Supporting Information

A supramolecular assembly bearing organic TADF chromophore: synthesis, characterization and light–driven cooperative acceptorless dehydrogenation of secondary amines

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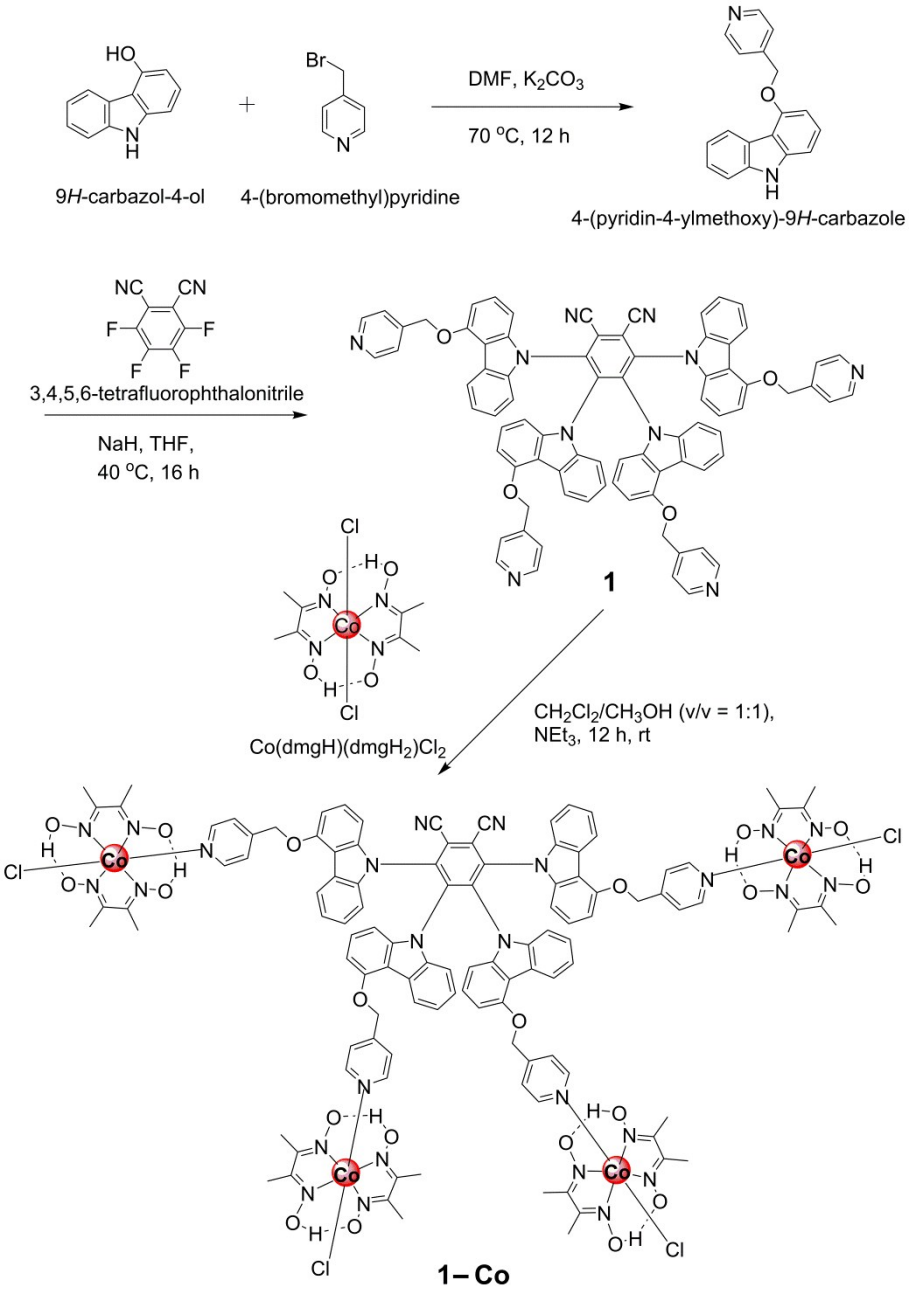


Scheme S1. Synthetic routes for **1** and **1-Co**.

2. Supplementary Figures

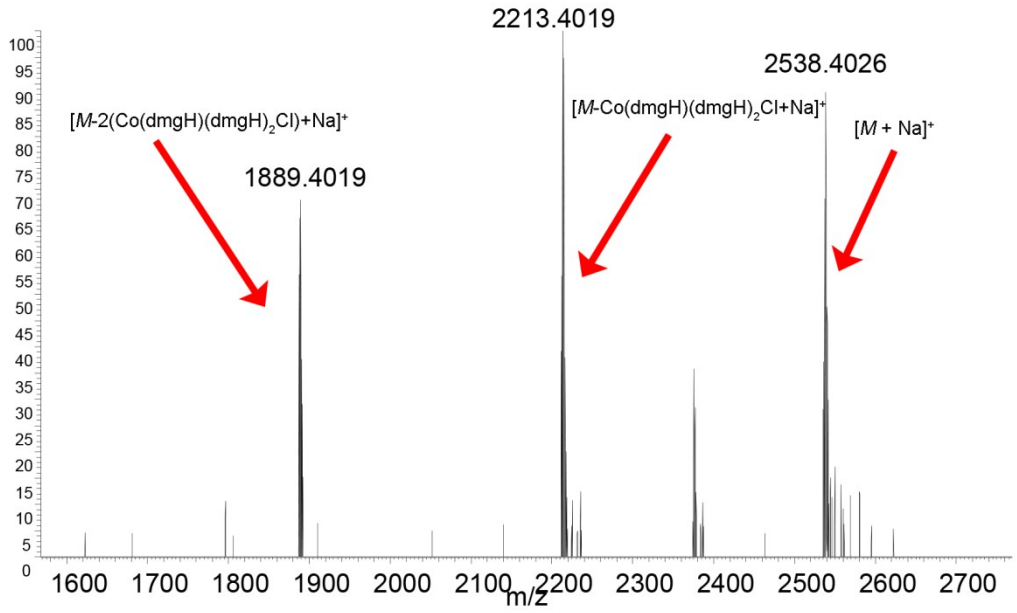


Fig. S1 HR-ESI-MS spectrum of assembly **1-Co** (*M* = **1-Co**).

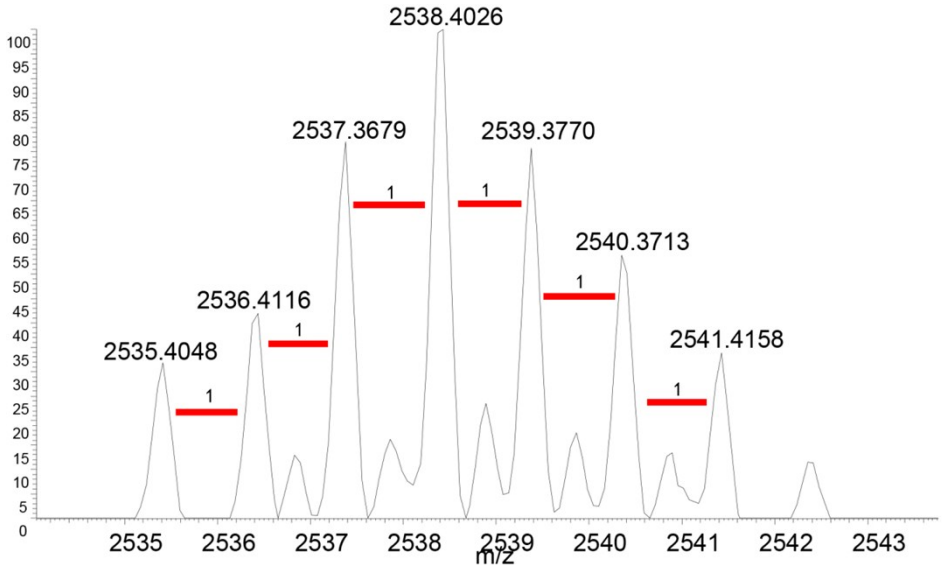


Fig. S2 Partial HR–ESI–MS spectrum of assembly **1-Co**.

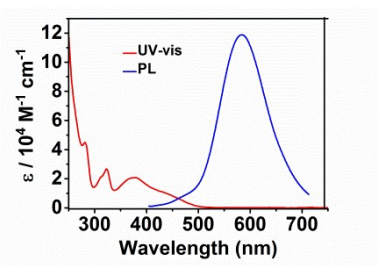


Fig. S3 UV-vis absorption and photoluminescence (PL) spectra of **1** in CH_2Cl_2 at room temperature, λ_{ex} = 400 nm.

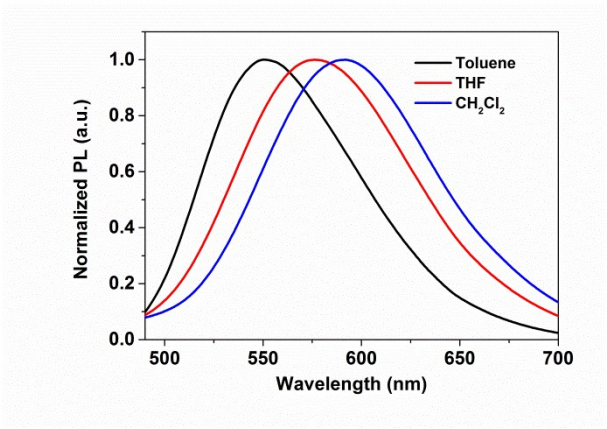


Fig. S4 PL spectra of chromophore **1** (10 μM) in various solvents (toluene, TFH and CH_2Cl_2).

