Electronic Supplementary Information

for

Acyclic Diaminocarbene-Based Thiele, Chichibabin and Müller Hydrocarbons

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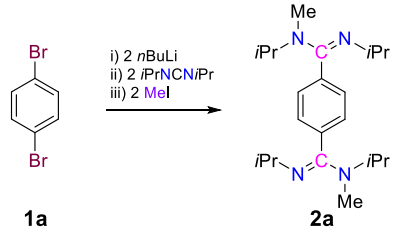
General considerations

All experiments were carried out under nitrogen atmosphere using standard Schlenk techniques or in a PL-HE-2GB Innovative Technology GloveBox and MBraun Unilab SP GloveBox. Hexane, diethyl ether, THF, and toluene were dried by PS-MD-5 Innovative Technology solvent purification system. 1,4-Dibromo benzene (Sigma Aldrich), 4,4'-dibromobiphenyl (Sigma Aldrich), 4,4''-dibromo-*p*-terphenyl (TCI), *N,N'*-diisopropylcarbodiimide, potassium (Sigma Aldrich)), *n*BuLi (Hychem Laboratories), MeI (Hychem Laboratories), MeOTf (Sigma Aldrich) were commercially purchased and used as it is except MeI which was distilled before used. KC_8 were synthesized according to literature procedure.[S1] Benzene-d6 was dried and distilled over potassium under nitrogen. Chloroform-d1 and CD_3CN was dried and distilled over CaH_2 under nitrogen. 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.

Elemental analyses were performed on a Perkin Elmer Analyser 240. Melting points were determined in closed NMR tubes under nitrogen atmosphere and are uncorrected. A Bruker Daltonics micrOTOF-Q instrument was used for electron spray mass spectrometry. All the ESI-MS data were recorded in positive operating mode. UV/Vis−NIR spectroelectrochemical measurements were recorded on a J&M TIDAS spectrometer instrument by using an optically transparent thin layer electrochemical (OTTLE) cell.[S2] Cyclic voltammetry was carried out in 0.1 M NBu_4PF_6/CH_3CN solutions using a three-electrode configuration (glassy carbon working, Pt wire counter electrodes, and Ag reference) and were performed using a Metrohm Autolab potentiostat. The ferrocene/ferrocenium (FcH/FcH+) couple served as internal reference. EPR spectrum at X-band frequency (ca. 9.5 GHz) were obtained with a Magnettech MS-5000 bench top EPR spectrometer equipped with a rectangular TE 102 cavity. The measurements were carried out in synthetic quarz glass tubes.

Experimental details and analytical data

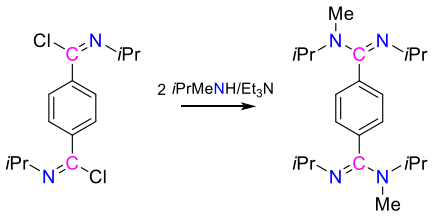
Synthesis of 2a



1a **2a**

*n*BuLi (5.8 mL, 9.32 mmol) was added dropwise to the solution of 1,4-dibromobenzene **1a** (1 g, 4.24 mmol) in a 100 mL Schlenk flask in 60 mL THF at −78 °C. The resulting mixture was stirred for 30 mins at −78 °C. After that *N,N'*-diisopropylcarbodiimide (1.1 g, 8.48 mol) in 20 ml THF was added at −78 °C and stirred for another 4hrs at −20 °C. After addition of MeI (0.8 mL, 12.72 mol) reaction mixture was stirred for 2 hrs at room temperature and refluxed for 2 hrs. After removing all the volatiles applying high vacuum the residue was dissolved in 50 ml DCM and 20 ml saturated NH_4Cl solution. The mixture was extracted with DCM (50 mL x 2) and then combined organic layers were dried by anhydrous Na_2SO_4. Subsequent removal of all the solvent, the resulting residue was dissolved in 20 mL of hot DCM and crystallization gives pure compound of **2a**. **Yield:** 1.1 gm (73 %).

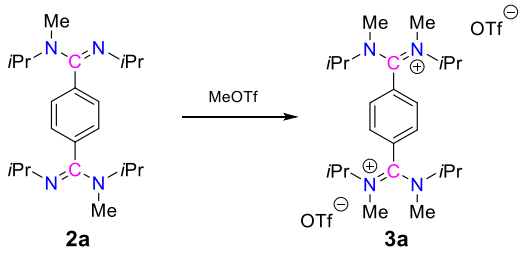
Alternative procedure for 2a



A **2a**

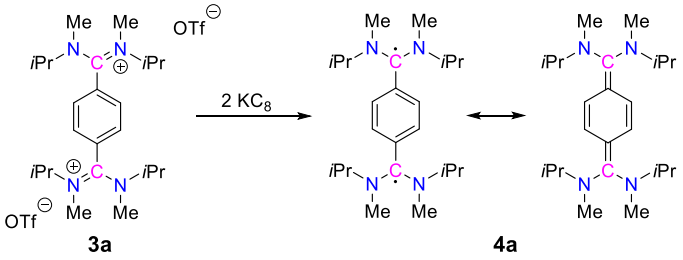
Isopropyl methyl amine (2.6 mL, 0.025 mol) was added to the solution of **A**[S3] (3.4 g, 0.012 mol) and Et_3N (6.62 mL, 0.0476 mol) in a 100 mL Schlenk flask in 60 mL toluene at 0 °C. The resulting mixture was heated for 6 hrs at 90 °C under static vacuum. After removing all the volatiles applying high vacuum the residue was dissolved in 30 ml DCM and 30 ml 2 M NaOH solution. The mixture was extracted with DCM (20 mL x 3) and then combined organic layers were dried by anhydrous Na_2SO_4. Subsequent removal of all the solvent, the resulting residue was dissolved in 20 mL of hot DCM and crystallization gives pure compound of **2a**. **Yield:** 3.8 gm (89 %). **M. P.**: 76°C. **^{1}H NMR** (300 MHz, $CDCl_3$, 298 K): δ = 7.11 (s, 4H, Ph*H*), 3.66 (br, 2H, $NCH_3CH(CH_3)_2$), 2.95 (sept, *J* = 6.20, 2H, $NCH(CH_3)_2$), 2.69 (s, 6H, $NCH_3CH(CH_3)_2$) 1.02 (d, *J* = 6.77, 12H, $NCH(CH_3)_2$) 0.95 (d, *J* = 6.2, 12H, $NCH_3CH(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75.4 MHz, $CDCl_3$, 298 K): δ = 159.41 (NCN), 135.68 (Ph*C*), 127.49 (Ph*C*), 49.98 ($NCH_3CH(CH_3)_2$), 47.40 ($NCH(CH_3)_2$), 28.28 ($NCH_3CH(CH_3)_2$), 25.56 ($NCH(CH_3)_2$), 19.98 ($NCH_3CH(CH_3)_2$) ppm. **Elemental analysis:** Anal. Calcd ($C_{22}H_{38}N_4$). C, 73.69; H, 10.68; N, 15.63, Found: C, 73.48; H, 10.65; N, 15.47. **ESI-MS**: Calcd (m/z) 358.3096, Found $[M+H]^+$ 359.3171.

Synthesis of 3a



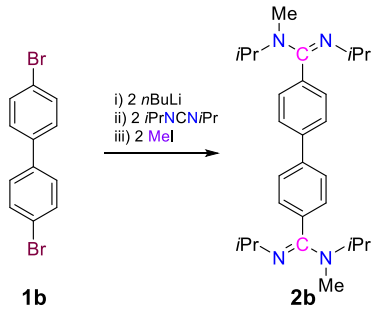
MeOTf (2.5 mL) in 10 mL hexane was added to **2a** (3.85 g, 0.010 mol) in 30 mL hexane at −78 °C. After stirring 30 mins the resulting mixture was slowly warmed to room temperature and stirred for further 6 hrs. Resulting white turbid solution was filtered and the residue was washed 30 mL Et_2O to get pure product of **3a** as white solid. **Yield:** 5.2 gm (76 %). **M. P.**: > 200 °C. **^{1}H NMR** (300 MHz, CD_3CN, 298 K): δ = 7.81 (s, 4H, Ph*H*), 3.49 (br, 4H, $NCH_3CH(CH_3)_2$), 3.17 (br, 12H, $NCH_3CH(CH_3)_2$) 1.20 (s, 24H, $NCH_3CH(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75.4 MHz, CD_3CN, 298 K): δ = 169.5 (N*C*N), 135.18 (Ph*C*), 131.40 (Ph*C*), 124.23 (CF_3SO_3), 119.98 (CF_3SO_3), 56.41 ($NCH_3CH(CH_3)_2$), 35.59 ($NCH_3CH(CH_3)_2$), 20.24 ($NCH_3CH(CH_3)_2$) ppm. **Elemental analysis:** Anal. calcd ($C_{26}H_{44}N_4F_6O_6S_2$). C, 45.47; H, 6.46; N, 8.16; S, 9.34, Found: C, 45.56; H, 6.47; N, 8.18, S, 9.37. **ESI-MS**: Calcd (m/z) 194.1778, Found 194.1790.

Synthesis of 4a



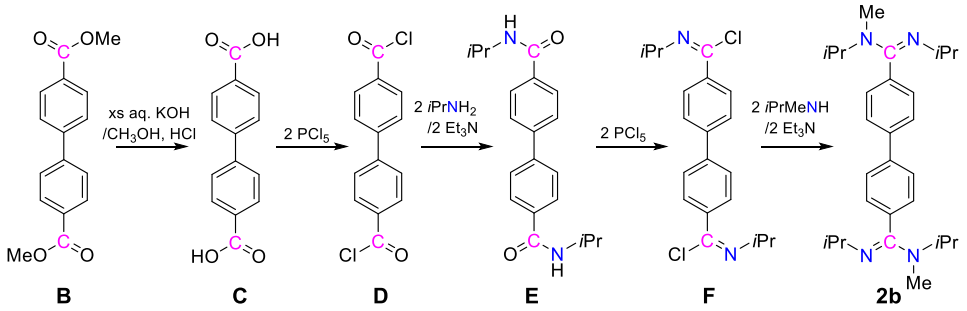
Compound **3a** (500 mg, 0.728 mol) and KC_8 (246 mg, 0.118 mol) was taken in a 50 mL Schlenk flask inside the GloveBox and then 20 mL of precooled (−78 °C) THF added on it at −78 °C. Then the reaction mixture was allowed to come to room temperature slowly and stirred for 4 hrs. Subsequently all the volatilities including solvent were removed under vacuum and the resulting residue was extracted with 20 mL of Toluene. After removal of all solvents from the resulting filtrate leads to compound **4a** as a pure yellow solid. Single crystals suitable for X-ray diffraction were obtained from saturated 1:1 benzene and hexane solution at room after 2 days. **Yield:** 250 mg (89 %). **M. P.**: 136 °C. **^{1}H NMR** (300 MHz, C_6D_6, 298 K): δ = 6.32 (d, 4H, Ph*H*), 3.54 (sept, 4H, $NCH_3CH(CH_3)_2$), 2.61 (s, 12H, $NCH_3CH(CH_3)_2$) 1.002 (s, 24H, $NCH_3CH(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75.4 MHz, C_6D_6, 298 K): δ = 147.39 (N*C*N), 122.77 (Ph*C*), 107.5 (Ph*C*), 50.25 ($NCH_3CH(CH_3)_2$), 32.38 ($NCH_3CH(CH_3)_2$), 20.13 ($NCH_3CH(CH_3)_2$) ppm. **UV/vis** (THF): λ_{max} (ε) = 436 (77185), 269 (8183) nm (L mol^{-1} cm^{-1}). **Elemental analysis:**Anal. calcd ($C_{24}H_{44}N_4$). C, 74.17; H, 11.41; N, 14.42; Found: C, 74.56; H, 11.21; N, 14.25. **ESI-MS**: Calcd (m/z) 388.3566, Found 388.6289.

Synthesis of 2b



*n*BuLi (4.4 mL, 7.04 mmol) was added dropwise to the solution of *p,p'*-dibromobiphenyl **1b** (1 g, 3.20 mmol) in a 100 mL Schlenk flask in 60 mL THF at −78 °C. The resulting mixture was stirred for 1 hr at −78 °C. After that *N,N'*-diisopropylcarbodiimide (0.81g, 6.4 mmol) in 20 ml THF was added at −78 °C and stirred for another 4hrs at −20 °C. After addition of MeI (0.6mL, 9.6 mmol) reaction mixture was stirred for 2 hrs at room temperature and refluxed for 4 hrs. After removing all the volatiles applying high vacuum the residue was dissolved in 50 ml DCM and 20 ml saturated NH_4Cl solution. The mixture was extracted with DCM (50 mL x 2) and then combined organic layers were dried by anhydrous Na_2SO_4. Subsequent removal of all the solvent, the resulting residue was dissolved in 20 mL of hot DCM and crystallization gives pure compound of **2b**. **Yield:** 1.2 gm (86 %).

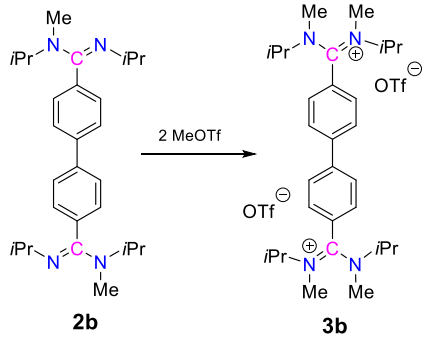
Alternative procedure for 2b



a) Dimethyl-*p,p'*-biphenyldicarboxylate **B** (25 gm, 0.185 mol) was taken in a 1-litre round Bottom flask. Then a freshly prepared KOH solution (40 gm KOH flakes in 200 ml water) was added to the 1-litre round bottom flask followed by the addition of 500 ml methanol at room temperature. Resulting white slurry was refluxed for 24 hours. All the volatiles including methanol was removed using rotary evaporator. Remaining residue was acidified with concentrated HCl to precipitate out all product from water. The total precipitate was filtered and washed with petroleum ether. Solid residue was dried to get pure product as white solids of biphenyl-*p,p'*-dicarboxylic acid, **C**. **Yield:** 23 gm (100 %). b) In a 500 ml Schlenk flask **C** (25 gm, 0.103 mole) was taken in 350 ml of toluene. Then PCl_5 (53.73 gm, 0.257 mole) was added into it at room temperature. Resulting solution was refluxed for 12 hrs. All volatilities were evaporated under high vacuum to get white crystalline residue of biphenyl-*p,p'*-dicarbonyldichloride **D** as pure product. c) Considering the previous reaction was 100 % conversion, 81 ml of trimethylamine (71.83 mL 0.51 mol) was added into it in 350 ml DCM. Then isopropylamine (35.4 ml 0.412 mole)

was added dropwise using a dropping funnel at 0 °C. After stirring for 12 hrs at room temperature resulting mixture was dried using rota-evaporator. 500 ml water was added into it and stirred for 1 hr and filtered. The residue was washed with petroleum ether and dried under high vacuum to get pure product as white solids of **E**. **Yield** : 28 gm (100%). d) Compound **E** (25 g, 0.077 mole) was taken in a 250 mL Schlenk flask and then 200 mL of dry toluene added at room temperature. Then PCl_5 (41.65 g, 0.2 mol) was added in a portion wise two times under nitrogen atmosphere. Then the resulting mixture was heated at 130 °C for 6 hrs until the reaction mixture became clear solution. After that all the volatilities including solvent were removed under vacuum. Subsequent extraction with hot pentane leads to **F** as white solid. Yield: 24.6 gm (88 %). **M. P.**: 42 °C. **^{1}H NMR** (300 MHz, $CDCl_3$, 298 K): δ = 8.07 (d, 4H, Biph*H*), 7.64 (d, 4H, Biph*H*), 4.18 (sept, 2H, NC*H*$(CH_3)_2$), 1.30 (d, 12H, NCH(C*H*$_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75.4 MHz, $CDCl_3$, 298 K): δ = 159.72 (N*C*Cl), 139.09 (Biph*C*), 135.75 (Biph*C*), 129.70 (Biph*C*), 127.09 (Biph*C*), 55.14 (N*C*H$(CH_3)_2$), 22.86 (NCH(*C*H$_3)_2$) ppm. e) Isopropyl methyl amine (4 mL, 0.038 mol) was added to the solution of *p,p'*-phenylene bridged *N,N'-iso*-propyl-*bis*-chloroimine (4.3 g, 0.012 mol) and Et_3N (7.24 mL, 0.051 mol) in a 100 mL Schlenk flask in 60 mL toluene at 0 °C. The resulting mixture was heated for 6 hrs at 90 °C under static vacuum. After removing all the volatiles applying high vacuum the residue was dissolved in 50 ml DCM and 50 ml 2 M NaOH solution. The mixture was extracted with DCM (50 mL x 3) and then combined organic layers were dried by anhydrous Na_2SO_4. Subsequent removal of all the solvent, the resulting residue was dissolved in 20 mL of hot DCM and crystallization gives pure compound of **2b**. **Yield:** 4.5 gm (86 %). **M. P.**: 101°C. **^{1}H NMR** (300 MHz, $CDCl_3$, 298 K): δ = 7.67 (d, 4H, Ar-*H*), 7.20 (d, 4H, Ar-*H*), 3.65 (br, 2H, $NCH_3CH(CH_3)_2$), 3.05 (sept, 2H, NC*H*$(CH_3)_2$), 2.76 (s, 6H, NC*H*$_3$CH$(CH_3)_2$), 1.03 (d, 12H, $NCH_3CH(CH_3)_2$), 0.98 (d, 12H, NCH(C*H*$_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75.4 MHz, $CDCl_3$, 298 K): δ = 159.72 (N*C*N), 139.94 (Ar-*C*), 135.49 (Ar-*C*), 128.02 (Ar-*C*), 127.09 (Ar-*C*), 50.05 (N*C*H$(CH_3)_2$), 47.65 ($NCH_3CH(CH_3)_2$) 28.18 ($NCH_3CH(CH_3)_2$), 25.59 (NCH(*C*H$_3)_2$) 20.06 ($NCH_3CH(CH_3)_2$) ppm. **Elemental analysis:** Anal. calcd ($C_{28}H_{42}N_4$). C, 77.37; H, 9.74; N, 12.89; Found: C, 77.13; H, 9.82; N, 12.91. **ESI-MS**: Calcd (m/z) 434.3409 Found $[M+H]^+$ 435.3479.

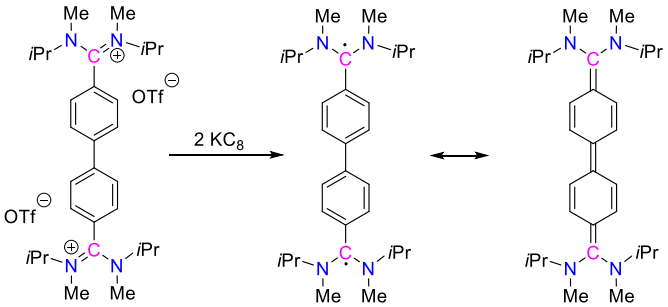
Synthesis of 3b



MeOTf (1.72 mL, 15.18 mmol) in 10 mL hexane was added to **2b** (3 g, 6.9 mmol) in 60 mL hexane at −78 °C. After stirring 30 mins the resulting mixture was slowly warmed to room temperature and stirred for further 6 hrs. Resulting white turbid solution was filtered and the residue was washed 30 mL Et_2O to get pure product of **3b** as

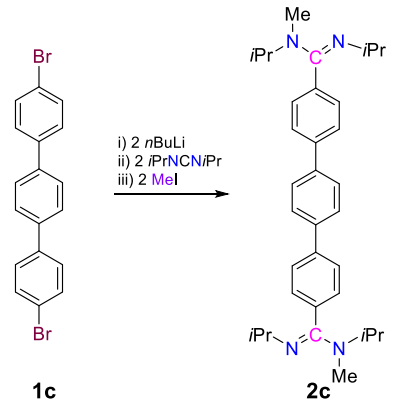
white solid. **Yield:** 4.6 g (87 %). **M. P.**: > 200 °C. **^{1}H NMR** (300 MHz, CD_3CN, 298 K): δ = 7.98 (d, 4H, Ar-*H*), 7.71 (d, 4H, Ar-*H*), 3.56 (br, 4H, $NCH_3CH(CH_3)_2$), 3.16 (s, 12H, $NCH_3CH(CH_3)_2$), 1.22 (d, 24H, $NCH_3CH(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75.4 MHz, CD_3CN, 298 K): δ = 170.89 (N*C*N), 144.29 (Ar-*C*), 131.03 (Ar-*C*), 129.32 (Ar-*C*), 124.30 (CF_3SO_3), 120.07 (CF_3SO_3), 56.33 ($NCH_3CH(CH_3)_2$), 35.43 ($NCH_3CH(CH_3)_2$), 20.36 ($NCH_3CH(CH_3)_2$) ppm. **Elemental analysis:** Anal. calcd ($C_{32}H_{48}N_4F_6O_6S_2$). C, 50.38; H, 6.34; N, 7.34; S, 8.41; Found C, 50.42; H, 6.60; N, 7.07; S, 8.83. **ESI-MS**: Calcd (m/z) 232.1934, Found 232.1960.

Synthesis of 4b



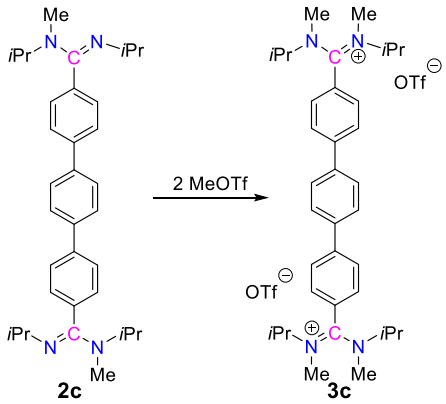
Compound **3b** (1 g, 1.31 mmol) and KC_8 (443 mg, 3.87 mmol) was taken in a 50 mL Schlenk flask inside the GloveBox and then 30 mL of precooled (−78 °C) THF added on it at −78 °C. Then the reaction mixture was allowed to come to room temperature slowly and stirred for 4 hrs. Subsequently all the volatilities including solvent were removed under vacuum and the resulting residue was extracted with 30 mL (x 3) of Toluene. After removal of all solvents from the resulting filtrate and washed with hexane leads to compound **4b** as a pure blue solid. Single crystals suitable for X-ray diffraction were obtained from saturated toluene solution at −30 °C after 3days. **Yield:** 320 mg (53 %). **M. P.**: 118 °C. **^{1}H NMR** (300 MHz, C_6D_6, 298 K): δ = 7.30 (d, 4H, Biph-*H*), 6.53 (d, 4H, Ar-*H*), 3.50 (sept, *J* = 6.62, 4H, $NCH_3CH(CH_3)_2$), 2.48 (s, 12H, $NCH_3CH(CH_3)_2$), 0.93 (d, 24H, $NCH_3CH(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75.4 MHz, C_6D_6, 298 K): δ = 150.00 (N*C*N), 125.82 (Ar-*C*), 125.18 (Ar-*C*), 120.76 (Ar-*C*), 110.54 (Ar-*C*), 51.03 ($NCH_3CH(CH_3)_2$), 31.8 ($NCH_3CH(CH_3)_2$), 20.01 ($NCH_3CH(CH_3)_2$) ppm. **UV/vis** (THF): λ_{max} (ε) = 591 (46656), 276 (2970) nm (L mol^{-1} cm^{-1}). **Elemental analysis:** Anal. calcd ($C_{30}H_{48}N_4$). C, 77.53; H, 10.41; N, 12.06; Found: C, 77.84; H 10.56, N, 12.32. **ESI-MS**: Calcd (m/z) 464.3879, Found 464.3803.

Synthesis of 2c



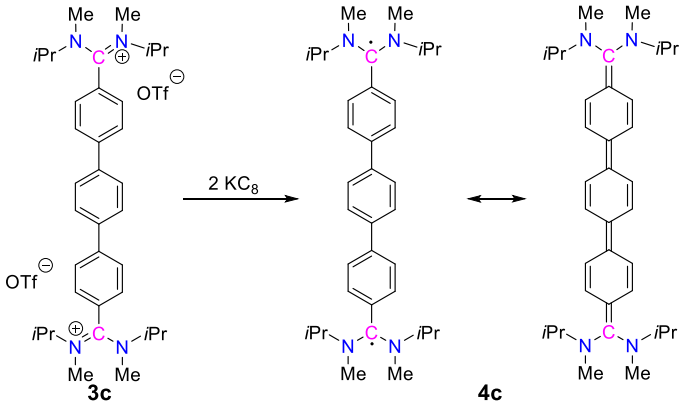
*n*BuLi (1.9 mL, 0.0029 mol) was added dropwise to the solution of *p,p''*-dibromo-*p*-terphenyl (0.5g, 0.0012 mol) in a 100 mL Schlenk flask in 60 mL THF at −78 °C. The resulting mixture was stirred for 3 hrs at −78 °C. After that *N,N'*-diisopropylcarbodiimide (0.323g, 0.0026 mol) in 20 ml THF was added at −78 °C and stirred for another 4hrs at −20 °C. After addition of MeI (0.24mL, 0.0038 mol) reaction mixture was stirred for 2 hrs at room temperature and refluxed for 6 hrs. After removing all the volatiles applying high vacuum the residue was dissolved in 50 ml DCM and 20 ml saturated NH_4Cl solution. The mixture was extracted with DCM (50 mL x 3) and then combined organic layers were dried by anhydrous Na_2SO_4. Subsequent removal of all the solvent, the resulting residue was dissolved in 20 mL of hot DCM and crystallization gives pure compound of **2c**. Yield: **Yield:** 0.36 gm (59 %). **M. P.**: 142 °C. **^{1}H NMR** (300 MHz, $CDCl_3$, 298 K): δ = 7.74 (s, 4H, Ar-*H*), 7.69 (d, 4H, Ar-*H*), 7.22 (d, 4H, Ar-*H*), 3.68 (br, 2H, $NCH_3CH(CH_3)_2$), 3.09 (sept, 2H, $NCH(CH_3)_2$), 2.79 (s, 6H, $NCH_3CH(CH_3)_2$), 1.04 (d, 12H, $NCH_3CH(CH_3)_2$), 1.01 (d, 12H, $NCH(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75.4 MHz, $CDCl_3$, 298 K): δ = 159.86 (NCN), 139.64 (Ar-*C*), 129.65 (Ar-*C*), 127.97 (Ar-*C*), 127.56 (Ar-*C*), 127.13 (Ar-*C*), 50.10 ($NCH(CH_3)_2$), 47.83 ($NCH_3CH(CH_3)_2$) 28.37 ($NCH_3CH(CH_3)_2$), 25.55 ($NCH(CH_3)_2$) 20.08 ($NCH_3CH(CH_3)_2$) ppm. **Elemental analysis:** Anal. calcd ($C_{34}H_{46}N_4$). C, 79.95; H, 9.08; N, 10.97, Found: C, 79.67; H, 8.60; N, 10.33. **ESI-MS**: Calcd (m/z) 510.37, Found $[M+H]^+$ 511.3795.

