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Supporting Information

Divergent synthesis of unsymmetrical azobenzenes via Cu-catalyzed C−N coupling

Yuzhou Wang, Rongrong Xie, Lingyu Huang, Ya-Nan Tian, Shihai Lv, Xiangfei Kong and Shiqing Li*

Guangxi Key Laboratory of Electrochemical and Magneto-Chemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, P. R. China.

E-mail: lisq@glut.edu.cn

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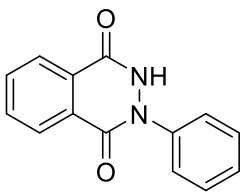
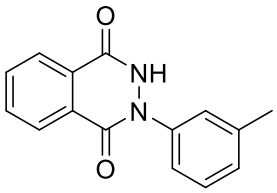
I. General remarks

NMR spectra were obtained on a BRUKER Ascend500. The ^{1}H NMR (500 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (126 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HR-MS) were obtained with a BRUKER solanX 70 FT-MS (ESI^+). Melting points were determined with SGW® X-4 and are uncorrected.

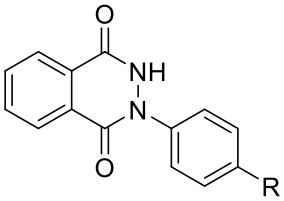
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Phthalic anhydride, arylhydrazine, arylboronic acids and copper salts were purchased from Beijing Innochem Chemical Engineering Reagent (China) Co., Ltd. TfOH and *m*-CPBA (purity of 75%) were purchased from Adamas-beta Ltd. N-aryl phthalic hydrazide (**1a**, **1c** and **1e**)[1] were prepared according to the literature procedures.



1a

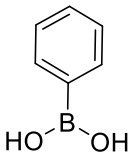


1b

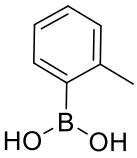


1c-g

1c, R = Me
1d, R = Et
1e, R = ^{t}Bu
1f, R = Br
1g, R = CN



2a



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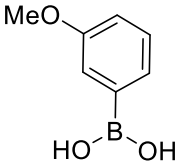

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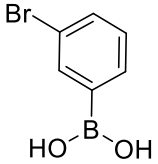
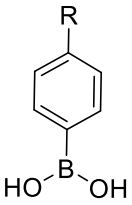
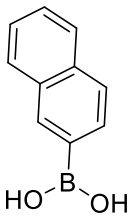


2d

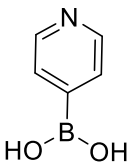


2e-n

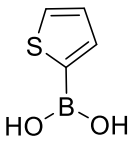
2e, R = Me
2f, R = ^{t}Bu
2g, R = Ph
2h, R = OMe
2i, R = Cl
2j, R = Br
2k, R = COOMe
2l, R = CF_3
2m, R = CN
2n, R = NO_2



2o



2p



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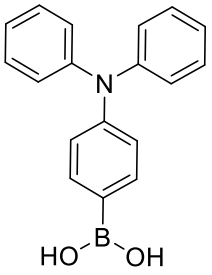
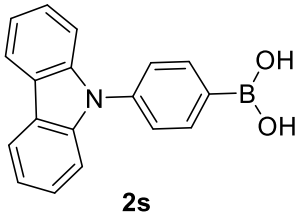
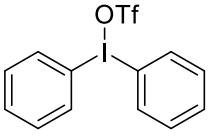


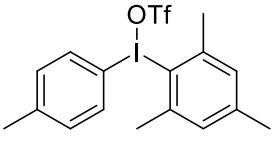
2r



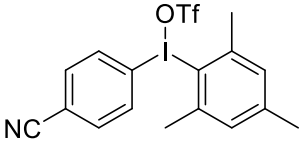
2s



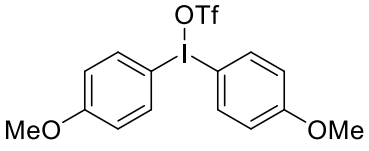
11a



11b

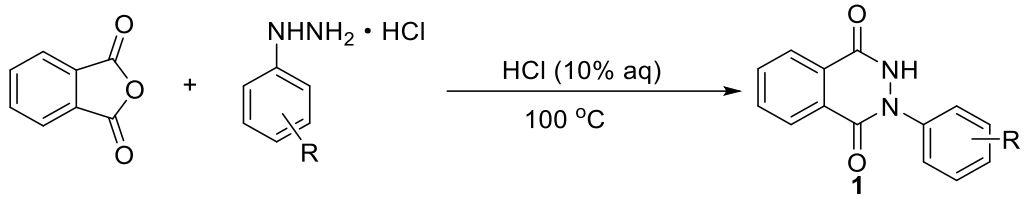


11c



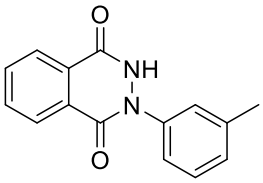
11d

II. General procedure for the synthesis of substrate 1.



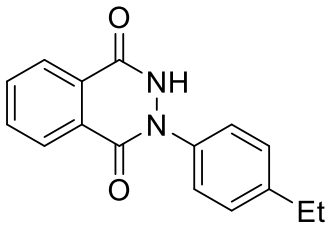
Compounds **1** were prepared according to modified literature procedure:[1] A solution of phthalic anhydride (PA, 1 mmol, 1 equiv, 148 mg) and phenylhydrazine or phenylhydrazine hydrochloride (1.0 mmol, 1equiv, 145 mg) in HCl (10% aq, 3 mL) was reacted at 100 °C for 9 h. The reaction mixture was cooled to room temperature, resulting solid was collected by filtration and recrystallized from ethanol to afford pure compounds **1**.

2-(*m*-tolyl)-2,3-dihydrophthalazine-1,4-dione (1c)



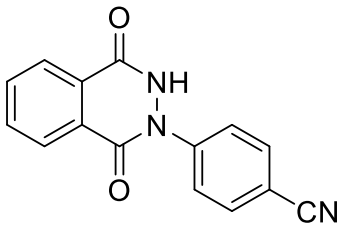
A brown solid (166 mg, 66% yield). M.p.: 223-225 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 11.80 (s, 1H), 8.30 (d, *J* = 7.5 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.98-7.91 (m, 2H), 7.44 (t, *J* = 6.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 1H) ppm. **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ = 157.28, 150.31, 141.67, 137.78, 133.53, 132.48, 129.25, 128.19, 127.68, 126.85, 126.42, 124.57, 124.17, 123.03, 20.90 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{15}H_{13}N_2O_2$ (M+H) 253.0977, found 253.0974.

2-(4-ethylphenyl)-2,3-dihydrophthalazine-1,4-dione (1d)



A white solid (245 mg, 92% yield). M.p.: 205-207 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 11.78 (s, 1H), 8.30 (d, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.98-7.90 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 2.66 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR (126 MHz, DMSO-*d*$_6$):** δ = 157.29, 150.29, 142.67, 139.50, 133.49, 132.45, 129.26, 127.65, 126.85, 125.78, 124.58, 124.16, 27.79, 15.60 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{16}H_{15}N_2O_2$ (M+H) 267.1134, found 267.1137. **HRMS (ESI) *m/z*:** calcd for $C_{16}H_{15}N_2O_2$ (M + H) 267.1134, found 267.1138.

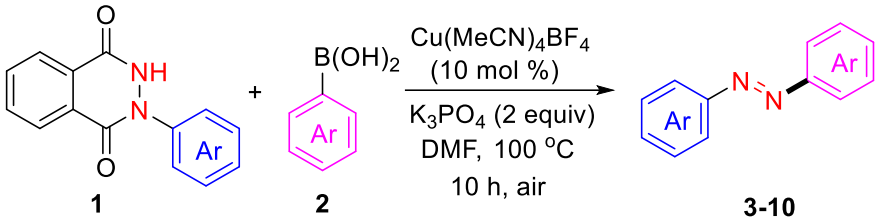
4-(1,4-dioxo-3,4-dihydrophthalazin-2(1*H*)-yl)benzonitrile (1g)



A yellow solid (234 mg, 89% yield). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.28 (s, 1H), 7.98-7.91 (m, 4H), 7.60 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ = 166.06, 150.75, 135.03, 133.62, 129.66, 123.61, 119.59, 112.27, 100.82 ppm.

HRMS (ESI) *m/z*: calcd for $C_{15}H_{10}N_3O_2$ (M+H) 264.0773, found 264.0775.

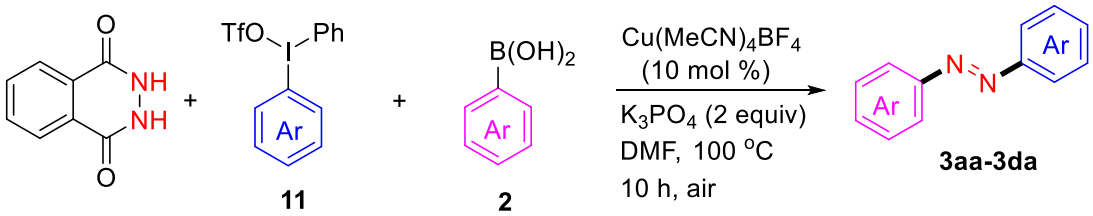
III. General procedure A for the synthesis of azobenzenes from 1 and 2.



1 **2** **3-10**

To a dry Schlenck tube with a magnetic stir bar was added **1** (0.2 mmol, 1 equiv), **2** (0.3 mmol, 1.5 equiv), $Cu(MeCN)_4BF_4$ (6.4 mg, 10 mol%), K_3PO_4 (85 mg, 2 equiv) and DMF (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was compeleted, the mixture was passed through a silica gel column (200-300 mesh), eluting with petroleum ether/EtOAc (100/1→50/1, v/v) to afford corresponding azobenzenes **3-10**.

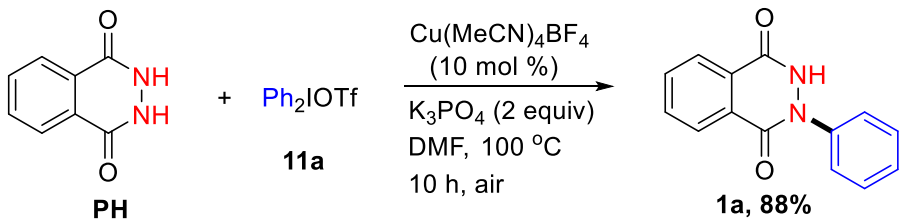
IV. General procedure B for three-component reaction to synthesize azobenzenes.



11 **2** **3aa-3da**

A mixture of phthalic hydrazide (32 mg, 0.2 mmol), diaryliodonium triflates **11** (0.2 mmol, 1 equiv), arylboronic acid **2** (0.2 mmol, 1 equiv), $Cu(MeCN)_4BF_4$ (10 mol%, 6.4 mg), K_3PO_4 (85 mg, 2 equiv) and DMF (1 mL) was stirred at 100 °C for 10 h under air. After the reaction was compeleted, the mixture was passed through a silica gel column (100-200 mesh), eluting with petroleum ether to afford **3aa-3da**.

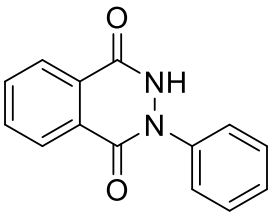
The reaction of PH and 11a (*path a*):



PH **11a** **1a, 88%**

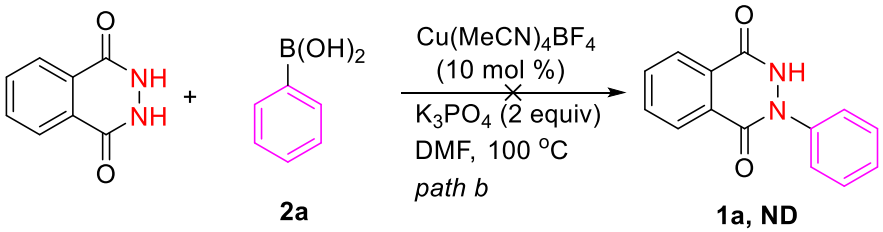
A mixture of phthalic hydrazide (0.2 mmol, 32.4 mg), diphenyliodonium triflate **11a** (0.2 mmol, 1 equiv, 86 mg), $Cu(MeCN)_4BF_4$ (10 mol%, 6.4 mg), K_3PO_4 (85 mg, 2 equiv) and DMF (1 mL) was stirred at 100 °C for 10 h under air. After the reaction was compeleted, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column (100-200 mesh), eluting with petroleum ether/EtOAc (10/1→5/1, v/v) to afford **1a** as a white solid (42 mg, 88% yield).

2-phenyl-2,3-dihydrophthalazine-1,4-dione (1a)[1]



^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ = 11.83 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.99-7.91 (m, 2H), 7.64 (d, *J* =8.0 Hz, 2H), 7.49 (t, *J* = 7.8 Hz 2H), 7.37 (t, *J* = 7.3 Hz ,1H) ppm. **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ = 157.33, 150.37, 141.75, 133.57, 132.50, 129.24, 128.41, 127.07, 126.87, 125.94, 124.62, 124.19 ppm.

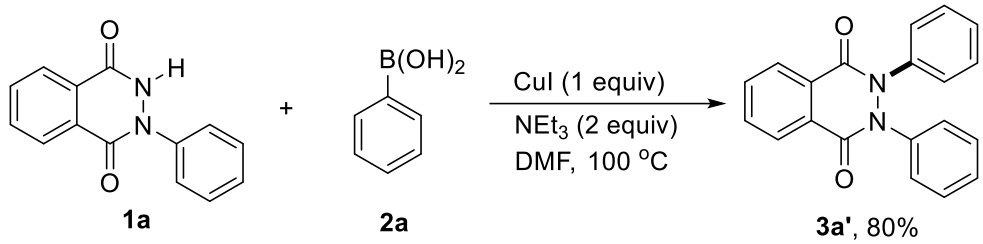
The reaction of PH and 2a (*path b*):



A mixture of phthalic hydrazide (0.2 mmol, 32.4 mg), phenylboronic acid **2a** (0.2 mmol, 1 equiv, 24.4 mg), $Cu(MeCN)_4BF_4$ (10 mol%, 6.3 mg), K_3PO_4 (85 mg, 2 equiv) and DMF (1 mL) was stirred at 100 °C for 10 h under air. The mixture was detected by TLC and **1a** was not observed.

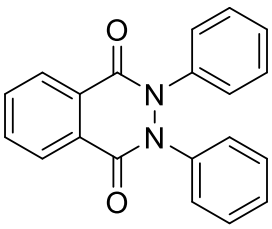
V. Mechanistic Experiments

Synthesis of 3a′:



The mixture of **1a** (0.2 mmol, 47.6mg, 1equiv), phenylboronic acid **2a** (0.2 mmol, 24.4 mg, 1 equiv), CuI (38.0 mg, 1 equiv), triethylamine (2 equiv) and DMF (1 mL) was heated at 100 °C for 9 h. Then the reaction was cooled, DMF was removed under reduced pressure, and the residue was purified by a silica gel column (100-200 mesh), eluting with petroleum ether/EtOAc (10/1→5/1, v/v) to afford **3a′** as a white solid (50.3 mg, 80% yield).

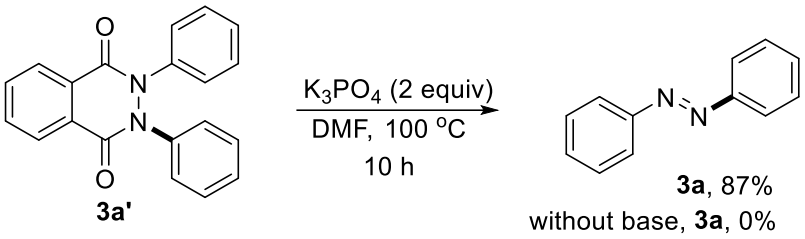
2,3-diphenyl-2,3-dihydrophthalazine-1,4-dione (3a')



M.p.: 175-177 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.45-8.42 (m, 2H), 7.91-7.88 (m, 2H), 7.32-7.26 (m, 8H), 7.19 (t, *J* = 7.3 Hz, 2H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 158.57, 137.79, 134.07, 129.74, 128.92, 128.81, 128.48, 128.41 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{15}N_2O_2$ (M + H) 315.1134, found

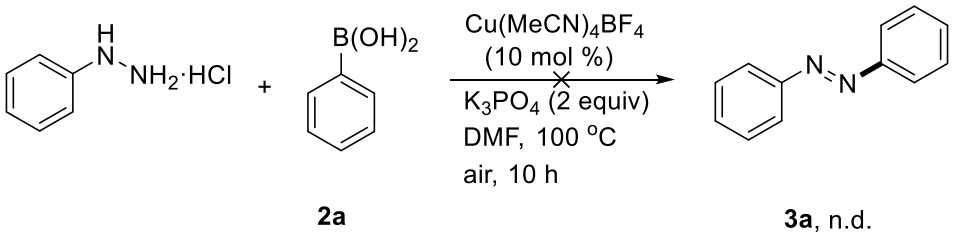
315.1135.

Deprotection of 3a′:



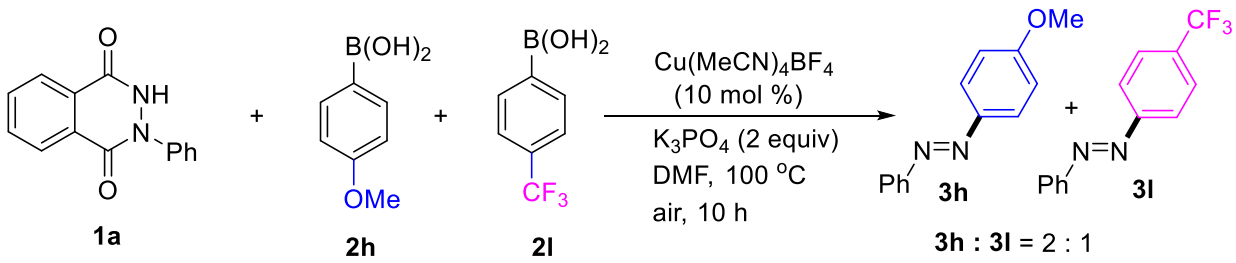
The mixture of **3a′** (0.2 mmol) with or without K_3PO_4 (2 equiv) in DMF (1 mL) was heated at 100 °C for 10 h. Then the reaction was cooled, the mixture was purified by a silica gel column (100-200 mesh), eluting with petroleum ether to afford **3a** (with K_3PO_4, 31.3 mg, 87% yield; without K_3PO_4, 0% yield).

The reaction of phenylhydrazine hydrochloride and 2a:



The mixture of phenylhydrazine hydrochloride (0.2 mmol, 28.9 mg), phenylboronic acid **2a** (0.2 mmol, 24.4 mg, 1 equiv), $Cu(MeCN)_4BF_4$ (10 mol%, 6.4 mg), K_3PO_4 (85 mg, 2 equiv) and DMF (1 mL) was stirred at 100 °C for 10 h under air. The mixture was detected by TLC and **3a** was not observed.

Competition experiments:



The mixture of **1a** (0.1 mmol, 23.8 mg), arylboronic acid **2h** (0.1 mmol, 15.2 mg, 1 equiv), **2l** (0.1 mmol, 19 mg, 1 equiv), $Cu(MeCN)_4BF_4$ (10 mol%, 3.2 mg), K_3PO_4 (42.5 mg, 2 equiv) and DMF (1 mL) was stirred at 100 °C for 10 h under air. The mixture was passed a silica gel column (100-200 mesh), eluting with petroleum ether/EtOAc (100/1→50/1, v/v) to afford the mixture of **3e** and **3l**. The ratio of **3e/3l** was determined to be 2.0/1 by ^{1}H NMR (see below).

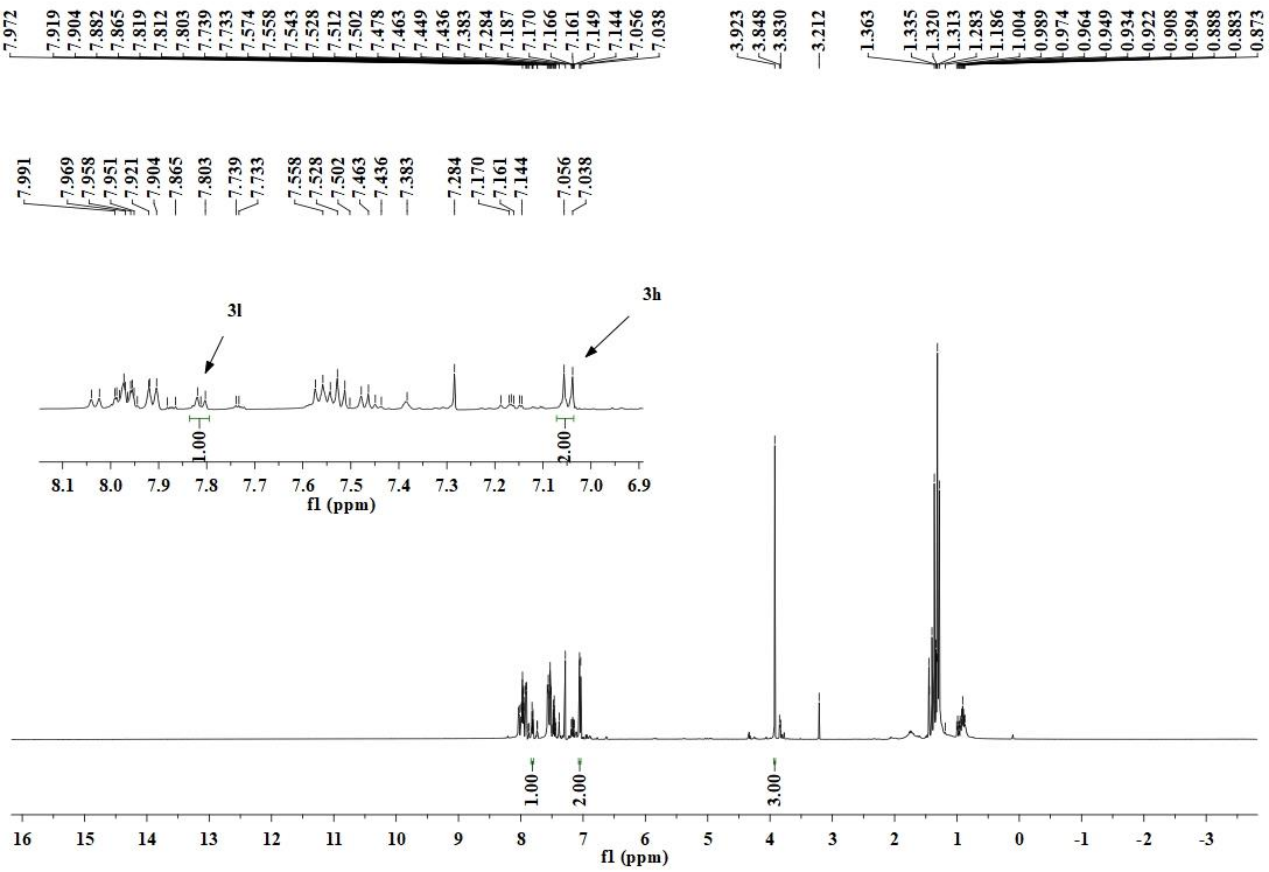
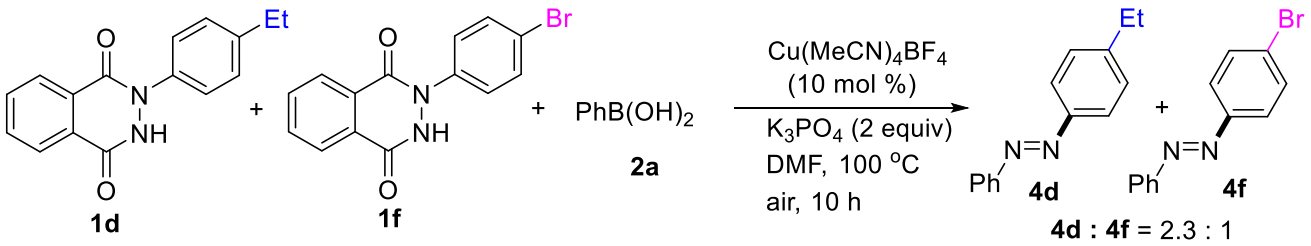


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) of the mixture of **3e** and **3l**



The mixture of **1d** (0.1 mmol, 26.6 mg), **1f** (0.1 mmol, 31.7 mg), phenylboronic acid **2a** (0.1 mmol, 12.2 mg, 1 equiv), $Cu(MeCN)_4BF_4$ (10 mol%, 3.2 mg), K_3PO_4 (42.5 mg, 2 equiv) and DMF (1 mL) was stirred at 100 °C for 10 h under air. The mixture was passed a silica gel column (100-200 mesh), eluting with petroleum ether/EtOAc (100/1→50/1, v/v) to afford the mixture of **4d** and **4f**. The ratio of **4d/4f** was determined to be 2.3/1 by ^{1}H NMR (see below).

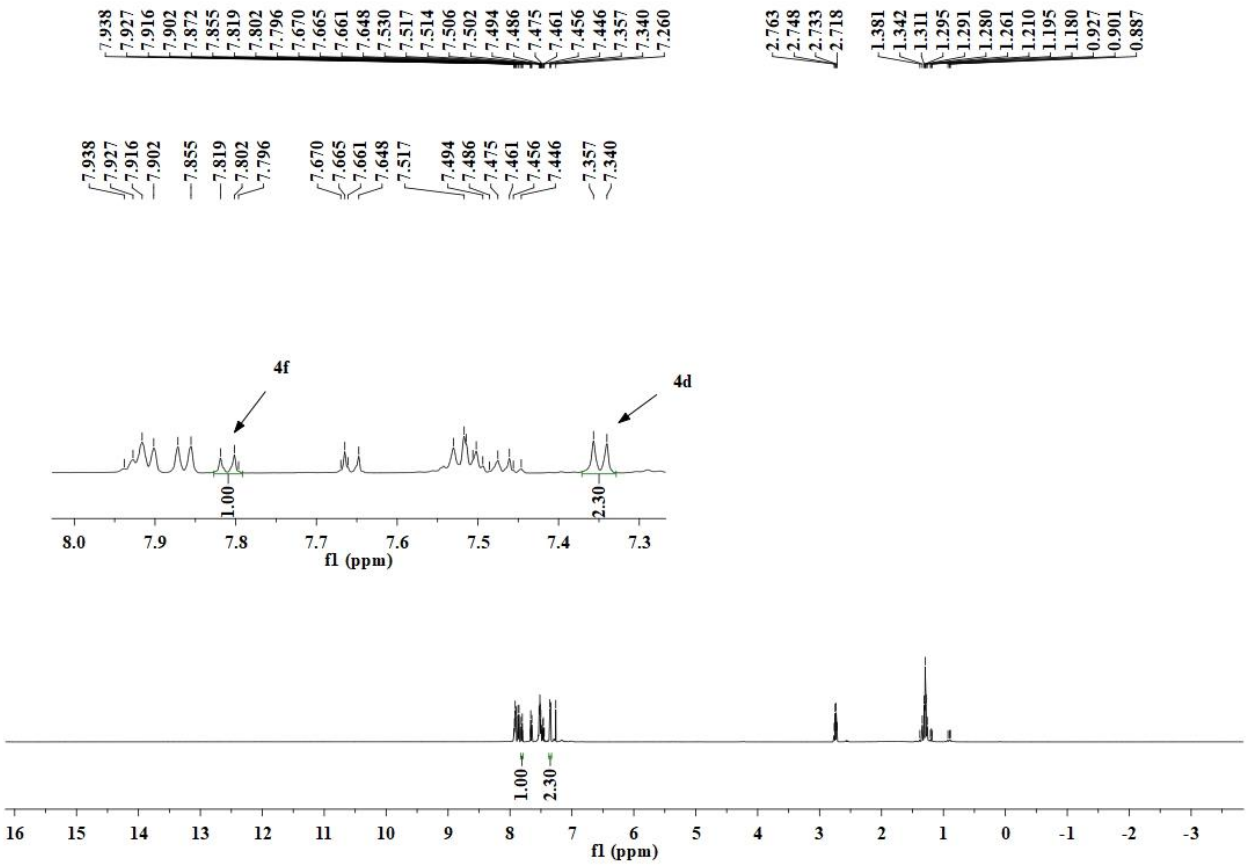
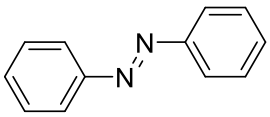


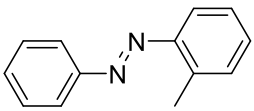
Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) of the mixture of **4d** and **4f**

VI. Experimental data for the described substances



(*E*)-1,2-diphenyldiazene (3a and 3aa)[2]

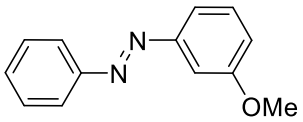
An orange solid (**3a** in general procedure A, 33 mg, 92% yield; **3aa** in general procedure B, 32 mg, 89% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 63-65 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.93 (d, J = 7.0 Hz, 4H), 7.53 (d, J =7.3 Hz, 4H), 7.48 (d, J = 7.3 Hz, 2H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$) :** δ = 152.81, 131.13, 129.23, 122.99 ppm.



(*E*)-1-phenyl-2-(o-tolyl)diazene (3b)[2]

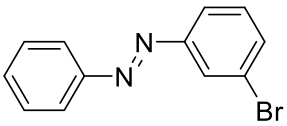
An orange solid (20 mg, 51% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 30/1, v/v). M.p.: 96-98 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.96 (d, J = 7.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 7.8 Hz, 2H), 7.49 (t, J = 7.3

Hz, 1H), 7.41-7.36 (m, 2H), 7.32-7.28 (m, 1H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 153.12, 150.87, 138.25, 131.38, 131.06, 130.91, 129.19, 126.56, 123.09, 115.58, 17.64 ppm.



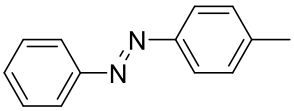
(*E*)-1-(3-methoxyphenyl)-2-phenyldiazene(3c)[3]

An orange solid (24 mg, 57% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 61-63 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.93 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.49-7.47 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.05 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H), 3.91 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.48, 154.05, 152.75, 131.17, 129.92, 129.23, 123.01, 117.94, 117.25, 105.91, 55.62 ppm.



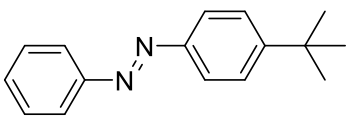
(*E*)-1-(3-bromophenyl)-2-phenyldiazene (3d)[4]

An orange solid (28 mg, 54% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 63-65 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.06 (t, *J* = 2.0 Hz, 1H), 7.93-7.91 (m, 2H), 7.90-7.87 (m, 1H), 7.61-7.59 (m, 1H), 7.55-7.50 (m, 3H), 7.41 (t, *J* = 8.0 Hz, 1H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 153.69, 152.51, 133.74, 131.68, 130.59, 129.31, 124.79, 123.27, 123.20, 123.10 ppm.



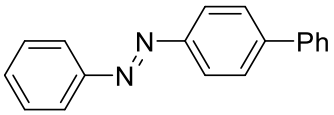
(*E*)-1-phenyl-2-(*p*-tolyl)diazene (3e and 4c)[4]

An orange solid (**3e**, 24 mg, 62% yield; **4c**, 24 mg, 62% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 63-65 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.91 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 152.88, 150.93, 141.69, 130.83, 129.88, 129.19, 123.00, 122.86, 21.64 ppm.



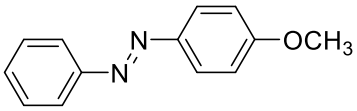
(*E*)-1-(4-(*tert*-butyl)phenyl)-2-phenyldiazene (**3f and 4e**)[4]

An orange solid (**3f**, 37 mg, 77% yield; **4e**, 30 mg, 63% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 41-43 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 7.90 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.55– 7.50 (m, 4H), 7.46 (t, *J* = 7.5 Hz, 1H), 1.38 (s, 9H) ppm. **^{13}C NMR (126 MHz, CDCl$_3$):** δ = 154.73, 152.98, 150.79, 130.82, 129.19, 126.16, 122.86, 122.73, 35.16, 31.42 ppm.



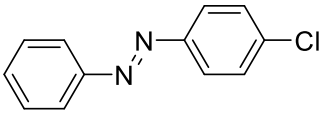
(*E*)-1-([1,1'-biphenyl]-4-yl)-2-phenyldiazene (3g)[5]

An orange solid (44 mg, 85% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 79-81 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.03 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 3H), 7.41 (t, *J* = 7.3 Hz, 1H) ppm. **^{13}C NMR (126 MHz, CDCl$_3$):** δ = 152.90, 151.92, 143.88, 140.34, 131.11, 129.25, 129.04, 128.04, 127.92, 127.34, 123.53, 123.01 ppm.



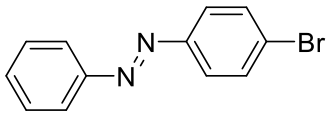
(*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (3h and **3da)**[4]

An orange solid (**3h** in general procedure A, 26 mg, 62% yield; **3da** in general procedure B, 36 mg, 85% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 56-58 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 7.96-7.94 (m, 2H), 7.92-7.89 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.04-7.02 (m, 2H), 3.89 (s, 3H) ppm. **^{13}C NMR (126 MHz, CDCl$_3$):** δ = 162.19, 152.90, 147.15, 130.48, 129.15, 124.88, 122.69, 114.34, 55.68 ppm.



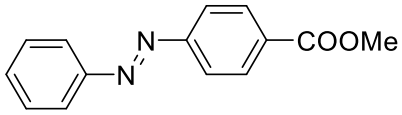
(*E*)-1-(4-chlorophenyl)-2-phenyldiazene (3i)[6]

An orange solid (33 mg, 77% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 76-78 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 7.92 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.55-7.48 (m, 5H) ppm. **^{13}C NMR (126 MHz, CDCl$_3$):** δ = 152.60, 151.12, 137.04, 131.42, 129.48, 129.28, 124.27, 123.07 ppm.



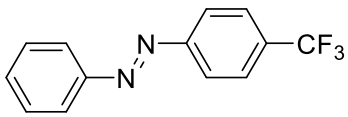
(*E*)-1-(4-bromophenyl)-2-phenyldiazene (3j and **4f)**[4]

An orange solid (**3j**, 33 mg, 64% yield; **4f**, 34 mg, 64% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 89-91 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 7.92 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 9.0 Hz, 2H), 7.54-7.47 (m, 3H) ppm. **^{13}C NMR (126 MHz, CDCl$_3$):** δ = 152.63, 151.51, 132.48, 131.47, 129.30, 125.51, 124.50, 123.09 ppm.



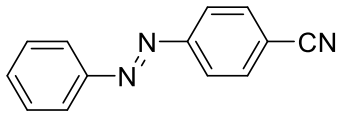
(*E*)-methyl 4-(phenyldiazenyl)benzoate (3k and **3ak)**[5]

An orange solid (**3k** in general procedure A, 28 mg, 58% yield; **3ak** in general procedure B, 40 mg, 83% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 115-117 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.20 (d, J = 7.5 Hz, 2H), 7.95 (d, J = 8.5 Hz, 4H), 7.56-7.51 (m, 3H), 3.96 (s, 3H) ppm. **^{13}C NMR (126 MHz, CDCl$_3$):** δ = 166.72, 152.73, 131.86, 130.78, 129.34, 123.30, 122.80, 120.91, 52.49 ppm.



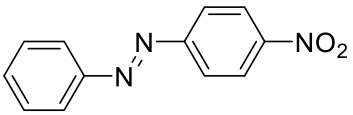
(*E*)-1-phenyl-2-(4-(trifluoromethyl)phenyl)diazene (**3l**)[4]

An orange solid (31 mg, 62% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 82-84 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.01 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.57-7.52 (m, 3H) ppm. **^{13}C NMR (126 MHz, CDCl$_3$):** δ = 154.59, 152.59, 131.97, 129.36, 126.45 (d, $J_{C\text{-}F}$ = 3.7 Hz), 123.32, 123.16 ppm.



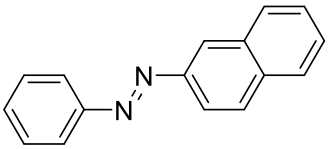
(*E*)-4-(phenyldiazenyl)benzonitrile[00] **(3m**, **4g** and **3ca)**[5]

An orange solid (**3m** in general procedure A, 25 mg, 60% yield; **4g** in general procedure A, 24 mg, 59% yield; **3ca** in general procedure B, 33 mg, 81% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 102-104 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.99 (d, J = 8.5 Hz, 2H), 7.97-7.95 (m, 2H), 7.82 (d, J = 8.5 Hz, 2H), 7.56-7.54 (m, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 154.68, 152.53, 133.38, 132.37, 129.42, 123.51, 123.47, 118.62, 114.12 ppm.



