Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Room-temperature Cu(II)-catalyzed aromatic C-H azidation for the synthesis of ortho-azido anilines with excellent regioselectivity

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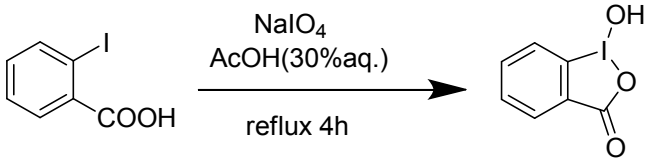
1. General methods

All manipulations were conducted under argon atmosphere (1 atm),unless otherwise noted. ^{1}H-NMR spectra were recorded with a Bruker AVANCE-500MHz spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ and $(CD_3)_2SO$ as an internal standard. ^{13}C-NMR spectra were obtained by the same NMR spectrometer. Mass spectra were recorded by PE SCLEX QSTAR spectrometer. Infrared spectra were recorded on a AVATAR 370 FT-IR.All materials obtained from commercial suppliers were used without further purification.

2. Synthesis of starting materials

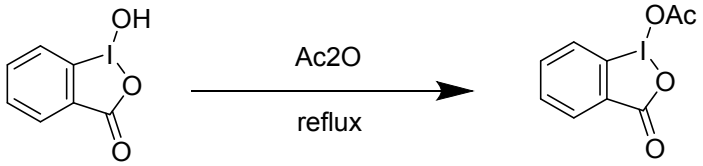
2.1 1-Hydroxy-1,2-benziodoxol-3-(1*H*)-one(2b)



2a **2b**

Following a reported procedure[1], in a 250 ml round bottom flask, $NaIO_4$ (17.3 g, 80.6 mmol, 1.0 equiv) and 2-iodobenzoic acid (20.0 g, 80.6 mmol, 1.0 equiv) were suspended in 30% (v:v) aq. AcOH (90 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (120 mL) and allowed to cool to room temperature, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 45 mL) and acetone (3 x 45 mL), and air-dried in the dark to give the pure product **2b.** (18.3 g, 73.1 mmol, 93% yield, reported 92%) as a colorless solid. **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) 8.02 (dd, *J* = 7.7, 1.4 Hz, 1 H, ArH), 7.97(m, 1 H, Ar*H*), 7.85 (dd, *J* = 8.2, 0.7 Hz, 1 H, ArH), 7.71 (td, *J* = 7.6, 1.2 Hz, 1 H, ArH). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) 167.7, 134.5, 131.5, 131.1, 130.4, 126.3 120.4. NMR data correspond to the reported values.[1]

2.2 1-Acetoxy-1,2-benziodoxol-3-(1*H*)-one(2c)

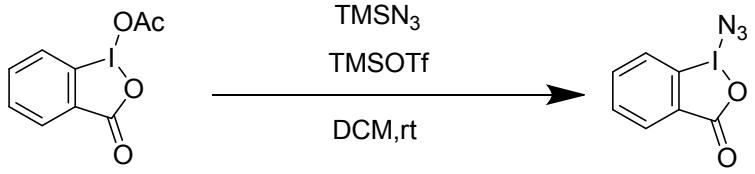


2b **2c**

Following a reported procedure[2], in a 100 ml round bottom flask,compound **2b** (18.3 g, 73.1 mmol, 1.00 equiv) was heated in Ac_2O (40 mL) to reflux until the solution turned clear (without suspension). The mixture was then left to cool down and white crystals started to form. The crystallization was continued at -18 °C. The crystal were then collected and dried overnight under high vacuum to give compound **2c** (15.9 g, 52.3 mmol, 87% yield, reported 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (dd, 1 H, *J* = 7.6, 1.4 Hz, ArH), 8.00 (dd, 1 H, *J* = 8.3, 0.5 Hz, ArH), 7.92 (dt, 1 H, *J* = 7.0, 1.7 Hz, ArH), 7.71 (td, 1 H, *J* = 7.6, 0.9 Hz, ArH),

2.25 (s, 3 H, $COCH_3$). NMR data correspond to the reported values.[2]

2.3 1-azido-1,2-benziodoxole-3-(1*H*)-one (2)



