Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Chemoselective Electrochemical Reduction of Nitroarenes with Gaseous Ammonia

Chang Liu, [a] Jin Li, [b] Na Wu, [a] and Xu Cheng*[a]

[1] *Institute of Chemistry and Biomedical Sciences, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, National Demonstration Center for Experimental Chemistry Education, Nanjing University, Nanjing, 210023, China*

[2] *Jiangsu Provincial Engineering Laboratory of Advanced Materials for Salt Chemical Industry, College of Chemical Engineering, Huaiyin Institute of Technology, Huaian 223003, China*

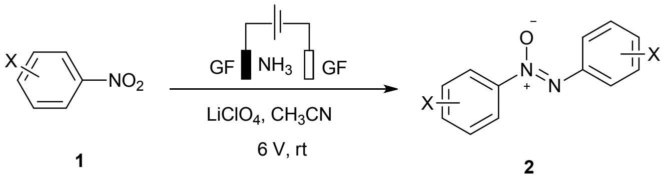
Contents

1. General Information

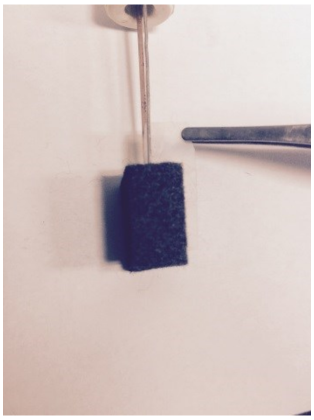
All reactions that required anhydrous conditions were carried with standard procedures. Unless otherwise noted, chemicals were commercial available and used without further purification. Solvents were dried by distillation over the appropriate drying reagents. Column chromatography was generally performed on silica gel (300-400 mesh). Reactions were monitored by GC/MS, ^{1}H NMR, or by TLC on silica gel plates. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured on 400 M spectrometer. Chemical shifts are recorded in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. High-resolution mass spectra (HRMS) was tested from Agilent mass spectrometer which is equipped with an ESI, APCI source and a Q-TOF detector, and all the sample were dissolved in MeOH.

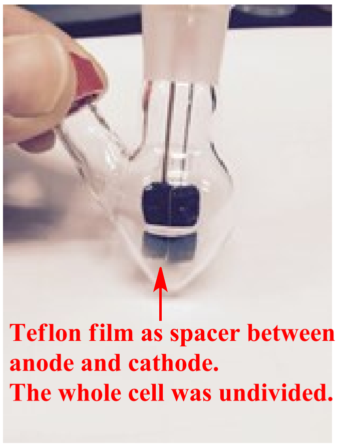
2. General procedure for preparation of the substrates

General procedure A for azoxybenzenes

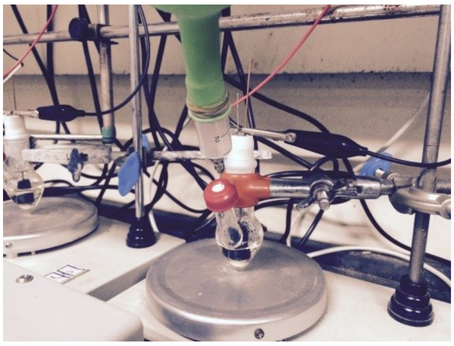


A 10 mL two-necked heart-shaped flask was charged with substrate **1** (0.2 mmol), $LiClO_4$ (0.1 mmol) and a magnetic stir bar. The flask was equipped with a rubber septum, through which graphite felt (2 cm x 1 cm x 0.5 cm) as anode and cathode were installed. Two electrodes were separated with a Teflon film that acted as a spacer between anode and cathode. The graphite felt anode attached to a platinum wire and cathode attached to a silver wire. A Teflon wire was tied around two electrodes. The flask was evacuated and backfilled with ammonia and 5 mL MeCN was added via syringe. The constant voltage electrolysis in this undivided cell was carried out under 6 V at room temperature. After the reaction finished as monitored with TLC and GC-MS analysis, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product **2**.[1]

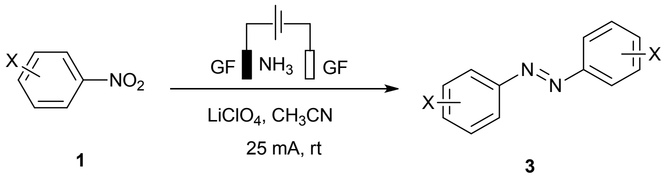




Teflon film as spacer between anode and cathode.
The whole cell was undivided.

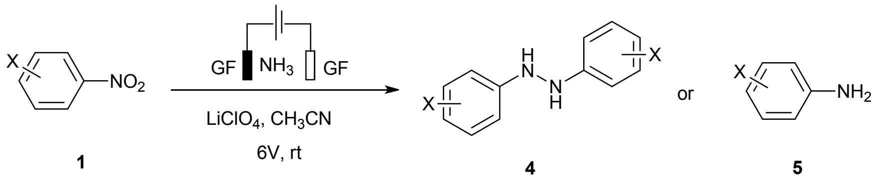


General procedure B for azobenzenes



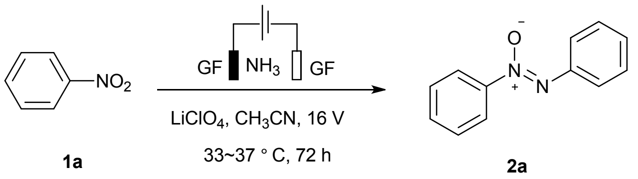
A 10 mL two-necked heart-shaped flask was charged with substrate **1** (0.2 mmol), $LiClO_4$ (0.1 mmol) and a magnetic stir bar. The flask was equipped with a rubber septum, through which graphite felt (2 cm x 1 cm x 0.5 cm) as anode and cathode were installed. Two electrodes were separated with a Teflon film that acted as a spacer between anode and cathode. The graphite felt anode attached to a platinum wire and cathode attached to a silver wire. A Teflon wire was tied around two electrodes. The flask was evacuated and backfilled with ammonia and 5 mL MeOH was added via syringe. The constant current electrolysis in this undivided cell was carried out under 25 mA at room temperature. After the reaction finished as monitored with TLC and GC-MS analysis, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product **3**.[1]

General procedure C for hydrazoarenes or aniline derivatives



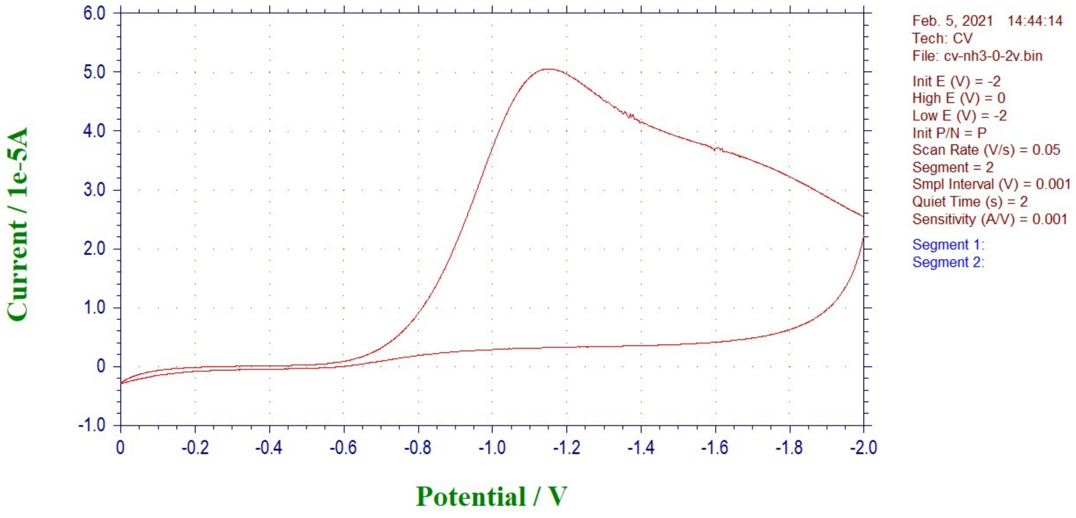
A 10 mL two-necked heart-shaped flask was charged with substrate **1** (0.2 mmol), $LiClO_4$ (0.1 mmol) and a magnetic stir bar. The flask was equipped with a rubber septum, through which graphite felt (2 cm x 1 cm x 0.5 cm) as anode and cathode were installed. Two electrodes were separated with a Teflon film that acted as a spacer between anode and cathode. The graphite felt anode attached to a platinum wire and cathode attached to a silver wire. A Teflon wire was tied around two electrodes. The flask was evacuated and backfilled with ammonia and 5 mL MeCN was added via syringe. The constant voltage electrolysis in this undivided cell was carried out under 6 V at room temperature. After the reaction finished as monitored with TLC and GC-MS analysis, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product **4** or **5**.[1]

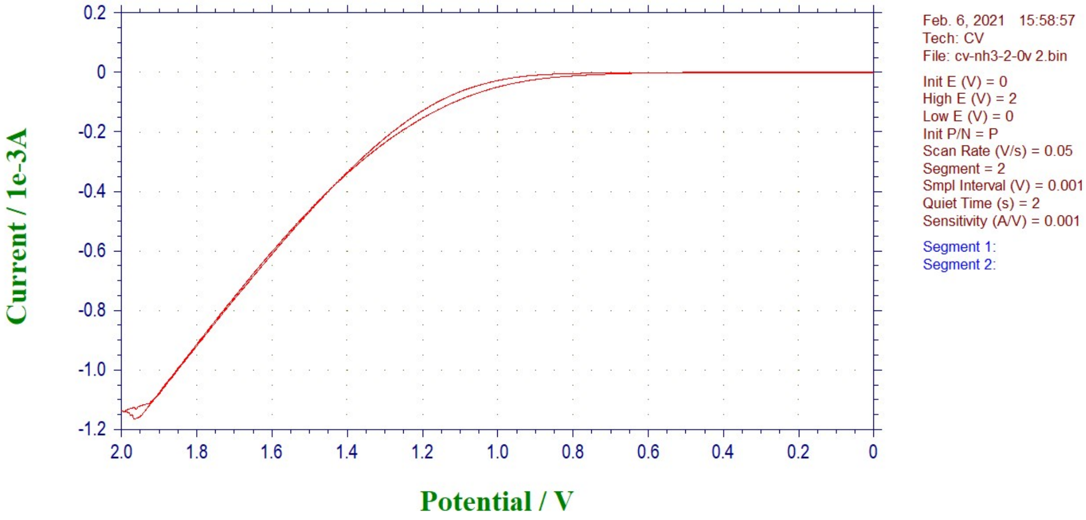
3. Gram scale reaction



A 500 mL cup was charged with the substrate **1a** (100 mmol, 12.3 g), LiCl (50 mmol, 2.11 g), MeCN (300 mL) and a magnetic stir bar. The cup was equipped with a plastic cover, graphite felt (8 cm x 5 cm x 1 cm) as anode and cathode. The graphite felt anode attached to a platinum wire and cathode attached to a silver wire. The cup was backfilled with ammonia for 3 times. The mixture was stirred under constant voltage electrolysis of 16 V. After the reaction was completed by monitoring with GC-MS analysis, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product **2a** (6.5 g, 66 %).

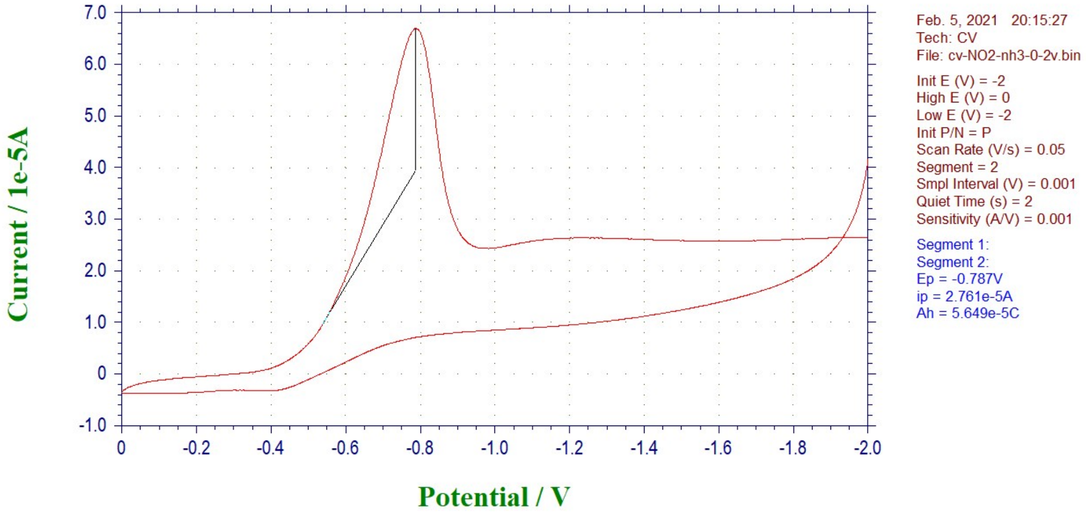
4. Cyclic voltammetry Experiments

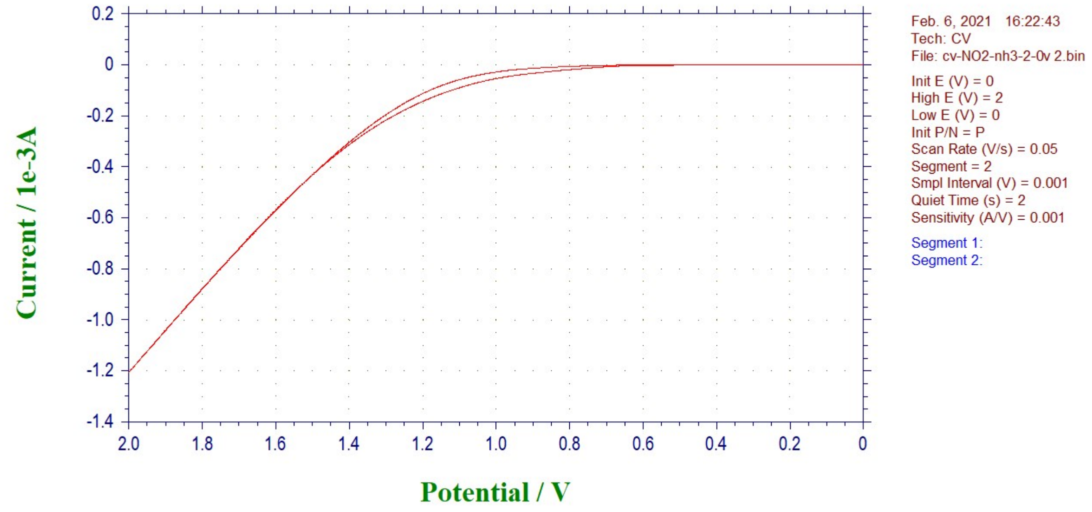




Blank sample using **glassy carbon** working electrode

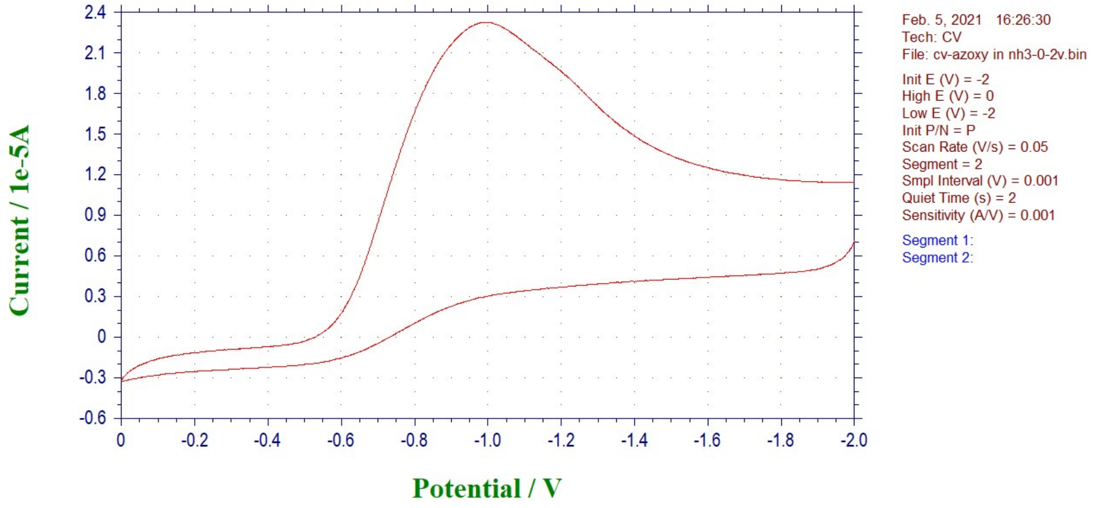
A solution of 5 mL MeCN saturated with ammonia gas was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.

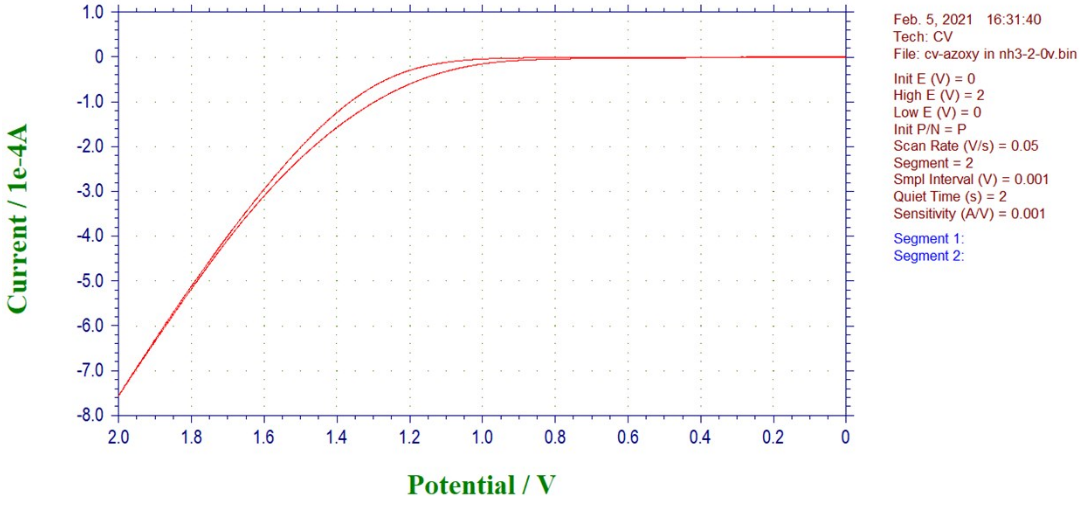




Blank sample using **glassy carbon** working electrode

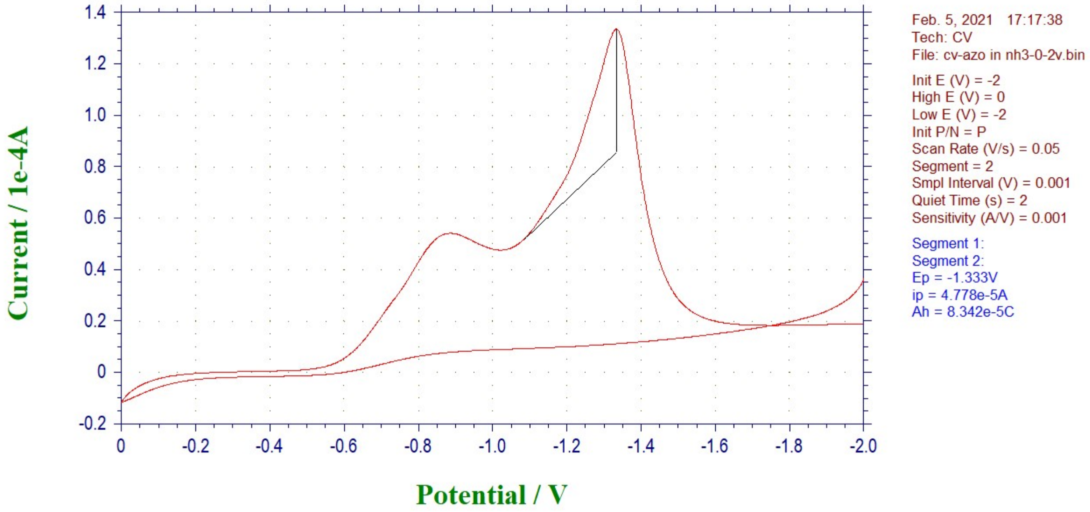
A solution of 5 mL MeCN saturated with ammonia gas was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.

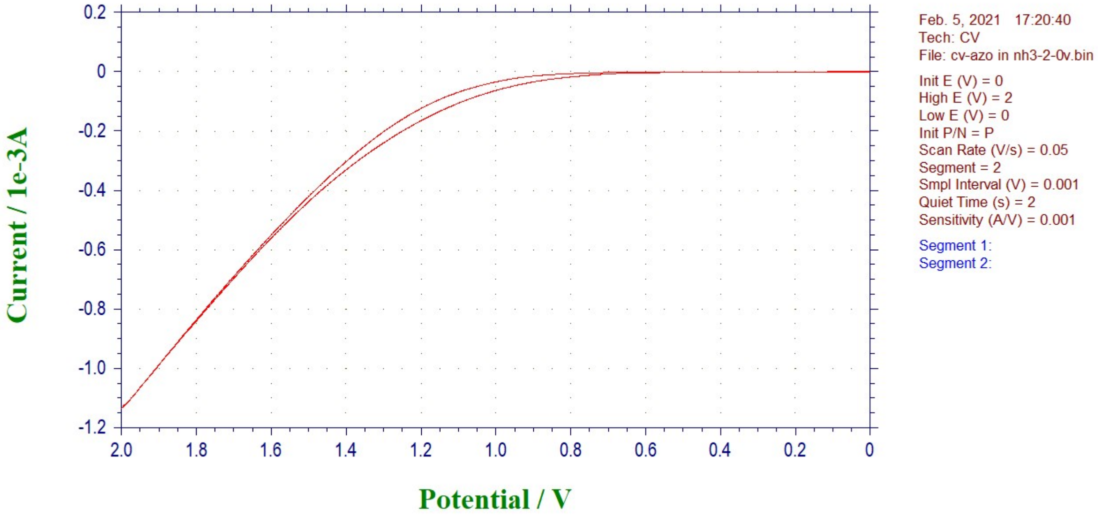




Cyclic voltammetry Experiment of **2a** under ammonia using **glassy carbon** working electrode

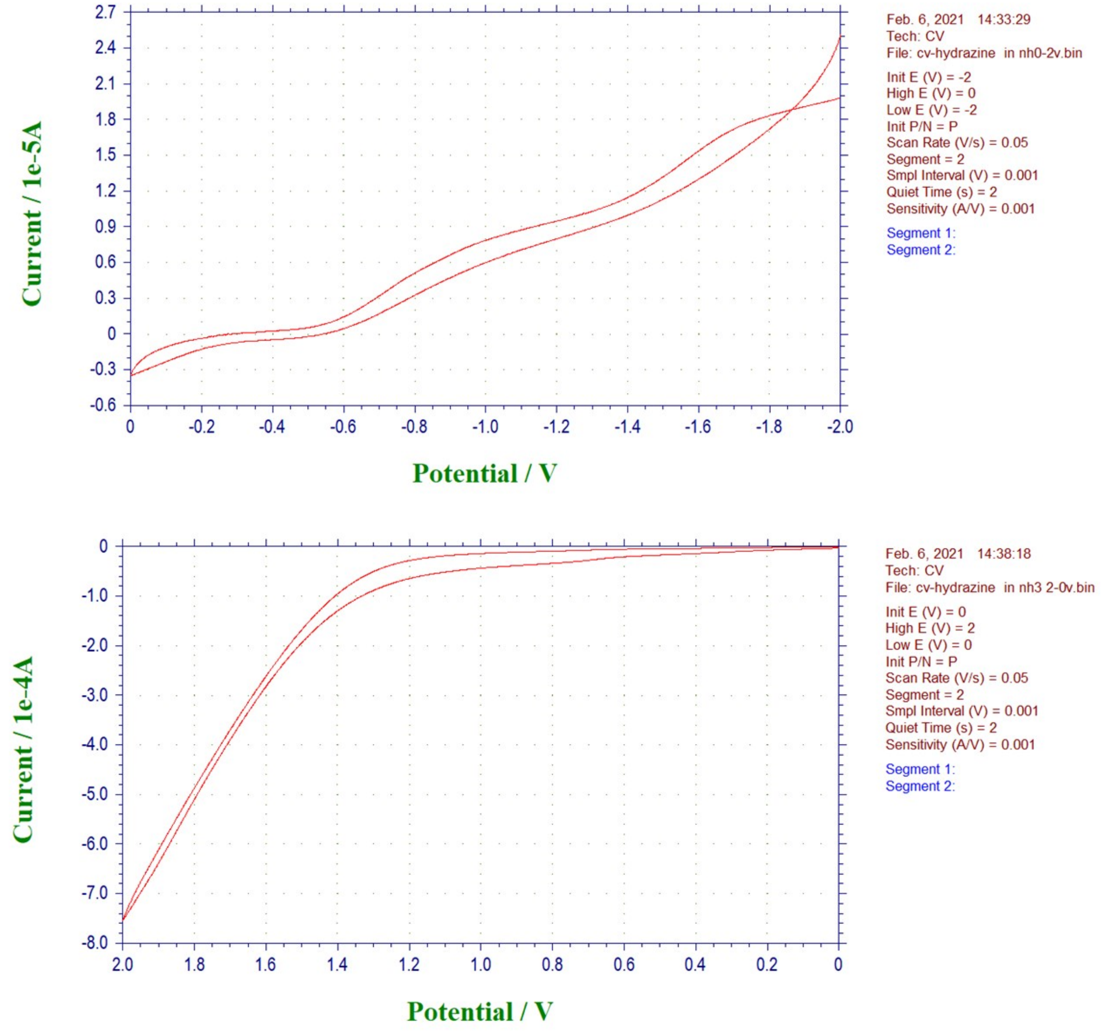
A solution of **2a** (0.1 mmol), $LiClO_4$ (0.1 mmol) in 5 mL MeCN saturated with ammonia gas was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.





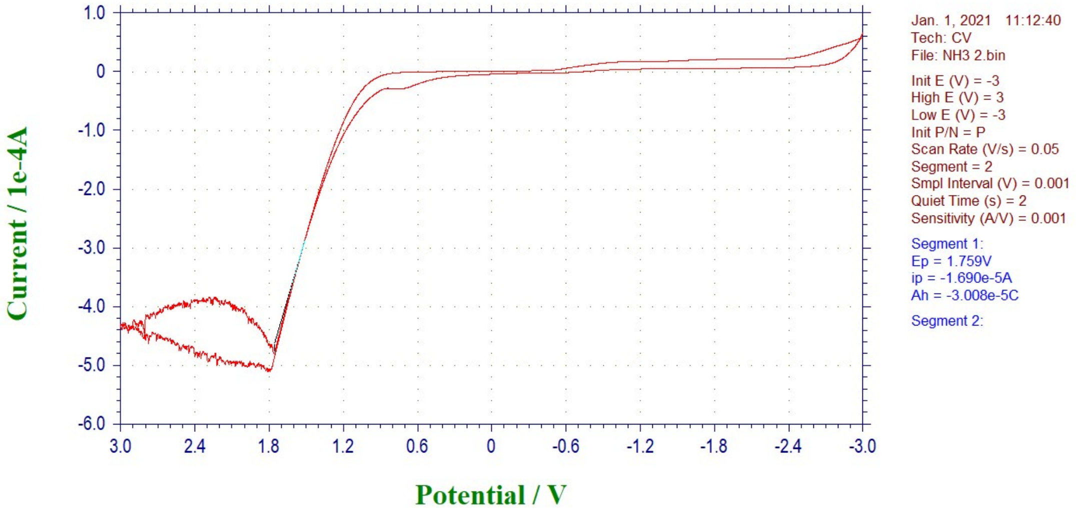
Cyclic voltammetry Experiment of **3a** under ammonia using **glassy carbon** working electrode

A solution of **3a** (0.1 mmol), $LiClO_4$ (0.1 mmol) in 5 mL MeCN saturated with ammonia gas was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.



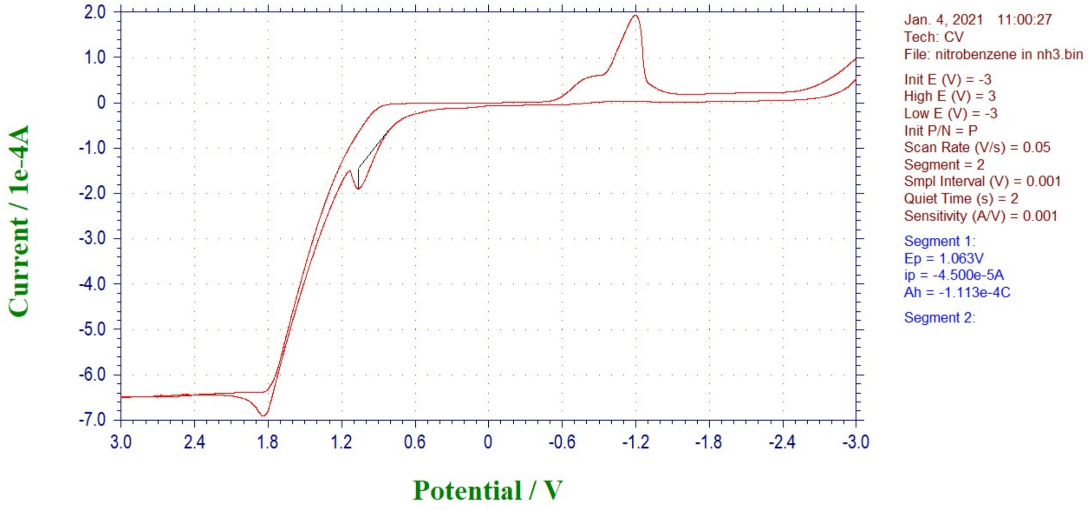
Cyclic voltammetry Experiment of **4a** under ammonia using **glassy carbon** working electrode

A solution of **4a** (0.1 mmol), $LiClO_4$ (0.1 mmol) in 5 mL MeCN saturated with ammonia gas was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.



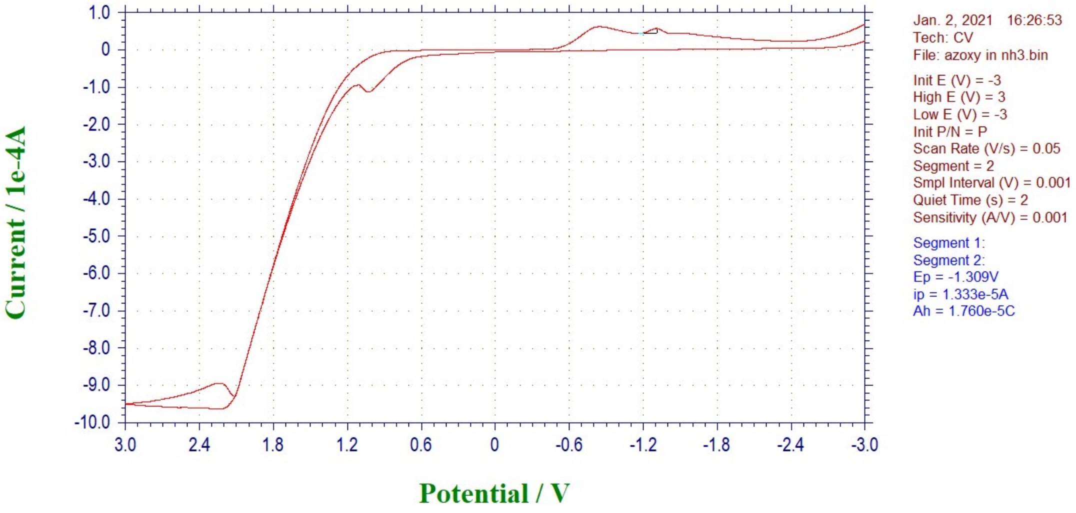
Blank sample using **glassy carbon** working electrode

A solution of 5 mL MeCN saturated with ammonia gas was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.



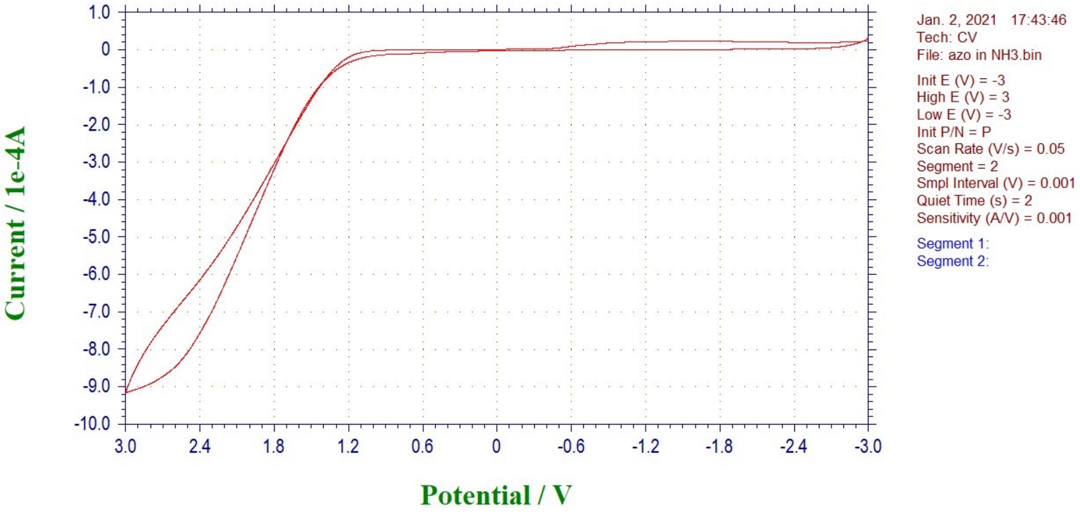
Cyclic voltammetry Experiment of **1a** under ammonia using **glassy carbon** working electrode

A solution of **1a** (0.2 mmol), $LiClO_4$ (0.1 mmol) in 5 mL MeCN saturated with ammonia gas was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.



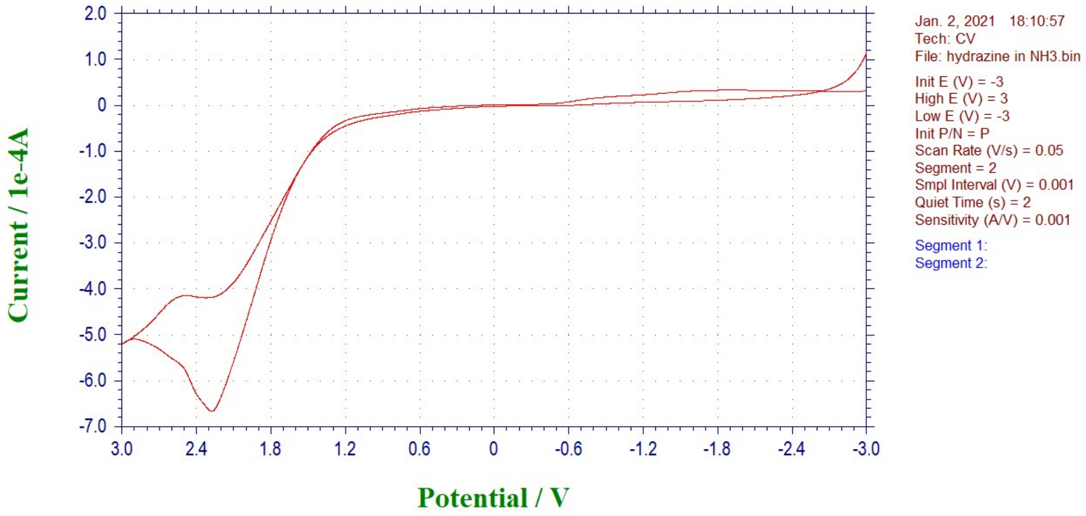
Cyclic voltammetry Experiment of **2a** under ammonia using **glassy carbon** working electrode

A solution of **2a** (0.1 mmol), $LiClO_4$ (0.1 mmol) in 5 mL MeCN saturated with ammonia gas was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.



Cyclic voltammetry Experiment of **3a** under ammonia using **glassy carbon** working electrode

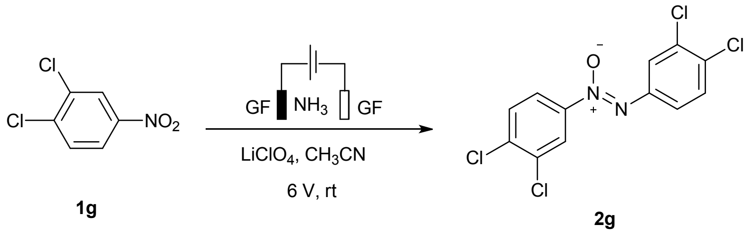
A solution of **3a** (0.1 mmol), $LiClO_4$ (0.1 mmol) in 5 mL MeCN saturated with ammonia gas was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.



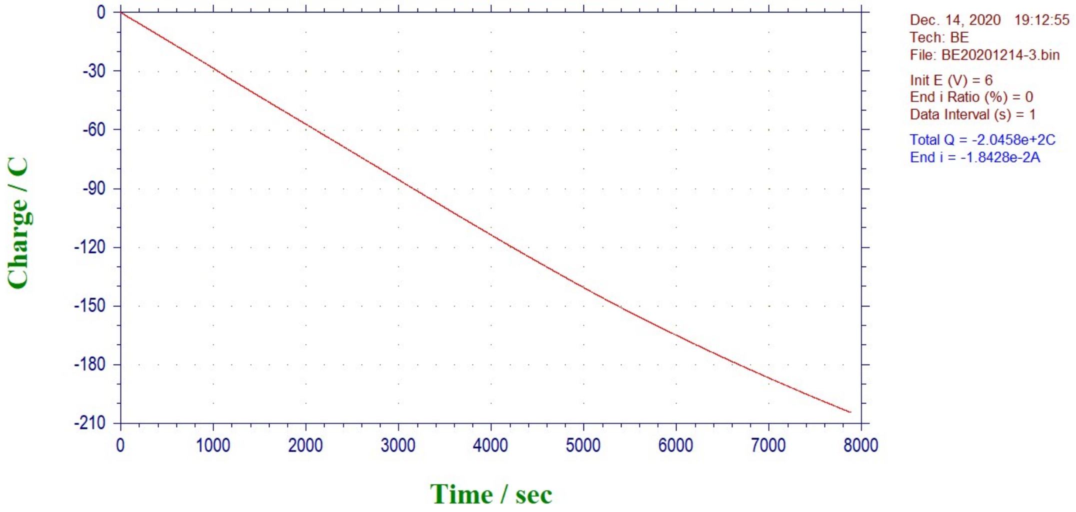
Cyclic voltammetry Experiment of **4a** under ammonia using **glassy carbon** working electrode

A solution of **4a** (0.1 mmol), $LiClO_4$ (0.1 mmol) in 5 mL MeCN saturated with ammonia gas was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.

5. Measure of Charge Consumption



1g (0.4 mmol), $LiClO_4$ (0.1 mmol) in 5 mL MeCN with graphite felt electrodes, under ammonia atmosphere, rt, 6V, 2.2 h. The NMR yield of **2g** was 78%.



Charge consumption was calculated as M*n*F/ Q, Q was read from the experiment as item "Total Q", M was the molar of **2g** obtained in the reaction ($1.56*10^{-4}$ mol), "n" was the number of electrons corresponds to the generation of one molecule of product, and F was Faraday's constant: 96485. Faradaic efficiency FE = $1.56*10^{-4}*3*96485/204.58$ = 22%.

6. Reaction profiles for the conversion of 1a

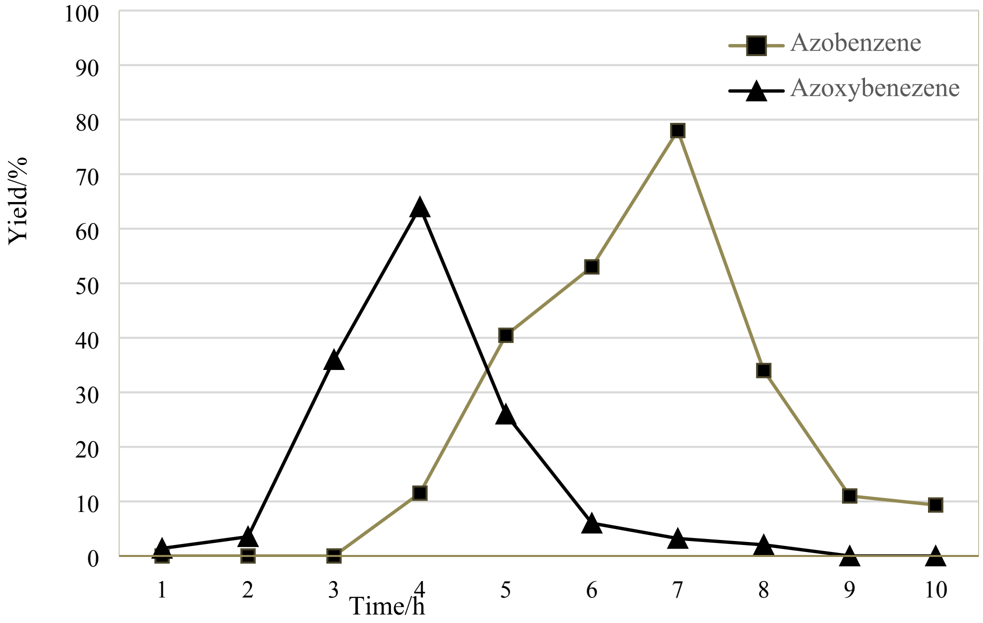


Figure S1. Reaction profiles for the conversion of **1a** in MeCN. Conditions: **1a** (0.2 mmol), $LiClO_4$ (0.1 mmol), MeCN (5 mL) GF electrodes, 6 V cell voltage, undivided cell, ammonia atmosphere, rt.

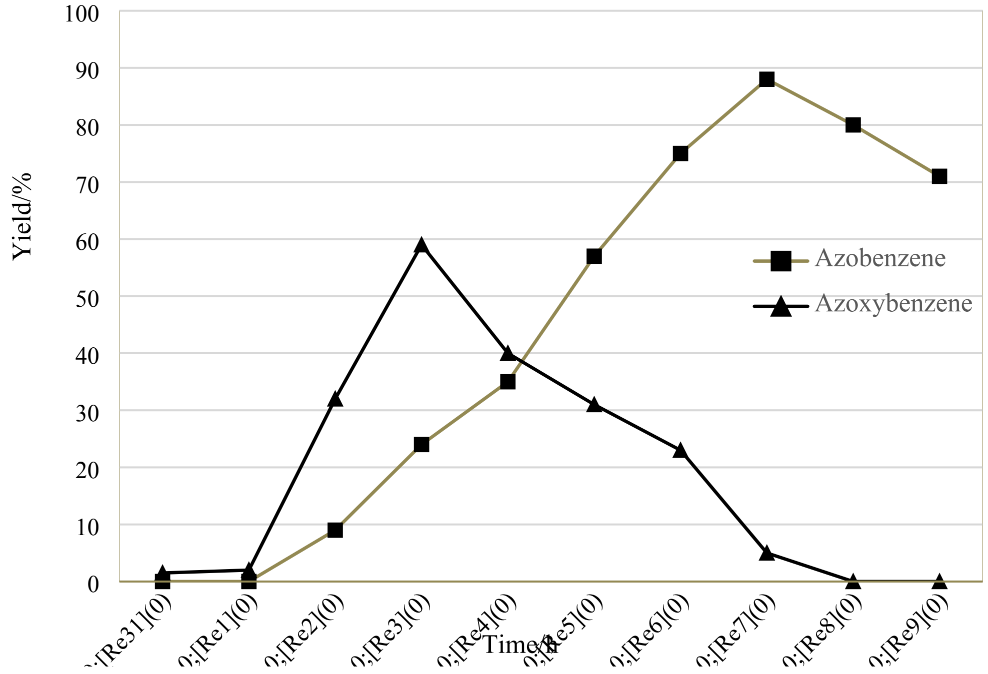


Figure S2. Reaction profiles for the conversion of **1a** in MeOH. Conditions: **1a** (0.2 mmol), $LiClO_4$ (0.1 mmol), MeOH (5 mL) GF electrodes, 25 mA, undivided cell, ammonia atmosphere, rt.