Synthesis of 3c



MeOTf (0.77 mL, 6.75 mmol) in 10 mL hexane was added to **2c** (1.5 g, 2.93 mmol) in 60 mL hexane at −78 °C. After stirring 30 mins the resulting mixture was slowly warmed to room temperature and stirred for further 12 hrs. Resulting white turbid solution was filtered and the residue was washed 30 mL of Et_2O to get pure product of **3c** as white solid. **Yield:** 2.2 gm (89 %). **M. P.**: > 200 °C. **^{1}H NMR** (300 MHz, CD_3CN, 298 K): δ = 7.99 (br, 4H, Ar-*H*), 7.97 (s, 4H, Ar-*H*), 7.69 (br, 4H, Ar-*H*), 3.63 (br, 4H, $NCH_3CH(CH_3)_2$), 3.17 (s, 12H, $NCH_3CH(CH_3)_2$), 1.24 (s, 24H, $NCH_3CH(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75.4 MHz, CD_3CN, 298 K): δ = 171.17 (NCN), 145.26 (Ar-*C*), 140.10 (Ar-*C*), 131.03 (Ar-*C*), 130.92 (Ar-*C*), 130.25 (CF_3SO_3), 128.91 ((Ar-*C*)), 56.31 ($NCH_3CH(CH_3)_2$), 35.40 ($NCH_3CH(CH_3)_2$), 20.40 ($NCH_3CH(CH_3)_2$) ppm. **Elemental analysis:** Anal. calcd ($C_{38}H_{52}N_4F_6O_6S_2$). C, 54.40; H, 6.25; N, 6.68. Found: C, 53.84; H, 6.22; N, 6.32. **ESI-MS**: Calcd (m/z) for 270.2091 Found 270.2056.

Synthesis of 4c



3c (513 mg, 0.61 mmol) and KC_8 (206 mg, 1.52 mmol) was taken in a 50 mL Schlenk flask inside the GloveBox and then 30 mL of Toluene added on it at room temperature and stirred for 16 hrs. Subsequently all the volatilities were removed under vacuum and the resulting residue was extracted with 30 mL (x 3) of hot Toluene. After removal of all solvents from the resulting filtrate and washed with hexane:toluene (1:2) leads to compound **4c** as a pure green solid. Single crystals suitable for X-ray diffraction were obtained from saturated hot toluene solution at room temperature after 1 day. **Yield:** 210 mg (64 %). **M. P.**: 118 °C. **UV/vis** (THF): λ_{max} (ε) = 343 (9695), 688 (44680) 879 (10572) nm (L mol^{-1} cm^{-1}). **Elemental analysis:** Anal. calcd ($C_{36}H_{52}N_4$). C, 79.95; H, 9.69; N, 10.36. Found C, 78.88; H, 9.31; N, 9.74 (this relatively large deviation of elemental analysis data even after repeating the measurements most likely due to the very air sensitivity nature of the compound). **ESI-MS**: Calcd (m/z) 540.4192 Found 540.4196.

NMR spectra

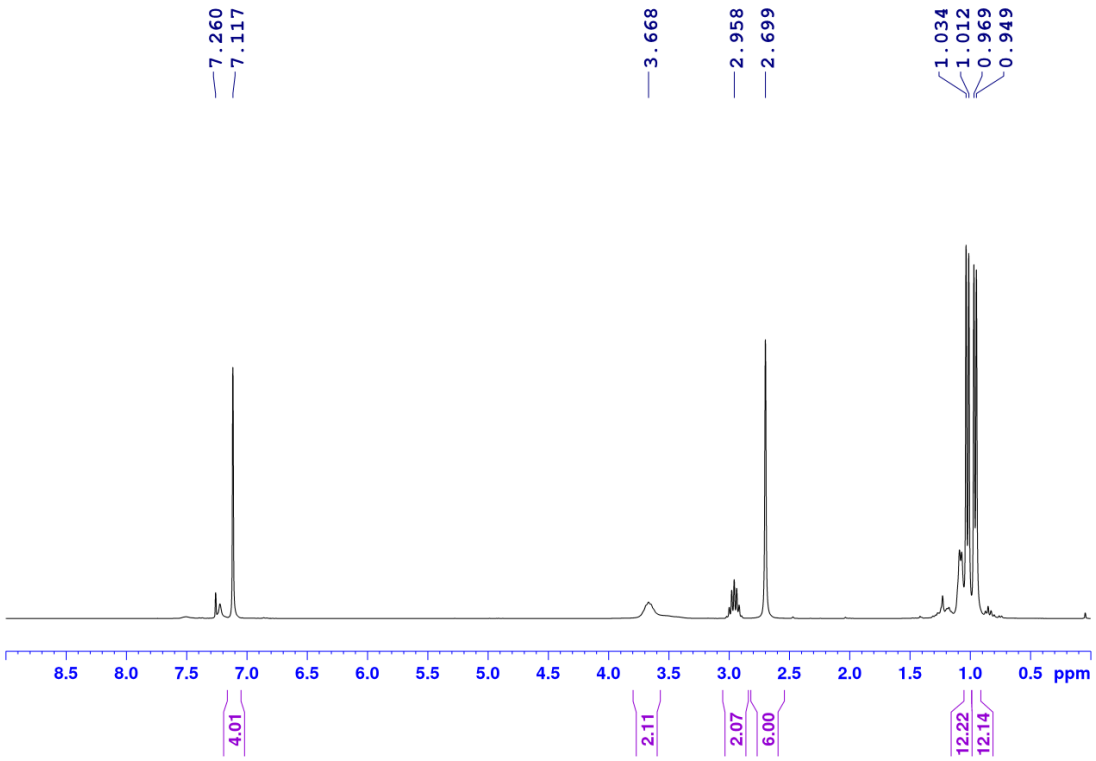


Fig. S1 ^{1}H NMR spectrum of **2a** in $CDCl_3$ at room temperature.

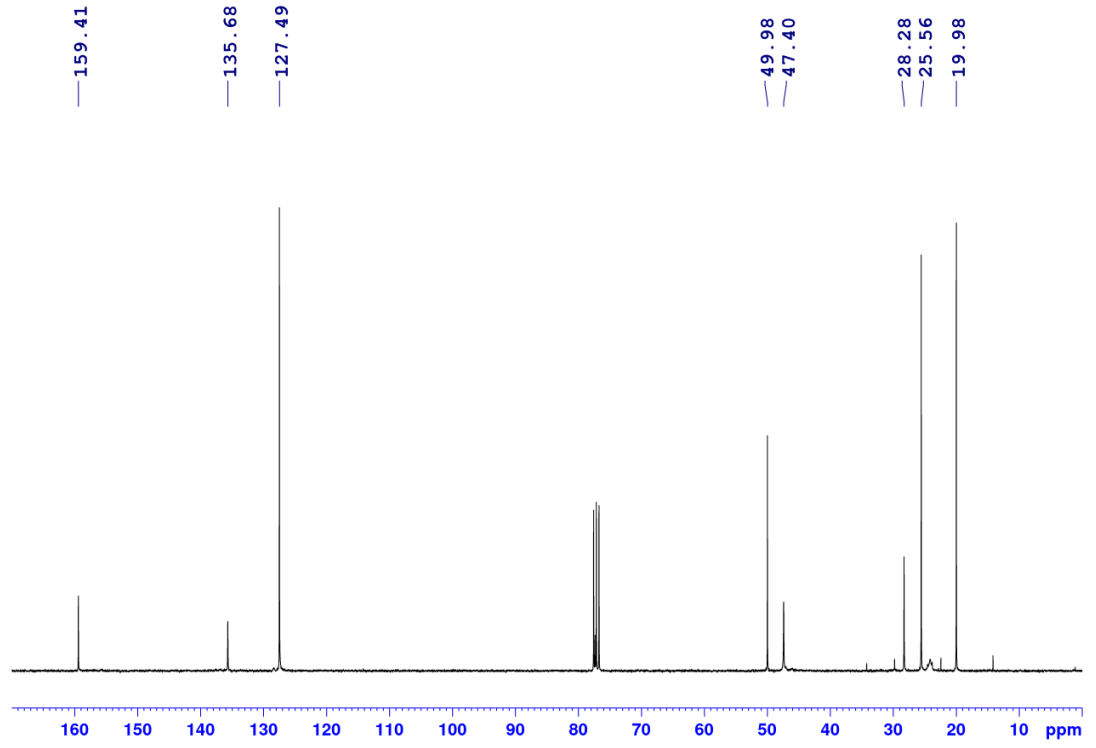


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in $CDCl_3$ at room temperature.

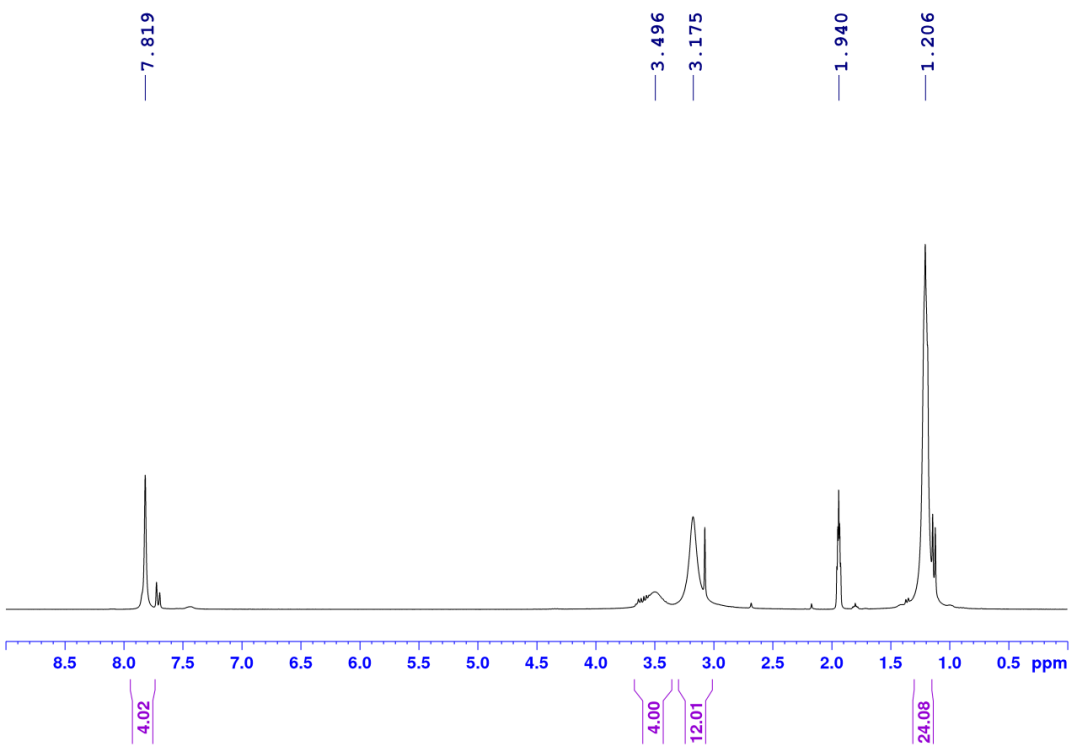


Fig. S3 ^{1}H NMR spectrum of **3a** in CD_3CN at room temperature.

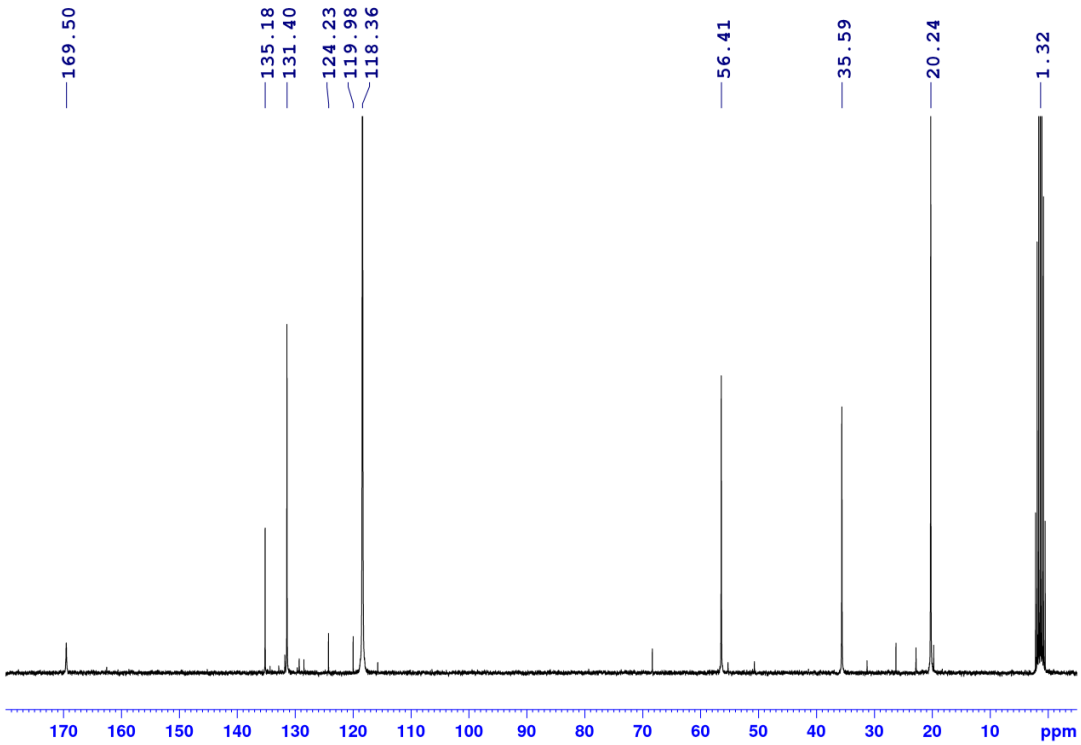


Fig. S4 $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in CD_3CN at room temperature.

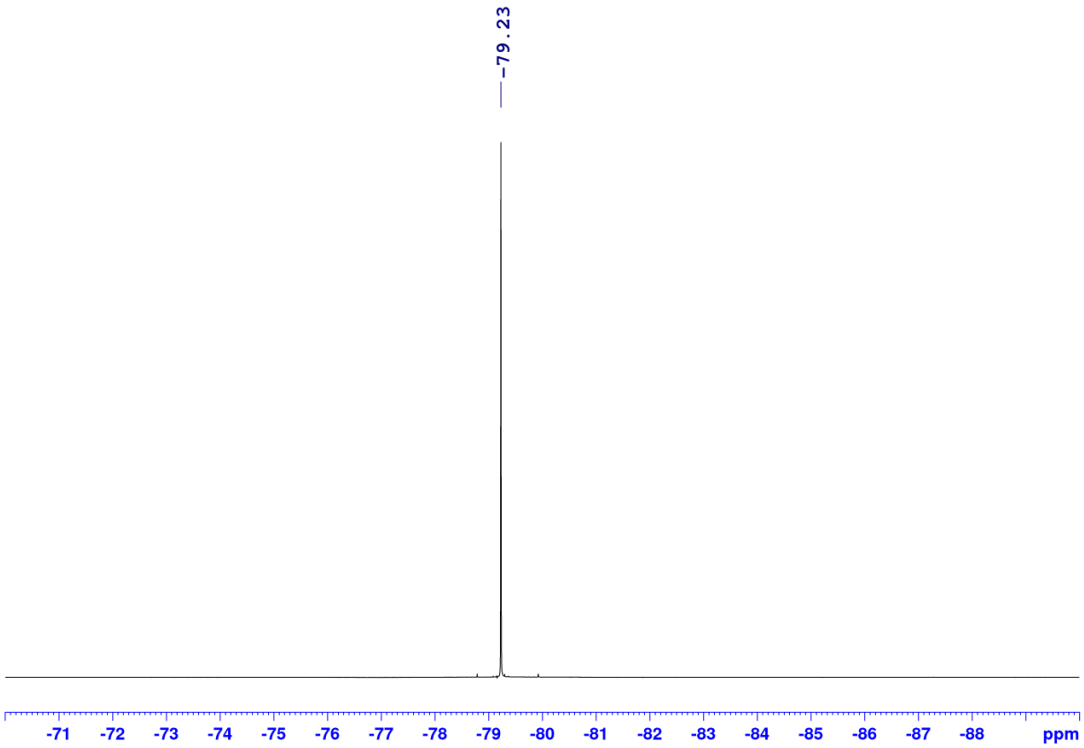


Fig. S5 $^{19}F\{^{1}H\}$ NMR spectrum of **3a** in CD_3CN at room temperature.

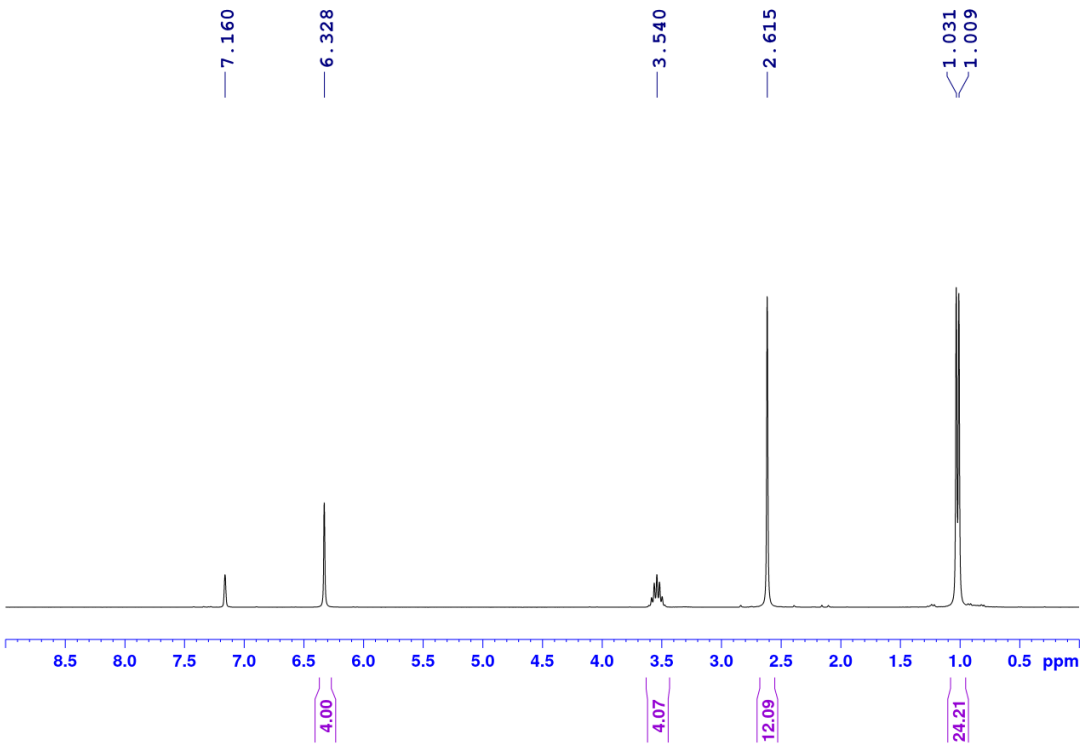


Fig. S6 ^{1}H NMR spectrum of **4a** in C_6D_6 at room temperature.

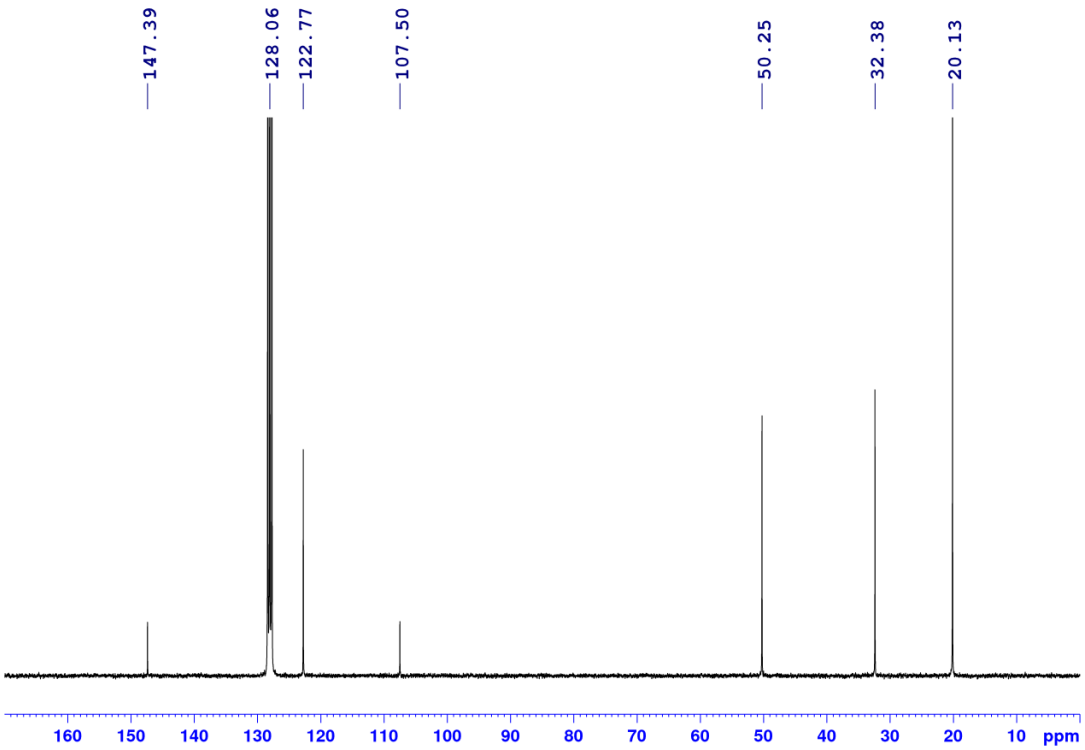


Fig. S7 $^{13}C\{^{1}H\}$ NMR spectrum of **4a** in C_6D_6 at room temperature.

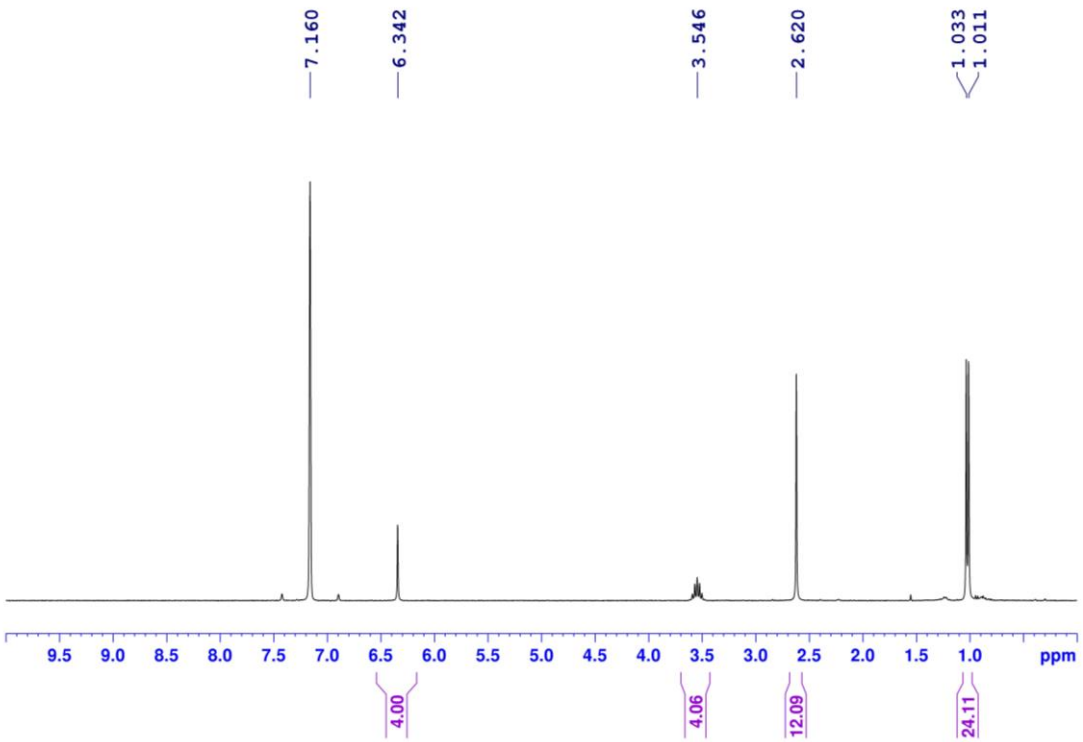


Fig. S8 ^{1}H NMR spectrum of **4a** after melting in C_6D_6 at room temperature.

