Supporting Information

Hydrogen Bonding Networks Enable Brønsted Acid-Catalyzed Carbonyl-Olefin Metathesis

T. Anh To, C. Pei, R. M. Koenigs*, T. Vinh Nguyen*
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**General Methods**

Reactions, unless otherwise stated, were conducted in screw-cap vials under ambient air. Acetonitrile (MeCN), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), and diethyl ether were batchwise dried over molecular sieves. Commercially available reagents were used as purchased unless otherwise noted. Analytical thin layer chromatography was performed using silica gel plates pre-coated with silica gel 60 F254 (0.2 mm). Flash chromatography employed 230-400 mesh silica gel. Solvents used for chromatography are quoted as volume/volume ratios.

NMR spectroscopy was performed at 298 K using either a Bruker Avance III 300 (300.13 MHz, 1H; 75.5 MHz, 13C; BBFO probe), an Avance I 300 (300.13 MHz, 1H; 75.5 MHz, 13C; BBFO probe) or an Avance III 400 (400.13 MHz, 1H; 100.6 MHz, 13C; BBFO probe or Prodigy cryoprobe). Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual solvent as an internal reference (δ 7.26 ppm for chloroform) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constant (J in Hz) and integration (number of protons). 13C NMR spectra were recorded at 298 K with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (δ 77.2 ppm for the central peak of deuterated chloroform).

Infrared spectra were obtained on a ThermoNicolet Avatar 370 FT-IR spectrometer and are reported in wavenumbers (cm⁻¹). HRMS were performed at the Bioanalytical Mass Spectrometry Facility within the Mark Wainwright Analytical Centre at the University of New South Wales on an Orbitrap LTQ XL (Thermo Fisher Scientific, San Jose, CA, USA) ion trap mass spectrometer.
$^1$H NMR Perturbation Studies between pTSA and Different H-bonding Solvents

pTSA and HFIP at different ratios (full spectra)

CD$_2$CN (400 MHz, 298K) at 0.5 M total concentration
pTSA and HFIP at different ratios (zoomed in spectra)

CD$_2$CN (400 MHz, 298K) at 0.5 M total concentration

pTSA - pure

pTSA : HFIP = 8 : 1

pTSA : HFIP = 4 : 1

pTSA : HFIP = 3 : 1

pTSA : HFIP = 2 : 1

pTSA : HFIP = 1 : 1

pTSA : HFIP = 1 : 2

pTSA : HFIP = 1 : 3

pTSA : HFIP = 1 : 4

pTSA : HFIP = 1 : 8

HFIP - pure

pTSA and iPrOH at 1 : 1 ratio (full spectra)

CD$_2$CN (400 MHz, 298K) at 0.5 M total concentration

pTSA : iPrOH = 1 : 1

iPrOH - pure

pTSA - pure
pTSA and CF$_3$CH$_2$OH at 1 : 1 ratio (full spectra)

pTSA and nCF$_3$CF$_2$CH$_2$OH at 1 : 1 ratio (full spectra)
**Table S3.** NMR perturbation of pTSA OH signal with different alcohols

CD$_3$CN, 400 MHz, 298K

|           | $\delta_A$ OH (ppm) in pure form | $\delta_B$ OH (ppm) in 1:1 mixture | $\delta_B$ | $[\delta_{A\text{pTSA}} - \delta_{A\text{alcohol}}]$ | $[\delta_{B} - \delta_{A\text{alcohol}}]$ |
|-----------|----------------------------------|-----------------------------------|-----------|-------------------------------------------------|---------------------------------|
| pTSA      | 7.59                             | -                                 | -         | -                                              | -                               |
| HFIP      | 5.48                             | 6.34                              | 6.34/2.11 = 3.00 | 1.25/0.86 = 1.45 |
| $i$PrOH   | 2.63                             | 6.20                              | 6.20/4.96 = 1.25 | 1.39/3.57 = 0.39 |
| TFE       | ~3.90                            | 5.99                              | 5.99/3.69 = 1.63 | 1.60/2.09 = 0.77 |
| $n$CF$_3$CF$_2$CH$_2$OH | 3.91                             | 5.96                              | 5.96/3.68 = 1.62 | 1.63/2.05 = 0.80 |

It is clear from these perturbations that the influence of the hydrogen bonding networks on pTSA with HFIP is the most significant one.
The studies were carried out in CD$_3$CN (298K, 400 MHz) at 0.5 M total solution concentration.

There is no detectable evidence for the binding of HFIP to the carbonyl groups or the alkene moiety of substrate 1a.
## Optimization Studies

**Table S1a – Optimization of the intramolecular COM reaction of 1a**

![Reaction Scheme](image)

| Entry[^a] | Variations from optimal conditions[^b] | Yield[^c] |
|-----------|----------------------------------------|-----------|
| 1         | None (HFIP = 100 µL)                    | 80%       |
| 2         | Neat                                   | n.p.      |
| 3         | DCE instead of HFIP                    | n.p.      |
| 4         | iPrOH instead of HFIP                  | n.p.      |
| 5         | TFE (CF<sub>3</sub>CH<sub>2</sub>OH) instead of HFIP | 15%       |
| 6         | CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>OH instead of HFIP | n.p.      |
| 7         | Catalyst A or B (10 mol%) instead of pTSA, in HFIP | n.p.      |
| 8         | pTSA and catalyst A or B (10 mol%, instead of HFIP), in DCE | n.p.      |
| 9         | Absence of pTSA                        | n.p.      |
| 10        | pTSA (5 mol%)                          | 73%       |
| 11        | TfOH (10 mol%) instead of pTSA, in HFIP | 66%       |
| 12        | TfOH (10 mol%) instead of pTSA, in DCE instead of HFIP | 36%       |
| 13        | HCl (10 mol%) instead of pTSA, in HFIP | traces    |
| 14        | TFA (10 mol%) instead of pTSA, in HFIP | traces    |
| 15        | HFIP (50 µL)                           | 56%       |
| 16        | HFIP (75 µL)                           | 62%       |
| 17        | HFIP (200 µL)                          | 80%       |

[^a]: Reaction conditions without other notes: 1a (0.2 mmol), Brønsted acid (10 mol%) and HFIP (100 µL) at RT for 4 h.

[^b]: Determined by <sup>1</sup>H NMR using methyl benzoate as an internal standard. n.p. = no product.

[^c]: HCl 4 M in dioxane.
**Table S1b** – Optimization of the intramolecular COM reaction of 1a

![Diagram]

| Acid                                | Yield of 2a (%) | Yield of 2a’ (%) | Total product yield (%) |
|-------------------------------------|-----------------|------------------|-------------------------|
| pTSA                                | 80%             | 7%               | 87%                     |
| Triflic                             | 66%             | 5%               | 71%                     |
| 2,4-Dinitrobenzenesulfonic          | 75%             | 4%               | 79%                     |
| 2-Nitrobenzenesulfonic              | 89%             | 4%               | 93%                     |
| 4-Nitrobenzenesulfonic              | 85%             | 5%               | 90%                     |
| 4-(CF₃)benzenesulfonic              | 82%             | 6%               | 88%                     |
| 4-Acetylbenzenesulfonic             | 82%             | 7%               | 89%                     |
| Benzenesulfonic                     | 74%             | 6%               | 80%                     |
| 4-Dodecylbenzenesulfonic            | 76%             | 6%               | 82%                     |
| 4-Hydroxybenzenesulfonic            | 75%             | 7%               | 82%                     |
| 10-Camphorsulfonic                  | 80%             | 5%               | 85%                     |
| Methylsulfonic                      | 78%             | 10%              | 88%                     |
| 2,4-Dinitrobenzoic                  | traces          | traces           | traces                  |
| Pentafluorobenzoic                  | traces          | traces           | traces                  |
| 2-Nitrobenzoic                      | traces          | traces           | traces                  |
| 3,5-Dinitrobenzoic                  | traces          | traces           | traces                  |
| 4-Nitrobenzoic                      | traces          | traces           | traces                  |
| Trifluoroacetic                     | traces          | traces           | traces                  |
| Trichloroacetic                     | traces          | traces           | traces                  |
| Dichloroacetic                      | traces          | traces           | traces                  |
| Chloroaacetic                      | traces          | traces           | traces                  |
| Acetic                              | traces          | traces           | traces                  |
| Diphenyl phosphate                  | 12%             | 0%               | 12%                     |
| Phosphomolybdic acid                | 13%             | 0%               | 13%                     |
| Phenylphosphinic acid               | traces          | traces           | traces                  |
Table S2 – Optimization of the intramolecular COM reaction of the nitrogen-bearing 1n

![Diagram of 1n and 2n with catalysis by solvent]

| Entry | Bronsted acid catalyst (amount) | Solvent (amount) | Yield of 2n<sup>b</sup> |
|-------|---------------------------------|------------------|-------------------------|
| 1     | AcOH                            | HFIP             | n.p.                    |
| 2     | PhCOOH                          | HFIP             | n.p.                    |
| 3     | TFA                             | HFIP             | trace                   |
| 4     | HBF<sub>4</sub>.OEt<sub>2</sub> | HFIP             | 68%                     |
| 5     | HCl<sup>c</sup>                 | HFIP             | 69%                     |
| 6     | H<sub>2</sub>SO<sub>4</sub>      | HFIP             | 69%                     |
| 7     | TfOH                            | HFIP             | 67%                     |
| 8     | pTSA                            | HFIP             | 73%, 73%<sup>d</sup>    |
| 9<sup>d</sup> | pTSA (5%)                  | HFIP             | 74%                     |
| 10<sup>d</sup> | pTSA (2%)              | HFIP             | 70%                     |
| 11<sup>d</sup> | pTSA (5%)                  | HFIP (100 µL)    | 78%                     |
| 12<sup>d</sup> | pTSA (5%)                  | HFIP (50 µL)     | 88%                     |
| 13<sup>d</sup> | pTSA (5%)                  | DCE (50 µL)      | n.p.                    |
| 14<sup>d</sup> | pTSA (5%)                  | iPrOH/DCE (50 µL/50 µL) | n.p.        |
| 15<sup>d</sup> | None                        | HFIP (50 µL)     | n.p.                    |
| 16<sup>d</sup> | TFA (5%)                   | HFIP (50 µL)     | 10%                     |
| 17<sup>d</sup> | HCl<sup>e</sup> (5%)       | HFIP (50 µL)     | 21%                     |
| 18<sup>d</sup> | TfOH (5%)                   | HFIP (50 µL)     | 83%                     |

<sup>a</sup> Reaction conditions without other notes: 1n (0.2 mmol), Bronsted acid (10 mol%) and HFIP (200 µL) at RT for 18 h. <sup>b</sup> Determined by <sup>1</sup>H NMR using mesitylene as an internal standard. n.p. = no product. <sup>c</sup> HCl 4 M in dioxane. <sup>d</sup> Reaction was carried out for 4 h.
Kinetic Studies and Reaction Order in HFIP solvent

Kinetic studies were carried out by monitoring the reaction of substrate 1a (0.2 mmol) and pTSA catalyst (0.02 mmol, 10 mol%) with varying amount of HFIP from 2 – 6 equivalents in CDCl₃. The volume of CDCl₃ was adjusted with the changing volume of HFIP so that the total volume of the reaction was fixed at 1.0 mL (the initial concentration of substrate 1a was 0.2 M for all kinetic runs). Conversion of substrate 1a was quantified by ¹H NMR spectroscopy analysis of aliquots of the reaction mixture in CDCl₃ with methyl benzoate as internal standard. We applied a standard error range of ±5% for conversion to all figures, as this is the commonly accepted error for ¹H NMR integration. We also applied a ± 10 seconds error range for reaction time under 10 minutes, and a ± 1 minute error range for time over 10 minutes.

![Conversion of 1a vs Time](image)

Initial rates were approximated within the range of the first 10% conversion. The following assumptions are made:

- The difference in polarity of the reaction medium was negligible and did not alter the reaction profile when the amount of HFIP was varied. Indeed, with the amount of CDCl₃ being 7 – 23 times the volume of HFIP (2 equivalents = 0.4 mmol = 0.042 mL; 6 equivalents = 1.2 mmol = 0.127 mL), the overall polarity of the reaction mixture does not change significantly.

- The reaction rate can be calculated as:

\[
rate = k[HFIP]^x[1a]^y[pTSA]^z
\]

Since [pTSA] remained the same over the course of the reaction, and [1a] can be approximated as negligibly changed in the first 10% conversion range, we can assume that:

\[
rate = k'[HFIP]^x
\]

or

\[
\ln[rate] = x\ln[HFIP] + \ln k' = x\ln[HFIP \text{ equivalent}] + \text{constant}
\]
with \([\text{HFIP}] = 0.2 \times [\text{HFIP equivalent}]\) M. Therefore, a plot of \(\ln[\text{rate}]\) vs. \(\ln[\text{HFIP equivalent}]\) should give the slope \(x\), which is the reaction order in HFIP.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{HFIP equiv} & \text{Initial rate} & \ln(\text{HFIP equiv}) & \ln(\text{initial rate}) \\
\hline
2 & 1.1296 & 0.6931 & 0.1219 \\
3 & 2.5974 & 1.0986 & 0.9545 \\
4 & 5.5556 & 1.3863 & 1.7148 \\
5 & 8.6420 & 1.6094 & 2.1566 \\
6 & 19.444 & 1.7918 & 2.9675 \\
\hline
\end{array}
\]

\(\ln(\text{initial rate})\) was plotted against \(\ln(\text{HFIP equivalent})\) to give the reaction order in HFIP:

The reaction order in HFIP is approximately 2.5.
Synthesis of Starting Materials

Synthesis of 5-bromo-2-methylpent-2-ene

To an oven-dried round bottom flask equipped with a stir bar and a reflux condenser was added a solution of CH$_3$MgBr (3 M in Et$_2$O, 60 mmol, 20 mL) under nitrogen. After that, a solution of cyclopropyl methyl ketone (50 mmol, 4.94 mL) in dry THF (7 mL) was added dropwise. The resulting mixture was refluxed under nitrogen for 30 minutes. The reaction mixture was then cooled to 0 °C and added slowly to a pre-cooled solution of sulfuric acid/water (15 mL/20 mL). The mixture was further stirred for 30 minutes. After the completion of the reaction, the reaction mixture was extracted with Et$_2$O (3×20 mL). The combined organic layer was washed with saturated NaHCO$_3$ and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was distilled under ambient pressure to remove solvents, then under vacuum to yield 5-bromo-2-methylpent-2-ene (82%, 6.683 g) as a colorless oil. Spectral data were in accordance with those previously reported.$^1$

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.18 – 5.09 (m, 1H), 3.34 (t, $J$ = 7.3 Hz, 2H), 2.56 (q, $J$ = 7.3 Hz, 2H), 1.72 (s, 3H), 1.63 (s, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 135.2, 121.1, 33.0, 32.0, 25.8, 18.1.

Synthesis of 6-bromo-2-methylhex-2-ene

To an oven-dried round bottom flask equipped with a stir bar and a reflux condenser was added magnesium turnings (50 mmol, 1.2 g) and an iodine grain. The flask was sealed by a septum then evacuated and backfilled with nitrogen for three times. 2 mL solution of 5-bromo-2-methylpent-2-ene (50 mmol, 8.15 g) in dry THF (50 mL) was added via syringe. The reaction was initiated by a heat gun then the rest of the halide solution was added portionwise in 30 minutes. After the Grignard reaction was completed, paraformaldehyde (52.5 mmol, 1.58 g) was added in one portion and the
The resulting mixture was stirred at room temperature overnight. The reaction was then quenched with saturated NH₄Cl solution (50 mL). The aqueous phase was extracted by Et₂O (3 × 50 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to get the crude alcohol which was used directly in the next step without further purification.

To an oven-dried round bottom flask equipped with a stir bar was added tosyl chloride (50 mmol, 9.53 g), DCM (250 mL), DMAP (5 mmol, 610 mg), triethylamine (55 mmol, 7.65 mL), and the crude alcohol. The resulting solution was stirred at room temperature overnight. The reaction was then quenched with water (250 mL) and organic layer was separated. The aqueous phase was extracted by DCM (2 × 100 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to get the crude tosylate which was used directly in the next step without further purification.

To an oven-dried round bottom flask equipped with a stir bar and a reflux condenser was added LiBr (100 mmol, 8.7 g), dried acetone (50 mL), and the crude tosylate. After being refluxed for 1 h, the reaction was cooled to room temperature, diluted with hexane (200 mL), washed with water (100 mL) and brine (100 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was distilled under ambient pressure to remove solvents, then under vacuum to yield 6-bromo-2-methylhex-2-ene (43% over three steps, 3.81 g) as a colorless oil. Spectral data were in accordance with those previously reported.¹

¹H NMR (400 MHz, CDCl₃) δ 5.07 (tdt, J = 7.2, 2.8, 1.4 Hz, 1H), 3.40 (t, J = 6.7 Hz, 2H), 2.13 (q, J = 7.2 Hz, 2H), 1.89 (p, J = 6.9 Hz, 2H), 1.70 (d, J = 1.0 Hz, 3H), 1.63 (s, 3H);
¹³C NMR (101 MHz, CDCl₃) δ 133.2, 122.5, 33.6, 32.9, 26.4, 25.7, 17.8.

Synthesis of 1-bromo-2-(2-methylprop-1-en-1-yl)benzene

To an oven-dried round bottom flask equipped with a stir bar was added isopropyltriphenylphosphonium iodide (24 mmol, 8.64 g) which was prepared according to
The flask was sealed by a septum then evacuated and back filled with nitrogen for three times. After the addition of anhydrous THF (80 mL), the suspension was cooled to 0 °C in an ice bath. A solution of LiHMDS (24 mL, 1 M in THF) was added dropwise via syringe and the reaction mixture was stirred for 30 minutes followed by adding slowly 2-bromobenzaldehyde (20 mmol, 2.4 mL). After that, the ice bath was removed, and the reaction was stirred at room temperature overnight. The reaction mixture was filtered to remove insoluble inorganic salt and triphenylphosphine oxide followed by washing the solid with Et₂O. The filtrate was then quenched with saturated NH₄Cl solution (50 mL). The aqueous phase was extracted by Et₂O (3 × 50 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes) to afford the product (75%, 3.17 g) as a colorless oil. Spectral data were in accordance with those previously reported.

**Synthesis of N-tosyl amines**

To an oven-dried round bottom flask equipped with a stir bar and a reflux condenser was added p-toluenesulfonamide (1.1 equiv) and K₂CO₃ (1.1 equiv). The flask was sealed, evacuated then back-filled with nitrogen. After that, anhydrous acetone (0.5 M) and alkyl bromides (1 equiv) was added via syringe. The reaction mixture was refluxed under nitrogen for 24 h. After the reaction was complete, the mixture was filtered and concentrated under reduced pressure to remove acetone. The residue was re-dissolved by ethyl acetate, washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was then purified by column chromatography (silica gel, hexanes/ethyl acetate = 80/20) to give the target products.

4-Methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: Prepared according to the general procedure from p-toluenesulfonamide and 3,3-dimethylallyl bromide in a 40 mmol scale to yield the
title compound (60%, 7.170 g) as a white solid. Spectral data were in accordance with those previously reported.\(^1\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.75 (dd, \(J = 8.4, 1.8\) Hz, 2H), 7.33 – 7.26 (m, 2H), 5.08 – 5.00 (m, 1H), 4.43 (t, \(J = 5.5\) Hz, 1H), 3.52 (t, \(J = 6.4\) Hz, 2H), 2.42 (s, 3H), 1.62 (s, 3H), 1.53 (s, 3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.3, 137.6, 137.1, 129.6, 127.2, 118.9, 41.0, 25.6, 21.5, 17.8.

4-methyl-N-(4-methylpent-3-en-1-yl)benzenesulfonamide: Prepared according to the general procedure from p-toluenesulfonamide and 5-bromo-2-methylpent-2-ene in a 10-mmol scale to yield the title compound (70%, 1.173 g) as a viscous pale-yellow oil. Spectral data were in accordance with those previously reported.\(^1\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 – 7.71 (m, 2H), 7.30 (d, \(J = 7.9\) Hz, 2H), 4.97 – 4.86 (m, 1H), 4.50 – 4.30 (m, 1H), 2.94 (qd, \(J = 6.6, 2.7\) Hz, 2H), 2.42 (s, 3H), 2.14 (q, \(J = 6.9\) Hz, 2H), 1.66 (s, 3H), 1.55 (s, 3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.3, 137.0, 135.7, 129.7, 127.1, 119.7, 42.9, 28.2, 25.8, 21.5, 17.9.

Synthesis of 2-(2-methylprop-1-en-1-yl)benzaldehyde

To an oven-dried round bottom flask equipped with a stir bar and a reflux condenser was added Pd(PPh\(_3\))\(_4\) (1 mol%, 115.5 mg) and Na\(_2\)CO\(_3\) (3 equiv, 3.18 g). The flask was sealed by a septum then evacuated and backfilled with nitrogen for three times. Toluene (35 mL), EtOH (10 mL), distilled water (5 mL), 2-bromobenzaldehyde (10 mmol, 1.17 mL), and 2,2-dimethylethenylboronic acid pinacol ester (1.2 equiv, 2 g) were added successively via syringe. The reaction was refluxed until completion of reaction was judged by TLC. After cooling down to room temperature, the resulting mixture was diluted by adding water (50 mL), extracted with Et\(_2\)O (3×50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes/DCM = 4/1 to 1/1) to afford the title compound (82%, 1307 mg) as a pale-yellow oil. Spectral data were in accordance with those previously reported.\(^4\)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.24 (d, $J = 0.8$ Hz, 1H), 7.91 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.56 (td, $J = 7.5, 1.5$ Hz, 1H), 7.41 – 7.34 (m, 1H), 7.25 (ddt, $J = 7.7, 1.4, 0.8$ Hz, 1H), 6.63 – 6.58 (m, 1H), 1.99 (d, $J = 1.6$ Hz, 3H), 1.68 (d, $J = 1.5$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.8, 142.2, 139.3, 133.8, 133.6, 130.8, 128.0, 126.8, 121.2, 26.1, 19.4.
Synthesis of Substrates in Scheme 3

**General procedure 1**

To an oven-dried round bottom flask equipped with a stir bar and a reflux condenser was added 1,3-dicarbonyl (2 mmol), K$_2$CO$_3$ (1.5 equiv, 414 mg), KI (0.75 equiv, 249 mg), anhydrous DMF (10 mL), and alkyl bromide (1.1 equiv). The reaction mixture was stirred at 55 °C under nitrogen overnight. After the reaction was complete, the mixture was quenched by water (20 mL), extracted by Et$_2$O (3×10 mL), washed with brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was then purified by column chromatography (silica gel, hexanes/ethyl acetate = 98/2 to 90/10) to afford the target products.

**General procedure 2**

To an oven-dried round bottom flask equipped with a stir bar and a reflux condenser was added deoxybenzoin (2 mmol, 392 mg), 'BuOK (1.5 equiv, 336 mg), anhydrous THF (10 mL), and alkyl bromide (1.5 equiv). The reaction mixture was refluxed under nitrogen overnight. After the reaction was complete, the mixture was quenched by water (20 mL), extracted by Et$_2$O (3×10 mL), washed with brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was then purified by column chromatography (silica gel, hexanes/ethyl acetate = 95/5) to afford the target products.

**General procedure 3**

To an oven-dried Schlenk flask equipped with a stir bar was added Pd(OAc)$_2$ (1 mol%, 4.4 mg), dicyclohexylphenylphosphine (2 mol%, 11 mg), sodium tert-butoxide (1.3 equiv, 250 mg), and
ketone (1.2 equiv, if ketone is a solid). The flask was sealed by a septum and evacuated and backfilled with nitrogen for three times. Degassed anhydrous toluene (2 mL), aryl halide (2 mmol, 422 mg), and ketone (1.2 equiv, if ketone is a liquid) were added successively via syringe. The reaction mixture was then stirred at 80 °C overnight. After the reaction was complete, the reaction was quenched by saturated NH₄Cl solution (10 mL), extracted by Et₂O (3 × 10 mL), washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was then purified by column chromatography (silica gel, hexanes/toluene = 1/1 to 1/5) to afford the target product.

**General procedure 4**

![Chemical structure]

To an oven-dried round bottom flask equipped with a stir bar and a reflux condenser was added secondary tosyl amides (2 mmol), K₂CO₃ (1.5 equiv, 414 mg), anhydrous acetone (10 mL), and bromoketones (1.5 equiv). The reaction mixture was refluxed under nitrogen overnight. After the reaction was complete, the mixture was filtered and concentrated under reduced pressure to remove acetone. The residue was re-dissolved by ethyl acetate, washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was then purified by column chromatography (silica gel, hexanes/ethyl acetate = 95/5 to 80/20) to afford the target products.

**General procedure 5**

![Chemical structure]

To an oven-dried round bottom flask equipped with a stir bar and a reflux condenser was added magnesium turnings (6 mmol, 144 mg) and a small iodine grain. The flask was sealed by a septum then evacuated and backfilled with nitrogen for three times. 1 mL solution of aryl bromide (6.6 mmol, 8.15 g) in dry THF (12 mL) was added via syringe. The reaction was initiated by a heat gun then the rest of the halide solution was added portionwise in 30 minutes. The mixture was stirred at room temperature until magnesium was completely dissolved. After the Grignard reaction was completed, citronellal (5 mmol, 900 µL) was added slowly and the resulting mixture was stirred at room temperature until judged completion by TLC. The reaction was then quenched with saturated NH₄Cl solution (20 mL), extracted by Et₂O (20 mL × 3). The combined organic layer was washed with brine,
dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure to obtain the crude alcohol which was used directly without further purification.

To an oven-dried round bottom flask equipped with a stir bar was added dry DCM (50 mL) and cooled to -78 °C. Oxalyl chloride (2 M in DCM, 3 mL) then DMSO (5.5 mmol, 390 µL) was added, and the reaction was stirred for 20 minutes. A solution of crude alcohol in DCM (5 mL) was added and the reaction was further stirred for 20 minutes, followed by adding triethylamine (25 mmol, 3.5 mL). The resulting mixture was allowed to warm to room temperature and stir overnight. The reaction was quenched with saturated NH$_4$Cl solution (20 mL), extracted by DCM (20 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate = 98/2 to 90/10) to afford the target product.

**General procedure 6**

![Chemical reaction diagram]

To an oven-dried round bottom flask equipped with a stir and a reflux condenser filled with anhydrous CaCl$_2$ granules was added toluene (5 mL), AcOH (10 mol%, 12 µL), piperidine (10 mol%, 20 µL), diketone (2 mmol), and 2-(2-methylprop-1-en-1-yl)benzaldehyde (2 mmol, 320 mg). The resulting solution was refluxed until completion of the reaction was judged by TLC. After cooling down to room temperature, the reaction was quenched by adding distilled water (10 mL), extracted by Et$_2$O (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes/EA = 9/1 to 4/1) to afford the product.
Ethyl 2-benzoyl-6-methylhept-5-enooate (1a): Prepared according to the general procedure 1 from ethyl benzoyleacetate and 5-bromo-2-methylpent-2-ene in a 10-mmol scale to yield the title compound (78%, 2137 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^5\)

\(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 8.05 - 7.94\) (m, 2H), 7.65 – 7.55 (m, 1H), 7.54 – 7.44 (m, 2H), 5.18 – 5.09 (m, 1H), 4.37 – 4.29 (m, 1H), 4.17 (qd, \(J = 7.1, 0.7\) Hz, 2H), 2.14 – 2.02 (m, 4H), 1.69 (d, \(J = 1.4\) Hz, 3H), 1.54 (d, \(J = 1.4\) Hz, 3H), 1.20 (t, \(J = 7.1\) Hz, 3H);

\(^1^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta 195.4, 170.1, 136.3, 133.4, 128.7, 128.6, 123.0, 61.3, 53.4, 29.0, 25.9, 25.7, 17.6, 14.0.\)

Ethyl 2-(4-methoxybenzoyl)-6-methylhept-5-enooate (1b): Prepared according to the general procedure 1 from ethyl 3-(4-methoxyphenyl)-3-oxopropanoate and 5-bromo-2-methylpent-2-ene to yield the title compound (77%, 469 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^5\)

\(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 8.02 - 7.96\) (m, 2H), 7.01 – 6.92 (m, 2H), 5.16 – 5.08 (m, 1H), 4.33 – 4.25 (m, 1H), 4.16 (qd, \(J = 7.1, 0.9\) Hz, 2H), 3.90 (s, 3H), 2.12 – 2.01 (m, 4H), 1.70 (d, \(J = 1.3\) Hz, 3H), 1.54 (d, \(J = 1.4\) Hz, 3H), 1.20 (t, \(J = 7.1\) Hz, 3H);

\(^1^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta 193.8, 170.3, 163.8, 133.2, 131.0, 129.4, 123.1, 113.84, 61.2, 55.5, 53.2, 29.1, 25.9, 25.7, 17.7, 14.1.\)

Ethyl 6-methyl-2-(4-nitrobenzoyl)hept-5-enooate (1c): Prepared according to the general procedure 1 from ethyl 3-(4-nitrophenyl)-3-oxopropanoate and 5-bromo-2-methylpent-2-ene to yield the title compound (20%, 122 mg) as a yellow oil.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.37 – 8.31 (m, 2H), 8.17 – 8.11 (m, 2H), 5.14 – 5.05 (m, 1H), 4.34 – 4.28 (m, 1H), 4.17 (q, $J$ = 7.1 Hz, 2H), 2.14 – 2.03 (m, 4H), 1.68 (d, $J$ = 1.3 Hz, 3H), 1.53 (d, $J$ = 1.3 Hz, 3H), 1.20 (t, $J$ = 7.1 Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.0, 169.3, 150.4, 140.9, 133.8, 129.6, 123.9, 122.8, 61.7, 53.9, 28.8, 25.8, 25.7, 17.7, 14.0;

ESI-HRMS: calcld for C$_{17}$H$_{21}$NO$_5$Na$: m/z = 342.1312$, found: $m/z = 342.1314$;
FTIR (neat): 2973, 2930, 1737, 1692, 1604, 1526, 1446, 1345, 1230 cm$^{-1}$.

2-(4-methylpent-3-en-1-yl)-1,3-diphenylpropane-1,3-dione (1d): Prepared according to the general procedure 1 from ethyl dibenzoylmethane and 5-bromo-2-methylpent-2-ene to yield the title compound (55%, 337 mg) as a colorless oil. Spectral data were in accordance with those previously reported.$^5$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 – 7.46 (m, 1H), 7.45 – 7.37 (m, 2H), 7.35 – 7.28 (m, 4H), 7.24 – 7.19 (m, 1H), 6.93 – 6.83 (m, 1H), 5.69 (s, $J = 1.5$ Hz, 3H), 1.69 (d, $J = 1.3$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.2, 136.2, 133.7, 133.4, 128.9, 128.6, 123.2, 56.2, 29.4, 26.5, 25.7, 17.8.

6-methyl-1,2-diphenylhept-5-en-1-one (1e): Prepared according to the general procedure 2 from deoxybenzoin and 5-bromo-2-methylpent-2-ene to yield the title compound (80%, 445 mg) as a colorless oil. Spectral data were in accordance with those previously reported.$^5$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 – 7.93 (m, 2H), 7.55 – 7.46 (m, 1H), 7.45 – 7.37 (m, 2H), 7.35 – 7.28 (m, 4H), 7.24 – 7.19 (m, 1H), 5.17 – 5.11 (m, 1H), 4.59 (t, $J = 7.2$ Hz, 1H), 2.35 – 2.21 (m, 1H), 2.03 – 1.95 (m, 2H), 1.93 – 1.83 (m, 1H), 1.69 (d, $J = 1.5$ Hz, 3H), 1.50 (d, $J = 1.3$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 200.1, 139.7, 137.0, 132.8, 132.5, 128.8, 128.6, 128.5, 128.3, 126.9, 123.8, 52.8, 34.1, 26.0, 25.7, 17.7.
Ethyl 3-(3-methoxyphenyl)-3-oxopropanoate (1f): Prepared according to the general procedure 1 from ethyl 3-(3-methoxyphenyl)-3-oxopropanoate and 5-bromo-2-methylpent-2-ene to yield the title compound (53%, 322 mg) as a colorless oil. Spectral data were in accordance with those previously reported.¹

¹H NMR (400 MHz, CDCl₃) δ 7.57 (dt, J = 7.7, 1.2 Hz, 1H), 7.53 (dd, J = 2.6, 1.6 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.14 (ddd, J = 8.2, 2.7, 0.9 Hz, 1H), 5.17 – 5.09 (m, 1H), 4.30 (td, J = 6.6, 1.4 Hz, 1H), 4.21 – 4.13 (m, 2H), 3.88 (s, 3H), 2.14 – 1.99 (m, 4H), 1.70 (d, J = 1.3 Hz, 3H), 1.55 (d, J = 1.5 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H);
¹³C NMR (101 MHz, CDCl₃) δ 195.2, 170.1, 159.9, 137.7, 133.4, 129.6, 123.0, 121.2, 120.1, 112.7, 61.3, 55.4, 53.6, 29.1, 25.9, 25.7, 17.7, 14.0.

Ethyl 2-(2-naphthoyl)-6-methylhept-5-enoate (1g): Prepared according to the general procedure 1 from ethyl 3-(naphthalen-2-yl)-3-oxopropanoate and 5-bromo-2-methylpent-2-ene to yield the title compound (70%, 454 mg) as a colorless oil. Spectral data were in accordance with those previously reported.⁵

¹H NMR (400 MHz, CDCl₃) δ 8.53 (d, J = 1.8 Hz, 1H), 8.06 (dd, J = 8.6, 1.8 Hz, 1H), 8.00 (dd, J = 8.0, 1.4 Hz, 1H), 7.96 – 7.85 (m, 2H), 7.66 – 7.56 (m, 2H), 5.21 – 5.13 (m, 1H), 4.56 – 4.43 (m, 1H), 4.23 – 4.13 (m, 2H), 2.19 – 2.09 (m, 4H), 1.71 (d, J = 1.4 Hz, 3H), 1.54 (d, J = 1.3 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H);
¹³C NMR (101 MHz, CDCl₃) δ 195.4, 170.2, 135.7, 133.7, 133.4, 132.5, 130.5, 129.7, 128.7, 128.6, 127.8, 126.9, 124.2, 123.1, 61.4, 53.5, 29.2, 26.0, 25.8, 17.7, 14.1.

2,6-dimethyl-1-phenylhept-5-en-1-one (1h)
An oven-dried round bottom flask equipped with a stir bar and a reflux condenser was evacuated and backfilled with nitrogen for three times. Propiophenone (5 mmol, 663 µL) and anhydrous THF (5 mL) was added via syringe, and the solution was cooled down to -78 °C. LiHMDS (1 M in THF, 5.5 mL) was added slowly. The resulting mixture was stirred for 30 min before warming up to room temperature. After 5-bromo-2-methylpent-2-ene (1.1 equiv) was added via syringe, the mixture was refluxed overnight. After the reaction was complete, the mixture was quenched by saturated NH₄Cl solution (10 mL), extracted by Et₂O (3 × 10 mL), washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was then purified by column chromatography (silica gel, hexanes/ethyl acetate = 98/2) to afford the target product (25%, 270 mg) as a colorless oil. Spectral data were in accordance with those previously reported.⁵

¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.93 (m, 2H), 7.61 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 5.15 – 5.07 (m, 1H), 3.50 (h, J = 6.8 Hz, 1H), 2.04 (q, J = 7.4 Hz, 2H), 1.95 – 1.85 (m, 1H), 1.68 (d, J = 1.5 Hz, 3H), 1.54 (d, J = 1.3 Hz, 3H), 1.22 (d, J = 6.8 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 204.5, 136.8, 132.8, 132.3, 128.6, 128.3, 123.9, 39.9, 33.7, 25.8, 25.7, 17.6, 17.3.

**Ethyl 2-(3,5-dichlorobenzoyl)-6-methylhept-5-enoate (1i):** To an oven-dried 20 mL vial equipped with a stir bar was added anhydrous THF (10 mL) and NaH (60% dispersion in mineral oil, 1.1 equiv, 88 mg). To this suspension, ethyl 3,5-dichlorobenzoylacetae (2 mmol, 522 mg) was added slowly and the solution was stirred for 15 minutes at room temperature. Next, homoprenyl iodide (2 mmol, 280 µL) was added. The vial was capped, and the reaction was stirred at 80 °C overnight. After cooling to room temperature, the reaction was quenched by saturated NH₄Cl solution (10 mL), extracted by Et₂O (3 × 10 mL), washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was then purified by column chromatography (silica gel, hexanes/ethyl acetate = 98/2 to 95/5) to afford the title compound (39%, 270 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 1.9 Hz, 2H), 7.58 (t, J = 1.9 Hz, 1H), 5.15 – 5.07 (m, 1H), 4.24 – 4.14 (m, 3H), 2.14 – 1.99 (m, 4H), 1.70 (d, J = 1.3 Hz, 3H), 1.54 (d, J = 1.5 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H);
13C NMR (101 MHz, CDCl3) δ 193.1, 169.3, 138.8, 135.7, 133.8, 133.0, 127.0, 122.8, 61.6, 53.4, 28.9, 25.7, 25.7, 17.7, 14.0;

ESI-HRMS: calcd for C17H20\textsubscript{35}Cl\textsubscript{2}O\textsubscript{3}H\textsuperscript{+}: m/z = 343.0862, found: m/z = 343.0861;

FTIR (neat): 3075, 2978, 2920, 1737, 1694, 1562, 1402, 1360, 1315, 1214 cm\textsuperscript{-1}.

4-methyl-N-(3-methylbut-2-en-1-yl)-N-(1-oxo-1-phenylpropan-2-yl)benzenesulfonamide (1j):
Prepared according to the general procedure 4 from 2'-bromopropiophenone and 4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide to yield the title compound (68%, 505 mg) as a white solid. Spectral data were in accordance with those previously reported.\textsuperscript{6}

1H NMR (400 MHz, CDCl3) δ 8.13 – 8.04 (m, 2H), 7.71 – 7.64 (m, 2H), 7.62 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 7.28 (d, J = 8.2 Hz, 2H), 5.56 (q, J = 6.8 Hz, 1H), 4.84 – 4.77 (m, 1H), 3.89 (dd, J = 15.5, 6.2 Hz, 1H), 3.62 (dd, J = 15.5, 7.8 Hz, 1H), 2.43 (s, 3H), 1.49 (d, J = 1.5 Hz, 3H), 1.47 (s, 3H), 1.26 (d, J = 6.9 Hz, 3H);

13C NMR (101 MHz, CDCl3) δ 198.1, 143.5, 137.1, 136.8, 135.8, 133.0, 129.6, 128.8, 128.4, 127.6, 120.4, 56.0, 42.6, 25.5, 21.5, 17.6, 13.2.

