Electronic Supplementary Information

for

Tethered CAAC-CAAC dimers: oxidation to persistent radical cations and bridging-unit dependent reactivity/stability of the dications

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Note added after first publication:
This Supplementary Information file replaces that originally published on 18 Dec 2020. The ESI has been updated to reflect the changes outlined in the correction notice.

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General considerations

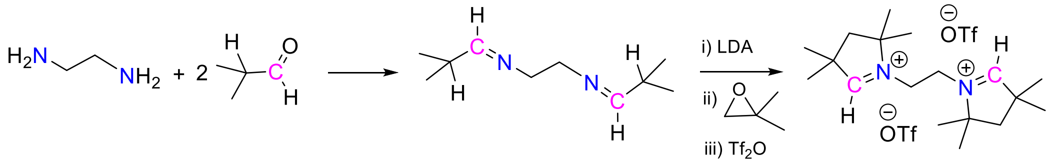
All experiments were carried out under an argon atmosphere using standard Schlenk techniques or in a PL-HE-2GB Innovative Technology GloveBox. Hexane, diethyl ether, THF, and toluene were dried by PS-MD-5 Innovative Technology solvent purification system. Acetonitrile was dried and distilled over CaH_2 under argon. Liquid compounds were distilled before use. All other chemicals were purchased commercially (ethylenediamine, - Alfa Aesar, (±)-*trans*-1,2-cyclohexanediamine - Sigma Aldrich, 1,3-diaminopropane - Sigma Aldrich, isobutyraldehyde - Avra Chemicals, potassium bis(trimethylsilyl)amide - Sigma Aldrich, potassium - Sigma Aldrich, graphite -Sigma Aldrich, isobutylene oxide - TCI Chemicals, triflic anhydride - TCI Chemicals, *n*BuLi - Hychem Laboratories, diisopropylamine - Avra Chemicals, AgOTf - Sigma Aldrich, *p*-TsOH - Sigma Aldrich, and used as received except ethylenediamine and diisopropylamine were distilled over KOH before use. KC_8 was synthesized according to the literature procedure.[S1] Benzene-d_6 was dried and distilled over potassium under argon. Chloroform-d_1 and acetonitrile-d_3 were dried and distilled over CaH_2 under argon. NMR spectra were recorded on a BrukerNanoBay 300 MHz NMR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (^1H) or the deuterated solvent itself ($^{13}C\{^1H\}$). $^{19}F\{^1H\}$ NMR spectra were referenced to external tol-CF_3. UV/Vis spectra were acquired using Jasco V-670 spectrometer using quartz cells with a path length of 0.1 cm. Melting points were determined in closed NMR tubes under argon atmosphere and are uncorrected.

Elemental analyses were performed on a Perkin Elmer Analyser 240. Melting points were determined in closed NMR tubes under argon atmosphere and are uncorrected. Cyclic voltammetry measurements were carried out in 0.1 M Bu_4NPF_6 solution using a three-electrode configuration (Pt or glassy carbon working electrode, Pt counter electrode, Ag wire as pseudo reference) and PAR VersaSTAT 4 or a PalmSens potentiostat at room temperature. The ferrocene/ferrocenium (FcH/FcH^+) couple served as internal reference. Mass spectrometry was performed on an Agilent 6210 ESI-TOF except **5**$^{\mathbf{Cy}}$. For **5**$^{\mathbf{Cy}}$ microTOFQ a Bruker Daltonics instrument was used. EPR spectra at X-band frequency (ca. 9.5 GHz) were obtained with a Magnettech MS-5000 benchtop EPR spectrometer equipped with a rectangular TE 102 cavity. The measurements were carried out in synthetic quartz glass tubes. For EPR spectroelectrochemistry a three-electrode setup was employed using two teflon-coated platinum wires (0.005″ bare, 0.008″ coated) as working and counter electrode and a Teflon-coated silver wire (0.005″ bare, 0.007″ coated) as pseudoreference electrode. Spectral simulations were performed with EasySpin 5.1.4[S2] and MatLab R2012a. UV/Vis spectroelectrochemistry was performed with an Avantes spectrometer consisting of a light source (AvaLight-DH-S-Bal), a UV/Vis detector (AvaSpec-ULS2048), and an NIR detector (AvaSpec-NIR256-TEC). The measurements were carried out in an optically transparent thin-layer electrochemical (OTTLE)[S3] cell (CaF_2 windows) with a platinum-mesh working electrode, a platinum-mesh counter electrode, and a silver-foil pseudoreference electrode. Anhydrous and degassed solvents with 0.1 M NBu_4PF_6 as electrolyte were used.

Computations were performed using the ORCA software package, versions 4.1.2 and 4.2.[S4] Geometries were optimized on the BP86/def2-TZVP level of theory. Grimme's dispersion correction with Becke-Johnson damping was employed.[S5] The optimized structures were verified to be minima by checking the absence of imaginary frequencies in numerical or analytical frequency calculations. Single-point energies were calculated at the B3LYP/def2-TZVP level of theory. Solvation was accounted for by using the CPCM model with THF as solvent. Spin population and EPR parameters for species $\mathbf{4}^{\mathbf{Pr}}$ were calculated using a TPSSh/EPR-III approach.

Experimental details and analytical data

Synthesis of 2^{Et}

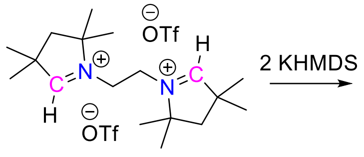


1^{Et} 2^{Et}

(a) Anhydrous sodium sulfate (113.6 g, 0.8 mol) was taken in a round-bottom flask and diethyl ether (250 mL) was added to it. Isobutyraldehyde (77 mL, 0.85 mol) and catalytic amounts of *p*-toluenesulfonic acid were added and round-bottom flask was kept at -10 °C. After 10 minutes, ethylenediamine (26.7 mL, 0.4 mol) was added dropwise with stirring at −10 °C. After 2 hours, the reaction mixture was warmed to room temperature and left for 12 hours at this temperature. Then the reaction mixture was filtered through filter paper or cotton containing anhydrous sodium sulfate. Sodium sulfate of the reaction mixture was washed with diethyl ether (3x20 mL) and filtered. The combined ether layers were collected and volatiles were evaporated on a rotary evaporator. The product $\mathbf{1^{Et}}$ was distilled through a Vigreux column at 50 to 70 °C and 0.33 torr as colorless liquid. Density: 0.836 g/mL. Yield: 57.888 g (86 %). **^{1}H NMR** (C_6D_6, 25 °C , 300 MHz): δ = 7.37-7.36 (d, 2H, 4.02 Hz, NC*H*C), 3.64 (s, 4H, CH_2CH_2), 2.35-2.20 (m, 2H, C*H*(CH_3)$_2$), 0.99-0.97 (d, 12H, 6.90 Hz, CH_3) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75.4 MHz): δ = 169.47 (H*C*=N), 61.74 (CH_2CH_2), 34.13 (*C*H(CH_3)$_2$), 19.43 (CH(CH_3)$_2$) ppm. (b) 44 mL (30.8 mmol) of 0.7 molar LDA in THF was added dropwise to a stirred solution of $\mathbf{1^{Et}}$ (2.44 g, 14.515 mmol) in Et_2O (50 mL) at 0°C. After half an hour the solution was warmed to room temperature and stirred for 12 hrs. Then solvent and volatile materials were removed under vacuum and the residue was dissolved in Et_2O (150 mL). Isobutylene oxide (2.7 mL, 30.4 mmol) was added dropwise at 0 °C. After stirring for 12 hrs at room temperature, triflic anhydride (5.1 mL, 30.3 mmol) was added to the reaction mixture dropwise at −78 °C. The solution was warmed to room temperature and stirred for 4 hrs at room temperature. It was then filtered. The residue was washed with ether, dissolved in acetonitrile and crystallized using ether diffusion. Colorless crystals were obtained as desired product $\mathbf{2^{Et}}$. **Yield:** 2.17 g (26 %). **M.P.:** > 200 °C. **^{1}H NMR** (D_2O, 25 °C, 300 MHz): δ = 8.87 (s, 2H, NC*H*C), 4.36 (s, 4H, CH_2CH_2), 2.28 (s, 4H, CH_2), 1.64 (s, 12H, CH_3), 1. 47 (s, 12H, CH_3) ppm. **^{13}C{^{1}H} NMR** (CD_3CN, 25 °C, 75.4 MHz): δ = 187.35 (*C*H), 80.81 (*C*(CH_3)$_2$), 48.95 (*C*(CH_3)$_2$), 48.41 (CH_2), 45.80 (CH_2-CH_2), 27.09 (CH_3), 26.23 (CH_3) ppm. **^{19}F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = −79.33 ppm. **ESI-MS:** [M] = $C_{20}H_{34}F_6N_2O_6S_2$; calcd. ([M]−($^-$OTf))$^+$: 427.2237; found: 427.2224; calcd. ([M]−($^-$OTf)$_2$−H$^+$)$^+$: 277.2633; found: 277.2626. **Elemental analysis** Calcd. (%) for $C_{20}H_{34}N_2F_6O_6S_2$: C 41.66, H 5.94, N 4.86, S 11.12; found: C 41.80, H 5.95, N 4.92, S 11.40.

Synthesis of 3^{Et}

Method I

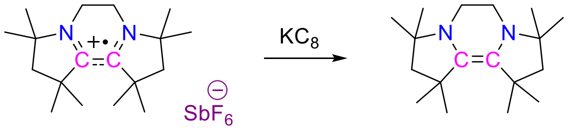


$\mathbf{2^{Et}}$ $\mathbf{3^{Et}}$

$\mathbf{2^{Et}}$ (1.16 g, 2 mmol) and **KHMDS** (798 mg, 4 mmol) were taken in a 100 mL Schlenk flask and 60 mL toluene was added at 0 °C with stirring. After half an hour, the reaction mixture was warmed to room temperature and stirred for another twelve hours at room temperature. Then toluene and other volatiles were removed under vacuum and the product was extracted with hexane (30 mL x 2). A colorless oily liquid was obtained as title compound after evaporating solvent. Yield 80%. The oily compound was dissolved in minimum amount (2 mL) of pentane and kept at −35 °C for crystallization. A colorless ppt. was obtained after 30 days and ^{1}H NMR shows the formation of targeted compound $\mathbf{3^{Et}}$ along with impurities. We tried to obtain pure $\mathbf{3^{Et}}$ in this route by crystallization as well as by sublimation, but did not succeed.

Note: In case of $\mathbf{3^{Et}}$ we did not obtain a pure compound by the reaction of $\mathbf{2^{Et}}$ and KHMDS. We carried out the 1-e oxidation of this crude product with an equivalent amount of $NOSbF_6$, obtained the corresponding radical cation $\mathbf{4^{Et}}$ and isolated it as a pure crystalline compound. It was then re-reduced using one equivalent of KC_8 to yield $\mathbf{3^{Et}}$ as a pure low-melting crystalline solid. Single crystals suitable for X-ray diffraction study obtained by the sublimation technique.

Method II

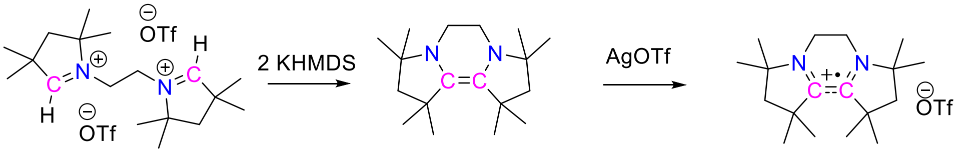


$\mathbf{4^{Et}}$ $\mathbf{3^{Et}}$

Benzene was added to a Schlenk flask containing $\mathbf{4^{Et}}$ **(SbF_6^-)** (509.14 mg, 1 mmol) and potassium graphite (540.72 mg, 4 mmol) at room temperature. After stirring for 12 hours the reaction mixture was filtered and the filtrate was evaporated to isolate $\mathbf{3^{Et}}$ as pure colorless low melting solid compound. **Yield:** 238 mg (86 %). **^{1}H NMR** (C_6D_6, 25 °C , 300 MHz): δ = 2.81 (s, 4H, CH_2CH_2), 1.63 (s, 4H, CH_2), 1.43 (s, 12H, CH_3), 1.04 (s, 12H, CH_3) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75.4 MHz): δ = 126.95 (C=C), 58.56 (CH_2), 58.23 ($C(CH_3)_2$), 41.10 (CH_2N), 39.10 ($C(CH_3)_2$), 31.93 ($C(CH_3)_2$), 26.20 ($C(CH_3)_2$) ppm. **ESI-MS**: [M] = $C_{18}H_{32}N_2$; calcd. ($[M]-2H)^+$: 274.2409; found: 274.2479.

Synthesis of 4^{Et}(OTf^{-})

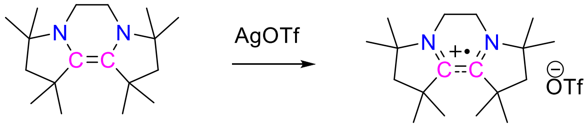
Method I



2^{Et} **3^{Et}** **4^{Et}**

3^{Et} was prepared from **2^{Et}** (576.6 mg, 1 mmol) and **KHMDS** (398 mg, 2 mmol) as crude product. THF (4 mL) was added to 25 mL Schlenk flask containing crude **3^{Et}** (obtained from 1 mmol of **2^{Et}**) and silver triflate (128.47 mg, 0.5 mmol) at −78 °C with stirring. Formation of the black colour of metallic silver was observed. After 10 minutes of stirring, the reaction mixture was warmed to room temperature. THF was evaporated and acetonitrile was added. It was filtered through a frit containing celite, but silver particles were also present in the filtrate. The filtrate was concentrated and kept at −30 °C with ether diffusion for crystallization. Yellow colored crystals of **4^{Et}(TfO^{-})** were obtained along with black silver particles after 12 hrs. Crystals (which were also suitable for a single crystal X-ray diffraction study) were washed with 5 mL of hexane. In this case, we were not able to remove black particles of silver and therefore the compound was not purified. This was mostly based on the impurity in **3^{Et}**.

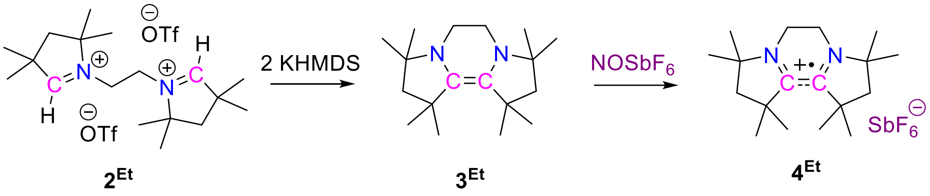
Method II



3^{Et} **4^{Et}**

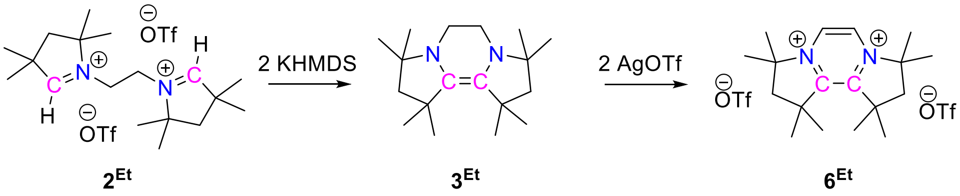
Silver triflate (46.0 mg, 0.179 mmol) was added to a THF solution of pure **3^{Et}** (50 mg, 0.180 mmol) at room temperature with stirring inside the glove box. Formation of the black colour of metallic silver was observed. After 2 minutes of stirring, THF was evaporated and acetonitrile was added. Black colored metallic silver particles were allowed to settle down from the solution and the supernatant was taken out from a dropper. The solution was concentrated and kept at −30 °C with ether diffusion for crystallization. Yellow crystals of **4^{Et}(TfO^{-})** were washed with hexane, the filtrate was concentrated and again kept for crystallization. **Yield:** 61 mg (80 %). **UV/Vis** (CH_3CN): $\lambda_{max}(\varepsilon)$ = 273 (4870.96), 331 (9651.81) nm (Lmol^{-1}cm^{-1}).

Synthesis of $4^{Et}(SbF_6^-)$



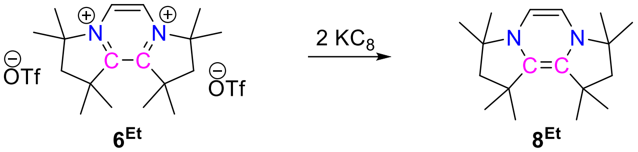
Nitrosonium hexafluoroantimonate (160 mg, 0.6 mmol) was added to a solution of crude 3^{Et} (obtained from 1 mmol of 2^{Et} and 2 mmol of KHMDS) in THF at −35 °C inside the glove box. It was stirred for half an hour and then the solvent was evaporated. Acetonitrile was added, concentrated and kept for crystallization with pentane diffusion at -30 °C. After 24 hours, bright yellow colored crystals of $4^{Et}(SbF_6^-)$ were obtained. **Yield:** 168 mg (55 %). **M.P.:** >195 °C. **ESI-MS:** [M] = $C_{18}H_{32}N_2$; calc. 276.2566; found: 276.2620. **Elemental analysis**: Calc. C 42.37, H 5.93, N 5.48; found C 42.79, H 7.28, N 5.54.

Synthesis of 6^{Et}



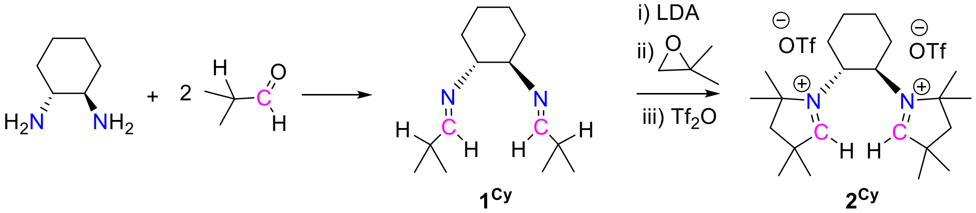
3^{Et} was prepared from 2^{Et} (1.16 g, 2 mmol) and **KHMDS** (798 mg, 4 mmol) as crude product. THF (10 mL) solution of crude 3^{Et} (obtained from 2 mmol of 1^{Et}) was added dropwise to a THF solution of silver triflate (1.054 g, 4.1 mmol in 20 mL of THF) at −78 °C with stirring. Immediately the black colour of metallic silver appeared and the particles precipitated out. After 10 minutes, the mixture was warmed to room temperature. The solvent and other volatiles were removed under vacuum and the residue was dissolved in acetonitrile and filtered. The filtrate was concentrated and kept for crystallization with ether diffusion at room temperature. Colorless crystals of 6^{Et} were obtained (along with some colored impurities) after 2 days which were suitable for single crystal X-ray diffraction study. Solvent was decanted and the crystals were washed with minimum amount of THF to remove the colored impurities and to isolate pure colorless product 6^{Et}. The decanted solvent was concentrated and some DCM was added and then again kept for crystallization layered with diethyl ether. **Yield:** 722 mg (63 %). **M.P.** > 200 °C. **^{1}H** NMR (CD_3CN, 25 °C , 300 MHz): δ = 9.54 (s, 2H, C*H*), 2.61 (s, 4H, C*H*$_2$), 1.91 (s, 12H, C*H*$_3$), 1.86 (s, 12H, C*H*$_3$) ppm. **^{13}C{^{1}H}** NMR (CD_3CN, 25 °C, 75.4 MHz): δ = 165.51 (*C*=N), 140.39 (*C*H), 81.10 (*C*(CH_3)$_2$), 52.44 (*C*H$_2$), 49.76 (*C*(CH_3)$_2$), 29.94 (C(*C*H$_3$)$_2$), 29.45 (C(*C*H$_3$)$_2$) ppm. **^{19}F{^{1}H}** NMR (CD_3CN, 25 °C, 282 MHz): δ = −79.24 ppm. **ESI-MS**: [M] = $C_{20}H_{30}F_6N_2O_6S_2$; calcd. ([M]–($^-$OTf)$_2$)$^+$: 274.2398; found: m/z = 274.2446, calcd. ([M]–($^-$OTf)$_2$): 137.1199; found: m/z = 137.1199. **Elemental analysis**: Calcd. (%) for $C_{20}H_{30}F_6N_2O_6S_2$: C 41.95, H 5.28, N 4.89, S 11.20; found C 41.98, H 5.76, N 4.94, S 11.33.

Reduction of 6^{Et} to 8^{Et}



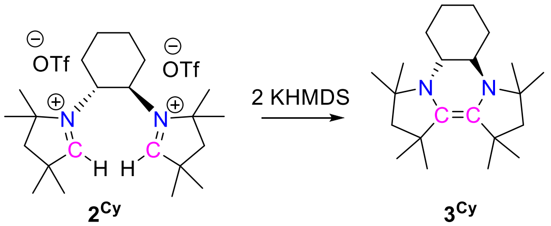
About 20 mL of toluene was added to a Schlenk flask containing KC_8 (30 mg, 0.222 mmol) and **6^{Et}** (32 mg, 0.056 mmol) and stirred at room temperature for 24 hours. Subsequently, the reaction mixture was filtered and after evaporation of the filtrate compound **8^{Et}** was obtained. **Yield:** 7 mg (46 %). **^{1}H NMR** (C_6D_6, 25 °C , 300 MHz): δ = 4.81 (s, 2H, C*H*=C*H*), 1.36 (s, 4H, C*H*$_2$), 1.28 (s, 12H, C*H*$_3$), 1.13 (s, 12H, C*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75.4 MHz): δ = 130.53 (*C*=*C*), 113.21 (H*C*=*C*H), 58.27 (*C*(CH$_3$)$_2$), 57.40 (*C*H$_2$), 38.38 (*C*(CH$_3$)$_2$), 30.93 (C(*C*H$_3$)$_2$), 26.41 (C(*C*H$_3$)$_2$) ppm.

Synthesis of 2^{Cy}



(a) Anhydrous sodium sulfate (85 g, 600 mmol) was taken in a round bottom flask and diethyl ether (250 mL) was added to it. (±)-*trans*-1,2-Cyclohexanediamine (30 mL, 249.84 mmol) and catalytic amounts of p-toluenesulfonic acid were added to round-bottom flask with stirring. After that, isobutyraldehyde (55 mL, 600 mmol) was added dropwise with stirring at room temperature and stirred for 12 hours. The reaction mixture was filtered through filter paper or cotton containing anhydrous sodium sulfate. Sodium sulfate of the reaction mixture was washed with diethyl ether (3x20 mL) and filtered. The combined ether layers were collected and volatiles were evaporated in a rotary evaporator. The product was distilled as colorless liquid. Density: 0.870-0.894 g/mL. **Yield:** 44.5 mg (80 %). **^{1}H NMR** (300 MHz, C_6D_6, 25 °C): δ = 7.40-7.41 (d, 2H, 4.10 Hz, *H*C=N), 3.05-3.14 (m, 2H, *H*C-N), 2.20-2.35 (m, 2H, *H*C(CH$_3$)$_2$), 1.57-1.82 (m, 4H, Cy-C*H*$_2$), 1.23-1.32 (m, 4H, Cy-C*H*$_2$), 0.99-1.01 (d, 6H, 6.90 Hz, C(C*H*$_3$)$_2$), 0.97-1.00 (d, 6H, 6.91 Hz, C(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75.4 MHz): δ = 168.30, 74.56, 34.59, 34.13, 25.51, 20.21, 20.13 ppm.[S6] (b) 39 mL (31.5 mmol) of 0.7 molar LDA in THF was added dropwise to a stirred solution of imine (3.335 g, 15 mmol) in Et_2O (50 mL) at −78 °C. After that the solution was kept for 2 hours in the same temperature bath (during this period the temperature was increasing). Then solvent and volatile materials were removed under vacuum and the residue was dissolved in Et_2O (240 mL). Isobutylene oxide (2.8 mL, 31.5 mmol) was added dropwise at 0 °C. After stirring for 12 h at room temperature, triflicanhydride (5.3 mL, 31.5 mmol) was added to above reaction mixture dropwise over 1 minute at −78 °C. The solution was warmed to room temperature and stirred for 8 hrs at room temperature. It was filtered and the residue containing the di-cation along with two molecules of lithium triflate was washed with ether. Yield: 17 % (2.4 g). Pure title compound without lithium triflate was obtained through precipitation by dissolving the residue in acetonitrile and layering with ether. Colorless crystals suitable for single crystal X-ray diffraction study were obtained by dissolving the residue in acetonitrile and diffusion with diethyl ether. **Yield:** 1.6 g (17 %). **M.P.:** > 200 °C. **^{1}H NMR** (CD_3CN, 25 °C , 300 MHz): δ = 9.33 (s, 2H, N=*H*C), 4.56-4.59 (m, 2H, C*H*C*H*), 2.50-2.46 (d, 2H, 12.08 Hz, Cy-C*H*$_2$), 2.30-2.14 (m, 4H, C*H*$_2$), 1.91-1.80 (m, 4H, Cy-C*H*$_2$), 1.72-1.69 (m, 2H, Cy-C*H*$_2$), 1.66 (s, 6H, C*H*$_3$), 1. 46 ppm (s, 6H, C*H*$_3$), 1.44 (s, 6H, C*H*$_3$), 1.42 (s, 6H, C*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (CD_3CN, 25 °C, 75.4 MHz): δ = 189.36 (N=*C*H), 81.85 (*C*(CH_3)$_2$), 61.55 (*C*H*C*H), 48.91 (*C*(CH_3)$_2$), 48.17 (*C*H$_2$), 38.89 (Cy-*C*H$_2$), 28.19 (*C*H$_3$), 27.76 (*C*H$_3$), 26.54 (*C*H$_3$), 25.64 (*C*H$_3$), 24.46 (Cy-*C*H$_2$) ppm. **^{19}F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = −79.28 ppm. **Elemental analysis** Calcd. (%) for $C_{24}H_{40}F_6N_2O_6S_2$: C 44.94, H 5.90, N 4.56, S 10.43; found C 44.98, H 6.05, N 4.59, S 10.52. **ESI-MS**: [M] = $C_{24}H_{40}F_6N_2O_6S_2$; calcd. ([M]–(OTf^-)$_2$)$^+$: 332.3181; found: 332.3294.

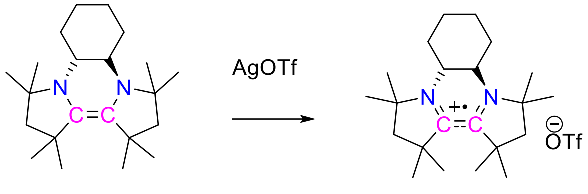
Synthesis of 3^{Cy}



2^{Cy} 3^{Cy}

2^{Cy} (1.1261 g, 2 mmol) and **KHMDS** (798 mg, 4 mmol) were taken in a 100 mL Schlenk flask and 60 mL toluene was added at 0 °C with stirring. After half an hour, the reaction mixture was warmed to room temperature and stirred for another 24 hours at room temperature. Then toluene and other volatiles were removed in vacuum and the product was extracted with hexane (30 mL x 2). A colorless oily liquid was obtained as title compound after evaporating solvent. The oily compound was dissolved in a minimum amount of pentane giving a concentrated solution and kept at −35 °C for crystallization. Colorless crystals were obtained after 7 days which were suitable for single crystal X-ray diffraction study. **Yield:** 463 mg (70 %). **M.P.:** 57 °C. **^{1}H NMR** (300 MHz, C_6D_6, 25 °C): δ = 2.97 (br, 2H, C*H*), 2.24-2.22 (m, 2H, Cy-C*H*$_2$), 1.74-1.70 (d, 2H, 12.43 Hz, C*H*$_2$), 1.57 (br. s, 2H, Cy-C*H*$_2$), 1.52 (s, 2H, C*H*$_2$), 1.48 (s, 6H, C(C*H*$_3$)$_2$), 1.42 (s, 6H, C(C*H*$_3$)$_2$), 1.28 (s, 6H, C(C*H*$_3$)$_2$), 1.17-1.19(m, 4H, Cy-C*H*$_2$CH), 1.11 (s, 6H, C(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75.4 MHz): δ = 131.39 (*C*=*C*), 62.75 (*C*H$_2$), 59.82 (*C*(CH_3)$_2$), 59.03 (*C*H), 39.10 (*C*(CH_3)$_2$), 34.62 (C(*C*H$_3$)$_2$), 34.17 (C(*C*H$_3$)$_2$), 32.99 (Cy-*C*H$_2$), 31.66 (C(*C*H$_3$)$_2$), 25.61(Cy-*C*H$_2$CH), 24.06 (C(*C*H$_3$)$_2$) ppm. **Elemental analysis** Calcd. (%) for $C_{22}H_{38}N_2$: C 79.94, H 11.59, N 8.47; found C 80.02, H 14.0, N 8.52. **ESI-MS**: [M] = $C_{22}H_{38}N_2$; calcd. ([M])$^+$: 330.3035; found: 330.3049.

