Supporting information

Photocatalytically Active Conjugated Porous Polymers via Click Chemistry for Heterogeneous Dehydrogenation of Hydrazo Aromatics

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Supporting Information section contains: 64 Pages, 106 Figures, 1 Tables

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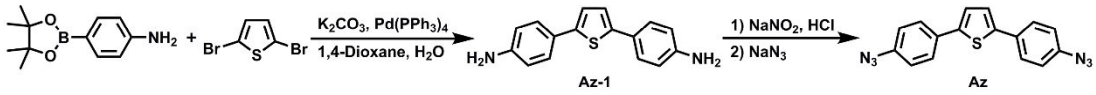
1. Synthesis of building blocks

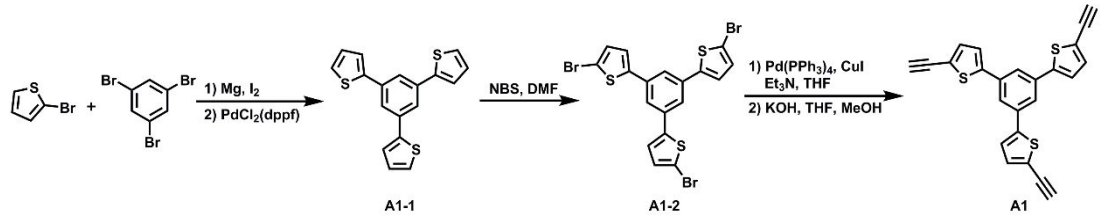
1.1. Synthesis of 2,5-bis(4-azidophenyl)thiophene (Az)



4,4'-(Thiophene-2,5-diyl)dianiline (Az-1) — To a solution of 4-aminophenylboronic acid pinacol ester (4.38 g, 20.00 mmol), 2,5-dibromothiophene (1.92 g, 8.01 mmol) and potassium carbonate (6.63 g, 48.00 mmol) in 80 mL 1,4-dioxane/water mixture (3:1 v/v) was added tetrakis(triphenylphosphine)palladium (0.46 g, 0.40 mmol) under a N_2 atmosphere. The mixture was stirred and heated to 110 °C for 12 h until the reaction was complete (monitored by TLC). After cooling to room temperature, the reaction mixture was extracted with dichloromethane (60 mL × 3). The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The residue was purified on a silica gel column (petroleum ether/dichloromethane 8:1, v/v) to afford **Az-1** as a light yellow powder (1.96 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.45 (m, 4H), 7.08 (s, 2H), 7.05-7.11 (m, 4H), 3.73 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.78, 142.51, 126.73, 125.39, 122.01, 115.34.

2,5-Bis(4-azidophenyl)thiophene (Az) — In a round-bottom flask equipped with a magnetic stirring bar, **Az-1** (1.96 g, 7.37 mmol) was suspended in HCl (6 N, 10 mL) cooled in an ice bath. Then 25 mL of aqueous solution of $NaNO_2$ (1.035 g, 15.00 mmol) was added dropwise. The reaction mixture was stirred for 0.5 h and 50 mL of aqueous solution of NaN_3 (2.15 g, 33.15 mmol) was added dropwise. After addition, the mixture was allowed to stir for another 16 h at room temperature. Then the mixture was extracted with ethyl acetate (80 mL × 3). The combined organic extracts were washed with H_2O and dried over anhydrous $MgSO_4$. The volatiles were removed under vacuum to give crude product, which was purified by column chromatography on silica gel (petroleum ether) to afford **Az** as a reddish brown solid (1.87 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.64 (m, 4H), 7.24 (s, 2H), 7.02-7.08 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.61, 139.18, 131.10, 126.95, 124.01, 119.56. HRMS (m/z): calcd for $C_{16}H_{11}N_6S$ 319.0766 $[M + H]^+$, found 319.0761.

1.2. Synthesis of 1,3,5-tris(5-ethynylthiophen-2-yl)benzene (A1)



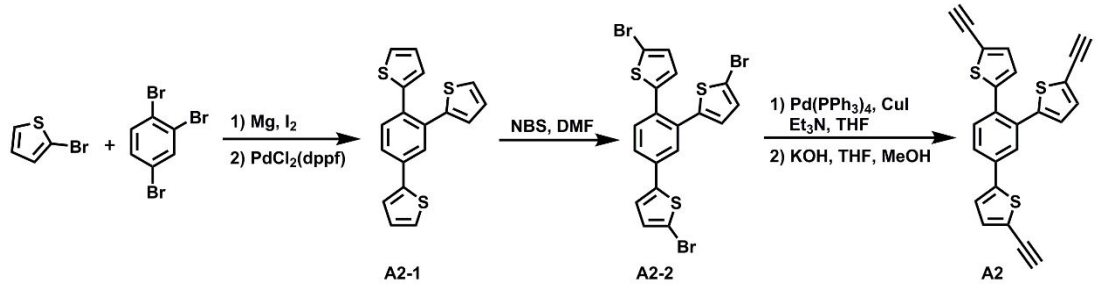
1,3,5-Tri(thiophen-2-yl)benzene (A1-1) — A1-1 was synthesized according to the published procedure.[1] Under a N_2 atmosphere, a solution of 2-bromothiophene (4.56 g, 27.98 mmol) in anhydrous THF (40 mL) was added dropwise to a suspension of magnesium (1.07 g, 44.03 mmol) in THF (10 mL). The reaction mixture was refluxed for 1 h to yield 2-thienylmagnesium bromide. The resulting solution containing 2-thienylmagnesium bromide was cooled and added dropwise to an ice cooled solution of 1,3,5-tribromobenzene (2.20 g, 7.00 mmol) and $PdCl_2$(dppf) (0.20 g, 0.28 mmol) in anhydrous THF (50 mL). Then the mixture was heated at 70 ^oC and stirred for 3 h under a N_2 atmosphere. Afterwards the reaction mixture was poured into water (500 mL), and extracted with dichloromethane (100 mL × 3). The organic phase was combined, washed with water, dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography (petroleum ether) to give compound **A1-1** as a white powder (2.22 g, 98%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 3H), 7.42 (dd, J_1 = 3.6, J_2 = 1.1 Hz, 3H), 7.34 (dd, J_1 = 5.1, J_2 = 1.1 Hz, 3H), 7.13 (dd, J_1 = 5.1, J_2 = 3.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.58, 135.73, 128.19, 125.46, 123.94, 122.77.

1,3,5-Tris(5-bromothiophen-2-yl)benzene (A1-2) — To a solution of **A1-1** (2.00g, 6.17 mmol) in DMF (20 mL) was added dropwise for 1 h a DMF solution (10 mL) of *N*-bromosuccinimide (3.51 g, 19.74 mmol). After being stirred in the dark overnight, the reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ (30 mL) and extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated to afford a residue, which was purified by chromatography on silica gel (petroleum ether) to give **A1-2** as a pale yellow powder (3.22 g, 93%). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.56 (s, 3H), 7.18 (d, J = 3.8 Hz, 3H), 7.11 (d, J = 3.8 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.36, 135.13, 131.16,

124.42, 122.05, 112.28.

1,3,5-Tris(5-ethynylthiophen-2-yl)benzene (A1) — To a solution of **A1-2** (3.22 g, 3.74 mmol), (trimethylsilyl)acetylene (4.00 mL, 28.30 mmol), $Pd(PPh_3)_4$ (0.40 g, 0.35 mmol) in Et_3N (30 mL) and THF (30 mL) was added CuI (0.10 g, 0.52 mmol), and the mixture was stirred under a N_2 atmosphere at 90 °C overnight. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated under vacuum. The residue was subsequently dissolved in tetrahydrofuran (50 mL) and methanol (50 mL), and an aqueous NaOH solution (2 M, 20 mL) was added dropwise. The mixture was stirred at room temperature for 3 h and extracted with dichloromethane (100 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated to give crude product, which was purified by column chromatography on silica gel (petroleum ether) to afford **A1** as a brown yellow powder (1.33 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 3H), 7.27-7.31 (m, 6H), 3.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.57, 135.17, 134.22, 123.82, 123.06, 122.11, 82.48, 76.82. HRMS (m/z): calcd for $C_{24}H_{13}S_3$ 397.0179 $[M + H]^+$, found 397.0176.

1.3. Synthesis of 1,2,4-tris(5-ethynylthiophen-2-yl)benzene (A2)



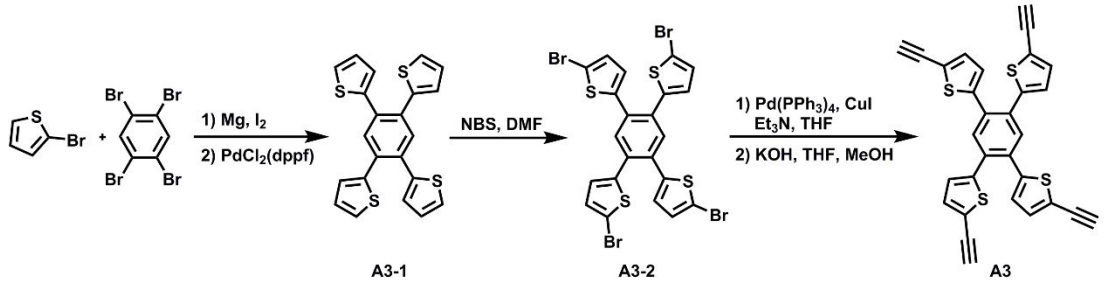
1,2,4-Tri(thiophen-2-yl)benzene (A2-1) — A2-1 was synthesized with a similar synthetic procedure to **A1-1** using 1,2,4-tribromobenzene (3.00 g, 9.53 mmol) and 2-bromothiophene (6.21 g, 38.08 mmol) as starting materials. The product was obtained as a white powder (2.95 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 2.0 Hz, 1H), 7.62 (dd, J_1 = 8.0, J_2 = 2.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.27-7.41 (m, 4H), 7.11 (dd, J_1 = 5.0, J_2 = 3.6 Hz, 1H), 6.94-7.04 (m, 3H), 6.91 (dd, J_1 = 3.6, J_2 = 1.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.30, 142.28, 142.26, 134.18, 133.96, 132.99, 131.41, 128.54, 128.21, 127.42, 127.09, 127.03, 126.25, 126.12, 125.38, 123.67.

1,2,4-Tris(5-bromothiophen-2-yl)benzene (A2-2) — Following a similar synthetic procedure to **A1-2** except **A2-1** (2.79 g, 8.59 mmol) was used instead of **A1-1**, the product was obtained as a pale

yellow powder (4.67 g, yield 97%). 1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.58 (m, 3H), 7.04-7.13 (m, 2H), 6.91-7.00 (m, 2H), 6.66-6.77 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.21, 143.02, 133.62, 133.31, 132.28, 131.40, 131.13, 130.09, 127.98, 127.59, 125.40, 124.07, 113.25.

1,2,4-Tris(5-ethynylthiophen-2-yl)benzene (A2) — Following a similar synthetic procedure to **A1** except **A2-2** (4.00 g, 7.13 mmol) was used instead of **A1-2**, the product was obtained as a yellow powder (2.57 g, 91%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.65 (m, 3H), 7.27 (d, J = 3.8 Hz, 1H), 7.23 (d, J = 3.8 Hz, 1H), 7.12-7.18 (m, 2H), 6.74-6.82 (m, 2H), 3.43 (s, 1H), 3.39 (s, 1H), 3.39 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.38, 143.46, 143.43, 134.31, 133.62, 133.38, 133.37, 133.35, 132.56, 131.59, 128.49, 127.47, 127.14, 125.81, 123.65, 123.01, 122.83, 122.04, 82.59, 82.34, 82.31, 76.91, 76.89, 76.82. HRMS (m/z): calcd for $C_{24}H_{13}S_3$ 397.0179 $[M + H]^+$, found 397.0175.

1.3. Synthesis of 1,2,4,5-tetrakis(5-ethynylthiophen-2-yl)benzene (A3)



1,2,4,5-Tetra(thiophen-2-yl)benzene (A3-1) — A3-1 was synthesized with a similar synthetic procedure to **A1-1** using 1,2,4,5-tribromobenzene (4.03 g, 10.22 mmol) and 2-bromothiophene (8.89 g, 54.53 mmol) as starting materials. The product was obtained as a white powder (4.94 g, 95%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 2H), 7.31 (dd, J_1 = 5.0 Hz, J_2 = 1.0 Hz, 4H), 6.95-7.01 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.62, 133.43, 133.28, 127.46, 127.08, 126.40.

1,2,4,5-Tetrakis(5-bromothiophen-2-yl)benzene (A3-2) — Following a similar synthetic procedure to **A1-2** except **A3-1** (2.47 g, 6.07 mmol) was used instead of **A1-1**, the product was obtained as a pale yellow powder (3.93 g, 90%). ^1H NMR (400 MHz, Chloroform-d) δ 7.50 (s, 2H), 6.96 (d, J = 3.8 Hz, 4H), 6.74 (d, J = 3.8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.20, 133.15, 132.71, 130.17, 128.03, 113.61.

1,2,4-Tetrakis(5-ethynylthiophen-2-yl)benzene (A3) — Following a similar synthetic procedure to **A1** except **A3-2** (3.10 g, 4.23 mmol) was used instead of **A1-2**, the product was obtained as a yellow powder (1.84 g, 87%). 1H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.17 (d, J = 3.4 Hz, 4H), 6.82 (d, J = 3.4 Hz, 4H), 3.39 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.57, 133.53, 133.41,

132.87, 127.55, 123.31, 82.46, 76.70. HRMS (m/z): calcd for $C_{30}H_{15}S_4$ 503.0057 $[M + H]^+$, found 503.0053.

2. Synthesis of hydrazo aromatics

All the substrates were synthesized according to the published procedures.[2-4]

References

(1) Cornacchio, A. L. P.; Price, J. T.; Jennings, M. C.; McDonald, R.; Staroverov, V. N.; Jones, N. D. *J. Org. Chem.* **2009**, *74*, 530-544.

(2) Wang, L.; Ishida, A.; Hashidoko, Y.; Hashimoto, M. *Angew. Chem. Int. Ed.* **2017**, 5*6*, 870–873.

(3) Lim, B. Y.; Jung, B. E.; Cho, C. G. *Org. lett.* **2014**, *16*, 4492-4495.

(4) Kim, M. H.; Kim, J. *J. Org. Chem.* **2018**, *83*, 1673-1679.

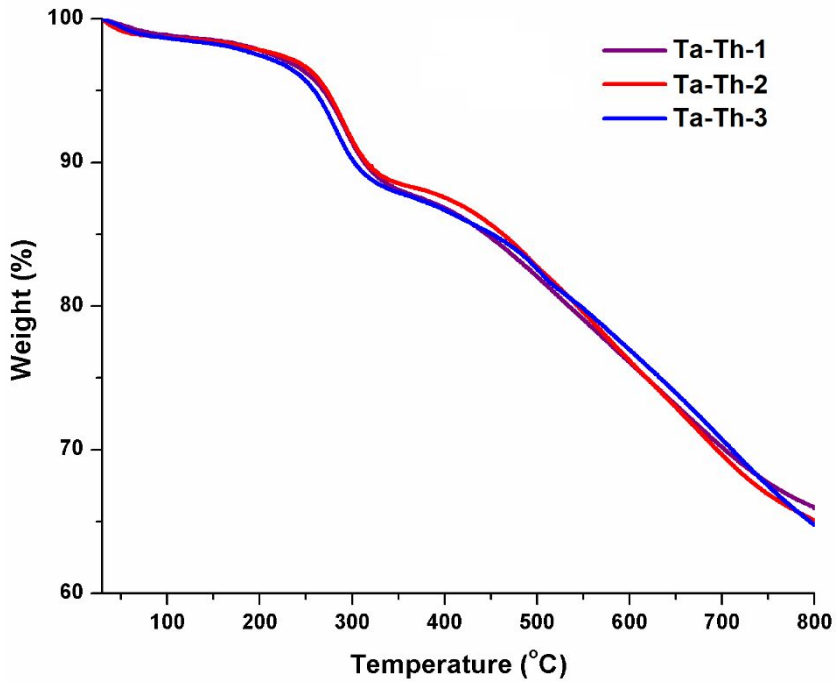


Figure S1. TGA curves.

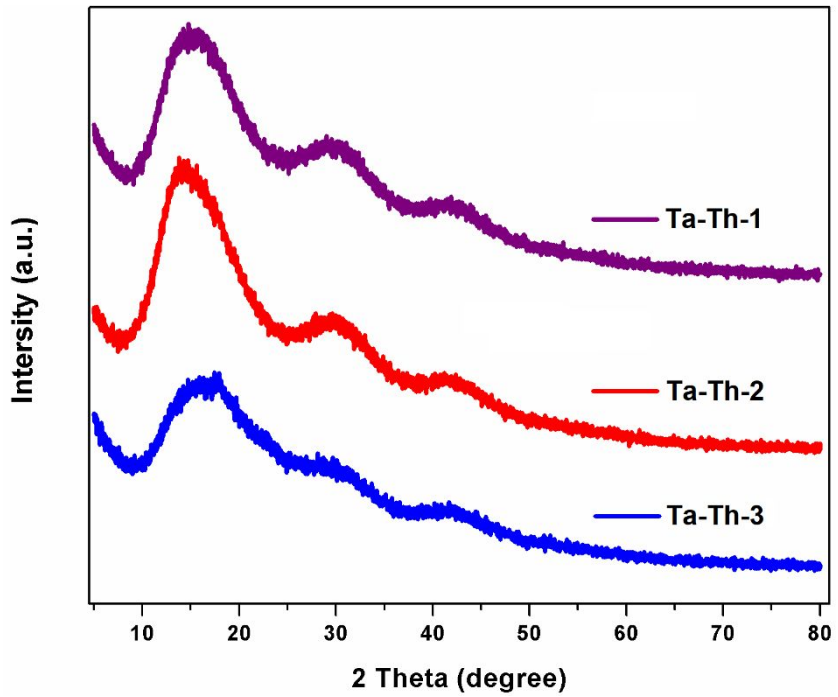


Figure S2. XRD patterns.

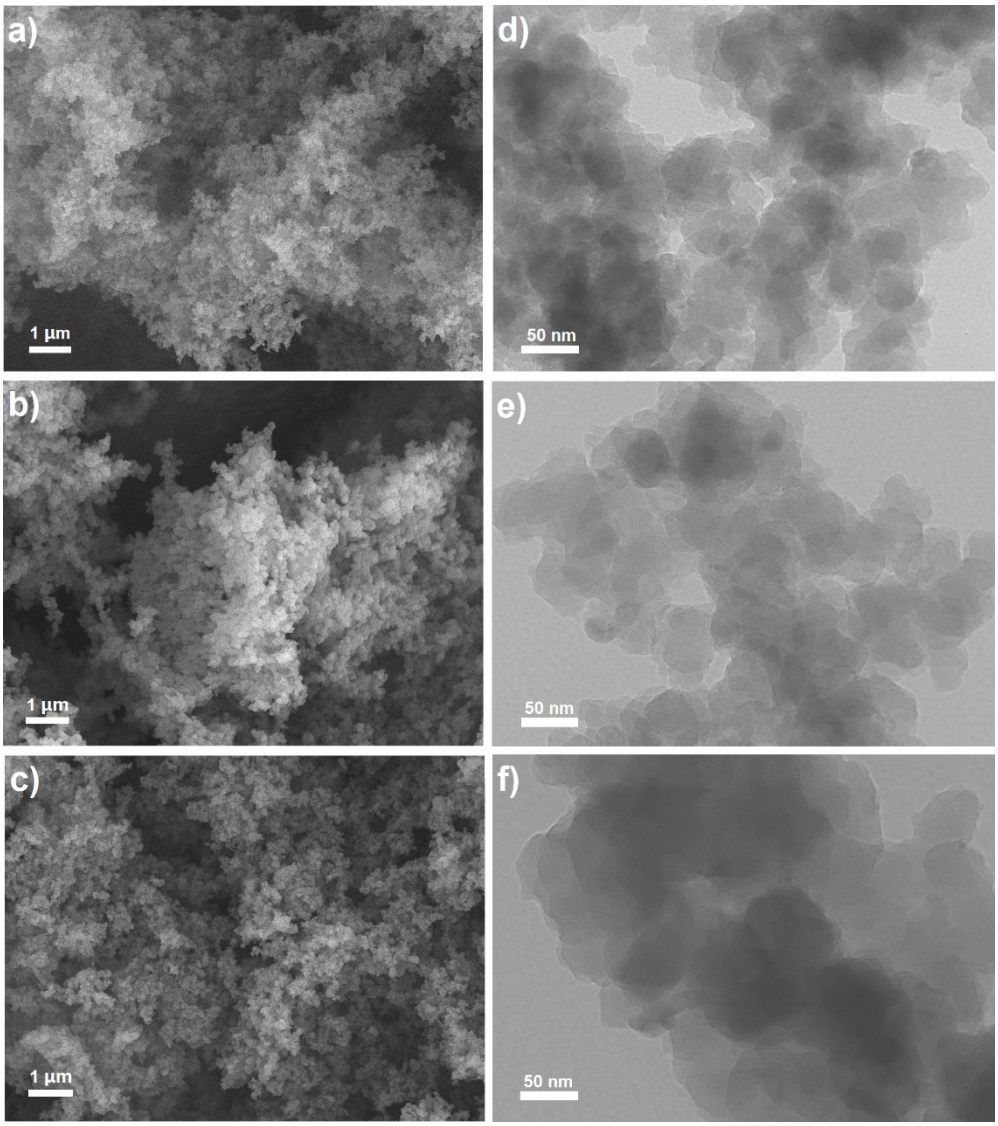


Figure S3. SEM images of (a) Ta-Th-1, (b) Ta-Th-2, and (c) Ta-Th-3, and TEM images of (d) Ta-Th-1, (e) Ta-Th-2, and (f) Ta-Th-3.

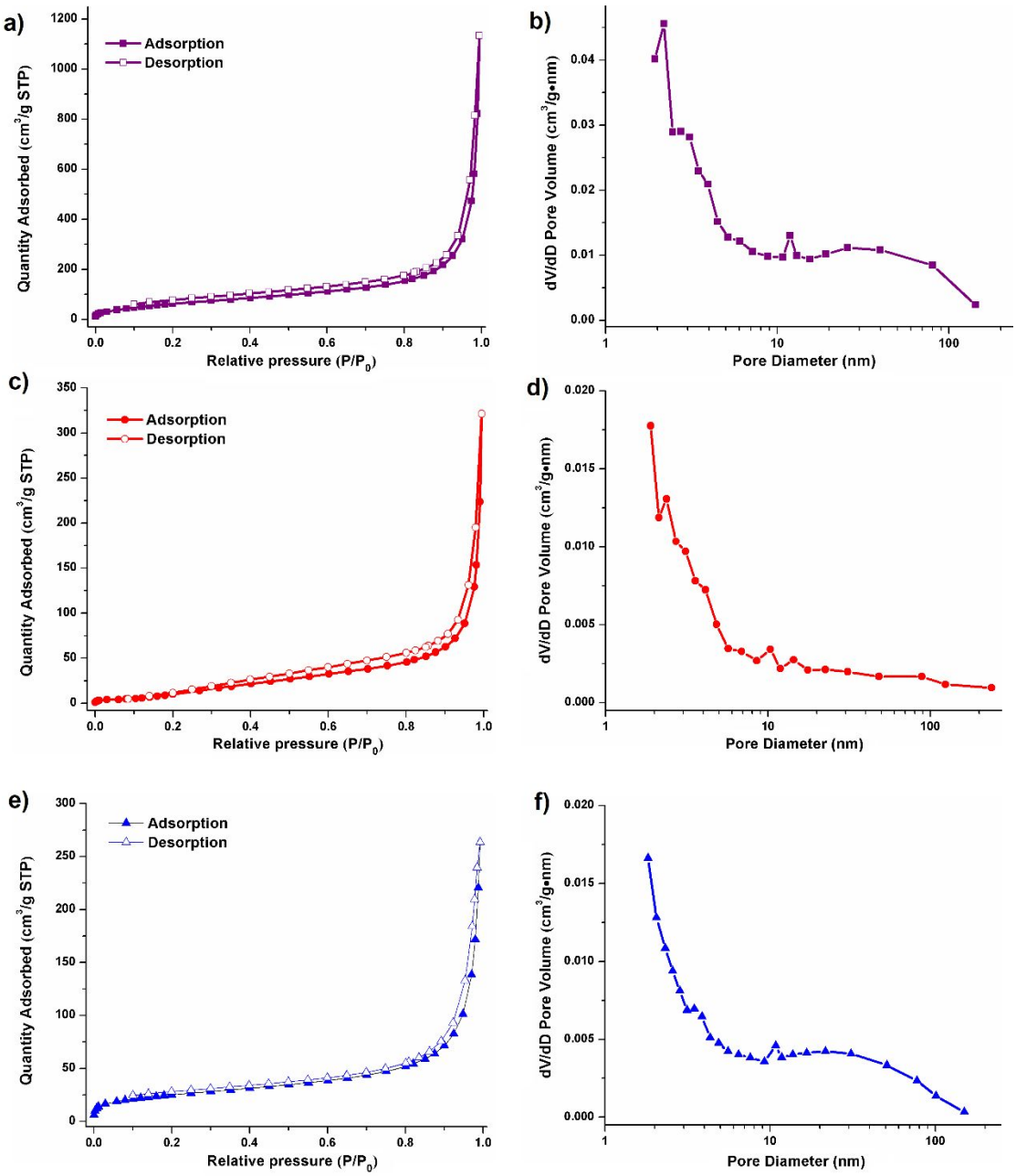


Figure S4. N_2 adsorption-desorption isotherms for (a) Ta-Th-1, (c) Ta-Th-2 and (e) Ta-Th-3, and pore size distributions for (b) Ta-Th-1, (d) Ta-Th-2, and (f) Ta-Th-3.

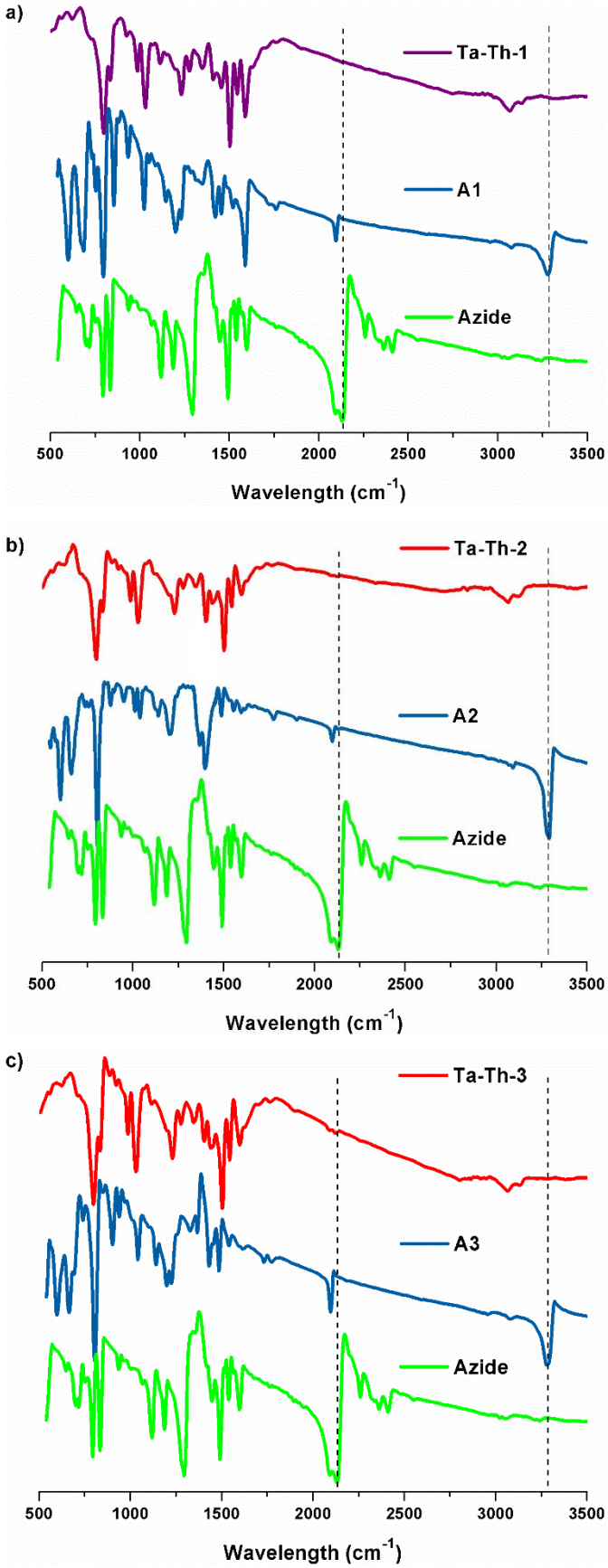

a)
Ta-Th-1
A1
Azide
500
1000
1500
2000
2500
3000
3500
Wavelength (cm-1)
b)
Ta-Th-2
A2
Azide
500
1000
1500
2000
2500
3000
3500
Wavelength (cm-1)
c)
Ta-Th-3
A3
Azide
500
1000
1500
2000
2500
3000
3500
Wavelength (cm-1)

Figure S5. IR spectra for (a) Ta-Th-1, (b) Ta-Th-2, (c) Ta-Th-3 and respective monomers.

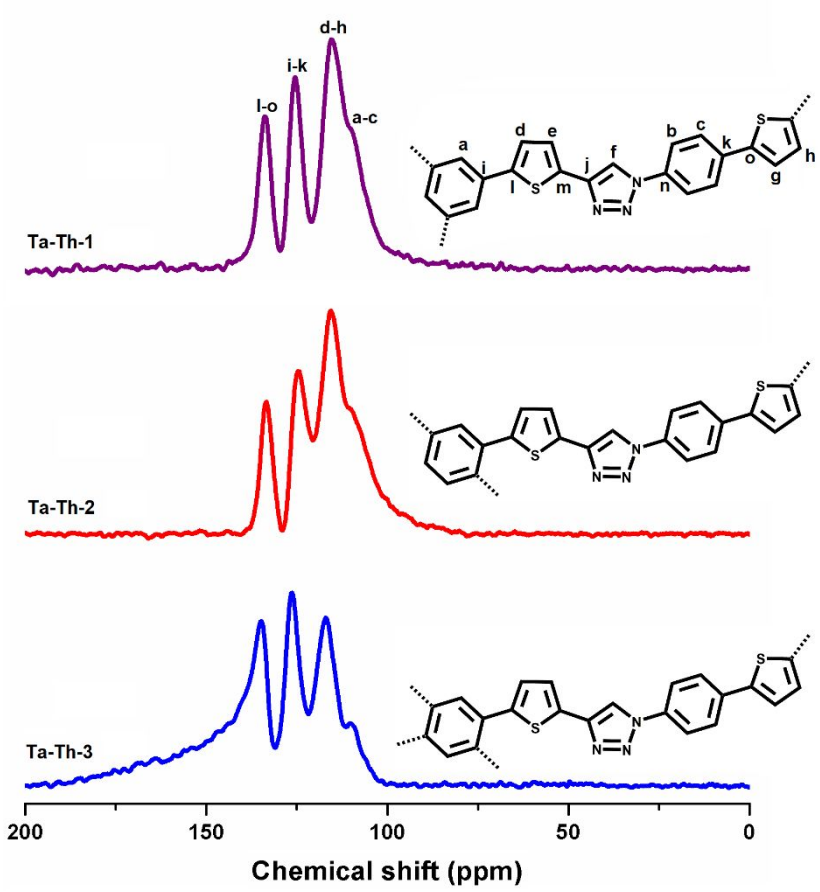


Figure S6. Solid-state ^{13}C NMR CP/MAS spectra.

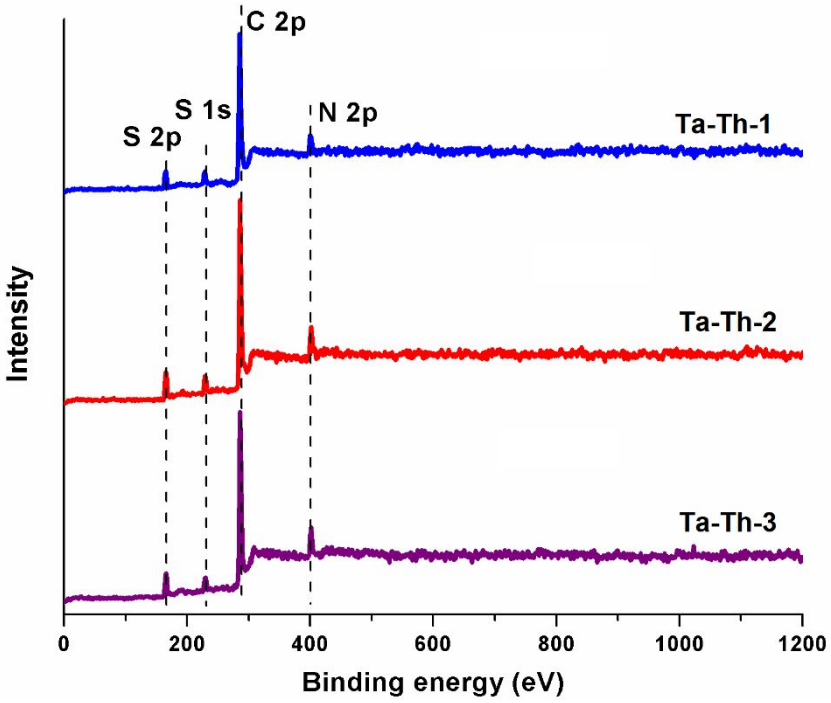


Figure S7. XPS survey spectra.

Table S1. Elemental distribution and peak positions measured by XPS.

Ta-Ths	Name	Peak BE	FWHM eV	Area (P) CPS. eV	Atomic %	Q
Ta-Th-1	N1s	399.00	3.15	8533.52	11.47	1
	S2p	163.23	2.51	5330.39	5.95	1
	C1s	283.86	2.00	38020.76	82.58	1
Ta-Th-2	N1s	398.87	3.15	9768.20	12.78	1
	S2p	163.14	2.40	5740.38	6.25	1
	C1s	283.71	1.79	38273.05	80.97	1
Ta-Th-3	N1s	399.00	3.15	7023.33	10.45	1
	S2p	163.25	2.47	4328.50	5.36	1
	C1s	284.02	2.22	34996.30	84.19	1

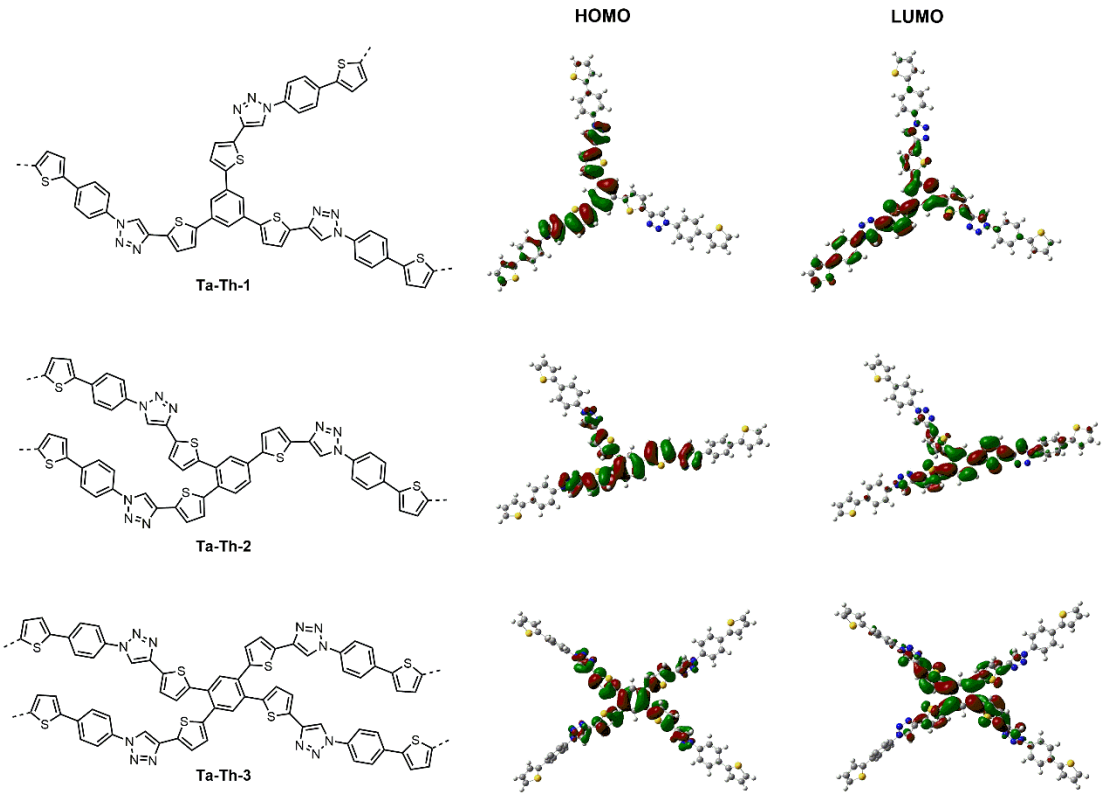


Figure S8. Calculated molecular orbital diagrams of Ta-Ths.

