Electronic Supplementary Information

for

Bis-[cyclic (alkyl)(amino)carbene]s derived diradicals

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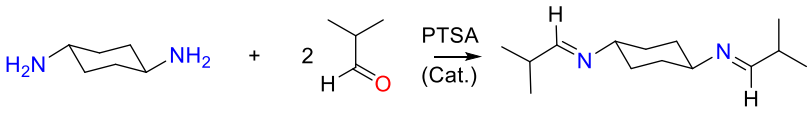
General Considerations

All experiments were carried out either under nitrogen or argon atmosphere using standard Schlenk techniques, PL-HE-2GB Innovative Technology glove box, and MBraun Unilab SP glove box. Hexane, diethyl ether, THF, and toluene were dried with a PS-MD-5 Innovative Technology solvent purification system. LiTMP was synthesised according to a literature procedure.[S1] All other employed chemicals were purchased commercially (potassium bis(trimethylsilyl)amide - Sigma Aldrich, TDAE - Sigma Aldrich, graphite - Sigma Aldrich, potassium - Sigma Aldrich, *trans*-1,4-cyclohexanediamine – TCI Chemicals, Cyclohexanecarboxaldehyde – Alfa Aesar, Isobutyraldehyde – Avra Chemicals, 2-Ethylbutyraldehyde – TCI Chemicals, 2-naphthoyl chloride – TCI Chemicals, Isobutylene oxide – TCI Chemicals, Triflic anhydride – TCI Chemicals, (NO)(SbF_6) - Sigma Aldrich, diisopropylamine - Avra Chemicals, ^{n}BuLi (1.6 M in hexane) - Hychem Laboratories, and AgOTf - Sigma Aldrich) and used as received except for diisopropylamine which was distilled under N_2 over KOH before use. Benzene-d_6 and THF-d_8 were dried and distilled over potassium under argon. CD_3CN was dried and distilled over CaH_2 under argon. NMR spectra were recorded on a BrukerNanoBay 300 MHz NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (^{1}H) or the deuterated solvent itself (^{13}C{^{1}H}). ^{19}F{^{1}H} NMR spectra were referenced to external tol-CF_3. Melting points were determined in sealed NMR tubes under argon atmosphere and are uncorrected. Elemental analyses of **1a-c**, **2a-c**, **3a-c, 4a-c** and **5a-c** were performed on an Elementar vario MICRO cube elemental analyzer. HRMS of **1a-c**, **3a-c**, and **5a-c** were performed on a Waters Xevo G2-XS QTOF (Waters Corporation) using electrospray ionization (ESI). HRMS of **2a-c**, and **4a-c** were performed on LCMS QTOF 6545B (Agilent Technologies) using electrospray ionization (ESI). Thermogravimetric analysis (TGA) was done on a Mettler Toledo TGA/SDTA851 analyzer with a heating rate of 5 Kmin^{-1} under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed using Mettler Toledo DSC 823e differential scanning calorimeter with dif-ferent sweep rates of 15, 10 and 5 min^{-1} in a nitrogen atmosphere. EPR measurements at X-band (9.38 GHz) were carried out using a Bruker ELEXSYS E580 CW EPR spectrometer equipped with an Oxford Instruments helium cryostat (ESR900) and a MercuryiTC temperature controller. The spectral simulations were performed using MATLAB 9.8.0.1323502 (R2020a) and the EasySpin 5.2.28 toolbox.[S2] The magnetic susceptibility measurements were performed with a Quantum Design MPMS-XL EverCool SQUID magnetometer, between 2 K and 300 K (**4a**, **4c**) and from 2 K to 268 K (**4b**) K for dc applied fields ranging from -5 to +5 T. Polycrystalline sample (19.7 mg for **4a** (**MK787**), 11.8 mg for **4b** (**MK785**), and 15.9 mg for **4c** (**MK784**),) was introduced in a polypropylene bag and subjected to the measurement. The temperature dependent data were measured using 1000 Oe and 10000 Oe dc magnetic fields. The isothermal magnetization data were acquired at 2.0, 5, and 6 K. *M vs H* measurements were performed at 100 K to check for the presence of impurities, where the sample was free from impurities. The magnetic data were corrected for the sample holder and the intrinsic diamagnetic contributions.

Experimental Details and Analytical Data

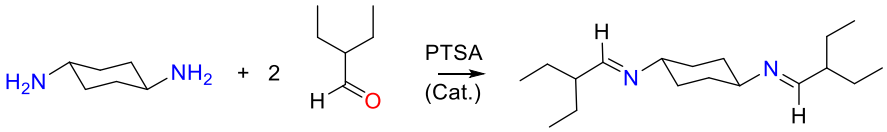
Synthesis of A



A

Anhydrous sodium sulfate (117.2 g, 825.3 mmol) was added to a one litre round-bottom flask and diethyl ether (500 mL) was added. (±)-*trans*-1,4-Cyclohexanediamine (30.000 g, 262.72 mmol) and catalytic amount of *p*-toluenesulfonic acid (10 mg, 0.05 mmol) were added to the round-bottom flask with stirring. After that, isobutyraldehyde (72.0 mL, 794 mmol) was added at room temperature and the mixture was stirred for 12 hours. The reaction mixture was then filtered through cotton containing anhydrous sodium sulfate. Sodium sulfate in the round-bottom flask of reaction mixture was washed with diethyl ether (3 × 100 mL) and filtered. The filtrates were combined and evaporated under reduced pressure to remove all the volatiles and then **A** was obtained as a white solid. **Yield:** 57 g (98%). **^{1}H NMR** (C_6D_6, 25 °C, 300 MHz): δ = 7.31 (d, 2H, $^{3}J_{H\text{-}H}$ = 4.2 Hz, *H*C=N), 2.82-2.83 (m, 2H, $^{Cy\text{-}B}$C*H*N), 2.19-2.34 (m, 2H, *H*C$(CH_3)_2$), 1.67-1.78 (m, 8H, $^{Cy\text{-}B}$CH_2), 0.98 (d, 12H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, C(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75.4 MHz): δ = 166.9 (H*C*=N), 69.8 ($^{Cy\text{-}B}$*C*HN), 34.6 (*C*H$(CH_3)_2$), 33.8 ($^{Cy\text{-}B}$*C*H$_2$), 20.0 (CH(*C*H$_3$)$_2$) ppm.

Synthesis of B

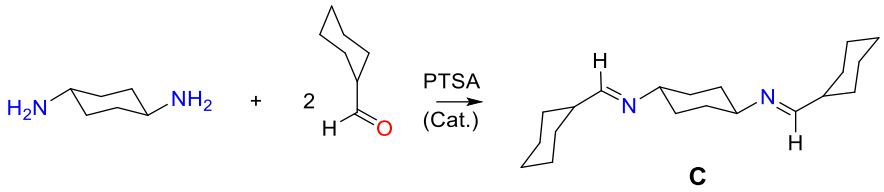


B

Anhydrous sodium sulfate (49.60 g, 349.3 mmol) was added to a 500 mL round-bottom flask and diethyl ether (300 mL) was added. (±)-*trans*-1,4-Cyclohexanediamine (10.00 g, 87.57 mmol) and catalytic amount of *p*-toluenesulfonic acid (10 mg, 0.05 mmol) were added to the round-bottom flask and stirred for 10 minutes. Then 2-ethylbutyraldehyde (22.6 mL, 184 mmol) was added at room temperature and the reaction mixture was stirred for 12 hours. The mixture was filtered through funnel containing anhydrous sodium sulfate over cotton. Sodium sulfate in the round-bottom flask of reaction mixture was washed with diethyl ether (3 × 30 mL) and filtered. The filtrates were combined and the volatiles from combined filtrates were removed under reduced pressure to give **B** as a white precipitate. **Yield:** 23.4 g (96%). **^{1}H NMR** (C_6D_6, 25 °C, 300 MHz): δ = 7.20 (d, 2H, $^{3}J_{H\text{-}H}$ = 6.1 Hz, *H*C=N), 2.76-2.93 (m, 2H, $^{Cy\text{-}B}$C*H*N), 1.96-2.07 (m, 2H, *H*C$(CH_2CH_3)_2$), 1.69-1.81 (m, 8H, $^{Cy\text{-}B}$CH_2), 1.27-1.47 (m, 8H, HC(CH_2CH$_3$)$_2$), 0.87 (t, 12H, $^{3}J_{H\text{-}H}$ = 7.4 Hz, HC(CH$_2$CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25

°C, 75.4 MHz): δ = 165.9 (H*C*=N), 70.2 ($^{Cy\text{-}B}$*C*HN), 48.6 (H*C*(C_2H_5)$_2$), 34.0 ($^{Cy\text{-}B}$*C*H$_2$), 25.9 (HC(*C*H$_2$CH$_3$)$_2$), 12.4 (HC(CH$_2$*C*H$_3$)$_2$) ppm.

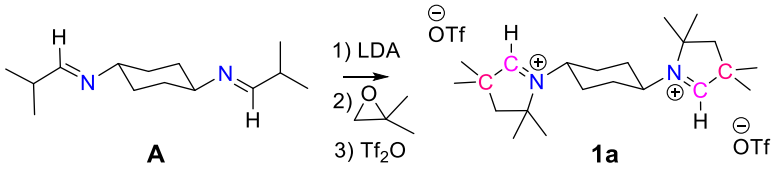
Synthesis of C



C

Anhydrous sodium sulfate (49.6 g, 349 mmol) was added to a 500 mL round-bottom flask and diethyl ether (300 mL) was added. (±)-*trans*-1,4-Cyclohexanediamine (10.00 g, 87.57 mmol) and catalytic amount of *p*-toluenesulfonic acid (10 mg, 0.05 mmol) were added to the R.B. and stirred for 10 minutes. After that cyclohexanecarboxaldehyde (22.3 mL, 184 mmol) was added at room temperature and the reaction mixture was stirred for 12 hours. The reaction mixture was then filtered through funnel containing anhydrous sodium sulfate over cotton. Sodium sulfate in the round-bottom flask of reaction mixture was washed with diethyl ether (3 × 30 mL) and filtered. The filtrates were combined and the volatiles from combined filtrates were removed under reduced pressure to give **C** as a white precipitate. **Yield:** 28 g (96%). **^{1}H NMR** (C_6D_6, 25 °C, 300 MHz): δ = 7.35 (d, 2H, $^3J_{H\text{-}H}$ = 4.2 Hz, *H*C=N), 2.85-2.87 (m, 2H, $^{Cy\text{-}B}$C*H*N), 2.02-2.12 (m, 2H, NC*H*CH$_2$CH$_2$), 1.53-1.82 (m, 20H, $^{Cy\text{-}B}$C*H*$_2$), 1.05-1.31 (m, 8H, $^{Cy\text{-}B}$C*H*$_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75.4 MHz): δ = 166.2 (H*C*=N), 70.0 ($^{Cy\text{-}B}$*C*HN), 43.9 (N*C*HCH$_2$CH$_2$), 33.9 ($^{Cy\text{-}B}$*C*H$_2$), 30.6 ($^{Cy\text{-}B}$*C*H$_2$), 27.1 ($^{Cy\text{-}B}$*C*H$_2$), 26.4 ($^{Cy\text{-}B}$*C*H$_2$) ppm.

Synthesis of 1a

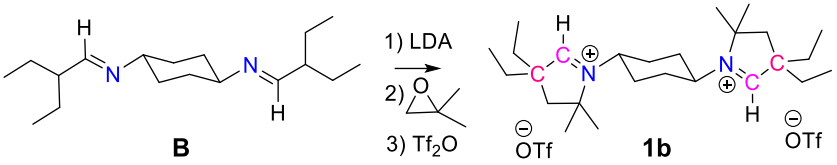


A **1a**

60 mL of a solution of LDA (120 mmol, 2.0 M) in THF was added dropwise to a solution of **A** (13.35 g, 60.00 mmol) in 100 mL of Et$_2$O at 0°C with stirring. After half an hour the mixture was warmed to room temperature and stirred for 6 hrs. Then the volatiles were removed under vacuum, residue was dissolved in 350 mL of Et$_2$O and isobutylene oxide (10.7 mL, 121 mmol) was added dropwise at 0 °C with stirring. After stirring the mixture for 12 hours at room temperature, triflic anhydride (20.3 mL, 121 mmol) was added dropwise at −78 °C. The reaction mixture was warmed to room temperature over 1 hour and stirred for 4 hrs at room temperature. The mixture was filtered and the residue obtained after filtration was washed with 250 mL of Et$_2$O (5 × 50 mL), dissolved in hot DMF (140 °C) and precipitated by layering with Et$_2$O. A white precipitate of **1a** was obtained as pure. **Yield:** 38.5%

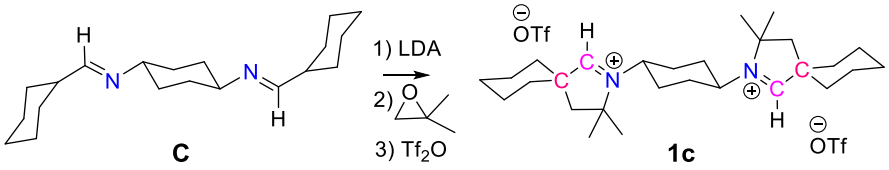
(14.57 g). **M.P.:** >180 °C. **1a** was crystallised by diffusing its saturated solution in DMF with Et_2O at room temperature. Crystals were suitable for single-crystal X-ray diffraction. **^{1}H NMR** (DMSO-d_6, 25 °C, 300 MHz): δ = 9.01 (s, 2H, N=*H*C), 3.86-4.01 (br, 2H, $^{Cy\text{-}B}$C*H*N), 2.11-2.24 (m, 4H, $^{bridged\text{-}Cy\text{-}B}$C*H*$_2$), 2.08 (s, 4H, C*H*$_2$), 1.87-2.02 (m, 4H, $^{bridged\text{-}Cy\text{-}B}$C*H*$_2$), 1.56 (s, 12H, C(C*H*$_3$)$_2$), 1.36 (s, 12H, C(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (DMSO-d_6, 25 °C, 75.4 MHz): δ = 183.9 (N=H*C*), 78.7 (*C*(CH$_3$)$_2$), 55.4 ($^{Cy\text{-}B}$*C*HN), 47.6 (*C*H$_2$), 46.56 (*C*(CH$_3$)$_2$), 31.8 ($^{bridged\text{-}Cy\text{-}B}$*C*H$_2$), 26.7 (C(*C*H$_3$)$_2$), 25.6 (C(*C*H$_3$)$_2$) ppm. **^{19}F{^{1}H} NMR** (DMSO-d_6, 25 °C, 282 MHz): δ = −77.8 ppm. **Elemental analysis:** calcd. (%) for $C_{24}H_{40}N_2F_6O_6S_2$: C, 45.71; H, 6.39; N, 4.44; S, 10.17; found: C, 45.75; H, 6.33; N, 4.44; S, 10.30. **HRMS-ESI (m/z):** Calculated for $C_{23}H_{40}N_2F_3O_3S_1$ [M-1OTf]$^+$: 481.2707, Found: 481.2718.

Synthesis of 1b



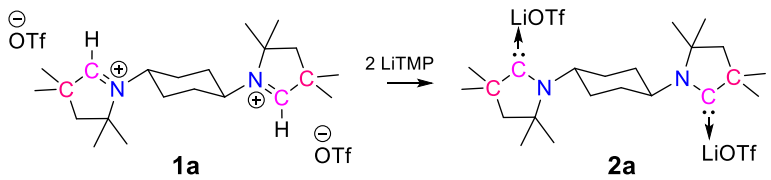
60 mL of a solution of LDA (120 mmol, 2.0 M) in THF was added dropwise to a solution of **B** (16.7 g, 60.0 mmol) in 100 mL of Et_2O at 0°C with stirring. After half an hour the mixture was warmed to room temperature and stirred for 10 hrs. Then the volatiles were removed under vacuum, residue was dissolved in 400 mL of Et_2O and isobutylene oxide (10.7 mL, 121 mmol) was added dropwise at 0 °C with stirring. After stirring the mixture for 12 hours at room temperature, triflic anhydride (20.3 mL, 121 mmol) was added dropwise at −78 °C. The reaction mixture was warmed to room temperature over 1 hour and stirred for 6 hrs at room temperature. The mixture was filtered and the residue obtained after filtration was washed with 300 mL of Et_2O (6 × 50 mL), dissolved in hot DMF (140 °C) and precipitated by layering with Et_2O. A white precipitate of **1b** was obtained as pure. **Yield:** 41.26% (17 g). **M.P.:** >180 °C. **1b** is also soluble in DCM and $CHCl_3$. We were not able to obtain single-crystal of **2b** suitable for single-crystal X-ray diffraction. **^{1}H NMR** (DMSO-d_6, 25 °C, 300 MHz): δ = 9.16 (s, 2H, N=*H*C), 3.84-3.99 (br, 2H, $^{Cy\text{-}B}$C*H*N), 2.10-2.24 (m, 4H, $^{bridged\text{-}Cy\text{-}B}$C*H*$_2$), 2.06 (s, 4H, C*H*$_2$), 1.91-2.03 (m, 4H, $^{bridged\text{-}Cy\text{-}B}$C*H*$_2$), 1.71 (q, 8H, $^3J_{H\text{-}H}$ = 7.5 Hz, C*H*$_2$CH$_3$), 1.56 (s, 12H, C(C*H*$_3$)$_2$), 0.89 (t, 12H, $^3J_{H\text{-}H}$ = 7.4 Hz, CH$_2$C*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (DMSO-d_6, 25 °C, 75.4 MHz): δ = 184.4 (N=H*C*), 78.4 (*C*(CH$_3$)$_2$), 55.8 ($^{Cy\text{-}B}$*C*HN), 54.8 (*C*(CH2CH$_3$)$_2$), 42.7 (*C*H$_2$), 32.0 ($^{bridged\text{-}Cy\text{-}B}$*C*H$_2$), 28.4 (*C*H$_2CH_3$), 27.0 (C(*C*H$_3$)$_2$), 8.6 (CH$_2$*C*H$_3$) ppm. **^{19}F{^{1}H} NMR** (DMSO-d_6, 25 °C, 282 MHz): δ = −77.8 ppm. **Elemental analysis:** calcd. (%) for $C_{28}H_{48}N_2F_6O_6S_2$: C, 48.97; H, 7.04; N, 4.08; S, 9.34; found: C, 48.93; H, 7.09; N, 4.08; S, 9.29. **HRMS-ESI (m/z):** Calculated for $C_{26}H_{48}N_2$ [M-2OTf]$^{2+}$: 194.1903, Found: 194.1910.

Synthesis of 1c



30.75 mL of a solution of LDA (61.5 mmol, 2.00 M) in THF was added dropwise to a solution of **C** (9.075 g, 30.00 mmol) in 80 mL of Et_2O at 0°C with stirring. After half an hour the mixture was warmed to room temperature and stirred for 6 hrs. Then the volatiles were removed under vacuum, residue was dissolved in 250 mL of Et_2O and isobutylene oxide (5.46 mL, 61.5 mmol) was added dropwise at 0 °C with stirring. After stirring the mixture for 12 hours at room temperature, triflic anhydride (10.4 mL, 61.8 mmol) was added dropwise at −78 °C. The reaction mixture was warmed to room temperature over 1 hour and stirred for 4 hrs at room temperature. The mixture was filtered and the residue obtained after filtration was washed with 300 mL of Et_2O (6 × 50 mL), dissolved in hot methanol (64 °C) and precipitated by layering with Et_2O. A white precipitate of **1c** was obtained as pure. **Yield:** 21.1%. **M.P.:** >180 °C. **1c** was crystallised by diffusing its saturated solution in methanol with Et_2O at room temperature. Crystals were suitable for single-crystal X-ray diffraction. **^{1}H NMR** (DMSO-d_6, 25 °C, 300 MHz): δ = 9.15 (s, 2H, N=*H*C), 3.84-4.05 (br, 2H, $^{Cy\text{-}B}CHN$), 2.16-2.27 (m, 4H, $^{bridged\text{-}Cy\text{-}B}CH_2$), 2.13 (s, 4H, CH_2), 1.94-2.08 (m, 4H, $^{bridged\text{-}Cy\text{-}B}CH_2$), 1.68-1.79 (m, 12H, $^{terminal\text{-}Cy\text{-}B}CH_2$), 1.59 (s, 12H, $C(CH_3)_2$), 1.36-1.56 (m, 8H, $^{terminal\text{-}Cy\text{-}B}CH_2$) ppm. **^{13}C{^{1}H} NMR** (DMSO-d_6, 25 °C, 75.4 MHz): δ = 183.2 (N=H*C*), 78.0 ($C(CH_3)_2$), 55.6 ($^{Cy\text{-}B}CHN$), 51.2 ($C(^{Cy\text{-}B}CH_2)_2$), 45.0 (CH_2), 33.6 ($^{terminal\text{-}Cy\text{-}B}CH_2$), 31.9 ($^{bridged\text{-}Cy\text{-}B}CH_2$), 27.1 ($C(CH_3)_2$), 24.4 ($^{terminal\text{-}Cy\text{-}B}CH_2$), 21.2 ($^{terminal\text{-}Cy\text{-}B}CH_2$) ppm. **^{19}F{^{1}H} NMR** (DMSO-d_6, 25 °C, 282 MHz): δ = −77.8 ppm. **Elemental analysis:** calcd. (%) for $C_{30}H_{48}N_2F_6O_6S_2$: C, 50.69; H, 6.81; N, 3.94; S, 9.02; found: C, 50.87; H, 6.77; N, 3.96; S, 9.07. **HRMS-ESI (m/z):** Calculated for $C_{28}H_{48}N_2$ $[M\text{-}2OTf]^{2+}$: 206.1903, Found: 206.1911.

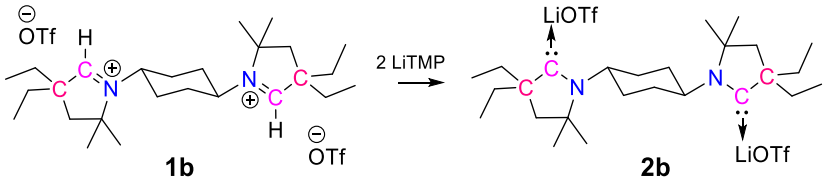
Synthesis of 2a



30 mL of THF was added to a mixture of **1a** (2.070 g, 3.282 mmol) and LiTMP (1.023 g, 6.950 mmol) at −35 °C with stirring and the reaction mixture was warmed to room temperature. After one hour stirring, about 50 mL of hexane was added to the reaction mixture and filtered. A white precipitate of the residue obtained after filtration was dried. The ^{1}H NMR spectrum of white residue showed the formation of **2a** as pure. **Yield:** 2.1 g (81%). **M.P.:** >175 °C (decomposed indicated by ^{1}H NMR, became

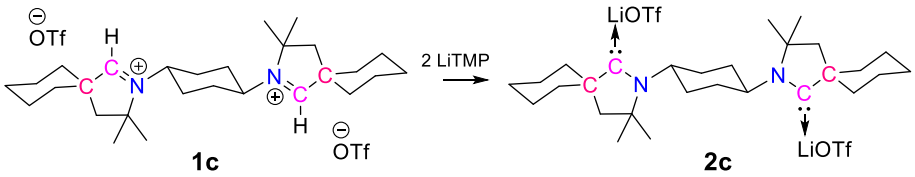
light yellow coloured at 165 °C). Suitable crystals for single-crystal X-ray diffraction were obtained by diffusing concentrated solution of **2a** in THF with pentane at room temperature for 24 hours. **^{1}H NMR** (THF-d_8, 25 °C, 300 MHz): δ = 3.60-3.63 (m, 4H, THF-CH_2OCH_2), 2.11-2.27 (m, 4H, NCH & $^{Cy\text{-}B}$CH_2), 1.79-1.89 (m, 6H, $^{Cy\text{-}B}$CH_2), 1.76-1.79 (m, 4H, THF-CH_2CH_2), 1.54 (s, 4H, CH_2), 1.32 (s, 12H, CH_3), 1.10 (s, 12H, CH_3) ppm. **^{13}C{^{1}H} NMR** (THF-d_8, 25 °C, 75.4 MHz): δ = (We were not able to get the resonance of carbenic carbon in this case due to the poor solubility of **2a**), 121.4 (q, $^{1}J_{C\text{-}F}$ = 319.2 Hz, $CF_3SO_3^-$), 79.4 ($C(CH_3)_2$), 68.0 (THF-CH_2OCH_2), 56.1 ($C(CH_3)_2$), 55.6 (CH), 51.4 (CH_2), 35.5 ($^{Cy\text{-}B}CH_2$), 28.8 ($C(CH_3)_2$), 28.0 ($C(CH_3)_2$), 26.2 (THF-CH_2CH_2) ppm. **^{7}Li NMR** (THF-d_8, 25 °C, 116.6 MHz): −23.8 ppm. **^{19}F{^{1}H} NMR** (THF-d_8, 25 °C, 282 MHz): δ = −79.4 ppm. Most likely due to high fluorine content, we were not able to get satisfactory elemental analysis data even after repeating measurements. **HRMS-ESI (m/z):** Calculated for $C_{32}H_{55}F_6Li_2N_2O_8S_2$ $[M+H]^+$: 787.3608, Found: 787.3560.

Synthesis of 2b



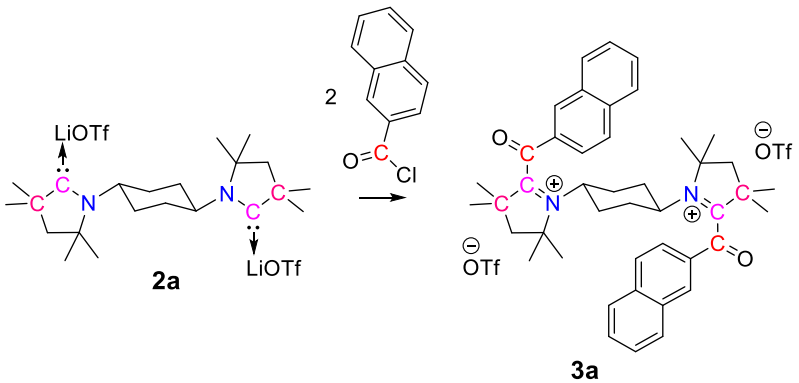
40 mL of THF was added to a mixture of **1b** (5.026 g, 7.318 mmol) and LiTMP (2.4 g, 16.305 mmol) at −35 °C with stirring and the reaction mixture was warmed to room temperature. After one hour of stirring, about 80 mL of pentane was added to the reaction mixture and filtered. A white precipitate of the residue obtained after filtration was dried. The ^{1}H NMR spectrum of white residue showed the formation of **2b** as pure. **Yield:** 5.367 g (87%). **M.P.:** 126 °C (decomposed). Suitable crystals for single-crystal X-ray diffraction were obtained by diffusing a concentrated solution of **2b** in THF with pentane at room temperature for 24 hours. **^{1}H NMR** (THF-d_8, 25 °C, 300 MHz): δ = 3.60-3.66 (m, 4H, THF-CH_2OCH_2), 2.09-2.24 (m, 4H, NCH & $^{Cy\text{-}B}$CH_2), 1.78-1.90 (m, 6H, $^{Cy\text{-}B}$CH_2), 1.74-1.77 (m, 4H, THF-CH_2CH_2), 1.51-1.55 (m, 8H, CH_2CH$_3$), 1.51 (s, 4H, CH_2), 1.33 (s, 12H, CH$_3$), 0.81 (t, 12H, $^{3}J_{H\text{-}H}$ = 6.7 Hz, CH$_2$CH_3) ppm. **^{13}C{^{1}H} NMR** (THF-d_8, 25 °C, 75.4 MHz): δ =296.2 (Li$C_{carbene}$), 121.3 (q, $^{1}J_{C\text{-}F}$ = 319.2 Hz, $CF_3SO_3^-$), 79.0 ($C(CH_3)_2$), 68.0 (THF-CH_2OCH_2), 64.3 ($C(CH_3)_2$), 55.9 (CH), 44.5 (CH_2), 35.8 ($^{Cy\text{-}B}CH_2$), 31.4 (CH_2CH_3), 28.6 ($C(CH_3)_2$), 26.2 (THF-CH_2CH_2), 9.6 (CH_2CH_3) ppm. **^{7}Li NMR** (THF-d_8, 25 °C, 116.6 MHz): −23.9 ppm. **^{19}F{^{1}H} NMR** (THF-d_8, 25 °C, 282 MHz): δ = −79.5 ppm. Most likely due to high fluorine content, we were not able to get satisfactory elemental analysis data even after repeating measurements. **HRMS-ESI (m/z):** Calculated for $C_{36}H_{62}F_6Li_2N_2O_8S_2$ $[M]^{2+}$: 421.2081, Found: 421.2050.

Synthesis of 2c



About 40 mL of THF was added to a mixture of **1c** (5.180 g, 7.287 mmol) and LiTMP (2.2 g, 14.947 mmol) at −35 °C with stirring and the reaction mixture was warmed to room temperature. After one hour stirring, about 80 mL of pentane was added to the reaction mixture and filtered. A white precipitate of the residue obtained after filtration was dried. The ^{1}H NMR spectrum of white residue showed the formation of **2c** as pure. **Yield:** 5.056 g (80%). **M.P.:** >170 °C (decomposed indicated by ^{1}H NMR, became yellow coloured at 145 °C). Suitable crystals for single-crystal X-ray diffraction were obtained by diffusing concentrated solution of **2c** in THF with pentane at room temperature for 24 hours. **^{1}H NMR** (THF-d_8, 25 °C, 300 MHz): δ = 3.60-3.63 (m, 4H, THF-CH_2OCH_2), 2.09-2.23 (m, 4H, NCH & $^{Cy\text{-}B}$CH_2), 1.82-1.92 (m, 6H, $^{bridged\text{-}Cy\text{-}B}CH_2$), 1.78-1.82 (m, 8H, $^{Cy\text{-}B}$CH_2), 1.75-1.77 (m, 4H, THF-CH_2CH_2), 1.56-1.62 (m, 2H, $^{Cy\text{-}B}$CH_2), 1.55 (s, 4H, CH_2), 1.38-1.40 (m, 6H, $^{Cy\text{-}B}$CH_2), 1.33 (s, 12H, CH_3), 1.09-1.12 (m, 4H, $^{Cy\text{-}B}$CH_2) ppm. **^{13}C{^{1}H} NMR** (THF-d_8, 25 °C, 75.4 MHz): δ = (We were not able to get the resonance of carbenic carbon in this case due to the poor solubility of the compound), 121.3 (q, $^{1}J_{C\text{-}F}$ = 319.2 Hz, $CF_3SO_3^-$), 77.9 ($C(CH_3)_2$), 68.0 (THF-CH_2OCH_2), 61.4 ($C(CH_3)_2$), 55.6 (CH), 48.8 (CH_2), 36.5 ($^{Cy\text{-}B}CH_2$), 35.7 ($^{Cy\text{-}B}CH_2$), 29.3 (C(CH_3)$_2$), 26.9 ($^{Cy\text{-}B}CH_2$), 26.2 (THF-CH_2CH_2), 23.5 ($^{Cy\text{-}B}CH_2$) ppm. **^{7}Li NMR** (THF-d_8, 25 °C, 116.6 MHz): −23.8 ppm. **^{19}F{^{1}H} NMR** (THF-d_8, 25 °C, 282 MHz): δ = −79.4 ppm. Most likely due to high fluorine content, we were not able to get satisfactory elemental analysis data even after repeating measurements. **HRMS-ESI (m/z):** Calculated for $C_{38}H_{64}F_6Li_2N_2O_8S_2$ $[M+2H]^{2+}$: 434.2159, Found: 434.2180.

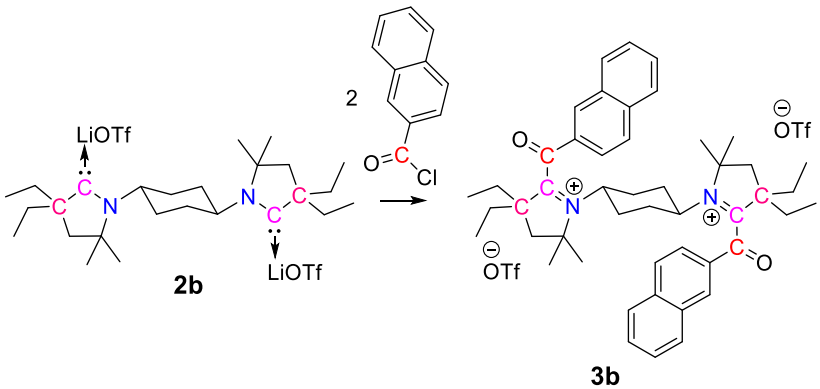
Synthesis of 3a



50 mL of THF was added to a mixture of **2a** (2.013 g, 2.558 mmol) and 2-naphthoyl chloride (1.300 g, 6.819 mmol) at room temperature with stirring. The reaction mixture became a clear solution. After

stirring the reaction mixture for 1 hour, precipitate started to appear. After 4 hours stirring, about 100 mL of diethyl ether was added to the reaction mixture and the precipitate was filtered. ^{1}H, ^{7}Li, ^{19}F NMR spectra of the precipitate showed the presence of **3a** along with lithium chloride. The precipitate was dissolved in about 40 mL of DCM, and combined with 200 mL of water in a separating funnel. DCM (5 × 40 mL) was added to the water layer, shaken well, allowed to stand and then DCM layer was collected. All DCM layers were combined and dried over anhydrous $MgSO_4$. The solution in DCM was concentrated to 10 mL and 200 mL of diethyl ether was added and sonicated to get the precipitate of **3a**. The precipitate was filtered and dried. ^{1}H, ^{7}Li, ^{19}F NMR spectra of the precipitate showed the presence of **3a** as pure. **Yield:** 1.704 g (71%). **M.P.:** >180 °C. We were not able to get the suitable crystals for single-crystal X-ray diffraction. **^{1}H NMR** (CD_3CN, 25 °C, 300 MHz): δ = 8.41 (s, 2H, H_{Ar}), 8.26 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, H_{Ar}), 8.00-8.14 (m, 4H, H_{Ar}), 7.90 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.2 Hz, H_{Ar}), 7.82 (t, 2H, $^{3}J_{H\text{-}H}$ = 7.2 Hz, H_{Ar}), 7.72 (t, 2H, $^{3}J_{H\text{-}H}$ = 7.3 Hz, H_{Ar}), 3.71-3.91 (m, 2H, C*H*), 2.33 (s, 4H, CH_2), 2.16-2.24 (br, 4H, $^{Cy\text{-}B}$CH_2), 1.75-1.87 (br, 4H, $^{Cy\text{-}B}$CH_2), 1.48-1.74 (br, 12H, CH_3), 1.35 (s, 6H, CH_3), 1.30 (s, 6H, CH_3) ppm. **^{13}C{^{1}H} NMR** (CD_3CN, 25 °C, 75.4 MHz): δ = 192.5 (*C*=N$^+$), 187.7 (*C*=N$^+$), 138.1 (C_{Ar}), 137.2 (HC_{Ar}), 133.1 (C_{Ar}), 132. (HC_{Ar}), 131.8 (HC_{Ar}), 130.9 (C_{Ar}), 130.5(HC_{Ar}), 129.0 (HC_{Ar}), 128.8 (HC_{Ar}), 124.0 (HC_{Ar}), 122.1 (q, $^{1}J_{C\text{-}F}$ = 320.8 Hz, *C*$F_3SO_3^-$), 83.5 (*C*$(CH_3)_2$), 61.7 (*C*H), 51.6 (*C*$(CH_3)_2$), 49.4 (*C*H_2), 32.0 ($^{Cy\text{-}B}$CH_2), 27.9 (C(*C*$H_3)_2$) ppm. **^{19}F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = −79.3 ppm. **Elemental analysis:** calcd. (%) for $C_{46}H_{52}N_2F_6O_8S_2$: C, 58.84; H, 5.58; N, 2.98; S, 6.83; found: C, 60.08; H, 5.72; N, 3.15; S, 5.79. **HRMS-ESI (m/z):** Calculated for $C_{44}H_{52}N_2O_2$ [M-2OTf]$^{2+}$: 320.2009, Found: 320.2010.

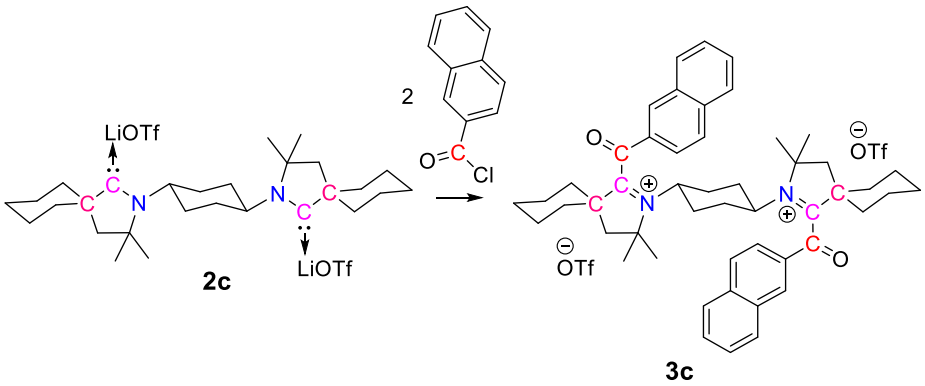
Synthesis of 3b



20 mL of THF was added to a mixture of **2b** (2.000 g, 2.373 mmol) and 2-naphthoyl chloride (1.200 g, 6.295 mmol) at −35 °C and the reaction mixture was warmed to room temperature. After 4 hours stirring, the reaction mixture was concentrated to 10 mL and 150 mL of diethyl ether was added. The mixture was sonicated for 2 minutes and filtered. The residue obtained after filtration was dissolved in 30 mL of DCM and combined with 150 mL of water in a separating funnel. DCM (3 × 40 mL) was added to the water layer, shaken well, allowed to stand and then DCM layer was collected. All DCM

layers were combined and dried over anhydrous $MgSO_4$. The solution in DCM was concentrated to 5 mL and 200 mL of diethyl ether was added to get the precipitate of **3b**. The precipitate of **3b** obtained after filtration was collected and dried. ^{1}H, ^{7}Li, ^{19}F NMR spectra of the precipitate showed the presence of **3b** as pure. **Yield:** 1.9 g (80%). **M.P.:** >180 °C. Suitable crystals for single-crystal X-ray diffraction were obtained by diffusing the concentrated solution of **3b** in acetonitrile with diethyl ether at room temperature for 10 days. **^{1}H NMR** (CD_3CN, 25 °C, 300 MHz): δ = 8.25-8.41 (br, 2H, H_{Ar}), 8.20 (d, 2H, $^{3}J_{H-H}$ = 8.3 Hz, H_{Ar}), 8.00- 8.15 (m, 4H, H_{Ar}), 7.83 (t, 4H, $^{3}J_{H-H}$ = 7.5 Hz, H_{Ar}), 7.72 (t, 2H, $^{3}J_{H-H}$ = 7.4 Hz, H_{Ar}), 3.74-3.93 (m, 2H, C*H*), 2.26-2.27 (m, 4H, CH_2), 2.14-2.26 (m, 4H, $^{Cy\text{-}B}CH_2$), 1.57-1.80 (m, 8H, CH_2), 1.57-1.80 (m, 12H, CH_3), 1.38-1.57 (m, 4H, CH_2), 0.91 (s, 6H, CH_3), 0.72 (s, 6H, CH_3) ppm. **^{13}C{^{1}H} NMR** (CD_3CN, 25 °C, 75.4 MHz): δ = 191.9 (C=N^+), 188.0 (C=N^+), 138.1 (C_{Ar}), 135.5 (HC_{Ar}), 132.9 (C_{Ar}), 132.3 (HC_{Ar}), 131.5 (HC_{Ar}), 131.4 (C_{Ar}), 130.7 (HC_{Ar}), 129.1 (HC_{Ar}), 124.4 (HC_{Ar}), 122.1 (q, $^{1}J_{C-F}$ = 321.2 Hz, $CF_3SO_3^-$), 83.2 ($C(CH_3)_2$), 79.4 ($C(CH_3)_2$), 61.8 (*C*H), 60.1 ($C(CH_3)_2$), 56.3 ($C(CH_3)_2$), 43.4 (CH_2), 43.0, 32.3 ($^{Cy\text{-}B}CH_2$), 31.7 (CH_2), 30.2 (CH_2), 29.8 (CH_2), 29.6 (CH_3), 27.5 (CH_3), 27.3 (CH_3), 9.2 (CH_3), 8.9 (CH_3) ppm. **^{19}F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = −79.3 ppm. **Elemental analysis:** calcd. (%) for $C_{50}H_{60}N_2F_6O_8S_2$: C, 60.35; H, 6.08; N, 2.82; S, 6.44; found: C, 59.48; H, 5.95; N, 2.89; S, 6.48. **HRMS-ESI (m/z):** Calculated for $C_{48}H_{60}N_2O_2$ $[M\text{-}2OTf]^{2+}$: 348.2322, Found: 348.2324.

Synthesis of 3c

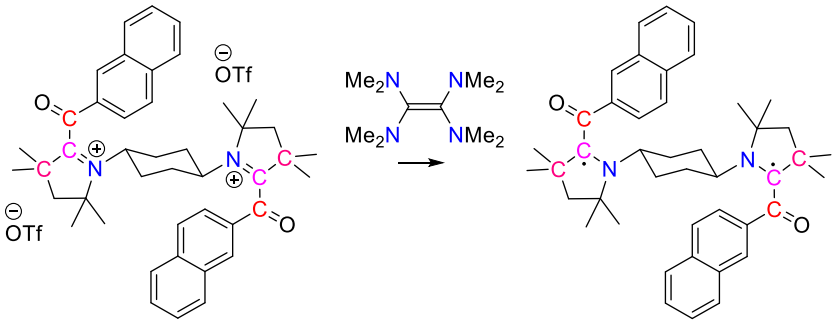


2c **3c**

20 mL of THF was added to a mixture of **2c** (1.068 g, 1.232 mmol) and 2-naphthoyl chloride (587 mg, 3.08 mmol) at −35 °C and the reaction mixture warmed to room temperature. After 4 hours stirring, the reaction mixture was concentrated to 5 mL and 50 mL of diethyl ether was added. The mixture was sonicated for 2 minutes and then filtered. The residue obtained after filtration was dissolved in 40 mL of DCM and combined with 150 mL of water in a separating funnel. DCM (3 × 20 mL) was added to the water layer, shaken well, allowed to stand and then DCM layer was collected. All DCM layers were combined and dried over anhydrous $MgSO_4$. The solution in DCM was concentrated to 5 mL and 200 mL of diethyl ether was added and sonicated for 5 minutes to get the precipitate of **3c**. The precipitate of **3c** obtained after filtration was dried. ^{1}H, ^{7}Li, ^{19}F NMR spectra of the precipitate showed

the presence of **3c** as pure. **Yield:** 1.02 g (81%). **M.P.:** >180 °C. We were not able to get the suitable crystals for single-crystal X-ray diffraction. **^{1}H NMR** (CD_3CN, 25 °C, 300 MHz): δ = 8.28-8.52 (br, 2H, H_{Ar}), 8.24 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, H_{Ar}), 8.00-8.17 (m, 4H, H_{Ar}), 7.77-7.94 (m, 4H, H_{Ar}), 7.65-7.76 (m, 2H, H_{Ar}), 3.67-3.92 (m, 2H, C*H*), 2.31-2.50 (m, 4H, CH_2), 2.12-2.19 (m, 2H, $^{Cy\text{-}B}CH_2$), 1.78-1.85 (br, 4H, $^{Cy\text{-}B}CH_2$), 1.70 (s, 6H, CH_3), 1.67 (s, 6H, CH_3), 1.46-1.59 (m, 12H, $^{Cy\text{-}B}CH_2$), 1.28-1.44 (m, 4H, $^{Cy\text{-}B}CH_2$), 1.08-1.25 (m, 4H, $^{Cy\text{-}B}CH_2$), 0.93-1.05 (m, 2H, $^{Cy\text{-}B}CH_2$) ppm. **^{13}C{^{1}H} NMR** (CD_3CN, 25 °C, 75.4 MHz): δ = 192.0 (C=N$^+$), 187.6 (C=N$^+$), 138.2 (C_{Ar}), 133.0 (C_{Ar}), 132.3 (HC_{Ar}), 131.4 (HC_{Ar}), 131.2 (C_{Ar}), 130.6 (HC_{Ar}), 129.09 (HC_{Ar}), 129.06 (HC_{Ar}), 124.2 (HC_{Ar}), 122.1 (q, $^{1}J_{C\text{-}F}$ = 321.1 Hz, $CF_3SO_3^-$), 83.2 ($C(CH_3)_2$), 61.8 (*C*H), 61.2 (*C*H), 56.7 ($C(CH_3)_2$), 44.2 (CH_2), 36.0 ($^{Cy\text{-}B}CH_2$), 35.4 ($^{Cy\text{-}B}CH_2$), 32.2 ($^{Cy\text{-}B}CH_2$), 28.6 (CH_3), 27.8 (CH_3), 24.5 ($^{Cy\text{-}B}CH_2$), 21.9 ($^{Cy\text{-}B}CH_2$) ppm. **^{19}F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = −79.3 ppm. **Elemental analysis:** calcd. (%) for $C_{52}H_{60}N_2F_6O_8S_2$: C, 61.28; H, 5.93; N, 2.75; S, 6.29; found: C, 61.63; H, 6.11; N, 2.92; S, 5.92. **HRMS-ESI (m/z):** Calculated for $C_{50}H_{60}N_2O_2$ $[M\text{-}2OTf]^{2+}$: 360.2322, Found: 360.2325.

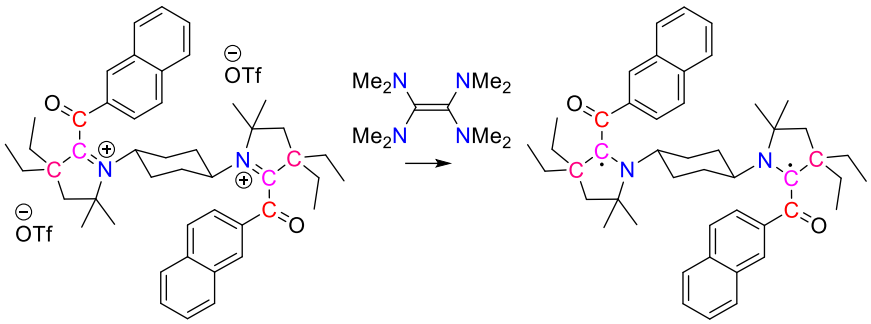
Synthesis of 4a



3a **4a**

TDAE (100 mg, 0.5 mmol) was added dropwise to a solution of **3a** in 10 mL of acetonitrile (417 mg, 0.444 mmol) at room temperature with stirring. After 2 hours, the mixture was filtered and the red-coloured residue obtained after filtration was washed with 5 mL of acetonitrile followed by 20 mL of pentane and dried under vacuum. The formation of the red-coloured residue as **4a** has been confirmed by the EPR spectroscopy. **Yield:** 245 mg (86%). **M.P.:** 145 °C (**4a** decomposed upon melting. The red colour changed to light yellow colour upon melting). **UV/Vis** (DCM): λ_{max} (ε) = 428 (2980), 286 (16200), 267 (16800) nm ($Lmol^{-1}cm^{-1}$). **HRMS-ESI (m/z):** Calculated for $C_{44}H_{53}N_2O_2$ $[M+H]^+$: 641.4102, Found: 641.4112; Calculated for $C_{44}H_{52}N_2O_2$ $[M]^{2+}$: 320.2009, Found: 320.2024.

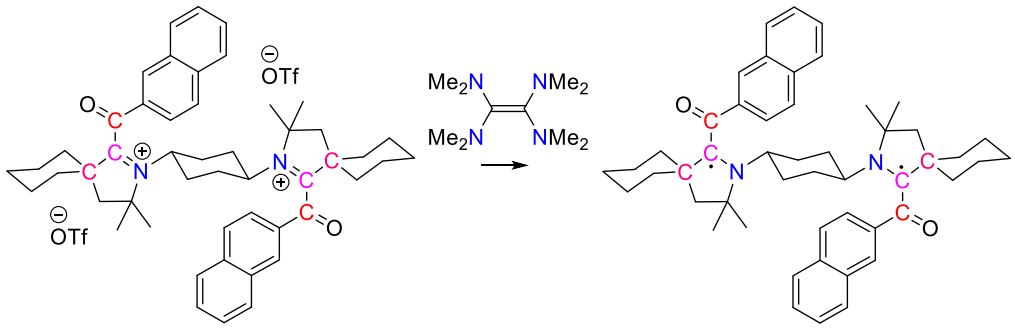
Synthesis of 4b



3b **4b**

TDAE (95 mg, 0.47 mmol) was added to a solution of **3b** (383 mg, 0.385 mmol) in 10 mL of acetonitrile at room temperature and shaken for 10 seconds. The black-coloured crystals of **4b** started to appear and then reaction mixture was allowed to stand at room temperature for 6 hours. The bright black-coloured crystals were collected by filtration and mother liquor was kept at −35 °C for 12 hours for further crystallisation. The crystals of **4b** were washed with, acetonitrile, pentane, and dried under vacuum. **Yield:** 190 mg (71%). **M. P.:** 155 °C (**4b** decomposed before melting. The black colour of crystals started to change into greenish yellow colour at 149 °C but black colour was stable up to 140 °C). **UV/Vis** (THF): λ_{max} (ε) = 540 (2170), 430 (2870), 326 (8020), 285 (13700), 270 (12300) nm ($Lmol^{-1}cm^{-1}$). **HRMS-ESI (m/z):** Calculated for $C_{48}H_{60}N_2O_2$ $[M]^{2+}$: 348.2322, Found: 348.2335.

Synthesis of 4c

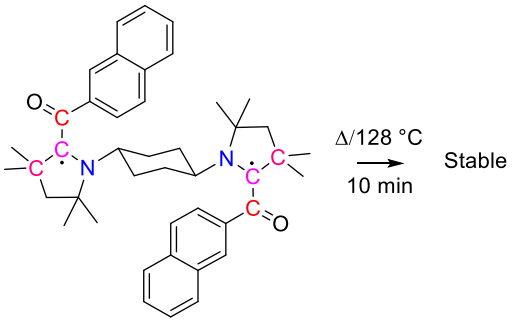


3c **4c**

TDAE (120 mg, 0.60 mmol) was added to a solution of **3c** (530 mg, 0.520 mmol) in 10 mL of acetonitrile at room temperature and shaken for 10 seconds. The black-coloured crystals of **4c** started to appear and then reaction mixture was allowed to stand at room temperature for 8 hours. The bright black-coloured crystals of **4c** obtained by filtration were washed with acetonitrile, pentane, and dried under vacuum. **Yield:** 250 mg (67%). Suitable crystals for single-crystal X-ray diffraction were obtained from its saturated solution in DCM at −35 °C. **M. P.:** 146 °C (**4c** decomposed upon melting. The black colour of crystals changed to yellow colour upon melting). **UV/Vis** (THF): λ_{max} (ε) = 542 (1430), 425 (2920), 326 (7990), 282 (14100), 270 (13400) nm ($Lmol^{-1}cm^{-1}$). **HRMS-ESI (m/z):**

Calculated for $C_{50}H_{60}N_2O_2$ $[M]^{2+}$: 360.2322, Found: 360.2340; Calculated for $C_{50}H_{61}N_2O_2$ $[M+H]^+$: 721.4728, Found: 721.4727.

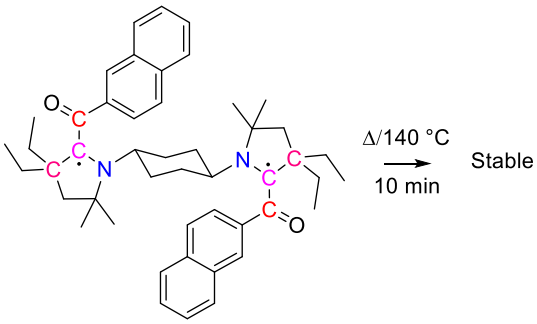
Thermal Stability of 4a



4a

About 4 mg of **4a** was taken in an NMR tube and held into the silicon oil bath the temperature of which was 128 °C (temperature measured by the thermometer) for 10 minutes. The color and the physical state of the crystals were the same as before heating. The UV/Vis spectrum of **4a** after heating at 128 °C for 10 minutes was measured which was the same as before heating (Fig. S62). When **4a** was heated at 140 °C, it was decomposed as colour and physical state were changed and also the UV/Vis spectrum was not the same as of **4a**.

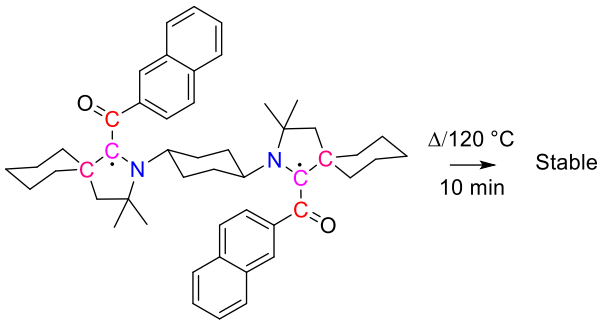
Thermal Stability of 4b



4b

About 2 mg of crystals of **4b** was taken in an NMR tube and held into the silicon oil bath the temperature of which was measured by the thermometer. The silicon oil bath was started to heat up to 140°C and kept at this temperature for 10 minutes. The color and the physical state of the crystals were the same as before heating. The UV/Vis spectrum of **4b** after heating at 140 °C for 10 minutes was measured which was the same as before heating (Fig. S63). When **4b** was heated at 150 °C, it was decomposed as colour and physical state were changed and also the UV/Vis spectrum was not the same as that of **4b**.

Thermal Stability of 4c



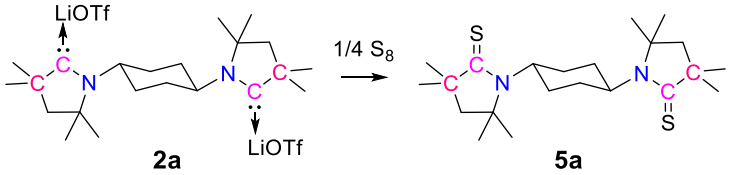
4c

About 2 mg of **4c** was taken in an NMR tube and held into the silicon oil bath the temperature of which was 120-124 °C (temperature measured by the thermometer) for 10 minutes. The color and the physical state of the crystals were the same as before heating. The UV/Vis spectrum of **4c** after heating at 120 °C for 10 minutes was measured which was the same as before heating (Fig. S64). When **4c** was heated at 130 °C, it was decomposed as colour was changed and also the UV/Vis spectrum was not the same as that of **4c**.

Table S1. Summary of melting points of **4a**, **4b**, and **4c**.

Compounds	Melting Point	Stable up to
4a	145 °C (decomposed)	128 °C
4b	155 °C (decomposed)	140 °C
4c	146 °C (decomposed)	120 °C

Synthesis of 5a

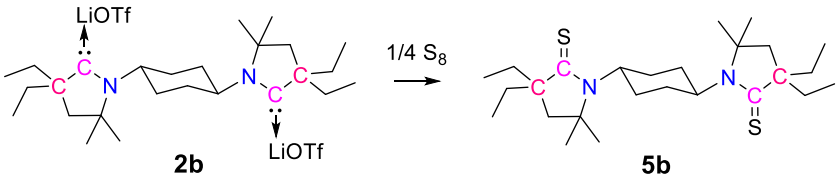


2a **5a**

20 mL of THF was added to a mixture of **2a** (338 mg, 0.429 mmol) and sulfur (38 mg, 1.2 mmol) at room temperature and then sonicated for 5 minutes. The reaction mixture was stirred for 6 hours and the volatiles were removed under vacuum. Then 30 mL of acetonitrile was added to the mixture and sonicated for 2 minutes. The mixture was filtered and a white precipitate obtained after filtration was dried. The ^{1}H NMR spectrum of the precipitate showed the formation of **5a**. Then the precipitate was dissolved in 60 mL of DCM and filtered. The filtrate was concentrated to 8 mL and the product was precipitated by layering the filtrate with acetonitrile. The precipitate obtained after filtration was dried to get **5a** as a white crystalline solid. **Yield:** 140 mg (87%). **M.P.:** >173 °C. Suitable crystals for

single-crystal X-ray diffraction were obtained by evaporating a solution of **5a** in DCM (6 mL) at room temperature. **^{1}H NMR** ($CDCl_3$, 25 °C, 300 MHz): δ = 3.47-3.73 (br, 4H, $^{Cy\text{-}B}CH_2$), 3.26-3.47 (br, 2H, $^{Cy\text{-}B}CHN$), 1.94 (S, 4H, CH_2), 1.50-1.68 (br, 4H, $^{Cy\text{-}B}CH_2$), 1.36 (s, 12H, $C(CH_3)_2$), 1.28 (s, 12H, $C(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** ($CDCl_3$, 25 °C, 75.4 MHz): δ = 208.5 (*C*=S), 68.3 ($C(CH_3)_2$), 56.3 (*C*H), 50.4 ($C(CH_3)_2$), 50.0 (CH_2), 31.0 ($C(CH_3)_2$), 28.3 ($C(CH_3)_2$), 26.4 ($^{Cy\text{-}B}CH_2$) ppm. **HRMS-ESI (m/z):** Calculated for $C_{22}H_{39}N_2S_2$ $[M+H]^+$: 395.2550, Found: 395.2556.

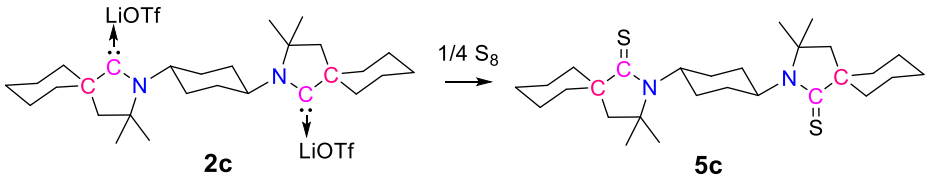
Synthesis of 5b



2b **5b**

20 mL of THF was added to a mixture of **2b** (310 mg, 0.37 mmol) and sulfur (40 mg, 1.2 mmol) at room temperature and then sonicated for 5 minutes. The reaction mixture was stirred for 6 hours and the volatiles were removed under vacuum. Then 30 mL of acetonitrile was added to the mixture and sonicated for 2 minutes. The mixture was filtered and a white precipitate obtained after filtration was dried. The ^{1}H NMR spectrum of the precipitate showed the formation of **5b**. Then the precipitate was dissolved in 50 mL of chloroform and filtered. The filtrate was evaporated under vacuum to get **5b** as a white solid. **Yield:** 130 mg (78%). **M.P.:** >173 °C. Suitable crystals for single-crystal X-ray diffraction study were obtained by keeping saturated solution of **5b** in THF-toluene (1:10) mixture at −35 °C for 24 hours. **^{1}H NMR** ($CDCl_3$, 25 °C, 300 MHz): δ = 3.55-3.69 (m, 4H, $^{Cy\text{-}B}CH_2$), 3.27-3.47 (br, 2H, $^{Cy\text{-}B}CHN$), 1.87 (s, 4H, CH_2), 1.68-1.80 (m, 4H, CH_2CH_3), 1.53-1.60 (m, 4H, CH_2CH_3), 1.46-1.52 (m, 4H, $^{Cy\text{-}B}CH_2$), 1.35 (s, 12H, $C(CH_3)_2$), 0.83 (t, 12H, $^{3}J_{H\text{-}H}$ = 7.3 Hz, CH_2CH_3) ppm. **^{13}C{^{1}H} NMR** ($CDCl_3$, 25 °C, 75.4 MHz): δ = 206.2 (*C*=S), 68.5 ($C(CH_3)_2$), 58.7 ($C(CH_3)_2$), 56.6 (*C*H), 41.4 (CH_2), 34.1 (CH_2CH_3), 28.5 ($C(CH_3)_2$), 26.5 ($^{Cy\text{-}B}CH_2$), 9.1 (CH_2CH_3) ppm. **Elemental analysis:** calcd. (%) for $C_{26}H_{46}N_2S_2$: C, 69.28; H, 10.29; N, 6.21; S, 14.22; found: C, 69.53; H, 10.33; N, 6.18; S, 15.08. **HRMS-ESI (m/z):** Calculated for $C_{26}H_{47}N_2S_2$ $[M+H]^+$: 451.3176, Found: 451.3186.