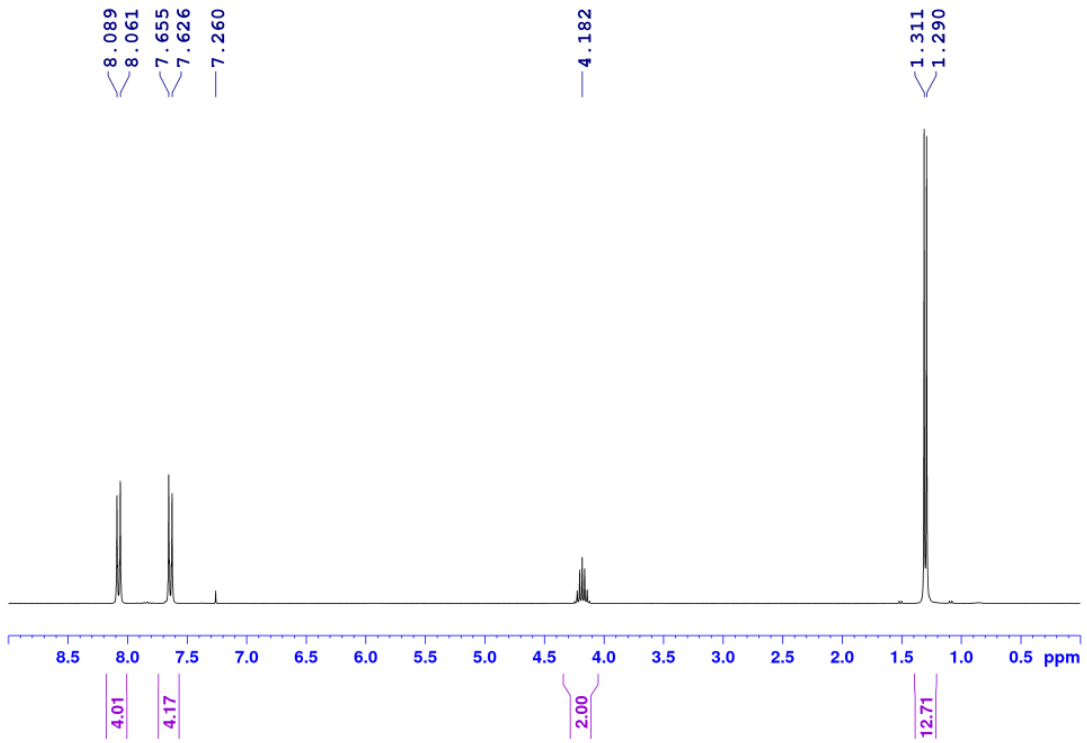


Fig. S9 ^{1}H NMR spectrum of **F** in $CDCl_3$ at room temperature.

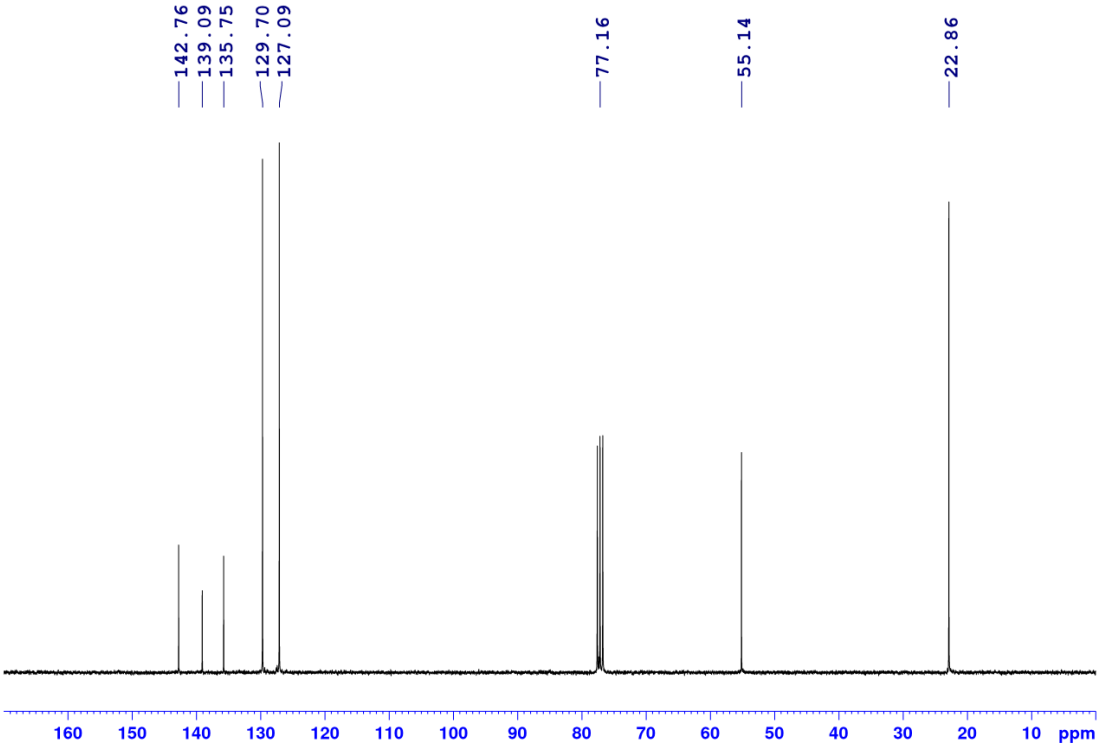


Fig. S10 $^{13}C\{^{1}H\}$ NMR spectrum of **F** in $CDCl_3$ at room temperature.

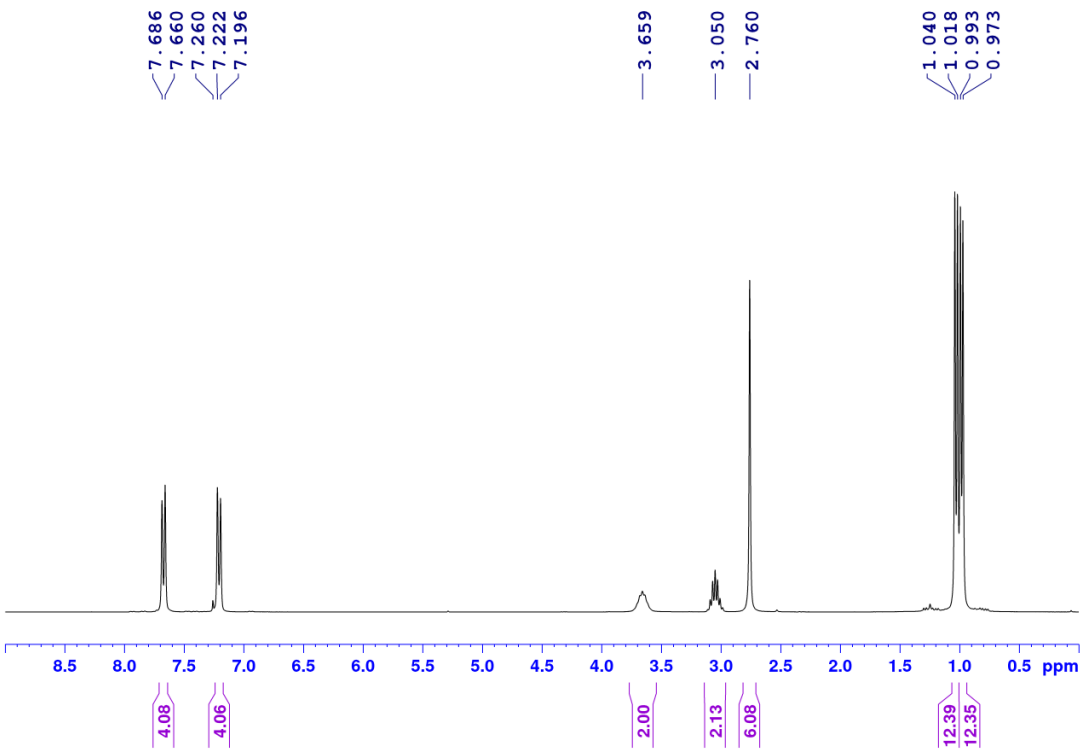


Fig. S11 ^{1}H NMR spectrum of **2b** in $CDCl_3$ at room temperature.

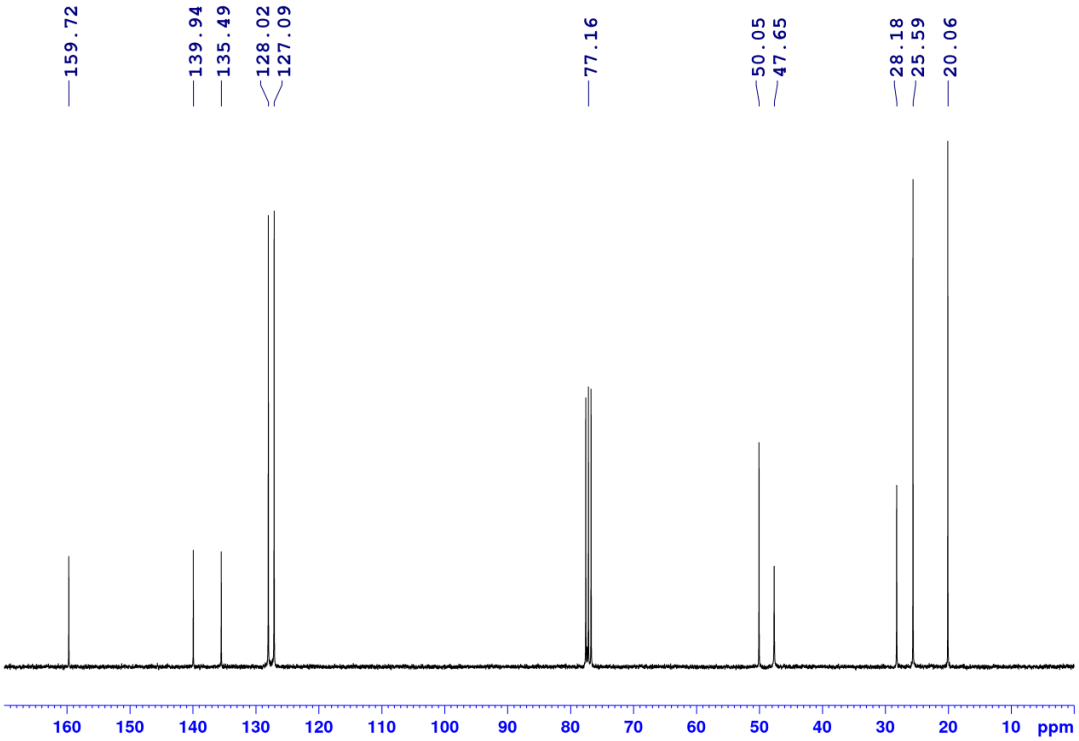


Fig. S12 $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in $CDCl_3$ at room temperature.

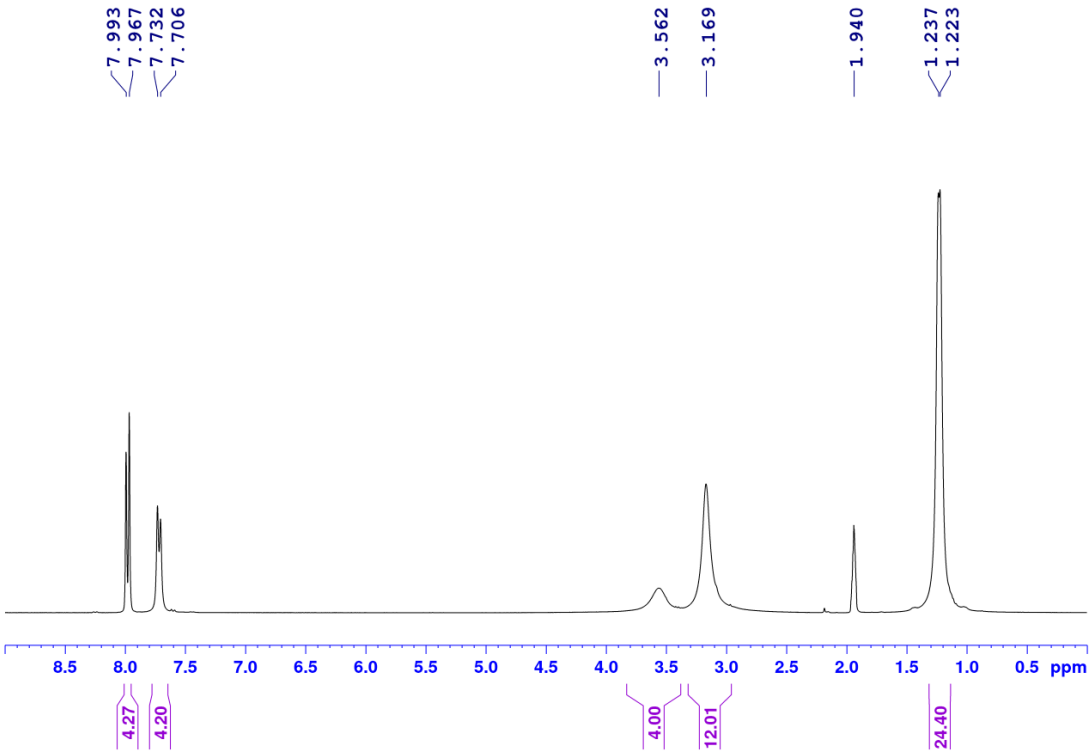


Fig. S13 ^{1}H NMR spectrum of **3b** in CD_3CN at room temperature.

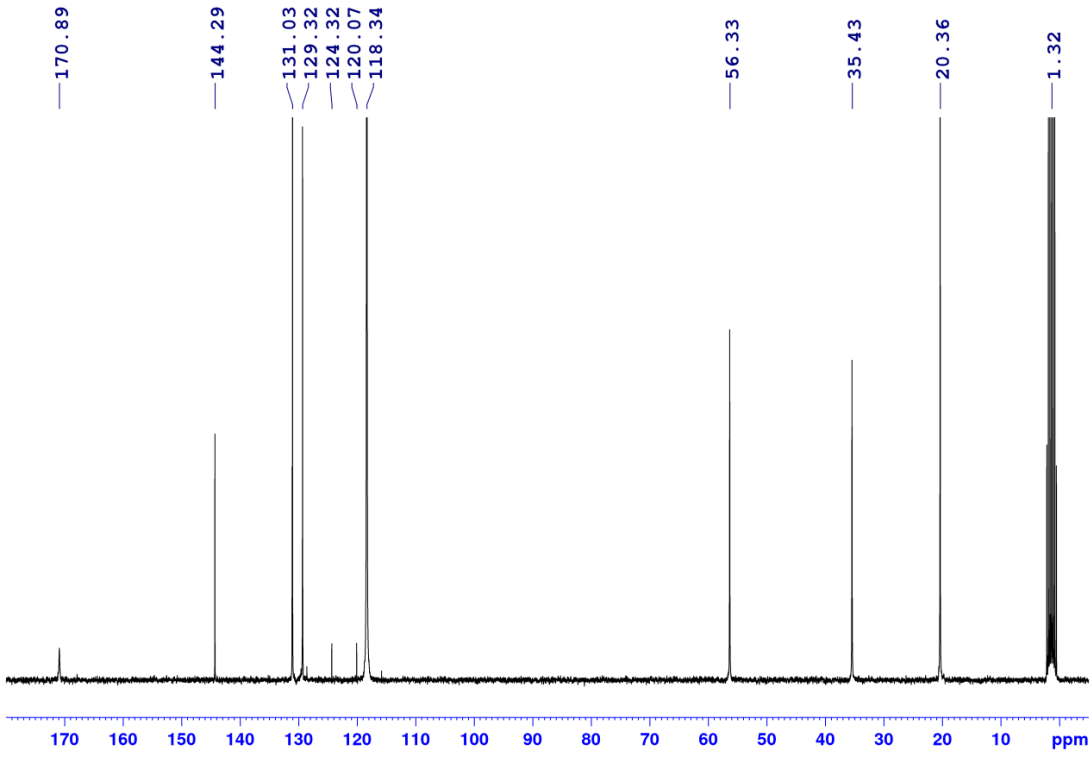


Fig. S14 $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in CD_3CN at room temperature.

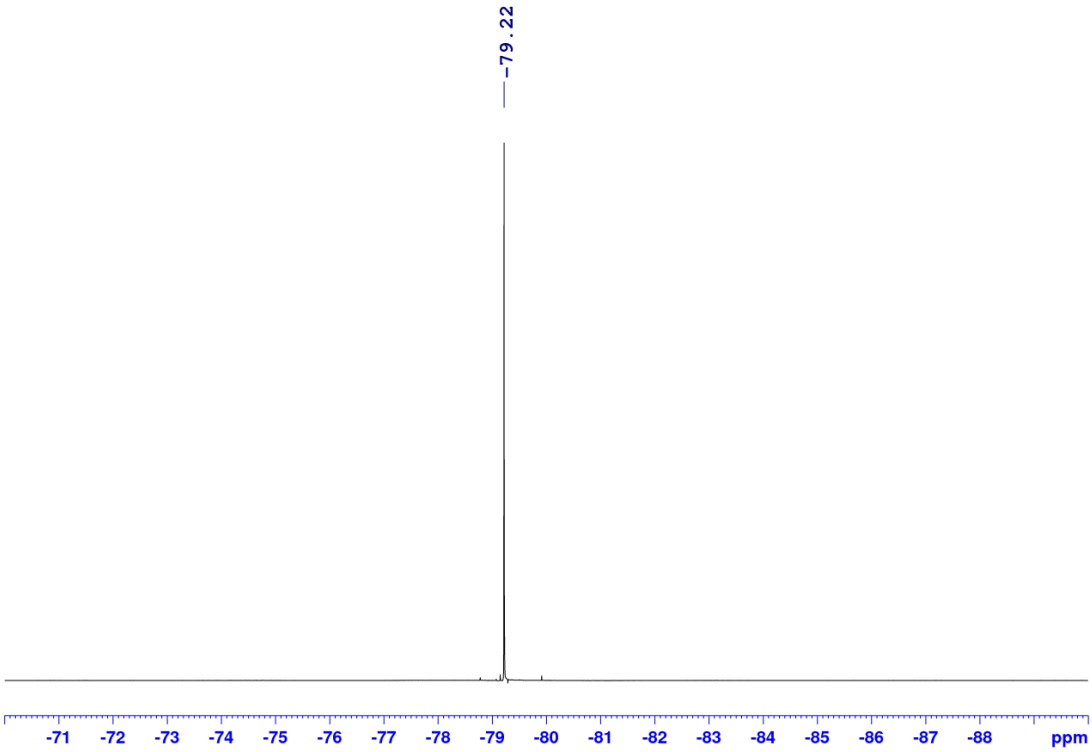


Fig. S15 $^{19}F\{^{1}H\}$ NMR spectrum of **3b** in CD_3CN at room temperature.

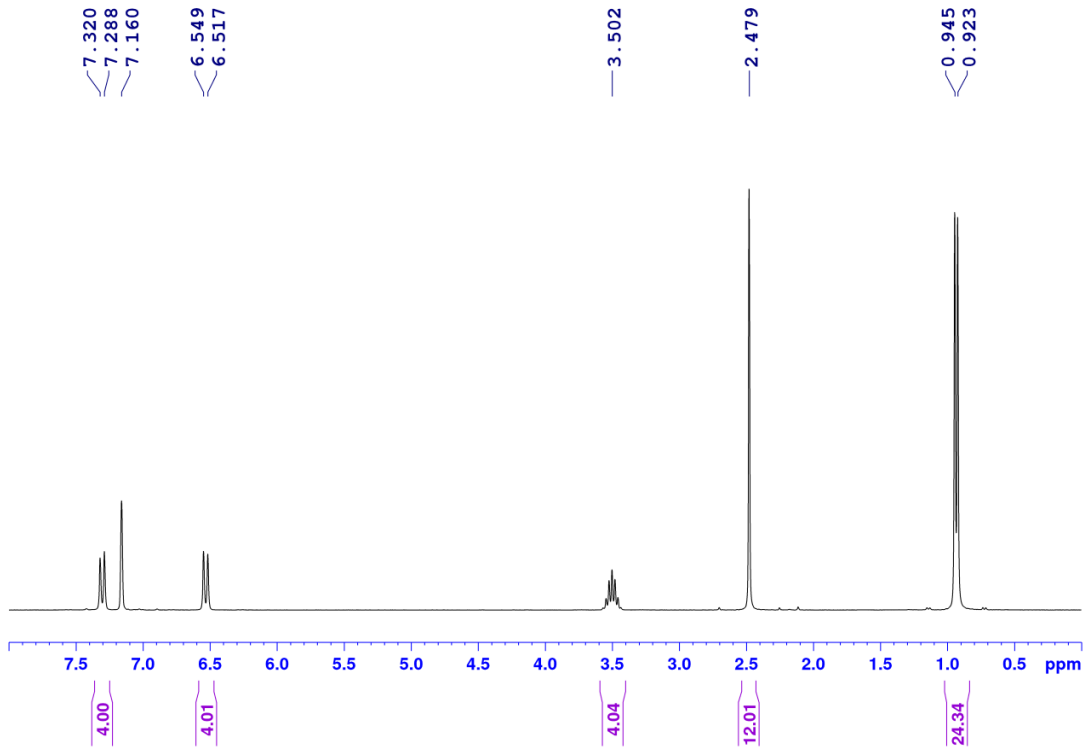


Fig. S16 ^{1}H NMR spectrum of **4b** in C_6D_6 at room temperature.

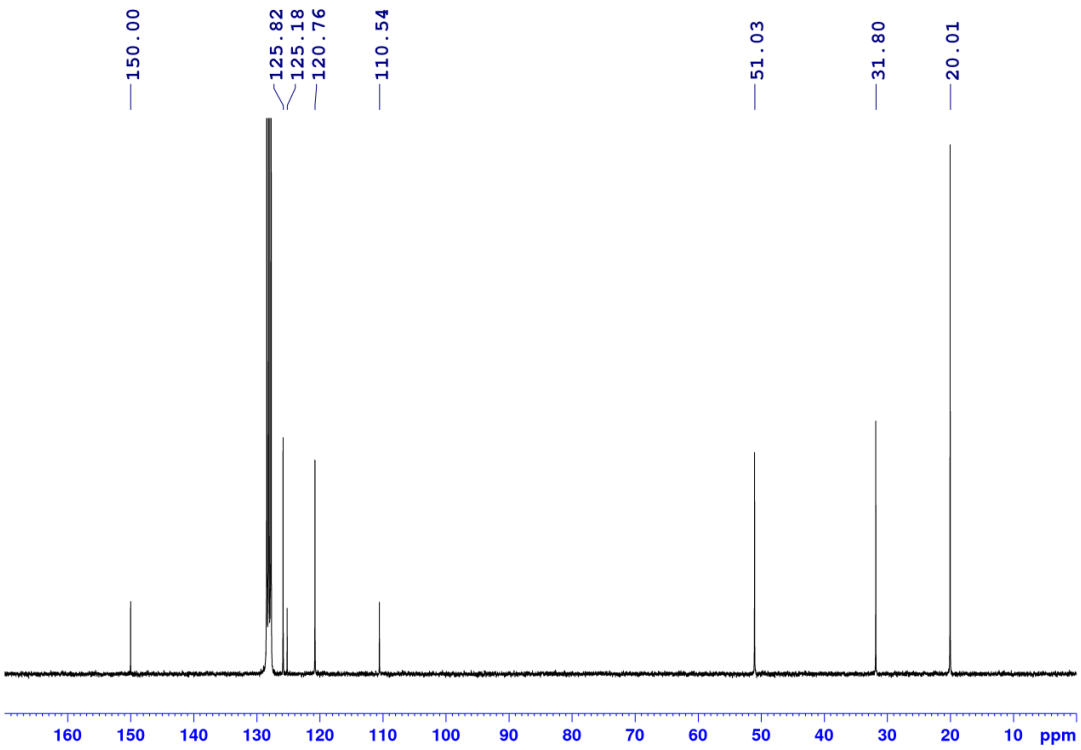


Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of **4b** in C_6D_6 at room temperature.

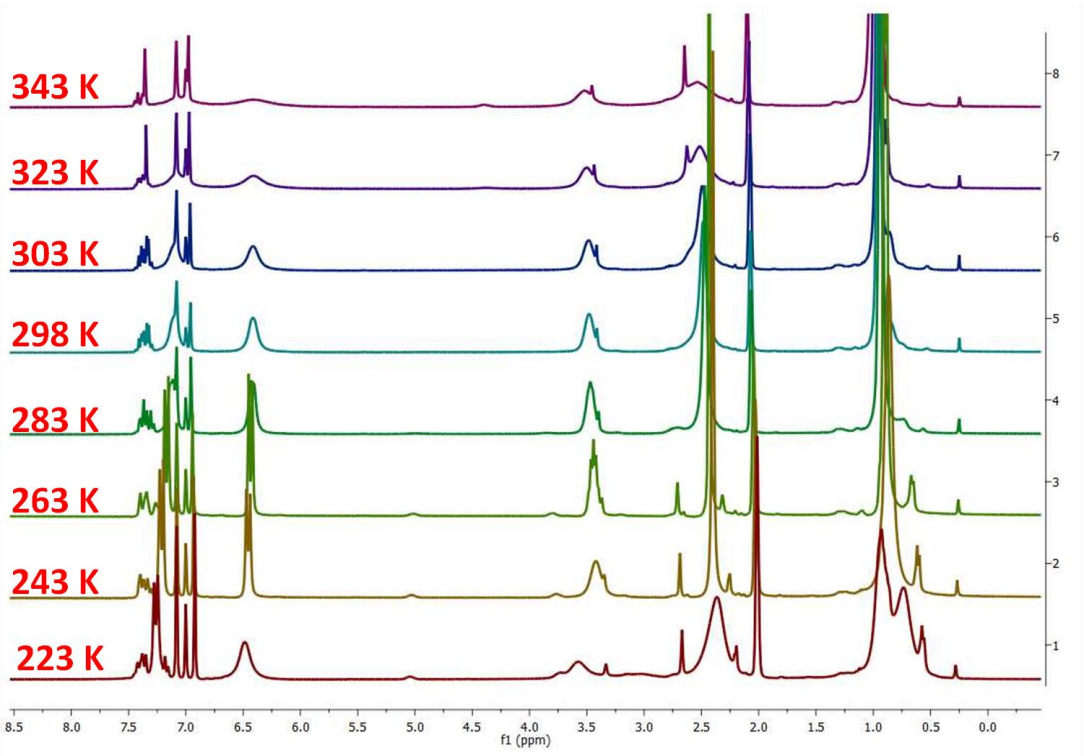


Fig. S18 Temperature-dependent ^{1}H NMR spectra of **4b** in Tol-d_8.

