Electronic Supplementary Information

for

Trisubstituted geminal diazaalkenes derived transient 1,2-carbodications

Debdeep Mandal,‡ Felix Stein, b Shubhadeep Chandra, bc Nicolás I. Neuman, bcd Pallavi Sarkar, e Shubhajit Das, § Abhinanda Kundu, a Arighna Sarkar, a Hemant Rawat, a Swapan K. Pati, ** Vadapalli Chandrasekhar, *sf Biprajit Sarkar, *bc and Anukul Jana* a

| 1. Content | S1 |
|-------------|----|
| 2. Experimental Details and Analytical Data | S2 |
| 3. Molecular Structures of 1·HOTf, 3iPr, 3Bu, 3Dip, 4Dip, 6H, and 10 | S10 |
| 4. Cyclic Voltammetry | S13 |
| 5. EPR Spectroscopy | S17 |
| 6. Computational Details | S35 |
| 7. NMR Spectra | S68 |
| 8. Crystallographic Details | S91 |
| 9. References | S102 |

‡Tata Institute of Fundamental Research Hyderabad, Gopanpally, Hyderabad-500107, Telangana, India
E-mail: ajana@tifrh.res.in

bInstitut für Chemie und Biochemie, Anorganische Chemie, Freie Universität Berlin, Fabeckstraße 34–36, 14195, Berlin Germany

bcdLehrstuhl für Anorganische Koordinationschemie, Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569, Stuttgart, Germany
E-mail: biprajit.sarkar@iac.uni-stuttgart.de

cdInstituto de Desarrollo Tecnológico para la Industria Química, CCT Santa Fe CONICET-UNL, Colectora Ruta Nacional 168, Km 472, Paraje El Pozo 3000 Santa Fe, Argentina.

dTheoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore-560064, India
E-mail: pati@jncasr.ac.in

fDepartment of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India
E-mail: vc@iitk.ac.in

‡Present Address: General and Inorganic Chemistry, Saarland University, Campus, C4.1, 66123 Saarbrücken, Germany

§Present Address: Laboratory for Computational Molecular Design Institute of Chemical Sciences and Engineering, Ecole Polytechnique Federale de Lausanne (EPFL), 1015 Lausanne, Switzerland

This journal is © The Royal Society of Chemistry 2020
Experimental details and analytical data

General Considerations

All experiments were carried out under an argon atmosphere using standard Schlenk techniques, PL-HE-2GB Innovative Technology GloveBox, and MBraun UNILAB GloveBox. n-Hexane, n-pentane, diethyl ether, THF, and toluene were dried by PS-MD-5 Innovative Technology solvent purification system. Methyl triflate, silver triflate, and KHMDs were purchased from Sigma-Aldrich. 1,2,4,5-tetramethylimidazole was purchased from TCI Chemicals. All these chemicals were used without further purification.

Dichloromethane and acetonitrile were dried and distilled over CaH$_2$. Benzene-$d_6$ was dried and distilled over potassium under argon. Chloroform-$d_1$ and acetonitrile-$d_3$ were dried and distilled over CaH$_2$ under argon.

NMR spectra were recorded on a BrukerNanoBay 300 MHz NMR spectrometer. $^1$H and $^{13}$C{$_{1H}$} NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (1H) or the deuterated solvent itself ($^{13}$C[1H]). $^{19}$F{$_{1H}$} NMR spectra were referenced to external tol-CF$_3$. Melting points were determined in closed NMR tubes under argon atmosphere and are uncorrected.

Synthesis of 1

a) At $-78$ °C, methyl triflate solution (6.94 g, 42.3 mmol, in 250 mL n-pentane) was added dropwise to a n-pentane suspension of 1,2,4,5-tetramethylimidazole (5.252 g, 42.3 mmol, in 200 mL n-pentane) by using a dropping funnel. After the completion of addition, the reaction mixture was allowed to reach room temperature slowly in an about 2.5 hrs and stirring was continued to another 2 hrs at room temperature. Then the reaction mixture was filtered which gave the desired 1,2,3,4,5-pentamethyl-1H-imidazol-3-ium triflate, 1·HOTf as a white solid residue. **Yield:** 11.20 g, 38.8 mmol (92 %). **M.P:** 77 °C. $^1$H NMR (300 MHz, CDCl$_3$, 298 K): $\delta$ = 2.19 (s, 6H, CC$_3$H$_3$), 2.60 (s, 3H, NC$_3$H$_3$N), 3.63 (s, 6H, NC$_3$H$_3$) ppm.

b) n-BuLi (1.6 M in n-hexane, 22 mL, 34.9 mmol) was added dropwise to 1·HOTf solution (10.07 g, 34.9 mmol, 40 mL THF) at $-78$ °C. Then the reaction mixture was stirred for 3 hrs at $-78$ °C that resulted in deep yellow colored solution. Subsequently, the reaction mixture was allowed to reach room temperature. Then all the volatiles were removed under vacuum and resulting residue was extracted using n-hexane (150 mL). Evaporation of filtrate gave the desired product 1 as pale yellow solid. **Yield:** 3.85 g, 27.8 mmol (80 %). **M.P:** 59 °C. $^1$H NMR (300 MHz, C$_6$D$_6$, 298 K): $\delta$ = 2.19 (s, 6H, CC$_3$H$_3$), 2.60 (s, 3H, NC$_3$H$_3$N), 3.63 (s, 6H, NC$_3$H$_3$) ppm.
298 K): $\delta = 1.48$ (s, 6H, CCH$_3$), 2.62 (s, 6H, NCH$_3$), 2.85 (s, 2H, CH$_2$) ppm. $^{13}$C$[^1H]$ NMR (75.4 MHz, C$_6$D$_{6}$, 298 K): $\delta = 8.60$ (2C, CCH$_3$), 29.29 (2C, NCH$_3$), 40.43 (1C, CH$_2$), 114.26 (2C, NCCH$_3$), 153.63 (NC(CH$_3$)N) ppm.$^{51}$

Synthesis of 3$^{iPr}$

Dry THF (30 mL) was added to a Schlenk flask containing 1 (1.59 g, 11 mmol) and 2$^{iPr}$ (3.60 g, 11 mmol) at room temperature. On stirring the reaction mixture overnight, a yellow colored solution was formed. Subsequently, all the volatilities were removed under vacuum and then the resulting residue was washed with n-hexane. The resulting white colored solids contain about 95 % of 3$^{iPr}$ and 5 % of 1·HOTf. **Total Yield:** 4.62 g; amount of compound 3$^{iPr}$ in the mixture is 4.389 g (9.63 mmol; **Yield:** 88 %). **M.P.:** 151 °C; $^1$H NMR (300 MHz, CDCl$_3$, 298 K): $\delta = 0.74$ (d, $J = 6.90$, 3H, CH(CH$_3$)$_2$), 0.88 (s, 3H, C(CH$_3$)$_2$), 0.99 (d, $J = 6.84$, 3H, CH(CH$_3$)$_2$), 1.05 (s, 3H, C(CH$_3$)$_3$), 1.16 (s, 3H, C(CH$_3$)$_2$), 1.20 (s, 3H, C(CH$_3$)$_2$), 1.67 (q, $J = 13.10$, 2H, CH$_2$C(CH$_3$)$_2$), 2.22 (s, 6H, NCCH$_3$), 2.92 (sep, 1H, CH(CH$_3$)$_2$), 3.26-2.93 (m, 1H, NCHCH$_2$; 2H, NCCH$_2$), 3.70 (s, 6H, N(CH$_3$)) ppm. $^{13}$C$[^1H]$ NMR (75.4 MHz, CDCl$_3$, 298 K): $\delta = 8.95$ (2C, NC(CH$_3$)$_2$), 20.78 (1C, CH(CH$_3$)$_2$), 24.91 (1C, CH(CH$_3$)$_2$), 25.82 (1C, C(CH$_3$)$_2$), 27.21 (1C, C(CH$_3$)$_3$), 28.81 (1C, C(CH$_3$)$_3$), 29.81 (1C, NCCH$_2$), 32.94 (2C, NCH$_3$), 33.64 (1C, C(CH$_3$)$_2$), 39.77 (1C, C(CH$_3$)$_2$), 46.36 (1C, CH(CH$_3$)$_2$), 52.45 (C(CH$_3$)$_2$CH$_2$), 65.87 (1C, NCHCH$_2$), 120.89 (1C, CF$_3$), 126.04 (2C, NC(CH$_3$)$_2$), 145.37 (1C, NCN) ppm. $^{19}$F$[^1H]$ NMR (169.2 MHz, CDCl$_3$, 298 K): $\delta = -78.45$ ppm. **HRMS (ESI-TOF) m/z:** [M]+ Calcd for [C$_{19}$H$_{36}$N$_2$]$:^+$ 306.2904; Found 306.2992.

Synthesis of 3$^{Bu}$

Dry THF (40 mL) was added to a Schlenk flask containing 1 (2.96 g, 21 mmol) and 2$^{Bu}$ (7.0 g, 21 mmol) at room temperature. On stirring the reaction mixture overnight, a yellow colored solution was formed. Subsequently, all the volatilities were removed under vacuum and then the resulting residue was washed with n-hexane. The resulting white colored solids contain about 90 % of 3$^{Bu}$ and 10 % of 1·HOTf. **Total Yield:** 9.20 g; amount of compound 3$^{Bu}$ in the mixture is 8.28 g (17.63 mmol; **Yield:** 84 %). **M.P.:** 155 °C; $^1$H NMR (300 MHz, C$_6$D$_{6}$, 298 K): $\delta = 0.86$ (s, 9H, C(CH$_3$)$_3$), 1.04 (s, 3H, C(CH$_3$)$_2$), 1.22 (s, 3H, C(CH$_3$)$_2$), 1.37 (s, 3H, C(CH$_3$)$_3$), 1.45 (s, 3H, C(CH$_3$)$_2$), 1.65 (d, $J = 13.03$, 1H, CH$_2$), 2.01 (d, $J = 13.03$, 1H, CH$_2$), 2.20 (s, 6H, NC(CH$_3$)$_2$), 2.88-3.16 (m, 2H, NCHCH$_2$), 3.29 (d, $J = 9.9$, Hz, 1H, NCHCH$_2$), 3.68 (s, 6H, N(CH$_3$)) ppm. $^{13}$C$[^1H]$ NMR (75.4 MHz, C$_6$D$_{6}$, 298 K): $\delta = 8.87$ (2C, C(CH$_3$)$_2$), 26.88 (1C, CHC(CH$_3$)$_2$), 29.34 (1C, CHC(CH$_3$)$_2$), 30.21 (1C, NC(CH$_3$)$_2$), 31.06 (3C, C(CH$_3$)$_2$), 31.72 (1C, NCCH$_3$), 32.47 (2C, N(CH$_3$)), 36.32 (2C, N(CH$_3$)$_2$), 50.80 (1C, C(CH$_3$)$_2$), 65.58 (1C, NCHCH$_2$), 114.26 (2C, NCCH$_3$), 153.63 (NC(CH$_3$)N), 163.17 (1C, NCN) ppm.
37.42 (1C, NC(CH\(_3\))\(_2\)), 40.33 (1C, NCHC(CH\(_3\))\(_2\)), 54.25 (1C, C(CH\(_3\))\(_3\)), 56.65 (1C, C(CH\(_3\))\(_2\)C(CH\(_3\))\(_2\)), 63.05 (1C, NC(CH\(_3\))\(_2\)), 67.75 (NCHC(CH\(_3\))\(_2\)), 120.89 (1C, CF\(_3\)), 125.82 (2C, NC(CH\(_3\))\(_2\)), 145.90 (1C, NCN) ppm. \(^{19}\)F\(^{\{+\} H}\) NMR (169.2 MHz, CDCl\(_3\), 298 K): \(\delta = -78.42\) ppm. HRMS (ESI-TOF) \(m/z\): \([M]^{+}\) Calcd for [C\(_{20}\)H\(_{38}\)N\(_3\)]\(^{+}\) 320.3060; Found 320.3094.

**Synthesis of 3\(^{\text{Dip}}\)**

Dry THF (100 mL) was added to a Schlenk flask containing 1 (3.453 g, 24.6 mmol) and 2\(^{\text{Dip}}\) (9.748 g, 22.3 mmol) at room temperature. On stirring the reaction mixture overnight, a yellow colored solution was formed. Subsequently, all the volatiles were removed under vacuum and then the resulting residue was washed with n-hexane. The resulting white colored solids contain about 89% of 3\(^{\text{Dip}}\) and 11% of 1-HOTf. **Total Yield:** 11.03 g; amount of compound 3\(^{\text{Dip}}\) in the mixture is 9.81 g (17.1 mmol; **Yield:** 77 %). \(^{1}H\) NMR (300 MHz, CD\(_2\)\(_{6}\), 298 K): \(\delta = 0.92\) (s, 3H, C(CH\(_3\))\(_2\)), 0.95 (d, \(J = 6.84\) Hz, 3H, C(CH\(_3\))\(_2\)), 1.04 (s, 3H, C(CH\(_3\))\(_2\)), 1.19-1.39 (m, 3H, C(CH\(_3\))\(_2\)), 1.39 (m, 3H, C(CH\(_3\))\(_2\)), 2.07-2.24 (m, 1H, C(CH\(_3\))\(_2\)), 2.17 (s, 6H, C(CH\(_3\))\(_2\)), 2.61 (m, 1H, NCCH\(_2\)), 2.96-3.70 (m, 1H, NCCH\(_2\)), 3.12 (sep, 1H, CH(CH\(_3\))\(_2\)), 3.39 (s, 6H, N(C(C\(_3\))\(_2\))), 3.87 (sep, 1H, CH(CH\(_3\))\(_2\)), 4.01 (q, \(J = 5.60\) Hz, 1H, NCHCH\(_2\)), 7.08-7.31 (m, 3H, Ar-\(H\)) ppm. \(^{13}\)C\(^{\{1\} H}\) NMR (75.4 MHz, CD\(_2\)\(_{6}\), 298 K): \(\delta = 8.94\) (2C, C(CH\(_3\))\(_2\)), 25.10 (1C, C(CH\(_3\))\(_2\)), 25.19 (2C, CH(CH\(_3\))\(_2\)), 25.24 (1C, C(CH\(_3\))\(_2\)), 25.85 (1C, CH(CH\(_3\))\(_2\)), 27.22 (1C, NCCH\(_2\)), 27.47 (1C, CH(CH\(_3\))\(_2\)), 28.77 (1C, C(CH\(_3\))\(_2\)), 29.02 (1C, CH(CH\(_3\))\(_2\)), 29.39 (1C, C(CH\(_3\))\(_2\)), 30.88 (1C, CH(CH\(_3\))\(_2\)), 32.74 (2C, NCH\(_3\)), 40.46 (1C, NCHC(CH\(_3\))\(_2\)), 57.02 (1C, C(CH\(_3\))\(_2\)CH\(_3\)), 61.64 (1C, NC(NCH\(_3\))\(_2\)), 70.04 (1C, NCHCH\(_2\)), 120.83 (1C, CF\(_3\)), 125.22 (1C, ArCH), 125.33 (1C, ArCH), 126.61 (2C, N(CH\(_3\))\(_2\)), 127.86 (1C, ArCH), 136.72 (1C, ArCCH(CH\(_3\))\(_2\)), 144.00 (1C, NCN), 151.56 (1C, ArCCH(CH\(_3\))\(_2\)), 152.59 (1C, NCAr) ppm. \(^{19}\)F\(^{\{+\} H}\) NMR (169.2 MHz, CDCl\(_3\), 298 K): \(\delta = -78.50\) ppm. HRMS (ESI-TOF) \(m/z\): \([M]^{+}\) Calcd for [C\(_{20}\)H\(_{38}\)N\(_3\)]\(^{+}\) 424.3686; Found 424.375.