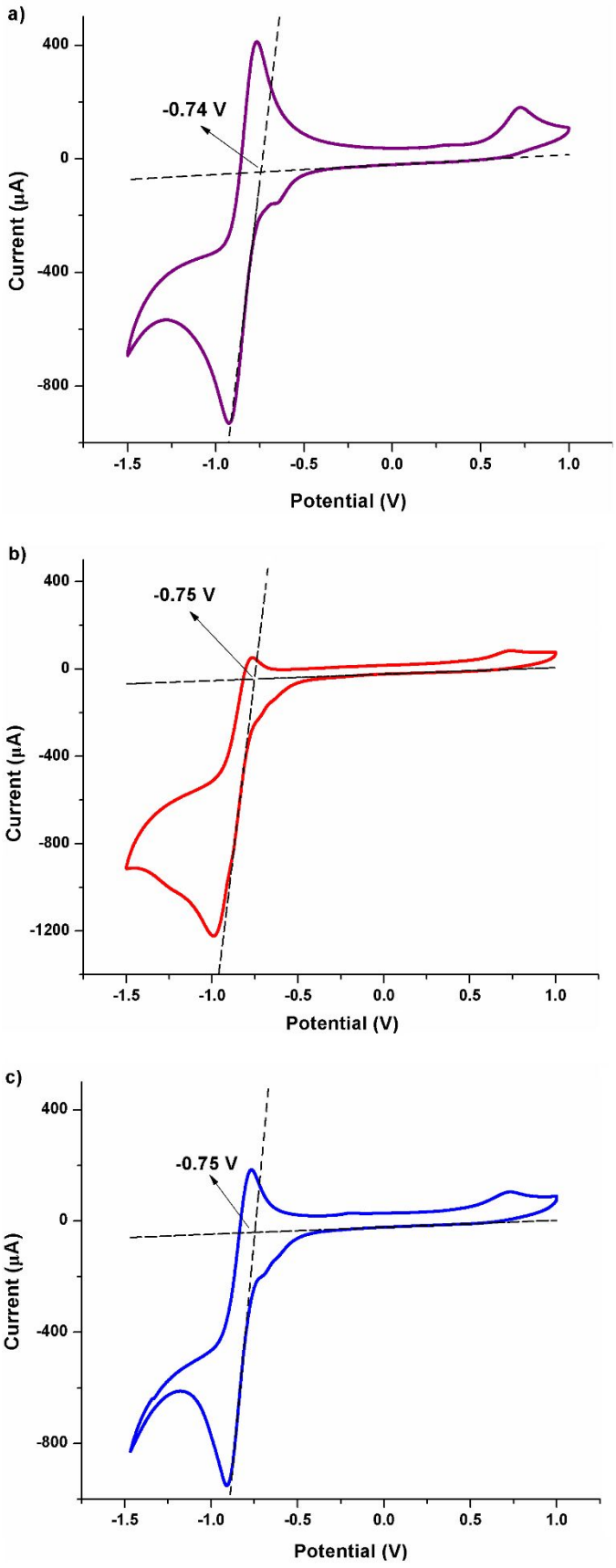


Figure S9. Cyclic voltammograms of (a) Ta-Th-2, (b) Ta-Th-2 and (c) Ta-Th-3.

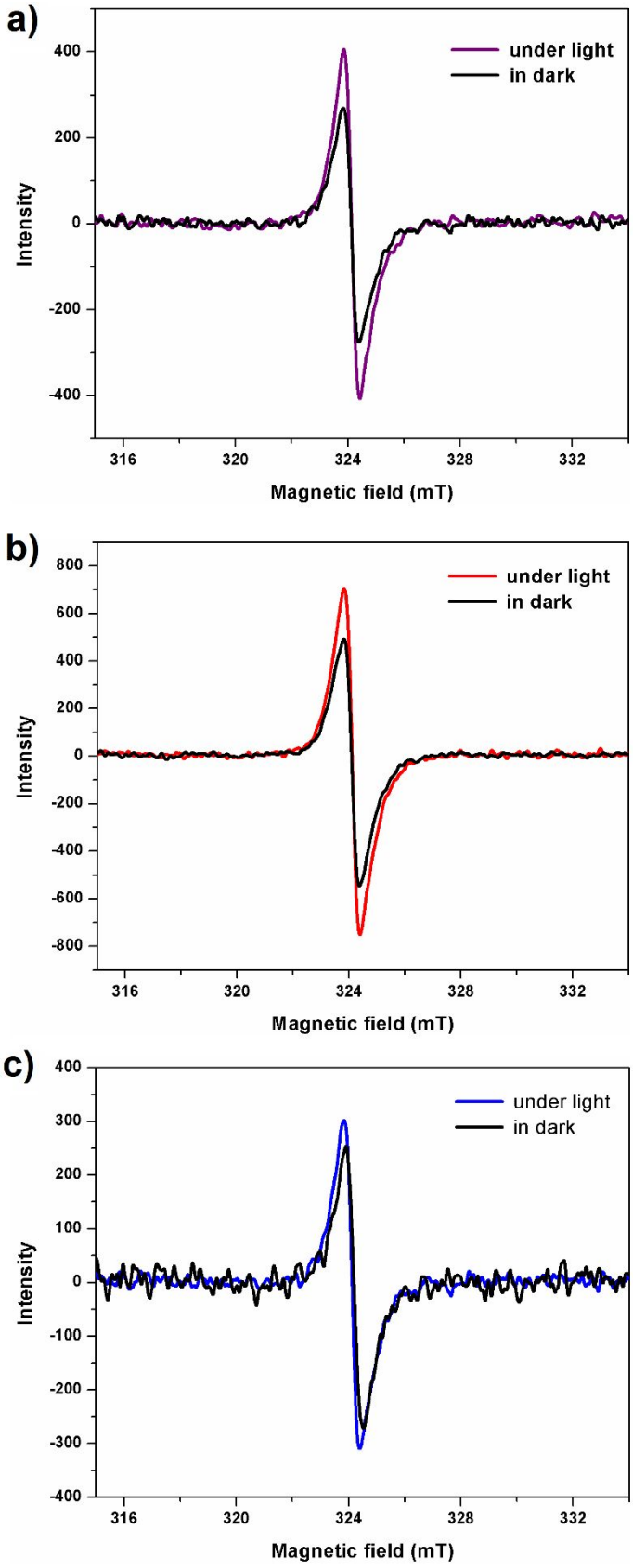


Figure S10. EPR spectra for (a) Ta-Th-1, (b) Ta-Th-2 and (c) Ta-Th-3 taken in darkness and under

light irradiation.

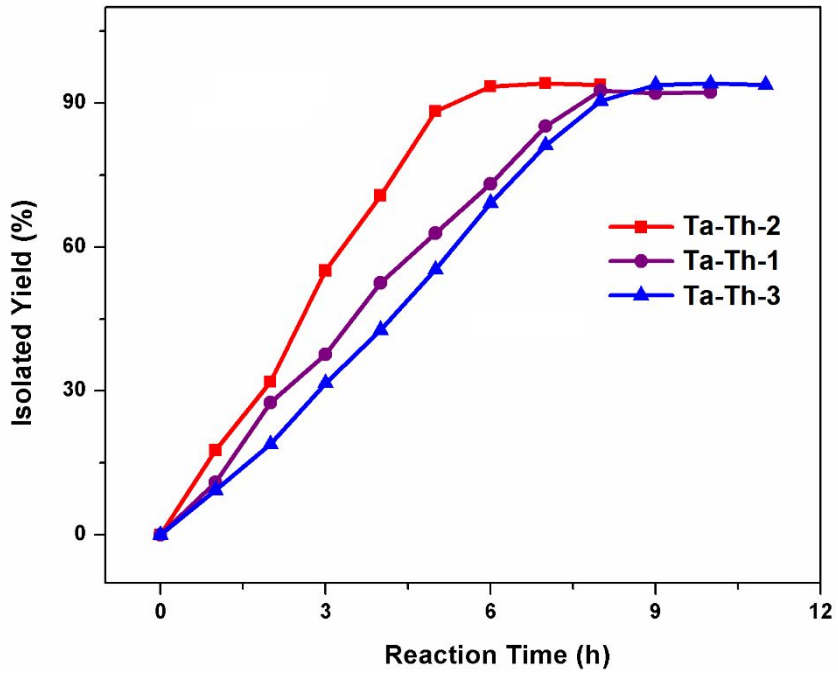


Figure S11. Yields of azobenzene as a function of time in the oxidative dehydrogenation of diphenylhydrazine. Reaction conditions: diphenylhydrazine (0.2 mmol), Ta-Th (5.0 mg), CH_3CN (2.0 mL), RT, air, 18 W white LED.

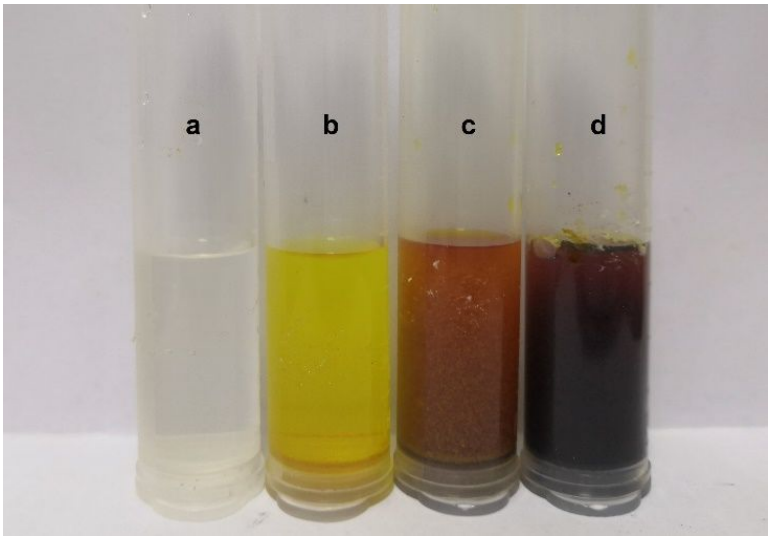


Figure S12. Photographs of (a) a solution containing starch (10 mg), KI (0.05 M) and CH_3COOH (0.05 M). (b) a solution of KI (0.05 M), CH_3COOH (0.05 M), diphenylhydrazine (0.2 mmol) with Ta-Th-2 after irradiation for 1 h in an open air atmosphere. (b) a solution of starch (10 mg), KI (0.05 M), CH_3COOH (0.05 M), diphenylhydrazine (0.2 mmol) with Ta-Th-2 after irradiation for 1 h in an open air atmosphere. (d) a solution of starch (10 mg), KI (0.05 M), CH_3COOH (0.05 M) and H_2O_2 (30%, 30 μL). The solvent used herein was 4 mL CH_3CN/H_2O (1:1), H_2O was added to make KI soluble in the solution. For (b) and (c), the solutions of starch/KI/CH_3COOH were added to the reaction mixture after 1 h irradiation.

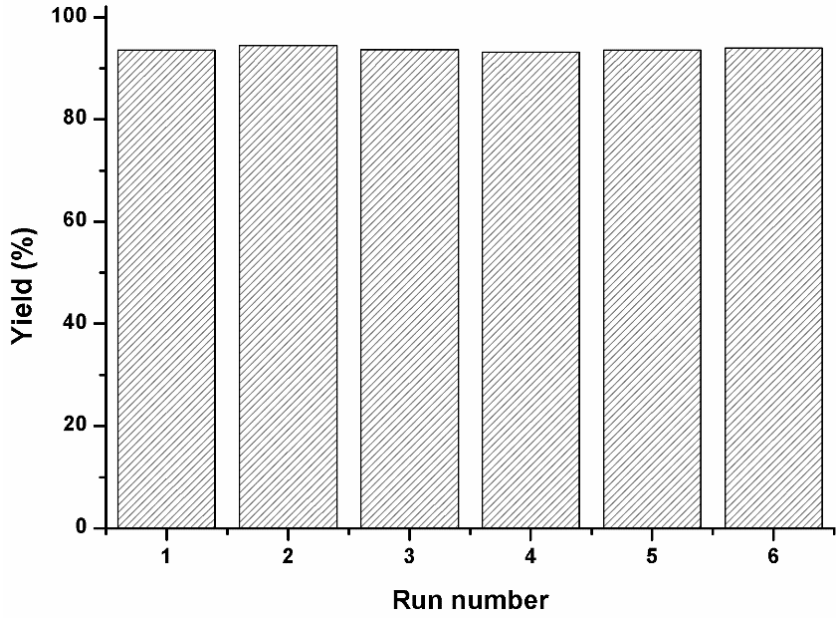


Figure S13. Recycling of Ta-Th-2 for the dehydrogenation of diphenylhydrazine.

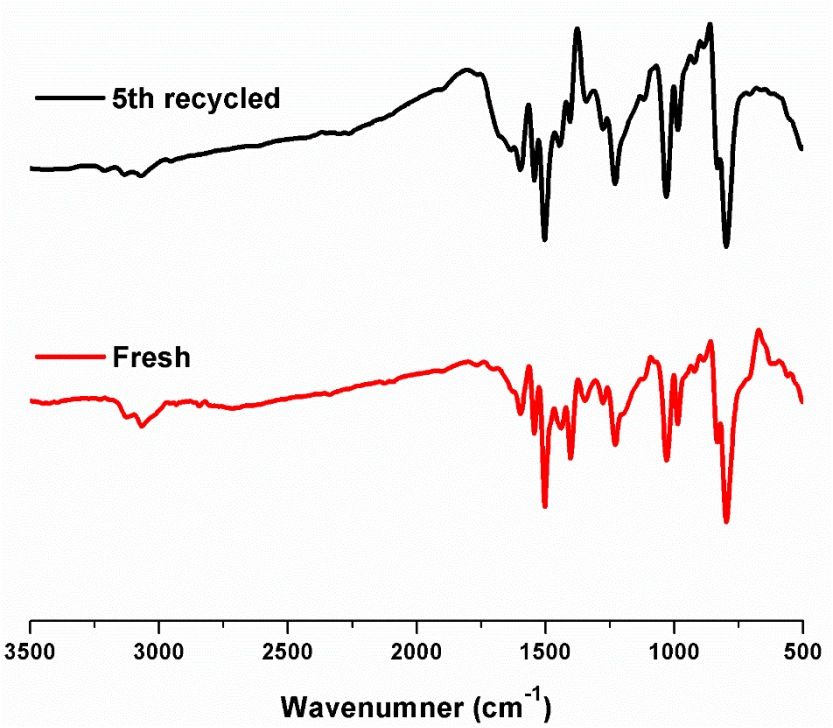


Figure S14. FT-IR spectra for fresh and recycled Ta-Th-2.

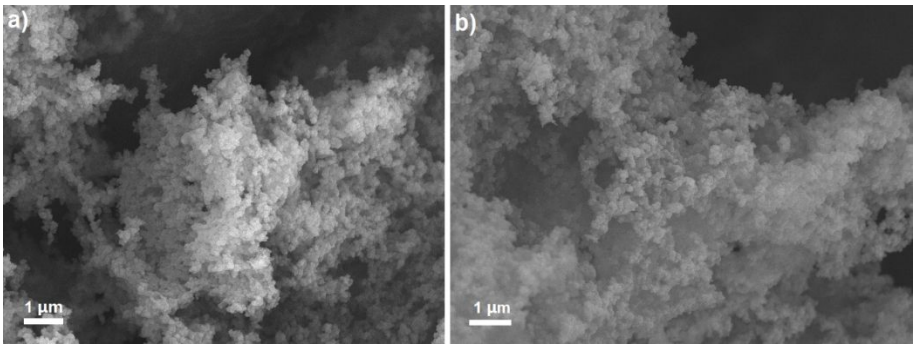


Figure S15. SEM images for (a) fresh and (b) 5th recycled Ta-Th-2.