4-methyl-N-(3-methylbut-2-en-1-yl)-N-(1-oxo-1-(p-tolyl)propan-2-yl)benzenesulfonamide (1k):
Prepared according to the general procedure 4 from 2'-bromo-4-methylpropiophenone and 4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide in a 10-mmol scale to yield the title compound (65%, 2503 mg) as a white solid. Spectral data were in accordance with those previously reported.\textsuperscript{6}

1H NMR (400 MHz, CDCl3) δ 8.03 – 7.94 (m, 2H), 7.72 – 7.64 (m, 2H), 7.33 – 7.23 (m, 4H), 5.56 (q, J = 6.9 Hz, 1H), 4.87 – 4.79 (m, 1H), 3.88 (dd, J = 15.6, 6.3, 1H), 3.65 (dd, J = 15.6, 7.6 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 1.50 (d, J = 1.3 Hz, 3H), 1.49 (d, J = 1.2 Hz, 3H), 1.25 (d, J = 6.9 Hz, 3H);

13C NMR (101 MHz, CDCl3) δ 197.7, 143.8, 143.4, 137.3, 136.3, 133.2, 129.6, 129.2, 128.9, 127.6, 120.6, 55.8, 42.6, 25.5, 21.7, 21.5, 17.6, 13.4.
4-methyl-N-(3-methylbut-2-en-1-yl)-N-(2-oxo-2-(p-tolyl)ethyl)benzenesulfonamide (1):
Prepared according to the general procedure 4 from 2′-bromo-4-methylacetophenone and 4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide to yield the title compound (61%, 453 mg) as a white solid. Spectral data were in accordance with those previously reported.\(^1\)

\[\text{\(^1\)H NMR (400 MHz, CDCl}_3\) \(\delta\) 7.87 – 7.81 (m, 2H), 7.80 – 7.74 (m, 2H), 7.36 – 7.25 (m, 4H), 5.08 – 5.00 (m, 1H), 4.65 (s, 2H), 3.91 (d, \(J = 7.5\) Hz, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 1.62 (d, \(J = 1.3\) Hz, 3H), 1.47 (d, \(J = 1.4\) Hz, 3H);

\[\text{\(^13\)C NMR (101 MHz, CDCl}_3\) \(\delta\) 194.1, 144.5, 143.2, 139.0, 137.0, 132.7, 129.5, 129.4, 128.1, 127.5, 118.4, 51.8, 45.5, 25.7, 21.7, 21.6, 17.6.\]

N-(2-(4-chlorophenyl)-2-oxoethyl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (1m): Prepared according to the general procedure 4 from 2′-bromo-4-chloroacetophenone and 4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide to yield the title compound (41%, 333 mg) as a yellow solid.

\[\text{\(^1\)H NMR (400 MHz, CDCl}_3\) \(\delta\) 7.94 – 7.88 (m, 2H), 7.78 – 7.73 (m, 2H), 7.50 – 7.44 (m, 2H), 7.34 (d, \(J = 8.1\) Hz, 2H), 5.04 – 4.95 (m, 1H), 4.57 (s, 2H), 3.87 (d, \(J = 7.5\) Hz, 2H), 2.46 (s, 3H), 1.60 (d, \(J = 1.2\) Hz, 3H), 1.47 (d, \(J = 1.4\) Hz, 3H);

\[\text{\(^13\)C NMR (101 MHz, CDCl}_3\) \(\delta\) 193.6, 143.5, 140.0, 139.4, 136.4, 133.5, 129.6, 129.6, 129.1, 127.5, 118.1, 52.5, 45.8, 25.7, 21.6, 17.6;

\text{ESI-HRMS: calcd for C}_{20}\text{H}_{22}\text{ClNO}_{3}\text{SNa}^{+}: m/z = 414.0901, found: m/z = 414.0905;

\text{FTIR (neat): 2969, 2878, 1684, 1589, 1490, 1429, 1400, 1346, 1277, 1235 cm}^{-1.}\]
2-(2-(2-methylprop-1-en-1-yl)phenyl)-1-phenylpropan-1-one (1n): Prepared according to the general procedure 3 from propiophenone and 1-bromo-2-(2-methylprop-1-en-1-yl)benzene to yield the title compound (50%, 264 mg) as a pale-yellow solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.90 – 7.80 (m, 2H), 7.49 – 7.42 (m, 1H), 7.37 – 7.30 (m, 2H), 7.20 – 7.11 (m, 4H), 6.48 – 6.42 (m, 1H), 4.81 (q, $J$ = 6.8 Hz, 1H), 1.98 (d, $J$ = 1.6 Hz, 3H), 1.72 (d, $J$ = 1.5 Hz, 3H), 1.48 (d, $J$ = 6.8 Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 201.0, 140.2, 137.4, 136.8, 136.5, 132.6, 130.8, 128.6, 128.3, 127.3, 126.8, 126.5, 123.6, 44.7, 26.0, 19.2, 18.1;

ESI-HRMS: calcd for C$_{19}$H$_{20}$OH$^+$: m/z = 265.1587, found: m/z = 265.1586;

FTIR (neat): 3059, 2970, 2933, 2869, 1681, 1596, 1484, 1446, 1381, 1333, 1307, 1222 cm$^{-1}$.

2-(2-(2-methylprop-1-en-1-yl)phenyl)-1,2-diphenylethan-1-one (1o): Prepared according to the general procedure 3 from deoxybenzoin and 1-bromo-2-(2-methylprop-1-en-1-yl)benzene to yield the title compound (85%, 554 mg) as a pale-yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 – 7.88 (m, 2H), 7.56 – 7.45 (m, 1H), 7.44 – 7.32 (m, 4H), 7.31 – 7.16 (m, 6H), 7.13 (dd, $J$ = 7.5, 1.9 Hz, 1H), 6.27 (d, $J$ = 1.4 Hz, 1H), 6.21 (s, 1H), 1.79 (d, $J$ = 1.6 Hz, 3H), 1.59 (d, $J$ = 1.5 Hz, 4H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.6, 138.00, 137.96, 137.6, 137.0, 132.8, 130.5, 129.7, 128.7, 128.63, 128.59, 128.55, 128.5, 127.0, 126.9, 126.8, 123.9, 56.6, 25.6, 19.0;

ESI-HRMS: calcd for C$_{24}$H$_{22}$OH$^+$: m/z = 327.1743, found: m/z = 327.1748;

FTIR (neat): 3062, 2965, 2910, 1678, 1596, 1497, 1449, 1378, 1327, 1300, 1242, 1212 cm$^{-1}$.
1-(4-chlorophenyl)-2-(2-(2-methylprop-1-en-1-yl)phenyl)-2-phenylethan-1-one (1p): Prepared according to the general procedure 3 from benzyl 4-chlorophenyl ketone and 1-bromo-2-(2-methylprop-1-en-1-yl)benzene to yield the title compound (60%, 431 mg) as a viscous colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 – 7.82 (m, 2H), 7.39 – 7.33 (m, 4H), 7.31 – 7.16 (m, 6H), 7.08 (dd, $J = 7.8, 1.6$ Hz, 1H), 6.24 (s, 1H), 6.12 (s, 1H), 1.81 (d, $J = 1.6$ Hz, 3H), 1.59 (d, $J = 1.4$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.4, 139.2, 137.9, 137.8, 137.6, 135.2, 130.6, 130.1, 129.6, 128.8, 128.62, 128.57, 127.2, 127.1, 126.9, 123.8, 56.7, 25.6, 19.0;

ESI-HRMS: calcd for C$_{24}$H$_{21}$ClOH$: m/z = 361.1354$, found: $m/z = 361.1353$;

FTIR (neat): 3065, 3030, 2974, 2911, 1686, 1588, 1486, 1447, 1399, 1276, 1206 cm$^{-1}$.

1-(4-methoxyphenyl)-2-(2-(2-methylprop-1-en-1-yl)phenyl)-2-phenylethan-1-one (1q): Prepared according to the general procedure 3 from benzyl 4-methoxyphenyl ketone and 1-bromo-2-(2-methylprop-1-en-1-yl)benzene to yield the title compound (43%, 306 mg) as a viscous colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97 – 7.88 (m, 2H), 7.38 – 7.30 (m, 2H), 7.27 – 7.20 (m, 4H), 7.20 – 7.10 (m, 3H), 6.92 – 6.81 (m, 2H), 6.26 (d, $J = 1.4$ Hz, 1H), 6.15 (s, 1H), 3.85 (s, 3H), 1.81 (d, $J = 1.5$ Hz, 3H), 1.61 – 1.58 (m, 3H);

$^{13}$C NMR (76 MHz, CDCl$_3$) $\delta$ 197.1, 163.2, 138.4, 138.1, 137.9, 137.4, 131.0, 130.4, 129.9, 129.6, 128.6, 128.5, 126.9, 126.82, 126.79, 123.9, 113.6, 56.2, 55.4, 25.6, 19.1;

ESI-HRMS: calcd for C$_{25}$H$_{24}$O$_2$H$: m/z = 357.1849$, found: $m/z = 357.1852$;

FTIR (neat): 3064, 3027, 2968, 2909, 1677 1598, 1510, 1443, 1420, 1377, 1313, 1260, 1210 cm$^{-1}$.  

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2-(2-(2-methylprop-1-en-1-yl)phenyl)-3,4-dihyronaphthalen-1(2H)-one (1r): Prepared according to the general procedure 3 from α-tetralone and 1-bromo-2-(2-methylprop-1-en-1-yl)benzene to yield the title compound (27%, 147 mg) as a viscous brown oil.

**1H NMR (400 MHz, CDCl₃)** \(\delta\) 8.12 (dd, \(J = 7.8, 1.6\) Hz, 1H), 7.53 (td, \(J = 7.5, 1.5\) Hz, 1H), 7.37 (t, \(J = 7.6\) Hz, 1H), 7.32 (d, \(J = 7.6\) Hz, 1H), 7.28 – 7.22 (m, 2H), 7.21 – 7.16 (m, 1H), 7.15 – 7.08 (m, 1H), 6.26 (s, 1H), 4.04 (dd, \(J = 12.1, 4.8\) Hz, 1H), 3.15 (ddd, \(J = 15.9, 11.3, 4.6\) Hz, 1H), 3.05 (dt, \(J = 16.6, 4.2\) Hz, 1H), 2.41 (dtd, \(J = 13.3, 11.6, 4.4\) Hz, 1H), 2.30 (dq, \(J = 13.3, 4.5\) Hz, 1H), 1.86 (d, \(J = 1.6\) Hz, 3H), 1.70 (d, \(J = 1.5\) Hz, 3H);

**13C NMR (101 MHz, CDCl₃)** \(\delta\) 198.4, 144.1, 138.9, 138.4, 136.7, 133.3, 133.2, 130.3, 128.8, 127.7, 127.6, 126.71, 126.69, 126.5, 123.8, 51.8, 30.8, 29.4, 25.9, 19.4;

**ESI-HRMS**: calcd for C₂₀H₂₀OH⁺: m/z = 277.1587, found: m/z = 277.1587;

**FTIR (neat)**: 3065, 3016, 2931, 2868, 1680, 1599, 1484, 1451, 1376, 1299, 1273, 1220 cm⁻¹.

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2-(2-(2-methylprop-1-en-1-yl)benzylidene)-1,3-diphenylpropane-1,3-dione (1s): Prepared according to the general procedure 6 from dibenzoylethane and 2-(2-methylprop-1-en-1-yl)benzaldehyde to yield the title compound (89%, 752 mg) as a pale-yellow solid.

**1H NMR (300 MHz, CDCl₃)** \(\delta\) 7.98 – 7.84 (m, 4H), 7.75 (s, 1H), 7.65 – 7.55 (m, 1H), 7.55 – 7.44 (m, 3H), 7.43 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 7.23 (td, \(J = 7.5, 1.4\) Hz, 1H), 7.12 (dt, \(J = 7.8, 0.8\) Hz, 1H), 7.08 – 6.98 (m, 1H), 6.24 (s, 1H), 1.86 (d, \(J = 1.5\) Hz, 3H), 1.65 (d, \(J = 1.5\) Hz, 3H);

**13C NMR (76 MHz, CDCl₃)** \(\delta\) 196.4, 194.9, 143.8, 139.5, 139.3, 138.4, 137.5, 136.7, 133.6, 132.5, 132.4, 130.1, 129.7, 129.6, 129.3, 129.0, 128.7, 128.4, 126.5, 122.9, 26.0, 19.5;

**ESI-HRMS**: calcd for C₂₆H₂₂O₂H⁺: m/z = 367.1693, found: m/z = 367.1685;

**FTIR (neat)**: 2981, 1667, 1637, 1496, 1449, 1368, 1259, 1234 cm⁻¹.
3-(2-(2-methylprop-1-en-1-yl)benzylidene)pentane-2,4-dione (1t): Prepared according to the general procedure 6 from acetylacetone and 2-(2-methylprop-1-en-1-yl)benzaldehyde to yield the title compound (77%, 373 mg) as an orange oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.70 (s, 1H), 7.43 – 7.33 (m, 1H), 7.32 – 7.27 (m, 1H), 7.27 – 7.19 (m, 2H), 6.30 (s, 1H), 2.40 (s, 3H), 2.20 (s, 3H), 1.98 (d, $J$ = 1.6 Hz, 3H), 1.69 (d, $J$ = 1.5 Hz, 3H);

$^{13}$C NMR (76 MHz, CDCl$_3$) $\delta$ 205.0, 196.5, 142.6, 140.0, 139.3, 138.9, 132.0, 130.2, 130.0, 128.7, 126.8, 122.6, 31.6, 26.9, 26.2, 19.6;

ESI-HRMS: calcd for C$_{16}$H$_{18}$O$_2$H$^+$: m/z = 243.1380, found: m/z = 243.1372;

FTIR (neat): 2969, 2911, 2854, 1688, 1657, 1594, 1475, 1442, 1377, 1354, 1296, 1235 cm$^{-1}$.

(E)-2-(2-(2-methylprop-1-en-1-yl)benzylidene)-1-phenylbutane-1,3-dione (1u): Prepared according to the general procedure 6 from acetylacetone and 2-(2-methylprop-1-en-1-yl)benzaldehyde to yield the title compound (69%, 420 mg) as a viscous pale-yellow oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.02 (s, 1H), 7.90 – 7.81 (m, 2H), 7.57 – 7.47 (m, 1H), 7.43 – 7.33 (m, 2H), 7.26 – 7.17 (m, 2H), 7.16 – 7.08 (m, 1H), 7.04 – 6.93 (m, 1H), 6.36 (s, 1H), 2.41 (s, 3H), 2.01 (d, $J$ = 1.5 Hz, 3H), 1.70 (d, $J$ = 1.4 Hz, 3H);

$^{13}$C NMR (76 MHz, CDCl$_3$) $\delta$ 197.8, 196.1, 141.0, 139.6, 138.5, 136.4, 133.8, 131.9, 130.2, 129.8, 129.1, 128.9, 128.7, 126.5, 122.8, 27.4, 26.2, 19.6;

ESI-HRMS: calcd for C$_{21}$H$_{20}$O$_2$H$^+$: m/z = 305.1536, found: m/z = 305.1536;

FTIR (neat): 2977, 2912, 2857, 1657, 1595, 1475, 1449, 1376, 1297, 1224 cm$^{-1}$.
4-methyl-N-(4-methylpent-3-en-1-yl)-N-(1-oxo-1-(p-tolyl)propan-2-yl)benzenesulfonamide (1v): Prepared according to the general procedure 4 from 2′-bromo-4-methylpropiophenone and 4-methyl-N-(4-methylpent-3-en-1-yl)benzenesulfonamide to yield the title compound (85%, 678 mg) as a yellow solid.

1H NMR (400 MHz, CDCl₃) δ 8.05 – 7.99 (m, 2H), 7.75 – 7.67 (m, 2H), 7.28 (d, J = 17.2 Hz, 4H), 5.61 (q, J = 6.9 Hz, 1H), 4.97 – 4.87 (m, 1H), 3.19 – 3.10 (m, 1H), 3.04 – 2.94 (m, 1H), 2.45 (s, 3H), 2.43 (s, 3H), 2.19 – 2.01 (m, 2H), 1.61 (d, J = 1.3 Hz, 3H), 1.54 (d, J = 1.4 Hz, 3H), 1.21 (d, J = 6.9 Hz, 3H);

13C NMR (101 MHz, CDCl₃) δ 197.4, 144.4, 143.5, 137.0, 134.4, 132.8, 129.6, 129.4, 129.0, 127.5, 120.1, 55.5, 44.5, 29.9, 25.6, 21.7, 21.5, 17.7, 13.8;

ESI-HRMS: calcd for C_{23}H_{29}NO_{3}SNa⁺: m/z = 422.1760, found: m/z = 422.1763;

FTIR (neat): 2968, 2925, 2876, 1683, 1605, 1437, 1381, 1334, 1310, 1228 cm⁻¹.

\[ \begin{align*}
\text{CHO} & + \text{Ts} \rightarrow \text{CHO} \\
\text{F} & \text{Ts}
\end{align*} \]

N-(2-formylphenyl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (1w): 4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (2 mmol, 478 mg) was dissolved in 10 ml of DMF, then NaOH (4.0 mmol, 80 mg) and 2-fluorobenzaldehyde (2.2 mmol, 273 mg) were successively added. The mixture was stirred at 120 °C overnight. The reaction was then quenched by adding water (20 mL), extracted with Et₂O (3 × 10 mL). The combined organic phase was washed by water and brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes/DCM/EA = 18/1/1 to 8/1/1) to afford the title compound (65%, 446 mg) as a viscous pale-yellow oil. Spectral data were in accordance with those previously reported.⁷

1H NMR (400 MHz, CDCl₃) δ 10.35 (d, J = 0.8 Hz, 1H), 8.02 – 7.96 (m, 1H), 7.57 – 7.51 (m, 2H), 7.49 – 7.44 (m, 2H), 7.33 – 7.29 (m, 2H), 6.81 – 6.76 (m, 1H), 5.13 – 5.06 (m, 1H), 4.54 (s, 1H), 3.91 (s, 1H), 2.47 (s, 3H), 1.58 (d, J = 1.3 Hz, 3H), 1.42 (d, J = 1.4 Hz, 3H);

13C NMR (101 MHz, CDCl₃) δ 190.4, 144.0, 141.7, 139.4, 136.3, 135.0, 134.0, 129.7, 128.6, 128.2, 128.1, 127.9, 117.3, 49.3, 25.6, 21.6, 17.6.
1-(3,5-dichlorophenyl)-3,7-dimethyloct-6-en-1-one (1x): Prepared according to the general procedure 5 from 1-bromo-3,5-dichlorobenzene and citronellal to yield the title compound (63%, 942 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^8\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (d, \(J = 2.0\) Hz, 2H), 7.56 (t, \(J = 1.9\) Hz, 1H), 5.15 – 5.06 (m, 1H), 2.93 (dd, \(J = 16.1, 5.6\) Hz, 1H), 2.72 (dd, \(J = 16.2, 8.1\) Hz, 1H), 2.26 – 2.12 (m, 1H), 2.12 – 1.94 (m, 2H), 1.71 (d, \(J = 1.3\) Hz, 3H), 1.63 (d, \(J = 0.9\) Hz, 3H), 1.49 – 1.37 (m, 1H), 1.37 – 1.26 (m, 1H), 0.98 (d, \(J = 6.6\) Hz, 3H);

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 197.7, 139.8, 135.6, 132.5, 131.8, 126.6, 124.2, 46.0, 37.0, 29.3, 25.7, 25.5, 19.9, 17.7.

3,7-dimethyl-1-(4-(trifluoromethyl)phenyl)oct-6-en-1-one (1y): Prepared according to the general procedure 5 from 1-bromo-4-(trifluoromethyl)benzene and citronellal to yield the title compound (33%, 485 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^8\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 (d, \(J = 7.8\) Hz, 2H), 7.75 (d, \(J = 8.1\) Hz, 2H), 5.15 – 5.08 (m, 1H), 3.01 (dd, \(J = 16.0, 5.5\) Hz, 1H), 2.79 (dd, \(J = 15.9, 8.1\) Hz, 1H), 2.28 – 2.13 (m, 1H), 2.13 – 1.94 (m, 2H), 1.70 (d, \(J = 1.4\) Hz, 3H), 1.63 (d, \(J = 1.5\) Hz, 3H), 1.50 – 1.39 (m, 1H), 1.38 – 1.27 (m, 1H), 1.00 (d, \(J = 6.7\) Hz, 3H);

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 199.4, 140.1, 134.2 (q, \(J = 32.3\) Hz), 131.7, 128.4, 125.6 (q, \(J = 3.5\) Hz), 124.2, 123.6 (q, \(J = 271\) Hz), 46.2, 37.1, 29.4, 25.7, 25.5, 19.9, 17.7;

\(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -63.1.
3,7-dimethyl-1-phenyloct-6-en-1-one (3a): Prepared according to the general procedure 5 from bromobenzene and citronellal to yield the title compound (54%, 621 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^9\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 – 7.93 (m, 2H), 7.61 – 7.53 (m, 1H), 7.52 – 7.44 (m, 2H), 5.16 – 5.08 (m, 1H), 2.99 (dd, \(J = 15.7, 5.5\) Hz, 1H), 2.77 (dd, \(J = 15.7, 8.1\) Hz, 1H), 2.27 – 2.15 (m, 1H), 2.14 – 1.96 (m, 2H), 1.70 (d, \(J = 1.3\) Hz, 3H), 1.62 (d, \(J = 1.3\) Hz, 3H), 1.51 – 1.38 (m, 1H), 1.36 – 1.26 (m, 1H), 0.99 (d, \(J = 6.6\) Hz, 3H);

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 200.5, 137.5, 132.8, 131.5, 128.6, 128.1, 124.4, 45.9, 37.2, 29.6, 25.7, 25.6, 20.0, 17.7.

1-(4-methoxyphenyl)-3,7-dimethyloct-6-en-1-one (3b): Prepared according to the general procedure 5 from commercial 4-methoxyphenyl magnesium bromide (0.5 M in THF) and citronellal to yield the title compound (38%, 494 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^9\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 – 7.91 (m, 2H), 7.01 – 6.90 (m, 2H), 5.16 – 5.08 (m, 1H), 3.89 (s, 3H), 2.93 (dd, \(J = 15.4, 5.6\) Hz, 1H), 2.71 (dd, \(J = 15.4, 8.2\) Hz, 1H), 2.26 – 2.13 (m, 1H), 2.13 – 1.93 (m, 2H), 1.70 (d, \(J = 1.3\) Hz, 3H), 1.62 (d, \(J = 1.3\) Hz, 3H), 1.49 – 1.39 (m, 1H), 1.35 – 1.25 (m, 1H), 0.98 (d, \(J = 6.6\) Hz, 3H);

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 199.1, 163.3, 131.5, 130.6, 130.4, 124.5, 113.7, 55.5, 45.6, 37.3, 29.8, 25.7, 25.6, 20.0, 17.7.

3,7-dimethyl-1-(p-tolyl)oct-6-en-1-one (3c): Prepared according to the general procedure 5 from 4-bromotoluene and citronellal to yield the title compound (57%, 695 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^9\)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 – 7.83 (m, 2H), 7.27 (d, $J = 6.4$ Hz, 2H), 5.16 – 5.08 (m, 1H), 2.96 (dd, $J = 15.5$, 5.5 Hz, 1H), 2.73 (dd, $J = 15.5$, 8.2 Hz, 1H), 2.43 (s, 3H), 2.27 – 2.13 (m, 1H), 2.13 – 1.92 (m, 2H), 1.70 (d, $J = 1.4$ Hz, 3H), 1.62 (d, $J = 1.3$ Hz, 3H), 1.49 – 1.38 (m, 1H), 1.36 – 1.25 (m, 2H), 0.98 (d, $J = 6.7$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 200.1, 143.6, 135.0, 131.5, 129.2, 128.3, 124.5, 45.8, 37.2, 29.7, 25.7, 25.6, 21.6, 19.9, 17.7.

1-(3,5-dimethylphenyl)-3,7-dimethyloct-6-en-1-one (3d): Prepared according to the general procedure 5 from 1-bromo-3,5-dimethylbenzene and citronellal to yield the title compound (56%, 722 mg) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 – 7.55 (m, 2H), 7.22 – 7.19 (m, 1H), 5.17 – 5.09 (m, 1H), 2.95 (dd, $J = 15.7$, 5.5 Hz, 1H), 2.74 (dd, $J = 15.7$, 8.2 Hz, 1H), 2.39 (d, $J = 0.7$ Hz, 6H), 2.35 – 2.13 (m, 2H), 2.14 – 1.96 (m, 2H), 1.70 (d, $J = 1.3$ Hz, 3H), 1.63 (d, $J = 1.3$ Hz, 3H), 1.50 – 1.37 (m, 1H), 1.36 – 1.25 (m, 1H), 0.98 (d, $J = 6.6$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 200.9, 138.2, 137.7, 134.5, 131.5, 125.9, 124.5, 46.0, 37.2, 29.6, 25.7, 25.6, 21.3, 20.0, 17.7;

ESI-HRMS: calcd for C$_{18}$H$_{26}$ONa$: m/z = 281.1876, found: m/z = 281.1878;

FTIR (neat): 2964, 2920, 1680, 1606, 1448, 1378, 1307 cm$^{-1}$.

1-(3-methoxyphenyl)-3,7-dimethyloct-6-en-1-one (3e): Prepared according to the general procedure 5 from commercial 3-methoxyphenyl magnesium bromide (0.5 M in THF) and citronellal to yield the title compound (70%, 910 mg) as a colorless oil. Spectral data were in accordance with those previously reported.$^9$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (ddd, $J = 7.6$, 1.6, 1.0 Hz, 1H), 7.50 (dd, $J = 2.7$, 1.5 Hz, 1H), 7.38 (t, $J = 7.9$ Hz, 1H), 7.12 (ddd, $J = 8.2$, 2.7, 1.0 Hz, 1H), 5.16 – 5.08 (m, 1H), 3.88 (s, 3H), 2.97 (dd, $J = 15.7$, 5.5 Hz, 1H), 2.75 (dd, $J = 15.7$, 8.2 Hz, 1H), 2.25 – 2.15 (m, 1H), 2.13 – 1.95 (m, 2H),
1.70 (d, $J = 1.3$ Hz, 3H), 1.62 (d, $J = 1.3$ Hz, 3H), 1.50 – 1.38 (m, 1H), 1.36 – 1.25 (m, 1H), 0.99 (d, $J = 6.6$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 200.2, 159.8, 138.9, 131.5, 129.5, 124.4, 120.8, 119.30, 112.4, 55.4, 46.0, 37.2, 29.6, 25.7, 25.6, 19.9, 17.7.

The following substrates were not reported in the main manuscript but relevant to our discussion, as they have the same substituents as substrates 1a, 1d and 1e. However, no COM products or interrupted COM products were formed from these substrates under our reaction conditions.

![Ethyl 2-benzoyl-7-methyloct-6-enoate (3f)](image)

Ethyl 2-benzoyl-7-methyloct-6-enoate (3f): Prepared according to the general procedure 1 from ethyl benzoylacetate and 6-bromo-2-methylhex-2-ene to yield the title compound (65%, 750 mg) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 – 7.98 (m, 2H), 7.64 – 7.56 (m, 1H), 7.55 – 7.46 (m, 2H), 5.14 – 5.07 (m, 1H), 4.31 (t, $J = 7.2$ Hz, 1H), 4.16 (qd, $J = 7.1$, 1.5 Hz, 2H), 2.13 – 1.93 (m, 4H), 1.69 (d, $J = 1.3$ Hz, 3H), 1.61 (d, $J = 1.3$ Hz, 3H), 1.46 – 1.37 (m, 2H), 1.19 (t, $J = 7.1$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.3, 170.1, 136.4, 133.4, 132.1, 128.7, 128.6, 123.9, 61.3, 54.3, 28.6, 27.8, 27.8, 25.7, 17.7, 14.0;

ESI-HRMS: calcd for C$_{18}$H$_{24}$O$_3$Na$: m/z = 311.1618$, found: $m/z = 311.1619$;

FTIR (neat): 2967, 2933, 2862, 1736, 1638, 1598, 1449, 1369, 1267, 1225 cm$^{-1}$.

![2-(5-methylhex-4-en-1-yl)-1,3-diphenylpropane-1,3-dione (3g)](image)

2-(5-methylhex-4-en-1-yl)-1,3-diphenylpropane-1,3-dione (3g): Prepared according to the general procedure 1 from dibenzoylemethane and 6-bromo-2-methylhex-2-ene to yield the title compound (56%, 358 mg) as a yellow oil.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 – 7.93 (m, 4H), 7.63 – 7.55 (m, 2H), 7.51 – 7.43 (m, 4H), 5.21 (t, $J = 6.7$ Hz, 1H), 5.13 – 5.07 (m, 1H), 2.21 – 2.11 (m, 2H), 2.11 – 2.01 (m, 2H), 1.68 (d, $J = 1.3$ Hz, 3H), 1.61 (d, $J = 1.3$ Hz, 3H), 1.55 – 1.43 (m, 2H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.2, 136.2, 133.4, 132.1, 128.9, 128.6, 123.9, 57.2, 29.2, 28.4, 27.9, 25.7, 17.8;

ESI-HRMS: calcd for C$_{22}$H$_{24}$O$_2$Na$^+$: m/z = 343.1668, found: m/z = 343.1669;

FTIR (neat): 3070, 2964, 2929, 2861, 1694, 1669, 1597, 1448, 1274, 1229 cm$^{-1}$.

7-methyl-1,2-diphenyloct-6-en-1-one (3h): Prepared according to the general procedure 2 from deoxybenzoin and 6-bromo-2-methylhex-2-ene to yield the title compound (79%, 461 mg) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 – 7.95 (m, 2H), 7.57 – 7.46 (m, 1H), 7.45 – 7.38 (m, 2H), 7.37 – 7.27 (m, 4H), 7.26 – 7.18 (m, 1H), 5.13 – 5.06 (m, 1H), 4.57 (t, $J = 7.3$ Hz, 1H), 2.26 – 2.15 (m, 1H), 2.10 – 1.94 (m, $J = 7.2$ Hz, 2H), 1.92 – 1.81 (m, 1H), 1.68 (d, $J = 1.3$ Hz, 3H), 1.60 (d, $J = 1.3$ Hz, 4H), 1.45 – 1.22 (m, 2H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 200.1, 139.8, 137.0, 132.8, 131.6, 128.8, 128.6, 128.5, 128.3, 127.0, 124.0, 53.6, 33.7, 28.0, 27.9, 25.7, 17.7;

ESI-HRMS: calcd for C$_{21}$H$_{24}$ONa$^+$: m/z = 315.1719, found: m/z = 315.1716;

FTIR (neat): 3064, 2927, 2861, 1678, 1598, 1493, 1448 cm$^{-1}$. 
Ethyl 2-benzoyl-5-methylhex-4-enoate (5a): Prepared according to the general procedure 1 from ethyl benzoylacetic acid and 3,3-dimethylallyl bromide to yield the title compound (58%, 300 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\textsuperscript{10}

\begin{align*}
^{1}H \text{ NMR (400 MHz, CDCl}_3) & \delta 8.05 – 7.96 (m, 2H), 7.64 – 7.56 (m, 1H), 7.54 – 7.45 (m, 2H), 5.17 – 5.09 (m, 1H), 4.32 (dd, J = 7.7, 6.8 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.80 – 2.64 (m, 2H), 1.67 (d, J = 1.4 Hz, 3H), 1.65 (d, J = 1.3 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); \\
^{13}C \text{ NMR (101 MHz, CDCl}_3) & \delta 195.1, 169.8, 136.4, 134.6, 133.4, 128.7, 128.6, 120.17, 61.3, 54.6, 27.8, 25.7, 17.8, 14.0.
\end{align*}

Ethyl 2-(4-methoxybenzoyl)-5-methylhex-4-enoate (5b): Prepared according to the general procedure 1 from ethyl 3-(4-methoxyphenyl)-3-oxopropanoate and 3,3-dimethylallyl bromide to yield the title compound (83%, 481 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\textsuperscript{10}

\begin{align*}
^{1}H \text{ NMR (400 MHz, CDCl}_3) & \delta 8.05 – 7.94 (m, 2H), 7.01 – 6.92 (m, 2H), 5.16 – 5.09 (m, 1H), 4.27 (dd, J = 7.9, 6.7 Hz, 1H), 4.16 (qd, J = 7.2, 0.8 Hz, 2H), 3.90 (s, 3H), 2.80 – 2.60 (m, 2H), 1.68 (d, J = 1.4 Hz, 3H), 1.65 (d, J = 1.2 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H); \\
^{13}C \text{ NMR (101 MHz, CDCl}_3) & \delta 193.4, 170.0, 163.8, 134.5, 131.0, 129.4, 120.3, 113.8, 61.3, 55.5, 54.3, 27.8, 25.8, 17.8, 14.0.
\end{align*}

Ethyl 5-methyl-2-(4-nitrobenzoyl)hex-4-enoate (5c): Prepared according to the general procedure 1 from ethyl 3-(4-nitrophenyl)-3-oxopropanoate and 3,3-dimethylallyl bromide to yield the title compound (68%, 415 mg) as a pale-yellow solid. Spectral data were in accordance with those previously reported.\textsuperscript{10}
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.37 – 8.30 (m, 2H), 8.18 – 8.12 (m, 2H), 5.14 – 5.07 (m, 1H), 4.31 (t, \(J = 7.3\) Hz, 1H), 4.16 (q, \(J = 7.1\) Hz, 2H), 2.80 – 2.67 (m, 2H), 1.67 (d, \(J = 1.3\) Hz, 3H), 1.65 (d, \(J = 1.3\) Hz, 3H), 1.19 (t, \(J = 7.1\) Hz, 3H);

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 193.8, 169.0, 150.4, 140.9, 135.3, 129.6, 123.9, 119.5, 61.7, 55.0, 27.5, 25.7, 17.8, 14.0.

2-(3-methylbut-2-en-1-yl)-1,3-diphenylpropane-1,3-dione (5d): Prepared according to the general procedure 1 from dibenzoylmethane and 3,3-dimethylallyl bromide to yield the title compound (87%, 506 mg) as a white solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.02 – 7.94 (m, 4H), 7.62 – 7.53 (m, 2H), 7.49 – 7.44 (m, 4H), 5.23 (t, \(J = 6.8\) Hz, 1H), 5.21 – 5.16 (m, 1H), 2.84 (t, \(J = 7.1\) Hz, 2H), 1.64 (d, \(J = 1.4\) Hz, 3H), 1.61 (d, \(J = 1.3\) Hz, 3H);

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 196.0, 136.2, 134.4, 133.4, 128.8, 128.6, 120.9, 57.4, 28.3, 25.7, 17.8;

ESI-HRMS: calcd for C\(_{20}\)H\(_{2}\)O\(_2\)Na\(^+\): m/z = 315.1356, found: m/z = 342.1354;

FTIR (neat): 3069, 2962, 2928, 2860, 1693, 1662, 1594, 1447, 1353, 1272 cm\(^{-1}\).

5-methyl-1,2-diphenylhex-4-en-1-one (5e): Prepared according to the general procedure 2 from deoxybenzoin and 3,3-dimethylallyl bromide to yield the title compound (87%, 459 mg) as a yellow solid. Spectral data were in accordance with those previously reported.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 – 7.94 (m, 2H), 7.53 – 7.47 (m, 1H), 7.43 – 7.38 (m, 2H), 7.36 – 7.26 (m, 4H), 7.25 – 7.19 (m, 1H), 5.14 – 5.07 (m, 1H), 4.57 (t, \(J = 7.3\) Hz, 1H), 2.96 – 2.85 (m, 1H), 2.59 – 2.49 (m, 1H), 1.65 (d, \(J = 1.4\) Hz, 3H), 1.58 (d, \(J = 1.3\) Hz, 3H);

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 199.9, 139.6, 137.0, 133.7, 132.8, 128.8, 128.7, 128.49, 128.3, 127.0, 121.6, 54.0, 32.8, 25.7, 17.8.
Ethyl 2-(3,5-dichlorobenzoyl)-5-methylhex-4-enoate (5x): Prepared according to the general procedure 1 from ethyl 3,5-dichlorobenzoylecetae and 3,3-dimethylallyl bromide to yield the title compound (54%, 358 mg) as a pale-yellow oil.

\[^1H\text{ NMR (400 MHz, CDCl}_3\] \(\delta\) 7.85 (d, \(J = 2.0\) Hz, 2H), 7.58 (t, \(J = 1.9\) Hz, 1H), 5.09 (tq, \(J = 7.4, 1.4\) Hz, 1H), 4.24 – 4.13 (m, 3H), 2.70 (tdt, \(J = 7.4, 5.6, 1.0\) Hz, 2H), 1.68 (d, \(J = 1.4\) Hz, 3H), 1.65 (d, \(J = 1.3\) Hz, 3H), 1.22 (t, \(J = 7.1\) Hz, 3H);

\[^{13}C\text{ NMR (101 MHz, CDCl}_3\] \(\delta\) 192.72, 169.01, 138.82, 135.75, 135.24, 133.05, 127.01, 119.63, 61.68, 54.66, 27.56, 25.74, 17.81, 14.00;

ESI-HRMS: calcd for C\textsubscript{16}H\textsubscript{18}35Cl\textsubscript{2}O\textsubscript{3}H\textsuperscript{+}: m/z = 329.0706, found: m/z = 329.0699;

FTIR (neat): 3077, 2980, 2918, 1737, 1695, 1565, 1410, 1369, 1318, 1214 cm\textsuperscript{-1}.

Methyl 5-methyl-2-(4-(trifluoromethyl)benzoyl)hex-4-enoate (5y): Prepared according to the general procedure 1 from methyl 4-(trifluoromethyl)benzoylecetae and 3,3-dimethylallyl bromide to yield the title compound (83%, 524 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^{10}\)

\[^1H\text{ NMR (400 MHz, CDCl}_3\] \(\delta\) 8.14 – 8.08 (m, 2H), 7.80 – 7.73 (m, 2H), 5.10 (tp, \(J = 7.4, 1.5\) Hz, 1H), 4.34 (t, \(J = 7.3\) Hz, 1H), 3.71 (s, 3H), 2.82 – 2.66 (m, 2H), 1.67 (d, \(J = 1.2\) Hz, 3H), 1.64 (d, \(J = 1.4\) Hz, 3H);

\[^{13}C\text{ NMR (101 MHz, CDCl}_3\] \(\delta\) 194.2, 169.7, 139.0, 135.2, 134.7 (q, \(J = 32.3\) Hz), 128.9, 125.8 (q, \(J = 4\) Hz), 123.5 (q, \(J = 271\) Hz), 119.6, 54.5, 52.6, 27.7, 25.7, 17.8;

\[^{19}F\text{ NMR (376 MHz, CDCl}_3\] \(\delta\) -63.22.
Ethyl 2-benzoylpent-4-ynoate (7a): Prepared according to the general procedure 1 from ethyl benzoylacetate and propargyl bromide to yield the title compound (44%, 202 mg) as a pale-yellow oil. Spectral data were in accordance with those previously reported.\textsuperscript{10}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.09 – 8.03 (m, 2H), 7.66 – 7.59 (m, 1H), 7.55 – 7.48 (m, 2H), 4.59 (t, \(J = 7.4\) Hz, 1H), 4.22 – 4.15 (m, 2H), 3.01 – 2.82 (m, 2H), 2.01 (t, \(J = 2.7\) Hz, 1H), 1.19 (tt, \(J = 7.2, 0.9\) Hz, 3H);
\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 193.3, 168.3, 135.9, 133.8, 128.9, 128.8, 80.6, 70.4, 61.9, 53.3, 18.4, 14.0.

Ethyl 2-(4-methoxybenzoyl)pent-4-ynoate (7b): Prepared according to the general procedure 1 from ethyl 3-(4-methoxyphenyl)-3-oxopropanoate and propargyl bromide to yield the title compound (81%, 421 mg) as a pale-yellow oil. Spectral data were in accordance with those previously reported.\textsuperscript{10}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.10 – 8.01 (m, 2H), 7.01 – 6.95 (m, 2H), 4.54 (dd, \(J = 7.8, 7.0\) Hz, 1H), 4.18 (qd, \(J = 7.1, 2.0\) Hz, 2H), 3.90 (s, 3H), 2.95 (ddd, \(J = 17.0, 7.8, 2.7\) Hz, 1H), 2.85 (ddd, \(J = 17.0, 7.0, 2.7\) Hz, 1H), 1.21 (t, \(J = 7.1\) Hz, 3H);
\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 191.6, 168.5, 164.1, 131.3, 128.9, 114.0, 80.8, 70.2, 61.8, 55.6, 53.0, 18.4, 14.0.

Ethyl 2-(4-nitrobenzoyl)pent-4-ynoate (7c): Prepared according to the general procedure 1 from ethyl 3-(4-nitrophenyl)-3-oxopropanoate and propargyl bromide to yield the title compound (51%, 281 mg) as a yellow oil. Spectral data were in accordance with those previously reported.\textsuperscript{10}
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.39 – 8.34 (m, 2H), 8.24 – 8.19 (m, 2H), 4.59 (t, $J = 7.4$ Hz, 1H), 4.20 (qd, $J = 7.1$, 0.7 Hz, 2H), 2.95 (dt, $J = 7.6$, 2.6 Hz, 2H), 2.01 (t, $J = 2.7$ Hz, 1H), 1.20 (t, $J = 7.1$ Hz, 3H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.3, 167.5, 150.7, 140.5, 129.9, 124.0, 80.0, 70.8, 62.3, 53.6, 18.2, 14.0.

1,3-diphenyl-2-(prop-2-yn-1-yl)propane-1,3-dione (7d): Prepared according to the general procedure 1 from dibenzoylmethane and propargyl bromide to yield the title compound (65%, 341 mg) as a pale-yellow solid. Spectral data were in accordance with those previously reported.$^{11}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 – 7.96 (m, 4H), 7.63 – 7.57 (m, 2H), 7.52 – 7.43 (m, 4H), 5.51 (t, $J = 7.0$ Hz, 1H), 3.04 (dd, $J = 7.0$, 2.7 Hz, 2H), 2.00 (t, $J = 2.7$ Hz, 1H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.4, 135.8, 133.8, 128.9, 128.8, 81.0, 70.9, 55.6, 19.1.

1,2-diphenylpent-4-yn-1-one (7e): Prepared according to the general procedure 2 from deoxybenzoin and propargyl bromide to yield the title compound (82%, 384 mg) as a pale-yellow solid. Spectral data were in accordance with those previously reported.$^{12}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 – 7.92 (m, 2H), 7.54 – 7.47 (m, 1H), 7.46 – 7.37 (m, 2H), 7.36 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 4.80 (t, $J = 7.3$ Hz, 1H), 3.06 (ddd, $J = 16.8$, 7.3, 2.6 Hz, 1H), 2.73 (ddd, $J = 16.8$, 7.3, 2.6 Hz, 1H), 1.96 (t, $J = 2.6$ Hz, 1H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.0, 138.1, 136.2, 133.1, 129.1, 128.9, 128.6, 128.2, 127.6, 82.2, 69.8, 53.0, 23.4.
Ethyl 2-benzoyl-4-methylpent-4-enoate (9a): Prepared according to the general procedure 1 from ethyl benzoylacetate and 3-bromo-2-methylprop-2-ene to yield the title compound (78%, 386 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\textsuperscript{10}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.07 – 7.98 (m, 2H), 7.66 – 7.57 (m, 1H), 7.56 – 7.46 (m, 2H), 4.82 – 4.78 (m, 1H), 4.76 – 4.72 (m, 1H), 4.57 (dd, J = 8.0, 6.7 Hz, 1H), 4.16 (qd, J = 7.1, 0.9 Hz, 2H), 2.84 – 2.67 (m, 2H), 1.79 (dd, J = 1.4, 0.8 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H);

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 194.6, 169.5, 142.1, 136.2, 133.5, 128.8, 128.7, 128.6, 112.2, 61.5, 52.8, 36.5, 22.7, 14.0.