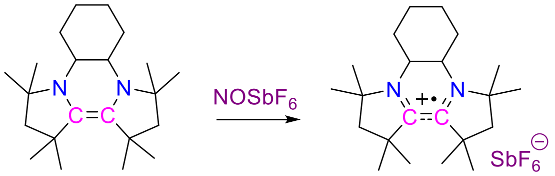
Synthesis of 4^{Cy}



3^{Cy} **4^{Cy}**

Silver triflate (155 mg, 0.603 mmol) solution in THF (10 mL) was added to a solution of powdered **3^{Cy}** (200 mg, 0.605 mmol) in THF (10 mL) dropwise at room temperature with stirring inside the GloveBox. An immediate formation of the black colour of metallic silver was observed. After 10 minutes stirring, the reaction mixture was standing for 10 minutes allowing the metallic silver to settle down. The pale yellow colored supernatant solution was taken out using a glass-pipette and then acetonitrile (10 mL) was added to the residue, stirred well and allowed to stand for 10 minutes to settle down metallic silver. The orange colored solution was taken out using a glass-pipette. The solution in THF was evaporated and the solution in acetonitrile was added to it. It was concentrated in vacuum and kept at −30 °C with pentane diffusion for crystallization. Orange colored crystals of **4^{Cy}** were obtained after 12 hrs and after collecting the resulting crystals (which were also suitable for a single crystal X-ray diffraction study) were washed with 5 mL of hexane. After concentrating the mother liquor, we kept it again at −30 °C with pentane diffusion for a second crop of crystals. After collecting the second crop of crystals the mother liquor was evaporated and the yellow powdered compound was obtained. **Total Yield:** 281 mg (97 %). **M.P.:** > 200 °C. **UV/Vis** (CH_3CN): $\lambda_{max}(\varepsilon)$ = 333 (10332), 424 (1624.2) nm ($Lmol^{-1}cm^{-1}$). **ESI-MS**: [M] = $C_{23}H_{38}F_3N_2O_3S$; calcd. ($[M]-(OTf^-))^+$: 330.3030; found: 330.3213. **Elemental analysis** Calcd. (%) for $C_{23}H_{38}F_3N_2O_3S$: C 57.84, H 7.60, N 5.87, S 6.71; found: C 57.90, H 8.19, N 6.49, S 7.03.

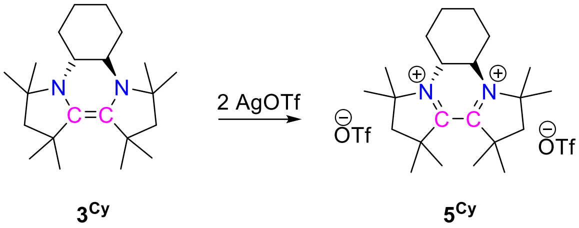
Synthesis of $4^{Cy}(SbF_6^-)$



3^{Cy} **4^{Cy}**

Nitrosonium hexafluoroantimonate (20 mg, 0.075) was added to a solution of **3^{Cy}** (30 mg, 0.091 mmol) in THF at −35 °C inside the glove box. It was then bringing outside and allowed to come room temperature with stirring. After stirring for 5 minutes at room temperature all the solvent was evaporated. Acetonitrile was added to the residue and concentrated until the volume of the solution about 1 mL and then 5 mL THF was added. The resulting solution kept for crystallization with diethyl ether diffusion at −30 °C. After 24 hours, orange colored crystals of **4^{Cy}**(SbF_6^-) were obtained. **Yield:** 20 mg (48 %).

Synthesis of 5^{Cy}



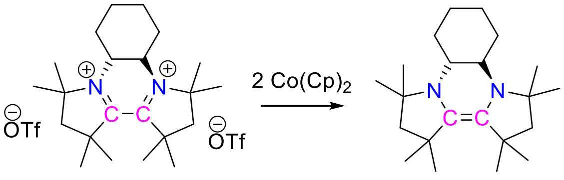
3^{Cy} 5^{Cy}

A THF (20 mL) solution of silver triflate (1.054 g, 4.1 mmol) was added dropwise to a THF (30 mL) solution of **3^{Cy}** (661.12 mg, 2 mmol) at room temperature with stirring. Immediately, black colored metallic silver precipitated out. After 10 minutes, solvent and other volatiles were removed under vacuum and the residue was dissolved in acetonitrile and filtered. The filtrate was concentrated and kept for crystallization with pentane diffusion at room temperature for 24 hours and then kept at −30 °C. Colorless crystals of **5^{Cy}** were obtained after 2 days which were also suitable for X-ray structural analysis. Crystals were washed with THF. The solvent was decanted, concentrated and some DCM was added and then again kept for crystallization layered with pentane. **Yield:** 1 g (80 %). **M.P.:** > 200 °C. **^{1}H NMR** (CD_3CN, 25 °C, 300 MHz): δ = 4.76 (br. s, 2H, Cy-C*H*), 2.96-3.0 (d, 2H, 10.77 Hz Cy-C*H*$_2$-CH), 2.39 (s, 4H, *C*H$_2$), 2.02 (br. m, 2H, Cy-C*H*$_2$), 1.88 (s, 6H, C*H*$_3$), 1.85 (s, 6H, C*H*$_3$), 1.77 (br. s, 12H, C*H*$_3$), 1. 64-1.41 (br. m, 4H, Cy-C*H*$_2$) ppm. **^{13}C{^{1}H} NMR** (CD_3CN, 25 °C, 75.4 MHz): δ = 176.41 (N^+=*C*), 123.81, 119.56, 115.33, 81.73, 62.58, 56.22, 51.46, 31.56, 29.46, 29.26, 28.45, 27.65, 24.96, 23.72 ppm. **^{19}F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = −79.19 ppm. **Elemental analysis** Calcd. (%) for $C_{24}H_{38}F_6N_2O_6S_2$: C 45.85, H 6.09, N 4.46, S 10.20; found: C 44.84, H 5.81, N 4.23, S 10.35. **ESI-MS:** [M] = $C_{24}H_{38}F_6N_2O_6S_2$; calcd. ([M]−(OTf$^-$)$_2$−H$^+$)$^+$: 329.2957; found: 329.2936; calcd. ([M−2H]−(OTf$^-$)$_2$−H$^+$)$^+$: 327.2800; found: 327.2795.

NOTE: Compound **5^{Cy}** decomposed to un-identified products in acetonitrile with time.

Reduction of 5^{Cy} to 3^{Cy}

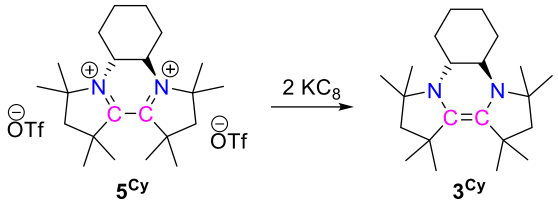
Method I



5^{Cy} 3^{Cy}

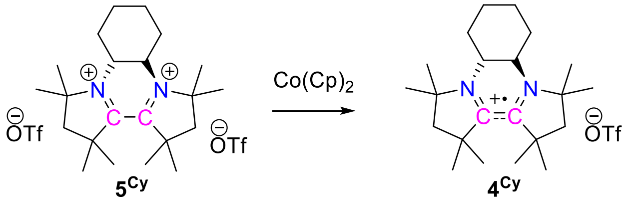
Acetonitrile or dichloromethane was added to a Schlenk flask containing cobaltocene (30.26 mg, 0.16 mmol) and **5^{Cy}** (50 mg, 0.08 mmol) and stirred at room temperature for 12 hours. The solvent was evaporated and pentane was added and filtered. The filtrate was evaporated and a ^{1}H NMR was measured. The obtained ^{1}H NMR spectrum matched with **3^{Cy}**. **Yield:** 20 mg (75 %).

Method II



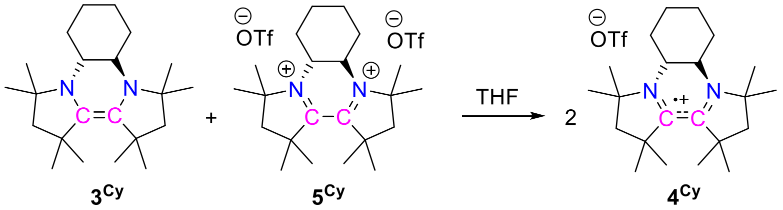
Either THF or benzene or toluene was added to a Schlenk flask containing potassium graphite (43 mg, 0.32 mmol) and **5^{Cy}** (50 mg, 0.08 mmol) and stirred at room temperature for 12 hours (in case of THF it was 4 hours). In case of THF, the solvent was evaporated and hexane was added and filtered. The filtrate was evaporated and ^1H NMR was measured. In case of benzene or toluene, it was filtered, the filtrate was evaporated and ^1H NMR was measured. The obtained ^1H NMR spectrum matched with **3^{Cy}**. **Yield**: 19 mg (71 %).

Reduction of 5^{Cy} to 4^{Cy}



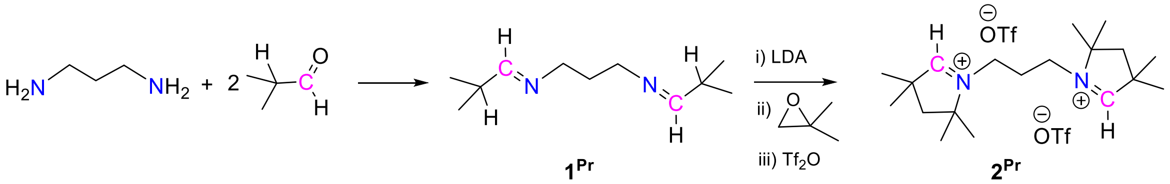
Acetonitrile was added to a Schlenk flask containing cobaltocene, $Co(Cp)_2$ (15.13 mg, 0.08 mmol) and **5^{Cy}** (50 mg, 0.08 mmol) and stirred at room temperature for 12 hours. The solvent was concentrated down to 2 mL and filtered through a dropper containing paper inside glove box. The filtrate was again concentrated to about 1 mL and kept at −30 °C for 12 hours. The resultant crystals were washed with THF and dried. The obtained UV/Vis spectrum was matched with **4^{Cy}** (Fig. S42). **Yield:** 27 mg (70 %).

1:1 Reaction of 3^{Cy} and 5^{Cy}



THF was added to a Schlenk flask containing **3^{Cy}** (50 mg, 0.151 mmol) and **5^{Cy}** (94 mg, 0.151 mmol) at room temperature with stirring. The solution slowly became yellow and after 24 hours of stirring at room temperature THF was evaporated. The resulting residue was dissolved in a minimum amount of 1:1 acetonitrile and THF (about 4 mL). Then the compound was precipitated out by layering with pentane at −30 °C. The obtained UV/Vis spectrum was matched with **4^{Cy}** (Fig. S41). **Yield:** 109 mg (75 %).

Synthesis of 2^{Pr}

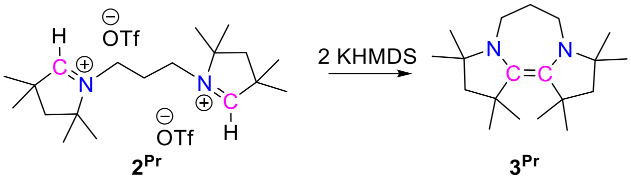


1^{Pr}

2^{Pr}

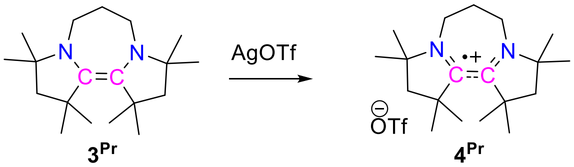
Anhydrous sodium sulfate (113.6 g, 0.8 mol) was taken in a round-bottom flask and diethyl ether (250 mL) was added to it. Isobutyraldehyde (77 mL, 0.85 mol) and catalytic amounts of p-toluenesulfonic acid were added and round-bottom flask was kept at -10 °C. After 10 minutes, propane-1,3-diamine (33.4 mL, 0.4 mol) was added dropwise with stirring at -10 °C. After 2 hours, the reaction mixture was warmed to room temperature and left for 12 hours at this temperature. Then the reaction mixture was filtered through filter paper or cotton containing anhydrous sodium sulfate. Sodium sulfate of the reaction mixture was washed with diethyl ether (3x20 mL) and filtered. The combined ether layers were collected and volatiles were evaporated in a rotary evaporator. The product was distilled at 70 °C and 0.2 torr as colorless liquid. Density: 0.84 g/mL. **Yield:** 59.8 g (82 %). **^{1}H NMR** (300 MHz, C_6D_6, 25 °C): δ = 7.37-7.35 (d, 2H, 4.05 Hz, *H*C=N), 3.45-3.41 (t, 4H, 6.82 Hz, H_2C-N), 2.35-2.20 (m, 4H, *H*C(CH_3)$_2$), 2.03-1.94 (quin, 2H, 6.78 Hz, CH_2CH2N), 0.99-0.96 (d, 12H, 0.89 Hz, CH(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75.4 MHz): δ = 168.90, 59.65, 34.65, 33.27, 19.95 ppm. (b) 60 mL (60 mmol) of 1.0 M LDA in THF was added dropwise to a stirred solution of **1^{Pr}** (5.460 g, 30 mmol) in Et_2O (50 mL) at 0 °C. After half an hour the solution was warmed to room temperature and stirred for 12 h. Then solvent and volatile materials were removed under vacuum and the residue was dissolved in Et_2O (150 mL). Isobutylene oxide (5.4 mL, 60 mmol) was added dropwise at 0 °C. After stirring for 12 hrs at room temperature, triflic anhydride (10.5 mL, 62.4 mmol) was added to above reaction mixture dropwise at –78 °C. The solution was warmed to room temperature and stirred for 4 h at room temperature. It was filtered. The residue was washed with ether, dissolved in acetonitrile and crystallized with ether diffusion. Colorless crystals were obtained as desired product **2^{Pr}**. **Yield:** 5.315 g (30 %). **M.P.:** > 200 °C. **^{1}H NMR** (CD_3CN, 25 °C, 300 MHz): δ = 8.53 (s, 2H, CH), 3.83-3.78 (t, 4H, 8.0 Hz, CH_2–CH$_2$–CH_2), 2.49-2.38 (quin, 2H, 7.70 Hz, CH$_2$–CH_2–CH$_2$), 2.15 (s, 4H, CH_2), 1.55 (s, 12H, CH$_3$), 1. 41 ppm (s, 12H, CH_3) ppm. **^{13}C{^{1}H} NMR** (CD_3CN, 25 °C, 75.4 MHz): δ = 185.24 (C*H*), 79.60 (*C*(CH_3)$_2$), 49.35 (*C*(CH_3)$_2$), 47.67 (*C*H$_2$), 45.96 (*C*H$_2$-CH$_2$–*C*H$_2$), 27.70 (CH$_2$–*C*H$_2$–CH$_2$), 27.24 (*C*H$_3$), 26.12 (*C*H$_3$) ppm. **^{19}F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = -79.32 ppm. **Elemental analysis** Calcd. (%) for $C_{21}H_{36}N_2F_6O_6S_2$: C 41.66, H 5.94, N 4.86, S 11.12; found: C 42.89, H 6.16, N 4.83, S 10.92. **ESI-MS:** [M] = $C_{21}H_{36}F_6N_2O_6S_2$; calcd. ([M]–(OTf$^-$))$^+$: 441.2393; found: 441.2385; calcd. ([M]–(OTf$^-$)$_2$–H$^+$)$^+$: 291.2790; found: 291.2788.

Synthesis of 3^{Pr}



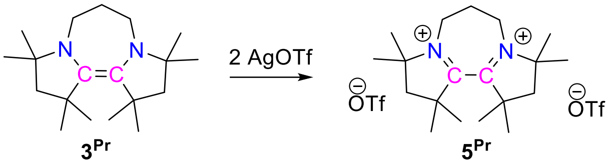
2^{Pr} (1.182 mg, 2 mmol) and **KHMDS** (798 mg, 4 mmol) were taken in a 100 mL Schlenk flask and 60 mL benzene was added at 0 °C with stirring. After half an hour, the reaction mixture was warmed to room temperature and stirred for another 24 hours at room temperature. Then benzene and other volatiles were removed in vacuum and the product was extracted with n-hexane (30 mL x2). A colorless oily liquid was obtained as title compound after evaporating the solvent. Yield: 494 mg (85 %). The oily compound was dissolved in minimum amount of n-hexane to give a concentrated solution and kept at −35 °C for crystallization. Colorless crystals were obtained after 7 days which were suitable for X-ray structural analysis. The product was also purified by sublimation. **Yield:** 238 mg (41 %). **M.P.:** 38 °C. **^{1}H NMR** (300 MHz, C_6D_6, 25 °C): δ = 3.36 (t, 4H, H_2C-N), 1.64 (s, 4H, H_2C), 1.36 (s, 12H, C(CH_3)$_2$), 1.34-1.30 (m, 2H, CH_2CH$_2$N), 1.12 (s, 12H, C(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75.4 MHz): δ = 127.97 (*C*=*C*), 59.99 (H$_2$*C*), 57.25 (*C*(CH$_3$)$_2$), 43.24 (H$_2$*C*-N), 39.57 (*C*(CH$_3$)$_2$), 30.25 (C(*C*H$_3$)$_2$), 28.18 (*C*(CH$_3$)$_2$), 27.87 (*C*H$_2$CH$_2$N) ppm. **Elemental analysis** Calcd. (%) for $C_{19}H_{34}N_2$: C 78.56, H 11.80, N 9.64; found C 77.92, H 13.76, N 9.19.

Synthesis of 4^{Pr}



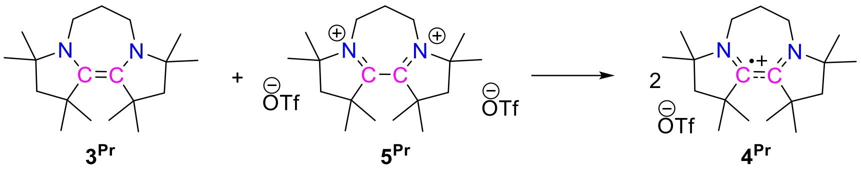
THF (15 mL) was added to a 50 mL Schlenk flask containing powdered **3^{Pr}** (100 mg, 0.344 mmol) and silver triflate (88 mg, 0.342 mmol) at room temperature with stirring inside the Glove Box. An immediate formation of black colored metallic silver was observed and the solution became red colored. After 30 seconds of stirring, the reaction mixture was allowed to stand for 10 minutes to settle down metallic silver. The intense-red supernatant solution was taken out using a glass-pipette and the residue was washed with THF (50 mL, 10 x 5 mL) until the solution obtained from washing the residue was colorless. The collected red solutions were mixed and evaporated. A yellow colored solid compound was obtained after evaporation. **Yield:** 109 mg (73 %) (110 mg). Suitable crystals for single crystal X-ray diffraction study were obtained by keeping concentrated solution of compound **4^{Pr}** in THF at −30 °C with pentane diffusion. Yellow colored crystals of **4^{Pr}** were obtained after 12 hrs. **M.P.:** 175 °C (decomposed). **UV/Vis** (THF): $\lambda_{max}(\varepsilon)$ = 305 (3243.18), 356 (7676.15), 441 (2122.08) nm (Lmol^{-1}cm^{-1}). **Elemental analysis** Calcd. (%) for $C_{20}H_{34}F_3N_2O_3S$: C 54.65, H 7.80, N 6.37, S 7.29; found: C 54.92, H 8.27, N 6.49, S 7.68. **ESI-MS:** [M] = $C_{20}H_{34}F_3N_2O_3S$; calcd. ([M]−(OTf$^-$))$^+$: 290.2717; found: 290.2762.

Synthesis of 5^{Pr}



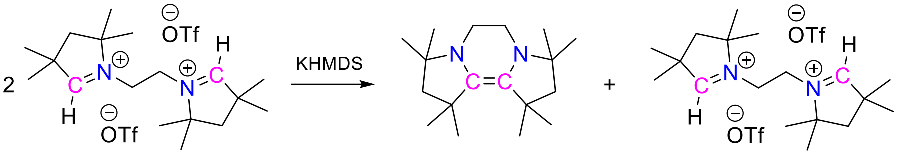
A THF (10 mL) solution of powdered $\mathbf{3^{Pr}}$ (290.50 mg, 1 mmol) was added dropwise to a THF (20 mL) solution of silver triflate (514 mg, 2 mmol) at −78 °C with stirring. Immediately, black colored metallic silver precipitated out. After 10 minutes, the reaction mixture was warmed to room temperature and further stirred for half an hour. Then solvent and other volatiles were removed under vacuum and the residue was dissolved in acetonitrile and filtered. The filtrate was concentrated and kept for crystallization with ether diffusion at room temperature. Colorless crystals of $\mathbf{5^{Pr}}$ were obtained after 24 hrs which were also suitable for X-ray structural analysis. The solvent was decanted, concentrated and some DCM was added and then again kept for crystallization layered with ether. **Yield:** 471 mg (80 %). **M.P.:** > 200 °C. ^{1}**H NMR** (300 MHz, C_6D_6, 25 °C): δ = 4.48-4.44 (dt, 2H, H_2C-N), 4.04-3.93 (m, 2H, H_2C-N), 2.94-2.80 (broad, m, 2H, H_2C-CH_2N), 2.62-2.51 (m, 4H, H_2C), 1.81 (s, 12H, C(CH_3)$_2$), 1.73-1.59 (s, 12H, C(CH_3)$_2$) ppm. ^{13}**C{^{1}H} NMR** (C_6D_6, 25 °C, 75.4 MHz): δ = 183.57 (*C*=N$^+$), 83.18 (*C*(CH_3)$_2$), 53.58 (*C*(CH_3)$_2$), 51.41 (C(*C*H_3)$_2$), 47.42 (C(*C*H_3)$_2$), 36.31 (C(*C*H_3)$_2$), 28.14 (H_2*C*), 27.86 (H_2*C*-N), 27.73 (H_2*C*-N), 26.80 (H_2*C*-CH_2N) ppm. ^{19}**F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = -79.26 ppm. **Elemental analysis** Calcd. (%) for $C_{21}H_{34}F_6N_2O_6S_2$: C 42.85, H 5.82, N 4.76, S 10.89; found C 42.89, H 5.85, N 4.81, S 10.90.

1:1 Reaction of 3^{Pr} and 5^{Pr}



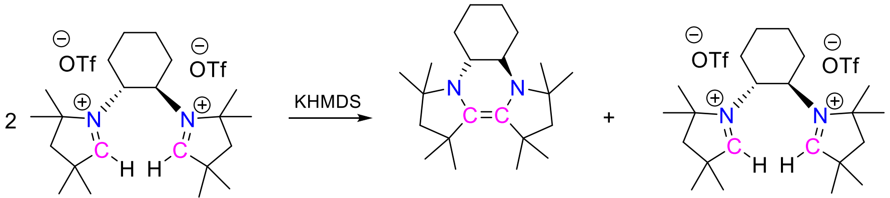
THF was added to a Schlenk flask containing $\mathbf{3^{Pr}}$ (50 mg, 0.172 mmol) and $\mathbf{5^{Pr}}$ (101 mg, 0.172 mmol) at room temperature with stirring. The solution slowly became yellow colored. After 24 hours stirring at room temperature THF was partially evaporated to give a concentrated solution. Subsequently, the compound was precipitated out by layering with pentane. The obtained UV/Vis spectrum was matched with $\mathbf{4^{Pr}}$ (Fig. S47). **Yield:** 134 mg (89 %).

1:1 Reaction of 2^{Et} and KHMDS



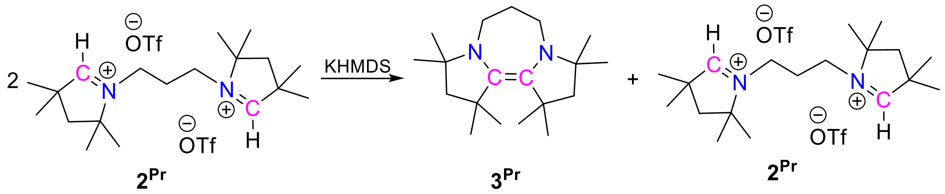
Toluene was added to a Schlenk flask containing **2** (1 eq.) and KHMDS (1 eq.) at 0 °C. After 12 hours stirring at room temperature, toluene and other volatiles were removed and the product was extracted with hexane. ^{1}H NMR of the resulting compound shows the formation of **3^{Et}**. Also, the presence of **2^{Et}** in the reaction mixture has been confirmed. From this result we cannot rule out the possibility of the formation of conjugated acid of **3^{Et}**. KHMDS is soluble in toluene and **2^{Et}** is not soluble in toluene. Therefore, in the reaction mixture there was always a local concentration of KHMDS higher than that of **2^{Et}**. This could be the reason to observe the same outcome as it was in case of 1:2 reactions of **1^{Et}** and KHMDS.

1:1 Reaction of 2^{Cy} and KHMDS



Toluene was added to a Schlenk flask containing **2^{Cy}** (1 eq.) and KHMDS (1 eq.) at 0 °C. After 12 hours stirring at room temperature, toluene and other volatiles were removed and the product was extracted with hexane. ^{1}H NMR of the resulting compound shows the formation of **3^{Cy}**. Also, the presence of **2^{Cy}** in the reaction mixture has been confirmed. From this result we cannot rule out the possibility of the formation of conjugated acid of **3^{Cy}**. KHMDS is soluble in toluene and **2^{Cy}** is not soluble in toluene. Therefore, in the reaction mixture there was always a local concentration of KHMDS higher than that of **2^{Cy}**. This could be the reason to observe the same outcome as it was in case of 1:2 reactions of **1^{Cy}** and KHMDS.

1:1 Reaction of $\mathbf{2^{Pr}}$ and KHMDS



Toluene was added to a Schlenk flask containing $\mathbf{2^{Pr}}$ (1 eq.) and KHMDS (1 eq.) at 0 °C. After 12 hours stirring at room temperature, toluene and other volatiles were removed and the product was extracted with hexane. ^{1}H NMR of the resulting compound shows the formation of $\mathbf{3^{Pr}}$. Also, the presence of $\mathbf{2^{Pr}}$ in the reaction mixture has been confirmed. From this result we cannot rule out the possibility of the formation of conjugated acid of $\mathbf{3^{Pr}}$. KHMDS is soluble in toluene and $\mathbf{2^{Pr}}$ is not soluble in toluene. Therefore, in the reaction mixture there was always a local concentration of KHMDS higher than that of $\mathbf{2^{Pr}}$. This could be the reason to observe the same outcome as it was in case of 1:2 reactions of $\mathbf{1^{Pr}}$ and KHMDS.

NMR Spectra

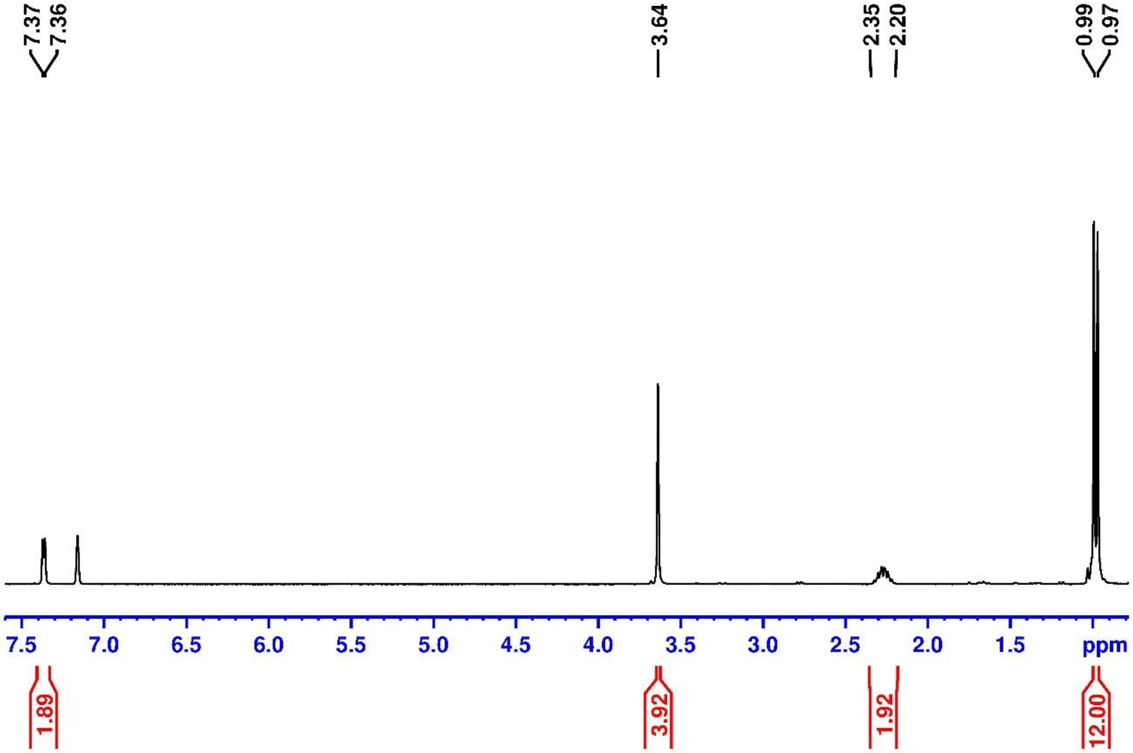


Fig. S1 ^{1}H NMR spectrum of compound $\mathbf{1^{Et}}$ in C_6D_6 at RT.

