Catalytic enantioselective addition of organoboron reagents to fluoroketones controlled by electrostatic interactions
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SUPPLEMENTARY INFORMATION

Ammonium-organofluorine electrostatic attraction as a stereochemistry controlling element:

To generate a broad range of enantiomerically of fluorooorganic compounds:

For synthesis of biologically active molecules:

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**Bibliography for Lewis base activation of Lewis acids**

The concept of Lewis base activation of Lewis acids is based on the following explanation by Guttmann: “[A]lthough a donor–acceptor interaction will result in a net transfer of electron density from the donor species to the acceptor species, it will, in the case of polyatomic species, actually lead to a net increase or “pileup” of electron density at the donor atom of the donor species and to a net decrease or “spillover” of electron density at the acceptor atom of the acceptor species. This results from the accompanying changes in the intramolecular charge distribution induced by the primary donor–acceptor interaction. These disperse the net change in electron density among all the atoms and in so doing, overcompensate for the initial changes induced at the donor and acceptor atoms. This result is important as it contradicts the usual assumption of the organic chemist that the net changes in formal charges remain localized on the donor and acceptor atoms.” See: (a) Jensen, W. B. *The Lewis Acid-Base Concepts*, Wiley-Interscience, New York, pp. 135–142 (1980). For the original exposition
of the concept, see: (b) Guttmann, V. *The Donor–Acceptor Approach to Molecular Interactions*; Chapter 1; Plenum Press, New York, (1978). Thus, electron donation to a Cu–alkoxide or Cu–B(pin) species by an Lewis basic species (e.g., an NHC) results in increase in electron density at the more electronegative (vs the transition metal) C (including that of the NHC), B and oxygen ligands and diminution of the same at the Cu center. For an excellent in depth review regarding this important concept, see: (c) Denmark, S. E. & Beutner, G. L. *Angew. Chem. Int. Edn* **47**, 1560–1638 (2008) and references cited therein.
2. General experimental part

Infrared (IR) spectra were recorded on a Bruker alpha spectrophotometer, \( \lambda_{\text{max}} \) in cm\(^{-1} \). Bands are characterized as broad (br), strong (s), medium (m), and weak (w). \(^1\)H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz), 500 (500 MHz) or 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl\(_3\): \( \delta \) 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). Well resolved ABX or AB splitting patterns where \( \Delta \delta_{AB}/J_{AB} < 4 \) are reported as follows: chemical shift, integration, actual multiplicity (ABX, AB\(_q\) = AB quartet), \( \Delta \delta_{AB} \) (calculated difference in chemical shift between A and B), and coupling constants. \(^{13}\)C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz), 500 (125 MHz) or 600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl\(_3\): \( \delta \) 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (singlet unless otherwise noted), and coupling constants (Hz). \(^{19}\)F NMR spectra were recorded on a Varian Unity INOVA 400 (376 MHz). Chemical shifts are reported in ppm with BF\(_3\)•OEt\(_2\) as an external standard (BF\(_3\)•OEt\(_2\): \( \delta \) 0.00 ppm). Data are reported as follows: chemical shift, integration, multiplicity, and coupling constants (Hz). High-resolution mass spectrometry was performed on a JEOL AccuTOF-DART (positive mode) or an Advion Expression CMS (ESI+ or ESI-) at the Mass Spectrometry Facility, Boston College. Enantiomer ratios (er) values were determined by HPLC analysis (high-performance liquid chromatography) using a Shimadzu LC-2010AHT chromatograph (Chiral Technologies Chiralcel OD-H (4.6 x 250 mm), Chiral Technologies Chiralcel OJ-H (4.6 x 250 mm), Chiral Technologies Chiralpak AD-H (4.6 x 250 mm), Chiral Technologies Chiralpak AS-H (4.6 x 250 mm) or Chiral Technologies Chiralpak AZ-H (4.6 x 250 mm)) and GLC analysis[Alltech Associated ChiralDex CDB/DA column (30m x 0.25 mm) in comparison with authentic racemic materials. Specific rotations were measured using either an Atago AP-300 Automated Polarimeter or a Rudolph Research Analytical Autopol IV Polarimeter. Melting points were determined using a Thomas Hoover Uni-melt capillary melting point apparatus. Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N\(_2\) in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques.

Solvents

Unless otherwise noted, solvents were purged with Argon and purified under a positive pressure of dry Argon by a modified Innovative Technologies purification system. Toluene (Fisher, ACS Grade) was passed successively through activated copper and alumina columns. Dichloromethane (Fisher, ACS Grade) and diethyl ether (Aldrich, Chromasolv®) were passed successively through two activated alumina columns. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl immediately prior to use. CDCl\(_3\) was purchased from Cambridge Isotope Laboratories and stored over activated 4Å molecular sieves prior to use. All work-up and purification procedures were carried out in
air with reagent grade solvents (purchased from Fisher).

**Reagents**

3-(1-Adamantyl)-2-hydroxy-5-methylbenzaldehyde was purchased from Matrix Scientific and used as received.

Allenyloboronic Acid Pinacol Ester was obtained from Frontier Scientific and distilled under vacuum prior to use.

Allylboronates: Allylboronic acid pinacol ester was purchased from Aldrich or obtained as a gift from Frontier Scientific, Inc and distilled prior to use. 2-(2-Methylallyl)boronic acid pinacol ester and 2-(2-chloroallyl)boronic acid pinacol ester were synthesized and purified in accordance with a procedure in the literature.²

Benzoyl Chloride was purchased from Aldrich and used as received.

Boc-Val-OH was purchased from Advanced ChemTech and used as received.

Boc-D-Val-OH was purchased from Advanced ChemTech and used as received.

tert-Butanol was purchased from Aldrich and distilled from sodium metal before use.

n-Butylamine was purchased from Aldrich and used as received.

tert-Butyldimethylsilyl Chloride was purchased from Strem and used as received.

3-tert-Butyl-2-hydroxybenzaldehyde was purchased from Aldrich and used as received.

Dess-Martin periodinane was purchased from Aldrich and used as received.

1,8-Diazabicycloundec-7-ene (DBU) was purchased from Aldrich and distilled from CaH₂ prior to use.

Dimethylamine (40 wt % in H₂O) was purchased from Aldrich and used as received.

Dimethyl sulfide was purchased from Aldrich and used as received.

1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide Hydrochloride (EDC•HCl) was purchased from Advanced ChemTech and used as received.

Hydrochloric Acid (4.0 M in 1,4-dioxane) was purchased from Aldrich and used as received.

1-Hydroxy-benzotriazole Hydrate (HOBt•H₂O) was purchased from Advanced ChemTech and used as received.

Hydroxylamine hydrochloride was purchased from Alfa Aesar and used as received.

[Hydroxy(tosyloxy)iodo]benzene was purchased from Aldrich and used as received.

4-Iodo-2-methyl-benzoic acid was purchased from Combi-Blocks and used as received.

Isopropylmagnesium chloride solution (1.3 M in thf) was purchased from Aldrich and used as received.

Pyridine was purchased from Aldrich and used as received.

(2) Zhang, P., Roundtree, I. A. and Morken, J. P. Org. Lett. 14, 1416–1419 (2012).
Magnesium Sulfate was purchased from Fisher and flame-dried under vacuum prior to use. Methanol was purchased from Acros (99.8% anhydrous) and distilled at 1 atm from sodium metal prior to use or used as received. Salicylaldehyde was purchased from Aldrich and used as received. Sodium Borohydride was purchased from Aldrich and used as received. Sodium tert-Butoxide was purchased from Strem and used as received. Sodium Hydride (60 wt% in oil) was purchased from Strem and used as received. Sodium Sulfate was purchased from Acros and used as received. Triethylamine was purchased from Aldrich and distilled from CaH₂ prior to use. Trimethyl phosphite was purchased from Aldrich and used as received. L-Valine Ethyl Ester Hydrochloride was purchased from Aldrich and used as received. Zinc methoxide (97%, powder) was purchased from Aldrich and used as received. Aminophenols 1a–1d

(S)-2-((3-(tert-Butyl)-2-hydroxybenzyl)amino)-N,N,3-trimethylbutanamide (1a, Figure 1b)
The title compound was synthesized in accordance to a procedure in the literature.³

(S)-2-((2-Hydroxybenzyl)amino)-N,N,3-trimethylbutanamide (1b, Figure 2a)
The title compound was synthesized analogous to 1a from salicylaldehyde and purified by silica gel chromatography (24 mm diameter column slurry packed with ~15 g of silica gel and eluted with 1:1 hexanes:ethyl acetate) affording 1b (386.0 mg, 1.54 mmol, 72% yield over 3 steps) as white solid. M.p. = 70–72 °C; IR (neat): 3304 (br, w), 2964 (w), 1637 (s), 1589 (m), 1490 (w), 1466 (m), 1398 (m), 1353 (w), 1256 (s), 1228 (w), 1125 (m), 1075 (w), 945 (m), 892 (m), 875 (w), 852 (w), 806 (m), 752 (s), 719 (w), 685 (m), 515 (m); 1H NMR (400 MHz, CDCl₃): δ 10.89 (1H, br s), 7.17 (1H, td, J = 7.7, 1.7 Hz), 6.92 (1H, d, J = 7.6 Hz), 6.85 (1H, d, J = 8.0 Hz), 6.76 (1H, td, J = 7.4, 1.2 Hz), 4.05 (1H, d, J = 13.8 Hz), 3.53 (1H, d, J = 13.8 Hz), 3.34 (1H, d, J = 6.0 Hz), 3.04 (3H, d, J = 0.9 Hz), 2.92 (3H, d, J = 0.9 Hz), 1.94–1.81 (1H, m), 0.98 (6H, d, J = 6.8 Hz); 13C NMR (100 MHz, CDCl₃): δ 173.4, 158.2, 129.0, 128.7, 122.6, 119.3, 116.5, 61.7, 51.4, 37.1, 35.9, 31.4, 20.1, 18.0; HRMS Calcd for C₁₄H₂₃N₂O₂ [M+H]⁺: 251.1760; Found: 251.1755; [α]D²⁵ = −22.7 (c = 0.44, CHCl₃)

(S)-2-((2-Hydroxy-3-(triphenylsilyl)benzyl)amino)-N,N,3-trimethylbutanamide (1c, Figure 3a)
The title compound was synthesized analogous to 1a except the reductive amination was performed in

³ Silverio, D. L., Torker, S., Pilyugina, T., Vieira, E. M., Snapper, M. L., Haeffner, F. & Hoveyda, A. H. *Nature* **494**, 216–221 (2013).
MeOH/toluene. 2-Hydroxy-3-(triphenylsilyl)benzaldehyde was synthesized according to a known procedure and the analytical data are fully consistent with those reported previously. Product \(1\text{c}\) was purified by silica gel chromatography (30 mm diameter column slurry packed with ~20 g of silica gel and eluted with 4:1 hexanes:ethyl acetate) affording \(1\text{c}\) (366.0 mg, 0.72 mmol, 72% yield over 2 steps) as colorless oil. IR (neat): 3294 (w), 3066 (br, w), 3047 (w), 1642 (s), 1596 (w), 1427 (s), 1398 (m), 1146 (m), 1107 (w), 823 (w), 743 (m), 701 (s), 508 (s) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.67–7.55 (6H, m), 7.44–7.28 (9H, m), 7.10 (1H, dd, \(J = 7.4, 1.7\) Hz), 7.01 (1H, dd, \(J = 7.4, 1.7\) Hz), 6.72 (1H, t, \(J = 7.4\) Hz), 4.17 (1H, d, \(J = 14.0\) Hz), 3.46 (1H, d, \(J = 14.1\) Hz), 3.23 (1H, d, \(J = 6.4\) Hz), 3.02 (3H, s), 2.82 (3H, s), 1.75 (1H, h, \(J = 6.8\) Hz), 0.79 (6H, t, \(J = 6.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 173.4, 163.3, 137.8, 136.3, 131.2, 129.1, 127.5, 121.7, 120.8, 119.0, 60.5, 50.7, 37.0, 35.7, 31.4, 19.9, 18.0; HRMS Calcd for \(C_{32}H_{36}N_2O_2Si\) [M+H]\(^+\): 509.2546; Found: 509.2617. \([\alpha]^{20}_D = -80.0\) (c = 1.0, CHCl\(_3\)).

\((R)-2-((3R,5R,7R)-Adamantan-1-yl)-2-hydroxy-5-methylbenzylamino)-N,N,3-trimethylbutanamide (1d, Figure 5)

The title compound was synthesized analogous to \(1\text{a}\) except the imine formation was performed at 30 °C for 18 h. Imine reduction required 13 equiv. of NaBH\(_4\), and the product was purified by silica gel chromatography (24 mm diameter column slurry packed with ~15 g of silica gel and eluted with 1:3 hexanes:diethyl ether) affording \(1\text{d}\) (189.1 mg, 0.47 mmol, 74% yield over 3 steps) as white foam. IR (CHCl\(_3\)): 3544 (br, w), 1641 (w), 1452 (w), 1296 (w), 1228 (w), 1157 (s), 1011 (w), 994 (w), 941 (w), 912 (w), 761 (w), 731 (m) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.71 (1H, s), 6.94 (1H, s), 6.60 (1H, s), 4.03 (1H, d, \(J = 13.5\) Hz), 3.41 (1H, d, \(J = 13.5\) Hz), 3.28 (1H, d, \(J = 13.5\) Hz), 3.04 (3H, s), 2.90 (3H, s), 2.62 (1H, s), 2.22 (3H, s), 2.06 (3H, s), 1.85–1.73 (7H, m), 0.95 (6H, t, \(J = 6.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 173.5, 154.7, 137.0, 127.2, 127.1, 126.6, 122.7, 61.1, 51.5, 40.4, 37.2, 37.0, 36.7, 35.7, 31.2, 29.2, 20.8, 20.0, 17.9; HRMS Calcd for \(C_{25}H_{39}N_2O_2\) [M+H]\(^+\): 399.3011; Found: 399.3009; \([\alpha]^{22}_D = +31.962\) (c = 0.98, CHCl\(_3\)).

(4) Thadani, A. N., Huang, Y. & Rawal, V. H. Org. Lett. 9, 3873–3876 (2007).
(5) Nomura, N., Ishii, R., Yamamoto, Y. & Kondo, T. Chem. Eur. J. 13, 4433–4451 (2007).
**Ketone Substrates**

**Acetophenone (2a, Figure 1a):** Purchased from Aldrich and distilled under vacuum from calcium hydride prior to use.

**Isobutyrophenone (2b, Figure 1a):** Purchased from Aldrich and distilled under vacuum from calcium hydride prior to use.

**2,2,2-Trifluoroacetophenone (3a, Figure 2a):** Purchased from Oakwood and distilled under vacuum from calcium chloride prior to use.

**2'-Methyl-2,2,2-trifluoroacetophenone (S1, not shown in the manuscript, see Chart S1):** Synthesized in accordance to a procedure in the literature\(^{(6)}\) using Knochel's procedure\(^{(7)}\) to generate the requisite Grignard. Analytical data are fully consistent with those reported previously\(^{(8)}\).

**2'-Methoxy-2,2,2-trifluoroacetophenone (S2, not shown in the manuscript, see Chart S1):** Purchased from Oakwood and distilled under vacuum (simple distillation) prior to use or used as received (no difference in results are observed).

**3'-Methyl-2,2,2-trifluoroacetophenone (S3, not shown in the manuscript, see Chart S1):** Purchased from Oakwood and used as received.

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(6) Shaw, D. A. and Tuominen, T. C. *Synth. Commun.* **15**, 1291–1297 (1985).

(7) Krasovskiy, A. and Knochel, P. *Angew. Chem. Int. Edn* **43**, 3333–3336 (2004).

(8) Chong, J. M. and Mar, E. K. *J. Org. Chem.* **56**, 893–896 (1991).
4’-Dimethylamino-2,2,2-trifluoroacetophenone (S4, not shown in the manuscript, see Chart S1): Purchased from Aldrich as orange-yellow solid. Dissolved in hot HPLC grade hexanes (Fisher) and filtered through a hot glass frit to remove dark orange solids. The fritted glass was washed with HPLC grade hexanes and minimal dichloromethane (Fisher, reagent grade) to recover maximum amount of S4. Concentration in vacuo affords S4 as a bright yellow solid.

4’-Bromo-2,2,2-trifluoroacetophenone (S5, not shown in the manuscript, see Chart S1): Purchased from Matrix and used as received.

4’-Trifluoromethyl-2,2,2-trifluoroacetophenone (S6, not shown in the manuscript, see Chart S1): Purchased from Oakwood and used as received.

tert-Butyl 2-(2,2,2-trifluoroacetyl)-1H-pyrrole-1-carboxylate (S7, not shown in the manuscript, see Chart S1): Synthesized from commercially available 2-(trifluoroacetyl)pyrrole (purchased from Oakwood) and protected with Boc group. IR (neat): 1755 (m), 1698 (m), 1423 (m), 1372 (m), 1302 (s), 1219 (m), 1135 (s), 1080 (m), 1038 (m), 917 (m), 876 (w), 837 (m), 729 (s), 591 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (1H, ddd, J = 2.9, 1.5, 0.7 Hz), 7.25–7.20 (1H, m), 6.32 (1H, ddd, J = 3.9, 3.0, 0.8 Hz), 1.58 (9H, s); ¹³C NMR (100 MHz, CDCl₃): δ 170.61 (q, J = 36.4 Hz), 148.17, 132.01, 126.67, 126.32 (q, J = 3.6 Hz), 116.62 (q, J = 290.3 Hz), 111.35, 86.34, 27.58; ¹⁹F NMR (376 MHz, CDCl₃): δ 80.1 (3F, s); HRMS Calculated for C₁₁H₁₂F₄N₃O₃ [M+H]⁺: 264.0848; Found: 264.0853.

2,2,2-trifluoro-1-(furan-2-yl)ethan-1-one (S8, not shown in the manuscript, see Chart S1): Synthesized in accordance to a procedure in the literature and analytical data are fully consistent with those reported previously.⁹

2,2,2-trifluoro-1-(furan-3-yl)ethan-1-one (S9, not shown in the manuscript, see Chart S1): Synthesized in accordance to a procedure in the literature. IR (neat): 1710 (s), 1607 (w), 1560 (m), 1518 (m), 1373 (w), 1244 (m), 1196 (m), 1141 (s), 1089 (m), 1020 (s), 992 (m), 872 (s), 833 (w), 749 (m), 731 (s), 597 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.25–8.23 (1H, m), 7.54 (1H, dd, J = 1.9, 1.3 Hz), 6.91 (1H, d, J = 2.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 175.6 (q, J = 37.3 Hz), 150.8 (q, J = 4.5 Hz), 145.0, 121.0, 116.3 (q, J = 289.8 Hz), 109.1; ¹⁹F NMR (376 MHz, CDCl₃): δ 77.95 (3F, s); HRMS Calculated for C₅H₃F₂O₂ [M+H]⁺: 165.0163; Found: 165.0170.

2-(Trifluoroacetyl)thiophene (S10, not shown in the manuscript, see Chart S1): Purchased from Aldrich and distilled under vacuum from calcium chloride prior to use or used as received (no difference in results are observed).

3-(Trifluoroacetyl)thiophene (S11, not shown in the manuscript, see Chart S1): Synthesized in accordance to a procedure in the literature using Knochel's procedure to generate the requisite Grignard. Analytical data are fully consistent with those reported previously.¹⁰

(E)-1,1,1-Trifluoro-4-phenylbut-3-en-2-one (S12, not shown in the manuscript, see Chart S1): Synthesized in accordance to a procedure in the literature and analytical data are fully consistent with

(9) Singh, R. P., Cao, G., Kirchmeier, R. L. & Shreeve, J. M. J. Org. Chem. 64, 2873–2876 (1999).
(10) Matsuda, T. & Harada, T. J. Org. Chem. 65, 157–163 (2000).
those reported previously.\textsuperscript{11}

1,1,1-Trifluoro-3-phenylacetone (S13, not shown in the manuscript, see Chart S1): Purchased from Oakwood and distilled under vacuum from calcium chloride or used as received (no difference in results are observed).

1-Cyclohexyl-2,2,2-trifluoro-ethanone (S14, not shown in the manuscript, see Chart S1): Purchased from Oakwood and distilled under vacuum from calcium chloride.

2,2,3,3,3-Pentfluoroacetophenone (S15, not shown in the manuscript, see Chart S1): Purchased from Matrix and used as received.

4,4,4,4,4,4-Heptafluoroacetophenone (S16, not shown in the manuscript, see Chart S1): Purchased from Alfa Aesar and used as received.

4′-Fluoro-2,2,2-trifluoroacetophenone (S17, not shown in the manuscript, see Chart S1): Purchased from Oakwood and used as received.

2-Fluoroacetophenone (S18, not shown in the manuscript, see Chart S1): Synthesized in accordance to a procedure in the literature and analytical data are fully consistent with those reported previously.\textsuperscript{12}

2,2-Difluoroacetophenone (S19, not shown in the manuscript, see Chart S1): Purchased from Alfa Aesar and distilled under vacuum (simple distillation) prior to use.

2,2-Difluoropropiophenone (S20, not shown in the manuscript, see Chart S1): Synthesized in accordance to a procedure in the literature and analytical data are fully consistent with those reported previously.\textsuperscript{13}

2,2-Difluoro-α-tetralone (S21, not shown in the manuscript, see Chart S1): Synthesized in accordance to a procedure in the literature and analytical data are fully consistent with those reported previously.\textsuperscript{12}

2′-Fluoroacetophenone (S22, not shown in the manuscript, see Chart S1): Purchased from Aldrich and distilled under vacuum from calcium chloride prior to use.

2′,6′-Difluoroacetophenone (S23, not shown in the manuscript, see Chart S1): Purchased from Oakwood and distilled under vacuum from calcium chloride prior to use.

2′,3′,4′,5′,6′-Pentafluoroacetophenone (S24, not shown in the manuscript, see Chart S1): Purchased from Aldrich and distilled under vacuum from calcium chloride prior to use.

Perfluoroacetophenone (S25, not shown in the manuscript, see Chart S1): Purchased from Oakwood and distilled under vacuum from calcium chloride.

3′,5′-Dichloro-2,2,2-trifluoroacetophenone (3r, Figure 5): Purchased from Oakwood and distilled under vacuum from calcium chloride.

\textsuperscript{(11)} Kawano, Y., Kaneko, N. & Mukaiyama, T. \textit{Bull. Chem. Soc. Jpn} \textbf{79}, 1133–1145 (2006).

\textsuperscript{(12)} Wei, Z.-L., Li, Z.-Y. & Lin, G.-Q. \textit{Tetrahedron} \textbf{54}, 13059–13072 (1998).

\textsuperscript{(13)} Pravst, I., Zupan, M. & Stavber, S. \textit{Synthesis} \textbf{18}, 3140–3146 (2005).
3. Catalytic Procedures

Procedure for small-scale catalytic enantioselective allyl additions to ketones 2a–2b and analytical data for the resultant homoallylic alcohols (Figure 1)

In a nitrogen-filled glove box, 1a (7.66 mg, 0.025 mmol) was added to a two-dram vial equipped with a stir bar and 1.0 mL of toluene was introduced. A solution was prepared by dissolving 4.81 mg NaOt-Bu in 8.0 mL toluene. Another two-dram vial equipped with a stir bar was charged with 0.2 mL of the solution of 1a (1.53 mg, 0.005 mmol) followed by the addition of 0.8 mL of the solution of NaOt-Bu (1.92 mg, 0.02 mmol). The vial was sealed with a cap (phenolic open top cap with a white PFTE/gray silicone septa) and electrical tape and removed from the glove box. Methanol (20 µL, 0.5 mmol), acetophenone 2a (24 µL, 0.2 mmol) and allylboronic acid pinacol ester (56 µL, 0.29 mmol) were added by syringe under N₂ in the order mentioned. The clear, colorless solution was allowed to stir at 22 °C for 4 h after which the cap was removed, and 9-methylantracene (6.4 mg, 0.033 mmol; solution in ethyl acetate) was added as an internal standard for ¹H NMR. The mixture was passed through a short plug of silica gel (eluted with Et₂O) and concentrated in vacuo taking care not to remove all solvent (product is volatile). The resulting yellow oil was purified by silica gel chromatography (10 mm diameter column slurry packed with ~2.5 g of silica gel and eluted with 95:5 pentanes:diethyl ether), affording S23 (26.0 mg, 0.16 mmol, 80% yield) as colorless oil.

The analytical data are fully consistent with those reported previously.¹⁴ ¹H NMR (400 MHz, CDCl₃): δ 7.46–7.43 (2H, m), 7.37–7.32 (2H, m), 7.27–7.22 (1H, m), 5.68–5.57 (1H, m), 5.17–5.10 (2H, m), 2.69 (1H, ddt, J = 14. 6.4, 0.8 Hz), 2.51 (1H, ddt, J = 13.6, 8.4, 0.8 Hz), 2.03 (1H, s), 1.55 (3H, s); HRMS Calcd for C₁₁H₁₃[M+H–H₂O]⁺: 145.1017; Found: 145.1016; [α]²³.₅D = −27.8 (c = 1.08, CHCl₃) for a 70:30 er sample. The enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AD-H, 99:1 hexanes:i-PrOH, 1.0 mL/min, 220 nm): tᵣ: 15 min (minor) and 16 min (major).

(14) Lou, S., Moquist, P. N. & Schaus, S. E. J. Am. Chem. Soc. 128, 12660–12661 (2006).
2-Methyl-3-phenylhex-5-en-3-ol (S27, not shown in the manuscript, see Chart S2)

The title compound was synthesized analogous to S26 except the reaction time was 18 h. The title compound was purified by silica gel chromatography to afford S27 (12.4 mg, 0.065 mmol, 33% yield) as colorless oil. The analytical data are fully consistent with those reported previously.\(^\text{15}\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.39–7.31 (4\text{H, m}), 7.24–7.21 (1\text{H, m}), 5.53–5.42 (1\text{H, m}), 5.15–5.05 (2\text{H, m}), 2.81 (1\text{H, dd, } J = 13.8, 5.4 \text{ Hz}), 2.54 (1\text{H, dd, } J = 13.8, 9.1 \text{ Hz}), 2.02 (1\text{H, hept, } J = 6.9 \text{ Hz}), 1.93 (1\text{H, s}), 0.95 (3\text{H, d, } J = 6.9 \text{ Hz}), 0.77 (3\text{H, d, } J = 6.9 \text{ Hz}); HRMS Calcd for C\(_{13}\)H\(_{17}\)[M+H–H\(_2\)O]+: 173.1330; Found: 173.1334; \([\alpha]^{23.5}_{23.5} = +54.5 (c = 0.55, \text{CHCl}_3)\) for a 65:35 er sample. The enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AD-H, 99:1 hexanes:i-ProOH, 1.0 mL/min, 220 nm): \(t_R:\) 6.6 min (major) and 7.0 min (minor).

| Peak # | Ret. Time | Area   | Area %  | Peak # | Ret. Time | Area   | Area %  |
|--------|-----------|--------|---------|--------|-----------|--------|---------|
| 1      | 10.8 min  | 985986 | 49.980  | 1      | 15.1 min  | 4093351| 29.699  |
| 2      | 11.6 min  | 9867754 | 50.020  | 2      | 16.1 min  | 9689529| 70.301  |

Procedure for small-scale catalytic enantioselective allyl additions to ketones that contain perfluoroalkyl group and analytical data for the resultant homoallylic alcohols 4a–4q, 5a–5b (Figure 2 & Table 1)

In a nitrogen-filled glove box, aminophenol 1a (7.66 mg, 0.025 mmol) was added to a two-dram vial equipped with a stir bar and dissolved in 1.0 mL of toluene. A second solution was prepared by dissolving 19.2 mg NaOt-Bu in 8.0 mL toluene. A two-dram vial equipped with a stir bar was charged with 0.2 mL of the stock solution of 1a (1.53 mg, 0.005 mmol) followed by 0.8 mL of the stock solution of NaOt-Bu (1.92 mg, 0.02 mmol). This vial was sealed with a cap (phenolic open top cap with a white PFTE/gray silicone septa) and electrical tape and removed from the glove box. Methanol (10 \(\mu\)L, 0.25 mmol) and trifluoroacetophenone 3a (28 \(\mu\)L, 0.2 mmol) were added by syringe under N\(_2\) in the stated order. The vessel was placed in a 0 °C ice/water bath and allowed to stir for 15 minutes. Allylboronic acid pinacol ester (42 \(\mu\)L, 0.22 mmol) was added by syringe under N\(_2\) and the mixture was allowed to stir at 4 °C for 4 h after which time the cap was removed and \(\alpha,\alpha,\alpha\)-trifluorotoluene

(15) Uccello-Barretta, G., Bernardini, R., Lazzaroni, R. & Salvadori, P. J. Organomet. Chem. 598, 174–178 (2000).
(24.4 µL, 0.2 mmol) was added as an internal standard. Following $^{19}$F NMR analysis of the reaction mixture, it was passed through a short plug of silica gel (eluted with Et$_2$O) and concentrated in vacuo being careful not to remove all of the solvent, as the product is volatile. The resulting pale yellow oil was purified by silica gel chromatography (10 mm diameter column slurry packed with ~2.5 g of silica gel in pentane and eluted with 9:1 pentane:Et$_2$O) to afford desired product 4a (40.2 mg, 0.186 mmol, 93% yield) as colorless oil.

(R)-1,1,1-Trifluoro-2-phenylpent-4-2-en-2-ol (4a, Figure 2a)

The analytical data are fully consistent with those reported previously.$^{16}$ $^1$H NMR (500 MHz, CDCl$_3$): δ 7.62–7.54 (2H, m), 7.45–7.32 (3H, m), 5.62–5.50 (1H, m), 5.30–5.18 (2H, m), 2.99 (1H, dd, $J = 14.3, 6.6$ Hz), 2.85 (1H, dd, $J = 14.3, 8.1$ Hz), 2.58 (1H, s); HRMS Calcd for C$_{11}$H$_{10}$F$_3$ [M+H–H$_2$O]$: 199.0735$; Found: 199.0734; [$\alpha$]$^{22.3}_{D}$ = +50.0 ($c = 2.20$, CHCl$_3$) for a 9:4:6 er sample. The enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): $t_R$ of 4a: 13 min (major) and 14 min (minor).

(R)-1,1,1-Trifluoro-2-(o-tolyl)pent-4-2-en-2-ol (4b, Figure 2b)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 4b (40.0 mg, 0.174 mmol, 87% yield) as colorless oil. IR (neat): 3544 (br, w), 1641 (w), 1452 (w), 1296 (w), 1228 (w), 1157 (s), 1011 (w), 994 (w), 941 (w), 912 (w), 761 (w), 731 (m) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.37–7.33 (1H, m), 7.19–7.06 (3H, m), 5.62–5.51 (1H, m), 5.22–5.13 (2H, m), 3.10 (1H, dd, $J = 14.6, 6.7$ Hz), 2.75 (1H, dd, $J = 14.6, 7.9$ Hz), 2.50–2.45 (4H, m); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.5, 134.3, 133.5, 131.0, 128.8, 128.7 (q, $J = 1.4$ Hz), 126.0 (q, $J = 286.3$ Hz), 125.8, 122.4, 78.0 (q, $J = 28.3$ Hz), 40.8 (q, $J = 1.2$ Hz), 23.1 (q, $J = 2.1$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): δ 75.73 (3F, s); HRMS Calcd for C$_{12}$H$_{12}$F$_3$ [M+H–H$_2$O]$: 213.0891$; Found: 213.0925. [$\alpha$]$^{22.4}_{D}$

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(16) Xie, Z., Li, G., Zhao, G. & Wang, J. Chin. J. Chem. 28, 1212–1216 (2010).
= +30.4 (c = 2.30, CHCl₃) for a 82:18 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tᵣ: 20 min (major) and 25 min (minor).

| Peak # | Ret. Time | Area  | Area % | Peak # | Ret. Time | Area  | Area % |
|--------|-----------|-------|--------|--------|-----------|-------|--------|
| 1      | 18.4 min  | 9445468 | 49.987 | 1      | 19.8 min  | 16531586 | 82.260 |
| 2      | 23.1 min  | 9450368 | 50.013 | 2      | 25.2 min  | 35651212 | 17.740 |

(R)-1,1,1-Trifluoro-2-(2-methoxyphenyl)pent-4-en-2-ol (4c, Figure 2b)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 4c (46.3 mg, 0.188 mmol, 94% yield) as pale yellow oil. IR (neat): 3452 (br, w), 3081 (w), 3015 (w), 2981 (w), 2947 (w), 2845 (w), 1603 (w), 1584 (w), 1438 (m), 1267 (m), 1238 (m), 1182 (m), 1156 (s), 1137 (m), 1022 (m), 912 (s), 753 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.37–7.31 (2H, m), 7.05–6.98 (2H, m), 6.07 (1H, s), 5.74 (1H, dddd, J = 17.2, 10.3, 7.2, 6.4 Hz), 5.25–5.06 (2H, m), 3.92–3.91 (3H, s), 3.06 (1H, dd, J = 15.0, 7.2 Hz), 2.85 (1H, dd, J = 14.9, 6.4 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 158.8, 131.9, 130.7, 130.3, 125.9 (q, J = 285.9 Hz), 123.2, 121.5, 119.3, 112.8, 78.4 (q, J = 28.5 Hz), 56.5–56.3 (m), 38.3–38.2 (m); ¹⁹F NMR (376 MHz, CDCl₃): δ 71.94 (3F, s); HRMS Calcd for C₁₂H₁₂F₃O [M+H–H₂O]⁺: 229.0840; Found: 229.0845. [α]²¹⁺ = –0.82 (c = 2.92, CHCl₃) for a 88:12 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tᵣ: 14 min (minor) and 17 min (major).

| Peak # | Ret. Time | Area  | Area % | Peak # | Ret. Time | Area  | Area % |
|--------|-----------|-------|--------|--------|-----------|-------|--------|
| 1      | 14.5 min  | 19479999 | 51.052 | 1      | 14.3 min  | 2288149 | 12.260 |
| 2      | 17.2 min  | 18677077 | 48.948 | 2      | 17.0 min  | 16476009 | 87.740 |
(R)-1,1,1-Trifluoro-2-(m-tolyl)pent-4-en-2-ol (4d, Table 1)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 4d (43.1 mg, 0.190 mmol, 94% yield) as colorless oil. IR (neat): 3549 (br, w), 2927 (w), 1642 (w), 1609 (w), 1370 (w), 1269 (m), 1230 (m), 1147 (s), 1023 (m), 993 (m), 785 (m), 708 (s), 646 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.41 (1H, s), 7.37 (1H, d, J = 6.4 Hz), 7.30 (1H, t, J = 7.6 Hz), 7.19 (1H, d, J = 7.6 Hz), 5.63–5.53 (1H, m), 5.29–5.22 (2H, m), 2.99 (1H, dd, J = 14.3, 6.5 Hz), 2.85 (1H, dd, J = 14.2, 8.1 Hz), 2.60 (1H, s), 2.40 (3H, s); ¹³C NMR (100 MHz, CDCl₃): δ 138.2, 136.9, 130.7, 129.4, 128.4, 127.2, 125.5 (q, J = 285.4 Hz), 123.6, 121.2, 75.9 (q, J = 28.3 Hz), 40.5, 21.5; ¹⁹F NMR (376 MHz, CDCl₃): δ 73.68 (3F, s); HRMS Calculated for C₁₂H₁₂F₃[M+H–H₂O]⁺: 213.0891; Found: 213.0896; [α]ᵢ₂₁.₅ = +61.7 (c = 1.94, CHCl₃) for a 92.5:7.5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): t_R: 21 min (major) and 23 min (minor).

| Peak # | Ret. Time | Area       | Area % | Peak # | Ret. Time | Area       | Area % |
|--------|-----------|------------|--------|--------|-----------|------------|--------|
| 1      | 20.8 min  | 17861454   | 49.109 | 1      | 20.8 min  | 22541369   | 92.482 |
| 2      | 22.9 min  | 18509371   | 50.891 | 2      | 23.0 min  | 1832304    | 7.518  |

(R)-2-(4-(Dimethylamino)phenyl)-1,1,1-trifluoropent-4-en-2-ol (4e, Table 1)

The title compound was synthesized analogous to 4a except the substrate was weighed out into the reaction vessel before any other components were added. The title compound was purified by silica gel chromatography to afford 4e (50.8 mg, 0.196 mmol, 98% yield) as colorless oil. IR (neat): 3543 (br, w), 2921 (br, w), 2854 (br, w), 2807 (br, w), 1614 (m), 1523 (m), 1445 (w), 1358 (w), 1269 (m), 1227 (m), 1145 (s), 994 (m), 944 (m), 814 (s), 710 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.39 (2H, d, J = 8.8 Hz), 6.73–6.70 (2H, m), 5.65–5.54 (1H, m), 5.26–5.18 (2H, m), 3.00–2.95 (1H, m), 2.97 (6H, s), 2.81–2.75 (1H, m), 2.46 (1H, br s); ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 131.1, 127.5, 125.7 (q, J = 285.4 Hz), 124.1, 121.6, 112.0, 75.7 (q, J = 28.2 Hz), 40.4, 40.0; ¹⁹F NMR (376 MHz, CDCl₃): 79.85 (3F, s); HRMS Calculated for C₁₃H₁₂F₃NO [M+H]⁺: 260.1262; Found: 260.1254; [α]ᵢ²⁶.⁰ᵢ = +59.8 (c = 1.17, CHCl₃) for a 93:7 e.r. sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with an authentic sample of racemic material (Chiralpak AD-H, 97:3 hexanes:i-PrOH, 0.8 mL/min, 220 nm): t_R: 15 min (major) and 19 min (minor).
The title compound was synthesized analogous to 4a except for the following changes: 1) The substrate was weighed out into the vessel before any other components were added. 2) The amount of aminophenol 1a was 1.0 mol% (vs. 2.5 mol%). The title compound was purified by silica gel chromatography to afford 4f (53.6 mg, 0.182 mmol, 91% yield) as colorless oil. The analytical data are fully consistent with those reported previously.\textsuperscript{15} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.55–7.52 (2H, m), 7.45 (2H, d, J = 8.4 Hz), 5.60–5.49 (1H, m), 5.29–5.23 (2H, m), 2.93 (2H, dd, J = 14.4, 6.7 Hz), 2.83 (2H, dd, J = 14.4, 7.9 Hz), 2.61 (1H, s); \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): δ 73.59 (3F, s); HRMS Calcd for C\textsubscript{11}H\textsubscript{9}BrF\textsubscript{3}\[M+H–H\textsubscript{2}O]\+: 276.9840; Found: 276.9828. \([\alpha]\)\textsuperscript{21}D\textsubscript{D} = +71.6 (c = 2.37, CHCl\textsubscript{3}) for a 96:4 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AD-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t\textsubscript{R}\): 19 min (major) and 21 min (minor).

### Table 1

| Peak # | Ret. Time | Area   | Area % |
|--------|-----------|--------|--------|
| 1      | 13.2 min  | 5392970| 49.807 |
| 2      | 16.9 min  | 5434675| 50.193 |

(R)-2-(4-Bromophenyl)-1,1,1-trifluoropent-4-en-2-ol (4f, Table 1)

The title compound was synthesized analogous to 4a, except for the following changes: 1) The substrate was weighed out into the vessel before any other components were added. 2) The amount of aminophenol 1a was 1.0 mol% (vs. 2.5 mol%). The title compound was purified by silica gel chromatography to afford 4f (53.6 mg, 0.182 mmol, 91% yield) as colorless oil. The analytical data are fully consistent with those reported previously.\textsuperscript{15} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.55–7.52 (2H, m), 7.45 (2H, d, J = 8.4 Hz), 5.60–5.49 (1H, m), 5.29–5.23 (2H, m), 2.93 (2H, dd, J = 14.4, 6.7 Hz), 2.83 (2H, dd, J = 14.4, 7.9 Hz), 2.61 (1H, s); \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): δ 73.59 (3F, s); HRMS Calcd for C\textsubscript{11}H\textsubscript{9}BrF\textsubscript{3}\[M+H–H\textsubscript{2}O]\+: 276.9840; Found: 276.9828. \([\alpha]\)\textsuperscript{21}D\textsubscript{D} = +71.6 (c = 2.37, CHCl\textsubscript{3}) for a 96:4 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AD-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t\textsubscript{R}\): 19 min (major) and 21 min (minor).

### Table 1

| Peak # | Ret. Time | Area   | Area % |
|--------|-----------|--------|--------|
| 1      | 19.4 min  | 29880388| 55.305 |
| 2      | 21.7 min  | 24147543| 44.695 |

(R)-1,1,1-Trifluoro-2-(4-(trifluoromethyl)phenyl)pent-4-en-2-ol (4g, Table 1)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 4g (51.6 mg, 0.183 mmol, 91% yield) as colorless oil. IR (neat): 3553 (br, w), 2965 (w), 1622
(w), 1445 (w), 1326 (s), 1270 (m), 1231 (w), 1160 (s), 1124 (s), 1068 (m), 941 (m), 834 (s), 731 (m), 708 (w), 415 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.72 (2H, d, J = 8.3 Hz), 7.67 (2H, d, J = 8.7 Hz), 5.61–5.47 (1H, m), 5.34–5.23 (2H, m), 2.97 (1H, dd, J = 14.5, 6.8 Hz), 2.89 (1H, dd, J = 14.4, 7.8 Hz), 2.70 (1H, s); ¹³C NMR (125 MHz, CDCl₃): δ 140.97, 131.00 (q, J = 32.6 Hz), 129.81, 127.18, 125.48 (q, J = 3.7 Hz), 125.16 (q, J = 284.2 Hz), 124.08 (q, J = 270.8 Hz), 75.84 (q, J = 28.5 Hz), 40.55; ¹⁹F NMR (376 MHz, CDCl₃): δ 90.06 (3F, s), 73.85 (3F, s); HRMS Calcd for C₁₂H₉F₆ [M+H–H₂O]⁺: 267.0608; Found: 267.0608; [α]²⁰D = +56.1 (c = 1.63, CHCl₃) for a 93.5:6.5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tₚ = 54 min (major) and 62 min (minor).

| Peak # | Ret. Time | Area | Area % | Peak # | Ret. Time | Area | Area % |
|-------|-----------|------|--------|-------|-----------|------|--------|
| 1     | 15.9 min  | 4486495 | 49.627 | 1     | 16.6 min  | 11859178 | 93.365 |
| 2     | 17.4 min  | 4553888 | 50.373 | 2     | 19.0 min  | 842754 | 6.635  |

**tert-Butyl (S)-2-(1,1,1-trifluoro-2-hydroxyprop-4-en-2-yl)-1H-pyrrole-1-carboxylate (4h, Table 1)**

The title compound was synthesized analogous to 4a except the substrate was weighed out into the reaction vessel before any other components were added. The title compound was purified by silica gel chromatography to afford 4h (43.3 mg, 0.142 mmol, 71% yield) as colorless oil. IR (neat): 3299 (br, w), 2984 (br), 2984 (w), 1718 (m), 1444 (w), 1398 (m), 1373 (m), 1337 (s), 1264 (m), 1145 (s), 1100 (m), 848 (w), 733 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.69 (1H, s), 7.28 (1H, dd, J = 3.6, 1.8 Hz), 6.39 (1H, s), 6.16 (1H, t, J = 3.5 Hz), 6.06–5.76 (1H, m), 5.27–5.03 (2H, m), 2.90 (3H, d, J = 6.8 Hz), 1.61 (9H, s); ¹³C NMR (100 MHz, CDCl₃): δ 151.9, 132.4, 130.3, 125.6 (q, J = 286.9 Hz), 125.4, 118.7, 118.5, 110.4, 86.6, 74.3 (q, J = 28.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ 73.85 (3F, s); HRMS Calculated for C₁₄H₁₉F₃NO₃ [M+H⁺]: 274.9685; Found: 306.1327; [α]²⁰D = −10.9 (c = 0.92, CHCl₃) for a >99:1 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with an authentic sample of racemic material (Chiralpak AD-H, 97:3 hexanes:i-PrOH, 0.8 mL/min, 220 nm): tₚ: 3 min (minor) and 5 min (major).
(S,E)-1-Phenyl-3-(trifluoromethyl)hexa-1,5-dien-3-ol (4i, Table 1)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 4i (45.4 mg, 0.187 mmol, 94% yield) as colorless oil. IR (neat): 3543 (br, w), 2921 (br, w), 2854 (br, w), 2807 (br, w), 1614 (m), 1523 (m), 1445 (w), 1358 (w), 1269 (m), 1227 (m), 1145 (s), 994 (m), 944 (m), 814 (s), 710 (w) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.44–7.40 (2H, m), 7.37–7.35 (2H, m), 7.32–7.26 (1H, m), 6.87 (1H, d, \(J = 16.0\) Hz), 6.21 (1H, d, \(J = 16.0\) Hz), 5.87–5.69 (1H, m), 5.28–5.23 (2H, m), 2.70–2.59 (2H, m), 2.32 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 135.8, 133.4, 130.5, 128.8, 128.5, 127.0, 125.4 (q, \(J = 283.7\) Hz), 124.8, 121.5, 75.3 (q, \(J = 28.3\) Hz), 39.7; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) 72.37 (3F, s); HRMS Calculated for C\(_{13}\)H\(_{12}\)F\(_3\) [M+H–H\(_2\)O]\(^+\): 225.0891; Found: 225.0891. \([\alpha]^{22}_D = +19.9\) (c = 1.00, CHCl\(_3\)) for a 96.5:3.5 e.r. sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with an authentic sample of racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t_R\): 14 min (major) and 15 min (minor).
(R)-1,1,1-trifluoro-2-(furan-2-yl)pent-4-en-2-ol (4j, Table 1)

The title compound was synthesized analogously to 4a except the reaction was performed at 22 °C. The title compound was purified by silica gel chromatography to afford 4j (31.7 mg, 0.154 mmol, 77% yield) as colorless oil. IR (neat): 3441 (br, w), 2982 (w), 2947 (w), 1642 (w), 1502 (w), 1439 (w), 1349 (w), 1327 (m), 1182 (s), 1151 (s), 1098 (m), 1070 (m), 980 (m), 848 (w), 740 (s), 708 (m), 596 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.45 (1H, s), 6.48 (1H, d, J = 3.4 Hz), 6.41 (1H, dd, J = 3.4, 1.9 Hz), 5.63 (1H, ddt, J = 17.2, 10.0, 7.2 Hz), 5.29–5.19 (2H, m), 2.97 (1H, dd, J = 14.2, 6.6 Hz), 2.81 (1H, s), 2.76 (1H, dd, J = 14.2, 7.9 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 149.8, 143.3, 130.3, 124.5 (q, J = 284.1 Hz), 110.9, 109.7, 74.2 (q, J = 29.8 Hz), 38.2; ¹⁹F NMR (376 MHz, CDCl₃): δ 72.86 (3F, s); HRMS Calcd for C₉H₈F₃O [M+H–H₂O]⁺: 189.0527; Found: 189.0519. [α]₂₀.₀° = 26.35 (c = 1.10, CHCl₃) for a 90:10 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tᵣ: 28 min (minor) and 29 min (major).

| Peak # | Ret. Time | Area | Area % |
|--------|-----------|------|--------|
| 1      | 27.8 min  | 1178749 | 49.585 |
| 2      | 29.1 min  | 1198502 | 50.415 |

(R)-1,1,1-trifluoro-2-(furan-3-yl)pent-4-en-2-ol (4k, Table 1)

The title compound was synthesized analogously to 4a except for the following changes: 1) Reaction time was 7 h. 2) The amount of aminophenol 1a was 5.0 mol%. 3) Reaction scale was 0.1 mmol. The title compound was purified by silica gel chromatography to afford 4k (18.1 mg, 0.088 mmol, 88% yield) as colorless oil. IR (neat): 3466 (br, w), 2985 (w), 2930 (w), 1643 (w), 1596 (w), 1504 (w), 1441 (w), 1330 (m), 1280 (m), 1159 (s), 1110 (m), 1075 (m), 1034 (m), 923 (m), 875 (w), 798 (m), 727 (m), 704 (m), 601 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.51 (1H, s), 7.43 (1H, t, J = 1.7 Hz), 7.43 (1H, t, J = 1.7 Hz), 6.43–6.42 (1H, m), 5.74–5.61 (1H, m), 5.29–5.20 (2H, m), 2.74 (2H, d, J = 7.3 Hz), 2.47 (1H, s); ¹³C NMR (125 MHz, CDCl₃): δ 143.7, 141.2, 130.4, 125.2 (q, J = 277.1 Hz), 123.6, 121.8, 109.0, 73.5 (q, J = 29.6 Hz), 40.3; ¹⁹F NMR (376 MHz, CDCl₃): δ 72.35 (3F, s); HRMS Calcd for C₉H₈F₃O [M+H–H₂O]⁺: 189.0527; Found: 189.0524. [α]₂₀.₀° = 32.48 (c = 1.03, CHCl₃) for a 98:2 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tᵣ: 17 min (major) and 19 min.
(S)-1,1,1-Trifluoro-2-(thiophen-2-yl)pent-4-en-2-ol (4l, Table 1)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 4l (31.5 mg, 0.142 mmol, 71% yield) as colorless oil. IR (neat): 3531 (br, w), 3083 (w), 2984 (w), 2957 (w), 2929 (w), 1642 (w), 1437 (w), 1274 (m), 1228 (w), 1154 (br, w), 1048 (m), 991 (m), 931 (m), 724 (m), 702 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.35 (1H, dd, J = 5.1, 1.2 Hz), 7.14–7.12 (1H, m), 7.05 (1H, dd, J = 5.1, 3.6 Hz), 5.71–5.60 (1H, m), 5.32–5.26 (2H, m), 2.97–2.91 (1H, m), 2.88–2.82 (2H, m); ¹³C NMR (100 MHz, CDCl₃): δ 141.2, 130.1, 127.3, 126.4, 125.9 (q, J = 1.2 Hz), 124.8 (q, J = 285.1 Hz), 122.5, 75.7 (q, J = 29.8 Hz), 41.4; ¹⁹F NMR (376 MHz, CDCl₃): δ 72.35 (3F, s); HRMS Calculated for C₉H₈F₃S [M+H–H₂O]⁺: 205.0300; Found: 205.0299. [α]²²⁺D = +52.0 (c = 0.96, CHCl₃) for a 84:16 e.r. sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with an authentic sample of racemic material (Chiralpak AS-H, 98:2 hexanes/i-PrOH, 0.5 mL/min, 220 nm): tR: 16 min (major) and 18 min (minor).
(R)-1,1,1-Trifluoro-2-(thiophen-3-yl)pent-4-en-2-ol (4m, Table 1)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 4m (43.8 mg, 0.197 mmol, 98% yield) as colorless oil. IR (neat): 3540 (br, w), 3115 (w), 3083 (w), 2928 (w), 2265 (m), 1510 (s), 1458 (m), 1432 (m), 1379 (m), 1275 (m), 1226 (m), 754 (s), 724 (s), 688 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.40–7.44 (1H, m), 7.38–7.29 (1H, m), 7.14–7.13 (1H, m), 5.65–5.43 (1H, m), 5.26–5.22 (2H, m), 2.92–2.83 (1H, m), 2.83–2.75 (1H, m), 2.63–2.55 (1H, m); ¹³C NMR (100 MHz, CDCl₃): δ 138.8, 130.4, 126.4, 126.0, 125.2 (q, J = 284.0 Hz), 123.9, 121.9, 75.4 (q, J = 29.1 Hz), 40.7; ¹⁹F NMR (376 MHz, CDCl₃): δ 73.03 (3F, s); HRMS Calculated for C₉H₈F₃S [M+H–H₂O]⁺: 205.0300; Found: 205.0305. [α]₂₂.₀° = +49.4 (c = 1.01, CHCl₃) for a 96.5:3.5 e.r. sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with an authentic sample of racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): t_R: 14 min (major) and 15 min (minor).

(R)-2-Benzyl-1,1,1-trifluoropent-4-en-2-ol (4n, Table 1)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 4n (44.0 mg, 0.191 mmol, 95% yield) as colorless oil. The analytical data are fully consistent with those reported previously.¹⁷ ¹H NMR (500 MHz, CDCl₃): δ 7.46–7.15 (5H, m), 5.92–5.68 (1H, m), 5.24–5.21 (1H, m), 5.15–5.09 (1H, m), 3.12 and 2.90 (2H, ABq, J_AB = 13.8 Hz), 2.52 (2H, dd, J = 14.4, 6.5 Hz), 2.33–2.23 (2H, m), 2.22 (1H, s); HRMS Calcd for C₁₂H₁₁F₃N₁O₁ [M+NH₄]⁺: 248.1262; Found: 248.1261. [α]₂₂.₀° = +52.0 (c = 0.96, CHCl₃) for a 94:6 e.r. sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with an authentic sample of racemic material (Chiralpak AD-H, 97:3 hexanes:i-PrOH, 0.8 mL/min, 220 nm): t_R: 9 min (minor) and 10 min (major).

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(R)-2-cyclohexyl-1,1,1-trifluoropent-4-en-2-ol (4o, Table 1)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 4o (39.1 mg, 0.176 mmol, 88% yield) as colorless oil. IR (neat): 3499 (br, w), 3082 (w), 2931 (s), 2856 (m), 1642 (w), 1452 (m), 1353 (m), 1316 (m), 1269 (m), 1146 (s), 955 (m), 895 (m), 676 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 5.93–5.74 (1H, m), 5.33–5.16 (2H, m), 2.54 (1H, dddt, J = 14.3, 6.4, 1.5, 0.7 Hz), 2.43–2.32 (1H, m), 2.25–2.14 (1H, m), 1.94–1.85 (2H, m), 1.94–1.65 (6H, m), 1.31–1.06 (5H, m); ¹³C NMR (125 MHz, CDCl₃): δ 131.5, 127.9, 125.6, 121.1, 76.5 (q, J = 25.4 Hz), 43.2, 36.5, 27.0–27.1 (m), 26.8, 26.8, 26.5; ¹⁹F NMR (376 MHz, CDCl₃): δ 78.90 (3F, s); HRMS Calcd for C₁₁H₁₈F₃O₁ [M+H⁺]: 223.1310; Found: 223.1303. [α]²²°D = −3.7 (c = 0.98, CHCl₃) for a 88:12 er sample. The enantiomeric purity of this compound was determined by GLC analysis in comparison with authentic racemic material after benzoylation (ChiralDEX CDB/DA column, 15 psi, 100 °C): tₚ: 543 min (major) and 561 min (minor).