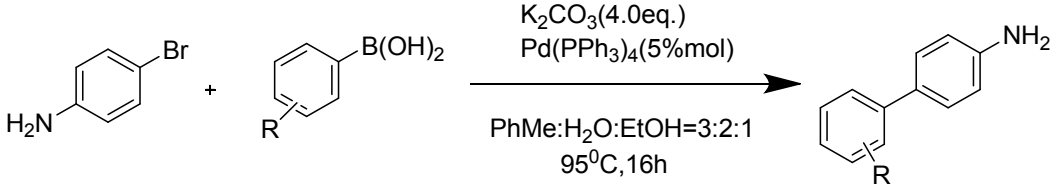
2c **2**

Following a reported procedure[3], in a 100 ml round bottom flask,compound **2c** (15.9 g, 52.3 mmol, 1.00 equiv) was stirred in dry DCM (45 mL) then $TMSN_3$ (10.7 mL, 78.5 mmol, 1.5 equiv) was cautiously added. A catalytic amount of TMSOTf (47 µL, 0.26 mmol, 0.005 equiv) was added last to the mixture which was then stirred for 30 minutes. The reaction mixture was then dried in vacuo to give a yellow precipitate, which was washed a few times with hexanes to give compound **2** (11.6 g, 40.1 mmol, 77% yield, reported 74%) as a pure pale yellow crystal. **^{1}H NMR** ($CDCl_3$/CF_3COOH, 20:1) δ 8.32(d, 1 H, *J* = 8 Hz, ArH), δ 8.05 (m, 2 H, ArH), δ 7.85(t, 1 H, *J* = 8 Hz, ArH). **^{13}C NMR** ($CDCl_3$/CF_3COOH, 20:1) δ 171.1, 137.3, 128.7, 126.7, 126.6, 118.8, 117.7. **IR** *vmax* 2052 (s), 1639 (s), 1564 (m), 1440 (w), 1347 (w), 1294 (m). NMR data correspond to the reported values.[4]

Coution:

The azidobenziodoxolone 2 can be stored at room temperature for in refrigerator for several months without noticeable decomposition. Shocks of the compound are not recommended. This compound 2 decomposes with explosion upheating to 138-140 °C

2.4 General Procedure for the Preparation of 4-Aminobiaryls (2)

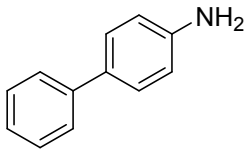


2d **2e** **2**

Following a reported procedure[5], in a 100 ml round bottom flask, phenylboronic acid (1.00 g, 8.16 mmol, 1.3 equiv), K_2CO_3 (3.47 g, 25.1mmol, 4.0 equiv), and $Pd(PPh_3)_4$ (0.363 g, 0.31 mmol, 0.05 equiv) were then dissolved in 30 mL of toluene, 20 mL of H_2O, and 10 mL of EtOH. 4-Bromoaniline (1.08 g, 6.28 mmol, 1.0 equiv) was added, and the resulting mixture was heated to 95 °C for 16 hours. After cooling, the biphasic solution was diluted with 100 mL of saturated aqueous NH_4Cl and 100 mL of CH_2Cl_2 and separated. The aqueous phase was extracted with an additional 2 × 100 mL of CH_2Cl_2, and the combined organic phases were washed 1 × 100 mL of water and 1 × 100 mL of saturated aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* to

afford a brown oil. Purification by column chromatography on silica gel afforded the product(**2-Aminobiaryls** was obtained by the same way).

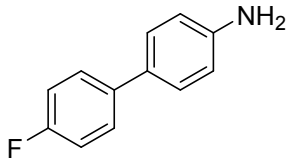
[1,1'-biphenyl]-4-amine(2g):



2g

^{1}H NMR ($CDCl_3$): δ 7.60 (m, 2H), 7.49-7.43 (m, 4H), 7.32 (m, 1H), 6.79 (dt, J = 2.7, 8.5 Hz, 2H), 3.74 (br s, 2H). **^{13}C NMR** ($CDCl_3$): δ 145.0, 141.3, 131.6, 128.8, 128.1, 126.5, 126.4, 115.5. NMR data correspond to the reported values.[6]

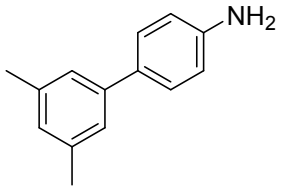
4'-fluoro-[1,1'-biphenyl]-4-amine(2h):