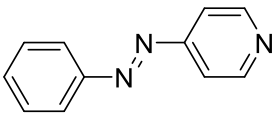
(*E*)-1-(4-nitrophenyl)-2-phenyldiazene (3n and **3an)**

An orange solid (**3n** in general procedure A, 36 mg, 78% yield; **3an** in general procedure B, 32 mg, 71% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 10/1, v/v). M.p.: 109-111 ºC. M.p.: 109-111 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.39 (d, J = 9.0 Hz, 2H), 8.04 (d, J = 9.0 Hz, 2H), 7.99-7.97 (m, 2H), 7.57-7.55 (m, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 155.86, 152.55, 148.87, 132.56, 129.46, 124.89, 123.59, 123.57 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{12}H_{10}N_3O_2$ (M + H) 228.0773, found 228.0775.



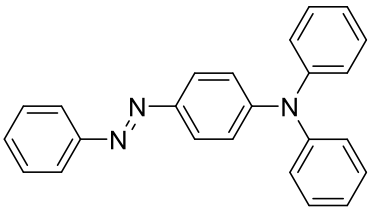
(*E*)-1-(naphthalen-2-yl)-2-phenyldiazene (3o)[7]

An orange solid (32 mg, 70% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 30/1, v/v). M.p.: 73-75 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.47 (s, 1H), 8.08 (dd, J = 9.0 Hz, 2.0 Hz, 1H), 8.04– 8.02 (m, 1H), 7.99 – 7.98 (m, 2H), 7.93 – 7.89 (m, 2H), 7.58 – 7.53 (m, 4H), 7.51 – 7.49 (m, 1H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 152.93, 150.41, 134.99, 133.69, 131.11, 129.53, 129.27, 128.09, 127.71, 126.88, 123.01, 117.28 ppm.



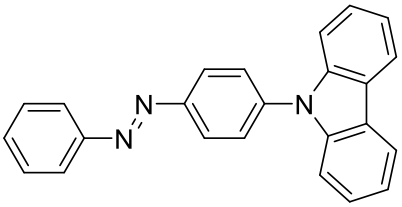
(*E*)-4-(phenyldiazenyl)pyridine (3p)[8]

An orange solid (23 mg, 60% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 80-82 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ =8.81 (d, J = 6.0 Hz, 2H), 7.97 (m, 2H), 7.55 (d, J =7.7 Hz, 2H), 7.55 (t, J = 3.3 Hz, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 157.46, 152.48, 151.29, 132.61, 129.42, 123.57, 116.48 ppm.



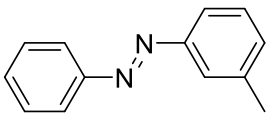
(*E*)-*N*,*N*-diphenyl-4-(phenyldiazenyl)aniline (3r).

An orange solid (48 mg, 68% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 89-91 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.88 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.50 (t, *J* =7.3 Hz, 2H), 7.43 (t, *J* = 7.3Hz ,1H), 7.32 (t, *J* = 7.5 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 4H), 7.12 (d, *J* = 8.0 Hz, 4H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 146.84, 146.79, 130.38, 129.72, 129.22, 125.80, 125.78, 124.60, 124.55, 122.55, 121.53, 121.49 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{24}H_{20}N_3$ (M + H) 350.1657, found 350.1659.



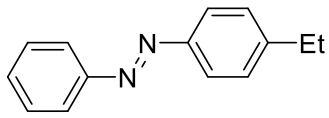
(*E*)-1-(4-(9*H*-fluoren-9-yl)phenyl)-2-phenyldiazene (3s)

An orange solid (36 mg, 52% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 117-119 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.19-8.16 (m, 4H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 3H), 7.46-7.43 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 2H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 152.82, 151.35, 140.69, 140.24, 131.42, 129.34, 127.48, 126.29, 124.54, 123.86, 123.13, 120.56, 120.53, 110.02 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{24}H_{18}N_3$ (M + H) 348.1501, found 348.1506.



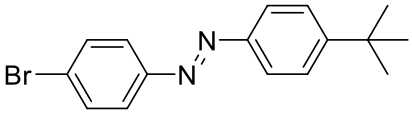
(*E*)-1-phenyl-2-(*m*-tolyl)diazene (4b)[2]

An orange solid (28 mg, 72% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 52-54 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.92 (d, *J* = 7.5 Hz, 2H), 7.73 (s, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 2.47 (s, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 152.92, 152.87, 139.13, 131.93, 131.03, 129.22, 129.05, 123.07, 122.95, 120.64, 77.41, 77.16, 76.91, 21.51 ppm.



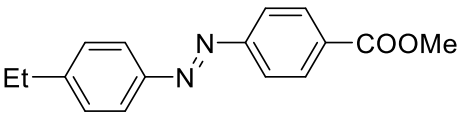
(*E*)-1-(4-ethylphenyl)-2-phenyldiazene (4d)[9]

An orange solid (37 mg, 87% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 73-75 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.91 (d, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 2.74 (q, *J* = 7.5 Hz, 2H), 1.30 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 152.93, 151.12, 147.96, 130.82, 129.19, 128.70, 123.09, 122.86, 28.99, 15.54 ppm.



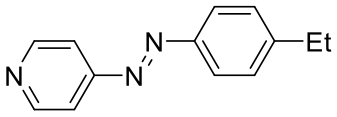
(*E*)-1-(4-bromophenyl)-2-(4-(*tert*-butyl)phenyl)diazene (4h)[10]

An orange solid (44 mg, 70% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 58-60 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.85 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 155.15, 151.66, 150.60, 132.41, 126.23, 125.14, 124.39, 122.84 , 35.21, 31.39 ppm.



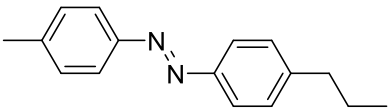
(*E*)-methyl 4-((4-ethylphenyl)diazenyl)benzoate (4i)

An orange solid (38 mg, 71% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 30/1, v/v). M.p.: 100-102 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.18 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 3.96 (s, 3H), 2.95 (q, *J* = 7.5 Hz, 2H), 1.30 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 166.76, 155.47, 151.07, 148.86, 131.68, 130.75, 128.81, 123.42, 122.67, 52.45, 29.06, 15.48 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{16}H_{17}N_2O_2$ (M + H) 269.1290, found 269.1295.



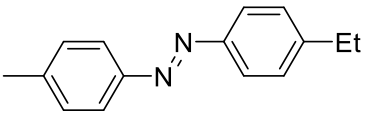
(*E*)-4-((4-ethylphenyl)diazenyl)pyridine (4j)

An orange solid (38 mg, 90% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 62-64 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.79 (d, *J* = 4.5 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 5.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.75 (q, *J* = 7.5 Hz, 2H), 1.30 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 157.63, 151.25, 150.90, 149.76, 128.91, 123.74, 116.45, 29.10, 15.43 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{13}H_{14}N_3$ (M + H) 212.1188, found 212.1185. **HRMS (ESI) *m/z*:** calcd for $C_{13}H_{14}N_3$ (M + H) 212.1188, found 212.1188.



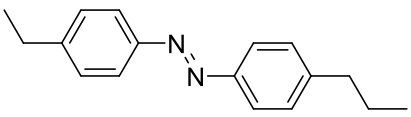
(*E*)-1-(4-propylphenyl)-2-(*p*-tolyl)diazene (5)

An orange solid (33 mg, 69% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 63-65 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.83 (t, *J* = 7.8, 4H), 7.31(dd, *J* =8.3 Hz, 1.8 Hz, 4H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 1.74-1.66 (m, 2H) , 0.97 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C **NMR (126 MHz, $CDCl_3$)** δ = 151.18, 151.01, 146.10, 141.33, 129.85, 129.27, 122.86, 122.84, 38.07, 24.56, 21.62, 13.93 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{16}H_{19}N_2$ (M + H) 239.1548, found 239.1545.



(*E*)-1-(4-ethylphenyl)-2-(*p*-tolyl)diazene (6)[9]

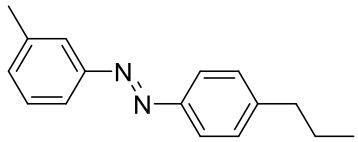
An orange solid (30 mg, 67% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 76-78 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.86-7.82 (m, 4H), 7.35-7.31 (m, 4H), 2.74 (q, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 1.30 (td, *J* = 7.5 Hz, 1.0 Hz, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 151.17, 151.02, 147.61, 141.32, 129.84, 128.65, 122.95, 122.87, 28.97, 21.61, 15.56 ppm.



(*E*)-1-(4-ethylphenyl)-2-(4-propylphenyl)diazene (7)

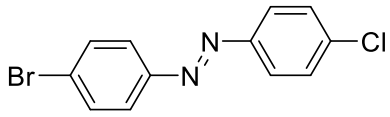
An orange solid (30 mg, 60% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 52-54 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.83 (dd, *J* = 8.3 Hz, 3.3Hz, 4H), 7.34-7.30 (m, 4H), 2.73 (m, 2H), 2.67 (t, *J* = 7.5 Hz, 2H),

1.69 (m, 2H), 1.29 (t, J = 7.8 Hz, 3H) , 0.97 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 151.21, 151.20, 147.62, 146.11, 129.27, 128.66, 122.95, 122.85, 38.08, 28.97, 24.57, 15.57, 13.93 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{17}H_{21}N_2$ (M + H) 253.1705, found 253.1703.



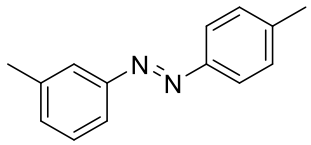
(*E*)-1-(4-propylphenyl)-2-(*m*-tolyl)diazene (8)

An orange solid (30 mg, 62 % yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 46-48 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.84 (d, J = 8.0, 2H), 7.72-7.71(m, 2H), 7.40 (t, J = 7.8 Hz, 1H), 7.32(d, J = 8.5 Hz, 2H), 7.28 (d, J =2.5, 1H) , 2.67 (t, J = 7.5, 2H), 2.46 (s, 3H), 1.74-1.66 (m, 2H), 0.97 (t, J =7.3, 3H) ppm, **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 153.00, 151.16, 146.35, 139.08, 131.63, 129.30, 129.01, 122.93, 120.52, 38.09, 24.55, 21.52, 13.94 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{16}H_{19}N_2$ (M + H) 239.1548, found 239.1549.



(*E*)-1-(4-bromophenyl)-2-(4-chlorophenyl)diazene (9)[11]

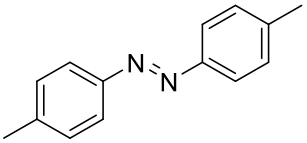
An orange solid (34 mg, 58% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 191-193 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.87 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 9.0 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 132.56, 129.58, 124.57, 124.36 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{12}H_9BrClN_2$ (M + H) 294.9638, found 294.9636.



(*E*)-1-(*m*-tolyl)-2-(*p*-tolyl)diazene (10)

A orange solid (28 mg, 67% yield), following the general procedure A, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 50-52 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.83 (d, J = 8.5 Hz, 2H), 7.71 (br, 2H), 7.40 (t, J = 7.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.28 (d, J =7.5 Hz, 1H), 2.46 (s, 3H), 2.44 (s, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 152.98, 150.97,

141.59, 139.09, 131.64, 129.88, 129.02, 122.95, 120.52, 21.63, 21.51 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{14}H_{15}N_2$ (M + H) 211.1235, found 211.1237.



(*E*)-1,2-di-*p*-tolyldiazene (3be)[6]

An orange solid (35 mg, 83% yield), following the general procedure B, purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 63-65 ºC **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.82 (d, *J* = 8.5 Hz, 4H), 7.31 (d, *J* = 8.0 Hz, 4H), 2.44 (s, 6H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 151.0, 141.3, 129.8, 122.9, 21.6 ppm.

VII. References

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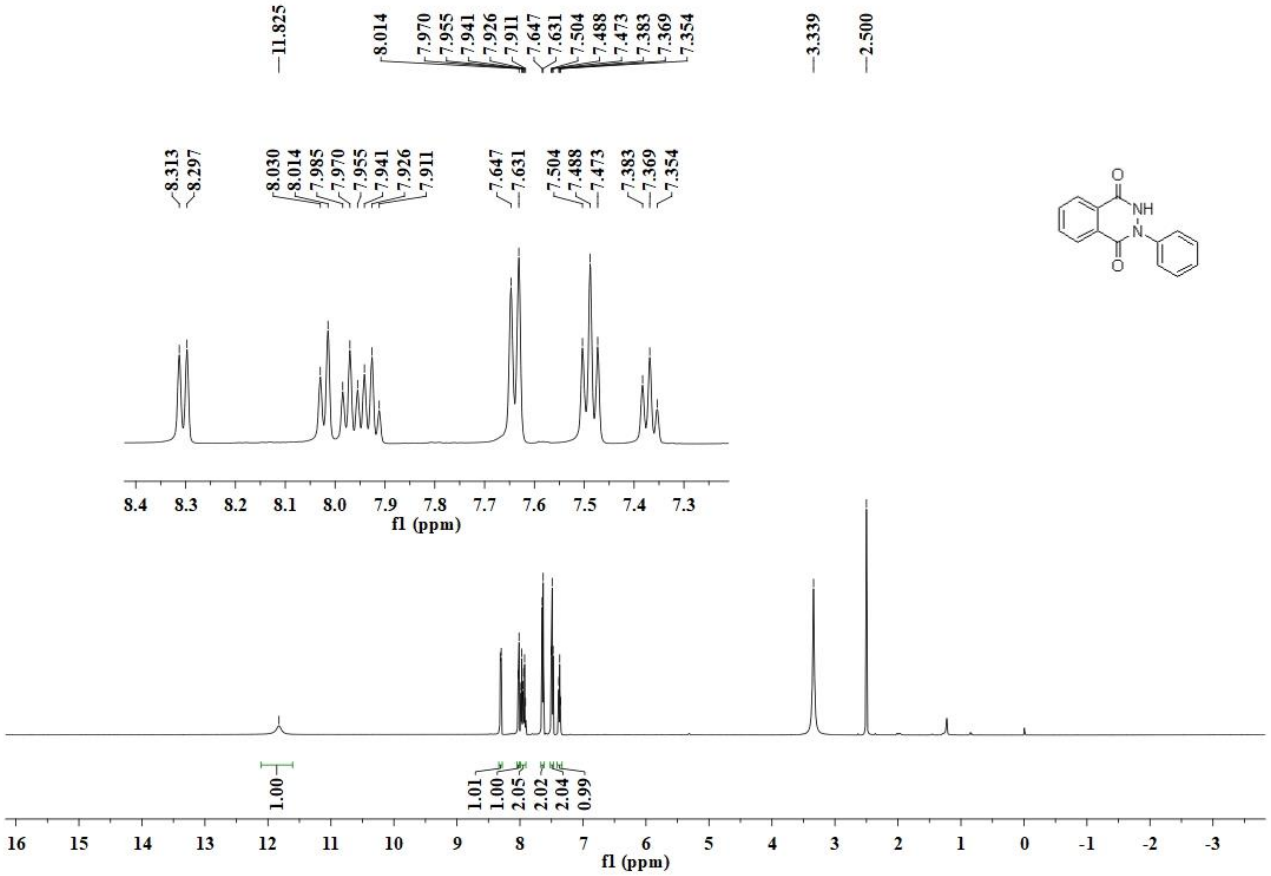
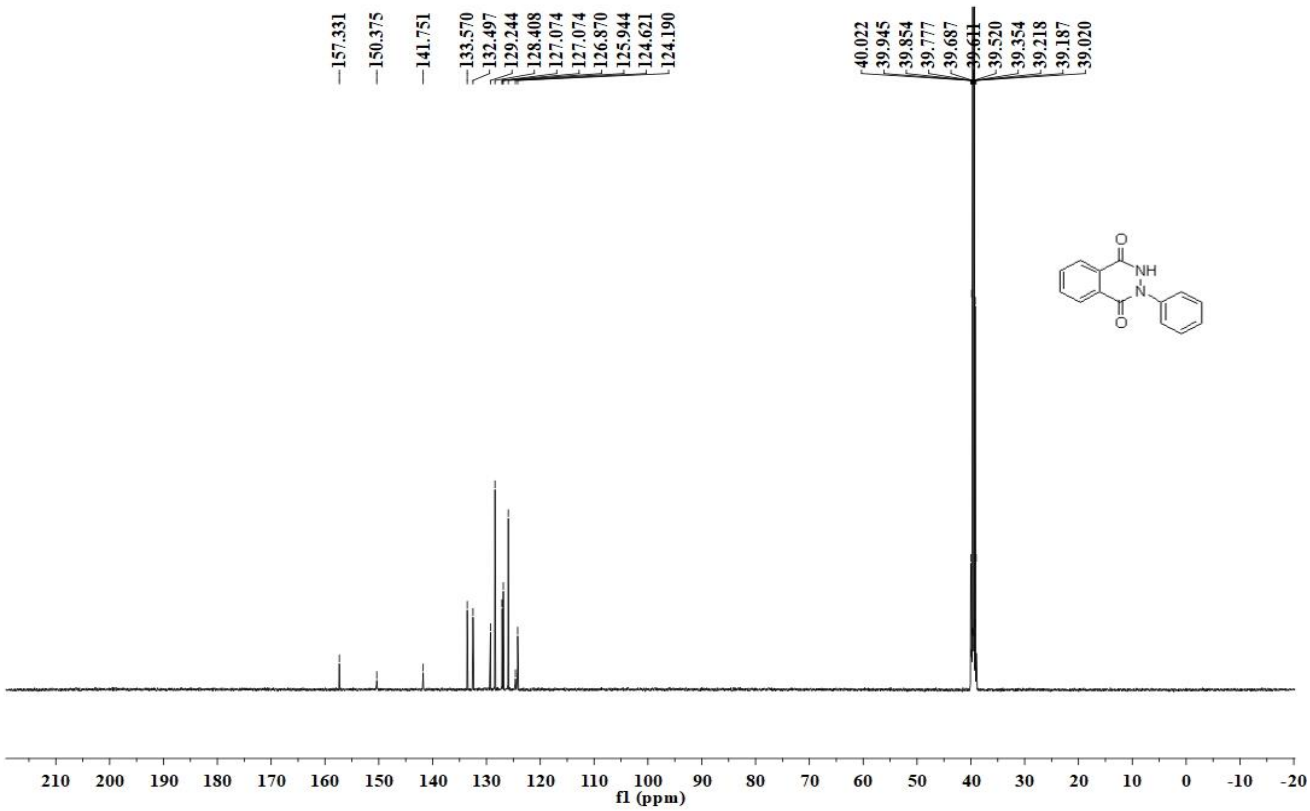
VIII. Copies of ^{1}H and ^{13}C NMR spectra

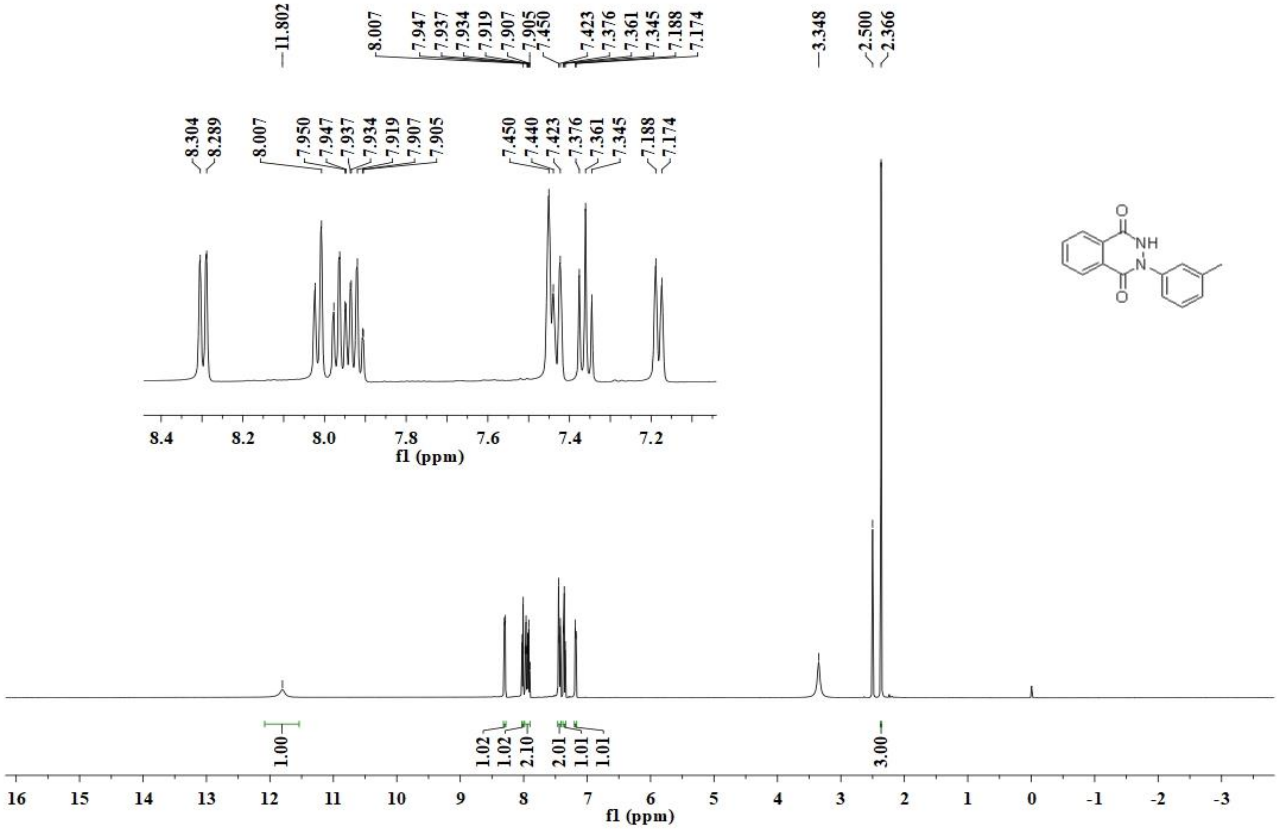
^{1}H NMR (500 MHz, DMSO-d_6) of **1a**



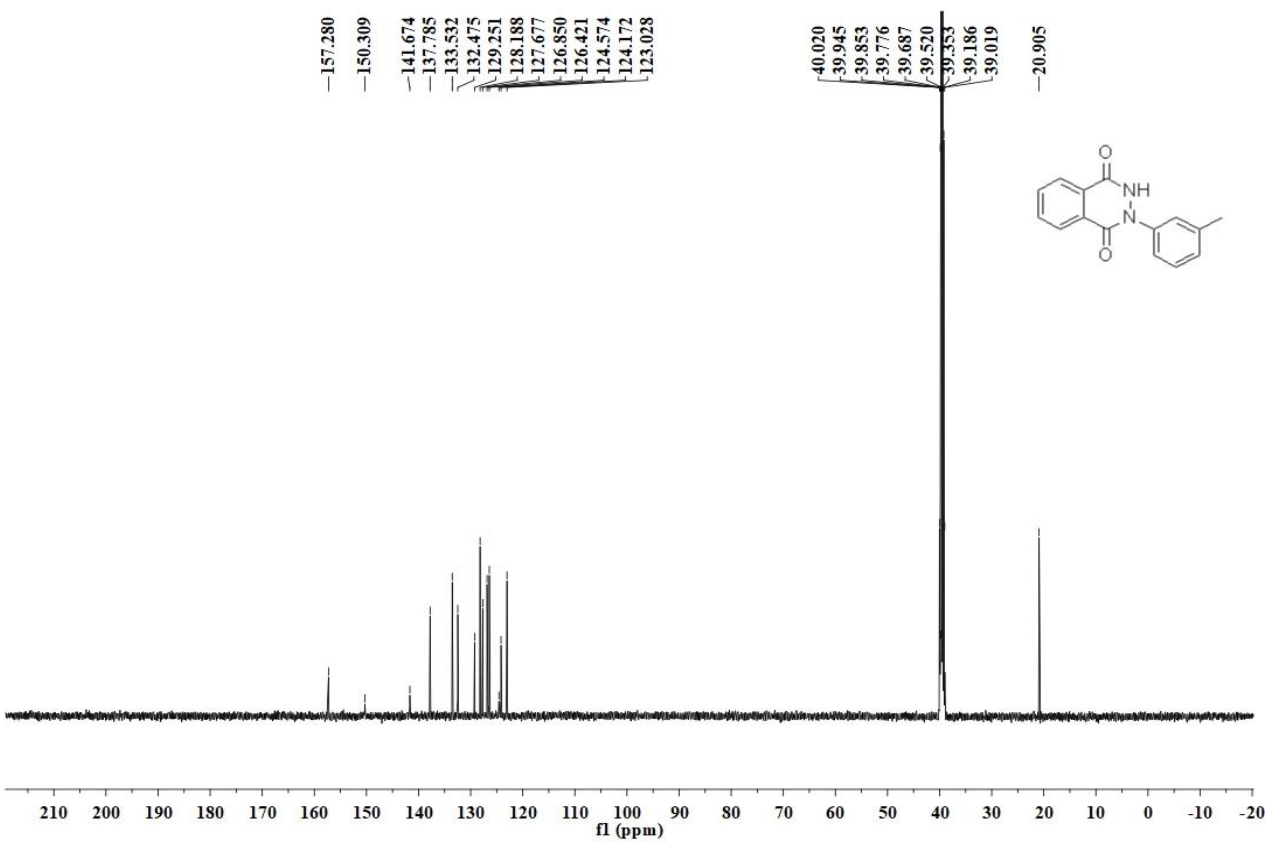
^{13}C NMR (126 MHz, DMSO-d_6) of **1a**



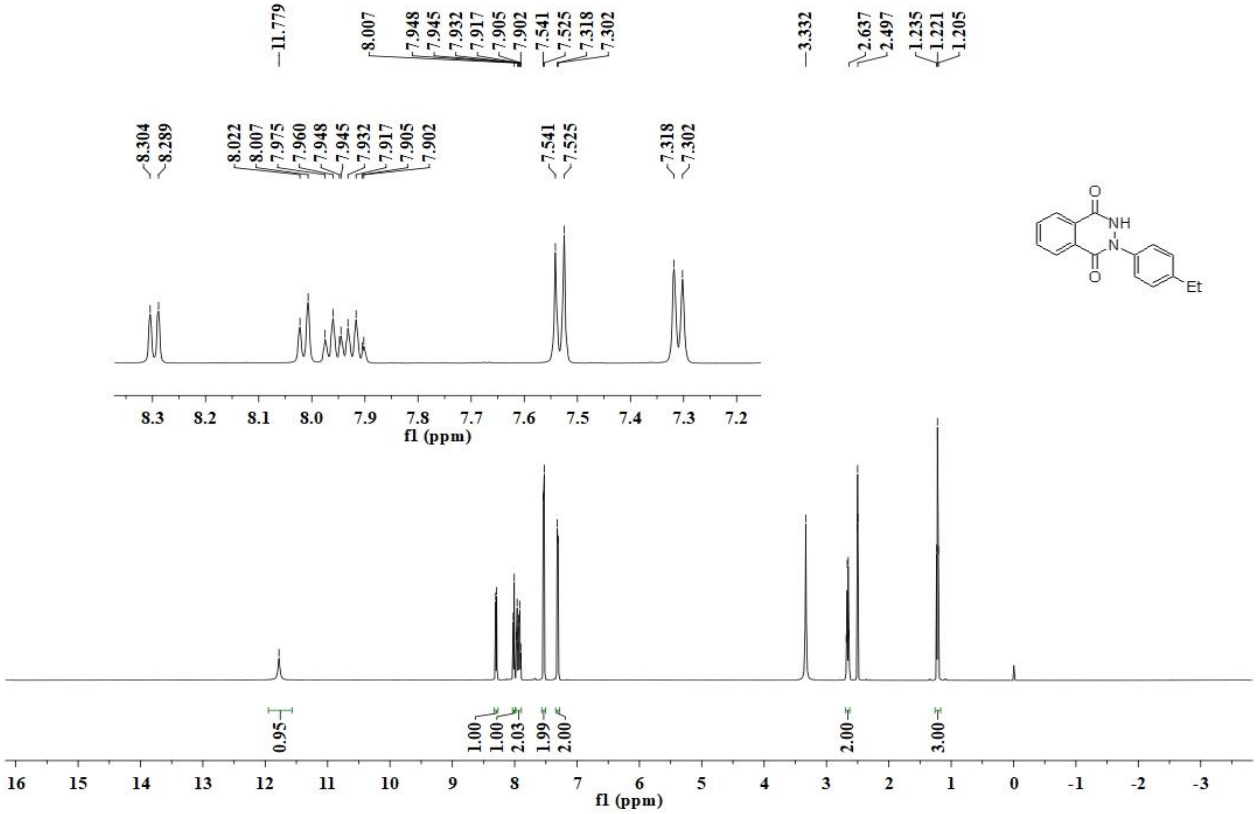
^{1}H NMR (500 MHz, DMSO-d_6) of **1b**



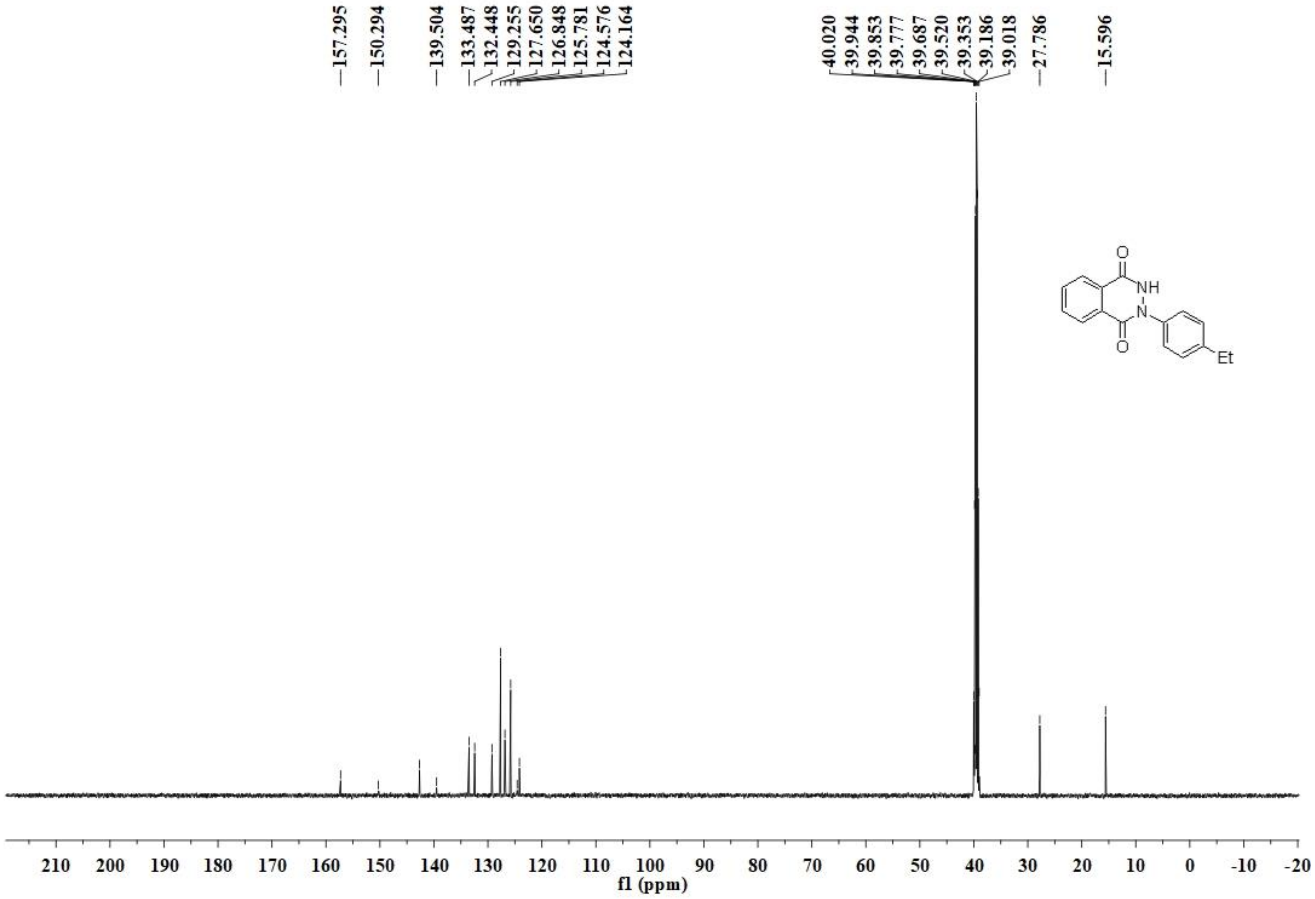
^{13}C NMR (126 MHz, DMSO-d_6) of **1b**



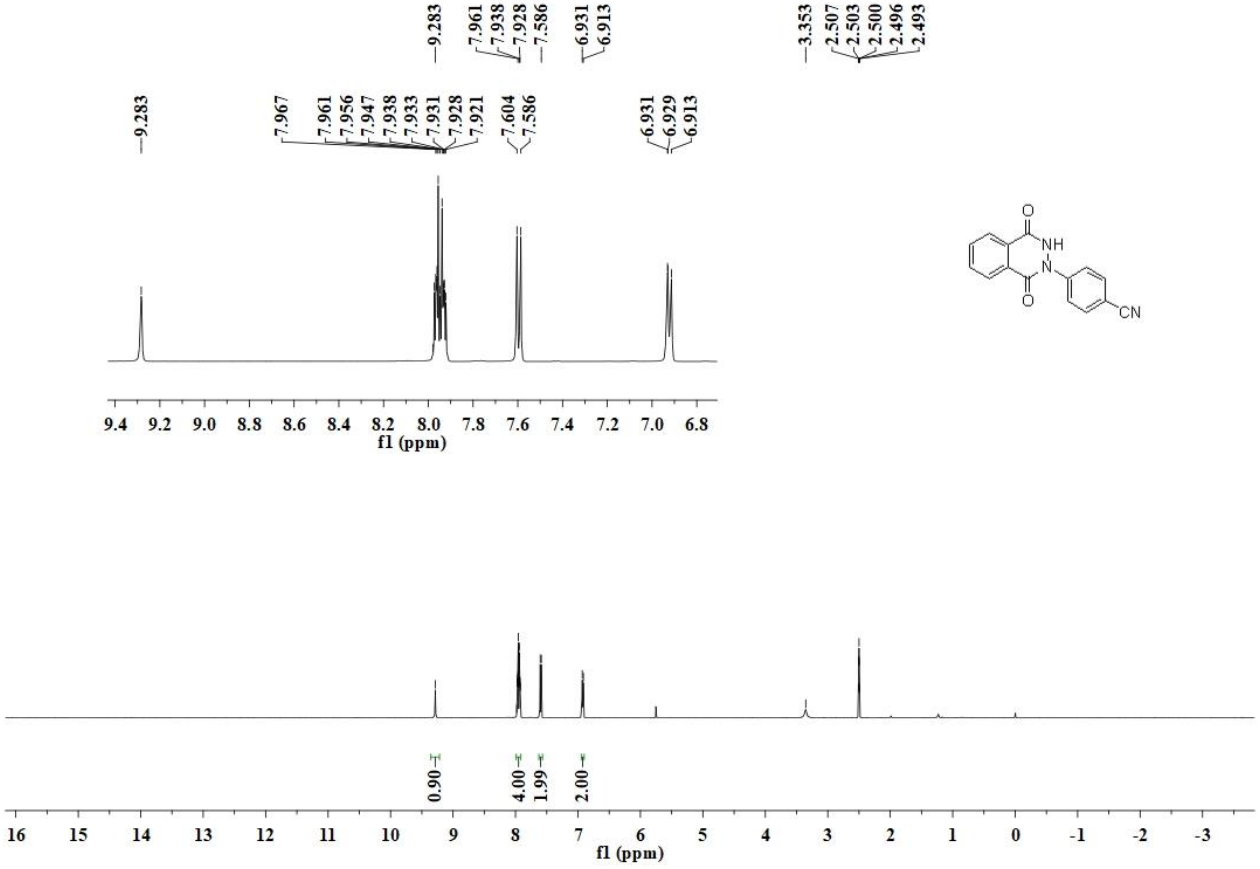
^{1}H NMR (500 MHz, DMSO-d_6) of **1d**



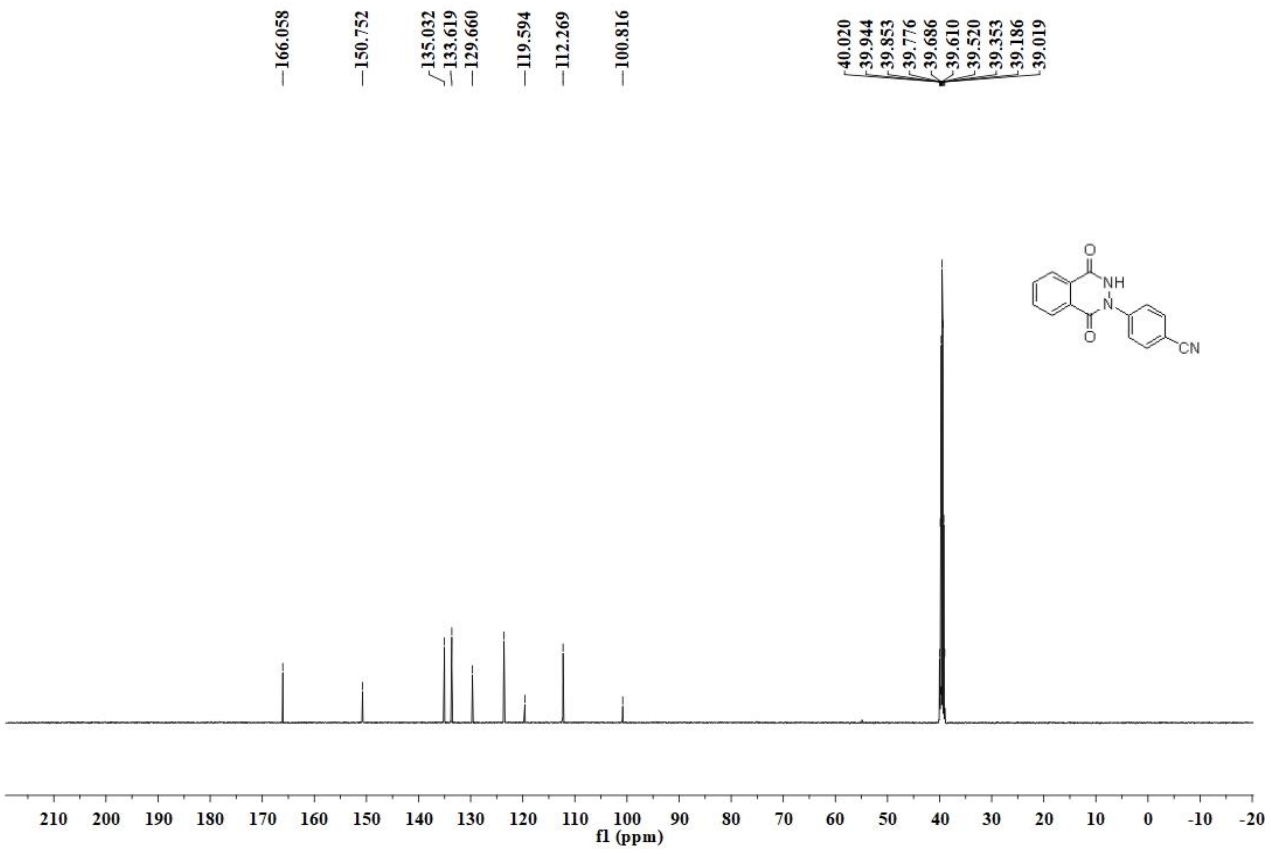
^{13}C NMR (126 MHz, DMSO-*d6*) of **1d**