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Peak # | Ret. Time | Area | Area % | Peak # | Ret. Time | Area | Area %
--- | --- | --- | --- | --- | --- | --- | ---
1 | 8.1 min | 2681627 | 49.814 | 1 | 9.2 min | 97054 | 6.287
2 | 9.5 min | 2701691 | 50.186 | 2 | 10.8 min | 1446604 | 93.713

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(Rao, W., Koh, M. J., Li, D., Hirao, H. & Chan, P. W. H. J. Am. Chem. Soc. 135, 7926–7932 (2013).
(R)-1,1,2,2-Pentafluoro-3-phenylhex-5-en-3-ol (4p, Table 1)

The title compound was synthesized analogously to 4a except that the amount of aminophenol 1a was 1.0 mol% (vs. 2.5 mol%). The title compound was purified by silica gel chromatography to afford 4p (45.1 mg, 0.169 mmol, 85% yield) as colorless oil. IR (neat): 3551 (br, w), 3068 (br, w), 3032 (w), 2986 (w), 1450 (w), 1339 (w), 1214 (m), 1173 (s), 1173 (s), 1132 (s), 1057 (m), 1001 (s), 983 (w), 937 (w), 849 (w), 765 (w), 713 (s), 699 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.56–7.53 (2H, m), 7.42–7.32 (3H, m), 5.49–5.38 (1H, m), 5.28–5.20 (2H, m), 3.08–3.03 (1H, m), 2.89 (1H, dd, J = 14.2, 8.3 Hz), 2.57 (1H, s); ¹³C NMR (100 MHz, CDCl₃): δ 134.1 (m), 134.1 (m), 131.3 (s), 118.9 (s), 118.9 (s), 107.2 (m), 997 (m), 937 (m), 937 (m), 710 (s) cm⁻¹; ¹⁹F NMR (376 MHz, CDCl₃): δ 74.86 (3F, s), 31.76 and 30.56 (2F, ABq, J_AB = 276.6 Hz); HRMS Calcd for C_{12}H_{10}F_{5} [M+H–H₂O]⁺: 249.0703; Found: 249.0699. [α]^{23.5}_D = +61.7 (c = 1.94, CHCl₃) for a 95:5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AD-H, 99:1 hexanes:i-PrOH, 1.0 mL/min, 220 nm): t_R: 7.2 min (minor) and 7.9 min (major).

| Peak # | Ret. Time | Area % | Area | Peak # | Ret. Time | Area % | Area |
|--------|-----------|--------|------|--------|-----------|--------|------|
| 1      | 7.4 min   | 50.769 | 3831929 | 1      | 7.2 min   | 4.959  | 239927 |
| 2      | 8.1 min   | 49.231 | 3715833 | 2      | 7.9 min   | 95.041 | 4598328 |

(R)-5,5,6,6,7,7-Heptafluoro-4-phenyleth-1-en-4-ol (4q, Table 1)

The title compound was synthesized analogously to 4a except that the amount of aminophenol 1a was 1.0 mol% (vs. 2.5 mol%). The title compound was purified by silica gel chromatography to afford 4q (56.6 mg, 0.179 mmol, 89% yield) as colorless oil. IR (neat): 3553 (br, w), 3068 (w), 1641 (w), 1450 (w), 1341 (m), 1213 (s), 1189 (s), 1116 (s), 1072 (m), 997 (m), 937 (m), 710 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.59–7.56 (2H, m), 7.42–7.34 (3H, m), 5.48–5.38 (1H, m), 5.29–5.20 (2H, m), 5.09–3.03 (1H, m), 2.91 (1H, dd, J = 14.1, 8.4 Hz), 2.65 (1H, s); ¹³C NMR (100 MHz, CDCl₃): Note: Peaks assigned as apparent due to complexity of the spectrum. δ 136.9–136.8, 130.4, 128.6, 128.4, 126.7–126.6, 122.8–121.9 (m), 122.5, 119.7–118.3 (m), 116.5–115.7 (m), 114.0–112.0 (m), 111.2–109.3 (m), 108.5–106.6 (m), 77.0–76.7 (m), 41.0 (t, J = 3.1 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ 71.87–71.81 (3F, m), 35.62 (1F, app. dq, J = 283.6, 19.9, 9.9 Hz), 34.24 (1F, app. dp, J = 283.5, 11.8 Hz), 31.33 (1F, app. ddd, J = 289.5, 11.3, 6.2 Hz), 28.59 (1F, app. dd, J = 289.4, 10.9 Hz); HRMS Calcd for C_{13}H_{10}F_{7} [M+H–H₂O]⁺: 299.0678; Found: 299.0678. [α]^{21.4}_D = +54.9 (c = 2.55, CHCl₃) for a 97:3 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with
authentic racemic material (Chiralpak AD-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): $t_R$: 9.8 min (minor) and 11 min (major).

| Peak # | Ret. Time | Area    | Area % | Peak # | Ret. Time | Area    | Area % |
|--------|-----------|---------|--------|--------|-----------|---------|--------|
| 1      | 9.7 min   | 1844689 | 49.535 | 1      | 9.8 min   | 962667  | 3.651  |
| 2      | 11.0 min  | 1879337 | 50.465 | 2      | 10.8 min  | 25407098| 96.349 |

(R)-1,1,1-Trifluoro-4-methyl-2-phenylpent-4-en-2-ol (5a, Table 1)
The title compound was synthesized analogous to 4a except for the following changes: 1) 2-(2-Methylallyl)boronic acid pinacol ester (60 µL, 0.28 mmol) was used. 2) Reaction temperature was 22 °C. The title compound was purified by silica gel chromatography. Three purifications were needed to obtain analytically pure compound 5a (41.1 mg, 0.179 mmol, 89% yield) as pale yellow oil. IR (neat): 3520 (br, w), 3076 (w), 3034 (w), 2973 (w), 2953 (w), 2924 (w), 1645 (w), 1450 (w), 1378 (w), 1265 (m), 1151 (s), 1073 (m), 911 (m), 721 (m), 699 (s) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62 (2H, d, $J$ = 7.4 Hz), 7.45–7.31 (3H, m), 4.99–4.96 (1H, m), 4.85 (1H, s), 2.97 (1H, app d, $J$ = 13.9 Hz), 2.87–2.83 (1H, m), 2.83 (1H, s), 1.40 (3H, s); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.8, 137.5, 128.6, 128.4, 126.6–126.5 (m), 125.5 (q, $J$ = 285.4 Hz), 118.2, 75.3 (q, $J$ = 28.2), 43.5, 23.9; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ 73.26 (3F, s); HRMS Calcd. for C$_{12}$H$_{12}$F$_3$ [M+H–H$_2$O]$^+$: 213.0891; Found: 213.0896. $[\alpha]_D^{21.0}$ = +88.7 $(c = 1.80$, CHCl$_3$) for a 96.5:3.5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): $t_R$: 11 min (major) and 12 min (minor).
The title compound was synthesized analogous to 4a except for the following changes: 1) 2-(2-chloroallyl)boronic acid pinacol ester (43 μL, 0.22 mmol) was used. 2) The reaction temperature was 22 ºC. The title compound was purified by silica gel chromatography to afford 5b (49.3 mg, 0.197 mmol, 98% yield) as pale yellow oil. IR (neat): 3567 (br, w), 1634 (w), 1451 (w), 1267 (m), 1145 (s), 1074 (m), 1012 (w), 968 (w), 896 (m), 765 (m), 721 (m), 697 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.61–7.58 (2H, m), 7.45–7.36 (3H, m), 5.32–5.30 (1H, m), 5.15 (1H, s), 3.26 and 3.18 (2H, ABq, JAB = 15.2 Hz), 3.09 (1H, s); ¹³C NMR (100 MHz, CDCl₃): δ 135.8, 134.6, 126.9, 128.4, 126.6–126.5 (m), 125.1 (q, J = 286.0 Hz), 118.9, 77.0 (q, J = 28.1 Hz, one peak is overlapping with CDCl₃), 44.4; ¹⁹F NMR (376 MHz, CDCl₃): δ 73.4 (3F, s); HRMS Calcd for C₁₁H₉ClF₃[M+H–H₂O]+: 233.03450; Found: 233.0349.

Peak # | Ret. Time | Area | Area % | Peak # | Ret. Time | Area | Area %
--- | --- | --- | --- | --- | --- | --- | ---
1 | 15.0 min | 2015694 | 49.795 | 1 | 14.9 min | 4093213 | 96.195
2 | 16.2 min | 2032268 | 50.205 | 2 | 16.1 min | 159791 | 3.805

Procedure for small-scale catalytic enantio- and regioselective allenyl additions to fluoroketones and analytical data for the resultant homoallenylic alcohols 6a–6n (Figure 3 & Table 2)

In a nitrogen-filled glove box, 1c (5.1 mg, 0.010 mmol) was added to a two-dram vial equipped with a stir bar and dissolved in 1.0 mL of toluene. A second solution was prepared by dissolving 19.2 mg NaOᵗ-Bu in 8.0 mL toluene. A two-dram vial equipped with a stir bar was charged with 0.2 mL of the solution of 1c (1.5 mg, 0.002 mmol) followed by 0.8 mL of the solution of NaOᵗ-Bu (1.9 mg, 0.02 mmol). This vial was sealed with a cap (phenolic open top cap with a white PFTE/gray silicone septa) and electrical tape and removed from the glove box. Methanol (10 μL, 0.25 mmol), trifluoroacetophenone 3a (28 μL, 0.20 mmol), and allenylboronic acid pinacol ester (40 μL, 0.22 mmol) were added by syringe under N₂ in the stated order and the mixture was allowed to stir at 22 ºC for 4 h after which time the cap was removed and 〈₄⁻trifluorotoluene (24.4 μL, 0.199 mmol) was added as an internal standard. Following ¹⁹F NMR analysis of the reaction mixture, it was passed through a short plug of silica gel (eluted with Et₂O) and concentrated in vacuo being careful not to remove all of the solvent (volatile product). The resulting pale yellow oil was purified by silica gel
chromatography (10 mm diameter column slurry packed with ~2.5 g of silica gel in pentane and eluted with 11:1 pentanes:diethyl ether) to afford 6a (43.0 mg, 0.201 mmol, >98% yield, >98:2 allene:propargyl) as pale yellow oil.

**(R)-1,1,1-Trifluoro-2-phenylpenta-3,4-dien-2-ol (6a, Figure 3a)**

IR (neat): 3548 (br, w), 3065 (w), 1959 (w), 1451 (w), 1264 (m), 1154 (s), 1073 (m), 1059 (m), 910 (m), 855 (m), 761 (m), 708 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.66–7.63 (2H, m), 7.44–7.36 (3H, m), 5.87 (1H, t, J = 6.7 Hz), 5.23–5.13 (2H, m), 2.83 (1H, s); ¹³C NMR (100 MHz, CDCl₃): δ 206.6, 136.9, 129.0, 128.4, 126.7 (q, J = 1.2 Hz), 124.8 (q, J = 285.9 Hz), 93.1, 82.4, 74.7 (q, J = 29.3 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ 73.40 (3F, s); HRMS Calcd for C₁₁H₁₀F₃O [M+H]⁺: 215.0684; Found: 215.0690. [α]²¹_D = +117 (c = 1.88, CHCl₃) for a 95.5:4.5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AS-H, 99:1 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tᵣ: 26 min (major) and 28 min (minor).

| Peak # | Ret. Time | Area  | Area % | Peak # | Ret. Time | Area  | Area % |
|-------|-----------|-------|--------|-------|-----------|-------|--------|
| 1     | 22.0 min  | 5074952| 49.895 | 1     | 25.7 min  | 10937018| 95.233 |
| 2     | 23.4 min  | 5096364| 50.105 | 2     | 28.1 min  | 547521 | 4.767  |

**(R)-1,1,1-Trifluoro-2-(o-tolyl)penta-3,4-dien-2-ol (6b, Figure 3a)**

The title compound was synthesized analogous to 6a and purified by silica gel chromatography to afford 6b (39.4 mg, 0.173 mmol, 86% yield, 98:2 allene:propargyl) as colorless oil. IR (neat): 3537 (br, w), 1958 (w), 1488 (w), 1458 (w), 1363 (w), 1262 (m), 1156 (s), 1078 (w), 1048 (w), 966 (w), 924 (m), 853 (m), 759 (m), 727 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.59 (1H, d, J = 7.8 Hz), 7.32–7.22 (3H, m), 5.82 (1H, s), 5.86–5.82 (1H, m), 5.22–5.12 (2H, m), 2.79–2.78 (1H, m), 2.60 (3H, s); ¹³C NMR (100 MHz, CDCl₃): δ 206.9, 138.4, 134.5, 133.2, 128.9, 128.0–127.9 (m), 125.6, 125.3 (q, J = 286.6 Hz), 93.4–93.3 (m), 81.6, 77.1 (q, J = 29.0 Hz), 22.5–22.4 (m); ¹⁹F NMR (376 MHz, CDCl₃): δ 74.60 (3F, s); HRMS Calcd. for C₁₂H₁₀F₃ [M+H–H₂O]⁺: 211.0735; Found: 211.0744; [α]²²⁵_D = +63.9 (c = 2.19, CHCl₃) for a 95:5 er sample (97:3 ratio of allene to propargyl addition). The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tᵣ: 35 min (minor) and 37 min (major).
The title compound was synthesized analogous to 6a and purified by silica gel chromatography to afford 6c (46.3 mg, 0.190 mmol, 95% yield, >98:2 allene:propargyl) as colorless oil. IR (neat): 3442 (br, w), 1961 (w), 1601 (w), 1585 (w), 1491 (w), 1465 (w), 1239 (s), 1158 (s), 1083 (m), 1050 (m), 1021 (m), 923 (m), 852 (m), cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.51–7.46 (1H, m), 7.39–7.34 (1H, m), 7.05–6.98 (2H, m), 5.82 (1H, s), 5.79 (1H, t, \(J = 6.8\) Hz), 5.10–4.99 (2H, m), 3.93 (1H, s); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 208.0, 158.0, 130.5, 130.1 (q, \(J = 1.2\) Hz), 125.1 (q, \(J = 287.2\) Hz), 124.8, 121.4, 112.5, 92.0 (q, \(J = 1.2\) Hz), 79.9, 77.5 (q, \(J = 29.4\) Hz), 56.3; \(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) 73.95 (3F, s); HRMS Calcd for C\(_{12}\)H\(_{10}\)F\(_3\)O \([\text{M+H–H}_2\text{O}]^+\): 227.0684; Found: 227.0688. \([\alpha]_{D}^{23}\) = +27.9 (\(c = 1.79\), CHCl\(_3\)) for a 97.5:2.5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t_R\) : 29 min (minor) and 40 min (major).

(R)-1,1,1-Trifluoro-2-(2-methoxyphenyl)penta-3,4-dien-2-ol (6c, Figure 3a)

(R)-1,1,1-Trifluoro-2-(4-fluorophenyl)penta-3,4-dien-2-ol (6d, Table 2)

The title compound was synthesized analogous to 6a and purified by silica gel chromatography to afford 6d (38.7 mg, 0.167 mmol, 83% yield, >98:2 allene:propargyl) as colorless oil. IR (neat): 3568 (br, w), 3490 (w, br), 3490 (w, br), 1958 (w), 1604 (w), 1510 (m), 1235 (m), 1156 (s), 1077 (m), 976 (w), 924 (m),
857 (m), 833 (s), 816 (m), 520 (m) cm⁻¹; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.62–7.59 (2H, m), 7.11–7.06 (2H, m), 5.82 (1H, t, \(J = 6.8\) Hz), 5.24–5.13 (2H, m), 2.80–2.79 (1H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 206.7, 163.1 (d, \(J = 248.0\) Hz), 132.7 (d, \(J = 3.1\) Hz), 128.9–128.6 (m), 124.7 (q, \(J = 285.2\) Hz, most downfield peak of quartet is overlapping with previous multiplet), 115.3 (d, \(J = 29.6\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ 73.19 (3F, s), 39.6–39.7 (1F, m); HRMS Calcd for C\(_{11}\)H\(_7\)F\(_3\) [M+H–H\(_2\)O]⁺: 215.0484; Found: 215.0490.

\([\alpha]^{D}_{22}\) = +124 (c = 2.01, CHCl\(_3\)) for a 97.5:2.5 er sample.

The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AS-H, 99:1 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t_R\): 20 min (major) and 22 min (minor).

| Peak # | Ret. Time | Area   | Area % | Peak # | Ret. Time | Area   | Area % |
|--------|-----------|--------|--------|--------|-----------|--------|--------|
| 1      | 21.3 min  | 12075799 | 50.224 | 1      | 20.6 min  | 19950901 | 97.444 |
| 2      | 23.0 min  | 11968299 | 49.776 | 2      | 22.2 min  | 523388  | 2.556  |

(R)-2-(4-(Dimethylamino)phenyl)-1,1,1-trifluoropenta-3,4-dien-2-ol (6e, Table 2)

The title compound was synthesized analogous to 6a except the substrate was weighed out into the reaction vessel before any other components were added. The title compound was purified by silica gel chromatography to afford 6e (49.6 mg, 0.193 mmol, 96% yield, >98:2 allene:propargyl) as white solid. M.p = 63–65 ºC. IR (neat): 3208 (br, w), 3005 (w), 2978 (w), 2894 (w), 2855 (w), 2815 (w), 2851 (w), 1976 (w), 1948 (w), 1608 (w), 1515 (w), 1474 (w), 1387 (w), 1313 (w), 1237 (w), 1189 (m), 1151 (s), 1125 (s), 1089 (m), 1047 (w), 976 (w), 924 (m), 859 (m), 826 (m), 815 (m), 740 (w), 699 (s) cm⁻¹; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.47 (2H, d, \(J = 9.2\) Hz), 6.72 (2H, d, \(J = 9.2\) Hz), 5.84 (1H, t, \(J = 6.7\) Hz), 5.20–5.10 (2H, m), 2.97 (6H, s), 2.73 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 206.6, 150.7, 127.6–127.5 (m), 125.0 (q, \(J = 285.8\) Hz), 124.2, 111.9, 93.2–93.1 (m), 81.9, 74.6 (q, \(J = 29.3\) Hz), 40.5, 40.4; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ 73.11 (3F, s); HRMS Calcd. for C\(_{13}\)H\(_{15}\)F\(_3\)NO [M+H]⁺: 258.1106; Found: 258.1093; \([\alpha]^{D}_{218}\) = +165 (c = 1.70, CHCl\(_3\)) for a 96:4 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AD-H, 97:3 hexanes:i-PrOH, 0.7 mL/min, 220 nm): \(t_R\): 21 min (major) and 23 min (minor).
Table 2: Retention times and areas for compounds.

| Peak # | Ret. Time | Area  | Area % | Peak # | Ret. Time | Area  | Area % |
|--------|-----------|-------|--------|--------|-----------|-------|--------|
| 1      | 21.2 min  | 1682618 | 49.959 | 1      | 20.8 min  | 10436412 | 96.351 |
| 2      | 24.8 min  | 1685397 | 50.041 | 2      | 24.3 min  | 395212  | 3.649  |

(R)-1,1,1-Trifluoro-2-(4-(trifluoromethyl)phenyl)penta-3,4-dien-2-ol (6f, Table 2)

The title compound was synthesized analogous to 6a and purified by silica gel chromatography to afford 6f (55.0 mg, 0.195 mmol, 97% yield, >98:2 allene:propargyl) as clear oil. IR (neat): 3567 (br, w), 1937 (w), 1621 (w), 1414 (w), 1325 (s), 1262 (m), 1160 (s), 1113 (s), 1067 (s), 1019 (m), 977 (m), 928 (m), 837 (s), 762 (w), 706 (m), 626 (w), 418 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.76 (2H, d, J = 8.4 Hz), 7.67 (2H, d, J = 8.4 Hz), 5.84 (1H, t, J = 6.7 Hz), 5.23 (1H, dd, J = 12.0, 6.7 Hz), 5.17 (1H, dd, J = 12.0, 6.6 Hz), 2.87 (1H, s); ¹³C NMR (125 MHz, CDCl₃): δ 206.74, 140.76, 131.18 (q, J = 32.6 Hz), 125.36 (app d, J = 3.4 Hz), 124.52 (q, J = 284.4 Hz), 122.97 (q, J = 270.8 Hz), 92.65, 82.80, 74.65 (q, J = 29.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ 90.04 (3F, s), 73.43 (3F, s); HRMS Calcd. for C₁₂H₇F₆ [M+H–H₂O]⁺: 265.0452; Found: 265.0454; [α]²⁰°D = +108.9 (c = 1.54, CHCl₃) for a 96.5:3.5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tₘ : 13 min (major) and 15 min (minor).
(R)-1,1,1-trifluoro-2-(furan-2-yl)penta-3,4-dien-2-ol (6g, Table 2)

The title compound was synthesized analogous to 6a and purified by silica gel to afford 6g (38.0 mg, 0.186 mmol, 93% yield, >98:2 allene:propargyl) as clear oil. IR (neat): 3491(br, w), 1979 (w), 1701 (w), 1612 (w), 1449 (w), 1264 (m), 1227 (w), 1147 (s), 1083 (m), 1067 (m), 1011 (m), 953 (m), 876 (m), 854 (m), 741 (s), 655 (w), 596 (m) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.46 (1H, dd, \(J = 1.8, 0.9\) Hz), 6.54 (1H, dd, \(J = 3.3, 0.9\) Hz), 6.41 (1H, dd, \(J = 3.4, 1.8\) Hz), 5.74 (1H, t, \(J = 6.7\) Hz), 5.25–5.15 (2H, m), 2.94 (1H, s); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 207.2, 149.4, 143.6, 124.0 (q, \(J = 286.0\) Hz), 110.8, 109.7, 82.3, 72.4 (q, \(J = 31.0\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) 73.09 (3F, s); HRMS Calcd. for C\(_9\)H\(_6\)F\(_3\)O\(_1\) [M+H–H\(_2\)O]\(^+\): 187.0371; Found: 187.0373; \([\alpha]_{22.0}^D = +112.3\) (c = 1.98, CHCl\(_3\)) for a 95:5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 99:1 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t_R\) : 82 min (major) and 92 min (minor).

### Peak Table

| Peak # | Ret. Time | Area    | Area % | Peak # | Ret. Time | Area    | Area % |
|--------|-----------|---------|--------|--------|-----------|---------|--------|
| 1      | 83.6 min  | 3913497 | 49.908 | 1      | 82.2 min  | 47202728| 94.569 |
| 2      | 91.2 min  | 3927962 | 50.092 | 2      | 91.8 min  | 2710810 | 5.431  |

(R)-1,1,1-trifluoro-2-(furan-3-yl)penta-3,4-dien-2-ol (6h, Table 2)

The title compound was synthesized analogous to 6a and purified by silica gel to afford 6h (37.5 mg, 0.182 mmol, 91% yield, >98:2 allene:propargyl) as clear oil. IR (neat): 3383(br, w), 2981 (w), 1960 (w), 1504 (w), 1474 (w), 1373 (w), 1162 (s), 1086 (m), 1070 (m), 1029 (m), 980 (m), 850 (s), 800 (m), 729 (m), 671 (m), 601 (m) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.56 (1H, s), 7.43 (1H, t, \(J = 1.6\) Hz), 6.50 (1H, s), 5.65 (1H, t, \(J = 6.6\) Hz), 5.23–5.13 (2H, m), 2.70 (1H, s); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 206.9, 143.6, 141.3, 124.6 (q, \(J = 283.8\) Hz), 123.3, 109.2, 92.1, 82.4, 71.9 (q, \(J = 30.7\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) 72.63 (3F, s); HRMS Calcd. for C\(_9\)H\(_6\)F\(_3\)O\(_1\) [M+H–H\(_2\)O]\(^+\): 187.0371; Found: 187.0373; \([\alpha]_{22.0}^D = +53.85\) (c = 1.43, CHCl\(_3\)) for a 98:2 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AZ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t_R\) : 22 min (major) and 26 min (minor).
(S)-1,1,1-Trifluoro-2-(thiophen-2-yl)penta-3,4-dien-2-ol (6i, Table 2)
The title compound was synthesized analogous to 6a and purified by silica gel to afford 6i (40.3 mg, 0.183 mmol, 92% yield, >98:2 allene:propargyl) as pale yellow oil. IR (neat): 3534 (br, w), 1980 (w), 1959 (w), 1434 (w), 1267 (w), 1164 (s), 1078 (w), 1047 (w), 996 (w), 890 (w), 853 (m), 716 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.37–7.35 (1H, m), 7.22–7.20 (1H, m), 7.06–7.03 (1H, m), 5.81 (1H, t, J=6.7 Hz), 5.27–5.18 (2H, m), 2.99 (1H, s); ¹³C NMR (100 MHz, CDCl₃): δ 206.5, 140.6, 127.2, 126.6, 126.5–126.4 (m), 124.3 (q, J = 285.6 Hz), 93.0, 82.9, 74.0 (q, J = 31.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ 72.80 (3F, s); HRMS Calcd. for C₉H₆F₃S [M+H–H₂O]⁺: 203.0142; Found: 203.0138; [α]²².⁴D = +104 (c = 2.30, CHCl₃) for a 91.5:8.5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tᵣ : 22 min (major) and 23 min (minor).
(R)-1,1,1-Trifluoro-2-(thiophen-3-yl)penta-3,4-dien-2-ol (6j, Table 2)

The title compound was synthesized analogous to 6a and purified by silica gel chromatography to afford 6j (38.7 mg, 0.176 mmol, 88% yield, >98:2 allene:propargyl) as colorless oil. IR (neat): 3540 (br, w), 3115 (w), 3083 (w), 2928 (w), 1275 (m), 1226 (w), 1150 (s), 1086 (m), 1019 (m), 995 (m), 920 (m), 854 (s), 724 (s), 688(s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.56–7.42 (1H, m), 7.42–7.29 (1H, m), 7.25–7.13 (1H, m), 5.76 (1H, t, J = 6.7 Hz), 5.28–5.05 (2H, m), 2.80 (1H, s); ¹³C NMR (100 MHz, CDCl₃): δ 206.6, 138.2, 126.2–126.1 (m), 124.6 (q, J = 285.5 Hz), 124.1 (m), 92.8–92.7 (m), 82.4, 73.9 (q, J = 30.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ 72.81; HRMS Calculated for C₉H₆F₃S [M+H–H₂O]⁺: 203.0142; Found: 203.0148. [α]D²³ = +82 (c = 0.97, CHCl₃) for a >99:1 e.r. sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with an authentic sample of racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tR: 19 min (major) and 20 min (minor).

(S,E)-1-Phenyl-3-(trifluoromethyl)hexa-1,4,5-trien-3-ol (6k, Table 2)

The title compound was synthesized analogous to 6a and purified by silica gel chromatography to afford 6k (38.7 mg, 0.176 mmol, 88% yield, >98:2 allene:propargyl) as colorless oil. IR (neat): 3440 (br, w), 3029 (w), 1965 (s), 1254 (m), 1161 (s), 963 (s), 854 (m), 748 (s), 690 (s), 500 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.47–7.40 (2H, m), 7.40–7.32 (2H, m), 7.32–7.27 (1H, m), 6.97 (1H, d, J = 16.0 Hz), 6.29 (1H, d, J = 15.9 Hz), 5.55 (1H, t, J = 6.7 Hz), 5.18 (2H, d, J = 6.7 Hz), 2.54 (1H, s); ¹³C NMR (100 MHz, CDCl₃): δ 207.22, 135.77, 133.56, 128.84, 128.12, 127.07, 124.7 (q, J = 284 Hz), 123.92, 109.53, 91.51, 83.40, 81.76, 74.1 (q, J = 29 Hz), 29.85, 24.65; ¹⁹F NMR (376 MHz, CDCl₃): δ 72.06 (3F, s); HRMS Calculated for C₁₃H₁₃F₃ [M+H–H₂O]⁺: 223.0727; Found: 223.0735; [α]D²³ = +173.3 (c = 0.98, CHCl₃) for a 95:5 e.r sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with an authentic sample of racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tR: 19 min (major) and 20 min (minor).
(S)-2-Benzyl-1,1,1-trifluoropenta-3,4-dien-2-ol (6l, Table 2)

The title compound was synthesized analogous to 6a and purified by silica gel chromatography to afford 6l (43.8 mg, 0.192 mmol, 96% yield, >98:2 allene:propargyl) as pale yellow oil. IR (neat): 3549 (br, w), 3066 (w), 1947 (w), 1456 (w), 1273 (m), 1164 (s), 1124 (m), 1088 (m), 1032 (m), 969 (m), 857 (m), 714 (m), 698 (s) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.33–7.21 (5H, m), 5.34–5.30 (1H, m), 5.02–4.97 (1H, m), 4.83–4.78 (1H, m), 3.18 (1H, d, \(J = 14.0\) Hz), 2.94 (1H, d, \(J = 13.6\) Hz), 2.29–2.27 (1H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 206.9, 134.0, 131.2, 128.2, 127.3, 125.4 (q, \(J = 285.7\) Hz), 91.3–91.2 (m), 81.5, 74.1 (q, \(J = 28.1\) Hz), 40.0; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) 71.86 (3F, s); HRMS Calcd. for C\(_{12}\)H\(_{12}\)F\(_3\)O [M+H]\(^+\): 229.0840; Found: 229.0849. \([\alpha]^{22.0}_{D} = +42.6\) (c = 1.64, CHCl\(_3\)) for a 94:6 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t_R\): 14 min (minor) and 15 min (major).

(S)-2-Cyclohexyl-1,1,1-trifluoropenta-3,4-dien-2-ol (6m, Table 2)

The title compound was synthesized analogous to 6a and purified by silica gel chromatography to afford 6m (43.8 mg, 0.192 mmol, 96% yield, >98:2 allene:propargyl) as a clear colorless oil. IR (neat): 3568 (br, w), 3484 (br, w), 2929 (s), 2856 (m), 1960 (w), 1453 (m), 1358 (s), 1154 (s), 1092 (m), 916
(m), 776 (m) cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 5.35 (1H, t, \(J = 6.7\) Hz), 5.14 (2H, d, \(J = 6.4\) Hz), 2.33 (1H, s), 1.93 (1H, d, \(J = 12.8\) Hz), 1.90–1.75 (3H, m), 1.68 (1H, d, \(J = 12.6\) Hz), 1.33–1.01 (6H, m); \(^13\)C NMR (125 MHz, CDCl₃): \(\delta\) 206.6, 125.7 (q, \(J = 287.2\) Hz), 90.5 (q, \(J = 2.1\) Hz), 81.7, 75.8 (q, \(J = 26.9\) Hz), 42.7, 27.2 (q, \(J = 12.8\) Hz), 26.5, 26.4, 26.3, 26.2; \(^19\)F NMR (376 MHz, CDCl₃): \(\delta\) 76.34 (3F, s); HRMS Calcd for C₁₁H₁₆F₃O \([\text{M+H}]^+\): 221.1153; Found: 221.1146. 

\([\alpha]_D^{20.0}\) for a 94:6 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material after benzoylation\(^17\) (Chiralpak AD-H, 99.5:0.5 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t_R\): 24 min (minor) and 25 min (major).

| Peak # | Ret. Time | Area | Area % |
|--------|-----------|------|--------|
| 1      | 23.9 min  | 38571019 | 48.346 |
| 2      | 25.0 min  | 41209647 | 51.654 |

\((R)-1,1,1,2,2\)-Pentafluoro-3-phenylhexa-4,5-dien-3-ol (6n, Table 2)

The title compound was synthesized analogous to 6a and purified by silica gel chromatography to afford 6n (46.3 mg, 0.175 mmol, 88% yield, >98:2 allene:propargyl) as pale yellow oil. IR (neat): 3559 (br, w), 1959 (w), 1496 (w), 1451 (w), 1336 (m), 1213 (s), 1172 (s), 1138 (s), 1060 (s), 869 (s), 715 (s), 697 (s) cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.64–7.61 (2H, m), 7.44–7.35 (3H, m), 5.99 (1H, t, \(J = 6.6\) Hz), 5.25 (1H, dd, \(J = 11.7, 6.7\) Hz), 5.16 (1H, dd, \(J = 11.7, 6.6\) Hz), 2.85 (1H, s); \(^13\)C NMR (100 MHz, CDCl₃): \(\delta\) 205.9, 137.1, 128.9, 128.4, 126.6 (t, \(J = 1.9\) Hz), 119.3 (qt, \(J = 288.4, 36.3\) Hz), 113.9 (tq, \(J = 261.9, 34.4\) Hz), 93.8–93.7 (m), 83.2, 74.2 (t, \(J = 23.9\) Hz); \(^19\)F NMR (376 MHz, CDCl₃): \(\delta\) 75.11 (3F, s), 30.2 and 29.9 (2F, ABq, \(J_{AB} = 276.8\) Hz); HRMS Calcd. for C₁₂H₁₀F₅O \([\text{M+H}]^+\): 265.0652; Found: 265.0653. \([\alpha]^{22.0}_{D}\) = 135 (c = 1.99, CHCl₃) for a 97:3 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t_R\): 32 min (minor) and 35 min (major).
**Procedure for gram-scale catalytic enantioselective allenyl addition to ketone to afford homoallenylalcohol 6c (Equation 1)**

A vial (8 mL, oven-dried, equipped with a magnetic stirring bar) was charged with NaOt-Bu (57.6 mg, 0.60 mmol) and aminophenol 1c (30.0 mg, 0.06 mmol) and sealed with a rubber septum. The vial was evacuated and charged with dry N₂. Toluene (3.00 mL) was added and stirred for 10 min. A round-bottom flask (50 mL, flame dried, equipped with a magnetic stirring bar) was sealed with a rubber septum and purged with dry N₂. Toluene (20 mL) was added. A 2.50 ml of the mixture of the NaOt-Bu (48 mg, 0.5 mmol, 10 mol%) and aminophenol 1c (25.2 mg, 0.05 mmol, 1.0 mol%) was added through a syringe to the round-bottom flask. MeOH (263 µl, 6.5 mmol, 1.3 equiv) from a septum-sealed bottle (Acros, 99.9% ExtraDry, used as received), 2'-methoxy-2,2,2-trifluoroacetophenone (785 µL, 5.00 mmol, Oakwood Chemicals, used as received) and allenylboronic acid pinacol ester (989 µL, 5.50 mmol, 1.1 equiv.) from a septum-sealed bottle (Frontier Scientific, used as received) are added sequentially. After four hours, the solvent was evaporated and the pale yellow oil residue was passed through silica gel using a fritted funnel. The resulting pale yellow oil was purified by Kugelrohr distillation under 0.5 torr at 105 ºC. The product was obtained in 96% yield (1.17 g, 4.79 mmol, 98:2 er, >98:2 allene:propargyl) as colorless oil.

**Procedure for small-scale catalytic enantioselective allyl and allenyl additions to perfluoroalkyl ketones to afford homoallylic alcohols 7–14,16 and homoallenyl alcohol 15 (Figure 4)**

1-Fluoro-2-phenylpent-4-en-2-ol (7, Figure 4a)

The title compound was synthesized analogously to 4a except for the following changes: 1) Reaction time was 16 h. 2) Reaction temperature was 22 ºC. The title compound was purified by silica gel chromatography to afford 7 (31.3 mg, 0.174 mmol, 87% yield) as colorless oil. IR (neat): 3565 (br, w), 3465 (br, w), 3064 (w), 2980 (w), 1707 (m), 1640 (w), 1600 (w), 1495 (w), 1448 (m), 1233 (m), 1089 (m), 1071 (s), 998 (m), 967 (s), 761 (m), 700 (s), 638 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.47–7.46 (2H, m), 7.40–7.36 (2H, m), 7.34–7.27 (1H, m), 5.75–5.52 (1H, m), 5.25–5.05 (2H, m), 4.49 (2H, d, J = 47.7 Hz), 2.74–2.71 (2H, m), 2.44 (1H, s); ¹³C NMR (100 MHz, CDCl₃): δ 141.7, 132.4, 128.6,
127.7, 125.7, 120.1, 88.6 (d, \(J = 177.0\) Hz), 75.2 (d, \(J = 18.0\) Hz), 42.6; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta -71.90\) (1F, t, \(J = 47.2\) Hz); HRMS Calculated for C\(_{11}\)H\(_{11}\)F \([M+H–H\_2O]^+\): 163.0923; Found: 163.0925; \([\alpha]^{23.0}\)_D = −14.9 (c = 1.82, CHCl\(_3\)) for a 65:35 e.r. sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with an authentic sample of racemic material (Chiralpak AZ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t_R\): 16 min (major) and 19 min (minor).

### 1,1-Difluoro-2-phenylpent-4-en-2-ol (8, Figure 4a)

The title compound was synthesized analogous to 4a except for the following changes: 1) Reaction time was 16 h. 2) Reaction temperature was 22 °C. The title compound was purified by silica gel chromatography to afford 8 (38.3 mg, 0.194 mmol, 97% yield) as colorless oil. IR (neat): 3555 (br, w), 3079 (w), 2980 (w), 1641 (w), 1496 (w), 1448 (m), 1346 (m), 1125 (m), 1063 (s), 996 (m), 970 (m), 923 (m), 763 (m), 699 (s), 643 (m), 563 (m) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.52\) (2H, dd, \(J = 3.6, 1.6\) Hz), 7.42–7.34 (2H, m), 7.33–7.31 (1H, m); 5.74 (1H, t, \(J = 56.4\)), 5.67–5.56 (1H, m), 5.25–5.17 (2H, m), 2.88 (1H, dd, \(J = 14.0, 8.0\) Hz), 2.74 (1H, dd, \(J = 14.3, 8.1\) Hz), 2.42 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 138.9, 131.4, 128.6, 128.3, 126.4, 121.2, 117.0\) (t, \(J = 248.9\)Hz), 75.6 (t, \(J = 21.2\) Hz), 39.8 (t, \(J = 2.3\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta 23.72\) and 22.07 (2F, d of ABq, \(2J_{F-F} = 277.9\) Hz, \(2J_{F-H} = 56.0\) Hz); HRMS Calculated for C\(_{11}\)H\(_{13}\)F\(_2\) \([M+H–H\_2O]^+\): 181.0828; Found: 181.0829. \([\alpha]^{21.0}\)_D = +9.88 (c = 1.01, CHCl\(_3\)) for a 58:42 e.r. sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with an authentic sample of racemic material (Chiralpak AS-H, 99:1 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \(t_R\): 20 min (major) and 21 min (minor).
(S)-2,2-Difluoro-3-phenylhex-5-en-3-ol (9, Figure 4a)

The title compound was synthesized analogous to 4a except for the following changes: 1) Reaction time was 16 h. 2) Reaction temperature was 22 ºC. The title compound was purified by silica gel chromatography to afford 9 (42.5 mg, 0.200 mmol, >98% yield) as colorless oil. IR (neat): 3555 (br, w), 3078 (w), 3010 (w), 2982 (w), 2950 (w), 1640 (w), 1497 (w), 1448 (w), 1385 (w), 1203 (m), 1142 (s), 1069 (m), 925 (s), 763 (m), 669 (s), 617 (m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.57–7.54 (2H, m), 7.39–7.29 (3H, m), 5.57–5.46 (1H, m), 5.22–5.12 (2H, m), 3.01 (1H, dd, J = 14.2, 6.0 Hz), 2.82 (1H, dd, J = 14.4, 8.5 Hz), 2.39 (1H, s), 1.41 (3H, t, J = 19.2 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 139.8 (app d, J = 3.8 Hz), 132.4, 128.3, 127.7, 126.6 (m), 124.6 (t, J = 247.6 Hz), 120.7, 77.3 (dd, J = 27.4, 25.1 Hz), 39.8 (t, J = 27.4, 25.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃): 50.73 and 49.35 (2F, q of ABq, Jᵢ=F = 245.2 Hz, Jᵢ=H = 19.0 Hz); HRMS Calcd. for C₁₂H₁₃F₂O [M−H]: 211.0935; Found: 211.0926; [α]²²D = +47.2 (c = 2.33, CHCl₃) for a 79:21 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tᵣ: 15 min (minor) and 18 min (major).

(5)-1-Allyl-2,2-difluoro-1,2,3,4-tetrahydronaphthalen-1-ol (10, Figure 4a)

The title compound was synthesized analogous to 4a except for the following changes: 1) Reaction time was 16 h. 2) Reaction temperature was 22 ºC. 3) The substrate was weighed out into the reaction vessel before any other components were added. The title compound was purified by silica gel chromatography. Three purifications were needed to obtain analytically pure 10 as colorless oil (35.1 mg, 0.156 mmol, 78% yield). IR (neat): 3587 (br, w), 3459 (br, w), 3076 (w), 3023 (w), 2948 (w), 2855 (w), 1640 (w), 1489 (w), 1454 (w), 1364 (w), 1340 (w), 1212 (w), 1146 (m), 1087 (m), 1057 (s), 1001

| Peak # | Ret. Time | Area  | Area % | Peak # | Ret. Time | Area  | Area % |
|--------|-----------|-------|--------|--------|-----------|-------|--------|
| 1      | 15.3 min  | 8897371 | 50.524 | 1      | 14.8 min  | 4666461 | 21.344 |
| 2      | 18.1 min  | 8712685 | 49.476 | 2      | 17.5 min  | 17196983 | 78.656 |
(m), 959 (s), 915 (m), 758 (s), 731 (s), 655 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.58–7.57 (1H, m), 7.29–7.23 (2H, m), 7.13–7.11 (1H, m), 5.78–5.68 (1H, m), 5.13–5.06 (2H, m), 3.12–2.97 (2H, m), 2.78 (1H, dd, J = 14.5, 6.1 Hz), 2.65 (1H, dd, J = 14.5, 8.5 Hz), 2.55 (1H, app d, J = 3.3 Hz), 2.46–2.30 (2H, m); ¹³C NMR (100 MHz, CDCl₃): δ 136.7 (app d, J = 3.8 Hz), 133.9 (app d, J = 1.6 Hz), 133.0, 128.3, 128.1, 127.3 (app d, J = 1.5 Hz ), 123.2 (dd, J = 250.2, 241.9 Hz), 119.3, 74.4 (dd, J = 23.7, 21.4 Hz), 28.4 (dd, J = 24.8, 23.3 Hz), 26.3 (dd, J = 7.6, 3.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ 43.27–43.16 and 42.63–42.53 (1F, m), 41.27–41.20 and 40.62–40.58 (1F, m); HRMS Calcd. for C₁₁H₁₃F₂ [M+H–H₂O⁺]: 207.0985; Found: 207.0986; [α] ²²_D +36.8 (c = 1.90, CHCl₃) for a 94:6 er sample.

The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): t_R: 26 min (major) and 44 min (minor).

2-(2-Fluorophenyl)pent-4-ene-2-ol (12, Figure 4b)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 12 (36.6 mg, 0.203 mmol, >98% yield) as colorless oil. The analytical data are fully consistent with those reported previously.¹⁹ ¹H NMR (400 MHz, CDCl₃): δ 7.56–7.52 (1H, m), 7.27–7.21 (1H, m), 7.15–7.11 (1H, m), 7.02 (2H, ddd, J = 12.2, 8.1, 1.3 Hz), 5.63–5.53 (1H, m), 5.17–5.09 (2H, m), 2.90 (1H, ddq, J = 13.8, 6.3, 1.2 Hz), 2.54 (1H, ddq, J = 13.8, 8.5, 0.9 Hz), 2.28 (1H, d, J = 1.8 Hz), 1.61 (3H, d, J = 1.1 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ 39.75 (1F, s); HRMS Calcd. for C₁₁H₁₂F [M+H–H₂O⁺]: 163.0923; Found: 163.0920; [α] ²⁴_D = −15.4 (c = 1.30, CHCl₃) for a 58:42 er sample.

The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AD-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): t_R: 17 min (minor) and 18 min (major).

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(19) Schneider, U., Ueno, M., Kobayashi, S. J. Am. Chem. Soc. 130, 13824–13825 (2008).
(S)-2-(2,6-Difluorophenyl)pent-4-ene-2-ol (13, Figure 4b)

The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 13 (14.6 mg, 0.074 mmol, 74% yield) as yellow oil. IR (neat): 3629 (br, w), 3484 (br, w), 2981 (w), 2943 (br, w), 1621 (m), 1574 (w), 1462 (s), 1351 (m), 1286 (m), 1262 (m), 1223 (m), 985 (s), 918 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.22–7.15 (1H, m), 6.90–6.82 (2H, m), 5.77–5.66 (1H, m), 5.14–5.09 (2H, m), 2.63 (1H, app ddt, J = 13.8, 6.4, 1.3 Hz), 2.47 (1H, app ddt, J = 13.8, 8.3, 1.0 Hz), 2.06 (1H, s), 1.71–1.70 (3H, m); ¹³C NMR (100 MHz, CDCl₃): δ 160.7 (dd, J = 247.0, 8.9 Hz), 133.4, 128.6 (t, J = 11.9 Hz), 122.1 (t, J = 13.7 Hz), 116.4, 112.9–112.6 (m), 74.9 (t, J = 2.8 Hz), 47.8 (t, J = 2.7 Hz), 28.8 (t, J = 4.8 Hz); ¹⁹F NMR (376 MHz, CDCl₃): 42.75–42.69 (2F, m); HRMS Calcd. for C₁₁H₁₁F₂ [M+H–H₂O⁺]: 181.0829; Found: 181.0830; [α]D²³ = –79.9 (c = 0.25, CHCl₃) for a 94.5:5.5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 99:1 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tₚ: 13 min (major) and 14 min (minor).

(S)-2-(Perfluorophenyl)pent-4-en-2-ol (14, Figure 4b)

The title compound was synthesized analogously to 4a and purified by silica gel chromatography to afford 14 (21.3 mg, 0.085 mmol, 85% yield) as colorless oil. IR (neat): 3466 (br, w), 2985 (w), 1650 (w), 1523 (m), 1483 (s), 1348 (w), 1305 (w), 1099 (m), 982 (s), 923 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 5.74–5.63 (1H, m), 5.20–5.14 (2H, m), 2.84–2.78 (2H, m), 2.56 (1H, dd, J = 13.9, 8.2 Hz),...
1.72 (3H, t, J = 2.1 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 146.3–145.9 (m), 143.8–143.5 (m), 141.4–141.1 (m), 139.4–139.0 (m), 138.9–138.5 (m), 136.9–136.6 (m), 132.3, 120.8, 120.1–119.8 (m), 75.5, 47.5 (t, J = 2.6 Hz), 28.9 (t, J = 4.3 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): δ 12.33 (2F, d, J = 18.8 Hz), –3.09 (1F, tt, J = 21.1, 2.5 Hz), –9.02––9.15 (2F, m); HRMS Calcd. for C$_{11}$H$_8$F$_5$[M+–H$_2$O]$^+$: 235.0546; Found: 235.0548; [$\alpha$]$^D_{21.5}$ = –6.49 (c = 1.54, CHCl$_3$) for a 95:5 er sample.

The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AD-H, 97.5:2.5 hexanes:i-PrOH, 0.5 mL/min, 220 nm): $t_R$ : 6.8 min (major) and 7.5 min (minor).

| Peak # | Ret. Time | Area | Area % | Peak # | Ret. Time | Area | Area % |
|--------|-----------|------|--------|--------|-----------|------|--------|
| 1      | 6.8 min   | 3208722 | 49.024 | 1      | 6.8 min   | 5530739 | 95.203 |
| 2      | 7.6 min   | 3336514 | 50.976 | 2      | 7.5 min   | 278683  | 4.797  |

(S)-2-(Perfluorophenyl)penta-3,4-dien-2-ol (15, Figure 4b)

The title compound was synthesized analogous to 6a except for the following changes: 1) The amount of NaOt-Bu was 20 mol% (vs. 10 mol%). 2) The amount of aminophenol 1c was 2.5 mol%. 3) i-PrOH was used (vs. MeOH). The title compound was purified by silica gel chromatography to afford 15 (46.5 mg, 0.186 mmol, 93% yield, >98:2 allene:propargyl) as colorless oil. IR (neat): 3438 (br, w), 2991 (w), 1958 (w), 1650 (m), 1523 (s), 1485 (s), 1302 (m), 1214 (m), 1080 (m), 984 (s), 857 (m), 741 (m) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ 5.61 (1H, tt, J = 6.6, 1.1 Hz), 5.03–4.89 (2H, m), 2.93 (1H, s), 1.84 (3H, t, J = 2.7 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 205.4, 146.6–145.9 (m), 143.9–143.7 (m), 142.0–141.2 (m), 139.7–138.6 (m), 136.7, 119.7–119.4 (m), 99.0, 80.6, 73.5, 29.2 (app t, J = 5.0 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): δ 13.45 (2F, d, J = 22.9 Hz), –2.55 (1F, app t, J = 21.8 Hz), –8.92––9.15 (2F, m); HRMS Calcd. for C$_{11}$H$_8$F$_5$[M+H]$^+$: 251.0495; Found: 251.0496; [$\alpha$]$^{22.5}$ = –19.96 (c = 1.00, CHCl$_3$) for a 90:10 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AD-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): $t_R$ : 16 min (minor) and 21 min (major).
The title compound was synthesized analogous to 4a and purified by silica gel chromatography to afford 16 (39.2 mg, 0.128 mmol, 64% yield) as colorless oil. IR (neat): 3632 (br, w), 1652 (w), 1528 (m), 1489 (s), 1355 (m), 1323 (m), 1180 (s), 1154 (s), 1120 (s), 1084 (m), 1025 (w), 983 (s), 930 (m), 824 (m), 745 (m), 713 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 5.80–5.67 (1H, m), 5.32 (1H, d, J = 16.8 Hz), 5.20 (1H, d, J = 10.2 Hz), 3.67 (1H, td, J = 7.0, 2.3 Hz), 3.30–3.16 (1H, m), 2.78 (1H, dd, J = 14.8, 5.7 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 147.6–147.3 (m), 145.1–144.8 (m), 143.2–142.8 (m), 140.6–140.2 (m), 139.7–139.3 (m), 137.2–136.7 (m), 130.04, 124.7 – 123.1 (m), 78.45 (q, J = 31.3 Hz), 38.5 (app t, J = 5.5 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ 70.96 (3F, t, J = 7.5 Hz), 14.75 (2F, s), 1.75 (1F, tt, J = 21.4, 4.6 Hz), –7.53 (2F, td, J = 22.0, 6.8 Hz); HRMS Calcd. for C₁₁H₁₅F₈[M+H⁺]: 289.0264; Found: 289.0268; [α]²⁰D = 3.42 (c = 1.45, CHCl₃) for a 59:41 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AD-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): t_R: 30.9 min and 32.5 min.
**Procedure for formal synthesis of fluralaner and analytical data (Figure 5)**

(S)-2-(3,5-Dichlorophenyl)-1,1,1-trifluoropent-4-en-2-ol (4r, Figure 5)

In a N₂ filled glove box, aminophenol 1d (6.7 mg, 0.017 mmol), Zn(OMe)₂ (8.5 mg, 0.067 mmol) and toluene (1.0 mL) were added to an oven-dried two-dram vial equipped with a stir bar. Methanol (33 µL, 0.82 mmol) was subsequently added to the vial to make a stock solution. A separate oven-dried two-dram vial equipped with a stir bar was charged with 0.3 mL of the stock solution containing 1d (2.0 mg, 0.005 mmol, 2.5 mol %), Zn(OMe)₂ (2.5 mg, 0.02 mmol, 10 mol %) and methanol (10 µL, 0.26 mmol, 1.3 equiv.). Pentane (0.45 mL), allylboronic acid pinacol ester (42 µL, 0.22 mmol, 1.1 equiv.) and 3',5'-dichloro-2,2,2-trifluoroacetophenone 3r (32 µL, 0.20 mmol, 1.0 equiv.) were subsequently added by syringe. This vial was sealed with a cap and electrical tape and removed from the glove box. The reaction mixture was allowed to stir at 22 ºC for 6 h after which the cap was removed and α,α,α-trifluorotoluene (24.4 µL, 0.199 mmol) was added as an internal standard. Following ¹⁹F NMR analysis of the unpurified mixture, it was passed through a short plug of silica gel (eluted with Et₂O) and concentrated in vacuo. The resulting clear colorless oil was purified by silica gel chromatography (10 mm diameter column slurry packed with 2.5 g of silica gel in hexanes and eluted with 40:1 hexanes:Et₂O) to afford desired product 4r (55.3 mg, 0.194 mmol, 97% yield) as colorless oil. IR (neat): 3379 (w, br), 2981 (w), 1590 (m), 1568 (m), 1439 (m), 1373 (m), 1271 (m), 1231 (m), 1163 (s), 1142 (s), 1024 (w), 1009 (m), 924 (m), 860 (m), 800 (s), 729 (m), 578 (w) cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.50–7.43 (2H, m), 7.41–7.35 (1H, m), 5.55 (1H, ddt, J = 17.4, 10.3, 7.5 Hz), 5.35–5.17 (2H, m), 2.90–2.82 (2H, m), 2.64 (1H, s); ¹³C NMR (100 MHz, CDCl₃): δ 140.6, 135.3, 129.6, 129.0, 125.5, 125.0 (q, J = 284.3 Hz), 122.8, 75.5 (q, J = 28.8 Hz), 40.4; ¹⁹F NMR (376 MHz, CDCl₃): δ 74.08 (3F, s); HRMS Calcd for C₁₁H₈Cl₂F₃ [M+H–H₂O]⁺: 266.9955; Found: 266.9949. [α]₂¹⁺ = −64.75 (c = 1.10, CHCl₃) for a 95:5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralpak AS-H, 98:2 hexanes:i-PrOH, 0.5 mL/min, 220 nm): tᵣ: 12 min (major) and 12.5 min (minor).
(S)-3-(3,5-Dichlorophenyl)-4,4,4-trifluoro-3-hydroxybutanal (S28, not shown in the manuscript, see Scheme S1)

A flame-dried 100 mL round-bottom flask equipped with a stir bar was charged with 4r (153 mg, 0.54 mmol, 1.0 equiv.), CH₂Cl₂ (10 mL) and MeOH (5 mL). The flask was cooled to −78 °C and O₃ was bubbled into the mixture until a blue coloration persisted (5 min). The cooling bath was removed and the flask was sealed with septum and purged with N₂ until the solution became clear. The solution was cooled to −78 °C again and dimethyl sulfide was added (79 µL, 1.08 mmol, 2 equiv.). The cooling bath was removed and the mixture was allowed to stir at 22 °C for 12 h, after which it was concentrated in vacuo to afford S28 as white solid which was subjected to the next step without purification.