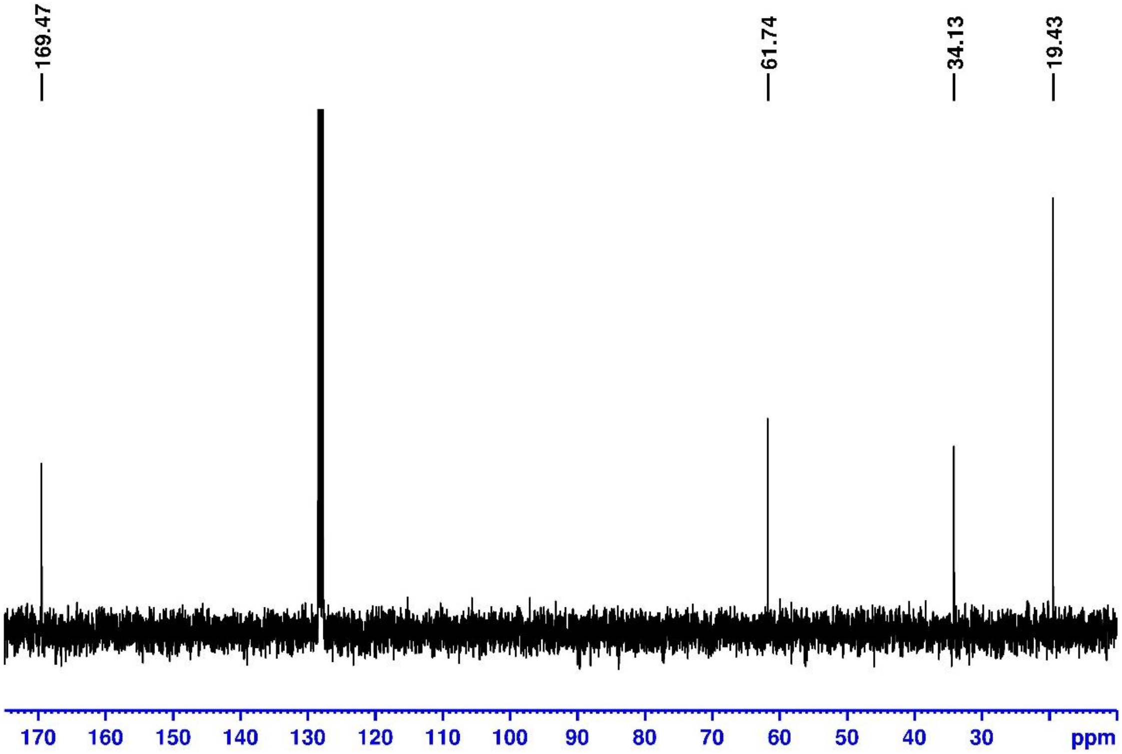


Fig. S2 $^{13}C\{^1H\}$ NMR spectrum of compound $\mathbf{1^{Et}}$ in C_6D_6 at RT.

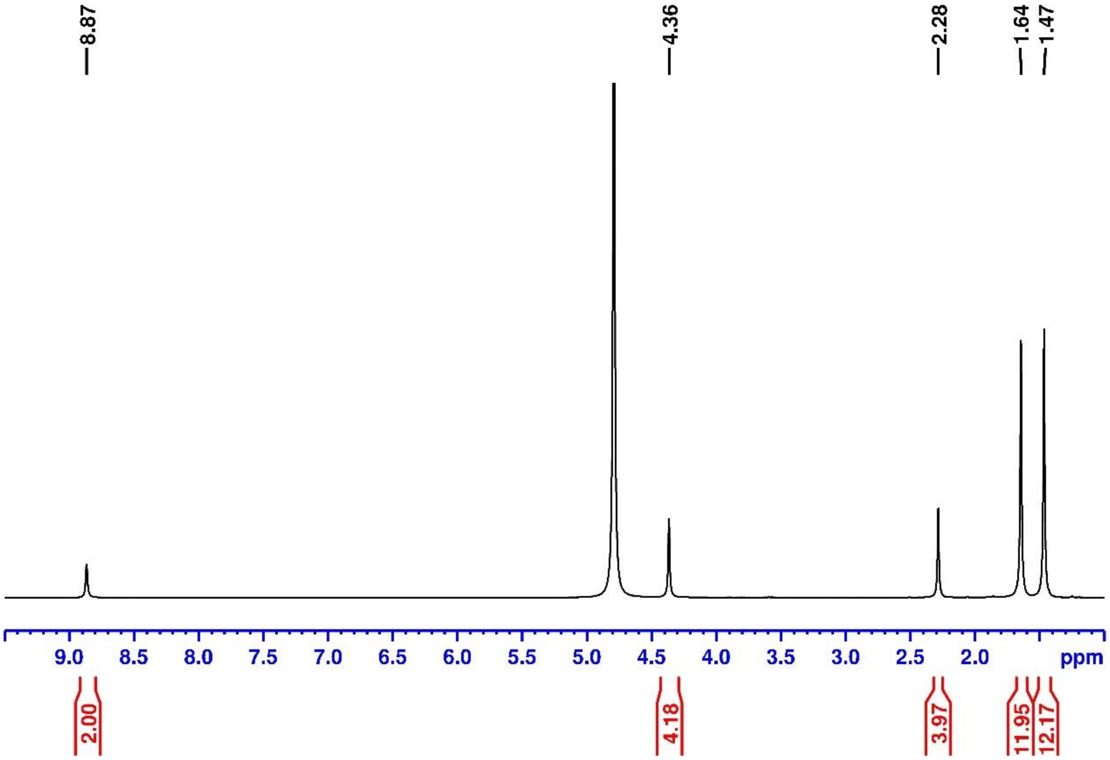


Fig. S3 ^1H NMR spectrum of compound $\mathbf{2^{Et}}$ in D_2O at RT.

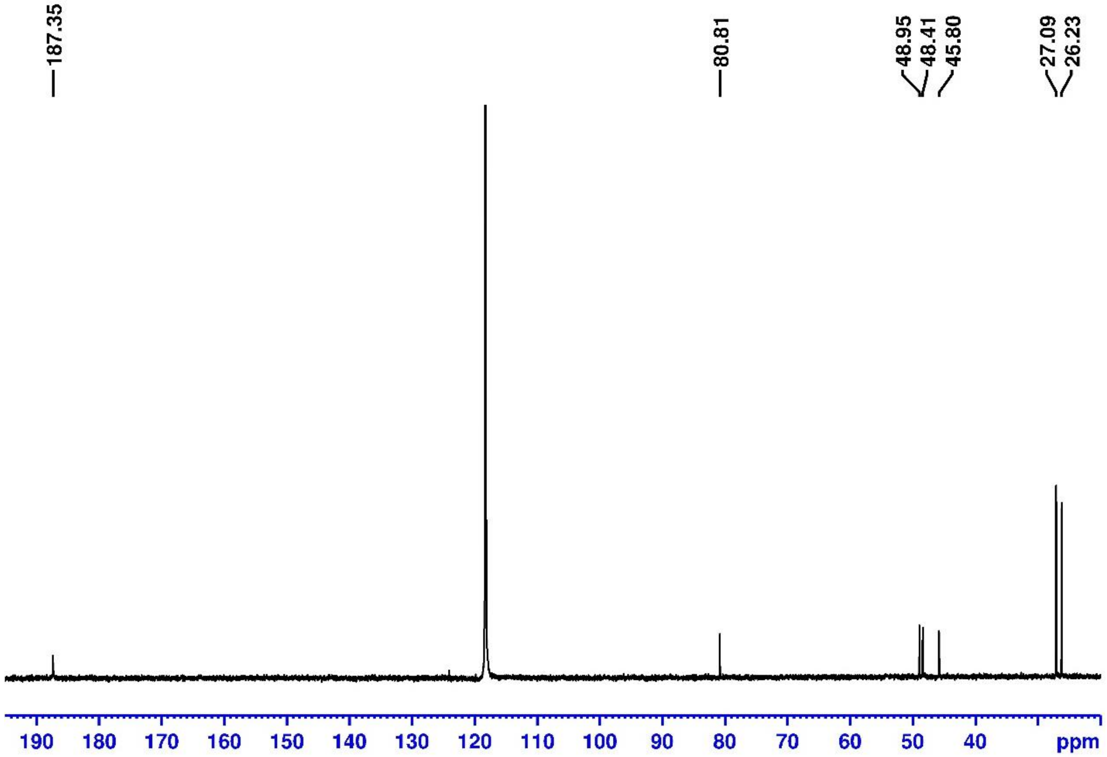


Fig. S4 $^{13}C\{^1H\}$ NMR spectrum of compound $\mathbf{2^{Et}}$ in CD_3CN at RT.

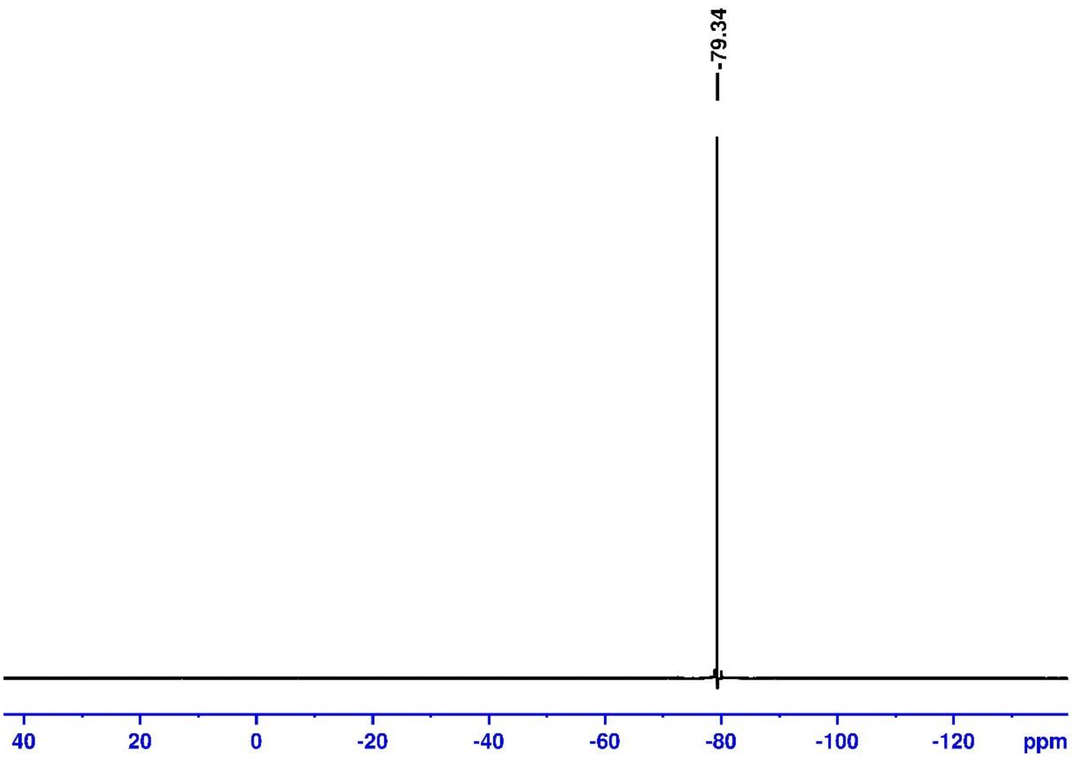


Fig. S5 $^{19}F\{^1H\}$ NMR spectrum of compound $\mathbf{2^{Et}}$ in CD_3CN at RT.

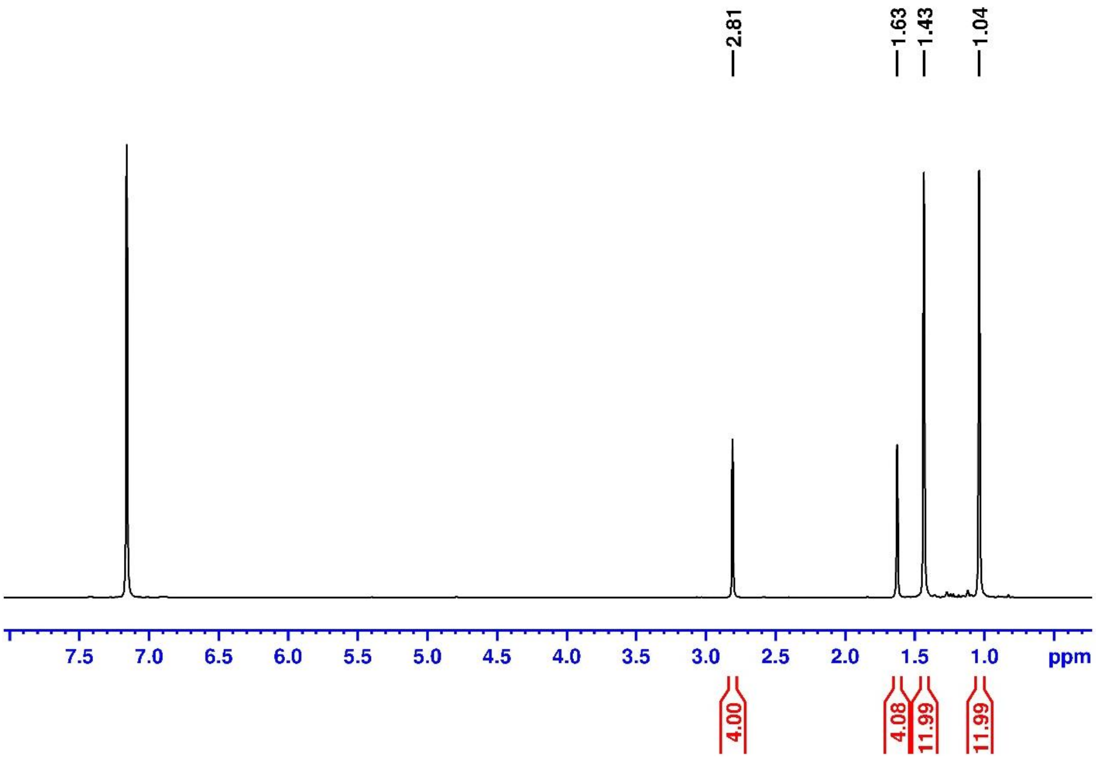


Fig. S6 ^1H NMR spectrum of pure $\mathbf{3^{Et}}$ in C_6D_6 at RT.

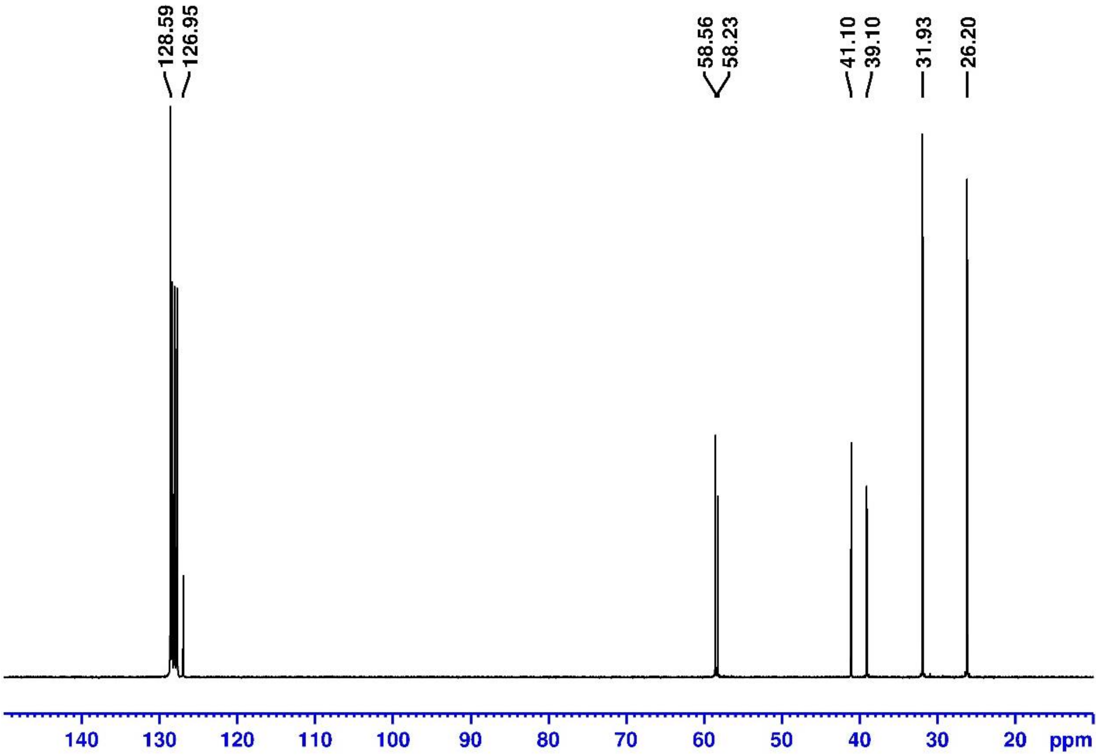


Fig. S7 $^{13}C\{^1H\}$ NMR spectrum of pure $\mathbf{3^{Et}}$ in C_6D_6 at RT (extra resonance at δ = 128.59 ppm due to the presence of C_6H_6 in $\mathbf{3^{Et}}$).

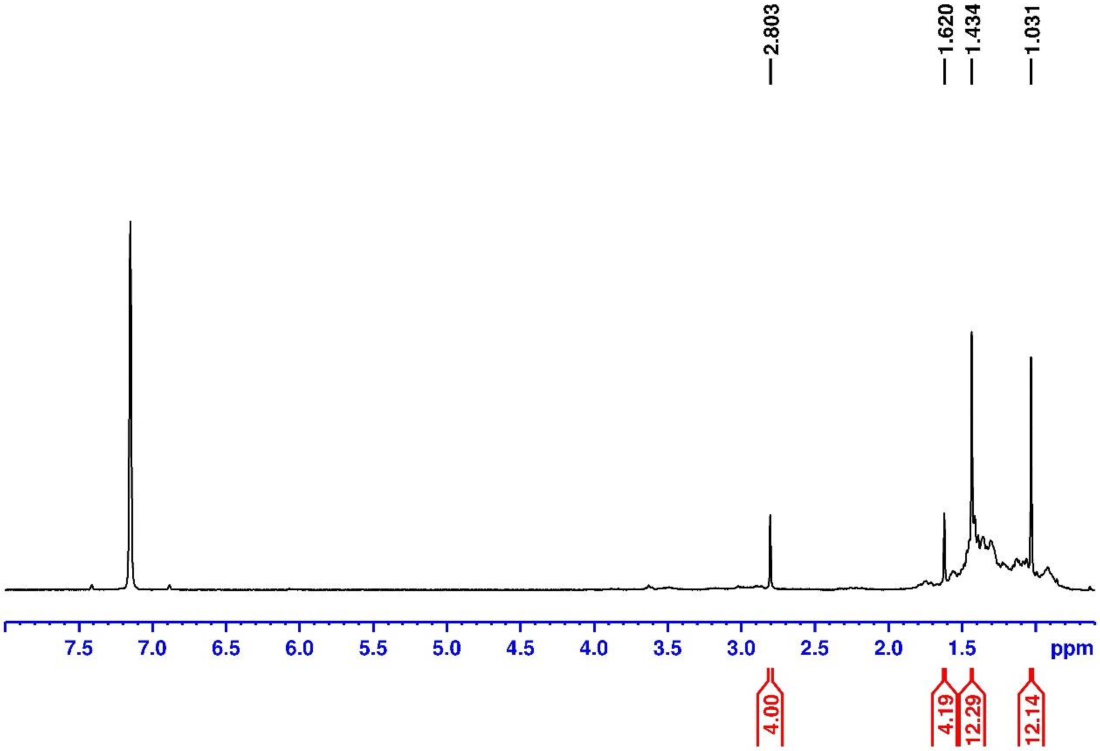


Fig. S8 ^1H NMR spectrum of crude $\mathbf{3^{Et}}$ in C_6D_6 at RT.

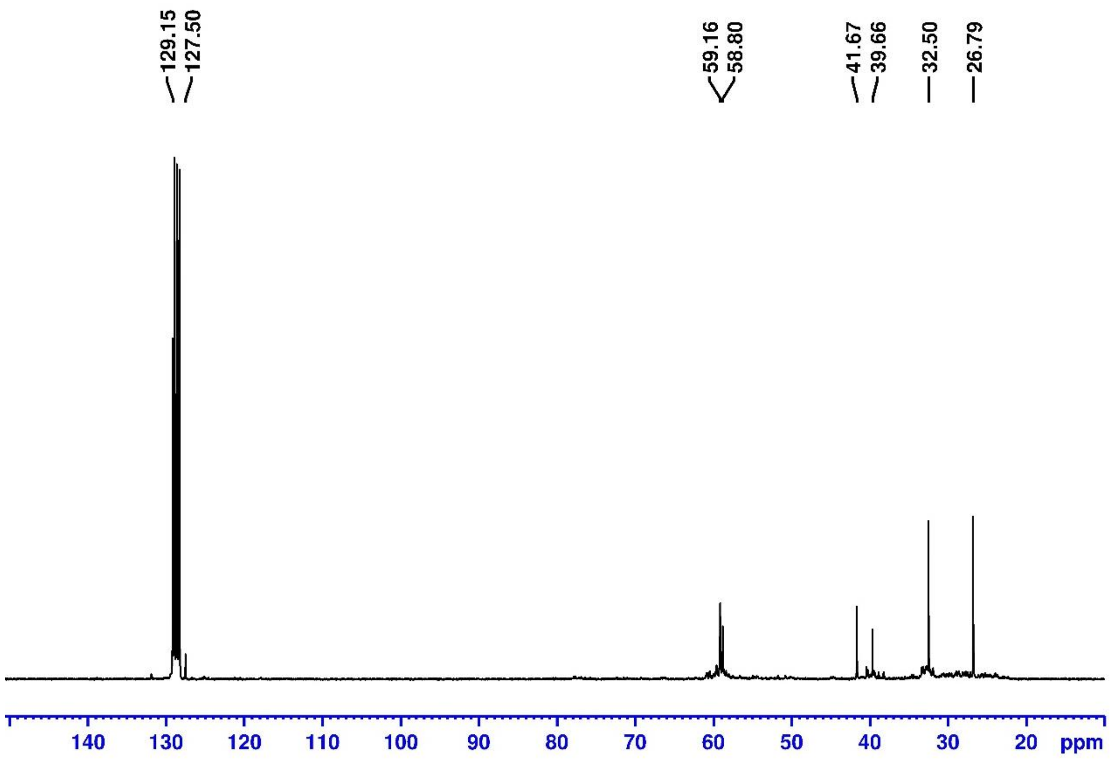


Fig. S9 $^{13}C\{^{1}H\}$ NMR spectrum of crude $\mathbf{3}^{\mathbf{Et}}$ in C_6D_6 at RT.

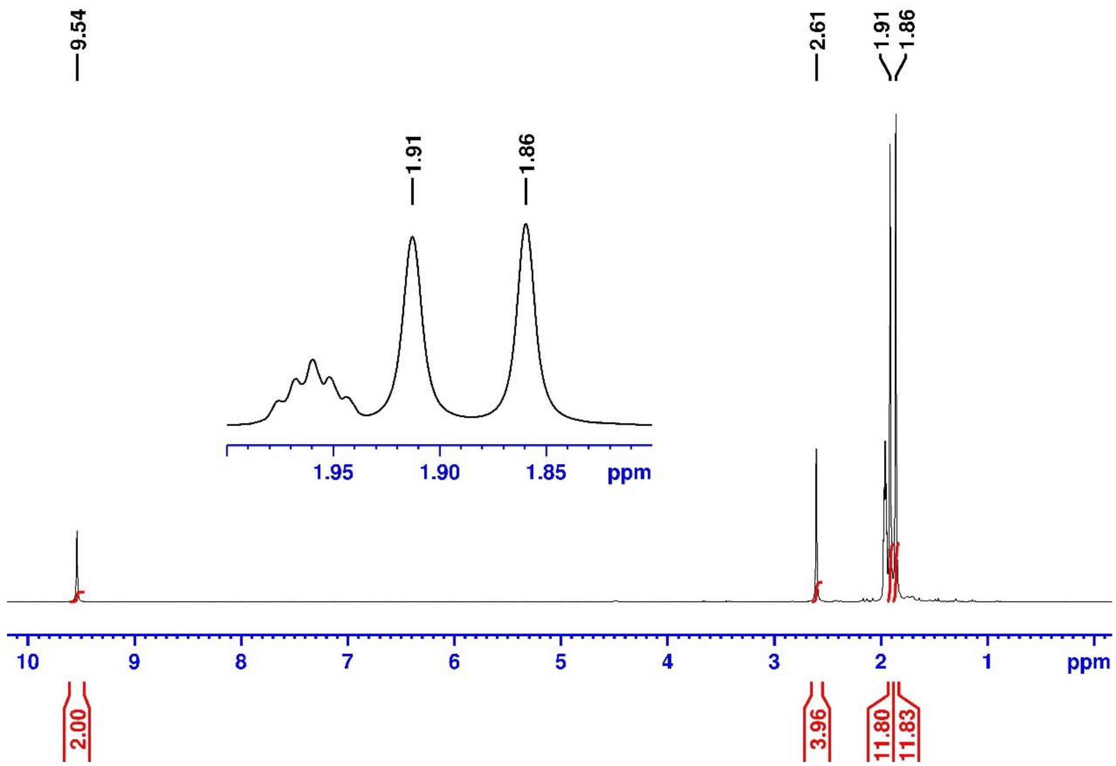


Fig. S10 ^{1}H NMR spectrum of compound $\mathbf{6}^{\mathbf{Et}}$ in CD_3CN at RT.

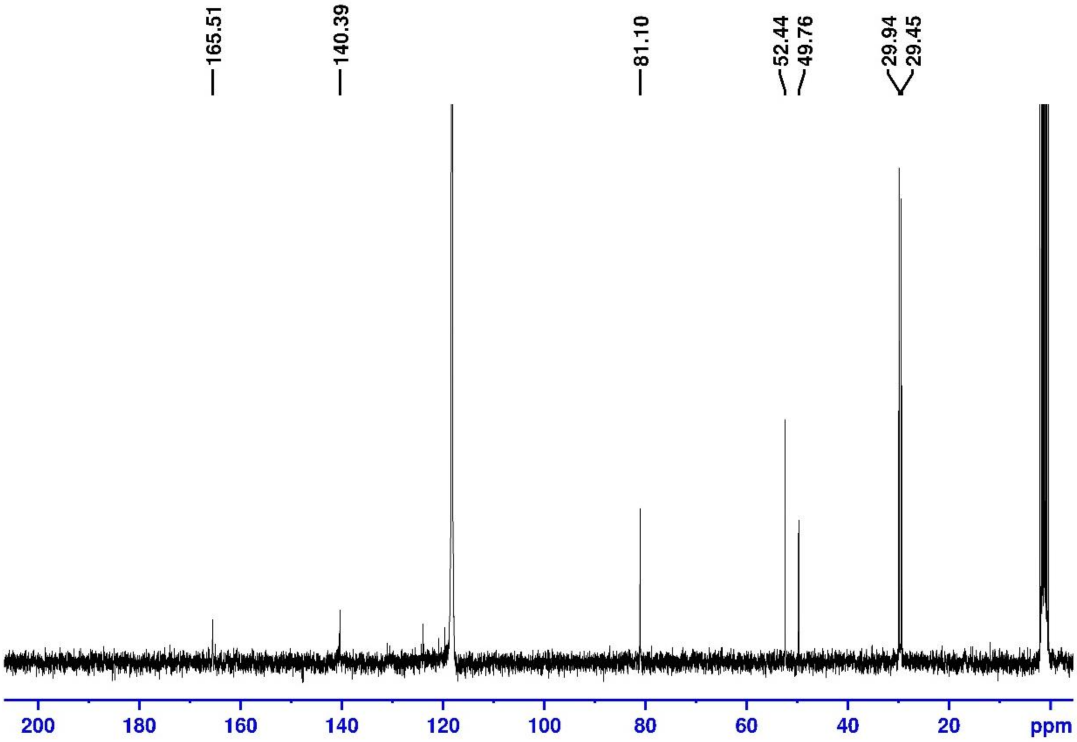


Fig. S11 $^{13}C\{^1H\}$ NMR spectrum of compound $\mathbf{6^{Et}}$ in CD_3CN at RT.

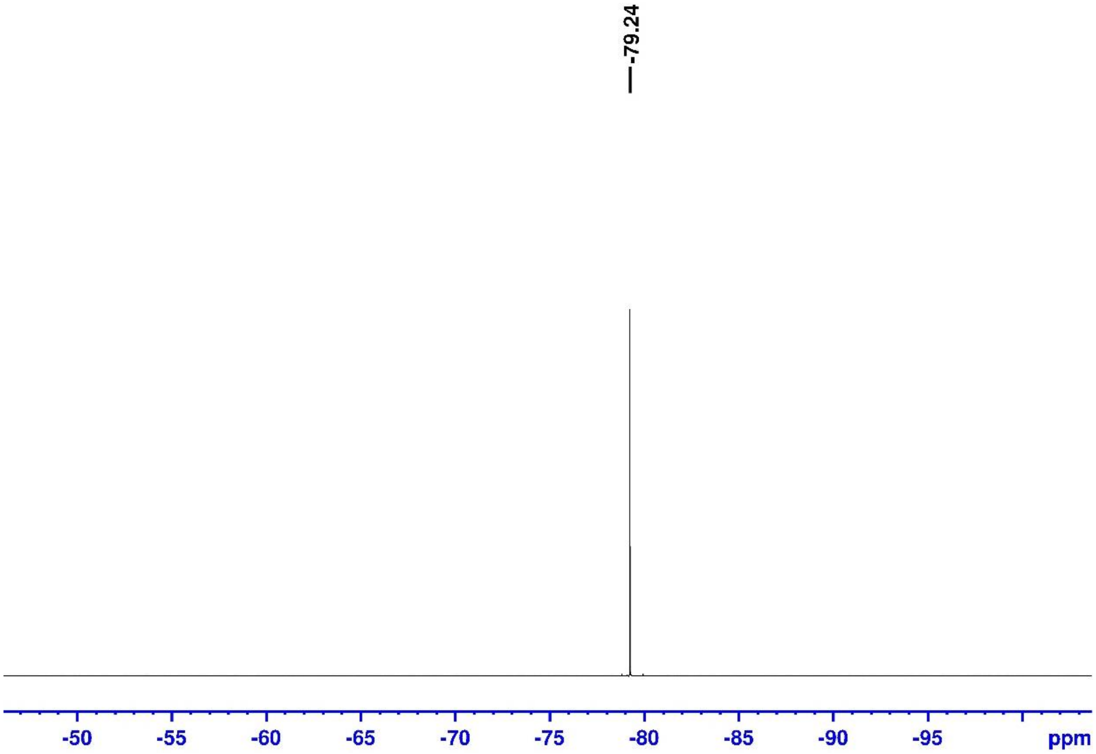


Fig. S12 $^{19}F\{^1H\}$ NMR spectrum of compound $\mathbf{6^{Et}}$ in CD_3CN at RT.