**Synthesis of 4\(^{\text{Pr}}\)**

Dry THF (50 mL) was added to a Schlenk flask containing 3\(^{\text{Pr}}\) (6.12 g, 13.4 mmol) and KHMDS (2.67 g, 13.4 mmol) at room temperature and stirred overnight. After removal of all the volatiles, the resulting solid was extracted with n-hexane (50 mL). Evaporation of n-hexane led to light yellow colored solid 4\(^{\text{Pr}}\) as the desired product. **Yield:** 3.004 g, 9.83 mmol (73 %). \(^{1}H\) NMR (300 MHz, CD\(_2\)\(_{6}\), 298 K): \(\delta = 1.10\) (s, 3H, C(CH\(_3\))\(_2\)), 1.14 (s, 6H, C(CH\(_3\))\(_2\)), 1.28 (s, 3H, C(CH\(_3\))\(_2\)), 1.37 (d, 3H, CH(CH\(_3\))\(_2\)), 1.43 (s, 3H, C(CH\(_3\))\(_2\)), 1.51 (d, 3H, CH(CH\(_3\))\(_2\)), 1.54 (s, 3H, C(CH\(_3\))\(_2\)), 1.60 (d
(J=12.64 Hz), 2H, CH₃), 1.77 (d, J = 12.58 Hz, 2H, CH₃), 2.59 (s, 3H, NCH₃), 2.86 (d, J = 10.66 Hz, 1H, NCH(CH₃)₂), 3.02 (s, 3H, NCH₃), 3.19 (sep, 1H, CH(CH₃)₂), 4.03 (d, J = 10.63 Hz, 1H, NCC) ppm. \(^{13}\text{C}[\text{H}]\text{NMR}\) (75.4 MHz, C₆D₆, 298 K): δ = 9.19 (2C, NCH₃), 20.10 (1C, CH(CH₃)₂), 26.20 (2C, C(CH₃)₂), 27.92 (1C, CH(CH₃)₂), 28.38 (1C, CH(CH₃)₂), 29.67 (1C, NCH₃), 31.32 (1C, C(CH₃)₂), 34.14 (1C, NCH₃), 38.41 (1C, CH(CH₃)₂), 45.50 (1C, CH(CH₃)₂), 55.71 (1C, CH₃), 57.79 (1C, NC(CH₃)₂), 64.05 (1C, NCCH), 65.00 (1C, NCH(CH₃)), 114.64 (1C, NCC(CH₃)), 115.61 (1C, NCC(CH₃)), 148.50 (1C, NCN) ppm. \(\text{HRMS (ESI-TOF) } m/z: [\text{M-H}]^+ \text{ Calcd for } [\text{C}_{19}\text{H}_{35}\text{N}_2]^+ 306.2904; \text{ Found } 306.2922.\)

### Synthesis of 4\(^{\text{tBu}}\)

\[\text{3}^{\text{tBu}} + \text{KHMDS} \rightarrow \text{4}^{\text{tBu}}\]

Dry THF (60 mL) was added to a Schlenk flask containing 3\(^{\text{tBu}}\) (5.136 g, 10.9 mmol) and KHMDS (2.183 g, 10.9 mmol) at room temperature and stirred for 10 h. After removal of all the volatiles, the resulting solid was extracted with n-hexane. Evaporation of n-hexane (50 mL) led to light yellow colored solid 4\(^{\text{tBu}}\) as the desired product. Crystals of compound, 3\(^{\text{tBu}}\) were obtained by keeping n-hexane solution of 3\(^{\text{tBu}}\) at −35 °C for 2 days. **Yield:** 2.44 g, 7.64 mmol (70 %). **M.P.:** 87 °C \(^{1}H\text{ NMR}\) (300 MHz, C₆D₆, 298 K): δ = 1.22 (s, 3H, C(CH₃)₂), 1.44 (s, 3H, NCH₃), 1.46 (s, 3H, HCC(CH₃)₂), 1.50 (s, 9H, C(CH₃)₃), 1.52 (s, 3H, NCH₃), 1.55 (s, 6H, NC(CH₃)₂), 1.61 (d, J = 12.36 Hz, 1H, CH₂), 2.10 (d, J = 12.36 Hz, 1H, CH₂), 2.58 (s, 3H, NCH₃), 2.92 (s, 3H, NCH₃), 2.977 (d, J = 10.84 Hz, 1H, NCH(CH₃)₂), 4.261 (d, J = 10.83 Hz, 1H, NCCCH) ppm. \(^{13}\text{C}[\text{H}]\text{NMR}\) (75.4 MHz, C₆D₆, 298 K): δ = 9.19 (1C, NC(CH₃)), 9.28 (1C, NC(CH₃)), 28.27 (1C, CHC(CH₃)₂), 29.59 (1C, NCH₃), 29.93 (1C, CHC(CH₃)₂), 32.80 (3C, C(CH₃)₃), 33.85 (1C, NC(CH₃)₃), 34.98 (1C, NCH₃), 35.12 (1C, NC(CH₃)₂), 38.92 (1C, CHC(CH₃)₂), 54.19 (1C, C(CH₃)₃), 58.77 (1C, CH₂), 59.57 (1C, NC(CH₃)₂), 68.71 (1C, NCCH), 70.37 (1C, HCCH), 115.11 (1C, NC(CH₃)), 116.04 (1C, NC(CH₃)), 148.26 (1C, NCN) ppm. **HRMS (ESI-TOF) m/z:** [M-H]^+ Calcd for [C₂₀H₃₇N₂]^+ 320.3060; Found 320.3084.

### Synthesis of 4\(^{\text{Dip}}\)

\[\text{3}^{\text{Dip}} + \text{nBuLi} \rightarrow \text{4}^{\text{Dip}}\]

n-BuLi (1.6 M in n-hexane, 4.31 mL, 6.901 mmol) was added dropwise to a Schlenk flask containing solution of 3\(^{\text{Dip}}\) (3.96 g, 6.901 mmol, 50 ml of THF) at −78 °C and the reaction mixture was stirred for 3 hrs at that temperature. After reaching room temperature, all volatiles were removed. The resulting residue was extracted with n-hexane (50 mL). Removal of the n-hexane gave a pale brown sticky solid compound. This sticky solid was redissolved in minimum quantity of n-hexane and kept at −35 °C to obtained crystals of 3\(^{\text{Dip}}\) after 2 days. **Yield:** 1.25 g, 3.08 mmol (43 %). **M.P.:** 129 °C. \(^{1}H\text{ NMR}\) (300 MHz, C₆D₆, 298 K): δ = 1.20 (s, 12H, CH(CH₃)₂), C(CH₃)₂), 1.41 (s, 12H, CH(CH₃)₂),
C(CH₃)ₛ, 1.53 (s, 3H, NC(CH₃)) 1.92 (q, J = 12.63 Hz, 2H, CH₂), 2.28 (s, 3H, NCH₃), 2.50 (d, J = 10.25 Hz, 1H, NCHC(CH₃)₂), 3.30 (s, 3H, NCH₃), 3.52 (sep, 1H, CH(CH₃)) 4.37 (sep, 1H, CH(CH₃)), 4.95 (NCCH), 7.07-7.30 (m, 3H, Ar-H) ppm. ¹³C{¹H} NMR (75.4 MHz, CD₃CN, 298 K): δ = 9.03 ( 2C, NC(CH₃)), 24.50 (1C, C(CH₃)₂), 25.14 (1C, C(CH₃)₂), 26.03 (1C, C(CH₃)₂), 26.25 (1C, CH(CH₃)), 26.62 (1C, CH(CH₃)), 27.78 (1C, CH(CH₃)), 28.79 (1C, CH(CH₃)), 29.34 (1C, CH(CH₃)), 29.43 (1C, CH(CH₃)), 30.25 (1C, NCH₃), 30.57 (1C, C(CH₃)₃), 33.37 (1C, NCH₃), 40.70 (HCC(CH₃)₂), 56.54 (1C, CH₂), 59.02 (1C, NC(CH₃)₂CH₃), 61.94 (1C, NCHCH), 69.56 (NCCH), 114.25 (1C, NC(CH₃)), 115.47 (1C, NC(CH₃)), 123.91 (1C, ArCH), 124.31 (1C, ArCH), 126.33 (1C, ArCH), 139.87 (1C, NCCCH(CH₃)), 148.91 (1C, NCN), 152.37 (1C, NCCCH(CH₃)), 153.54 (1C, NCCCH(CH₃)) ppm. HRMS (ESI-TOF) m/z: [M-H]⁺ Calcd for [C₂₈H₄₅N₃⁺]⁺ 424.3686; Found 424.3695.

**Synthesis of 6^{Pr}**

AgOTf solution (1.688 g, 6.57 mmol, in 20 mL THF) was added to a solution of 4^{Pr} (1.004 g, 3.28 mmol, 25 mL THF) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C followed by stirred for another 1 h at room temperature. During the time, a color change from green color solution to faint yellow colored solution with precipitation of dark black color metallic silver was observed. After evaporation of all the volatiles, the sample was extracted in 40 mL of dry acetonitrile. Removal of all the volatiles gave brown color sticky solid which was redissolved in minimum quantity of acetonitrile. Diffusion of diethyl ether over the concentrated acetonitrile solution at room temperature gave pale yellow colored crystals of compound, 6^{Pr} after 3 days. **Yield:** 1.20 g, 3.94 mmol (61%). **M.P:** 165 °C. ¹H NMR (300 MHz, 298 K): δ = 1.32 (s, 3H, C(CH₃)), 1.38 (d, J = 6.94 Hz, 3H, CH(CH₃)), 1.56 (d, J = 6.94 Hz, 3H, CH(CH₃)), 1.61 (s, 3H, C(CH₃)), 1.81 (s, 3H, C(CH₃)), 1.86 (s, 3H, C(CH₃)), 2.08 (d, J = 4.70 Hz, 2H, CH₂), 2.30 (s, 3H, NC(CH₃)), 2.33 (s, 3H, NC(CH₃)), 2.86 (sep, 1H, CH(CH₃)), 3.70 (s, 3H, N(CH₃)), 3.93 (s, 3H, N(CH₃)), 4.39 (d, J = 6.56 Hz, 1H, NCHC(CH₃)), 4.649 (d, J = 6.58 Hz, 1H, NCCH) ppm. ¹³C{¹H} NMR (75.4 MHz, CD₃CN, 298 K): δ = 9.31 (1C, NC(CH₃)), 9.52 (1C, NC(CH₃)), 19.08 (1C, CH(CH₃)), 22.24 (1C, CH(CH₃)), 25.24 (1C, CH(CH₃)), 27.29 (1C, C(CH₃)), 28.45 (1C, C(CH₃)), 28.73 (1C, C(CH₃)), 35.54 (1C, N(CH₃)), 35.90 (1C, N(CH₃)), 40.15 (1C, C(CH₃)), 45.90 (1C, NCCCH(CH₃)), 51.55 (1C, CH₂), 62.83 (1C, CH(CH₃)), 65.71 (1C, NCCCH(CH₃)), 82.19 (1C, C(CH₃)), 132.28 (2C, NC(CH₃)), 133.20 (1C, NCN) ppm. ¹⁹F{¹H} NMR(169.2 MHz, CD₃CN, 298 K): δ = -79.33 ppm. HRMS (ESI-TOF) m/z: [M⁺] Calcd for [C₂₀H₃₁F₃N₅O₅S₂]⁺ 545.2346; Found 454.234. Anal. Calcd for C₂₁H₃₆F₆N₅O₆S₂ (603.64): C, 41.79; H, 5.84; N, 6.96; S, 10.62. Found: C, 41.78; H, 6.05; N, 7.00; S, 10.89.
Synthesis of 6

AgOTf solution (1.941 g, 7.55 mmol, 20 mL THF) was added to a solution of 4Bu (1.207 g, 3.77 mmol, 25 mL THF) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C followed by stirred for another 1 h at room temperature. During the time, a color change from green color solution to faint yellow colored solution with precipitation of dark black color metallic silver was observed. After evaporation of all the volatiles, the sample was dried and extracted with 40 mL of acetonitrile. Removal of all the volatiles gave pale brown sticky solid which was washed with THF and pentane. The residue obtained was dissolved in minimum amount of acetonitrile. Diffusion of diethyl ether over the concentrated acetonitrile solution gave off white colored crystals of compound, 6 after two weeks. **Yield**: 1.32 g (2.289 mmol, 61 %). **M.P.:** 154 °C. **1H NMR** (300 MHz, 298 K): 1.38 (s, 3H, C(CH3)2), 1.53 (s, 3H, C(CH3)2), 1.53 (s, 6H, C(CH3)2), 1.68 (s, 6H, C(CH3)2), 1.81 (d, 1H, CH2), 2.07 (d, 1H, CH2), 2.25 (s, 6H, NCH3), 3.72 (s, 6H, NCH3), 4.20 (brs, 1H, CH2), 4.47 (brs, 1H, CH), 9.60 (brs, 1H, NH) **13C{1H} NMR** (75.4 MHz, CD3CN, 298 K): δ = 8.81 (2C, NC(CH3)), 26.06 (1C, C(CH3)), 26.53 (2C, C(CH3)), 28.25 (1C, C(CH3)), 34.24 (2C, N(CH3)), 40.99 (2C, C(CH3)), 48.72 (1C, CH2), 58.63 (2C, NCH3, HNCHMe2), 119.48 (2C, N(CH3)), 123.72 (1C, NCN) ppm. **19F{1H} NMR** (169.2 MHz, CD3CN, 298 K): δ = −79.47 ppm. **HRMS** (ESI-TOF) m/z: [M]+ Calcd for [C16H29N3−H]+ 262.2278; Found: 262.2278.

Synthesis of 9

AgOTf solution (0.363 g, 1.416 mmol, in 20 mL THF) was added to a solution of 4Dip (0.300 g, 0.708 mmol, in 25 mL THF) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C followed by stirred for another 1 h at room temperature. During the time, a color change from green color solution to faint yellow colored solution with precipitation of dark black color metallic silver was observed. After evaporation of all the volatiles, the sample was dried and extracted with 20 mL of acetonitrile. Removal of all the volatiles gave pale yellow colored crystals of compound, 9 after 4 days. **Yield**: 0.032 g (0.044 mmol, 6 %). **1H NMR** (300 MHz, CD3CN, 298 K): δ = 1.17-1.21 (m, 6H, CH(CH3)2), 1.42 (d, 6H, CH(CH3)2), 1.60 (s, 3H, CH2=C-CH3), 2.15 (s, 6H, NCCCH3), 2.35-2.55 (m, 4H; 3H, N=C(CH3)2, 1H, CH2CHCH2), 2.66-2.92 (m, 3H, CH(CH3)2, 1H, CH2CHCH2), 2.95-3.14 (m, 5H; 3H, N=C(CH3)2, 2H, CH2CHCH2), 3.50 (s, 6H, NCH3), 4.37 (s, 1H, C=CH2), 4.59 (s, 1H, C=CH2), 5.20 (br s, 1H, CH2CHCH2), 7.53-7.63 (m, 2H, Ar-CH), 7.67-7.74 (m, 1H, Ar-CH) ppm. **13C{1H} NMR** (75.4 MHz, CD3CN, 298 K):
K): δ = 8.74 (2C, NCCH$_3$), 22.48 (1C, CH$_2$=C(CH$_3$)$_2$), 23.53 (1C, CH(CH$_3$)$_2$), 24.82 (1C, CH(CH$_3$)$_2$), 25.25 (1C, CH(CH$_3$)$_2$), 25.62 (1C, CH(CH$_3$)$_2$), 27.03 (1C, N=C(CH$_3$)$_2$), 28.10 (1C, CH$_2$CHCH$_2$), 29.47 (1C, CH(CH$_3$)$_2$), 29.80 (1C, CH(CH$_3$)$_2$), 30.38 (1C, N=C(CH$_3$)$_2$), 33.71 (2C, NCH$_3$), 42.35 (1C, CH$_2$CHCH$_2$), 62.69(1C, CH$_2$CHCH$_2$), 112.04 (1C, C=CH$_2$), 127.87 (1C, ArCH), 128.19 (1C, ArCH), 128.54 (2C, NCCH$_3$), 133.39(1C, ArCH), 134.33 (1C, C-N=C(CH$_3$)$_2$), 138.65 (1C, CH$_2$CH(CH$_3$)$_2$), 144.36 (2C, C(CH$_3$)$_2$), 201.50(1C, N=C(CH$_3$)$_2$) ppm; $^{13}$C($^1$H) resonance for NCN could not obtained.

$^{19}$F($^1$H) NMR (169.2 MHz, CD$_3$CN, 298 K): δ = −79.32 ppm. HRMS (ESI-TOF) m/z: [M]$^+$ Calcd for [C$_{28}$H$_{45}$N$_3$−H]$^+$ 423.3530; Found: 422.3497. Anal. Calcd for C$_{36}$H$_{45}$F$_6$N$_3$O$_6$S$_2$ (721.8154): C, 49.92; H, 6.28; N, 5.82; S, 8.88. Found: C, 50.01; H, 5.882; N, 5.891; S, 9.669. Anal. Calcd for C$_{36}$H$_{45}$F$_6$N$_3$O$_6$S$_2$ (721.82): C 49.92; H 6.28; N 5.82; S 8.88. Found C, 50.01; H, 5.88; N, 5.89; S, 9.67.

**1:1 Reaction of AgOTf and 4$^{i}$pr**

AgOTf solution (0.433 g, 1.685 mmol, in 10 mL THF) was added to a solution of 4$^{i}$pr (0.515 g, 1.685 mmol, 15 mL THF) at −78 °C. The reaction mixture was allowed to reach room temperature in 4 hrs followed by stirred for another 1 h at room temperature. During the time, the formation of orange solution with precipitation of dark black color metallic silver was observed. Then the reaction mixture was very slowly filtered using D4 frit. On evaporation of all the volatiles, blackish-orange color solid. $^1$H NMR spectrum of this solid in THF-$d_8$ indicated formation of compound 3$^{i}$pr along with some unidentified product.

**1:1 Reaction of AgOTf and 4$^{i}$bu**

AgOTf solution (0.187 g, 0.729 mmol, in 10 mL THF) was added to a solution of 4$^{i}$bu (0.233 g, 0.729 mmol, 10 mL THF) at −78 °C. The reaction mixture was allowed to reach room temperature in 3 hrs followed by stirred for another 1 h at room temperature. During the time, the formation of dark brown color solution with precipitation of dark black color metallic silver was observed. The reaction mixture was very slowly filtered using D4 frit. On evaporation of all the volatiles orange-red color oily compound. $^1$H NMR spectrum of this solid in THF-$d_8$ indicated formation of compound 3$^{i}$bu along with some unidentified product.

**1:1 Reaction of AgOTf and 4$^{i}$io**

AgOTf solution (0.198 g, 0.771 mmol, in 10 mL THF) was added to a solution of 4$^{i}$io (0.327 g, 0.771 mmol, 10 mL THF) at −78 °C. The reaction mixture was allowed to reach RT in 3 hrs followed by stirred for another 2 hrs at room temperature. During the time, the formation of yellow color solution with precipitation of dark black color metallic silver was observed. The reaction mixture was very slowly filtered using D4 frit. On evaporation of all the volatiles yellow color solid compound has been formed. $^1$H NMR spectrum of this solid in THF-$d_8$ indicated formation of compound 3$^{i}$io along with some unidentified product.
Synthesis of compound 10

THF was added to a Schlenk flask containing $6^\text{iPr}$ (0.500 g, 0.823 mmol) and KHMDS (0.152 g, 0.823 mmol) at 0 °C. An instant light-violet coloration was observed which changed to light orange and finally to a yellow within 30 minutes and during that time the reaction mixture reached to room temperature. Then after stirring the reaction mixture for another 3 hrs at room temperature all the volatiles were evaporated under vacuum. The resulting residue was extracted with warm toluene. Then after removal of all volatiles of the filtrate a pale yellow colored solids was obtained as compound 10. Yield: 0.148 g, 0.325 mmol (39 %). M.P.: 106 °C.

$^1\text{H NMR}$ (300 MHz, CDCl$_3$, 298 K): $\delta = 0.89$ (d, 6H, CH(C$_2$H$_3$)$_2$), 1.15 (s, 6H, C(C$_2$H$_3$)$_2$), 1.36 (s, 6H, C(C$_2$H$_3$)$_2$), 1.72 (s, 2H, C$_2$H), 2.29 (s, 6H, NCC$_3$H$_3$), 3.52 (sep, 1H, C$_2$H(CH$_3$)$_2$), 3.75 (s, 6H, NC$_3$H$_3$), 5.54 (s, 1H, C$_2$H) ppm.

$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (75.4 MHz, CDCl$_3$, 298 K): $\delta = 8.99$ (2C, C$_2$C$_3$H$_3$), 23.05 (2C, CH(C$_2$H$_3$)$_2$), 29.04 (2C, C(C$_2$H$_3$)$_2$), 30.72 (2C, C(C$_2$H$_3$)$_2$), 31.49 (C(CH$_3$)$_2$), 32.83 (2C, NCC$_3$H$_3$), 49.26 (C$_2$H(CH$_3$)$_2$), 50.36 (C$_2$H), 57.01 (NC$_3$H$_3$)$_2$, 124.39 (NCCCH$_3$), 127.22 (2C, C(CH$_3$)$_3$), 134.10 (CH), 142.23 (NC) ppm.