Methyl 4-((S)-3-(3,5-dichlorophenyl)-4,4,4-trifluoro-1,3-dihydroxybutyl)-2-methylbenzoate (S29, not shown in the manuscript, see Scheme S1)

The title compound S29 was prepared from S28 following a literature procedure.²⁰ 4-Iodo-2-methylbenzoic acid methyl ester²¹ (297 mg, 1.075 mmol, 2.5 equiv.) was added to a flame-dried 100 mL round-bottom flask equipped with a stir bar. The flask was sealed, evacuated and purged with N₂. Tetrahydrofuran (2 mL) was added and the mixture was allowed to cool to −25 °C (4:1 ethylene glycol: ethanol with dry ice). Isopropylmagnesium chloride lithium chloride complex solution (1.3 M in thf; 0.9 mL, 1.19 mmol, 2.7 equiv.) was added dropwise and the mixture was allowed to stir for 30 min. Compound S28 (125 mg, 0.44 mmol, 1.0 equiv.) was added to a flame-dried 15 mL round-bottom flask and the flask was evacuated and purged with N₂. Tetrahydrofuran (2.5 mL) was added to this flask and the solution was allowed to cool to −25 °C. This solution was added dropwise to the flask containing the Grignard reagent. The resulting mixture was allowed to stir at −25 °C for 3 h. Saturated NH₄Cl solution was added to the mixture and the aqueous layer was extracted with EtOAc (3x5 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo to afford S29 as colorless oil, which was subjected to the next step without purification.

Methyl (S)-4-(3-(3,5-dichlorophenyl)-4,4,4-trifluoro-3-hydroxybutanoyl)-2-methylbenzoate (17, Figure 5)

17 was prepared from S29 following a literature procedure.¹⁹ Dess-Martin Periodinane (456 mg, 1.07 mmol, 2.5 equiv.) was added to a solution of S29 (188 mg, 0.43 mmol, 1.0 equiv.) in CH₂Cl₂ (8 mL) at

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(20) Oonishi, Y., Yokoe, T., Hosotani, A. & Sato, Y. Angew. Chem. Int. Edn 53, 1135–1139 (2014).
(21) Prepared by methylation of 4-iodo-2-methylbenzoic acid following a literature procedure: Hirose, Y., Ohta, E., Kawai, Y. & Ohta, S. J. Nat. Prod. 76, 554–558 (2013)
0 °C. The mixture was allowed to warm to 22 °C and stir for 3 h. A saturated solution of NH₄Cl was added and the aqueous layer was washed with EtOAc (3 x 5 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The resulting pale yellow oil was purified by silica gel chromatography (8:1 hexanes:diethyl ether) to afford 17 (131.4 mg, 0.302 mmol, 56% overall yield for 3 steps) as colorless oil.

IR (neat): 3444 (w, br), 2955 (w), 2927 (w), 1720 (m), 1677 (w), 1589 (m), 1435 (w), 1259 (s), 1166 (s), 1085 (s), 961 (w), 801 (m), 752 (s), 706 (m), 699 (m), 638 (m), 540 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.01–7.98 (1H, m), 7.84–7.73 (2H, m), 7.49 (2H, d, J = 1.8 Hz), 7.35 (1H, t, J = 1.9 Hz), 5.63 (1H, s), 3.94 (3H, s), 3.86 (1H, d, J = 17.6 Hz), 3.69 (1H, d, J = 17.5 Hz), 2.66 (3H, s); ¹³C NMR (100 MHz, CDCl₃): δ 198.7, 166.9, 141.1, 140.8, 137.8, 135.3, 135.1, 131.1, 129.1, 125.3, 125.1, 124.0 (q, J = 283.6 Hz), 75.9 (q, J = 29.6 Hz), 52.3, 40.5, 21.6; ¹⁹F NMR (376 MHz, CDCl₃): δ 72.91 (3F, s); HRMS Calculated for C₁₉H₁₆Cl₂F₃O₄ [M+H]+: 435.0378; Found: 435.0387.

Scheme S2: Transformation of 17 to 18

(S)-5-(3,5-Dichlorophenyl)-3-(4-(methoxycarbonyl)-3-methylphenyl)-5-(trifluoromethyl)-4,5-dihydroisoxazole 2-oxide (S30, not shown in the manuscript, see Scheme S2)

The title compound S30 was prepared from 17 following a literature procedure. A flame-dried 100 mL round-bottom flask equipped with a stir bar was charged with 17 (104.5 mg, 0.24 mmol, 1.0 equiv.) and hydroxylamine hydrochloride (33.3 mg, 0.48 mmol, 2 equiv.). The flask was sealed, evacuated and purged with N₂. Pyridine (2 mL) was added and the mixture was allowed to stir at 50 °C for 12 h. The mixture was allowed to cool to 22 °C and pyridine was removed under reduced pressure. Water (10 mL) was added and the aqueous layer was washed with EtOAc (3 x 5 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The resulting pale yellow oil was transferred to a flame-dried 100 mL round-bottom flask equipped with a stir bar. [Hydroxy(tosyloxy)iodo]benzene (109.8 mg, 0.28 mmol, 1.2 equiv.) was added. The vessel was sealed, evacuated and purged with N₂. MeOH (2 mL) was added and the mixture was allowed to stir at 22 °C for 30 min. Water (10 mL) was added and the aqueous layer was washed with EtOAc (3 x 5 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo to afford S30 as colorless oil, which was subjected to the next step without purification.

(22) Kawai, H., Okusu, S., Tokunaga, E. & Shibata, N. Eur. J. Org. Chem. 6506–6509 (2013).
Methyl (S)-4-(5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4,5-dihydroisoxazol-3-yl)-2-methylbenzoate (18, Figure 5)

The title compound 18 was prepared from S30 following a previously reported procedure. A flame-dried 100 mL round-bottom flask equipped with a stir bar was charged with S30. The flask was connected to a reflux condenser and the apparatus was sealed, evacuated and purged with N₂. Trimethyl phosphite (4 mL) was added by syringe and the mixture was heated to reflux and allowed to stir for 2 h. The mixture was allowed to cool to 22 °C and diluted with diethyl ether. The organic layer was washed with an aqueous solution of 1M HCl (3x2 mL), brine, dried over Na₂SO₄ and concentrated in vacuo. The resulting pale yellow oil was purified by silica gel chromatography (19:1 hexanes:diethyl ether) to afford 18 (41.2 mg, 0.095 mmol, 40% yield over 3 steps) as colorless oil. The analytical data are fully consistent with those reported previously.¹²³¹H NMR (400 MHz, CDCl₃): δ 7.96 (1H, d, J = 8.6 Hz), 7.57–7.50 (4H, m), 7.43 (1H, t, J = 1.8 Hz), 4.09 (1H, d, J = 17.1 Hz), 3.91 (3H, s), 3.71 (1H, dd, J = 17.3, 1.0 Hz), 2.63 (3H, s); [α]²⁰.₀ = 21.16 (c = 1.68, CHCl₃).

(23) US2010/179194 A1 filled 28 Mar 2008, issued 15 Jul 2010.
4. Determination of absolute stereochemistry

Scheme S3: Transformation of 4a to S31

(R)-5,5,5-Trifluoro-4-hydroxy-4-phenylpentan-2-one (S31, not shown in the manuscript, see Scheme S3)

Compound 4a was converted to S31 in accordance to a procedure in the literature. The title compound was purified by silica gel chromatography (10 mm diameter column slurry packed with ~2.5 g of silica gel and eluted with 1:1 hexanes:dichloromethane) affording S31 (41.6 mg, 0.179 mmol, 90% yield) as colorless oil. The analytical data are fully consistent with those reported previously and comparison of the specific rotation of S31 and its HPLC trace with data in literature establishes the absolute stereochemistry of 4a.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.58–7.55 (2H, m), 7.42–7.34 (3H, m), 5.44 (1H, s), 3.37 and 3.21 (2H, ABq, $J_{AB} = 17.1$ Hz), 2.21 (3H, s); HRMS Calcd for C$_{11}$H$_{12}$F$_3$O$_2$ [M+H]$^+$: 233.07894; Found: 233.07928; $[\alpha]_{D}^{23.4}= -20.0$ ($c = 1.0$, CHCl$_3$) for a 94:6 e.r. sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OD-H, 99:1 hexanes:i-PrOH, 1.0 mL/min, 220 nm): $t_R$: 13 min (major) and 25 min (minor).

| Peak # | Ret. Time | Area      | Area %   | Peak # | Ret. Time | Area      | Area %   |
|--------|-----------|-----------|----------|--------|-----------|-----------|----------|
| 1      | 13.6 min  | 3503987   | 48.378   | 1      | 13.4 min  | 3720387   | 93.561   |
| 2      | 25.6 min  | 3739315   | 51.624   | 2      | 25.4 min  | 256051    | 6.439    |

(24) McCombs, J. R., Michel, B. W., Sigman, M. S. J. Org. Chem. 76, 3609–3613 (2011).
(25) Duangdee, N., Harnying, W., Rulli, G., Neudörfl, J.-M., Gröger, H., Berkessel, A. J. Am. Chem. Soc. 134, 11196–11205 (2012).
(R)-5,5,5-Trifluoro-4-hydroxy-4-phenylpentan-2-one (S31, not shown in the manuscript, see Scheme S4)

Compound 5a was converted to S31 in accordance to a procedure in the literature and purified as above to obtain S31 (18.8 mg, 0.0810 mmol, 67% yield) as colorless oil.\(^{26}\)

| Peak # | Ret. Time | Area  | Area % | Peak # | Ret. Time | Area  | Area % |
|--------|-----------|-------|--------|--------|-----------|-------|--------|
| 1      | 12.9 min  | 688668| 49.233 | 1      | 12.9 min  | 1107272| 98.457 |
| 2      | 21.8 min  | 710117| 50.767 | 2      | 21.9 min  | 17352 | 1.543 |

(R)-(1,1,1-Trifluoro-2-methoxypenta-3,4-dien-2-yl)benzene (S32, not shown in the manuscript, see Scheme S5)

The title compound was synthesized in accordance to a procedure in the literature\(^{24}\) and purified by silica gel chromatography (10 mm diameter column slurry packed with \~2.5 g of silica gel and eluted with 99:1 pentanes:diethyl ether) affording S32 (33.1 mg, 0.145 mmol, 73% yield as a 95:5 ratio of allene to propargyl product) as pale yellow oil. IR (neat): 2945 (br, w), 2838 (w), 1981 (w), 1958 (w), 1489 (w) 1450 (w), 1276 (m), 1165 (s), 1094 (s), 1078 (s), 1082 (m), 974 (w), 849 (m), 762 (m), 714 (m), 669 (s) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.59–7.56 (2H, m), 7.44–7.36 (3H, m), 5.54 (1H, t, \(J = 6.8\) Hz), 5.06–4.96 (2H, m), 3.38–3.37 (3H, m); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 210.7, 134.3, 129.1, 128.8 (m), 128.2, 124.5 (q, \(J = 284.7\) Hz, one peak overlaps with m at 128.8), 87.4 (q, \(J = 1.4\) Hz), 82.4 (q, \(J = 27.7\) Hz), 79.1, 52.6; \(^19\)F NMR (376 MHz, CDCl\(_3\)): 75.59 (3F, s); HRMS Calcd for C\(_{12}\)H\(_{12}\)O\(_3\) [M+H]: 229.08402; Found: 229.08391; \([\alpha]^{21.8}_{D} = +22.2\) (c = 1.35, CHCl\(_3\)) for a 95:5 e.r.

\(\alpha\) (26) Román, J. G. and Soderquist, J. A. J. Org. Chem. 72, 9772–9775 (2007).
sample (based on e.r. of 6a). (95:5 allene:propargyl).

(S)-3,3,3-Trifluoro-2-methoxy-2-phenylpropanoic acid (Mosher’s Acid) (S33, not shown in the manuscript, see Scheme S5)

The title compound was synthesized in accordance to a procedure in the literature\(^{27}\) and purified by silica gel chromatography (10 mm diameter column slurry packed with ~2.5 g of silica gel and eluted with 99:1 dichloromethane:acetic acid affording S33 (18.4 mg, 0.0786 mmol, 37% yield) as colorless sticky oil. The analytical data are fully consistent with those reported previously; comparison of the specific rotation of S33 and its HPLC trace with data in literature establishes the absolute stereochemistry of 6a.\(^ {28,29} \)\(^ \text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.27 (1H, br s), 7.59–7.57 (2H, m), 7.46–7.41 (3H, m), 3.57 (3H, s); HRMS Calcd for C\(_{10}\)H\(_{10}\)F\(_3\)O\(_3\)\([\text{M+H]}^+\): 235.0582; Found: 235.0574; \([\alpha]\)\(^ {23.7} \)\(_D = -58.3 \) (c = 1.15, CHCl\(_3\)) for a 95:5 e.r. sample (based on e.r. of 6a).

Scheme S6: Transformation of 13 to S36 and S26 to S36

(S)-1,3-Difluoro-2-(2-methoxypentan-2-yl)benzene (S35, not shown in the manuscript, see Scheme S6)

A 10 mL Schlenk flask equipped with a stirbar was charged with S34\(^ {30} \) (25 mg, 0.12 mmol), 10 wt% Pd/C (13 mg, 10 mol% Pd), and tetrahydrofuran (1.5 mL). The flask was purged with N\(_2\) gas followed by H\(_2\) gas, sealed with a rubber septum, and connected to a balloon of H\(_2\) gas by a needle in order to keep the H\(_2\) pressure above the solution at ~1 atm. The mixture was allowed to stir at 22 °C for 6 h after which the balloon was removed and the reaction vessel was purged with N\(_2\) to remove excess H\(_2\) (IMPORTANT! Opening a Pd/C reduction without first removing H\(_2\) gas can lead to fires) and the vessel was opened. The cloudy black mixture was passed through a short plug of Celite (eluted with

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(27) Chong, J. M. & Loewirth, R. Synth. Comm. 23, 2145–2150 (1993).
(28) Dale, J. A., Dull, D. L. & Mosher, H. S. J. Org. Chem. 34, 2543–2549 (1969).
(29) Chavda, S., Coulbeck, E., Dingjan, M., Eames, J. & Motevalli, M. Tetrahedron: Asymmetry. 19, 1274–1284 (2008).
(30) Compound S34 was prepared from 13 in accordance to a procedure in the literature, passed through a short plug of silica gel (elute with pentanes), concentrated \textit{in vacuo}, and used without purification; see: Chong, J. M. & Loewirth, R. Synth. Comm. 23, 2145–2150 (1993).
diethyl ether) and carefully concentrated in vacuo to minimize loss of volatile S35 to afford colorless oil, which was purified by silica gel chromatography (10 mm diameter column slurry packed with ~2.5 g of silica gel and eluted with 10 mL pentanes, 30 mL 99:1, 10 mL 49:1 pentanes:diethyl ether) affording S35 (19.0 mg, 0.089 mmol, 74% yield) as colorless oil. IR (neat): 2961 (m), 2933 (w), 2874 (w), 2827 (w), 1619 (m), 1460 (s), 1286 (m), 1230 (w), 1087 (m), 986 (m), 789 (m) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.23–7.15 (1H, m), 6.88–6.80 (2H, m), 3.16 (3H, s), 1.99 (1H, td, \(J = 12.8, 4.7\) Hz), 1.81 (1H, td, \(J = 12.9, 4.6\) Hz), 1.70–1.68 (3H, m), 1.43–1.31 (1H, m), 1.24–1.15 (1H, m), 0.85 (1H, app t, \(J = 7.3\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 161.8 (dd, \(J = 250.9, 9.1\) Hz), 128.9 (t, \(J = 11.6\) Hz), 119.4 (t, \(J = 14.4\) Hz), 112.8–112.5 (m), 80.4 (t, \(J = 3.3\) Hz), 51.1, 44.5 (t, \(J = 2.4\) Hz), 24.2 (t, \(J = 6.3\) Hz), 17.8, 14.5; \(^19\)F NMR (376 MHz, CDCl\(_3\)): 44.80–44.75 (2F, m); HRMS Calcd for C\(_9\)H\(_9\)F\(_2\)O \([\text{M}–\text{C}_3\text{H}_7]^+\): 171.0622; Found: 171.0624; \([\alpha]^{21.6}_{D} = -26.3\) (\(c = 0.38\), CHCl\(_3\)) for a 94:6 e.r. sample (based on e.r. of 13).

(S)-(2-Methoxypentan-2-yl)benzene (S36, From S35, not shown in the manuscript, see Scheme S6)

In a nitrogen-filled glove box, a 5 mL Schlenk flask equipped with a stirbar was charged with Ni(PCy\(_3\))\(_2\)Cl\(_2\)\(^{31}\) (2.8 mg, 4.0 \(\mu\)mol), connected to a reflux condenser, and the entire apparatus was sealed with a rubber septum and electrical tape and removed from the glove box. Nitrogen gas was connected to the apparatus with a needle and tetrahydrofuran (300 \(\mu\)L) was added through syringe followed by dropwise addition of a 1.0 M solution of LiEt\(_3\)BH (320 \(\mu\)L, 0.32 mmol) in tetrahydrofuran. Compound S35 (8.5 mg, 0.040 mmol) was added dropwise as a solution in tetrahydrofuran (200 \(\mu\)L) and the orange solution was heated to reflux and allowed to stir for 14 h during which time the solution darkens from orange to black. The mixture was cooled to 0 \(^\circ\)C, and following removal of the reflux condenser, the solution was diluted dropwise with diethyl ether (3 mL) followed by water (1 mL), causing a color change from black to yellow as well as bubbling. The layers were separated and the aqueous layer was washed with diethyl ether (3 x 5 mL) and the combined organic layers are dried over MgSO\(_4\) and carefully concentrated in vacuo to minimize loss of volatile S36 to afford yellow oil (>98% consumption of S35 by \(^1\)H NMR). The product was purified by silica gel chromatography (10 mm diameter column slurry packed with ~2.5 g of silica gel and eluted with 49:1 pentanes:diethyl ether) to afford S36 (3.3 mg, 0.019 mmol, 46% yield) as colorless oil.

(31) Procedure is based on a report in the literature. See: Zhao, W., Wu, J. & Cao, S. Adv. Synth. Catal. 354, 574–578 (2012).
In a nitrogen-filled glove box, a 10 mL Schlenk flask equipped with a stirbar was charged with Crabtree’s catalyst$^{32}$ (32 mg, 0.04 mmol), sealed with a rubber septum and electrical tape, and removed from the glove box. The vessel was purged with H$_2$ gas and connected to a balloon of H$_2$ gas with a needle in order to keep the H$_2$ pressure above the solution at ~1 atm. S37 (65 mg, 0.4 mmol) was added by syringe in a solution of dichloromethane (2.5 mL). The orange solution was allowed to stir at 22 ºC for 18 h after which time the solution was transferred to a 15 mL round-bottom flask and concentrated in vacuo to afford green oil. Diethyl ether (5 mL) was added to this, which causes a gummy green precipitate to form. This mixture was passed through a short plug of Celite® (eluted with diethyl ether) and concentrated in vacuo to give an olive green oil which was used without purification.

In a nitrogen-filled glove box, a round-bottom flask equipped with a stirbar was charged with NaH (24.0 mg, 1.00 mmol), sealed with a rubber septum and electrical tape, and removed from the glove box. Nitrogen gas was connected to the apparatus with a needle and tetrahydrofuran (400 µL) and methyl iodide (100. µL, 1.61 mmol) were added through syringe followed by dropwise addition of the olive green oil from the previous step (~0.4 mmol from previous reduction; transferred to reaction vessel with 3 x 200 µL of tetrahydrofuran) by syringe with a rate slow enough that the bubbling from H$_2$ gas generation subsided between additions. The cloudy yellow solution was allowed to stir at 22 ºC for 12 h during which time it becomes a cloudy tan. The mixture was cooled to 0 ºC, and water was added dropwise through a syringe with a rate slow enough that H$_2$ gas evolution subsides between additions. At this time, water was added, the septum and nitrogen line were removed and the solution was diluted with diethyl ether (3 mL) and water (0.5 mL). The aqueous and organic layers were separated and the organic layer was washed sequentially with a solution of saturated aqueous NH$_4$Cl (1 mL), an aqueous solution of Na$_2$S$_2$O$_3$ (5 wt%, 1 mL), and brine (1 mL). The organic layer was dried over MgSO$_4$, carefully concentrated in vacuo to minimize loss of volatile S36 to afford a yellow oil,

(S)-(2-methoxypentan-2-yl)benzene (S36, From S26, not shown in the manuscript, see Scheme S6)

(32) Crabtree, R. H., Felkin, H. & Morris, G. E. J. Organomet. Chem. 141, 205–215 (1977).
which was purified by silica gel chromatography (19 mm diameter column slurry packed with ~6 g of silica gel and eluted with 100 mL of pentanes and 100 mL 99:1 pentanes:diethyl ether) to afford **S36** (50.5 mg, 0.28 mmol, 71% yield over 2 steps) as pale yellow oil. The analytical data are fully consistent with those reported previously.  

\[ \text{IR (neat): 2958 (m), 2935 (m), 2872 (w), 2824 (w), 1494 (w), 1446 (m), 1371 (w), 1225 (m), 1072 (s), 764 (s), 669 (s) cm}^{-1}; \]  
\[ ^1\text{H NMR (400 MHz, CDCl}_3\text{): }\delta 7.39–7.32 (4H, m), 7.26–7.22 (1H, m), 3.09–3.08 (3H, m), 1.78–1.70 (2H, m), 1.53 (3H, s), 1.33–1.12 (2H, m), 0.86 (3H, t, } J = 7.4 \text{ Hz);} \]  
\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): }\delta 145.5, 128.2, 126.7, 126.3, 79.2, 50.4, 45.3, 23.1, 17.3, 14.6; \]  
\[ \text{HRMS Calcd for C}_{11}\text{H}_{15}\text{O [M + H]}^+; 163.1123; \text{ Found: 163.1118; }[^{11}\text{C}]_{D} = -24.8 (c = 2.42, CHCl}_3\text{) for an 80:20 e.r. sample.} \]

The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H, 99:1 hexanes:i-PrOH, 0.5 mL/min, 220 nm): \( t_{R} \): 9 min (minor) and 10 min (major).

| Peak # | Ret. Time | Area     | Area % | Peak # | Ret. Time | Area     | Area % |
|--------|-----------|----------|--------|--------|-----------|----------|--------|
| 1      | 9.3 min   | 9477321  | 47.873 | 1      | 9.2 min   | 3163935  | 20.582 |
| 2      | 10.4 min  | 10319634 | 52.127 | 2      | 10.1 min  | 12208618 | 79.418 |

5. **NMR spectra of products**

... are displayed on the following pages.

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(33) Tramontini, M., Angiolini, L., Fouquey, C & Jacques, J *Tetrahedron* **29**, 4183–4187 (1973).
$^1$H NMR of

![Chemical Structure](image)

1b
$^{13}$C NMR of 1b
$^1$H NMR of

![Chemical Structure of 1c](image)
$^{13}$C NMR of

![Chemical structure diagram](image)

*1c*
$^{1}$H NMR of

\[
\begin{align*}
\text{Me} & \quad \text{OH} \\
\text{H} & \quad \text{N} \quad \text{Me}_2 \\
\end{align*}
\]

1d
$^{13}$C NMR of 1d
$^1$H NMR of S7
$^{13}$C NMR of $\text{F}_3\text{C}\text{BocN}$
$^{19}$F NMR of $F_3C$-BocN
$^{1}H$ NMR of

![Diagram of a molecular structure](image)
$^{13}$C NMR of $\text{F}_3\text{C} \overset{\text{O}}{\underset{\text{O}}{\text{C}}}$

S9
$^{19}$F NMR of $F_3C\text{O}+\text{S9}$
$^1H$ NMR of

![Structure](image)
$^1$H NMR of HO

$^1$Pr

S27
$^1$H NMR of \( \text{HO}_{\text{F}_3\text{C}} \text{CH} = \text{CH} \text{Ph} \)
$^1$H NMR of 4b
$^{13}$C NMR of $\text{HO}_2$, $\text{F}_3\text{C}$, $\text{Me}$

4b
\(^{19}\text{F NMR of} \ \begin{align*} &\text{HO} \\
&\text{F}_3\text{C} \\
&\text{Me} \\
\end{align*} \)
$^1$H NMR of

4c
$^{13}$C NMR of

\begin{align*}
\text{HO} & , \\
\text{F}_3\text{C} & , \\
\text{MeO} & \\
\text{4c} & 
\end{align*}
$^{19}$F NMR of 4c
$^1$H NMR of

![Chemical Structure](image)

4d
$^{13}$C NMR of $\text{HO}_\text{F}_3\text{C}$

4d
$^{19}\text{F NMR of}$

$\text{F}_3\text{C}$

$\text{HO}$

$\text{Me}$

$4d$
$^1$H NMR of $\text{HO, F}_3\text{C-}\text{NMe}_2$ (4e)
$^1$H NMR of \( \text{HO}_2 \cdot \text{F}_3 \text{C} \cdot \text{NMe}_2 \)
$^1$H NMR of $\text{HO, } F_3\text{C}$

$\text{Br}$

4f
$^{13}$C NMR of $\text{HO-}\text{CF}_3\text{CF}_3\text{C}$

4g
$^{19}$F NMR of $\text{HO, } F_3C$, $\text{CF}_3$ $4g$
$\text{^1H NMR of}$

![Chemical structure](image)

4h
$^{13}$C NMR of $\text{F}_3\text{C} - \text{HO}_2 - \text{BocN}$

4h
$^{19}$F NMR of $\text{F}_3\text{C}\text{HO}$

$\text{F}_3\text{C}\text{BocN}$

4h
$^{19}\text{F} \text{NMR of } \text{HO}_2, \text{F}_2\text{C} = \text{Ph}$

4i
$^1\text{H NMR of } \text{HO}_2\text{CCH} = \text{CCH}_2\text{F}_3\text{C} = \text{CCH}_2\text{O}$

$4j$
$^{13}$C NMR of \( \text{HO-} \begin{array}{c} \text{F}_3\text{C} \\ \text{O} \end{array} \text{4j} \)
$^{19}$F NMR of $\text{HO,} \text{F}_3\text{C}$

4j
$^1$H NMR of

\[ \text{HO}_2\text{C} - \text{CH}_2\text{CF}_3\text{CH} = \text{CH}_2 \]

4k
$\text{^{13}C NMR of }$ 

$\text{HO}_2$ 

$\text{F}_3\text{C}$ 

$\text{4k}$
$^{19}$F NMR of HO$_2$-C\(\text{F}_3\)C-\(\text{HO}_2\)
$^1$H NMR of

![Chemical Structure](image)
$^{13}$C NMR of $\text{HO}_2\text{C}_3\text{F}_3\text{C}_4\text{l}$
$^{19}$F NMR of \( \text{HO}_x \text{F}_3 \text{C} \text{S} \)
$^1$H NMR of $\text{HO-F}_3\text{C}$
$^{13}$C NMR of $\text{HO,} \quad \text{F}_3\text{C}$

4m
$^{19}$F NMR of HO$_2$F with $F_2C$ and 4m
$^1$H NMR of

![Chemical Structure](image)
$^1$H NMR of \( \text{HO} \quad \text{F}_3\text{C} \quad \text{4o} \)
\[ ^{19}\text{F} \text{NMR of } \text{HO, } \text{F}_3\text{C} \]
$^1$H NMR of $C_2F_5$-HO-4p

The NMR spectrum shows peaks at the following chemical shifts:
- 1.92 ppm
- 2.71 ppm
- 1.00 ppm
- 1.88 ppm
- 1.00 ppm
- 0.94 ppm
- 0.81 ppm
$^{13}$C NMR of $C_2F_5$HO,

4p
$^{19}\text{F NMR of}$

$$\text{C}_{2}\text{F}_{5}\text{HO,}$$

$4p$
$^1$H NMR of

$C_3F_7$ 

4q
$^{13}$C NMR of $\text{C}_3\text{F}_7\text{HO}$
$^{19}$F NMR of \( \text{C}_3\text{F}_7\text{HO} \), 4q
$^1$H NMR of 5a
$^{13}$C NMR of

![Chemical Structure](attachment:image.png)
$^{19}$F NMR of 5a
$^1$H NMR of

![Chemical structure](image)

Lee, et al., SI, Page S119
$^{13}$C NMR of

\[
\begin{align*}
\text{Cl} & \quad \text{HO} \quad \text{F}_3\text{C} \\
\end{align*}
\]

5b
$^{19}\text{F NMR of}$

$\text{Cl}$

$\text{HO}$

$\text{F}_2\text{C}$

$\text{5b}$
$^1$H NMR of $\text{F}_3\text{C-}\text{HO-}\text{C}=\text{C}=\text{C}$

6a
$^{13}$C NMR of $\text{HO, } \text{F}_3\text{C} \rightarrow \equiv$
$^{19}$F NMR of $\text{HO} \cdot \text{CC} \cdot \text{HO}$

6a
$^1$H NMR of \( \text{HO} \cdots \text{C}^\bullet \cdots \text{HO} \)
$^{13}$C NMR of $\text{F}_3\text{C}$

$\text{HO}$

$\text{MeO}$

$\text{6b}$
$^{19}$F NMR of

![Chemical Structure](image)
$^1$H NMR of $\text{H}_3\text{C} - \text{C}=\text{C} - \text{Me}$
$^{13}$C NMR of $\text{HO, F}_{3}\text{C}=-\equiv$}

6c
$^{19}$F NMR of $\text{F}_{3}\text{C}-\text{HO}$

6c
$^1$H NMR of \( \text{HO,} \quad \text{F}_3\text{C} \quad \text{F} \quad \text{6d} \)

![NMR spectrum of compound 6d]
$^{13}$C NMR of $\text{HO,} \uparrow \rightleftharpoons \downarrow \leftarrow \uparrow \rightleftharpoons \downarrow \text{F}$

6d
$^{19}$F NMR of $\text{HO}_2\text{C}-\text{H}-\text{F}$

$6\text{d}$
$^1$H NMR of $\text{HO}_2\text{C}_3\text{F} \equiv \equiv \text{NMe}_2$

6e
$\text{^{13}C NMR of } \text{HO, disposed of } \text{F}_3\text{C} \equiv \equiv \text{NMe}_2$
$^{19}$F NMR of $\text{F}_3\text{C} = \text{HO}$, $\text{NMe}_2$
$^{13}$C NMR of $\text{HO, } F_3C\text{CF}_3$
$^{19}$F NMR of 6f
$^{1}$H NMR of $\text{HO-F}_{3}\text{C}$
\(^{19}\text{F} \text{NMR of } \text{HO} \text{F}_3\text{C} \text{C} \text{F}_3\text{C} \text{O} \text{6h} \)
\(^1\text{H NMR of} \quad \begin{array}{c} \text{HO} \\ \begin{array}{c} \text{F}_3\text{C} \\ \begin{array}{c} \equiv \equiv \end{array} \\ \begin{array}{c} \text{S} \\ \begin{array}{c} \text{6j} \end{array} \end{array} \end{array} \end{array} \quad \end{array}
$^{13}$C NMR of $\text{HO-} - \text{C}_3\text{F}_3\text{C}-\text{S}$

6j
$^{19}$F NMR of $\text{HO, F}_3\text{C} = \equiv$ $\equiv$ 6j
$^1$H NMR of $\text{HO-F}_3\text{C-Ph}$

6k
$^{13}$C NMR of \( \text{HO,} \quad \text{F}_3\text{C} \quad \text{Ph} \)
$^{19}\text{F NMR of } \text{HO, } \begin{array}{c} \text{F}_3\text{C} \\ \text{Ph} \end{array}$

$6k$
$^1$H NMR of $\text{HO,F}_3\text{C} \equiv \text{Ph}$

61
$^{13}$C NMR of $\text{HO,} \begin{array}{c} \text{Ph} \\ \text{F}_3\text{C} \end{array}$

61
$^{19}$F NMR of HO$_2$C\(\text{Ph}\)F$_3$C

61
$^1$H NMR of $\text{HO, C} \equiv \text{C}$

6m
$^{13}\text{C NMR of } \text{HO-F}_3\text{C}$

6m
$^{19}$F NMR of $\text{HO,} - \equiv - \equiv$ $\text{F}_3\text{C}$

6m
\(^1\)H NMR of \(\text{HO}_2\)C\(\text{C}_2\text{F}_5\) with peaks at 1.97, 3.03, 1.00, 1.03, 1.07, and 0.94 ppm.
$^{13}$C NMR of $\text{C}_2\text{F}_5\text{HO}$
\(^{19}\text{F NMR of}\)

\[
\text{HO, } \overset{\text{C}_2\text{F}_5}{\rightleftharpoons}\text{C}_2\text{F}_5
\]

6n
$^1$H NMR of HO\(\text{FH}_2\text{C}\)
$^{13}$C NMR of
\[ \text{HO} - \text{FH}_2\text{C} - \text{C}_7 \]
$^{19}$F NMR of $\text{FH}_2\text{C}$

![Chemical Structure](image)
$^1$H NMR of $\text{HO}$

$\text{F}_2\text{HC}$

8
$^{13}$C NMR of HO- \( \text{F}_2\text{HC} \)
$^{19}$F NMR of $\text{F}_2\text{HC} \text{HO}$

8
$^1$H NMR of $\text{HO}_2\text{F}_2\text{MeC}$

9
$^{13}$C NMR of $\text{F}_2\text{MeC}$

![Diagram of molecular structure and NMR spectrum](image-url)
$^{19}\text{F} \text{NMR of } \text{HO}_2 \text{F}_{2}\text{MeC}$
$^1$H NMR of HOO-F

10
$^{13}$C NMR of 10
$^{19}$F NMR of \( \text{HO, } \text{F} \text{F} \text{F} \) 10
$^1$H NMR of

![NMR spectrum of compound 12](image-url)
$^1$H NMR of

![Chemical Structure](image)

13
$^1$H NMR of

\begin{array}{c}
\text{Me} \\
\text{HO} \\
\text{F} \\
13
\end{array}

\begin{array}{c}
\text{C} \\
\text{NMR}
\end{array}
$^{19}$F NMR of Compound 13
$^1$H NMR of

![Chemical Structure](image)

**14**
$^{13}$C NMR of $14$
$^1$H NMR of

15
$\text{^{13}C NMR of}$

![Chemical structure of compound 15 with peaks from NMR spectrum]
$^{19}$F NMR of

![Chemical Structure](image)

**15**
$^{1}$H NMR of

![Chemical Structure](image)

16
$^{13}$C NMR of

16

![NMR spectrum](image-url)
$^{19}$F NMR of

![Diagram of a chemical structure with 16 labeled as a peak.](image-url)
$^1$H NMR of $\text{Cl}_4\text{Cl}^3\text{C}_3\text{OH}$
$^{19}$F NMR of \( \text{ClF}_3C\text{OH} \)
$^{19}$F NMR of

![Chemical Structure](attachment:chemical_structure.png)
\(^1\text{H NMR of MeO}_{\leftarrow\text{F}_3\text{C}}\)
$^{19}$F NMR of MeO, $\text{MeO}^- \cdots \cdots 
\begin{array}{c}
\text{F}_3\text{C} \\
\text{S32}
\end{array}$
$^1$H NMR of

![Chemical structure]
$^{13}$C NMR of MeMeO\textsubscript{2}F

S35
$^{19}\text{F}	ext{ NMR of}\text{ S35}$
6. Density functional theory (DFT) calculations

General Methods

DFT computations\(^\text{34}\) were performed with the Gaussian 09 suite of programs.\(^\text{35}\) Geometries were optimized by application of the M06-2X functional on the charged species (charge +1, multiplicity 1).\(^\text{36}\) For simplicity, all calculations were carried out with the L-\text{tert}-leucine-derived catalyst (not the L-valine-derived catalyst). The 6-31G(d,p) basis set was used for all atoms and the effect of a polar medium (toluene) was modeled by means of an integral equation formalism variant of the polarizable continuum model (IEFPCM).\(^\text{37}\) Stationary points were probed through vibrational analysis and Gibbs free energy corrections were performed under standard conditions (298.15 K, 1.0 atm). Through single point energy calculations in toluene and the larger 6-311++G(2df,2pd) basis set we evaluated the performance of a selected number of density functionals, including those that account for dispersion\(^\text{34,38}\) (M06-2X,\(^\text{35}\) oB97XD,\(^\text{39}\) M06,\(^\text{36}\) MN12SX\(^\text{40}\) and PBE0-D3BJ\(^\text{34b}\)) and those that do not (B3LYP\(^\text{41}\), PBE0\(^\text{42}\) and BP86\(^\text{43}\)). Additionally, atoms in molecules (AIM) calculations, carried out

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\(^{37}\) Scalmani, G.; Frisch, M. J. J. Chem. Phys. \textbf{132}, 114110 (2010).

\(^{38}\) For selected examples highlighting the importance of including treatment of dispersion interactions, see: (a) Torker, S.; Merki, D.; Chen. P. J. Am. Chem. Soc. \textbf{130}, 4808–4814 (2008). (b) Minenkov, Y.; Occhipinti, G.; Singstad, A.; Jensen, V. R. Dalton Trans. \textbf{41}, 5526–5541 (2012). (c) Minenkov, Y.; Occhipinti, G.; Jensen, V. R. Organometallics \textbf{32}, 2099–2111 (2013). (d) Khan, R. K. M.; Torker, S.; Hoveyda, A. H. J. Am. Chem. Soc. \textbf{136}, 14337–14340 (2014). (e) Torker, S.; Koh, M. J.; Khan, R. K. M.; Hoveyda, A. H. Organometallics \textbf{35}, 543–562 (2016).

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\(^{41}\) (a) Becke, A. D. J. Chem. Phys. \textbf{98}, 5648–5652 (1993); Lee, C., Yang, W. & Parr, R. G. Phys. Rev. B. \textbf{37}, 785–789 (1988). (b) Vosko, S. H., Wilk, L. & Nusair, M. Can. J. Phys. \textbf{58}, 1200–1211 (1980). (c) Stephens, P. J., Devlin, F. J., Chabalowski, C. F. & Frisch, M. J. J. Phys. Chem. \textbf{98}, 11623–11627 (1994).

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to obtain the electron density at the bond critical point (BCP), have been performed at the B3LYP/6-31G(d,p) level (Figures S9 and S10). Gibbs free energies are provided in Section 7 and a file for convenient viewing of computed geometries with the program Mercury 3.3 is appended as separate “coordinates.xyz” file in Section 8.

**Computationally investigated reactions**

The following modes of reactions with activated catalyst species cat1−cat4 involving fluorine-containing substrates (1,1,1-trifluoroacetone, 2,2,2-trifluoroacetophenone, 2,2,2-trifluoro-2’-methylacetophenone and 2’,6’-difluoroacetophenone) have been investigated (Figures S1–S8). Transition states II and IV lead to the major enantiomer, whereas III and V generate the minor isomer. Due to the high electrophilicity of the fluoro-ketones, some of the transition states occur rather early (i.e., longer C–C distances), rendering optimization difficult due to lack of structural rigidity; a decrease in magnitude or loss of the imaginary frequency is thus observed. Hence, we performed constrained optimizations at several C–C bond distances (typically in 0.1 Å intervals) and employed the corresponding free energy corrections to provide an estimate of the free energy barrier. The highest free energy value from a C–C bond-distance scan for each density functional was chosen as free energy barrier. For energy and Gibbs free energy values as a function of the density functional and the C–C distance, see Tables S1–S8. For a graphical representation including a summary of the free energy values, see Figures S1–S8.

**Analysis of various density functionals: The need for including dispersion**

Comparison of the relative energies of modes IIa–Va for allyl addition with protonated species cat1 to 1,1,1-trifluoroacetone (Figure S1) indicates that addition via IVa is favored with all investigated density functionals and that Va is the most competitive approach leading to the minor enantiomer. Modeling the transformation with 2,2,2-trifluoroacetophenone as substrate (IIb–Vb, Figure S2) demonstrates that proper treatment of dispersion is necessary in order to predict the correct trend. Although IVb is still favored with M06-2X, ωB97XD, M06, MN12SX and PBE0-D3BJ (all of which account for dispersion), mode IIb is the energetically lowest transition state with functionals B3LYP, PBE0 and BP86. The latter three density functionals treat the interaction between the axial phenyl group and the phenol unit of the catalyst in IVb as overly repulsive; this may be attributed to lack of treatment of dispersion forces. There are similar trends for allenyl addition to 2,2,2-trifluoroacetophenone (IIId–Vd, Figure S4) with active species cat2 and allyl addition to 2,2,2-

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(43) (a) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **38**, 3098–3100 (1988). (b) Perdew, J. P.; Yue, W. *Phys. Rev. B* **33**, 8800–8802 (1986).

(44) *Organometallics* **33**, 835–835 (2014). The “coordinates.xyz” file can be generated by copying all the coordinates in Section 8 into a text file without empty lines and changing the extension to “.xyz”.


trifluoroacetophenone promoted by triphenylsilyl-substituted cat4 (IIi–Vi, Figure S7). When the substrate’s aryl ring is more sizeable, mode of addition IVe is disfavored with all density functionals except ωB97XD (Figure S3). The same applies when the active species is changed from cat1 to cat4 (IIj–Vj, Figure S8). In modeling allenyl addition to 2,2,2-trifluoroacetophenone with triphenylsilyl-substituted catalyst cat3 all attempts to locate transition state IVe resulted in conversion to structure IIe (Figure S5). In the corresponding allyl addition (Figure S7), mode of addition IVi can be located, presumably as a result of the more severe eclipsing interactions imposed by the terminal CH2 group on the allyl nucleophile, which prohibits collapse to the corresponding boat structure. After single-point energy calculation, transition state IVi remains energetically more accessible compared to IIi (Figure S7). Modeling the allylation reaction with 2’,6’-difluoroacetophenone as substrate (IIh–Vh, Figure S6) again demonstrates that proper treatment of dispersion is crucial. As in the case of 2,2,2-trifluoroacetophenone (IIb–Vb, Figure S2), structure Vh with an axial aryl group is disfavored with all density functionals that do not account for dispersion (B3LYP, PBE0 and BP86).

**Structural attributes of allyl vs. allenyl addition**

Comparison of transition states for allyl vs. allenyl addition (Schemes S7 and S8) reveals a number of features that can explain the enhancement in performance when the allenyl additions are promoted through active species cat3 rather than cat2 (IVd vs IIe in Figures S4 and S5, respectively). In contrast, there is little improvement when the corresponding allyl additions are carried out with cat4 (IVi in Figure S7) as compared to cat1 (IVb in Figure S2). The following interactions in Schemes S7 and S8 are characteristic:

For allyl additions promoted by cat1, transition state IVb is favored, mainly due to the more favored chair structure, allowing for a shorter O–HN+ distance (2.53 Å) and a longer O–O distance (2.51 Å) as compared to mode of addition IIb (2.79 and 2.38 Å, respectively; Scheme S7). As a result of the more severe eclipsing interaction between the phenoxide oxygen and the hydrogen on the α carbon atom on the propargyl group in IVd (dihedral angle of 33º) vs. IVb (dihedral angle of 53º; Scheme S7), the O–HN+ distance increases (2.60 Å) whereas the O–O distance decreases (2.48 Å) compared to the transition state for allyl addition IVb. This structural adjustment furthermore leads to a longer N+H–F distance of 4.23 Å (vs. 4.11 Å in IVb). Overall, the repulsive forces (O–O) are increased relative to those that are attractive (O–HN+ and N+H–F) in the most favorable mode for allenyl addition IVd, potentially causing a diminution in enantioselectivity compared to the corresponding allyl additions.

Analysis of the transition states with the triphenylsilyl-substituted catalysts (cat3 and cat4) reveals a number of structural alterations (Scheme S8). Mode of addition IVi is still favored over IIi; nonetheless there is steric repulsion between the phenyl group on the substrate and the Ph3Si moiety on the catalyst. This leads to a distortion, which is confirmed by reduction of dihedral angles H–C–B–O
(45°) and H–C–C–C⁺ (36°) in IVi (vs. 53 and 40° in IVb, respectively; Schemes S7 and S8). This adjustment is paralleled by the decrease in the N⁺H–F distance to 3.89 Å (vs. 4.11 Å in IVb).

**Scheme S7.** Comparison of structural attributes of transition states for allyl vs allenyl addition derived from active species cat1 and cat2 (cf. Figures S2 and S4)

| Transition State | Newman Projection | Distance (Å) | Newman Projection | Distance (Å) | Newman Projection | Distance (Å) |
|------------------|--------------------|--------------|--------------------|--------------|--------------------|--------------|
| Iib              | Newman projection | 2.00         |                    | 2.00         | Newman projection | 2.79         |
|                  |                    |              | stronger e–e repulsion due to small O–O distance (2.38 Å) relative to IVb (2.53 Å) |              | stronger e–e repulsion due to small O–O distance (2.38 Å) relative to IVb (2.53 Å) |              |
|                  |                    |              |                    |              |                    |              |
| IVb              | Newman projection | 4.11         | shorter O–H (2.53 Å) and longer O–O distance (2.53 Å) than in Iib (2.79 Å and 2.38 Å, respectively) contributes to greater stability | 2.53         | shorter O–H (2.53 Å) and longer O–O distance (2.53 Å) than in Iib (2.79 Å and 2.38 Å, respectively) contributes to greater stability | 2.53         |
|                  |                    |              |                    |              |                    |              |
| Vb               | Newman projection | 2.33         | e–e repulsion reduces dihedral angle to 43° (vs 53° in IVb) | 2.53         | e–e repulsion reduces dihedral angle to 43° (vs 53° in IVb) | 2.53         |
|                  |                    |              |                    |              |                    |              |
| Vd               | Newman projection | 2.42         |                    | 2.42         | Newman projection | 2.55         |
|                  |                    |              | stronger eclipsing interaction (33°) leads to shorter O–O (2.48 Å) and longer O–H distance (2.60 Å) relative to IVb (2.51 and 2.53 Å, respectively) |              | stronger eclipsing interaction (33°) leads to shorter O–O (2.48 Å) and longer O–H distance (2.60 Å) relative to IVb (2.51 and 2.53 Å, respectively) |              |

Overall, destabilization of IVi is minimal and the energy difference relative to the most favored minor approach VI is still 2.8, 1.9 and 2.1 kcal/mol with density functionals oB97XD, M06 and PBE0-D3BJ, respectively (Figure S7). Transition state IIe emerges as the most preferential in the corresponding allenyl addition (Scheme S8). Due to the linear structure of the propargyl nucleophile, the CF₃ group is not subject to unfavorable gauche interaction with the alkyne; such an interaction, on the other hand, does exist between the CF₃ and the alkene in III (Scheme S8). The longer N⁺H–F distance of 2.26 Å in IIe (vs. 2.10 Å in III) can allow for a more favorable π–π stacking interaction.
with one of the phenyl substituents on the Ph$_3$Si group (i.e., more intimate contact with the substrate). The possibility of π−π stacking interaction is further supported by comparison with structure IIID (N$^+$H–F distance of 2.21 Å; Scheme S7). Additionally, the longer O–HN$^+$ distance (2.91 Å) and the shorter O–O distance (2.34 Å) in IIE (vs. 2.84 and 2.36 Å in IIID, respectively), imply an attractive π−π stacking interaction, positioning the substrate more proximal to the Ph$_3$Si group.

The above-mentioned structural trends underscore the weak nature of the N$^+$H–F hydrogen-bonding interaction. Not only is interaction of the carbonyl lone pairs and the proton preferred (e.g.; IVb vs. IIb in Scheme 7), other weak forces like π−π stacking or C–H/π interactions can successfully compete or disrupt the weak N$^+$H–F H-bond (e.g.; IIID vs. IIE in Schemes 7 and 8).