Synthesis of 5c



2c **5c**

20 mL of THF was added to a mixture of **2c** (294 mg, 0.339 mmol) and sulfur (38 mg, 1.2 mmol) at room temperature and then sonicated for 5 minutes. The reaction mixture was stirred for 6 hours

and the volatiles were removed under vacuum. Then 30 mL of acetonitrile was added to the mixture and sonicated for 2 minutes. The mixture was filtered and a white precipitate obtained after filtration was dried. The ^{1}H NMR spectrum of the precipitate showed the formation of **5c**. Then the precipitate was dissolved in 60 mL of chloroform and filtered. The filtrate was evaporated under vacuum to get **5c** as a white solid. The white solid was washed with about 2 mL of DCM. **Yield:** 148 mg (92%). **M.P.:** >173 °C. Suitable crystals for single-crystal X-ray diffraction were obtained by evaporating its saturated solution in 10 mL of DCM at room temperature. **^{1}H NMR** ($CDCl_3$, 25 °C, 300 MHz): δ = 3.47-3.73 (br, 4H, $^{Cy\text{-}B}CH_2$), 3.25-3.47 (br, 2H, $^{Cy\text{-}B}CHN$), 1.96-2.09 (m, 4H, $^{Cy\text{-}B}CH_2$), 1.93 (s, 4H, CH_2), 1.62-1.74 (br, 6H, $^{Cy\text{-}B}CH_2$), 1.51-1.59 (m, 6H, $^{Cy\text{-}B}CH_2$), 1.35 (s, 12H, $C(CH_3)_2$), 1.27-1.31 (m, 8H, $^{Cy\text{-}B}CH_2$) ppm. **^{13}C{^{1}H} NMR** ($CDCl_3$, 25 °C, 75.4 MHz, we were not able to get all resonances of carbon due to the poor solubility): δ = 68.8, 56.4, 55.2, 38.2, 28.7, 26.6, 25.3, 22.7. **HRMS-ESI (m/z):** Calculated for $C_{28}H_{47}N_2S_2$ $[M+H]^+$: 475.3176, Found: 475.3185.

NMR Spectra

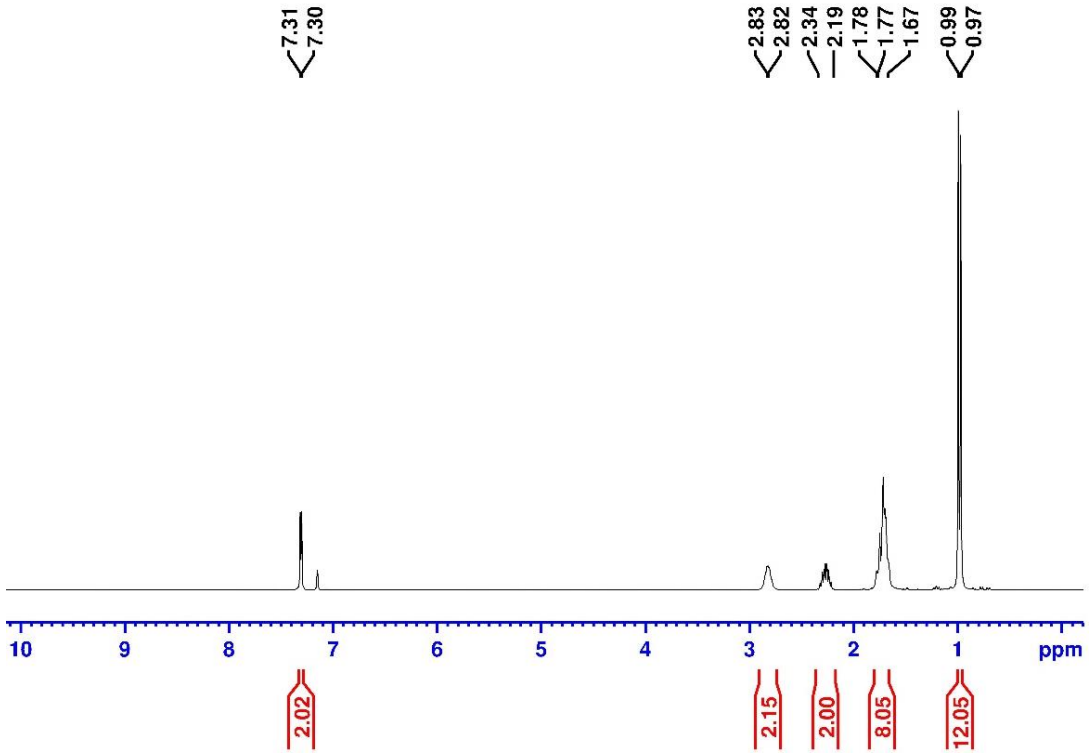


Fig. S1 ^{1}H NMR spectrum of **A** in C_6D_6 at room temperature.

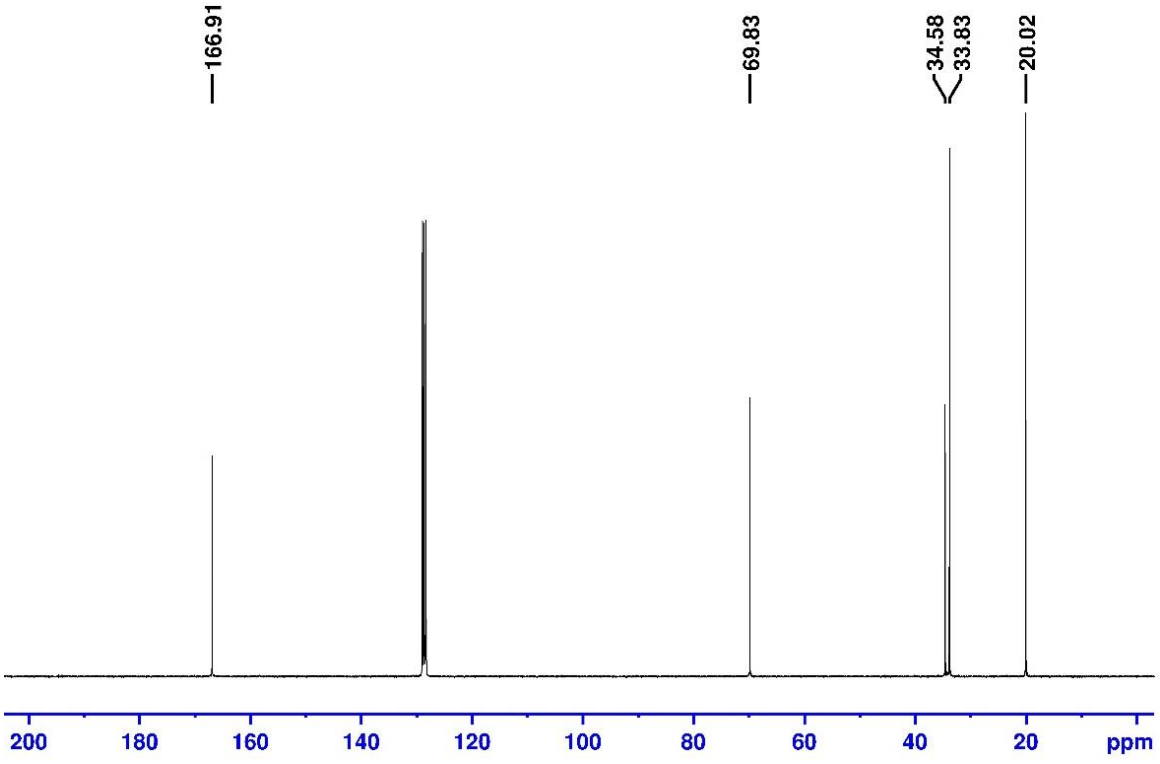


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of **A** in C_6D_6 at room temperature.

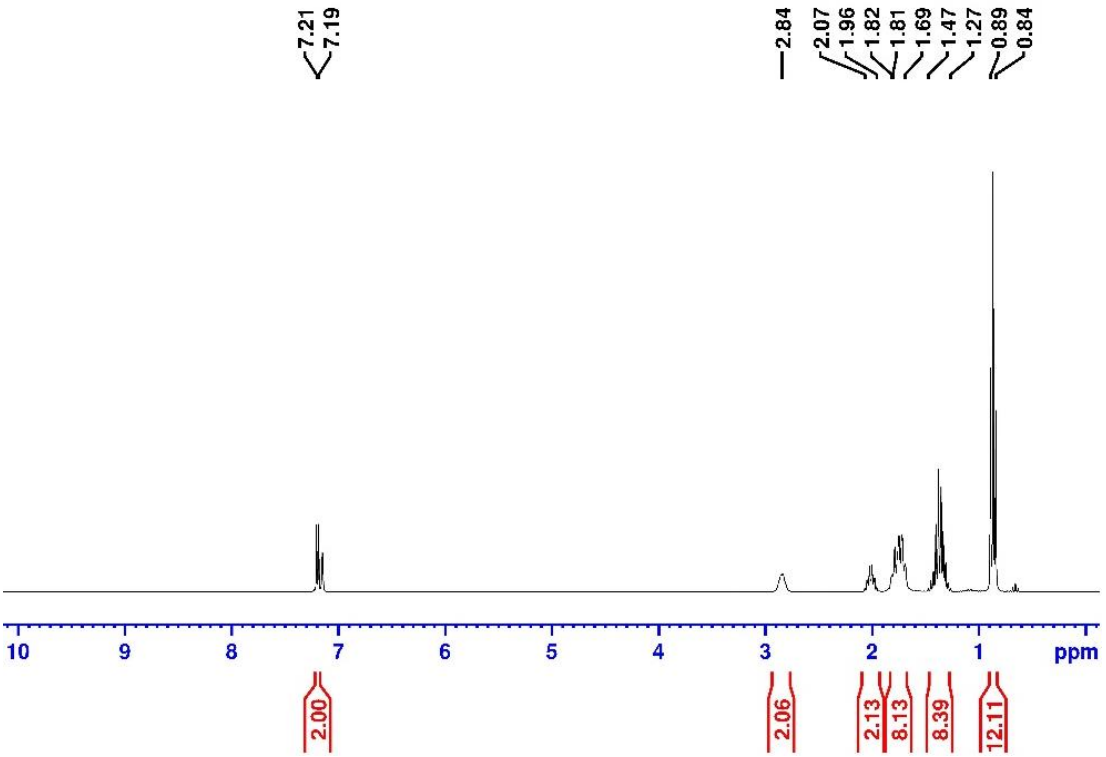


Fig. S3 ^{1}H NMR spectrum of **B** in C_6D_6 at room temperature.

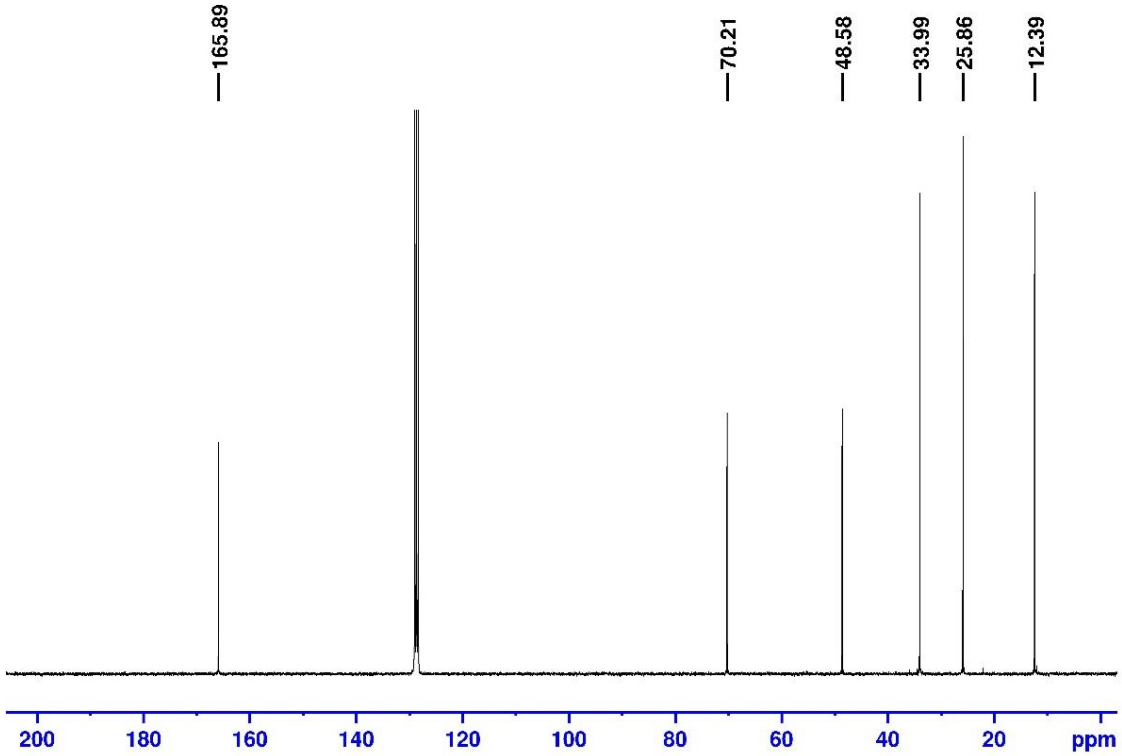


Fig. S4 $^{13}C\{^{1}H\}$ NMR spectrum of **B** in C_6D_6 at room temperature.

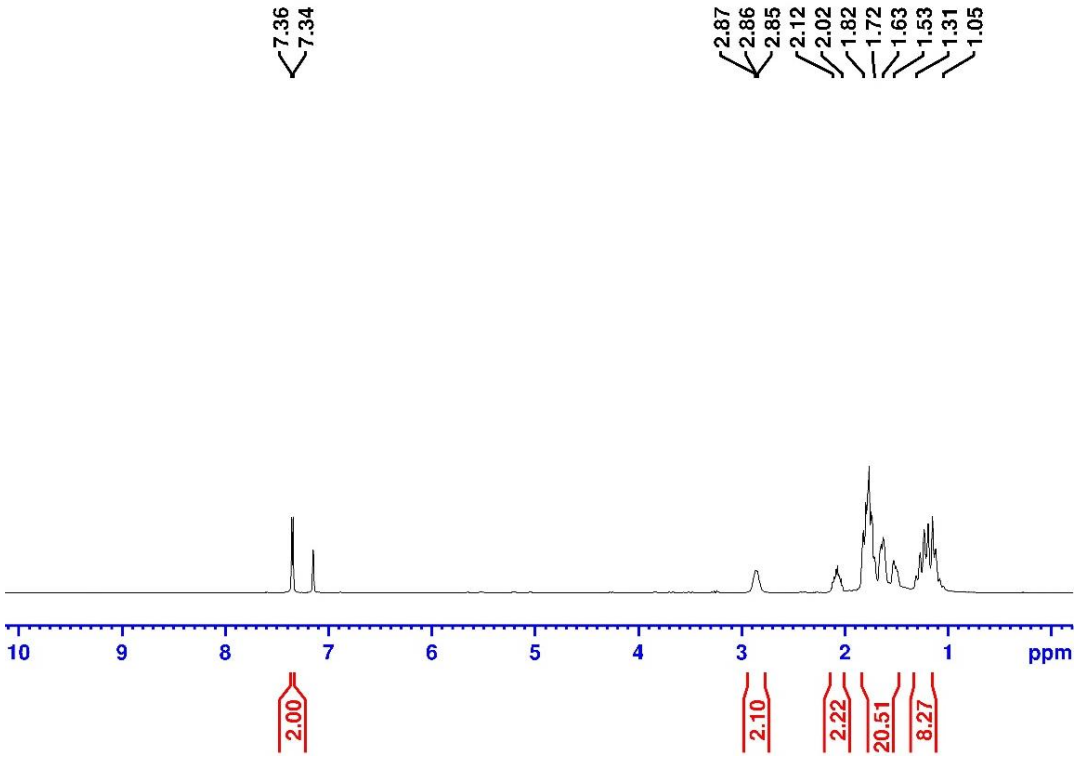


Fig. S5 ^{1}H NMR spectrum of **C** in C_6D_6 at room temperature.

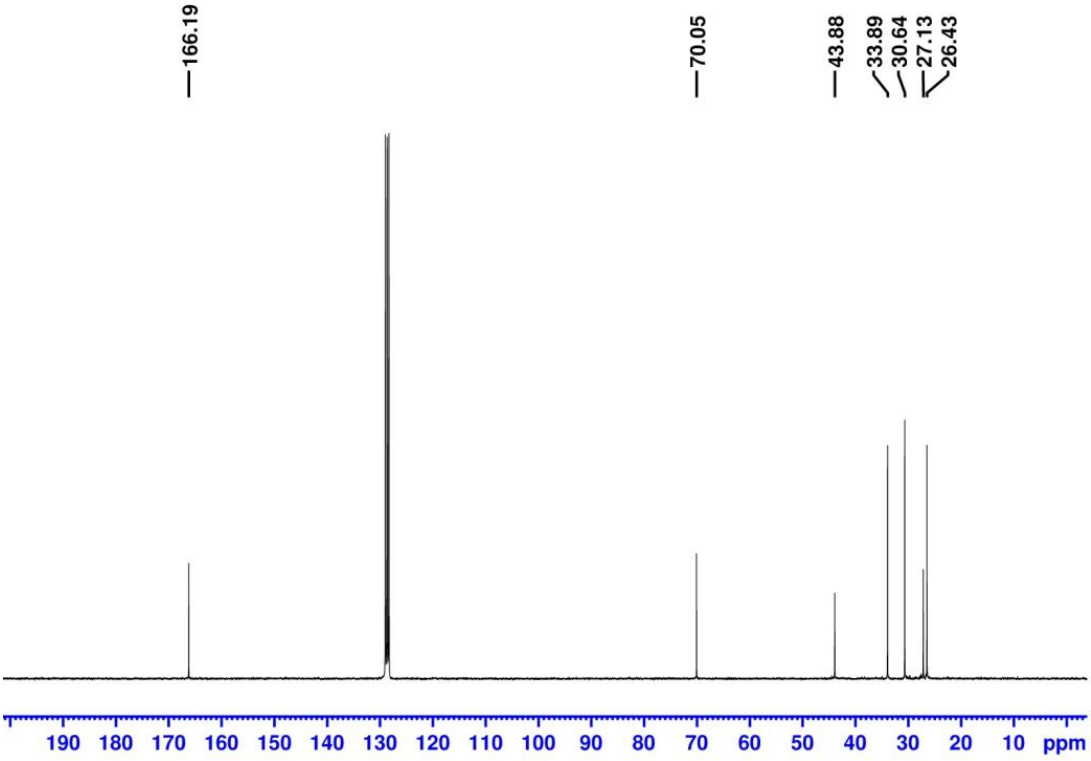


Fig. S6 $^{13}C\{^{1}H\}$ NMR spectrum of **C** in C_6D_6 at room temperature.

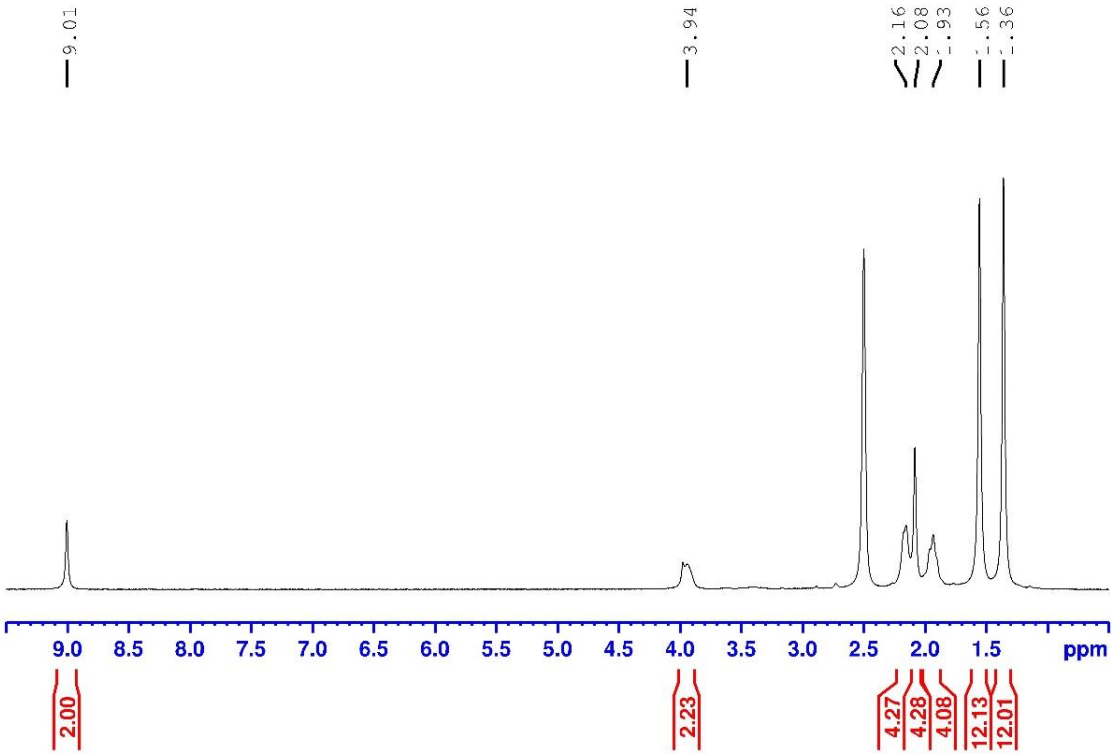


Fig. S7 ^{1}H NMR spectrum of **1a** in $(CD_3)_2SO$ at room temperature.

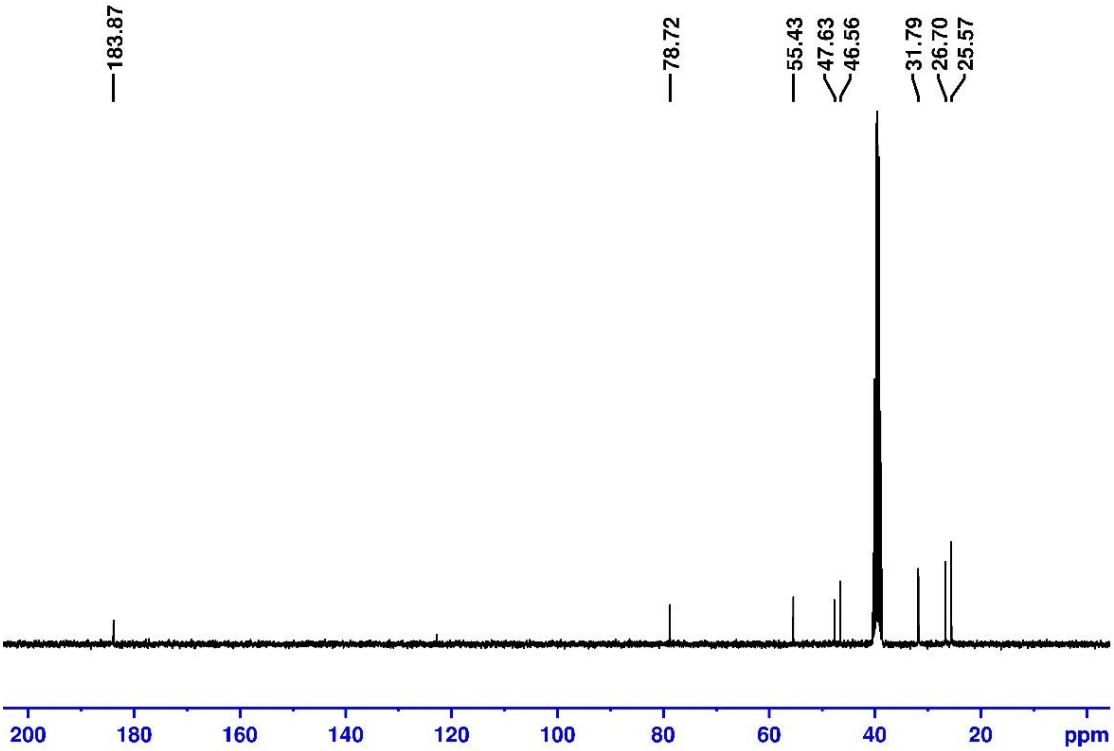


Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of **1a** in $(CD_3)_2SO$ at room temperature.

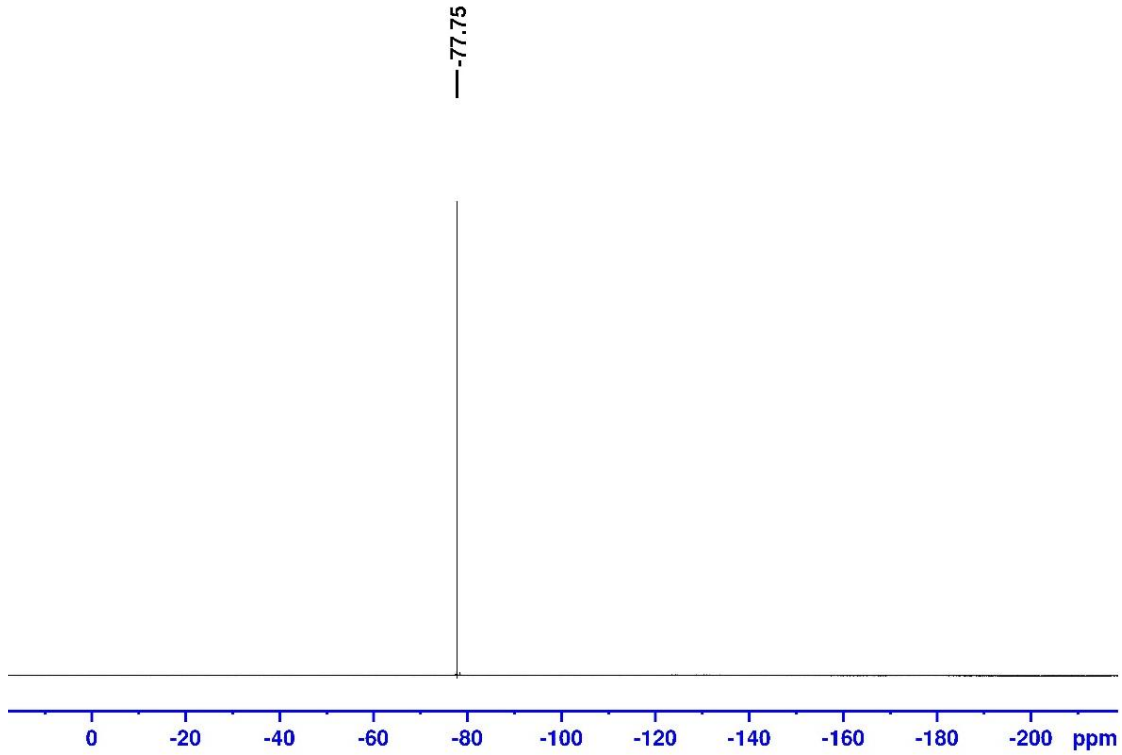


Fig. S9 $^{19}F\{^{1}H\}$ NMR spectrum of **1a** in $(CD_3)_2SO$ at room temperature.

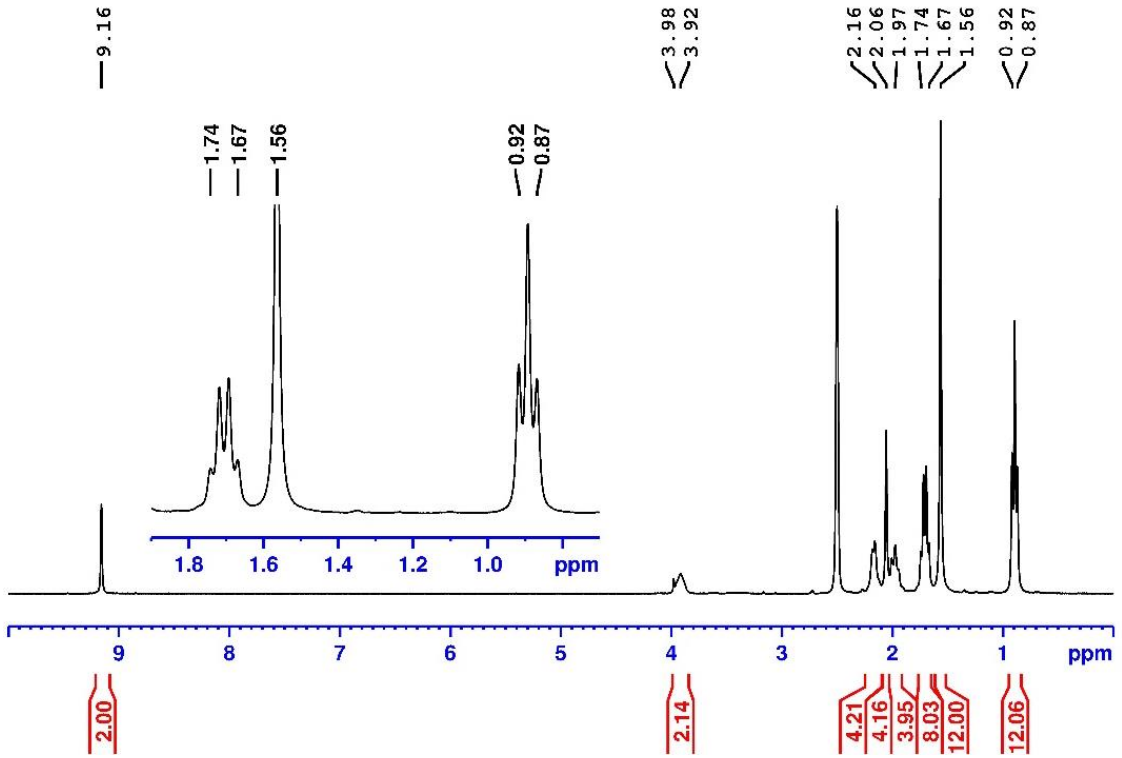


Fig. S10 ^{1}H NMR spectrum of **1b** in $(CD_3)_2SO$ at room temperature.

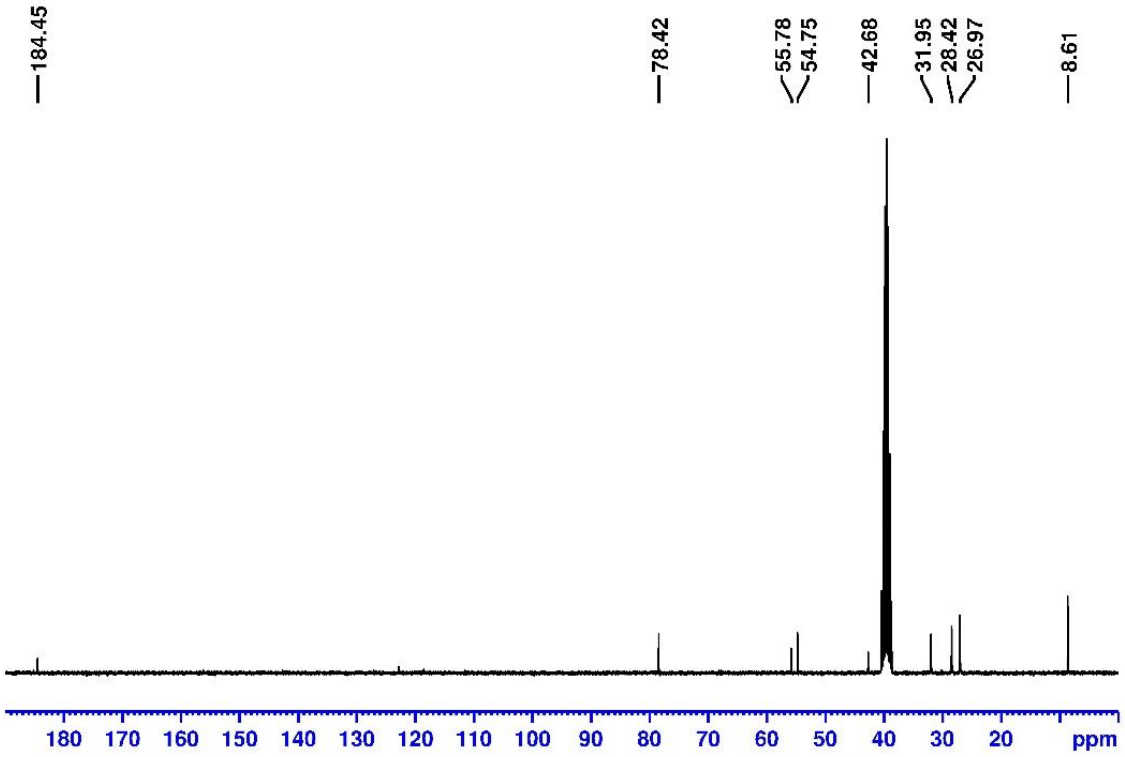


Fig. S11 $^{13}C\{^{1}H\}$ NMR spectrum of **1b** in $(CD_3)_2SO$ at room temperature.

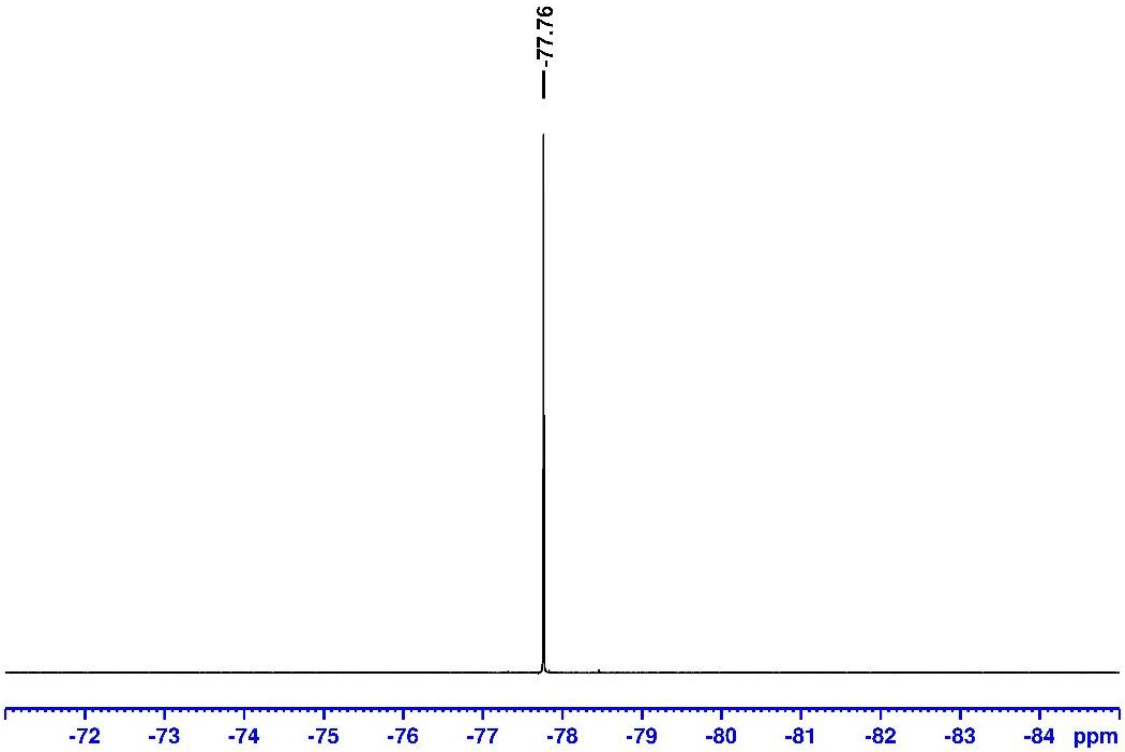


Fig. S12 $^{19}F\{^{1}H\}$ NMR spectrum of **1b** in $(CD_3)_2SO$ at room temperature.

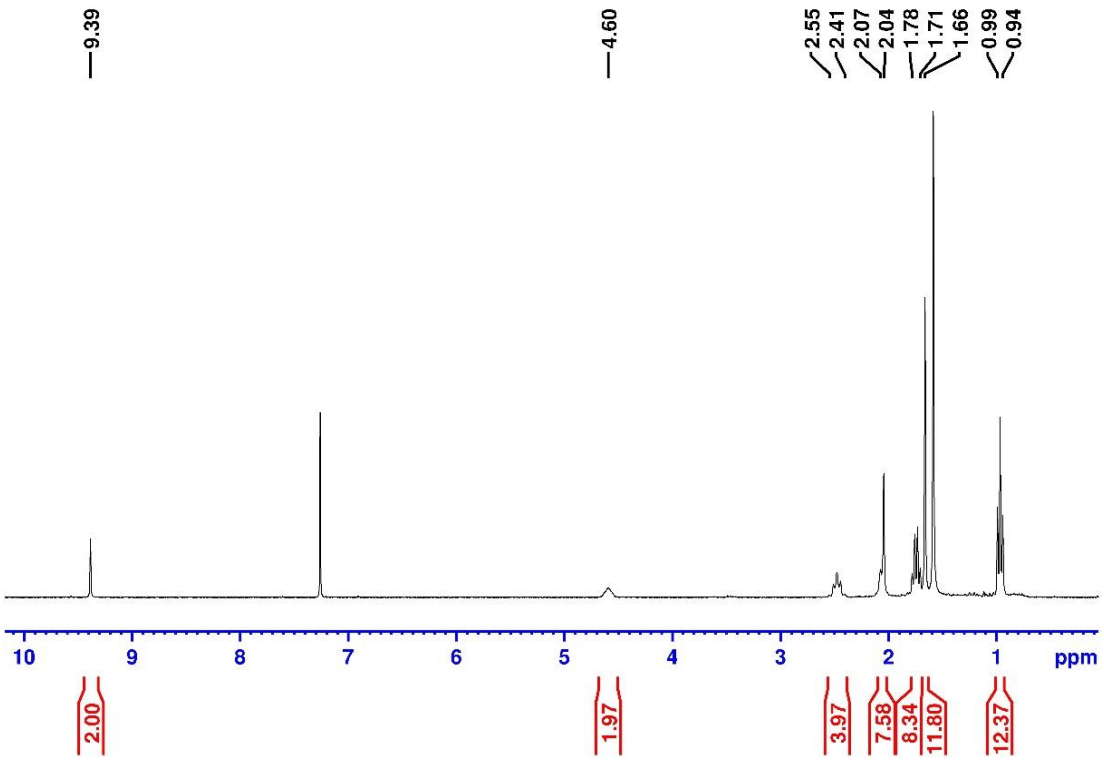


Fig. S13 ^{1}H NMR spectrum of **1b** in $CDCl_3$ at room temperature.

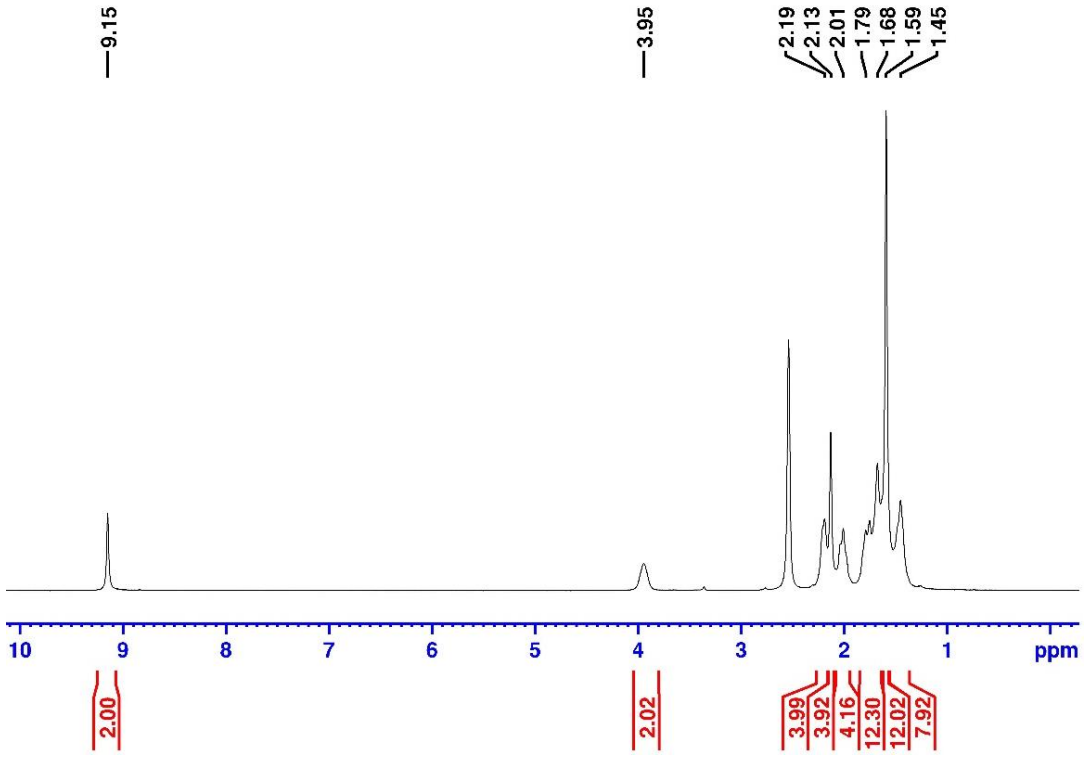


Fig. S14 ^{1}H NMR spectrum of **1c** in $(CD_3)_2SO$ at room temperature.

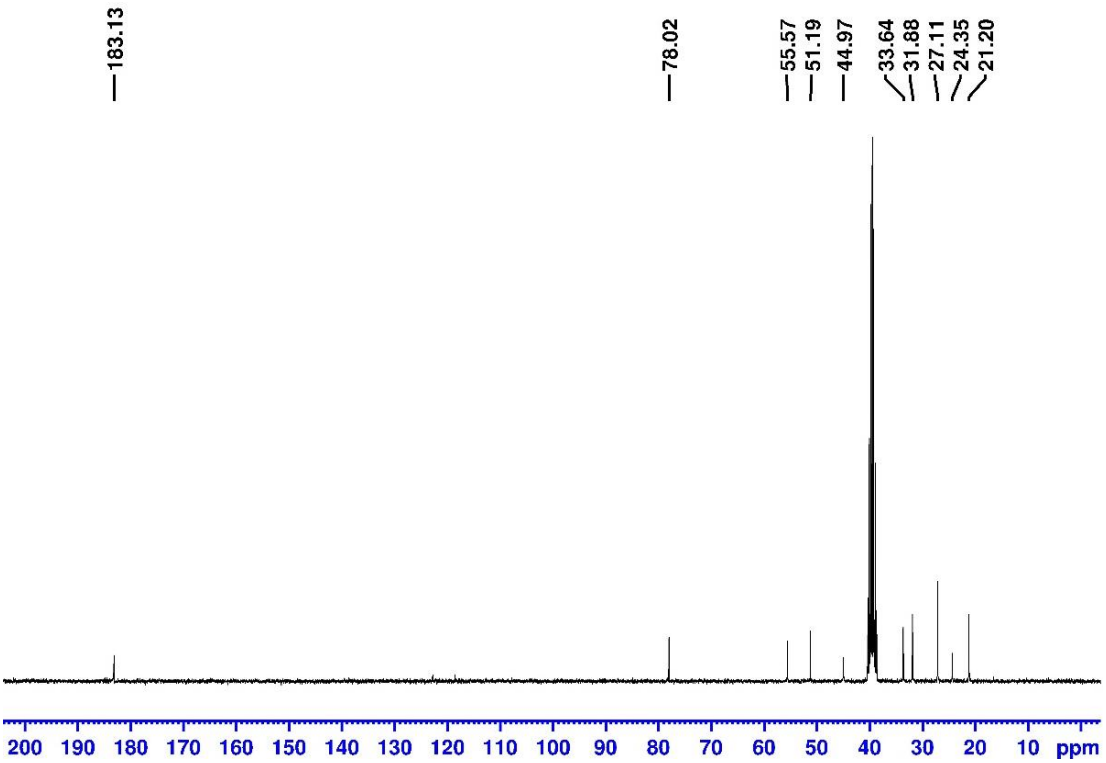


Fig. S15 $^{13}C\{^{1}H\}$ NMR spectrum of **1c** in $(CD_3)_2SO$ at room temperature.

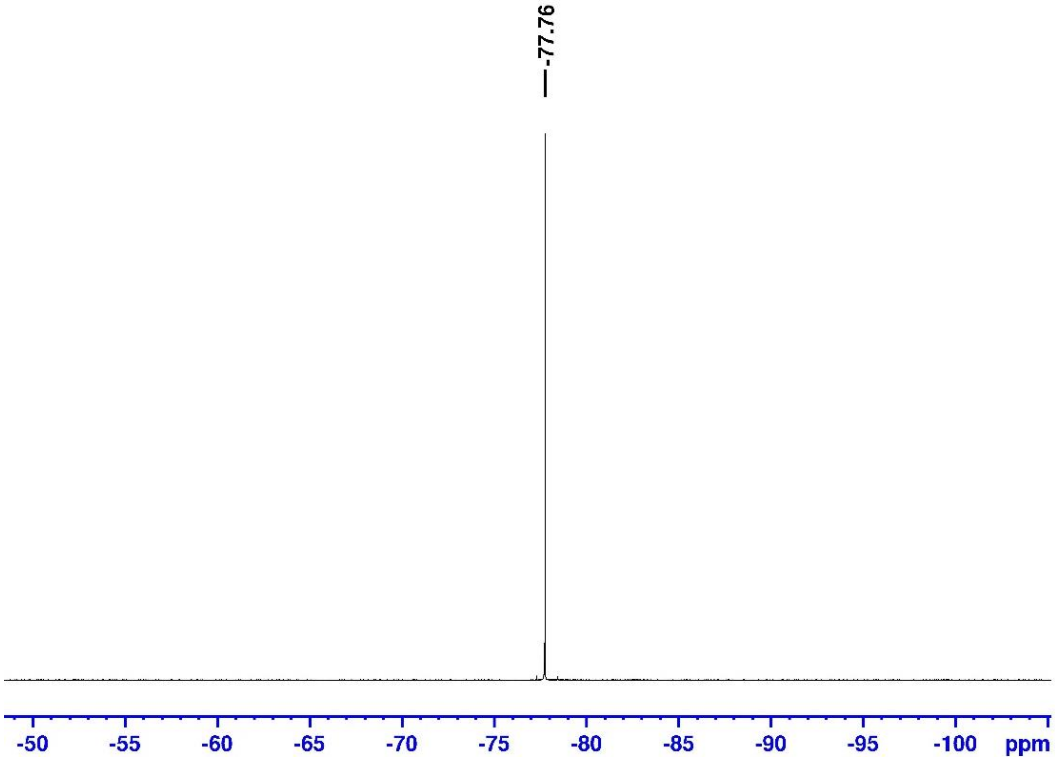


Fig. S16 $^{19}F\{^{1}H\}$ NMR spectrum of **1c** in $(CD_3)_2SO$ at room temperature.

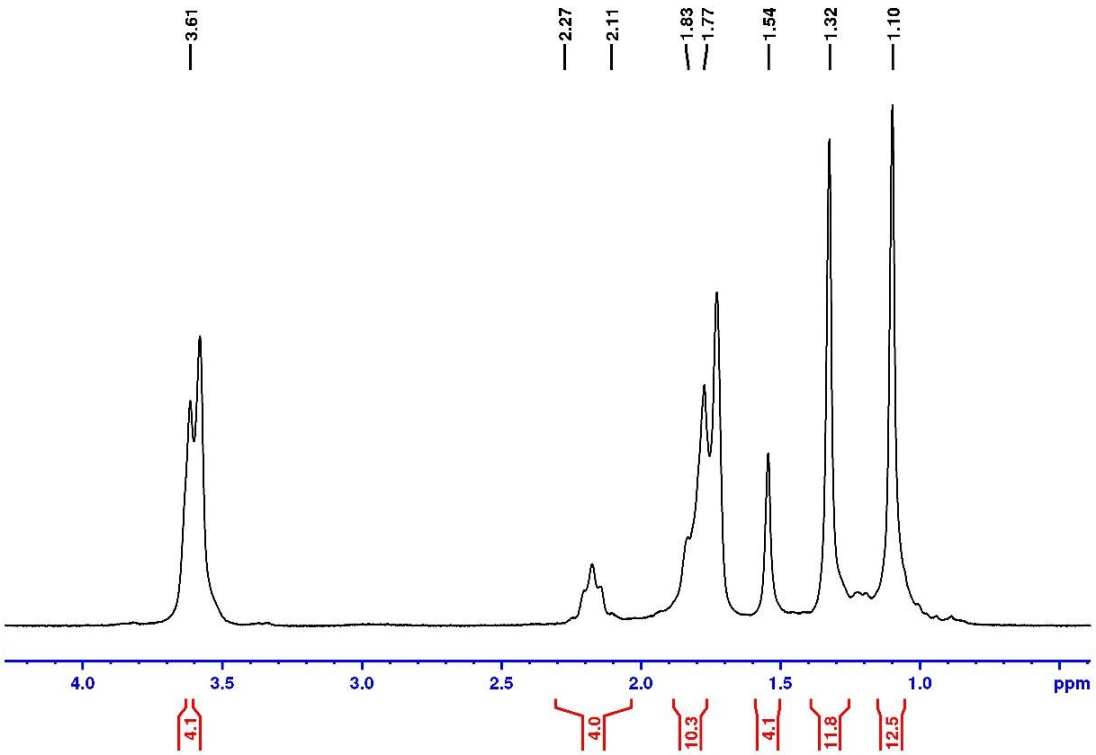


Fig. S17 ^{1}H NMR spectrum of **2a** in THF-d_8 at room temperature.

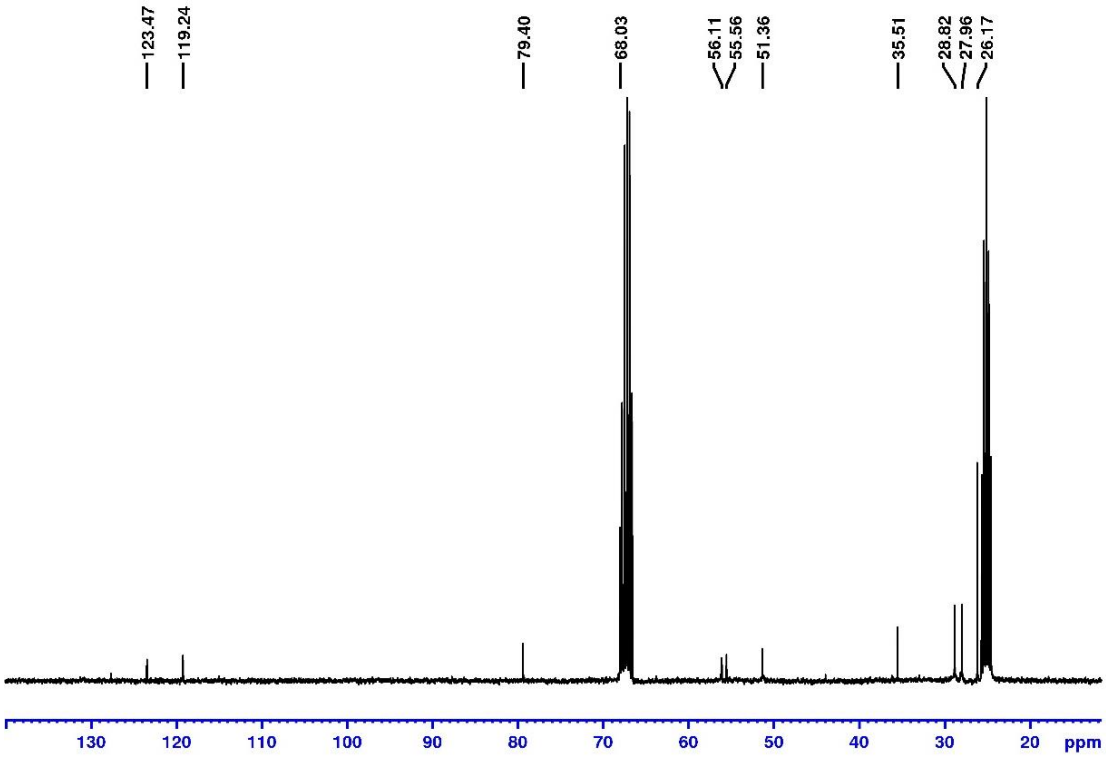


Fig. S18 ^{13}C{^{1}H} NMR spectrum of **2a** in THF-d_8 at room temperature.

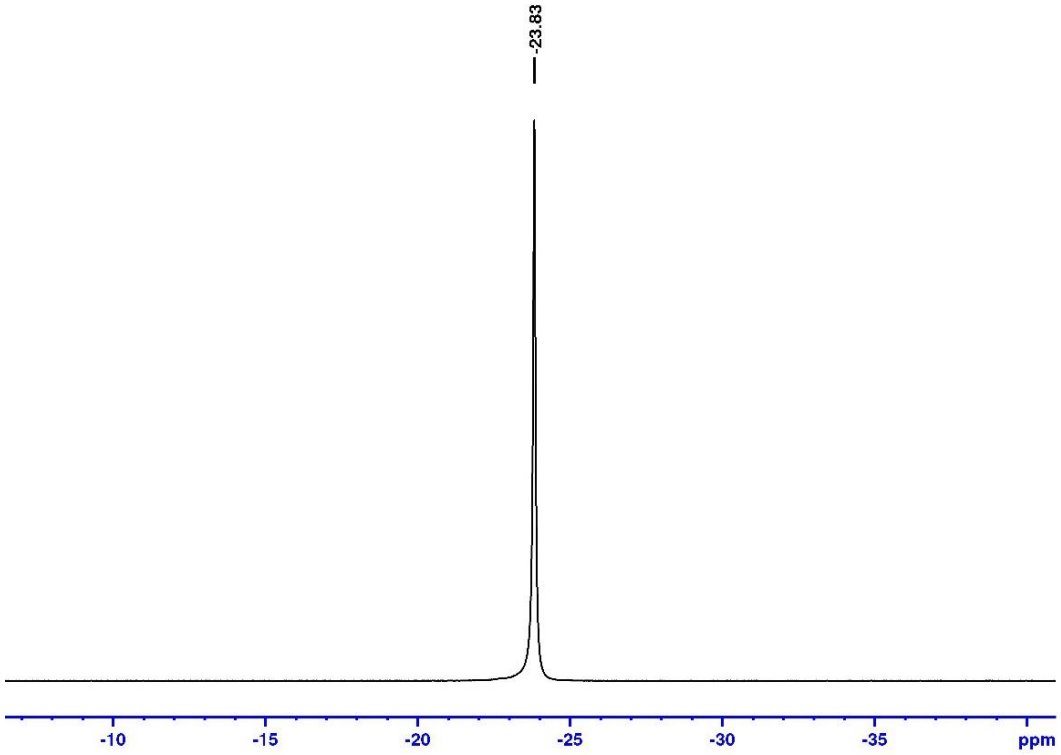


Fig. S19 ^{7}Li NMR spectrum of **2a** in THF-d_8 at room temperature.

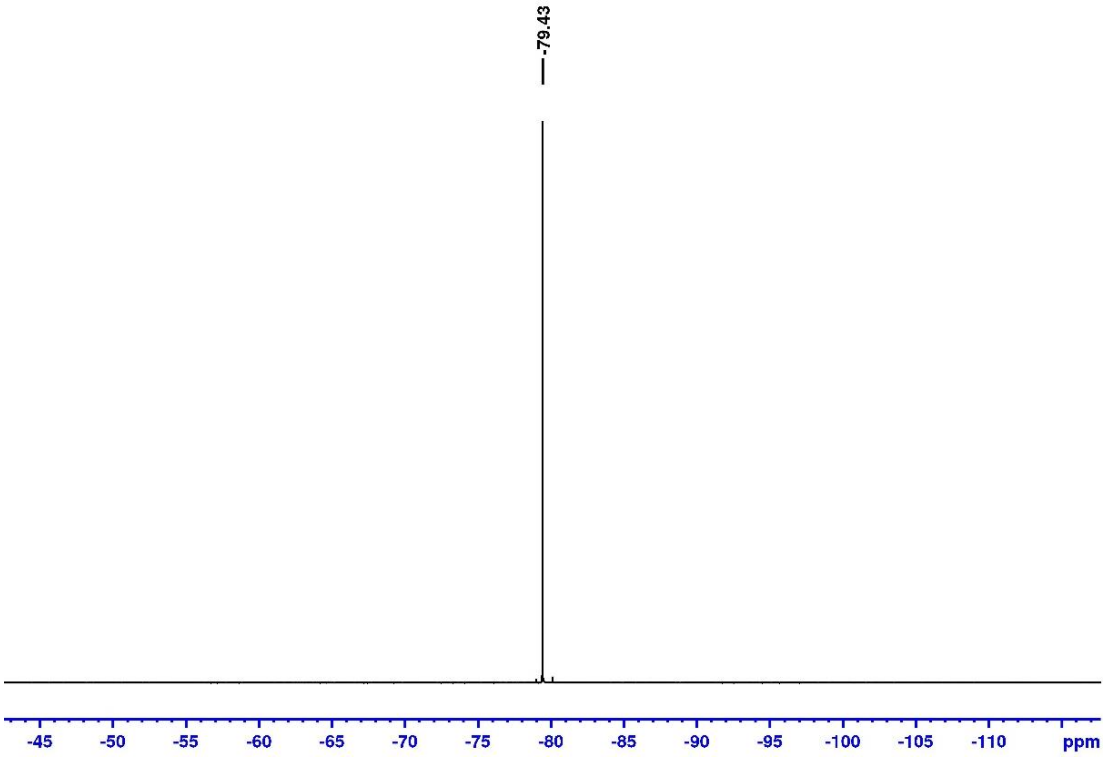


Fig. S20 ^{19}F{^{1}H} NMR spectrum of **2a** in THF-d_8 at room temperature.

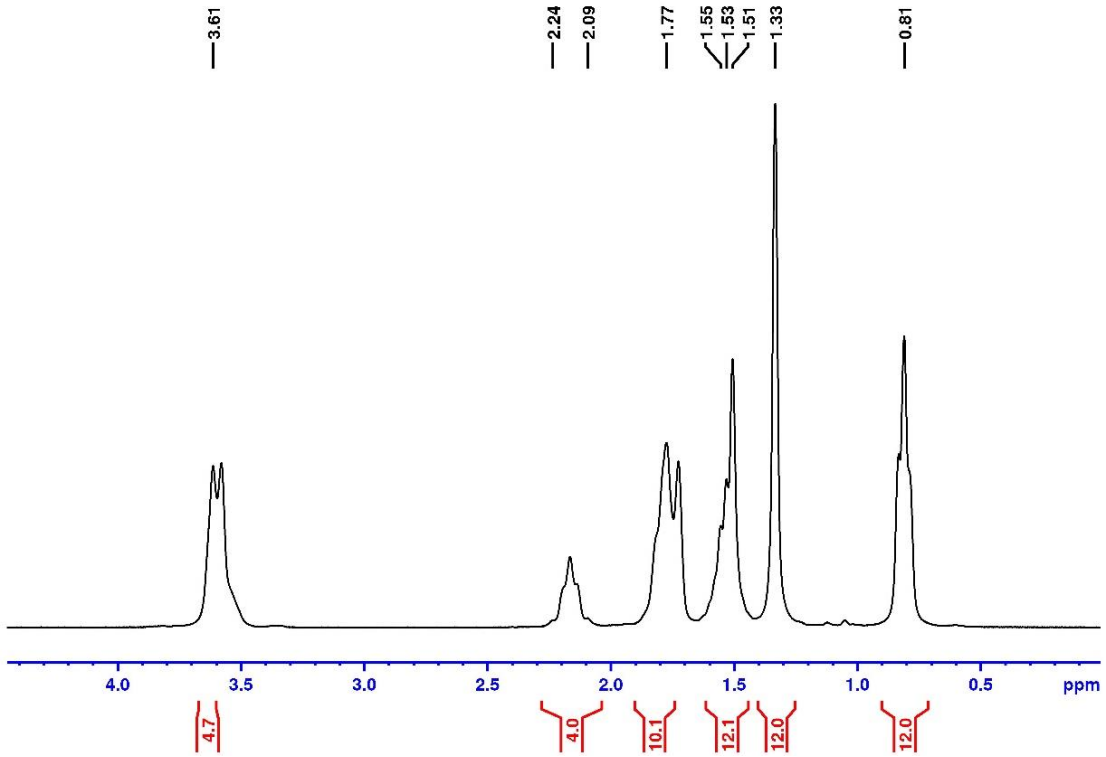


Fig. S21 ^{1}H NMR spectrum of **2b** in THF-d_8 at room temperature.