$^{19}\text{F}\{^1\text{H}\} \text{NMR}$ (169.2 MHz, CDCl$_3$, 298 K): $\delta = -78.34$ ppm.

HRMS (ESI-TOF) m/z: [M]$^+$ Calcd for [C$_{19}$H$_{34}$N$_3$]$^+$ 304.2747; Found 304.2781. Anal. Calcd for C$_{20}$H$_{34}$F$_3$N$_3$O$_3$S (453.57): C, 52.96; H, 7.56; N, 9.26; S, 7.07. Found: C, 52.98; H, 9.02; N, 9.27; S, 7.54.

Deprotonation of $6^\text{th}$ with KHMDS

THF was added into the solid mixture of $6^\text{th}$ (0.20 g, 3.561 mmol) and KHMDS (0.071 g, 3.561 mmol) at 0 °C. The reaction mixture was allowed to reach room temperature in 30 min and stirred for another 3hrs at room temperature. Then the resulting black turbid solution obtained was evaporated and the residue was extracted with DCM. After removal of DCM, a brown color sticky compound was obtained. We have failed to get any crystal of the resulting compound but $^1\text{H NMR}$ spectrum of it indicates the formation of compound 11. $^1\text{H NMR}$ (300 MHz, CDCl$_3$, 298 K): $\delta = 1.36$ (s, 3H, C(CH$_3$)$_2$), 1.38 (s, 3H, C(CH$_3$)$_2$), 1.40 (s, 3H, C(CH$_3$)$_2$), 1.42 (s, 3H, C(CH$_3$)$_2$), 1.54 (m, 2H, CH$_2$), 2.19 (s, 6H, NCCCH$_3$), 2.35 (s, 1H, NCHCM$_2$), 3.22 (s, 1H, CH), 3.77 (s, 6H, NCH$_3$) ppm. $^{19}\text{F}\{^1\text{H}\} \text{NMR}$ (169.2 MHz, CDCl$_3$, 298 K): $\delta = -78.47$ ppm.
Molecular structures of 1·HOTf, 3\textsuperscript{iPr}, 3\textsuperscript{iBu}, 3\textsuperscript{Dip}, 4\textsuperscript{Dip}, 6\textsuperscript{H}, and 10

**Figure S1.** Solid state molecular structure of 1·HOTf with thermal ellipsoids at 50% probability level. All H atoms and triflate anion are omitted for clarity.

**Figure S2.** Solid state molecular structure of 3\textsuperscript{iPr} with thermal ellipsoids at 50% probability level. All H atoms except at C4 and C5 and triflate anion are omitted for clarity.
**Figure S3.** Solid state molecular structure of 3^Bu with thermal ellipsoids at 50% probability level. All H atoms except at C4 and C5 and triflate anion are omitted for clarity.

**Figure S4.** Solid state molecular structure of 3^Dip with thermal ellipsoids at 50% probability level. All H atoms except at C4 and C5 and triflate anion are omitted for clarity.
Figure S5. Solid state molecular structure of $4^{\text{Dip}}$ with thermal ellipsoids at 50% probability level. All H atoms except at C4 and C5 are omitted for clarity.

Figure S6. Solid state molecular structure of $6^\text{H}$ with thermal ellipsoids at 50% probability level. Two triflate anions and all H atoms except at C8, C9 and N3 were omitted for clarity.

Figure S7. Solid state molecular structure of 10 with thermal ellipsoids at 50% probability level. Triflate anion and all H atoms except at C9 were omitted for clarity.
Cyclic Voltammetry

Cyclic voltammograms were recorded with a PAR VersaStat 4 potentiostat (Ametek) by working in anhydrous and degassed THF distilled from sodium-benzophenone with 0.1 M NBu₄PF₆ (dried, > 99.0 %, electrochemical grade, Fluka) as electrolyte. Concentrations of the complexes were about 1x10⁻⁴m. A three-electrode setup was used with a glassy carbon, gold or platinum working electrode, a coiled platinum wire as counter electrode, and a coiled silver wire as a pseudoreference electrode. The ferrocene/ferrocenium couple was used as internal reference.

Table S1. Redox potentials \(E_{1/2}\) of \(4^R\) vs. FcH/FcH⁺ measured in THF at 100 mVs⁻¹ with 0.1 M Bu₄NPF₆ at room temperature.

|        | \(E_{1/2}(1^{st} \text{Red})\) | \(E_{1/2}(1^{st} \text{Ox})\) | \(E_{1/2}(2^{nd} \text{Ox})\) | \(E_{1/2}(3^{rd} \text{Ox})\) |
|--------|---------------------------------|-------------------------------|-----------------------------|-------------------------------|
| \(4^{iPr}\) | −3.24                           | −0.87                         | 0.10                        | 0.45                          |
| \(4^{tBu}\) | −3.25                           | −0.91                         | −0.03                       | -                             |
| \(4^{Dip}\) | −3.13                           | −0.86                         | 0.18                        | -                             |

All values given were measured with GCWE at 100 mVs⁻¹, given in Volts.

Figure S8. Cyclic voltammogram of \(4^{iPr}\) in THF/0.1 M Bu₄NPF₆ measured at 100 mV s⁻¹.
Figure S9. Cyclic voltammogram of 4\(^{\text{Pr}}\) in THF/0.1 M Bu\(_4\)NPF\(_6\) (only first oxidation) measured at different scan rates.

Figure S10. Cyclic voltammogram of 4\(^{\text{Bu}}\) in THF/0.1 M Bu\(_4\)NPF\(_6\) measured at 100 mV s\(^{-1}\).
Figure S11. Cyclic voltammogram of $4^{\text{Bu}}$ in THF/0.1 M Bu$_4$NPF$_6$ (only first oxidation) measured at different scan rates.

Figure S12. Cyclic voltammogram of $4^{\text{Dip}}$ in THF/0.1 M Bu$_4$NPF$_6$ measured at 100 mV s$^{-1}$. 
Figure S13. Cyclic voltammogram of 4Dip in THF/0.1 M Bu₄NPF₆ (only first oxidation) measured at different scan rates.
EPR Spectroscopy

EPR spectra at X-band frequency (ca. 9.5 GHz) were obtained with a Magnettech MS-5000 bench top EPR spectrometer equipped with a rectangular TE 102 cavity. The measurements were carried out in synthetic quartz glass tubes. Compounds 4′Pr, 4′Bu, and 4′Dip were dissolved in dry and degassed THF (2 mmol/l) in Schlenk tubes under strictly anaerobic conditions, at room temperature. The oxidized species were generated by the addition of one equivalent of AgOTf to the solutions, immediate transfer to an EPR tube inside a large Schlenk tube, and transfer of the closed EPR tube to the spectrometer. Time between mixing and acquisition was approximately one minute. In the case of 4′Pr and 4′Bu, the generated radical signals were very weak and disappeared fast. In the case of 4′Dip we obtained EPR signal which was seen to decay within a time-span of about 2 minutes. Simulation of the obtained EPR spectrum was carried out using the EasySpin program (Figure S14). 52

![EPR Spectra](image)

Figure S14. EPR spectra obtained after the in situ oxidation of 4′Dip with AgOTf together with simulation. The hyperfine splittings included in the simulation arose from three 14N (A(14N, MHz) = 5.77, 6.04, 5.93) and two 1H nuclei (A(1H, MHz) = 6.00, 6.07).

The following calculations were performed using the ORCA program package, version 4.2. 33 Geometry optimization and single point calculations were performed using the TPSSh 54 and the ωB97x-V functional. 55 Relativistic effects were taken into account using the ZORA approximation as implemented in ORCA. 56 Ahlrichs basis sets (def2-SVP/def2-TZVP/def2-QZVPP) were used, as well as their contractions for use with the ZORA approximation. 57 Solvation was taken into account using the SMD method 58 together with the CPCM model 59 using THF, MeCN or DCM as pseudo solvent. Dispersion corrections were included using the D3 dispersion correction model. 510 The resolution-of-the-identity (RI) approximation 511 with matching basis sets, 512 as well as the RIJCOSX approximation (combination of RI and chain-of-spheres algorithm for exchange integrals) were used to reduce the time of calculations.

We have calculated the hyperfine coupling constants of 8′Dip at the different level of theory and different combinations, which leads to the following results (Table S2). The first calculations based on Structure 1 (8′Dip without solvent) show that there isn’t a great difference between pseudo-solvents of different
polarities. There are slight differences when changing the basis set, but from a chemical point of view all these results are clearly compatible. **Structure 2** is the result of a geometry optimization of **Structure 1** using the TPSSh/def2-TZVP level with THF pseudo-solvent. Calculations coded adX are all based on this structure. These series of calculations were performed with the TPSSh functional, with and without the ZORA relativistic Hamiltonian, and with various basis sets, from def2-TZVP to ZORA-def2-TZVP and ZORA-def2-QZVPP. While ZORA-def2-TZVP is quite similar to def2-TZVP, ZORA-def2-QZVPP is considerably larger than def2-TZVP and contains more and steeper s-type primitives for describing the regions near the nuclei. Also one of the calculations was performed with the ωB97x-V functional. All calculations with **Structure 1** or **Structure 2** seem to predict a much larger hyperfine interaction in the H atoms bridging the two moieties. They also somewhat overestimate the N hyperfine interactions.

**Table S2.** Calculated isotropic hyperfine splittings for the three N atoms and the two H atoms.

|               | $^{14}$N | $^{15}$N | $^{14}$N | $^{1H}$ | $^{1H}$ | Method/Basis set (Annotations) | SMD solvent |
|---------------|---------|---------|---------|--------|--------|-------------------------------|------------|
| **Experiment** |         |         |         |        |        |                               |            |
| 8Dip          | 14.7    | 14.5    | 13.2    | 9.94   | −58.3  | M06-2X/EPR-II                 |            |
| 8Dip          | 15.5    | 8.21    | 7.49    | 12.9   | −40.9  | TPSSh/ZORA-def2-TZVP          | DCM        |
| 8Dip          | 15.5    | 8.16    | 7.44    | 12.6   | −40.8  | TPSSh/ZORA-def2-TZVP          | MeCN       |
| 8Dip          | 15.5    | 8.23    | 7.52    | 13.0   | −40.4  | TPSSh/ZORA-def2-TZVP          | THF        |
| 8Dip          | 15.0    | 8.19    | 7.47    | 13.5   | −41.7  | TPSSh/ZORA-def2-TZVP/ZORA-def2-QZVPP | THF        |
| **Structure 1** |         |         |         |        |        |                               |            |
| ad            | 9.11    | 5.96    | 5.34    | 19.4   | −35.5  | TPSSh/def2-TZVP (optimized, Structure 2) | THF        |
| ad2           | 9.41    | 7.85    | 7.07    | 19.4   | −35.5  | TPSSh/ZORA-def2-TZVP (based on ad optimized structure) | THF        |
| ad8           | 9.41    | 7.90    | 7.11    | 19.4   | −35.5  | TPSSh/ZORA-def2-TZVP with orbital contribution | THF        |
| ad3           | 9.09    | 7.87    | 7.11    | 20.3   | −36.1  | TPSSh/ZORA-def2-TZVP/ZORA-def2-QZVPP | THF        |
| ad7           | 9.08    | 7.87    | 7.11    |        |        | TPSSh/ZORA-def2-QZVPP         | THF        |
| ad6           | 8.51    | 9.85    | 8.90    | 15.0   | −34.5  | wB97x-V/ZORA-def2-TZVP*       | THF        |
| **Structure 2** |         |         |         |        |        |                               |            |
| ai2 (with CF$_3$SO$_3$) | 9.24 | 8.56 | 7.42 | 22.5 | 36.7 | TPSSh/ZORA-def2-TZVP* | THF |

We also optimized the structures of hypothetical variations were the 34H atom had dissociated giving a neutral radical (8$^{Dip}$ – H$^+$) (Figure S17), where an additional proton had bound to 5C, giving a dicationic radical (8$^{Dip}$ + H$^+$) (Figure S18), which leads to the following results (Table S3).
Table S3. Calculated isotropic hyperfine splittings for the three N atoms and the two H atoms.

| Method/Basis set (Annotations) | SMD solvent |
|--------------------------------|-------------|
| **14N** | **14N** | **14N** | **1H** | **1H** |
| Experiment                  | 5.77  | 6.04  | 5.93  | 6.00  | 6.07  |
| Calculated                  | 0N    | 1N    | 2N    | 34H   | 35H   |
| ah (8Dip – H+)               | 30.0  | 19.2  | 25.9  | 28.8  | -     |
|                            |        |       |       |       | TPSSh/def2-SVP |
| af2 (8Dip + H+)              | 42.4  | 0.0   | -0.1  | 146   | 5.8   | THF |
|                            |        |       |       |       | TPSSh/ZORA-def2-TZVP* |
| ag2 (8Dip + H+ + 3 THF)      | 52.2  | -0.2  | -0.26 | 114   | 10.9  | THF |
|                            |        |       |       |       | PBE/def2-SVP optimization |
| ag3 (8Dip + H+ + 3 THF)      | 39.2  | 0.05  | -0.02 | 148   | 5.5   | THF |

*These single point calculations were performed on intermediate structures obtained during geometry optimizations of the corresponding molecules. This was done to qualitatively observe the effect of small conformational changes on the hyperfine couplings.

Though we have performed all our experiments strictly maintaining an atmosphere without oxygen, it is possible that there could be an adventitious source of oxygen and the possibility of formation of hydroxyl-substituted radical cation 8Dip-OH. Subsequently, we have consider the calculation of EPR-fine coupling constants of 8Dip-OH. In this case the H atom of O-H moiety was renumbered to 76H. The calculated hyperfine splittings for alcohol radical 8Dip-OH seem to be quite more similar to experiment (Table S4).

![Spin Density Diagram](image_url)

Table S4. Calculated isotropic hyperfine splittings for the three N atoms and the two H atoms.

| Method/Basis set (Annotations) | SMD solvent |
|--------------------------------|-------------|
| **14N** | **14N** | **14N** | **1H** | **1H** |
| Experiment                  | 5.77  | 6.04  | 5.93  | 6.00  | 6.07  |
| Calculated                  | 0N    | 1N    | 2N    | 34H   | 35H   |
| aj (8Dip-OH)                 | 10.1  | 17.3  | 14.3  | 5.01  | 3.52  |
|                            |        |       |       |       | TPSSh/def2-SVP optimization |
|                            |        |       |       |       | (76H) |
| aj2 (8Dip-OH)                | 7.33  | 9.24  | 6.90  | 6.09  | 5.05  |
|                            |        |       |       |       | TPSSh/ZORA-def2-TZVP (based on aj 5th structure) |
| aj3 (8Dip-OH)                | 8.14  | 9.34  | 7.20  | 5.17  | 4.47  |
|                            |        |       |       |       | TPSSh/ZORA-def2-TZVP (based on aj final structure) |

Figures S15 and S19 show the spin density of 8Dip and 8Dip-OH. In the first case a considerable negative spin density can be observed in 34H, which is in accordance to the large negative hyperfine value of −34 to −36 MHz. In the case of 8Dip-OH the O atom shares a large part of the spin density of 5C, and the O-bound H
atom (76H) doesn’t show an appreciable spin density, which is compatible with the calculated hyperfine value of 4.5-5.5 MHz. The calculated hyperfine splitting in 35H also decreases considerably from 15-20 MHz in the case of 8\textsuperscript{Dip} to 5-6 MHz in the case of 8\textsuperscript{Dip-OH}. The hyperfine values in the N atoms also decrease slightly in the latter radical (basically because the spin density is now shared by one more atom).

All these effects point to 8\textsuperscript{Dip-OH} as a closer candidate to produce the EPR signal shown in Figure S14, while the calculations on 8\textsuperscript{Dip} itself don’t seem to be in agreement with experiment. It would also be possible for other species to give the EPR signal shown in Figure S14. From experiments we find that compound 8\textsuperscript{Dip} has a limited stability and it leads to the hydrogen abstracted product 3\textsuperscript{Dip}.

\textbf{Figure S15.} Spin density plot (isovalue = 0.003) of the radical species 8\textsuperscript{Dip} (optimized at TPSSh/def2-TZVP level, spin density calculated at TPSSh/ZORA-def2-TZVP level).
Figure S16. Spin density plot (isovalue = 0.003) of radical species $8^{\text{Dip}}$ with a triflate counterion.

Figure S17. Spin density plot (isovalue = 0.003) of neutral radical species $8^{\text{Dip}} - \text{H}^+$, where the H atom in the bridging C has dissociated as a proton.
Figure S18. Spin density plot (isovalue = 0.003) of hypothetical dicationic radical species $8^\text{Dip} + H^+$, solvated with 3 THF molecules, where an extra proton bound to the C atom bridging the NHC and the CAAC.