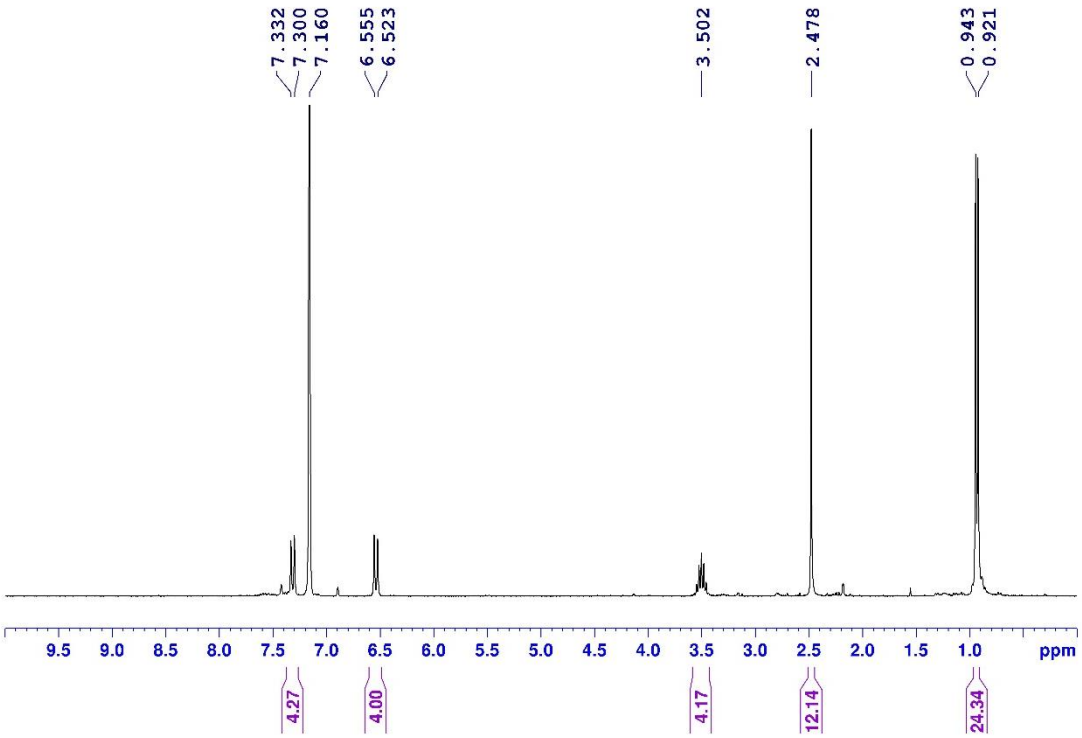


Fig. S19 ^{1}H NMR spectrum of **4b** after melting in C_6D_6 at room temperature.

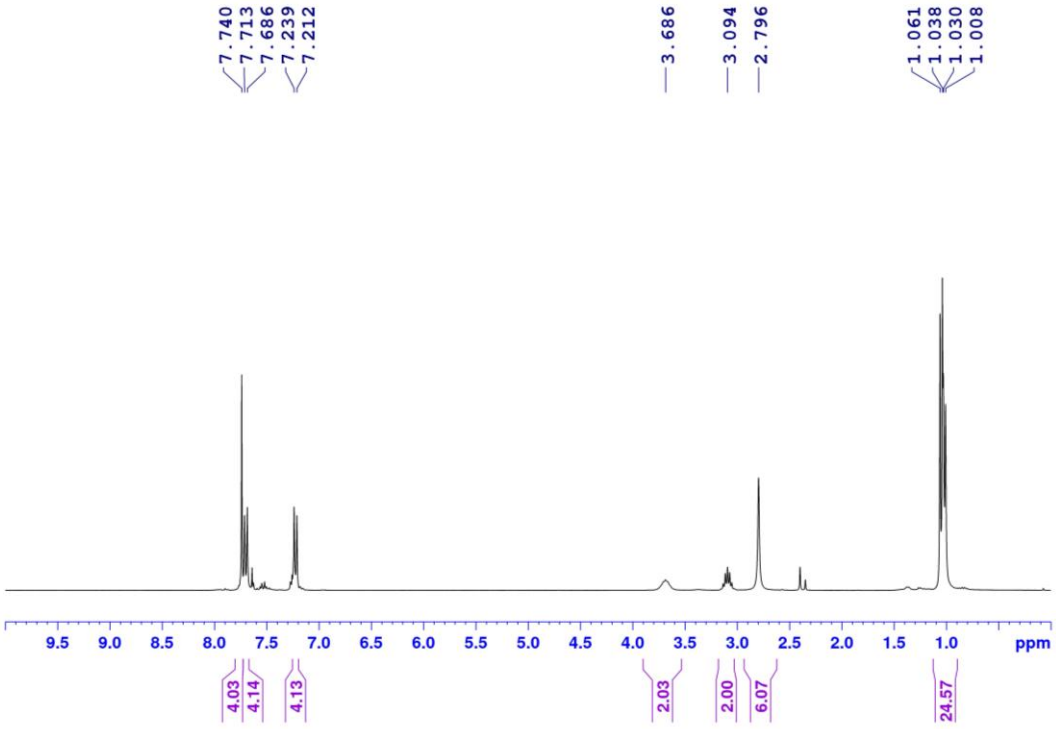


Fig. S20 ^{1}H NMR spectrum of **2c** in $CDCl_3$ at room temperature.

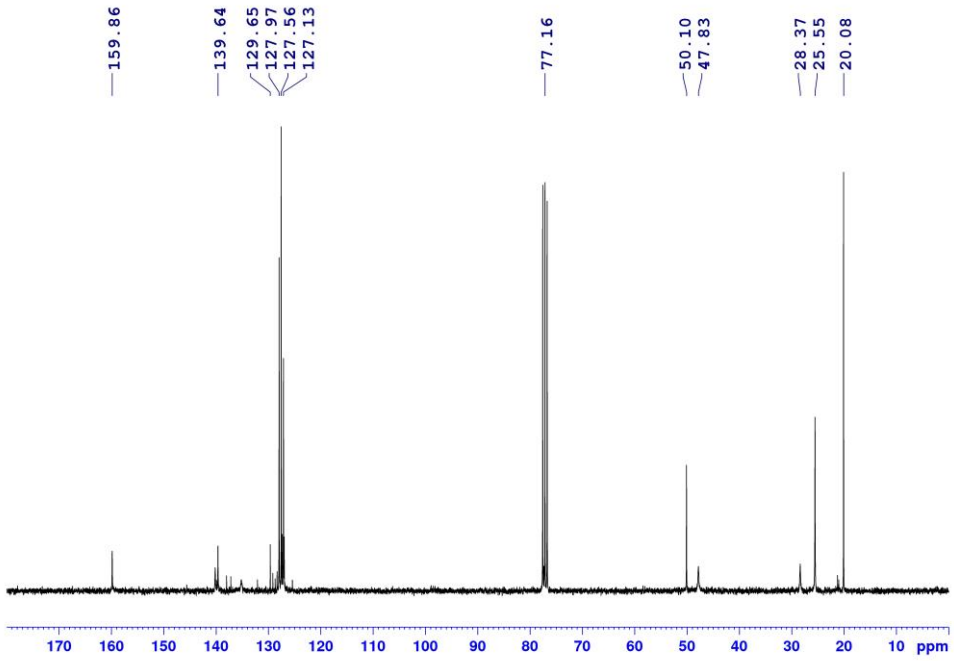


Fig. S21 $^{13}C\{^{1}H\}$ NMR spectrum of **2c** in $CDCl_3$ at room temperature.

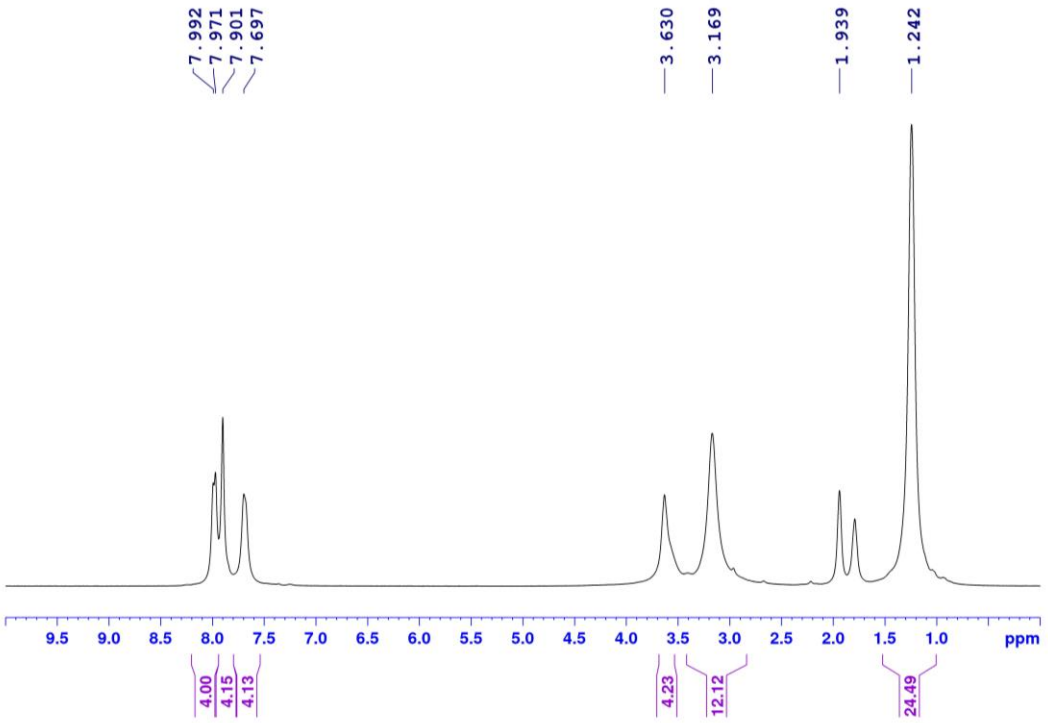


Fig. S22 ^{1}H NMR spectrum of **3c** in CD_3CN at room temperature.

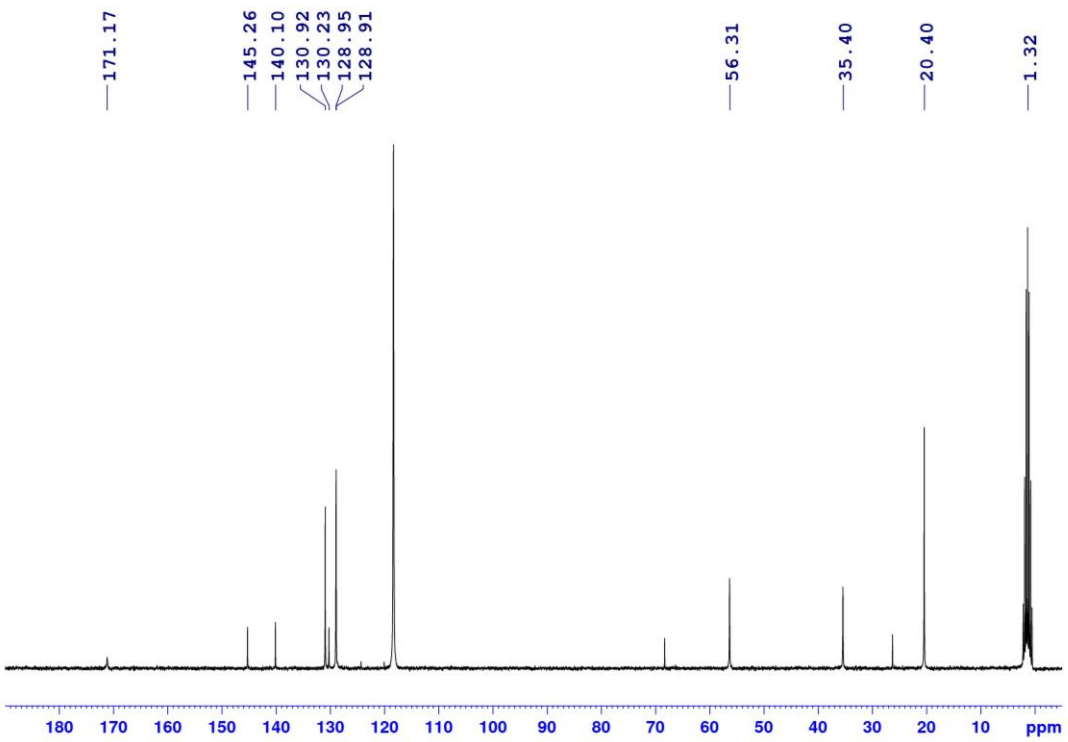


Fig. S23 $^{13}C\{^{1}H\}$ NMR spectrum of **3c** in CD_3CN at room temperature.

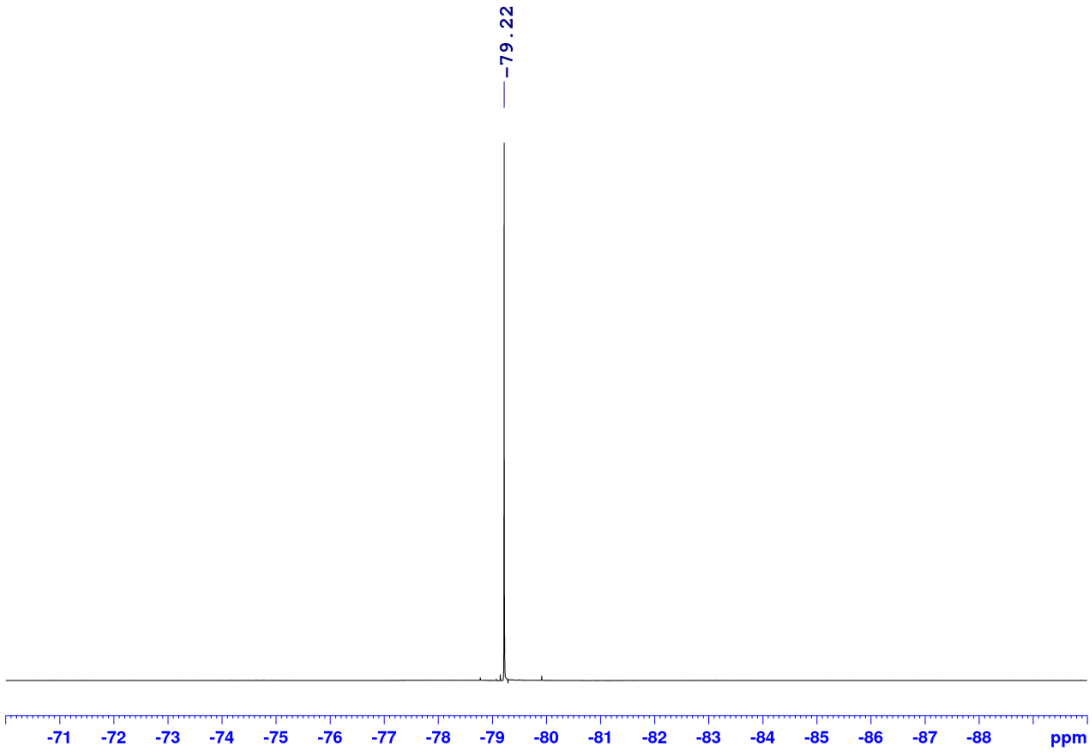


Fig. S24 $^{19}F\{^{1}H\}$ NMR spectrum of **3c** in CD_3CN at room temperature.

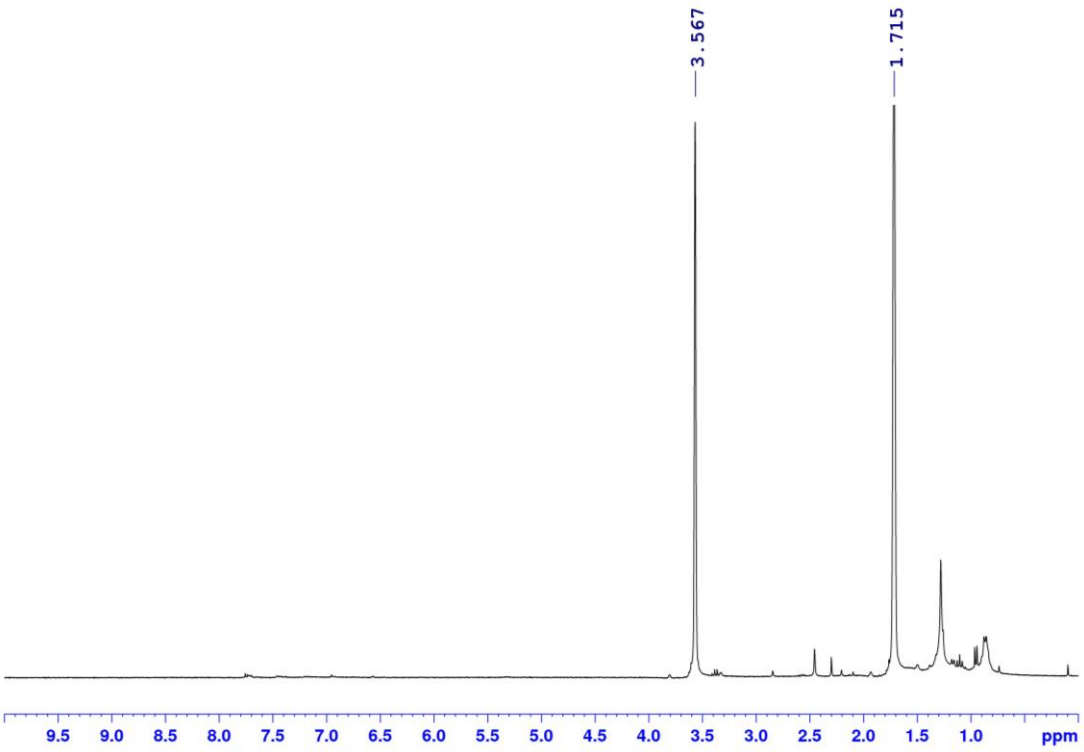


Fig. S25 ^{1}H NMR spectrum of **4c** in THF-d8 at RT.

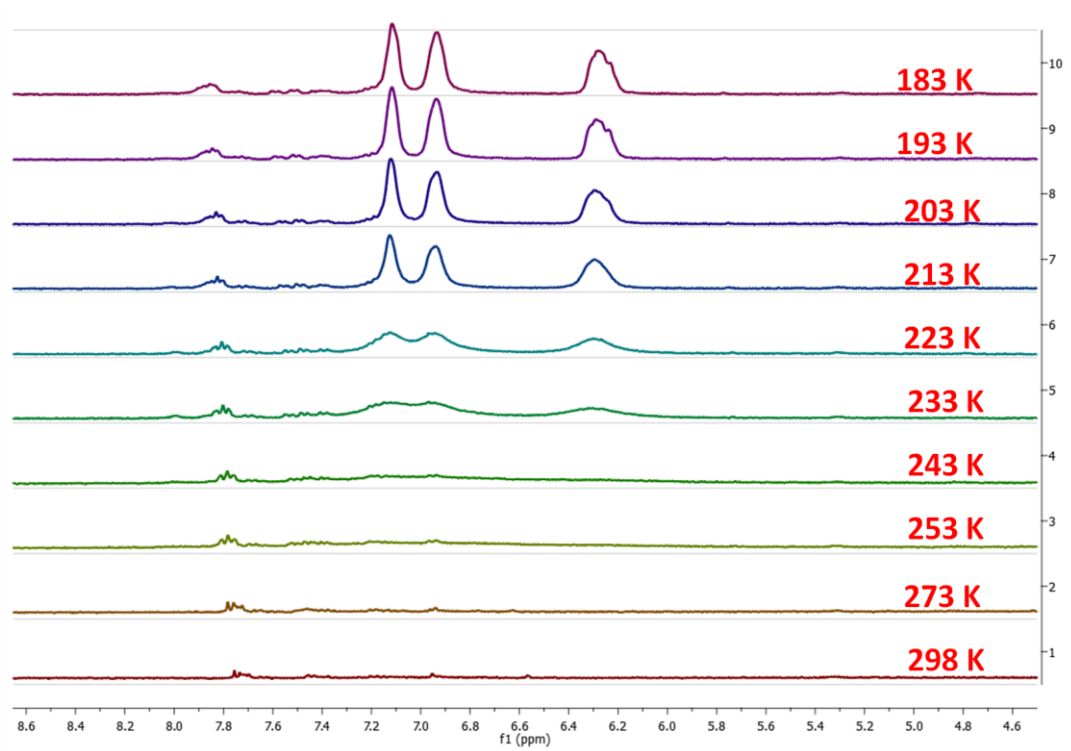


Fig. S26 Selected region of the VT-^{1}H NMR spectra of **4c** in THF-d8.

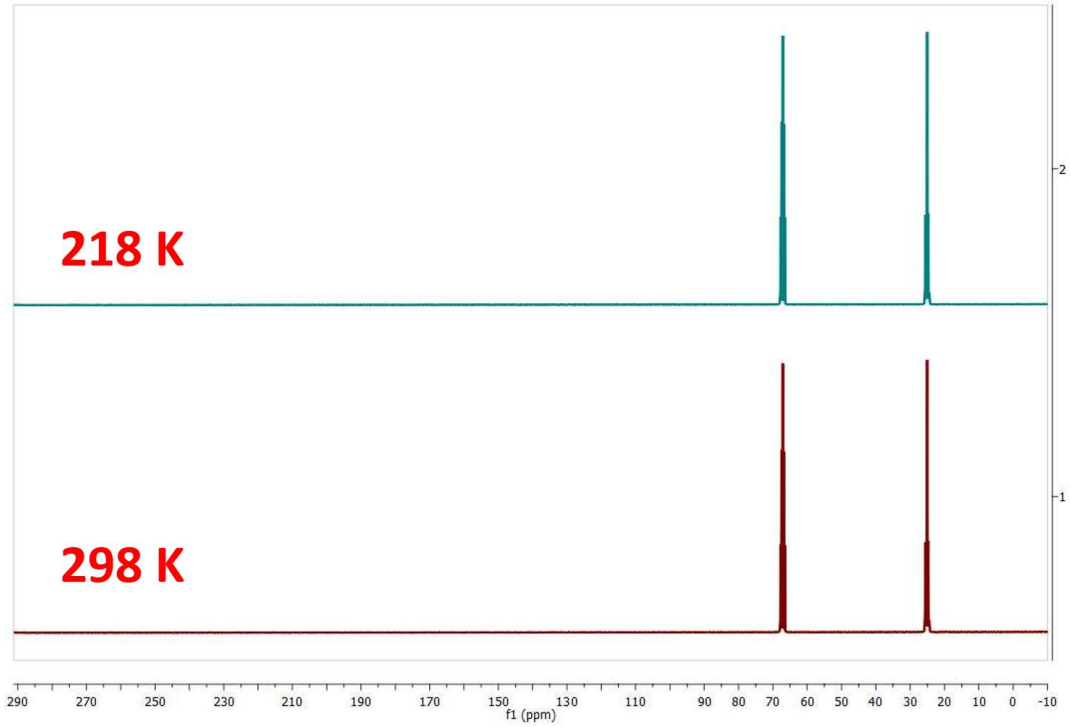


Fig. S27 $^{13}C\{^{1}H\}$ NMR spectra of **4c** in THF-d8 at 298 K and 218 K.

UV/Vis spectra

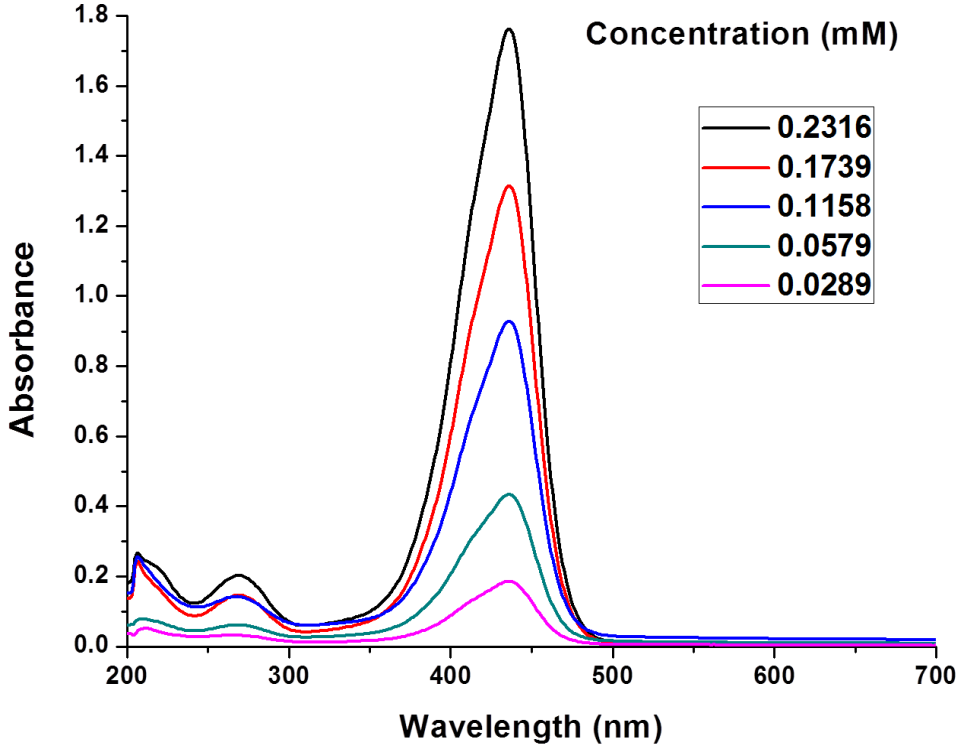


Fig. S28 UV/Vis spectra of **4a** in THF at different concentrations.