^{1}H NMR and ^{13}C NMR spectra for building blocks

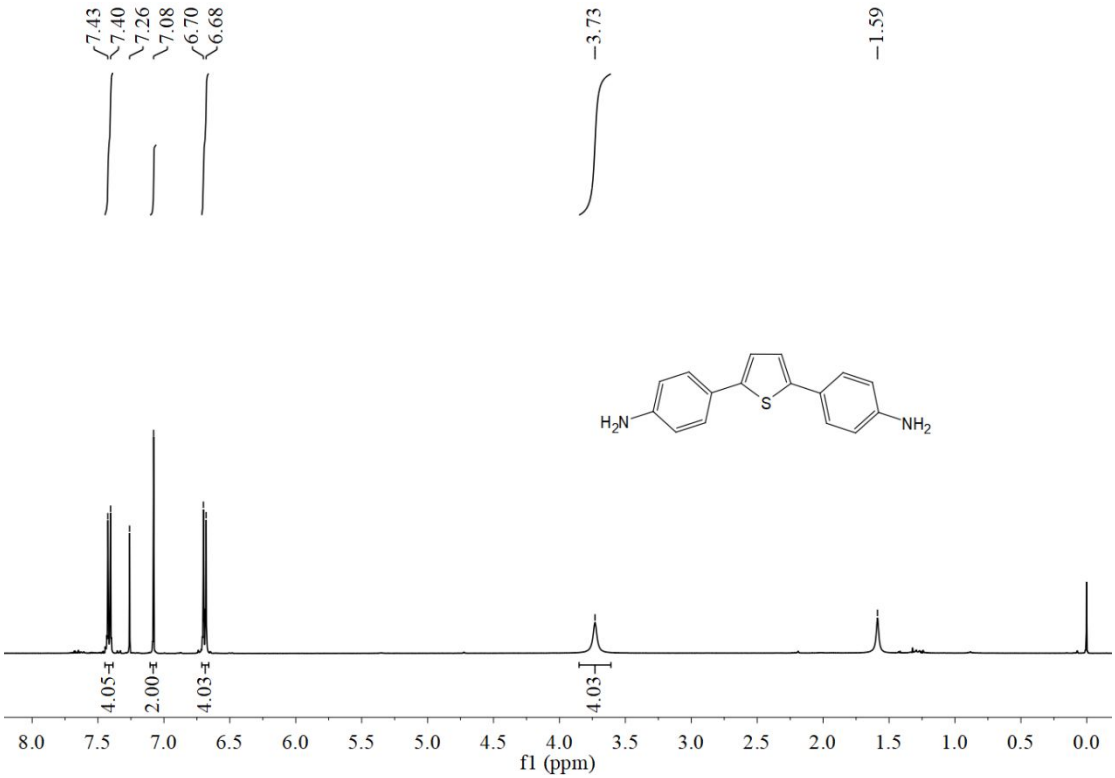


Figure S16. ^{1}H NMR spectrum ($CDCl_3$) of **Az-1**

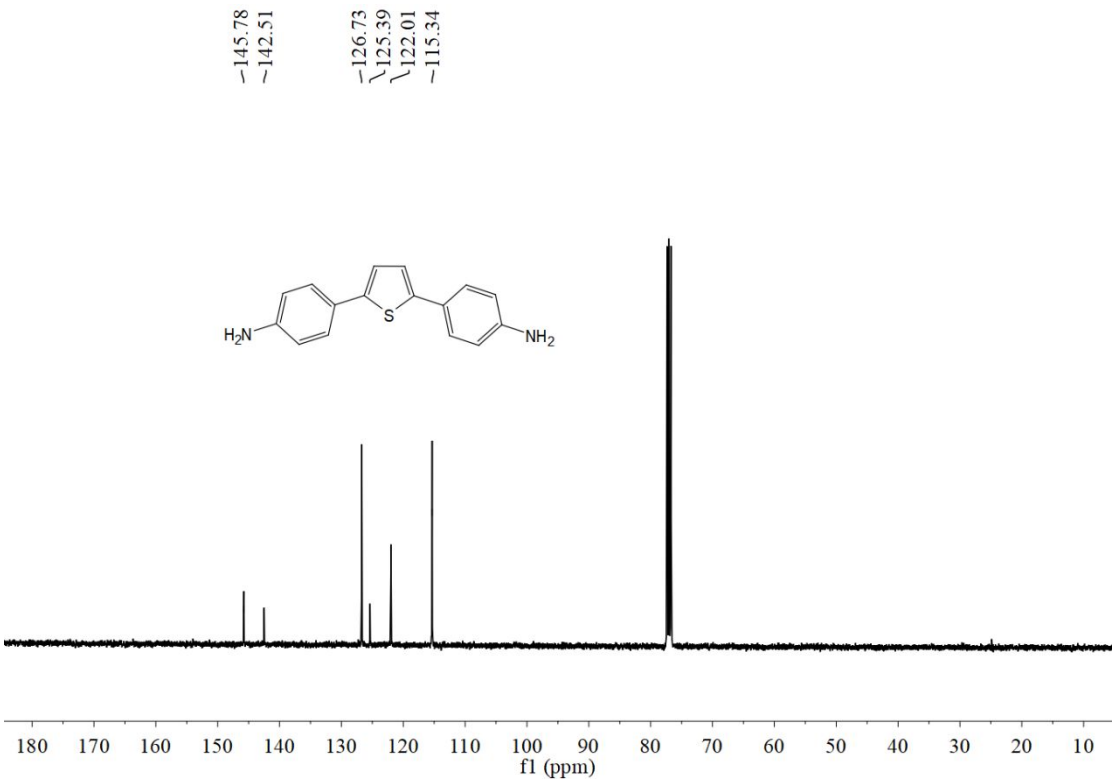


Figure S17. ^{13}C NMR spectrum ($CDCl_3$) of **Az-1**

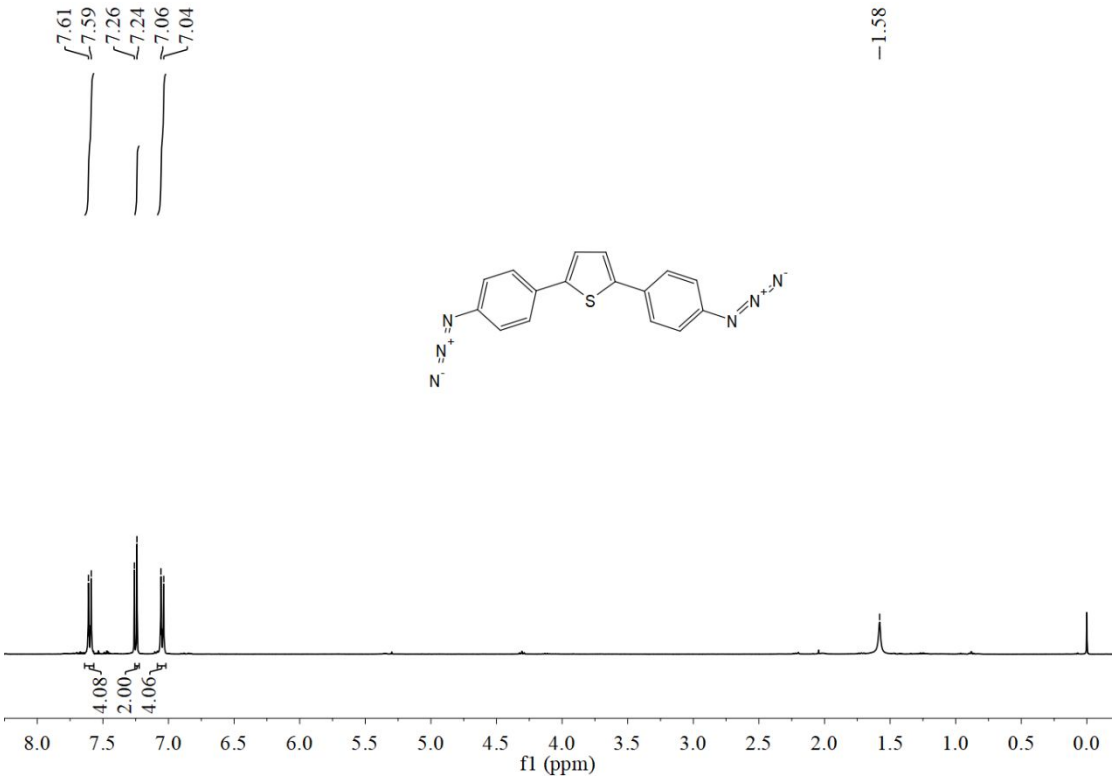


Figure S18. ^{1}H NMR spectrum ($CDCl_3$) of **Az**

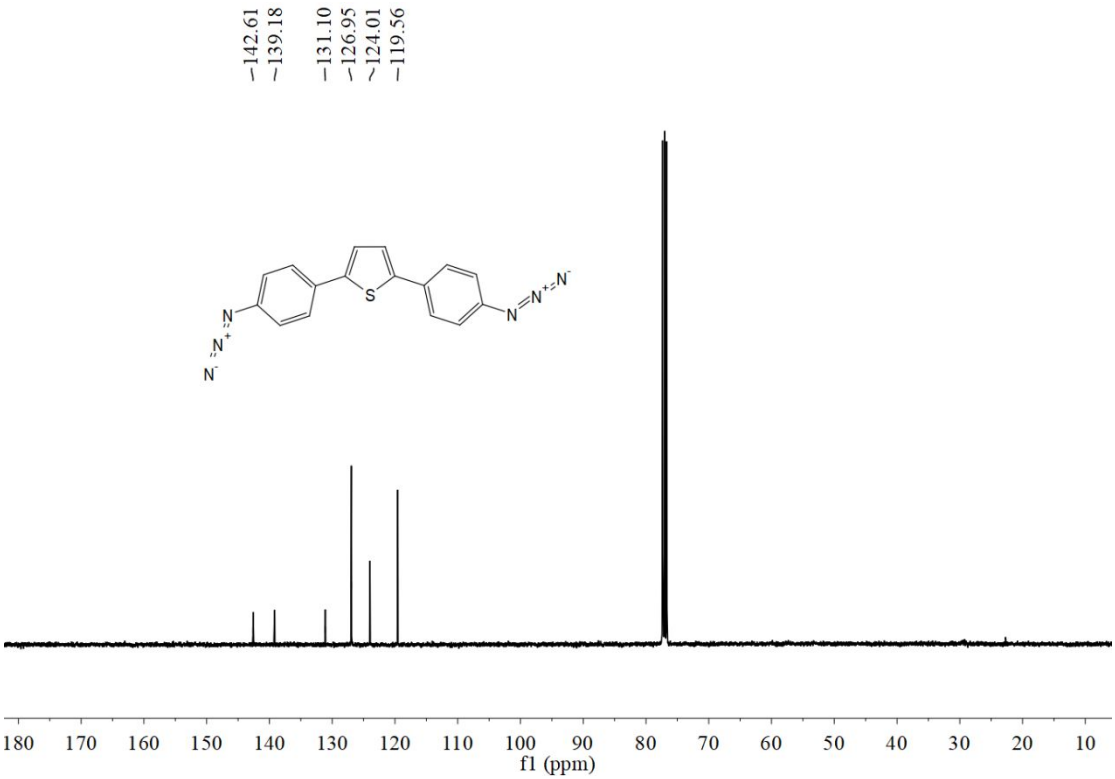


Figure S19. ^{13}C NMR spectrum ($CDCl_3$) of **Az**

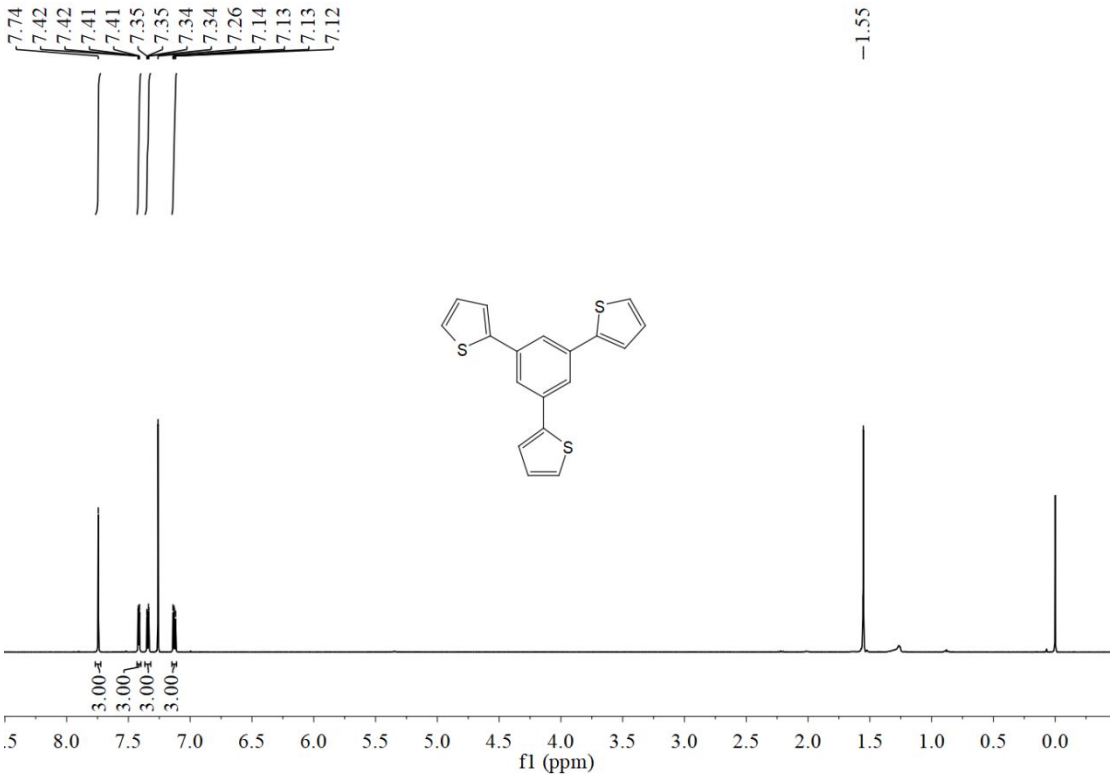


Figure S20. ^{1}H NMR spectrum ($CDCl_3$) of **A1-1**

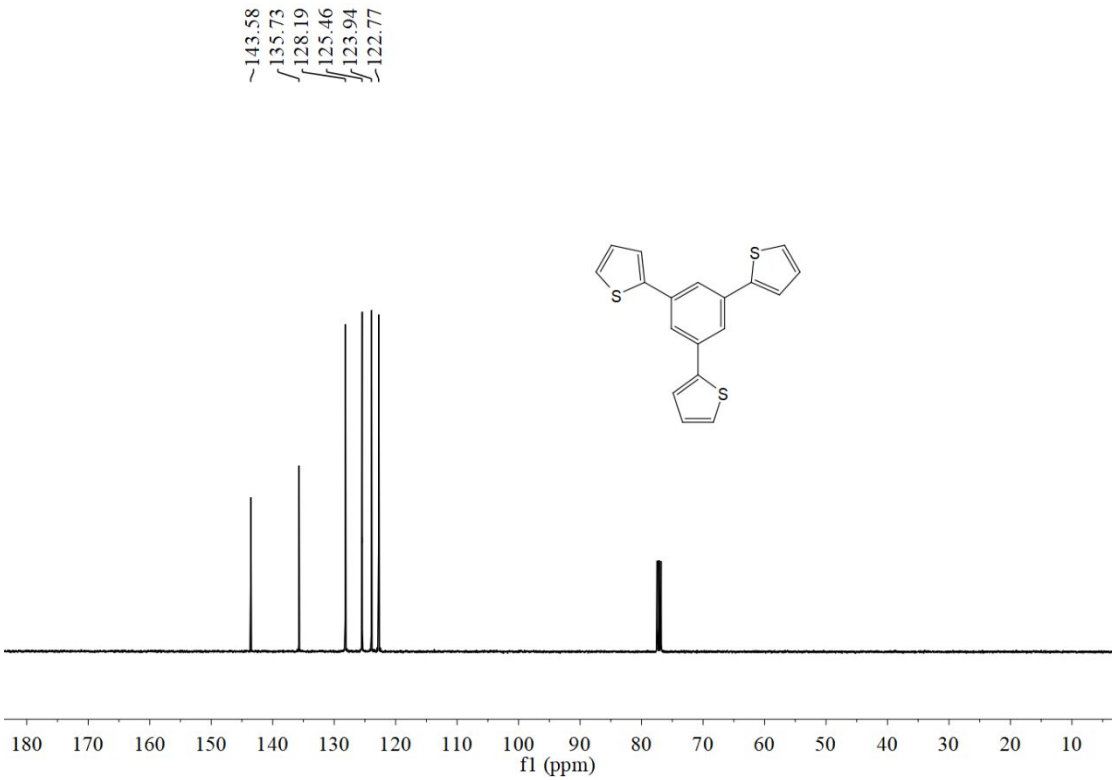


Figure S21. ^{13}C NMR spectrum ($CDCl_3$) of **A1-1**

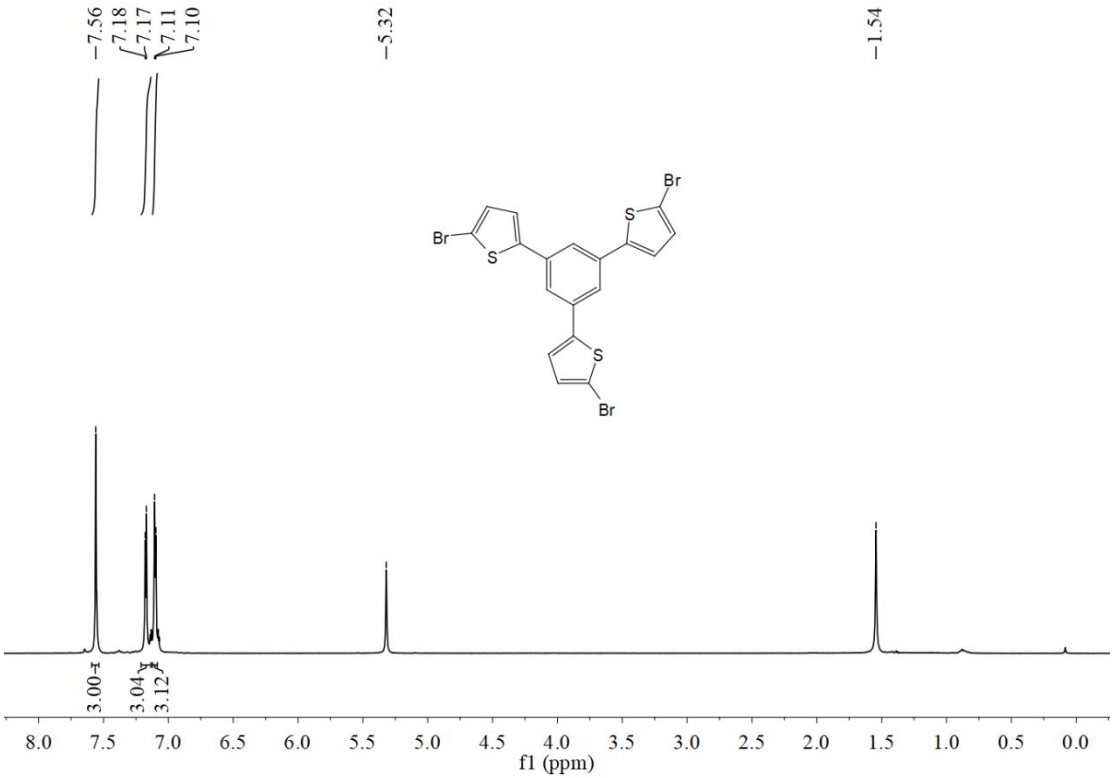


Figure S22. ^{1}H NMR spectrum (CD_2Cl_2) of **A1-2**

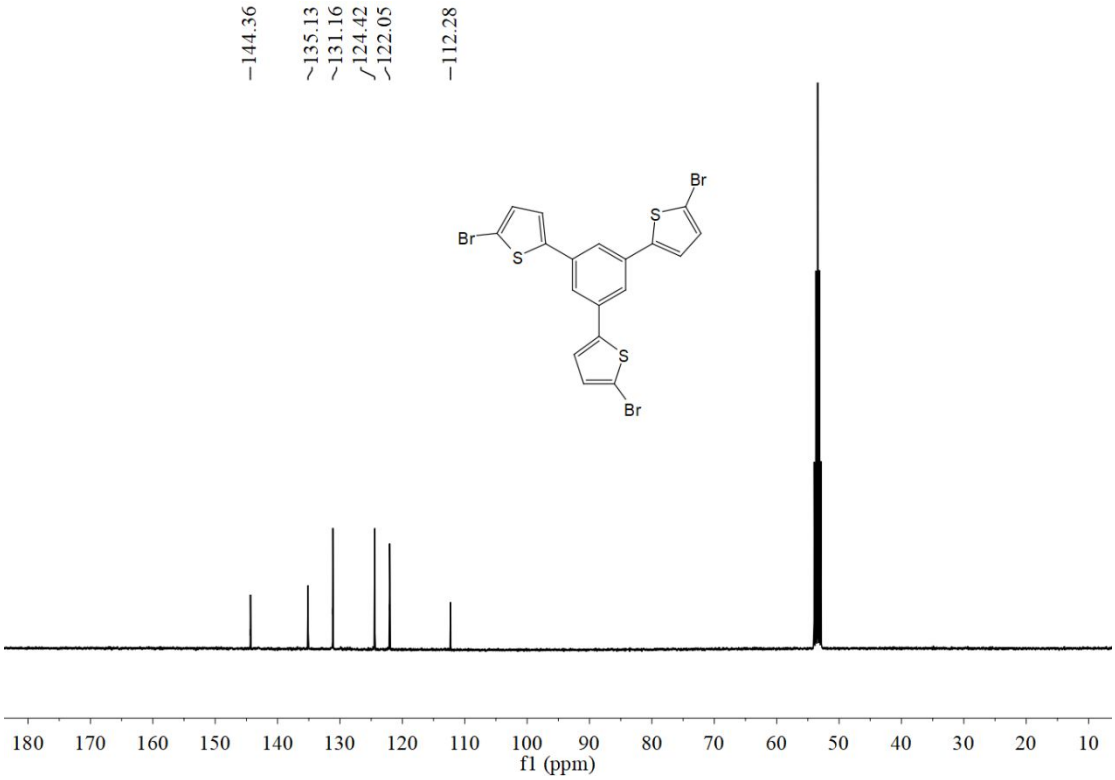


Figure S23. ^{13}C NMR spectrum (CD_2Cl_2) of **A1-2**

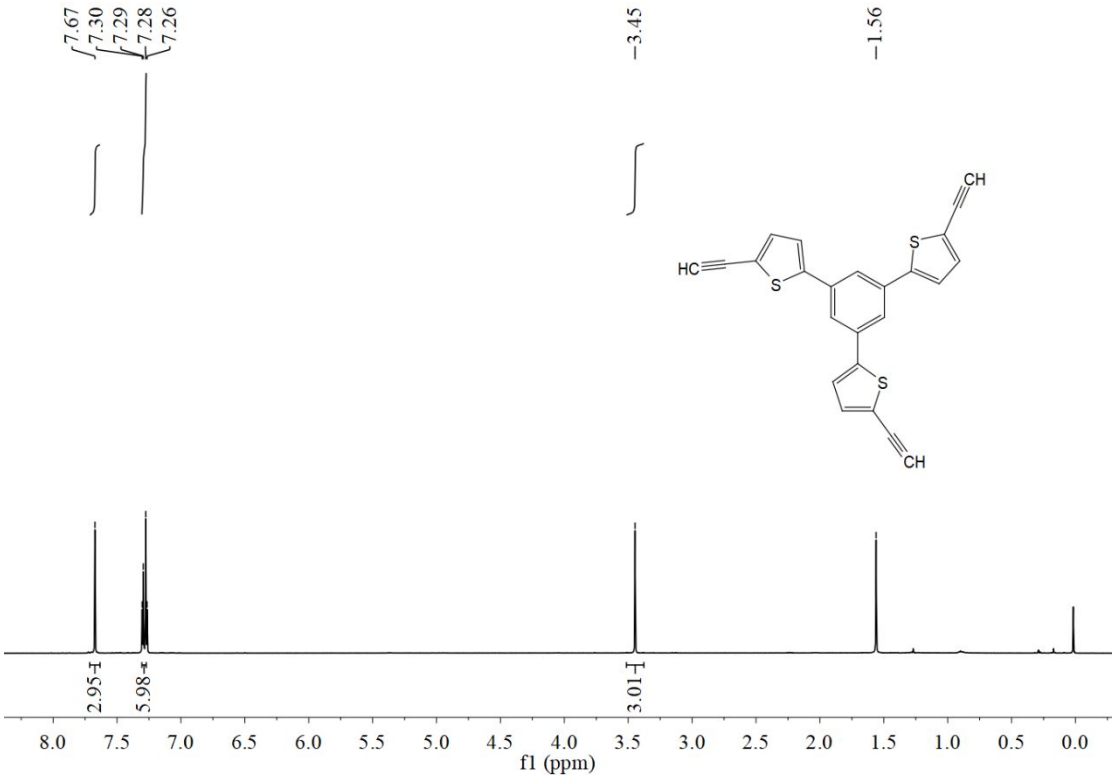


Figure S24. ^{1}H NMR spectrum ($CDCl_3$) of **A1**

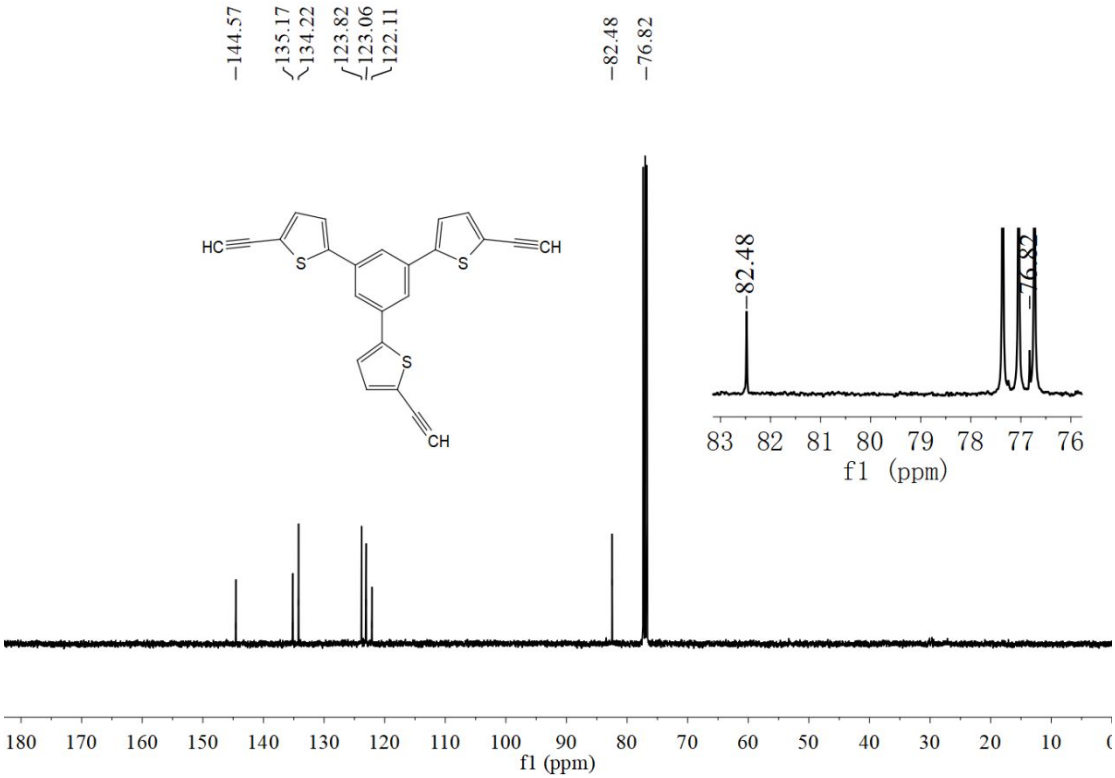


Figure S25. ^{13}C NMR spectrum ($CDCl_3$) of **A1**

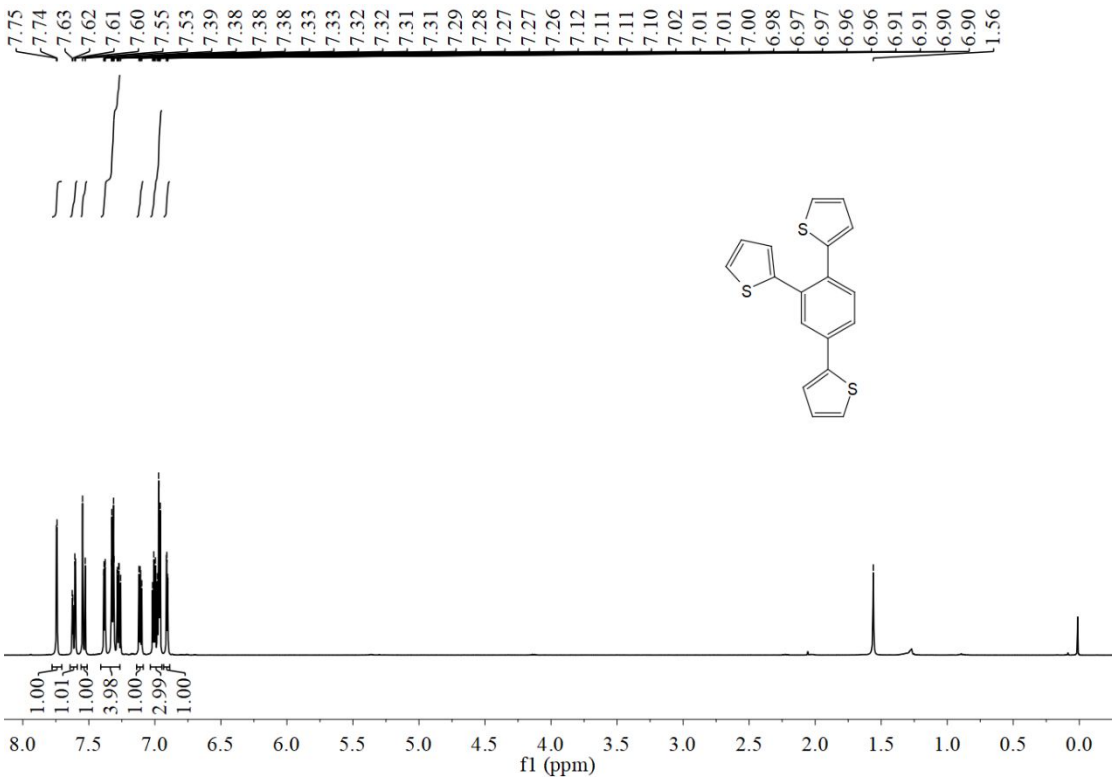


Figure S26. ^{1}H NMR spectrum ($CDCl_3$) of **A2-1**

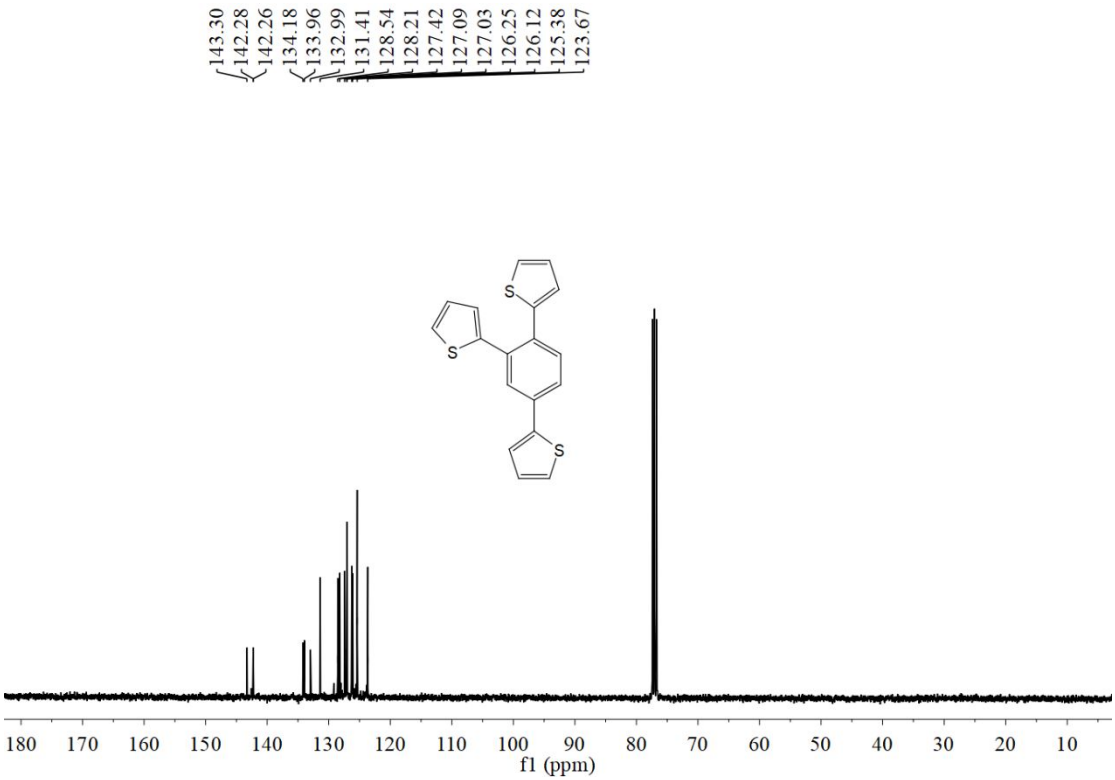


Figure S27. ^{13}C NMR spectrum ($CDCl_3$) of **A2-1**

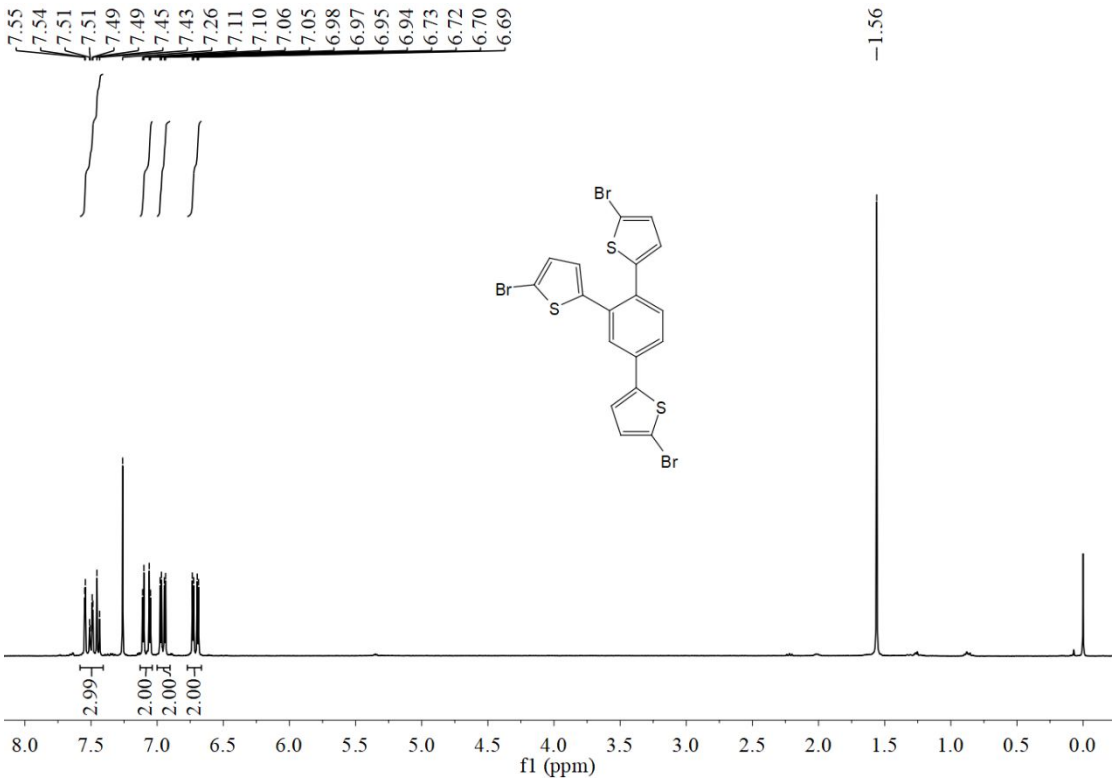


Figure S28. ^{1}H NMR spectrum ($CDCl_3$) of **A2-2**

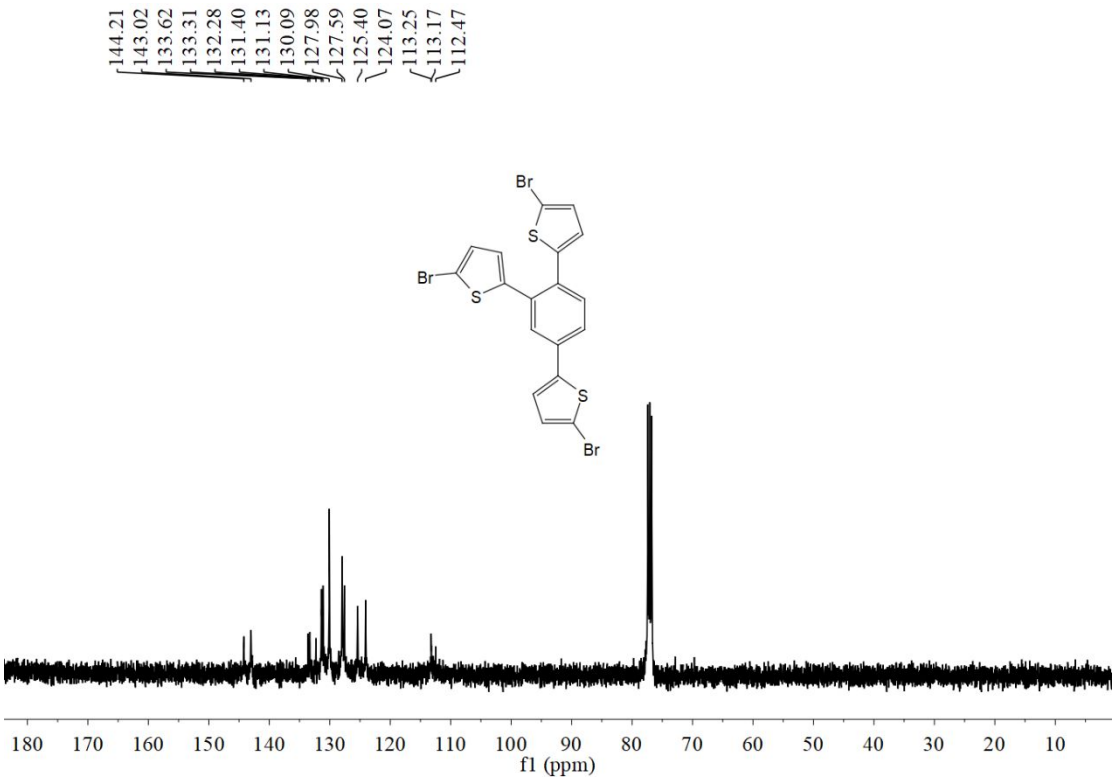


Figure S29. ^{13}C NMR spectrum ($CDCl_3$) of **A2-2**

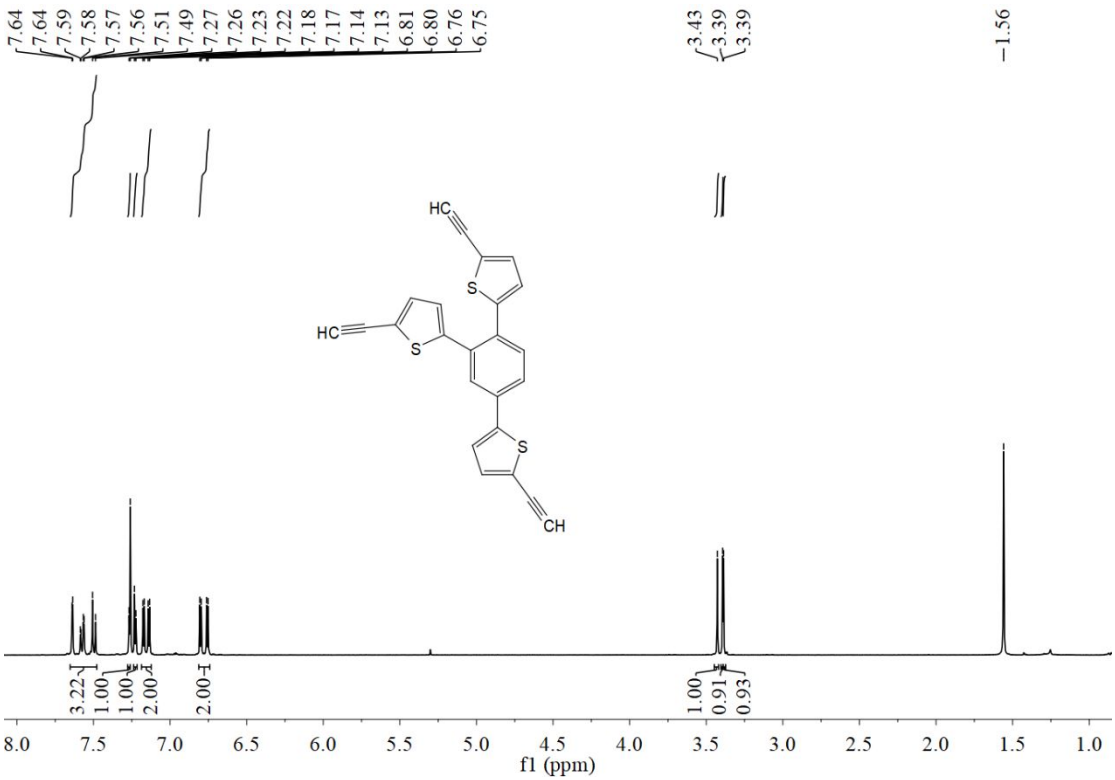