Ethyl 2-(4-methoxybenzoyl)-4-methylpent-4-enoate (9b): Prepared according to the general procedure 1 from ethyl 3-(4-methoxyphenyl)-3-oxopropanoate and 3-bromo-2-methylprop-2-ene to yield the title compound (85%, 469 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\textsuperscript{10}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.06 – 7.99 (m, 2H), 7.00 – 6.93 (m, 2H), 4.81 – 4.77 (m, 1H), 4.75-4.71 (m, 1H), 4.52 (dd, J = 8.0, 6.5 Hz, 1H), 4.16 (qd, J = 7.1, 1.2 Hz, 2H), 3.90 (s, 3H), 2.83 – 2.64 (m, 2H), 1.81 – 1.76 (m, 3H), 1.20 (t, J = 7.1 Hz, 3H);

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 193.0, 169.7, 163.9, 142.3, 131.0, 129.2, 113.9, 112.03, 61.4, 55.5, 52.5, 36.5, 22.7, 14.0.

Ethyl 4-methyl-2-(4-nitrobenzoyl)pent-4-enoate (9c): Prepared according to the general procedure 1 from ethyl 3-(4-nitrophenyl)-3-oxopropanoate and 3-bromo-2-methylprop-2-ene to yield a mixture of ketone form and enol form of the title compound (40%, 233 mg, 100/13 ratio) as a white solid. Spectral data were in accordance with those previously reported.\textsuperscript{10}
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 13.25 (s, 0.13H), 8.41 – 8.31 (m, 2H), 8.30 – 8.22 (m, 0.26H), 8.23 – 8.14 (m, 2H), 7.81 – 7.69 (m, 0.26H), 4.89 – 4.86 (m, 0.13H), 4.83 – 4.79 (m, 1H), 4.73 – 4.69 (m, 1.13H), 4.55 (t, $J$ = 7.3 Hz, 1H), 4.31 (q, $J$ = 7.1 Hz, 0.26H), 4.17 (q, $J$ = 7.1 Hz, 2H), 2.90 – 2.67 (m, 2.26H), 1.81 – 1.77 (m, 3H), 1.76 – 1.73 (m, 0.39H), 1.33 (t, $J$ = 7.1 Hz, 0.39H), 1.20 (t, $J$ = 7.1 Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.3, 168.8, 150.5, 141.6, 140.8, 129.6, 129.0, 124.0, 123.4, 112.6, 110.2, 61.9, 61.2, 53.3, 36.3, 34.4, 23.2, 22.6, 14.1, 14.0. (some signals of the enol form were missing)

2-(2-methylallyl)-1,3-diphenylpropane-1,3-dione (9d): Prepared according to the general procedure 1 from dibenzoylmethane and 3-bromo-2-methylprop-2-ene to yield the title compound (89%, 495 mg) as a yellow oil. Spectral data were in accordance with those previously reported.$^{13}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 – 7.96 (m, 4H), 7.63 – 7.55 (m, 2H), 7.52 – 7.43 (m, 4H), 5.46 (t, $J$ = 6.6 Hz, 1H), 4.83 – 4.79 (m, 1H), 4.74 – 4.70 (m, 1H), 2.91 – 2.85 (m, 2H), 1.81 (dd, $J$ = 1.5, 0.8 Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.5, 142.6, 136.0, 133.5, 128.9, 128.6, 112.0, 55.8, 36.6, 23.0.

4-methyl-1,2-diphenylpent-4-en-1-one (9e): Prepared according to the general procedure 2 from deoxybenzoin and 3-bromo-2-methylprop-2-ene to yield the title compound (92%, 460 mg) as a colorless oil. Spectral data were in accordance with those previously reported.$^{10}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 – 7.97 (m, 2H), 7.57 – 7.46 (m, 1H), 7.46 – 7.38 (m, 2H), 7.38 – 7.27 (m, 4H), 7.26 – 7.16 (m, 1H), 4.84 (dd, $J$ = 8.3, 6.2 Hz, 1H), 4.75 – 4.71 (m, 1H), 4.65 – 4.61 (m, 1H), 3.09 – 2.98 (m, 1H), 2.56 – 2.47 (m, 1H), 1.74 (t, $J$ = 1.1 Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 199.3, 143.3, 139.3, 136.9, 132.9, 128.9, 128.7, 128.6, 128.6, 128.2, 127.1, 111.9, 52.0, 41.8, 23.1.
General Procedure for Reaction in COM Substrate Scope (Scheme 3)

To a solution of compound 1 (0.2 mmol) in HFIP in a screw-cap vial equipped with a stirrer bar was added pTSA. The reaction mixture was stirred at indicated temperature for 4 h or 18 h. The solvent was then evaporated off and the residue was directly purified by flash column chromatography (silica-gel, hexanes/ethyl acetate) to obtain the metathesis product.

Ethyl 2-phenylcyclopent-2-ene-1-carboxylate (2a) and ethyl 2-phenylcyclopent-1-ene-1-carboxylate (2’a): Prepared according to the general procedure from 1a using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided a mixture of 2a (major) and 2’a (minor) (12/1, 76%, 33 mg) as a colorless oil. Spectral data were in accordance with those previously reported.14 When performed on 2 mmol scale, the reaction yielded a mixture of 2a/2’a (8/1, 80%).

1H NMR (400 MHz, CDCl3) δ 7.49 – 7.42 (m, 2H), 7.32 (dd, J = 8.5, 6.8 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.38 – 6.34 (m, 1H), 4.18 – 4.05 (m, 2.2H), 4.03 – 3.96 (m, 1H), 2.93 – 2.83 (m, 0.32H), 2.75 (dddt, J = 17.8, 9.1, 6.6, 2.5 Hz, 1H), 2.63 – 2.52 (m, 1H), 2.38 (dtd, J = 13.1, 9.1, 6.7 Hz, 1H), 2.28 (ddt, J = 13.1, 8.8, 4.4 Hz, 1H), 2.02 (p, J = 7.7 Hz, 0.16H), 1.17 (t, J = 7.1 Hz, 3.24H);

13C NMR (101 MHz, CDCl3) δ 175.3, 166.3, 153.1, 141.2, 137.2, 135.5, 133.1, 130.1, 128.3, 127.8, 127.74, 127.71, 127.2, 125.8, 60.5, 60.0, 51.3, 40.2, 35.2, 32.5, 29.3, 22.0, 14.1, 14.0.

Ethyl 2-(4-methoxyphenyl)cyclopent-2-ene-1-carboxylate (2b) and ethyl 2-(4-methoxyphenyl)cyclopent-1-ene-1-carboxylate (2’b): Prepared according to the general procedure from 1b using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided a mixture of 2b and 2’b
(1/1.2, 64%, 31 mg) as a colorless oil. Spectral data were in accordance with those previously reported.¹

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.37 (m, 2H), 7.37 – 7.32 (m, 2H), 6.91 – 6.83 (m, 4H), 6.23 (td, J = 2.6, 1.5 Hz, 1H), 4.18 – 4.07 (m, 4.4H), 3.95 (dddt, J = 9.4, 4.1, 2.7, 1.5 Hz, 1H), 3.84 (s, 3.6H), 3.82 (s, 3H), 2.85 (tdd, J = 7.7, 5.7, 2.1 Hz, 4.8H), 2.78 – 2.67 (m, 1H), 2.61 – 2.49 (m, 1H), 2.41 – 2.32 (m, 1H), 2.27 (qd, J = 9.2, 8.8, 4.9 Hz, 1H), 1.98 (p, J = 7.7 Hz, 2.4H), 1.25 – 1.13 (m, 6.6H);

¹³C NMR (101 MHz, CDCl₃) δ 175.4, 166.5, 159.4, 158.8, 152.6, 140.5, 129.4, 129.2, 128.3, 128.0, 127.9, 127.0, 113.7, 113.1, 60.5, 59.9, 55.2 (2C), 51.4, 40.0, 35.3, 32.4, 29.3, 21.9, 14.2, 14.1.

Phenyl(2-phenylcyclopent-2-en-1-yl)methanone (2d): Prepared according to the general procedure from 1d using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided 2d (71%, 35 mg) as a colorless oil. Spectral data were in accordance with those previously reported.⁵ When performed on 1 mmol scale, the reaction yielded 74% of 2d.

¹H NMR (400 MHz, CDCl₃) δ 8.13 – 8.07 (m, 2H), 7.65 – 7.60 (m, 1H), 7.56 – 7.50 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 6.52 – 6.48 (m, 1H), 5.03 – 4.95 (m, 1H), 2.78 – 2.63 (m, 2H), 2.63 – 2.53 (m, 1H), 2.21 – 2.12 (m, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 201.2, 141.6, 136.5, 135.6, 133.1, 130.2, 128.73, 128.69, 128.4, 127.1, 125.8, 53.5, 32.4, 30.1.

1,2-diphenylcyclopent-1-ene (2’e): Prepared according to the general procedure from 1e using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes provided 2’e (61%, 27 mg) as a colorless oil. Spectral data were in accordance with those previously reported.¹⁴
\( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.29 – 7.17 (m, 10H), 2.96 (t, \( J = 7.6 \) Hz, 4H), 2.10 (p, \( J = 7.5 \) Hz, 2H);

\( ^13 \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 138.5, 137.6, 128.2, 128.1, 126.6, 39.2, 22.2.

Ethyl 2-(3-methoxyphenyl)cyclopent-2-ene-1-carboxylate (2f) and ethyl 2-(3-methoxyphenyl)cyclopent-1-ene-1-carboxylate (2'f): Prepared according to the general procedure from 1f using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided a mixture of 2f (major) and 2'f (minor) (20/1, 33%, 16 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^{14}\)

\( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.23 (t, \( J = 7.9 \) Hz, 1H), 7.07 – 6.98 (m, 2H), 6.80 (ddd, \( J = 8.2, 2.5, 0.9 \) Hz, 1H), 6.36 (td, \( J = 2.6, 1.6 \) Hz, 1H), 4.20 – 4.05 (m, 2.1H), 4.01 – 3.93 (m, 1H), 3.83 (s, 3.15H), 2.90 – 2.81 (m, 0.2H), 2.74 (dddt, \( J = 17.8, 9.1, 6.6, 2.5 \) Hz, 1H), 2.63 – 2.50 (m, 1H), 2.37 (ddt, \( J = 13.0, 9.1, 6.6 \) Hz, 1H), 2.26 (ddt, \( J = 13.2, 8.9, 4.5 \) Hz, 1H), 2.01 (p, \( J = 7.7 \) Hz, 0.1H), 1.18 (t, \( J = 7.1 \) Hz, 3.15H);

\( ^13 \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 175.3, 159.6, 141.1, 136.9, 130.5, 129.3, 118.4, 112.9, 111.4, 60.6, 55.2, 51.3, 32.5, 29.3, 14.1. (Signals of 2'f were not high enough to report.)

Ethyl 2-(naphthalen-2-yl)cyclopent-2-ene-1-carboxylate (2g) and ethyl 2-(naphthalen-2-yl)cyclopent-1-ene-1-carboxylate (2'g): Prepared according to the general procedure from 1g using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided a mixture of 2g and 2'g (11/1, 80%, 43 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^{14}\)

\( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.86 – 7.77 (m, 4H), 7.69 (dd, \( J = 8.6, 1.8 \) Hz, 1H), 7.52 – 7.42 (m, 2H), 6.52 (td, \( J = 2.7, 1.5 \) Hz, 1H), 4.21 – 4.05 (m, 3H), 2.99 (tt, \( J = 7.7, 2.4 \) Hz, 0.18H), 2.92 (tt, \( J = 7.8, 2.4 \) Hz, 0.18H), 2.87 – 2.75 (m, 1H), 2.69 – 2.58 (m, 1H), 2.50 – 2.39 (m, 1H), 2.39 – 2.28 (m, 1H), 2.07 (p, \( J = 7.7 \) Hz, 0.18H), 1.18 (t, \( J = 7.1 \) Hz, 3H), 1.11 (t, \( J = 7.1 \) Hz, 0.27H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.4, 141.1, 133.5, 132.8, 132.7, 130.9, 128.2, 127.9, 127.6, 126.2, 125.8, 124.4, 124.4, 60.6, 51.3, 32.7, 29.4, 14.2. (Signals of 2$^g$ were not high enough to report.)

(2-methylcyclopent-1-en-1-yl)benzene (2'h): Prepared according to the general procedure from 1h using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes provided 2'h (30%, 9.5 mg) as a colorless oil. Spectral data were in accordance with those previously reported.$^{14}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.30 (m, 4H), 7.25 – 7.20 (m, 1H), 2.80 – 2.73 (m, 2H), 2.56 – 2.49 (m, 2H), 1.98 – 1.89 (m, 2H), 1.89 – 1.86 (m, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.8, 135.2, 134.8, 128.0, 127.6, 126.0, 40.1, 37.3, 21.9, 15.5.

Ethyl 2-(3,5-dichlorophenyl)cyclopent-2-ene-1-carboxylate (2i): Prepared according to the general procedure from 1i using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (98/2 to 95/5) provided 2 (22%, 12.5 mg) as a colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J$ = 1.8 Hz, 2H), 7.23 (t, $J$ = 1.9 Hz, 1H), 6.43 – 6.38 (m, 1H), 4.25 – 4.03 (m, 2H), 3.97 – 3.86 (m, 1H), 2.84 – 2.66 (m, 1H), 2.66 – 2.50 (m, 1H), 2.46 – 2.20 (m, 2H), 1.21 (t, $J$ = 7.1 Hz, 3H);

$^{13}$C NMR (76 MHz, CDCl$_3$) $\delta$ 174.60, 139.04, 138.47, 134.89, 133.29, 127.03, 124.39, 60.82, 50.98, 32.54, 29.11, 14.12.

ESI-HRMS: calced for C$_{14}$H$_{14}$Cl$_2$O$_2$H$^+$: m/z = 285.0444, found: m/z = 285.0443;

FTIR (neat): 2950, 2906, 2830, 1730, 1592, 1555, 1487, 1355, 1250 cm$^{-1}$. 
2-methyl-3-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole (2j): Prepared according to the general procedure from 1j using HFIP (50 µL) and pTSA (5 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (9/1) provided the title compound (75%, 47 mg) as a white solid. Spectral data were in accordance with those previously reported.\(^{14}\)

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 – 7.75 (m, 2H), 7.39 – 7.23 (m, 7H), 5.84 (q, \(J = 2.0\) Hz, 1H), 5.08 – 4.99 (m, 1H), 4.36 – 4.25 (m, 2H), 2.42 (s, 3H), 1.50 (d, \(J = 6.4\) Hz, 3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.4, 143.4, 135.1, 133.0, 129.8, 128.7, 128.2, 127.29, 126.3, 118.8, 62.9, 54.8, 22.1, 21.5.

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2-methyl-3-(p-tolyl)-1-tosyl-2,5-dihydro-1H-pyrrole (2k): Prepared according to the general procedure from 1k using HFIP (50 µL) and pTSA (5 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (9/1) provided the title compound (84%, 55 mg) as a white solid. Spectral data were in accordance with those previously reported.\(^{14}\)

When performed on 1 mmol scale, the reaction yielded 85% of 2k.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 – 7.73 (m, 2H), 7.31 (d, \(J = 8.2\) Hz, 2H), 7.23 – 7.09 (m, 4H), 5.79 (q, \(J = 2.0\) Hz, 1H), 5.06 – 4.96 (m, 1H), 4.35 – 4.23 (m, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 1.49 (d, \(J = 6.4\) Hz, 3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.4, 143.3, 138.2, 135.2, 130.1, 129.8, 129.4, 127.3, 126.2, 117.8, 62.9, 54.7, 22.1, 21.5, 21.2.

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3-(p-tolyl)-1-tosyl-2,5-dihydro-1H-pyrrole (2l): Prepared according to the general procedure from 1l using HFIP (50 µL) and pTSA (5 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (9/1) provided the title compound (62%, 39 mg) as a white solid. Spectral data were in accordance with those previously reported.\(^{14}\)
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 – 7.76 (m, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 8.3$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 5.98 – 5.94 (m, 1H), 4.49 (td, $J = 4.5$, 2.0 Hz, 2H), 4.31 (td, $J = 4.5$, 2.2 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.5, 138.4, 137.2, 134.1, 129.8, 129.7, 129.4, 127.5, 125.3, 117.8, 55.7, 55.0, 21.5, 21.2.

3-(4-chlorophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole (2m): Prepared according to the general procedure from 1m using HFIP (50 µL) and pTSA (5 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (9/1) provided the title compound (56%, 37 mg) as a pale-yellow solid. Spectral data were in accordance with those previously reported.$^1$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 – 7.76 (m, 2H), 7.38 – 7.27 (m, 4H), 7.25 – 7.19 (m, 2H), 6.02 (p, $J = 2.1$ Hz, 1H), 4.46 (td, $J = 4.5$, 2.0 Hz, 2H), 4.31 (td, $J = 4.5$, 2.2 Hz, 2H), 2.44 (s, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.7, 136.3, 134.2, 134.0, 131.0, 129.9, 128.9, 127.5, 126.7, 119.6, 55.6, 54.8, 21.5.

1-methyl-2-phenyl-1H-indene (2n) and 3-methyl-2-phenyl-1H-indene (2’n): Prepared according to the general procedure from 1i using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes provided a mixture of 2n and 2’n (1/1.25, 70%, 28.8 mg) as a pale-yellow solid. Spectral data were in accordance with those previously reported.$^{15}$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.62 – 7.55 (m, 2H), 7.55 – 7.22 (m, 18.25H), 7.30 – 7.21 (m, 3H), 7.13 (d, $J = 1.5$ Hz, 1H), 3.97 (q, $J = 7.6$ Hz, 1H), 3.79 (q, $J = 2.2$ Hz, 2.5H), 2.35 (t, $J = 2.1$ Hz, 3.75H), 1.40 (d, $J = 7.5$ Hz, 3H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.5, 149.5, 147.5, 143.5, 142.5, 140.4, 137.6, 135.5, 134.7, 128.7, 128.4, 128.32, 128.28, 127.4, 126.9, 126.8, 126.7, 126.4, 125.9, 124.9, 124.8, 123.4, 122.9, 121.1, 119.2, 44.1, 41.0, 17.2, 12.0.

1,2-diphenyl-1$H$-indene (2o): Prepared according to the general procedure from 1o using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (98/2 to 95/5) provided 2o (95%, 50.7 mg) as a white solid. Spectral data were in accordance with those previously reported.$^{16}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 – 7.50 (m, 2H), 7.44 (dt, $J = 7.5, 0.9$ Hz, 1H), 7.39 (d, $J = 1.8$ Hz, 1H), 7.31 – 7.10 (m, 11H), 5.01 (s, 1H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.9, 149.2, 143.2, 140.0, 135.0, 128.9, 128.5, 128.0, 127.9, 127.3, 127.0, 126.7, 126.6, 125.5, 123.8, 121.2, 56.3.

2-(4-chlorophenyl)-1-phenyl-1$H$-indene (2p): Prepared according to the general procedure from 1p using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (95/5) provided 2p (91%, 54.9 mg) as a white solid. Spectral data were in accordance with those previously reported.$^{16}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 – 7.42 (m, 3H), 7.38 (d, $J = 1.8$ Hz, 1H), 7.33 – 7.20 (m, 6H), 7.20 – 7.12 (m, 3H), 4.96 (s, 1H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.1, 148.6, 143.0, 139.6, 133.5, 133.1, 129.0, 128.7, 128.6, 127.8, 127.1, 126.9, 125.8, 123.9, 121.2, 56.3.
2-(4-methoxyphenyl)-1-phenyl-1H-indene (2q): Prepared according to the general procedure from 1q using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/DCM (4/1) provided 2q (85%, 50.4 mg) as a white solid. Spectral data were in accordance with those previously reported.\textsuperscript{17}

\[
{^1}H \text{ NMR (400 MHz, CDCl}_3\) \delta 7.51 – 7.44 (m, 2H), 7.41 (dt, \(J = 7.5, 1.0 \text{ Hz}, 1H\)), 7.29 – 7.23 (m, 4H), 7.23 – 7.15 (m, 4H), 7.10 (td, \(J = 7.4, 1.1 \text{ Hz}, 1H\)), 6.87 – 6.78 (m, 2H), 4.98 – 4.94 (m, 1H), 3.79 (s, 3H);
\]

\[
{^{13}}C \text{ NMR (101 MHz, CDCl}_3\) \delta 159.0, 149.6, 148.9, 143.6, 140.3, 128.9, 127.89, 127.86, 127.0, 126.7, 126.1, 125.0, 123.7, 120.7, 113.9, 56.3, 55.2.
\]

6,11-dihydro-5H-benzo[a]fluorene (2'r): Prepared according to the general procedure from 1r using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (98/2) provided 2'r (92%, 40.1 mg) as a white solid.

\[
{^1}H \text{ NMR (400 MHz, CDCl}_3\) \delta 7.52 (dt, \(J = 7.3, 0.9 \text{ Hz}, 1H\)), 7.39 – 7.20 (m, 6H), 7.20 – 7.13 (m, 1H), 3.70 (t, \(J = 2.7 \text{ Hz}, 2H\)), 3.06 (t, \(J = 8.2 \text{ Hz}, 2H\)), 2.80 (tt, \(J = 8.0, 2.6 \text{ Hz}, 2H\));
\]

\[
{^{13}}C \text{ NMR (101 MHz, CDCl}_3\) \delta 145.1 143.5, 139.1, 138.9, 135.6, 133.6, 127.8, 126.7, 126.5, 124.9, 123.9, 122.8, 118.8, 36.0, 28.6, 20.7;
\]

ESI-HRMS: calcd for C\textsubscript{17}H\textsubscript{14}H\textsuperscript{+}: m/z = 219.1168, found: m/z = 219.1168;

FTIR (neat): 3060, 2928, 2882, 2830, 1604, 1489, 1459, 1396 1288, 1259 cm\textsuperscript{-1}.

Phenyl(3-phenylnaphthalen-2-yl)methanone (2s) and phenyl(3-phenyl-4-(prop-1-en-2-yl)naphthalen-2-yl)methanone (2's'): Prepared according to the general procedure from 1s using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting hexanes/ethyl acetate (95/5 to 90/10) provided an inseparable mixture of 2s
and 2’s (97%, 64.8 mg, 3/1 ratio) as a pale-yellow solid. Spectral data of 2s were in accordance with those previously reported.\textsuperscript{18}

\textbf{1H NMR (300 MHz, CDCl\textsubscript{3})}: \(\delta\) 8.07 (s, 0.75H), 8.01 – 7.90 (m, 3H), 7.78 – 7.71 (m, 1.5H), 7.70 – 7.53 (m, 2.5H), 7.52 – 7.43 (m, 1H), 7.42 – 7.13 (m, 7H), 5.44 (p, \(J = 1.6\) Hz, 0.25H), 5.05 (dt, \(J = 2.1, 1.1\) Hz, 0.25H), 1.82 (t, \(J = 1.3\) Hz, 0.75H);

\textbf{13C NMR (76 MHz, CDCl\textsubscript{3})}: \(\delta\) 198.3, 140.4, 138.6, 137.7, 137.4, 134.1, 132.9, 131.6, 130.0, 129.4, 129.2, 129.1, 128.4, 128.3, 128.2, 128.0, 127.8, 127.2, 126.8 (signals according to the major product);

\textbf{13C NMR (76 MHz, CDCl\textsubscript{3})}: \(\delta\) 142.1, 141.2, 139.0, 138.5, 138.1, 132.7, 131.84, 131.79, 130.6, 129.9, 128.7, 128.0, 127.6, 127.0, 126.8, 126.6, 126.4, 122.0, 119.0, 24.9 (signals according to the minor product, other signals are unclear or missing);

\textbf{ESI-HRMS}: calcd for C\textsubscript{23}H\textsubscript{16}OH\textsuperscript{+}: m/z = 309.1274, found: m/z = 309.1272 (for the major product);

\textbf{ESI-HRMS}: calcd for C\textsubscript{26}H\textsubscript{20}OH\textsuperscript{+}: m/z = 349.1587, found: m/z = 349.1586 (for the minor product);

\textbf{FTIR (neat)}: 3058, 2968, 2866, 1657, 1596, 1490, 1449, 1314, 1276, 1221 cm\textsuperscript{-1}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{diagram.png}
\caption{Structures of 1-(3-methylnaphthalen-2-yl)ethan-1-one (2t) and 1-(3-methyl-4-(prop-1-en-2-yl)naphthalen-2-yl)ethan-1-one (2t').}
\end{figure}

\textbf{1-(3-methylnaphthalen-2-yl)ethan-1-one (2t) and 1-(3-methyl-4-(prop-1-en-2-yl)naphthalen-2-yl)ethan-1-one (2t')}: Prepared according to the general procedure from 1t using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting hexanes/ethyl acetate (95/5 to 90/10) provided an inseparable mixture of 2t and 2t’ (92%, 35.3 mg, 4/1 ratio) as a pale-yellow solid. Spectral data of 2t were in accordance with those previously reported.\textsuperscript{19}

\textbf{1H NMR (300 MHz, CDCl\textsubscript{3})}: \(\delta\) 8.26 (s, 1H), 8.06 (s, 0.25H), 7.97 – 7.92 (m, 0.25H), 7.92 – 7.86 (m, 1.25H), 7.82 – 7.76 (m, 1H), 7.70 – 7.65 (m, 1H), 7.61 – 7.45 (m, 2.5H), 5.56 (p, \(J = 1.6\) Hz, 0.25H), 4.96 (dd, \(J = 2.1, 1.0\) Hz, 0.25H), 2.74 (s, 3H), 2.73 (s, 0.75H), 2.70 (d, \(J = 1.1\) Hz, 3H), 2.55 (s, 0.75H), 2.10 (dd, \(J = 1.5, 1.0\) Hz, 0.75H);

\textbf{13C NMR (76 MHz, CDCl\textsubscript{3})}: \(\delta\) 201.5, 136.3, 134.8, 134.6, 131.0, 130.6, 130.0, 128.6, 128.2, 126.9, 125.9, 29.5, 21.9; (signals according to the major product);

\textbf{13C NMR (76 MHz, CDCl\textsubscript{3})}: \(\delta\) 128.7, 128.1, 127.9, 125.8, 125.7, 116.9, 30.2, 24.5, 17.6 (signals according to the minor product, other signals are unclear or missing);

\textbf{ESI-HRMS}: calcd for C\textsubscript{13}H\textsubscript{12}OH\textsuperscript{+}: m/z = 185.0961, found: m/z = 185.0958 (for the major product);
ESI-HRMS: calcd for C_{16}H_{16}OH^+: m/z = 225.1274, found: m/z = 225.1271 (for the minor product); 
FTIR (neat): 3056, 2968, 2930, 1678, 1492, 1432, 1355, 1270, 1236 cm\(^{-1}\).

(3-methylnaphthalen-2-yl)(phenyl)methanone (2u) and (3-methyl-4-(prop-1-en-2-ylnaphthalen-2-yl)(phenyl)methanone (2u’): Prepared according to the general procedure from 1u using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting hexanes/ethyl acetate (95/5 to 90/10) provided an inseparable mixture of 2u and 2’u (82%, 40.2 mg, 4/1 ratio) as a viscous pale-yellow oil.

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\] \( \delta \): 8.12 (s, 1H), 8.02 (s, 0.25H), 7.99 – 7.94 (m, 1.25H), 7.93 – 7.88 (m, 1H), 7.87 (s, 1H), 7.64 – 7.54 (m, 2.5H), 7.52 – 7.41 (m, 5H), 5.47 – 5.42 (m, 0.25H), 5.04 – 5.01 (m, 1H), 2.15 (s, 3H), 2.00 (s, 0.75H), 1.78 – 1.75 (m, 0.75H);
\[^{13}\text{C NMR (101 MHz, CDCl}_3\] \( \delta \): 204.3, 141.0, 139.3, 137.5, 134.1, 131.8, 129.5, 129.0, 128.8, 128.7, 128.5, 128.0, 127.8, 127.7, 126.8, 30.5 (signals according to the major product);
\[^{13}\text{C NMR (101 MHz, CDCl}_3\] \( \delta \): 204.4, 142.1, 141.2, 140.3, 139.7, 133.5, 132.1, 131.9, 129.1, 127.9, 127.4, 126.6, 126.3, 119.1, 30.4, 24.7 (signals according to the minor product, other signals are unclear or missing);
ESI-HRMS: calcd for C_{18}H_{14}OH^+: m/z = 247.1117, found: m/z = 247.1123 (for the major product); 
ESI-HRMS: calcd for C_{21}H_{18}OH^+: m/z = 287.1430, found: m/z = 287.1435 (for the minor product); 
FTIR (neat): 3058, 2972, 2928, 1684, 1628, 1590, 1447, 1352, 1270, 1206 cm\(^{-1}\).

\[6\text{-methyl-5-(p-tolyl)-1-tosyl-1,2,3,6-tetrahydropyridine (2v): Prepared according to the general procedure from 1v using HFIP (100 µL) and pTSA (10 mol%) at 60 °C for 18 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (9/1) provided the title compound (21%, 14.3 mg) as a white solid.\]
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 – 7.73 (m, 2H), 7.27 – 7.23 (m, 2H), 7.21 – 7.14 (m, 4H), 5.76 – 5.70 (m, 1H), 5.12 – 4.94 (m, 1H), 3.92 (ddt, $J = 14.2, 6.7, 1.1$ Hz, 1H), 3.25 (ddd, $J = 14.2, 11.8, 4.7$ Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 2.21 – 1.93 (m, 2H), 1.22 (d, $J = 6.7$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.0, 140.3, 138.5, 137.4, 136.7, 129.6, 129.3, 126.8, 126.1, 121.8, 50.8, 37.0, 24.5, 21.5, 21.1, 19.4;

ESI-HRMS: calcld for C$_{20}$H$_{23}$NO$_2$SH$: m/z = 342.1522$, found: m/z = 342.1526;

FTIR (neat): 3026, 2980, 2926, 2877, 1599, 1510, 1450, 1379, 1344, 1214 cm$^{-1}$.

1-tosyl-1,2-dihydroquinoline (2w): Prepared according to the general procedure from 1w using HFIP (100 µL) and pTSA (10 mol%) at 60 °C for 18 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (9/1) provided the title compound (20%, 11.4 mg) as a white solid. Spectral data were in accordance with those previously reported.$^7$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 – 7.70 (m, 1H), 7.34 – 7.27 (m, 3H), 7.20 (td, $J = 7.5, 1.3$ Hz, 1H), 7.12 – 7.06 (m, 2H), 6.95 (dd, $J = 7.5, 1.6$ Hz, 1H), 6.05 (dt, $J = 9.6, 1.9$ Hz, 1H), 5.60 (dt, $J = 9.6, 4.1$ Hz, 1H), 4.46 (dd, $J = 4.1, 1.7$ Hz, 2H), 2.37 (s, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.4, 136.3, 135.0, 129.5, 129.0, 128.0, 127.3, 126.9, 126.7, 126.4, 125.9, 124.0, 45.4, 21.5.

$3',5'$-dichloro-3-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (2x) and $3',5'$-dichloro-5-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (2'x): Prepared according to the general procedure from 1x using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 18 h. Purification by flash column chromatography eluting hexanes provided an inseparable mixture of 2x and 2'x (33%, 15.9 mg, 7/1 ratio) as a colorless oil. Spectral data of 2x were in accordance with those previously reported.$^8$
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 (d, $J = 1.8$ Hz, 2.3H), 7.22 (t, $J = 1.8$ Hz, 1.15H), 6.20 – 6.13 (m, 1H), 6.03 – 5.99 (m, 0.15H), 2.44 – 2.36 (m, 1H), 2.36 – 2.18 (m, 3H), 2.05 – 1.92 (m, 1H), 1.87 – 1.73 (m, 2H), 1.32 – 1.20 (m, 1H), 1.10 – 1.06 (m, 3.45H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.6, 134.7, 134.3, 127.0, 126.3, 123.6, 35.7, 30.1, 28.8, 25.9, 21.9. (Signals corresponding to the major isomer)

3-methyl-4'--(trifluoromethyl)-2,3,4,5-tetrahydro-1',1'-biphenyl (2y) and 5-methyl-4'- (trifluoromethyl)-2,3,4,5-tetrahydro-1',1'-biphenyl (2'y): Prepared according to the general procedure from 1y using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 18 h. Purification by flash column chromatography eluting hexanes provided an inseparable mixture of 2y and 2'y (32%, 15.9 mg, 2.6/1 ratio) as a colorless oil. Spectral data of the mixture were in accordance with those previously reported.  

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 – 7.54 (m, 2H), 7.53 – 7.46 (m, 2H), 6.24 – 6.18 (m, 0.73H), 6.09 – 6.04 (m, 0.2H), 2.60 – 2.44 (m, 1H), 2.43 – 2.35 (m, 1H), 2.35 – 2.19 (m, 2H), 2.12 – 2.00 (m, 1H), 2.00 – 1.75 (m, 2H), 1.35 – 1.23 (m, 1H), 1.13 – 1.07 (m, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.0, 135.3, 133.2, 128.4 (q, $J = 32.0$ Hz), 126.6, 125.24, 125.17, 125.1 (q, $J = 4.0$ Hz), 124.4 (q, $J = 272.7$ Hz), 35.8, 30.2, 28.9, 26.0, 21.9 (signals corresponding to the major isomer);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 31.0, 30.7, 27.3, 21.8, 21.7 (signals corresponding to the minor isomer, other signals are unclear or missing);

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.33.
General Procedure for Variation of Chain Length Investigation

To a solution of substrate (0.2 mmol) in HFIP in a screw-cap vial equipped with a stirrer bar was added pTSA. The reaction mixture was stirred at indicated temperature for 4 h or 18 h. The solvent was then evaporated off and the residue was purified by flash column chromatography (silica-gel, hexanes/ethyl acetate) without work-up to obtain the product.

3,9,9-trimethyl-2,3,4,9-tetrahydro-1H-fluorene (4a): Prepared according to the general procedure from 3a using HFIP/PhCl (0.2 mL/1.8 mL) and pTSA (10 mol%) at room temperature for 18 h. Purification by flash column chromatography eluting with hexanes provided 4a (25%, 10.6 mg) as a colorless oil. Spectral data were in accordance with those previously reported.9

1H NMR (400 MHz, CDCl3) δ 7.34 – 7.30 (m, 1H), 7.25 (td, J = 7.3, 1.2 Hz, 1H), 7.20 – 7.13 (m, 2H), 2.60 – 1.52 (m, 1H), 2.34 – 2.17 (m, 2H), 2.06 – 1.80 (m, 3H), 1.51 – 1.33 (m, 1H), 1.23 (s, 3H), 1.22 (s, 3H), 1.12 (d, J = 6.5 Hz, 3H);

13C NMR (101 MHz, CDCl3) δ 153.9, 150.1, 143.6, 131.9, 126.2, 124.0, 120.9, 117.7, 48.4, 31.4, 30.4, 29.0, 24.0, 23.9, 21.7, 21.2.

7-methoxy-3,9,9-trimethyl-2,3,4,9-tetrahydro-1H-fluorene (4b): Prepared according to the general procedure from 3b using HFIP/PhCl (0.2 mL/1.8 mL) and pTSA (10 mol%) at room temperature for 18 h. Purification by flash column chromatography eluting with hexanes provided 4b (10%, 5.2 mg) as a colorless oil. Spectral data were in accordance with those previously reported.9

1H NMR (400 MHz, CDCl3) δ 7.07 (d, J = 8.1 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.78 (dd, J = 8.1, 2.4 Hz, 1H), 3.85 (s, 3H), 2.57 – 2.48 (m, 1H), 2.32 – 2.14 (m, 2H), 2.03 – 1.78 (m, 3H), 1.50 – 1.34 (m, 1H), 1.21 (s, 3H), 1.20 (s, 3H), 1.10 (d, J = 6.5 Hz, 3H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.5, 155.8, 147.9, 136.8, 131.4, 117.8, 110.6, 108.5, 55.6, 48.4, 31.4, 30.5, 29.0, 24.2, 24.1, 21.7, 21.2.

3,7,9,9-tetramethyl-2,3,4,9-tetrahydro-1H-fluorene (4c): Prepared according to the general procedure from 3c using HFIP/PhCl (0.2 mL/1.8 mL) and pTSA (10 mol%) at room temperature for 18 h. Purification by flash column chromatography eluting with hexanes provided 4c (44%, 19.9 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^9\)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 (dd, $J = 1.5$, 0.8 Hz, 1H), 7.11 – 7.02 (m, 2H), 2.60 – 2.52 (m, 1H), 2.43 (s, 3H), 2.34 – 2.17 (m, 2H), 2.08 – 1.80 (m, 3H), 1.51 – 1.36 (m, 1H), 1.24 (s, 3H), 1.23 (s, 3H), 1.13 (d, $J = 6.5$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.2, 149.0, 141.0, 133.5, 131.8, 126.8, 122.0, 117.4, 48.3, 31.4, 30.5, 29.1, 24.1, 24.0, 21.8, 21.6, 21.2.

3,6,8,9,9-pentamethyl-2,3,4,9-tetrahydro-1H-fluorene (4d): Prepared according to the general procedure from 3d using HFIP/PhCl (0.2 mL/1.8 mL) and pTSA (10 mol%) at room temperature for 18 h. Purification by flash column chromatography eluting with hexanes provided 4d (57%, 27.3 mg) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.87 (d, $J = 1.6$ Hz, 1H), 6.76 (d, $J = 1.6$ Hz, 1H), 2.60 – 2.48 (m, 1H), 2.49 (s, 3H), 2.38 (s, 3H), 2.29 – 2.17 (m, 2H), 2.04 – 1.80 (m, 3H), 1.52 – 1.37 (m, 1H), 1.32 (s, 3H), 1.31 (s, 3H), 1.12 (d, $J = 6.4$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.5, 147.5, 144.6, 136.0, 132.0, 131.6, 127.4, 116.3, 49.2, 31.5, 30.4, 29.0, 21.7, 21.6, 21.5, 21.3, 20.9, 18.6;

ESI-HRMS: calcd for C$_{18}$H$_{24}$H$: m/z = 241.1951, found: m/z = 241.1950;

FTIR (neat): 2958, 2925, 2870, 1639, 1459, 1385, 1302 cm$^{-1}$.
6-methoxy-3,9,9-trimethyl-2,3,4,9-tetrahydro-1H-fluorene (4e): Prepared according to the general procedure from 3e using HFIP/PhCl (0.2 mL/1.8 mL) and pTSA (10 mol%) at room temperature for 18 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (100/0 to 98/2) provided 4e (23%, 11.1 mg) as a colorless oil and 4e’ (12%, 5.8 mg) as a white solid. Spectral data of both were in accordance with those previously reported.9

\[ \text{MeO} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.21 (d, $J = 8.0$ Hz, 1H), 6.76 (d, $J = 2.4$ Hz, 1H), 6.70 (dd, $J = 8.1$, 2.4 Hz, 1H), 3.85 (s, 3H), 2.58 – 2.49 (m, 1H), 2.34 – 2.16 (m, 2H), 2.03 – 1.79 (m, 3H), 1.50 – 1.33 (m, 1H), 1.21 (s, 3H), 1.20 (s, 3H), 1.12 (d, $J = 6.4$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.9, 151.6, 146.2, 145.1, 131.7, 121.2, 109.0, 104.0, 55.5, 47.8, 31.3, 30.4, 29.0, 24.2, 24.1, 21.7, 21.3.

\[ \text{MeO} \]

8-methoxy-3,9,9-trimethyl-2,3,4,9-tetrahydro-1H-fluorene (4e’)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.27 – 7.18 (m, 1H), 6.83 (d, $J = 7.4$ Hz, 1H), 6.71 (d, $J = 8.2$ Hz, 1H), 3.92 – 3.88 (m, 3H), 2.60 – 2.46 (m, 1H), 2.34 – 2.14 (m, 2H), 2.05 – 1.79 (m, 3H), 1.52 – 1.35 (m, 1H), 1.34 – 1.27 (m, 6H), 1.15 – 1.05 (m, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.3, 151.2, 145.5, 139.2, 131.4, 127.7, 110.8, 107.3, 55.2, 49.2, 31.4, 30.5, 29.0, 21.7, 21.40, 21.37, 20.8.
Ethyl 2,2-dimethyl-6-phenyl-3,4-dihydro-2\(H\)-pyran-5-carboxylate (6a): Prepared according to the general procedure from 5a using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided 6a (70%, 36.7 mg) as a pale-yellow oil. Spectral data were in accordance with those previously reported.\(^{20}\)

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.00 (m, 5H), 3.94 (q, \(J = 7.1\) Hz, 2H), 2.52 (t, \(J = 6.7\) Hz, 2H), 1.78 (t, \(J = 6.8\) Hz, 2H), 1.39 (s, 6H), 0.93 (t, \(J = 7.1\) Hz, 3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 168.8, 162.0, 137.8, 128.6, 128.5, 127.6, 101.9, 76.2, 59.6, 32.3, 26.4, 20.2, 13.7.