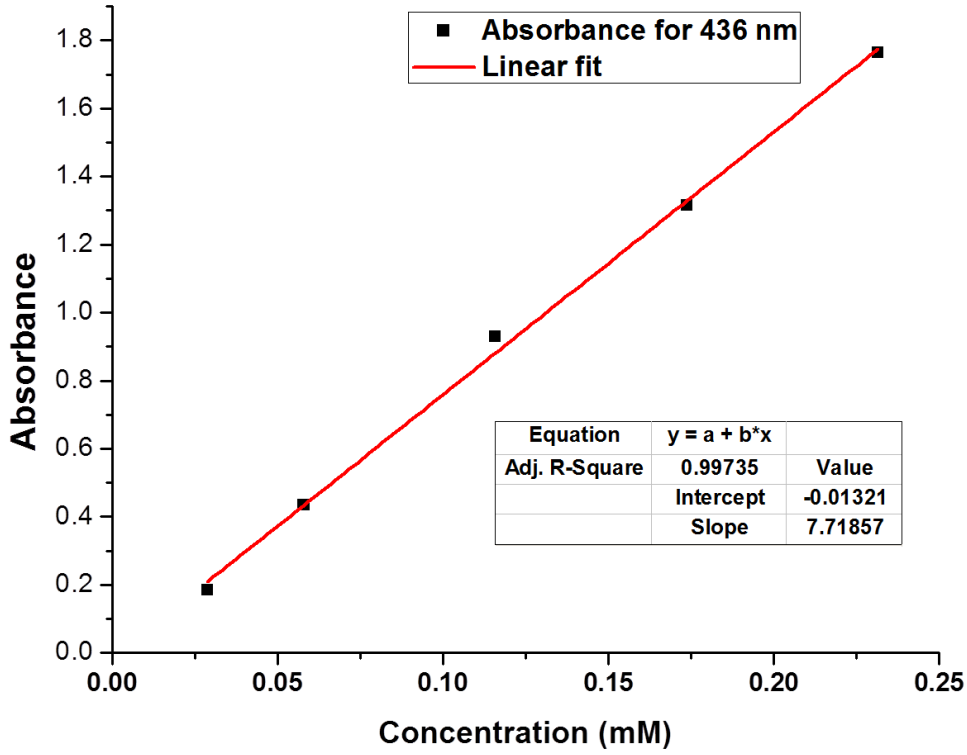


Fig. S29 Linear regression of **4a** at 436 nm.

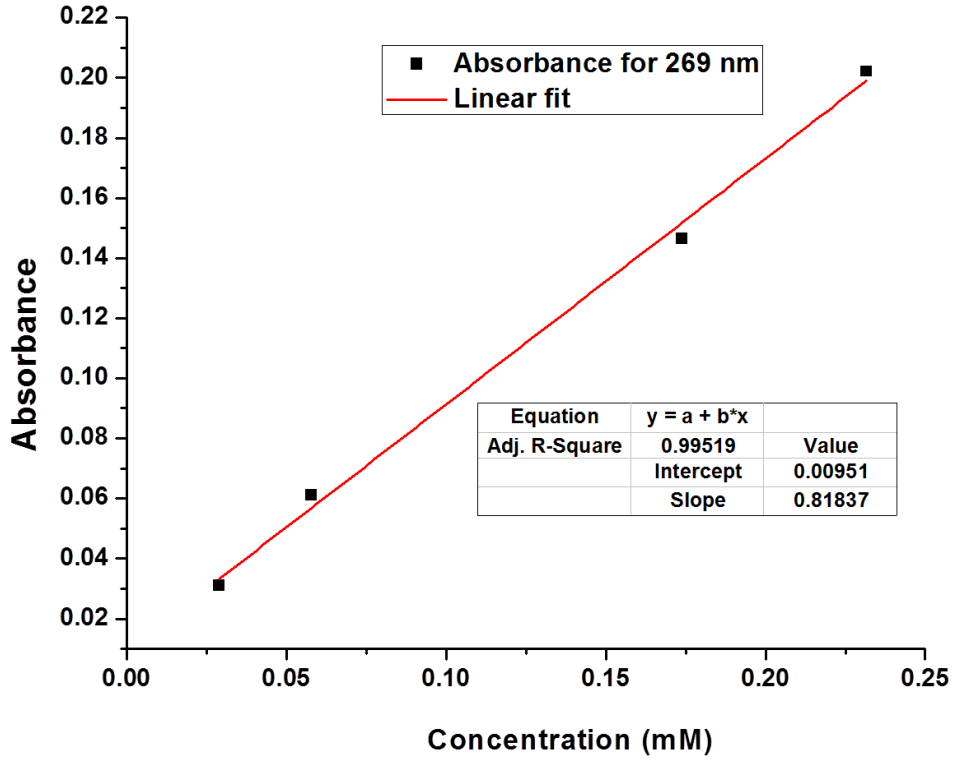


Fig. S30 Linear regression of **4a** at 269 nm.

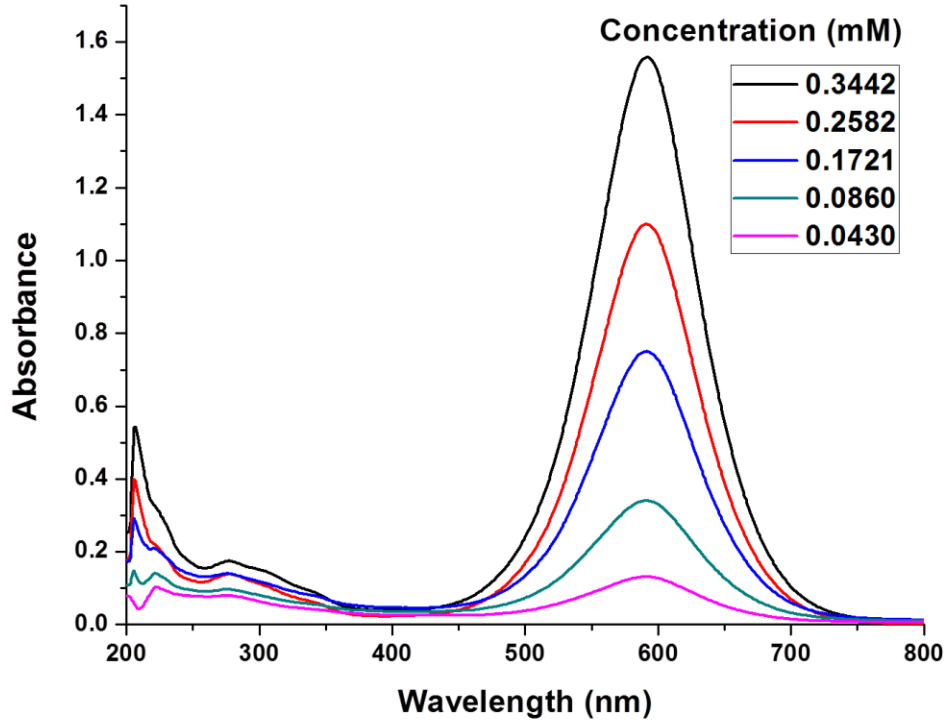


Fig. S31 UV/Vis spectra of **4b** in THF at different concentrations.

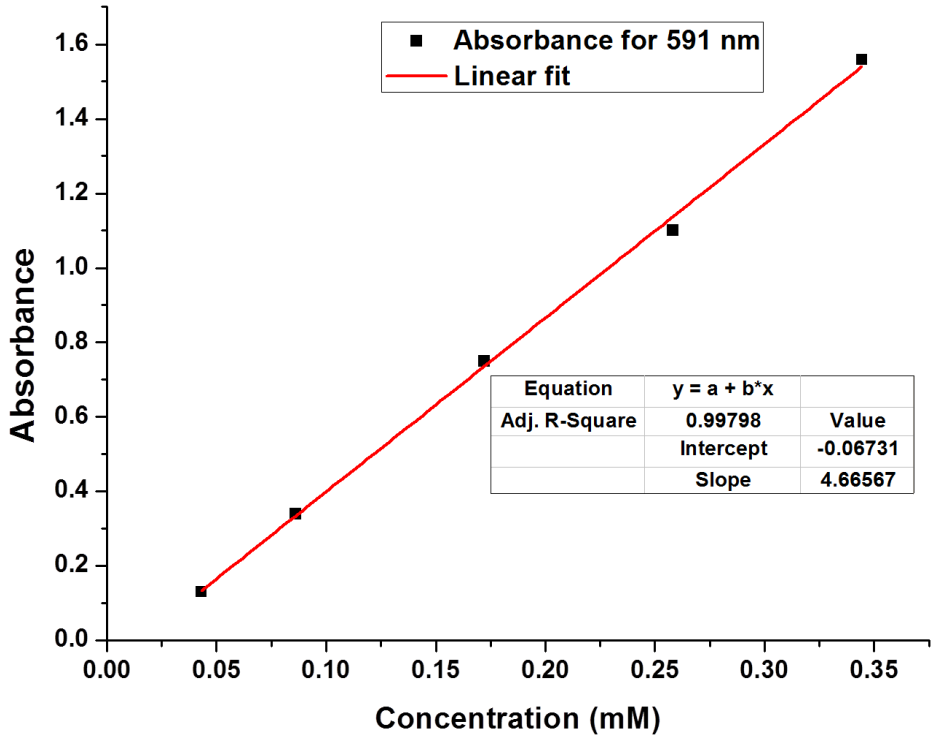


Fig. S32 Linear regression of **4b** at 591 nm.

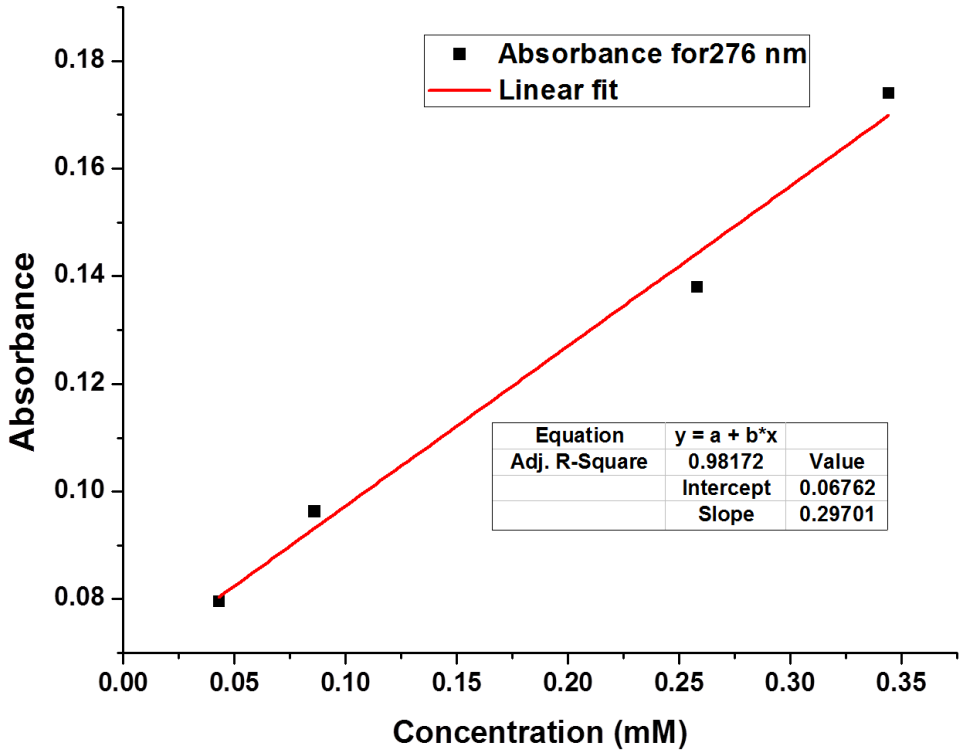


Fig. S33 Linear regression of **4b** at 276 nm.

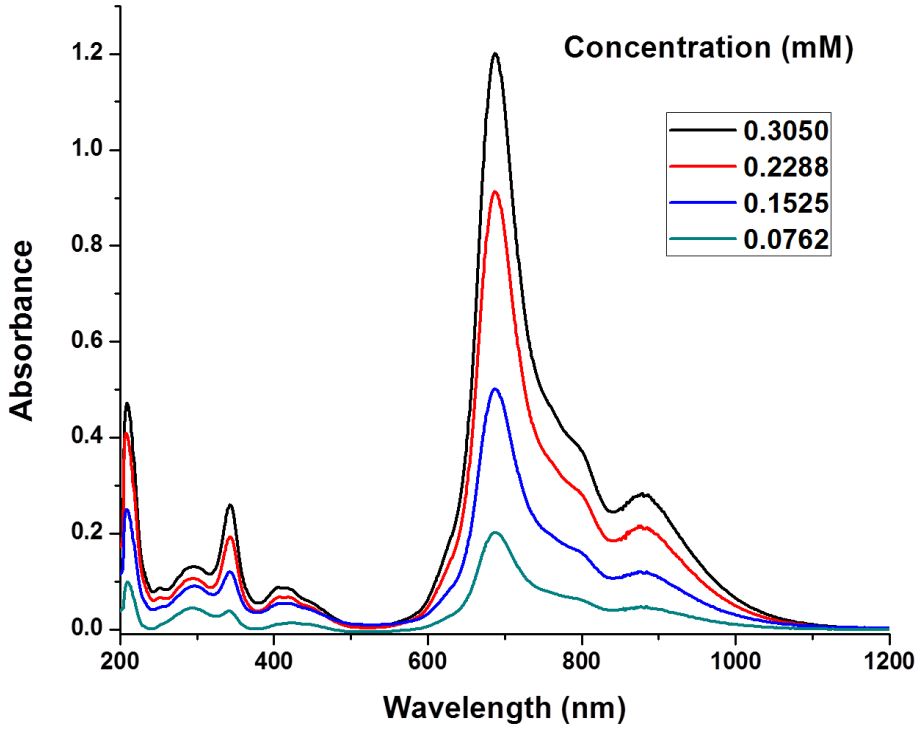


Fig. S34 UV/Vis spectra of **4c** in THF at different concentrations.

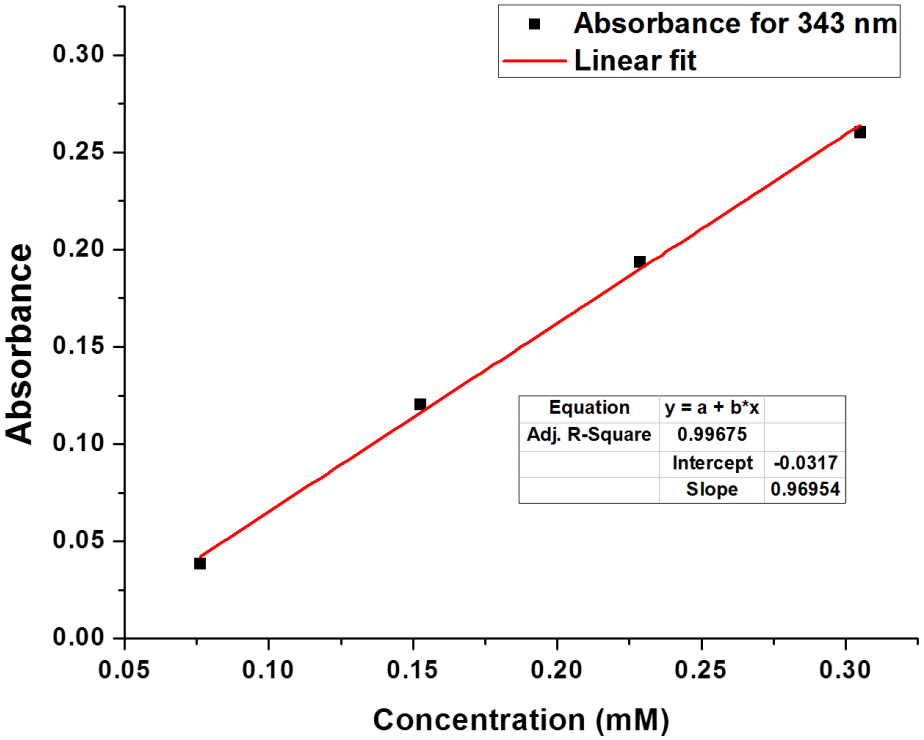


Fig. S35 Linear regression of **4c** at 343 nm.

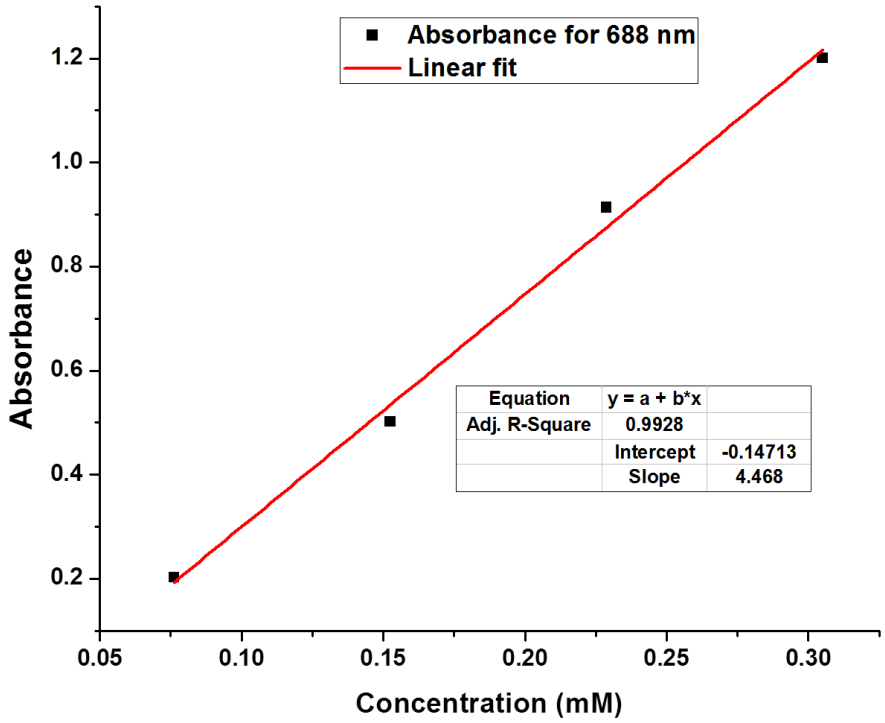


Fig. S36 Linear regression of **4c** at 688 nm.

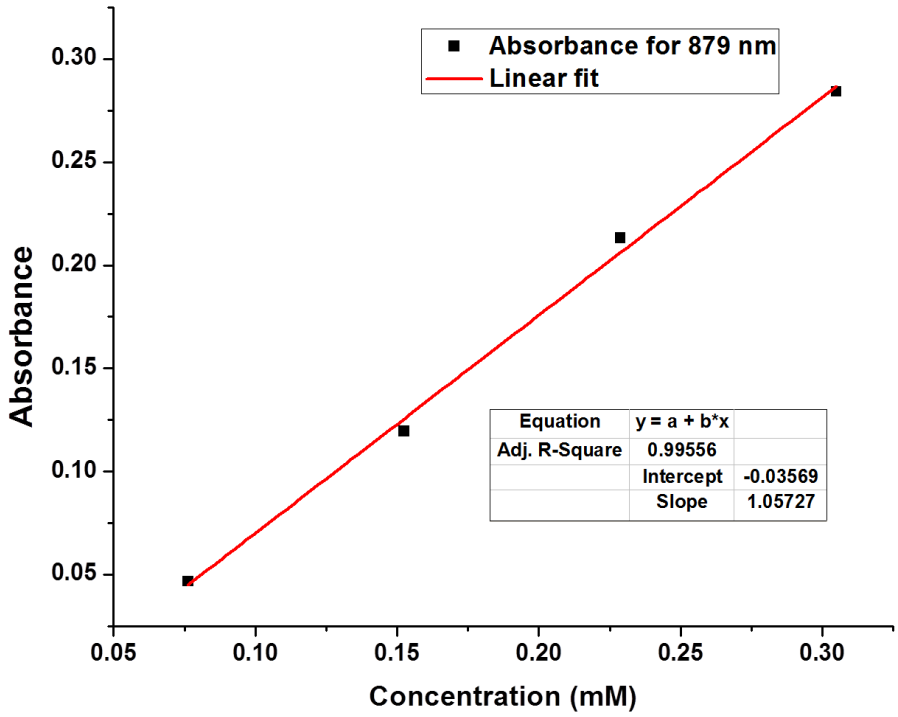


Fig. S37 Linear regression of **4c** at 879 nm.

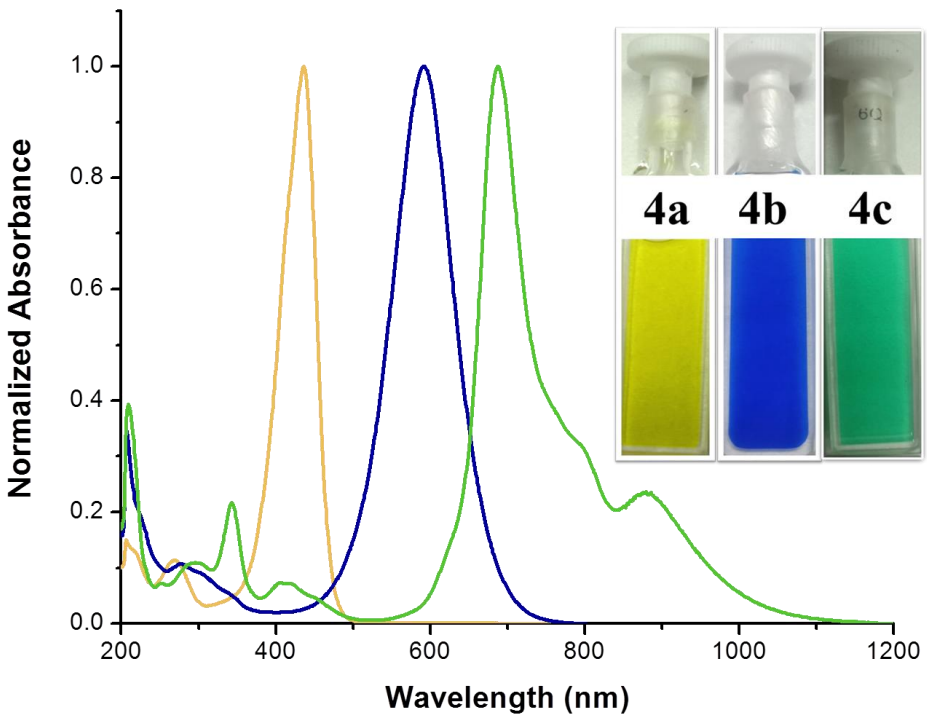


Fig. S38 Comparison of UV/Vis spectra of **4a**, **4b** and **4c** in THF at room temperature.

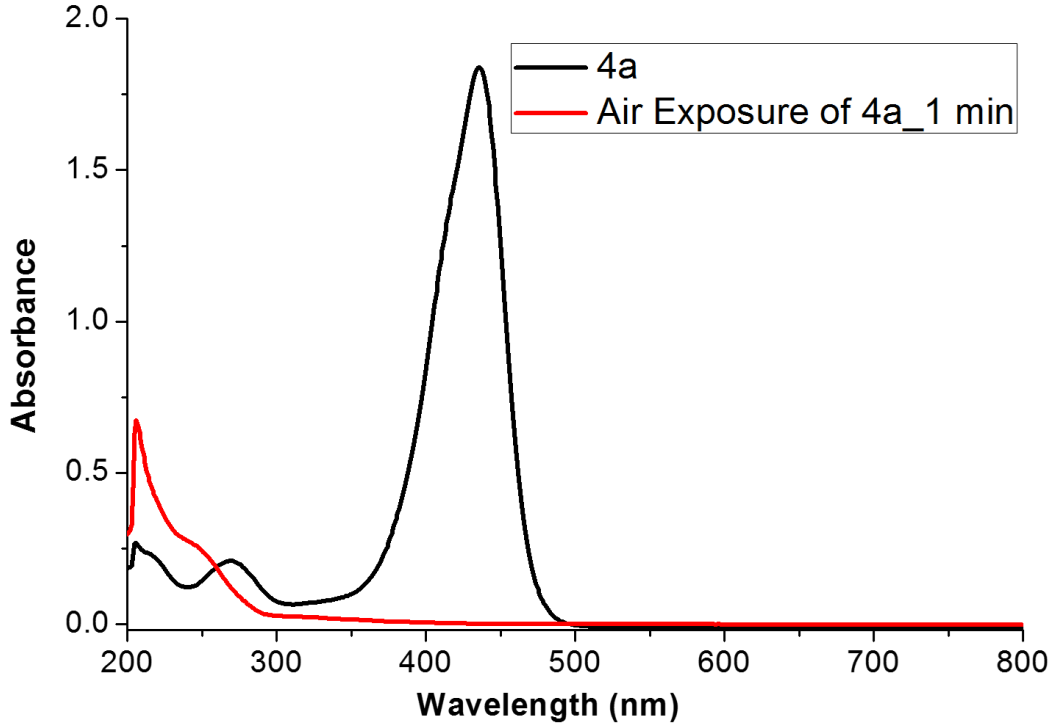


Fig. S39 UV/Vis spectra of **4a** in THF before and after exposing to air.

