Supplementary information for

Visible-Light-Promoted Oxidative Dehydrogenation of Hydrazobenzenes and Transfer Hydrogenation of Azobenzenes

Xianya Wang,[a,b,#] Xianjin Wang,[a,#] Chungu Xia,*[,a] Lipeng Wu*[,a]

[a]State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou, 730000 (P. R. China)

[b]University of Chinese Academy of Sciences, Beijing, 100049 (China)

[#]these authors contributed equally to this work

Email: cgxia@licp.cas.cn; lipengwu@licp.cas.cn

General Information

Manipulations for oxidative dehydrogenation were carried out under ambient conditions or under an atmosphere of dry and deoxygenated N_2 in a glovebox (H_2O and O_2 < 0.1 ppm) for transfer hydrogenation reactions. Glassware was pre-dried in an oven at 150 °C for several hours and cooled prior to use. All solvents were purchased as super dry standard solvent and used as received. Azobenzene and hydrazobenzene were prepared according to literature report.[2] Eosin Y was purchased from Macklin company. ^{1}H NMR, ^{13}C NMR spectra were recorded on Zhongke-Niujin 400 at room temperature using tetramethylsilane as an internal reference and $CDCl_3$ or CD_3CN as a solvent. Chemical shifts (δ) are given in parts per million (ppm). Coupling constants (*J*) are given in Hertz (Hz) and are referenced to tetramethylsilane (δ 0.00). Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ 77.0). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 100-200 mesh silica gel in petroleum (bp. 60-90 °C). High-Resolution MS analyses were performed on Agilent 6530 Accurate – Mass Q-TOF LC/MS with ESI mode or Waters Micro Mass GCT Premier with EI mode.

General procedure for the preparation of symmetrical hydrazobenzene

In a 100 mL pressure tube was added amine (1.0 g), toluene (60 mL), activated MnO_2 (10 equiv). The mixture was heated at reflux temperature and monitored by TLC. Then, the reaction mixture was filtered through Celite pad and washed with toluene for three times. The filtrate was subjected to vacuum to afford the crude azobenzene which was directly dissolved in EtOH (50 mL) with 5 weight % of Pd/C and 10 mol% pyridine. The solution was reduced with hydrogen balloon and monitored using TLC. After all the azobenzene was converted the reaction mixture was quickly filtered, and the solvent was removed to get the desired hydrazobenzene in quantitative yield.

General procedure for the preparation of unsymmetrical hydrazobenzene

To a solution of nitrosobenzene (0.5 g, 4.7 mmol) in glacial acetic acid (12 mL) and EtOH (3 mL), the amine (1.0 equiv) was added. The reaction mixture was stirred at 40 °C for 12 h. Then, the

mixture was poured into ice water and filtered to afford azobenzene crude product which was directly used for the next step without purification. The crude product was dissolved in EtOH (50 mL) with 5 weight % of Pd/C and 10 mol% pyridine. The solution was reduced with hydrogen balloon and monitored using TLC. After all the azobenzene was converted the reaction mixture was quickly filtered, and the solvent was removed to get the desired hydrazobenzene in quantitative yield.

General procedure for the Eosin Y – catalyzed synthesis of azobenzene from hydrazobenzene

Under ambient condition, a 20 mL sample vial was charged with 0.2 mmol of hydrazobenzene, 2 mol% of Eosin Y and 1.0 mL of MeCN, then sealed and put on a 22 W white compact fluorescent lamp plate for the time shown and analyzed by ^{1}H NMR using CH_2Br_2 as internal standard. Isolated products were obtained after flash chromatography using petroleum: ethyl acetate (10:1) as eluent.

General procedure for the Eosin Y – catalyzed transfer hydrogenation of azobenzene

In a glovebox, 20 mL sample vial was charged with 0.2 mmol of azobenzene, 2 mol% of Eosin Y, 1.0 mL of MeCN and the corresponding hydrogen donor (0.42 mmol), then sealed and put on a 22 W white compact fluorescent lamp plate for the time shown and analyzed by ^{1}H NMR using CH_2Br_2 as internal standard.

Procedure for the luminescence quenching experiments

A Shimadazu fluorescence spectrometer (RF-5301) was used to record the emission intensities. All the experiments were performed in quartz cuvette using degassed MeCN as solvent. Eosin Y solutions were excited at 698 nm and the emission intensities at 554 nm were recorded. In a typical experiment, the emission spectrum of $5x10^{-4}$ M solution of Eosin Y in CH_3CN was collected. Then, appropriate amount of hydrazobenzene was added to the measured solution and the spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 554 nm. With O_2 quenching experiments saturated the solution of Eosin Y by O_2 bubble for 20 min and then the spectrum was collected.

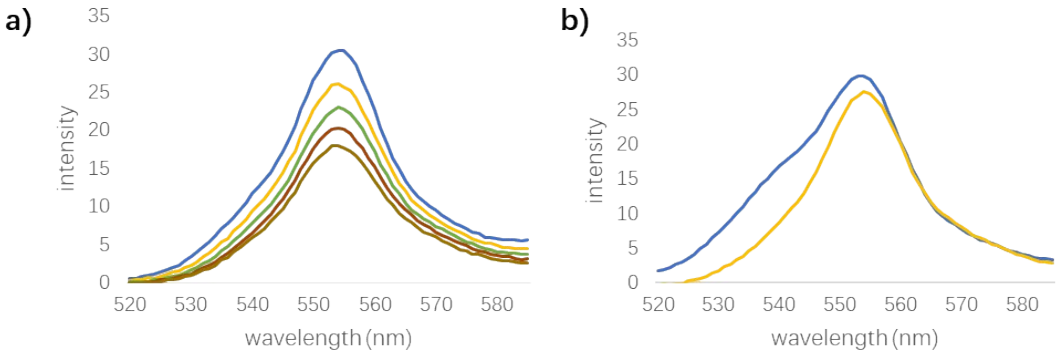
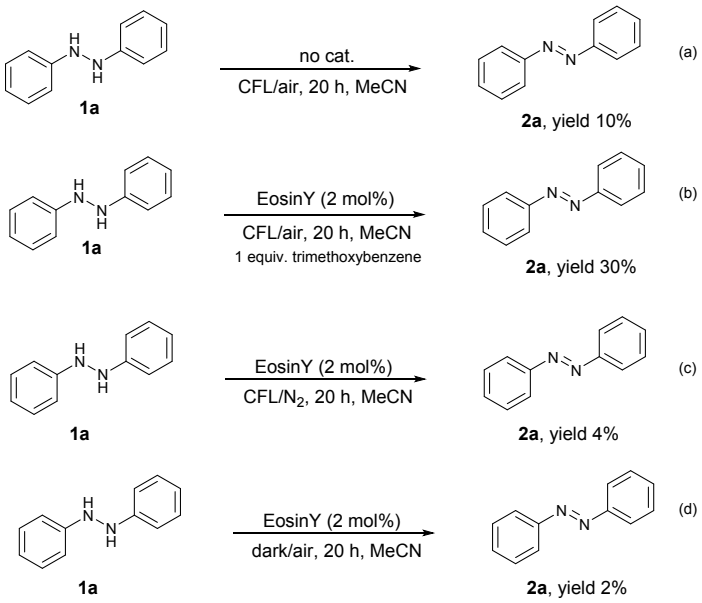
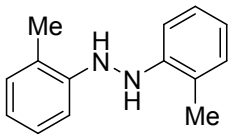


Figure S1: Luminescence quenching of Eosin Y by a) hydrazobenzene; b) azobenzene.



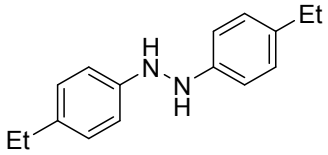
Scheme S1. Control experiments showed the crucial role of Eosin Y, air, light.

Products Characterization



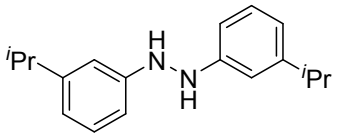
1b

1,2-Di-o-tolylhydrazine 1b: light yellow oil obtained in 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.10 (m, 4H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.2 Hz, 2H), 5.60 (s, 2H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 130.4, 127.3, 121.2, 119.4, 111.0, 17.2.



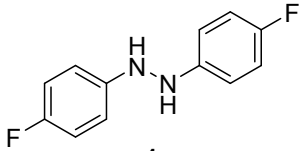
1d

1,2-Bis(4-ethylphenyl)hydrazine 1d: light yellow oil obtained in 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.4 Hz, 4H), 6.62 (d, *J* = 8.2 Hz, 4H), 3.52 (s, 2H), 2.54 (q, *J* = 7.6 Hz, 4H), 1.18 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 224.9, 144.1, 134.5, 128.6, 115.3, 28.0, 16.0.



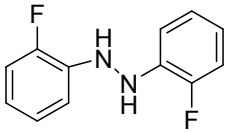
1e

1,2-Bis(3-isopropylphenyl)hydrazine 1e: light yellow oil obtained in 39% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.7 Hz, 2H), 6.82 (s, 3H), 6.80 – 6.74 (m, 3H), 5.62 (s, 2H), 2.95- 2.88 (m, 2H), 1.30 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 149.2, 129.3, 118.1, 110.7, 110.0, 34.3, 24.0.



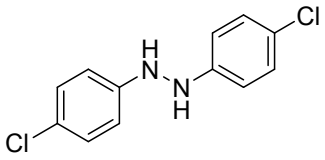
1g

1,2-Bis(4-fluorophenyl)hydrazine 1g: brown solid obtained in 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (t, *J* = 8.7 Hz, 4H), 6.83 (dd, *J* = 8.9, 4.5 Hz, 4H), 5.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.24 (d, *J* = 237.3 Hz), 144.94 – 144.84 (d, *J* = 2.0 Hz), 115.89 (d, *J* = 22.6 Hz), 113.41 (d, *J* = 7.6 Hz).



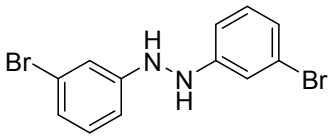
1h

1,2-Bis(2-fluorophenyl)hydrazine 1h: light yellow oil obtained in 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.01 (m, 6H), 6.85-6.79 (m, 2H), 5.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 136.5 (d, *J* = 10.0 Hz), 124.8 (d, *J* = 3.2 Hz), 119.8 (d, *J* = 6.9 Hz), 115.0 (d, *J* = 17.8 Hz), 113.7.



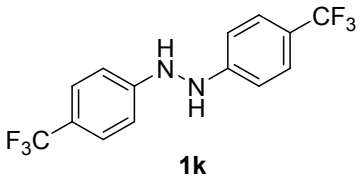
1i

1,2-Bis(4-chlorophenyl)hydrazine 1i: yellow solid obtained in 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 4H), 6.81 (d, *J* = 8.8 Hz, 4H), 5.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 129.3, 124.8, 113.5.



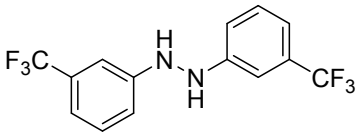
1j

1,2-Bis(3-bromophenyl)hydrazine 1j: yellow solid obtained in 48% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 1.9 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.79 (dd, *J* = 8.8, 1.5 Hz, 2H), 5.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 130.8, 123.4, 123.1, 115.2, 110.9.



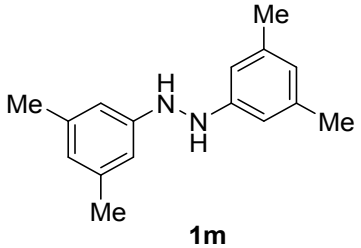
1k

1,2-Bis(4-(trifluoromethyl)phenyl)hydrazine 1k: yellow solid obtained in 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 4H), 6.98 – 6.89 (m, 4H), 6.00 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 126.9 (d, *J* = 2.8 Hz), 124.6 (q, *J* = 270.8 Hz), 122.2 (q, 34.6 Hz), 111.7.



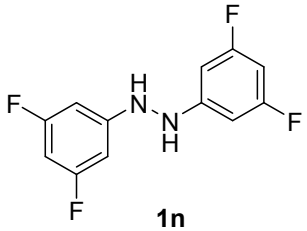
1l

1,2-Bis(3-(trifluoromethyl)phenyl)hydrazine 1l: yellow solid obtained in 32% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (tt, *J* = 7.4, 1.0 Hz, 2H), 7.13 – 7.07 (m, 4H), 7.02 – 6.92 (m, 2H), 5.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 131.9 (q, J = 32.1 Hz), 130.0, 124.2 (q, J = 272.4 Hz), 116.9 (q, J = 3.9 Hz), 115.3 (d, J = 1.6 Hz), 108.9 (q, J = 4.0 Hz).



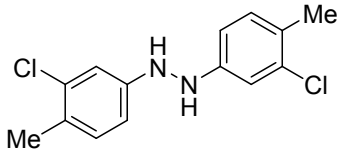
1m

1,2-Bis(3,5-dimethylphenyl)hydrazine 1m: yellow solid obtained in 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 6H), 5.51 (s, 2H), 2.30 (s, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 139.1, 121.8, 110.1, 21.5.



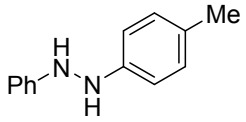
1n

1,2-Bis(3,5-difluorophenyl)hydrazine 1n: yellow solid obtained in 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 – 6.27 (m, 6H), 5.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.42 (d, *J* = 15.1 Hz), 162.98 (d, *J* = 15.1 Hz), 150.64 (t, *J* = 12.4 Hz), 95.51 (t, *J* = 26.1 Hz), 95.29 (d, *J* = 29.4 Hz), 95.29 (d, *J* = 11.4 Hz); HRMS-ESI: m/z $(M+H)^+$ calcd for $C_{12}H_8F_4N_2$:257.0702; found: 257.0697.



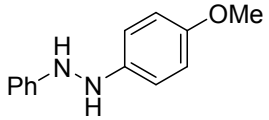
1o

1,2-Bis(3-chloro-4-methylphenyl)hydrazine 1o: yellow solid obtained in 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 2.2 Hz, 2H), 6.67 (dd, *J* = 8.2, 2.3 Hz, 2H), 5.60 (s, 2H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 135.1, 131.5, 127.1, 112.9, 110.9, 19.0; HRMS-ESI: m/z $(M+H)^+$ calcd for $C_{11}H_{14}Cl_2N_2$:281.0612; found: 281.0605



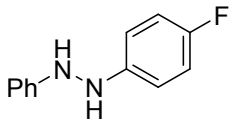
3a

1-Phenyl-2-(p-tolyl)hydrazine 3a: yellow solid obtained in 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.5 Hz, 2H), 7.07 – 7.00 (m, 2H), 6.86 (d, *J* = 8.3 Hz, 3H), 6.77 (d, *J* = 8.0 Hz, 2H), 5.60 (s, 1H), 5.54 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 129.9, 129.3, 119.8, 112.5, 112.4, 20.5.



3c

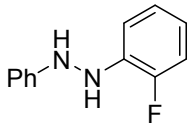
1-(4-Methoxyphenyl)-2-phenylhydrazine 3c: yellow solid obtained in 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.9 Hz, 2H), 6.88 – 6.82 (m, 3H), 6.80 (s, 4H), 5.59 (s, 1H), 5.45 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ142.8, 129.4, 119.8, 114.9, 113.7, 112.4, 55.7.



3d

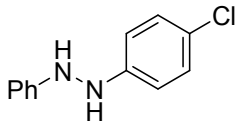
1-(4-Fluorophenyl)-2-phenylhydrazine 3d: yellow solid obtained in 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 5H), 5.67 (s, 1H), 5.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2 (d, *J* = 237.0 Hz), 148.7, 145.1, 129.4, 120.1, 115.8 (d, *J* =

22.6 Hz), 113.4 (d, *J* = 7.6 Hz), 112.4.



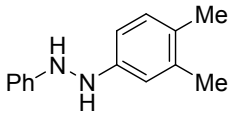
3e

1-(2-Fluorophenyl)-2-phenylhydrazine 3e: yellow solid obtained in 34% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 3H), 7.15 – 6.97 (m, 3H), 6.98 – 6.86 (m, 3H), 6.80 (s, 1H), 5.94 (s, 1H), 5.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6 (d, *J* = 239.1 Hz), 148.5, 136.9 (d, *J* = 9.8 Hz), 129.4, 124.8 (d, *J* = 3.5 Hz), 120.3, 119.4 (d, *J* = 6.9 Hz), 114.9 (d, *J* = 17.8 Hz), 113.8 (d, *J* = 2.9 Hz), 112.4.



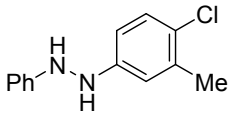
3f

1-(4-Chlorophenyl)-2-phenylhydrazine 3f: yellow solid obtained in 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 4H), 6.95 – 6.81 (m, 5H), 5.70 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ129.4, 129.4, 129.3, 120.2, 119.9, 113.6, 112.4.



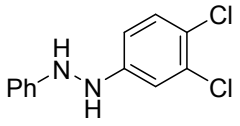
3g

1-(3,4-Dimethylphenyl)-2-phenylhydrazine 3g: yellow solid obtained in 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.95 – 6.87 (m, 3H), 6.74 (s, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.62 (s, 1H), 5.53 (s, 1H), 2.26 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 147.0, 137.6, 130.4, 129.4, 128.0, 119.8, 114.0, 112.4, 109.9, 20.0, 18.8. HRMS-ESI: m/z $(M+H)^+$ calcd for $C_{14}H_{16}N_2$:213.1392; found: 213.1387.



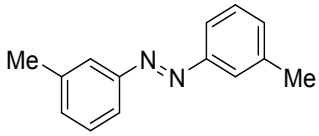
3h

1-(4-Chloro-3-methylphenyl)-2-phenylhydrazine 3h: yellow solid obtained in 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (q, *J* = 7.7, 6.7 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.93 – 6.83 (m, 3H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.65 (s, 1H), 5.58 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 148.1, 135.1, 131.5, 129.4, 126.9, 120.2, 112.9, 112.4, 110.9, 19.0. HRMS-ESI: m/z $(M+H)^+$ calcd for $C_{13}H_{13}ClN_2$:233.0846; found: 233.0840.



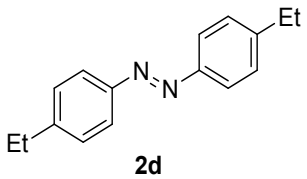
3i

1-(3,4-Dichlorophenyl)-2-phenylhydrazine 3i: yellow oil obtained in 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 3H), 7.04 (s, 1H), 6.92 (t, *J* = 7.0 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 1H), 5.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 148.0, 133.2, 130.9, 129.5, 122.4, 120.5, 113.8, 112.4, 111.8.



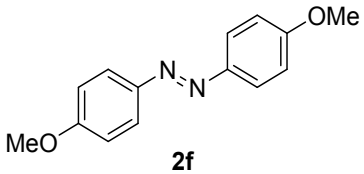
2c

1,2-Di-m-tolyldiazene 2c: yellow solid obtained in 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 4H), 7.47 (s, 2H), 7.35 (s, 2H), 2.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 139.0, 131.7, 128.9, 122.9, 120.5, 21.4.



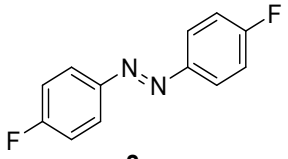
2d

1,2-Bis(4-ethylphenyl)diazene 2d: yellow solid obtained in 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 4H), 7.40 (d, *J* = 8.3 Hz, 4H), 2.79 (q, *J* = 7.6 Hz, 4H), 1.35 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 147.5, 128.5, 122.8, 28.9, 15.4.



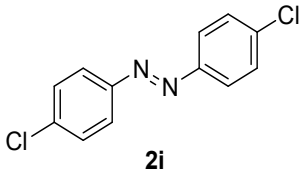
2f

1,2-Bis(4-methoxyphenyl)diazene 2f: yellow solid obtained in 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 4H), 7.05 (d, *J* = 8.9 Hz, 4H), 3.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ161.6, 147.2, 124.4, 114.2, 55.6.



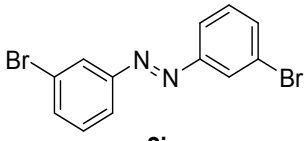
2g

1,2-Bis(4-fluorophenyl)diazene 2g: yellow solid obtained in 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.6, 5.3 Hz, 4H), 7.24 (t, *J* = 8.5 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (d, *J* = 252.3 Hz), 163.2, 149.0, 124.8 (d, *J* = 9.0 Hz), 116.1 (d, *J* = 22.9 Hz).



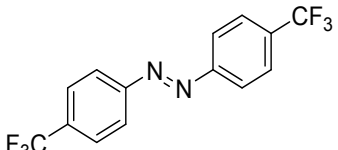
2i

1,2-Bis(4-chlorophenyl)diazene 2i: yellow solid obtained in 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 4H), 7.54 (d, *J* = 7.5 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ149.3, 137.3, 129.4, 124.2.



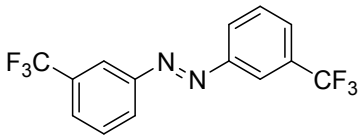
2j

1,2-Bis(3-bromophenyl)diazene 2j: yellow solid obtained in 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.70 – 7.64 (m, 2H), 7.46 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 134.1, 130.5, 124.8, 123.2.



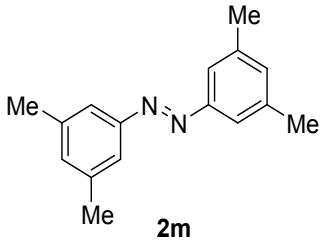
2k

1,2-Bis(4-(trifluoromethyl)phenyl)diazene 2k: yellow solid obtained in 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 4H), 7.86 (d, *J* = 8.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 133.0 (d, *J* = 32.7 Hz), 126.4 (d, *J* = 4.0 Hz), 123.3, 122.8 (q, *J* = 272.5 Hz).