**Scheme S8.** Comparison of structural attributes of transition states for allyl vs allenyi addition derived from active species cat3 and cat4 (cf. Figures S5 and S7)
Electrostatic interaction energy between proton and fluorine in toluene

The electrostatic interaction energy (V) in eV between two charges can be evaluated based on Eq. (1), wherein $q_1$ and $q_2$ are the partial atomic charges, $\epsilon$ is the dielectric constant of the medium ($\epsilon = 2.38$ for toluene) and $R$ is the distance between the two charges in Å.

$$V = \frac{14.4 (q_1 \cdot q_2)}{\epsilon \cdot R} \text{ [in eV]} \quad \text{Eq. (1)}$$

Through the use of the natural atomic charges on the proton and the closest fluorine atom of $+0.46$ and $-0.34$ for $q_1$ and $q_2$ still yields the significant electrostatic interaction energy of 5.3 kcal/mol in toluene for transition state IIb ($R = 4.11$ Å). Yet, the comparable electrostatic interaction energy in the minor approach Vb ($R = 4.96$ Å) amounts to 4.4 kcal/mol, resulting in the excess electrostatic interaction energy of 0.9 kcal/mol in favor of the major approach (5.3–4.4 kcal/mol).
Figure S1. Comparison of single point free energies ($\Delta G$ in kcal/mol) for transition states IIa–Va relative to cat1 for reaction with 1,1,1-trifluoroacetone with various density functionals after optimization with M06-2X in toluene (PCM) as a function of various C–C bond distances (cf. Table S1-1).
**Figure S2.** Comparison of single point free energies (ΔG in kcal/mol) for transition states IIb–Vb relative to cat1 for reaction with 2,2,2-trifluoroacetophenone with various density functionals after optimization with M06-2X in toluene (PCM) as a function of various C–C bond distances (cf. Table S2-1).
Figure S3. Comparison of single point free energies (ΔG in kcal/mol) for transition states IIc–Vc relative to cat1 for reaction with 2,2,2-trifluoro-2'-methylacetophenone with various density functionals after optimization with M06-2X in toluene (PCM) as a function of various C–C bond distances (cf. Table S3-1).
Figure S4. Comparison of single point free energies (ΔG in kcal/mol) for transition states IId–Vd relative to cat2 for reaction with trifluoroacetophenone with various density functionals after optimization with M06-2X in toluene (PCM) as a function of various C–C bond distances (cf. Table S4-1).
Figure S5. Comparison of single point free energies (ΔG in kcal/mol) for transition states Ile and Ve relative to cat3 for reaction with 2,2,2-trifluoracetophenone with various density functionals after optimization with M06-2X in toluene (PCM) as a function of various C–C bond distances (cf. Table S5-1).
**Figure S6.** Comparison of single point free energies ($\Delta G$ in kcal/mol) for transition states IIh-Vh relative to cat1 for reaction with 2',6'-difluoroacetophenone with various density functionals after optimization with M06-2X in toluene (PCM) as a function of various C–C bond distances (cf. Table S6-1).
Figure S7. Comparison of single point free energies ($\Delta G$ in kcal/mol) for transition states III–VI relative to cat4 for reaction with 2,2,2-trifluoroacetophenone with various density functionals after optimization with M06-2X in toluene (PCM) as a function of various C–C bond distances (cf. Table S7-1).
Figure S8. Comparison of single point free energies (ΔG in kcal/mol) for transition states IIj–Vj relative to cat4 for reaction with 2,2,2-trifluoro-2'-methylacetophenone with various density functionals after optimization with M06-2X in toluene (PCM) as a function of various C–C bond distances (cf. Table S8-1).
Bond critical points from AIM calculations

Figure S9. Atom in molecules (AIM) calculation at the B3LYP/6-31G(d,p) level of theory with 2,2,2-trifluoroacetophenone as substrate
Figure S10. Atom in molecules (AIM) calculation at the B3LYP/6-31G(d,p) level of theory with phosphinoylimine as substrate.
7. Tables of energies and Gibbs free energies

Table S1-1. After optimization with M06-2X/6-31G(d,p) in toluene (PCM) [IIa–Va in Figure 1 and S1]

| structure | E [hartree] | ΔE [kcal/mol] | G [hartree] | ΔG [kcal/mol] | ΔG_{corr} [kcal/mol] | FREQ [cm⁻¹] |
|-----------|-------------|---------------|-------------|---------------|-----------------------|-------------|
| cat1      | -1634.95295531 | 0.0          | -1634.418996 | 0.0          | 0.0                   | 17.24       |
| IIa_2.20 Å | -1634.98565462 | -20.5         | -1634.419171 | -0.1         | 20.4                  | -264.61     |
| IIa_2.30 Å | -1634.98373547 | -19.1         | -1634.417157 | 1.2          | 20.2                  | -209.85     |
| IIa_2.40 Å | -1634.98164890 | -18.0         | -1634.416065 | 1.8          | 19.8                  | -183.10     |
| IIa_2.50 Å | -1634.98034825 | -17.2         | -1634.415568 | 2.2          | 19.3                  | -161.03     |
| IIa_2.60 Å | -1634.97940186 | -16.6         | -1634.415676 | 2.1          | 18.7                  | -125.68     |
| IIa_2.70 Å | -1634.97870911 | -16.2         | -1634.415335 | 2.3          | 18.5                  | -77.02      |
| IIa_2.80 Å | -1634.97814497 | -15.8         | -1634.415309 | 2.3          | 18.1                  | -25.05      |
| IIIa_2.20 Å | -1634.98197061 | -18.2         | -1634.413134 | 3.7          | 21.9                  | -240.68     |
| IIIa_2.30 Å | -1634.97985173 | -16.9         | -1634.411591 | 4.6          | 21.5                  | -193.84     |
| IIIa_2.40 Å | -1634.97831927 | -15.9         | -1634.409833 | 5.7          | 21.7                  | -161.50     |
| IIIa_2.50 Å | -1634.97714943 | -15.2         | -1634.409063 | 6.2          | 21.4                  | -140.91     |
| IIIa_2.70 Å | -1634.97556913 | -14.2         | -1634.408717 | 6.5          | 20.6                  | -62.70      |
| IIIa_2.80 Å | -1634.97494690 | -13.8         | -1634.408939 | 6.3          | 20.1                  | -15.74      |
| IVa_2.20 Å  | -1634.98818087 | -22.1         | -1634.420956 | -1.2         | 20.9                  | -250.58     |
| IVa_2.30 Å  | -1634.98649647 | -21.0         | -1634.418958 | 0.0          | 21.1                  | -195.78     |
| IVa_2.40 Å  | -1634.98530982 | -20.3         | -1634.417999 | 0.6          | 20.9                  | -174.57     |
| IVa_2.50 Å  | -1634.98450896 | -19.8         | -1634.417516 | 0.9          | 20.7                  | -147.96     |
| IVa_2.60 Å  | -1634.98398308 | -19.5         | -1634.417156 | 1.2          | 20.6                  | -84.72      |
| IVa_2.70 Å  | -1634.98356904 | -19.2         | -1634.419153 | -0.1         | 19.1                  | 21.91       |
| IVa_2.80 Å  | -1634.98313144 | -18.9         | -1634.420318 | -0.8         | 18.1                  | 22.17       |
| Va_2.20 Å   | -1634.98446620 | -19.8         | -1634.417965 | 0.6          | 20.4                  | -267.92     |
| Va_2.30 Å   | -1634.98230728 | -18.4         | -1634.415930 | 1.9          | 20.3                  | -205.35     |
| Va_2.40 Å   | -1634.98072474 | -17.4         | -1634.414262 | 3.0          | 20.4                  | -174.08     |
| Va_2.50 Å   | -1634.97953987 | -16.7         | -1634.413717 | 3.3          | 20.0                  | -157.90     |
| Va_2.60 Å   | -1634.97869883 | -16.2         | -1634.413923 | 3.2          | 19.3                  | -124.51     |
| Va_2.70 Å   | -1634.97811284 | -15.8         | -1634.413809 | 3.3          | 19.0                  | -76.91      |
| Va_2.80 Å   | -1634.97765306 | -15.5         | -1634.417042 | 1.2          | 16.7                  | 5.04        |

E …… electronic energy in toluene (PCM) in hartree with 6-31G(d,p)  
G …… sum of electronic and thermal free energies in toluene (PCM) in hartree with 6-31G(d,p)  
ΔE …… relative electronic energy in kcal/mol in toluene (PCM) with 6-31G(d,p)  
ΔG …… relative free energy in kcal/mol in toluene (PCM) with 6-31G(d,p)  
ΔG_{corr} …… gas phase thermal correction to free energy in kcal/mol obtained with 6-31G(d,p) (ΔG = ΔE + ΔG_{corr})
Table S1-2. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIa–Va in Figure 1 and S1]

|                  | M062X/6-311++G(2df,2pd) (toluene) | ωB97XD/6-311++G(2df,2pd) (toluene) | M06/6-311++G(2df,2pd) (toluene) |
|------------------|----------------------------------|----------------------------------|----------------------------------|
|                  | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] |
|                  | -1635.48447390 | 0.0 | 0.0 | -1635.66239430 | 0.0 | 0.0 | -1635.09276162 | 0.0 | 0.0 |
|                  | -1635.50531317 | -13.1 | 7.3 | -1635.67597693 | -8.5 | 11.9 | -1635.10871161 | -10.0 | 10.4 |
|                  | -1635.50338512 | -11.9 | 8.4 | -1635.67432728 | -7.5 | 12.8 | -1635.10677123 | -8.8 | 11.5 |
|                  | -1635.50200803 | -11.0 | 8.8 | -1635.67341851 | -6.9 | 12.9 | -1635.10577979 | -8.2 | 11.7 |
|                  | -1635.50104316 | -10.4 | 8.9 | -1635.67299348 | -6.7 | 12.7 | -1635.10532047 | -7.9 | 11.5 |
|                  | -1635.50039243 | -10.0 | 8.7 | -1635.67278383 | -6.5 | 12.2 | -1635.10479230 | -7.5 | 11.1 |
|                  | -1635.50003284 | -9.8 | 8.7 | -1635.67269676 | -6.5 | 12.0 | -1635.10445284 | -7.3 | 11.1 |
|                  | -1635.49979997 | -9.6 | 8.5 | -1635.67258919 | -6.4 | 11.7 | -1635.10403568 | -7.1 | 11.0 |
|                  | -1635.50363251 | -12.0 | 9.9 | -1635.67493864 | -7.9 | 14.0 | -1635.10788381 | -9.5 | 12.4 |
|                  | -1635.50178277 | -10.9 | 10.7 | -1635.67345071 | -6.9 | 14.6 | -1635.10580289 | -8.2 | 13.3 |
|                  | -1635.50056283 | -10.1 | 11.6 | -1635.67272324 | -6.5 | 15.2 | -1635.10486948 | -7.6 | 14.1 |
|                  | -1635.49970624 | -9.6 | 11.9 | -1635.67244317 | -6.3 | 15.1 | -1635.10446935 | -7.3 | 14.1 |
|                  | -1635.49871480 | -8.9 | 11.7 | -1635.67230596 | -6.2 | 14.4 | -1635.10408920 | -7.1 | 13.5 |
|                  | -1635.49836959 | -8.7 | 11.4 | -1635.67219242 | -6.1 | 14.0 | -1635.10376420 | -6.9 | 13.2 |
|                  | -1635.51001023 | -16.0 | 4.9 | -1635.68184752 | -12.2 | 8.7 | -1635.11483759 | -13.9 | 7.0 |
|                  | -1635.50864492 | -15.2 | 5.9 | -1635.68073967 | -11.5 | 9.6 | -1635.11338217 | -12.9 | 8.1 |
|                  | -1635.50779925 | -14.6 | 6.3 | -1635.68032742 | -11.3 | 9.7 | -1635.11287980 | -12.6 | 8.3 |
|                  | -1635.50733067 | -14.3 | 6.4 | -1635.68038986 | -11.3 | 9.4 | -1635.11284912 | -12.6 | 8.1 |
|                  | -1635.50711197 | -14.2 | 6.4 | -1635.68062895 | -11.4 | 9.2 | -1635.11289100 | -12.6 | 8.0 |
|                  | -1635.50703075 | -14.2 | 5.0 | -1635.68085950 | -11.6 | 7.5 | -1635.11285167 | -12.6 | 6.5 |
|                  | -1635.50689544 | -14.1 | 4.0 | -1635.68094933 | -11.6 | 6.5 | -1635.11270772 | -12.5 | 5.6 |
|                  | -1635.50526925 | -13.0 | 7.4 | -1635.67591158 | -8.5 | 11.9 | -1635.10936869 | -10.4 | 10.0 |
|                  | -1635.50345695 | -11.9 | 8.4 | -1635.67434367 | -7.5 | 12.8 | -1635.10752648 | -9.3 | 11.1 |
|                  | -1635.50223879 | -11.1 | 9.2 | -1635.67357437 | -7.0 | 13.4 | -1635.10665793 | -8.7 | 11.7 |
|                  | -1635.50141137 | -10.6 | 9.4 | -1635.67308586 | -6.8 | 13.1 | -1635.10628034 | -8.5 | 11.5 |
|                  | -1635.50090684 | -10.3 | 9.0 | -1635.67362997 | -6.8 | 12.5 | -1635.10605295 | -8.3 | 11.0 |
|                  | -1635.50059875 | -10.1 | 8.9 | -1635.67324555 | -6.8 | 12.2 | -1635.10575216 | -8.2 | 10.9 |
|                  | -1635.50039391 | -10.0 | 8.7 | -1635.67321504 | -6.8 | 9.9 | -1635.10538688 | -7.9 | 8.8 |

$E_{sp}$ ...... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
$\Delta E_{sp}$ ...... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
$\Delta G_{sp}$ ...... relative single point free energy in toluene in kcal/mol ($\Delta G_{sp} = \Delta E_{sp}/6-311++G(2df,2pd) + \Delta G_{corr}/6-31G(d,p)$)
### Table S1-3. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIa–Va in Figure 1 and S1]

|       | MN12SX/6-311++G(2df,2pd) (toluene) | PBE0-D3BJ/6-311++G(2df,2pd) (toluene) | B3LYP/6-311++G(2df,2pd) (toluene) |
|-------|-----------------------------------|--------------------------------------|-------------------------------------|
|       | $E_\text{sp}$ [hartree] | $\Delta E_\text{sp}$ [kcal/mol] | $\Delta G_\text{sp}$ [kcal/mol] | $E_\text{sp}$ [hartree] | $\Delta E_\text{sp}$ [kcal/mol] | $\Delta G_\text{sp}$ [kcal/mol] | $E_\text{sp}$ [hartree] | $\Delta E_\text{sp}$ [kcal/mol] | $\Delta G_\text{sp}$ [kcal/mol] |
| -1634.83014358 | 0.0 | 0.0 | -1634.35379129 | 0.0 | 0.0 | -1636.14850960 | 0.0 | 0.0 |
| -1634.8478158 | -9.2 | 11.2 | -1634.37629846 | -14.1 | 6.3 | -1636.14307977 | 3.4 | 23.9 |
| -1634.8326388 | -8.2 | 12.0 | -1634.37423212 | -12.8 | 7.4 | -1636.14186966 | 4.2 | 24.4 |
| -1634.8429810 | -7.6 | 12.2 | -1634.37266575 | -11.8 | 8.0 | -1636.14129444 | 4.6 | 24.5 |
| -1634.84173093 | -7.3 | 12.1 | -1634.37142433 | -11.1 | 8.3 | -1636.14082734 | 4.9 | 24.2 |
| -1634.84134550 | -7.0 | 11.6 | -1634.37040179 | -10.4 | 8.3 | -1636.14071223 | 4.9 | 23.6 |
| -1634.84111027 | -6.9 | 11.6 | -1634.36939774 | -9.8 | 8.7 | -1636.14055398 | 5.0 | 23.5 |
| -1634.84083502 | -6.7 | 11.4 | -1634.36848861 | -9.2 | 8.9 | -1636.14039336 | 5.1 | 23.3 |
| -1634.84333814 | -8.3 | 13.6 | -1634.37486010 | -13.2 | 8.7 | -1636.14094172 | 4.8 | 26.7 |
| -1634.84170920 | -7.3 | 14.3 | -1634.37288795 | -12.0 | 9.5 | -1636.14002616 | 5.4 | 26.9 |
| -1634.84086060 | -6.7 | 14.9 | -1634.37155648 | -11.1 | 10.5 | -1636.13956577 | 5.6 | 27.3 |
| -1634.84037379 | -6.4 | 15.0 | -1634.37051594 | -10.5 | 10.9 | -1636.13934131 | 5.8 | 27.2 |
| -1634.83980456 | -6.1 | 14.6 | -1634.36873362 | -9.4 | 11.3 | -1636.13914775 | 5.9 | 26.6 |
| -1634.83948810 | -5.9 | 14.2 | -1634.36790326 | -8.9 | 11.3 | -1636.13897962 | 6.0 | 26.1 |
| -1634.85065605 | -12.9 | 8.0 | -1634.38127610 | -17.2 | 3.6 | -1636.14638618 | 1.4 | 22.2 |
| -1634.84956686 | -12.2 | 8.9 | -1634.37976598 | -16.3 | 4.8 | -1636.14572482 | 1.8 | 22.9 |
| -1634.84090362 | -11.9 | 9.0 | -1634.37847872 | -15.7 | 5.3 | -1636.14555202 | 1.9 | 22.8 |
| -1634.84898382 | -11.8 | 8.9 | -1634.37805096 | -15.2 | 5.5 | -1636.14566764 | 1.8 | 22.5 |
| -1634.84000119 | -11.8 | 8.8 | -1634.37746351 | -14.9 | 5.8 | -1636.14583322 | 1.7 | 22.3 |
| -1634.84896472 | -11.8 | 7.3 | -1634.37686559 | -14.5 | 4.6 | -1636.14597072 | 1.6 | 20.7 |
| -1634.84878456 | -11.7 | 6.4 | -1634.37623379 | -14.1 | 4.0 | -1636.14606895 | 1.6 | 19.7 |
| -1634.84569144 | -9.8 | 10.7 | -1634.37579421 | -13.8 | 6.6 | -1636.14194710 | 4.2 | 24.6 |
| -1634.84422119 | -8.8 | 11.5 | -1634.37380143 | -12.6 | 7.8 | -1636.14089623 | 4.8 | 25.2 |
| -1634.84341393 | -8.3 | 12.1 | -1634.37237072 | -11.7 | 8.7 | -1636.14042287 | 5.1 | 25.5 |
| -1634.84293636 | -8.1 | 11.9 | -1634.37126522 | -11.0 | 9.0 | -1636.14024410 | 5.2 | 25.2 |
| -1634.84274362 | -7.9 | 11.4 | -1634.37013843 | -10.4 | 9.0 | -1636.14017833 | 5.3 | 24.6 |
| -1634.84248605 | -7.7 | 11.3 | -1634.36943487 | -9.8 | 9.2 | -1636.14013058 | 5.3 | 24.3 |
| -1634.84222091 | -7.6 | 9.1 | -1634.36863446 | -9.3 | 7.4 | -1636.14012050 | 5.3 | 22.0 |

$E_\text{sp}$ .... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)

$\Delta E_\text{sp}$ .... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)

$\Delta G_\text{sp}$ .... relative single point free energy in toluene in kcal/mol ($\Delta G_\text{sp} = \Delta E_\text{sp}/6-311++G(2df,2pd) + \Delta G_{\text{corr}}/6-31G(d,p)$)
Table S1-4. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIa–Va in Figure 1 and S1]

| E(sp) | ΔE(sp) | ΔG(sp) | E(sp) | ΔE(sp) | ΔG(sp) |
|-------|--------|--------|-------|--------|--------|
|       | [hartree] | [kcal/mol] | [kcal/mol] | [hartree] | [kcal/mol] | [kcal/mol] |
| -1634.26700827 | 0.0 | 0.0 | -1636.09524563 | 0.0 | 0.0 |
| -1634.27698939 | -6.3 | 14.1 | -1636.09864643 | -2.1 | 18.3 |
| -1634.27497386 | -5.0 | 15.2 | -1636.09697416 | -1.1 | 19.2 |
| -1634.27353348 | -4.1 | 15.7 | -1636.09573807 | -0.3 | 19.5 |
| -1634.27245446 | -3.4 | 15.9 | -1636.09472903 | 0.3 | 19.7 |
| -1634.27169950 | -2.9 | 15.7 | -1636.09394289 | 0.8 | 19.5 |
| -1634.27090305 | -2.4 | 16.0 | -1636.09307374 | 1.4 | 19.8 |
| -1634.27018853 | -2.0 | 16.1 | -1636.09227505 | 1.9 | 20.0 |
| -1634.27544438 | -5.3 | 16.6 | -1636.09741463 | -1.4 | 20.5 |
| -1634.27362625 | -4.2 | 17.4 | -1636.09606899 | -0.5 | 21.0 |
| -1634.27240042 | -3.4 | 18.3 | -1636.09508460 | 0.1 | 21.8 |
| -1634.27148848 | -2.8 | 18.6 | -1636.09427535 | 0.6 | 22.0 |
| -1634.27004772 | -1.9 | 18.7 | -1636.09282724 | 1.5 | 22.2 |
| -1634.26938217 | -1.5 | 18.6 | -1636.09211997 | 2.0 | 22.1 |
| -1634.28121297 | -8.9 | 12.0 | -1636.10233181 | -4.4 | 16.4 |
| -1634.27974947 | -8.0 | 13.1 | -1636.10113169 | -3.7 | 17.4 |
| -1634.27882279 | -7.4 | 13.5 | -1636.10038857 | -3.2 | 17.7 |
| -1634.27823754 | -7.0 | 13.7 | -1636.09989267 | -2.9 | 17.8 |
| -1634.27777346 | -6.8 | 13.9 | -1636.09941114 | -2.6 | 18.0 |
| -1634.27734088 | -6.5 | 12.6 | -1636.09891312 | -2.3 | 16.8 |
| -1634.27690867 | -6.2 | 11.9 | -1636.09844166 | -2.0 | 16.1 |
| -1634.27614515 | -5.7 | 14.7 | -1636.09729783 | -1.3 | 19.1 |
| -1634.27425783 | -4.5 | 15.8 | -1636.09569348 | -0.3 | 20.1 |
| -1634.27298514 | -3.8 | 16.6 | -1636.09460679 | 0.4 | 20.8 |
| -1634.27205834 | -3.2 | 16.8 | -1636.09376038 | 0.9 | 20.9 |
| -1634.27130877 | -2.7 | 16.6 | -1636.09298724 | 1.4 | 20.8 |
| -1634.27065016 | -2.3 | 16.8 | -1636.09224542 | 1.9 | 20.9 |
| -1634.27008028 | -1.9 | 14.8 | -1636.09162742 | 2.3 | 19.0 |

E(sp) ..... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
ΔE(sp) ..... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
ΔG(sp) ..... relative single point free energy in toluene in kcal/mol (ΔG(sp) = ΔE(sp)/6-311++G(2df,2pd) + ΔG_corr/6-31G(d,p))

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Table S2-1. After optimization with M06-2X/6-31G(d,p) in toluene (PCM) [IIb–Vb in Figure 1 and S2]

| structure | $E$ [hartree] | $\Delta E$ [kcal/mol] | $G$ [hartree] | $\Delta G$ [kcal/mol] | $\Delta G_{corr}$ [kcal/mol] | FREQ [cm$^{-1}$] |
|-----------|----------------|-------------------|---------------|-------------------|--------------------------|--------------|
| cat1      | -1826.62108164 | 0.0              | -1826.036762  | 0.0              | 0.0                      | 17.24        |
| IIb_2.10 Å | -1826.65380539 | -20.5            | -1826.039005  | -1.4             | 19.1                     | -316.60      |
| IIb_2.20 Å | -1826.65213306 | -19.5            | -1826.036272  | 0.3              | 19.8                     | -228.68      |
| IIb_2.30 Å | -1826.65127270 | -18.9            | -1826.036173  | 0.4              | 19.3                     | -171.41      |
| IIb_2.40 Å | -1826.65087319 | -18.7            | -1826.036323  | 0.3              | 19.0                     | -141.48      |
| IIb       | -1826.65079465 | -18.6            | -1826.036291  | 0.3              | 18.9                     | -121.49      |
| IIb_2.60 Å | -1826.65093769 | -18.7            | -1826.037427  | -0.4             | 18.3                     | -53.76       |
| IIIb_2.10 Å | -1826.64826758 | -17.1            | -1826.031029  | 3.6              | 20.7                     | -330.28      |
| IIIb_2.20 Å | -1826.64476510 | -14.9            | -1826.027870  | 5.6              | 20.4                     | -264.39      |
| IIIb_2.30 Å | -1826.64220239 | -13.3            | -1826.025477  | 7.1              | 20.3                     | -209.60      |
| IIIb_2.46 Å | -1826.63916164 | -11.3            | -1826.023708  | 8.2              | 19.5                     | -147.83      |
| IIIb_2.60 Å | -1826.63815671 | -10.7            | -1826.022525  | 8.9              | 19.6                     | -91.40       |
| IIIb_2.70 Å | -1826.63778129 | -10.5            | -1826.021368  | 9.7              | 20.1                     | -73.88       |
| IVb_2.10 Å | -1826.65657214 | -22.3            | -1826.039579  | -1.8             | 20.5                     | -322.96      |
| IVb_2.20 Å | -1826.6543696  | -20.7            | -1826.037900  | -0.7             | 20.0                     | -255.24      |
| IVb_2.30 Å | -1826.65268384 | -19.8            | -1826.036947  | -0.1             | 19.7                     | -187.15      |
| IVb_2.40 Å | -1826.65183025 | -19.3            | -1826.035601  | 0.7              | 20.0                     | -154.12      |
| IVb_2.46 Å | -1826.65152132 | -19.1            | -1826.035153  | 1.0              | 20.1                     | -140.11      |
| IVb_2.60 Å | -1826.65122151 | -18.9            | -1826.035182  | 1.0              | 19.9                     | -78.85       |
| IVb_2.70 Å | -1826.65119652 | -18.9            | -1826.035715  | 0.7              | 19.6                     | -34.99       |
| IVb       | -1826.65119860 | -18.9            | -1826.035872  | 0.6              | 19.5                     | -32.13       |
| Vb_2.10 Å | -1826.65229374 | -19.6            | -1826.036061  | 0.4              | 20.0                     | -328.84      |
| Vb_2.20 Å | -1826.65075545 | -18.6            | -1826.035105  | 1.0              | 19.7                     | -240.76      |
| Vb_2.30 Å | -1826.64996451 | -18.1            | -1826.034523  | 1.4              | 19.5                     | -174.17      |
| Vb_2.40 Å | -1826.64962722 | -17.9            | -1826.034230  | 1.6              | 19.5                     | -139.37      |
| Vb_2.50 Å | -1826.64958431 | -17.9            | -1826.035736  | 0.6              | 18.5                     | -115.75      |
| Vb_2.60 Å | -1826.64986642 | -18.1            | -1826.035902  | 0.5              | 18.6                     | -44.83       |
| Vb_2.70 Å | -1826.65016027 | -18.2            | -1826.037041  | -0.2             | 18.1                     | 20.91        |

$E$: electronic energy in toluene (PCM) in hartree with 6-31G(d,p)

$G$: sum of electronic and thermal free energies in toluene (PCM) in hartree with 6-31G(d,p)

$\Delta E$: relative electronic energy in kcal/mol in toluene (PCM) with 6-31G(d,p)

$\Delta G$: relative free energy in kcal/mol in toluene (PCM) with 6-31G(d,p)

$\Delta G_{corr}$: gas phase thermal correction to free energy in kcal/mol obtained with 6-31G(d,p) ($\Delta G = \Delta E + \Delta G_{corr}$)
Table S2-2. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIb-Vb in Figure 1 and S2]

| M062X/6-311++G(2df,2pd) (toluene) | ωB97XD/6-311++G(2df,2pd) (toluene) | M06/6-311++G(2df,2pd) (toluene) |
|------------------------------------|------------------------------------|---------------------------------|
| E_{sp} [hartree] | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] | E_{sp} [hartree] | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] | E_{sp} [hartree] | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] |
| -1827.20607178 | 0.0 | 0.0 | -1827.38549978 | 0.0 | 0.0 | -1826.73579183 | 0.0 | 0.0 |
| -1827.22715852 | -13.2 | 5.9 | -1827.40117697 | -9.8 | 9.3 | -1826.75296327 | -10.8 | 8.4 |
| -1827.22569021 | -12.3 | 7.5 | -1827.39973656 | -8.9 | 10.9 | -1826.75142319 | -9.8 | 10.0 |
| -1827.22519185 | -12.0 | 7.3 | -1827.3952387 | -8.8 | 10.5 | -1826.75121512 | -9.7 | 9.6 |
| -1827.22514735 | -12.0 | 7.0 | -1827.3996159 | -9.1 | 9.9 | -1826.75178236 | -10.0 | 8.9 |
| -1827.22531042 | -12.1 | 6.9 | -1827.40055488 | -9.4 | 9.5 | -1826.75240708 | -10.4 | 8.5 |
| -1827.22581979 | -12.4 | 5.9 | -1827.40153981 | -10.1 | 8.3 | -1826.75328615 | -11.0 | 7.3 |
| -1827.22381523 | -11.1 | 9.5 | -1827.39907452 | -8.5 | 12.1 | -1826.74969609 | -8.7 | 11.9 |
| -1827.22057372 | -9.1 | 11.3 | -1827.39585234 | -6.5 | 13.9 | -1826.74614674 | -6.5 | 13.9 |
| -1827.21824810 | -7.6 | 12.7 | -1827.39375503 | -5.2 | 15.2 | -1826.74374854 | -5.0 | 15.3 |
| -1827.21630793 | -6.4 | 13.1 | -1827.39246893 | -4.4 | 15.2 | -1826.74306430 | -4.6 | 15.0 |
| -1827.21563560 | -6.0 | 13.6 | -1827.39250685 | -4.4 | 15.3 | -1826.74304537 | -4.6 | 15.1 |
| -1827.21547572 | -5.9 | 14.2 | -1827.39265749 | -4.5 | 15.6 | -1826.74327167 | -4.7 | 15.4 |
| -1827.23311761 | -17.0 | 3.5 | -1827.40847641 | -14.4 | 6.1 | -1826.75889329 | -14.5 | 6.0 |
| -1827.23080444 | -15.5 | 4.5 | -1827.40610403 | -12.9 | 7.1 | -1826.75622945 | -12.8 | 7.2 |
| -1827.22953888 | -14.7 | 5.0 | -1827.40493748 | -12.2 | 7.5 | -1826.75497956 | -12.0 | 7.7 |
| -1827.22886083 | -14.3 | 5.7 | -1827.40458561 | -12.0 | 8.0 | -1826.75474067 | -11.9 | 8.1 |
| -1827.22864158 | -14.2 | 5.9 | -1827.40465172 | -12.0 | 8.1 | -1826.75486579 | -12.0 | 8.1 |
| -1827.22854962 | -14.1 | 5.8 | -1827.40522113 | -12.4 | 7.5 | -1826.75458604 | -12.4 | 7.5 |
| -1827.22868922 | -14.2 | 5.4 | -1827.40573043 | -12.7 | 6.9 | -1826.75598796 | -12.7 | 6.9 |
| -1827.22871611 | -14.2 | 5.2 | -1827.40580201 | -12.7 | 6.7 | -1826.75606200 | -12.7 | 6.7 |
| -1827.22683918 | -13.0 | 7.0 | -1827.40007860 | -9.1 | 10.9 | -1826.75258996 | -10.5 | 9.5 |
| -1827.22559123 | -12.2 | 7.4 | -1827.39882767 | -8.4 | 11.3 | -1826.75110047 | -9.6 | 10.1 |
| -1827.22514015 | -12.0 | 7.6 | -1827.39864238 | -8.2 | 11.3 | -1826.75088477 | -9.5 | 10.1 |
| -1827.22514503 | -12.0 | 7.5 | -1827.39910736 | -8.5 | 11.0 | -1826.75153834 | -9.9 | 9.6 |
| -1827.22541416 | -12.1 | 6.4 | -1827.39988203 | -9.0 | 9.5 | -1826.75252566 | -10.5 | 8.0 |
| -1827.22604087 | -12.5 | 6.1 | -1827.40102267 | -9.7 | 8.9 | -1826.75394748 | -11.4 | 7.2 |
| -1827.22662635 | -12.9 | 5.2 | -1827.40194903 | -10.3 | 7.7 | -1826.75472486 | -11.9 | 6.2 |

E_{sp} ..... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
ΔE_{sp} ..... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
ΔG_{sp} ..... relative single point free energy in toluene in kcal/mol (ΔG_{sp} = ΔE_{sp}/6-311++G(2df,2pd) + ΔG_corr/6-31G(d,p))
Table S2-3. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIb–Vb in Figure 1 and S2]

| MN12SX/6-311++G(2df,2pd) (toluene) | PBE0-D3BJ/6-311++G(2df,2pd) (toluene) | B3LYP/6-311++G(2df,2pd) (toluene) |
|-------------------------------------|---------------------------------------|----------------------------------|
|                                     |                                       |                                  |
| E_sp [hartree]                      | ΔE_sp [kcal/mol]                      | ΔG_sp [kcal/mol]                 |
| -1826.47837797                      | 0.0                                   | 0.0                              |
| -1826.49253190                      | -8.9                                  | 10.2                             |
| -1826.49171018                      | -8.4                                  | 11.4                             |
| -1826.49181922                      | -8.4                                  | 10.9                             |
| -1826.49241657                      | -8.8                                  | 10.2                             |
| -1826.49300974                      | -9.2                                  | 9.8                              |
| -1826.49400243                      | -9.8                                  | 8.5                              |
| -1826.48804516                      | -6.1                                  | 14.6                             |
| -1826.48524813                      | -4.3                                  | 16.1                             |
| -1826.48326156                      | -3.1                                  | 17.3                             |
| -1826.48270224                      | -2.7                                  | 16.8                             |
| -1826.48258339                      | -2.6                                  | 17.0                             |
| -1826.48274055                      | -2.7                                  | 17.4                             |
| -1826.49909445                      | -13.0                                 | 7.5                              |
| -1826.49728493                      | -11.9                                 | 8.2                              |
| -1826.49645118                      | -11.3                                 | 8.4                              |
| -1826.49624021                      | -11.2                                 | 8.8                              |
| -1826.49628840                      | -11.2                                 | 8.9                              |
| -1826.49676868                      | -11.5                                 | 8.4                              |
| -1826.49698392                      | -11.7                                 | 7.9                              |
| -1826.49702750                      | -11.7                                 | 7.8                              |
| -1826.49307350                      | -9.2                                  | 10.8                             |
| -1826.49237479                      | -8.8                                  | 10.9                             |
| -1826.49255809                      | -8.9                                  | 10.6                             |
| -1826.49322253                      | -9.3                                  | 10.2                             |
| -1826.49405865                      | -9.8                                  | 8.7                              |
| -1826.49510255                      | -10.5                                 | 8.1                              |
| -1826.49582196                      | -10.9                                 | 7.1                              |

E_sp = single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)

ΔE_sp = relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)

ΔG_sp = relative single point free energy in toluene in kcal/mol (ΔG_sp = ΔE_sp/6-311++G(2df,2pd) + ΔG_corr/6-31G(d,p))
Table S2-4. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIb–Vb in Figure 1 and S2]

|                   | PBE0/6-311++G(2df,2pd) (toluene) | BP86/6-311++G(2df,2pd) (toluene) |
|-------------------|----------------------------------|----------------------------------|
|                   | E<sub>sp</sub> [hartree] | ΔE<sub>sp</sub> [kcal/mol] | ΔG<sub>sp</sub> [kcal/mol] | E<sub>sp</sub> [hartree] | ΔE<sub>sp</sub> [kcal/mol] | ΔG<sub>sp</sub> [kcal/mol] |
| -1825.83404479    | 0.0                             | 0.0                             | -1827.88627299             | 0.0                             | 0.0                             |
| -1825.84407515    | -6.3                            | 12.8                            | -1827.88856896             | -1.4                            | 17.7                            |
| -1825.84234720    | -5.2                            | 14.6                            | -1827.88741355             | -0.7                            | 19.1                            |
| -1825.84175896    | -4.8                            | 14.5                            | -1827.88714578             | -0.5                            | 18.8                            |
| -1825.84163792    | -4.8                            | 14.2                            | -1827.88720792             | -0.6                            | 18.4                            |
| -1825.84169754    | -4.8                            | 14.1                            | -1827.88730759             | -0.6                            | 18.3                            |
| -1825.84180992    | -4.9                            | 13.5                            | -1827.88735979             | -0.7                            | 17.6                            |
| -1825.83496612    | -0.6                            | 20.1                            | -1827.87909738             | 4.5                             | 25.2                            |
| -1825.83195251    | 1.3                             | 21.8                            | -1827.87671132             | 6.0                             | 26.4                            |
| -1825.82963189    | 2.8                             | 23.1                            | -1827.87484645             | 7.2                             | 27.5                            |
| -1825.82780973    | 3.9                             | 23.4                            | -1827.87336239             | 8.1                             | 27.6                            |
| -1825.82729320    | 4.2                             | 23.9                            | -1827.87312706             | 8.2                             | 27.9                            |
| -1825.82738213    | 4.2                             | 24.3                            | -1827.87339875             | 8.1                             | 28.2                            |
| -1825.84210664    | -5.1                            | 15.4                            | -1827.88487820             | 0.9                             | 21.4                            |
| -1825.83995339    | -3.7                            | 16.3                            | -1827.88335575             | 1.8                             | 21.9                            |
| -1825.83866523    | -2.9                            | 16.8                            | -1827.88252642             | 2.4                             | 22.1                            |
| -1825.83807128    | -2.5                            | 17.5                            | -1827.88227295             | 2.5                             | 22.5                            |
| -1825.83789318    | -2.4                            | 17.7                            | -1827.88223893             | 2.5                             | 22.6                            |
| -1825.83775069    | -2.3                            | 17.6                            | -1827.88253838             | 2.5                             | 22.4                            |
| -1825.83774845    | -2.3                            | 17.2                            | -1827.88228672             | 2.5                             | 22.1                            |
| -1825.83775874    | -2.3                            | 17.1                            | -1827.88230347             | 2.5                             | 21.9                            |
| -1825.84219524    | -5.1                            | 14.9                            | -1827.88640849             | -0.1                            | 19.9                            |
| -1825.84092987    | -4.3                            | 15.3                            | -1827.88561846             | 0.4                             | 20.1                            |
| -1825.84042198    | -4.0                            | 15.5                            | -1827.88547404             | 0.5                             | 20.0                            |
| -1825.84037990    | -4.0                            | 15.5                            | -1827.88563848             | 0.4                             | 19.9                            |
| -1825.84054287    | -4.1                            | 14.5                            | -1827.88587128             | 0.3                             | 18.8                            |
| -1825.84109610    | -4.4                            | 14.2                            | -1827.88650372             | -0.1                            | 18.5                            |
| -1825.84137446    | -4.6                            | 13.5                            | -1827.88674519             | -0.3                            | 17.8                            |

E<sub>sp</sub> ...... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)

ΔE<sub>sp</sub> ...... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)

ΔG<sub>sp</sub> ...... relative single point free energy in toluene in kcal/mol (ΔG<sub>sp</sub> = ΔE<sub>sp</sub>/6-311++G(2df,2pd) + ΔG<sub>corr</sub>/6-31G(d,p))
Table S3-1. After optimization with M06-2X/6-31G(d,p) in toluene (PCM) \([IIc\sim Vc\text{ in Figure 2 and S3}]\)

| structure     | \(E\) [hartree] | \(\Delta E\) [kcal/mol] | \(G\) [hartree] | \(\Delta G\) [kcal/mol] | \(\Delta G_{\text{corr}}\) [kcal/mol] | FREQ [\(\text{cm}^{-1}\)] |
|---------------|-----------------|--------------------------|-----------------|-------------------------|----------------------------------------|------------------------|
| catl          | -1865.91825336  | 0.0                      | -1865.304382    | -1865.307228            | 0.0                                    | 0.0                    |
| IIc_2.20 Å    | -1865.95025976  | -20.1                    | -1865.307307    | -1865.307307            | 0.0                                    | 20.0                   |
| IIc_2.30 Å    | -1865.94972664  | -19.7                    | -1865.306392    | -1865.306392            | 0.5                                    | 20.3                   |
| IIc_2.40 Å    | -1865.94959465  | -19.7                    | -1865.306419    | -1865.306419            | 0.5                                    | 20.2                   |
| IIc_2.50 Å    | -1865.94959561  | -19.7                    | -1865.306444    | -1865.306444            | 0.5                                    | 20.2                   |
| IIc_2.60 Å    | -1865.94974932  | -19.8                    | -1865.307320    | -1865.307320            | -0.1                                   | 19.7                   |
| IIIc_2.20 Å   | -1865.93878692  | -12.9                    | -1865.293839    | -1865.293839            | 8.4                                    | 21.3                   |
| IIIc_2.30 Å   | -1865.93697750  | -11.7                    | -1865.292042    | -1865.292042            | 9.5                                    | 21.3                   |
| IIIc_2.40 Å   | -1865.93580058  | -11.0                    | -1865.291231    | -1865.291231            | 10.0                                   | 21.0                   |
| IIIc_2.50 Å   | -1865.93506334  | -10.5                    | -1865.291022    | -1865.291022            | 10.2                                   | 20.7                   |
| IIIc_2.60 Å   | -1865.93469208  | -10.3                    | -1865.292529    | -1865.292529            | 9.2                                    | 19.5                   |
| IIIe          | -1865.93462016  | -10.3                    | -1865.292990    | -1865.292990            | 8.9                                    | 19.2                   |
| IVc_2.20 Å    | -1865.94797922  | -18.7                    | -1865.302471    | -1865.302471            | 3.0                                    | 21.6                   |
| IVc_2.30 Å    | -1865.94644647  | -17.7                    | -1865.301721    | -1865.301721            | 3.5                                    | 21.1                   |
| IVc_2.40 Å    | -1865.94534623  | -17.0                    | -1865.301903    | -1865.301903            | 3.3                                    | 20.3                   |
| IVc_2.60 Å    | -1865.94433855  | -16.4                    | -1865.300952    | -1865.300952            | 3.9                                    | 20.3                   |
| IVc           | -1865.94425012  | -16.3                    | -1865.301573    | -1865.301573            | 3.5                                    | 19.9                   |
| Vc_2.05 Å     | -1865.95021040  | -20.1                    | -1865.306032    | -1865.306032            | 0.8                                    | 20.8                   |
| Vc_2.10 Å     | -1865.94926545  | -19.5                    | -1865.304680    | -1865.304680            | 1.6                                    | 21.1                   |
| Vc_2.15 Å     | -1865.94862431  | -19.1                    | -1865.303963    | -1865.303963            | 2.0                                    | 21.1                   |
| Vc_2.20 Å     | -1865.94820140  | -18.8                    | -1865.303532    | -1865.303532            | 2.3                                    | 21.1                   |
| Vc_2.30 Å     | -1865.94777374  | -18.5                    | -1865.303557    | -1865.303557            | 2.3                                    | 20.8                   |
| Vc            | -1865.94769245  | -18.5                    | -1865.304721    | -1865.304721            | 1.6                                    | 20.0                   |
| Vc_2.40 Å     | -1865.94769877  | -18.5                    | -1865.304745    | -1865.304745            | 1.6                                    | 20.0                   |

\(E\) …… electronic energy in toluene (PCM) in hartree with 6-31G(d,p)
\(G\) …… sum of electronic and thermal free energies in toluene (PCM) in hartree with 6-31G(d,p)
\(\Delta E\) …… relative electronic energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
\(\Delta G\) …… relative free energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
\(\Delta G_{\text{corr}}\) gas phase thermal correction to free energy in kcal/mol obtained with 6-31G(d,p) \((\Delta G = \Delta E + \Delta G_{\text{corr}})\)
### Table S3-2. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIc–Vc in Figure 2 and S3]

|                | M062X/6-311++G(2df,2pd) (toluene) | ΩB97XD/6-311++G(2df,2pd) (toluene) | M06/6-311++G(2df,2pd) (toluene) |
|----------------|-----------------------------------|-----------------------------------|----------------------------------|
|                | $E_p$ [hartree] | $\Delta E_p$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] | $E_p$ [hartree] | $\Delta E_p$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] | $E_p$ [hartree] | $\Delta E_p$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] |
| -1866.51357009 | 0.0 | 0.0 | 0.0 | -1866.7018054 | 0.0 | 0.0 | -1866.03022045 | 0.0 | 0.0 |
| -1866.53436375  | -13.0 | 7.0 | -9.4 | 10.6 | -1866.71608506 | -9.5 | 10.8 | -1866.04648395 | -10.2 | 9.8 |
| -1866.53417306  | -12.9 | 7.3 | -9.0 | 10.3 | -1866.71619083 | -9.9 | 10.2 | -1866.04657613 | -10.3 | 10.0 |
| -1866.53432181  | -13.0 | 7.2 | -9.5 | 10.2 | -1866.71685315 | -9.9 | 10.2 | -1866.04729886 | -10.7 | 9.5 |
| -1866.53434545  | -13.0 | 7.1 | -9.2 | 10.2 | -1866.71692443 | -9.9 | 10.2 | -1866.04737331 | -10.8 | 9.4 |
| -1866.53478364  | -13.3 | 6.4 | -10.6 | 9.1 | -1866.71796215 | -10.6 | 9.1 | -1866.04840424 | -11.4 | 8.3 |
| -1866.53537121  | -13.7 | 5.7 | -11.2 | 8.1 | -1866.71900173 | -11.2 | 8.1 | -1866.04973999 | -11.2 | 7.4 |
| -1866.52482165  | -7.1 | 14.2 | -4.7 | 16.6 | -1866.70857231 | -4.7 | 16.6 | -1866.03666249 | -4.0 | 17.2 |
| -1866.52238666  | -6.1 | 15.2 | -3.9 | 17.4 | -1866.70722124 | -3.9 | 17.4 | -1866.03503849 | -3.0 | 18.3 |
| -1866.52229652  | -5.5 | 15.6 | -3.5 | 17.5 | -1866.70673204 | -3.5 | 17.5 | -1866.03444401 | -2.7 | 18.4 |
| -1866.52180643  | -5.2 | 15.5 | -3.6 | 17.1 | -1866.70682225 | -3.6 | 17.1 | -1866.03453030 | -2.7 | 18.0 |
| -1866.52171162  | -5.1 | 14.4 | -3.9 | 15.6 | -1866.70728357 | -3.9 | 15.6 | -1866.03496863 | -3.0 | 16.6 |
| -1866.52183432  | -5.2 | 14.0 | -4.2 | 15.0 | -1866.70779185 | -4.2 | 15.0 | -1866.03531798 | -3.2 | 16.0 |
| -1866.53492311  | -13.4 | 8.2 | -11.3 | 10.3 | -1866.71913860 | -11.3 | 10.3 | -1866.04738234 | -10.8 | 10.9 |
| -1866.53359465  | -12.6 | 8.6 | -10.7 | 10.4 | -1866.71813785 | -10.7 | 10.4 | -1866.04611005 | -10.0 | 11.2 |
| -1866.53227218  | -12.0 | 8.3 | -10.5 | 9.8 | -1866.71872832 | -10.5 | 9.8 | -1866.04570775 | -9.7 | 10.6 |
| -1866.53211791  | -11.6 | 8.7 | -11.0 | 9.3 | -1866.71866685 | -11.0 | 9.3 | -1866.04661974 | -10.3 | 10.0 |
| -1866.53236443  | -11.8 | 8.1 | -11.5 | 8.3 | -1866.71943093 | -11.5 | 8.3 | -1866.04730991 | -10.7 | 9.1 |
| -1866.53490012  | -13.4 | 7.4 | -9.6 | 11.2 | -1866.71686669 | -9.6 | 11.2 | -1866.04725208 | -10.7 | 10.1 |
| -1866.53410790  | -12.9 | 8.2 | -9.0 | 12.0 | -1866.71548111 | -9.0 | 12.0 | -1866.04611500 | -10.0 | 11.1 |
| -1866.53360577  | -12.6 | 8.5 | -8.7 | 12.4 | -1866.71493767 | -8.7 | 12.4 | -1866.04546790 | -9.6 | 11.5 |
| -1866.53332632  | -12.4 | 8.7 | -8.5 | 12.6 | -1866.71469679 | -8.5 | 12.6 | -1866.04520830 | -9.4 | 11.7 |
| -1866.53320307  | -12.3 | 8.5 | -8.7 | 12.1 | -1866.71492726 | -8.7 | 12.1 | -1866.04552923 | -9.6 | 11.2 |
| -1866.5339278  | -12.4 | 7.6 | -9.1 | 10.9 | -1866.71562482 | -9.1 | 10.9 | -1866.04635860 | -10.1 | 9.9 |
| -1866.53343836  | -12.5 | 7.6 | -9.2 | 10.8 | -1866.71575386 | -9.2 | 10.8 | -1866.04650150 | -10.2 | 9.8 |

$E_p$ ….. single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)

$\Delta E_p$ …. relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)

$\Delta G_{sp}$ … relative single point free energy in toluene in kcal/mol ($\Delta G_{sp} = \Delta E_p / 6-311++G(2df,2pd) + \Delta G_{corr}/6-31G(d,p)$)
Table S3-3. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIc–Vc in Figure 2 and S3]

| Energy (hartree) | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] | Energy (hartree) | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] | Energy (hartree) | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] |
|-----------------|-------------------|-------------------|-----------------|-------------------|-------------------|-----------------|-----------------|-------------------|
| MN12SX/6-311++G(2df,2pd) (toluene) | | | | | | | | |
| -1865.76667153  | 0.0               | 0.0               | -1865.21213219  | 0.0               | 0.0               | -1867.27084624  | 0.0               | 0.0               |
| -1865.78101862  | -9.0              | 11.0              | -1865.23473492  | -14.2             | 5.9               | -1865.23698473  | 8.7               | 28.7              |
| -1865.78138101  | -9.2              | 11.0              | -1865.23448024  | -14.0             | 6.3               | -1865.2769909   | 8.2               | 28.5              |
| -1865.78205037  | -9.7              | 10.5              | -1865.23450840  | -14.0             | 6.1               | -1865.25865722  | 7.6               | 27.8              |
| -1865.78211642  | -9.7              | 10.5              | -1865.23451817  | -14.0             | 6.1               | -1865.25874396  | 7.6               | 27.8              |
| -1865.78305137  | -10.3             | 9.4               | -1865.23467594  | -14.1             | 5.6               | -1865.25898702  | 6.9               | 26.6              |
| -1865.78396993  | -10.9             | 8.5               | -1865.23478300  | -14.2             | 5.2               | -1865.26097634  | 6.2               | 25.6              |
| -1865.76925739  | -1.6              | 19.7              | -1865.22657730  | -9.1              | 12.2              | -1865.24413772  | 16.8              | 38.0              |
| -1865.76809161  | -0.9              | 20.4              | -1865.22482847  | -8.0              | 13.3              | -1865.24328211  | 17.3              | 38.6              |
| -1865.76754747  | -0.5              | 20.5              | -1865.22364584  | -7.2              | 13.8              | -1865.24303195  | 17.5              | 38.5              |
| -1865.76742945  | -0.5              | 20.2              | -1865.22285589  | -6.7              | 14.0              | -1865.24316102  | 17.4              | 38.1              |
| -1865.76762505  | -0.6              | 18.9              | -1865.22229631  | -6.4              | 13.2              | -1865.24355251  | 17.1              | 36.7              |
| -1865.76785003  | -0.7              | 18.5              | -1865.22205854  | -6.2              | 13.0              | -1865.24399576  | 16.8              | 36.1              |
| -1865.78105319  | -9.0              | 12.6              | -1865.23513936  | -14.4             | 7.2               | -1865.24696476  | 13.3              | 34.9              |
| -1865.78009071  | -8.4              | 12.7              | -1865.23385214  | -13.6             | 7.5               | -1865.24922832  | 13.6              | 34.7              |
| -1865.77958161  | -8.1              | 12.2              | -1865.23301399  | -13.1             | 7.2               | -1865.24936292  | 13.5              | 33.8              |
| -1865.77978832  | -8.2              | 12.1              | -1865.23265673  | -12.9             | 7.4               | -1865.25220772  | 11.7              | 32.0              |
| -1865.78038465  | -8.6              | 11.3              | -1865.23258604  | -12.8             | 7.0               | -1865.25324537  | 11.0              | 30.9              |
| -1865.78140822  | -9.2              | 11.6              | -1865.23465197  | -14.1             | 6.7               | -1865.25663427  | 8.9               | 29.7              |
| -1865.78084703  | -8.9              | 12.2              | -1865.23404873  | -13.8             | 7.3               | -1865.25626499  | 9.1               | 30.2              |
| -1865.78061024  | -8.7              | 12.4              | -1865.23366544  | -13.5             | 7.6               | -1865.25620719  | 9.2               | 30.3              |
| -1865.78061155  | -8.7              | 12.4              | -1865.23344268  | -13.4             | 7.7               | -1865.25639886  | 9.1               | 30.2              |
| -1865.78106505  | -9.0              | 11.8              | -1865.23332050  | -13.3             | 7.5               | -1865.25726146  | 8.5               | 29.4              |
| -1865.78176802  | -9.5              | 10.6              | -1865.23343157  | -13.4             | 6.7               | -1865.25833197  | 7.9               | 27.9              |
| -1865.78187846  | -9.5              | 10.5              | -1865.23345808  | -13.4             | 6.7               | -1865.25849920  | 7.7               | 27.8              |

E_{sp} ...... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
ΔE_{sp} .... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
ΔG_{sp} .... relative single point free energy in toluene in kcal/mol (ΔG_{sp} = ΔE_{sp}/6-311++G(2df,2pd) + ΔG_{corr}/6-31G(d,p))
Table S3-4. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIc–Vc in Figure 2 and S3]

|                  | PBE0/6-311++G(2df,2pd) (toluene) | BP86/6-311++G(2df,2pd) (toluene) |
|------------------|----------------------------------|----------------------------------|
|                  | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] |
| -1865.11150831  | 0.0 | 0.0 | -1867.21068652 | 0.0 | 0.0 |
| -1865.11542068  | -2.5 | 17.6 | -1867.20598242 | 3.0 | 23.0 |
| -1865.11518220  | -2.3 | 18.0 | -1867.20603235 | 2.9 | 23.2 |
| -1865.11532222  | -2.4 | 17.8 | -1867.20633304 | 2.7 | 22.9 |
| -1865.11534407  | -2.4 | 17.8 | -1867.20636267 | 2.7 | 22.9 |
| -1865.11568907  | -2.6 | 17.1 | -1867.20675797 | 2.5 | 22.2 |
| -1865.11602890  | -2.8 | 16.5 | -1867.20709690 | 2.3 | 21.6 |
| -1865.10416357  | 4.6 | 25.9 | -1867.19534186 | 9.6 | 30.9 |
| -1865.10243314  | 5.7 | 27.0 | -1867.19398118 | 10.5 | 31.8 |
| -1865.10136244  | 6.4 | 27.4 | -1867.19313651 | 11.0 | 32.1 |
| -1865.10073131  | 6.8 | 27.5 | -1867.19257679 | 11.4 | 32.1 |
| -1865.10038704  | 7.0 | 26.5 | -1867.19215831 | 11.6 | 31.2 |
| -1865.10033744  | 7.0 | 26.2 | -1867.19201824 | 11.7 | 30.9 |
| -1865.11086033  | 0.4 | 22.0 | -1867.20026376 | 6.5 | 28.2 |
| -1865.10954868  | 1.2 | 22.4 | -1867.19941039 | 7.1 | 28.2 |
| -1865.10882690  | 1.7 | 22.0 | -1867.19902745 | 7.3 | 27.7 |
| -1865.10968738  | 1.1 | 21.4 | -1867.20058721 | 6.3 | 26.6 |
| -1865.10991149  | 1.0 | 20.9 | -1867.2009498 | 6.1 | 26.0 |
| -1865.11633170  | -3.0 | 17.8 | -1867.20617369 | 2.8 | 23.6 |
| -1865.11553825  | -2.5 | 18.5 | -1867.20560074 | 3.2 | 24.3 |
| -1865.11500693  | -2.2 | 18.9 | -1867.20529481 | 3.4 | 24.5 |
| -1865.11470625  | -2.0 | 19.1 | -1867.20519976 | 3.4 | 24.6 |
| -1865.11458990  | -1.9 | 18.9 | -1867.20539877 | 3.3 | 24.1 |
| -1865.11482083  | -2.1 | 18.0 | -1867.20583421 | 3.0 | 23.1 |
| -1865.11486958  | -2.1 | 17.9 | -1867.20590562 | 3.0 | 23.0 |

$E_{sp}$ .... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
$\Delta E_{sp}$ .... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
$\Delta G_{sp}$ .... relative single point free energy in toluene in kcal/mol ($\Delta G_{sp} = \Delta E_{sp}/6-311++G(2df,2pd) + \Delta G_{corr}/6-31G(d,p)$)
Table S4-1. After optimization with M06-2X/6-31G(d,p) in toluene (PCM) [IIId–Vd in Figure 2 and S4]

| structure   | E [hartree] | ΔE [kcal/mol] | G [hartree] | ΔG [kcal/mol] | ΔG<sub>corr</sub> [kcal/mol] | FREQ [cm<sup>-1</sup>] |
|-------------|-------------|---------------|-------------|---------------|------------------------------|-------------------------|
| cat2        | -1825.37628709 | 0.0           | -1824.813066 | 0.0           | 0.0                          | 23.61                   |
| IIId_2.10 Å | -1825.40293719 | -16.7         | -1824.811705 | 0.9           | 17.6                         | -218.30                 |
| IIId_2.15 Å | -1825.40284458 | -16.7         | -1824.812254 | 0.5           | 17.2                         | -180.96                 |
| IIId_2.25 Å | -1825.40295088 | -16.7         | -1824.813194 | -0.1          | 16.7                         | -122.17                 |
| IIId_2.35 Å | -1825.4031913  | -17.0         | -1824.813554 | -0.2          | 16.6                         | -75.21                  |
| IVd_2.10 Å  | -1825.40412544 | -17.5         | -1824.811240 | 1.1           | 18.6                         | -305.59                 |
| IVd_2.15 Å  | -1825.40335987 | -17.0         | -1824.810976 | 1.3           | 18.3                         | -259.35                 |
| IVd_2.25 Å  | -1825.4027128  | -16.4         | -1824.811224 | 1.2           | 17.6                         | -190.28                 |
| IVd_2.35 Å  | -1825.4027215  | -16.3         | -1824.812071 | 0.6           | 16.9                         | -147.67                 |
| IVd         | -1825.4031913  | -17.0         | -1824.813554 | -0.2          | 16.6                         | -75.21                  |
| Vd_2.10 Å   | -1825.40183214 | -16.0         | -1824.809483 | 2.2           | 18.3                         | -281.62                 |
| Vd_2.15 Å   | -1825.40145891 | -15.8         | -1824.808941 | 2.6           | 18.4                         | -237.30                 |
| Vd_2.25 Å   | -1825.40119710 | -15.6         | -1824.808902 | 2.6           | 18.2                         | -174.71                 |
| Vd          | -1825.40119619 | -15.6         | -1824.808930 | 2.6           | 18.2                         | -170.72                 |
| Vd_2.35 Å   | -1825.40133045 | -15.7         | -1824.810479 | 1.6           | 17.3                         | -137.33                 |

E …… electronic energy in toluene (PCM) in hartree with 6-31G(d,p)
G …… sum of electronic and thermal free energies in toluene (PCM) in hartree with 6-31G(d,p)
ΔE …… relative electronic energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
ΔG …… relative free energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
ΔG<sub>corr</sub> … gas phase thermal correction to free energy in kcal/mol obtained with 6-31G(d,p) (ΔG = ΔE + ΔG<sub>corr</sub>)
Table S4-2. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IId–Vd in Figure 2 and S4]

| M062X/6-311++G(2df,2pd) (toluene) | ωB97XD/6-311++G(2df,2pd) (toluene) | M06/6-311++G(2df,2pd) (toluene) |
|-----------------------------------|-----------------------------------|-----------------------------------|
| E<sub>sp</sub> [hartree] | ΔE<sub>sp</sub> [kcal/mol] | ΔG<sub>sp</sub> [kcal/mol] | E<sub>sp</sub> [hartree] | ΔE<sub>sp</sub> [kcal/mol] | ΔG<sub>sp</sub> [kcal/mol] | E<sub>sp</sub> [hartree] | ΔE<sub>sp</sub> [kcal/mol] | ΔG<sub>sp</sub> [kcal/mol] |
| -1825.96449449 | 0.0 | 0.0 | -1826.12944114 | 0.0 | 0.0 | -1825.49228579 | 0.0 | 0.0 |
| -1825.97971575 | -9.6 | 8.0 | -1826.13866068 | -5.8 | 11.8 | -1825.50331841 | -6.9 | 10.7 |
| -1825.97984790 | -9.6 | 7.5 | -1826.13870201 | -5.8 | 11.4 | -1825.50342957 | -7.0 | 10.2 |
| -1825.97985642 | -9.6 | 7.5 | -1826.13870967 | -5.8 | 11.4 | -1825.50344036 | -7.0 | 10.2 |
| -1825.98039104 | -10.0 | 6.7 | -1826.13946297 | -6.3 | 10.4 | -1825.50432804 | -7.6 | 9.1 |
| -1825.98124458 | -10.5 | 6.3 | -1826.14070776 | -7.1 | 9.7 | -1825.50570026 | -8.4 | 8.4 |
| -1825.98353988 | -12.0 | 6.7 | -1826.14452852 | -9.5 | 9.1 | -1825.50690087 | -9.2 | 9.4 |
| -1825.98292845 | -11.6 | 6.7 | -1826.14378536 | -9.0 | 9.3 | -1825.50612595 | -8.7 | 9.6 |
| -1825.98228153 | -11.2 | 6.4 | -1826.14301869 | -8.5 | 9.1 | -1825.50537323 | -8.2 | 9.4 |
| -1825.98233394 | -11.1 | 5.8 | -1826.14291025 | -8.5 | 8.5 | -1825.50559014 | -8.3 | 8.6 |
| -1825.98227678 | -11.2 | 5.6 | -1826.14300223 | -8.5 | 8.3 | -1825.50573275 | -8.4 | 8.3 |
| -1825.97916836 | -9.2 | 9.1 | -1826.13799609 | -5.4 | 12.9 | -1825.50288863 | -6.7 | 11.6 |
| -1825.97899181 | -9.1 | 9.3 | -1826.13773043 | -5.2 | 13.2 | -1825.50267159 | -6.5 | 11.9 |
| -1825.97911125 | -9.2 | 9.1 | -1826.13795477 | -5.3 | 12.9 | -1825.50307916 | -6.8 | 11.5 |
| -1825.97913631 | -9.2 | 9.0 | -1826.13800120 | -5.4 | 12.9 | -1825.50314141 | -6.8 | 11.4 |
| -1825.97959132 | -9.5 | 7.9 | -1826.13884466 | -5.9 | 11.4 | -1825.50424881 | -7.5 | 9.8 |
| -1825.96449449 | 0.0 | 0.0 | -1826.12944114 | 0.0 | 0.0 | -1825.49228579 | 0.0 | 0.0 |