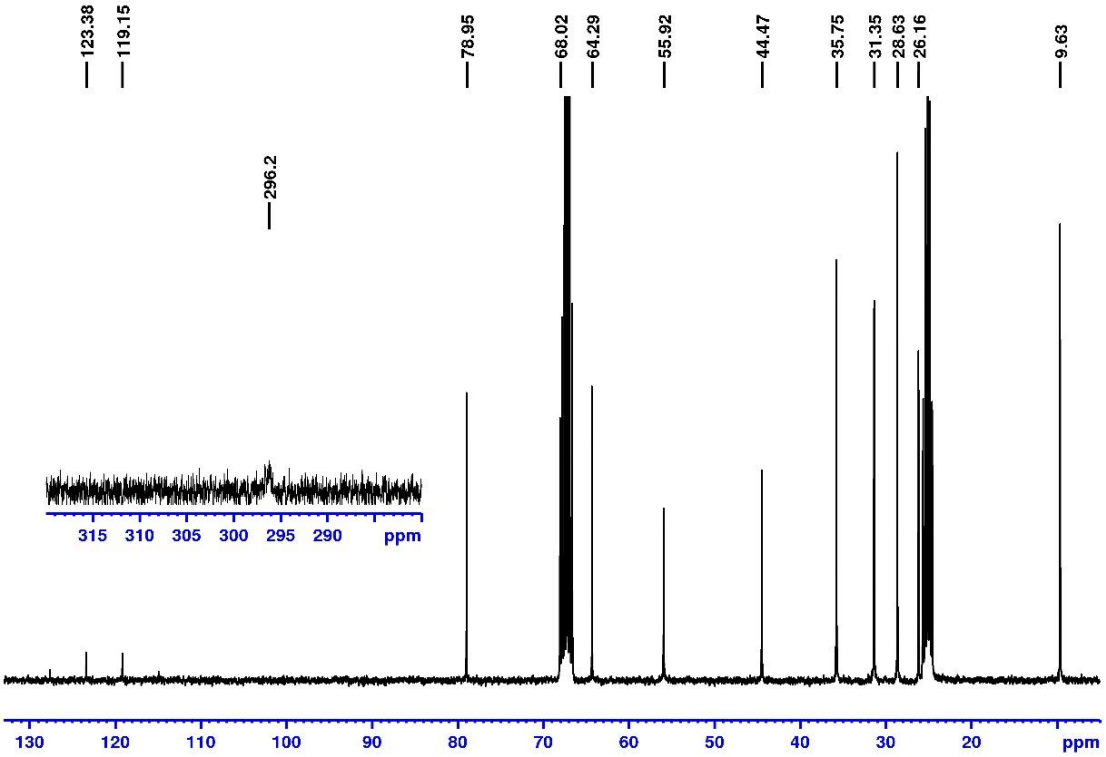


Fig. S22 ^{13}C{^{1}H} NMR spectrum of **2b** in THF-d_8 at room temperature.

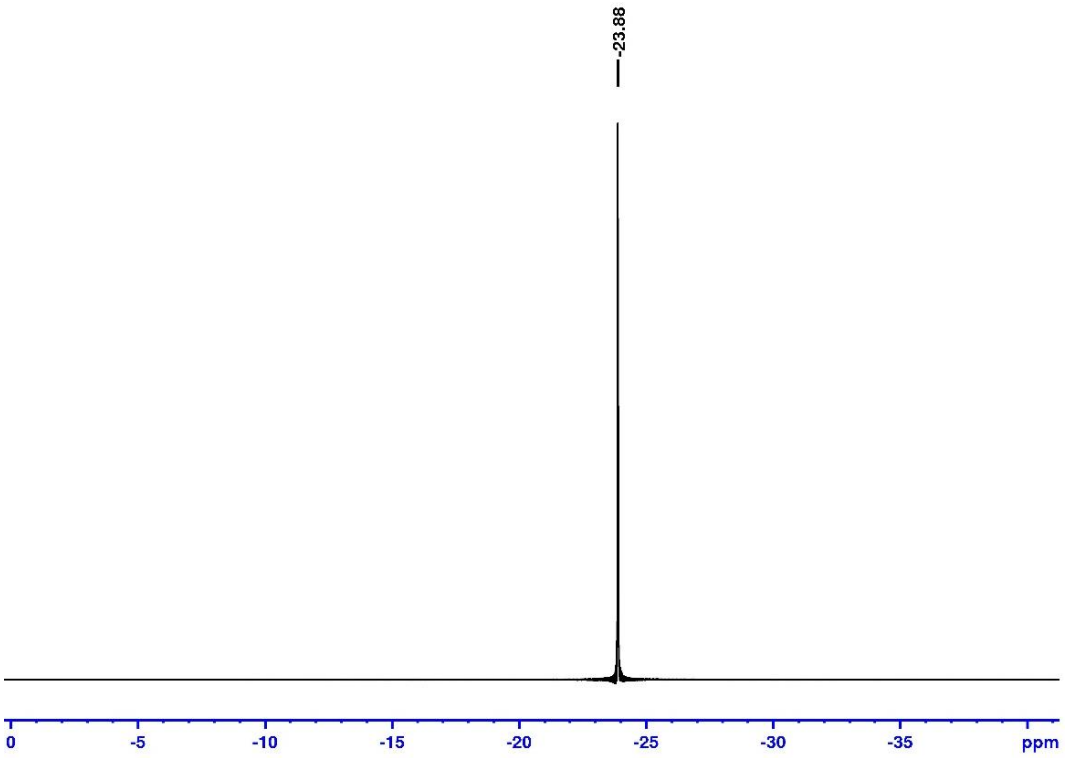


Fig. S23 ^{7}Li NMR spectrum of **2b** in THF-d_8 at room temperature.

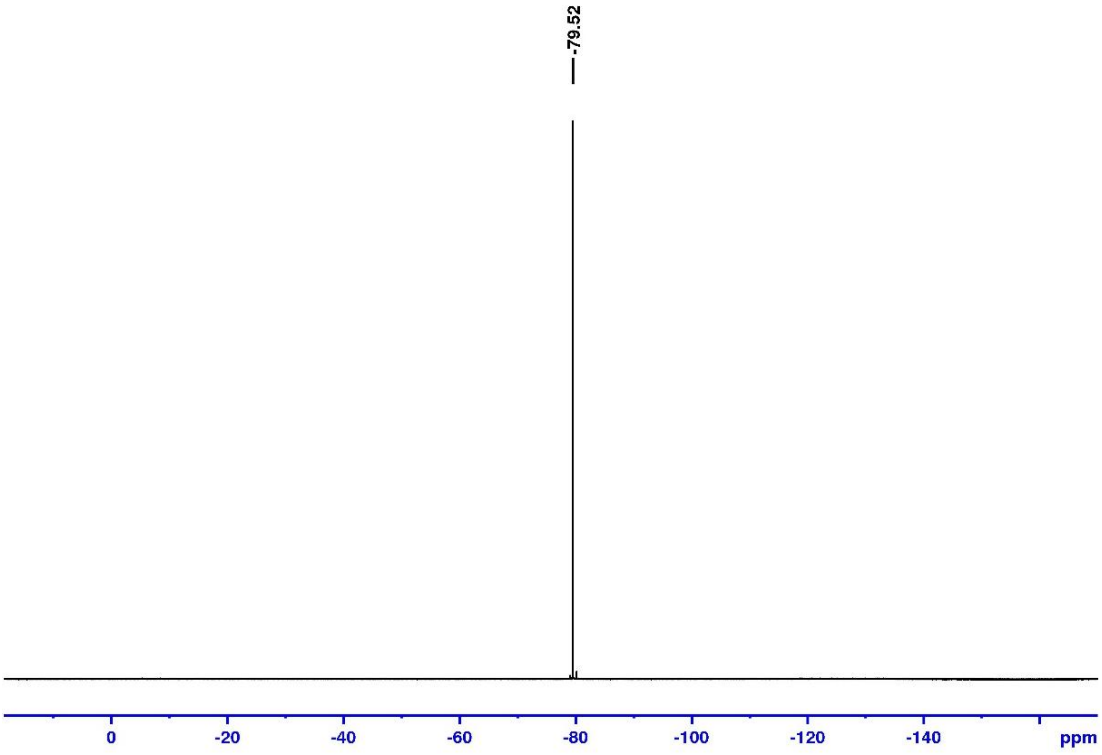


Fig. S24 ^{19}F{^{1}H} NMR spectrum of **2b** in THF-d_8 at room temperature.

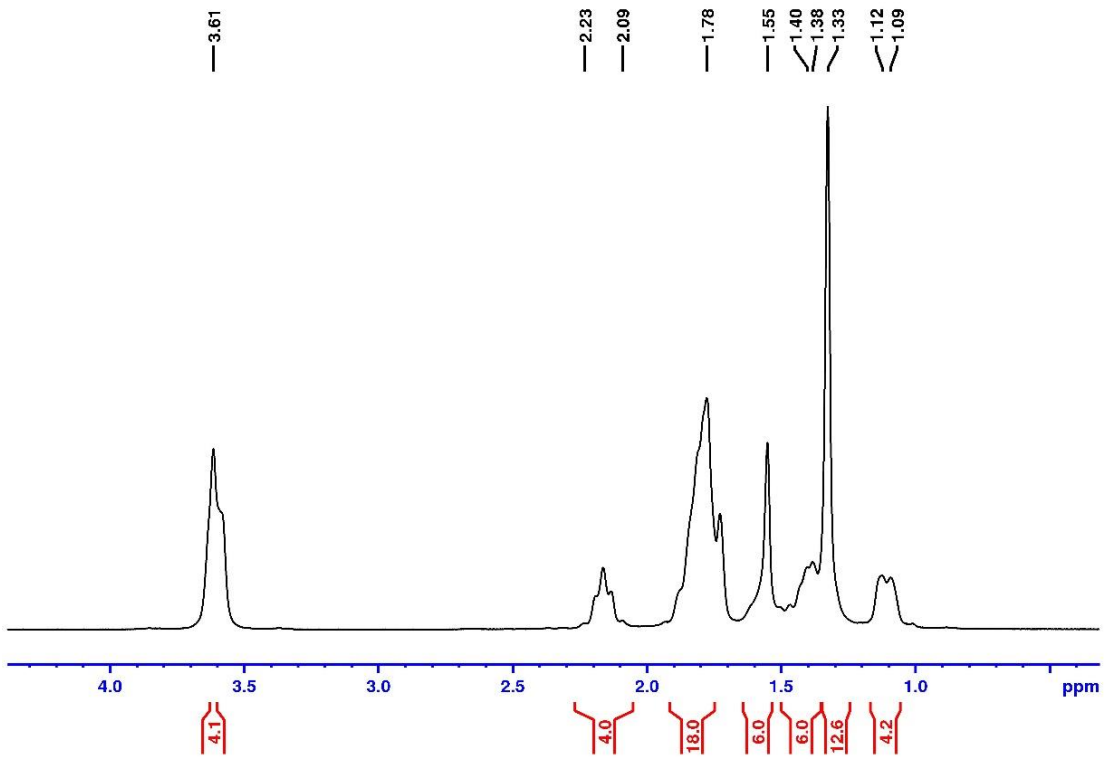


Fig. S25 ^{1}H NMR spectrum of **2c** in THF-d_8 at room temperature.

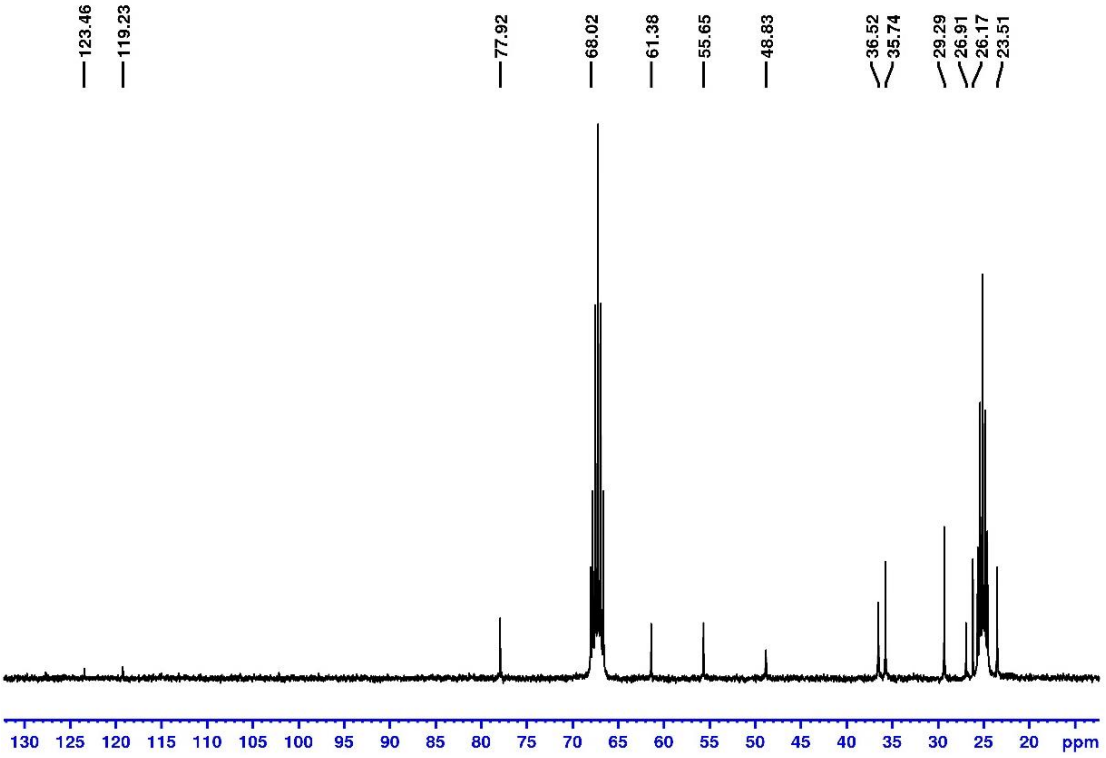


Fig. S26 $^{13}C\{^{1}H\}$ NMR spectrum of **2c** in THF-d_8 at room temperature.

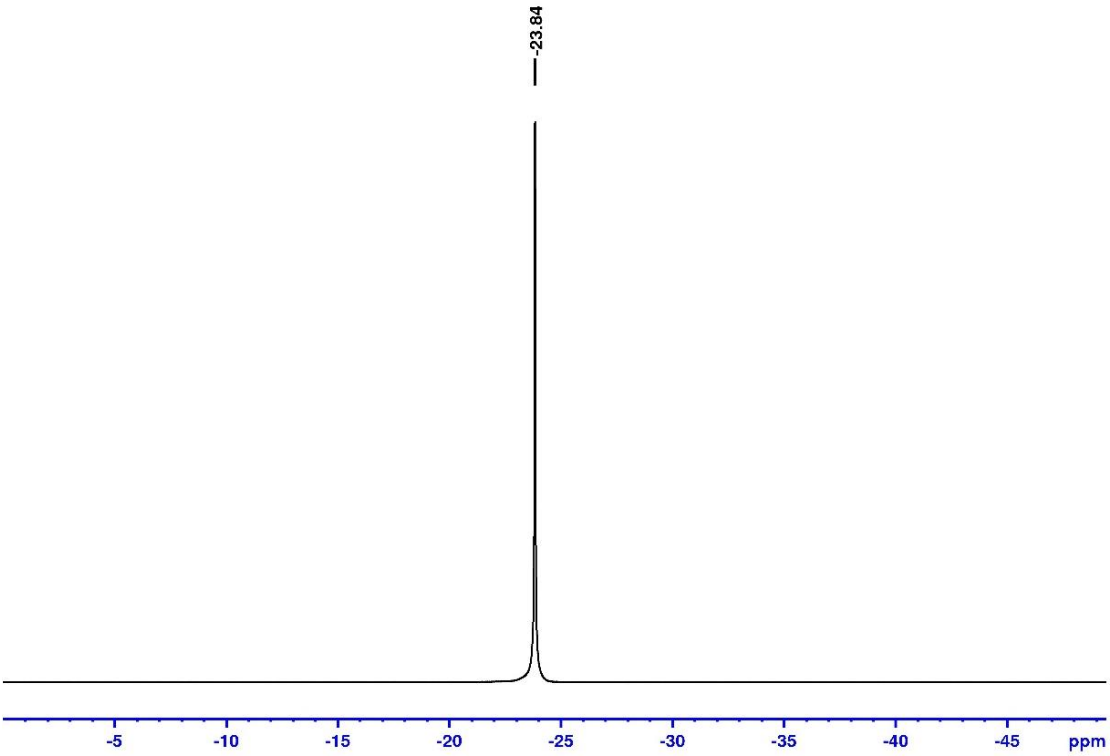


Fig. S27 ^{7}Li NMR spectrum of **2c** in THF-d_8 at room temperature.

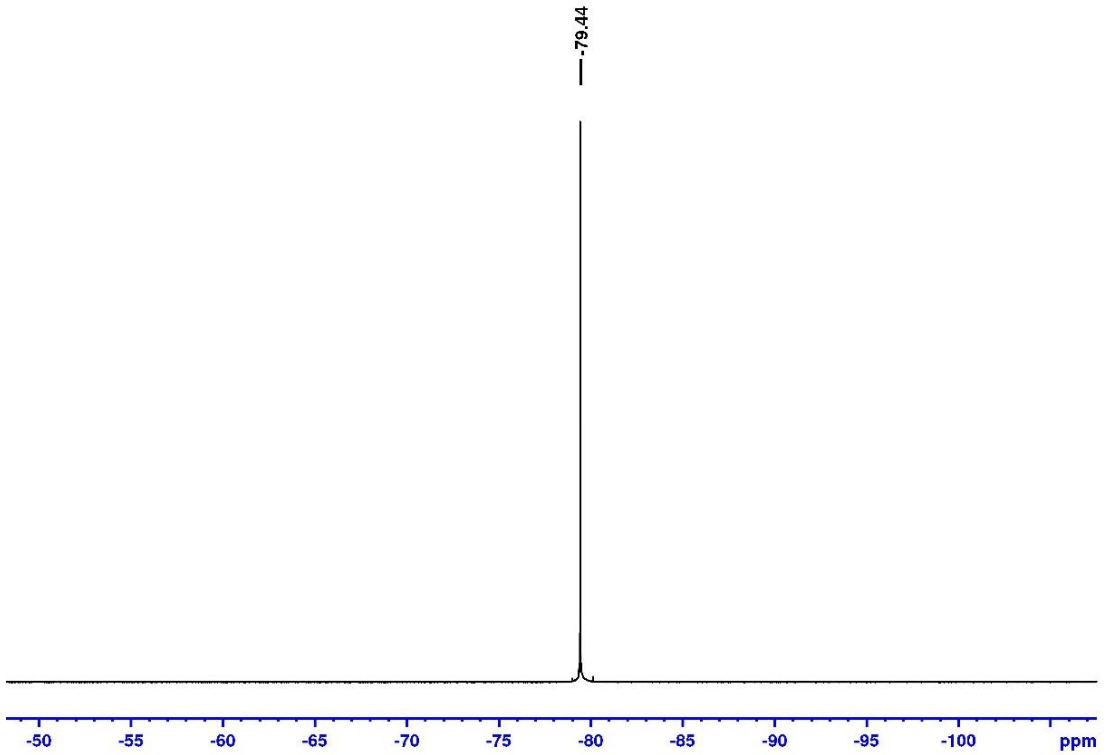


Fig. S28 ^{19}F{^{1}H} NMR spectrum of **2c** in THF-d_8 at room temperature.

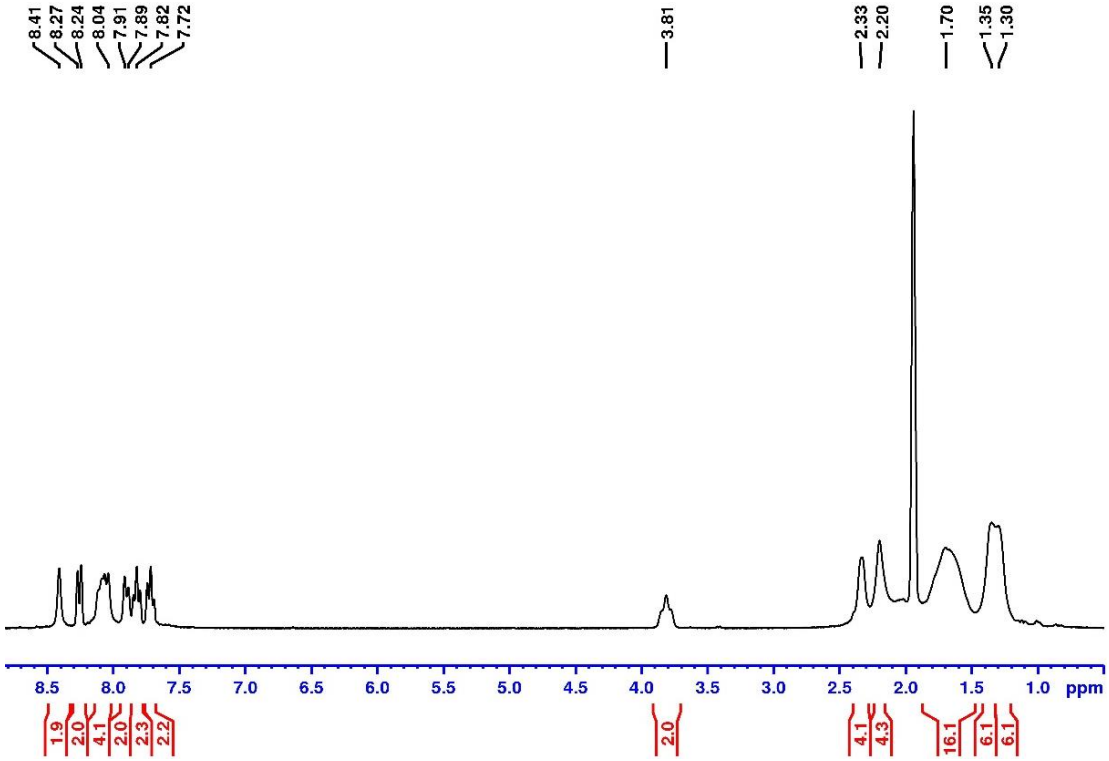


Fig. S29 ^{1}H NMR spectrum of **3a** in CD_3CN at room temperature.

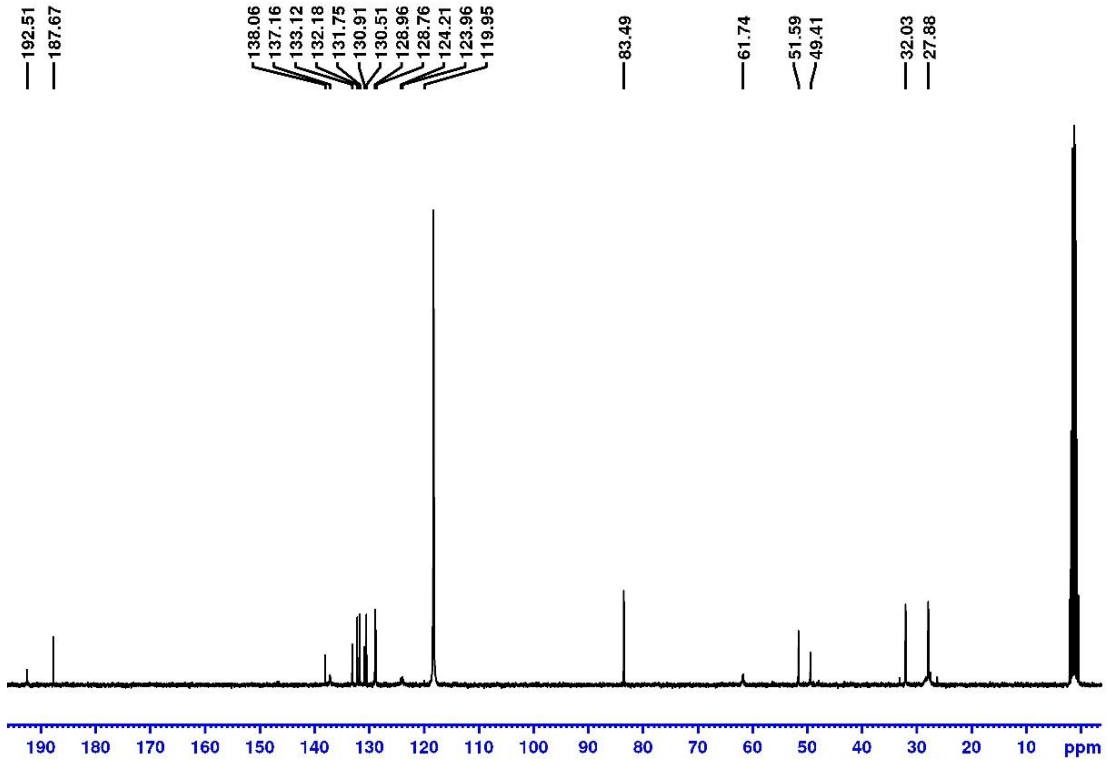


Fig. S30 $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in CD_3CN at room temperature.

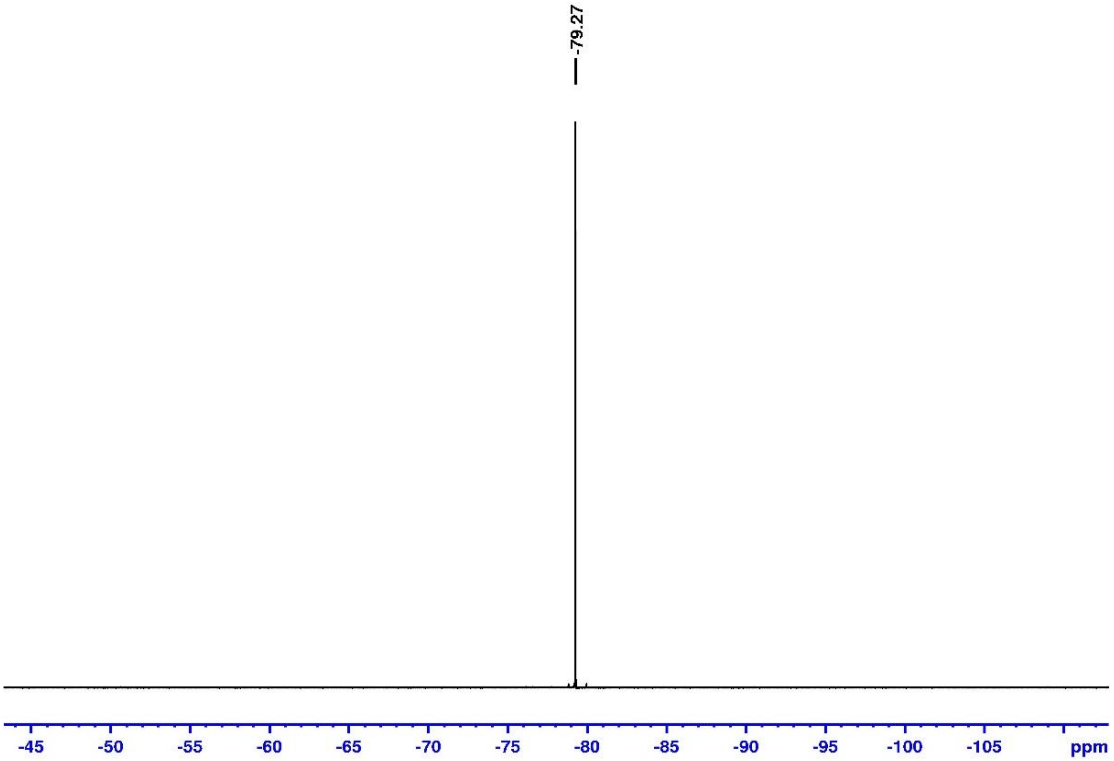


Fig. S31 $^{19}F\{^{1}H\}$ NMR spectrum of **3a** in CD_3CN at room temperature.

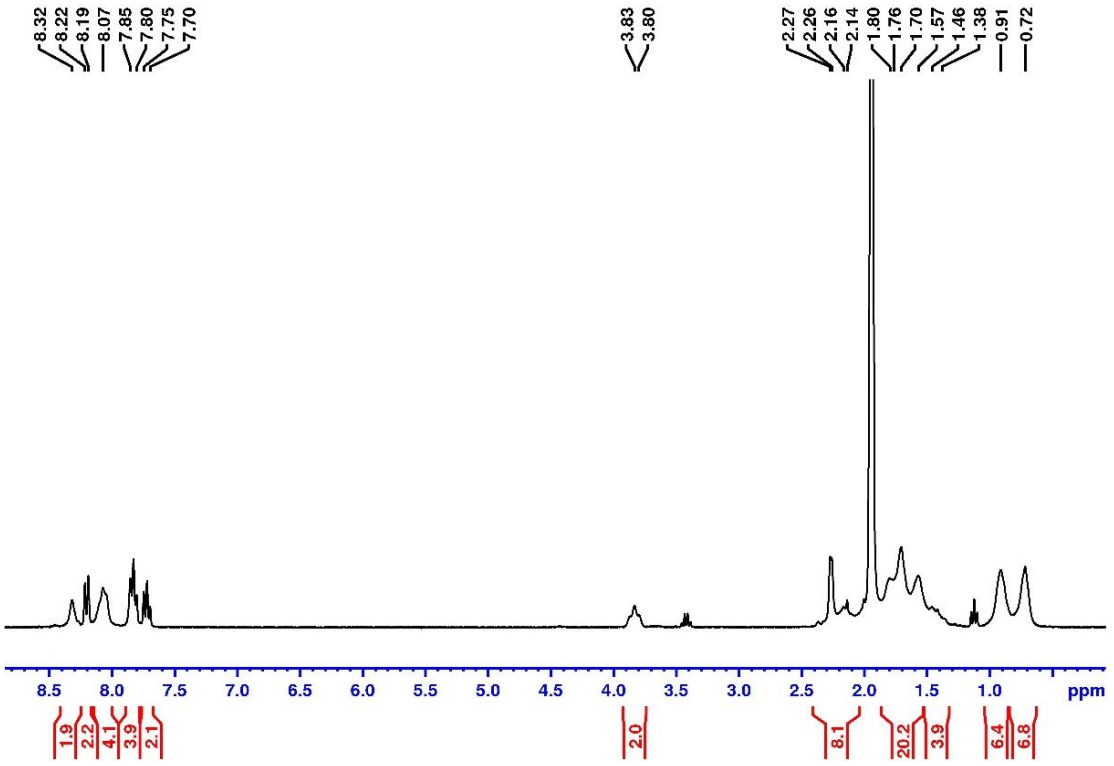


Fig. S32 ^{1}H NMR spectrum of **3b** (contains residual diethyl ether) in CD_3CN at room temperature.

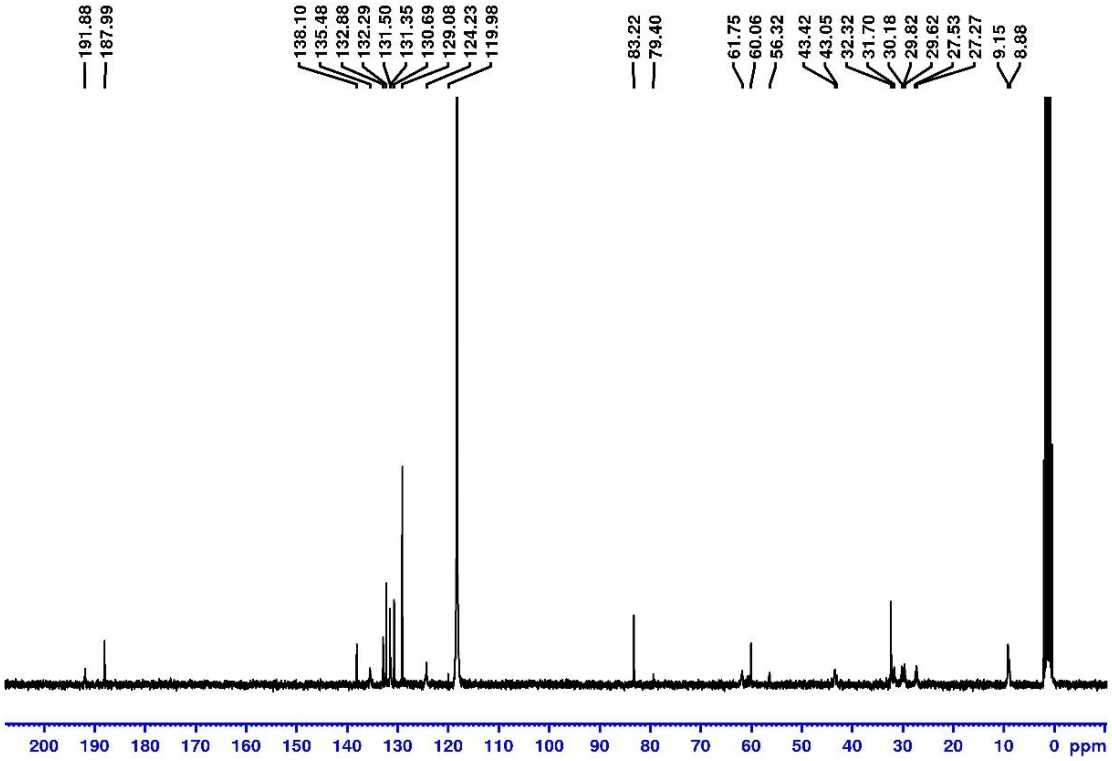


Fig. S33 $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in CD_3CN at room temperature.

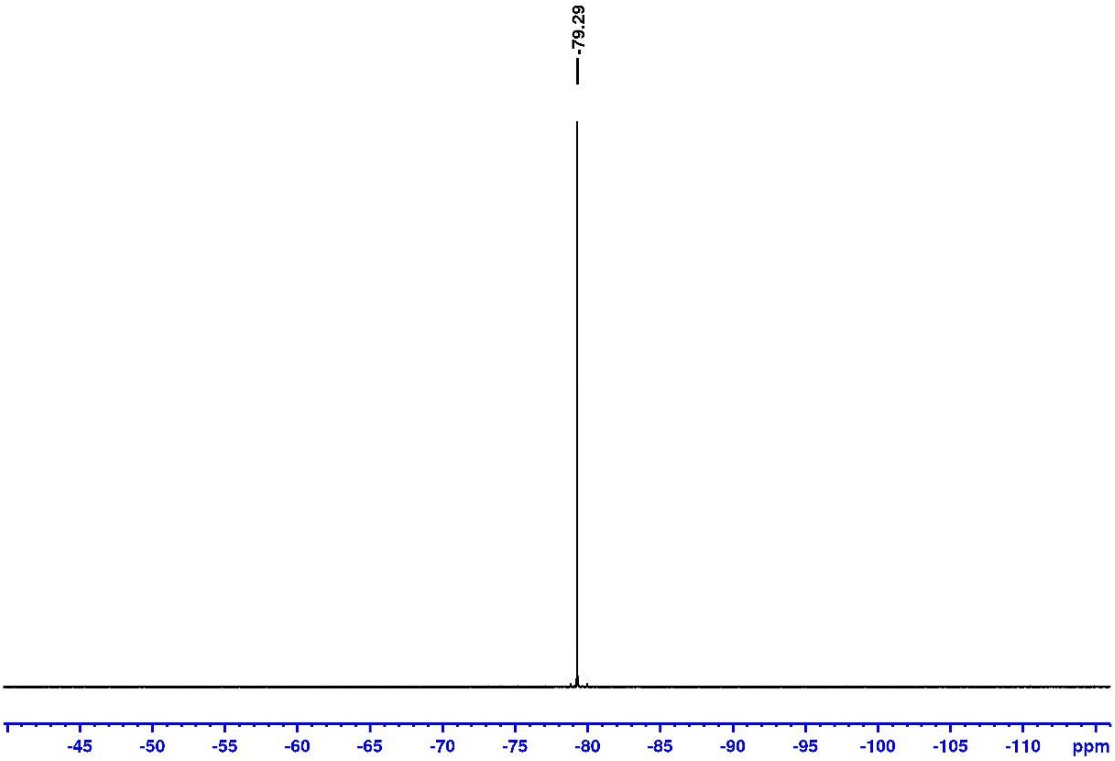


Fig. S34 $^{19}F\{^{1}H\}$ NMR spectrum of **3b** in CD_3CN at room temperature.

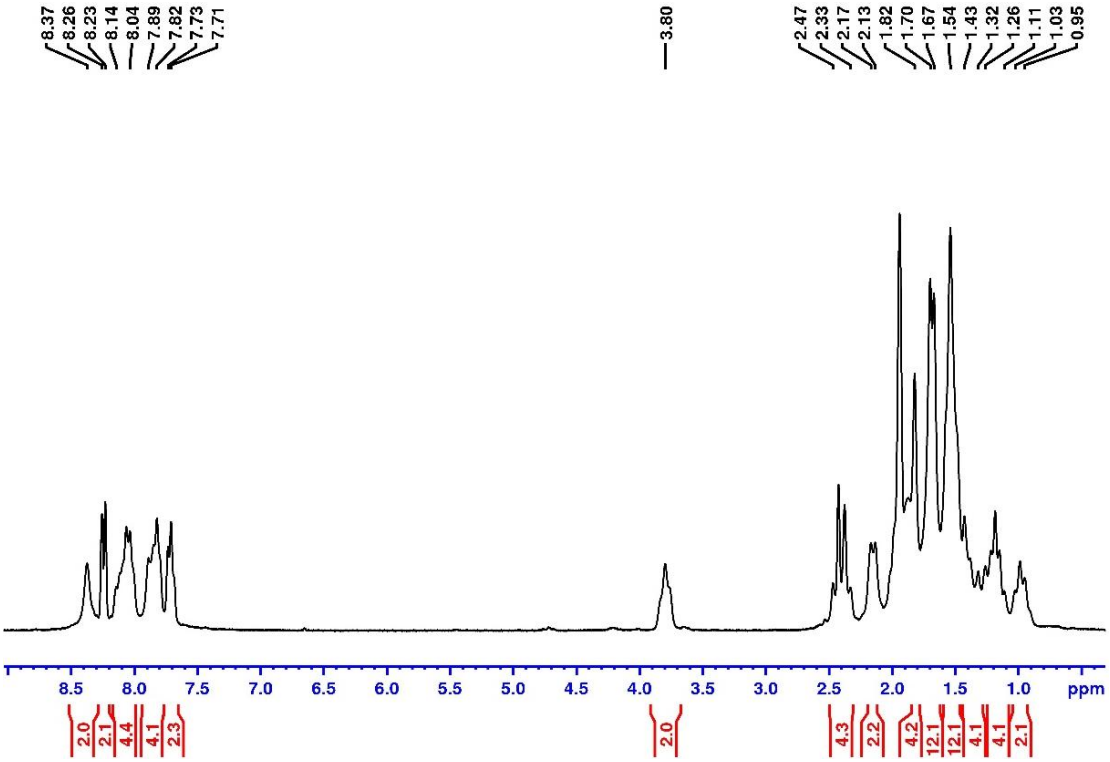


Fig. S35 ^{1}H NMR spectrum of **3c** in CD_3CN at room temperature.

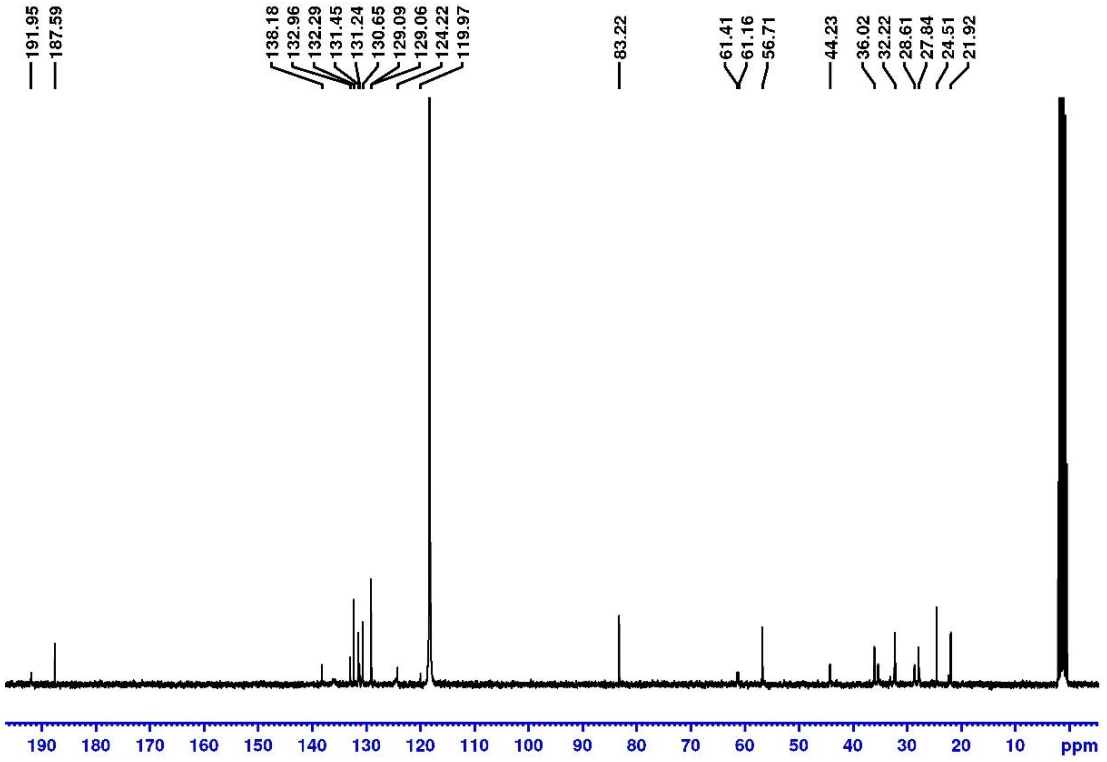


Fig. S36 $^{13}C\{^{1}H\}$ NMR spectrum of **3c** in CD_3CN at room temperature.

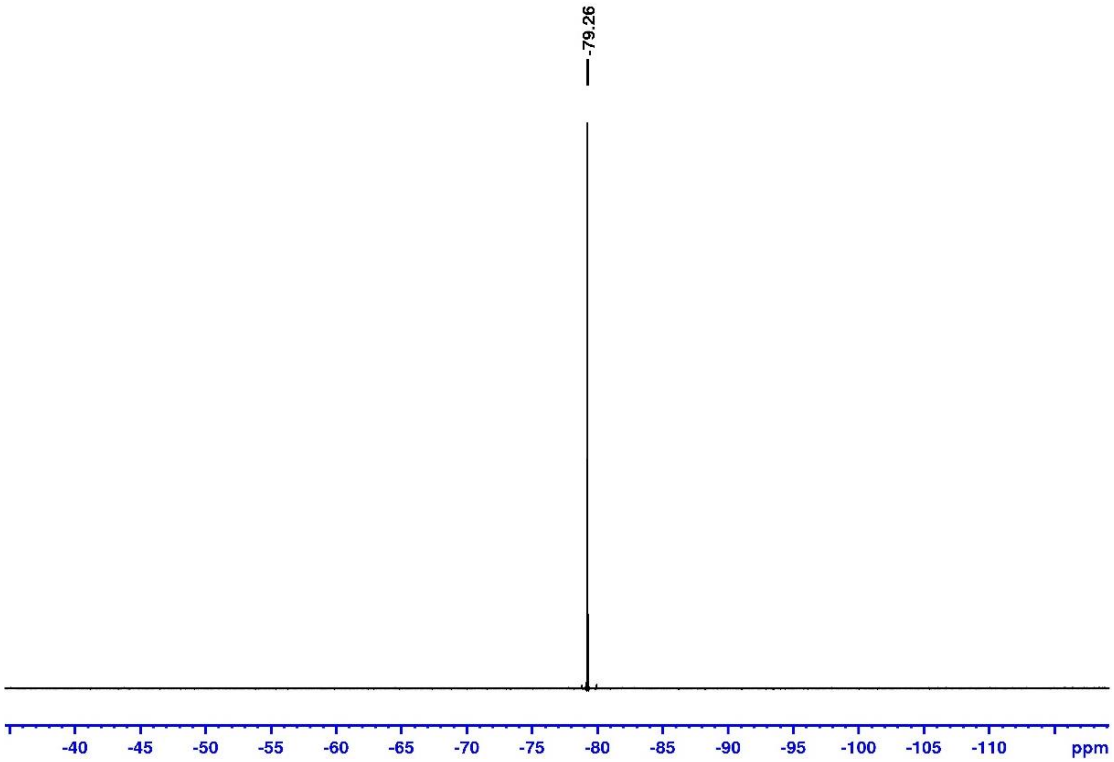


Fig. S37 $^{19}F\{^{1}H\}$ NMR spectrum of **3c** in CD_3CN at room temperature.

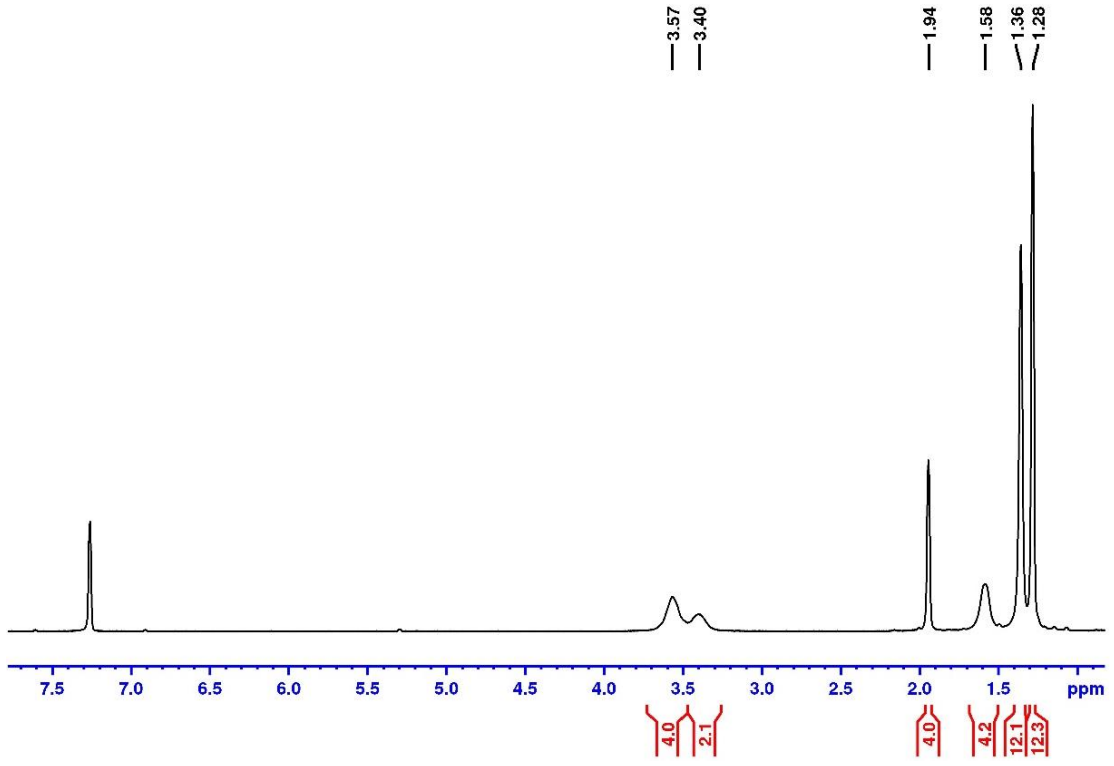


Fig. S38 ^{1}H NMR spectrum of **5a** in $CDCl_3$ at room temperature.

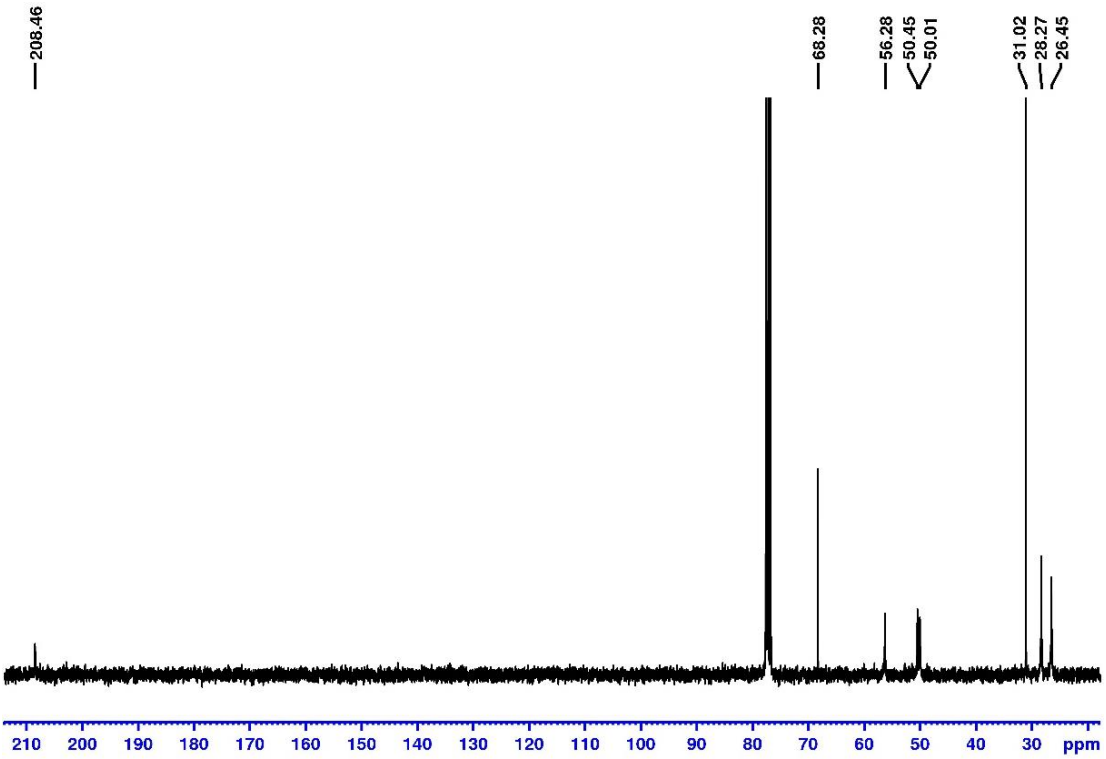


Fig. S39 $^{13}C\{^{1}H\}$ NMR spectrum of **5a** in $CDCl_3$ at room temperature.

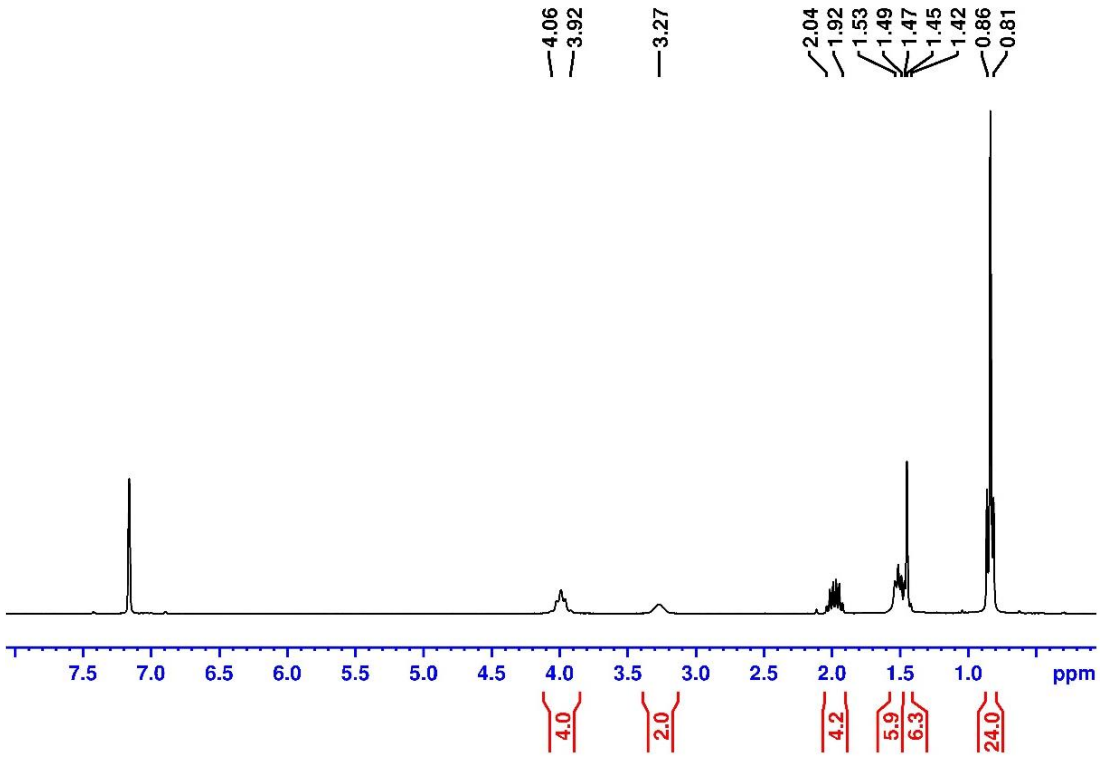


Fig. S40 ^{1}H NMR spectrum of **5b** in C_6D_6 at room temperature.

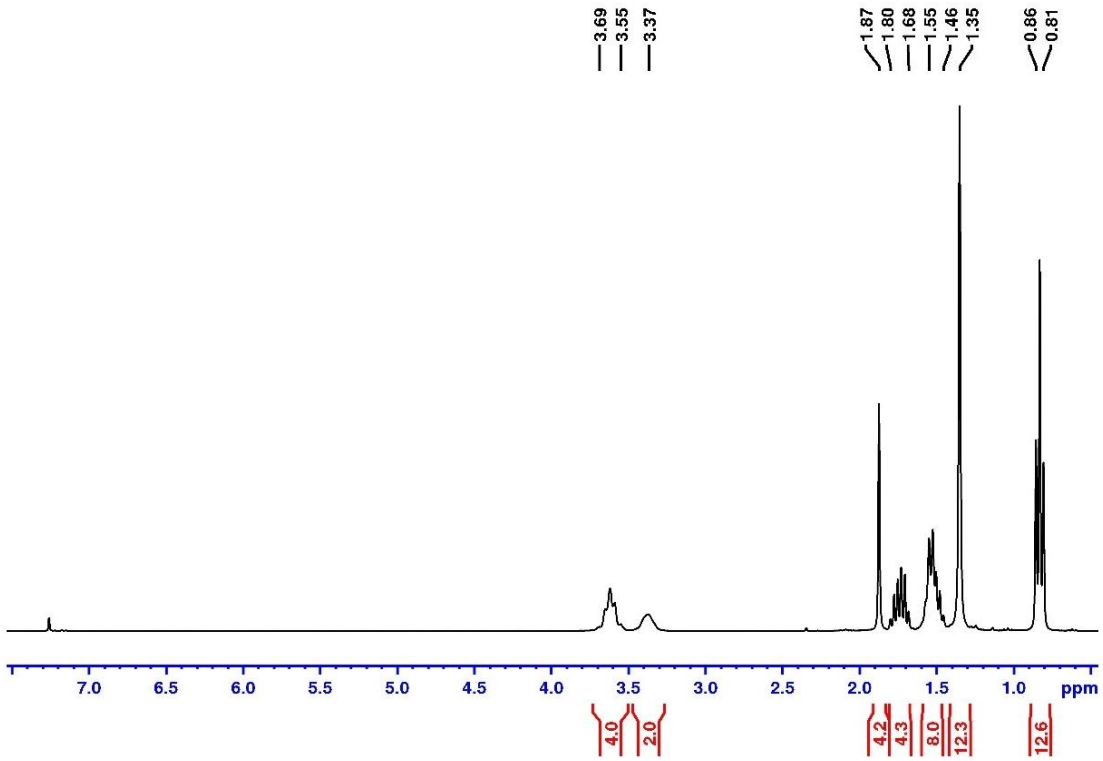


Fig. S41 ^{1}H NMR spectrum of **5b** in $CDCl_3$ at room temperature.

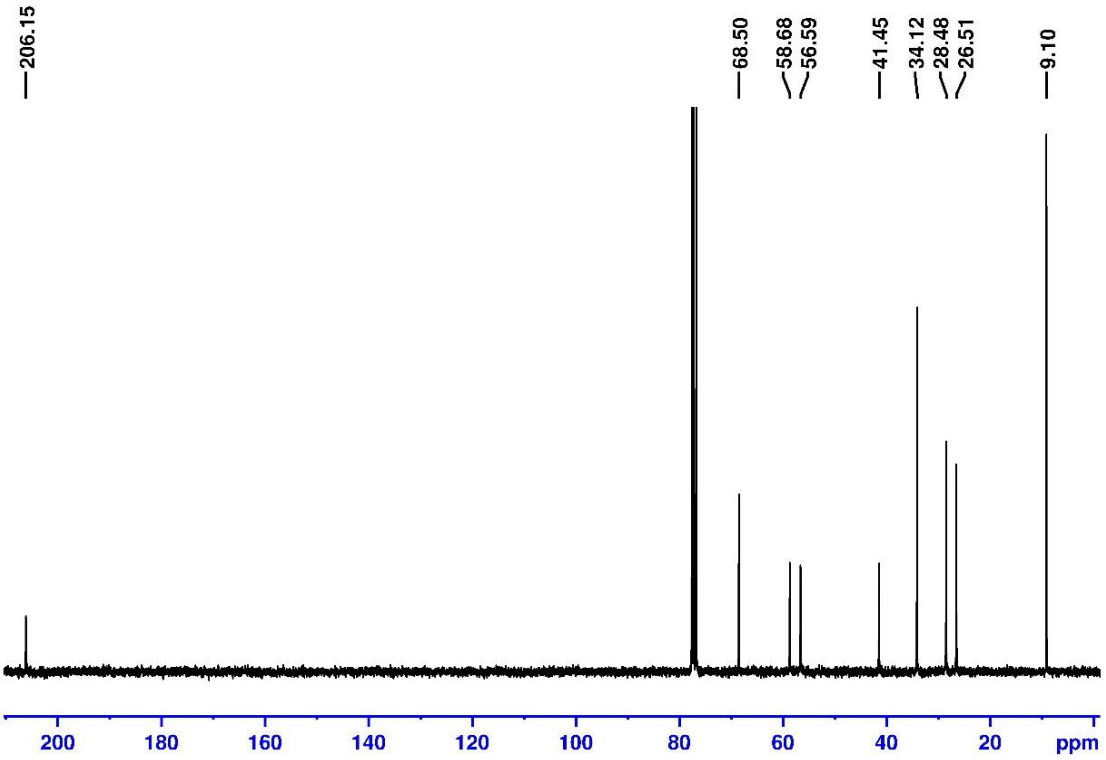


Fig. S42 $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in $CDCl_3$ at room temperature.