Ethyl 6-(4-methoxyphenyl)-2,2-dimethyl-3,4-dihydro-2\(H\)-pyran-5-carboxylate (6b): Prepared according to the general procedure from 5b using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) then preparative TLC eluting with hexanes/DCM (1/9) provided 6b (50%, 29 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^{20}\)

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.31 – 7.26 (m, 2H), 6.91 – 6.84 (m, 2H), 3.98 (q, \(J = 7.1\) Hz, 2H), 3.83 (s, 3H), 2.50 (t, \(J = 6.8\) Hz, 2H), 1.76 (t, \(J = 6.8\) Hz, 2H), 1.37 (s, 6H), 1.02 (t, \(J = 7.1\) Hz, 3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 168.9, 161.8, 160.0, 130.05, 130.01, 113.0, 101.3, 76.1, 59.6, 55.3, 32.3, 26.4, 20.4, 13.9;

ESI-HRMS: caleed for C_{17}H_{22}O_{4}H\(^{+}\): m/z = 291.1591, found: m/z = 291.1589;

FTIR (neat): 2980, 2940, 1685, 1603, 1510, 1459, 1370, 1297, 1246 cm\(^{-1}\).
Ethyl 2,2-dimethyl-6-(4-nitrophenoxyyl)-3,4-dihydro-2H-pyran-5-carboxylate (6c): Prepared according to the general procedure from 5c using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided 6c (80%, 48.8 mg) as a viscous yellow oil. Spectral data were in accordance with those previously reported.20

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 – 8.18 (m, 2H), 7.53 – 7.45 (m, 2H), 3.98 (q, $J$ = 7.1 Hz, 2H), 2.53 (t, $J$ = 6.7 Hz, 2H), 1.81 (t, $J$ = 6.7 Hz, 2H), 1.40 (s, 6H), 1.01 (t, $J$ = 7.1 Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.7, 159.8, 147.7, 144.2, 129.6, 122.9, 103.5, 60.0, 32.1, 26.4, 20.1, 13.9.

(2,2-dimethyl-6-phenyl-3,4-dihydro-2H-pyranyl-5-yl)(phenyl)methanone (6d): Prepared according to the general procedure from 5d using HFIP (100 µL) and pTSA (10 mol%) at room temperature or 50 °C for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided 6d (50%, 29.2 mg, at room temperature) or (92%, 53.7 mg, at 50 °C) as a white solid. Spectral data were in accordance with those previously reported.21

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 – 7.46 (m, 2H), 7.25 – 7.15 (m, 3H), 7.12 – 6.99 (m, 5H), 2.69 (t, $J$ = 6.8 Hz, 2H), 1.88 (t, $J$ = 6.8 Hz, 2H), 1.51 (s, 6H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.9, 156.0, 139.5, 136.2, 131.1, 129.5, 129.2, 129.1, 127.61, 127.57, 110.8, 76.0, 32.4, 26.3, 21.7.
2,2-dimethyl-5,6-diphenyl-3,4-dihydro-2H-pyran (6e): Prepared according to the general procedure from 5e using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (99/1 to 98/2) provided 6e (40%, 21 mg) as a pale-yellow oil. Spectral data were in accordance with those previously reported.20

1H NMR (400 MHz, CDCl₃) δ 7.24 – 7.06 (m, 10H), 2.53 (t, J = 6.8 Hz, 2H), 1.91 (t, J = 6.8 Hz, 2H), 1.45 (s, 6H);
13C NMR (101 MHz, CDCl₃) δ 147.9, 142.1, 137.3, 129.6, 129.5, 128.0, 127.5, 127.4, 125.6, 110.3, 73.6, 33.6, 26.4, 25.8.

(4,4-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)(phenyl)methanone (6e‘): Prepared according to the general procedure from 5e using HFIP (100 µL) and pTSA (10 mol%) at room temperature or 50 °C for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (99/1 to 98/2) provided 6e′ (33%, 17.4 mg, at room temperature) or (83%, 43.8 mg, at 50 °C) as a pale-yellow oil. Spectral data were in accordance with those previously reported.20

1H NMR (400 MHz, CDCl₃) δ 8.08 – 7.99 (m, 2H), 7.65 – 7.57 (m, 1H), 7.55 – 7.49 (m, 2H), 7.45 (dd, J = 8.0, 1.3 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.10 (td, J = 7.5, 1.4 Hz, 1H), 6.91 (dd, J = 7.7, 1.3 Hz, 1H), 4.84 (t, J = 6.5 Hz, 1H), 2.22 (dddd, J = 13.7, 9.6, 6.5, 3.2 Hz, 1H), 2.12 (ddddd, J = 13.7, 8.3, 6.4, 3.2 Hz, 1H), 1.82 (dddd, J = 13.4, 9.4, 3.2 Hz, 1H), 1.67 (dd, J = 13.5, 8.4, 3.2 Hz, 1H), 1.41 (s, 3H), 1.35 (s, 3H);
13C NMR (101 MHz, CDCl₃) δ 202.5, 146.5, 136.7, 133.7, 133.0, 129.3, 128.8, 128.7, 127.1, 126.8, 125.6, 48.3, 36.0, 33.8, 31.8, 31.6, 24.0.
Ethyl 6-(3,5-dichlorophenyl)-2,2-dimethyl-3,4-dihydro-2H-pyran-5-carboxylate (6x): Prepared according to the general procedure from 5x using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided 6x (76%, 50.0 mg) as a colorless oil.

\[ \text{1H NMR (300 MHz, CDCl}_3\text{)} \delta 7.35 (t, J = 1.9 Hz, 1H), 7.21 (d, J = 2.0 Hz, 2H), 3.99 (q, J = 7.2 Hz, 2H), 2.50 (t, J = 6.7 Hz, 2H), 1.77 (t, J = 6.7 Hz, 2H), 1.38 (s, 6H), 1.02 (t, J = 7.1 Hz, 3H); \]

\[ \text{13C NMR (76 MHz, CDCl}_3\text{)} \delta 167.9, 159.0, 140.4, 134.1, 128.5, 127.2, 103.3, 60.0, 32.1, 26.3, 20.2, 13.8; \]

ESI-HRMS: calcld for C\text{16}H\text{18}Cl\text{2}O\text{3}H\text{+}: m/z = 329.0706, found: m/z = 329.0701;

FTIR (neat): 2980, 2939, 1687, 1628, 1586, 1562, 1436, 1370, 1295, 1261, 1232 cm\text{−1}.

Methyl 2,2-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyran-5-carboxylate (6y): Prepared according to the general procedure from 5y using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided 6y (77%, 48.3 mg) as a colorless oil. Spectral data were in accordance with those previously reported.

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 7.66 – 7.60 (m, 2H), 7.48 – 7.42 (m, 2H), 3.52 (s, 3H), 2.53 (t, J = 6.7 Hz, 2H), 1.80 (t, J = 6.7 Hz, 2H), 1.39 (s, 6H); \]

\[ \text{13C NMR (101 MHz, CDCl}_3\text{)} \delta 168.4, 161.0, 141.1, 130.6 (q, J = 32.0 Hz), 128.9, 128.7 (q, J = 4.0 Hz), 124.1 (q, J = 271.0 Hz), 102.5, 51.1, 32.1, 26.3, 20.1. \]

Ethyl 5-methyl-2-phenylfuran-3-carboxylate (8a): Prepared according to the general procedure from 7a using HFIP (100 µL) and pTSA (10 mol%) at room temperature or 50 °C for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided 8a (22%, 10.1
mg, at room temperature) or (91%, 41.9 mg, at 50 °C) as a pale-yellow oil. Spectral data were in accordance with those previously reported.²⁰

¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.94 (m, 2H), 7.48 – 7.41 (m, 2H), 7.41 – 7.36 (m, 1H), 6.46 (q, J = 1.1 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.38 (d, J = 1.0 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 163.8, 155.9, 151.1, 130.1, 128.9, 128.1, 128.0, 114.53, 108.8, 60.4, 14.2, 13.4.

**Ethyl 2-(4-methoxyphenyl)-5-methylfuran-3-carboxylate (8b):** Prepared according to the general procedure from 7b using HFIP (100 µL) and pTSA (10 mol%) at room temperature or 50 °C for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided 8b (37%, 19.2 mg, at room temperature) or (88%, 45.8 mg, at 50 °C) as a colorless oil. Spectral data were in accordance with those previously reported.²⁰

¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.92 (m, 2H), 7.01 – 6.92 (m, 2H), 6.43 (q, J = 1.0 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 2.36 (d, J = 1.1 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 164.0, 160.1, 156.3, 150.4, 129.7, 122.8, 113.4, 113.3, 108.6, 60.2, 55.3, 14.3, 13.3.

**Ethyl 5-methyl-2-(4-nitrophenyl)furan-3-carboxylate (8c):** Prepared according to the general procedure from 7c using HFIP (100 µL) and pTSA (10 mol%) at room temperature or 50 °C for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1 to 9/1) provided 8c (10%, 5.5 mg, at room temperature) or (64%, 35.2 mg, at 50 °C) as a yellow solid. Spectral data were in accordance with those previously reported.²⁰

¹H NMR (400 MHz, CDCl₃) δ 8.30 – 8.21 (m, 4H), 6.53 (q, J = 1.0 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.41 (d, J = 1.0 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H);
\[
{^{13}\text{C NMR (101 MHz, CDCl}_3} \delta 163.3, 152.9, 152.7, 147.3, 135.7, 128.4, 123.4, 117.6, 109.9, 60.9, 14.2, 13.4.
\]

(5-methyl-2-phenylfuran-3-yl)(phenyl)methanone (8d): Prepared according to the general procedure from 7d using HFIP (100 µL) and pTSA (10 mol%) at room temperature or 50 °C for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided 8d (35%, 18.3 mg, at room temperature) or (97%, 50.8 mg, at 50 °C) as a colorless oil. Spectral data were in accordance with those previously reported.\(^{11}\)

\[
{^1\text{H NMR (400 MHz, CDCl}_3} \delta 7.89 – 7.82 (m, 2H), 7.73 – 7.65 (m, 2H), 7.51 (ddt, J = 8.0, 6.9, 1.3 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.34 – 7.24 (m, 3H), 6.32 (q, J = 1.0 Hz, 1H), 2.43 (d, J = 1.0 Hz, 3H);
\]

\[
{^{13}\text{C NMR (101 MHz, CDCl}_3} \delta 192.0, 154.5, 151.2, 138.2, 132.7, 130.0, 129.7, 128.6, 128.25, 128.23, 127.3, 121.8, 109.8, 13.4.
\]

5-methyl-2,3-diphenylfuran (8e): Prepared according to the general procedure from 7e using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes provided 8e (85%, 39.6 mg) as a colorless oil. Spectral data were in accordance with those previously reported.\(^{12}\)

\[
{^1\text{H NMR (400 MHz, CDCl}_3} \delta 7.56 – 7.48 (m, 2H), 7.45 – 7.40 (m, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.26 (m, 3H), 7.26 – 7.20 (m, 1H), 6.19 (q, J = 1.1 Hz, 1H), 2.42 (d, J = 1.0 Hz, 3H);
\]

\[
{^{13}\text{C NMR (101 MHz, CDCl}_3} \delta 151.3, 146.8, 134.7, 131.5, 128.59, 128.56, 128.3, 127.0, 126.9, 125.9, 123.2, 110.1, 13.6.
\]
Ethyl 5,5-dimethyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (10a): Prepared according to the general procedure from 9a using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1 to 4/1) provided 10a (53%, 26 mg) as a yellow oil. Spectral data were in accordance with those previously reported.20

\[ \text{1}^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.80 – 7.72 (m, 2H), 7.46 – 7.34 (m, 3H), 4.14 (q, J = 7.1 Hz, 2H), 2.95 (s, 2H), 1.52 (s, 6H), 1.22 (t, J = 7.1 Hz, 3H); \]

\[ \text{1}^3\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 165.7, 164.1, 130.6, 130.1, 129.2, 127.6, 101.7, 85.6, 59.6, 44.3, 28.2, 14.3. \]

3-benzoyl-5,5-dimethylidihydrofuran-2(3H)-one (10’a): Prepared according to the general procedure from 9a using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1 to 4/1) provided a mixture of ketone form and enol form of 10’a (33%, 14.4 mg, 100/15 ratio) as a pale-yellow oil. Spectral data were in accordance with those previously reported.22

\[ \text{1}^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 12.00 (s, 0.15H), 8.12 – 8.04 (m, 2H), 7.75 – 7.70 (m, 0.3H), 7.66 – 7.58 (m, 1H), 7.55 – 7.49 (m, 2H), 7.49 – 7.44 (m, 0.45H), 4.80 (dd, J = 9.7, 8.5 Hz, 1H), 3.01 (s, 0.3H), 2.81 (dd, J = 13.1, 8.6 Hz, 1H), 2.31 (dd, J = 13.1, 9.7 Hz, 1H), 1.58 (s, 3H), 1.52 (s, 3H), 1.49 (s, 0.9H); \]

\[ \text{1}^3\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 193.0, 176.5, 171.8, 164.8, 135.0, 134.0, 133.8, 130.8, 129.5, 128.7, 128.5, 127.5, 96.4, 83.9, 83.7, 49.7, 40.3, 37.5, 28.6, 28.51, 28.49. \]

Ethyl 2-(4-methoxyphenyl)-5,5-dimethyl-4,5-dihydrofuran-3-carboxylate (10b): Prepared according to the general procedure from 9b using HFIP (100 µL) and pTSA (10 mol%) at room temperature or 50 °C for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1 to 4/1) provided 10b (48%, 21 mg) as a yellow oil. Spectral data were in accordance with those previously reported.21

\[ \text{1}^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.05 (s, 0.15H), 8.13 – 7.78 (m, 1H), 7.47 – 7.31 (m, 4H), 4.14 (q, J = 7.1 Hz, 2H), 2.94 (s, 2H), 1.52 (s, 6H), 1.22 (t, J = 7.1 Hz, 3H); \]

\[ \text{1}^3\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 176.5, 171.8, 164.8, 135.0, 134.0, 133.8, 130.8, 129.5, 128.7, 128.5, 127.5, 96.4, 83.9, 83.7, 49.7, 40.3, 37.5, 28.6, 28.51, 28.49. \]
acetate (19/1 to 4/1) provided 10b (14%, 7.7 mg, room temperature condition) or (24%, 13.2 mg, 50 °C condition) as a colorless oil. Spectral data were in accordance with those previously reported.20

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 7.83 – 7.76 (m, 2H), 6.94 – 6.87 (m, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 2.93 (s, 2H), 1.50 (s, 6H), 1.25 (t, J = 7.1 Hz, 3H); \]

\[ ^13C \text{ NMR (101 MHz, CDCl}_3 \delta 165.9, 163.9, 161.1, 131.0, 122.9, 112.9, 100.3, 85.0, 59.5, 55.3, 44.4, 28.2, 14.4. \]

3-(4-methoxybenzoyl)-5,5-dimethylidihydrofuran-2(3H)-one (10b): Prepared according to the general procedure from 9b using HFIP (100 µL) and pTSA (10 mol%) at room temperature or 50 °C for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1 to 4/1) provided a mixture of ketone form and enol form of 10b (18%, 10 mg, 10/1 ratio, at room temperature condition) or (35%, 17.4 mg, 10/1 ratio, at 50 °C) as a viscous yellow oil.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 12.08 (s, 0.1H), 8.10 – 8.03 (m, 2H), 7.74 – 7.63 (m, 0.2H), 7.02 – 6.95 (m, 2H), 4.74 (dd, J = 9.7, 8.4 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 0.3H), 3.00 (s, 0.2H), 2.83 (dd, J = 13.1, 8.4 Hz, 1H), 2.28 (dd, J = 13.1, 9.7 Hz, 1H), 2.06 (s, 0.2H), 1.57 (s, 3H), 1.52 (s, 3H), 1.50 (s, 0.6H); \]

\[ ^13C \text{ NMR (101 MHz, CDCl}_3 \delta 191.1, 172.1, 164.2, 132.0, 129.4, 128.7, 114.9, 113.9, 83.8, 55.6, 49.4, 40.5, 37.4, 28.7, 28.6, 28.50 (some signals of enol form were missing); \]

ESI-HRMS: caled for C_{14}H_{16}O_{4}H\(^+\): m/z = 249.1121, found: m/z = 249.1118;

FTIR (neat): 2976, 2845, 1754, 1617, 1598, 1510, 1458, 1422, 1378, 1342, 1300, 1263, 1236 cm\(^{-1}\).

Ethyl 5,5-dimethyl-2-(4-nitrophenyl)-4,5-dihydrofuran-3-carboxylate (10c): Prepared according to the general procedure from 9c using HFIP (100 µL) and pTSA (10 mol%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1 to 4/1)
provided 10c (82%, 48 mg) as a yellow oil. Spectral data were in accordance with those previously reported.\textsuperscript{20}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.26 – 8.20 (m, 2H), 8.00 – 7.95 (m, 2H), 4.16 (q, \(J = 7.1\) Hz, 2H), 2.98 (s, 2H), 1.53 (s, 6H), 1.24 (t, \(J = 7.1\) Hz, 3H); 
\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 165.1, 161.0, 148.4, 136.7, 130.4, 122.7, 104.5, 86.4, 60.0, 44.4, 28.2, 14.2.

5,5-dimethyl-3-(4-nitrobenzoyl)dihydrofuran-2(3H)-one (10’c): Prepared according to the general procedure from 9c using HFIP (100 µL) and pTSA (10 mol\%) at room temperature for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1 to 4/1) provided a mixture of ketone form and enol form of 10’c (16%, 8.4 mg, 1/2 ratio) as a viscous yellow oil.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 12.03 (s, 1H), 8.42 – 8.24 (m, 4H), 7.95 – 7.85 (m, 2H), 4.80 (dd, \(J = 9.5, 8.7\) Hz, 0.5H), 3.04 (s, 2H), 2.91 (dd, \(J = 13.2, 8.6\) Hz, 0.5H), 2.33 (dd, \(J = 13.2, 9.5\) Hz, 0.5H), 1.60 (s, 1.5H), 1.56 (s, 1.5H), 1.54 (s, 6H); 
\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 191.4, 176.0, 170.8, 161.8, 150.7, 148.7, 140.1, 139.6, 130.7, 128.5, 123.8, 123.7, 99.3, 84.3, 84.2, 50.5, 40.2, 36.8, 28.7, 28.5, 28.4; 
ESI-HRMS: calcd for C\textsubscript{13}H\textsubscript{13}NO\textsubscript{5}H\textsuperscript{+}: m/z = 264.0866, found: m/z = 264.0862; 
FTIR (neat): 3122, 2986, 2934, 1670, 1631, 1593, 1514, 1451, 1411, 1399, 1343, 1267, 1218 cm\textsuperscript{-1}.

(5,5-dimethyl-2-phenyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (10d): Prepared according to the general procedure from 9d using HFIP (100 µL) and pTSA (10 mol\%) at room temperature or 50 °C for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (19/1) provided 10d (46%, 25.6 mg, at room temperature) or (82%, 45.6 mg, at 50 °C) as a white solid.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.41 (m, 2H), 7.25 – 7.15 (m, 4H), 7.11 – 7.03 (m, 4H), 3.14 (s, 2H), 1.61 (s, 6H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.8, 165.3, 139.4, 130.9, 130.6, 129.8, 129.3, 128.8, 127.6, 111.9, 86.3, 45.4, 28.0.

ESI-HRMS: calcd for C$_{19}$H$_{18}$O$_2$H$: m/z = 279.1380$, found: $m/z = 279.1374$;

FTIR (neat): 3068, 2978, 2934, 1677, 1597, 1571, 1492, 1449, 1368, 1257 cm$^{-1}$.

2,2-dimethyl-4,5-diphenyl-2,3-dihydrofuran (10e): Prepared according to the general procedure from 9e using HFIP (100 µL) and pTSA (10 mol%) at room temperature or 50 °C for 4 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (98/2) provided 10e (66%, 33 mg, at room temperature) or (96%, 48 mg, at 50 °C) as a colorless oil. Spectral data were in accordance with those previously reported.$^{20}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 – 7.46 (m, 2H), 7.34 – 7.29 (m, 3H), 7.26 – 7.18 (m, 4H), 7.16 – 7.10 (m, 1H), 3.02 (s, 2H), 1.55 (s, 6H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.2, 136.3, 132.5, 128.5, 128.19, 128.15, 127.0, 125.6, 109.0, 82.4, 48.4, 28.3.
### Table S4. Comparison between three catalytic systems: pTSA/HFIP, TfOH/DCE, and pTSA/DCE\(^{[a]}\)

| Product | pTSA/HFIP | pTSA/DCE | TfOH/DCE |
|---------|-----------|----------|----------|
| 4a      | 30%       | ND       | 25%      |
| 2a      | 78%\(^{[b]}\) | ND (10%) | 36%\(^{[b]}\) |
| 6a      | 73%       | traces   | ND (8%)  |
| 8a      | 24% (93%) | ND       | 67%      |
| 10a     | 56%       | traces   | 76%      |

| Product | pTSA/HFIP | pTSA/DCE | TfOH/DCE |
|---------|-----------|----------|----------|
| 4d      | 58%       | ND       | 37%      |
| 2e'     | 77%\(^{[b]}\) | ND (ND) | 24%\(^{[b]}\) |
| 6e      | 42% (trace) | ND (trace) | 45% (7%) |
| 6e'     | 84%       | ND       | 87%      |
| 10e     | 67% (96%) | 9%       | 90% (96%) |

\(^{[a]}\) Reaction condition: Substrate (0.2 mmol), pTSA or TfOH (10 mol%), HFIP or DCE (100 \(\mu\)L) at RT for 4 h. Yields in parentheses are of reactions carried out at 50 °C. Yields were determined by \(^1\)H NMR integration using mesitylene as an internal standard. ND = not detected. \(^{[b]}\) Overall yields of two olefin isomers 2/2'.

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**Comparison of Cyclization Reactions Using Three Different Catalytic Systems**
NMR Spectra

5-bromo-2-methylpent-2-ene: $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1-bromo-2-methylhex-2-ene: $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1-bromo-2-(2-methylprop-1-en-1-yl)benzene: $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
4-Methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
4-methyl-N-(4-methylpent-3-en-1-yl)benzenesulfonamide: $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(2-methylprop-1-en-1-yl)benzaldehyde: $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-benzoyl-6-methylhept-5-enoate (1a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(4-methoxybenzoyl)-6-methylhept-5-enoate (1b): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 6-methyl-2-(4-nitrobenzoyl)hept-5-enoate (1c): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(4-methylpent-3-en-1-yl)-1,3-diphenylpropane-1,3-dione (1d): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
6-methyl-1,2-diphenylhept-5-en-1-one (1e): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
**Ethyl 3-(3-methoxyphenyl)-3-oxopropanoate (1f):** $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(2-naphthoyl)-6-methylhept-5-enoate (1g): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2,6-dimethyl-1-phenylhept-5-en-1-one (1h): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(3,5-dichlorobenzoyl)-6-methylhept-5-enoate (1i): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
4-methyl-N-(3-methylbut-2-en-1-yl)-N-(1-oxo-1-phenylpropan-2-yl)benzenesulfonamide (1j):

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
4-methyl-N-(3-methylbut-2-en-1-yl)-N-(1-oxo-1-(p-tolyl)propan-2-yl)benzenesulfonamide (1k):

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
4-methyl-N-(3-methylbut-2-en-1-yl)-N-(2-oxo-2-(p-tolyl)ethyl)benzenesulfonamide (11): \( ^1\)H NMR (400 MHz, CDCl\(_3\)) and \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)).
N-(2-(4-chlorophenyl)-2-oxoethyl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (1m): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(2-(2-methylprop-1-en-1-yl)phenyl)-1-phenylpropan-1-one (1n): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(2-(2-methylprop-1-en-1-yl)phenyl)-1,2-diphenylethan-1-one (1o): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1-(4-chlorophenyl)-2-(2-(2-methylprop-1-en-1-yl)phenyl)-2-phenylethan-1-one (1p): \(^1\)H NMR (400 MHz, CDCl\(_3\)) and \(^{13}\)C NMR (101 MHz, CDCl\(_3\)).
1-(4-methoxyphenyl)-2-(2-(2-methylprop-1-yl)phenyl)-2-phenylethan-1-one (1q): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(2-(2-methylprop-1-en-1-yl)phenyl)-3,4-dihyronaphthalen-1(2H)-one (1r): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(2-(2-Methylprop-1-en-1-yl)benzylidene)-1,3-diphenylpropane-1,3-dione (1s): $^1$H NMR (300 MHz, CDCl$_3$) and $^{13}$C NMR (76 MHz, CDCl$_3$).
3-(2-(2-methylprop-1-en-1-yl)benzylidene)pentane-2,4-dione (I): $^1$H NMR (300 MHz, CDCl$_3$) and $^{13}$C NMR (76 MHz, CDCl$_3$).
(E)-2-(2-(2-methylprop-1-en-1-yl)benzylidene)-1-phenylbutane-1,3-dione (1u): $^1$H NMR (300 MHz, CDCl$_3$) and $^{13}$C NMR (76 MHz, CDCl$_3$).
4-methyl-N-(4-methylpent-3-en-1-yl)-N-(1-oxo-1-(p-tolyl)propan-2-yl)benzenesulfonamide (1v): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
N-(2-formylphenyl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (1w): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1-(3,5-dichloro phenyl)-3,7-dimethyl oct-6-en-1-one (1x): \(^1H\) NMR (400 MHz, CDCl\(_3\)) and \(^{13}C\) NMR (101 MHz, CDCl\(_3\)).

![NMR Spectra](image)

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3,7-dimethyl-1-(4-(trifluoromethyl)phenyl)oct-6-en-1-one (1y): $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (101 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$).
3,7-dimethyl-1-phenyloct-6-en-1-one (3a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1-(4-methoxyphenyl)-3,7-dimethyloct-6-en-1-one (3b): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
**3,7-dimethyl-1-(p-tolyl)oct-6-en-1-one (3c):** $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1-(3,5-dimethylphenyl)-3,7-dimethyloct-6-en-1-one (3d): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1-(3-methoxyphenyl)-3,7-dimethyloct-6-en-1-one (3e): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-benzoyl-7-methyloct-6-enoate (3f): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(5-methylhex-4-en-1-yl)-1,3-diphenylpropane-1,3-dione (3g): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
7-methyl-1,2-diphenyloct-6-en-1-one (3h): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-benzoyl-5-methylhex-4-enoate (5a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(4-methoxybenzoyl)-5-methylhex-4-enoate (5b): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 5-methyl-2-(4-nitrobenzoyl)hex-4-enoate (5c): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(3-methylbut-2-en-1-yl)-1,3-diphenylpropane-1,3-dione (5d): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
5-methyl-1,2-diphenylhex-4-en-1-one (5e): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(3,5-dichlorobenzoyl)-5-methylhex-4-enoate (5x): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Methyl 5-methyl-2-(4-(trifluoromethyl)benzoyl)hex-4-enoate (5y): $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (101 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$).
Ethyl 2-benzoylpent-4-ynoate (7a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(4-methoxybenzoyl)pent-4-ynoate (7b): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(4-nitrobenzoyl)pent-4-ynoate (7c): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1,3-diphenyl-2-(prop-2-yn-1-yl)propane-1,3-dione (7d): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1,2-diphenylpent-4-yn-1-one (7e): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-benzoyl-4-methylpent-4-enoate (9a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(4-methoxybenzoyl)-4-methylpent-4-enoate (9b): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 4-methyl-2-(4-nitrobenzoyl)pent-4-enoate (9c): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(2-methylallyl)-1,3-diphenylpropane-1,3-dione (9d): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
4-methyl-1,2-diphenylpent-4-en-1-one (9e): \(^1\)H NMR (400 MHz, CDCl\(_3\)) and \(^{13}\)C NMR (101 MHz, CDCl\(_3\)).
Ethyl 2-phenylcyclopent-2-ene-1-carboxylate (2a) and ethyl 2-phenylcyclopent-1-ene-1-carboxylate (2’a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(4-methoxyphenyl)cyclopent-2-ene-1-carboxylate (2b) and ethyl 2-(4-methoxyphenyl)cyclopent-1-ene-1-carboxylate (2'b): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Phenyl(2-phenylcyclopent-2-en-1-yl)methanone (2d): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1,2-diphenylcyclopent-1-ene (2’e): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(4-methoxyphenyl)cyclopent-2-ene-1-carboxylate (2f) and ethyl 2-(4-methoxyphenyl)cyclopent-1-ene-1-carboxylate (2'f): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(naphthalen-2-yl)cyclopent-2-ene-1-carboxylate (2g) and ethyl 2-(naphthalen-2-yl)cyclopent-1-ene-1-carboxylate (2'g): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
(2-methylcyclopent-1-en-1-yl)benzene (2'h): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(3,5-dichlorophenyl)cyclopent-2-ene-1-carboxylate (2i): $^1$H NMR (300 MHz, CDCl$_3$) and $^{13}$C NMR (76 MHz, CDCl$_3$).
2-methyl-3-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole (2j): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-methyl-3-(p-tolyl)-1-tosyl-2,5-dihydro-1H-pyrrole (2k): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
3-(p-toly1)-1-tosyl-2,5-dihydro-1H-pyrrole (2l): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
3-(4-chlorophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole (2m): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1-methyl-2-phenyl-1H-indene (2n) and 3-methyl-2-phenyl-1H-indene (2’n): \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) and \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}).
1,2-diphenyl-1H-indene (2o): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(4-chlorophenyl)-1-phenyl-1H-indene (2p): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2-(4-methoxyphenyl)-1-phenyl-1H-indene (2q): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
6,11-dihydro-5H-benzo[α]fluorene (2'R): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Phenyl(3-phenylnaphthalen-2-yl)methanone (2s) and phenyl(3-phenyl-4-(prop-1-en-2-yl)naphthalen-2-yl)methanone (2s’): $^1$H NMR (300 MHz, CDCl$_3$) and $^{13}$C NMR (76 MHz, CDCl$_3$).
1-(3-methylnaphthalen-2-yl)ethan-1-one (2t) and 1-(3-methyl-4-(prop-1-en-2-yl)naphthalen-2-yl)ethan-1-one (2t')

$^1$H NMR (300 MHz, CDCl$_3$) and $^{13}$C NMR (76 MHz, CDCl$_3$).
(3-methylnaphthalen-2-yl)(phenyl)methanone (2u) and (3-methyl-4-(prop-1-en-2-yl)naphthalen-2-yl)(phenyl)methanone (2u'): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
6-methyl-5-(p-tolyl)-1-tosyl-1,2,3,6-tetrahydropyridine (2v): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
1-tosyl-1,2-dihydroquinoline (2w): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
3',5'-dichloro-3-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (2x) and 3',5'-dichloro-5-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (2'x): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
3-methyl-4'-(trifluoromethyl)-2,3,4,5-tetrahydro-1,1'-biphenyl (2y) and 5-methyl-4'-
(trifluoromethyl)-2,3,4,5-tetrahydro-1,1'-biphenyl (2'y): $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (101 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$).
and
3,9,9-trimethyl-2,3,4,9-tetrahydro-1H-fluorene (4a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
7-methoxy-3,9,9-trimethyl-2,3,4,9-tetrahydro-1H-fluorene (4b): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
3,7,9,9-tetramethyl-2,3,4,9-tetrahydro-1H-fluorene (4c): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
3,6,8,9,9-pentamethyl-2,3,4,9-tetrahydro-1H-fluorene (4d): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
6-methoxy-3,9,9-trimethyl-2,3,4,9-tetrahydro-1H-fluorene (4e): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
8-methoxy-3,9,9-trimethyl-2,3,4,9-tetrahydro-1H-fluorene (4e'): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2,2-dimethyl-6-phenyl-3,4-dihydro-2H-pyran-5-carboxylate (6a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 6-(4-methoxyphenyl)-2,2-dimethyl-3,4-dihydro-2H-pyran-5-carboxylate (6b): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2,2-dimethyl-6-(4-nitrophenyl)-3,4-dihydro-2H-pyran-5-carboxylate (6c): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
(2,2-dimethyl-6-phenyl-3,4-dihydro-2'H-pyran-5-yl)(phenyl)methanone (6d): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2,2-dimethyl-5,6-diphenyl-3,4-dihydro-2H-pyran (6e): $^{1}$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
(4,4-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)(phenyl)methanone (6c’): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 6-(3,5-dichlorophenyl)-2,2-dimethyl-3,4-dihydro-2H-pyran-5-carboxylate (6x): $^1$H NMR (300 MHz, CDCl$_3$) and $^{13}$C NMR (76 MHz, CDCl$_3$).
Methyl 2,2-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyran-5-carboxylate (6y):

$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (101 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$).
Ethyl 5-methyl-2-phenylfuran-3-carboxylate (8a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 2-(4-methoxyphenyl)-5-methylfuran-3-carboxylate (8b): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 5-methyl-2-(4-nitrophenyl)furan-3-carboxylate (8c): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
(5-methyl-2-phenylfuran-3-yl)(phenyl)methanone (8d): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
5-methyl-2,3-diphenylfuran (8e): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 5,5-dimethyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (10a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
3-benzoyl-5,5-dimethyldihydrofuran-2(3H)-one (10’a): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
**Ethyl 2-(4-methoxyphenyl)-5,5-dimethyl-4,5-dihydrofuran-3-carboxylate (10b):** $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
3-(4-methoxybenzoyl)-5,5-dimethyldihydrofuran-2(3H)-one (10’b): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
Ethyl 5,5-dimethyl-2-(4-nitrophenyl)-4,5-dihydrofuran-3-carboxylate (10c): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
5,5-dimethyl-3-(4-nitrobenzoyl)dihydrofuran-2(3\(H\))-one (10’c): \(^1\)H NMR (400 MHz, CDCl\(_3\)) and \(^{13}\)C NMR (101 MHz, CDCl\(_3\)).
(5,5-dimethyl-2-phenyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (10d): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
2,2-dimethyl-4,5-diphenyl-2,3-dihydrofuran (10e): $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (101 MHz, CDCl$_3$).
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Computational Supporting Information

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Computational Details

All calculations were performed using the Gaussian 16, Revision C.01 package. All structures were optimized at the B3LYP level of theory, in which all atoms were described with the def2-SVP basis set. Analytical frequency calculations were carried out at the same level of theory to confirm each stationary point as either an intermediate (no imaginary frequencies) or a transition state (only one imaginary frequency). Key transition-state structures were confirmed to connect corresponding reactants and products by intrinsic reaction coordinate (IRC) calculations. Single point energies were then refined using def2-TZVP basis set at the B3LYP level and the SMD solvation model in HFIP based on the optimized geometries in combination with D3 dispersion corrections with a Becke-Johnson damping scheme (D3BJ). Due to the unavailable solvent parameters of HFIP in Gaussian 16, the parameters of isopropanol were used and the dielectric constant of the solvent was modified to the dielectric constant of HFIP ($\varepsilon = 16.7$) in the calculations. Standard state concentrations of 1.0 mol/L were used for all species in calculations. The given Gibbs free energies in HFIP were calculated in Table S2 according to the formula: $G_{\text{sol}} = TCG + E_{\text{sol}} + 1.89$ (kcal/mol). We have sampled the different HFIP binding modes of all intermediates and transition states to confirm them as the optimal structure with lowest Gibbs energy, in which we put the samples of pTSA with one HFIP molecular in Figure 22 as a model. The CYLview software was employed to show the 3D structures of the studied species.

Non-Covalent Interactions (NCI) analysis in Figure S23 was performed for the qualitative study of hydrogen bonds with Multiwfn program and visualized by VMD program at B3LYP-D3BJ/def2-TZVP level based on the optimized geometries. The pTSA with one molecule HFIP (pTSA-HFIP), pTSA with three molecules HFIP (pTSA-3HFIP) and 1a with one molecule HFIP (1HFIP-1a-1) were chosen as the models. In the gradient isosurfaces, blue indicates strong attractive interactions, the green indicates Van der Waals interaction and red indicates strong non-bonded overlap.

For more detailed quantitative analysis of hydrogen binding modes, we have performed the energy decomposition analysis (EDA) calculation according to Symmetry-Adapted Perturbation Theory (SAPT) with PSI4 program. The EDA was calculated with scaled SAPTO method (sSAPT0) with jun-cc-pVDZ basis set. The SAPT input files of PSI4 were generated with help of Multiwfn program.
**Figure S1.** Relative energy profile of COM reaction of 1a with inexplicit solvent model.

**Figure S2.** Relative energy profile of COM reaction of 1a using 1-unit HFIP as explicit solvent model.
Figure S3. Relative energy profile of COM reaction of 1a using 2-unit HFIP as explicit solvent model.

Figure S4. Relative energy profile of COM reaction of 1a using 3-unit HFIP as explicit solvent model.
Figure S5. Relative energy profile of COM reaction of 1a using 4-unit HFIP as explicit solvent model.

Figure S6. Relative energy profile of COM reaction of 1a using 3-unit TFE as explicit solvent model.
Figure S7. Relative energy profile of COM reaction of 1a using 3-unit iPrOH as explicit solvent model.

Figure S8. Relative energy profile of interrupted COM reaction of 1a.
Figure S9. Relative energy profile of 7-endo-trig cyclization of 1a.

Figure S10. Relative energy profile of 5-exo-dig cyclization of 7a.
Figure S11. Relative energy profile of COM process and 6-endo-trig cyclization of 5a.

Figure S12. Relative energy profile of COM reaction of 3a.
Figure S13. Relative energy profile of interrupted COM reaction of 3a.

Figure S14. Relative energy profile of 8-endo-trig cyclization of 3a.
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Figure S18. Relative energy profile of 5-exo-trig cyclization of 9b.

Figure S19. Relative energy profile of 5-exo-trig cyclization of 9c.
Figure S20. Relative energy profile of 5-exo-dig cyclization of 7b.

Figure S21. Figure S20. Relative energy profile of 5-exo-dig cyclization of 7c.
Figure S22. Sampling the HFIP binding modes of pTSA with one HFIP molecule.