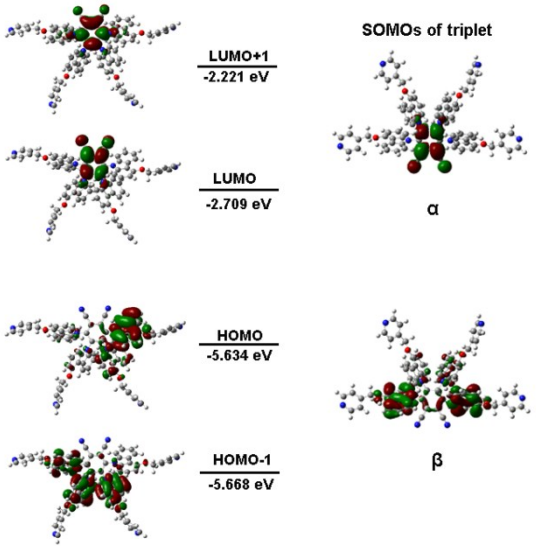


Fig. S5 Frontier orbitals for optimized chromophore **1** by DFT calculations B3LYP/6-31G(d) level for C, H, N, O atom.

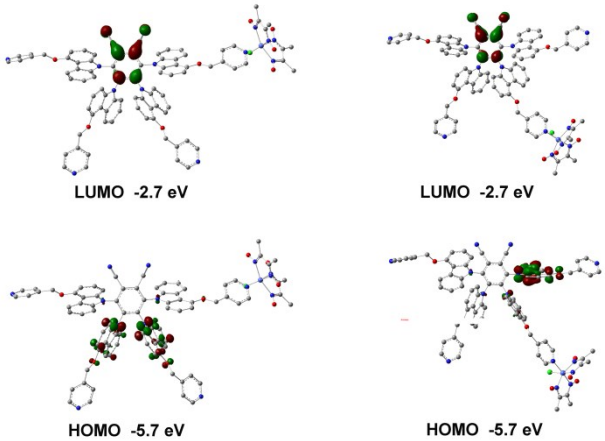


Fig. S6 DFT calculations of species containing **1** and one Co^{III} moiety. DFT calculations were carried out using Gaussian 09 program. Geometry optimizations were performed with the B3LYP functional using the LANL2DZ basis set for Co and the 6-31G basis set for the other atoms, respectively. Polarization functions were added for Co (ξd = 2.78) to the standard LANL2DZ

basis set.

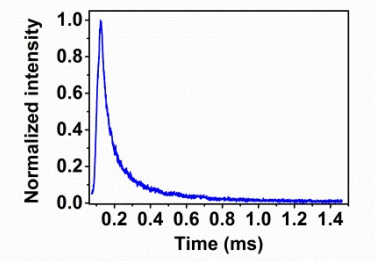


Fig. S7 Transient PL decay of **1** in degassed CH_2Cl_2 at room temperature.

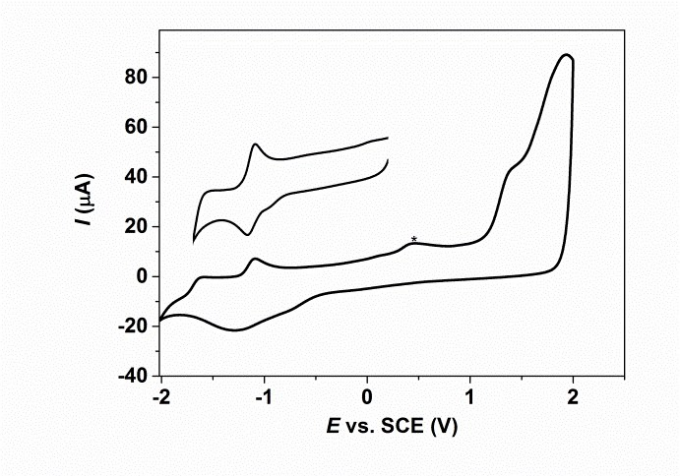


Fig. S8 Cyclic voltammogram of **1** (0.5 mmol) in CH_3CN at room temperature under N_2. Tetra–nbutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte.

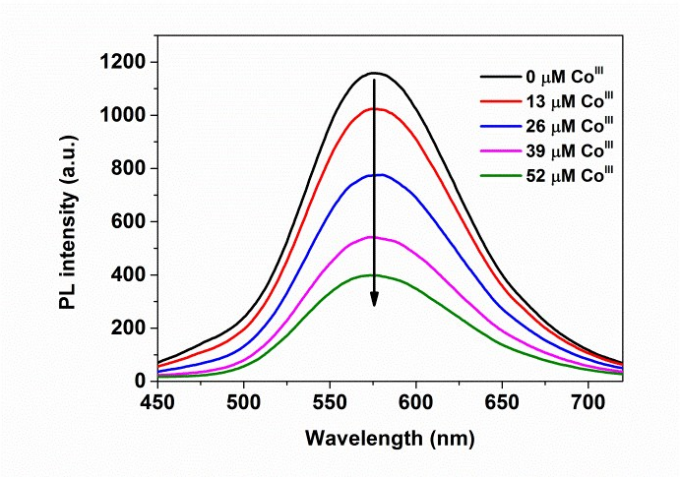


Fig. S9 Emission quenching titration experiments of **1** (10 μM) upon addition of $Co(dmgH)_2PyCl$ (0 – 52 μM) in degassed THF (λ_{ex} = 400 nm).

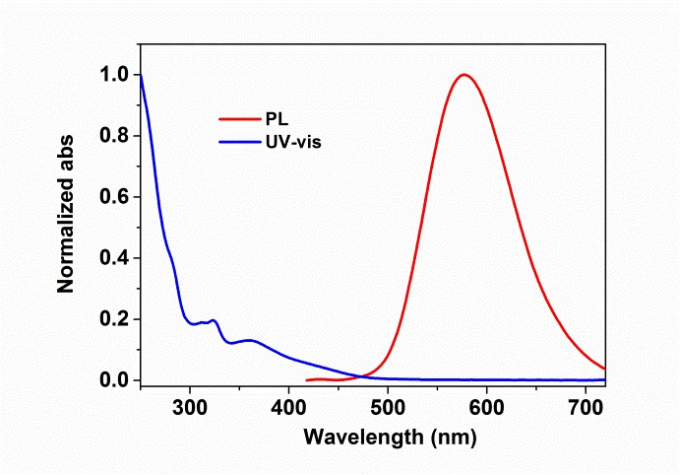


Fig. S10 UV-vis absorption and photoluminescence (PL) spectra of **1-Co** (10 μM) in CH_2Cl_2 at room temperature, λ_{ex} = 400 nm.

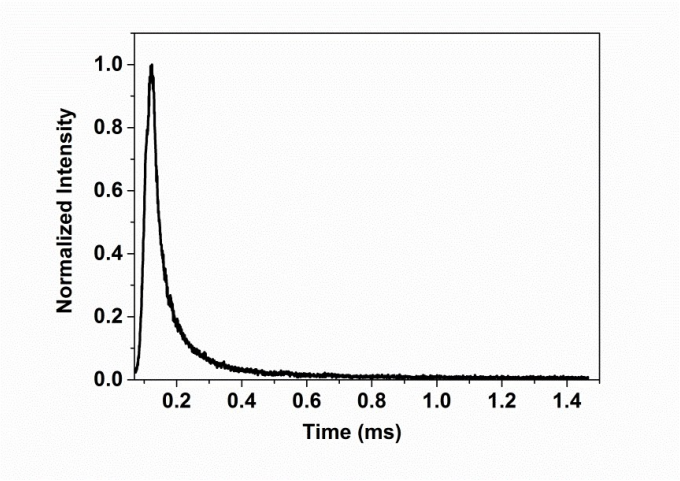


Fig. S11 Transient PL decay of **1-Co** in degassed CH_2Cl_2 at room temperature.

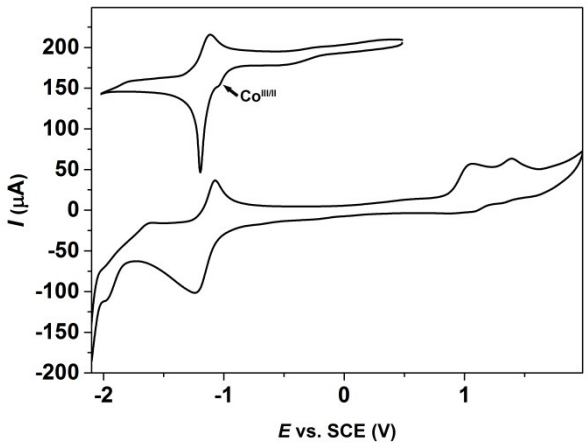


Fig. S12 Cyclic voltammogram of **1-Co** (0.5 mmol) in CH_3CN at room temperature under N_2. Tetra–nbutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte.