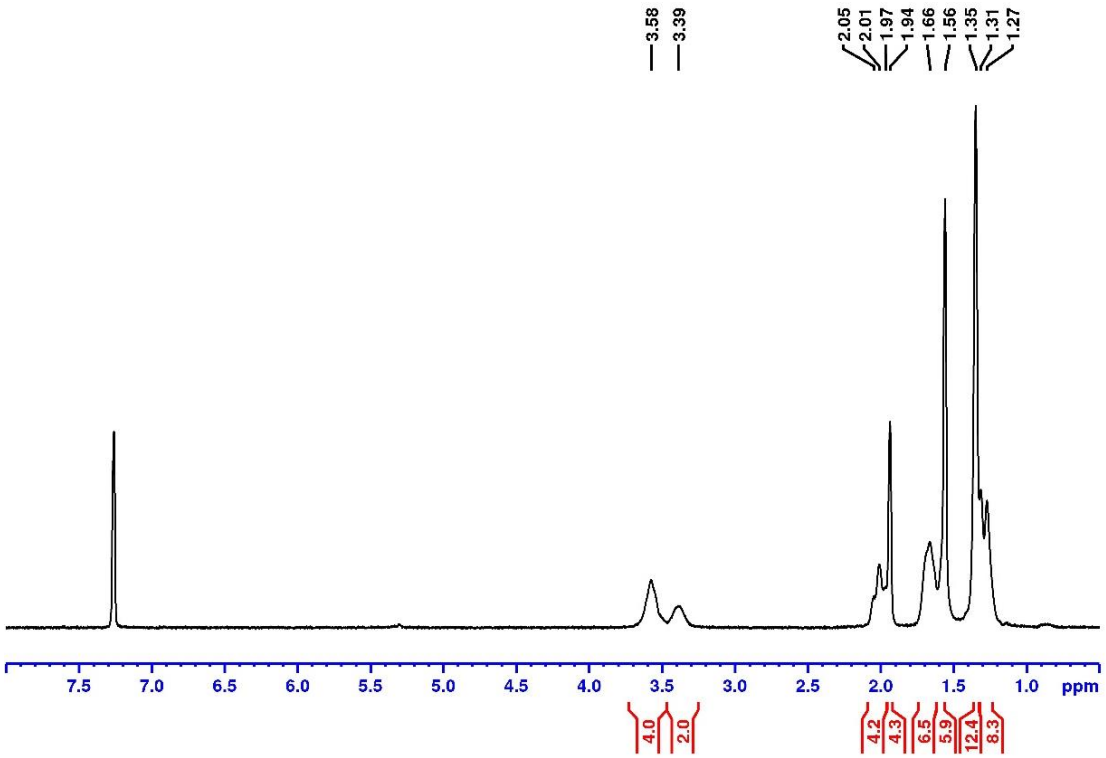


Fig. S43 ^{1}H NMR spectrum of **5c** in $CDCl_3$ at room temperature.

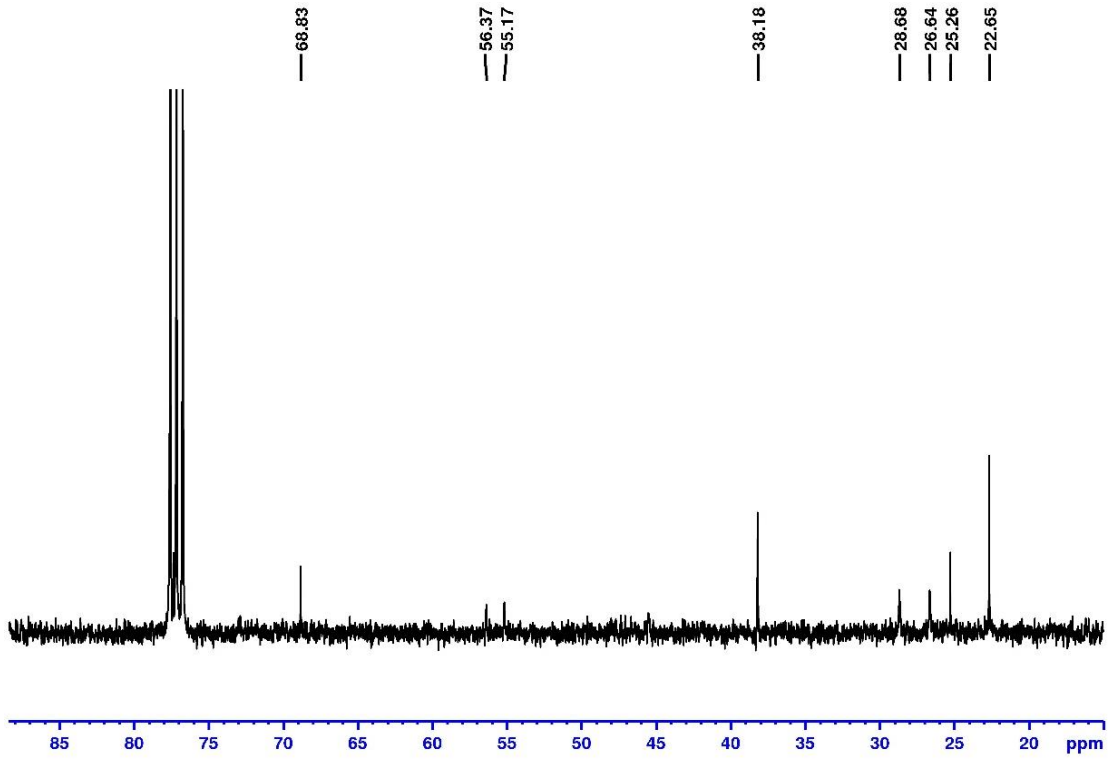


Fig. S44 $^{13}C\{^{1}H\}$ NMR spectrum of **5c** in $CDCl_3$ at room temperature.

UV/Vis Spectra

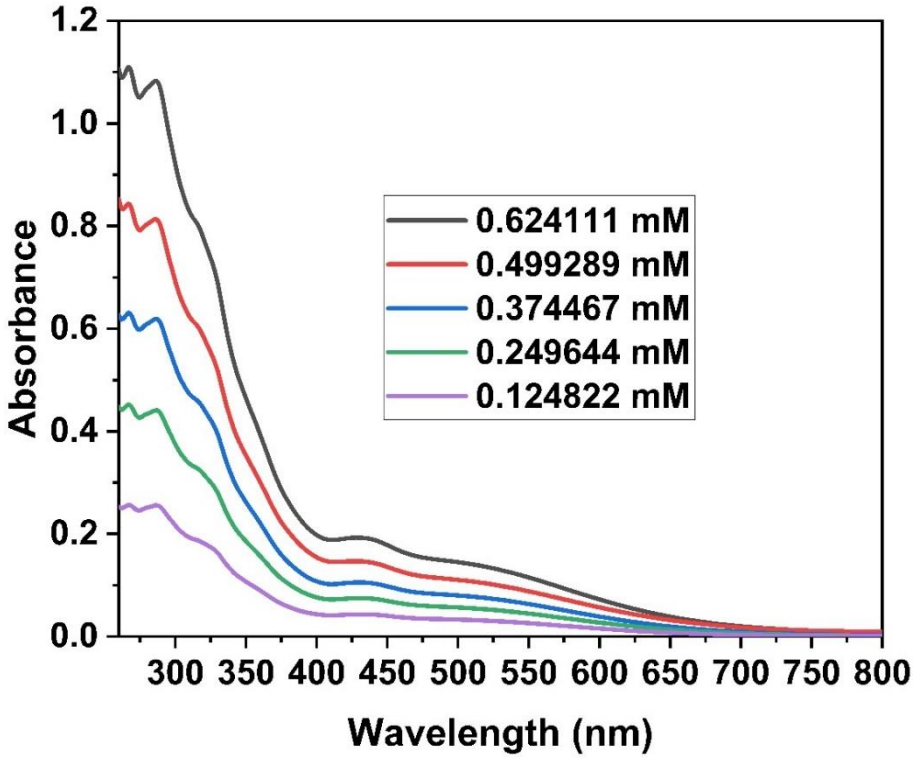


Fig. S45 UV/Vis spectra of **4a** in DCM at room temperature.

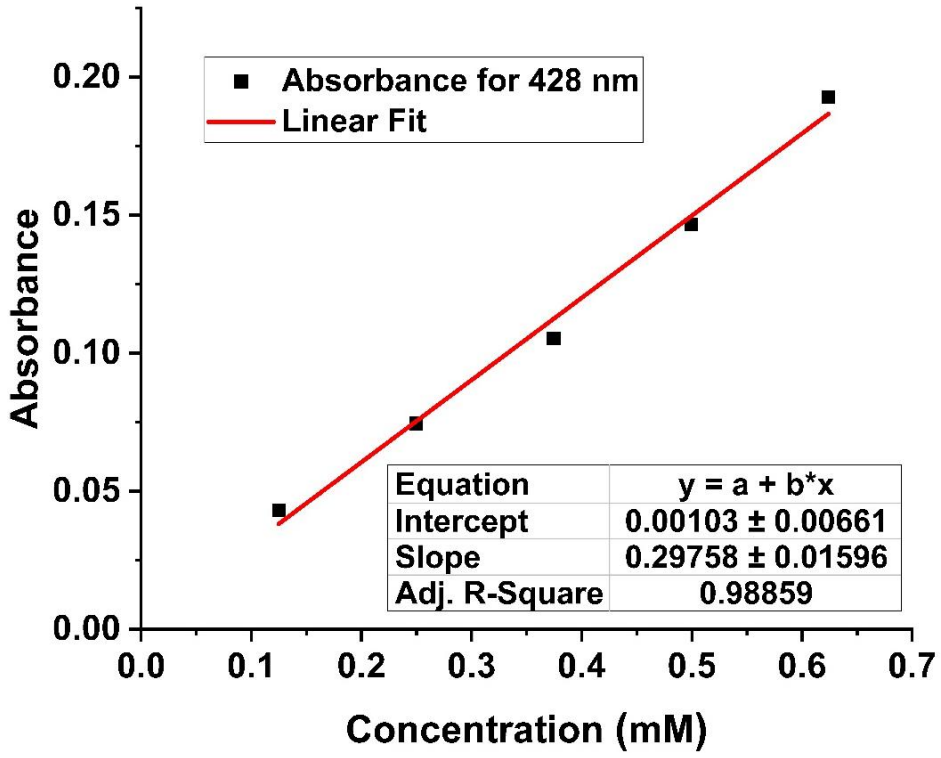


Fig. S46 Linear regression of **4a** at 428 nm (ε = 2980 $Lmol^{-1}cm^{-1}$).

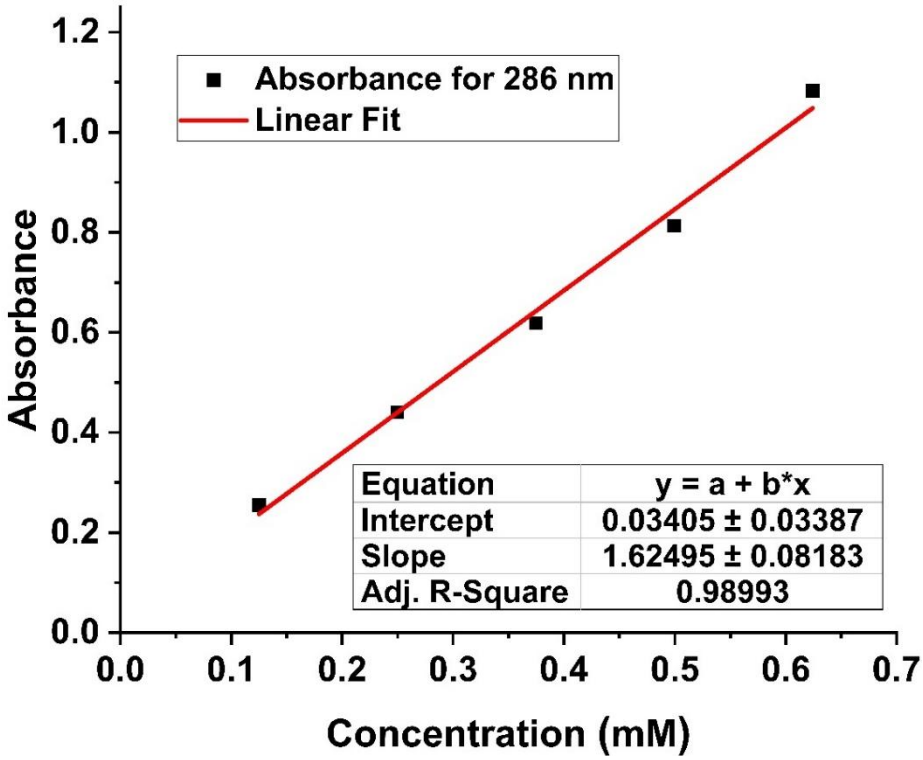


Fig. S47 Linear regression of **4a** at 286 nm (ε = 16200 $Lmol^{-1}cm^{-1}$).

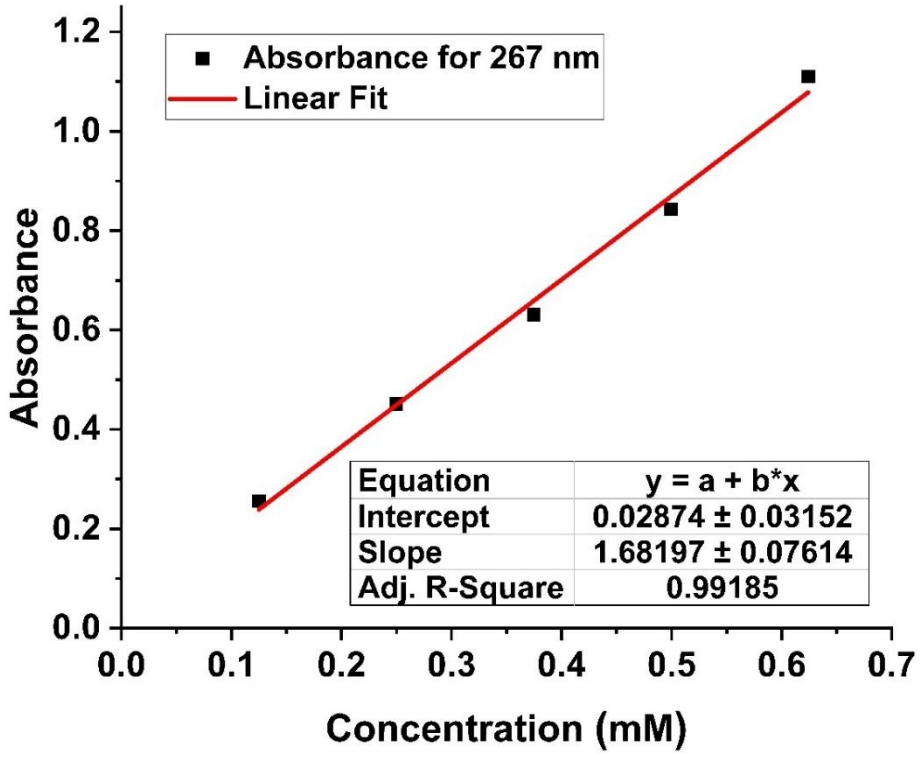


Fig. S48 Linear regression of **4a** at 267 nm (ε = 16800 $Lmol^{-1}cm^{-1}$).

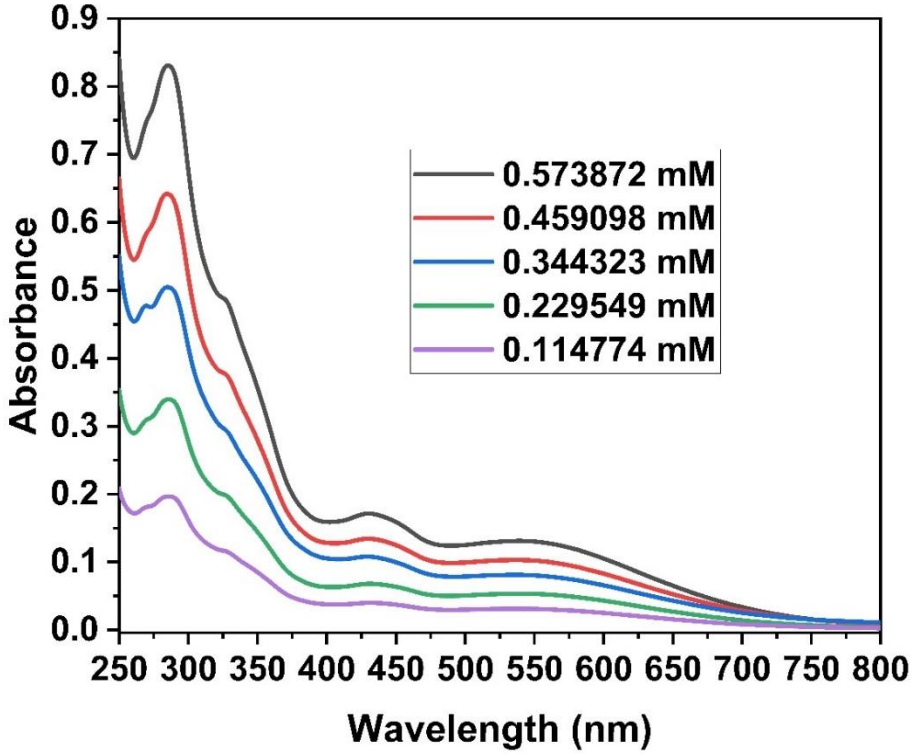


Fig. S49 UV/Vis spectra of **4b** in THF at room temperature.

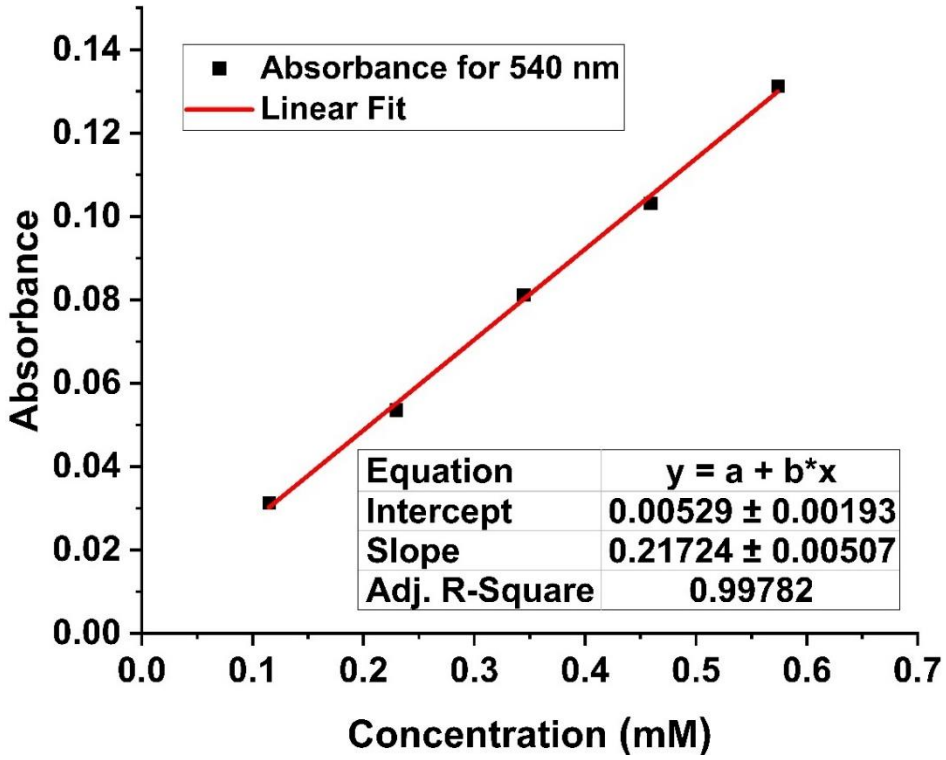


Fig. S50 Linear regression of **4b** at 540 nm (ε = 2170 $Lmol^{-1}cm^{-1}$).

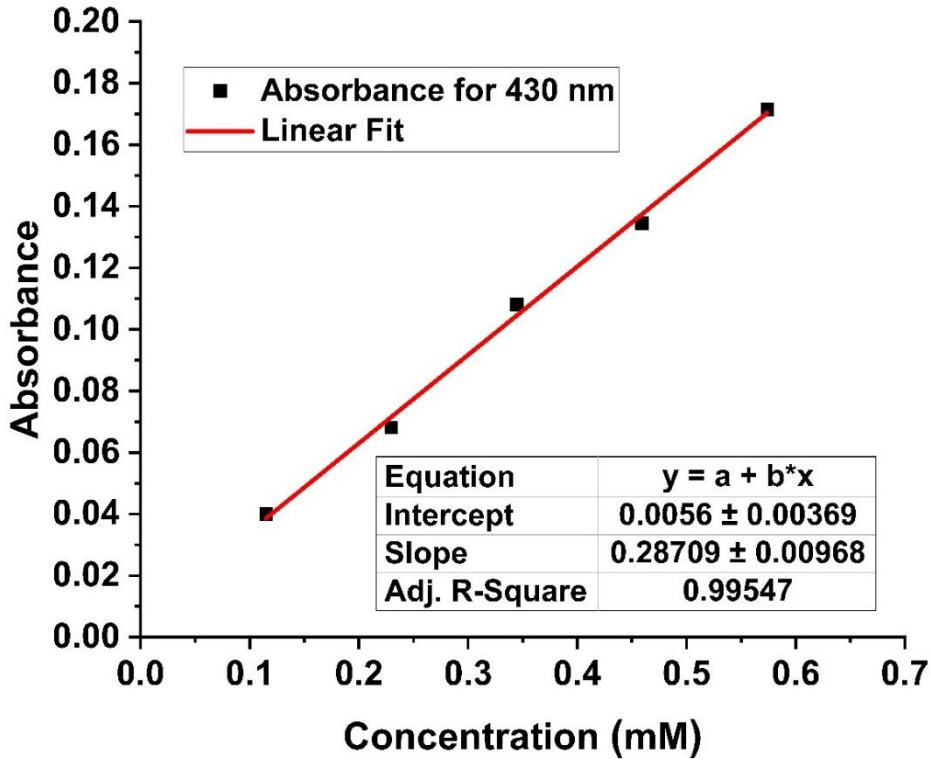


Fig. S51 Linear regression of **4b** at 430 nm (ε = 2870 $Lmol^{-1}cm^{-1}$).

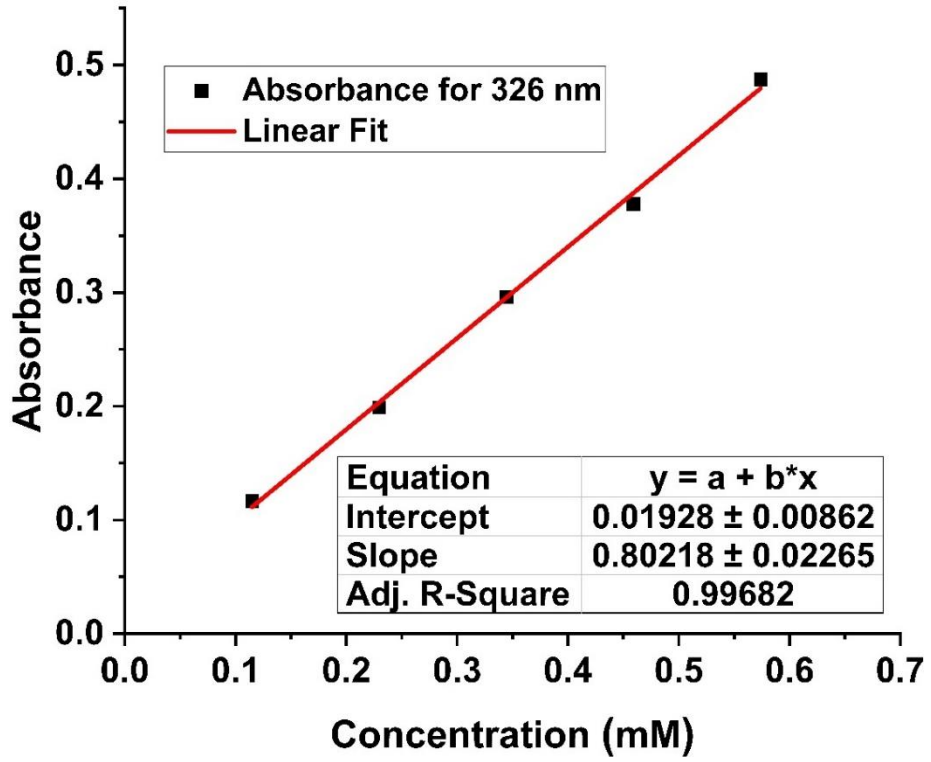


Fig. S52 Linear regression of **4b** at 326 nm (ε = 8020 $Lmol^{-1}cm^{-1}$).

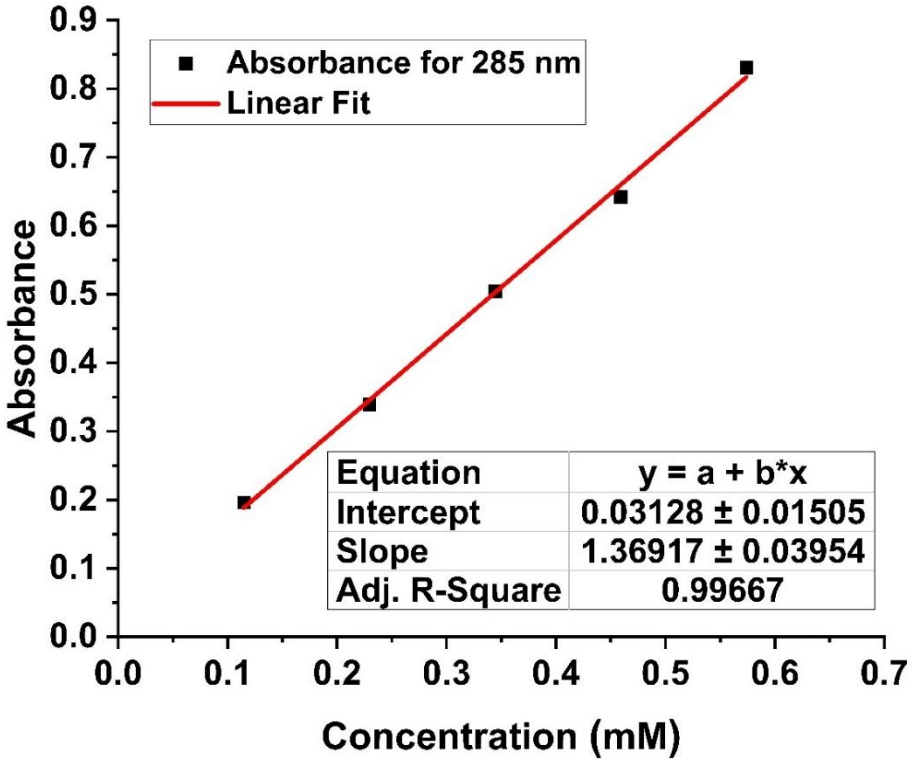


Fig. S53 Linear regression of **4b** at 285 nm (ε = 13700 $Lmol^{-1}cm^{-1}$).

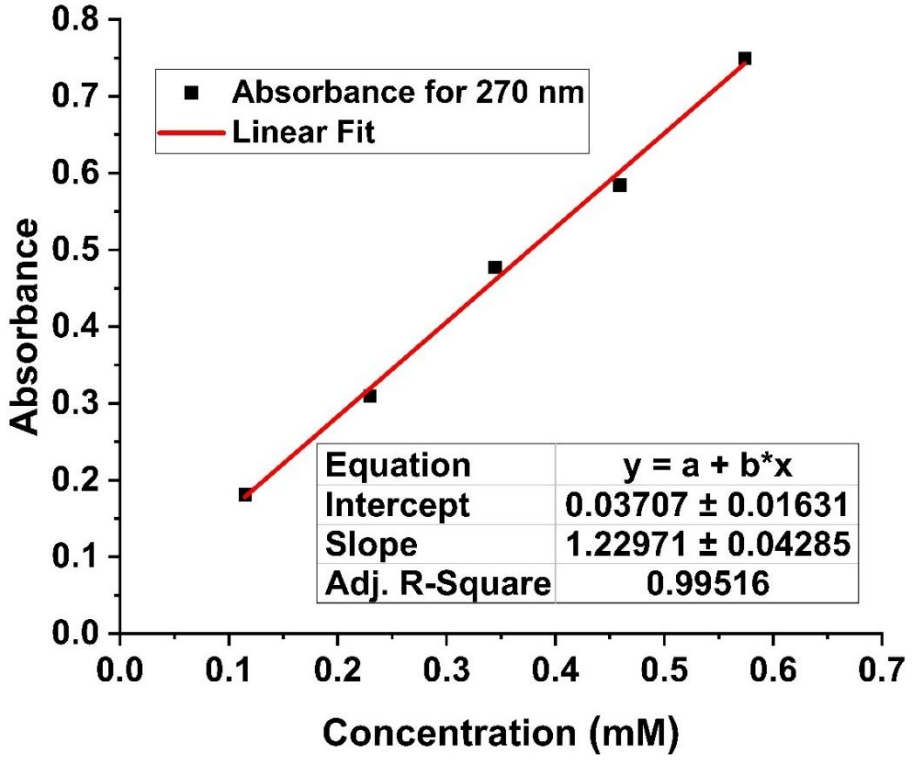


Fig. S54 Linear regression of **4b** at 270 nm (ε = 12300 $Lmol^{-1}cm^{-1}$).

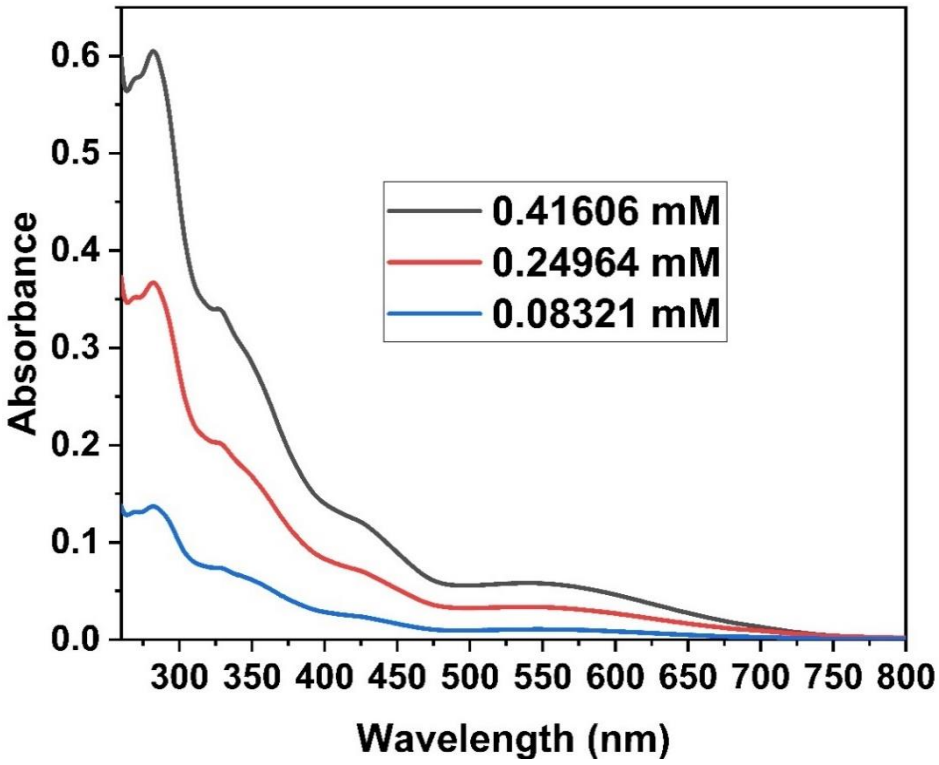


Fig. S55 UV/Vis spectra of **4c** in THF at room temperature.

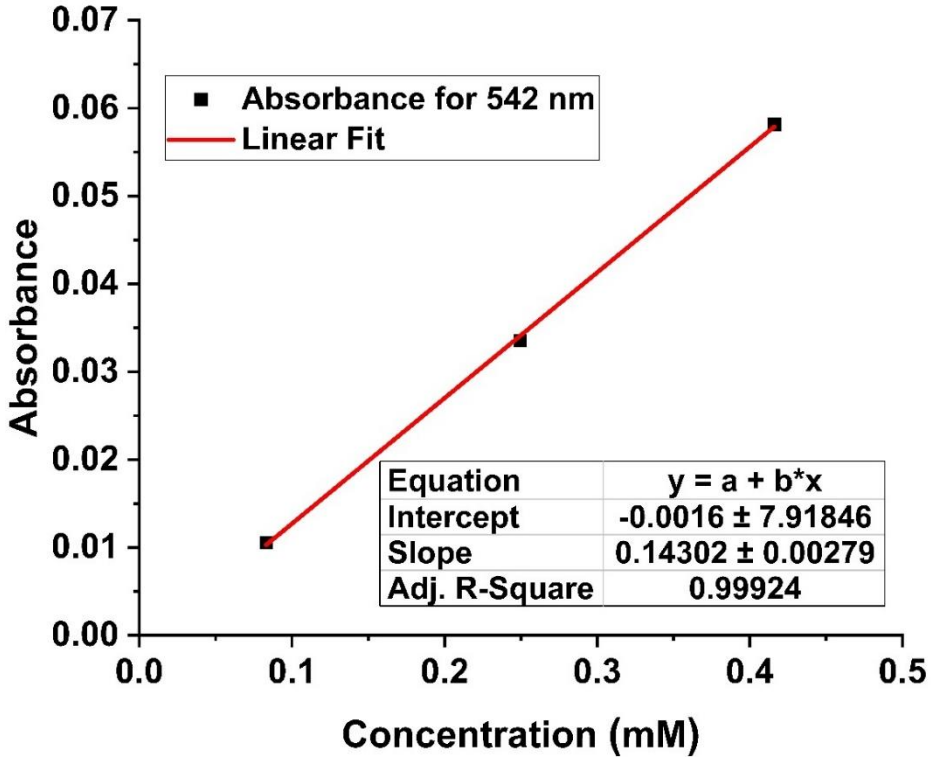


Fig. S56 Linear regression of **4c** at 542 nm (ε = 1430 $Lmol^{-1}cm^{-1}$).

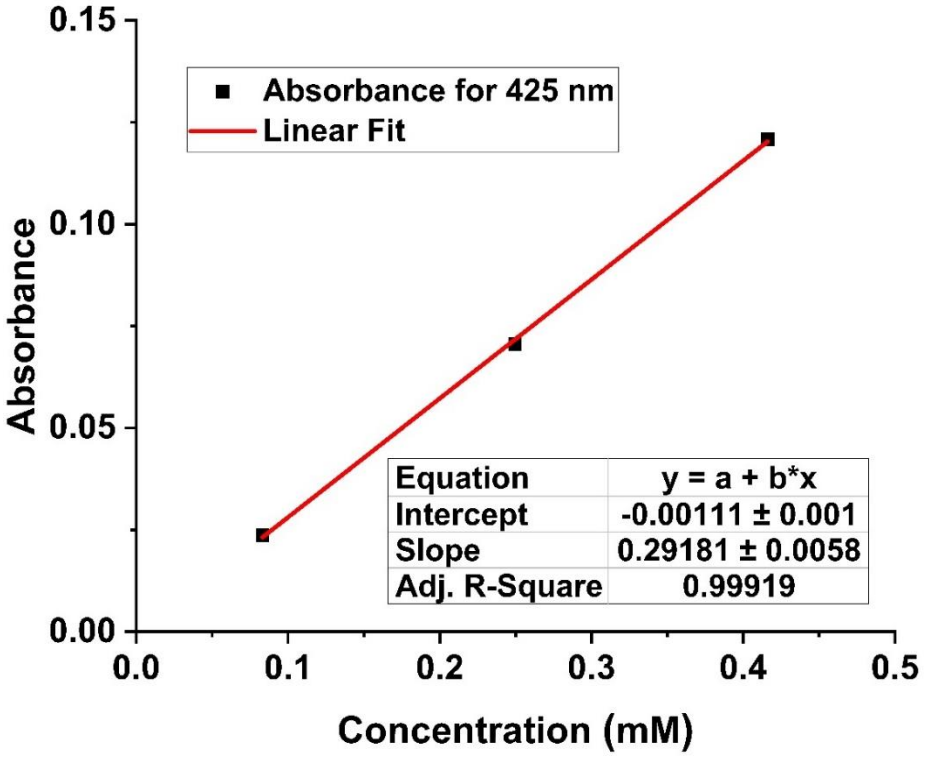


Fig. S57 Linear regression of **4c** at 425 nm (ε = 2920 $Lmol^{-1}cm^{-1}$).

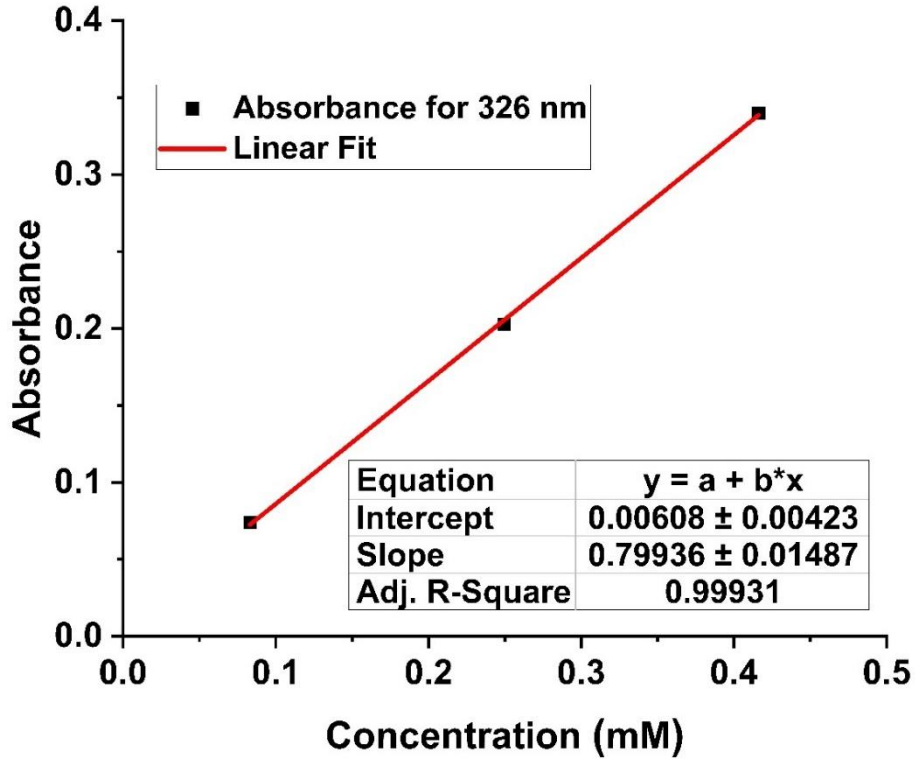


Fig. S58 Linear regression of **4c** at 326 nm (ε = 7990 $Lmol^{-1}cm^{-1}$).

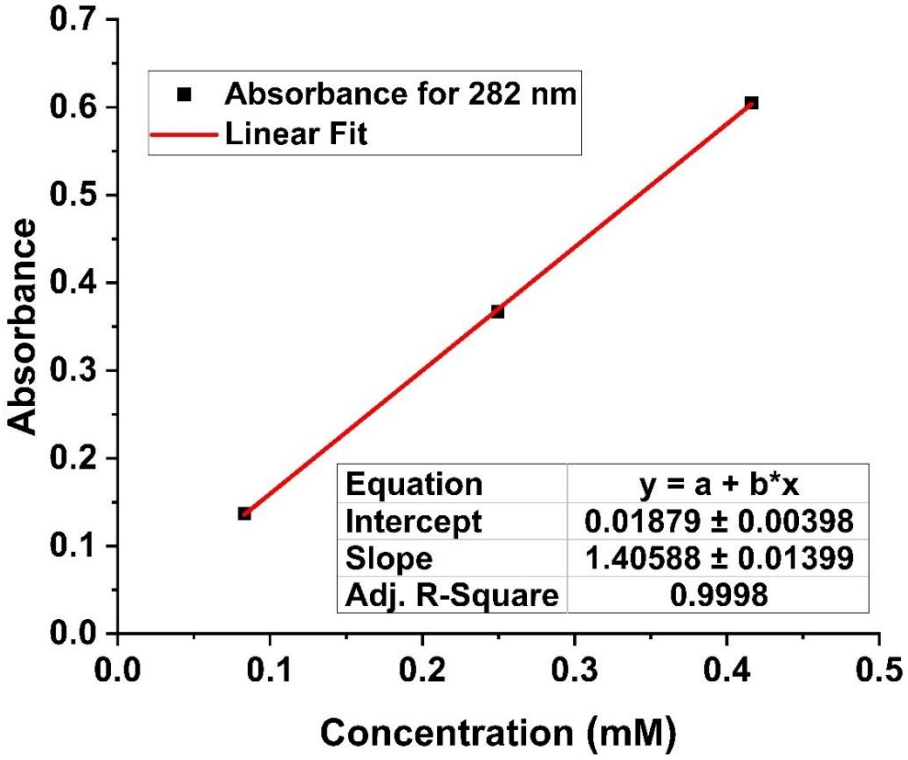


Fig. S59 Linear regression of **4c** at 282 nm (ε = 14100 $Lmol^{-1}cm^{-1}$).

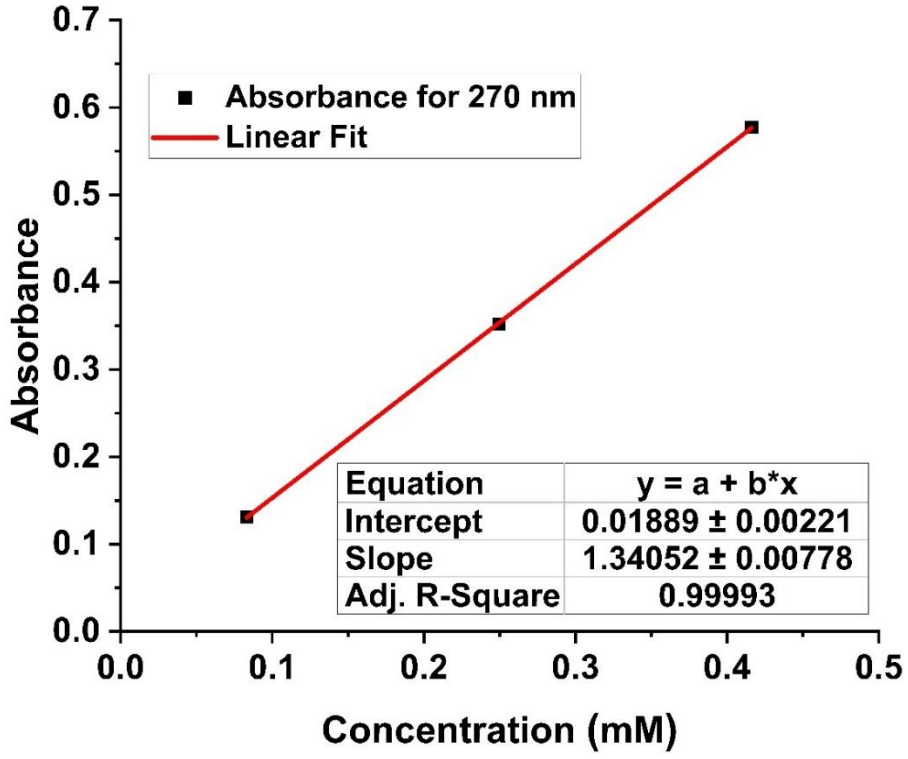


Fig. S60 Linear regression of **4c** at 270 nm (ε = 13400 $Lmol^{-1}cm^{-1}$).

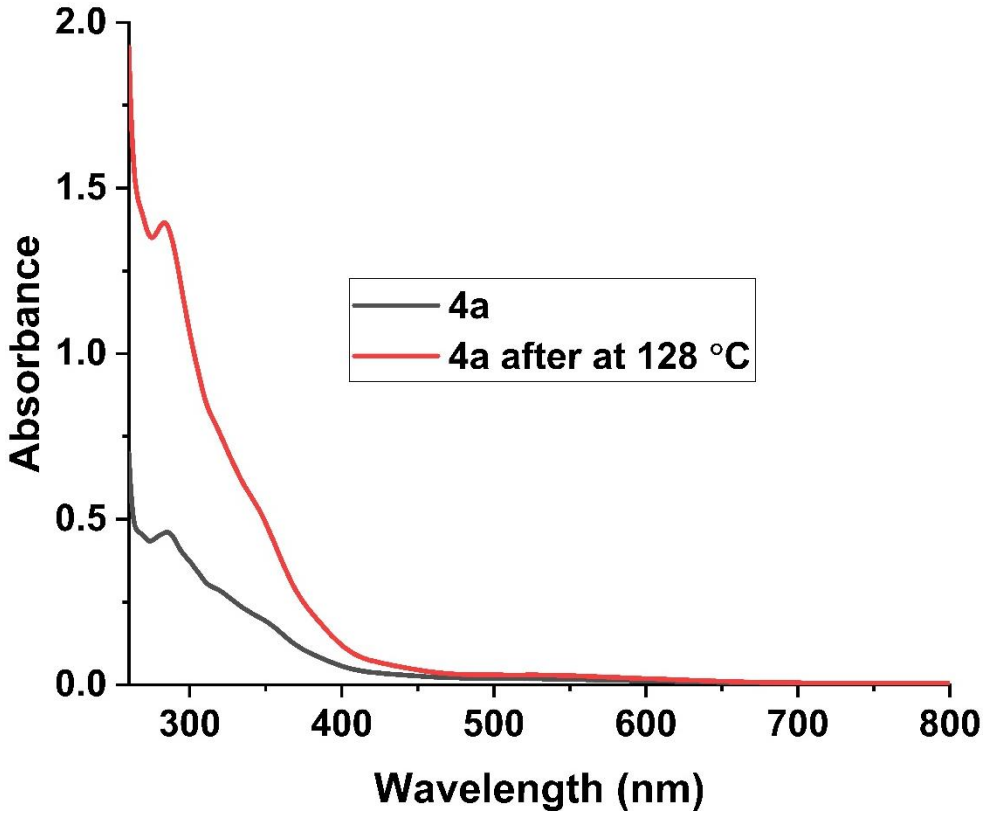


Fig. S61 Overlay of UV/Vis spectra of **4a** before heating (black) and after heating at 128 °C for 10 minutes (red) in DCM at room temperature.

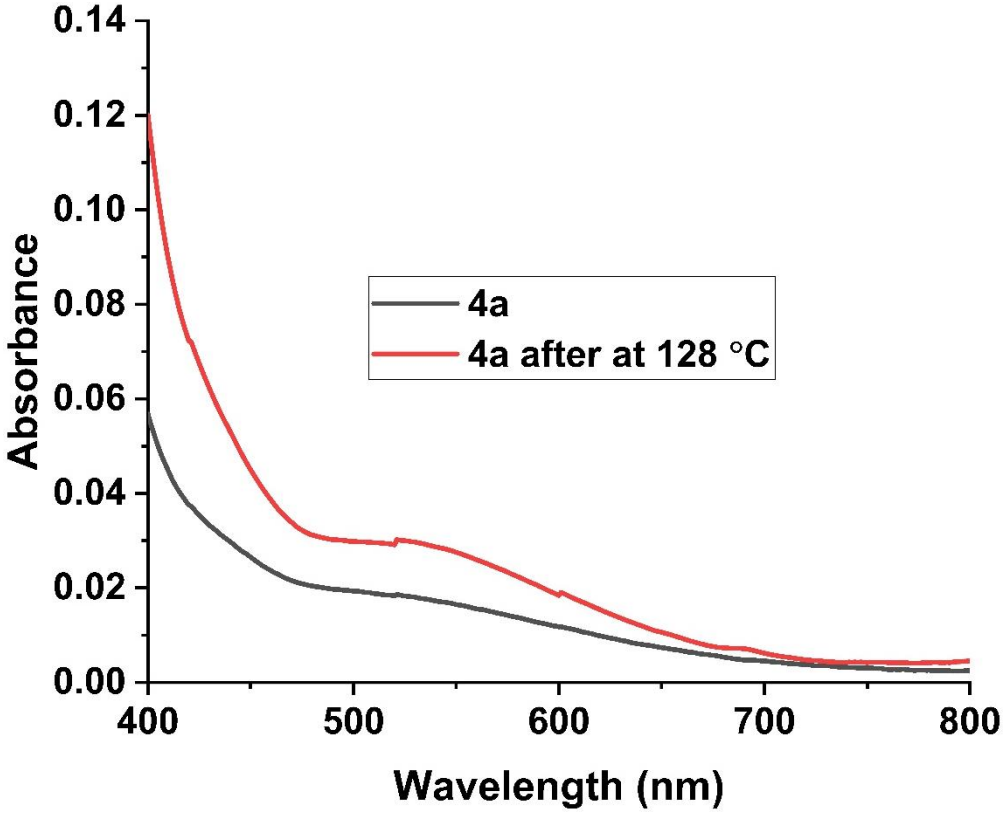


Fig. S62 Overlay of UV/Vis spectra of **4a** before heating (black) and after heating at 128 °C for 10 minutes (red) in DCM in selected region at room temperature.

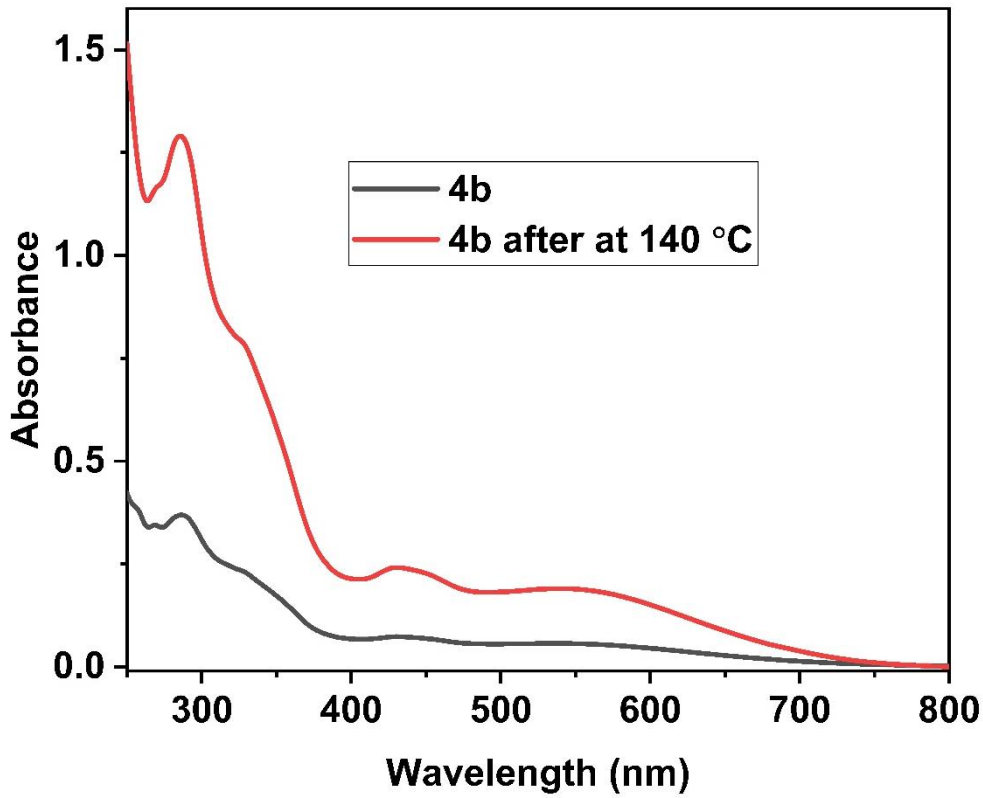


Fig. S63 Overlay of UV/Vis spectra of **4b** before heating (black) and after heating at 140 °C for 10 minutes (red) in DCM at room temperature.

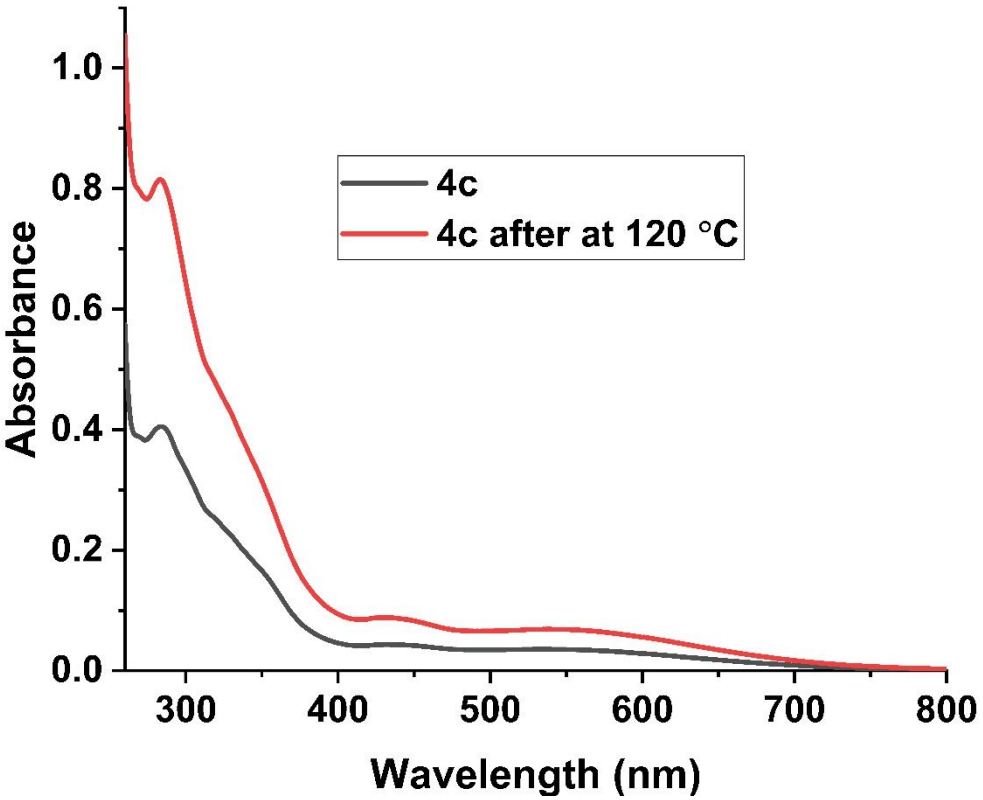


Fig. S64 Overlay of UV/Vis spectra of **4c** before heating (black) and after heating at 120 °C for 10 minutes (red) in DCM at room temperature.

Molecular Structures of 1a, 1c, 2a, 2b, 2c, 3b, 4c, 5a, 5b and 5c

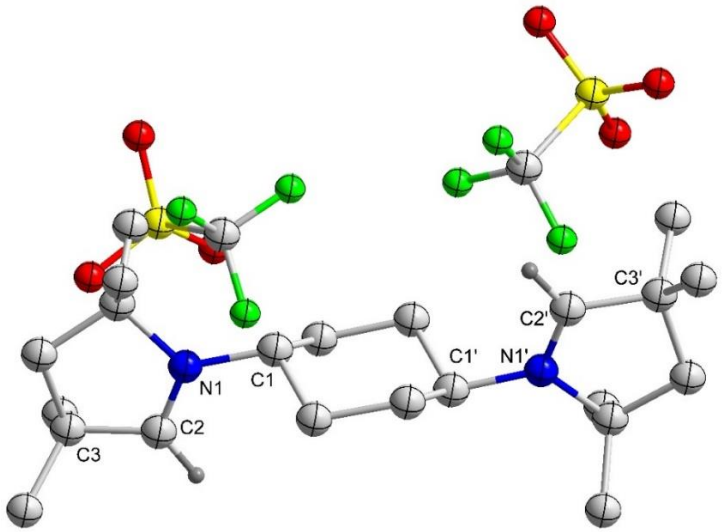


Fig. S65 Molecular structure of **1a** in solid-state with thermal ellipsoids at a 50% probability level. All hydrogen atoms except for those on C2 and C2' are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.493(2), N1–C2 1.274(3), C2–C3 1.496(3); C1–N1–C2 123.77(16), N1–C2–C3 114.02(17).

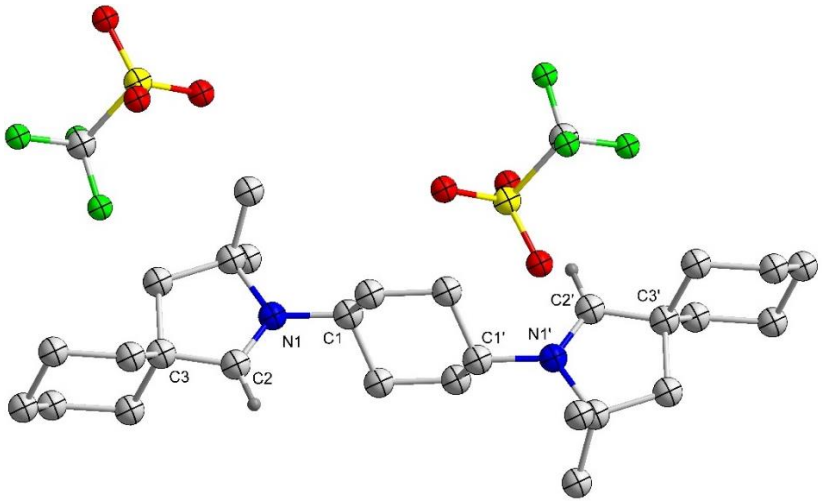


Fig. S66 Molecular structure of **1c** in solid-state with thermal ellipsoids at a 50% probability level. All hydrogen atoms except for those on C2 and C2' are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.492(2), N1–C2 1.275(2), C2–C3 1.483(3); C1–N1–C2 124.56(15), N1–C2–C3 115.34(17).

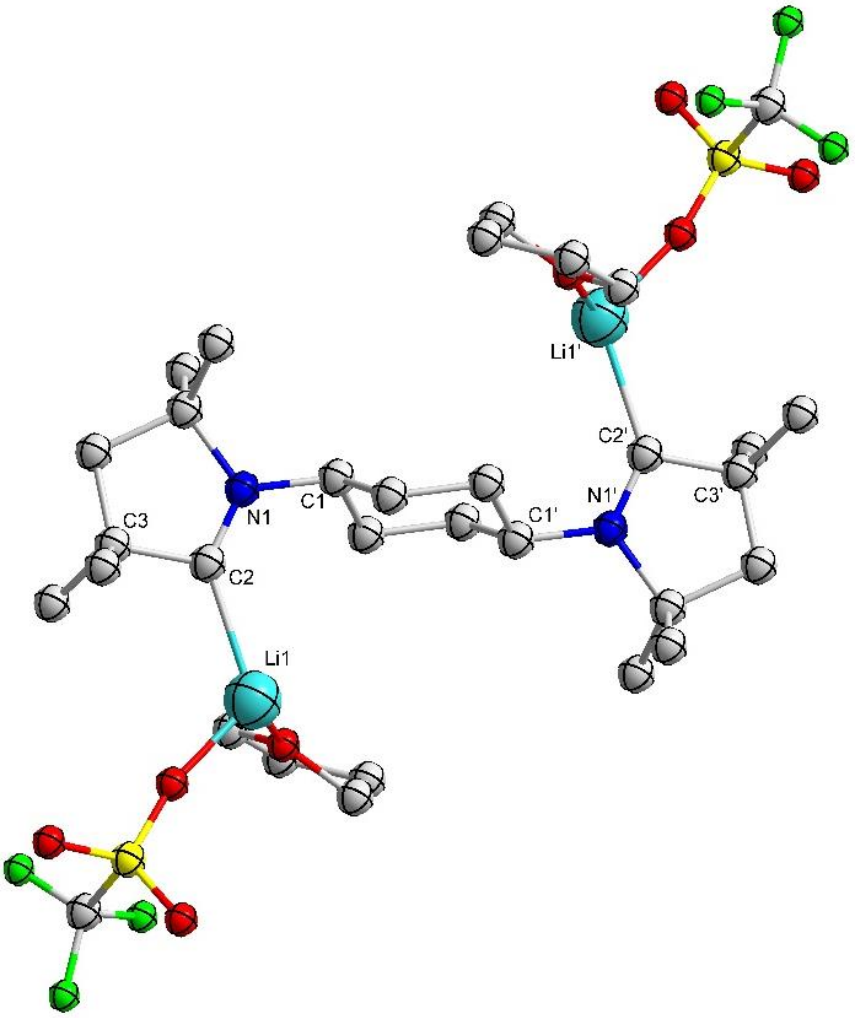


Fig. S67 Molecular structure of **2a** in solid-state in different orientations with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.491(19), N1–C2 1.2995(19), C2–C3 1.524(2), C2–Li1 2.227(3); N1–C2–Li1 135.57(13), N1–C2–C3 106.90(13).