Figure S23. Non-Covalent Interactions (NCI) analysis of hydrogen bonding complexes pTSA-HFIP, pTSA-3HFIP and 1HFIP-1a-1
Table S1. Energy decomposition analysis (EDA). The interaction energy ($E_{int}$) of two highlighted fragments (red and green fragments) in different complexes has been decomposed to electrostatics ($E_{ele}$), exchange ($E_{exc}$), induction ($E_{ind}$) and dispersion ($E_{dis}$) components. The EDA indicates similar hydrogen bond modes between HFIP with substrate 1a and pTSA, which reflected by similar electrostatics component (-68.5 kJ/mol vs. -61.9 kJ/mol). For three HFIP molecules with pTSA complex, electrostatics energy of -86.6 kJ/mol between one of the HFIP and pTSA indicates a strong hydrogen bond. Furthermore, for the interaction of substrate 1a with pTSA and pTSA-3HFIP complex, the interaction energy difference between pTSA-1a and cat-1a-1 indicated HFIP would enhance the hydrogen bond dramatically, which facilitated the COM reaction.

| Name          | $E_{ele}$ (kJ/mol) | $E_{exc}$ (kJ/mol) | $E_{ind}$ (kJ/mol) | $E_{dis}$ (kJ/mol) | $E_{tot}$ (kJ/mol) |
|---------------|-------------------|-------------------|-------------------|-------------------|--------------------|
| 1HFIP-1a-1    | -68.5             | 61.7              | -26.3             | -21.1             | -54.2              |
| pTSA-HFIP     | -61.9             | 51.4              | -18.1             | -21.3             | -50.0              |
| pTSA-1a       | -74.2             | 76.5              | -33.8             | -28.4             | -59.9              |
| cat-1a-1      | -159.7            | 192.6             | -100.5            | -87.4             | -155.1             |
| pTSA-3HFIP-1  | -55.6             | 45.3              | -18.3             | -19.3             | -47.9              |
| pTSA-3HFIP-2  | -66.4             | 67.0              | -24.8             | -26.8             | -51.0              |
| pTSA-3HFIP-3  | -86.6             | 98.1              | -38.8             | -34.7             | -61.9              |
### Computed energies of all stationary points

**Table S2.** Thermal correction to Gibbs free energies ($TCG$, in Hartree), thermal correction to enthalpies ($TCH$, in Hartree), sum of electronic and thermal free energies ($G$, in Hartree), single point energies in gas phase computed at the B3LYP-D3BJ/def2-TZVP level ($E_{gas}$, in Hartree) and single point energies in HFIP computed at the B3LYP-D3BJ/def2-TZVP level ($E_{sol}$, in Hartree).

| Name       | $TCG$/a.u. | $TCH$/a.u. | $G$/a.u. | $E_{gas}$/a.u. | $E_{sol}$/a.u. |
|------------|------------|------------|----------|----------------|----------------|
| 1a         | 0.299841   | 0.377235   | -885.796641 | -887.156282 | -887.178432   |
| pTSA       | 0.103725   | 0.153607   | -894.772697 | -895.682173 | -895.700884   |
| pTSA-1a    | 0.421758   | 0.533154   | -1780.570581 | --            | -1782.892512  |
| TS1        | 0.431184   | 0.530247   | -1780.511995 | -1782.823305 | -1782.865887  |
| INT1       | 0.432455   | 0.534068   | -1780.545144 | -1782.855899 | -1782.887263  |
| TS2        | 0.431973   | 0.529789   | -1780.505359 | -1782.814629 | -1782.856664  |
| INT2       | 0.433642   | 0.534232   | -1780.555391 | -1782.860903 | -1782.892800  |
| TS3        | 0.434960   | 0.532428   | -1780.498548 | -1782.819176 | -1782.867427  |
| INT3       | 0.432612   | 0.532709   | -1780.518820 | -1782.830345 | -1782.873148  |
| TS4        | 0.432230   | 0.531519   | -1780.518804 | -1782.829800 | -1782.871734  |
| acetone    | 0.054312   | 0.089406   | -192.959042  | -193.247711  | -193.257096   |
| 2a         | 0.225387   | 0.284810   | -692.853286  | -693.902666  | -693.919638   |
| pTSA-HFIP-1| 0.148760   | 0.228562   | -1683.949942 | -1685.871824 | -1685.893858  |
| pTSA-HFIP-2| 0.151069   | 0.228930   | -1683.951986 | --            | -1685.892599  |
| pTSA-HFIP-3| 0.149460   | 0.228599   | -1683.949380 | --            | -1685.894111  |
| pTSA-HFIP-4| 0.149297   | 0.228745   | -1683.951018 | --            | -1685.893163  |
| pTSA-HFIP-5| 0.150892   | 0.228490   | -1683.954237 | --            | -1685.892730  |
| pTSA-HFIP-6| 0.150057   | 0.228732   | -1683.949025 | --            | -1685.891423  |
| pTSA-HFIP-7| 0.149987   | 0.228658   | -1683.954006 | --            | -1685.892963  |
| pTSA-HFIP-8| 0.150049   | 0.228820   | -1683.951260 | --            | -1685.893472  |
| pTSA-HFIP-9| 0.148896   | 0.228736   | -1683.955842 | --            | -1685.893197  |
| pTSA-HFIP-10| 0.148697 | 0.228619    | -1683.950984 | --            | -1685.893035  |
| pTSA-HFIP-11| 0.149732  | 0.228736    | -1683.953769 | --            | -1685.891014  |
| pTSA-HFIP-12| 0.146847  | 0.228477    | -1683.947188 | --            | -1685.889861  |
| 1HFIP-TS1  | 0.477392   | 0.605863   | -2569.702855 | -2573.025612 | -2573.065749  |
| 1HFIP-INT1 | 0.477698   | 0.606892   | -2569.702968 | -2573.026486 | -2573.068530  |
| 1HFIP-TS2  | 0.479767   | 0.605483   | -2569.692416 | -2573.018574 | -2573.061839  |
| 1HFIP-INT2 | 0.480941   | 0.609002   | -2569.738529 | -2573.055526 | -2573.088762  |
| 1HFIP-TS3  | 0.482801   | 0.607603   | -2569.691564 | -2573.026609 | -2573.073238  |
| 1HFIP-INT3 | 0.480822   | 0.608498   | -2569.709367 | -2573.038169 | -2573.077805  |
| 1HFIP-TS4  | 0.480119   | 0.607133   | -2569.709761 | -2573.037362 | -2573.076399  |

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|                  |       |       |                  |                  |                  |                  |
|------------------|-------|-------|------------------|------------------|------------------|------------------|
| **pTSA-2HFIP**   | 0.192632 | 0.303498 | -2473.122469 | -2476.054714 | -2476.083545 |                  |
| **2HFIP-TS1**    | 0.525838 | 0.681137 | -3358.886417 | -3363.226827 | -3363.268601 |                  |
| **2HFIP-INT1**   | 0.525541 | 0.682069 | -3358.886891 | -3363.227316 | -3363.270693 |                  |
| **2HFIP-TS2**    | 0.527276 | 0.680500 | -3358.876315 | -3363.219289 | -3363.265254 |                  |
| **2HFIP-INT2**   | 0.526934 | 0.683502 | -3358.918770 | -3363.249006 | -3363.284429 |                  |
| **2HFIP-TS3**    | 0.526427 | 0.682511 | -3358.881214 | -3363.226929 | -3363.273381 |                  |
| **2HFIP-INT3**   | 0.529830 | 0.683703 | -3358.889949 | -3363.237289 | -3363.281028 |                  |
| **2HFIP-TS4**    | 0.528556 | 0.682318 | -3358.890256 | -3363.235292 | -3363.278024 |                  |
| **pTSA-3HFIP**   | 0.241605 | 0.378482 | -3262.307321 | -3266.253140 | -3266.279449 |                  |
| **3HFIP-TS1**    | 0.574677 | 0.756629 | -4148.065682 | -4153.422910 | -4153.467552 |                  |
| **3HFIP-INT1**   | 0.574790 | 0.757452 | -4148.068990 | -4153.426682 | -4153.471978 |                  |
| **3HFIP-TS2**    | 0.576369 | 0.755391 | -4148.059860 | -4153.420161 | -4153.466164 |                  |
| **3HFIP-INT2**   | 0.576185 | 0.757312 | -4148.084995 | -4153.440150 | -4153.483144 |                  |
| **3HFIP-TS3**    | 0.578535 | 0.757159 | -4148.062225 | -4153.428054 | -4153.469840 |                  |
| **3HFIP-INT3**   | 0.577013 | 0.758971 | -4148.070893 | -4153.432959 | -4153.479746 |                  |
| **3HFIP-TS4**    | 0.574925 | 0.757469 | -4148.070333 | -4153.429327 | -4153.475904 |                  |
| **pTSA-4HFIP**   | 0.291936 | 0.453267 | -4051.494590 | -4056.455976 | -4056.484672 |                  |
| **4HFIP-TS1**    | 0.623497 | 0.831724 | -4937.245834 | -4943.618594 | -4943.664732 |                  |
| **4HFIP-INT1**   | 0.623773 | 0.832443 | -4937.246206 | -4943.619063 | -4943.667438 |                  |
| **4HFIP-TS2**    | 0.622994 | 0.830572 | -4937.236630 | -4943.610082 | -4943.662447 |                  |
| **4HFIP-INT2**   | 0.625865 | 0.833478 | -4937.263826 | -4943.635212 | -4943.680589 |                  |
| **4HFIP-TS3**    | 0.627461 | 0.832783 | -4937.243502 | -4943.622074 | -4943.668883 |                  |
| **4HFIP-INT3**   | 0.625658 | 0.833614 | -4937.248673 | -4943.626148 | -4943.674686 |                  |
| **4HFIP-TS4**    | 0.625158 | 0.832641 | -4937.248563 | -4943.623957 | -4943.671162 |                  |
| **1a-TFE**       | 0.299841 | 0.377235 | -885.796641 | -887.156282 | -887.178573 |                  |
| **pTSA-3TFE**    | 0.246279 | 0.353967 | -2251.972617 | -2254.689686 | -2254.714698 |                  |
| **3TFE-TS1**     | 0.572223 | 0.731835 | -3137.709805 | -3141.834242 | -3141.886304 |                  |
| **3TFE-INT1**    | 0.572067 | 0.732672 | -3137.710225 | -3141.834638 | -3141.888747 |                  |
| **3TFE-TS2**     | 0.576875 | 0.731011 | -3137.706464 | -3141.835116 | -3141.884215 |                  |
| **3TFE-INT2**    | 0.576971 | 0.733307 | -3137.733790 | -3141.855239 | -3141.898240 |                  |
| **3TFE-TS3**     | 0.577069 | 0.732967 | -3137.707927 | -3141.836039 | -3141.890502 |                  |
| **3TFE-INT3**    | 0.574733 | 0.734381 | -3137.715858 | -3141.843607 | -3141.895149 |                  |
| **3TFE-TS4**     | 0.572293 | 0.732861 | -3137.715799 | -3141.839989 | -3141.891562 |                  |
| **acetone-TFE**  | 0.054312 | 0.089406 | -192.959042 | -193.247711 | -193.257267 |                  |
| **2a-TFE**       | 0.225387 | 0.284810 | -692.853286 | -693.902666 | -693.919817 |                  |
| **1a-iPrOH**     | 0.299841 | 0.377235 | -885.796641 | -887.156282 | -887.178726 |                  |
| **pTSA-3/iPrOH** | 0.399584 | 0.501538 | -1477.188919 | -1479.107462 | -1479.132571 |                  |

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| 3/PrOH-TS1     | 0.727827 | 0.880185 | -2362.914588 | -2366.243329 | -2366.293185 |
|---------------|----------|----------|---------------|--------------|--------------|
| 3/PrOH-INT1   | 0.726576 | 0.880914 | -2362.917530  | -2366.245351 | -2366.297491 |
| 3/PrOH-TS2    | 0.730651 | 0.879542 | -2362.909015  | -2366.242354 | -2366.294228 |
| 3/PrOH-INT2   | 0.730449 | 0.881895 | -2362.956360  | -2366.279171 | -2366.318667 |
| 3/PrOH-TS3    | 0.734513 | 0.881762 | -2362.914895  | -2366.249871 | -2366.300794 |
| 3/PrOH-INT3   | 0.729726 | 0.882997 | -2362.920101  | -2366.248852 | -2366.302850 |
| 3/PrOH-TS4    | 0.728644 | 0.881517 | -2362.920068  | -2366.246340 | -2366.299344 |
| 3/PrOH-acetone| 0.054312 | 0.089406 | -192.959042   | -193.247711  | -193.257244  |
| 3/PrOH-2a     | 0.225387 | 0.284810 | -692.853286   | -693.902666  | -693.919848  |
| 3HFIP-TS5     | 0.574825 | 0.757095 | -4148.022663  | -4153.380602 | -4153.431661 |
| 3HFIP-TS6     | 0.570247 | 0.753052 | -4148.065888  | -4153.413412 | -4153.458047 |
| 3HFIP-INT4    | 0.575590 | 0.758787 | -4148.093023  | -4153.443079 | -4153.480990 |
| H2O           | 0.003570 | 0.025012 | -76.354746    | -76.463448   | -76.475491   |
| 3HFIP-INT5    | 0.547421 | 0.728877 | -4071.694889  | -4076.935797 | -4076.979353 |
| 3HFIP-TS7     | 0.545333 | 0.724353 | -4071.693761  | -4076.931280 | -4076.972551 |
| 3HFIP-INT6    | 0.545261 | 0.729709 | -4071.717287  | -4076.946625 | -4076.987581 |
| 3HFIP-TS8     | 0.542201 | 0.723832 | -4071.716618  | -4076.941569 | -4076.981325 |
| 3HFIP-INT7    | 0.547259 | 0.728642 | -4071.722925  | -4076.957277 | -4077.003719 |
| 3HFIP-TS9     | 0.546183 | 0.727497 | -4071.696479  | -4076.924590 | -4076.972942 |
| 3HFIP-INT8    | 0.551754 | 0.729364 | -4071.717002  | -4076.951332 | -4076.994477 |
| 3HFIP-TS10    | 0.550424 | 0.725364 | -4071.716419  | -4076.948697 | -4076.989538 |
| 11            | 0.283762 | 0.349633 | -809.448676   | -810.697910  | -810.715634  |
| 3HFIP-TS11    | 0.562276 | 0.752602 | -4148.078177  | -4153.413666 | -4153.457500 |
| 3HFIP-INT9    | 0.575669 | 0.759725 | -4148.077089  | -4153.427512 | -4153.476175 |
| 3HFIP-TS12    | 0.571789 | 0.754485 | -4148.071315  | -4153.417644 | -4153.458644 |
| 12            | 0.308636 | 0.378100 | -885.780035   | -887.151560  | -887.170996  |
| 7a            | 0.200662 | 0.265024 | -766.779882   | -767.894117  | -767.913093  |
| 7a-TS1        | 0.461524 | 0.639324 | -4029.057606  | -4034.147289 | -4034.188857 |
| 7a-INT1       | 0.473404 | 0.647178 | -4029.113860  | -4034.217665 | -4034.257829 |
| 7a-TS2        | 0.466367 | 0.641372 | -4029.094183  | -4034.188266 | -4034.225555 |
| 7a-INT2       | 0.467640 | 0.645385 | -4029.109917  | -4034.198324 | -4034.237002 |
| 7a-TS3        | 0.465717 | 0.640720 | -4029.106406  | -4034.193134 | -4034.232559 |
| 7a-INT3       | 0.472077 | 0.645430 | -4029.119836  | -4034.215282 | -4034.254633 |
| 7a-TS4        | 0.468332 | 0.641944 | -4029.114831  | -4034.207407 | -4034.249271 |
| 8a            | 0.204826 | 0.266369 | -766.843091   | -767.954505  | -767.969823  |
| 7a-TS5        | 0.466001 | 0.639555 | -4029.044934  | -4034.135231 | -4034.171891 |
| 5a            | 0.274929 | 0.347569 | -846.537167   | -847.825156  | -847.845727  |
|      |          |          |          |          |          |          |
|------|----------|----------|----------|----------|----------|----------|
| 5a-TS1 | 0.539618 | 0.722514 | -4108.781717 | -4114.051499 | -4114.095900 |
| 5a-INT1 | 0.545934 | 0.728317 | -4108.788839 | -4114.065380 | -4114.108392 |
| 5a-TS2 | 0.533686 | 0.722582 | -4108.821501 | -4114.082850 | -4114.127170 |
| 5a-INT2 | 0.549217 | 0.730073 | -4108.838366 | -4114.116795 | -4114.161347 |
| 5a-TS3 | 0.543029 | 0.724325 | -4108.827412 | -4114.099807 | -4114.140325 |
| 6a | 0.281452 | 0.348347 | -846.539411 | -847.833658 | -847.85331 |
|      | 0.290747 | 0.359062 | -697.383152 | -698.506654 | -698.524671 |
| 3a-TS1 | 0.567796 | 0.738730 | -3959.655527 | -3964.778503 | -3964.819538 |
| 3a-INT1 | 0.568004 | 0.739638 | -3959.655406 | -3964.778627 | -3964.820868 |
| 3a-TS2 | 0.568257 | 0.738691 | -3959.645677 | -3964.769990 | -3964.813950 |
| 3a-INT2 | 0.567239 | 0.740415 | -3959.677407 | -3964.793218 | -3964.829255 |
| 3a-TS3 | 0.569758 | 0.740218 | -3959.656689 | -3964.784331 | -3964.823451 |
| 3a-INT3 | 0.570125 | 0.741811 | -3959.663496 | -3964.792144 | -3964.833070 |
| 3a-TS4 | 0.565678 | 0.739607 | -3959.661699 | -3964.785706 | -3964.826626 |
| 13 | 0.216751 | 0.266878 | -504.443643 | -505.257983 | -505.269904 |
| 3a-TS5 | 0.563864 | 0.735072 | -3959.653006 | -3964.771314 | -3964.811306 |
| 3a-INT4 | 0.569051 | 0.740417 | -3959.679391 | -3964.801428 | -3964.836375 |
| 3a-INT5 | 0.540931 | 0.712777 | -3883.289015 | -3888.294536 | -3888.334745 |
| 3a-TS6 | 0.536006 | 0.706716 | -3883.280849 | -3888.281639 | -3888.319483 |
| 3a-INT6 | 0.536441 | 0.711151 | -3883.306764 | -3888.300274 | -3888.337231 |
| 3a-TS7 | 0.535691 | 0.706212 | -3883.300504 | -3888.294830 | -3888.330536 |
| 3a-INT7 | 0.540781 | 0.711678 | -3883.316633 | -3888.320003 | -3888.358280 |
| 3a-TS8 | 0.541748 | 0.710253 | -3883.297256 | -3888.300358 | -3888.340336 |
| 3a-INT8 | 0.541621 | 0.711141 | -3883.317555 | -3888.318664 | -3888.355129 |
| 3a-TS9 | 0.540241 | 0.707365 | -3883.318010 | -3888.316369 | -3888.350602 |
| 4a | 0.276560 | 0.331988 | -621.046372 | -622.062418 | -622.075648 |
| 3a-TS10 | 0.569388 | 0.739861 | -3959.628400 | -3964.756567 | -3964.799882 |
| 3a-T11 | 0.552080 | 0.734481 | -3959.667958 | -3964.766058 | -3964.804988 |
| 3a-INT9 | 0.565253 | 0.741699 | -3959.666204 | -3964.781843 | -3964.829053 |
| 3a-TS12 | 0.562371 | 0.735802 | -3959.647855 | -3964.759223 | -3964.794038 |
| 14 | 0.300573 | 0.360265 | -697.362240 | -698.499467 | -698.513454 |
| cat-1a-1 | 0.568745 | 0.757677 | -4148.105215 | -- | -4153.484457 |
| cat-1a-2 | 0.565143 | 0.757421 | -4148.105181 | -- | -4153.480611 |
| cat-1a-3 | 0.568157 | 0.757823 | -4148.086651 | -- | -4153.476281 |
| cat-1a-4 | 0.564023 | 0.757481 | -4148.091123 | -- | -4153.473720 |
| cat-acetone | 0.317622 | 0.468319 | -3455.270616 | -- | -3459.557557 |
| 1HFIP-1a-1 | 0.344469 | 0.452541 | -1674.975587 | -- | -1677.372912 |
Single point energies in HFIP were calculated at M06-2X-D3 and B3LYP-D3BJ, respectively

| Name | $TCG$/a.u. | $TCH$/a.u. | $G$/a.u. | $E_{M06-2X}$/a.u. | $E_{sol}$/a.u. |
|------|------------|------------|----------|-------------------|--------------|
| 7b   | 0.229882   | 0.300062   | -881.191460 | -882.064366       | -882.494331  |
| 7b-TS1 | 0.490996   | 0.674277   | -4143.469851 | -4147.222532      | -4148.770655 |
| 7b-INT1 | 0.502305   | 0.682415   | -4143.531423 | -4147.301160      | -4148.845293 |
| 7b-TS2 | 0.494987   | 0.676508   | -4143.508647 | -4147.263370      | -4148.808430 |
| 7b-TS3 | 0.496829   | 0.680338   | -4143.520706 | -4147.275389      | -4148.816961 |
| 7b-INT2 | 0.49385    | 0.675737   | -4143.518392 | -4147.268877      | -4148.812753 |
| 7b-INT3 | 0.501601   | 0.680506   | -4143.531305 | -4147.290498      | -4148.835600 |
| 7b-TS4 | 0.496427   | 0.676674   | -4143.527153 | -4147.281881      | -4148.828855 |
| 8b   | 0.233776   | 0.301351   | -881.252819  | -882.118865       | -882.548583  |
| 7c   | 0.199031   | 0.270255   | -971.125532 | -972.047403       | -972.506030  |
|      |       |       |             |             |             |
|------|-------|-------|-------------|-------------|-------------|
| 7c-TS1 | 0.460908 | 0.644797 | 4233.399275 | 4237.203057 | 4238.780878 |
| 7c-INT1 | 0.472336  | 0.652091 | 4233.453228 | 4237.272350 | 4238.844922 |
| 7c-TS2 | 0.464954  | 0.646450 | 4233.435616 | 4237.241884 | 4238.816130 |
| 7c-INT2 | 0.465997  | 0.650763 | 4233.456884 | 4237.261703 | 4238.832383 |
| 7c-TS3 | 0.464445  | 0.645943 | 4233.451484 | 4237.254194 | 4238.827419 |
| 7c-INT3 | 0.470901  | 0.650509 | 4233.463341 | 4237.273607 | 4238.847444 |
| 7c-TS4 | 0.468550  | 0.648014 | 4233.457226 | 4237.268172 | 4238.844856 |
| 8c    | 0.203319  | 0.271708 | -971.192009 | -972.106835 | -972.566704 |
Coordinates of all stationary points

1a  
C  -4.43194700  -0.34751300  -1.42801100  
C  -3.07961900  -0.44058400  -1.08699200  
C  -2.70279100  -0.77260500  0.22720700  
C  -3.70526300  -1.01025700  1.18650200  
C  -5.05191700  -0.91691100  0.84347400  
C  -5.41831400  -0.58551400  -0.46715200  
H  -4.71441800  -0.08727800  -2.45105200  
H  -2.32763300  -0.23756600  -1.85072300  
H  -3.39451600  -1.27020100  2.20010300  
H  -5.82168900  -1.10340800  1.59667200  
H  -6.47480700  -0.51293700  -0.73858700  
C  -1.27379200  -0.90906800  0.67173700  
O  -1.00598600  -1.25840600  1.80279500  
C  -0.14300400  -0.62486400  -0.34173300  
H  -0.36324700  -1.17494200  -1.26944200  
C  1.22257500  -1.06770500  0.21139600  
H  1.44735100  -0.48372900  1.11577800  
H  1.12994700  -2.11342700  0.54585000  
C  2.36962900  -0.94235600  -0.80592100  
H  2.47236800  0.10391700  -1.13397400  
H  2.09870600  -1.51403000  -1.71445800  
C  3.67258900  -1.46953900  -0.26922800  
C  3.65109300  -2.53163300  0.00998400  
C  4.83182200  -0.81269300  -0.07942000  
C  5.05698900  0.64529700  -0.39452900  
H  5.86288900  0.76226700  -1.14111600  
H  4.16383100  1.15210100  -0.78319300  
H  5.39063800  1.18971400  0.50683500  
C  6.04007000  -1.52259100  0.48182900  
H  6.38349400  -1.04295900  1.41621400  
C  5.81974100  -2.58166600  0.69714100  
H  6.89122400  -1.47427800  -0.22135400  
C  -0.13501600  0.84896000  -0.74462000  
O  -0.29807500  1.26490400  -1.86701600  
O  0.08518600  1.64072600  0.31575000  
C  0.11658500  3.06150000  0.08157400  
H  -0.83320000  3.36269500  -0.38895400  
H  0.91861200  3.28374900  -0.64049700  
C  0.33933200  3.75031800  1.41121000

pTSA  
S  -1.90854400  -0.00691500  -0.13298600  
O  -2.35156800  -1.23281800  -0.77353400  
O  -2.37901000  1.31511400  -0.54375700  
C  -0.12439600  0.00143500  -0.80602200  
C  2.67442300  0.00942000  0.02161000  
C  0.55795600  1.21898400  -0.88606300  
C  0.56410600  -1.21578000  -0.03605400  
C  1.95592700  -1.20079100  0.01852400  
C  1.95371100  1.21259400  -0.03426400  
H  -0.00051900  2.15492000  -0.14474000  
H  0.00962900  -2.15570800  -0.05440400  
H  2.49926000  -2.14924000  0.05399400  
H  2.49304000  2.16355200  -0.04228900  
C  4.18181700  0.00122200  0.06386900  
H  4.59991600  -0.41827900  -0.86691700  
H  4.59085800  1.01421400  0.18810700  
H  4.55430100  -0.62250700  0.89250700  
O  -2.30430100  -0.17582800  1.45503100  
H  -2.51237100  0.70943900  1.79910200

pTSA-1a  
S  -2.14670400  -1.36546100  -0.73978500  
O  -1.93442400  -0.30210000  -1.72822700  
O  -1.85272700  -2.75024600  -1.10332400  
C  -3.81599900  -1.25384300  -0.12134900  
C  -6.43537600  -1.09174800  0.85467500  
C  -4.43928800  -2.40539600  0.36208400  
C  -4.47682400  -0.02288300  -0.13339700  
C  -5.77992000  0.04867500  0.35777500  
C  -5.77460500  -2.31469700  0.84802500  
H  -3.90386900  -3.35629000  0.34686900  
H  -3.97199900  0.86027700  -0.52842400  
H  -6.30137200  1.01000500  0.35356300  
H  -6.23746400  -3.21352300  1.22863700  
C  -7.85658500  -1.00486200  1.35281200
| Atoms | X       | Y       | Z       |
|-------|---------|---------|---------|
| O     | 0.15199700 | 1.29299700 | 8.25276100 |
| H     | 8.29799180 | 0.63950100 | 0.59698900 |
| H     | 8.09046100 | 0.66269100 | 0.55690900 |
| C     | 7.71136600 | 0.58544600 | 0.08648500 |
| H     | 5.76165700 | 2.19258100 | 0.95901900 |
| C     | 7.11366000 | 0.58544600 | 0.08648500 |
| C     | 8.09046100 | 0.66269100 | 0.09469600 |
| C     | 7.97991800 | 1.52568900 | 0.59698900 |
| H     | 8.25276100 | 0.23327800 | 0.58295300 |
| O     | 1.29299700 | 0.48879800 | 1.32747200 |
| H     | 0.15199700 | 1.26838500 | 2.20543900 |

**TS4**

| Atoms | X       | Y       | Z       |
|-------|---------|---------|---------|
| C     | -1.65943200 | -1.00840200 | 3.40014000 |
| C     | -1.53167900 | -0.47829600 | 2.11926700 |
| C     | -2.38808800 | -0.91957400 | 1.07744400 |
| C     | -3.38108800 | -1.89000000 | 1.37634100 |
| C     | -3.51941000 | -2.38863600 | 2.66378200 |
| C     | -2.65207600 | -1.95269800 | 3.67756200 |
| H     | -0.97362700 | -0.68483600 | 4.18573800 |
| H     | -0.72147800 | 0.22108400 | 1.90362200 |
| H     | -4.07554800 | -2.21288400 | 0.59903400 |
| H     | -4.30454900 | -3.11419100 | 2.88814900 |
| H     | -2.75577600 | -2.35400800 | 4.68914900 |
| O     | -0.40624500 | -1.69813100 | -2.67560900 |
C    4.94163700
O    0.38346000
S    1.28356300
F    2.47257800
F    3.38782600
F    4.27257800
H    0.76614100
O    1.06713300
C    2.36922100
C    4.94163700
F    2.85007400
H    0.59307100
C    -2.87291000
C    5.27756200
C    4.00174100
C    -1.27081000
C    -0.43587100
H    0.85485400
C    1.42187800
C    -2.62181500
H    0.29422700
C    2.36922100
H    -2.03827100
C    1.10090600
C    -6.58012900
H    2.73725900
C    2.65748000
C    1.33375100
H    2.69851000
C    0.82906700
C    -1.33375100
H    1.81269000
C    0.25988000
O    -0.44149200
C    0.35223180
F    -2.02911600
F    2.65748000
C    5.27756200
O    1.28356300
F    -2.62953500
H    -5.60272300
S    1.28356300
F    3.38782600
C    5.27756200
F    4.27257800
F    3.38782600
F    4.27257800
H    2.60233100
H    0.85485400
C    3.26689100
H    -0.62771800
C    3.26689100
F    4.47396300
F    3.38782600
F    2.47257800
H    2.60233100
H    0.85485400
C    3.26689100
F    4.47396300
F    3.38782600
F    2.47257800
H    2.60233100
H    0.85485400

pTSA-HFIP-11
S  -1.10090600
O  -0.51316600
O  -0.54227700
C  -2.85584800
C  -5.62650700
C  -3.54573100
C  -3.51532900
C  -4.89970500
C  -4.92678000
H  -3.00280200
H  -2.94957900
H  -5.42488700
H  -5.47522300
H  -7.11998400
H  -7.38251500

S32
C -3.41083900 2.88500100 0.22341800  H -1.50611400 0.29612600 1.37651200
C -4.02893400 4.13173800 0.17026100  C -3.13702900 1.68808500 2.01104500
C -1.93015000 5.21437000 0.65356900  H -3.33176600 1.58857500 3.08739000
H -0.22811500 3.88493500 0.92645100  H -2.37756200 2.46580300 1.86270500
H -3.98483200 1.96988100 0.06222200  C -4.40545200 2.01519200 1.20730700
H -5.10133500 4.18842700 -0.03894000  H -4.62587700 3.09043500 1.19881200
H -1.34575800 6.12282700 0.82636500  H -5.27251100 1.48217000 1.62679500
C -3.99355900 6.65849300 0.33021400  C -4.09800400 1.46946000 -0.20030700
H -3.28325800 7.48765600 0.46409500  H -4.97171800 1.17124000 -0.79566900
H -4.50850100 6.80555300 -0.63378300  C -3.46320300 2.72686600 -1.18879700
H -4.76076100 6.74265100 1.11849200  C -4.70472300 3.49946300 -1.64708900
O -1.44338300 0.60263000 -0.81314300  H -5.34831200 2.88729000 -2.29622200
C -3.12785300 -2.01838900 -0.23882900  H -5.29494300 3.85663600 -0.79145500
O -2.97152200 -1.99858900 1.13786300  H -4.36805100 4.38132500 -2.21240200
C -2.48380000 -3.29358900 -0.79402800  C -2.68818000 2.16710700 -2.38138600
F -3.08315900 -4.41492700 -0.38693300  H -1.75129600 1.60891400 -2.07685000
F -2.47642400 -3.30073100 -2.14406600  H -3.28518300 1.46031000 -2.97476600
F -1.19191100 -3.36523800 -0.40487500  H -2.42464200 3.01428100 -3.03414700
C -4.61475500 -1.89332300 -0.60573500  C -3.13819800 -0.86320200 2.15722600
F -4.80457200 -1.92539300 -1.93837900  O -4.22442200 -0.91181800 2.67936500
F -5.36750700 -2.85693000 -0.06486800  O -2.24166100 -1.84680100 2.16798800
F -5.08414700 -0.71407600 -0.16143900  C -2.59272300 -3.08029700 2.83817700
H -2.61729400 -1.17213400 -0.73524200  H -3.26474300 -3.64752800 2.17271500
H -2.65375300 -1.09401400 1.39038600  H -3.15850900 -2.83451600 3.74901000
C -1.31460900 -3.83562500 3.13271200  H -1.55597700 -4.80103500 3.60439900
1HFIP-INT3
C -1.42696100 -2.38705500 -1.85956300  H -0.74264500 -4.02691200 2.21363600
C -1.70193400 -1.41694200 -0.89913500  H -0.67280200 -3.26520200 3.82128300
C -2.92463200 -0.69234300 -0.94246700  S 0.69074600 1.42645400 -0.03295500
C -3.86943100 -1.00900900 -1.96124600  O 0.59010500 0.35607700 1.00698000
C -3.60469500 -2.00847300 -2.88317400  O 0.79623100 0.87720800 -1.42475600
C -2.37595900 -2.68925900 -2.84044600  C 2.21917100 2.30689200 0.28924000
H -0.45435800 -2.87845100 -1.84080200  C 4.56725500 3.75378700 0.81328300
H -0.94423800 -1.17051100 -0.15546600  C 2.53811700 2.65541100 1.60678400
H -4.83024400 -0.49369500 -1.99012700  C 3.05689200 2.66697800 -0.76600500
H -4.34755400 -2.26346100 -3.64220000  C 4.22401500 3.38721700 -0.49607600
H -2.15942400 -3.46144400 -3.58336100  C 3.70417200 3.37487100 1.85823700
C -3.18867700 0.34923300 0.00802300  H 1.87997400 2.35278900 2.42352300
O -2.70828800 3.57512800 -0.42187700  H 2.79681000 2.37282500 -1.78379800
C -2.60985000 0.37555100 1.39461100  H 4.88304000 3.66567400 -1.32311000
S38
H 3.95474700  3.64615000  2.88802200  H 4.41094600  -3.36597600  1.10523800
C 5.83641600  4.51490900  1.10732000  H 5.21159600  -1.84803700  1.59146300
H 6.31383000  4.87892500  0.18579000  C 4.03763400  -1.63879100  -0.21155300
H 5.64234200  5.38340500  1.75748800  H 4.89234900  -1.47403500  -0.87636500
H 6.56796400  3.87705100  1.63260800  C 3.17779900  -2.90397000  -1.27258600
O -0.40504900  2.43552300  0.10176800  C 4.36441900  -3.71832900  -1.77978900
H -1.79219700  3.21544500  -0.30722000  H 5.01861800  -3.12596100  -2.43487500
C 2.44965300  -1.88501800  -0.47246400  H 4.95493500  -4.13106600  -0.95035400
O 1.69058700  -1.65654500  -1.61227600  H 3.96159400  -4.56575300  -2.35670000
C 2.13054700  -3.29560100  0.03508600  C 2.41779000  -2.20012400  -2.38511600
F 2.35939800  -4.24054100  -0.88359100  F 1.52293700  -1.67840900  -2.01962000
F 2.83231300  -3.60520200  1.13287300  H 3.05100800  -1.49398900  -2.93879300
F 0.82051900  -3.37044300  0.36036800  H 2.08220600  -2.97659300  -3.09268800
C 3.94486700  -1.68117900  -0.77139200  C 3.20411500  0.68135000  2.17124700
F 4.69223900  -1.97678000  0.33884900  O 4.30017700  0.67142500  2.67638700
F 4.41356800  -2.55287300  -1.67301800  O 2.35350200  1.70516500  2.22006600
F 4.13415100  -0.44619500  -1.26159800  C 2.77620800  2.90358400  2.90922800
H 2.19194700  -1.19923300  0.35487100  H 3.50307200  3.42799100  2.26663400
H 1.38731000  -0.71261200  -1.61067000  C 3.30198900  2.61136000  3.83060700

1HFIP-TS4
C 1.62091900  2.35811900  -1.86012800  C 1.01383200  3.98504200  2.25254400
C 1.82845000  1.35609800  -0.91410600  H 0.85078400  3.21491000  3.84894900
C 3.02256600  0.59107200  -0.93330300  S -0.79722500  -1.45856900  0.03229500
C 4.01151900  0.89462800  -1.90871800  O -0.63002400  -0.39360900  1.06349800
C 3.81366100  1.92219900  -2.81958000  O -0.81597500  -0.92085300  -1.36881500
C 2.61141800  2.64740900  -2.80302700  C -2.40252000  -2.20290600  0.32068900
H 0.66797400  2.88688400  -1.86597000  C -4.87775400  -3.43819800  0.79688800
H 1.03882700  1.12446400  -0.19968900  C -2.79075700  -2.49109000  1.63413300
H 4.95412200  0.34486700  -1.91527600  C -3.23309200  -2.51858300  -0.75418500
H 4.59129100  2.16446500  -3.54754200  C -4.46394100  -3.13346200  -0.50796800
H 2.44824800  3.44336000  -3.53430400  C -4.01986700  -3.10593400  1.86174100
C 3.21739000  -0.48884900  0.00345700  C -2.13570500  -2.22288900  2.46527800
O 2.42265300  -3.67450000  -0.47286200  H -2.91799900  -2.27103300  -1.76884600
C 2.61288900  -0.50873000  1.38580800  H -5.11751200  -3.37653900  -1.35033500
H 1.51647900  -0.37474800  1.36227900  H -4.32474700  -3.33003000  2.88821200
C 3.06034000  -1.86212100  1.98202100  C -6.21473100  -4.08420300  1.06467500
H 3.27848000  -1.78612700  3.05572200  H -6.69037000  -4.43231200  0.13610200
H 2.24541200  -2.58394100  1.84475100  H -6.11499700  -4.94784300  1.74203100
C 4.29317400  -2.27504800  1.15828800  C -6.90749000  -3.37434100  1.54854500

S39
C 3.91349600 -0.99275800 -2.64605100
H 3.03127800 0.78815000 -3.49681500
H 2.59088200 1.84769800 -1.32250100
H 4.32586500 -1.57255200 0.67943200
H 4.72906900 -2.63613100 -1.49883000
H 4.08410800 -1.47268100 -3.61241300
C 3.14969500 0.90902100 1.18621000
O 2.07912800 1.84711800 1.14276300
C 4.38124500 1.71219100 1.73278100
H 4.39740600 2.66743200 1.19216400
C 4.07175600 1.87218900 3.23109600
H 4.95087500 2.16906100 3.82188800
H 3.30918000 2.65748400 3.34078300
C 3.51701200 0.50062000 3.65244900
H 2.88355800 0.55404500 4.54992600
H 4.35073500 -0.17549500 3.87930900
C 2.77687000 -0.05853200 2.41826800
H 3.08701000 -1.08762100 2.19280600
C 1.29025200 -0.01408900 2.40226800
O 0.46669300 0.79044900 3.29975400
H -0.25759000 0.12406800 3.80606100
H 1.01641000 1.40480500 4.01827600
H -0.18843000 1.40743100 2.64314100
C 0.60253200 -0.90708100 1.46406600
H 1.14928200 -1.06570700 0.52120500
H 0.59799700 -1.89927200 1.96408400
H -0.43853600 -0.62395500 1.28249300
C 5.70064100 0.99776000 1.49267500
O 6.08026500 0.01989200 2.09978900
O 6.40189000 1.57724600 0.51344400
C 7.65241500 0.96096200 0.14513400
H 7.45343900 -0.07863300 -0.16011400
H 8.30203400 0.92074200 1.03416000
C 8.26222700 1.77655900 -0.97488200
H 9.22043000 1.33061400 -1.28354900
H 7.59488300 1.80257800 -1.84972800
H 8.45138000 2.81210800 -0.65267600
H 1.46894500 1.78635400 0.36047600
S -1.26478300 1.65034900 -0.37904700
O -1.55896700 1.74373900 1.09455700
O 0.16800300 1.93045100 -0.69209300
C -2.23556200 2.92445100 -1.17762400
C -3.77844500 4.88418900 -2.46185500
C -1.62010000 3.82479400 -2.04625800
C -3.61422200 2.98500700 -0.93476600
C -4.37001600 3.96193300 -1.57835900
C -2.39640700 4.79873400 -2.68167900
H -0.54660500 3.75993100 -2.21618800
C -4.09193100 2.28383700 -0.24784500
H -5.44608400 4.01053600 -1.38887600
H -1.91414700 5.50612200 -3.36197700
C -4.61966800 5.93338100 -3.14543200
H -5.11911700 6.58479500 -2.40893000
H -4.01540900 6.57190000 -3.80614800
H -5.41426400 5.47120600 -3.75459500
O -1.73443800 0.33931500 -0.93799000
C -4.01666300 -0.49532600 1.44438800
O -3.94407600 0.81361000 1.89918800
C -3.56654400 -1.46366500 2.55152200
F -4.31199700 -1.37428700 3.65427500
F -3.56690700 -2.73978600 2.14939100
F -2.29072500 -1.16056000 2.90809500
C -5.45376400 -0.75420500 0.97171200
F -5.60072100 -2.01053400 0.52133500
F -6.35332000 -0.55671700 1.94044500
F -5.75109600 0.07588600 -0.03975400
H -3.36578500 -0.68814100 0.57219300
H -3.06110600 1.18648900 1.66055400
C -0.45655700 -2.58439100 -2.08619600
O 0.13295000 -1.42249900 -1.62716400
C 0.54417500 -3.28473400 -3.01860900
F 1.68365200 -3.60303700 -2.38973100
F 0.02784900 -4.41428200 -3.52773000
F 0.85185300 -2.47901800 -4.0415700
C -0.90378500 -3.47284200 -0.90845000
C -1.50913000 -4.59304100 -1.31574500
F 0.12511100 -3.82014700 -0.11698500
F -1.77574500 -2.78938400 -0.14456800
H -1.36544700 -2.40782300 -2.69218300
H -0.56043700 -0.73604700 -1.44197200
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | 0.489139  | 0.569002  |           |
| H       | 0.643275  | 0.654734  |           |
| C       | 0.484749  |           |           |
| H       | 1.764000  |           |           |
| H       | 1.180320  |           |           |
| C       | 2.997465  |           |           |
| H       | 4.911763  |           |           |
| C       | 4.019790  |           |           |
| H       | 3.604421  |           |           |
| H       | 2.304972  | 3.686310  | 0.020431  |
| 2HFIP   |           |           |           |
| H       | 0.769997  | 2.014179  | 1.983064  |

**2HFIP-TS3**

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 3.161154  | 1.702732  | 1.927590  |
| C       | 3.488883  | 0.650239  | 1.092866  |
| C       | 3.249709  | 0.739410  | -0.314105 |
| C       | 2.696420  | 1.951717  | -0.831833 |
| C       | 2.382524  | 3.002241  | 0.011663  |
| C       | 2.597663  | 2.870041  | 1.391728  |
| H       | 3.301036  | 1.610551  | 3.005911  |
| H       | 3.887703  | -0.269680  | 1.516823 |
| H       | 2.532255  | 2.059340  | -1.902809 |
| H       | 1.933289  | 3.913186  | -0.382315 |
| C       | 2.304972  | 3.686310  | 0.020431  |
| C       | 3.511360  | -0.361568  | -1.160470 |
| O       | 1.549549  | -1.886376  | -1.119131 |
| C       | 4.409678  | -1.521648  | -0.783928 |
| H       | 4.035701  | -2.001513  | 0.130418  |
| C       | 4.385733  | -2.460359  | -2.014940 |
| H       | 5.345443  | -2.974630  | -2.163934 |
| H       | 3.604210  | -3.215557  | -1.857070 |
| C       | 4.019790  | -1.524587  | -3.174273 |
| H       | 3.633803  | -2.049533  | -4.057029 |
| C       | 4.911673  | -0.959144  | -3.486310 |
| C       | 2.997465  | -0.551637  | -2.554494 |
| H       | 2.912404  | 0.386255  | -3.119966 |
| C       | 1.510698  | -1.150643  | -2.342644 |
| C       | 1.130430  | -2.123939  | -3.459612 |
| H       | 1.180320  | -1.652202  | -4.453726 |
| H       | 1.764503  | -3.020957  | -3.455275 |
| H       | 0.094863  | -2.448960  | -3.278438 |
| C       | 0.484749  | -0.020431  | -2.286446 |
| H       | 0.643275  | 0.654734  | -1.437803 |
| H       | 0.489139  | 0.569020  | -3.215977 |
| H       | -0.516215 | -0.453535  | -2.160270 |