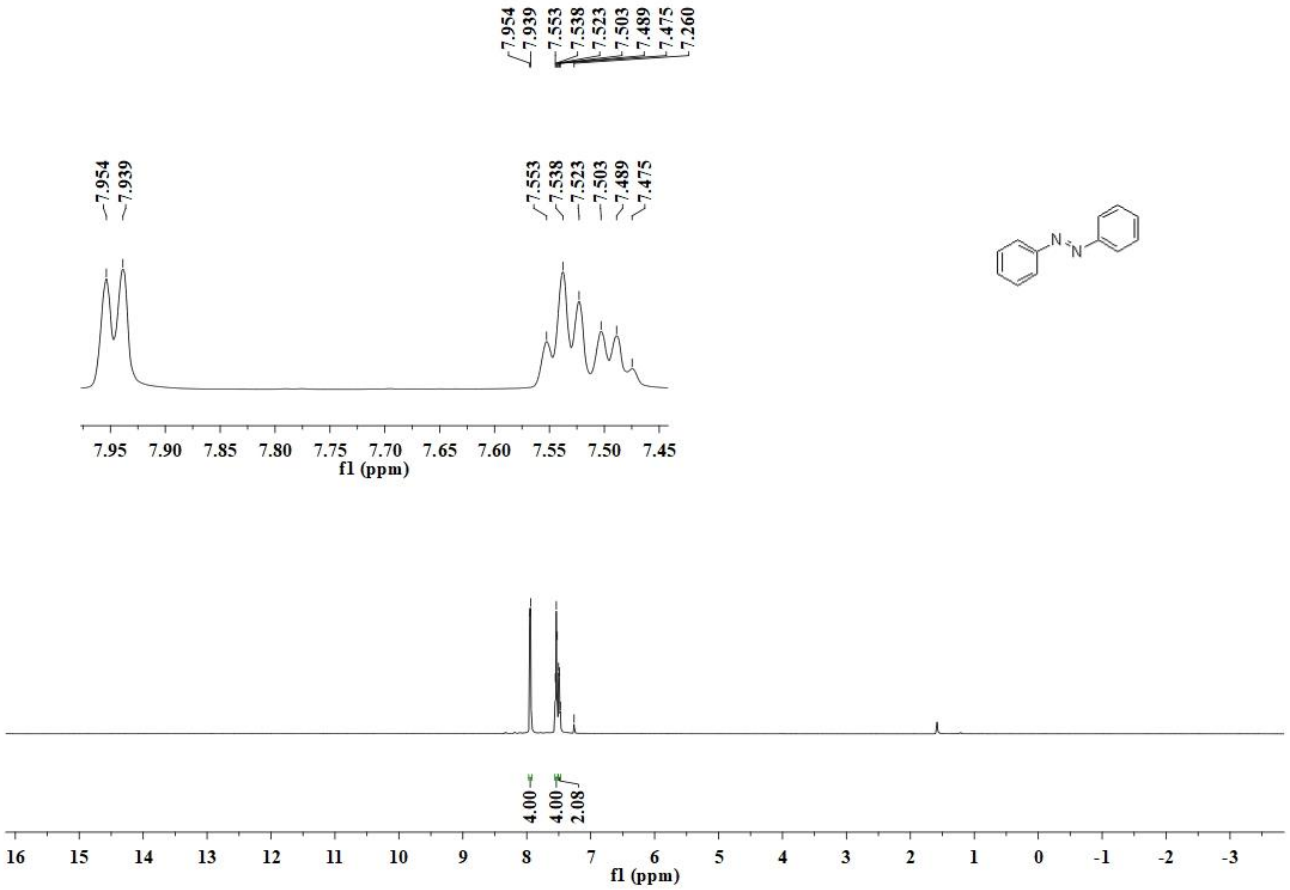
^{1}H NMR (500 MHz, DMSO-d_6) of **1g**



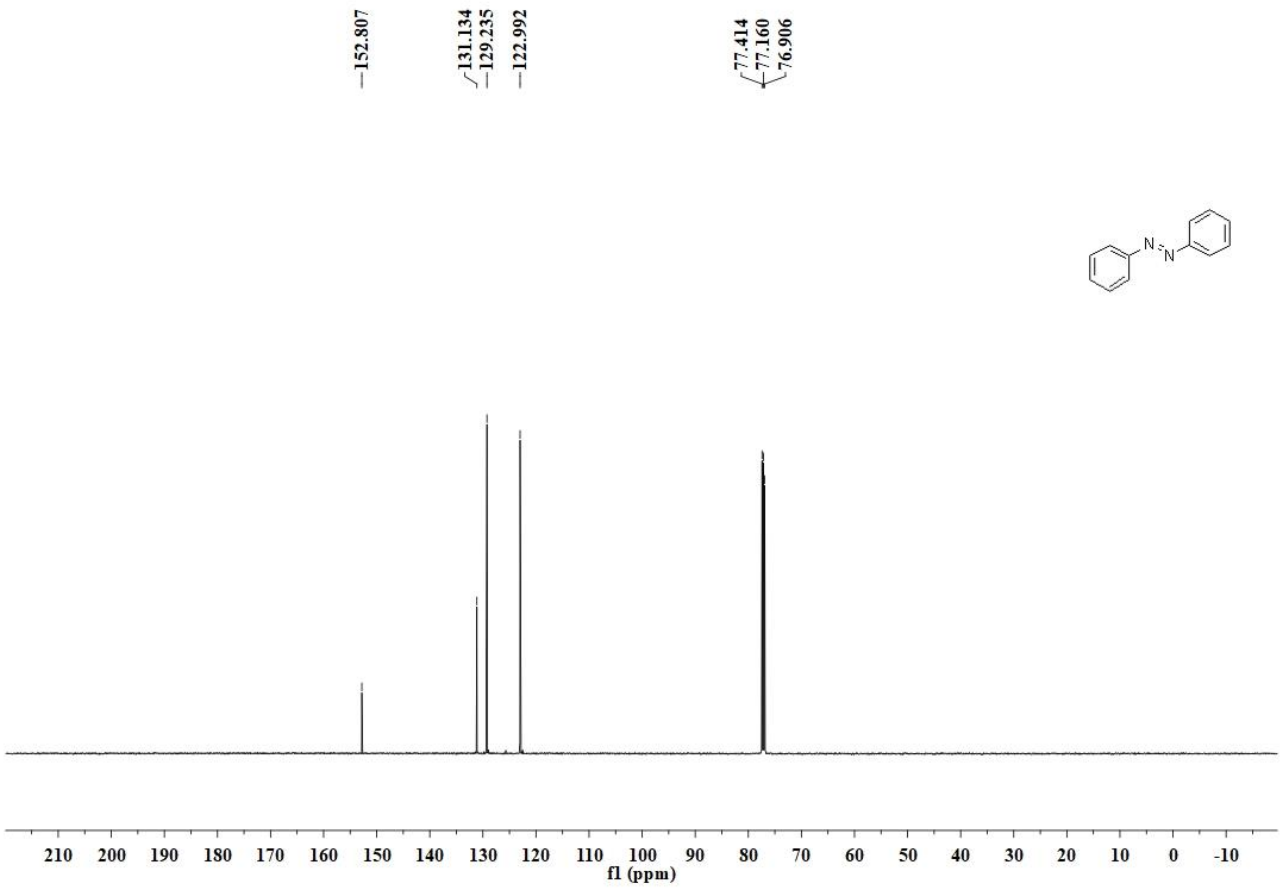
^{13}C NMR (126 MHz, DMSO-d_6) of **1g**



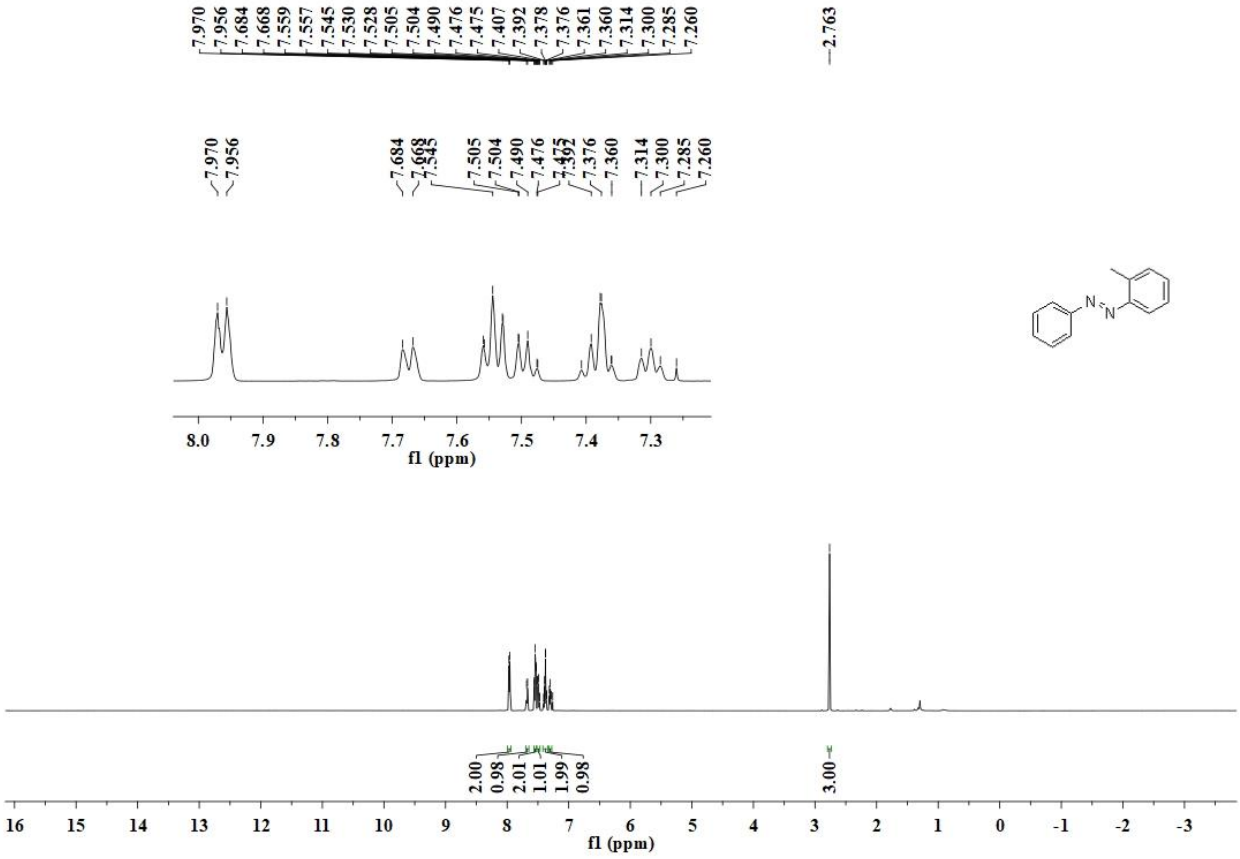
^{1}H NMR (500 MHz, $CDCl_3$) of **3a** or **3aa**



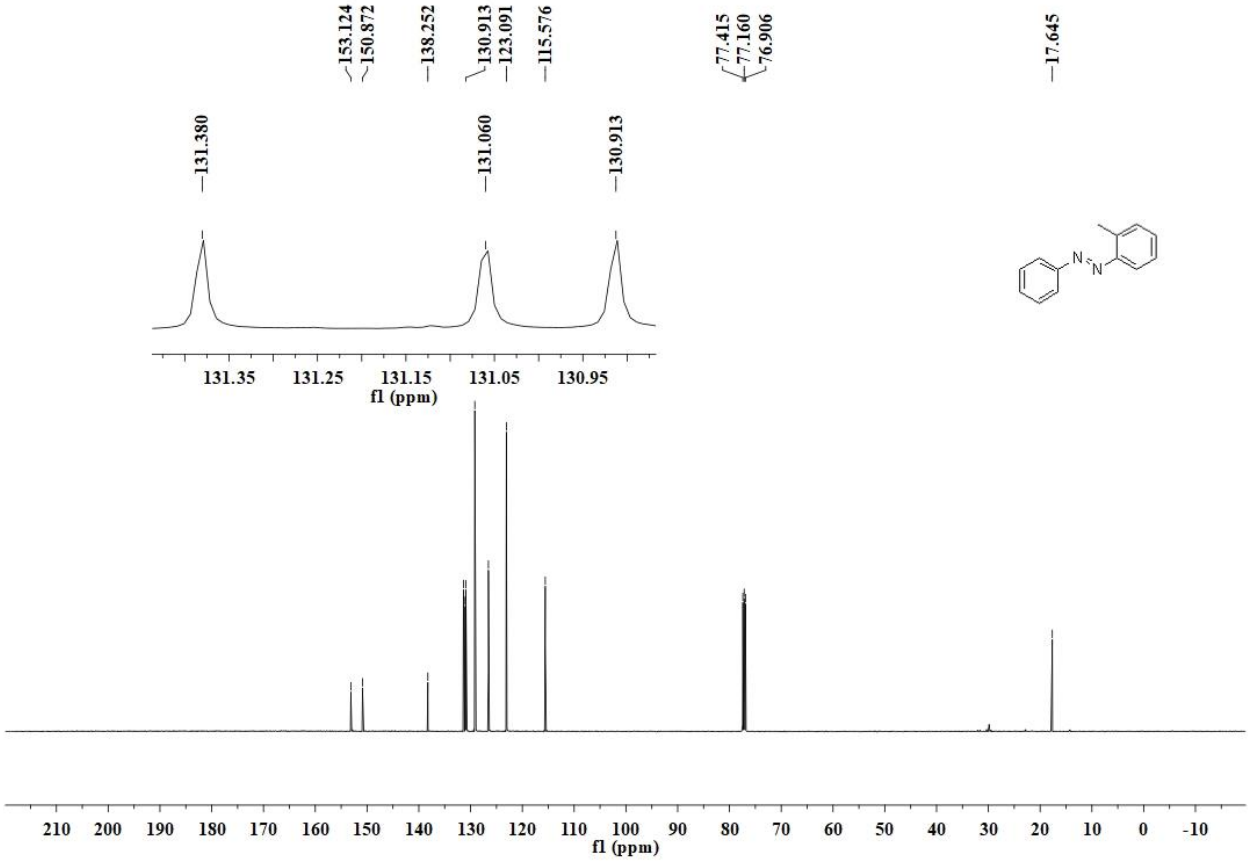
^{13}C NMR (126 MHz, $CDCl_3$) of **3a** or **3aa**



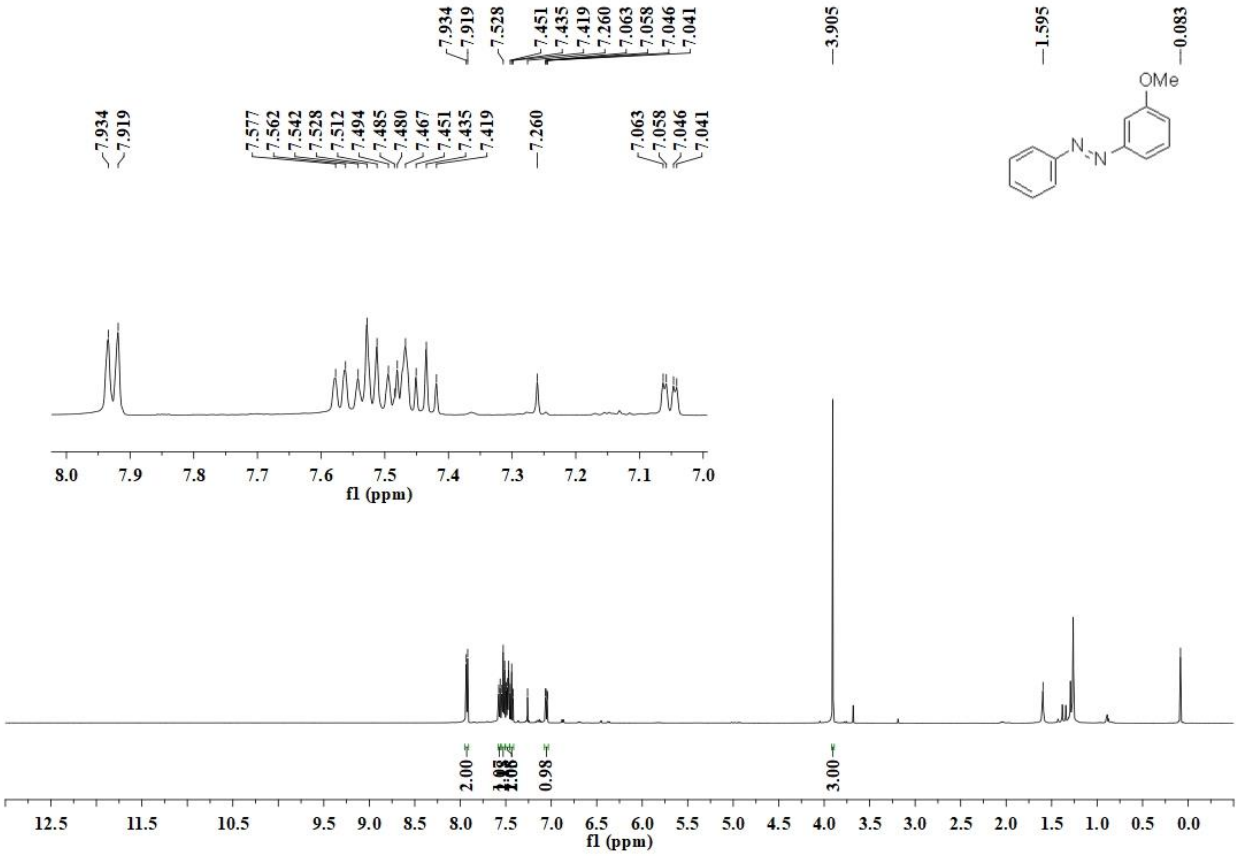
^{1}H NMR (500 MHz, $CDCl_3$) of **3b**



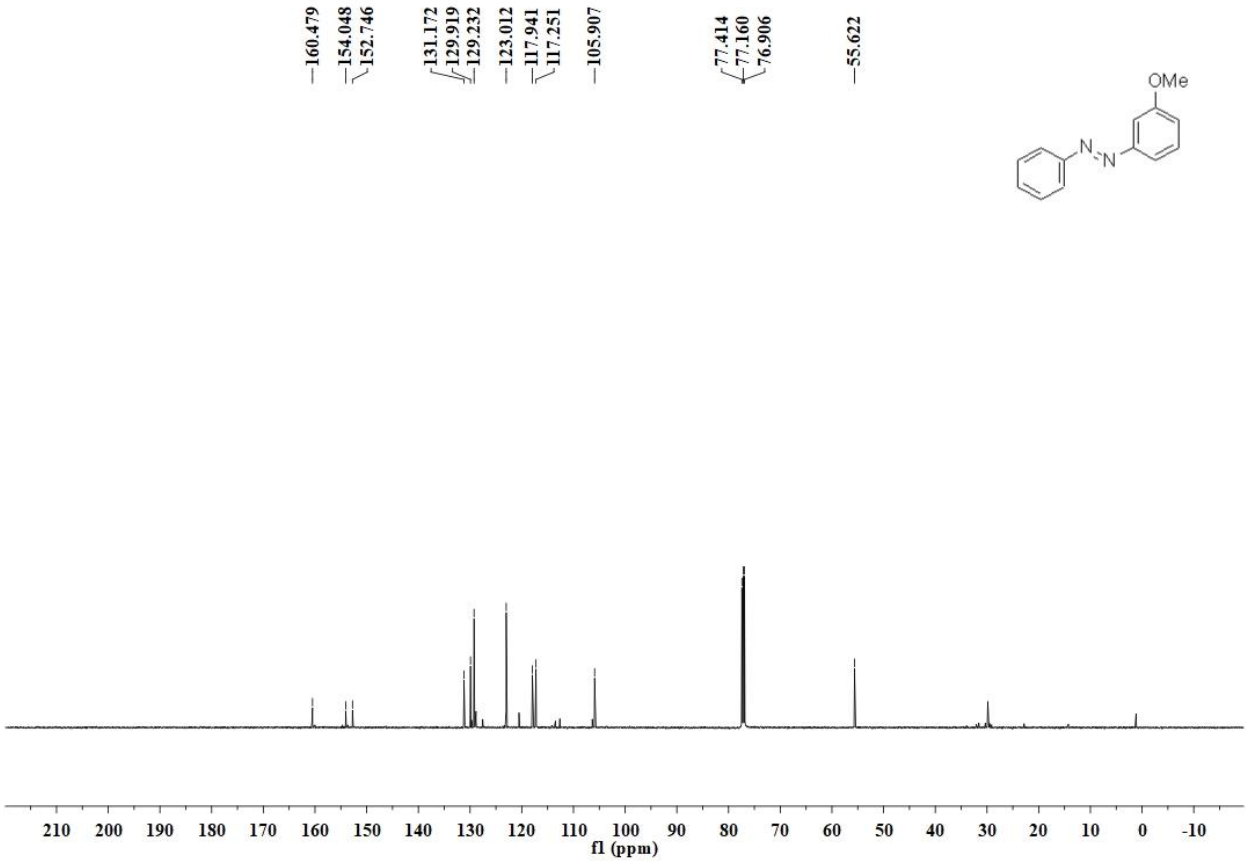
^{13}C NMR (126 MHz, $CDCl_3$) of **3b**



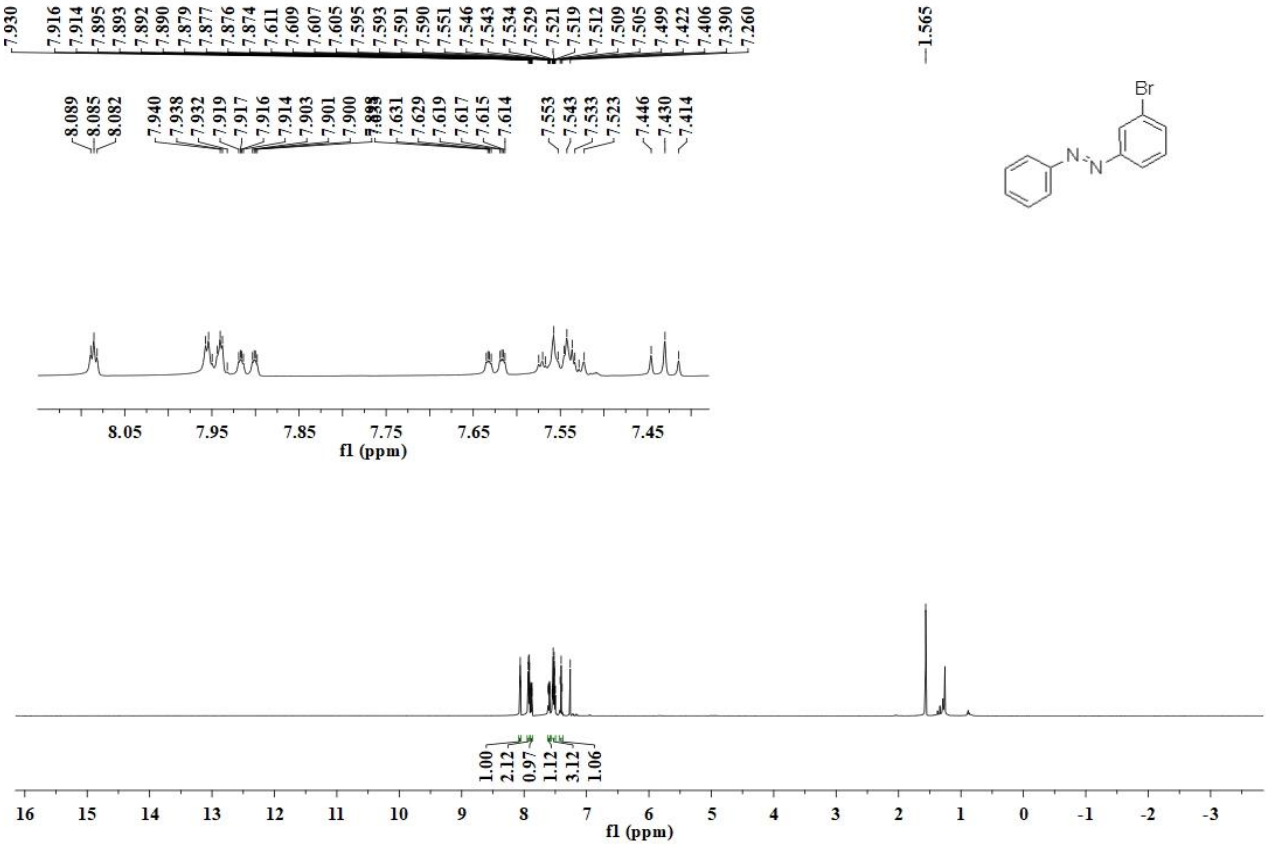
^{1}H NMR (500 MHz, $CDCl_3$) of **3c**



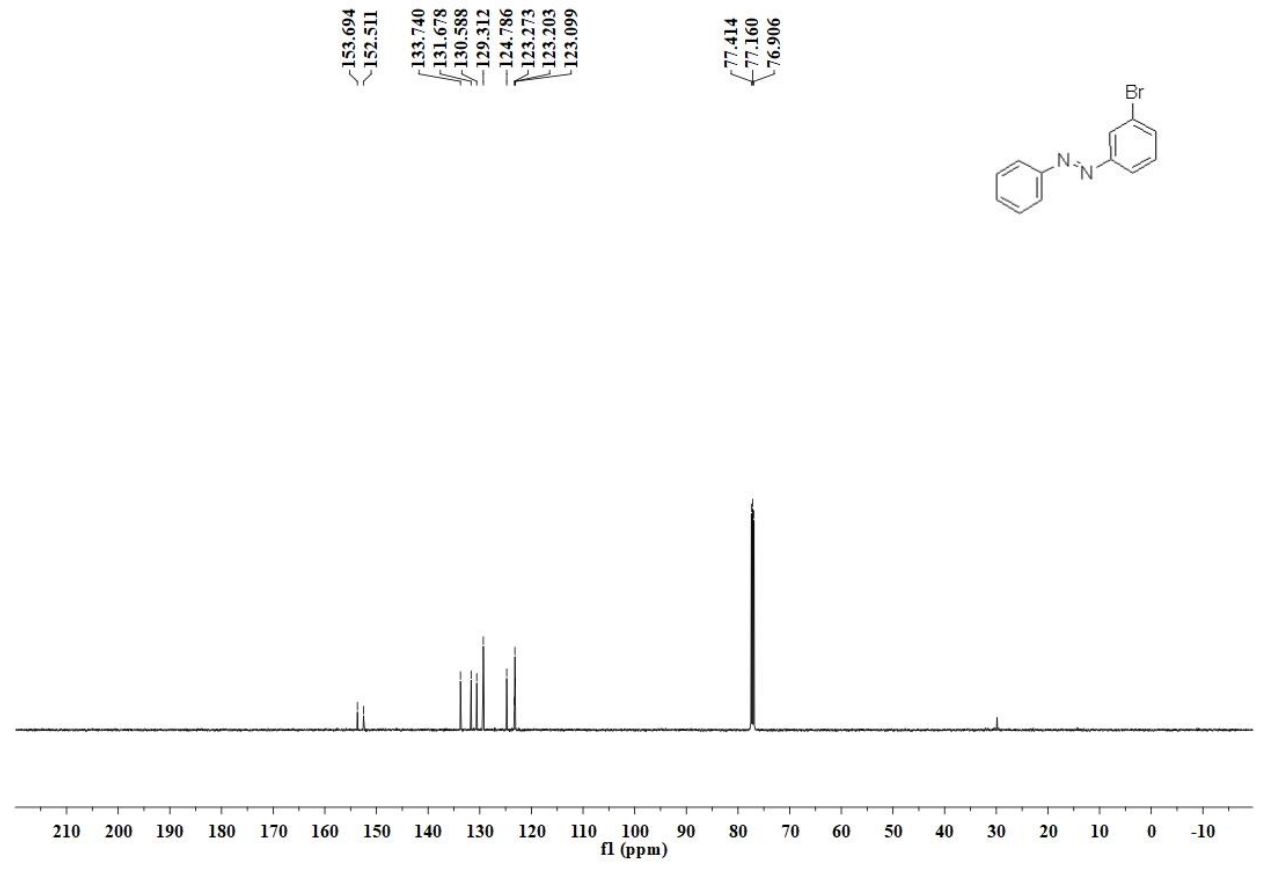
^{13}C NMR (126 MHz, $CDCl_3$) of **3c**



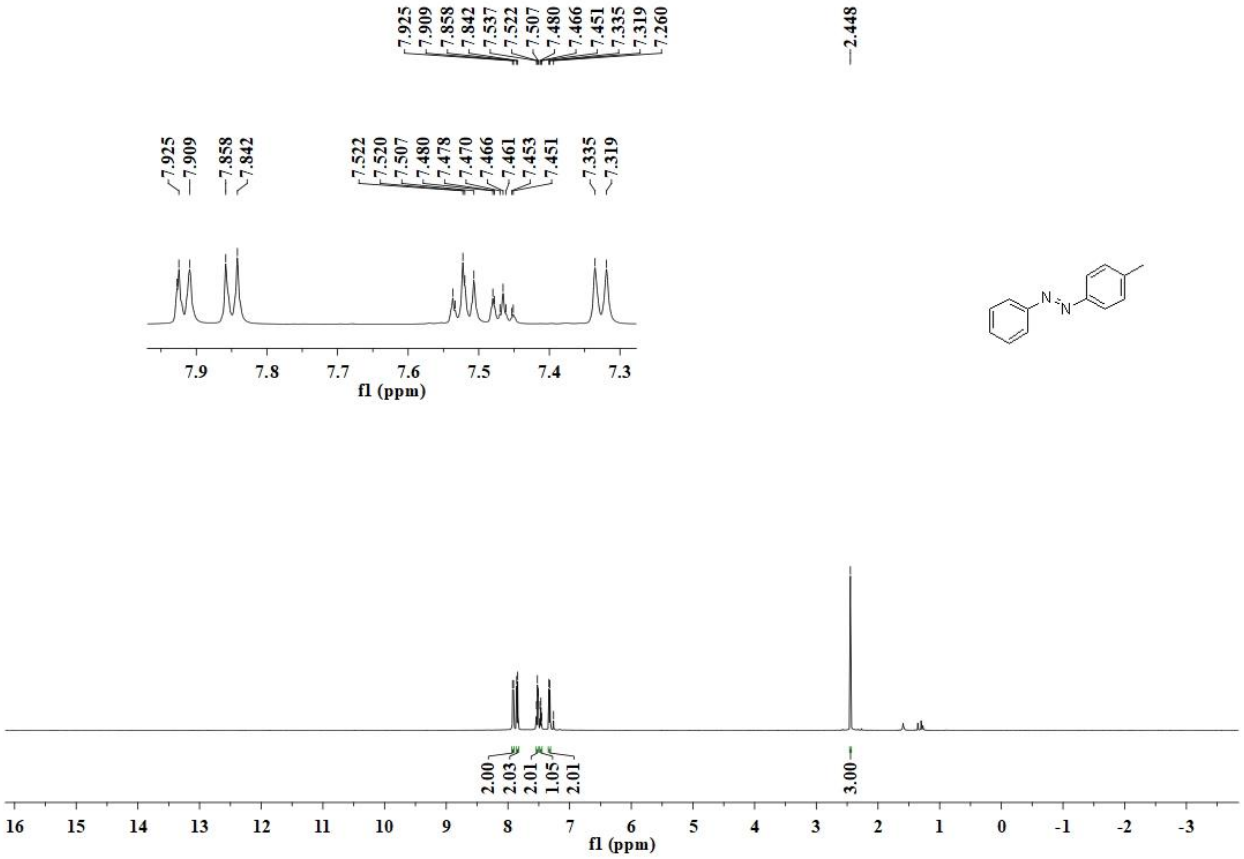
^{1}H NMR (500 MHz, $CDCl_3$) of **3d**



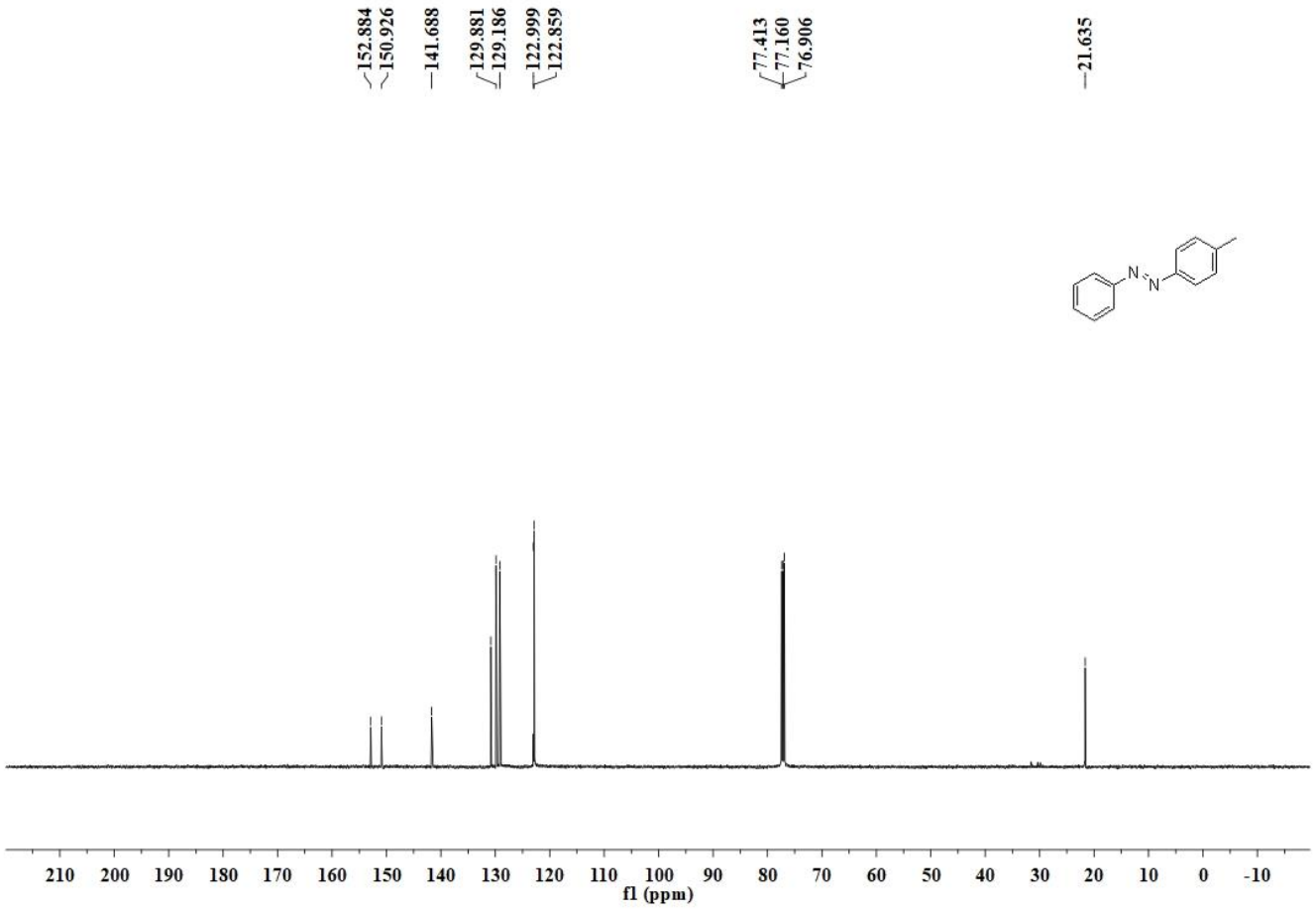
^{13}C NMR (126 MHz, $CDCl_3$) of **3d**