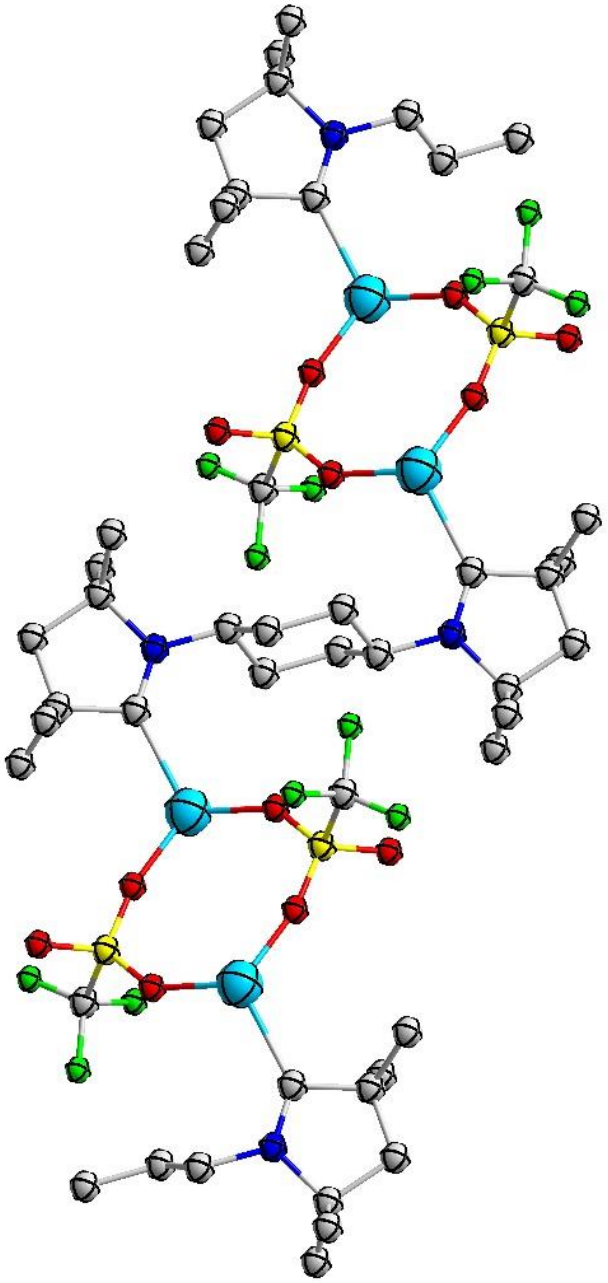


Fig. S68 Polymeric subunit of molecular structure of **2a** in solid-state in different orientations with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.491(19), N1–C2 1.2995(19), C2–C3 1.524(2), C2–Li1 2.227(3); N1–C2–Li1 135.57(13), N1–C2–C3 106.90(13).

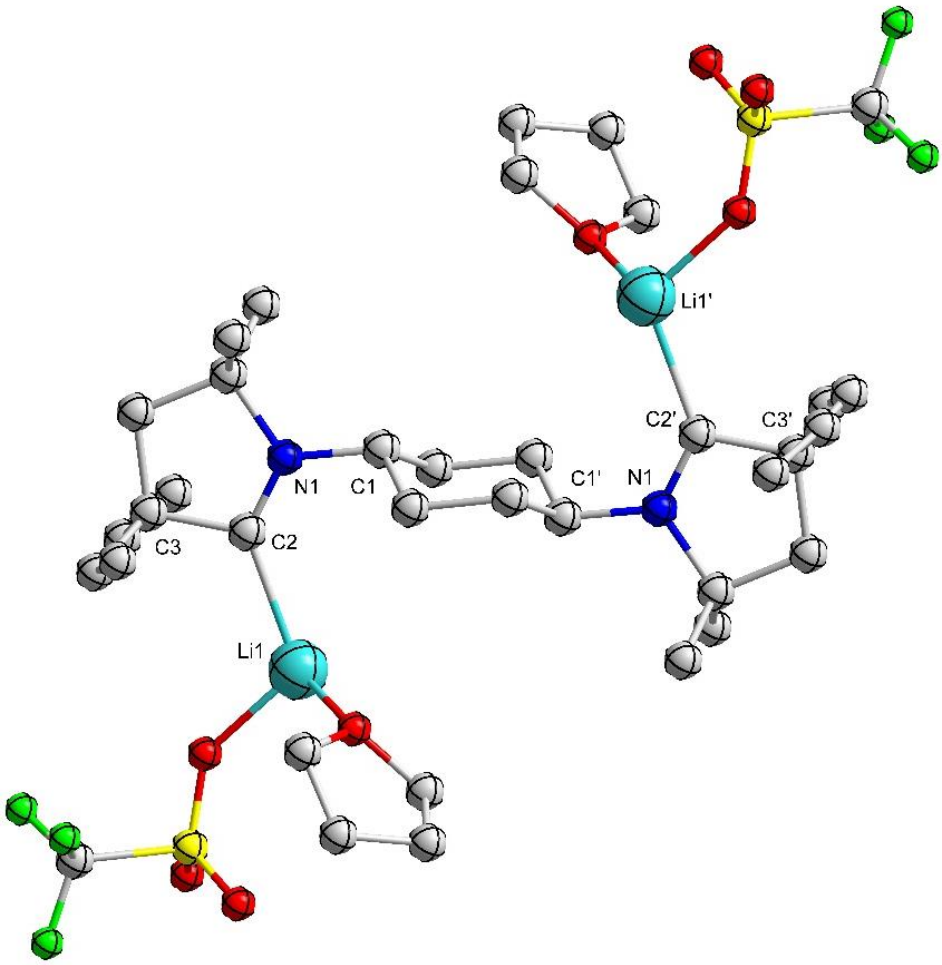


Fig. S69 Molecular structure of **2b** in solid-state with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.4804(17), N1–C2 1.2977(18), C2–C3 1.522(2), C2–Li1 2.234(3); N1–C2–Li1 133.29(12), N1–C2–C3 107.13(12).

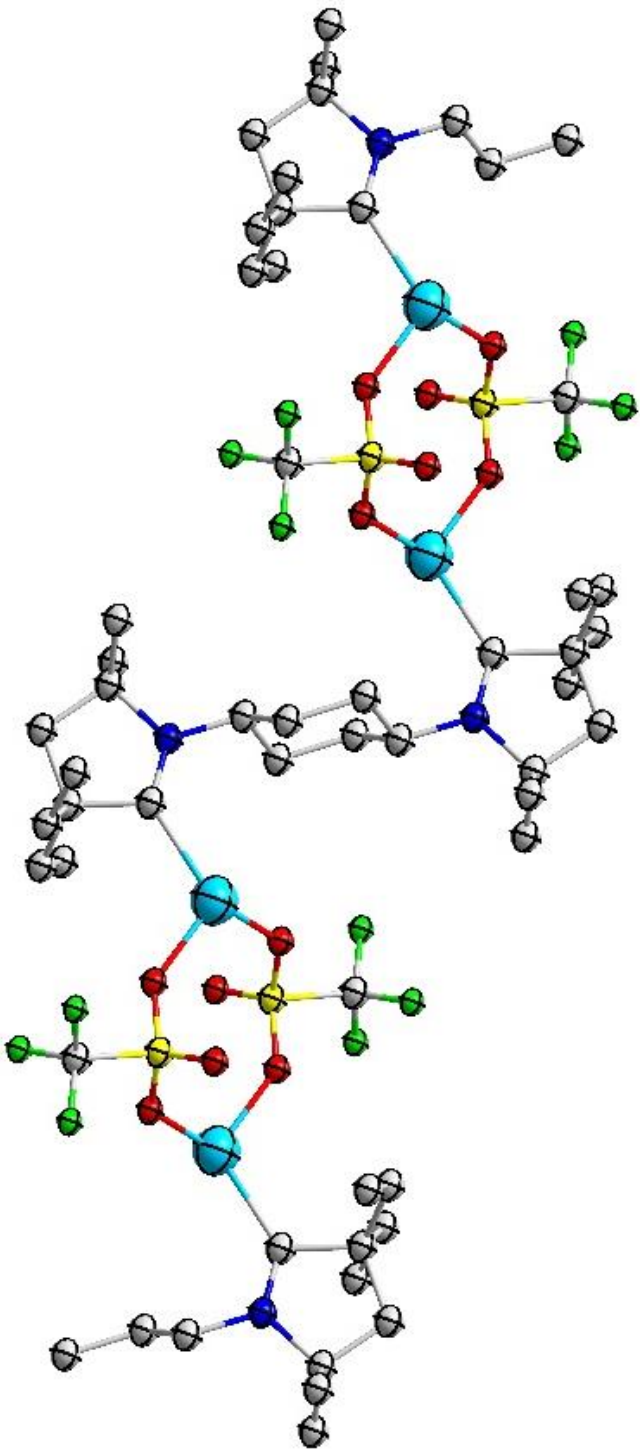


Fig. S70 Polymeric subunit of molecular structure of **2b** in solid-state with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.4804(17), N1–C2 1.2977(18), C2–C3 1.522(2), C2–Li1 2.234(3); N1–C2–Li1 133.29(12), N1–C2–C3 107.13(12).

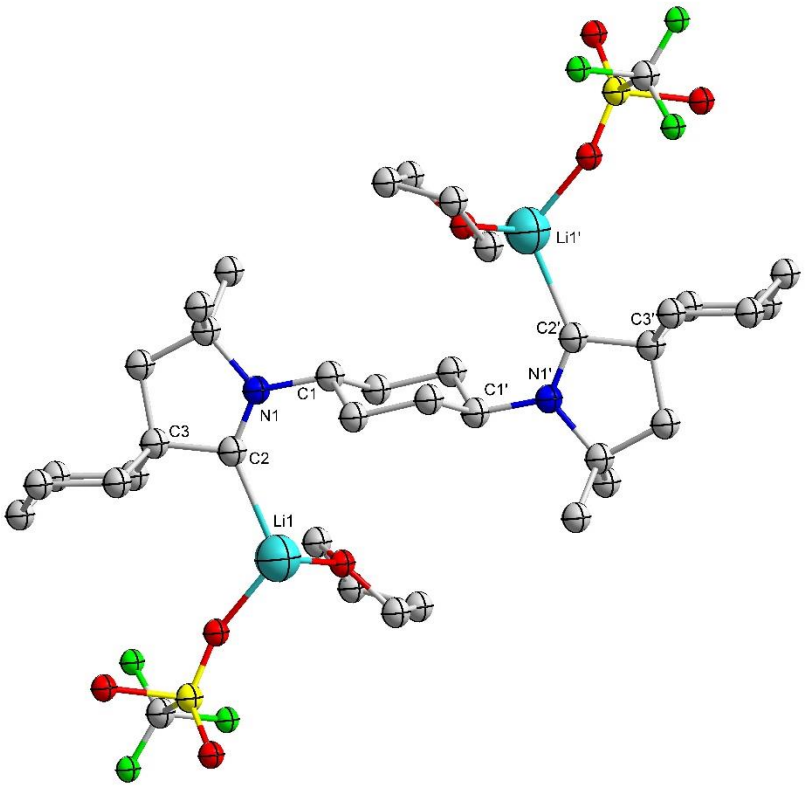


Fig. S71 Molecular structure of **2c** in solid-state with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.486(2), N1–C2 1.304(2), C2–C3 1.525(2), C2–Li1 2.255(3); N1–C2–Li1 134.84(15), N1–C2–C3 107.13(14).

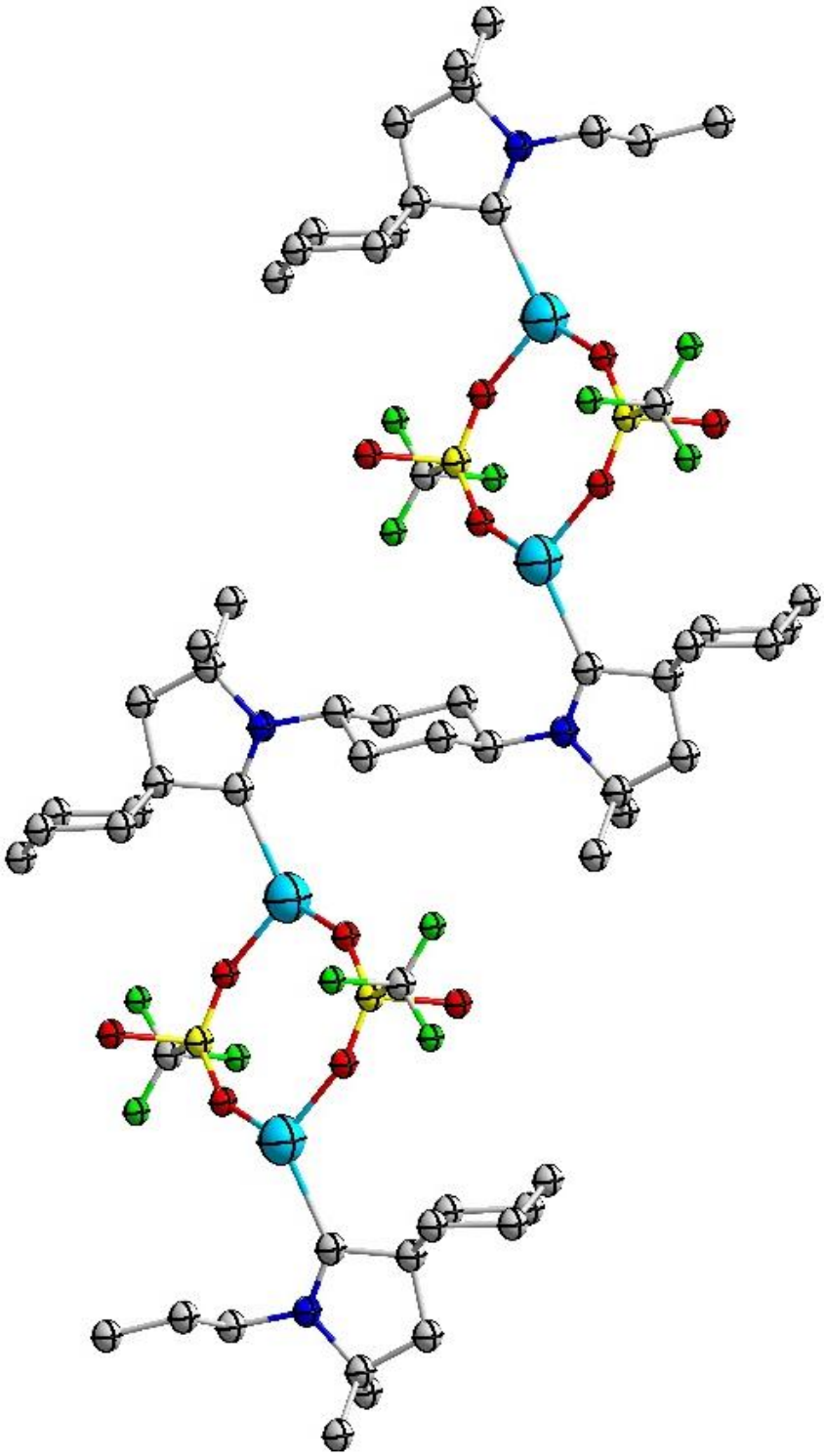


Fig. S72 Polymeric subunit of molecular structure of **2c** in solid-state with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.486(2), N1–C2 1.304(2), C2–C3 1.525(2), C2–Li1 2.255(3); N1–C2–Li1 134.84(15), N1–C2–C3 107.13(14).

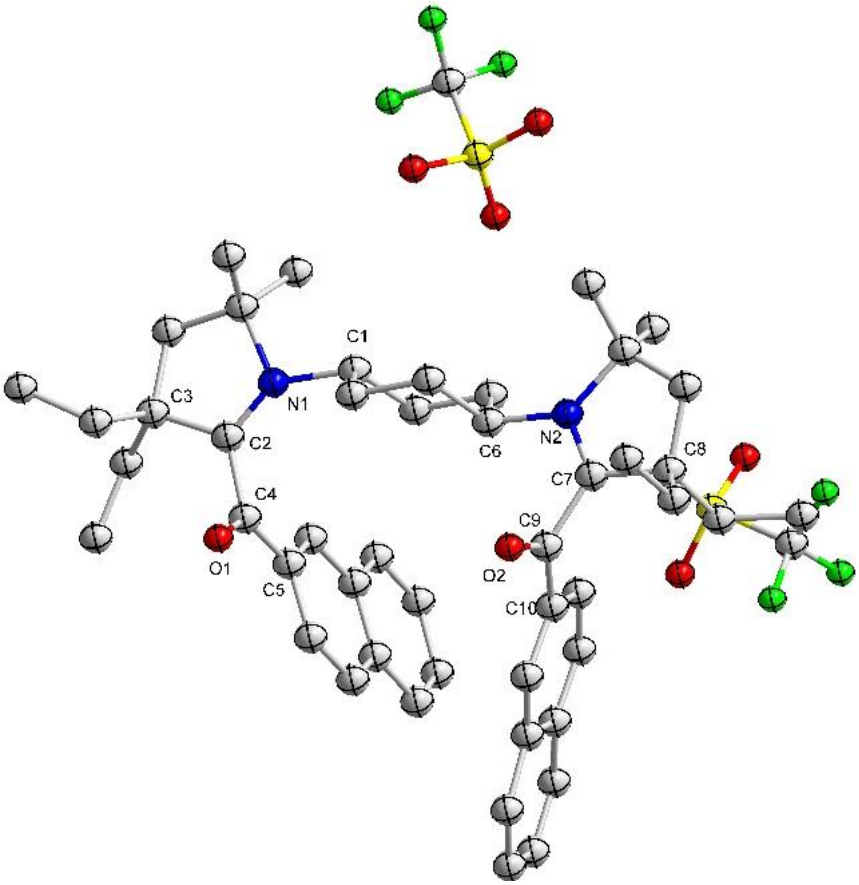


Fig. S73 Molecular structure of **3b** in solid-state with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.515(6), N1–C2 1.280(3), C2–C3 1.508(3), C2–C4 1.530(4), C4–C5 1.459(5), C4–O1 1.221(4); N1–C2–C4 123.2(2), C2–C4–C5 118.2(3), N2–C7–C9 124.2(4), C7–C9–C10 122.7(5).

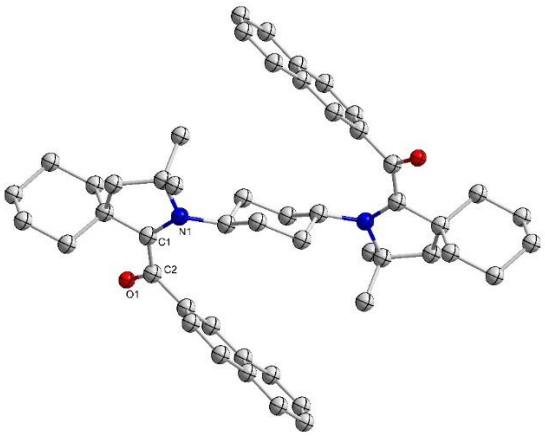


Fig. S74 Molecular structure of **4c** in solid-state in different orientations with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.366(2), C1–C2 1.434(2), C2–O1 1.258(2); N1–C1–C2 126.87(14), C1–C2–O1 120.46(14).

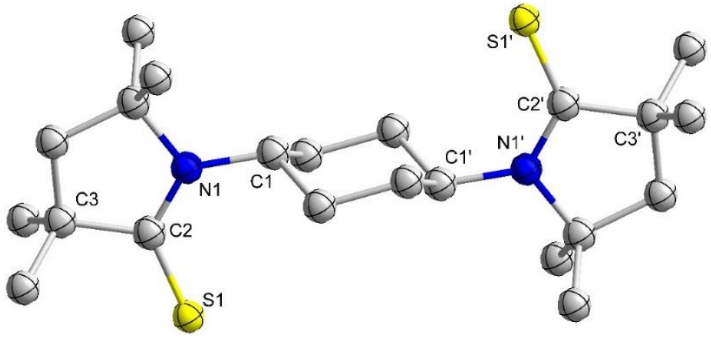


Fig. S75 Molecular structure of **5a** in solid-state with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.481(2), N1–C2 1.328(2), C2–C3 1.526(2), C2–S1 1.6675(19); N1–C2–S1 128.22(14), N1–C2–C3 109.73(15).

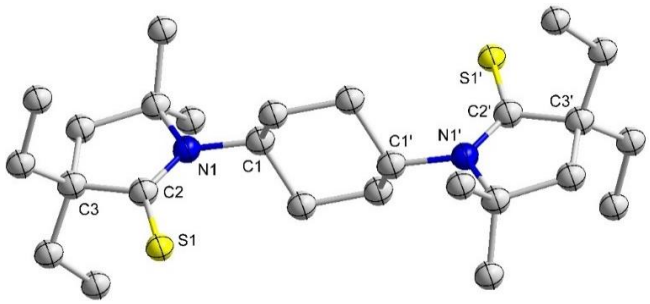


Fig. S76 Molecular structure of **5b** in solid-state with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.476(2), N1–C2 1.330(3), C2–C3 1.527(3), C2–S1 1.663(2); N1–C2–S1 128.06(16), N1–C2–C3 110.17(18).

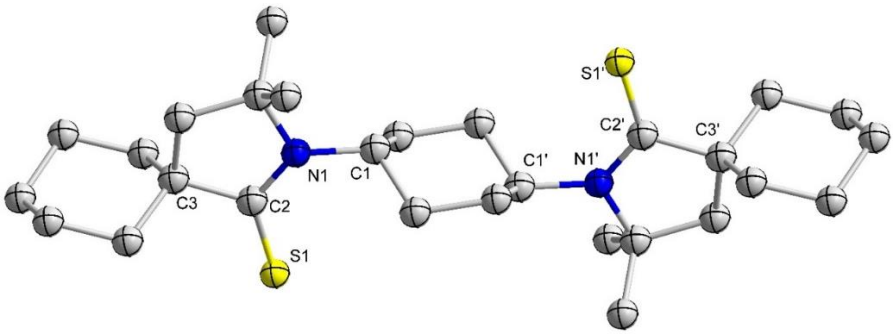


Fig. S77 Molecular structure of **5c** in solid-state with thermal ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–C1 1.481(2), N1–C2 1.327(2), C2–C3 1.529(2), C2–S1 1.663(18); N1–C2–S1 127.41(13), N1–C2–C3 109.80(15).

Crystallographic Details

Single-crystal X-ray diffraction data of **1a**, **1c**, **2a**, **2b**, **2c**, **3b** and **5b** were collected using a Rigaku diffractometer with graphite-monochromated molybdenum *Kα* radiation, *λ* = 0.71073 Å. Single-crystal X-ray diffraction data of **4c** was collected using a Rigaku diffractometer with graphite-monochromated copper *Kα* radiation, *λ* = 1.54184 Å. Data integration and reduction were processed with CrysAlisPro software.[S3] An empirical absorption correction was applied to the collected reflections with SCALE3 ABSPACK integrated with CrysAlisPro. The structures were solved by direct methods using SHELXT[S4] and refined by the full matrix least-squares method based on F^2 by using SHELXL[S5] through the Olex2[S6] interface. All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms, unless stated otherwise, were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for the aromatic carbon atoms. Individual reflections which were clear outliers were removed from the refinements with OMIT instructions.

Single-crystal X-ray diffraction data of **5a** and **5c** were collected using a Bruker APEX-II CCD diffractometer with graphite-monochromated molybdenum *Kα* radiation, λ = 0.71073 Å. Data were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Empirical absorption corrections were carried out using Int.Tab. Vol. C (1992) p. 523, Tab. 6.3.3.3 for values of muR in the range 0-2.5, and Int.Tab. Volume II (1959) p.302; Table 5.3.6 B for muR in the range 2.6-10.0. The structures were solved and refined using the Bruker SHELXTL Software Package[S4] using Direct Methods and refined with the SHELXL refinement package[S5] using least square minimisation with WinGX.[S7] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in geometrically calculated positions or found in the Fourier difference map and included in the refinement process using riding models.

Crystal and structure refinement data of all these compounds are summarized in tables EPR-S12. In the structure of **1a**, the hydrogen on C7 was found and refined freely. In the structure of **1c**, all atoms of the triflate anion are disordered, which was modelled with SAME, SIMU and DELU constraints. Occupancies are 55% and 45%. Five reflections were omitted as outliers. In the structure of **2a**, there are three moieties which are disordered. i) All atoms of the triflate anion are disordered over two orientations. This was modelled including all eight atoms to allow for a better orientation of the oxygen and fluorine atoms. This was modelled with SAME, SIMU and DELU constraints. Occupancies are 64% and 36%. ii) The THF molecule is disordered entirely over two orientations. This was also modelled with SAME, SIMU and DELU constraints. Occupancies are 73% and 27%. iii) There is a disordered ring pucker in the N-heterocycle (only the C3 atom). This was

modelled without any constraints or restraints. Occupancies are 73% and 27%. The Li and triflate ions form an eight-membered square ring-type arrangement. One reflex was omitted as the outlier. In the structure of **2b**, the hydrogen on C11 was found and refined freely. In the structure of **2c,** all atoms of the triflate anion are disordered, which was modelled with SAME, SIMU and DELU constraints. Occupancies are 65% and 35%. The THF molecule is disordered entirely, which was modelled with SAME and with SIMU for only two carbon atoms of the major occupancy (C17' and C18'). Occupancies are 27% and 73%. The structure is essentially a coordination polymer through the Li and triflate ions which form squares (2Li + 2S + 4O). In the structure of **5a**, absorption correction is carried out and 2 reflections are omitted as affected by beamstop/outliers. The structure of **3b** exhibits three types of disorder. The central cyclohexane ring (C1-C6) is present in two different orientations with regard to the ring pucker. Both are in chair conformation while four of the atoms point into opposite directions. This was modelled with SAME, SIMU and DELU constraints (relatively mild values). Occupancies are 54% and 46%. One naphthyl-formyl substituent is disordered by a small slide and a flip by 180° of the naphthyl moiety. This was modelled with SAME (for the naphthyl) and SADI (for the formyl moiety) plus SIMU and DELU constraints (also relatively mild values). Occupancies are 81% and 19%. The third disorder affects two ethyl substituents on the same carbon atom. This was modelled with SADI, SIMU and DELU constraints (again relatively mild values). Occupancies are 56% and 44%. Further, there is some fraction of co-crystallised solvent. SQUEEZE finds ca. 15 electrons per cell and a void size of 110 $Å^3$. These values are actually split over two sites, *i.e.* two voids with roughly 8 electrons each and void size 55 $Å^3$. The density most likely belongs to acetonitrile since it is in specific symmetry related positions and the resultant molecule would be linear. In the cell, there are four cations and eight anions, hence, four electrons per formula were squeezed away. In each cell there is only a fraction of acetonitrile (*ca*. 68% of one molecule) and this is distributed over two voids. It was not included in the sum formula for the refinements. With regard to the refinement of **4c**, all three B-alerts go back to electron density close to C14, close to C21 and close to the atoms of the naphthalene moiety. Presumably the 5-ring has a bit of ring pucker disorder (10%) affecting C14 and C21, and the disorder of the naphthalene is a flip (8%). Modelling only one of those did not really improve the overall refinement and modelling all renders the solution messy and difficult to navigate without any actual benefit. We have therefore refrained from modelling the disorder but are prepared to submit an alternative refinement with disorder modelling.

Table S2. Crystal data and structure refinement for **1a** (CCDC 2189381)

Identification code	aj0698
Empirical formula	$C_{24}H_{40}F_6N_2O_6S_2$
Formula weight	630.70
Temperature/K	120(2)
Crystal system	monoclinic
Space group	*C*2/*c*
a/Å	22.6531(9)
b/Å	10.6359(4)
c/Å	13.5057(5)
α/°	90
β/°	112.830(4)
γ/°	90
Volume/Å^3	2999.1(2)
Z	4
ρ_{calc}g/cm^3	1.397
μ/mm^{-1}	0.254
F(000)	1328.0
Crystal size/mm^3	0.235 × 0.146 × 0.131
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.844 to 57.846
Index ranges	-29 ≤ h ≤ 30, -13 ≤ k ≤ 14, -14 ≤ l ≤ 18
Reflections collected	20113
Independent reflections	3602 [R_{int} = 0.0373, R_{sigma} = 0.0304]
Data/restraints/parameters	3602/0/189
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.1177
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.1236
Largest diff. peak/hole / e Å^{-3}	0.41/-0.43

Table S3. Crystal data and structure refinement for **1c** (CCDC 2189382)

Identification code	AJ0857
Empirical formula	$C_{30}H_{48}F_6N_2O_6S_2$
Formula weight	710.82
Temperature/K	230.00(10)
Crystal system	triclinic
Space group	*P*-1
a/Å	6.6145(5)
b/Å	8.4668(5)
c/Å	15.3473(8)
α/°	88.298(5)
β/°	79.536(5)
γ/°	88.611(5)
Volume/Å^3	844.68(9)
Z	1
ρ_{calc}g/cm^3	1.397
μ/mm^{-1}	0.235
F(000)	376.0
Crystal size/mm^3	0.13 × 0.12 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.4 to 57.94
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 11, -20 ≤ l ≤ 16
Reflections collected	11531
Independent reflections	3862 [R_{int} = 0.0349, R_{sigma} = 0.0429]
Data/restraints/parameters	3862/0/210
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0500, wR_2 = 0.1100
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1168
Largest diff. peak/hole / e Å^{-3}	0.31/-0.40

Table S4. Crystal data and structure refinement for **2a** (CCDC 2189383)

Identification code	aj2066
Empirical formula	$C_{16}H_{27}LiNO_4F_3S$
Formula weight	393.38
Temperature/K	250(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.4316(6)
b/Å	17.5255(9)
c/Å	10.7728(6)
α/°	90
β/°	101.125(5)
γ/°	90
Volume/Å^3	2117.7(2)
Z	4
ρ_{calc}g/cm^3	1.234
μ/mm^{-1}	0.196
F(000)	832.0
Crystal size/mm^3	0.441 × 0.351 × 0.226
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.296 to 57.728
Index ranges	-15 ≤ h ≤ 14, -23 ≤ k ≤ 22, -14 ≤ l ≤ 11
Reflections collected	17333
Independent reflections	4849 [R_{int} = 0.0294, R_{sigma} = 0.0319]
Data/restraints/parameters	4849/855/368
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0489, wR_2 = 0.1324
Final R indexes [all data]	R_1 = 0.0717, wR_2 = 0.1443
Largest diff. peak/hole / e Å^{-3}	0.26/-0.25

Table S5. Crystal data and structure refinement for **2b** (CCDC 2189384)

Identification code	aj2045
Empirical formula	$C_{18}H_{31}LiF_3O_4SN$
Formula weight	421.44
Temperature/K	250(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.8035(3)
b/Å	11.8153(2)
c/Å	16.7982(3)
α/°	90
β/°	104.459(2)
γ/°	90
Volume/Å^3	2268.51(8)
Z	4
ρ_{calc}g/cm^3	1.234
μ/mm^{-1}	0.188
F(000)	896.0
Crystal size/mm^3	0.292 × 0.26 × 0.161
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.008 to 58.012
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -21 ≤ l ≤ 22
Reflections collected	33844
Independent reflections	5483 [R_{int} = 0.0381, R_{sigma} = 0.0312]
Data/restraints/parameters	5483/0/262
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1222
Final R indexes [all data]	R_1 = 0.0593, wR_2 = 0.1299
Largest diff. peak/hole / e Å^{-3}	0.41/-0.34

Table S6. Crystal data and structure refinement for **2c** (CCDC 2189385)

Identification code	aj2090
Empirical formula	$C_{19}H_{31}LiNO_4F_3S$
Formula weight	433.45
Temperature/K	250(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	10.0875(3)
b/Å	11.4427(4)
c/Å	11.5307(4)
α/°	94.430(3)
β/°	113.237(3)
γ/°	109.486(3)
Volume/Å^3	1118.94(7)
Z	2
ρ_{calc}g/cm^3	1.286
μ/mm^{-1}	0.192
F(000)	460.0
Crystal size/mm^3	0.26 × 0.22 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.424 to 57.988
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	19792
Independent reflections	5163 [R_{int} = 0.0562, R_{sigma} = 0.0522]
Data/restraints/parameters	5163/679/383
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0549, wR_2 = 0.1449
Final R indexes [all data]	R_1 = 0.0843, wR_2 = 0.1589
Largest diff. peak/hole / e Å^{-3}	0.55/-0.42

Table S7. Crystal data and structure refinement for **3b** (CCDC 2189387)

Identification code	aj1917_sq
Empirical formula	$C_{50}H_{60}F_6N_2O_8S_2$
Formula weight	995.12
Temperature/K	250(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	22.9053(8)
b/Å	14.0233(6)
c/Å	16.6472(7)
α/°	90
β/°	106.774(4)
γ/°	90
Volume/Å^3	5119.7(4)
Z	4
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	0.178
F(000)	2096.0
Crystal size/mm^3	0.34 × 0.29 × 0.26
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.572 to 52.744
Index ranges	-28 ≤ h ≤ 25, -17 ≤ k ≤ 16, -17 ≤ l ≤ 20
Reflections collected	55981
Independent reflections	10444 [R_{int} = 0.0435, R_{sigma} = 0.0363]
Data/restraints/parameters	10444/403/824
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0588, wR_2 = 0.1591
Final R indexes [all data]	R_1 = 0.0964, wR_2 = 0.1787
Largest diff. peak/hole / e Å^{-3}	0.25/-0.29

Table S8. Crystal data and structure refinement for **4c** (CCDC 2214291).

Identification code	mk784
Empirical formula	$C_{50}H_{60}N_2O_2$
Formula weight	721.00
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.0791(2)
b/Å	12.04020(10)
c/Å	12.44240(10)
α/°	90
β/°	92.7730(10)
γ/°	90
Volume/Å^3	1957.07(4)
Z	2
ρ_{calc}g/cm^3	1.224
μ/mm^{-1}	0.561
F(000)	780.0
Crystal size/mm^3	0.207 × 0.169 × 0.119
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.766 to 157.700
Index ranges	-16 ≤ h ≤ 16, -14 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	24580
Independent reflections	4194 [R_{int} = 0.0325, R_{sigma} = 0.0221]
Data/restraints/parameters	4194/0/336
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0585, wR_2 = 0.1574
Final R indexes [all data]	R_1 = 0.0618, wR_2 = 0.1607
Largest diff. peak/hole / e Å^{-3}	0.65/-0.24

Table S9. Crystal data and structure refinement for **5a** (CCDC 2190724)

Identification code	mk755_test
Empirical formula	$C_{22}H_{38}N_2S_2$
Formula weight	394.66
Temperature/K	296(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.2307(7)
b/Å	7.8541(6)
c/Å	15.9582(12)
α/°	90
β/°	100.261(3)
γ/°	90
Volume/Å^3	1138.45(15)
Z	2
ρ_{calc}g/cm^3	1.151
μ/mm^{-1}	0.242
F(000)	432.0
Crystal size/mm^3	0.272 × 0.104 × 0.102
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.188 to 48.908
Index ranges	-10 ≤ h ≤ 10, -9 ≤ k ≤ 9, -18 ≤ l ≤ 18
Reflections collected	15963
Independent reflections	1859 [R_{int} = 0.0303, R_{sigma} = 0.0214]
Data/restraints/parameters	1859/0/122
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0446, wR_2 = 0.1144
Final R indexes [all data]	R_1 = 0.0487, wR_2 = 0.1189
Largest diff. peak/hole / e Å^{-3}	0.30/-0.20

Table S10. Crystal data and structure refinement for **5b** (CCDC 2189386)

Identification code	aj1386
Empirical formula	$C_{26}H_{46}N_2S_2$
Formula weight	450.77
Temperature/K	298(2)
Crystal system	orthorhombic
Space group	*Cmce*
a/Å	12.2275(10)
b/Å	7.8196(6)
c/Å	27.4908(19)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2628.5(3)
Z	4
ρ_{calc}g/cm^3	1.139
μ/mm^{-1}	0.218
F(000)	992.0
Crystal size/mm^3	0.25 × 0.19 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.928 to 57.878
Index ranges	-16 ≤ h ≤ 15, -8 ≤ k ≤ 10, -37 ≤ l ≤ 34
Reflections collected	17331
Independent reflections	1688 [R_{int} = 0.0473, R_{sigma} = 0.0279]
Data/restraints/parameters	1688/0/81
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0443, wR_2 = 0.1175
Final R indexes [all data]	R_1 = 0.0616, wR_2 = 0.1235
Largest diff. peak/hole / e Å^{-3}	0.28/-0.20

Table S11. Crystal data and structure refinement for **5c** (CCDC 2189389).

Identification code	MK756
Empirical formula	$C_{28}H_{46}N_2S_2$
Formula weight	474.79
Temperature/K	297(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.1244(5)
b/Å	12.4798(8)
c/Å	17.3975(11)
α/°	90
β/°	93.516(2)
γ/°	90
Volume/Å^3	1327.21(16)
Z	2
ρ_{calc}g/cm^3	1.188
μ/mm^{-1}	0.219
F(000)	520.0
Crystal size/mm^3	0.12 × 0.063 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.716 to 42.366
Index ranges	-6 ≤ h ≤ 6, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17
Reflections collected	16670
Independent reflections	1458 [R_{int} = 0.0312, R_{sigma} = 0.0175]
Data/restraints/parameters	1458/0/147
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0692
Final R indexes [all data]	R_1 = 0.0324, wR_2 = 0.0719
Largest diff. peak/hole / e Å^{-3}	0.16/-0.11

EPR Spectroscopy

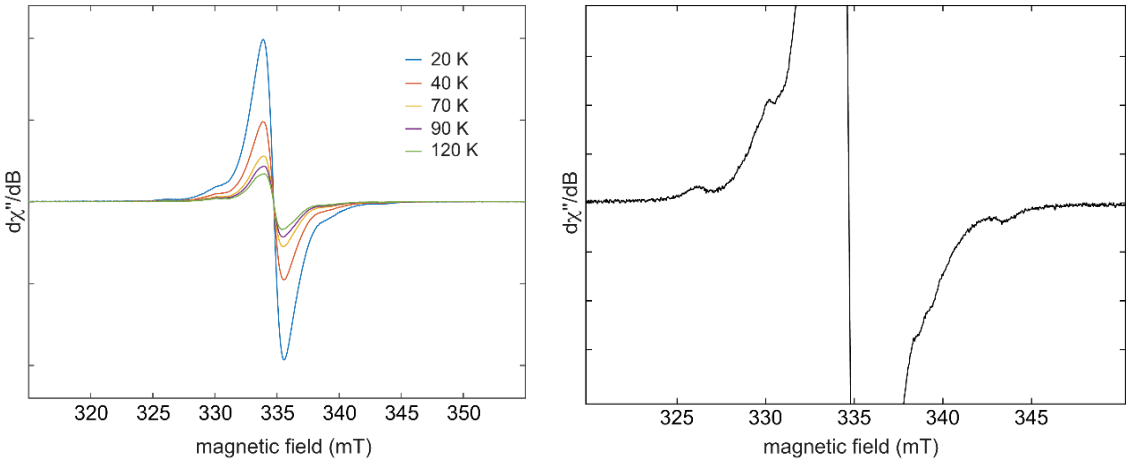


Fig. S78 Left: Variable temperature X-band EPR spectra of **4a** in dichloromethane between 20 and 140 K for the *g* = 2 region. Right: Zoomed in view of the weak zero-field splittings at 120 K. The weak and poorly resolved zero-field splittings in the *g* = 2 region suggest a value of around 242 MHz for the parameter *D*.

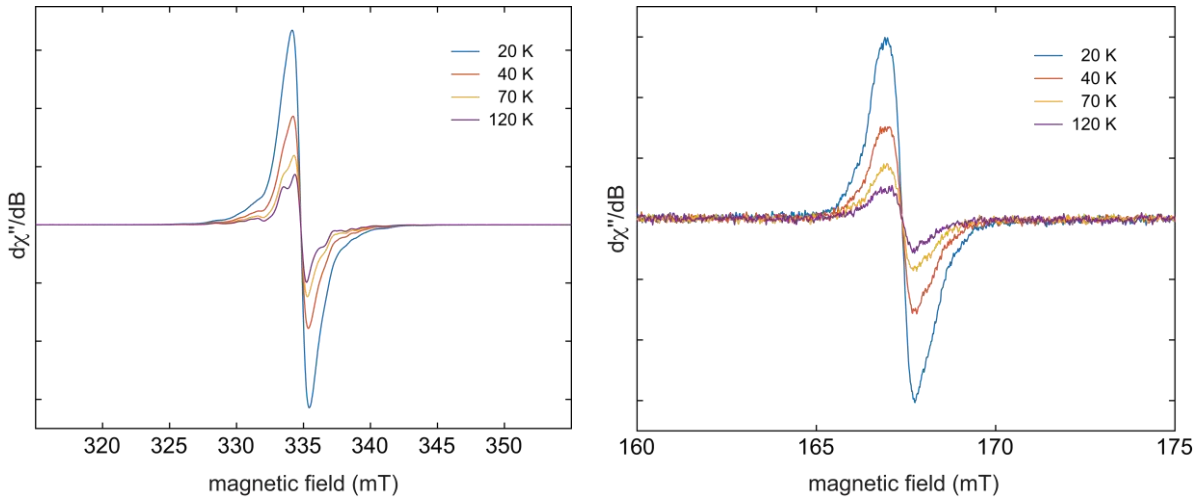


Fig. S79 Variable temperature X-band EPR spectra of **4b** in frozen THF solution between 20 and 120 K for the g = 2 (left) and the half-field region (right). The zero-field splittings are not well resolved.

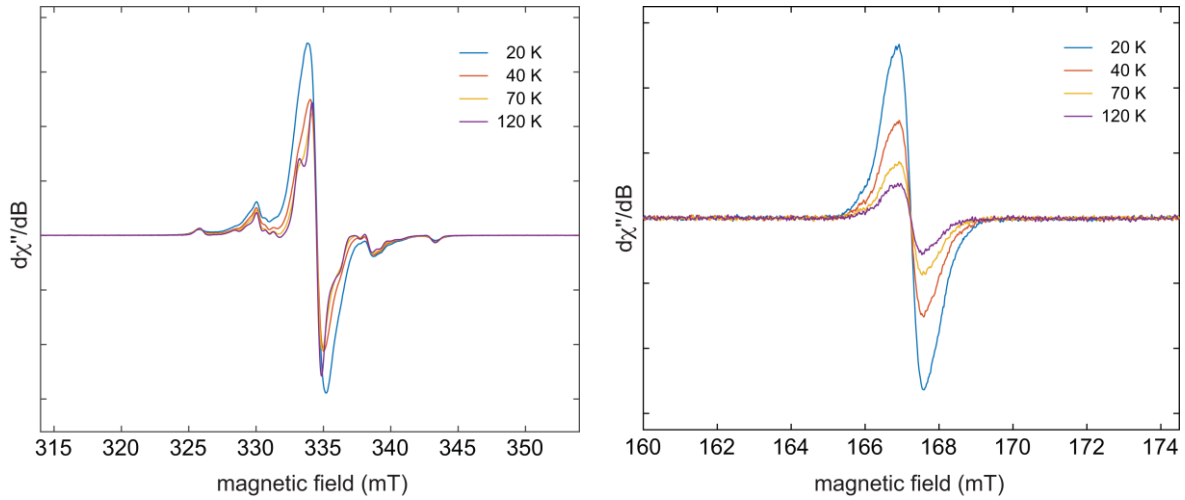


Fig. S80 Variable temperature X-band EPR spectra of **4c** in frozen THF solution between 20 and 120 K for the g = 2 (left) and the half-field region (right).

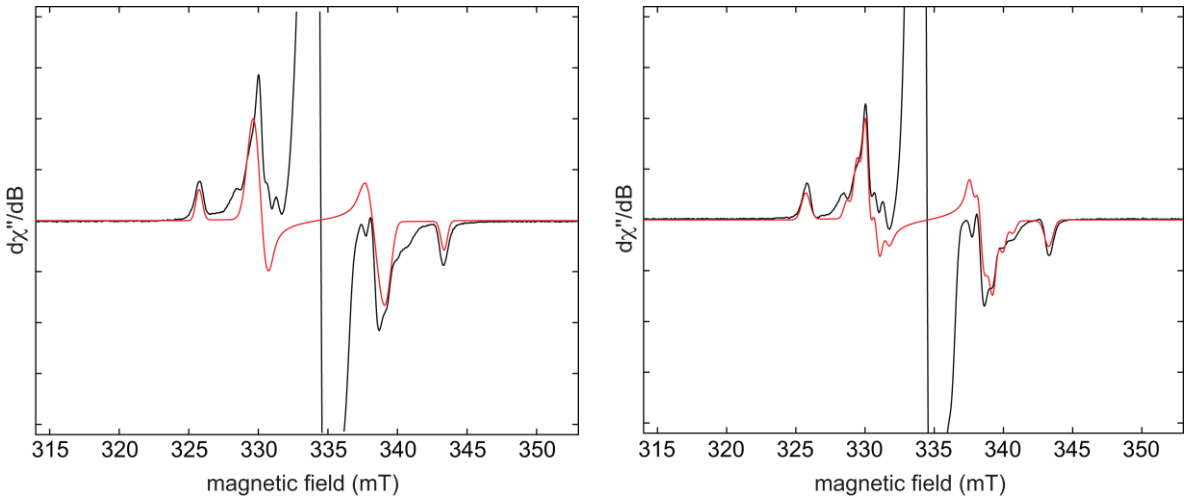
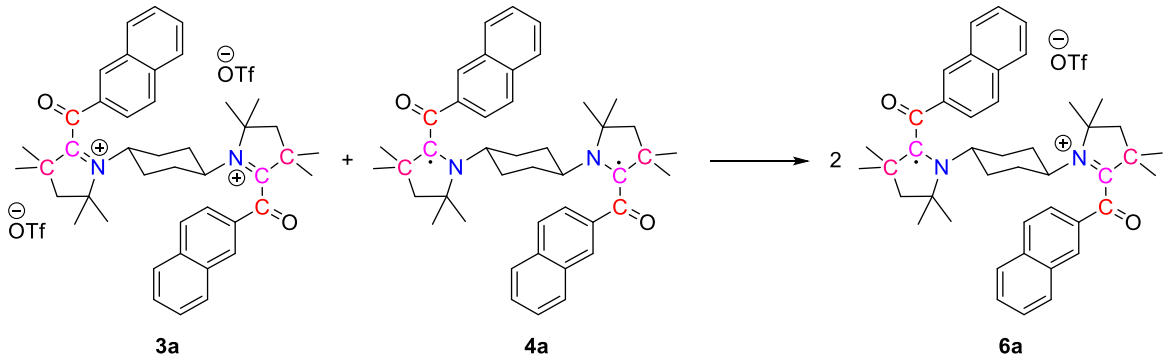


Fig. S81 Experimental (black) and simulated (red) X-band EPR spectra of **4c** in frozen THF solution at 70 K (left) and 120 K (right), showing the zero-field splittings. The simulation on the right contains the same zero-field splitting parameters but in addition some nitrogen hyperfine couplings. The simulated zero-field parameters are D = 247 MHz and E = 3.4 MHz. Using the point-dipole approximation, an interspin distance of 6.8 Å can be estimated.

Comproportionation reaction of 3a and 4a



3a **4a** **6a**

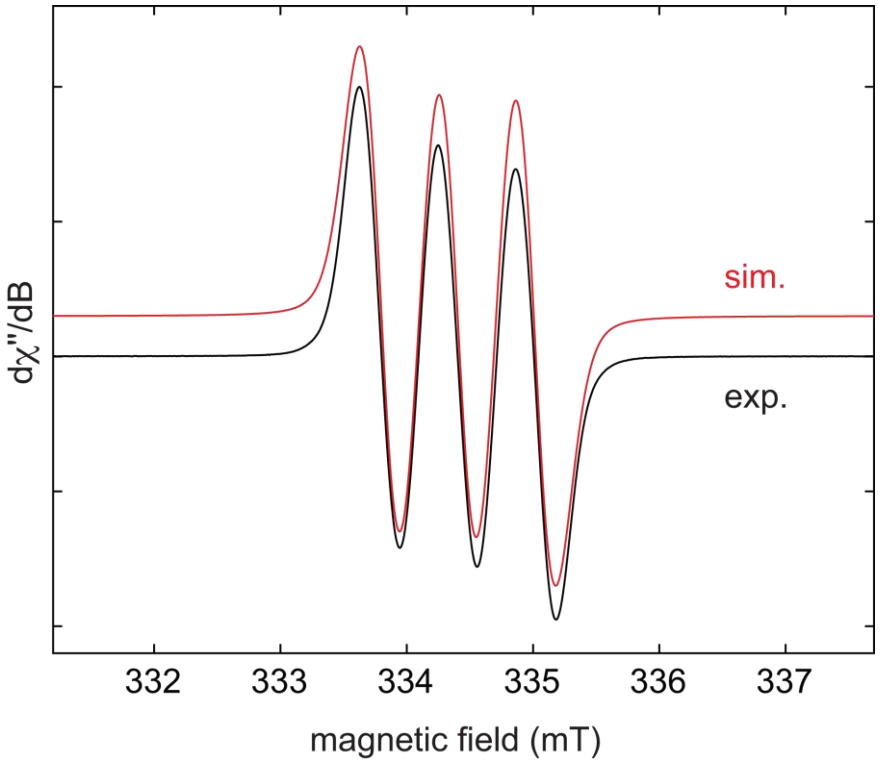


Fig. S82 Experimental (black) and simulated (red) EPR spectra of **6a** obtained by 1:1 reaction of **3a** and **4a** in dichloromethane. Best-fit simulation parameters: g_{iso} = 2.0043 and $a(^{14}N)$ = 17.1 MHz.

Magnetic Study of 4a, 4b, and 4c

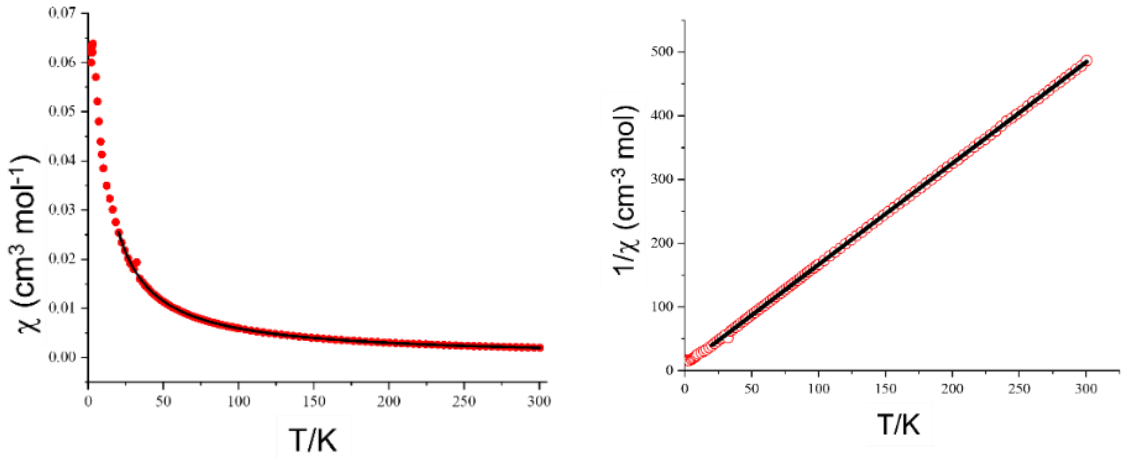


Fig. S83 Plot of magnetic susceptibility versus temperature for **4a**.

As per Curie-Weiss law: $\chi = C/(T - \theta_{CW})$, $1/\chi = T/C - \theta_{CW}/C$

From the above plot: y = 1.59*x + 7.56, 1/C = 1.59, C = 0.629, $\theta_{CW}/C = -7.56$, $\theta_{CW} = -4.75$

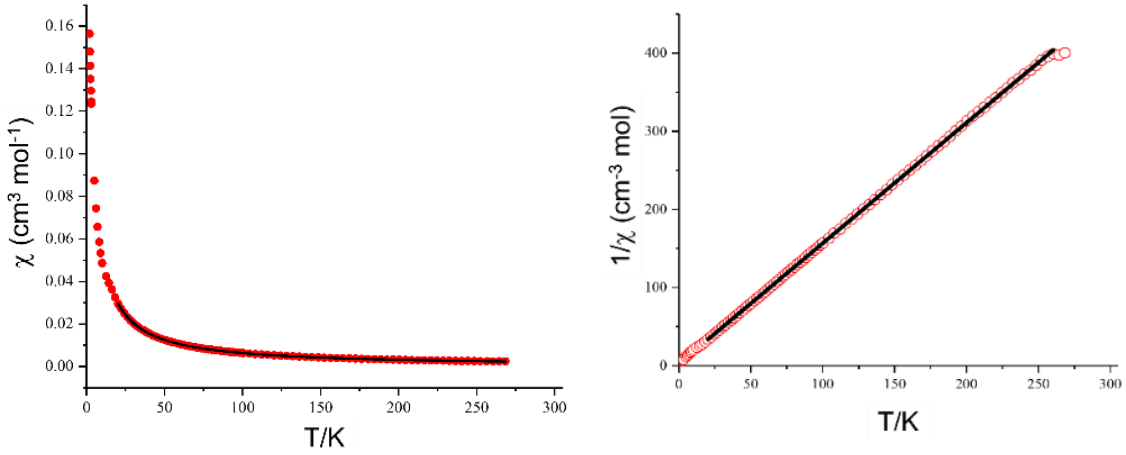


Fig. S84 Plot of magnetic susceptibility versus temperature for **4b**.

As per Curie Weiss law: $\chi = C/(T - \theta_{CW})$, $1/\chi = T/C - \theta_{CW}/C$

From the above plot: y = 1.54*x + 2.69, 1/C = 1.54, C = 0.65, $\theta_{CW}/C = -2.69$, $\theta_{CW} = -1.75$

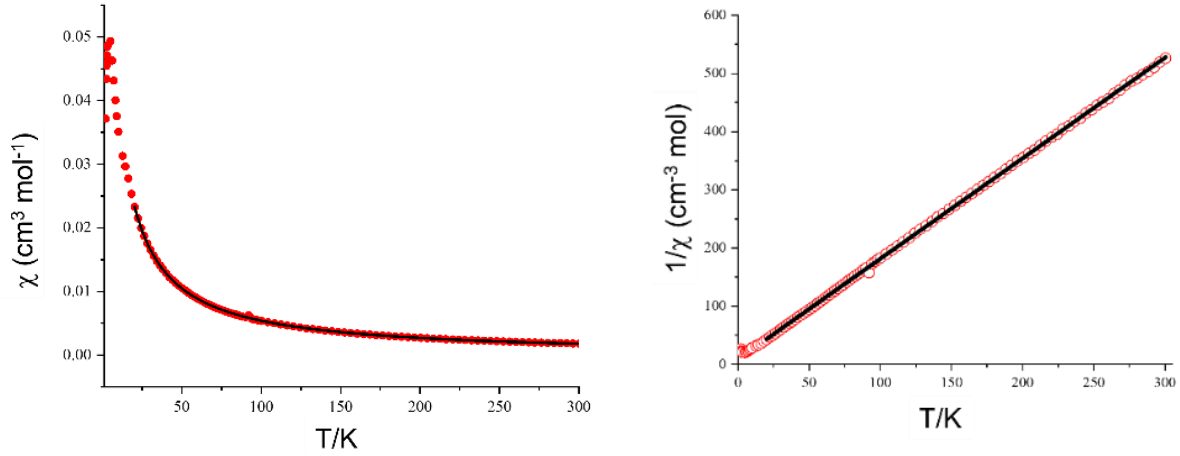


Fig. S85 Plot of magnetic susceptibility versus temperature for **4c**.

As per curie Weiss law: $\chi = C/(T - \theta_{CW})$, $1/\chi = T/C - \theta_{CW}/C$

From the above plot: y = 1.73*x + 8.66, 1/C = 1.73, C = 0.58, θ_{CW}/C = -8.66, θ_{CW} = −5.0

Cyclic Voltammetry

All electrochemical measurements were carried out using an AUTOLAB PGSTA12 potentiostat/galvanostat controlled by the software NOVA. A glassy carbon electrode was used as working electrode. As counter and reference electrode (together with internal referencing versus decamethylferrocene/decamethylferrocenium (DFc/DFc^+) and calculated for ferrocene/ferrocenium (Fc/Fc^+)) a platinum wire electrode was used. All measurements were undertaken inside a glove box (argon atmosphere). For the measurements the investigated compound (1.4 mg for **3a**, 2.3 mg for **3b**, and 2.1 mg for **3c**) was dissolved in 5 ml of electrolyte solution (0.1 $mol \cdot l^{-1}$ Bu_4NPF_6 in acetonitrile) in a double walled electrochemical cell. Cyclic voltammetry was performed using +/-0.00244 V/step (positive/negative measurement direction). Differential pulse voltammetry (DPV) was performed with the following parameters: modulation step: +/- 0.005 V, modulation amplitude: 0.01 V, modulation time: 1 s, interval time: 2 s and referenced against DFc/DFc^+ but calculated for Fc/Fc^+.

Table S12. Summary of the electrochemical results of **3a**/**3b**/**3c** relative to the potential of Fc/Fc^+.