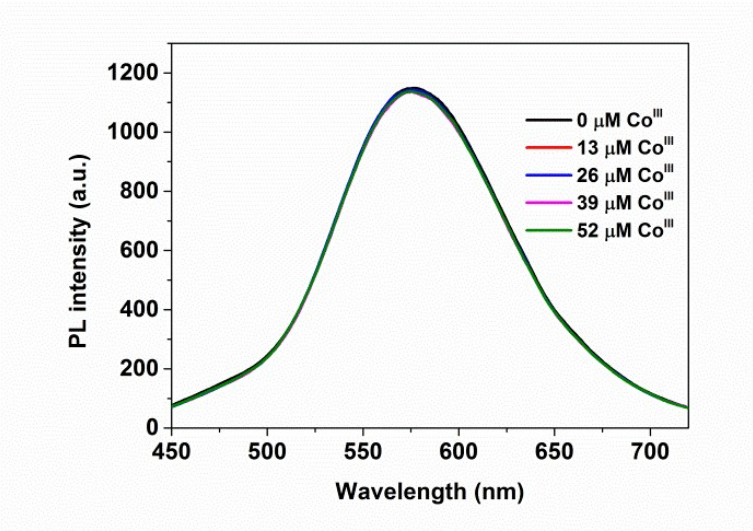


Fig. S13 Emission quenching titration experiments of **1** (10 μM) upon addition of **2a** (0 – 52 μM) in degassed THF (λ_{ex} = 400 nm).

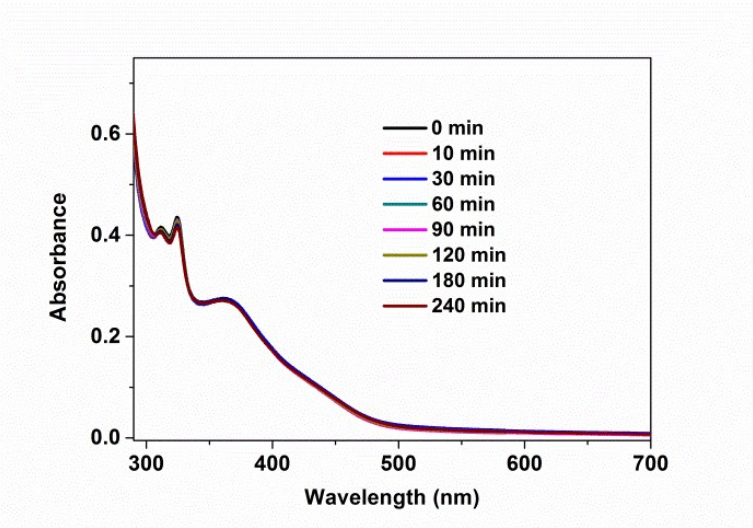


Fig. S14 UV-vis absorption spectra of **1-Co** upon blue light irradiation at room temperature.

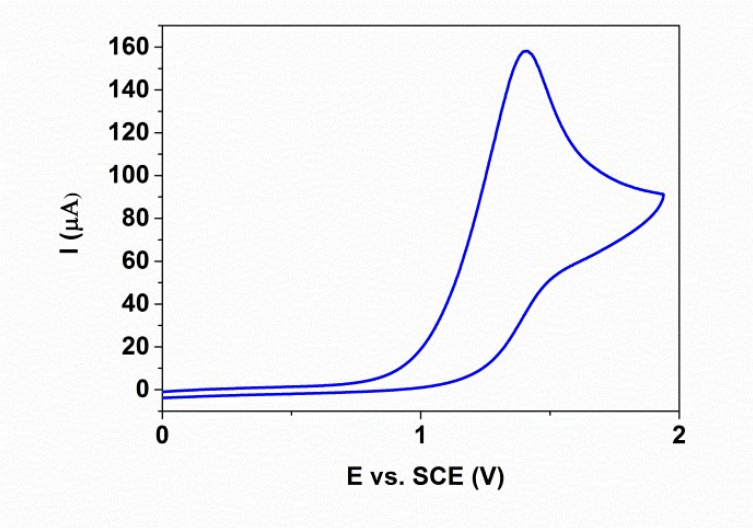


Fig. S15 Cyclic voltammogram of **2a**.

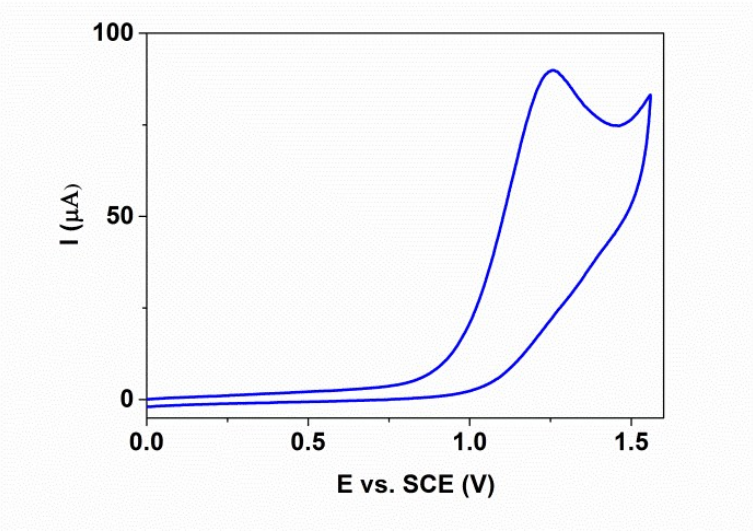


Fig. S16 Cyclic voltammogram of **2b**.

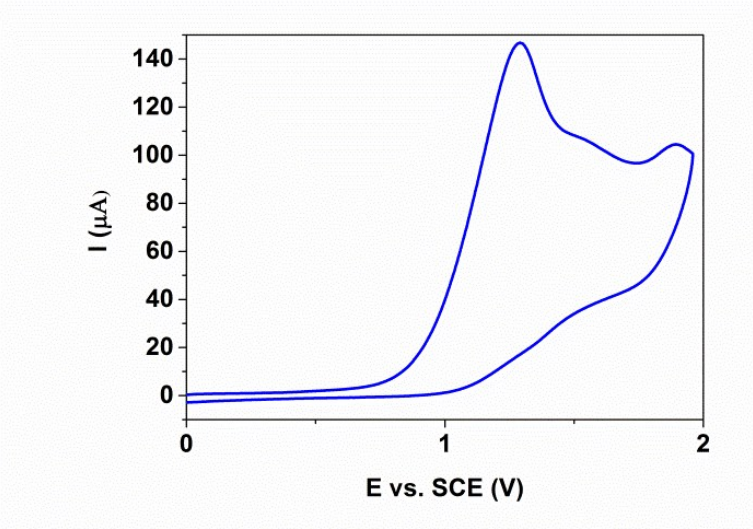


Fig. S17 Cyclic voltammogram of **2c**.

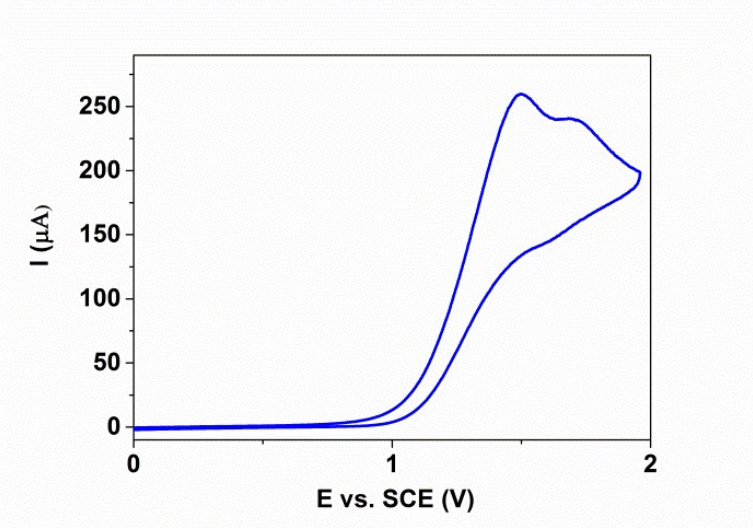


Fig. S18 Cyclic voltammogram of **2d**.

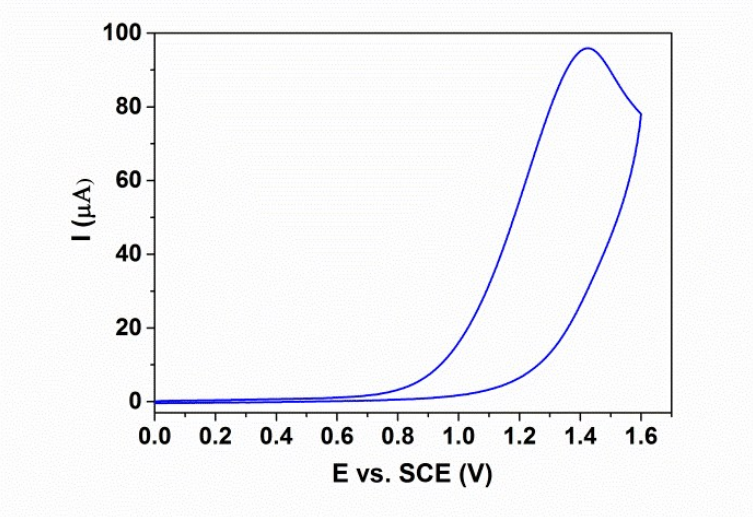


Fig. S19 Cyclic voltammogram of **2e**.