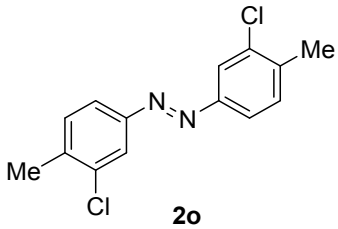
2l

1,2-Bis(3-(trifluoromethyl)phenyl)diazene 2l: yellow solid obtained in 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 2H), 8.19 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.73 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 131.9 (d, *J* = 33.1 Hz), 129.8, 127.9 (q, *J* = 3.2 Hz), 126.5, 123.8 (q, *J* = 272.6 Hz), 119.77 (q, *J* = 3.9 Hz).



2m

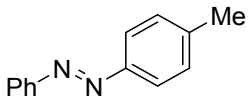
1,2-Bis(3,5-dimethylphenyl)diazene 2m: yellow solid obtained in 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 4H), 7.17 (s, 2H), 2.47 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 138.8, 132.5, 120.6, 21.3. HRMS-ESI: m/z $(M+H)^+$ calcd for $C_{16}H_{18}N_2$: 239.1548; found: 239.1552.



2o

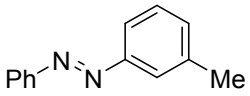
1,2-Bis(3-chloro-4-methylphenyl)diazene 2o: yellow solid obtained in 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.5 Hz, 2H), 7.78 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 2.50 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 139.3, 135.2, 131.3, 122.5, 122.2, 20.2. HRMS-ESI: m/z

$(M+H)^+$ calcd for $C_{16}H_{18}N_2$:279.0456; found: 279.0447.



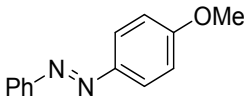
4a

1-Phenyl-2-(p-tolyl)diazene 4a: yellow solid obtained in 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.48 (m, 3H), 7.37 (d, *J* = 8.1 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.7, 129.8, 129.1, 122.9, 122.7, 21.5.



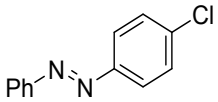
4b

1-Phenyl-2-(m-tolyl)diazene 4b: yellow solid obtained in 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 2H), 7.79 (s, 2H), 7.56 (dt, *J* = 13.6, 6.6 Hz, 3H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 139.0, 131.8, 130.9, 129.1, 128.9, 123.0, 122.8, 120.5, 21.4.



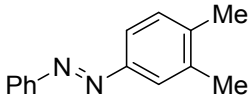
4c

1-(4-Methoxyphenyl)-2-phenyldiazene 4c: yellow solid obtained in 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.7 Hz, 2H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.52 (dt, *J* = 26.3, 7.1 Hz, 3H), 7.07 (d, *J* = 8.8 Hz, 2H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 162.1, 152.8, 147.1, 130.4, 129.0, 124.8, 122.6, 114.2, 55.6.



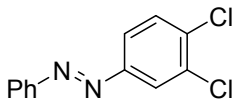
4f

1-(4-Chlorophenyl)-2-phenyldiazene 4f: yellow solid obtained in 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 14.5, 8.0 Hz, 4H), 7.55 (t, *J* = 9.3 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ152.5, 151.1, 136.9, 131.3, 129.4, 129.2, 124.1, 123.0.



4g

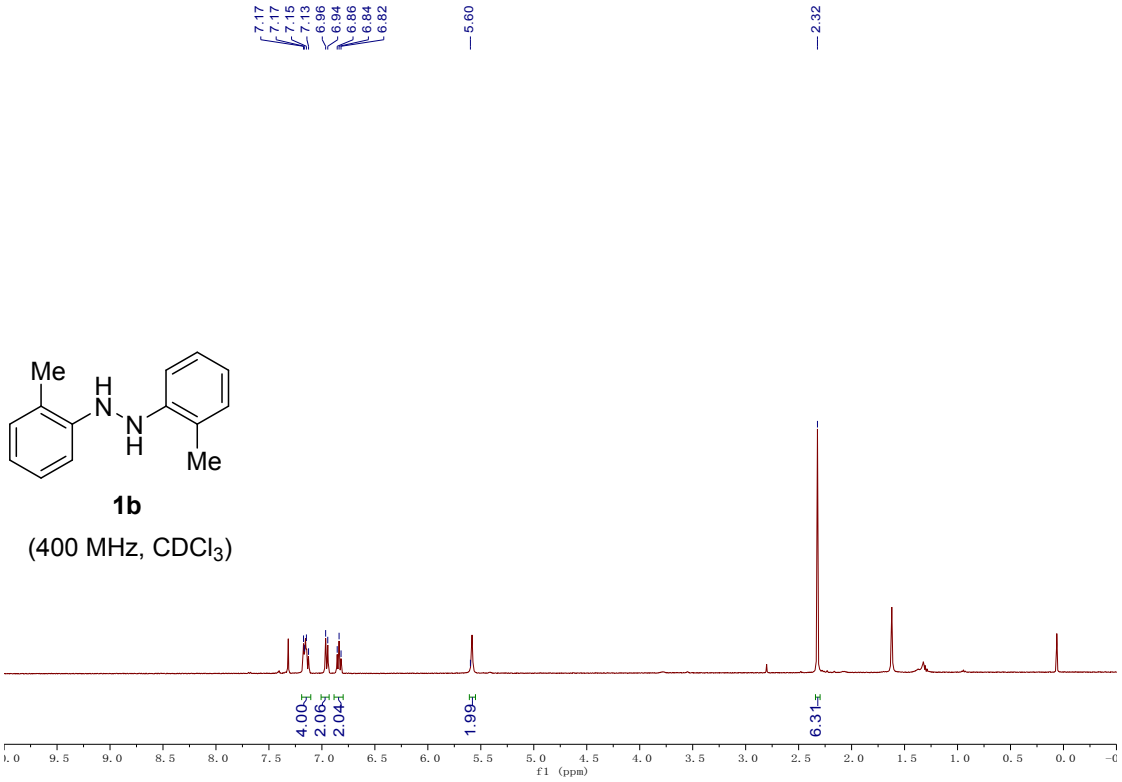
1-(3,4-Dimethylphenyl)-2-phenyldiazene 4g: brown solid obtained in 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.85 – 7.74 (m, 2H), 7.56 (dt, *J* = 24.0, 7.1 Hz, 3H), 7.39 – 7.32 (m, 1H), 2.45 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 152.9, 151.2, 140.3, 137.5, 130.6, 130.3, 129.1, 123.6, 122.7, 120.9, 19.9. HRMS-ESI: m/z $(M+H)^+$ calcd for $C_{14}H_{14}N_2$:211.1235; found: 211.1231.



4i

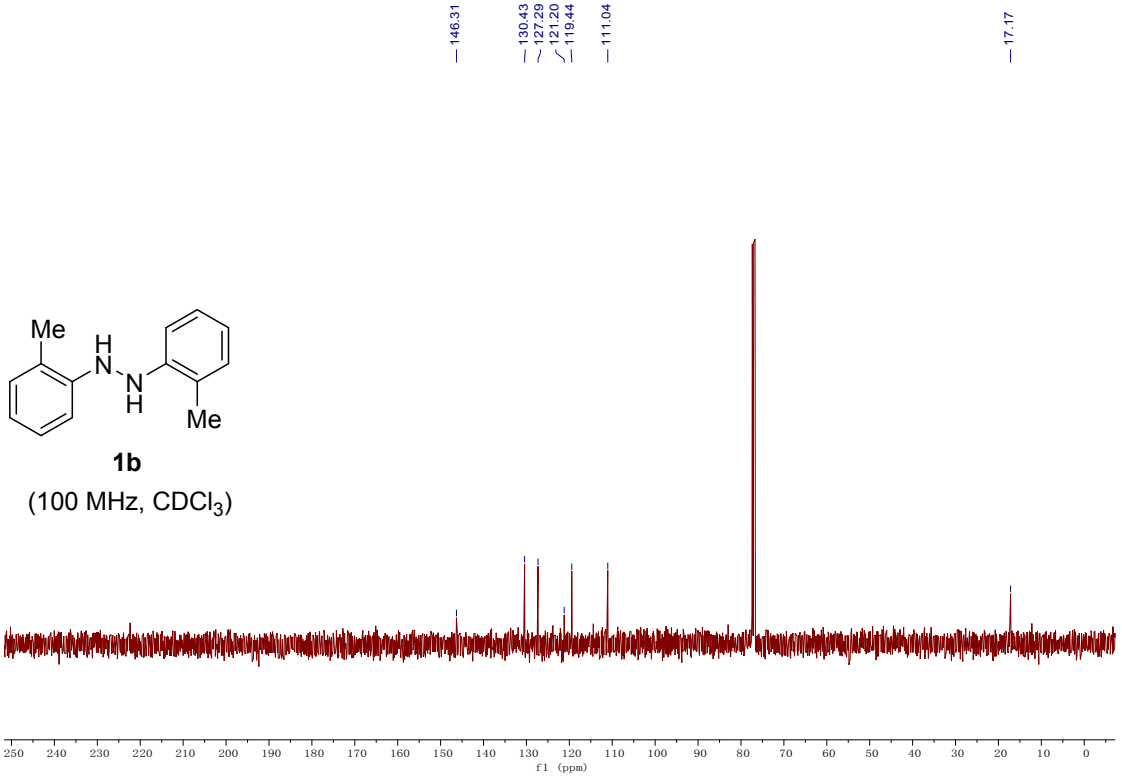
1-(3,4-Dichlorophenyl)-2-phenyldiazene 4i: yellow solid obtained in 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 1H), 7.96 (d, *J* = 6.2 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.5, 134.9, 133.5, 131.8, 130.9, 129.2, 123.9, 123.1, 122.9. HRMS-ESI: m/z $(M+NH_4)^+$ calcd for $C_{12}H_8Cl_2N_2$:268.0408; found: 268.0115.

NMR Spectra



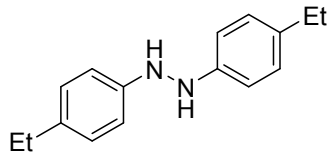
1b

(400 MHz, $CDCl_3$)



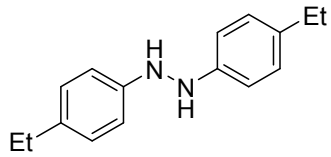
1b

(100 MHz, $CDCl_3$)



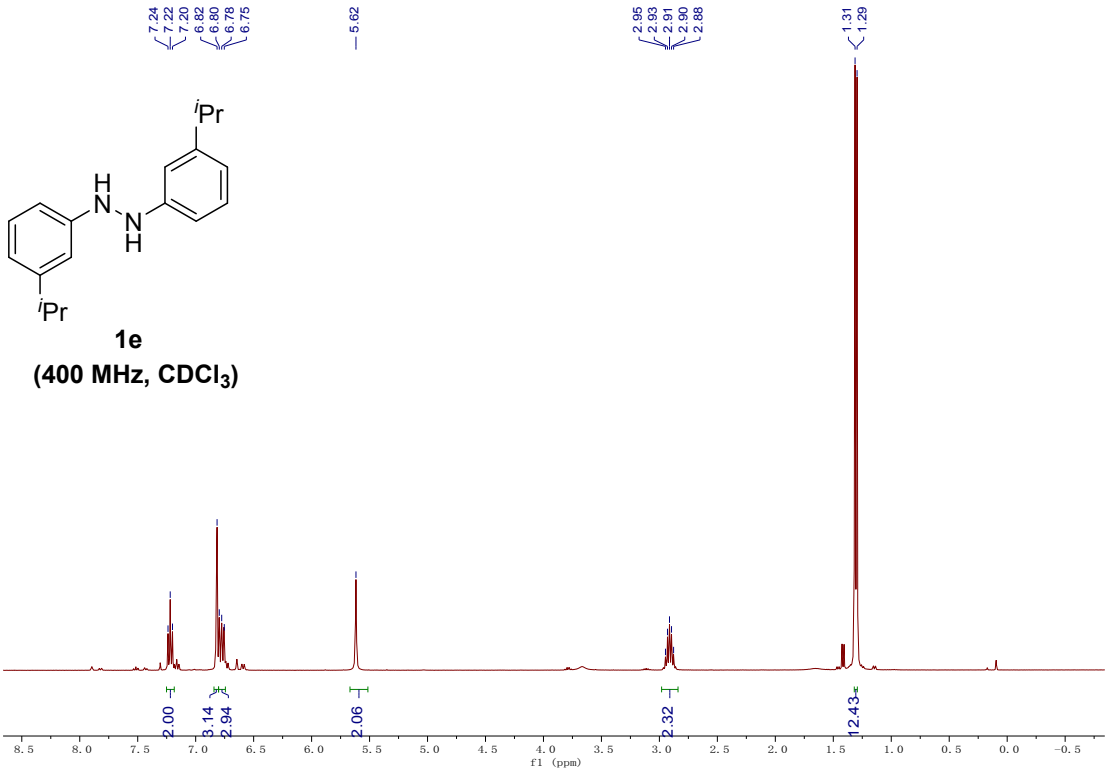
1d

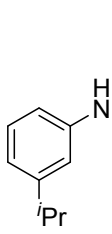
(400 MHz, $CDCl_3$)



1d

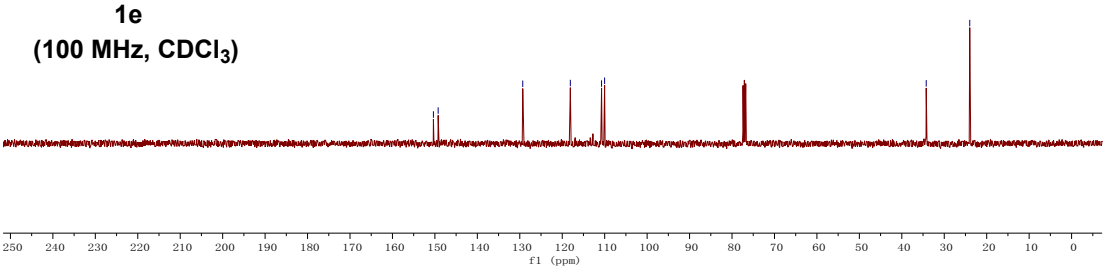
(100 MHz, $CDCl_3$)





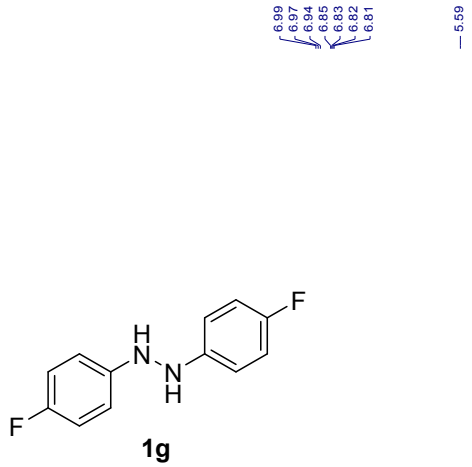
1e

(400 MHz, $CDCl_3$)



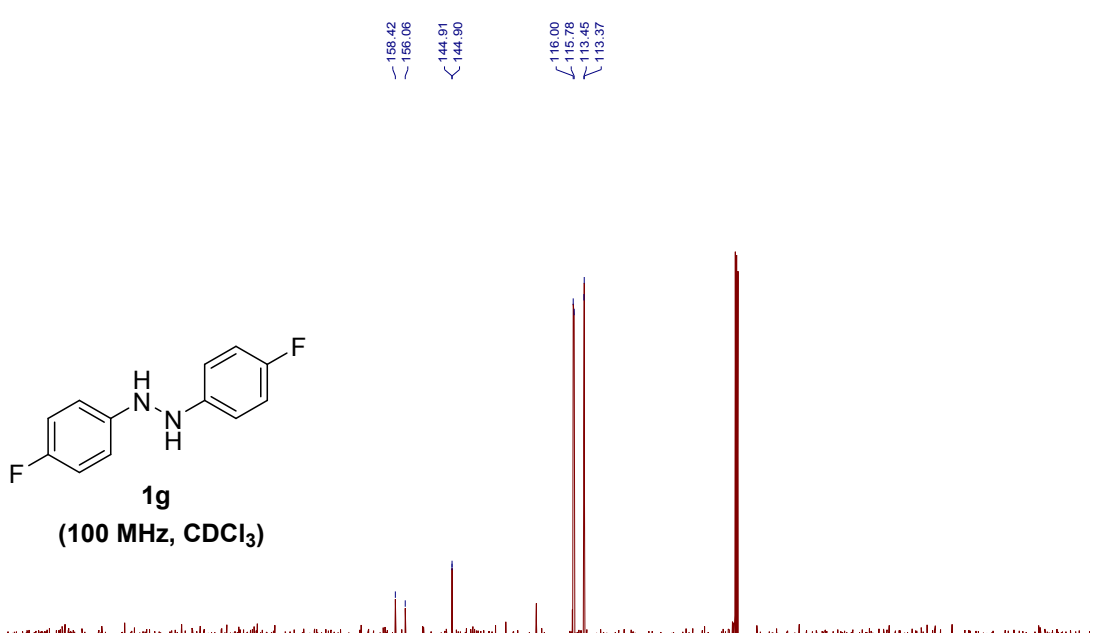
1e

(100 MHz, $CDCl_3$)



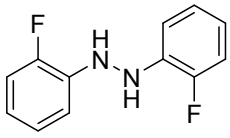
1g

(400 MHz, $CDCl_3$)



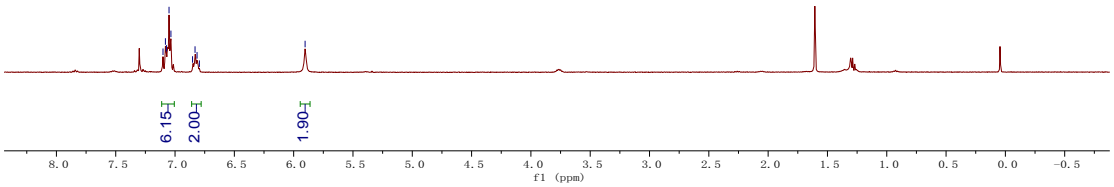
1g

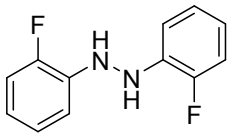
(100 MHz, $CDCl_3$)



1h

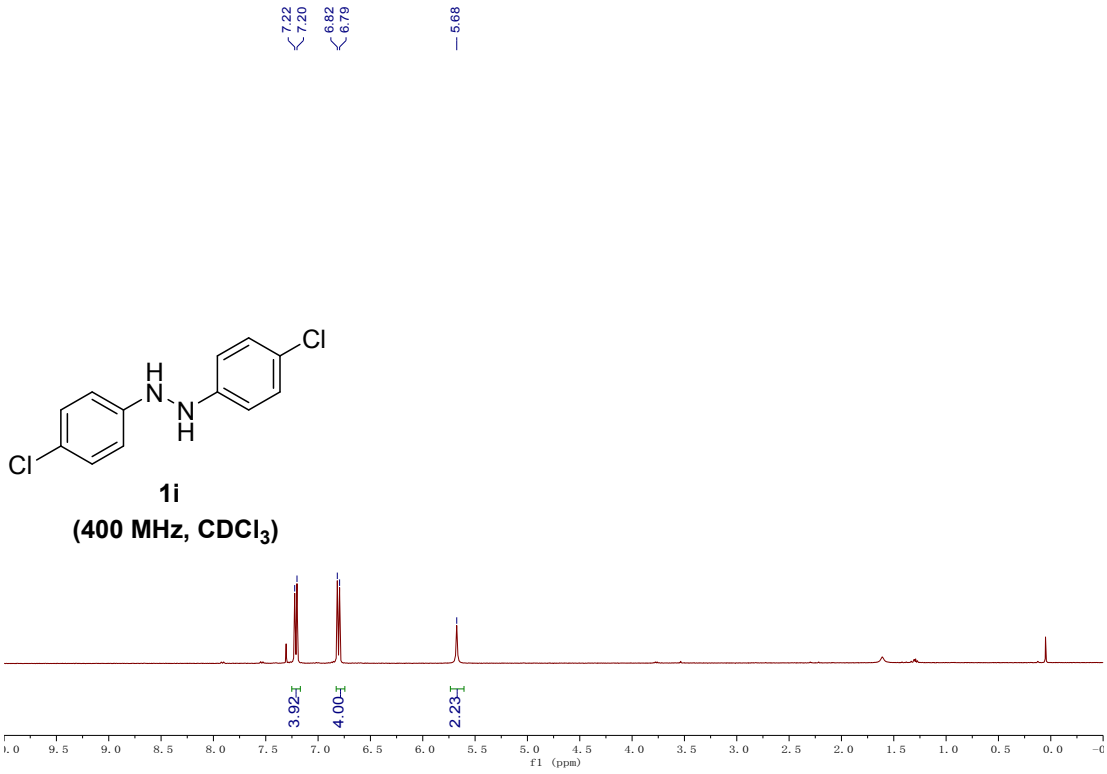
(400 MHz, $CDCl_3$)