Figure S19. Spin density plot (isovalue = 0.003) of $8^\text{Dip}\cdot\text{OH}$. 
Cartesian coordinates of the computed structures

Structure 1

N       -1.50672000  0.60184900  0.09153000
N        2.50321700 -0.89564000 -1.20263900
N        2.86088600  1.06389300 -0.32101600
C       -1.27578700 -0.72011500  0.60658800
C       -0.38783500  1.42571800 -0.35943500
C        0.54218900  0.54852800 -1.13380400
C       -1.73949200 -1.83340600 -0.14029400
C        1.89771900  2.06641100 -2.52867700
C        0.03504500  0.15907300  2.66648700
C        0.02333200 -3.34663800  1.46104900
C        3.81628300 -0.87262600 -0.80182300
C        4.04198700  0.36153000 -0.24425800
C        2.87732600  1.60417600  1.95737000
C        0.26993400  3.81391700 -1.32406500
C        1.78778500 -2.05712700 -1.72559300
C        1.76137200 -2.25631300 -2.64402400
C        3.98642700  0.90230600 -0.13322100
C        2.69526500  2.43515300  0.14381900
C        3.88746600 -2.42150600 -1.33587100
C        0.54949000  0.11142800  4.08476600
C        4.73782400 -2.02885700 -0.97390500
C        1.56746900  0.08256100  2.74418200
C        5.27569000  0.93722800  0.35661000
H        0.30998600 -2.43293500  3.09066900
H       -0.51916400 -4.35627400  1.79690700
H       -1.82733800 -3.97332800 -0.25857400
H        0.15843300  1.90274900  0.46949000
H        0.05048300 -0.14957200 -1.79998800
H       -2.70762100 -0.65203700 -1.60801600
H       -1.98527100  3.50876100  0.57799100
H       -3.14410100  3.25741400 -0.72511600
H       -0.71559600  1.93408200 -3.19915800
H       -2.10759500  1.11998400 -2.46923200
H       -2.23323800  2.80576700 -2.98284500
H       -0.23587400  1.11734100  2.22951900
H       -3.06857500  0.63044800  2.41555600
| Atom | X         | Y        | Z         |
|------|-----------|----------|-----------|
| H    | -2.014197 | 2.061615 | 2.442925  |
| H    | -3.742080 | 2.242783 | 2.152348  |
| H    | 0.102282  | 4.187567 | -0.365657 |
| H    | 0.574425  | 3.641580 | -1.999443 |
| H    | -0.876682 | 4.606108 | -1.769213 |
| H    | 0.910515  | -2.252998| -1.104574 |
| H    | 1.485032  | -1.878189| -2.757704 |
| H    | 2.451482  | -2.916518| -1.694296 |
| H    | -0.866900 | -1.669629| -2.865734 |
| H    | -1.456421 | -3.294366| -2.485466 |
| H    | -2.394073 | -2.228121| -3.533950 |
| H    | -3.986206 | 0.893909 | -1.223831 |
| H    | -4.172687 | -0.109415| 0.231773  |
| H    | -4.817448 | 1.530896 | 0.193490  |
| H    | 1.970932  | 2.940122 | -0.487583 |
| H    | 2.359400  | 2.444610 | 1.182779  |
| H    | 3.651131  | 2.948240 | 0.064819  |
| H    | -3.760693 | -3.507031 | -1.334119 |
| H    | -4.426633 | -2.151765| -0.427307 |
| H    | -4.510803 | -2.164863| -2.195322 |
| H    | -1.638520 | 0.144946 | 4.074434  |
| H    | -0.248170 | -0.803970| 4.599050  |
| H    | -0.185313 | 0.957573 | 4.672655  |
| H    | 4.411509  | -2.887251| -0.382033 |
| H    | 4.796547  | -2.332194| -2.021165 |
| H    | 5.739855  | -1.758234| -0.647817 |
| H    | 1.885909  | -0.808963| 3.289131  |
| H    | 2.019143  | 0.033295 | 1.750920  |
| H    | 1.968516  | 0.949593 | 3.276871  |
| H    | 5.664451  | 1.764685 | -0.242239 |
| H    | 5.081833  | 1.304042 | 1.367069  |
| H    | 6.051010  | 0.176526 | 0.418942  |

**Structure 2**

| Atom | X         | Y        | Z         |
|------|-----------|----------|-----------|
| N    | -1.540978 | 0.509222 | 0.142946  |
| N    | 2.739351  | -0.702087| -1.491076 |
| N    | 2.920136  | 1.039888 | -0.174265 |
| C    | -1.473551 | -0.777943| 0.770498  |
| C    | -0.344090 | 1.243505 | -0.263813 |
| C    | 0.620198  | 0.324323 | -0.916386 |
| C    | -2.039310 | -1.887502| 0.091193  |
| C    | 1.998411  | 0.266262 | -0.846642 |
| C    | -0.952544 | 2.340733 | -1.200783 |
| C    | -0.845887 | -0.990668| 2.021963  |
| C    | -2.658115 | 1.465348 | 0.397239  |
| C    | -2.012261 | -3.149079| 0.687468  |
| C    | -0.831016 | -2.275347| 2.571460  |
| Atom | X    | Y    | Z    |
|------|------|------|------|
| H    | -4.097819 | -3.397623 | -1.208460 |
| H    | -4.715442  | -1.844611  | -0.639648  |
| H    | -4.485733  | -2.127214  | -2.370421  |
| H    | -1.780117  | 0.453450   | 4.201878   |
| H    | -0.530607  | -0.627428  | 4.827085   |
| H    | -0.221237  | 1.107971   | 4.724082   |
| H    | 4.966085   | -2.470783  | -1.435599  |
| H    | 5.123981   | -1.429008  | -2.857722  |
| H    | 6.100691   | -1.115892  | -1.418183  |
| H    | 1.541500   | -1.127101  | 3.476885   |
| H    | 2.904616   | 1.413248   | -0.199170  |
| N    | 1.262253    | -0.349051   | 0.814675   |
| C    | 0.555662    | 1.006390    | -0.983309  |
| C    | -1.670451   | -1.538248   | 0.140792   |
| C    | 1.914947    | 0.655238    | -0.765810  |
| C    | -1.023222   | 3.102511    | -0.658824  |
| C    | -0.529914   | -0.461406   | 2.031338   |
| C    | -2.765110   | 1.744769    | 0.491968   |
| C    | -1.287561   | -2.787150   | 0.654660   |
| C    | -0.153522   | -1.734746   | 2.489265   |
| C    | -2.555097   | -1.544199   | -1.100634  |
| C    | -2.255827   | 3.180336    | 0.260376   |
| C    | -1.397161   | 2.974691    | -2.142659  |
| C    | -0.145248   | 0.719309    | 2.918008   |
| C    | -0.515079   | -2.893617   | 1.808117   |
| C    | 3.819725    | -0.551193   | -0.693872  |
| C    | 4.081801    | 0.682346    | -0.138453  |
| C    | -3.266449   | 1.561339    | 1.928631   |
| C    | -0.175428   | 4.366762    | -0.486841  |
| C    | 1.780090    | -1.734884   | -1.566065  |
| C    | -1.954284   | -2.322103   | -2.281889  |
| C    | -3.934595   | 1.410907    | -0.448897  |
| C    | 2.805803    | 2.817830    | 0.168598   |
| C    | -3.944077   | -2.113029   | -0.755815  |
| C    | -0.768063   | 0.588399    | 4.318936   |
| C    | 4.718386    | -1.722464   | -0.879350  |
| C    | 1.379336    | 0.872555    | 3.031673   |
| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 5.338148 | 1.241445 | 0.427964 |
| H    | 0.424616 | -1.816641 | 3.412806 |
| H    | -0.211744 | -3.873806 | 2.183343 |
| H    | -1.598090 | -3.694658 | 0.131475 |
| H    | 0.203769 | 2.090519 | -0.823555 |
| O    | -0.088761 | 0.295020 | -1.926520 |
| H    | -2.697788 | -0.500850 | -1.418123 |
| H    | -1.942398 | 3.612172 | 1.224916 |
| H    | -3.035973 | 3.858210 | 2.451532 |
| H    | -0.494393 | 2.926462 | 2.770998 |
| H    | -2.008031 | 2.089171 | -2.363347 |
| H    | -1.977628 | 3.858210 | -2.451532 |
| H    | -0.550437 | 1.636315 | 2.472089 |
| H    | -3.505955 | 0.507154 | 2.137847 |
| H    | -2.535559 | 2.668017 | 0.088761 |
| H    | -4.187507 | 2.068782 | -1.405623 |
| H    | 0.219500 | 4.462163 | 0.536896 |
| H    | 0.661742 | 4.403202 | -1.201532 |
| H    | -0.799821 | 5.252100 | -0.686351 |
| H    | 0.848913 | -1.866241 | -2.591672 |
| H    | 1.557942 | -2.591672 | 1.224916 |
| H    | 2.421180 | -2.068782 | -2.363347 |
| H    | -0.983364 | -2.591672 | 1.224916 |
| H    | -1.813352 | -2.068782 | -2.363347 |
| H    | -2.634223 | -2.068782 | -2.363347 |
| H    | -3.653936 | -2.068782 | -2.363347 |
| H    | -4.340726 | 1.468229 | -1.509148 |
| H    | -4.748324 | 2.132728 | -0.278692 |
| H    | 2.017555 | 3.282419 | -0.426760 |
| H    | 2.587601 | 2.935138 | 1.239242 |
| H    | 3.755557 | 3.314195 | -0.620210 |
| H    | -3.879233 | -3.192340 | -0.541977 |
| H    | -4.379257 | -2.591672 | 1.224916 |
| H    | -4.638922 | -1.600107 | 3.566053 |
| H    | -1.856499 | 0.437008 | 4.267712 |
| H    | -0.336427 | -0.261535 | 4.870985 |
| H    | -0.575822 | 1.500922 | 4.906082 |
| H    | 4.392328 | -2.584840 | -0.275385 |
| H    | 4.753943 | -2.037197 | -1.933968 |
| H    | 5.737344 | -1.460174 | -0.568012 |
| H    | 1.824633 | 0.018185 | 3.566053 |
| H    | 1.854848 | 0.918539 | 2.042161 |
| H    | 1.639222 | 1.787966 | 3.586465 |
| H    | 5.719480 | 2.079530 | -0.178543 |
| H    | 5.184959 | 1.608933 | 1.454827 |
| H    | 6.113669 | 0.465874 | 0.455700 |
| H    | -1.034772 | 0.328528 | -1.626740 |
### \(8^{\text{Dip} + H^* (THF)_3}\)

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| N       | -1.160499994843 | 0.814467287481 | 0.320705225870 |
| N       | 2.854461457693   | -0.512175842344 | -0.320792010939 |
| N       | 3.179072011661   | 1.613034915338  | 0.055399037021  |
| C       | -0.883278321877  | -0.534745252014 | 0.714784052378  |
| C       | -0.15098198266   | 1.731579085950  | -0.227361005033 |
| C       | 0.969424144597   | 1.056904023160  | -1.033935084668 |
| C       | -1.353057012209  | -1.622153168516 | -0.095068809492 |
| C       | 2.264657958807   | 0.710327850764  | -0.389823183071 |
| C       | -1.024231032275  | 2.749678012264  | -1.054520079654 |
| C       | -0.122943221083  | -0.790332042331 | 1.904832246450  |
| C       | -2.453477926441  | 1.537041887318  | 0.586246898596  |
| C       | -1.083222124462  | -2.936279139693 | 0.32666936757  |
| C       | 0.105356015212   | -2.13002978876  | 2.264697117924  |
| C       | -0.2928909095701 | -1.442560993750 | -1.450191200504 |
| C       | -2.232092144253  | 2.905813437114  | -0.099006946579 |
| C       | -1.439388046965  | 2.189259196838  | -2.423902209994 |
| C       | 0.3810900197931 | 0.283225188855  | 2.866572208214  |
| C       | -0.368193063018  | -3.197431287138 | 1.497976964443  |
| C       | 4.149693155195   | -0.388724081925 | 0.174590920585  |
| C       | 4.351033456540   | 0.962789849426  | 0.426297254136  |
| C       | -2.608129448284  | 1.703523166563  | 2.11456248583  |
| C       | -0.295208936836  | 4.07732462153   | -1.270679989857 |
| C       | 2.259737139569   | -1.79446307311  | -0.665767951335 |
| C       | -1.103248837451  | -1.838452252336 | -2.614970122582 |
| C       | -3.702953254753  | 0.807632963310  | 0.073501132354  |
| C       | 2.957470042629   | 3.051811233404  | 0.130896225958  |
| C       | -3.353725375162  | -2.217028302156 | -1.551230187719 |
| C       | -0.313971974554  | 0.169092768968  | 4.236734345819  |
| C       | 5.04704579935    | -1.556293884814 | 0.353995766605 |
| C       | 1.904179241725   | 0.209508152183  | 3.066006413108  |
| C       | 5.531438435604   | 1.670243209373  | 0.983745268486  |
| H       | 0.659671300249   | -2.340810269179 | 3.189897390644  |
| H       | -0.173243106132  | -4.234380565416 | 1.808758000185  |
| H       | -1.42860080096   | -3.775056101477 | -0.294479201410 |
| H       | 0.26750274433    | 3.30314038445   | 0.619236866653  |
| H       | 1.247924309796   | 1.769879347701  | -1.848184880299 |
| H       | -2.252613355443  | -0.367842218502 | -1.567451057932 |
| H       | -1.971739301105  | 3.661587469199  | 0.671133808639  |
| H       | -3.132523993307  | 3.254253281781  | -0.623194054121 |
| H       | -0.569539185313  | 2.056642086466  | -3.098319034287 |
| H       | -1.96831276296   | 1.21783975724   | -2.361459294612 |
| H       | -2.12796245221   | 2.902267330368  | -2.919258153479 |
| H       | 0.148834805522   | 1.277342860599  | 2.439353127311  |
| H       | -2.763139232124  | 0.72788068595   | 2.611651122876  |
| H       | -1.735477005566  | 2.217751158279  | 2.556874398300  |
| H       | -3.502544305366  | 2.331445419403  | 2.294074392902  |
C 3.222506351082  1.229361301078  -3.723189521932
H 1.593796147274  4.027440510422  -3.914701414223
H 3.350877343208  4.086881593999  -4.287212563602
H 2.454067959073  3.161520606666  -6.384843661421
H 1.255315328432  2.159825299894  -5.494528340486
H 4.330660132453  1.825483176317  -5.507193687646
H 3.11837396289  0.548275785094  -5.818469485234
H 4.203831162831  0.987482847396  -3.262402082238
H -0.243890914760  5.742887627937  1.706562231504
O 0.702099144542  3.970500509252  2.328286231227
C 0.567011834772  3.780718497380  3.758865064528
C 0.424204887293  5.175522302762  4.370468549364
C 1.164486287059  6.050755542923  3.351877488208
C 0.845051086587  5.230851488386  5.392762337311
H -0.644810944742  5.461885429179  4.422384489433
H 2.262793138182  5.977012576566  3.494613525936
H 0.87740072392  7.119080798649  3.393996292988
H 1.478608018775  5.545705601414  1.21354138738
H 0.572031080979  0.161484787659  -1.541113906249

8\text{Dip} + \text{CF}_3\text{SO}_3^-

N -1.160499994843  0.814467287481  0.320705225870
N 2.854461457693 -0.512175842344 -0.320792010939
N 3.179072011661  1.613034915338  0.055399037021
C -0.883278321877 -0.534745252014  0.714784052378
C -0.159098198266  1.731579085950 -0.227361005303
C 0.969424144597  1.056904023160 -1.033935084668
C -1.353057012209 -1.622153168516 -0.095068809492
C 2.264657958807  0.710327850764 -0.389823183071
C -1.024231032275  2.749678012264 -1.054520079654
C -0.122943210183 -0.790332042331  1.904832246450
C -2.453477926441  1.537041887318  0.586246898596
C -1.083222124462 -2.936279139693  0.326666936757
C 0.105356015121 -2.130020978876  2.264697117924
C -2.029809095701 -1.442560993750 -1.450191200504
C -2.223092144253  2.905813347114 -0.099006946579
C -1.439388046965  2.189259196838 -2.423902209994
C 0.381090170931  0.283225188855  2.866572208214
C -0.368193063018 -3.197431287138  1.497976964443
C 4.149693155195 -0.388724081925  0.174590920585
C 4.351033456540  0.962789849426  0.426297254136
C -2.608129448828  1.703523166563  2.114546248583
C -0.295208936836  4.07732462153  -1.270679989857
C 2.259737139569 -1.797446307311 -0.665767951335

S30
|  |  |  |  |
|---|---|---|---|
| H | 2.458177020412 | 0.224298127116 | 2.111943225696 |
| H | 2.253229317761 | 1.06759115805 | 3.674527440469 |
| H | 5.960546697286 | 2.393394083235 | 0.259374111888 |
| H | 5.275548444723 | 2.289263234243 | 1.907270166036 |
| H | 6.322921456452 | 0.941850305683 | 1.236478205900 |
| H | 3.929485039037 | -0.246789248772 | 0.934572001800 |
| O | 3.115453264432 | -3.633146308774 | 1.983445231030 |
| C | 3.3993764838079 | -3.54204023470 | 3.931092168246 |
| H | 3.912277253254 | -4.92051914951 | 3.800918251329 |
| C | 3.089198135223 | -5.832981642111 | 2.881475427078 |
| C | 3.054599997506 | -5.02152373176 | 1.586398249333 |
| H | 4.128390066682 | -2.720906116059 | 3.553215143667 |
| C | 2.464475288030 | -3.284015268619 | 3.944571353229 |
| C | 3.765623033884 | -5.126833233259 | 4.878775576841 |
| C | 4.994821501660 | -5.011510164562 | 3.573327054193 |
| O | 2.603797020590 | -5.963073518650 | 3.28649464031 |
| H | 3.532148068207 | -6.837600307184 | 2.739951205250 |
| H | 2.134535389987 | -5.181605195240 | 0.98517113387 |
| H | 2.515419483737 | 0.402571063000 | -3.482546167949 |
| O | 2.710155310682 | 2.452815396525 | -3.143847328081 |
| C | 2.471170438584 | 3.410086456421 | -4.195893504096 |
| C | 2.283014059220 | 2.579654949692 | -5.45888458525 |
| C | 3.316884055086 | 1.46631150098 | -5.235543173876 |
| H | 3.2224062351082 | 1.229361301078 | 3.723189521932 |
| H | 1.593796147274 | 4.027440510422 | -3.91470141232 |
| H | 3.350877343208 | 4.089688159399 | -4.287212563602 |
| H | 2.454067959073 | 3.16152060666 | -6.384843661421 |
| H | 1.255315328432 | 2.159825999894 | -5.49452834086 |
| H | 4.330660132453 | 1.825483176317 | -5.50719368764 |
| H | 3.111837362989 | 0.548275785094 | -5.818469485234 |
| H | 4.203831628319 | 0.987482847396 | -3.262402082238 |
| H | -0.243890914760 | 5.742887627937 | 1.706562231504 |
| O | 0.702009144542 | 3.970500509252 | 2.328286231227 |
| C | 0.567011834772 | 3.780718497380 | 3.758865064528 |
| C | 0.424204887293 | 5.175523207262 | 4.370468549364 |
| C | 1.164486287059 | 6.050755542923 | 3.351877488208 |
| C | 0.757841088420 | 5.386261321227 | 2.041728284057 |
| H | -0.312069053167 | 3.133765443134 | 3.959593107796 |
| H | 1.476843212649 | 3.25814322093 | 4.128702281259 |
| H | 0.845051086587 | 5.230851488386 | 5.392762263731 |
| H | -0.644810944742 | 5.468188542917 | 4.422328448943 |
| H | 2.262793138182 | 5.977012576566 | 3.494613525936 |
| H | 0.877470072392 | 7.119080798649 | 3.393962929888 |
| H | 1.478608018775 | 5.545705610141 | 1.213534138738 |
| H | 0.572031080979 | 0.161484787659 | -1.541113906249 |
\[ \text{Dip} - H^+ \]