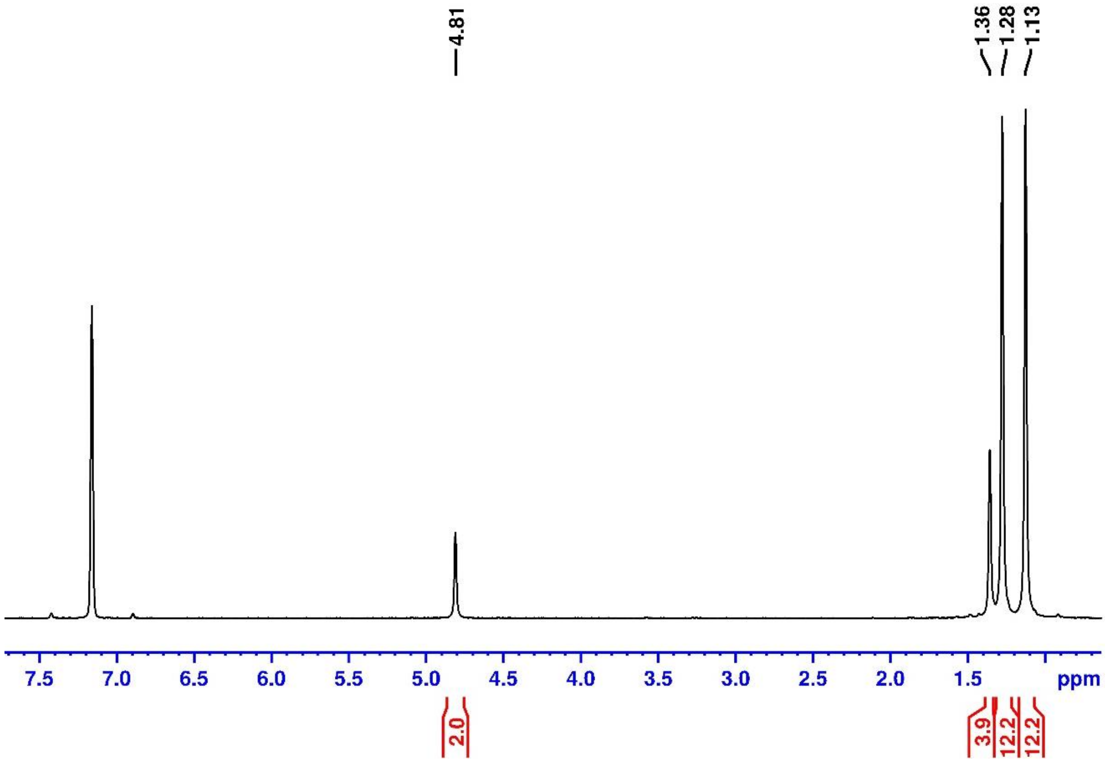


Fig. S13 ^{1}H NMR spectrum of compound $\mathbf{8^{Et}}$ in C_6D_6 at RT.

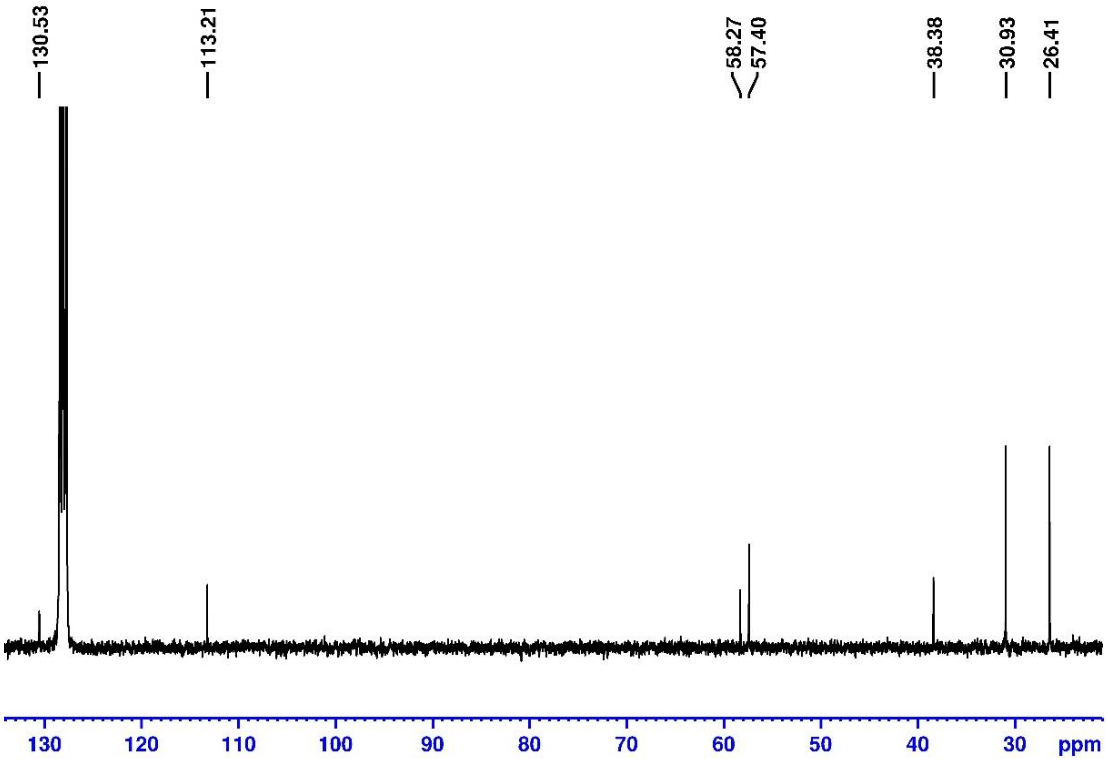


Fig. S14 $^{13}C\{^1H\}$ NMR spectrum of compound $\mathbf{8^{Et}}$ in C_6D_6 at RT.

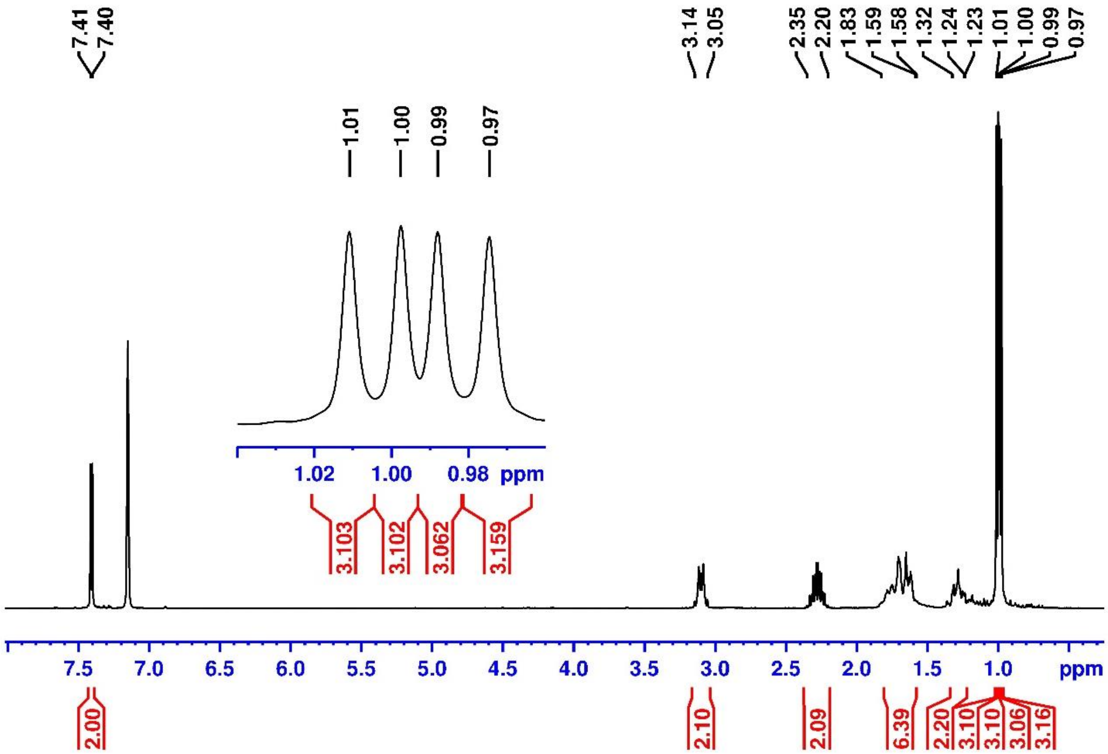


Fig. S15 ^{1}H NMR spectrum of compound $\mathbf{1^{Cy}}$ in C_6D_6 at RT.

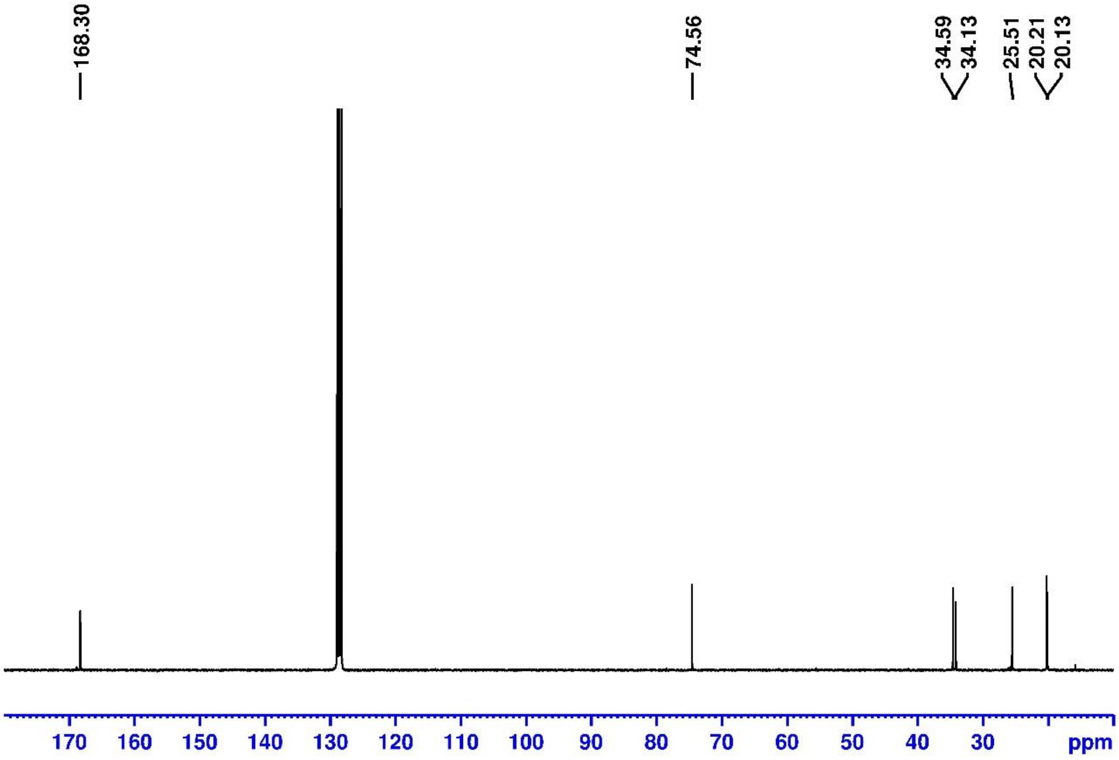


Fig. S16 $^{13}C\{^1H\}$ NMR spectrum of compound $\mathbf{1^{Cy}}$ in C_6D_6 at RT.

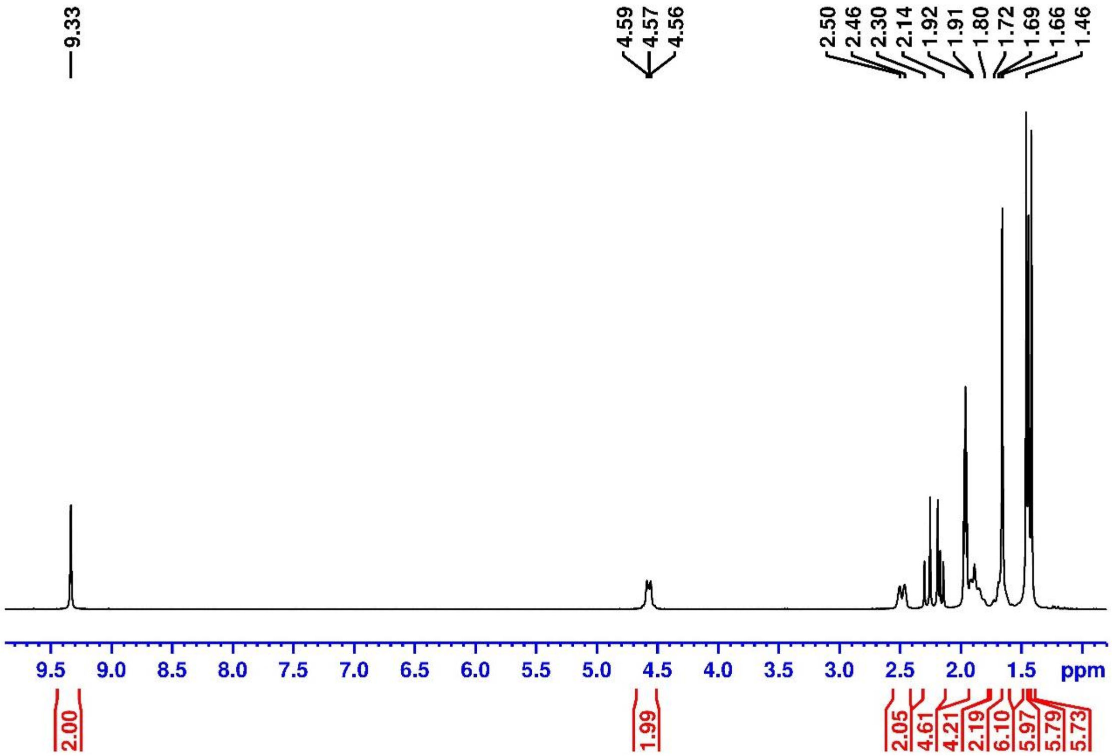


Fig. S17 ^{1}H NMR spectrum of compound **2^{Cy}** in CD_3CN at RT.

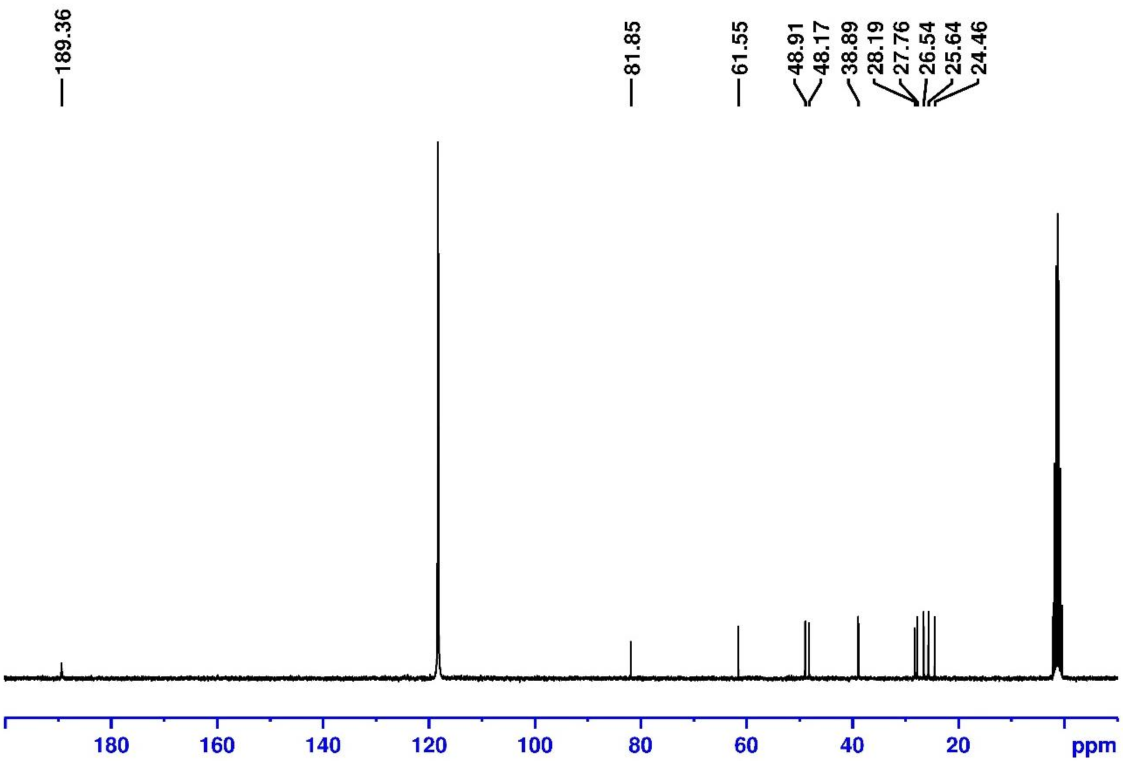


Fig. S18 ^{13}C{^{1}H} NMR spectrum of compound **2^{Cy}** in CD_3CN at RT.

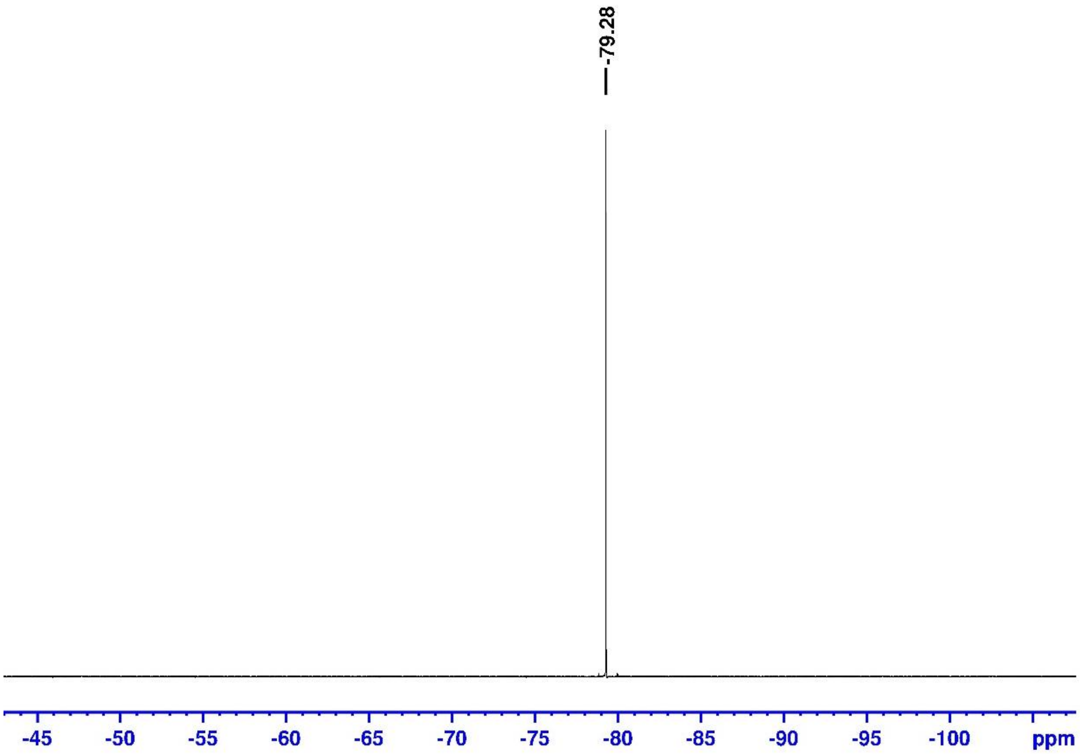


Fig. S19 $^{19}F\{^1H\}$ NMR spectrum of compound $\mathbf{2^{Cy}}$ in CD_3CN at RT.

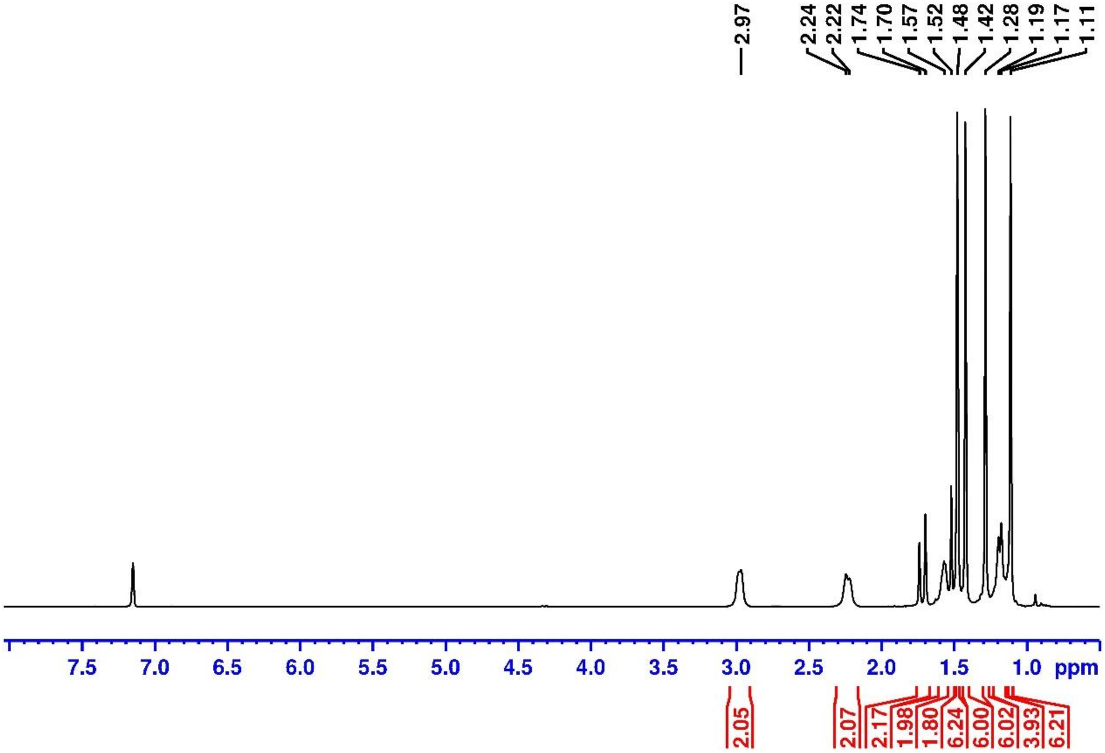


Fig. S20 ^1H NMR spectrum of compound $\mathbf{3^{Cy}}$ in C_6D_6 at RT.

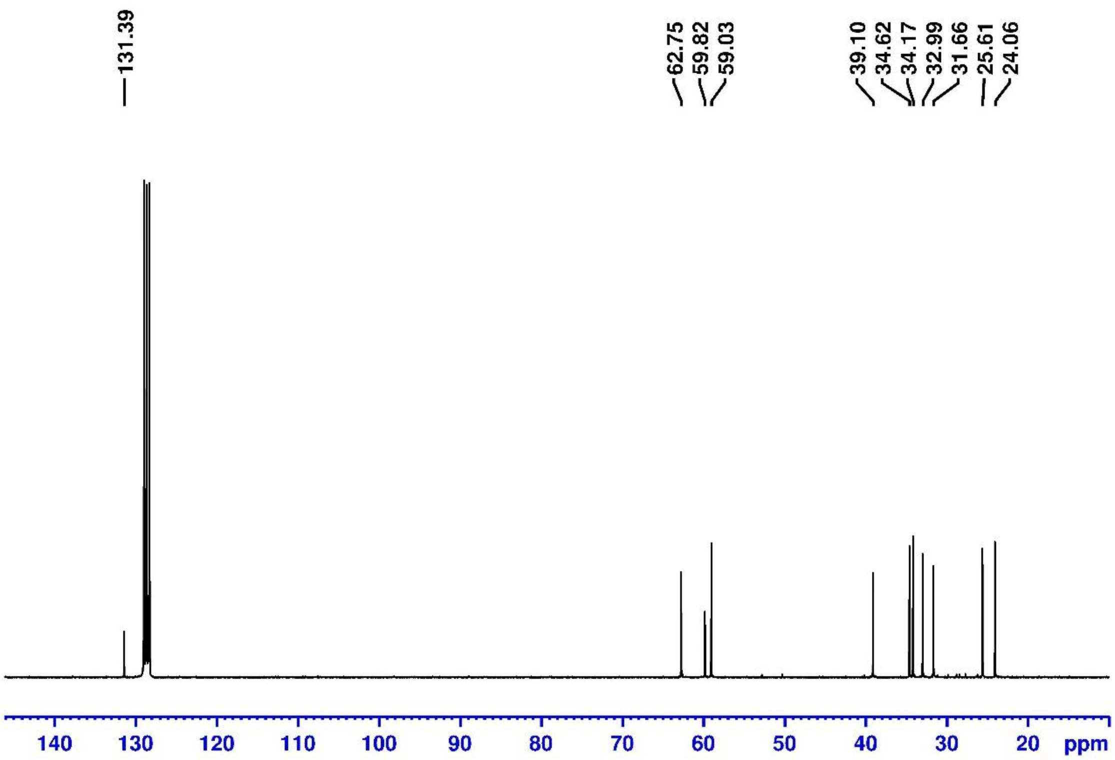


Fig. S21 $^{13}C\{^1H\}$ NMR spectrum of compound $\mathbf{3^{Cy}}$ in C_6D_6 at RT.

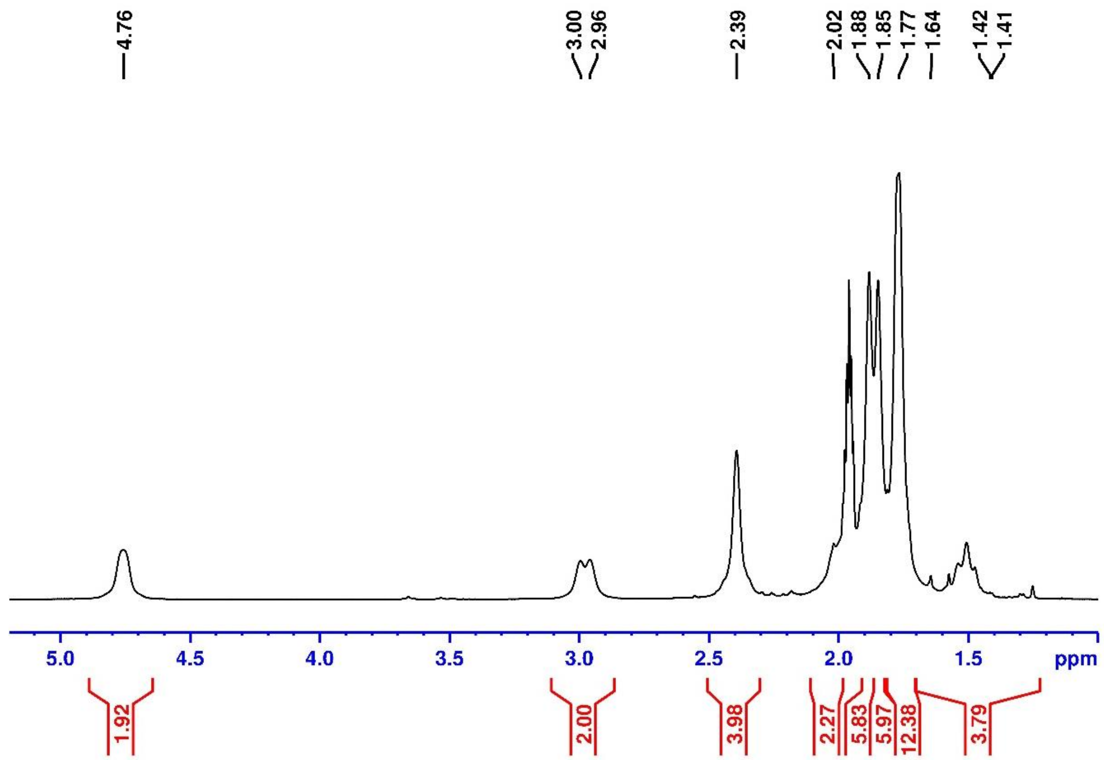


Fig. S22 ^1H NMR spectrum of compound $\mathbf{5^{Cy}}$ in CD_3CN at RT.