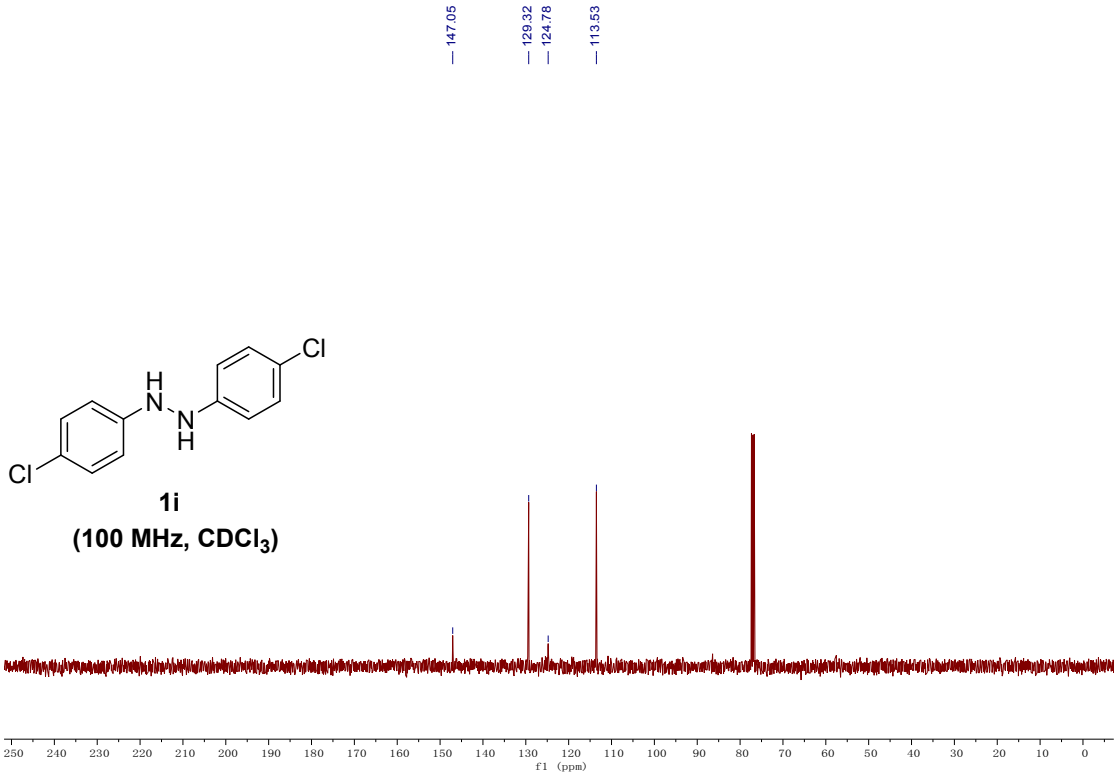
1h

(100 MHz, $CDCl_3$)



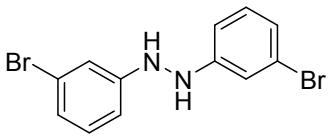
1i

(400 MHz, $CDCl_3$)



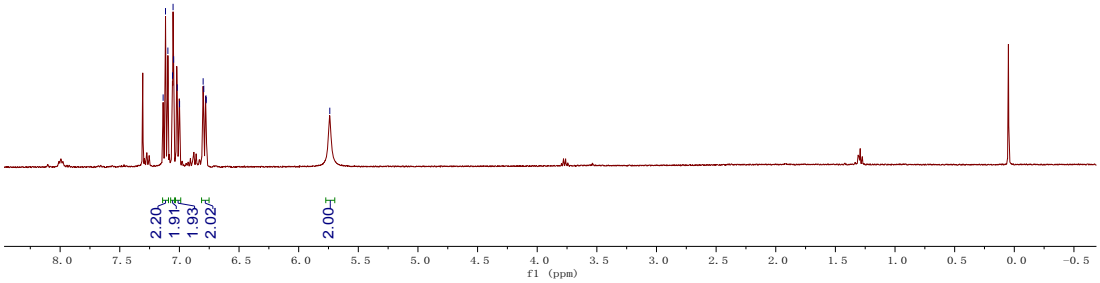
1i

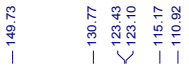
(100 MHz, $CDCl_3$)

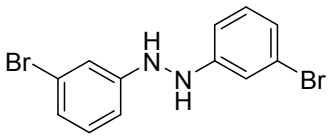


1j

(400 MHz, $CDCl_3$)

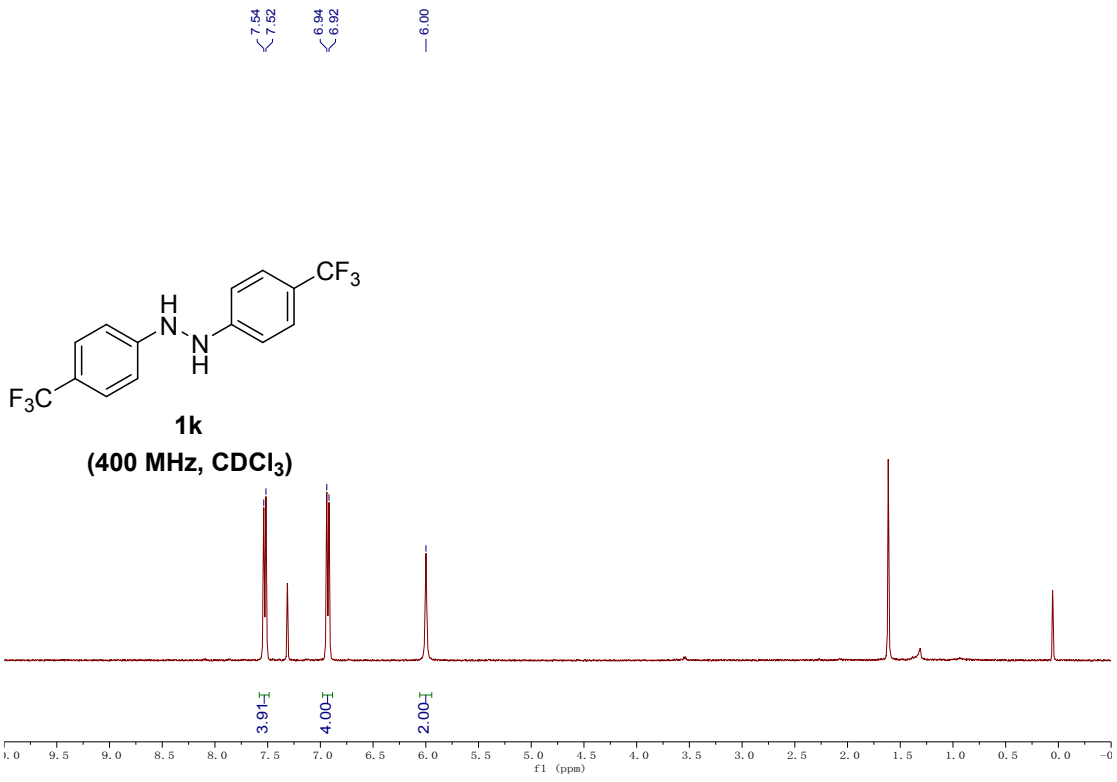






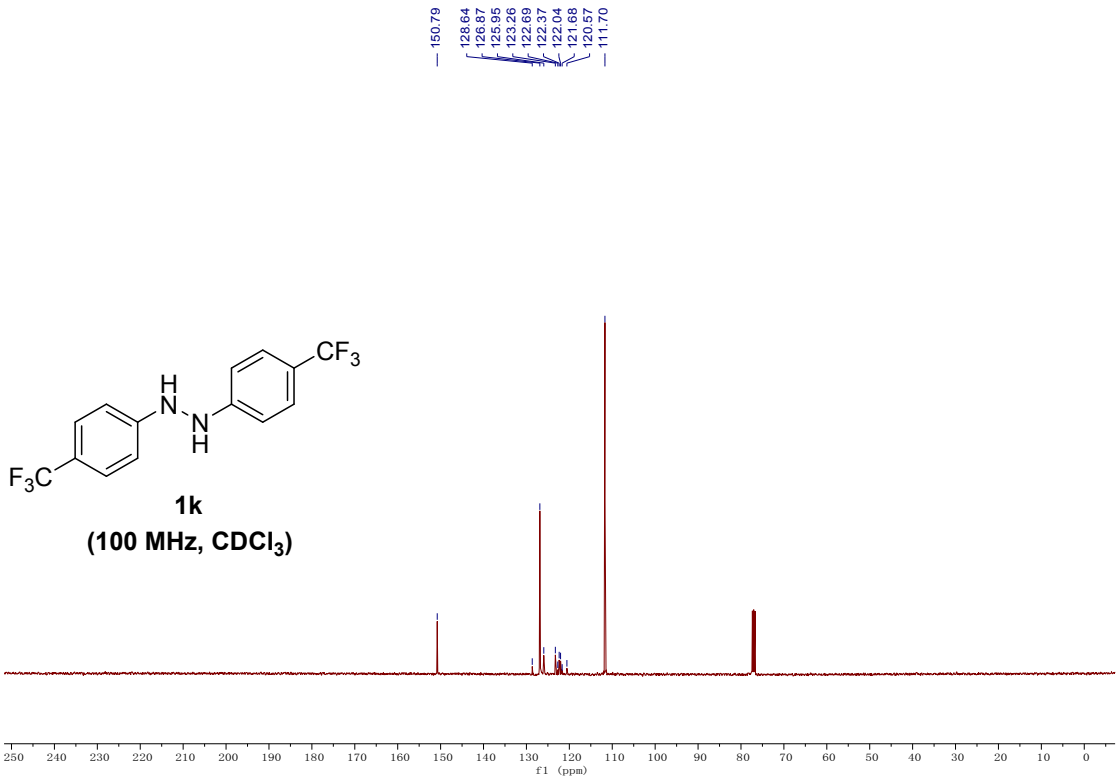
1j

(100 MHz, $CDCl_3$)



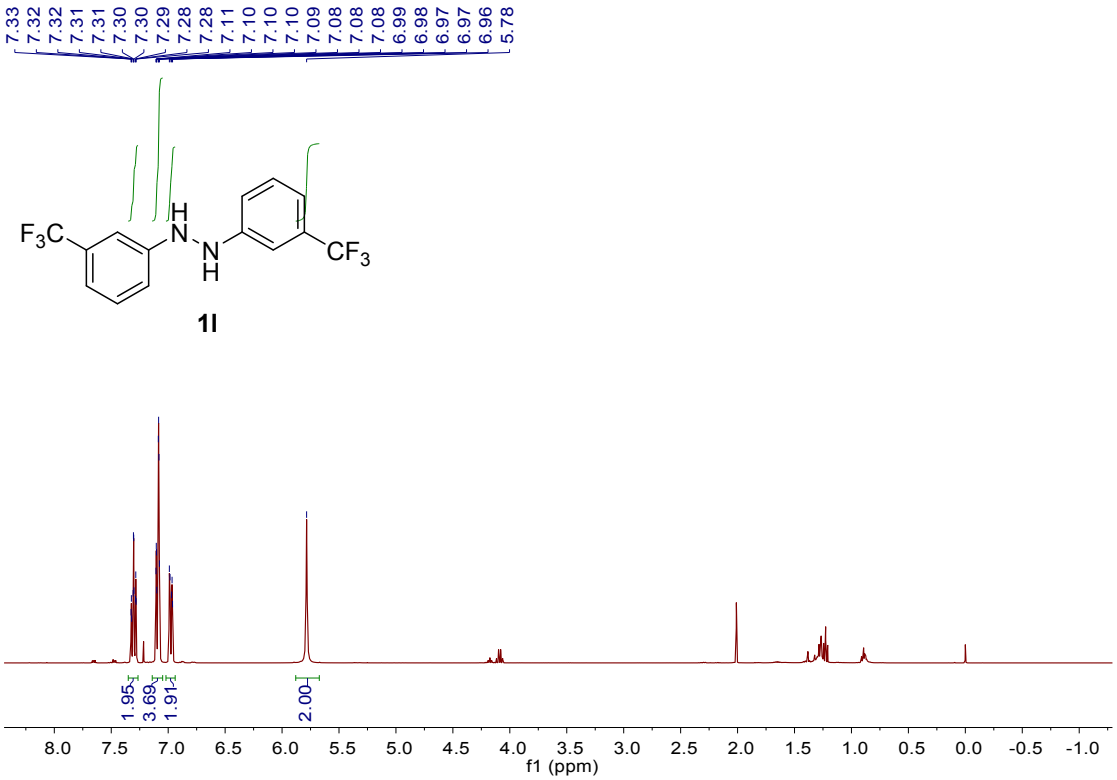
1k

(400 MHz, $CDCl_3$)



1k

(100 MHz, $CDCl_3$)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7.29
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7.28
7.11
7.10
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6.97
6.96
5.78
F3C
H
N
N
H
CF3
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1.95
3.69
1.91
2.00
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
1.5
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0.0
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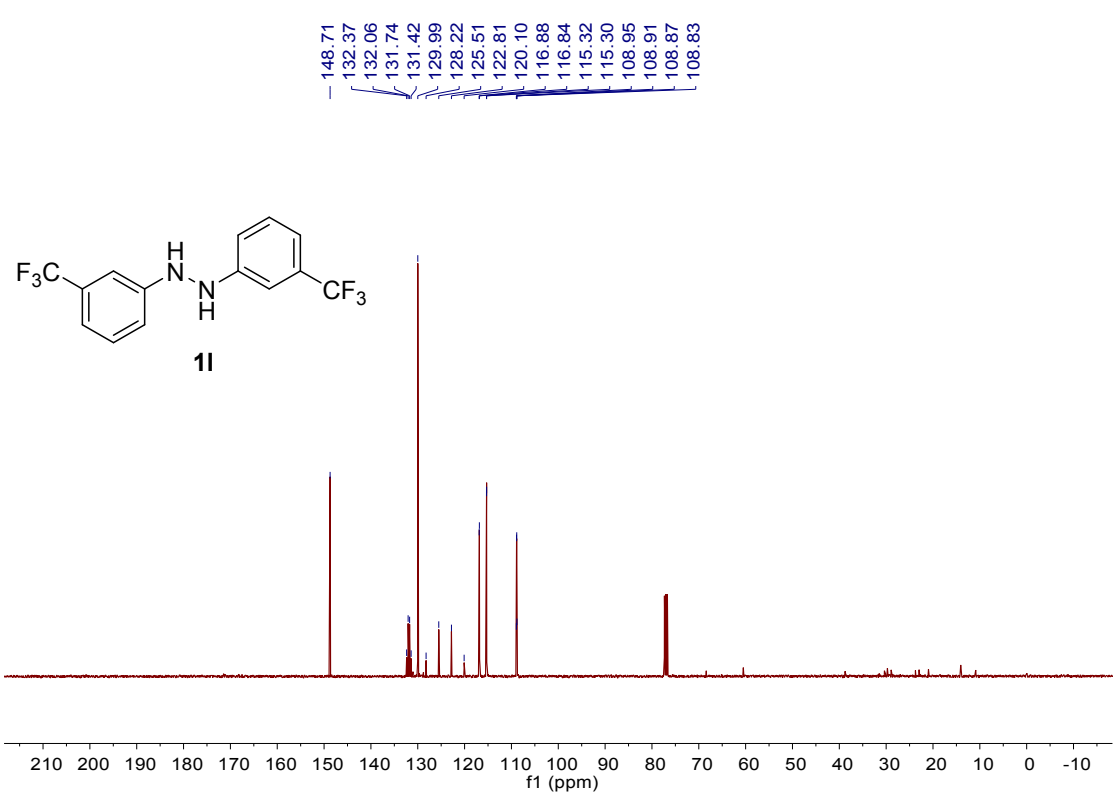
-1.0
f1 (ppm)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120.10
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115.30
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CF3
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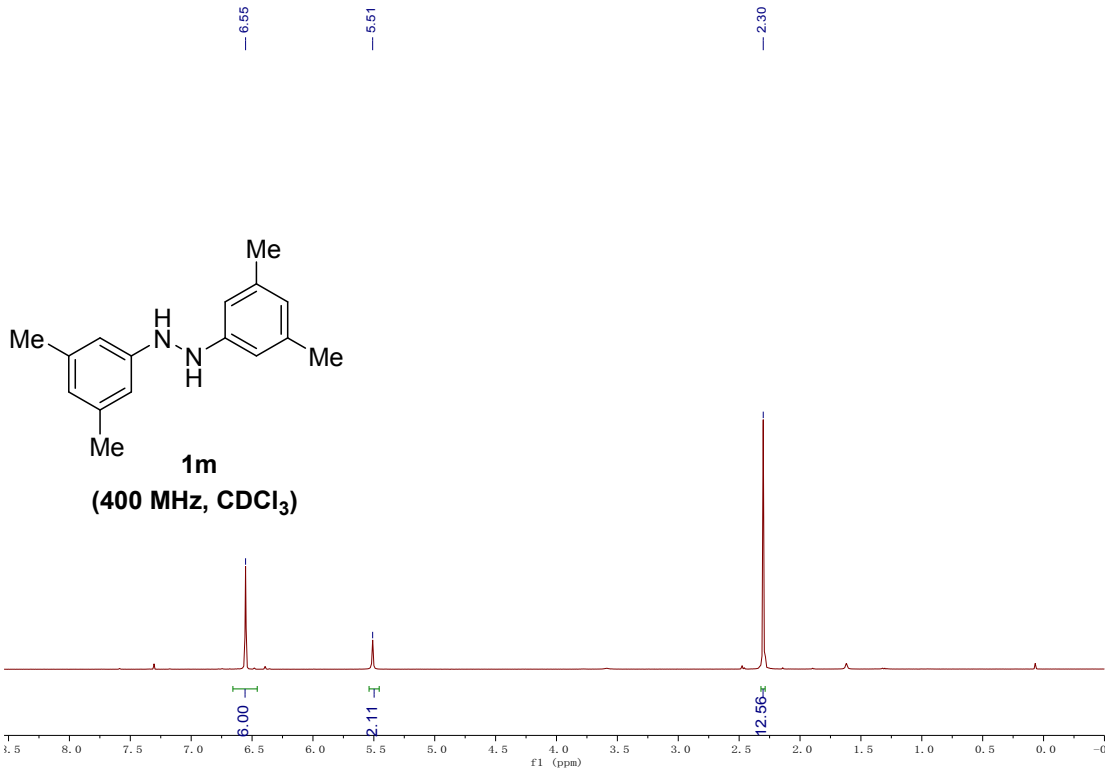
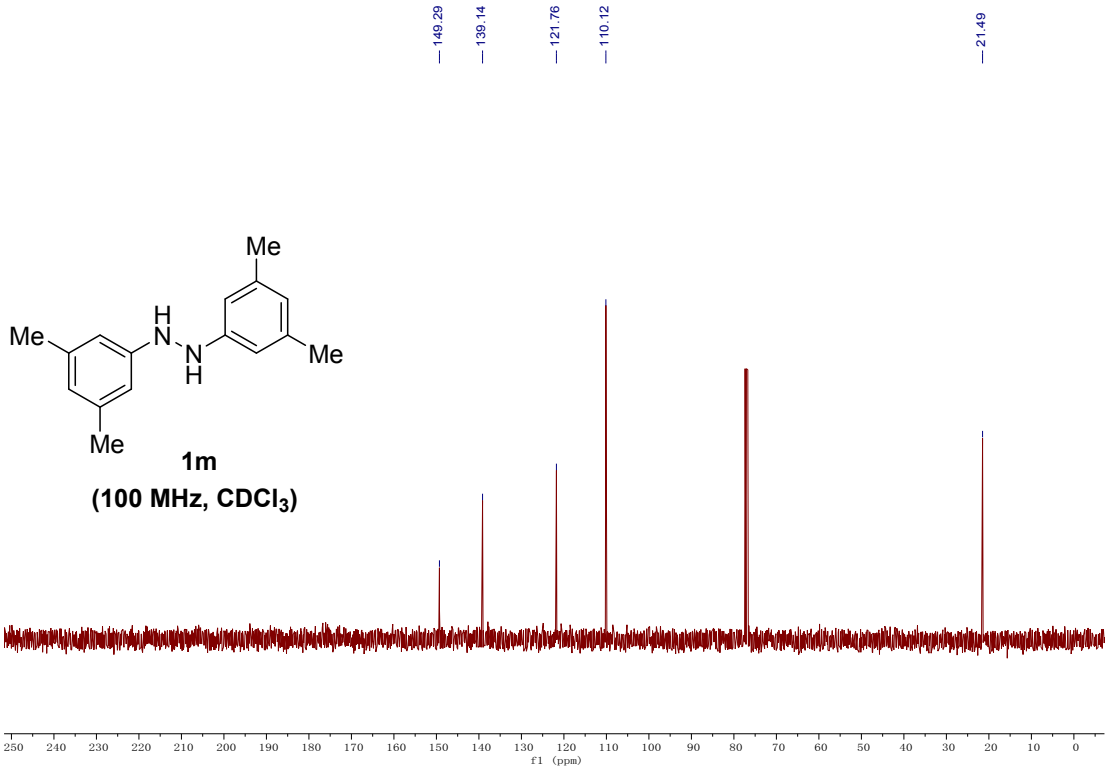
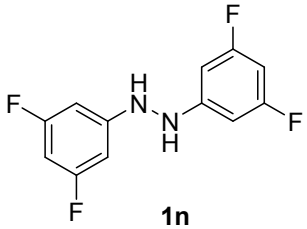
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

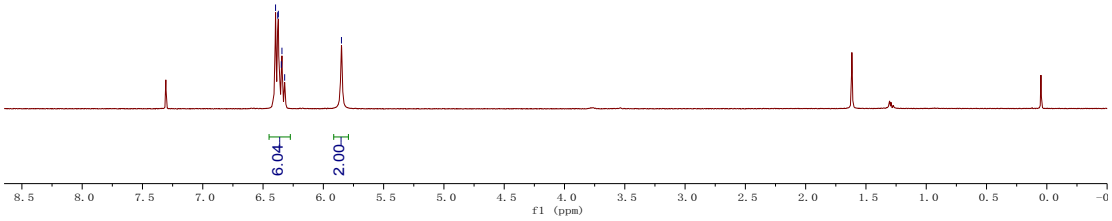

6.55
5.51
2.30
Me
Me
Me
Me
H
N
N
H
1m
(400 MHz, CDCl3)
6.00
2.11
12.56
f1 (ppm)

