Supporting Information for

Oxidative Dehydrogenation of Hydrazines and Diarylamines Using a Polyoxomolybdate-based Iron Catalyst

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1. Experimental techniques

All chemicals were obtained from Energy Chemical, or Alfa Aesar and used as received unless indicated otherwise. Reactions were monitored by thin layer chromatography on precoated aluminium-backed plates (Merck Kieselgel 60 with fluorescent indicator UV254). Flash column chromatography was performed with silica gel (200-300 mesh), applying head pressure by means of low pressure argon line (0.1-0.3 atm). Brine denotes a saturated aq. solution of NH_4Cl. ^1H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ or in the solvent indicated using Varian 400M Hz or Bruker 600M Hz pectrometers. Data are expressed as chemical shifts in part per million (ppm) relative to residual chloroform and $CDCl_3$ (^1H δ=7.26, ^{13}C δ=77.2, respectively; likewise for other solvents where applicable) as internal standard on the δ scale. ESI mass spectra were obtained using a Bruker Daltonics MicroTof and the instrument was calibrated using sodium formicates clusters.

2. Synthesis of the $FeMo_6$ catalyst [1]

A mixture of $[N(C_4H_9)_4]_4[Mo_8O_{26}]$ (2.16 g, 1 mmol), $[Fe(acac)_3]$ (530 mg, 1.5 mmol, acac=acetylacetonate) and $(HOCH_2)_3CNH_2$ (370 mg, 3 mmol) in 40 mL of acetonitrile was refluxed for 24 h. The red suspension was cooled to room temperature, and a yellow-orange solid was removed by filtration. A microcrystalline solid were grown by slow ether diffusion into an acetonitrile solution. Yield: 0.97 g (48%). IR: ν_{max} =2964 (ν CH, s), 2937 (ν CH, s), 2873 (ν CH, s), 1669 (w), 1486 (δ CH, m), 1386 (δ CH, w), 1154 (w), 1129 (w), 1042 (ν CO, s), 937 (ν Mo O, vs), 922 (ν MoO, vs), 902 (ν MoO, vs), 808 (w), 664 (ν MoOMo, br., vs), 613 (w), 563 (m), 528 (w),487 (w), 452 (w), 408 (w)cm^{-1}. Spectral data were in accordance with the literature.[1]

Figure S1. Photographs of the $FeMo_6$ catalyst

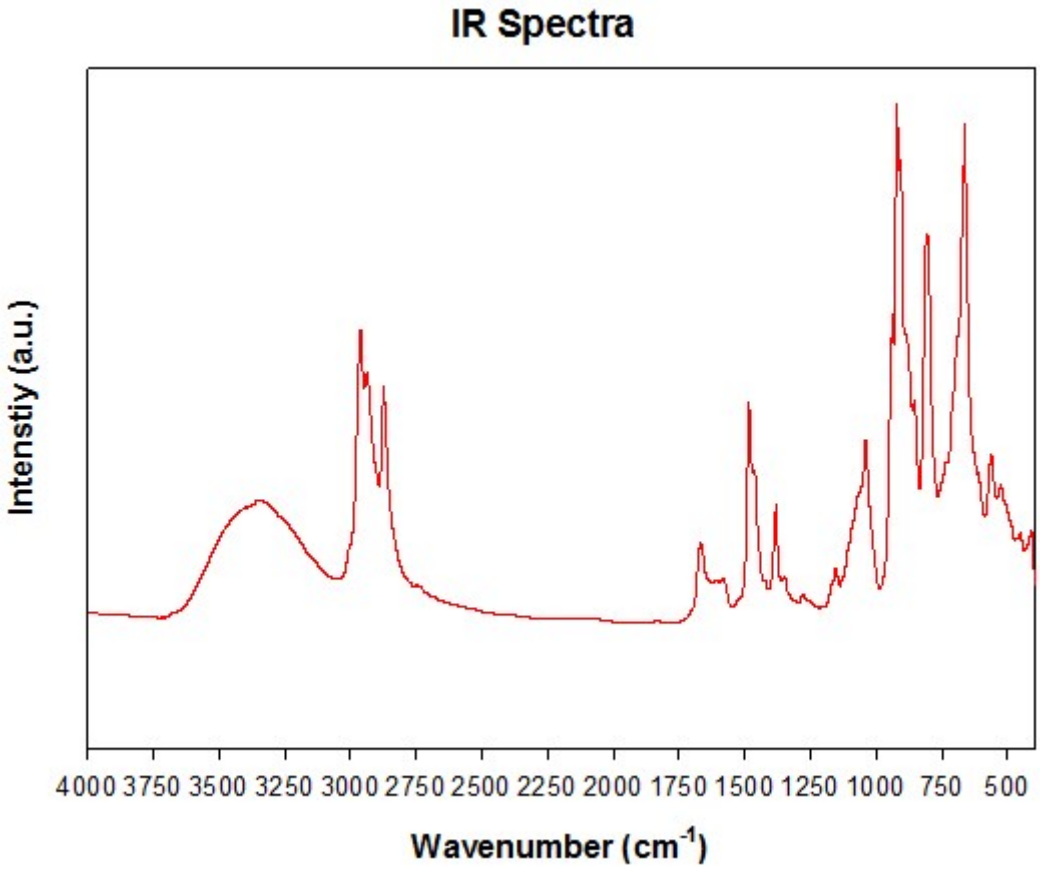


Figure S2. IR spectrum of the $FeMo_6$ catalyst

3. Cyclic voltammogram of the $FeMo_6$ catalyst

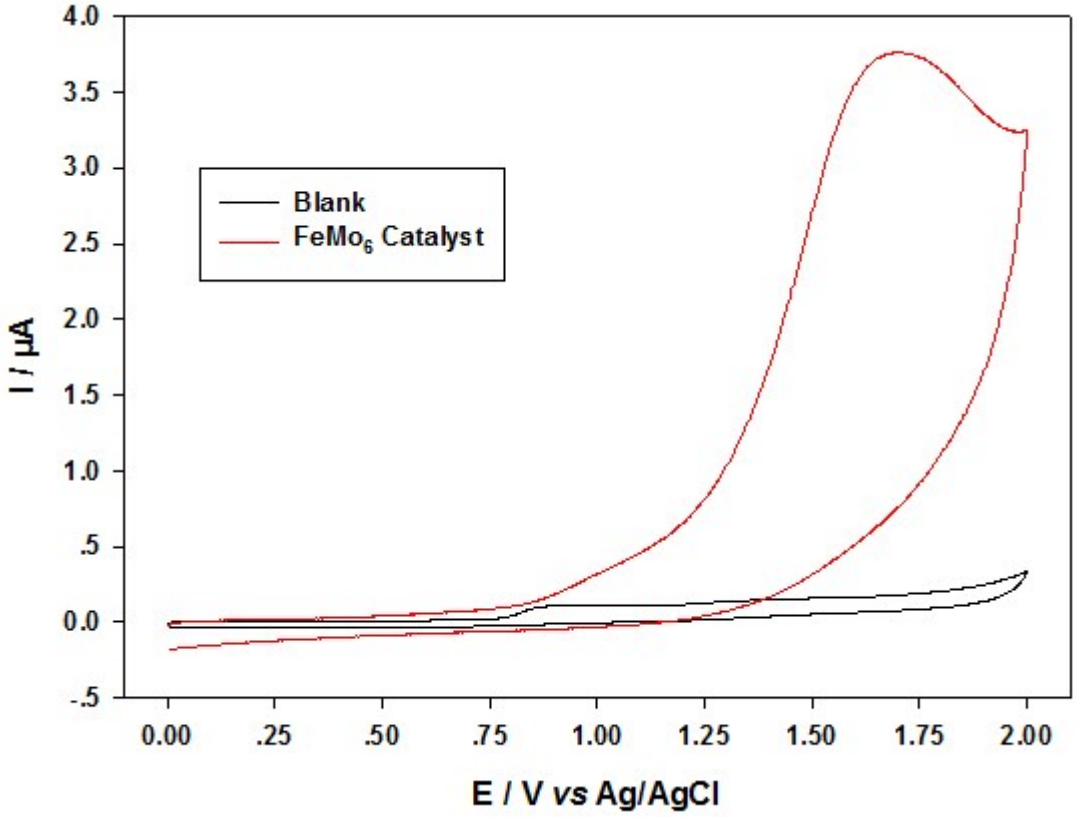


Figure S3. CVs of the $FeMo_6$ catalyst

Cyclic voltammogram of conditions: 2 mM $FeMo_6$ in an electrolyte of Bu_4NBF_4 (0.1 M) in MeCN; Working electrode, glassy carbon; Counter Electrode, glassy carbon; Reference Electrode, Ag/AgCl in saturated KCl in EtOH; scan rate, 100 mV/s. E_{ox} = 1.69 V.

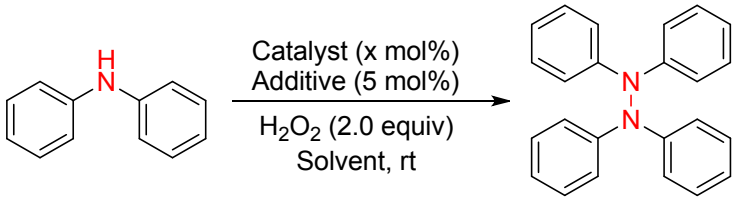
4. The pH value of the reaction solution

Table S1. The pH value of the reaction solution[a]

Entry	Mixture	pH
1	$FeMo_6$ (0.01mol)+$NaHSO_3$(0.1mol)	5.83
2	$[N(C_4H_9)_4]_4[Mo_8O_{26}]$ (0.01mol) + $NaHSO_3$(0.1mol)	5.35
3	$Fe(acac)_3$(0.01mol) + $NaHSO_3$(0.1mol)	5.61
[a] The solvent is H_2O (2mL)/ EtOH(0.4 mL).		

5. Optimization of the reaction conditions for oxidative dehydrogenation of diarylamine

Table S2. Optimization of Conditions[a]



Entry	Solvent	Catalyst	Additive	Time	Yield(%)[b]
1	H_2O/EtOH(5:1)	$FeMo_6$ (0.5 mol%)	$NaHSO_3$	0.5 h	24
2	H_2O/EtOH(5:1)	$FeMo_6$ (0.5 mol%)	$NaHSO_3$	2h	32
3	H_2O/EtOH(5:1)	$FeMo_6$ (0.5 mol%)	$NaHSO_3$	4h	41
4	H_2O/EtOH(5:1)	$FeMo_6$ (1 mol%)	$NaHSO_3$	2h	47
5	H_2O/EtOH(5:1)	$FeMo_6$ (2mol%)	$NaHSO_3$	2h	68(61)[c]
6	H_2O/EtOH(5:1)	$FeMo_6$ (2mol%)	$NaHSO_3$	4h	73
7	H_2O/EtOH(5:1)	$FeMo_6$ (2mol%)	$NaHSO_3$	8h	77
8	H_2O/EtOH(5:1)	$FeMo_6$ (3mol%)	$NaHSO_3$	2h	70
9	H_2O/EtOH(5:1)	$FeMo_6$ (3mol%)	Na_2SO_3	2h	63
10	H_2O/EtOH(5:1)	$FeMo_6$ (3mol%)	$NaHCO_3$	2h	34

[a]Reaction conditions: air atmosphere, diphenylamine (0.2 mmol), H_2O_2 (2.0 eq, 46 mg), solvent (1 mL), temperature (~28 °C), in a 10 mL glass tube. [b]Conversion yields were determined by ^{1}H NMR using 1,2-dichloroethane as the internal standard. [c]Isolated yield.

6. General procedure for the synthesis of azo compounds

Under open air atmosphere, hydrazine (0.2 mmol), $FeMoO_6$ catalyst (2.1 mg, 0.5 mol%), $NaHSO_3$ (1.1 mg, 5 mol%), H_2O_2 (46 mg), H_2O (1 mL) and ethanol (0.2 mL) were added into a 10 mL tube (capped a balloon). Then the mixture was stirring 0.5 h at room temperhature. Afterwards, the reaction mixture was quenched with water (1 mL) and the crude mixture was extracted with ethyl acetate (2 x 3 mL). The combined organic fractions were dried over anhydrous Na_2SO_4, concentrated in vacuo and the

residue was purified by flash column chromatography on silica gel (Petroleum ether/Ethyl acetate).

7. Gram-scale reaction

Under open air atmosphere, 1,2-diphenylhydrazine (10 mmol), $FeMoO_6$ catalyst (102 mg, 0.5 mol%), $NaHSO_3$ (52 mg, 5 mol%), H_2O_2 (2.3 g), H_2O (10 mL) and ethanol (2 mL) were added into a 20 mL tube (capped a balloon). Then the mixture was stirring 2 h at room temperhature. Afterwards, the reaction mixture was quenched with water (10 mL) and the crude mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic fractions were dried over anhydrous Na_2SO_4, concentrated in vacuo and the residue was further purified through recrystallization in ethyl acetate/hexane (1.71g, 94%).

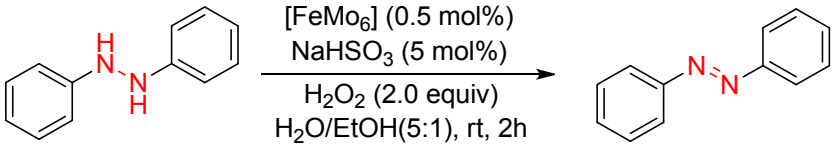
8. General procedure for the synthesis of tetraarylhydrazines

Under open air atmosphere, diarylamine (0.2 mmol), $FeMoO_6$ catalyst (8.4 mg, 2 mol%), $NaHSO_3$ (2.2 mg, 10 mol%), H_2O_2 (46 mg), H_2O (1 mL) and ethanol (0.2 mL) were added into a 10 mL tube (capped a balloon). Then the mixture was stirring 2 h at room temperhature. Afterwards, the reaction mixture was quenched with water (1 mL) and the crude mixture was extracted with ethyl acetate (2 x 3 mL). The combined organic fractions were dried over anhydrous Na_2SO_4, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (Petroleum ether/Ethyl acetate).

9. Recyclability of the $FeMo_6$ catalysts

1,2-diphenylhydrazine (10 mmol), $FeMoO_6$ catalyst (102 mg, 0.5 mol%), $NaHSO_3$ (52 mg, 5 mol%), H_2O_2 (2.3 g), H_2O (10 mL), ethanol (2 mL), under air, room temperature, t = 2 h. In each run, ethyl ether (10 mL) added to the mixture solution. Then the catalyst was separated by filtration, washed thoroughly with ethyl acetate, water, and ethyl acetate and dried under vacuum. Then, the dried catalyst was used further, without any purification or reactivation. The filtrate was evaporated under vacuum, and the residue was purified by column chromatography.

Table S3. Recycling of $FeMo_6$ catalyst



Run	1st	2nd	3rd	4th	5th	6th
Yield (%)	94	92	93	91	92	90

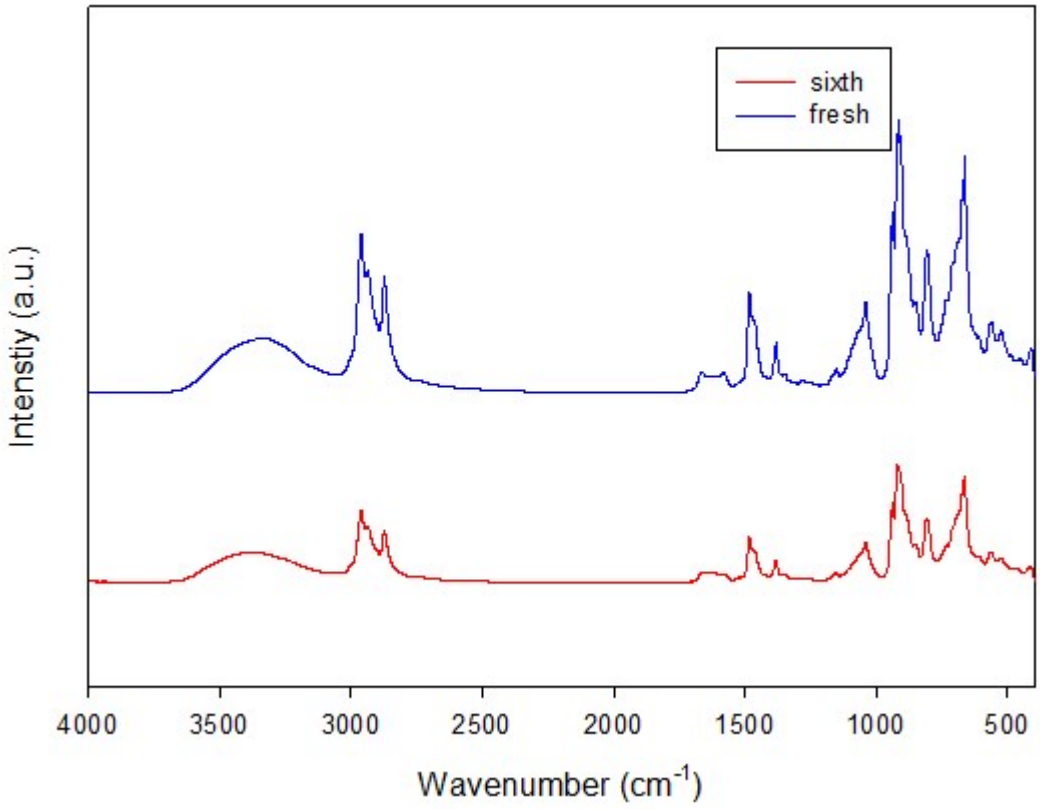
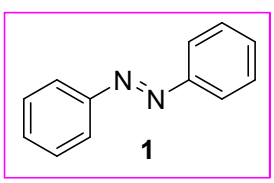


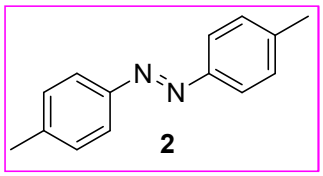
Figure S4. IR spectrums of the $FeMo_6$ catalyst

10. Analytic data



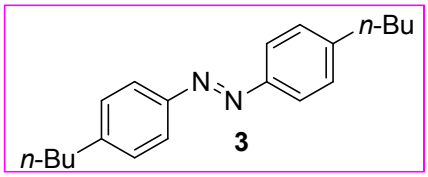
(E)-1,2-diphenyldiazene **(1)**. The crude product was purified by

column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a red solid (34.9 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J*=7.6 Hz, 4H), 7.47-7.56 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 131.0, 129.1, 122.9. Spectral data were in accordance with the literature. [2]



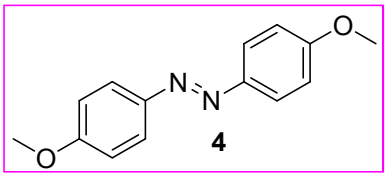
2

(E)-1,2-di-p-tolyldiazene **(2)**. The crude product was purified by column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a yellow solid (40.0 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J*=8.4 Hz, 4H), 7.32 (d, *J*=8.8 Hz, 4H), 2.44 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.9, 141.2, 129.8, 122.8, 21.5. Spectral data were in accordance with the literature. [2]



3

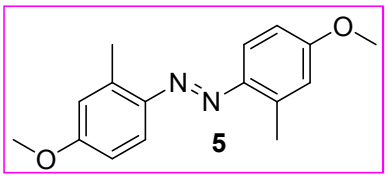
(E)-1,2-bis(4-butylphenyl)diazene **(3)**. The crude product was purified by column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a red oil (53.0 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J*=8.4 Hz, 4H), 7.32 (d, *J*=8.4 Hz, 4H), 2.69 (t, *J*=8.0 Hz, 4H), 1.64-1.69 (m, 4H), 1.35-1.44 (m, 4H), 0.96 (t, *J*= 7.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.0, 146.2, 129.1, 122.7, 35.6, 33.5, 22.4, 14.0. Spectral data were in accordance with the literature. [3]



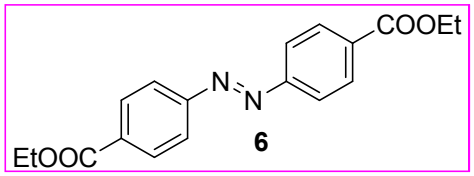
4

(E)-1,2-bis(4-methoxyphenyl)diazene **(4)**. The crude product was purified by column chromatography on silica gel (PE/EA = 8:1) to afford the title compound as a yellow solid (46.5 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ

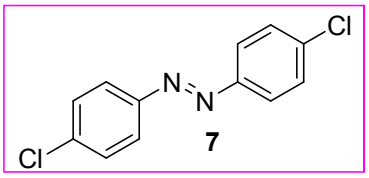
7.88 (d, *J*=9.2 Hz, 4H), 7.00 (d, *J*=8.8 Hz, 4H), 3.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.6, 147.1, 124.4, 114.2, 55.6. Spectral data were in accordance with the literature. [2]



(E)-1,2-bis(4-methoxy-2-methylphenyl)diazene **(5)**. The crude product was purified by column chromatography on silica gel (PE/EA = 5:1) to afford the title compound as a yellow solid (49.7 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J*=8.8 Hz, 2H), 6.77-6.83 (m, 4H), 3.86 (s, 6H), 2.72 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.2, 145.5, 139.9, 117.3, 115.2, 112.3, 55.4, 17.9. Spectral data were in accordance with the literature. [4]

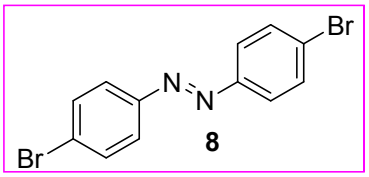


(E)-diethyl 4,4'-(diazene-1,2-diyl)dibenzoate **(6)**. The crude product was purified by column chromatography on silica gel (PE/EA = 10:1) to afford the title compound as a white solid (58.0 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J*=8.4 Hz, 4H), 7.97 (d, *J*=8.8 Hz, 4H), 4.41 (q, *J*=7.2 Hz, 4H), 1.413 (t, *J*=7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 154.8, 132.7, 130.6, 122.9, 61.3, 14.3. Spectral data were in accordance with the literature. [2]

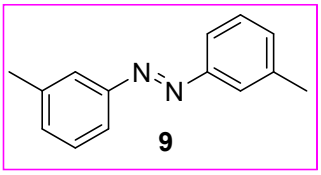


(E)-1,2-bis(4-chlorophenyl)diazene **(7)**. The crude product was purified by column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a yellow solid (45.0 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J*=8.8 Hz, 4H), 7.49 (d, J=8.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.8, 137.2, 129.4, 124.2. Spectral data were in accordance with the

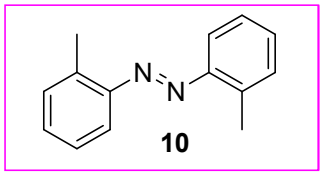
literature. [2]



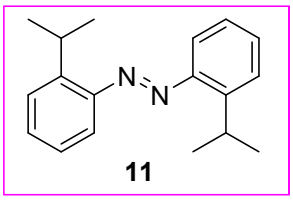
(E)-1,2-bis(4-bromophenyl)diazene **(8)**. The crude product was purified by column chromatography on silica gel (PE/EA = 10:1) to afford the title compound as a yellow solid (62.2 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J*=8.8 Hz, 4H), 7.65 (d, *J*=8.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 132.4, 125.7, 124.4. Spectral data were in accordance with the literature. [2]



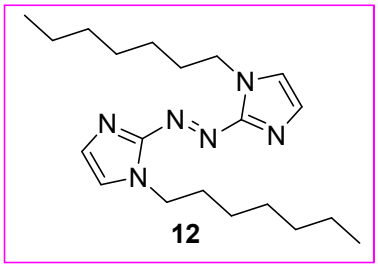
(E)-1,2-di-m-tolyldiazene **(9).** The crude product was purified by column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a yellow solid (39.5 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71-7.73 (m, 4H), 7.38 (t, *J*=7.8 Hz, 2H), 7.26 (d, *J*=7.8 Hz, 2H), 2.44 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.9, 139.0, 131.8, 129.0, 122.9, 120.6, 21.4. Spectral data were in accordance with the literature. [2]



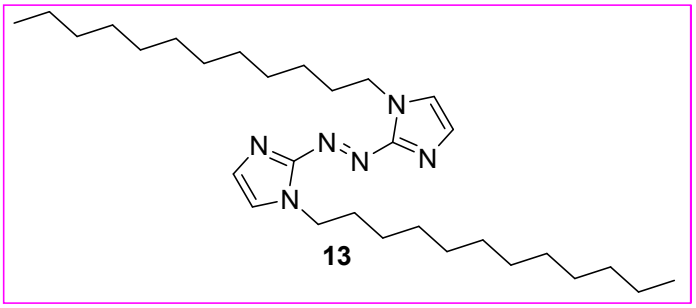
(E)-1,2-di-o-tolyldiazene **(10).** The crude product was purified by column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a yellow solid (39.6 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.66 (m, 2H), 7.32-7.36 (m, 4H), 7.27-7.30 (m, 2H), 2.75 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 138.1, 131.3, 130.7, 126.4, 115.8, 17.7. Spectral data were in accordance with the literature. [2]



(E)-1,2-bis(2-isopropylphenyl)diazene **(11).** The crude product was purified by column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a yellow solid (47.3 mg, 89%).^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J*=8.4 Hz, 2H), 7.41-7.47 (m, 4H), 7.26 (t, J= 7.8 Hz, 2H), 4.15-4.19 (m, 2H), 1.35 (d, J= 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.1, 148.1, 131.1, 126.4, 126.3, 115.6, 27.4, 23.9. Spectral data were in accordance with the literature. [5]

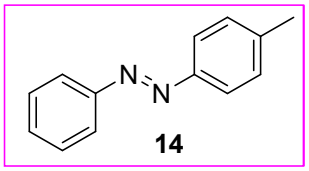


(E)-1,2-bis(1-heptyl-1H-imidazol-2-yl)diazene **(12)**. The crude product was purified by column chromatography on silica gel (PE/EA = 3:1) to afford the title compound as a red solid (64.4 mg, 90%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J*=3.6 Hz, 2H), 7.18 (d, *J*=3.6 Hz, 2H) 4.44 (m, 4H), 1.84 (s, 4H), 1.22-1.29 (m, 16H), 0.82-0.83 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 130.8, 123.0, 45.8, 31.6, 31.2, 28.8, 26.4, 22.5, 14.0. HRMS (ESI): calcd. for $C_{20}H_{34}N_6$ $[M+H]^+$: 359.2918; found: 359.2914.



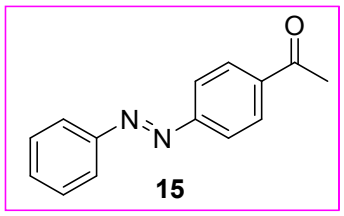
(E)-1,2-bis(1-dodecyl-1H-imidazol-2-yl)diazene **(13)**. The crude product was purified by column

chromatography on silica gel (PE/EA = 3:1) to afford the title compound as a red solid (86.6 mg, 87%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 2H), 7.19 (s, 2H) 4.45 (t, J=6.8 Hz, 4H), 1.83-1.87 (m, 4H), 1.19-1.29 (m, 36H), 0.84-0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 130.9, 123.0, 45.9, 31.9, 31.2, 29.6, 29.5, 29.4, 29.3, 29.1, 26.5, 22.7, 14.1. HRMS (ESI): calcd. for $C_{30}H_{54}N_6$ $[M+H]^+$: 499.4483; found: 499.4482.