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 5.834484  | -1.006350  | -0.519391 |
| O       | 6.556260  | -0.553846  | -1.372520 |
| O       | 6.177721  | -1.139040  | 0.766260  |
| C       | 7.506245  | -0.700241  | 1.137989  |
| H       | 7.595710  | 0.373320   | 0.907829  |
| H       | 8.236050  | -1.230715  | 0.506818  |
| C       | 7.701224  | -0.991271  | 2.609866  |
| H       | 8.709079  | -0.674917  | 2.919812  |
| H       | 6.967326  | -0.447739  | 3.224479 |
| H       | 7.598799  | -2.067278  | 2.817494 |
| O       | 1.043541  | -1.433863  | -0.403559 |
| H       | -0.542785 | 0.133345   | 1.596055  |
| O       | -1.651475 | 0.241995   | 0.583594  |
| C       | -2.164028 | -2.468573  | 5.027497  |
| C       | -1.697517 | -2.138968  | 2.653770  |
| C       | -1.148055 | -0.390321  | 4.248978  |
| C       | -1.638922 | -1.193897  | 5.283174  |
| C       | -2.185980 | -2.923527  | 3.695737  |
| H       | -0.749071 | 0.605771   | 4.445755  |
| H       | -1.616813 | -0.816699  | 6.309419  |
| H       | -2.600179 | -3.909633  | 3.466928  |
| C       | -2.704065 | -3.339840  | 6.139228  |
| H       | -2.192591 | -4.310397  | 6.169887  |
| H       | -2.581327 | -2.856231  | 7.122299  |
| H       | -3.778191 | -3.540114  | 5.996330  |
| O       | -0.191098 | 1.456330   | 2.193504  |
| C       | -3.400744 | -1.991153  | -1.259611 |
| O       | -2.062232 | -1.888441  | -0.922179 |
| C       | -3.595129 | -1.632561  | -2.744972 |
| C       | -2.903150 | -2.448407  | -3.556271 |
| F       | -4.884130 | -1.684737  | -3.108777 |
| F       | -3.161230 | -0.380269  | -2.958806 |
| C       | -3.891714 | -3.407770  | -0.916177 |
| F       | -5.194275 | -3.560381  | -1.199973 |
| F       | -3.211866 | -4.353183  | -1.570986 |
| F       | -3.737963 | -3.629971  | 0.400402  |
| H       | -4.047190 | -1.297560  | -0.691552 |
|     |      |      |      |      |      |      |      |      |      |      |      |
|-----|------|------|------|------|------|------|------|------|------|------|------|
| H   | 7.23 | -0.99| 0.28 | 2.05 |
| H   | 7.98 | -2.26 | -0.69| 16.50|
| C   | 7.56 | -2.85 | 1.36 | 44.70|
| H   | 8.55 | -2.56 | 1.75 | 12.15|
| H   | 6.81 | -2.65 | 2.14 | 48.30|
| H   | 7.57 | -3.94 | 1.17 | 31.00|
| H   | 1.22 | -1.98 | -0.29| 30.23|
| S   | -1.04 | -0.99 | 1.57 | 05.80|
| O   | -2.27 | -0.46 | 0.88 | 64.10|
| O   | -0.32 | -1.95 | 0.65 | 55.50|
| C   | -1.61 | -1.95 | 2.70 | 89.80|
| C   | -2.56 | -3.41 | 5.16 | 48.10|
| C   | -2.15 | -3.23 | 2.77 | 66.30|
| C   | -1.53 | -1.40 | 4.25 | 05.40|
| C   | -2.01 | -2.14 | 5.33 | 74.40|
| C   | -2.62 | -3.94 | 3.86 | 23.00|
| H   | -2.19 | -3.66 | 1.76 | 94.70|
| H   | -1.09 | -0.41 | 4.38 | 81.40|
| H   | -1.95 | -1.71 | 6.34 | 07.20|
| H   | -3.05 | -4.94 | 3.70 | 33.60|
| C   | -3.08 | -4.21 | 6.33 | 58.20|
| H   | -2.52 | -5.16 | 6.45 | 57.50|
| H   | -3.01 | -3.65 | 2.77 | 43.40|
| H   | -4.14 | -4.49 | 6.19 | 36.70|
| O   | -0.17 | 0.06 | 2.12 | 09.80|
| C   | -3.01 | 2.50 | 78.63 | 0.71 | 96.84 | 0.08 | 12.67 | 0.26 | 67.32 | 0.74 | 98.60 |
| F   | -3.19 | 4.38 | 36.76 | 0.74 | 98.60 |
| F   | -4.99 | 3.78 | 84.22 | -0.30 | 26.53 | 0.17 | 94.30 |
| F   | -4.21 | 2.55 | 41.84 | 1.30 | 09.42 |
| C   | -2.52 | 3.32 | 24.88 | -1.92 | 59.35 |
| F   | -3.54 | 3.89 | 57.04 | -2.58 | 03.46 |
| F   | -1.66 | 4.28 | 03.26 | -1.57 | 40.92 |
| F   | -1.89 | 2.50 | 73.28 | -2.79 | 55.59 |
| H   | -3.68 | 1.72 | 86.82 | -1.13 | 01.15 |
| H   | -2.11 | 1.12 | 20.89 | 0.34 | 76.50 |
| C   | -2.97 | 2.45 | 07.77 | -1.50 | 45.85 |
| O   | -1.59 | -2.59 | 92.25 | -1.58 | 99.23 |
| C   | -3.44 | 1.61 | 14.32 | -2.70 | 129.30 |

|     |      |      |      |      |      |      |      |      |      |      |      |
|-----|------|------|------|------|------|------|------|------|------|------|------|
| F   | -3.01 | -2.10 | 09.82 | -3.86 | 63.10 |
| F   | -4.77 | -1.50 | 19.99 | -2.75 | 22.90 |
| F   | -2.93 | -0.36 | 12.76 | -2.59 | 97.30 |
| C   | -3.64 | -3.83 | 31.57 | -1.43 | 34.77 |
| F   | -4.96 | -3.72 | 80.17 | -1.22 | 47.84 |
| F   | -3.46 | -4.54 | 89.40 | -2.54 | 64.00 |
| F   | -3.12 | -4.52 | 58.40 | -0.40 | 78.38 |
| H   | -3.27 | -1.89 | 52.82 | -0.59 | 96.52 |
| H   | -1.17 | -2.43 | 39.99 | -0.70 | 66.10 |
| C   | 0.91 | 3.24 | 09.60 | 0.93 | 08.28 |
| O   | 1.33 | 1.91 | 80.16 | 0.89 | 94.56 |
| C   | 1.22 | 3.86 | 92.63 | 2.29 | 99.70 |
| F   | 2.54 | 3.87 | 31.70 | 2.57 | 50.30 |
| F   | 0.78 | 5.13 | 16.99 | 2.38 | 19.30 |
| F   | 0.61 | 3.15 | 62.19 | 3.25 | 96.60 |
| C   | 1.61 | 3.95 | 84.36 | -0.22 | 95.48 |
| O   | 1.27 | 5.25 | 03.51 | -0.28 | 07.06 |
| C   | 2.95 | 3.88 | 29.40 | -0.14 | 88.44 |
| F   | 1.26 | 3.39 | 24.74 | -1.40 | 61.20 |
| H   | -0.17 | 3.35 | 88.67 | 0.76 | 35.75 |
| H   | 0.73 | 1.33 | 51.55 | 1.42 | 14.90 |

### 3HFIP-INT2

|     |      |      |      |      |      |      |      |      |      |      |
|-----|------|------|------|------|------|------|------|------|------|------|
| C   | -4.03 | -0.47 | 65.92 | 2.10 | 14.97 |
| C   | -3.81 | 0.05 | 84.05 | 0.83 | 34.40 |
| C   | -3.40 | -0.76 | 94.65 | -0.23 | 10.49 |
| C   | -3.23 | -2.13 | 86.02 | 0.00 | 33.60 |
| C   | -3.45 | -2.67 | 41.75 | 1.27 | 54.26 |
| C   | -3.85 | -1.84 | 71.90 | 2.32 | 54.28 |
| H   | -4.33 | 0.17 | 94.30 | 2.92 | 01.00 |
| H   | -3.94 | 1.13 | 06.20 | 0.67 | 46.90 |
| H   | -2.91 | -2.80 | 34.24 | -0.79 | 28.00 |
| H   | -3.28 | -3.73 | 94.18 | 1.44 | 35.00 |
| H   | -4.02 | -2.26 | 73.28 | 3.31 | 29.29 |
| F   | -4.23 | -0.15 | 51.06 | -1.59 | 60.15 |
| O   | -2.07 | 0.83 | 65.07 | -1.60 | 86.90 |
| C   | -4.47 | 0.56 | 59.61 | -2.16 | 57.19 |
| H   | -4.57 | 1.56 | 07.22 | -1.71 | 13.50 |
| O   | -4.22 | 0.62 | 23.83 | -3.69 | 19.80 |
| H   | -5.16 | 0.68 | 54.50 | -4.25 | 96.40 |

S52
| Atoms | X   | Y   | Z   |
|-------|-----|-----|-----|
| C     | -2.70835300 | -0.40589900 | -2.04908900 |
| F     | -1.64440300 | -2.26221500 | -2.63700700 |
| F     | -1.36858600 | -2.73579600 | -3.58951700 |
| F     | -2.12549500 | -0.73199800 | -3.13215200 |
| H     | -3.05155700 | -0.97375700 | -4.33010200 |
| C     | -2.51230300 | -1.43549800 | -5.17047500 |
| C     | -3.09531900 | -1.61082100 | -4.06139200 |
| C     | -3.44973800 | -0.00209500 | -4.65764600 |
| C     | -0.93860800 | 0.14211500  | -3.53689600 |
| H     | -0.29277600 | 0.39706500  | -2.68493200 |
| C     | -0.32339700 | -0.33234600 | -4.31994500 |
| C     | -1.33773800 | 1.08353700  | -3.94555100 |
| C     | -0.36909700 | -3.65586300 | 0.41779600  |
| O     | -0.12100400 | -3.70104400 | 1.59447500  |
| C     | -0.19653200 | -4.68261000 | -0.42654300 |
| O     | 0.36944600  | -5.89624400 | 0.12663100  |
| H     | -0.30153200 | -6.26359600 | 0.91890000  |
| H     | 1.33050000  | -5.64232600 | 0.59911100  |
| C     | 0.52570600  | -6.89472900 | -0.99934800 |
| H     | 0.95878200  | -7.82834200 | -0.60857500 |
| C     | -0.44614900 | -7.13332200 | -1.45834700 |
| H     | 1.19580600  | -6.50761100 | -1.78230600 |
| S     | -0.40549100 | 1.23690000  | 0.49851000  |
| O     | -0.10233500 | 0.17753100  | 1.50993900  |
| C     | 0.56458800  | 1.24313900  | -0.64064700 |
| C     | -0.27574300 | 2.82289800  | 1.31176200  |
| C     | -0.02719300 | 5.27013400  | 2.65909600  |
| C     | -1.42019600 | 3.45927400  | 1.79592000  |
| C     | 0.99250600  | 3.39280100  | 1.47902900  |
| C     | 1.10470000  | 4.60981000  | 2.14830200  |
| C     | 1.28457900  | 4.67742900  | 2.46636400  |
| C     | -2.40569900 | 3.02075500  | 1.63732100  |
| O     | 1.88349600  | 2.90628300  | 1.07819700  |
| H     | 2.09482300  | 5.05819000  | 2.26681600  |
| H     | -2.18106600 | 5.17862500  | 2.84090600  |
| C     | 0.11704500  | 6.57350900  | 3.40395800  |
| H     | -0.84809100 | 7.09004700  | 3.50981900  |
| H     | 0.51596400  | 6.40252000  | 4.41881300  |
| C     | 0.81754900  | 7.25305200  | 2.89336700  |
| O     | -1.81939000 | 1.11482900  | -0.00663500 |

3HFIP-INT3

| Atoms | X   | Y   | Z   |
|-------|-----|-----|-----|
| C     | 3.15078600 | -1.60836400 | -1.35814400 |
| C     | 1.81303100 | -1.78935500 | -1.03534900 |
| C     | 0.86091000 | -2.13196700 | -2.03769900 |
| C     | 1.32471800 | -2.32203700 | -3.37391500 |
| C     | 2.66453700 | -2.16424400 | -3.68182000 |
| C     | 3.57719400 | -1.79424500 | -2.67758000 |
| C     | 3.84955500 | -1.30368500 | -0.57814400 |
| C     | 1.50621200 | -1.61210800 | -0.00646000 |
| C     | 0.62752500 | -2.62895000 | -4.15369600 |
| C     | 3.01355800 | -2.32274700 | -4.70426500 |
| C     | 4.62877900 | -1.64376600 | -2.93313600 |
| C     | -0.51517700 | -2.26391200 | -1.69619700 |
| O     | -2.88820900 | -0.13249200 | -2.14104900 |
| O     | -0.99971900 | -2.44618100 | -0.28294200 |
| H     | -0.73545900 | -1.57660100 | 0.34599600  |
| H     | -2.53946800 | -2.63427700 | -0.40005600 |
| H     | -2.91345700 | -3.41095300 | 0.28211300  |
| H     | -3.04283500 | -1.70267300 | -0.12155100 |
| H     | -2.78525100 | -2.97335500 | -1.87808900 |
| H     | -3.78052100 | -2.64750600 | -2.20479400 |

S55
|   |   | 4HFIP-INT2   |
|---|---|-------------|
| C | 1.10825200 | -4.09720400 | 3.70689800 | C | -4.84718400 | 2.37808100 | -0.21861600 |
| H | 1.67456000 | -3.35502800 | 1.76060600 | F | -6.16896700 | 2.45366000 | -0.03385400 |
| H | -2.04402100 | -1.84941600 | 3.35636700 | F | -4.36076100 | 3.62425100 | -0.26640100 |
| H | -1.71613500 | -3.23488600 | 5.40543000 | F | -4.62944700 | 1.81581800 | -1.42119300 |
| H | 2.00222900 | -4.72008400 | 3.79778800 | H | -4.64338900 | 0.53067600 | 0.81052900 |
| O | 0.37773200 | -4.91550300 | 5.98630900 | H | -2.38683700 | 0.70905100 | 0.95413400 |
| H | -0.45009300 | -4.80413400 | 6.70118900 | F | 4.03047500 | -0.15878800 | 1.51499000 |
| H | 0.46529100 | -5.98463100 | 5.73134400 | O | 2.92951100 | 0.10973000 | 2.31626200 |
| H | 1.31091500 | -4.63068200 | 6.50012700 | C | 4.91917000 | 1.09469900 | 1.48588200 |
| O | -1.73565600 | -0.82654500 | 1.14021900 | F | 5.24730600 | 1.51688900 | 2.70677300 |
| C | -3.76990500 | -2.06392200 | -1.01651200 | F | 6.05070200 | 0.87328300 | 0.79939200 |
| O | -2.75151800 | -2.75622700 | -1.65330800 | F | 4.26537100 | 2.09926900 | 0.87260700 |
| C | -4.76959100 | -1.61507900 | -2.08788800 | C | 4.79114400 | -1.40030900 | 2.02600900 |
| F | -5.23227300 | -2.62606100 | -2.82013800 | F | 5.69910000 | -1.81643600 | 1.13034700 |
| F | -5.81753600 | -0.98551900 | -1.53038900 | F | 5.42334000 | -1.17639100 | 3.18277500 |
| F | -4.17546400 | -0.74454000 | -2.92749600 | F | 3.92778800 | -2.40977100 | 2.22714200 |
| C | -4.42497900 | -2.90529800 | 0.98070000 | H | 3.76402700 | -0.37124500 | 0.46559800 |
| F | -5.19784400 | -2.13343200 | 0.88714000 | H | 2.12261300 | -0.25788800 | 1.89573900 |
| F | -5.18359200 | -3.89947700 | -0.37142000 | F | 3.47131400 | -3.44606900 | 0.86915400 |
| F | -3.47131400 | -3.44606900 | 0.86915400 | H | -3.41405700 | -1.14821200 | -0.51382400 |
| H | -1.95963700 | -2.76691800 | -1.06895300 | C | 2.02050500 | -3.28234100 | -2.48673900 |
| O | 1.03669700 | -2.32266600 | -2.32112300 | C | 2.23687500 | -3.46173500 | -3.99730100 |
| F | 2.52267800 | -2.29329800 | -4.59601700 | F | 3.23683300 | -4.31211600 | -4.25359000 |
| F | 1.12454400 | -3.94420900 | -4.55879300 | C | 3.29977700 | -2.88119500 | -1.72860700 |
| F | 4.24834700 | -3.81716900 | -1.80461800 | C | 3.80910600 | -1.72459000 | -2.16990400 |
| F | 3.80910600 | -1.72459000 | -2.16990400 | F | 2.99171300 | -2.71246100 | -0.42644200 |
| H | 1.72923700 | -4.27532400 | -2.09649300 | O | 0.91287400 | 1.36248400 | -1.33717000 |
| H | 0.56676900 | -2.41546000 | -1.44847500 | C | 1.95834200 | 3.60905900 | -1.43405100 |
| C | -4.17284800 | 1.53007500 | 0.86850900 | H | 2.63436200 | 3.19579200 | -0.67499900 |
| O | -2.81390000 | 1.52228200 | 0.59665600 | F | 2.48303800 | 3.40030000 | -2.87495600 |
| C | -4.44698300 | 2.03292300 | 2.29899300 | H | 3.16653500 | 4.20329900 | -3.18767000 |
| F | -4.08053800 | 3.30788200 | 2.47775100 | H | 3.05667300 | 2.46496900 | -2.90610100 |
| F | -5.74452600 | 1.92656300 | 2.61448700 | C | 1.21800000 | 3.32842700 | -3.74889600 |
| F | -3.74992500 | 1.28003300 | 3.16463200 | H | 1.38301900 | 2.80441800 | -4.70249800 |
C 0.695961 0.00 0.469637
F 6.159995 0.253266 0.417306
F 4.488134 1.326767 -1.278887
C 4.724230 -0.373465 2.027131
F 5.693369 -1.255317 1.758395
F 5.233096 0.5776180 2.815818
F 3.770067 -1.017995 2.729436
H 3.762700 -0.660571 0.140278
H 2.213993 0.548518 1.160576

4HFIP-TS3
C 0.111993 0.405078 0.126689
C -0.848152 3.269244 0.752730
C -0.582329 2.699081 2.032040
C 0.667329 2.978690 2.657307
C 1.606014 3.781557 2.030855
C 1.338618 4.301730 0.756722
H -0.078638 4.447533 -0.872566
H -1.776998 3.034515 0.233370
H 0.881015 2.577568 3.647410
H 2.565740 3.982498 2.508767
H 2.102912 4.888767 0.245037
C -1.551035 1.870218 2.671468
O -1.472422 -0.222405 1.856630
C -3.032092 1.956597 2.392144
H -3.216829 1.699328 1.341100
C -3.684000 0.970711 3.390941
H -4.679239 1.307580 3.715388
H -3.795946 -0.002453 2.894355
C -2.674718 0.901273 4.545736
H -2.795550 0.017827 5.185947
H -2.788556 1.792666 5.182068
C -1.297118 0.958551 3.855040
H -0.510897 1.321603 4.530532
C -0.821754 -0.372129 3.142777
C -1.303897 -1.646949 3.827455
H -0.895192 -1.726769 4.847602
H -2.399346 -1.696568 3.878313
C -0.966466 -2.513206 3.242865
C 0.695961 -0.416917 2.965234
H 1.081826 0.446110 2.405273
H 1.207607 -0.458545 3.938910
H 0.983403 -1.324747 2.413160
C -3.530694 3.391472 2.633820
O -3.591822 3.914267 3.719244
O -3.910127 3.969621 1.492670
C -4.449563 5.308746 1.569606
H -3.673344 5.976645 1.976491
H -5.285469 5.305227 2.286653
C -4.887111 5.710283 0.177623
H -5.335151 6.715577 0.203049
H -4.033477 5.729800 -0.516839
H -5.632187 5.003676 -0.217185
H -0.929306 -0.524838 1.093710
S 0.769042 -1.202765 -1.232100
O 0.916743 -2.568219 -0.618281
O -0.390448 -0.472815 -0.605917
C 0.373158 -1.441955 -2.956343
C -0.303564 -1.760338 -5.658543
C -0.640791 -2.338680 -3.312615
C 1.057123 -0.708836 -3.926149
C 0.712484 -0.875420 -5.269949
C -0.969413 -2.490810 -4.656950
H -1.170277 -2.905680 -2.546397
H 1.846923 -0.017745 -3.629734
H 1.248400 -0.302403 -6.031244
H -1.760895 -3.191258 -4.937726
C -0.695090 -1.916238 -7.106130
H -1.665178 -1.427844 -7.302273
H 0.047556 -1.463678 -7.779027
H -0.806811 -2.977157 -7.380657
C 2.039239 -0.429589 -1.186236
C 3.979168 -1.805343 0.991370
C 3.012544 -2.777500 1.198273
C 4.684557 -1.567844 2.332186
C 5.083660 -2.701106 2.908613
C 5.757831 -0.775816 2.179959
C 3.845270 -0.949437 3.183411
C 4.956593 -2.210976 -0.130998
F 5.666997 -1.144738 -0.558875
| Atom | X | Y | Z |
|------|---|---|---|
| C    | 3.34701400 | 0.39536800 | 2.46588900 |
| O    | 1.98824900 | 0.06566800 | 2.50536600 |
| C    | 4.19174900 | -0.61717400 | 3.22175200 |
| F    | 4.07640200 | -1.85593400 | 2.69478000 |
| F    | 5.49223600 | -0.27590800 | 3.16618100 |
| F    | 3.84798900 | -0.70556200 | 4.51382000 |
| H    | 3.50435600 | 1.37176700 | 2.95168500 |
| H    | 1.75843300 | -0.49883500 | 1.73035900 |
| C    | -0.90132800 | 2.21549600 | -3.28855800 |
| O    | -1.32366900 | 1.02440500 | -2.69591100 |
| C    | -1.93887300 | 3.28536200 | -3.01319700 |
| F    | -2.08487600 | 3.52401700 | -1.68617700 |
| F    | -1.57824800 | 4.44738300 | -3.58447900 |
| F    | -3.15175700 | 2.95960500 | -3.48207300 |
| H    | -0.81746600 | 2.14357200 | -4.39198200 |
| H    | -0.55627200 | 0.42546800 | -2.57441900 |
| H    | 0.06340200 | 2.58565800 | -2.89620900 |
| H    | 3.92121100 | 3.37340600 | -0.95887900 |
| H    | 3.72984400 | 0.46090500 | 1.43392200 |

### 3TFE-INT2

| Atom | X | Y | Z |
|------|---|---|---|
| C    | -3.26682500 | -1.15283000 | -2.15918300 |
| C    | -2.99877600 | -0.95650600 | -0.80424600 |
| C    | -2.94170100 | 0.34154700 | -0.26332400 |
| C    | -3.15659100 | 1.43285000 | -1.11324300 |
| C    | -3.41807200 | 1.23761700 | -2.47320200 |
| C    | -3.47818800 | -0.05342200 | -2.99938600 |
| H    | -3.31403500 | -2.16878700 | -2.56044700 |
| H    | -2.83367300 | -1.82366200 | -0.16018300 |
| H    | -3.11503100 | 2.45050000 | -0.72485200 |
| H    | -3.56139600 | 2.10473700 | -3.12092700 |
| H    | -3.68641700 | -0.20452500 | -4.06177600 |
| C    | -2.69153000 | 0.49689900 | 1.22259800 |
| O    | -1.34896900 | 0.01004900 | 1.59882000 |
| C    | -3.76439300 | -0.20131200 | 2.11525800 |
| H    | -3.53690700 | -1.27270600 | 2.19626800 |
| C    | -3.67691600 | 0.52959100 | 3.47483500 |
| H    | -4.61991000 | 0.47456900 | 4.03920000 |
| C    | -2.90624800 | 0.04263300 | 4.08926700 |
| C    | -3.28483700 | 1.97578600 | 3.12052000 |
C -1.85481500 -1.96422200 2.32979300          C -2.42364700 -0.03282000 0.50843000
O -1.80477000 -0.91452400 1.34488600          C -3.28625900 -1.03038200 1.00015300
C -0.93028300 -3.11456800 1.93624000          C -3.41125500 -1.25213600 2.37155300
C -1.51722600 -1.34826400 3.67990600          C -2.68690000 -0.47368500 3.28029000
H -2.89668500 -2.33343600 2.35659900          H -1.27147600 1.15086700 3.49776600
H -2.10726500 -1.27239400 0.46078200          H -1.05496100 1.56113600 1.09910600
C -3.15430600 -1.60139700 -2.08139900        H -3.87411900 -1.63976400 0.31554500
O -2.16469900 -1.88990900 -1.07654800        H -4.07784800 -2.04012000 2.73077800
C -4.10401500 -2.79090500 -2.14805600        H -2.78630800 -0.64801600 4.35463600
C -3.86640900 -0.28534100 -1.78242800        C -2.33941100 0.33915400 -0.95042500
H -2.62988200 -1.51313800 -3.05077000        O -1.23315700 0.94706100 -1.36286200
H -1.29901800 -1.51290500 -1.33886800        C -3.55739400 1.09646000 -1.55944300
C -2.39872300 2.84268900 0.46811800          H -3.37962100 2.14337400 -1.27565500
O -2.13147700 2.64714200 -0.91268700        C -3.54746900 0.90438400 -3.09241500
C -1.46432700 3.89721100 1.06494900          H -4.57781500 0.78161300 -3.45313600
C -3.86682200 3.23249100 0.59091000          H -3.13008600 1.79230600 -3.58666400
H -2.24515300 1.89182000 1.02093100          H -2.69707800 -0.34328400 -3.41487400
H -1.19181200 2.41321200 -1.00835100        H -1.69670600 -0.03511100 -3.74149600
H -1.59474900 -2.10176300 4.47880500          H -3.14418900 -0.93305700 -4.23135700
H -2.20633700 -0.52224600 3.91153800          C -2.59523300 -1.19363200 -2.16085100
H -0.48928100 -0.95036000 3.68116100          H -3.56443100 -1.54985100 -1.79488800
H -1.01285300 -3.94677800 2.65331400          C -1.51854400 -2.07478700 -1.94136200
H 0.11866300 -2.77689700 1.91789300          C -0.23080100 -1.88882500 -2.64919400
H -3.15899100 0.55251400 -1.67892800        H -0.38563700 -1.92050400 -3.74163700
H -1.19004800 -3.49059600 0.93481800          H 0.16295300 -0.87359300 -2.44665200
H -4.43779200 -0.36504600 -0.84175400        H 0.54267400 -2.61753800 -2.37290000
H -4.57597600 -0.03531500 -2.58794400        C -1.60526600 -3.17276900 -0.95685600
H -4.61839100 -2.92530100 -1.18193100        H -2.62606500 -3.37957700 -0.61447700
H -4.87041100 -2.63873800 -2.92410400        H -1.15322200 -4.08487400 -1.38211100
H -3.55315000 -3.71655500 -2.37440500        H -0.96076100 -2.94087800 -0.07452500
H -0.41400700 3.58209100 0.96172500          C -4.88964900 0.68428800 -0.94532600
H -1.66898800 4.05464100 2.13694100          O -5.52904300 -0.29019800 -1.27522100
H -1.58882200 4.85854600 0.53946800          O -5.27819100 1.54224400 0.00080000
H -4.15197000 3.38057800 1.64457500          C -6.50665800 1.24900500 0.69701700
H -4.51211000 2.45020600 0.16242700          H -6.40221700 0.26852800 1.18857800
H -4.05711300 4.16837800 0.04031200          H -7.31842500 1.15961700 -0.04238100
C -3.86433500 2.36097700 1.69355100          C -6.75433500 2.36097700 1.69355100
3/PrOH-TS1                                      S77
H -7.68543100 2.16526100 2.24762900          H -7.68543100 2.16526100 2.24762900
C -1.83802100 0.52610500 2.80335400          C -5.92825800 2.43036400 2.41740900
C -1.70279000 0.74874100 1.43085300          H -6.85263000 3.33272300 1.18578800
H 4.87334400 2.95327900 2.18277400
H 3.49465800 2.21940000 0.43421100
C 0.28406400 2.41155600 2.38029900
O -0.21690400 1.74086100 1.22317000
C -0.54757800 3.67305300 2.57121500
C 0.23899900 1.48902800 3.59845700
H 1.33364100 2.70957300 2.19183600
H 0.31300500 0.93296200 1.09417400
C 1.00506600 2.62930300 -1.71120000
O 0.45423200 1.36073400 -2.16491900
H 2.25227800 2.89977000 -2.53595900
C -0.04626200 3.72197800 -1.82107800
H 1.28011500 2.52440200 -0.65142400
H 1.26466300 0.24468400 -1.92745200
H 0.62109900 1.99717300 4.49922700
H 0.85659500 0.59266600 3.42693400
H -0.79546700 1.15902900 3.78918700
H 5.66236500 3.93286400 -0.62531200
H 5.87736200 2.27308000 -0.00851800
H 6.78354200 3.61903800 0.73218100
H 4.31244400 5.63911000 0.80352700
H 5.44585800 5.38076500 2.16284800
H 2.75149100 3.80445000 -2.16070500
H 2.96698700 2.06913300 -2.44337000
H 2.00009400 3.03612000 -3.60031500
H 3.69141600 5.13302500 2.39519800
H 0.36889400 4.67309800 -1.45339400
H -0.92157000 3.47949500 -1.19948500
H -0.37086600 3.86436100 -2.86453500
H -0.50573600 4.30337600 1.66962300
H -0.17310700 4.26450600 3.42153500
H -1.60294100 3.41797900 2.76493700

3PrOH-TS3
C 0.41918800 2.99553900 -0.20683600
C 1.29619100 1.93372100 -0.01775200
C 2.32132100 1.67502200 -0.96909400
C 2.45866500 2.55070700 -2.08607500
C 1.61826400 3.64265300 -2.22781000
C 0.58635100 3.85467900 -1.29673700
H -0.40931900 3.12377100 0.49066400
H 1.15657500 1.26767700 0.83222300
H 3.25264000 2.38255400 -2.81373700
H 1.74620500 4.32644000 -3.06976800
H -0.09863800 4.69563800 -1.43401100
C 3.16966200 0.53814400 -0.81572500
O 2.00822100 -1.41821800 -1.51179300
C 3.51932800 -0.07527300 0.50481800
H 2.58607200 -0.35092600 1.04562900
C 4.44790500 -1.25914900 0.16756500
H 5.19276100 -1.43259400 0.95502300
H 3.83236200 -2.16059400 0.05226500
C 5.08339000 -0.84684300 -1.16777600
H 5.51982600 -1.68157200 -1.73092000
H 5.89094100 -0.12245000 -0.97648600
C 3.94041400 -0.13840700 -1.92545100
H 4.31201500 0.56605900 -2.68381800
C 2.86573200 -1.09700800 -2.60259300
C 3.49233900 -2.36992500 -3.18240000
H 4.25095100 -2.14576700 -3.95005500
H 3.94962600 -2.98931700 -2.39930600
H 2.69794400 -2.96884800 -3.65403000
C 2.08704100 -0.37042700 -3.70737300
H 1.58287900 0.52971100 -3.33236200
H 2.74416400 -0.09385300 -4.54747500
H 1.29565000 -1.03801900 -4.07817600
C 4.26120100 0.97109000 1.37613000
O 5.46173000 1.08148500 1.40956300
O 3.42083100 1.71623700 2.09045700
C 3.99968800 2.72971200 2.94302400
H 4.59057000 3.41813500 2.31751500
H 4.69935200 2.23958000 3.63888800
C 2.87183800 3.43341700 3.66558000
H 3.28387300 4.20511400 4.33417600
H 2.18833000 3.92137600 2.95427100
H 2.28900000 2.72375500 4.27192000
H 1.08983300 -1.68003000 -1.82574200
S -2.26041700 0.26605400 -0.12902500
O -2.98564200 -1.02061000 0.07422800
O -1.43861900 0.66392000 1.06095000

S82
| Atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | -1.3331000 | -2.88161800 | 5.05878100 |
| C    | -3.12866700 | -1.30294400 | 4.74115200 |
| H    | -3.18325300 | -0.30322900 | 2.81490500 |
| H    | 0.02384900 | -3.12635200 | 3.38521300 |
| H    | -0.80952200 | -3.61154100 | 5.68284300 |
| C    | -2.98335100 | -2.54640000 | 6.94901900 |
| H    | -3.77251200 | -1.84643400 | 7.25980900 |
| O    | -3.40353200 | -3.56583000 | 6.99460600 |
| H    | -2.17254500 | -2.49933900 | 7.69385700 |
| O    | 0.19843700 | -0.27250500 | 1.56178900 |
| C    | -3.05485900 | 2.11704100 | -0.93760500 |
| O    | -1.87821900 | 1.71115500 | -0.33153500 |
| C    | -4.05271000 | 2.63847300 | 0.11371300 |
| F    | -3.57954000 | 3.69966400 | 0.77490000 |
| F    | -5.22636500 | 2.97653000 | -0.43710000 |
| F    | -4.28991500 | 1.66762800 | 1.01292700 |
| C    | -2.68678100 | 3.16599800 | -1.99748300 |
| F    | -3.77180300 | 3.64085100 | -2.62032700 |
| F    | -2.01796600 | 4.19797400 | -1.47569300 |
| C    | -1.89731200 | 2.60189100 | -2.93296500 |
| H    | -3.56789100 | 1.30049000 | -1.47854900 |
| H    | -1.97041300 | 0.78635500 | 0.03322500 |
| C    | -2.51607700 | -2.97805200 | -1.76031700 |
| O    | -1.12760700 | -3.00308700 | -1.69097400 |
| C    | -2.92134100 | -2.14186300 | -2.98133700 |
| F    | -2.28288600 | -2.52323100 | -4.09154100 |
| F    | -4.23865400 | -2.20367700 | -3.21316000 |
| F    | -2.61297200 | -0.84461100 | -2.76842000 |
| C    | -3.07117300 | -4.41294300 | -1.80404500 |
| F    | -4.40809500 | -4.42757800 | -1.69312500 |
| F    | -2.74385700 | -5.05162900 | -2.93527500 |
| F    | -2.56936000 | -5.11232800 | -0.77726900 |
| H    | -2.96806000 | -2.48305100 | -0.88288900 |
| H    | -0.85657900 | -2.94270100 | -0.73585700 |
| C    | 0.57087100 | 3.23940200 | 1.14966700 |
| O    | 1.38370200 | 2.13818400 | 1.39098100 |
| C    | 0.39042900 | 4.05526200 | 2.44057400 |
| F    | 1.54543700 | 4.56159200 | 2.89309900 |
| F    | -0.46518500 | 5.07433700 | 2.26738500 |

**3HFIP-INT4**

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | 4.61665200 | 2.64511400 | -0.79372900 |
| C    | 3.87845200 | 1.46166000 | -0.68590200 |
| C    | 4.01501800 | 0.44302400 | -1.64051500 |
| C    | 4.90671400 | 0.64641200 | -2.70918200 |
| C    | 5.64438200 | 1.82690400 | -2.81703700 |
| C    | 5.50429900 | 2.83152100 | -1.85505400 |
| H    | 4.47789000 | 3.42892900 | -0.04729400 |
| H    | 3.16482200 | 1.34962900 | 0.10307400 |
| C    | 5.02937800 | -0.11836000 | -3.48052700 |
| H    | 6.32926400 | 1.96163400 | -3.65827200 |
| H    | 6.07874600 | 3.75762100 | -1.93768000 |
| C    | 3.22206000 | -0.86042200 | -1.52985300 |
| O    | 2.52255500 | -0.93343900 | -0.27814600 |
| C    | 4.13525700 | -2.12169300 | -1.62858800 |
| O    | 4.79445900 | -2.00871800 | -2.49751800 |
| C    | 3.15445700 | -3.29959000 | -1.87858400 |
| C    | 3.61608100 | -4.04864500 | -2.53802400 |
| H    | 2.91231900 | -3.80693200 | -0.93298000 |
| C    | 1.88487800 | -2.65290400 | -2.48681300 |
| H    | 1.04924800 | -2.77653000 | -1.78774200 |
| O    | 1.58778600 | -3.11730200 | -3.43807900 |
| C    | 2.19454800 | -1.15247700 | -2.67219400 |
| H    | 2.78137100 | -1.03213000 | -3.60208300 |
| C    | 0.99764500 | -0.22104900 | -2.80620400 |
| C    | -0.26779900 | -0.65613000 | -2.70951800 |
| H    | -0.54149800 | -1.68686700 | -2.48204000 |
| C    | 1.16387200 | -0.59356000 | 0.22514400 |
| O    | 1.09895200 | 0.03689700 | -2.85463100 |
| C    | 1.27849200 | 1.22726600 | -3.13830100 |
| H    | 1.65363200 | 1.78364400 | -2.26568800 |
| H    | 2.04163700 | 1.32188100 | -3.92857600 |
3HFIP-TS7

C 5.22190900 0.28130300 -2.55719400
C 4.01456400 0.96091500 -2.42791600
C 3.50679800 1.27848600 -1.14563900
C 4.24568900 0.89036000 -0.00503300
C 5.43225940 0.17724800 -0.14238100
C 5.92455300 -0.12396300 -1.41622000
H 5.61268100 0.05485300 -3.55181200
H 3.46916180 1.28037900 -3.31622200
H 3.86322700 1.10907600 0.99082500
H 5.96002000 -0.16852400 0.74801600
H 6.85566700 -0.68627000 -1.52038600
C 2.28370500 2.05918100 -1.01486600
C 2.14894300 3.12718600 0.06268000
H 2.34072700 2.70280500 1.05825000
C 0.71610000 3.68693300 -0.10755700
H 0.04932500 3.20135800 0.61690000
H 0.67107700 4.76993400 0.06705800
C 0.30412200 3.29715300 -1.53429200
H 0.59952300 4.07282500 -2.25871200
H -0.77514300 3.12376500 -1.64016300
C 1.11937300 2.02324700 -1.80754200
H 0.61600700 1.25867600 -0.85765900
C 0.91581200 1.23107800 -3.07229600
C 0.55569500 1.86745800 -4.19905800
H 0.41460600 2.94939800 -4.24512800
H 0.38823500 1.30789700 -5.12334400
C 1.02273200 -0.27477800 -3.00785900
H 1.87042500 -0.62361400 -2.40150200
H 0.11386400 -0.70755900 -2.56294400
H 1.12178200 -0.70293200 -4.01537700
C 3.21181400 4.20039200 -0.21004800
O 3.14394300 4.99522800 -1.11489900
O 4.21378400 4.1401800 0.67119600
C 5.29989500 5.07760700 0.49344500
H 4.89000300 6.09919300 0.53599900
H 5.72040100 4.93748400 -0.51493500
C 6.32042600 4.8220600 1.58111300
H 7.16212000 5.52371000 1.47401600
H 5.87900300 4.96365500 2.57954200
H 6.71573400 3.79691400 1.51856700
S 0.07439000 -0.39918500 1.00517700
O -0.36961100 0.64549000 -0.05142800
O -0.06236200 -1.77622400 0.48017900
C -1.10197100 -0.19870100 2.33127400
C -3.04518600 0.22563300 4.30622400
C -0.95305100 0.86815600 3.22424500
H -2.18664800 -1.07586100 2.42677600
H -3.14682600 -0.85560400 3.41440300
H -1.92651700 1.07198400 4.20270500
H -0.08276400 1.52357600 3.15851100
H -2.28375500 -1.91257100 1.73449900
H -4.00143700 -1.53347800 3.48153300
H -1.81614900 1.90586800 4.90099200
C -4.12752700 0.48092900 5.32287400
H -3.80732000 1.20072000 6.08977600
H -5.02339400 0.89245200 4.82702100
H -4.43424900 -0.44926000 5.82594200
O 1.42109000 -0.02864300 1.50910000
C -3.61672300 1.76246600 0.43210300
O -2.95380500 1.29828200 -0.69796500
C -3.74859300 3.29455100 0.37356400
F 4.40294000 3.71552600 -0.70688500
F -4.37047000 3.77672600 1.45946900
F -2.51379500 3.83778600 0.34312000
C -4.97254300 1.04462300 0.54862700
F -5.58788000 1.36956600 1.69920300
F -5.79503400 1.33347400 -0.45882800
H -3.08165300 1.54356100 1.37165900
H -2.02548500 1.07638200 -0.47094900
C -2.72956900 -2.05642200 -1.81378600
|   | 3HFIP-TS8 |
|---|-----------|
| H | -4.79983300 -2.40353700 5.05196100 |
| H | -3.68009100 -3.71410900 5.47410300 |
| O | 1.59465700 -0.99424900 1.63571900 |
| C | -3.66488300 1.82784200 1.17938400 |
| O | -2.71830500 1.24958500 0.34068400 |
| C | -3.59982100 3.36436500 1.10140800 |
| F | -3.84224100 3.82590600 -0.12406700 |
| F | -4.45484700 3.93913700 1.95268900 |
| F | -2.35483100 3.75298400 1.45013300 |
| C | -5.03208700 1.24989500 0.78100200 |
| F | -6.00826200 1.76939900 1.53410600 |
| F | -5.31650700 1.48129100 -0.50025800 |
| F | -5.02774900 -0.07909400 0.97293000 |
| H | -3.52033100 1.56816000 2.24481500 |
| H | -1.81578700 1.37030000 0.68877800 |
| C | -2.78049300 -0.33812100 -2.56925700 |
| O | -1.47562600 -0.79944000 -2.71433400 |
| C | -3.13321100 0.44461900 -3.84005700 |
| F | -2.93459900 -0.26578000 -4.95041300 |
| F | -4.41371300 0.84201300 -3.81916500 |
| F | -2.36891800 1.54992800 -3.91858000 |
| C | -3.74153600 -1.50948200 -2.29947700 |
| F | -4.97392000 -1.08666300 -1.99182000 |
| F | -3.83326900 -2.35723400 -3.32485100 |
| F | -3.27985900 -2.20963700 -1.23693500 |
| H | -2.90991600 0.36562100 -1.72855700 |
| H | -1.08935300 -0.97740800 -1.83981800 |
| C | 2.43227100 -3.84139300 -0.07628000 |
| O | 3.24045000 -3.11769200 0.79237300 |
| C | 3.35662300 -4.63824000 -1.00703700 |
| F | 4.21262900 -5.40598600 -0.33126800 |
| F | 2.64616000 -5.42421400 -1.82852600 |
| F | 4.07160000 -3.79509000 -1.76808800 |
| C | 1.45112500 -4.73661900 0.70505300 |
| F | 0.55112900 -5.31073300 -0.09992100 |
| F | 2.06495300 -5.69488100 1.40148600 |
| F | 0.77332700 -3.96734400 1.58684400 |
| H | 1.80445100 -3.20484800 -0.72779900 |
| H | 2.71005300 -2.40159400 1.18806600 |