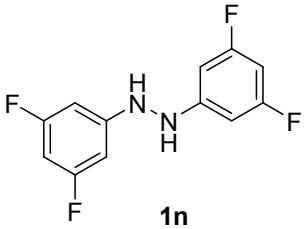

149.29
139.14
121.76
110.12
21.49
Me
Me
Me
Me
H
N
N
H
1m
(100 MHz, CDCl3)
f1 (ppm)



1n

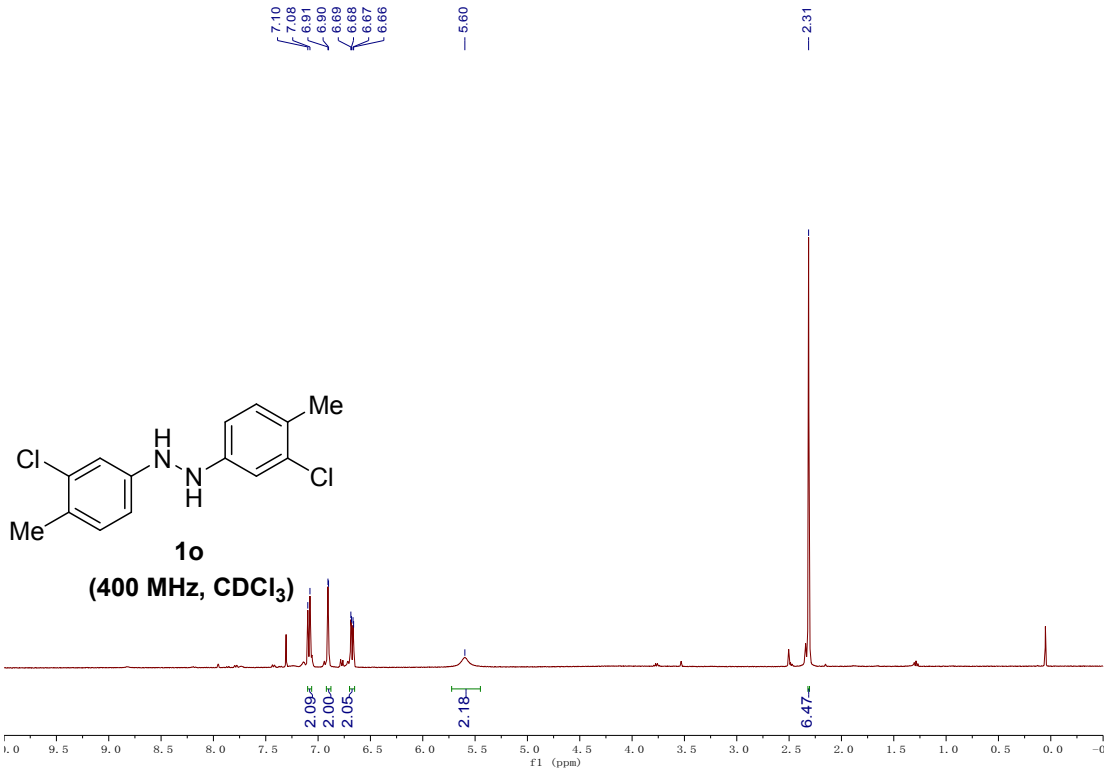
(400 MHz, $CDCl_3$)

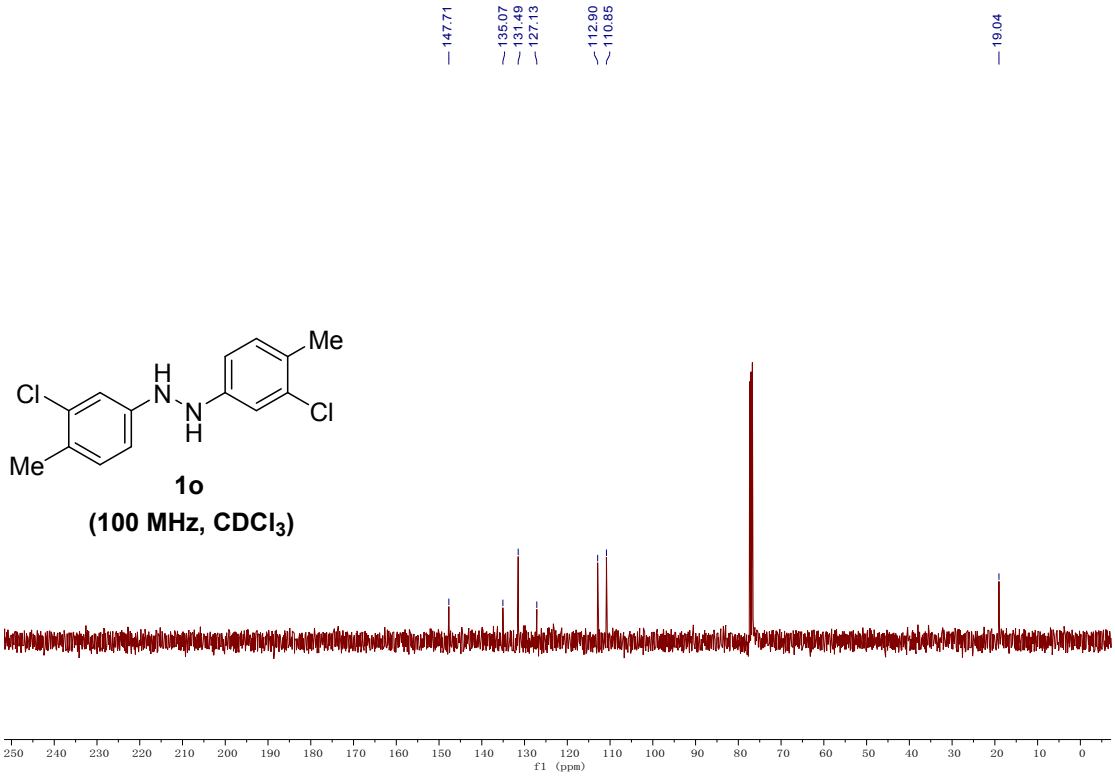


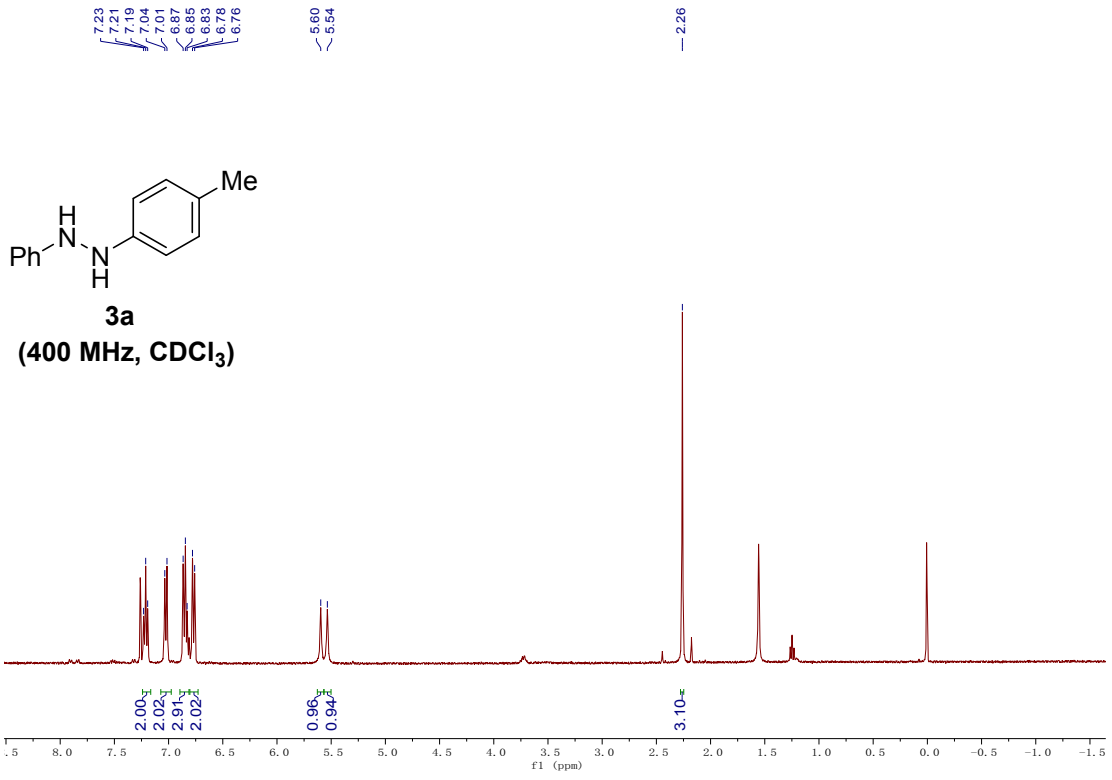


1n

(400 MHz, $CDCl_3$)

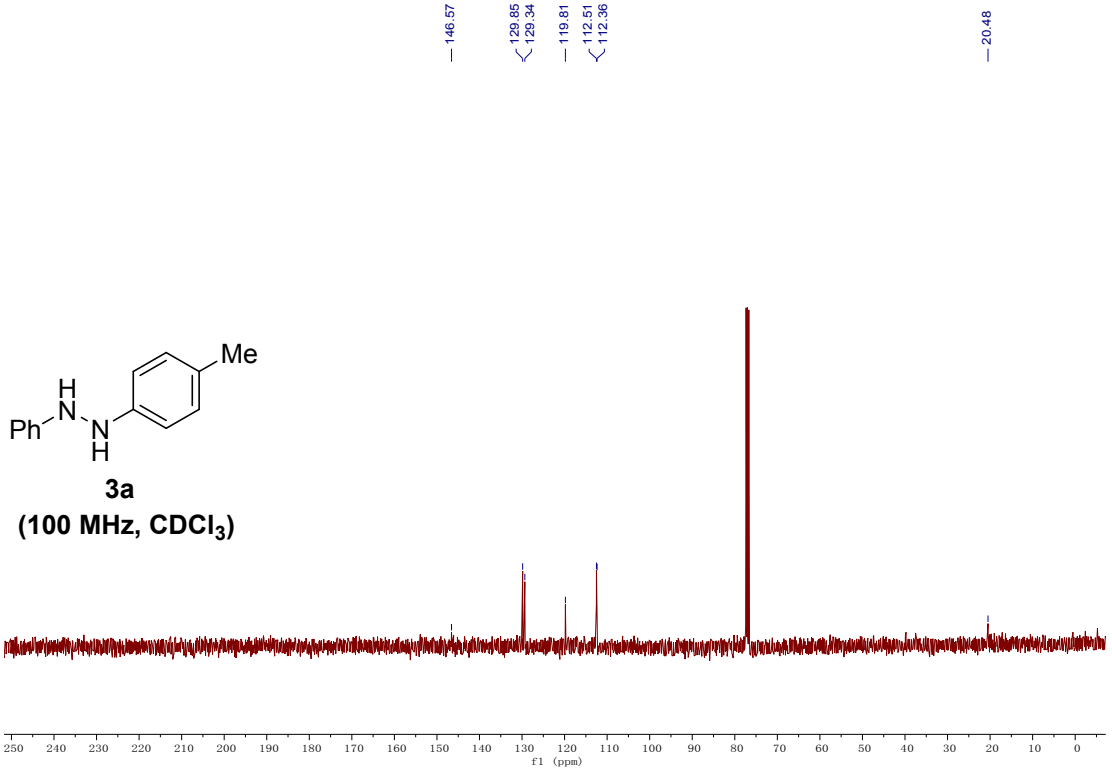

7.10
7.08
6.91
6.90
6.69
6.68
6.67
6.66
5.60
2.31
Me
Cl
H
N
N
H
Cl
Me
1o
(400 MHz, CDCl3)
2.09
2.00
2.05
2.18
6.47
f1 (ppm)


147.71
135.07
131.49
127.13
112.90
110.85
19.04
Me
Cl
H
N
N
H
Cl
Me
1o
(100 MHz, CDCl3)
f1 (ppm)



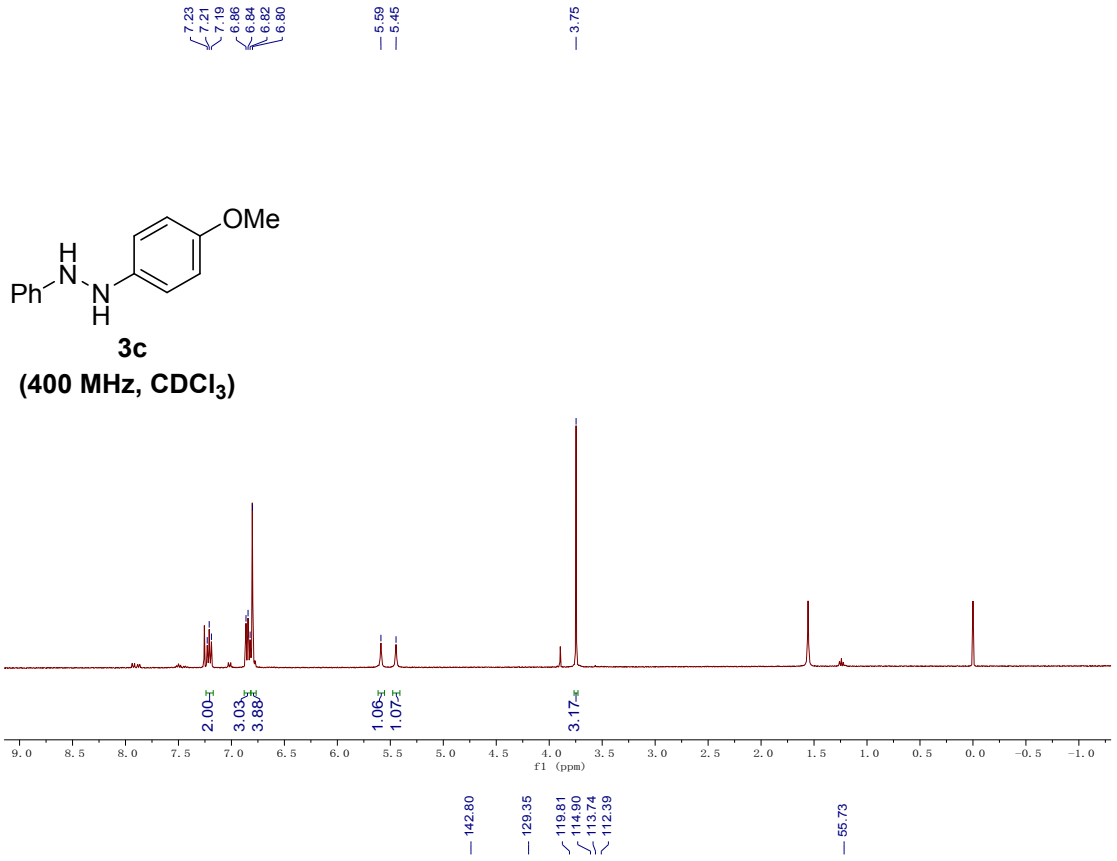
3a

(400 MHz, $CDCl_3$)



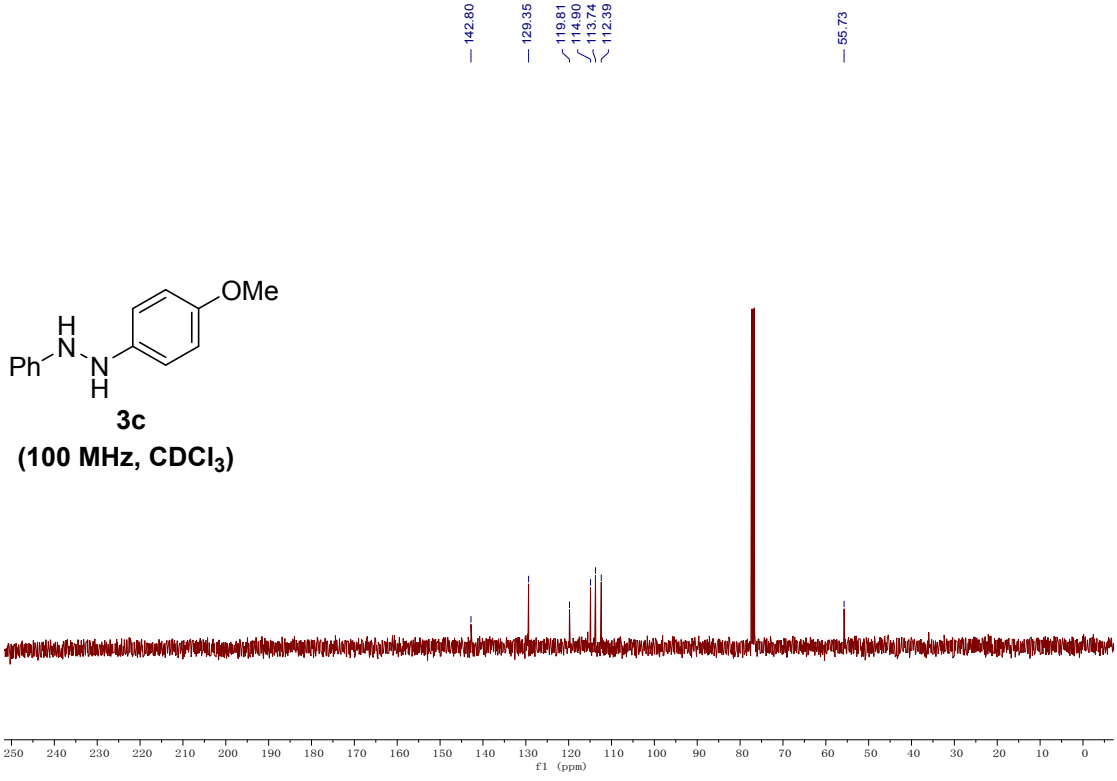
3a

(100 MHz, $CDCl_3$)



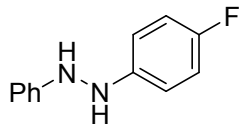
3c

(400 MHz, $CDCl_3$)



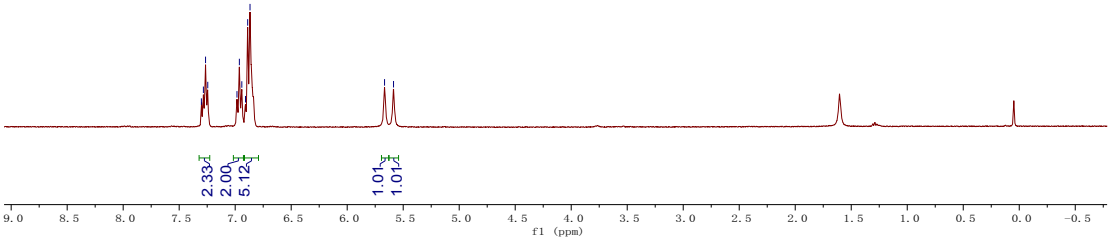
3c

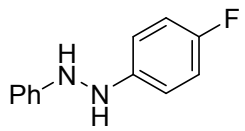
(100 MHz, $CDCl_3$)



3d

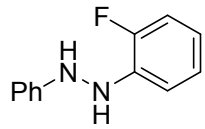
(400 MHz, $CDCl_3$)





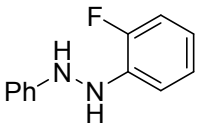
3d

(100 MHz, $CDCl_3$)



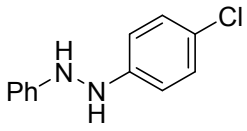
3e

(400 MHz, $CDCl_3$)



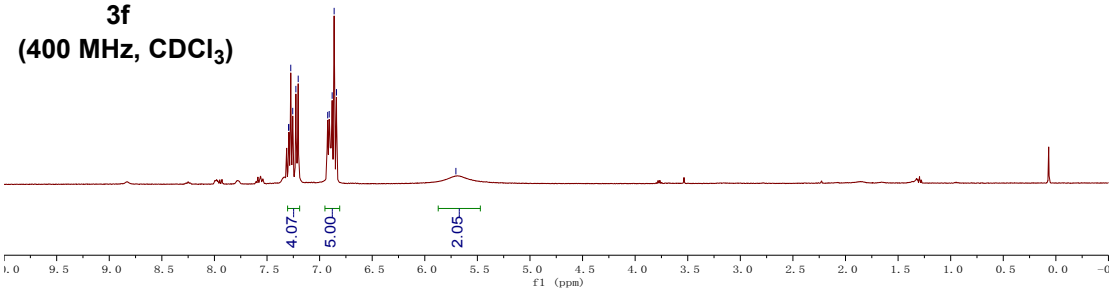
3e

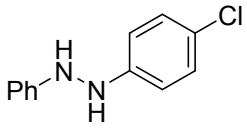
(100 MHz, $CDCl_3$)