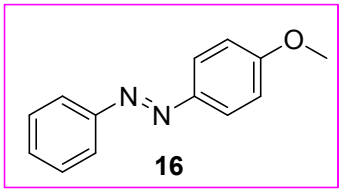
14

(E)-1-phenyl-2-(p-tolyl)diazene **(14)**. The crude product was purified by column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a red solid (36.8 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J*=6.4 Hz, 2H), 7.89 (d, J=5.2 Hz, 2H), 7.48-7.56 (m, 3H), 7.35 (d, J=6.4 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.8, 150.8, 141.6, 130.7, 129.8, 129.1, 122.9, 122.8, 21.6. Spectral data were in accordance with the literature. [6]



15

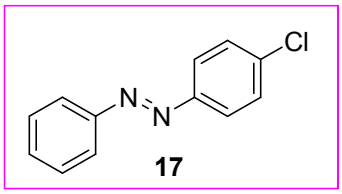
(E)-1-(4-(phenyldiazenyl)phenyl)ethanone **(15)**. The crude product was purified by column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a red solid (40.4 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J*= 8.4 Hz, 2H), 7.95-7.99 (m, 4H), 7.53-7.55 (m, 3H), 2.67 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.5, 155.0, 152.5, 138.3, 131.8, 129.4, 129.2, 123.2, 122.9, 26.9. Spectral data were in accordance with the literature. [7]



16

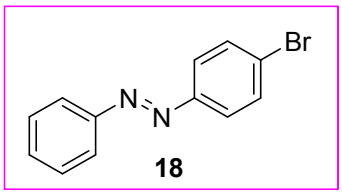
(E)-1-(4-methoxyphenyl)-2-phenyldiazene **(16)**. The crude

product was purified by column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a yellow solid (39.0 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J*= 9.2 Hz, 2H), 7.88 (d, *J*=7.6 Hz, 2H), 7.49-7.53 (m, 3H), 7.02 (d, *J*=9.2 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.0, 152.7, 147.0, 130.3, 129.0, 129.2, 124.7, 122.5, 114.2, 55.6. Spectral data were in accordance with the literature. [2]



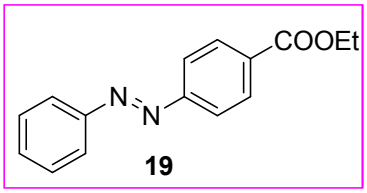
17

(E)-1-(4-chlorophenyl)-2-phenyldiazene **(17)**. The crude product was purified by column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a yellow solid (39.3 mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, *J*=7.2 Hz, 2H), 7.85 (d, *J*=8.4 Hz, 2H), 7.49-7.51 (m, 3H), 7.45 (d, *J*=8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.5, 151.0, 136.9, 131.3, 129.4, 129.2, 124.2, 122.9. Spectral data were in accordance with the literature. [6]



18

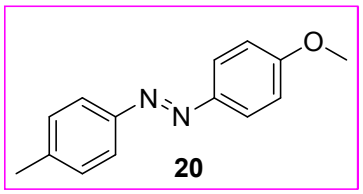
(E)-1-(4-bromophenyl)-2-phenyldiazene **(18)**. The crude product was purified by column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a yellow solid (45.2 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, *J*=7.8 Hz, 2H), 7.78 (d, *J*=8.4 Hz, 2H), 7.63 (d, J=8.4 Hz, 2H), 7.48-7.52 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.5, 151.4, 132.4, 131.4, 129.2, 125.4, 124.4, 122.9. Spectral data were in accordance with the literature. [6]



19

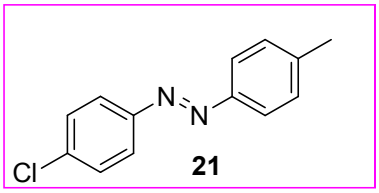
(E)-ethyl 4-(phenyldiazenyl)benzoate **(19)**. The crude product was purified by column chromatography on silica gel (PE/EA = 8:1) to afford

the title compound as a red solid (42.8 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J*=8.8 Hz, 2H), 7.94-7.97 (m, 4H), 7.52-7.53 (m, 2H), 4.39-74.44 (m, 2H), 1.43 (t, J=7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1, 155.0, 152.5, 132.1, 131.7, 130.6, 129.2, 123.2, 122.6, 61.3, 14.4. Spectral data were in accordance with the literature. [2]



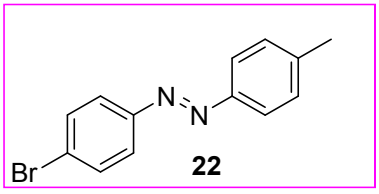
20

(E)-1-(4-methoxyphenyl)-2-(p-tolyl)diazene **(20)**. The crude product was purified by column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a yellow solid (40.7 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J*=6.8 Hz, 2H), 7.78 (d, *J*=6.4 Hz, 2H), 7.28 (d, *J*=6.4 Hz, 2H), 7.00 (d, *J*=6.4 Hz, 2H), 3.87 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.8, 150.8, 147.0, 140.8, 129.7, 124.6, 122.5, 114.2, 55.5, 21.5. Spectral data were in accordance with the literature. [2]



21

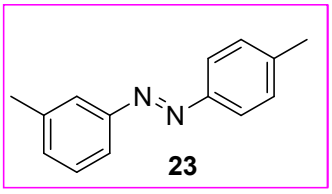
(E)-1-(4-chlorophenyl)-2-(p-tolyl)diazene **(21)**. The crude product was purified by column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a yellow solid (43.2 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.86 (m, 4H), 7.47 (d, *J*=8.8 Hz, 2H), 7.31 (d, *J*=8.8 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 150.6, 141.9, 136.5, 129.8, 129.3, 124.0, 122.9, 21.5. Spectral data were in accordance with the literature. [8]



22

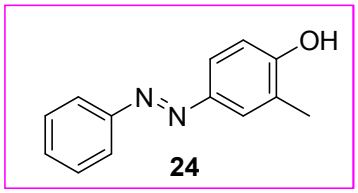
(E)-1-(4-bromophenyl)-2-(p-tolyl)diazene **(22)**. The crude product was purified by column chromatography on silica gel (PE/EA = 40:1)

to afford the title compound as a yellow solid (57.3 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J*=8.0 Hz, 2H), 7.77 (d, *J*=8.4 Hz, 2H), 7.62 (d, *J*=8.4 Hz, 2H), 7.30 (d, *J*=8.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.4, 150.6, 142.0, 132.3, 129.8, 125.0, 124.2, 122.9, 21.5. Spectral data were in accordance with the literature. [8]



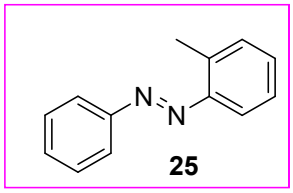
23

(E)-1-(m-tolyl)-2-(p-tolyl)diazene **(23)**. The crude product was purified by column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a yellow solid (37.8 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J*=8.0 Hz, 2H), 7.71 (s, 2H), 7.40 (t, J=8.0 Hz, 1H), 7.27-7.32 (m, 3H), 2.46 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.8, 150.8, 141.4, 138.9, 131.5, 129.7, 128.9, 122.8, 122.7, 21.5, 21.4. Spectral data were in accordance with the literature.[9]

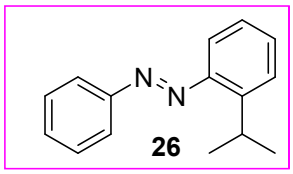


24

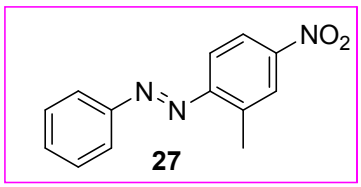
(E)-2-methyl-4-(phenyldiazenyl)phenol **(24)**. The crude product was purified by column chromatography on silica gel (PE/EA = 5:1) to afford the title compound as a yellow solid (38.2 mg, 90%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J*=8.0 Hz, 2H), 7.67 (d, *J*=8.8 Hz, 1H), 7.43-7.52 (m, 3H), 6.78 (s, 1H), 6.71 (d, *J*=8.8 Hz, 1H), 5.32 (s, 1H), 2.70 (2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.1, 153.0, 145.2, 141.2, 130.3, 129.0, 122.7, 117.3, 117.2, 113.7, 17.7. HRMS (ESI): calcd. for $C_{13}H_{12}N_2O$ $[M+H]^+$: 213.1022; found: 213.1021.



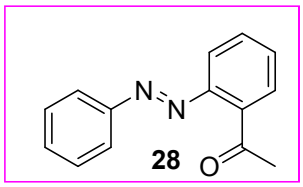
(E)-1-phenyl-2-(o-tolyl)diazene **(25)**. The crude product was purified by column chromatography on silica gel (PE/EA = 50:1) to afford the title compound as a red oil (37.1 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J*=6.8 Hz, 2H), 7.66 (d, *J*=7.6 Hz, 1H), 7.37-7.41 (m, 2H), 7.28-7.31 (m, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.0, 150.7, 131.3, 131.0, 130.8, 129.1, 126.5, 123.0, 115.4, 17.8. Spectral data were in accordance with the literature. [9]



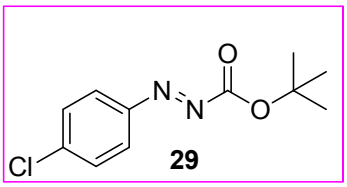
(E)-1-(2-isopropylphenyl)-2-phenyldiazene **(26)**. The crude product was purified by column chromatography on silica gel (PE/EA = 10:1) to afford the title compound as a red oil (40.8 mg, 91%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J*=7.2 Hz, 2H), 7.64 (d, *J*=7.2 Hz, 1H), 7.46-7.56 (m, 5H), 7.27-7.31 (m, 1H), 4.10-4.17 (m, 1H), 1.37 (d, *J*=6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.0, 149.6, 148.0, 131.3, 130.8, 129.1, 126.4, 126.3, 123.0, 115.3, 27.8, 23.9. HRMS (ESI): calcd. for $C_{15}H_{16}N_2$ $[M+H]^+$: 225.1386; found: 225.1386.



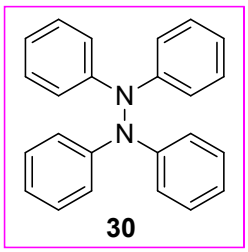
(E)-1-(2-methyl-4-nitrophenyl)-2-phenyldiazene**(27)**. The crude product was purified by column chromatography on silica gel (PE/EA = 4:1) to afford the title compound as a red solid (39.5 mg, 82%).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.12-8.14 (m, 1H), 7.96 (d, *J*=6.4 Hz, 2H), 7.69 (d, *J*=8.8 Hz, 1H), 7.55-7.56 (m, 3H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0, 152.7, 138.9, 132.2, 129.3, 126.4, 123.5, 122.0, 116.7, 17.7. Spectral data were in accordance with the literature. [10]



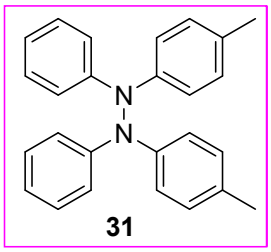
28 (E)-1-(2-(phenyldiazenyl)phenyl)ethanone **(28)**. The crude product was purified by column chromatography on silica gel (PE/EA = 4:1) to afford the title compound as a red oil (38.1 mg, 85%).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J*=8.0 Hz, 1H), 8.16 (d, *J*=7.6 Hz, 1H), 7.91 (d, *J*=8.0 Hz, 2H), 7.75-7.77 (m, 1H), 7.64-7.66 (m, 1H), 7.52-7.59 (m, 3H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.8, 152.3, 150.3, 138.2, 131.8, 130.8, 129.3, 128.7, 128.3, 125.6, 123.3, 122.4, 118.5, 32.7. Spectral data were in accordance with the literature.[11]



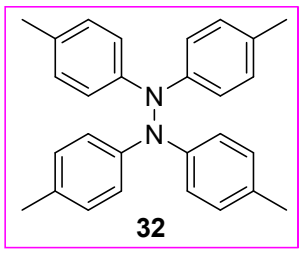
29 (E)-tert-butyl 2-(4-chlorophenyl)diazenecarboxylate **(29)**. The crude product was purified by column chromatography on silica gel (PE/EA = 4:1) to afford the title compound as a red oil (41.0 mg, 86%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J*=8.8 Hz, 2H), 7.48 (d, *J*=8.8 Hz, 2H), 1.65 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.9, 149.9, 139.7, 129.6, 124.9, 85.3, 27.8. Spectral data were in accordance with the literature.[12]



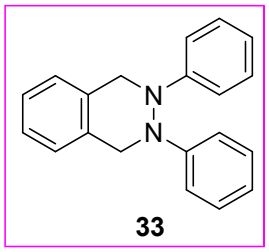
30 1,1,2,2-tetraphenylhydrazine **(30)**. The crude product was purified by column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a white solid (41.0 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.32 (m, 8H), 7.18-7.22 (m, 8H), 6.88-6.92 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.5, 129.1, 122.0, 118.1. Spectral data were in accordance with the literature.[13]



1,2-diphenyl-1,2-di-p-tolylhydrazine **(31)**. The crude product was purified by column chromatography on silica gel (PE/EA = 50:1) to afford the title compound as a white solid (47.3 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.28 (m, 12H), 7.01 (d, *J*=8.4 Hz, 4H), 6.86 (t, *J*=7.2 Hz, 2H), 2.25 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.9, 140.9, 131.7, 129.6, 129.0, 121.4, 118.6, 117.4, 20.7. Spectral data were in accordance with the literature.[13]



1,1,2,2-tetra-p-tolylhydrazine **(32)**. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 50:1) to afford the title compound as a white solid (48.6 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J*=8.4 Hz, 8H), 7.02 (d, *J*=8.0 Hz, 8H), 2.27 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.4, 130.9, 129.6, 117.9, 20.7. Spectral data were in accordance with the literature.[13]



2,3-diphenyl-1,2,3,4-tetrahydrophthalazine **(33)**. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 50:1) to afford the title compound as a light yellow solid (38.9 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.25 (m, 4H), 7.16 (m, 4H), 6.992 (d, *J*=6.4 Hz, 4H), 6.79-6.82 (m, 2H), 4.67 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.2, 132.5, 129.4, 126.7,

126.6, 119.1, 113.4, 45.1. Spectral data were in accordance with the literature.[14]

11. References.

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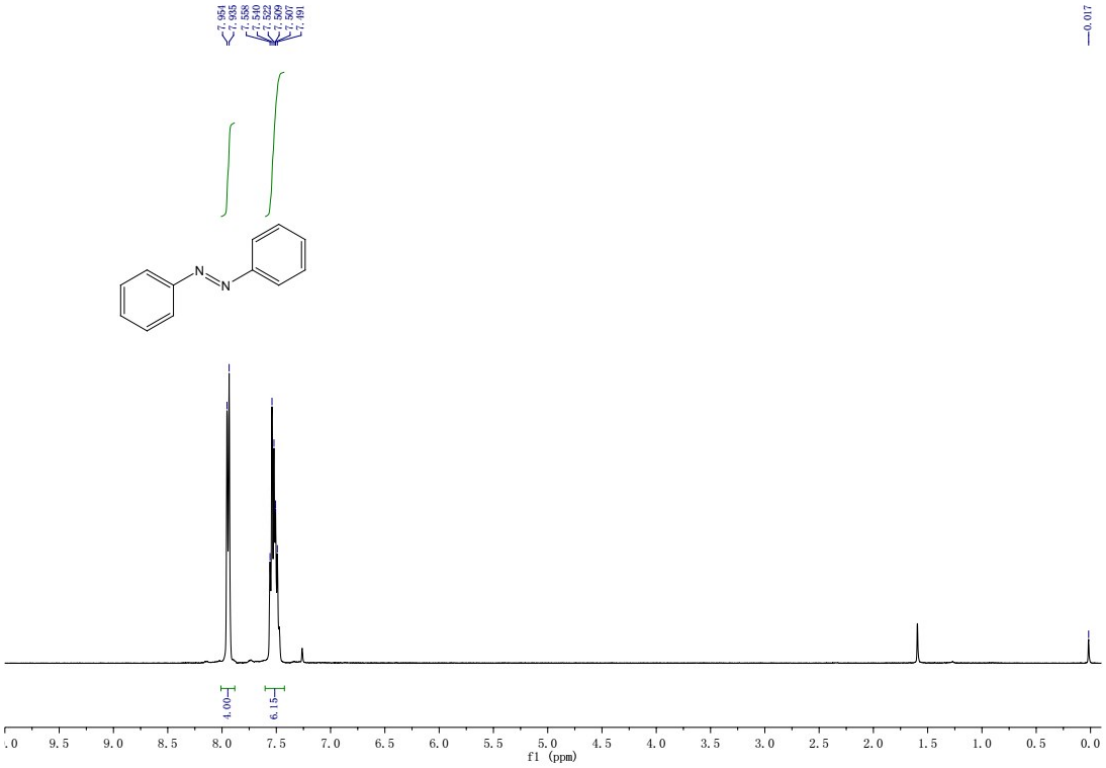
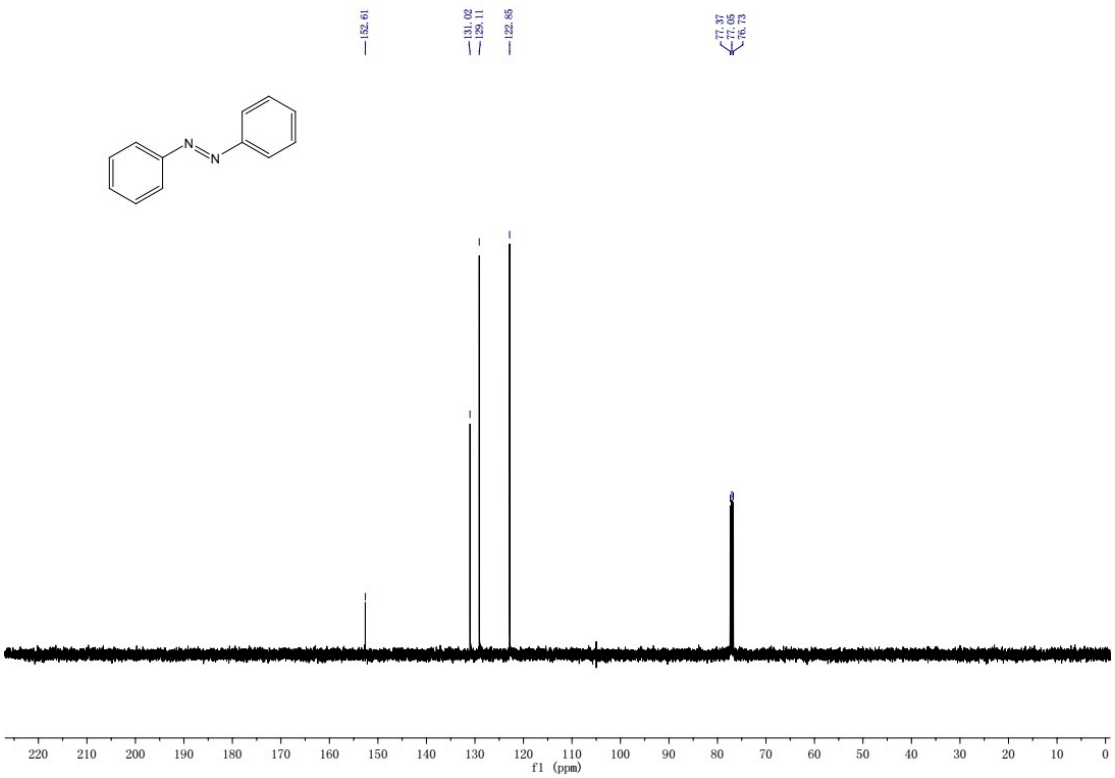
12. ^{1}H and ^{13}C NMR spectra copies