Figure S30. ^{1}H NMR spectrum ($CDCl_3$) of **A2**

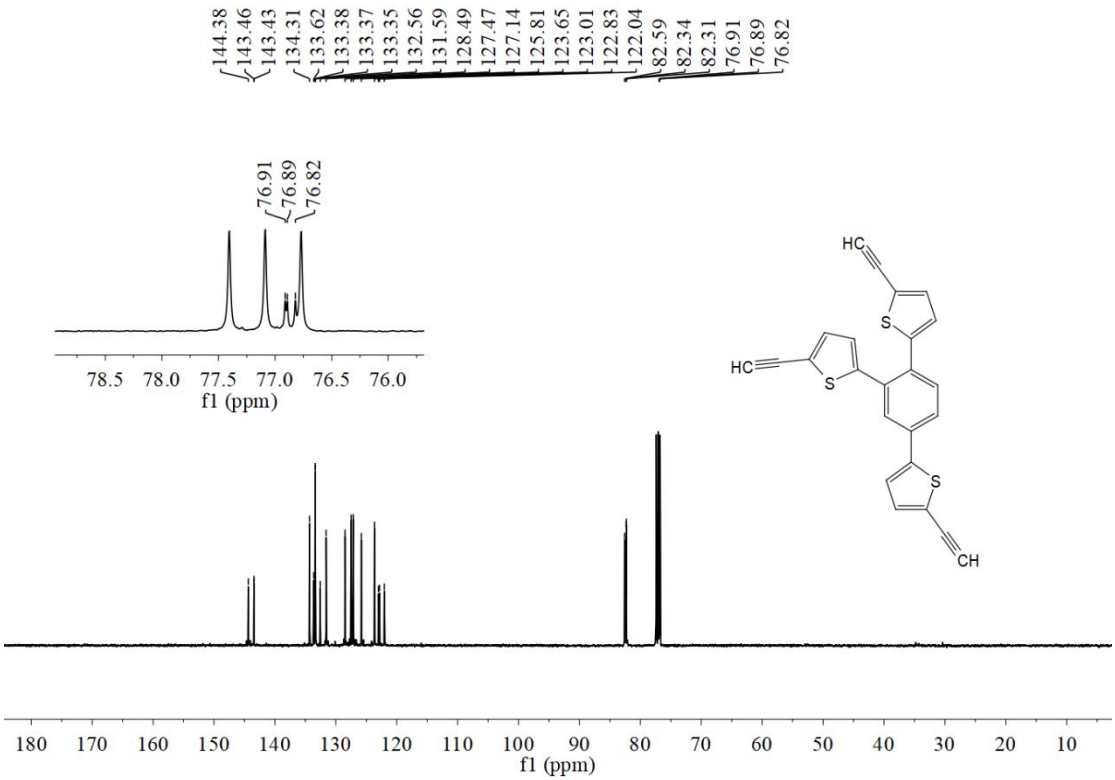


Figure S31. ^{13}C NMR spectrum ($CDCl_3$) of **A2**

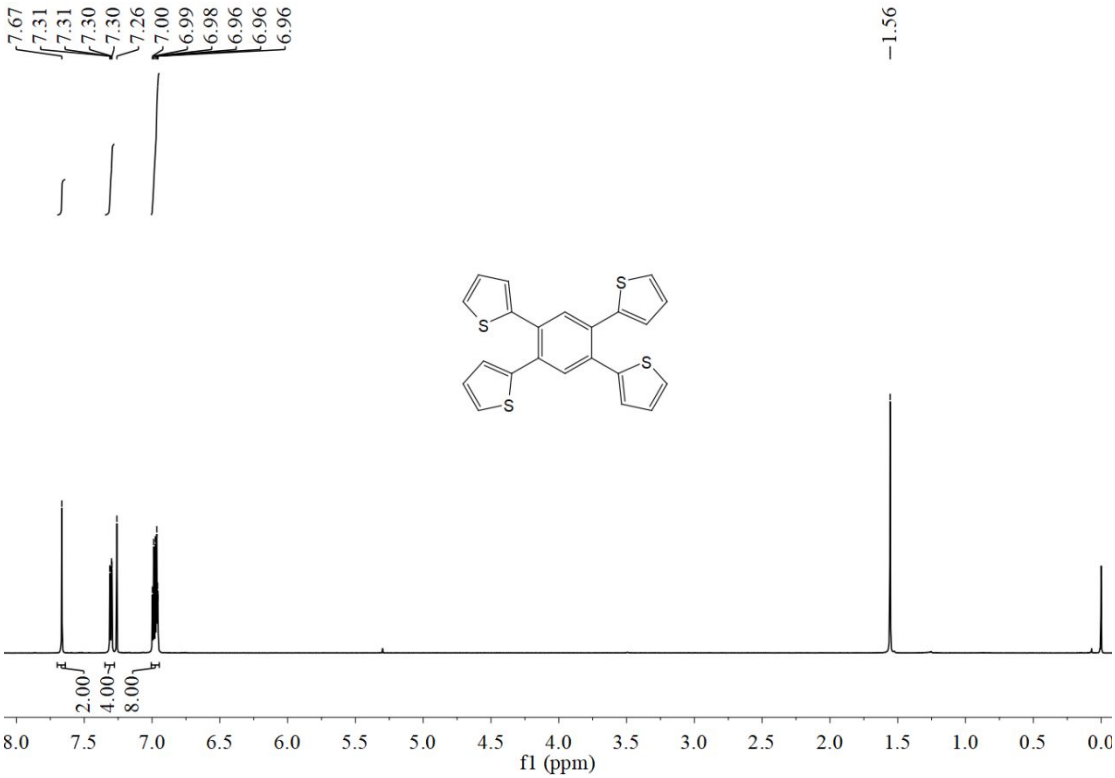


Figure S32. ^{1}H NMR spectrum ($CDCl_3$) of **A3-1**

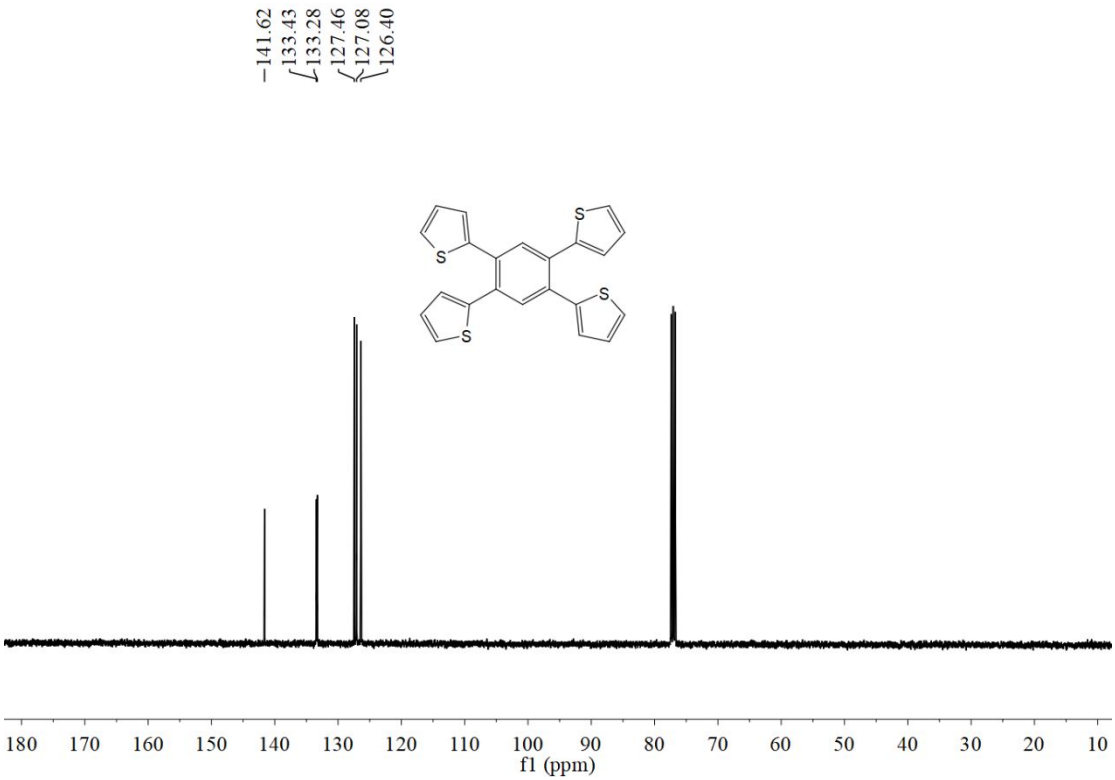


Figure S33. ^{13}C NMR spectrum ($CDCl_3$) of **A3-1**

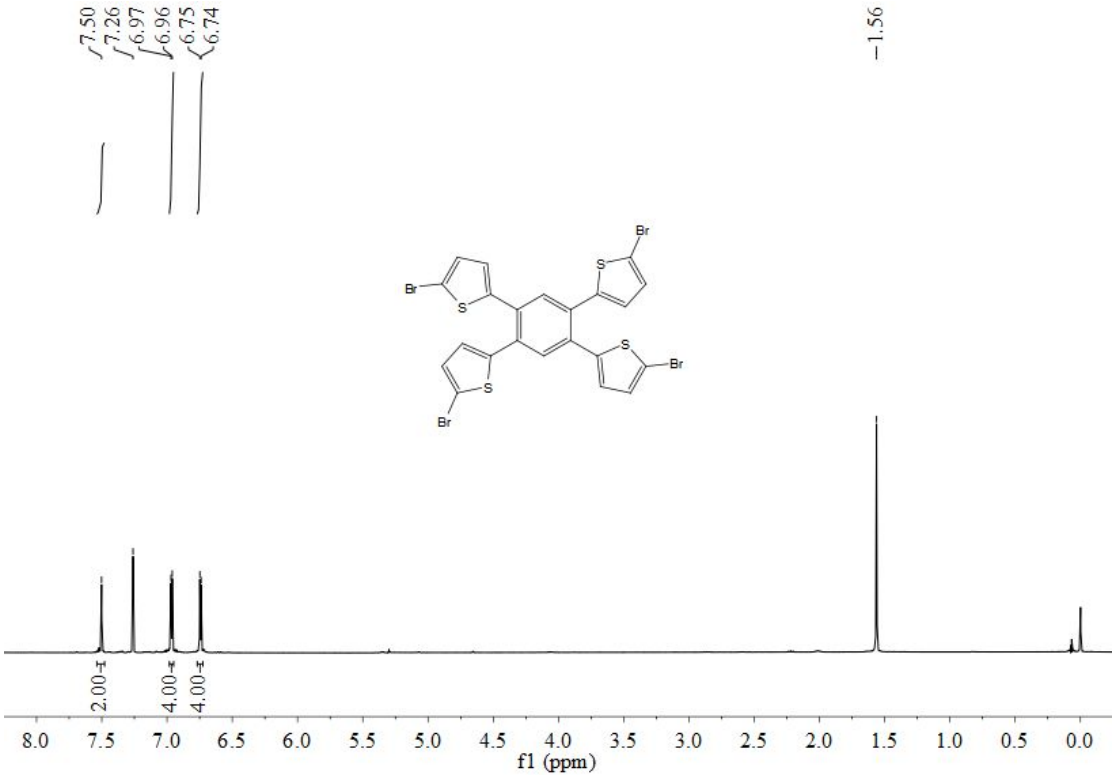


Figure S34. ^{1}H NMR spectrum ($CDCl_3$) of **A3-2**

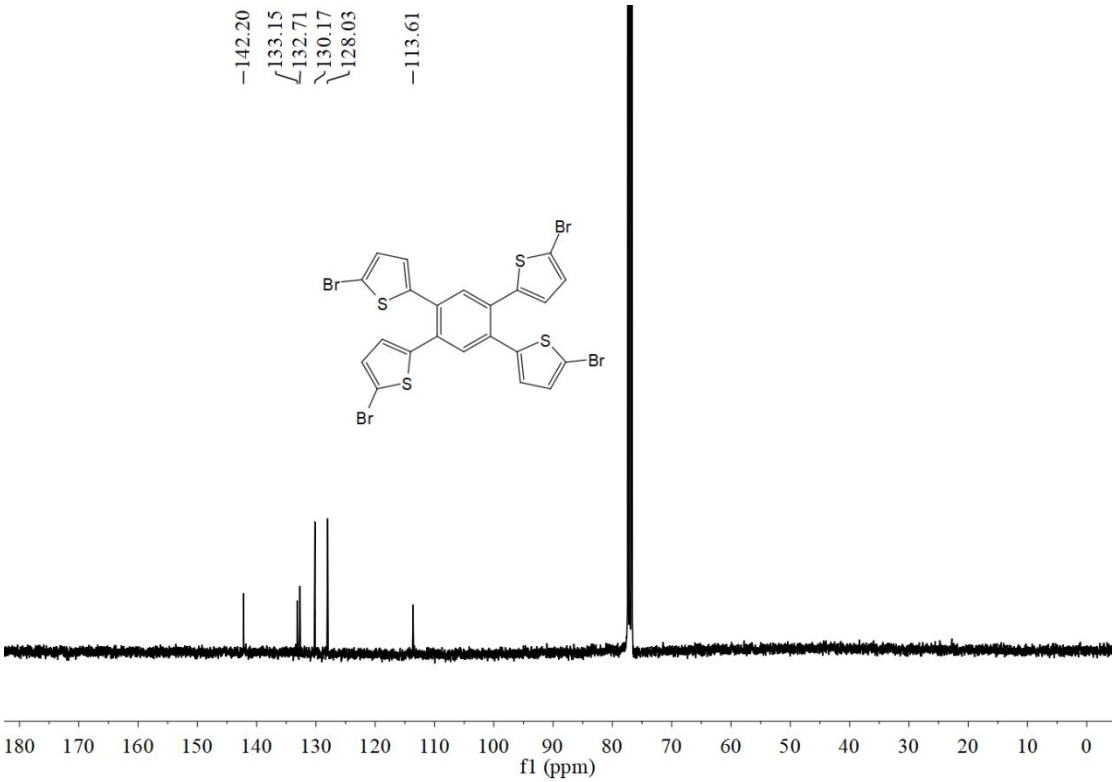


Figure S35. ^{13}C NMR spectrum ($CDCl_3$) of **A3-2**

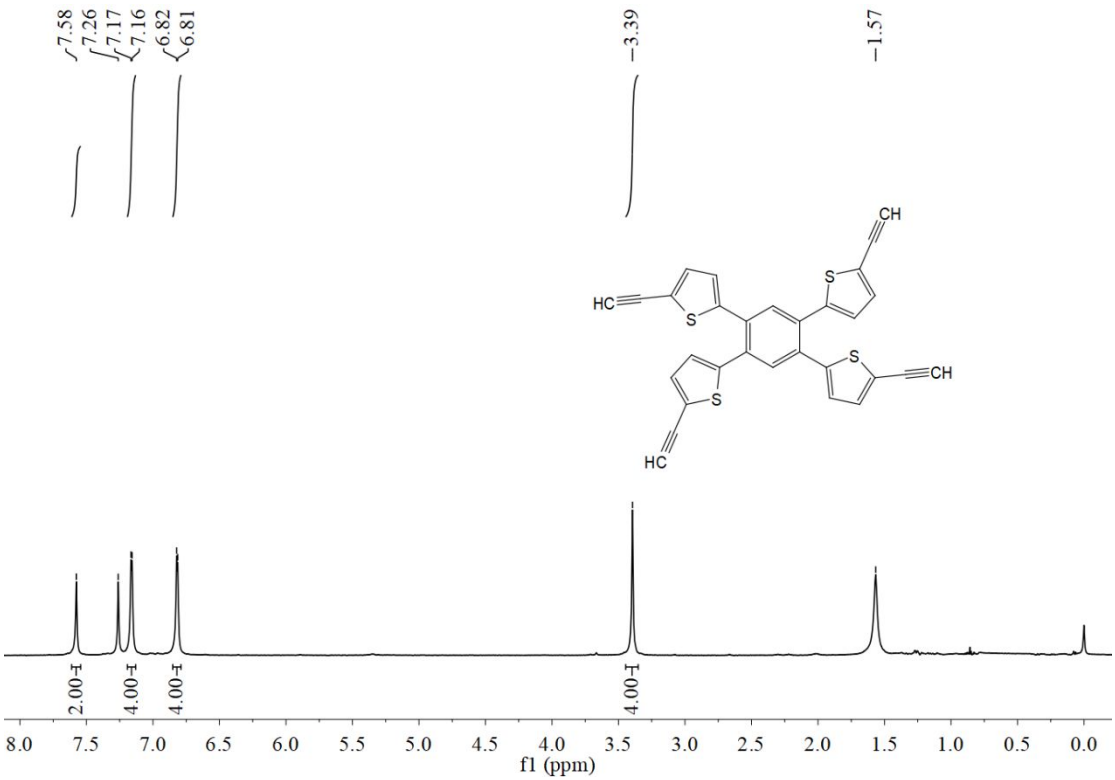


Figure S36. ^{1}H NMR spectrum ($CDCl_3$) of **A3**

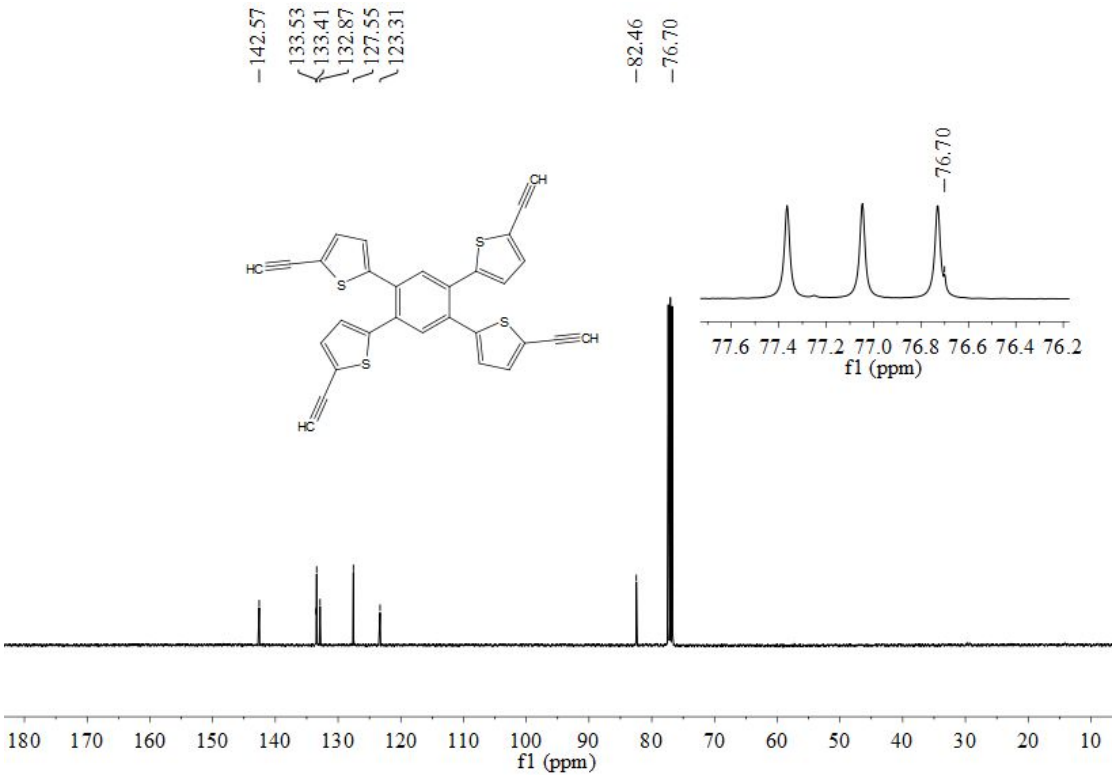


Figure S37. ^{13}C NMR spectrum ($CDCl_3$) of **A3**

[1]H NMR spectra for hydrazo aromatics

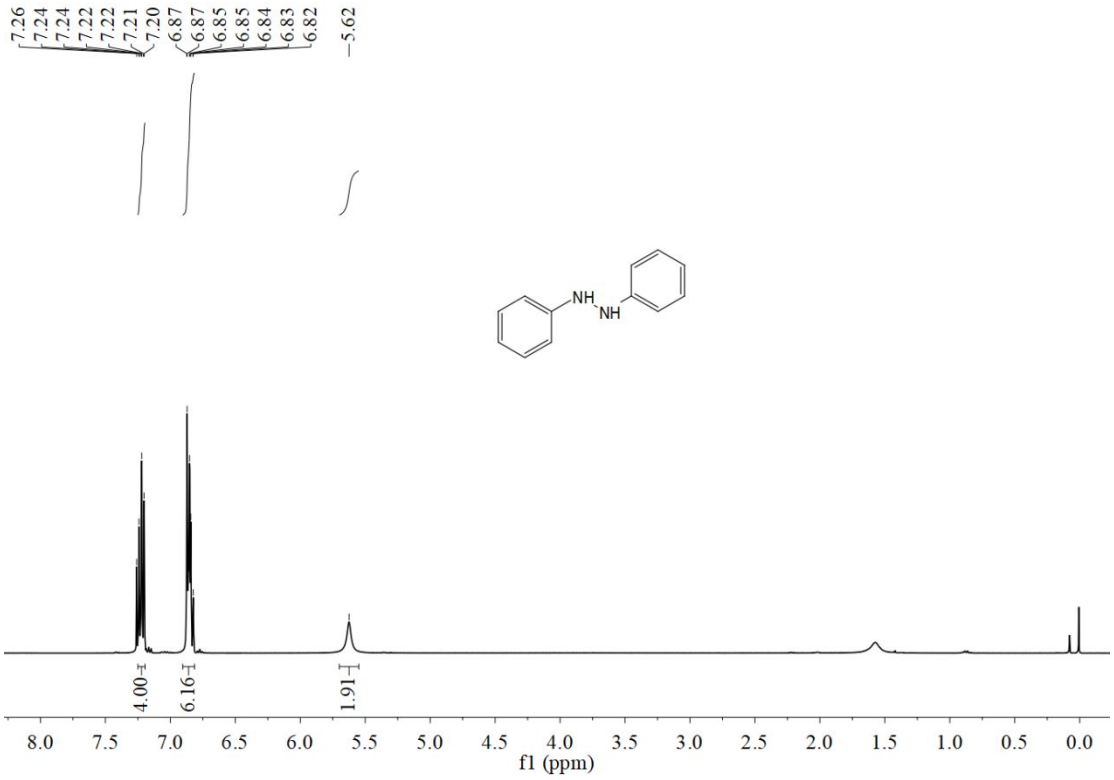


Figure S38. [1]H NMR spectrum ($CDCl_3$) of **1a**

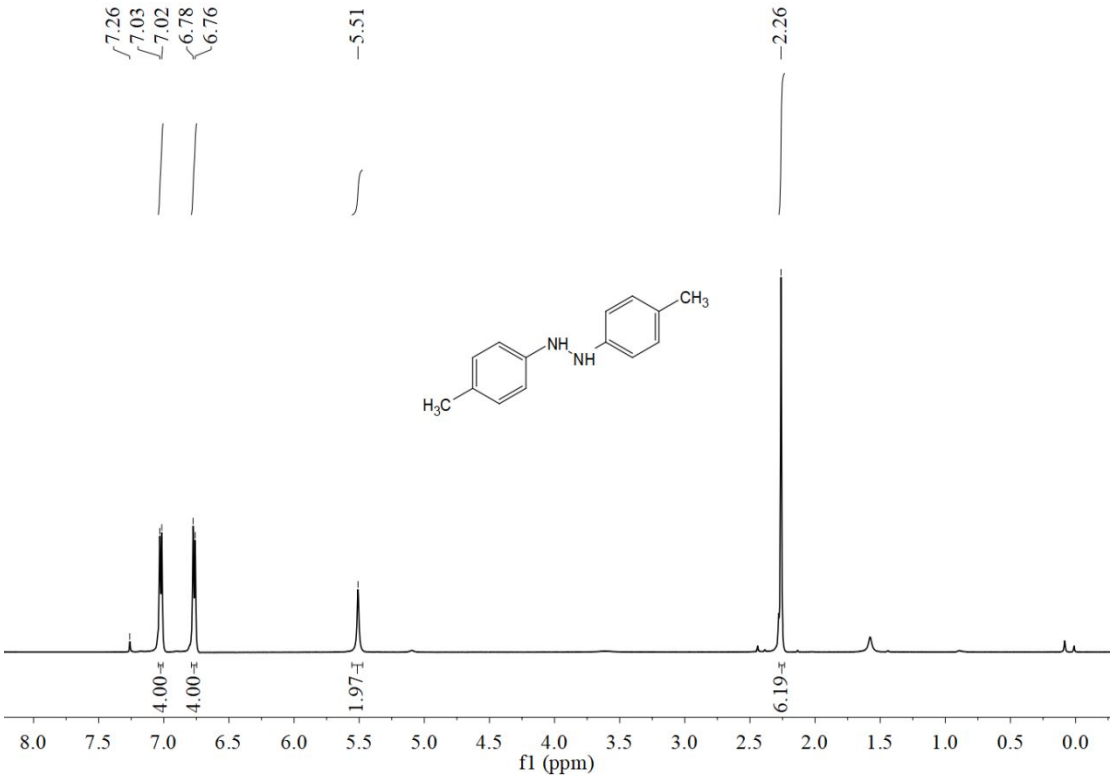


Figure S39. [1]H NMR spectrum ($CDCl_3$) of **1b**

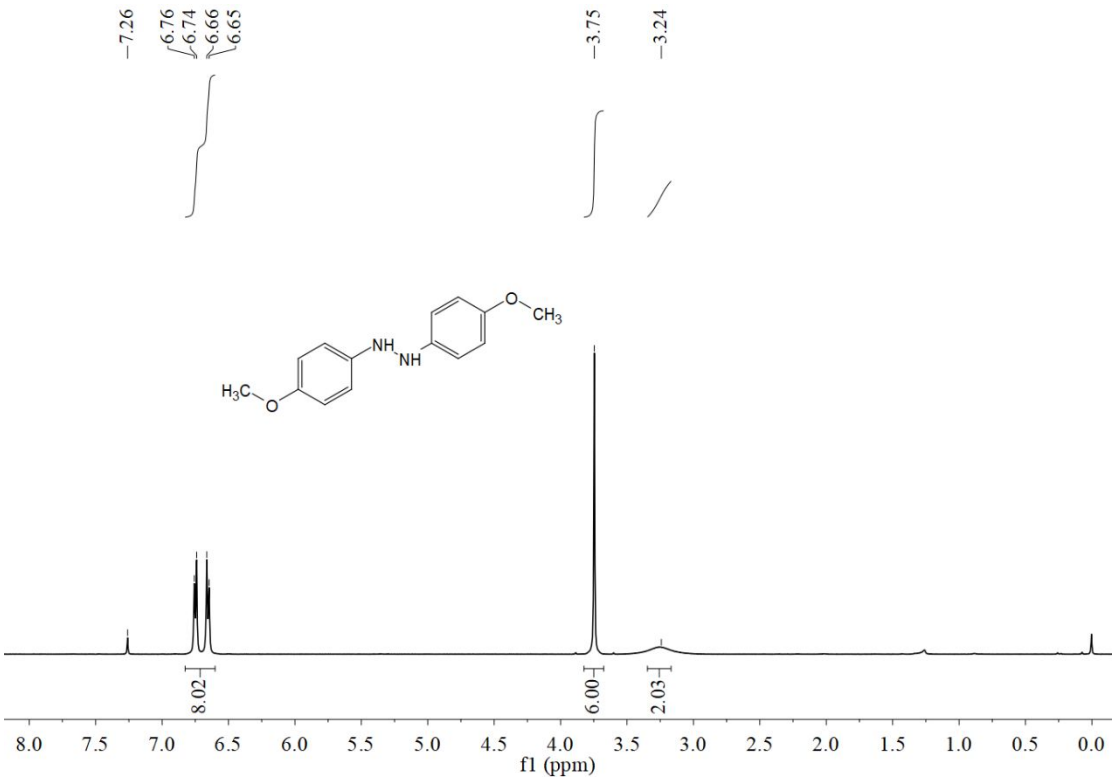


Figure S40. ^{1}H NMR spectrum ($CDCl_3$) of **1c**

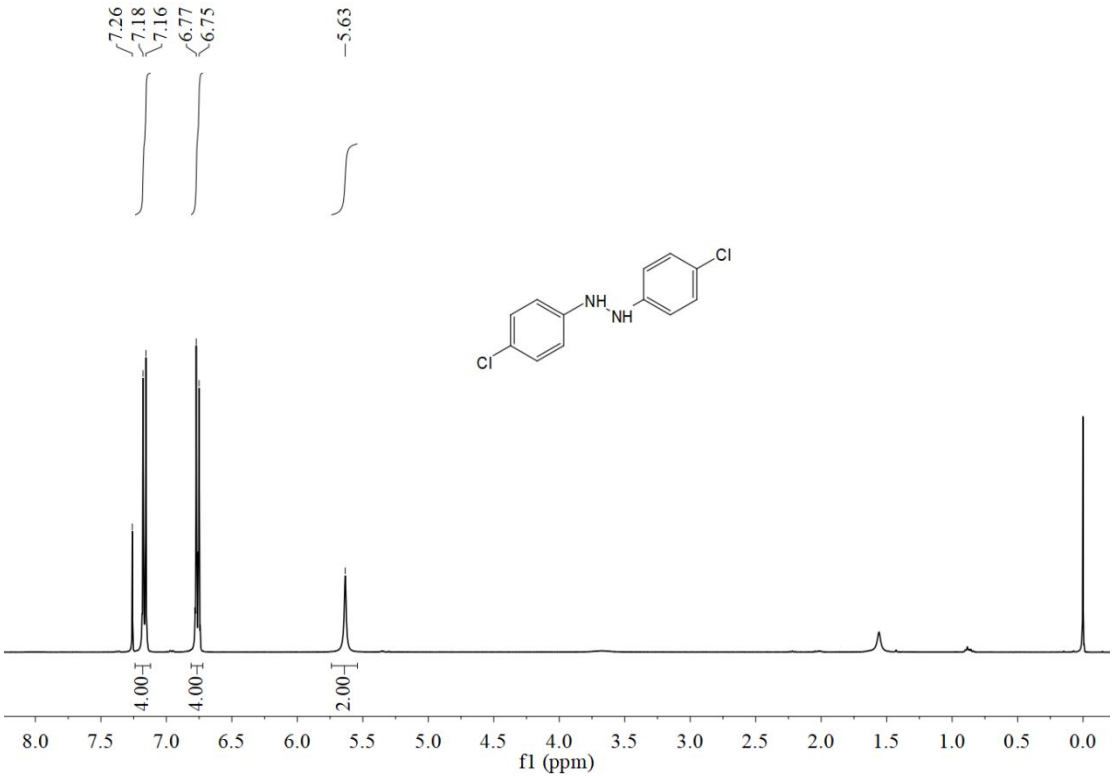


Figure S41. ^{1}H NMR spectrum ($CDCl_3$) of **1d**

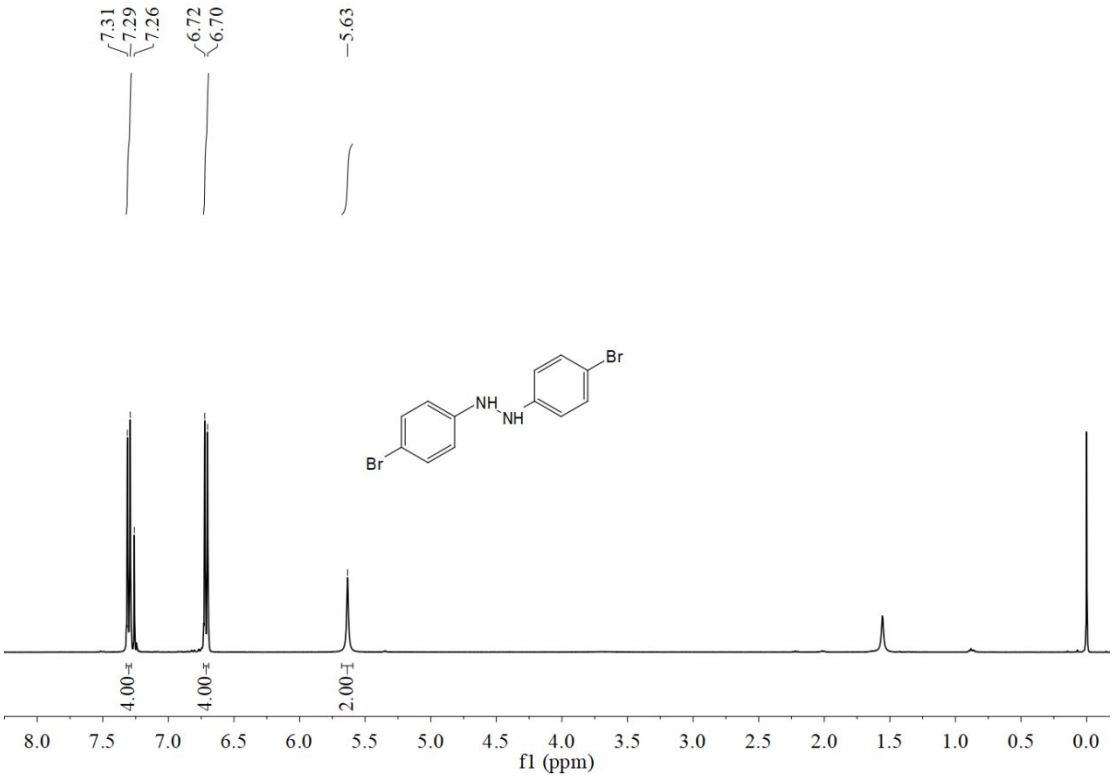


Figure S42. ^{1}H NMR spectrum ($CDCl_3$) of **1e**

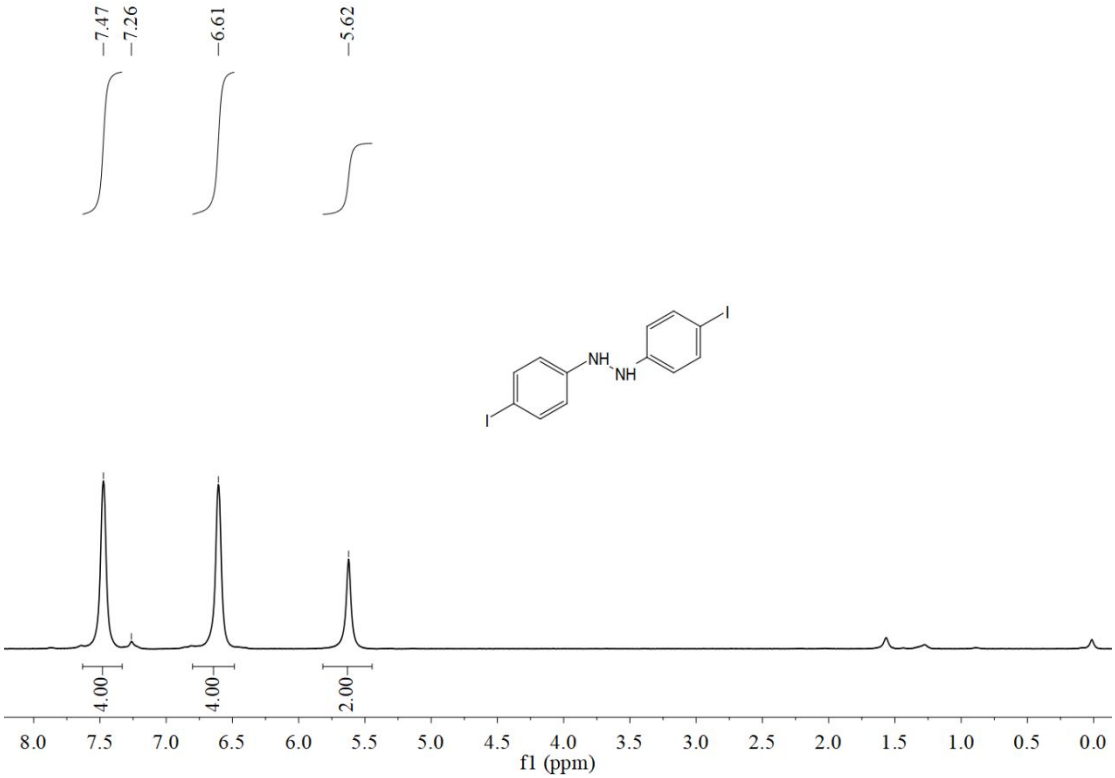


Figure S43. ^{1}H NMR spectrum ($CDCl_3$) of **1f**

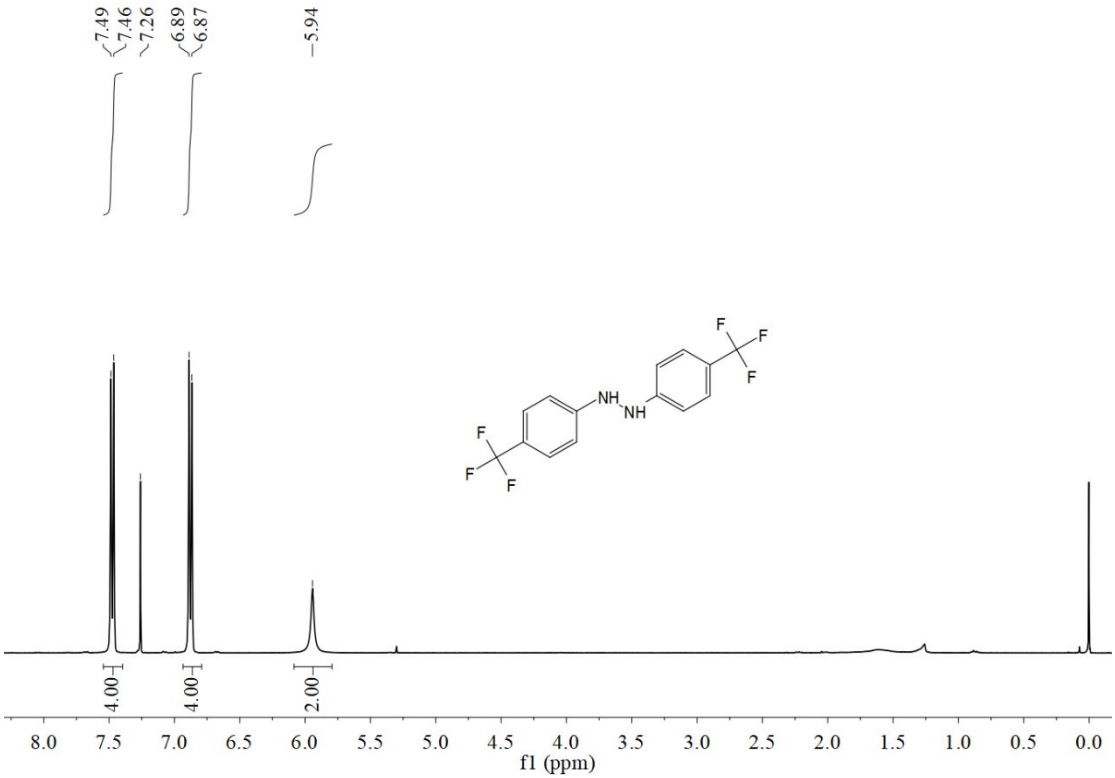


Figure S44. ^{1}H NMR spectrum ($CDCl_3$) of **1g**

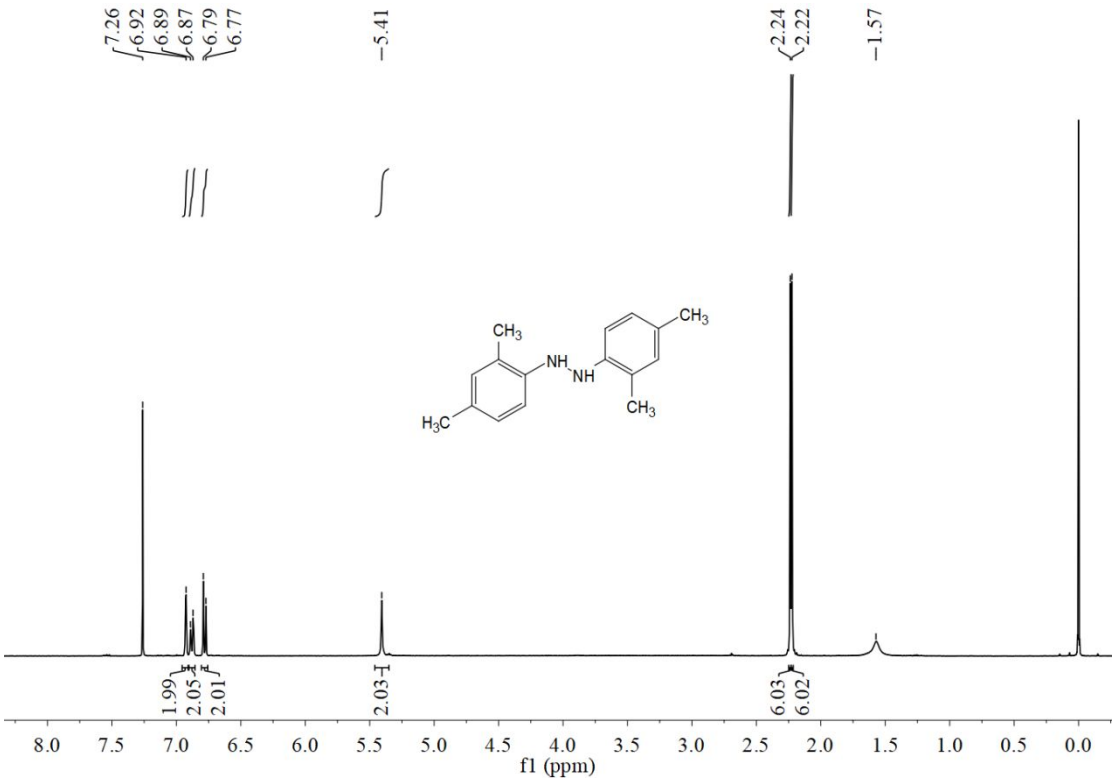