3f

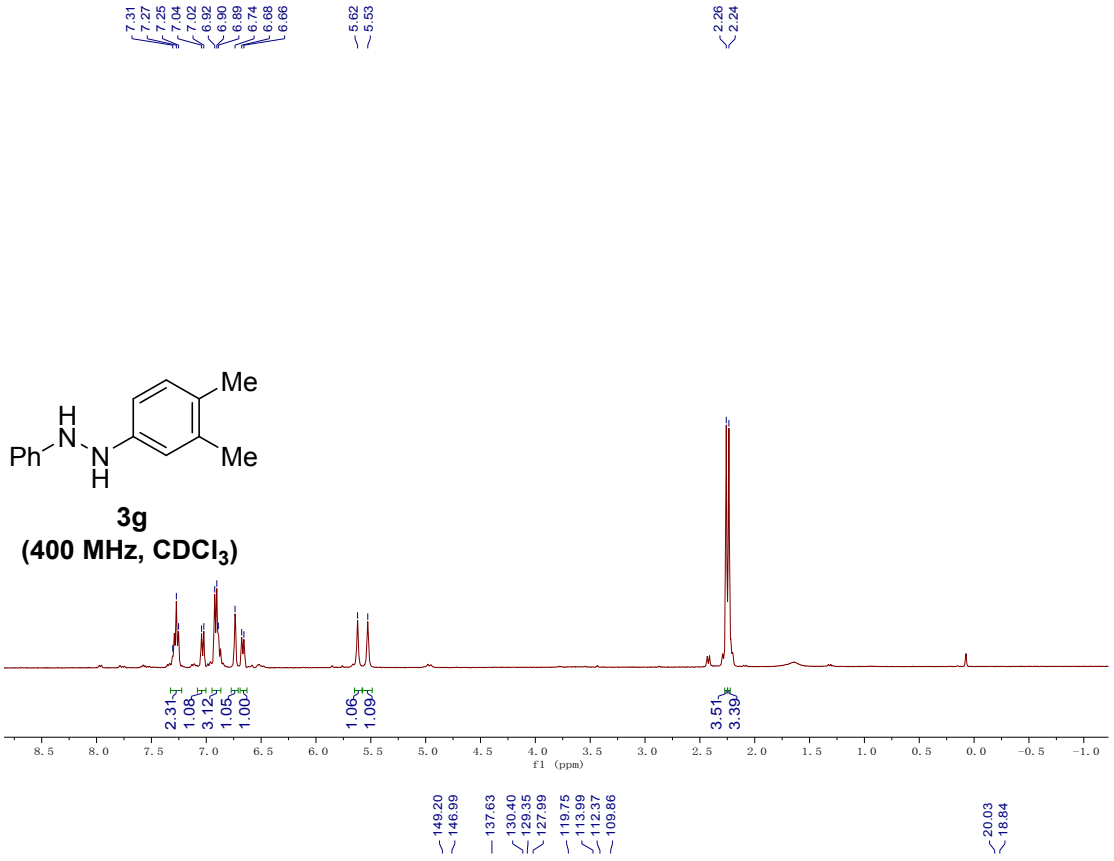
(400 MHz, $CDCl_3$)

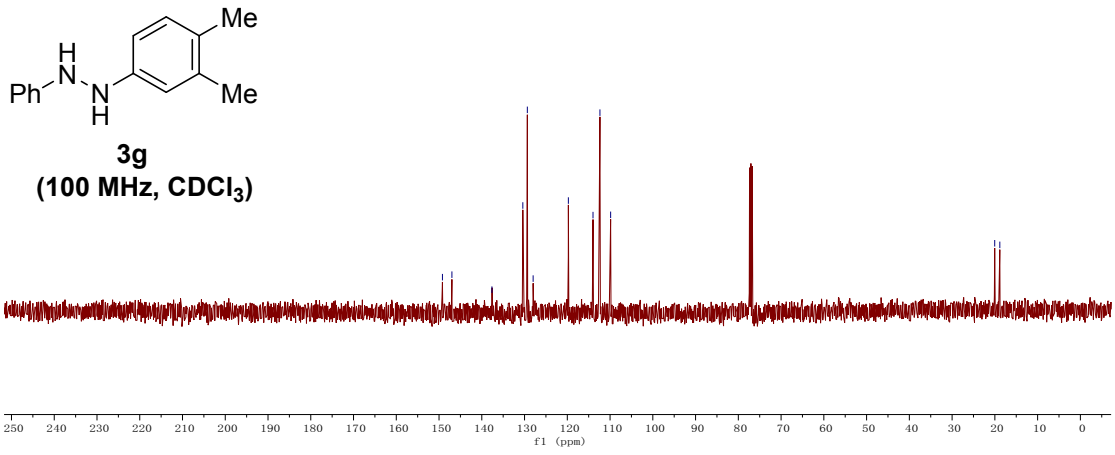


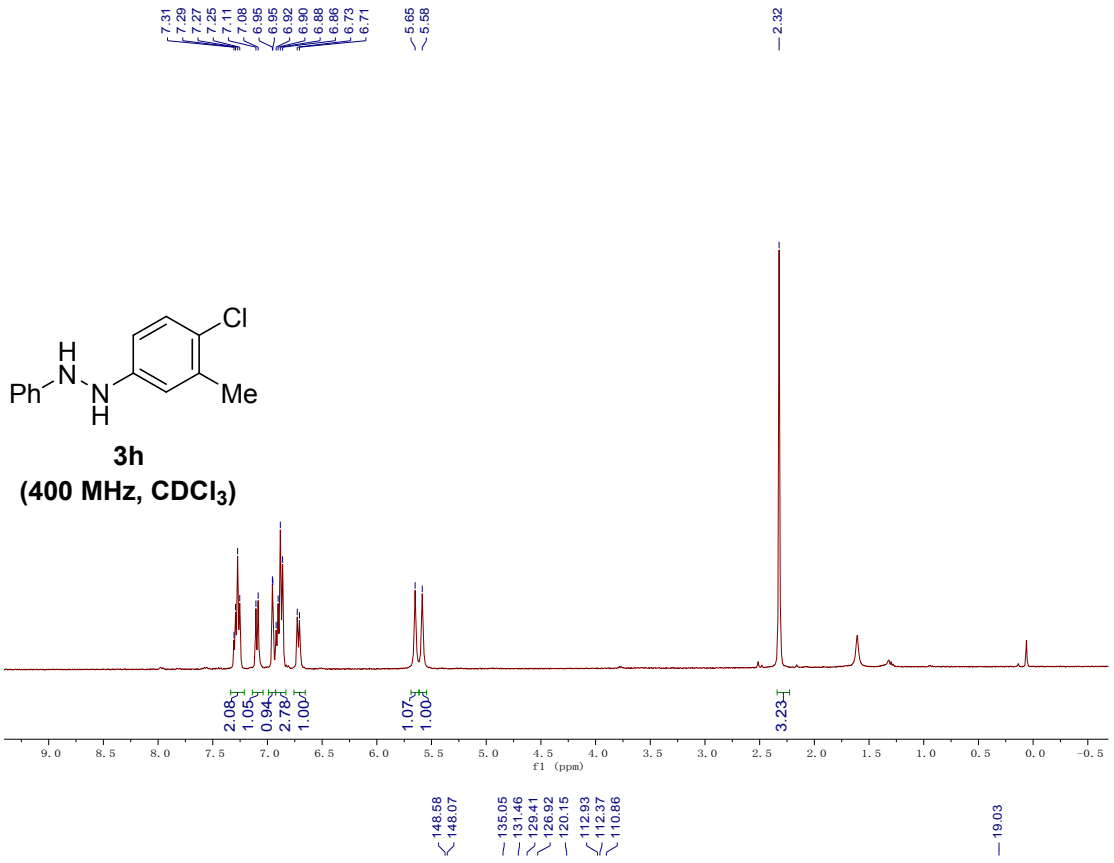


3f

(100 MHz, $CDCl_3$)

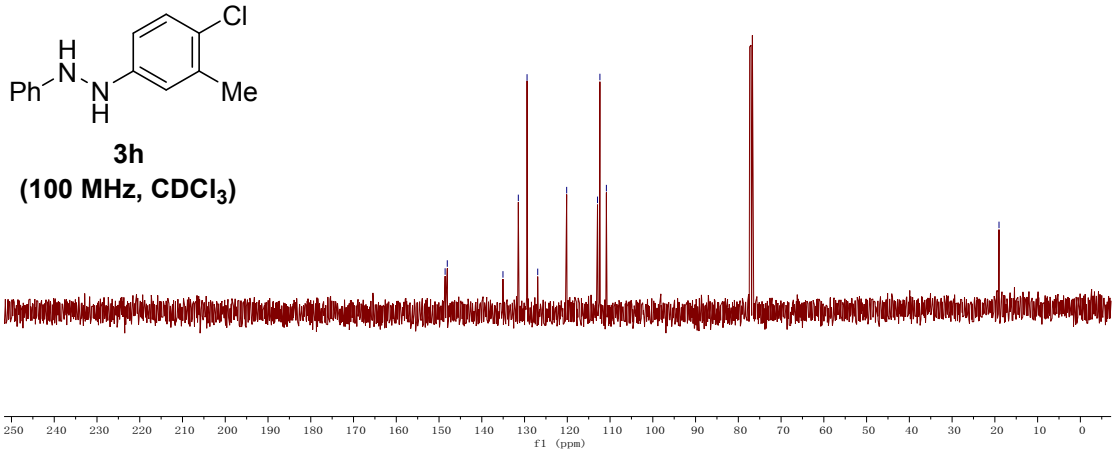

7.31
7.27
7.25
7.04
7.02
6.92
6.90
6.89
6.74
6.68
6.66
5.62
5.53
2.26
2.24
Me
Me
Ph
H
N
N
H
3g
(400 MHz, CDCl3)
2.31
1.08
3.12
1.05
1.00
1.06
1.09
3.51
3.39
f1 (ppm)


149.20
146.99
137.63
130.40
129.35
127.99
119.75
113.99
112.37
109.86
20.03
18.84
Me
Me
Ph
H
N
N
H
3g
(100 MHz, CDCl3)
f1 (ppm)



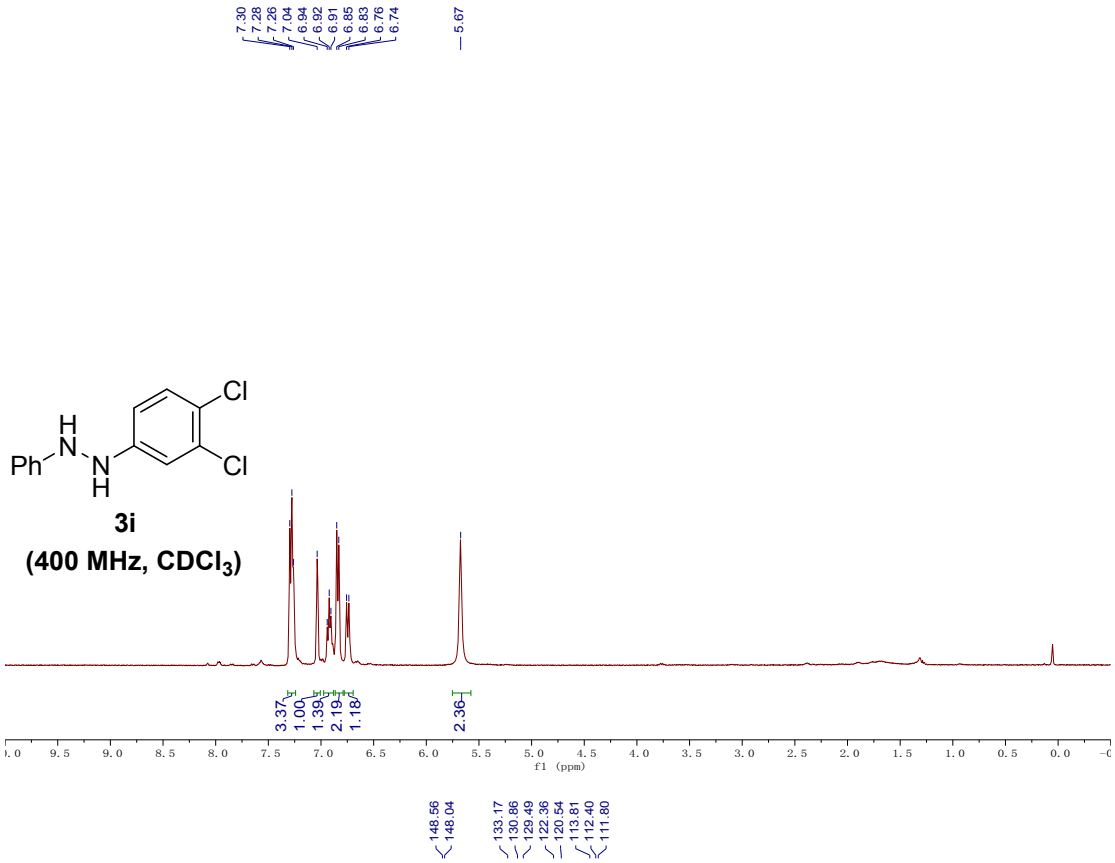
3h

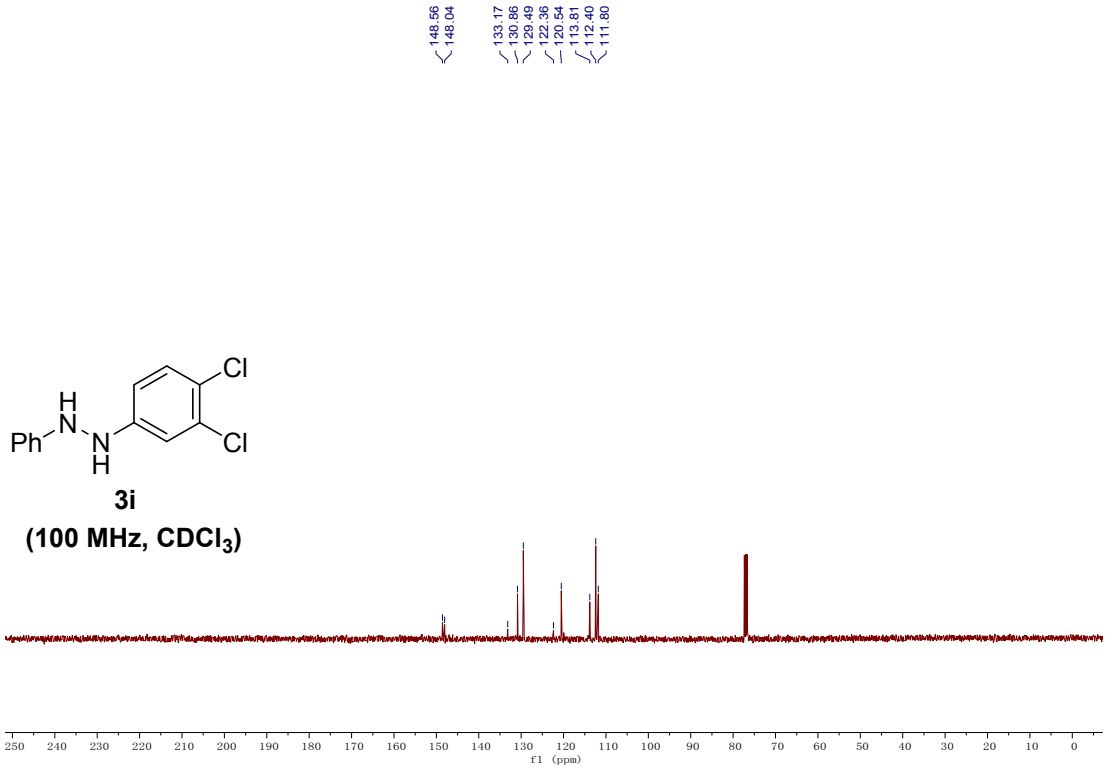
(400 MHz, $CDCl_3$)

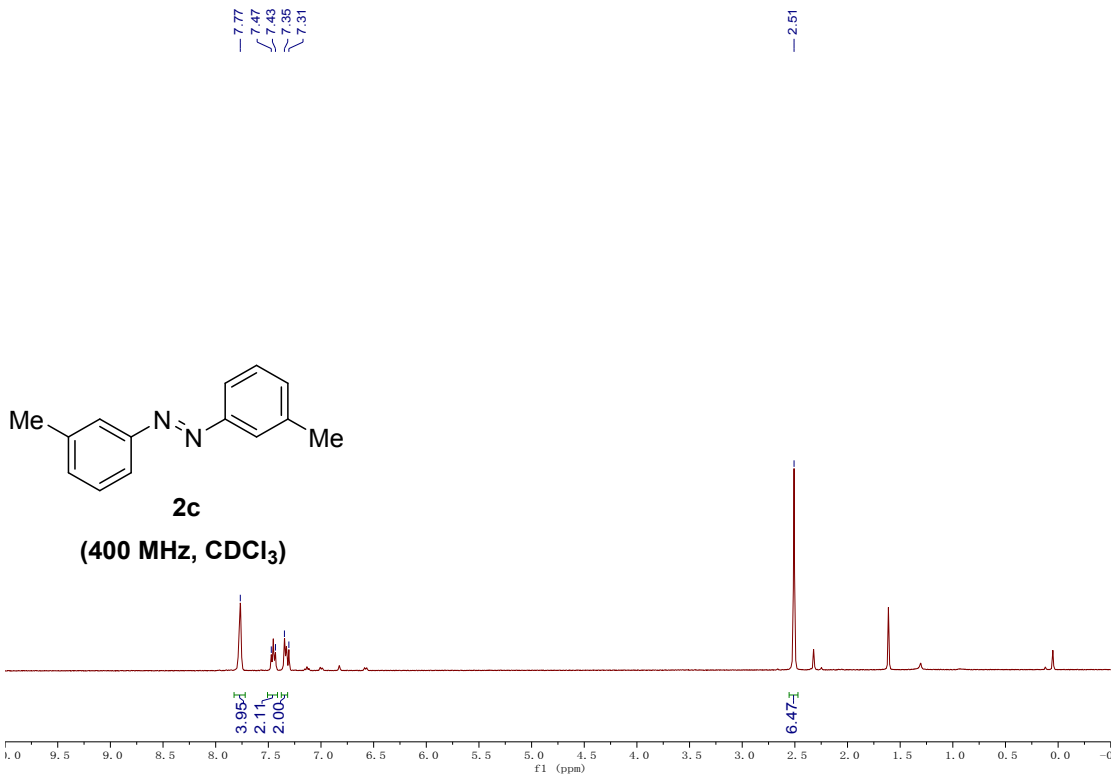


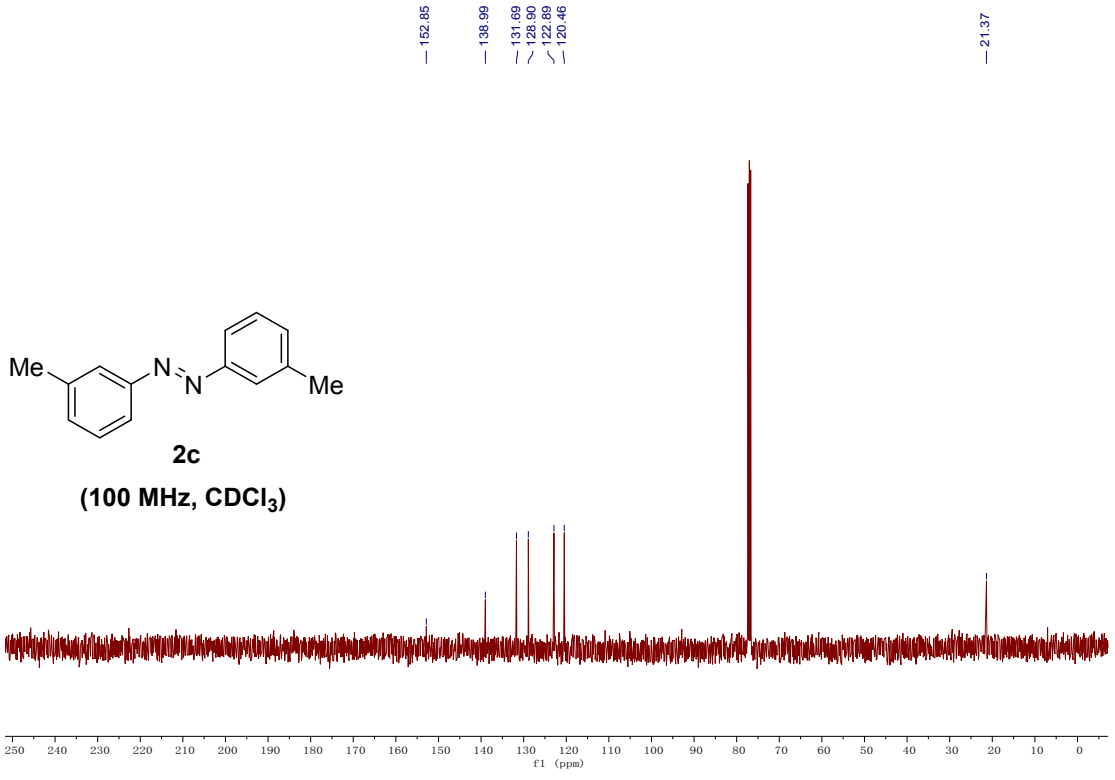
3h

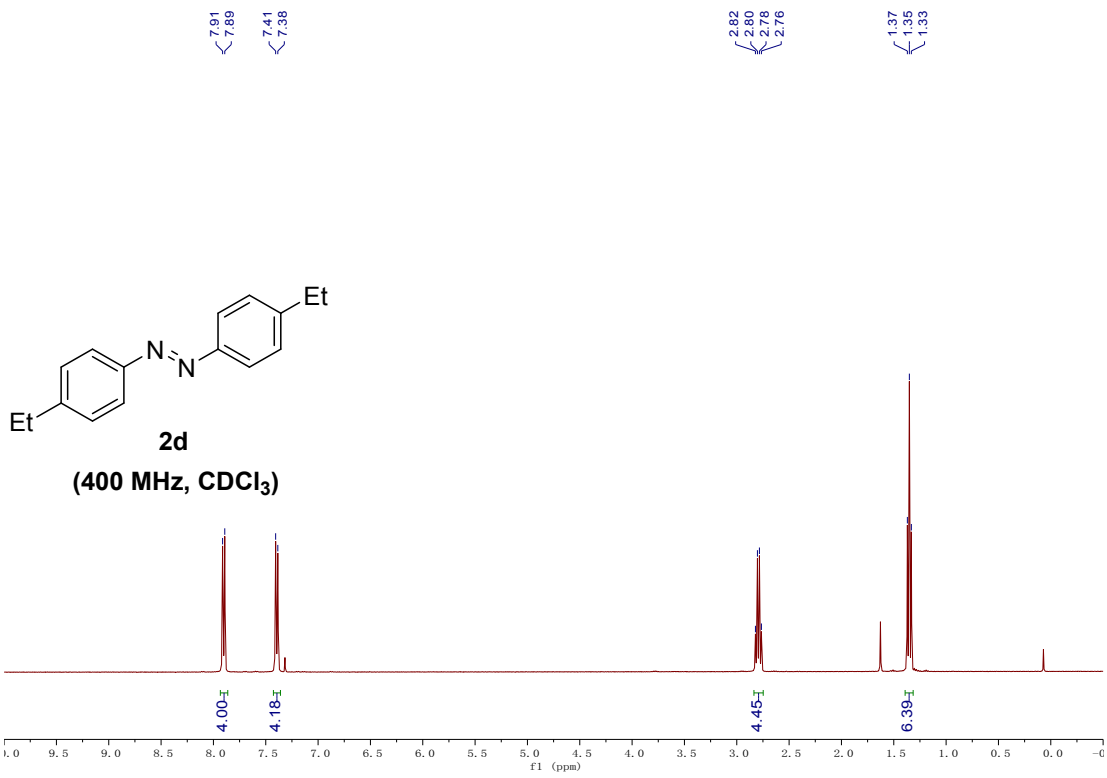
(100 MHz, $CDCl_3$)