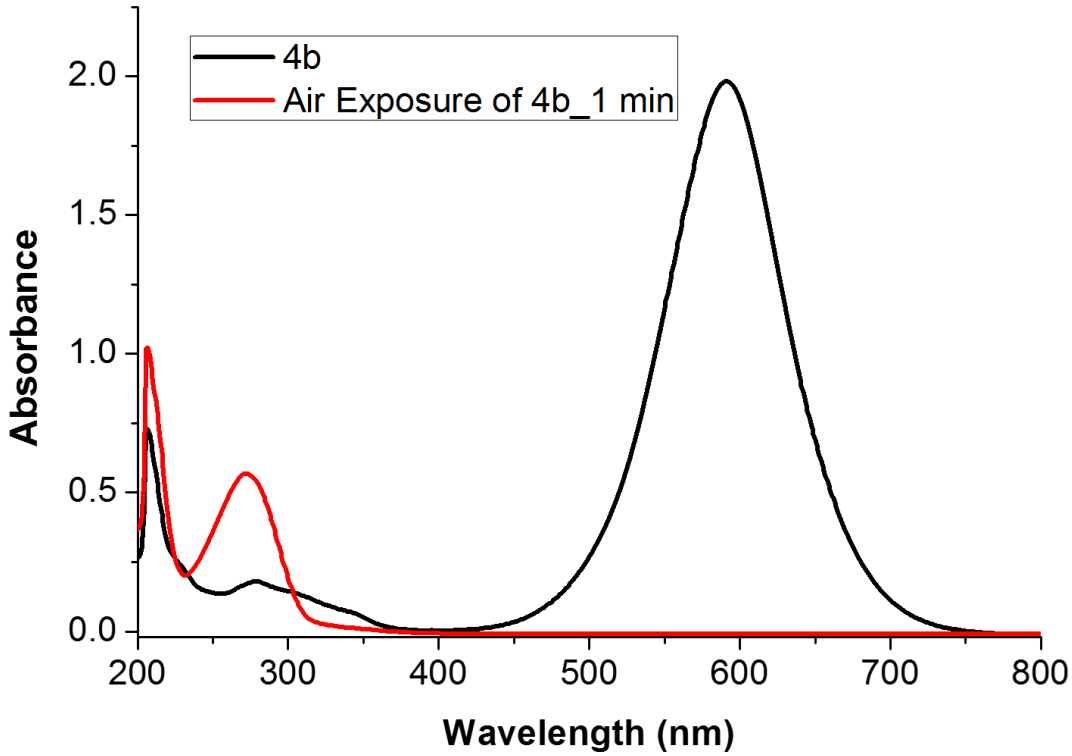


Fig. S40 UV/Vis spectra of **4b** in THF before and after exposing to air.

Cyclic Voltammetry

Table S1 Redox potentials ($E_{1/2}$) of **3a**-**3c** *vs.* FcH/FcH$^+$ in CH_3CN/0.1 M Bu_4NPF_6 measured at GC working electrode at 100 mVs^{-1}.

	$E_{1/2}$(1st Red)	Peak-to-peak separation (ΔE)
3a	−1.42	40 mV
3b	−1.61	45 mV
3c	−1.82	50 mV

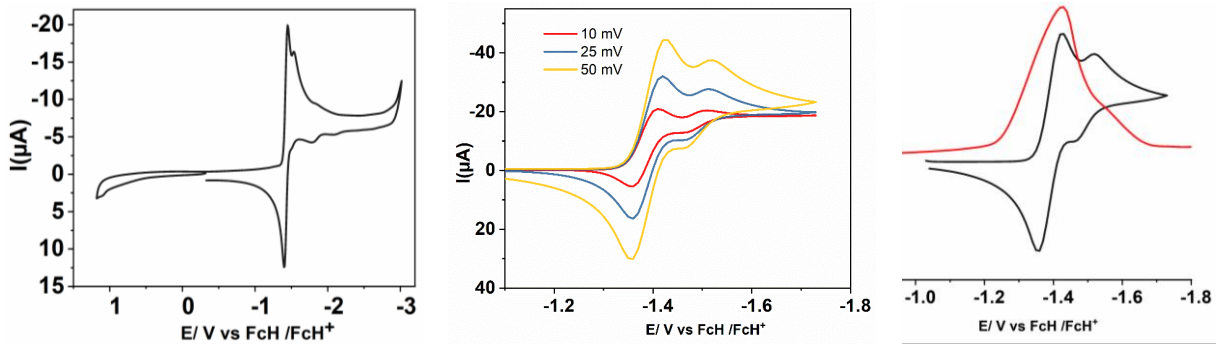


Fig. S41 Cyclic voltammogram of **3a** in CH_3CN/0.1 M Bu_4NPF_6 at 100 mVs^{-1} (left), Cyclic voltammograms of **3a** at different scan rates (middle), and Differential pulse voltammogram (DPV) of a 0.1 mM solution of **3a** in CH_3CN/0.1 M Bu_4NPF_6 at 10 mVs^{-1} (right).

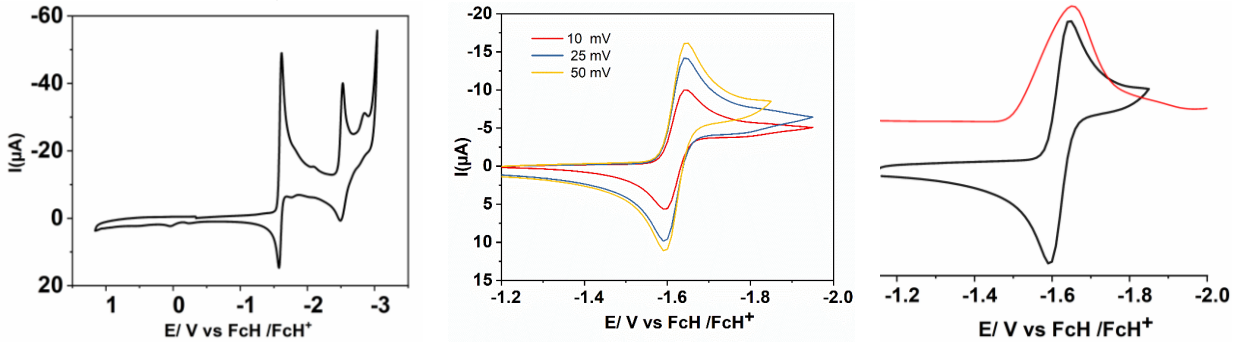


Fig. S42 Cyclic voltammogram of **3b** in CH_3CN/0.1 M Bu_4NPF_6 at 100 mVs^{-1} (left), Cyclic voltammograms of **3b** at different scan rates (middle), and Differential pulse voltammogram (DPV) of a 0.1 mM solution of **3b** in CH_3CN/0.1 M Bu_4NPF_6 at 10 mVs^{-1} (right).

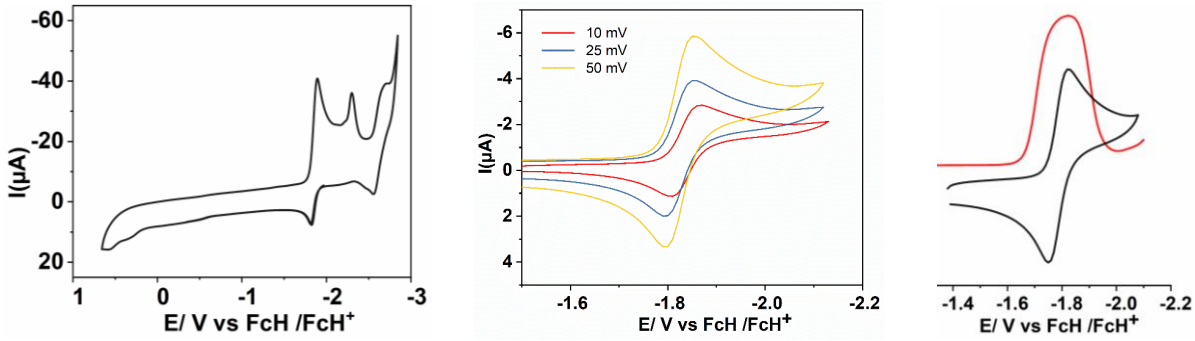


Fig. S43 Cyclic voltammogram of **3c** in CH_3CN/0.1 M Bu_4NPF_6 at 100 mVs^{-1} (left), Cyclic voltammograms **3c** at different scan rates (middle), and Differential pulse voltammogram (DPV) of a 0.1 mM solution of **3c** in CH_3CN/0.1 M Bu_4NPF_6 at 10 mVs^{-1} (right).

UV-Vis-NIR-spectroelectrochemistry

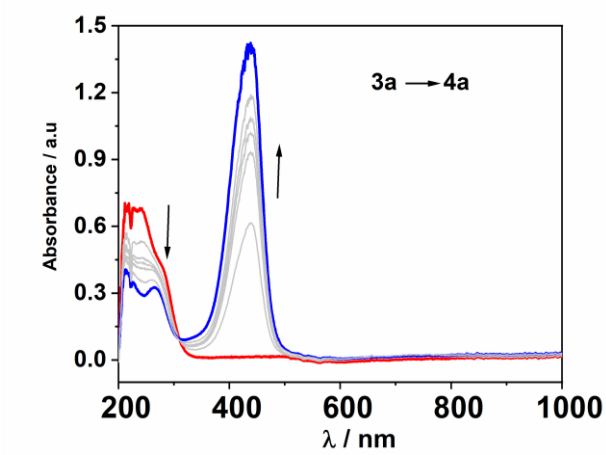


Fig. S44 Changes in the UV-Vis-NIR spectrum of **3a** during spectroelectrochemistry in CH_3CN/0.1 M Bu_4NPF_6 (measured at the potential of −1.45 V with the scan rate of 10 mVs^{-1}).

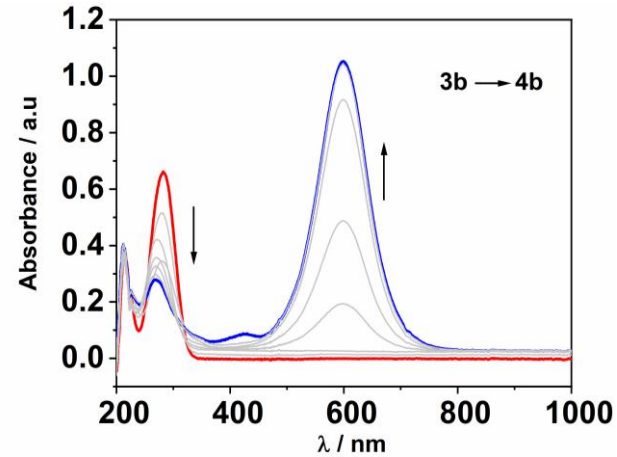


Fig. S45 Changes in the UV-Vis-NIR spectrum of **3b** during spectroelectrochemistry in CH_3CN/0.1 M Bu_4NPF_6 (measured at the potential of −1.6 V with the scan rate of 10 mVs^{-1}).

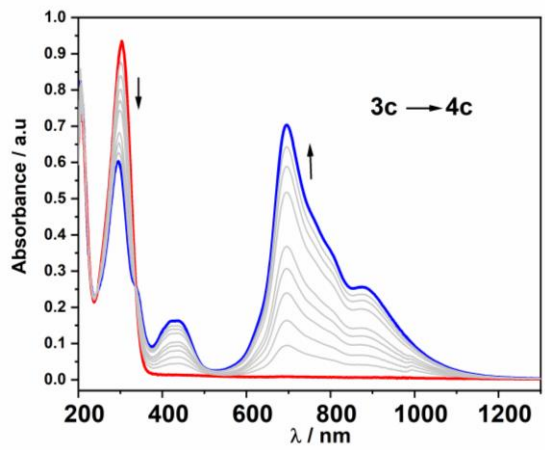


Fig. S46 Changes in the UV-Vis-NIR spectrum of **3c** during spectroelectrochemistry in CH_3CN/0.1 M Bu_4NPF_6 (measured at the potential of −1.75 V with the scan rate of 10 mVs^{-1}).

EPR spectroscopy

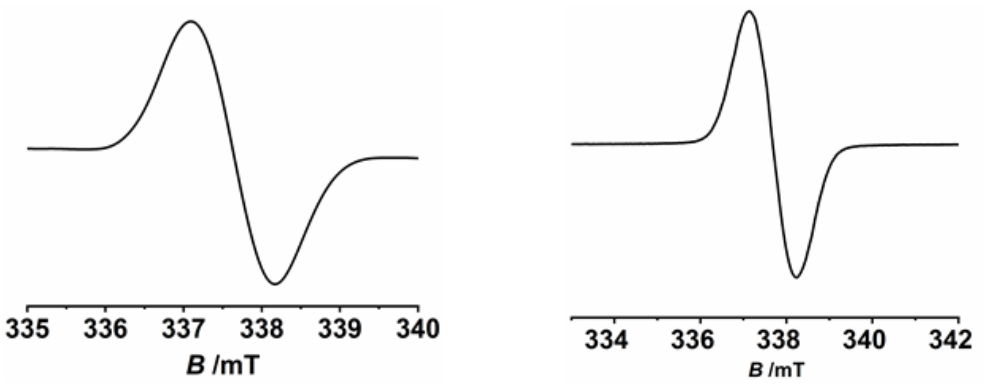


Fig. S47 EPR spectra of **4b** (left) and **4c** (right) at 25 °C in THF.

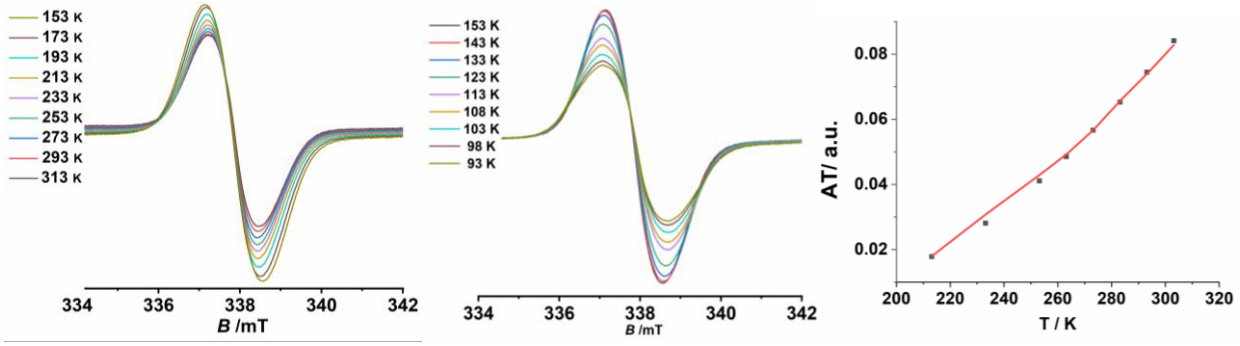


Fig. S48 Variable temperature EPR spectra of **4b** in the solid state (left and middle) and representations of the temperature dependence of the double integral EPR intensity (A) of **4b** in solid state (right). Black points represent the experimental results and the red line corresponds to the fit with the Bleaney-Bowers equation. Analysis of the variable temperature EPR data gives a singlet-triplet gap of $\Delta E_{S\text{-}T} = -2.3$ kcal mol^{-1}.[S4]

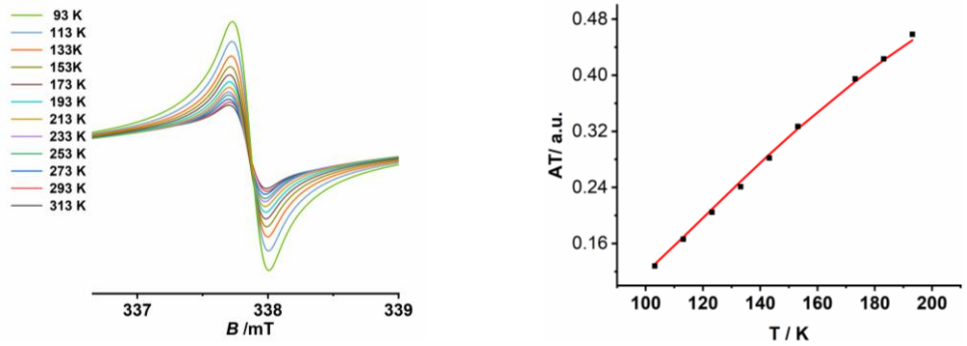


Fig. S49 Variable temperature EPR spectra of **4c** in the solid state (left) and representations of the temperature dependence of the double integral EPR intensity (A) of **4c** in solid state (right). Black points represent the experimental results and the red line corresponds to the fit with the Bleaney-Bowers equation. Analysis of the variable temperature EPR data gives a singlet-triplet gap of $\Delta E_{S\text{-}T} = -0.65$ kcal mol^{-1}.[S4]

Theoretical calculations

All calculations were performed with the ORCA program package, version 4.0.1.2.[S5] The geometries of all species were optimized using the PBE0 functional[S6] and the def2-TZVP basis set.[S7] Solvation was taken into account using the SMD method together with the CPCM model[S8] using THF as solvent, and dispersion corrections were included using the D3 dispersion correction model.[S9]The resolution-of-the-identity (RI) approximation[S10] with matching basis sets[S11],as well as the RIJCOSX approximation (combination of RI and chain-of-spheres algorithm for exchange integrals) were used to reduce the time of calculations. Low-lying excitation energies were calculated with time-dependent DFT (TD-DFT). For all calculations spin densities were calculated according to the Löwdin population analysis.[S12] The absence of imaginary frequency confirmed that the optimized geometries represent local minima. Biradical character (*y*) which can vary from 0 (closed-shell system) to 1 (pure biradical system) was obtained by calculating natural occupation number from the broken symmetry approach.[S13]

Table S2 For compound **4a** electronic energies (E in Hartrees) and relative energies (ΔEr in kcalmol^{-1}) of the different electronic states: Singlet closed-shell (SCS) and triplet (T) states, biradical character (*y*).

Methods	E (Hartees)		$\Delta E_{S\text{-}T}$ (kcal mol^{-1})	*y*
	SCS	T		
PBE0/ def2-TZVP	−1159.09346962	−1159.04891617	−27.96	0

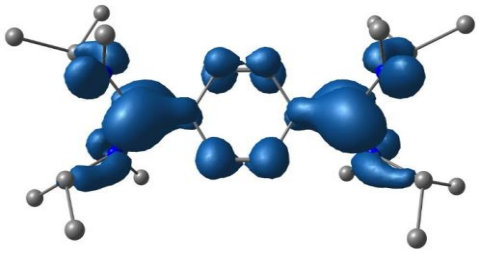
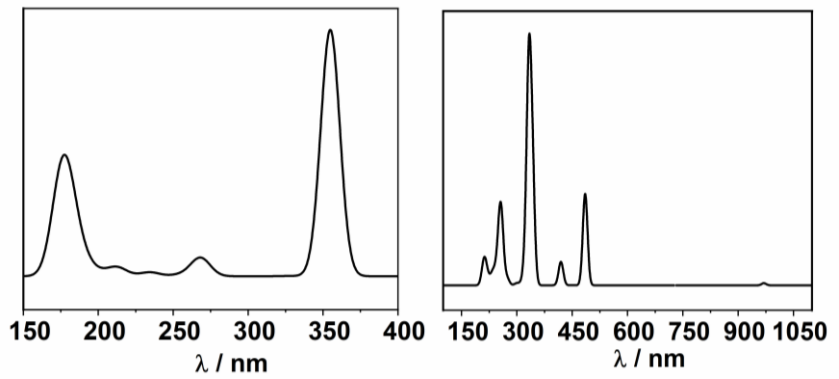


Fig. S50 Spin density of the triplet state of **4a**, plot at an isovalue of 0.004. Hydrogen atoms are omitted for clarity.

Table S3 Full TD-DFT results [PBEO/def2-TZVP] for compound **4a** as a singlet closed-shell species.

Singlet Closed Shells				Triplet state		
	λ(nm)	Oscillator strength	Transition	λ(nm)	Oscillator strength	Transition
1	354.8	1.8406	HOMO > LUMO (c= 0.95)	969.4	0.0043	SOMO (*α*) > LUMO(c= 0.98)
2	267.6	0.1069	HOMO-1 > LUMO (c= -0.95)	484.9	0.1824	SOMO (*α*) > LUMO+2(c= 0.85)
				332.3	0.4149	SOMO (*α*) > LUMO+7(c= -0.73) HOMO-2(*β*) > LUMO (*β*)



(a) (b)

Fig. S51 Calculated TD-DFT spectra of compound **4a** for (a) singlet closed shell species (b) triplet state.

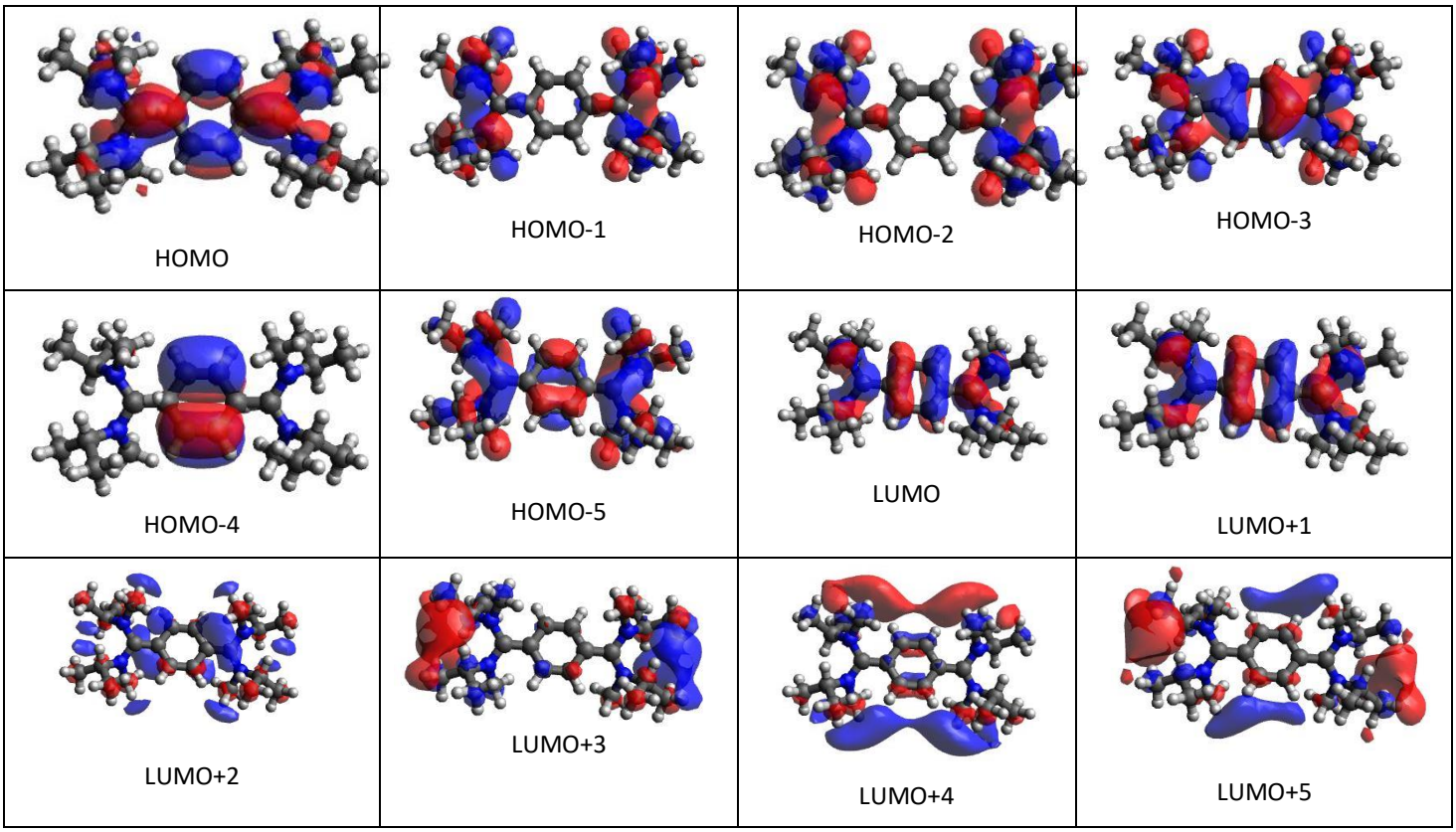


Fig. S52 Molecular Orbitals of compound **4a** for singlet closed shell species.

Table S4 Orbital energies of compound **4a** for singlet closed shell.

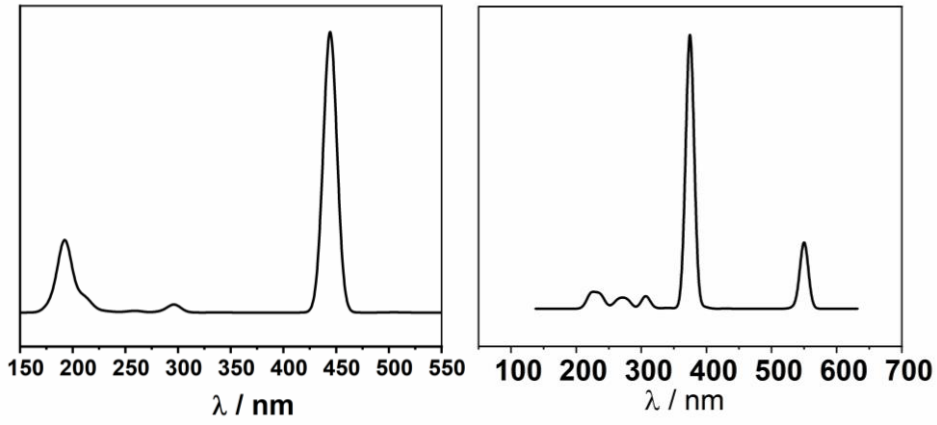
Orbital	Energy (Eh)	Energy (ev)	Orbitals	Energy (Eh)	Energy (ev)
HOMO	−0.137890	−3.752	LUMO	−0.019041	−0.518
HOMO-1	−0.220716	−6.006	LUMO+1	0.014900	0.405
HOMO-2	−0.221623	−6.031	LUMO+2	0.033215	0.904
HOMO-3	−0.233223	−6.346	LUMO+3	0.041862	1.139
HOMO-4	−0.259978	−7.074	LUMO+4	0.056474	1.537
HOMO-5	−0.275147	−7.487	LUMO+5	0.063174	1.719

Table S5 For Compound **4b** electronic energies (E in Hartrees) and relative energies (ΔEr in kcal mol^{-1}) of the different electronic states: Singlet closed-shell (SCS) and triplet (T) states, the biradical character (*y*).

Methods	E (Hartees)		ΔE_{S-T} (kcal mol^{-1})	*y*
	SCS	T		
PBE0/ def2-TZVP	−1389.95891	−1389.95293455	−3.7	0.43

Table S6 Full TD-DFT results [PBEO/def2-TZVP] for compound **4b** for singlet closed shell and triplet state.