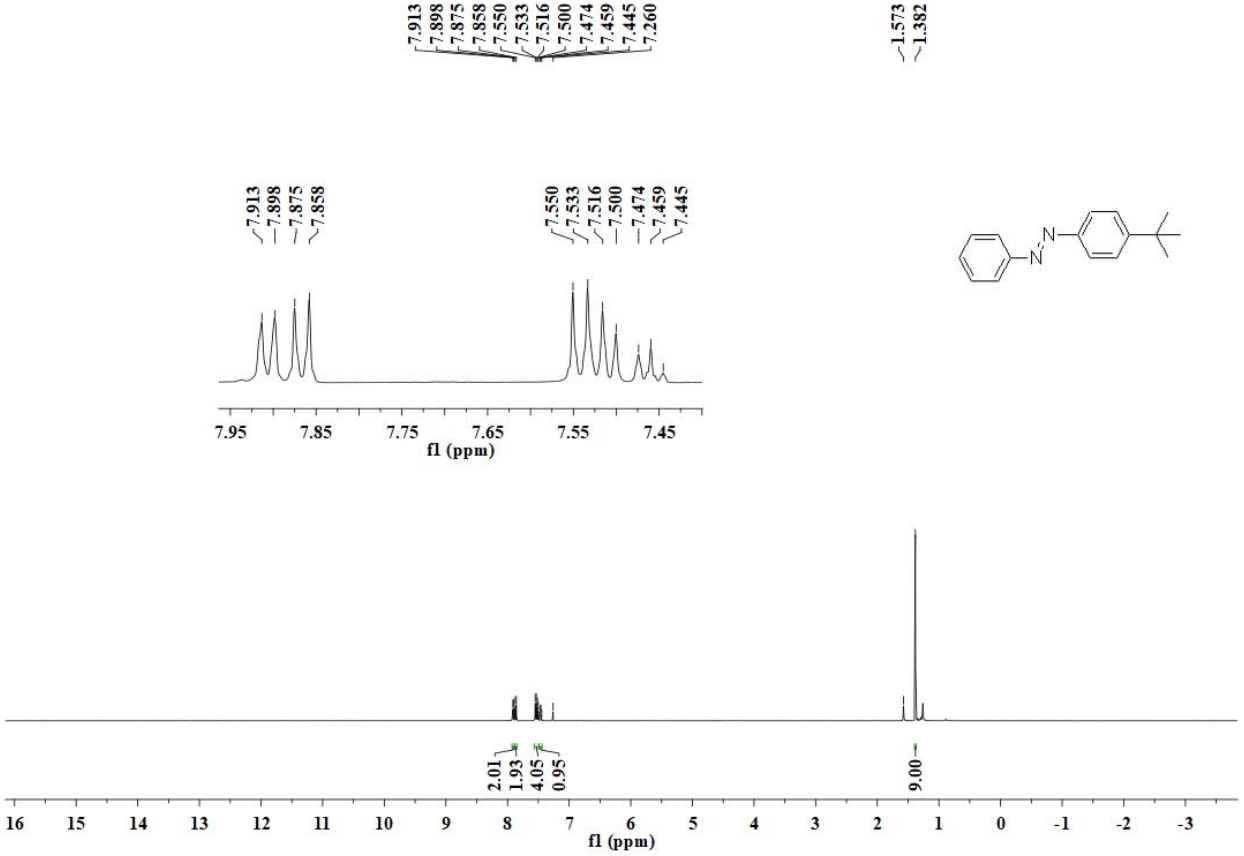
^{1}H NMR (500 MHz, $CDCl_3$) of **3e** or **4c**



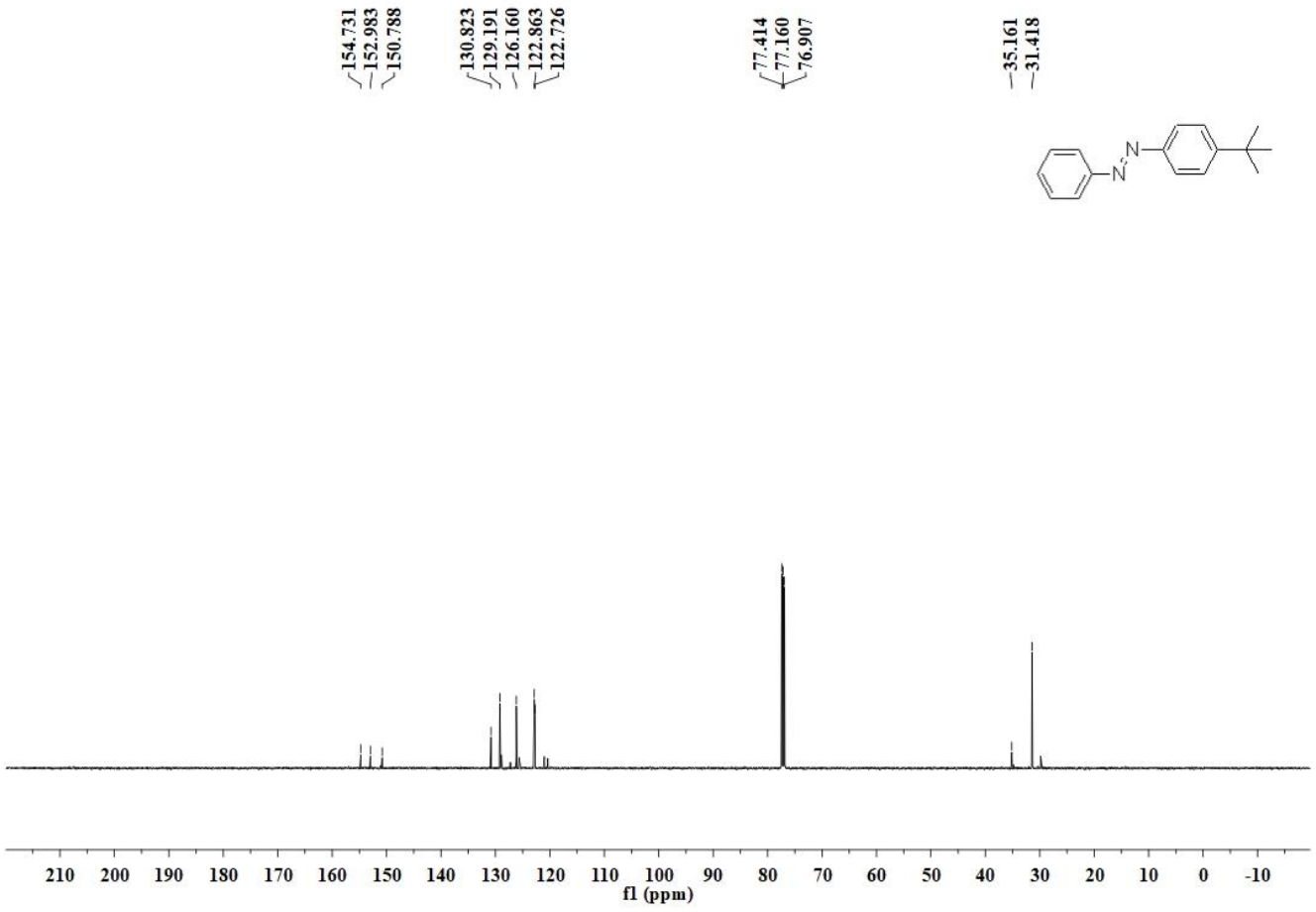
^{13}C NMR (126 MHz, $CDCl_3$) of **3e** or **4c**



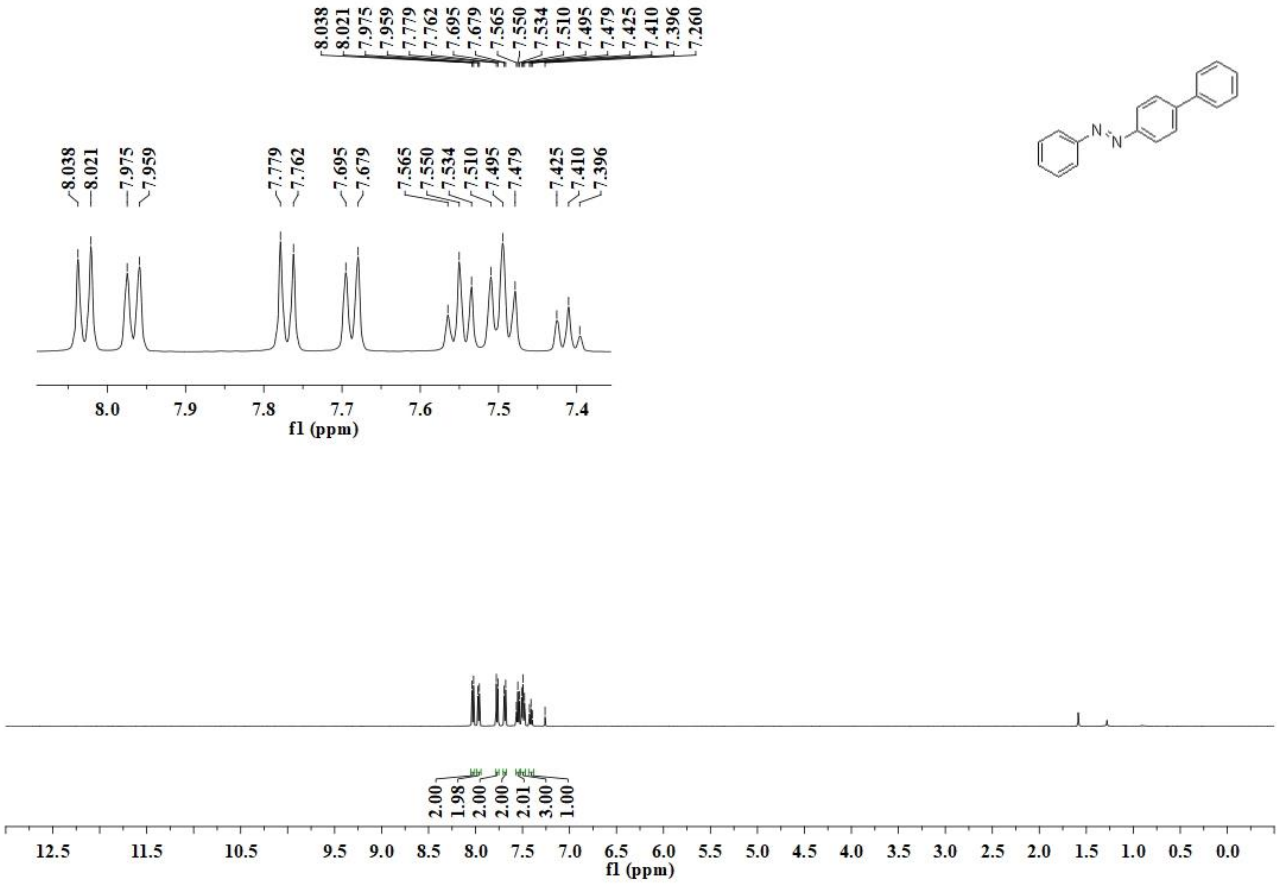
^{1}H NMR (500 MHz, $CDCl_3$) of **3f** or **4e**



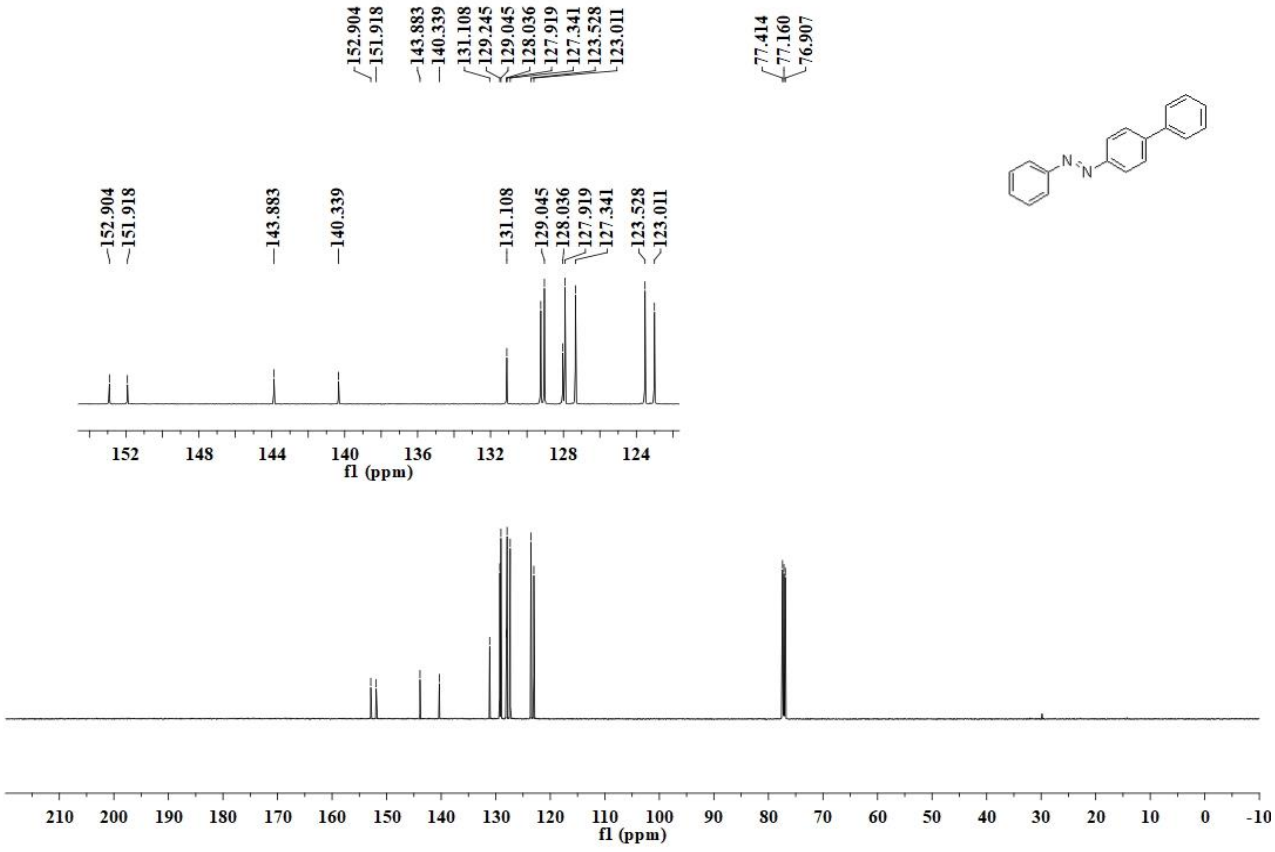
^{13}C NMR (126 MHz, $CDCl_3$) of **3f** or **4e**



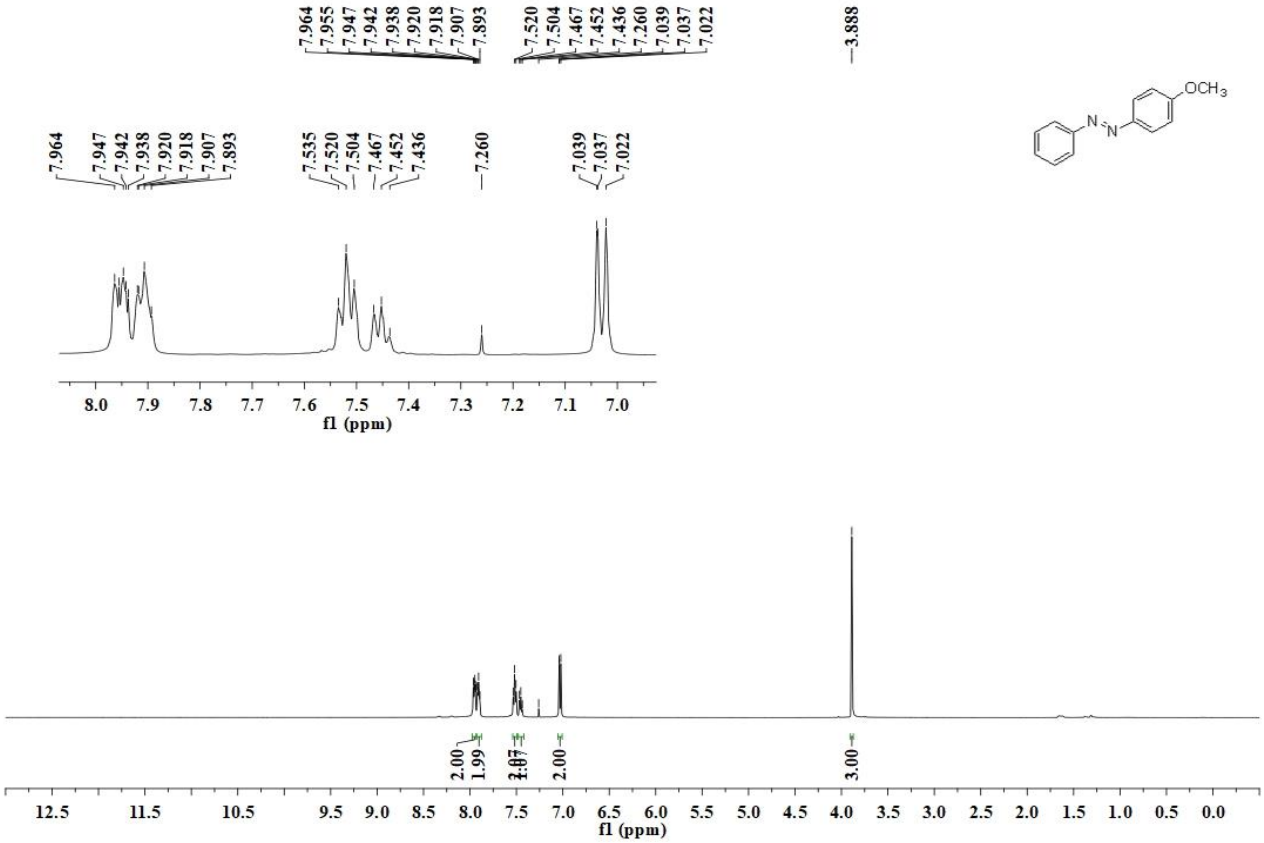
^{1}H NMR (500 MHz, $CDCl_3$) of **3g**



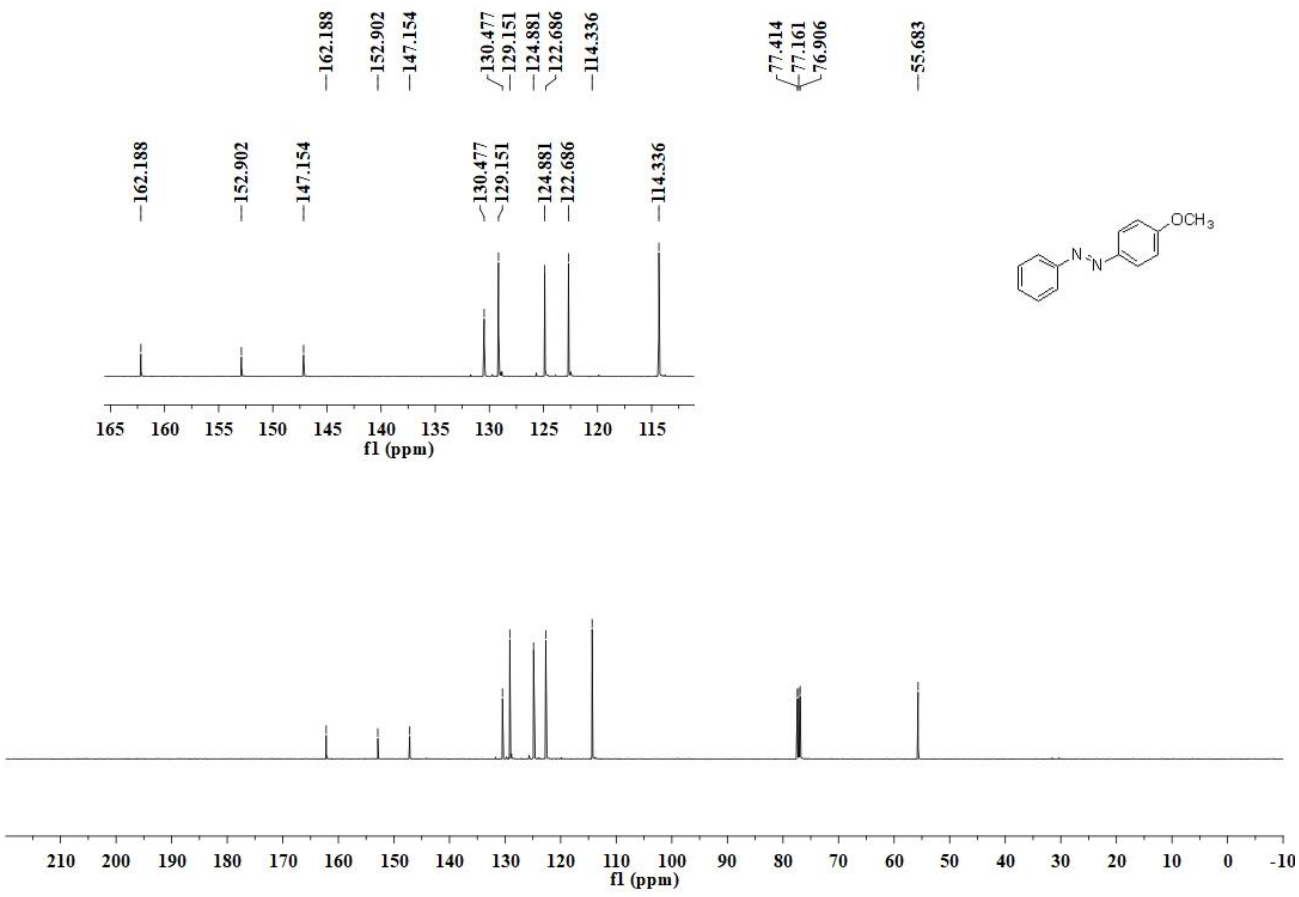
^{13}C NMR (126 MHz, $CDCl_3$) of **3g**



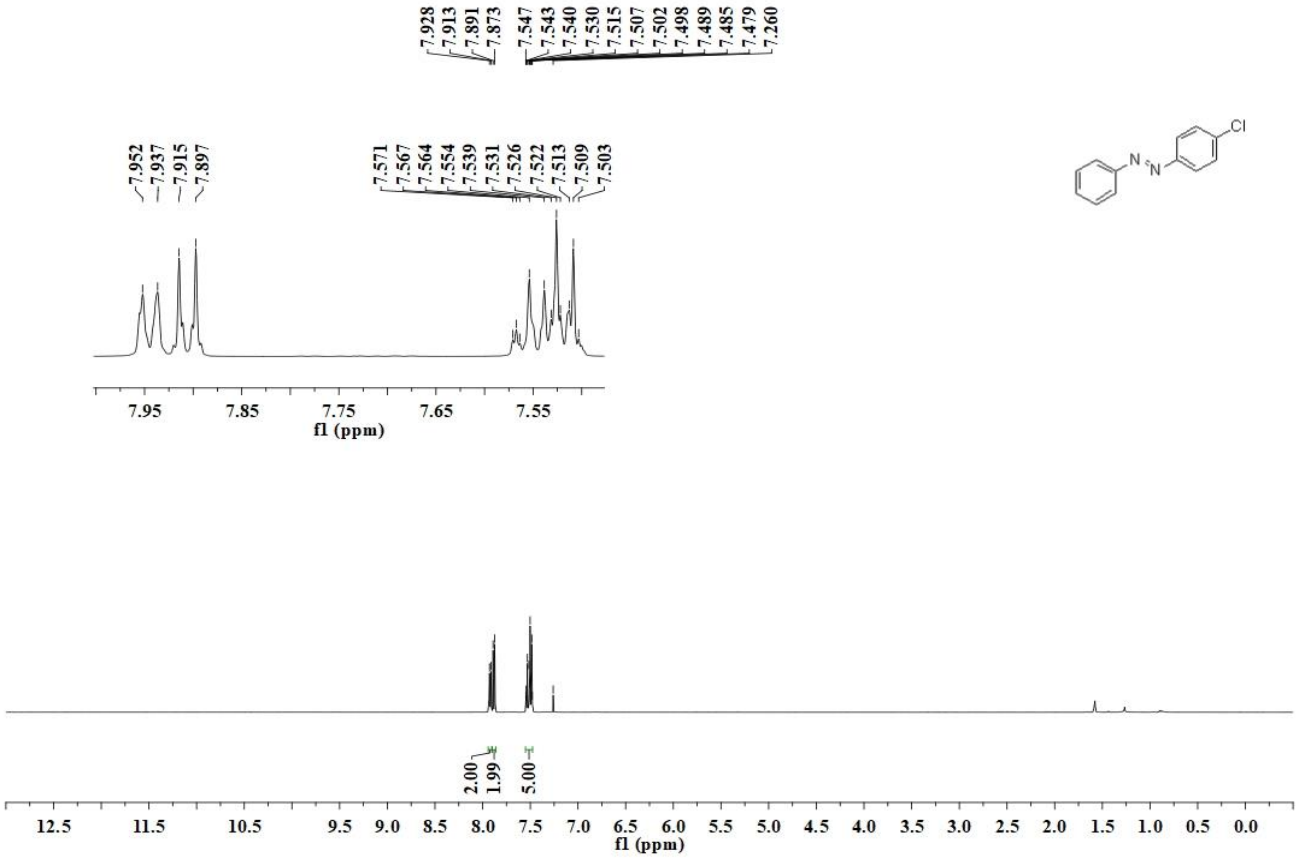
^{1}H NMR (500 MHz, $CDCl_3$) of **3h**



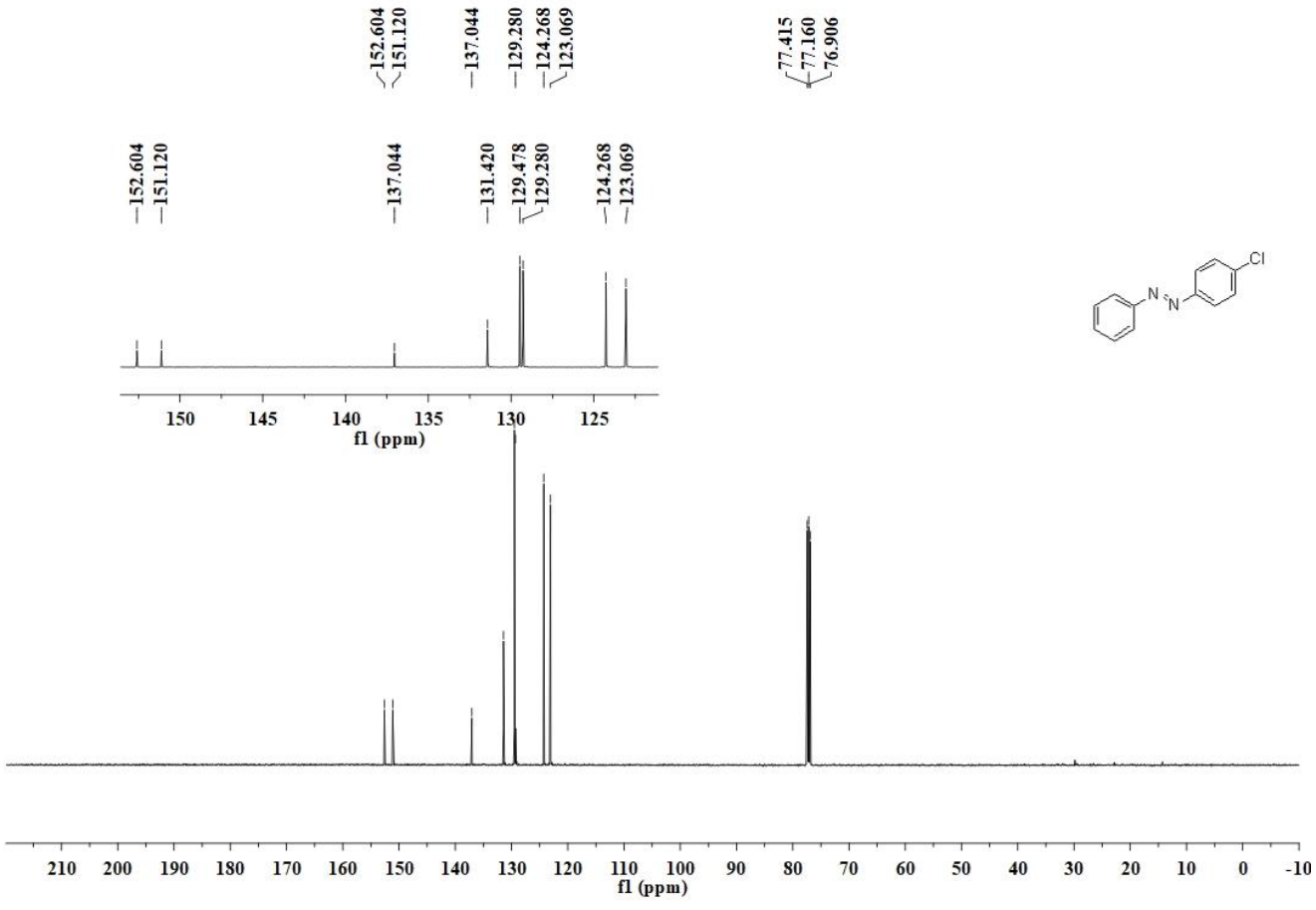
^{13}C NMR (126 MHz, $CDCl_3$) of **3h**



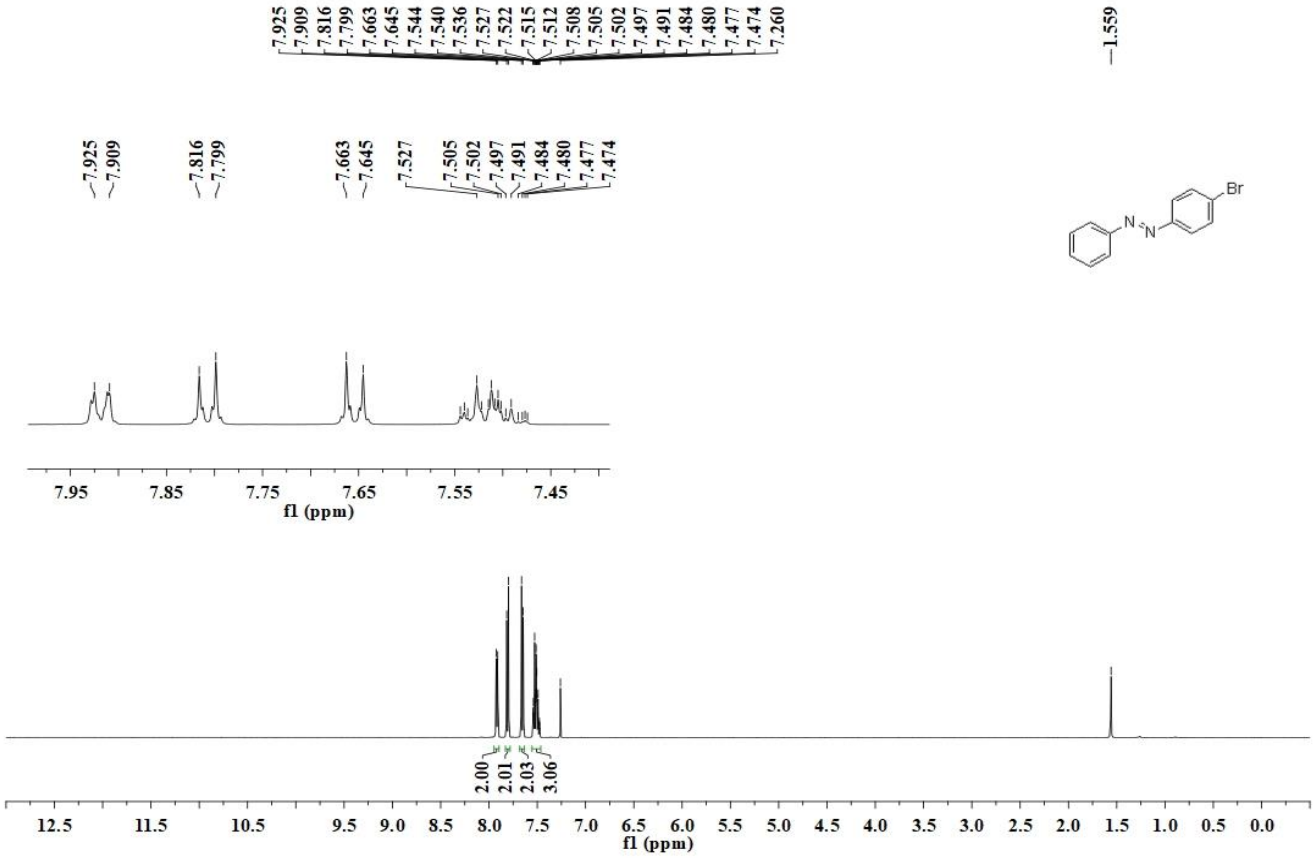
^{1}H NMR (500 MHz, $CDCl_3$) of **3i**



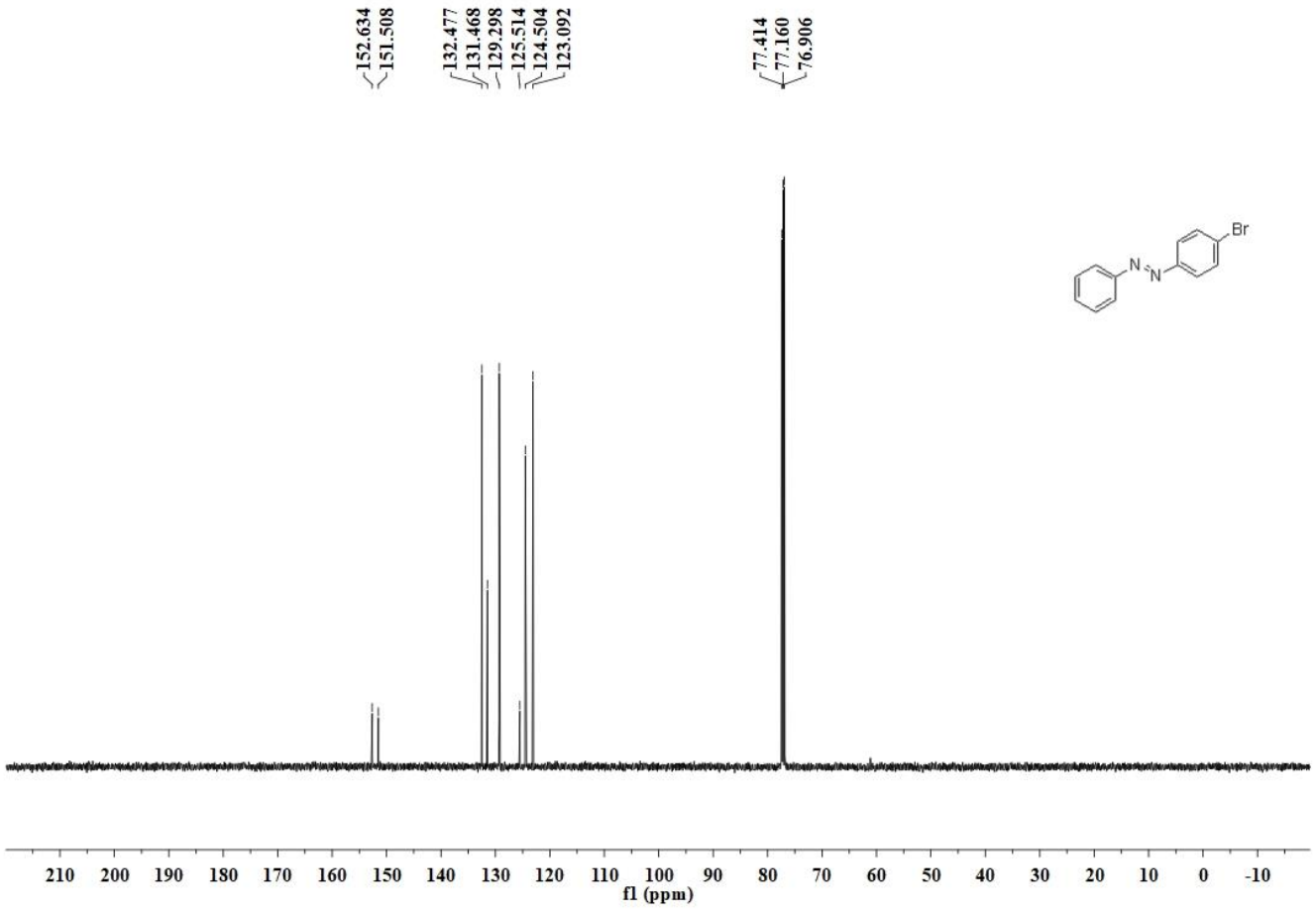
^{13}C NMR (126 MHz, $CDCl_3$) of **3i**