E<sub>sp</sub> ....... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)

ΔE<sub>sp</sub> ....... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)

ΔG<sub>sp</sub> ....... relative single point free energy in toluene in kcal/mol (ΔG<sub>sp</sub> = ΔE<sub>sp</sub>/6-311++G(2df,2pd) + ΔG<sub>corr</sub>/6-31G(d,p))
Table S4-3. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIa–Vd in Figure 2 and S4]  

| MN12SX/6-311++G(2df,2pd) (toluene) | PBE0-D3BJ/6-311++G(2df,2pd) (toluene) | B3LYP/6-311++G(2df,2pd) (toluene) |
|------------------------------------|---------------------------------------|-----------------------------------|
| E_{sp} [hartree] | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] | E_{sp} [hartree] | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] | E_{sp} [hartree] | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] |
| -1825.24058547 | 0.0 | 0.0 | -1824.67980946 | 0.0 | 0.0 | -1826.69135594 | 0.0 | 0.0 |
| -1825.25139757 | -6.8 | 10.8 | -1824.69938402 | -12.3 | 5.3 | -1826.67928433 | 7.6 | 25.2 |
| -1825.25153850 | -6.9 | 10.3 | -1824.69941705 | -12.3 | 4.9 | -1826.67972880 | 7.3 | 24.5 |
| -1825.25154869 | -6.9 | 10.3 | -1824.69942187 | -12.3 | 4.9 | -1826.67975475 | 7.3 | 24.5 |
| -1825.25220569 | -7.3 | 9.4 | -1824.69974296 | -12.5 | 4.1 | -1826.6809143 | 6.5 | 23.2 |
| -1825.25327726 | -8.0 | 8.8 | -1824.70035774 | -12.9 | 3.9 | -1826.68244585 | 5.6 | 22.4 |
| -1825.25513475 | -9.1 | 9.5 | -1824.70254378 | -14.3 | 4.3 | -1826.67442575 | 10.6 | 29.2 |
| -1825.25449588 | -8.7 | 9.6 | -1824.70181607 | -13.8 | 4.5 | -1826.67405191 | 10.9 | 29.2 |
| -1825.25392075 | -8.4 | 9.2 | -1824.70088512 | -13.2 | 4.4 | -1826.67378605 | 11.0 | 28.6 |
| -1825.25407553 | -8.5 | 8.5 | -1824.70062886 | -13.1 | 3.9 | -1826.67456784 | 10.5 | 27.5 |
| -1825.25415358 | -8.5 | 8.3 | -1824.70063579 | -13.1 | 3.7 | -1826.67471648 | 10.4 | 27.2 |
| -1825.25097217 | -6.5 | 11.8 | -1824.69791449 | -11.4 | 6.9 | -1826.67843818 | 8.1 | 26.4 |
| -1825.25080002 | -6.4 | 12.0 | -1824.69764178 | -11.2 | 7.2 | -1826.67859320 | 8.0 | 26.4 |
| -1825.25106893 | -6.6 | 11.7 | -1824.69755880 | -11.1 | 7.1 | -1826.67940121 | 7.5 | 25.7 |
| -1825.2511050 | -6.6 | 11.6 | -1824.69756992 | -11.1 | 7.1 | -1826.67947693 | 7.5 | 25.7 |
| -1825.25185848 | -7.1 | 10.3 | -1824.69784253 | -11.3 | 6.0 | -1826.68059502 | 6.8 | 24.1 |
| -1825.24058547 | 0.0 | 0.0 | -1824.67980946 | 0.0 | 0.0 | -1826.69135594 | 0.0 | 0.0 |

E_{sp} .... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)  
ΔE_{sp} ... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)  
ΔG_{sp} ... relative single point free energy in toluene in kcal/mol (ΔG_{sp} = ΔE_{sp}/6-311++G(2df,2pd) + ΔG_{corr}/6-31G(d,p))
Table S4-4. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [II-d-Vd in Figure 2 and S4]

|                     | PBE0/6-311++G(2df,2pd) (toluene) | BP86/6-311++G(2df,2pd) (toluene) |
|---------------------|----------------------------------|----------------------------------|
|                     | E_{sp} [hartree] | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] | E_{sp} [hartree] | ΔE_{sp} [kcal/mol] | ΔG_{sp} [kcal/mol] |
| -1824.58423613      | 0.0 | 0.0 | -1826.63445782 | 0.0 | 0.0 |
| -1824.58925031      | -3.1 | 14.4 | -1826.63239856 | 1.3 | 18.9 |
| -1824.58923455      | -3.1 | 14.0 | -1826.63251302 | 1.2 | 18.4 |
| -1824.58923803      | -3.1 | 14.0 | -1826.63252239 | 1.2 | 18.4 |
| -1824.58951041      | -3.3 | 13.3 | -1826.63300739 | 0.9 | 17.6 |
| -1824.59013686      | -3.7 | 13.1 | -1826.63371601 | 0.5 | 17.2 |
| -1824.58676803      | -1.6 | 17.0 | -1826.62961010 | 3.0 | 21.7 |
| -1824.58596529      | -1.1 | 17.2 | -1826.62891820 | 3.5 | 21.8 |
| -1824.58491639      | -0.4 | 17.2 | -1826.62804734 | 4.0 | 21.6 |
| -1824.58489186      | -0.4 | 16.5 | -1826.62806404 | 4.0 | 20.9 |
| -1824.58491310      | -0.4 | 16.4 | -1826.62808363 | 4.0 | 20.8 |
| -1824.58787124      | -2.3 | 16.0 | -1826.63157340 | 1.8 | 20.1 |
| -1824.58754341      | -2.1 | 16.3 | -1826.63134927 | 2.0 | 20.3 |
| -1824.58742320      | -2.0 | 16.2 | -1826.63137345 | 1.9 | 20.2 |
| -1824.58743601      | -2.0 | 16.2 | -1826.63139393 | 1.9 | 20.1 |
| -1824.58775434      | -2.2 | 15.1 | -1826.63176731 | 1.7 | 19.0 |
| -1824.58423613      | 0.0 | 0.0 | -1826.63445782 | 0.0 | 0.0 |

E_{sp} ...... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
ΔE_{sp} ..... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
ΔG_{sp} ..... relative single point free energy in toluene in kcal/mol (ΔG_{sp} = ΔE_{sp}/6-311++G(2df,2pd) + ΔG_{corr}/6-31G(d,p))
Table S5-1. After optimization with M06-2X/6-31G(d,p) in toluene (PCM) [IIe–Ve in Figure S5]

| structure | $E$ [hartree] | $\Delta E$ [kcal/mol] | $G$ [hartree] | $\Delta G$ [kcal/mol] | $\Delta G_{\text{corr}}$ [kcal/mol] | FREQ [cm$^{-1}$] |
|-----------|-------------|----------------|-------------|----------------|----------------|----------------|
| cat3      | -2651.76749863 | 0.0          | -2651.068851 | 0.0           | 0.0            | 16.73          |
| IIe       | -2651.80282411 | -22.2        | -2651.075829 | -4.4          | 17.8           | -177.66        |
| IIe_2.20 Å | -2651.80298705 | -22.3        | -2651.076028 | -4.5          | 17.8           | -133.18        |
| IIe_2.50 Å | -2651.80430440 | -23.1        | -2651.075398 | -4.1          | 19.0           | -16.80         |
| Ve_2.05 Å | -2651.80286098 | -22.2        | -2651.070908 | -1.3          | 20.9           | -301.30        |
| Ve_2.10 Å | -2651.80233153 | -21.9        | -2651.070960 | -1.3          | 20.5           | -254.83        |
| Ve_2.15 Å | -2651.80203392 | -21.7        | -2651.071075 | -1.4          | 20.3           | -211.06        |
| Ve_2.20 Å | -2651.80189599 | -21.6        | -2651.070983 | -1.3          | 20.2           | -177.73        |
| Ve       | -2651.80186286 | -21.6        | -2651.071248 | -1.5          | 20.1           | -151.41        |
| Ve_2.30 Å | -2651.80190503 | -21.6        | -2651.071614 | -1.7          | 19.9           | -127.16        |
| Ve_2.40 Å | -2651.80214194 | -21.7        | -2651.072196 | -2.1          | 19.6           | -120.47        |
| Ve_2.50 Å | -2651.80256000 | -22.0        | -2651.073070 | -2.6          | 19.4           | -75.16         |

E …… electronic energy in toluene (PCM) in hartree with 6-31G(d,p)
G …… sum of electronic and thermal free energies in toluene (PCM) in hartree with 6-31G(d,p)
$\Delta E$ … relative electronic energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
$\Delta G$ … relative free energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
$\Delta G_{\text{corr}}$ … gas phase thermal correction to free energy in kcal/mol obtained with 6-31G(d,p) ($\Delta G = \Delta E + \Delta G_{\text{corr}}$)
Table S5-2. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIe−Ve in Figure S5]

|                  | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] |                  | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] |                  | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] |
|------------------|--------------------|-----------------------------|-----------------------------|------------------|--------------------|-----------------------------|-----------------------------|------------------|--------------------|-----------------------------|-----------------------------|
| M062X/6-311++G(2df,2pd) (toluene) | -2652.54290086 | 0.0                         | 0.0                         | $\omega$B97XD/6-311++G(2df,2pd) (toluene) | -2652.73487316 | 0.0                         | 0.0                         | M06/6-311++G(2df,2pd) (toluene) | -2651.85424152 | 0.0                         | 0.0                         |
|                  | -2652.56688769     | -15.1                       | 2.7                         |                  | -2652.75248765 | -11.1                       | 6.7                         |                  | -2651.87094571 | -10.5                       | 7.3                         |
|                  | -2652.56730411     | -15.3                       | 2.5                         |                  | -2652.75288711 | -11.3                       | 6.5                         |                  | -2651.87153428 | -10.9                       | 6.9                         |
|                  | -2652.56967733     | -16.8                       | 2.2                         |                  | -2652.75642236 | -13.5                       | 5.5                         |                  | -2651.87413118 | -12.5                       | 6.5                         |
|                  | -2652.56713075     | -15.2                       | 5.7                         |                  | -2652.75237774 | -11.0                       | 9.9                         |                  | -2651.87177853 | -11.0                       | 9.9                         |
|                  | -2652.56676650     | -15.0                       | 5.6                         |                  | -2652.75182992 | -10.6                       | 9.9                         |                  | -2651.87123289 | -10.7                       | 9.9                         |
|                  | -2652.56660730     | -14.9                       | 5.4                         |                  | -2652.75144630 | -10.4                       | 9.9                         |                  | -2651.87089783 | -10.5                       | 9.8                         |
|                  | -2652.56663047     | -14.9                       | 5.4                         |                  | -2652.75141473 | -10.4                       | 9.9                         |                  | -2651.87097155 | -10.5                       | 9.7                         |
|                  | -2652.56675364     | -15.0                       | 5.1                         |                  | -2652.75160519 | -10.5                       | 9.6                         |                  | -2651.87127126 | -10.7                       | 9.4                         |
|                  | -2652.56696435     | -15.1                       | 4.8                         |                  | -2652.75196933 | -10.7                       | 9.1                         |                  | -2651.87176451 | -11.0                       | 8.9                         |
|                  | -2652.56751114     | -15.4                       | 4.2                         |                  | -2652.75294180 | -11.3                       | 8.3                         |                  | -2651.87296418 | -11.7                       | 7.9                         |
|                  | -2652.56819160     | -15.9                       | 3.5                         |                  | -2652.75408122 | -12.1                       | 7.3                         |                  | -2651.87420019 | -12.5                       | 6.8                         |
|                  | -2652.54290086     | 0.0                         | 0.0                         |                  | -2652.73487316 | 0.0                         | 0.0                         |                  | -2651.85424152 | 0.0                         | 0.0                         |

$E_{sp}$ …… single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
$\Delta E_{sp}$ … relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
$\Delta G_{sp}$ … relative single point free energy in toluene in kcal/mol ($\Delta G_{sp} = \Delta E_{sp}/6-311++G(2df,2pd) + \Delta G_{corr}/6-31G(d,p)$)
Table S5-3. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIe–Ve in Figure S5]

|           | MN12SX/6-311++G(2df,2pd) (toluene) | PBE0-D3BJ/6-311++G(2df,2pd) (toluene) | B3LYP/6-311++G(2df,2pd) (toluene) |
|-----------|-----------------------------------|---------------------------------------|-----------------------------------|
| E<sub>sp</sub> [hartree] | ΔE<sub>sp</sub> [kcal/mol] | ΔG<sub>sp</sub> [kcal/mol] | E<sub>sp</sub> [hartree] | ΔE<sub>sp</sub> [kcal/mol] | ΔG<sub>sp</sub> [kcal/mol] | E<sub>sp</sub> [hartree] | ΔE<sub>sp</sub> [kcal/mol] | ΔG<sub>sp</sub> [kcal/mol] |
| -2651.59804808 | 0.0 | 0.0 | -2650.75928277 | 0.0 | 0.0 | -2653.49942277 | 0.0 | 0.0 |
| -2651.61778831 | -12.4 | 5.4 | -2650.78652994 | -17.1 | 0.7 | -2653.49029842 | 5.7 | 23.5 |
| -2651.61831863 | -12.7 | 5.0 | -2650.78679033 | -17.3 | 0.5 | -2653.49083606 | 5.4 | 23.2 |
| -2651.62105475 | -14.4 | 4.6 | -2650.78823487 | -18.2 | 0.8 | -2653.49600544 | 2.1 | 21.1 |
| -2651.61801060 | -12.5 | 8.4 | -2650.78609093 | -16.8 | 4.1 | -2653.49074068 | 5.4 | 26.3 |
| -2651.61758877 | -12.3 | 8.3 | -2650.78556902 | -16.5 | 4.0 | -2653.49054999 | 5.6 | 26.1 |
| -2651.61738255 | -12.1 | 8.1 | -2650.78518593 | -16.3 | 4.0 | -2653.49048680 | 5.6 | 25.9 |
| -2651.61743165 | -12.2 | 8.1 | -2650.78504644 | -16.2 | 4.1 | -2653.49071105 | 5.5 | 25.7 |
| -2651.61761648 | -12.3 | 7.8 | -2650.78503324 | -16.2 | 3.9 | -2653.49107602 | 5.2 | 25.3 |
| -2651.61792703 | -12.5 | 7.4 | -2650.78509476 | -16.2 | 3.7 | -2653.49157034 | 4.9 | 24.8 |
| -2651.61874960 | -13.0 | 6.6 | -2650.78537417 | -16.4 | 3.3 | -2653.49269605 | 4.2 | 23.9 |
| -2651.61968573 | -13.6 | 5.8 | -2650.78573120 | -16.6 | 2.8 | -2653.49391564 | 3.5 | 22.8 |
| -2651.59804808 | 0.0 | 0.0 | -2650.75928277 | 0.0 | 0.0 | -2653.49942277 | 0.0 | 0.0 |

E<sub>sp</sub> ...... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
ΔE<sub>sp</sub> ..... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
ΔG<sub>sp</sub> ..... relative single point free energy in toluene in kcal/mol (ΔG<sub>sp</sub> = ΔE<sub>sp</sub>/6-311++G(2df,2pd) + ΔG<sub>corr</sub>/6-31G(d,p))
Table S5-4. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIe−Ve in Figure S5]

|                   | PBE0/6-311++G(2df,2pd) (toluene) | BP86/6-311++G(2df,2pd) (toluene) |
|-------------------|----------------------------------|----------------------------------|
|                   | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] |
| -2650.61400922   | 0.0                          | 0.0                           | -2653.43695891            | 0.0                          | 0.0                           |
| -2650.62326433   | -5.8                         | 12.0                          | -2653.43718920            | -0.1                         | 17.6                          |
| -2650.62323663   | -5.8                         | 12.0                          | -2653.43724592            | -0.2                         | 17.6                          |
| -2650.62563934   | -7.3                         | 11.7                          | -2653.44013706            | -2.0                         | 17.0                          |
| -2650.62378310   | -6.1                         | 14.8                          | -2653.43793216            | -0.6                         | 20.3                          |
| -2650.62316289   | -5.7                         | 14.8                          | -2653.43737298            | -0.3                         | 20.3                          |
| -2650.62269661   | -5.5                         | 14.8                          | -2653.43690120            | 0.0                          | 20.3                          |
| -2650.62249533   | -5.3                         | 14.9                          | -2653.43673801            | 0.1                          | 20.4                          |
| -2650.62245453   | -5.3                         | 14.8                          | -2653.43673508            | 0.1                          | 20.2                          |
| -2650.62251600   | -5.3                         | 14.5                          | -2653.43683260            | 0.1                          | 19.9                          |
| -2650.62285770   | -5.6                         | 14.1                          | -2653.43720048            | -0.2                         | 19.5                          |
| -2650.62334056   | -5.9                         | 13.5                          | -2653.43767521            | -0.4                         | 18.9                          |
| -2650.61400922   | 0.0                          | 0.0                           | -2653.43695891            | 0.0                          | 0.0                           |

$E_{sp}$ …… single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
$\Delta E_{sp}$ … relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
$\Delta G_{sp}$ … relative single point free energy in toluene in kcal/mol ($\Delta G_{sp} = \Delta E_{sp}/6-311++G(2df,2pd) + \Delta G_{corr}/6-31G(d,p)$)
Table S6-1. After optimization with M06-2X/6-31G(d,p) in toluene (PCM) [IIh–Vh in Figure 4 and S6]

| structure | E [hartree] | ΔE [kcal/mol] | G [hartree] | ΔG [kcal/mol] | ΔG_{corr} [kcal/mol] | FREQU [cm^{-1}] |
|-----------|-------------|---------------|-------------|---------------|---------------------|-----------------|
| cat1      | -1727.39595761 | 0.0          | -1726.803700 | 0.0          | 0.0                 | 17.24           |
| IIh_2.10 Å | -1727.42795953 | -20.1        | -1726.802417 | 0.8          | 20.9                | -304.76         |
| IIh_2.20 Å | -1727.42791491 | -20.1        | -1726.802373 | 0.8          | 20.9                | -275.68         |
| IIh_2.30 Å | -1727.42807813 | -20.2        | -1726.802861 | 0.5          | 20.7                | -218.46         |
| IIh_2.40 Å | -1727.42875986 | -20.6        | -1726.804312 | -0.4         | 20.2                | -153.76         |
| IIh_2.50 Å | -1727.42974178 | -21.2        | -1726.807528 | -2.4         | 18.8                | -134.93         |
| IIh_2.60 Å | -1727.43109658 | -22.1        | -1726.808770 | -3.2         | 18.9                | -78.47          |
| IIh_2.70 Å | -1727.42563237 | -18.6        | -1726.800269 | 2.2          | 20.8                | -242.00         |
| IIh_2.80 Å | -1727.42429225 | -17.8        | -1726.799845 | 2.4          | 20.2                | -183.41         |
| IIh_2.90 Å | -1727.42345791 | -17.3        | -1726.799826 | 2.4          | 19.7                | -170.16         |
| IIh_3.00 Å | -1727.42306361 | -17.0        | -1726.799971 | 2.3          | 19.3                | -161.93         |
| IIh_3.10 Å | -1727.42302875 | -17.0        | -1726.800379 | 2.1          | 19.1                | -146.06         |
| IIh_3.20 Å | -1727.42308998 | -17.0        | -1726.801526 | 1.4          | 18.4                | -109.65         |
| Vh_2.15 Å | -1727.43503324 | -24.5        | -1726.810580 | -4.3         | 20.2                | -250.11         |
| Vh_2.20 Å | -1727.43462757 | -24.3        | -1726.809703 | -3.8         | 20.5                | -215.57         |
| Vh_2.30 Å | -1727.43452214 | -24.2        | -1726.809563 | -3.7         | 20.5                | -178.59         |
| Vh_2.40 Å | -1727.43457184 | -24.2        | -1726.809671 | -3.7         | 20.5                | -159.77         |
| Vh_2.50 Å | -1727.43515982 | -24.6        | -1726.810059 | -4.0         | 20.6                | -151.44         |
| Vh_2.60 Å | -1727.43621492 | -25.3        | -1726.811528 | -4.9         | 20.3                | -110.12         |
| IVh_2.15 Å | -1727.43365006 | -23.7        | -1726.811144 | -4.7         | 19.0                | -302.27         |
| IVh_2.20 Å | -1727.43375833 | -23.7        | -1726.811351 | -4.8         | 18.9                | -255.67         |
| IVh_2.30 Å | -1727.43405391 | -23.9        | -1726.812890 | -5.8         | 18.1                | -217.47         |
| IVh_2.40 Å | -1727.43461458 | -25.4        | -1726.813586 | -6.2         | 19.2                | -129.77         |
| IVh_2.50 Å | -1727.43772046 | -26.2        | -1726.816240 | -7.9         | 18.3                | -63.15          |

E ........ electronic energy in toluene (PCM) in hartree with 6-31G(d,p)
G ........ sum of electronic and thermal free energies in toluene (PCM) in hartree with 6-31G(d,p)
ΔE .......... relative electronic energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
ΔG .......... relative free energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
ΔG_{corr} gas phase thermal correction to free energy in kcal/mol obtained with 6-31G(d,p) (ΔG = ΔE + ΔG_{corr})
Table S6-2. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIIh–Vh in Figure 4 and S6]

|                  | M062X/6-311++G(2df,2pd) (toluene) | ωB97X/6-311++G(2df,2pd) (toluene) | M06/6-311++G(2df,2pd) (toluene) |
|------------------|-----------------------------------|----------------------------------|---------------------------------|
|                  | E₀ [hartree]                      | ΔE₀ [kcal/mol]                   | ΔG₀ [kcal/mol]                  | E₀ [hartree]                      | ΔE₀ [kcal/mol]                   | ΔG₀ [kcal/mol]                  |
| -1727.94253411   | 0.0                               | 0.0                              | 0.0                             | -1727.94752980                    | 0.0                              | 0.0                             |
| -1727.96436447   | -13.7                             | 7.2                              | 10.7                            | -1727.94933037                    | -11.3                            | 9.6                             |
| -1727.96440740   | -13.7                             | 7.2                              | 10.7                            | -1727.94932402                    | -11.2                            | 9.6                             |
| -1727.96478874   | -14.0                             | 6.7                              | 10.2                            | -1727.94935740                    | -11.4                            | 9.2                             |
| -1727.96578736   | -14.6                             | 5.6                              | 8.9                             | -1727.94950020                    | -12.3                            | 7.9                             |
| -1727.96708640   | -15.4                             | 3.4                              | 6.3                             | -1727.94970039                    | -13.6                            | 5.2                             |
| -1727.96866377   | -16.4                             | 2.5                              | 4.8                             | -1727.94947567                    | -15.2                            | 3.7                             |
| -1727.96104350   | -11.6                             | 9.2                              | 12.6                            | -1727.48882016                    | -8.5                             | 12.3                            |
| -1727.96017037   | -11.1                             | 9.1                              | 12.3                            | -1727.48810337                    | -8.0                             | 12.2                            |
| -1727.95983256   | -10.9                             | 8.8                              | 11.6                            | -1727.48838569                    | -8.2                             | 11.5                            |
| -1727.95993863   | -10.9                             | 8.4                              | 10.8                            | -1727.48919606                    | -8.7                             | 10.6                            |
| -1727.96010484   | -11.0                             | 8.0                              | 10.3                            | -1727.48957774                    | -8.9                             | 10.1                            |
| -1727.96045805   | -11.2                             | 7.1                              | 9.2                             | -1727.49015283                    | -9.3                             | 9.1                             |
| -1727.97167982   | -18.3                             | 1.9                              | 5.2                             | -1727.49960249                    | -15.2                            | 5.0                             |
| -1727.97144617   | -18.1                             | 2.4                              | 6.1                             | -1727.49820314                    | -14.4                            | 6.1                             |
| -1727.97155143   | -18.2                             | 2.3                              | 6.0                             | -1727.49815077                    | -14.3                            | 6.2                             |
| -1727.97174424   | -18.3                             | 2.2                              | 5.8                             | -1727.49833779                    | -14.4                            | 6.0                             |
| -1727.97252923   | -18.8                             | 1.8                              | 5.3                             | -1727.49956411                    | -15.2                            | 5.4                             |
| -1727.97376284   | -19.6                             | 0.8                              | 4.0                             | -1727.50156050                    | -16.5                            | 3.9                             |
| -1727.97065977   | -17.6                             | 1.3                              | 4.5                             | -1727.49987313                    | -15.4                            | 3.6                             |
| -1727.97092547   | -17.8                             | 1.1                              | 4.3                             | -1727.49997944                    | -15.5                            | 3.5                             |
| -1727.97138058   | -18.1                             | 0.0                              | 3.2                             | -1727.50041201                    | -15.7                            | 2.4                             |
| -1727.97356957   | -19.5                             | -0.3                             | 2.0                             | -1727.50391891                    | -17.9                            | 1.2                             |
| -1727.97518494   | -20.5                             | -2.2                             | -0.2                            | -1727.50590072                    | -19.2                            | -0.8                            |

E₀ …… single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
ΔE₀ …… relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
ΔG₀ …… relative single point free energy in toluene in kcal/mol (ΔG₀ = ΔE₀/6-311++G(2df,2pd) + ΔGcore/6-31G(d,p))
### Table S6-3. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [III–Vh in Figure 4 and S6]

| MN12SX/6-311++G(2df,2pd) (toluene) | PBE0-D3BJ/6-311++G(2df,2pd) (toluene) | B3LYP/6-311++G(2df,2pd) (toluene) |
|-------------------------------------|---------------------------------------|----------------------------------|
| **E_p** [hartree] | **ΔE_p** [kcal/mol] | **ΔG_p** [kcal/mol] | **E_p** [hartree] | **ΔE_p** [kcal/mol] | **ΔG_p** [kcal/mol] | **E_p** [hartree] | **ΔE_p** [kcal/mol] | **ΔG_p** [kcal/mol] |
| -1727.24025310 | 0.0 | 0.0 | -1726.73211414 | 0.0 | 0.0 | -1728.65731580 | 0.0 | 0.0 |
| -1727.25539238 | -9.5 | 11.4 | -1726.75717819 | -15.7 | 5.2 | -1728.65087634 | 4.0 | 24.9 |
| -1727.25557604 | -9.6 | 11.3 | -1726.75726604 | -15.8 | 5.1 | -1728.65110627 | 3.9 | 24.8 |
| -1727.25630255 | -10.1 | 10.6 | -1726.75764782 | -16.0 | 4.7 | -1728.65193242 | 3.4 | 24.1 |
| -1727.25784482 | -11.0 | 9.2 | -1726.75851121 | -16.6 | 3.6 | -1728.65356907 | 2.4 | 22.6 |
| -1727.25972574 | -12.2 | 6.6 | -1726.75958883 | -17.2 | 1.6 | -1728.65432420 | 1.2 | 20.0 |
| -1727.26172789 | -13.5 | 5.4 | -1726.76079596 | -18.0 | 0.9 | -1728.65748132 | -0.1 | 18.8 |
| -1727.25029172 | -6.3 | 14.5 | -1726.75262929 | -12.9 | 7.9 | -1728.63940425 | 11.2 | 32.0 |
| -1727.24981911 | -6.0 | 14.2 | -1726.75159218 | -12.2 | 8.0 | -1728.63927633 | 11.3 | 31.5 |
| -1727.24993980 | -6.1 | 13.6 | -1726.75105740 | -11.9 | 7.8 | -1728.63972924 | 11.0 | 30.7 |
| -1727.25049100 | -6.4 | 12.9 | -1726.75083197 | -11.7 | 7.6 | -1728.64044211 | 10.6 | 29.9 |
| -1727.25080080 | -6.6 | 12.5 | -1726.75078745 | -11.7 | 7.4 | -1728.64073714 | 10.4 | 29.5 |
| -1727.25131165 | -6.9 | 11.5 | -1726.75076317 | -11.7 | 6.7 | -1728.64121037 | 10.1 | 28.5 |
| -1727.26256292 | -14.0 | 6.2 | -1726.76220359 | -18.9 | 1.3 | -1728.64673612 | 6.6 | 26.8 |
| -1727.26217651 | -13.8 | 6.7 | -1726.76128445 | -18.3 | 2.2 | -1728.64618652 | 7.0 | 27.5 |
| -1727.26251601 | -14.0 | 6.6 | -1726.76120971 | -18.3 | 2.3 | -1728.64662700 | 6.7 | 27.2 |
| -1727.26288374 | -14.2 | 6.3 | -1726.76128306 | -18.3 | 2.2 | -1728.64711842 | 6.4 | 26.9 |
| -1727.26429688 | -15.1 | 5.5 | -1726.76183728 | -18.7 | 2.0 | -1728.64905919 | 5.2 | 25.8 |
| -1727.26606441 | -16.2 | 4.2 | -1726.76276470 | -19.2 | 1.1 | -1728.65113566 | 3.9 | 24.2 |
| -1727.26282787 | -14.2 | 4.8 | -1726.76357159 | -19.7 | -0.8 | -1728.65589345 | 0.9 | 19.9 |
| -1727.26329320 | -14.5 | 4.5 | -1726.76386463 | -19.9 | -1.0 | -1728.65641969 | 0.6 | 19.5 |
| -1727.26396014 | -14.9 | 3.3 | -1726.76428354 | -20.2 | -2.0 | -1728.65714139 | 0.1 | 18.2 |
| -1727.26710364 | -16.8 | 2.3 | -1726.76628440 | -21.4 | -2.3 | -1728.66129143 | -2.5 | 16.7 |
| -1727.26902056 | -18.1 | 0.3 | -1726.76741542 | -22.2 | -3.8 | -1728.66322824 | -3.7 | 14.6 |
| -1727.24025310 | 0.0 | 0.0 | -1726.73211414 | 0.0 | 0.0 | -1728.65731580 | 0.0 | 0.0 |

**E_p** .... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)

**ΔE_p** .... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)

**ΔG_p** .... relative single point free energy in toluene in kcal/mol (ΔG_p = ΔE_p/6-311++G(2df,2pd) + ΔG_cor/6-31G(d,p))
### Table S6-4. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIh–Vh in Figure 4 and S6]

| PBE0/6-311++G(2df,2pd) (toluene) | BP86/6-311++G(2df,2pd) (toluene) |
|----------------------------------|----------------------------------|
| $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] |
| -1726.63529987 | 0.0 | 0.0 | -1728.59922361 | 0.0 | 0.0 |
| -1726.64567292 | -6.5 | 14.4 | -1728.60242040 | -2.0 | 18.9 |
| -1726.64566178 | -6.5 | 14.4 | -1728.60248220 | -2.0 | 18.8 |
| -1726.64590632 | -6.7 | 14.0 | -1728.60285214 | -2.3 | 18.4 |
| -1726.64674833 | -7.2 | 13.0 | -1728.60375715 | -2.8 | 17.4 |
| -1726.64788946 | -7.9 | 10.9 | -1728.60483702 | -3.5 | 15.3 |
| -1726.64921361 | -8.7 | 10.1 | -1728.6060694 | -4.3 | 14.6 |
| -1726.65554046 | -0.2 | 20.6 | -1728.5943314 | 4.9 | 25.7 |
| -1726.6348056 | 0.5 | 20.7 | -1728.59065520 | 5.4 | 25.6 |
| -1726.63423359 | 0.7 | 20.4 | -1728.59035779 | 5.6 | 25.3 |
| -1726.63421609 | 0.7 | 20.0 | -1728.59024625 | 5.6 | 25.0 |
| -1726.63424365 | 0.7 | 19.7 | -1728.59020093 | 5.7 | 24.7 |
| -1726.63433921 | 0.6 | 19.0 | -1728.59017753 | 5.7 | 24.1 |
| -1726.64392033 | -5.4 | 14.8 | -1728.59811078 | 0.7 | 20.9 |
| -1726.64308967 | -4.9 | 15.6 | -1728.59726703 | 1.2 | 21.7 |
| -1726.64305067 | -4.9 | 15.7 | -1728.59732346 | 1.2 | 21.7 |
| -1726.64319704 | -5.0 | 15.5 | -1728.59752042 | 1.1 | 21.6 |
| -1726.64415044 | -5.6 | 15.1 | -1728.59865217 | 0.4 | 21.0 |
| -1726.64541386 | -6.3 | 14.0 | -1728.59993817 | -0.4 | 19.9 |
| -1726.65126283 | -10.0 | 9.0 | -1728.60272674 | -5.1 | 13.9 |
| -1726.65137835 | -10.1 | 8.8 | -1728.60748425 | -5.2 | 13.7 |
| -1726.65168922 | -10.3 | 7.9 | -1728.60784860 | -5.4 | 12.7 |
| -1726.65387779 | -11.7 | 7.5 | -1728.61013905 | -6.8 | 12.3 |
| -1726.65511919 | -12.4 | 5.9 | -1728.61121306 | -7.5 | 10.8 |

$E_{sp}$ .... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
$\Delta E_{sp}$ .... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
$\Delta G_{sp}$ .... relative single point free energy in toluene in kcal/mol ($\Delta G_{sp} = \Delta E_{sp}/6-311++G(2df,2pd) + \Delta G_{corr}/6-31G(d,p)$)
Table S7-1. After optimization with M06-2X/6-31G(d,p) in toluene (PCM) [III–VI in Figure S7]

| structure  | $E$ [hartree] | $\Delta E$ [kcal/mol] | $G$ [hartree] | $\Delta G$ [kcal/mol] | $\Delta G_{\text{corr}}$ [kcal/mol] | FREQ [cm$^{-1}$] |
|------------|---------------|------------------------|---------------|------------------------|--------------------------------------|-----------------|
| cat4       | -2653.01837897 | 0.0                    | -2652.294420  | 0.0                    | 0.0                                  | 19.59           |
| III_2.20 Å | -2653.05221601 | -21.2                  | -2652.298185  | -2.4                   | 18.9                                 | -237.72         |
| III_2.30 Å | -2653.05163267 | -20.9                  | -2652.297027  | -1.6                   | 19.2                                 | -175.69         |
| III        | -2653.05149303 | -20.8                  | -2652.296356  | -1.2                   | 19.6                                 | -145.71         |
| III_2.40 Å | -2653.05149444 | -20.8                  | -2652.296333  | -1.2                   | 19.6                                 | -144.54         |
| III_2.50 Å | -2653.05167380 | -20.9                  | -2652.296617  | -1.4                   | 19.5                                 | -116.81         |
| III_2.60 Å | -2653.05207835 | -21.1                  | -2652.297061  | -1.7                   | 19.5                                 | -43.84          |
| IVI_2.20 Å | -2653.05265637 | -21.5                  | -2652.299434  | -3.1                   | 18.4                                 | -251.00         |
| IVI_2.30 Å | -2653.05103258 | -20.5                  | -2652.296516  | -1.3                   | 19.2                                 | -186.43         |
| IVI_2.40 Å | -2653.04995982 | -19.8                  | -2652.296073  | -1.0                   | 18.8                                 | -146.55         |
| IVI_2.50 Å | -2653.04928160 | -19.4                  | -2652.295730  | -0.8                   | 18.6                                 | -120.87         |
| IVI_2.60 Å | -2653.04887891 | -19.1                  | -2652.295462  | -0.7                   | 18.5                                 | -90.49          |
| V1i_2.10 Å | -2653.05392855 | -22.3                  | -2652.299457  | -3.2                   | 19.1                                 | -294.73         |
| V1i_2.15 Å | -2653.05300906 | -21.7                  | -2652.298440  | -2.5                   | 19.2                                 | -247.04         |
| V1i_2.20 Å | -2653.05230108 | -21.3                  | -2652.297792  | -2.1                   | 19.2                                 | -210.29         |
| V1i_2.30 Å | -2653.05129176 | -20.7                  | -2652.297670  | -2.0                   | 18.6                                 | -155.70         |
| V1i_2.40 Å | -2653.05064811 | -20.2                  | -2652.296759  | -1.5                   | 18.8                                 | -131.93         |
| V1i_2.50 Å | -2653.05028624 | -20.0                  | -2652.296866  | -1.5                   | 18.5                                 | -106.72         |
| V1i_2.60 Å | -2653.05011191 | -19.9                  | -2652.297241  | -1.8                   | 18.1                                 | -54.76          |

$E$ ……. electronic energy in toluene (PCM) in hartree with 6-31G(d,p)
$G$ …… sum of electronic and thermal free energies in toluene (PCM) in hartree with 6-31G(d,p)
$\Delta E$ … relative electronic energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
$\Delta G$ … relative free energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
$\Delta G_{\text{corr}}$ gas phase thermal correction to free energy in kcal/mol obtained with 6-31G(d,p) ($\Delta G = \Delta E + \Delta G_{\text{corr}}$)
Table S7-2. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIIi–Vi in Figure S7]

|            | M062X/6-311++G(2df,2pd) (toluene) | ΩB97XD/6-311++G(2df,2pd) (toluene) | M06/6-311++G(2df,2pd) (toluene) |
|------------|-----------------------------------|-----------------------------------|-----------------------------------|
|            | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] | $E_{sp}$ [hartree] | $\Delta E_{sp}$ [kcal/mol] | $\Delta G_{sp}$ [kcal/mol] |
| -2653.78983468 | 0.0 | 0.0 | 0.0 | -2653.99491231 | 0.0 | 0.0 | -2653.10054549 | 0.0 | 0.0 |
| -2653.81244615 | -14.2 | 4.7 | 11.9 | -2654.01338380 | -11.6 | 7.3 | -2653.12006872 | -12.3 | 6.6 |
| -2653.81211223 | -14.0 | 5.3 | 11.7 | -2654.01329535 | -11.5 | 7.7 | -2653.11995260 | -12.2 | 7.1 |
| -2653.81220976 | -14.0 | 5.5 | 11.9 | -2654.01381797 | -11.9 | 7.7 | -2653.12053213 | -12.5 | 7.0 |
| -2653.81223687 | -14.1 | 5.5 | 11.9 | -2654.01389584 | -11.9 | 7.7 | -2653.12061511 | -12.6 | 7.0 |
| -2653.81268114 | -14.3 | 5.2 | 11.9 | -2654.01484719 | -12.5 | 7.0 | -2653.12157815 | -13.2 | 6.3 |
| -2653.81334781 | -14.8 | 4.7 | 11.9 | -2654.01589244 | -13.2 | 6.3 | -2653.12247900 | -13.8 | 5.7 |
| -2653.81633037 | -16.6 | 1.7 | 11.9 | -2654.01925424 | -15.3 | 3.1 | -2653.12408371 | -14.8 | 3.6 |
| -2653.81488403 | -15.7 | 3.5 | 11.9 | -2654.01802755 | -14.5 | 4.7 | -2653.12286025 | -14.0 | 5.2 |
| -2653.81399178 | -15.2 | 3.6 | 11.9 | -2654.01753720 | -14.2 | 4.6 | -2653.12252205 | -13.8 | 5.0 |
| -2653.81347976 | -14.8 | 3.7 | 11.9 | -2654.01753384 | -14.2 | 4.4 | -2653.12266886 | -13.9 | 4.7 |
| -2653.81327412 | -14.7 | 3.8 | 11.9 | -2654.01774206 | -14.3 | 4.2 | -2653.12298528 | -14.1 | 4.4 |
| -2653.81481503 | -15.7 | 3.5 | 11.9 | -2654.01514320 | -12.7 | 6.5 | -2653.12164033 | -13.2 | 5.9 |
| -2653.81404867 | -15.2 | 4.0 | 11.9 | -2654.01413592 | -12.1 | 7.1 | -2653.12037666 | -12.4 | 6.8 |
| -2653.81350605 | -14.9 | 4.3 | 11.9 | -2654.01354845 | -11.7 | 7.5 | -2653.11970342 | -12.0 | 7.1 |
| -2653.81280716 | -14.4 | 4.2 | 11.9 | -2654.01297230 | -11.3 | 7.3 | -2653.11908394 | -11.6 | 7.0 |
| -2653.81243758 | -14.2 | 4.6 | 11.9 | -2654.01295594 | -11.3 | 7.3 | -2653.11919085 | -11.7 | 7.1 |
| -2653.81231003 | -14.1 | 4.4 | 11.9 | -2654.01313815 | -11.4 | 7.1 | -2653.11957810 | -11.9 | 6.5 |
| -2653.81241174 | -14.2 | 4.0 | 11.9 | -2654.01364636 | -11.8 | 6.4 | -2653.12012027 | -12.3 | 5.9 |

$E_{sp}$ ...... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)

$\Delta E_{sp}$ ...... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)

$\Delta G_{sp}$ ...... relative single point free energy in toluene in kcal/mol ($\Delta G_{sp} = \Delta E_{sp}/6-311++G(2df,2pd) + \Delta G_{cor}/6-31G(d,p)$)
Table S7-3. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [III\text{v} in Figure S7]

| MN12SX/6-311++G(2df,2pd) (toluene) | PBE0-D3BJ/6-311++G(2df,2pd) (toluene) | B3LYP/6-311++G(2df,2pd) (toluene) |
|-------------------------------------|---------------------------------------|----------------------------------|
| $E_{\text{sp}}$ [hartree] | $\Delta E_{\text{sp}}$ [kcal/mol] | $\Delta G_{\text{sp}}$ [kcal/mol] | $E_{\text{sp}}$ [hartree] | $\Delta E_{\text{sp}}$ [kcal/mol] | $\Delta G_{\text{sp}}$ [kcal/mol] | $E_{\text{sp}}$ [hartree] | $\Delta E_{\text{sp}}$ [kcal/mol] | $\Delta G_{\text{sp}}$ [kcal/mol] |
| -2652.84132885 | 0.0 | 0.0 | -2652.01452698 | 0.0 | 0.0 | -2654.75580687 | 0.0 | 0.0 |
| -2652.85846285 | -10.8 | 8.1 | -2652.04198113 | -17.2 | 1.6 | -2654.74775797 | 5.2 | 24.0 |
| -2652.85869800 | -10.9 | 8.3 | -2652.04154219 | -17.0 | 2.3 | -2654.74791617 | 5.0 | 24.2 |
| -2652.85930559 | -11.3 | 8.3 | -2652.04145915 | -16.9 | 2.7 | -2654.74863316 | 4.5 | 24.1 |
| -2652.85935806 | -11.3 | 8.2 | -2652.04146246 | -16.9 | 2.7 | -2654.74872279 | 4.4 | 24.0 |
| -2652.86032317 | -11.9 | 7.6 | -2652.04155425 | -17.0 | 2.6 | -2654.74971237 | 3.8 | 23.3 |
| -2652.86130734 | -12.5 | 7.0 | -2652.04167394 | -17.0 | 2.5 | -2654.75065609 | 3.2 | 22.7 |
| -2652.86148325 | -12.6 | 5.7 | -2652.04608285 | -19.8 | -1.4 | -2654.74058871 | 9.5 | 27.9 |
| -2652.86058855 | -12.1 | 7.1 | -2652.04482106 | -19.0 | 0.2 | -2654.74062311 | 9.5 | 28.7 |
| -2652.86022841 | -11.9 | 6.9 | -2652.04394294 | -18.5 | 0.3 | -2654.74080507 | 9.4 | 28.2 |
| -2652.86029500 | -11.9 | 6.7 | -2652.04337200 | -18.1 | 0.5 | -2654.74134724 | 9.1 | 27.6 |
| -2652.86053277 | -12.1 | 6.4 | -2652.04293546 | -17.8 | 0.7 | -2654.74175534 | 8.8 | 27.3 |
| -2652.86063304 | -12.1 | 7.0 | -2652.04309121 | -17.9 | 1.2 | -2654.74744078 | 5.2 | 24.4 |
| -2652.85993498 | -11.7 | 7.5 | -2652.04234352 | -17.5 | 1.8 | -2654.74755372 | 5.2 | 24.4 |
| -2652.85957219 | -11.4 | 7.7 | -2652.04179076 | -17.1 | 2.1 | -2654.74750675 | 5.2 | 24.4 |
| -2652.85932012 | -11.3 | 7.3 | -2652.04093771 | -16.6 | 2.0 | -2654.74773933 | 5.1 | 23.7 |
| -2652.85953021 | -11.4 | 7.4 | -2652.04038580 | -16.2 | 2.6 | -2654.74820684 | 4.8 | 23.6 |
| -2652.85993400 | -11.7 | 6.8 | -2652.03981636 | -15.9 | 2.6 | -2654.74859269 | 4.5 | 23.0 |
| -2652.86039895 | -12.0 | 6.2 | -2652.03953691 | -15.7 | 2.4 | -2654.74933565 | 4.1 | 22.2 |

$E_{\text{sp}}$ ....... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)  
$\Delta E_{\text{sp}}$ ..... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)  
$\Delta G_{\text{sp}}$ ..... relative single point free energy in toluene in kcal/mol ($\Delta G_{\text{sp}} = \Delta E_{\text{sp}}/6-311++G(2df,2pd) + \Delta G_{\text{corr}}/6-31G(d,p)$)
Table S7-4. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [III–VI in Figure S7]

|                  | PBE0/6-311++G(2df,2pd) (toluene) | BP86/6-311++G(2df,2pd) (toluene) |
|------------------|----------------------------------|----------------------------------|
|                  | E<sub>sp</sub> [hartree] | ΔE<sub>sp</sub> [kcal/mol] | ΔG<sub>sp</sub> [kcal/mol] | E<sub>sp</sub> [hartree] | ΔE<sub>sp</sub> [kcal/mol] | ΔG<sub>sp</sub> [kcal/mol] |
| -2651.86782460   | 0.0 | 0.0 | -2654.69215956 | 0.0 | 0.0 |
| -2651.87668590   | -5.6 | 13.3 | -2654.69234326 | -0.1 | 18.8 |
| -2651.87615215   | -5.2 | 14.0 | -2654.69208337 | 0.0 | 19.3 |
| -2651.87611185   | -5.2 | 14.4 | -2654.69218048 | 0.0 | 19.6 |
| -2651.87612488   | -5.2 | 14.4 | -2654.69220193 | 0.0 | 19.6 |
| -2651.87634683   | -5.3 | 14.2 | -2654.69245640 | -0.2 | 19.3 |
| -2651.87661030   | -5.5 | 14.0 | -2654.69267474 | -0.3 | 19.2 |
| -2651.87344894   | -3.5 | 14.8 | -2654.68759557 | 2.9 | 21.2 |
| -2651.87237800   | -2.9 | 16.3 | -2654.68704051 | 3.2 | 22.4 |
| -2651.87164049   | -2.4 | 16.4 | -2654.68668442 | 3.4 | 22.2 |
| -2651.87132274   | -2.2 | 16.4 | -2654.68662058 | 3.5 | 22.0 |
| -2651.87103308   | -2.0 | 16.5 | -2654.68646538 | 3.6 | 22.1 |
| -2651.87794571   | -6.4 | 12.8 | -2654.69268298 | -0.3 | 18.8 |
| -2651.87744346   | -6.0 | 13.2 | -2654.69248984 | -0.2 | 19.0 |
| -2651.87688974   | -5.7 | 13.5 | -2654.69216178 | 0.0 | 19.2 |
| -2651.87614276   | -5.2 | 13.4 | -2654.69176604 | 0.2 | 18.9 |
| -2651.87573593   | -5.0 | 13.8 | -2654.69156949 | 0.4 | 19.2 |
| -2651.87533297   | -4.7 | 13.8 | -2654.69125814 | 0.6 | 19.1 |
| -2651.87531800   | -4.7 | 13.4 | -2654.69132984 | 0.5 | 18.7 |

E<sub>sp</sub> ...... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
ΔE<sub>sp</sub> ...... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
ΔG<sub>sp</sub> ...... relative single point free energy in toluene in kcal/mol (ΔG<sub>sp</sub> = ΔE<sub>sp</sub>/6-311++G(2df,2pd) + ΔG<sub>corr</sub>/6-31G(d,p))
Table S8-1. After optimization with M06-2X/6-31G(d,p) in toluene (PCM) [IIj–Vj in Figure S8]

| structure   | E [hartree] | ΔE [kcal/mol] | G [hartree] | ΔG [kcal/mol] | ΔG_{corr} [kcal/mol] | FREQ [cm\(^{-1}\)] |
|-------------|-------------|---------------|-------------|---------------|----------------------|-----------------|
| cat4        | -2692.31555069 | 0.0          | -2691.564886 | 0.0          | 0.0                 | 19.59          |
| IIj_2.20 Å  | -2692.35159026 | -22.6        | -2691.569601 | -3.0         | 19.7                | -220.78        |
| IIj_2.30 Å  | -2692.35116400 | -22.3        | -2691.569029 | -2.6         | 19.7                | -160.04        |
| IIj_2.40 Å  | -2692.35109175 | -22.3        | -2691.568936 | -2.5         | 19.8                | -138.05        |
| IIj_2.50 Å  | -2692.35131776 | -22.4        | -2691.569820 | -3.1         | 19.3                | -109.89        |
| IIj_2.60 Å  | -2692.35174823 | -22.7        | -2691.570811 | -3.7         | 19.0                | -47.24         |
| IIIj_2.20 Å | -2692.33344968 | -11.2        | -2691.552320 | 7.9          | 19.1                | -280.06        |
| IIIj_2.30 Å | -2692.33152224 | -10.0        | -2691.551314 | 8.5          | 18.5                | -218.40        |
| IIIj_2.40 Å | -2692.33026060 | -9.2         | -2691.550990 | 8.7          | 18.0                | -182.65        |
| IIIj_2.50 Å | -2692.32949923 | -8.8         | -2691.550596 | 9.0          | 17.7                | -146.44        |
| IIIj_2.60 Å | -2692.32908417 | -8.5         | -2691.550603 | 9.0          | 17.5                | -126.58        |
| IIIj        | -2692.32895554 | -8.4         | -2691.551384 | 8.5          | 16.9                | -114.27        |
| IVj_2.20 Å  | -2692.34972585 | -21.4        | -2691.563532 | 0.8          | 22.3                | -210.38        |
| IVj_2.30 Å  | -2692.34826123 | -20.5        | -2691.562509 | 1.5          | 22.0                | -163.02        |
| IVj_2.40 Å  | -2692.34721744 | -19.9        | -2691.562265 | 1.6          | 21.5                | -140.09        |
| IVj_2.50 Å  | -2692.34650482 | -19.4        | -2691.562004 | 1.8          | 21.2                | -114.86        |
| IVj_2.60 Å  | -2692.34602683 | -19.1        | -2691.562224 | 1.7          | 20.8                | -85.86         |
| Vj_2.20 Å   | -2692.34936718 | -21.2        | -2691.566074 | -0.7         | 20.5                | -205.25        |
| Vj_2.30 Å   | -2692.34864126 | -20.8        | -2691.565258 | -0.2         | 20.5                | -148.56        |
| Vj_2.40 Å   | -2692.34825063 | -20.5        | -2691.565361 | -0.3         | 20.2                | -131.45        |
| Vj_2.50 Å   | -2692.34812286 | -20.4        | -2691.565535 | -0.4         | 20.0                | -105.38        |
| Vj_2.60 Å   | -2692.34816941 | -20.5        | -2691.566205 | -0.8         | 19.6                | -40.80         |