	Epk (100 mV/s) [V]	*Epa* (100 mV/s) [V]	$E_{1/2}$ (100 mV/s) [V]
3a	−1.70(vw)	−1.60	−1.65
	– 1.12	–1.05 (vw)	–1.09
	– 0.99	–0.94	–0.96
3b	−2.01	−1.66 (vw)	−1.84
	−1.14	−0.97	−1.06
3c	−1.68	−1.57	−1.63
	−1.18	−1.12	−1.15
	–1.06 (vw)	–1.02	–1.04

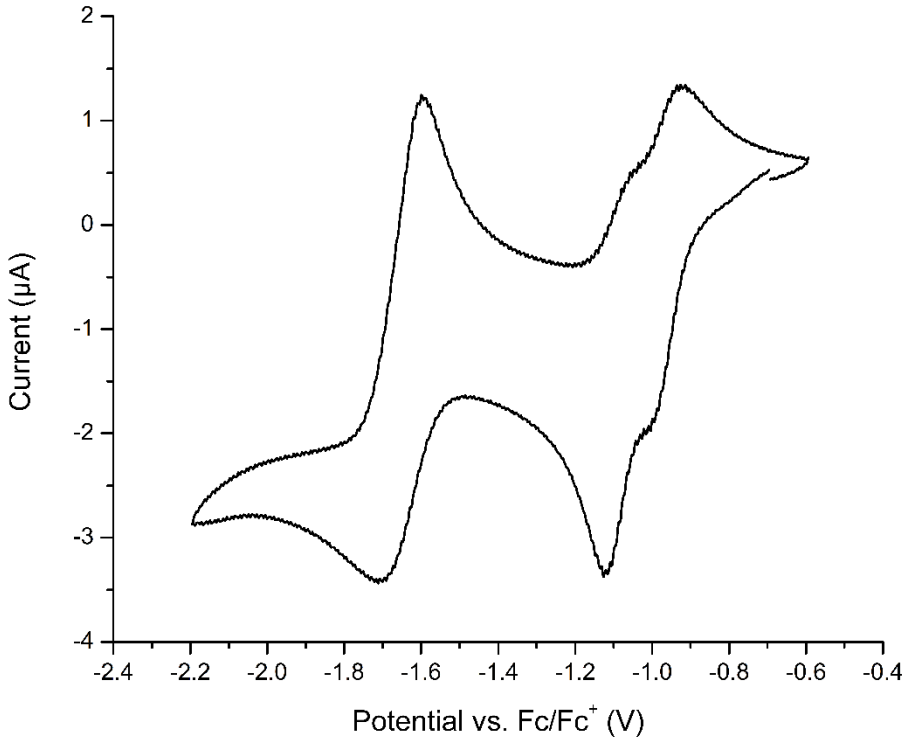


Fig. S86 Cyclic Voltammogram of **3a** at 100 mV/s in CH_3CN (0.1 M [nBu$_4$N][PF_6]) at room temperature.

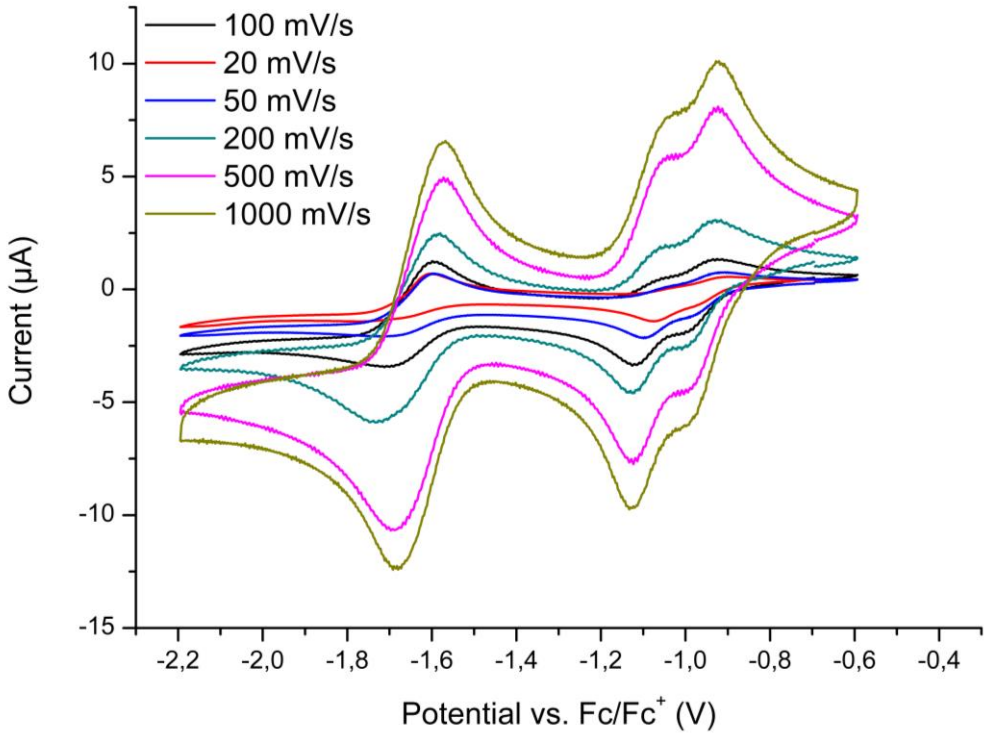


Fig. S87 Cyclic voltammograms of **3a** at various scan rates in CH_3CN (0.1 M [nBu$_4$N][PF_6]) at room temperature.

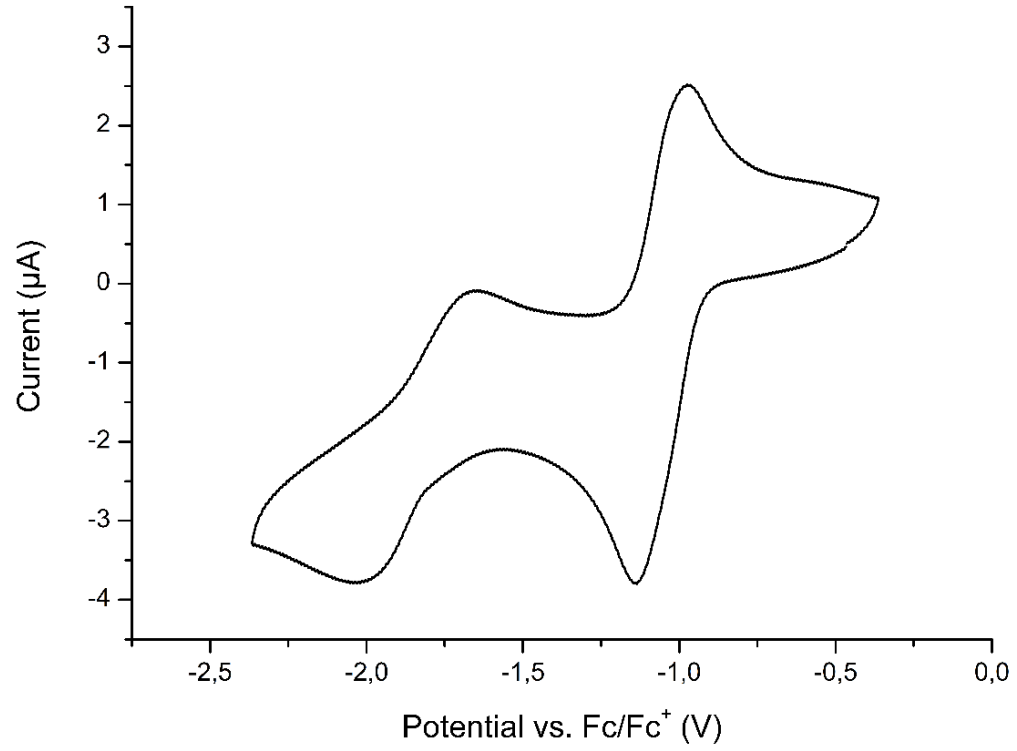


Fig. S88 Cyclic Voltammogram of **3b** at 100 mV/s in CH_3CN (0.1 M [nBu$_4$N][PF_6]) at room temperature.

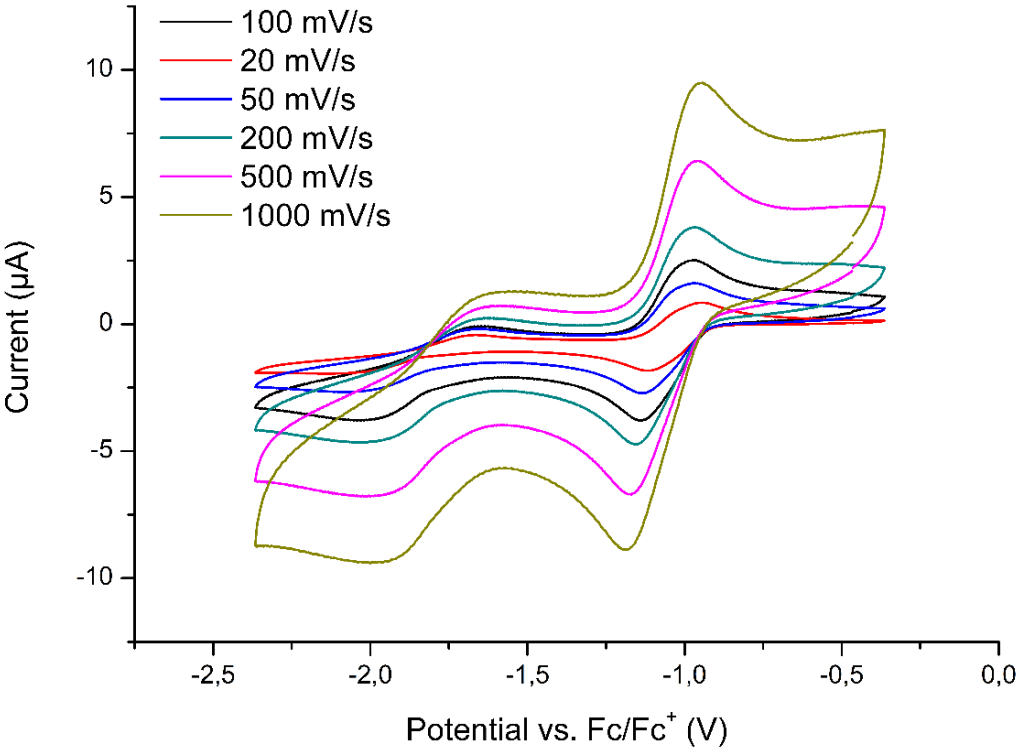


Fig. S89 Cyclic voltammograms of **3b** at various scan rates in CH_3CN (0.1 M [nBu$_4$N][PF_6]) at room temperature.

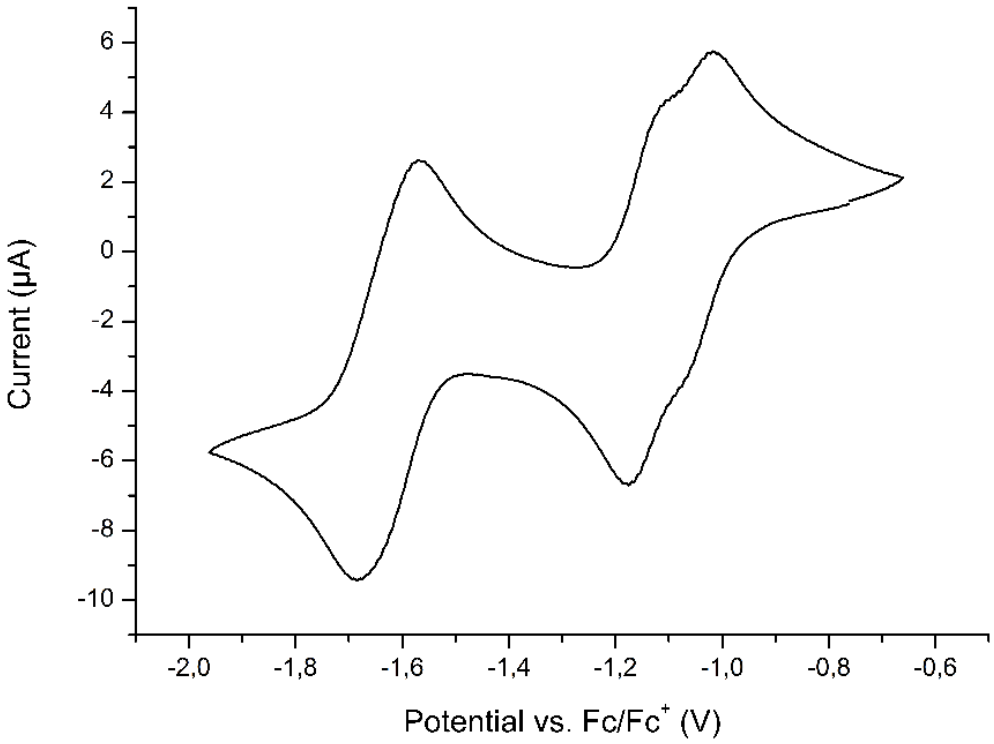


Fig. S90 Cyclic Voltammogram of **3c** at 100 mV/s in CH_3CN (0.1 M [nBu$_4$N][PF$_6$]) at room temperature.

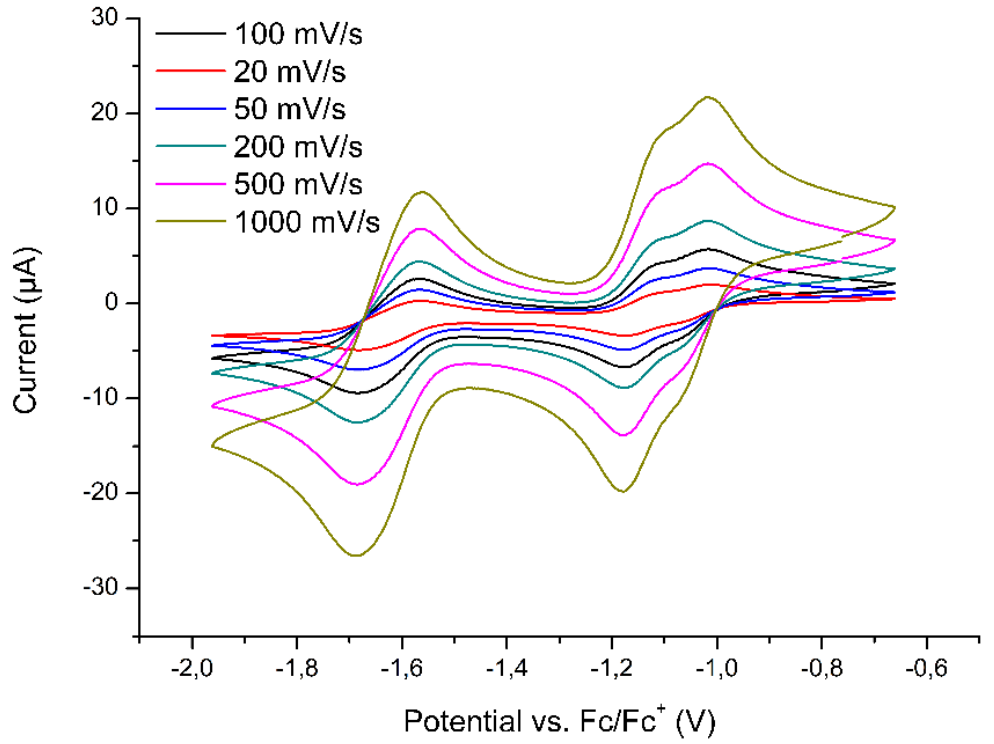


Fig. S91 Cyclic voltammograms of **3c** at various scan rates in CH_3CN (0.1 M [nBu$_4$N][PF$_6$]) at room temperature.

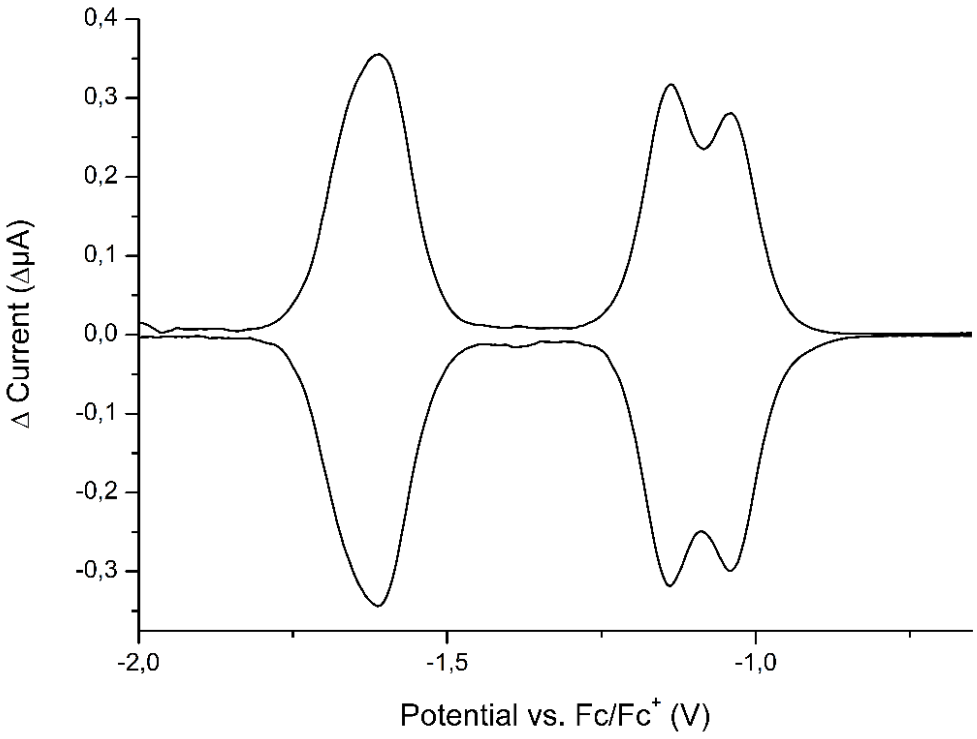


Fig. S92 Differential pulse voltammograms of **3c** at room temperature in CH_3CN (0.1 mol/L Bu_4NPF_6).

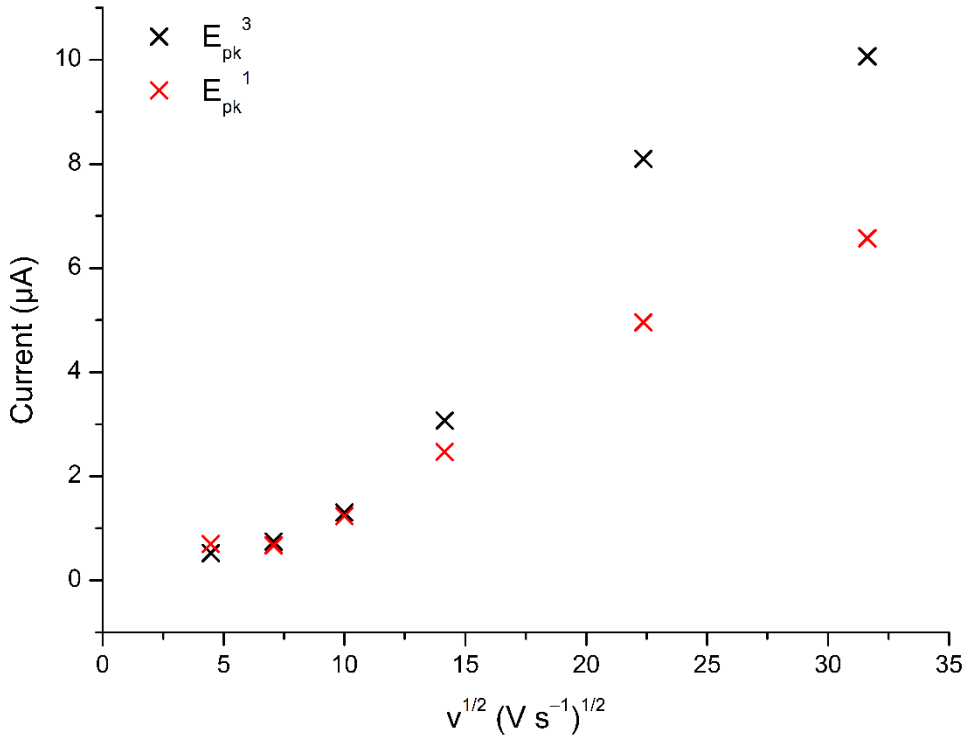


Fig. S93 Randles-Sevcik analysis plot of **3a**.

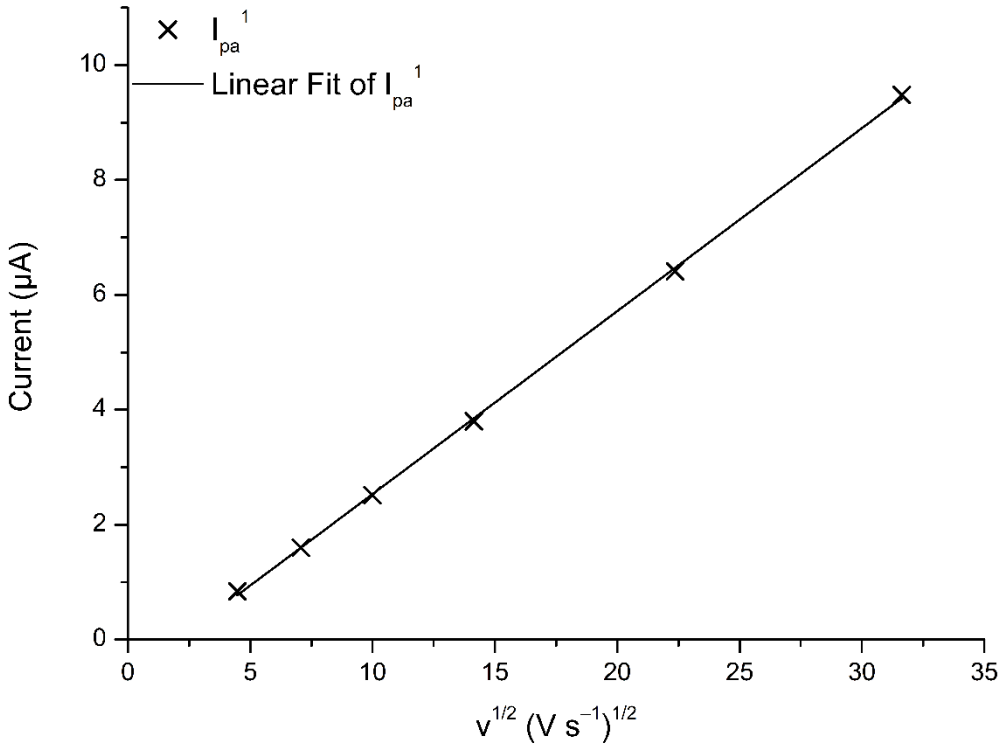


Fig. S94 Randles-Sevcik analysis plot of **3b**.

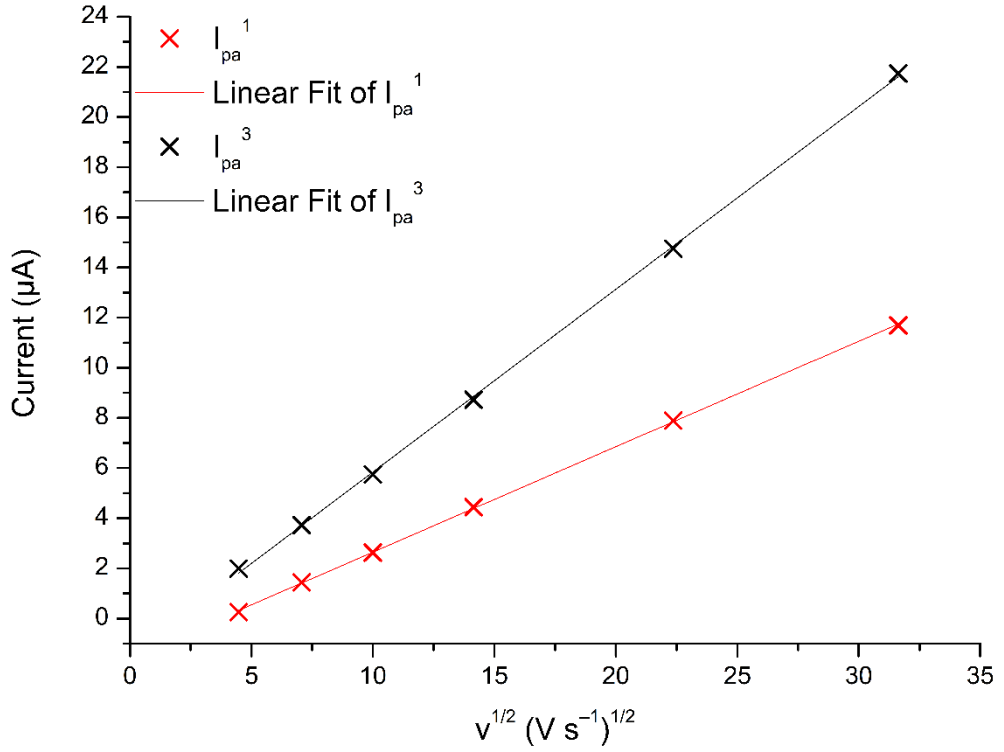


Fig. S95 Randles-Sevcik analysis plot of **3c**.

TGA and DSC Study

Table S13. Summary of TGA results of **4a**, **4b**, and **4c** (the heating rate is 5 °C/minute).

Compounds	Onset Temperature (°C) at Weight Loss Started	Weight Loss (%)
4a	127	7.01
4b	188	3.55
4c	127	3.55

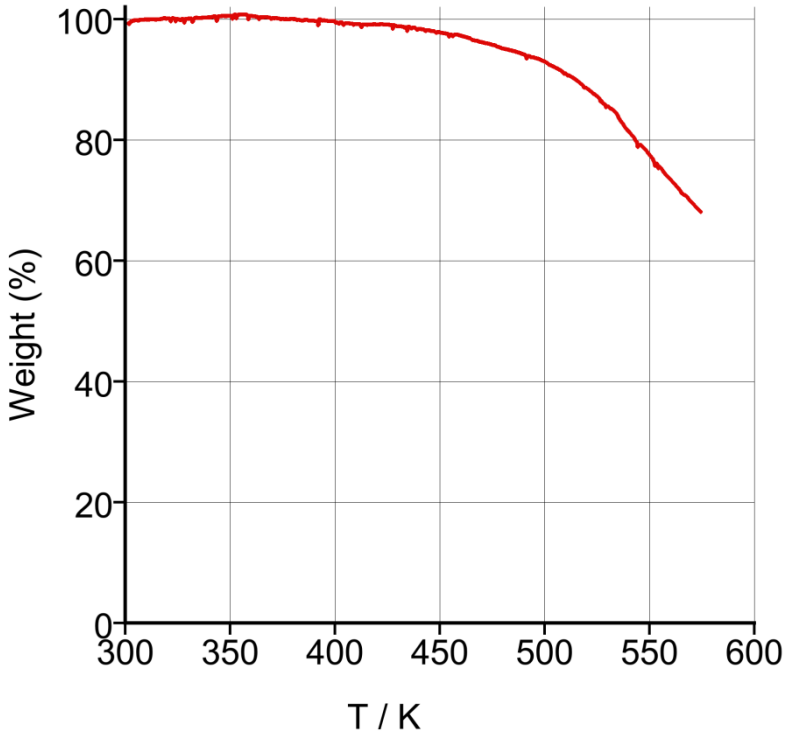


Fig. S96 TGA plot of **4a**.

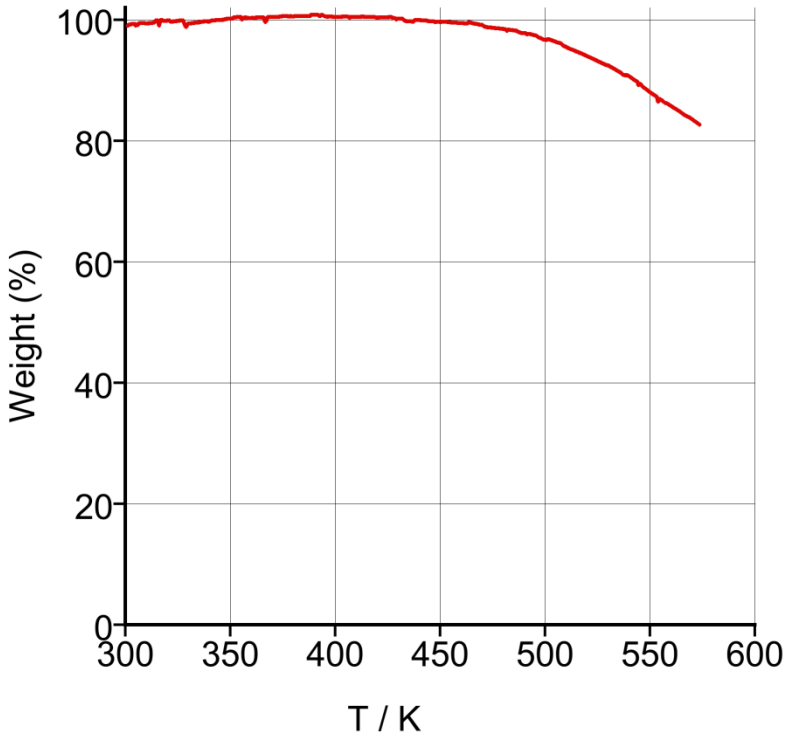


Fig. S97 TGA plot of **4b**.

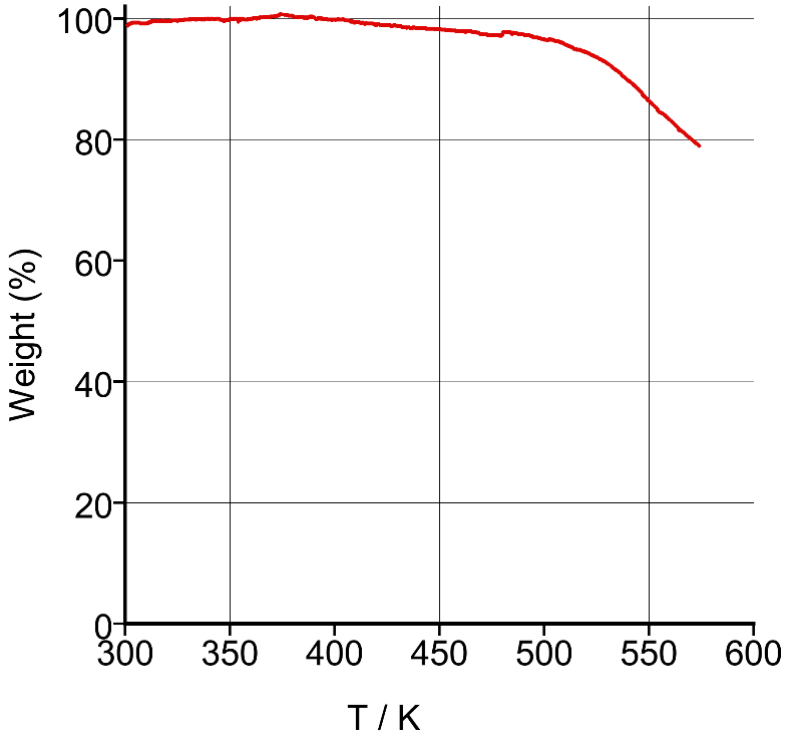


Fig. S98 TGA plot of **4c**.

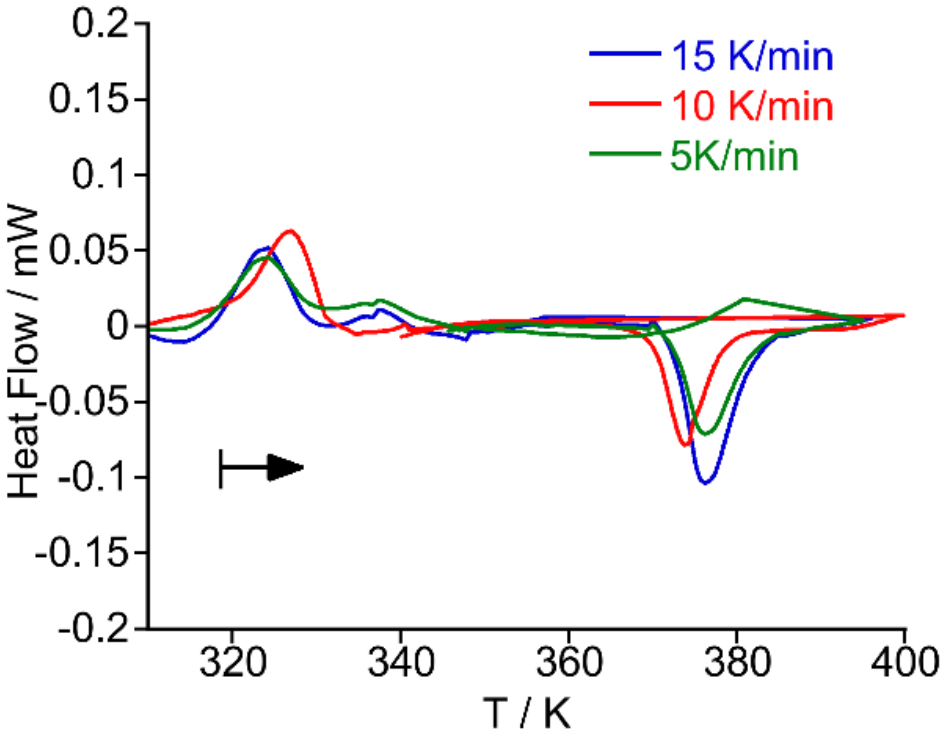


Fig. S99 DSC plots of **4a** (heating).

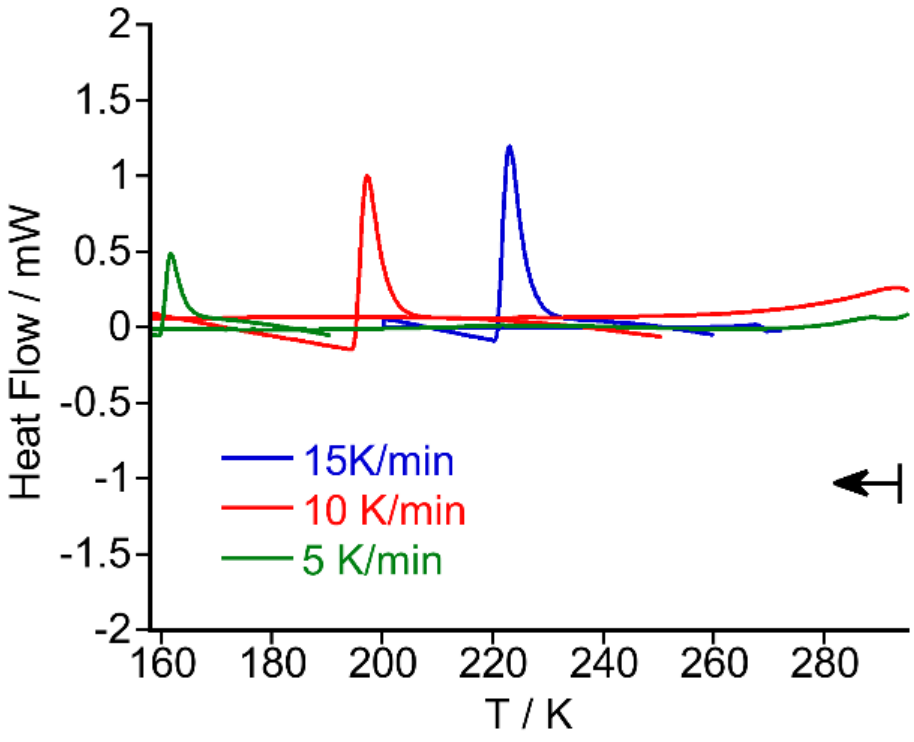


Fig. S100 DSC plots of **4a** (cooling).

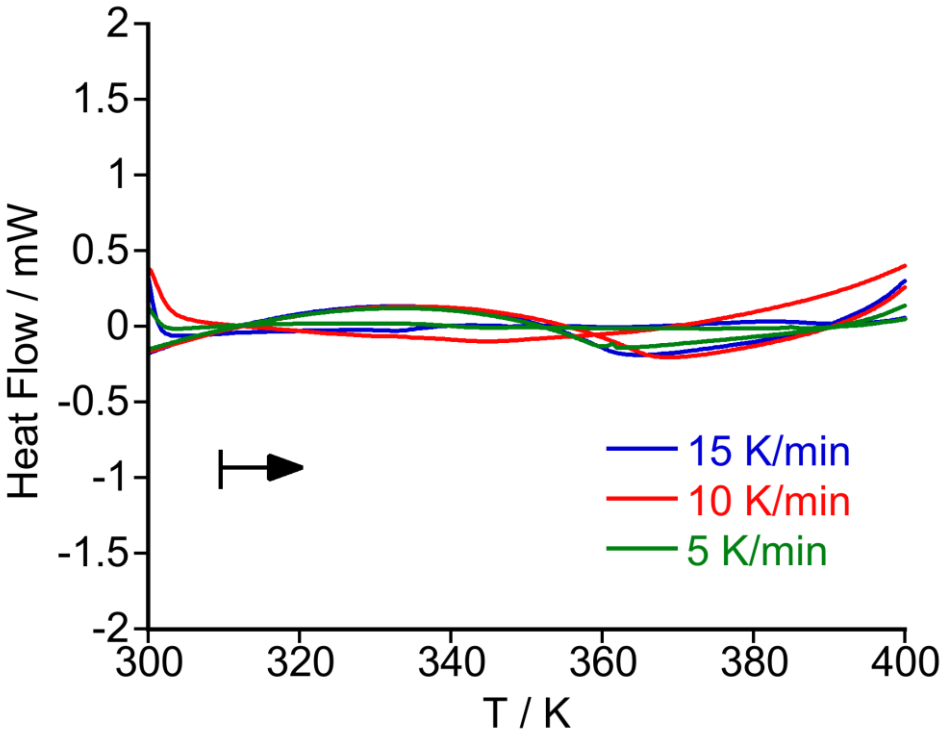


Fig. S101 DSC plots of **4b** (heating).

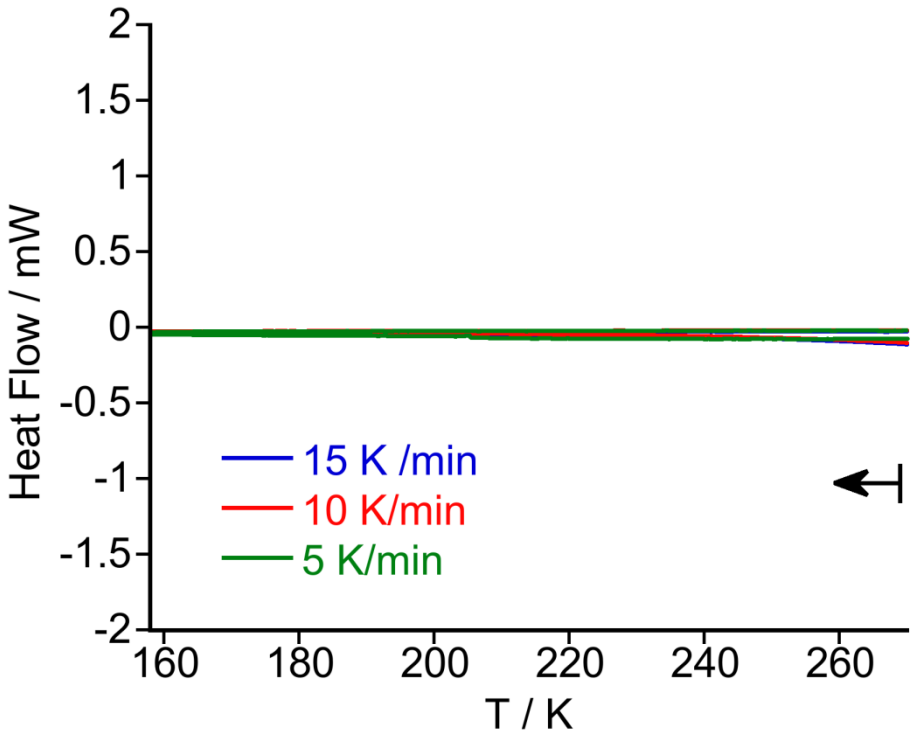


Fig. S102 DSC plots of **4b** (cooling).

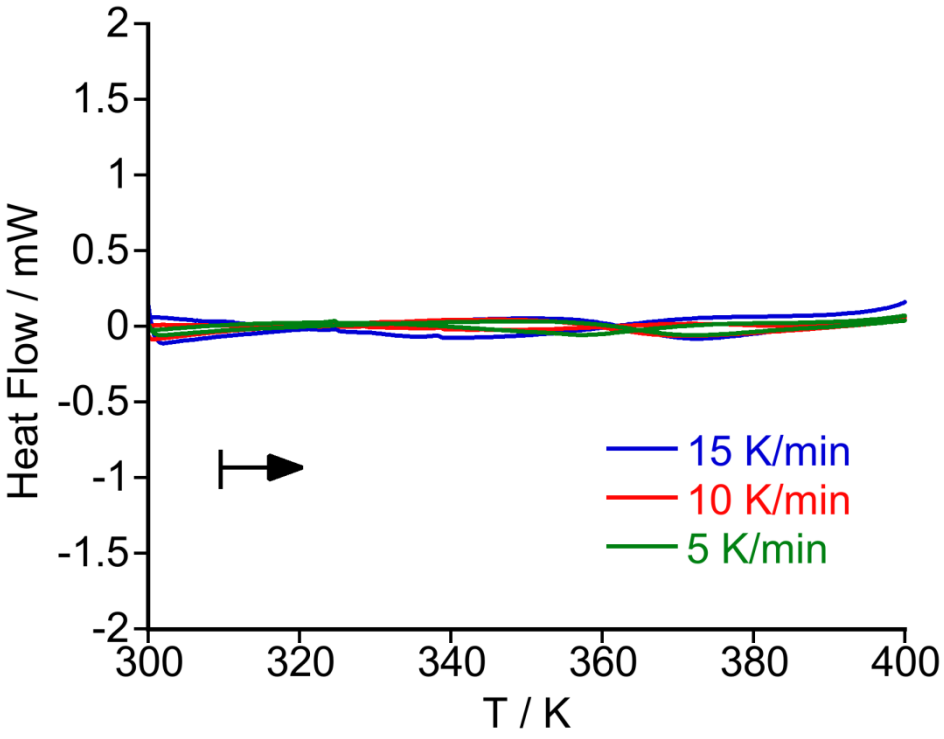


Fig. S103 DSC plots of **4c** (heating).

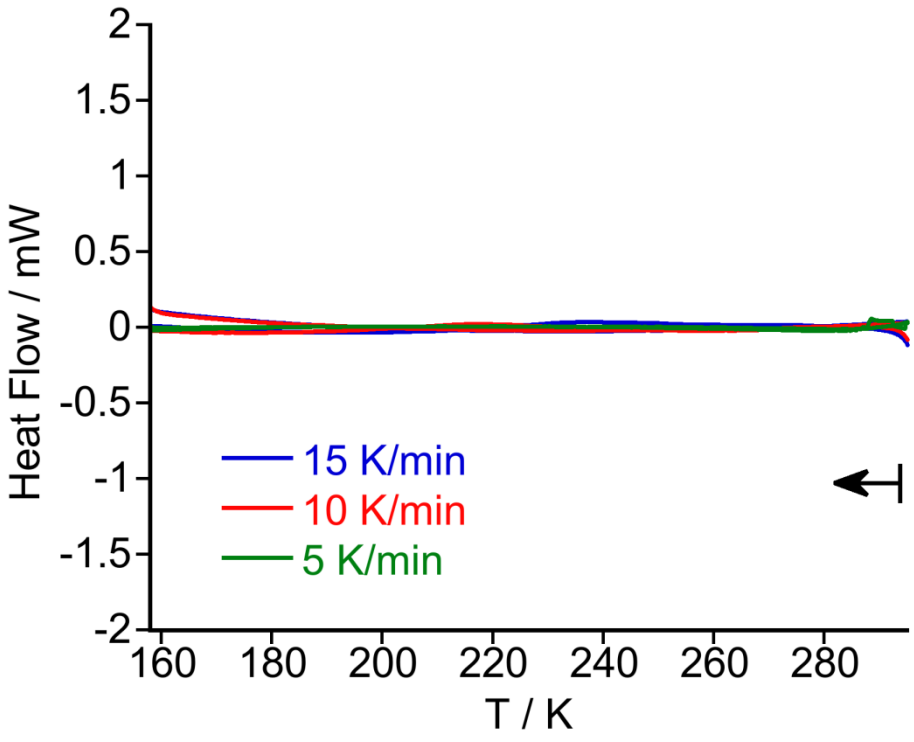


Fig. S104 DSC plots of **4c** (cooling).

Quantum Chemical Calculations

The DFT calculations were performed using Gaussian 16 (Revision C.01) suite[S8] of electronic structure Programs. The multireference CASSCF calculations were performed using ORCA–4.2.1.[S9]

The geometries were optimized in the gas phase with PBE0 and ωB97XD functionals and Def2SVP basis-set. To verify the stationary point frequency analysis was performed on optimized geometries. The singlet geometries were optimized with spin-unrestricted broken-symmetry (BS) wavefunctions. Single point energy calculations were performed on optimized geometries using triple-zeta basis set def2-TZVPP. NEVPT2//CASSCF(6,6)/def2-TZVP calculations were performed on DFT (PBE0/def2SVP) optimized geometries of singlet and triplet states. Spin density plots are visualized with Chemcraft software.

TD-DFT calculations were performed at B3LYP/def2SVP level on PBE0/def2SVP optimized geometry. The solvent effect was accounted with polarizable continuum model (PCM) including THF as the solvent.

Table S14. Summary of calculated exchange coupling for **4a**/**4b**/**4c**.

		J^a(cm^{-1})	$\Delta E_{ST}{}^b$ / kJmol^{-1}	$\Delta E_{ST}{}^c$ / kJmol^{-1}
4a	PBE0	–1.54	–0.037	–0.030
	ωB97XD	–1.10	–0.026	–
4b	PBE0	–1.29	–0.031	–0.055
	ωB97XD	–0.88	–0.021	–
4c	PBE0	–0.88	–0.021	–0.043
	ωB97XD	–0.22	–0.0053	–

[a]The exchange coupling constant $J = (E_{BS}–E_T)/(S^2(T)–S^2(BS))$. $S^2(BS)$ and $S^2(T)$ are the eigenvalues of the spin operator for broken-symmetry singlet and triplet states, respectively. [b]Energy difference between singlet and triplet state $\Delta E_{ST} = 2J$. [c]Adiabatic singlet-triplet energy gap from multi-reference NEVPT2//CASSCF(6,6)/def2-TZVP calculations.

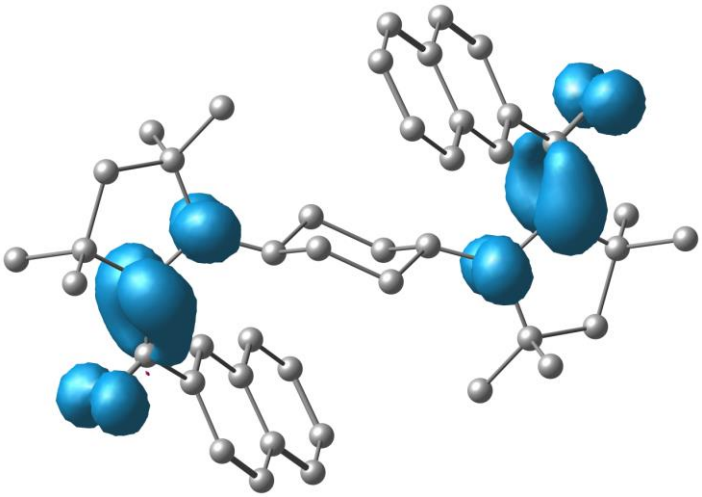


Fig. S105 Spin-density plot of **4a** (at isovalue of 0.005 and hydrogens are omitted for clarity).

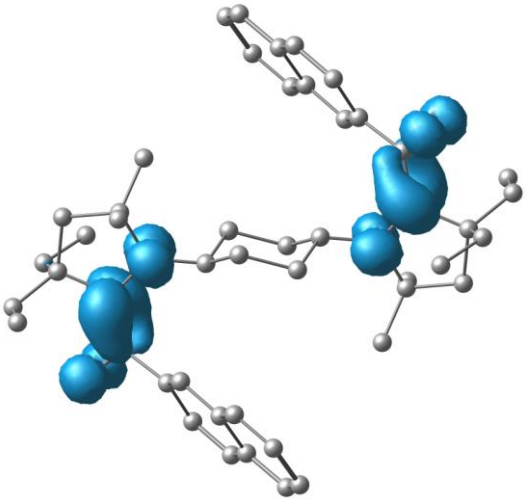


Fig. S106 Spin-density plot of **4b** (at isovalue of 0.005 and hydrogens are omitted for clarity).

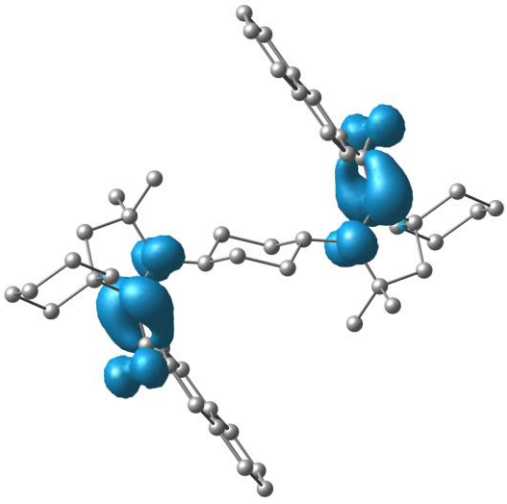


Fig. S107 Spin-density plot of **4c** (at isovalue of 0.005 and hydrogens are omitted for clarity).

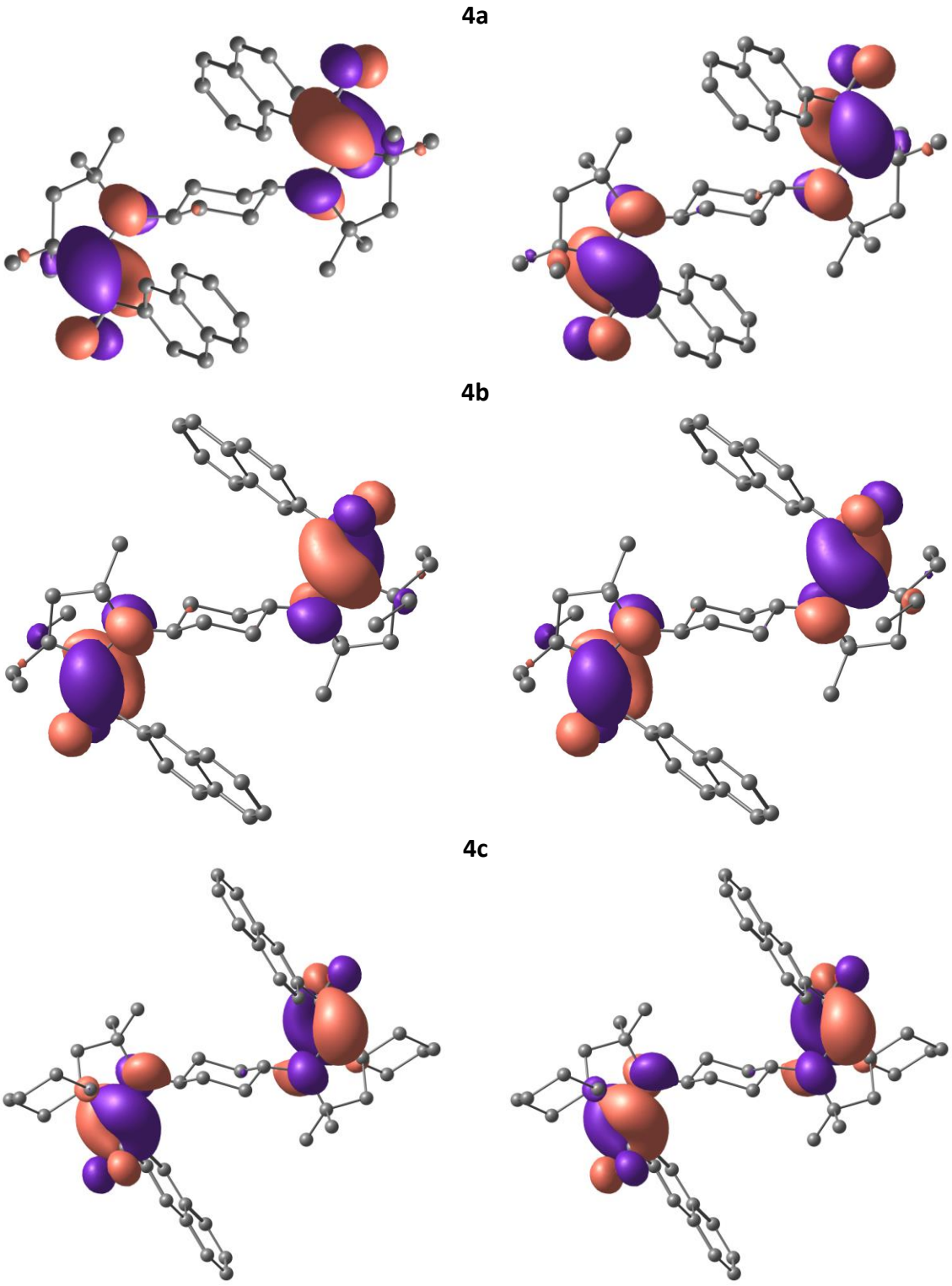
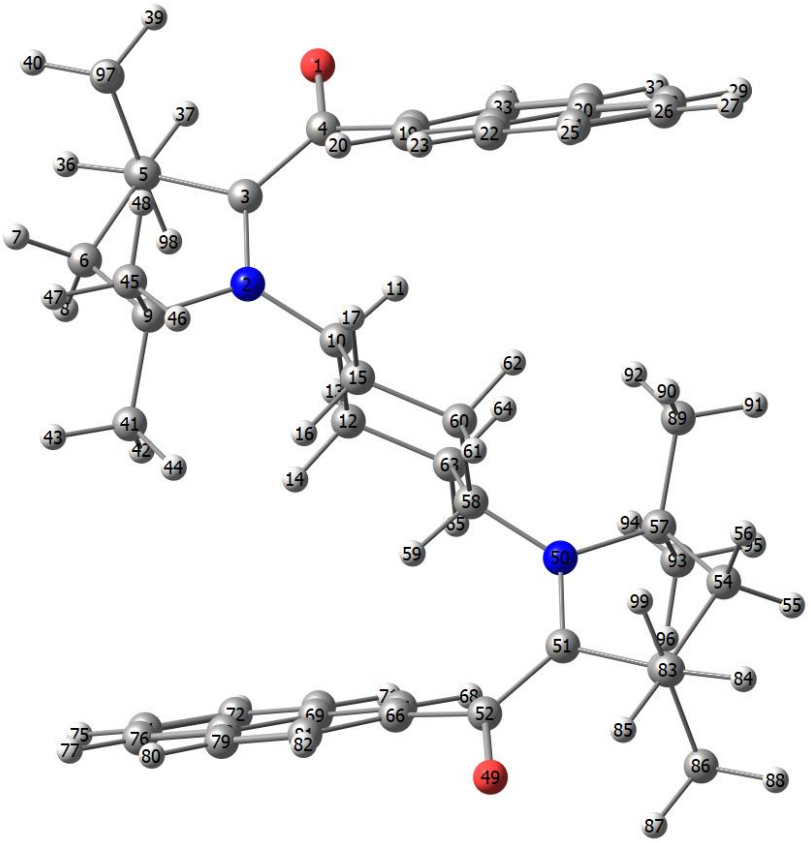


Fig. S108 NOs of **4a**, **4b**, and **4c** obtained from CASSCF(6,6) calculations.

Table S15. Isotropic Fermi contact couplings constants of **4a**.