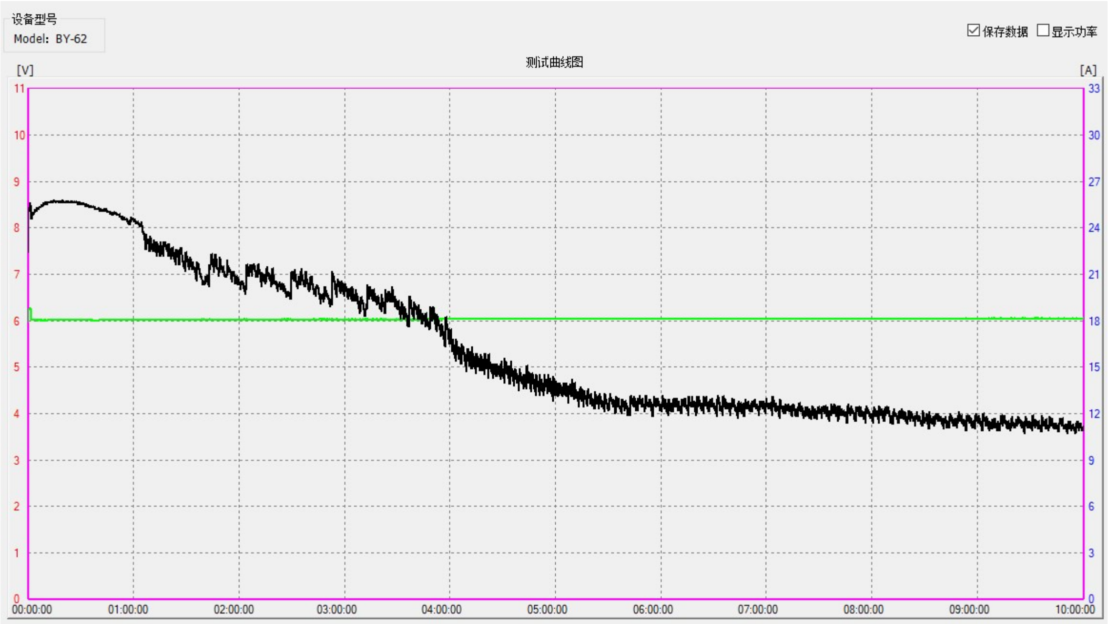


Figure S3. Chronoamperogram for the conversion of **1a**. Conditions: **1a** (0.2 mmol), $LiClO_4$ (0.1 mmol), MeCN (5 mL) GF electrodes, 6 V cell voltage, undivided cell, ammonia atmosphere, rt.

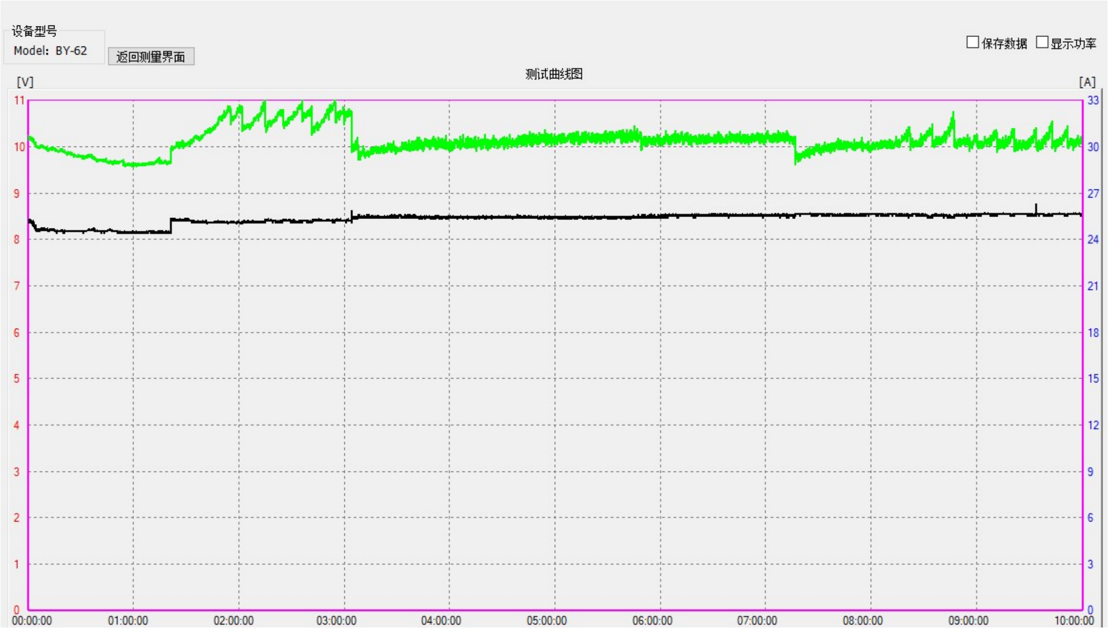
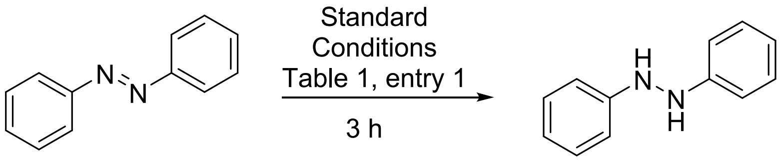


Figure S4. Chronopotentiogram for the conversion of **1a**. Conditions: **1a** (0.2 mmol), $LiClO_4$ (0.1 mmol), MeOH (5 mL) GF electrodes, 25 mA, undivided cell, ammonia atmosphere, rt.

7. Study of Species in reactions under controlled conditions

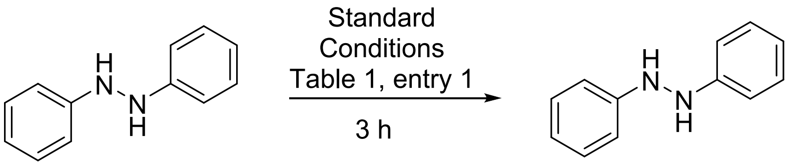
7.1) The tolerance of products in electrochemical reactions.

Products **3a**, **4a** and **5a** were used as substrates in reaction with standard conditions for 3 hours. It was found the **3a** was reduced to **4a** partially, **4a** remained intact, and compound **5a** partially underwent dehydrogenative cross-coupling to give hydrazine.



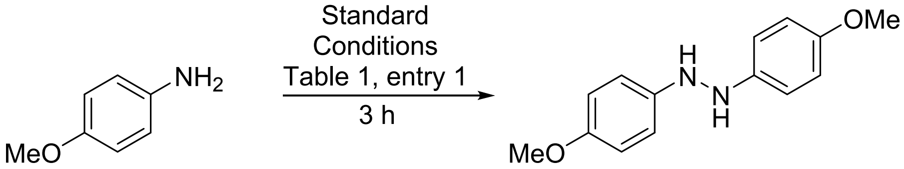
3a

4a, partial conversion



4a

4a

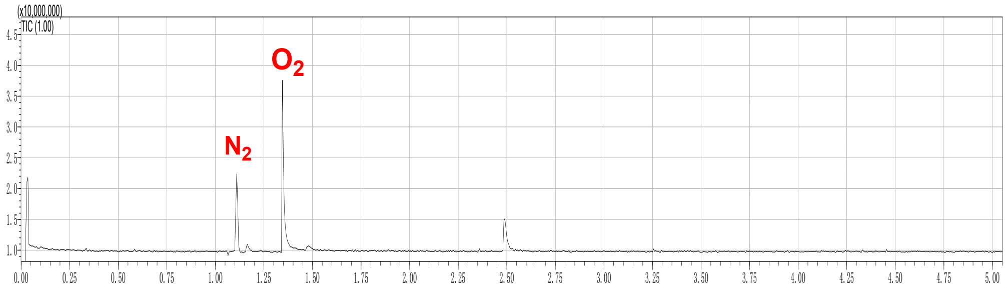


4a

partially conversion

7.2) Detection of N_2 generated in reaction.

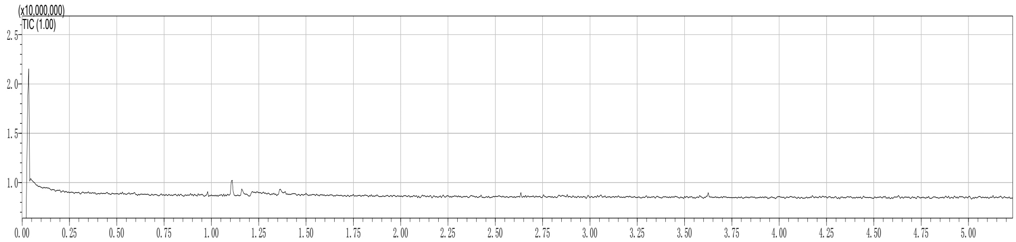
Detection of air with GC-MS



峰表 TIC

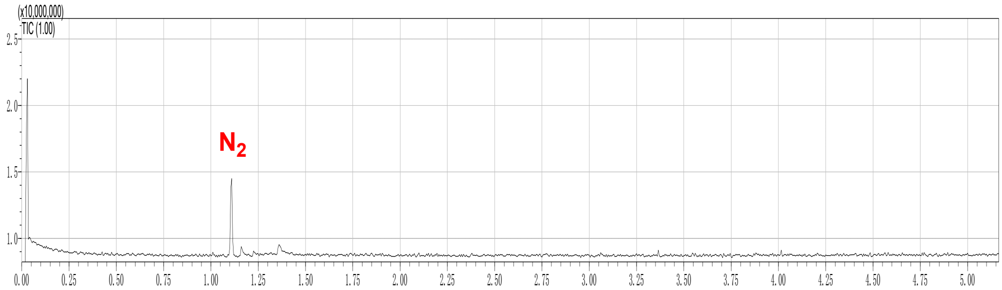
峰号	保留时间	I.Time	F.Time	峰面积	峰面积%	峰高	峰高%	积/高度	标记	名称
1	1.110	1.095	1.130	8895565	26.26	12772766	27.75	0.70	MI	
2	1.346	1.340	1.385	18747094	55.34	27946062	60.70	0.67	MI	
3	2.489	2.475	2.525	6235421	18.41	5317028	11.55	1.17	MI	
				33878080	100.00	46035856	100.00			

Detection of NH_3 with GC-MS



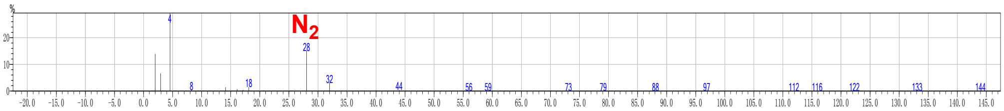
Detection of N_2 from the reaction with GC-MS

The atmosphere of headspace in reaction mixture was collected as the above figure and analyzed by GC-MS. The N_2 was detected as the major species without significant O_2, suggesting N_2 was produced in the reaction.

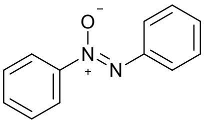


峰表 TIC

峰号	保留时间	I. Time	F. Time	峰面积	峰面积%	峰高	峰高%	积/高度	标记	名称
1	1. 108	1. 095	1. 120	3829306	100. 00	5766350	100. 00	0. 66	MI	
				3829306	100. 00	5766350	100. 00			

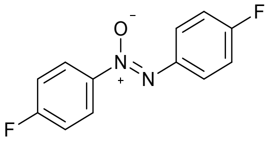


8. Synthesis and characterization of compounds



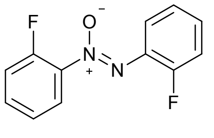
Azoxybenzene (2a)

Follow a general procedure A and reacted for 4 h, **2a** was obtained as a yellow solid in 65% yield (12.9 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.32 (m, 2H), 8.29 (d, *J* = 7.5 Hz, 2H), 7.57 – 7.45 (m, 5H), 7.45 – 7.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.35, 144.00, 131.56, 129.57, 128.77, 128.68, 125.50, 122.33. Spectroscopic data matches with previously reported data. Spectroscopic data matches with previously reported data.[2]



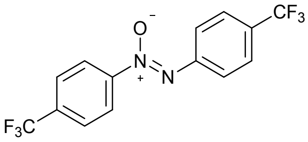
4, 4'-Difluoroazoxybenzene (2b)

Follow a general procedure A reacted for 4 h. **2b** was obtained as a light yellow solid in 57% yield (13.3 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (ddd, *J* = 24.0, 8.9, 5.1 Hz, 4H), 7.26 – 7.07 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.94 (d, *J* = 197.7 Hz), 162.43 (d, *J* = 197.4 Hz), 144.43, 140.45 (d, *J* = 3.3 Hz), 128.14 (d, *J* = 8.4 Hz), 124.69 (d, *J* = 9.2 Hz), 115.95 (d, *J* = 5.8 Hz), 115.73 (d, *J* = 5.0 Hz). Spectroscopic data matches with previously reported data.[2]



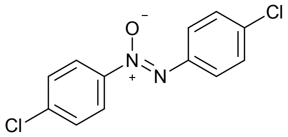
2, 2'-Difluoroazoxybenzene (2c)

Follow a general procedure A and reacted for 3 h. **2c** was obtained as a light yellow solid in 72% yield (16.8 mg). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.34 – 8.23 (m, 1H), 7.97 – 7.88 (m, 1H), 7.55 – 7.47 (m, 1H), 7.42 – 7.34 (m, 1H), 7.33 – 7.18 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.85 (d, *J* = 167.7 Hz), 154.29 (d, *J* = 170.8 Hz), 132.49 (d, *J* = 8.0 Hz), 132.35 (d, *J* = 9.2 Hz), 130.68 (d, *J* = 8.4 Hz), 125.53 (d, *J* = 1.3 Hz), 124.41 (d, *J* = 4.2 Hz), 124.04 (d, *J* = 4.2 Hz), 117.73 (d, *J* = 20.2 Hz), 116.24 (d, *J* = 20.1 Hz). Spectroscopic data matches with previously reported data.[3]



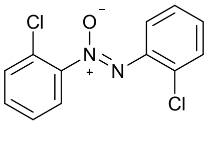
4, 4'-Ditrifluoromethylazoxybenzene (2d)

Follow a general procedure A and reacted for 4 h. **2b** was obtained as a white solid in 86% yield (28.7 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.4 Hz, 2H), 8.23 (d, *J* = 8.3 Hz, 2H), 7.78 (dd, *J* = 23.1, 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.28 , 146.14 , 134.05 (q, *J* = 33.0 Hz), 131.33 (q, *J* = 32.8 Hz), 127.74 (d, *J* = 28.3 Hz), 126.42 (q, *J* = 3.7 Hz), 126.08 (q, *J* = 3.8 Hz), 125.87 , 125.03 (d, *J* = 28.7 Hz), 123.18 , 122.32 (d, *J* = 29.1 Hz), 119.61 (d, *J* = 29.6 Hz). Spectroscopic data matches with previously reported data.[2]



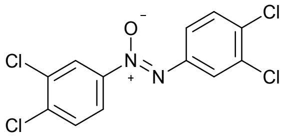
4, 4'-Dichloroazoxybenzene (2e)

Follow a general procedure A and reacted for 7 h. **2e** was obtained as a yellow solid in 73% yield (19.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9.0 Hz, 2H), 8.15 (d, *J* = 8.9 Hz, 2H), 7.46 (dd, *J* = 12.7, 9.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.69, 142.37, 138.22, 135.39, 129.16, 129.10, 127.20, 123.84. Spectroscopic data matches with previously reported data.[2]



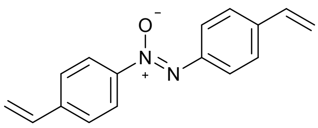
2, 2'-Dichloroazoxybenzene (2f)

Follow a general procedure A and reacted for 5 h. **2f** was obtained as a yellow solid in 40% yield (10.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.58 – 7.49 (m, 2H), 7.48 – 7.35 (m, 3H), 7.31 (td, *J* = 7.7, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.37, 140.99, 131.25, 131.14, 130.37, 129.84, 129.66, 127.67, 127.14, 126.89, 125.27, 123.47. Spectroscopic data matches with previously reported data.[3]



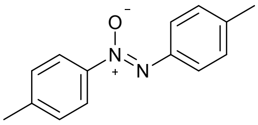
3, 3', 4, 4'-Tetrachloroazoxybenzene (2g)

Follow a general procedure A and reacted for 4 h. **2g** was obtained as a yellow solid in 76% yield (25.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (t, *J* = 2.4 Hz, 2H), 8.14 (dd, *J* = 8.8, 2.6 Hz, 1H), 8.00 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.78, 142.68, 136.93, 133.89, 133.42, 132.94, 130.72, 130.59, 127.41, 125.45, 124.59, 121.63. HRMS (ESI): calcd. for $C_{12}H_6Cl_4N_2O$: ($[M-H]^+$): 332.9156, found: 332.9167.



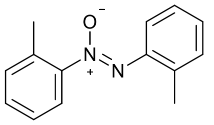
4, 4'-Divinylazoxybenzene (2h)

Follow a general procedure A and reacted for 4 h. **2h** was obtained as a green solid in 47% yield (11.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 26.8, 8.4 Hz, 4H), 7.52 (d, *J* = 7.9 Hz, 4H), 6.77 (dt, *J* = 18.2, 10.0 Hz, 2H), 5.87 (dd, *J* = 17.6, 9.0 Hz, 2H), 5.38 (dd, *J* = 23.4, 10.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.63, 143.67, 140.94, 138.99, 136.29, 135.67, 126.61, 126.20, 122.73, 116.72, 115.56. Spectroscopic data matches with previously reported data.[3]



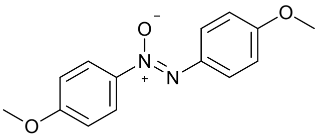
4, 4'-Dimethylazoxybenzene (2i)

Follow a general procedure A and reacted for 5.5 h. **2i** was obtained as a yellow solid in 70% yield (15.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.9 Hz, 2H), 8.15 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 4H), 2.45 (d, *J* = 9.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.24, 141.95, 141.86, 140.03, 129.32, 125.68, 122.16, 21.59, 21.33. Spectroscopic data matches with previously reported data.[3]



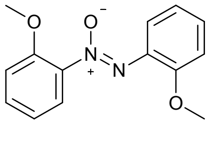
2, 2'-Dimethylazoxybenzene (2j)

Follow a general procedure A and reacted for 5 h. **2j** was obtained as a light yellow solid in 68% yield (15.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.18 (m, 6H), 2.53 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.60, 142.92, 134.24, 131.92, 131.36, 130.91, 130.15, 128.71, 126.73, 126.19, 123.72, 121.67, 18.58, 18.54. Spectroscopic data matches with previously reported data.[3]



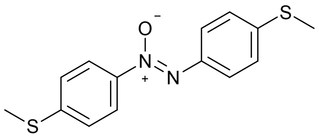
4, 4'-Dimethoxyazoxybenzene (2k)

Follow a general procedure A and reacted for 5 h. **2k** was obtained as a yellow solid in 77% yield (19.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 13.8, 9.2 Hz, 4H), 6.96 (t, *J* = 8.7 Hz, 4H), 3.87 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.97, 160.31, 138.13, 127.92, 123.89, 113.85, 113.71, 55.79, 55.60.Spectroscopic data matches with previously reported data.[3]



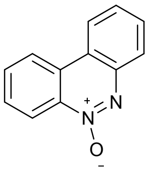
2, 2'-Dimethoxyazoxybenzene (2l)

Follow a general procedure A and reacted for 6 h. **2l** was obtained as a yellow solid in 64% yield (16.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.13 – 6.91 (m, 4H), 3.90 (d, *J* = 7.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.53, 152.01, 139.84, 133.65, 131.16, 129.84, 124.89, 123.23, 120.55, 120.36, 113.14, 111.84, 56.45, 56.11. Spectroscopic data matches with previously reported data.[4]



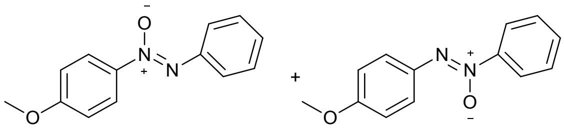
4, 4'-Dimethylthioazoxybenzene (2m)

Follow a general procedure A and reacted for 6 h. **2m** was obtained as a yellow solid in 68% yield (19.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (t, J = 7.8 Hz, 4H), 7.31 (dd, J = 8.7, 4.0 Hz, 4H), 2.55 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.27, 143.81, 141.30, 141.18, 126.33, 125.62, 125.45, 122.63, 15.30. Spectroscopic data matches with previously reported data.[4]



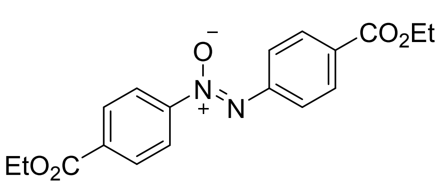
Benzo[c]cinnoline-N-oxide (2n)

Follow a general procedure A and reacted for 4 h. **2n** was obtained as a yellow solid in 40% yield (7.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.48 (d, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.92 (t, *J* = 7.6 Hz, 1H), 7.73 (ddt, *J* = 30.6, 15.1, 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.38, 137.24, 132.64, 130.56, 129.99, 128.92, 128.72, 126.46, 122.44, 122.38, 121.29, 118.31. Spectroscopic data matches with previously reported data.[5]



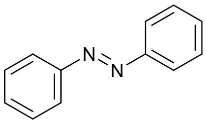
4-Methoxyazoxybenzene + 4'-Methoxybenzene (2o+2o')

Follow a general procedure A and reacted for 12 h. **2o+2o'** was obtained as a yellow solid in 45% yield (20.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.21 (m, 3H), 8.12 (d, *J* = 7.5 Hz, 1H), 7.58 – 7.33 (m, 3H), 6.98 (t, *J* = 9.1 Hz, 2H), 3.88 (d, *J* = 1.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.38, 160.65, 148.53, 144.33, 138.08, 131.24, 129.31, 128.86, 128.78, 128.16, 125.48, 124.19, 122.29, 113.93, 113.79, 55.84, 55.63. Spectroscopic data matches with previously reported data.[3]



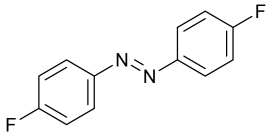
DiethylAzoxybenzene-4, 4'-dicarboxylate (2p)

Follow a general procedure A and reacted for 4 h. **2p** was obtained as a white solid in 52% yield (17.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$ δ 8.38 (d, *J* = 8.8 Hz, 2H), 8.23 – 8.03 (m, 6H), 4.42 (dq, *J* = 9.6, 7.1 Hz, 5H), 1.47 – 1.39 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.89, 165.42, 150.93, 147.01, 133.73, 131.16, 130.45, 130.28, 125.45, 122.63, 61.78, 61.41, 14.47, 14.43.



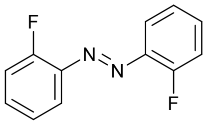
Azobenzene (3a)

Follow a general procedure B and reacted for 7 h. **3a** was obtained as an orange solid in 82% yield (14.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 4H), 7.51 (dt, *J* = 12.7, 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.68, 130.96, 129.07, 122.83. Spectroscopic data matches with previously reported data.[3]



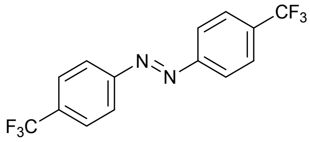
4, 4'-Difluoroazobenzene (3b)

Follow a general procedure B and reacted for 4 h. **3b** was obtained as an orange solid in 53% yield (11.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.87 (m, 4H), 7.20 (t, *J* = 8.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.78, 163.27, 149.15, 149.12, 125.00, 124.94, 124.91, 116.32, 116.09. Spectroscopic data matches with previously reported data.[4]



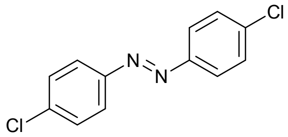
2, 2'-Difluoroazobenzene (3c)

Follow a general procedure B and reacted for 11 h. **3c** was obtained as an orange solid in 50% yield (10.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (t, *J* = 7.8 Hz, 2H), 7.53 – 7.42 (q, 2H), 7.25 (dt, *J* = 21.4, 8.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.51 (d, *J* = 258.4 Hz), 141.02 (d, *J* = 6.7 Hz), 133.14 (d, *J* = 8.3 Hz), 124.51 (d, *J* = 3.9 Hz), 118.06 , 117.22 (d, *J* = 19.8 Hz). Spectroscopic data matches with previously reported data.[6]



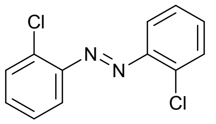
4, 4'-Ditrifluoromethylazobenzene (3d)

Follow a general procedure B and reacted for 14 h. **3c** was obtained as an orange solid in 47% yield (15.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 4H), 7.81 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.25, 133.15 (q, *J* = 32.6 Hz), 126.56 (q, *J* = 3.8 Hz), 123.96 (q, *J* = 273.7 Hz), 123.47. Spectroscopic data matches with previously reported data.[6]



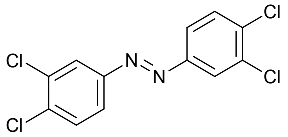
4, 4'-Dichloroazobenzene (3e)

Follow a general procedure B and reacted for 6 h. **3e** was obtained as an orange solid in 50% yield (12.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 4H), 7.49 (d, *J* = 8.7 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.96, 137.39, 129.56, 124.34. Spectroscopic data matches with previously reported data.[4]



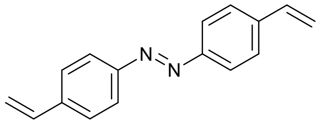
2, 2'-Dichloroazobenzene (3f)

Follow a general procedure B and reacted for 12 h. **3f** was obtained as an orange solid in 68% yield (17.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.60 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.41 (dtd, *J* = 24.4, 7.4, 1.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.93, 135.98, 132.38, 130.88, 127.53, 118.24. Spectroscopic data matches with previously reported data.[6]



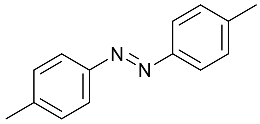
3, 3', 4, 4'-Tetrachloroazobenzene (3g)

Follow a general procedure B and reacted for 4 h. **3g** was obtained as a yellow solid in 44% yield (14.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.18, 135.86, 133.84, 131.17, 124.22, 123.20. Spectroscopic data matches with previously reported data.[7]



4, 4'-Divinylazoxybenzene (3h)

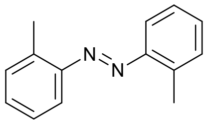
Follow a general procedure B and reacted for 6 h. **3h** was obtained as an orange solid in 73% yield (17.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 4H), 7.56 (d, *J* = 8.4 Hz, 4H), 6.80 (dd, *J* = 17.6, 10.9 Hz, 2H), 5.88 (d, *J* = 17.6 Hz, 2H), 5.37 (d, *J* = 10.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.33, 140.28, 136.33, 127.07, 123.35, 115.69. HRMS (ESI): calcd. for $C_{16}H_{14}N_2$: ($[M+H]^+$): 235,1235, found: 235.1228.



4, 4'-Dimethylazobenzene (3i)

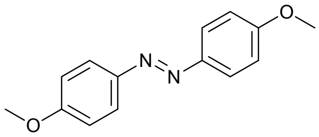
Follow a general procedure B and reacted for 7.5 h. **3i** was obtained as an orange solid in 71% yield (14.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 4H), 7.34 (d, *J* = 8.1 Hz, 4H), 2.47

(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.96, 141.31, 129.83, 122.86, 21.61. Spectroscopic data matches with previously reported data.[4]



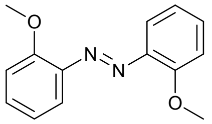
2, 2'-Dimethylazobenzene (3j)

Follow a general procedure B and reacted for 11 h. **3j** was obtained as an orange solid in 79% yield (16.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.9 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.26 (tt, J = 8.6, 2.9 Hz, 2H), 2.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.22, 138.14, 131.39, 130.81, 126.49, 115.98, 17.76. Spectroscopic data matches with previously reported data.[4]



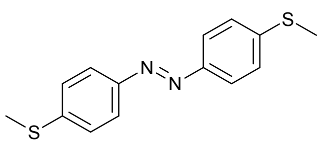
4, 4'-Dimethoxylazobenzene (3k)

Follow a general procedure B and reacted for 3 h. **3k** was obtained as an orange solid in 33% yield (8.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.8 Hz, 4H), 7.00 (d, J = 8.8 Hz, 4H), 3.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.71, 147.24, 124.47, 114.31, 55.68. Spectroscopic data matches with previously reported data.[4]



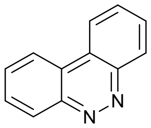
2, 2'-Dimethoxylazobenzene (3l)

Follow a general procedure B and reacted for 6 h. **3l** was obtained as an orange solid in 64% yield (15.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.9 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 7.00 (t, J = 7.6 Hz, 2H), 4.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.02, 143.19, 132.29, 120.98, 117.72, 112.79, 56.53. Spectroscopic data matches with previously reported data.[4]



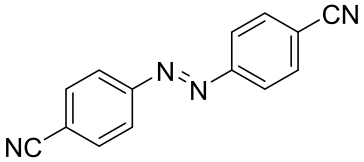
4, 4'-Dimethylthioazoxybenzene (3m)

Follow a general procedure B and reacted for 6 h. **3m** was obtained as an orange solid in 87% yield (23.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.6 Hz, 4H), 7.33 (d, J = 8.7 Hz, 4H), 2.55 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.18, 142.72, 126.15, 123.38, 15.47. Spectroscopic data matches with previously reported data.[4]



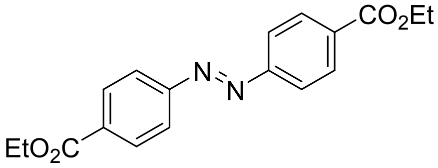
Benzo[c]cinnoline (3n)

Follow a general procedure B and reacted for 6 h. **3n** was obtained as a yellow solid in 69% yield (12.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 – 8.70 (dd, 2H), 8.54 (dd, *J* = 6.1, 3.4 Hz, 2H), 7.88 (dd, *J* = 6.3, 3.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.41, 131.63, 131.38, 129.32, 121.51, 120.98. Spectroscopic data matches with previously reported data.[6]



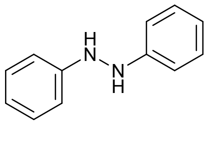
4, 4'-Dicyanoazobenzene (3o)

Follow a general procedure B and reacted for 6 h. **3o** was obtained as a yellow solid in 61% yield (14.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.9 Hz, 4H), 7.89 (d, *J* = 8.9 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.15, 133.61, 124.43, 118.45, 116.93.



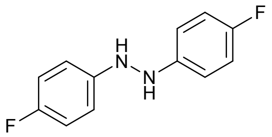
DiethylAzobenzene-4, 4'-dicarboxylate (3p)

Follow a general procedure B and reacted for 10 h. **3p** was obtained as an orange solid in 48% yield (15.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 4H), 7.98 (d, *J* = 8.5 Hz, 4H), 4.42 (q, *J* = 7.1 Hz, 4H), 1.43 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.09, 154.98, 132.87, 130.77, 123.02, 61.52, 14.49.



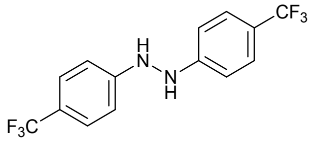
Hydrazobenzene (4a)

Follow a general procedure C and reacted overnight. **4a** was obtained as a colorless liquid in 96% yield (17.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.5 Hz, 4H), 6.91 – 6.84 (m, 6H), 5.60 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.96, 129.42, 119.94, 112.43. Spectroscopic data matches with previously reported data.[8]



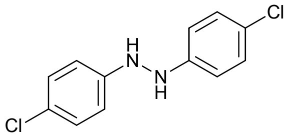
Hydrazo(4-fluorobenzene) (4b)

Follow a general procedure C and reacted overnight. **4b** was obtained as a colorless liquid in 90% yield (19.8 mg). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.17 (d, *J* = 8.8 Hz, 4H), 6.76 (d, *J* = 8.8 Hz, 4H), 5.62 (br, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.33 (d, *J* = 237.3 Hz), 145.03 (d, *J* = 2.1 Hz), 115.98 (d, *J* = 22.7 Hz), 113.53 (d, *J* = 7.7 Hz). Spectroscopic data matches with previously reported data.[8]



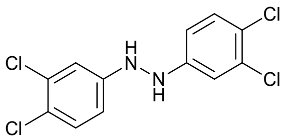
Hydrazo(4-(trifluoromethyl)benzene) (4c)

Follow a general procedure C and reacted overnight. **4c** was obtained as a yellow liquid in 31% yield (9.9 mg). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, *J* = 8.2 Hz, 4H), 6.88 (d, *J* = 8.2 Hz, 4H), 5.94 (br, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.85 , 127.04 (d, *J* = 3.9 Hz), 124.68 (q, *J* = 2.9 H$_Z$), 122.38 (q, *J* = 32.8 Hz), 111.82. Spectroscopic data matches with previously reported data.[8]



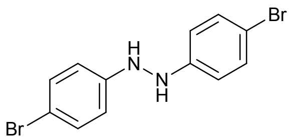
Hydrazo(4-chlorobenzene) (4d)

Follow a general procedure C and reacted overnight. **4d** was obtained as a yellow liquid in 59% yield (14.9 mg). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.17 (d, *J* = 8.8 Hz, 4H), 6.76 (d, *J* = 8.8 Hz, 4H), 5.62 (br, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.18, 129.44, 124.89, 113.66. Spectroscopic data matches with previously reported data.[4]



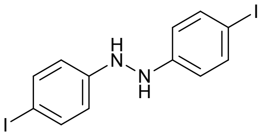
Hydrazo(3,4-dichlorobenzene) (4e)

Follow a general procedure C and reacted overnight. **4e** was obtained as a yellow liquid in 47% yield (15.1 mg). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 2.7 Hz, 2H), 6.66 (dd, *J* = 8.7, 2.7 Hz, 2H), 5.69 (br, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.73, 133.41, 131.10, 123.16, 113.93, 111.95. HRMS (ESI): calcd. for $C_{12}H_8Cl_4N_2$: ([M-H]$^+$): 318.9364, found: 318.9371.



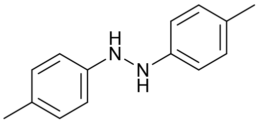
Hydrazo(4-bromobenzene) (4f)

Follow a general procedure C and reacted for 4 h. **4f** was obtained as a yellow liquid in 56% yield (19.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 4H), 6.71 (d, *J* = 8.8 Hz, 4H), 5.63 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.59, 132.33, 114.11. Spectroscopic data matches with previously reported data.[4]



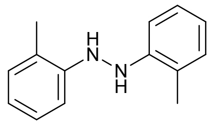
Hydrazo(4-iodobenzene) (4g)

Follow a general procedure C and reacted for 5 h. **4f** was obtained as a yellow liquid in 40% yield (17.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz, 4H), 6.61 (d, *J* = 8.7 Hz, 4H), 5.63 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.08, 138.07, 114.50, 81.38. HRMS (ESI): calcd. for $C_{12}H_6Cl_4N_2O$: ([M+H]$^+$): 436.9012, found: 436.9051.



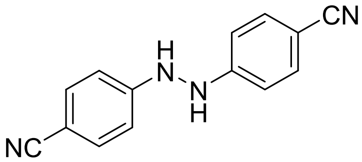
Hydrazo(4-methylbenzene) (4h)

Follow a general procedure C and reacted overnight. **4h** was obtained as a yellow liquid in 85% yield (18.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 7.4 Hz, 4H), 6.77 (d, *J* = 7.2 Hz, 4H), 5.50 (br, 2H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.87, 129.94, 129.20, 112.62, 20.62. Spectroscopic data matches with previously reported data.[4]



Hydrazo(2-methylbenzene) (4i)

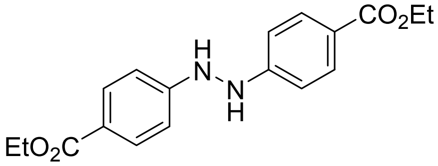
Follow a general procedure C and reacted overnight. **4i** was obtained as a yellow liquid in 71% yield (15.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 11.4, 7.4 Hz, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 2H), 5.53 (br, 2H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.40, 130.51, 127.38, 121.29, 119.52, 111.14, 17.26. Spectroscopic data matches with previously reported data.[4]



Hydrazo(4-cyanobenzene) (4j)

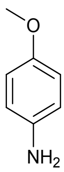
Follow a general procedure C and reacted for 9 h. **4j** was obtained as a white solid in 76% yield (17.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.7 Hz, 4H), 6.84 (d, *J* = 8.8 Hz, 4H), 6.14

(br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.21, 134.14, 119.63, 112.17, 103.07.



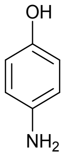
Diethyl 4,4'-(hydrazine-1,2-diyl)dibenzoate (4k)

Follow a general procedure C and reacted for 12 h. **3p** was obtained as a white solid in 73% yield (23.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 4H), 6.79 (d, J = 8.5 Hz, 4H), 4.31 (q, J = 7.1 Hz, 4H), 6.16 (br, 1H), 1.34 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 166.69, 152.10, 131.64, 121.94, 111.29, 60.63, 14.50.



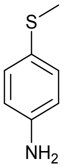
4-methoxyaniline (5a)

Follow a general procedure C and reacted overnight. **5a** was obtained as a black liquid in 49% yield (12.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 3.37 (br, 2H). ^{13}C NMR (100 MHz, CDCl3) δ 152.88, 139.86, 116.48, 114.84, 55.76. HRMS (ESI): calcd. for $C_{12}H_6Cl_4N_2O$: ([M+Na]$^+$): 146.0582, found: 146.0586.



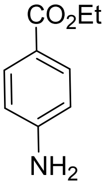
4-Aminophenol (5b)

Follow a general procedure C and reacted for 5.5 h. **5c** was obtained as a black liquid in 47% yield (10.3 mg). ^{1}H NMR (400 MHz, DMSO) δ 8.35 (br, 1H), 6.52 – 6.38 (m, 4H), 4.38 (br, 2H). ^{13}C NMR (100 MHz, DMSO) δ 148.25, 140.66, 115.57, 115.28. Spectroscopic data matches with previously reported data.[9]



4-methylthioaniline (5c)

Follow a general procedure C and reacted overnight. **5c** was obtained as a yellow liquid in 38% yield (10.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.65 – 6.60 (m, 2H), 3.38 (br, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.21, 131.20, 125.95, 115.87, 18.91. HRMS (ESI): calcd. for $C_{12}H_6Cl_4N_2O$: ([M+H]$^+$): 140.0534, found: 140.0528.



4-Ethoxycarbonylaniline (5d)

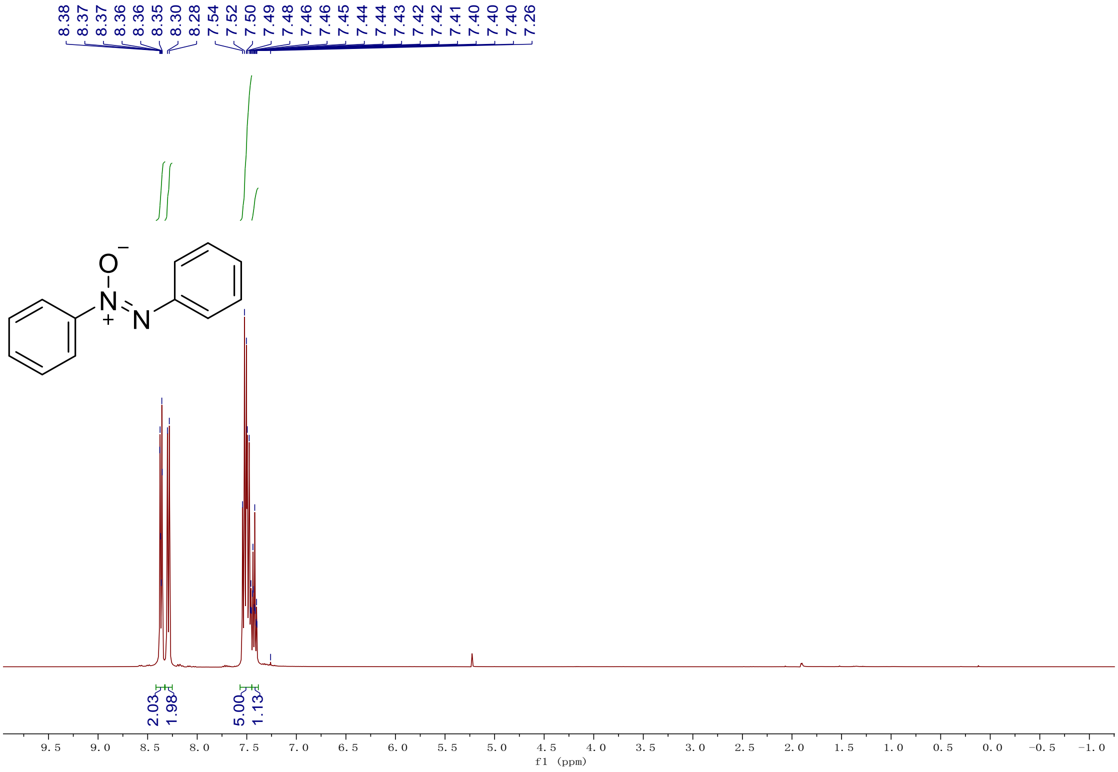
Follow a general procedure C and reacted for 12 h. **5d** was obtained as a white solid in 24% yield (7.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.04 (br, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.84, 150.81, 131.68, 120.25, 113.91, 60.46, 14.57.