E …… electronic energy in toluene (PCM) in hartree with 6-31G(d,p)
G …… sum of electronic and thermal free energies in toluene (PCM) in hartree with 6-31G(d,p)
ΔE …… relative electronic energy in kcal/mol in toluene (PCM) with 6-31G(d,p)
ΔG …… relative free energy in kcal/mol with 6-31G(d,p)
ΔG_{corr} gas phase thermal correction to free energy in kcal/mol obtained with 6-31G(d,p) (ΔG = ΔE + ΔG_{corr})
### Table S8-2. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIj−Vj in Figure S8]

|        | M062X/6-311++G(2df,2pd) (toluene) | 6-311++G(2df,2pd) (toluene) | M06/6-311++G(2df,2pd) (toluene) |
|--------|-----------------------------------|-------------------------------|----------------------------------|
|        | \( E_{sp} \) [hartree] | \( \Delta E_{sp} \) [kcal/mol] | \( \Delta G_{sp} \) [kcal/mol] | \( E_{sp} \) [hartree] | \( \Delta E_{sp} \) [kcal/mol] | \( \Delta G_{sp} \) [kcal/mol] | \( E_{sp} \) [hartree] | \( \Delta E_{sp} \) [kcal/mol] | \( \Delta G_{sp} \) [kcal/mol] |
| -2693.0973299 | 0.0 | 0.0 | -2693.31049757 | 0.0 | 0.0 | -2692.39497411 | 0.0 | 0.0 |
| -2693.12224984 | -15.6 | 4.0 | -2693.33101138 | -12.9 | 6.8 | -2692.41483099 | -12.5 | 7.2 |
| -2693.12220029 | -15.6 | 4.1 | -2693.33125867 | -13.0 | 6.7 | -2692.41505114 | -12.6 | 7.1 |
| -2693.12237034 | -15.7 | 4.0 | -2693.33177169 | -13.3 | 6.4 | -2692.41559648 | -12.9 | 6.8 |
| -2693.12247397 | -15.8 | 4.0 | -2693.33203066 | -13.5 | 6.2 | -2692.41586298 | -13.1 | 6.6 |
| -2693.12297235 | -16.1 | 3.3 | -2693.33303022 | -14.1 | 5.2 | -2692.41686219 | -13.7 | 5.6 |
| -2693.12357739 | -16.5 | 2.5 | -2693.33406736 | -14.8 | 4.2 | -2692.41777572 | -14.3 | 4.7 |
| -2693.10704700 | -6.1 | 13.0 | -2693.31849730 | -5.0 | 14.1 | -2692.40199853 | -4.4 | 14.7 |
| -2693.10537939 | -5.0 | 13.5 | -2693.31712242 | -4.2 | 14.4 | -2692.40027989 | -3.3 | 15.2 |
| -2693.10439462 | -4.4 | 13.5 | -2693.31666300 | -3.9 | 14.1 | -2692.39967252 | -2.9 | 15.0 |
| -2693.10391495 | -4.1 | 13.6 | -2693.31677618 | -3.9 | 13.8 | -2692.39977125 | -3.0 | 14.7 |
| -2693.10378263 | -4.0 | 13.4 | -2693.31727698 | -4.3 | 13.2 | -2692.40021142 | -3.3 | 14.2 |
| -2693.10390895 | -4.1 | 12.8 | -2693.31788341 | -4.6 | 12.2 | -2692.40061213 | -3.5 | 13.3 |
| -2693.12304636 | -16.1 | 6.2 | -2693.33338641 | -14.4 | 7.9 | -2692.41509591 | -12.6 | 9.7 |
| -2693.12179953 | -15.4 | 6.7 | -2693.33243283 | -13.8 | 8.3 | -2692.41384936 | -11.8 | 10.2 |
| -2693.12101890 | -14.9 | 6.7 | -2693.33215790 | -13.6 | 7.9 | -2692.41356281 | -11.7 | 9.9 |
| -2693.12056626 | -14.6 | 6.7 | -2693.33232802 | -13.7 | 7.5 | -2692.41372892 | -11.8 | 9.5 |
| -2693.12037340 | -14.5 | 6.3 | -2693.33273645 | -14.0 | 6.8 | -2692.41406836 | -12.0 | 8.8 |
| -2693.12121806 | -15.0 | 5.5 | -2693.32998003 | -12.2 | 8.2 | -2692.41392520 | -11.9 | 8.6 |
| -2693.12088270 | -14.8 | 5.8 | -2693.32988027 | -12.2 | 8.4 | -2692.41375432 | -11.8 | 8.7 |
| -2693.12082016 | -14.7 | 5.5 | -2693.33022370 | -12.4 | 7.8 | -2692.41415448 | -12.0 | 8.2 |
| -2693.12096365 | -14.8 | 5.2 | -2693.33089542 | -12.8 | 7.2 | -2692.41485423 | -12.5 | 7.6 |
| -2693.12126352 | -15.0 | 4.6 | -2693.33167464 | -13.3 | 6.4 | -2692.41560699 | -12.9 | 6.7 |

\( E_{sp} \) .... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)  
\( \Delta E_{sp} \) .... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)  
\( \Delta G_{sp} \) .... relative single point free energy in toluene in kcal/mol (\( \Delta G_{sp} = \Delta E_{sp} / 6-311++G(2df,2pd) + \Delta G_{corr}/6-31G(d,p) \))
Table S8-3. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [IIj–Vj in Figure S8]

|          | MN12SX/6-311++G(2df,2pd) (toluene) | PBE0-D3BJ/6-311++G(2df,2pd) (toluene) | B3LYP/6-311++G(2df,2pd) (toluene) |
|----------|-----------------------------------|--------------------------------------|-----------------------------------|
|          | E_sp [hartree] | ΔE_sp [kcal/mol] | ΔG_sp [kcal/mol] | E_sp [hartree] | ΔE_sp [kcal/mol] | ΔG_sp [kcal/mol] | E_sp [hartree] | ΔE_sp [kcal/mol] | ΔG_sp [kcal/mol] |
| -2692.12962241 | 0.0 | 0.0 | -2691.29549284 | 0.0 | 0.0 | -2694.08236697 | 0.0 | 0.0 |
| -2692.14844446 | -11.8 | 7.8 | -2691.32347357 | -17.6 | 2.1 | -2694.06972785 | 7.9 | 27.6 |
| -2692.14983906 | -12.1 | 7.6 | -2691.32335826 | -17.5 | 2.3 | -2694.07049607 | 7.4 | 27.2 |
| -2692.14950108 | -12.5 | 7.3 | -2691.32340314 | -17.5 | 2.2 | -2694.07118905 | 7.0 | 26.8 |
| -2692.14975702 | -12.6 | 7.1 | -2691.32343853 | -17.5 | 2.2 | -2694.07148215 | 6.8 | 26.6 |
| -2692.15070418 | -13.2 | 6.1 | -2691.32358492 | -17.6 | 1.7 | -2694.07251463 | 6.2 | 25.5 |
| -2692.15153429 | -13.7 | 5.2 | -2691.32370310 | -17.7 | 1.3 | -2694.07359048 | 5.5 | 24.5 |
| -2692.13093988 | -0.8 | 18.3 | -2691.31154027 | -10.1 | 9.0 | -2694.05978338 | 14.2 | 33.3 |
| -2692.12972646 | -0.1 | 18.5 | -2691.30988571 | -9.0 | 9.5 | -2694.05916103 | 14.6 | 33.1 |
| -2692.12921086 | 0.3 | 18.2 | -2691.30878282 | -8.3 | 9.6 | -2694.05900987 | 14.6 | 32.6 |
| -2692.12917335 | 0.3 | 18.0 | -2691.30810242 | -7.9 | 9.8 | -2694.05942900 | 14.4 | 32.1 |
| -2692.12938756 | 0.1 | 17.6 | -2691.30765691 | -7.6 | 9.8 | -2694.05991569 | 14.1 | 31.5 |
| -2692.12968798 | 0.0 | 16.8 | -2691.30731994 | -7.4 | 9.5 | -2694.06029782 | 13.8 | 30.7 |
| -2692.14810470 | -11.6 | 10.7 | -2691.32382820 | -17.8 | 4.5 | -2694.05709956 | 15.9 | 38.2 |
| -2692.14716281 | -11.0 | 11.0 | -2691.32257060 | -17.0 | 5.0 | -2694.05663576 | 16.1 | 38.2 |
| -2692.14675857 | -10.8 | 10.8 | -2691.32180981 | -16.5 | 5.0 | -2694.05681196 | 16.0 | 37.6 |
| -2692.14669540 | -10.7 | 10.5 | -2691.32133187 | -16.2 | 5.0 | -2694.05722574 | 15.8 | 37.0 |
| -2692.14668375 | -10.8 | 10.0 | -2691.32100136 | -16.0 | 4.8 | -2694.05775460 | 15.4 | 36.2 |
| -2692.14767904 | -11.3 | 9.1 | -2691.32321135 | -16.8 | 3.6 | -2694.06916778 | 8.3 | 28.8 |
| -2692.14779762 | -11.4 | 9.1 | -2691.32193212 | -16.6 | 3.9 | -2694.06986888 | 7.8 | 28.4 |
| -2692.14823592 | -11.7 | 8.5 | -2691.32170999 | -16.5 | 3.8 | -2694.07077346 | 7.3 | 27.5 |
| -2692.14886358 | -12.1 | 8.0 | -2691.32162032 | -16.4 | 3.6 | -2694.07173945 | 6.7 | 26.7 |
| -2692.14950893 | -12.5 | 7.2 | -2691.32157246 | -16.4 | 3.3 | -2694.07271500 | 6.1 | 25.7 |

E_sp ........ single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)
ΔE_sp ........ relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)
ΔG_sp ........ relative single point free energy in toluene in kcal/mol (ΔG_sp = ΔE_sp/6-311++G(2df,2pd) + ΔG_corr/6-31G(d,p))
**Table S8-4. Single point in toluene (PCM) with 6-311++G(2df,2pd) basis set [Hlj–Vj in Figure S8]**

|                | PBE0/6-311++G(2df,2pd) (toluene) | BP86/6-311++G(2df,2pd) (toluene) |
|----------------|----------------------------------|----------------------------------|
|                | E\(_{\text{sp}}\) [hartree]     | \(\Delta E_{\text{sp}}\) [kcal/mol] | \(\Delta G_{\text{sp}}\) [kcal/mol] | E\(_{\text{sp}}\) [hartree] | \(\Delta E_{\text{sp}}\) [kcal/mol] | \(\Delta G_{\text{sp}}\) [kcal/mol] |
| -2691.14528812 | 0.0                              | 0.0                              | 0.0                              | -2694.01657309 | 0.0                              | 0.0                              |
| -2691.15145410  | -3.9                             | 15.8                             | 2.2                              | -2694.01306421 | 2.1                              | 21.9                             |
| -2691.15130102  | -3.8                             | 16.0                             | 2.1                              | -2694.01317086 | 0.0                              | 0.0                              |
| -2691.15138741  | -3.8                             | 15.9                             | 2.0                              | -2694.01334828 | 0.0                              | 0.0                              |
| -2691.15144841  | -3.9                             | 15.9                             | 2.0                              | -2694.01342345 | 0.0                              | 0.0                              |
| -2691.15171923  | -4.0                             | 15.3                             | 1.8                              | -2694.01368000 | 1.6                              | 20.6                             |
| -2691.15202243  | -4.2                             | 14.8                             | 1.6                              | -2694.01397255 | 1.6                              | 20.6                             |
| -2691.14060153  | 2.9                              | 22.1                             | 8.2                              | -2694.00349160 | 8.2                              | 27.3                             |
| -2691.13904551  | 3.9                              | 22.5                             | 8.9                              | -2694.00239011 | 8.9                              | 27.4                             |
| -2691.13810346  | 4.5                              | 22.5                             | 9.3                              | -2694.00172209 | 9.3                              | 27.3                             |
| -2691.13763910  | 4.8                              | 22.5                             | 9.5                              | -2694.00138230 | 9.5                              | 27.3                             |
| -2691.13740331  | 4.9                              | 22.4                             | 9.7                              | -2694.00113541 | 9.7                              | 27.1                             |
| -2691.13721505  | 5.1                              | 22.0                             | 9.9                              | -2694.00083200 | 9.9                              | 26.8                             |
| -2691.14310558  | 1.4                              | 23.7                             | 8.8                              | -2694.00258986 | 8.8                              | 31.1                             |
| -2691.14177642  | 2.2                              | 24.2                             | 9.3                              | -2694.00171290 | 9.3                              | 31.3                             |
| -2691.14110827  | 2.6                              | 24.1                             | 9.5                              | -2694.00139717 | 9.5                              | 31.0                             |
| -2691.14075125  | 2.8                              | 24.1                             | 9.6                              | -2694.00128748 | 9.6                              | 30.8                             |
| -2691.14056746  | 3.0                              | 23.8                             | 9.6                              | -2694.00124647 | 9.6                              | 30.4                             |
| -2691.15087763  | -3.5                             | 17.0                             | 2.9                              | -2694.01201670 | 2.9                              | 23.3                             |
| -2691.15061381  | -3.3                             | 17.2                             | 2.8                              | -2694.01211805 | 2.8                              | 23.3                             |
| -2691.15058845  | -3.3                             | 16.9                             | 2.7                              | -2694.01231613 | 2.7                              | 22.9                             |
| -2691.15071685  | -3.4                             | 16.6                             | 2.5                              | -2694.01256947 | 2.5                              | 22.5                             |
| -2691.15091938  | -3.5                             | 16.1                             | 2.3                              | -2694.01284353 | 2.3                              | 22.0                             |

\(E_{\text{sp}}\) ....... single point electronic energy in toluene (PCM) in hartree with 6-311++G(2df,2pd)

\(\Delta E_{\text{sp}}\) ....... relative single point electronic energy in toluene (PCM) in kcal/mol with 6-311++G(2df,2pd)

\(\Delta G_{\text{sp}}\) ....... relative single point free energy in toluene in kcal/mol (\(\Delta G_{\text{sp}} = \Delta E_{\text{sp}}/6\text{-}311\text{++G}(2\text{df},2\text{pd}) + \Delta G_{\text{corr}}/6\text{-}31\text{G}(d,p)\))
8. Geometries of computed structures (M06-2X/6-31G** toluene(PCM))

17
CF3AP / electronic energy: -682.36238539 a.u. / lowest freq: 31.00 cm-1
O 1.051418 1.975684 0.000819
C 0.743151 0.888151 0.000099
C -0.656343 0.314666 0.000095
C -1.670867 1.279680 -0.000086
C -3.081042 0.889384 -0.000111
C -0.930866 -1.046483 0.000084
C -2.191966 -1.431077 0.000089
C -3.325151 -8.467684 -0.000085
H -0.807718 -1.803900 0.000025
H -1.389677 2.327590 -0.000100
H -3.786718 1.637267 -0.000022
H -2.575347 -2.485089 0.000015
H -4.360557 -0.759083 -0.000089
C 1.879158 -0.239085 -0.000085
F 1.794966 -1.025921 -1.082421
F 3.067485 -0.346279 -0.000010
F 1.794968 -1.025929 1.082487

63
cat1 / electronic energy: -1144.25877588 a.u. / lowest freq: 17.24 cm-1
H -4.338875 2.465172 1.026426
H -5.696914 0.695184 2.488110
H 0.812258 2.899060 -4.330787
C -3.848273 1.765463 0.337393
H -4.571218 1.585923 -0.441780
C -2.839819 1.585438 2.904077
C -4.658991 -0.606785 1.888196
H -3.983400 2.748864 -1.275458
H -5.446119 -0.312742 1.891228
H 1.945981 2.671519 -2.927334
C -0.068979 2.896971 -3.463557
C -3.416383 0.835948 1.105151
C -2.932508 0.870268 2.292817
H 0.921238 2.788314 -2.578420
H -4.424887 -0.950335 2.480532
H -1.802228 3.620899 -3.143771
H -1.491724 1.326118 1.786614
C -2.168463 -0.821442 2.770933
C -2.798833 -0.523603 1.556736
C 0.785489 2.756263 -1.072816
H -4.242116 -2.073760 0.588741
O -1.072193 1.013768 -0.512353
C -3.348055 -1.826042 -0.625184
C -1.639083 -0.254977 -0.579746
B 0.192545 1.388822 -0.852738
C -2.762587 -2.747180 -0.869728
H -0.082785 -1.192625 1.716267
H 0.648588 -0.880922 0.682240
C -3.224447 -3.718126 -0.908933
N 1.074572 0.658821 -1.172932
H 0.048299 -0.156184 -2.974258
C -1.591325 -2.452082 -1.554339
C 0.248489 -0.788045 -2.183919
H 1.948301 0.736636 -1.628483
C 1.528729 -0.567774 0.138746
C 3.142985 1.149258 0.031827
C 2.341227 0.576012 0.773781
H 0.735677 3.153990 -0.450200
H -1.122497 -3.189246 -2.199429
N 2.126041 0.927835 2.852713
H 1.087251 3.171985 -1.191803
H 0.827512 -1.646582 -2.437948
C 2.957886 1.936619 2.627218
C 1.289233 0.234773 3.026839
C 1.539255 -3.184069 -0.201846
C 2.497962 -2.130895 2.169873
C 2.489774 -1.851927 -0.097518
C 3.176197 -2.035583 1.115766
C 2.166225 -3.994179 -0.679642
H 3.873751 -1.214510 1.585163
H 2.988568 1.164315 -2.130976
C 3.438334 -1.719434 -1.144485
H 3.579572 -2.597394 1.258821
H 0.078995 -0.852820 -0.956951
H 0.453836 -2.616063 -1.163430
H 0.638199 0.958991 3.509920
H 1.928985 -0.231914 3.787116
H 0.673326 -0.353146 2.565729
H 2.324633 2.652860 3.214772
C 3.443976 2.533979 1.826385
H 3.715995 1.545334 3.238116
H 1.636181 2.976065 -0.854752
H -0.067413 3.468081 -0.772885

08
Ib2_1.0A / electronic energy: -1826.65388359 a.u. / lowest freq: -316.60 cm-1
C -0.559755 3.726948 -1.790147
C 1.132341 5.432651 -1.896685
C -2.396254 -1.897515 -1.868326
C 0.853791 3.924341 -1.129196
C -1.982951 3.280131 -2.855174

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H 5.123473 -0.781577 -0.698705
C 3.483980 -1.234675 1.293033
C 4.785443 -1.598286 0.547425
H 4.768584 -0.169076 2.653423
H 4.691517 -2.588093 -0.059491
H 2.193328 -2.676960 2.760828
H 3.184967 -2.411057 2.173938
H 5.567833 -1.770950 1.289202
H 2.959988 -3.333583 1.575644
H 3.913462 -2.616183 2.883716
O -1.423084 -0.159248 0.158973
C -2.456282 -0.919993 0.142246
C -3.768869 -0.258689 -0.019680
C -3.562995 1.067573 -3.408031
C -4.953718 1.743211 -0.654685
C -4.976255 -0.899773 0.264123
C -6.169962 -0.289385 0.893623
C -6.461728 1.358265 -0.368821
H -5.083227 -1.922659 0.617499
H -2.808711 1.554733 -0.867315
H -4.948134 2.768240 -1.886876
H -7.180334 -0.817620 0.319640
H -7.099451 1.343847 -0.502884
C -2.368298 -2.184843 1.017373
F -3.186293 -3.162428 6.644172
F -1.124148 -2.680957 1.024923
F -2.669593 -1.828727 2.267519
C 3.379393 -0.631358 3.481882
C 4.828990 -1.887347 -2.554318
H 3.632991 0.824841 -1.853787
H 2.676821 -4.030145 -2.314914
C 3.981950 -3.383503 3.284544
H 2.288585 -2.962077 -3.687514
H 0.877776 -0.124224 -2.898648
H 0.877786 -1.131351 -2.310261
C -3.634737 -2.851326 -1.750524
C -2.859339 -1.114272 -3.254483
H -6.832111 -3.818582 -1.448685
C 1.024332 5.815480 -2.167843
C 2.966443 5.662432 -0.771371
H 0.368832 5.642441 -0.936235
H 0.658842 4.190539 -2.716133
C 1.335258 4.144387 -1.079130
H -0.884581 2.641394 -1.867611
C 0.515955 3.732272 -3.078313
C 1.719791 2.280273 -2.194269
H 2.889526 3.440480 -1.687971

IIb_2.40Å / electronic energy: -1826.6588731 a.u. / lowest freq: -141.48 cm^{-1}

C -0.574231 3.159617 -1.742647
C 1.095474 5.427688 -1.149660
C -2.415758 -2.340477 -3.197869
C 0.834424 3.915859 -1.153980
C 1.920176 2.728300 -2.867474
C -1.688680 -2.185159 -1.776327
C 0.892548 3.115192 -0.249291
C -0.217584 -0.915957 -1.878711
C 1.386973 5.160689 1.248934
C 0.431139 1.136670 -0.598219
C 1.217752 4.992566 1.360872
C 0.723114 1.937077 0.473769
B -0.013502 -0.191127 -0.419296
C 3.132126 3.545444 2.651784
C 0.085081 1.374157 1.747991
C 2.595139 0.451733 -0.243873
C 1.547487 4.398311 3.494299
C 0.956744 0.866955 0.699671
C -0.344288 -0.552179 2.424131
C 1.352444 2.193760 2.837608
C 0.682779 -0.186923 1.958383
C 0.783918 -1.852086 0.833941
C 2.386864 -0.925180 0.289621
C 1.641526 -3.054482 -0.512967
C 2.331492 -2.675729 -0.815551
C 3.966409 9.880835 1.492782
C 1.251549 1.752888 3.826122
C 0.301617 -2.081276 -1.974166
C 0.306691 0.251534 2.894875
C 1.325667 -4.684343 2.756587
C 2.973764 -3.151983 -2.073117
C 3.792888 -0.853849 -2.494143
C 8.292655 0.014382 2.125449
C 5.122769 -0.772166 -0.115437
C 3.492144 -1.230569 1.281847
C 4.795012 -1.509617 0.532889
C 4.779077 -1.185833 2.637634
C 4.698436 -2.580139 -0.648677
C 2.212695 -2.268735 2.755693
C 3.121462 -2.427681 2.168157
C 5.579578 -1.759896 1.270992
C 2.980245 -3.331744 1.571627
C 3.933183 -2.687082 2.878880
C -1.424066 -0.154210 8.175142
C -2.461036 -0.894633 0.184836
C -3.759799 -0.244523 -0.086135
C -3.754334 1.061466 -0.524738

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\text{IIb}, 2.60\text{Å} / \text{electronic energy:} \quad 80

H  
H  1.150058  5.786126  3.013499
H  0.714907
H  2.216480
H  3.586401
H  4.763032
F  
H  
H  
H  
C  
H  2.964065  5.571683
H  4.675755
C  4.778539  5.106864  1.330285
H  3.10
N  2.984381
C  2.378336  0.690038
H  1.591015  3.639353  3.85684
O  0.984098  0.893082  0.892051
C  3.04967  3.652201  2.534301
C  1.78548  2.706286  2.846669
C  0.683351  0.125152  1.963913
H  0.609038  1.867880  0.813186
C  2.783336  0.948847  0.288092
C  1.628599  0.376014  0.531521
C  2.319178  2.953414  2.820643
C  3.954378  0.864476  1.486175
C  1.26962  1.728424  3.835575
N  2.943381  2.018033  1.938833
C  3.186637  8.218144  2.899027
C  1.338258  0.492187  2.756784
C  2.917129  3.162618  2.887774
C  3.697263  0.861997  2.530482
C  3.834958  0.022264  2.17883
N  5.168664  0.814109  0.317671
C  3.481249  1.263841  2.742336
C  4.778539  1.629048  0.515222
C  4.786499  0.281684  2.652516
C  4.675755  2.539972  0.679659
C  2.894111  2.296473  2.753860
C  3.113998  2.459917  2.161860
H  5.571683  1.806364  1.246778
C  2.964065  3.162721  1.544157
C  3.927721  2.645456  2.669109
O  1.437084  0.120542  0.902808
C  2.486832  0.812991  0.265153
C  3.773283  1.855751  0.622470
C  3.678746  1.908729  0.574884
C  4.954449  1.755526  0.822823
C  4.992531  0.781966  0.371693
C  6.18103  3.10312  0.125430
C  6.369961  1.486111  0.473644
H  5.021385  1.759464  0.837100
H  2.889980  1.556965  0.827682
H  4.941408  2.734685  0.283941
H  7.123833  8.569695  0.399940
H  7.099599  1.661853  0.667123
C  2.422365  2.125674  1.071111
F  3.222401  3.079243  0.628290
F  1.177155  2.688221  1.185157
F  2.775643  1.828063  2.324936
C  3.309071  0.624141  0.518165
C  4.760692  1.084445  0.287998
C  3.584401  0.813499  1.871815
C  2.625558  0.406432  2.333777
C  3.92226  3.117206  3.321389
C  2.116488  2.973576  3.696839
C  8.743559  1.149756  2.450311
O  8.719497  1.127362  2.335860
C  3.847176  2.973781  1.885499
C  2.894227  1.281382  2.483585
C  6.23488  3.048626  1.432689
C  1.550958  5.786126  2.157285
C  2.39322  5.186053  0.745235
C  8.46329  5.948585  0.536873
H  0.552787  4.195174  2.747480

\text{Lee, et al., SI, Page S252}
IIIb_2.10Å / electronic energy: -1826.64826758 a.u. / lowest freq: -338.28 cm⁻¹

C    3.530068
C    5.620362
H    3.852000
H    5.996121
H    2.648367
H    3.684134
H    2.440347
F
C
H
C
C
C
C
O
H
C    0.448131
C    1.460460
N    0.807992
H    1.970450
C    0.185875
C    2.398917
C    0.140739
C    0.938112
C    0.845401
C    2.21252
C    2.285781
H    2.477314
C    1.794568
N    0.887992
C    1.256312
N    0.928089
C    0.185987
C    1.984386
C    1.854607
C    0.840945
C    2.701303
C    0.481311
C    0.775089
H    1.442572
H    0.887443
H    0.998871
C    0.765899
H    1.787813
C    0.808635
C    0.959925
C    2.247888
C    1.081780
C    0.308441
C    3.628488
C    3.385625
C    4.418982
C    4.428998
C    3.748859
H    2.592137
H    0.777491
H    0.938518
H    0.995529
C    2.861144
F    2.922185
F    2.128299
F    0.907115
H    2.596757
H    2.648367
H    2.698324
H    0.862444
H    0.699668
H    0.278344
H    0.348785
H    0.492681
H    2.097801
H    1.968528
H    5.996121
H    2.189487
H    5.755728
H    3.502000
H    3.488246
H    2.337348
H    4.473820
H    2.970806
H    4.539144

IIIb_2.20Å / electronic energy: -1826.64476510 a.u. / lowest freq: -264.39 cm⁻¹

C    3.410168
C    5.628362
C    0.243245
C    4.134575
C    0.828696
C    1.587786
C    3.530686
C    3.861754
C    2.231558
C    1.543050
C    1.899614
C    0.872398
C    0.457733
C    1.385703
C    0.949736
C    0.380786
C    2.430284
C    0.565684
C    1.789885
C    2.455821
C    0.713854
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11lb_2.60A / electronic energy: -1826.6315671 a.u. / lowest freq: -91.40 cm^-1

C  0.807682  4.435854  0.669470
H  1.826378  4.274646  -2.32846
H  -0.016354  4.574743  -0.73891
H  -0.074473  2.622784  -2.94422
C  -0.763163  3.399819  -1.55110
H  0.873160  5.336447  -0.54527
H  -3.587751  3.485510  -0.82818
H  -0.788553  4.354936  -2.08391
O  -9.940079  -1.627623  -0.36848
C  -2.388936  -1.627337  -0.31492
C  -3.089923  -8.480142  -0.467667
C  -2.881311  -8.994449  -1.713514
C  -3.784605  1.127370  -2.168193
C  -4.158667  -8.305013  0.322517
C  -4.965439  8.983443  -0.118428
C  -4.738177  1.582737  -1.35868
H  -4.333816  5.918171  1.289655
C  -2.118485  -8.380970  -2.394594
H  -3.543157  1.563135  -3.148341
H  -5.780483  1.124581  0.510825
H  -5.376113  2.392593  -1.691612
C  -2.812334  -3.266898  -0.275796
F  -2.908538  -3.228483  -1.586107
F  -2.028364  -3.976533  -0.284826
F  -4.018712  -3.184290  -0.310229
H  2.091811  1.099642  -1.574224
H  2.087395  3.856933  3.819930
H  2.395658  2.259183  1.809888
H  -4.728363  3.176015  3.292930
H  -0.044120  3.684392  4.182881
H  -0.656218  1.933045  4.182123
H  0.824757  -1.657202  2.192557
H  0.294145  0.949082  2.413152
H  -3.415385  -1.933953  2.568971
H  -1.842592  -2.867658  2.297980
H  -2.186064  0.283125  3.126187
H  5.923655  -2.064647  3.634690
H  6.252434  -1.717726  0.833557
H  5.941392  -2.854210  -0.124495
H  3.778457  -3.798386  1.740476
H  3.649585  -3.924175  -0.021180
H  2.341082  -3.172835  0.918140
H  4.145721  -1.544362  2.840690
H  2.759680  -0.822186  2.684665
H  4.373951  -0.892750  1.853811

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1826.63815671 a.u. / lowest freq: -91.40 cm^-1
|        | x      | y      | z      |
|--------|--------|--------|--------|
| H      | 2.374640 | 2.182485 | 1.987772 |
| H      | 2.067641 | 3.494219 | 3.138240 |
| H      | 1.918807 | 1.798752 | 3.651963 |
| F      |        |        |        |
| C      |        |        |        |
| H      | 1.006581 | 5.361585 |
| C      | 0.904176 | 4.449374 | 0.164052 |
| H      | 1.826292 | 4.326496 | 0.741735 |
| C      | 1.832737 | 3.292605 |
| C      | 0.383462 | 1.176519 |
| H      | 1.675196 | 2.655135 |
| H      | 2.622645 | 0.859190 |
| C      |        |        |        |
| C      | 0.662903 | 1.942841 | 0.059550 |
| H      | 0.544099 | 0.363802 |
| C      |        |        |        |
| H      | 0.286869 | 0.064134 | 2.413814 |
| H      | -1.885438 | -2.848478 | 2.374570 |
| H      | -2.197978 | -2.712426 | 2.862434 |
| C      | 0.604441 | -2.745142 | 2.851388 |
| H      | 6.222200 | -1.316144 | 0.633671 |
| C      | 5.922471 | -1.808055 | 1.919629 |
| H      | 3.749024 | -3.030113 | 1.793931 |
| H      | 3.621884 | -3.936387 | 0.853610 |
| C      | 2.318959 | -3.182198 | 0.884848 |
| H      | 4.139213 | -1.591103 | 2.833569 |
| H      | 2.756998 | -0.851077 | 0.894142 |
| C      | 4.375716 | -0.129774 | 1.856998 |

**IIlb_2.70Å** / electronic energy: -1826.63778129 a.u. / lowest freq: -73.88 cm⁻¹

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Ivb_2.10Å / electronic energy: 80

H    1.907842    1.397726    1.738502
H    2.132374    2.638827    2.991319
H
H    2.832427
H    1.454456
H    1.298374
H
H
H
F    3.825344
H
H    4.204176
C    4.933772    0.602841    0.816492
C    3.723036    1.349738    0.167284
C    2.762779    2.933872    0.801951
F    3.825344    3.336760    0.832927
F    4.053349    4.716222    0.802472
4.933772    0.602841    0.816492
C    2.770253    1.587075    0.851712
4.724176    1.237757    1.639144
C    2.044328    0.340726    1.735917
H    3.587458    2.257119    1.830876
C    5.751007    0.676306    1.529524
5.460408    2.423111    0.884135
C    2.762779    2.933872    0.801951
H    3.825344    3.336760    0.832927
H    4.053349    4.716222    0.802472
2.970253    1.587075    0.851712
2.770253    1.587075    0.851712
H    0.618354    3.984768    0.871984
F    3.066441    2.610856    0.245867
H    1.293538    0.225119    3.390816
H    4.795557    0.482590    2.646883
H    3.354418    0.995154    1.883813
H    3.967585    3.148164    2.147335
5.083128    2.040449    2.989993
H    3.426354    2.255167    3.598941
-1.071818    1.803587    2.179196
-0.816338    2.613288    1.359880
2.795419    2.879558    1.364449
1.907842    1.397726    ...
H 1.044237 4.839674 2.825939
H -0.067832 5.251273 1.514293
H 1.673343 5.087017 1.195836

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IVb_2.30Å / electronic energy: -1826.65413696 a.u. / lowest freq: -255.24 cm⁻¹

C 1.952634 2.470333 1.931986
C 0.023391 4.673760 1.031994
C 1.859816 -2.656459 1.794364
C 0.642051 3.175124 1.548944
C -0.319319 2.682939 2.438384
C 0.963098 -1.661185 2.099947
C 0.299977 2.912862 0.667774
C -0.372513 -1.643094 1.554920
H 0.477762 4.950919 -0.576631
O 0.224378 0.566900 1.669791
C 0.237524 3.938171 -0.877119
C -0.866548 1.681352 -0.935540
B -0.767414 -0.770725 -0.119691
C -0.334239 3.714083 -2.281385
C -0.596992 1.184491 -1.790857
H -2.447834 8.644594 0.176797
H -0.163283 4.548067 -2.983768
C -1.395337 -0.775146 -0.942886
H -0.028511 -0.589552 -2.497886
C -0.518279 2.441215 -2.680634
C -0.826898 -0.841228 -2.117123
H -1.518125 -1.745331 -1.219442
C 2.693798 -0.283395 -0.346053
O -2.955673 -2.574414 0.167170
C -3.094884 -1.430684 0.684777
H -3.359897 2.143146 -1.293583
H -0.834983 2.258412 3.626929
N -3.585995 -1.166683 1.831385
H -2.928076 1.484493 -2.797525
H -1.610854 0.633826 -2.965238
C -4.019149 -2.208919 2.667198
N -3.729234 8.137982 2.459333
C -3.747328 1.356964 -2.824546
H -5.158048 -0.881727 0.241747
C -3.874057 -0.818122 -1.343694
C -5.186084 0.829161 -5.338384
C -4.699546 1.598182 -2.584839
H -5.424564 -0.931083 1.068423
C -3.552287 -1.235798 -3.643229
C -0.164586 -1.142410 -2.379537
H -0.683414 0.787380 -1.213781
H -4.377416 -2.187341 -1.893959
H -4.889775 -0.926842 -3.613790
O 0.866003 -1.561449 -0.687783
C 2.083159 -1.711489 -0.879717
C 2.998748 -0.541842 -0.664452
C 2.828611 0.472168 -1.012476
C 3.787465 1.540263 -1.076814
C 4.091646 -0.491865 0.885774
C 4.971385 0.582117 0.747376
C 4.782747 1.597610 0.389427
H 4.265627 -1.79185 1.530388
C 2.985261 4.812539 -1.721266
H 3.535365 2.321939 -1.866974
H 5.81078 0.622598 1.432310
C 5.764660 2.430781 -0.231266
C 2.723342 -2.964694 -0.802389
F 3.848772 -3.349917 -1.273772
F 1.864419 -3.979260 -0.856140
F 3.008774 -2.660860 -2.848863
O 3.183318 0.348190 3.482917
H -4.784756 0.328723 2.677776
H -3.355898 0.943979 1.832933
H -3.942288 -3.285471 2.181120
H -5.055237 -2.119619 2.978233
H -3.388763 -2.396964 3.560454
H -1.93648 -1.031478 2.159724
H -0.779254 -2.622725 1.338101
C 1.328514 -0.777399 -2.692795
C 1.492674 -3.597119 1.840143
H 2.556134 -2.659348 2.219915
H -0.380456 2.928777 3.479668
H -8.652687 1.682910 2.357855
H -1.458978 3.718647 2.514710
H 2.144198 -2.20522 2.999991
H 2.793637 2.891619 1.374384
H 1.917463 1.397766 1.729585
H 1.046822 4.818354 2.875855
H -0.082184 5.242513 1.580361
H 1.665733 5.983922 1.242725

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IVb_2.38Å / electronic energy: -1826.65413696 a.u. / lowest freq: -187.15 cm⁻¹

C 1.964676 2.467881 1.962880
C 8.815964 4.663440 1.873623
C 1.664128 -2.671924 1.830871
C 0.644898 3.163171 1.575663
C -0.498087 2.650692 2.471919
C 0.908399 -1.661162 2.681427
C 0.329141 2.929680 -0.181874
C -0.359187 -1.631913 1.517680
H 0.451219 4.975957 -0.510199

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O  0.134718  0.57619  0.46276
C  0.214388  3.970765 -0.825624
C -0.012223  1.641703 -0.381947
B -0.182037  0.756163  0.189664
C  0.167387  3.766749 -2.152152
C  0.466656  1.274788 -1.686158
H -2.515944  0.630859  0.212828
H -0.286561  4.685187 -2.838360
N  -1.361242  0.647988 -9.545768
H -0.031448 -0.533180 -2.512772
C  0.538591  2.498902 -2.576381
C -0.104468  0.642968 -2.220878
H -1.579945  1.179296  1.245832
H  2.695457  0.279318 -3.349488
O  -2.939336 -2.580847  0.697652
C  0.308542  1.461170  0.573987
C -0.587566  2.711188 -2.141718
H  0.817672  2.331314 -3.594820
N  -0.576285  1.244145  1.889899
H -0.080549  1.450732 -2.796660
H  1.626264  0.887337 -2.984440
C  -0.994033  2.192881  2.685889
C  0.764516  0.639431  2.491777
C  0.749523  1.480130 -1.981188
H  -5.137749  8.208940  2.897311
C  0.881057  0.614540  1.13264
C  0.581386  0.606480 -0.846434
H  4.708139  1.662375 -2.437222
H  5.425687  0.983788 -0.642880
H -1.784649  1.182888 -3.642888
H -0.044656 -1.088814 -2.377763
H -0.068287  0.237987  1.163155
H -4.215618 -2.059977 -1.990866
H -0.928792  0.848880 -3.097267
O  0.869902  1.549199 -0.639252
C  2.085131 -1.693408 -8.239162
C  3.083856 -0.536334 -1.088118
H  2.088214  0.587126 -2.802489
C  3.699598  1.571180 -1.068189
C  4.416884  0.588420  0.793978
C  4.908118  0.553494 -0.694484
C  4.793426  1.597111 -0.287983
H  4.294358  1.329772  1.436873
H  1.973714  4.718624 -1.711299
C  3.534918  2.474542 -1.787848
H  5.852453  0.751722  1.362254
H  5.498215  2.348071 -2.248046
C  2.712580 -2.967393 -0.814233
F  3.781518 -3.158831 -8.110951
F  1.837423 -3.976292 -2.845232
F  3.095166 -2.710588 -2.043465
H  1.315259  0.806143  3.478380
C -0.757445  0.233903  2.712973
H -3.311464  0.859277  1.983467
C -3.991038 -3.282728  1.582896
H -4.998955 -2.216489  2.597120
H -3.387279 -2.531396 -3.447597
H -1.042819 -1.051544 -2.143238
H  0.758868 -2.625591  1.387193
H  1.335829  0.767525  2.595528
H  1.507587  3.613923  1.425881
H  2.861615 -2.662737  2.553273
H  0.277085  2.838972  3.517887
H  0.626389  1.569652 -2.381397
H  1.441593  3.140780  2.207688
H  2.136381  2.597691 -3.912354
H  2.797561  2.980928 -1.387585
H  1.937227  1.391906  1.718443
H  1.045928  4.791224  2.955668
H  0.096737  5.228130  1.652818
H  1.648651  5.180620  1.382355

Ivb_2.4A / electronic energy: -1826.65183025 a.u. / lowest freq: -154.12 cm-1
C  1.967443  2.472145  1.044886
C  0.796905  4.656889  0.928665
C  1.876565  2.673847  1.880249
C  0.637651  3.163950  1.597415
C -0.492499  2.623684  2.495890
C  0.997189 -1.656628  2.075811
C  0.724083  2.948495  0.922788
C -0.342873  2.655062  1.759939
H  8.410254  4.998848 -4.465539
C  0.814268  0.582466  0.457142
C  0.181944  0.991771 -0.791861
C -0.021628  1.653938 -0.373574
B  0.184042 -0.747281  0.184685
C  2.072383  3.799856 -2.117283
C  0.428269  1.452886 -1.677872
C  2.457458  4.622199  0.226418
C  0.258268  4.648886  2.793332
N  1.394396 -0.735351 -0.962540
C  0.034665  0.497934 -2.522727
C  0.562235  2.539992 -5.554185
C  0.828578  0.869317 -2.123814
C  1.573222  1.784105 -2.612631
C  2.695479  0.183724 -3.335807
| Column | Row | Value |
|--------|-----|-------|
| 1      | 1   | -3.962490 |
| 2      | 1   | -1.586196 |
| 3      | 1   | -2.419748 |
| 4      | 1   | -2.861668 |
| 5      | 1   | -0.956296 |
| 6      | 1   | -2.161473 |
| 7      | 1   | -3.463323 |
| 8      | 1   | -3.548887 |
| 9      | 1   | -4.651268 |
| 10     | 1   | -2.084448 |
| 11     | 1   | -0.062180 |
| 12     | 1   | -4.357147 |
| 13     | 1   | -3.735905 |
| 14     | 1   | -1.318335 |
| 15     | 1   | -2.153884 |
| 16     | 1   | -4.748174 |
| 17     | 1   | -1.767043 |
| 18     | 1   | -2.849335 |
| 19     | 1   | 1.529276  |
| 20     | 1   | 2.659691  |
| 21     | 1   | 3.862914  |
| 22     | 1   | 3.711548  |
| 23     | 1   | 0.813419  |
| 24     | 1   | 5.133234  |
| 25     | 1   | 6.384349  |
| 26     | 1   | 0.675626  |
| 27     | 1   | 5.274365  |
| 28     | 1   | 6.075296  |
| 29     | 1   | 7.218291  |
| 30     | 1   | 6.937723  |
| 31     | 1   | 2.769593  |
| 32     | 1   | 3.134377  |
| 33     | 1   | 1.606857  |
| 34     | 1   | 3.689562  |
| 35     | 1   | 3.190893  |
| 36     | 1   | 4.417188  |
| 37     | 1   | 3.646151  |
| 38     | 1   | 3.804346  |
| 39     | 1   | 3.085328  |
| 40     | 1   | 1.812242  |
| 41     | 1   | 0.555392  |
| 42     | 1   | 0.723833  |
| 43     | 1   | 1.186046  |
| 44     | 1   | 3.067611  |
| 45     | 1   | 3.499561  |
| 46     | 1   | 3.348843  |
| 47     | 1   | 2.439273  |
| 48     | 1   | 3.933427  |
| 49     | 1   | 1.159464  |
| 50     | 1   | 0.857993  |
| 51     | 1   | 0.311813  |
| 52     | 1   | 1.291224  |
| 53     | 1   | 3.976681  |
| 54     | 1   | 2.482273  |

**Vb = 2.48 A**: 
**Electronic energy**: -1826.64962722 a.u. 
**Lowest freq**: -139.37 cm^-1

-0.879349 3.621821 1.687211
-0.032231 4.562379 0.896343
2.768516 0.748966 2.484974
2.876683 2.838566 9.559279
2.978596 2.237784 1.763626
1.433886 0.856093 2.440862
1.919382 1.274942 0.452225
0.825985 0.873846 1.836614
-2.969652 4.728073 1.508152
0.862675 0.918373 0.435119
-2.429689 3.338240 1.596334
-1.282569 1.525082 0.648952
B 8.313468 0.266688 0.334415
-2.284893 2.788875 2.870317
-1.177783 0.921092 1.986456
-2.459298 0.707977 0.028213
-2.695789 3.163480 3.731667
-0.934322 1.212890 0.774671
0.858380 0.388592 2.295474
-1.653855 1.566183 0.802025
-0.495385 0.443245 2.056885
-0.077164 2.097695 0.854594
-1.978668 1.621983 0.323571
-0.785453 3.444532 0.596368
-1.684221 0.621664 0.806685
-2.967137 0.476791 1.759885
-1.508763 1.096227 3.997986
-2.392244 2.591446 1.953733
-0.880806 0.851212 3.678199
-0.977714 0.000087 2.856394
-2.315059 3.585730 2.979567
-3.442482 1.649296 2.858724
-3.553322 2.713722 2.329461
-0.643555 2.294624 0.866170
-2.896180 2.386630 1.398179
-4.055573 0.684054 8.656880
-4.378556 1.756285 2.878474
-3.712872 3.010422 0.092965
-3.313539 2.590069 2.784360
H  4.760825  -3.624425  -1.186891
H  2.333563  -8.142917  -0.785716
H  6.996138  -2.590682  -1.235856
C  2.761842  1.822191  0.190718
F  3.156082  2.326295  -0.982659
F  3.597800  2.348615  -0.581890
F  3.605394  2.180280  1.115681
H  -3.162213  -1.131541  3.234899
H  -4.649972  -2.198890  2.477312
H  -3.681252  -8.989977  1.534815
H  -1.291801  -4.342324  2.645148
H  -2.980451  -4.352982  3.215882
H  -1.757928  -3.695583  3.965761
H  -0.498494  -9.832280  2.372116
H  -0.808493  -1.893964  1.763553
H  1.096139  1.800730  2.794984
H  3.128849  -1.246656  2.173722
H  3.849648  8.457361  2.863130
H  -3.135232  -2.620711  2.885522
H  -2.357326  -1.388187  1.925131
H  -3.948525  1.965876  1.337337
H  -1.098802  4.118285  2.627444
H  -0.294809  4.335796  1.685856
H  -0.867070  2.752162  1.853380
H  -2.344850  4.885224  1.598685
H  -0.489092  4.348347  -0.472587
H  -2.571928  5.346894  0.379935
B  8.0.486415  1.217990  3.399102  4.116020
C  1.555568  2.390175  0.478125
F  3.622351  2.222319  1.087826
H  -2.834365  4.491751  3.375972
H  -4.136028  -2.463329  2.620851
H  -3.399180  -1.814172  1.746523
H  -2.179998  -4.640796  2.300460
H  -2.649022  -4.297413  3.314860
H  -1.112727  -3.445530  3.617817
H  -0.484645  -8.780855  2.348440

VdW 2.60 A /
VdW 2.60 A /

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H 0.851916 -1.871297 1.708585
H 1.037194 1.016054 2.788684
H 3.144989 -1.142128 2.186807
H 3.434583 0.536788 2.913553
H -3.157241 2.574350 2.961377
H -2.508184 1.283415 1.994655
H -3.928588 1.917952 1.542847
H -1.185905 -0.692153 2.695217
H -0.359988 4.352685 1.388841
H -0.279700 2.757856 1.869340
H -3.277680 4.845132 2.881211
H -4.124738 4.151057 0.618296
H -2.663381 5.353806 0.499590

Vb = 2.78A / electronic energy: -1826.6581027 a.u. / lowest freq: 20.91 cm-1
C -0.898435 3.636937 1.720816
C -3.112971 4.520652 1.064478
C -2.732593 -0.170793 2.540166
C -2.238977 3.647678 1.064234
C -2.84324 -2.193747 1.919590
C 1.486597 -0.061139 2.443403
C -0.204769 2.727380 -0.859134
C 0.854787 -0.863178 1.737657
H -3.15954 -4.262743 -1.336990
O -0.52246 8.540746 0.438884
C -2.681939 3.344630 -2.476083
C -1.291681 1.548583 -0.685858
B 0.094088 -0.624983 0.377230
C -2.581526 2.817331 -2.758310
C -1.245286 8.967225 -1.877764
C -2.656962 -0.810344 0.116331
C -2.969355 3.339308 -3.519737
N -0.611656 -1.728966 -0.887568
O 0.472951 -0.272384 -2.340918
C -1.844751 -1.615228 -2.957234
C -0.582815 -8.170779 -2.073959
O -0.855628 -0.292883 -0.903638
C -0.951487 -1.674853 -0.617688
O -0.687529 -3.479159 -0.449355
C -1.538828 -0.732017 0.727392
C -0.415512 -8.468822 -1.630384
C -1.799979 1.164138 3.965230
C -2.186484 -2.829670 1.902536
C -2.958527 -8.320683 -3.015514
C -1.046521 -0.928142 -2.873824
C -1.78261 -3.874014 2.833285
C -3.192284 -1.918729 2.427690
C -3.612233 -1.805225 2.435513
C -4.537953 -2.199595 0.037695
C -2.897298 -2.355526 1.179972
C -4.012443 -3.077363 -0.613847
C -4.449931 -1.760176 -2.758581
C -3.638758 -3.998160 -0.651539
C -1.349854 -2.928750 -2.839769
C -2.164095 -3.663225 -2.258184
C -4.746673 -3.490389 -1.339973
C -1.746871 -4.169557 -1.645429
C -2.875247 -3.795194 -2.961638
C 0.524966 -0.147916 0.362799
C 2.647655 8.355514 -0.180080
C 3.858117 -0.394795 0.396588
C 3.741084 -1.779221 -0.620856
C 4.867794 -3.301500 -0.953126
C 5.118752 0.225147 -0.460838
C 6.329558 -8.356934 -0.756380
C 6.216749 -1.907889 -0.975668
C 5.229053 1.289725 0.295392
C 2.766936 -2.525280 -0.551662
C 4.780229 -3.597822 -1.870815
C 7.211546 -0.061198 0.816374
C 6.999065 -2.497373 -1.282858
C 2.735972 1.877603 0.131585
F 3.131028 2.422536 -1.024819
F 1.569891 2.855092 0.456746
F 3.623656 2.381215 1.676445
H -2.834843 -1.491126 3.370885
H -4.121168 -2.462939 2.621825
H -3.485158 -1.187179 1.743234
H -1.234773 -4.648187 2.298983
H -2.657228 -2.497322 3.310576
H -1.161280 -3.453757 3.653349
H -8.488403 -0.917152 2.348886
H -0.871574 -3.871555 1.684650
H -1.087872 -1.089062 2.884166
C 3.548228 -1.125668 2.330872
C 3.399617 8.545784 2.996802
C -3.132776 2.584165 2.917292
C -2.336694 1.289562 2.060443
H -3.988193 1.929319 1.464634
H -1.078822 4.694359 2.697573
H -0.348376 4.359826 1.184613
H -0.264913 2.759983 1.864454
H -3.253834 4.853888 2.986234
H -4.300796 4.235176 6.838352
H -2.647494 5.341753 0.510981
| Atom | x | y | z |
|------|---|---|---|
| H    | -5.17736 | 2.90326 | 2.915294 |
| H    | -7.08358 | 0.536751 | 0.81992 |
| H    | -7.211887 | 1.779087 | -0.816292 |
| C    | -2.478823 | 2.125276 | 0.839798 |
| F    | -3.313755 | -0.06164 | -0.321588 |
| F    | -1.250192 | -2.684633 | 0.791714 |
| F    | -2.786656 | -1.964684 | -2.127769 |
| H    | 3.438377 | -0.621874 | -3.316460 |
| H    | 4.831288 | -1.385389 | -2.461351 |
| C    | 3.792427 | -0.157328 | -1.642589 |
| H    | 2.389913 | -2.886178 | -3.760933 |
| H    | 2.415455 | -0.056844 | -2.420452 |
| F    | 3.901257 | -3.461388 | -3.211867 |
| H    | 0.556449 | -0.090197 | -2.495994 |
| H    | 0.769882 | -1.159027 | -2.317648 |
| F    | -3.235724 | -2.526468 | -2.189779 |
| F    | -2.853722 | -0.574367 | -2.485278 |
| C    | -0.840755 | -2.946564 | -1.675519 |
| H    | 2.234916 | 5.525243 | -2.974802 |
| C    | 3.086265 | 3.595224 | -0.558881 |
| C    | 1.426746 | 5.582163 | -0.338984 |
| H    | 0.349948 | 2.454076 | -2.814627 |
| H    | 0.528289 | 4.773135 | -1.765459 |
| H    | 0.599293 | 2.780275 | -1.993858 |
| C    | 2.725457 | 3.299277 | -2.862976 |
| C    | 2.371821 | 1.847823 | -2.086617 |
| H    | 3.518687 | 2.819928 | -1.349890 |
| C    | -2.673218 | 2.041224 | -1.008881 |
| H    | -3.098646 | 2.959547 | -1.486644 |
| H    | -2.181766 | 1.456519 | -1.27332 |
| C    | -1.975349 | 2.185514 | -0.800172 |

B3

I1C2.60 A / electronic energy: -1865.9580722 a.u. / lowest freq: 22.38 cm⁻¹

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| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | -2.45797  | -0.405737 | -2.416108 |
| H    | 3.935656  | -3.436590 | -3.213385 |
| H    | -0.563082 | 0.623912  | -2.498399 |
| H    | 0.775916  | -1.151698 | -2.325680 |
| H    | -3.178535 | -2.621966 | -2.154596 |
| H    | -2.842987 | 0.835831  | -2.568964 |
| H    | 0.705822  | -2.975633 | -1.675129 |
| H    | 2.171866  | 5.553281  | 2.062770 |
| H    | 3.013339  | 5.248282  | -0.539560 |
| C    | 3.345468  | 5.862776  | -0.532699 |
| H    | 0.315043  | 4.245921  | -2.822447 |
| H    | -0.754823 | 4.340966  | -1.293641 |
| H    | -2.869819 | 2.762682  | -2.069628 |
| H    | 2.710675  | 3.313573  | -2.846924 |
| H    | 2.179162  | 1.874444  | -1.997362 |
| H    | 3.492648  | 2.872251  | -1.325744 |
| C    | -2.685585 | 2.069973  | -0.636888 |
| H    | 3.025286  | 2.917654  | -1.537724 |
| H    | -2.114623 | 1.413341  | 1.754280 |
| H    | -1.987337 | 2.195429  | -0.241837 |

*IIIc_2.20Å / electronic energy: ~106.53876892 a.u. / lowest freq: ~275.94 cm⁻¹*
H -3.387684 -4.063556 -0.351257
H -2.98887 -3.189372 -1.167513
H -4.533257 -1.460130 -2.613322
H -3.049077 -0.743174 -1.962929
H -4.637988 -0.130386 -1.447844
C 2.566042 -1.473189 2.680967
C 2.145788 -0.023392 3.515765
H 3.394855 -2.116878 2.917653
H 1.813788 -2.118663 2.158152

IIIc_2.30A / electronic energy: -1865.93697750 a.u. / lowest freq: -212.98 cm⁻¹
C -3.256222 -3.313195 -0.961252
C -5.681232 -2.438214 -0.371849
C 2.348391 -1.271729 -2.642784
C -4.322822 -2.043585 -0.571218
C -4.082812 -1.014992 -2.718232
C 1.646863 -0.234731 -2.554646
C 2.542377 -1.424610 0.782872
C 0.072053 -0.433269 -2.198849
H -3.383586 -1.629699 1.582162
O -1.427988 -1.111221 -0.359847
C -4.284486 -2.774899 1.876382
C -2.214491 -0.958566 0.745889
B -0.136693 -0.578848 -0.542511
C -3.759087 -0.691096 3.077624
C -1.086823 -0.325906 1.873368
H -1.784943 1.619243 0.897976
H -4.722515 -6.684171 3.577556
N 0.057137 -0.786916 0.844350
H 0.422989 -6.693448 1.961538
C 2.462316 -2.738482 3.872686
C 0.761243 -1.569261 1.810432
H 1.036933 1.082992 -4.108973
H 0.792529 1.937085 0.678356
O 1.048422 2.199125 -1.351421
O -0.140899 -2.951176 -2.174841
C -2.547715 2.864647 0.583833
H -2.045334 0.261050 3.869234
H -0.949288 2.782177 -2.783059
H -1.383535 2.295896 2.954967
H -0.205485 0.855221 2.570698
C -0.294416 3.385522 -3.493186
C -2.481313 2.684567 -2.373583
C -1.622799 3.037010 2.230613
H -0.915169 4.369391 -1.435664
C -6.168781 3.148351 1.071832
C -0.988533 4.406019 0.343138
H -1.638032 3.984589 2.787525
H -0.259034 4.690616 -8.461880
H 1.351683 2.481492 2.224124
C 0.818094 3.131237 1.594581
H -0.121487 5.267077 1.026421
C 1.528235 -3.228338 -0.706810
H 0.846188 4.214983 2.211547
O 0.393117 -1.594813 -0.179625
C 2.708981 -4.492836 -0.362491
C 3.062828 -0.379378 0.296217
H 3.076262 -0.390976 1.712980
C 3.744216 0.673770 2.321712
C 3.638672 0.811941 -4.335689
C 4.302822 1.652584 -0.199841
C 4.344447 1.693270 1.587795
H 3.685791 0.597800 -1.515684
C 3.797449 0.695955 3.439543
C 4.737342 2.428415 -0.397313
H 4.847965 2.584666 2.099486
C 2.982127 -2.876211 -0.481583
F 3.162096 -3.357174 0.736803
F 3.208662 -3.756256 -1.381919
F 4.061589 -2.765837 1.124797
H -2.681218 2.180118 -3.253314
H -2.484592 -3.839299 -2.415361
H -2.817978 2.158573 -1.466285
H 0.341852 2.547164 -4.282864
H 0.897986 3.591183 -2.777455
H -0.449394 4.176884 -3.806368
H -0.345695 -1.399890 -2.532669
H -0.506685 0.356246 -2.544146
H 3.349017 -1.98783 -2.877438
H 1.978817 -2.842826 -2.778028
H 1.818682 0.789717 -2.612871
H -5.984214 2.626265 1.389393
H -6.225151 -1.573987 -0.119675
H -5.715639 -3.195985 0.699132
H -3.805897 -3.755374 -1.856192
H -3.497545 4.652674 -0.156394
H -2.387486 -3.109988 -1.713314
H -4.543214 -1.441661 -2.614887
H -3.056982 -0.732164 -1.963564
H -4.642589 -0.113145 -1.447493
C 2.554263 -1.475088 2.629154
H 2.123338 -1.625819 3.527285
H 3.348079 -2.11363 2.946653
H 1.89519 -2.126174 2.173950