Figure S45. ^{1}H NMR spectrum ($CDCl_3$) of **1h**

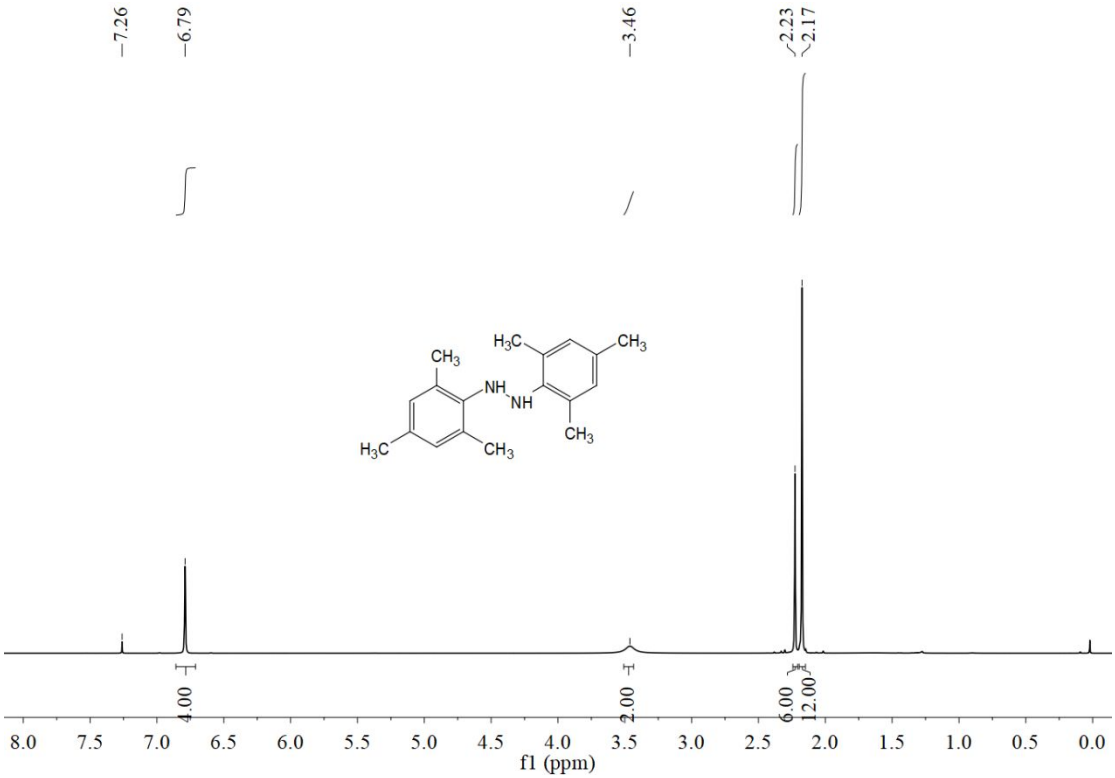


Figure S46. ^{1}H NMR spectrum of ($CDCl_3$) **1i**

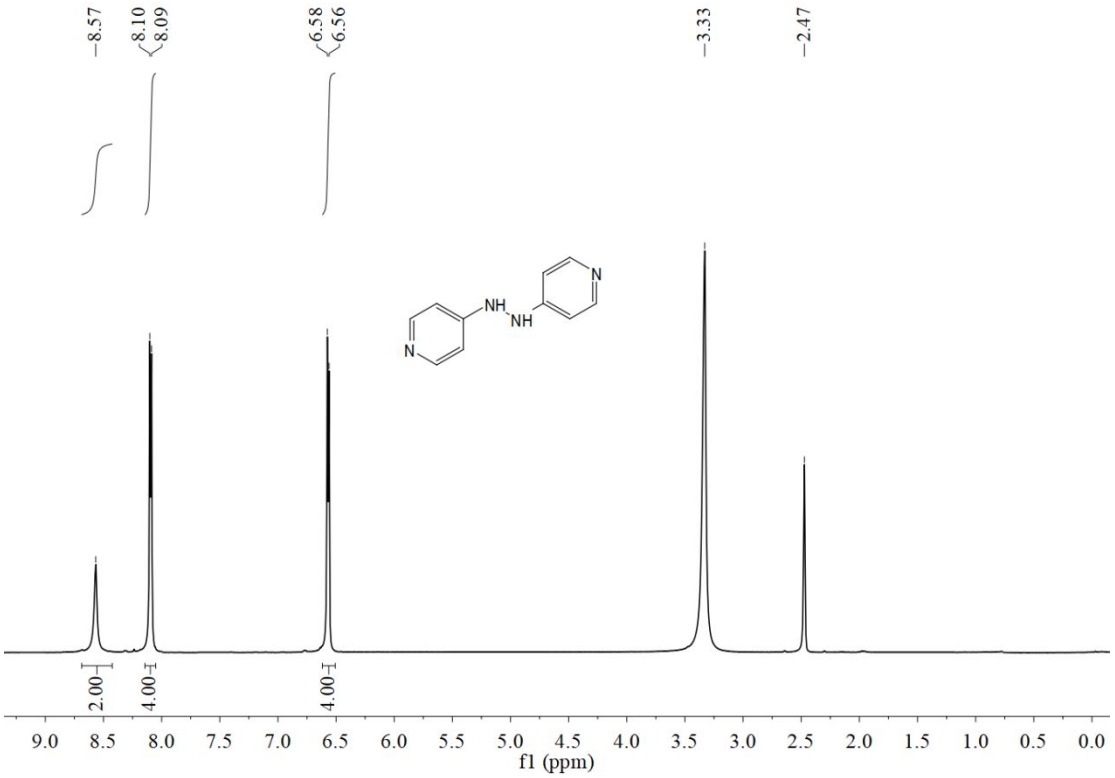


Figure S47. ^{1}H NMR spectrum (DMSO-d_6) of **1j**

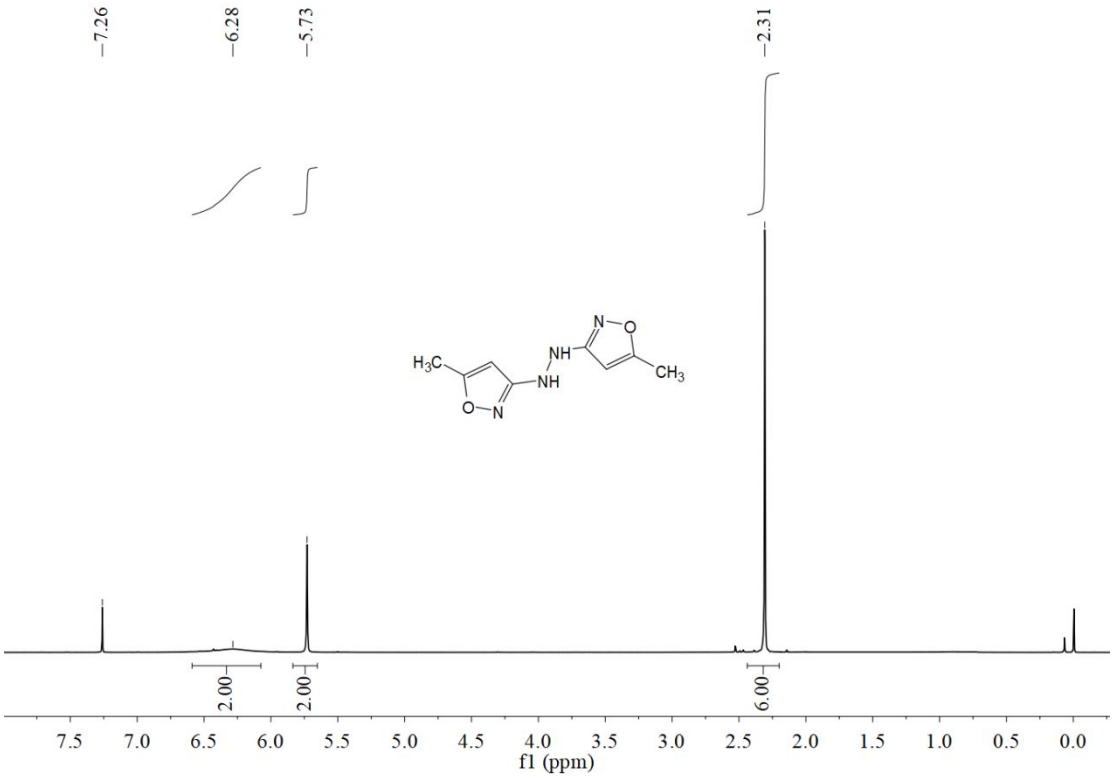


Figure S48. ^{1}H NMR spectrum ($CDCl_3$) of **1k**

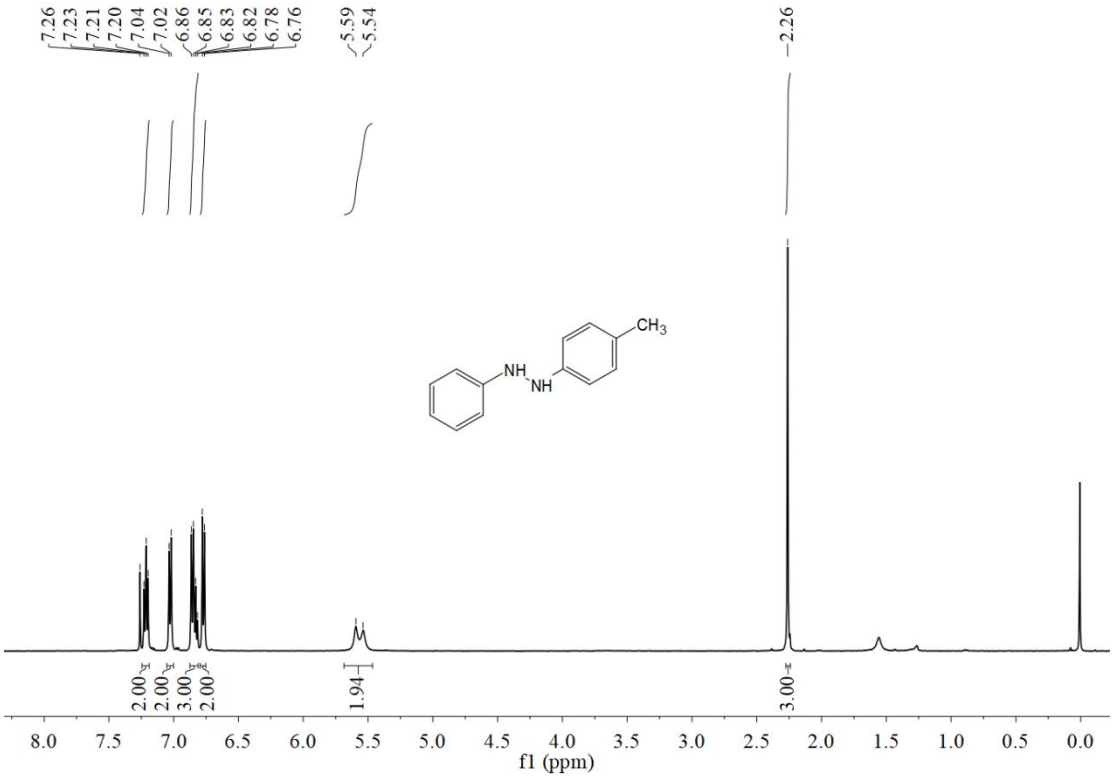


Figure S49. ^{1}H NMR spectrum ($CDCl_3$) of **3a**

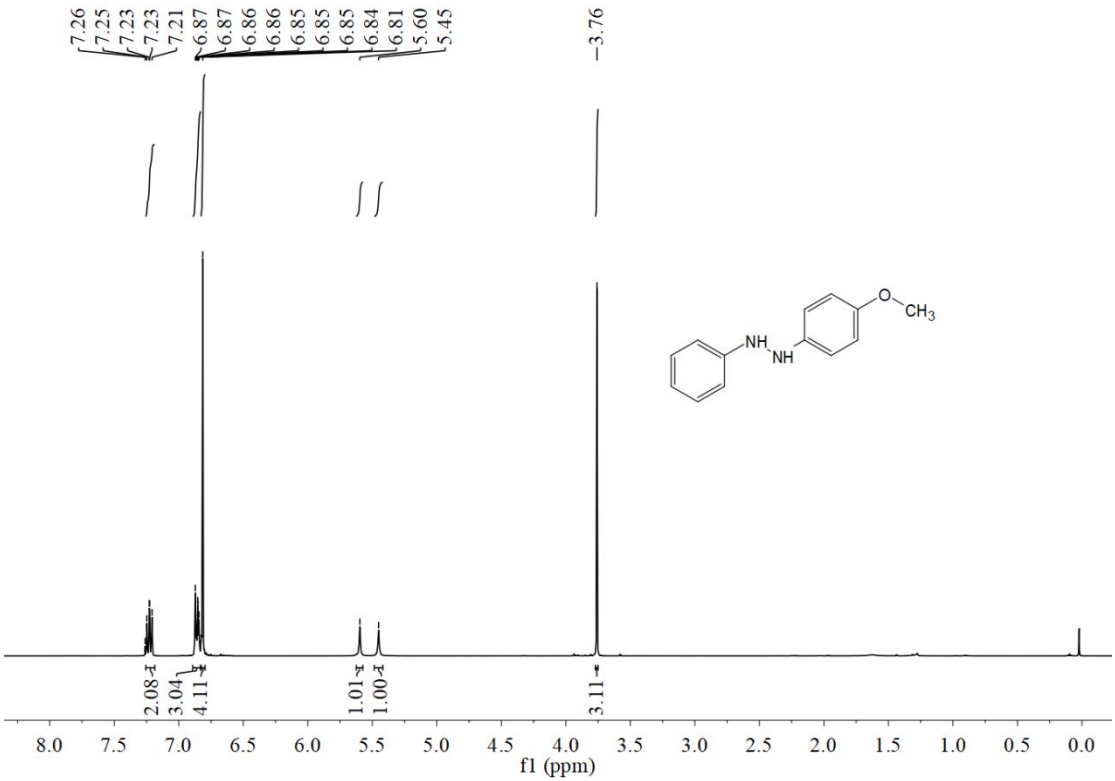


Figure S50. ^{1}H NMR spectrum ($CDCl_3$) of **3b**

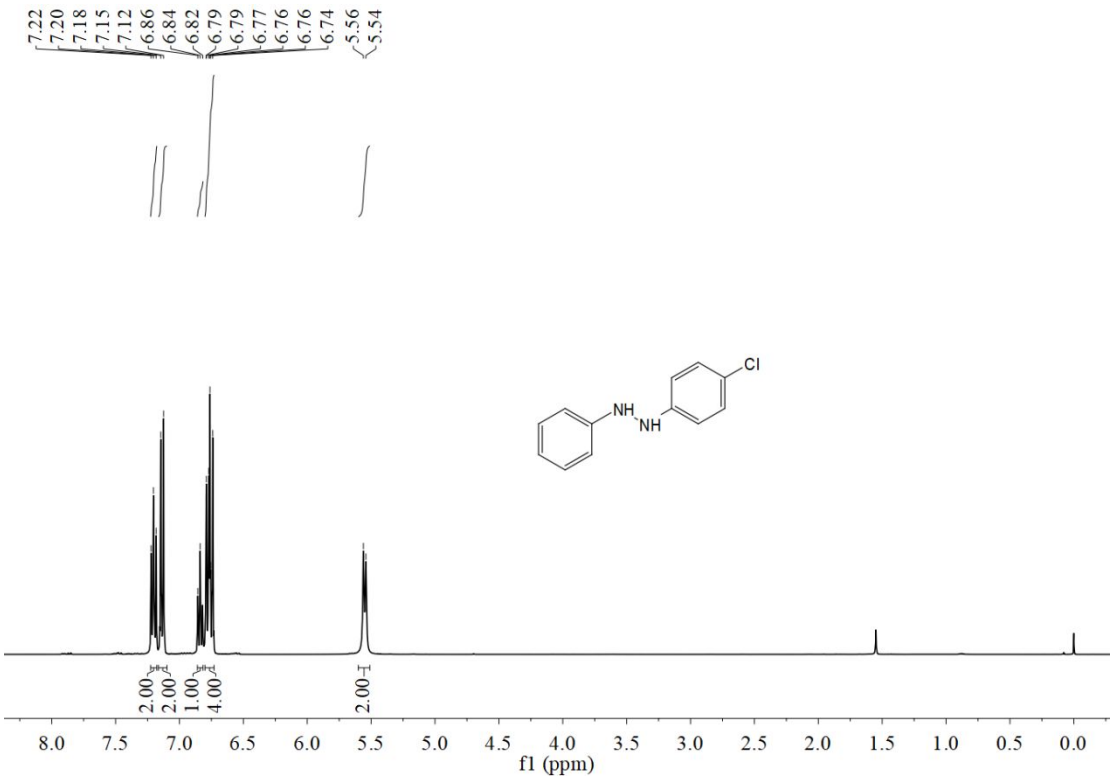


Figure S51. ^{1}H NMR spectrum ($CDCl_3$) of **3c**

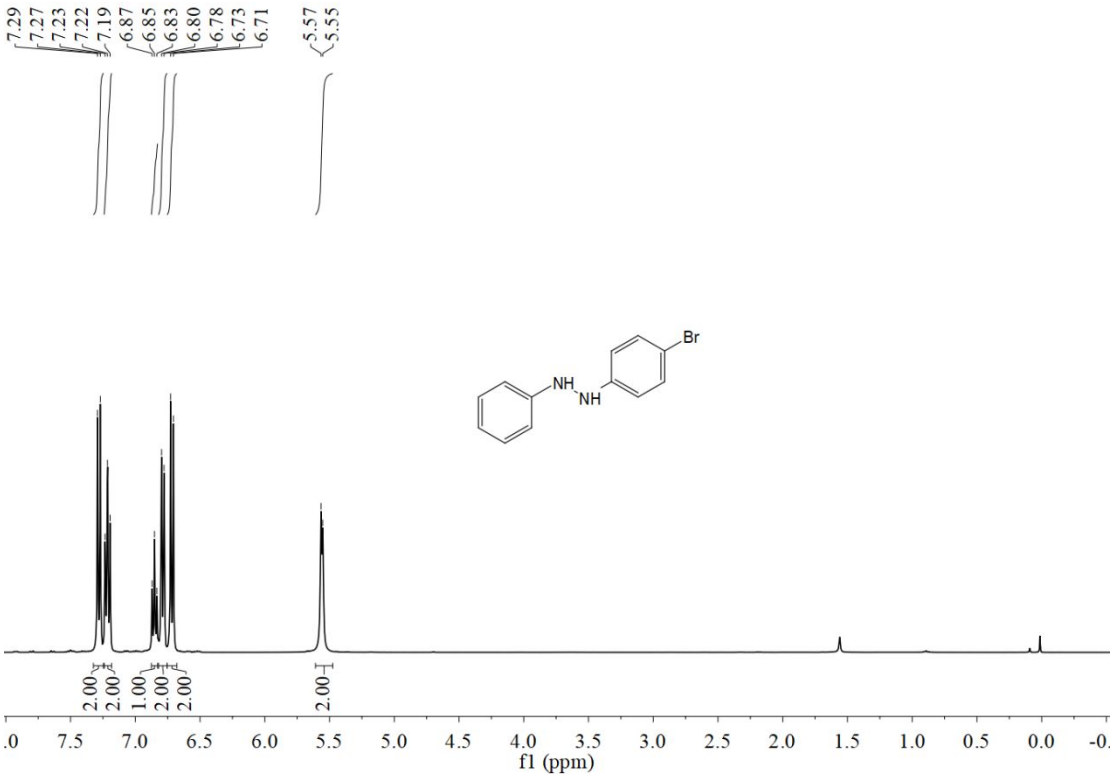


Figure S52. ^{1}H NMR spectrum ($CDCl_3$) of **3d**

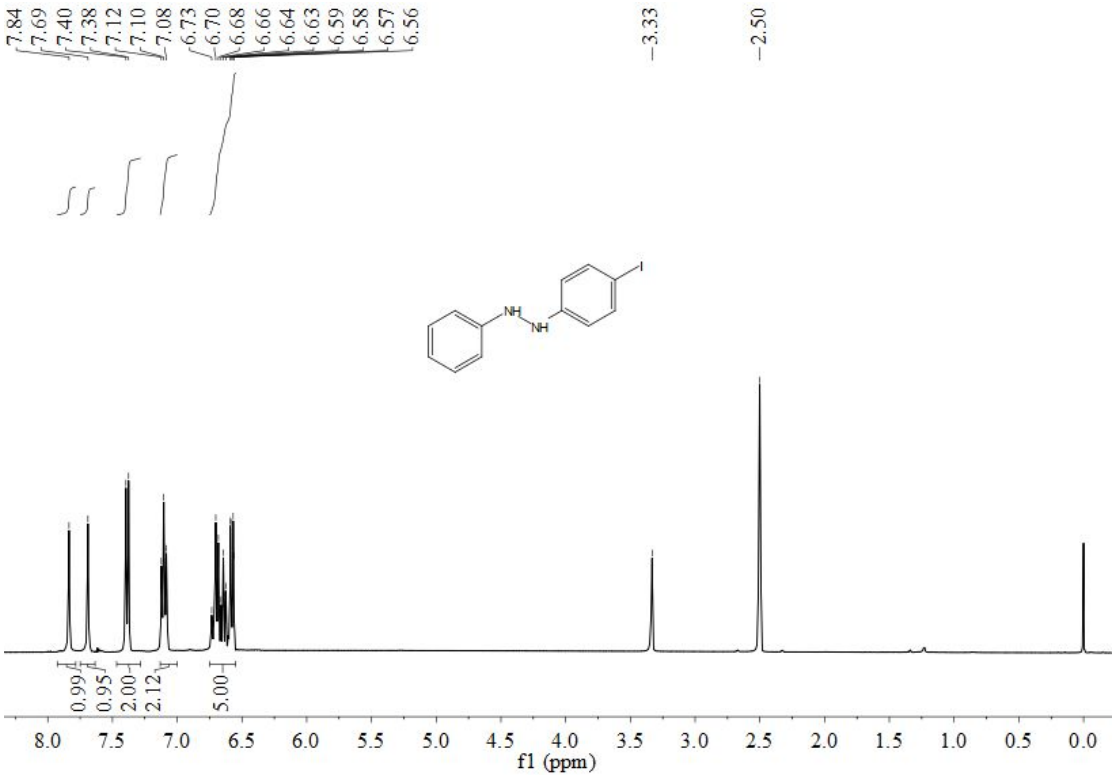


Figure S53. ^{1}H NMR spectrum (DMSO-d_6) of **3e**

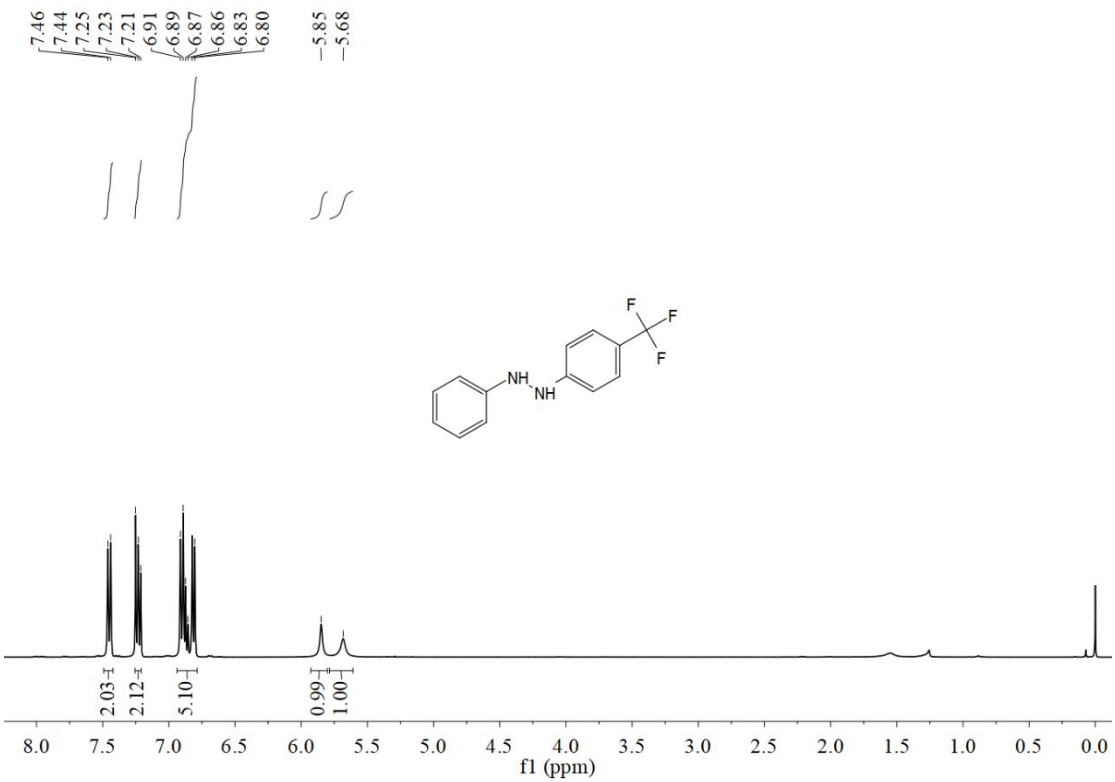


Figure S54. ^{1}H NMR spectrum ($CDCl_3$) of **3f**

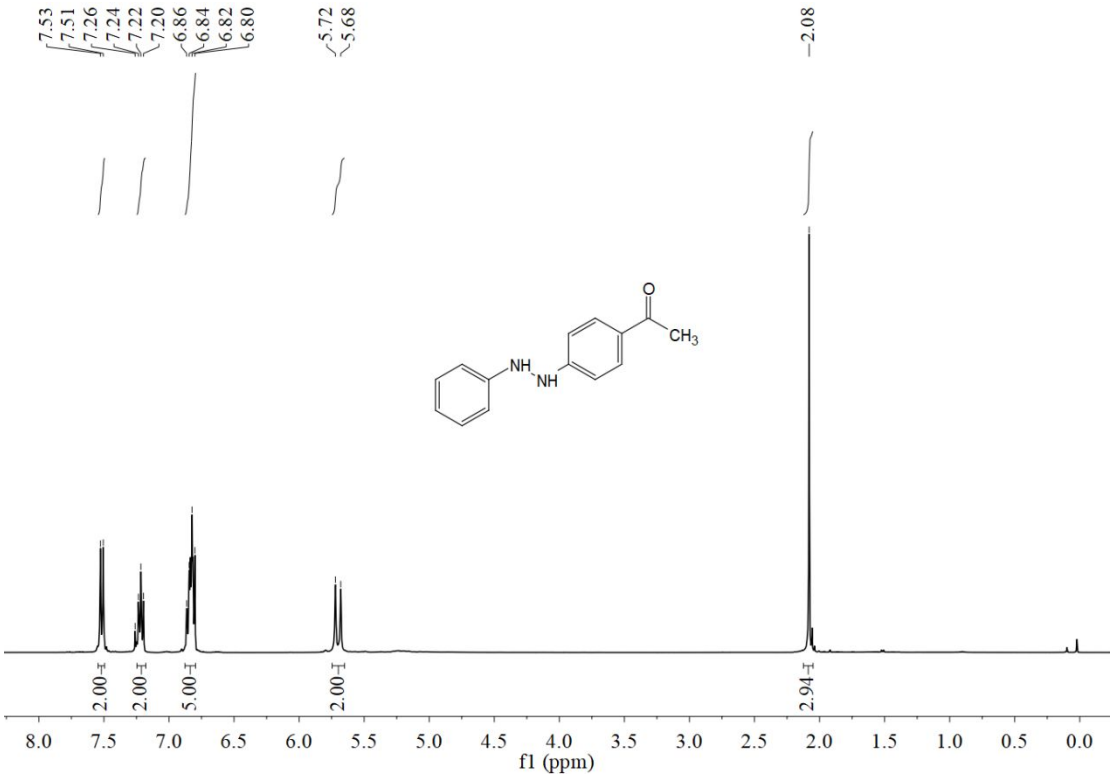


Figure S55. ^{1}H NMR spectrum ($CDCl_3$) of **3g**

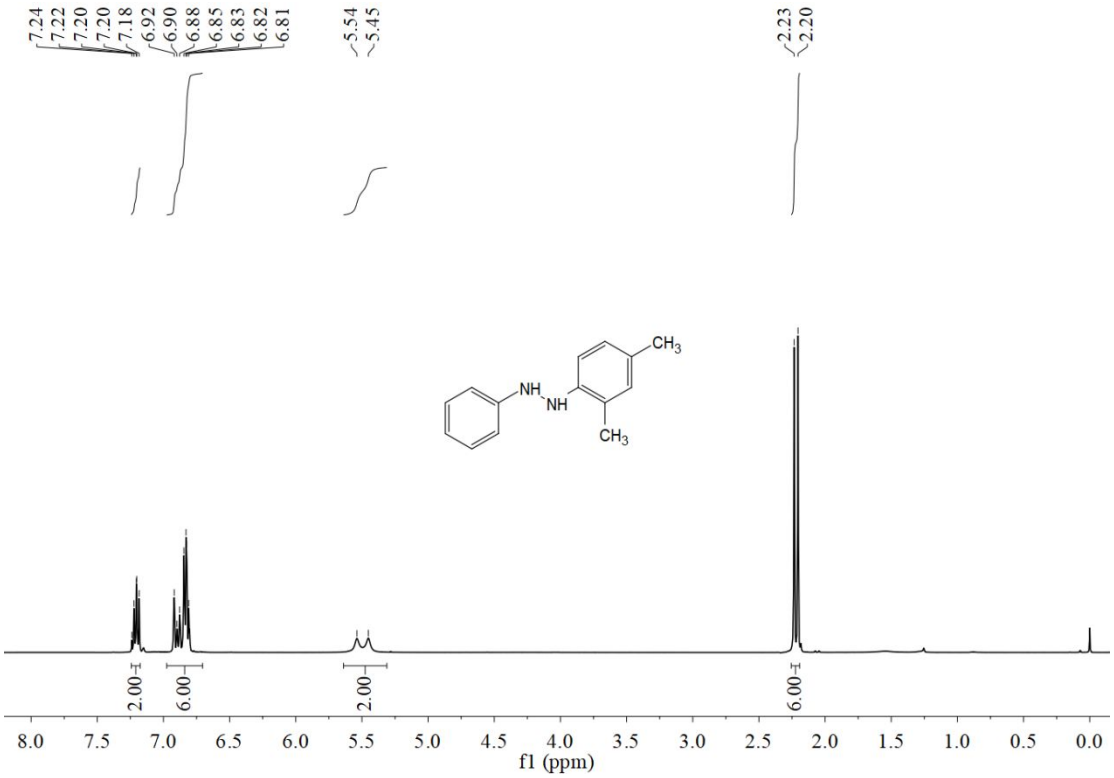


Figure S56. ^{1}H NMR spectrum ($CDCl_3$) of **3h**

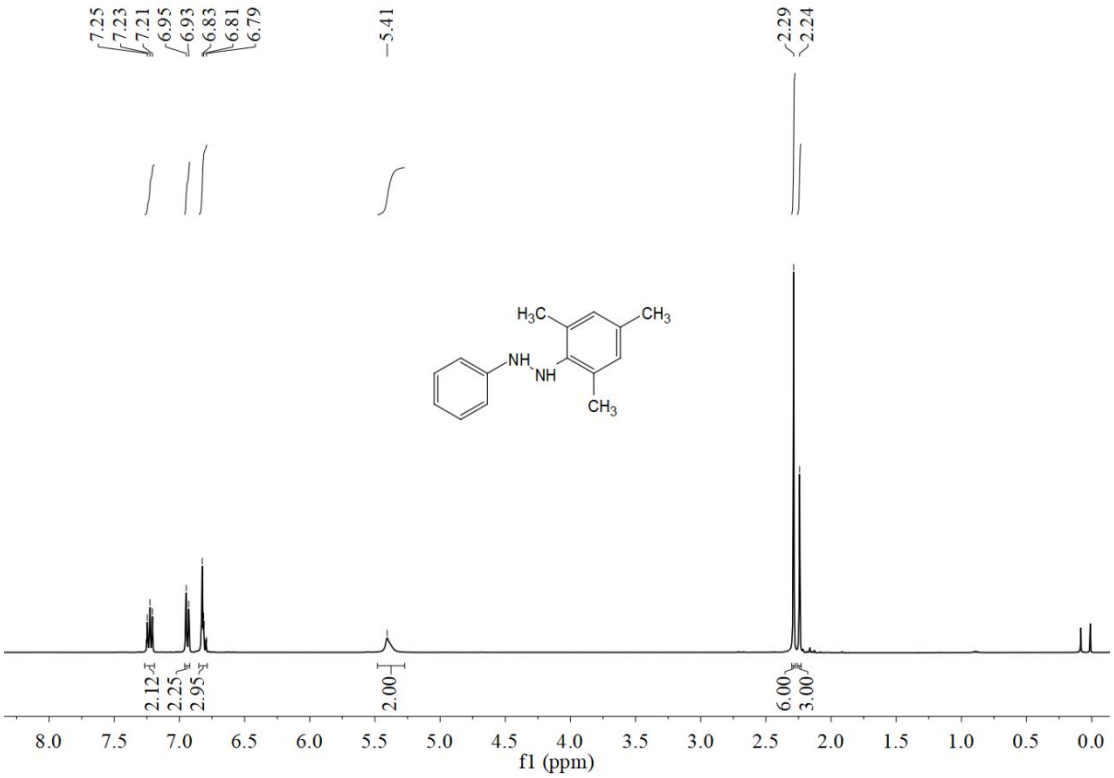


Figure S57. ^{1}H NMR spectrum ($CDCl_3$) of **3i**

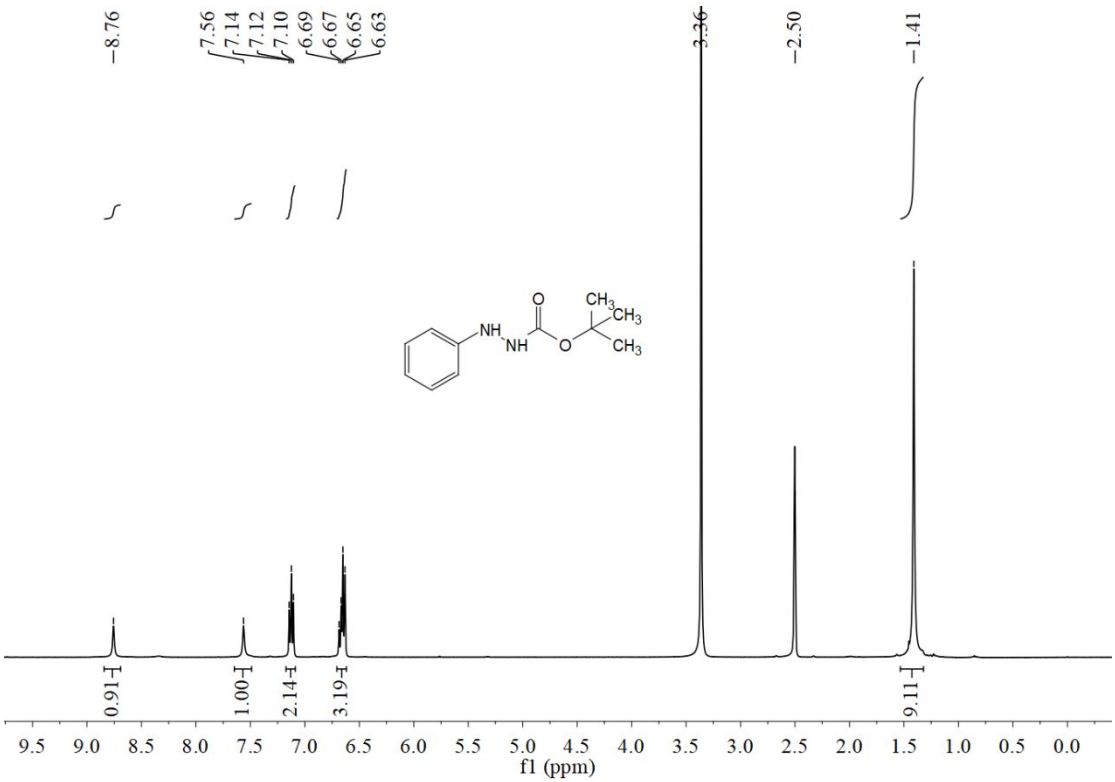


Figure S58. ^{1}H NMR spectrum (DMSO-d_6) of **3j**

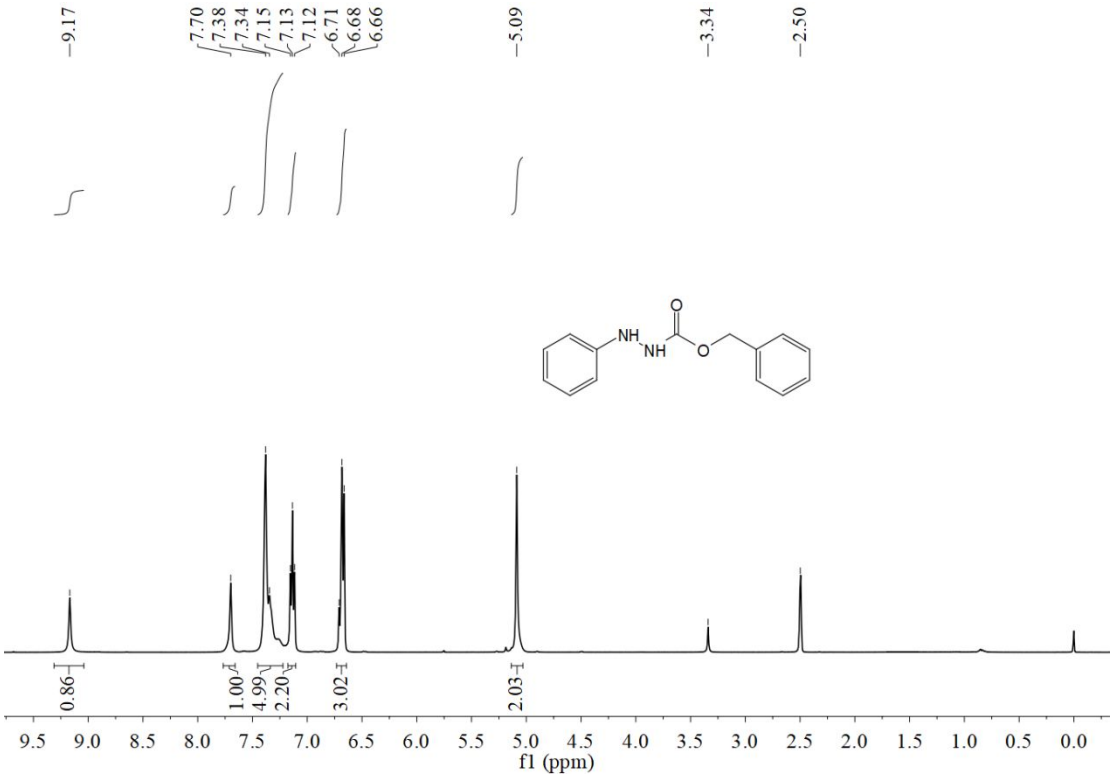


Figure S59. ^{1}H NMR spectrum (DMSO-d_6) of **3k**

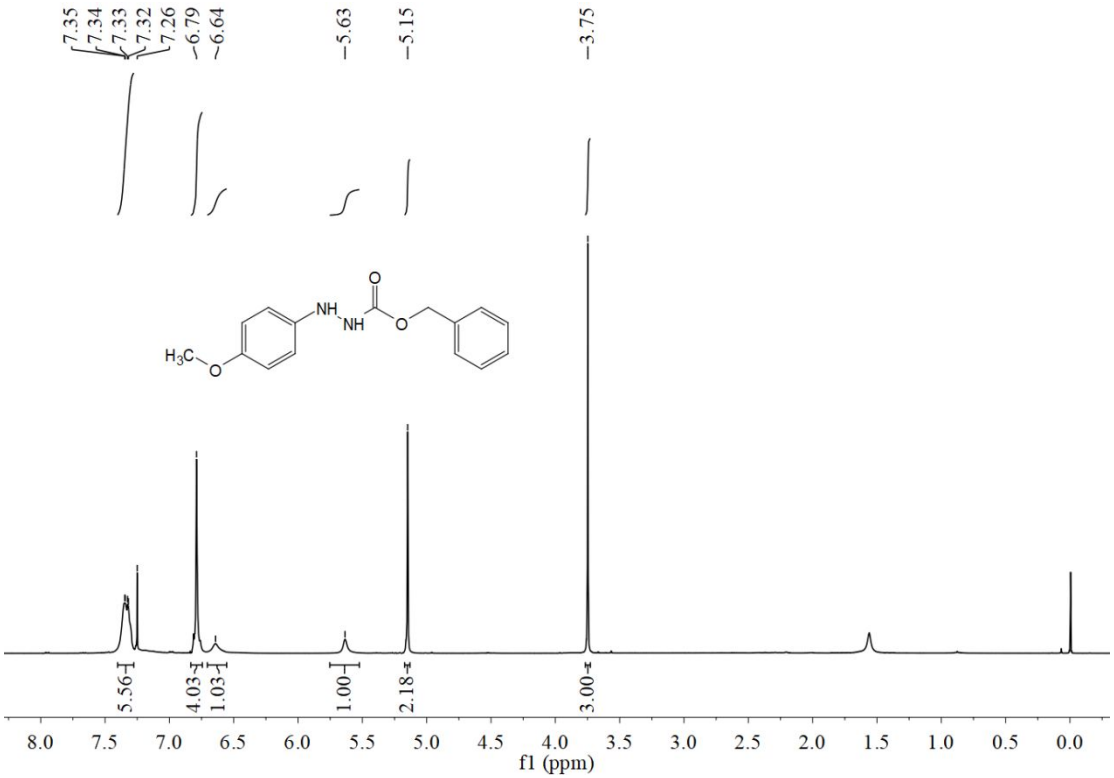


Figure S60. ^{1}H NMR spectrum ($CDCl_3$) of **3l**