N  -1.499966670899  0.588217554671  0.083553912554
N  2.421495511866  -0.928882817196  -0.889223099093
N  2.879334905105  1.137473376030  -0.342931199505
C  -1.257778119349  -0.740451265663  0.543554994855
C  -0.421887620120  1.44361702362  -0.457861618684
C  0.582150008334  0.677193417318  -1.269261265652
C  -1.802375064208  -1.829208552256  -0.201767876562
C  1.857239103030  0.326703449988  -0.807749382305
C  -1.250180721585  2.52671645234  -1.211783620398
C  -0.455766605955  -1.02842052855  1.686085717854
C  -2.65854223151  1.413564726391  0.519116001965
C  -1.573704345484  -3.148256432920  0.218668739541
C  -0.234135532175  -2.366747892039  2.055020158198
C  -2.552856355449  -1.605520069225  -1.505025605399
C  -2.379753481287  2.766321695100  -0.19280968078
C  -1.787413106670  2.000647195863  -2.545396543769
C  0.192618931104  0.046458058221  2.550937558744
C  -0.794602502731  -3.424096953266  1.342151727461
C  3.762827014591  -0.900659677798  -0.493755711484
C  4.052570079623  0.392855368708  -0.158250985491
C  -2.715422252228  1.623456532080  2.041733575830
C  -0.443184887683  3.801684499985  -1.462416782487
C  1.68356141868  -2.085022391507  -1.352569639963
C  -1.635556699056  -1.86743391025  -2.708165644612
C  -4.009847483602  0.817704264713  0.091867816313
C  2.763087363754  2.563059951164  -0.115200299576
C  -3.854337107084  -2.409631887120  -1.602900112665
C  -0.363650605513  0.037130250853  3.985440770523
C  4.613981613568  -2.122465915292  -0.458263793393
C  1.72102782078  -0.108520495161  2.603507614191
C  5.313875165336  1.010966675352  0.337866973233
H  0.386741783950  -2.581939937054  2.928810861178
H  -0.615809914788  -4.45817046970  1.652931704849
H  -1.991120947027  -3.975067308911  -0.36169532983
H  0.093925786634  1.988672443895  0.373100123648
H  -2.800662123497  -0.541180047362  -1.533710716356
H  -2.041126080348  3.50636337572  0.550602577458
H  -3.288831310763  3.173645828150  -0.662998766791
H  -0.955805768094  1.778379395826  -3.229691519769
H  -2.362978562494  1.075632135180  -2.408435417360
H  -2.442998100202  2.749911908608  -3.02043668424
H  -0.03434245106  1.019315504810  2.095672083643
H  -2.891607583864  0.669448908279  2.562561466195
H  -1.785437687999  2.068453322664  2.423823891761
H  -3.544065139855  2.303473110021  2.300241953739
H  -0.014187242046  4.199902550935  -0.527684439981
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | 0.380641428624 | 3.61212096671 | -2.171121121438 |
| H    | -1.080203697434 | 4.589018224024 | -1.899293348185 |
| H    | 0.758380849214  | -2.203775587132 | -0.773559769424 |
| H    | 1.421738927357  | -1.965419866671 | -2.415571901740 |
| H    | 2.301755400671  | -2.981723823483 | -1.231070543592 |
| H    | -0.767672143352 | -1.190893819316 | -2.663694117783 |
| H    | -1.751621211156 | -2.91025296215055 | -2.725230023361 |
| H    | -2.17521374295  | -1.678920657902 | -3.651990310611 |
| H    | -4.127139091665 | 0.794212499098  | -1.000550350383 |
| H    | -4.133154778632 | -0.204756140487 | 0.481695761979  |
| H    | -4.828738163707  | 1.430096752827  | 0.502394000896 |
| H    | 1.983877030965   | 2.963125359889  | -0.773776732096 |
| H    | 2.502964466058   | 2.792403783349  | 0.930094633096 |
| H    | 3.713180663445   | 3.056183825012  | -0.360427916066 |
| H    | -3.667271891208  | -3.49391245385  | -1.678728566561 |
| H    | -4.503283042850  | -2.242442039540 | -0.728153715574 |
| H    | -4.417936806954  | -2.113006871966 | -2.502934832132 |
| H    | -1.460218880195  | 0.105714268210  | 4.008133478492 |
| H    | -0.07549013874   | -0.888355248404 | 4.511068298537 |
| H    | 0.042753817478   | 0.885703012032  | 4.560580767840 |
| H    | 4.200951380242   | -2.888336739288 | 0.220101751531 |
| H    | 4.718977277074   | -2.582997233197 | -1.454966495999 |
| H    | 5.620424899796   | -1.867000835742 | -0.100221937543 |
| H    | 2.0101990903562  | -1.020676019517 | 3.151104464874 |
| H    | 2.157408018221   | -0.170115139413 | 1.600153153566 |
| H    | 2.177758058508   | 0.747625850805  | 3.126901485037 |
| H    | 5.7135181891794  | 1.760827241680  | -0.366149909660 |
| H    | 5.167385144205   | 1.51362735696   | 1.308787101912 |
| H    | 6.083285126774   | 0.238604963220  | 0.471946729521 |
Computational Details

All electronic structure calculations are performed at the DFT level. Starting from the molecular structure obtained from X-ray diffraction, geometry optimizations are carried out using B3LYP-D3\textsuperscript{13,14} exchange-correlation functional paired with 6-31g(d,p) basis set for all atoms. The restricted and unrestricted DFT methods are employed for closed and open shell molecules respectively. To refine the electronic energies further, we have performed single-point calculations on optimized geometries using M062X\textsuperscript{15,16} functional with a larger basis set, 6-311++G(d,p). The stationary points are characterized by vibrational analysis to recognize the structures as minima (all positive frequencies). All thermochemical data are estimated within the ideal gas-rigid rotor-harmonic oscillator approximation at 298.15 K. SMD\textsuperscript{17} model is used to take into account solvent effects at the B3LYP/6-31G(d,p) level. All DFT calculations are performed using the Gaussian 16\textsuperscript{18} suite of programs. NPA charges are calculated with NBO 3.0 Package as implemented within the Gaussian 16 package.

![Figure S20](image.png)

**Figure S20.** Numbering scheme for NPA charge analysis for 4\textsuperscript{Pr}.

**Table S5.** NPA charge analysis for 4\textsuperscript{Pr}, 6\textsuperscript{Pr}, and 8\textsuperscript{Pr}.

|       | 4\textsuperscript{Pr} | 6\textsuperscript{Pr} | 8\textsuperscript{Pr} |
|-------|------------------------|------------------------|------------------------|
| N1    | -0.20880               | -0.16056               | N 1                   | -0.09955               |
| N2    | -0.21715               | -0.15817               | N 2                   | -0.10601               |
| C5    | 0.19620                | 0.20037                | C5                    | 0.13912                |
| C10   | -0.24036               | -0.05998               | C10                   | 0.13303                |
| C12   | -0.03249               | -0.00412               | C12                   | -0.05689               |
| N3    | -0.26872               | -0.14286               | N3                    | -0.16674               |
Figure S21. Numbering scheme for NPA charge analysis for $4^tBu$.

Figure S22. Numbering scheme for NPA charge analysis for $6^H$.

Table S6. NPA charge analysis for $4^tBu$, $6^tBu$, $6^H$, and $8^tBu$.

|       | $4^tBu$ | $6^tBu$ | $6^H$  | $8^tBu$ |
|-------|---------|---------|--------|---------|
| N1    | -0.21013| -0.16066| N1     | -0.15889|
| N2    | -0.21845| -0.16028| N2     | -0.16024|
| C5    | 0.19450 | 0.20872 | C5     | 0.19751 |
| C10   | -0.23733| -0.06093| C10    | -0.05956|
| C12   | -0.02897| -0.00508| C7     | -0.00419|
| N3    | -0.27208| -0.14546| N3     | -0.22740|
|       |         |         | N1     | -0.10317|
|       |         |         | N2     | -0.10972|
|       |         |         | C5     | 0.14353 |
|       |         |         | C10    | 0.11914 |
|       |         |         | C12    | -0.05356|
|       |         |         | N3     | -0.15021|
Figure S23. Numbering scheme for NPA charge analysis for $4^\text{Dip}$.

Table S7. NPA charge analysis for $4^\text{Dip}$, $6^\text{Dip}$, and $8^\text{Dip}$.

|       | $4^\text{Dip}$ |       | $6^\text{Dip}$ |       | $8^\text{Dip}$ |
|-------|----------------|-------|----------------|-------|----------------|
| N2    | -0.20749       | N2    | -0.15199       | N1    | -0.09470       |
| N3    | -0.21212       | N3    | -0.15518       | N2    | -0.10479       |
| C8    | 0.20020        | C8    | 0.17857        | C8    | 0.13360        |
| C6    | -0.23895       | C6    | -0.05371       | C6    | 0.20544        |
| C5    | -0.02146       | N5    | -0.04893       | C5    | -0.05115       |
| N1    | -0.27626       | N1    | -0.18699       | N1    | -0.24772       |
Figure S24. Frontier-orbitals of 4^irr.

Figure S25. Frontier-orbitals of 4^bu.

Figure S26. Frontier-orbitals of 4^Dip.
Figure S27. Frontier-orbitals of $6^{\text{Ir}}$.

Figure S28. Frontier-orbitals of $6^{\text{Bu}}$.

Figure S29. Frontier-orbitals of $6^{\text{H}}$. 
Figure S30. Frontier-orbitals of 6^{Dip}.

Figure S31. Frontier-orbitals of 8^{iPr}.
Figure S32. Frontier-orbitals of 8$^{\text{Bu}}$. 
Figure S33. Frontier-orbitals of $8^{Dip}$. 
Figure S34. Spin densities of $8^{\text{pr}}$ at B3LYP/6-31g(d,p), iso-value 0.013.

Figure S35. Spin densities of $8^{\text{tBu}}$ at B3LYP/6-31g(d,p), iso-value 0.013.
Figure S36. Spin densities of $8^\text{Dip}$ at B3LYP/6-31g(d,p), iso-value 0.013.
Table S8. Mulliken spin densities for $^{8}\text{Pr}$, $^{8}\text{Bu}$, and $^{8}\text{Dip}$.

|     | $^{8}\text{Pr}$ |     | $^{8}\text{Bu}$ |     | $^{8}\text{Dip}$ |
|-----|-----------------|-----|-----------------|-----|-----------------|
| N1  | 0.136150        | N1  | 0.139815        | N1  | 0.033157        |
| N2  | 0.130804        | N2  | 0.134900        | N2  | 0.140336        |
| N3  | 0.165410        | N3  | 0.138896        | N3  | 0.130881        |
| C10 | 0.532545        | C10 | 0.549403        | C6  | 0.650273        |
| C4  | 0.076318        | C4  | 0.084007        | C19 | 0.084835        |
| C8  | 0.092992        | C8  | 0.100154        | C20 | 0.107506        |

Natural bond orbital (NBO) analysis of $^{6}\text{Pr}$

Figure S37. Numbering scheme for NBO analysis for $^{6}\text{Pr}$ (carbon atoms are coloured as grey and nitrogens are coloured as blue).

Natural bond orbital (NBO) analysis revealed that the Wiberg bond index values for N2-C56 bond and N2-C5 bond are 0.8367 and 0.8670, respectively. The computed bond order for N2-C56 bond is 0.9315 and the N2-C5 bond has bond order of value 0.9548. These findings indicate that in the $^{6}\text{Pr}$ molecule the N2-C56 and N2-C5 possess quite similar characteristics. These conclusions are also verified even by the M06-2X/6-311g(d,p) level of theory.
Cartesian coordinates of the computed structures

B3LYP/6-31g(d,p) optimized structures are given in standard XYZ format

4\(^{1}Pr\)

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| N    | 2.43257000| -0.63445000| -1.09950000|
| N    | 2.23371800| 0.71899600 | 0.64357400 |
| N    | -1.96792100| -0.35086000| 0.57057100 |
| C    | 3.70466500| -0.51233500| -0.51207800|
| C    | 1.49580800| 0.11221900 | -0.38122900|
| C    | -2.96402600| -0.50948400| -0.53629300|
| C    | -1.41263700| -1.54023600| 1.23181900 |
| C    | 3.59147400| 0.32830000 | 0.54040700 |
| C    | -1.88603000| 1.73389500 | -0.53201200|
| C    | 0.16458300| 0.17647500 | -0.67601300|
| H    | -0.12622500| -0.29566800| -1.60618800|
| C    | -0.96995100| 0.69144100 | 0.17472100 |
| H    | -0.58334900| 1.13367800 | 1.09234500 |
| C    | -4.40568700| -0.56530800| 0.01444000 |
| H    | -4.58914400| -1.45243900| 0.62145600 |
| H    | -5.12165600| -0.57900600| -0.81586400|
| H    | -4.61528100| 0.31245400 | 0.62996700 |
| C    | 2.03576800| -1.56802400| -2.12313400|
| H    | 1.63178000| -1.04794100| -3.00119500|
| H    | 1.25556500| -2.24309300| -1.74395000|
| H    | 2.89450100| -2.15907800| -2.44145400|
| C    | 4.88979100| -1.24596900| -1.03885400|
| H    | 4.76538600| -2.33506200| -0.97683300|
| H    | 5.78334500| -0.98458100| -0.46890600|
| H    | 5.08357300| -0.99944800| -2.09033300|
| C    | -2.78350800| 0.79878800 | -1.36409400|

S46
H  -2.28432000  0.57234400  -2.31313500
H  -3.74517900  1.25831200  -1.61582900
C   4.62171900  0.80575500  1.50588500
H   4.83222200  1.87905900  1.40760900
H   5.56388100  0.27692300  1.34756500
H   4.30997800  0.62927900  2.54268500
C   1.79116800  1.91196100  1.34032500
H  1.21948300  2.55103200  0.65846800
H   2.65663600  2.47305900  1.69562600
H   1.16180900  1.67811800  2.20552300
C  -2.72269500  -1.73260300  -1.44995000
H  -1.69854000  -1.74438600  -1.83140100
H  -3.40417100  -1.69409600  -2.30689500
H  -2.89810200  -2.68080300  -0.93508000
C  -0.44702100  -1.12699000  2.35701200
H   0.46358900  -0.66060400  1.97985000
H  -0.14521100  -2.01094900  2.92784000
H  -0.94580900  -0.43214100  3.04237900
C  -2.69199000  2.51002000  0.52742800
H  -3.13943300  1.83039500  1.25496500
H  -3.48773700  3.10316400  0.06222400
H  -2.03804800  3.20173000  1.07233800
C  -2.50086200  -2.42837000  1.85580000
H  -3.10813700  -1.84702800  2.55749100
H  -2.03194000  -3.25159300  2.40497400
H  -3.16781100  -2.87475300  1.11734400
C  -1.13146400  2.73227200  -1.41499200
H  -0.47242200  3.37169500  -0.81533400
H  -1.83786800  3.38754800  -1.93841600
H  -0.51037400  2.22337500  -2.15604500
|   |    |    |    |
|---|----|----|----|
| H | -0.83417500 | -2.15613500 | 0.51855400 |
| 4tBu |    |    |    |
| N | -2.53669500 | -0.41769700 | 1.17181000 |
| N | -2.28351800 | 0.62139500  | -0.77133800 |
| N | 1.91631400  | -0.33161700 | -0.38012100 |
| C | -3.79492800 | -0.38159500 | 0.54667100  |
| C | -1.58011500 | 0.21566200  | 0.37371600  |
| C | 2.96821100  | -0.23877300 | 0.67271700  |
| C | 1.52602200  | -1.57874400 | -1.07982700 |
| C | -3.64783100 | 0.25928000  | -0.63416600 |
| C | 1.75921500  | 1.91111200  | 0.34589700  |
| C | -0.26469000 | 0.35644600  | 0.70362500  |
| H | 0.01053400  | 0.01540400  | 1.69504700  |
| C | 0.89064800  | 0.73327000  | -0.19068700 |
| H | 0.51745500  | 1.01378700  | -1.17380000 |
| C | 4.40510800  | -0.23771200 | 0.09229400  |
| H | 4.70347000  | -1.20956300 | -0.30079700 |
| H | 5.11832600  | 0.02272400  | 0.88279200  |
| H | 4.50390100  | 0.49719100  | -0.70889100 |
| C | -2.21071200 | -1.00654000 | 2.44572200  |
| H | -1.88027600 | -0.24414200 | 3.16470400  |
| H | -1.40068000 | -1.73894800 | 2.33718000  |
| H | -3.08519700 | -1.51238700 | 2.85480700  |
| C | -4.99531800 | -1.02155700 | 1.15488700  |
| H | -4.85060400 | -2.09779600 | 1.31615900  |
| H | -5.86267600 | -0.89889500 | 0.50359300  |
| H | -5.24696300 | -0.57713800 | 2.12614100  |
| C | 2.68503100  | 1.15375000  | 1.31002800  |
|  |  |  |  |
|---|---|---|---|
| C | 0.96272900 | 3.00179200 | 1.06930400 |
| H | 0.27420400 | 3.51062100 | 0.38423900 |
| H | 1.64206300 | 3.75995400 | 1.4770300 |
| H | 0.36603900 | 2.58958700 | 1.88642400 |