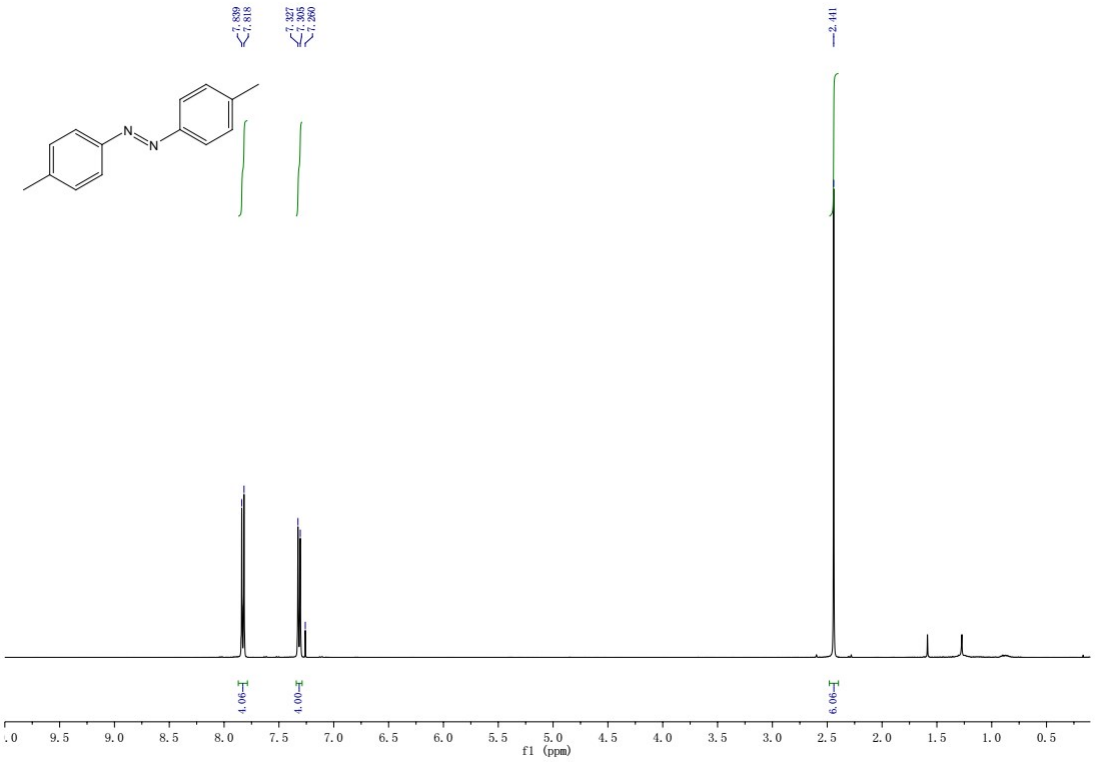
400 MHz ^{1}H NMR for Compound 1



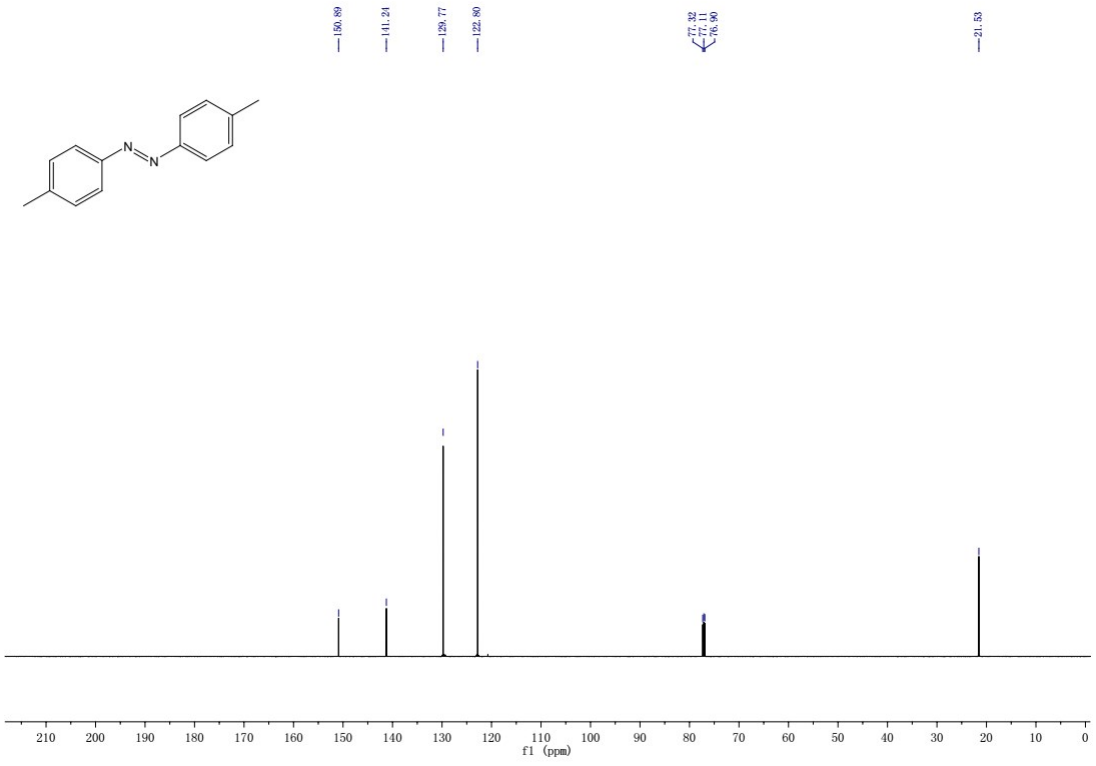
100 MHz ^{13}C NMR for Compound 1



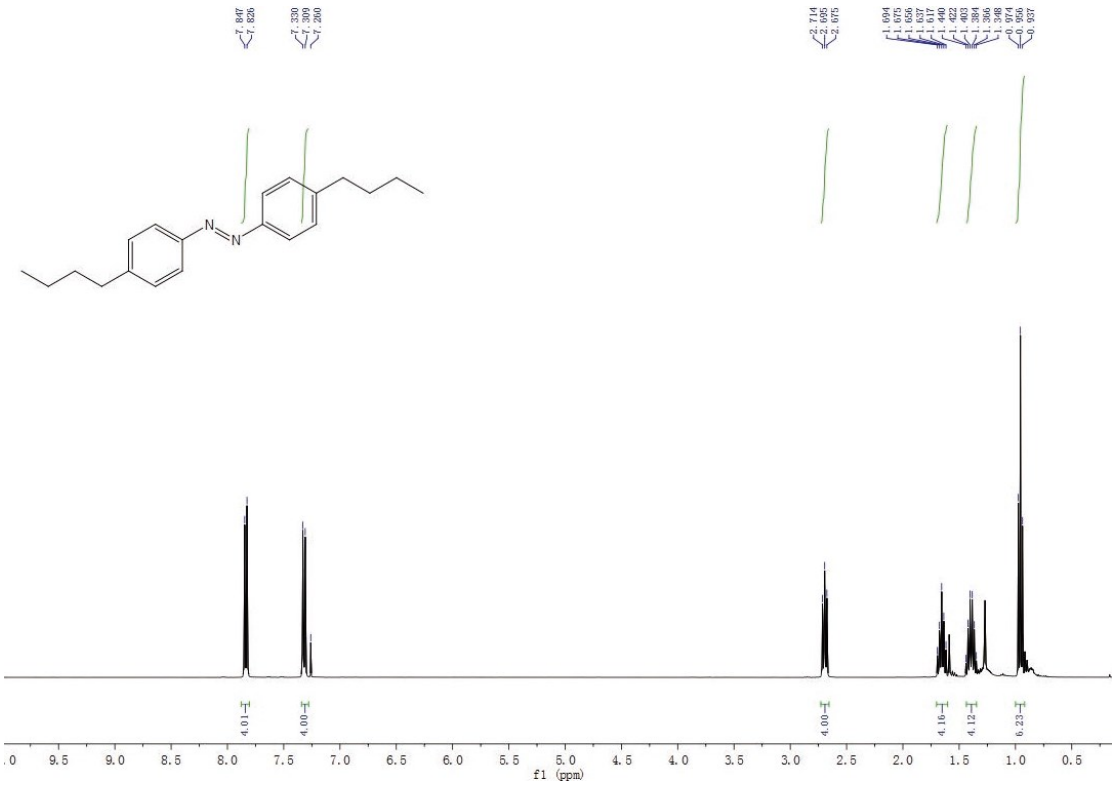
400 MHz ^{1}H NMR for Compound 2



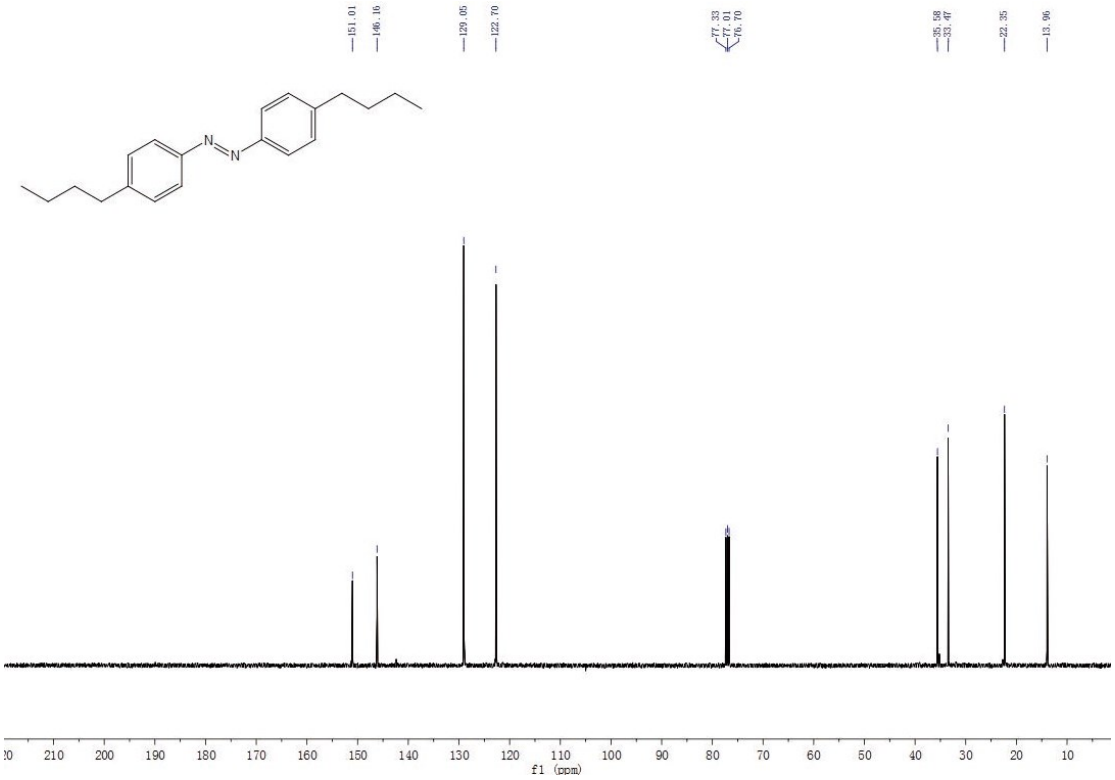
100 MHz ^{13}C NMR for Compound 2



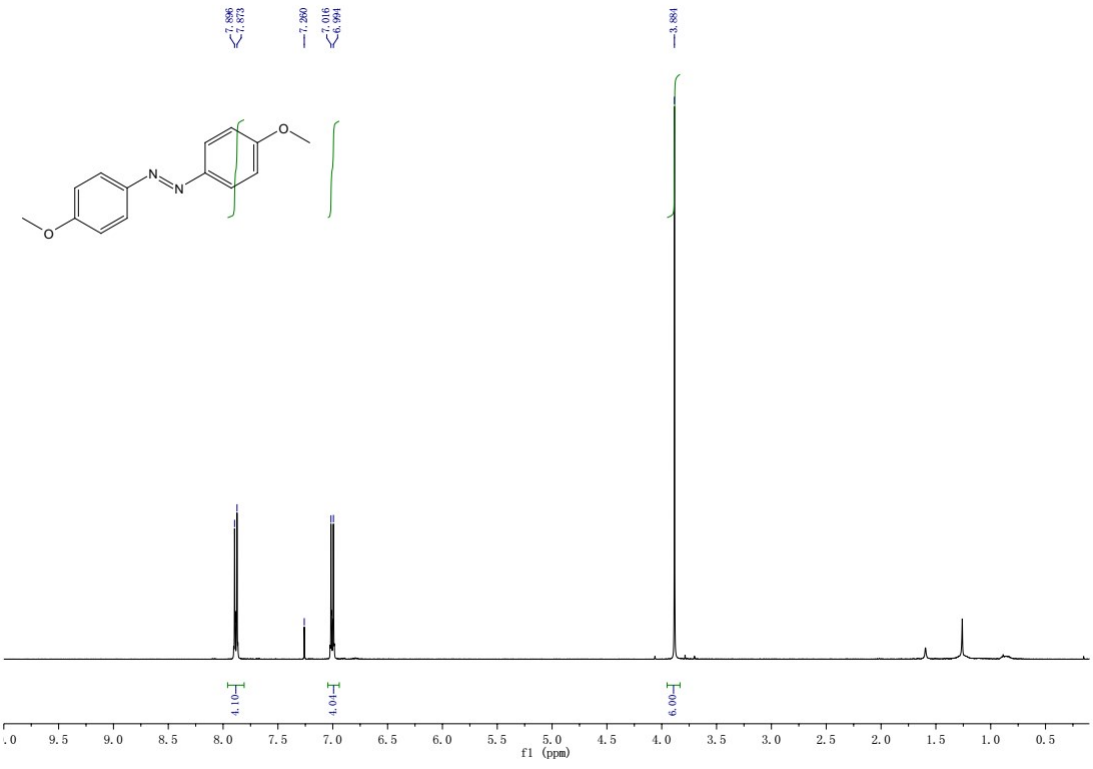
400 MHz ^{1}H NMR for Compound 3



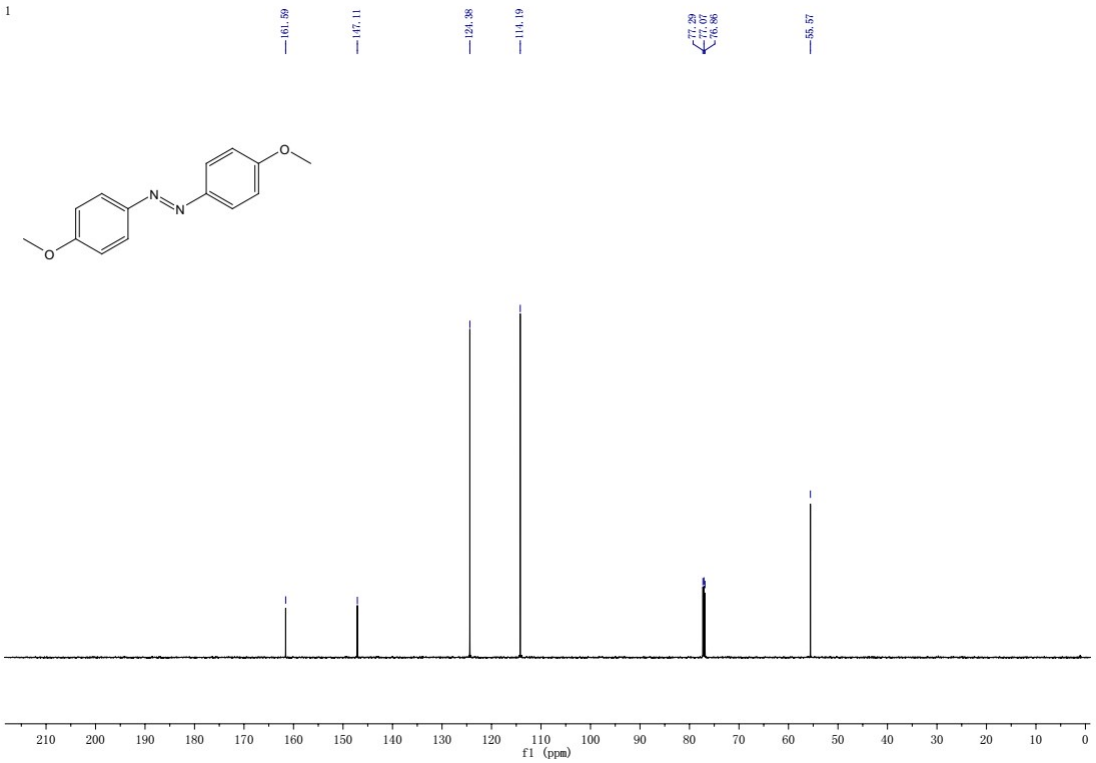
100 MHz ^{13}C NMR for Compound 3



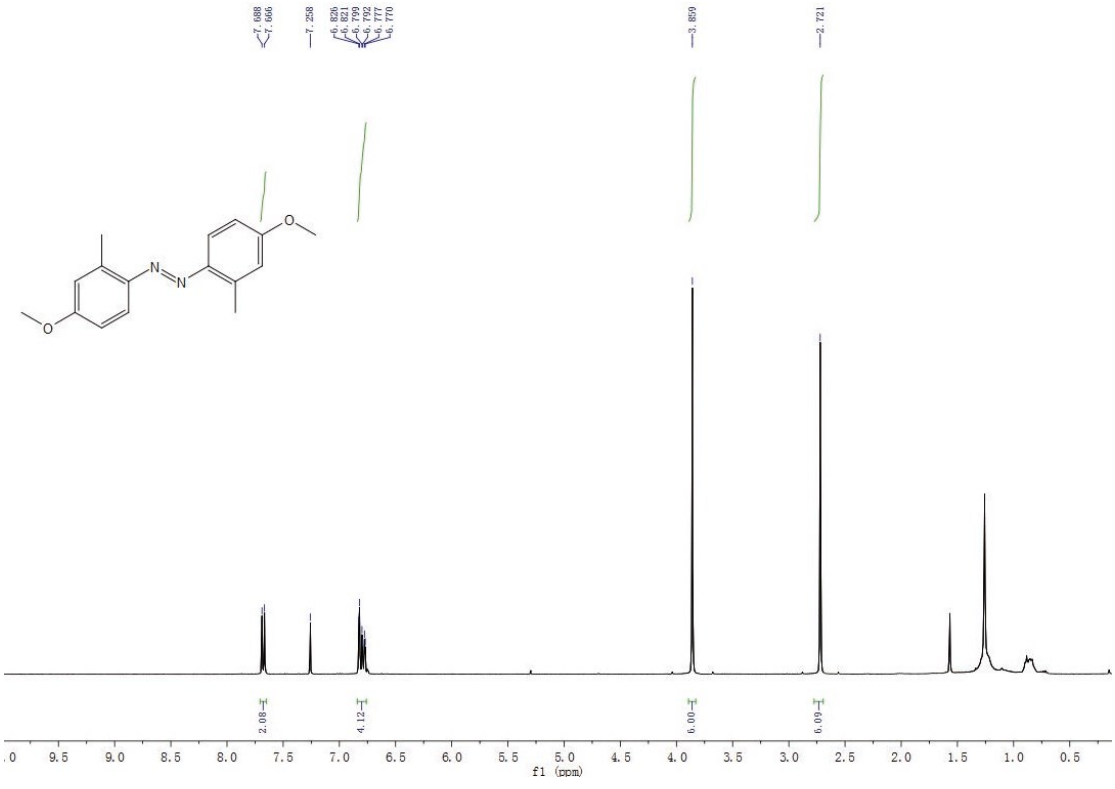
400 MHz ^{1}H NMR for Compound 4



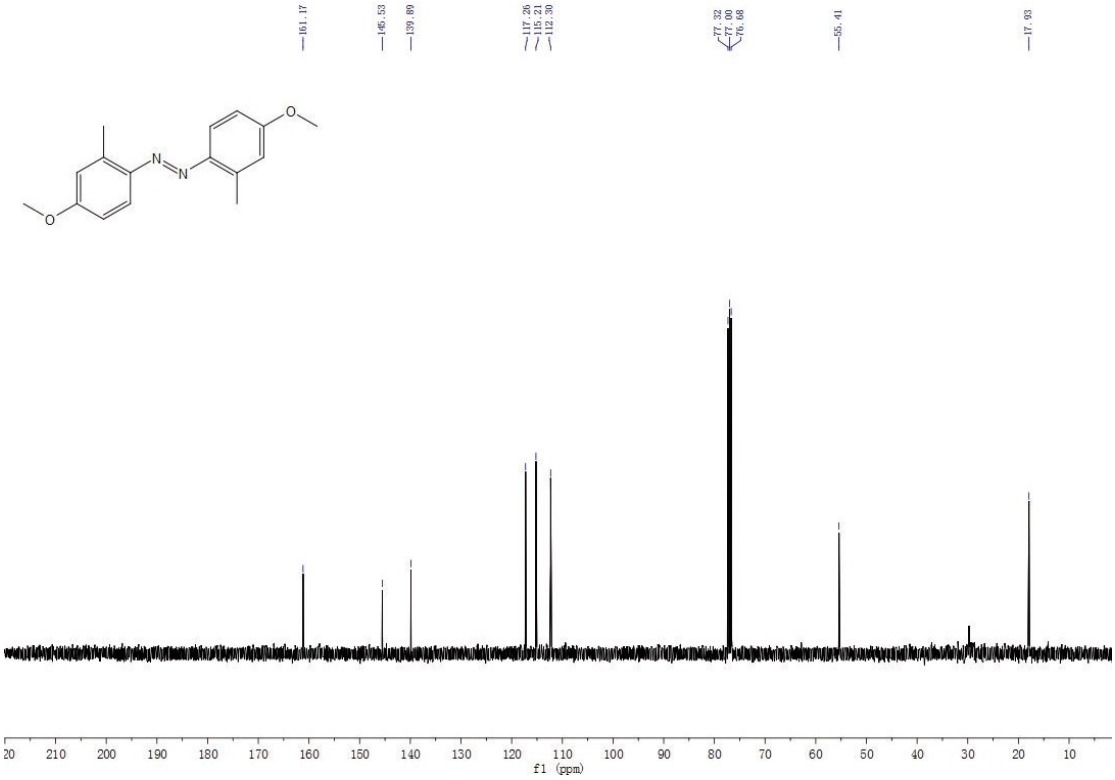
100 MHz ^{13}C NMR for Compound 4



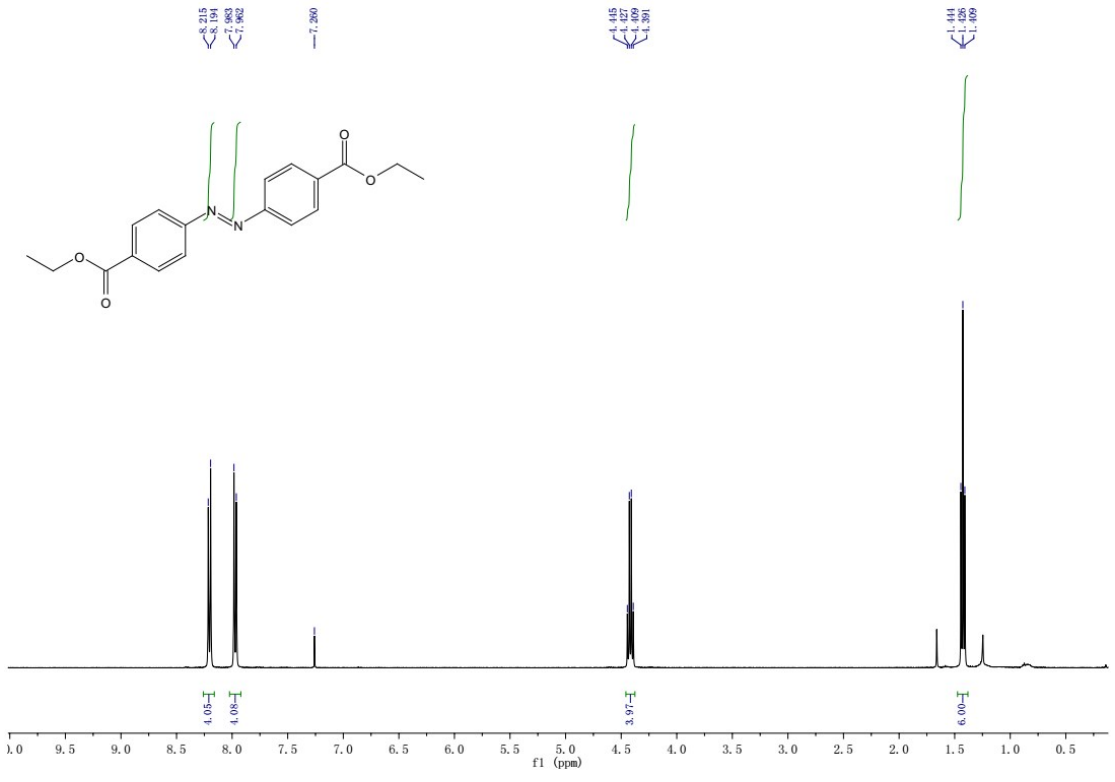
400 MHz ^{1}H NMR for Compound 5



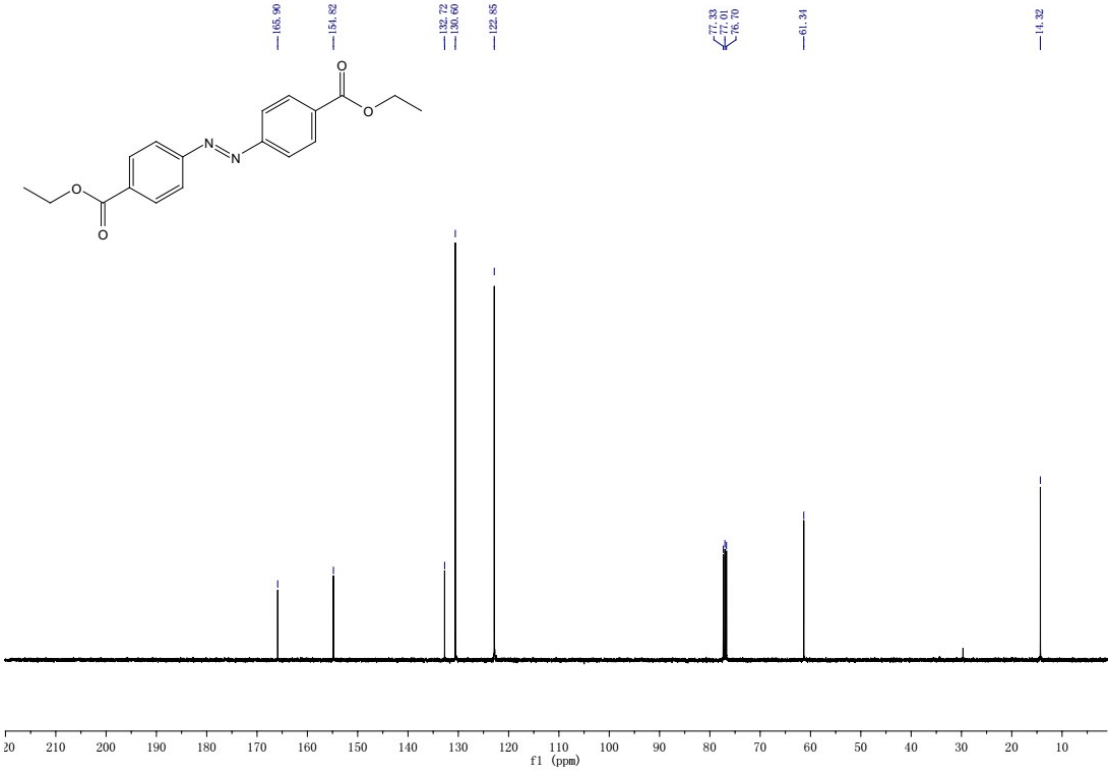
100 MHz ^{13}C NMR for Compound 5



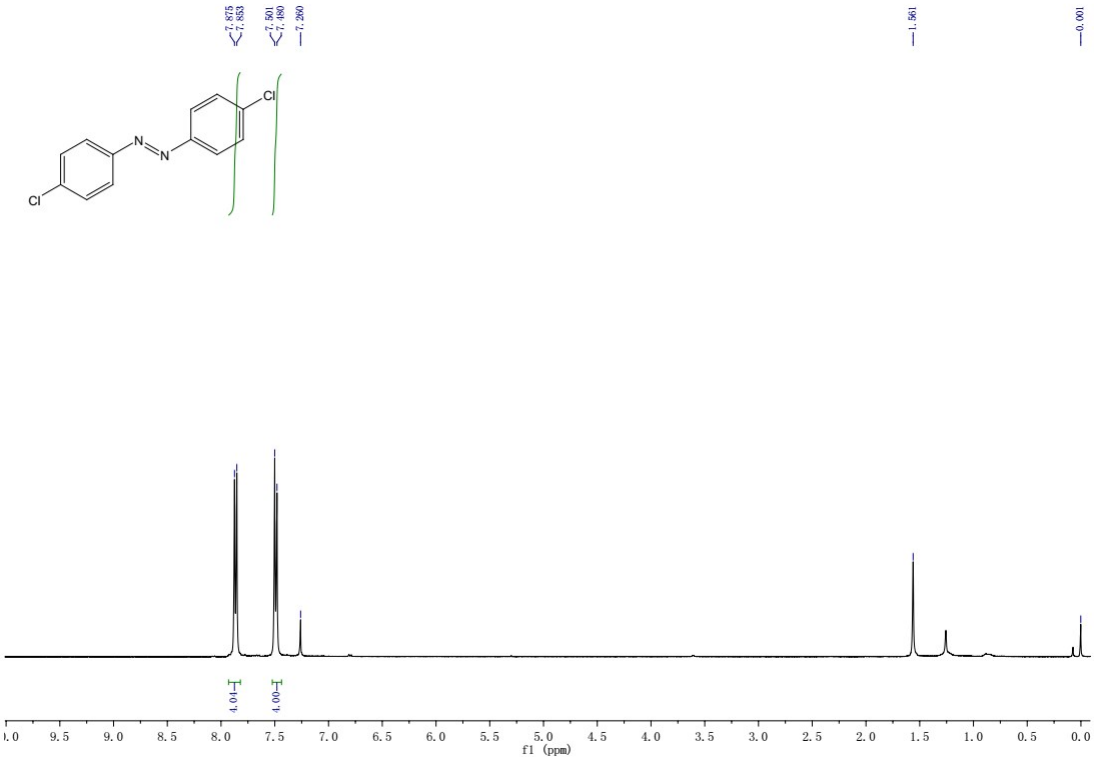