^{1}H NMR and ^{13}C NMR spectra for azo aromatics

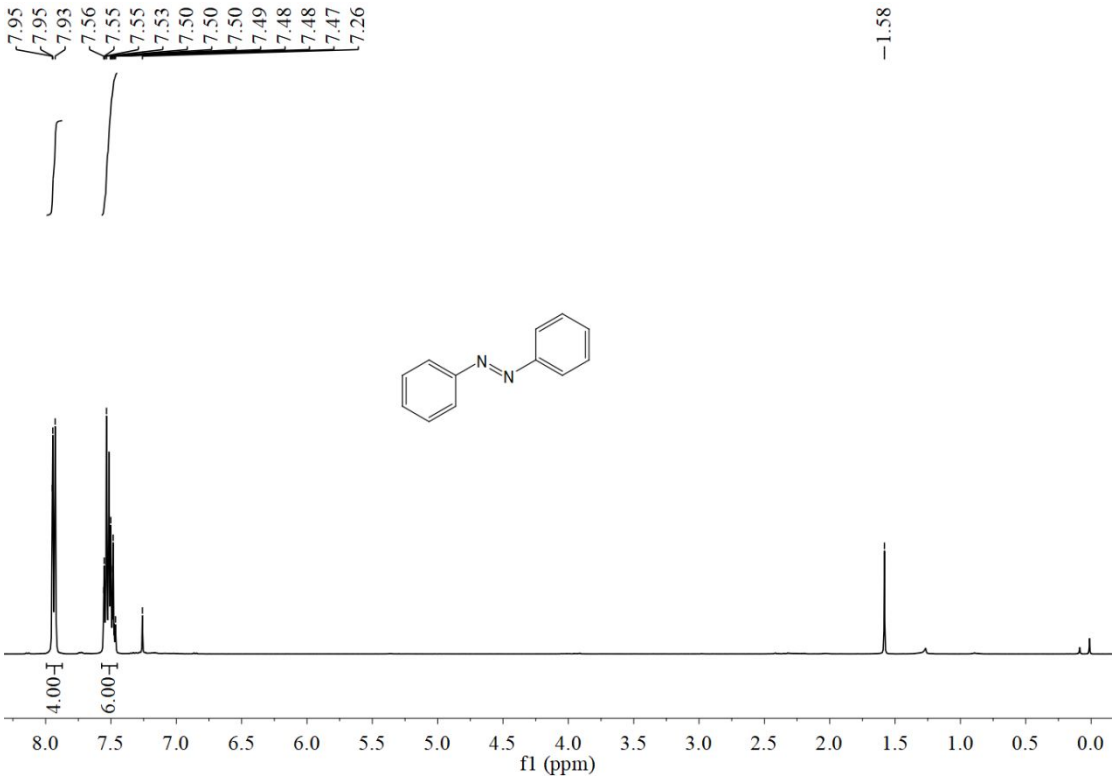


Figure S61. ^{1}H NMR spectrum ($CDCl_3$) of **2a**

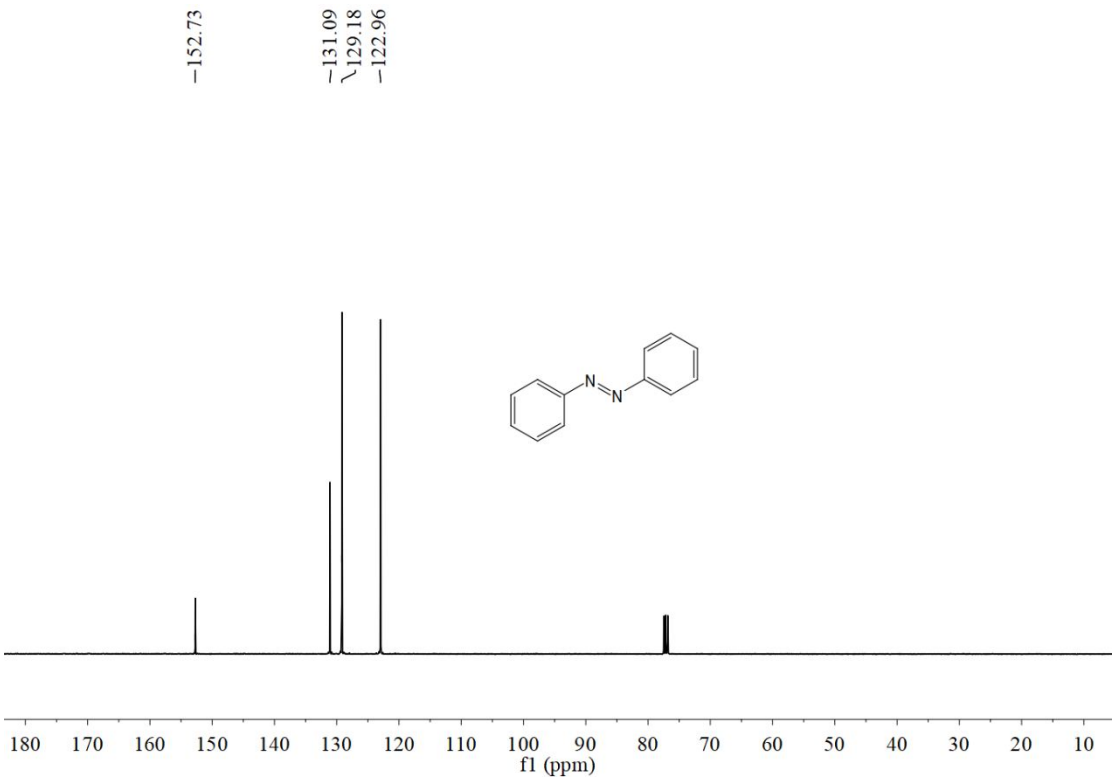


Figure S62. ^{13}C NMR spectrum ($CDCl_3$) of **2a**

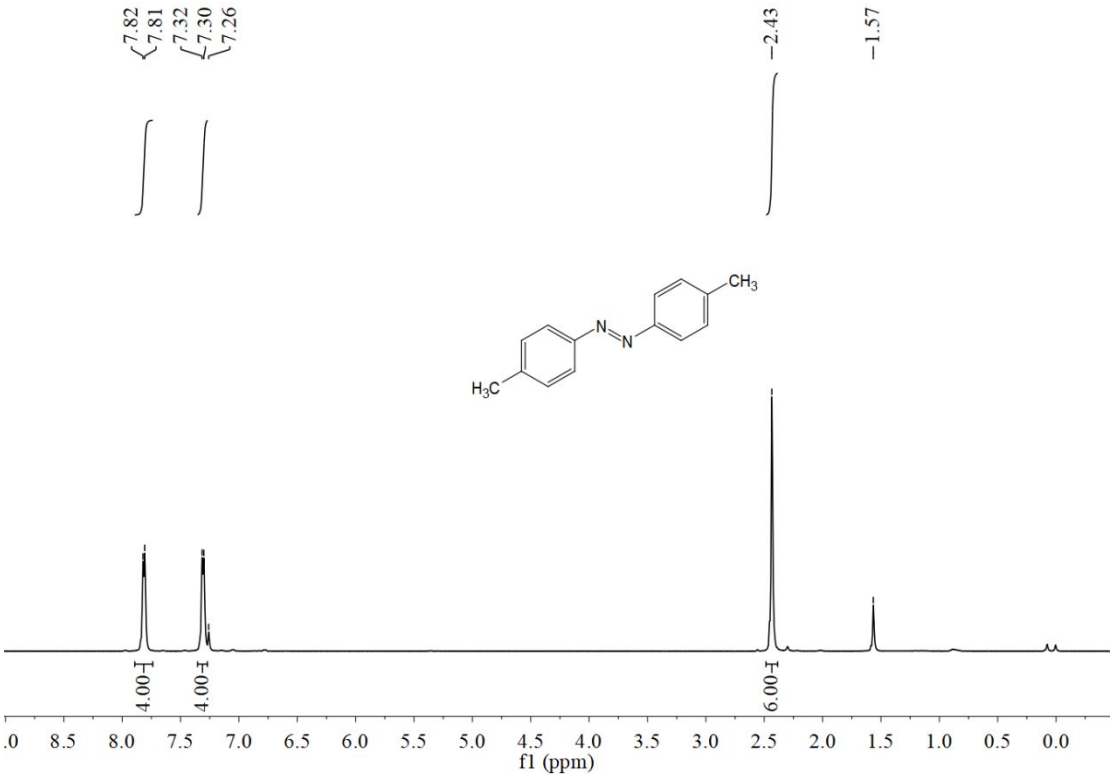


Figure S63. ^{1}H NMR spectrum ($CDCl_3$) of **2b**

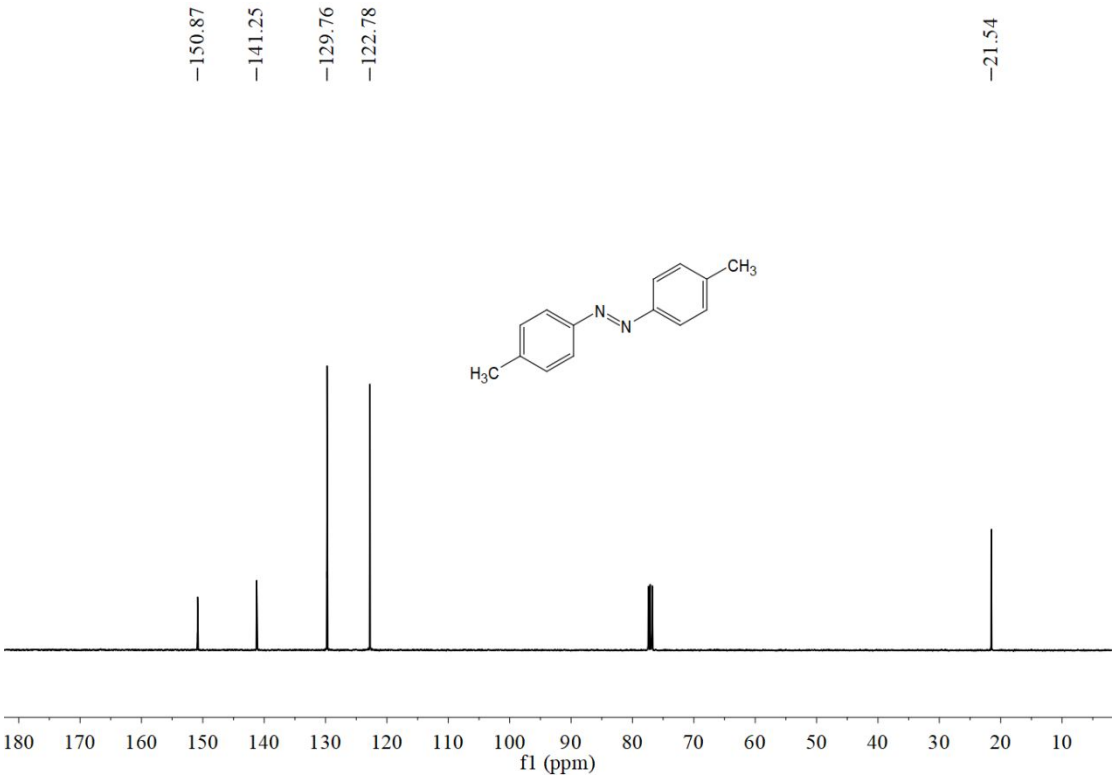


Figure S64. ^{13}C NMR spectrum ($CDCl_3$) of **2b**

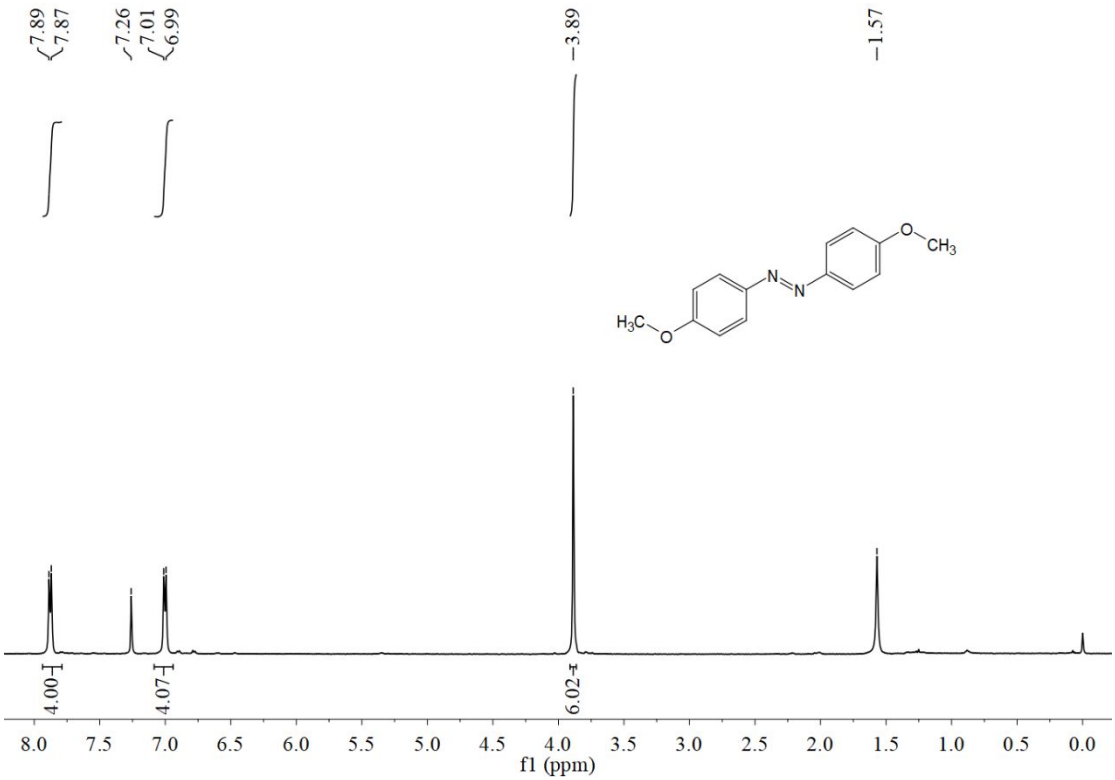


Figure S65. ^{1}H NMR spectrum ($CDCl_3$) of **2c**

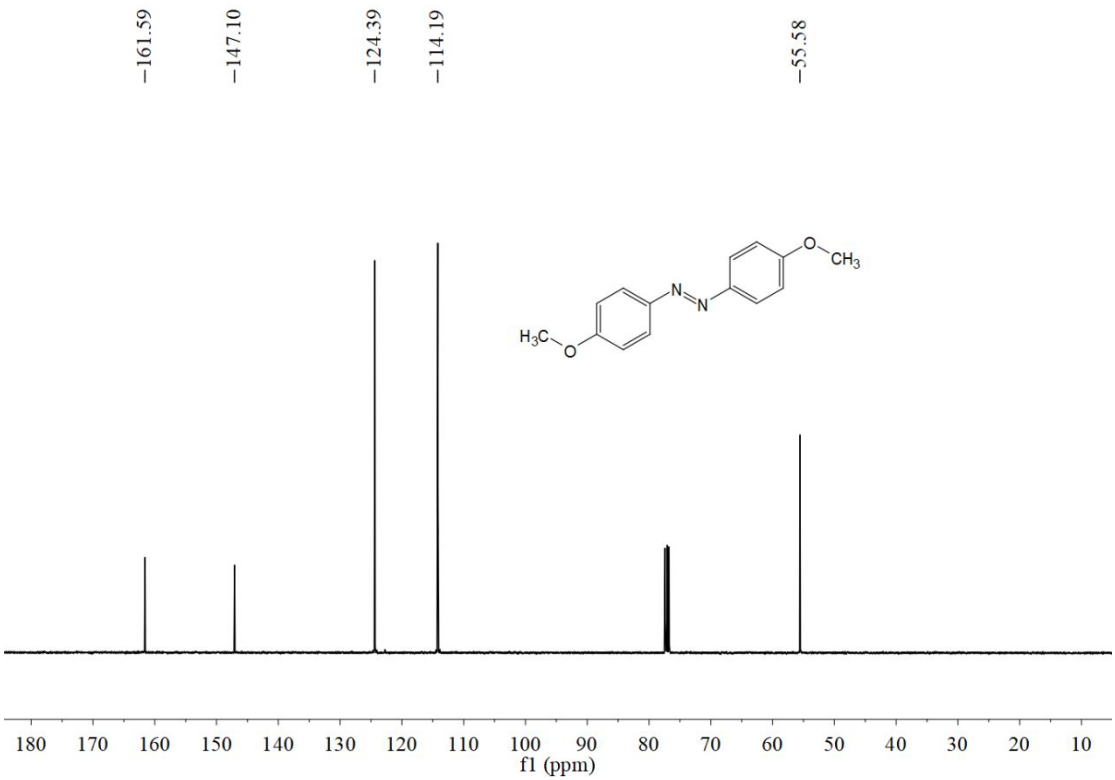


Figure S66. ^{13}C NMR spectrum ($CDCl_3$) of **2c**

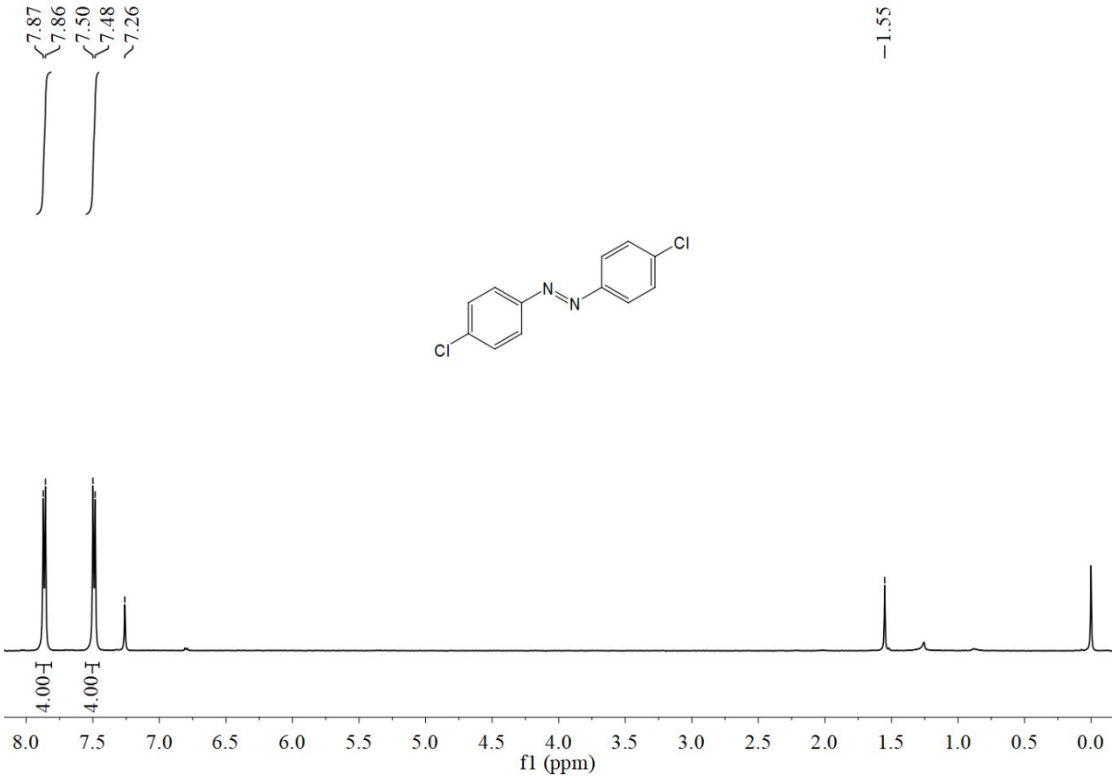


Figure S67. ^{1}H NMR spectrum ($CDCl_3$) of **2d**

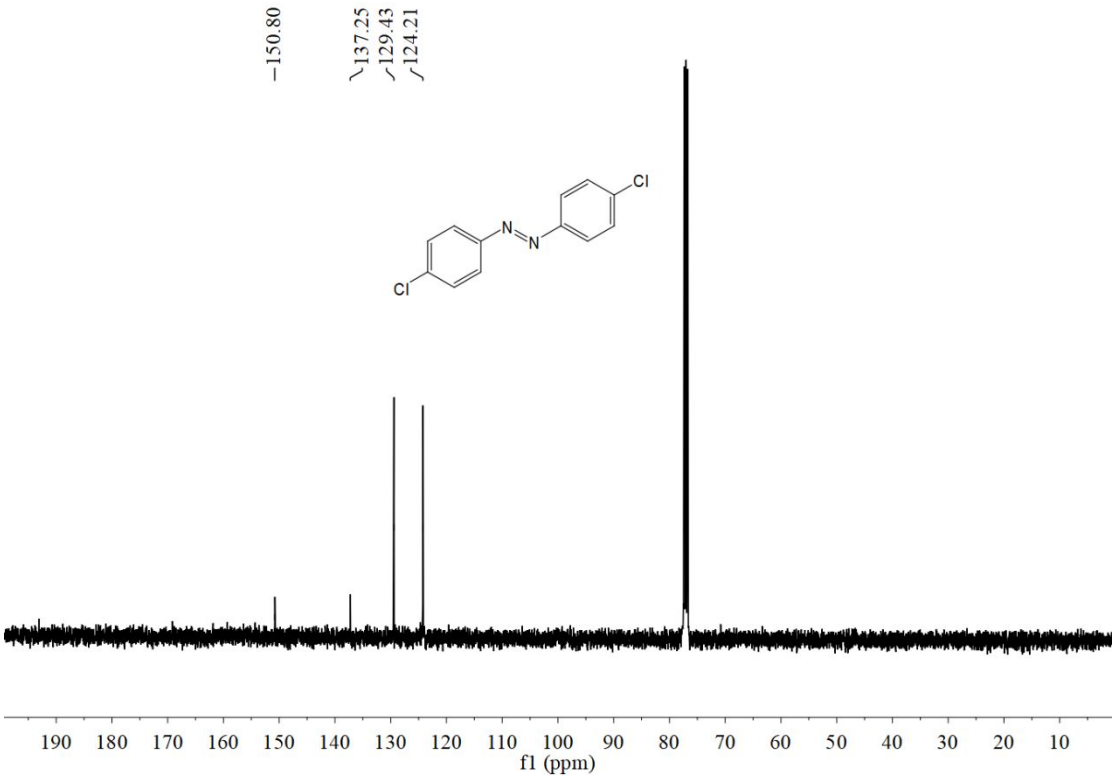


Figure S68. ^{13}C NMR spectrum ($CDCl_3$) of **2d**

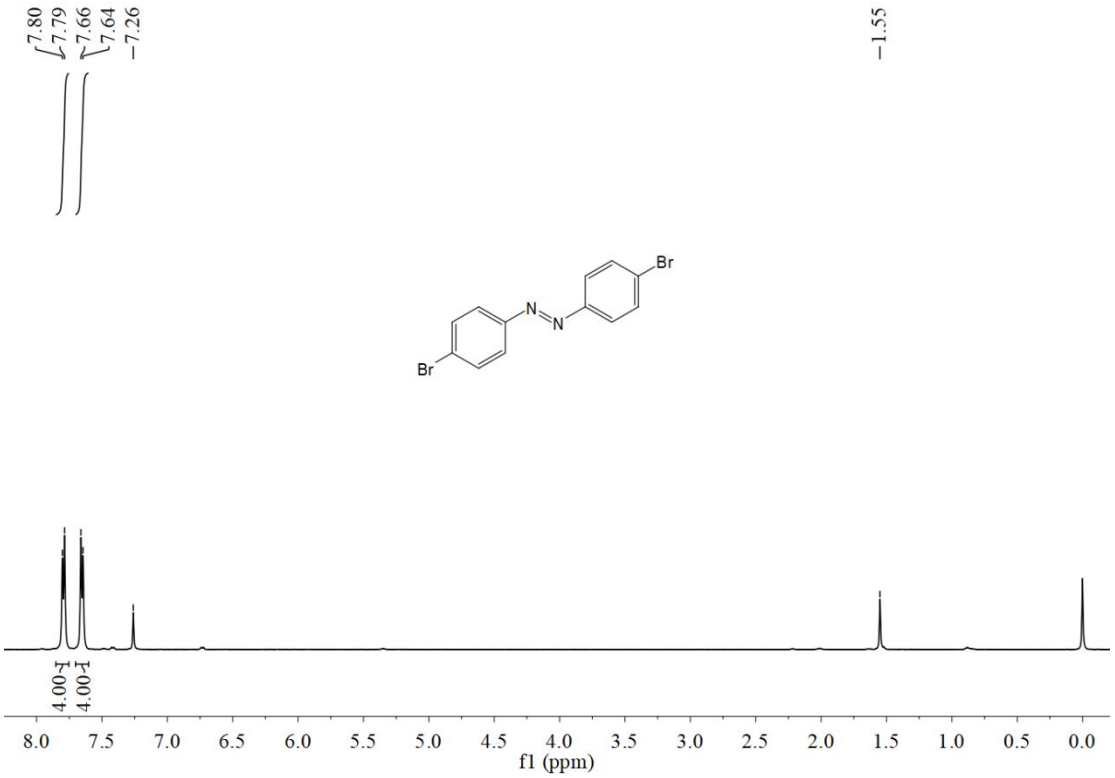


Figure S69. ^{1}H NMR spectrum ($CDCl_3$) of **2e**

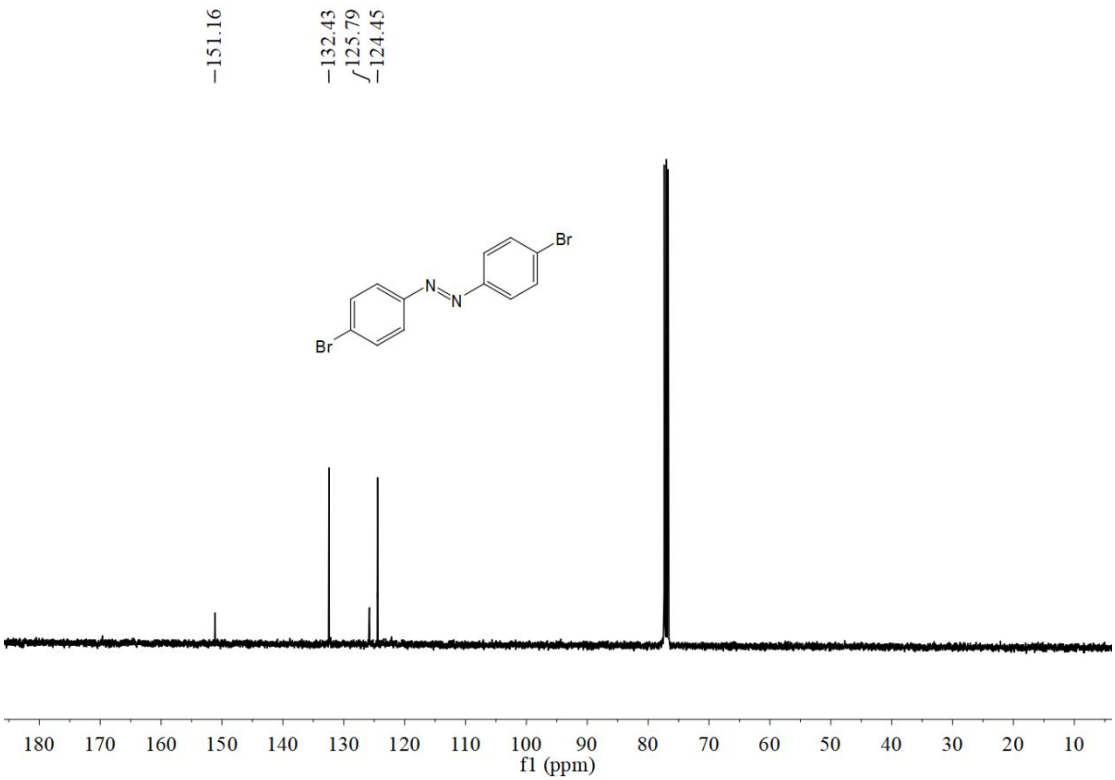


Figure S70. ^{13}C NMR spectrum ($CDCl_3$) of **2e**

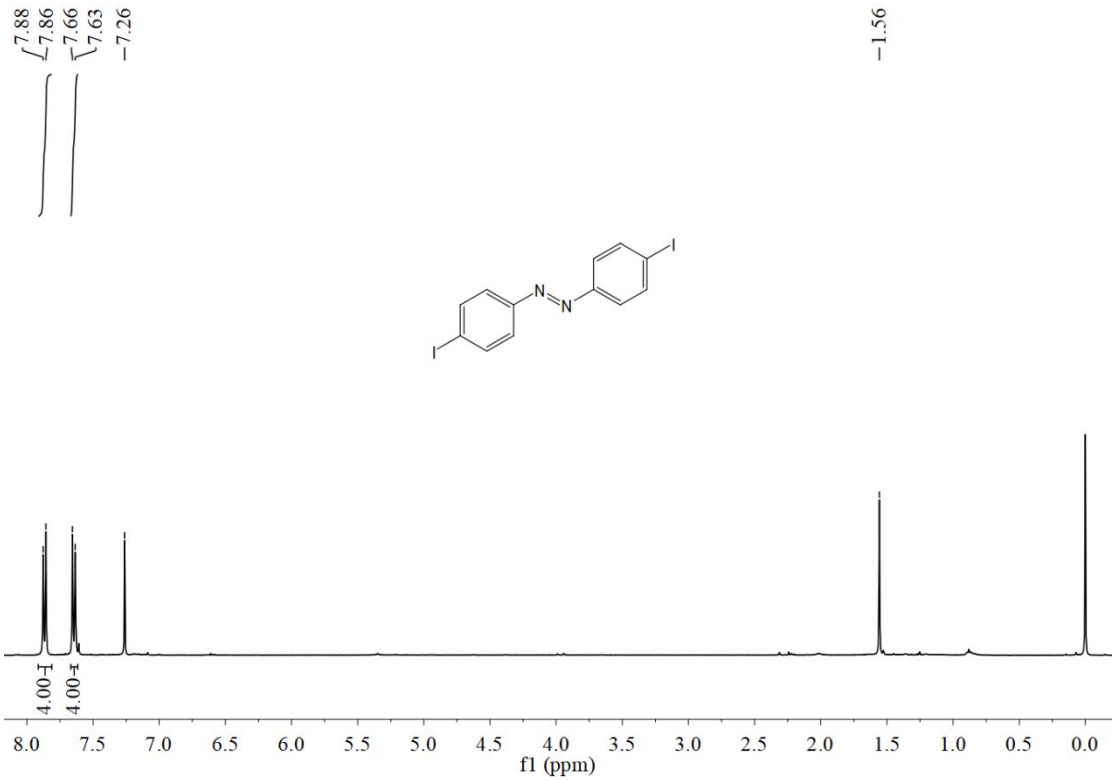


Figure S71. ^{1}H NMR spectrum ($CDCl_3$) of **2f**

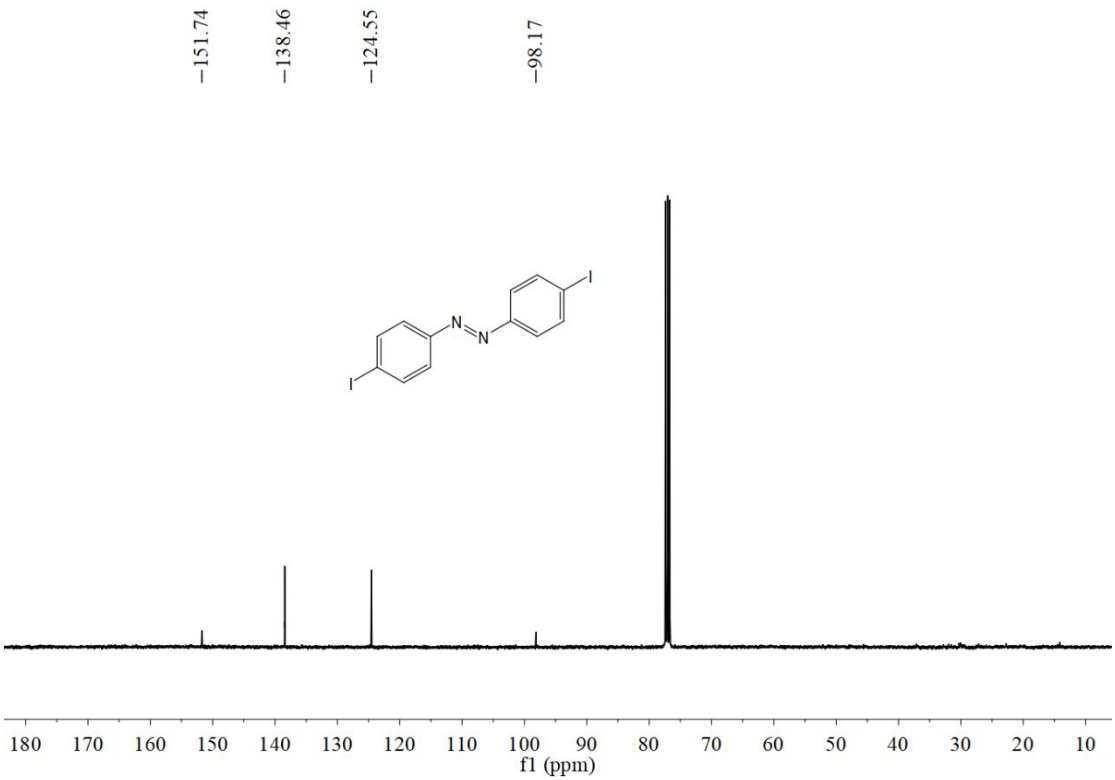


Figure S72. ^{13}C NMR spectrum ($CDCl_3$) of **2f**

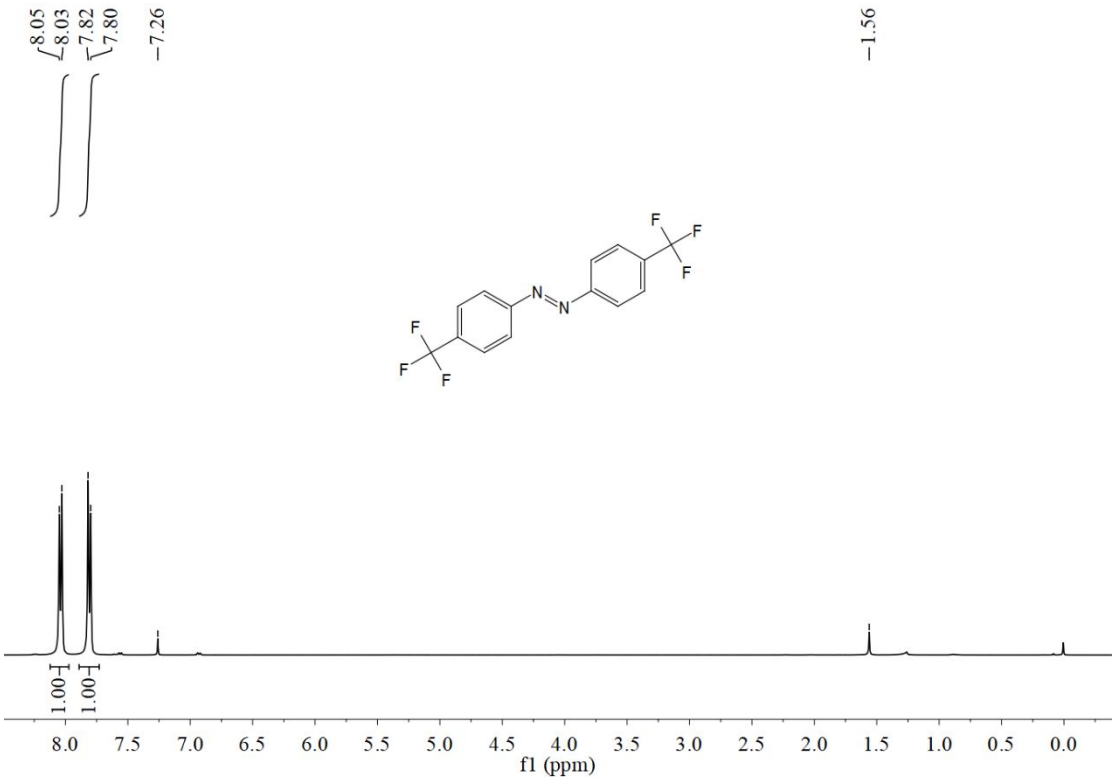


Figure S73. ^{1}H NMR spectrum ($CDCl_3$) of **2g**

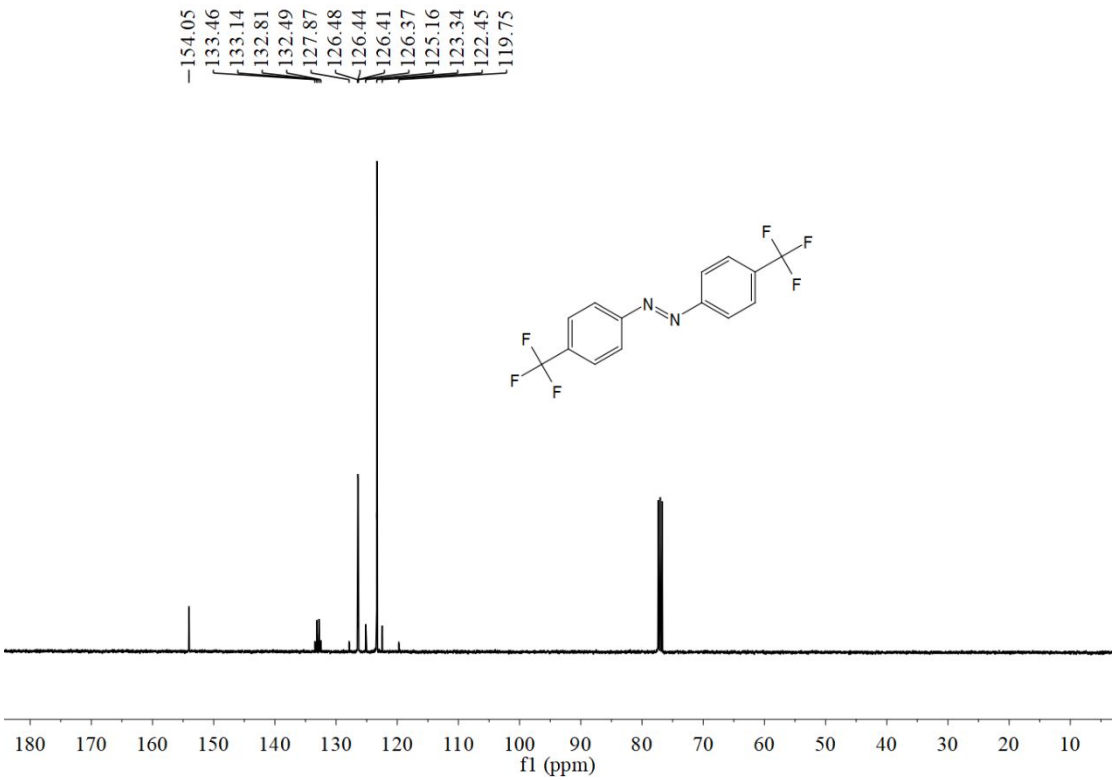


Figure S74. ^{13}C NMR spectrum ($CDCl_3$) of **2g**

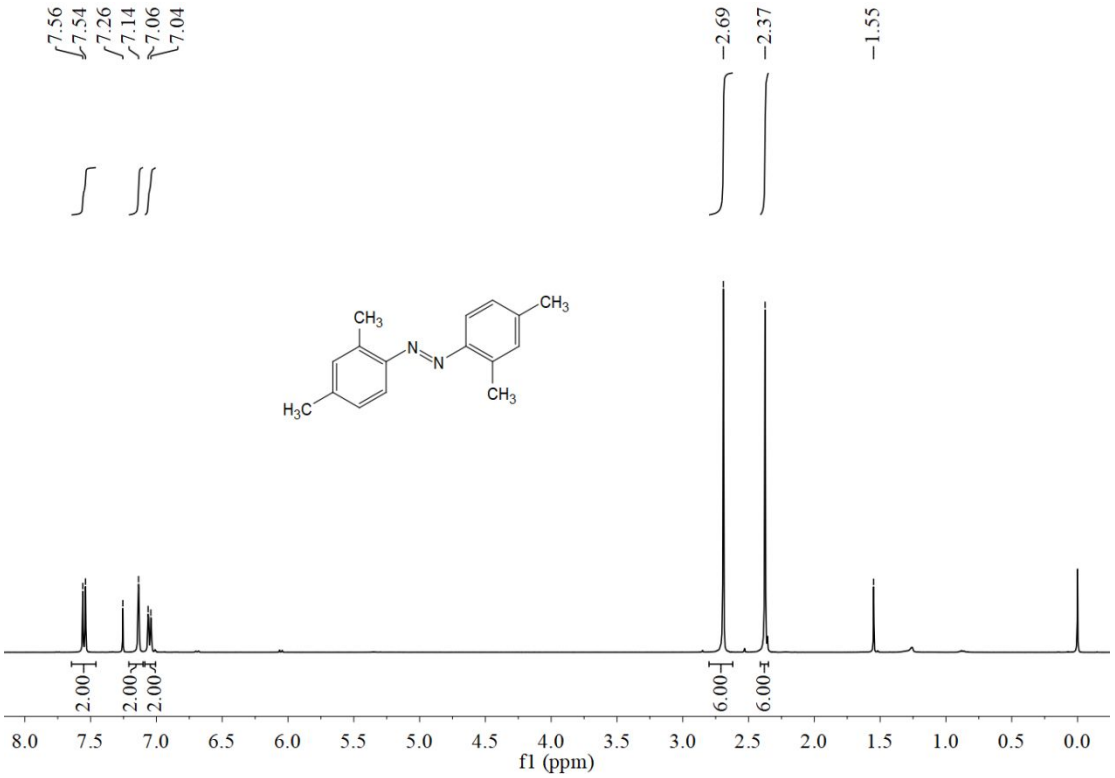


Figure S75. ^{1}H NMR spectrum ($CDCl_3$) of **2h**