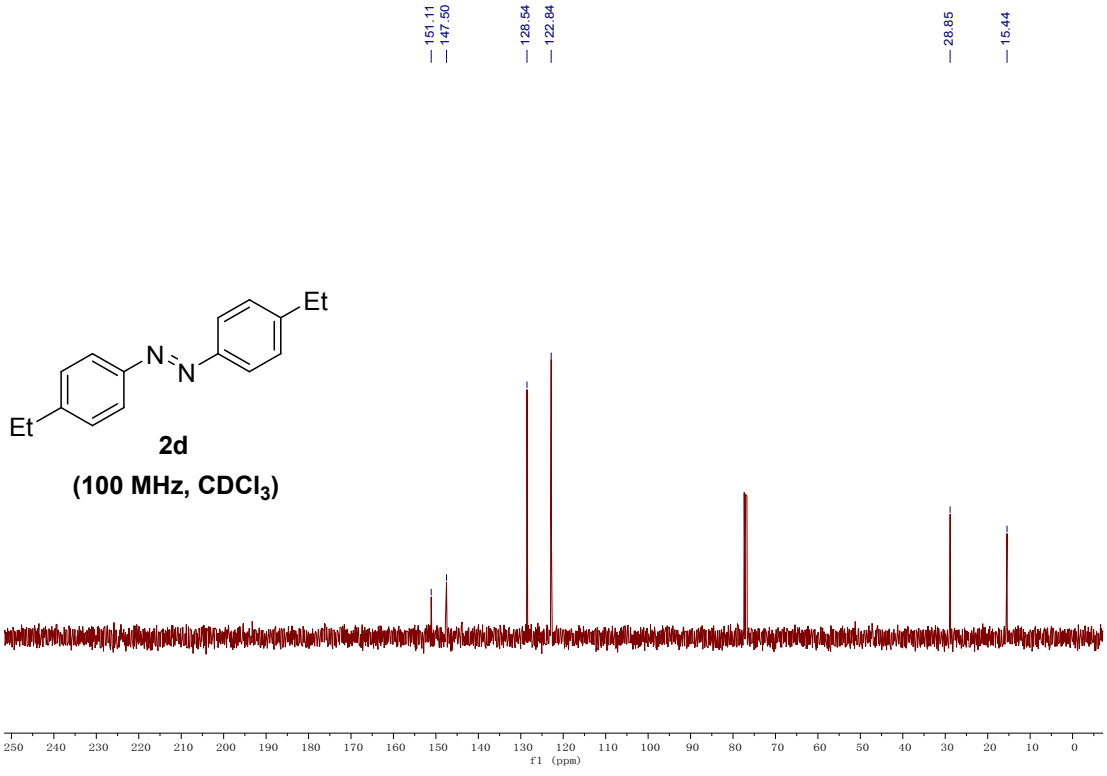

7.30
7.28
7.26
7.04
6.94
6.92
6.91
6.85
6.83
6.76
6.74
5.67
Cl
H
N
Ph
N
H
Cl
3i
(400 MHz, CDCl3)
3.37
1.00
1.39
2.19
1.18
2.36
f1 (ppm)

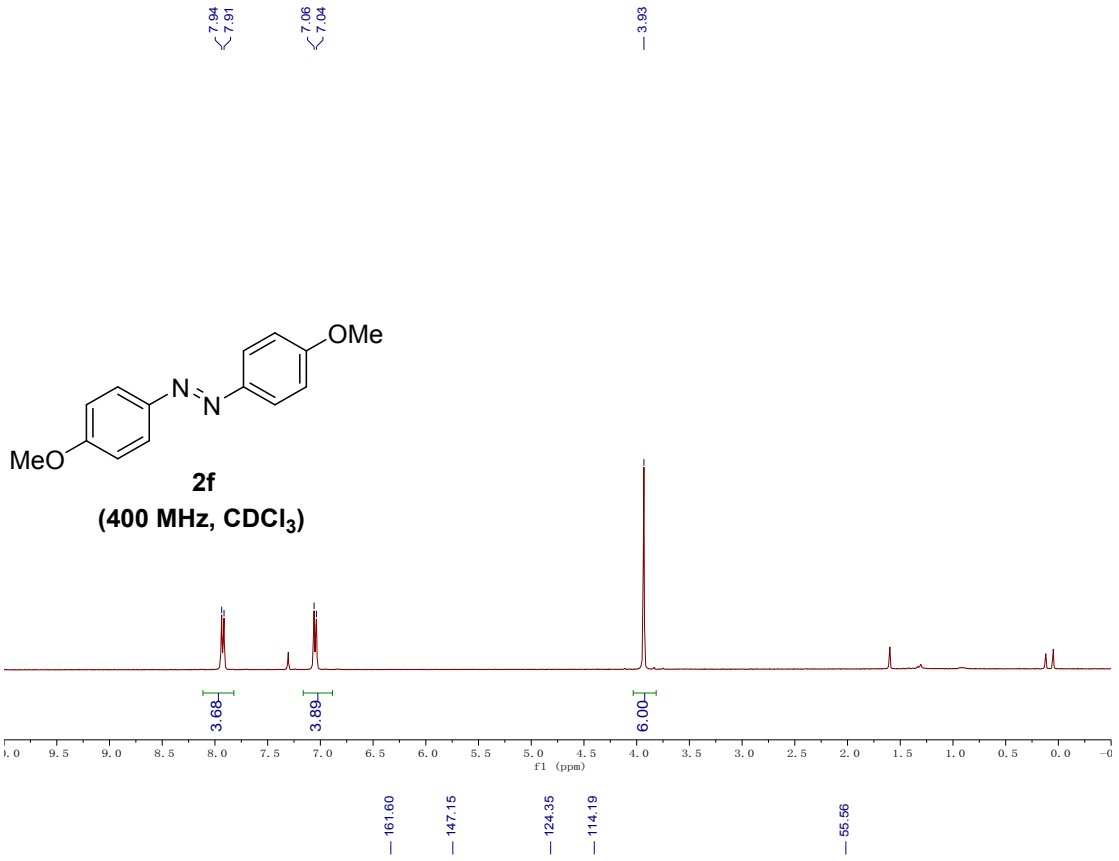

148.56
148.04
133.17
130.86
129.49
122.36
120.54
113.81
112.40
111.80
Cl
H
N
Ph
N
H
Cl
3i
(100 MHz, CDCl3)
f1 (ppm)

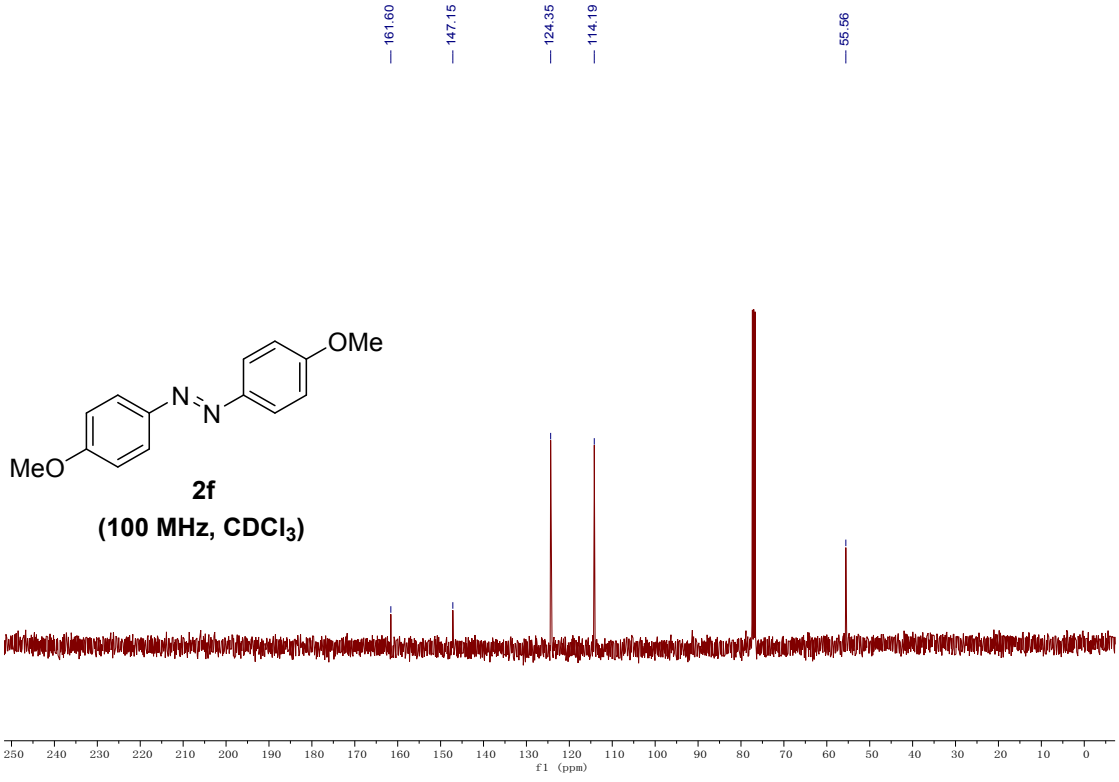

7.77
7.47
7.43
7.35
7.31
2.51
Me
N
N
Me
2c
(400 MHz, CDCl3)
3.95
2.11
2.00
6.47
f1 (ppm)

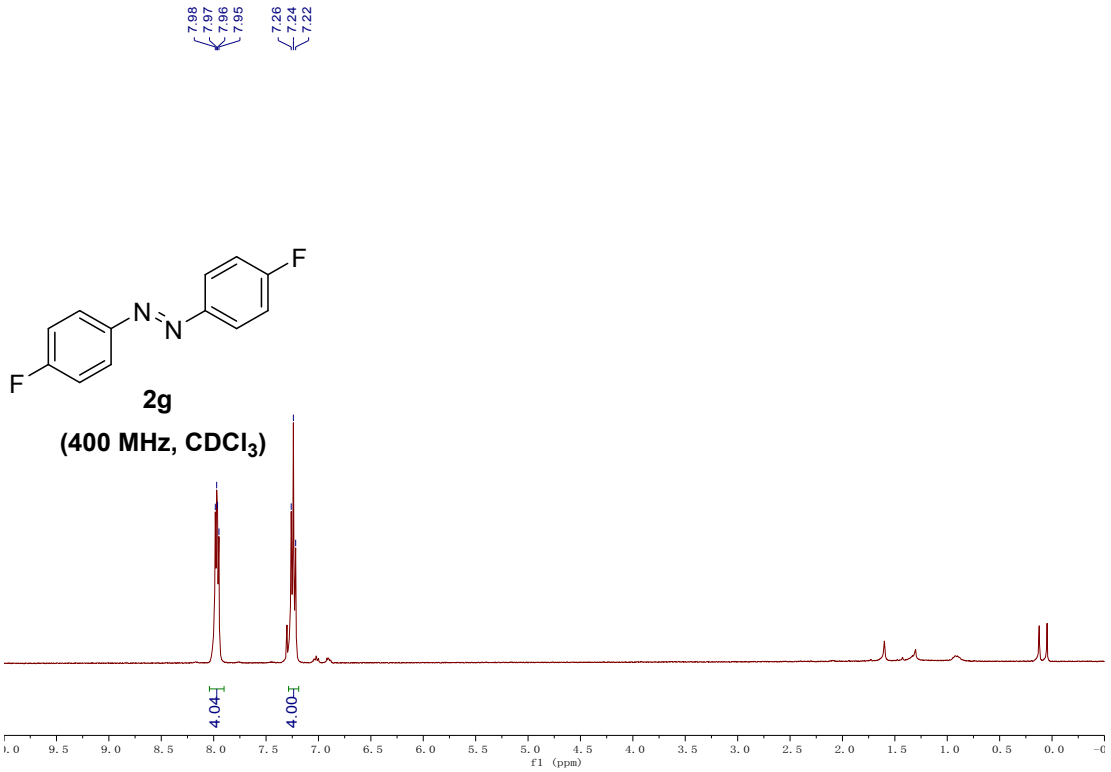

152.85
138.99
131.69
128.90
122.89
120.46
21.37
Me
N
N
Me
2c
(100 MHz, CDCl3)
f1 (ppm)

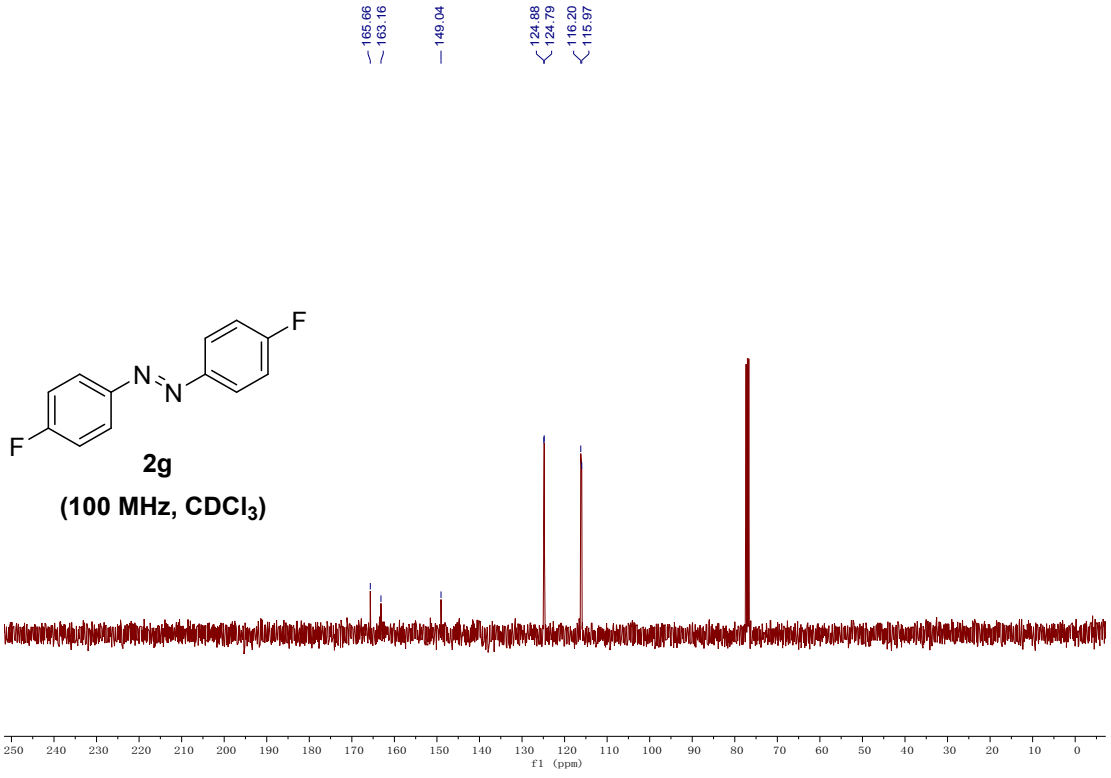

7.91
7.89
7.41
7.38
2.82
2.80
2.78
2.76
1.37
1.35
1.33
Et
N
N
Et
2d
(400 MHz, CDCl3)
4.00
4.18
4.45
6.39
f1 (ppm)

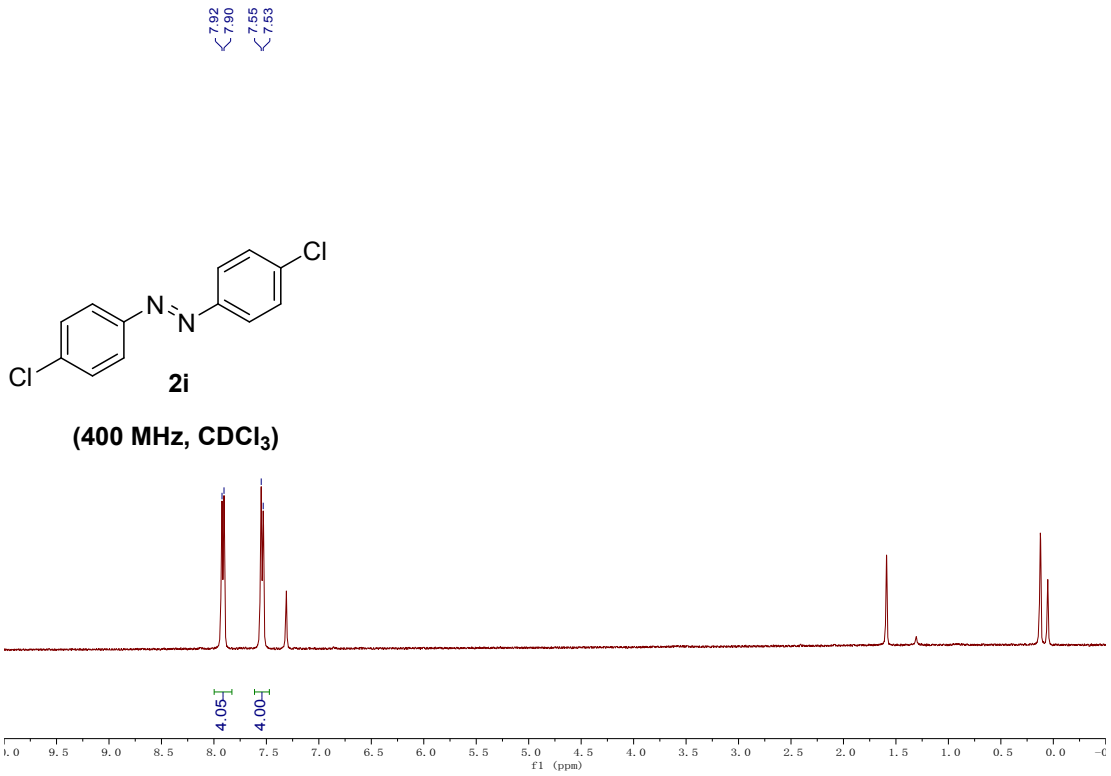

151.11
147.50
128.54
122.84
28.85
15.44
Et
N
N
Et
2d
(100 MHz, CDCl3)
f1 (ppm)

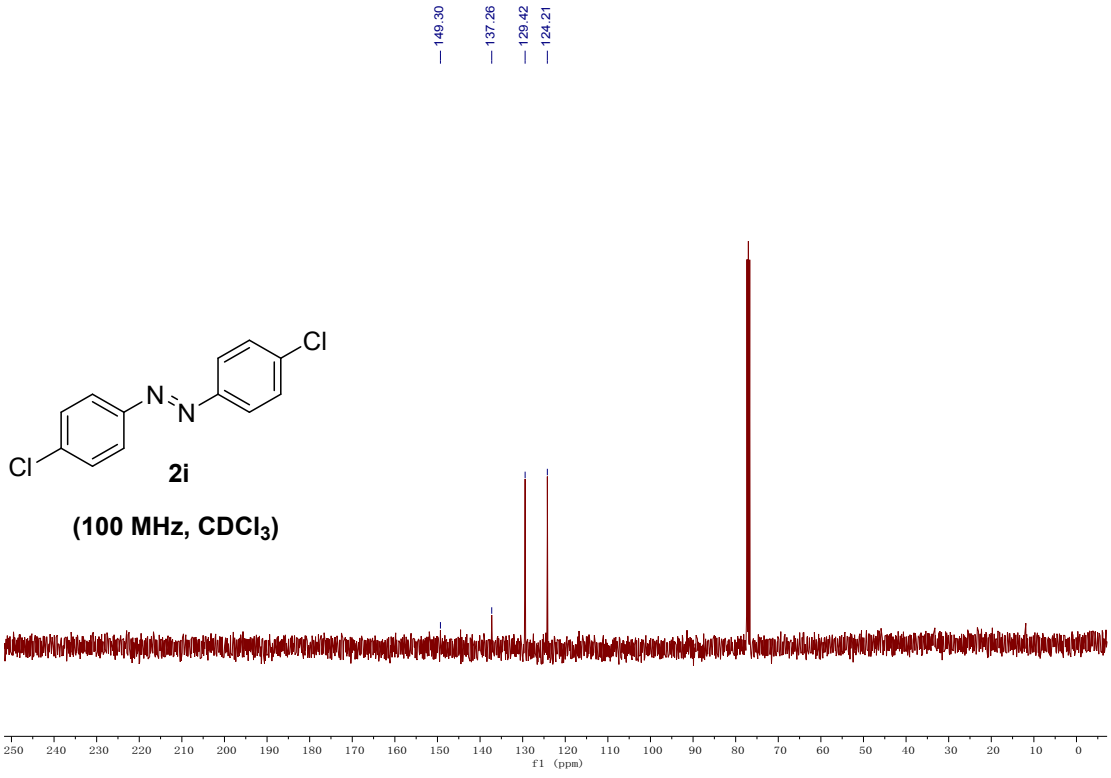

7.94
7.91
7.06
7.04
3.93
OMe
N
N
MeO
2f
(400 MHz, CDCl3)
3.68
3.89
6.00
f1 (ppm)