9. Reference

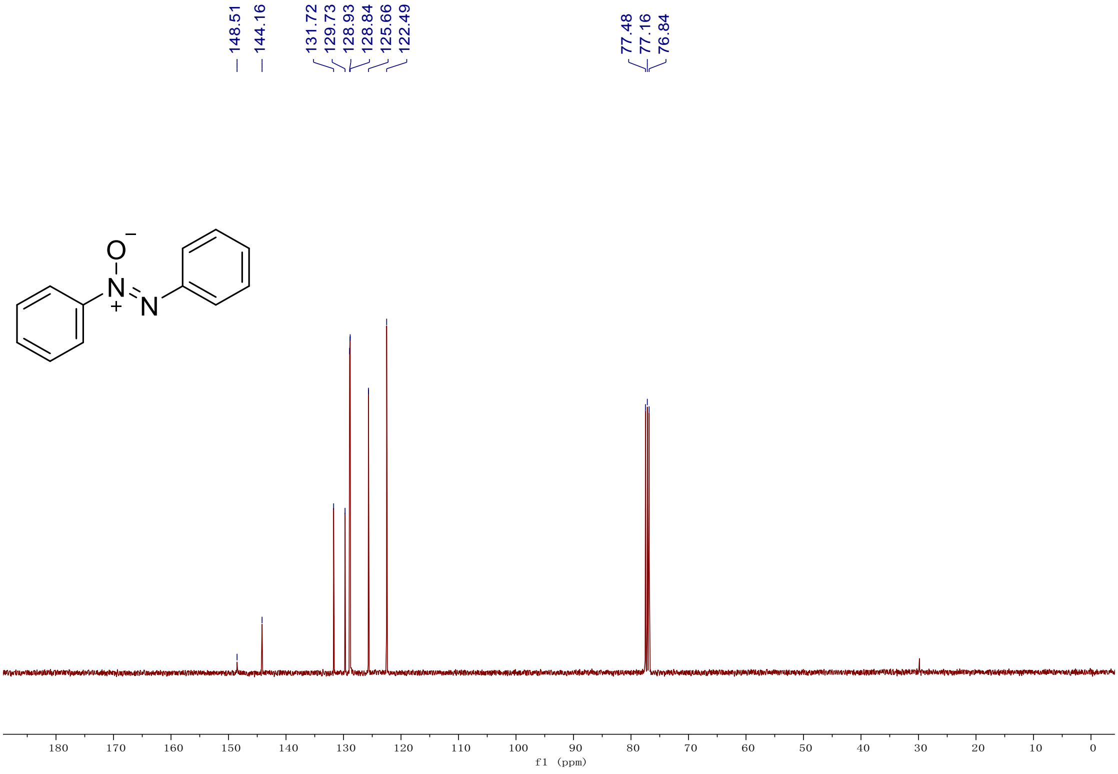
1. J. Li, L. He, X. Liu, X. Cheng and G. Li, *Angew. Chem. Int. Ed*., 2019, **58**, 1759.
2. G. S. G. De Carvalho, L. H. Chagas, C. G. Fonseca, P. P. de Castro, A. C. Sant'Ana, A. A. Leitão and G. W. Amarante. *New. J. Chem*., 2019, **43**, 5863
3. X. Chong, C. Liu, Y. Huang, C. Huang and B. Zhang, *Natl. Sci. Rev*., 2019, **7**, 285
4. Z. Yan, X. Xie, Q. Song, F. Ma, X. Sui, Z. Huo and M. Ma. *Green. Chem*., 2020, **22**, 1301
5. J. R. Hwu, A. R. Das, C. W. Yang, J.-J. Huang and M.-H. Hsu. *Org Lett*., 2005, **7**, 3211
6. N. Sakai, S. Asama, S. Anai and T. Konakahara. *Tetrahedron*., 2014, **70**, 2027
7. X. Liu, H.-Q. Li, S. Y, Y. -M. Liu, H. -Y. He and Y. Cao. *Angew Chem Int Ed*., 2014, **53**, 7624-7628
8. F. Wang, O. Planas and J. Cornella. *J. Am. Chem. Soc*., 2019, **141**, 4235
9. N. García, P. García-García, M. A. Fernández-Rodríguez, R. Rubio, M. R. Pedrosa, F. J. Arnáiz and R. Sanz. *Adv. Synth. Catal*., 2012, **354**, 321

10. NMR Spectra

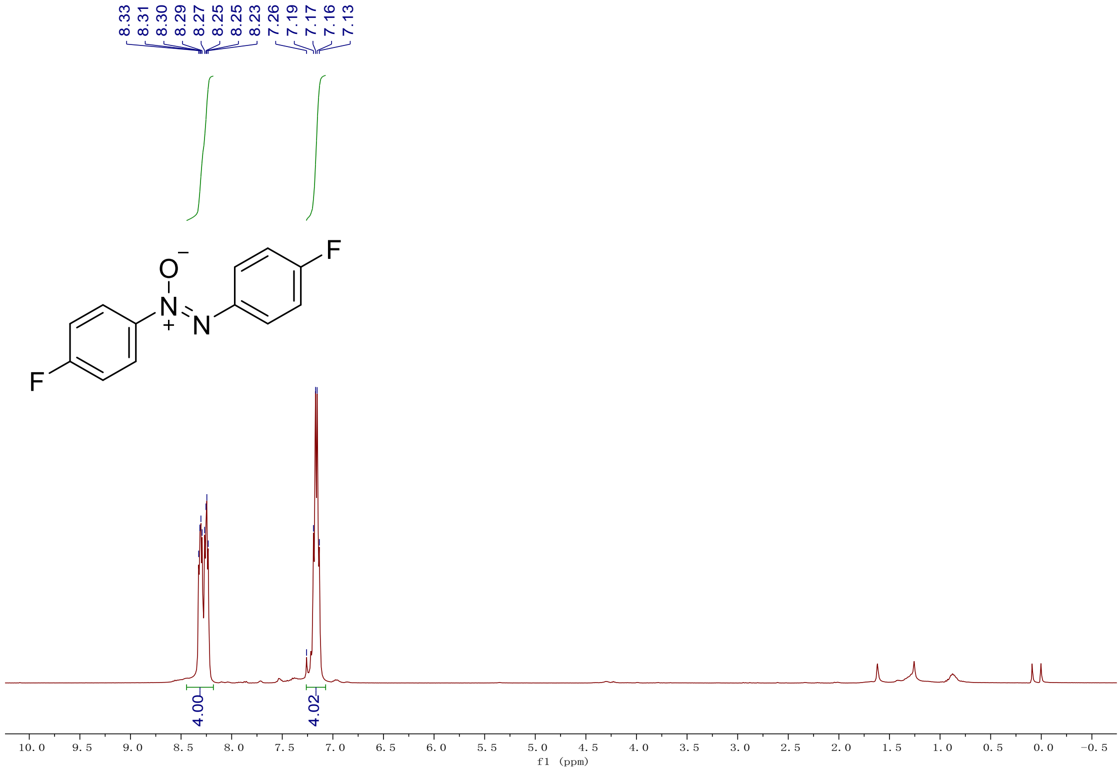
^{1}H NMR (400 MHz, $CDCl_3$) of **2a**



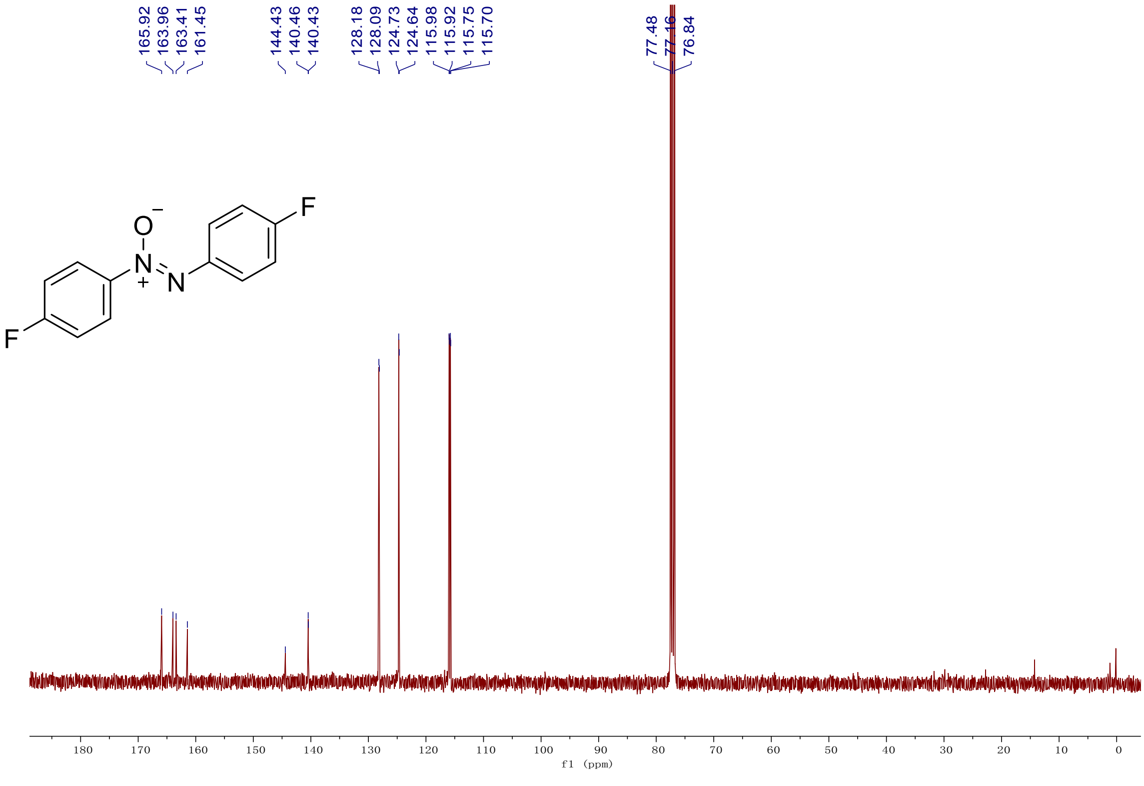
^{13}C NMR (100 MHz, $CDCl_3$) of **2a**



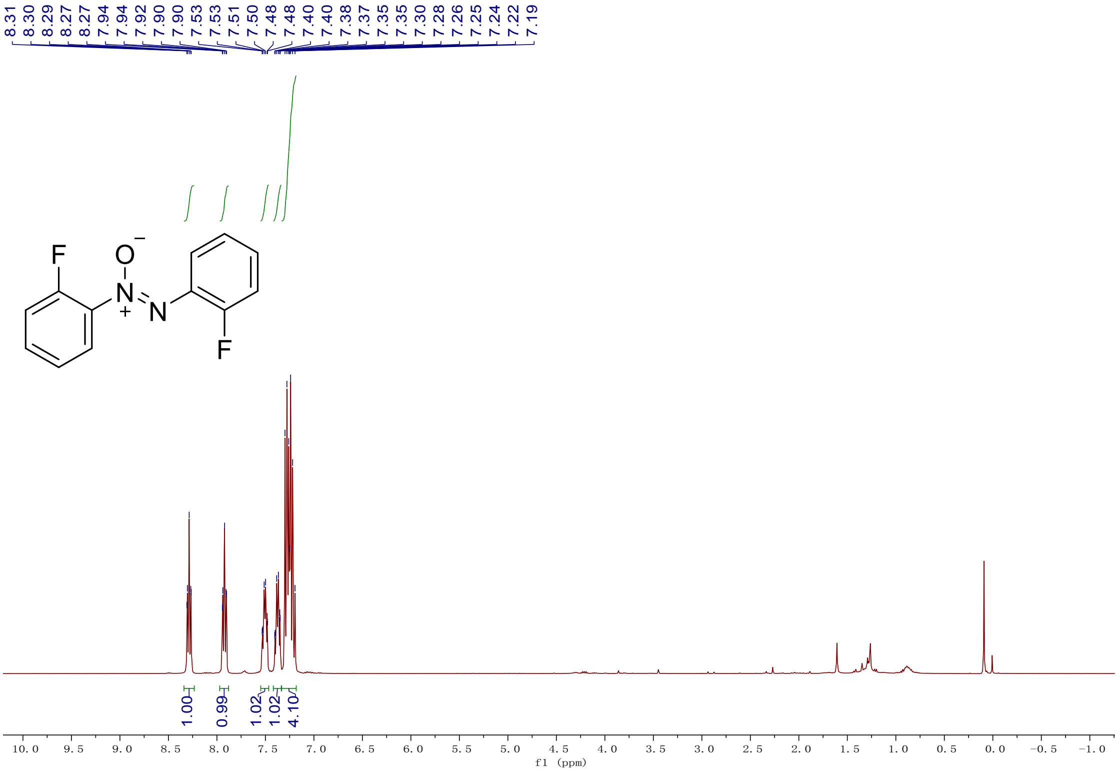
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



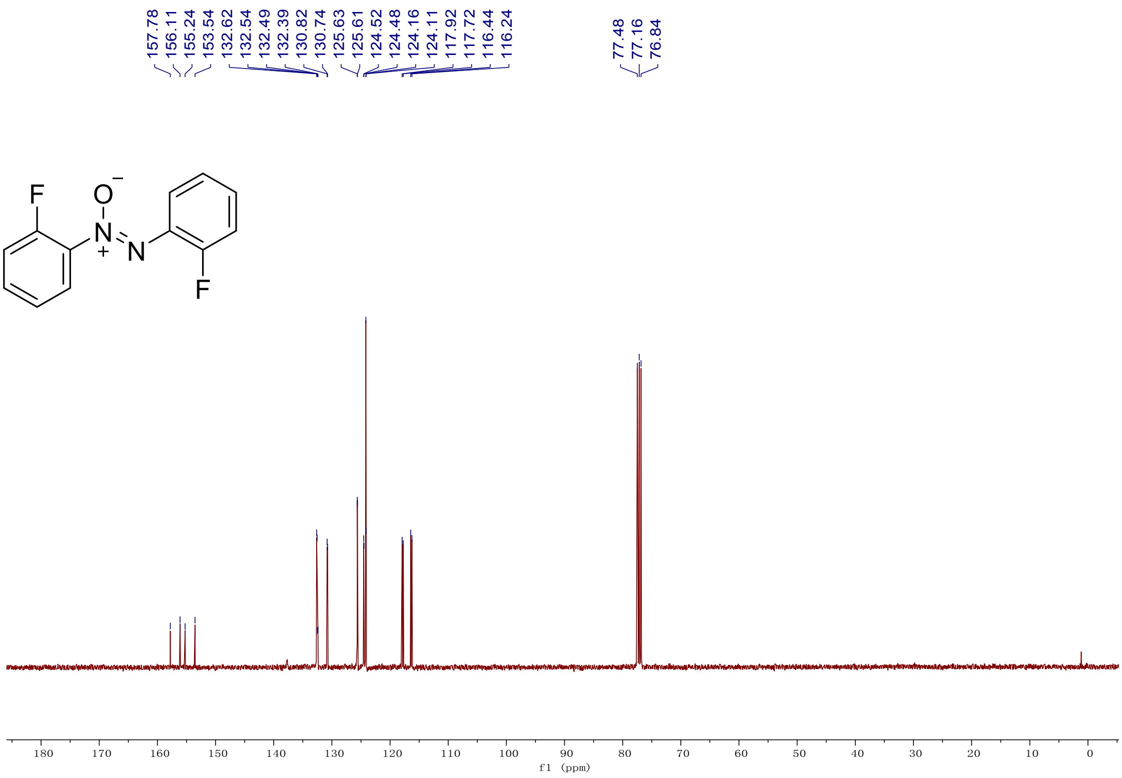
^{13}C NMR (100 MHz, CDCl$_3$) of **2b**



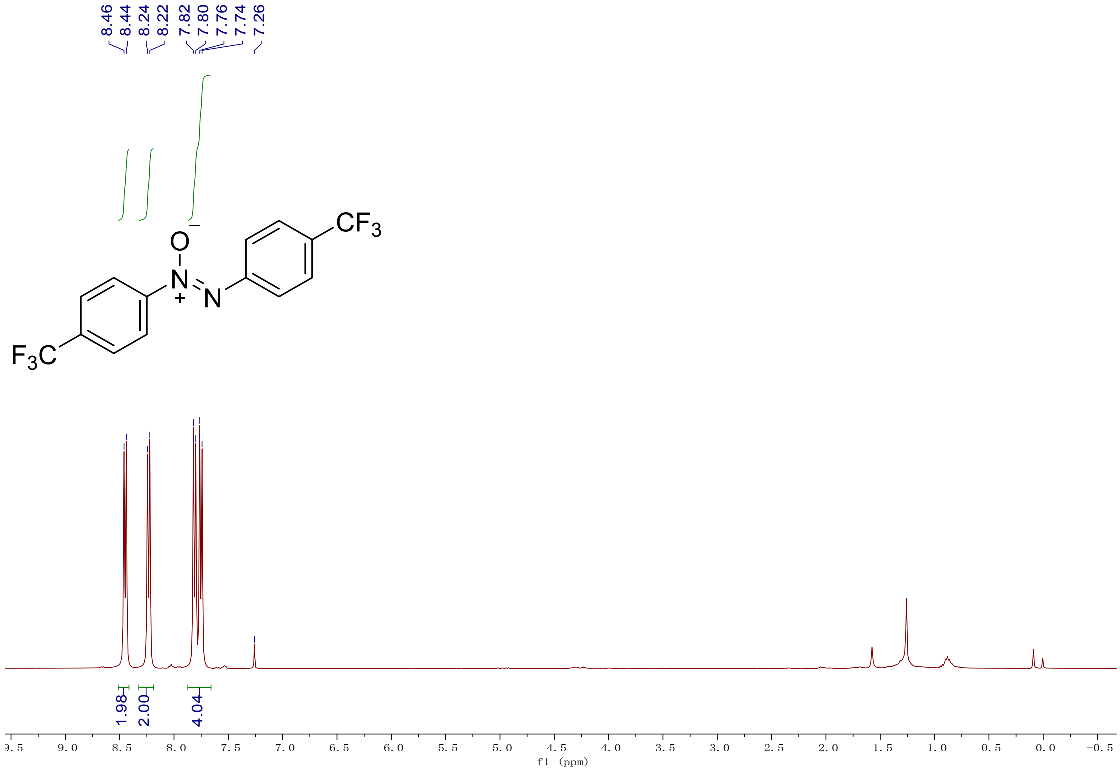
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**



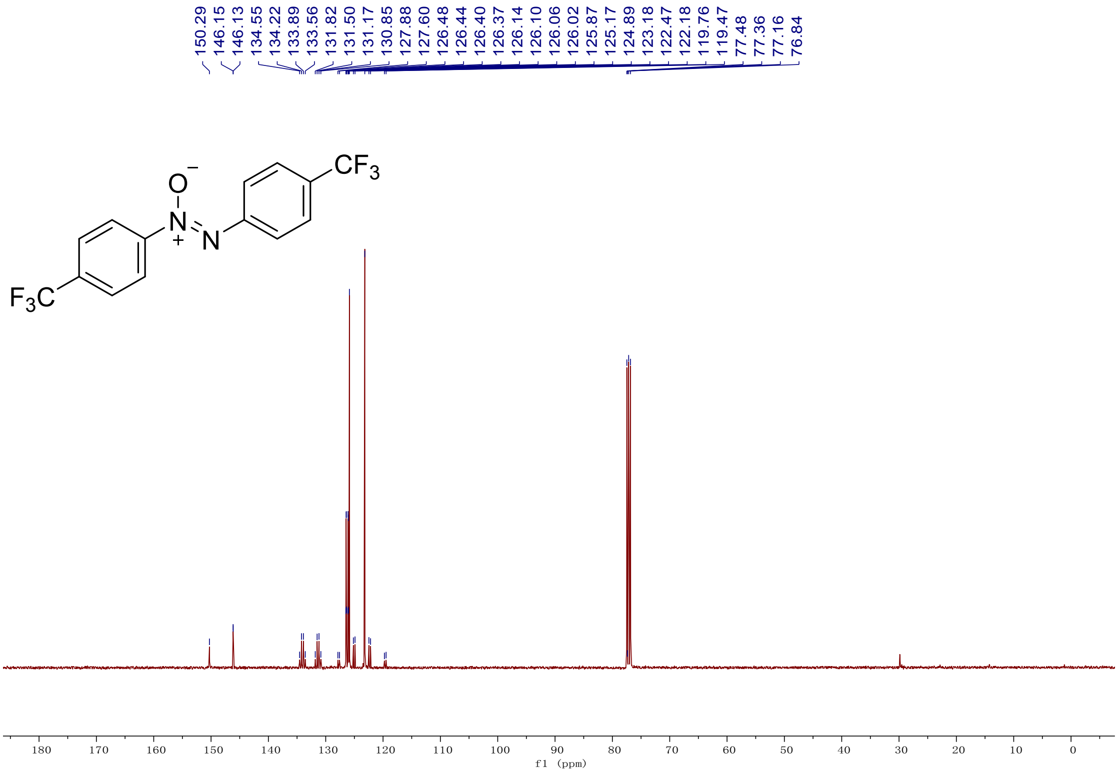
^{13}C NMR (100 MHz, $CDCl_3$) of **2c**



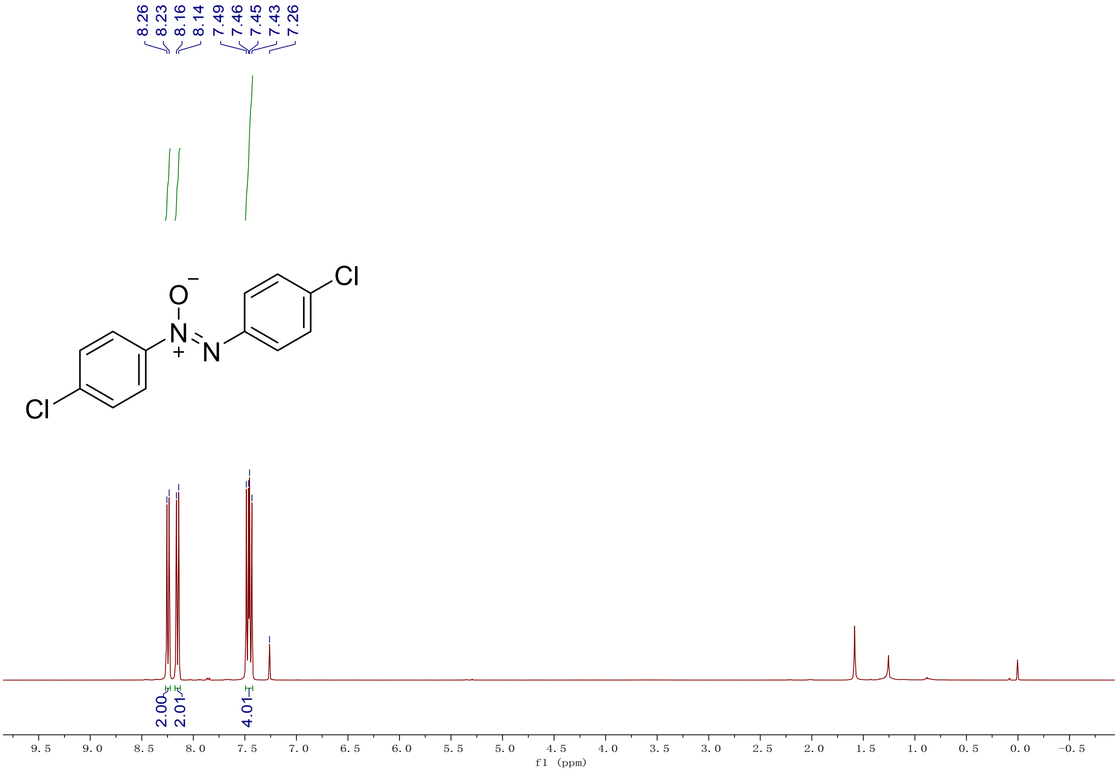
^{1}H NMR (400 MHz, CDCl$_3$) of **2d**



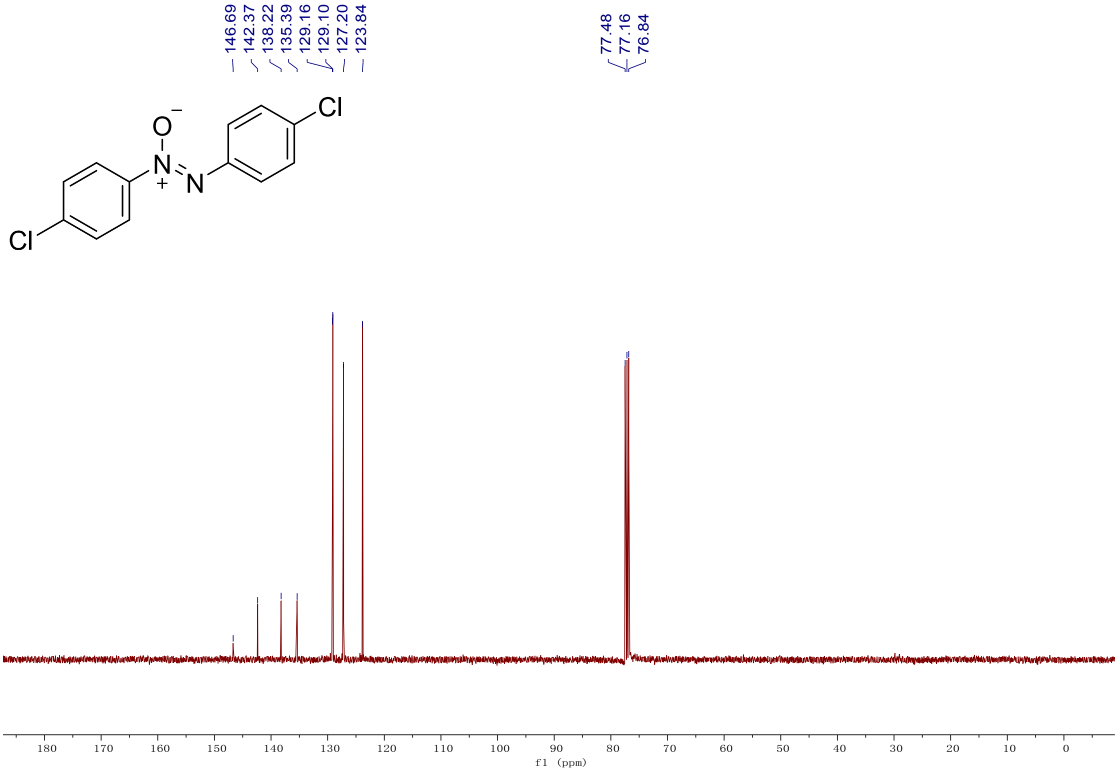
^{13}C NMR (100 MHz, CDCl$_3$) of **2d**



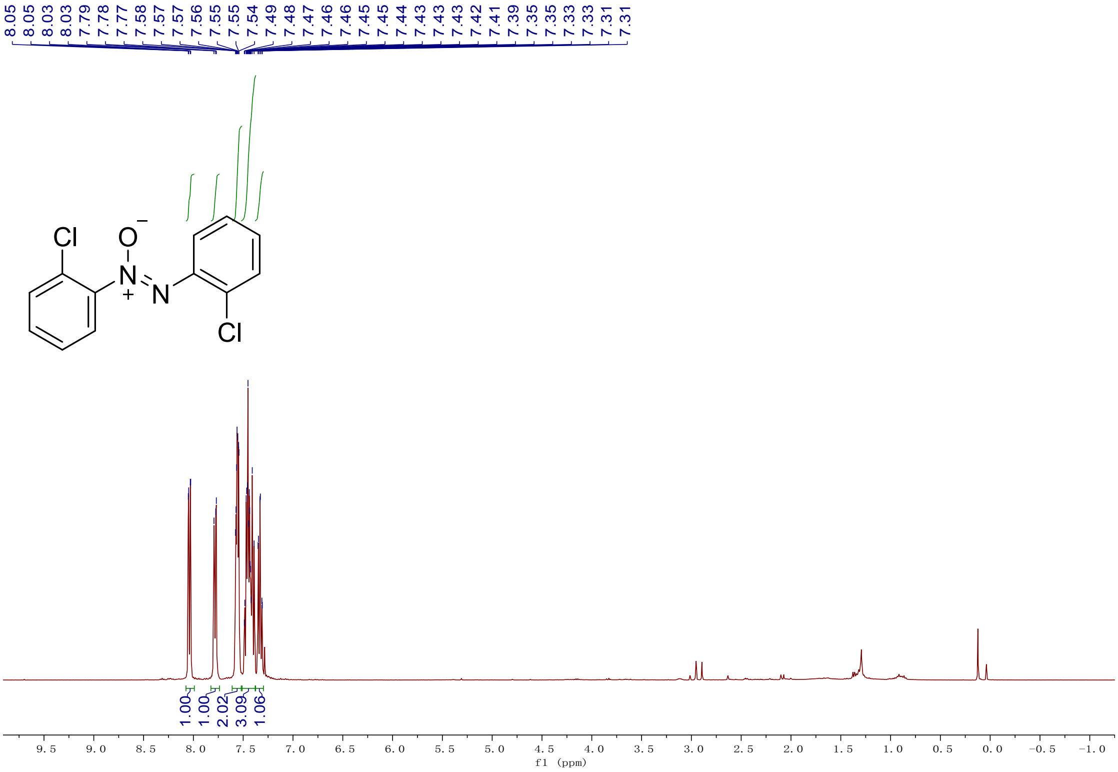
^{1}H NMR (400 MHz, CDCl$_3$) of **2e**



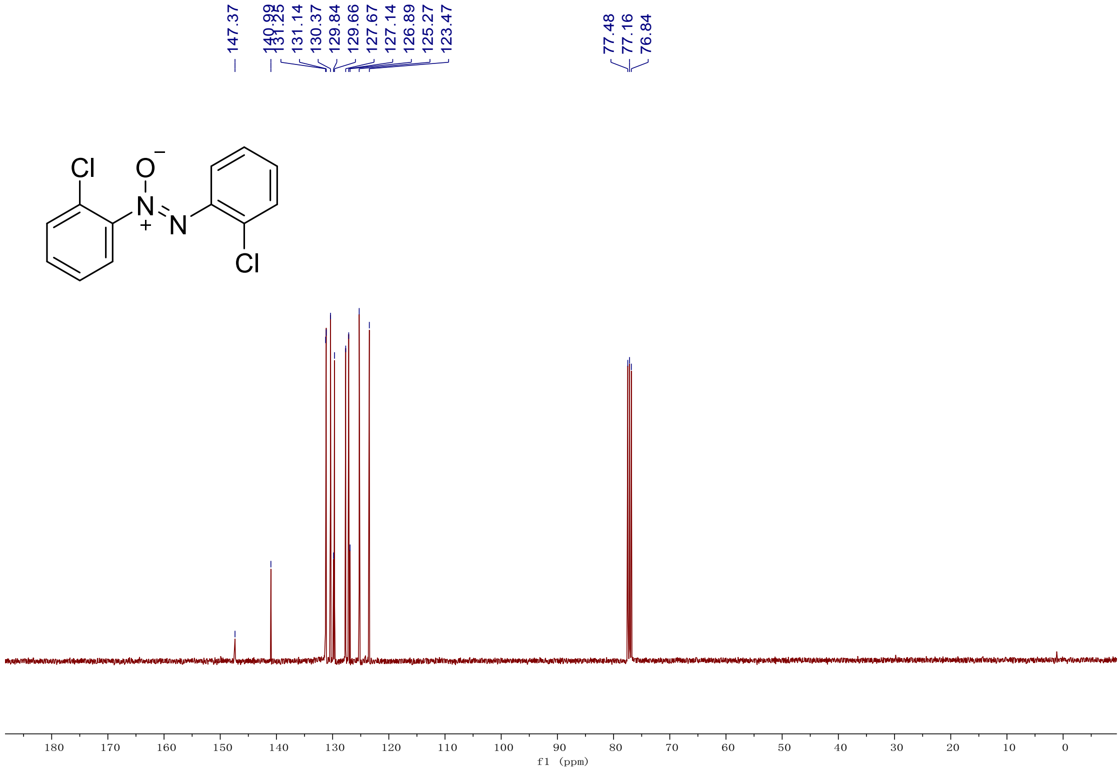
^{13}C NMR (100 MHz, CDCl$_3$) of **2e**



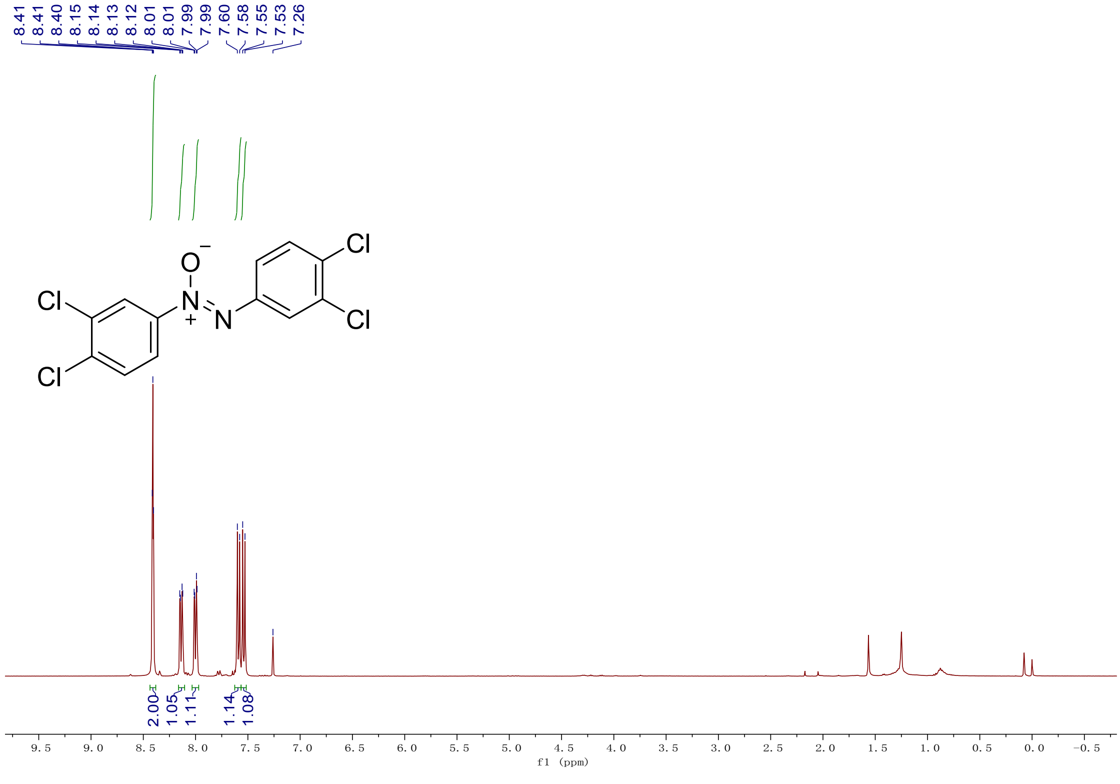
^{1}H NMR (400 MHz, CDCl$_3$) of **2f**



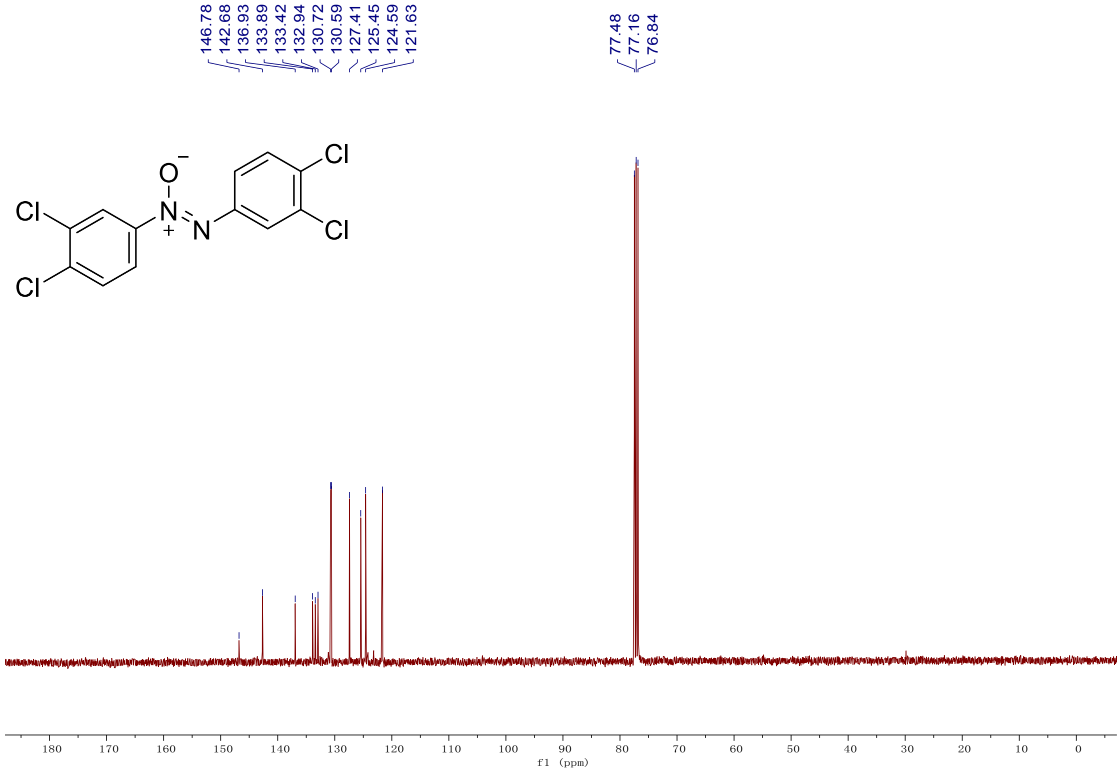
^{13}C NMR (100 MHz, CDCl$_3$) of **2f**



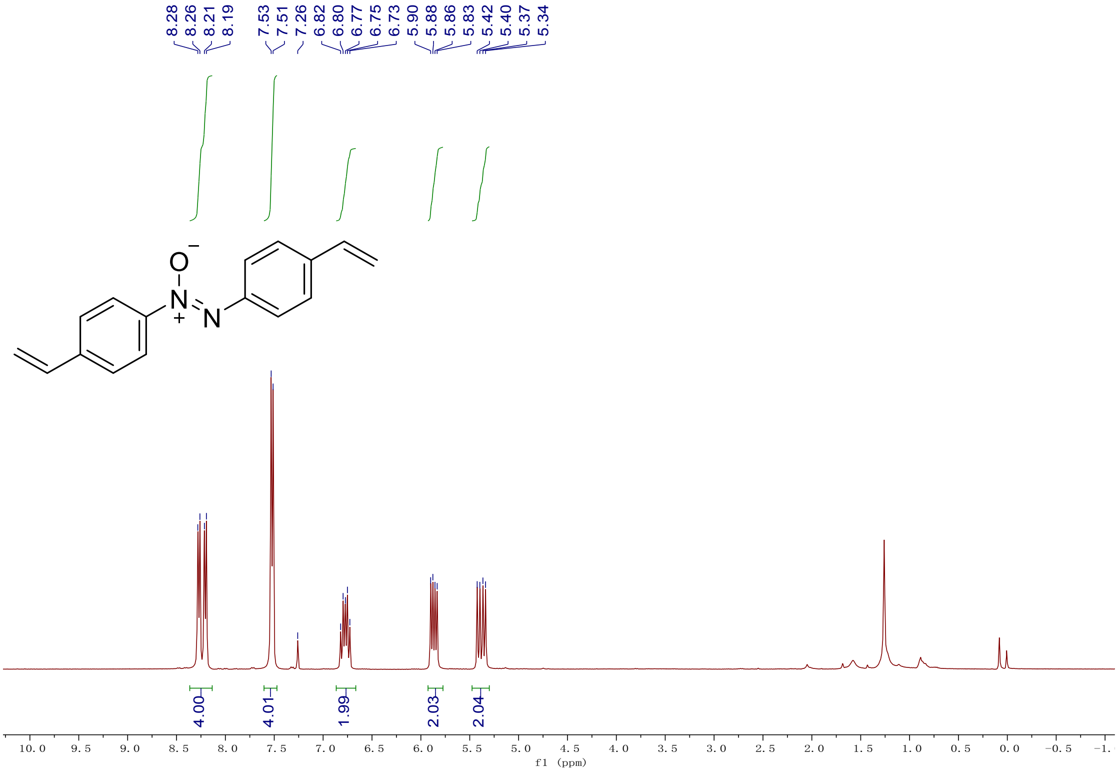
^{1}H NMR (400 MHz, $CDCl_3$) of **2g**



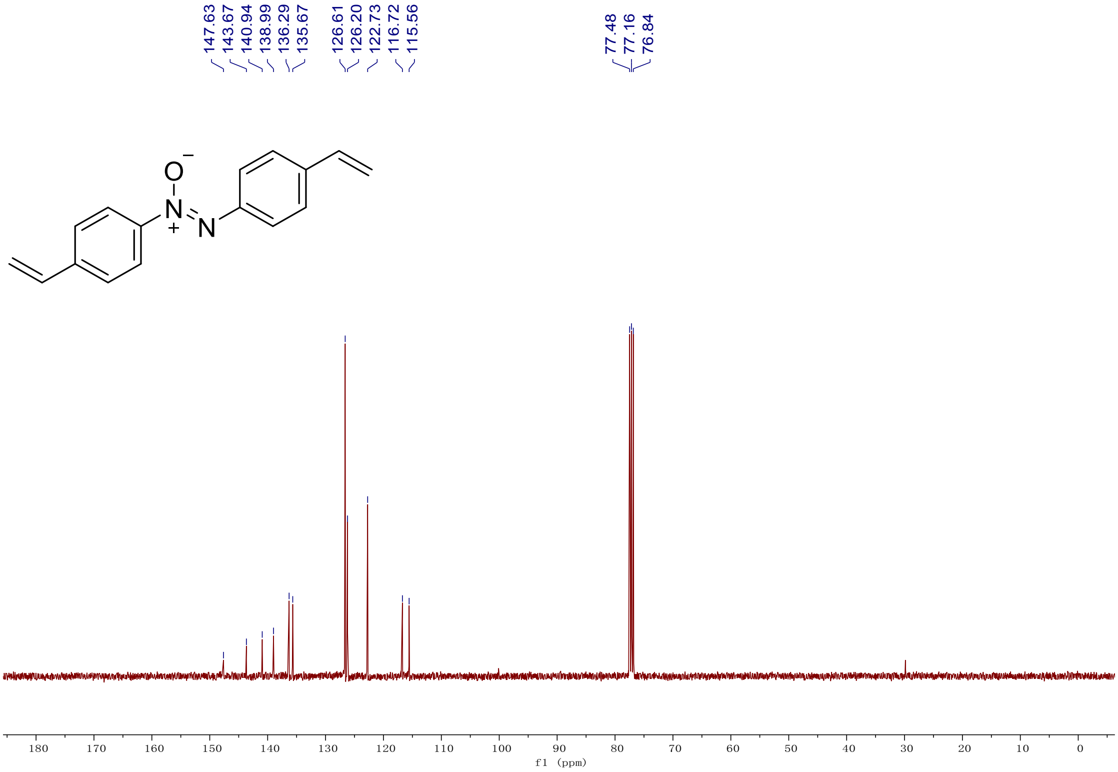
^{13}C NMR (100 MHz, CDCl$_3$) of **2g**