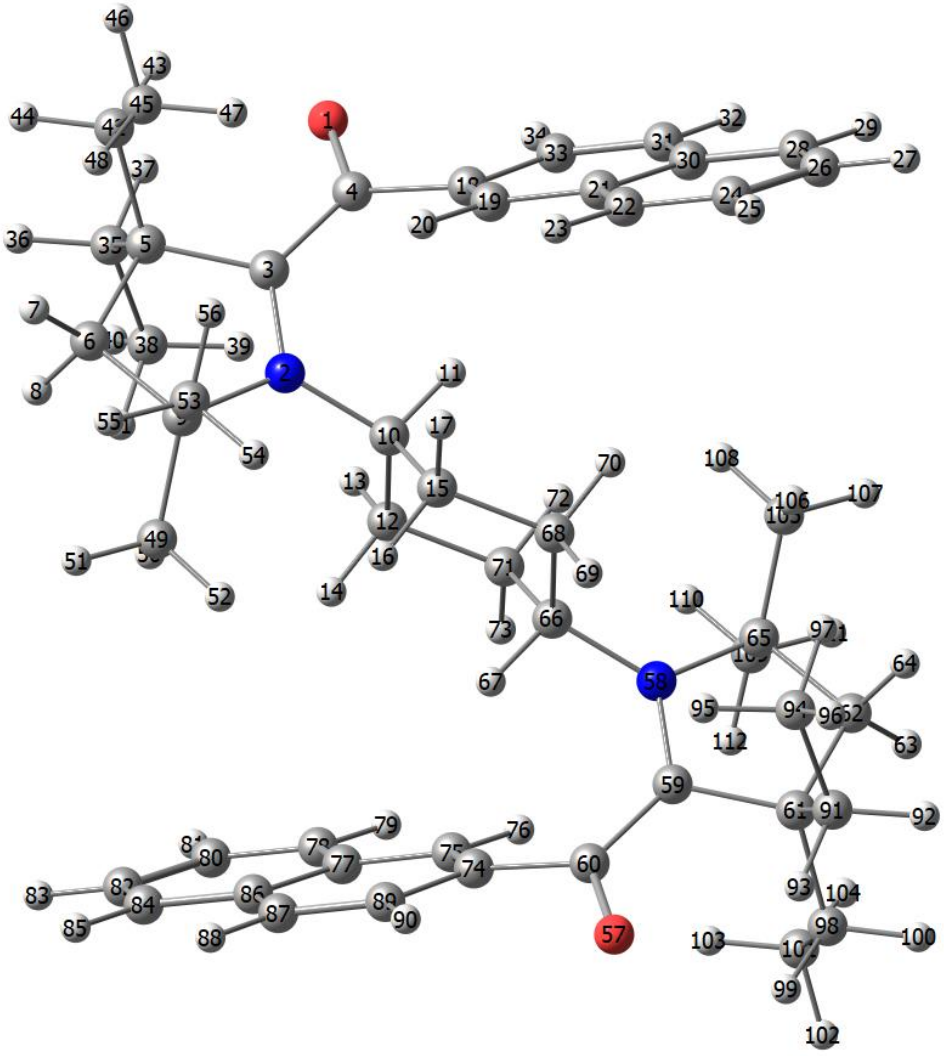


Atom	a.u.	MegaHertz	Gauss	10(-4) cm-1
1 O(17)	0.03424	-10.37737	-3.70290	-3.46152
2 N(14)	0.04095	6.61628	2.36085	2.20695
3 C(13)	0.01383	7.77303	2.77361	2.59280
4 C(13)	-0.00881	-4.95049	-1.76646	-1.65130
5 C(13)	-0.00354	-1.99133	-0.71056	-0.66424
6 C(13)	0.00312	1.75379	0.62579	0.58500
7 H(1)	-0.00013	-0.28663	-0.10228	-0.09561
8 H(1)	-0.00014	-0.31109	-0.11100	-0.10377
9 C(13)	-0.00590	-3.31436	-1.18265	-1.10555
10 C(13)	-0.00333	-1.87317	-0.66840	-0.62482
11 H(1)	0.00110	2.46682	0.88022	0.82284
12 C(13)	0.01269	7.13132	2.54463	2.37875
13 H(1)	-0.00011	-0.23807	-0.08495	-0.07941
14 H(1)	-0.00025	-0.55289	-0.19728	-0.18442
15 C(13)	0.00470	2.63985	0.94196	0.88056
16 H(1)	0.00008	0.17113	0.06106	0.05708
17 H(1)	0.00039	0.87625	0.31267	0.29229
18 C(13)	-0.00486	-2.73279	-0.97513	-0.91156
19 C(13)	0.00573	3.21942	1.14877	1.07388
20 H(1)	-0.00024	-0.53913	-0.19237	-0.17983
21 C(13)	-0.00057	-0.32064	-0.11441	-0.10695
22 C(13)	0.00049	0.27717	0.09890	0.09246
23 H(1)	-0.00009	-0.21183	-0.07559	-0.07066
24 C(13)	-0.00053	-0.29528	-0.10536	-0.09849
25 H(1)	0.00005	0.11271	0.04022	0.03760
26 C(13)	0.00060	0.33913	0.12101	0.11312
27 H(1)	-0.00011	-0.25310	-0.09031	-0.08443

28	C(13)	-0.00058	-0.32729	-0.11678	-0.10917
29	H(1)	0.00006	0.12928	0.04613	0.04312
30	C(13)	0.00084	0.47179	0.16835	0.15737
31	C(13)	-0.00049	-0.27739	-0.09898	-0.09253
32	H(1)	0.00024	0.52844	0.18856	0.17627
33	C(13)	0.00334	1.87802	0.67012	0.62644
34	H(1)	-0.00016	-0.36766	-0.13119	-0.12264
35	C(13)	0.01312	7.37241	2.63066	2.45917
36	H(1)	0.00232	5.17423	1.84629	1.72594
37	H(1)	-0.00004	-0.09642	-0.03441	-0.03216
38	C(13)	0.00822	4.61891	1.64814	1.54070
39	H(1)	-0.00016	-0.36415	-0.12994	-0.12147
40	H(1)	0.00032	0.71201	0.25406	0.23750
41	C(13)	0.00215	1.20902	0.43141	0.40329
42	H(1)	-0.00006	-0.13882	-0.04953	-0.04631
43	H(1)	-0.00018	-0.39846	-0.14218	-0.13291
44	H(1)	-0.00007	-0.14934	-0.05329	-0.04981
45	C(13)	0.00948	5.32987	1.90183	1.77785
46	H(1)	-0.00003	-0.06235	-0.02225	-0.02080
47	H(1)	0.00115	2.57478	0.91875	0.85885
48	H(1)	-0.00031	-0.69200	-0.24692	-0.23083
49	O(17)	0.03424	-10.37747	-3.70294	-3.46155
50	N(14)	0.04096	6.61638	2.36089	2.20699
51	C(13)	0.01383	7.77306	2.77362	2.59281
52	C(13)	-0.00881	-4.94967	-1.76616	-1.65103
53	C(13)	-0.00354	-1.99148	-0.71061	-0.66429
54	C(13)	0.00312	1.75400	0.62587	0.58507
55	H(1)	-0.00013	-0.28663	-0.10228	-0.09561
56	H(1)	-0.00014	-0.31108	-0.11100	-0.10377
57	C(13)	-0.00590	-3.31415	-1.18257	-1.10548
58	C(13)	-0.00333	-1.87349	-0.66851	-0.62493
59	H(1)	0.00110	2.46656	0.88013	0.82275
60	C(13)	0.01269	7.13179	2.54480	2.37891
61	H(1)	-0.00011	-0.23813	-0.08497	-0.07943
62	H(1)	-0.00025	-0.55290	-0.19729	-0.18443
63	C(13)	0.00470	2.64024	0.94210	0.88069
64	H(1)	0.00008	0.17102	0.06102	0.05705
65	H(1)	0.00039	0.87622	0.31266	0.29228
66	C(13)	-0.00486	-2.73249	-0.97502	-0.91146
67	C(13)	0.00573	3.21971	1.14887	1.07398
68	H(1)	-0.00024	-0.53905	-0.19235	-0.17981
69	C(13)	-0.00057	-0.32047	-0.11435	-0.10690
70	C(13)	0.00049	0.27711	0.09888	0.09243
71	H(1)	-0.00009	-0.21179	-0.07557	-0.07064
72	C(13)	-0.00053	-0.29521	-0.10534	-0.09847
73	H(1)	0.00005	0.11269	0.04021	0.03759
74	C(13)	0.00060	0.33905	0.12098	0.11310
75	H(1)	-0.00011	-0.25304	-0.09029	-0.08441
76	C(13)	-0.00058	-0.32721	-0.11676	-0.10915
77	H(1)	0.00006	0.12925	0.04612	0.04311
78	C(13)	0.00084	0.47173	0.16833	0.15735
79	C(13)	-0.00049	-0.27731	-0.09895	-0.09250
80	H(1)	0.00024	0.52843	0.18856	0.17626
81	C(13)	0.00334	1.87786	0.67007	0.62639
82	H(1)	-0.00016	-0.36761	-0.13117	-0.12262
83	C(13)	0.01312	7.37204	2.63053	2.45905
84	H(1)	0.00232	5.17390	1.84618	1.72583
85	H(1)	-0.00004	-0.09652	-0.03444	-0.03220
86	C(13)	0.00822	4.61938	1.64831	1.54086
87	H(1)	-0.00016	-0.36410	-0.12992	-0.12145
88	H(1)	0.00032	0.71223	0.25414	0.23757
89	C(13)	0.00215	1.20886	0.43135	0.40323
90	H(1)	-0.00006	-0.13880	-0.04953	-0.04630

91	H(1)	-0.00018	-0.39852	-0.14220	-0.13293
92	H(1)	-0.00007	-0.14933	-0.05329	-0.04981
93	C(13)	0.00948	5.32962	1.90174	1.77777
94	H(1)	-0.00003	-0.06238	-0.02226	-0.02081
95	H(1)	0.00115	2.57470	0.91872	0.85883
96	H(1)	-0.00031	-0.69203	-0.24693	-0.23084
97	H(1)	-0.00006	-0.12638	-0.04510	-0.04216
98	H(1)	-0.00010	-0.23322	-0.08322	-0.07779
99	H(1)	-0.00010	-0.23322	-0.08322	-0.07779
100	H(1)	-0.00006	-0.12638	-0.04510	-0.04216

Table S16. Isotropic Fermi contact couplings constants of **4b**.

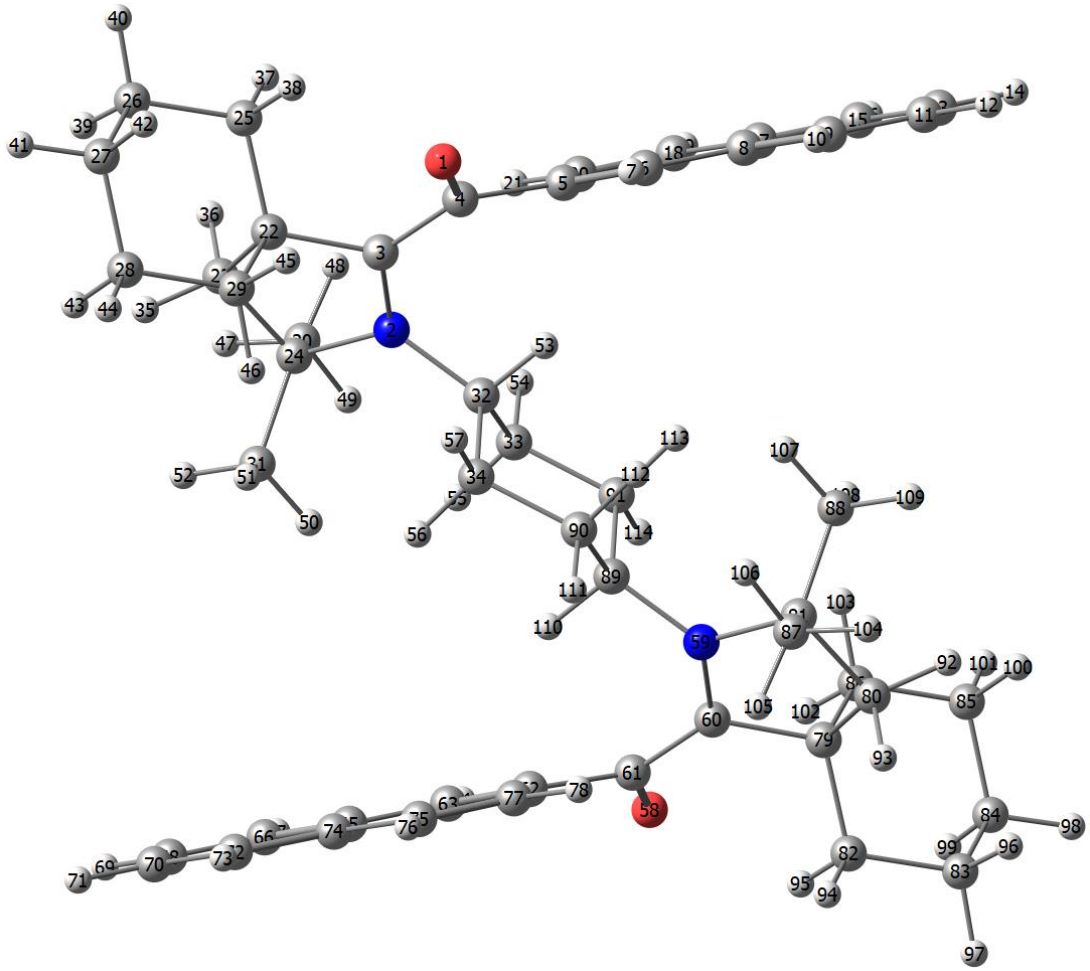


	Atom	a.u.	MegaHertz	Gauss	10(-4) cm-1
1	O(17)	0.03537	-10.72016	-3.82522	-3.57586
2	N(14)	0.04015	6.48652	2.31455	2.16367
3	C(13)	0.01327	7.45852	2.66138	2.48789
4	C(13)	-0.00879	-4.93912	-1.76240	-1.64751
5	C(13)	-0.00385	-2.16174	-0.77136	-0.72108
6	C(13)	0.00225	1.26688	0.45205	0.42258
7	H(1)	-0.00016	-0.35769	-0.12763	-0.11931
8	H(1)	-0.00018	-0.39263	-0.14010	-0.13097

9	C(13)	-0.00625	-3.51197	-1.25316	-1.17147
10	C(13)	-0.00304	-1.70776	-0.60937	-0.56965
11	H(1)	0.00126	2.81905	1.00591	0.94033
12	C(13)	0.01151	6.46775	2.30785	2.15741
13	H(1)	-0.00012	-0.27875	-0.09947	-0.09298
14	H(1)	-0.00023	-0.50866	-0.18150	-0.16967
15	C(13)	0.00397	2.22906	0.79538	0.74353
16	H(1)	0.00007	0.14596	0.05208	0.04869
17	H(1)	0.00037	0.82240	0.29345	0.27432
18	C(13)	-0.00499	-2.80278	-1.00010	-0.93491
19	C(13)	0.00544	3.05609	1.09049	1.01940
20	H(1)	-0.00031	-0.69046	-0.24637	-0.23031
21	C(13)	-0.00098	-0.54885	-0.19584	-0.18308
22	C(13)	0.00066	0.37227	0.13284	0.12418
23	H(1)	-0.00012	-0.27394	-0.09775	-0.09138
24	C(13)	-0.00068	-0.38189	-0.13627	-0.12738
25	H(1)	0.00007	0.14623	0.05218	0.04878
26	C(13)	0.00079	0.44261	0.15793	0.14764
27	H(1)	-0.00015	-0.33134	-0.11823	-0.11052
28	C(13)	-0.00076	-0.42606	-0.15203	-0.14212
29	H(1)	0.00007	0.16497	0.05887	0.05503
30	C(13)	0.00102	0.57481	0.20511	0.19173
31	C(13)	-0.00069	-0.38924	-0.13889	-0.12984
32	H(1)	0.00025	0.55016	0.19631	0.18351
33	C(13)	0.00348	1.95890	0.69898	0.65342
34	H(1)	-0.00020	-0.43603	-0.15559	-0.14544
35	C(13)	0.01402	7.87918	2.81149	2.62821
36	H(1)	0.00140	3.12414	1.11477	1.04210
37	H(1)	-0.00026	-0.57523	-0.20526	-0.19188
38	C(13)	0.00018	0.10267	0.03663	0.03425
39	H(1)	-0.00007	-0.16641	-0.05938	-0.05551
40	H(1)	-0.00004	-0.09857	-0.03517	-0.03288
41	H(1)	0.00010	0.21835	0.07791	0.07283
42	C(13)	0.00523	2.94218	1.04984	0.98141
43	H(1)	-0.00015	-0.32512	-0.11601	-0.10845
44	H(1)	-0.00025	-0.56989	-0.20335	-0.19010
45	C(13)	0.00168	0.94704	0.33793	0.31590
46	H(1)	-0.00006	-0.13903	-0.04961	-0.04637
47	H(1)	0.00019	0.42129	0.15033	0.14053
48	H(1)	0.00020	0.43761	0.15615	0.14597
49	C(13)	0.00363	2.04121	0.72835	0.68087
50	H(1)	-0.00010	-0.21627	-0.07717	-0.07214
51	H(1)	-0.00007	-0.15291	-0.05456	-0.05100
52	H(1)	-0.00008	-0.18004	-0.06424	-0.06006
53	C(13)	0.01112	6.25041	2.23030	2.08491
54	H(1)	-0.00008	-0.17940	-0.06401	-0.05984
55	H(1)	0.00135	3.02564	1.07962	1.00924
56	H(1)	-0.00025	-0.56305	-0.20091	-0.18781
57	O(17)	0.03537	-10.71988	-3.82512	-3.57577
58	N(14)	0.04014	6.48539	2.31415	2.16329
59	C(13)	0.01327	7.46061	2.66213	2.48859
60	C(13)	-0.00879	-4.93955	-1.76255	-1.64766
61	C(13)	-0.00385	-2.16155	-0.77130	-0.72102
62	C(13)	0.00225	1.26567	0.45162	0.42218
63	H(1)	-0.00016	-0.35797	-0.12773	-0.11941
64	H(1)	-0.00018	-0.39271	-0.14013	-0.13100
65	C(13)	-0.00625	-3.51402	-1.25389	-1.17215
66	C(13)	-0.00303	-1.70265	-0.60755	-0.56794
67	H(1)	0.00126	2.82685	1.00869	0.94294
68	C(13)	0.01150	6.46492	2.30684	2.15647
69	H(1)	-0.00012	-0.27789	-0.09916	-0.09270
70	H(1)	-0.00023	-0.50863	-0.18149	-0.16966
71	C(13)	0.00396	2.22563	0.79416	0.74239

72	H(1)	0.00007	0.14671	0.05235	0.04894
73	H(1)	0.00037	0.82222	0.29339	0.27426
74	C(13)	-0.00498	-2.80056	-0.99931	-0.93417
75	C(13)	0.00544	3.05501	1.09010	1.01904
76	H(1)	-0.00031	-0.69003	-0.24622	-0.23017
77	C(13)	-0.00098	-0.54881	-0.19583	-0.18306
78	C(13)	0.00066	0.37216	0.13280	0.12414
79	H(1)	-0.00012	-0.27386	-0.09772	-0.09135
80	C(13)	-0.00068	-0.38181	-0.13624	-0.12736
81	H(1)	0.00007	0.14618	0.05216	0.04876
82	C(13)	0.00079	0.44253	0.15791	0.14761
83	H(1)	-0.00015	-0.33128	-0.11821	-0.11050
84	C(13)	-0.00076	-0.42601	-0.15201	-0.14210
85	H(1)	0.00007	0.16494	0.05885	0.05502
86	C(13)	0.00102	0.57465	0.20505	0.19168
87	C(13)	-0.00069	-0.38887	-0.13876	-0.12971
88	H(1)	0.00025	0.55012	0.19630	0.18350
89	C(13)	0.00349	1.95911	0.69906	0.65349
90	H(1)	-0.00020	-0.43606	-0.15560	-0.14545
91	C(13)	0.01403	7.88367	2.81309	2.62971
92	H(1)	0.00140	3.12537	1.11521	1.04251
93	H(1)	-0.00026	-0.57536	-0.20530	-0.19192
94	C(13)	0.00018	0.10270	0.03665	0.03426
95	H(1)	-0.00007	-0.16631	-0.05935	-0.05548
96	H(1)	-0.00004	-0.09872	-0.03522	-0.03293
97	H(1)	0.00010	0.21772	0.07769	0.07262
98	C(13)	0.00524	2.94460	1.05071	0.98221
99	H(1)	-0.00015	-0.32540	-0.11611	-0.10854
100	H(1)	-0.00025	-0.56954	-0.20323	-0.18998
101	C(13)	0.00168	0.94681	0.33785	0.31582
102	H(1)	-0.00006	-0.13906	-0.04962	-0.04638
103	H(1)	0.00019	0.42113	0.15027	0.14047
104	H(1)	0.00020	0.43780	0.15622	0.14603
105	C(13)	0.00363	2.04167	0.72852	0.68103
106	H(1)	-0.00010	-0.21625	-0.07716	-0.07213
107	H(1)	-0.00007	-0.15256	-0.05444	-0.05089
108	H(1)	-0.00008	-0.18003	-0.06424	-0.06005
109	C(13)	0.01112	6.25257	2.23107	2.08563
110	H(1)	-0.00008	-0.17926	-0.06396	-0.05980
111	H(1)	0.00135	3.02620	1.07982	1.00943
112	H(1)	-0.00025	-0.56273	-0.20079	-0.18770

Table S17. Isotropic Fermi contact couplings constants of **4c**.



	Atom	a.u.	MegaHertz	Gauss	10(-4) cm-1
1	O(17)	0.03501	-10.61278	-3.78690	-3.54004
2	N(14)	0.03820	6.17144	2.20212	2.05857
3	C(13)	0.01535	8.62872	3.07894	2.87823
4	C(13)	-0.01003	-5.64044	-2.01265	-1.88145
5	C(13)	-0.00366	-2.05939	-0.73484	-0.68694
6	C(13)	0.00440	2.47448	0.88296	0.82540
7	H(1)	-0.00050	-1.11740	-0.39872	-0.37272
8	C(13)	-0.00133	-0.74597	-0.26618	-0.24883
9	C(13)	0.00101	0.56710	0.20236	0.18916
10	H(1)	-0.00015	-0.32752	-0.11687	-0.10925
11	C(13)	-0.00075	-0.42172	-0.15048	-0.14067
12	H(1)	0.00008	0.17616	0.06286	0.05876
13	C(13)	0.00095	0.53471	0.19080	0.17836
14	H(1)	-0.00018	-0.40726	-0.14532	-0.13585
15	C(13)	-0.00089	-0.50176	-0.17904	-0.16737
16	H(1)	0.00008	0.18586	0.06632	0.06200
17	C(13)	0.00109	0.61212	0.21842	0.20418
18	C(13)	-0.00089	-0.50186	-0.17908	-0.16740
19	H(1)	0.00010	0.23193	0.08276	0.07736
20	C(13)	0.00316	1.77711	0.63412	0.59278
21	H(1)	-0.00010	-0.22770	-0.08125	-0.07595
22	C(13)	-0.00235	-1.32000	-0.47101	-0.44031
23	C(13)	0.00239	1.34069	0.47839	0.44720

24	C(13)	-0.00660	-3.70756	-1.32295	-1.23671
25	C(13)	0.00383	2.15109	0.76756	0.71753
26	C(13)	-0.00016	-0.09084	-0.03241	-0.03030
27	C(13)	0.00023	0.12970	0.04628	0.04326
28	C(13)	0.00509	2.86030	1.02063	0.95409
29	C(13)	0.01513	8.50706	3.03553	2.83765
30	C(13)	0.01074	6.03863	2.15473	2.01427
31	C(13)	0.00684	3.84689	1.37266	1.28318
32	C(13)	0.00253	1.42141	0.50719	0.47413
33	C(13)	0.00116	0.65096	0.23228	0.21714
34	C(13)	0.00731	4.10680	1.46541	1.36988
35	H(1)	-0.00029	-0.64931	-0.23169	-0.21659
36	H(1)	-0.00011	-0.23766	-0.08480	-0.07928
37	H(1)	-0.00015	-0.34435	-0.12287	-0.11486
38	H(1)	-0.00017	-0.38988	-0.13912	-0.13005
39	H(1)	0.00010	0.23455	0.08369	0.07824
40	H(1)	0.00002	0.04688	0.01673	0.01564
41	H(1)	-0.00002	-0.03670	-0.01310	-0.01224
42	H(1)	-0.00000	-0.00831	-0.00296	-0.00277
43	H(1)	-0.00008	-0.18656	-0.06657	-0.06223
44	H(1)	0.00075	1.66576	0.59438	0.55564
45	H(1)	0.00006	0.14135	0.05044	0.04715
46	H(1)	-0.00030	-0.66290	-0.23654	-0.22112
47	H(1)	0.00112	2.51310	0.89674	0.83828
48	H(1)	-0.00013	-0.28008	-0.09994	-0.09343
49	H(1)	-0.00014	-0.32119	-0.11461	-0.10714
50	H(1)	-0.00010	-0.22817	-0.08142	-0.07611
51	H(1)	-0.00014	-0.32193	-0.11487	-0.10738
52	H(1)	0.00020	0.43731	0.15604	0.14587
53	H(1)	0.00285	6.38005	2.27656	2.12816
54	H(1)	0.00042	0.94456	0.33704	0.31507
55	H(1)	0.00004	0.09713	0.03466	0.03240
56	H(1)	-0.00022	-0.49044	-0.17500	-0.16359
57	H(1)	-0.00037	-0.83257	-0.29708	-0.27771
58	O(17)	0.03501	-10.61282	-3.78692	-3.54005
59	N(14)	0.03820	6.17136	2.20209	2.05854
60	C(13)	0.01535	8.62875	3.07895	2.87824
61	C(13)	-0.01003	-5.64035	-2.01262	-1.88142
62	C(13)	-0.00366	-2.05925	-0.73479	-0.68689
63	C(13)	0.00440	2.47448	0.88295	0.82540
64	H(1)	-0.00050	-1.11738	-0.39871	-0.37272
65	C(13)	-0.00133	-0.74594	-0.26617	-0.24882
66	C(13)	0.00101	0.56710	0.20235	0.18916
67	H(1)	-0.00015	-0.32751	-0.11687	-0.10925
68	C(13)	-0.00075	-0.42172	-0.15048	-0.14067
69	H(1)	0.00008	0.17616	0.06286	0.05876
70	C(13)	0.00095	0.53470	0.19079	0.17836
71	H(1)	-0.00018	-0.40725	-0.14532	-0.13585
72	C(13)	-0.00089	-0.50175	-0.17904	-0.16737
73	H(1)	0.00008	0.18586	0.06632	0.06200
74	C(13)	0.00109	0.61212	0.21842	0.20418
75	C(13)	-0.00089	-0.50183	-0.17907	-0.16739
76	H(1)	0.00010	0.23192	0.08276	0.07736
77	C(13)	0.00316	1.77731	0.63419	0.59285
78	H(1)	-0.00010	-0.22770	-0.08125	-0.07595
79	C(13)	-0.00235	-1.31987	-0.47096	-0.44026
80	C(13)	0.00239	1.34077	0.47842	0.44723
81	C(13)	-0.00660	-3.70752	-1.32293	-1.23669
82	C(13)	0.00383	2.15122	0.76761	0.71757
83	C(13)	-0.00016	-0.09082	-0.03241	-0.03029
84	C(13)	0.00023	0.12971	0.04628	0.04327
85	C(13)	0.00509	2.86029	1.02062	0.95409
86	C(13)	0.01513	8.50698	3.03550	2.83762

87	C(13)	0.01074	6.03865	2.15474	2.01428
88	C(13)	0.00684	3.84682	1.37264	1.28316
89	C(13)	0.00253	1.42131	0.50716	0.47410
90	C(13)	0.00116	0.65093	0.23227	0.21713
91	C(13)	0.00731	4.10673	1.46538	1.36986
92	H(1)	-0.00029	-0.64931	-0.23169	-0.21659
93	H(1)	-0.00011	-0.23767	-0.08481	-0.07928
94	H(1)	-0.00015	-0.34434	-0.12287	-0.11486
95	H(1)	-0.00017	-0.38986	-0.13911	-0.13004
96	H(1)	0.00010	0.23452	0.08368	0.07823
97	H(1)	0.00002	0.04686	0.01672	0.01563
98	H(1)	-0.00002	-0.03670	-0.01310	-0.01224
99	H(1)	-0.00000	-0.00831	-0.00296	-0.00277
100	H(1)	-0.00008	-0.18656	-0.06657	-0.06223
101	H(1)	0.00075	1.66578	0.59439	0.55564
102	H(1)	0.00006	0.14136	0.05044	0.04715
103	H(1)	-0.00030	-0.66290	-0.23654	-0.22112
104	H(1)	0.00112	2.51319	0.89677	0.83831
105	H(1)	-0.00013	-0.28009	-0.09994	-0.09343
106	H(1)	-0.00014	-0.32118	-0.11460	-0.10713
107	H(1)	-0.00010	-0.22816	-0.08141	-0.07611
108	H(1)	-0.00014	-0.32192	-0.11487	-0.10738
109	H(1)	0.00020	0.43725	0.15602	0.14585
110	H(1)	0.00285	6.38066	2.27678	2.12836
111	H(1)	0.00042	0.94460	0.33706	0.31508
112	H(1)	0.00004	0.09711	0.03465	0.03239
113	H(1)	-0.00022	-0.49044	-0.17500	-0.16359
114	H(1)	-0.00037	-0.83257	-0.29708	-0.27771

Table S18. Summary of TD-DFT calculated first ten transitions for **4a**.

HOMO: 173

LUMO: 174

Excitation energies and oscillator strengths:

Excited State 1: 1.152-A 1.9916 eV 622.55 nm f=0.0012 <S**2>=0.082

173A ->174A 0.75107

173B ->174B 0.65856

Excited State 2: 1.153-A 1.9918 eV 622.46 nm f=0.0000 <S**2>=0.082

173A ->174A -0.65881

173B ->174B 0.75129

Excited State 3: 2.332-A 2.2165 eV 559.36 nm f=0.0000 <S**2>=1.110

173A ->175A 0.68998

173B ->175B 0.67733

Excited State 4: 2.335-A 2.2198 eV 558.53 nm f=0.0905 <S**2>=1.113

173A ->175A -0.67747

173B ->175B 0.69011

Excited State 5: 2.388-A 2.4915 eV 497.63 nm f=0.0036 <S**2>=1.175

168A ->174A -0.19995

170A ->174A 0.87819

172A ->174A -0.32004

171B ->175B 0.12082

Excited State 6: 2.388-A 2.4915 eV 497.63 nm f=0.0024 <S**2>=1.176

171A ->175A -0.12102

168B ->174B -0.19985

170B ->174B 0.87810

172B ->174B -0.32015

Excited State 7: 2.242-A 2.6958 eV 459.91 nm f=0.0000 <S**2>=1.007

173A ->176A 0.72613

173B ->176B 0.67794

Excited State 8: 2.228-A 2.6963 eV 459.83 nm f=0.0006 <S**2>=0.991

173A ->176A -0.68173

173B ->176B 0.72965

Excited State 9: 3.440-A 2.7400 eV 452.49 nm f=0.0113 <S**2>=2.708

167A ->177A 0.11086

170A ->174A 0.13359

171A ->175A 0.51529

172A ->174A 0.16945

172A ->176A -0.30781

173A ->175A 0.14841

168B ->178B -0.11684

170B ->174B 0.20192

171B ->175B -0.34144

172B ->174B 0.25602

172B ->176B 0.46454

Excited State 10: 3.431-A 2.7400 eV 452.49 nm f=0.0005 <S**2>=2.694

168A ->178A -0.11564

170A ->174A -0.20194

171A ->175A 0.33975

172A ->174A -0.25591

172A ->176A 0.46355

167B ->177B 0.10955

170B ->174B 0.13364

171B ->175B 0.51418

172B ->174B 0.16930

172B ->176B 0.30630

173B ->175B 0.14483

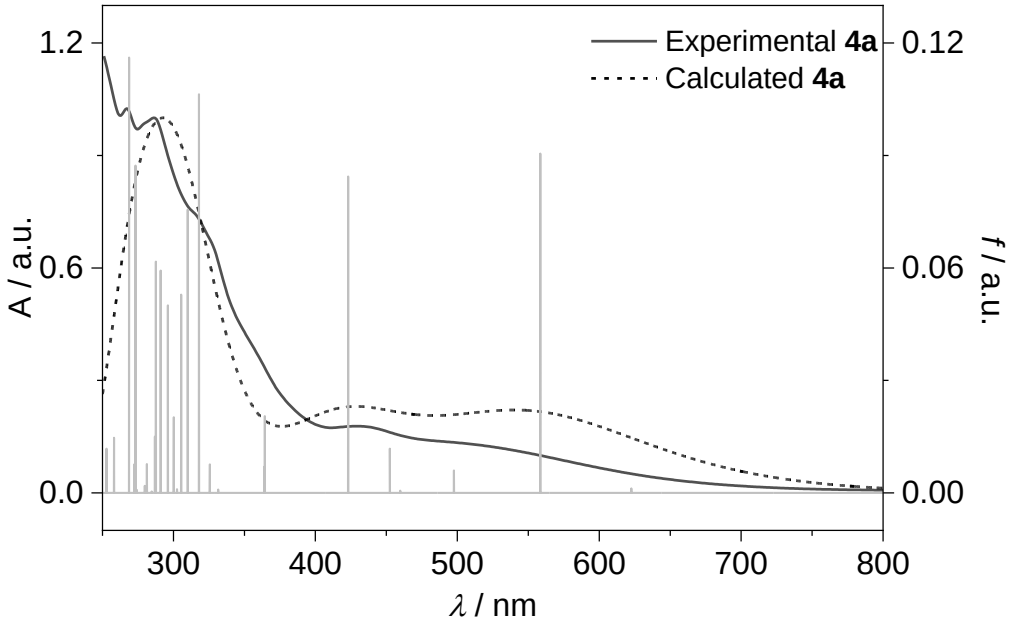


Fig. S109 TD-DFT calculated electronic absorption spectra of **4a**. *f* = oscillator strength.

Table S19. Summary of TD-DFT calculated first ten transitions for **4b**.

HOMO: 189

LUMO: 190

Excited State 1: 1.181-A 1.9569 eV 633.58 nm f=0.0011 <S**2>=0.099

189A -> 190A 0.23995

189B -> 190B 0.96878

Excited State 2: 1.181-A 1.9575 eV 633.37 nm f=0.0004 <S**2>=0.099

189A -> 190A 0.96892

189B -> 190B -0.24058

Excited State 3: 2.318-A 2.1143 eV 586.40 nm f=0.0000 <S**2>=1.094

189A -> 191A 0.67135

189B -> 191B 0.69998

Excited State 4: 2.321-A 2.1184 eV 585.27 nm f=0.1076 <S**2>=1.096

189A -> 191A 0.69983

189B -> 191B -0.67122

Excited State 5: 2.414-A 2.5333 eV 489.41 nm f=0.0021 <S**2>=1.207

186A -> 190A -0.15219

187A -> 191A 0.13703

184B -> 190B -0.19227

186B -> 190B 0.88946

188B -> 190B -0.23057

188B -> 192B 0.10995

Excited State 6: 2.414-A 2.5336 eV 489.36 nm f=0.0042 <S**2>=1.207

184A -> 190A -0.19247

186A -> 190A 0.88968

188A -> 190A -0.22998

188A -> 192A -0.10979

186B -> 190B 0.15344

187B -> 191B -0.13681

Excited State 7: 2.218-A 2.6321 eV 471.04 nm f=0.0002 <S**2>=0.980

189A -> 192A 0.15364

189B -> 192B 0.98709

Excited State 8: 2.217-A 2.6328 eV 470.92 nm f=0.0003 <S**2>=0.979

189A -> 192A 0.98724

189B -> 192B -0.15463

Excited State 9: 3.419-A 2.7308 eV 454.02 nm f=0.0002 <S**2>=2.672

183A -> 193A 0.10341

186A -> 190A 0.15348

187A -> 191A 0.47583

188A -> 190A 0.22147

188A -> 192A 0.34087

189A -> 191A -0.11784

184B -> 190B 0.10545

184B -> 194B -0.10541

186B -> 190B -0.19205

187B -> 191B 0.37928

188B -> 190B -0.27763

188B -> 192B 0.42757

Excited State 10: 3.422-A 2.7312 eV 453.95 nm f=0.0165 <S**2>=2.677

184A -> 190A -0.10489

184A -> 194A -0.10614

186A -> 190A 0.19076

187A -> 191A -0.37958

188A -> 190A 0.27668

188A -> 192A 0.42774

183B -> 193B 0.10419

186B -> 190B 0.15171

187B -> 191B 0.47601

188B -> 190B 0.22045

188B -> 192B -0.34102

189B -> 191B -0.12035

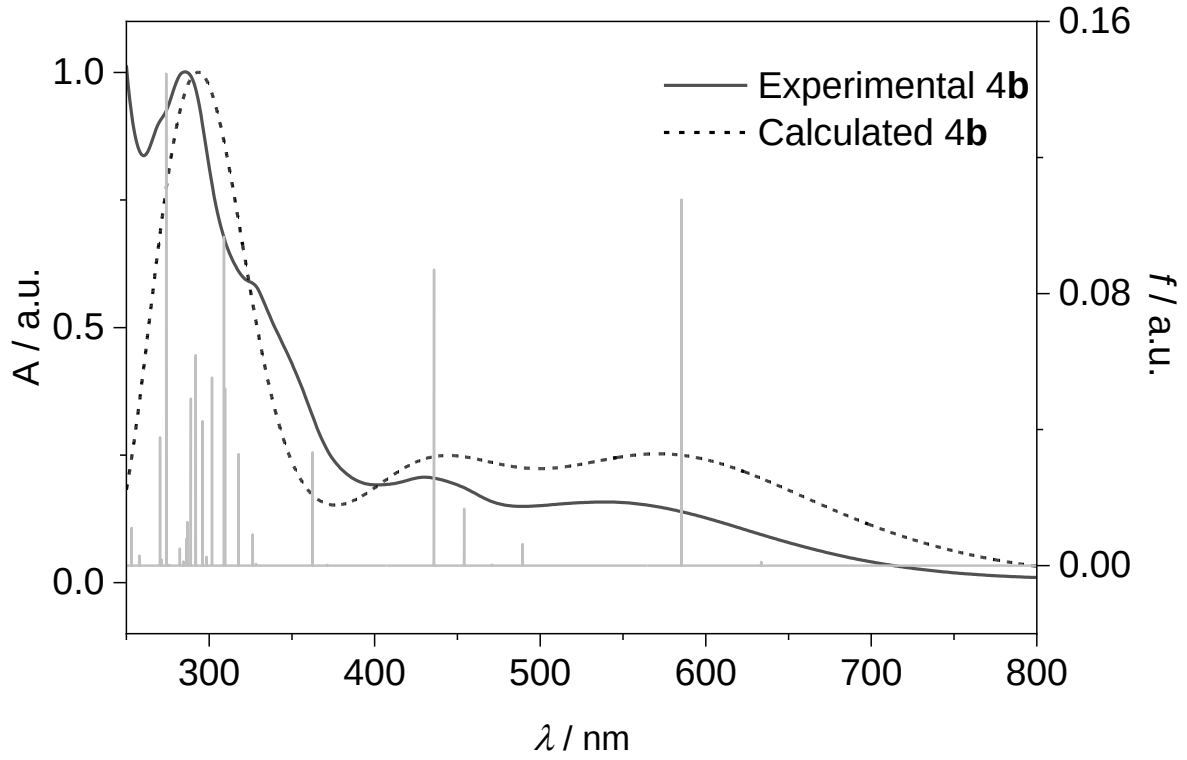


Fig. S110 TD-DFT calculated electronic absorption spectra of **4b**. *f* = oscillator strength.

Table S20. Summary of TD-DFT calculated first ten transitions for **4c**.

HOMO: 195

LUMO: 196

*Excited State 1: 1.206-A 1.8989 eV 652.92 nm f=0.0005 <S**2>=0.114*

195A -> 196A 0.56103

195B -> 196B 0.82742

*Excited State 2: 1.206-A 1.8990 eV 652.89 nm f=0.0000 <S**2>=0.114*

195A -> 196A 0.82745

195B -> 196B -0.56108

*Excited State 3: 2.334-A 2.1547 eV 575.42 nm f=0.0000 <S**2>=1.112*

195A -> 197A 0.68063

195B -> 197B 0.68444

*Excited State 4: 2.337-A 2.1592 eV 574.20 nm f=0.2085 <S**2>=1.116*

195A -> 197A 0.68452

195B -> 197B -0.68071

*Excited State 5: 2.495-A 2.4838 eV 499.17 nm f=0.0000 <S**2>=1.307*

192A -> 196A -0.46217

192A -> 198A -0.10197

193A -> 197A -0.14559

194A -> 196A -0.44933

195A -> 199A 0.12160

192B -> 196B 0.47458

192B -> 198B -0.10469

193B -> 197B -0.14183

194B -> 196B 0.46133

195B -> 199B 0.11849

*Excited State 6: 2.493-A 2.4842 eV 499.10 nm f=0.0128 <S**2>=1.304*

192A -> 196A 0.47591

192A -> 198A 0.10462

193A -> 197A -0.14069

194A -> 196A 0.46068

195A -> 199A 0.11703

192B -> 196B 0.46356

192B -> 198B -0.10189

193B -> 197B 0.14449

194B -> 196B 0.44866

195B -> 199B -0.12022

*Excited State 7: 3.221-A 2.7221 eV 455.47 nm f=0.0299 <S**2>=2.344*

192A -> 196A 0.35128

193A -> 197A 0.37493

194A -> 196A -0.15137

194A -> 198A 0.32583

195A -> 197A -0.10116

195A -> 198A -0.15701

192B -> 196B 0.35446

193B -> 197B -0.37151

194B -> 196B -0.15277

194B -> 198B -0.32883

195B -> 197B 0.10023

195B -> 198B 0.15697

*Excited State 8: 3.266-A 2.7222 eV 455.46 nm f=0.0000 <S**2>=2.417*

192A -> 196A -0.36273

193A -> 197A 0.38195

194A -> 196A 0.15669

194A -> 198A -0.33777

195A -> 197A -0.10169

192B -> 196B 0.35961

193B -> 197B 0.38522

194B -> 196B -0.15537

194B -> 198B -0.33490

195B -> 197B -0.10256

*Excited State 9: 2.296-A 2.7328 eV 453.69 nm f=0.0001 <S**2>=1.067*

193A -> 197A -0.10061

195A -> 198A -0.53652

195A -> 199A -0.14541

193B -> 197B 0.11437

195B -> 198B 0.76779

195B -> 199B 0.18766

*Excited State 10: 2.218-A 2.7329 eV 453.68 nm f=0.0000 <S**2>=0.980*

195A -> 198A 0.79298

195A -> 199A 0.15271

195B -> 198B 0.57188

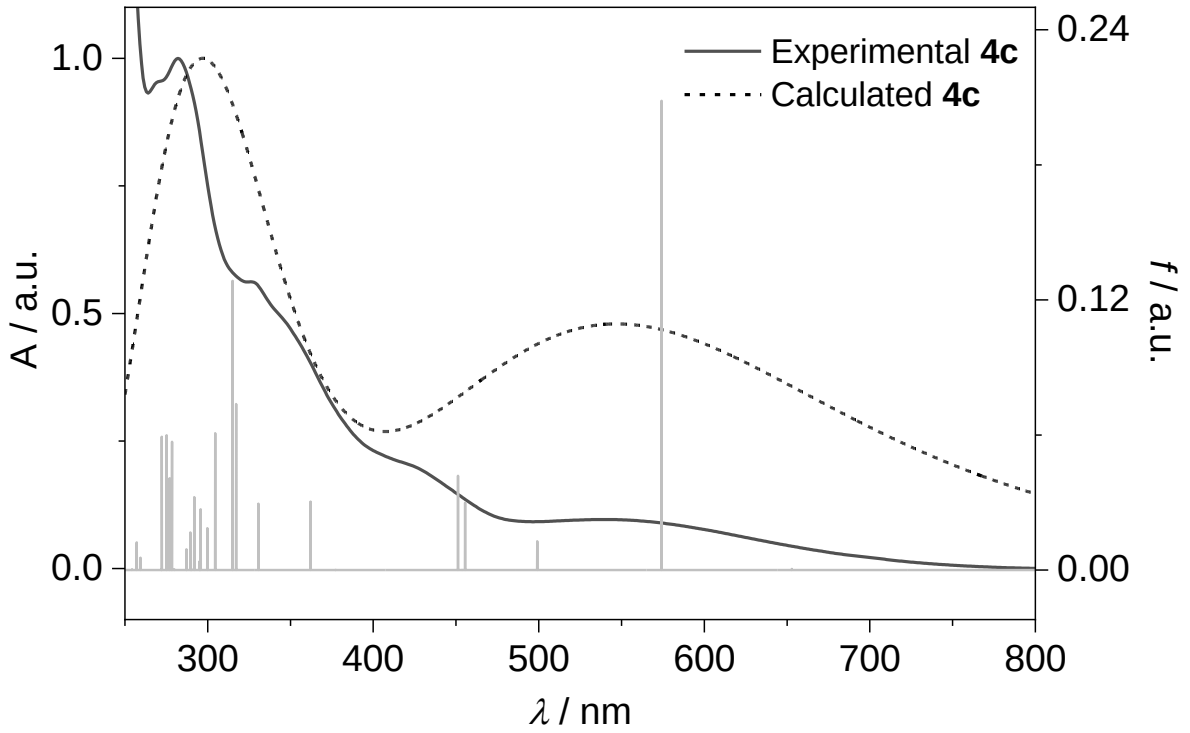


Fig. S111 TD-DFT calculated electronic absorption spectra of **4c**. *f* = oscillator strength.

Cartesian Coordinates

4a, UwB97XD/def2SVP, BSS

O	5.131945000	0.922467000	1.718954000
N	2.738542000	-0.825144000	-0.350774000
C	3.894039000	-0.426493000	0.264875000
C	4.159191000	0.808043000	0.953407000
C	4.972049000	-1.491232000	0.123469000
C	4.271541000	-2.552538000	-0.753219000
H	4.925615000	-2.930530000	-1.552248000
H	3.985954000	-3.415452000	-0.133179000
C	2.995504000	-1.909907000	-1.329797000
C	1.430318000	-0.247408000	-0.062530000
H	1.638866000	0.624489000	0.562116000
C	0.524256000	-1.125016000	0.812449000
H	1.098780000	-1.491991000	1.676643000
H	0.156340000	-2.006470000	0.268589000
C	0.675967000	0.300942000	-1.278430000
H	0.329004000	-0.521940000	-1.925176000
H	1.345674000	0.927948000	-1.882427000
C	3.287187000	2.018866000	0.747350000
C	3.003963000	2.504060000	-0.508018000
H	3.421398000	2.006003000	-1.387694000
C	2.123225000	3.603464000	-0.692329000
C	1.752915000	4.064498000	-1.985162000
H	2.196316000	3.585547000	-2.862020000
C	0.843895000	5.083472000	-2.134142000
H	0.559998000	5.422454000	-3.132678000
C	0.271841000	5.702302000	-0.995348000
H	-0.446758000	6.514254000	-1.125693000
C	0.621727000	5.287265000	0.266857000
H	0.183823000	5.764128000	1.147464000
C	1.548274000	4.226147000	0.452922000
C	1.913150000	3.752341000	1.744755000
H	1.495488000	4.248337000	2.624779000
C	2.766825000	2.689310000	1.888539000
H	3.050024000	2.325738000	2.878375000
C	5.337058000	-2.087318000	1.493915000
H	6.028027000	-2.935860000	1.361038000
H	5.810706000	-1.328106000	2.128000000
C	6.234212000	-0.926779000	-0.546241000
H	6.666996000	-0.126900000	0.069566000
H	6.986463000	-1.722291000	-0.665744000
C	1.881590000	-2.951822000	-1.424967000
H	1.670144000	-3.410750000	-0.449612000
H	2.213188000	-3.751037000	-2.104894000
H	0.943815000	-2.546239000	-1.829363000
C	3.257647000	-1.296621000	-2.715180000
H	2.353155000	-0.826044000	-3.124574000
H	3.582481000	-2.075977000	-3.421021000
H	4.047634000	-0.533452000	-2.660571000
O	-5.131928000	-0.922091000	-1.718964000
N	-2.738388000	0.825191000	0.350875000
C	-3.893939000	0.426640000	-0.264747000
C	-4.159175000	-0.807814000	-0.953400000
C	-4.971919000	1.491376000	-0.123124000
C	-4.271334000	2.552553000	0.753657000
H	-4.925346000	2.930460000	1.552776000
H	-3.985774000	3.415537000	0.133700000
C	-2.995256000	1.909835000	1.330047000
C	-1.430205000	0.247405000	0.062560000
H	-1.638806000	-0.624479000	-0.562088000
C	-0.524137000	1.124999000	0.812432000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.872627 (Hartree/Particle)
Thermal correction to Energy= 0.916041
Thermal correction to Enthalpy= 0.916985
Thermal correction to Gibbs Free Energy= 0.798151
Sum of electronic and zero-point Energies= -1965.111389
Sum of electronic and thermal Energies= -1965.067975
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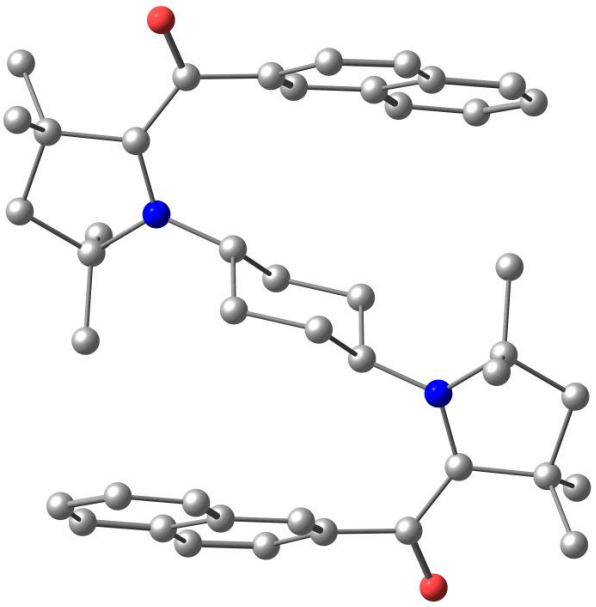

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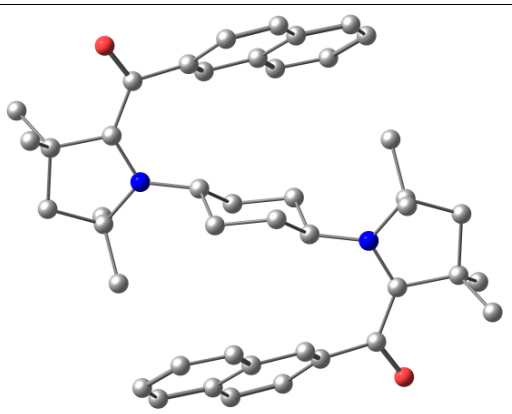
C	-0.675830000	-0.300938000	1.278455000	
H	-0.328829000	0.521974000	1.925147000	
H	-1.345510000	-0.927906000	1.882516000	
C	-3.287268000	-2.018727000	-0.747452000	
C	-3.003904000	-2.503937000	0.507878000	
H	-3.421112000	-2.005797000	1.387614000	
C	-2.123308000	-3.603475000	0.692064000	
C	-1.752861000	-4.064546000	1.984844000	
H	-2.196033000	-3.585500000	2.861766000	
C	-0.844003000	-5.083683000	2.133692000	
H	-0.560002000	-5.422698000	3.132188000	
C	-0.272247000	-5.702636000	0.994816000	
H	0.446232000	-6.514710000	1.125057000	
C	-0.622271000	-5.287562000	-0.267340000	
H	-0.184602000	-5.764524000	-1.148010000	
C	-1.548665000	-4.226287000	-0.453271000	
C	-1.913686000	-3.752453000	-1.745052000	
H	-1.496253000	-4.248534000	-2.625136000	
C	-2.767204000	-2.689280000	-1.888713000	
H	-3.050518000	-2.325689000	-2.878509000	
C	-5.337049000	2.087651000	-1.493451000	
H	-6.028039000	2.936146000	-1.360398000	
H	-5.810708000	1.328517000	-2.127621000	
C	-6.234028000	0.926822000	0.546607000	
H	-6.666818000	0.126983000	-0.069251000	
H	-6.986306000	1.722293000	0.666223000	
C	-1.881321000	2.951721000	1.425257000	
H	-1.669963000	3.410802000	0.449956000	
H	-2.212826000	3.750840000	2.105343000	
H	-0.943509000	2.546058000	1.829491000	
C	-3.257259000	1.296366000	2.715372000	
H	-2.352733000	0.825691000	3.124590000	
H	-3.581968000	2.075640000	3.421362000	
H	-4.047289000	0.533241000	2.660759000	
H	6.013790000	-0.517121000	-1.543751000	
H	4.436435000	-2.458142000	2.008208000	
H	-4.436478000	2.458583000	-2.007758000	
H	-6.013540000	0.517078000	1.544066000	
4a, UwB97XD/def2SVP, Triplet				
O	5.131891000	0.922473000	1.719016000	- Thermochemistry -
N	2.738543000	-0.825119000	-0.350793000	-------------------
C	3.894026000	-0.426468000	0.264885000	Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
C	4.159162000	0.808064000	0.953432000	
C	4.972049000	-1.491190000	0.123460000	Zero-point correction= 0.872631
C	4.271573000	-2.552476000	-0.753280000	(Hartree/Particle)
H	4.925659000	-2.930405000	-1.552330000	Thermal correction to Energy= 0.916044
H	3.986018000	-3.415432000	-0.133284000	Thermal correction to Enthalpy= 0.916988
C	2.995514000	-1.909859000	-1.329829000	Thermal correction to Gibbs Free Energy= 0.797119
C	1.430323000	-0.247389000	-0.062562000	Sum of electronic and zero-point Energies= -1965.111382
H	1.638859000	0.624531000	0.562055000	Sum of electronic and thermal Energies= -1965.067969
C	0.524304000	-1.124973000	0.812504000	Sum of electronic and thermal Enthalpies= -1965.067024
H	1.098903000	-1.491812000	1.676707000	Sum of electronic and thermal Free Energies= -
H	0.156424000	-2.006507000	0.268747000	1965.186893
C	0.675928000	0.300938000	-1.278464000	
H	0.329010000	-0.521948000	-1.925229000	Charge = 0 Multiplicity = 3
H	1.345619000	0.927984000	-1.882435000	
C	3.287168000	2.018888000	0.747355000	
C	3.003940000	2.504075000	-0.508016000	
H	3.421384000	2.006025000	-1.387690000	
C	2.123182000	3.603463000	-0.692332000	
C	1.752863000	4.064483000	-1.985167000	

H	2.196267000	3.585531000	-2.862023000
C	0.843833000	5.083448000	-2.134153000
H	0.559931000	5.422420000	-3.132691000
C	0.271774000	5.702279000	-0.995363000
H	-0.446833000	6.514223000	-1.125712000
C	0.621663000	5.287250000	0.266845000
H	0.183753000	5.764113000	1.147449000
C	1.548221000	4.226143000	0.452915000
C	1.913110000	3.752354000	1.744751000
H	1.495442000	4.248349000	2.624773000
C	2.766800000	2.689336000	1.888540000
H	3.050006000	2.325772000	2.878377000
C	5.337041000	-2.087315000	1.493894000
H	6.028038000	-2.935830000	1.361005000
H	5.810649000	-1.328109000	2.128017000
C	6.234215000	-0.926695000	-0.546207000
H	6.666982000	-0.126837000	0.069638000
H	6.986476000	-1.722194000	-0.665733000
C	1.881611000	-2.951789000	-1.424988000
H	1.670195000	-3.410730000	-0.449633000
H	2.213199000	-3.750991000	-2.104934000
H	0.943820000	-2.546211000	-1.829352000
C	3.257623000	-1.296545000	-2.715204000
H	2.353136000	-0.825907000	-3.124544000
H	3.582384000	-2.075896000	-3.421085000
H	4.047651000	-0.533416000	-2.660608000
O	-5.131877000	-0.922095000	-1.719024000
N	-2.738390000	0.825167000	0.350894000
C	-3.893927000	0.426615000	-0.264754000
C	-4.159148000	-0.807833000	-0.953424000
C	-4.971919000	1.491334000	-0.123111000
C	-4.271366000	2.552491000	0.753722000
H	-4.925390000	2.930334000	1.552863000
H	-3.985838000	3.415518000	0.133810000
C	-2.995266000	1.909786000	1.330082000
C	-1.430210000	0.247385000	0.062594000
H	-1.638801000	-0.624522000	-0.562025000
C	-0.524185000	1.124955000	-0.812486000
H	-1.098769000	1.491801000	-1.676696000
H	-0.156312000	2.006481000	-0.268715000
C	-0.675791000	-0.300935000	1.278490000
H	-0.328835000	0.521981000	1.925201000
H	-1.345456000	-0.927942000	1.882525000
C	-3.287250000	-2.018748000	-0.747459000
C	-3.003880000	-2.503952000	0.507874000
H	-3.421098000	-2.005820000	1.387609000
C	-2.123265000	-3.603475000	0.692063000
C	-1.752807000	-4.064532000	1.984844000
H	-2.195982000	-3.585487000	2.861766000
C	-0.843938000	-5.083660000	2.133697000
H	-0.559932000	-5.422667000	3.132193000
C	-0.272178000	-5.702612000	0.994823000
H	0.446309000	-6.514679000	1.125067000
C	-0.622206000	-5.287546000	-0.267335000
H	-0.184533000	-5.764507000	-1.148003000
C	-1.548612000	-4.226283000	-0.453270000
C	-1.913648000	-3.752464000	-1.745052000
H	-1.496208000	-4.248542000	-2.625135000
C	-2.767181000	-2.689304000	-1.888716000
H	-3.050502000	-2.325719000	-2.878513000
C	-5.337033000	2.087648000	-1.493425000
H	-6.028053000	2.936117000	-1.360357000
H	-5.810653000	1.328521000	-2.127633000



C	-6.234031000	0.926737000	0.546579000
H	-6.666804000	0.126920000	-0.069318000
H	-6.986319000	1.722196000	0.666219000
C	-1.881341000	2.951687000	1.425282000
H	-1.670014000	3.410782000	0.449981000
H	-2.212837000	3.750792000	2.105387000
H	-0.943513000	2.546028000	1.829482000
C	-3.257233000	1.296287000	2.715400000
H	-2.352713000	0.825551000	3.124562000
H	-3.581869000	2.075556000	3.421428000
H	-4.047304000	0.533203000	2.660799000
H	6.013803000	-0.516998000	-1.543704000
H	4.436415000	-2.458183000	2.008150000
H	-4.436461000	2.458626000	-2.007696000
H	-6.013551000	0.516954000	1.544024000

4a, UPBE0/def2SVP, BSS

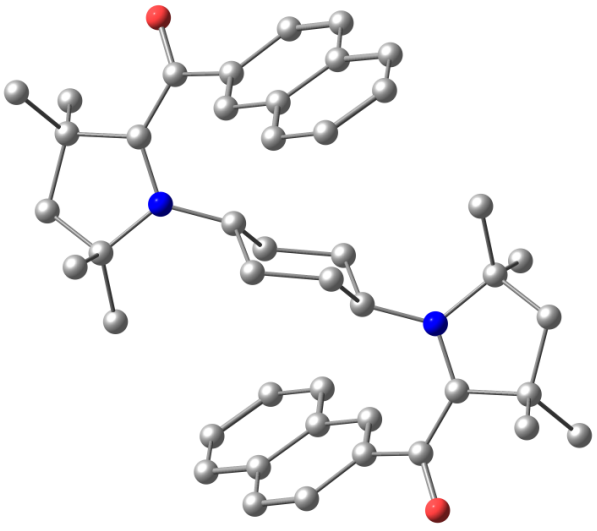
O	4.943142000	-1.352681000	1.896428000
N	2.202943000	-1.825976000	-0.396961000
C	3.377208000	-1.982219000	0.285923000
C	4.107776000	-1.000343000	1.042038000
C	3.894423000	-3.405686000	0.158107000
C	2.878811000	-4.035875000	-0.817401000
H	3.370661000	-4.615896000	-1.612120000
H	2.222994000	-4.730646000	-0.271092000
C	2.022137000	-2.899674000	-1.407542000
C	1.242702000	-0.770812000	-0.084361000
H	1.801409000	-0.064065000	0.543081000
C	0.070749000	-1.242697000	0.787792000
H	0.465131000	-1.809791000	1.645767000
H	-0.592502000	-1.920893000	0.230678000
C	0.746448000	0.049043000	-1.276345000
H	0.127260000	-0.569570000	-1.946606000
H	1.601763000	0.407040000	-1.867886000
C	3.963330000	0.476312000	0.805448000
C	3.935160000	1.029223000	-0.459598000
H	3.957256000	0.377699000	-1.337820000
C	3.885901000	2.433514000	-0.653877000
C	3.848130000	3.017439000	-1.947684000
H	3.872636000	2.361441000	-2.822398000
C	3.781095000	4.382800000	-2.103936000
H	3.750579000	4.818307000	-3.105659000
C	3.754196000	5.229304000	-0.971375000
H	3.703434000	6.312420000	-1.106780000
C	3.797591000	4.693774000	0.295957000
H	3.784567000	5.346434000	1.173213000
C	3.865740000	3.290527000	0.490680000
C	3.929658000	2.701193000	1.782391000
H	3.939177000	3.355619000	2.658586000
C	3.994752000	1.338688000	1.935184000
H	4.079757000	0.884289000	2.924638000
C	3.850641000	-4.127520000	1.513825000
H	4.129763000	-5.186454000	1.383807000
H	4.541753000	-3.652269000	2.221138000
C	5.326584000	-3.437021000	-0.388817000
H	6.007254000	-2.915313000	0.298106000
H	5.669260000	-4.478750000	-0.494374000
C	0.584848000	-3.379195000	-1.590625000
H	0.152809000	-3.744130000	-0.648741000
H	0.592673000	-4.221955000	-2.298467000
H	-0.080414000	-2.611822000	-2.009567000
C	2.585080000	-2.424937000	-2.754226000
H	2.001207000	-1.588229000	-3.163990000
H	2.560268000	-3.244847000	-3.488595000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.867798
(Hartree/Particle)
Thermal correction to Energy= 0.912111
Thermal correction to Enthalpy= 0.913055
Thermal correction to Gibbs Free Energy= 0.789926
Sum of electronic and zero-point Energies= -1963.378819
Sum of electronic and thermal Energies= -1963.334507
Sum of electronic and thermal Enthalpies= -1963.333562
Sum of electronic and thermal Free Energies= -1963.456691