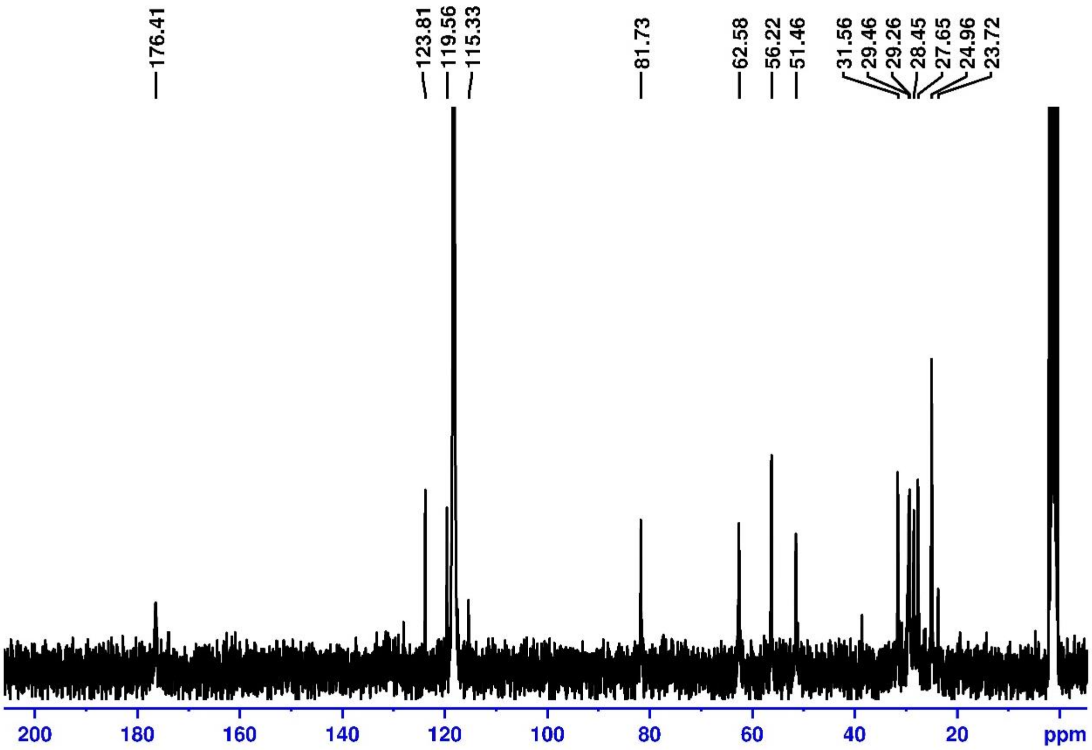


Fig. S23 $^{13}C\{^1H\}$ NMR spectrum of compound $\mathbf{5^{Cy}}$ in CD_3CN at RT.

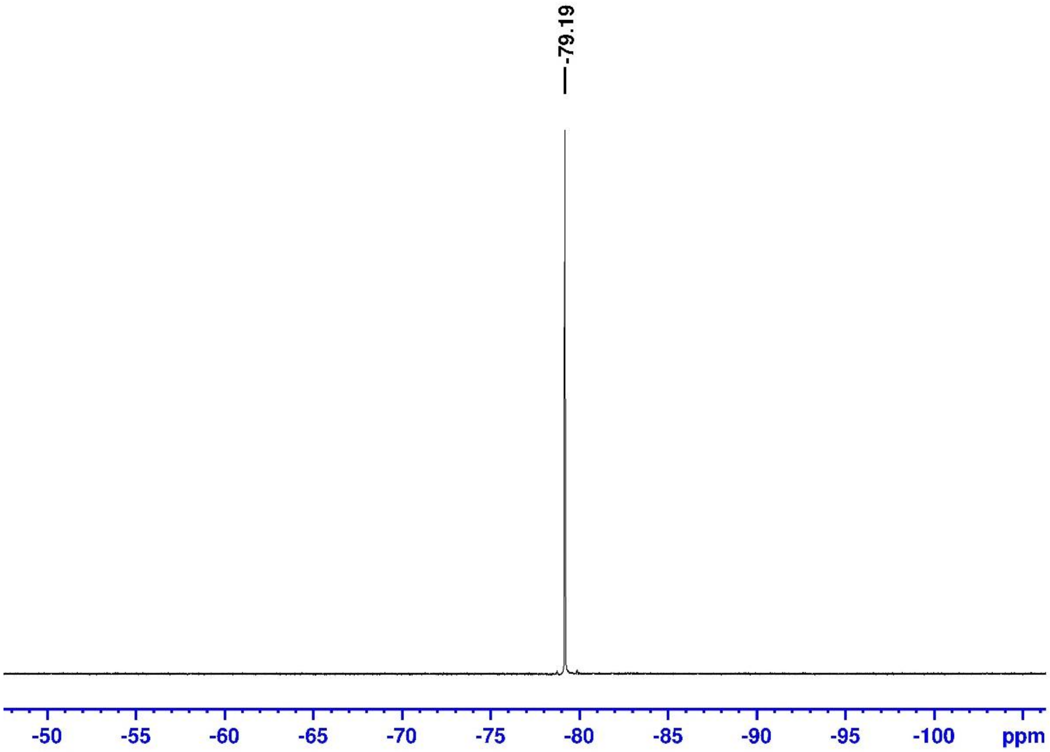


Fig. S24 $^{19}F\{^1H\}$ NMR spectrum of compound $\mathbf{5^{Cy}}$ in CD_3CN at RT.

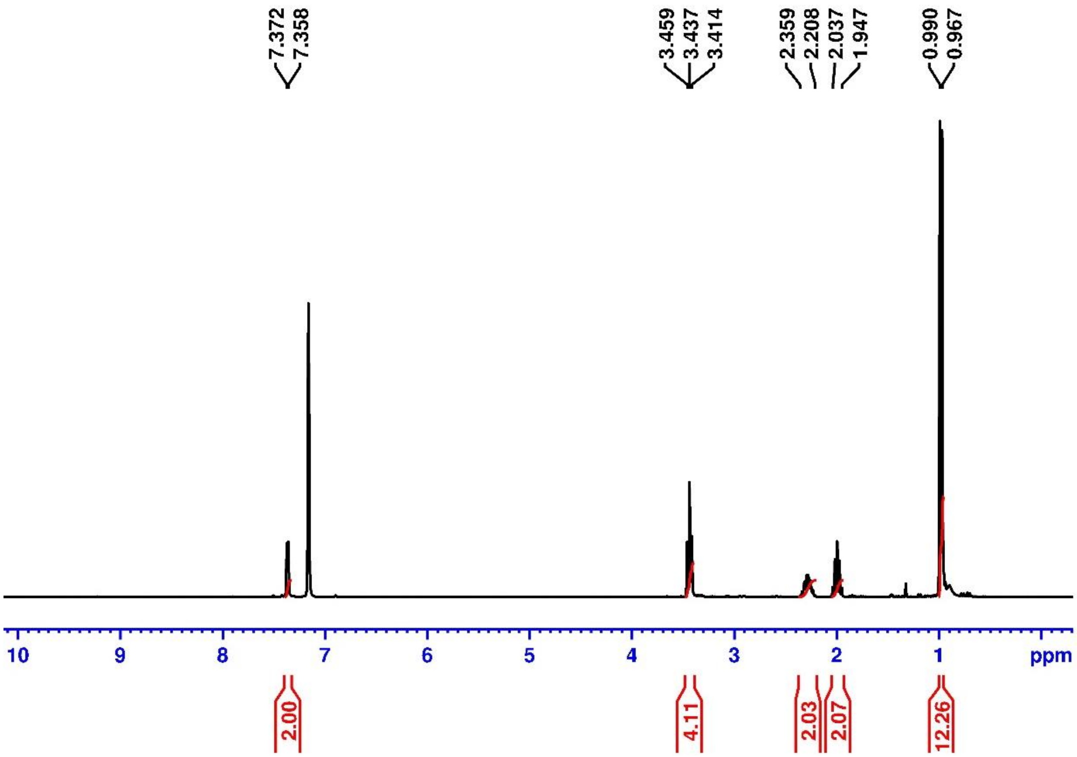


Fig. S25 ^{1}H NMR spectrum of compound **1^{Pr}** in C_6D_6 at RT.

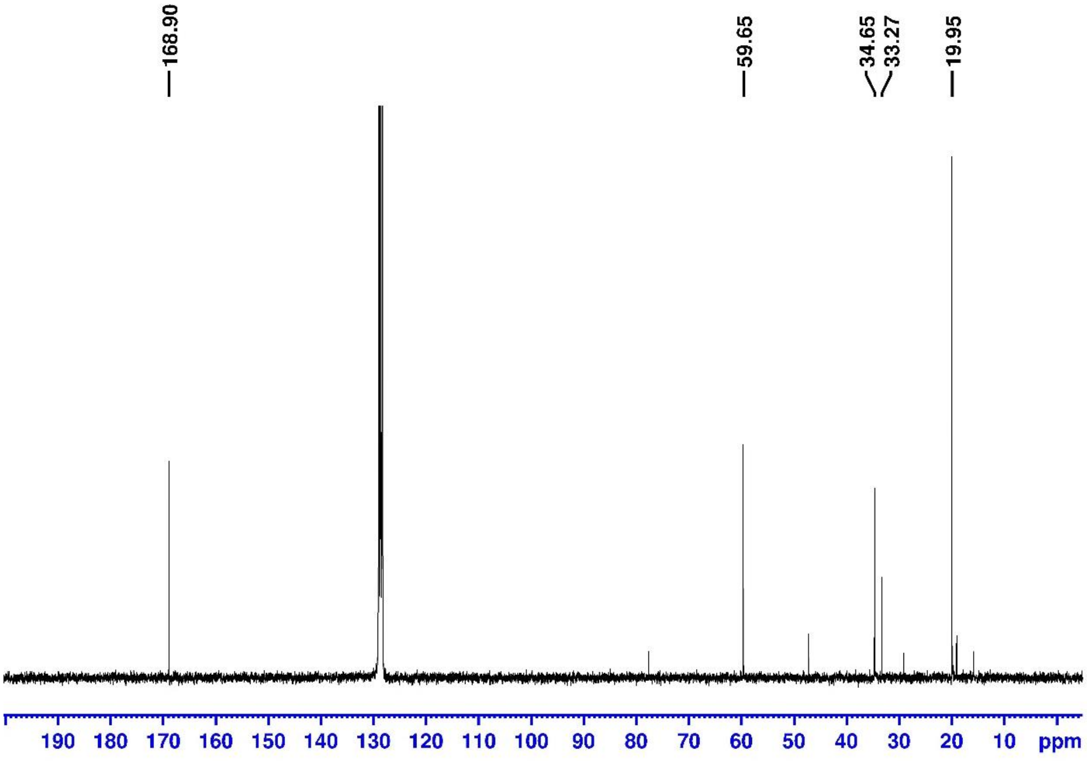


Fig. S26 $^{13}C\{^1H\}$ NMR spectrum of compound **1^{Pr}** in C_6D_6 at RT.

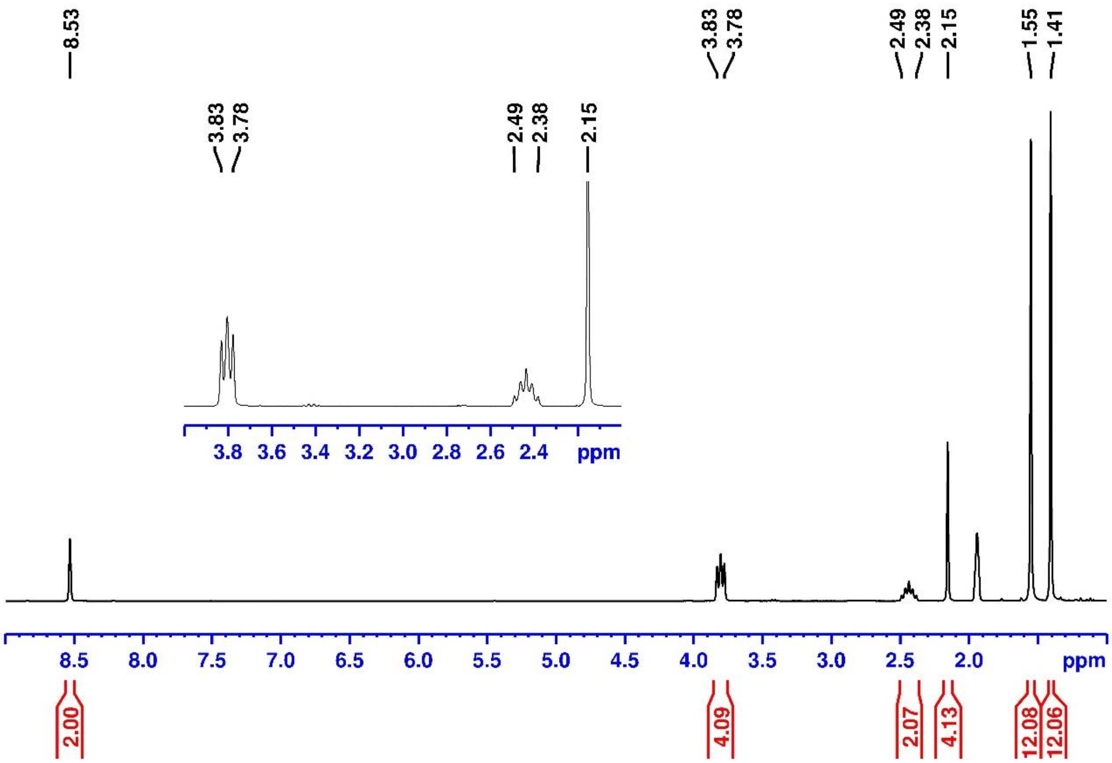


Fig. S27 ^{1}H NMR spectrum of compound **2^{Pr}** in CD$_3$CN at RT.

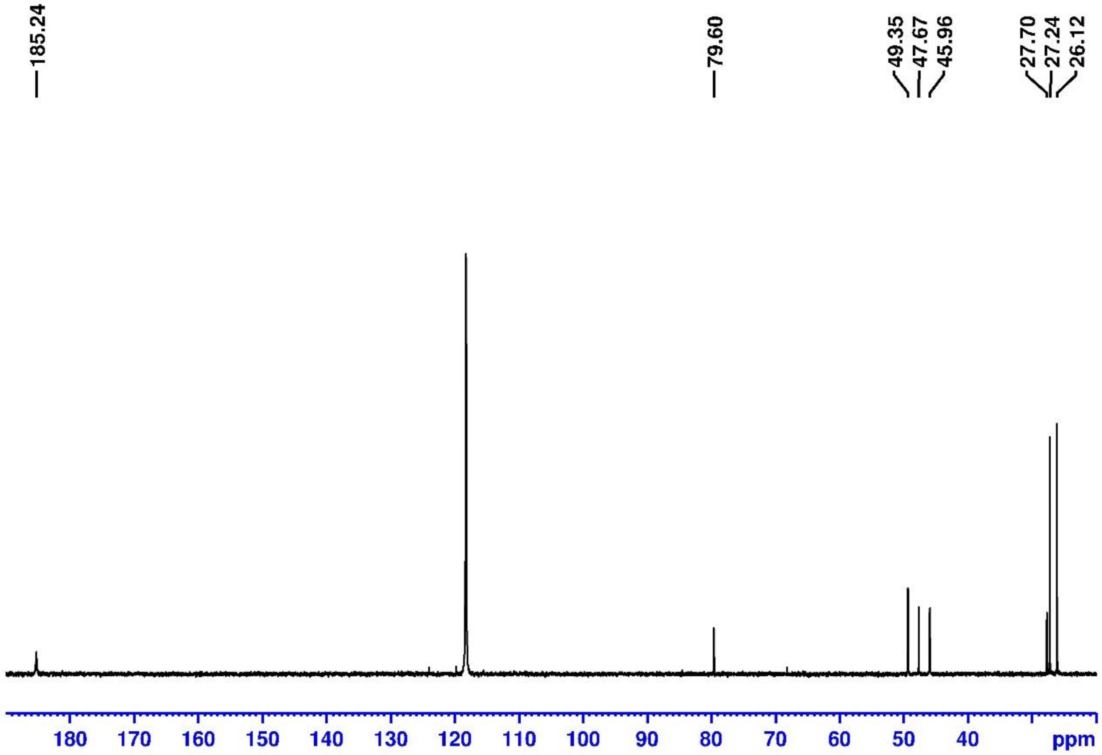


Fig. S28 ^{13}C{^{1}H} NMR spectrum of compound **2^{Pr}** in CD$_3$CN at RT.

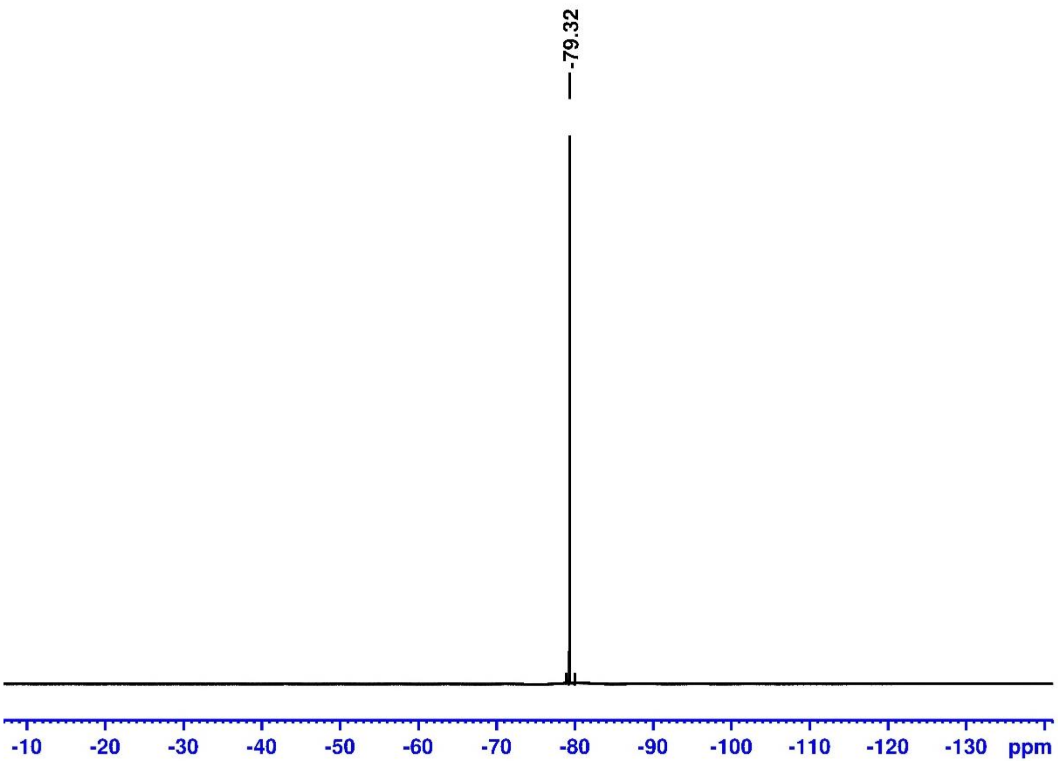


Fig. S29 $^{19}F\{^1H\}$ NMR spectrum of compound **2**

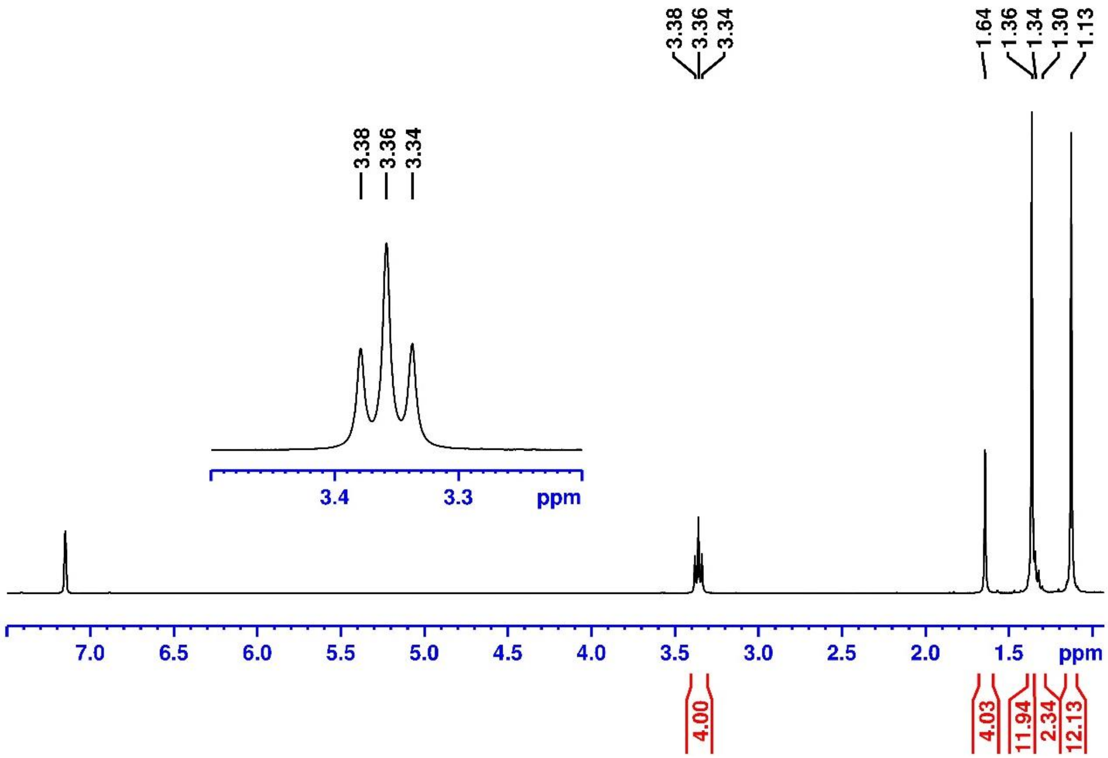


Fig. S30 ^1H NMR spectrum of compound $\mathbf{3^{Pr}}$ in C_6D_6 at RT.

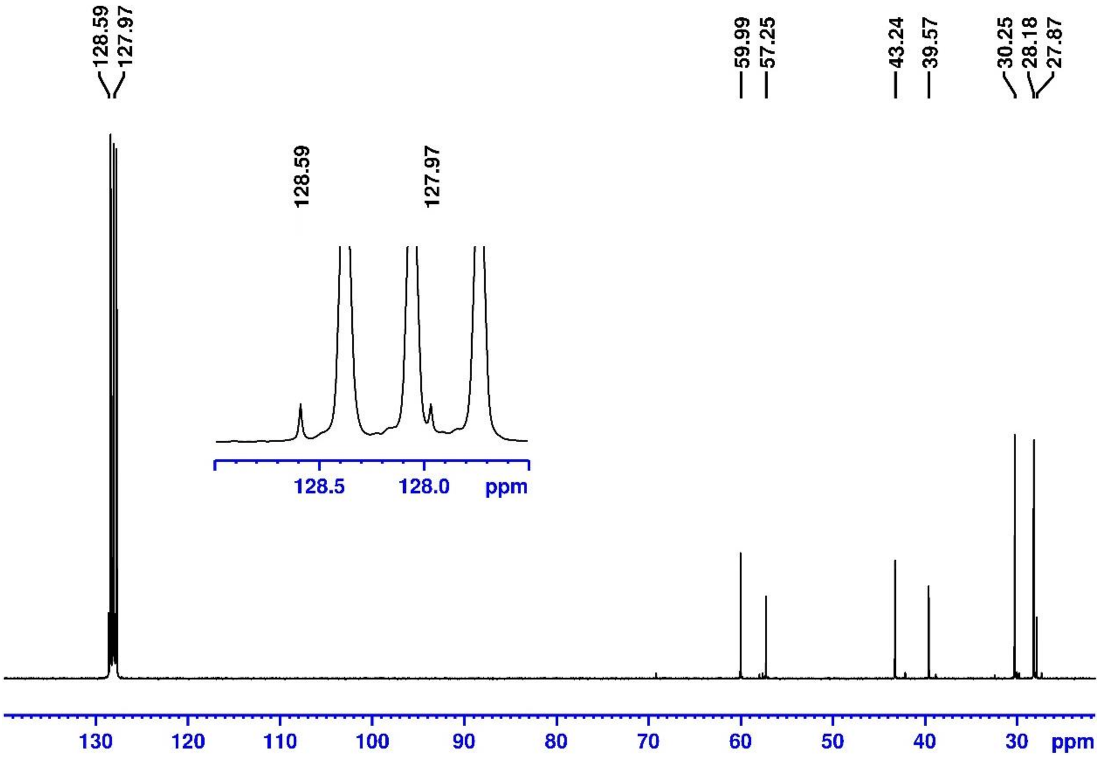


Fig. S31 $^{13}C\{^1H\}$ NMR spectrum of compound $\mathbf{3^{Pr}}$ in C_6D_6 at RT (extra resonance at δ = 128.59 ppm due to the presence of C_6H_6 in $\mathbf{3^{Pr}}$).

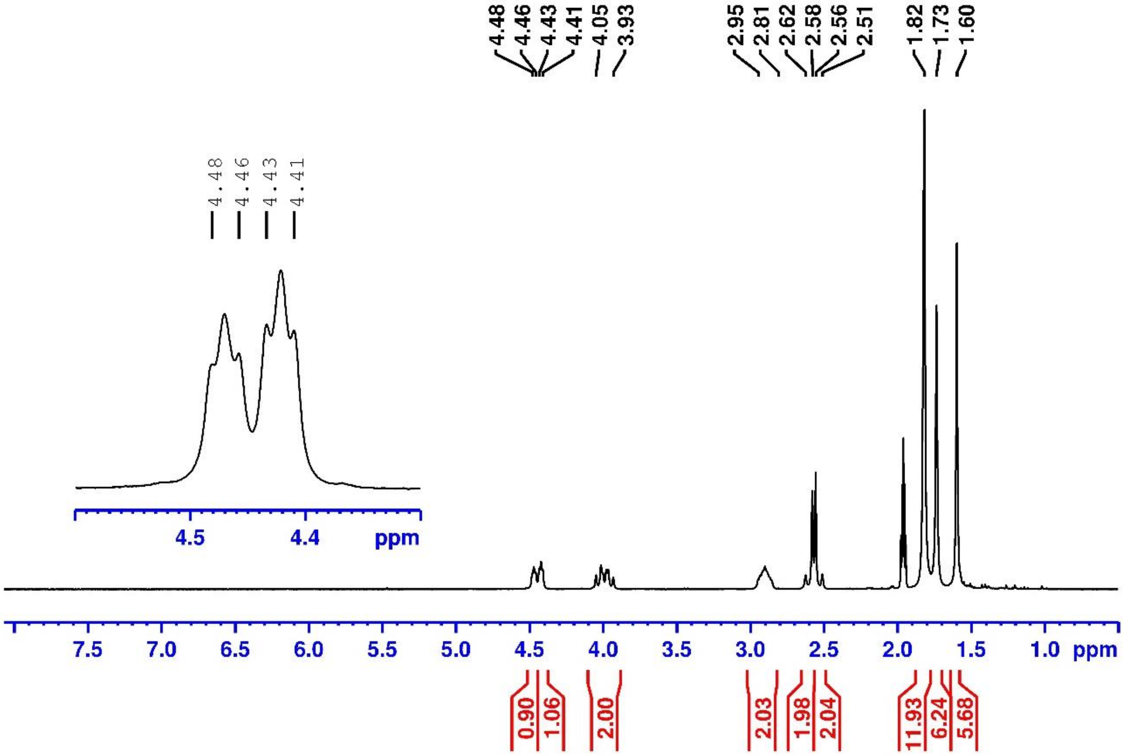


Fig. S32 ^1H NMR spectrum of compound $\mathbf{5^{Pr}}$ in CD_3CN at RT.

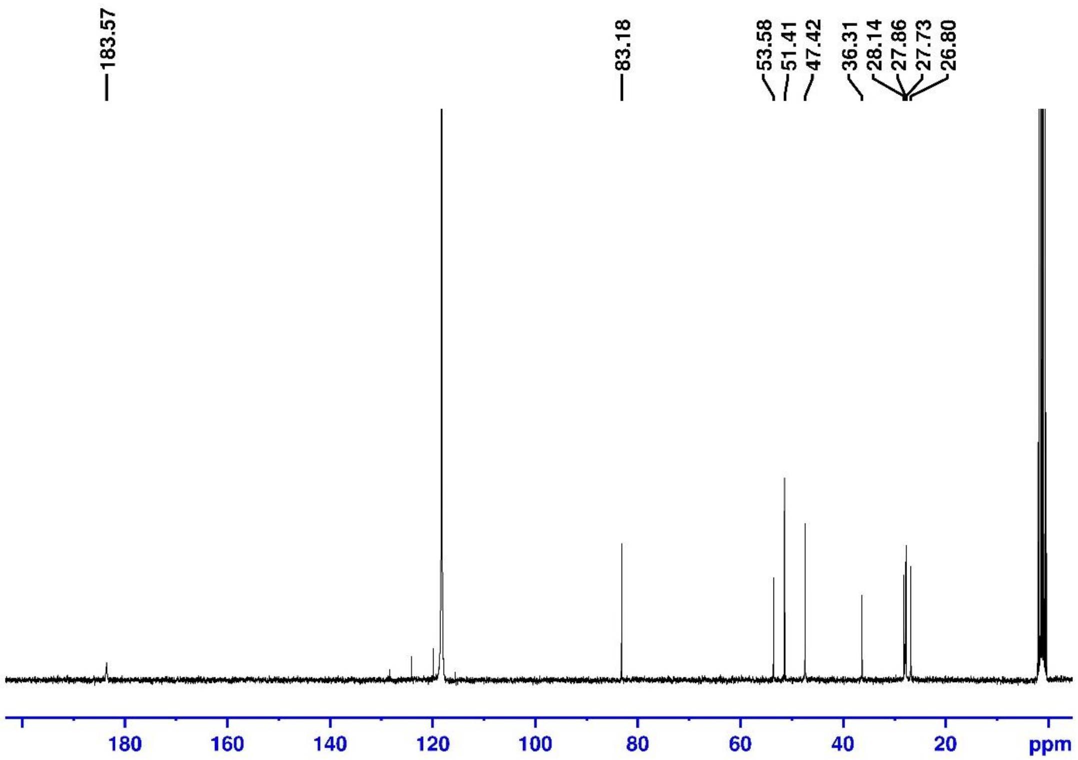


Fig. S33 $^{13}C\{^1H\}$ NMR spectrum of compound $\mathbf{5^{Pr}}$ in CD_3CN at RT.