IIIc_2.40A / electronic energy: -1865.93588058 a.u. / lowest freq: -160.88 cm⁻¹
IIIc_2.60Å / electronic energy: -1865.93469208 a.u. / lowest freq: -126.72 cm

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| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 1.444191 | -0.063856 |
| O    | -1.183866 | 2.415399 | 1.320845 |
| C    | 0.12544 | 2.897444 | 0.366519 |
| H    | 2.655744 | 2.089071 | -0.155418 |
| H    | 2.006982 | 0.197558 | -0.916379 |
| N    | 0.912288 | 2.38354 | 2.28799 |
| H    | 1.809199 | 2.292744 | -0.952828 |
| H    | 0.059329 | 0.892666 | -0.561877 |
| C    | 0.619849 | 3.13152 | 2.484841 |
| C    | 2.30482 | 2.691138 | 2.376349 |
| C    | 1.647543 | 3.088485 | -2.233289 |
| H    | 2.004876 | 4.357676 | 0.133896 |
| C    | 0.631779 | 3.143969 | -0.803837 |
| C    | 1.028953 | 4.437197 | -3.313319 |
| H    | 1.670823 | 3.952323 | -2.784496 |
| H    | 0.298717 | 4.701983 | 0.437619 |
| C    | -1.133908 | 2.82676 | -2.232467 |
| C    | -0.792351 | 3.313878 | -2.144412 |
| C    | 1.053869 | 5.258491 | -0.856969 |
| C    | -1.580964 | 3.454145 | -0.797352 |
| C    | -0.824354 | 2.211782 | -2.246578 |
| C    | -0.941597 | -1.068824 | 0.284647 |
| C    | -2.193725 | -1.514585 | 0.272879 |
| C    | -2.972334 | -2.409244 | -0.373286 |
| C    | -3.952388 | -9.243446 | 1.787165 |
| C    | -3.171963 | 0.637592 | 2.486792 |
| C    | -3.638548 | 0.682142 | 0.359437 |
| C    | -4.361267 | 1.836561 | -0.288738 |
| C    | -4.380745 | 1.660378 | 1.678610 |
| C    | -3.564764 | 5.387979 | 1.348329 |
| C    | -3.778437 | 6.425843 | 3.491231 |
| C    | -4.827971 | 2.423889 | 0.294790 |
| C    | -4.687172 | 2.474564 | 2.196831 |
| C    | -2.928113 | -2.853028 | 0.531360 |
| F    | -3.242727 | -3.379268 | -0.673854 |
| F    | -2.463446 | -3.719313 | 1.624891 |
| F    | -4.807732 | -2.656772 | 1.844899 |
| C    | 2.618552 | 2.186815 | 3.265435 |
| C    | 2.886473 | 3.685610 | 2.471113 |
| C    | 2.791532 | 2.195170 | 1.506018 |
| C    | 8.189968 | 2.304642 | 4.245774 |
| C    | 0.737297 | 3.660029 | 3.233199 |
| C    | 0.855449 | 4.140598 | 3.883136 |
| C    | 0.382341 | -1.780801 | 2.552767 |
| C    | 0.528265 | 0.364730 | 2.581140 |
| C    | -3.368373 | -1.043825 | 3.132449 |
| C    | -1.984449 | -2.253410 | 2.899385 |
| C    | -1.383832 | 0.813091 | 2.665462 |
| C    | 5.998772 | -2.806954 | 1.293683 |
| C    | 6.233478 | -1.592483 | 0.685759 |
| C    | 5.786679 | -3.216194 | -0.411264 |
| C    | 3.823269 | -3.733062 | 1.883321 |
| C    | 3.796871 | -4.047457 | 0.935310 |
| C    | 2.319434 | -0.073951 | 1.219348 |
| C    | 4.584817 | -1.411714 | 2.681756 |
| C    | 3.86449 | -0.781263 | 1.959899 |
| C    | 4.677829 | -0.100032 | 1.415274 |
| C    | 2.539435 | -1.539857 | -2.672165 |
| C    | -2.087651 | -1.123976 | 3.575990 |
| C    | -3.376087 | -2.172288 | -2.981616 |
| C    | -1.891213 | -2.191621 | -2.191388 |

83

**llc / electronic energy**: -1865.9346/2016 a.u. / lowest freq: -102.59 cm⁻¹
Lee, et al., SI, Page S283

C 2.084376 -1.685190 -0.158366
C 2.938042 -0.564284 0.285599
C 3.192037 0.427087 -0.763769
C 4.143557 1.487190 -0.454197
C 3.656738 -0.567525 1.484587
C 4.601748 0.488610 1.678692
C 4.045622 1.480196 0.740832
H 3.482988 -1.334387 2.147394
H 4.339913 2.176829 -1.156691
H 5.342859 0.835597 2.637182
H 5.580555 2.181258 0.938339
C 2.701145 -2.851231 -0.905698
F 3.737157 -3.317696 -0.214326
F 1.861878 -3.852046 -1.599944
F 3.153011 -2.184877 -2.072894
H -3.234436 0.084669 3.481440
H -4.818133 0.115731 2.739596
H -3.336217 0.881471 1.948869
H -5.159251 -2.130451 3.626880
H -3.741588 -2.582149 3.483411
H -4.174046 -3.231946 2.815299
H -1.124298 -1.123161 2.168263
H -0.964455 -2.658452 1.222773
H 1.233932 -1.172249 2.722584
H 1.283475 -3.764123 1.050382
H 2.028483 -3.120555 2.645142
H -8.641588 3.836575 3.345585
H -9.194855 1.784179 2.268450
H -1.643264 3.288000 1.893320
H 1.844721 2.673926 3.121246
H 2.637168 2.798987 1.541694
H 1.654934 1.726535 1.927347
H 0.858204 4.783557 2.790874
H -0.336222 5.281991 1.386152
H 1.617071 5.048510 1.287873
C 2.618486 8.477463 -2.159890
H 2.294885 1.477968 -2.364845
H 1.825811 -8.243915 2.336949
H 3.416671 0.717073 -2.875953

B3

1Vc_2.3A /

energy: -1865.94644647 a.u. / lowest freq: -165.65 cm-1

C 1.734311 2.341478 2.872763
C 0.726926 4.675431 1.759726
C 1.629573 -2.992184 1.651569
C 0.842398 3.175447 1.527865
C -0.753758 2.767284 2.320164
C 0.838668 -1.957286 2.047745
C 0.828158 2.866254 0.704675
C -0.498897 -1.749991 1.482830
H 0.598817 4.689150 -0.655925
O -0.098984 0.541482 0.588899
O 0.322275 3.860337 -0.937862
C -0.054541 1.568152 -0.397738
B -0.282331 -0.790884 1.129338
C 0.066816 3.138629 -2.712286
C -0.476215 1.323295 -1.988285
H -2.491312 0.622453 0.266430
H -0.093667 4.411785 -2.593332
N -1.586257 -0.784413 -0.932418
H -0.396446 -0.646151 -2.545849
O -0.441678 2.155483 -2.647871
C -0.981587 -0.035177 -2.117482
H -1.728998 -1.751620 -2.832800
C -2.780891 0.863905 -0.380756
O -3.140941 -2.566658 0.684101
C -2.227960 1.440843 0.584919
H -3.417787 2.249295 1.169721
H -0.759061 2.159149 -3.668542
H -3.691248 2.130082 1.830641
H -3.013468 1.516301 2.725781
H -1.759741 0.056619 -2.870624
C -4.148984 2.174457 2.617271
C -3.778556 0.040947 2.534832
C -3.739528 1.583656 -0.914394
C -5.311185 1.680949 0.364882
C -3.955805 0.119682 -1.272516
C -5.239185 0.247595 -0.426283
H -4.609198 1.844759 -3.334821
H -5.548125 0.699599 0.026768
H -3.265552 1.125190 3.800136
H -4.280866 -0.959735 -2.334876
H -6.052331 0.571986 1.079582
H -4.469896 1.915423 -1.870381
H -5.047862 0.864567 2.960766
O -0.087375 -1.958440 -0.653183
C 2.085043 -1.675966 -0.196890
C 2.926384 -5.538862 0.185493
C 3.187061 4.444814 -0.776575
C 4.141787 1.419882 -0.466833
C 3.659284 -0.576999 1.380658
C 4.085688 0.396460 1.680180
C 4.846388 1.486687 0.731961
H 3.485292 -1.538222 2.112769
H 4.337917 2.192584 -1.191933
H 5.515111 0.363070 2.596515
H 5.582781 2.176679 0.936453
H  -0.973682 -2.686888 1.166939
H  1.237539 -1.217937 2.785172
H  1.199886 -3.840186 1.085261
H  2.588479 -3.210834 2.129125
H  -0.625763 3.026645 3.397836
H  -0.912355 1.670473 2.939294
H  -1.632263 3.639994 1.505133
H  1.861882 2.624518 3.156820
H  2.644497 2.754827 1.576322
H  1.655743 1.337874 1.949983
H  8.073926 4.829223 2.869262
H  -0.121338 5.261787 1.473749
H  1.613171 5.067800 1.287598
C  2.688429 0.309067 -2.183670
H  2.181771 1.519993 -2.365315
H  1.548171 -0.216776 1.303638
H  3.413752 0.790762 -1.290669

B3

IVC_2.60Å / electronic energy: -1805.94433855 a.u. / lowest freq: -74.01 cm^-1

C  1.921653 2.551783 1.932881
C  8.697913 4.673000 1.986899
C  1.646669 -2.929900 1.898334
C  0.356723 1.832162 1.643897
C  -0.523341 2.596110 2.569151
C  0.952399 -1.016736 2.070473
C  0.373343 2.978552 0.175297
C  -0.424276 -1.640490 1.452318
C  0.754483 5.050897 -0.371488
O  0.909404 6.608838 0.864721
C  0.935415 4.064722 -8.712890
C  -0.184999 1.696973 -0.341870
B  -0.258912 -0.788851 0.116161
C  -0.388758 3.876419 -2.030981
C  -0.809678 1.516572 -1.631583
H  -2.547089 0.685181 0.301802
H  -0.474447 4.735316 -2.687660
H  -1.474341 -0.694143 -0.964279
H  -0.844772 -4.806225 2.519386
H  -0.736764 2.614987 -2.482198
H  -0.995489 0.383380 -2.096248
H  -1.644673 -1.659690 -1.261888
C  -2.773558 -0.279123 -0.294300
O  -0.000178 -2.621149 -0.001818
C  -3.148811 -1.517450 0.545656
C  -3.556918 2.800279 1.124877
H  -1.113073 2.701775 -3.491741
H  -3.622999 -1.382047 1.785994
H  -3.162411 1.582272 -2.794764
H  -1.762578 0.814806 -2.653334
C  -4.091144 -2.585625 2.533197
C  -3.746094 -0.521597 2.563853
C  -3.861878 1.457982 -1.870932
C  -5.196464 0.811389 0.488881
C  -3.979899 0.051949 -2.513680
C  -5.263859 0.075437 -0.397441
C  -4.399083 1.752528 -2.558769
H  -5.580598 -9.905580 0.031311
H  -3.326266 -1.103915 3.807093
C  -4.164789 -1.013217 -2.343377
C  -6.100916 0.364964 -1.030812
C  -4.558067 1.955786 -1.908887
C  -5.028458 -0.733383 -2.964438
O  0.828585 -1.497635 -0.004062
C  2.092045 -1.640812 -0.326455
C  2.973476 -0.335454 -0.018821
C  3.137088 0.446099 -1.021243
C  4.139589 1.428072 -0.764832
C  3.708733 -5.557415 1.128278
C  4.728795 0.427025 1.343936
C  4.901523 1.433955 0.394254
H  3.643962 -1.364721 1.657785
H  4.383348 2.189966 -1.523659
H  5.338648 0.496951 2.245386
H  5.641835 2.111374 0.558029
H  2.806289 2.946145 -0.847268
F  3.676667 -3.336267 -0.004115
F  1.731288 -3.525694 -0.953111
F  3.138264 -2.689999 -2.073659
F  -3.398983 -0.256143 3.582312
C  -4.797608 0.306976 2.893866
C  -3.535245 0.786615 2.629169
C  -4.948425 -2.436050 2.985960
C  -3.716395 -2.781066 3.326534
F  -4.030799 -3.430151 1.849852
F  -1.023058 -1.087055 2.132153
F  -0.876094 -2.684593 1.207708
H  -1.356985 -0.974214 2.624978
C  -2.322375 -3.793489 1.836987
C  -2.619129 -3.057001 2.360876
C  -0.755098 2.894842 3.686751
C  -0.619964 1.514856 2.446213
C  -1.493752 3.056765 2.346558
C  -2.174265 6.328777 2.991562
C  -2.70922 2.989153 1.341273
H  1.989951 1.450878 1.692118
H  0.958542 4.773136 3.943478
| Atom | X       | Y       | Z     |
|------|---------|---------|-------|
| C    | 1.208967| 0.896158| 1.526831|
| H    | 2.491677| -0.786047| -0.065344|
| C    | 2.824567| 3.151887| 3.868750|
| N    | 0.859369| -1.177210| 0.719553|
| C    | -0.551439| -0.336416| 2.244424|
| C    | 1.798841| 1.484142| 3.673411|
| C    | 0.513062| -4.393234| 0.203841|
| C    | 0.015055| -2.025085| 0.773483|
| C    | 1.951255| -1.668413| 2.080443|
| C    | 0.642428| -3.485039| -0.652416|
| C    | 1.598659| 2.649594| -0.854616|
| O    | 3.963717| -0.588935| 1.761217|
| H    | 1.648813| 0.990833| 4.036399|
| C    | 2.364740| -2.655432| -1.983999|
| C    | 2.853835| -0.997799| 3.070186|
| O    | 0.952382| -1.043227| 2.812852|
| C    | 1.959954| -3.236089| -0.834126|
| C    | 3.426321| -1.791784| -2.343973|
| C    | 3.511210| -1.421299| 2.313284|
| C    | 4.596468| -2.443057| 0.860639|
| C    | 2.821845| -2.410652| 1.354628|
| C    | 3.968392| -1.324249| 0.614351|
| C    | 4.218281| -1.965322| 2.843896|
| O    | 3.594485| -3.987889| -0.075386|
| C    | 1.784538| -3.043570| 2.690597|
| C    | 2.041516| -3.465136| 2.124335|
| C    | 4.598664| -3.609556| 1.354415|
| C    | 1.612349| -4.234096| 1.449564|
| C    | 2.670208| -3.957176| 2.846219|
| O    | -1.445018| 0.629199| 0.212895|
| C    | -2.578282| 0.423090| -0.273179|
| O    | -3.816082| -0.225350| 0.220922|
| C    | -3.821854| -1.576050| 0.647113|
| C    | -5.091323| -2.111163| 1.998889|
| O    | -5.018341| 0.514667| 0.241491|
| C    | -6.192767| -0.045182| 0.730285|
| C    | -6.284282| -1.365099| 1.335829|
| O    | -5.927831| 1.543243| -0.091625|
| C    | -5.446939| -3.145698| 1.428651|
| C    | -7.907789| 0.550480| 0.718533|
| C    | -7.199815| -1.810912| 1.495380|
| C    | -2.598878| 1.961262| -0.439381|
| F    | -2.936065| 2.511766| 0.727385|
| F    | -1.399756| 2.420494| -0.797872|
| C    | 4.679865| 2.177721| -1.361515|
| C    | 3.214771| -1.296034| -3.292261|
| H    | 4.323525| -2.190395| -2.459156|
| C    | 3.680219| -1.031852| -1.587453|
| C    | 2.841438| -4.218284| -3.288291|
| C    | 1.622952| -3.694346| -3.931394|
| C    | 1.168765| 4.727008| 2.668874|
| H    | 0.680544| -0.576183| -2.418158|
| C    | -0.569286| -1.778721| 1.809696|
| O    | -1.058763| 1.976839| -2.988869|
| C    | -2.936921| -1.206967| 2.065451|
| C    | 3.441219| 0.466873| 2.634800|
| C    | 3.548732| 2.634583| -2.684280|
| H    | 2.624933| 1.136468| -1.816160|
| C    | 4.458518| 1.917183| -1.187757|
| C    | 1.512464| 4.219112| -2.520680|
| O    | 0.603515| 4.383025| -1.087439|
| C    | 0.611339| 2.837685| -1.873548|
| C    | 3.621395| 4.881886| -1.738885|
| C    | 4.219554| 4.287681| -0.194688|
| C    | 2.878677| 5.328487| -0.164595|
| C    | 3.617952| -2.487192| 0.659878|
| C    | 1.969917| -2.236319| 1.499316|
| C    | -2.025982| -2.446122| -2.592728|
| C    | -2.948297| -3.520431| 0.797174|

B3

Vc.2.15A / electronic energy: -1865.94862431 a.u. / lowest freq: -260.26 cm⁻¹
\begin{verbatim}
H  3.971225  -0.586495  1.750877
H  1.614786  0.592669  4.634118
N  2.297089  -2.635549  -2.003875
H  2.865381  -0.955293  3.062265
H  0.963548  -1.043549  2.812359
C  1.945485  -3.626194  -3.896588
C  3.413907  -1.793449  -2.353986
H  3.521627  -1.418862  2.305236
H  4.593344  -2.406169  6.649979
C  2.029136  -2.899084  3.341989
C  3.966436  -3.104543  6.038511
C  4.333775  -1.941949  2.830899
H  3.598751  -3.968575  -0.638976
H  1.190898  -3.043681  2.689584
C  2.026388  -3.464785  2.129411
H  4.608475  -3.673883  1.341560
H  1.628414  -4.252778  1.449618
H  2.687923  -3.953558  2.843434
O  -1.443763  -0.929937  0.223812
C  -2.567389  -0.426895  -0.245483
C  -3.813373  -0.223410  -0.233240
C  -3.819609  -1.571416  0.669285
C  -5.003916  -2.186460  1.108475
H  -5.018867  0.513250  -2.308802
C  -6.165228  -0.045998  -0.608887
C  -6.286912  -1.364289  1.126384
H  -5.028801  1.389950  -0.112127
H  -5.847422  -3.138230  1.445588
H  -7.184362  0.545161  0.600387
H  -7.127385  -1.877782  1.475685
C  -2.195948  1.963519  -0.433888
F  -2.952998  2.222910  0.724469
F  -1.392978  2.420798  -0.757687
F  -0.452984  2.168164  -1.375974
H  3.195397  -1.291544  -3.382229
H  4.322085  -2.391112  -2.478584
H  3.609815  -0.332833  -1.608963
H  2.825515  -4.221791  -3.295672
H  1.602353  -0.397773  -3.932862
H  1.156441  -0.272340  -2.665910
H  0.663436  -0.581518  -2.422970
H  -0.579024  -1.700668  -1.885957
H  -1.088637  1.073942  -2.901898
H  -2.946961  -1.223163  -2.045292
C  -3.548971  0.420556  -2.694858
H  3.543819  2.673531  -2.610493
C  -2.633388  1.337975  -1.822239
H  4.157248  1.926522  -1.193980
H  1.584962  4.218418  -2.522992
H  0.598260  4.361624  -1.087859
H  8.687295  2.385478  -1.874662
H  3.614487  4.884781  -1.710637
H  4.316493  4.291941  -0.292158
H  2.873917  5.303191  -0.170832
C  -6.103497  -4.781393  0.781318
C  -0.957231  -2.280895  1.536925
H  -2.012444  -2.447344  -0.218270
H  -2.933295  -3.589443  0.854587

B3

\end{verbatim}
|       |       |       |       |
|-------|-------|-------|-------|
| 83    | 1.362627 | 2.445358 | 0.639732 |
|       | 2.977070 | 2.584159 |       |
| H     | 7.173005 |       |       |
|       | 5.096180 |       |       |
| H     | 5.009991 | 1.58  |       |
| O     | 1.444377 |       |       |
| C     |       |       |       |
| C     |       |       |       |
| H     |       |       |       |
| C     |       |       |       |
| C     |       |       |       |
| H     |       |       |       |
| N     |       |       |       |
| H     | 0.490929 |       |       |
| C     |       |       |       |
| C     |       |       |       |
| C     |       |       |       |
| H     | 2.940208 |       |       |
| C     | 2.620896 |       |       |
| H     |       |       |       |
| H     |       |       |       |
| H     | 0.62  |       |       |
| H     | 5.079867 |       |       |
| F     | 1.347091 | 1.548818 | 0.188836 |
|       | 0.020516 | 3.898253 | 3.614305 |
|       | 3.910815 | 0.086474 | 1.890690 |
|       | 3.132658 | -0.582865 |      |
|       | 1.003516 | 0.953881 | 0.554398 |
|       | 2.697513 | 0.812798 |      |
|       | 0.407327 | 0.293613 | 1.163671 |
|       | 0.821327 |      | 0.121207 |
|       | 0.159692 | 0.356457 |    |
|       | 2.131792 | -2.908885 |    |
|       | 0.922982 | -1.508029 |    |
|       | 0.818611 | 0.122187 |    |
|       | 3.196011 | 3.780183 |    |
|       | 0.535432 | 8.608309 |    |
|       | 2.806780 | -0.821327 |    |
|       | 1.628274 | -0.274521 |    |
|       | 3.429330 | 0.546730 |    |
|       | 2.697513 | 0.812798 |    |
|       | 0.594390 | 1.680839 |    |
|       | 1.647740 | 4.008665 |    |
|       | 2.758457 | 1.980742 |    |
|       | 2.929381 | 0.853881 | 3.529994 |
|       | 0.813516 | -0.827125 |    |
|       | 1.884806 | 3.758684 | 2.964635 |
|       | 3.888718 | 1.911479 | 2.488842 |
|       | 3.561646 | 1.384216 | -0.257520 |
|       | 2.36287 | -0.939228 |    |
|       | 2.357827 | -1.339428 |    |
|       | 3.981183 | 3.132658 | -0.582865 |
|       | 1.896000 | -2.702628 |    |
|       | 3.684574 | 3.910815 | 0.864741 |
|       | 3.164824 | -3.601053 | -2.721489 |
|       | 2.079163 | 3.430828 | -2.154384 |
|       | 4.638555 | 3.614385 | -1.313613 |
|       | 1.56238 | 0.016723 | 5.00813 |
|       | 2.756916 | 3.892523 | -2.878712 |
|       | 1.444377 | 8.205416 | -2.701713 |
|       | 2.561826 | 0.499947 | 8.196513 |
|       | 3.81081 | 0.89836 | -0.29086 |
|       | 3.443364 | -1.534081 | -0.699569 |
|       | 5.062487 | 2.691596 | 1.969827 |
|       | 0.987876 | 8.551549 | -0.252819 |
|       | 6.11139 | 0.818100 | -0.634245 |
|       | 6.237722 | 1.347691 | 1.045830 |
|       | 0.809991 | 1.568200 | 0.665859 |
|       | 5.096188 | 3.132658 | -1.834264 |
|       | 7.11978 | 0.571699 | -0.68857 |
|       | 7.173665 | 1.886888 | -1.344469 |
|       | 2.575711 | 2.008169 | 0.354343 |
|       | 2.970768 | 2.584159 | -0.780342 |
|       | 1.362627 | 2.445158 | 0.839732 |
|   | 3.468143 | 0.462626 | 2.801123 |
| H | 3.584856 | 2.573786 | 2.720172 |
| H | 2.598549 | 1.960878 | 1.889459 |
| H | 4.129914 | 1.980174 | 2.116689 |
| H | 1.483775 | 4.172464 | 2.595651 |
| H | 6.629571 | 4.186770 | 1.657241 |
| H | 8.579686 | 2.822433 | 1.886621 |
| H | 3.927943 | 4.826419 | 1.846381 |
| H | 4.559899 | 4.245287 | 3.646441 |
| H | 2.934888 | 5.386018 | 0.294794 |
| C | 2.672935 | -2.450866 | -0.765123 |
| H | 1.976221 | -2.160598 | -1.597346 |
| H | 2.032479 | -2.434141 | 0.152834 |
| H | 2.946578 | -3.478498 | -0.937486 |

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CIFAP / electronic energy: -682.362385389 a.u. / lowest freq: 31.00 cm⁻¹
G 1.815148 1.975684 0.006019
C 0.742351 0.888151 0.006899
C 6.565243 0.314666 0.008085
C 6.769676 1.279680 0.007466
C 3.081402 0.889384 0.006811
C 0.983066 0.146438 0.006314
C 0.213586 -0.413077 0.004899
C 0.352551 0.466784 0.006895
H 1.207178 1.883090 0.006225
H 1.389677 2.217590 0.006810
H 0.708106 1.673767 0.006822
H 3.253347 -2.485899 0.006015
H 4.366087 -0.775903 0.006899
C 1.879158 -0.396985 0.006895
F 0.794969 -1.051521 -1.082421
F 0.607485 0.346279 -0.006010
F 1.794082 -1.025929 1.882487

B4

cat4 / electronic energy: -1970.65687313 a.u. / lowest freq: 19.59 cm⁻¹
C 2.166538 1.981066 0.311480
C -0.066899 0.457359 -0.373733
C 4.326095 0.367871 -2.666223
Si -2.772914 0.055250 -0.821348
C -1.475566 0.897926 1.491555
C 3.088973 3.210671 -1.913441
C 1.316686 -0.562130 -1.539133
C 2.250886 2.761585 -0.678340
H -2.753425 -0.503273 -2.123997
C 0.445194 1.092813 -1.161922
C 1.768134 -1.672142 -2.271843
C -0.043901 -0.160088 1.777689
B 1.731632 1.338793 0.812738
C -0.925514 2.344515 3.164522
C 0.870865 -0.851780 -2.500275
H 1.731838 -0.878634 0.194169
H -1.308919 -3.150936 -3.722835
H 2.725718 1.822880 -1.342871
H 2.428987 0.441993 -3.381980
C 0.408266 -1.592333 -3.365815
C 2.383784 -0.384161 -2.662247
H 3.674090 0.587275 -1.419899
C 2.709083 -0.690166 0.853448
C 4.529096 0.884185 0.425744
C 3.526157 -3.245939 0.884469
C 1.615585 -3.185549 -0.582885
H 1.068884 -2.580283 -3.965319
N 3.074158 0.455054 2.130812
H 2.614481 -2.937719 -2.037158
H 2.949491 -1.180880 -2.963480
C 3.831968 1.128731 3.604921
H 1.921269 -0.216910 2.766891
H 2.644655 -3.093819 -0.595884
H 2.709349 -2.285558 1.724090
C 3.583745 -2.061187 -0.210793
C 3.672276 -2.580862 1.227139
H 3.079518 -4.869618 -0.796887
C 4.314477 -1.949368 1.835188
H 4.837412 -1.546120 -1.686807
C 4.085335 -1.934470 -0.863819
C 4.138951 -3.575877 1.183906
C 5.545841 -1.124887 -0.286175
C 5.338480 -2.927999 -0.921391
H 1.373542 0.597747 3.200379
H 2.247278 -0.940108 3.472195
H 1.236094 -0.614861 2.047192
H 4.749778 1.649986 2.581678
H 4.736872 0.694535 3.895585
H 3.267833 2.131223 3.373627
H 1.466181 4.321464 -0.462131
H 2.929298 2.751545 0.179386
H 4.823886 3.377658 -2.976964
H 4.945715 2.667524 -1.266471
H 2.411923 3.628259 -2.723202
H -3.159561 2.761898 -0.552479
C -3.886033 1.346028 0.111322
C -2.062438 4.667550 0.803982
C -0.012351 3.862128 1.362858
C -1.081792 2.493130 1.615420
H -0.283918 1.813649 1.380516
H -1.974938 5.734510 0.595993
|        |        |        |
|--------|--------|--------|
| C      | 0.967981 | 1.073977 | 1.360699  |
| C      | 3.16455  | 1.734747 | -0.78964  |
| C      | 3.683875 | 3.016189 | -0.607669  |
| C      | 4.347476 | 3.129588 | -0.576261  |
| C      | 4.582623 | 2.353712 | 1.560141   |
| H      | 5.029636 | 2.587377 | 2.479556   |
| C      | 4.18852  | 3.26240  | 2.048578   |
| H      | 2.658565 | 1.583365 | -1.733172  |
| C      | 3.76472  | 3.767297 | 1.853389   |
| C      | 4.752594 | 4.235183 | -0.727680  |
| H      | -4.695838| 0.537155 | -0.487355  |

V1.2, 1.5 Å / electronic energy: -2653.8500986 a.u. / lowest freq: -247.04 cm⁻¹

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### Table 1:

| C       | 6.072206 | -3.852991 | -1.440688 |
|---------|---------|-----------|-----------|
| C       | 4.745479 | -4.178837 | -1.715543 |
| H       | 2.694792 | -3.571136 | -1.570238 |
| C       | 4.873339 | -5.885734 | -2.276385 |
| H       | 5.595181 | -0.861200 | 0.087930  |
| H       | 7.464664 | -2.481959 | -0.578926 |
| H       | 8.689714 | -4.527150 | -1.736693 |
| C       | 3.989986 | 1.993838  | 1.445820  |
| C       | 3.359672 | 1.776640  | 0.735785  |
| C       | 3.654188 | 3.059949  | -0.587310 |
| C       | 4.278848 | 3.326215  | 0.795861  |
| C       | 4.395915 | 2.775552  | 1.682800  |
| H       | 4.884375 | 2.861641  | 2.642751  |
| H       | 4.010624 | 0.336294  | 2.219158  |
| H       | 2.692221 | 1.555398  | -1.692870 |
| C       | 3.571807 | 3.820274  | -1.278865 |
| H       | 4.668219 | 4.160177  | 0.885682  |
| H       | -4.888848| 4.723262  | -0.478552 |

**Total energy: -2653.8523018 a.u. / lowest freq: -210.29 cm⁻¹**

### Table 2:

- **Energy Calculation**
  - ** molecular energy:** -2653.8523018 a.u. / lowest freq: -210.29 cm⁻¹
  - **nic energy:** 2653.05230108 a.u. / lowest freq: -210.29 cm⁻¹
|   |   |   |
|---|---|---|
| C | 1.069349 | -1.571944 | 1.456434 |
| C | 1.008945 | -2.069544 | -0.697474 |
| C | 1.354621 | -1.103428 | 2.274841 |
| C | 1.259992 | -0.972957 | -0.180952 |
| C | 2.553731 | 0.762814 | 0.281666 |
| C | 1.208675 | -0.642366 | 2.299178 |
| C | 1.545969 | 0.723083 | 0.156260 |
| C | -0.814405 | 0.683661 | 1.798631 |
| C | 1.383769 | -2.453022 | -2.689691 |
| O | 1.070968 | 3.441289 | 0.858647 |
| H | 2.125543 | -3.343276 | 3.283886 |
| H | -0.573671 | 0.760876 | -4.544923 |
| N | -0.343543 | 0.313657 | 5.253985 |
| C | -0.606465 | 0.211266 | -5.265971 |
| H | -1.271115 | 2.380877 | -2.839397 |
| C | -0.996228 | 4.165193 | 3.262151 |
| C | 1.047050 | 3.262184 | 2.087766 |
| C | 1.380841 | -0.739080 | 5.284412 |
| C | -1.228838 | 3.856830 | 0.189952 |
| C | 0.810417 | -4.155161 | -1.330175 |
| C | 0.780033 | 0.542932 | -5.583915 |
| C | 0.950496 | 0.511616 | 0.989584 |
| C | 0.308729 | 0.541255 | 0.271610 |
| C | -0.543987 | 3.060892 | -2.398099 |
| C | -1.840138 | 0.753136 | 0.513120 |
| C | 0.491380 | 0.760892 | 0.124889 |
| C | 0.341800 | 0.561496 | -0.939230 |
| H | -1.645118 | 0.629031 | -2.415850 |
| C | -0.593948 | -0.281812 | -3.065988 |
| C | 0.314683 | -1.435944 | 0.624614 |
| C | -0.531197 | -1.657186 | -0.310990 |
| C | -0.512094 | 0.538883 | -6.477555 |
| C | -0.647787 | 0.897999 | 0.053958 |
| C | -0.581433 | -2.930692 | 0.333488 |
| C | -1.638957 | -3.060867 | -6.684414 |
| C | -0.789491 | -1.973892 | 0.159910 |
| C | -0.321981 | 0.414868 | 0.082779 |
| C | -0.242784 | 0.168869 | -1.126928 |
| C | -0.877651 | 0.478085 | -0.790473 |
| C | -0.252286 | 2.069366 | 1.288168 |
| C | 0.186855 | 2.680601 | 0.283654 |
| C | -0.228789 | 2.275596 | -1.028280 |
| C | -0.934898 | -2.329975 | 0.370973 |
| C | -0.598384 | -0.342385 | 1.032834 |
| H | 1.224453 | 2.687229 | -0.353236 |
| C | 1.646985 | 1.616849 | 2.122636 |
| C | 1.367369 | 2.655111 | 1.241484 |
| C | -1.873801 | 4.169696 | 3.662839 |
| C | -0.213758 | 4.916003 | 3.650881 |
| C | 1.022960 | 3.371917 | 4.068747 |
| C | 0.857448 | 0.380645 | -2.06678 |
| C | -0.646665 | 1.411184 | 1.947853 |
| C | -1.377252 | 1.234090 | 2.574569 |
| C | -0.457584 | 0.418490 | 2.493879 |

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V1.2_30A / electronic energy: -2653.85129176 a.u. / lowest freq: -155.78 cm⁻¹
| x       | y       | z       | Energy [a.u.] | Frequency [cm⁻¹] |
|---------|---------|---------|---------------|-----------------|
| -1.89348 | 4.63167 | 3.649626 |
| -0.330589 | 4.91266 | 3.655926 |
| -1.066668 | 3.77780 | 4.982545 |
| -0.912017 | 1.835285 | 2.269127 |
| -2.626648 | 1.421641 | 1.927414 |
| -1.431851 | -1.231875 | 2.599153 |
| -4.22977 | -0.382743 | 2.988444 |
| -3.73647 | -2.05778 | 2.672881 |
| 1.859789 | -3.128231 | 1.641583 |
| 1.367408 | -3.609286 | 2.798487 |
| 0.852089 | -2.870629 | 3.883223 |
| 0.855817 | -1.490716 | 3.643896 |
| 1.368222 | -0.930876 | 2.469152 |
| 1.356868 | -0.150377 | 3.247931 |
| 0.858552 | -3.115832 | 4.713418 |
| 0.469555 | -0.848714 | 4.427899 |
| 2.325551 | -3.701522 | 0.883248 |
| 1.375128 | -4.763229 | 2.923866 |
| 5.384039 | -1.718171 | -0.428814 |
| 3.796141 | -3.359591 | -1.373812 |
| 6.428238 | -2.552416 | -0.822493 |
| 6.154756 | -3.741838 | -1.492847 |
| 4.355614 | -4.096412 | -1.67289 |
| 2.778910 | -3.544285 | -1.684719 |
| 4.618692 | -0.208166 | -2.294877 |
| 5.619987 | -0.789899 | 0.889959 |
| 7.455187 | -2.727741 | -0.696622 |
| 6.967943 | -4.390763 | -1.891217 |
| 3.831577 | 1.67453 | 1.539946 |
| 3.108807 | 1.792775 | 0.659582 |
| 3.662497 | 3.673497 | -0.389985 |
| 4.255996 | 3.357762 | 0.852244 |
| 4.312948 | 2.355231 | 1.816099 |
| 4.768779 | 2.566954 | 2.783126 |
| 3.989189 | 0.386520 | 2.384711 |
| 2.754844 | 1.540627 | 1.639558 |
| 3.606244 | 3.846532 | -1.152881 |
| 4.684188 | 4.353073 | 1.644483 |
| 4.85825 | 0.432186 | -0.780058 |

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V1.2, 5.8A / electronic energy: -2653.8582864 a.u. / lowest freq: -106.72 cm⁻¹

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| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | 1.300519 | 1.925514 | 0.004901 |
| H    | 2.775425 | 2.772914 | 0.0     |
| H    | 4.581189 | 4.347664 | 1.113328 |
| H    | 2.545037 | 2.88962 | 2.335303 |
| H    | 4.710028 | 2.558759 | 2.23836 |
| H    | 4.331868 | 2.210992 | 0.649896 |
| H    | 7.468185 | 2.210992 | 0.649896 |
| C    | 1.095027 | 3.476644 | 1.133328 |
| C    | 0.384978 | 0.398067 | -0.748835 |
| C    | 0.982744 | 1.879863 | 0.000823 |
| C    | 0.872555 | 0.888117 | 0.00081 |
| C    | 0.554510 | 0.649588 | 0.000895 |
| C    | 1.379098 | 0.851385 | 0.00082 |
| C    | 2.956011 | 2.810702 | 0.00087 |
| C    | 0.663560 | 1.350237 | 0.00089 |
| C    | 1.985287 | 1.967655 | 0.00086 |
| C    | 3.056359 | 1.185747 | 0.00081 |
| H    | 0.924466 | 1.969514 | 0.00081 |
| H    | 3.859350 | 0.803575 | 0.00081 |
| H    | 1.572466 | 3.049798 | 0.00081 |
| H    | 4.003176 | 1.645993 | 0.00084 |
| H    | 0.035179 | 2.281999 | 0.00084 |
| H    | 2.051723 | 1.019446 | 1.083361 |
| C    | 3.134598 | 0.495561 | 0.00082 |
| F    | 0.917484 | 1.004441 | 0.583374 |
| C    | 1.786385 | 2.373770 | 0.00088 |
| H    | 2.723683 | 2.738134 | 0.00082 |
| H    | 1.751464 | 2.749233 | 0.873454 |
| H    | 1.374619 | 2.782127 | 0.873454 |

**References:**

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| Chem. | E (a.u.) | Freq (cm⁻¹) |
|-------|---------|-------------|
| H     | 0.012475 | 2.995569    |
| C     | 0.501632  | 2.047192   |
| N     | 0.052064  | 0.807825    |
| O     | 0.806651  | 4.358653    |
| Si    | 2.357951  | 1.312123    |
| C     | 2.343772  | 1.764490    |
| H     | 2.093073  | 0.871350    |
| C     | 2.084132  | 0.876558    |
| C     | 1.955632  | 0.885451    |
| C     | 1.903978  | 0.706971    |
| C     | 1.870041  | 0.655371    |
| C     | 1.608288  | 0.517597    |
| C     | 1.344283  | 1.256193    |
| O     | 0.976297  | 0.871787    |
| C     | 0.878207  | 0.887825    |
| C     | 0.445083  | 0.852664    |
| B     | 1.384888  | 0.422646    |
| C     | 1.425284  | 0.369434    |
| C     | 0.824211  | 0.456135    |
| C     | 0.736414  | 0.481896    |
| C     | 1.886613  | 0.501632    |
| N     | 1.639156  | 1.733171    |
| C     | 2.441356  | 0.584576    |
| C     | 2.169899  | 2.794500    |
| C     | 1.563503  | 1.220743    |
| C     | 2.574777  | 2.113446    |
| C     | 0.712459  | 0.736185    |
| C     | 1.537280  | 3.306048    |
| N     | 1.325988  | 3.116673    |
| N     | 0.592338  | 3.714896    |
| C     | 0.012457  | 2.995569    |

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IIj_2.50Å / electronic energy: 104

C    3.237595    1.914608
C    2.858634
H    0.151442
H    0.486865
C    1.287846
C    0.729665
C    0.919725
C    1.683278
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
H
C    1.406286    4.385602    2.173380
H    0.995769    2.926465    3.699153
C    4.249423    0.835682    2.173380
H    2.474362    2.817197    1.355771
H    2.823306    4.885516    2.841377
H    0.805983    0.574125    3.553765
H    1.383479    3.511954    3.920883
H    1.180993    0.345554    2.142255
H    1.296695    1.414725    2.808798
H    4.810355    0.916967    2.378732
H    3.314163    1.780398    2.362447
H    3.773178    1.291685    1.978796
C    0.878897    0.829716    0.316258
H    0.496635    0.387148    0.683430
H    0.031414    0.281281    1.131376
H    0.616995    2.549774    0.552533
C    2.247596    3.287545    1.507632
C    1.682375    3.910525    2.633535
C    0.919725    3.240295    3.586700
C    0.729665    1.863489    3.475821
C    1.287846    1.697322    2.484628
H    1.388322    0.895556    2.323780
H    0.486865    0.738359    4.420891
H    0.314142    1.313170    4.225357
C    2.058634    3.314700    0.851127
H    1.851027    4.979151    2.726793
C    3.327353    1.941680    0.022184
|  C  |  1.680688 |  -3.921737 |  2.624554 |
|  C  |  0.988817  |  -3.255789  |  3.572116 |
|  C  |  0.712694  |  -1.879663  |  3.460581 |
|  H  |  1.273699  |  -1.182188  |  2.393870 |
|  H  |  1.118754  |  -0.189466  |  2.312450 |
|  H  |  0.473568  |  -3.881664  |  4.483299 |
|  H  |  0.327298  |  -1.353225  |  2.876361 |
|  H  |  2.865468  |  -3.749197  |  0.847196 |
|  H  |  1.852730  |  -4.896684  |  2.716888 |
|  C  |  3.245946  |  -1.911035  |  -0.410988 |
|  C  |  3.669773  |  1.155659  |  1.831783 |
|  C  |  4.001952  |  2.439818  |  2.167697 |
|  C  |  4.077584  |  3.462068  |  1.240643 |
|  C  |  3.657246  |  3.196676  |  -0.061818 |
|  H  |  2.938899  |  1.712491  |  -1.436671 |
|  H  |  4.485165  |  4.460116  |  1.514888 |
|  H  |  3.663562  |  3.966620  |  -0.879854 |
|  H  |  3.695932  |  8.167555  |  2.582827 |
|  H  |  4.143259  |  2.639929  |  3.292833 |
|  C  |  5.627725  |  -1.309183  |  -0.243255 |
|  C  |  4.278726  |  -2.982897  |  -1.318114 |
|  C  |  5.427101  |  -3.676144  |  -1.628460 |
|  H  |  6.081254  |  -3.180699  |  -1.330891 |
|  C  |  6.780719  |  -1.992351  |  -0.621318 |
|  H  |  5.720126  |  -0.772635  |  0.133948 |
|  H  |  3.866669  |  -3.378763  |  -1.607747 |
|  C  |  5.345964  |  -4.604349  |  -2.245781 |
|  H  |  7.578257  |  -3.719626  |  -1.610877 |
|  H  |  7.756182  |  -1.605275  |  -0.340227 |

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II1_1-280 / electronic energy: -2692 33344968 a.u. / lowest freq: -288.06 cm-1
Lee, et al., SI, Page S325
| X  | Y  | Z   | Atomic Number | Atomic Symbol | 1Vj_2.30Å / electronic energy | 104 cm^−1 |
|----|----|-----|---------------|---------------|-------------------------------|-----------|
| -1.39456 | 2.985529 | -1.427465 | 1 | H | 8.497743 | 5.210186 | -0.821197 | 0.889668 | 6.018672 | 1.586138 |

Lee, et al., SI, Page S329
F2PhAP / electronic energy: -583.137181810 a.u. / lowest freq: 55.63 cm⁻¹
cat1 / electronic energy: -1144.2587580 a.u. / lowest freq: 17.24 cm⁻¹

H -4.338875 2.465172 1.826262
H -0.069214 0.695184 2.483110
H 0.125270 2.899060 -4.530787
C -3.648273 1.765463 0.337383
C -4.571210 1.585923 -0.041700
C -2.839819 1.585438 2.908477
C -4.658991 -0.060785 1.881196
C -3.984480 2.748646 -0.127548
C -5.446419 -0.317247 1.991228
C 1.945901 2.671519 -2.937734
C -0.069797 2.896971 -3.463557
C -3.416383 0.859548 1.105011
C -2.393550 0.870618 2.203817
C 0.921238 2.788384 -2.578420
H -4.424887 -0.905035 2.480532
H -1.302228 3.620899 -3.143771
H -1.491724 1.326318 1.786614
H -2.166663 -0.621442 2.770933
C -2.988333 -0.523683 0.156736
C 0.785489 2.756263 -1.978216
H -4.342116 -2.073760 0.588741
O -1.072293 1.013768 -0.512353
C -3.348055 -1.802042 -0.625184
C -1.639983 -0.254977 -0.579746
B 0.392545 1.188822 -0.852738
C -2.762587 -2.747380 -0.609728
C -0.082785 -1.190625 -1.486267
H 0.614585 -0.889222 0.682420
H -3.324447 -3.721826 -0.589833
N 1.074572 0.856821 -1.172932
H 0.048299 -0.151684 -2.974258
C -1.591325 -2.452082 -1.554339
C 0.848469 -0.788045 -2.183919
H 1.940381 0.760363 -1.628483
C 1.528729 -0.567774 0.137846
O 3.142985 1.149258 0.031827
C 2.341327 0.576012 -0.772781
N 0.753677 3.153900 -0.546280
H -1.122497 -3.189246 -2.199429
N 2.126841 0.927835 2.652713
H 1.087251 -3.179185 -1.191833
H 0.827812 -1.664582 -2.437948
C 2.957096 1.983619 2.627218
C 1.289233 0.234773 3.024639
C 1.539255 -3.184069 -0.218466
C 2.497062 -2.130895 2.169873
C 2.480774 -1.851927 -0.997758
C 3.176397 -2.035583 1.315766
C 2.166225 -3.991479 -0.679422
H 3.873751 -1.214510 1.585163
H 2.968568 -1.642315 -2.306076
C 3.438334 -3.179413 -1.448675
C 3.759772 -2.957194 1.258821
H 0.478995 -0.852280 -0.956591
C 0.453836 -2.616963 -1.163430
H 0.638199 0.558991 3.089920
C 1.928885 -0.231014 3.287116
H 0.673326 -0.335146 2.565729
C 2.324633 2.652860 3.214772
C 3.443976 2.533979 1.826385
H 3.715995 1.545134 3.283116
H 1.636381 2.976065 -0.547526
H -0.047613 3.468801 -0.772895

IIIh -10A / electronic energy: -1727.42795953 a.u. / lowest freq: -304.76 cm⁻¹

C -0.218586 3.811186 -1.602681
C 1.775082 5.224135 -1.287582
C -2.471584 -1.661188 -1.951289
C -1.252088 3.784646 -1.168386
C -2.182071 2.955656 -2.244842
C -1.115795 -1.886951 -1.983480
C 1.532791 3.195267 0.249640
C -0.886324 -0.780445 -1.936370
H 2.166087 4.950585 1.174916
O 0.451588 1.121936 -0.584267
H 1.942188 3.928512 1.331186
O 0.942123 1.874512 0.521226
B -0.098186 -1.808461 -0.306944

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\begin{tabular}{ccc}
C & -3.867688 & -0.358121 \ 0.283296 \\
& -1.736147 & -0.445915 \ 1.780657 \\
H & -1.153845 & -1.723854 \ 0.111130 \\
& -4.462529 & -0.234371 \ 3.780342 \\
N & 0.875999 & -0.243229 \ 0.511787 \\
& 0.018484 & -1.392119 \ 1.884869 \\
& -2.856699 & -0.275668 \ 2.626848 \\
C & -0.235888 & -0.367432 \ 1.781156 \\
& 1.382927 & -0.377761 \ 5.247879 \\
H & -0.078652 & -1.063317 \ 0.297459 \\
& 1.946195 & -1.700557 \ 0.917643 \\
& 0.774998 & -2.069411 \ -0.915883 \\
& -0.628219 & -3.588872 \ 3.246668 \\
H & -1.931346 & -0.084212 \ 3.886019 \\
& 0.268399 & -2.874160 \ -0.188880 \\
& -1.884247 & -2.742694 \ 2.165772 \\
C & 0.149972 & -0.152720 \ 2.643942 \\
& 1.548183 & -3.290741 \ -0.975326 \\
C & -1.189673 & -3.285460 \ -0.648897 \\
& -0.794999 & -2.652636 \ 2.586274 \\
H & -0.664228 & -3.700389 \ 0.646396 \\
& 0.777645 & -2.668034 \ 1.482953 \\
& 0.292199 & -4.187699 \ 0.928813 \\
H & -0.773334 & -1.762770 \ 3.212169 \\
C & 0.993399 & -4.708483 \ 0.284847 \\
& 1.754692 & -1.388994 \ 2.534541 \\
C & 1.669182 & -2.377695 \ 2.665792 \\
& 0.453803 & -4.798469 \ 1.759628 \\
H & -1.955280 & -4.375137 \ 3.981543 \\
C & 1.780623 & -2.844031 \ -1.298770 \\
& 0.942486 & -2.697380 \ -3.873657 \\
H & -2.184458 & -3.152846 \ -2.675883 \\
& 0.962467 & -4.436123 \ -3.199084 \\
& -0.613565 & -1.155341 \ -2.752789 \\
H & -0.385983 & -0.576061 \ -2.494757 \\
C & -0.097989 & -2.018254 \ -3.131629 \\
C & 1.286597 & -2.786051 \ 3.193669 \\
H & 2.126268 & -0.800175 \ -2.551664 \\
& -6.559938 & -1.089194 \ -1.717775 \\
& -6.361783 & -0.087669 \ -0.353785 \\
& -6.362242 & -1.751639 \ -0.083287 \\
& -4.186681 & -2.483385 \ -2.485314 \\
& -4.384346 & -3.14622 \ -0.803894 \\
& -3.092280 & -2.498675 \ -1.664395 \\
H & -4.602186 & -0.929996 \ -2.891852 \\
& -3.018889 & -0.777892 \ -0.338389 \\
& -4.351223 & 1.132985 \ -1.433181 \\
C & 2.783992 & -1.553583 \ 0.123495 \\
& 2.762614 & -1.786540 \ 1.589671 \\
& 3.586274 & -1.153381 \ 2.418666 \\
H & 3.789968 & -0.687189 \ -0.311973 \\
& 4.363097 & -0.609985 \ 0.564967 \\
& 4.527148 & -0.489845 \ 1.928943 \\
& 3.902558 & -0.472271 \ -1.614494 \\
& 1.879292 & -2.691323 \ 1.968931 \\
& 3.495462 & -1.390111 \ 3.741767 \\
C & 5.372191 & -0.856798 \ 1.505037 \\
& 5.186627 & -0.266896 \ 2.616891 \\
& 2.074789 & -3.799152 \ -0.854973 \\
& 3.056035 & -3.925494 \ -1.312211 \\
& 2.099086 & -4.249989 \ -0.144828 \\
& 1.300354 & -4.291017 \ -1.441777 \\
\end{tabular}

\textbf{BB}

I\textsuperscript{2+}H \textsuperscript{48A} / electronic energy: -1727.42345791 a.u. / lowest freq: -170.16 cm\textsuperscript{-1}

\begin{tabular}{ccc}
C & 0.059358 & -0.451154 \ 2.264992 \\
& 0.235633 & -0.763646 \ -0.667753 \\
& 0.584621 & -0.282542 \ -0.448587 \\
& 1.746175 & -2.161316 \ -0.681849 \\
& 1.946884 & -1.893125 \ -2.964651 \\
& 1.449481 & -0.646458 \ -2.649397 \\
& -0.091594 & -2.352858 \ -1.459634 \\
& -0.807552 & -0.576549 \ -1.731497 \\
C & 1.378979 & -4.25695 \ 1.784877 \\
& 1.135379 & -1.730743 \ 0.693675 \\
& -0.472902 & -0.193795 \ 3.777133 \\
& 0.278549 & -0.294276 \ 0.511140 \\
& 0.176175 & -1.735341 \ 1.879456 \\
& -2.49655 & -0.242898 \ 2.943141 \\
& -0.243244 & -2.167564 \ 1.785480 \\
& 1.297788 & -0.243143 \ 0.524254 \\
C & -0.087687 & -1.699898 \ 0.282970 \\
& 0.958066 & -1.688263 \ -0.923486 \\
& 0.780846 & -2.083596 \ -0.931487 \\
& 0.827087 & 3.540536 \ 3.215842 \\
& -1.933658 & -0.841479 \ 3.886147 \\
\end{tabular}
| Atomic  | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| C       | 1.580024     | -0.58613     | 1.115287     |
| H       | 0.221036     | -0.887278    | 2.783150     |
| C       | 0.354785     | 2.919078     | 2.080037     |
| C       | 0.956048     | 8.470722     | 2.119398     |
| H       | 1.851918     | -1.340403    | 1.683499     |
| C       | 2.657799     | 0.048124     | 0.263832     |
| O       | 3.251753     | -2.326167    | 0.377987     |
| C       | 3.167287     | -1.349988    | -0.370839    |
| H       | 3.606673     | 2.693330     | 5.021324     |
| O       | 0.839835     | 3.059814     | 2.979883     |
| N       | 3.510383     | -1.394124    | -1.672139    |
| C       | 2.925635     | 2.245516     | 2.235664     |
| H       | 1.749153     | 0.784256     | 2.794326     |
| C       | 4.038805     | -2.441637    | -2.213525    |
| C       | 3.77962    | -0.329184    | -2.653853    |
| C       | 5.535692    | 2.121153    | 1.854183    |
| H       | 4.812962    | -1.332062    | -0.879935    |
| C       | 5.858838    | 8.651880    | 1.086830    |
| O       | 5.056164    | 8.638685    | 0.037791    |
| C       | 4.492553    | 3.203268    | 1.584422    |
| O       | 5.480589    | -0.313600    | -2.275456    |
| H       | 3.587816    | -0.190903    | -3.020390    |
| C       | 4.291243    | -0.25297     | 2.250221    |
| H       | 5.082844    | 1.285062    | 0.525958    |
| H       | 4.652182    | -1.409999    | 2.066991    |
| O       | 5.338027    | 0.392788     | 2.718448    |
| H       | -0.588895   | -1.721388    | 1.248352    |
| C       | -1.789901   | -2.162582    | 1.052879    |
| C       | 2.775439    | -0.687413    | -3.494895    |
| H       | 4.362124    | -0.844733    | -3.039593    |
| H       | 2.897512    | 0.554469     | -2.241393    |
| H       | 4.215196    | -3.336320    | -1.309779    |
| C       | 5.474878    | -2.839183    | -2.741184    |
| H       | 3.323833    | -3.072885    | -2.920190    |
| H       | 0.874363    | -1.512253    | -1.833645    |
| H       | 1.126842    | -2.050320    | -0.656461    |
| H       | -1.519863   | -2.040832    | -1.986236    |
| H       | -0.731485   | -4.392949    | -0.616752    |
| C       | -2.368889   | -6.452157    | -0.825681    |
| C       | -0.994894   | 1.690999     | -3.913896    |
| H       | 0.557549    | 0.748083     | -2.519642    |
| H       | 0.889655    | 2.181218     | -2.831494    |
| H       | -2.769918   | 1.138711     | 1.137423     |
| C       | -3.191812   | 3.971699     | 1.591345     |
| H       | 2.516557    | 0.510234     | -1.617169    |
| C       | -1.963216   | 3.544386     | 3.786320     |
| C       | -0.731844   | 4.392966     | -2.693521    |
| C       | -2.415166   | 4.214888     | -2.550685    |
| C       | -2.859803   | -1.194588    | 0.627185     |
| C       | -2.928612   | 8.827640     | 1.387978     |
| C       | -3.934071   | 0.957186     | 1.119784     |
| C       | -3.928902   | -1.455083    | -2.302727    |
| C       | -4.958518   | -0.555894    | -0.457850    |
| C       | -4.955511   | 0.655169     | 0.225589     |
| F       | -3.937802   | -2.625195    | -0.882128    |
| F       | -2.999008   | 0.284662     | 2.238895     |
| H       | -0.984956   | 1.881449     | 1.683915     |
| H       | -5.744372   | -0.821771    | -1.151311    |
| H       | -5.723652   | 3.116735     | 0.626333     |
| C       | -2.243968   | -3.362684    | 2.081777     |
| C       | -1.442233   | 3.942229     | 2.236936     |
| C       | -2.525983   | -2.723858    | 2.929822     |
| C       | -3.126383   | 3.749574     | 1.619122     |