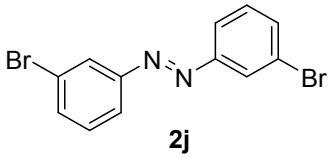

161.60
147.15
124.35
114.19
55.56
OMe
N
N
MeO
2f
(100 MHz, CDCl3)
f1 (ppm)


7.98
7.97
7.96
7.95
7.26
7.24
7.22
F
N
N
F
2g
(400 MHz, CDCl3)
4.04
4.00
f1 (ppm)


165.66
163.16
149.04
124.88
124.79
116.20
115.97
F
N
N
F
2g
(100 MHz, CDCl3)
f1 (ppm)

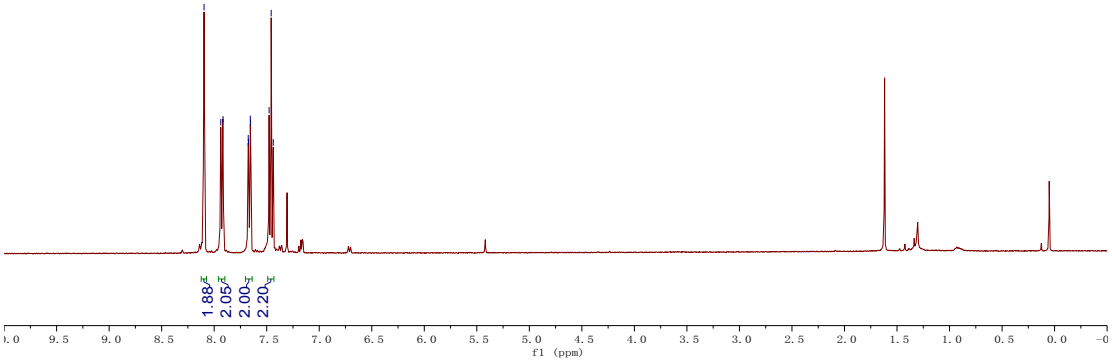

7.92
7.90
7.55
7.53
Cl
N
N
Cl
2i
(400 MHz, CDCl3)
4.05
4.00
f1 (ppm)

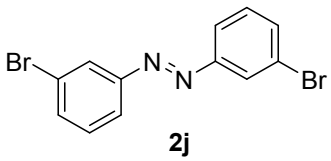

149.30
137.26
129.42
124.21
Cl
N
N
Cl
2i
(100 MHz, CDCl3)
f1 (ppm)



2j

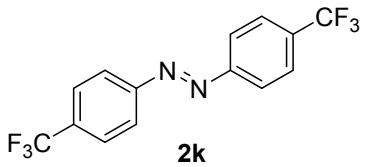
(400 MHz, $CDCl_3$)





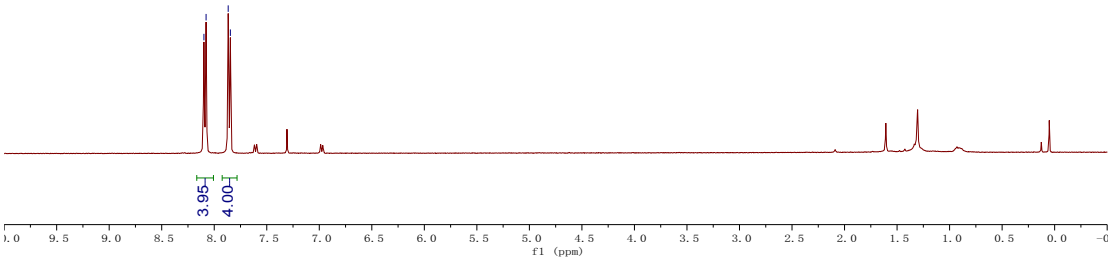
2j

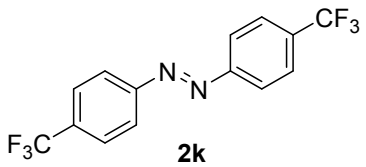
(100 MHz, $CDCl_3$)



2k

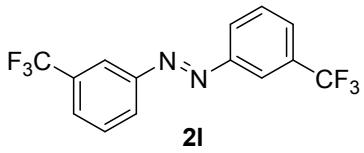
(400 MHz, $CDCl_3$)





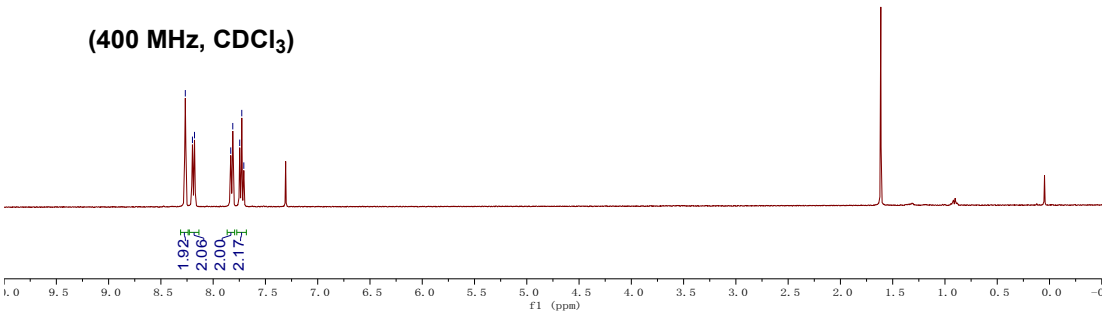
2k

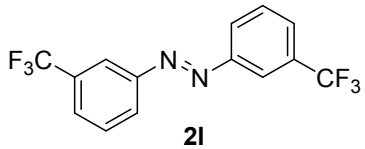
(100 MHz, $CDCl_3$)



2l

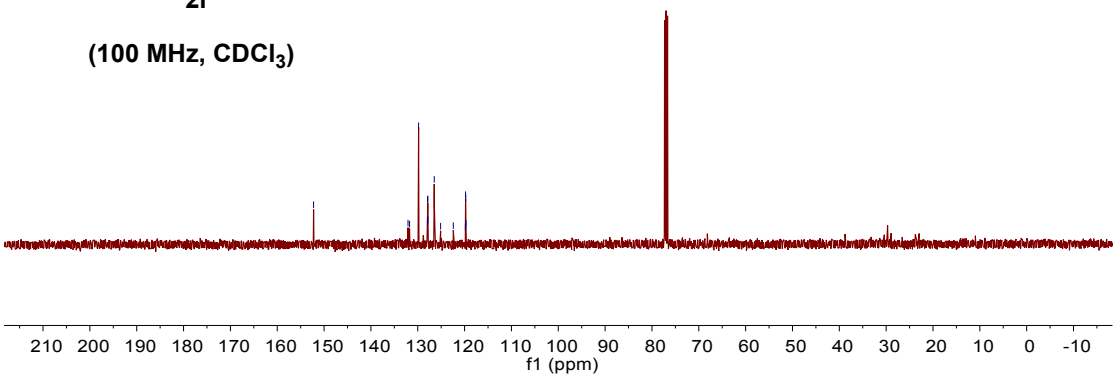
(400 MHz, $CDCl_3$)

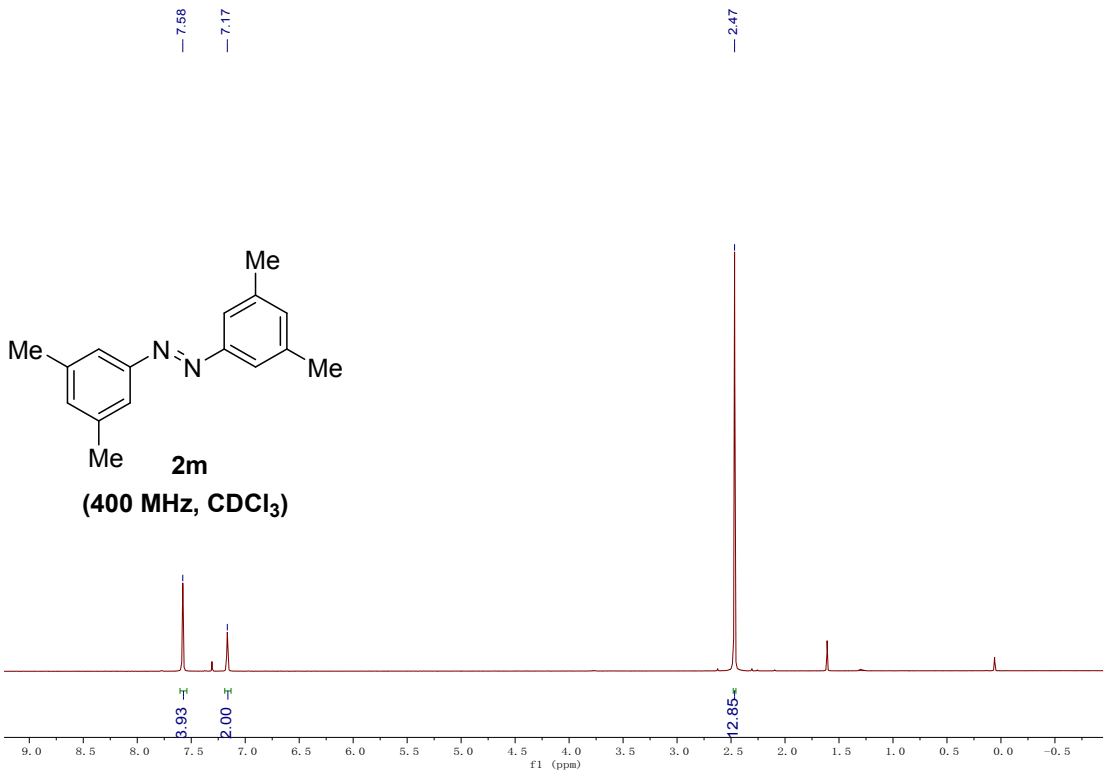


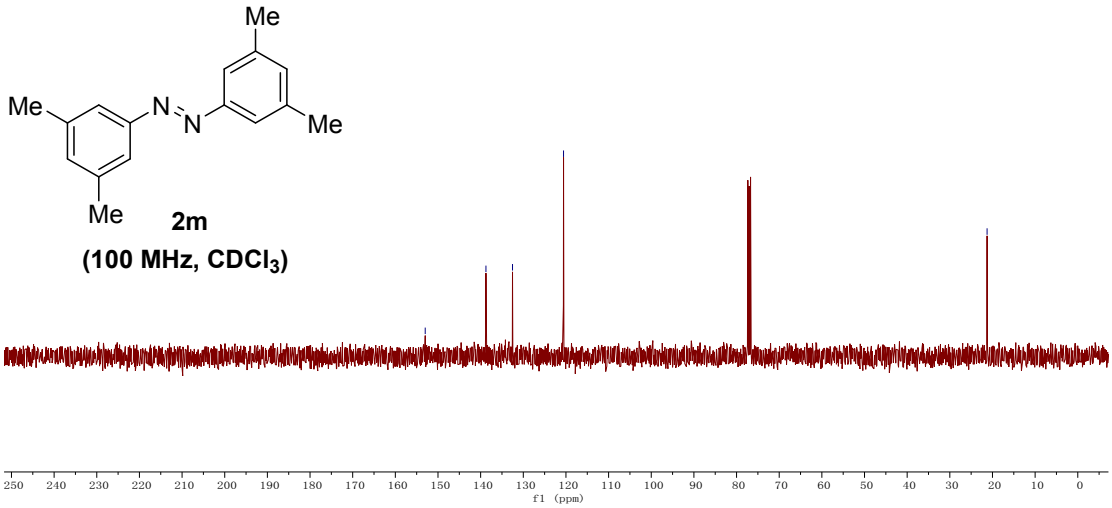


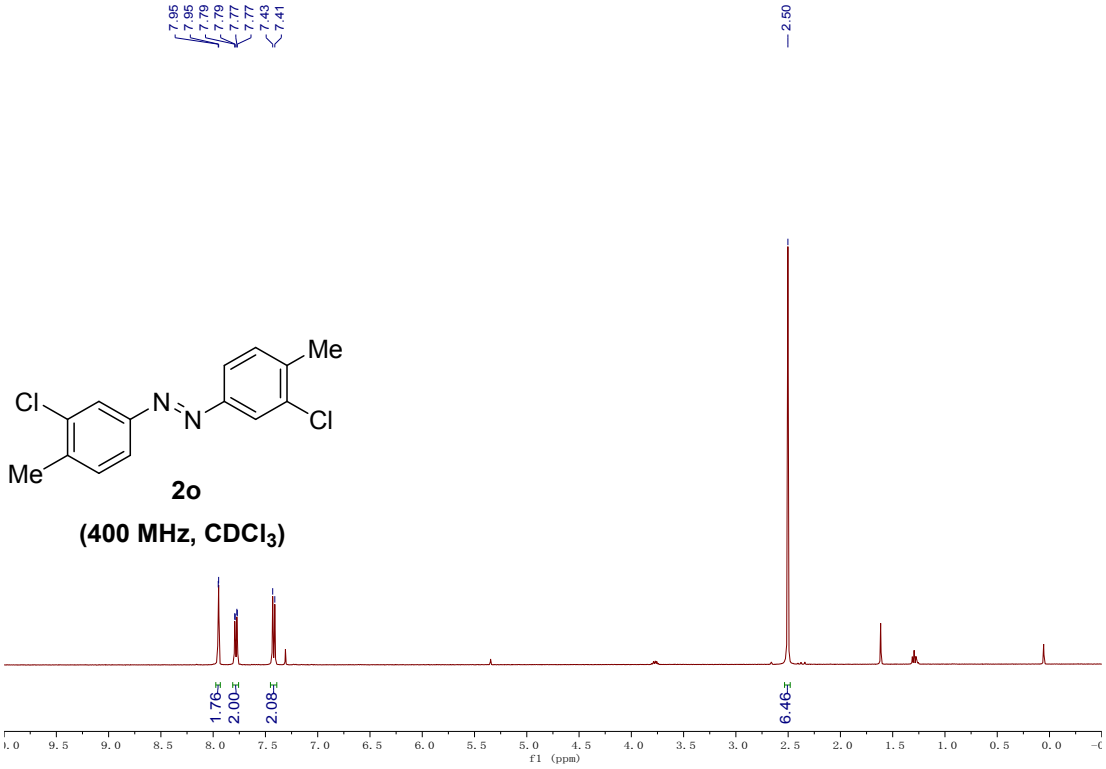
2l

(100 MHz, $CDCl_3$)



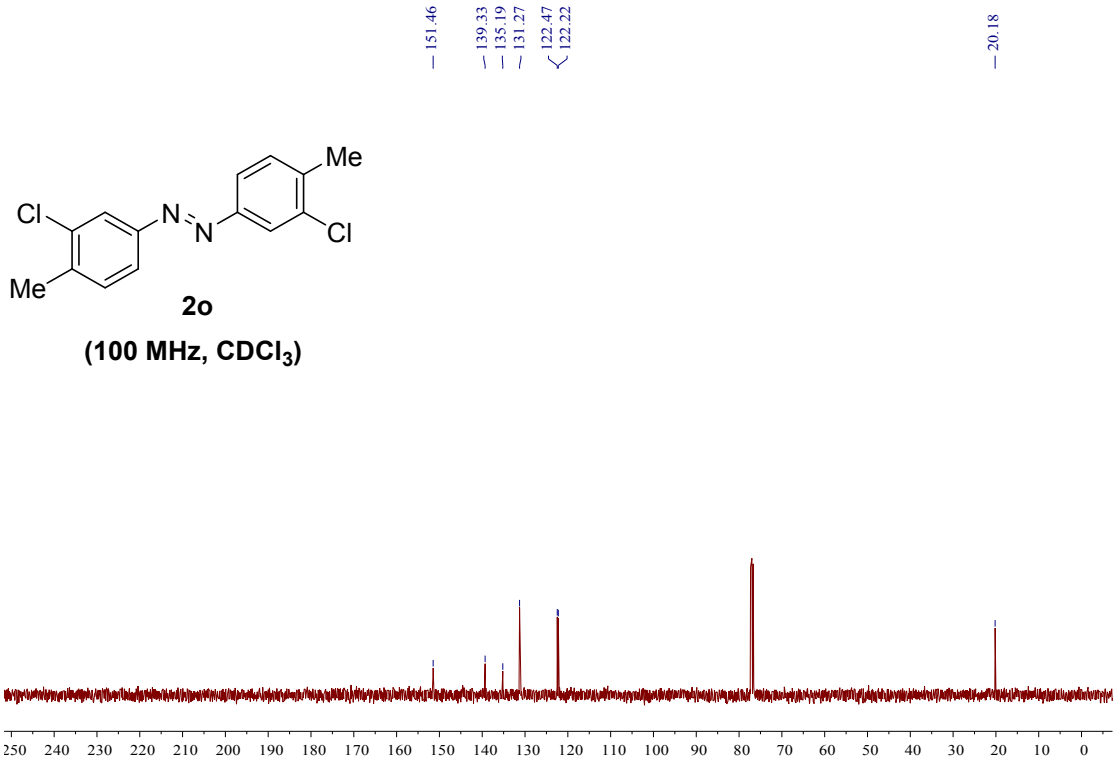

7.58
7.17
2.47
Me
Me
N
N
Me
Me
2m
(400 MHz, CDCl3)
3.93
2.00
12.85
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


152.99
138.76
132.53
120.57
21.26
Me
Me
N
N
Me
Me
2m
(100 MHz, CDCl3)
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



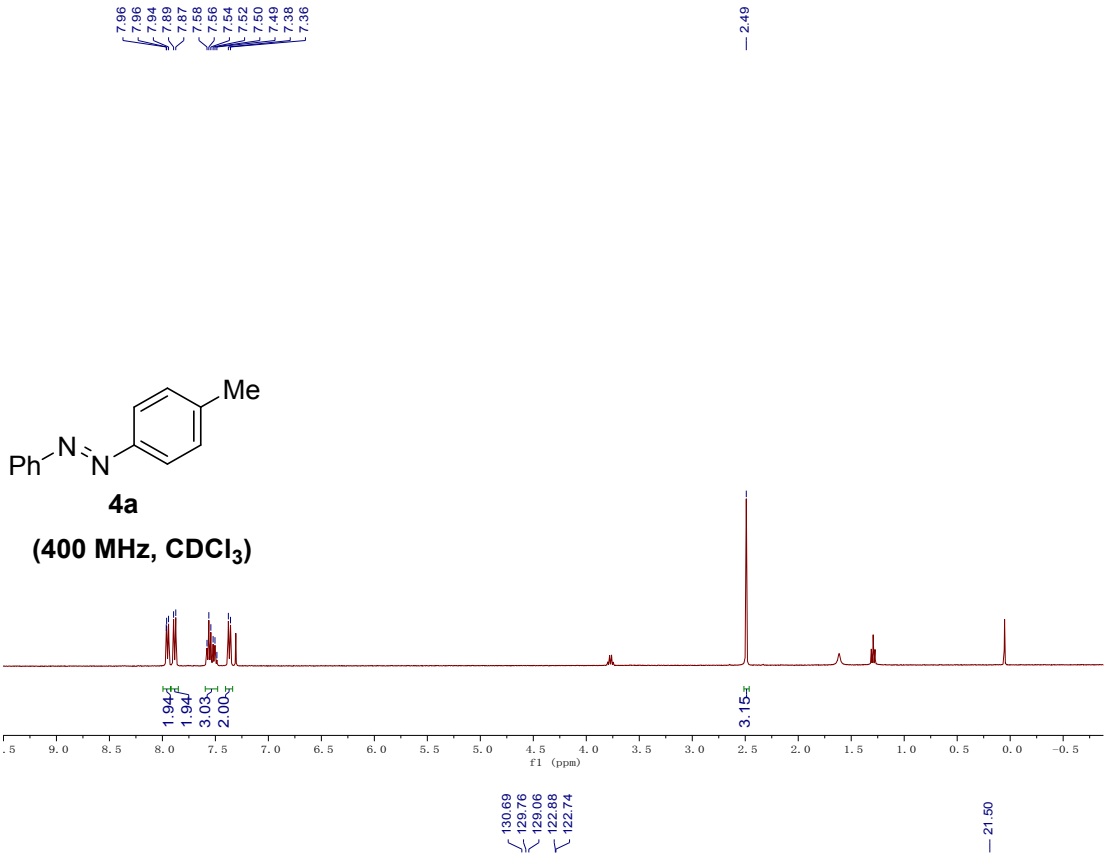
2o

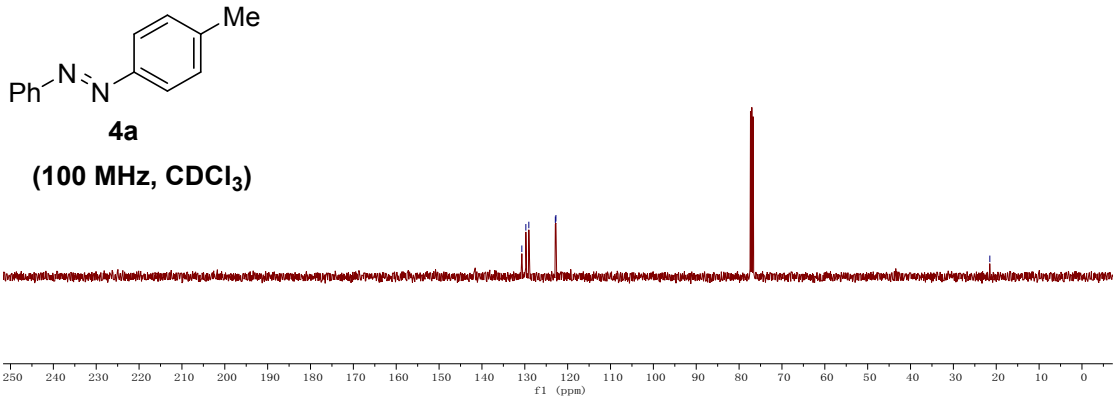
(400 MHz, $CDCl_3$)