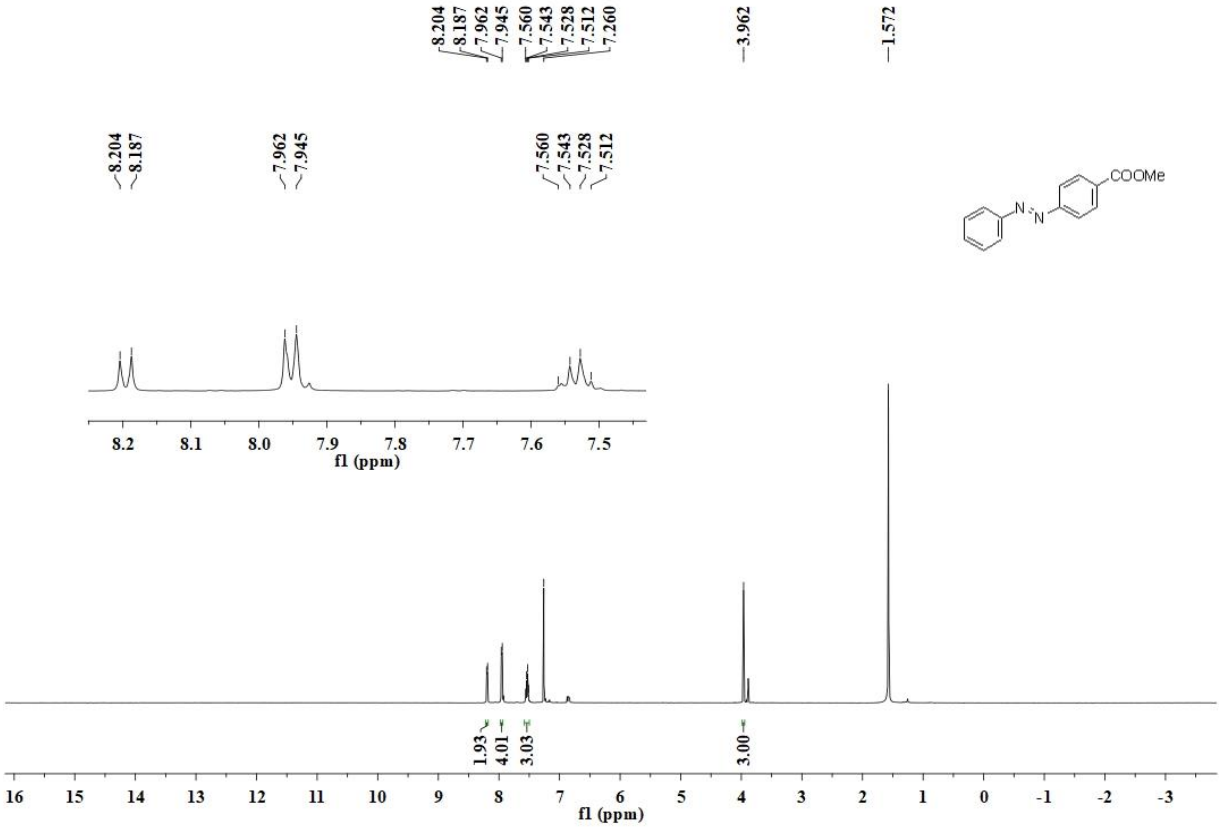
^{1}H NMR (500 MHz, $CDCl_3$) of **3j**



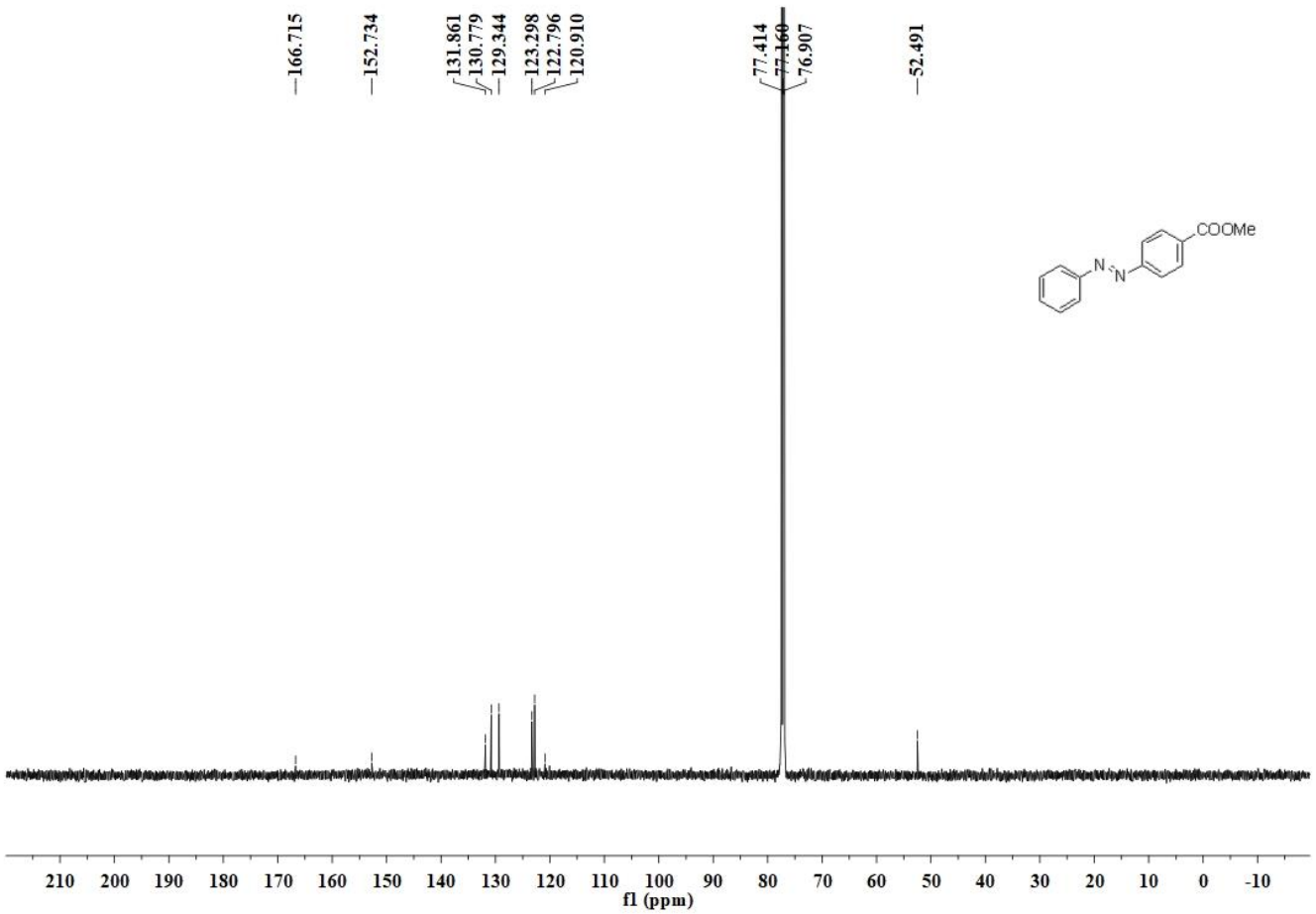
^{13}C NMR (126 MHz, $CDCl_3$) of **3j**



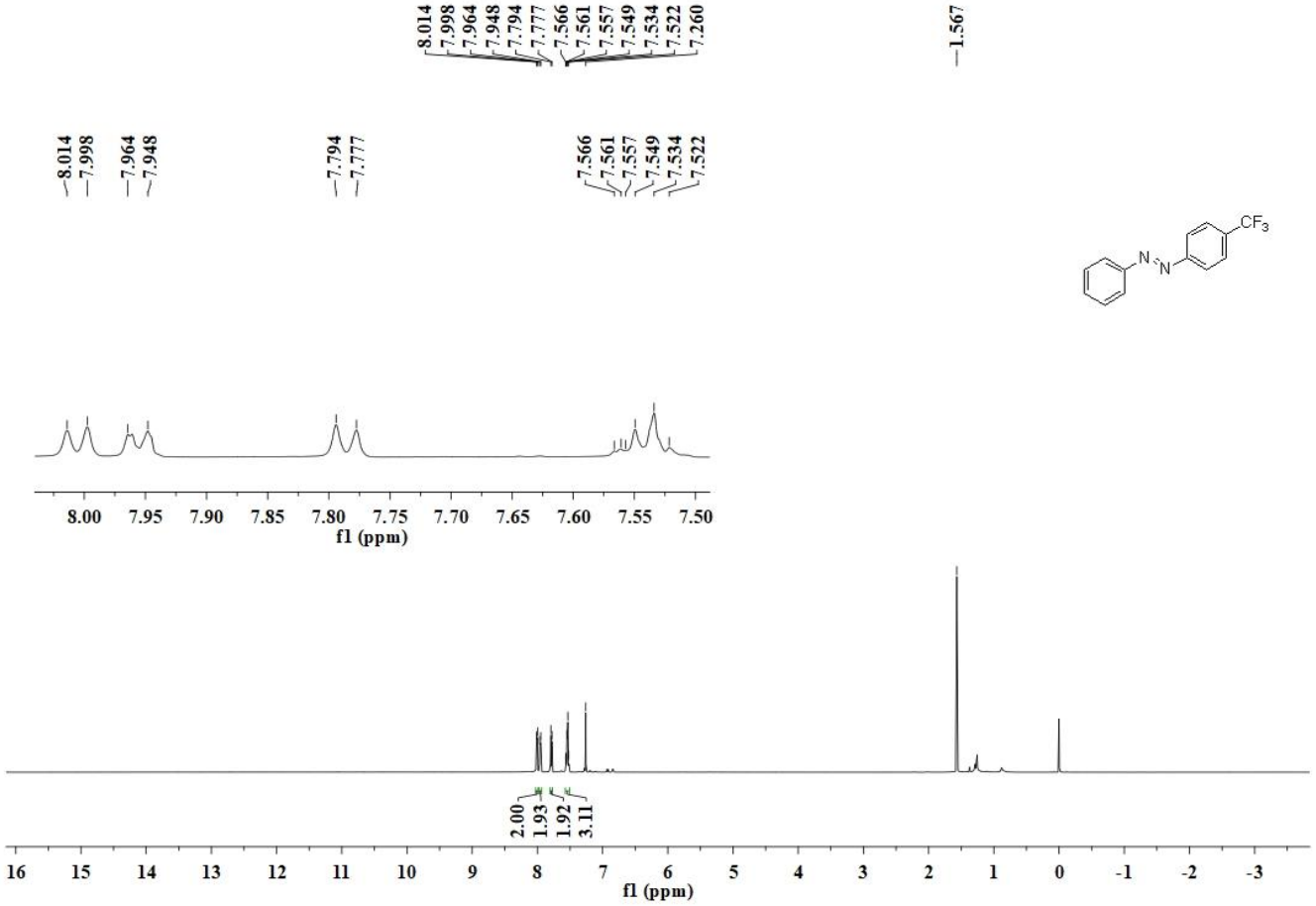
^{1}H NMR (500 MHz, $CDCl_3$) of **3k** or **3ak**



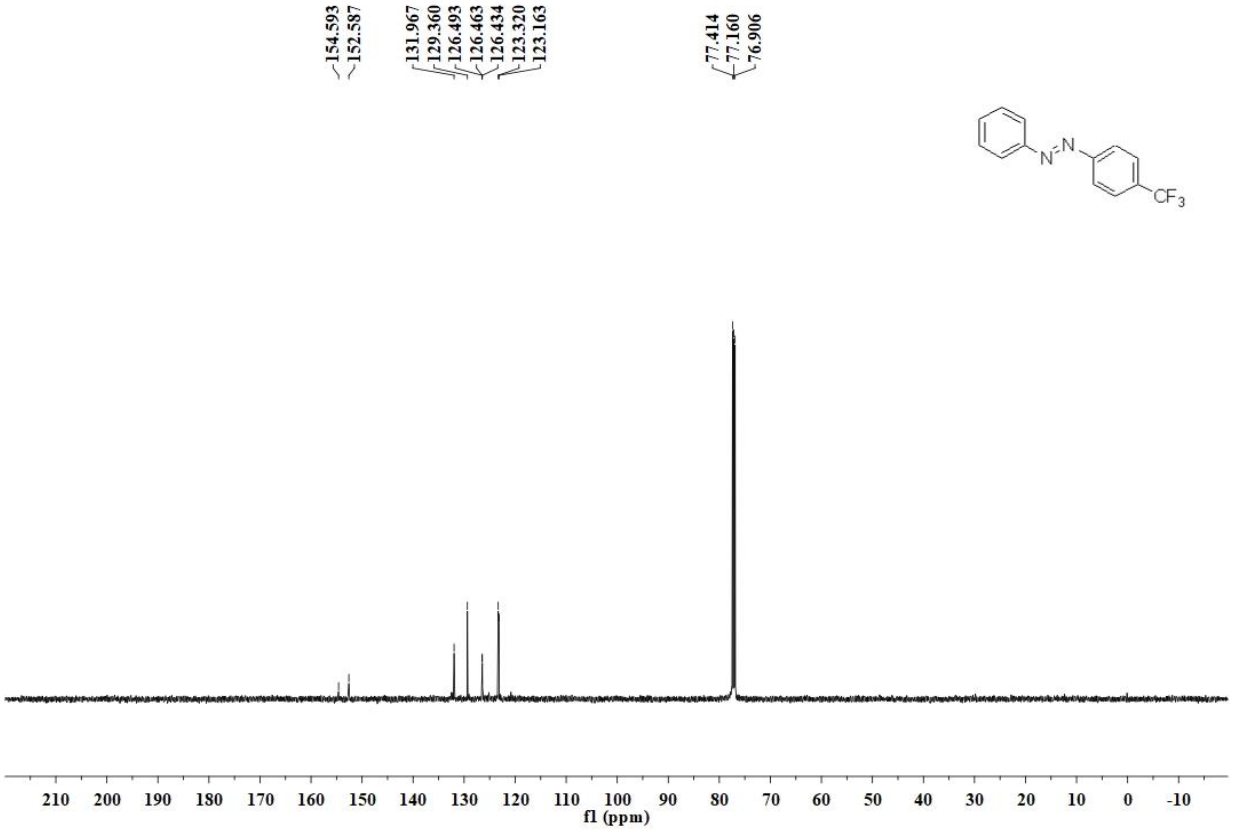
^{13}C NMR (126 MHz, $CDCl_3$) of **3k** or **3ak**



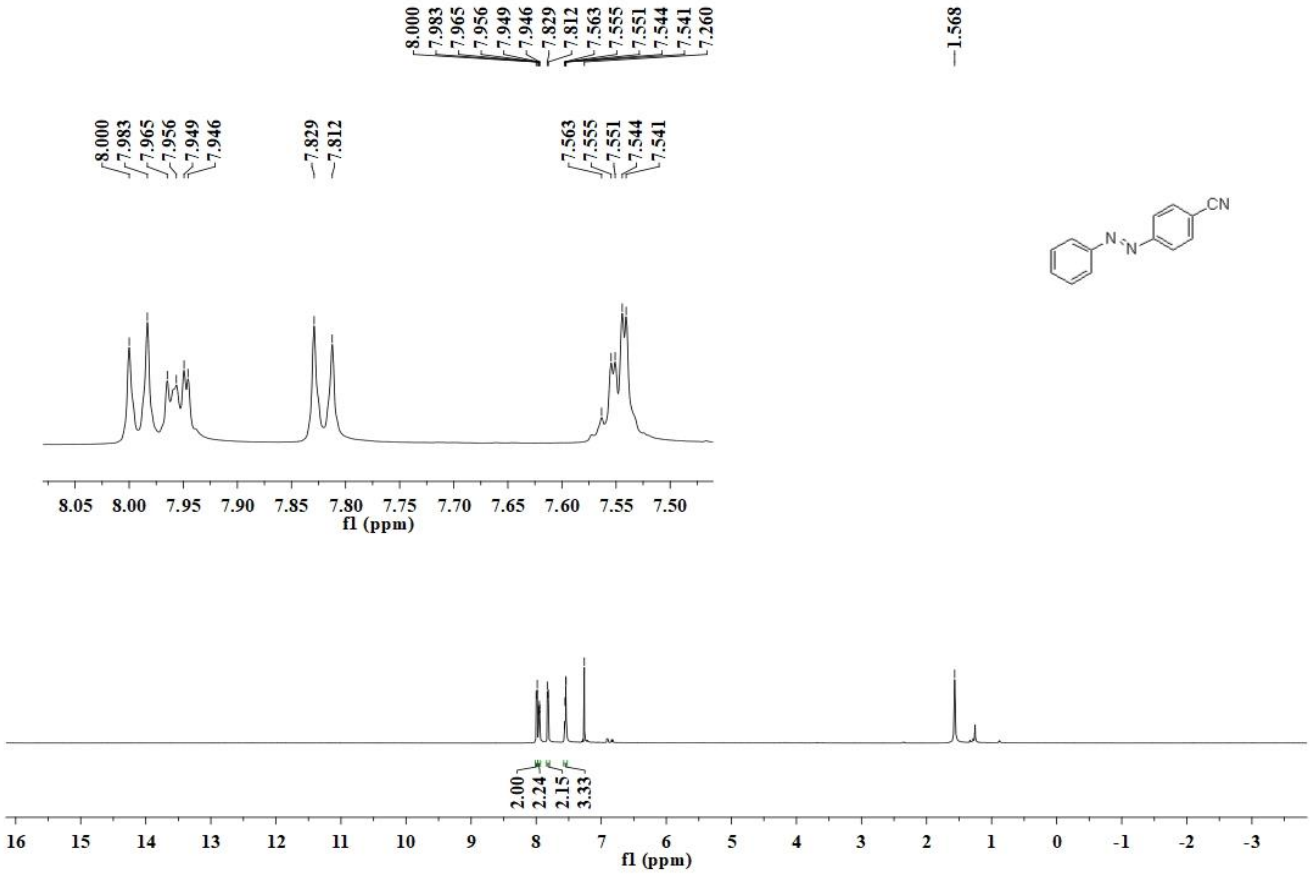
^{1}H NMR (500 MHz, $CDCl_3$) of **3l**



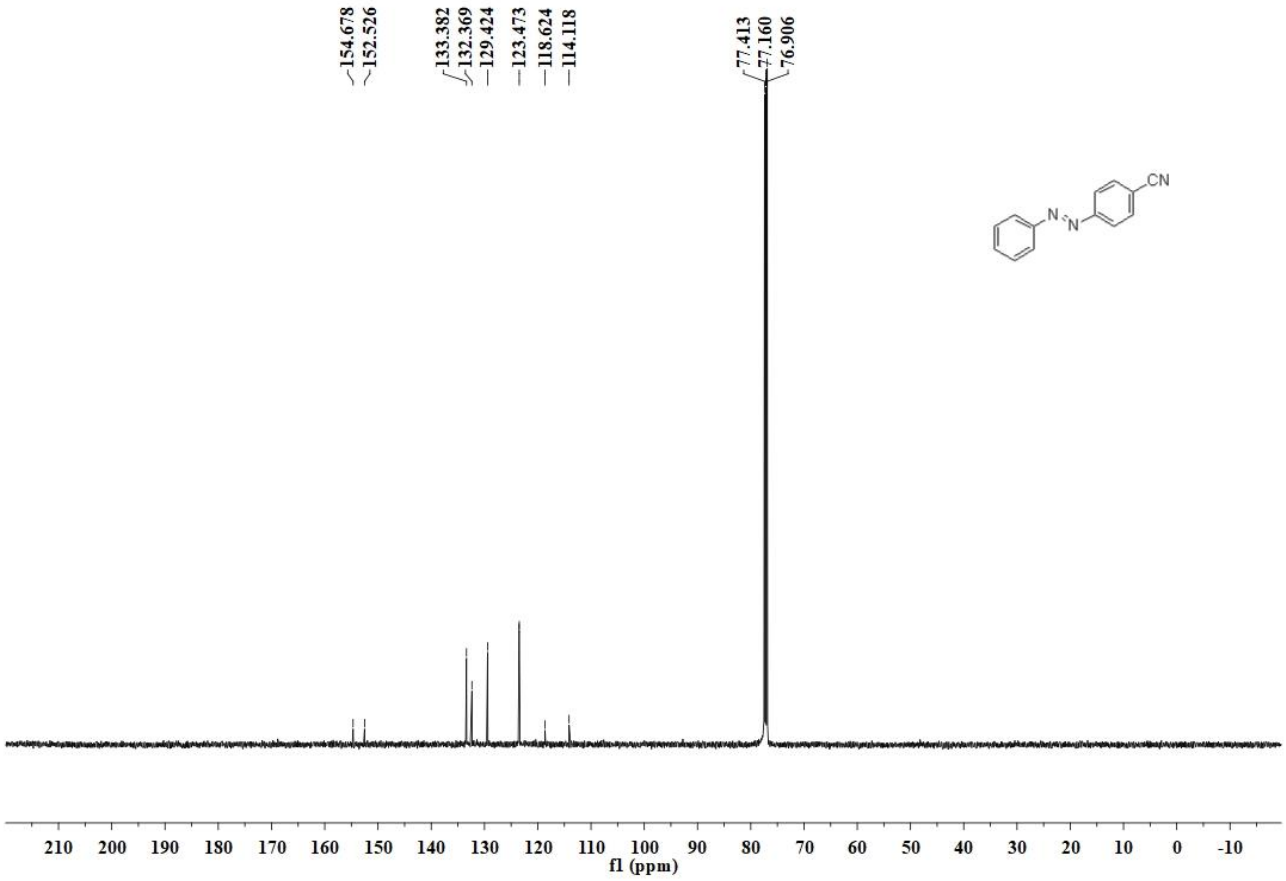
^{13}C NMR (126 MHz, $CDCl_3$) of **3l**



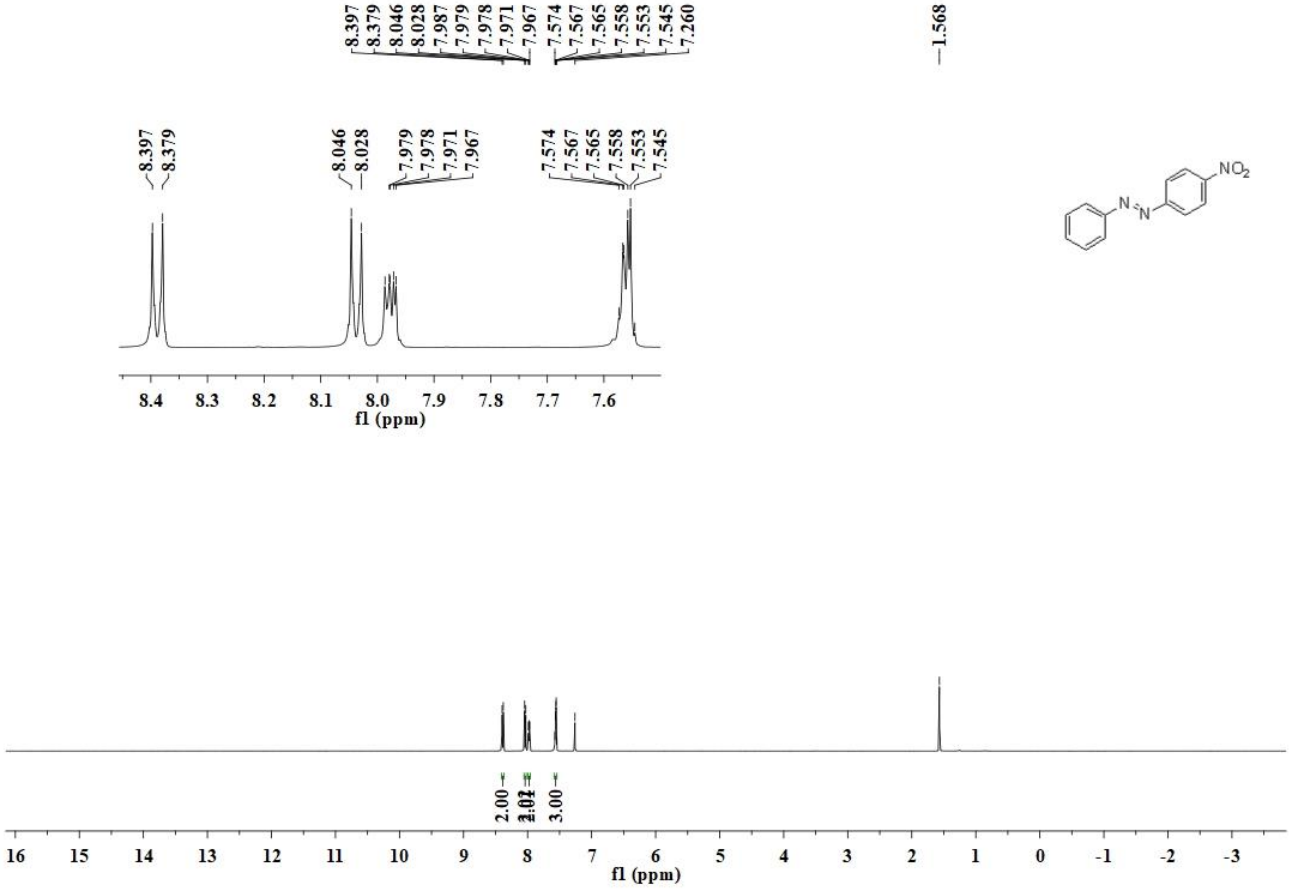
^{1}H NMR (500 MHz, $CDCl_3$) of **3m**, **4g** or **3ca**



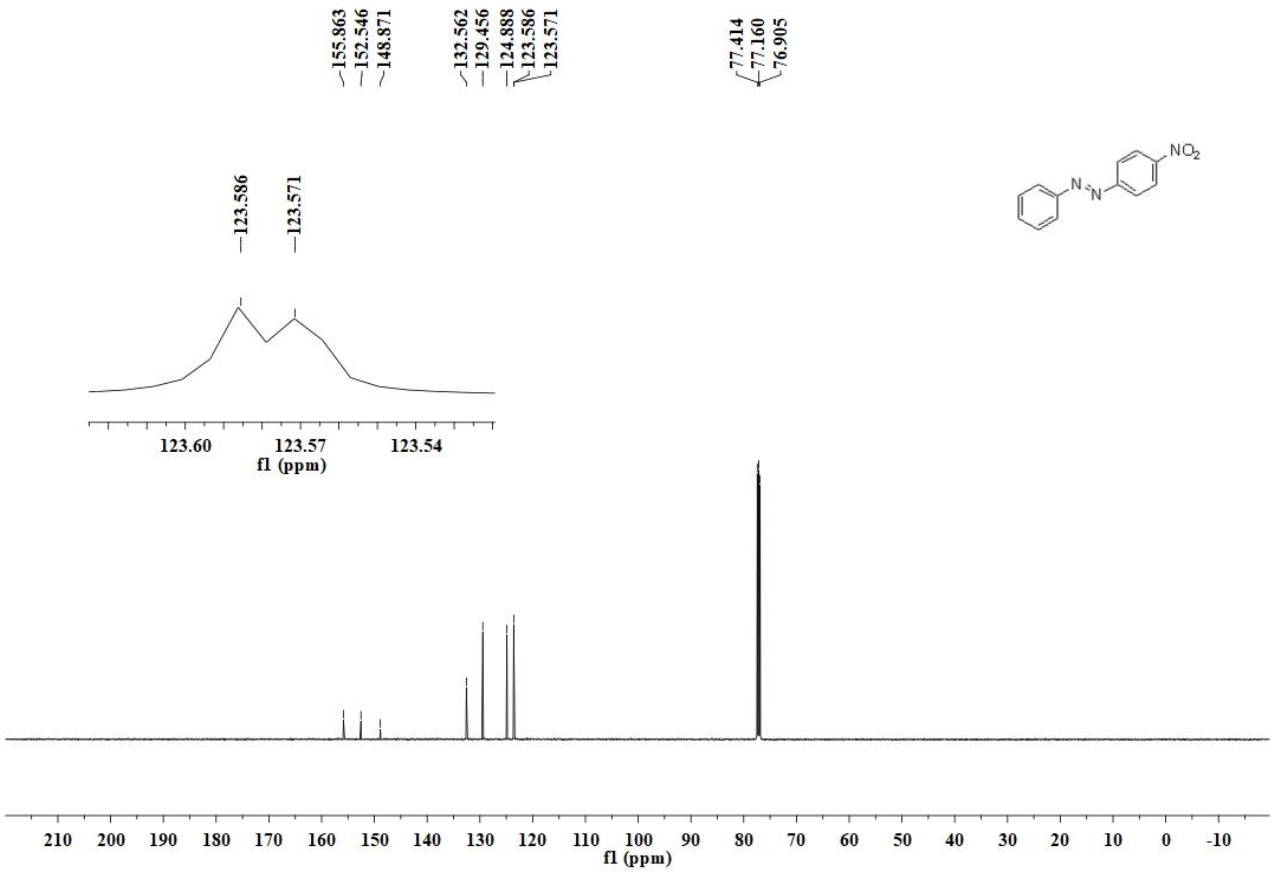
^{13}C NMR (126 MHz, $CDCl_3$) of **3m**, **4g** or **3ca**



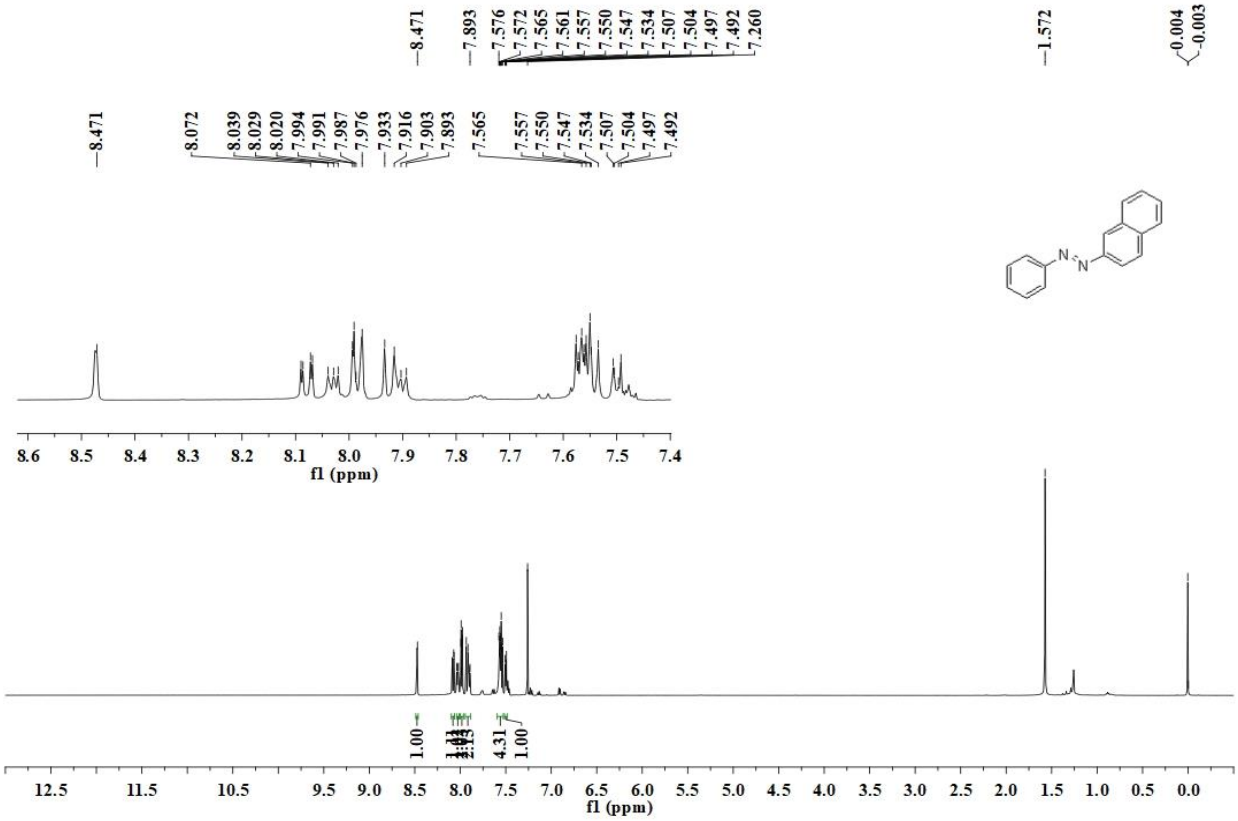
^{1}H NMR (500 MHz, $CDCl_3$) of **3n** or **3an**



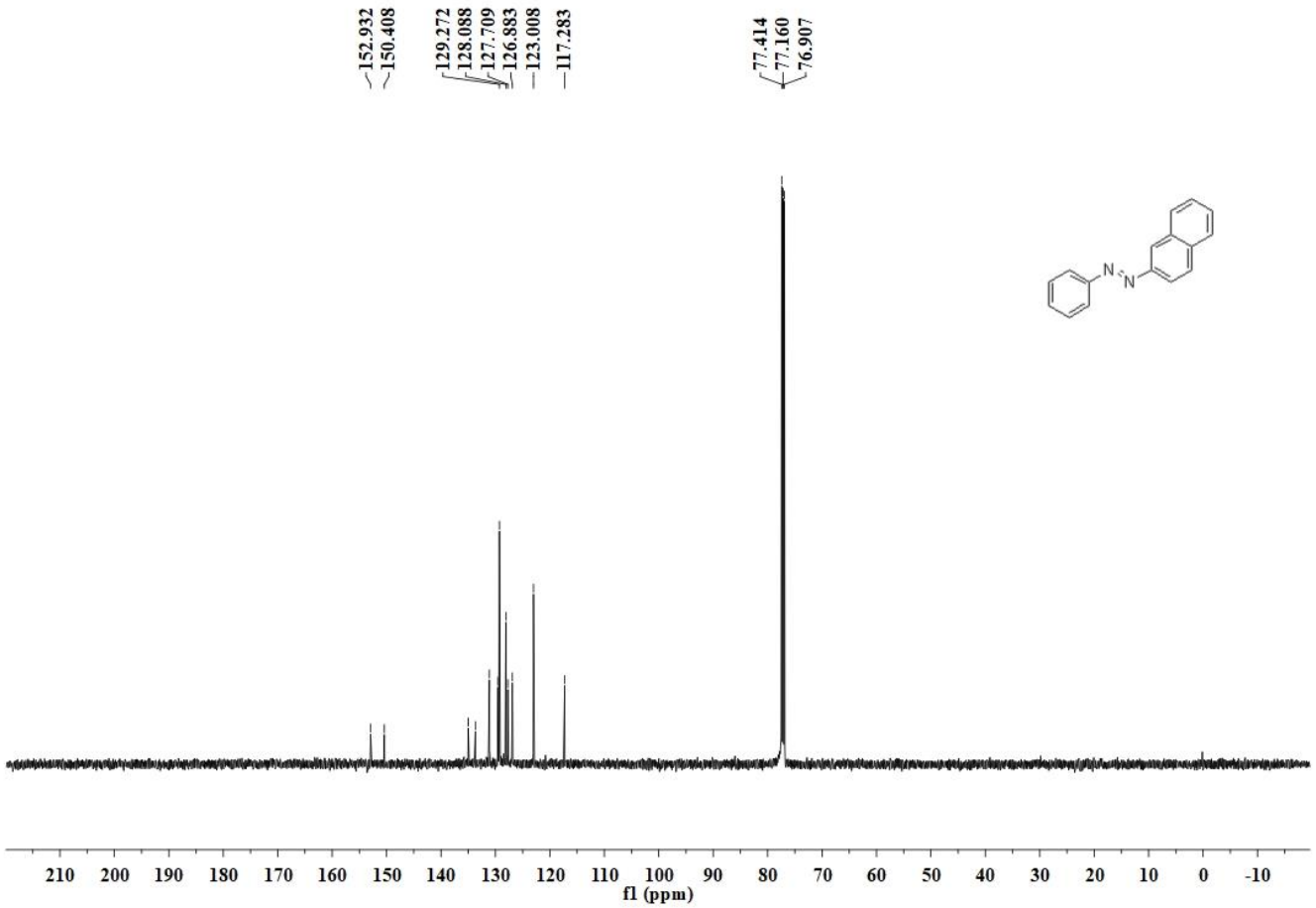
^{13}C NMR (126 MHz, $CDCl_3$) of **3n** or **3an**