	Singlet Closed Shells			Triplet state		
	λ(nm)	Oscillator strength	Transition	λ(nm)	Oscillator strength	Transition
1	444.5	4.0864	HOMO > LUMO (c= 0.96)	549.9	0.3506	SOMO (α) > LUMO+1(c= -0.90)
2	298.05	0.0047	HOMO-3 > LUMO (c= 0.97)	374.5	1.3959	SOMO (***β***) > LUMO (c= 0.87) SOMO (*α*) > LUMO+1(c= -0.35)



(a) (b)

Fig. S53 Calculated TD-DFT spectra of compound **4b** for (a) singlet closed shell species (b) triplet state .

Table S7 Orbital energies of compound **4b** for singlet closed shell.

Orbital	Energy (Eh)	Energy (ev)	Orbitals	Energy (Eh)	Energy (ev)
HOMO	−0.127721	−3.4755	LUMO	−0.050709	−1.3799
HOMO-1	−0.217195	−5.9102	LUMO+1	−0.001884	−0.0513
HOMO-2	−0.231366	−6.2958	LUMO+2	0.016274	0.4428
HOMO-3	−0.231580	−6.3016	LUMO+3	0.023091	0.6283
HOMO-4	−0.259214	−7.0536	LUMO+4	0.038226	1.0402
HOMO-5	−0.265674	−7.2293	LUMO+5	0.039513	1.0752

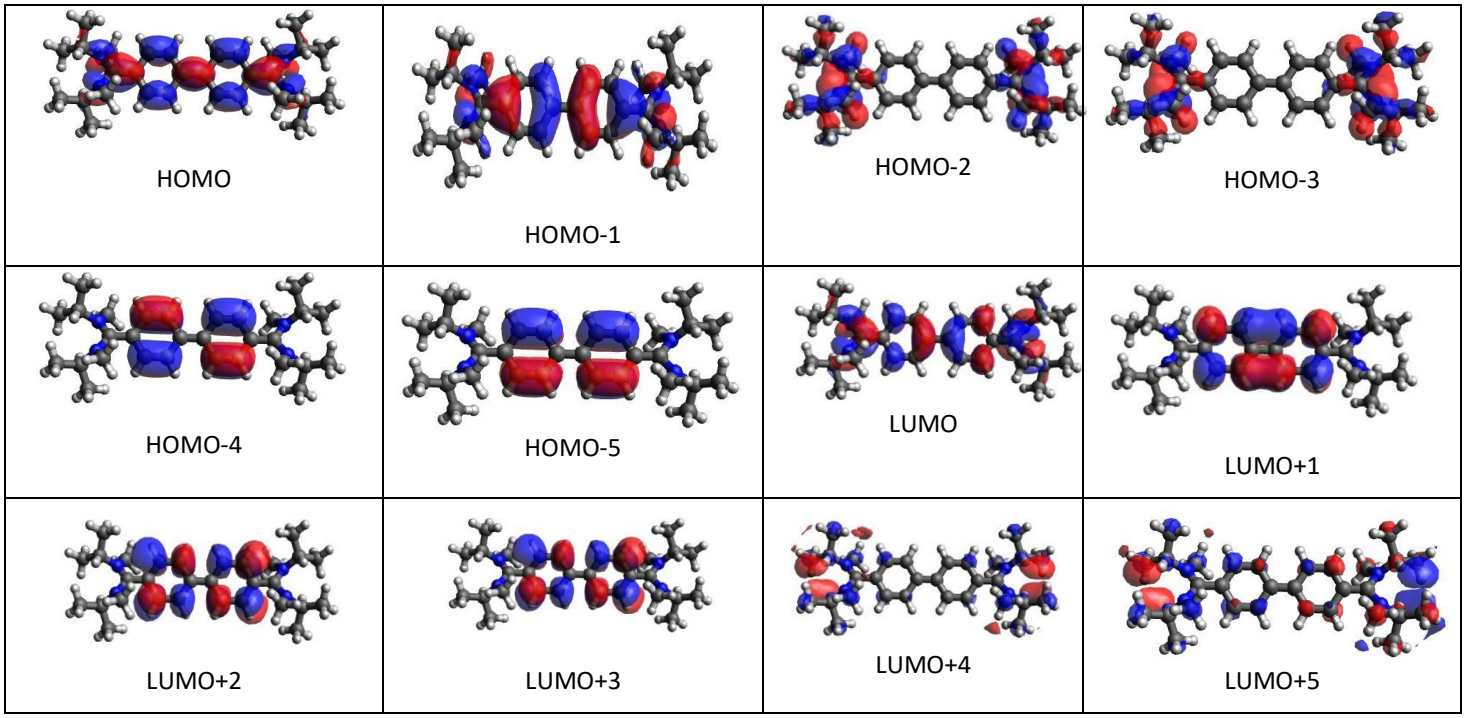


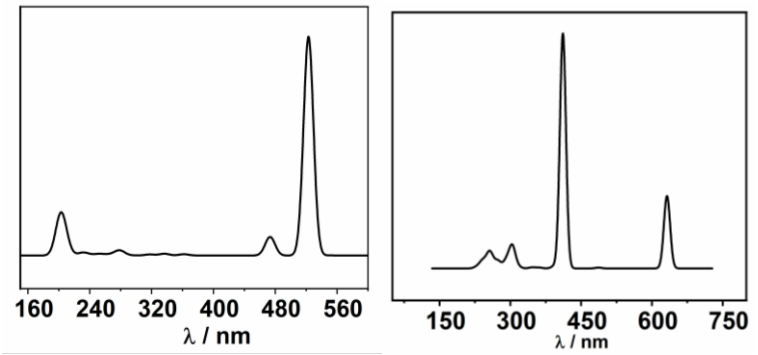
Fig. S54 Molecular Orbitals of compound **4b** for singlet closed shell species.

Table S8 For Compound **4c** electronic energies (E in Hartrees) and relative energies (ΔEr in kcal mol^{-1}) of the different electronic states: Singlet closed-shell (SCS) and triplet (T) states, the biradical character (*y*).

Methods	E (Hartees)		ΔE_{S-T} (kcal mol^{-1})	*y*
	SCS	T		
PBE0/ def2-TZVP	−1620.826533957609	−1620.825963790546	−0.37	0.65

Table S9 Full TD-DFT results [PBEO/def2-TZVP] for compound **4c** as a singlet closed-shell species.

	Singlet Closed Shells			Triplet state		
	λ(nm)	Oscillator strength	Transition	λ(nm)	Oscillator strength	Transition
1	522.9	6.5985	HOMO > LUMO(c= 0.93)	631.7	0.3029	SOMO (α) > LUMO (c= 0.66) SOMO (α) > LUMO+1 (c= -0.63)
2	473.2	0.5618	HOMO-1 > LUMO(c= 0.60) HOMO > LUMO+1(c= 0.75)	411.2	1.7935	SOMO (β) > LUMO (c= 0.88) SOMO (α) > LUMO (c= 0.31)



(a) (b)

Fig. S55 Calculated TD-DFT spectra of compound **4c** for (a) singlet closed shell species (b) triplet state.

Table S10 Orbital energies of compound **4c** for singlet closed shell.

Orbital	Energy (Eh)	Energy (ev)	Orbitals	Energy (Eh)	Energy (ev)
HOMO	−0.123644	−3.3645	LUMO	−0.070922	−1.9299
HOMO-1	−0.205711	−5.5977	LUMO+1	−0.013875	−0.3776
HOMO-2	−0.230752	−6.2791	LUMO+2	−0.010008	−0.2723
HOMO-3	−0.238000	−6.4763	LUMO+3	0.005816	0.1583
HOMO-4	−0.250472	−6.8157	LUMO+4	0.026535	0.7221
HOMO-5	−0.259285	−7.0555	LUMO+5	0.032616	0.8875

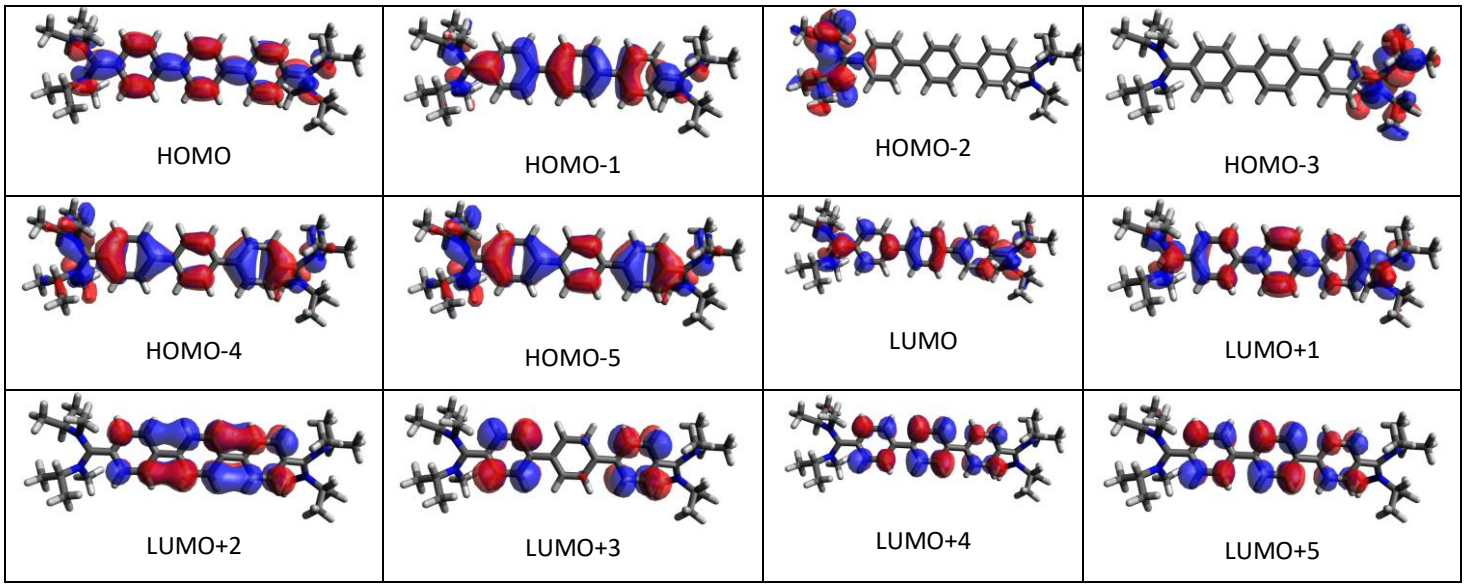


Fig. S56 Molecular Orbitals of compound **4c** for singlet closed shell species.

Cartesian coordinates of the computed structures

4a closed shell singlet

N	2.13073017943489	5.53295548139003	3.77925122312602
N	3.66283603948416	4.40404436156721	2.42515795853206
C	3.37086439933754	4.92349267847463	3.67802056958129
C	1.71383534671174	6.54231977320971	2.80798914916294
H	2.40931869642844	6.43823152827990	1.97251633930546
C	2.71798262925648	3.45914490342903	1.83106684585421
H	1.73827159651970	3.76059962985954	2.20332508648006
C	6.06243350962541	3.71025285966605	5.93212987350364
H	6.76095601135341	2.88259204351614	5.99040494701197
C	4.23040392689414	4.83529078928109	4.75303914091814
C	5.23338164906778	3.79800162137400	4.86922301073509
H	5.28030022315938	3.03434763491699	4.10182441483846
C	1.31133168344273	5.33608419275948	4.94597987263308
H	1.74132925918209	4.53605043818671	5.54587776718466
H	0.29682056164773	5.04049558048573	4.65594889893659
H	1.23324948437428	6.22444399509841	5.58369087155703
C	5.01394936775444	4.40521364117423	1.92274996916240
H	5.61580113103797	5.07305348163644	2.53586056212689
H	5.04252238039623	4.76855858844736	0.89031188402246
H	5.49185932903862	3.41854296732376	1.94020497797758
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H	0.15367620173024	5.30308859240034	1.92163665320910
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H	3.96766632658089	1.68420844825070	2.00938734166147
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H	2.53513313565661	4.58506514616997	-0.00888765112929
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H	1.19161355788119	8.09793405084539	4.23401816226004
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C	8.53414808694333	2.94243990283630	8.97789763141283
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C	4.18124495187382	5.77113680627938	5.85573207963192
H	3.48303501679912	6.59901191870932	5.79736747898671
C	6.01300412838749	4.64585965303211	7.03486834737972
C	5.00987224058872	5.68295495460416	6.91890854119524
H	4.96294293356560	6.44636379341216	7.68654587078110
C	8.93125813028227	4.15069328074156	6.84009560533823
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H	9.94642318306500	4.44502214194386	7.12891232176160
H	9.00754235520312	3.26362734671072	6.20038541957026
C	5.22620353922702	5.06763858357751	9.86450398341780
H	4.62784545500437	4.39761369479438	9.25034726982656
H	5.19790551582811	4.70370166584292	10.89672522723327
H	4.74421472858841	6.05230207242086	9.84680755938310
C	9.94593452826139	3.16134709377804	9.50759622823529
H	10.09406994346033	4.18314034763041	9.86293236180963
H	10.12736376049348	2.48400841549861	10.34491051510379
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H	6.26507928409610	7.79193312429427	9.79054311150570
H	7.98985212931242	8.13239574573240	9.93959376295738
H	7.34470864450171	7.52309436517319	8.40886889813543
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H	7.70341613410178	4.88722125742235	11.79771025908881
H	8.35654482374837	6.53161867560349	11.87176201343659
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C	8.39949994304055	1.53179227002528	8.41121299013758
H	9.05673070278315	1.38905139009227	7.54960221999539
H	8.68450143109829	0.79448662884853	9.16672916027093
H	7.37298311838471	1.32946279380787	8.09692995872419

4aTriplet

N	2.09876676173462	5.53231955391043	3.75691250746598
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C	4.24064030527635	4.83870749259362	4.76595642590049
C	5.13083358220482	3.75639495375686	4.92165246263542
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C	5.01670981968147	4.42638838093665	1.91522973715894
H	5.60675191131715	5.09467389426549	2.53958213323039
H	5.07825159368212	4.78787502416977	0.88343049670695
H	5.49079824297895	3.43764413886981	1.94976730799678
C	0.24443679011557	6.36915925241007	2.32701538580022
H	0.08061795828756	5.35279648822592	1.96220830298393
H	0.03859631020276	7.06130369688418	1.50763017553536
H	-0.48140001557662	6.57374860974067	3.11818873020066
C	2.99317211814859	2.03155155263192	2.30877898925930
H	4.00116474842753	1.69355033614897	2.05259921732529
H	2.28564719810796	1.33006650619081	1.85972461748356
H	2.87650583058319	1.98300795029715	3.39413750616133
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H	2.58002618554542	4.52554226876137	-0.06896665253165
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H	3.68776009141767	3.14048816228007	-0.12898237618291
C	1.85296878541923	7.96974340513479	3.38428517084380
H	1.22237270068757	8.12182148081636	4.26422609188594
H	1.56552155612945	8.71822654741589	2.64061058970653
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N	8.14679316754173	3.95258312266134	8.03173569463358
N	6.58661425369011	5.05110635556034	9.40567802531068
C	6.89478589500673	4.53342917255575	8.15413131387334
C	8.57542796147553	2.91973753457550	8.97234900843066
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C	5.11140465268529	5.72152546198101	6.86815756963976
H	5.10697056825204	6.51233165395268	7.60935568091660
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H	9.94812493806140	4.49088057977635	7.10288299758863
H	9.02323148792781	3.26294757411726	6.22102890139396
C	5.22326208453472	5.04579315918708	9.87301916030692
H	4.63642793499253	4.37504250204140	9.24826938519332
H	5.16160785394637	4.68471193334504	10.90493416000217
H	4.74569537863911	6.03282936165328	9.83719668931395
C	10.00546248350360	3.11853702392068	9.45734560210171
H	10.16700823906871	4.13488897416498	9.82321052043596
H	10.21466223217735	2.42584606743770	10.27541260401410
H	10.73053815313589	2.91710221096784	8.66466376871933
C	7.24038746493118	7.44699767908186	9.48377923284486
H	6.23114743109494	7.78208240122489	9.73893506077930
H	7.94542646233709	8.15013255924243	9.93416415965153
H	7.35828021562533	7.49658868712132	8.39859912667144

C	7.49161916990322	5.97322609196501	11.50776246449284
H	7.65653809456257	4.95249414217436	11.86042628865360
H	8.28494726483986	6.60774523959559	11.90744877526139
H	6.54555734369514	6.33501572742262	11.91974001293217
C	8.39903526862824	1.51482276212959	8.40135165142344
H	9.02949715821061	1.36426489665953	7.52105841769754
H	8.68828269812901	0.76644130577704	9.14441435292384
H	7.36014083008304	1.33487251245078	8.11485362482574

4b closed shell singlet

N	3.29153277082113	4.75501405415423	17.20785859855165
N	5.15933285299051	3.84622892391922	18.26156001889049
C	4.14986060342543	0.52215974952226	14.40390295708397
C	4.22568125982332	3.74552974559356	17.26117587129475
C	4.21579584757778	2.69285492487323	16.34402389358012
C	4.61657803486012	0.35013247638873	15.75580161689426
H	4.94603914773707	-0.62801897980414	16.08520048899492
C	4.66111562064018	1.36656392108702	16.65727408632927
H	5.00779819400738	1.15586593821753	17.66337829876125
C	3.75696441995280	2.87413491856461	14.99797482733691
H	3.45320339430604	3.86561040365894	14.68209615878079
C	3.74158091556137	1.86568137877710	14.08915364622365
H	3.40957657810995	2.09907476414496	13.08467405559218
C	3.71615278707927	6.15711669030528	17.16726169989100
H	4.78938330922687	6.13525813893092	17.36681235229391
C	6.51807438971662	3.40206207373206	18.06658095678027
H	6.73319438209579	2.43478026743467	18.53273252541913
H	7.20874396890424	4.13784469361777	18.48735440201416
H	6.71605973126265	3.31576955473402	16.99928700872703
C	1.91691527014241	4.46397267838788	16.87690729660267
H	1.66765206190778	4.61784863745245	15.82135034493444
H	1.25763813671406	5.10128696548686	17.47254251476865
H	1.70264997286253	3.42579052627500	17.12831055871900
C	4.76782631330182	4.23947957192795	19.61593123604368
H	3.72661068202577	4.55059193122522	19.52840609803020

C	3.50434102139678	6.74497670221140	15.77554471822057
H	3.98929415368536	6.13032671983052	15.01487955632679
H	3.92957897091234	7.75000942175360	15.72555349959790
H	2.44100451709301	6.81951626530357	15.53396979428357
C	3.05113489458428	7.02097570386727	18.22740850926003
H	1.98082651943555	7.13593532763230	18.03789704432322
H	3.49828608105272	8.01752195661141	18.21857615304816
H	3.17993198846801	6.60083314176275	19.22533334407026
C	5.57125365580746	5.41398041498288	20.15802092980461
H	6.59884106003885	5.12776093957189	20.39590712516958
H	5.10980595264886	5.77483442938004	21.08012021969110
H	5.59901576058475	6.24029143015754	19.44660206977273
C	4.82161896965338	3.05129618957559	20.56853327936189
H	4.22298012600084	2.22121556319692	20.18719811761085
H	4.42591784391865	3.34225695124466	21.54462697922084
H	5.84594068392247	2.69888271193272	20.71510622130693
N	4.96866843060677	-4.75394934551506	10.66467865375447
N	3.10195406077895	-3.84732171885266	9.60750844189942
C	4.09869725106458	-0.52600203353007	13.47118118031490
C	4.03223192425798	-3.74675913010672	10.61088049977989
C	4.03781684338089	-2.69533926073655	11.52969136011791
C	3.63282061864174	-0.35365969915903	12.11904085338045
H	3.30298027238639	0.62432778420430	11.78962206407376
C	3.59053597014821	-1.36970491827985	11.21700627535711
H	3.24515222013781	-1.15871172683638	10.21051069480743
C	4.49501311858978	-2.87716766214846	12.87611681815786
H	4.80061938328313	-3.86826503040930	13.19145439731036
C	4.50801103872468	-1.86925515462720	13.78563770179453
H	4.83994593646586	-2.10261755191607	14.79015471175815
C	4.54781047891175	-6.15735982999971	10.70100225816344
H	3.47479819780183	-6.13797141394362	10.50012312038647
C	1.74159702285420	-3.40607815046902	9.79842944802886
H	1.52539180376061	-2.44068813714541	9.32894726909711
H	1.05360843587508	-4.14469078744702	9.37824311551332
H	1.54105392072553	-3.31707280150149	10.86498563627759

C	6.34178032668840	-4.46006824552902	10.99939677016741
H	6.58948012773915	-4.61820412058821	12.05467064594938
H	7.00418783839031	-5.09254538754564	10.40207597244482
H	6.55320578055625	-3.42006594175988	10.75322766959495
C	3.49898312113585	-4.23709658364224	8.25369928393746
H	4.54051806049681	-4.54602707832597	8.34429347412031
C	4.75956069119687	-6.74827119001623	12.09145017833734
H	4.27259332675582	-6.13663119859279	12.85326574333075
H	4.33639369193041	-7.75431024120027	12.13834839421039
H	5.82280798034081	-6.82129729328297	12.33384212177026
C	5.21667258452117	-7.01673220502138	9.63960214523565
H	6.28712768280897	-7.12873060717276	9.83005932660911
H	4.77264866257087	-8.01468988813588	9.64578157700163
H	5.08763000967182	-6.59484892690298	8.64244345649446
C	2.70014963117782	-5.41232486191532	7.70647562092566
H	1.67252352052029	-5.12814601427700	7.46629413508459
H	3.16527243747521	-5.76984387313941	6.78492986117401
H	2.67247098702194	-6.24041760802260	8.41584718935894
C	3.44622782326617	-3.04692863672783	7.30349033609345
H	4.04082524301344	-2.21607504012465	7.68943895146505
H	3.84739592794852	-3.33471130727599	6.32868755802691
H	2.42166377212010	-2.69699500000404	7.15278501508366

4b Triplet

N	3.29117660759687	4.75353427842767	17.20729517727909
N	5.15929839915856	3.84565178810519	18.26146889244795
C	4.15369134779664	0.52248838450573	14.40293011841553
C	4.22639313603999	3.74531748244620	17.26085281886080
C	4.21765770072927	2.69260814236542	16.34329566163617
C	4.62068428197660	0.35051433246919	15.75473449192604
H	4.95078434431453	-0.62741501985938	16.08408350851087
C	4.66449625982740	1.36696230338814	16.65631197767803
H	5.01182355143888	1.15653042227166	17.66225096786360
C	3.75928657257392	2.87407053354579	14.99733956951489
H	3.45462647453303	3.86530512133575	14.68162501749166

C	3.74470043897463	1.86576228008615	14.08826317967840
H	3.41244118662389	2.09916859699750	13.08388840160867
C	3.71393556216878	6.15637717865772	17.16568389440087
H	4.78737988845594	6.13596685363264	17.36408299666111
C	6.51807336857945	3.40060235110556	18.06849456863170
H	6.73471331003648	2.44027557192386	18.54789294035633
H	7.20955728927056	4.14277197237280	18.47669094787083
H	6.71303371446384	3.29891874368125	17.00211228349036
C	1.91655307095405	4.46089823973902	16.87745886275105
H	1.66594381547310	4.61628983474226	15.82248875782699
H	1.25693455716525	5.09623507371627	17.47483018063976
H	1.70399486730680	3.42206410661740	17.12745375028686
C	4.76775301628163	4.24201324759601	19.61508007603521
H	3.72694393180561	4.55395230616695	19.52647051789345
C	3.50002542784737	6.74288429379979	15.77377985927052
H	3.98498343558468	6.12843783034028	15.01296428039632
H	3.92408599911855	7.74835582450912	15.72272173463645
H	2.43643336203277	6.81620083151122	15.53304743157754
C	3.04852598737286	7.02010915715241	18.22553523126520
H	1.97730720935355	7.13071690523583	18.03864041075494
H	3.49185456872573	8.01832060065943	18.21296299823203
H	3.18140051977033	6.60327480996241	19.22428932476461
C	5.57250497331482	5.41618421963307	20.15555951423729
H	6.59963869616640	5.12886847045593	20.39415918244725
H	5.11127652553685	5.77905131847096	21.07699472043779
H	5.60164142243315	6.24171543416586	19.44327933734437
C	4.81943179581643	3.05517894288407	20.56947236575496
H	4.22241824254338	2.22421266139682	20.18754377168936
H	4.42017645705819	3.34747545042099	21.54372218269523
H	5.84333001546998	2.70353486611257	20.72047978113286
N	4.97007178008424	-4.75500020555568	10.66325111087911
N	3.10244282110046	-3.84704864209152	9.60831153604215
C	4.10277523566622	-0.52577367153062	13.47041047058639
C	4.03456358678249	-3.74654173882667	10.61039086926822
C	4.04212305832291	-2.69485740016462	11.52846412208774

C	3.63545102525490	-0.35372911305349	12.11871264876198
H	3.30394271242618	0.62391549516917	11.78993382503934
C	3.59388892784468	-1.36921381044642	11.21627332584190
H	3.24690401638786	-1.15863434660549	10.21024937729082
C	4.50059221892276	-2.87627793470992	12.87467284778334
H	4.80653898896280	-3.86732657941266	13.18968367806581
C	4.51339391663857	-1.86868178854164	13.78440163826881
H	4.84587908098162	-2.10211764217893	14.78869144249918
C	4.54702681323383	-6.15772929830494	10.70322194284528
H	3.47393597356408	-6.13699013722042	10.50301144252258
C	1.74306213595290	-3.40446515666096	9.80115967734753
H	1.52570597724203	-2.44129124969144	9.32755603205115
H	1.05292239558845	-4.14462652865981	9.38710179158788
H	1.54579401809596	-3.30970671334486	10.86779909063868
C	6.34378877541078	-4.46254564130008	10.99610124580214
H	6.59254002139866	-4.61820450936169	12.05155621769819
H	7.00493475843761	-5.09740405513998	10.39989430468649
H	6.55664580953977	-3.42343153329454	10.74739349779673
C	3.49690038325148	-4.23733641662744	8.25387852004231
H	4.53775945843936	-4.54899722382149	8.34317729769447
C	4.75877936752558	-6.74619664934438	12.09457869339056
H	4.27237457875771	-6.13281703158596	12.85534945892447
H	4.33494838832746	-7.75186342883382	12.14391973781127
H	5.82199106989718	-6.81948625932944	12.33705969339505
C	5.21350253134508	-7.01972829773197	9.64259890769677
H	6.28445100226289	-7.13122055774041	9.83058179046704
H	4.76980878269088	-8.01779582087281	9.65180102610557
H	5.08218938281338	-6.59989619679162	8.64484665744382
C	2.69444324050391	-5.41061008767412	7.70774545664925
H	1.66709328165148	-5.12411324024551	7.46901758060435
H	3.15711601234724	-5.76951045812283	6.78550613094848
H	2.66564495593922	-6.23861697174666	8.41720070235018
C	3.44583900721606	-3.04718609404964	7.30364416806050
H	4.04265360519634	-2.21747932973555	7.68862646173551
H	3.84529064864343	-3.33589663778890	6.32839349478538