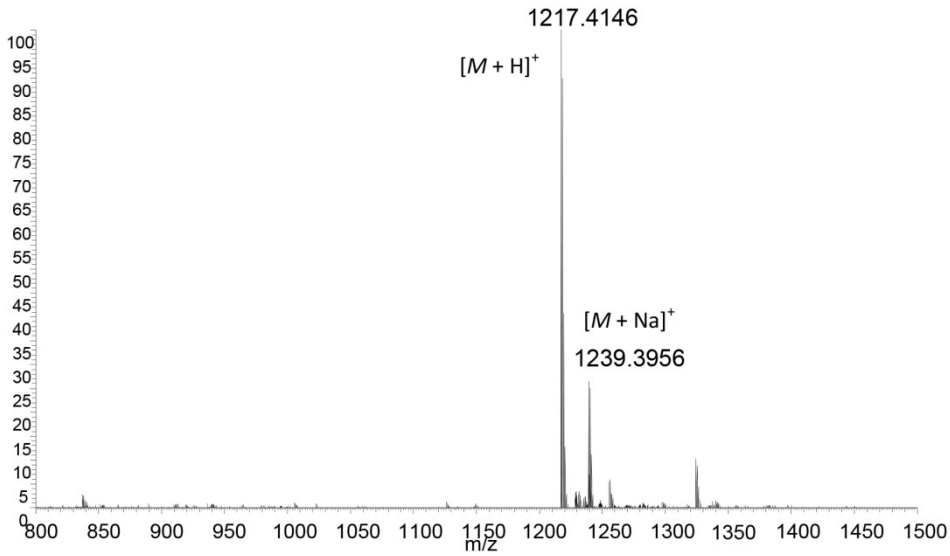


Fig. S20 HR-ESI-MS spectrum of chromophore **1** (*M* = **1**).

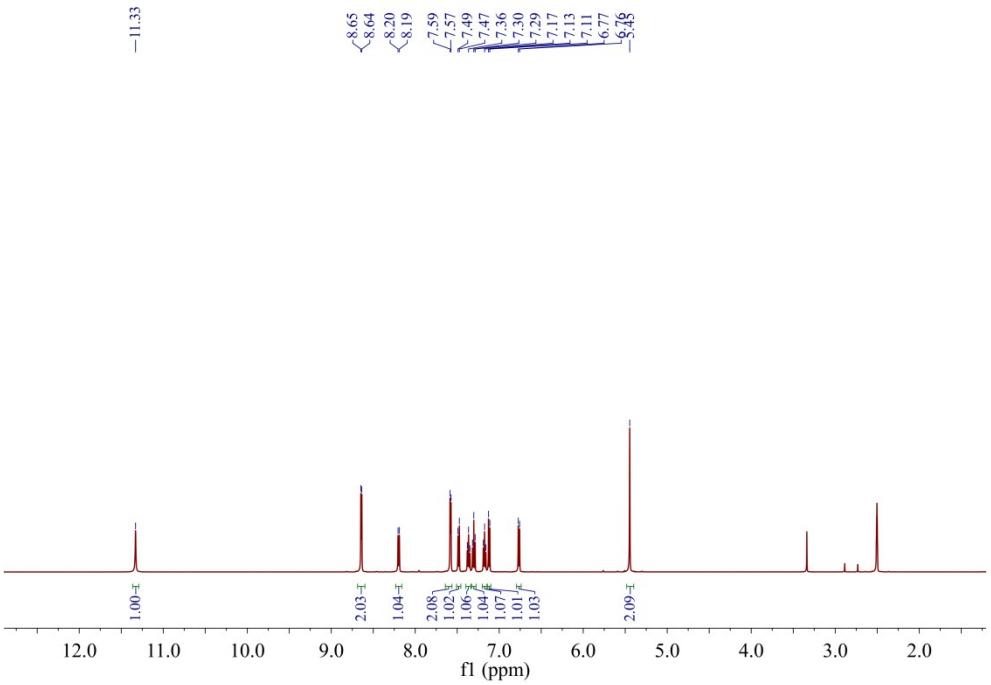


Fig. S21 ^{1}H NMR spectrum of 4-(pyridin-4-ylmethoxy)-9H-carbazole in DMSO-d_6.

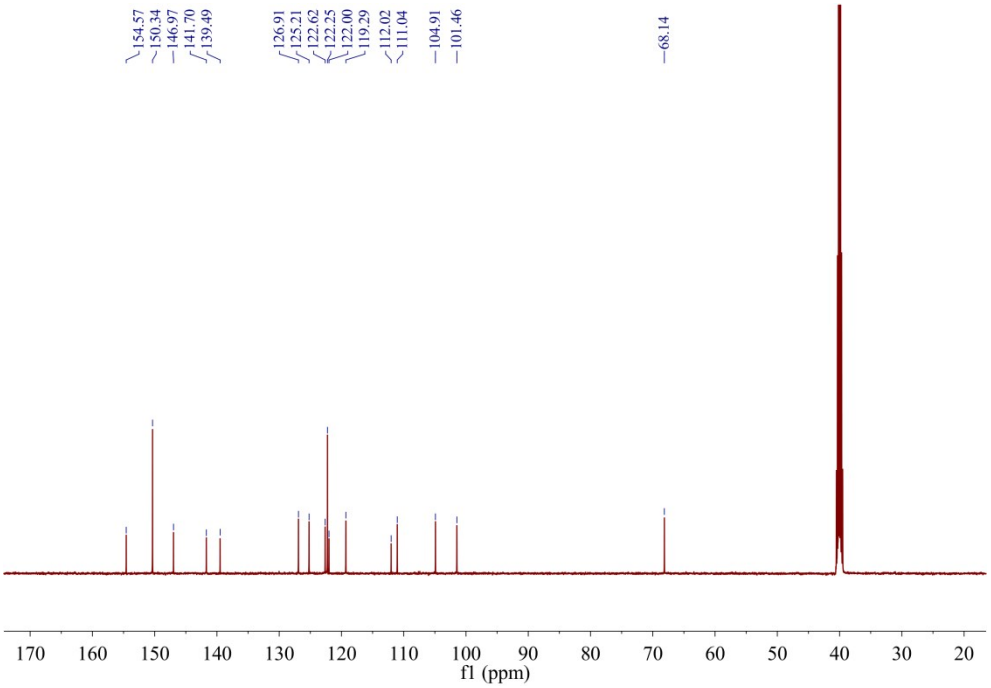


Fig. S22 ^{13}C NMR spectrum of 4-(pyridin-4-ylmethoxy)-9H-carbazole in DMSO-d_6.

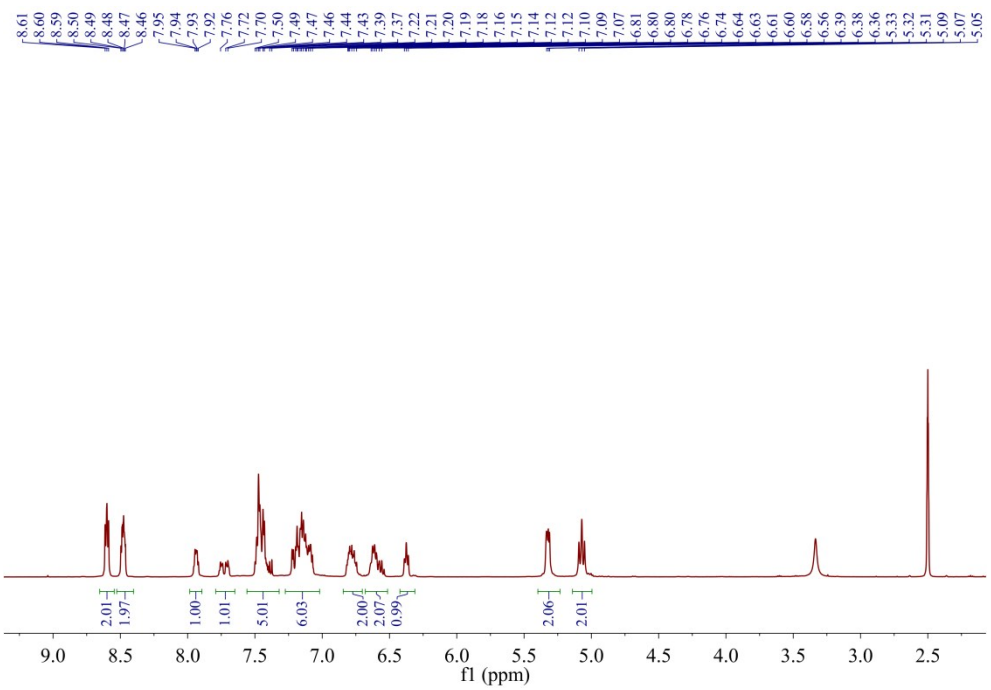


Fig. S23 ^{1}H NMR spectrum of **1** in DMSO-d_6.