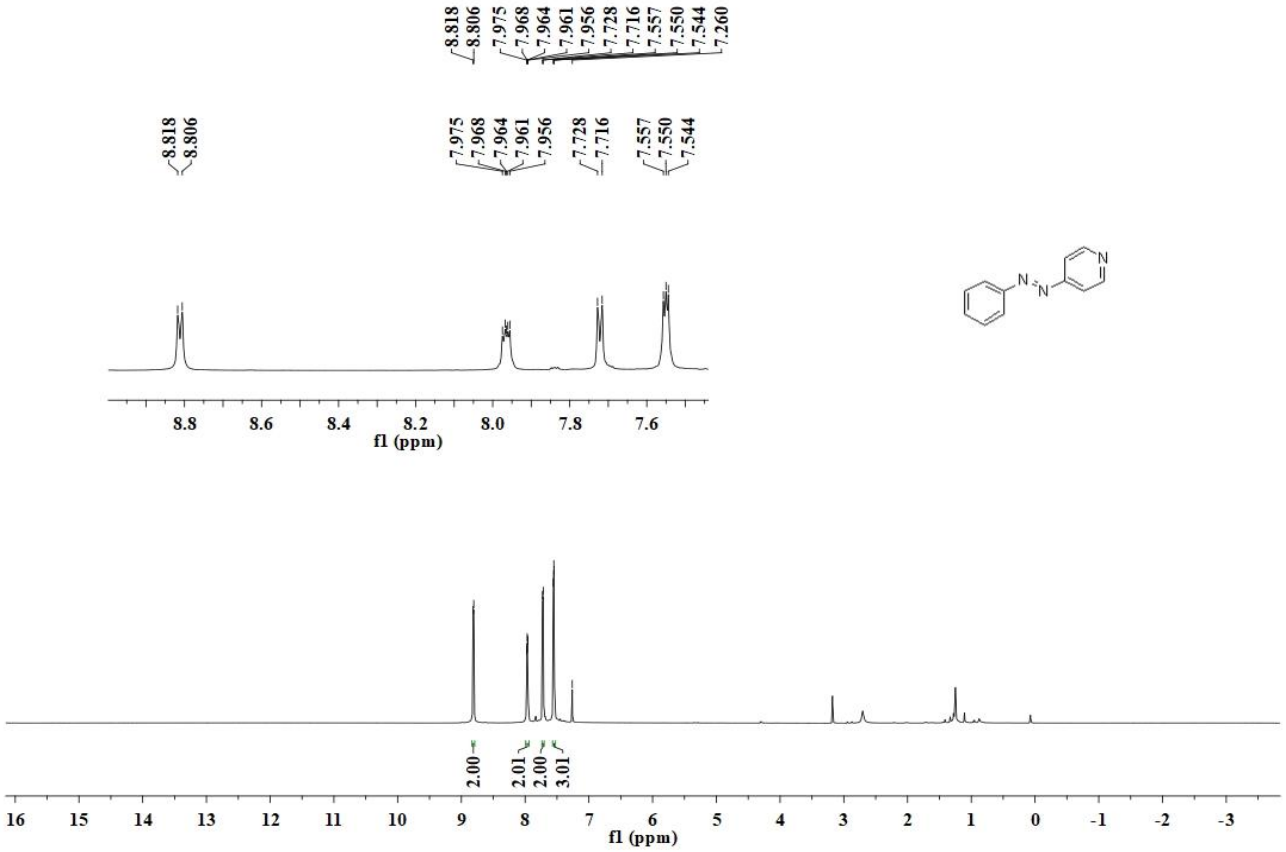
^{1}H NMR (500 MHz, $CDCl_3$) of **3o**



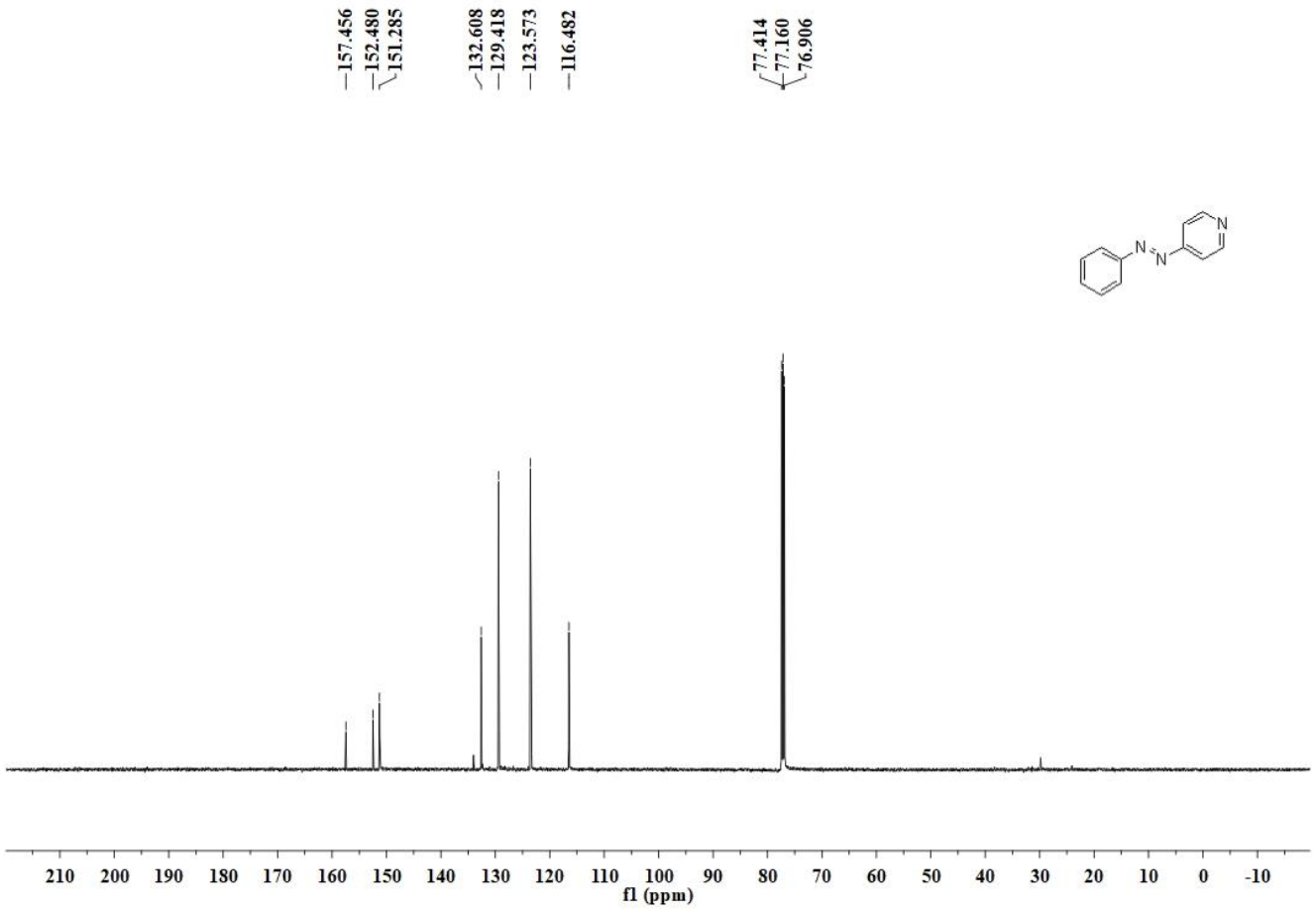
^{13}C NMR (126 MHz, $CDCl_3$) of **3o**



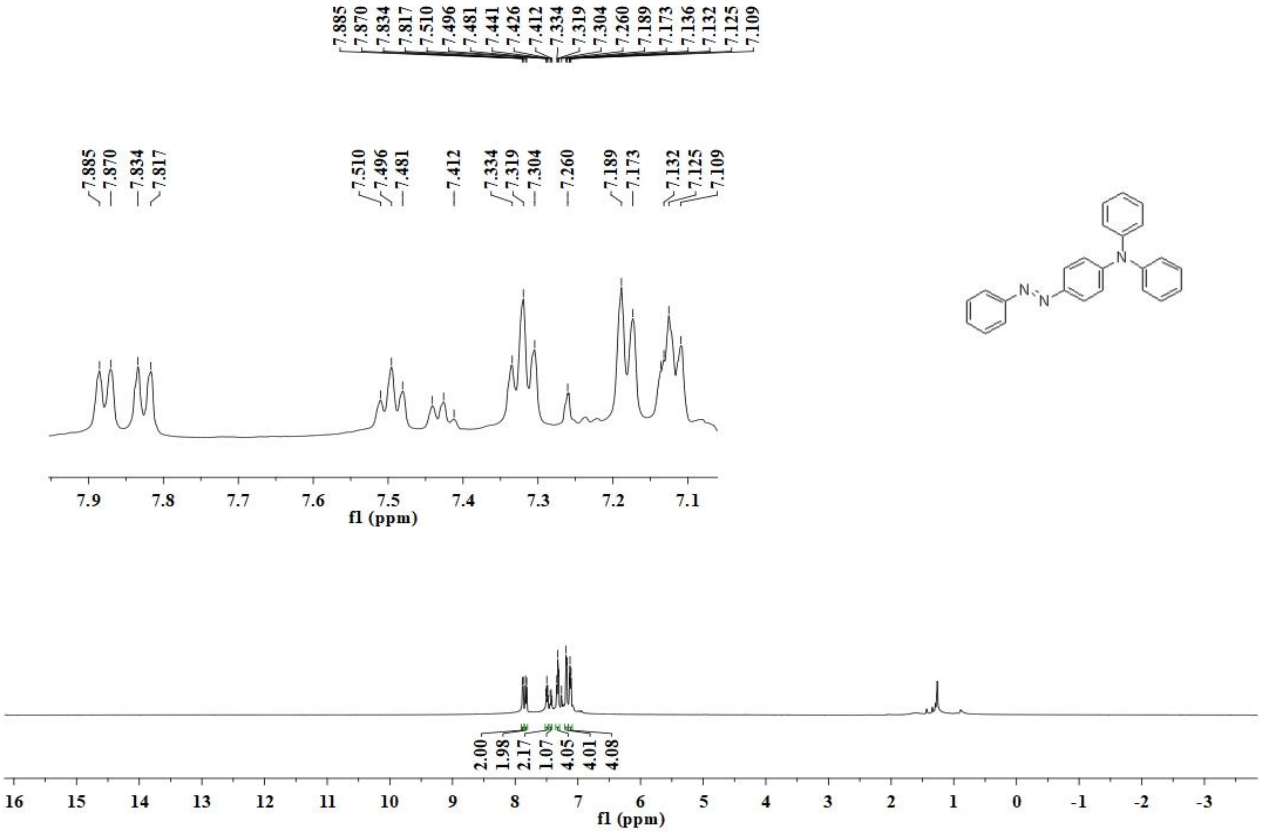
^{1}H NMR (500 MHz, $CDCl_3$) of **3p**



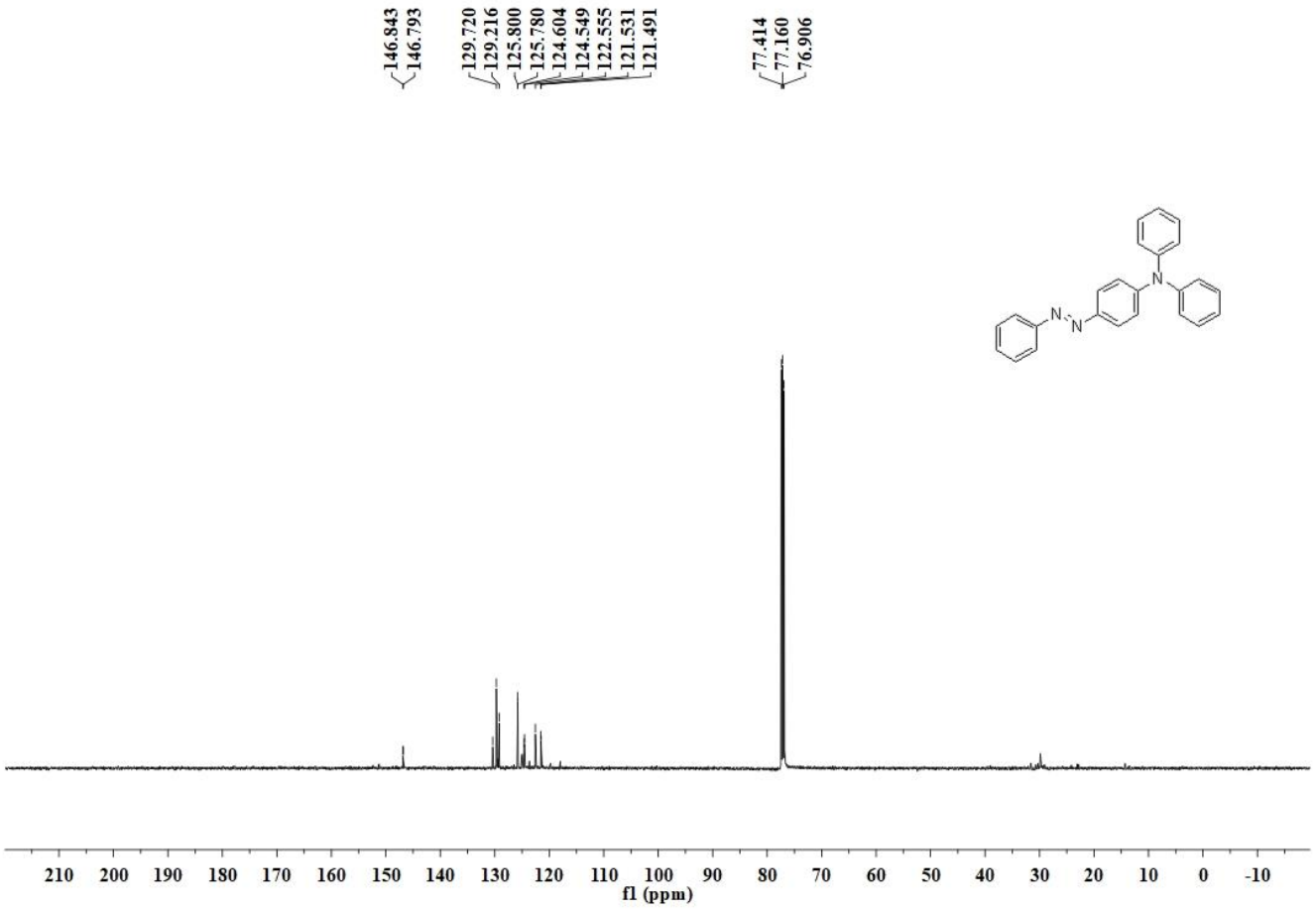
^{13}C NMR (126 MHz, $CDCl_3$) of **3p**



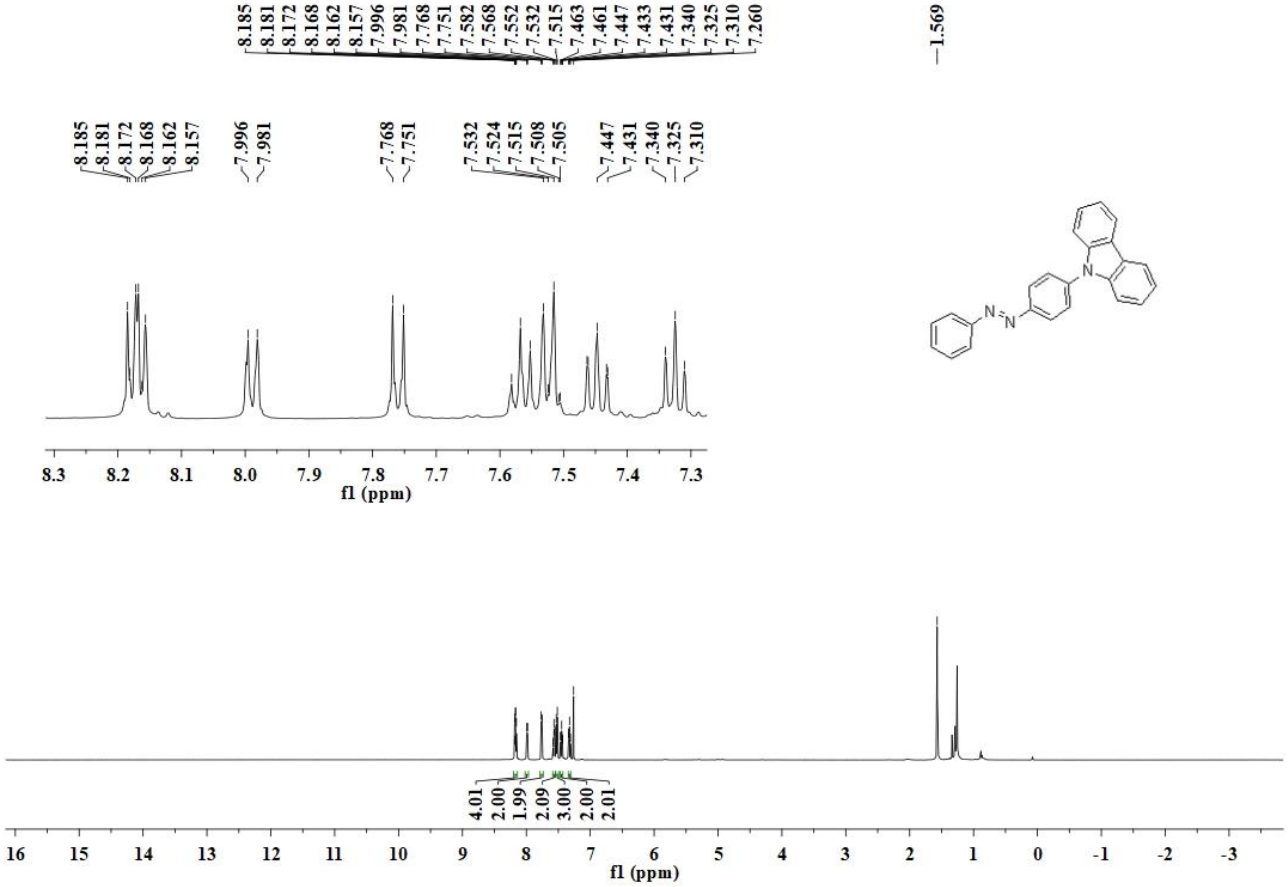
^{1}H NMR (500 MHz, $CDCl_3$) of **3r**



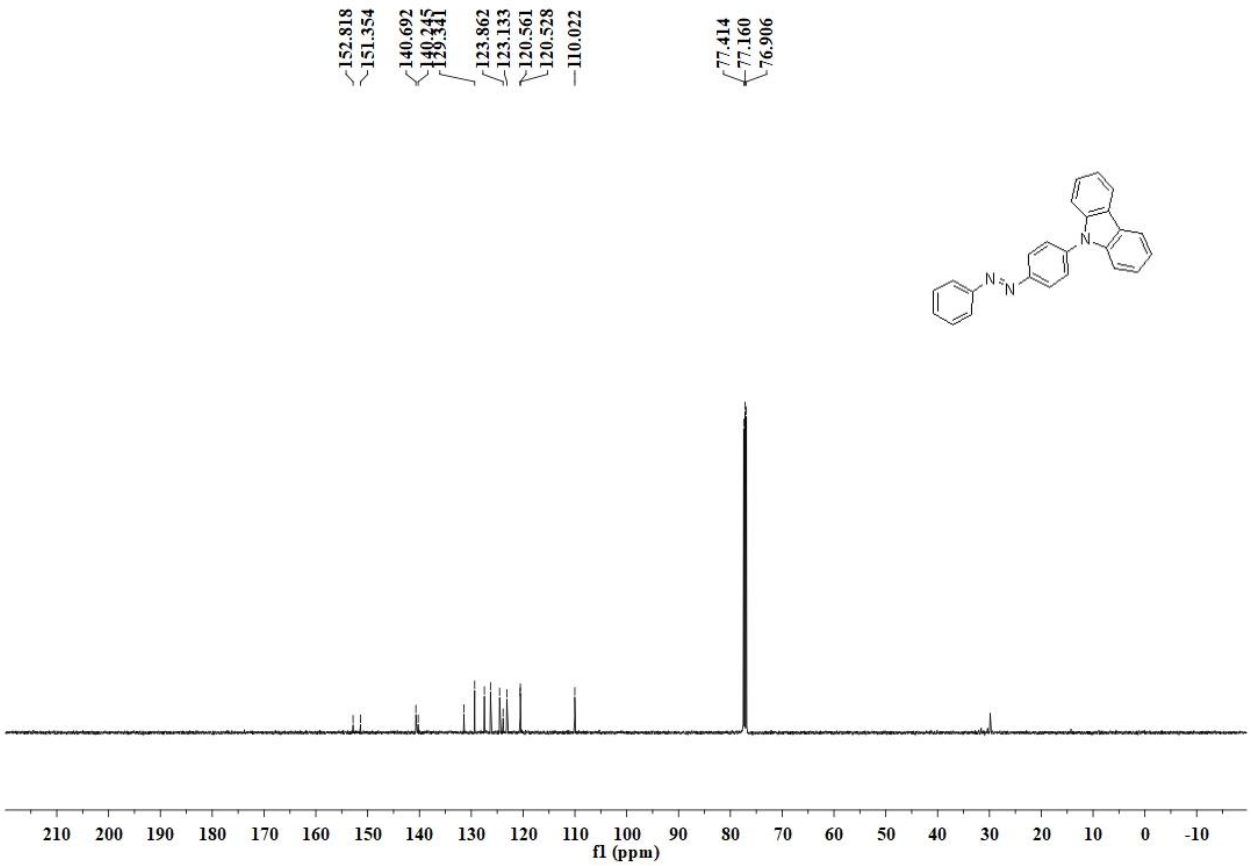
^{13}C NMR (126 MHz, $CDCl_3$) of **3r**



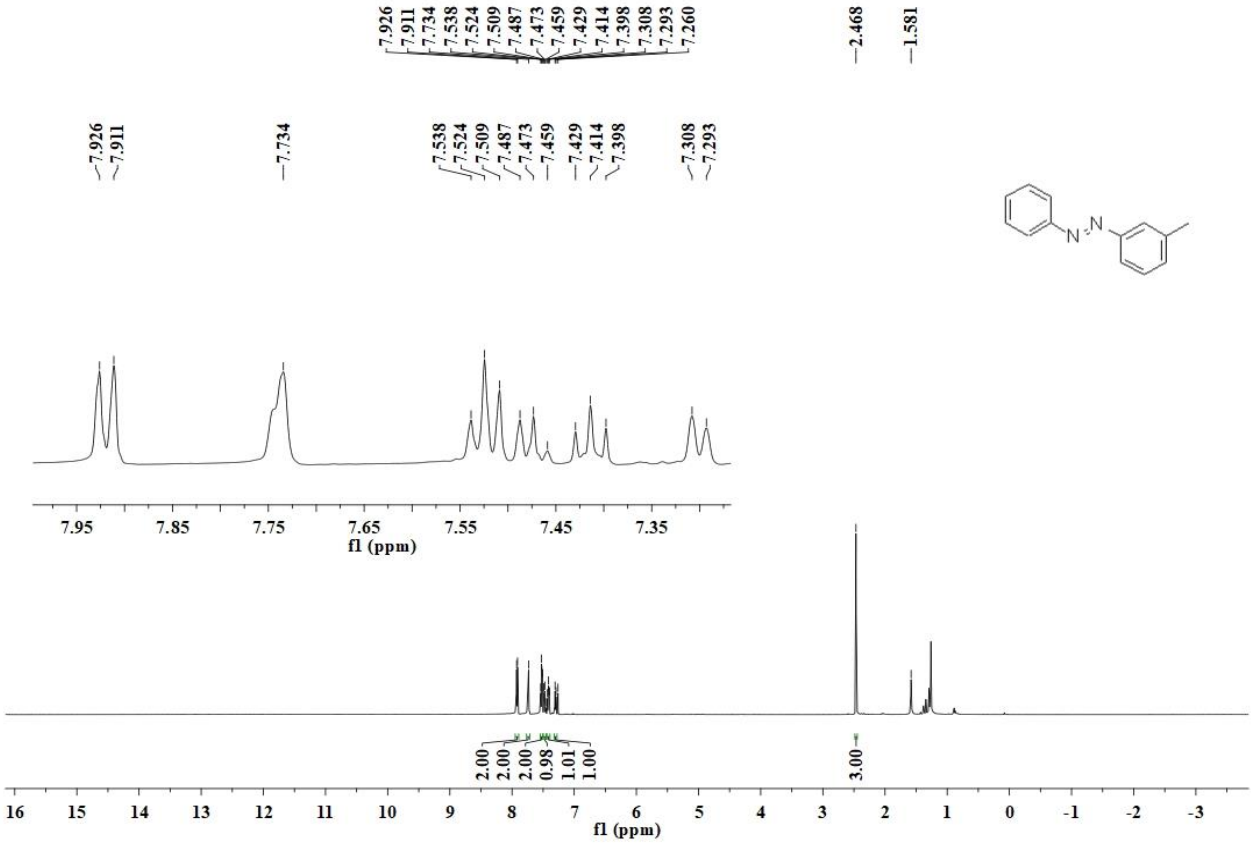
^{1}H NMR (500 MHz, $CDCl_3$) of **3s**



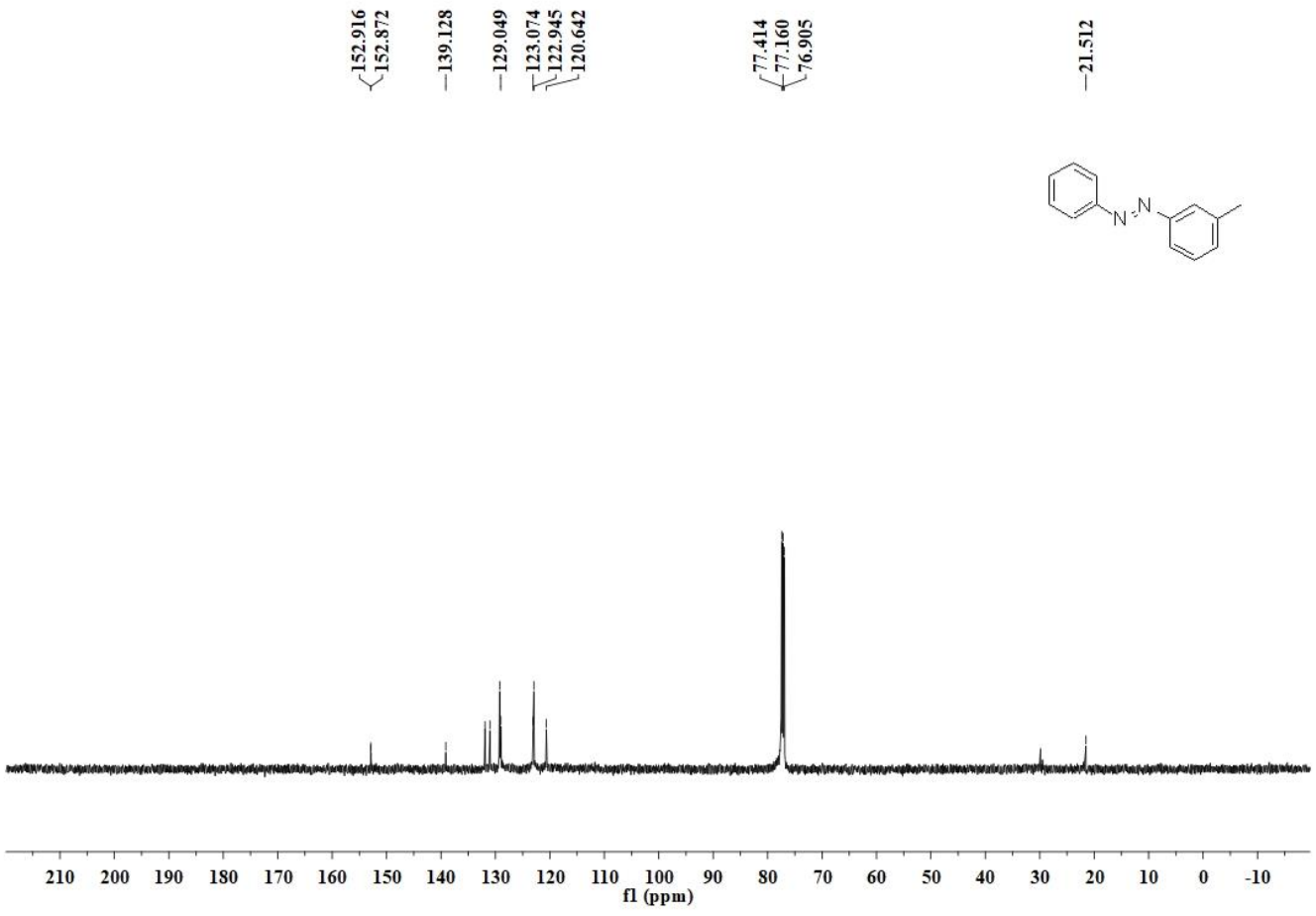
^{13}C NMR (126 MHz, $CDCl_3$) of **3s**



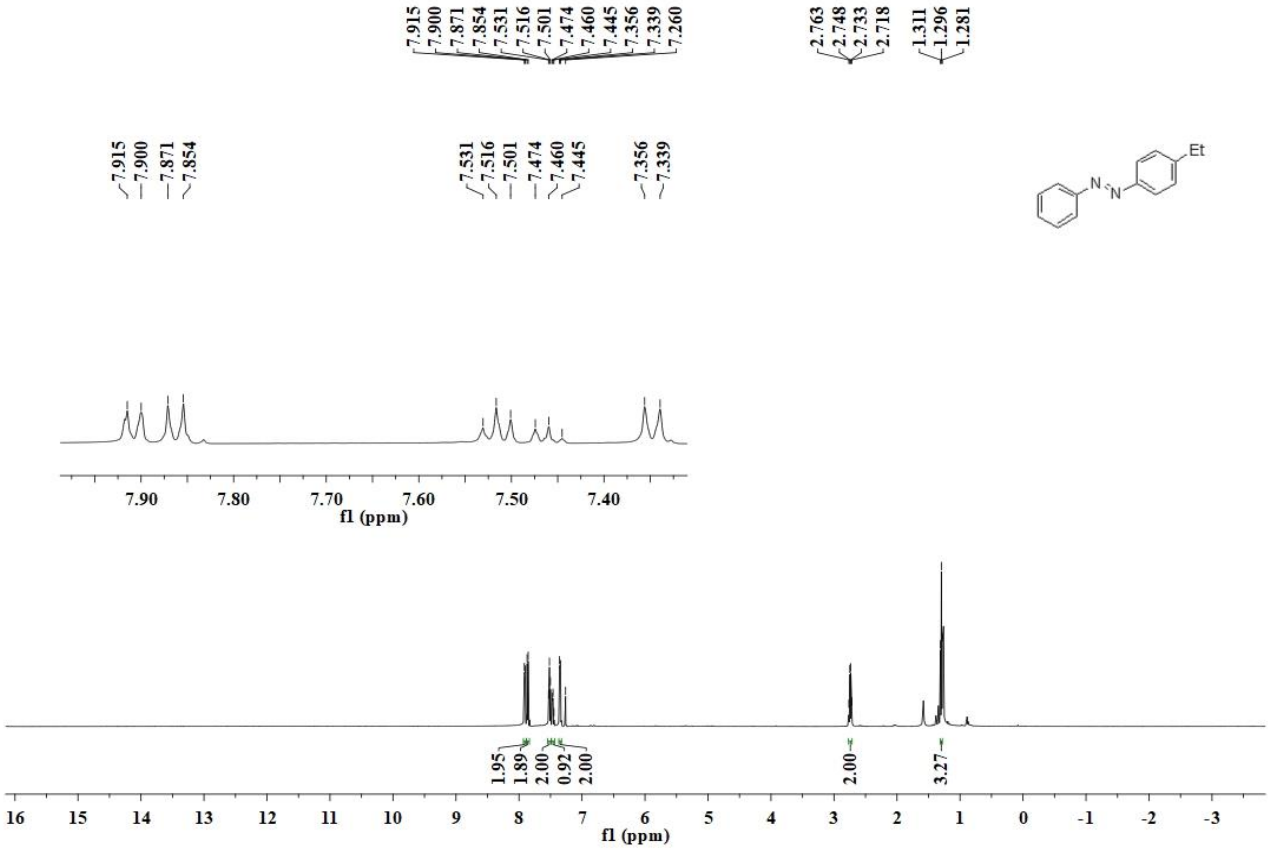
^{1}H NMR (500 MHz, $CDCl_3$) of **4b**



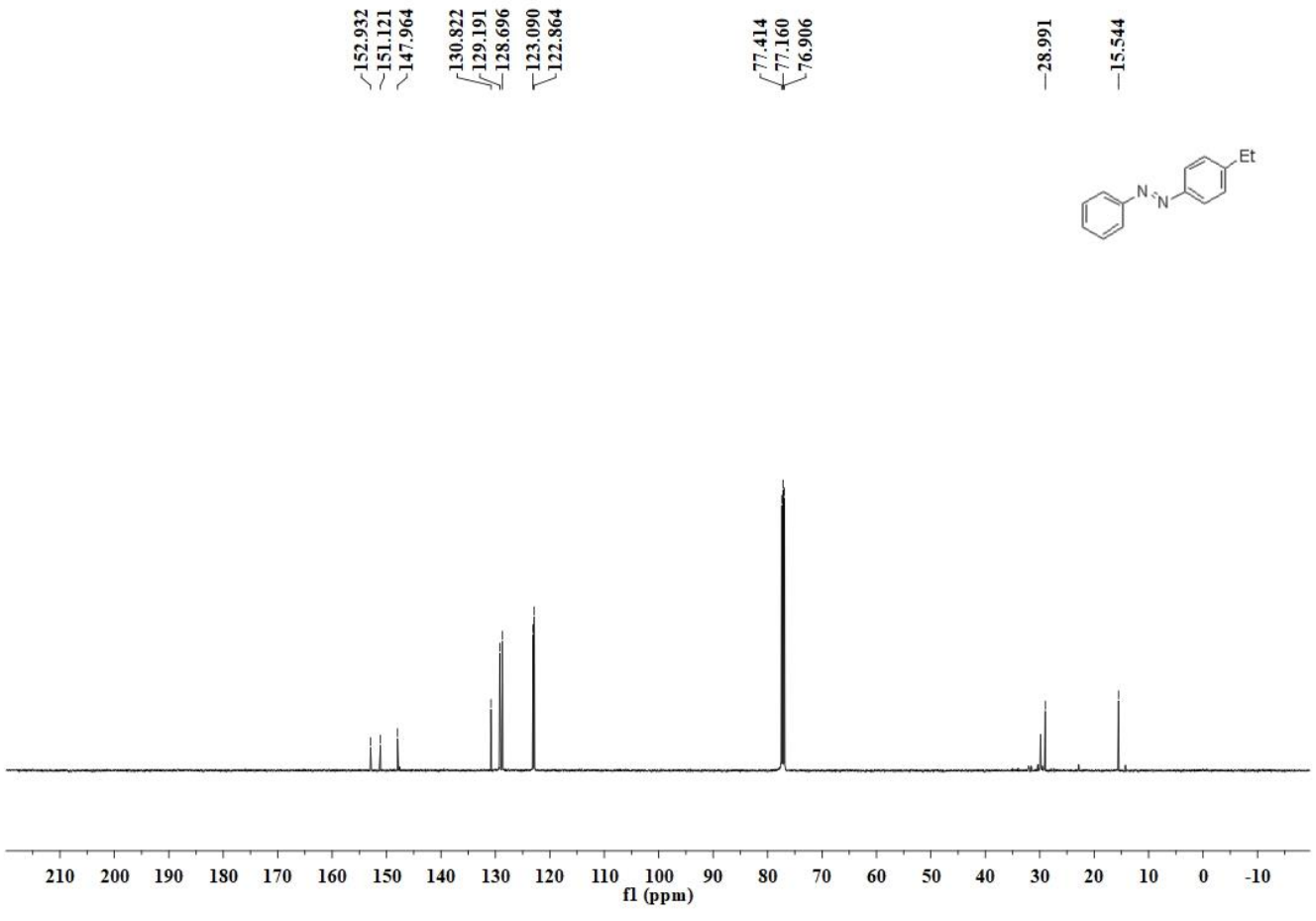
^{13}C NMR (126 MHz, $CDCl_3$) of **4b**