S93
C  -5.35974700  1.77478800  0.50512700
F  -5.71603400  2.02252600  -0.75618600
F  -6.22277600  2.40410700  1.31708500
F  -5.47992200  0.45739700  0.72144900
C  -3.70275700  3.72392300  0.68207000
F  -4.41500200  4.39581000  1.59252400
F  -4.00680500  4.19977200  -0.52657000
F  -2.39659500  4.00673800  0.90704700
H  -3.71837200  1.94582800  1.85012900
H  -2.34350100  1.10413100  0.45875600
C  -3.54368000  -1.60283700  -1.48751000
O  -2.52095000  -2.47730800  -1.14450300
C  -4.87106500  -2.28441000  -1.12982200
F  -5.00415600  -3.47564900  -1.72154200
F  -5.92167500  -1.52889800  -1.48146100
F  -4.93098900  -2.47827500  0.19708900
C  -3.44232500  -1.21404200  -2.97247400
F  -4.35037700  -0.29081100  -3.31932200
F  -3.58033800  -2.25727100  -3.79444100
F  -2.22085400  -0.67996800  -3.20221300
H  -3.52496600  -0.65005600  -0.92866900
H  -1.73259000  -1.96734500  -0.85406300
H  1.11485000  5.86146800  0.74016500

3HFIP-TS10
C  -0.10014700  2.37232600  -1.20174100
C  1.10448200  2.67943400  -0.47943300
C  2.38196600  2.41324800  -1.12402100
C  2.43793300  1.61041300  -2.26831600
C  1.23732400  1.20134000  -2.84990100
C  -0.02321000  1.58928000  -2.33967000
H  -1.07345300  2.64332200  -0.78928800
H  1.07981300  1.57513200  0.17416000
H  3.39579100  1.32179700  -2.70246300
H  1.27194600  0.56158400  -3.73490700
H  -0.93732500  1.24944400  -2.82949900
C  3.39994800  3.10466600  -0.37231400
C  4.91120200  3.15755800  -0.33485800
H  5.35562400  3.31994500  -1.32760100
C  5.14979800  4.36349700  0.63131300

S98
| X   | Y   | Z   |
|-----|-----|-----|
| 0.27640700 | 5.00962100 | 1.15553500 |
| 2.03995000 | 5.82965200 | 0.20115100 |
| 2.21184100 | 4.82043500 | 2.11200500 |
| 1.18586300 | 2.43294400 | 0.92437700 |
| 4.80103700 | 0.93249400 | 3.47106900 |
| 4.82043500 | 2.11200500 | 4.91349600 |
| 0.99391800 | 2.89637400 | 4.06090900 |
| 0.52839700 | -3.12758000 | -0.31623500 |
| 0.46943100 | -4.03522900 | 0.05084400 |
| 1.77649000 | -3.55605200 | -0.78482100 |
| 2.01995300 | -4.92552100 | -0.86926300 |
| -0.19894900 | -5.40145000 | -0.04747500 |
| -1.44396300 | -3.68630600 | 0.39818800 |
| 2.54247700 | -2.83888000 | -1.08409800 |
| 2.99385500 | -5.26660200 | -1.23089300 |
| -0.97496600 | -6.11615800 | 0.23804900 |
| 1.33154400 | -7.34561200 | -0.61277200 |
| 1.55229500 | -7.62882800 | -1.6537600 |
| 2.21322200 | -7.62327400 | -0.01185300 |
| 0.48139800 | -7.95260600 | -0.27014300 |
| 3.91854300 | 3.19854300 | 0.38334900 |
| 3.09323600 | 3.12763800 | 0.79434000 |
| 4.18553000 | 2.63179100 | -1.24306500 |
| 4.03522900 | 0.05084400 | -1.40065800 |
| 0.48139800 | -7.95260600 | -0.27014300 |
| 0.38334900 | 3.12763800 | 0.79434000 |
| 4.18553000 | 2.63179100 | -1.24306500 |
| 4.03522900 | 0.05084400 | -1.40065800 |
| 0.48139800 | -7.95260600 | -0.27014300 |
| 0.38334900 | 3.12763800 | 0.79434000 |
| 4.18553000 | 2.63179100 | -1.24306500 |
| 4.03522900 | 0.05084400 | -1.40065800 |
| 0.48139800 | -7.95260600 | -0.27014300 |
| 0.38334900 | 3.12763800 | 0.79434000 |
| 4.18553000 | 2.63179100 | -1.24306500 |
| 4.03522900 | 0.05084400 | -1.40065800 |
| 0.48139800 | -7.95260600 | -0.27014300 |
| 0.38334900 | 3.12763800 | 0.79434000 |
| 4.18553000 | 2.63179100 | -1.24306500 |
| 4.03522900 | 0.05084400 | -1.40065800 |
| 0.48139800 | -7.95260600 | -0.27014300 |
| 0.38334900 | 3.12763800 | 0.79434000 |
| 4.18553000 | 2.63179100 | -1.24306500 |
| 4.03522900 | 0.05084400 | -1.40065800 |
| 0.48139800 | -7.95260600 | -0.27014300 |

**3HFIP-TS12**

| X   | Y   | Z   |
|-----|-----|-----|
| 1.41580100 | 0.25233900 | 0.76663400 |

S102
|   |   |   |   |
|---|---|---|---|
| H | -3.52650700 | -0.73170600 | -0.27284000 |
| H | -2.38713600 | -1.69190400 | 1.28309800 |
| C | -2.62863100 | 1.49421700 | -2.69714300 |
| O | -2.23895000 | 0.92672100 | -1.49232700 |
| C | -4.10613600 | 1.89476000 | -2.56151000 |
| F | -4.31252600 | 2.69332500 | -1.50824200 |
| F | -4.53808800 | 2.53192000 | -3.65876100 |
| F | -4.85188600 | 0.79612100 | -2.39968000 |
| C | -1.70725400 | 2.67284200 | -3.06876400 |
| F | -1.96000000 | 3.13019300 | -4.29911600 |
| F | -1.82556400 | 3.70233900 | -2.21139400 |
| F | -0.43099700 | 2.26342000 | -3.03111600 |
| H | -2.57721100 | 0.78930400 | -3.54714900 |
| H | -1.53338900 | 0.24996700 | -1.63263100 |
| C | 0.45695500 | -0.56874500 | 5.84274900 |
| C | 0.19975300 | 0.35169900 | 4.82811300 |
| C | 0.84636100 | 0.24410700 | 3.58121900 |
| C | 1.73446100 | -0.82901400 | 3.36716800 |
| C | 1.98331900 | -1.75136200 | 4.38111800 |
| C | 1.35073100 | -1.62157300 | 5.62285300 |
| H | -0.40536900 | -0.46746200 | 6.80577200 |
| H | -0.50039000 | 1.16957400 | 4.99664600 |
| H | 2.20436700 | -0.97025900 | 2.39406800 |
| H | 2.66393500 | -2.58577400 | 4.19686300 |
| H | 1.54654300 | -2.34845600 | 6.41518100 |
| C | 0.55892600 | 1.24587700 | 2.53055800 |
| O | -0.63510100 | 1.76041000 | 2.65205200 |
| C | 1.43728700 | 1.50663200 | 1.43919600 |
| C | 0.93123900 | 2.31570300 | 0.23897300 |
| H | 1.66312600 | 2.20657300 | -0.57397500 |
| H | 0.00760100 | 1.84215300 | -0.12231000 |
| C | 0.67270500 | 3.80144900 | 0.51529000 |
| H | 0.02596600 | 4.19631200 | -0.28392100 |
| H | 1.61565100 | 4.37005600 | 0.45606200 |
| C | 0.05015400 | 4.05361400 | 1.89135600 |
| H | 0.82582200 | 3.97795500 | 2.67288400 |
| C | -1.11608000 | 3.14786000 | 2.30562900 |
| C | -2.21968900 | 2.99118600 | 1.26723100 |
| H | -2.66840100 | 3.97601100 | 1.06601700 |
| H | -1.86828200 | 2.57869900 | 0.31611000 |

H -3.00636600 2.32425900 1.64598900
H -1.70081200 3.62244300 3.63893400
H -2.45818600 2.91249100 4.00083500
H -0.91652400 3.72962300 4.40406000
H -2.18356400 4.60177400 3.50274300
C 2.91553000 1.61882800 1.67676500
O 3.74204700 1.54545400 0.79163700
O 3.24441200 1.86390100 2.95474700
C 4.65058000 1.93720300 3.26916200
H 5.11442200 2.70860100 2.63477300
H 5.12126100 0.97588200 3.00665900
C 4.78368700 2.25123300 4.74406700
H 5.84855600 2.31592400 5.01615900
H 4.30780000 3.21634600 4.98770300
H 4.31637000 1.46786300 5.35998100
H -0.32101700 5.09015000 1.94477600
C 0.21242560 2.26632800 -1.28610300
C 1.28775600 1.17802300 -1.03166700
C 0.46605600 1.15597800 0.10901000
C 0.48573000 2.26569600 0.97382400
C 1.33032500 3.34690100 0.72652800
C 2.15668500 3.35130000 -0.40369600
H 2.74773100 2.27140700 -2.18405900
H 1.25557200 0.34515700 -1.73704400
H -0.17035800 2.26720300 1.84603400
H 1.34671200 4.19398100 1.41735500
H 2.81320900 4.20233100 -0.60292900
C -0.47397600 0.03868000 0.38716400
O -1.69766600 0.45363000 0.85075200
C -0.26979900 -1.30189200 0.27580800
C -1.45414600 -2.21566600 0.51916500
H -1.11174000 -3.25788700 0.56440700
H -1.86977100 -1.95831000 1.50768700
H -2.56734700 -2.09039200 -0.54427600
H -3.50282500 -2.49895600 -0.12658100
H -2.31530000 -2.72713100 -1.40824100
C -2.79092500 -0.66388500 -1.07085000
H -1.97735700 -0.40827400 -1.76909200
| Atom | x        | y        | z       |
|------|----------|----------|---------|
| C    | -3.08544300 | 1.55384300 | 1.87487400 |
| O    | -3.13304700 | 0.49048400 | 2.44922000 |
| O    | -4.15407400 | 2.25674400 | 1.49304500 |
| C    | -5.44575700 | 1.66255600 | 1.75866000 |
| H    | -5.52343600 | 0.73450900 | 1.17152000 |
| H    | -5.49106900 | 1.38389400 | 2.82270900 |
| C    | -6.51241000 | 2.66853700 | 1.38389000 |
| H    | -7.50770200 | 2.24240700 | 1.58351600 |
| H    | -6.45972800 | 2.92837000 | 0.31563200 |
| C    | -6.40892400 | 3.59410200 | 1.97072200 |
| O    | 0.47485800  | 2.53524900 | 1.73301200 |
| C    | 1.92562400  | 2.53580600 | 1.98344400 |
| H    | 2.20551800  | 3.44638000 | 2.53941500 |
| H    | 2.47658400  | 2.56622600 | 1.02671800 |
| H    | 2.22314700  | 1.64716400 | 2.55077400 |
| C    | 1.16887600  | -0.36952800 | -0.50176200 |
| H    | -0.14211200 | -0.44840700 | 0.30975800 |
| C    | 2.32707600  | -0.69795900 | 0.37159600 |
| O    | 0.99839200  | 1.63774300 | 1.73812300 |
| C    | 0.62134700  | 3.63020300 | 3.66556100 |
| H    | 1.02109700  | -2.98252000 | 1.34568100 |
| C    | 0.81598300  | 1.17284200 | 2.07332200 |
| H    | 0.63315500  | 2.27406100 | 5.02823600 |
| C    | -3.18590600 | 4.07382500 | 0.73542900 |
| H    | 1.18933600  | 3.95228800 | 2.03036300 |
| H    | 0.82745000  | 2.21636200 | 3.53621000 |
| C    | 0.49413000  | 1.99443600 | 0.50759200 |
| H    | 0.83525500  | 0.50139190 | -2.01278500 |
| C    | 0.35732000  | 4.70511300 | 4.68427500 |
| H    | 1.01411400  | 5.57899800 | 4.53092800 |
| H    | 0.49846400  | 4.33415200 | 5.71195000 |
| H    | 0.68305500  | 5.06542200 | 4.59404200 |
| O    | 1.26760900  | 0.95020500 | 1.17591900 |
| O    | 0.86186900  | 2.62441010 | 2.77636000 |
| C    | 0.20635490  | 2.78611200 | 2.10314400 |
| O    | 1.02989400  | 1.68756200 | 3.98588400 |
| C    | 1.82482700  | 2.18007400 | 4.93252100 |
| O    | -0.14904000 | -1.37279500 | 4.54399400 |
| C    | 1.57930400  | -0.52249100 | 3.55806300 |
| H    | 0.35901700  | -4.02260700 | 3.15972900 |

7a-TS4

| Atom | x        | y        | z       |
|------|----------|----------|---------|
| C    | -3.77602500 | 5.07489700 | -1.50655600 |
| C    | 0.83012300  | 4.39635020 | -2.31458600 |
| C    | -3.18590600 | 4.07382500 | -0.73542900 |
| H    | 1.18933600  | 3.95228800 | 2.03036300 |
| C    | -2.09179300 | 4.37782700 | 0.09583300 |
| H    | 0.82745000  | 2.21636200 | 3.53621000 |
| C    | -1.59079600 | 5.69482900 | 0.12126500 |
| H    | 0.49413000  | 1.99443600 | 0.50759200 |
| C    | -2.18989300 | 6.69029900 | -0.64912200 |
| H    | 0.83525500  | 0.50139190 | -2.01278500 |
| C    | -3.28594600 | 6.38405600 | -1.46293000 |
| H    | -4.61989200 | 4.82744200 | -2.15613000 |
| H    | 1.95592800  | 5.07489700 | 0.78926000 |
| H    | -0.73153000 | 5.93638200 | 0.74945800 |
| H    | -0.68305500 | 5.06542200 | -4.59404200 |
| H    | -1.79768200 | 7.09391000 | -0.61654400 |
| O    | 1.26760900  | 0.95020500 | 1.17591900 |
| O    | 0.86186900  | 2.62441010 | 2.77636000 |
| C    | 0.20635490  | 2.78611200 | 2.10314400 |
| C    | 1.02989400  | 1.68756200 | 3.98588400 |
| C    | 1.82482700  | 2.18007400 | 4.93252100 |
| O    | -0.14904000 | -1.37279500 | 4.54399400 |
| C    | 1.57930400  | -0.52249100 | 3.55806300 |
| H    | 0.35901700  | -4.02260700 | 3.15972900 |
F  -4.85962500  0.78728400  1.57453400  H  0.11023700  2.33227100  1.48724000
C  -5.08081800  -0.52346200  -1.90506400  H  -1.42420400  0.26475300  -1.96603700
F  -5.66728200  -1.70730300  -1.66662900  H  -3.33017000  1.85225600  -2.07582700
F  -5.99040700  0.28993000  -2.44428900  H  -3.53699400  3.67841100  -0.38662700
F  -4.12192100  -0.73122900  -2.88292100  C  0.62818900  0.25946900  -0.16003300
H  -3.89300000  -0.75873500  -0.19199800  O  1.76217500  0.98731500  -0.01593500
H  -2.76362700  0.89404000  -1.08243000  C  0.63709200  -1.09975100  -0.29823800
C  1.18549500  4.21559900  -1.30266200  C  1.94135000  -1.84660900  -0.47902600
O  1.49790000  2.97994500  -0.76307600  H  1.82222800  -2.55315200  -1.31535300
C  -0.29207300  4.58388200  -1.05146000  H  2.14000300  -2.48132400  0.40388700
F  -0.53809200  4.86482100  0.24086000  C  3.10422300  -0.89282200  -0.73507000
F  -0.67051500  5.63932800  -1.78013900  H  3.06612100  -0.52521500  -1.77425300
F  -1.07233900  3.54543100  -1.39118200  C  3.04048900  0.32671700  0.19443600
C  2.16218800  5.23895300  -0.70409700  C  3.15188200  -0.04941200  1.67686600
C  1.83616300  6.48908000  -1.07172600  H  3.10522500  0.85498500  2.30242700
F  2.17655200  5.19279500  0.63307800  H  2.33955000  -0.72124300  1.98873400
F  3.40115800  4.99280800  -1.13895500  H  4.11044100  -0.55531300  1.87234200
H  1.32311400  4.26475500  -2.39918400  C  4.08227600  1.37659600  -0.18294900
H  1.21701600  2.26294200  -1.37461800  H  3.97404600  1.66650700  -1.23877400
C  4.52291900  -1.03111700  -0.01646200  C  3.96157300  2.27889300  0.43550900
O  3.75377400  -0.39515700  -0.99014700  H  5.09809400  0.98112600  -0.02979200
C  5.34210300  -2.13480400  -0.69644500  C  -0.55598700  -1.97719200  -0.27570800
F  6.14539400  -1.66694200  -1.65492700  O  -0.55725600  -3.10479100  -0.72871500
F  6.09556700  -2.80278600  0.18962600  O  -1.62586700  -1.45741700  0.36165500
F  4.50549900  -3.02460300  -1.26253300  C  -2.80964400  -2.26531100  0.40097100
C  5.38589500  0.00872600  0.71659500  H  -2.56321700  -3.24448400  0.84271300
F  6.09618800  -0.55133400  1.70809400  H  -3.14955600  -2.46040900  -0.63032300
F  6.23794100  0.63736000  -0.09750500  C  -3.85533300  -1.52403700  1.20917300
F  4.58370700  0.93765200  1.26603400  H  -4.78107600  -2.11834200  1.26274500
H  3.91511200  -1.52006200  0.76226700  H  -3.50131000  -1.34228900  2.23577900
H  2.83849300  -0.30881400  -0.66527500  H  -4.09182700  -0.55108500  0.75199300
H  4.07152400  -1.40473600  -0.61043800

6a
C  -1.72974600  3.11020100  0.66085400
C  -0.65527800  2.22036400  0.71730300
C  -0.54811000  1.16965600  -0.20885100
C  -1.51880500  1.05399700  -1.21734200
C  -2.58689100  1.94987100  -1.28026700
H  -2.70001900  2.97703100  -0.33693100
H  -1.80722900  3.91492800  1.39655700

3a
C  -4.65326900  1.93671300  0.50334900
C  -3.40432400  1.32951600  0.34921600
C  -3.30962000  -0.00445600  -0.08391100
C  -4.49128900  -0.71567800  -0.35941800
C  -5.73706600  -0.11066600  -0.20389000
C  -5.82062300  1.21852200  0.22829000

S120
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| H    | -4.71506000 | 2.97467800 | 0.83983600 |
| H    | -2.50431900 | 1.90651800 | 0.56837100 |
| H    | -4.39954200 | -1.74986300 | -0.69679600 |
| H    | -6.64856500 | -0.67393800 | -0.41979100 |
| H    | -6.79696500 | 1.69478800 | 0.35055600 |
| C    | -1.99778700 | -0.71971200 | -0.27750300 |
| O    | -1.98234000 | -1.86818800 | -0.67970900 |
| C    | -0.70521500 | 0.03514600 | 0.01407700 |
| H    | -0.66843800 | 0.88424800 | -0.69386600 |
| C    | 1.99787500 | -1.07971200 | -0.27750300 |
| O    | 1.80449500 | 0.11608300 | -0.21215200 |
| H    | 1.90188700 | 0.71995200 | 0.70951600 |
| H    | 1.62673800 | 0.81494900 | -1.02664000 |
| C    | 3.13953800 | -0.60158300 | -0.48435200 |
| H    | 3.00349900 | -1.25904200 | -1.36476700 |
| C    | 3.38807300 | -1.26703500 | 0.35519600 |
| C    | 4.26740900 | 0.35479000 | -0.76188200 |
| H    | 4.11875700 | 0.98751500 | -1.64744200 |
| C    | 5.40627000 | 0.54024900 | -0.06755000 |
| C    | 5.78987800 | -0.22346700 | 1.17594190 |
| H    | 6.74036300 | -0.76523900 | 1.02133100 |
| C    | 5.96371900 | 0.46891400 | 2.01853900 |
| H    | 5.03410600 | -0.95477400 | 1.49111100 |
| C    | 6.42265200 | 1.56564000 | -0.50751100 |
| H    | 6.60179500 | 2.31379800 | 0.28590200 |
| H    | 7.40044900 | 1.09298700 | -0.71220700 |
| H    | 6.10553700 | 2.09893000 | -1.41548100 |
| H    | -0.77503500 | 0.49857300 | 1.01473000 |
| C    | 0.68714800 | -1.79949300 | 1.06688100 |
| H    | 0.80602500 | -1.26834400 | 2.02793700 |
| C    | 1.55114700 | -2.47090700 | 0.94802900 |

3a-TSI

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | -1.82418000 | 2.54147900 | 2.86665400 |
| C    | -0.64039600 | 2.59284000 | 2.12521800 |
| C    | -0.47089600 | 3.55543000 | 1.11669900 |
| C    | -1.51034100 | 4.47643200 | 0.89017800 |
| C    | -2.69235400 | 4.41881600 | 1.62796100 |

H: Hydrogen, C: Carbon, O: Oxygen

S121
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | 1.9023000 | 6.1513790 | -1.89184400 |
| F    | -1.05023900 | -4.25354700 | -4.13595100 |
| H    | 3.50300800 | 5.42720000 | -2.08525800 |
| F    | -0.14383600 | -4.77691100 | -2.24169100 |
| C    | 1.40371700 | 5.06958000 | 0.65273600 |
| H    | -1.33784900 | -2.70831000 | -2.14172800 |
| H    | 0.67746900 | 5.86725800 | 0.42896700 |
| F    | 0.56056700 | -2.01942700 | -1.93561800 |
| C    | 2.73364500 | 5.35093700 | -0.05469500 |
| C    | 3.44757900 | -0.84321400 | -0.13525800 |
| H    | 3.42984200 | 4.54156600 | 0.22294100 |
| O    | 4.08106000 | -0.21150000 | 1.04715900 |
| S    | 0.61622600 | -1.15627700 | 0.69897900 |
| O    | -0.82909400 | -0.94224900 | 0.39094400 |
| O    | 1.32849400 | -1.87691700 | -0.39859000 |
| C    | 0.70237700 | -2.18375200 | 2.16086500 |
| O    | 0.85060700 | -3.83307900 | 4.42512700 |
| C    | 1.95613800 | -2.50629800 | 2.69773400 |
| F    | 6.00172900 | -2.46657900 | -0.90801000 |
| C    | -0.47233200 | -2.66588600 | 2.73867000 |
| C    | -0.38809500 | -3.48636800 | 3.86768400 |
| C    | 2.01682800 | -3.32600900 | 3.82170100 |
| H    | 2.87405500 | -2.11778400 | 2.25399900 |
| H    | -1.44035600 | -2.39621200 | 2.31617300 |
| H    | -1.30889000 | -3.86251400 | 4.32149900 |
| H    | 2.99502700 | -3.57817200 | 4.24052500 |
| O    | 1.33547800 | 0.12791100 | 1.04908900 |
| C    | -4.09443200 | 0.06678100 | 0.31403200 |
| O    | -2.88175600 | 0.72412500 | 0.44501400 |
| C    | -4.60047300 | -0.41473600 | 1.68753200 |
| F    | -4.85731100 | 0.59660100 | 2.52528600 |
| F    | -5.70958400 | -1.15488700 | 1.57481900 |
| F    | -3.65439200 | -1.18275000 | 2.25975000 |
| C    | -5.07030100 | 1.03099000 | -0.37756600 |
| F    | -6.28561900 | 0.48572800 | -0.50471400 |
| F    | -5.19840700 | 2.18585800 | 0.28517700 |
| F    | -4.62024000 | 1.32018800 | -1.61049600 |
| H    | -4.04726800 | -0.83014400 | -0.33004700 |
| H    | -2.13202500 | 0.80325300 | 0.52152600 |
| C    | -1.20673900 | -2.68513600 | -2.33674300 |
| O    | -0.04067000 | -2.03715200 | -2.71792500 |
| C    | -2.41151600 | -1.90403800 | -2.87903700 |
| F    | -2.47870800 | -1.89425100 | -4.21022200 |
| F    | -3.56917900 | -2.40058600 | -2.40566500 |
| F    | -2.34672200 | -0.61827400 | -2.46845100 |
| C    | -1.18102500 | -4.14928700 | -2.81062100 |
| F    | -2.30157600 | -4.80013000 | -2.45202300 |
H 6.24572100  -4.45635700  -0.43730800  O  -1.73077700  -1.77955400  -0.27025500  C  -0.68357300  -1.19144000  -2.63164200  C  -0.75696600  -1.50999800  -5.41355800  C  -1.85163100  -1.65933300  -3.23680000  C  0.45373800  -0.88021200  -3.38807700  C  0.40434100  -1.04316800  -4.77076500  C  -1.87751100  -1.81185700  -4.62467300  H  -2.72767100  -1.89746400  -2.63427800  H  1.36781700  -0.52295600  -2.91101100  H  1.29219200  -0.80446100  -5.36271200  H  -2.79212800  -2.17457600  -5.10067200  C  4.00877000  3.85706600  -0.46094500  C  2.78293400  3.25007200  -0.16228900  C  1.80242700  3.95683100  0.54520300  C  2.06624300  5.27857900  0.94404200  C  3.28775700  5.88178200  0.64067300  C  4.26522400  5.17046500  -0.06403200  H  4.76308800  3.28284500  -1.00279400  H  2.61552900  2.21793000  -0.47056700  C  1.31221600  5.84623300  1.49747600  H  3.47803500  6.90963500  0.95975900  C  5.22419500  5.63960400  -0.29757800  C  0.43902400  3.36082700  0.85769100  O  0.54090900  1.85841000  0.80517300  C  0.08919200  3.28102100  2.38388100  H  0.86010400  3.78895700  2.97635000  C  0.38348200  1.74633300  2.31941400  C  -0.71032900  0.75906800  2.66422600  H  -0.87821500  0.78316200  3.75212600  H  -1.66364200  0.98121000  2.17067000  H  -0.41062300  -0.26716200  2.40976000  C  1.72736800  1.34121500  2.89657600  H  2.52701400  2.02650500  2.58366500  C  1.66017300  1.36124200  3.99590700  H  1.99305400  0.32088900  2.58952500  H  -0.12864400  1.28061500  0.16503700  C  -1.31300700  3.74685600  2.84115100  H  -1.20747800  4.35111700  3.75534100  H  -1.91840400  2.87571600  3.12755900  C  -2.10470600  4.53388300  1.78750300  H  -1.70425800  5.56014200  1.68293600  C  -3.14482900  4.64359600  2.13431600  C  -0.63190900  3.87786000  -1.07941000  H  -0.52567200  3.32470100  -1.05683500  H  -2.07247100  3.84539700  0.41787000  H  -2.38619800  2.79790600  0.54911600  O  -0.65318600  -0.95475800  -0.86502500  O  0.71405600  -1.27074300  -0.36397400  S125
|     |     |     |     |
|-----|-----|-----|-----|
| F   | -5.80454100 | 0.09983900 | 1.72359000 |
| F   | -4.02968000 | 1.33876700 | 1.80109700 |
| C   | -5.52165000 | -0.34929800 | -1.17124200 |
| F   | -6.29405600 | -1.24600550 | -0.54313400 |
| F   | -6.31268000 | 0.60289400 | -1.67242000 |
| C   | -9.31705000 | -0.97587200 | -2.20459500 |
| H   | -3.86778700 | -0.64343900 | 0.13716200 |
| C   | -2.71597700 | 0.89991800 | -0.86495700 |
| C   | -0.78030100 | -1.69678800 | -6.90939500 |
| H   | -0.36103500 | -0.82043900 | -7.42687600 |
| H   | -0.17126600 | -2.56822300 | -7.20526500 |
| H   | -1.80135800 | -1.86159500 | -7.78243800 |
| C   | -0.37260200 | 4.92286100 | -0.34337600 |
| C   | -3.03750200 | 4.48043400 | -0.58504700 |
| H   | -2.98812100 | 3.97306400 | -1.56066700 |
| H   | -4.07589800 | 4.39912800 | -0.22927700 |
| H   | -2.80863000 | 5.54906200 | -0.73970400 |

**3a-TS3**

|     |     |     |     |
|-----|-----|-----|-----|
| C   | -0.23092100 | -0.08085400 | -2.86202400 |
| C   | 0.44319300 | -1.08312800 | -2.17920400 |
| C   | -0.05791900 | -2.42008200 | -2.16732800 |
| C   | -1.24205200 | -2.69795700 | -2.91592900 |
| C   | -1.88136200 | -1.69964300 | -3.63026300 |
| C   | -1.39017800 | -0.38693500 | -3.58675500 |
| H   | 0.11351500 | 0.95145700 | -2.79098300 |
| H   | 1.31718600 | -0.81782400 | -1.58647300 |
| H   | -1.63615300 | -3.71266100 | -2.95952500 |
| H   | -2.78672700 | -1.92626400 | -4.19601500 |
| H   | -1.92942100 | 0.41034800 | -4.10255400 |
| C   | 0.59924500 | -3.44183000 | -1.40993500 |
| O   | -0.01282300 | -3.18816300 | 1.04106900 |
| C   | -0.11890100 | -4.66598100 | -0.94599400 |
| H   | -0.98343700 | -4.86394700 | -1.59098600 |
| C   | -0.76108100 | -4.26594500 | 0.49444400 |
| C   | -0.67374300 | -5.43186700 | 1.48173900 |
| H   | -1.20636300 | -6.32423700 | 1.11988600 |
| H   | 0.36766000 | -5.70270500 | 1.70078900 |
| C   | -2.22667600 | -3.86675500 | 0.29801200 |

**S126**
C  -4.19243400  0.17377700  -0.56734500  C  3.10179700  -3.29292500  -2.30369700
O  -3.21515300  -0.74847200  -0.91302900  H  3.34494200  -2.89075300  -0.18833600
C  -4.80204900  0.71455600  -1.86711900  H  1.01619500  -2.27526400  0.16420700
F  -5.22326600  -0.26895600  -2.67428100  H  0.21565000  -2.99283400  -4.06460700
F  -5.83902700  1.52809500  -1.62990300  H  2.56462400  -3.62411800  -4.37938600
F  -3.87582800  1.41799500  -2.54049100  H  4.14927200  -3.57139800  -2.45452600
C  -5.23064400  -0.47078500  0.36624600  C  -0.96211000  -2.17334600  -1.72129400
F  -6.11482100  0.42210600  0.82881500  C  -1.91396500  -1.93597400  -2.82794400
F  -5.90859100  -1.46255500  -0.22159100  H  -1.54618200  -2.39495800  -3.75293000
F  -4.59329300  -0.99735600  1.43472900  C  -3.32697200  -2.48308700  -2.48050300
H  -3.78061500  1.04516200  -0.02757800  H  -3.80803000  -2.82771100  -3.40800900
H  -2.45410300  -0.67834000  -0.28754600  H  -3.94539200  -1.67089100  -2.07480400
C  3.88969700  0.4136400  0.07951600  C  -3.25740100  -3.61877000  -1.45700800
O  2.85212600  -0.49825400  0.22316200  H  -2.65188600  -4.44846900  -1.86788200
C  4.74037900  0.44829700  1.36174700  H  -4.26513500  -4.02561200  -1.27704600
F  5.28886400  -0.74012500  1.64372300  C  -1.56437300  -2.01509500  -0.38744100
F  5.72650500  1.35069000  1.27884700  H  -2.12588800  -1.06621500  -0.40380000
F  3.95759200  0.79181500  2.39866000  C  -2.64619300  -3.14656900  -0.12726700
C  4.69117700  0.03979800  -1.17674400  H  -3.43110100  -2.64593500  0.45933200
F  5.69274100  0.89832600  -1.39346300  O  -2.69102900  0.36178800  -2.20724400
F  5.21297400  -1.19462800  -0.09666500  C  -2.00899400  -0.33513100  -3.20836600
F  3.88655100  0.06314700  -2.24982100  C  -2.86633300  -0.24308100  -4.47822500
H  3.53686600  1.44505700  -0.08589200  H  -2.42769400  -0.81951700  -5.30674000
H  2.04110300  -0.02787900  0.55044100  H  -3.88984100  -0.59783000  -4.29749900
C  -1.27188800  0.98101500  7.26863000  H  -2.92904400  0.81923400  -4.78047000
H  -1.68458100  0.04595400  7.68135400  C  -0.61915600  0.26030700  -3.45558000
H  -0.31526600  1.82476000  7.77193400  H  -0.01696600  0.29900300  -2.53542800
H  -1.97214900  1.78870600  7.54123100  H  -0.06053900  -0.30728600  -4.21361900
C  4.09613800  -4.16626500  0.13649500  H  -0.73561100  1.29053900  -3.82571200
H  4.47003400  -4.87445100  0.89326000  S  -0.20628100  1.38863600  0.60047400
H  4.64634100  -4.35924000  -0.80071800  O  -0.24441600  0.77842000  1.95918700
H  4.34636200  -3.14938900  0.47066800  O  0.74242400  0.69210900  -0.32838700
H  2.54856200  -3.51182600  -2.08068800  C  0.38290300  3.06374200  0.80236100
C  1.34149400  5.67221900  1.17673800  C  -0.49489300  4.14065700  0.67981700
C  2.65578600  -2.92642700  -1.03257100  C  1.73348100  3.26422900  1.11605300
C  1.32571300  -2.57324800  -0.83692200  C  2.20140400  4.56392100  1.29407100
C  0.40450500  -2.56427400  -1.92516400  C  -0.00679200  5.43724100  0.86965900
C  0.89011900  -2.95475200  -3.21015400  H  -1.54467900  3.96213000  0.44247500
C  2.21279200  -3.32087400  -3.39104600  H  2.41551000  2.41762700  1.21434600
| 3a-INT7 | 1.35486900 5.82106000 -0.28034600 | C 3.44299700 4.62512400 0.43770100 |
|---------|----------------------------------|----------------------------------|
| C -2.34259100 5.01619900 -1.07532200 | H 0.94494600 -2.57235500 1.09225700 |
| C -1.36632600 4.17745400 -0.48937700 | H -0.11891300 -5.79263700 -2.66337900 |
| C -1.22204500 4.17595000 0.91881900 | H 1.05146800 -4.96012100 1.40388800 |
| C -2.06116800 4.96117200 1.70606700 | H 0.83608100 -7.00963100 -0.40504700 |
| C -3.02242900 5.78858200 1.11248300 | H 1.22930400 -7.46741000 -1.32574400 |
| H -3.89102500 6.47990800 -0.74681500 | H 1.57721100 -7.15298000 0.39533100 |
| H -2.42975900 5.05741300 -2.16284800 | H -0.50665600 3.50272400 1.39395400 |
| H -1.96547800 4.92420500 2.79354700 | H -0.80592700 -0.52399900 0.11008500 |
| H -3.66743200 6.41176300 1.73689800 | C 1.45779500 0.91024100 2.36749700 |
| C -0.47105100 3.39777900 -1.34798400 | O 0.42844900 1.36113600 1.54694000 |
| C -0.91430200 2.72083500 -2.50833600 | C 2.25395700 2.14312400 2.81347500 |
| C -2.20712400 2.17472400 -2.62955900 | F 1.47341300 3.06506900 3.39847400 |
| C -2.59831100 1.49649100 -3.89850300 | F 3.22653100 1.81962200 3.67048600 |
| H -2.22607700 1.99706400 -4.80160600 | F 2.82584900 2.72985100 1.74658000 |
| H -2.14861500 0.48375200 -3.85740800 | C 0.90063400 0.10076200 3.55134600 |
| H -3.68643700 1.35687100 -3.95950400 | F 1.88134600 -0.43353800 4.29008500 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| F    | 0.124437 | 0.834538 | 4.356503 |
| F    | 0.150876 | -0.911175 | 3.076782 |
| H    | 2.172922 | 0.2577080 | 1.835885 |
| H    | 0.025730 | 0.614575 | 1.030629 |
| C    | 3.790338 | -1.1236490 | -0.736274 |
| O    | 2.821319 | -0.2301560 | -0.3089180 |
| C    | 4.863542 | -0.3898830 | -1.5618140 |
| F    | 5.491635 | 0.5555950 | -0.8555210 |
| F    | 5.786549 | -1.2354130 | -2.0417290 |
| F    | 4.277980 | 0.2084690 | -2.6146860 |
| C    | 4.363545 | -1.8454340 | 0.4938630 |
| F    | 5.320746 | -2.7197690 | 0.1574700 |
| F    | 4.876020 | -0.9868750 | 1.3830490 |
| F    | 3.383449 | -2.5277260 | 1.1091150 |
| H    | 3.385948 | -1.9120570 | -1.3964930 |
| H    | 2.016050 | -0.3181600 | -0.8891190 |
| C    | -4.057501 | -1.5521100 | 0.1778220 |
| O    | -4.160716 | -1.2545500 | -1.1775310 |
| C    | -5.100862 | -0.7139890 | 0.9271080 |
| F    | -6.335033 | -0.8861110 | 0.4470640 |
| F    | -5.118109 | -1.0065010 | 2.2353140 |
| F    | -4.800724 | 0.5941200 | 0.8116530 |
| C    | -4.225572 | -3.0655770 | 0.4044990 |
| F    | -3.989780 | -3.4041430 | 1.6807840 |
| F    | -5.448093 | -3.5016290 | 0.0804710 |
| F    | -3.339861 | -3.7242380 | -0.3610440 |
| H    | -3.073742 | -1.2810050 | 0.6027730 |
| H    | -3.260044 | -1.2963230 | -1.5796080 |
| C    | 3.381159 | 3.3722620 | -1.7486530 |
| H    | 3.713790 | 3.1324150 | -0.7276010 |
| H    | 4.099155 | 2.9145930 | -2.4452350 |
| H    | 3.427068 | 4.4676430 | -1.8784270 |
| H    | 1.249293 | 4.4456420 | -0.6896430 |

**3a-TS8**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -2.175020 | -3.9547570 | 2.5218690 |
| C    | -1.592790 | -4.1117530 | 1.2278020 |
| C    | -2.158536 | -3.3959640 | 0.1067730 |
| C    | -3.354272 | -2.6691260 | 0.2752110 |
| C    | -3.881177 | -2.5286410 | 1.5500600 |
3a-INT8