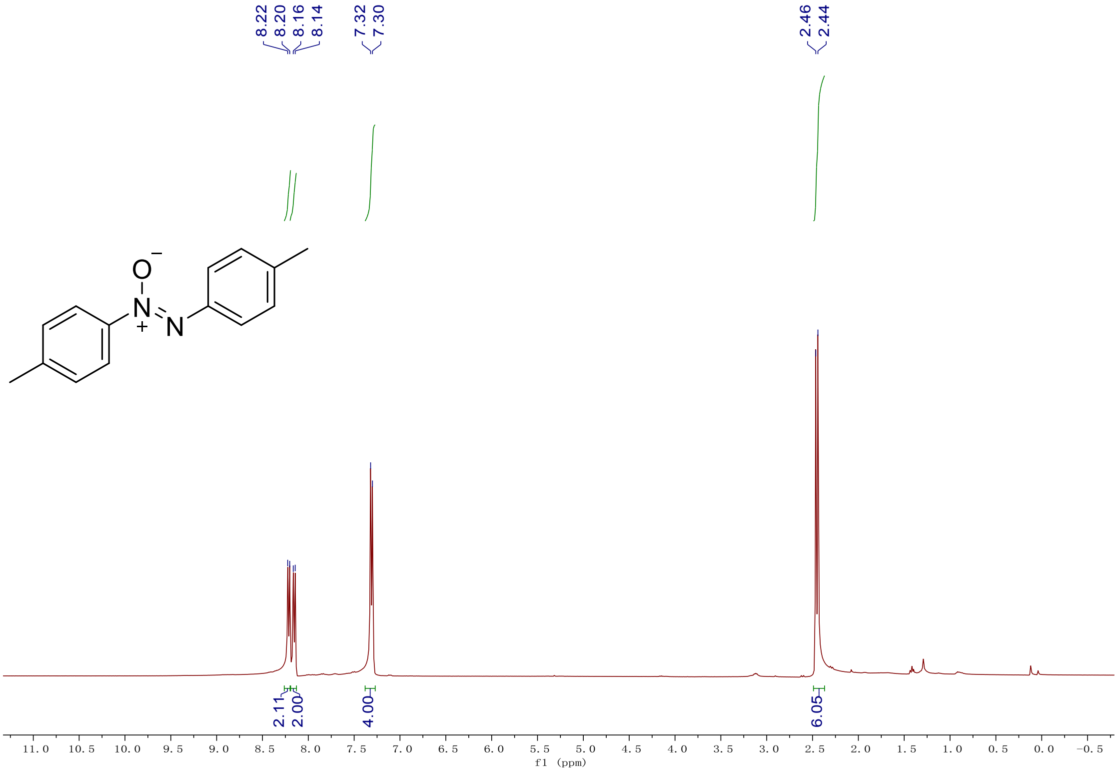
^{1}H NMR (400 MHz, CDCl$_3$) of **2h**



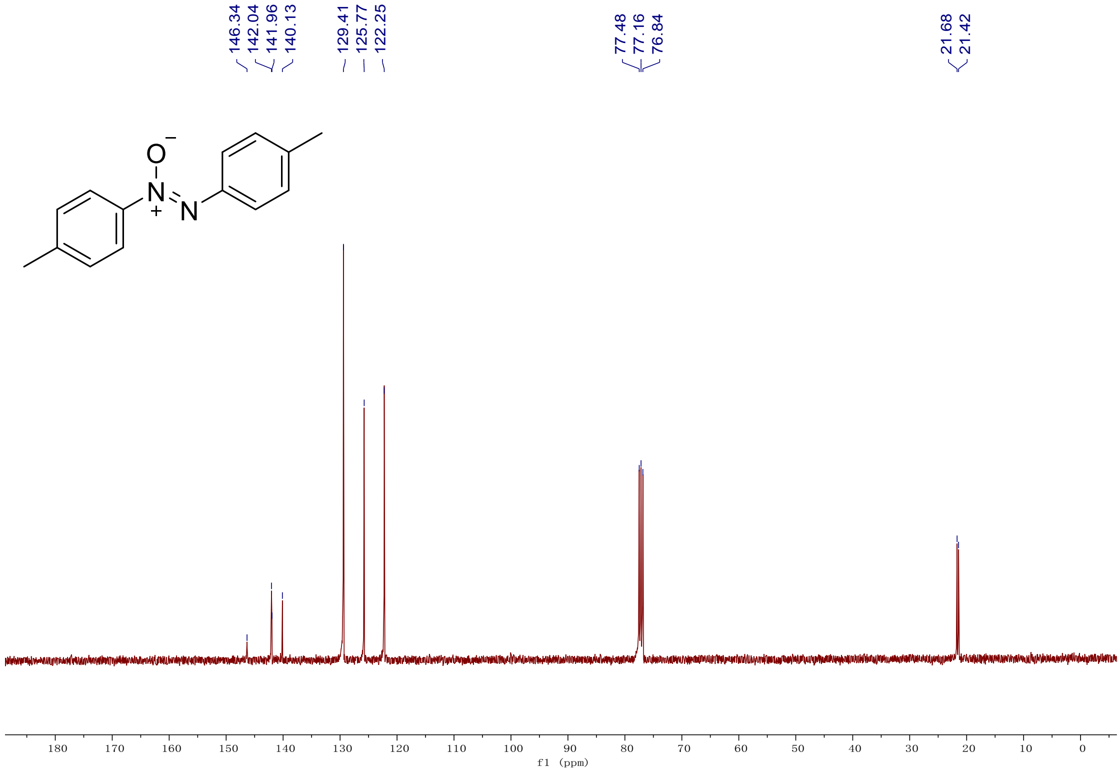
^{13}C NMR (100 MHz, CDCl$_3$) of **2h**



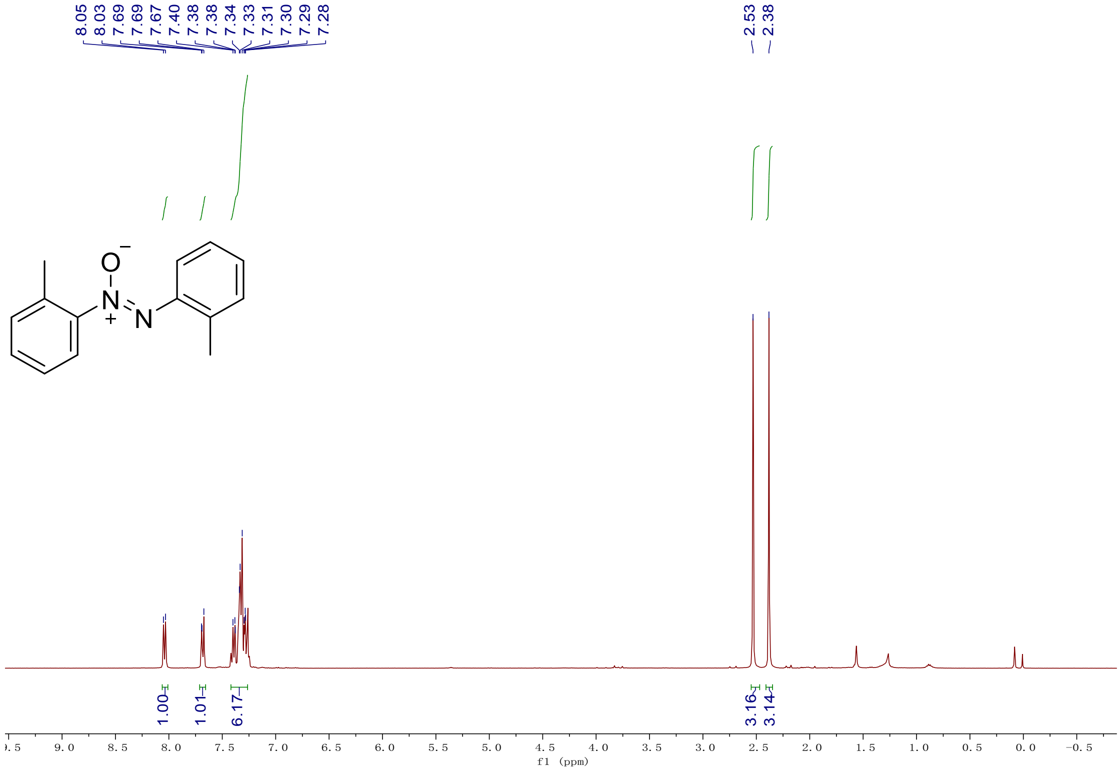
^{1}H NMR (400 MHz, $CDCl_3$) of **2i**



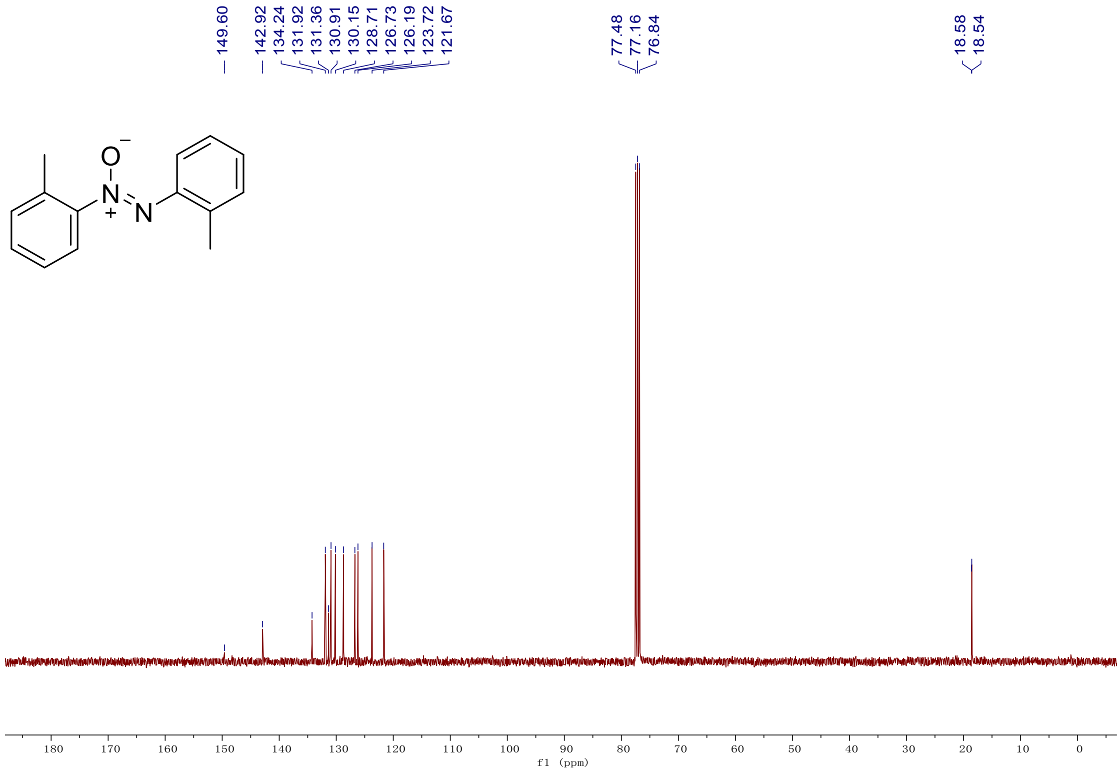
^{13}C NMR (100 MHz, $CDCl_3$) of **2i**



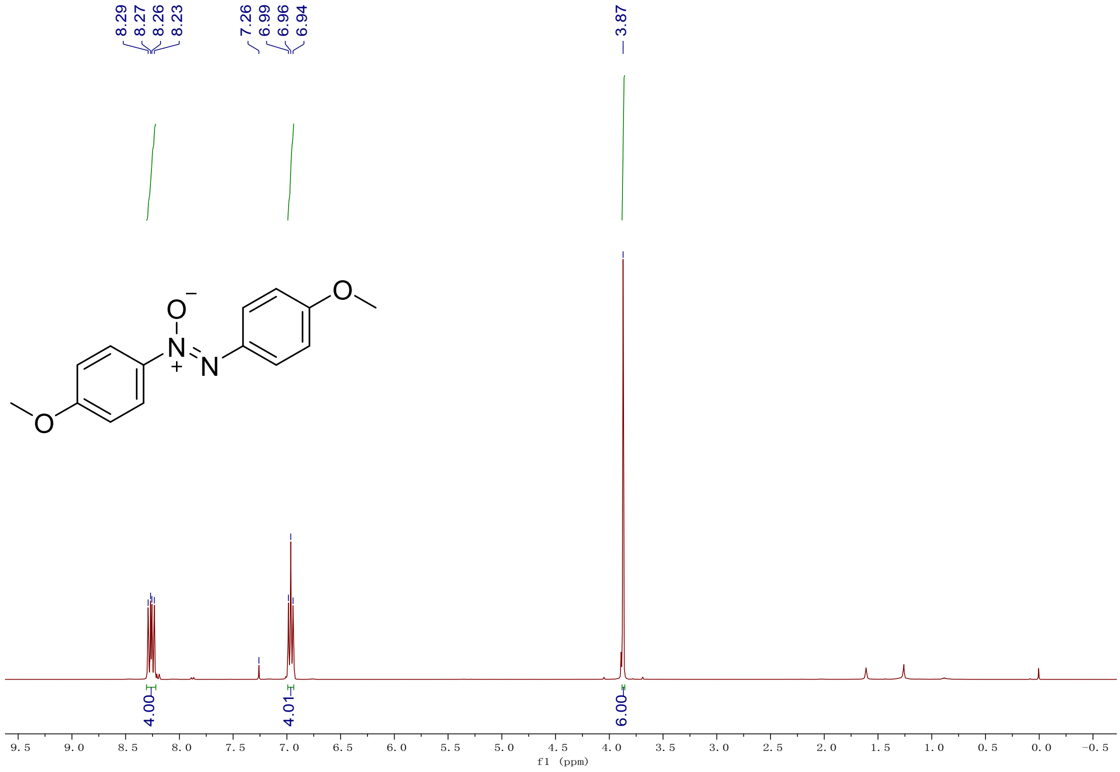
^{1}H NMR (400 MHz, CDCl$_3$) of **2j**



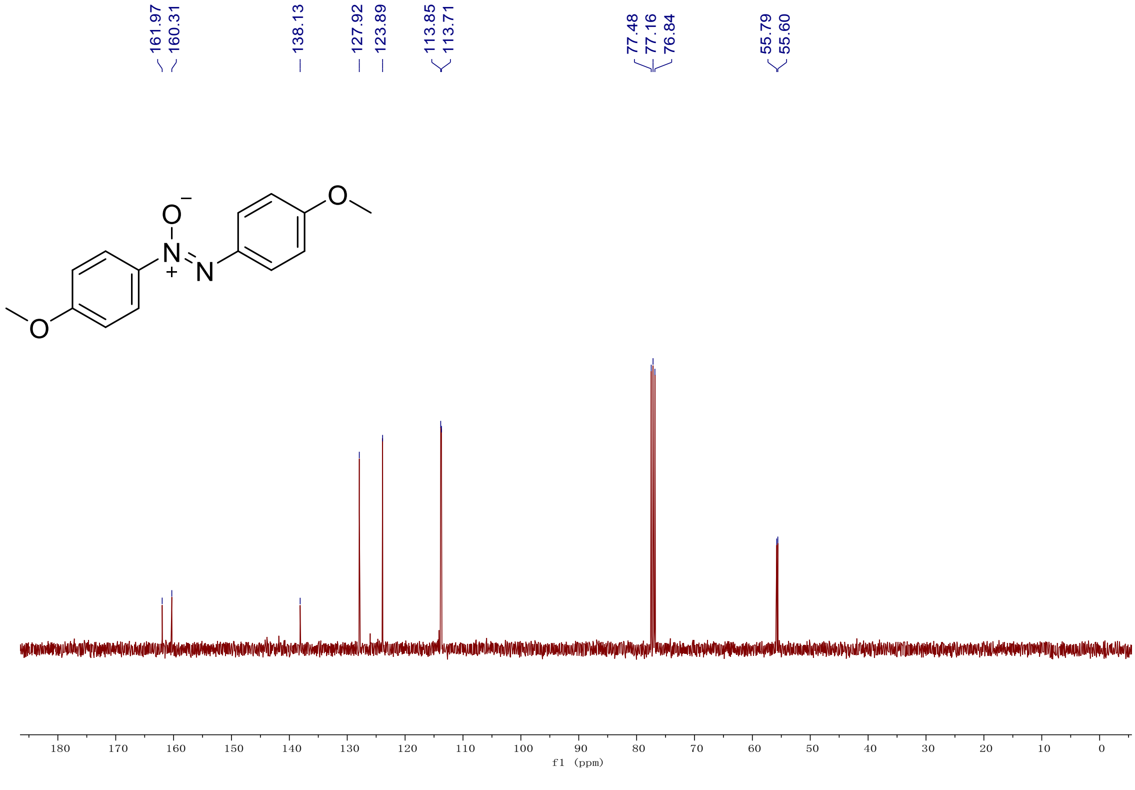
^{13}C NMR (100 MHz, CDCl$_3$) of **2j**



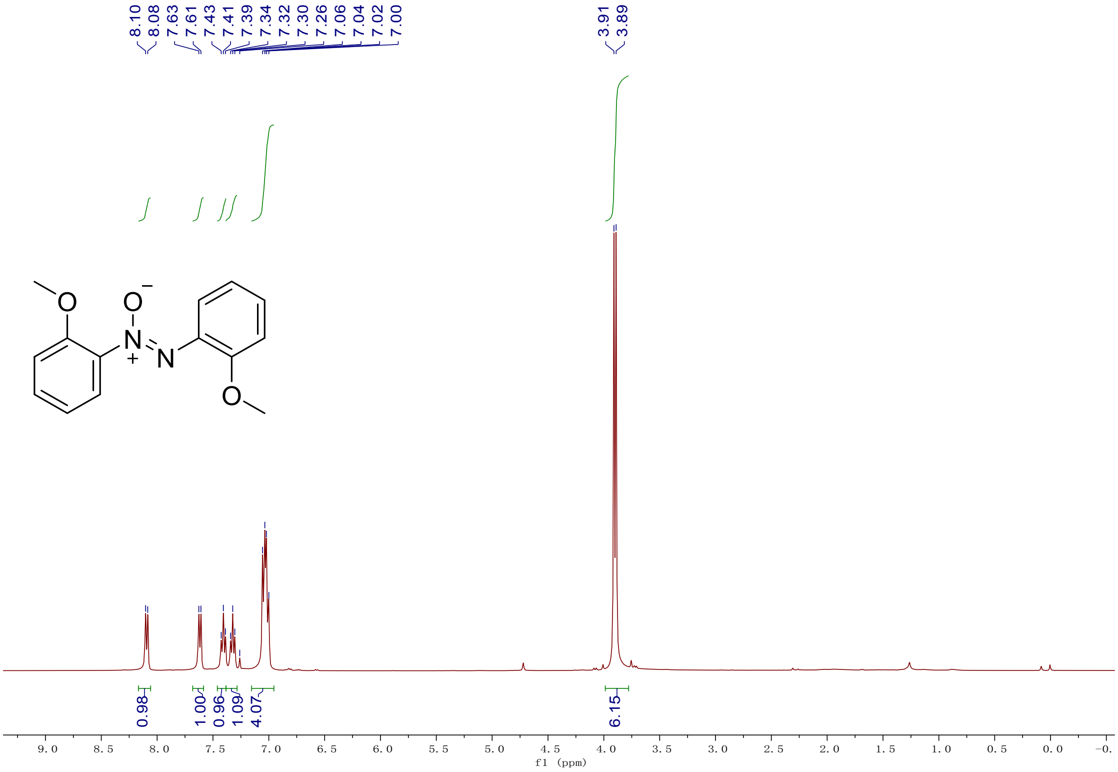
^{1}H NMR (400 MHz, CDCl$_3$) of **2k**



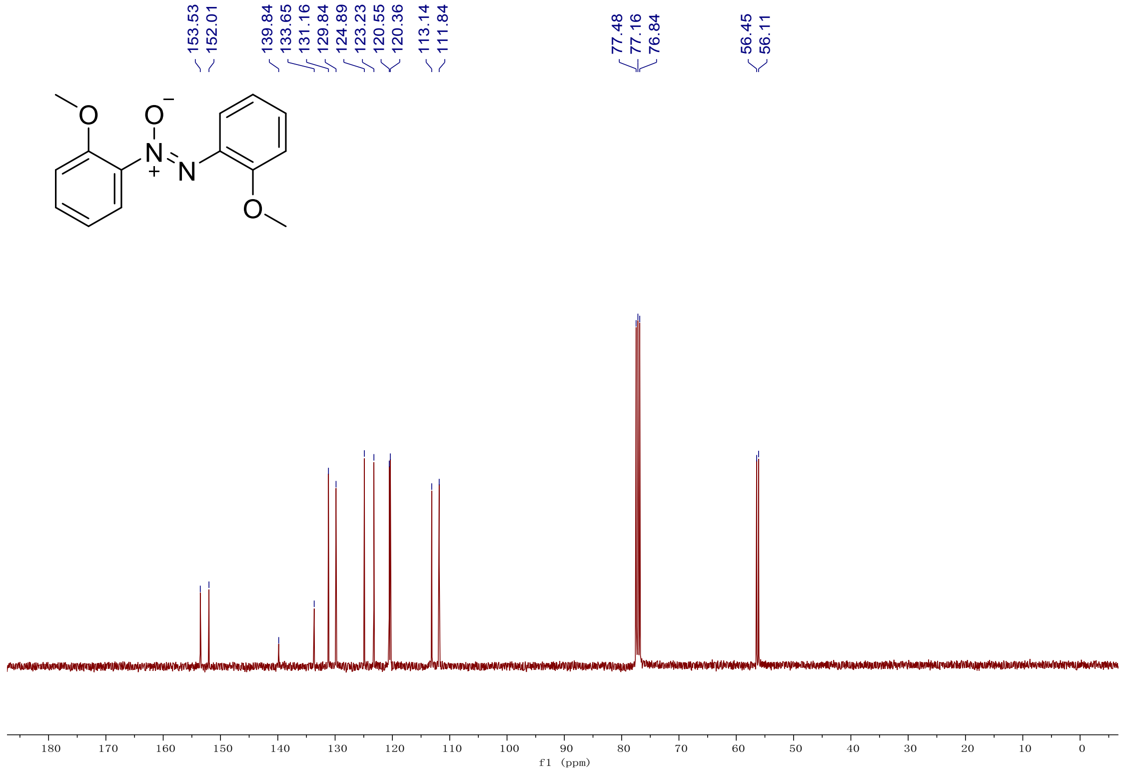
^{13}C NMR (100 MHz, $CDCl_3$) of **2k**



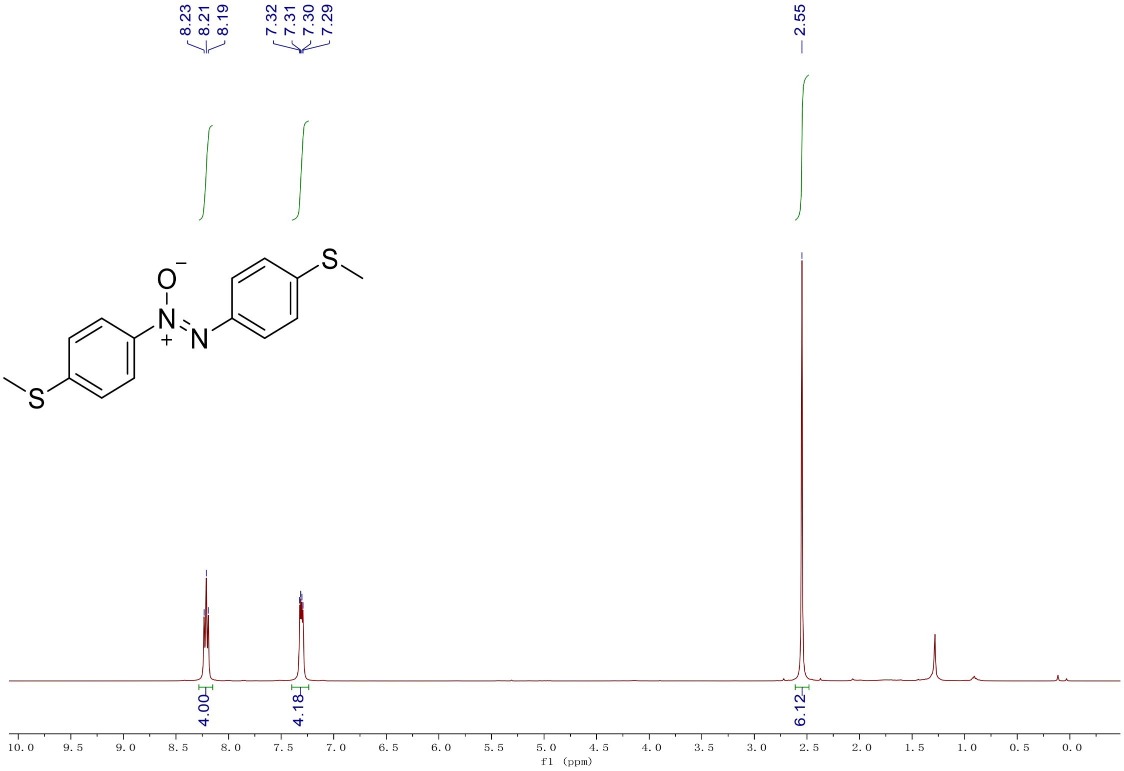
^{1}H NMR (400 MHz, CDCl$_3$) of **2l**



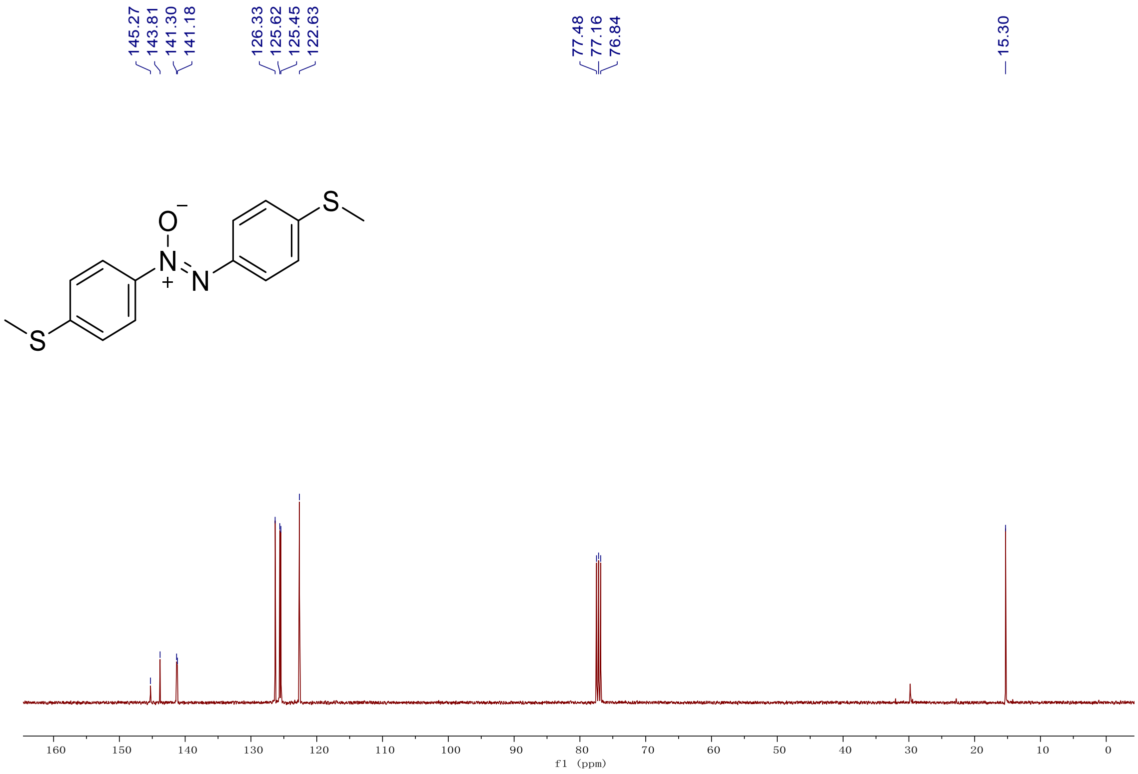
^{13}C NMR (100 MHz, CDCl$_3$) of **2l**



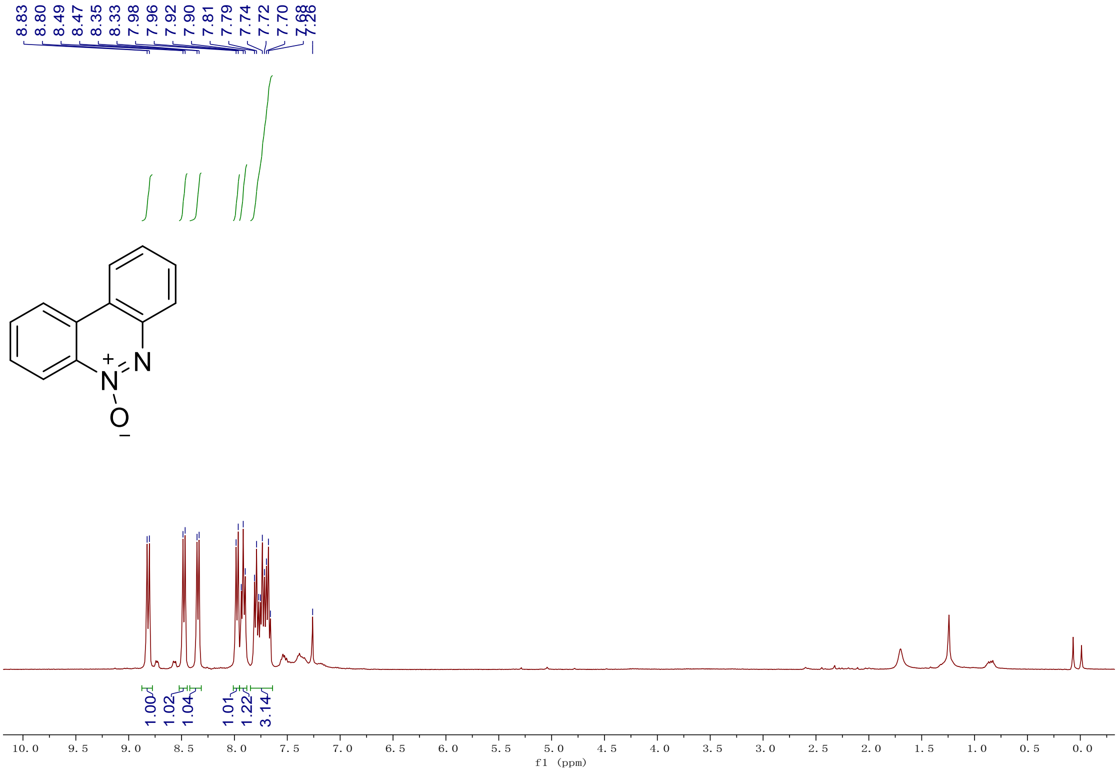
^{1}H NMR (400 MHz, CDCl$_3$) of **2m**



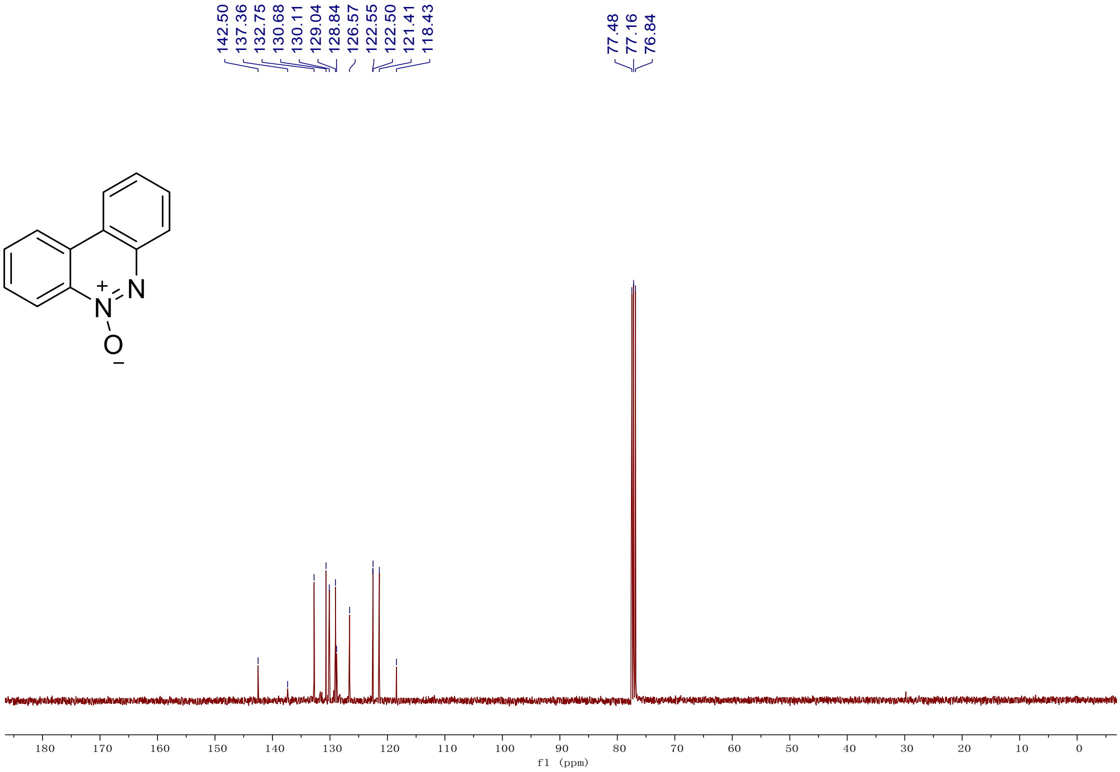
^{13}C NMR (100 MHz, CDCl$_3$) of **2m**



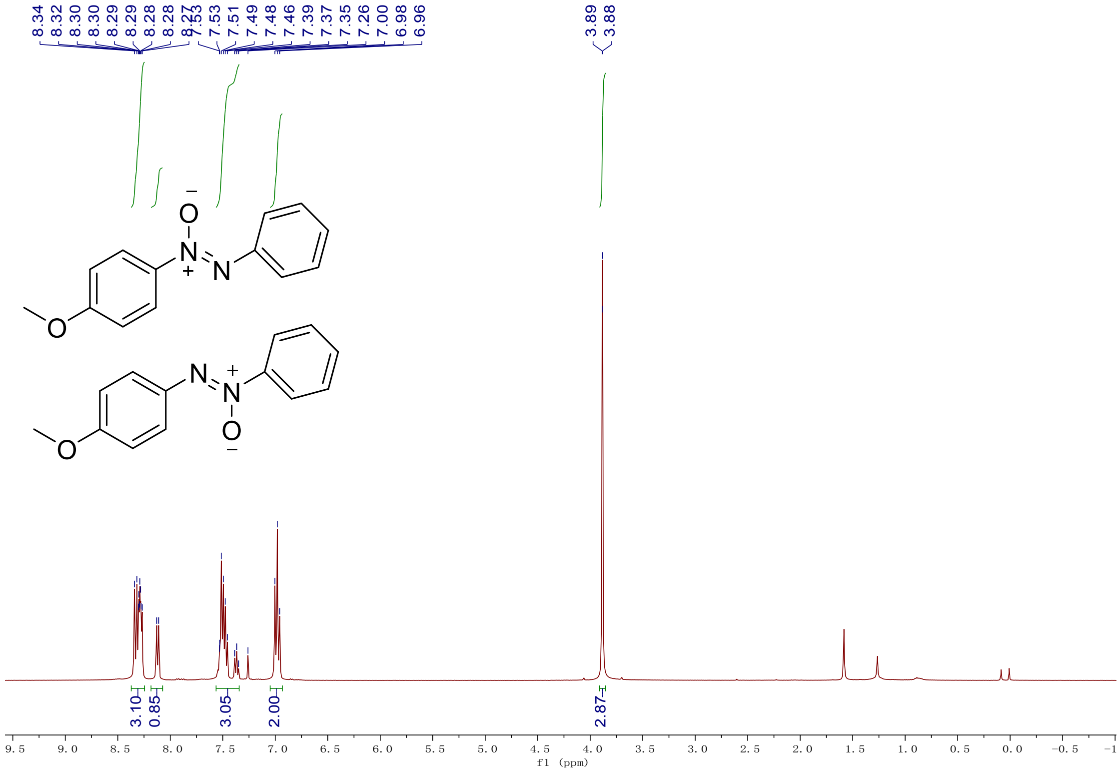
^{1}H NMR (400 MHz, CDCl$_3$) of **2n**



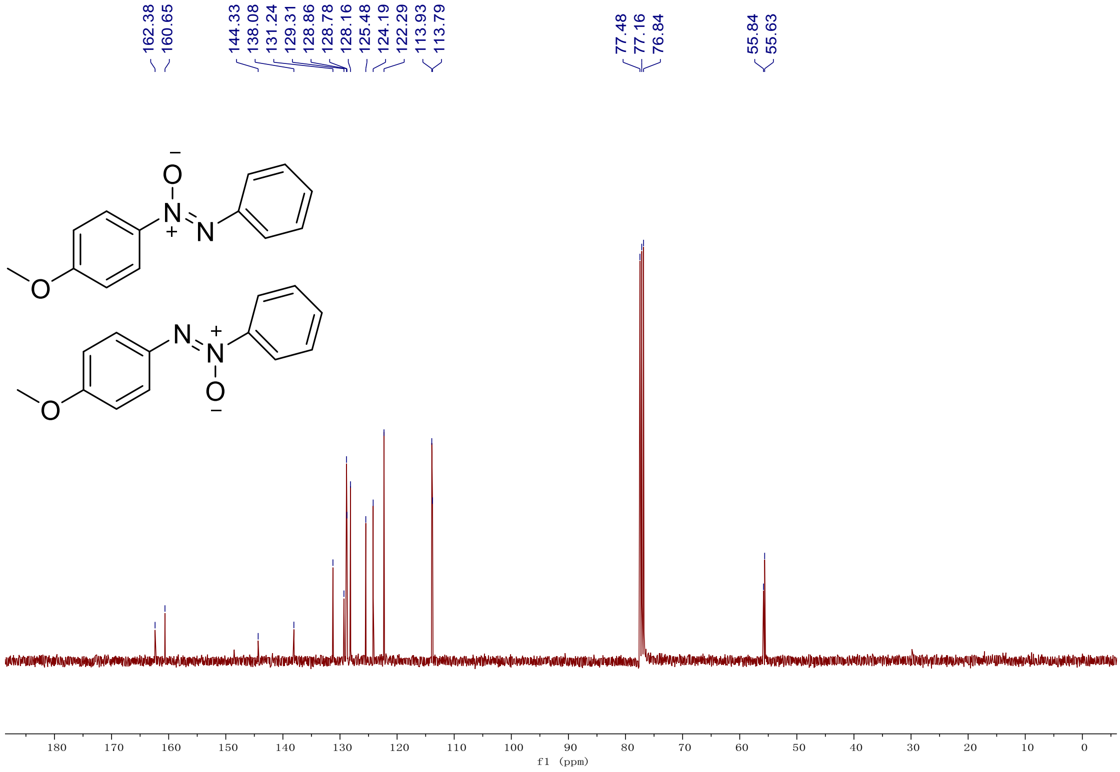
^{13}C NMR (100 MHz, $CDCl_3$) of **2n**



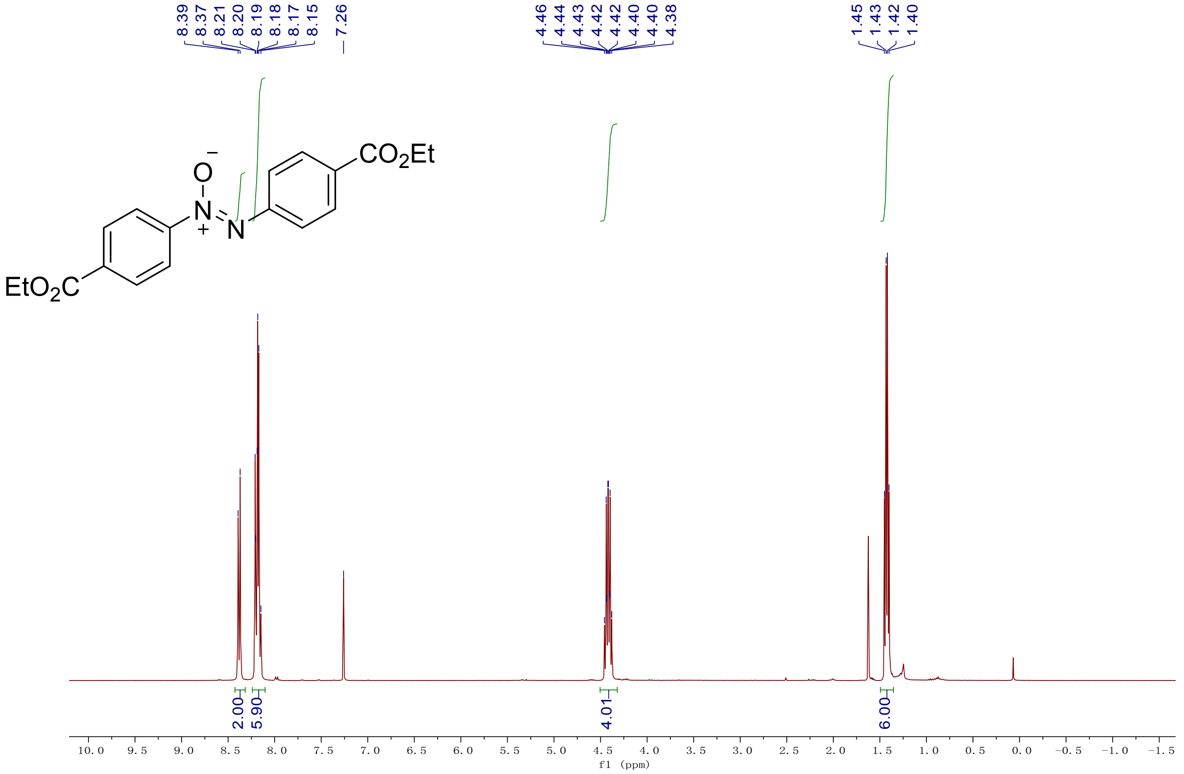
^{1}H NMR (400 MHz, CDCl$_3$) of **2o+2o’**



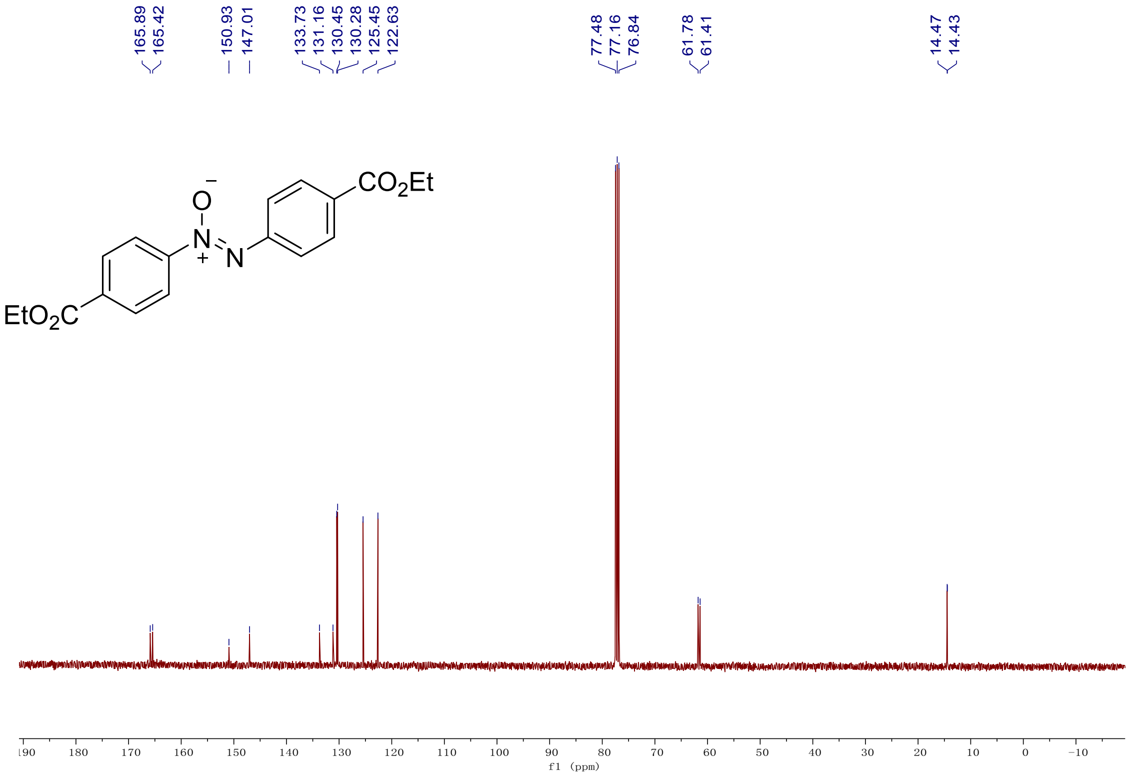
^{13}C NMR (100 MHz, CDCl$_3$) of **2o+2o’**