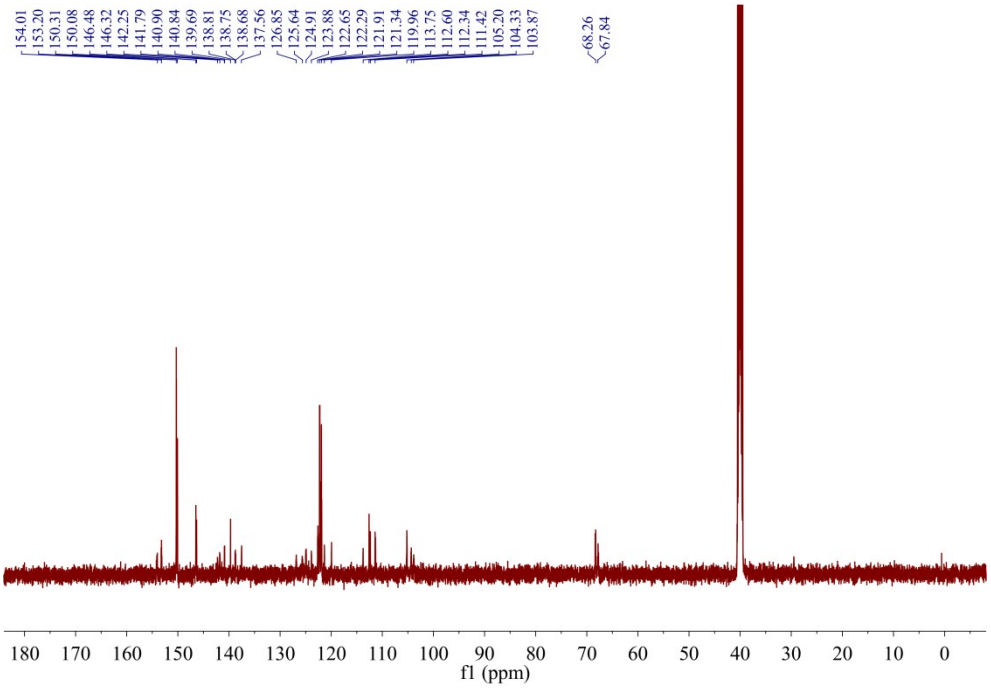


Fig. S24 ^{13}C NMR spectrum of **1** in DMSO-d_6.

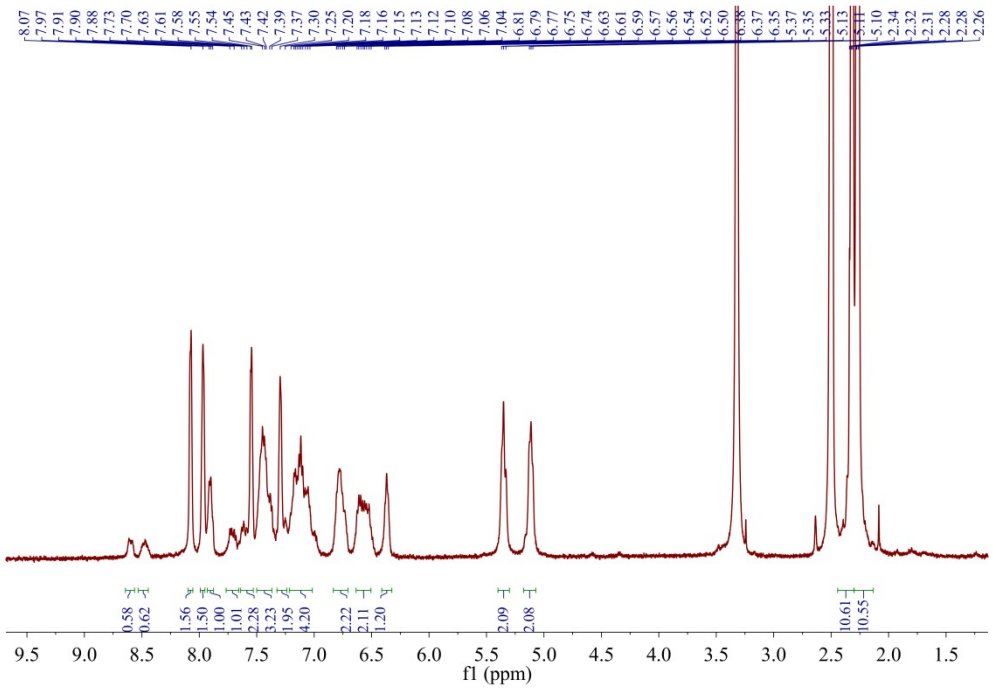


Fig. S25 ^{1}H NMR spectrum of **1-Co** in DMSO-d_6.

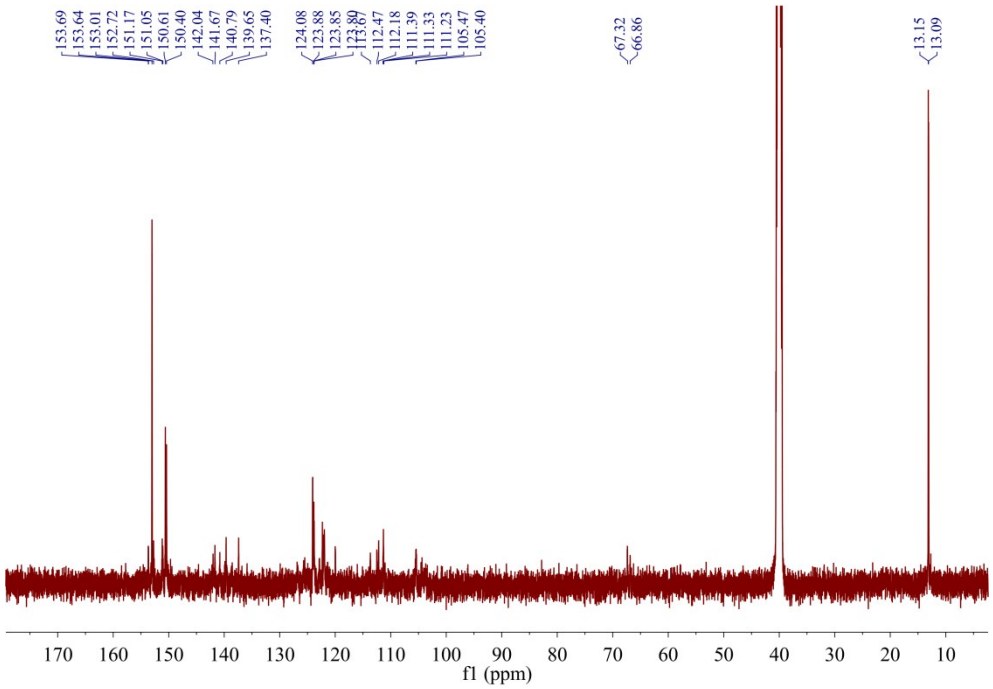
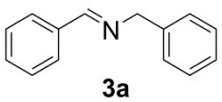


Fig. S26 ^{13}C NMR spectrum of **1-Co** in DMSO-d_6.

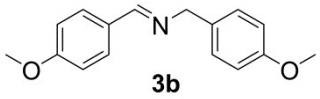
Characterization of products



3a

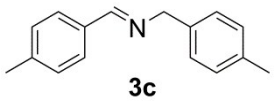
3a: ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.36 (s, 1H), 7.77 (d, 2H, J = 3.0 Hz), 7.38-7.39 (m, 3H), 7.32 (d, 4H, J = 4.0 Hz), 7.24 (d, 1H, J = 4.0 Hz), 4.8 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 161.97, 139.44, 136.31,

130.79, 128.65, 128.55, 128.35, 128.04, 127.03, 65.10. HR–MS (m/z): found 196.1139 for [*M* + H]$^+$ (calcd. 196.1126, $C_{14}H_{14}N^+$).



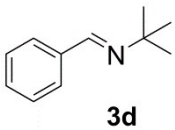
3b

3b: ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.29 (s, 1H), 7.70 (d, 2H, J = 9.0 Hz), 7.23 (d, 2H, J = 8.5 Hz), 6.87-6.93 (m, 4H), 4.72 (s, 2H), 3.83 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 161.68, 160.97, 158.65, 131.67, 129.83, 129.19, 113.98, 113.91, 64.42, 55.37, 55.31. HR–MS (m/z): found 256.1342 for [*M* + H]$^+$ (calcd. 256.1338, $C_{16}H_{18}NO_2^+$).



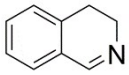
3c

3c: ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.34 (s, 1H), 7.65 (d, 2H, J = 8.0 Hz), 7.21 (d, 4H, 6.0 Hz), 7.14 (d, 2H, J = 8.0 Hz), 4.77 (s, 2H), 2.38 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 161.71, 140.99, 136.53, 136.36, 133.63, 129.31, 129.17, 128.25, 127.97, 64.82, 21.52, 21.12. HR–MS (m/z): found 224.1472 for [*M* + H]$^+$ (calcd. 224.1439, $C_{16}H_{18}N^+$).



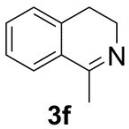
3d

3d: ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.27 (s, 1H), 7.74-7.75 (m, 2H), 7.38-7.40 (m, 3H), 1.30 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 155.20, 137.18, 130.19, 128.53, 127.93, 57.26, 29.76. HR–MS (m/z): found 162.1291 for [*M* + H]$^+$ (calcd. 162.1283, $C_{11}H_{16}N^+$).



3e

3e: ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.35 (s, 1H), 7.34-7.38 (m, 1H), 7.26-7.32 (m, 2H), 7.5 (d, 1H, J = 7.5 Hz), 3.76-3.80 (m, 2H), 2.74 (t, 2H, J = 7.5 Hz). ^{13}C NMR (125 MHz, CDCl3), δ (ppm): 160.41, 136.35, 131.13, 127.44, 127.28, 127.11, 47.33, 25.03. HR–MS (m/z): found 132.0864 for [*M* + H]$^+$ (calcd. 132.0808, $C_9H_{10}N^+$).