### $\text{4Dip}$

|  |  |  |  |
|---|---|---|---|
| N | -1.49253100 | 0.63947200 | 0.07821400 |
| N | 2.69580900 | -0.82578100 | -1.37551300 |
| N | 2.93233300 | 0.91952600 | -0.04585700 |
| C | -1.42474700 | -0.70163700 | 0.58072200 |
| C | -0.28954500 | 1.39085200 | -0.36962300 |
| C | 0.67343200 | 0.51206000 | 1.09556900 |
| C | -2.01784200 | -1.74452800 | -0.18819700 |
| C | 1.99402200 | 0.25807500 | 0.83941100 |
| C | -0.95110900 | 2.55815600 | -1.1756200 |
| C | -0.77013200 | -1.04386900 | 1.79653800 |
| C | -2.57982900 | 1.57872200 | 0.45598700 |
| C | -1.99800300 | -3.05993200 | 0.29038500 |
| C | -0.77396300 | 2.37676200 | 2.22975500 |
| C | -2.63315100 | -1.50864700 | -1.56377600 |
| C | -2.16257900 | 2.88970200 | -0.2786200 |
| C | -1.39402700 | 2.10809800 | -2.57620500 |
| C | 0.00519700 | -0.04842700 | 2.65728400 |
| C | -1.39155000 | -3.38203100 | 1.49775900 |
| C | 4.00314600 | -0.86329700 | -0.85793600 |
| C | 4.15340100 | 0.20963700 | -0.04916500 |
| C | -2.67426800 | 1.83251700 | 1.97399600 |
| C | -0.01122200 | 3.75848900 | -1.32308500 |
| C | 2.01233300 | -1.91613000 | -2.03151500 |
|   |   |   |   |
|---|---|---|---|
| H | -1.75099800 | -3.25915400 | -2.54381900 |
| H | -2.23671200 | -1.97078700 | -3.65728000 |
| H | -4.00813300 | 0.99118800  | -1.09886700 |
| H | -4.19352300 | 0.11671200  | 0.43336900  |
| H | -4.73373000 | 1.79556000  | 0.29849300  |
| H | 2.20170900  | 2.87166100  | -0.09340200 |
| H | 2.16641700  | 2.12747000  | 1.51928900  |
| H | 3.70378800  | 2.65014800  | 0.81357700  |
| H | -4.16291900 | -3.07854200 | -1.57625600 |
| H | -4.71693200 | -1.55629400 | -0.87357100 |
| H | -4.52236300 | -1.70669400 | -2.62701500 |
| H | -1.60585300 | 0.31029300  | 4.10783700  |
| H | -0.42468600 | -0.89336700 | 4.63062300  |
| H | -0.00076000 | 0.82052100  | 4.65454400  |
| H | 4.63930100  | -2.92748000 | -0.88158500 |
| H | 5.11081000  | -1.99949700 | -2.31053000 |
| H | 5.94316500  | -1.74318000 | -0.77340900 |
| H | 1.65748900  | -1.36231600 | 3.23378700  |
| H | 1.91879100  | -0.52292500 | 1.70177000  |
| H | 2.07157000  | 0.35362500  | 3.23685300  |
| H | 5.72955800  | 1.62984000  | 0.38027700  |
| H | 5.09304000  | 0.78594200  | 1.79770600  |
| H | 6.14333700  | -0.06195000 | 0.65879600  |

### $^{69}$Pr

|   |   |   |   |
|---|---|---|---|
| N  | 2.05349300 | 1.18458300 | 0.22423800 |
| N  | -1.18119100 | -0.44012300 | 0.26775800 |
| N  | 2.13803000  | -0.76745700 | -0.73542700 |
| C  | 1.29650200  | 0.22355000  | -0.36106600 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | -1.14921700 | 1.04241900 | 0.14580800 |
| H       | -0.81708600 | 1.54896400 | 1.0496800  |
| C       | 3.43429200  | -0.45281900| -0.36208300|
| C       | 3.38231400  | 0.78123700 | 0.24731800 |
| C       | 1.60314600  | 2.50709700 | 0.68994900 |
| H       | 0.81319300  | 2.87895800 | 0.04021400 |
| H       | 2.44389000  | 3.19710000 | 0.63163600 |
| H       | 1.26164000  | 2.45505500 | 1.72635900 |
| C       | -2.44731200 | 0.97508800 | -0.52128100|
| C       | -2.39522200 | 1.56329000 | -0.56046500|
| C       | -0.65045800 | 1.03894000 | 1.57928800 |
| H       | 0.30664300  | -0.52256600| 1.70454300 |
| C       | -1.52121100 | 0.68318100 | 2.78652500 |
| H       | -1.83215800 | 0.36476400 | 2.78565300 |
| H       | -0.92267400 | -0.84608300| 3.68695100 |
| H       | -2.40684600 | -1.31085200| 2.86890700 |
| C       | -2.05506000 | -2.11404300| -1.46275300|
| H       | -1.31871800 | -1.80791300| -2.21094200|
| H       | -2.94709900 | -2.41775600| -2.01694900|
| H       | -1.68868200 | -2.99199700| -0.92881800|
| C       | -3.52242500 | -1.45378900| 0.45950200 |
| H       | -3.22262100 | -2.34524900| 1.01011500 |
| H       | -4.39929600 | -1.72465800| -0.13396700|
| H       | -3.83164200 | -0.68236000| 1.16250300 |
| C       | -2.90526000 | 0.29230300 | -1.29538600|
| H       | -3.99329900 | 0.30077500 | -1.38432500|
| H       | -2.51713700 | 0.26698300 | 2.31846800 |
| C       | 4.58715400  | 1.35571900 | -0.63942600|
| H       | 4.46607100  | -2.32559600| -0.14542700|
| H       | 5.51295200  | -0.91077800| -0.27489000|
C -1.33839500  0.23352800  0.37843300
C  2.46245900  -0.74029100  0.83414300
C  0.93689900  -1.28487200  -1.47231200
C -3.44727200  0.74791100  -0.17973200
C  2.25224900  1.75918200  0.44902200
C  0.11810700  0.31492500  0.61192500
H  0.34831500  0.29972500  1.67140400
C  1.09317500  1.05073200  -0.23709200
H  0.76192800  1.42165000  -1.19997100
C  3.70631600  -1.27078600  0.11133200
H  3.56500300  -2.24708600  -0.34848800
H  4.47288700  -1.39502600  0.88091000
H  4.10533200  -0.57406200  -0.62245000
C -1.76006700  -1.96567600  1.53747600
H -2.24283500  -1.97437700  2.51649100
H -0.68219600  -1.98644900  1.66629100
H -2.07287300  -2.84638300  0.97356200
C -4.59435400  -1.38152100  0.79787100
H -4.45869700  -2.37231700  0.35191500
H -5.53356600  -0.97462000  0.42318400
H -4.69601300  -1.50812000  1.88086000
C  2.75812900  0.66651900  1.42668000
H  2.27554900  0.77769200  2.40268800
H  3.82928800  0.77139200  1.60824500
C -4.56727300  1.55355800  -0.74578500
H -4.73736000  2.46948800  -0.16916100
H -5.49155000  0.97582700  -0.72012800
H -4.37851800  1.83202100  -1.78680000
C -1.69666700  2.47128400  -0.73766900
H -0.86190300  2.85629900  -0.15594400
|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| H | -2.52499800 | 3.17133500 | -0.64735500 |
| H | -1.42368200 | 2.38204400 | -1.79204000 |
| C | 2.03309200  | -1.74324900 | 1.90658400  |
| H | 1.19164800  | -1.39330600 | 2.50976900  |
| H | 2.86905400  | -1.87218400 | 2.59916700  |
| H | 1.79923700  | -2.72547600 | 1.49443800  |
| C | -0.41933400 | -0.91370000 | -2.10223900 |
| H | -1.27562900 | -1.25534100 | -1.52253800 |
| H | -0.47128700 | -1.43128000 | -3.06237700 |
| H | -0.52192400 | 0.15049100  | -2.32508900 |
| C | 0.90252200  | -2.77013300 | -1.10192400 |
| H | 1.85803100  | -3.14990200 | -0.74648700 |
| H | 0.64744500  | -3.33796200 | -2.00016200 |
| H | 0.13662200  | -2.98226100 | -0.35271000 |
| C | 3.30148400  | 2.17151700  | -0.60066000 |
| H | 3.64457200  | 1.33306800  | -1.20997700 |
| H | 4.17367000  | 2.60634900  | -0.10640900 |
| H | 2.89312400  | 2.92919700  | -1.27665100 |
| C | 2.02556700  | -0.96279700 | -2.50956900 |
| H | 2.08426700  | 0.10941300  | -2.71530700 |
| H | 1.75384300  | -1.45669100 | -3.44536600 |
| H | 3.01127500  | -1.32466900 | -2.23792000 |
| C | 1.75817700  | 3.00595900  | 1.20253900  |
| H | 1.38494000  | 3.76776800  | 0.51061900  |
| H | 2.58310900  | 3.45608400  | 1.76088100  |
| H | 0.96657000  | 2.76457500  | 1.92057000  |

|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| N | -1.92563700 | -1.10817200 | -0.00070200 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| N       | -1.97259400 | 1.06114800 | -0.18412900 |
| N       | 1.20693500  | 0.66274700 | 0.55840600  |
| H       | 0.76823900  | 1.06250800 | 1.38899600  |
| C       | -1.15547000 | -0.01412700 | -0.19300800 |
| C       | 2.60233700  | -1.22943400 | -0.16855600 |
| C       | 1.24080700  | -0.81799500 | 0.39939700  |
| H       | 0.81959300  | -1.37701600 | 1.23026900  |
| C       | -3.24948000 | -0.72035600 | 0.15784800  |
| C       | 0.30454800  | -0.01085500 | -0.44409200 |
| H       | 0.61303500  | 0.20294700  | -1.46512100 |
| C       | -3.27857200 | 0.65271400  | 0.04455600  |
| C       | 3.18666600  | 0.12346300  | -0.68508600 |
| H       | 4.27257700  | 0.14862000  | -0.57339700 |
| H       | 2.98254300  | 0.23762300  | -1.75423000 |
| C       | 2.54443200  | 1.29860000  | 0.09510400  |
| C       | -1.58488000 | 2.46050500  | -0.40579900 |
| H       | -1.79251900 | 3.04814200  | 0.49079600  |
| H       | -2.15935100 | 2.86371000  | -1.24134300 |
| H       | -0.52603800 | 2.51703800  | -0.64805700 |
| C       | 3.28558300  | 1.68572200  | 1.37855600  |
| H       | 2.75703500  | 2.47623600  | 1.92131300  |
| H       | 4.26839900  | 2.07885000  | 1.10772000  |
| H       | 3.43963500  | 0.83828700  | 2.04802800  |
| C       | 2.43110900  | -2.24561600 | -1.31143200 |
| H       | 1.99956200  | -3.18354000 | -0.94793900 |
| H       | 3.40639100  | -2.48593100 | -1.74225100 |
| H       | 1.80074200  | -1.85796000 | -2.11887400 |
| C       | -4.35165300 | -1.69774400 | 0.38643500  |
| H       | -4.51820300 | -2.32759000 | -0.49443700 |
| H       | -5.28326600 | -1.17095100 | 0.59415800  |
|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| H | -4.139835 | -2.350287 | 1.238856  |
| C | -4.413566 | 1.615391  | 0.120094  |
| H | -4.256382 | 2.360923  | 0.906394  |
| H | -5.341508 | 1.088407  | 0.342470  |
| H | -4.551931 | 2.144926  | -0.828613 |
| C | 3.449765  | -1.856927 | 0.956324  |
| H | 3.566996  | -1.19919  | 1.820341  |
| H | 4.447747  | -2.090816 | 0.578016  |
| H | 3.000808  | -2.792227 | 1.304167  |
| C | -1.487310 | -2.51376  | -0.011934 |
| H | -0.528379 | -2.601222 | -0.518115 |
| H | -2.220055 | -3.102897 | -0.562782 |
| H | -1.416587 | -2.893356 | 1.009949  |
| C | 2.268307  | 2.524728  | -0.770824 |
| H | 1.681265  | 2.283257  | -1.662311 |
| H | 3.223249  | 2.927562  | -1.118525 |
| H | 1.769565  | 3.318039  | -0.205976 |

**6Dip**

|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| N | -1.393447 | 0.270485  | -0.691044 |
| N | 2.974362  | -1.390634 | 0.544809  |
| N | 3.109118  | 0.678778  | -0.213778 |
| C | -1.823047 | 0.187501  | 0.678477  |
| C | -0.022041 | 0.329424  | -1.101839 |
| C | 0.886718  | -0.532867 | -0.370806 |
| C | -2.451752 | -0.996248 | 1.154400  |
| C | 2.226998  | -0.380256 | -0.047627 |
| C | -0.097366 | -0.099317 | -2.692693 |
| C | -1.619526 | 1.297028  | 1.545667  |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -2.32876600 | 0.65190900 | -1.81785200 |
| C       | -2.95292200 | -1.00857600 | 2.46074600 |
| C       | -2.12997500 | 1.21694700 | 2.84492300 |
| C       | -2.47862000 | -2.30211400 | 0.36755700 |
| C       | -1.37535900 | 0.69539700 | -3.03364800 |
| C       | -0.24659400 | -1.61390600 | -2.87968500 |
| C       | -0.86684200 | 2.56726700 | 1.15883400 |
| C       | -2.80694800 | 0.08803900 | 3.29998500 |
| C       | 4.25736200  | -0.98793000 | 0.72589200 |
| C       | 4.34467800  | 0.33096800 | 0.24197400 |
| C       | -2.93816500 | 2.03883400 | -1.52627300 |
| C       | 1.12724900  | 0.40411700 | -3.45253000 |
| C       | 2.43730100  | -2.70689400 | 0.92353800 |
| C       | -1.49814100 | -3.31930400 | 0.98916900 |
| C       | -3.48231000 | -0.33982600 | -2.01829200 |
| C       | 2.79445600  | 2.00791000 | -0.75526200 |
| C       | -3.87722600 | -2.93613700 | 0.26548900 |
| C       | -1.69030400 | 3.84826100 | 1.38919700 |
| C       | 5.32236600  | -1.83293400 | 1.33038900 |
| C       | 0.47059000  | 2.63885100 | 1.92539200 |
| C       | 5.52669500  | 1.23331300 | 0.20685200 |
| H       | -2.01623600 | 2.06676200 | 3.50963100 |
| H       | -3.20281100 | 0.06122600 | 4.30999000 |
| H       | -3.44463600 | -1.90110500 | 2.83201100 |
| H       | 0.33447000  | 1.36468300 | -1.17092700 |
| H       | 0.43591900  | -1.45377900 | -0.01707400 |
| H       | -2.12453700 | -2.08658700 | -0.64222400 |
| H       | -1.09702700 | 1.73111600 | -3.25255000 |
| H       | -1.84857400 | 0.28600600 | -3.93023300 |
| H       | 0.69250800  | -2.13718000 | -2.67834800 |
|    |          |          |          |          |
|----|----------|----------|----------|----------|
| H  | -1.02526900 | -2.04264100 | -2.24956100 |          |
| H  | -0.51345400 | -1.81448400 | -3.92128300 |          |
| H  | -0.64404800 | 2.53283100  | 0.08947900  |          |
| H  | -3.54811200 | 2.01269100  | -0.62067500 |          |
| H  | -2.16715700 | 2.80350500  | -1.41076400 |          |
| H  | -3.58103900 | 2.33041100  | -2.36105400 |          |
| H  | 1.22908000  | 1.49174200  | -3.39505300 |          |
| H  | 2.04943200  | -0.06993100 | -3.09970700 |          |
| H  | 1.02065900  | 0.14390100  | -4.51008500 |          |
| H  | 1.71982500  | -2.59029400 | 1.73806800  |          |
| H  | 1.95914100  | -3.17492500 | 0.06224700  |          |
| H  | 3.25508800  | -3.34051400 | 1.25688700  |          |
| H  | -0.48608000 | -2.90885700 | 1.08388200  |          |
| H  | -1.81651000 | -3.60855800 | 1.99468600  |          |
| H  | -1.44519100 | -4.22572100 | 0.37849900  |          |
| H  | -3.14345500 | -1.33520100 | -2.30605700 |          |
| H  | -4.08798200 | -0.41580100 | -1.11466200 |          |
| H  | -4.12550800 | 0.03662900  | -2.81774400 |          |
| H  | 2.80657400  | 1.98333700  | -1.84445400 |          |
| H  | 1.81877300  | 2.32379900  | -0.39092700 |          |
| H  | 3.53743500  | 2.71682500  | -0.39738700 |          |
| H  | -4.23213200 | -3.27943400 | 1.24128300  |          |
| H  | -4.61959000 | -2.24070900 | -0.13004000 |          |
| H  | -3.84532300 | -3.80961600 | -0.39253400 |          |
| H  | -2.65080400 | 3.80432400  | 0.87093100  |          |
| H  | -1.89086000 | 4.01445400  | 2.45083800  |          |
| H  | -1.14218600 | 4.72061800  | 1.02069100  |          |
| H  | 5.05391800  | -2.13907500 | 2.34719000  |          |
| H  | 5.49635800  | -2.73736700 | 0.73673000  |          |
| H  | 6.26229900  | -1.28504600 | 1.38574600  |          |
| Atom | x     | y     | z     |
|------|-------|-------|-------|
| H    | 0.29793300 | 2.72170300 | 3.00201000 |
| H    | 1.07723500 | 1.73746000 | 1.76992400 |
| H    | 1.05049900 | 3.51650100 | 1.62016700 |
| H    | 5.67820700 | 1.65212200 | -0.79312600 |
| H    | 5.41186000 | 2.06622500 | 0.91077700 |
| H    | 6.43032800 | 0.69081100 | 0.48305500 |