400 MHz ^{1}H NMR for Compound 6



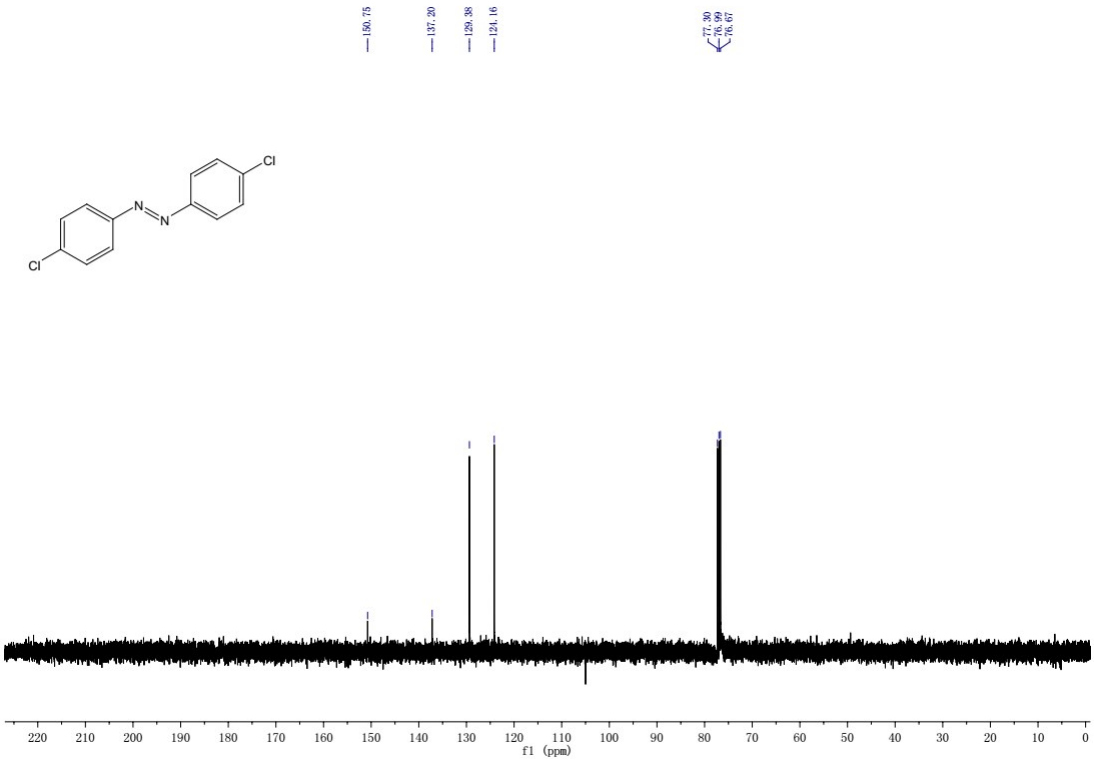
100 MHz ^{13}C NMR for Compound 6



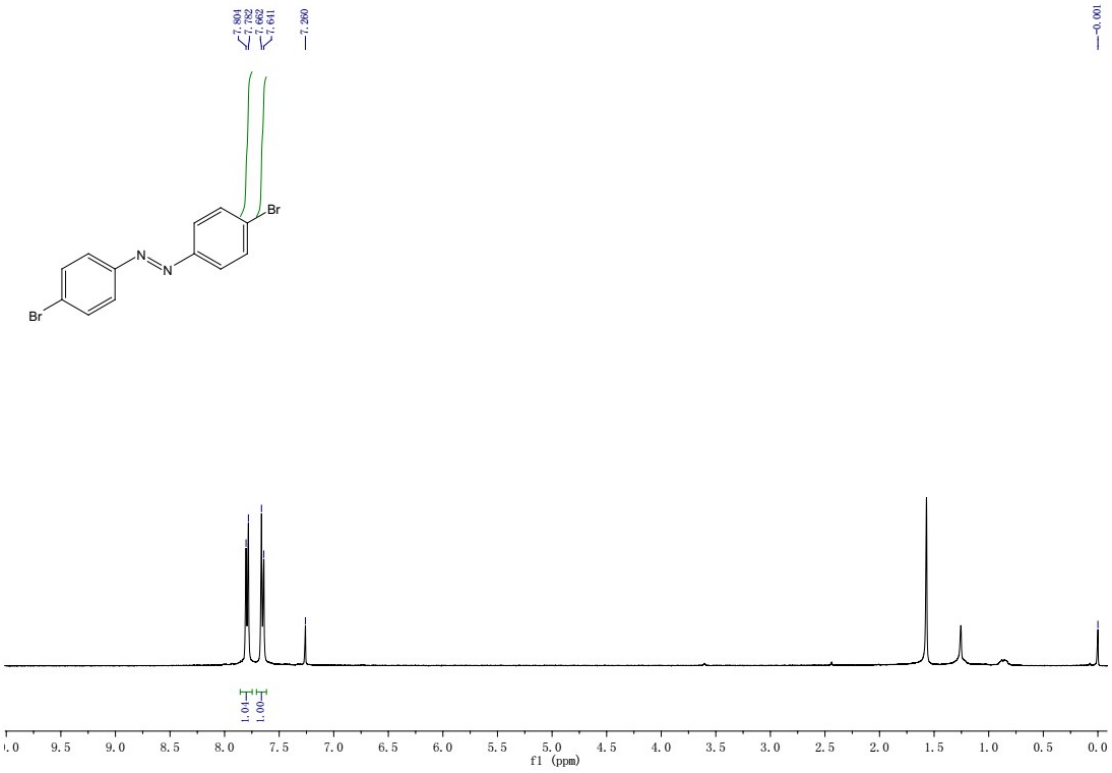
400 MHz ^{1}H NMR for Compound 7



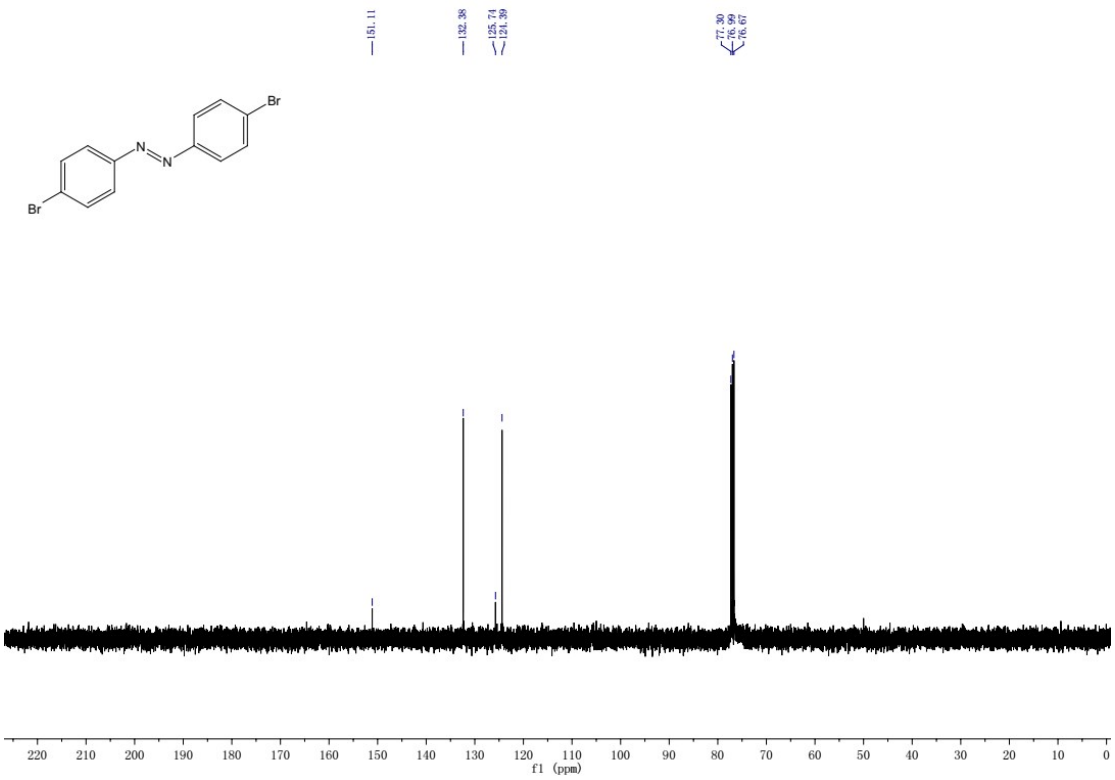
100 MHz ^{13}C NMR for Compound 7



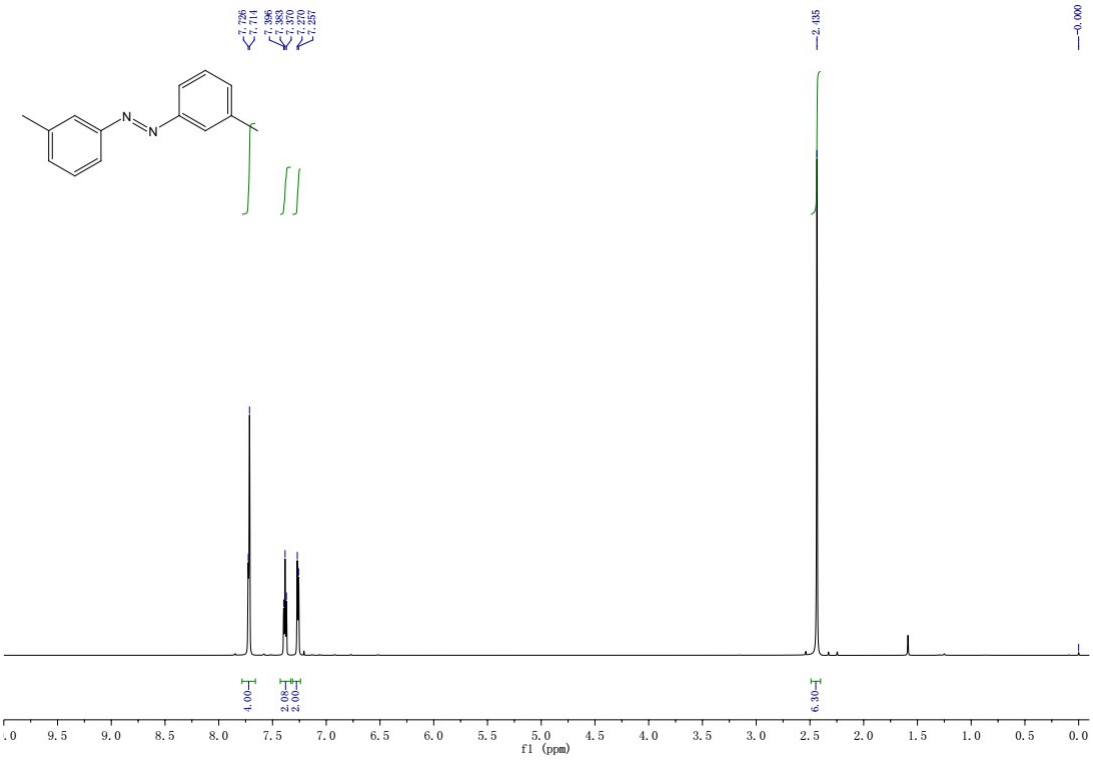
400 MHz ^{1}H NMR for Compound 8



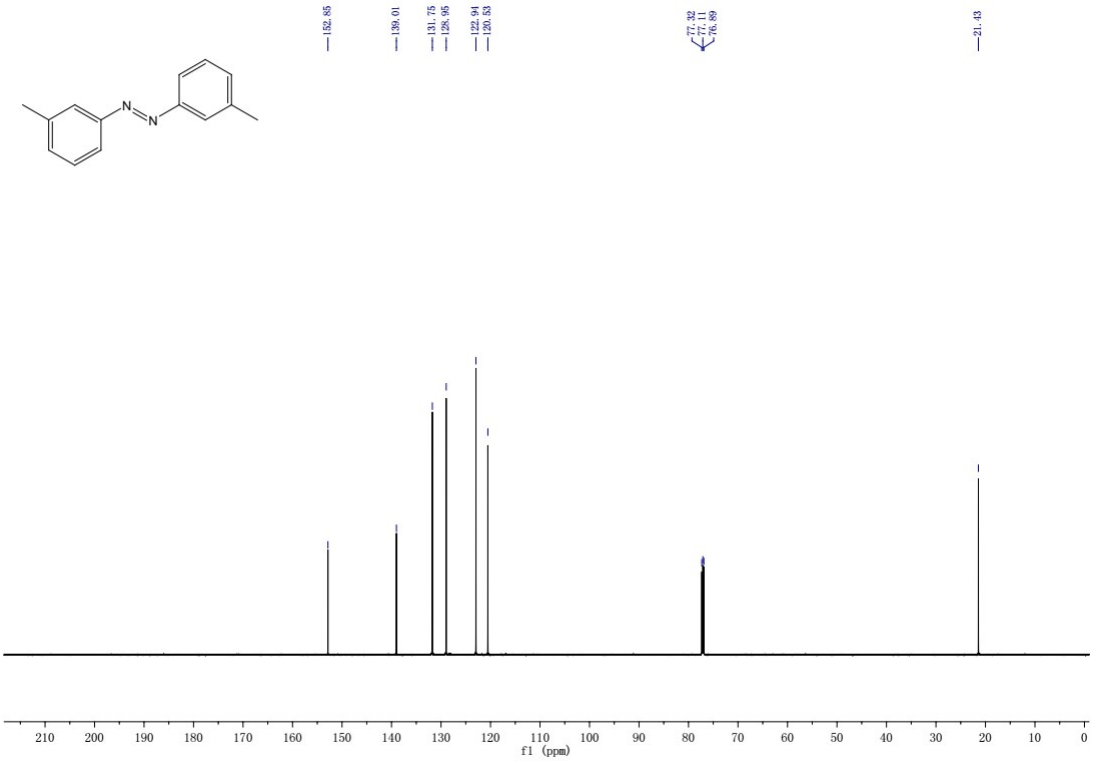
100 MHz ^{13}C NMR for Compound 8



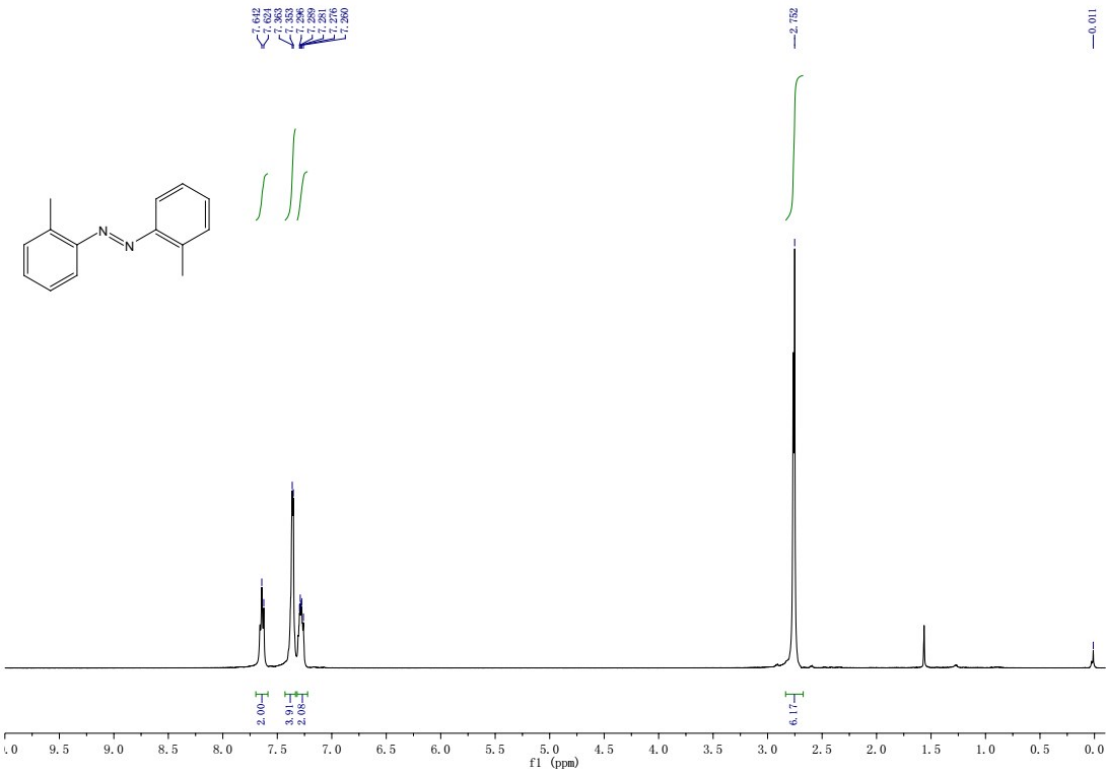
600 MHz ^{1}H NMR for Compound 9



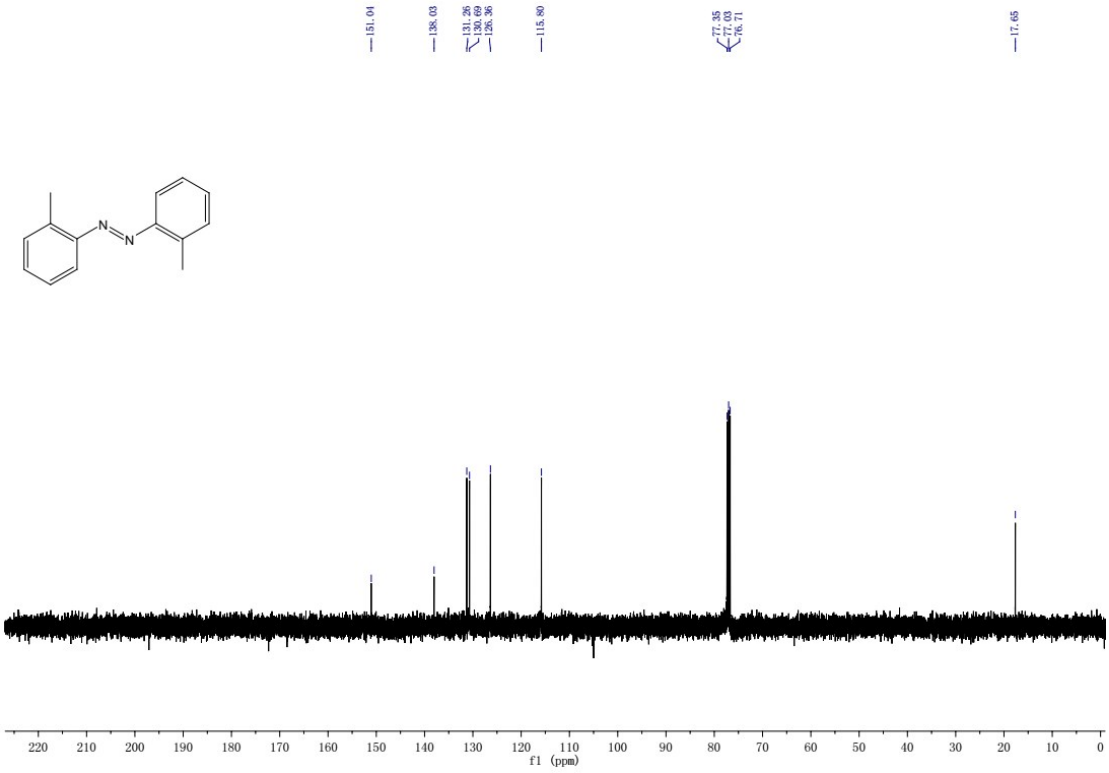
150 MHz ^{13}C NMR for Compound 9



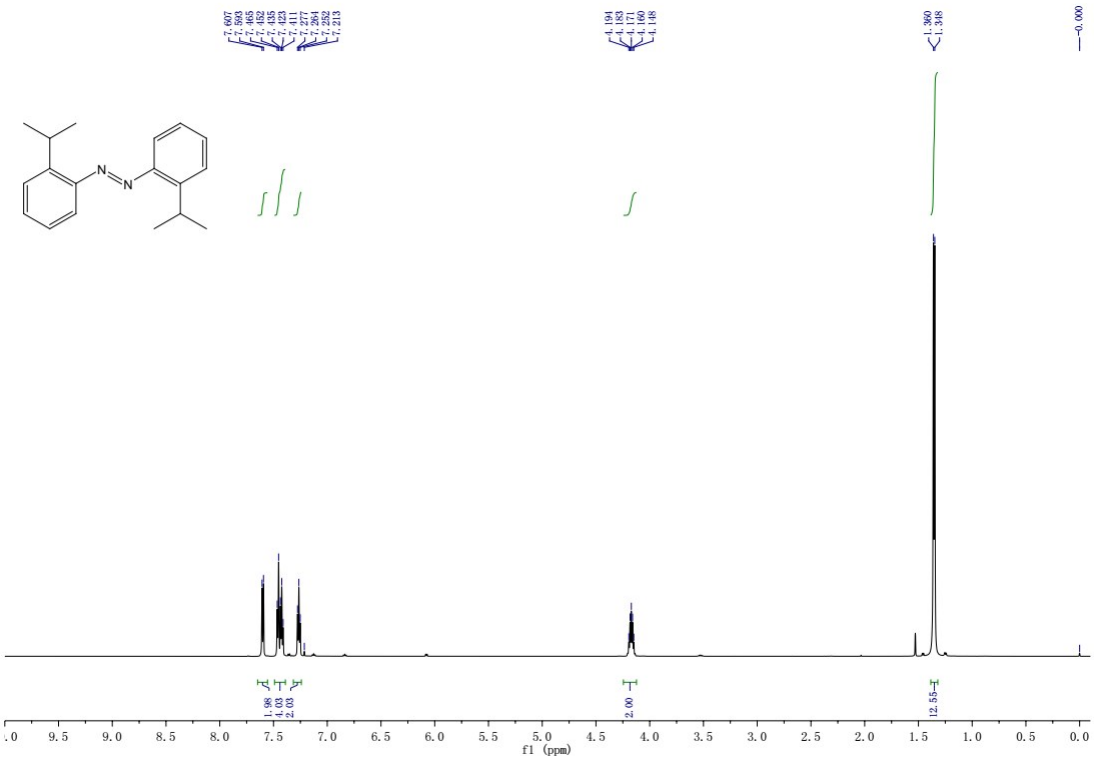
400 MHz ^{1}H NMR for Compound 10



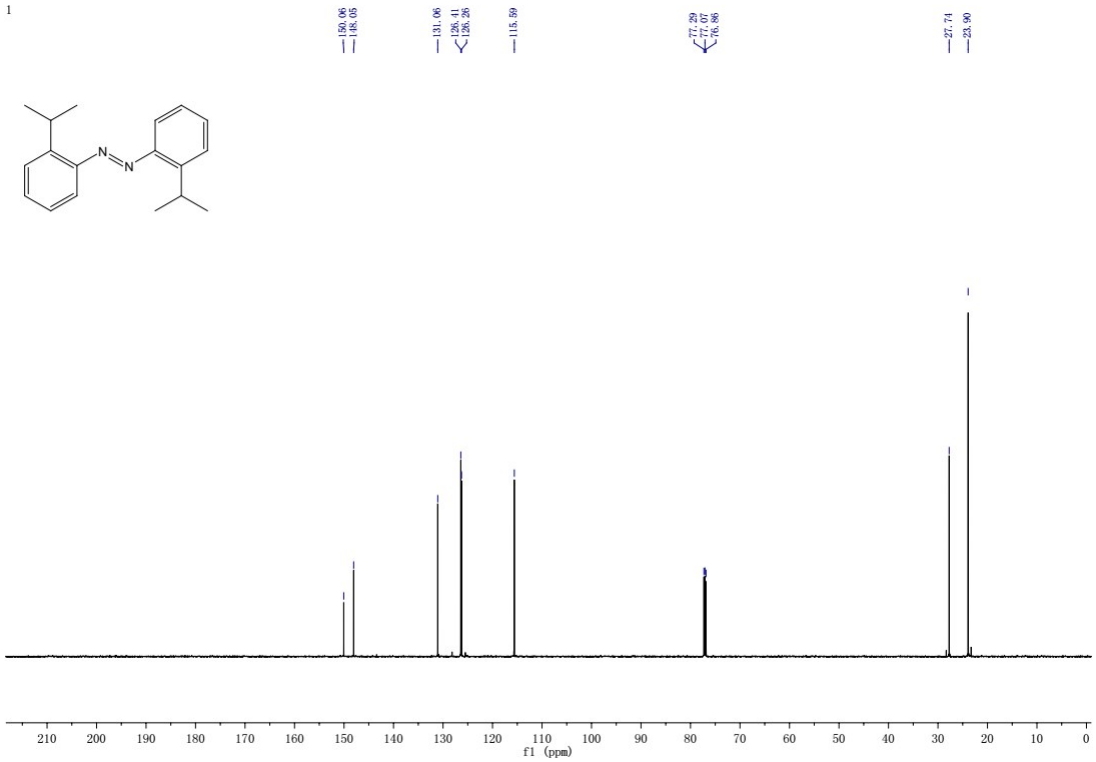
100 MHz ^{13}C NMR for Compound 10



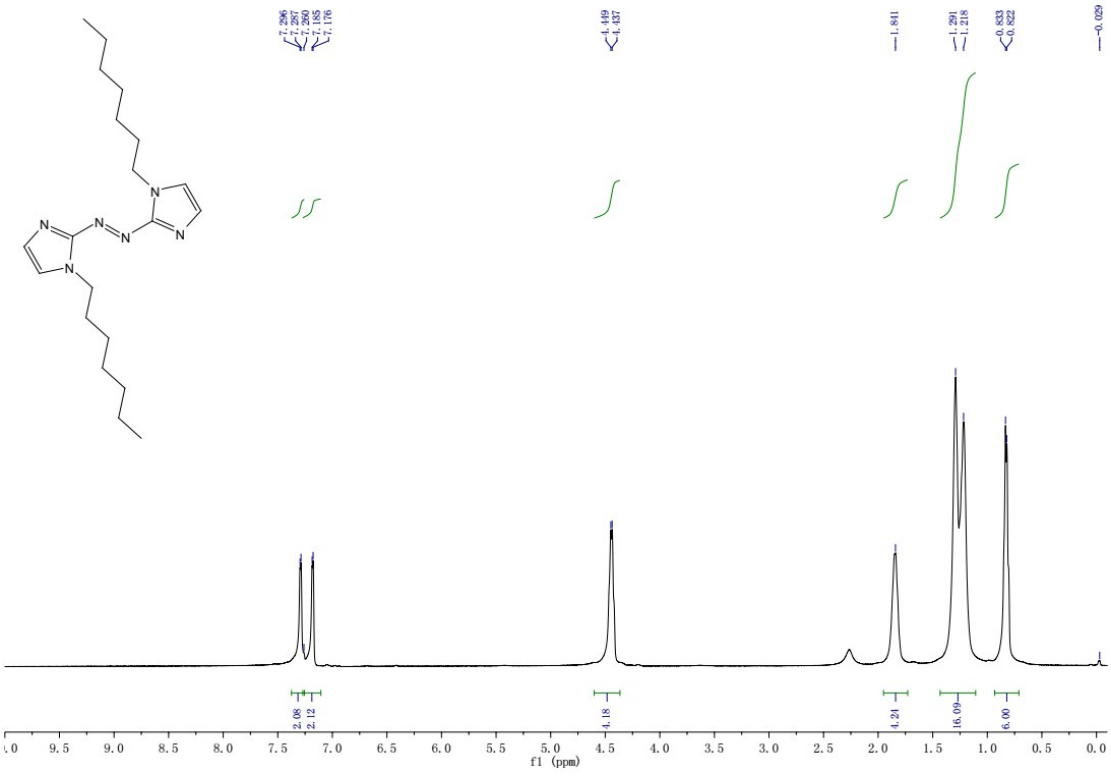
600 MHz ^{1}H NMR for Compound 11



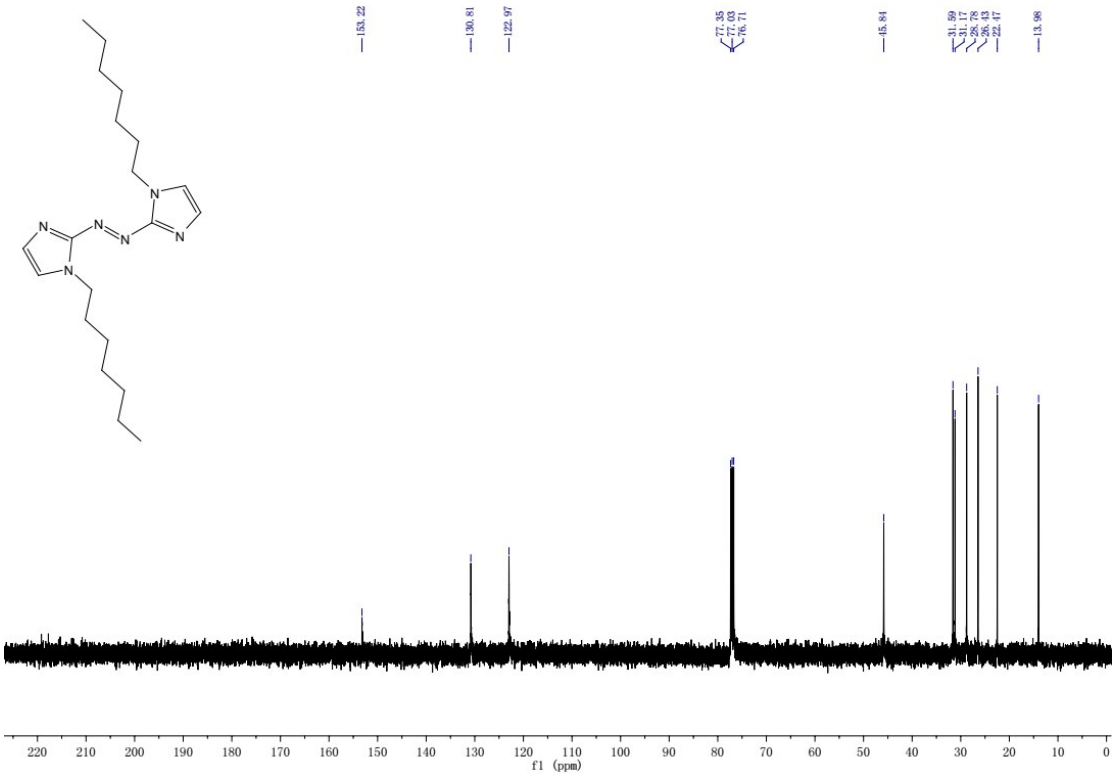