3f

3f: ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.40 (d, 1H, J = 5.0 Hz), 7.26-7.29 (m, 1H), 7.19-7.23 (m, 1H), 7.10 (d, 1H, J = 5.0 Hz), 3.57-3.60 (m, 2H), 2.63 (t, 2H, J = 7.5 Hz), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 164.54, 137.40, 130.70, 129.51, 127.46, 126.93, 125.39, 46.8, 26.03, 23.22. HR–MS (m/z): found 146.0876 for [*M* + H]$^+$ (calcd. 146.0964, $C_{10}H_{12}N^+$).

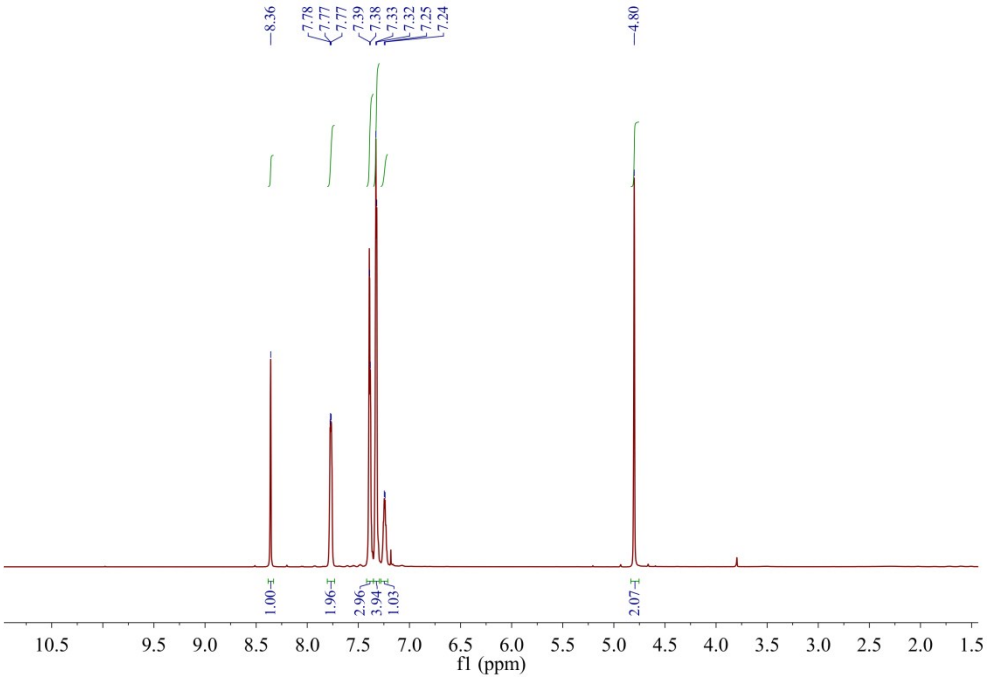


Fig. S27 ^{1}H NMR spectrum of **3a** in $CDCl_3$.

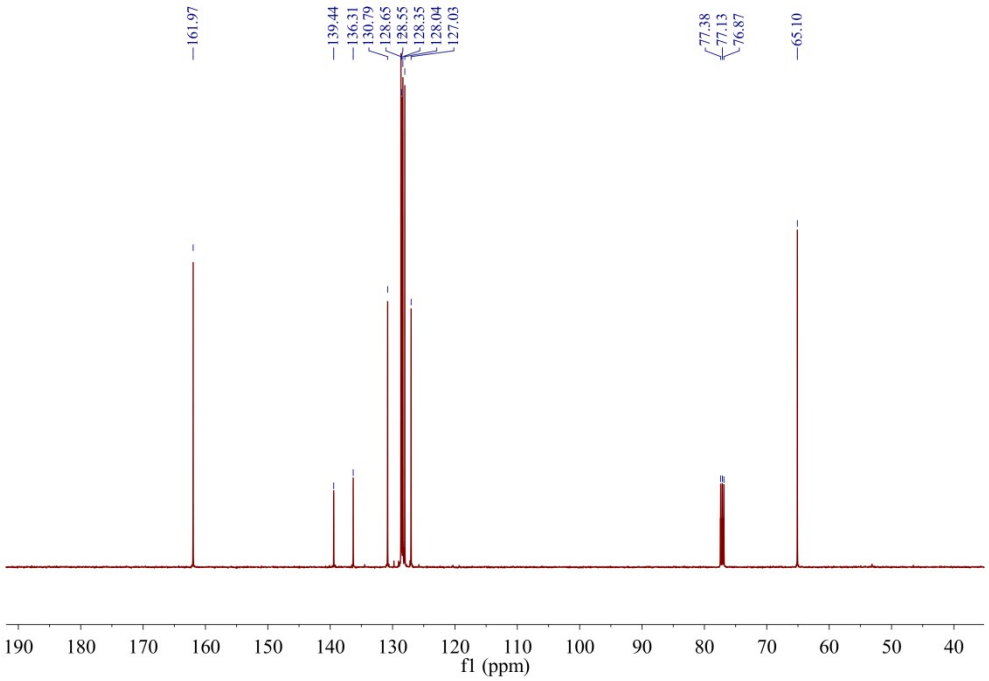


Fig. S28 ^{13}C NMR spectrum of **3a** in $CDCl_3$.

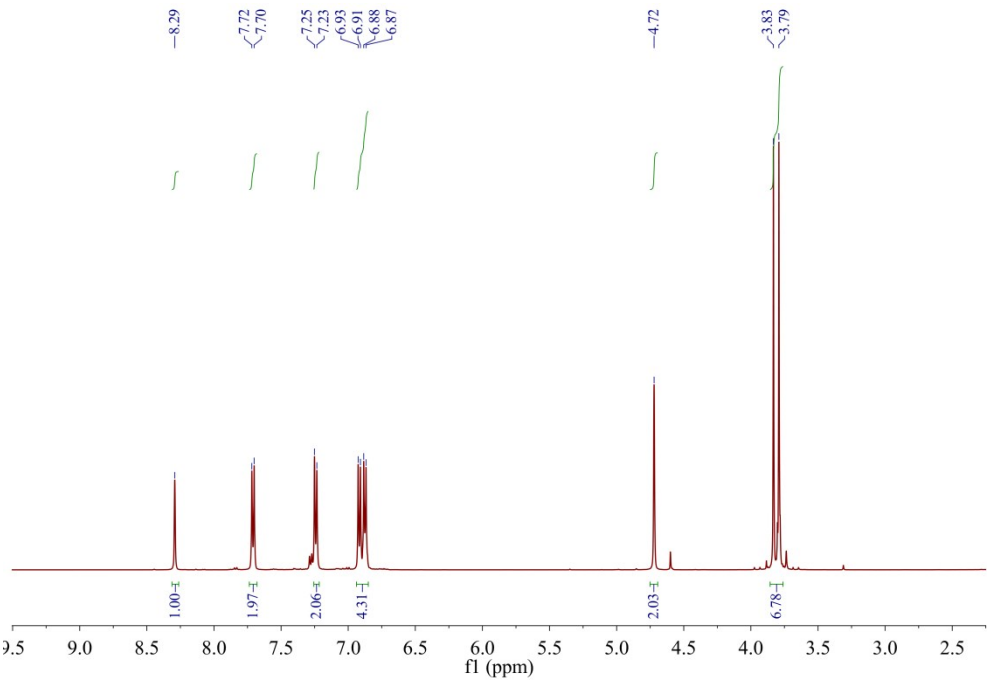


Fig. S29 ^{1}H NMR spectrum of **3b** in $CDCl_3$.

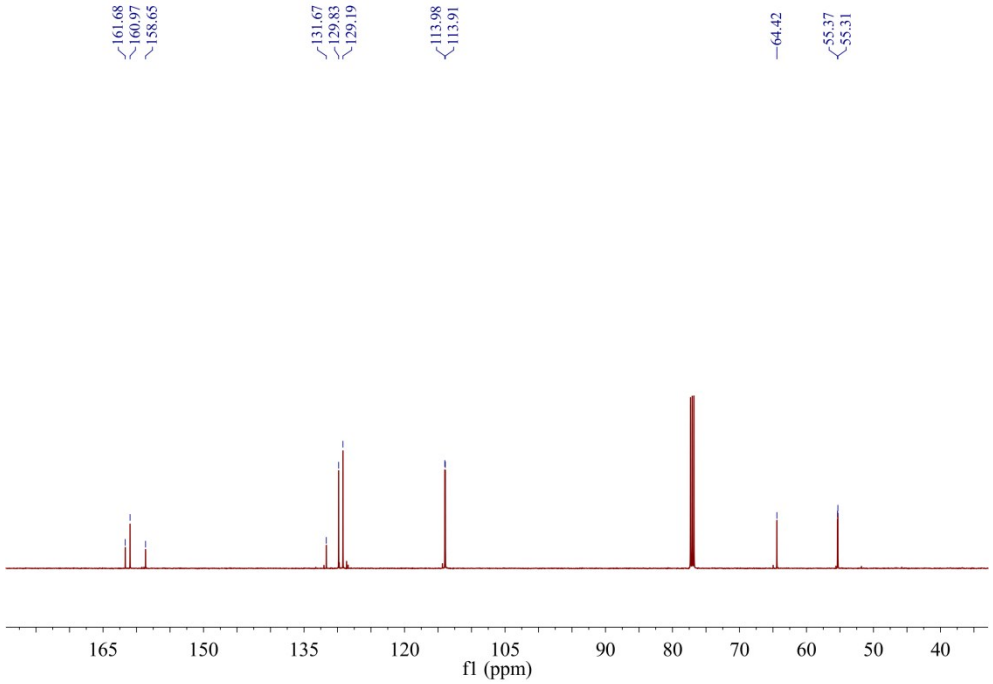


Fig. S30 ^{13}C NMR spectrum of **3b** in $CDCl_3$.