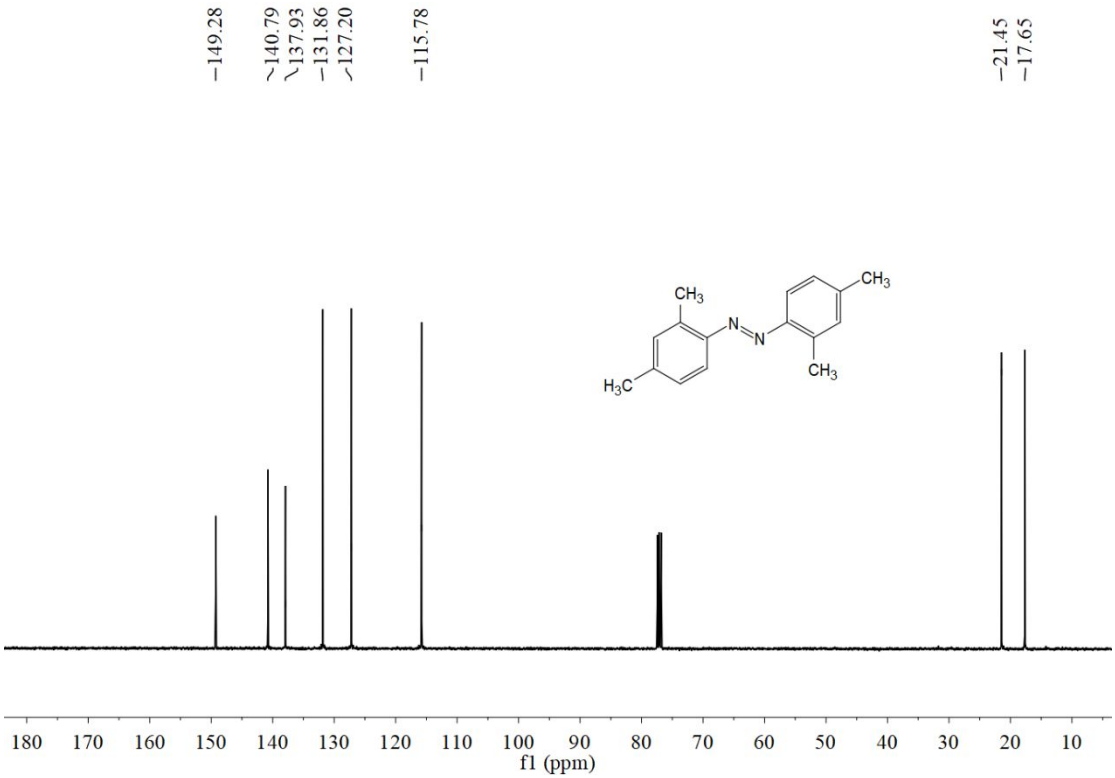


Figure S76. ^{13}C NMR spectrum ($CDCl_3$) of **2h**

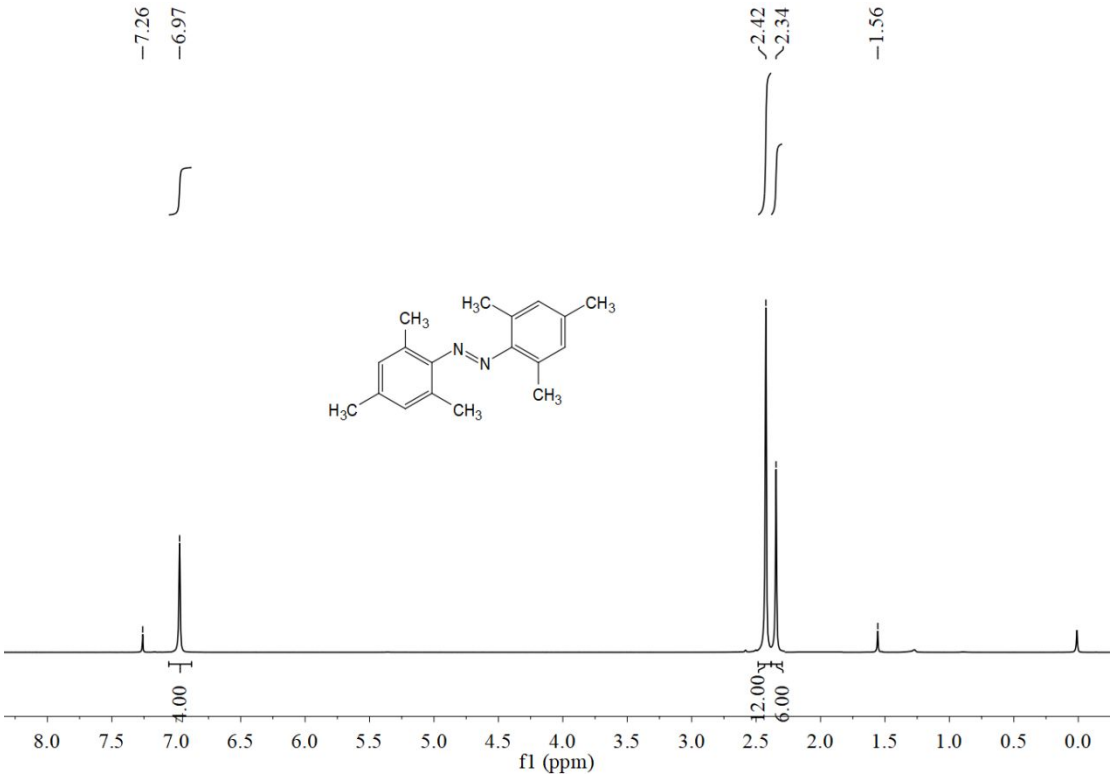


Figure S77. ^{1}H NMR spectrum ($CDCl_3$) of **2i**

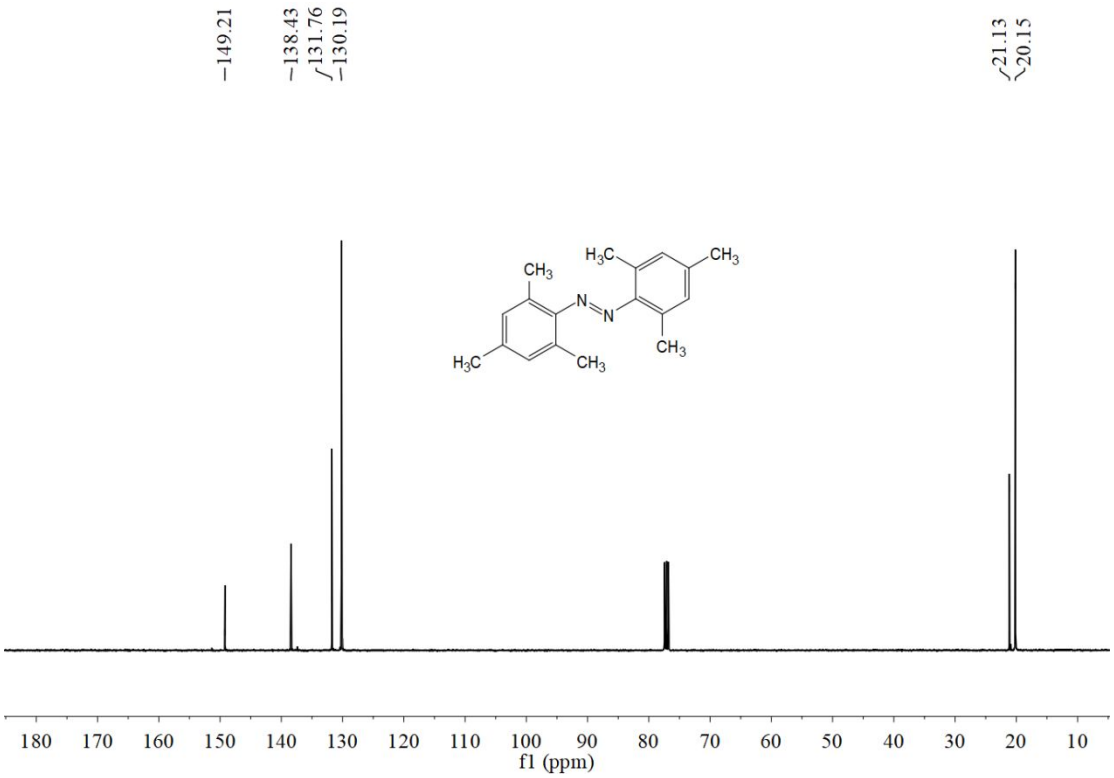


Figure S78. ^{13}C NMR spectrum ($CDCl_3$) of **2i**

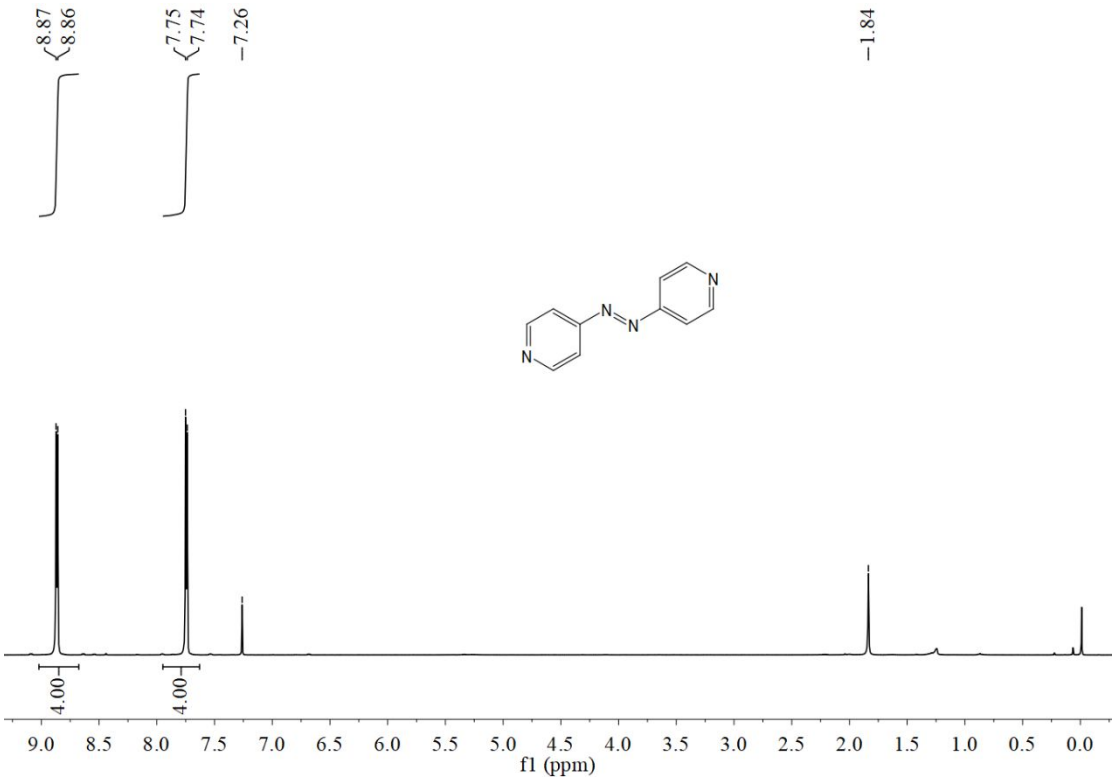


Figure S79. ^{1}H NMR spectrum ($CDCl_3$) of **2j**

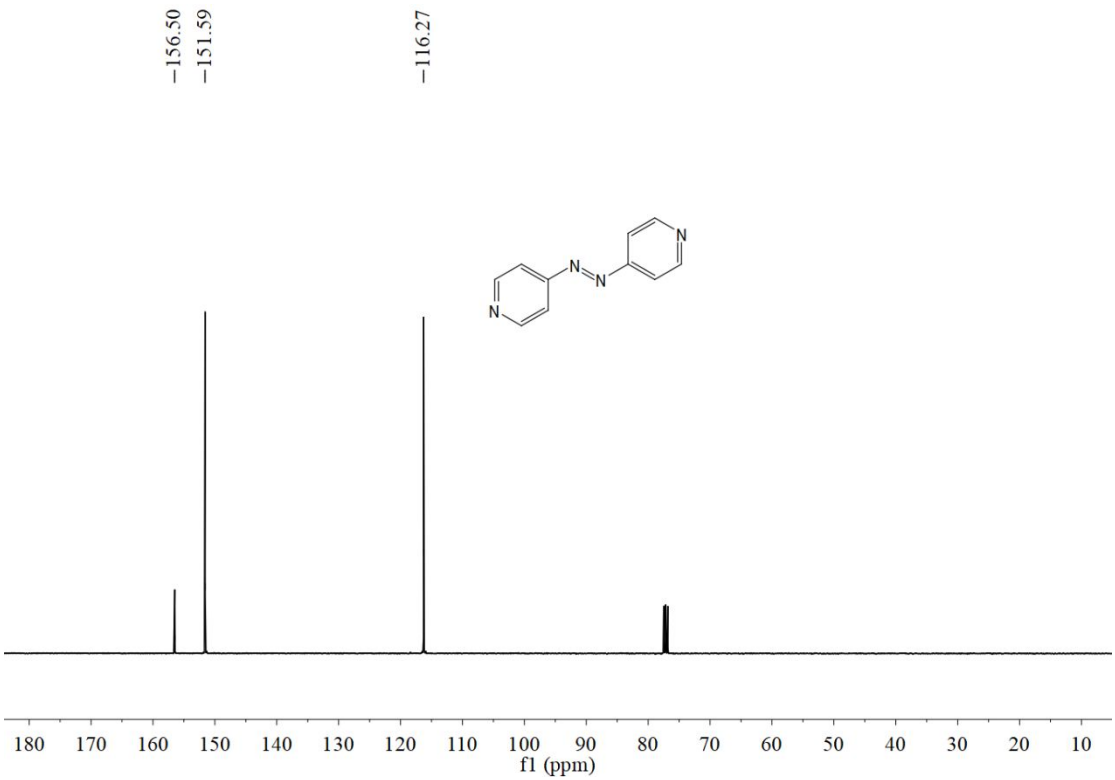


Figure S80. ^{13}C NMR spectrum ($CDCl_3$) of **2j**

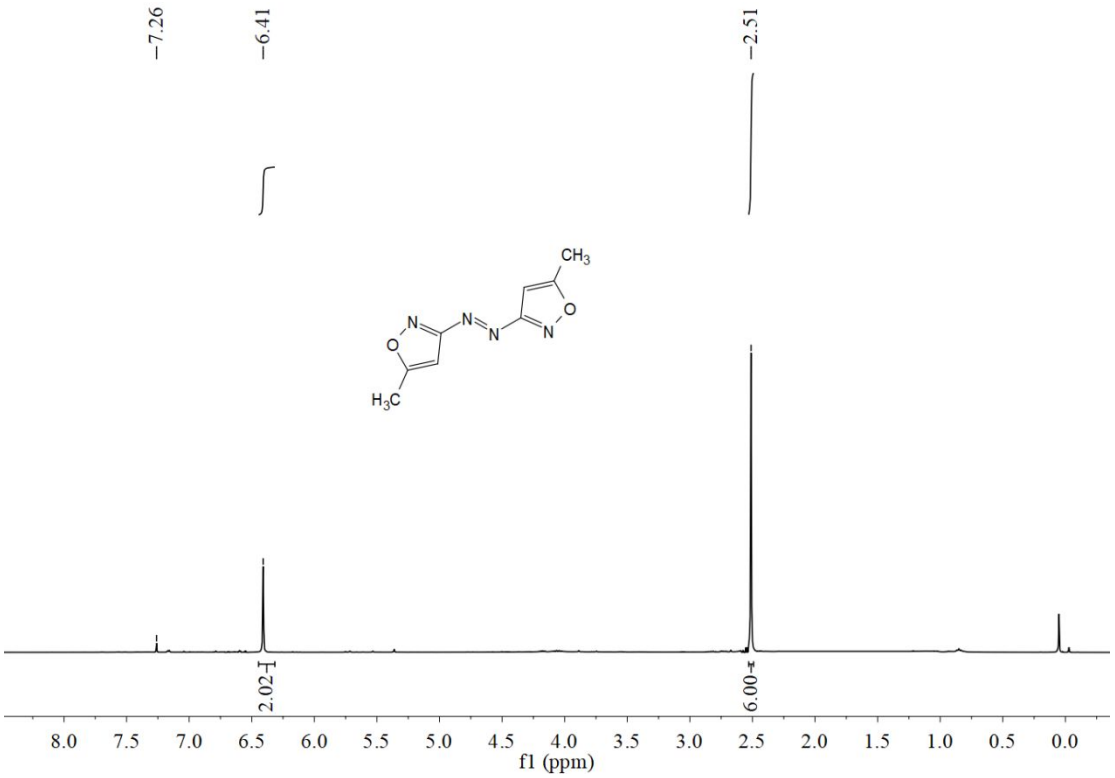


Figure S81. ^{1}H NMR spectrum ($CDCl_3$) of **2k**

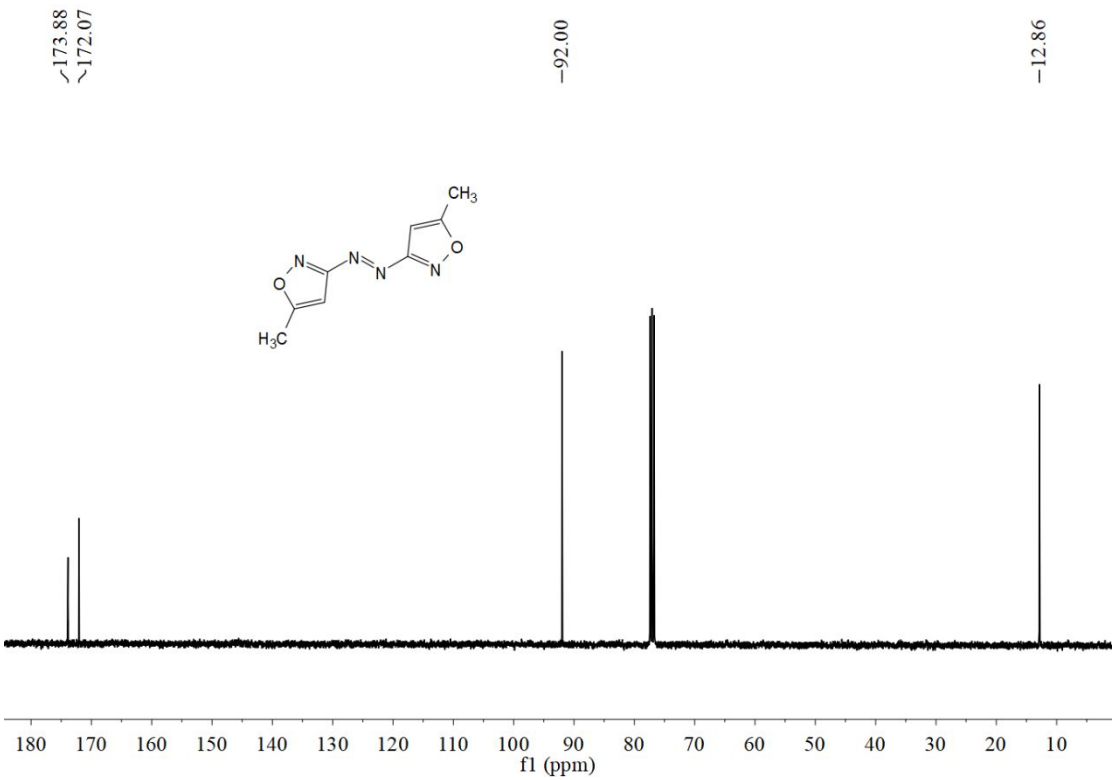


Figure S82. ^{13}C NMR spectrum ($CDCl_3$) of **2k**

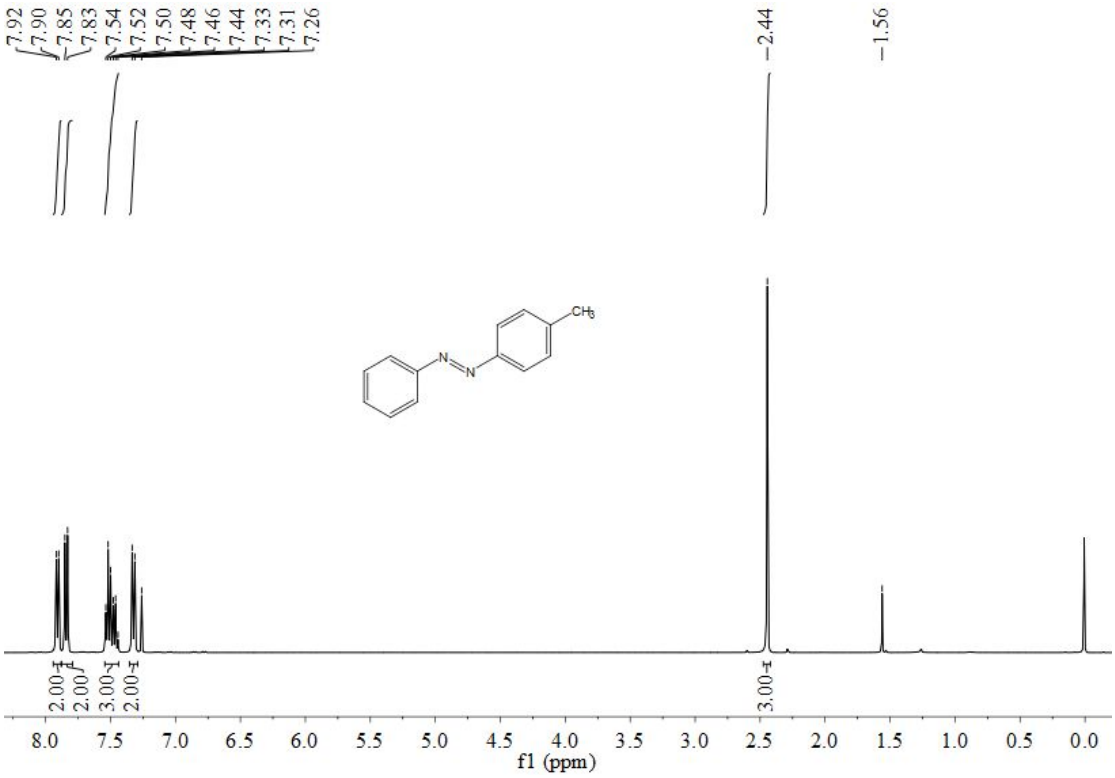


Figure S83. ^{1}H NMR spectrum ($CDCl_3$) of **4a**

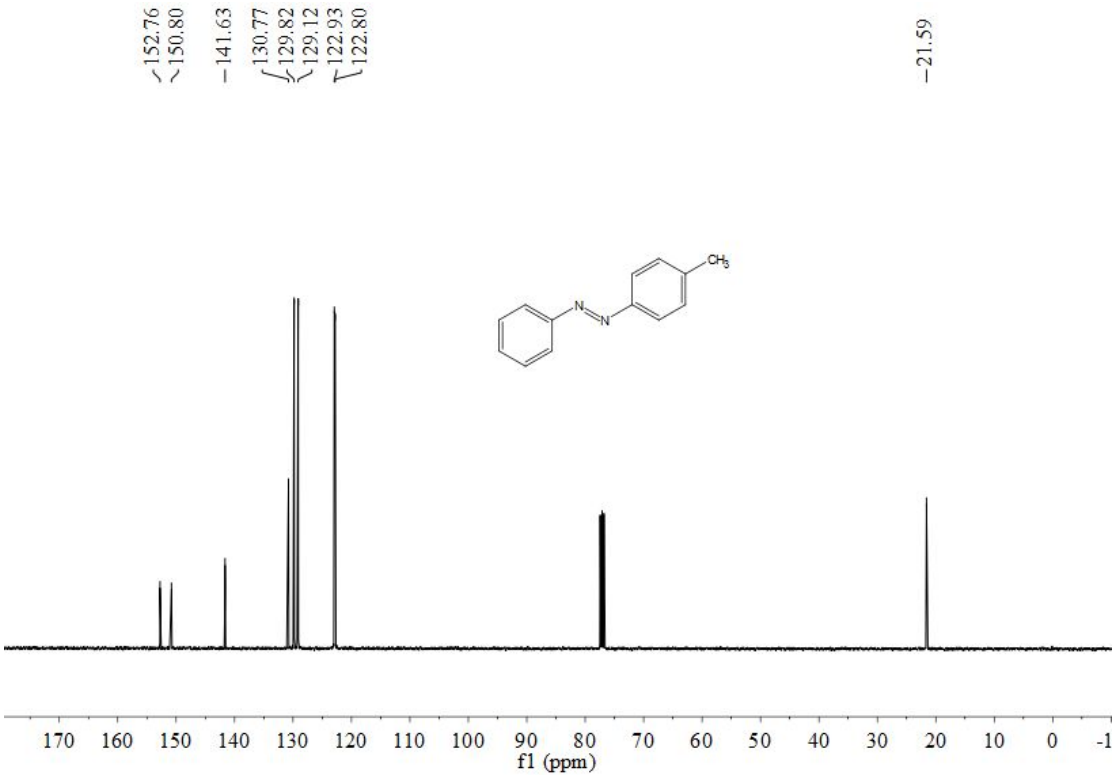


Figure S84. ^{13}C NMR spectrum ($CDCl_3$) of **4a**

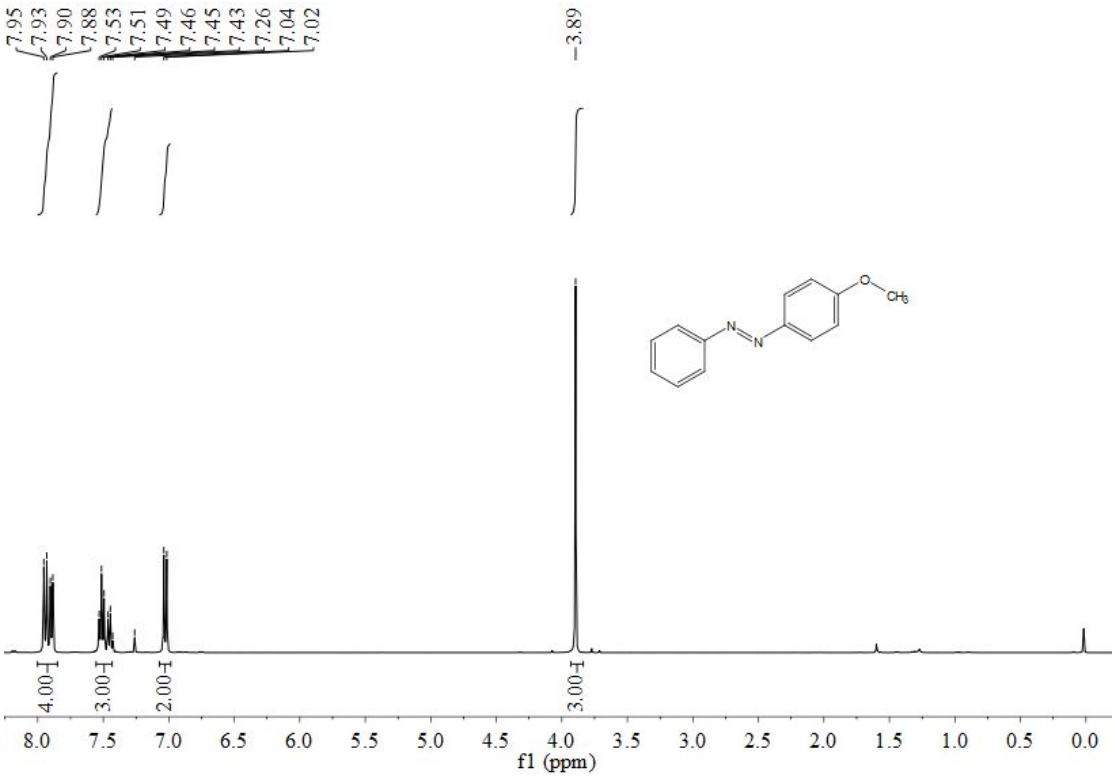


Figure S85. ^{1}H NMR spectrum ($CDCl_3$) of **4b**

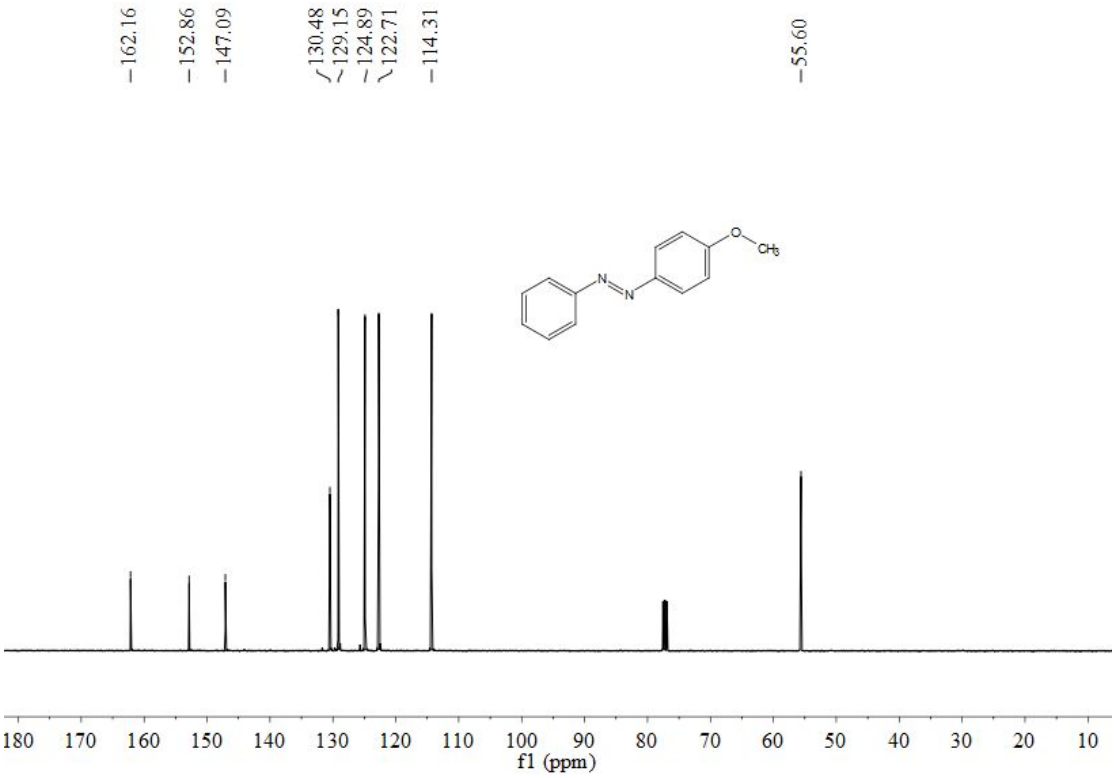


Figure S86. ^{13}C NMR spectrum ($CDCl_3$) of **4b**

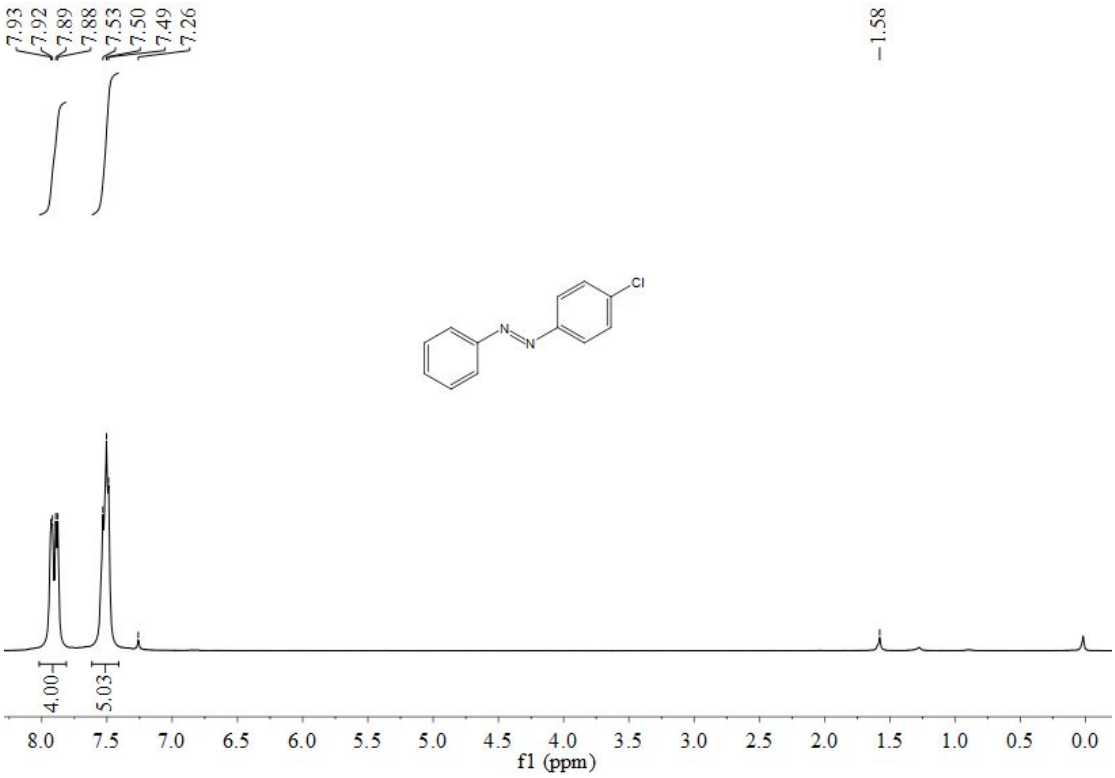


Figure S87. ^{1}H NMR spectrum ($CDCl_3$) of **4c**

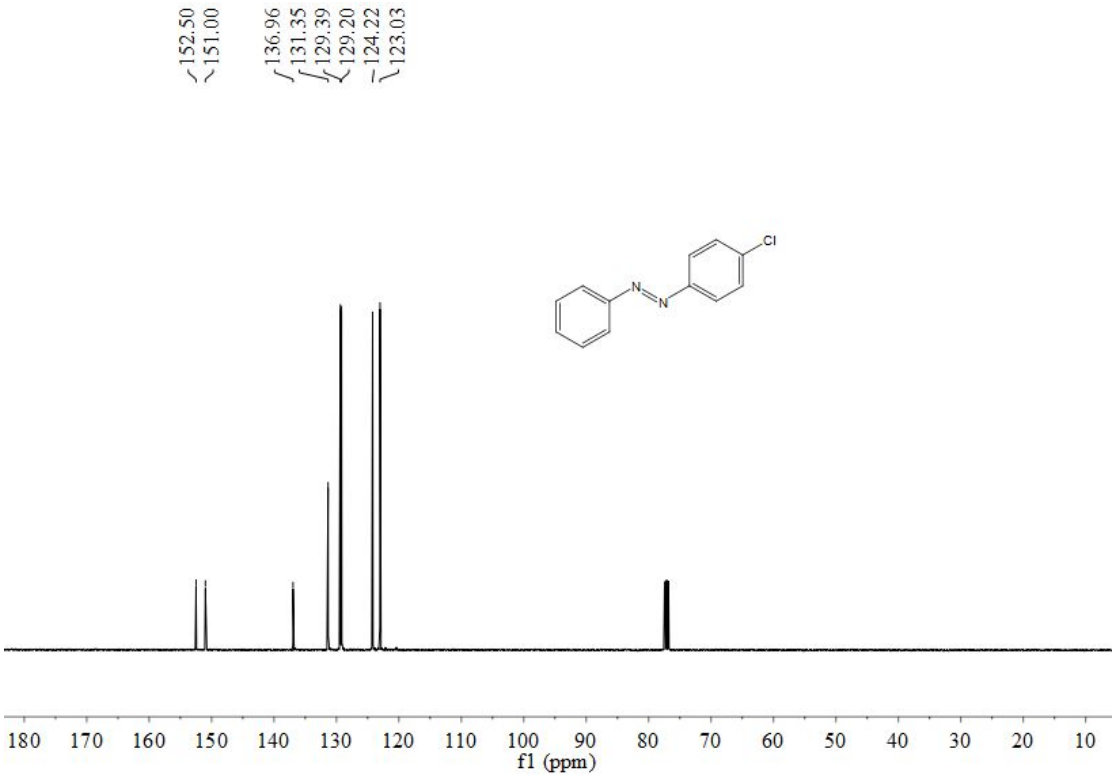


Figure S88. ^{13}C NMR spectrum ($CDCl_3$) of **4c**

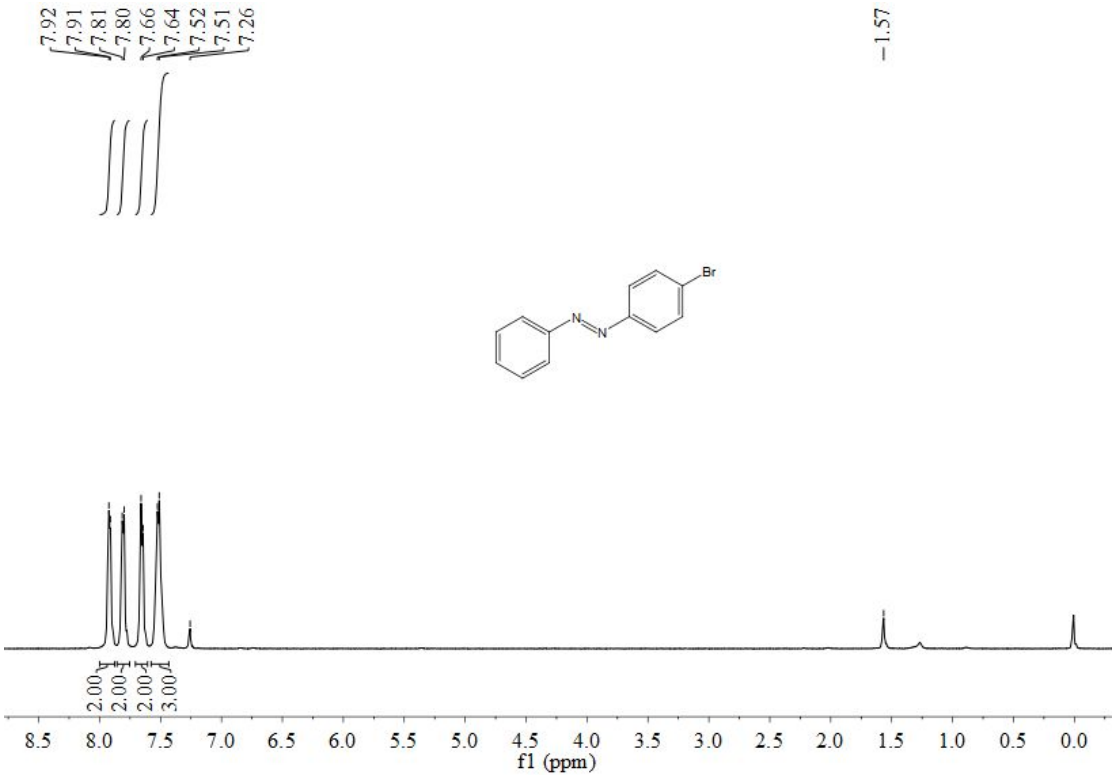


Figure S89. ^{1}H NMR spectrum ($CDCl_3$) of **4d**

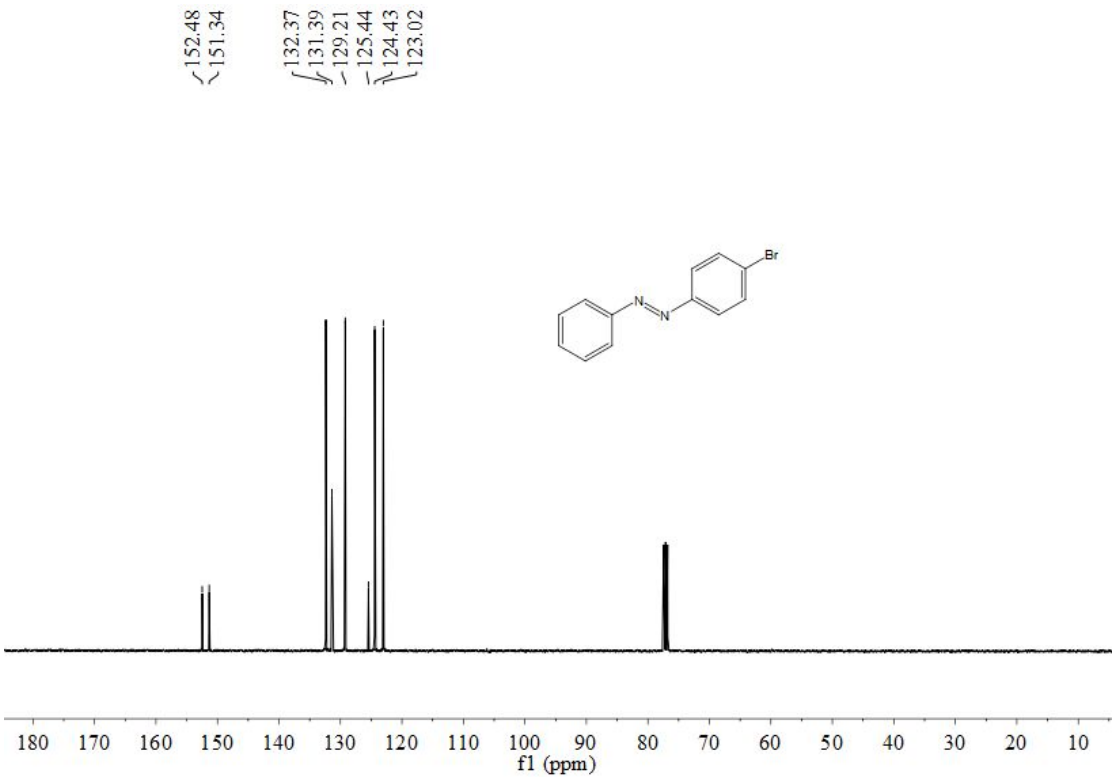


Figure S90. ^{13}C NMR spectrum ($CDCl_3$) of **4d**

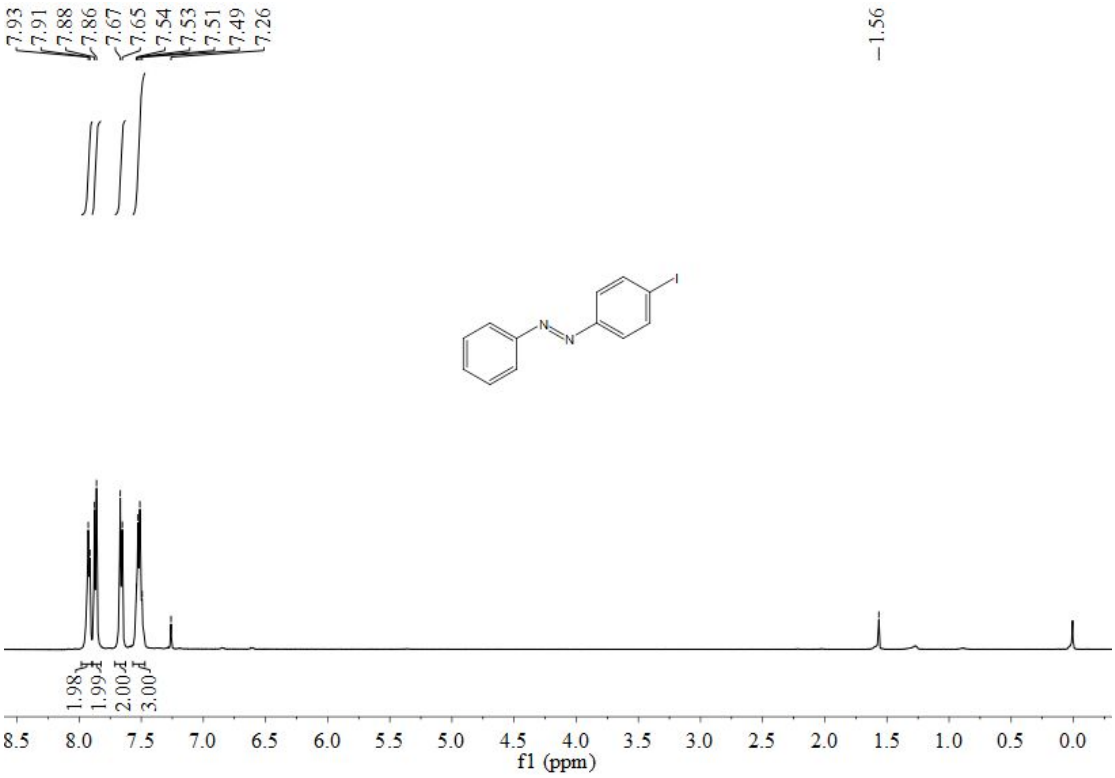