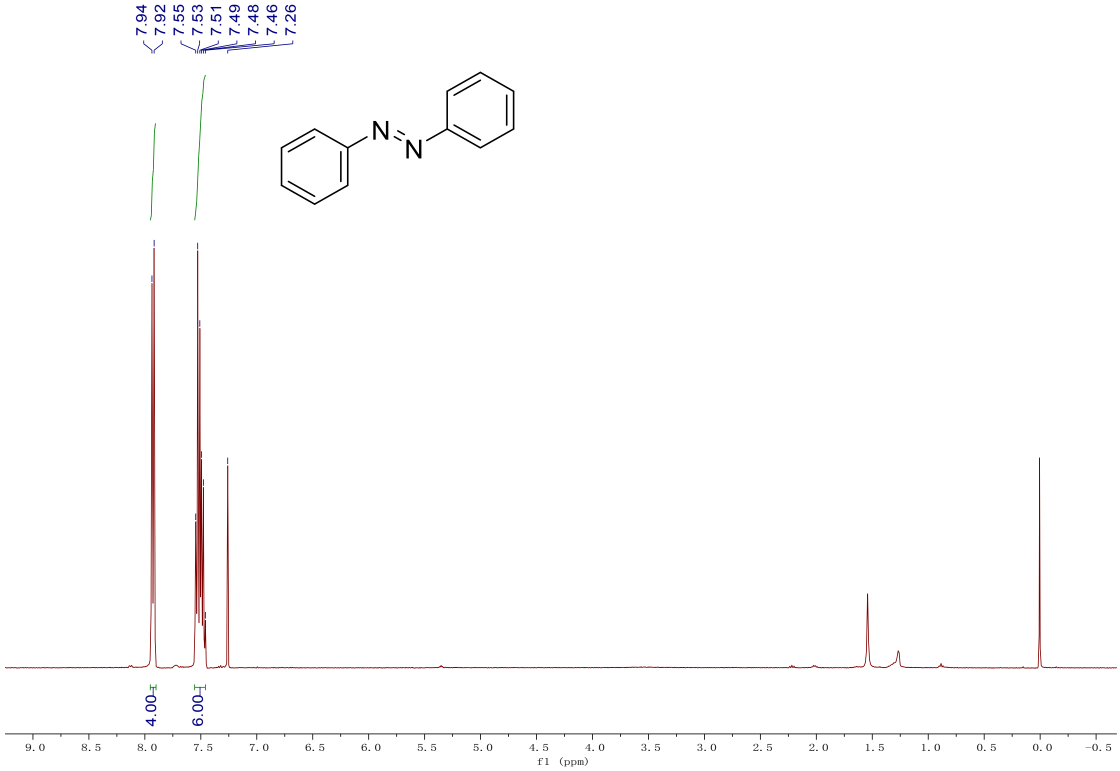
^{1}H NMR (400 MHz, $CDCl_3$) of **2p**



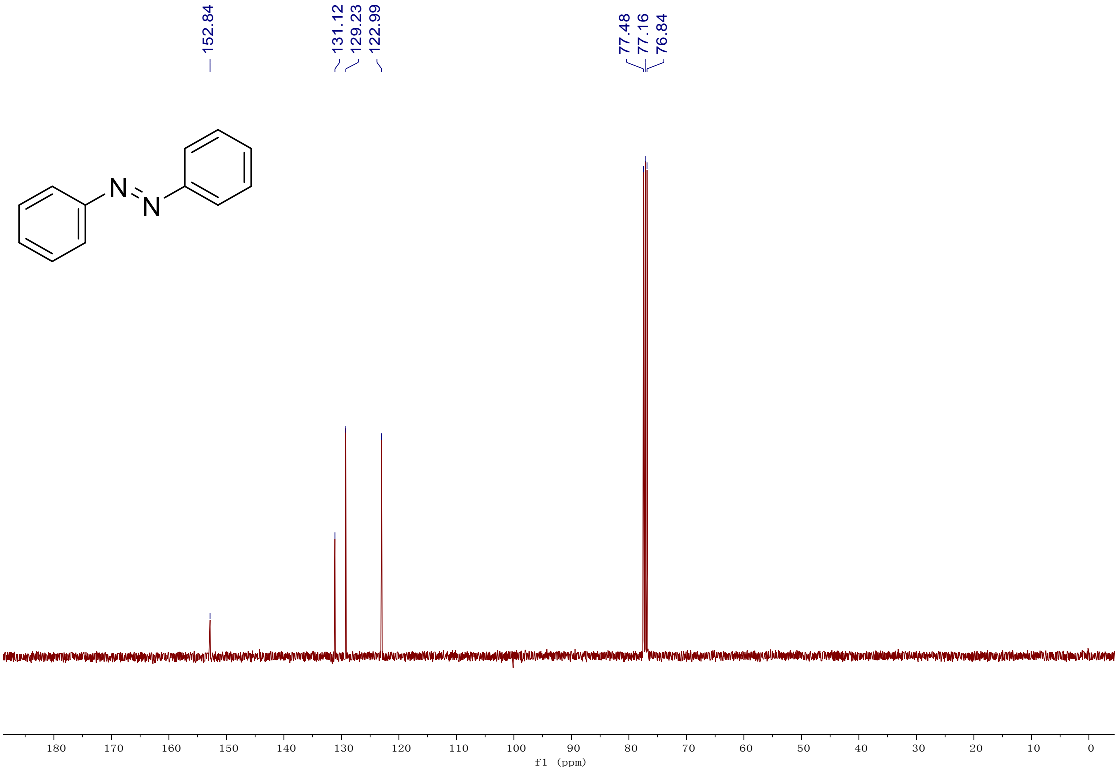
^{13}C NMR (100 MHz, CDCl$_3$) of **2p**



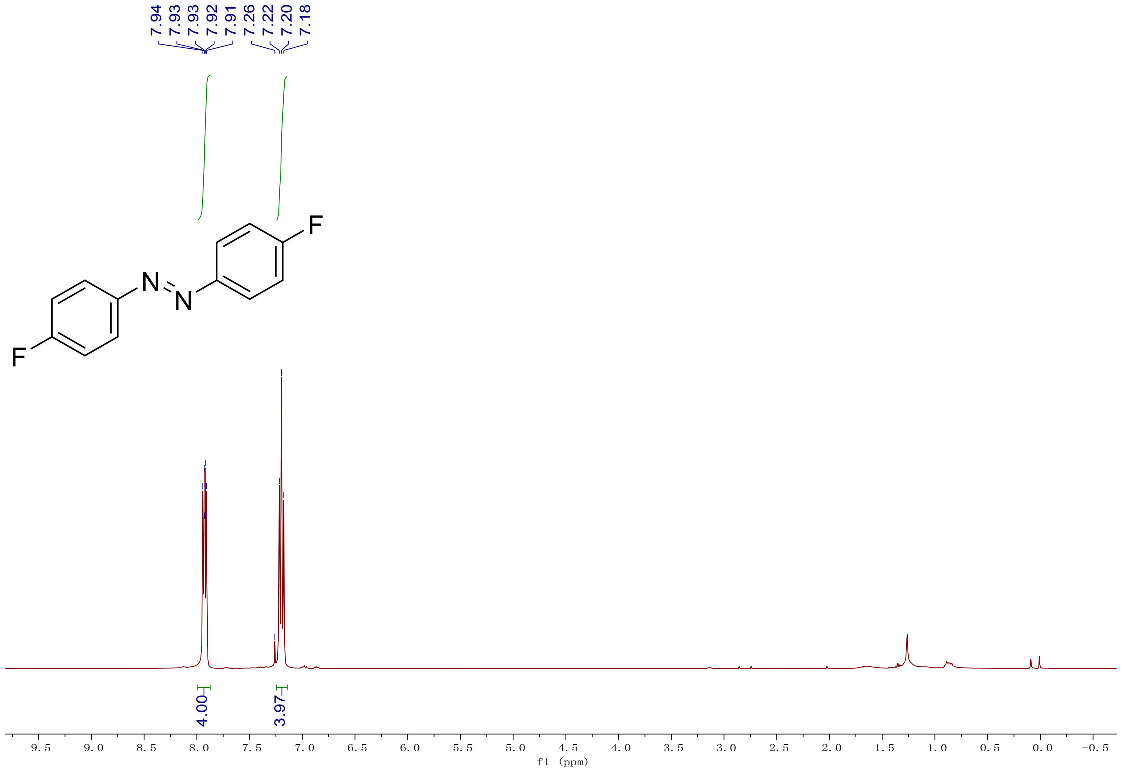
^{1}H NMR (400 MHz, CDCl$_3$) of **3a**



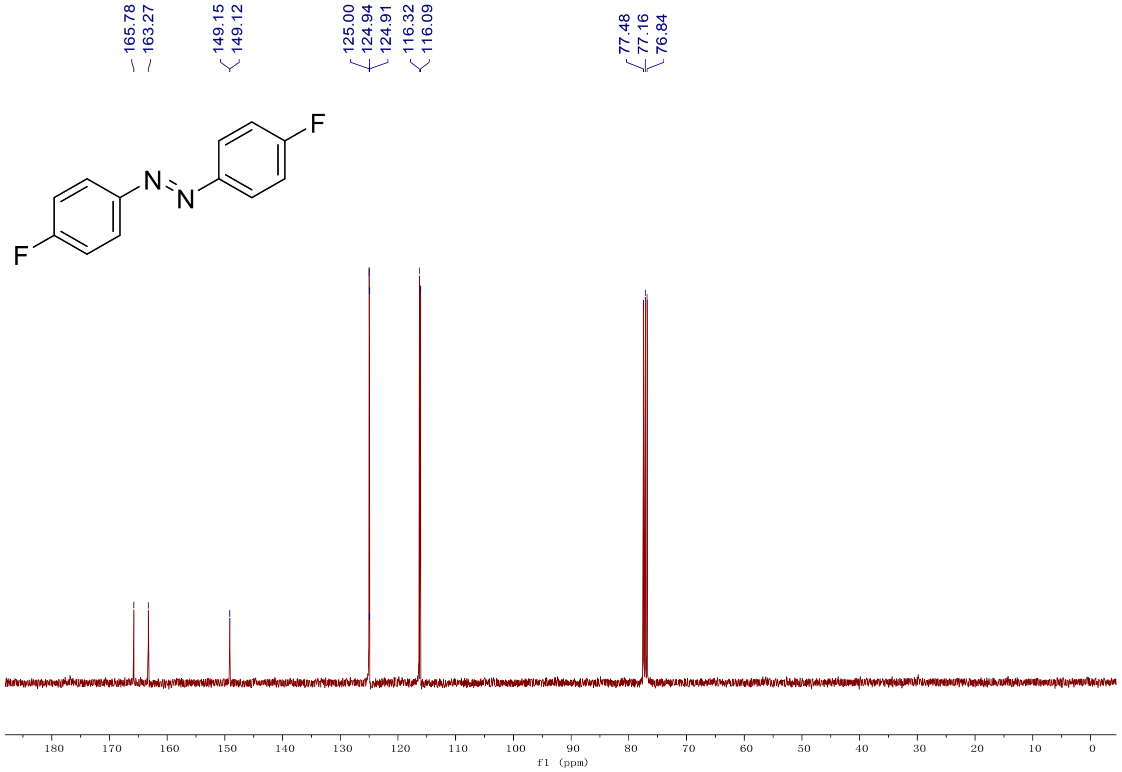
^{13}C NMR (100 MHz, CDCl$_3$) of **3a**



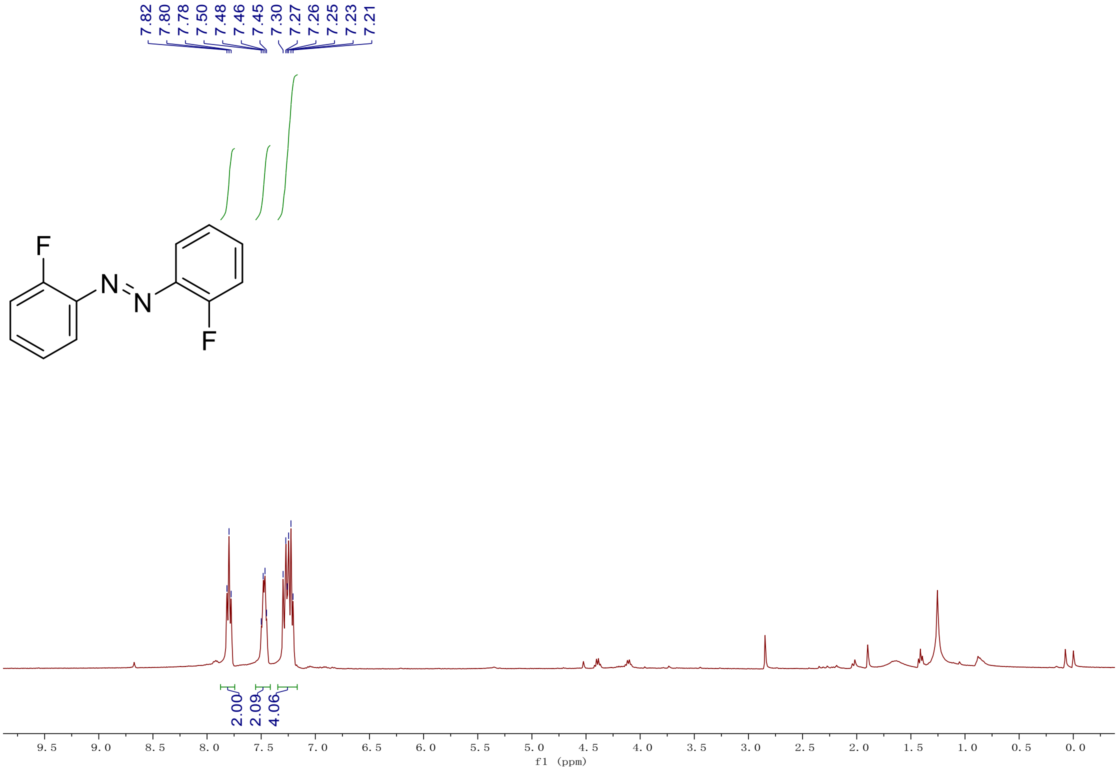
^{1}H NMR (400 MHz, CDCl$_3$) of **3b**



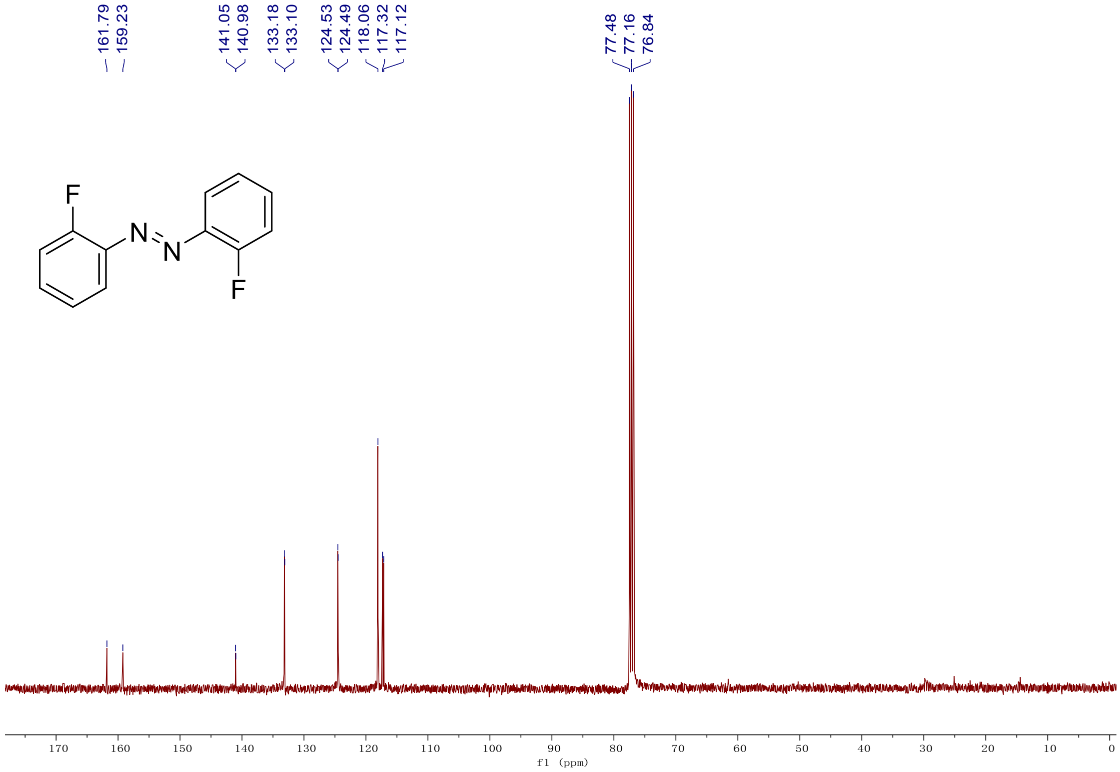
^{13}C NMR (100 MHz, CDCl$_3$) of **3b**



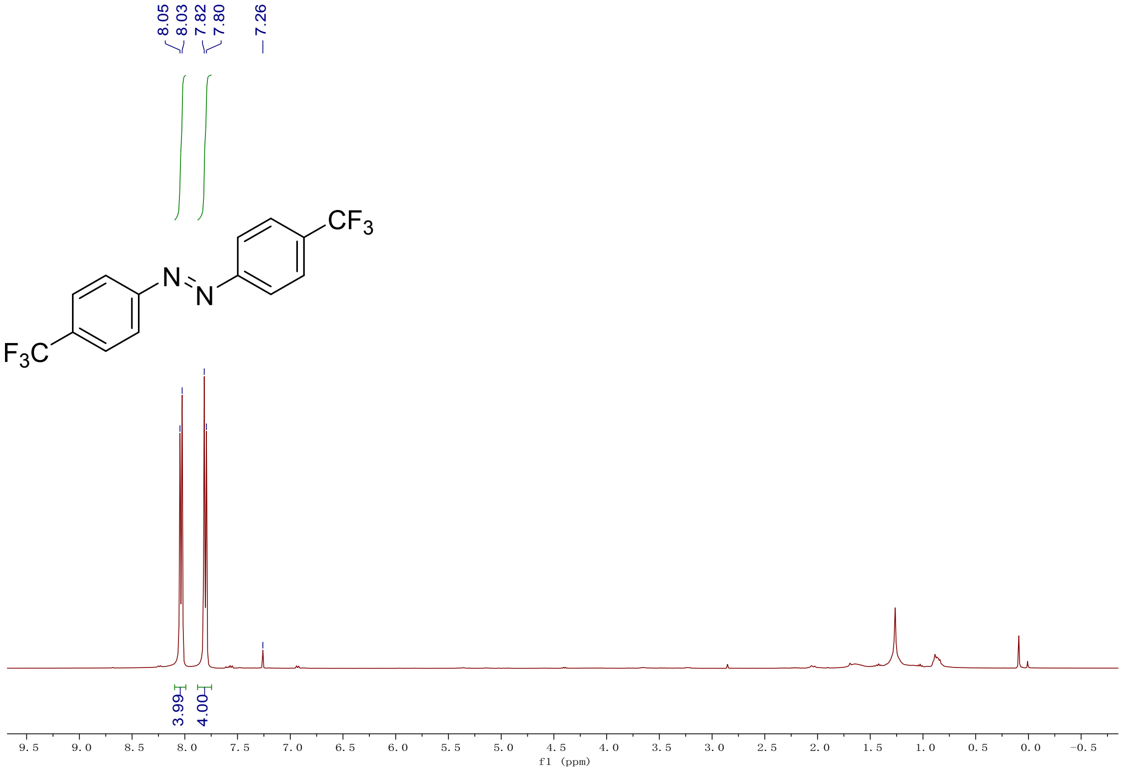
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



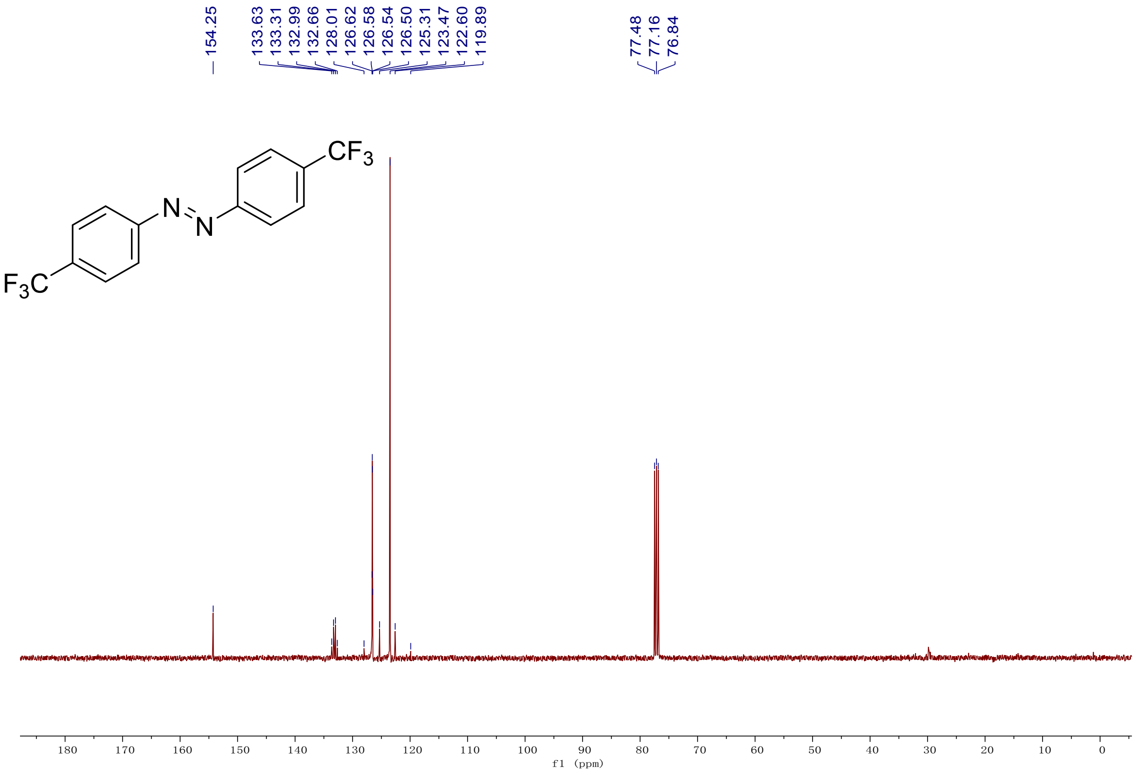
^{13}C NMR (100 MHz, $CDCl_3$) of **3c**



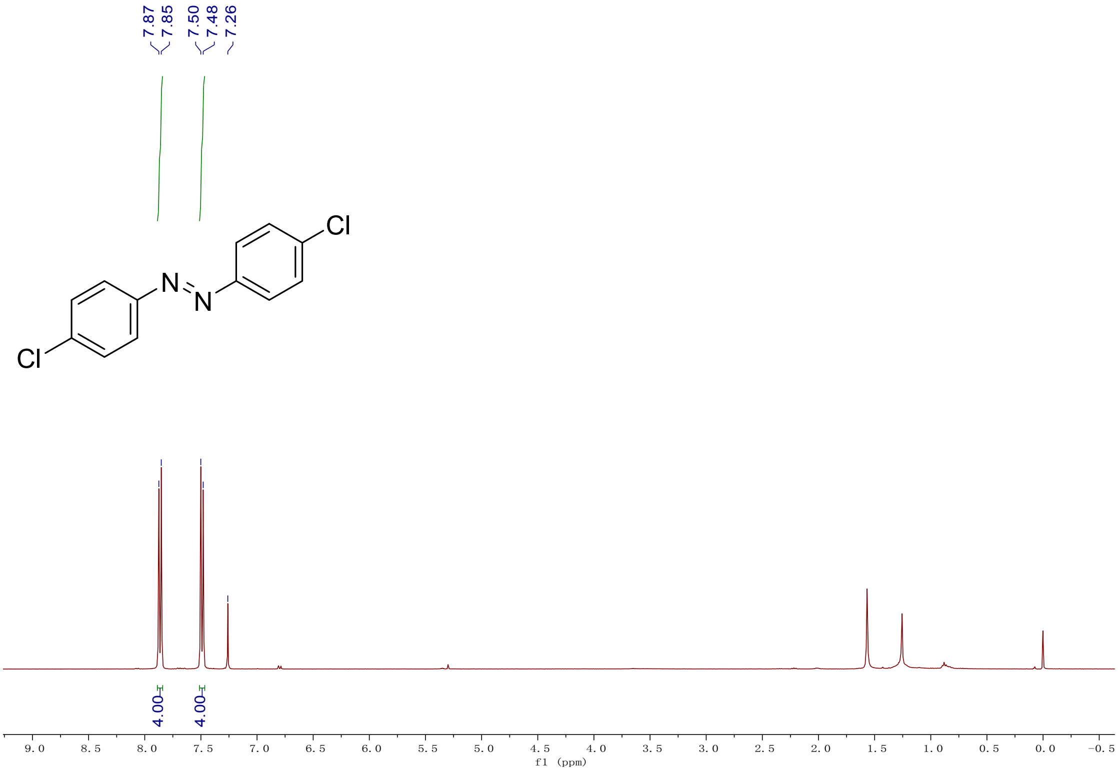
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



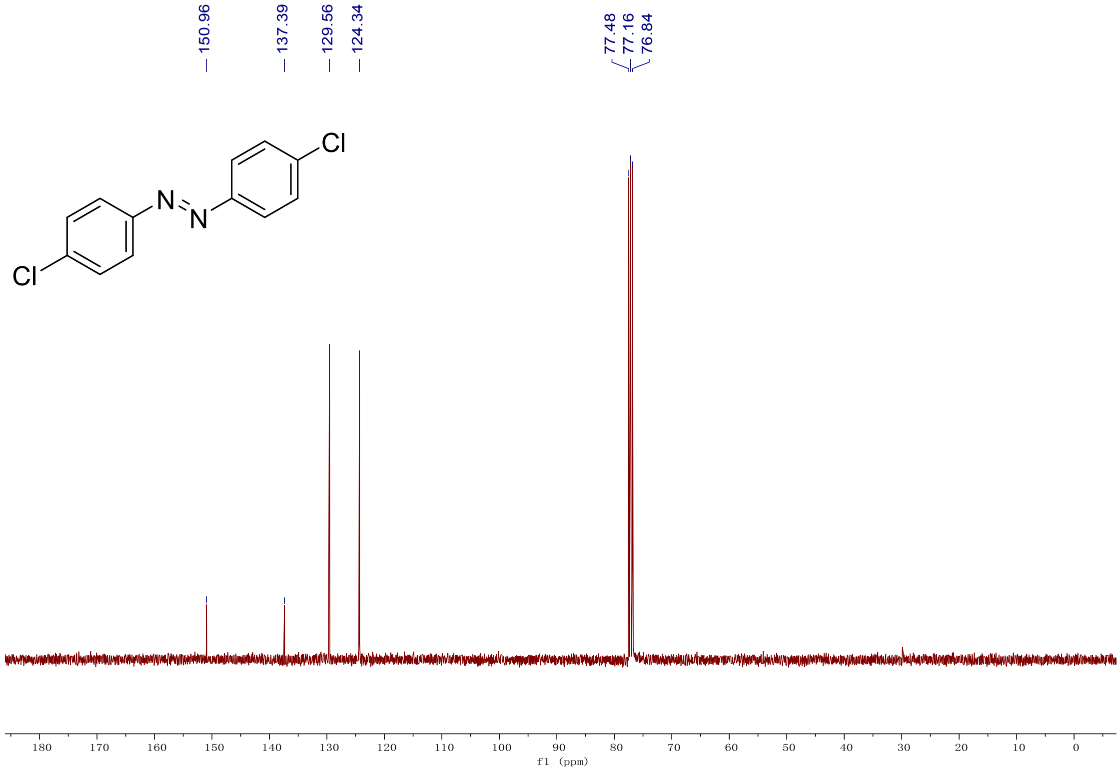
^{13}C NMR (100 MHz, CDCl$_3$) of **3d**



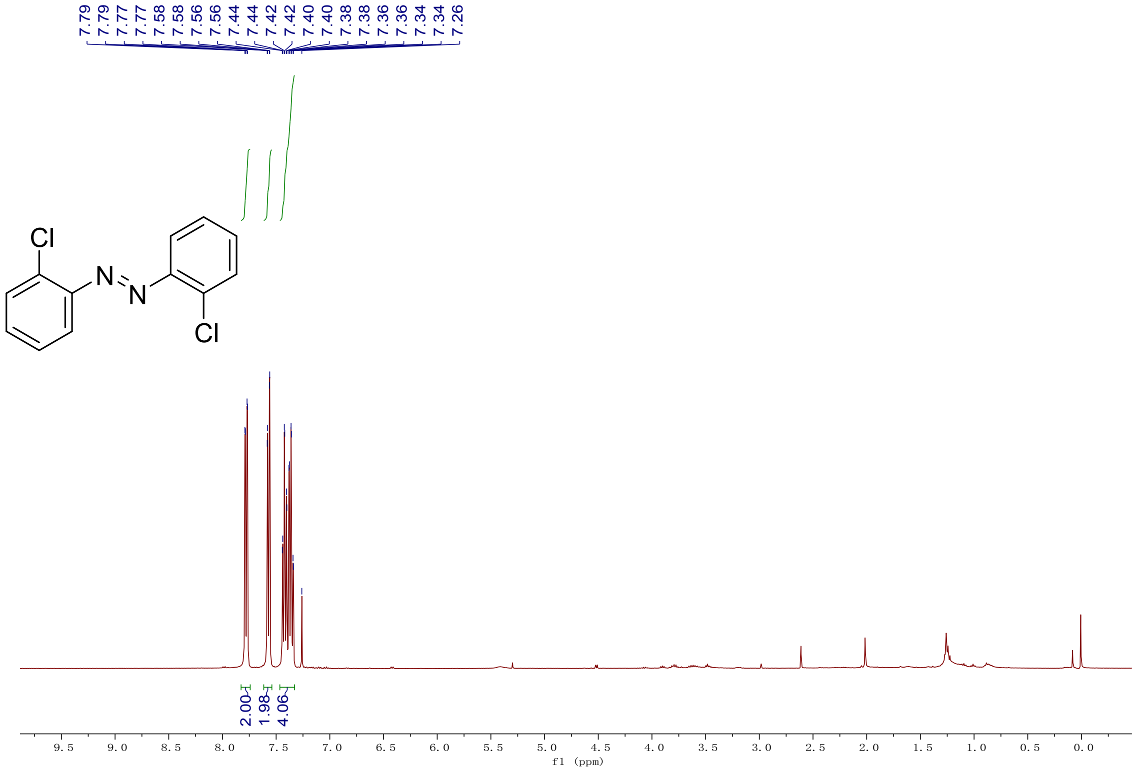
^{1}H NMR (400 MHz, CDCl$_3$) of **3e**



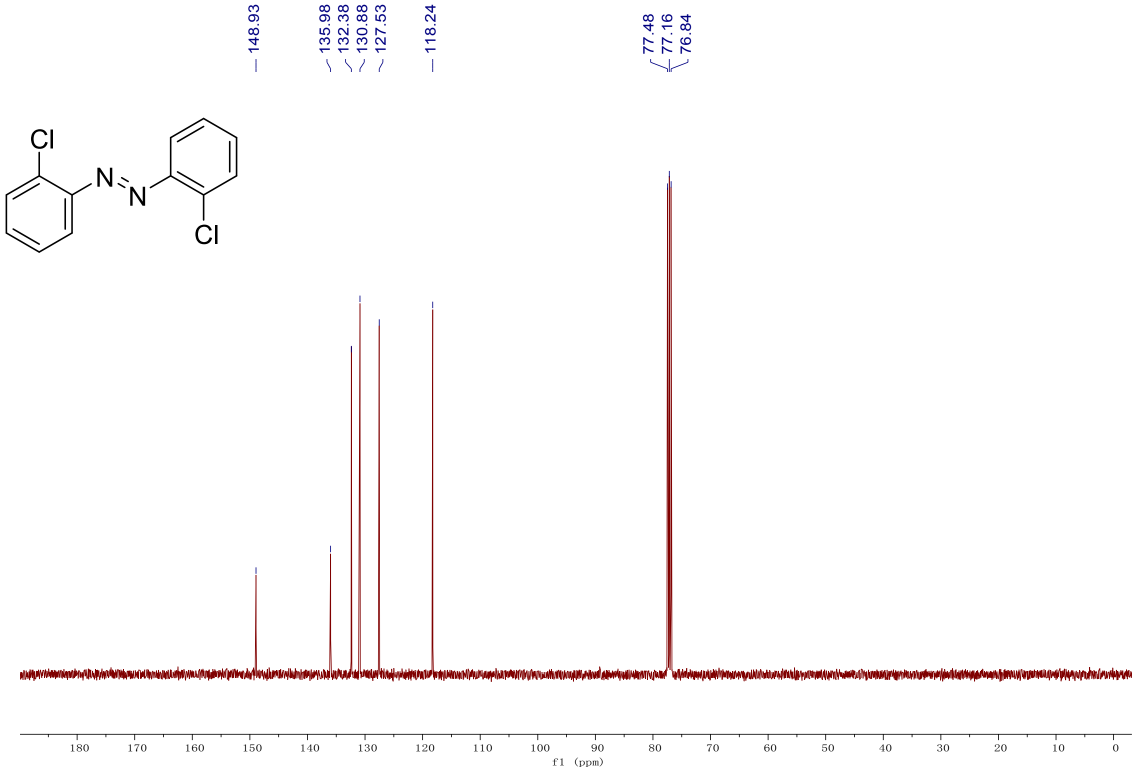
^{13}C NMR (100 MHz, CDCl$_3$) of **3e**



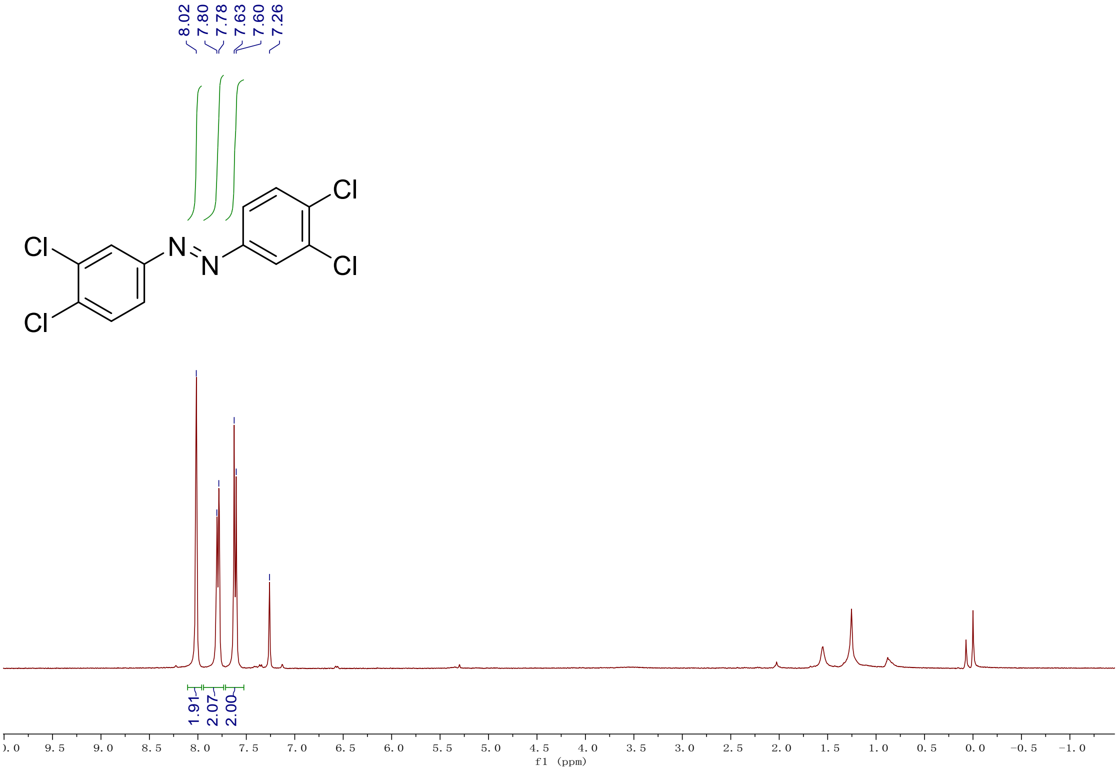
^{1}H NMR (400 MHz, CDCl$_3$) of **3f**



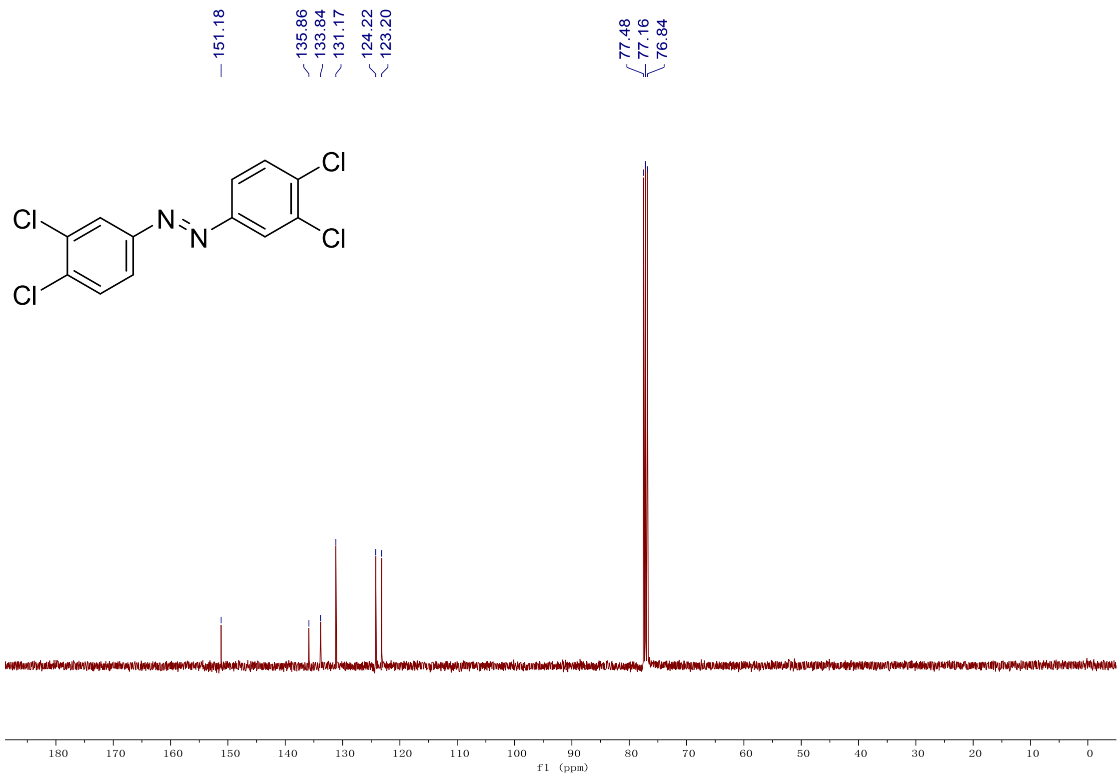
^{13}C NMR (100 MHz, CDCl$_3$) of **3f**



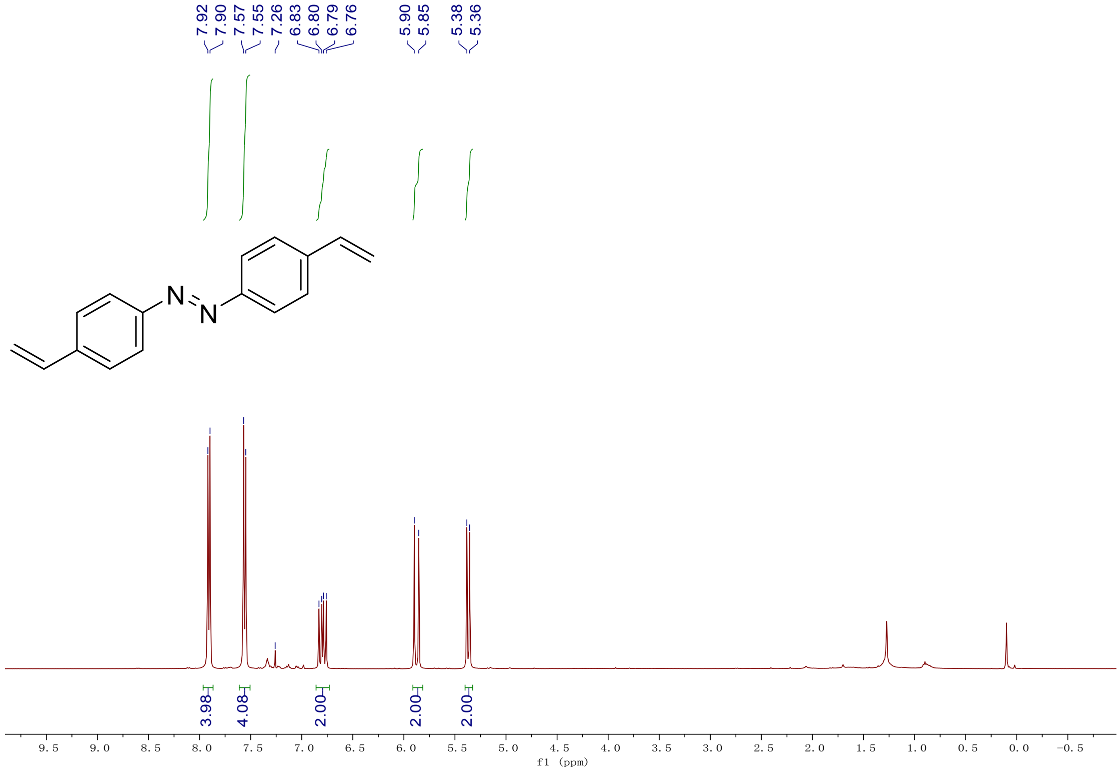
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