150 MHz ^{13}C NMR for Compound 11



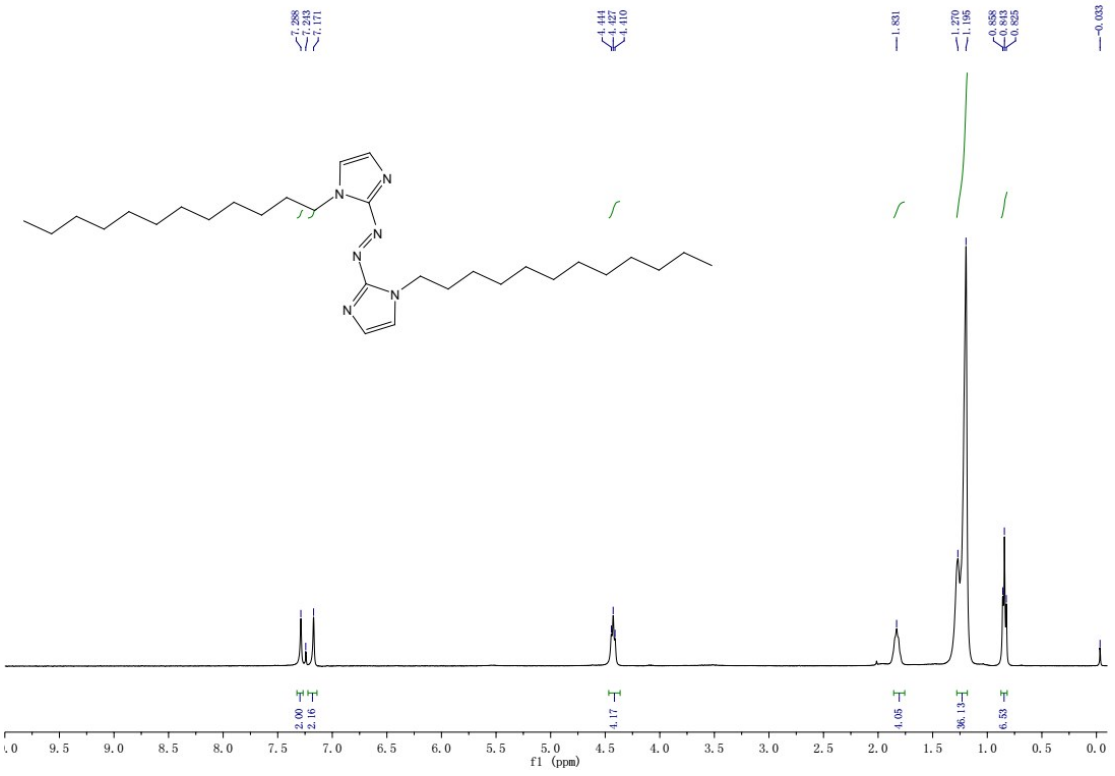
400 MHz ^{1}H NMR for Compound 12

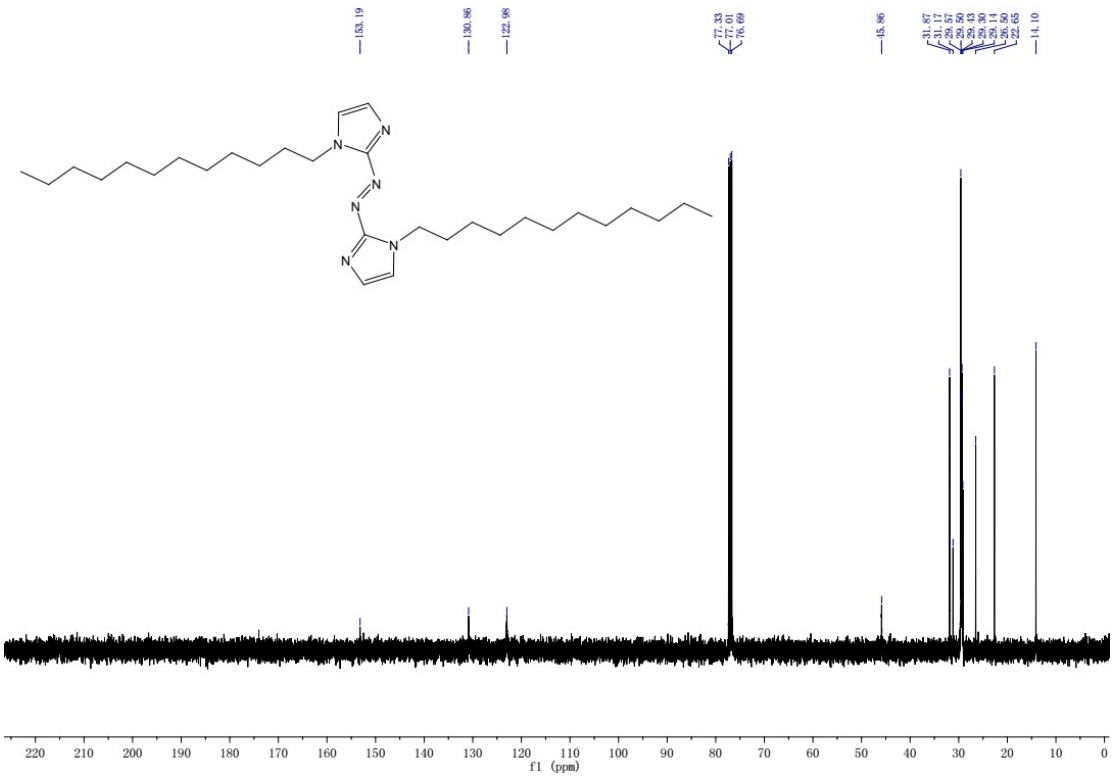


100 MHz ^{13}C NMR for Compound 12

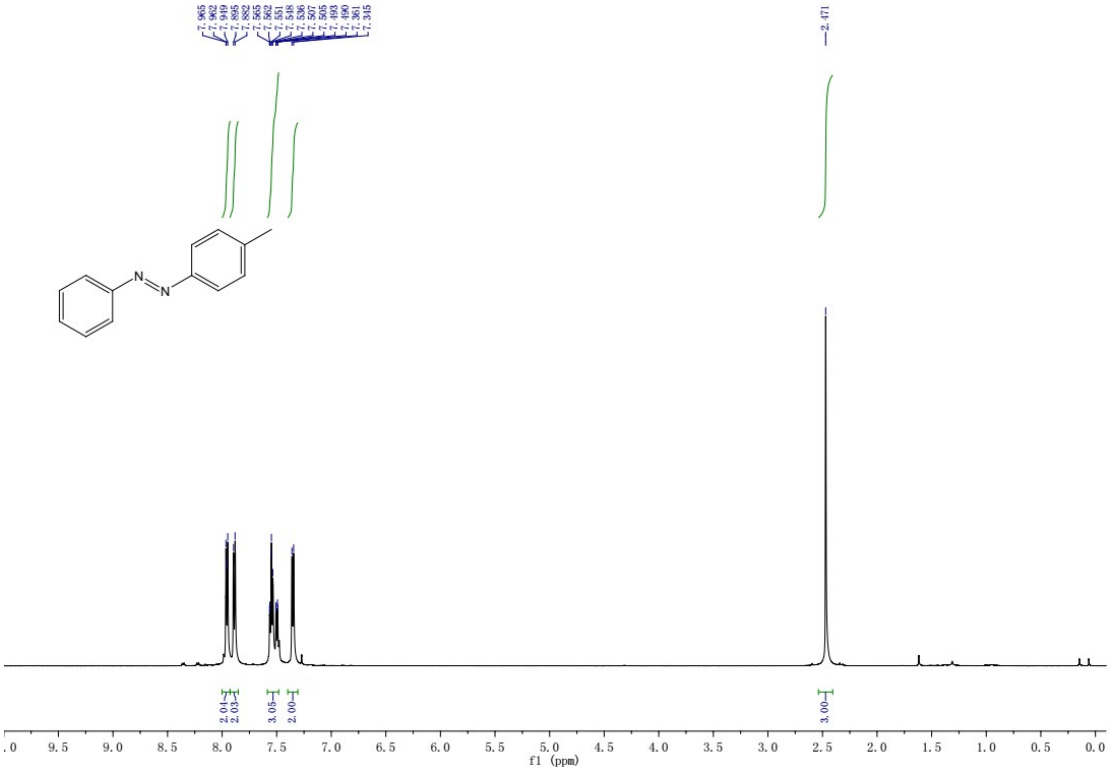


400 MHz ^{1}H NMR for Compound 13

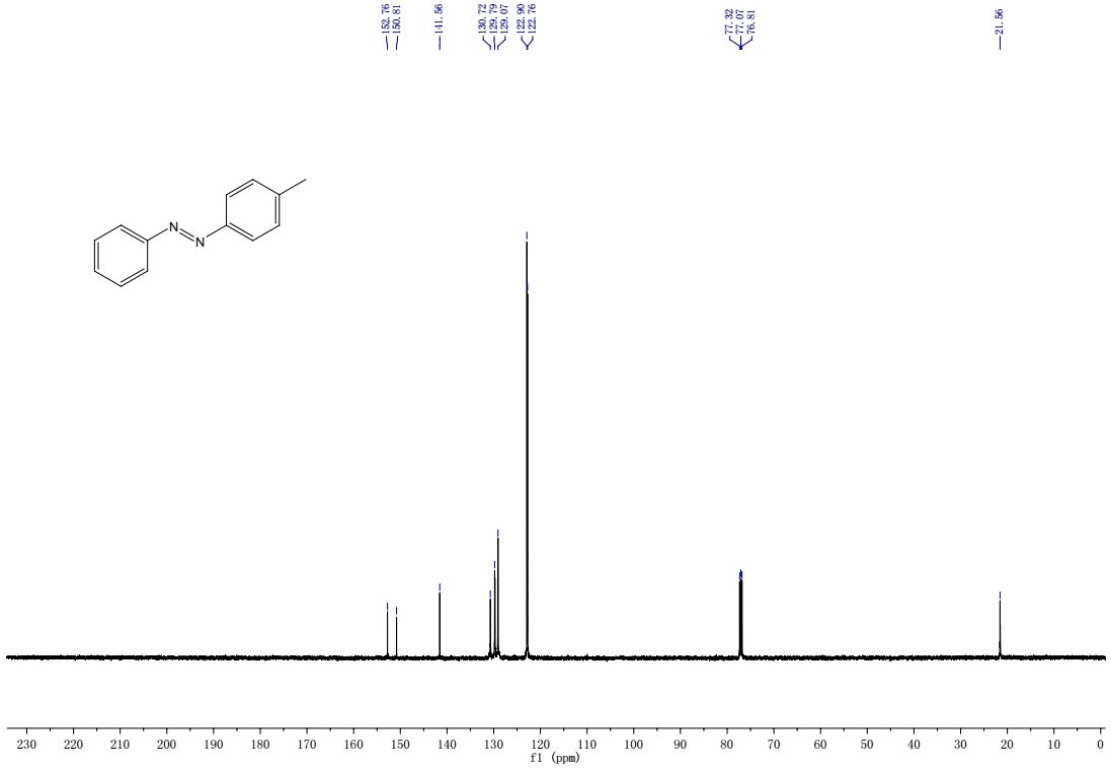




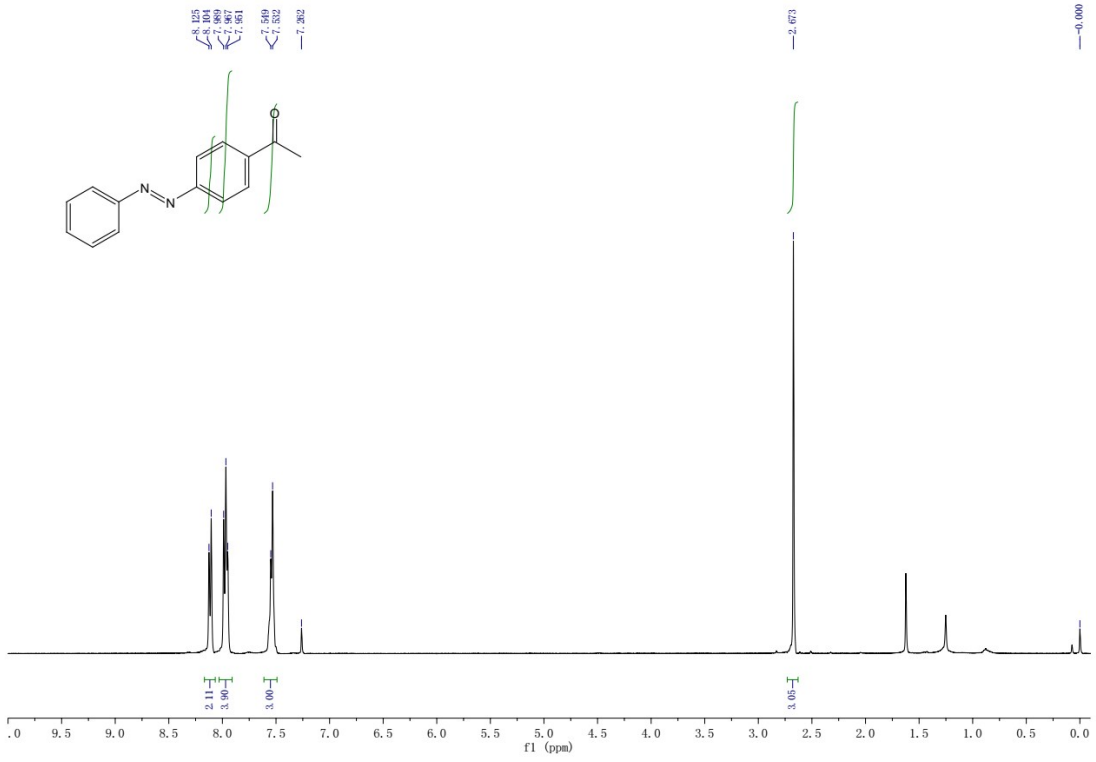
400 MHz ^{1}H NMR for Coumpound 14



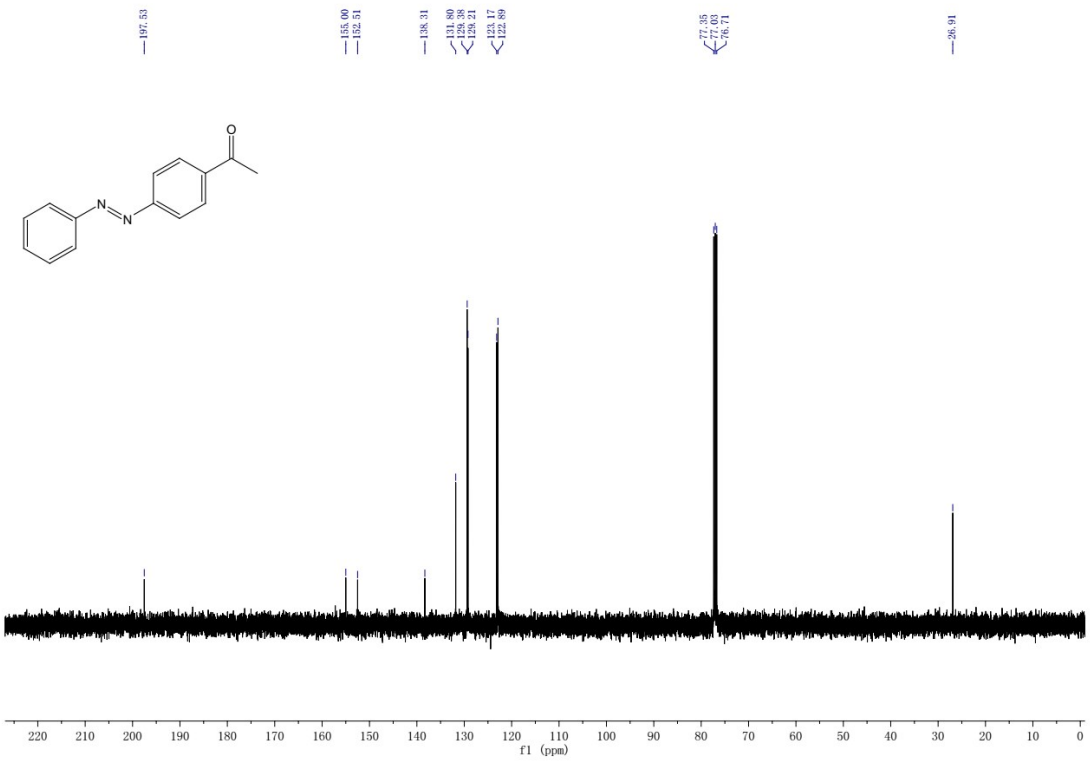
100 MHz ^{13}C NMR for Compound 14



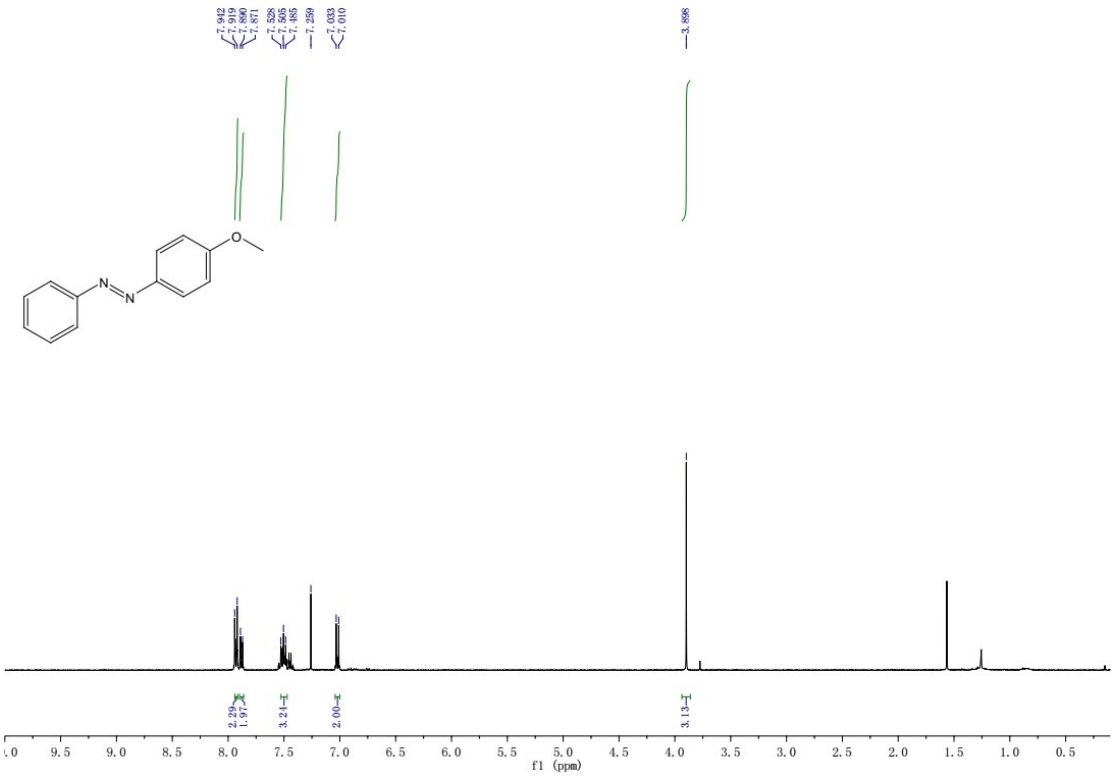
400 MHz ^{1}H NMR for Compound 15



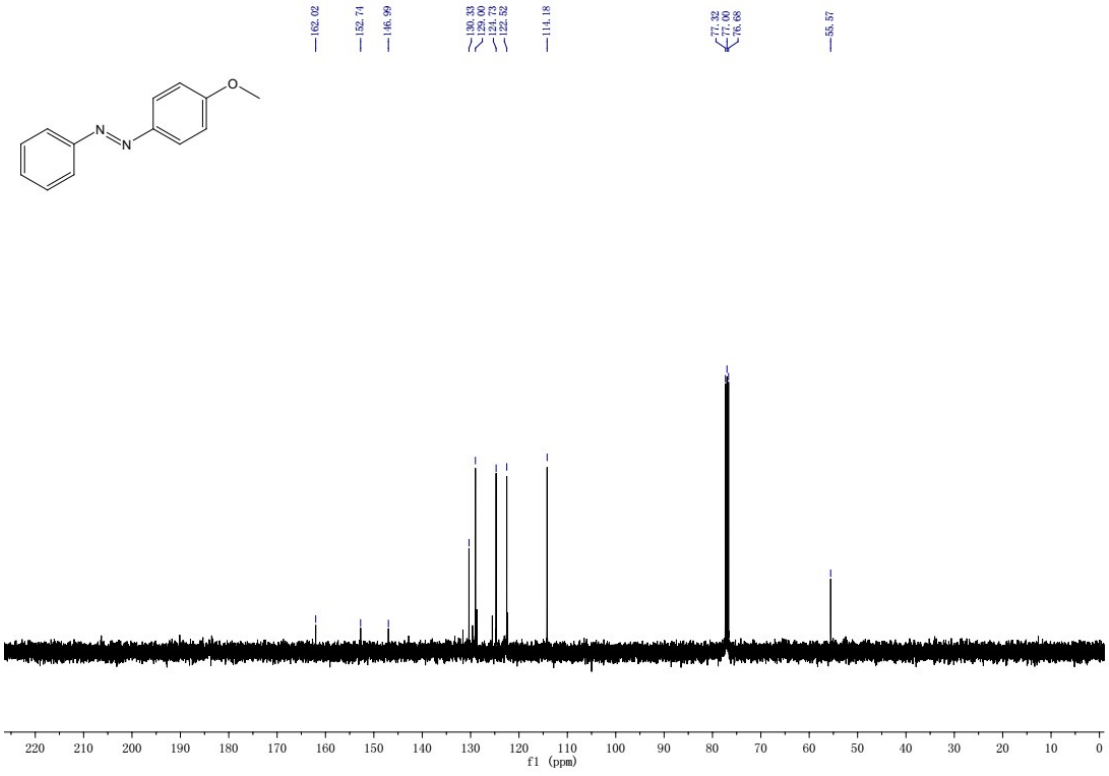
100 MHz ^{13}C NMR for Compound 15



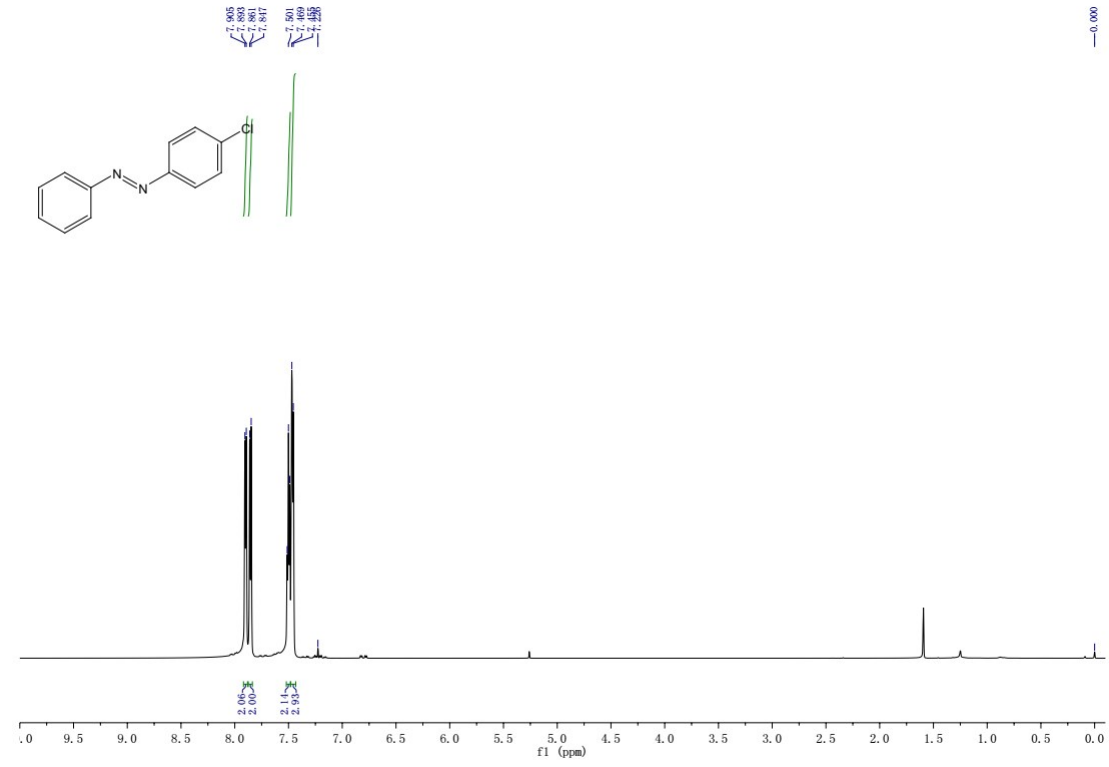
400 MHz ^{1}H NMR for Compound 16



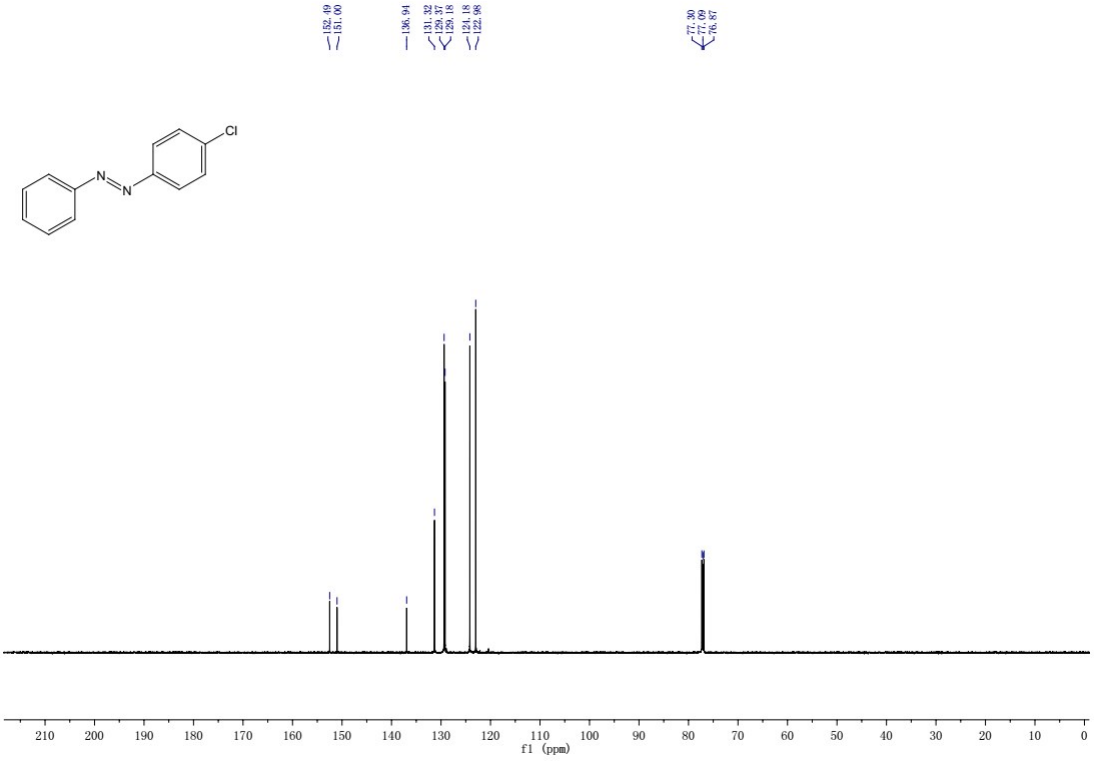
100 MHz ^{13}C NMR for Compound 16



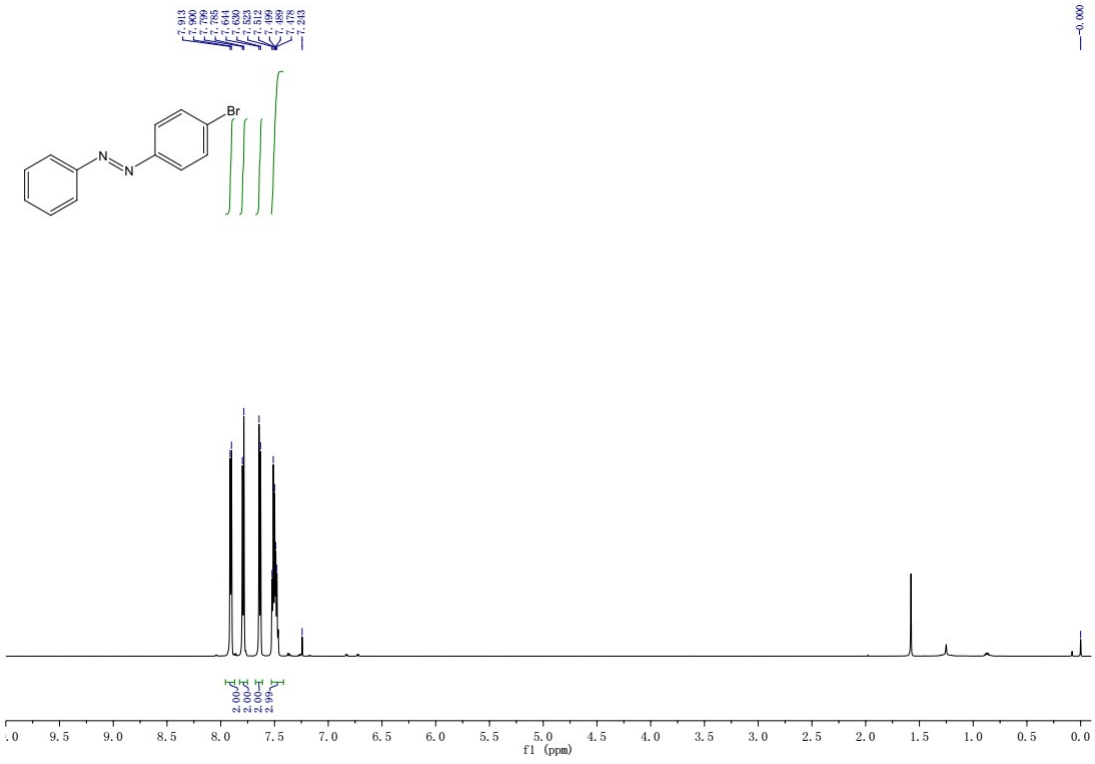