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| N    | 2.39124100 | -0.75926400 | -0.99126600 |
| N    | 2.27410000 | 0.81003700 | 0.54270400 |
| N    | -1.91876600 | -0.36004400 | 0.52757600 |
| C    | 3.66588900 | -0.58924900 | -0.48919900 |
| C    | 1.50914500 | 0.09376200 | -0.35612900 |
| C    | -2.94220800 | -0.52142600 | -0.56095000 |
| C    | -1.41964500 | -1.51661500 | 1.30174200 |
| C    | 3.59295200 | 0.39278500 | 0.47525400 |
| C    | -1.87386000 | 1.73271500 | -0.58980400 |
| C    | 0.15133500 | 0.16366700 | -0.63582100 |
| H    | -0.16001300 | -0.39626400 | -1.50827200 |
| C    | -0.97881500 | 0.72643000 | 0.18352100 |
| H    | -0.61380500 | 1.18424700 | 1.10100800 |
| C    | -4.37897400 | -0.53680900 | 0.00737700 |
| H    | -4.58890100 | -1.42274700 | 0.60459100 |
| H    | -5.09265600 | -0.52491100 | -0.82245100 |
| H    | -4.56466600 | 0.34240400 | 0.62656200 |
| C    | 1.98349500 | -1.73007400 | -2.00289800 |
| H    | 1.63022900 | -1.21729100 | -2.90139300 |
| H    | 1.18658600 | -2.36527800 | -1.60881500 |
| H    | 2.83448200 | -2.35385700 | -2.26679700 |
|   |   |   |   |
|---|---|---|---|
| H | -3.21433500 | -2.79337000 | 1.25114100 |
| C | -1.08590600 | 2.70151100 | -1.47884300 |
| H | -0.43210700 | 3.35083900 | -0.88456400 |
| H | -1.77375900 | 3.35307200 | -2.02639800 |
| H | -0.46664300 | 2.17659100 | -2.21293800 |
| H | -0.87468600 | -2.21688300 | 0.64512000 |

|   |   |   |   |
|---|---|---|---|
| N | -2.48150800 | -0.57389800 | 1.08787800 |
| N | -2.32580500 | 0.79856000 | -0.62126300 |
| N | 1.85564300 | -0.32720400 | -0.35871600 |
| C | -3.74214100 | -0.47965800 | 0.52844900 |
| C | -1.58536800 | 0.20373200 | 0.38008500 |
| C | 2.93708600 | -0.29351600 | 0.68505100 |
| C | 1.49390000 | -1.49379900 | -1.21300600 |
| C | -3.64516100 | 0.37704100 | -0.54429300 |
| C | 1.76762500 | 1.90115900 | 0.47974000 |
| C | -0.23422800 | 0.31134200 | 0.68331800 |
| H | 0.06507700 | -0.14720900 | 1.61736300 |
| C | 0.90857700 | 0.78648600 | -0.17415900 |
| H | 0.55335000 | 1.12637600 | -1.14383200 |
| C | 4.36419200 | -0.26395200 | 0.08258600 |
| H | 4.67479100 | -1.22623700 | -0.32053100 |
| H | 5.07395000 | -0.00545400 | 0.87417800 |
| H | 4.45260500 | 0.48335300 | -0.70699400 |
| C | -2.10631700 | -1.39188100 | 2.23732000 |
| H | -1.77781300 | -0.75616000 | 3.06382900 |
| H | -1.30090800 | -2.07700700 | 1.96255000 |
| H | -2.96719600 | -1.97197700 | 2.56175600 |
H  1.91544900  3.26856500 -1.21135600
C  2.76024300 -2.17464000 -1.76960700
H  3.39828100 -1.45751300 -2.29034600
H  2.46500200 -2.95014700 -2.48143500
H  3.34264100 -2.66390700 -0.98779900
C  0.94962300  2.93623300  1.26108700
H  0.27243500  3.49392500  0.60361700
H  1.61738900  3.66669000  1.72819400
H  0.35034200  2.47670900  2.05303800

8Dip
N  -1.52788700  0.59090100  0.08496700
N  2.55243400 -0.90383100 -1.18834600
N  2.85494500  1.07102600 -0.27965200
C  -1.28738000 -0.71769700  0.63809500
C  -0.40808100  1.39759100 -0.40399900
C   0.54823800  0.49382600 -1.11599300
C  -1.69920000 -1.86215500 -0.10442700
C   1.90210500  0.27166800 -0.87260700
C  -1.12897800  2.48950100 -1.26764300
C  -0.56696900 -0.90180600  1.85067600
C  -2.72341500  1.44995000  0.36656100
C  -1.38982400 -3.14047900  0.37846800
C  -0.28209100 -2.20313000  2.28589600
C  -2.47044000 -1.77950000 -1.41939200
C  -2.34315300  2.77355000 -0.35432100
C  -1.55370900  1.94022700 -2.63973400
C  -0.04313400  0.24336100  2.71432800
C  -0.68612500 -3.31863800  1.56381900
| Atomic Number | X     | Y     | Z     |
|---------------|-------|-------|-------|
| C             | 3.86681100 | -0.84591300 | -0.77966300 |
| C             | 4.05839700 | 0.39521900  | -0.20799600 |
| C             | -2.94441000 | 1.69378700  | 1.86970500  |
| C             | -0.28278600 | 3.74982500  | -1.47400200 |
| C             | 1.87334100  | -2.08404100 | -1.72464300 |
| C             | -1.68295500 | -2.35242000 | -2.61331000 |
| C             | -4.02206700 | 0.85325400  | -0.19778200 |
| C             | 2.65884500  | 2.44644100  | 0.17244000  |
| C             | -3.83665100 | -2.48664400 | -1.32030600 |
| C             | -0.67795400 | 0.24702600  | 4.11829700  |
| C             | 4.82661100  | -1.97317900 | -0.95300400 |
| C             | 1.49319400  | 0.19550400  | 2.84359500  |
| C             | 5.28397700  | 0.98998200  | 0.39579400  |
| H             | 0.26413000  | -2.34371800 | 3.21350600  |
| H             | -0.46020000 | -4.31770500 | 1.92430300  |
| H             | -1.70976800 | -4.01136400 | -0.18553000 |
| H             | 0.11574100  | 1.92084900  | 0.41175600  |
| H             | 0.07306900  | -0.23273900 | -1.76159200 |
| H             | -2.64539700 | -0.72670300 | -1.62675300 |
| H             | -2.06214500 | 3.52815200  | 0.38856500  |
| H             | -3.18421100 | 3.18279600  | -0.92108600 |
| H             | -0.68335100 | 1.75681500  | -3.27883800 |
| H             | -2.11109800 | 1.00693700  | -2.55074600 |
| H             | -2.19166000 | 2.66679000  | -3.15155000 |
| H             | -0.30647500 | 1.18477600  | 2.23237000  |
| H             | -3.14310300 | 0.75117600  | 2.38684000  |
| H             | -2.08270900 | 2.17392400  | 2.33823500  |
| H             | -3.80903800 | 2.34765800  | 2.01959500  |
| H             | 0.05727600  | 4.17339600  | -0.52241700 |
| H             | 0.58895300  | 3.55054900  | -2.10860000 |
| X         | Y         | Z          |
|-----------|-----------|------------|
| -0.873204 | 4.520768  | -1.978701  |
| 1.012197  | -2.330620 | -1.098991  |
| 1.543828  | -1.897278 | -2.748845  |
| 2.566347  | -2.922138 | -1.727483  |
| -0.776757 | -1.776333 | -2.823286  |
| -1.387922 | -3.393230 | -2.444318  |
| -2.297387 | -2.325460 | -3.518577  |
| -3.996394 | 0.753653  | -1.284235  |
| -4.220611 | -0.127230 | 0.240004   |
| -4.863675 | 1.504765  | 0.055044   |
| 1.983598  | 2.958131  | -0.507276  |
| 2.249409  | 2.461620  | 1.185178   |
| 3.617380  | 2.962809  | 0.164812   |
| -3.717795 | -3.571852 | -1.238169  |
| -4.406170 | -2.152733 | -0.450063  |
| -4.433765 | -2.287303 | -2.215822  |
| -1.767477 | 0.285936  | 4.070176   |
| -0.401945 | -0.652284 | 4.677459   |
| -0.330864 | 1.113110  | 4.691587   |
| 4.520684  | -2.853773 | -0.377499  |
| 4.911602  | -2.267368 | -2.004049  |
| 5.819169  | -1.681835 | -0.608881  |
| 1.815734  | -0.666263 | 3.435715   |
| 1.979502  | 0.115687  | 1.868538   |
| 1.864716  | 1.092984  | 3.350897   |
| 5.646365  | 1.847929  | -0.181825  |
| 5.097540  | 1.326877  | 1.420547   |
| 6.086229  | 0.252531  | 0.428141   |
NMR Spectra

Figure S38. $^1$H NMR spectrum of 1-HOTf in CDCl$_3$ at 298 K.

Figure S39. $^{13}$C($^1$H) NMR spectrum of 1-HOTf in CDCl$_3$ at 298 K.
Figure S40. $^{19}\text{F}(^{1}\text{H})$ NMR spectrum of 1·HOTf in CDCl$_3$ at 298 K.

Figure S41. $^{1}\text{H}$ NMR spectrum of compound 1 in C$_6$D$_6$ at 298 K.
**Figure S42.** $^{13}$C($^1$H) NMR spectrum of compound 1 in C$_6$D$_6$ at 298 K.

**Figure S43.** $^1$H NMR spectrum of compound 3$_{pr}$ in CDCl$_3$ at 298 K.
Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 3$^{\text{ipr}}$ in CDCl$_3$ at 298 K.

Figure S45. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of compound 3$^{\text{ipr}}$ in CDCl$_3$ at 298 K.
Figure S46. $^1$H NMR spectrum of compound 3^Bu in CDCl$_3$ at 298 K.

Figure S47. $^{13}$C($^1$H) NMR spectrum of compound 3^Bu in CDCl$_3$ at 298 K.
Figure S48. $^{19}$F($^1$H) NMR spectrum of compound $3^{\text{Bu}}$ in CDCl$_3$ at 298 K.

Figure S49. $^1$H NMR spectrum of compound $3^{\text{Dip}}$ in CDCl$_3$ at 298 K.
Figure S50. $^{13}$C($^1$H) NMR spectrum of compound $3^{\text{Dip}}$ in CDCl$_3$ at 298 K.

Figure S51. $^{19}$F($^1$H) NMR spectrum of compound $3^{\text{Dip}}$ in CDCl$_3$ at 298 K.
Figure S52. $^1$H NMR spectrum of compound 4$i$Pr in C$_6$D$_6$ at 298 K.

Figure S53. $^{13}$C($^1$H) NMR spectrum of compound 4$i$Pr in C$_6$D$_6$ at 298 K.
Figure S54. $^1$H NMR spectrum of compound 4$^{tBu}$ in C$_6$D$_6$ at 298 K.

Figure S55. $^{13}$C($^1$H) NMR spectrum of compound 4$^{tBu}$ in C$_6$D$_6$ at 298 K.
Figure S56. $^1$H NMR spectrum of compound 4Dip in C$_6$D$_6$ at 298 K.

Figure S57. $^{13}$C($^1$H) NMR spectrum of compound 4Dip in C$_6$D$_6$ at 298 K.
Figure S58. $^1$H NMR spectrum of compound 6$i$Pr in CD$_3$CN at 298 K.

Figure S59. $^{13}$C($^1$H) NMR spectrum of compound 6$i$Pr in CD$_3$CN at 298 K.
Figure S60. $^{19}$F$[^1]$H NMR spectrum of compound 6$^{pr}$ in CD$_3$CN at 298 K.

Figure S61. $^1$H NMR spectrum of compound 6$^h$ in CD$_3$CN at 298 K.
Figure S62. $^{13}$C($^1$H) NMR spectrum of compound 6$^H$ in CD$_3$CN at 298 K.

Figure S63. $^{19}$F($^1$H) NMR spectrum of compound 6$^H$ in CD$_3$CN at 298 K.
Figure S64. $^1$H NMR of the crude reaction mixture of 1:1 Reaction of AgOTf and 4-iPr in THF-$d_8$ at 298K.

Figure S65. $^{19}$F($^1$H) NMR of the crude reaction mixture of 1:1 Reaction of AgOTf and 4-iPr in THF-$d_8$ at 298K.
Figure S66. $^1$H NMR of 3$^{iPr}$ in THF-$d_8$ at 298K.

Figure S67. $^{19}$F($^1$H) NMR of 3$^{iPr}$ in THF-$d_8$ at 298K.
Figure S68. $^1$H NMR of the crude reaction mixture of 1:1 Reaction of AgOTf and 4$^{tBu}$ in THF-$_d^8$ at 298K.

Figure S69. $^{19}$F($^1$H) NMR of the crude reaction mixture of 1:1 Reaction of AgOTf and 4$^{tBu}$ in THF-$_d^8$ at 298K.
Figure S70. $^1$H NMR of $3^\text{Bu}$ in THF-$d_8$ at 298K.

Figure S71. $^{19}$F($^1$H) NMR of $3^\text{Bu}$ in THF-$d_8$ at 298K.
Figure S72. $^1$H NMR of the crude reaction mixture of 1:1 reaction of AgOTf and 4Dip in THF-$d_8$ at 298K.

Figure S73. $^{19}$F($^1$H) NMR of the crude reaction mixture of 1:1 Reaction of AgOTf and 4Dip in THF-d8 at 298K.
Figure S74. $^1$H NMR of 3Dip in THF-$d_8$ at 298K.

Figure S75. $^{19}$F($^1$H) NMR of 3Dip in THF-$d_8$ at 298K.
Figure S76. $^1$H NMR of compound 9 in CD$_3$CN at 298K.

Figure S77. $^{13}$C($^1$H) NMR of compound 9 in CD$_2$CN at 298K.
Figure S78. $^{19}$F-$^1$H NMR of compound 9 in CD$_3$CN at 298K.

Figure S79. $^1$H NMR spectrum of compound 10 in CDCl$_3$ at 298.
Figure S80. $^{13}\text{C}^{[1\text{H}]}$ NMR spectrum of compound 10 in CDCl$_3$ at 298 K.

Figure S81. $^{19}\text{F}^{[1\text{H}]}$ NMR spectrum of compound 10 in CDCl$_3$ at 298 K.
Figure S82. $^1$H NMR of 11 in CDCl$_3$ at 298K.

Figure S83. $^{19}$F($^1$H) NMR of 11 in CDCl$_3$ at 298K.
Crystallographic Details

Single crystal X-ray data of 1-HOTf, 3Pr, 3\textsuperscript{t}Bu, 3\textsuperscript{Dip}, 4\textsuperscript{t}Bu, 4\textsuperscript{Dip}, 6\textsuperscript{Pr}, 6\textsuperscript{H}, 9, and 10 were collected at 120 K on a Rigaku Xtalab Pro using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Data integration and reduction were processed with CrysAlis Pro software. The structure was solved by direct methods using ShelXT瞿瞿 and programs and refined by full matrix least-squares method based on $F^2$ using SHELXL瞿瞿 in the Olex-2瞿瞿 software. All non-hydrogen-atoms were refined with anisotropic displacement parameters. Hydrogens were fixed in their ideal geometries and their contributions included in the refinement. Crystal data and structure refinement for all these molecular structures are in Tables S9-S18.
Table S9. Crystal data and structure refinement for 1-HOTf (CCDC: 1951977)

| Parameter                        | Value                      |
|----------------------------------|----------------------------|
| Identification code              | AJ0622                     |
| Empirical formula                | C₉H₁₅F₃N₂O₃S              |
| Formula weight                   | 288.29                     |
| Temperature/K                    | 119.98(10)                 |
| Crystal system                   | orthorhombic               |
| Space group                      | Pnma                       |
| a/Å                              | 8.5710(17)                 |
| b/Å                              | 6.9720(14)                 |
| c/Å                              | 21.017(4)                  |
| α/°                              | 90                         |
| β/°                              | 90                         |
| γ/°                              | 90                         |
| Volume/Å³                        | 1255.9(4)                  |
| Z                                | 4                          |
| ρ<sub>calc</sub>/cm³             | 1.525                      |
| μ/mm⁻¹                           | 0.298                      |
| F(000)                           | 600.0                      |
| Crystal size/mm³                 | 0.14 × 0.23 × 0.19         |
| Radiation                        | MoKα (λ = 0.71073)         |
| 2Θ range for data collection/*   | 5.13 to 57.728             |
| Index ranges                     | -9 ≤ h ≤ 11, -8 ≤ k ≤ 9, -27 ≤ l ≤ 26 |
| Reflections collected            | 15371                      |
| Independent reflections          | 1670 [R<sub>int</sub> = 0.0374, R<sub>sigma</sub> = 0.0215] |
| Data/restraints/parameters       | 1670/0/108                 |
| Goodness-of-fit on F²            | 1.099                      |
| Final R indexes [I>=2σ (I)]     | R<sub>1</sub> = 0.0441, wR<sub>2</sub> = 0.1276 |
| Final R indexes [all data]      | R<sub>1</sub> = 0.0491, wR<sub>2</sub> = 0.1310 |
| Largest diff. peak/hole/e Å⁻³   | 0.50/-0.51                 |
Table S10. Crystal data and structure refinement for 3\textsuperscript{Pr} (CCDC: 1951948)

| Description                           | Value                                |
|---------------------------------------|--------------------------------------|
| Identification code                   | AJ0629                               |
| Empirical formula                     | C\textsubscript{20}H\textsubscript{36}F\textsubscript{3}N\textsubscript{3}O\textsubscript{3}S |
| Formula weight                        | 455.58                               |
| Temperature/K                         | 120.00(10)                           |
| Crystal system                        | monoclinic                           |
| Space group                           | P2\textsubscript{1}/n                 |
| a/Å                                   | 11.5596(6)                           |
| b/Å                                   | 16.1768(9)                           |
| c/Å                                   | 12.4775(8)                           |
| α/°                                   | 90                                   |
| β/°                                   | 95.002(6)                            |
| γ/°                                   | 90                                   |
| Volume/Å\textsuperscript{3}           | 2324.4(2)                            |
| Z                                      | 4                                    |
| ρ\textsubscript{calc}/cm\textsuperscript{3} | 1.302                                |
| μ/mm\textsuperscript{-1}              | 0.188                                |
| F(000)                                | 976.0                                |
| Crystal size/mm\textsuperscript{3}    | 0.14 × 0.13 × 0.11                   |
| Radiation                             | MoKα (λ = 0.71073)                   |
| 2Θ range for data collection/°        | 6.01 to 57.93                        |
| Index ranges                          | -15 ≤ h ≤ 15, -22 ≤ k ≤ 22, -12 ≤ l ≤ 16 |
| Reflections collected                 | 5448                                 |
| Independent reflections               | 5448 [R\textsubscript{int} = ?, R\textsubscript{sigma} = 0.0445] |
| Data/restraints/parameters            | 5448/564/337                         |
| Goodness-of-fit on F\textsuperscript{2} | 1.071                               |
| Final R indexes [I>=2σ (I)]          | R\textsubscript{1} = 0.1055, wR\textsubscript{2} = 0.2703 |
| Final R indexes [all data]            | R\textsubscript{1} = 0.1269, wR\textsubscript{2} = 0.2841 |
| Largest diff. peak/hole / e Å\textsuperscript{3} | 1.21/-0.64 |
Table S11. Crystal data and structure refinement for \(3^\text{Bu}\) (CCDC: 1951949)