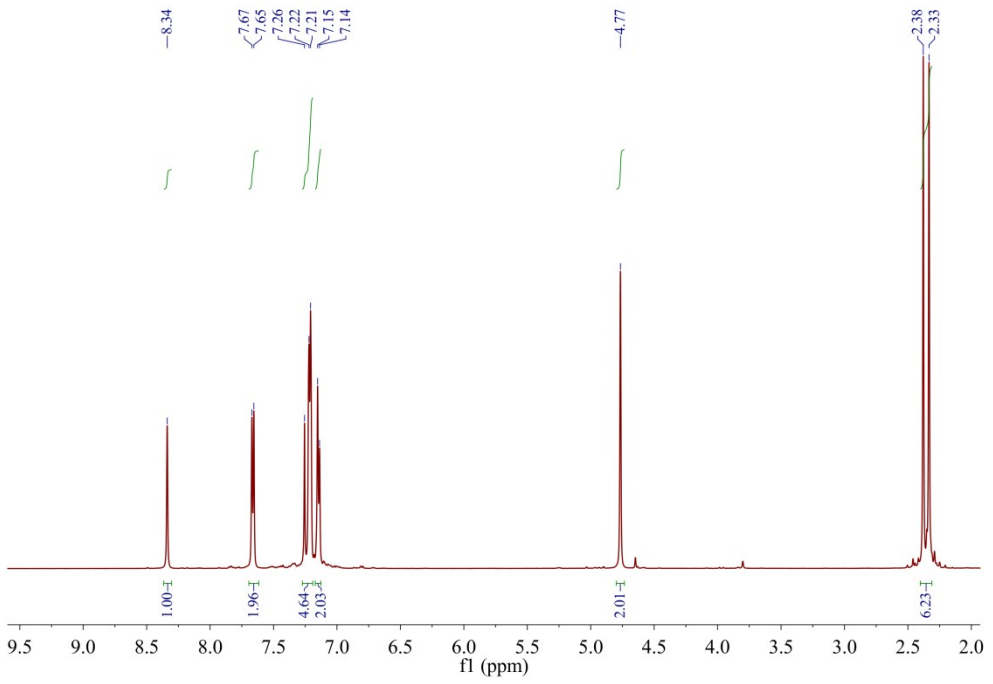


Fig. S31 ^{1}H NMR spectrum of **3c** in $CDCl_3$.

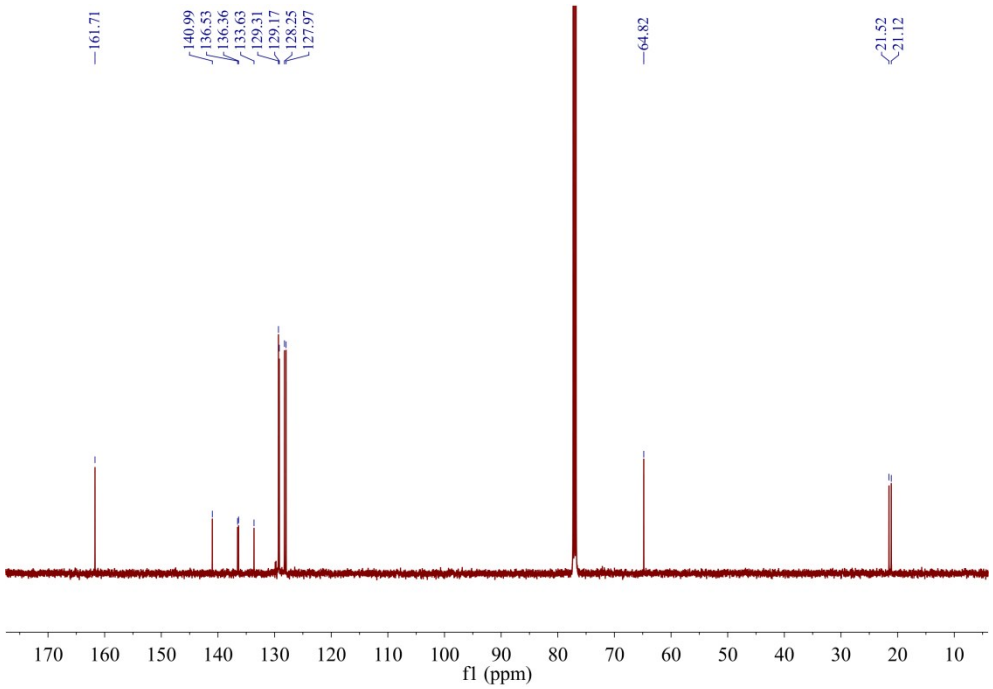


Fig. S32 ^{13}C NMR spectrum of **3c** in $CDCl_3$.

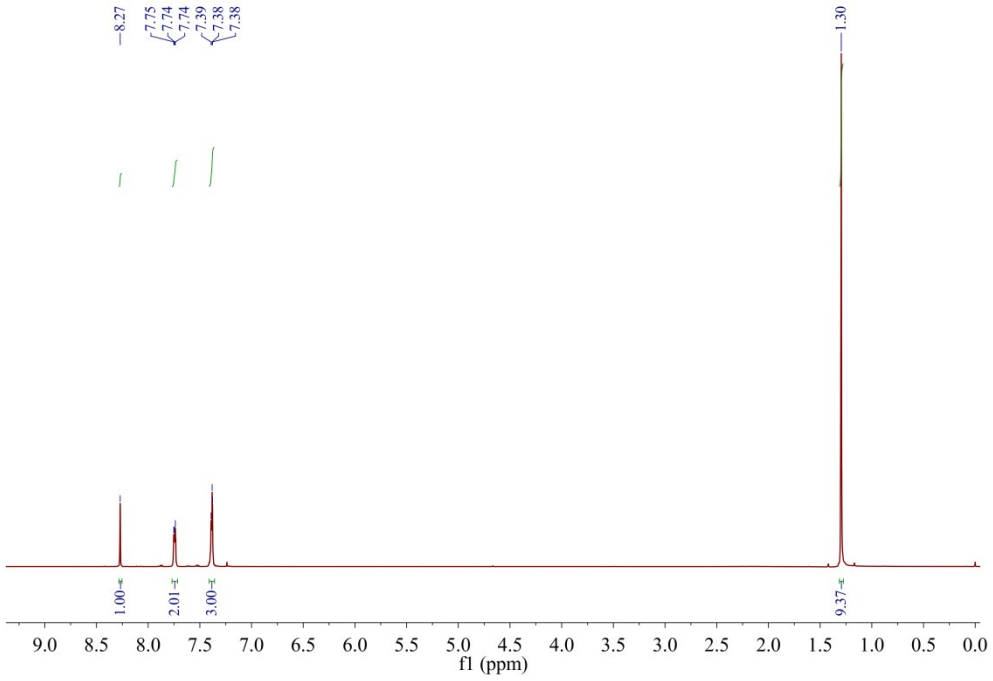


Fig. S33 ^{1}H NMR spectrum of **3d** in $CDCl_3$.

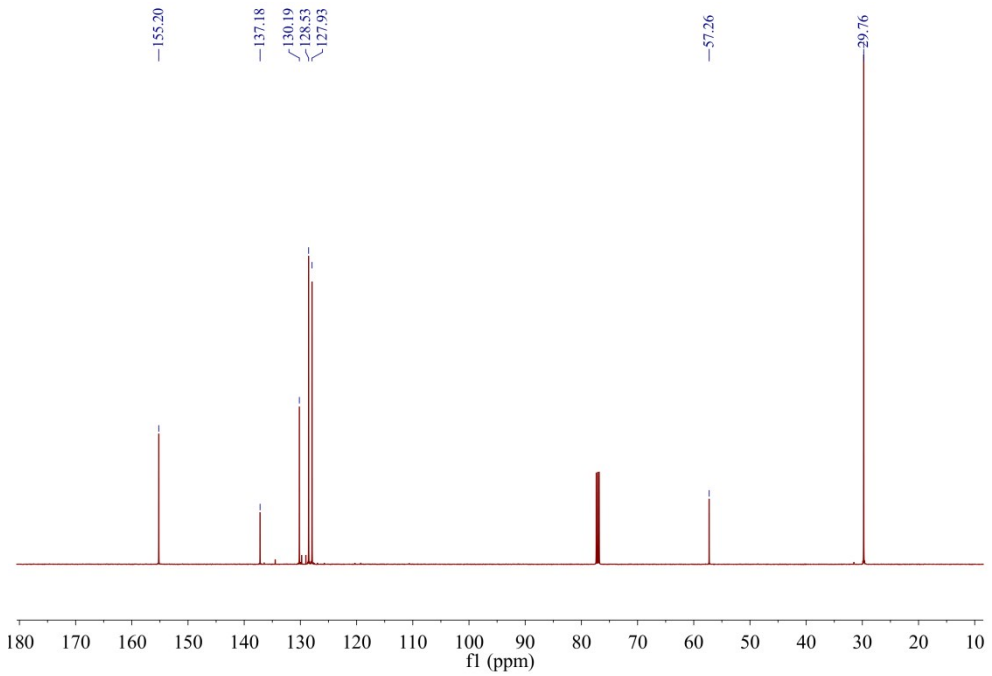


Fig. S34 ^{1}H NMR spectrum of **3d** in $CDCl_3$.