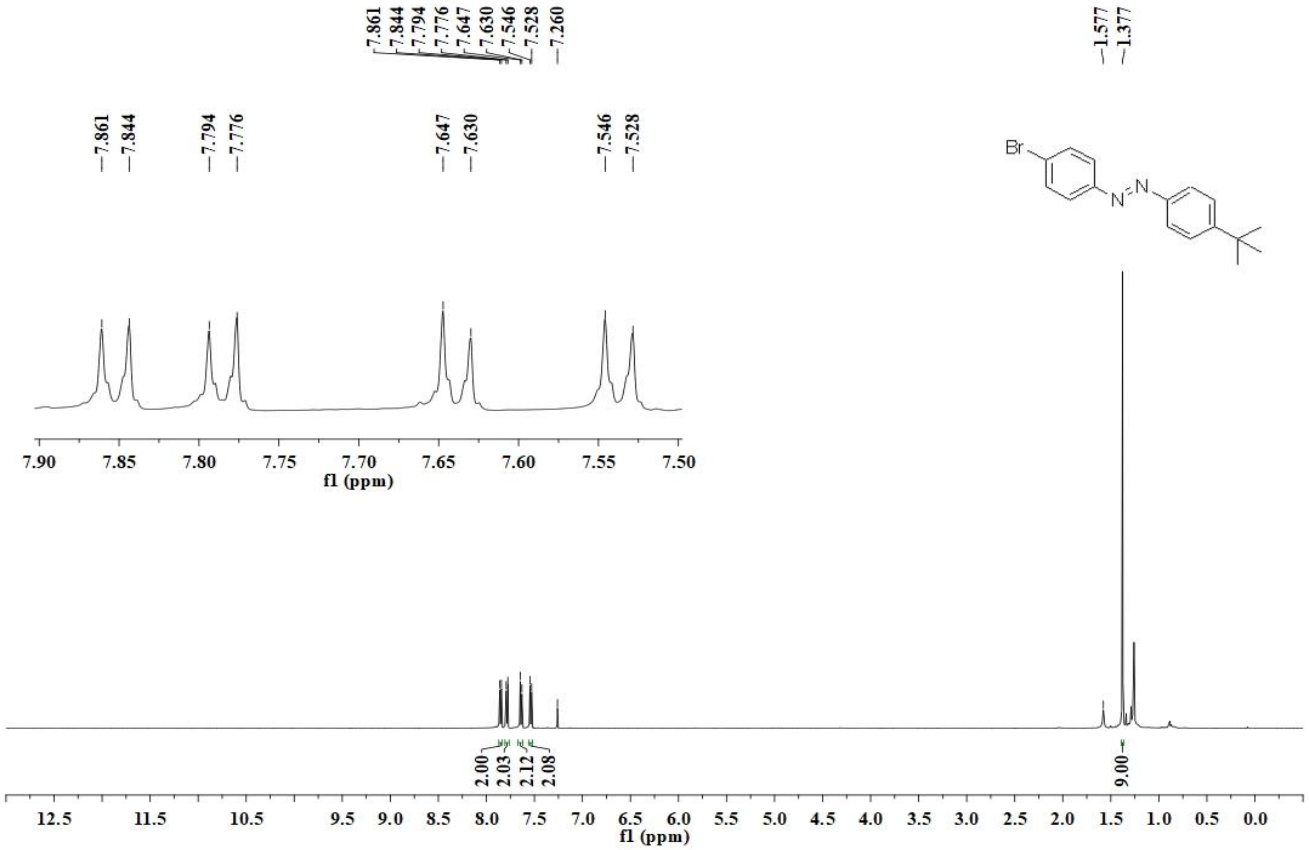
^{1}H NMR (500 MHz, $CDCl_3$) of **4d**



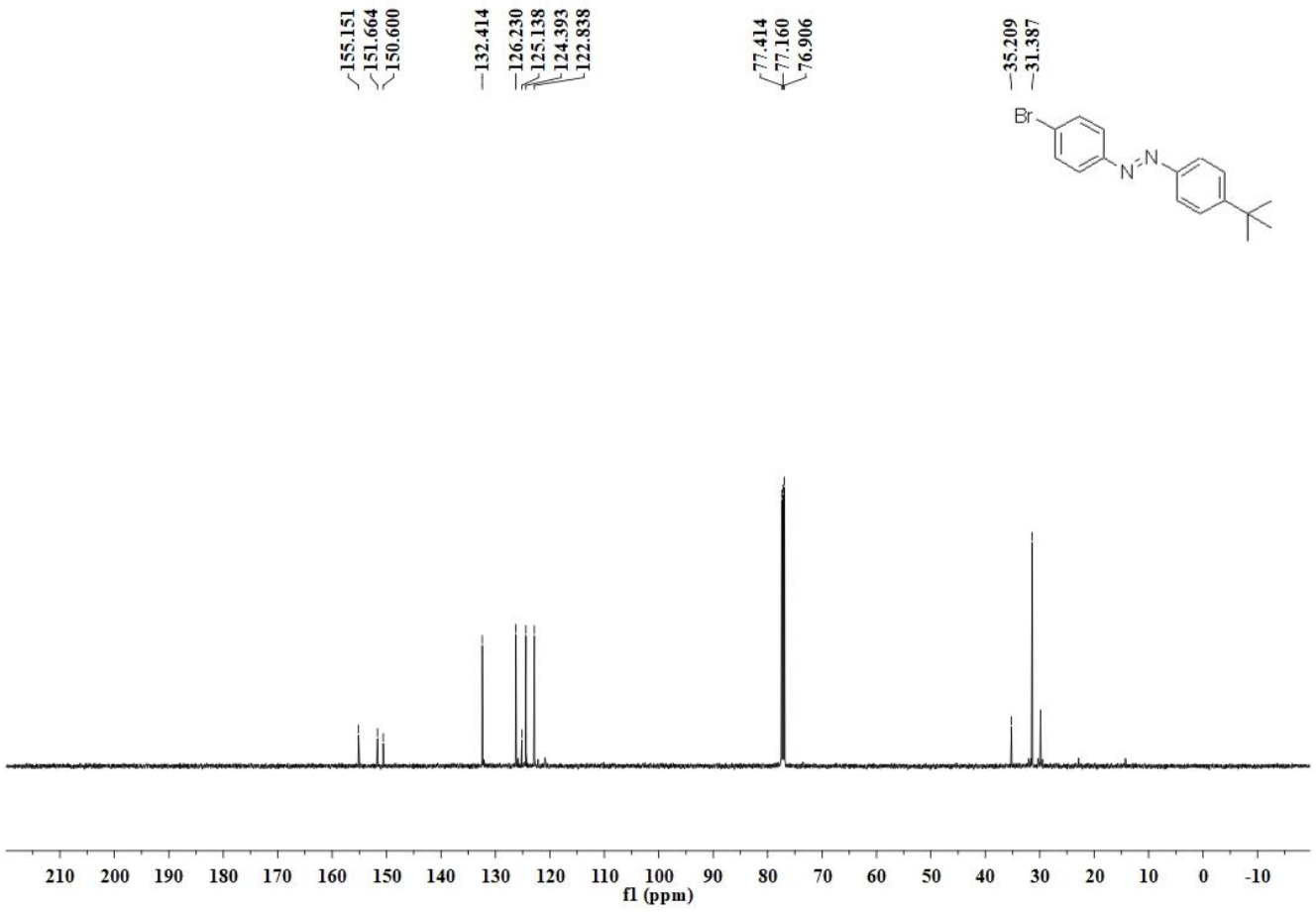
^{13}C NMR (126 MHz, $CDCl_3$) of **4d**



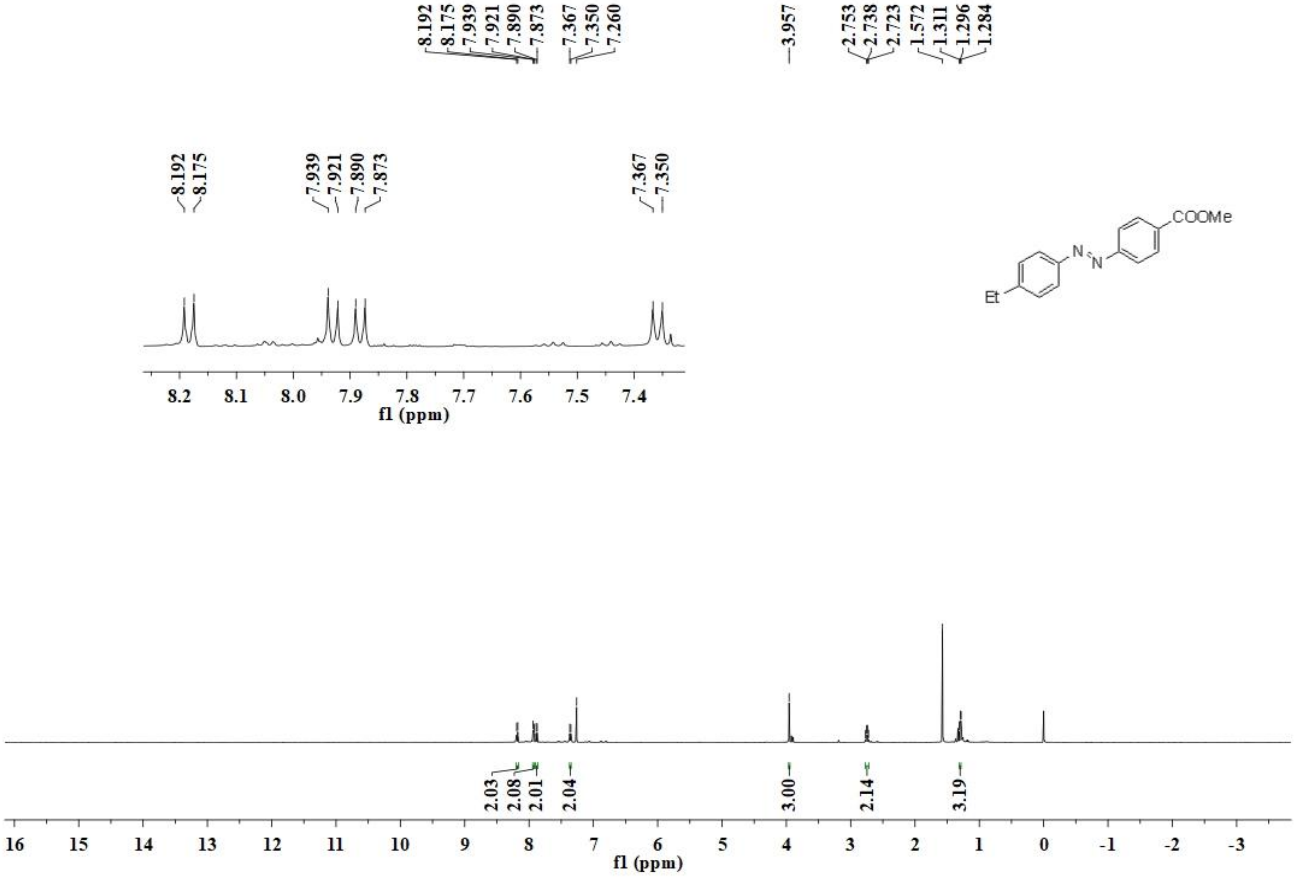
^{1}H NMR (500 MHz, $CDCl_3$) of **4h**



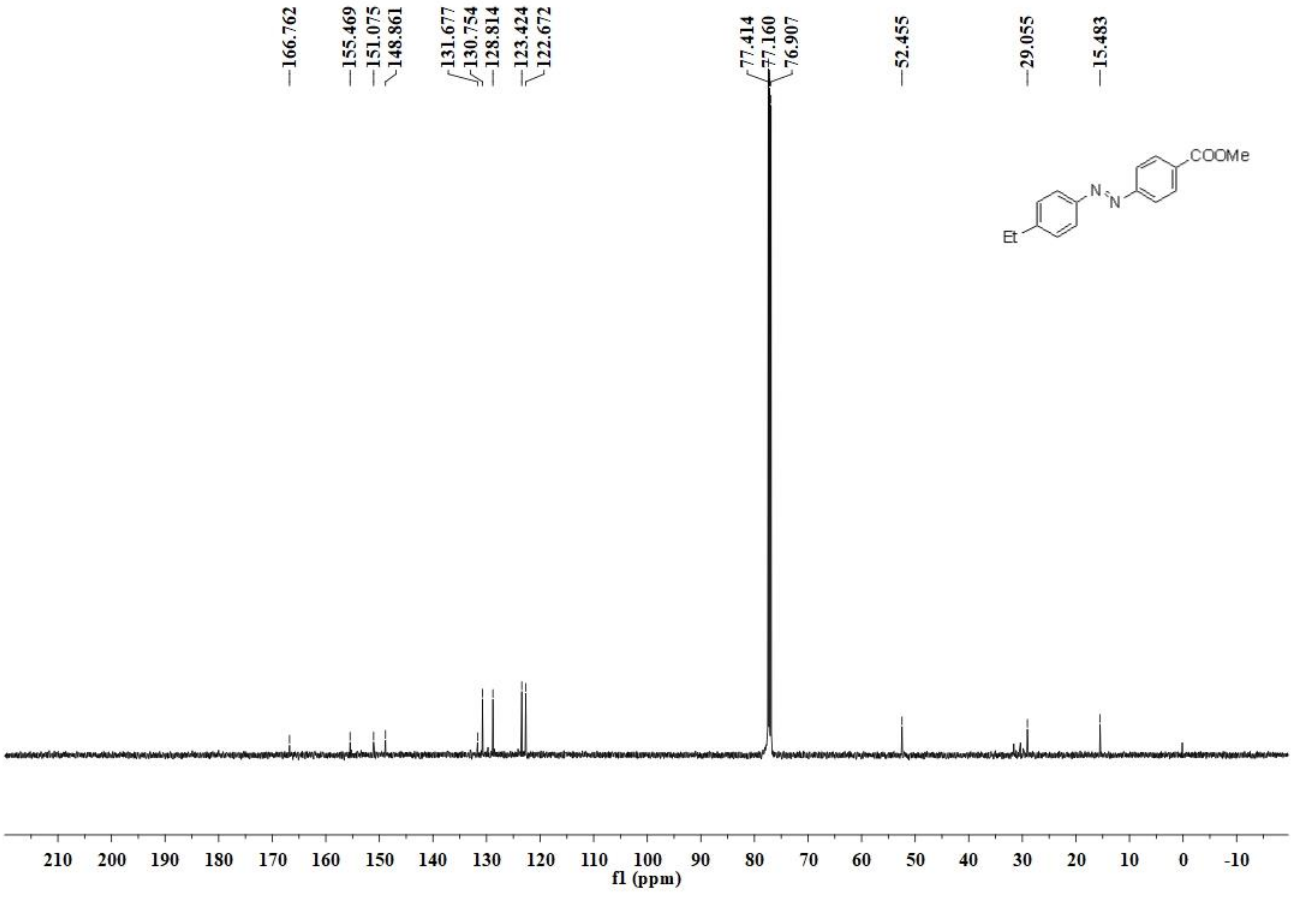
^{13}C NMR (126 MHz, $CDCl_3$) of **4h**



^{1}H NMR (500 MHz, $CDCl_3$) of **4i**



^{13}C NMR (126 MHz, $CDCl_3$) of **4i**



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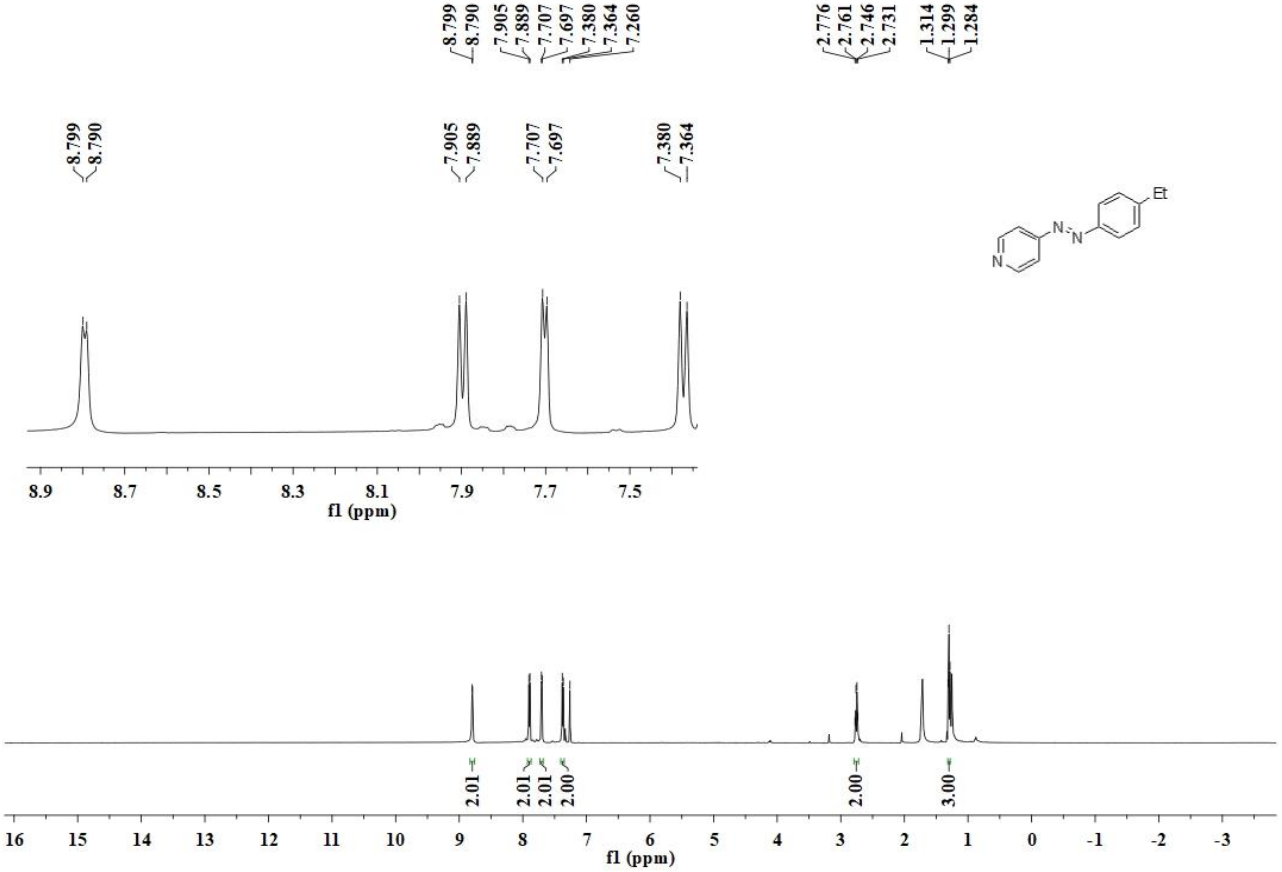
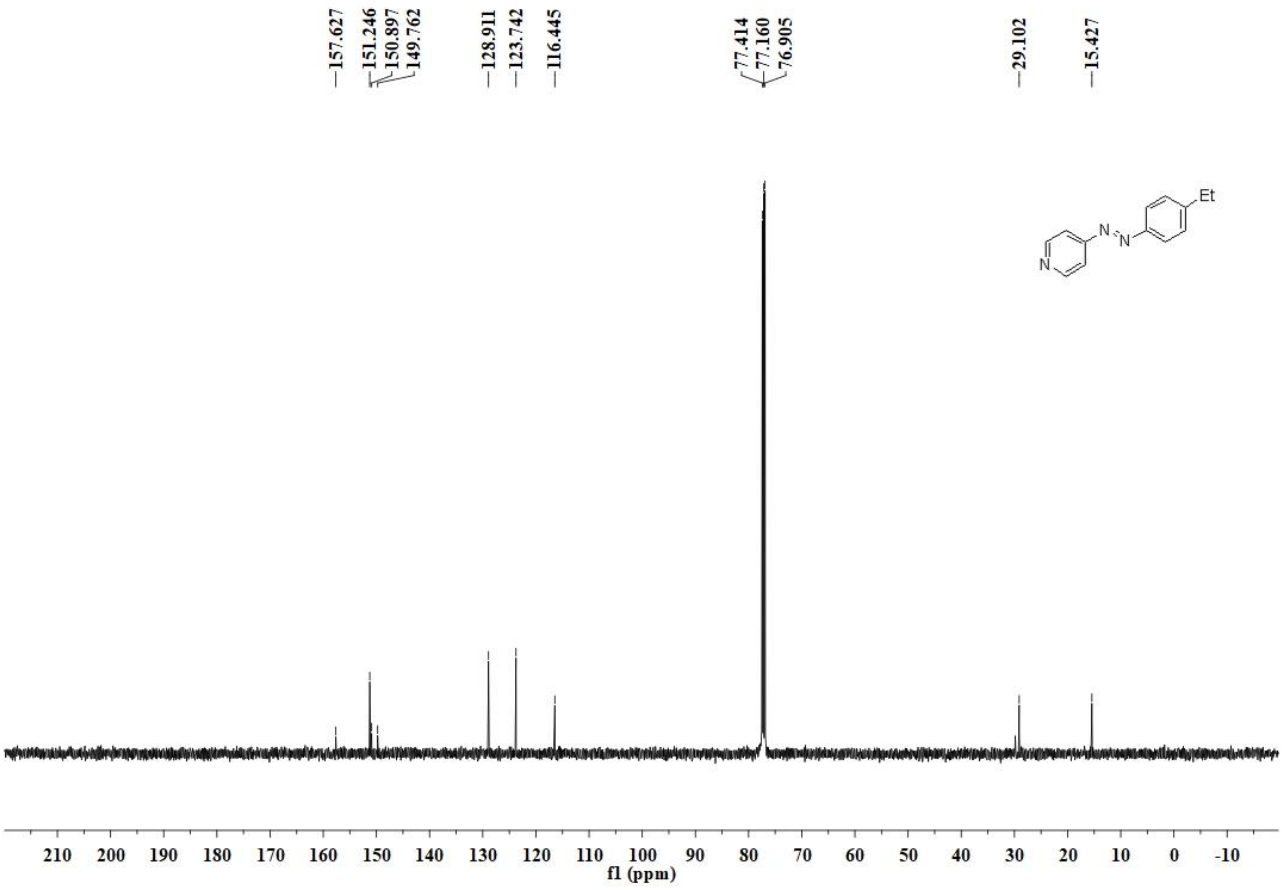
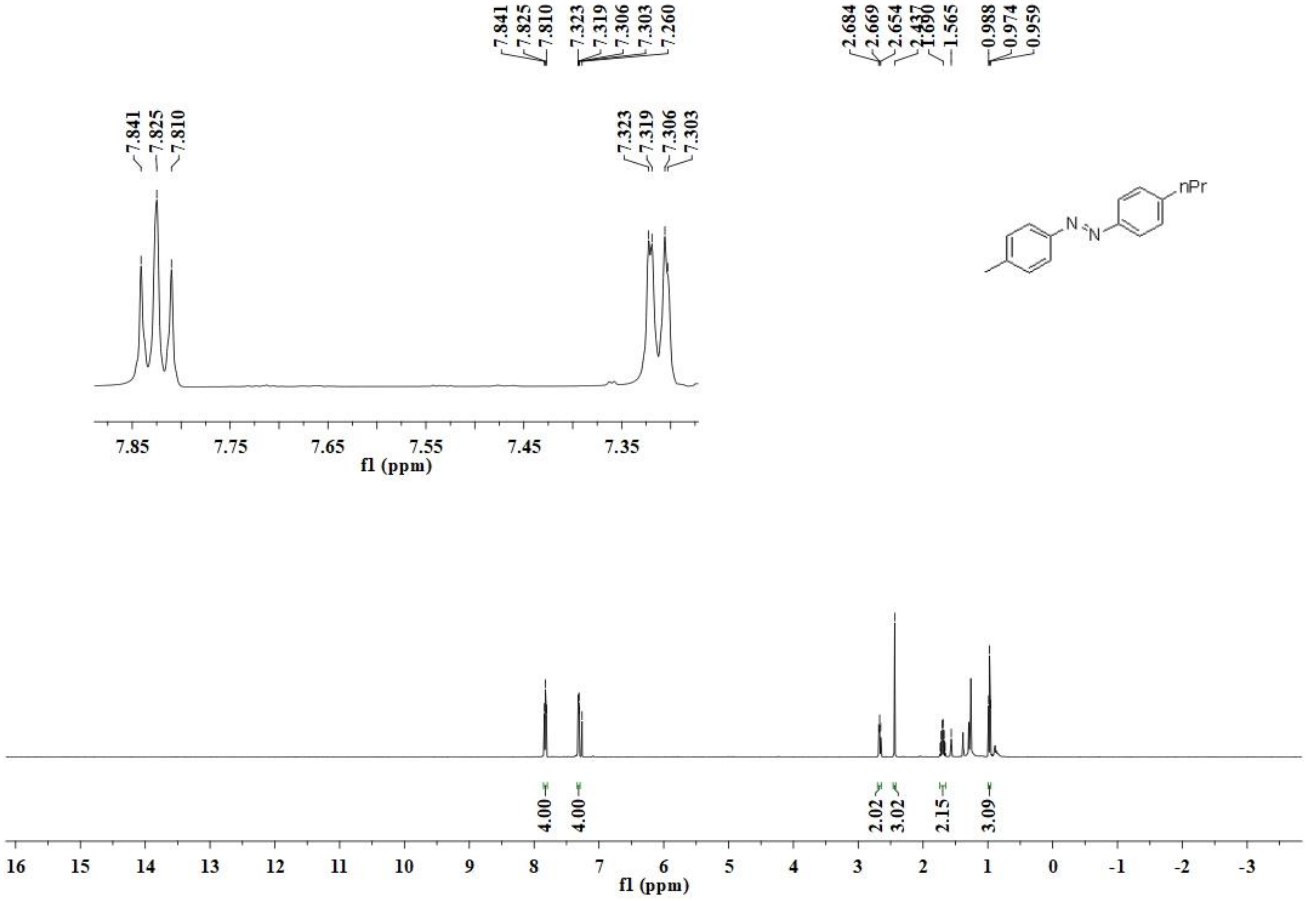


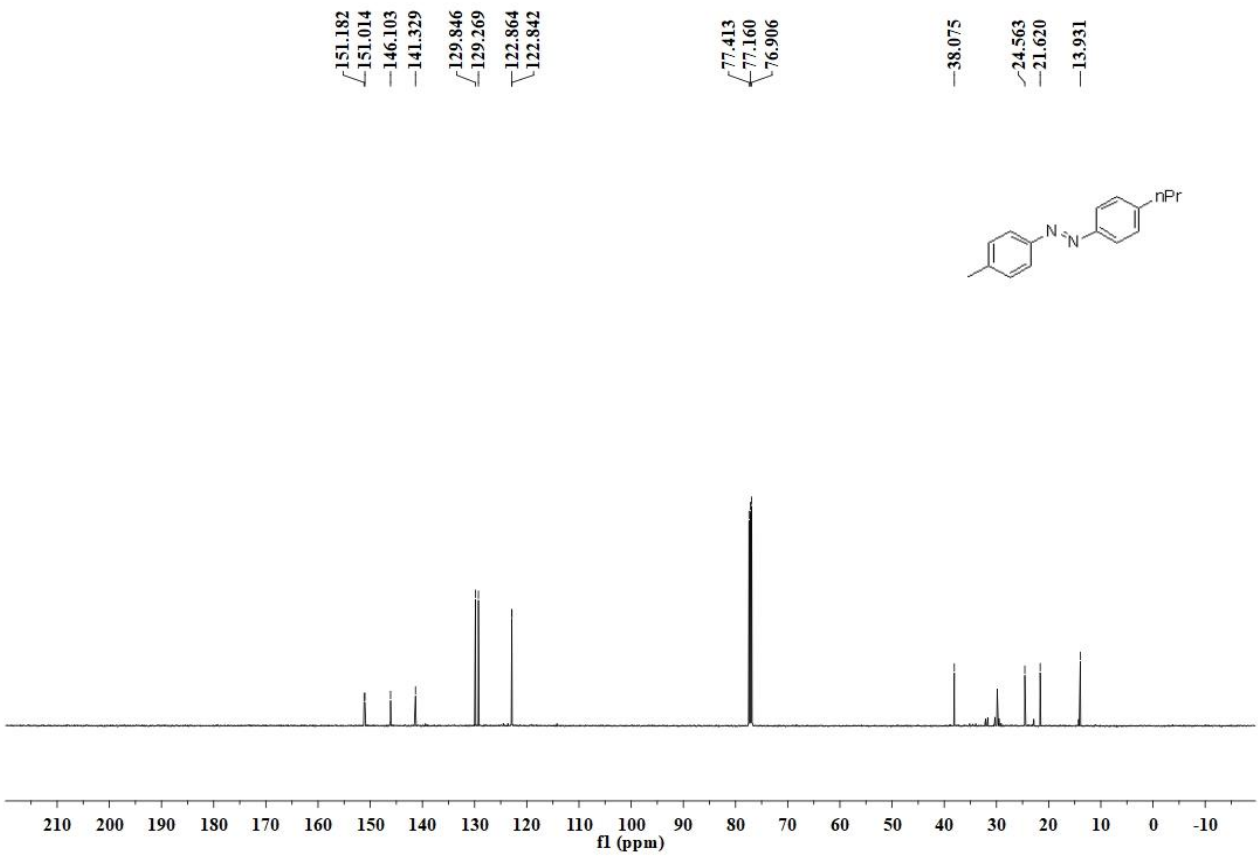
^{13}C NMR (126 MHz, $CDCl_3$) of **4j**