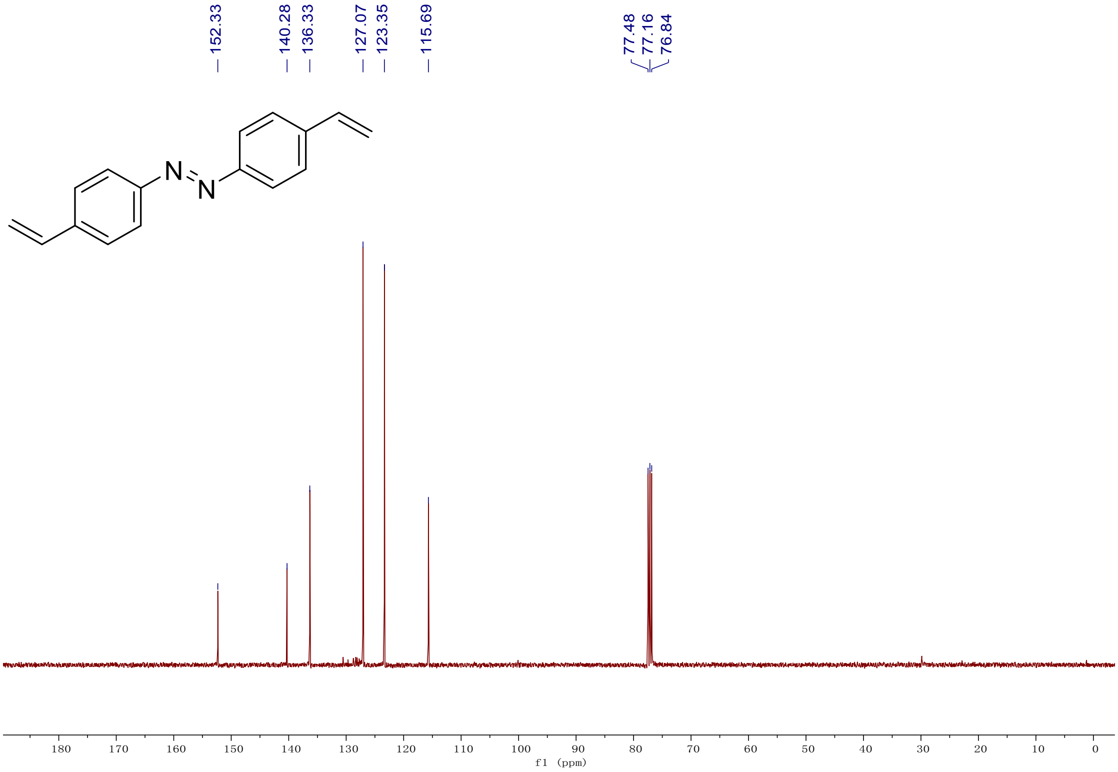
^{13}C NMR (100 MHz, $CDCl_3$) of **3g**



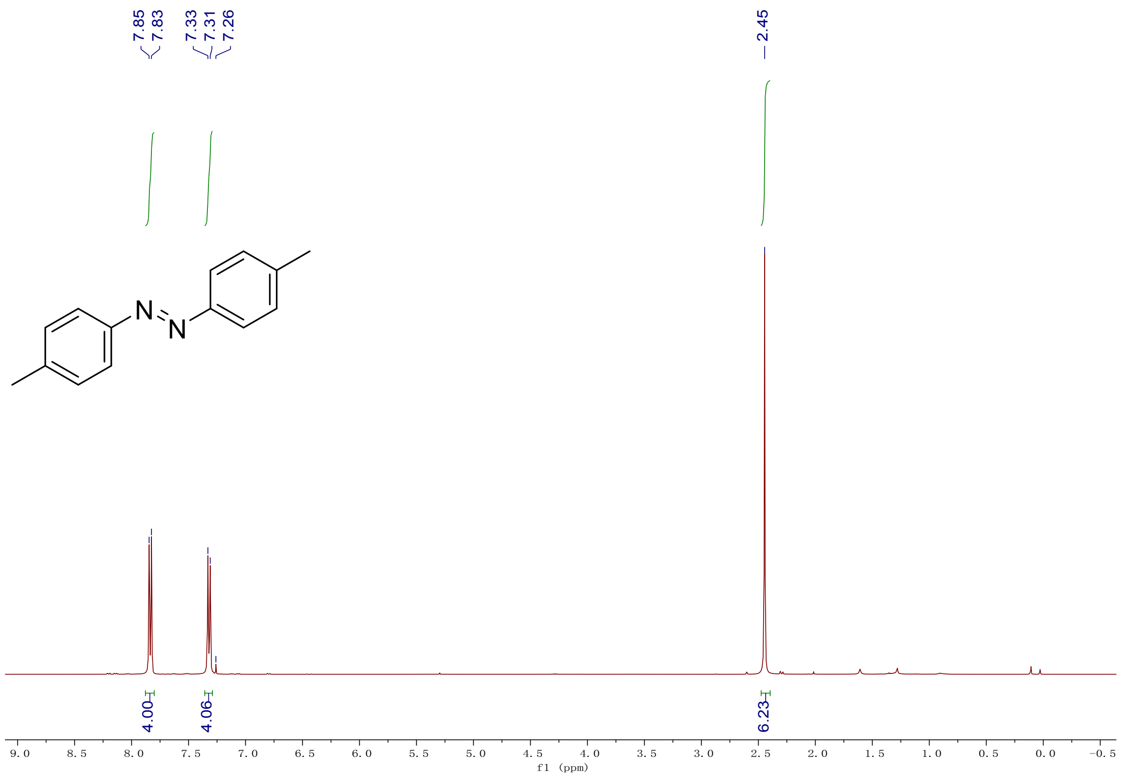
^{1}H NMR (400 MHz, CDCl$_3$) of **3h**



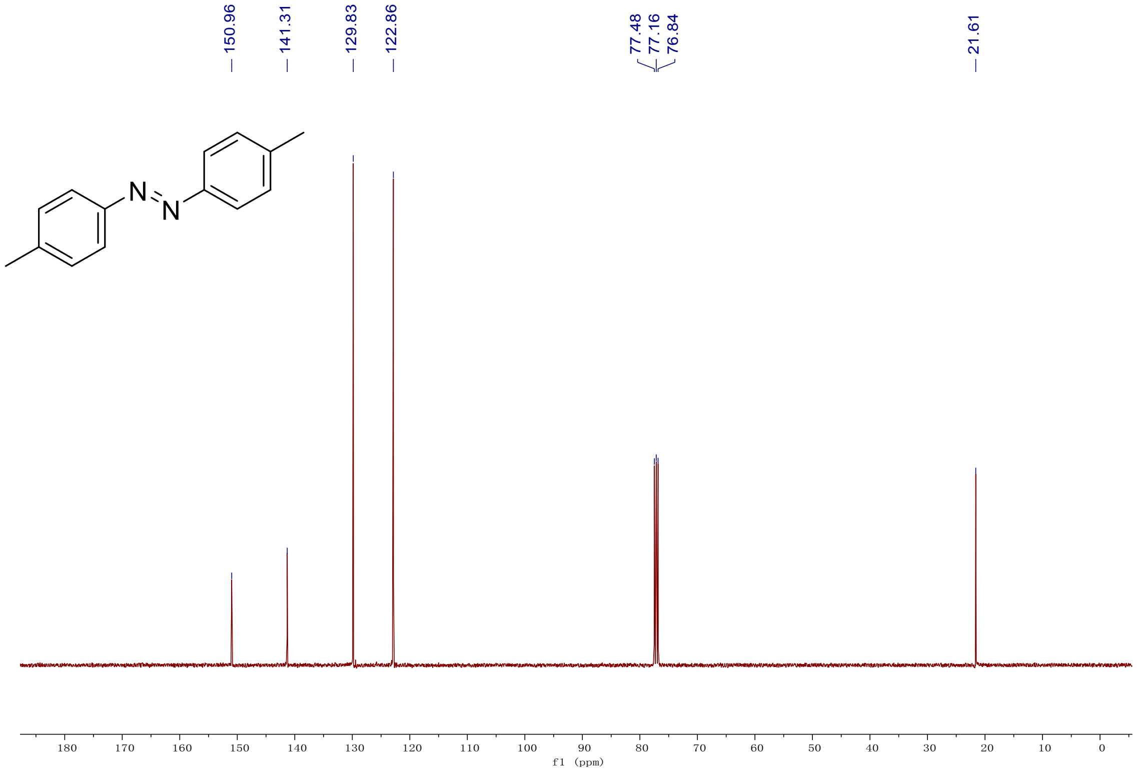
^{13}C NMR (100 MHz, CDCl$_3$) of **3h**



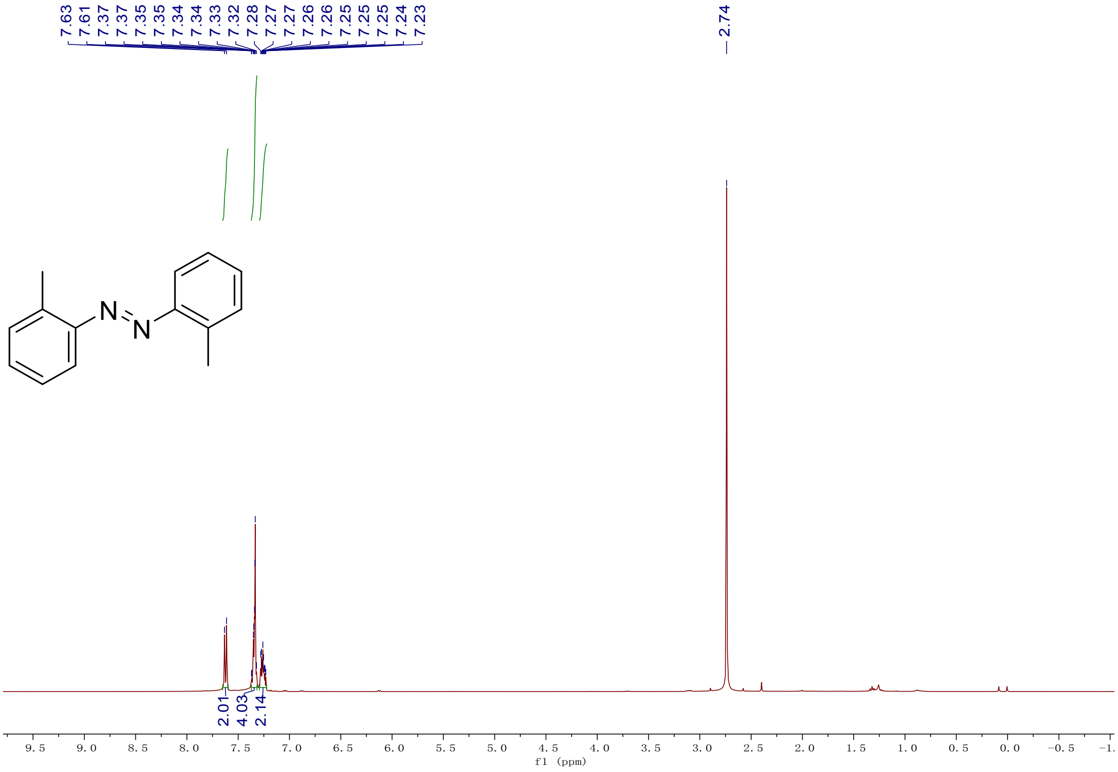
^{1}H NMR (400 MHz, CDCl$_3$) of **3i**



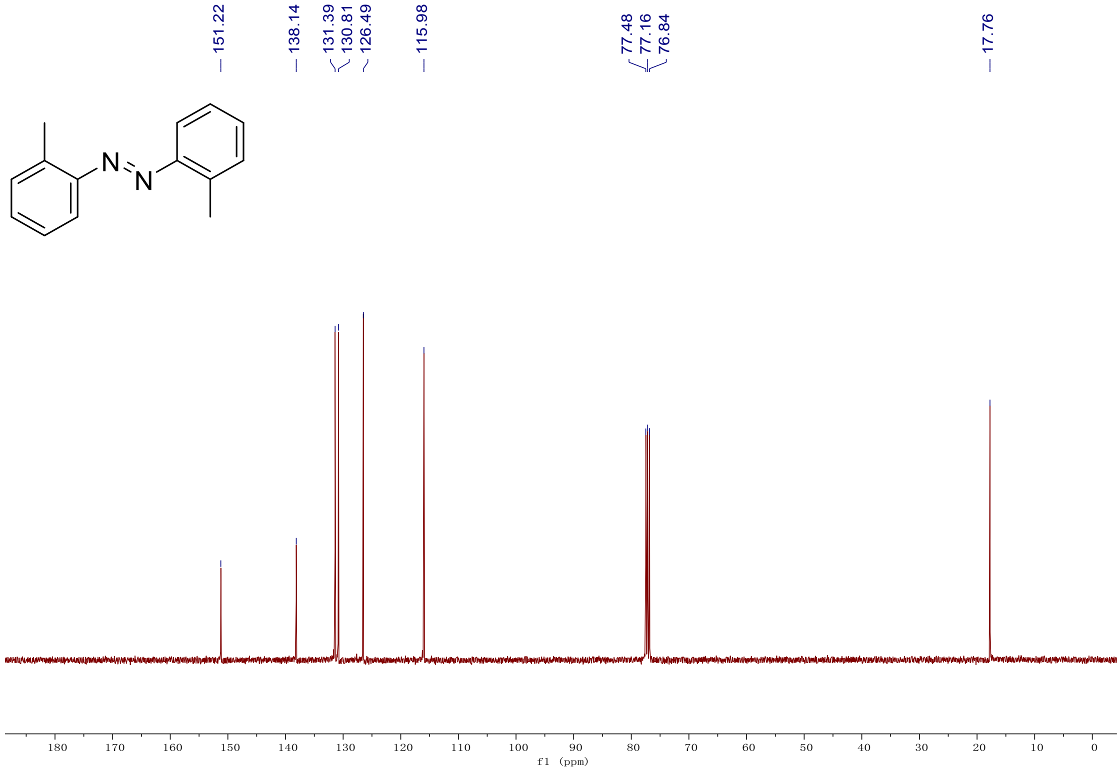
^{13}C NMR (100 MHz, CDCl$_3$) of **3i**



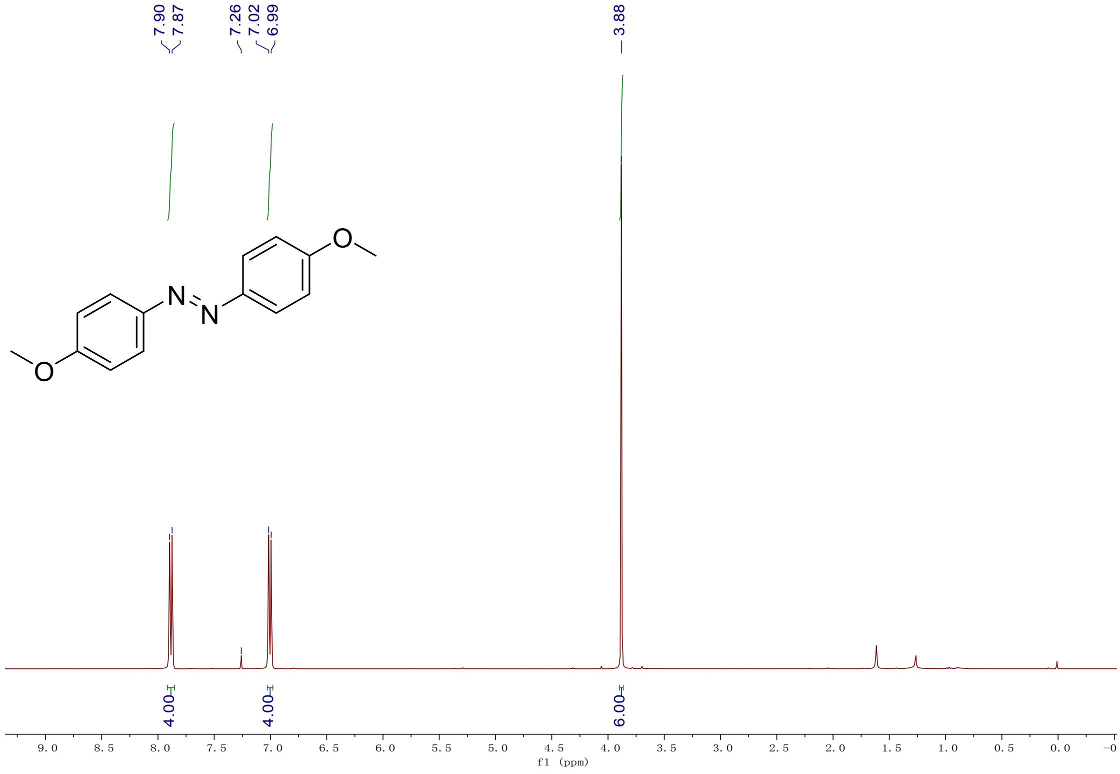
^{1}H NMR (400 MHz, CDCl$_3$) of **3j**



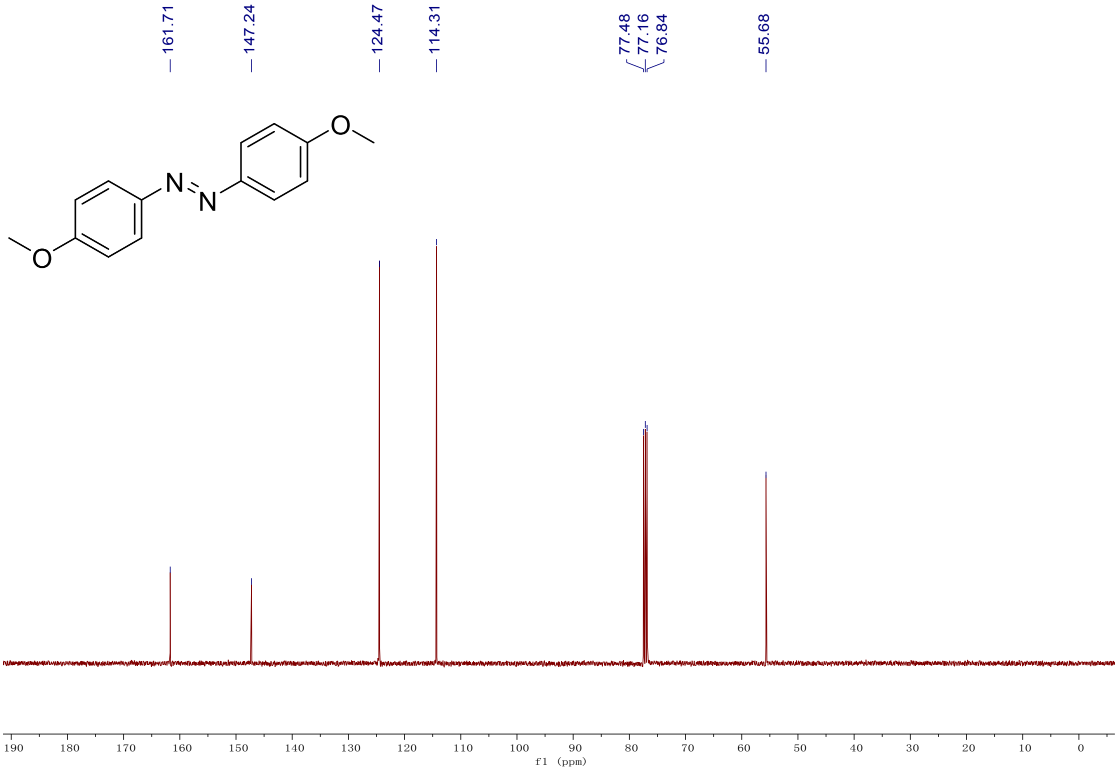
^{13}C NMR (100 MHz, CDCl$_3$) of **3j**



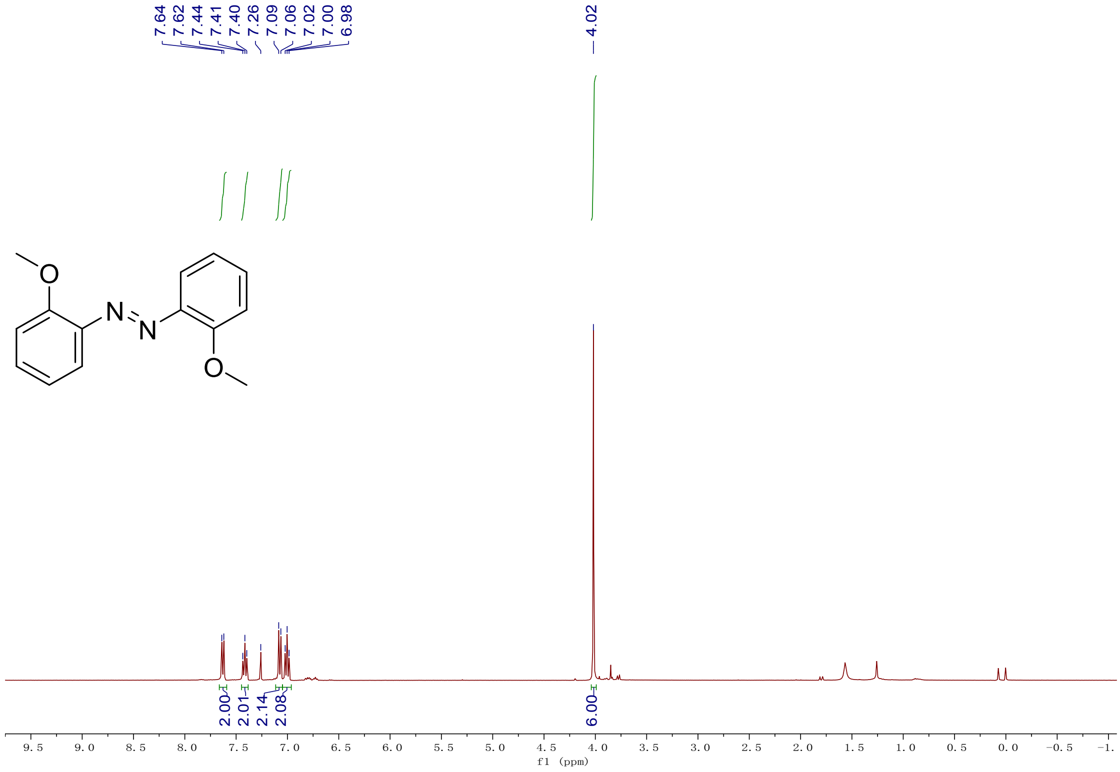
^{1}H NMR (400 MHz, CDCl$_3$) of **3k**



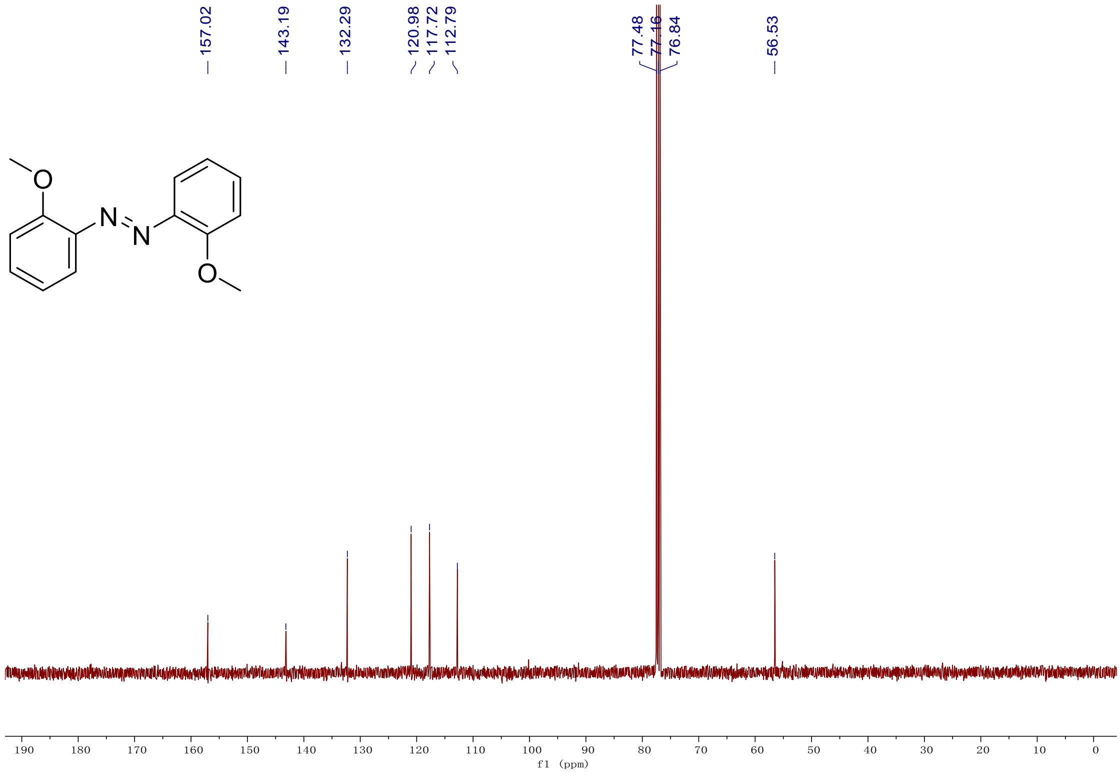
^{13}C NMR (100 MHz, CDCl$_3$) of **3k**



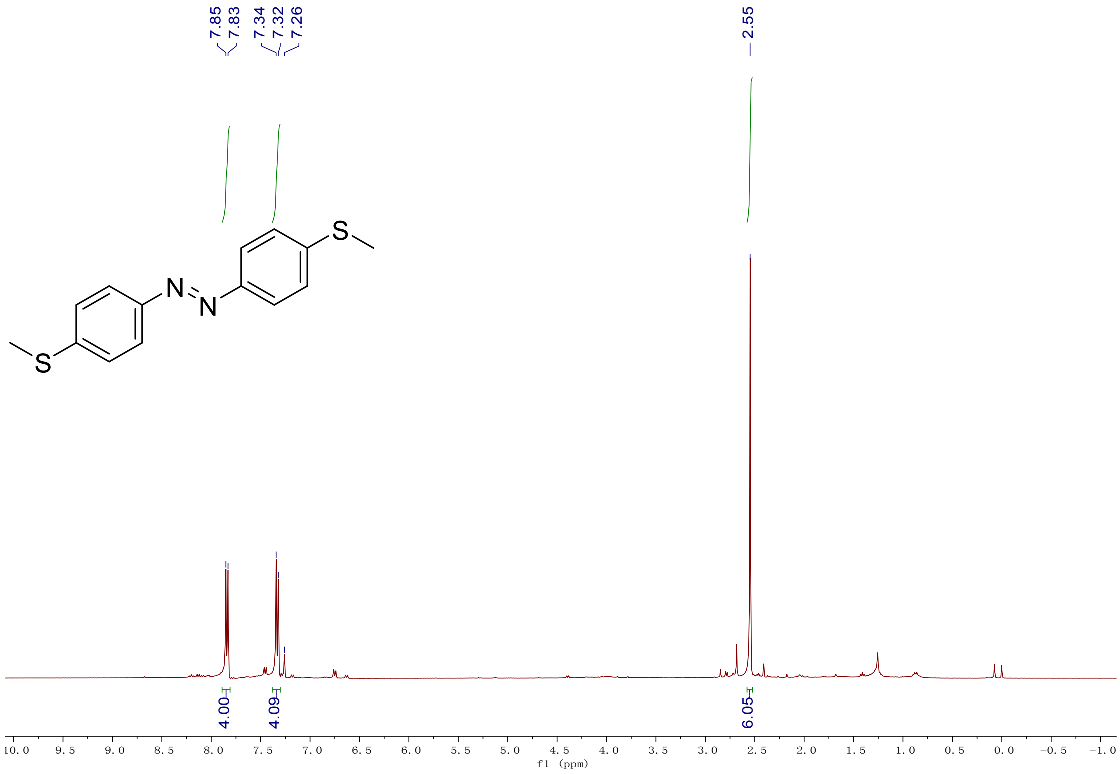
^{1}H NMR (400 MHz, CDCl$_3$) of **3l**



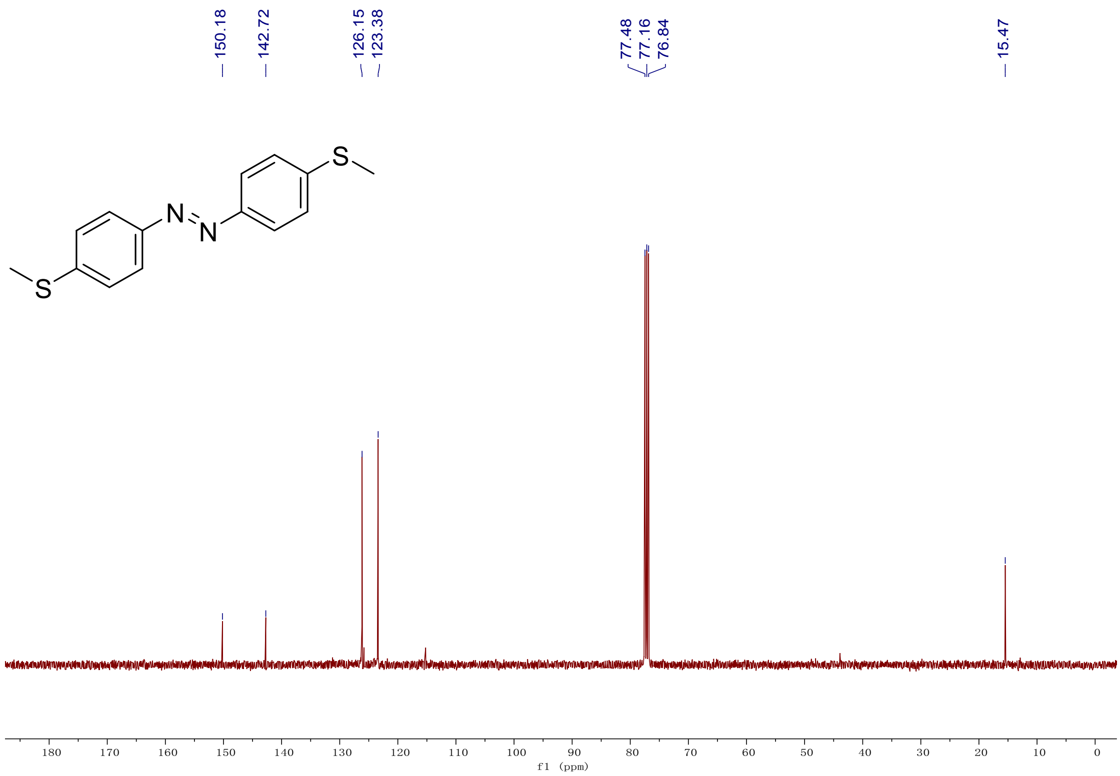
^{13}C NMR (100 MHz, CDCl$_3$) of **3l**



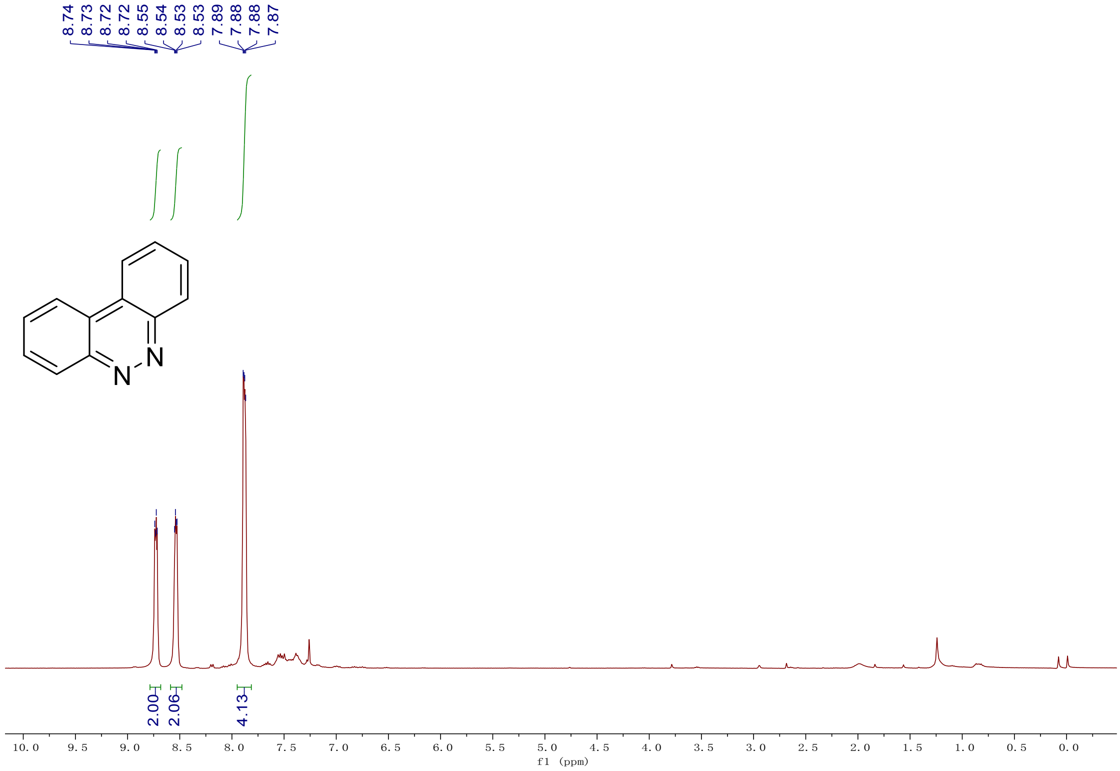
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



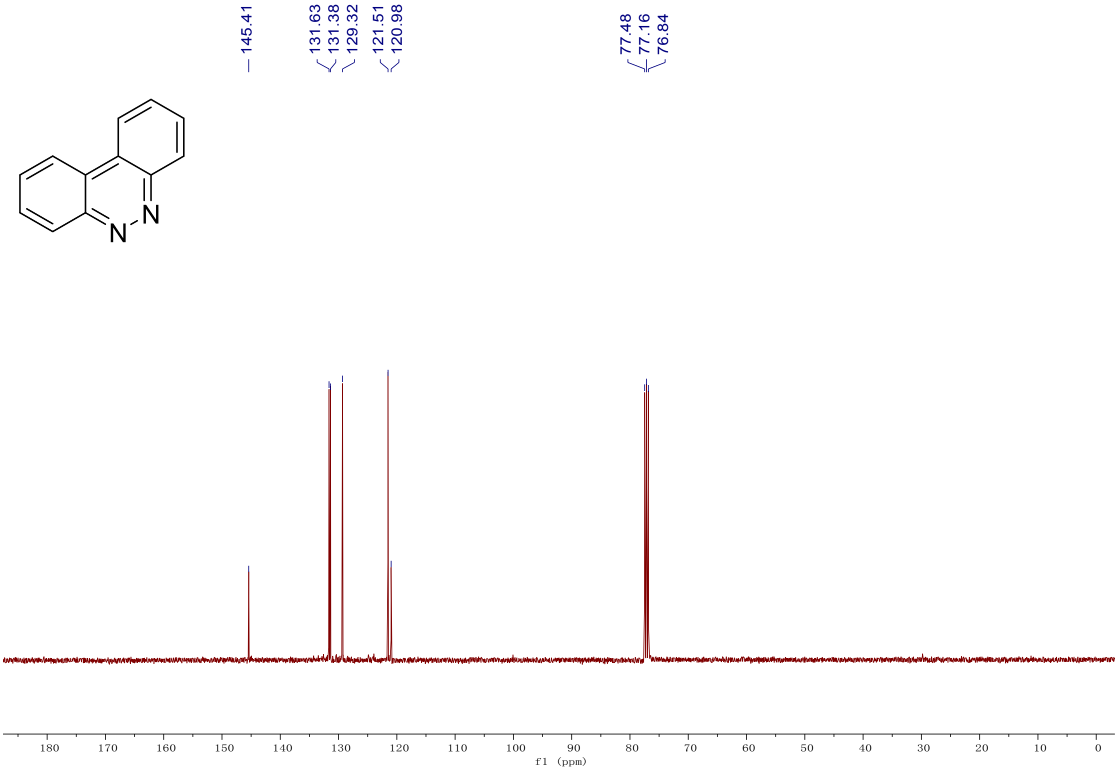
^{13}C NMR (100 MHz, $CDCl_3$) of **3m**



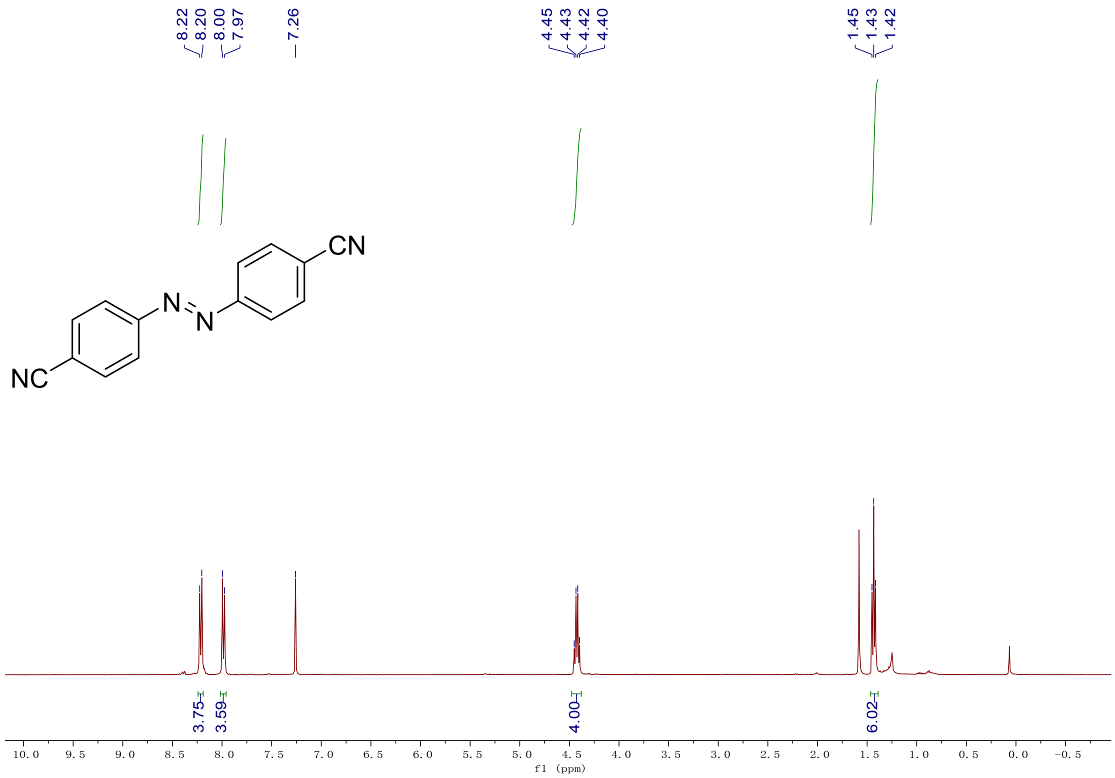
^{1}H NMR (400 MHz, CDCl$_3$) of **3n**



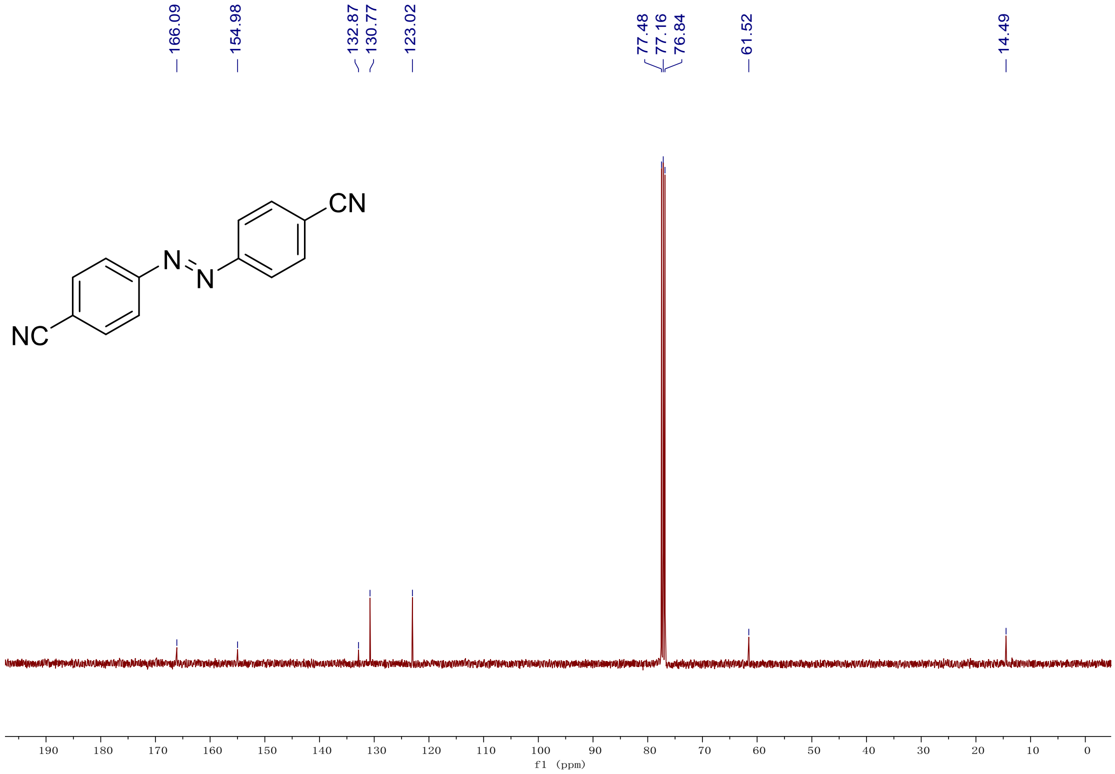
^{13}C NMR (100 MHz, CDCl$_3$) of **3n**



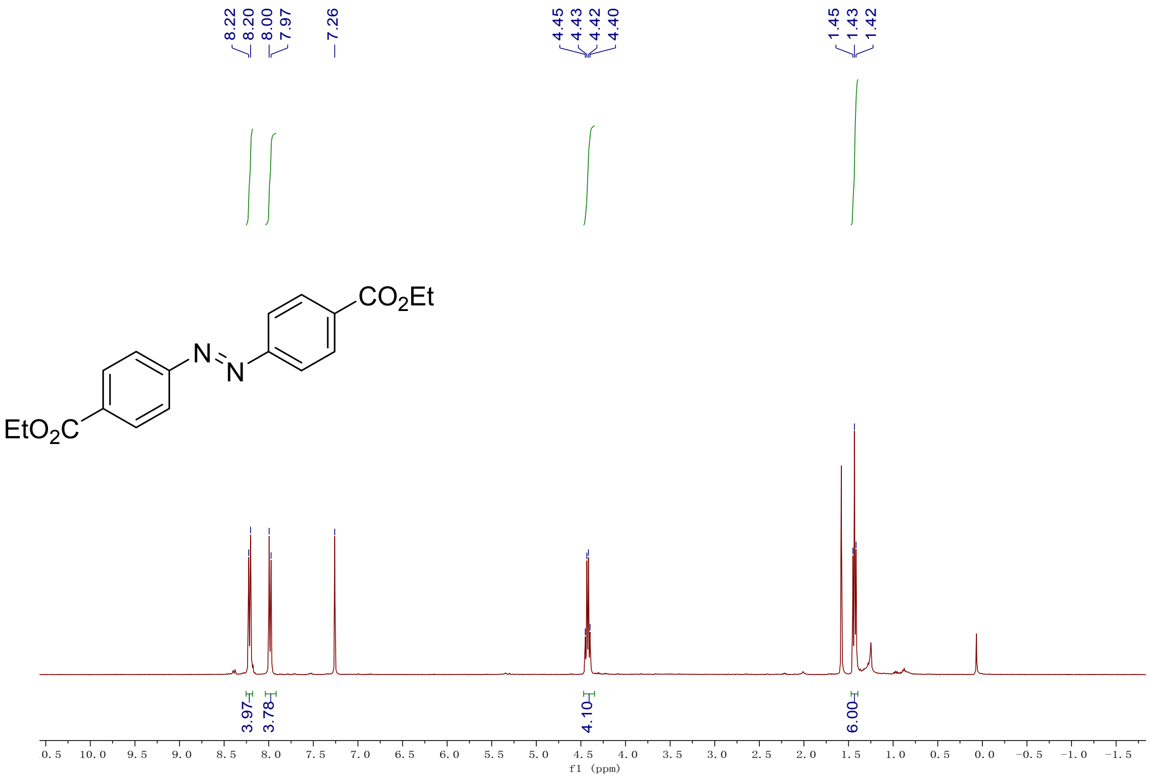
^{1}H NMR (400 MHz, CDCl$_3$) of **3o**



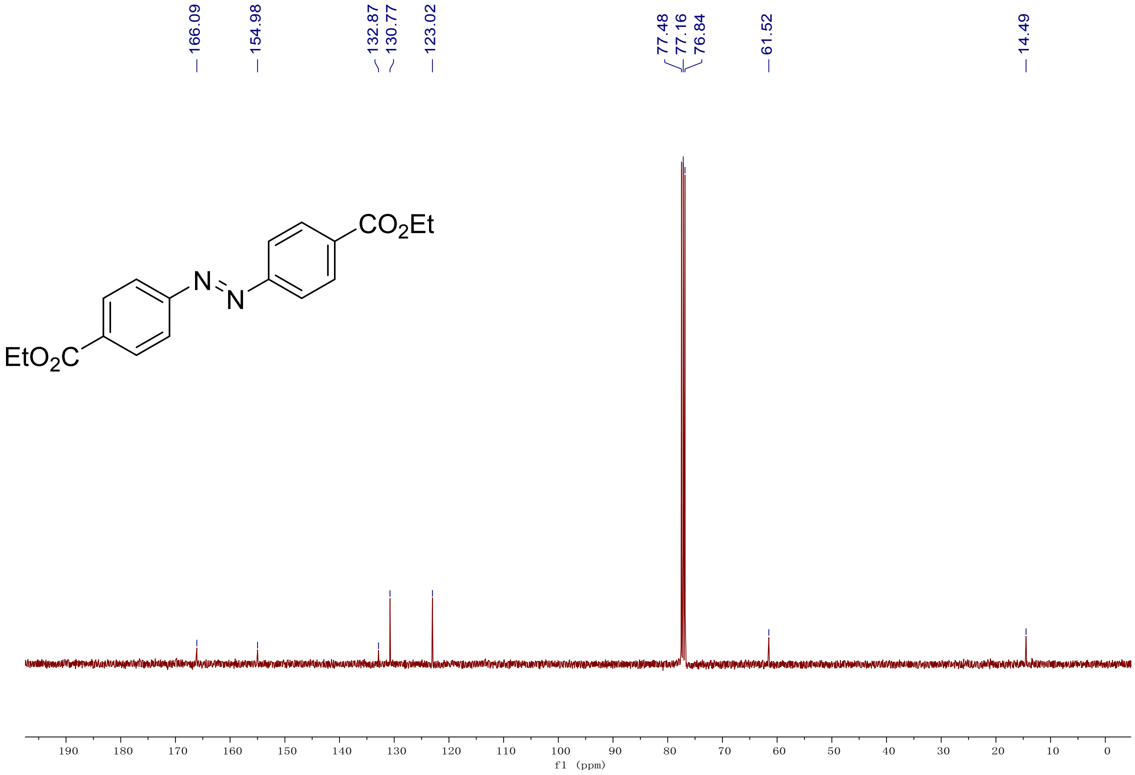
^{13}C NMR (100 MHz, CDCl$_3$) of **3o**