600 M ^{1}H NMR for Compound 17



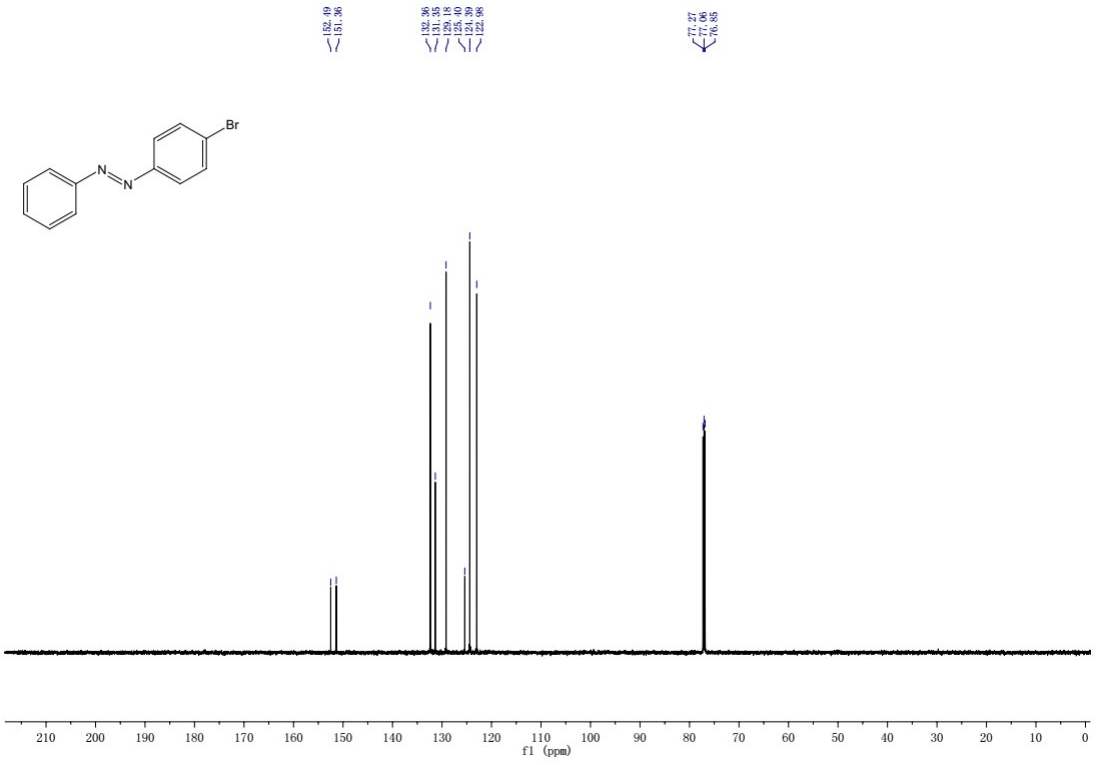
150 M ^{13}C NMR for Compound 17



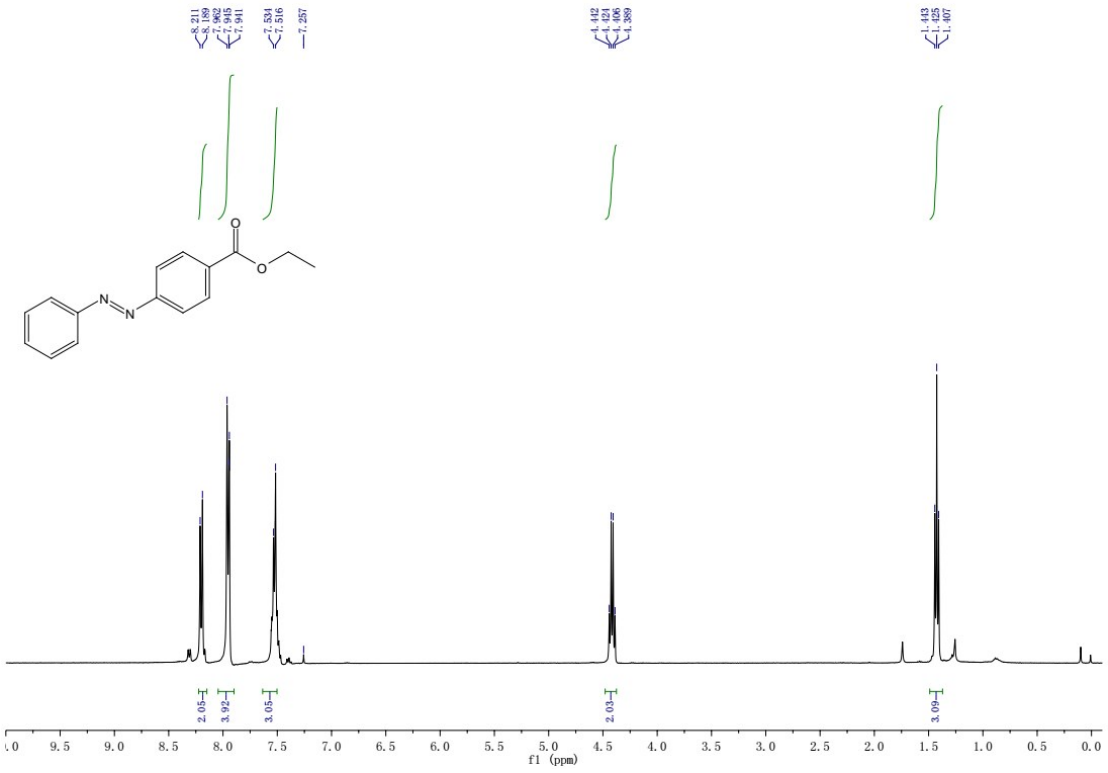
600 MHz ^{1}H NMR for Compound 18



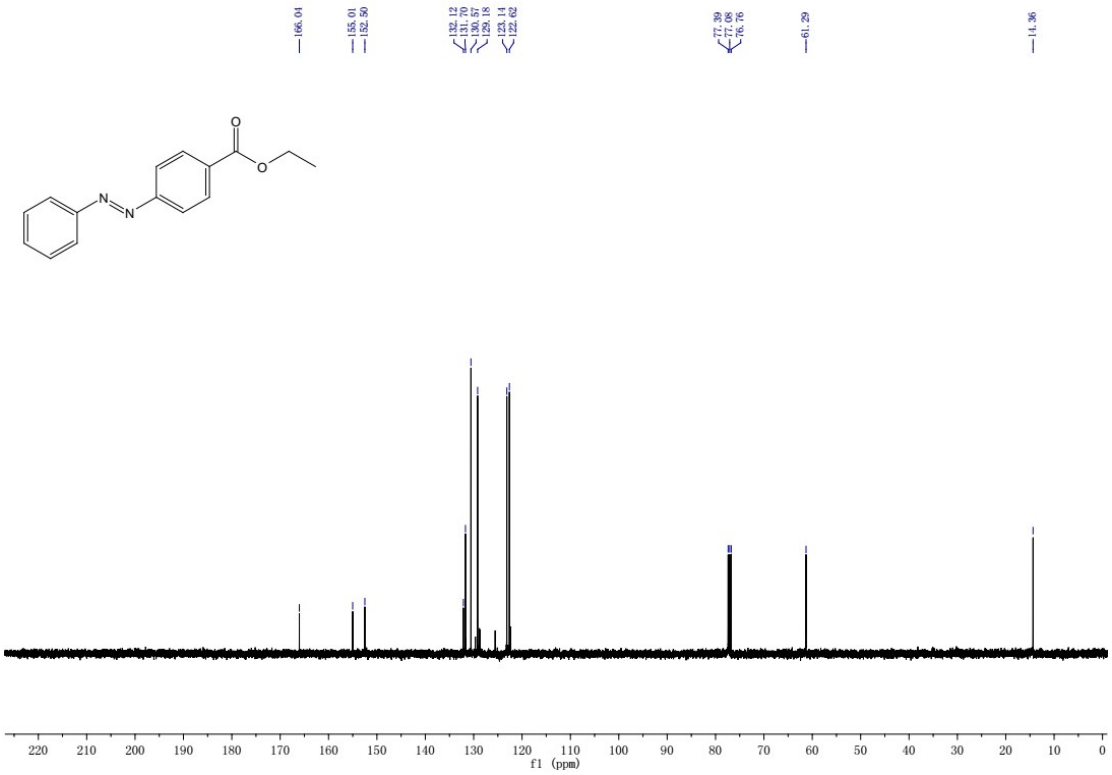
150 MHz ^{13}C NMR for Compound 18



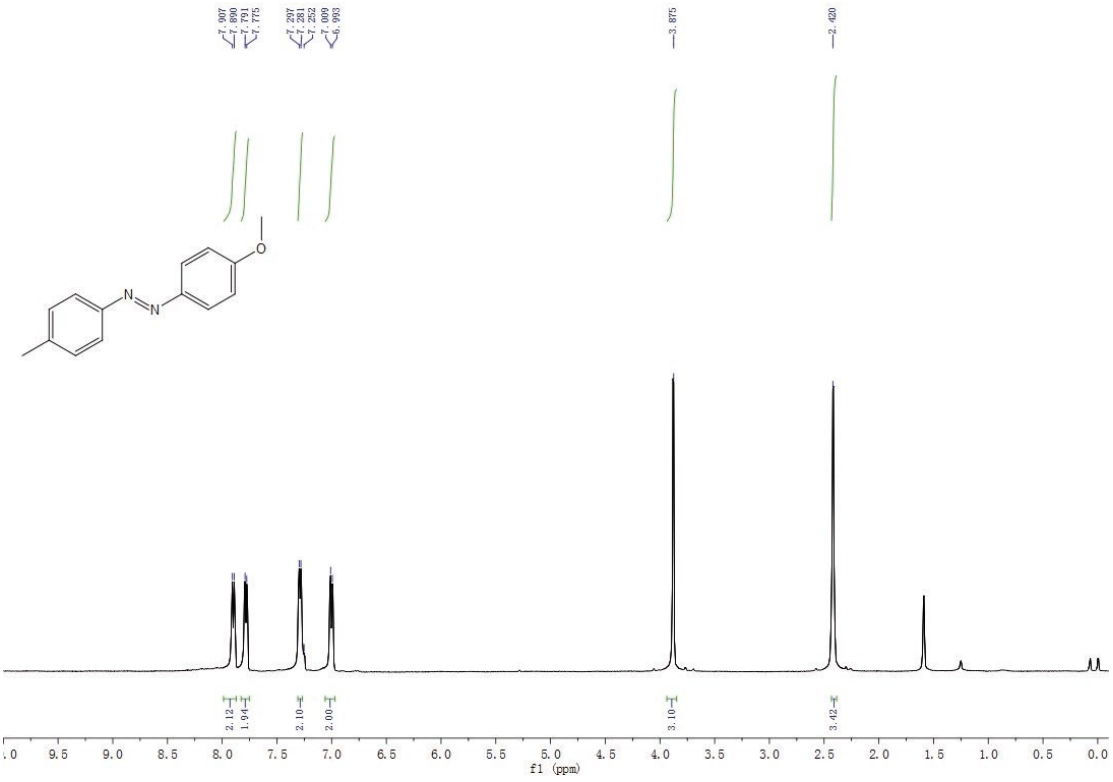
400 MHz ^{1}H NMR for Compound 19



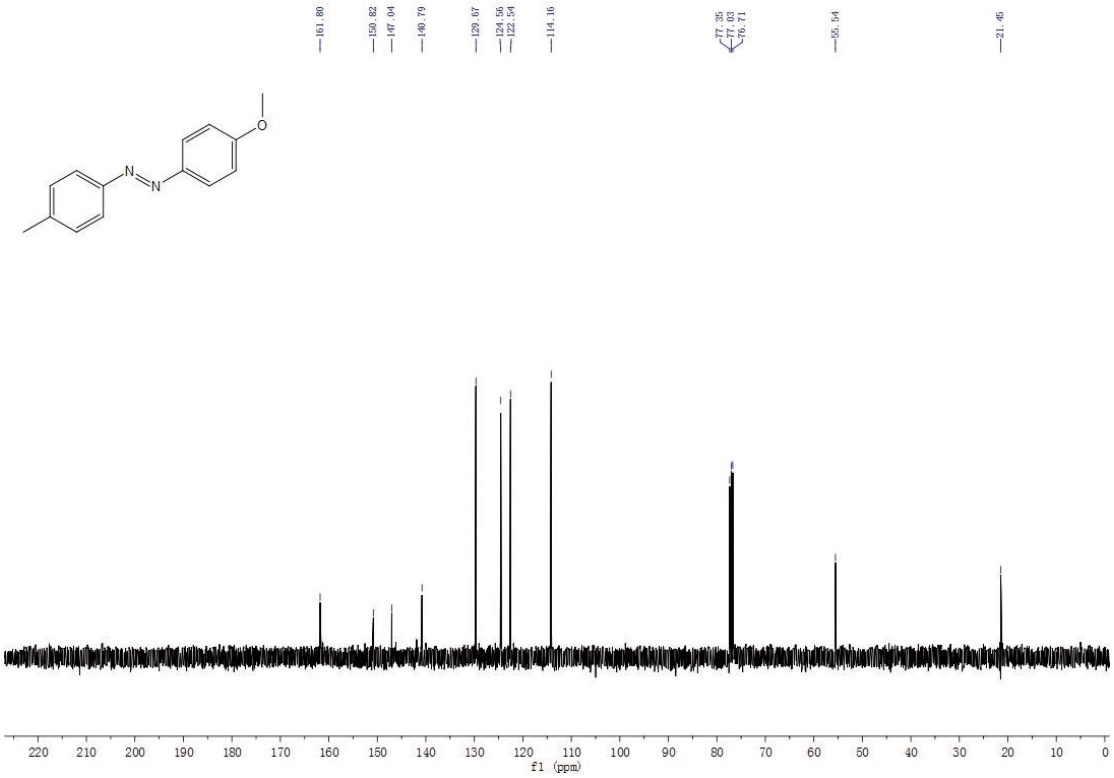
100 MHz ^{13}C NMR for Compound 19



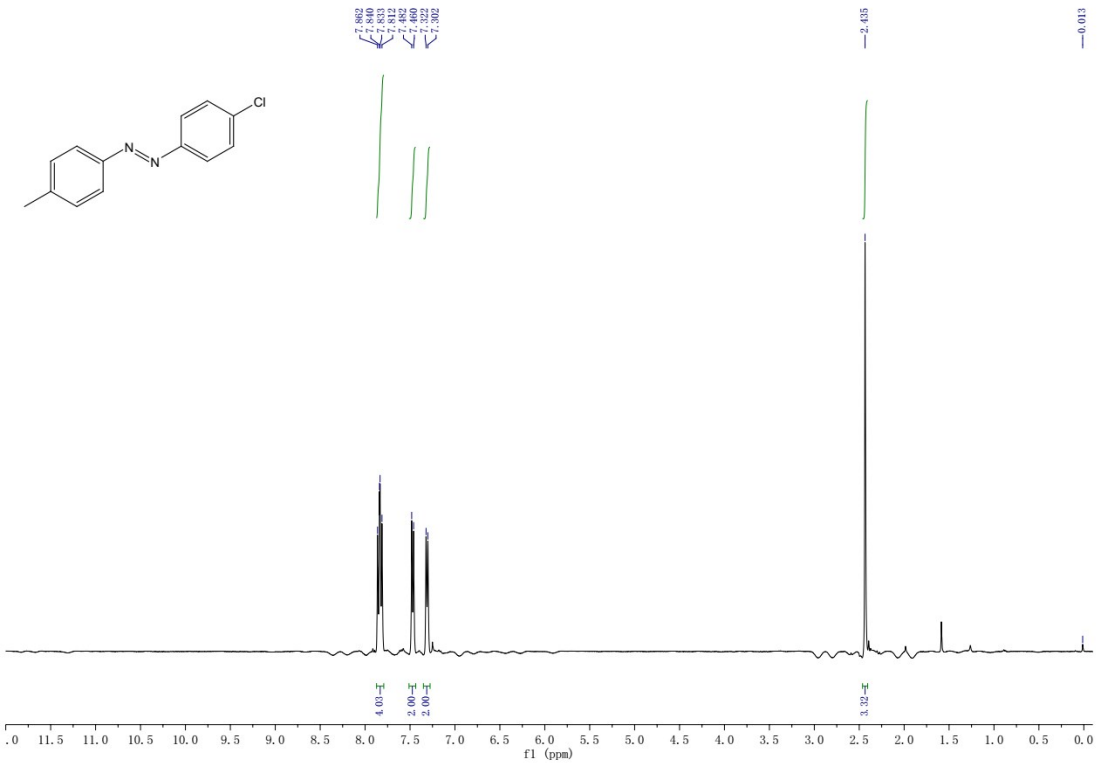
400 MHz ^{1}H NMR for Compound 20



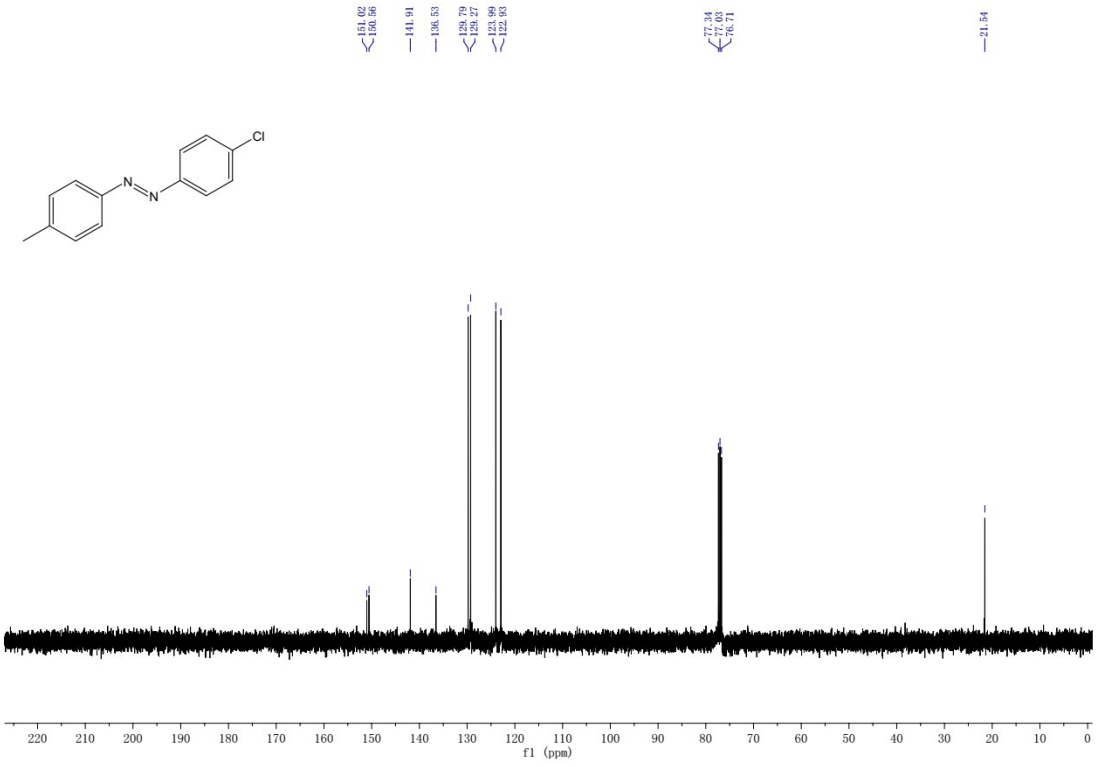
100 MHz ^{13}C NMR for Compound 20



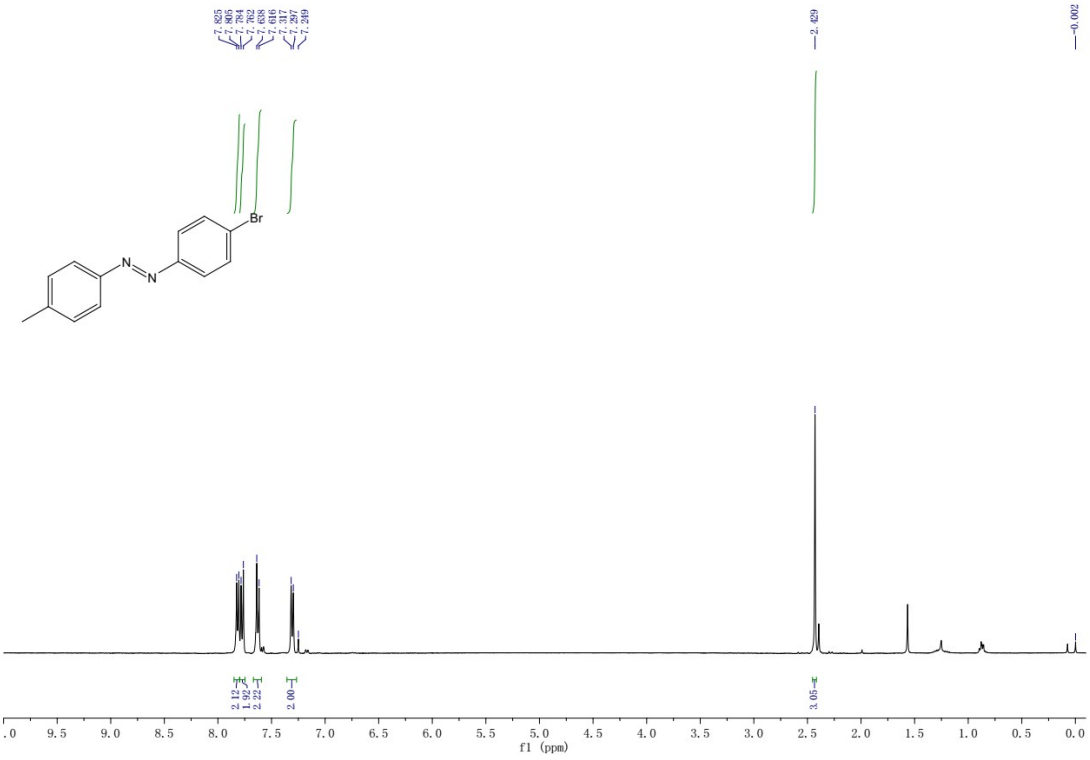
400 MHz ^{1}H NMR for Compound 21



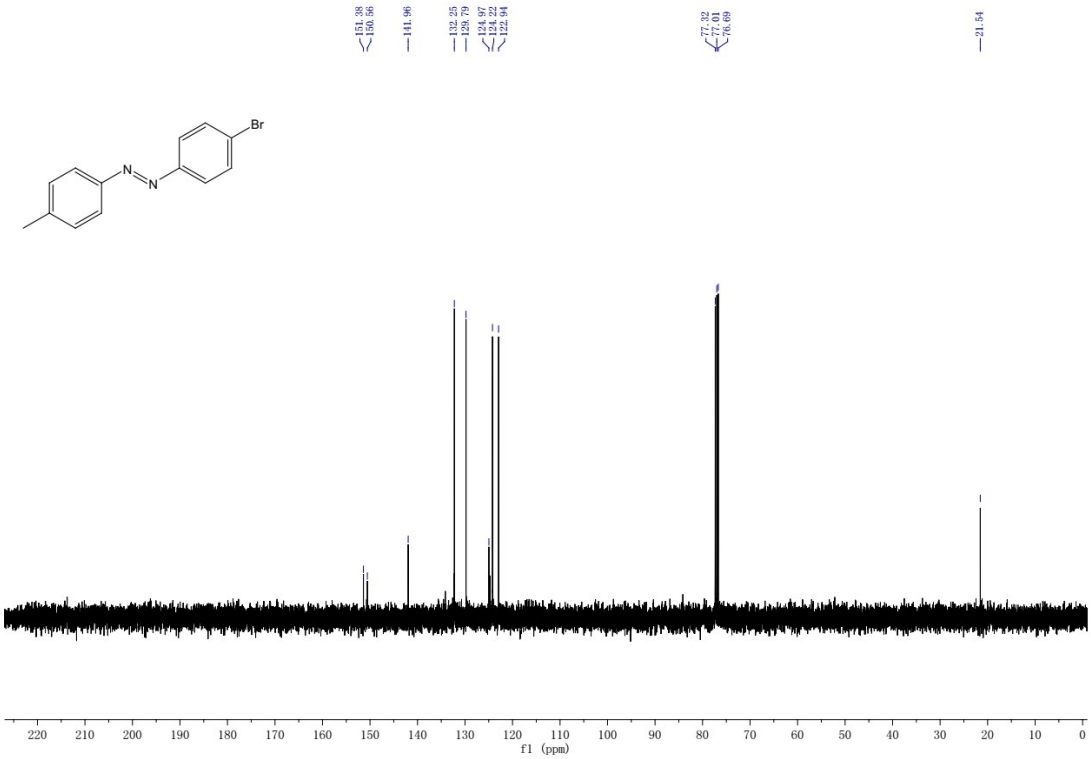
100 MHz ^{13}C NMR for Compound 21



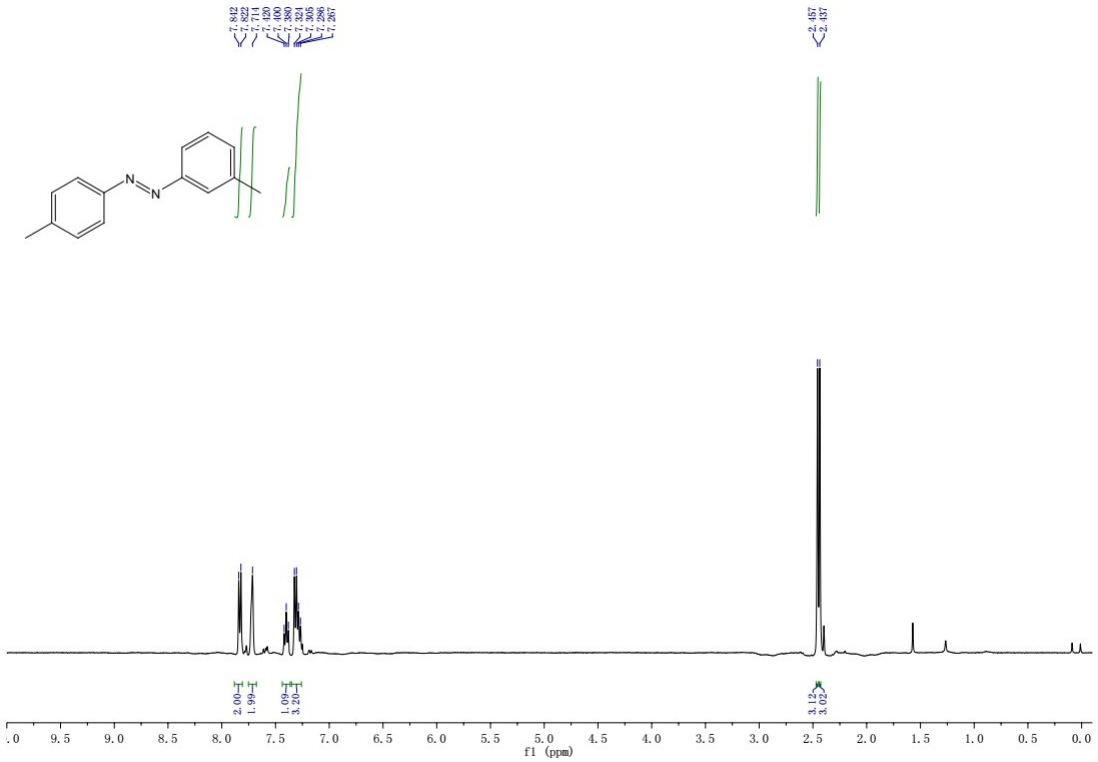
400 MHz ^{1}H NMR for Compound 22