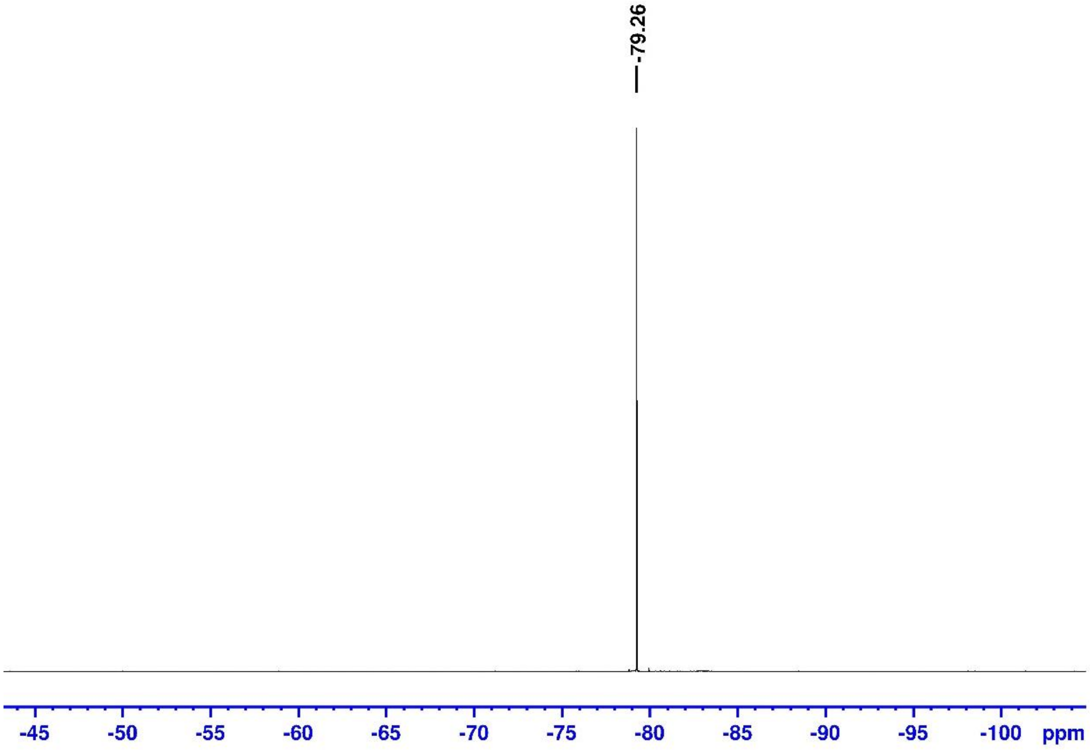


Fig. S34 $^{19}F\{^1H\}$ NMR spectrum of compound $\mathbf{5^{Pr}}$ in CD_3CN at RT.

UV/Vis spectra

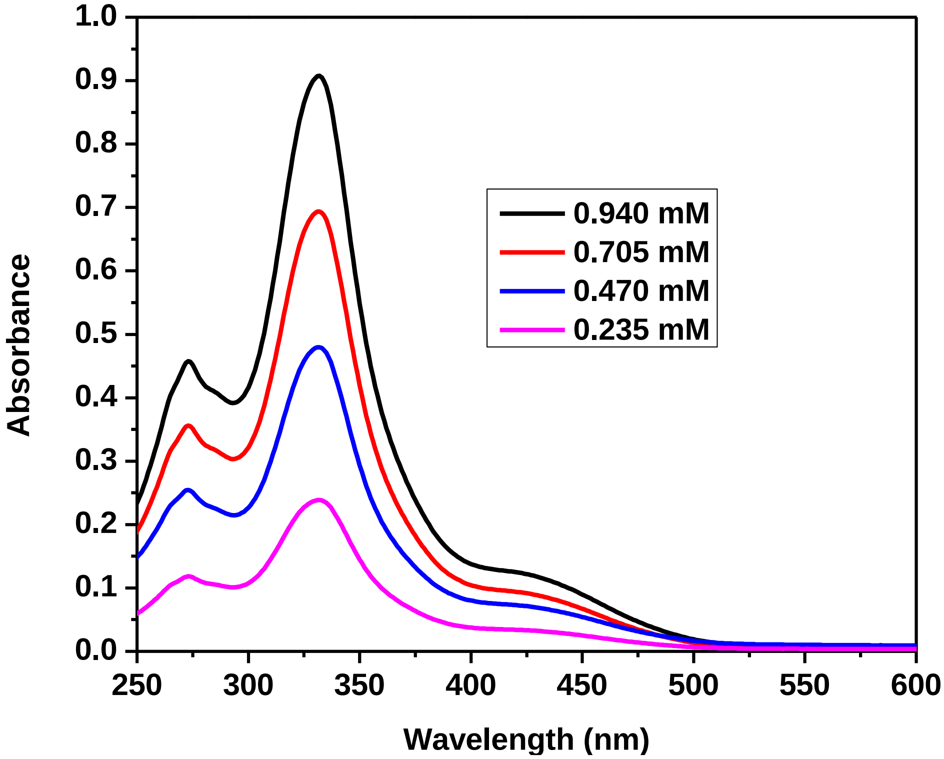
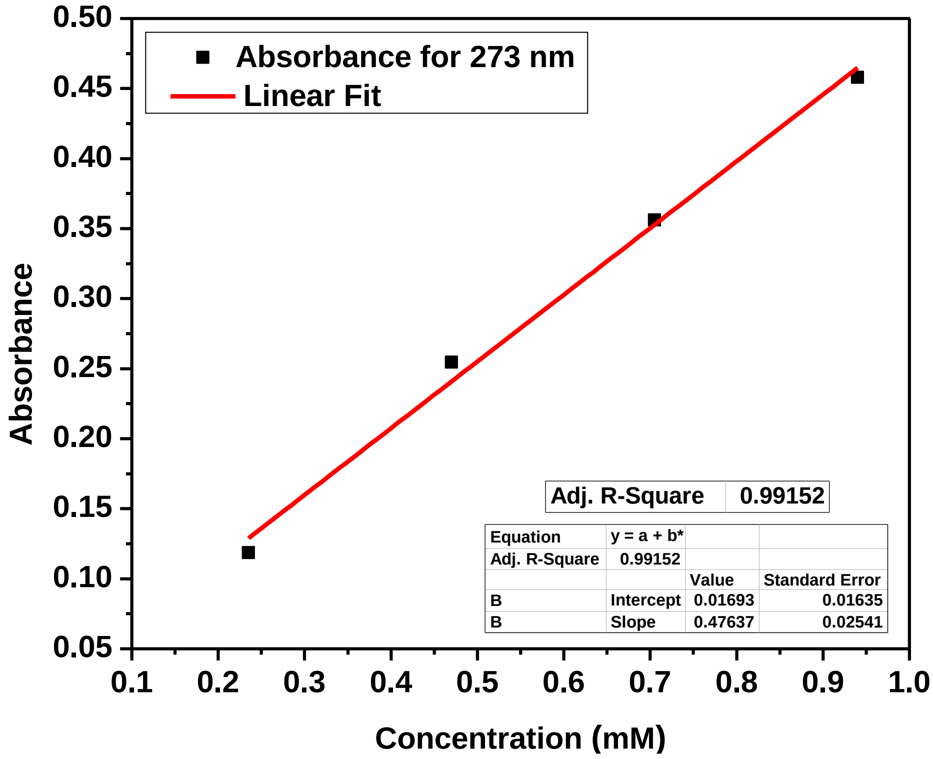


Fig. S35 UV/Vis spectrum of **4**$^{\mathbf{Et}}$ in acetonitrile at various concentrations at room temperature.



Adj. R-Square 0.99152

Equation	y = a + b*		
Adj. R-Square	0.99152		
		Value	Standard Error
B	Intercept	0.01693	0.01635
B	Slope	0.47637	0.02541

Fig. S36 Linear regression of **4**$^{\mathbf{Et}}$ at 273 nm.

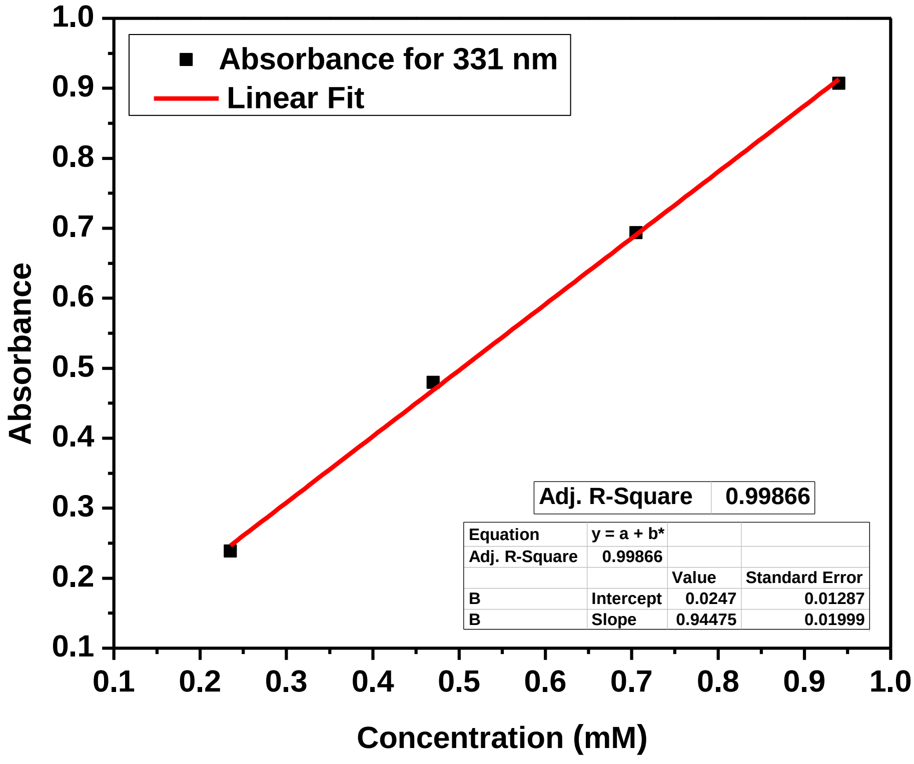


Fig. S37 Linear regression of $\mathbf{4}^{\mathrm{Et}}$ at 331 nm.

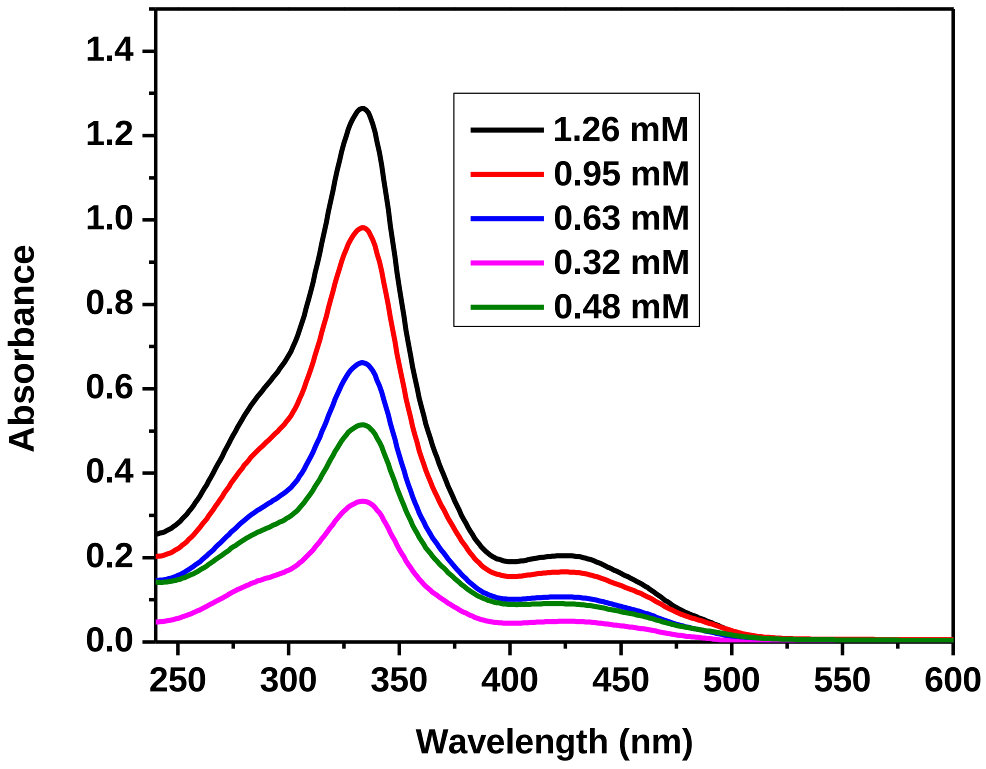


Fig. S38 UV/Vis spectrum of $\mathbf{4}^{\mathrm{Cy}}$ in acetonitrile at various concentrations at room temperature.

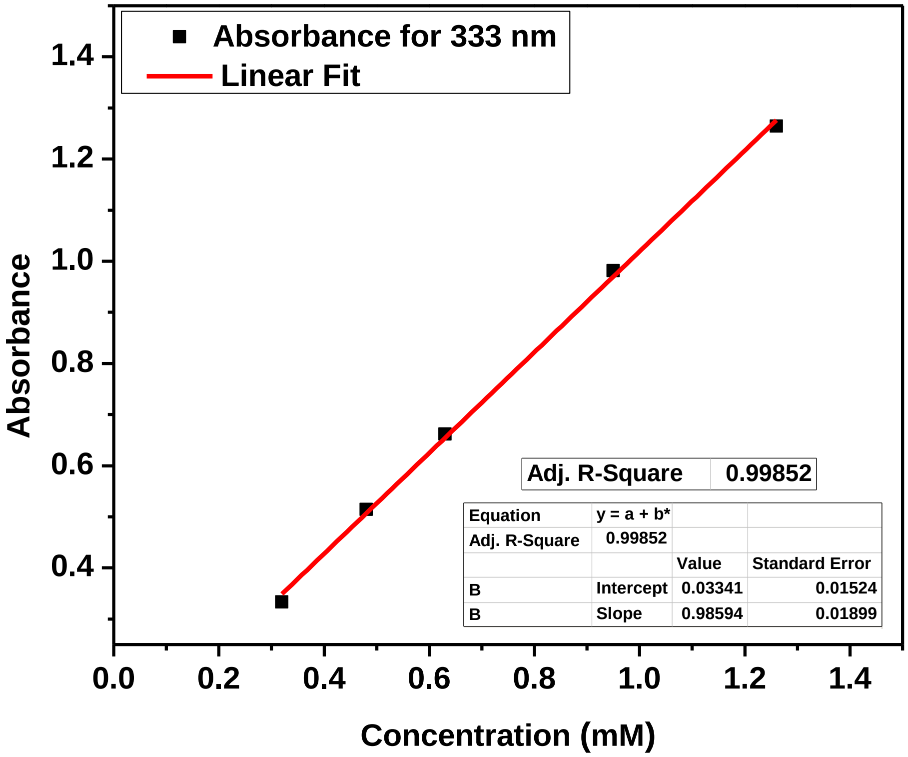


Fig. S39 Linear regression of **4**^{Cy} at 333 nm.

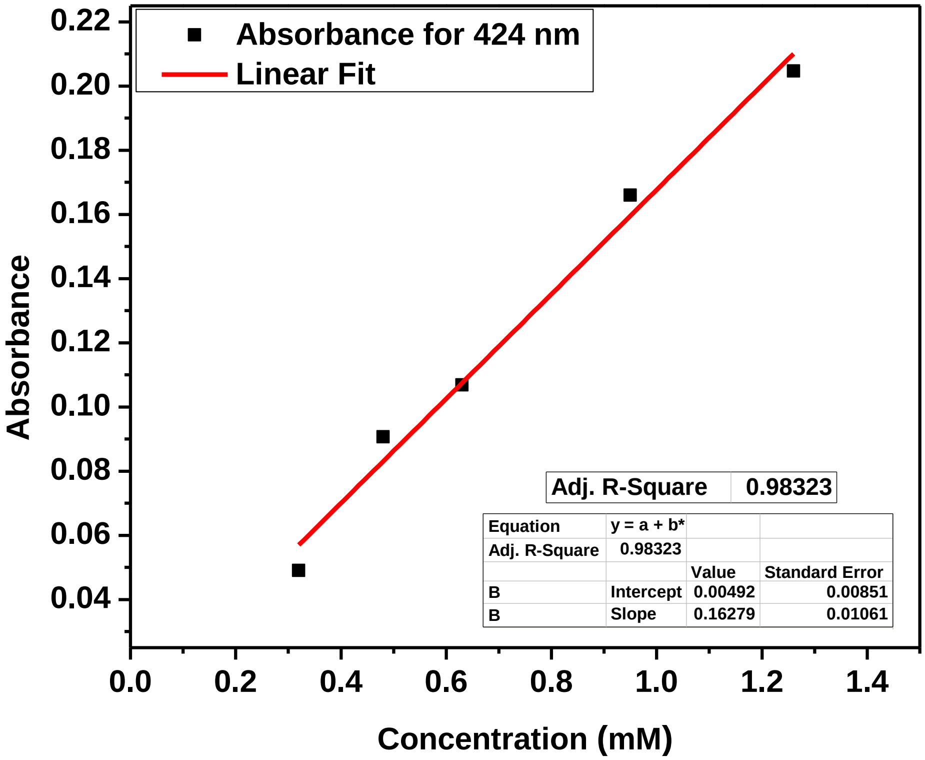


Fig. S40 Linear regression of **4**^{Cy} at 424 nm.

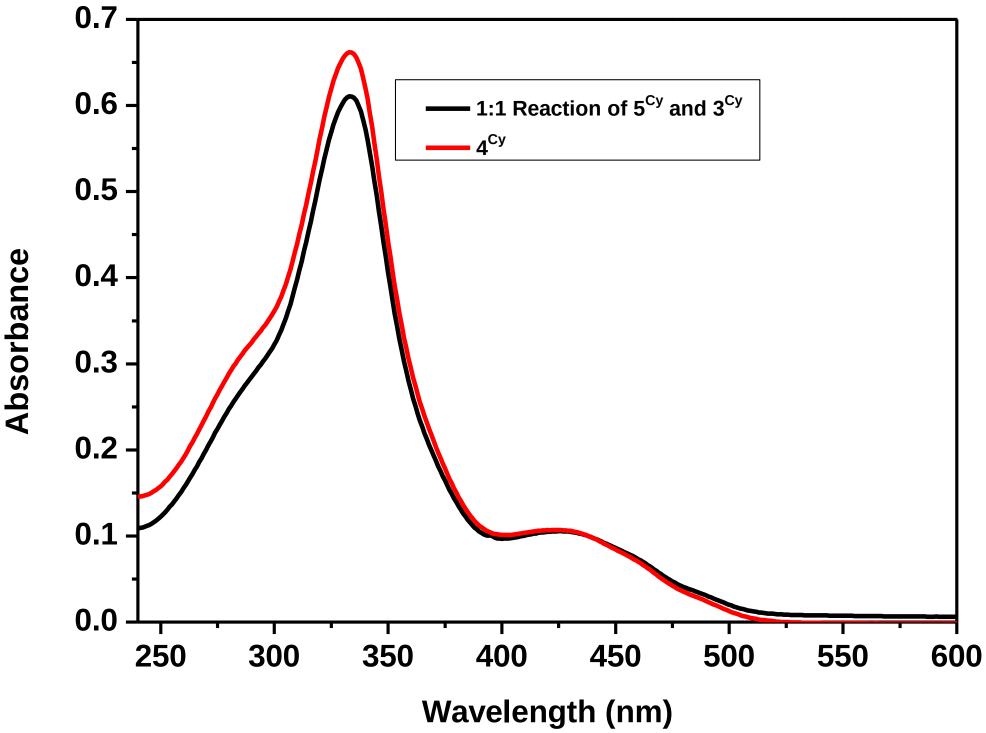


Fig. S41 Comparison of UV/Vis spectrum from 1:1 reaction of $\mathbf{5^{Cy}}$ and $\mathbf{3^{Cy}}$ with UV/Vis spectrum of $\mathbf{4^{Cy}}$ in acetonitrile at room temperature.

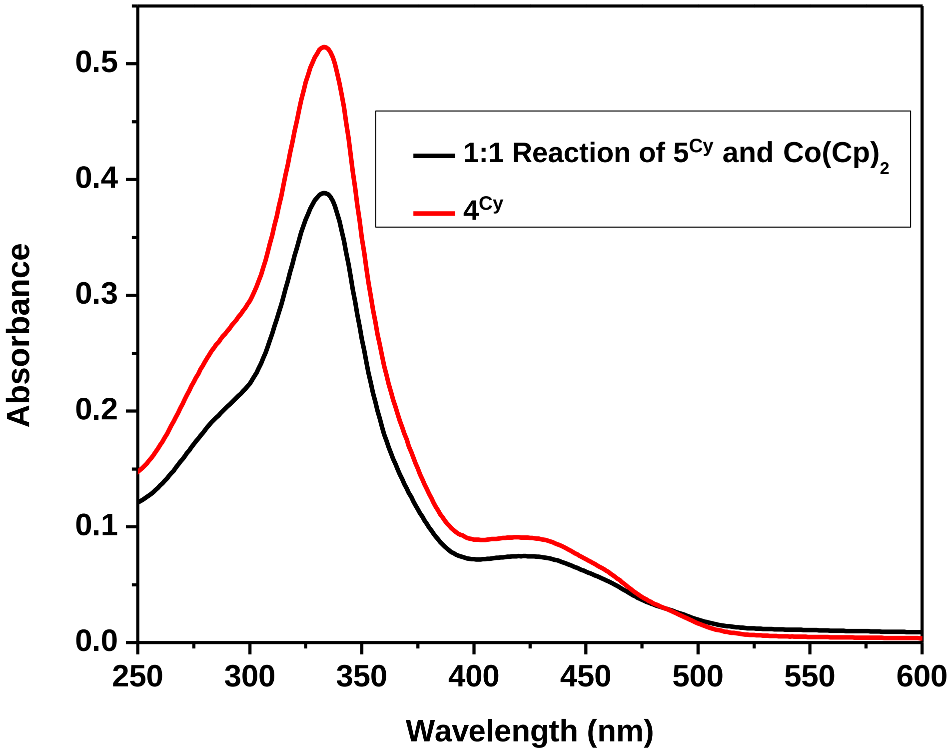


Fig. S42 Comparison of UV/Vis spectrum of 1-e reduced product of $\mathbf{5^{Cy}}$ with $\mathbf{4^{Cy}}$ in acetonitrile at room temperature.

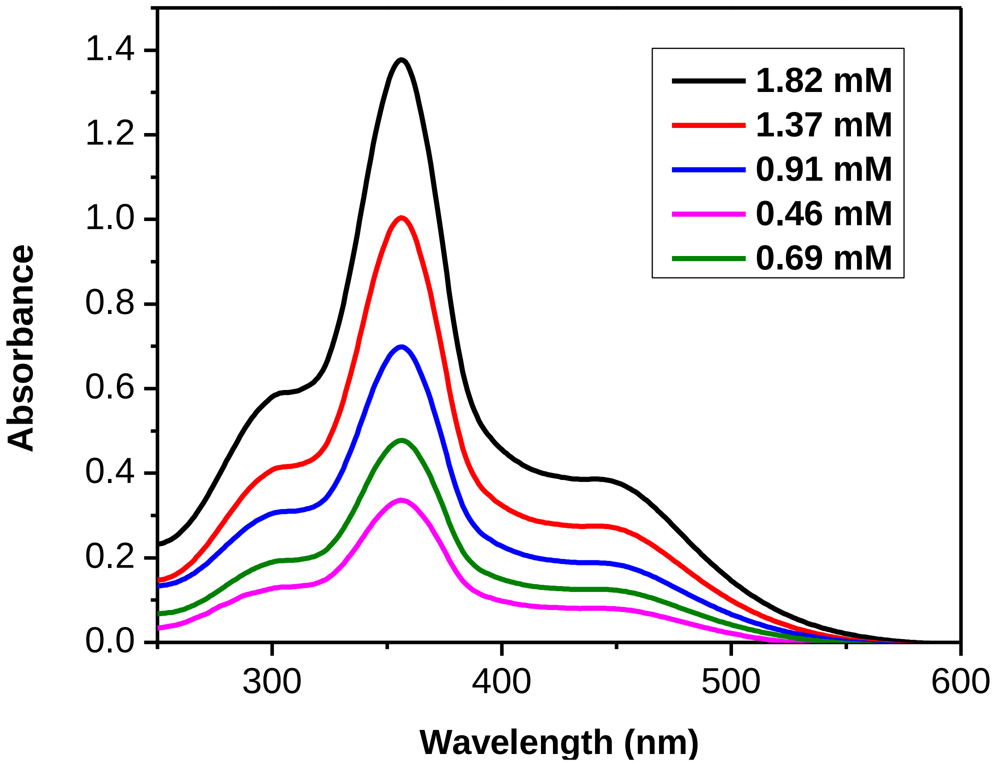
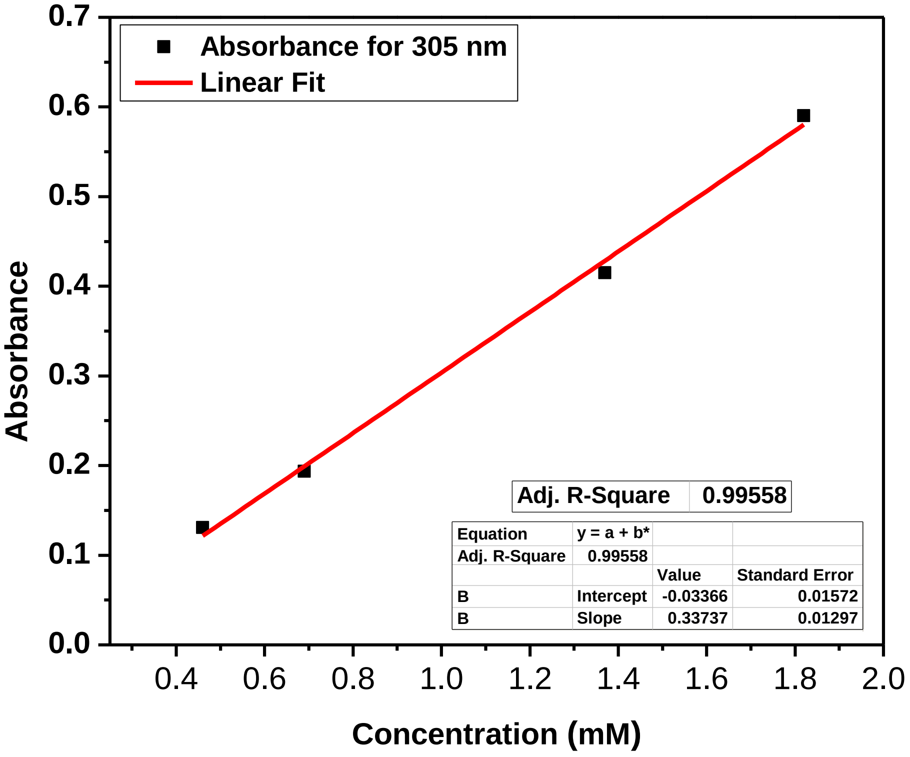


Fig. S43 UV/Vis spectrum of $\mathbf{4^{Pr}}$ in THF at various concentrations at room temperature.



Equation	y = a + b*		
Adj. R-Square	0.99558		
		Value	Standard Error
B	Intercept	-0.03366	0.01572
B	Slope	0.33737	0.01297

Fig. S44 Linear regression of $\mathbf{4^{Pr}}$ at 305 nm.

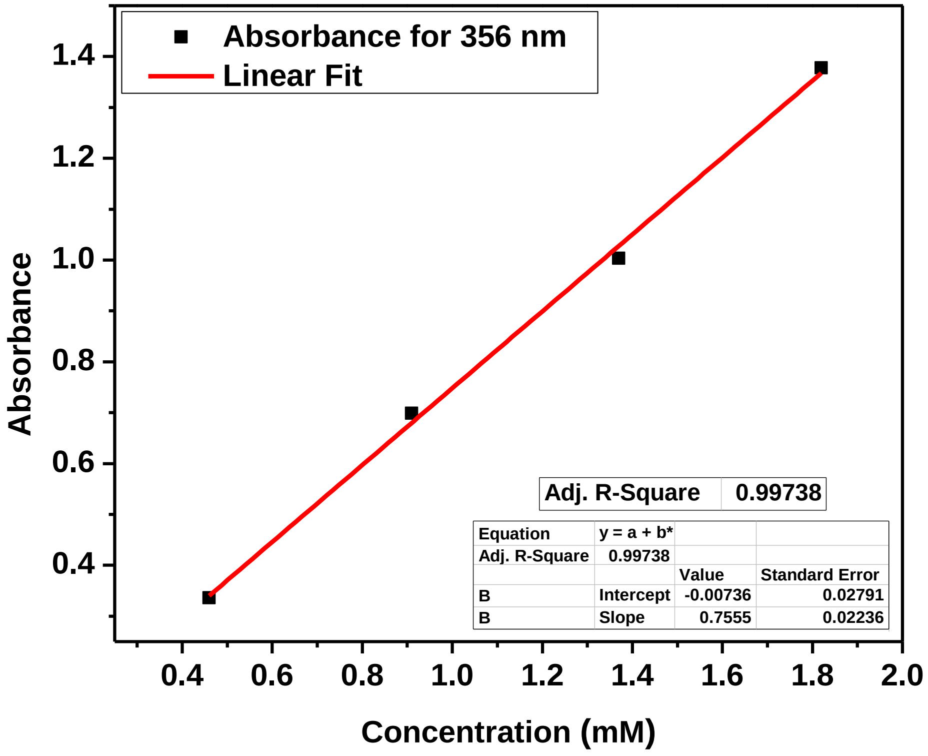


Fig. S45 Linear regression of **4**^{Pr} at 356 nm.