**VH:** 2.38 Å / electronic energy: -172.43457184 a.u. / lowest freq: -159.77 cm⁻¹

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*Lee, et al., SI, Page S352*
| Atom  | Type  | X       | Y       | Z       |
|-------|-------|---------|---------|---------|
| C     | 2.073198 | 1.297178 | 3.681215 |
| C     | 3.377613  | 1.966199 | 1.535242 |
| C     | 2.383347  | 0.523748 | 1.557277 |
| C     | 2.036657  | 3.583242 | 3.734632 |
| C     | 0.817247  | 4.376537 | 2.795522 |
| C     | 2.472253  | 4.215824 | 2.189191 |
| C     | 2.870808  | 1.287141 | 0.712349 |
| C     | 2.913648  | 0.856587 | 1.317324 |
| C     | 3.941888  | 0.562045 | 1.140385 |
| C     | 4.017482  | 1.546786 | 0.623888 |
| C     | 5.063079  | 0.681215 | 0.249887 |
| C     | 5.016138  | 0.592728 | 0.337385 |
| C     | 4.106979  | -2.779318 | 0.505557 |
| C     | 1.936288  | 0.719497 | -2.173899 |
| H     | 3.882351  | 1.921462 | -1.640332 |
| C     | 5.890913  | 0.992082 | 0.856542 |
| C     | 5.832411  | 1.285444 | -0.179644 |
| C     | 2.157286  | 3.377529 | -1.836745 |
| H     | 1.387124  | -4.049968 | 1.940879 |
| H     | 2.459958  | 3.588827 | -2.833810 |
| C     | 3.865517  | -3.872940 | 1.373230 |

 vibrational energy: -1727.4336586 a.u. / lowest freq: 302.27 cm^-1
Lee, et al., SI, Page S358
| Atom | x      | y      | z      |
|------|--------|--------|--------|
| N    | 1.624047 | 0.453061 | 1.029924 |
| H    | 0.408297  | 0.551237  |        |
| C    | 0.267973  |        |        |
| O    | 2.908965  |        |        |
| C    | 1.386020  | 0.455625 | 1.495261 |
| H    | 2.036987  | 0.351123 | 1.495261 |
| C    | 0.356175  | 1.621812 | 1.589768 |
| C    | 0.268257  | 1.430000 |        |
| N    | 1.121955  | 0.453061 | 1.029924 |
| H    | 0.408297  | 0.551237  |        |
| C    | 0.267973  |        |        |

Electronic energy: -682.362305839 a.u. / lowest freq: 31.00 cm⁻¹

Cat2 / electronic energy: -1143.6398125 a.u. / lowest freq: 23.61 cm⁻¹
IId_2.10Å / electronic energy: -1825.4829379 a.u. / lowest freq: \(218.30\) cm\(^{-1}\)

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | 1.84476 | 3.352394 | -0.346459 |
| H    | 0.928884 | 2.538159 | 1.460390 |
| C    | 2.319253 | -0.973941 | -0.918818 |
| C    | 0.659349 | -1.138087 | -2.766274 |
| C    | 1.519089 | 2.885698 | -1.241468 |
| H    | 2.381989 | 0.923785 | -3.035238 |
| C    | 2.234445 | 1.680591 | 5.054931 |
| H    | 2.958627 | 1.163859 | -2.285128 |
| H    | 2.176268 | 3.623282 | -1.70188 |
| C    | 3.617444 | 0.708412 | -2.154928 |
| C    | 3.075213 | 2.925165 | 9.862926 |
| H    | 3.445694 | 1.882020 | 0.654719 |
| H    | 3.561217 | 1.984970 | 2.806566 |
| H    | 3.969998 | 0.967783 | -0.290368 |
| H    | 4.146773 | 2.601220 | -0.375992 |
| H    | 0.082164 | -2.178365 | 9.238869 |
| C    | 1.240787 | -1.661683 | -0.698785 |
| C    | 0.312287 | -8.462387 | -2.523882 |
| H    | 2.923848 | -3.285145 | -1.845779 |
| C    | 2.963659 | -2.982463 | -2.809076 |
| C    | 1.579634 | -3.760743 | -2.083392 |
| H    | 0.131722 | -2.865161 | 2.776843 |
| H    | 1.338378 | -2.671188 | 1.532383 |
| C    | 3.464588 | -0.425761 | 4.476826 |
| H    | -1.808518 | -2.744670 | -1.396889 |
| C    | -1.662444 | 1.997589 | 7.726760 |
| H    | -2.472879 | -1.296030 | -2.143829 |
| C    | -4.276985 | -2.639546 | 8.804545 |
| H    | -4.488461 | -1.850880 | 1.679891 |
| H    | -2.930819 | -1.960225 | 1.579730 |
| C    | -5.321188 | -1.745930 | -1.217120 |
| H    | -4.743753 | -0.257882 | 1.976682 |
| H    | -5.598757 | -0.197597 | -0.415820 |

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I1d_2.35Å / electronic energy: 78

H 0.626844 3.586881 2.588496
C 0.598126 1.340726 1.725183
H 2.684055 0.329051 0.645486
C 0.694241 4.275462 3.423659
N 1.062177 -0.892240 0.770015
H -0.383684 -0.522296 2.234692
C 0.678936 2.226096 2.884750
C 0.612355 -0.145575 1.986848
H 0.948481 -1.983113 0.911858
C 2.518076 -0.780165 0.486649
O 2.341752 -2.884313 -0.467481
C 2.735938 1.738896 -0.781245
H 3.924612 1.121430 1.79538
H 0.768437 1.821768 0.811426
N 3.223824 -1.380036 -1.859148
H 2.919314 0.542669 3.079555
H 1.262596 -0.382288 2.823566
C 3.593855 -2.343538 -2.038895
C 3.722415 -0.050802 -2.277241
C 3.757218 0.353851 -2.414080
H 5.191617 -0.334716 0.169532
C 3.579884 -0.91076 1.538585
C 4.931737 -1.160730 0.843993
H 4.638597 0.191649 0.843767
H 4.958466 2.096612 0.278377
H 2.533257 -2.077345 2.075111
C 3.276688 -2.167626 2.395185
O 5.719492 -1.216477 0.689361
H 3.206974 -3.064631 1.776393
H 4.008851 -2.86682 3.114552
O -1.223359 -0.384629 0.135981
C -3.282762 -1.159866 -0.839403
C -3.658519 -0.553640 0.079112
C -3.751946 0.835318 -0.097519
C -4.982867 1.461789 0.017753
C -5.803408 -1.389916 0.374891
F -6.024888 -0.686724 0.498867
C -6.128253 0.710295 0.316464
H -4.747485 -2.382041 0.519872
H -5.505189 2.534485 -0.120577
H -6.913388 -2.462682 0.740294
H -7.082933 1.282117 0.418990
C -2.115878 -2.622437 0.480473
F -2.917873 -3.608737 -0.268988
F -0.849896 -2.997386 0.186385
F -2.341554 -2.677327 1.715932
C 3.369258 0.121285 -3.299982
H 4.813111 0.843880 -2.279217
H 3.295138 0.720213 -1.634722
C 5.502268 3.486675 -2.361750
C 4.612189 -2.384799 -3.225420
H 2.891032 -2.363887 -3.672446
H 0.566016 -0.548177 -2.597885
H 0.645184 -2.149396 -1.796872
H -3.498974 -1.866096 -0.484773
C 3.384413 3.882133 -3.124583
H 1.473058 2.538385 -2.559961
C 2.416294 3.645164 -1.680802
H -1.357557 3.727789 -2.807499
H -1.889093 3.651787 -1.260743
C -1.806214 2.219914 -1.942657
H 0.356019 5.673453 -2.288823
H 1.340556 5.749242 -0.860661
H -0.278998 5.726192 -0.680329
H -2.855175 1.486687 -0.319596

TB
IId_2.35A / electronic energy: -1825.48331913 a.u. / lowest freq: -75.21 cm⁻¹

C 1.049926 3.289475 1.879555
C 0.268281 5.311475 1.291970
C 2.481384 -1.643352 2.272896
C -0.777487 3.777527 1.269377
C -1.458992 3.116139 2.143861
C 1.276915 -1.472479 2.284724
C -0.626422 3.240175 -0.160893
C -0.908848 -1.222656 0.827678
H 0.647916 5.160786 -1.134925
O -0.417888 0.905720 0.639643
C -5.518238 4.888824 -1.265595
C -0.873626 1.855744 -0.842374
B -0.092467 -0.368339 0.415517
C -0.636343 3.688998 -2.569802
C -6.801914 1.552370 -1.723376
H -2.683684 0.325714 -0.638526
H -0.781084 4.385026 -3.397669
H -1.074785 -0.881776 -0.766887
H 0.354242 -0.580951 -2.263285
H -0.685797 2.244271 -2.796873
C -0.636186 -1.220692 -1.999952
H -0.963081 -1.895115 -0.936113
C -2.526088 -0.697151 -0.481597
C -2.339432 -2.094635 -0.431328
C -2.732966 -1.755017 0.690180
H -3.946687 1.245463 -1.727887
H -0.793014 1.854987 -3.862282
C 3.380514 -1.426263 1.859014
H -1.940316 0.681980 -3.629470

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Ivd_2.10A / electronic energy: -1825.48412544 a.u. / lowest freq: -385.59 cm⁻¹

C 1.984859 -2.410805 1.851723
C 0.789061 -2.731252 0.916432
C 0.842951 2.888729 0.128815
C 0.516708 -1.742968 1.541990
H 0.778244 4.424915 -0.314146
O 0.055316 0.488606 0.538574
C 0.790927 0.852118 -0.819835
C 0.039075 1.539714 -0.398888
B -0.338774 -0.813144 0.129622
C 0.318829 3.632162 -2.154510
C -0.374328 1.313430 -1.659938
H -2.482436 0.784190 1.343911
H 0.365228 4.557239 -2.856365
N -1.433199 -0.787384 -0.951161
H -0.037666 -0.646028 -2.492699
C -0.323258 2.387191 -2.569390
C -0.858913 -0.027699 -2.888283
H -1.662767 -1.746682 -1.241887
C -2.711864 -0.218990 -0.373737
O -1.342388 -2.472222 0.154887
C 3.358015 -1.323569 0.583387
H -2.896807 1.491466 -2.822185
H -1.590423 0.060699 -2.889190
C -0.093980 -2.091883 2.682422
C -3.628689 0.838426 2.430711
C -3.671494 1.470800 -2.063884
H -5.117365 0.973036 0.194445
C -3.866588 0.899778 -1.388729
C -2.002847 0.386447 -0.884599
H -4.604456 1.750978 -2.559318
C -5.466362 -0.743867 -1.261611
C -3.188828 1.149694 3.868672
H -0.513429 -1.045282 -2.427954
H -0.581189 0.493819 -1.261773
H -4.254353 1.972760 -1.944962
H -4.981568 0.761993 -3.646798
O -0.842913 -1.573738 -0.858925
C 0.205884 -1.722127 -0.128164
C 3.983599 0.557988 -0.676319
C 2.817045 4.010381 -1.073256
C 3.721459 1.460672 -1.196659
C 4.084647 -0.795112 -0.781826
1825.40247128 a.u. / lowest freq: 190.28 cm⁻¹

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Vd_2.15Å / electronic energy: -1825.40145891 a.u. / lowest freq: -237.30 cm

-2.45714 0.110069
-2.45287 0.235173 1.466971
-2.418162 0.942821 0.727616
-2.414708 -1.637345 2.917110
-3.756999 -3.771015 0.182483
-3.817080 -2.882521 2.884761
-2.285589 -3.293343 2.293850
-4.783988 -3.356424 1.473496
-1.886396 -4.885226 1.655265
-2.910894 -3.744148 2.991195
-1.525488 -0.251752 0.320870
-2.645489 -0.247770 -0.312017
-3.854629 -0.559440 0.153255
-3.785586 -1.952146 -2.211114
-4.855388 -2.757084 0.472834
-5.118994 -0.677555 0.332528
-6.213999 -0.796966 0.595627
-6.061498 -2.179222 0.626617
-5.257718 1.090450 0.287995
-4.848988 -3.833788 0.525744
-7.188992 0.340801 0.748717
-6.921758 -2.880595 0.863581
-2.748981 1.781612 0.634183
-3.067018 2.025932 1.282585
-1.599948 2.725204 -2.693937
-3.697727 2.381060 -0.709989
-3.396365 -1.087187 -3.199166
-4.443231 -2.095158 -3.367555
-3.680989 -0.794849 -1.493993
-1.433269 -4.202162 -2.586716
-3.128984 -4.087959 -3.325853
-1.886477 -3.049082 3.858186
-0.858493 -0.713025 -2.489496
-0.534442 -2.093115 -1.884248
-3.685211 0.633480 -2.579702
-0.647653 3.855559 -1.863233
-2.768261 4.597387 -1.163123
-1.988923 3.771185 -1.146838
-2.821334 -2.240356 -1.938346
-3.008159 -2.611593 -2.946385
-2.297737 1.285188 -2.018991
-3.789729 2.675751 -1.447557
-2.901921 4.913846 -2.280793
-3.750338 4.580610 -0.787321
-2.213364 5.393182 -0.645467
-0.837478 3.948977 -2.846291
-0.021385 -1.383242 -1.205685
-0.095095 2.576495 -2.044845
-2.726298 -2.395252 -0.692990

Vd_2.15Å / electronic energy: -1825.40145891 a.u. / lowest freq: -237.30 cm

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| Atom | x | y | z |
|------|---|---|---|
| C    | 0.742151 | 0.808151 | 0.000009 |
| O    | 1.051410 | 1.975604 | 0.000019 |
| H    | 2.736944 | -2.388888 | -0.113613 |

Vd_2.35Å / lowest freq: -182.2273845 a.u. / lowest freq: 137.33 cm⁻¹

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C 1.606395 0.037692 1.486792
C -0.028280 -0.33855 -1.743664
H 3.243952 0.384075 2.951829
O -0.133558 -0.178156 0.629937
C 2.189939 0.096596 2.792474
C 0.336081 -0.719383 1.598162
B -1.535966 -0.118385 -0.148444
C 1.362775 -0.183789 3.897383
C -0.594626 -0.485886 2.413881
H -0.598683 -2.558772 4.417329
H 1.766616 -0.043837 4.918185
H -2.222396 -1.124297 0.850659
H -2.587058 0.892642 2.334742
C 0.028878 -0.394412 3.762087
H -1.971339 -0.884183 2.229186
H -3.235455 -1.199315 0.689491
C -1.675696 -2.784456 0.538488
O -3.621233 -2.922170 0.785661
C -2.394083 -0.361485 -0.770360
H 0.324551 -3.655797 2.153510
H -0.632148 -0.565341 4.553917
N -1.692174 -3.468265 -1.834638
C -1.874166 -2.957746 3.463731
C -2.318339 -1.526446 2.964802
C -2.425631 -3.945194 -3.089679
C -0.29283 -3.588441 -1.963338
C -0.895156 -3.768789 2.738136
H -0.619572 -5.178397 0.441549
C -1.912252 -3.846231 1.584534
C -1.624467 -5.73527 0.852477
H -0.937568 -4.781816 3.366995
C -2.355143 -5.78396 0.065412
C -3.627834 -3.011659 2.692841
C -3.358636 -3.808016 2.114695
H -1.674966 -5.931911 1.573362
H -4.067389 -4.019581 1.299871
H -3.498942 -4.757155 2.784578
O -1.878324 1.169496 0.353820
C -2.785825 2.061616 -0.630139
C -2.427336 3.450688 0.137919
C -0.878978 3.629667 0.01978
H -0.190124 4.982053 0.180382
C -3.135866 4.497799 0.415419
C -2.637363 5.782285 0.592765
C -1.789223 6.024521 0.474689
H -4.280172 4.319424 0.513594
H -4.39949 2.873186 -0.275383
H 0.672662 5.172177 -0.678882
H -3.31724 5.934536 0.824443
H -0.887476 7.030827 0.69372
C -1.800037 1.781553 0.229164
F -4.364443 0.484386 -0.034773
F -4.275596 1.896948 1.527339
F -5.039735 2.419785 -0.481486
C 4.735662 1.792014 1.354912
C 0.536523 -0.036420 0.672828
C 6.925259 3.313467 0.460415
C 7.133231 1.431166 1.290730
C 0.026541 2.163290 1.739888
H 8.121008 1.717280 1.591277
C 6.165323 3.016562 2.319959
C 5.500094 -0.981559 -0.563349
C 7.777948 -0.243248 0.119265
C 3.089921 2.678347 1.725281
C 2.555424 2.810223 -1.197418
C 1.347425 1.142546 -2.223310
C 8.653241 2.694585 -3.964151
C 1.076851 3.419778 0.839631
C 2.036159 3.777880 -2.663336
C 2.398417 4.802882 -0.013743
H 6.074862 4.165386 -0.388383
C 3.128998 3.113868 -0.483334
H 8.054765 0.168686 -2.384466
H -0.070594 1.883588 -0.844885
C 3.089158 1.698311 -2.023317
C 2.722056 -2.650387 -0.021851
C 3.188228 -2.978785 -2.744118
C 2.838782 -3.931663 0.555698
C 3.078822 -4.694687 -1.506264
C 2.753989 -4.880136 0.918889
C 3.163173 -5.093132 -2.340767
C 3.186191 -0.835653 -2.855991
C 3.274818 -3.184235 -0.862121
C 2.546337 -2.529367 1.645974
H 0.012113 -3.258837 -2.986029
H 0.166627 -4.500882 1.742621
H 0.244645 -2.768240 -1.321955
H -3.476028 -4.684485 -2.746285
H -1.989983 -4.847722 3.358440
H -2.353676 -3.283146 -3.812513
H -1.34561 -6.057261 -2.320736
H -2.847877 -1.049955 -1.872137
H 3.224667 3.072196 -2.470322

99

H 2.20A / electronic energy: -2651.829785 a.u. / lowest freq: -133.18 cm^-1
C 2.185642 1.515474 -1.250197
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| Atom | x     | y     | z     |
|------|-------|-------|-------|
| H    | -0.025378 | -2.684195 | -1.396320 |
| H    | -3.716472 | -3.657816 | -2.82859 |
| H    | -2.308546 | -4.754613 | -3.327290 |
| H    | -2.353464 | -3.654951 | -3.858763 |
| H    | -1.289126 | -8.306343 | -2.327917 |
| H    | -2.919728 | -7.853861 | -1.880786 |
| H    | -2.897561 | -3.821745 | -2.698746 |

Ve_2.05A / electronic energy: -2651.80286098 a.u. / lowest freq: 381.38 cm⁻¹
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Ve_2.50Å / electronic energy: 99

| X  | Y  | Z      | Energy (a.u.) |
|----|----|--------|---------------|
| 0.558379 | 0.775618 | 0.548219 | 0.559829 | 0.347556 | 0.338955 | 0.132366 | 0.447243 | 2.548805 | 1.104212 | 1.256729 | 1.923627 | 2.544771 |

99

Ve_2.50Å / electronic energy: -2651.80256000 a.u. / lowest freq: -75.16 cm⁻¹

| X  | Y  | Z      | Energy (a.u.) |
|----|----|--------|---------------|
| 1.791772 | -1.823434 | 1.441363 | 4.301726 | 4.067577 | 3.925583 | 3.659787 | 2.109666 | 2.684786 | 0.132366 | 0.447243 | 2.548805 | 1.104212 | 1.256729 | 1.923627 | 2.544771 |

75.16 cm⁻¹
Ila_2.3A / electronic energy: -1634.98337347 a.u. / lowest freq: -209.85 cm⁻¹

C  3.040087  -2.618183  -1.889841
C  -5.243288  -1.682167  -1.238327
C  3.063242  -1.778643  -2.152588
C  -3.733812  -1.488759  -1.237589
C  -3.494269  -0.142195  -0.828892
C  2.487452  -0.551083  -0.975179
C  -3.285084  -1.996848  0.187867
C  1.046057  -0.364399  -1.939113
H  -0.743335  -1.556546  1.176493
O  -1.082092  -0.788832  -0.638483
C  -3.028987  -1.186422  1.389579
C  -1.853113  -0.883755  0.430489
B  0.878777  -0.613893  -0.487294
C  3.568387  -1.958088  2.666359
C  -1.376468  -0.652151  1.718893
C  -1.013938  1.164717  0.093694
C  -2.236994  -1.195517  3.467891
N  0.859461  0.479190  0.782098
H  0.789597  -1.064285  2.119213
C  -2.237668  -0.743782  2.894927
C  0.854793  -0.206913  1.930587
N  1.539344  0.670574  0.853585
C  -0.083845  1.816461  0.361318
O  2.148234  2.151834  -0.557720
O  0.948558  2.139692  -0.737780
H  -2.21854  2.580899  1.815872
H  -1.863268  -0.548964  3.811424
O  0.453977  2.958172  -1.886797
H  -1.255858  1.756424  3.624777
C  0.134533  0.455592  2.787785
C  1.480852  3.358019  -2.773886
C  -0.946424  3.142667  -2.179668
C  -1.301993  2.648085  2.194660
H  -1.136924  3.120415  0.269999
C  -0.070525  2.069330  1.527486
C  -0.246449  -0.628280  -0.991834
C  -1.487568  3.584812  3.090788
H  0.624996  4.575266  0.341445
O  1.423639  1.970878  2.897287
C  1.229174  2.289180  2.356657
H  -0.377211  4.994118  1.780121
C  2.093257  3.186683  1.715317
C  1.154348  3.694083  3.269527
O  0.333576  -1.916089  -0.667585
C  2.226482  -2.379281  -0.096388
C  2.373231  -3.627782  -0.234782
C  3.315588  -1.787899  0.760162
F  4.525065  -2.121578  0.422993
F  3.280417  -0.372558  -0.966670
F  3.078789  -2.057872  2.031346
H  -1.181989  2.720647  -3.177896
H  -1.289012  4.281937  -2.858592
H  -1.614672  2.634122  -1.488886
H  2.385058  3.594923  -2.316885
C  0.964339  4.334598  -3.668176
C  1.448338  2.983091  3.664776
C  0.539997  -1.227883  -2.589563
H  0.874756  0.624015  2.343893
C  4.130727  -1.925196  -0.874720
C  2.949342  -2.582189  -2.625597
C  3.180526  0.294092  -1.665973
H  -5.589592  -1.811981  -2.760188
H  -5.897112  -0.084090  -0.057994
H  -5.429387  -2.596352  -0.691124
H  -3.440228  -2.708314  -0.897652
H  -1.313269  -3.525879  -1.389167
H  -1.961257  -2.472357  -1.964307
H  -3.936225  -0.748434  -3.874933
H  -2.429966  0.665493  -2.287889
C  -0.972288  -0.725164  -1.614688
C  1.639868  -4.241715  -0.938174
H  2.171601  -4.299168  0.751325
C  3.381097  -4.143588  -0.536516

IIa_2.4A / electronic energy: -1634.98166498 a.u. / lowest freq: -183.10 cm⁻¹

C  -3.029276  -2.669832  -1.963850
C  -5.238103  -1.687810  -1.250772
C  3.094293  -1.751620  -2.189726
C  -3.788004  -1.460882  -1.247778
C  -3.495989  -0.135185  -2.087496
C  2.510722  -0.543817  -1.970614
C  -3.283573  -1.290086  0.179837
C  1.066284  -0.357496  -1.979785
H  -0.771842  -1.750956  1.164523
O  -1.082396  -0.173958  -0.644257
H  -0.027782  -1.316019  1.298957
C  -1.854247  -0.877134  0.424215

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\begin{align*}
\text{H} & \quad 1.144855 \quad 4.324876 \quad 0.270831 \\
\text{C} & \quad -0.082881 \quad 2.877962 \quad 1.537765 \\
\text{C} & \quad -0.268297 \quad 4.76743 \quad 0.913776 \\
\text{H} & \quad -1.443987 \quad 3.906671 \quad 3.689352 \\
\text{H} & \quad 0.613784 \quad 4.589571 \quad 0.337216 \\
\text{H} & \quad 1.399614 \quad 1.979420 \quad 2.917287 \\
\text{C} & \quad 2.89393 \quad 2.98272 \quad 2.753389 \\
\text{H} & \quad -0.481627 \quad 5.08024 \quad 1.72011 \\
\text{H} & \quad 2.073358 \quad 3.128439 \quad 1.751897 \\
\text{C} & \quad 1.114584 \quad 3.689361 \quad 3.126477 \\
\text{O} & \quad 0.170919 \quad -1.925397 \quad -0.649865 \\
\text{C} & \quad 2.175355 \quad -2.419590 \quad -0.890817 \\
\text{C} & \quad 2.335493 \quad -3.884870 \quad -0.261654 \\
\text{H} & \quad 3.248271 \quad -2.750696 \quad -0.789137 \\
\text{F} & \quad 4.487953 \quad -2.165933 \quad 0.423851 \\
\text{F} & \quad 3.542543 \quad -0.416548 \quad 0.736025 \\
\text{F} & \quad 3.072527 \quad -2.211949 \quad 2.660991 \\
\text{H} & \quad -1.081951 \quad 2.735626 \quad -3.186882 \\
\text{H} & \quad -1.175889 \quad 4.219256 \quad -2.237077 \\
\text{H} & \quad -1.587321 \quad 2.645882 \quad -1.585746 \\
\text{H} & \quad 2.425786 \quad 3.399819 \quad -2.285265 \\
\text{H} & \quad 1.121285 \quad 4.555188 \quad -3.637841 \\
\text{C} & \quad 1.492558 \quad 2.927482 \quad -3.642444 \\
\text{H} & \quad 0.578062 \quad -1.189933 \quad -2.585492 \\
\text{H} & \quad 0.776671 \quad 6.318562 \quad -3.509824 \\
\text{C} & \quad 4.109829 \quad -1.843998 \quad -2.847378 \\
\text{H} & \quad 2.549879 \quad -2.347610 \quad 2.680884 \\
\text{H} & \quad 3.135796 \quad 6.389776 \quad -1.637864 \\
\text{C} & \quad -5.168333 \quad -1.814547 \quad -2.295762 \\
\text{H} & \quad -5.806308 \quad -0.866788 \quad -8.225508 \\
\text{C} & \quad -5.472736 \quad -2.612232 \quad -1.723871 \\
\text{F} & \quad -3.417502 \quad -2.744221 \quad -2.929854 \\
\text{C} & \quad -3.201083 \quad -3.512185 \quad -1.348354 \\
\text{H} & \quad -1.942649 \quad -2.439133 \quad -1.993529 \\
\text{C} & \quad 3.942908 \quad -0.251751 \quad -3.083805 \\
\text{F} & \quad 2.437355 \quad 8.99607 \quad -2.217397 \\
\text{C} & \quad 3.893382 \quad 7.346221 \quad -6.138662 \\
\text{H} & \quad 1.585733 \quad -4.335965 \quad -9.69198 \\
\text{H} & \quad 2.162793 \quad -4.75587 \quad -0.785153 \\
\text{H} & \quad 3.342878 \quad -4.13188 \quad -0.593752 \\
\end{align*}

\text{IIa, 2.68A / electronic energy: -1634.79481B a.u. / lowest freq: -125.68 cm-1}
| Atom | C | H | N | C | H | N | C | H |
|------|---|---|---|---|---|---|---|---|
|      |  3.363494 |  3.17685 |  3.618484 |  3.543765 |  3.533366 |  3.543765 |  3.543765 |  3.543765 |
|      | -0.421695 | -0.421695 | -0.421695 | -0.421695 | -0.421695 | -0.421695 | -0.421695 | -0.421695 |
|      |  4.041526 |  0.783169 |  1.534919 |  1.534919 |  1.534919 |  1.534919 |  1.534919 |  1.534919 |
|      |  1.475613 |  2.375418 |  1.654254 |  1.654254 |  1.654254 |  1.654254 |  1.654254 |  1.654254 |
|      |  2.693782 |  4.498717 |  8.618787 |  8.618787 |  8.618787 |  8.618787 |  8.618787 |  8.618787 |
|      |  3.236986 |  4.171853 |  8.618787 |  8.618787 |  8.618787 |  8.618787 |  8.618787 |  8.618787 |

Ila_2.80Å / electronic energy: -1634.97814497 a.u. / lowest freq: 25.05 cm⁻¹
Illea (4,4A) / electronic energy: -1634.978192 a.u. / lowest freq: -161.50 cm⁻¹

\[
\begin{array}{ccc}
1 & 1.362134 & 3.936358
-0.125963 \\
0 & -1.743852 & -1.800761
-0.260579 \\
C & -2.958012 & -0.599411
-0.412869 \\
& -3.343311 & 0.633593
-1.175396 \\
& -3.921203 & 1.782588
-0.547543 \\
F & -5.177861 & 1.412745
-0.837934 \\
& -5.845185 & 2.386977
-1.03869 \\
& -3.596088 & 2.77922
0.260540 \\
H & 1.483996 & 2.631030
0.480295 \\
& 2.355733 & 3.087773
2.392889 \\
& 2.144862 & 2.115753
1.875735 \\
& -1.144752 & 4.627387
1.780379 \\
& 0.214716 & 4.978076
2.828152 \\
& 0.924915 & 3.666043
3.261334 \\
& -1.079988 & 0.326885
2.366358 \\
& -0.498487 & 1.037299
2.199560 \\
& -0.488653 & 0.211558
1.639272 \\
& -0.479639 & 1.144161
2.654726 \\
& 2.728976 & 1.804075
1.584242 \\
& 3.887439 & -0.009113
2.727227 \\
& 4.749086 & -3.254340
1.485851 \\
& 3.728548 & -4.624783
1.083565 \\
& 1.481869 & -3.92019
2.569772 \\
& 1.218226 & -4.646289
1.302153 \\
& 0.448664 & -2.973998
1.879596 \\
& 2.906882 & 1.982885
3.343629 \\
& 1.940849 & -0.982048
2.390469 \\
& 3.691941 & 1.085139
2.099858 \\
& 2.182987 & 8.459520
-2.323178 \\
& 2.838583 & 1.533386
-0.821644 \\
& 4.199777 & 0.786865
-1.960856 \\
\end{array}
\]
IIIa \_2.50Å / electronic energy: 1634.9715943 a.u. / lowest freq: -140.91 cm\(^{-1}\)

C 1.348673 -3.558846 1.960135
C 3.812175 -3.691116 1.711295
C 3.658422 -0.082749 1.818594
H 2.686311 -2.778459 1.520880
H 2.887315 -1.349986 2.427854
H 2.598938 0.754078 1.798222
H 2.464265 -2.30641 0.059261
C 3.19793 0.196878 1.756183
H 4.140884 -3.445844 -0.678971
O 0.536869 -2.162875 0.586212
C 3.342389 -2.761025 -0.956656
C 1.442066 -1.449961 -0.347203
B -0.567214 0.193848 0.135570
C 3.238045 -2.339585 -2.262650
C 1.349282 -0.846486 -1.659811
C 1.589375 1.899885 0.264935
H 3.941054 -2.785143 -3.085557
N -0.126788 0.847464 -0.854620
H -0.641013 -0.516424 -2.342539
C 2.249083 -1.406839 2.619444
O -0.720343 -0.082487 -2.025722
H -0.921289 1.433182 -1.139914
C 0.853108 1.866368 -0.324550
C 0.185789 2.997024 0.684240
O -0.054825 2.772186 0.532530
H 3.338459 1.382767 -1.335167
H 2.369789 -0.082129 -3.645386
N -0.378863 3.290825 1.687961
H 2.416731 1.246981 -2.832741
H 0.582289 0.626265 -2.851600
H -0.581712 4.216842 2.465857
C 1.622535 2.984258 2.379586
C 2.749832 1.948458 -2.669335
H 3.017736 3.555667 0.080994
H 4.612868 2.735749 -1.392566
C 2.294152 3.993939 -6.606274
H 3.418837 2.651875 -2.563380
H 1.509932 4.576784 -0.170870
H 0.823447 2.572075 3.028052
C 0.649357 3.129787 -2.439018
C 2.845378 4.499578 -1.396815
H -0.180052 3.979295 -1.960144
C 1.222718 3.936958 -3.136852
O 1.78124 1.039215 -2.79854
C -2.913539 6.48673 0.582366
C -3.324958 5.597753 -1.219361
C -3.897744 -1.82752 -0.573739
F -5.141275 -1.439918 -0.384642
F -3.862122 -2.280534 -1.831668
F -3.550842 -2.884441 0.249357
H 1.387458 2.731662 3.401584
H 2.277935 3.206160 2.392546
H 2.159724 2.155979 1.913670
H 2.347775 4.618830 1.719485
O 0.099998 5.027852 2.821862
H -1.087064 3.694952 3.225381
H -1.36558 6.618754 2.580745
H -0.528959 1.043259 2.199269
H -4.668939 0.382471 1.737926
H -3.513788 -1.118816 2.119674
H -2.767988 1.884130 1.475895
H 3.078393 -3.984775 2.764725
H 4.748604 -3.381556 4.486856
H 3.721979 -4.618260 1.224452
H 1.471567 -3.891221 2.996135
H 1.218432 -4.446051 3.314454
H 0.446682 -2.948534 1.898199
H 2.968181 -1.879126 3.459593
H 1.944678 -0.881208 2.466541
H 3.696684 -0.980754 2.116937
H -3.048878 0.450680 -2.283625
H -2.814387 1.490493 -0.849349
H -4.408466 0.738836 -1.123396

Illia \_2.50Å / electronic energy: -1634.97356913 a.u. / lowest freq: -62.70 cm\(^{-1}\)

C 1.351689 -3.554595 1.964629
C 3.818857 -3.677795 1.746338
C -3.677626 -0.364460 1.912689
C 2.683281 -2.765956 1.538989
C 2.790245 -1.534621 2.446293
C -2.683281 0.765722 1.711235
C 2.482876 -2.313941 0.676323
C -1.281618 0.285638 1.726821
H 4.179914 -3.420444 -0.638214
| Symbol | X       | Y       | Z       |
|--------|---------|---------|---------|
| H      | 0.632031| 0.633712|         |
| H      | 2.465179| 1.263605|         |
| N      | 0.304284| 3.309805| 1.666157|
| O      |         |         |         |
| H      | 1.575667| 1.327626| 0.290831|
| B      | 1.465085|         |         |
| C      | 2.314567|         |         |
| N      | 1.577899| 4.575400| -0.45895|
| H      | 2.577589| -0.521745|         |
| C      | 2.359839| 3.335754| -2.429746|
| O      | 2.854317| 4.589449| -1.359227|
| H      | -0.069001| 3.938375| -1.972159|
| C      | 1.682586| 3.935083| -3.319665|
| O      | -1.731669| 1.832256| -3.120768|
| H      | -2.899012| -6.908281| -3.592148|
| C      | 3.342631| 0.748647| -1.243838|
| O      | -3.880482| -1.863192| -0.868226|
| H      | -5.119559| -1.454797| -0.875277|
| F      | -3.921729| -2.297478| -1.853877|
| F      | -3.515339| -2.287653| -0.201671|
| H      | 1.705213| 2.725194| 3.421825|
| O      | 2.208717| 3.884128| 2.416520|
| H      | 2.101089| 2.761177| 1.942156|
| C      | 1.325486| 4.589664| 1.851434|
| H      | 0.082382| 5.039230| 2.788442|
| C      | -1.076743| 3.680668| 3.282323|
| H      | -1.129748| 8.634319| 3.176113|
| H      | -0.548387| 1.014579| 2.194446|
| F      | -4.826882| 1.044784| 1.865127|
| H      | -3.548796| -1.077128| 2.108679|
| H      | -2.717545| 1.813192| 1.462577|
| C      | 0.879034| 3.967900| 2.808552|
| H      | 4.755337| 3.173568| 1.488441|
| C      | 3.743106| 4.957542| 1.158366|
| C      | 1.468421| 3.884974| 3.963638|
| C      | 1.229969| 4.434447| 3.338019|
| C      | -0.446168| -2.950878| 1.892122|
| H      | 2.934487| -1.861257| 3.481265|
| H      | 0.922591| -8.876281| 2.415653|
| C      | 3.678328| -9.968792| 2.145116|
| H      | -3.192581| -8.405933| -3.254661|
| H      | -2.801984| 1.459192| -0.878615|
| H      | -4.888421| -0.719450| -0.878668|

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Ilia_2.80Å / electronic energy: -1634.9749469 a.u. / lowest freq: -15.74 cm^-1
Iva_2.50Å / electronic energy: -1634.9853982 a.u. / lowest freq: -147.96 cm⁻¹

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| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| H       | -4.137065 | 2.147574 | -0.080172 |
| H       | -4.971426  | -0.617036 | 0.099641  |
| H       | -2.963352  | -0.777759 | -0.087920 |
| C       | -3.778789  | -0.655117 | -0.368651 |
| H       | -5.496234  | 0.771180  | -0.852122 |
| H       | -4.062381  | -1.460876 | -0.010878 |
| H       | -4.624977  | -0.730134 | -0.915873 |
| O       | 1.279365   | -1.583970 | -0.165948 |
| C       | 2.446462   | -2.081621 | -0.016850 |
| C       | 2.804182   | -3.138699 | -1.796413 |
| C       | 3.592867   | -1.127534 | -0.475170 |
| F       | 4.128808   | -0.539933 | -1.551333 |
| F       | 3.189152   | -0.193857 | 0.364969  |
| F       | 4.525229   | -1.875285 | 0.183314  |
| H       | -2.354378  | -0.581215 | 3.460950  |
| H       | -4.154673  | 0.113990  | 2.821878  |
| H       | -2.657147  | 0.532480  | 2.092333  |
| H       | -3.628936  | -3.520953 | 1.537467  |
| H       | -4.547140  | -2.577518 | 2.761979  |
| H       | -2.826216  | -3.051689 | 3.063681  |
| H       | -8.492904  | 1.564985  | 1.986222  |
| H       | -8.299778  | -2.912837 | 0.763451  |
| H       | 1.846549   | -1.448538 | 2.295445  |
| H       | 1.887258   | -4.170421 | 0.870683  |
| H       | 3.228628   | -3.473445 | 1.839589  |
| H       | 0.895281   | 2.538691  | 3.615287  |
| H       | -0.298841  | 1.335438  | 2.362364  |
| H       | -0.992853  | 2.069881  | 2.252830  |
| H       | 2.589388   | 2.262859  | 3.233591  |
| H       | 3.237758   | 2.337284  | 1.586821  |
| H       | 2.183418   | 0.995019  | 2.064986  |
| H       | 1.551720   | 4.190752  | 3.244978  |
| H       | 0.537666   | 4.099624  | 1.927780  |
| H       | 2.281369   | 4.749275  | 1.677136  |
| H       | 1.996051   | -3.846551 | -1.963899 |
| H       | 3.664597   | -3.728544 | -1.296662 |
| H       | 3.237061   | -2.848477 | -2.762181 |
9. X-ray crystallographic data of 17

Table S9-1. Crystal data and structure refinement for C_{10}H_{7}Cl_{2}F_{3}O_{2}

| Parameter                          | Value                        |
|------------------------------------|------------------------------|
| Identification code                | C10H7Cl2F3O2                 |
| Empirical formula                  | C10 H7 Cl2 F3 O2             |
| Formula weight                     | 287.06                       |
| Temperature                        | 100(2) K                     |
| Wavelength                         | 1.54178 Å                    |
| Crystal system                     | Orthorhombic                 |
| Space group                         | P2_12_12                     |
| Unit cell dimensions               | a = 6.2490(4) Å, α= 90º.    |
|                                    | b = 9.8370(6) Å, β= 90º.    |
|                                    | c = 18.7718(10) Å, γ = 90º. |
| Volume                             | 1153.93(12) Å³               |
| Z                                  | 4                            |
| Density (calculated)               | 1.652 Mg/m³                  |
| Absorption coefficient             | 5.368 mm⁻¹                   |
| F(000)                             | 576                          |
| Crystal size                       | 0.340 x 0.080 x 0.050 mm³    |
| Theta range for data collection    | 4.711 to 70.124º.            |
| Index ranges                       | -7<=h<=7, -11<=k<=11, -22<=l<=22 |
| Reflections collected              | 21833                        |
| Independent reflections            | 2174 [R(int) = 0.0850]       |
| Completeness to theta =            | 67.679º 100.0 %              |
| Absorption correction              | Semi-empirical from equivalents |
| Max. and min. transmission         | 0.7533 and 0.5812            |
| Refinement method                  | Full-matrix least-squares on F² |
| Data / restraints / parameters     | 2174 / 1 / 158               |
| Goodness-of-fit on F²              | 1.104                        |
| Final R indices [I>2sigma(I)]      | R1 = 0.0477, wR2 = 0.1231    |
| R indices (all data)               | R1 = 0.0508, wR2 = 0.1249    |
| Absolute structure parameter       | 0.04(3)                      |
| Extinction coefficient             | na                           |
| Largest diff. peak and hole        | 0.590 and -0.259 e.Å⁻³      |
Table S9-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for C_{10}H_{7}Cl_{2}F_{3}O_{2}. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

|    | x     | y     | z     | U(eq) |
|----|-------|-------|-------|-------|
| Cl(1) | 4358(3) | 5185(2) | 1457(1) | 53(1) |
| Cl(2) | 10519(2) | 8213(2) | 2676(1) | 50(1) |
| F(1)  | 2513(4) | 6298(4) | 4193(2) | 40(1) |
| F(2)  | 5227(5) | 7185(3) | 4724(2) | 33(1) |
| F(3)  | 3532(5) | 5515(3) | 5204(2) | 39(1) |
| O(1)  | 9760(6) | 2652(4) | 4618(2) | 38(1) |
| O(2)  | 4503(6) | 3794(3) | 4085(2) | 30(1) |
| C(1)  | 9085(8) | 3653(5) | 4328(3) | 34(1) |
| C(2)  | 7654(7) | 4689(5) | 4674(2) | 23(1) |
| C(3)  | 5701(7) | 4999(4) | 4199(2) | 22(1) |
| C(4)  | 6306(7) | 5582(4) | 3469(2) | 22(1) |
| C(5)  | 5185(7) | 5160(5) | 2867(2) | 29(1) |
| C(6)  | 5747(7) | 5715(3) | 2210(2) | 32(1) |
| C(7)  | 7386(8) | 6632(5) | 2131(3) | 32(1) |
| C(8)  | 8458(8) | 7026(5) | 2741(3) | 31(1) |
| C(9)  | 7913(7) | 6550(5) | 3410(2) | 25(1) |
| C(10) | 4200(7) | 6010(5) | 4582(2) | 28(1) |

Table S9-3. Bond lengths [Å] and angles [°] for C_{10}H_{7}Cl_{2}F_{3}O_{2}.

| Bond | Length [Å] | Angle [°] |
|------|------------|-----------|
| Cl(1)-C(6) | 1.738(5) |          |
| Cl(2)-C(8) | 1.743(5) |          |
| F(1)-C(10) | 1.334(6) |          |
| F(2)-C(10) | 1.336(6) |          |
| F(3)-C(10) | 1.339(6) |          |
| O(1)-C(1) | 1.201(6) |          |
| O(2)-C(3) | 1.418(5) |          |
| O(2)-H(2O) | 0.83(3) |          |
| C(1)-C(2) | 1.504(7) |          |
| C(1)-H(1) | 0.9500 |          |
| C(2)-C(3) | 1.543(6) |          |
| C(2)-H(2A) | 0.9900 |          |
| C(2)-H(2B) | 0.9900 |          |
| C(3)-C(10) | 1.529(6) |          |
| C(3)-C(4) | 1.533(6) |          |
| C(4)-C(9) | 1.388(6) |          |
| C(4)-C(5) | 1.393(6) |          |
| C(5)-C(6) | 1.394(6) |          |
| C(5)-H(5) | 0.9500 |          |
| C(6)-C(7) | 1.373(8) |          |
C(7)-C(8)  1.382(7)
C(7)-H(7)  0.9500
C(8)-C(9)  1.383(6)
C(9)-H(9)  0.9500
C(3)-O(2)-H(2O)  108(5)
O(1)-C(1)-C(2)  124.6(4)
O(1)-C(1)-H(1)  117.7
C(2)-C(1)-H(1)  117.7
C(1)-C(2)-C(3)  110.8(4)
C(1)-C(2)-H(2A)  109.5
C(3)-C(2)-H(2A)  109.5
C(1)-C(2)-H(2B)  109.5
H(2A)-C(2)-H(2B)  108.1
O(2)-C(3)-C(10)  107.4(3)
O(2)-C(3)-C(4)  108.0(3)
C(10)-C(3)-C(4)  108.9(4)
O(2)-C(3)-C(2)  109.8(3)
C(10)-C(3)-C(2)  109.2(4)
C(4)-C(3)-C(2)  113.3(3)
C(9)-C(4)-C(5)  120.3(4)
C(9)-C(4)-C(3)  120.4(4)
C(5)-C(4)-C(3)  119.3(4)
C(4)-C(5)-C(6)  118.3(4)
C(4)-C(5)-H(5)  120.8
C(6)-C(5)-H(5)  120.8
C(7)-C(6)-C(5)  122.7(4)
C(7)-C(6)-Cl(1)  118.9(4)
C(5)-C(6)-Cl(1)  118.4(4)
C(6)-C(7)-C(8)  117.2(4)
C(6)-C(7)-H(7)  121.4
C(8)-C(7)-H(7)  121.4
C(7)-C(8)-C(9)  122.6(5)
C(7)-C(8)-Cl(2)  119.2(4)
C(9)-C(8)-Cl(2)  118.2(4)
C(8)-C(9)-C(4)  118.8(4)
C(8)-C(9)-H(9)  120.6
C(4)-C(9)-H(9)  120.6
F(1)-C(10)-F(2)  107.4(4)
F(1)-C(10)-F(3)  106.7(4)
F(2)-C(10)-F(3)  107.0(4)
F(1)-C(10)-C(3)  111.3(4)
F(2)-C(10)-C(3)  112.4(4)
F(3)-C(10)-C(3)  111.8(4)

Symmetry transformations used to generate equivalent atoms:
Table S9-4. Anisotropic displacement parameters (Å² x 10³) for C₁₀H₇Cl₂F₃O₂. The anisotropic displacement factor exponent takes the form: \(-2\pi²[ h² a^* a U_{11} + ... + 2 h k a^* b^* U_{12} ]\)

|    | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|----|--------|--------|--------|--------|--------|--------|
| Cl(1) | 71(1) | 60(1) | 28(1) | 2(1) | -13(1) | -23(1) |
| Cl(2) | 47(1) | 59(1) | 44(1) | 21(1) | -6(1) | -26(1) |
| F(1) | 18(1) | 57(2) | 45(2) | -1(2) | -2(1) | 10(1) |
| F(2) | 33(2) | 25(1) | 42(2) | -10(1) | 3(1) | 4(1) |
| F(3) | 38(2) | 47(2) | 32(1) | 3(1) | 16(1) | 4(1) |
| O(1) | 39(2) | 34(2) | 41(2) | 10(2) | 0(2) | 8(2) |
| O(2) | 37(2) | 26(2) | 27(2) | 3(1) | -3(1) | -14(2) |
| C(1) | 34(2) | 38(3) | 29(2) | 7(2) | 4(2) | 9(2) |
| C(2) | 23(2) | 25(2) | 22(2) | 4(2) | 2(2) | 1(2) |
| C(3) | 21(2) | 20(2) | 24(2) | -2(2) | 0(2) | -3(2) |
| C(4) | 25(2) | 19(2) | 22(2) | 1(2) | 1(2) | 2(2) |
| C(5) | 31(2) | 25(2) | 30(2) | -1(2) | -1(2) | -4(2) |
| C(6) | 37(2) | 32(2) | 26(2) | -1(2) | -6(2) | 0(2) |
| C(7) | 40(3) | 31(2) | 27(2) | 9(2) | 1(2) | 0(2) |
| C(8) | 32(2) | 31(2) | 30(3) | 10(2) | -2(2) | -3(2) |
| C(9) | 21(2) | 27(2) | 27(2) | 2(2) | -4(2) | 0(2) |
| C(10) | 21(2) | 33(2) | 31(2) | -3(2) | 3(2) | 0(2) |

Table S9-5. Hydrogen coordinates (x 10⁴) and isotropic displacement parameters (Å² x 10³) for C₁₀H₇Cl₂F₃O₂

|    | x     | y     | z     | U(eq) |
|----|-------|-------|-------|-------|
| H(2O) | 4610(110) | 3310(60) | 4440(20) | 45 |
| H(1) | 9485 | 3800 | 3846 | 40 |
| H(2A) | 8469 | 5536 | 4759 | 28 |
| H(2B) | 7159 | 4341 | 5141 | 28 |
| H(5) | 4066 | 4510 | 2903 | 34 |
| H(7) | 7768 | 6981 | 1677 | 39 |
| H(9) | 8626 | 6880 | 3822 | 30 |
### Table S9-6. Torsion angles [°] for C_{10}H_{7}Cl_{2}F_{3}O_{2}

| Bond                        | Torsion Angle [°] |
|-----------------------------|-------------------|
| O(1)-C(1)-C(2)-C(3)         | -130.6(5)         |
| C(1)-C(2)-C(3)-O(2)         | 60.1(5)           |
| C(1)-C(2)-C(3)-C(10)        | 177.7(4)          |
| C(1)-C(2)-C(3)-C(4)         | -60.7(5)          |
| O(2)-C(3)-C(4)-C(9)         | -163.6(4)         |
| C(10)-C(3)-C(4)-C(9)        | 80.0(5)           |
| C(2)-C(3)-C(4)-C(9)         | -41.7(5)          |
| O(2)-C(3)-C(4)-C(5)         | 18.2(5)           |
| C(10)-C(3)-C(4)-C(5)        | -98.3(5)          |
| C(2)-C(3)-C(4)-C(5)         | 140.1(4)          |
| C(9)-C(4)-C(5)-C(6)         | 1.1(7)            |
| C(3)-C(4)-C(5)-C(6)         | 179.3(4)          |
| C(4)-C(5)-C(6)-C(7)         | 1.6(8)            |
| C(4)-C(5)-C(6)-Cl(1)        | 179.8(4)          |
| C(5)-C(6)-C(7)-C(8)         | -1.6(8)           |
| Cl(1)-C(6)-C(7)-C(8)        | -179.8(4)         |
| C(6)-C(7)-C(8)-C(9)         | -1.0(8)           |
| C(6)-C(7)-C(8)-Cl(2)        | -178.7(4)         |
| C(7)-C(8)-C(9)-C(4)         | 3.7(7)            |
| Cl(2)-C(8)-C(9)-C(4)        | -178.6(4)         |
| C(5)-C(4)-C(9)-C(8)         | -3.6(7)           |
| C(3)-C(4)-C(9)-C(8)         | 178.2(4)          |
| O(2)-C(3)-C(10)-F(1)        | -60.3(5)          |
| C(4)-C(3)-C(10)-F(1)        | 56.4(5)           |
| C(2)-C(3)-C(10)-F(1)        | -179.3(4)         |
| O(2)-C(3)-C(10)-F(2)        | 179.3(3)          |
| C(4)-C(3)-C(10)-F(2)        | -64.0(5)          |
| C(2)-C(3)-C(10)-F(2)        | 60.2(5)           |
| O(2)-C(3)-C(10)-F(3)        | 58.9(5)           |
| C(4)-C(3)-C(10)-F(3)        | 175.6(4)          |
| C(2)-C(3)-C(10)-F(3)        | -60.2(5)          |

Symmetry transformations used to generate equivalent atoms:

### Table S9-7. Hydrogen bonds for C_{10}H_{7}Cl_{2}F_{3}O_{2} [Å and °]

| D-H...A          | d(D-H) [Å] | d(H...A) [Å] | d(D...A) [Å] | <(DHA) [°] |
|------------------|------------|--------------|--------------|------------|
| O(2)-H(2O)...O(1)#1 | 0.83(3)    | 2.00(3)      | 2.825(5)     | 173(6)     |

Symmetry transformations used to generate equivalent atoms:  #1 x-1/2,-y+1/2,-z+1