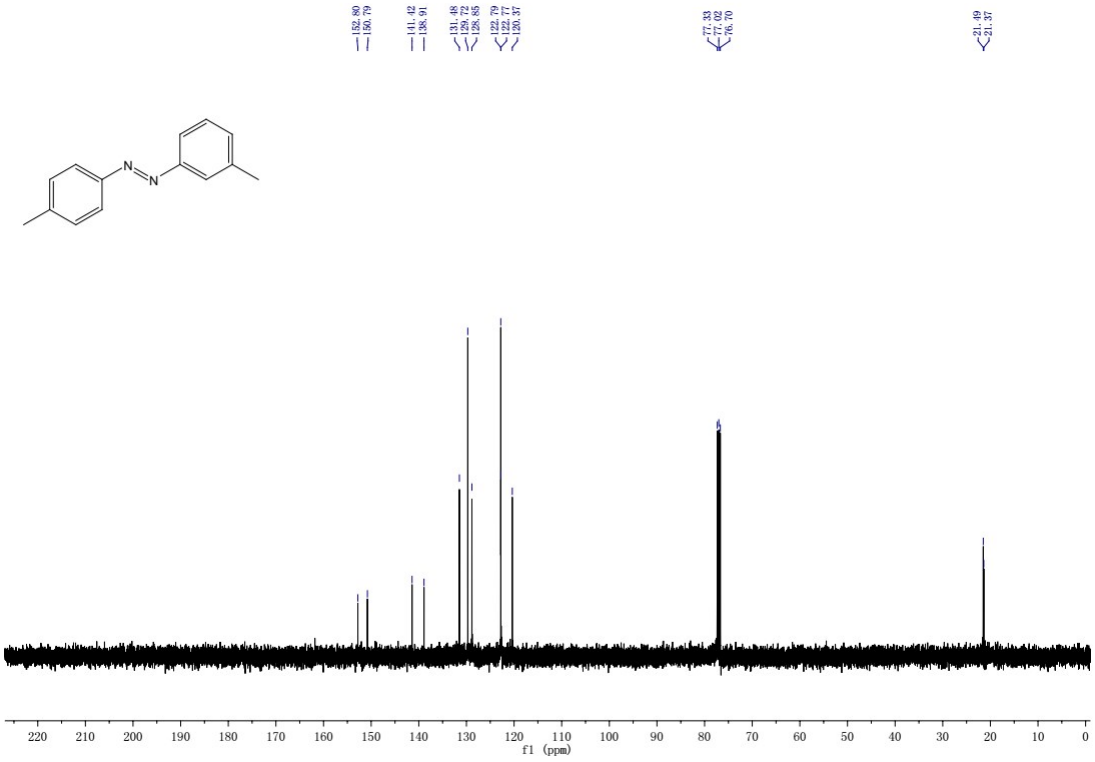
100 MHz ^{13}C NMR for Compound 22



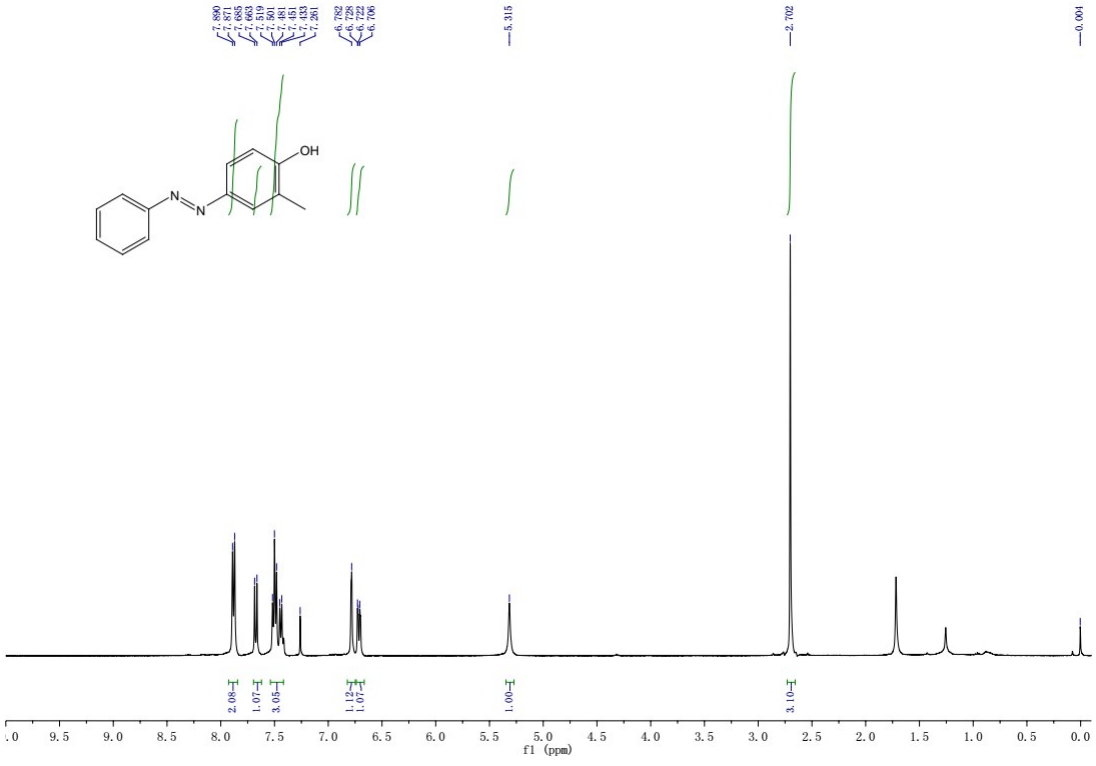
400 MHz ^{1}H NMR for Compound 23



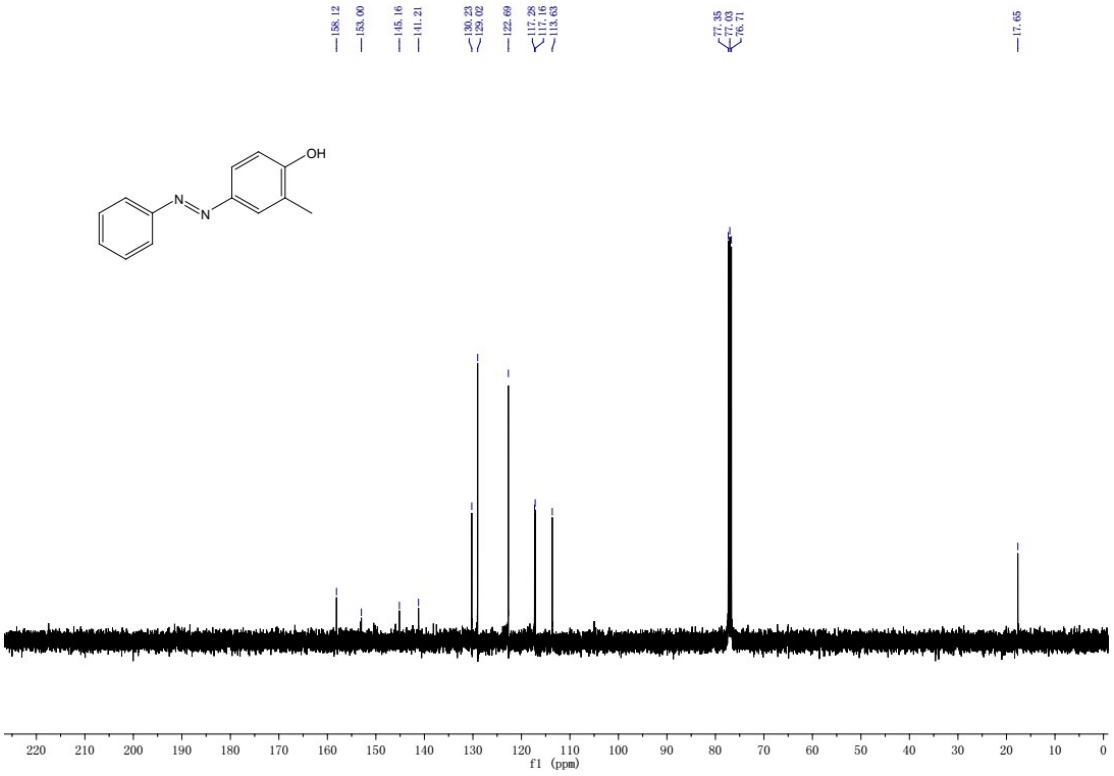
100 MHz ^{13}C NMR for Compound 23



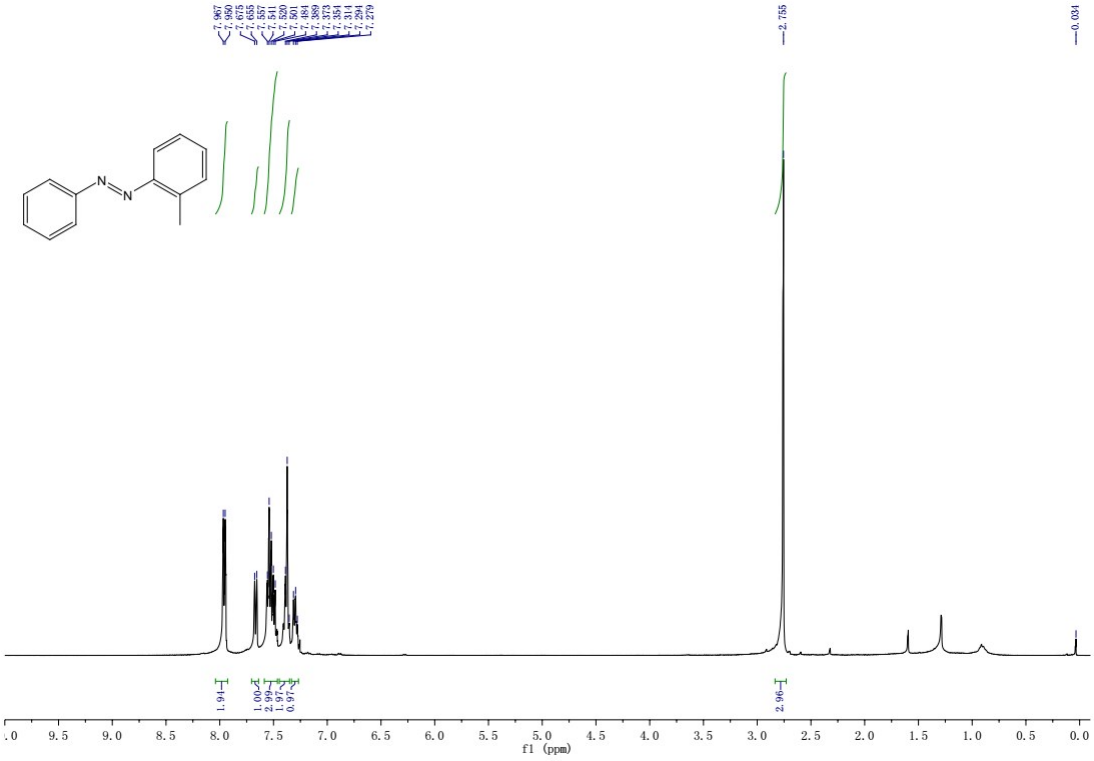
400 MHz ^{1}H NMR for Coumpound 24



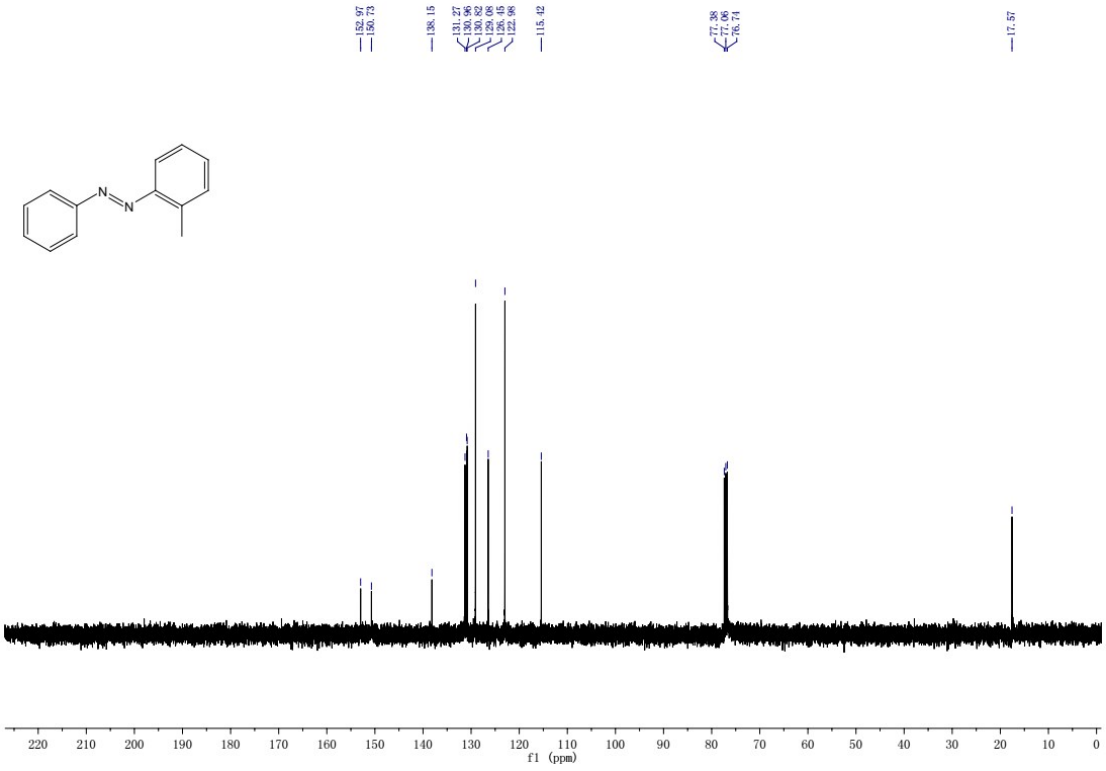
100 MHz ^{13}C NMR for Compound 24



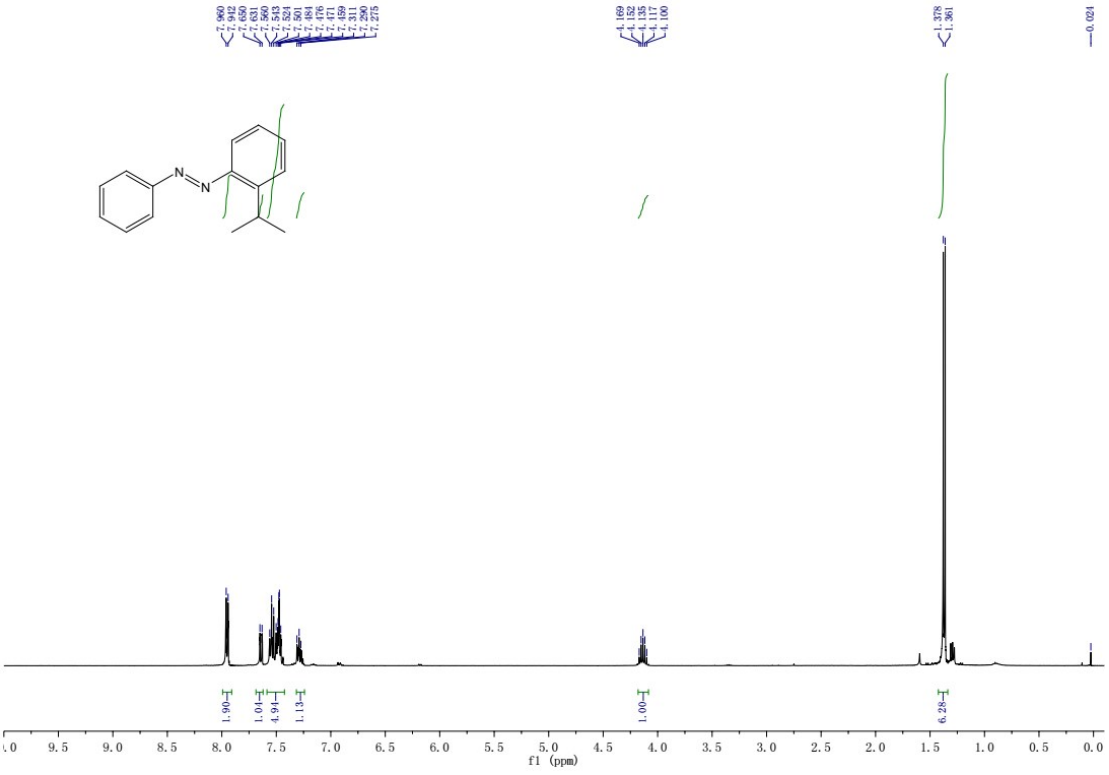
400 MHz ^{1}H NMR for Coumpound 25



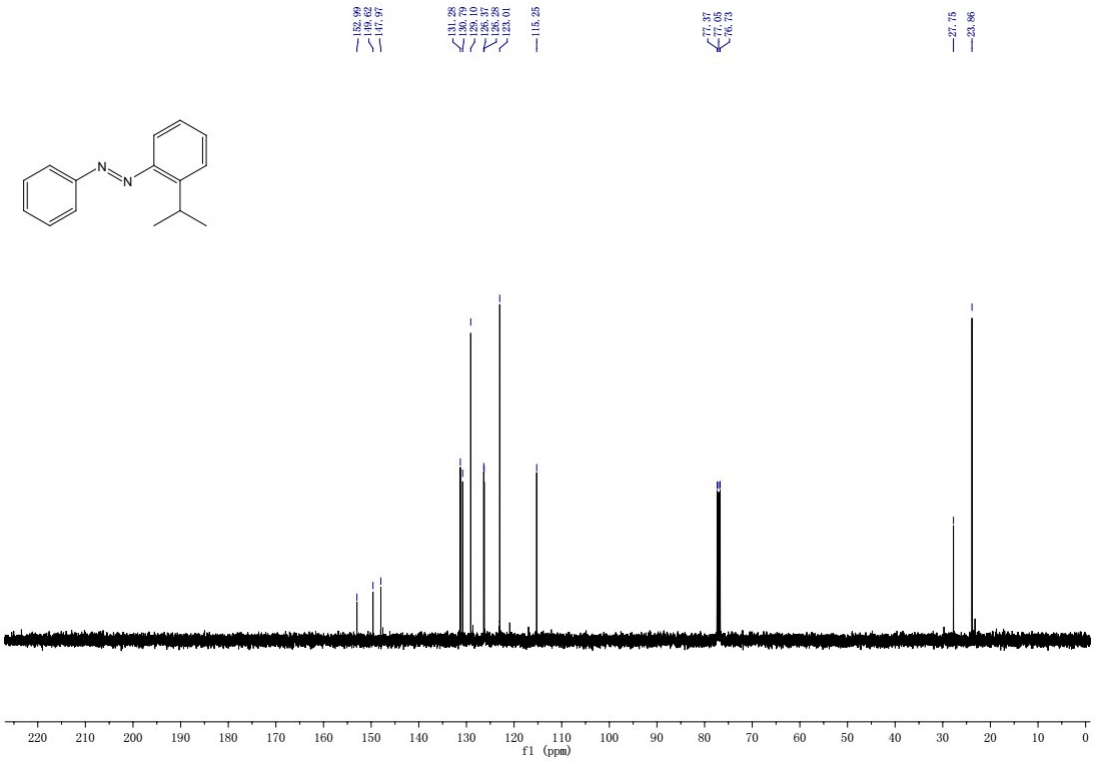
100 MHz ^{13}C NMR for Compound 25



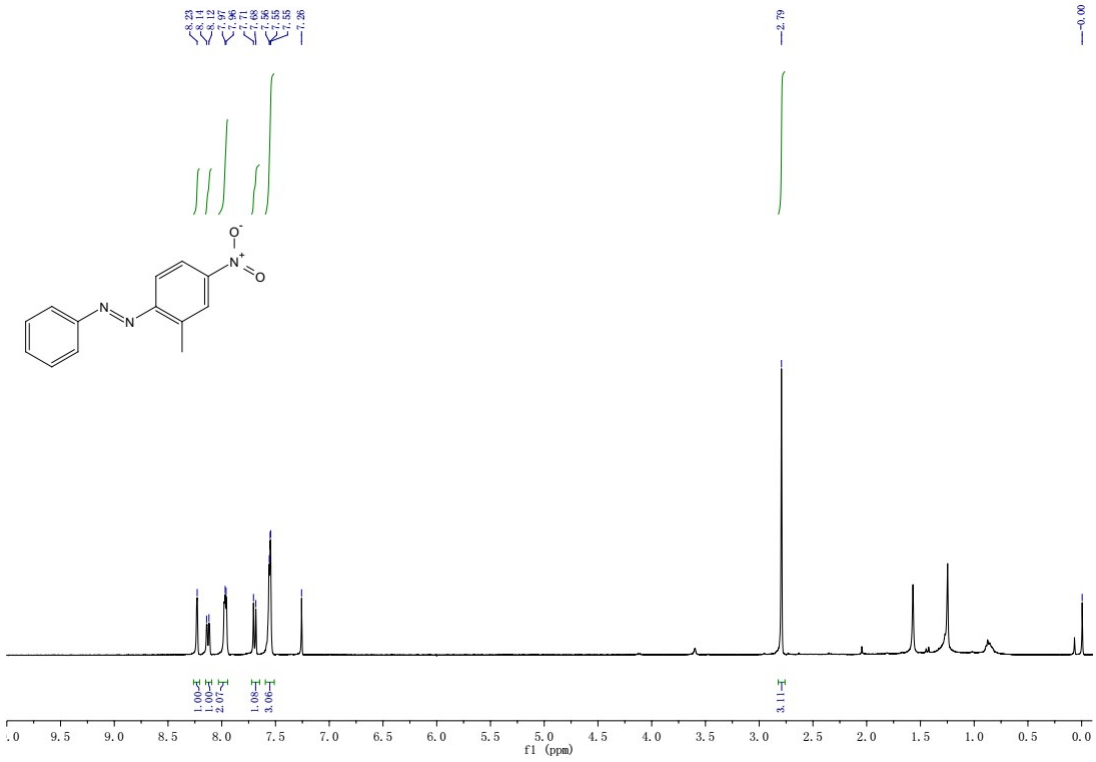
400 MHz ^{1}H NMR for Coumpound 26



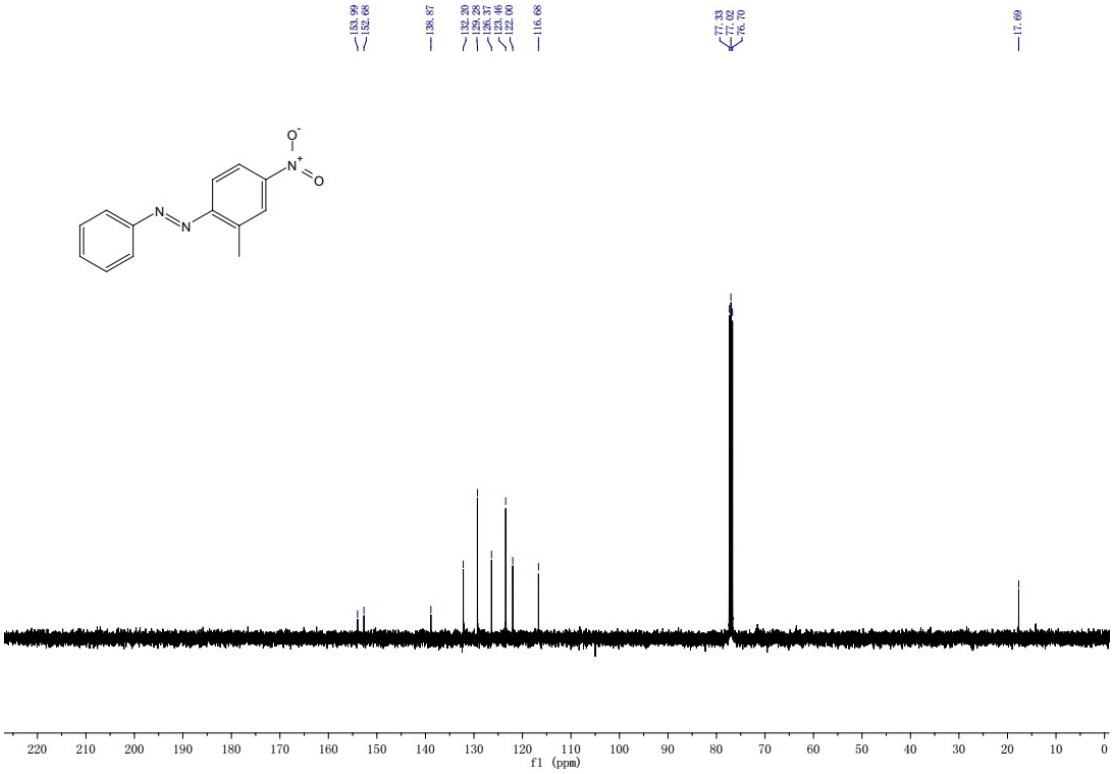
100 MHz ^{13}C NMR for Compound 26



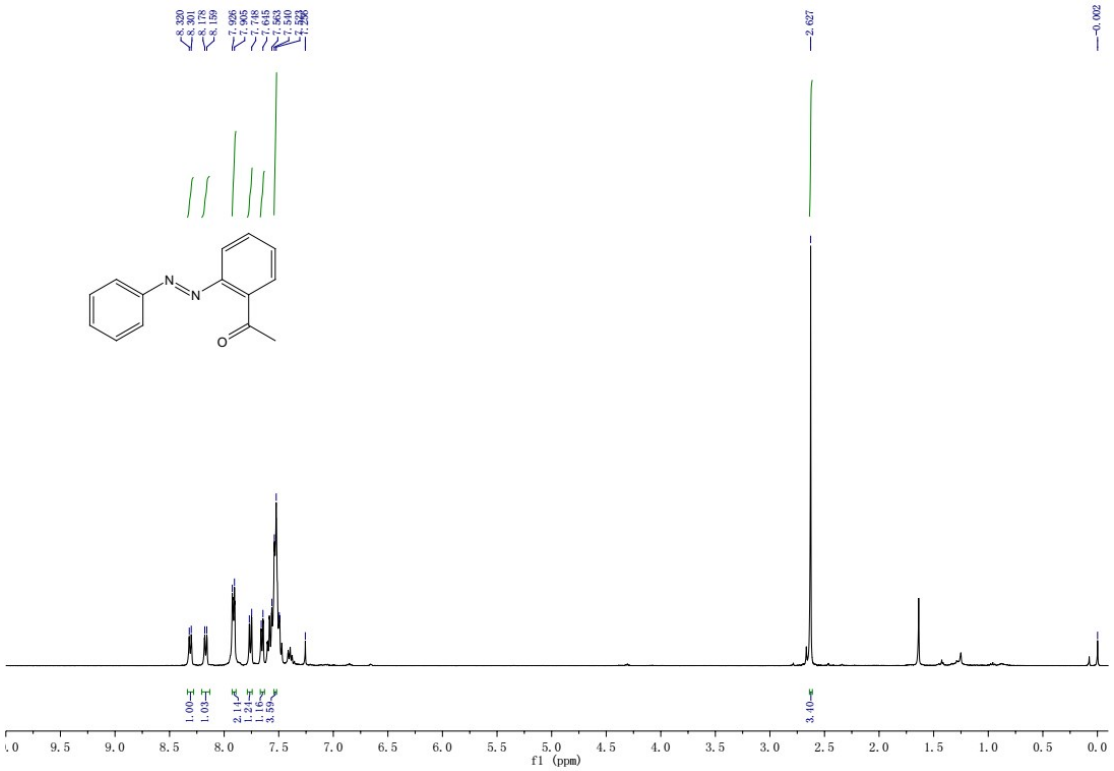
400 MHz ^{1}H NMR for Coumpound 27



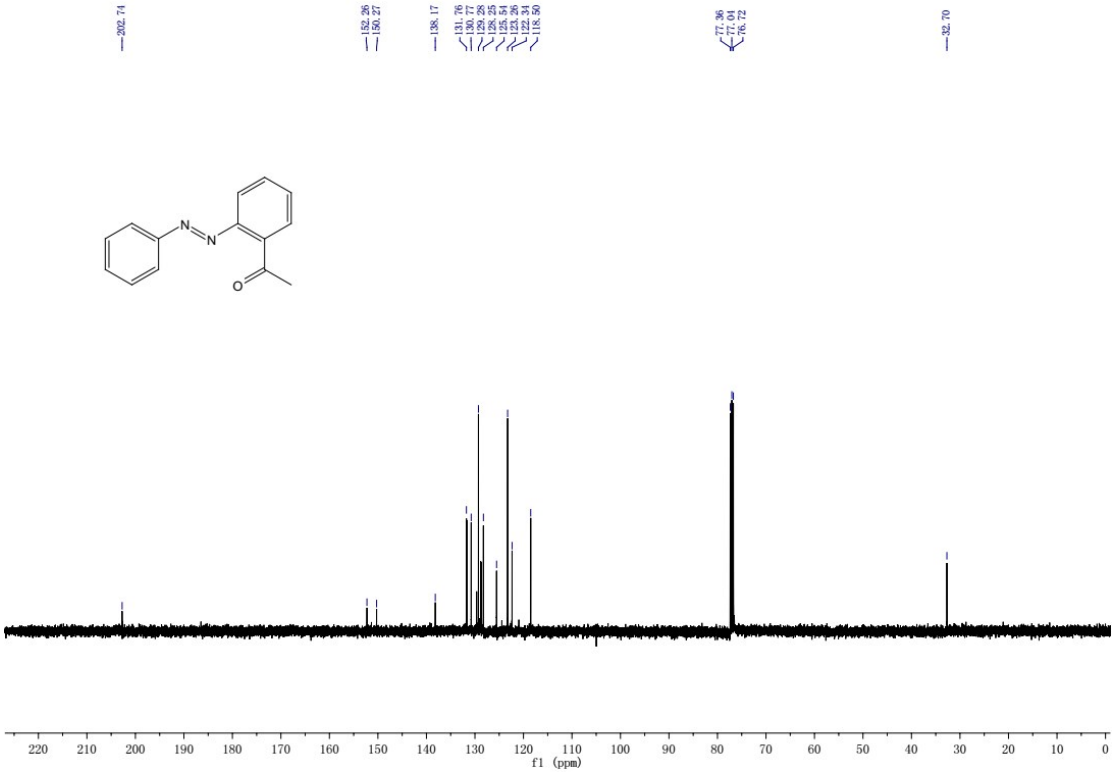
100 MHz ^{13}C NMR for Compound 27