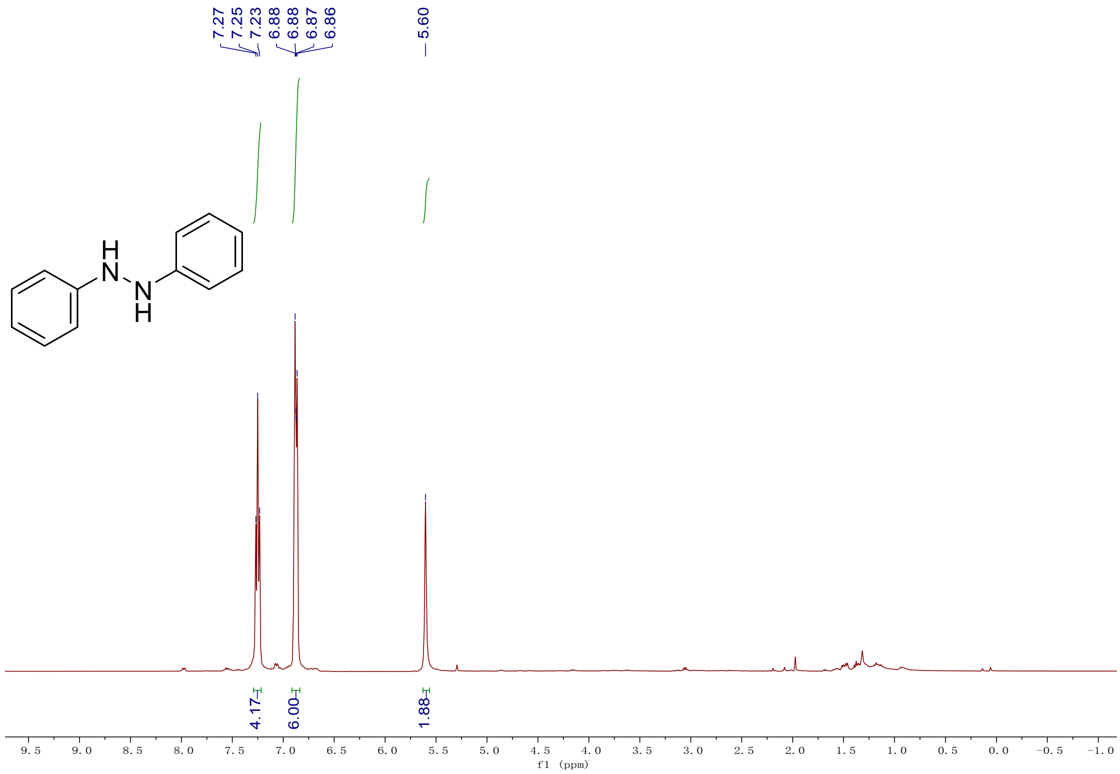
^{1}H NMR (400 MHz, CDCl$_3$) of **3p**



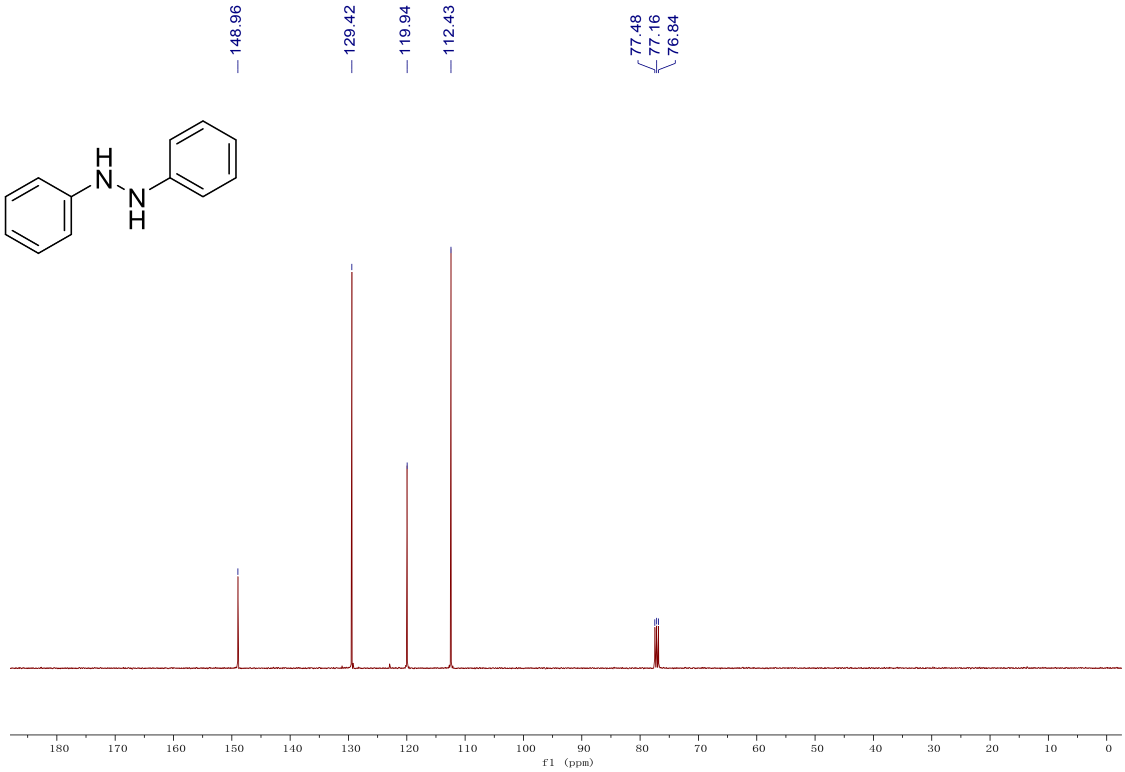
^{13}C NMR (100 MHz, CDCl$_3$) of **3p**



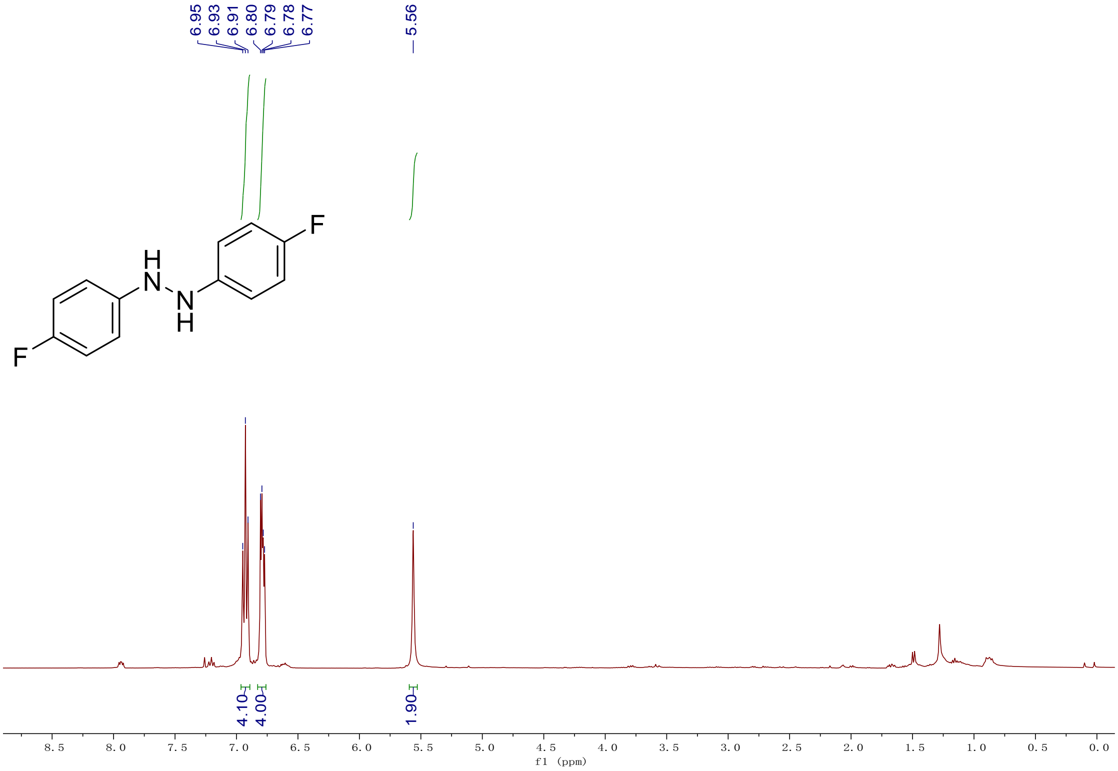
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



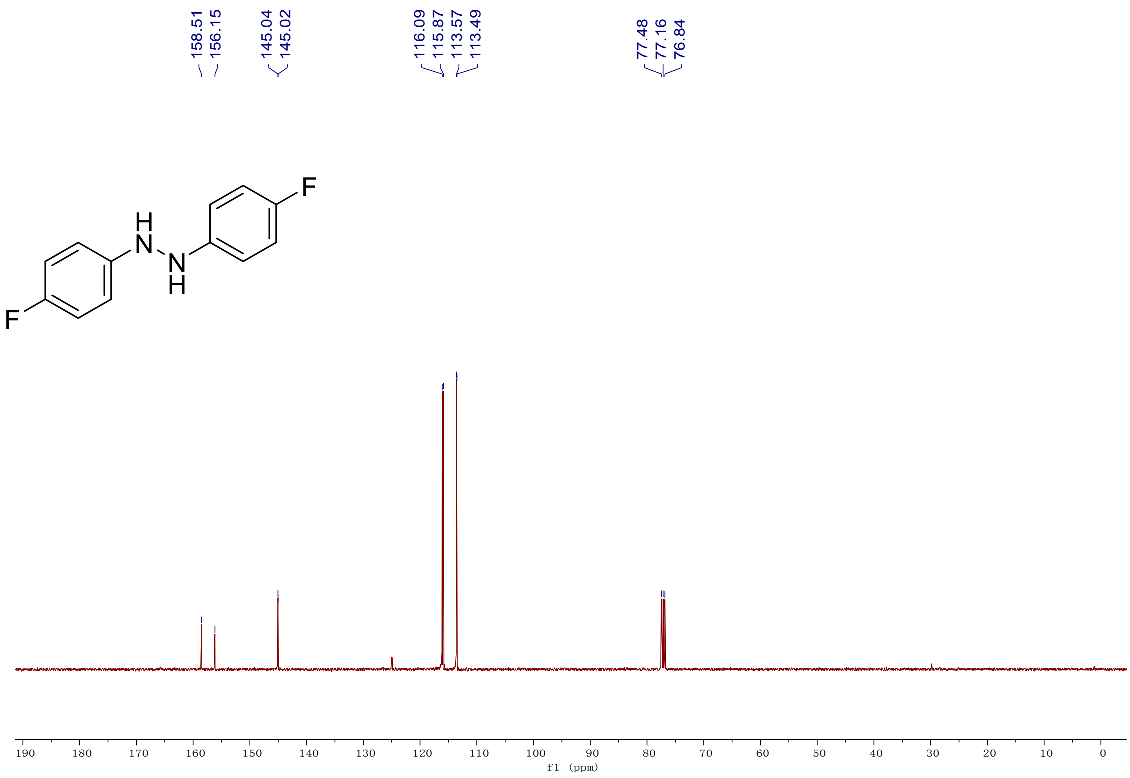
^{13}C NMR (100 MHz, $CDCl_3$) of **4a**



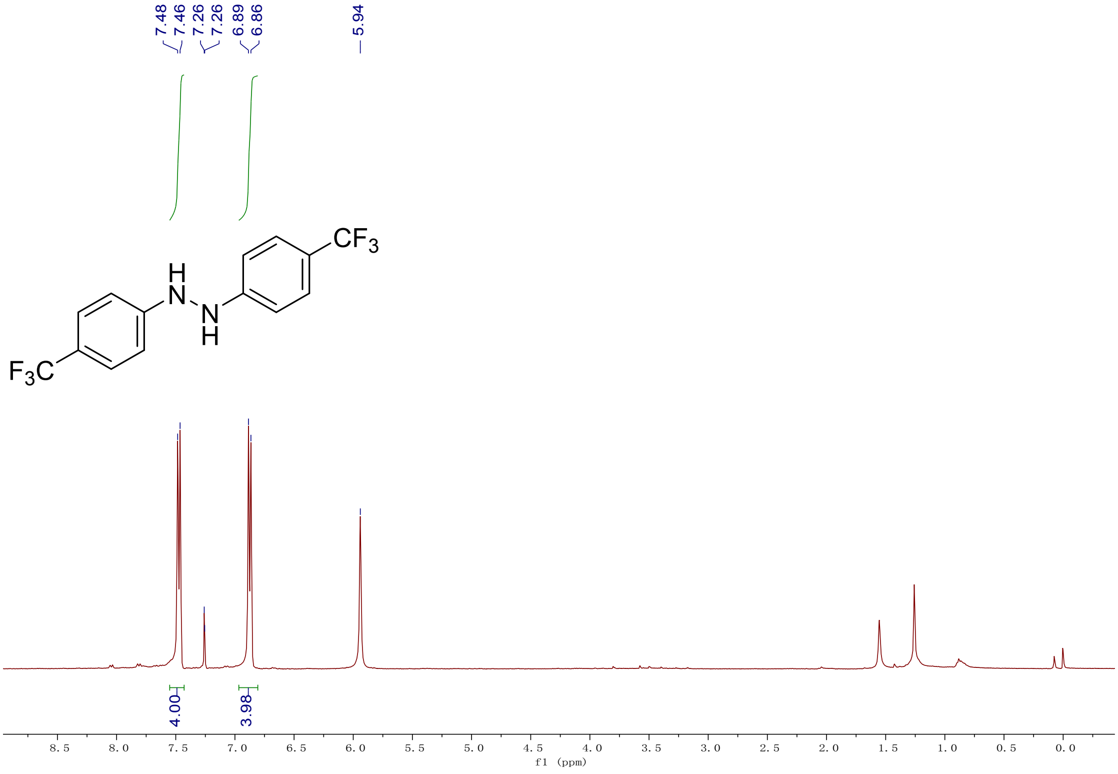
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



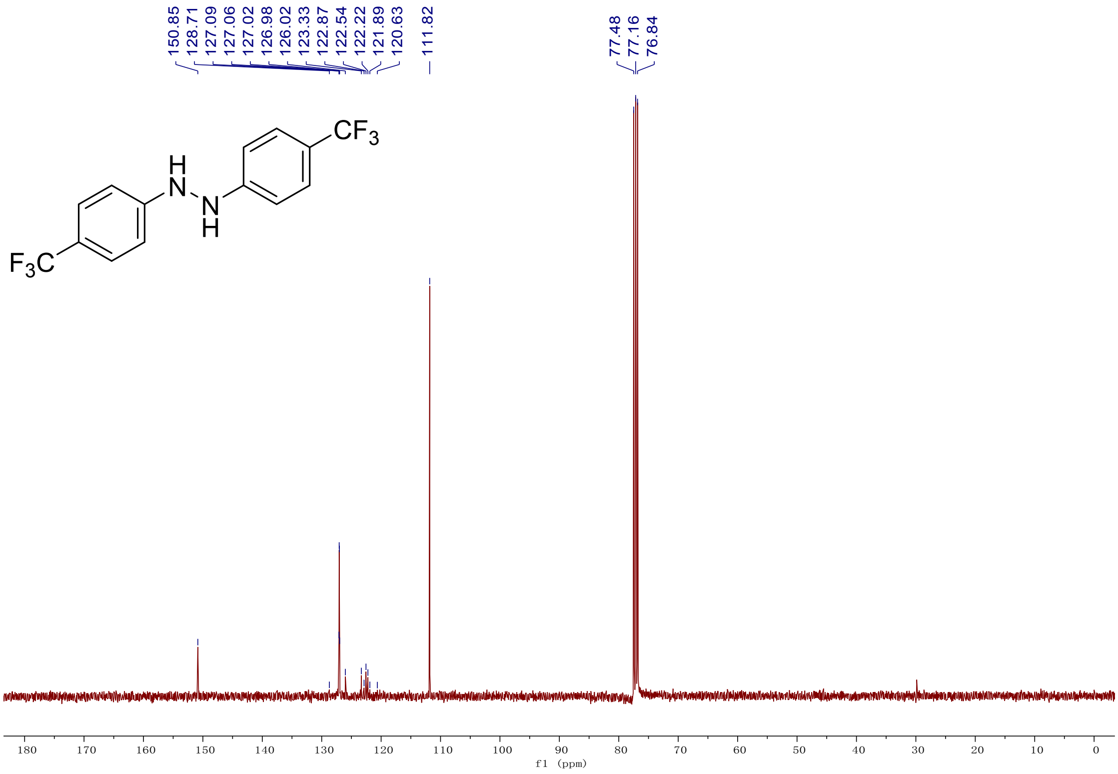
^{13}C NMR (100 MHz, $CDCl_3$) of **4b**



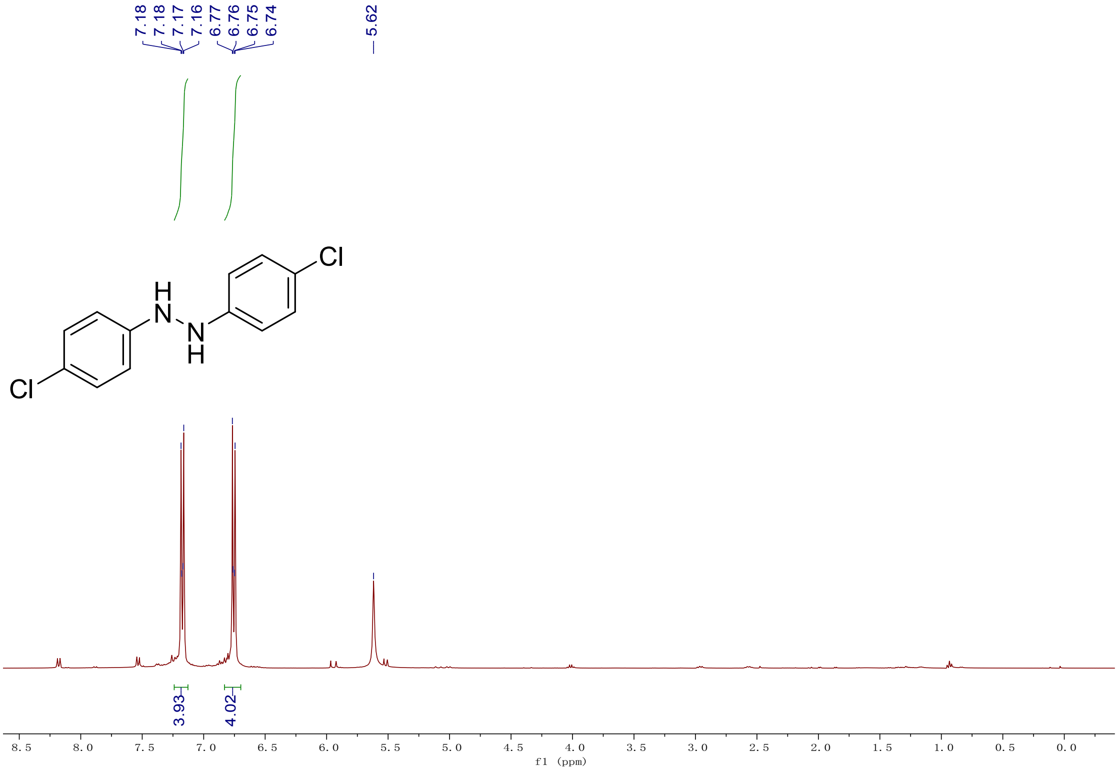
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



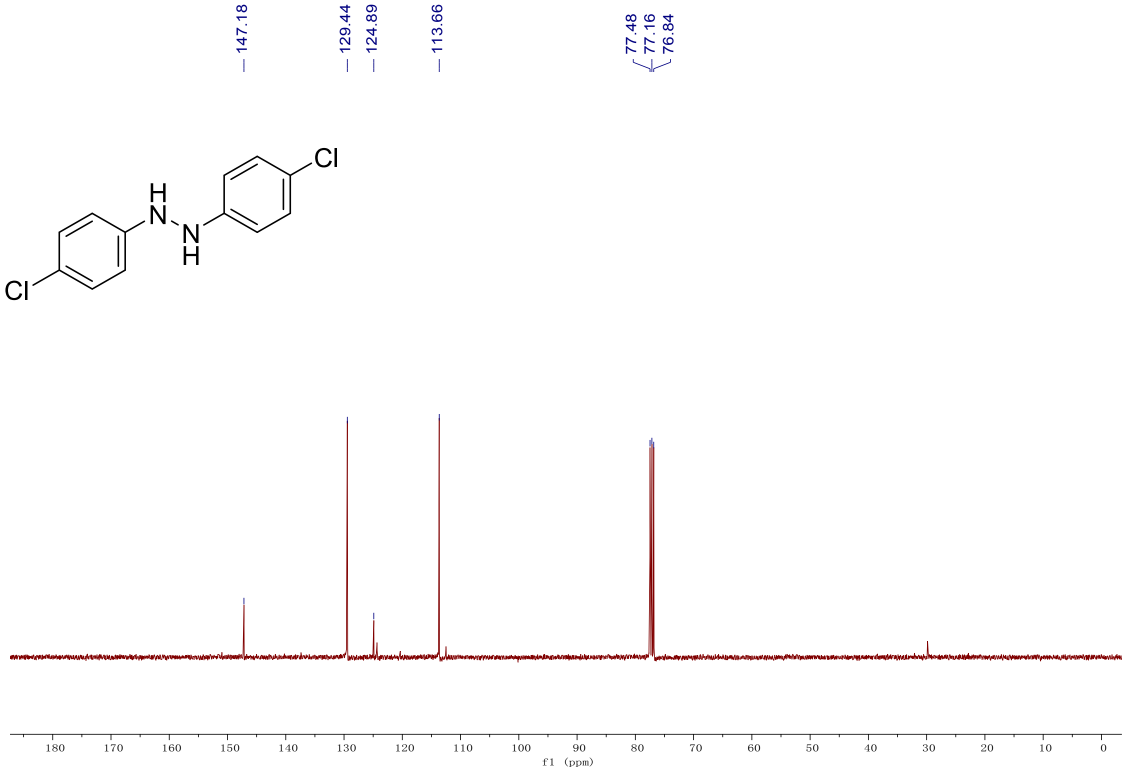
^{13}C NMR (100 MHz, CDCl$_3$) of **4c**



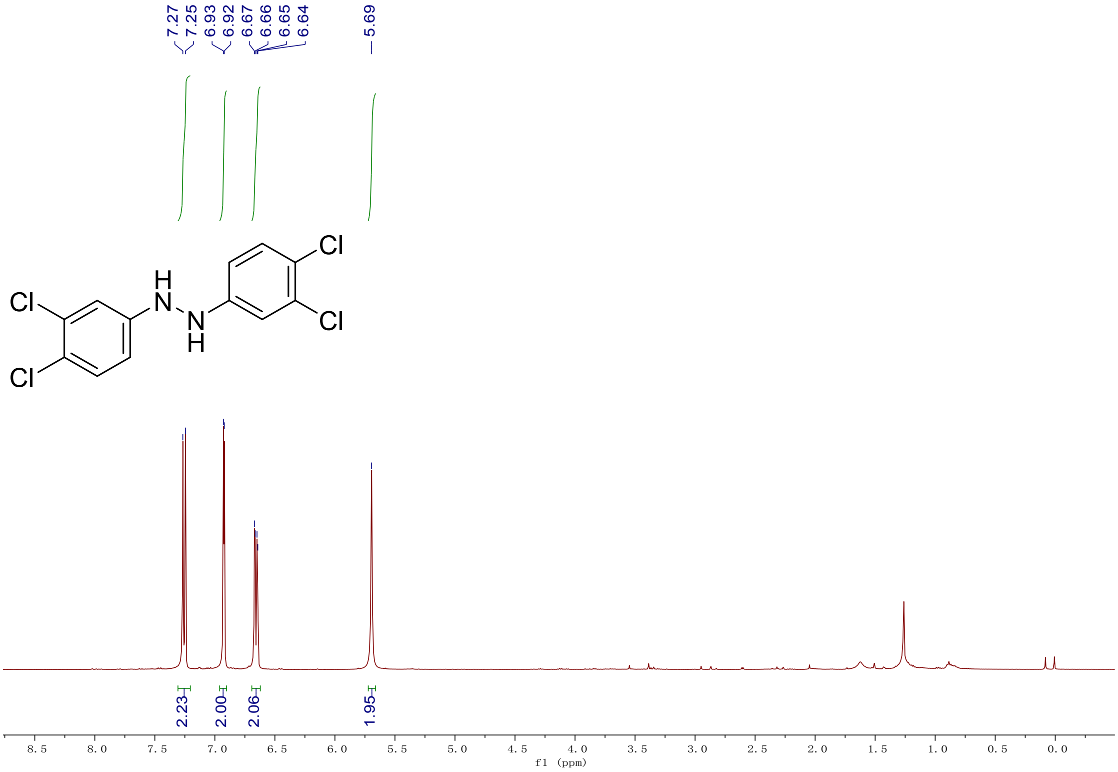
^{1}H NMR (400 MHz, CDCl$_3$) of **4d**



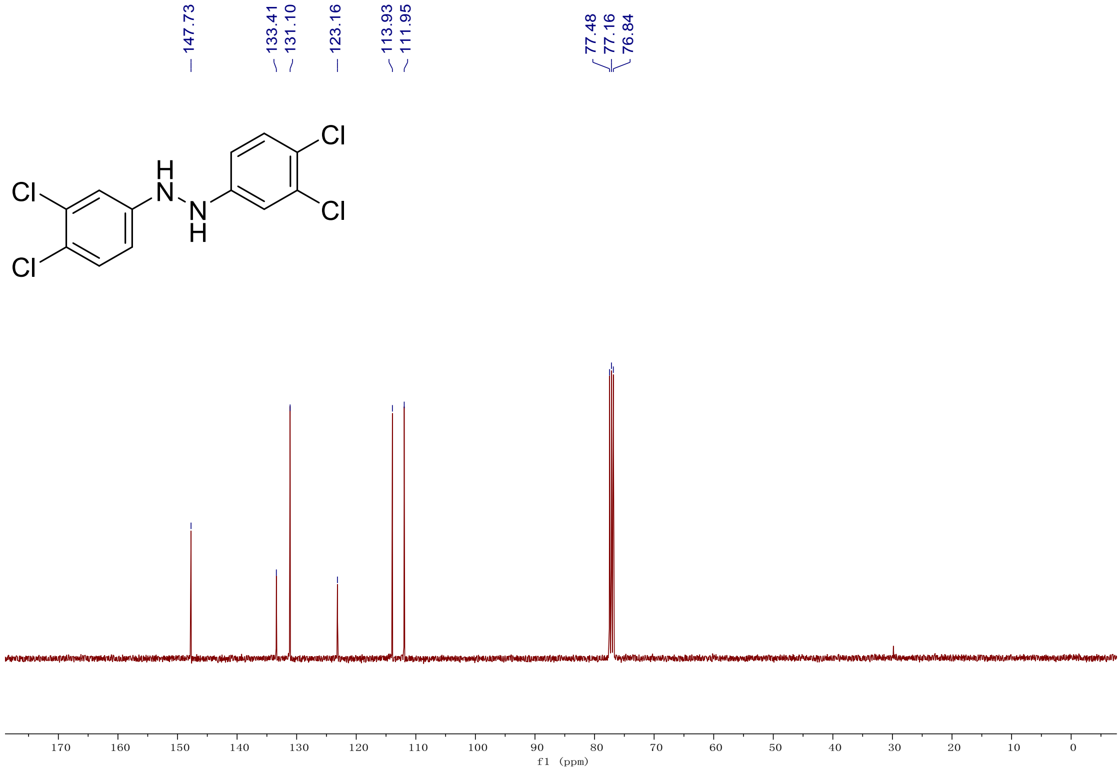
^{13}C NMR (100 MHz, $CDCl_3$) of **4d**



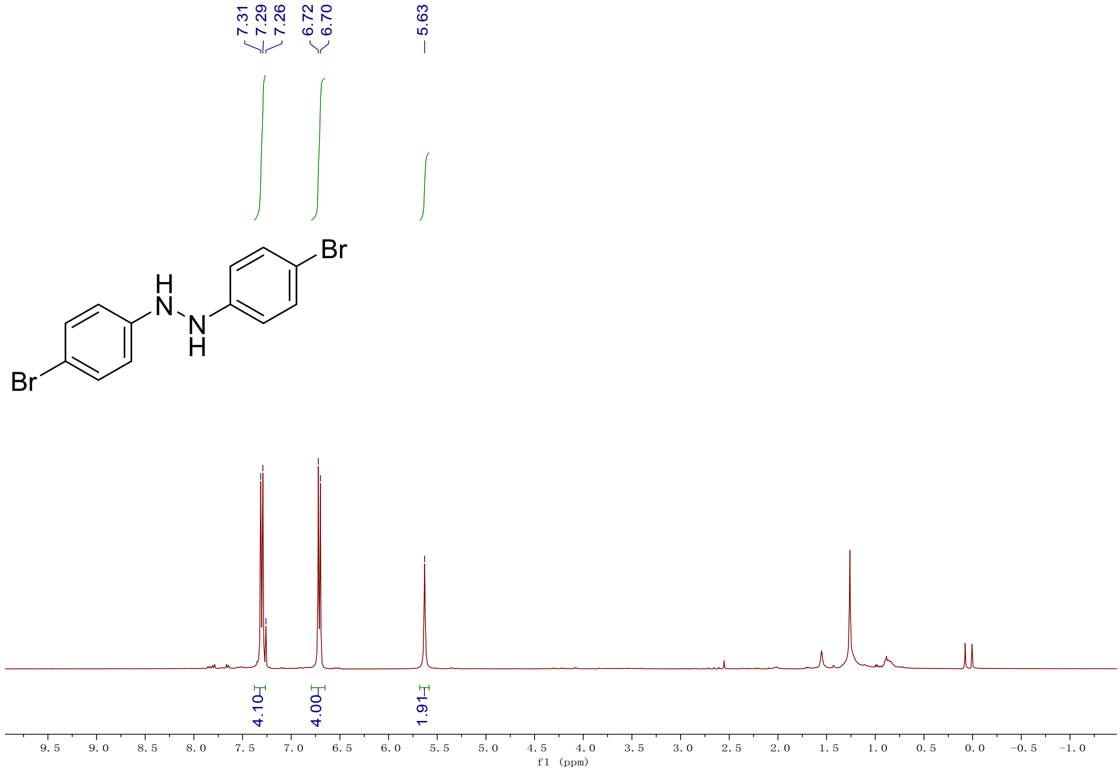
^{1}H NMR (400 MHz, $CDCl_3$) of **4e**



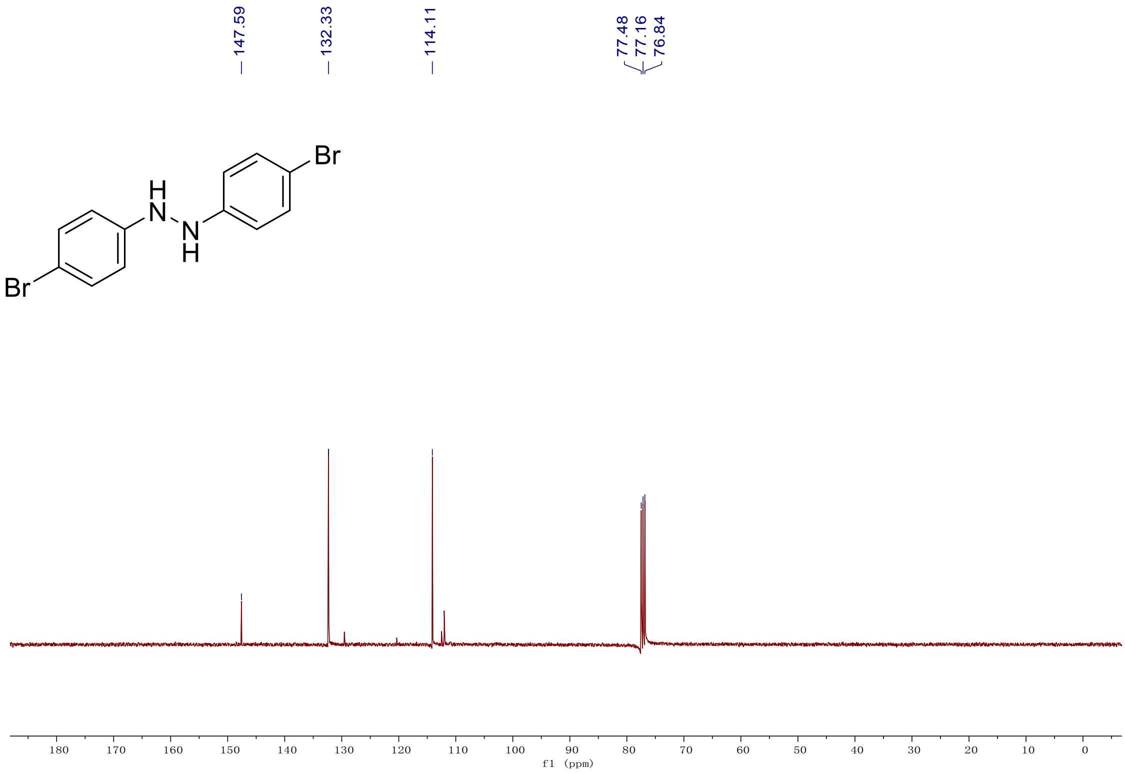
^{13}C NMR (100 MHz, $CDCl_3$) of **4e**



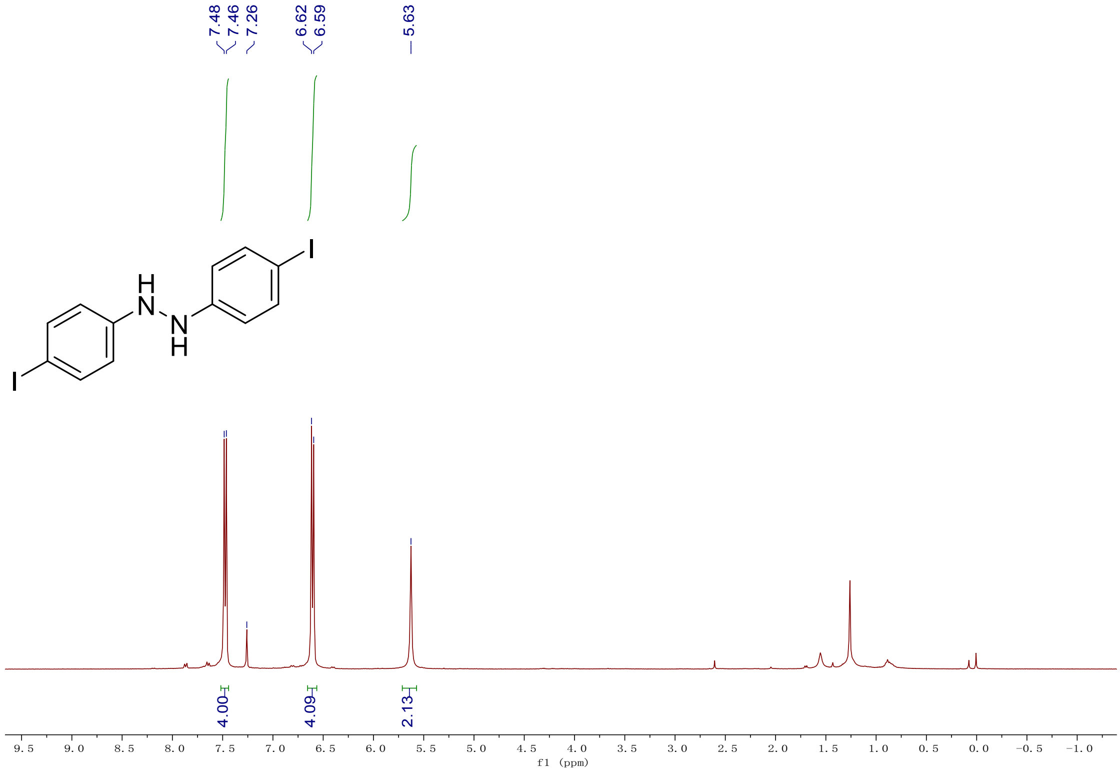
¹H NMR (400 MHz, $CDCl_3$) of **4f**



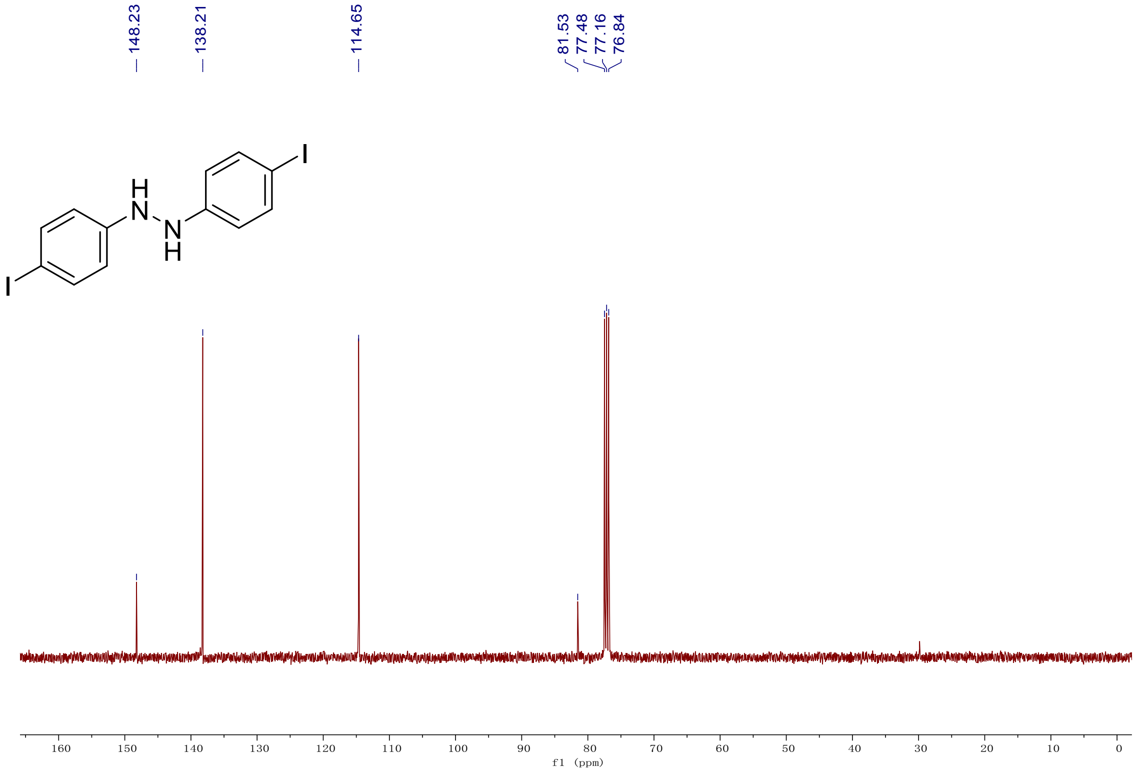
^{13}C NMR (100 MHz, $CDCl_3$) of **4f**



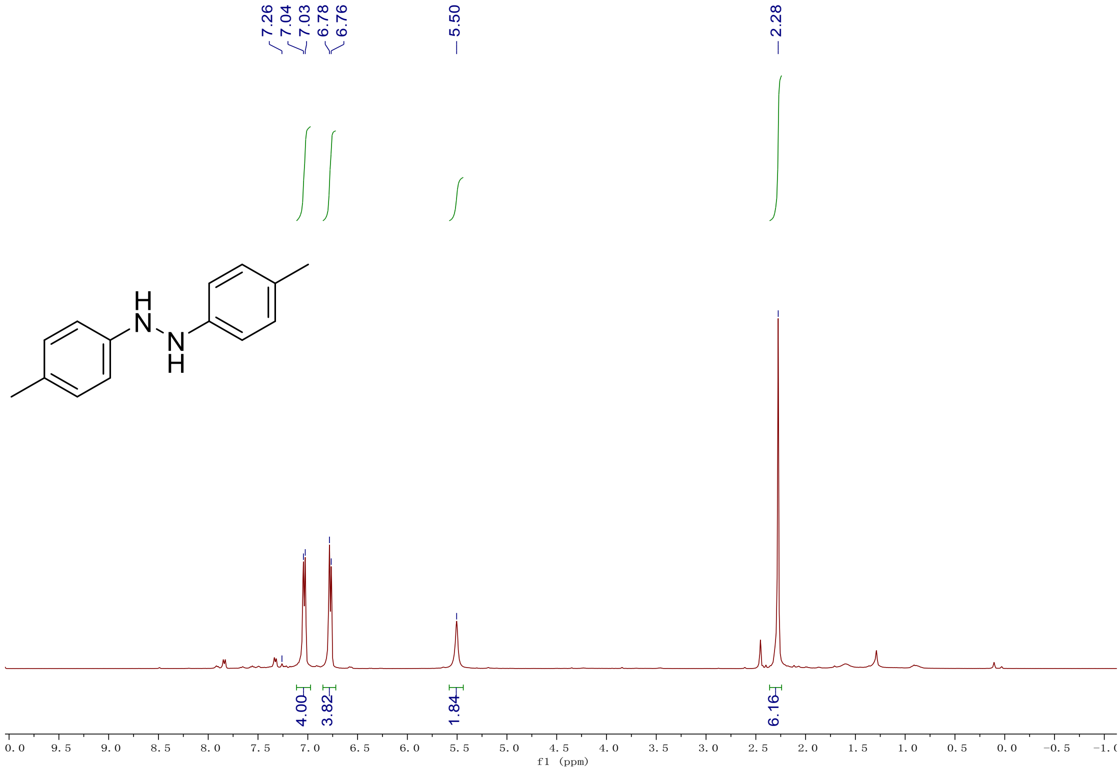
^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