| Property                         | Value                      |
|----------------------------------|----------------------------|
| Identification code              | AJ0662                     |
| Empirical formula                | \(\text{C}_{21}\text{H}_{38}\text{F}_3\text{N}_3\text{O}_3\text{S}\) |
| Formula weight                   | 469.60                     |
| Temperature/K                    | 119.99(10)                 |
| Crystal system                   | monoclinic                 |
| Space group                      | \(\text{P2}_1/\text{n}\)   |
| \(a/\text{Å}\)                   | 8.4819(3)                  |
| \(b/\text{Å}\)                   | 26.6123(7)                 |
| \(c/\text{Å}\)                   | 11.1305(4)                 |
| \(\alpha/°\)                     | 90                         |
| \(\beta/°\)                      | 104.586(4)                 |
| \(\gamma/°\)                     | 90                         |
| Volume/\(\text{Å}^3\)            | 2431.44(14)                |
| \(Z\)                            | 4                          |
| \(\rho_{\text{calc}}/\text{cm}^3\) | 1.283                      |
| \(\mu/\text{mm}^{-1}\)           | 0.182                      |
| \(F(000)\)                       | 1008.0                     |
| Crystal size/mm\(^3\)            | \(0.13 \times 0.12 \times 0.11\) |
| Radiation                        | MoK\(\alpha\) (\(\lambda = 0.71073\)) |
| 2\(\Theta\) range for data collection\(^\ast\) | 5.194 to 58.094 |
| Index ranges                     | -11 \(\leq\) h \(\leq\) 11, -33 \(\leq\) k \(\leq\) 35, -14 \(\leq\) l \(\leq\) 14 |
| Reflections collected            | 32338                      |
| Independent reflections          | 5795 \([R_{\text{int}} = 0.0356, R_{\text{sigma}} = 0.0270]\) |
| Data/restraints/parameters       | 5795/0/291                 |
| Goodness-of-fit on \(F^2\)       | 1.047                      |
| Final R indexes [I\(>\)=2\(\sigma\) (I)] | \(R_1 = 0.0368, wR_2 = 0.0940\) |
| Final R indexes [all data]       | \(R_1 = 0.0435, wR_2 = 0.0968\) |
| Largest diff. peak/hole / e \(\text{Å}^3\) | 0.36/-0.44                |
Table S12. Crystal data and structure refinement for 3\textsuperscript{Di} (CCDC: 1951950)

| Property                        | Value                  |
|---------------------------------|------------------------|
| Identification code             | AJ0687                 |
| Empirical formula               | C\textsubscript{29}H\textsubscript{46}F\textsubscript{3}N\textsubscript{3}O\textsubscript{3}S |
| Formula weight                  | 573.75                 |
| Temperature/K                   | 185.84(10)             |
| Crystal system                  | orthorhombic           |
| Space group                     | P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} |
| a/Å                            | 7.4452(4)              |
| b/Å                            | 18.8437(9)             |
| c/Å                            | 21.3251(10)            |
| α/°                            | 90                     |
| β/°                            | 90                     |
| γ/°                            | 90                     |
| Volume/Å\textsuperscript{3}    | 2991.8(3)              |
| Z                              | 4                      |
| \(\rho_{\text{calc}}/\text{cm}^3\) | 1.274                  |
| \(\mu/\text{mm}^{-1}\)         | 0.161                  |
| F(000)                          | 1232.0                 |
| Crystal size/mm\textsuperscript{3} | 0.13 \times 0.12 \times 0.11 |
| Radiation                       | MoKα (λ = 0.71073)     |
| 2Θ range for data collection/* | 5.77 to 57.85          |
| Index ranges                    | -9 ≤ h ≤ 10, -25 ≤ k ≤ 25, -28 ≤ l ≤ 21 |
| Reflections collected           | 27094                  |
| Independent reflections         | 6944 [R\text{int} = 0.0401, R\text{sigma} = 0.0345] |
| Data/restraints/parameters      | 6944/0/365             |
| Goodness-of-fit on \(P^2\)     | 1.047                  |
| Final R indexes [I => 2σ (I)]   | R\textsubscript{1} = 0.0377, wR\textsubscript{2} = 0.0925 |
| Final R indexes [all data]      | R\textsubscript{1} = 0.0419, wR\textsubscript{2} = 0.0945 |
| Largest diff. peak/hole / e Å\textsuperscript{3} | 0.30/-0.51 |
| Flack parameter                 | 0.38(8)                |
| Property                                      | Value                                      |
|----------------------------------------------|--------------------------------------------|
| Identification code                          | AJ0718                                     |
| Empirical formula                            | C_{20}H_{37}N_{3}                          |
| Formula weight                               | 319.52                                     |
| Temperature/K                                | 120.02(10)                                 |
| Crystal system                               | monoclinic                                 |
| Space group                                  | P2_{1}/c                                   |
| a/Å                                         | 15.1826(9)                                 |
| b/Å                                         | 8.4655(5)                                  |
| c/Å                                         | 16.3019(10)                                |
| α/°                                         | 90                                         |
| β/°                                         | 108.622(6)                                 |
| γ/°                                         | 90                                         |
| Volume/Å\(^3\)                              | 1985.6(2)                                  |
| Z                                           | 4                                          |
| \(\rho_{\text{calc}}\)/cm\(^3\)            | 1.069                                      |
| μ/mm\(^{-1}\)                               | 0.063                                      |
| F(000)                                       | 712.0                                      |
| Crystal size/mm\(^3\)                       | 0.13 × 0.12 × 0.1                         |
| Radiation                                    | MoKα (λ = 0.71073)                         |
| 2θ range for data collection/*               | 5.488 to 57.98                             |
| Index ranges                                 | -20 ≤ h ≤ 20, -9 ≤ k ≤ 11, -21 ≤ l ≤ 21   |
| Reflections collected                        | 27507                                      |
| Independent reflections                      | 4758 [R_{int} = 0.0578, R_{sigma} = 0.0491]|
| Data/restraints/parameters                   | 4758/46/241                                |
| Goodness-of-fit on F\(^2\)                   | 1.051                                      |
| Final R indexes [l>=2σ (l)]                  | R_1 = 0.0776, wR_2 = 0.1949                |
| Final R indexes [all data]                   | R_1 = 0.1097, wR_2 = 0.2127                |
| Largest diff. peak/hole / e Å\(^3\)         | 0.59/-0.47                                 |
**Table S14.** Crystal data and structure refinement for $4^{\text{th}}$ (CCDC: 1951954)

| Property                          | Value                      |
|----------------------------------|----------------------------|
| Identification code              | AJ0705                     |
| Empirical formula                | C$_{38}$H$_{53}$N$_{3}$    |
| Formula weight                   | 423.69                     |
| Temperature/K                    | 119.96(10)                 |
| Crystal system                   | triclinic                  |
| Space group                      | P-1                        |
| $a$/Å                            | 9.4090(3)                  |
| $b$/Å                            | 10.8582(4)                 |
| $c$/Å                            | 13.6751(5)                 |
| $\alpha$/°                       | 73.417(3)                  |
| $\beta$/°                        | 88.835(3)                  |
| $\gamma$/°                       | 73.820(3)                  |
| Volume/Å$^3$                     | 1283.31(8)                 |
| Z                                | 2                          |
| $\rho$$_{\text{calc}}$/cm$^3$   | 1.0964                     |
| $\mu$/mm$^{-1}$                  | 0.064                      |
| F(000)                           | 468.2                      |
| Crystal size/mm$^3$              | 0.13 × 0.12 × 0.11         |
| Radiation                        | Mo Kα (λ = 0.71073)        |
| 2θ range for data collection/*   | 5.16 to 50                 |
| Index ranges                     | -12 ≤ h ≤ 11, -13 ≤ k ≤ 13, -18 ≤ l ≤ 17 |
| Reflections collected            | 22678                      |
| Independent reflections          | 4504 [R$_{\text{int}}$ = 0.0289, R$_{\text{sigma}}$ = 0.0274] |
| Data/restraints/parameters       | 4504/0/292                 |
| Goodness-of-fit on F$^2$          | 1.032                      |
| Final R indexes [I>=2σ (I)]      | R$_1$ = 0.0378, wR$_2$ = 0.0944 |
| Final R indexes [all data]       | R$_1$ = 0.0422, wR$_2$ = 0.0974 |
| Largest diff. peak/hole / e Å$^3$| 0.28/-0.21                |

S97
Table S15. Crystal data and structure refinement for \( ^{6}\text{Pr} \) (CCDC: 1951955)

| Parameter                      | Value                          |
|--------------------------------|--------------------------------|
| Identification code            | AJ0641                         |
| Empirical formula              | \( \text{C}_{31}\text{H}_{35}\text{F}_{6}\text{N}_{3}\text{O}_{6}\text{S}_{2} \) |
| Formula weight                 | 603.64                         |
| Temperature/K                  | 119.99(10)                     |
| Crystal system                 | monoclinic                     |
| Space group                    | \( \text{P2}_1/\text{n} \)     |
| \( a/\text{Å} \)               | 17.8930(6)                     |
| \( b/\text{Å} \)               | 8.3124(2)                      |
| \( c/\text{Å} \)               | 19.3921(6)                     |
| \( \alpha/\text{°} \)          | 90                             |
| \( \beta/\text{°} \)           | 107.751(4)                     |
| \( \gamma/\text{°} \)          | 90                             |
| Volume/\( \text{Å}^3 \)        | 2746.94(15)                    |
| \( Z \)                        | 4                              |
| \( \rho_{\text{calc}}/\text{g/cm}^3 \) | 1.460                         |
| \( \mu/\text{mm}^{-1} \)       | 0.275                          |
| \( F(000) \)                   | 1264.0                         |
| Crystal size/mm\(^3\)         | 0.13 × 0.11 × 0.11             |
| Radiation                      | MoK\( \alpha \) (\( \lambda = 0.71073 \)) |
| 2\( \Theta \) range for data collection/\( ^{\circ} \) | 5.374 to 58.024               |
| Index ranges                   | \(-24 \leq h \leq 22, -11 \leq k \leq 10, -26 \leq l \leq 25 \) |
| Reflections collected          | 24504                          |
| Independent reflections        | 6419 [\( R_{\text{int}} = 0.0366, R_{\text{sigma}} = 0.0355 \)] |
| Data/restraints/parameters     | 6419/0/353                     |
| Goodness-of-fit on \( F^2 \)   | 1.066                          |
| Final R indexes [\( I \geq 2\sigma (I) \)] | \( R_1 = 0.0394, wR_2 = 0.0934 \) |
| Final R indexes [all data]     | \( R_1 = 0.0500, wR_2 = 0.0986 \) |
| Largest diff. peak/hole / e \( \text{Å}^3 \) | 0.31/-0.47                    |
Table S16. Crystal data and structure refinement for 6H (CCDC: 1951956)

| Property                        | Value                                          |
|---------------------------------|------------------------------------------------|
| Identification code             | AJ0722                                         |
| Empirical formula               | C_{36}H_{58}F_{12}N_{6}O_{12}S_{4}             |
| Formula weight                  | 1123.12                                        |
| Temperature/K                   | 119.96(10)                                     |
| Crystal system                  | triclinic                                      |
| Space group                     | P-1                                            |
| a/Å                             | 8.2515(2)                                      |
| b/Å                             | 15.1873(5)                                     |
| c/Å                             | 20.3300(5)                                     |
| α/°                             | 81.547(2)                                      |
| β/°                             | 87.795(2)                                      |
| γ/°                             | 80.681(2)                                      |
| Volume/Å³                       | 2486.50(12)                                    |
| Z                               | 2                                              |
| ρ_{calc}/g/cm³                  | 1.500                                          |
| μ/mm⁻¹                          | 0.298                                          |
| F(000)                          | 1168.0                                         |
| Crystal size/mm³                | 0.13 × 0.12 × 0.11                             |
| Radiation                       | MoKα (λ = 0.71073)                             |
| 2Θ range for data collection/*  | 5.21 to 57.998                                 |
| Index ranges                    | -10 ≤ h ≤ 11, -20 ≤ k ≤ 19, -26 ≤ l ≤ 27      |
| Reflections collected           | 40324                                          |
| Independent reflections         | 11593 [R_{int} = 0.0287, R_{sigma} = 0.0313]   |
| Data/restraints/parameters      | 11593/0/647                                    |
| Goodness-of-fit on F²           | 1.028                                          |
| Final R indexes [I>=2σ (I)]     | R₁ = 0.0540, wR₂ = 0.1370                      |
| Final R indexes [all data]      | R₁ = 0.0682, wR₂ = 0.1445                      |
| Largest diff. peak/hole / e Å³ | 1.11/-0.85                                     |
| Identification code        | AJ0723            |
|---------------------------|-------------------|
| Empirical formula         | C$_{30}$H$_{45}$F$_{6}$N$_{3}$O$_{6}$S$_{2}$       |
| Formula weight            | 721.81            |
| Temperature/K             | 120.03(10)        |
| Crystal system            | monoclinic        |
| Space group               | P2$_1$/n          |
| a/Å                       | 11.4405(6)        |
| b/Å                       | 19.9990(8)        |
| c/Å                       | 16.0796(8)        |
| α/*                       | 90                |
| β/*                       | 107.195(5)        |
| γ/*                       | 90                |
| Volume/Å$^3$              | 3514.6(3)         |
| Z                         | 4                 |
| $\rho$$_{calc}$/cm$^3$    | 1.364             |
| $\mu$/mm$^{-1}$           | 0.228             |
| F(000)                    | 1520.0            |
| Crystal size/mm$^3$       | 0.13 x 0.12 x 0.11|
| Radiation                 | MoKα (λ = 0.71073) |
| 2Θ range for data collection/$^\circ$ | 5.522 to 58.034 |
| Index ranges              | -12 ≤ h ≤ 15, -27 ≤ k ≤ 24, -21 ≤ l ≤ 21       |
| Reflections collected     | 28458             |
| Independent reflections   | 8163 [R$_{int}$ = 0.0331, R$_{sigma}$ = 0.0369] |
| Data/restraints/parameters| 8163/49/435       |
| Goodness-of-fit on F$^2$  | 1.082             |
| Final R indexes [I≥2σ(I)] | R$_1$ = 0.0438, wR$_2$ = 0.1095 |
| Final R indexes [all data]| R$_1$ = 0.0602, wR$_2$ = 0.1153 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.37/-0.34 |
**Table S18. Crystal data and structure refinement for 10 (CCDC: 1951958)**

| Property                      | Value                                      |
|-------------------------------|--------------------------------------------|
| Identification code           | AJ0742                                     |
| Empirical formula             | C_{20}H_{34}F_{3}N_{3}O_{3}S               |
| Formula weight                | 453.56                                     |
| Temperature/K                 | 119.98(10)                                 |
| Crystal system                | monoclinic                                 |
| Space group                   | P2\(_1\)/n                                 |
| a/Å                           | 9.3281(5)                                  |
| b/Å                           | 23.9120(12)                                |
| c/Å                           | 11.1067(6)                                 |
| α/°                           | 90                                         |
| β/°                           | 111.055(6)                                 |
| γ/°                           | 90                                         |
| Volume/Å\(^3\)               | 2312.0(2)                                  |
| Z                             | 4                                          |
| ρ\(_{calc}\)/cm\(^3\)        | 1.303                                      |
| μ/mm\(^{-1}\)                | 0.189                                      |
| F(000)                        | 968.0                                      |
| Crystal size/mm\(^3\)        | 0.14 × 0.13 × 0.12                         |
| Radiation                     | MoKα (λ = 0.71073)                         |
| 2Θ range for data collection/°| 4.98 to 57.784                             |
| Index ranges                  | -12 ≤ h ≤ 9, -30 ≤ k ≤ 32, -15 ≤ l ≤ 14   |
| Reflections collected         | 18853                                      |
| Independent reflections       | 5363 [R\(_{int}\) = 0.0333, R\(_{sigma}\) = 0.0365] |
| Data/restraints/parameters    | 5363/0/281                                 |
| Goodness-of-fit on F\(^2\)    | 1.058                                      |
| Final R indexes [I>2σ (I)]    | R\(_1\) = 0.0388, wR\(_2\) = 0.0898       |
| Final R indexes [all data]    | R\(_1\) = 0.0534, wR\(_2\) = 0.0945       |
| Largest diff. peak/hole / e Å\(^3\) | 0.27/-0.39        |
References

S1  N. Kuhn, H. Bohnen, J. Kreutzberg, D. Bläser and R. Boese, *J. Chem. Soc., Chem. Commun.*, 1993, 1136–1137.
S2  S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42–55.
S3  F. Neese, *Comput. Mol. Sci.* 2018, **8**, 1327–1332.
S4  V. N. Staroverov, G. E. Scuseria, J. Tao and J. P. Perdew, *J. Chem. Phys.*, 2003, **119**, 12129–12137.
S5  N. Mardirossian and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2014, **16**, 9904–9924.
S6  (a) E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597–4610; (b) E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, **101**, 9783–9792.
S7  F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297–3305.
S8  A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.
S9  V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.
S10  (a) S. J. Grimme, *Comput. Chem.*, 2006, **27**, 1787–1799; (b) S. J. Grimme, *Comput. Chem.*, 2004, **25**, 1463–1473; (c) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; (d) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
S11  (a) T. Petrenko, S. Kossmann and F. Neese, *J. Chem. Phys.*, 2011, **134**, 54116; (b) F. Neese and G. Olbrich, *Chem. Phys. Lett.*, 2002, **362**, 170–178; (c) R. Izsak and F. Neese, *J. Chem. Phys.*, 2011, **135**, 144105; (d) J. L. Whitten, *J. Chem. Phys.*, 1973, **58**, 4496–4501; (e) O. Vahtras, J. Almlöf and M. W. Feyereisen, *Chem. Phys. Lett.*, 1993, **213**, 514–518; (f) F. Neese, F. Wennmohs, A. Hansen and U. Becker, *Chem. Phys.*, 2009, **356**, 98–109; (g) F. Neese, *J. Comput. Chem.*, 2003, **24**, 1740–1747.
S12  (a) K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **242**, 652–660; (b) K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, **97**, 119–124; (c) F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.
S13  (a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789; (b) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200–206.
S14  (a) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465; (b) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104–154104-19; (c) S. Grimme, *J. Comput. Chem.*, 2004, **25**, 1463–1476; (d) S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787–1799.
S15  Y. Zhao and D. G. Truhlar, *Theor. Chim. Acta*, 2008, **120**, 215–241
S16  Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 157–167.
S17  A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.

Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria; M. A. Robb; J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Williams; F. Ding; F. Lippari, F. Egid, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Hevd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J.
W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

S19 G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3–8.

S20 G. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3–8.

S21 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.