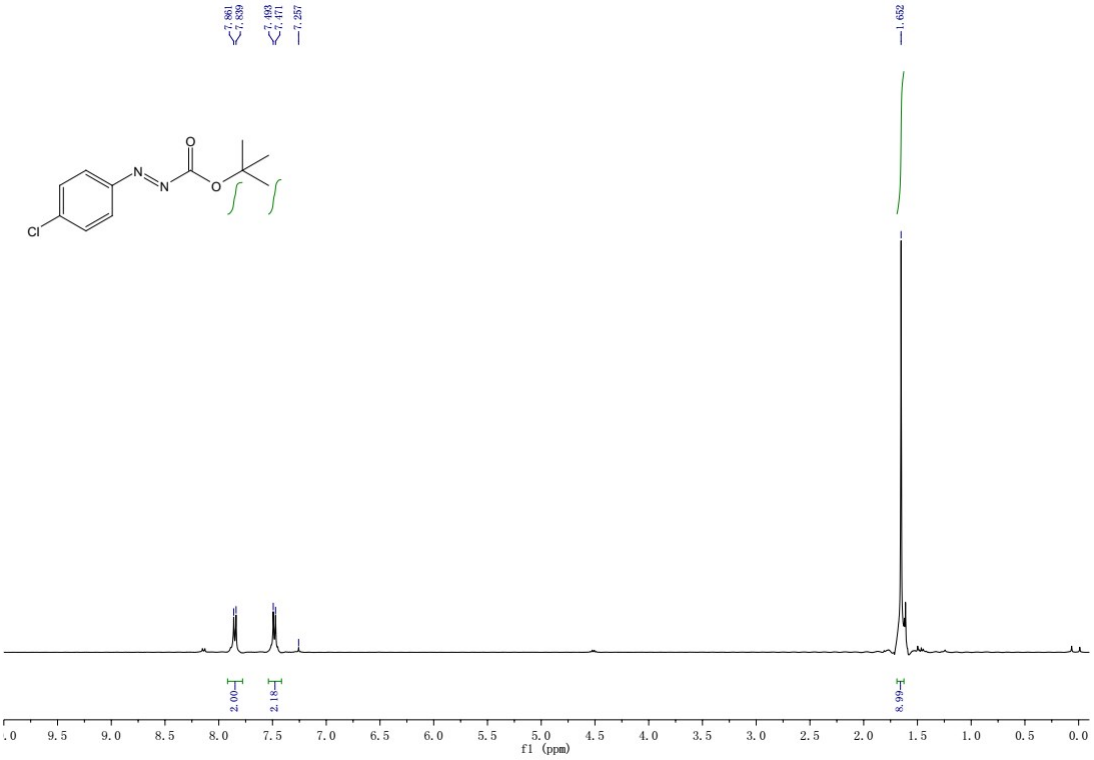
400 MHz ^{1}H NMR for Coumpound 28



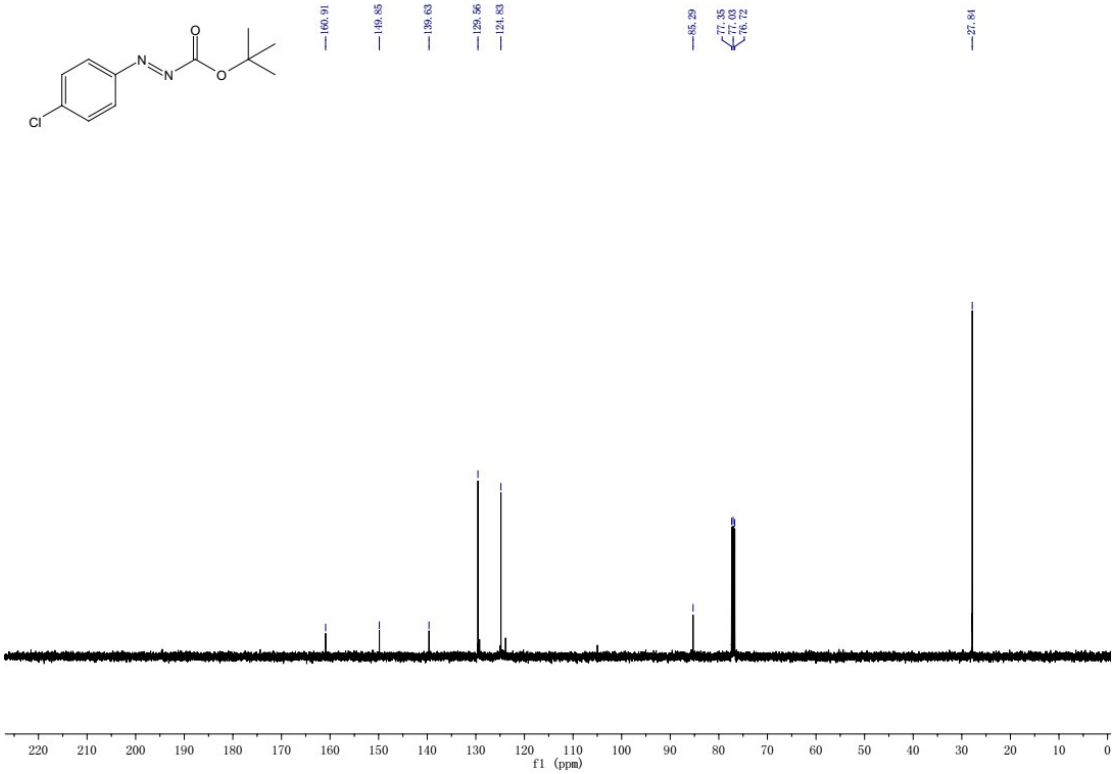
100 MHz ^{13}C NMR for Compound 28



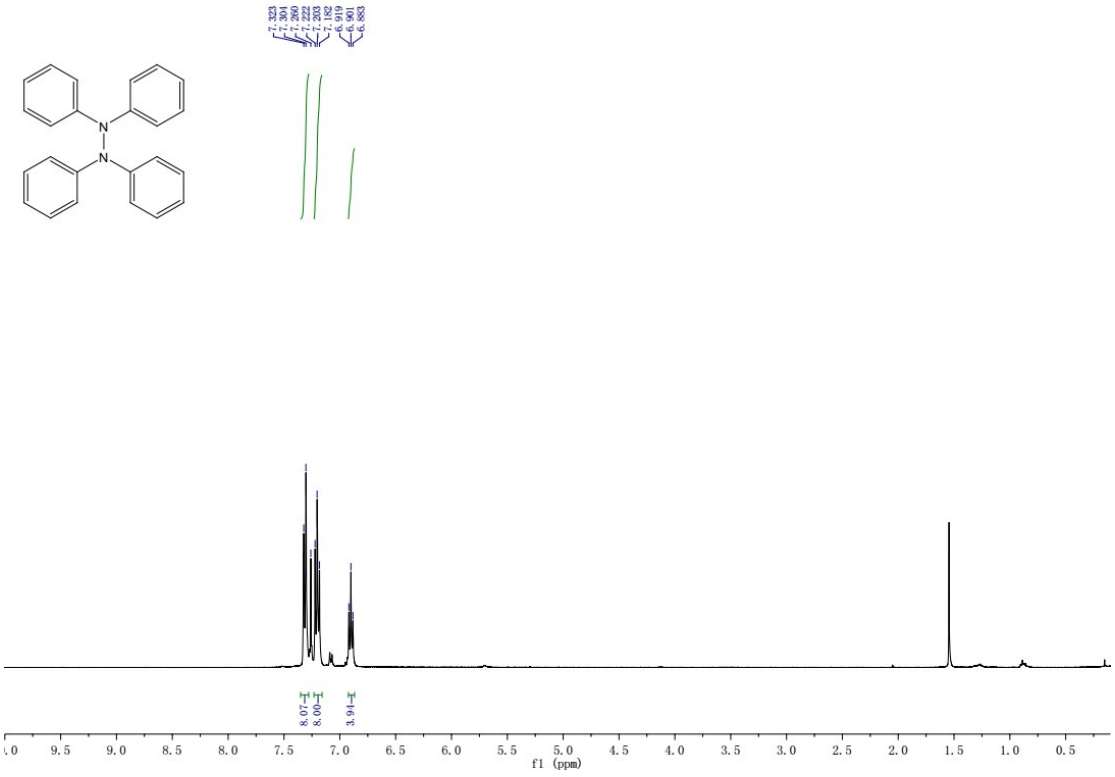
400 MHz ^{1}H NMR for Coumpound 29



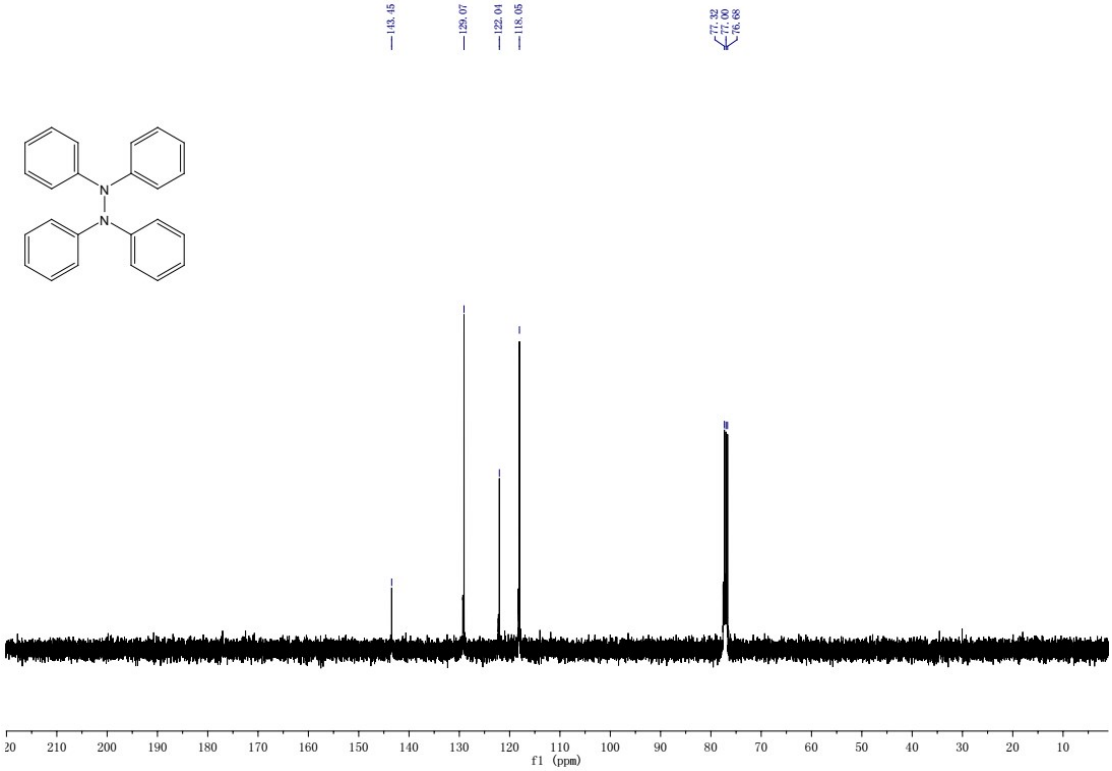
100 MHz ^{13}C NMR for Compound 29



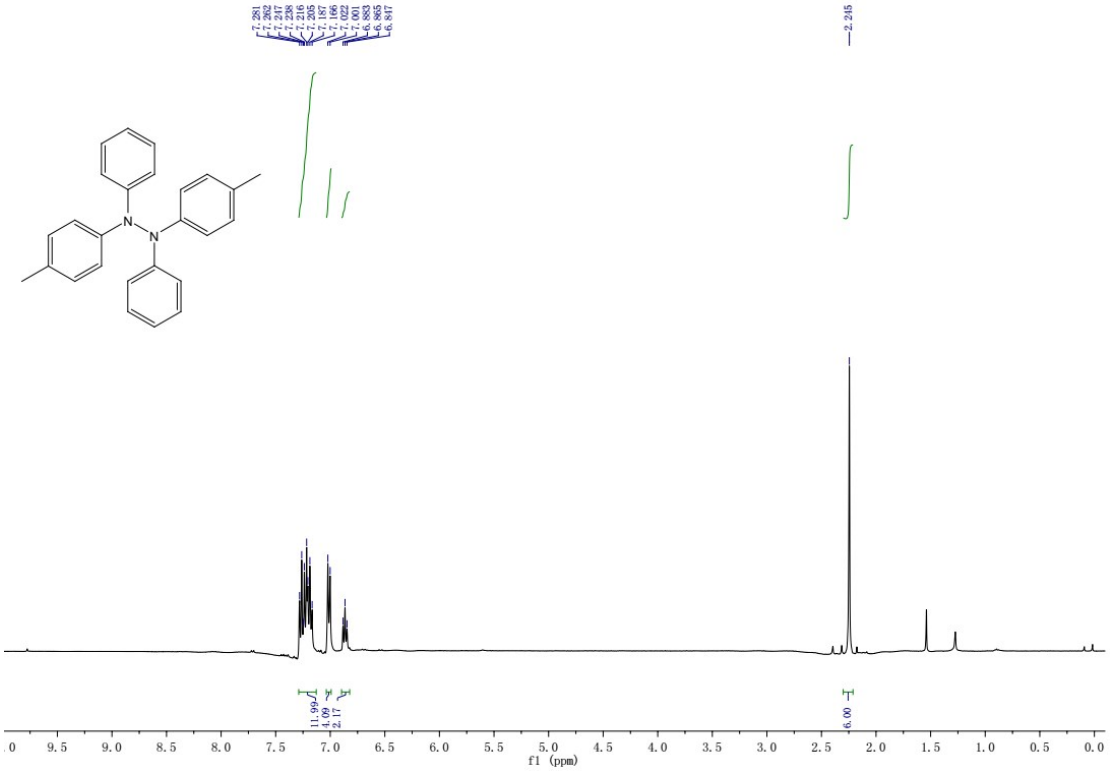
400 MHz ^{1}H NMR for Compound 30



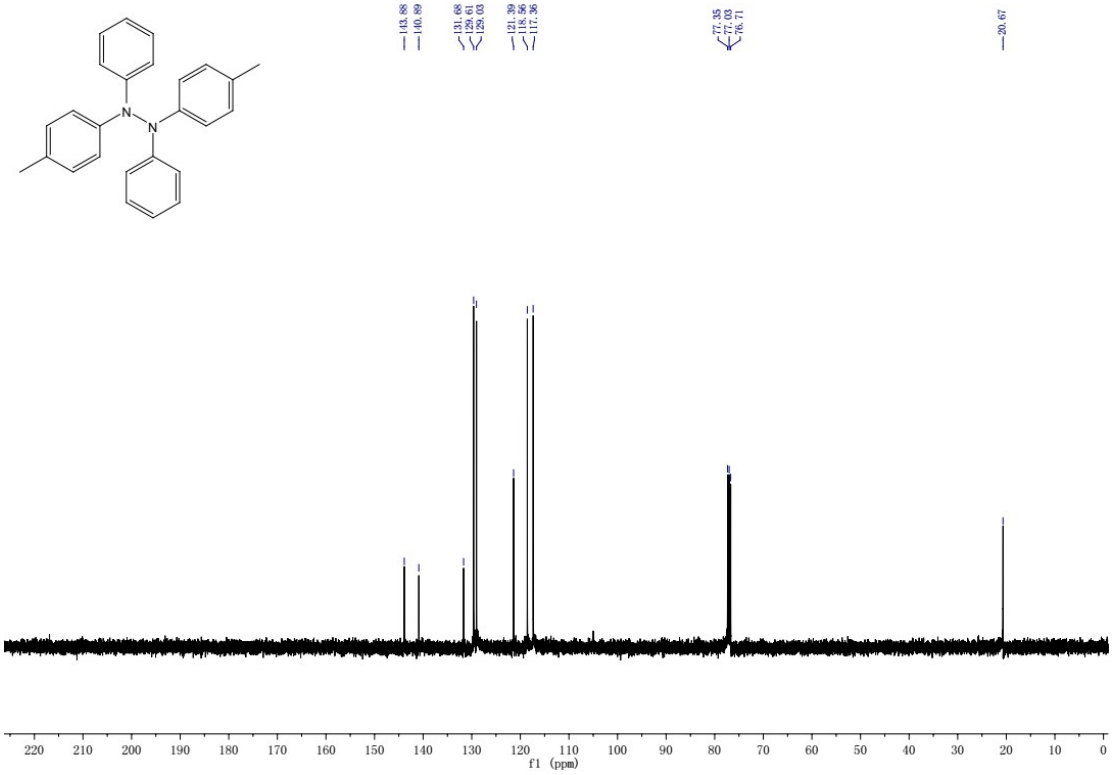
100 MHz ^{13}C NMR for Compound 30



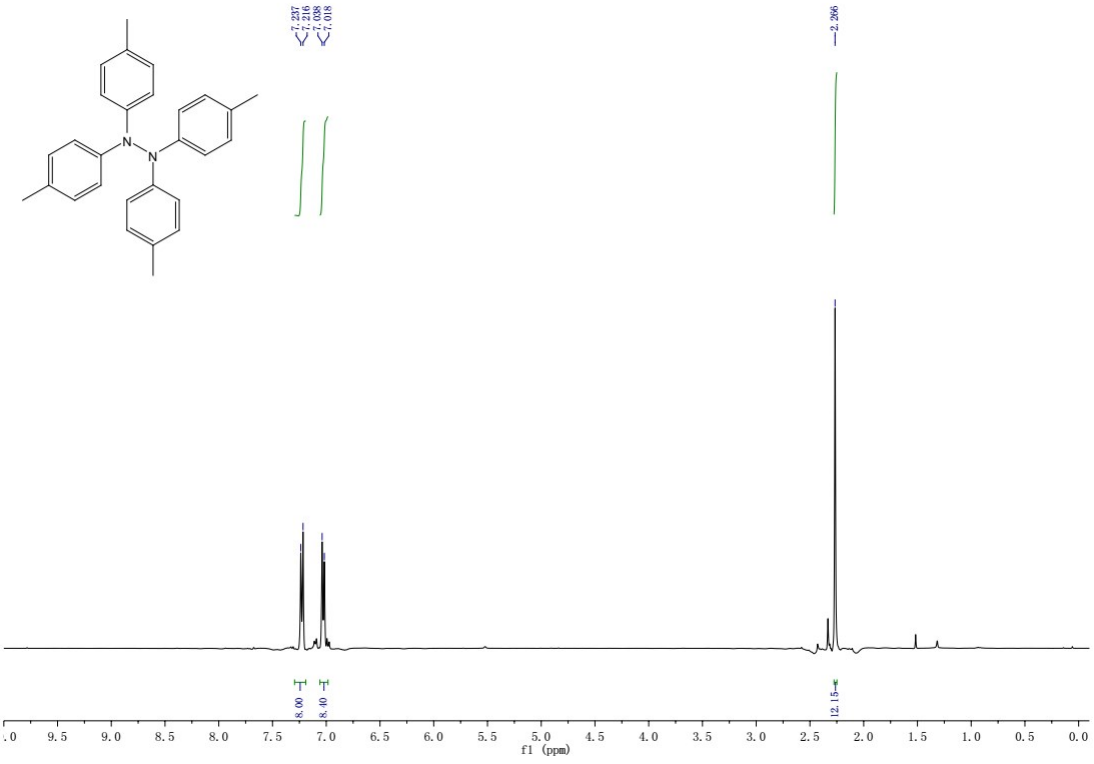
400 MHz ^{1}H NMR for Compound 31



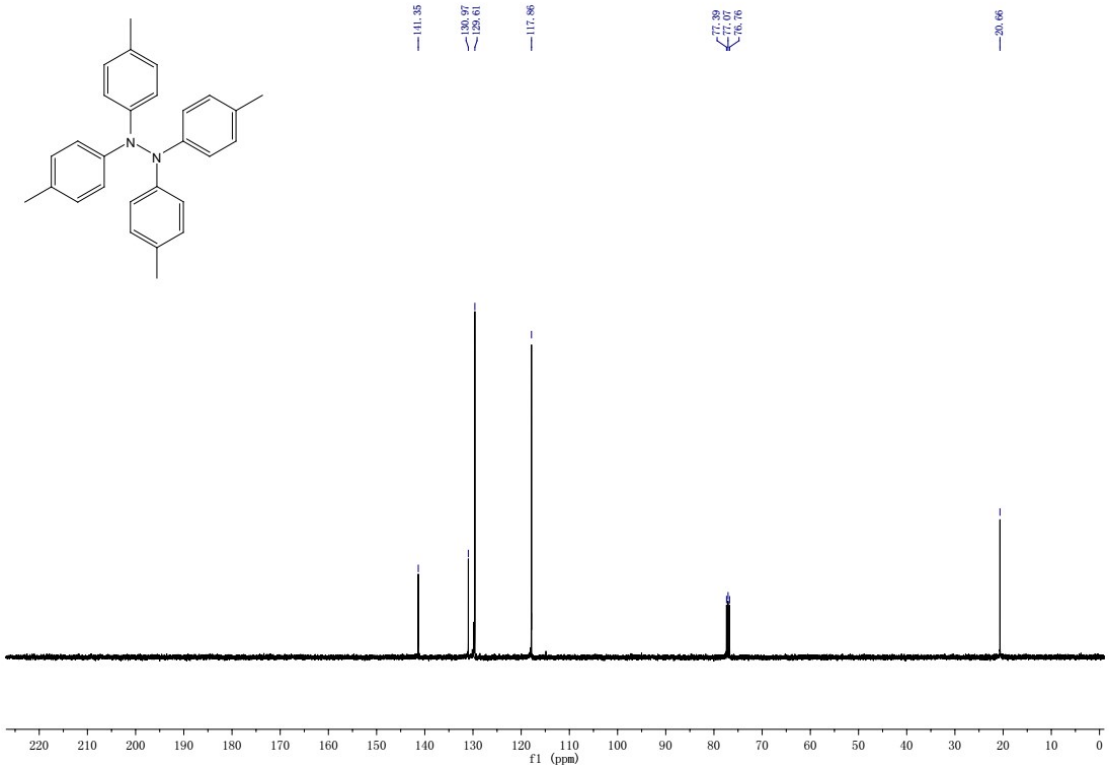
100 MHz ^{13}C NMR for Compound 31



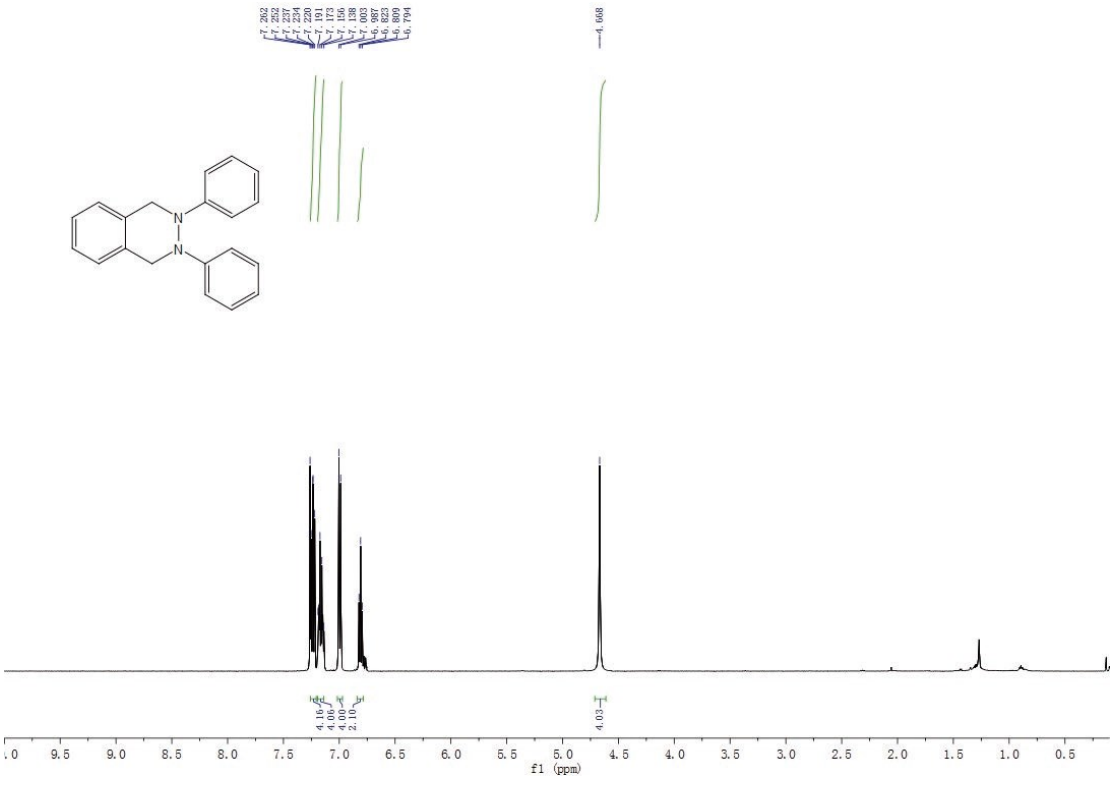
400 MHz ^{1}H NMR for Compound 32



100 MHz ^{13}C NMR for Compound 32



400 MHz ^{1}H NMR for Compound 33



100 MHz ^{13}C NMR for Compound 33