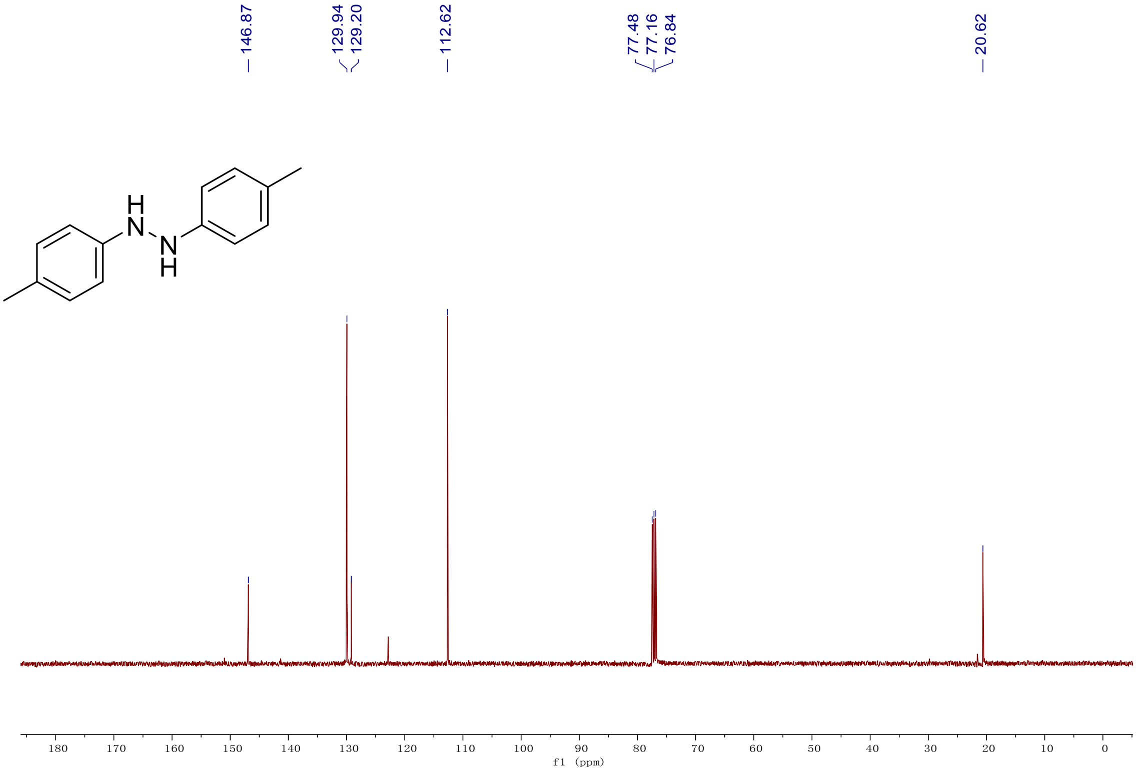
^{13}C NMR (100 MHz, CDCl$_3$) of **4g**



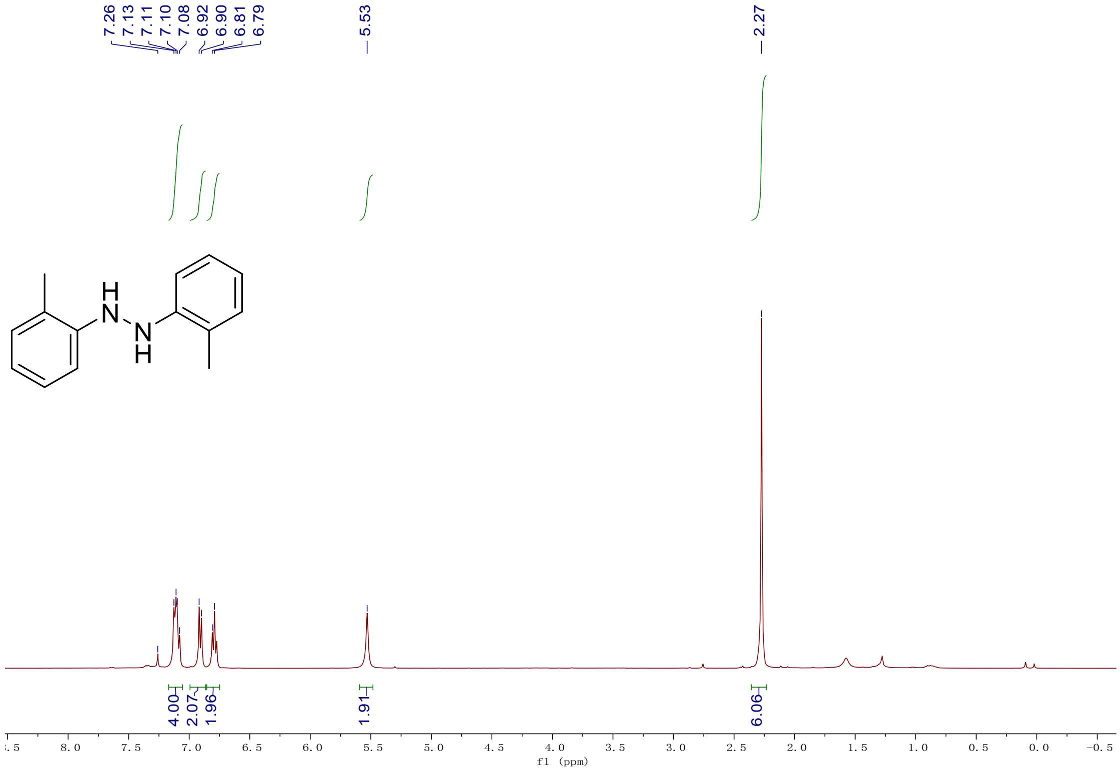
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



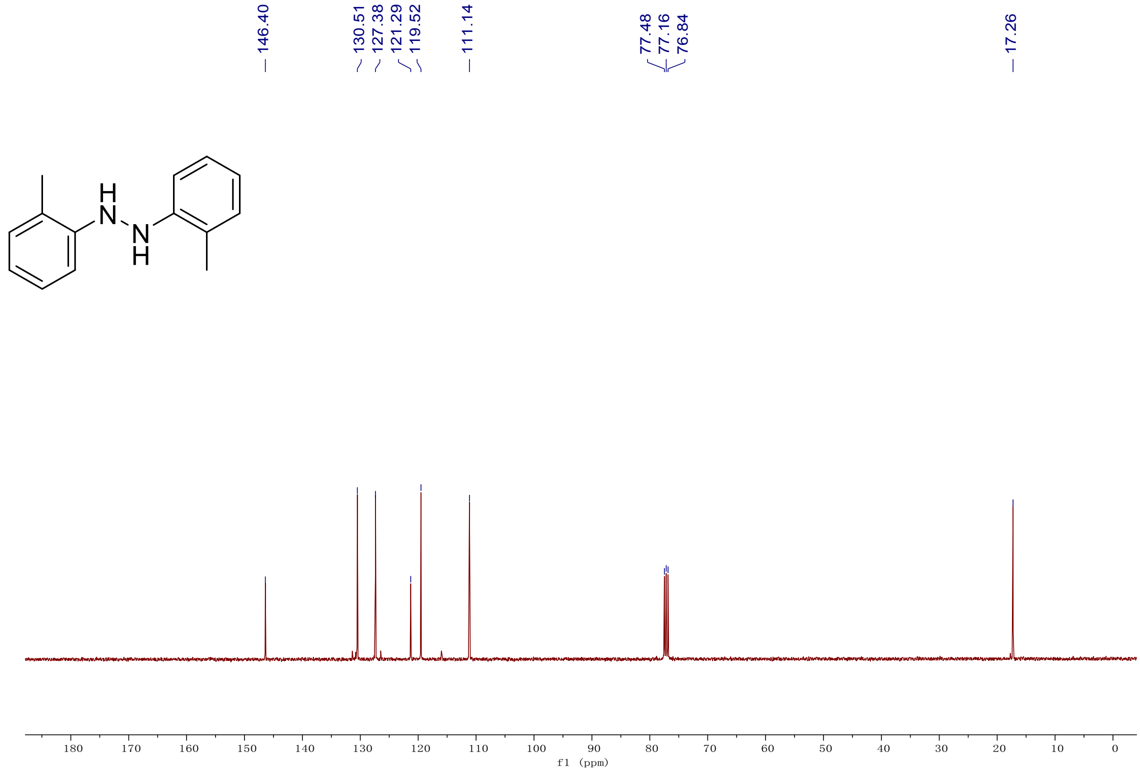
^{13}C NMR (100 MHz, $CDCl_3$) of **4h**



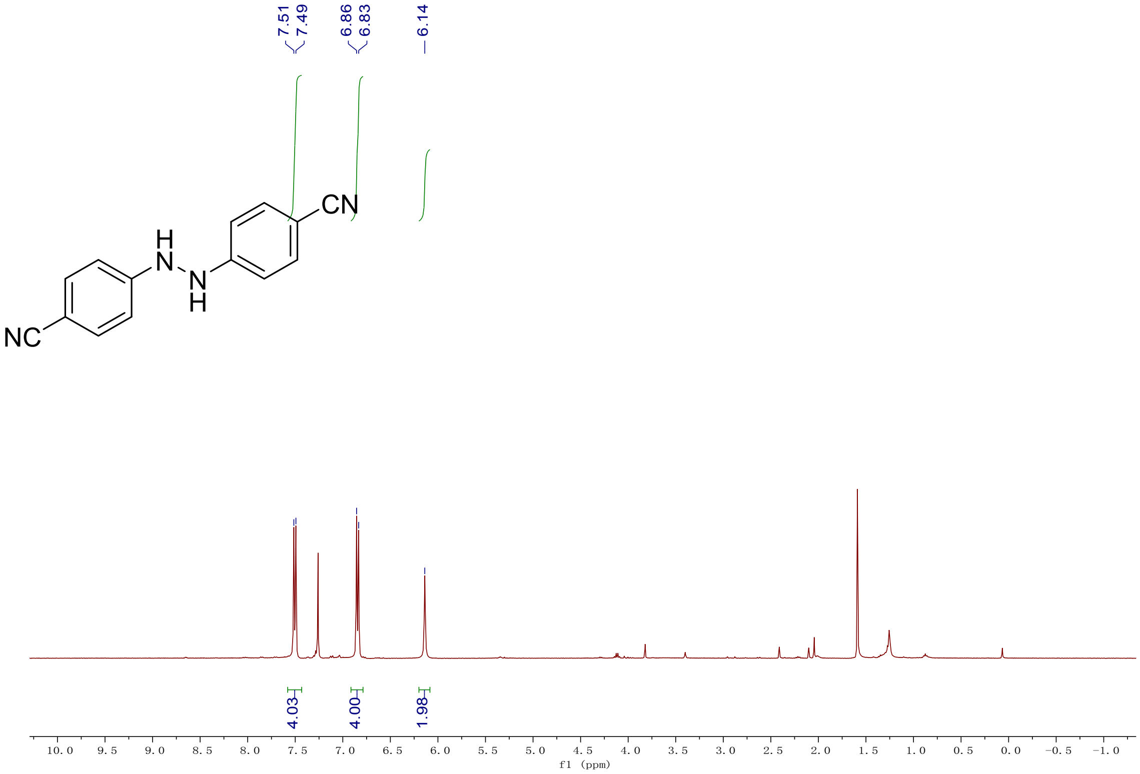
^{1}H NMR (400 MHz, CDCl$_3$) of **4i**



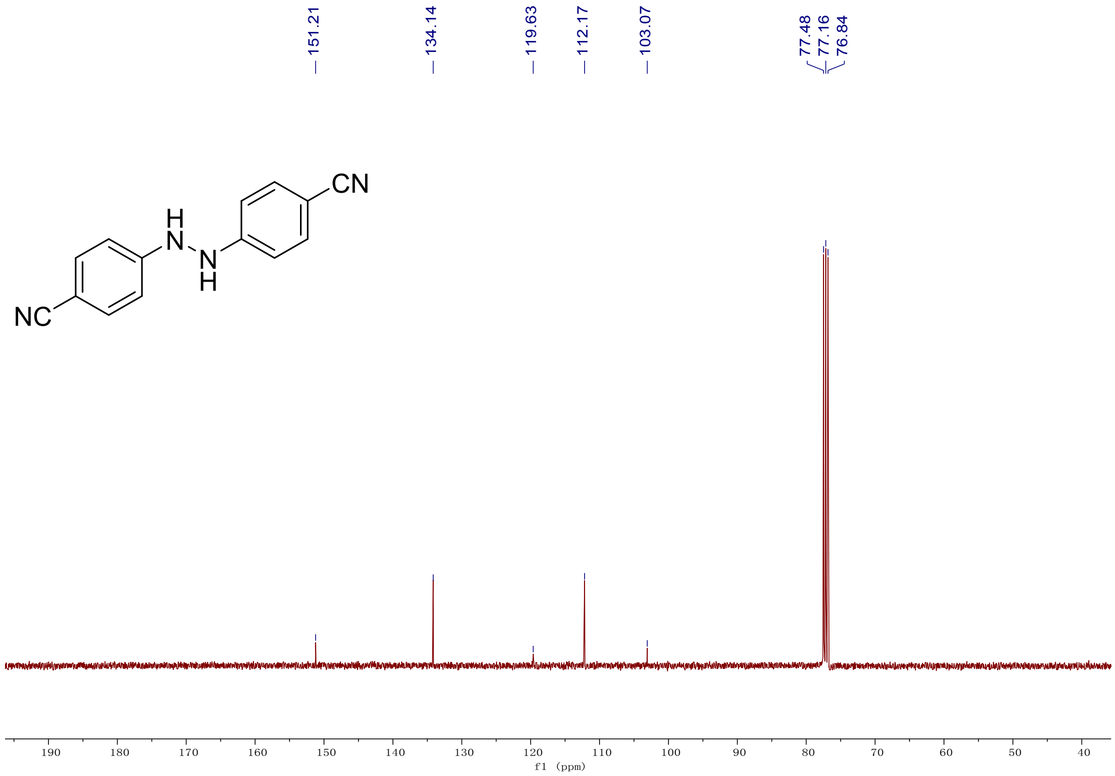
^{13}C NMR (100 MHz, CDCl$_3$) of **4i**



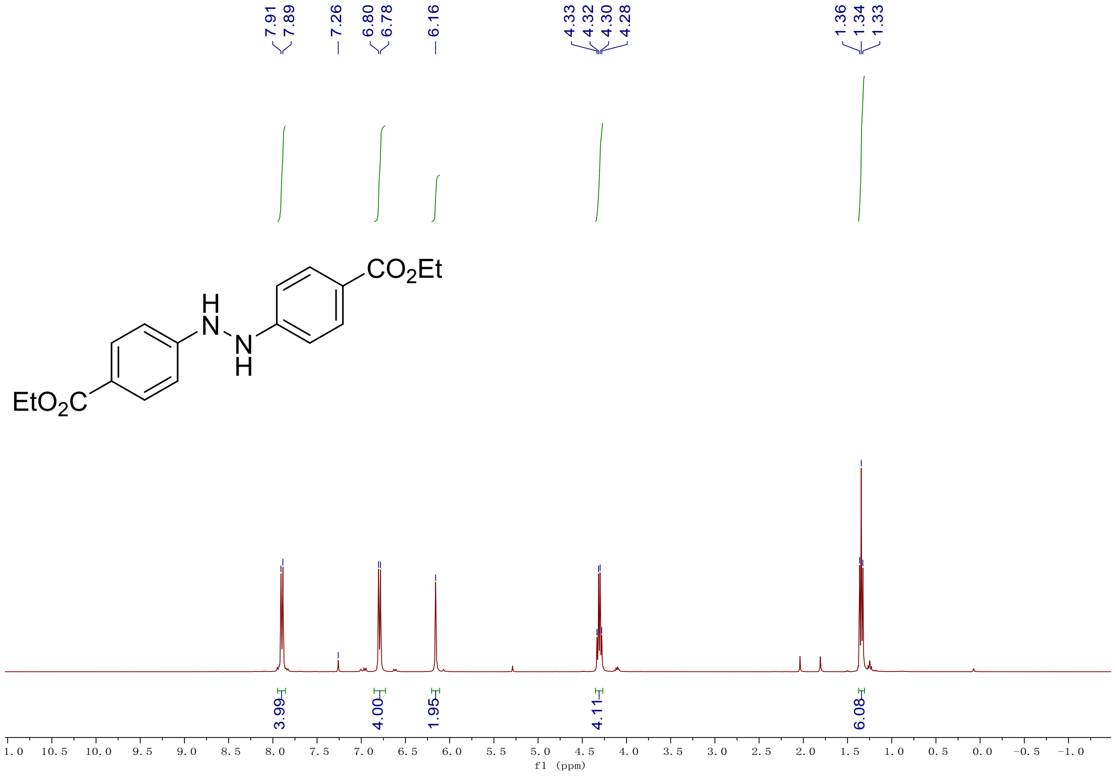
^{1}H NMR (400 MHz, CDCl$_3$) of **4j**



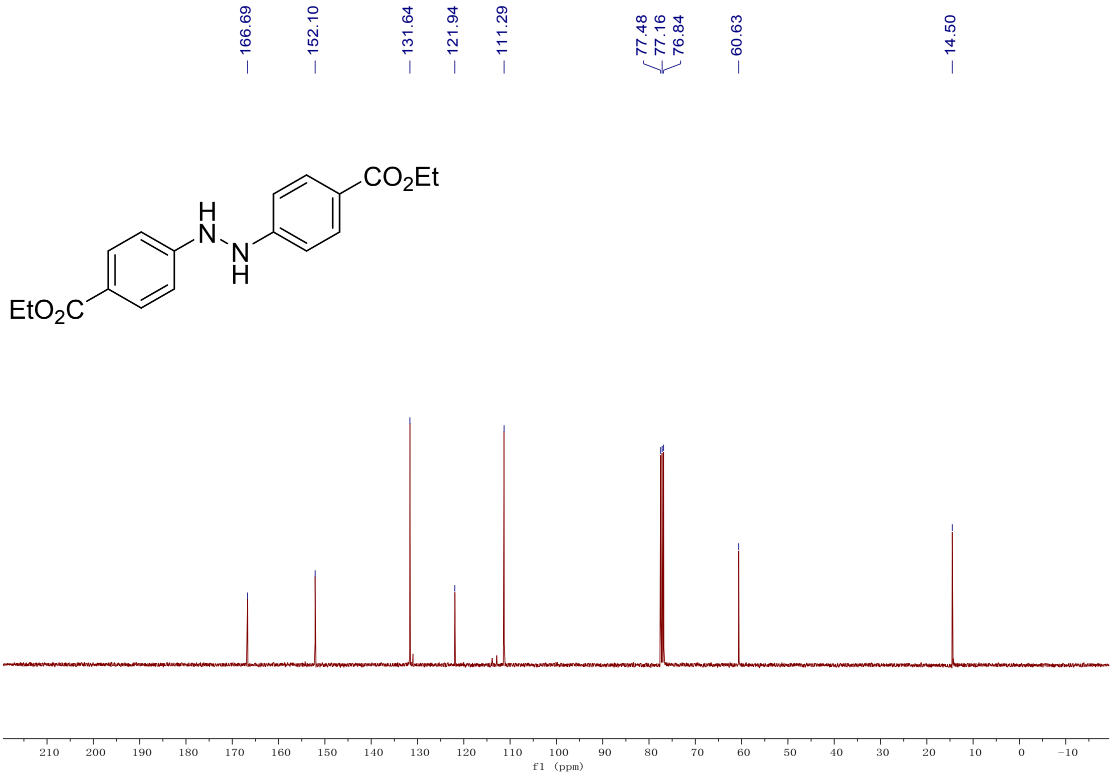
^{13}C NMR (100 MHz, $CDCl_3$) of **4j**



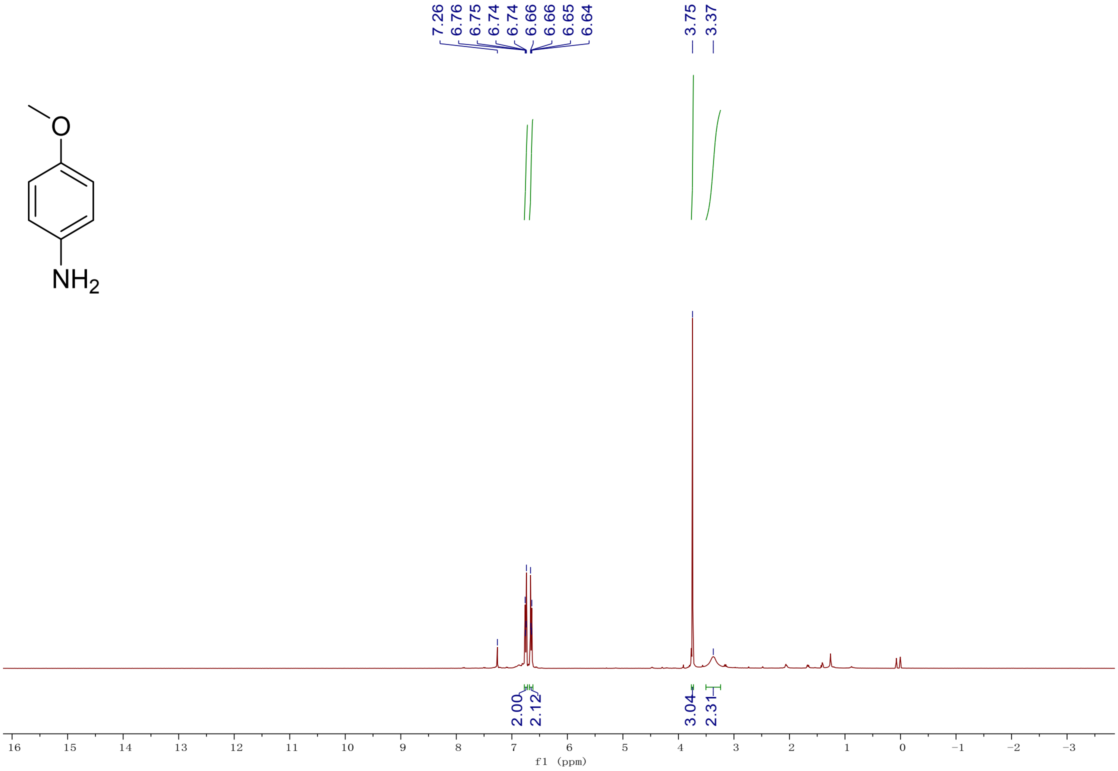
^{1}H NMR (400 MHz, $CDCl_3$) of **4k**



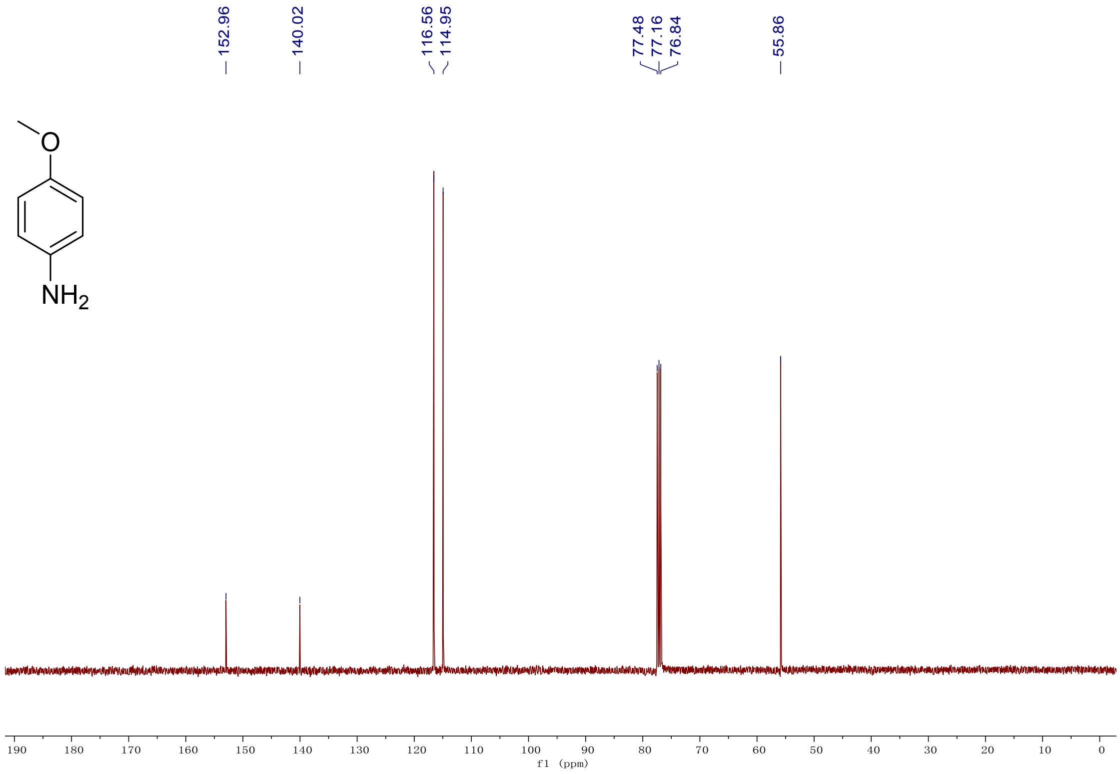
^{13}C NMR (100 MHz, CDCl$_3$) of **4k**



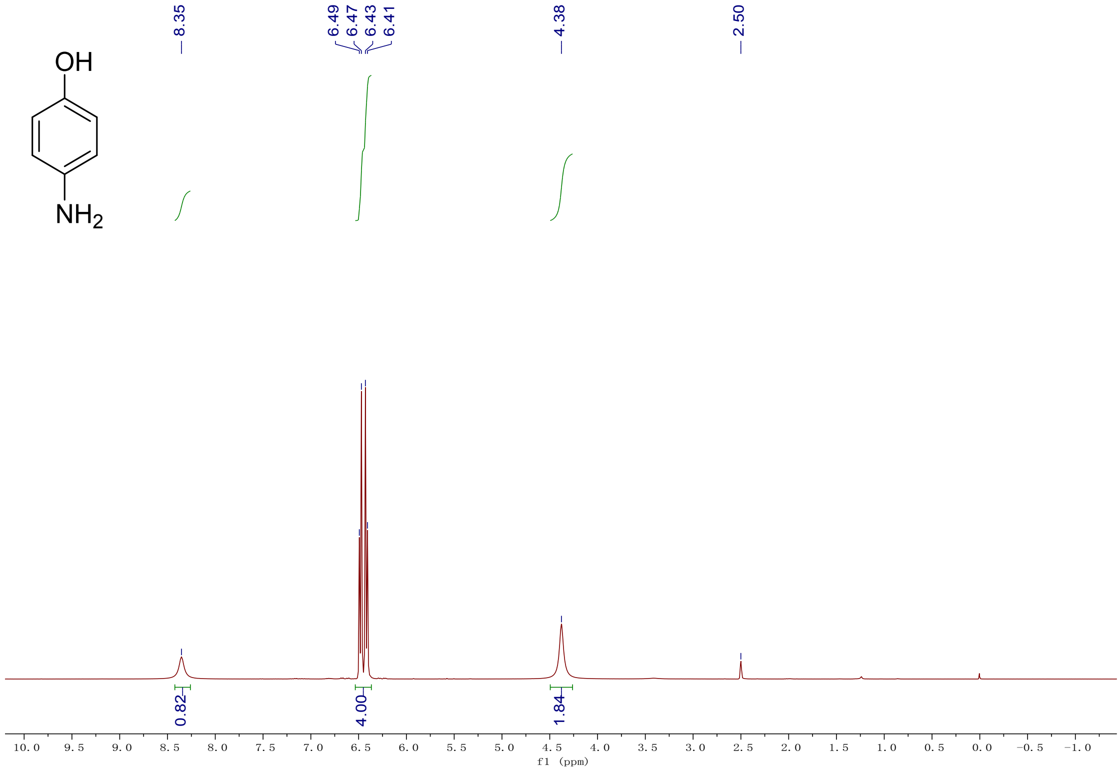
^{1}H NMR (400 MHz, CDCl$_3$) of **5a**



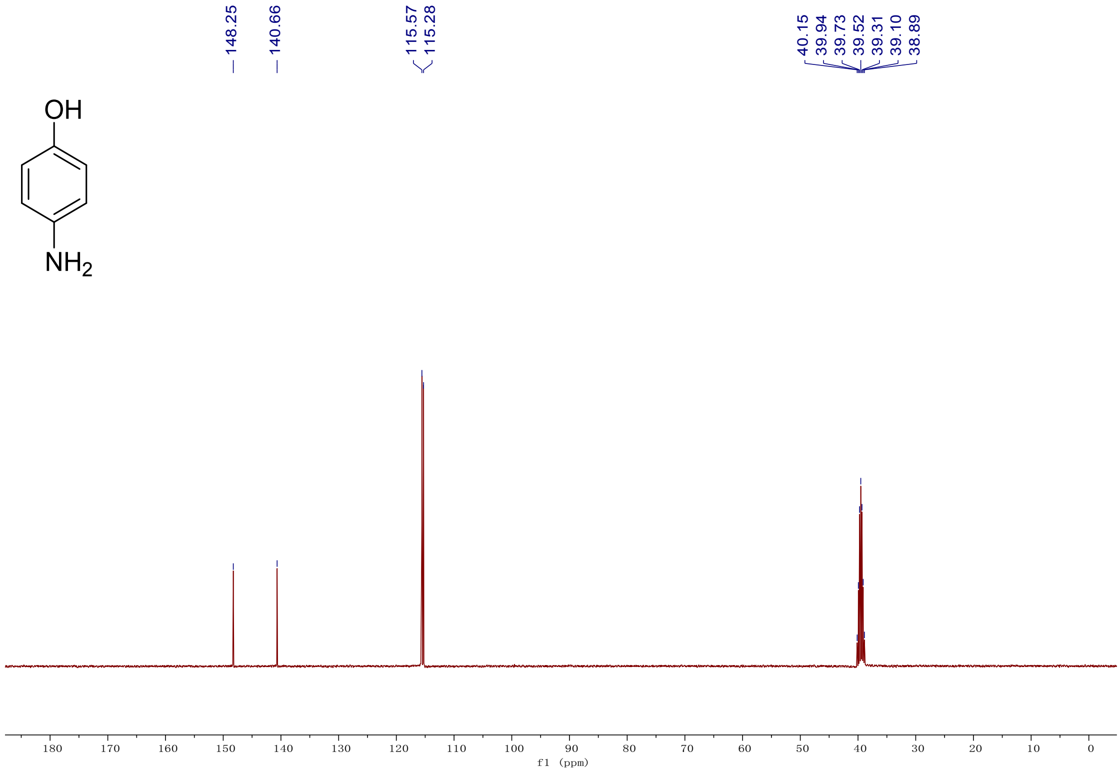
^{13}C NMR (100 MHz, CDCl$_3$) of **5a**



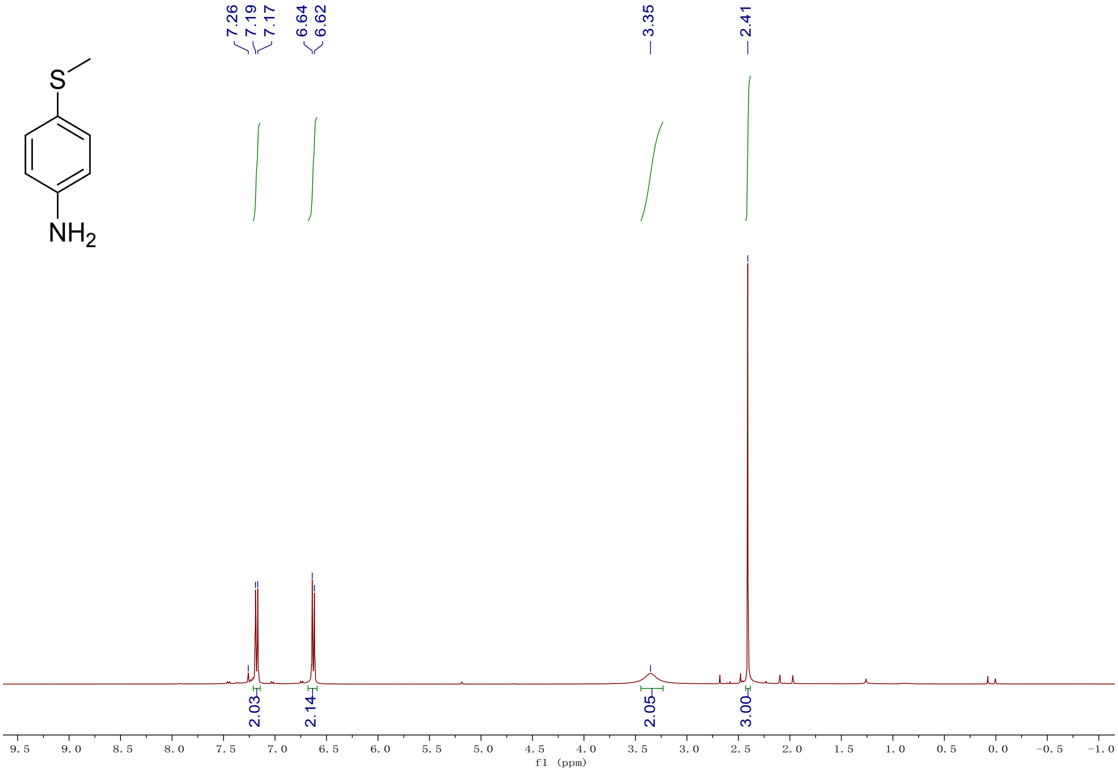
^{1}H NMR (400 MHz, DMSO) of **5b**



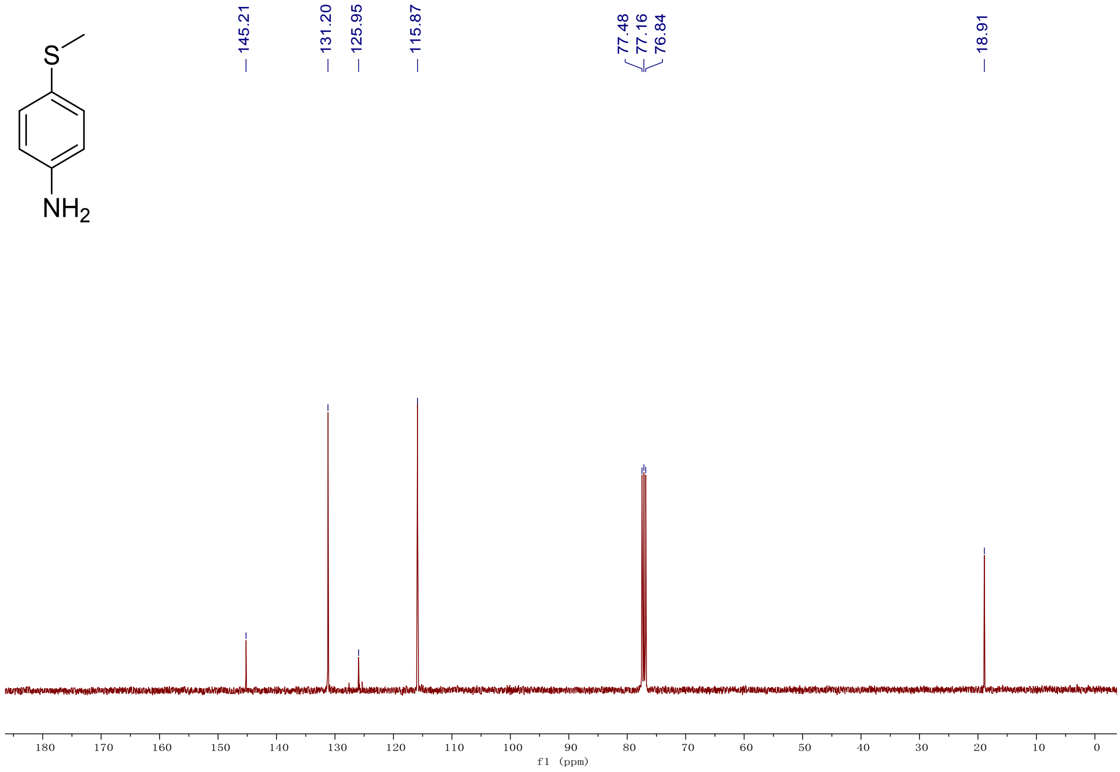
^{13}C NMR (100 MHz, DMSO) of **5b**



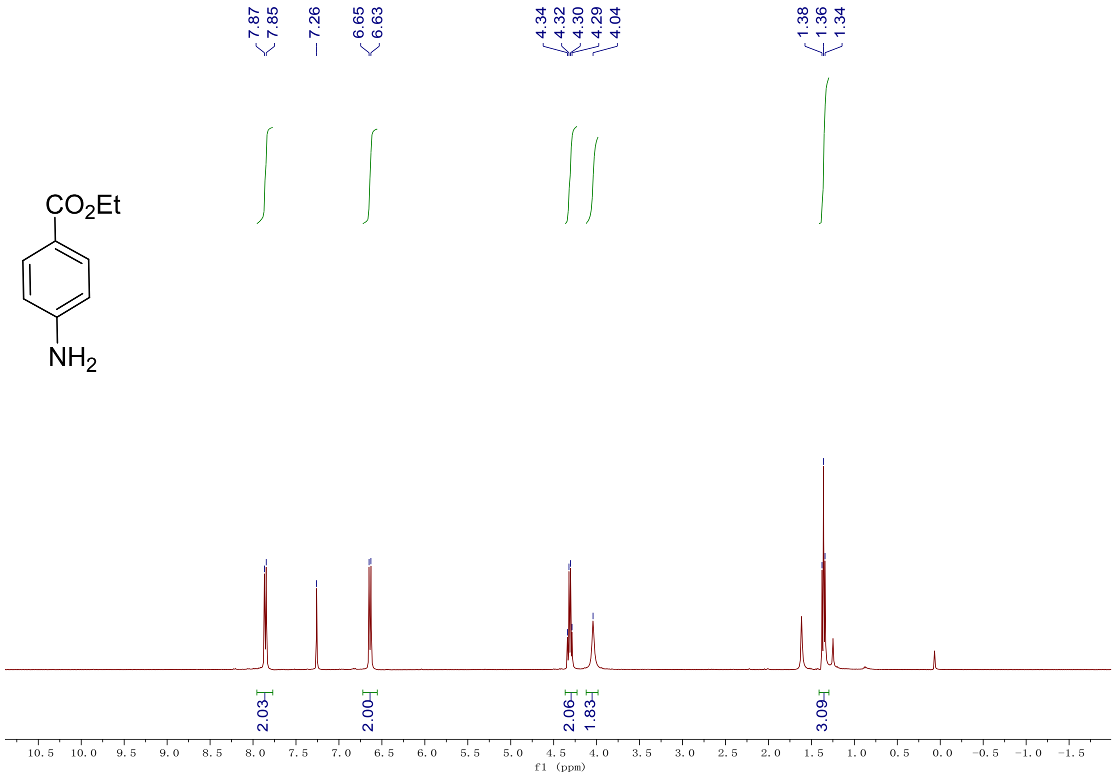
^{1}H NMR (400 MHz, CDCl$_3$) of **5c**



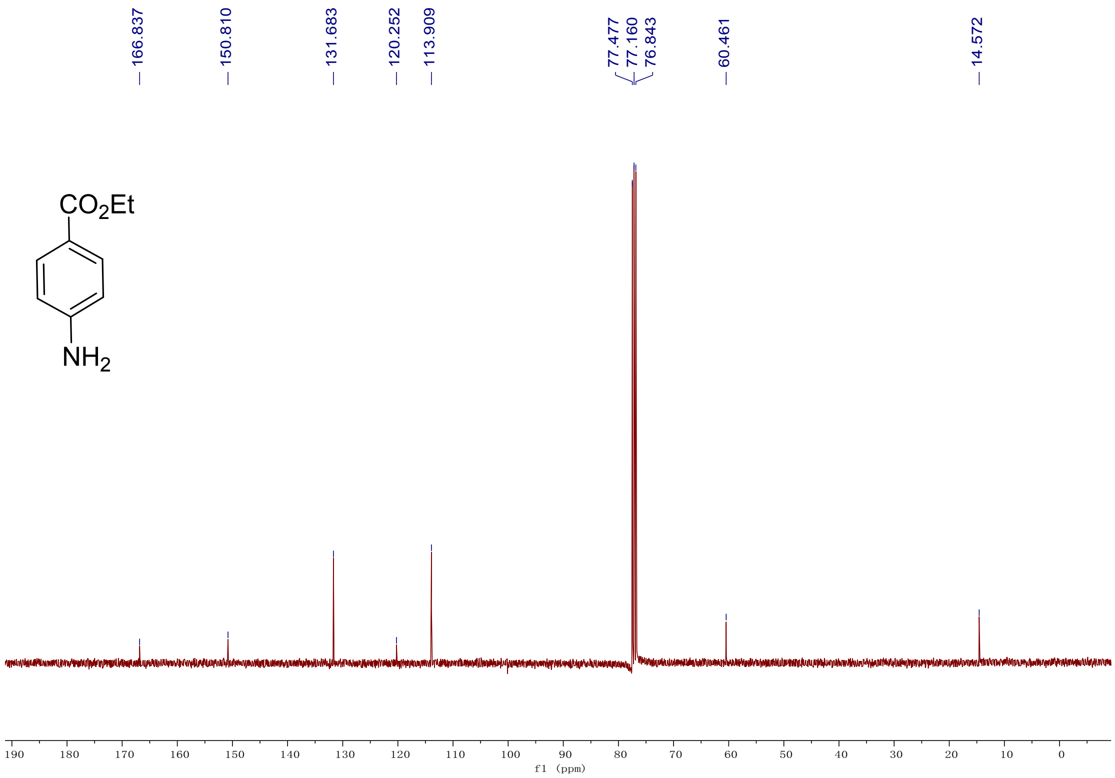
^{13}C NMR (100 MHz, CDCl$_3$) of **5c**



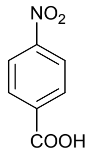
^{1}H NMR (400 MHz, $CDCl_3$) of **5d**

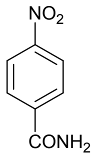


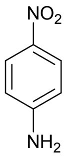
^{13}C NMR (100 MHz, $CDCl_3$) of **5d**

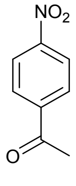


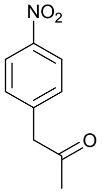
11. Substrates failed to deliver corresponding products


form insoluble salt


NR


decomposed


NR


NR