Figure S91. ^{1}H NMR spectrum ($CDCl_3$) of **4e**

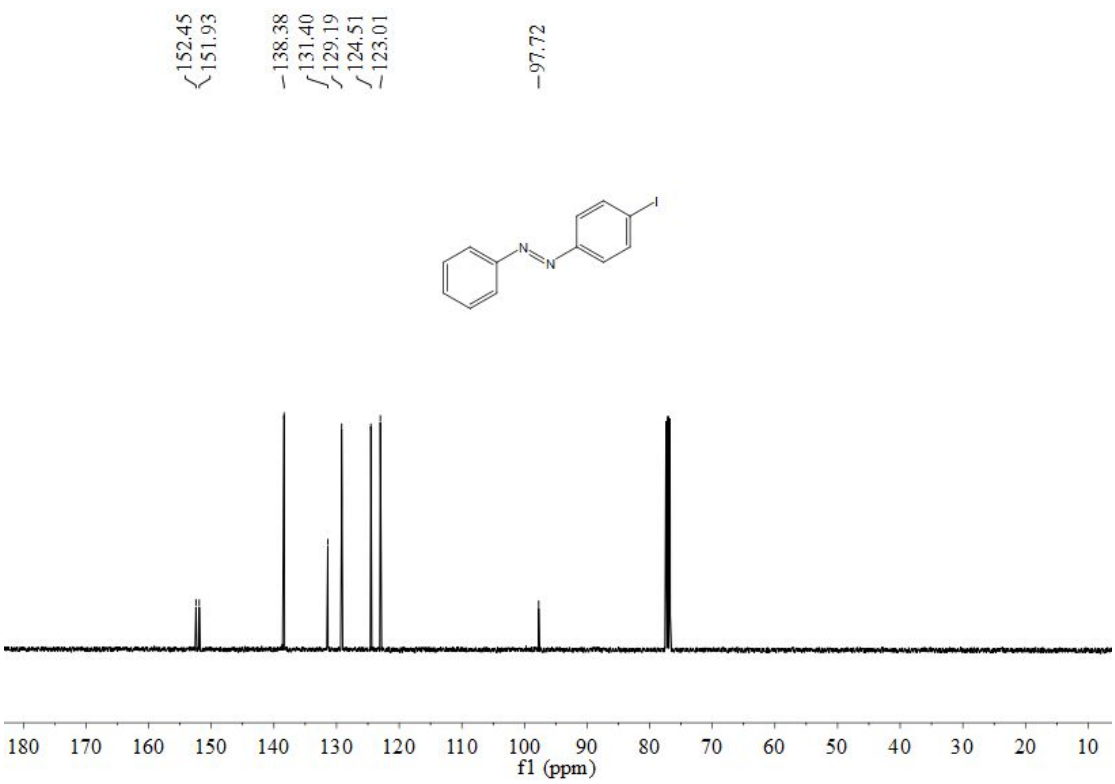


Figure S92. ^{13}C NMR spectrum ($CDCl_3$) of **4e**

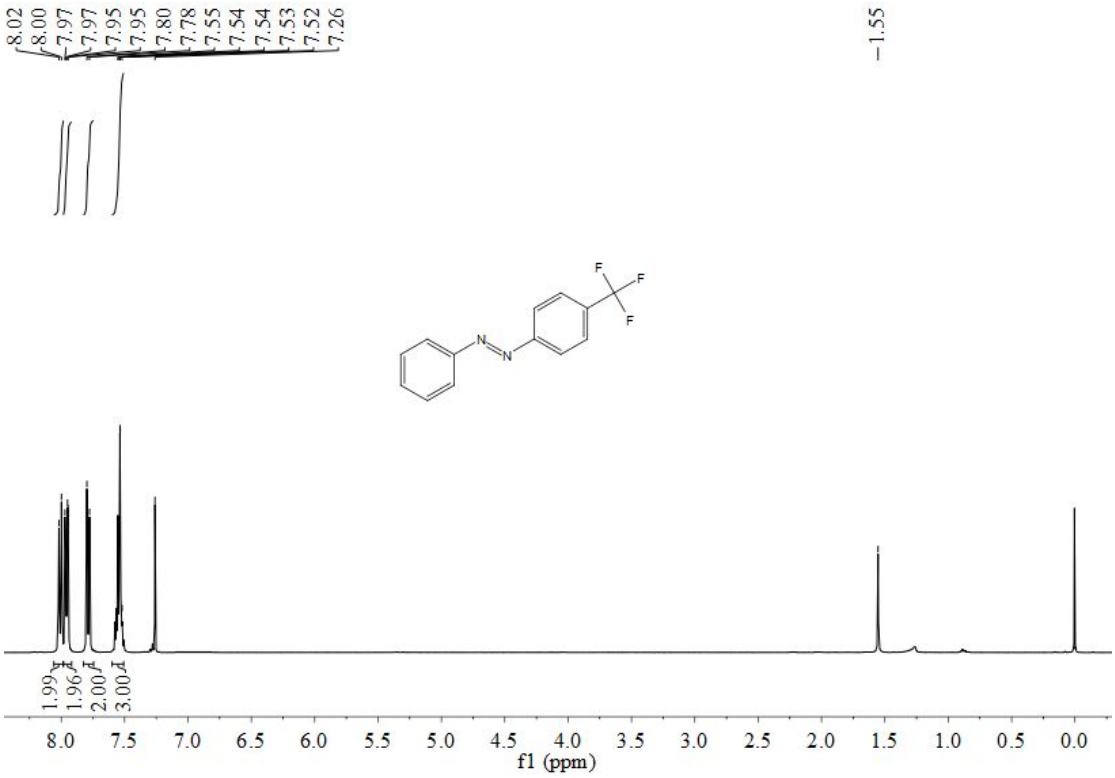


Figure S93. ^{1}H NMR spectrum ($CDCl_3$) of **4f**

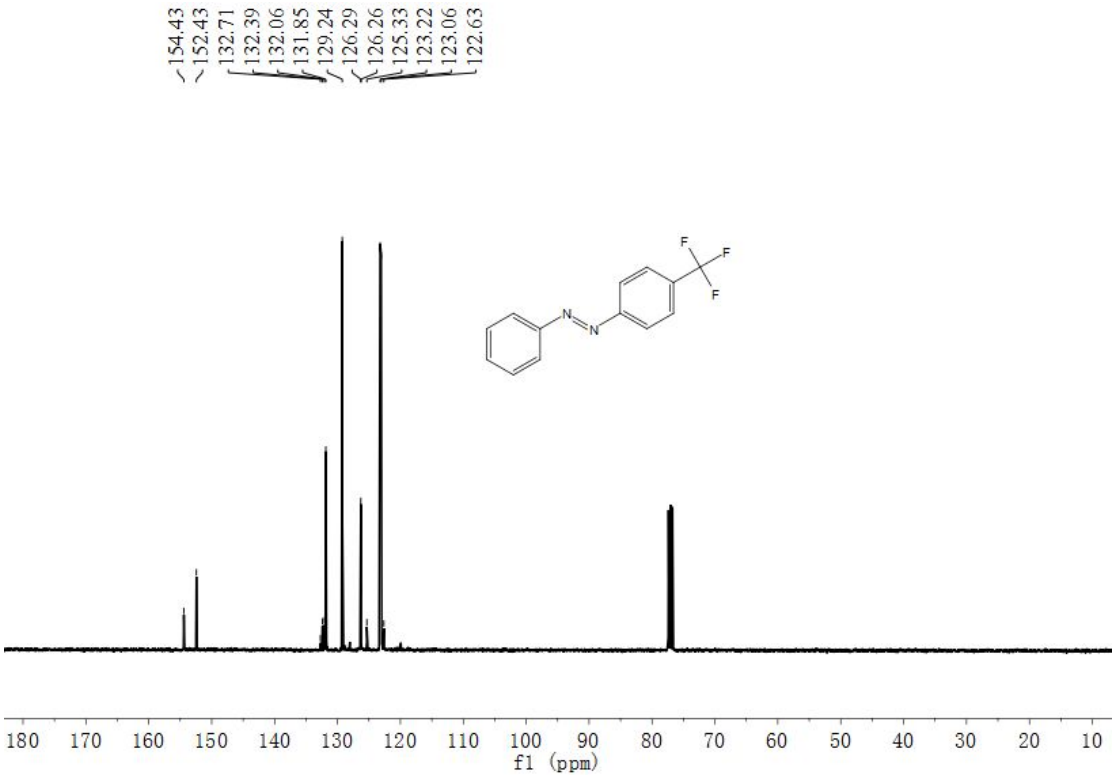


Figure S94. ^{13}C NMR spectrum ($CDCl_3$) of **4f**

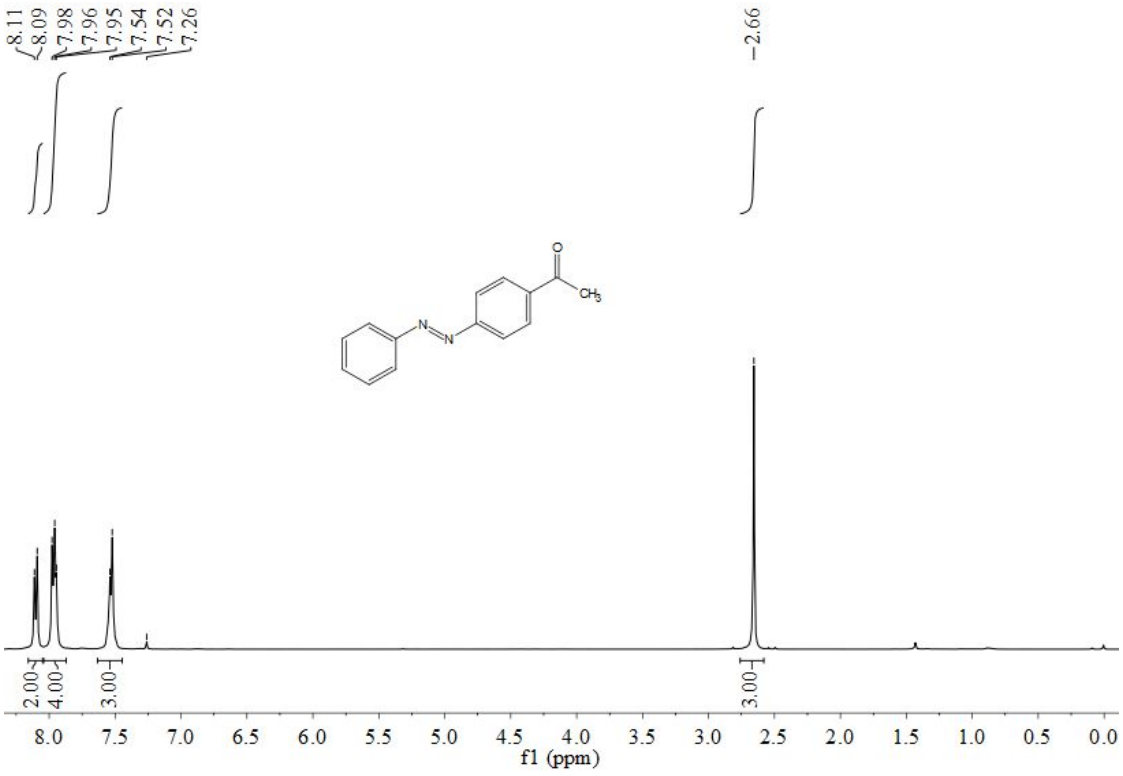


Figure S95. ^{1}H NMR spectrum ($CDCl_3$) of **4g**

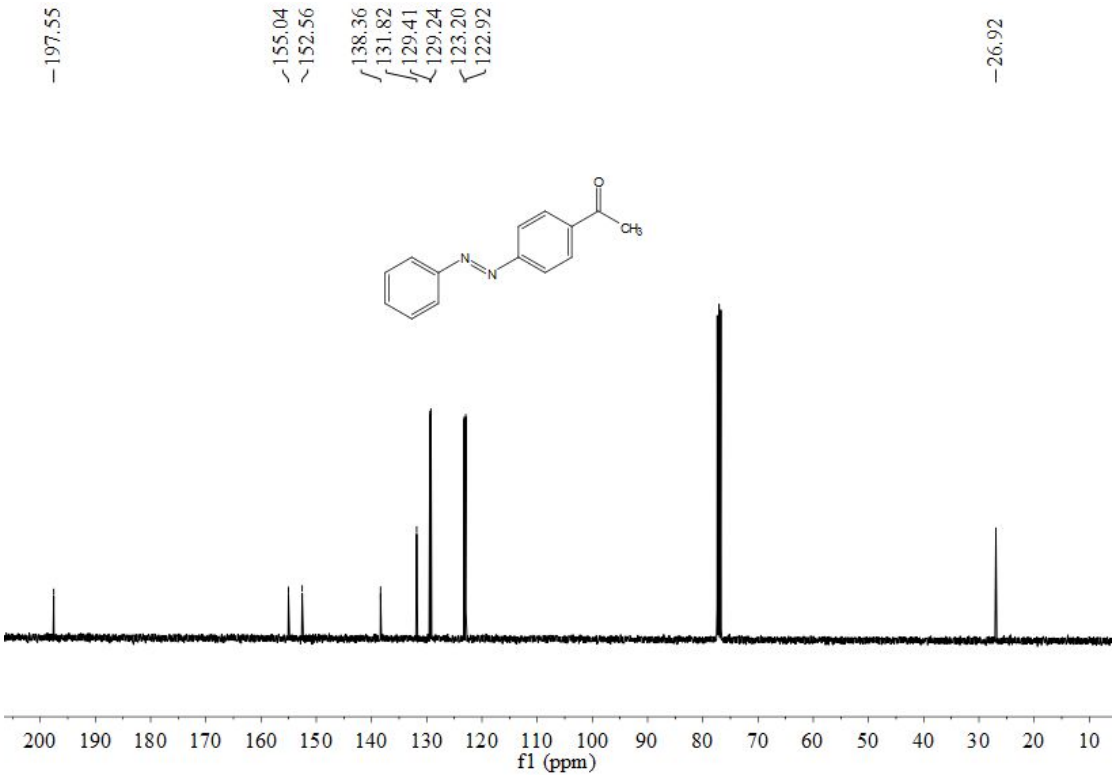


Figure S96. ^{13}C NMR spectrum ($CDCl_3$) of **4g**

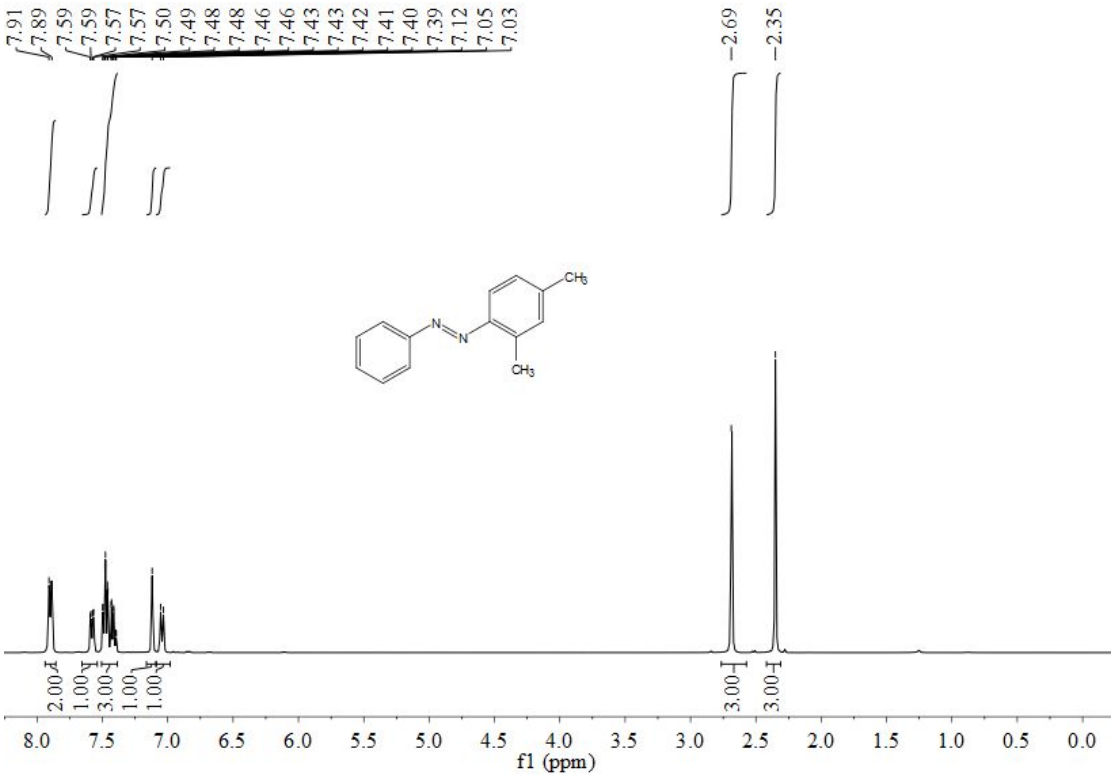


Figure S97. ^{1}H NMR spectrum ($CDCl_3$) of **4h**

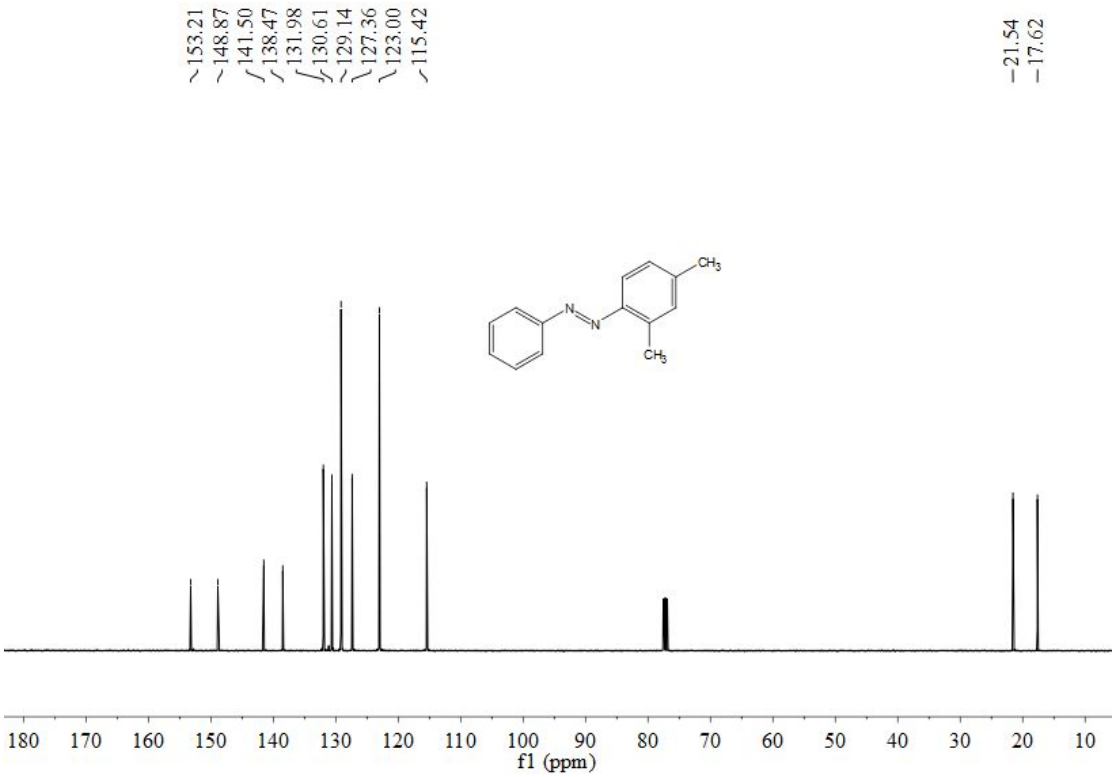


Figure S98. ^{13}C NMR spectrum ($CDCl_3$) of **4h**

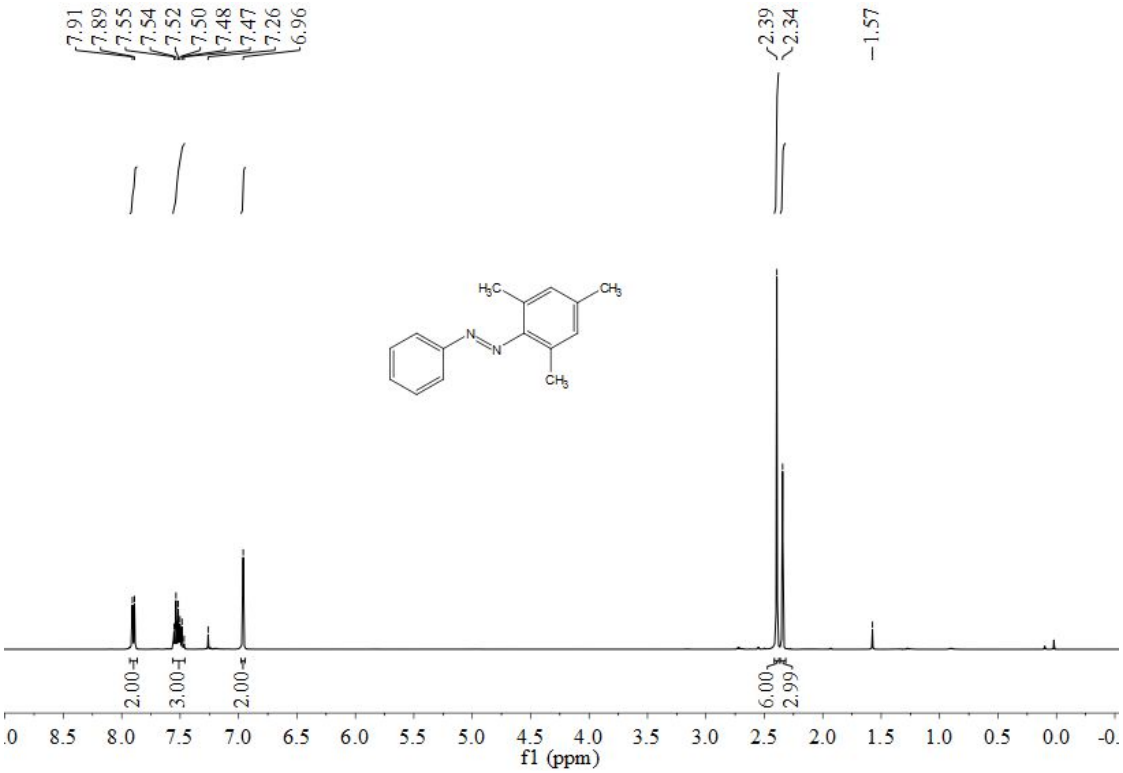


Figure S99. ^{1}H NMR spectrum ($CDCl_3$) of **4i**

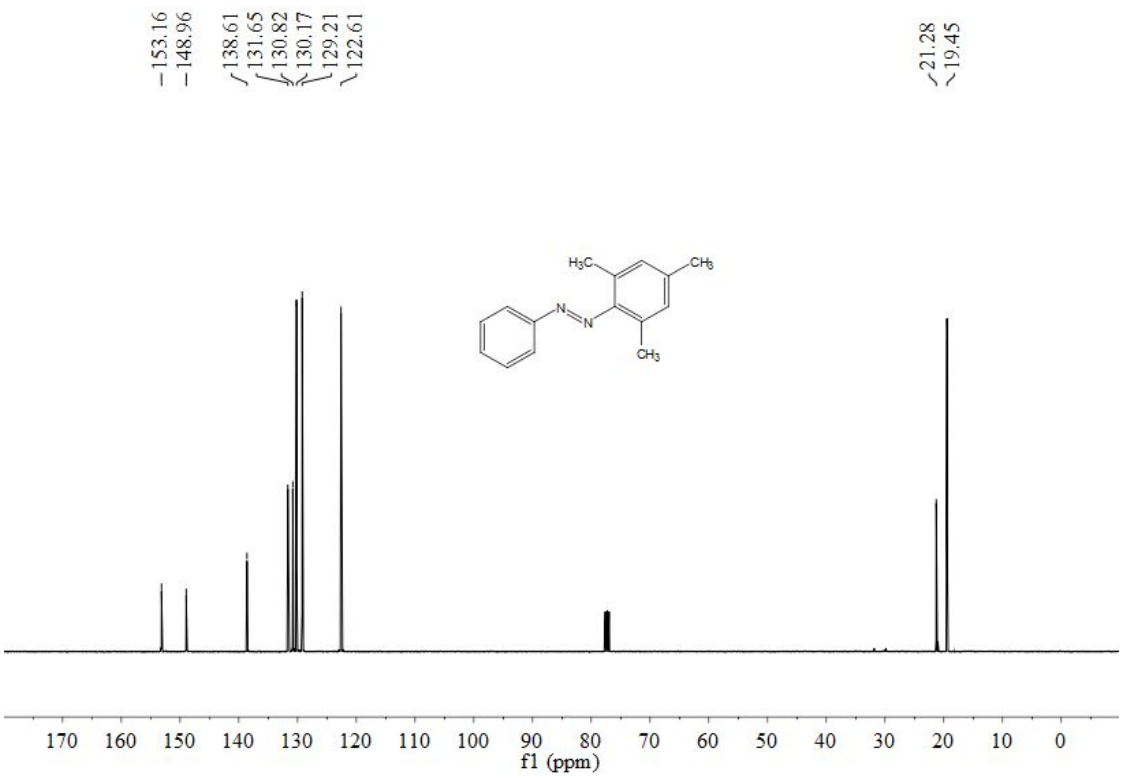


Figure S100. ^{13}C NMR spectrum ($CDCl_3$) of **4i**

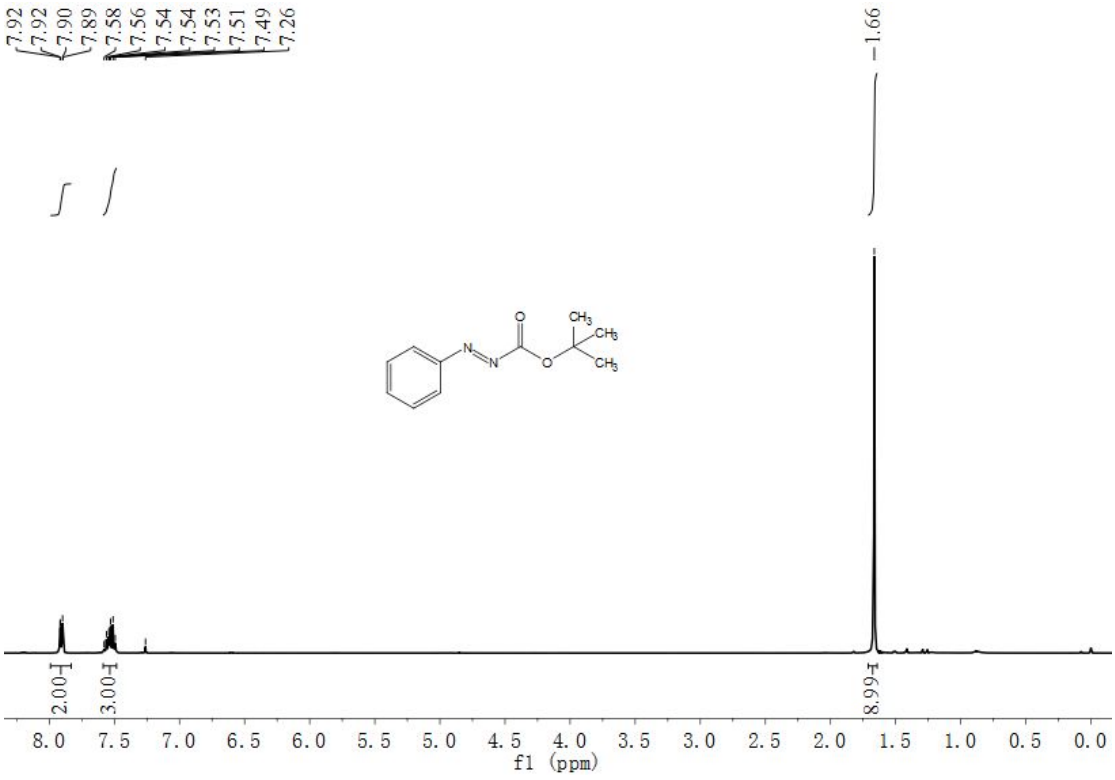


Figure S101. ^{1}H NMR spectrum ($CDCl_3$) of **4j**

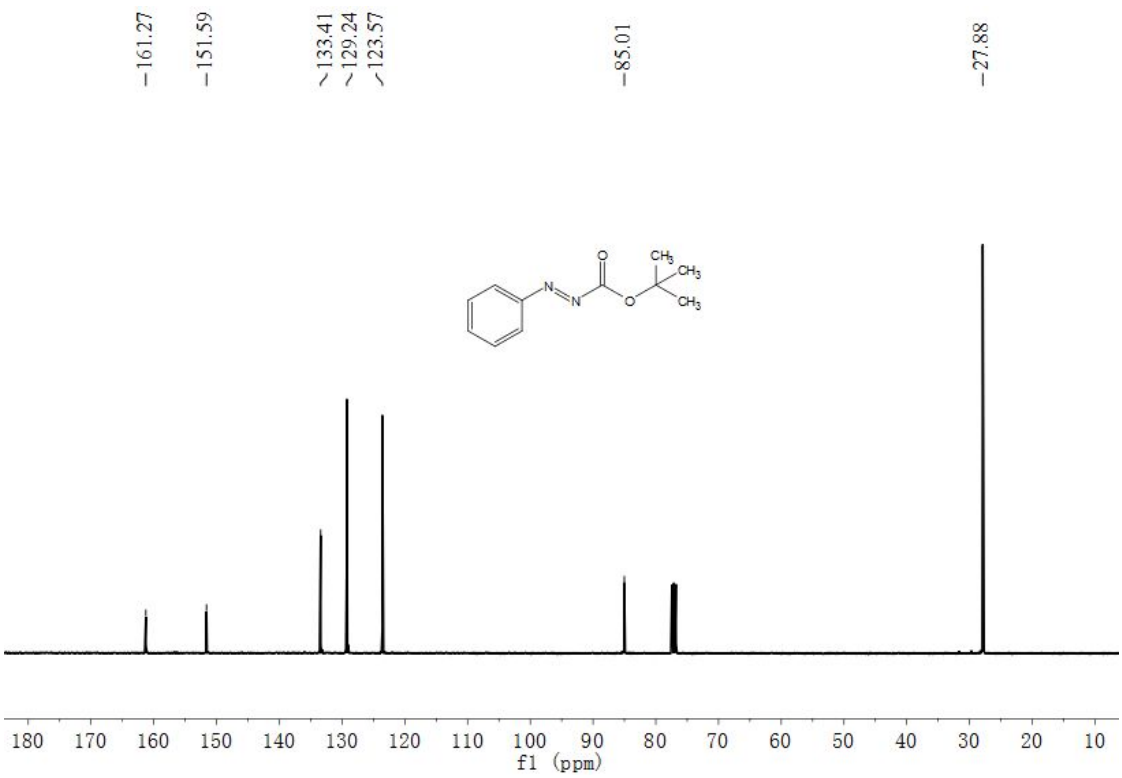


Figure S102. ^{13}C NMR spectrum ($CDCl_3$) of **4j**

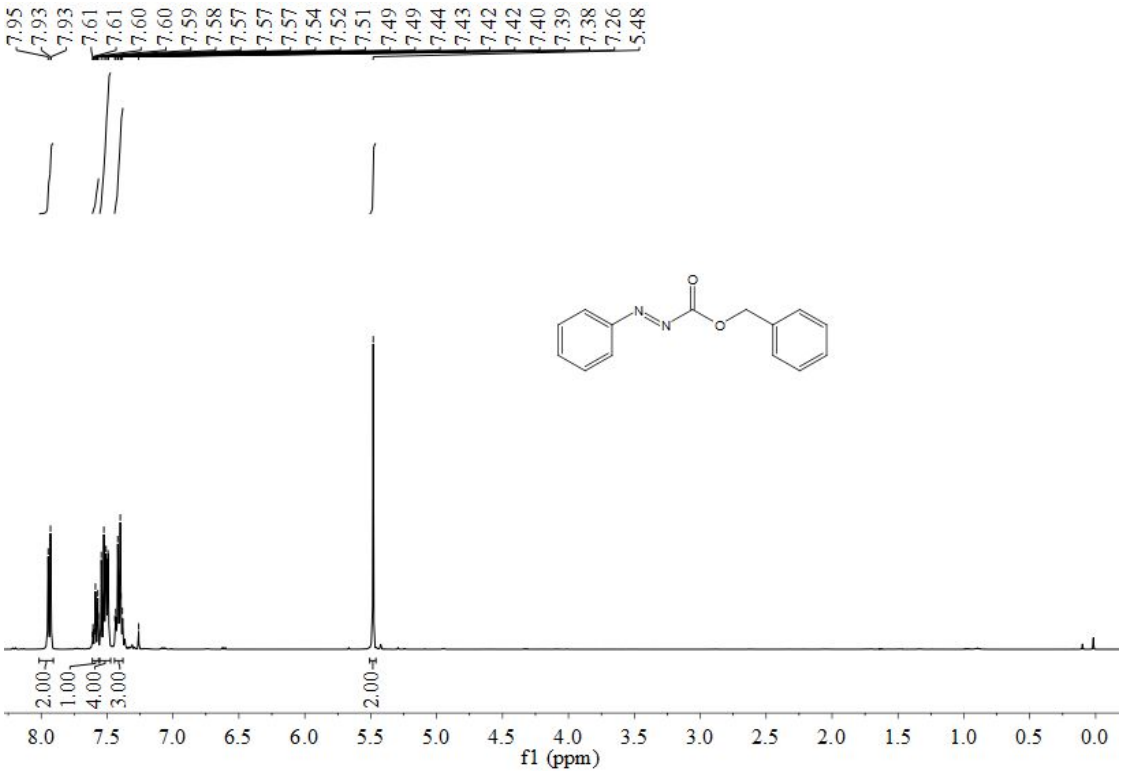


Figure S103. ^{1}H NMR spectrum ($CDCl_3$) of **4k**

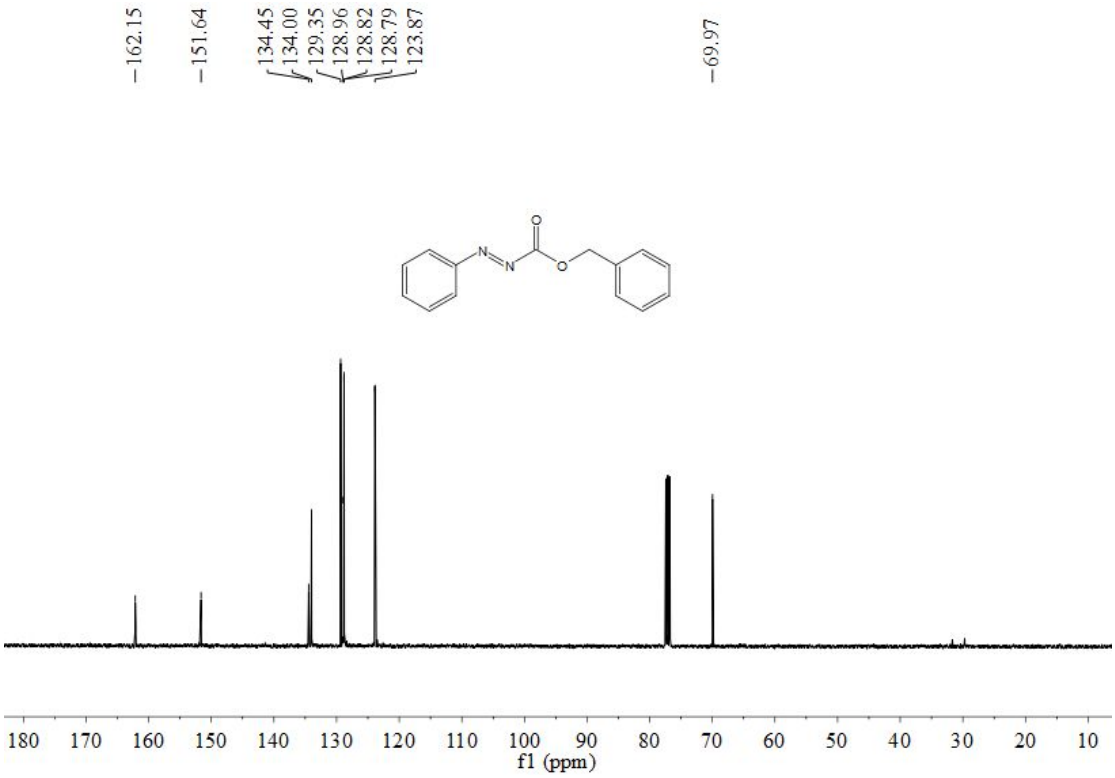


Figure S104. ^{13}C NMR spectrum ($CDCl_3$) of **4k**

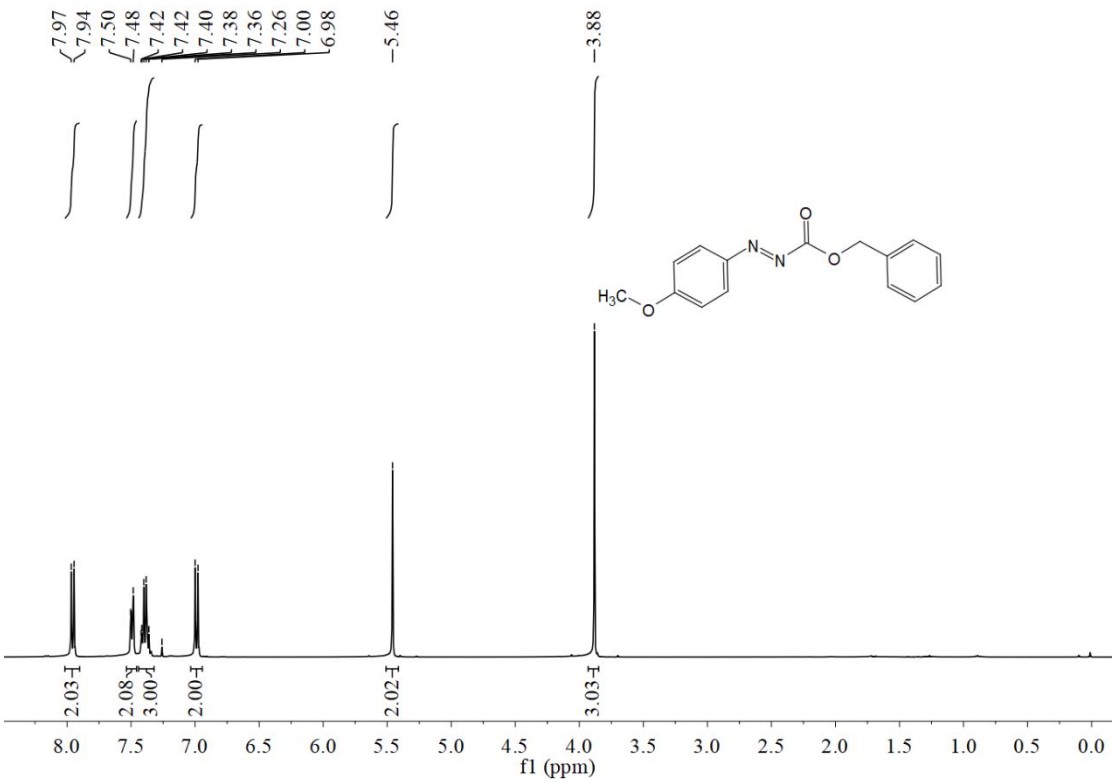


Figure S105. ^{1}H NMR spectrum ($CDCl_3$) of **4l**

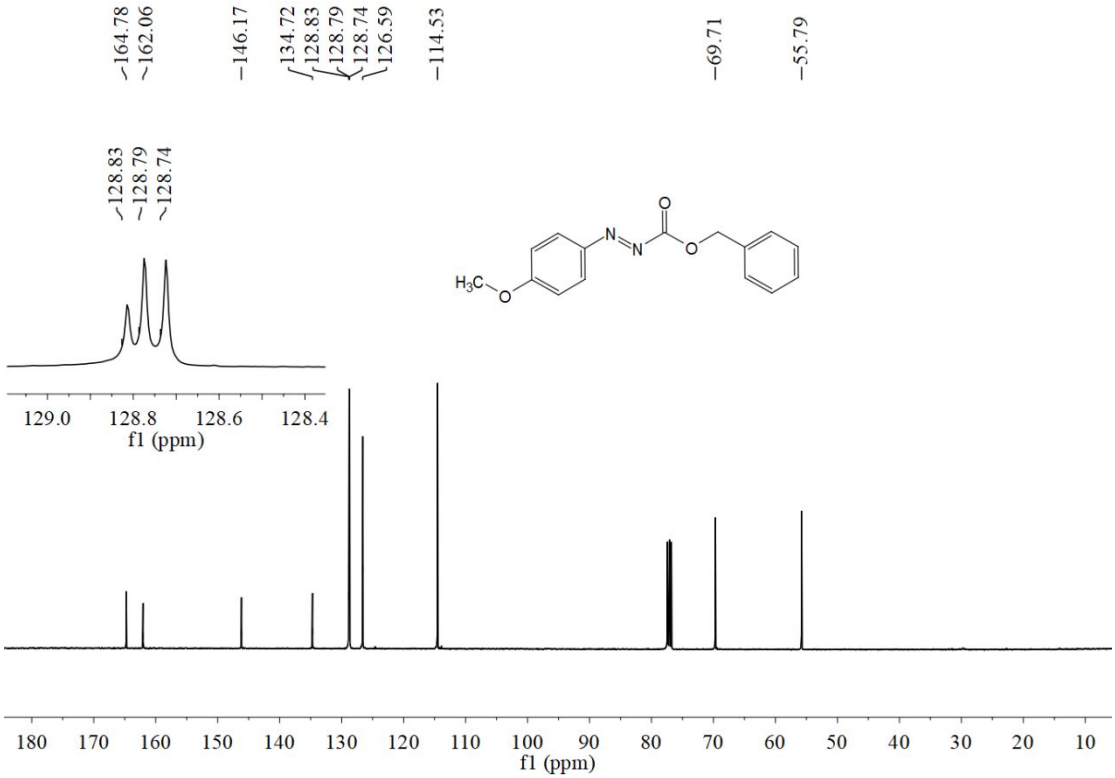


Figure S106. ^{13}C NMR spectrum ($CDCl_3$) of **4l**