H	2.42193792366029	-2.69495283977777	7.15374940010886

4c closed shell singlet

N	2.88159392456077	4.86479674551098	3.29473332625858
N	0.94041899284121	3.96581152098699	4.21185596893216
C	2.22245829237863	4.40918075051795	4.39572237057014
C	3.68133702445454	4.39639203798465	8.43670918723694
C	2.79779338507761	4.38222975626778	5.68476383431038
C	4.14864155481331	5.34821129262928	7.47368941962731
H	4.84139192370284	6.12199069731067	7.78327975997838
C	4.01883526118460	4.44984637768088	9.81365153396038
C	3.74153191837976	5.33732340606223	6.16973113206260
H	4.11525540297917	6.10591324328315	5.50204658261386
C	2.38393414110899	3.39293985250021	6.62224901895228
H	1.71831263340173	2.60588302555352	6.28794216870593
C	2.80921626457495	3.38902980822245	7.91388352795569
H	2.45004883431019	2.59794132200339	8.55887012051622
C	0.60843738009637	3.02296115516770	3.13752972365751
H	1.41701779626834	3.10405978468111	2.41103777580878
C	5.04687786796285	5.56756352956740	11.73923898124315
H	5.63839068919187	6.40202088279130	12.09727806007220
C	4.79495689778024	5.49643571152794	10.39836776886640
H	5.19512538052472	6.28161968297215	9.76691921520833
C	2.19135522427644	5.67537586687243	2.28185409044449
H	1.12819992614123	5.51221698654468	2.44943539774102
C	-0.07520188893940	4.21308920963183	5.21138265092413
H	-0.38211124306751	3.30994962051402	5.74643280247819
H	-0.96051330875933	4.64466251094517	4.73674374956921
H	0.30697579128087	4.92452966989601	5.93899352334229
C	4.32146313718912	4.79135419231882	3.20652454285272
H	4.80114057063536	5.76888283535596	3.30695745739142
H	4.61332651208461	4.36514818588257	2.24345834357983
H	4.69553729595540	4.14411785603605	3.99529444847567
C	2.47527294792678	7.15712028481686	2.49208966710504
H	2.22241333431014	7.46329909913670	3.50995310311376

H	1.87102936082919	7.74705517004334	1.79964474841771
H	3.52323728299129	7.39931133522059	2.29793312606366
C	-0.70318464914528	3.35044630989479	2.44135250817078
H	-1.55889532464501	3.11996626184101	3.08019208288561
H	-0.79017135459414	2.74021366898246	1.54060711561796
H	-0.76323227242099	4.40085179871683	2.14720536121075
C	0.58685341594862	1.59386357334526	3.66738992914651
H	1.56284142159729	1.30725638292790	4.06509335529287
H	0.32225599252403	0.90285271348138	2.86339953666767
H	-0.15681130089464	1.47680863815809	4.45916489623182
C	2.52574746409694	5.25792399292964	0.85976427322727
H	3.56386941876766	5.48793484844435	0.60730133457735
H	1.89307173296308	5.81511444117514	0.16690899512783
H	2.35045592024875	4.19247442919318	0.69610945770281
N	4.73031908594940	4.18259574800639	19.20934144281316
N	6.50345340132887	5.63067545109960	18.85168302500434
C	5.49246895722170	4.88112593079160	18.30293262461051
C	4.79261124577082	4.67641227011344	14.06586809473395
C	5.24969566498238	4.82577245851576	16.92701465821179
C	4.35151430248669	3.66014483037509	14.97548663688252
H	3.84097521721616	2.78631105762106	14.59028447397077
C	4.56846564132741	4.59352690596937	12.67130234665330
C	4.56328331951444	3.72689528560165	16.31717457382698
H	4.22006954245613	2.90928185971995	16.94079830525270
C	5.67575576230888	5.85418281768728	16.02666756264158
H	6.16369099888138	6.73352144676479	16.43076427042915
C	5.46210449342408	5.78222894041317	14.68443505941376
H	5.79807837002976	6.61066139655261	14.07244053948298
C	6.18608560765921	6.53549633629070	19.96063289996951
H	5.28265404574086	6.12768943479925	20.41365061938839
C	3.56285297725340	3.46539494082361	10.74175439375738
H	2.97897717903620	2.62505256042509	10.38768387969556
C	3.82625733750634	3.52680864160981	12.07713255358840
H	3.43116619946930	2.73575536704621	12.70224891779149
C	5.38631710109802	3.35308215491712	20.22444848678436

H	6.43435431624522	3.65689274448051	20.20991848566107
C	7.78916026806027	5.76755624215915	18.21288398291183
H	7.97665012811580	6.77817768250063	17.83452244678859
H	8.58658843791434	5.51699527178581	18.91940557673189
H	7.84913712552568	5.07596677913783	17.37512587831495
C	3.29893360243656	4.08947603549032	19.07394117385007
H	2.95031623346686	3.07542660820225	18.85238173204398
H	2.81004721551646	4.42402475804953	19.99497258239908
H	2.97577460003905	4.74132533628850	18.26525776590315
C	5.31341711134181	1.87886589671334	19.84322458524129
H	5.72945797404055	1.71110585148317	18.84724930264827
H	5.88248702001336	1.27921990783036	20.55701965157547
H	4.28250258176927	1.51655139762004	19.85573432484772
C	7.27113929184865	6.56125929809554	21.02158097570419
H	8.18436886806922	7.03816022260574	20.65751036660135
H	6.91989075158935	7.13295637165259	21.88307167044169
H	7.52117430783478	5.55308433839669	21.36017816510781
C	5.85624413854419	7.93537711924787	19.44892446922839
H	5.06603144461469	7.89361077985516	18.69573065937069
H	5.50438370987501	8.56292322676182	20.27166446009106
H	6.73234643770754	8.41559837913971	19.00461618843964
C	4.85597669203031	3.57232298744102	21.63190861791543
H	3.81626993310057	3.24796091122710	21.72651153430929
H	5.44816033107761	2.98318831256227	22.33469104187504
H	4.92679105536752	4.61978724080171	21.93028302319753

4c Triplet

N	2.86284916947918	4.90209176386685	3.26364287463683
N	0.93215439858963	3.93525108067388	4.16262841974598
C	2.21062659084167	4.41322149790600	4.37041198385300
C	3.63780686803387	4.42520745276391	8.41456578313437
C	2.77708925201311	4.39635973727159	5.66958842369037
C	4.10730910505955	5.36857560630904	7.47620579682417
H	4.77803533950078	6.15723324061042	7.79974130236212
C	3.97141738217814	4.48076957094154	9.84149441018426

C	3.71025678342101	5.35628069208302	6.15690116635939
H	4.07830458263390	6.13055656027925	5.49342625204015
C	2.37031241052824	3.40427856741203	6.60309288542775
H	1.72319310662605	2.60436780859350	6.26557137214152
C	2.78624899140629	3.42007642581897	7.90786360564300
H	2.44951382752279	2.62095859986943	8.55676197897283
C	0.66923018340008	2.92586458224415	3.13568596074772
H	1.48752894423683	3.01951487176702	2.41903885878751
C	5.26409872143966	5.35400940949005	11.71643589171232
H	6.07159510163958	5.99478525306997	12.05219099780750
C	4.98859982634683	5.29758394801689	10.36028441716127
H	5.59249420290931	5.89787820174925	9.68948097545923
C	2.16042154982468	5.76337633810086	2.30858555833339
H	1.10037049943359	5.55679821994006	2.45592249845498
C	-0.10217102820856	4.18672247061095	5.13569962362323
H	-0.35977034562027	3.31031134731707	5.74063896816098
H	-1.01275853874672	4.53097920828562	4.63686653784924
H	0.23114919725398	4.97070591019780	5.81268993320495
C	4.29845083791169	4.82909935798571	3.15953703298200
H	4.78319570393020	5.80672113872799	3.25294884772583
H	4.59051207172504	4.39933900082322	2.19675057715782
H	4.68215205239358	4.18546014831460	3.94753504556873
C	2.40073236274978	7.23784520865922	2.60966479632572
H	2.12435818727352	7.47586488496768	3.63977765778680
H	1.79675374489980	7.85797386751105	1.94321587961016
H	3.44733328427338	7.51222056472589	2.45135753383543
C	-0.64036158857812	3.16606745219758	2.39963233808994
H	-1.50015303024328	2.92447504522766	3.02959988071902
H	-0.68528668539003	2.52053790590116	1.52037534733508
H	-0.73459582553016	4.20228383749170	2.06655356327738
C	0.69919511758003	1.51713836168725	3.71861173750585
H	1.68113137412704	1.28443430176131	4.13660046453205
H	0.46905776096127	0.78234828608326	2.94267748240908
H	-0.04712395704480	1.40287941377659	4.50921098669108
C	2.51081304950039	5.44054542798854	0.86586846245873

H	3.54746381259769	5.69943866041010	0.63461209433447
H	1.87412708692771	6.02573488533299	0.19985388200920
H	2.35308256938609	4.38286476337253	0.64207151147701
N	4.74769085588320	4.14942316686708	19.22248248319725
N	6.53267325965761	5.60332938815633	18.86320342966028
C	5.52050907676861	4.84435975931560	18.31623548848905
C	4.81004234546350	4.65529332514311	14.09050643876337
C	5.27864277197542	4.78595687897014	16.92289086666644
C	4.37835430097902	3.63864117915023	14.96527946387627
H	3.87460142346878	2.76737136388095	14.56236520818781
C	4.54462061071012	4.59219610841751	12.64957443095116
C	4.59596974587512	3.69332200648249	16.32055924727286
H	4.25703318182461	2.87244602223963	16.94164317166622
C	5.70758312483010	5.81210428963615	16.03698803616020
H	6.20191545367090	6.68634667511222	16.44287510098637
C	5.48236662102976	5.74231927739653	14.68262852931653
H	5.81233846975510	6.56889935663342	14.06283500280772
C	6.19358740242731	6.56195977354471	19.91647639848262
H	5.28072124054169	6.17440177309703	20.37111686113337
C	3.25546600674792	3.71860491666164	10.77907191918174
H	2.43726968061840	3.08785752433408	10.45518866569322
C	3.53269190284582	3.77261016793064	12.13034166557004
H	2.92143154366392	3.18172531258906	12.80205554358110
C	5.38973896403260	3.32446202150909	20.24651686516811
H	6.44435512747407	3.60513103368297	20.21786481149816
C	7.83077711205341	5.69562583429521	18.24530443058837
H	8.05008809000363	6.69345810194834	17.84849706169880
H	8.61593478196177	5.43889058367164	18.96417402778887
H	7.88730744770870	4.98734101077560	17.42077890526456
C	3.31502344320509	4.08950022203795	19.09221131230242
H	2.94236346080908	3.07915835321377	18.89135670163335
H	2.82988724097069	4.45497809823074	20.00410426861576
H	3.00444539658294	4.73073592335585	18.26982759049004
C	5.27914644698771	1.84311843589745	19.90458481262365
H	5.67611619891762	1.64052188350708	18.90721697676450

H	5.84399503733288	1.24787157163791	20.62556761567356
H	4.24024165927113	1.50510096363914	19.94242830607936
C	7.25760963554611	6.63373000516570	20.99697497069388
H	8.18074513576252	7.08679970432074	20.62652906193744
H	6.89643445956726	7.24764077953293	21.82469894067498
H	7.49472318630531	5.64039281594158	21.38507642101165
C	5.87566716032287	7.93924898974997	19.33805857662238
H	5.09732922084676	7.86579688095228	18.57497371893573
H	5.51369033215215	8.60580334892126	20.12516875067226
H	6.76002812843789	8.39694030681702	18.88563691580645
C	4.87595520646657	3.58698093926229	21.65380225292794
H	3.82659025499395	3.29834671801851	21.75936363354712
H	5.45183668140996	2.99285960331513	22.36607101266494
H	4.98261812064570	4.63776672710526	21.92976250852040

Molecular structures of 2b, 2c, 3a, 3b and 3c

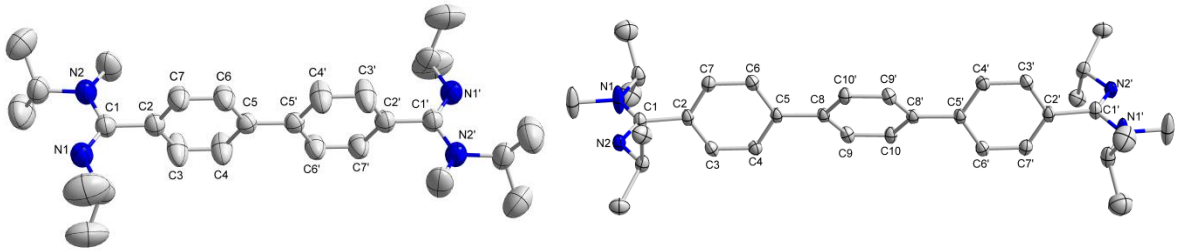

Fig. S57 Solid-state structures of **2b** (left) and **2c** (right). Hydrogen atoms are omitted for clarity.

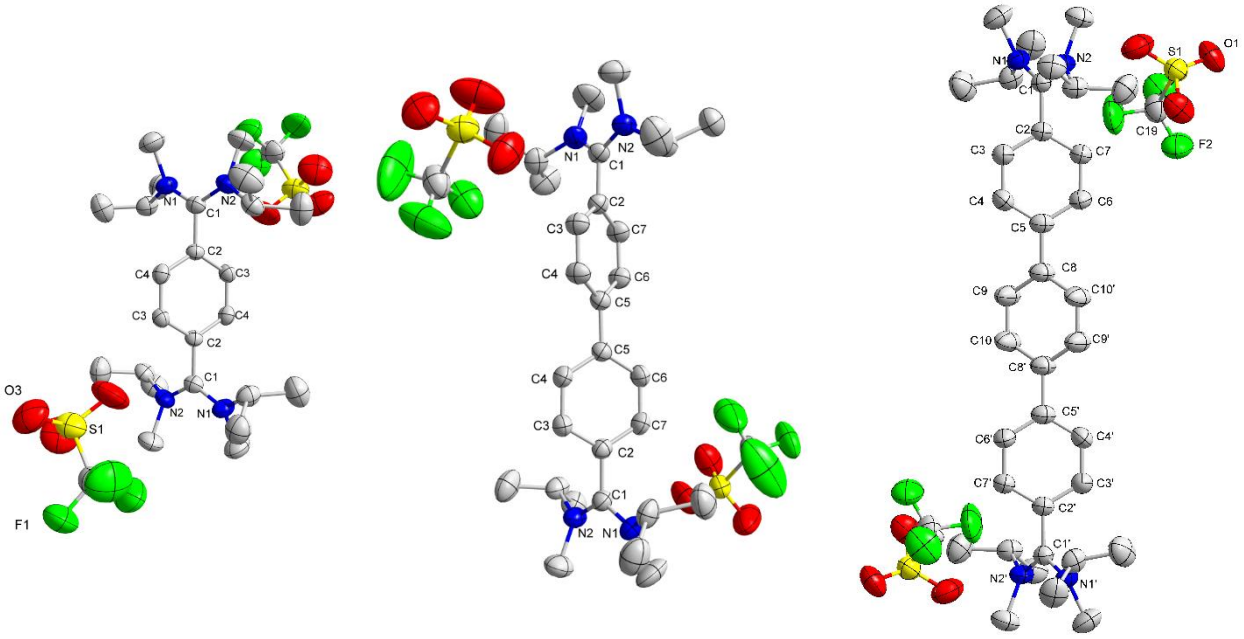

Fig. S58 Solid-state structures of **3a** (left), **3b** (middle) and **3c** (right). Hydrogen atoms are omitted for clarity.

Crystallographic details

Single-crystal X-ray diffraction data of **2b**, **3a**, **3b**, **3c** and **4b** were collected at 298 K, **2c** was collected at 197 K, whereas **4a** and **4c** were collected at 240K using a XtaLAB AFC12 (RINC): Kappa single diffractometer with graphite-monochromated molybdenum *Kα* radiation, λ = 0.71073 Å. Data were integrated using CrysAlisPro 1.171.39.29d (Rigaku Oxford Diffraction, 2017) software.[S14] Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The structure was solved with the SHELXT structure solution program[S15] using Direct Methods and refined with the SHELXL refinement package[S16] using Least Squares minimisation in the Olex-2 software.[S17] All the non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were placed in geometrically calculated positions or found in the Fourier difference map and included in the refinement process using riding model.

Table S11 Crystal data and structure refinement for **2b** (CCDC: 2010337).

Identification code	AJ1043
Empirical formula	$C_{28}H_{42}N_4$
Formula weight	434.65
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.4471(5)
b/Å	8.8406(6)
c/Å	10.0062(7)
α/°	96.010(6)
β/°	105.100(6)
γ/°	104.691(5)
Volume/Å^3	686.09(8)
Z	1
ρ_{calc}g/cm^3	1.052
μ/mm^{-1}	0.062
F(000)	238.0
Crystal size/mm^3	0.32 × 0.16 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.684 to 58.026
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 10, -12 ≤ l ≤ 13
Reflections collected	11405
Independent reflections	3151 [R_{int} = 0.0778, R_{sigma} = 0.0624]
Data/restraints/parameters	3151/0/150
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0723, wR_2 = 0.2174
Final R indexes [all data]	R_1 = 0.0917, wR_2 = 0.2363
Largest diff. peak/hole / e Å^{-3}	0.35/-0.28

Table S12 Crystal data and structure refinement for **2c** (CCDC: 2010338)**.**

Identification code	AJ1409-1
Empirical formula	$C_{34}H_{46}N_4$
Formula weight	510.75
Temperature/K	197.19(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.6157(5)
b/Å	22.4602(17)
c/Å	10.2356(8)
α/°	90
β/°	93.229(7)
γ/°	90
Volume/Å^3	1518.5(2)
Z	2
ρ_{calc}g/cm^3	1.117
μ/mm^{-1}	0.066
F(000)	556.0
Crystal size/mm^3	0.26 × 0.21 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.43 to 56.534
Index ranges	-8 ≤ h ≤ 8, -29 ≤ k ≤ 26, -13 ≤ l ≤ 13
Reflections collected	11800
Independent reflections	3482 [R_{int} = 0.0700, R_{sigma} = 0.0612]
Data/restraints/parameters	3482/0/177
Goodness-of-fit on F^2	1.193
Final R indexes [I>=2σ (I)]	R_1 = 0.0601, wR_2 = 0.1645
Final R indexes [all data]	R_1 = 0.0840, wR_2 = 0.1934
Largest diff. peak/hole / e Å^{-3}	0.31/-0.38

Table S13 Crystal data and structure refinement for **3a** (CCDC: 1983573).

Identification code	AJ0927
Empirical formula	$C_{26}H_{44}F_6N_4O_6S_2$
Formula weight	686.77
Temperature/K	297.91(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.7348(5)
b/Å	13.5132(7)
c/Å	14.3175(9)
α/°	67.708(6)
β/°	77.216(5)
γ/°	89.130(4)
Volume/Å^3	1694.54(18)
Z	2
ρ_{calc}g/cm^3	1.346
μ/mm^{-1}	0.233
F(000)	724.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.352 to 58.056
Index ranges	-12 ≤ h ≤ 12, -17 ≤ k ≤ 18, -19 ≤ l ≤ 18
Reflections collected	24009
Independent reflections	7789 [R_{int} = 0.0898, R_{sigma} = 0.0874]
Data/restraints/parameters	7789/0/409
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0834, wR_2 = 0.2056
Final R indexes [all data]	R_1 = 0.1557, wR_2 = 0.2327
Largest diff. peak/hole / e Å^{-3}	0.48/-0.28

Table S14 Crystal data and structure refinement for **3b** (CCDC: 1983580).

Identification code	AJ0988
Empirical formula	$C_{32}H_{48}F_6N_4O_6S_2$
Formula weight	762.86
Temperature/K	293
Crystal system	monoclinic
Space group	C2/c
a/Å	13.8834(7)
b/Å	9.6798(5)
c/Å	29.2643(14)
α/°	90
β/°	100.514(5)
γ/°	90
Volume/Å^3	3866.8(3)
Z	4
ρ_{calc}g/cm^3	1.310
μ/mm^{-1}	0.211
F(000)	1608.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.492 to 58.12
Index ranges	-18 ≤ h ≤ 17, -13 ≤ k ≤ 13, -39 ≤ l ≤ 39
Reflections collected	29846
Independent reflections	4630 [R_{int} = 0.0296, R_{sigma} = 0.0219]
Data/restraints/parameters	4630/0/232
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0656, wR_2 = 0.1952
Final R indexes [all data]	R_1 = 0.0834, wR_2 = 0.2073
Largest diff. peak/hole / e Å^{-3}	0.51/-0.45

Table S15 Crystal data and structure refinement for **3c** (CCDC: 1983581).

Identification code	AJ1304
Empirical formula	$C_{38}H_{52}F_6N_4O_6S_2$
Formula weight	838.95
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.2064(3)
b/Å	8.6379(3)
c/Å	18.5201(7)
α/°	86.324(3)
β/°	89.745(3)
γ/°	69.232(3)
Volume/Å^3	1224.75(8)
Z	1
ρ_{calc}g/cm^3	1.137
μ/mm^{-1}	0.173
F(000)	442.0
Crystal size/mm^3	0.23 × 0.21 × 0.19
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.648 to 57.742
Index ranges	-11 ≤ h ≤ 10, -8 ≤ k ≤ 11, -22 ≤ l ≤ 24
Reflections collected	18070
Independent reflections	5615 [R_{int} = 0.1174, R_{sigma} = 0.0860]
Data/restraints/parameters	5615/58/319
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0644, wR_2 = 0.1887
Final R indexes [all data]	R_1 = 0.0834, wR_2 = 0.2047
Largest diff. peak/hole / e Å^{-3}	0.28/-0.36

Table S16 Crystal data and structure refinement for **4a** (CCDC: 1983587).

Identification code	AJ0888
Empirical formula	$C_{24}H_{44}N_4$
Formula weight	388.63
Temperature/K	240.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.8244(13)
b/Å	9.4809(18)
c/Å	11.8030(14)
α/°	90
β/°	92.827(11)
γ/°	90
Volume/Å^3	1209.8(3)
Z	2
ρ_{calc}g/cm^3	1.067
μ/mm^{-1}	0.063
F(000)	432.0
Crystal size/mm^3	0.14 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.514 to 50.052
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 11, -12 ≤ l ≤ 14
Reflections collected	2045
Independent reflections	2045 [R_{int} = ?, R_{sigma} = 0.1273]
Data/restraints/parameters	2045/0/134
Goodness-of-fit on F^2	1.002
Final R indexes [I>=2σ (I)]	R_1 = 0.1025, wR_2 = 0.2537
Final R indexes [all data]	R_1 = 0.1376, wR_2 = 0.2803
Largest diff. peak/hole / e Å^{-3}	0.34/-0.39

Table S17 Crystal data and structure refinement for **4b** (CCDC: 1983586).

Identification code	AJ1012R
Empirical formula	$C_{30}H_{48}N_4$
Formula weight	464.72
Temperature/K	299.83(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.2696(4)
b/Å	12.3840(7)
c/Å	27.8702(13)
α/°	90
β/°	90.000(4)
γ/°	90
Volume/Å^3	2854.2(3)
Z	4
ρ_{calc}g/cm^3	1.081
μ/mm^{-1}	0.064
F(000)	1024.0
Crystal size/mm^3	0.26 × 0.19 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.728 to 57.916
Index ranges	-8 ≤ h ≤ 11, -13 ≤ k ≤ 16, -35 ≤ l ≤ 37
Reflections collected	22115
Independent reflections	3456 [R_{int} = 0.0836, R_{sigma} = 0.0477]
Data/restraints/parameters	3456/0/160
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0558, wR_2 = 0.1408
Final R indexes [all data]	R_1 = 0.0797, wR_2 = 0.1535
Largest diff. peak/hole / e Å^{-3}	0.18/-0.17

Table S18 Crystal data and structure refinement for **4c** (CCDC: 1983588).

Identification code	AJ1295
Empirical formula	$C_{36}H_{52}N_4$
Formula weight	540.81
Temperature/K	240.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.1170(8)
b/Å	9.2664(5)
c/Å	11.9686(7)
α/°	90
β/°	108.222(6)
γ/°	90
Volume/Å^3	1592.49(16)
Z	2
ρ_{calc}g/cm^3	1.128
μ/mm^{-1}	0.066
F(000)	592.0
Crystal size/mm^3	0.29 × 0.18 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.672 to 57.31
Index ranges	-19 ≤ h ≤ 19, -12 ≤ k ≤ 8, -15 ≤ l ≤ 15
Reflections collected	15048
Independent reflections	3681 [R_{int} = 0.0358, R_{sigma} = 0.0435]
Data/restraints/parameters	3681/0/187
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0564, wR_2 = 0.1513
Final R indexes [all data]	R_1 = 0.0837, wR_2 = 0.1625
Largest diff. peak/hole / e Å^{-3}	0.22/-0.18

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