H  2.59180200    -0.93760300    -0.66570100
H  -2.24132700    -3.95465500    -2.83479100
C  -0.89326200    -2.68586700    -4.82529000
H  -1.67966800    -1.93009800    -4.97795200
H  -0.03636900    -2.41223000    -5.46118600
H  -1.28047100    -3.65525800    -5.18424800
H  0.38934600    -1.33176500    -2.60697100
C  -1.04170500    -1.43900500    -2.32174800
C  -1.86860800    -0.24907800    -2.55706800
C  -1.27119600    1.00279900    -2.73217800
C  0.11540300    1.06397500    -2.83343900
C  0.94498800    -0.09434900    -2.80335700
H  1.02584700    -2.21484800    -2.51494400
H  -0.99727700    -1.41348600    -1.16861400
H  -1.87152800    1.90941900    -2.80163700
H  0.59275000    2.03864600    -2.95293200
H  2.02581500    0.02043100    -2.87799600
C  -3.25370400    -0.63489900    -2.56928800
C  -3.32815200    -2.00237000    -2.57442400
C  -1.95836200    -2.66586700    -2.62986900
C  -1.79408700    -3.81197000    -1.61742100
C  -2.03679400    -3.48012200    -0.59814300
H  -2.43130400    -4.69661300    -1.88244300
H  -0.75014000    -4.16307000    -1.61162400
C  -1.67548900    -3.17481900    -4.06437900
H  -1.74951800    -2.36032500    -4.80085300
H  -0.66258000    -3.60305900    -4.12152700
C  -4.63269700    -2.73369000    -2.53491200
C  -4.56662500    -3.58691900    -1.83050300
C  -4.81238600    -3.18766700    -3.52903600
C  -5.79861600    -1.80827400    -2.14995500
H  -5.76690000    -1.61712600    -1.06232400
H  -6.75538900    -2.31714600    -2.35042800
H  -4.44259900    0.28199100    -2.55171300
H  -4.28853700    1.11838100    -3.25542600
C  -5.74901900    -0.46120200    -2.89135200
H  -5.73766400    -0.68175100    -3.97650500
H  -2.39108100    -3.96265100    -4.34736400

S139
| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | -3.46759100 | 4.66154100 | -0.79965800 |
| C       | -4.83625300 | 2.68662900 | 0.61804500  |
| H       | -3.44220800 | 1.28899000 | -0.19300800 |
| C       | -4.57581800 | 5.00358400 | -0.02539700 |
| H       | -2.94190100 | 5.42599100 | -1.37030300 |
| C       | -5.26176700 | 4.01794500 | 0.69000500  |
| H       | -5.36678100 | 1.90739000 | 1.16996000  |
| H       | -4.90757100 | 6.04388700 | 0.01615800  |
| H       | -6.13001300 | 4.28422700 | 1.29816400  |
| H       | -2.17523400 | 0.93417200 | -1.76206300 |
| C       | -0.98897600 | 0.09717500 | -3.87299200 |
| H       | -0.89317800 | -0.77130300 | -3.20441900 |
| H       | -2.04091700 | 0.16822900 | -1.89946000 |
| H       | -0.37669700 | -0.10577100 | -4.76572100 |
| S       | -2.56370500 | -0.21356900 | 1.38293700  |
| C       | -0.65989700 | 1.51126600 | -0.21651200 |
| C       | -2.99011000 | 1.09024600 | 0.69235600  |
| C       | -2.13433600 | 1.52096600 | -0.52164700 |
| H       | -1.64251800 | -0.04012600 | 1.96121500  |
| H       | -2.99007000 | 1.90161400 | 1.44304300  |
| H       | -3.33495100 | -0.45407400 | 2.13382500  |
| H       | -4.03674300 | 0.99526600 | 0.34881100  |
| H       | -2.29545800 | 0.76967900 | -1.31338400 |
| C       | -0.95798300 | -1.79007300 | -0.03955100 |
| C       | -2.38390300 | -1.43547100 | 0.45724900  |
| H       | -3.03809000 | -1.33165000 | -0.42544500 |
| H       | -2.74374100 | -2.33484800 | 0.98516300  |
| C       | -0.02278400 | -2.12341200 | 1.12998700  |
| C       | -0.44563600 | -2.95069600 | 1.72114200  |
| H       | 0.96671900  | -2.43121700 | 0.76368000  |
| H       | 0.12262900 | -1.26779300 | 1.80481000  |
| C       | -1.05173400 | -2.98541500 | -0.99309800 |
| H       | -1.66711700 | -2.72590600 | -1.86769600 |
| H       | -0.05124300 | -3.27058600 | 1.35107300  |
| H       | -1.50392000 | -3.85447000 | -0.49161400 |
| O       | -0.40193900 | -0.73859600 | -0.87991200 |
| C       | 0.12313600 | 0.42196800 | -0.35252000 |
| C       | 1.59426300 | 0.42090200 | -0.13015800 |

**cat-1a-1**

**S147**
cat-1a-3

C -0.68920200  4.09450300 -1.74529100
C -1.32074700  3.37318200 -0.72951600
C -2.60263400  3.73875800 -0.28372400
C -3.24345500  4.83955000 -0.88246000
C -2.61625200  5.55660800 -1.89847400
C -1.33684900  5.18544200 -2.33113100
H  0.31072100  3.80113200 -2.06663100
H -0.78687900  2.52782600 -0.29526800
H -4.23906100  5.11131600 -0.52730600
H -3.12254100  6.41062500 -2.35555900
H -0.84231100  5.75016900 -3.12581100
C -3.34184900  3.01507700  0.80070100
O -4.46752400  3.33570900  1.11559300
C -2.66438900  1.80817000  1.50227000
H -2.39057100  1.09205500  0.71522400
C -3.64394900  1.12927300  2.48305700
H -3.97785100  1.87548400  3.21922300
H -4.53892900  0.85088600  1.90714900
C -3.07160200 -0.10680200  3.20017400
H -2.24811400  0.19144200  3.86903900
H -2.62671400 -0.78092300  2.44627100
C -4.12825500 -0.86690100  3.95684500
H -4.86869300 -1.36466900  3.31807000
F -4.28272400 -0.98402400  5.28845900
C -3.37664600 -0.35606700  6.31798500

H  3.13102600  0.02937100
F  2.74576600  2.29554400
H  2.78072100  0.99964700

S150
F 4.78971900 2.62543200 -2.77627000  C -3.41737800 1.91731800 -2.15753200
F 3.24178300 1.11768400 -2.95517600  C -3.94267300 2.93584800 -2.94941400
C 3.44226900 3.73462700 -0.31638500  C -4.96127900 3.95434000 -1.00778300
F 4.65791500 4.23102000 -0.57651100  H -4.64693900 2.93211200 0.87952600
F 2.53196000 4.61538500 -0.73853600  H -2.83077200 1.10860700 -2.59740300
F 3.31999500 3.62391700 1.01646600  H -3.75180600 2.92450700 -4.02537800
H 4.04700400 1.71090200 -0.51968900  H -5.57142800 4.74269600 -0.55985700
H 1.93679800 0.94563800 -0.77183300  C -5.23279300 5.09196400 -3.25338900
C 4.47580700 -2.13243800 1.08170700  H -6.15442800 5.52810100 -2.84085300
O 3.70623900 -2.06754400 2.23690300  H -4.48481600 5.90159200 -3.31656100
C 5.52781700 -1.01816200 1.15574000  H -5.43526400 4.75342600 -4.28024900
F 6.25626200 -1.07390900 2.26755900  O -1.54264300 1.33642200 0.59123700
F 6.35562300 -1.05644100 0.10328200  H -0.98709100 0.74787200 1.21556900
F 4.90715400 0.18279100 1.13372300  C -0.31897900 -2.87788000 -1.76142500
C 5.08349700 -3.53740600 0.91653100  O -0.31463100 -1.57571700 -1.28124600
F 5.71015100 -3.66578300 -0.26260300  C -0.63912000 -2.89581800 -3.26735400
F 5.95658300 -3.83904200 1.88498100  F 0.31902000 -2.32917200 -4.00521800
F 4.09128900 -4.44279400 0.95004000  F -0.83289000 -4.14225100 -3.71625000
H 3.89711400 -1.93786500 0.16138200  F -1.77675800 -2.20523800 -3.47208100
H 2.78484700 -2.29215100 2.01439000  C 1.04428700 -3.49433000 -1.41830800
C -3.50521500 -1.33801500 -1.76185900  F 1.16374700 -4.72548200 -1.92901200
O -2.69506600 -0.23457700 -1.51428400  F 2.06108500 -2.75209400 -1.87553700
C -4.64577000 -1.41761100 -0.73039100  F 1.17510600 -3.58456700 -0.08588200
F -5.36591900 -0.29984100 -0.67253500  H -1.07506400 -3.52298300 -1.27831700
F -5.46811700 -2.44433900 -0.97945300  H -1.22650500 -1.28531000 -1.08992700
F -4.10129300 -1.61966100 0.48883800  C -4.24331900 -2.81186100 1.39686200
C -4.00089800 -1.25109500 -3.21452900  O -4.07650000 -2.04539200 2.54549200
F -4.64453800 -2.38198900 -3.55890100  C -3.05883400 -3.78153300 1.25785800
F -4.82090400 -0.22562500 -3.41435700  F -2.99357300 -4.67077000 2.24617000
F -2.95642800 -1.11563700 -4.04205900  F -3.10841300 -4.45142600 0.90163200
H -2.96749800 -2.29890300 -1.68763600  F -1.90628300 -3.08070900 1.25589300
H -1.98518200 -0.46789300 -0.89331300  C -5.60755200 -3.51895500 1.45042300
F -5.80205300 -4.28762700 0.36692000  F -5.73952700 -4.28629300 2.53362100

**cat-1a-4**
S -2.98384100 0.67937500 0.23777200  F -6.57820700 -2.59383400 1.47524400
O -2.76351200 -0.54049400 -0.55749500  H -4.23947800 -2.21173500 0.47209100
O -3.75438000 0.54248100 1.48129100  H -4.05763200 -1.10335700 2.29580000
C -3.67093900 1.94466100 -0.78184100  C 0.17091600 4.30817200 0.30114700
C -4.71209200 3.97227900 -2.39149900  O 0.43831900 3.12037600 -0.36500400
C -4.44542200 2.94905000 -0.19286900  C 1.51064400 4.87398800 0.79521000
| Atoms | x    | y    | z    |
|-------|------|------|------|
| S     | -0.22768700 | -0.06072000 | 1.52465400 |
| O     | 1.11350400  | 0.29494300  | 1.01186900  |
| O     | -0.98685400 | 0.99656700  | 2.21636900  |
| C     | -0.08264600 | -1.45484800 | 2.62582900  |
| C     | 0.12733100  | -3.56779700 | 4.44908200  |
| C     | -1.21932800 | -2.21960500 | 2.92053100  |
| C     | 1.15117300  | -1.72217700 | 3.22112000  |
| C     | 1.24339200  | -2.77925700 | 4.13081300  |
| C     | -1.09909300 | -3.27179200 | 3.82493900  |
| H     | -2.17919600 | -2.00836500 | 2.44555600  |
| H     | 2.02345700  | -1.11281300 | 2.98360200  |
| H     | 2.20663100  | -2.99029100 | 4.60286100  |
| H     | -1.98211300 | -3.87666500 | 4.04831200  |
| C     | 0.22382100  | -4.69650300 | 5.44430400  |
| C     | -0.33141000 | -4.45415500 | 6.36638600  |
| H     | -0.21442700 | -5.62395700 | 5.04184900  |
| H     | 1.26630700  | -4.90289000 | 5.72671900  |
| O     | -1.09872600 | -0.61217300 | 0.33592800  |
| C     | 4.14944300  | 1.06715200  | 0.65380500  |
| O     | 3.20128900  | 2.05723100  | 0.86189900  |
| C     | 5.14705900  | 1.56460300  | -0.40259800 |
| F     | 5.68790700  | 2.73921200  | -0.08163400 |
| F     | 6.14281400  | 0.67957800  | -0.58228600 |
| F     | 4.52455700  | 1.70902600  | -1.58601800 |
| C     | 4.83615000  | 0.68281600  | 1.97929000  |
| F     | 5.61087600  | -0.40435400 | 1.83675000  |
| F     | 5.58727700  | 1.66854400  | 2.47892500  |
| F     | 3.89476400  | 0.38428000  | 2.89677300  |
| H     | 3.71897000  | 0.13269300  | 0.25263900  |
| H     | 2.34427000  | 1.61926400  | 1.03442300  |
| C     | -1.93549800 | 4.19107100  | 1.14320300  |
| O     | -2.08945400 | 2.91041500  | 0.64137000  |
| C     | -0.50008800 | 4.71554400  | 0.92623100  |
| F     | -0.24086400 | 4.98245800  | -0.36547400 |
| F     | -0.26894400 | 5.82873200  | 1.63060200  |
| F     | 0.37823200  | 3.78249400  | 1.32757500  |
| C     | -2.99816100 | 5.07645500  | 0.47535700  |
| F     | -2.82751900 | 6.36716900  | 0.80559200  |
| F     | -2.95994200 | 4.98361300  | -0.85893000 |
| F     | -4.21689900 | 4.70685000  | 0.87968000  |
| S     | 4.21689900  | 4.70685000  | 0.87968000  |
| C     | 3.18984800  | -1.41978700 | 0.13257000  |
| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| H       | -3.34148900 | -2.27119900 | -2.05336100 |
| H       | -3.51851300 | -3.52211300 | -0.79248600 |
| H       | -4.81951300 | -2.32622700 | -1.05320800 |
| C       | -1.51446300 | 1.59552400 | 0.25197100 |
| O       | 3.69336500  | 3.37384500  | 3.62303300 |
| C       | 1.89559800  | -0.17959500 | 3.46083700 |
| O       | 1.74854300  | 1.93122000 | 4.25462400 |
| C       | 1.48809300 | 5.06166900 | 0.74389300 |
| O       | 5.54933200 | -0.64419900 | 3.51971000 |
| C       | 2.39784400 | -0.20417600 | 0.75315700 |
| C       | 1.02819200 | -1.83377700 | 0.68182400 |
| C       | 0.49094500 | -0.74722800 | -0.04352300 |
| C       | 1.38268000 | 0.09681400 | -0.72168300 |
| C       | 2.76227300 | -1.09635000 | -0.66770300 |
| C       | 3.28285000 | -1.17912200 | 0.07948000 |
| H       | 1.51446300 | 1.59552400 | 0.25197100 |
| C       | 2.39784400 | -0.20417600 | 0.75315700 |
| C       | 1.02819200 | -1.83377700 | 0.68182400 |
| C       | 0.49094500 | -0.74722800 | -0.04352300 |
| C       | 1.38268000 | 0.09681400 | -0.72168300 |
| C       | 2.76227300 | -1.09635000 | -0.66770300 |
| C       | 3.28285000 | -1.17912200 | 0.07948000 |
| H       | 2.81746700 | -2.87302900 | 1.32271800 |
| H       | 0.34929200 | -2.51635200 | 1.19414800 |
| C       | 0.99407100 | 0.92571500 | -1.31032400 |
| H       | 3.42021300 | 0.56383500 | -1.21703100 |
| C       | -0.97061700 | -0.58909300 | -0.11930600 |
| O       | -1.63442800 | -1.76962300 | -0.08760600 |
| C       | -1.81381300 | 0.48522200 | -0.22571900 |
| C       | -3.22794800 | -0.03338800 | -0.37663500 |
| H       | -3.60387600 | 0.12041500 | -1.40411400 |
| C       | -3.93136200 | 0.48470200 | 0.29278000 |
| C       | -3.08351500 | -1.53288100 | -0.02899900 |
| C       | -3.52327500 | -1.84118400 | 1.40223100 |
| H       | -3.26841100 | -2.87770000 | 1.67184900 |
| H       | -3.02683700 | -1.16327100 | 2.11376200 |
| H       | -4.61195100 | -1.71004000 | 1.50554300 |
| C       | -3.72765300 | -2.47055500 | -1.04245600 |
| O       | -3.27829200 | -1.09836000 | 0.65437700 |
| C       | -3.16297000 | -3.20828000 | -0.50391000 |
| F       | -3.39069900 | -3.97131000 | 0.57039600 |
| F       | -3.56877700 | -3.88241200 | -1.58807800 |
| F       | -1.82467800 | -3.05263900 | -0.60383000 |
| C       | -5.33917700 | -1.89559800 | -0.17959500 |
| F       | -5.93303300 | -2.59085500 | -1.16009700 |
| F       | -5.65211300 | -2.47067600 | 0.98566300 |
| F       | -5.85794800 | -0.66017200 | -0.17828400 |
| H       | -3.66502600 | -1.33554100 | -1.38368700 |
| C       | -2.37764700 | -0.80127100 | 0.41120900 |
| O       | 5.83767700 | -2.64150900 | -1.51446300 |
| C       | 1.75972500 | -2.21060500 | -1.79524100 |
| H       | 7.81897200 | -3.04137800 | -1.51331400 |
| H       | 7.29541500 | -1.99285500 | -2.86860800 |
| H       | 7.42080400 | -1.31963400 | -1.20169700 |

10b

9c
O  -2.29619000  0.83919800  0.38151100  C  -2.74302900  -2.47785200  -1.23639600
C  -3.11197100  2.64714700  1.65505400  O  -1.66680600  -3.34762600  -0.92582500
F  -4.28409200  2.02543400  1.81446300  C  -2.40089200  -1.70283300  -2.29658200
F  -3.33025600  3.96697900  1.68599200  C  -0.98258100  -2.02535400  -2.68376700
F  -2.33847200  2.33576700  2.71059800  H  -0.30510000  -1.16134600  -2.56440600
C  -3.13428800  2.69205300  -0.91330200  H  -0.88238000  -2.36141500  -3.73016200
F  -3.12123200  4.02391100  -1.02774800  C  -3.15973700  -0.76314800  -3.14378100
F  -4.41491400  2.28644500  -0.93821000  O  -2.67661500  -0.28990700  -4.15033600
F  -2.52235400  2.17469300  -1.98663400  O  -4.40846500  -0.51571600  -2.72877000
H  -1.42589500  2.73856600  0.35569600  C  -5.19285500  0.36948900  -3.55417500
H  -1.46435400  0.54581700  -0.03565400  H  -4.66375500  1.33087500  -3.63624300
C  2.89292400  3.24503000  -0.82997500  H  -5.25358500  -0.05762300  -4.56811100
O  2.55530200  2.31379700  -1.79791700  C  -6.55743300  0.52355900  -2.91778700
C  1.63595200  3.72007500  -0.07702200  H  -7.18743500  1.17261200  -3.54574800
F  0.75940800  4.34600600  -0.86330200  H  -6.47636800  0.98362800  -1.92186400
F  1.93283700  4.52403200  0.94933800  H  -7.05954100  -0.45072100  -2.81473400
F  1.00015200  2.63520200  0.43720800  C  -0.62608200  -3.10082600  -1.71130800
C  3.64906200  4.39166400  -1.51940400  C  0.59076400  -3.71822400  -1.48579300
F  3.95663100  5.35961100  -0.64033000  H  1.33712700  -3.66374400  -2.28305400
F  2.93798000  4.93911600  -2.50617100  H  0.58554300  -4.62681800  -0.87477600
F  4.79186200  3.92677000  -2.03446600  H  1.15051000  -2.83755400  -0.54948900
H  3.57639200  2.85030400  -0.05554400  S  1.52196900  -0.67100500  0.38220000
H  2.57226800  1.42567400  -1.39553600  O  1.76720400  -2.21594300  0.31033100
O  -6.95322800  -3.30539100  2.46905000  O  0.20177700  -0.36637900  -0.21496200
C  -7.73986800  -2.24583900  2.97180800  C  1.50286700  -0.32625600  2.12691700
H  -8.47125200  -2.69791400  3.65473400  C  1.49876600  0.22536700  4.86921800
H  -7.13144800  -1.51347200  3.53156300  C  0.30669300  0.03352700  2.74835500
H  -8.27969600  -1.71839300  2.16549200  C  2.70287400  -0.42324900  2.84529700
C  2.68526800  -1.50420000  4.21028300  C  0.31807900  0.31244000  4.11720300
C  -5.72576600  -1.72825800  0.95456500  H  -0.62025500  0.11078600  2.18018200
C  -4.65462500  -1.55387900  0.07992900  H  3.63008700  -0.72000400  2.35131300
C  -3.88961600  -2.65019100  -0.35262800  H  3.61645600  -0.22841300  4.77799200
C  -4.21512200  -3.93604400  0.13685500  H  -0.61548300  0.60986500  4.60094300
C  -5.28783800  -4.11830700  0.99463000  C  1.51192700  0.53113800  6.34525600
C  -6.05861500  -3.01469100  1.41194600  H  0.50339600  0.74987000  6.72401900
H  -6.27791000  -0.85005300  1.28814500  H  2.15161600  1.40315000  6.56144400
H  -4.38115600  -0.55070300  -0.23667800  H  1.91838200  -0.31556900  6.92228800
H  -3.61971800  -4.79847700  -0.16847200  O  2.68120800  0.02473800  -0.22089900
H  -5.5503600  -5.10853400  1.36805700  C  5.08826000  -2.26018500  -0.23939100

S182
| At  | X       | Y       | Z       |
|-----|---------|---------|---------|
| O   | 4.42697 | -2.78891 | 0.86469 |
| C   | 5.19740 | -3.31128 | -1.35684 |
| F   | 5.93409 | -4.36759 | -1.00949 |
| F   | 5.70815 | -2.79333 | -2.48070 |
| F   | 3.95528 | -3.76082 | -1.64847 |
| C   | 6.44614 | -1.73951 | 0.24598 |
| F   | 7.16662 | -1.24719 | -0.77203 |
| F   | 7.16903 | -2.68674 | 0.84739 |
| F   | 6.25491 | -0.74560 | 1.12905 |
| H   | 4.56286 | -1.39334 | -0.67866 |
| C   | 3.46524 | -2.72813 | 0.70412 |
| C   | -2.36544 | 2.07848 | 0.43290 |
| O   | -2.23811 | 0.69785 | 0.33947 |
| C   | -3.19520 | 2.38191 | 1.68925 |
| F   | -4.36679 | 1.73399 | 1.69094 |
| F   | -3.44488 | 3.69164 | 1.80815 |
| F   | -2.51524 | 1.99360 | 2.78130 |
| C   | -2.98601 | 2.65092 | -0.85548 |
| F   | -2.96723 | 3.98680 | -0.86169 |
| F   | -4.26307 | 2.25640 | -1.02033 |
| F   | -2.29106 | 2.21684 | -1.91425 |
| H   | -1.40160 | 2.59775 | 0.56222 |
| H   | -1.34013 | 0.44358 | 0.04167 |
| C   | 2.73324 | 3.30203 | -0.70427 |
| O   | 2.38319 | 2.34868 | -1.64393 |
| C   | 1.50066 | 3.72413 | 0.11663 |
| F   | 0.54194 | 4.28057 | -0.62860 |
| F   | 1.81007 | 4.57114 | 1.10437 |
| F   | 0.96012 | 2.62032 | 0.69183 |
| C   | 3.39450 | 4.47682 | -1.44129 |
| F   | 3.72145 | 5.45971 | -0.58503 |
| F   | 2.59735 | 4.99438 | -2.37846 |
| F   | 4.51829 | 4.05903 | -2.03292 |
| H   | 3.47653 | 2.94419 | 0.03253 |
| H   | 2.46471 | 1.46509 | -1.23144 |
| O   | -7.07790 | -3.28747 | 2.25289 |
| C   | -7.89467 | -2.23550 | 2.72651 |
| H   | -8.64740 | -2.69685 | 3.37903 |
| H   | -7.31475 | -1.49968 | 3.31078 |
| H   | -8.40697 | -1.71263 | 1.89985 |

**7b-INT3**

| At  | X       | Y       | Z       |
|-----|---------|---------|---------|
| C   | -6.63769 | 0.80281 | -0.30294 |
| C   | -5.35444 | 0.45128 | 0.11049 |
| C   | -4.49995 | 1.39647 | 0.70659 |
| C   | -4.97183 | 2.72270 | 0.86071 |
| C   | -6.24767 | 3.07619 | 0.45584 |
| C   | -7.09992 | 2.11908 | -0.13029 |
| H   | -7.26543 | 0.04458 | -0.77041 |
| H   | -5.00118 | -0.56456 | -0.04538 |
| H   | -4.32858 | 3.48195 | 1.30745 |
| H   | -6.61811 | 4.09552 | 0.57776 |
| C   | -3.15414 | 1.05241 | 1.14121 |
| O   | -2.27310 | 2.19728 | 1.15730 |
| C   | -2.43159 | -0.01613 | 1.56909 |
| C   | -1.03649 | 0.44220 | 1.84548 |
| H   | -0.25677 | -0.08175 | 1.23687 |
| H   | -0.68643 | 0.26606 | 2.87920 |
| C   | -2.74176 | -1.43685 | 1.87531 |
| O   | -2.00744 | -2.08510 | 2.58532 |
| O   | -3.85059 | -1.90677 | 1.30355 |
| C   | -4.07161 | -3.33291 | 1.41592 |
| H   | -3.25219 | -3.83252 | 0.87653 |
| H   | -4.00412 | -3.67123 | 2.47672 |
| C   | -5.42509 | -3.65254 | 0.81948 |
| O   | -5.61936 | -4.73262 | 0.90885 |
| C   | -5.45783 | -3.38825 | -0.24785 |
| H   | -6.22982 | -3.11519 | 1.34528 |
| C   | -1.08438 | 1.86543 | 1.53195 |
| C   | -0.00378 | 2.84852 | 1.53112 |
| C   | -0.38550 | 3.87035 | 1.66771 |
| H   | 0.46417 | 2.80881 | 0.52094 |
| H   | 0.76917 | 2.52737 | 2.25814 |
| S   | 1.95708 | -0.41670 | -0.49060 |
| O   | 1.15393 | -1.27912 | 0.45288 |
| C   | 3.11803 | -1.49731 | -1.31099 |
| C   | 5.02734 | -3.12224 | -2.56598 |
| C   | 3.66592 | -2.57939 | -0.61431 |
| C   | 3.51133 | -1.20154 | -2.62037 |
| C   | 4.46311 | -2.02546 | -3.23682 |
C 4.61354600 -3.38146800 -1.24733100  C -0.80280000 -3.55934100 -2.44276700
H 3.35139700 -2.78967400 0.40842900  F -0.72219600 -3.47909200 -3.77879300
H 3.07738500 -0.36007700 -3.14881900  F -1.68339900 -4.52249200 -2.13932700
H 4.77159300 -1.80286000 -4.26107100  F 0.39776200 -3.94160200 -1.98209700
H 5.04146000 -4.22933200 -0.70522100  H -0.44001100 -1.46838600 -2.16993500
C 6.03383400 -4.01775400 -3.24386300  H -0.28716600 -2.08686600 -0.07875500
H 6.86141900 -4.27812400 -2.56542200  O -8.32038700 2.55588200 -0.49461100
H 6.46018500 -3.54384200 -4.14008900  C -9.23484000 1.66350700 -1.10198100
H 5.56517800 -4.96570100 -3.56050300  H -10.14475300 2.24306500 -1.30418700
O 1.10036200 0.19368600 -1.55865800  H -8.84288800 1.26497400 -2.05390100
C 2.34016000 -0.37423700 3.54696900  H -9.48565100 0.82097500 -0.43410000
O 2.28253100 0.83817400 2.87479800
C 1.68869100 -0.16552600 4.91990400 7b-TS4
F 2.29584500 0.77920400 5.63783800  C 5.65027000 2.55954300 0.55591500
F 1.67544700 -1.29518200 5.63396000  C 4.57576200 1.91401900 -0.05408000
F 0.40172700 0.22263600 4.75783800  C 3.64167000 2.62877700 -0.82295800
C 3.78900700 -0.88960600 3.65186900  C 3.80409000 4.02799900 -0.94636300
F 3.83732500 -2.10068100 4.22617100  C 4.87263400 4.67559600 -0.34826200
F 4.58038100 -0.06766800 4.34427300  C 5.81262300 3.94809800 0.40825100
F 4.30055500 -1.00685900 2.41416800  H 6.34741100 1.97360200 1.15448300
H 1.77069000 -1.17973400 3.04357800  H 4.44829600 0.84247400 0.08705900
H 2.53332000 0.71542100 1.92207500  H 3.08194400 4.60875600 -1.52280500
C 2.47767500 3.26375200 -1.63426500  H 5.00853400 5.75413100 -0.44578300
O 1.14657900 2.87403300 -1.51435300  C 2.50008600 1.97214300 -1.44795100
C 2.63602800 4.61113800 -0.91859700  O 1.35127800 2.78487500 -1.53568400
F 1.78101400 5.53241700 -1.37055800  C 2.18572300 0.74976200 -1.97690900
F 3.87852500 5.09143800 -1.05219400  C 0.74666400 0.77824800 -2.30463800
F 2.40131400 4.45497900 0.39829500  H 0.18621700 0.20270900 -1.33629100
C 2.89398800 3.32334300 -3.11557500  H 0.32034000 0.18522900 -3.12119000
F 4.21014100 3.53784600 -3.24797200  C 2.96603400 -0.47793300 -2.25683600
F 2.24664800 4.27272900 -3.79702900  O 2.43556300 -1.47732600 -2.68631500
F 2.61513400 2.14231700 -3.69966800  O 4.27853100 -0.36146900 -2.02961900
H 3.17004200 2.56085800 -1.13681200  C 5.08220900 -1.53359000 -2.29129000
H 1.09662200 1.89018400 -1.62282000  H 4.76478300 -2.33051800 -1.60120600
C -1.17563600 -2.20905700 -1.80790400  H 4.87271800 -1.88222900 -3.31435100
O -1.18120900 -2.32390800 -0.42228100  C 6.53639000 -1.15879100 -2.10198900
C -2.54905100 -1.69094100 -2.24745300  H 7.17305300 -2.03360100 -2.30566800
F -3.55357900 -2.48020900 -1.82934000  H 6.73267100 -0.82597900 -1.07121300
F -2.63922000 -1.58825300 -3.57831900  H 6.83024400 -0.35004700 -2.78859100
F -2.75940800 -0.46878700 -1.72876800  C 0.35395400 2.12123600 -2.07578600
S184
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | -0.93743400 | 2.80684200 | -2.25715000 |
| H       | -0.80565300 | 3.67697500 | -2.92193200 |
| H       | -1.30218600 | 3.19666700 | -1.29087100 |
| H       | -1.68268400 | 2.12558400 | -2.68232600 |
| S       | -1.41041700 | 0.15610100 | 0.57086900 |
| O       | -0.36851700 | -0.60519400 | -0.28151700 |
| O       | -2.66623900 | 0.33309800 | -0.20477200 |
| C       | -1.72422200 | -0.92970300 | 1.94526400 |
| C       | -2.12263700 | -2.68576900 | 4.08650400 |
| C       | -2.41695300 | -2.12786800 | 1.72778700 |
| C       | -1.24903000 | -0.58170300 | 3.21173200 |
| C       | -1.45715600 | -1.46388600 | 4.27479000 |
| C       | -2.60626700 | -2.99321700 | 2.80161300 |
| H       | -2.80723600 | -2.38170700 | 0.74003300 |
| H       | -0.73458100 | 0.36965100 | 3.35639400 |
| H       | -1.09199500 | -1.19601200 | 5.26977100 |
| H       | -3.13607300 | -3.93463900 | 2.63573500 |
| C       | -2.28828100 | -0.66632300 | 5.21805400 |
| C       | -3.82900700 | -4.12525600 | 5.21121000 |
| H       | -2.13062100 | -3.19143500 | 6.19728200 |
| H       | -1.55412800 | -4.48443900 | 5.11866700 |
| O       | -0.82161400 | 1.41937000 | 1.08069100 |
| C       | -2.53816500 | -2.27868900 | -2.39681400 |
| O       | -3.59474300 | -1.78725300 | -1.64453200 |
| C       | -2.38499900 | -1.49204100 | -3.71094200 |
| F       | -3.41617200 | -1.63775000 | -4.53956100 |
| F       | -1.26363800 | -1.82685900 | -4.36728500 |
| F       | -2.28272400 | -0.17201100 | -3.41544700 |
| C       | -2.78831400 | -3.77701400 | -2.61434100 |
| F       | -1.84137900 | -4.31441200 | -3.39746200 |
| F       | -3.97553900 | -4.01494800 | -3.17561300 |
| F       | -2.75421500 | -4.41109700 | -1.43353500 |
| H       | -1.56036400 | -2.20048400 | -1.88663800 |
| H       | -3.31789000 | -0.96131100 | -1.18969200 |
| C       | -3.52255200 | 3.42834300 | 0.78536300 |
| O       | -2.16774400 | 3.74917400 | 0.75506100 |
| C       | -4.24228800 | 4.36137100 | -0.19508000 |
| F       | -4.02573800 | 5.65063200 | 0.07413800 |
| F       | -5.56501700 | 4.14865700 | -0.18685800 |
| F       | -3.80170100 | 4.12680400 | -1.44546100 |
| Atom | xyz coordinates       | Atom | xyz coordinates       |
|------|-----------------------|------|-----------------------|
| O    | 0.26005500 -0.22056300 -0.29071000 | C    | 1.54736300 -0.34347200 2.06312400 |
| H    | 0.05960070          | N    | 1.57061100 0.12581300 4.81499800 |
| O    | 0.26005500 -0.22056300 -0.29071000 | C    | 0.36763000 0.05932600 2.69283200 |
| O    | 0.26005500 -0.22056300 -0.29071000 | C    | 2.74404900 -0.52206500 2.77226300 |
| O    | 0.26005500 -0.22056300 -0.29071000 | C    | 2.73748500 -0.29026100 4.14451300 |
| S    | 0.39487600 0.29710400 4.06791200 | N    | 0.06279900 0.64245100 6.68597300 |
| C    | 0.359457800 -1.52291200 0.86033600 | O    | 0.26005500 -0.22056300 -0.29071000 |
C 3.07127700 3.24464600 -0.65229700 H -6.88602200 1.93510500 -3.47495300
O 2.70967800 2.34320700 -1.63999900 H -6.23073000 1.52217600 -1.87052300
C 1.83365700 3.69497100 0.14647200 H -6.85050000 0.23273400 -2.94391600
F 0.93455400 4.33915300 -0.59899900 C -0.57602000 -2.81512100 -1.96148800
F 2.15482600 4.46966900 1.18667900 C 0.60329100 -3.51442700 -1.76041300
F 1.12139000 2.59346600 0.64613400 H 1.37304900 -3.42377800 -2.53216300
C 3.80896500 4.41296100 -1.32567200 H 0.52395200 -4.48475900 -1.25861900
F 4.13983900 5.35270200 -0.42490700 H 1.16531100 -2.78775900 -0.74725600
F 3.07129200 4.98971800 -2.27535400 S 1.60802300 -0.72657200 0.39983200
F 4.93718000 3.96458400 -1.88518600 O 1.79462400 -2.26494200 0.21143600
H 3.77451300 2.82764600 0.09223100 O 0.30282500 -0.33127400 -0.18453600
H 2.73015600 1.44322800 -1.26604900 C 1.57993700 -0.50650500 2.16368800
N -7.16628300 -3.03898000 2.03702300 C 1.56038900 -0.15828700 4.93939200
O -7.69463900 -2.05099500 2.51358400 C 0.38674600 -0.16240000 2.80000900
O -7.50138300 -4.19091100 2.25504800 C 2.76923700 -0.68780400 2.88350500

7c-TS3
C -5.70211300 -1.50431100 0.65880400 H -0.53172400 -0.02025000 2.23074600
C -4.57529100 -1.27773400 -0.12857300 H 3.69382200 -0.97191000 2.37728000
C -3.88320000 -2.36229800 -0.69728500 H 3.66649400 -0.65963200 4.83329400
C -4.32085600 -3.67895500 -0.44861300 H -0.50469600 0.29974200 4.68196000
C -5.45300800 -3.91074000 0.32708400 C 1.56553200 0.03743300 6.43391100
C -6.12882700 -2.81552100 0.86666200 H 0.55851900 0.25074600 6.81956700
H -6.24297900 -0.68116300 1.12440600 H 2.22244400 0.87618700 6.71899500
H -4.20308500 -0.26648500 -0.27076400 H 1.94740900 -0.85860200 6.94990900
H -3.77335500 -4.52355600 -0.87006700 O 2.79208500 -0.02321000 -0.14391300
H -5.81966200 -4.91740000 0.52471000 C 5.11336200 -2.39186100 -0.31521900
C -2.67641800 -2.14714300 -1.50280600 O 4.42253500 -2.98143600 0.73852500
O -1.65619800 -3.09041500 -1.12406100 C 5.18666500 -3.35045500 -1.51563400
C -2.26463500 -1.28021900 -2.45736800 F 5.87152400 -4.46404700 -1.25401400
C -0.84872200 -1.63004100 -2.82688400 F 5.72865900 -2.76476800 -2.59025800
H -0.14461500 -0.81299500 -2.58745100 F 3.92723800 -3.71815500 -1.85066300
H -0.71886400 -1.85472500 -3.89946400 C 6.48827600 -1.97046300 0.21665600
C -2.95578100 -0.21188100 -3.21323600 F 7.23453900 -1.42219000 -0.75418100
C -2.41522100 0.34639300 -4.14162100 F 7.16766500 -2.99399400 0.73788300
C -4.20198200 0.03680000 -2.80400700 F 6.33147500 -1.04735300 1.17957800
C -4.92994900 1.04969300 -3.53640400 H 4.62814800 -1.47026700 -0.68359300
H -4.35743200 1.98776100 -3.48975800 H 3.46523000 -2.86828800 0.57944500
H -4.97858800 0.74499100 -4.59394500 C -2.16483400 2.15981200 0.65407400
C -6.30275900 1.18719700 -2.91587400 O -2.08666500 0.79850100 0.38035800
F 1.83682000 1.49554700 -5.60161000 C 4.50457900 2.90193900 -1.15640200
F 0.43322600 0.08745300 -4.74100800 C 5.70718400 3.29903000 -0.57884400
C 3.93116900 0.83237800 -3.66944500 C 6.40034900 2.38735900 0.21709400
F 4.08708600 2.04922100 -4.20996700 H 6.48790100 0.43119500 1.10521000
F 4.62773300 -0.04169500 -4.39790000 H 4.31868100 -0.28496800 0.07127600
F 4.46893500 0.86288300 -2.43740800 H 3.94826200 3.60616300 -1.77665300
H 1.95894000 1.29746000 -3.01743100 H 6.11642000 4.29707800 -0.73185200
H 2.56482900 -0.69855000 -1.96438700 C 2.73313200 1.21054800 -1.55858600
C 2.42842700 -3.40352800 1.50145800 O 1.80301300 2.27056500 -1.65908500
O 1.12309300 -2.92753200 1.40308900 C 2.15186100 0.08865900 -2.06592900
C 2.49869400 -4.73224100 0.73841600 C 0.75005500 0.43526900 -2.39535400
F 1.58951100 -5.61290700 1.16365700 H 0.08486600 -0.00870300 -1.49693100
F 3.70899200 -5.29263600 0.84582200 H 0.24018700 -0.01177100 -3.25869800
F 2.26708700 -4.51044200 -0.57084200 C 2.63894500 -1.29349400 -2.32062900
C 2.84599300 -3.53967000 2.97747500 O 1.89913600 -2.14271200 -2.75804000
F 4.14656700 -3.83901200 3.09330400 O 3.93390100 -1.47145200 -2.05823900
F 2.14358800 -4.46987900 3.62929800 C 4.45967200 -2.80442500 -2.27649500
F 2.64271000 -2.36394300 3.60204000 H 3.95169300 -3.48820100 -1.57937500
H 3.16095500 -2.72788700 1.02358100 H 4.19803000 -3.11182600 -3.29853900
H 1.13313100 -1.94951900 1.56232000 C 5.95539800 -2.76429700 -2.05311300
C -0.95467900 2.19700300 1.93753400 H 6.37912500 -3.76567900 -2.22474400
O -0.95549400 2.34832900 0.55472400 H 6.19967500 -2.46445500 -1.02262100
C -2.32498900 1.65723200 2.36029800 H 6.44293600 -2.06100200 -2.74548200
F -3.33388200 2.46089000 1.98003000 C 0.67851800 1.84924700 -2.17602100
F -2.40932700 1.49384600 3.68330700 C -0.42175200 2.80439000 -2.35969000
F -2.53538000 0.45813100 1.78560800 H -0.09175900 3.62788200 -3.01537600
C -0.59305400 3.53381900 2.60643100 H -0.68171000 3.26404700 -1.38752800
F -0.53924700 3.42689800 3.94112600 H -1.30282700 2.31168000 -2.78411200
F -1.46793800 4.50259100 2.30354200 S -1.43044400 0.36024400 0.50664200
F 0.61567100 3.92319700 2.17547100 O -0.70886500 -0.69860200 -0.33959500
H -0.21573300 1.45119100 2.28107000 O -2.61491200 0.88525000 -0.22642100
H -0.06197800 2.11393500 0.20602100 C -1.98983400 -0.51724500 1.95036400
N -8.46541300 -1.93803500 0.38117500 C -2.79362500 -1.98347600 4.19390900
O -0.90699100 -1.05966400 0.94258400 C -2.96599400 -1.51182900 1.80470100
O -8.88871600 -3.04894000 0.11062300 C -1.42833800 -0.22450700 3.19505300
C -1.84037800 -0.95949900 4.30951600
7e-TS4
C 5.92109700 1.10007900 0.45827300 C -3.35505200 -2.23534100 2.92841400
C 4.71944500 0.70718800 -0.12545000 H -3.41979200 -1.71624600 0.83261200
C 4.00655000 1.59943600 -0.94863800 H -0.68805400 0.57211100 3.28378800
H -1.40774700 -0.73300600 5.28756000
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