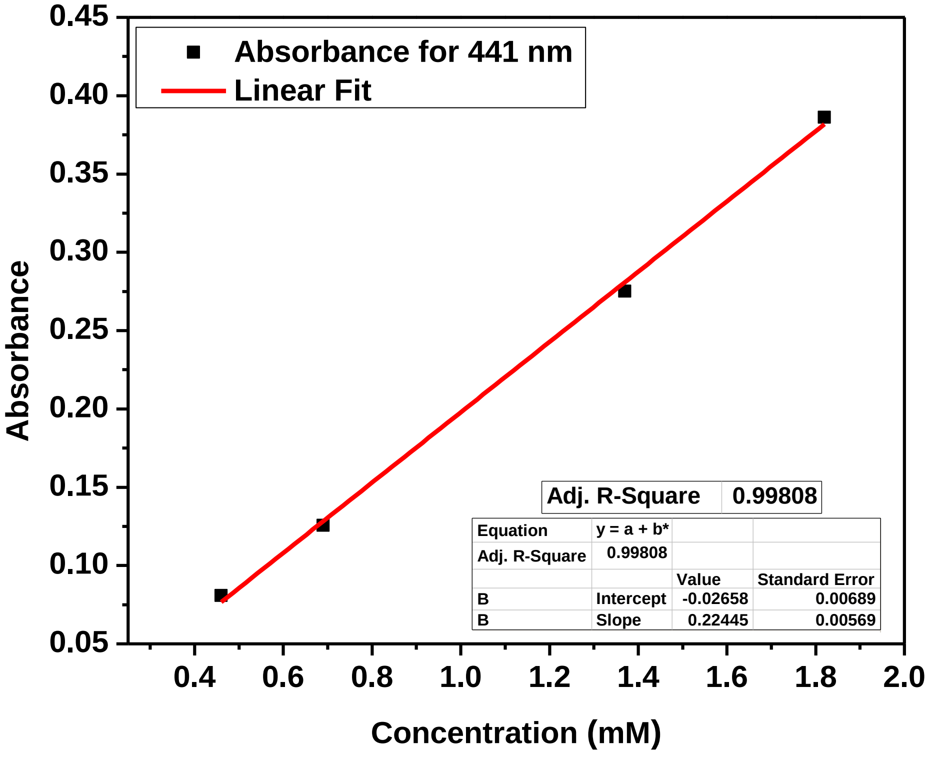


Fig. S46 Linear regression of **4**^{Pr} at 441 nm.

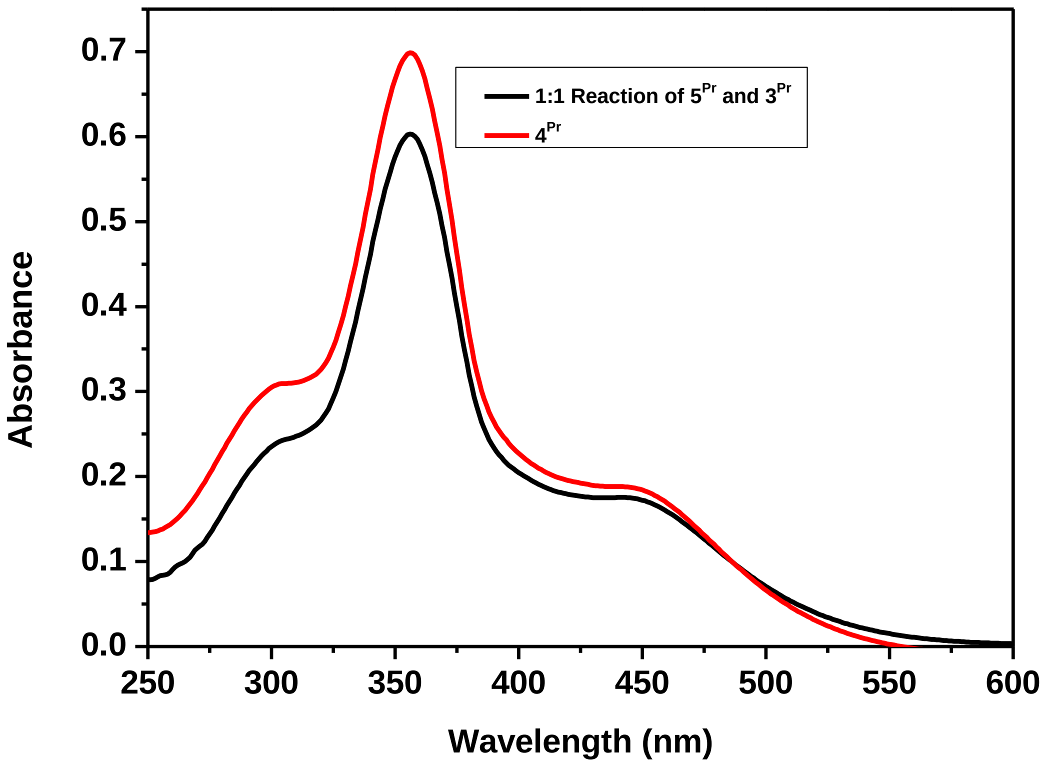


Fig. S47 Comparison of UV/Vis spectrum from comproportionation product of $\mathbf{5}^{\mathrm{Pr}}$ and $\mathbf{3}^{\mathrm{Pr}}$ with UV/Vis spectrum of $\mathbf{4}^{\mathrm{Pr}}$ in acetonitrile at room temperature.

Cyclic voltammetry

Table S1 Summary of the electrochemical data.

$\mathbf{3}^{\mathrm{Et}}$				
	$E_{1/2}$ [V vs FcH/FcH$^+$]	ΔEp (100 mV/s) [mV]	ΔEp (25 mV/s) [mV]	ΔEp (250 mV/s) [mV]
1st Oxidation	−1.01	430	260	590
2nd Oxidation	−0.22	420	240	570
$\mathbf{3}^{\mathrm{Cy}}$				
1st Oxidation	−0.84	452	280	630
2nd Oxidation	−0.15	436	275	635
$\mathbf{3}^{\mathrm{Pr}}$				
1st Oxidation	−1.03	350	210	375
2nd Oxidation	−0.34	310	215	380
$\mathbf{6}^{\mathrm{Et}}$				
1st Reduction	−0.24	80	75	80
2nd Reduction	−1.27	76	75	73

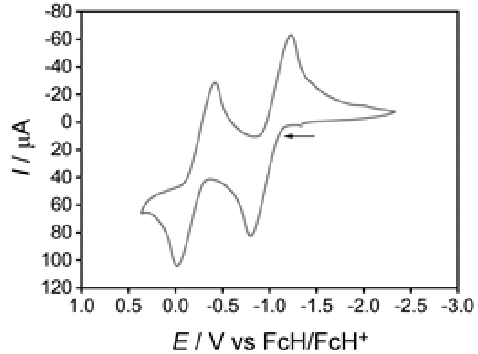


Fig. S48 CV of $\mathbf{3}^{\mathrm{Et}}$ in THF/0.1 M Bu_4NPF_6 measured at GC working electrode at 100 mVs^{-1}.

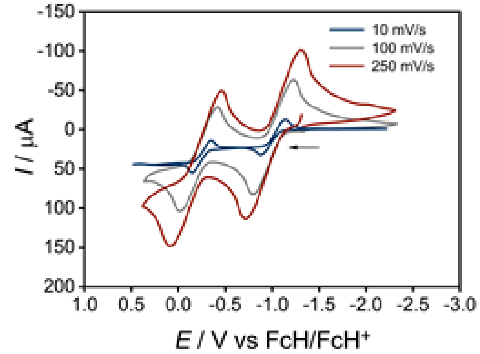


Fig. S49 CV of $\mathbf{3}^{\mathbf{Et}}$ in THF/0.1 M Bu_4NPF_6 measured at GC working electrode at various scan rates.

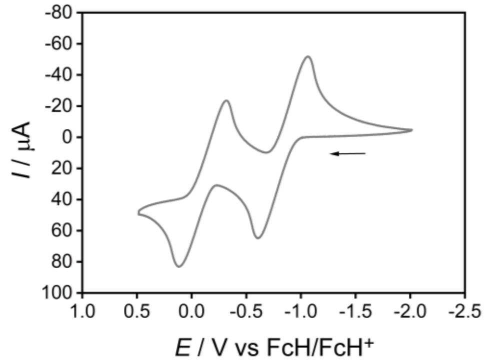


Fig. S50 CV of $\mathbf{3}^{\mathbf{Cy}}$ in THF/0.1 M Bu_4NPF_6 measured at GC working electrode at 100 mVs^{-1}.

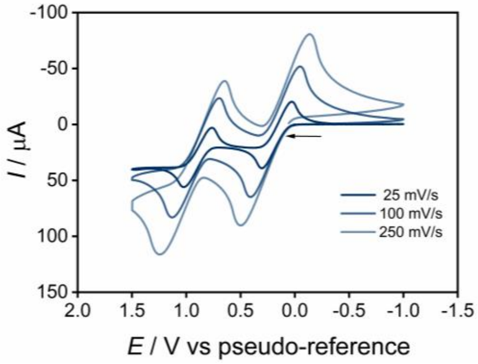


Fig. S51 CV of $\mathbf{3}^{\mathbf{Cy}}$ in THF/0.1 M Bu_4NPF_6 measured at GC working electrode at various scan rates.

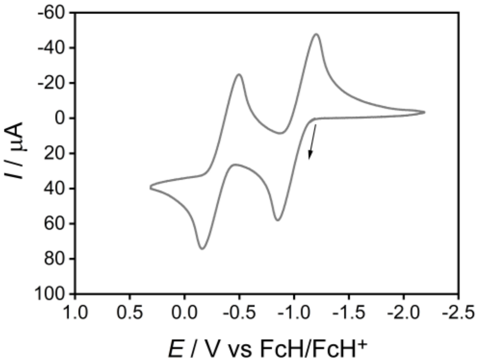


Fig. S52 CV of $\mathbf{3}^{\mathrm{Pr}}$ in THF/0.1 M Bu_4NPF_6 measured at GC working electrode at 100 mVs^{-1}.

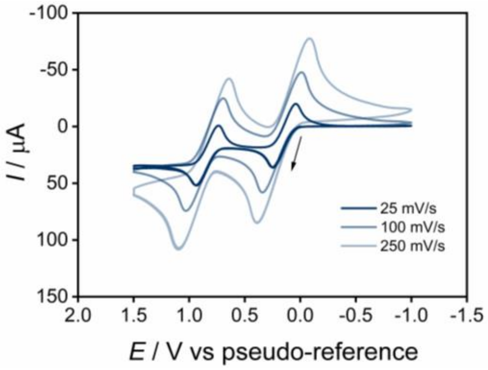


Fig. S53 CV of $\mathbf{3}^{\mathrm{Pr}}$ in THF/0.1 M Bu_4NPF_6 measured at GC working electrode at various scan rates.

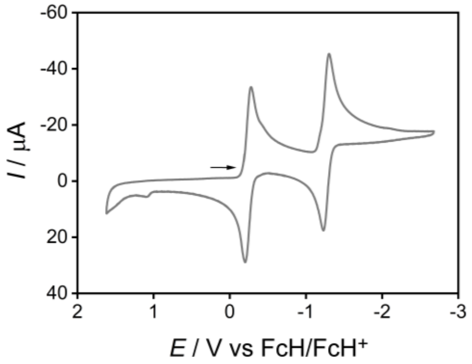


Fig. S54 CV of $\mathbf{6}^{\mathrm{Et}}$ in CH_3CN/0.1 M Bu_4NPF_6 measured at GC working electrode at 100 mVs^{-1}.

UV-Vis-NIR-spectroelectrochemistry

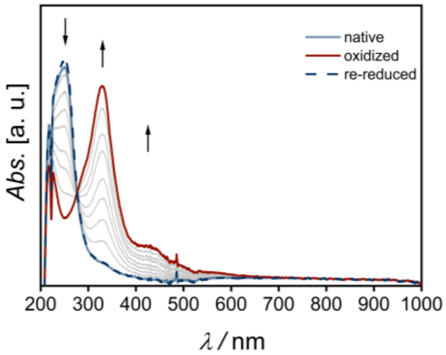


Fig. S55 Changes in the UV-Vis-NIR spectrum of $\mathbf{3}^{\mathbf{Et}}$ during spectroelectrochemistry in THF/0.1 M Bu_4NPF_6.

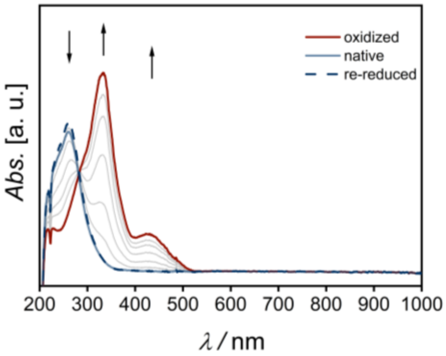


Fig. S56 Changes in the UV-Vis-NIR spectrum of $\mathbf{3}^{\mathbf{Cy}}$ during spectroelectrochemistry in THF/0.1 M Bu_4NPF_6.

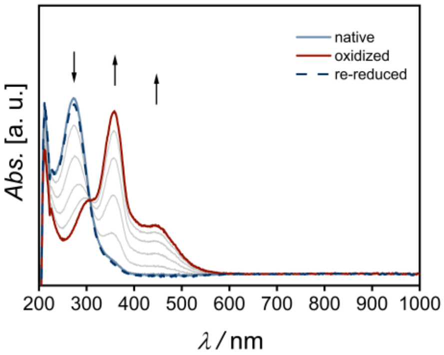


Fig. S57 Changes in the UV-Vis-NIR spectrum of $\mathbf{3}^{\mathbf{Pr}}$ during spectroelectrochemistry in THF/0.1 M Bu_4NPF_6.

EPR spectroscopy

Compound	g(exp)
4^{Et}	2.003
4^{Cy}	2.003
4^{Pr}	2.003
7^{Et}	2.005

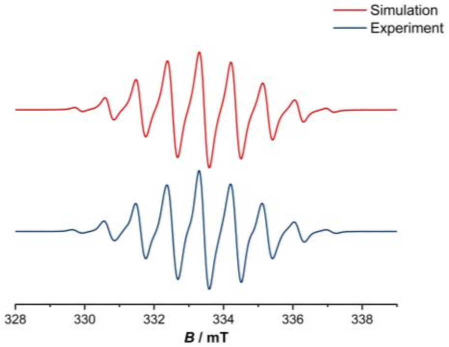


Fig. S58 EPR spectrum upon first oxidation of **3^{Et}** (**4^{Et}**) by spectroelectrochemically at 25 °C in THF.

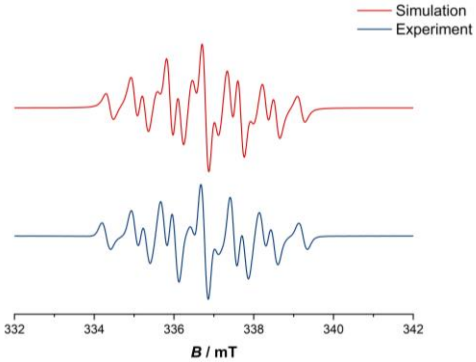


Fig. S59 EPR spectrum of **4^{Cy}** at 25 °C in THF.

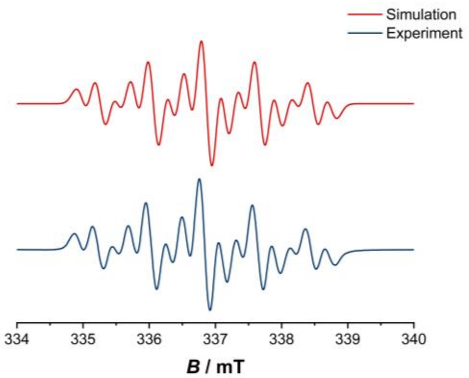


Fig. S60 EPR spectrum upon first reduction of **6^Et^** (**7^Et^**) by spectroelectrochemically at 25 °C in CH_3CN.

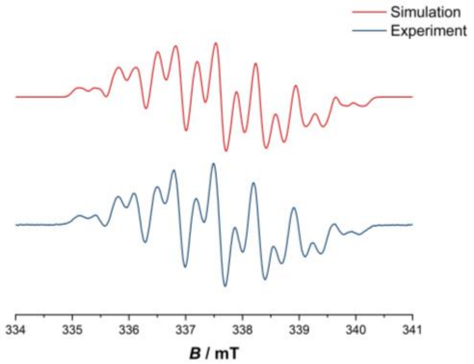


Fig. S61 EPR spectrum of **4^Pr^** at 25 °C in THF.

Solid-state molecular structures of 2^{Et}, 2^{Cy}, 2^{Pr}, 3^{Et}, 4^{Et}, and 6^{Et}

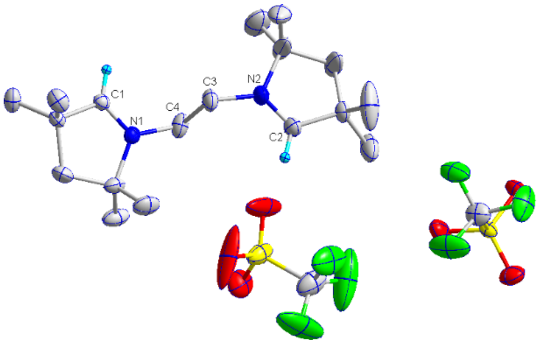


Fig. S62 Solid-state molecular structure of $\mathbf{2^{Et}}$. Hydrogen atoms except C1-H and C2-H are omitted for clarity.

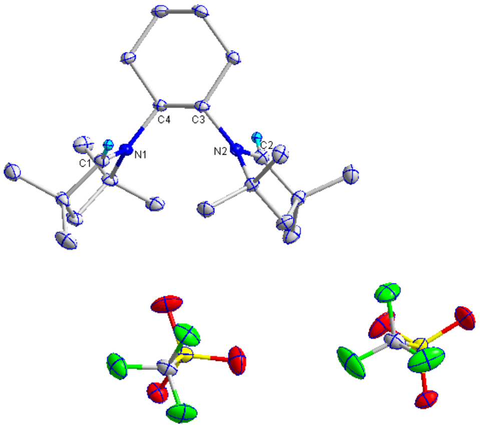


Fig. S63 Solid-state molecular structure of $\mathbf{2^{Cy}}$. Hydrogen atoms except C1-H and C2-H are omitted for clarity.

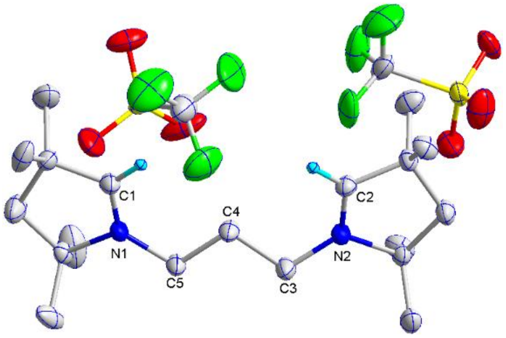


Fig. S64 Solid-state molecular structure of $\mathbf{2^{Pr}}$. Hydrogen atoms except C1-H and C2-H are omitted for clarity.

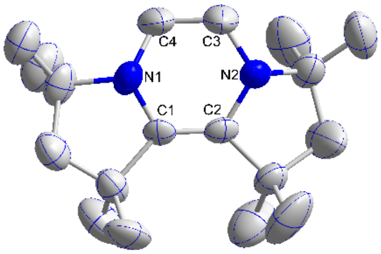


Fig. S65 Solid-state molecular structure of 3^{Et}. Hydrogen atoms are omitted for clarity.

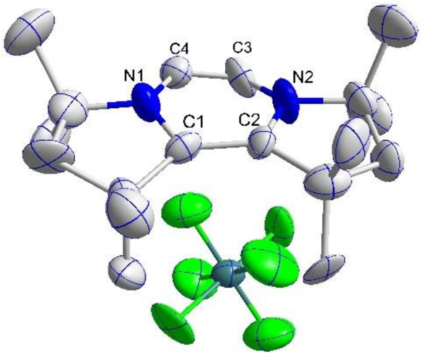


Fig. S66 Solid-state molecular structure of 4^{Et}. Hydrogen atoms are omitted for clarity.

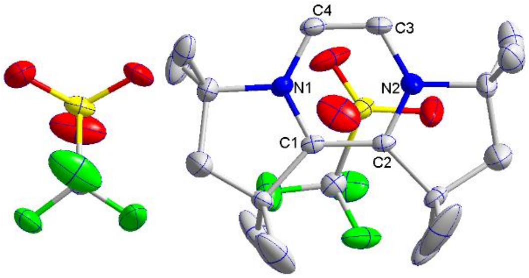


Fig. S67 Solid-state molecular structure of 6^{Et}. Hydrogen atoms are omitted for clarity.

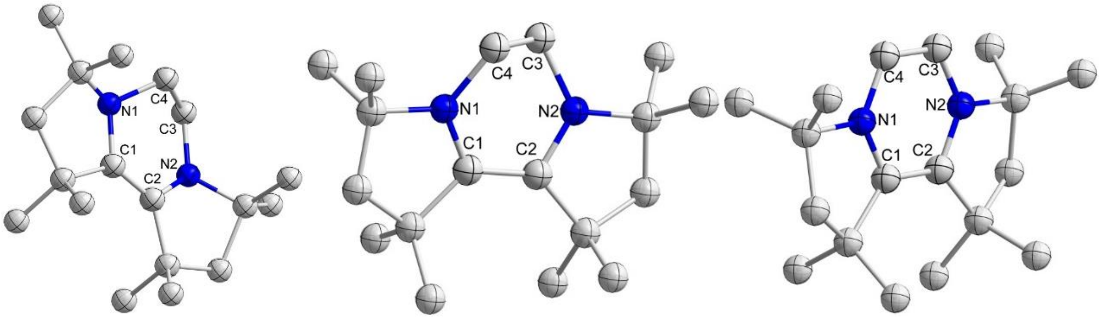


Fig. S68 Side-on-view of the solid-state molecular structures of $\mathbf{3}^{\mathbf{Et}}$ (left), $\mathbf{4}^{\mathbf{Et}}$ (middle) and $\mathbf{6}^{\mathbf{Et}}$ (right). All hydrogen atoms, SbF_6^- counter anion for $\mathbf{4}^{\mathbf{Et}}$ and two OTf^- counter anions for $\mathbf{6}^{\mathbf{Et}}$ are omitted for clarity.

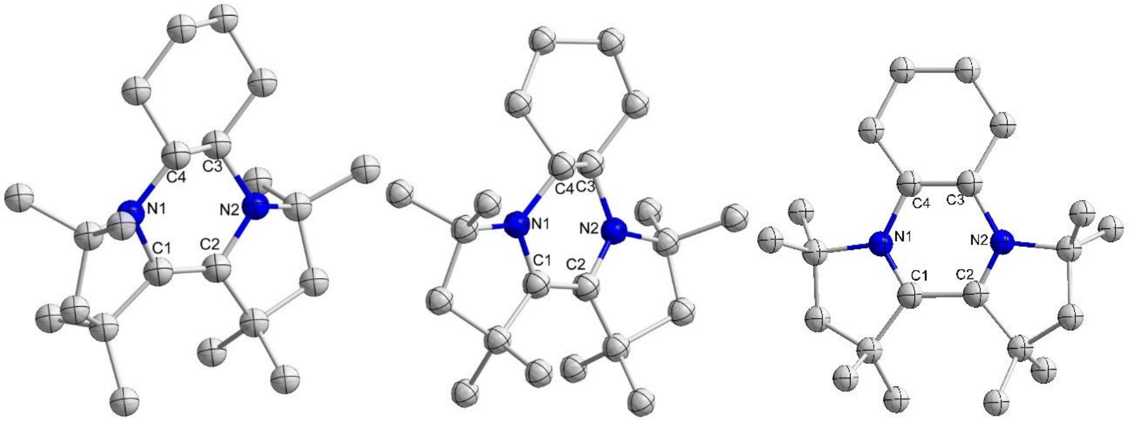


Fig. S69 Side-on-view of the solid-state molecular structures of $\mathbf{3}^{\mathbf{Cy}}$ (left), $\mathbf{4}^{\mathbf{Cy}}$ (middle) and $\mathbf{5}^{\mathbf{Cy}}$ (right). All hydrogen atoms, SbF_6^- counter anion for $\mathbf{4}^{\mathbf{Cy}}$ and two OTf^- counter anions for $\mathbf{5}^{\mathbf{Cy}}$ are omitted for clarity.

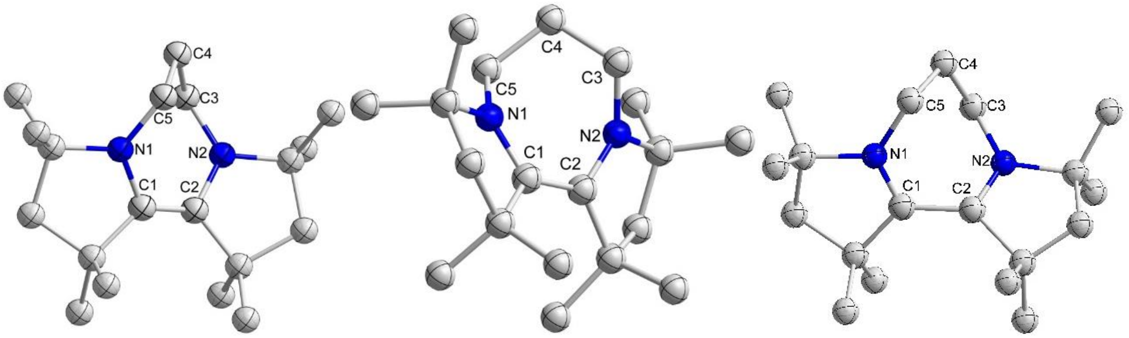


Fig. S70 Side-on-view of the solid-state molecular structures of $\mathbf{3}^{\mathbf{Pr}}$ (left), $\mathbf{4}^{\mathbf{Pr}}$ (middle) and $\mathbf{5}^{\mathbf{Pr}}$ (right). All hydrogen atoms, OTf^- counter anion for $\mathbf{4}^{\mathbf{Pr}}$ and two OTf^- counter anions for $\mathbf{5}^{\mathbf{Pr}}$ are omitted for clarity.

Crystallographic details

Single-crystal X-ray diffraction data of **2^{Et}**, **3^{Et}**, **6^{Et}**, **2^{Cy}**, **3^{Cy}**, **4^{Cy}**, **5^{Cy}**, **2^{Pr}**, **3^{Pr}**, **4^{Pr}**, and **5^{Pr}** were collected using a Rigaku diffractometer with graphite-monochromated molybdenum *Kα* radiation, λ = 0.71073 Å. Data integration and reduction were processed with CrysAlisPro software.[S7] An empirical absorption correction was applied to the collected reflections with SCALE3 ABSPACK integrated with CrysAlisPro.

Single-crystal X-ray diffraction data of **4^{Et}** were collected using an STOE-IPDS II diffractometer equipped with a normal-focus, 2.4 kW, sealed-tube X-ray source with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å) at low temperature (170 K). The program XArea was used for integration of diffraction profiles; numerical absorption corrections were carried out with the programs X-Shape and X-Red32; all from STOE ©.

The structures were solved by direct methods using SHELXT[S8] program and refined by full matrix least-squares method based on F^2 by using SHELXL[S9] program through Olex2[S10] interface. All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms 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. Crystal data and structure refinement of all these compounds are summarized in Tables S2-S13.

Specifics in the refinement

In case of **2^{Et}** three carbon atoms of the cation are disordered over two positions (ring pucker). This was modelled using free variables for the occupancies 53%:47% and no constraints or restraints. One anion is heavily disordered over two positions, which was modelled using free variables for the occupancies and SAME, SIMU and DELU constraints.

In case of **3^{Et}** the structure was refined with a TWIN component and BASF of 0.04. The ethylene spacer is disordered over two positions (ring pucker). This was modelled using free variables for the occupancies 79%:21% and no constraints or restraints. One of the two five-membered rings including half of the ring atom's methyl substituents is disordered over two positions (ring pucker). This was modelled using free variables for the occupancies 54%:46% and no constraints or restraints. The data was cut at 0.84 Å resolution. A remaining B-Alert in the checkcif points towards a close distance of two methyl hydrogen atoms which results from not optimal calculated positions. Other close distances are due to disorder issues. Locating and freely refining the respective sets of hydrogen atoms did not result in an improvement of the structure.

In case of **4^{Et}** the measured crystal was of poor quality (though the best one of all those tested). The diffraction was weak and several domains were present. Two strong domains could be separated during data integration while at least one, or possibly more, weaker domains could not be considered. Using the hklf5 for the refinement did not lead to an acceptable solution. Therefore, only the separated data for one of the two stronger domains was used for the final solution. The data was cut at 0.85 Å resolution. All this results in a rather low data completeness and several related issues including the respective A, B and C Alerts in the checkcif. The ethylene spacer is disordered over two positions. This was modelled using free variables for the occupancies 51%:49% and SADI, SIMU and DELU constraints.