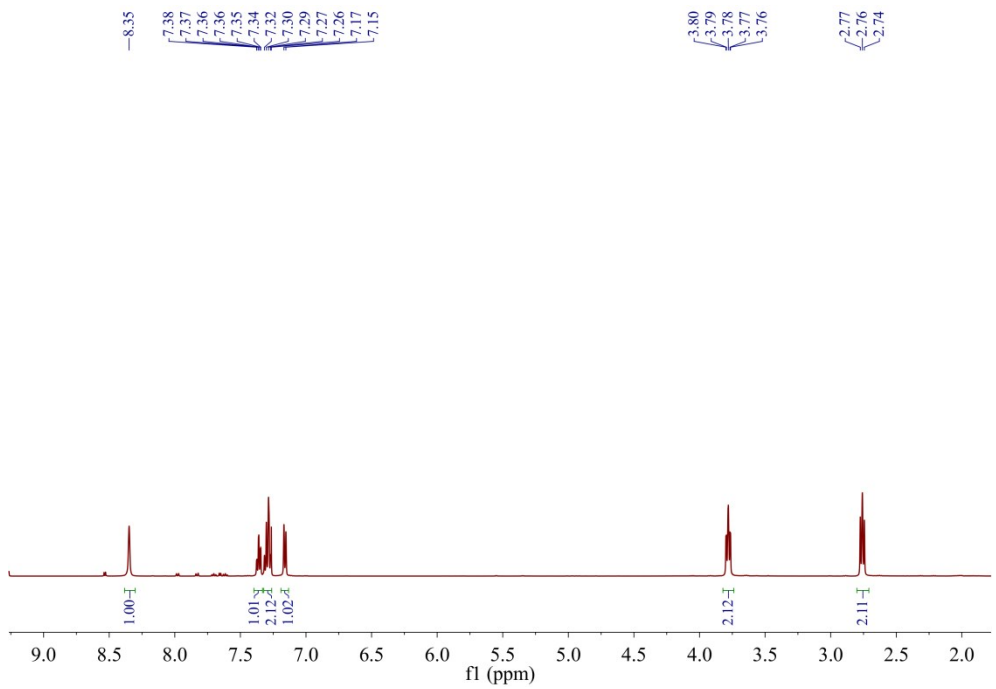


Fig. S35 ^{1}H NMR spectrum of **3e** in $CDCl_3$.

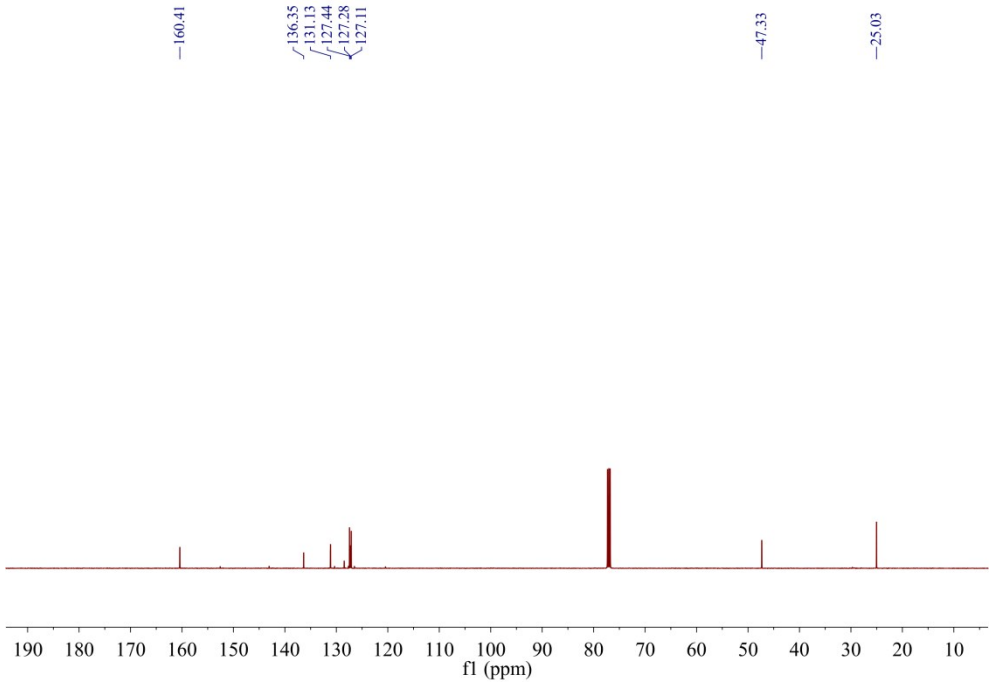


Fig. S36 ^{13}C NMR spectrum of **3e** in $CDCl_3$.

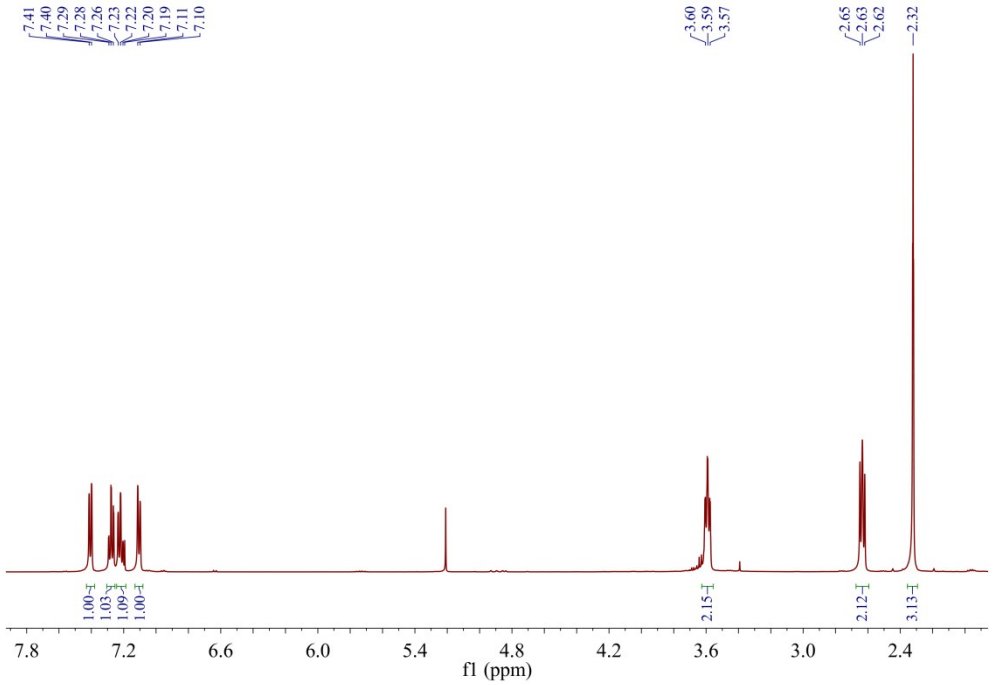


Fig. S37 ^{1}H NMR spectrum of **3f** in $CDCl_3$.

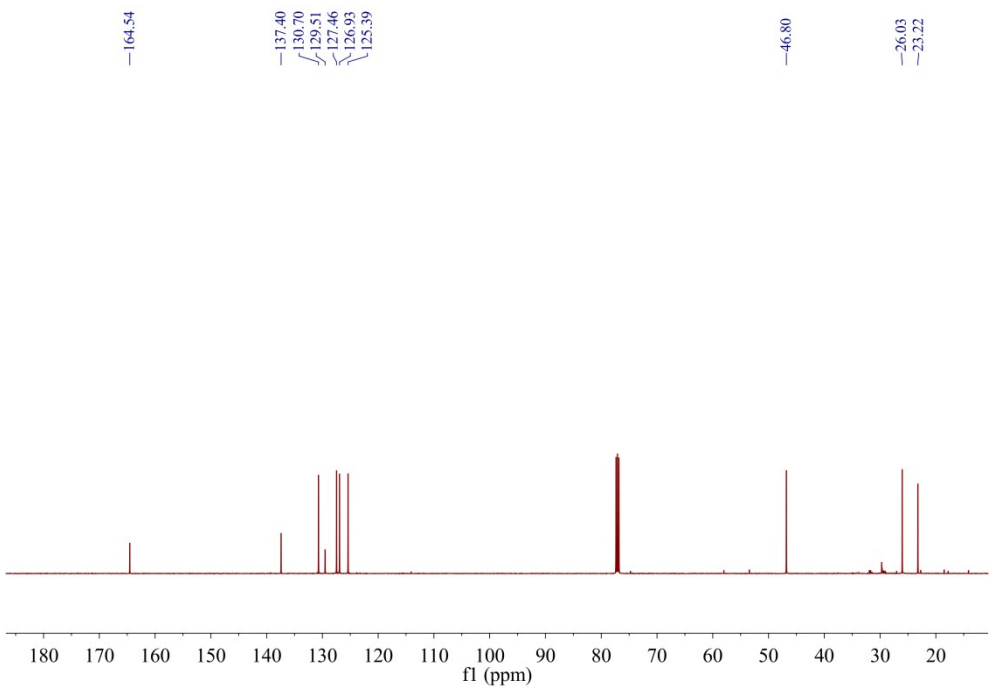


Fig. S38 ^{13}C NMR spectrum of **3e** in $CDCl_3$.