Charge = 0 Multiplicity = 1

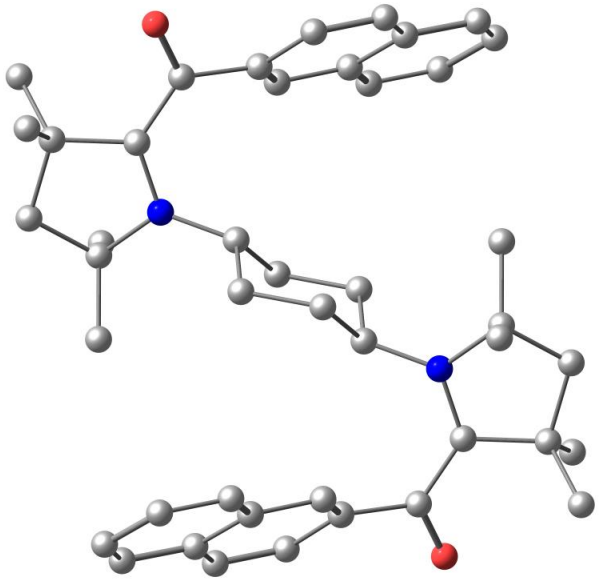


H	3.629381000	-2.095743000	-2.647062000	
O	-4.943219000	1.352704000	-1.896334000	
N	-2.203020000	1.826009000	0.397055000	
C	-3.377301000	1.982241000	-0.285808000	
C	-4.107864000	1.000370000	-1.041930000	
C	-3.894527000	3.405703000	-0.157970000	
C	-2.878892000	4.035900000	0.817509000	
H	-3.370722000	4.615938000	1.612227000	
H	-2.223079000	4.730656000	0.271176000	
C	-2.022220000	2.899699000	1.407646000	
C	-1.242767000	0.770862000	0.084452000	
H	-1.801458000	0.064116000	-0.543006000	
C	-0.070804000	1.242754000	-0.787684000	
H	-0.465168000	1.809865000	-1.645657000	
H	0.592454000	1.920932000	-0.230557000	
C	-0.746510000	-0.048989000	1.276441000	
H	-0.127325000	0.569639000	1.946693000	
H	-1.601821000	-0.406981000	1.867988000	
C	-3.963319000	-0.476294000	-0.805446000	
C	-3.935216000	-1.029300000	0.459558000	
H	-3.957443000	-0.377846000	1.337829000	
C	-3.885857000	-2.433603000	0.653731000	
C	-3.848141000	-3.017624000	1.947495000	
H	-3.872781000	-2.361697000	2.822259000	
C	-3.780995000	-4.382992000	2.103648000	
H	-3.750519000	-4.818573000	3.105339000	
C	-3.753928000	-5.229406000	0.971024000	
H	-3.703076000	-6.312527000	1.106350000	
C	-3.797270000	-4.693782000	-0.296270000	
H	-3.784121000	-5.346371000	-1.173576000	
C	-3.865529000	-3.290525000	-0.490890000	
C	-3.929393000	-2.701096000	-1.782561000	
H	-3.938794000	-3.355454000	-2.658808000	
C	-3.994582000	-1.338585000	-1.935252000	
H	-4.079546000	-0.884120000	-2.924680000	
C	-3.850794000	4.127541000	-1.513688000	
H	-4.129908000	5.186476000	-1.383657000	
H	-4.541935000	3.652295000	-2.220975000	
C	-5.326672000	3.437029000	0.389000000	
H	-6.007360000	2.915321000	-0.297904000	
H	-5.669347000	4.478756000	0.494573000	
C	-0.584931000	3.379213000	1.590739000	
H	-0.152886000	3.744151000	0.648858000	
H	-0.592753000	4.221968000	2.298587000	
H	0.080321000	2.611830000	2.009679000	
C	-2.585167000	2.424952000	2.754327000	
H	-2.001289000	1.588248000	3.164091000	
H	-2.560366000	3.244861000	3.488697000	
H	-3.629463000	2.095748000	2.647155000	
H	5.395931000	-2.956844000	-1.377150000	
H	2.836567000	-4.094381000	1.942879000	
H	-2.836736000	4.094400000	-1.942780000	
H	-5.395986000	2.956848000	1.377333000	
4a, UPBE0/def2SVP, Triplet				
O	4.943036000	-1.352787000	1.896508000	- Thermochemistry -
N	2.202919000	-1.825989000	-0.397003000	----------
C	3.377152000	-1.982268000	0.285930000	Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
C	4.107730000	-1.000412000	1.042069000	
C	3.894353000	-3.405734000	0.158082000	Zero-point correction= 0.867798
C	2.878779000	-4.035883000	-0.817493000	(Hartree/Particle)
H	3.370666000	-4.615840000	-1.612236000	Thermal correction to Energy= 0.912111
H	2.222967000	-4.730709000	-0.271248000	Thermal correction to Enthalpy= 0.913055
C	2.022095000	-2.899664000	-1.407591000	Thermal correction to Gibbs Free Energy= 0.788886

C	1.242718000	-0.770794000	-0.084425000
H	1.801460000	-0.064001000	0.542933000
C	0.070869000	-1.242638000	0.787905000
H	0.465460000	-1.809557000	1.645903000
H	-0.592384000	-1.920995000	0.230984000
C	0.746361000	0.049031000	-1.276413000
H	0.127234000	-0.569628000	-1.946687000
H	1.601660000	0.407096000	-1.867932000
C	3.963363000	0.476242000	0.805449000
C	3.935169000	1.029151000	-0.459601000
H	3.957224000	0.377627000	-1.337823000
C	3.885939000	2.433443000	-0.653883000
C	3.848132000	3.017364000	-1.947691000
H	3.872582000	2.361362000	-2.822404000
C	3.781135000	4.382727000	-2.103947000
H	3.750592000	4.818229000	-3.105671000
C	3.754308000	5.229237000	-0.971389000
H	3.703574000	6.312354000	-1.106798000
C	3.797730000	4.693711000	0.295943000
H	3.784759000	5.346374000	1.173197000
C	3.865843000	3.290462000	0.490670000
C	3.929797000	2.701132000	1.782382000
H	3.939367000	3.355560000	2.658574000
C	3.994856000	1.338627000	1.935177000
H	4.079880000	0.884226000	2.924629000
C	3.850516000	-4.127613000	1.513775000
H	4.129664000	-5.186538000	1.383735000
H	4.541586000	-3.652371000	2.221135000
C	5.326537000	-3.437058000	-0.388788000
H	6.007186000	-2.915391000	0.298186000
H	5.669203000	-4.478786000	-0.494382000
C	0.584797000	-3.379178000	-1.590639000
H	0.152786000	-3.744118000	-0.648743000
H	0.592594000	-4.221932000	-2.298488000
H	-0.080477000	-2.611799000	-2.009549000
C	2.585007000	-2.424895000	-2.754275000
H	2.001189000	-1.588110000	-3.163964000
H	2.560085000	-3.244756000	-3.488693000
H	3.629342000	-2.095796000	-2.647143000
O	-4.943115000	1.352809000	-1.896412000
N	-2.202998000	1.826023000	0.397096000
C	-3.377247000	1.982290000	-0.285815000
C	-4.107819000	1.000439000	-1.041961000
C	-3.894460000	3.405751000	-0.157945000
C	-2.878864000	4.035908000	0.817602000
H	-3.370732000	4.615880000	1.612345000
H	-2.223057000	4.730720000	0.271333000
C	-2.022181000	2.899690000	1.407695000
C	-1.242784000	0.770846000	0.084516000
H	-1.801509000	0.064054000	-0.542859000
C	-0.070924000	1.242697000	-0.787797000
H	-0.465497000	1.809633000	-1.645792000
H	0.592335000	1.921036000	-0.230862000
C	-0.746423000	-0.048975000	1.276509000
H	-0.127300000	0.569699000	1.946774000
H	-1.601719000	-0.407036000	1.868034000
C	-3.963351000	-0.476224000	-0.805447000
C	-3.935223000	-1.029228000	0.459561000
H	-3.957409000	-0.377775000	1.337832000
C	-3.885892000	-2.433532000	0.653736000
C	-3.848138000	-3.017550000	1.947502000
H	-3.872722000	-2.361618000	2.822264000
C	-3.781028000	-4.382919000	2.103658000

Sum of electronic and zero-point Energies= -1963.378814
Sum of electronic and thermal Energies= -1963.334502
Sum of electronic and thermal Enthalpies= -1963.333557
Sum of electronic and thermal Free Energies= -1963.457726

Charge = 0 Multiplicity = 3

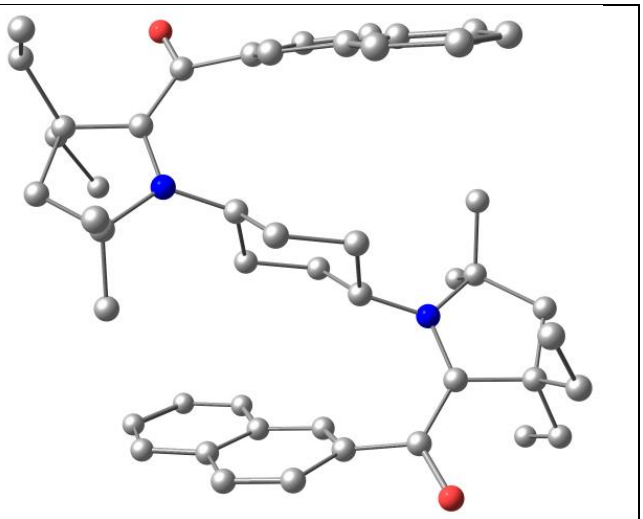


H	-3.750525000	-4.818495000	3.105351000	
C	-3.754033000	-5.229339000	0.971038000	
H	-3.703208000	-6.312461000	1.106367000	
C	-3.797405000	-4.693718000	-0.296257000	
H	-3.784308000	-5.346312000	-1.173561000	
C	-3.865629000	-3.290460000	-0.490880000	
C	-3.929531000	-2.701035000	-1.782552000	
H	-3.938981000	-3.355396000	-2.658797000	
C	-3.994686000	-1.338524000	-1.935246000	
H	-4.079670000	-0.884056000	-2.924671000	
C	-3.850672000	4.127635000	-1.513637000	
H	-4.129813000	5.186560000	-1.383584000	
H	-4.541771000	3.652397000	-2.220972000	
C	-5.326627000	3.437064000	0.388970000	
H	-6.007295000	2.915397000	-0.297985000	
H	-5.669294000	4.478790000	0.494581000	
C	-0.584883000	3.379198000	1.590754000	
H	-0.152867000	3.744142000	0.648862000	
H	-0.592678000	4.221947000	2.298610000	
H	0.080382000	2.611809000	2.009662000	
C	-2.585097000	2.424909000	2.754375000	
H	-2.001273000	1.588129000	3.164064000	
H	-2.560186000	3.244769000	3.488796000	
H	-3.629427000	2.095799000	2.647236000	
H	5.395925000	-2.956835000	-1.377095000	
H	2.836421000	-4.094503000	1.942779000	
H	-2.836593000	4.094523000	-1.942680000	
H	-5.395983000	2.956836000	1.377277000	

4b, UwB97XD/def2SVP, Broken symmetry singlet

O	-4.893051000	-1.292635000	1.930618000	- Thermochemistry -
N	-2.814596000	0.471196000	-0.420078000	---
C	-3.906503000	0.000809000	0.255165000	Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
C	-4.002636000	-1.180304000	1.069308000	
C	-5.084438000	0.943969000	0.098649000	Zero-point correction= 0.988695
C	-4.595571000	1.909404000	-1.006779000	(Hartree/Particle)
H	-5.285168000	1.924325000	-1.862141000	Thermal correction to Energy= 1.037020
H	-4.556208000	2.938905000	-0.623106000	Thermal correction to Enthalpy= 1.037964
C	-3.182737000	1.465832000	-1.456266000	Thermal correction to Gibbs Free Energy= 0.909289
C	-1.447075000	0.077270000	-0.092405000	Sum of electronic and zero-point Energies= -2122.103164
H	-1.555084000	-0.783298000	0.570846000	Sum of electronic and thermal Energies= -2122.054839
C	-0.663942000	1.095053000	0.749431000	Sum of electronic and thermal Enthalpies= -2122.053895
H	-1.289239000	1.435437000	1.587149000	Sum of electronic and thermal Free Energies= -
H	-0.388363000	1.986525000	0.168652000	2122.182570
C	-0.611690000	-0.433181000	-1.270349000	
H	-0.344430000	0.396258000	-1.946501000	Charge = 0 Multiplicity = 1
H	-1.193292000	-1.156946000	-1.857325000	
C	-3.037904000	-2.321906000	0.891546000	
C	-2.709549000	-2.816182000	-0.349875000	
H	-3.174616000	-2.389588000	-1.243002000	
C	-1.711439000	-3.814505000	-0.505668000	
C	-1.288557000	-4.263581000	-1.786608000	
H	-1.786459000	-3.865945000	-2.674810000	
C	-0.260622000	-5.166137000	-1.910557000	
H	0.064078000	-5.494026000	-2.900276000	
C	0.383033000	-5.678027000	-0.756908000	
H	1.197065000	-6.397601000	-0.867395000	
C	-0.016383000	-5.275691000	0.494677000	
H	0.476947000	-5.670395000	1.386549000	
C	-1.065639000	-4.330988000	0.654594000	
C	-1.481408000	-3.864131000	1.933637000	
H	-1.008436000	-4.282415000	2.825970000	
C	-2.446465000	-2.897292000	2.049730000	

H	-2.765866000	-2.532515000	3.027975000
C	-5.345851000	1.712056000	1.421549000
H	-6.083787000	2.502866000	1.198689000
H	-5.818093000	1.014897000	2.127213000
C	-4.116246000	2.319775000	2.083757000
H	-3.437204000	1.531780000	2.442728000
H	-4.405361000	2.927127000	2.953942000
H	-3.544316000	2.970820000	1.402876000
C	-6.390204000	0.213888000	-0.284933000
H	-6.685631000	-0.407725000	0.572016000
H	-7.174826000	0.980722000	-0.406116000
C	-6.332982000	-0.659442000	-1.531536000
H	-7.294217000	-1.170730000	-1.687121000
H	-5.560260000	-1.439019000	-1.437201000
H	-6.121976000	-0.080459000	-2.444075000
C	-2.241959000	2.670508000	-1.515052000
H	-2.170380000	3.178961000	-0.543595000
H	-2.642739000	3.390871000	-2.243942000
H	-1.226784000	2.405228000	-1.842035000
C	-3.235892000	0.785947000	-2.834175000
H	-2.236579000	0.499770000	-3.187622000
H	-3.669718000	1.473612000	-3.576260000
H	-3.861702000	-0.116443000	-2.795934000
O	4.893070000	1.291906000	-1.930824000
N	2.814473000	-0.470965000	0.420478000
C	3.906395000	-0.000945000	-0.254993000
C	4.002696000	1.179965000	-1.069419000
C	5.084214000	-0.944231000	-0.098285000
C	4.595284000	-1.909286000	1.007446000
H	5.284909000	-1.923996000	1.862788000
H	4.555847000	-2.938902000	0.624088000
C	3.182480000	-1.465487000	1.456821000
C	1.446972000	-0.076991000	0.092776000
H	1.554985000	0.783576000	-0.570460000
C	0.663829000	-1.094752000	-0.749068000
H	1.289137000	-1.435166000	-1.586766000
H	0.388199000	-1.986212000	-0.168287000
C	0.611597000	0.433514000	1.270704000
H	0.344331000	-0.395876000	1.946910000
H	1.193217000	1.157313000	1.857627000
C	3.038188000	2.321786000	-0.891858000
C	2.709859000	2.816320000	0.349468000
H	3.174871000	2.389851000	1.242683000
C	1.711787000	3.814711000	0.505066000
C	1.288857000	4.263984000	1.785922000
H	1.786758000	3.866519000	2.674201000
C	0.260868000	5.166500000	1.909698000
H	-0.063888000	5.494518000	2.899356000
C	-0.382776000	5.678180000	0.755947000
H	-1.196851000	6.397727000	0.866296000
C	0.016717000	5.275688000	-0.495562000
H	-0.476600000	5.670233000	-1.387511000
C	1.066014000	4.331001000	-0.655298000
C	1.481814000	3.863930000	-1.934253000
H	1.008899000	4.282104000	-2.826669000
C	2.446828000	2.897025000	-2.050158000
H	2.766254000	2.532067000	-3.028326000
C	5.345494000	-1.712768000	-1.420937000
H	6.083313000	-2.503616000	-1.197837000
H	5.817843000	-1.015939000	-2.126846000
C	4.115774000	-2.320518000	-2.082900000
H	3.436867000	-1.532529000	-2.442139000
H	4.404747000	-2.928257000	-2.952861000



H	3.543751000	-2.971202000	-1.401754000
C	6.390098000	-0.214198000	0.285041000
H	6.685549000	0.407143000	-0.572095000
H	7.174636000	-0.981093000	0.406379000
C	6.333073000	0.659481000	1.531409000
H	7.294410000	1.170628000	1.686830000
H	5.560496000	1.439178000	1.436892000
H	6.121992000	0.080787000	2.444111000
C	2.241581000	-2.670077000	1.515733000
H	2.170041000	-3.178670000	0.544347000
H	2.642252000	-3.390348000	2.244771000
H	1.226407000	-2.404650000	1.842600000
C	3.235641000	-0.785427000	2.834638000
H	2.236338000	-0.499173000	3.188050000
H	3.669440000	-1.473019000	3.576807000
H	3.861481000	0.116938000	2.796287000

4b, UwB97XD/def2SVP, Triplet

O	-4.893008000	-1.292656000	1.930656000
N	-2.814598000	0.471164000	-0.420090000
C	-3.906490000	0.000775000	0.255176000
C	-4.002608000	-1.180336000	1.069326000
C	-5.084441000	0.943909000	0.098634000
C	-4.595592000	1.909330000	-1.006815000
H	-5.285187000	1.924213000	-1.862180000
H	-4.556257000	2.938841000	-0.623167000
C	-3.182746000	1.465780000	-1.456286000
C	-1.447077000	0.077243000	-0.092436000
H	-1.555067000	-0.783360000	0.570773000
C	-0.663994000	1.094991000	0.749503000
H	-1.289354000	1.435218000	1.587239000
H	-0.388468000	1.986554000	0.168836000
C	-0.611646000	-0.433155000	-1.270390000
H	-0.344433000	0.396298000	-1.946543000
H	-1.193220000	-1.156948000	-1.857354000
C	-3.037880000	-2.321936000	0.891546000
C	-2.709506000	-2.816196000	-0.349878000
H	-3.174576000	-2.389607000	-1.243005000
C	-1.711370000	-3.814492000	-0.505674000
C	-1.288461000	-4.263539000	-1.786615000
H	-1.786361000	-3.865900000	-2.674818000
C	-0.260508000	-5.166073000	-1.910566000
H	0.064210000	-5.493941000	-2.900286000
C	0.383144000	-5.677968000	-0.756917000
H	1.197191000	-6.397525000	-0.867405000
C	-0.016291000	-5.275653000	0.494669000
H	0.477038000	-5.670358000	1.386541000
C	-1.065567000	-4.330974000	0.654588000
C	-1.481363000	-3.864145000	1.933633000
H	-1.008390000	-4.282428000	2.825966000
C	-2.446442000	-2.897328000	2.049728000
H	-2.765859000	-2.532567000	3.027974000
C	-5.345885000	1.712022000	1.421514000
H	-6.083841000	2.502804000	1.198621000
H	-5.818116000	1.014868000	2.127190000
C	-4.116312000	2.319801000	2.083725000
H	-3.437262000	1.531839000	2.442754000
H	-4.405467000	2.927189000	2.953872000
H	-3.544377000	2.970826000	1.402829000
C	-6.390189000	0.213787000	-0.284936000
H	-6.685599000	-0.407818000	0.572024000
H	-7.174830000	0.980599000	-0.406133000
C	-6.332944000	-0.659563000	-1.531524000
H	-7.294168000	-1.170875000	-1.687101000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.988694 (Hartree/Particle)

Thermal correction to Energy= 1.037019

Thermal correction to Enthalpy= 1.037963

Thermal correction to Gibbs Free Energy= 0.908248

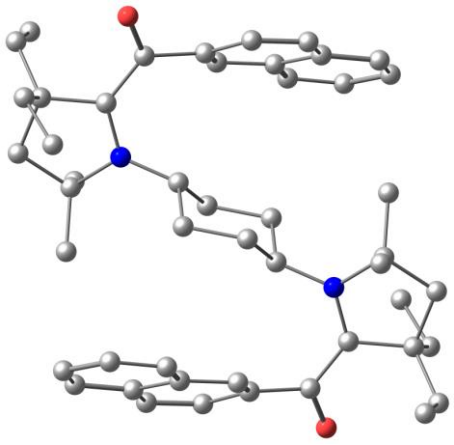
Sum of electronic and zero-point Energies= -2122.103162

Sum of electronic and thermal Energies= -2122.054836

Sum of electronic and thermal Enthalpies= -2122.053892

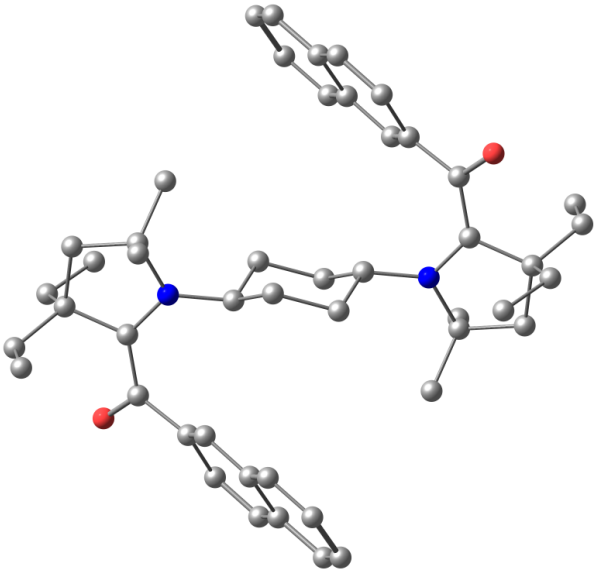
Sum of electronic and thermal Free Energies= -2122.183607

Charge = 0 Multiplicity = 3



H	-5.560206000	-1.439121000	-1.437175000
H	-6.121951000	-0.080591000	-2.444072000
C	-2.241980000	2.670467000	-1.515062000
H	-2.170429000	3.178927000	-0.543606000
H	-2.642748000	3.390822000	-2.243967000
H	-1.226794000	2.405194000	-1.842014000
C	-3.235876000	0.785884000	-2.834189000
H	-2.236561000	0.499682000	-3.187613000
H	-3.669667000	1.473553000	-3.576290000
H	-3.861705000	-0.116493000	-2.795960000
O	4.893026000	1.291919000	-1.930862000
N	2.814474000	-0.470932000	0.420495000
C	3.906381000	-0.000912000	-0.254999000
C	4.002669000	1.179993000	-1.069435000
C	5.084215000	-0.944174000	-0.098266000
C	4.595303000	-1.909213000	1.007489000
H	5.284925000	-1.923884000	1.862834000
H	4.555891000	-2.938840000	0.624157000
C	3.182487000	-1.465434000	1.456846000
C	1.446974000	-0.076961000	0.092813000
H	1.554968000	0.783641000	-0.570382000
C	0.663880000	-1.094687000	-0.749136000
H	1.289252000	-1.434943000	-1.586850000
H	0.388302000	-1.986237000	-0.168467000
C	0.611553000	0.433491000	1.270749000
H	0.344333000	-0.395911000	1.946957000
H	1.193144000	1.157319000	1.857662000
C	3.038166000	2.321813000	-0.891861000
C	2.709818000	2.816336000	0.349467000
H	3.174833000	2.389876000	1.242684000
C	1.711720000	3.814701000	0.505064000
C	1.288766000	4.263951000	1.785919000
H	1.786664000	3.866487000	2.674201000
C	0.260758000	5.166447000	1.909695000
H	-0.064015000	5.494449000	2.899353000
C	-0.382883000	5.678127000	0.755942000
H	-1.196972000	6.397658000	0.866290000
C	0.016628000	5.275651000	-0.495567000
H	-0.476689000	5.670195000	-1.387517000
C	1.065946000	4.330986000	-0.655302000
C	1.481770000	3.863939000	-1.934257000
H	1.008855000	4.282109000	-2.826674000
C	2.446806000	2.897054000	-2.050160000
H	2.766247000	2.532108000	-3.028328000
C	5.345523000	-1.712739000	-1.420896000
H	6.083362000	-2.503559000	-1.197763000
H	5.817861000	-1.015916000	-2.126819000
C	4.115833000	-2.320547000	-2.082860000
H	3.436919000	-1.532591000	-2.442156000
H	4.404844000	-2.928323000	-2.952784000
H	3.543806000	-2.971211000	-1.401699000
C	6.390082000	-0.214103000	0.285047000
H	6.685517000	0.407230000	-0.572102000
H	7.174638000	-0.980977000	0.406398000
C	6.333039000	0.659598000	1.531398000
H	7.294365000	1.170768000	1.686810000
H	5.560445000	1.439278000	1.436869000
H	6.121971000	0.080915000	2.444112000
C	2.241599000	-2.670034000	1.515750000
H	2.170087000	-3.178635000	0.544366000
H	2.642255000	-3.390297000	2.244804000
H	1.226414000	-2.404612000	1.842584000
C	3.235623000	-0.785361000	2.834659000

H	2.236318000	-0.499083000	3.188047000	
H	3.669385000	-1.472958000	3.576844000	
H	3.861482000	0.116990000	2.796318000	
4b, UPBE0/def2SVP, Broken symmetry singlet				
O	-5.034118000	0.202186000	1.981177000	- Thermochemistry -
N	-2.590773000	1.213464000	-0.448199000	----------
C	-3.760071000	1.092432000	0.249090000	Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
C	-4.192683000	0.001825000	1.082447000	
C	-4.627352000	2.326649000	0.087622000	Zero-point correction= 0.982566
C	-3.884509000	3.111878000	-1.014800000	(Hartree/Particle)
H	-4.541674000	3.321032000	-1.870995000	Thermal correction to Energy= 1.032126
H	-3.557385000	4.088565000	-0.629171000	Thermal correction to Enthalpy= 1.033070
C	-2.652662000	2.293159000	-1.467039000	Thermal correction to Gibbs Free Energy= 0.898517
C	-1.396553000	0.437241000	-0.113162000	Sum of electronic and zero-point Energies= -2120.207335
H	-1.768327000	-0.396493000	0.495336000	Sum of electronic and thermal Energies= -2120.157776
C	-0.399470000	1.176957000	0.790565000	Sum of electronic and thermal Enthalpies= -2120.156832
H	-0.939628000	1.617938000	1.641638000	Sum of electronic and thermal Free Energies= -
H	0.087167000	2.005722000	0.255506000	2120.291385
C	-0.677982000	-0.215596000	-1.294313000	
H	-0.213427000	0.548356000	-1.939889000	Charge = 0 Multiplicity = 1
H	-1.398606000	-0.767177000	-1.916128000	
C	-3.729366000	-1.412530000	0.885343000	
C	-3.530739000	-1.975238000	-0.360980000	
H	-3.654944000	-1.364250000	-1.259539000	
C	-3.167276000	-3.337712000	-0.510716000	
C	-2.948977000	-3.926807000	-1.784345000	
H	-3.079304000	-3.311006000	-2.678690000	
C	-2.578902000	-5.247127000	-1.896746000	
H	-2.411898000	-5.686754000	-2.883087000	
C	-2.415306000	-6.042552000	-0.738826000	
H	-2.123627000	-7.090799000	-0.839656000	
C	-2.626846000	-5.502373000	0.509463000	
H	-2.507419000	-6.116978000	1.405942000	
C	-3.007147000	-4.144324000	0.659275000	
C	-3.248251000	-3.554111000	1.929431000	
H	-3.147624000	-4.174428000	2.824520000	
C	-3.613355000	-2.235601000	2.038710000	
H	-3.831922000	-1.785348000	3.009240000	
C	-4.699962000	3.150053000	1.400047000	
H	-5.212132000	4.097801000	1.153355000	
H	-5.348695000	2.601010000	2.096678000	
C	-3.380691000	3.442328000	2.092202000	
H	-2.912752000	2.514828000	2.455890000	
H	-3.540720000	4.091081000	2.966829000	
H	-2.656073000	3.954223000	1.438108000	
C	-6.083003000	1.982862000	-0.297255000	
H	-6.527356000	1.454318000	0.559381000	
H	-6.629716000	2.937693000	-0.392026000	
C	-6.289916000	1.153319000	-1.553275000	
H	-7.360217000	0.943841000	-1.701608000	
H	-5.777520000	0.180311000	-1.485000000	
H	-5.933895000	1.661548000	-2.463414000	
C	-1.414924000	3.188437000	-1.504500000	
H	-1.217554000	3.653428000	-0.528598000	
H	-1.593996000	3.996841000	-2.229498000	
H	-0.508998000	2.658256000	-1.829747000	
C	-2.882635000	1.687848000	-2.858806000	
H	-2.010115000	1.121129000	-3.210874000	
H	-3.074493000	2.490465000	-3.587982000	
H	-3.753246000	1.017163000	-2.854629000	
O	5.032380000	-0.204735000	-1.981696000	
N	2.588774000	-1.212708000	0.448727000	
C	3.758039000	-1.093089000	-0.248859000	

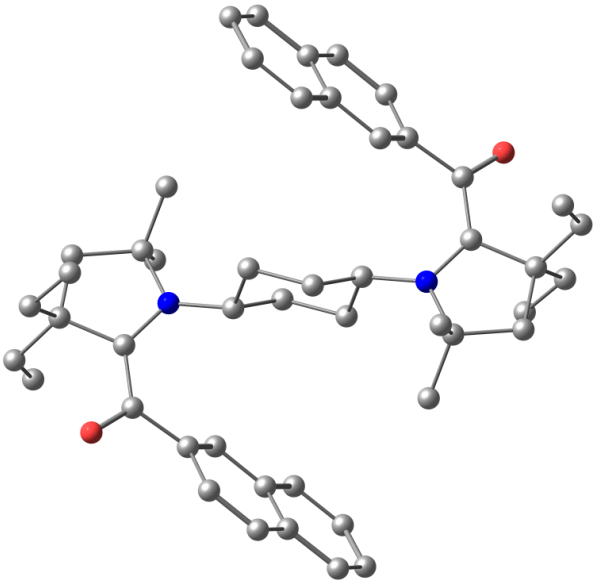


C	4.191488000	-0.003207000	-1.082726000	
C	4.624272000	-2.327992000	-0.087004000	
C	3.880908000	-3.112099000	1.015857000	
H	4.537989000	-3.321371000	1.872088000	
H	3.552981000	-4.088708000	0.630717000	
C	2.649730000	-2.292215000	1.467838000	
C	1.395115000	-0.435750000	0.113322000	
H	1.767510000	0.397824000	-0.495037000	
C	0.398075000	-1.175140000	-0.790712000	
H	0.938354000	-1.615899000	-1.641821000	
H	-0.088586000	-2.004060000	-0.255926000	
C	0.676559000	0.217428000	1.294302000	
H	0.211916000	-0.546312000	1.940050000	
H	1.397264000	0.769049000	1.915988000	
C	3.729878000	1.411739000	-0.885824000	
C	3.532447000	1.974999000	0.360439000	
H	3.656052000	1.364034000	1.259096000	
C	3.171211000	3.338086000	0.510005000	
C	2.954472000	3.927852000	1.783591000	
H	3.084131000	3.312036000	2.678023000	
C	2.586769000	5.248846000	1.895845000	
H	2.420991000	5.689000000	2.882158000	
C	2.424041000	6.044281000	0.737811000	
H	2.134238000	7.093060000	0.838522000	
C	2.634072000	5.503437000	-0.510444000	
H	2.515304000	6.118035000	-1.407016000	
C	3.011975000	4.144703000	-0.660103000	
C	3.251615000	3.553810000	-1.930219000	
H	3.151610000	4.174078000	-2.825410000	
C	3.614668000	2.234721000	-2.039335000	
H	3.832229000	1.783940000	-3.009845000	
C	4.696061000	-3.152060000	-1.399055000	
H	5.207383000	-4.100158000	-1.151947000	
H	5.345258000	-2.603932000	-2.095974000	
C	3.376498000	-3.443451000	-2.091018000	
H	2.909462000	-2.515696000	-2.455209000	
H	3.535886000	-4.092838000	-2.965293000	
H	2.651391000	-3.954279000	-1.436632000	
C	6.080271000	-1.985265000	0.297526000	
H	6.524934000	-1.457430000	-0.559389000	
H	6.626206000	-2.940513000	0.392576000	
C	6.288087000	-1.155410000	1.553188000	
H	7.358589000	-0.946782000	1.701270000	
H	5.776507000	-0.181995000	1.484615000	
H	5.931780000	-1.662988000	2.463578000	
C	1.411288000	-3.186535000	1.505528000	
H	1.213583000	-3.651739000	0.529792000	
H	1.589744000	-3.994828000	2.230804000	
H	0.505721000	-2.655614000	1.830562000	
C	2.880168000	-1.686704000	2.859441000	
H	2.008126000	-1.119125000	3.211311000	
H	3.071310000	-2.489269000	3.588862000	
H	3.751350000	-1.016762000	2.855098000	
4b, UPBE0/def2SVP, Triplet				
O	-5.034068000	0.202195000	1.981192000	- Thermochemistry -
N	-2.590772000	1.213452000	-0.448249000	-------------------
C	-3.760045000	1.092424000	0.249080000	Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
C	-4.192655000	0.001814000	1.082441000	
C	-4.627351000	2.326620000	0.087588000	Zero-point correction= 0.982567
C	-3.884530000	3.111849000	-1.014850000	(Hartree/Particle)
H	-4.541697000	3.320941000	-1.871058000	Thermal correction to Energy= 1.032127
H	-3.557461000	4.088565000	-0.629251000	Thermal correction to Enthalpy= 1.033071
C	-2.652639000	2.293174000	-1.467050000	Thermal correction to Gibbs Free Energy= 0.897477

C	-1.396568000	0.437199000	-0.113252000
H	-1.768356000	-0.396647000	0.495082000
C	-0.399641000	1.176811000	0.790740000
H	-0.940004000	1.617498000	1.641837000
H	0.086955000	2.005778000	0.255954000
C	-0.677843000	-0.215469000	-1.294426000
H	-0.213338000	0.548574000	-1.939929000
H	-1.398391000	-0.767076000	-1.916303000
C	-3.729376000	-1.412547000	0.885315000
C	-3.530672000	-1.975239000	-0.361006000
H	-3.654815000	-1.364240000	-1.259566000
C	-3.167197000	-3.337710000	-0.510740000
C	-2.948798000	-3.926780000	-1.784364000
H	-3.079054000	-3.310961000	-2.678707000
C	-2.578719000	-5.247099000	-1.896763000
H	-2.411642000	-5.686707000	-2.883100000
C	-2.415215000	-6.042548000	-0.738847000
H	-2.123533000	-7.090795000	-0.839675000
C	-2.626843000	-5.502391000	0.509438000
H	-2.507484000	-6.117014000	1.405913000
C	-3.007150000	-4.144344000	0.659247000
C	-3.248344000	-3.554153000	1.929397000
H	-3.147779000	-4.174484000	2.824482000
C	-3.613448000	-2.235643000	2.038674000
H	-3.832072000	-1.785400000	3.009195000
C	-4.700006000	3.150052000	1.399993000
H	-5.212231000	4.097762000	1.153267000
H	-5.348712000	2.600990000	2.096634000
C	-3.380762000	3.442435000	2.092152000
H	-2.912768000	2.514979000	2.455880000
H	-3.540846000	4.091210000	2.966752000
H	-2.656168000	3.954354000	1.438049000
C	-6.082988000	1.982775000	-0.297297000
H	-6.527333000	1.454238000	0.559347000
H	-6.629730000	2.937587000	-0.392098000
C	-6.289857000	1.153196000	-1.553301000
H	-7.360149000	0.943683000	-1.701645000
H	-5.777433000	0.180205000	-1.484996000
H	-5.933837000	1.661415000	-2.463446000
C	-1.414912000	3.188476000	-1.504397000
H	-1.217624000	3.653437000	-0.528465000
H	-1.593939000	3.996901000	-2.229383000
H	-0.508951000	2.658320000	-1.829587000
C	-2.882525000	1.687905000	-2.858849000
H	-2.010005000	1.121161000	-3.210875000
H	-3.074296000	2.490549000	-3.588017000
H	-3.753163000	1.017253000	-2.854755000
O	5.032319000	-0.204768000	-1.981713000
N	2.588757000	-1.212689000	0.448784000
C	3.757999000	-1.093087000	-0.248846000
C	4.191453000	-0.003210000	-1.082721000
C	4.624246000	-2.327975000	-0.086961000
C	3.880898000	-3.112071000	1.015920000
H	4.537979000	-3.321282000	1.872165000
H	3.553018000	-4.088709000	0.630814000
C	2.649683000	-2.292220000	1.467859000
C	1.395121000	-0.435694000	0.113414000
H	1.767536000	0.397991000	-0.494780000
C	0.398237000	-1.174975000	-0.790888000
H	0.938723000	-1.615439000	-1.642022000
H	-0.088384000	-2.004101000	-0.256378000
C	0.676411000	0.217318000	1.294415000
H	0.211815000	-0.546510000	1.940091000

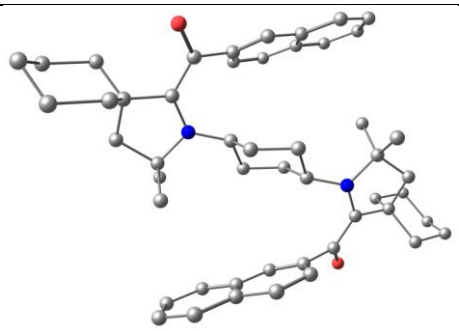
Sum of electronic and zero-point Energies= -2120.207331
Sum of electronic and thermal Energies= -2120.157771
Sum of electronic and thermal Enthalpies= -2120.156827
Sum of electronic and thermal Free Energies= -2120.292420

Charge = 0 Multiplicity = 3



H	1.397040000	0.768965000	1.916162000	
C	3.729895000	1.411748000	-0.885800000	
C	3.532395000	1.974999000	0.360460000	
H	3.655933000	1.364027000	1.259121000	
C	3.171163000	3.338088000	0.510019000	
C	2.954335000	3.927837000	1.783598000	
H	3.083917000	3.312005000	2.678030000	
C	2.586645000	5.248835000	1.895846000	
H	2.420800000	5.688976000	2.882154000	
C	2.424016000	6.044291000	0.737813000	
H	2.134222000	7.093074000	0.838519000	
C	2.634124000	5.503462000	-0.510435000	
H	2.515430000	6.118074000	-1.407006000	
C	3.012017000	4.144724000	-0.660087000	
C	3.251738000	3.553845000	-1.930196000	
H	3.151800000	4.174126000	-2.825385000	
C	3.614775000	2.234753000	-2.039305000	
H	3.832387000	1.783976000	-3.009805000	
C	4.696073000	-3.152078000	-1.398988000	
H	5.207443000	-4.100141000	-1.151843000	
H	5.345247000	-2.603939000	-2.095920000	
C	3.376535000	-3.443570000	-2.090954000	
H	2.909451000	-2.515857000	-2.455190000	
H	3.535972000	-4.092985000	-2.965198000	
H	2.651448000	-3.954411000	-1.436556000	
C	6.080234000	-1.985201000	0.297574000	
H	6.524893000	-1.457379000	-0.559351000	
H	6.626191000	-2.940433000	0.392659000	
C	6.288012000	-1.155305000	1.553216000	
H	7.358507000	-0.946649000	1.701308000	
H	5.776413000	-0.181903000	1.484609000	
H	5.931704000	-1.662865000	2.463615000	
C	1.411245000	-3.186554000	1.505438000	
H	1.213618000	-3.651731000	0.529673000	
H	1.589649000	-3.994867000	2.230705000	
H	0.505647000	-2.655651000	1.830411000	
C	2.880039000	-1.686748000	2.859492000	
H	2.008000000	-1.119136000	3.211318000	
H	3.071086000	-2.489340000	3.588907000	
H	3.751254000	-1.016847000	2.855230000	
4c, UwB97XD/def2SVP, Broken symmetry singlet				
O	-4.282864000	-2.857116000	-0.982474000	- Thermochemistry -
N	-2.794701000	-0.053582000	0.714285000	----------
C	-3.718264000	-0.952934000	0.242768000	Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
C	-3.481232000	-2.298332000	-0.212523000	
C	-2.270993000	-3.081182000	0.224096000	Zero-point correction= 1.007867
C	-1.506592000	-3.715444000	-0.727571000	(Hartree/Particle)
H	-1.803853000	-3.651820000	-1.777266000	Thermal correction to Energy= 1.054393
C	-0.323466000	-4.417099000	-0.374211000	Thermal correction to Enthalpy= 1.055337
C	0.514399000	-5.023359000	-1.351119000	Thermal correction to Gibbs Free Energy= 0.929885
H	0.227495000	-4.956751000	-2.403532000	Sum of electronic and zero-point Energies= -2198.235841
C	1.660273000	-5.684209000	-0.981315000	Sum of electronic and thermal Energies= -2198.189316
H	2.294469000	-6.146813000	-1.740641000	Sum of electronic and thermal Enthalpies= -2198.188372
C	2.024295000	-5.773382000	0.384887000	Sum of electronic and thermal Free Energies= -
H	2.936307000	-6.303542000	0.667460000	2198.313824
C	1.237496000	-5.194586000	1.350783000	
H	1.517746000	-5.260384000	2.405056000	Charge = 0 Multiplicity = 1
C	0.047606000	-4.500630000	0.999795000	
C	-0.788304000	-3.883490000	1.972459000	
H	-0.518438000	-3.965412000	3.028309000	
C	-1.911306000	-3.192133000	1.596048000	
H	-2.533954000	-2.698690000	2.346524000	
C	-5.086732000	-0.312179000	0.123104000	

C	-4.911075000	0.925181000	1.019958000
C	-3.407604000	1.251755000	1.079234000
C	-6.226834000	-1.212114000	0.640318000
C	-7.595611000	-0.551996000	0.474927000
C	-7.862499000	-0.199922000	-0.988552000
C	-6.750727000	0.680947000	-1.558119000
C	-5.374184000	0.046474000	-1.358652000
C	-3.045632000	1.693524000	2.504151000
C	-3.035705000	2.367572000	0.093886000
C	-1.370334000	-0.224646000	0.419466000
C	-0.391688000	0.485353000	1.352171000
C	-1.022833000	0.015048000	-1.056898000
H	-5.487037000	1.796527000	0.680281000
H	-5.267699000	0.682438000	2.033236000
H	-6.041094000	-1.462412000	1.698108000
H	-6.206693000	-2.155699000	0.076696000
H	-7.655026000	0.363525000	1.090870000
H	-8.379453000	-1.227129000	0.852912000
H	-8.839458000	0.298047000	-1.094988000
H	-7.917032000	-1.133309000	-1.575661000
H	-6.787264000	1.673169000	-1.074071000
H	-6.917910000	0.861427000	-2.631920000
H	-5.312029000	-0.891036000	-1.931122000
H	-4.586453000	0.709864000	-1.747914000
H	-3.747992000	2.479873000	2.820633000
H	-3.135697000	0.850875000	3.205402000
H	-2.034995000	2.113125000	2.578329000
H	-1.965695000	2.614200000	0.129311000
H	-3.296878000	2.105492000	-0.939856000
H	-3.581121000	3.283943000	0.361152000
H	-1.160699000	-1.281412000	0.592644000
H	-0.649324000	0.270531000	2.399140000
H	-0.419936000	1.578711000	1.218193000
H	-1.094683000	1.085916000	-1.305602000
H	-1.750121000	-0.517345000	-1.689375000
O	4.283072000	2.856767000	0.982153000
N	2.794595000	0.053476000	-0.714790000
C	3.718179000	0.952781000	-0.243224000
C	3.481274000	2.298132000	0.212263000
C	2.270957000	3.081139000	-0.223878000
C	1.506699000	3.714996000	0.728182000
H	1.804071000	3.650860000	1.777815000
C	0.323592000	4.416935000	0.375301000
C	-0.514106000	5.022796000	1.352594000
H	-0.227093000	4.955649000	2.404943000
C	-1.659947000	5.683956000	0.983228000
H	-2.294015000	6.146258000	1.742845000
C	-2.024089000	5.773853000	-0.382892000
H	-2.936071000	6.304250000	-0.665117000
C	-1.237455000	5.195441000	-1.349155000
H	-1.517808000	5.261795000	-2.403366000
C	-0.047613000	4.501177000	-0.998623000
C	0.788134000	3.884421000	-1.971672000
H	0.518156000	3.966887000	-3.027451000
C	1.911112000	3.192780000	-1.595729000
H	2.533646000	2.699669000	-2.346517000
C	5.086673000	0.312042000	-0.123743000
C	4.910937000	-0.925279000	-1.020623000
C	3.407471000	-1.251901000	-1.079675000
C	6.226656000	1.212058000	-0.641093000
C	7.595500000	0.552034000	-0.475888000
C	7.862597000	0.199950000	0.987551000
C	6.750964000	-0.681020000	1.557231000



C	5.374348000	-0.046644000	1.357962000
C	3.045415000	-1.693874000	-2.504507000
C	3.035796000	-2.367637000	-0.094144000
C	1.370196000	0.224619000	-0.420086000
C	0.391502000	-0.485359000	-1.352769000
C	1.022649000	-0.015022000	1.056293000
H	5.486985000	-1.796625000	-0.681086000
H	5.267384000	-0.682474000	-2.033950000
H	6.040760000	1.462354000	-1.698855000
H	6.206523000	2.155634000	-0.077455000
H	7.654904000	-0.363472000	-1.091856000
H	8.379245000	1.227231000	-0.853958000
H	8.839609000	-0.297941000	1.093857000
H	7.917123000	1.133330000	1.574673000
H	6.787525000	-1.673229000	1.073161000
H	6.918292000	-0.861512000	2.631008000
H	5.312206000	0.890833000	1.930481000
H	4.586712000	-0.710103000	1.747298000
H	3.747953000	-2.480051000	-2.821016000
H	3.135173000	-0.851257000	-3.205835000
H	2.034885000	-2.113760000	-2.578549000
H	1.965823000	-2.614455000	-0.129419000
H	3.297022000	-2.105372000	0.939538000
H	3.581347000	-3.283953000	-0.361328000
H	1.160620000	1.281393000	-0.593330000
H	0.649122000	-0.270595000	-2.399754000
H	0.419710000	-1.578707000	-1.218734000
H	1.094484000	-1.085894000	1.304996000
H	1.749944000	0.517342000	1.688783000

4c, UwB97XD/def2SVP, Triplet

O	-4.282858000	-2.857109000	-0.982473000
N	-2.794699000	-0.053542000	0.714245000
C	-3.718253000	-0.952909000	0.242740000
C	-3.481215000	-2.298308000	-0.212545000
C	-2.270976000	-3.081159000	0.224078000
C	-1.506563000	-3.715412000	-0.727585000
H	-1.803801000	-3.651767000	-1.777285000
C	-0.323455000	-4.417093000	-0.374213000
C	0.514420000	-5.023351000	-1.351113000
H	0.227541000	-4.956714000	-2.403532000
C	1.660270000	-5.684235000	-0.981297000
H	2.294473000	-6.146838000	-1.740618000
C	2.024257000	-5.773446000	0.384912000
H	2.936250000	-6.303635000	0.667495000
C	1.237451000	-5.194650000	1.350801000
H	1.517675000	-5.260476000	2.405079000
C	0.047585000	-4.500658000	0.999800000
C	-0.788333000	-3.883519000	1.972456000
H	-0.518489000	-3.965463000	3.028311000
C	-1.911316000	-3.192137000	1.596035000
H	-2.533973000	-2.698699000	2.346507000
C	-5.086732000	-0.312172000	0.123097000
C	-4.911073000	0.925210000	1.019921000
C	-3.407605000	1.251798000	1.079170000
C	-6.226811000	-1.212113000	0.640354000
C	-7.595601000	-0.552017000	0.474979000
C	-7.862525000	-0.199975000	-0.988501000
C	-6.750778000	0.680900000	-1.558107000
C	-5.374222000	0.046449000	-1.358660000
C	-3.045620000	1.693608000	2.504071000
C	-3.035719000	2.367587000	0.093784000
C	-1.370332000	-0.224617000	0.419465000
C	-0.391689000	0.485435000	1.352145000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 1.007867 (Hartree/Particle)

Thermal correction to Energy= 1.054392

Thermal correction to Enthalpy= 1.055336

Thermal correction to Gibbs Free Energy= 0.928845

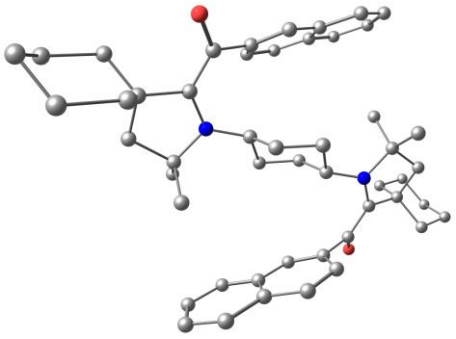
Sum of electronic and zero-point Energies= -2198.235841

Sum of electronic and thermal Energies= -2198.189315

Sum of electronic and thermal Enthalpies= -2198.188371

Sum of electronic and thermal Free Energies= -2198.314862

Charge = 0 Multiplicity = 3



C	-1.022828000	0.014986000	-1.056911000
H	-5.487047000	1.796543000	0.680232000
H	-5.267681000	0.682488000	2.033210000
H	-6.041045000	-1.462386000	1.698145000
H	-6.206669000	-2.155708000	0.076750000
H	-7.655015000	0.363515000	1.090906000
H	-8.379425000	-1.227153000	0.852994000
H	-8.839493000	0.297979000	-1.094925000
H	-7.917057000	-1.133374000	-1.575591000
H	-6.787318000	1.673130000	-1.074077000
H	-6.917986000	0.861358000	-2.631908000
H	-5.312065000	-0.891070000	-1.931113000
H	-4.586508000	0.709843000	-1.747950000
H	-3.747985000	2.479958000	2.820538000
H	-3.135668000	0.850978000	3.205346000
H	-2.034988000	2.113225000	2.578228000
H	-1.965707000	2.614211000	0.129188000
H	-3.296906000	2.105476000	-0.939946000
H	-3.581129000	3.283967000	0.361031000
H	-1.160692000	-1.281375000	0.592700000
H	-0.649324000	0.270661000	2.399122000
H	-0.419944000	1.578786000	1.218115000
H	-1.094695000	1.085834000	-1.305696000
H	-1.750124000	-0.517464000	-1.689336000
O	4.283069000	2.856751000	0.982158000
N	2.794591000	0.053439000	-0.714762000
C	3.718167000	0.952755000	-0.243201000
C	3.481258000	2.298104000	0.212289000
C	2.270942000	3.081116000	-0.223850000
C	1.506670000	3.714956000	0.728210000
H	1.804016000	3.650787000	1.777848000
C	0.323582000	4.416925000	0.375321000
C	-0.514128000	5.022775000	1.352611000
H	-0.227144000	4.955587000	2.404966000
C	-1.659943000	5.683973000	0.983236000
H	-2.294020000	6.146266000	1.742851000
C	-2.024046000	5.773924000	-0.382891000
H	-2.936007000	6.304353000	-0.665122000
C	-1.237402000	5.195521000	-1.349151000
H	-1.517727000	5.261914000	-2.403367000
C	-0.047587000	4.501216000	-0.998609000
C	0.788170000	3.884469000	-1.971655000
H	0.518218000	3.966969000	-3.027439000
C	1.911128000	3.192799000	-1.595705000
H	2.533672000	2.699700000	-2.346492000
C	5.086672000	0.312031000	-0.123743000
C	4.910932000	-0.925307000	-1.020599000
C	3.407468000	-1.251940000	-1.079626000
C	6.226633000	1.212053000	-0.641131000
C	7.595489000	0.552049000	-0.475946000
C	7.862621000	0.199990000	0.987492000
C	6.751011000	-0.680987000	1.557208000
C	5.374383000	-0.046631000	1.357961000
C	3.045401000	-1.693949000	-2.504446000
C	3.035803000	-2.367651000	-0.094064000
C	1.370192000	0.224596000	-0.420099000
C	0.391500000	-0.485434000	-1.352756000
C	1.022642000	-0.014952000	1.056292000
H	5.486989000	-1.796644000	-0.681053000
H	5.267364000	-0.682520000	-2.033934000
H	6.040711000	1.462330000	-1.698894000
H	6.206500000	2.155637000	-0.077507000
H	7.654891000	-0.363465000	-1.091902000

H	8.379216000	1.227250000	-0.854043000	
H	8.839642000	-0.297887000	1.093785000	
H	7.917147000	1.133378000	1.574600000	
H	6.787575000	-1.673202000	1.073150000	
H	6.918365000	-0.861463000	2.630983000	
H	5.312241000	0.890853000	1.930469000	
H	4.586765000	-0.710096000	1.747322000	
H	3.747946000	-2.480124000	-2.820942000	
H	3.135143000	-0.851347000	-3.205794000	
H	2.034877000	-2.113850000	-2.578471000	
H	1.965827000	-2.614464000	-0.129319000	
H	3.297041000	-2.105358000	0.939609000	
H	3.581346000	-3.283976000	-0.361230000	
H	1.160613000	1.281363000	-0.593401000	
H	0.649119000	-0.270719000	-2.399750000	
H	0.419715000	-1.578776000	-1.218670000	
H	1.094495000	-1.085805000	1.305078000	
H	1.749944000	0.517469000	1.688730000	

4c, UPBE0/def2SVP, Broken symmetry singlet

O	-4.854571000	-1.396952000	-1.362829000	
N	-2.737233000	0.556276000	0.750121000	
C	-3.867906000	0.058470000	0.159742000	
C	-4.036875000	-1.242963000	-0.435584000	
C	-3.300587000	-2.450844000	0.066172000	
C	-3.098078000	-3.500506000	-0.809181000	
H	-3.451598000	-3.392245000	-1.837695000	
C	-2.463460000	-4.698028000	-0.397944000	
C	-2.228234000	-5.774381000	-1.294326000	
H	-2.552662000	-5.671835000	-2.333290000	
C	-1.607962000	-6.925213000	-0.866313000	
H	-1.434444000	-7.746386000	-1.566113000	
C	-1.195604000	-7.054866000	0.480567000	
H	-0.705983000	-7.974629000	0.809961000	
C	-1.412203000	-6.031225000	1.374795000	
H	-1.097846000	-6.131310000	2.417328000	
C	-2.046973000	-4.831434000	0.964178000	
C	-2.295733000	-3.755170000	1.857484000	
H	-2.005556000	-3.863897000	2.906259000	
C	-2.900770000	-2.600900000	1.423573000	
H	-3.091874000	-1.786947000	2.127204000	
C	-4.956954000	1.106998000	0.112216000	
C	-4.502283000	2.038549000	1.249012000	
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H	-5.025269000	1.749234000	2.174007000	
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H	-5.842604000	3.702924000	-0.751226000	
H	-6.021756000	3.260259000	-2.446002000	

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 1.001755 (Hartree/Particle)

Thermal correction to Energy= 1.049358

Thermal correction to Enthalpy= 1.050302

Thermal correction to Gibbs Free Energy= 0.918901

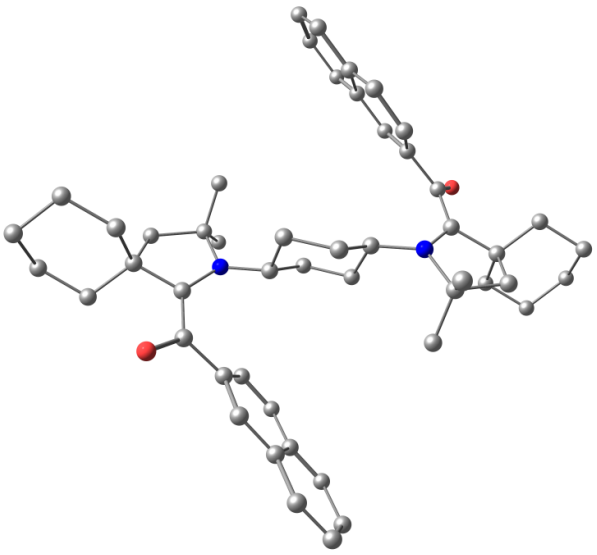
Sum of electronic and zero-point Energies= -2196.288779

Sum of electronic and thermal Energies= -2196.241177

Sum of electronic and thermal Enthalpies= -2196.240233

Sum of electronic and thermal Free Energies= -2196.371634

Charge = 0 Multiplicity = 1



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H	-3.078536000	2.632688000	3.456573000
H	-3.149895000	0.855795000	3.375626000
H	-1.597080000	1.707998000	3.153684000
H	-1.115368000	2.907758000	0.951063000
H	-2.431476000	3.162968000	-0.224185000
H	-2.484215000	3.944963000	1.369523000
H	-1.563506000	-1.020201000	0.173914000
H	-0.709231000	-0.337787000	2.370393000
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H	2.552644000	5.671781000	2.333379000
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H	1.434439000	7.746353000	1.566237000
C	1.195598000	7.054870000	-0.480456000
H	0.705983000	7.974642000	-0.809834000
C	1.412191000	6.031244000	-1.374702000
H	1.097836000	6.131349000	-2.417233000
C	2.046954000	4.831441000	-0.964105000
C	2.295715000	3.755195000	-1.857430000
H	2.005544000	3.863943000	-2.906205000
C	2.900751000	2.600916000	-1.423540000
H	3.091863000	1.786982000	-2.127191000
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C	2.202793000	-3.021862000	-0.841191000
C	1.416913000	-0.051588000	-0.361981000
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H	4.743962000	-3.094680000	-1.065163000
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H	0.709237000	0.337772000	-2.370397000	
H	0.069248000	-1.159522000	-1.670195000	
H	0.675127000	-1.699162000	0.866757000	
H	1.707749000	-0.541590000	1.722996000	
4c, UPBE0/def2SVP, Triplet				
O	-4.854472000	-1.397515000	-1.362646000	- Thermochemistry -
N	-2.737271000	0.556135000	0.750073000	----------
C	-3.867889000	0.058127000	0.159761000	Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
C	-4.036719000	-1.243371000	-0.435471000	
C	-3.300257000	-2.451139000	0.066294000	Zero-point correction= 1.001756
C	-3.097633000	-3.500781000	-0.809060000	(Hartree/Particle)
H	-3.451225000	-3.392576000	-1.837555000	Thermal correction to Energy= 1.049358
C	-2.462791000	-4.698195000	-0.397858000	Thermal correction to Enthalpy= 1.050302
C	-2.227440000	-5.774509000	-1.294253000	Thermal correction to Gibbs Free Energy= 0.917866
H	-2.551953000	-5.672021000	-2.333197000	Sum of electronic and zero-point Energies= -2196.288777
C	-1.606939000	-6.925234000	-0.866279000	Sum of electronic and thermal Energies= -2196.241174
H	-1.433322000	-7.746375000	-1.566092000	Sum of electronic and thermal Enthalpies= -2196.240230
C	-1.194477000	-7.054815000	0.480576000	Sum of electronic and thermal Free Energies= -
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C	-1.411194000	-6.031209000	1.374816000	
H	-1.096757000	-6.131242000	2.417329000	Charge = 0 Multiplicity = 3
C	-2.046194000	-4.831527000	0.964237000	
C	-2.295076000	-3.755296000	1.857550000	
H	-2.004811000	-3.863966000	2.906307000	
C	-2.900332000	-2.601128000	1.423673000	
H	-3.091536000	-1.787214000	2.127324000	
C	-4.957091000	1.106502000	0.112220000	
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C	-0.337291000	0.115740000	1.438862000	
C	-0.910510000	0.628319000	-0.967967000	
H	-4.744268000	3.094336000	1.064865000	
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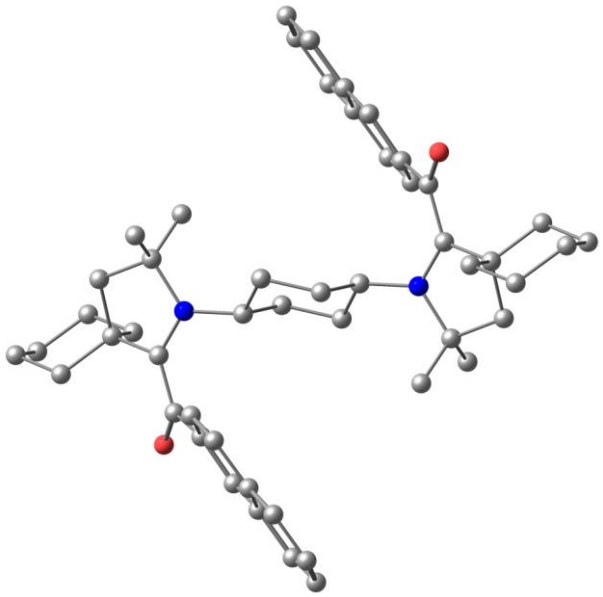

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N	2.737256000	-0.556114000	-0.750122000
C	3.867877000	-0.058136000	-0.159792000
C	4.036712000	1.243341000	0.435486000
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C	3.097634000	3.500740000	0.809145000
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