In case of **6^{Et}** both five-membered rings including half of the ring atom's methyl substituents are disordered over two positions each (ring pucker). This was modelled using free variables for the occupancies (71%:29% for both disordered moieties) and SAME constraints.

In case of **3^{Cy}** one of the five-membered rings including half of the ring atom's methyl substituents are disordered over two positions each (ring pucker). This was modelled using free variables for the occupancies (83%:17%) and SIMU and DELU constraints.

In case of **4^{Cy}** the structure was refined as racemic twin (BASF 0.5). The anion is heavily disordered and was refined in three different orientations. The occupancies were refined with free variables for the major occupancy and the sum of the two lesser occupancies (40%:60%). The two lesser occupancies were split into 70% vs. 30% (of their 60% joint share) and SADI and SIMU constraints applied. The six-membered ring is disordered over two positions. This was modelled using free variables for the occupancies (50%:50%) and SIMU and SAME constraints. Both five-membered rings including half of the ring atom's methyl substituents are disordered over two positions each (ring pucker). This was modelled using free variables for the occupancies (roughly 50%:50% for both disordered moieties) and SIMU and DELU constraints.

In case of **5^{Cy}** the structure was refined as non-merohedral twin with two considered domains (BASF: 0.36) by employing the hklf5 file. To clean the refinement up several reflexes were omitted from the refinement. The entire cyclohexyl ring is disordered over two conformations (alternating up and down positions) with occupancies of 66% and 34%. Both triflate anions are disordered over two positions each with occupancies of 95% and 5% and of 78% and 22%, respectively. All disorders were treated with SAME, SIMU and DELU constraints. For the disordered triflate anions also DFIX as anti-bumping restraint was used.

In case of **2^{Pr}** the two anions are disordered over two positions each. This was modelled using free variables for the occupancies (92%:8% and 89%:11%) and SAME, SIMU and DELU constraints.

In case of **4^{Pr}** the structure was refined with a TWIN component and BASF of 0.20.

In case of **5^{Pr}** the structure was refined as racemic twin (BASF 0.43). Both anions are disordered over two positions each. This was modelled using free variables for the occupancies (52%:48% and 51%:49%) and SAME, SIMU and DELU constraints. In one of the five-membered rings three carbon atoms including their methyl substituents are disordered over two positions. This was modelled using free variables for the occupancies (51%:49%) and SAME constraints.

Table S2 Crystal data and structure refinement for **2^{Et}** (CCDC: 1971751)

Identification code	aj0063
Empirical formula	$C_{20}H_{34}F_6N_2O_6S_2$
Formula weight	576.61
Temperature/K	120.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.2198(6)
b/Å	24.3160(12)
c/Å	11.2287(6)
α/°	90
β/°	104.852(6)
γ/°	90
Volume/Å^3	2697.2(3)
Z	4
ρ_{calc}g/cm^3	1.420
μ/mm^{-1}	0.276
F(000)	1208.0
Crystal size/mm^3	0.23 × 0.21 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.032 to 52.998
Index ranges	$-12 \le h \le 12, -30 \le k \le 30, -13 \le l \le 14$
Reflections collected	25848
Independent reflections	5580 [R_{int} = 0.0304, R_{sigma} = 0.0245]
Data/restraints/parameters	5580/421/445
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0547, wR_2 = 0.1388
Final R indexes [all data]	R_1 = 0.0630, wR_2 = 0.1447
Largest diff. peak/hole / e Å^{-3}	0.71/-0.49

Table S3 Crystal data and structure refinement for $\mathbf{3}^{\mathbf{Et}}$ (CCDC: 1971752)

Identification code	AJ1150
Empirical formula	$C_{18}H_{32}N_2$
Formula weight	276.45
Temperature/K	240.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.3706(9)
b/Å	8.1457(4)
c/Å	18.6134(11)
α/°	90
β/°	91.043(7)
γ/°	90
Volume/Å^3	1723.72(19)
Z	4
ρ_{calc}g/cm^3	1.065
μ/mm^{-1}	0.062
F(000)	616.0
Crystal size/mm^3	0.19 × 0.17 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5 to 50.054
Index ranges	$-11 \le h \le 13$, $-9 \le k \le 9$, $-22 \le l \le 22$
Reflections collected	12263
Independent reflections	2958 [R_{int} = 0.0628, R_{sigma} = 0.0537]
Data/restraints/parameters	2958/0/219
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0750, wR_2 = 0.2041
Final R indexes [all data]	R_1 = 0.0859, wR_2 = 0.2127
Largest diff. peak/hole / e Å^{-3}	0.23/-0.30

Table S4 Crystal data and structure refinement for **4^{Et}** (CCDC: 1971753)

Identification code	MK0385
Empirical formula	$C_{18}H_{32}F_6N_2Sb$
Formula weight	512.20
Temperature/K	170.15
Crystal system	monoclinic
Space group	C2/c
a/Å	13.286(3)
b/Å	16.169(3)
c/Å	20.044(4)
α/°	90
β/°	91.44(3)
γ/°	90
Volume/Å^3	4304.7(15)
Z	8
ρ_{calc}g/cm^3	1.581
μ/mm^{-1}	1.337
F(000)	2072.0
Crystal size/mm^3	0.11 × 0.101 × 0.073
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.476 to 49.402
Index ranges	$-15 \le h \le 14$, $-18 \le k \le 17$, $-23 \le l \le 23$
Reflections collected	8280
Independent reflections	2171 [R_{int} = 0.1623, R_{sigma} = 0.1225]
Data/restraints/parameters	2171/77/271
Goodness-of-fit on F^2	0.955
Final R indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.1021
Final R indexes [all data]	R_1 = 0.1493, wR_2 = 0.1355
Largest diff. peak/hole / e Å^{-3}	0.54/-0.69

Table S5 Crystal data and structure refinement for **6^{Et}** (CCDC: 1971754)

Identification code	AJ0678
Empirical formula	$C_{20}H_{30}F_6N_2O_6S_2$
Formula weight	572.58
Temperature/K	120.15
Crystal system	triclinic
Space group	P-1
a/Å	10.4927(3)
b/Å	11.3753(4)
c/Å	12.8459(4)
α/°	67.712(3)
β/°	72.257(3)
γ/°	66.569(3)
Volume/Å^3	1280.14(8)
Z	2
ρ_{calc}g/cm^3	1.485
μ/mm^{-1}	0.290
F(000)	596.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.008 to 57.75
Index ranges	$-10 \le h \le 14$, $-14 \le k \le 15$, $-17 \le l \le 17$
Reflections collected	25226
Independent reflections	5944 [R_{int} = 0.0364, R_{sigma} = 0.0359]
Data/restraints/parameters	5944/6/393
Goodness-of-fit on F^2	1.110
Final R indexes [I>=2σ (I)]	R_1 = 0.0502, wR_2 = 0.1244
Final R indexes [all data]	R_1 = 0.0646, wR_2 = 0.1317
Largest diff. peak/hole / e Å^{-3}	1.06/-0.59

Table S6 Crystal data and structure refinement for **2^{Cy}** (CCDC: 1971755)

Identification code	AJ0759
Empirical formula	$C_{24}H_{40}F_6N_2O_6S_2$
Formula weight	630.70
Temperature/K	120
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.2936(4)
b/Å	16.1144(4)
c/Å	16.1904(5)
α/°	90
β/°	91.094(3)
γ/°	90
Volume/Å^3	2945.95(16)
Z	4
ρ_{calc}g/cm^3	1.422
μ/mm^{-1}	0.259
F(000)	1328.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.032 to 58.058
Index ranges	-15 ≤ h ≤ 11, -21 ≤ k ≤ 17, -21 ≤ l ≤ 21
Reflections collected	26173
Independent reflections	6921 [R_{int} = 0.0302, R_{sigma} = 0.0285]
Data/restraints/parameters	6921/0/370
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0412, wR_2 = 0.1057
Final R indexes [all data]	R_1 = 0.0488, wR_2 = 0.1098
Largest diff. peak/hole / e Å^{-3}	0.65/-0.58

Table S7 Crystal data and structure refinement for **3**^{Cy} (CCDC: 1971756)

Identification code	AJ0776
Empirical formula	$C_{22}H_{38}N_2$
Formula weight	330.54
Temperature/K	173.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.3676(6)
b/Å	20.7476(10)
c/Å	11.0903(7)
α/°	90
β/°	109.300(7)
γ/°	90
Volume/Å^3	2034.3(2)
Z	4
ρ_{calc}g/cm^3	1.079
μ/mm^{-1}	0.062
F(000)	736.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.008 to 58.098
Index ranges	-10 ≤ h ≤ 12, -28 ≤ k ≤ 27, -13 ≤ l ≤ 15
Reflections collected	32939
Independent reflections	4975 [R_{int} = 0.0827, R_{sigma} = 0.0504]
Data/restraints/parameters	4978/60/255
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0583, wR_2 = 0.1546
Final R indexes [all data]	R_1 = 0.0834, wR_2 = 0.1662
Largest diff. peak/hole / e Å^{-3}	0.23/-0.21

Table S8 Crystal data and structure refinement for $\mathbf{4^{Cy}}$ (CCDC: 1971757)

Identification code	AJ1208
Empirical formula	$C_{22}H_{38}F_6N_2Sb$
Formula weight	566.29
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	15.5683(14)
b/Å	15.5783(14)
c/Å	10.020(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2430.2(6)
Z	4
ρ_{calc}g/cm^3	1.548
μ/mm^{-1}	1.192
F(000)	1156.0
Crystal size/mm^3	0.23 × 0.19 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.23 to 60.06
Index ranges	$-21 \le h \le 20$, $-20 \le k \le 20$, $-13 \le l \le 10$
Reflections collected	25957
Independent reflections	5714 [R_{int} = 0.0925, R_{sigma} = 0.0467]
Data/restraints/parameters	5714/1208/513
Goodness-of-fit on F^2	0.984
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.0980
Final R indexes [all data]	R_1 = 0.0606, wR_2 = 0.1079
Largest diff. peak/hole / e Å^{-3}	0.74/-0.73
Flack parameter	0.50(6)

Table S9 Crystal data and structure refinement for **5^{Cy}** (CCDC: 1971758)

Identification code	AJ0779r
Empirical formula	$C_{24}H_{38}F_6N_2O_6S_2$
Formula weight	628.68
Temperature/K	173.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.0963(7)
b/Å	12.0415(5)
c/Å	14.8878(6)
α/°	90
β/°	92.041(4)
γ/°	90
Volume/Å^3	2883.8(2)
Z	4
ρ_{calc}g/cm^3	1.448
μ/mm^{-1}	0.265
F(000)	1320.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.986 to 57.752
Index ranges	$-21 \le h \le 21$, $-15 \le k \le 15$, $0 \le l \le 20$
Reflections collected	6920
Independent reflections	6920 [R_{int} = ? R_{sigma} = 0.0446]
Data/restraints/parameters	6920/1720/571
Goodness-of-fit on F^2	1.104
Final R indexes [I>=2σ (I)]	R_1 = 0.0869, wR_2 = 0.2236
Final R indexes [all data]	R_1 = 0.1050, wR_2 = 0.2316
Largest diff. peak/hole / e Å^{-3}	0.677/-0.580

Table S10 Crystal data and structure refinement for **2**$^{\mathbf{Pr}}$ (CCDC: 1971759)

Identification code	AJ0121
Empirical formula	$C_{21}H_{36}F_6N_2O_6S_2$
Formula weight	590.64
Temperature/K	120.01
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.0062(6)
b/Å	12.0297(5)
c/Å	23.0723(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2777.2(2)
Z	4
ρ_{calc}g/cm^3	1.413
μ/mm^{-1}	0.269
F(000)	1240.0
Crystal size/mm^3	0.479 × 0.124 × 0.104
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.892 to 52
Index ranges	-12 ≤ h ≤ 11, -14 ≤ k ≤ 14, -28 ≤ l ≤ 27
Reflections collected	30895
Independent reflections	5416 [R_{int} = 0.0403, R_{sigma} = 0.0295]
Data/restraints/parameters	5416/754/488
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0427, wR_2 = 0.1019
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.1051
Largest diff. peak/hole / e Å^{-3}	0.58/-0.20
Flack parameter	0.14(3)

Table S11 Crystal data and structure refinement for **3^{Pr}** (CCDC: 1971760)

Identification code	AJ0605
Empirical formula	$C_{19}H_{34}N_2$
Formula weight	290.48
Temperature/K	120.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.6542(3)
b/Å	11.7196(5)
c/Å	35.0170(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3551.6(2)
Z	8
ρ_{calc}g/cm^3	1.087
μ/mm^{-1}	0.063
F(000)	1296.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.25 to 58.158
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 15$, $-47 \leq l \leq 45$
Reflections collected	23351
Independent reflections	4236 [R_{int} = 0.0469, R_{sigma} = 0.0385]
Data/restraints/parameters	4236/0/198
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1184
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1258
Largest diff. peak/hole / e Å^{-3}	0.34/-0.27

Table S12 Crystal data and structure refinement for **4**$^{\mathbf{Pr}}$ (CCDC: 1971761)

Identification code	AJ0625
Empirical formula	$C_{20}H_{34}F_3N_2O_3S$
Formula weight	439.55
Temperature/K	119.98(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.7269(5)
b/Å	16.6330(3)
c/Å	16.7087(4)
α/°	90
β/°	90.073(2)
γ/°	90
Volume/Å^3	4370.75(19)
Z	8
ρ_{calc}g/cm^3	1.336
μ/mm^{-1}	0.197
F(000)	1880.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.18 to 57.914
Index ranges	$-21 \le h \le 19$, $-22 \le k \le 22$, $-22 \le l \le 22$
Reflections collected	72306
Independent reflections	10578 [R_{int} = 0.0485, R_{sigma} = 0.0374]
Data/restraints/parameters	10578/0/540
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.0894
Final R indexes [all data]	R_1 = 0.0482, wR_2 = 0.0929
Largest diff. peak/hole / e Å^{-3}	0.41/-0.34

Table S13 Crystal data and structure refinement for **5^{Pr}** (CCDC: 1971762)

Identification code	AJ0650
Empirical formula	$C_{21}H_{34}F_6N_2O_6S_2$
Formula weight	588.62
Temperature/K	120.02(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.9365(2)
b/Å	16.2526(3)
c/Å	18.4341(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2677.39(9)
Z	4
ρ_{calc}g/cm^3	1.460
μ/mm^{-1}	0.279
F(000)	1232.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.012 to 56.544
Index ranges	$-11 \le h \le 10$, $-21 \le k \le 20$, $-24 \le l \le 24$
Reflections collected	40905
Independent reflections	6385 [R_{int} = 0.0355, R_{sigma} = 0.0227]
Data/restraints/parameters	6385/332/511
Goodness-of-fit on F^2	1.128
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.0968
Final R indexes [all data]	R_1 = 0.0452, wR_2 = 0.0981
Largest diff. peak/hole / e Å^{-3}	0.35/-0.46
Flack parameter	0.43(9)

Theoretical calculations

Calculations on (formal) H_2 loss

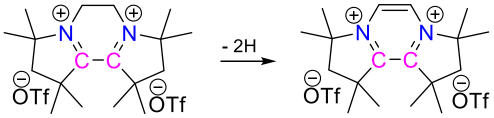
Single point energies were calculated at B3LYP/def2-TZVP level of theory including numerical frequencies to calculate vibrational contributions to free enthalpies. Solvation was accounted for by calculating the electronic single point energy including the CPCM solvent model (THF). The free enthalpy of H_2 loss was calculated according to the following formula.[S11]

$$\Delta G_r = \left(G_{H_2} + G_{II} + E_{H_2}^{solv} + E_{II}^{solv} - E_{H_2}^{unsolv} - E_{II}^{unsolv} + G_{corr}\right) - \left(G_I + E_I^{solv} - E_I^{unsolv}\right)$$

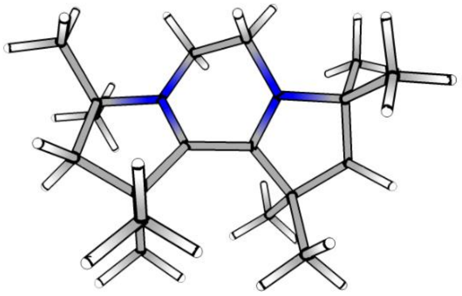
where G refers to the free enthalpies of species as obtained from gas phase calculations, E^{solv} to the electronic energy including solvent effects and E^{unsolv} to the gas phase electronic energy. G_{corr} corrects for the difference between ideal gas standard conditions and standard solution conditions and is equal to $RT\ln(RT/p) = 1.89\ kcal/mol$ for each species. According to these contributions, a weakly exergonic reaction with

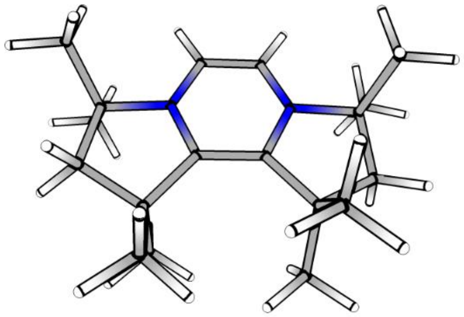
$$\Delta G_r = 0.92\ kcal/mol$$

is calculated. However, potentially important contributions such as removal of dihydrogen (if it is indeed formed) from equilibrium are ignored.



5^{Et} 6^{Et}





Representative calculation of EPR parameters for 4$^{\mathrm{Pr}}$

Löwdin analysis reveals 82 % of spin population on N-C-C-N moiety, with 22 % on each N atom and 19 % on each C atom. This is also apparent in the spin density plot below. A comparison of the experimentally observed and calculated hyperfine coupling parameters is given in Table S13.

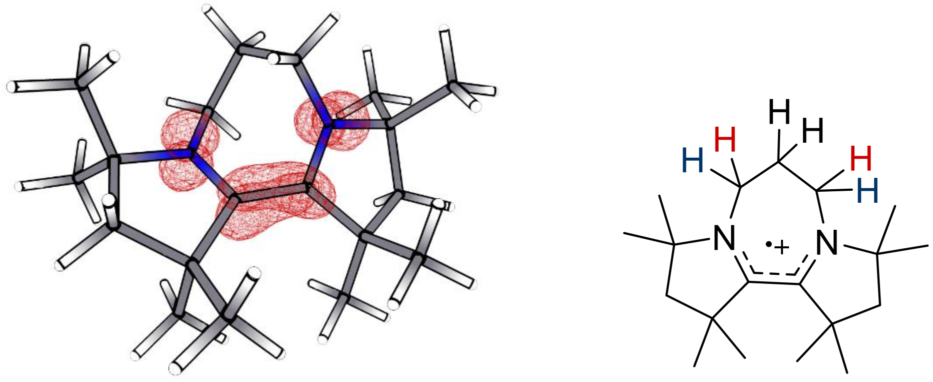


Fig. S71 Spin density plot and assignment of protons for **4**$^{\mathrm{Pr}}$.

Table S14 Experimental and calculated EPR parameters for **4**$^{\mathrm{Pr}}$.

	g	A_N	A_{H1}	A_{H2}	A_{H3}
Experimental	2.003	19.8	18.2	8.3	3.8
Calculated	2.003	16.8	20.2	9.7	-0.7

Coordinates of optimized structures

5$^{\text{Et}}$

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N	-1.23047541868310	-0.47934258833124	0.69818161279097
C	-0.34351924877641	-1.64958106046950	0.79178062775164
C	0.52899322926414	-1.66585212950475	-0.44825433361770
N	1.19739369941826	-0.35829704757332	-0.54088873888337
C	-2.66350844456145	-0.48600433493181	1.19843589346981
C	-3.19355384671980	0.79969541655191	0.53312616323941
C	-1.97511204849483	1.64204610775242	0.03171643027934
C	-0.83571440472060	0.65652434092845	0.19241809442676
C	0.60363656265765	0.75371114949603	-0.20521692685955
C	1.55109733066235	1.93576168415719	-0.20809362028169
C	2.90464663488930	1.25423237151951	-0.59359389586785
C	2.61682327248770	-0.18956585581333	-1.05136418732979
C	1.63859169638955	2.51080340967018	1.22724014598378
C	1.18806247393937	3.04046926733326	-1.22162727118719
C	3.54722657288374	-1.21313960882814	-0.40113634849037
C	2.56794539433615	-0.35946709827942	-2.57641546400108
C	-2.60344456497960	-0.41247762276671	2.73082063633341
C	-1.82463112496488	2.93219227332913	0.86402936532876
C	-2.14406749126908	1.97188195890515	-1.47196905880851
C	-3.39331022084326	-1.74224636317938	0.72382105733238
H	-0.96203487025832	-2.55133946406230	0.84673151272082
H	0.24969611563801	-1.57890261885828	1.71698152580097
H	1.29561770713432	-2.44424476162135	-0.37707917811967
H	-0.05556545910901	-1.83728690674019	-1.36574503260881
H	-3.80322099962294	1.37588899845381	1.23779723507958
H	-3.83257299268784	0.53730279580032	-0.31920721403114
H	3.56844260641771	1.23872659377308	0.27980520693933
H	3.41328895513453	1.81585211565825	-1.38488152540730
H	1.90498903695306	1.73404583319452	1.95737827587895
H	0.71080730440372	2.99602330380847	1.54641247154293
H	2.43457193509158	3.26813989968747	1.23909369439365
H	1.08437704999649	2.64601394334386	-2.24077951180906
H	2.00984478810049	3.76881409622235	-1.22415866725072

H	0.27714938854064	3.58349981382268	-0.95342825545051
H	3.47169729097144	-1.19870253289787	0.69491869607678
H	4.57835429258310	-0.94168343931759	-0.66444330421678
H	3.38522073057884	-2.23355892986092	-0.77289460035409
H	2.24335316367904	-1.36766103012035	-2.86801333272950
H	3.58245753020872	-0.21525396711925	-2.97110853467642
H	1.90734243627986	0.38090082643653	-3.04674195180532
H	-2.08768287154149	0.49422971087497	3.07383796225996
H	-2.11124154850873	-1.29282746281748	3.16620207890489
H	-3.63209130079545	-0.38928157194808	3.11441126879415
H	-1.66601173427554	2.71888619470452	1.92910303096754
H	-2.76195939625108	3.49634961747161	0.76941517088094
H	-1.02052673407326	3.58156759040550	0.50549074993934
H	-2.26104345786723	1.06020401448125	-2.07410415548633
H	-1.31201683931219	2.55901286050790	-1.87320656134930
H	-3.06041721101144	2.56747343023004	-1.58544169880088
H	-3.30923445402159	-1.88023424043305	-0.36298965547606
H	-4.45891156951985	-1.61827131270021	0.95913457348243
H	-3.05970894577076	-2.65088767034584	1.24225954430048

6^{Et}

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N	-1.33176324144722	-0.60618629361335	-0.02290392322018
C	-0.72200699631258	0.60879441222711	-0.00011074648204
C	0.70594799620932	0.61836726167503	0.01492155577970
N	1.33203115042318	-0.58834301037039	0.03426376308824
C	0.69453182684614	-1.77637176648597	0.02079691211289
C	-0.67832849252204	-1.78555347883725	-0.01242833099454
C	1.73180544455938	1.73909891131090	-0.06400094556943
C	3.04943019642598	0.99810929450980	0.30589578738946
C	2.86505004791392	-0.50181833800015	0.03744127163890
C	-2.86577698911493	-0.54039688877043	-0.02677058991061
C	-3.07027387976170	0.95773266798323	-0.29079559619224
C	-1.76295924091217	1.71530429723939	0.08208287169816
C	3.36102876212295	-0.97578826930574	-1.33454556320997

C	3.41803118323667	-1.37563723113828	1.16324018262145
C	1.53199902712539	2.90708602889143	0.91502992183324
C	1.77638461776919	2.26022817727353	-1.52665004351549
C	-1.57878684305134	2.88946607169161	-0.89260987209215
C	-1.81493873956693	2.23063920636688	1.54658211949834
C	-3.40601564492495	-1.41822217473032	-1.15565742231723
C	-3.35637937483027	-1.02520157881669	1.34337738092690
H	1.29446865430725	-2.68300937629415	0.03984224650033
H	-1.26605038278475	-2.70010104180241	-0.03389115922013
H	3.26241106136173	1.15155140859056	1.37237702894510
H	3.89540239988009	1.40166457886890	-0.26172967862502
H	-3.92191172571520	1.34808988982128	0.27759143505843
H	-3.28475004528354	1.11156004450919	-1.35692585571129
H	2.95516988987690	-0.37900404674057	-2.15963525996409
H	3.12249599622059	-2.03408051483541	-1.50871590527807
H	4.45447853086297	-0.87932562690655	-1.35076911058791
H	2.95650372513454	-1.13592979954933	2.13054486052203
H	4.49428078432958	-1.17204367914806	1.24556095039650
H	3.31380211692870	-2.45005675743651	0.96002934861035
H	1.40386596902892	2.55639261586638	1.94744266181111
H	0.69451399267031	3.55675884560437	0.64539984742212
H	2.43918932799975	3.52579813471879	0.88500631589204
H	1.95798972805745	1.45787810198766	-2.25203480298283
H	2.60195044650083	2.98064342079466	-1.60192320295212
H	0.85290063932447	2.77496336937582	-1.80706855602508
H	-1.44588288899640	2.54434857685704	-1.92629607480782
H	-0.75014773861473	3.54937047634025	-0.62039670686956
H	-2.49423262402125	3.49578888700674	-0.86044581051238
H	-1.98506178686123	1.42329088273273	2.26919672833125
H	-2.65069514090892	2.93894030331339	1.62430891628863
H	-0.89887246313013	2.75751793921620	1.82881515440574
H	-2.94711333242495	-1.16925684684818	-2.12187429441867
H	-4.48489121345890	-1.22912623629880	-1.23815331023937
H	-3.28720282747075	-2.49174007621699	-0.95567296611302
H	-2.95969106354672	-0.42521916894826	2.17060647828152

H	-3.10338136201835	-2.08058339206265	1.51477012568659
H	-4.45107947743623	-0.94399821161643	1.35877186307220

4$^{\mathrm{Pr}}$

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N	-1.34084708222978	1.11173326819224	-0.65323117729752
C	-0.37752952575259	1.75670236444217	-1.53997211002307
C	0.86220123825975	2.27513189919049	-0.80559767383962
C	1.28657885634871	1.24535377370539	0.24530663966604
N	1.18585122131958	-0.13152626008617	-0.22809605741584
C	-2.59425348376182	1.80419831726358	-0.22783455454829
C	-3.22489906317328	0.72406936207895	0.66960576416910
C	-2.60748876749925	-0.64114071989004	0.26035562636430
C	-1.22953348550146	-0.17784405353910	-0.22527685772240
C	0.02223108859660	-0.84143673216440	-0.24741483780801
C	0.37177126316104	-2.33127357424946	-0.33344926367630
C	1.75389075326942	-2.24640133951315	-1.03734627764693
C	2.39622413037511	-0.90653358605449	-0.63488065826723
C	0.53100126988415	-2.94108117149887	1.07911220475010
C	-0.57260009147735	-3.19859939545514	-1.16885503024808
C	3.40143320057711	-1.02964443017332	0.51955513611328
C	3.06841242938327	-0.21809011961726	-1.83022196395997
C	-2.23786121681300	3.06664244561011	0.56800824096692
C	-2.61627524433579	-1.58520172371369	1.46468050517573
C	-3.41782848772636	-1.26575756648356	-0.89981552454291
C	-3.46503582102193	2.18461447146238	-1.43423381267245
H	-0.89094159546132	2.56891951188098	-2.06732374095305
H	-0.07732770428543	1.01418407280560	-2.29400508337833
H	0.66181827495638	3.23102249642821	-0.30225721430996
H	1.65922860197753	2.45320192854056	-1.54056617498316
H	0.64241986034410	1.33541058761038	1.13243321309794
H	2.31856565700133	1.41831108941176	0.57168289832570
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H	-2.97014489211649	0.93067499412589	1.71942489036154
H	1.60175844219406	-2.26327333149162	-2.12646944970318

H	2.38783048031849	-3.10226787850879	-0.77596420831894
H	1.14106045399106	-2.30978133902472	1.73588349182229
H	1.02011937294456	-3.92179818082287	0.99528562689618
H	-0.43651563466658	-3.09071420887861	1.56759909714390
H	-0.81542084716711	-2.72574803712917	-2.13011549039291
H	-1.50503071848883	-3.42237959334977	-0.63853717472998
H	-0.08580089182126	-4.16126083607786	-1.37890646898833
H	2.96058042949457	-1.49473168124148	1.40825332260316
H	3.81255968934052	-0.05214014901588	0.80634789466497
H	4.24565565179926	-1.65064982881568	0.19294566076963
H	3.50687785740509	0.75015540549362	-1.55083967674961
H	2.35475649483048	-0.06524157764242	-2.65137285197569
H	3.88436523872244	-0.85237936380856	-2.20274705733311
H	-1.56925899183059	2.82987098590922	1.40700597444008
H	-3.15607725257397	3.50797085280491	0.97910036508900
H	-1.76269558840665	3.82848993382987	-0.06570486707257
H	-1.94345727916281	-1.23641704631947	2.25982677968695
H	-2.33752569395111	-2.60822703182240	1.18823873689831
H	-3.63342332476683	-1.63162654701530	1.87825399523235
H	-3.36960159514353	-0.65950686733058	-1.81202289823167
H	-4.47170004994204	-1.34998012675714	-0.59931504342019
H	-3.06020637656775	-2.26918976159816	-1.14920250790538
H	-3.72556270818110	1.31645435709759	-2.04969539216701
H	-2.97086688312718	2.92846440304329	-2.07399297056278
H	-4.39687105429444	2.63879413376282	-1.07309360022132

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