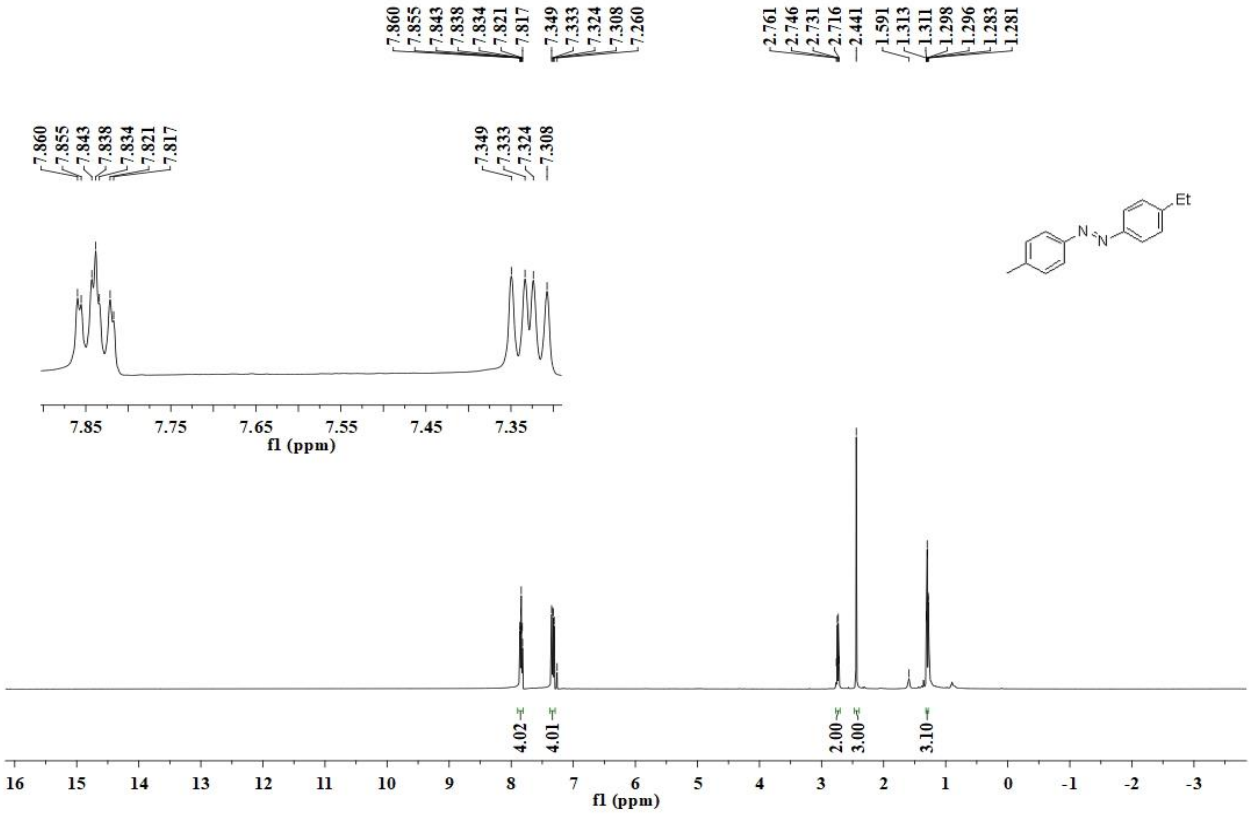
^{1}H NMR (500 MHz, $CDCl_3$) of **5**



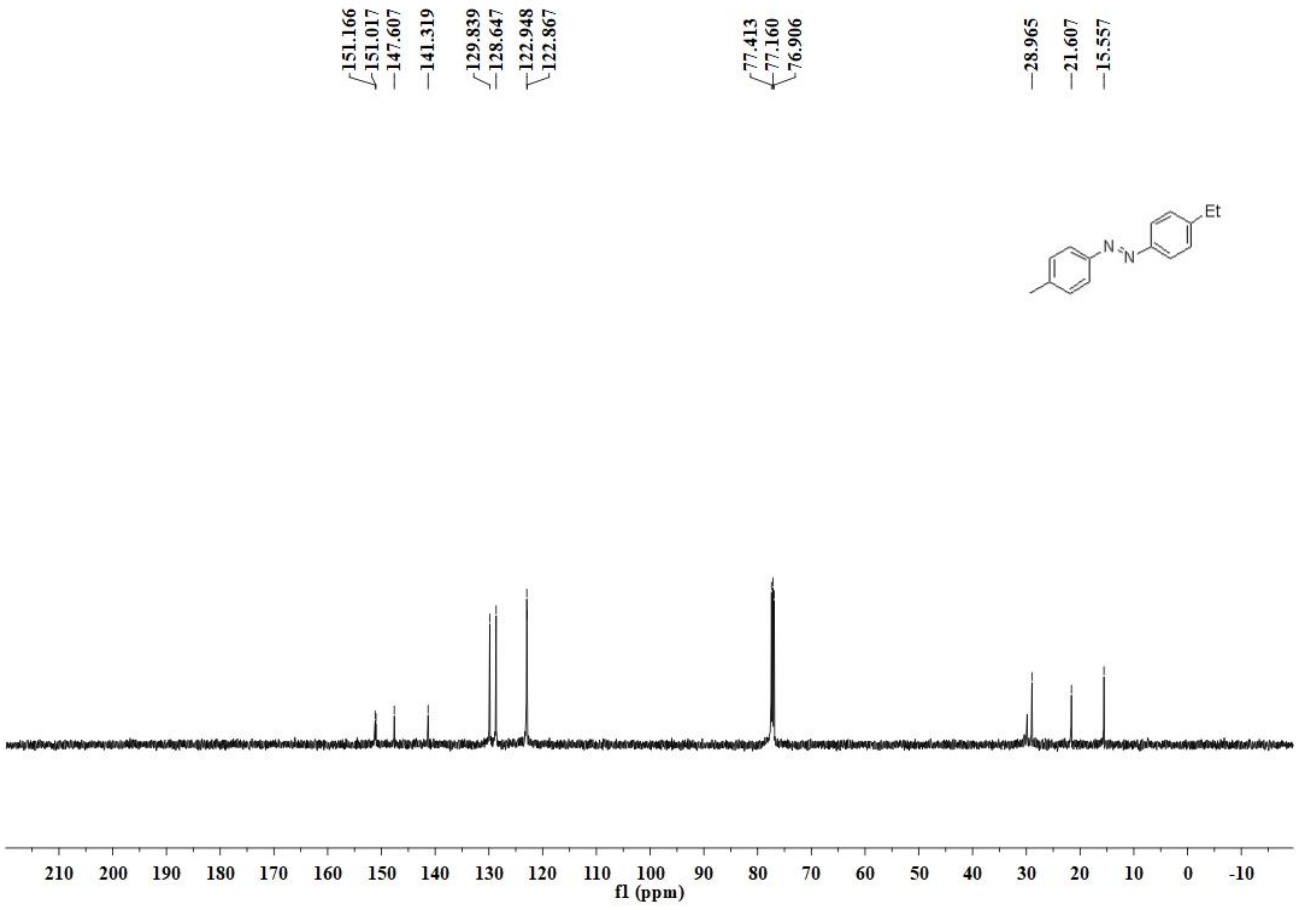
^{13}C NMR (126 MHz, $CDCl_3$) of **5**



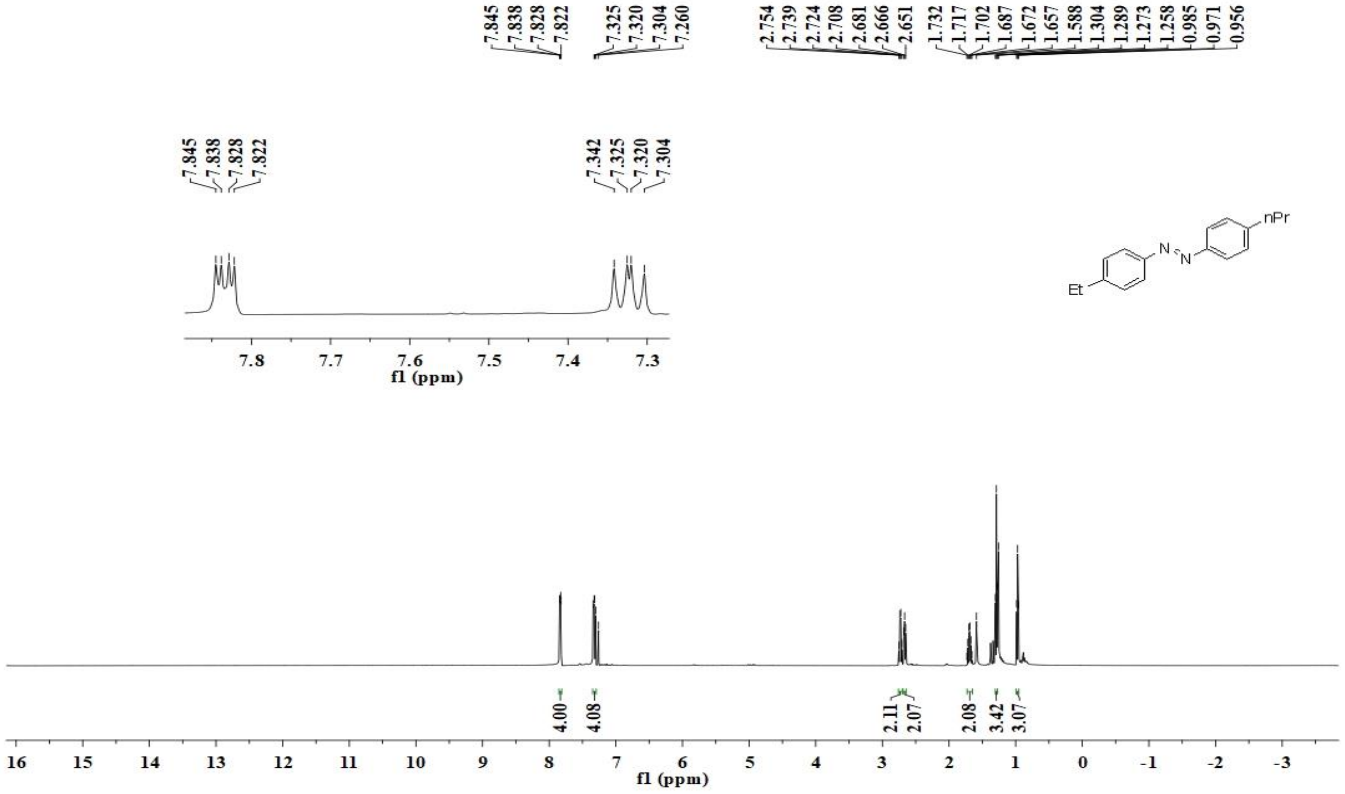
^{1}H NMR (500 MHz, $CDCl_3$) of **6**



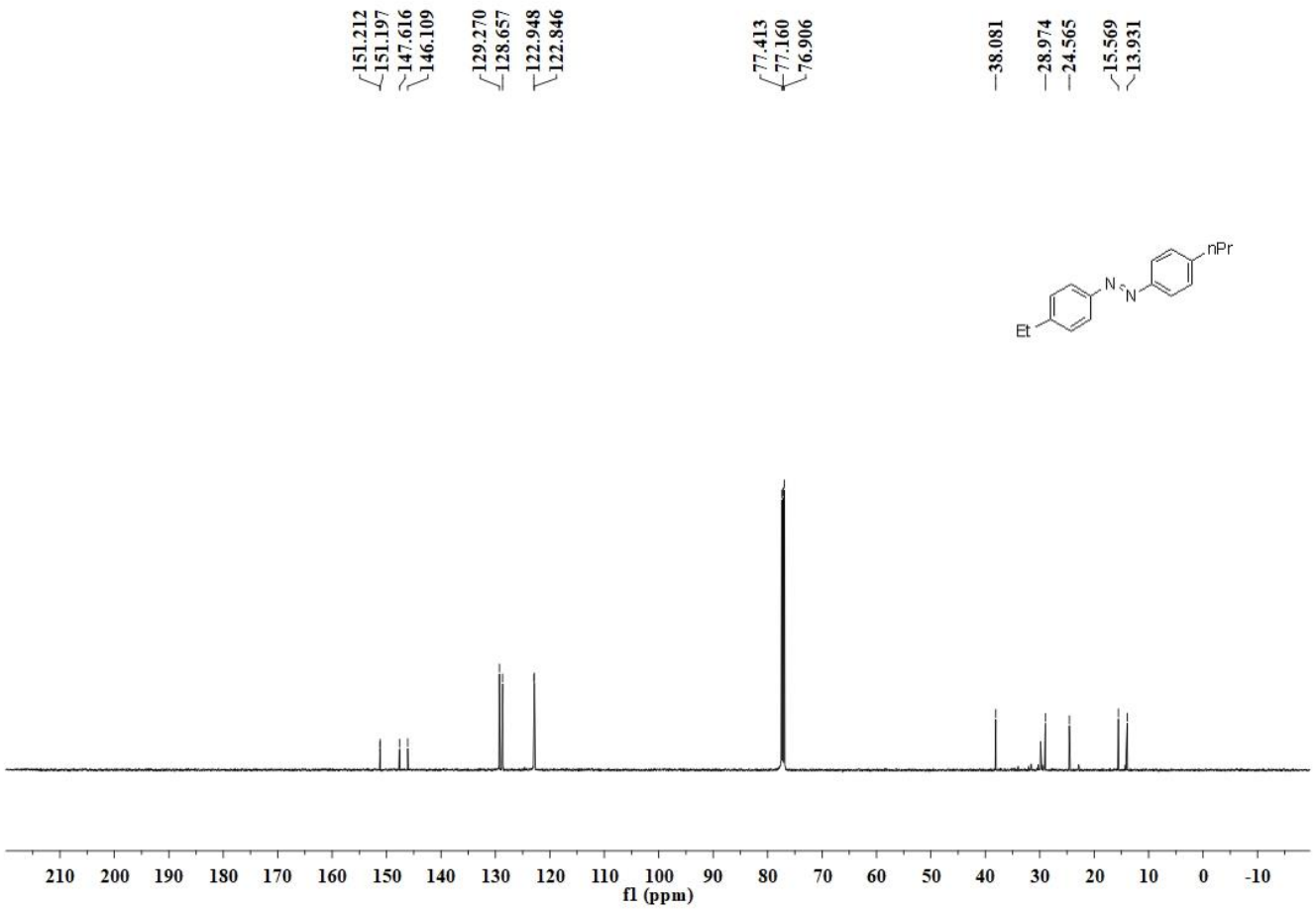
^{13}C NMR (126 MHz, $CDCl_3$) of **6**



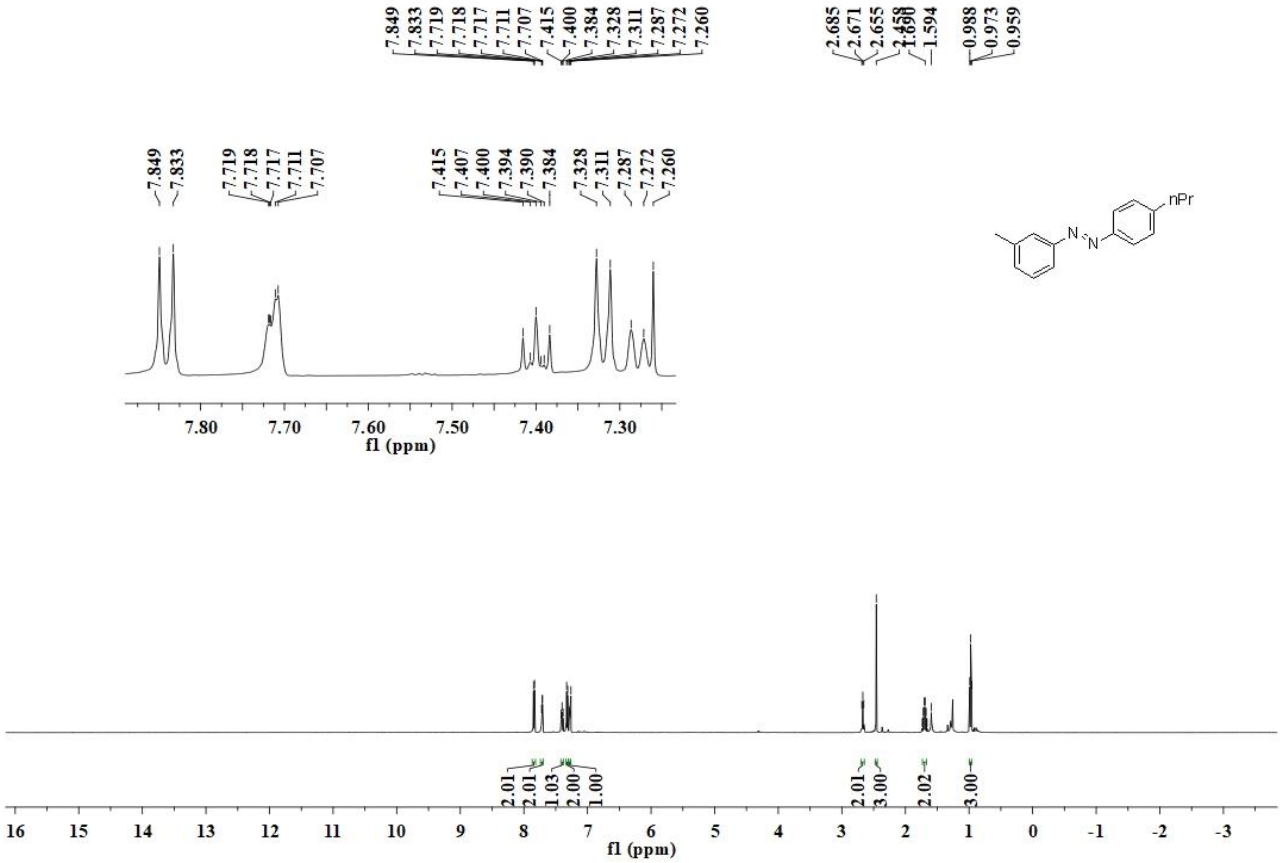
^{1}H NMR (500 MHz, $CDCl_3$) of **7**



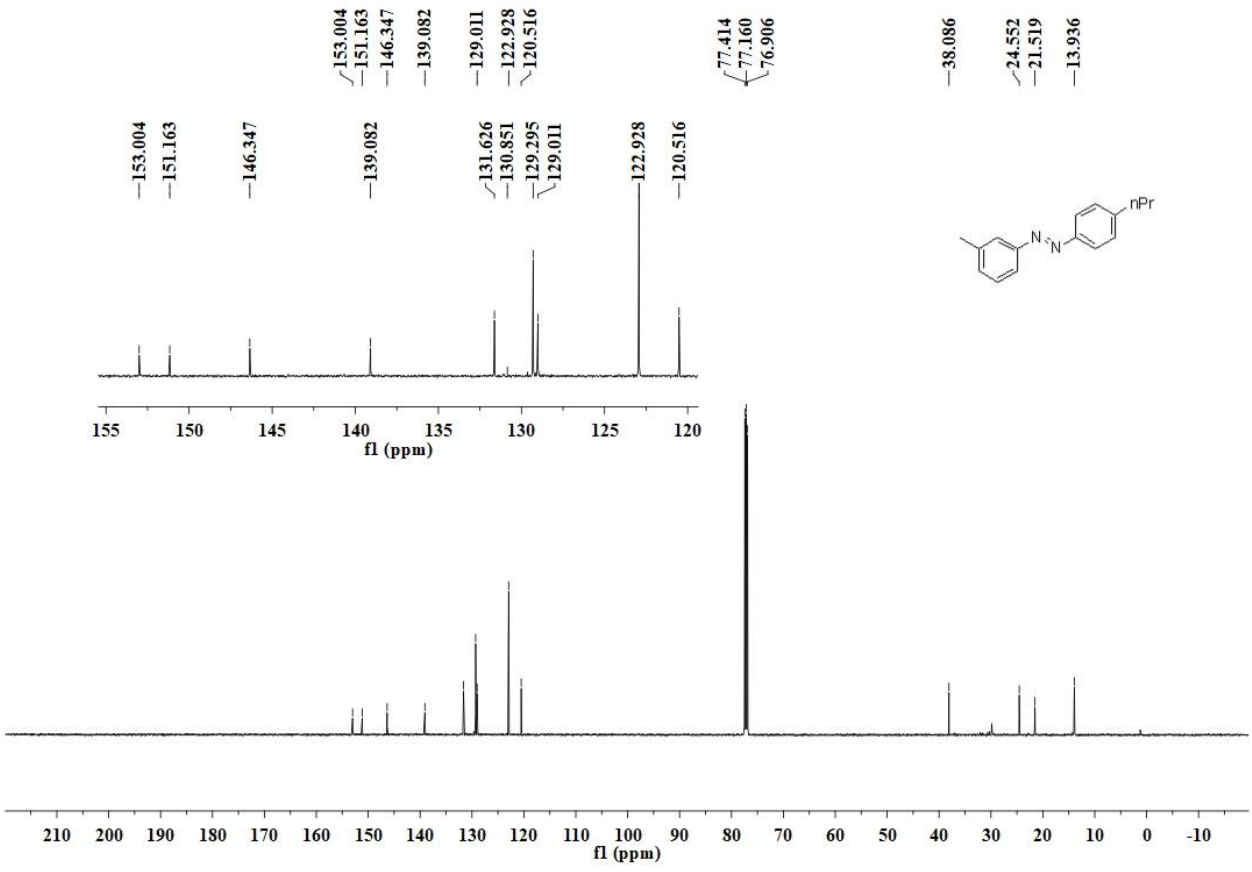
^{13}C NMR (126 MHz, $CDCl_3$) of **7**



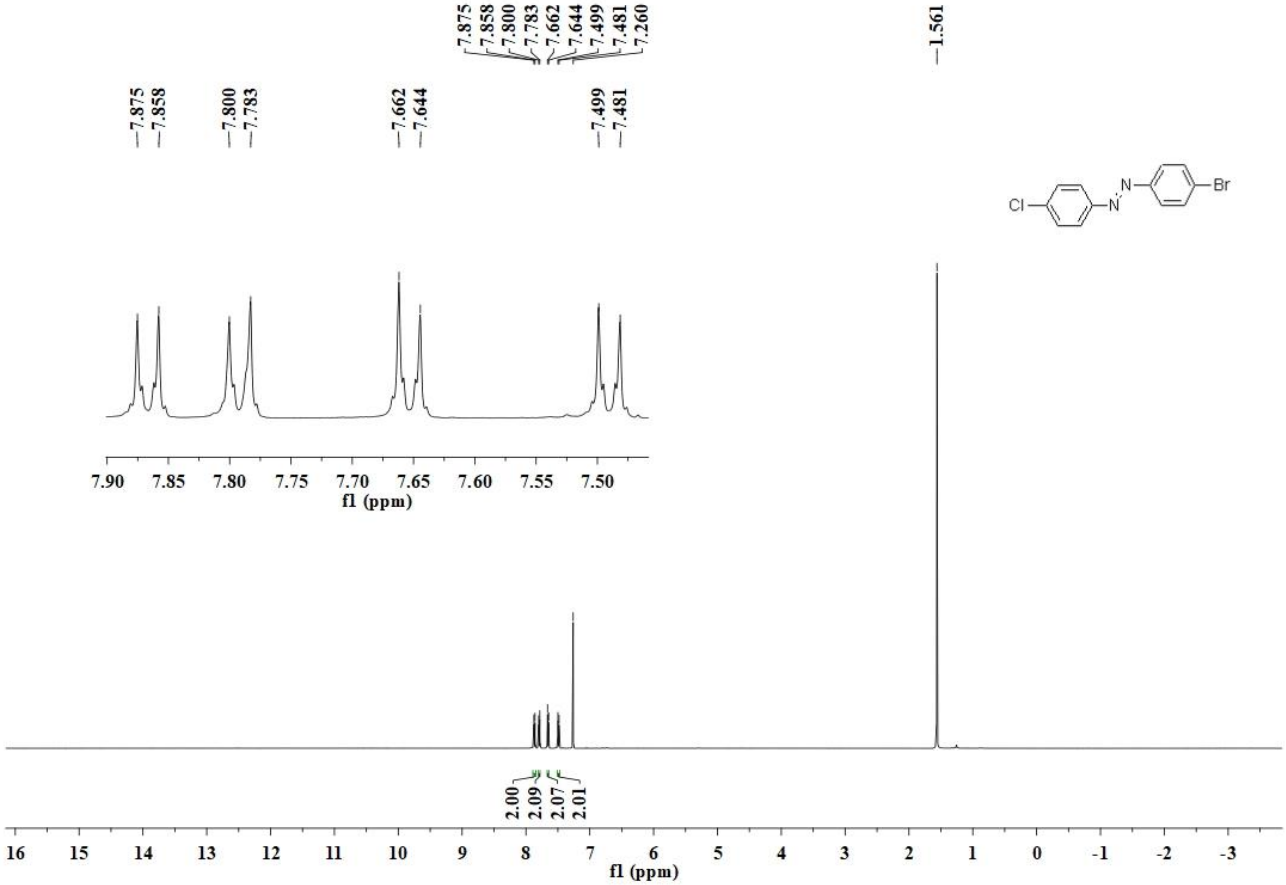
^{1}H NMR (500 MHz, $CDCl_3$) of **8**



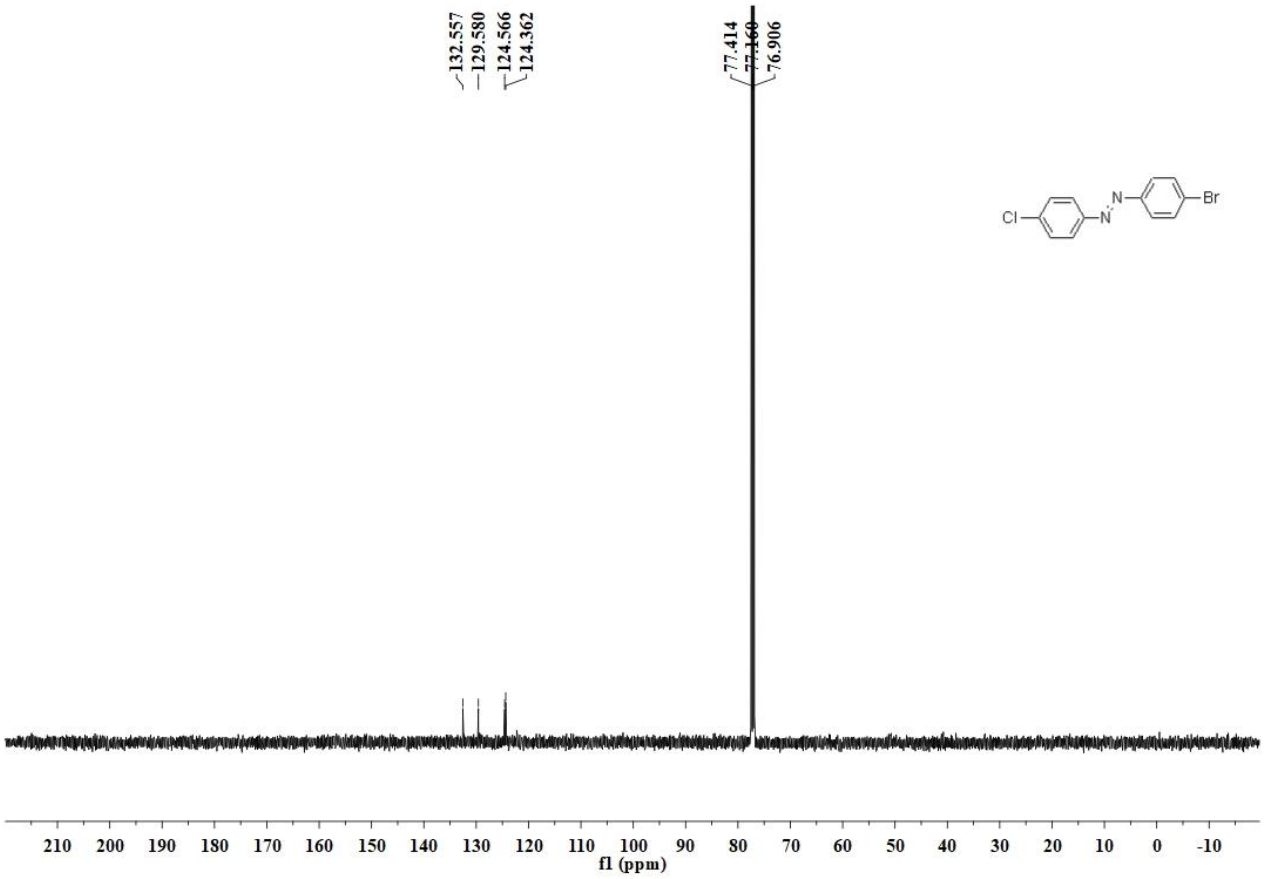
^{13}C NMR (126 MHz, $CDCl_3$) of **8**



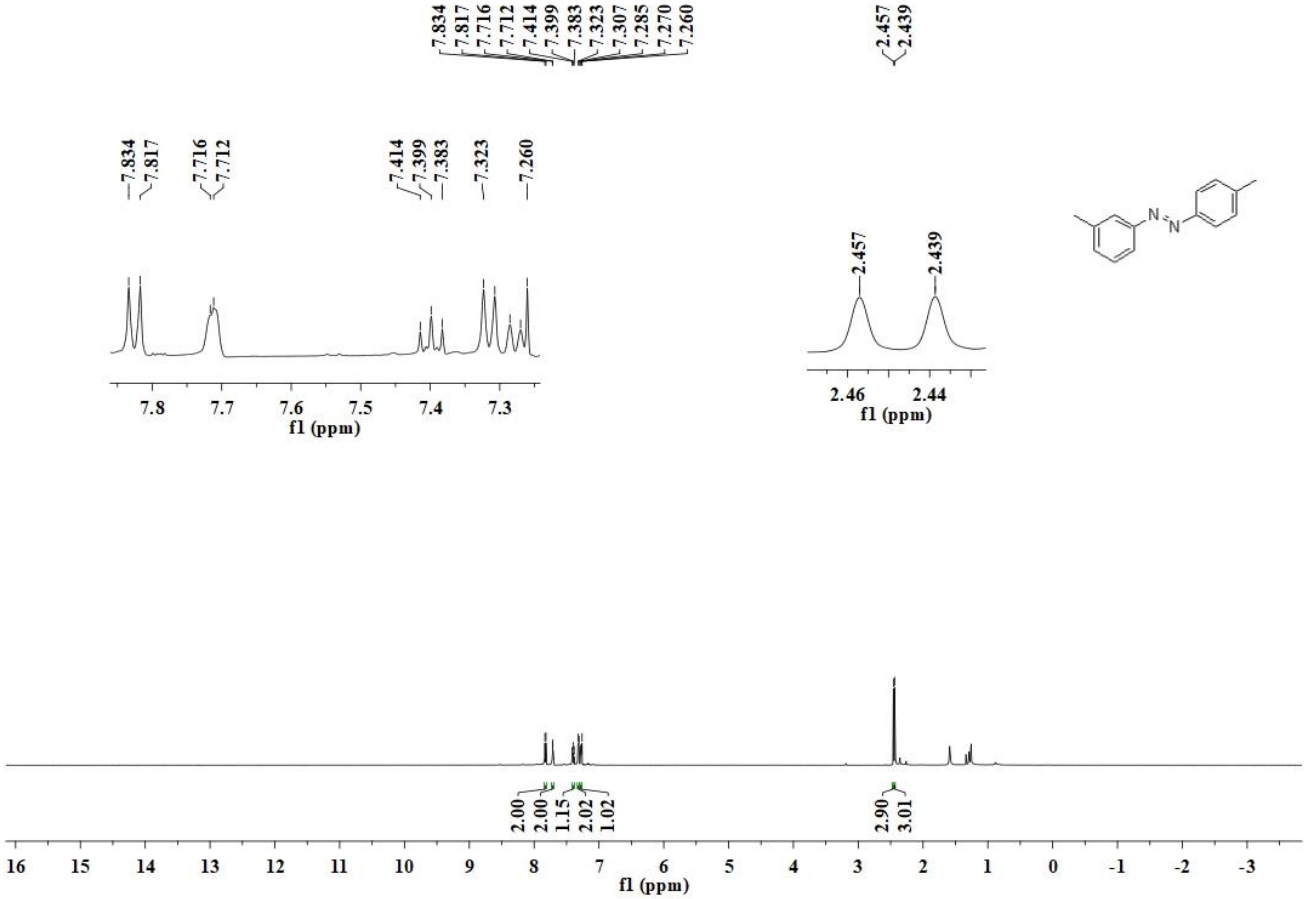
^{1}H NMR (500 MHz, $CDCl_3$) of **9**



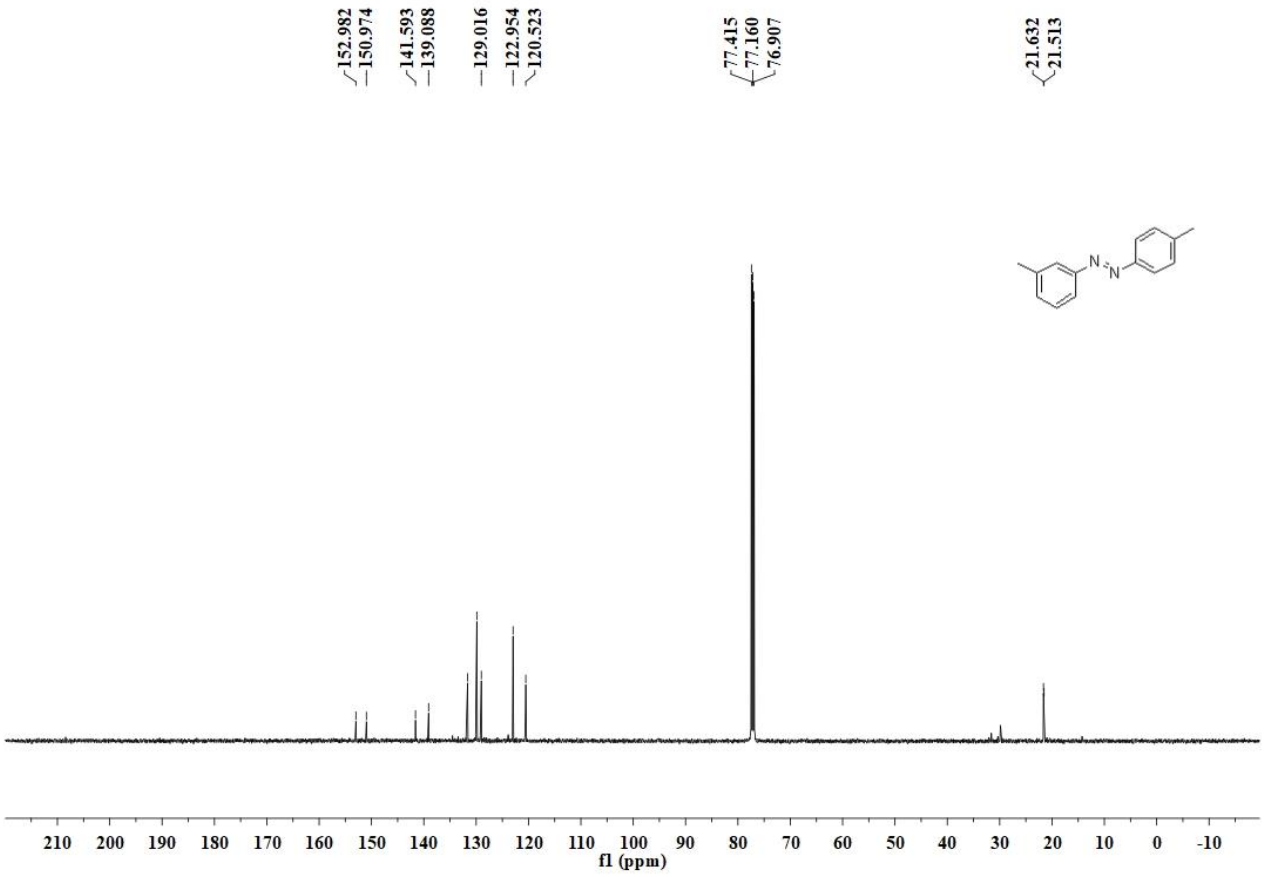
^{13}C NMR (126 MHz, $CDCl_3$) of **9**



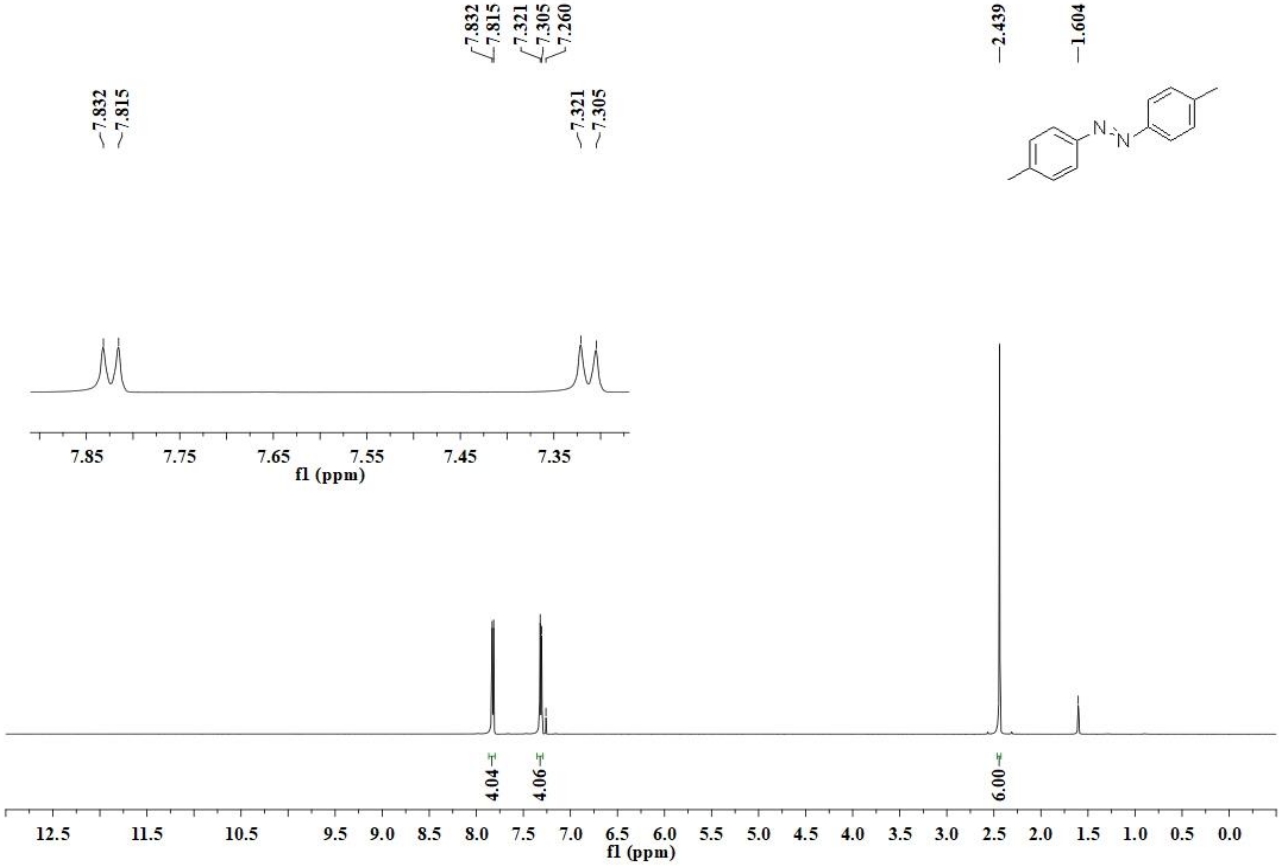
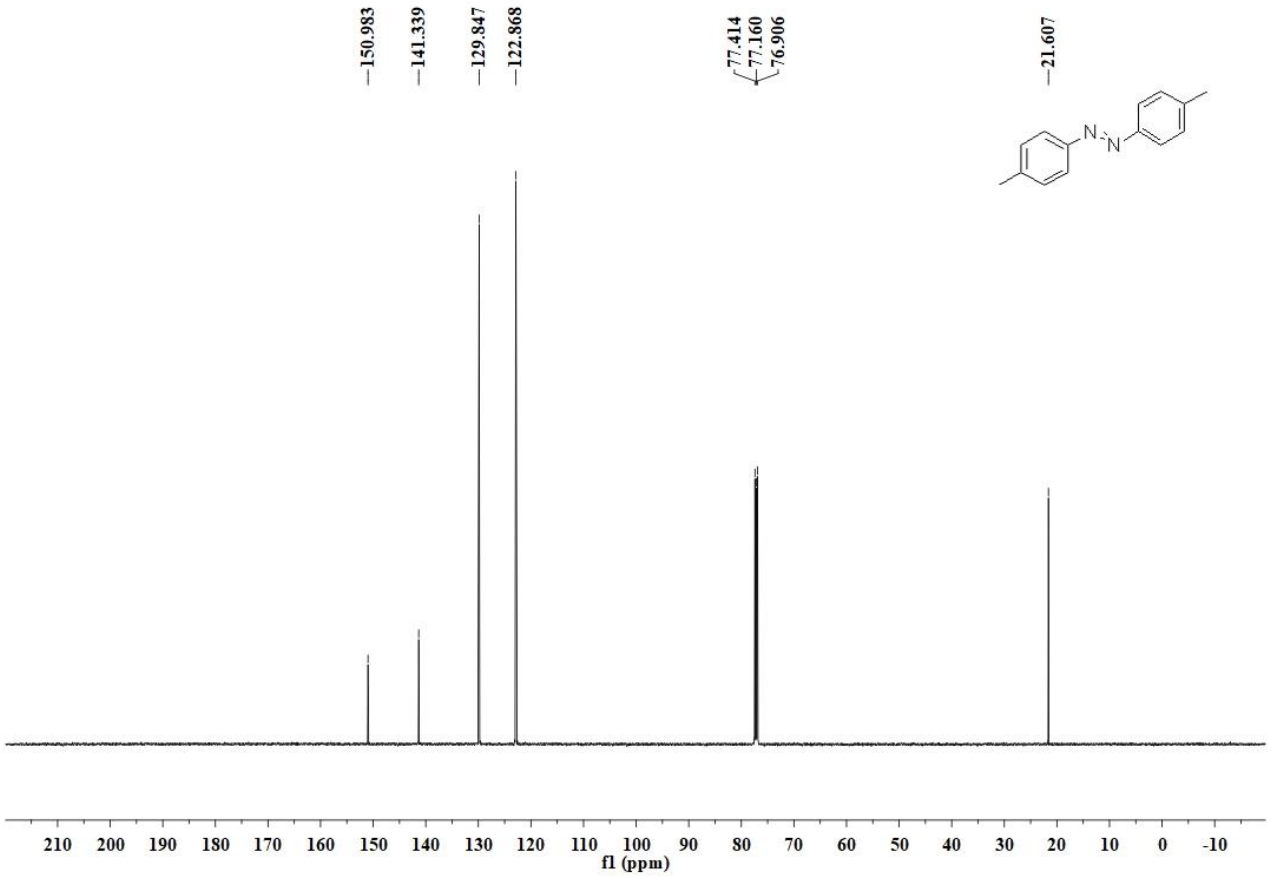
^{1}H NMR (500 MHz, $CDCl_3$) of **10**



^{13}C NMR (126 MHz, $CDCl_3$) of **10**



^{1}H NMR (500 MHz, $CDCl_3$) of **3be**



^{13}C NMR (126 MHz, $CDCl_3$) of **3be**