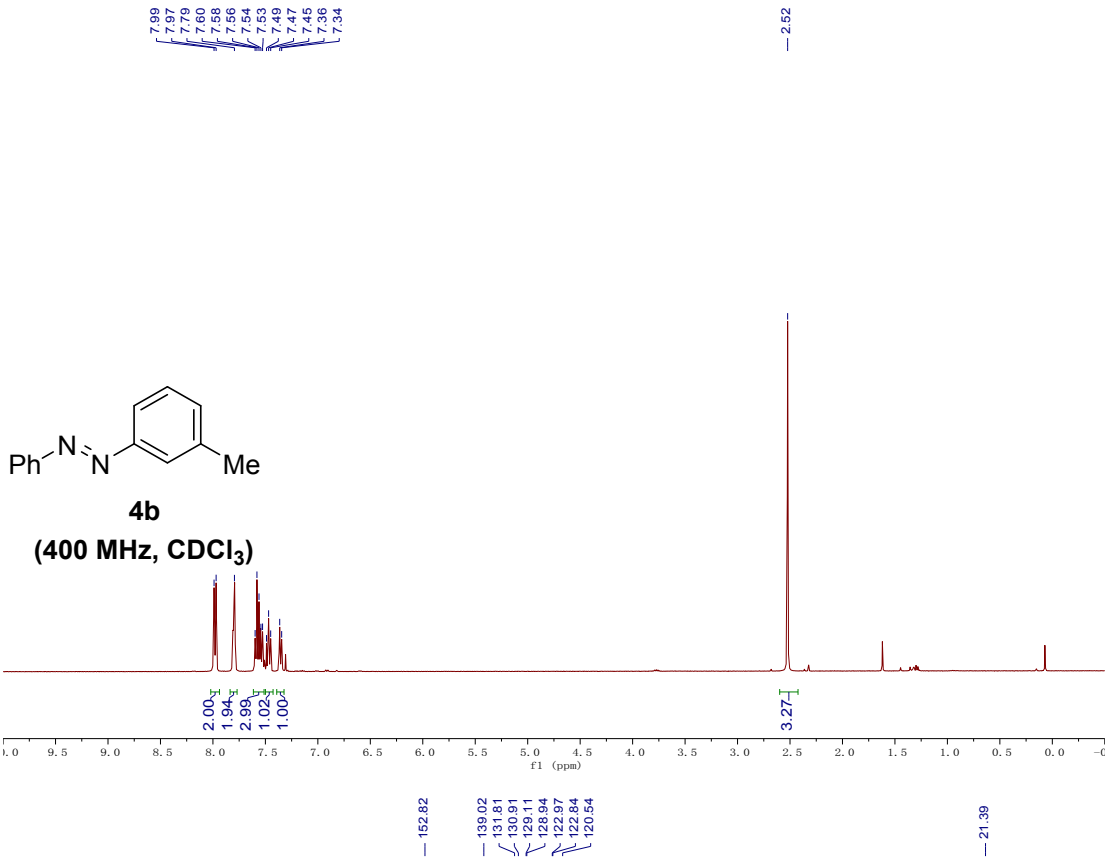


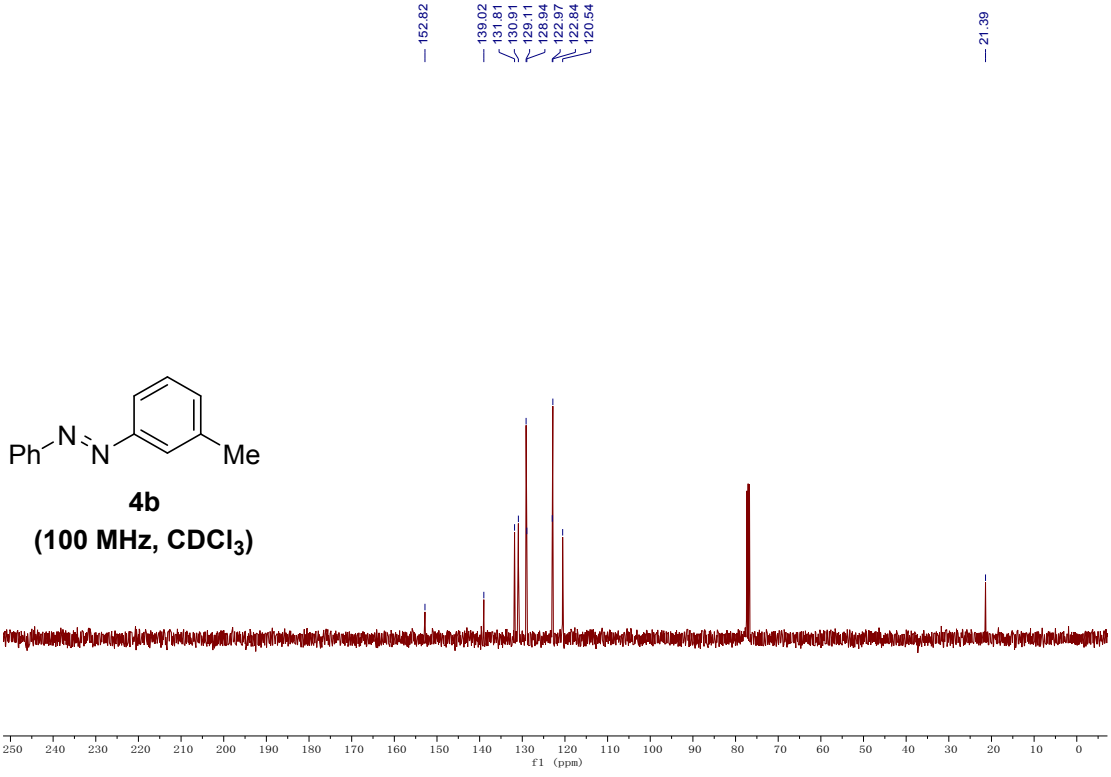
2o

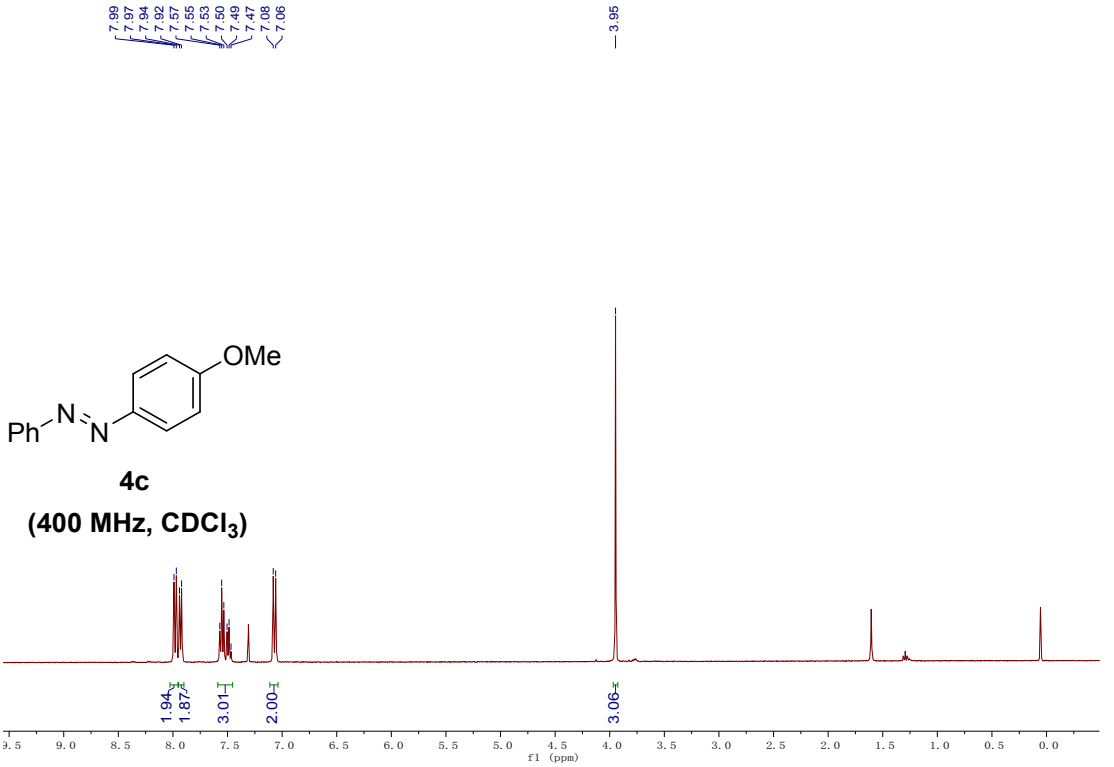
(100 MHz, $CDCl_3$)


7.96
7.96
7.94
7.89
7.87
7.58
7.56
7.54
7.52
7.50
7.49
7.38
7.36
2.49
Me
Ph
N
N
4a
(400 MHz, CDCl3)
1.94
1.94
3.03
2.00
3.15
f1 (ppm)
130.69
129.76
129.06
122.88
122.74
21.50


Me
Ph
N
N
4a
(100 MHz, CDCl3)
f1 (ppm)

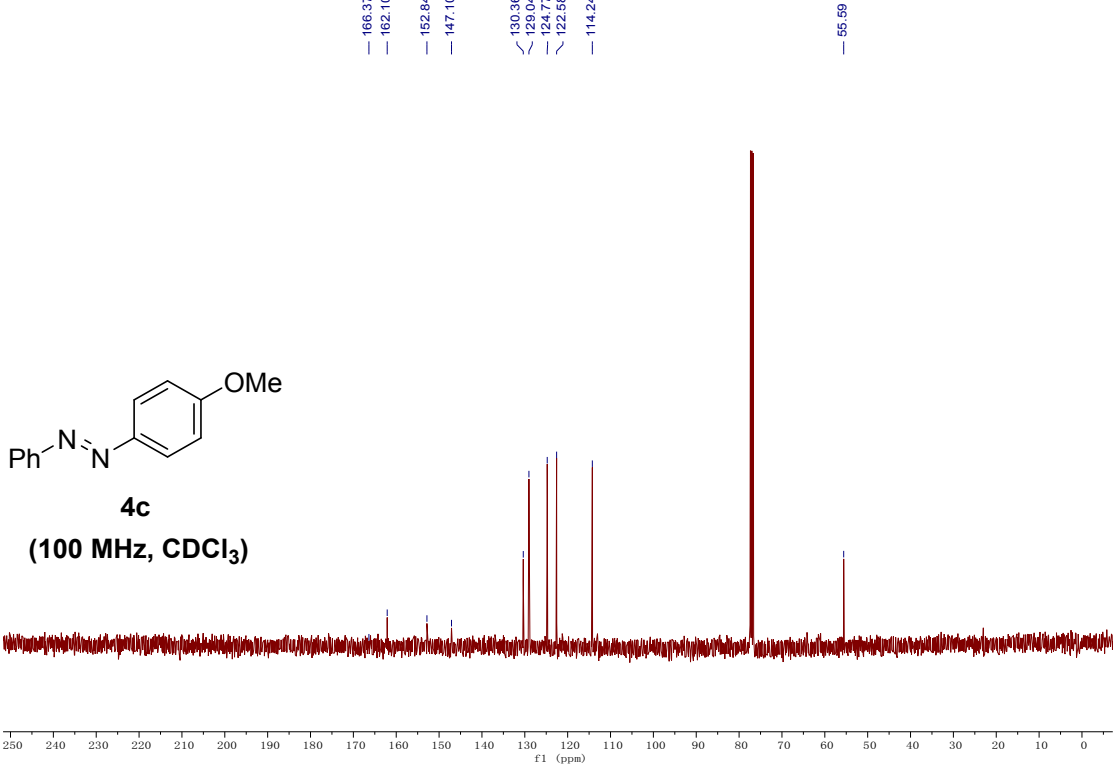

7.99
7.97
7.79
7.60
7.58
7.56
7.54
7.53
7.49
7.47
7.45
7.36
7.34
2.52
Ph
N
N
Me
4b
(400 MHz, CDCl3)
2.00
1.94
2.99
1.02
1.00
3.27
f1 (ppm)


152.82
139.02
131.81
130.91
129.11
128.94
122.97
122.84
120.54
21.39
Ph
N
N
Me
4b
(100 MHz, CDCl3)
f1 (ppm)



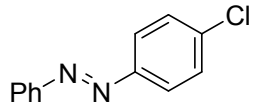
4c

(400 MHz, $CDCl_3$)



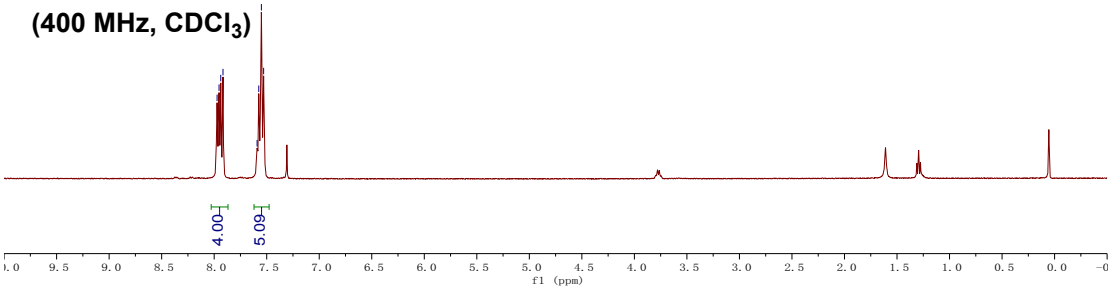
4c

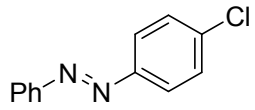
(100 MHz, $CDCl_3$)



4f

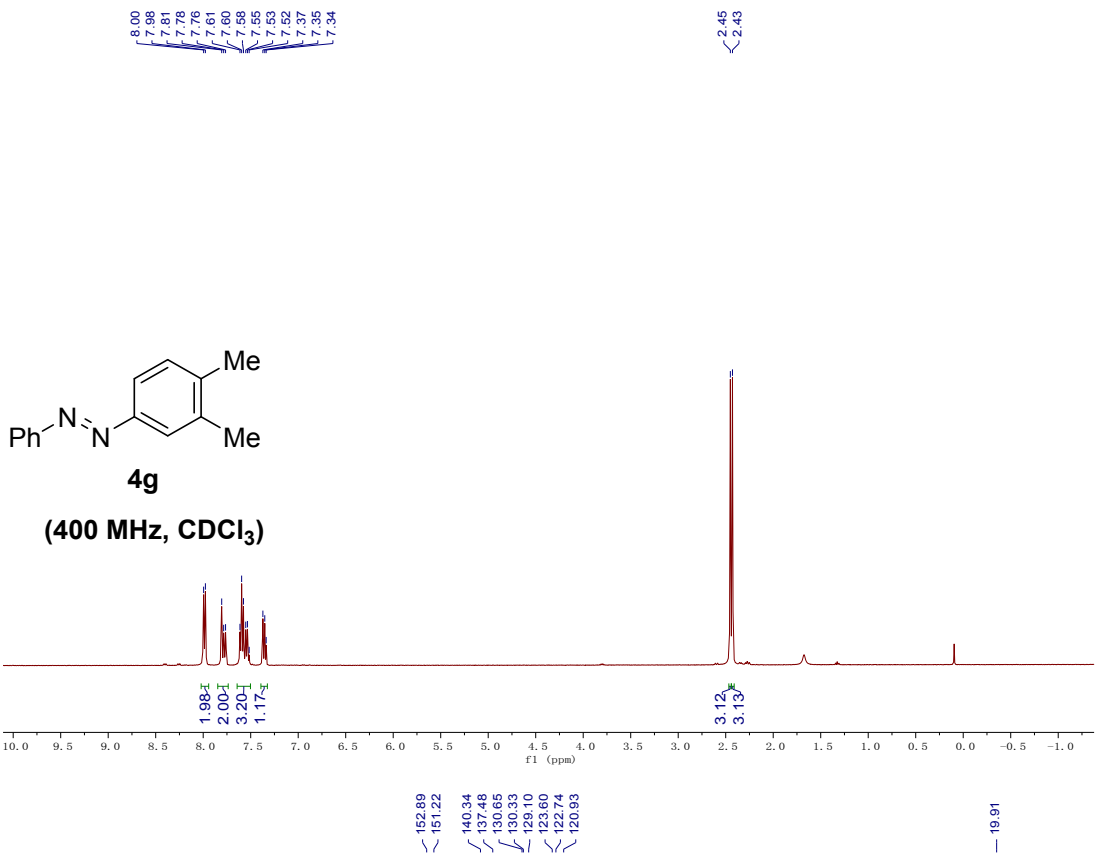
(400 MHz, $CDCl_3$)

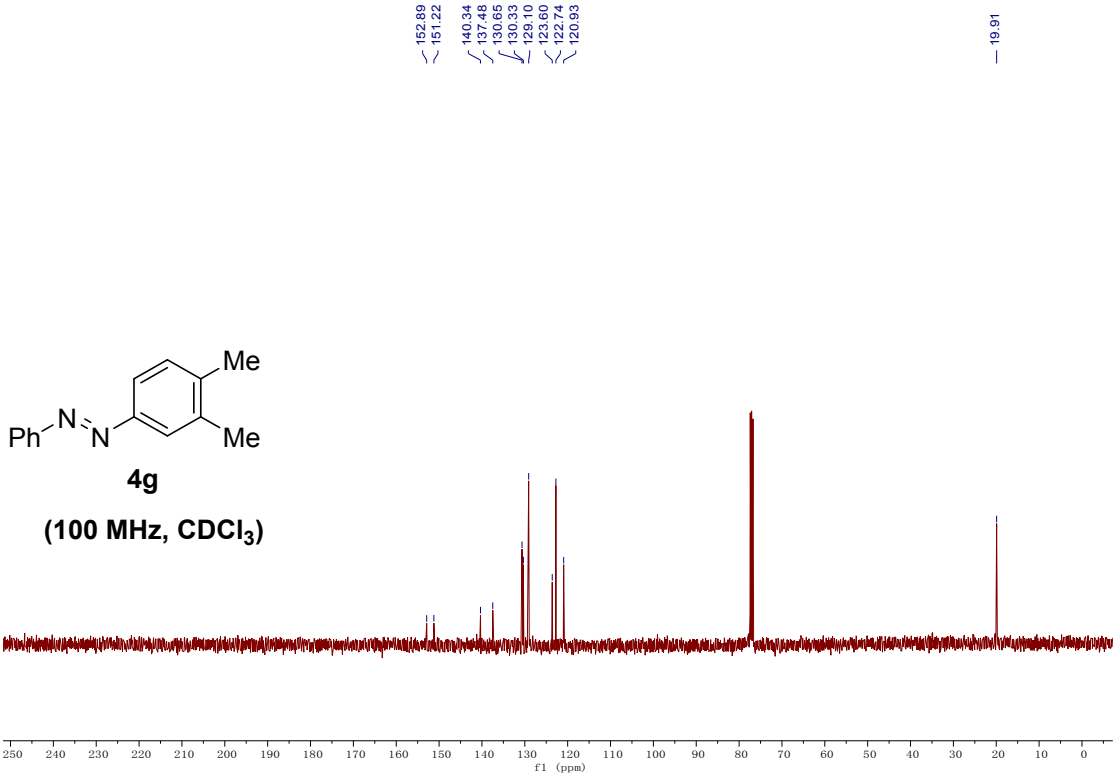


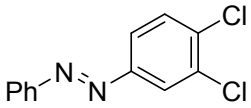


4f

(100 MHz, $CDCl_3$)

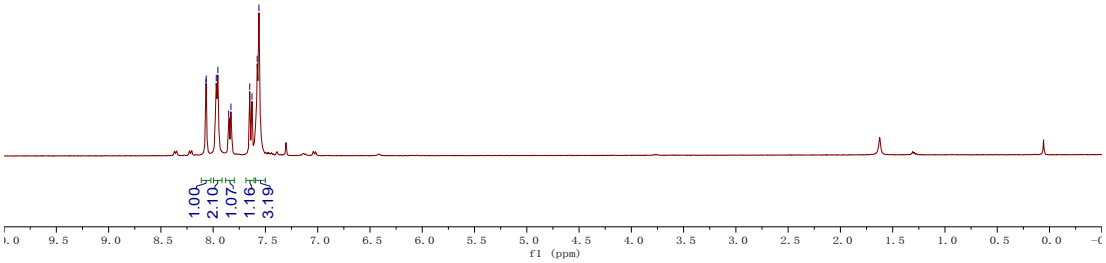

8.00
7.98
7.81
7.78
7.76
7.61
7.60
7.58
7.55
7.53
7.52
7.37
7.35
7.34
2.45
2.43
Me
Me
Ph
N
N
4g
(400 MHz, CDCl3)
1.98
2.00
3.20
1.17
3.12
3.13
f1 (ppm)

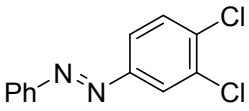

152.89
151.22
140.34
137.48
130.65
130.33
129.10
123.60
122.74
120.93
19.91
Me
Me
Ph
N
N
4g
(100 MHz, CDCl3)
f1 (ppm)



4i

(400 MHz, $CDCl_3$)





4i

(100 MHz, $CDCl_3$)