2h

^{1}H NMR (360 MHz, $CDCl_3$): δ 6.75 (d, J = 8.7 Hz, 2 H), 7.07 (t, J_{HF} = 8.8 Hz, J = 8.8 Hz, 2 H), 7.35 (d, J = 8.7 Hz, 2 H), 7.47 (dd, J_{HF} = 5.3 Hz, J = 8.9 Hz, 2 H); **^{13}C NMR** (91 MHz, $CDCl_3$): δ 115.4 (d, J_{CF} = 21.3 Hz), 115.4 127.8 (d, J_{CF} = 7.8 Hz), 127.9, 130.6, 137.3 (d, J_{CF} = 3.2 Hz), 145.8, 161.8 (d, J_{CF} = 245.0 Hz). NMR data correspond to the reported values.[7]

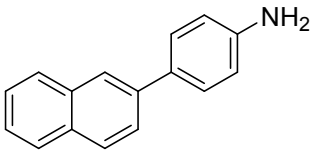
3',5'-dimethyl-[1,1'-biphenyl]-4-amine(2i):



2i

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, J = 8.4 Hz, 2 H), 7.18 (s, 2H), 6.94 (s, 1H), 6.76 (d, J = 8.4 Hz, 2H), 3.71 (br s, 2H), 2.38 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 145.8, 141.3, 138.2, 131.9, 128.1, 128.0, 124.5, 115.4, 21.5.

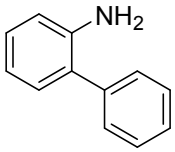
4-(naphthalen-2-yl)aniline(2j):



2j

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (s, 1H); 7.88 (m, 3H),
7.75 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 6.8 Hz, 1H), 7.48 (t, *J* = 6.9 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 3.64 (br s, 2H); **^{13}C NMR** (75MHz, $CDCl_3$) : δ 146.0. 138.5, 133.8, 132.1, 128.3, 128.1 127.6, 127.5, 126.1, 125.4, 125.3, 124.5, 115.5. NMR data correspond to the reported values.[8]

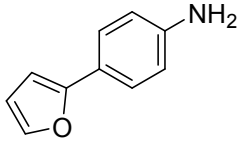
[1,1'-biphenyl]-2-amine(2k):



2k

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 4H), 7.36 (m, 1H), 7.16 (m, 2H), 6.84 (td, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.77 (brs, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.46, 139.48, 130.43, 129.06, 128.78, 128.46, 127.60, 127.13,
118.62, 115.56. NMR data correspond to the reported values.[9]

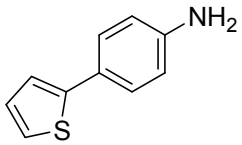
4-(furan-2-yl)aniline(2l):



2l

^{1}H NMR (200 MHz, DMSO-d6): δ 7.56 (dd, *J* = 1.8 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 6.56 (dd, *J* = 3.3Hz, 1H), 6.47 (dd, *J* = 1.8, 3.3 Hz, 1H), 3.54 (br s, 2H). NMR data correspond to the reported values.[10]

4-(thiophen-2-yl)aniline(2m):



2m

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37-7.47 (m, 2H), 7.11-7.21 (m, 2H), 7.03 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.64-6.75 (m, 2H), 3.73 (br s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 146.2, 145.2, 120.8, 127.3, 125.3, 123.2, 121.4, 115.5. NMR data correspond to the reported values.[11]

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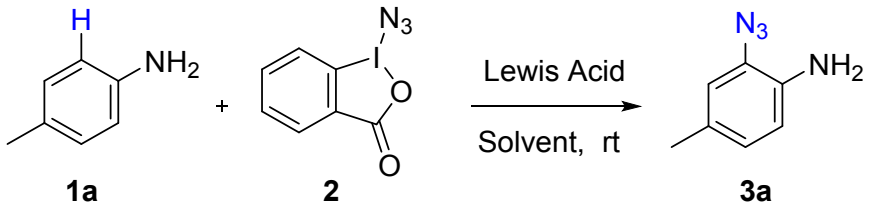
3. General procedures and characterization of products

Table S1. Optimization of reaction conditions [a]



1a **2** **3a**

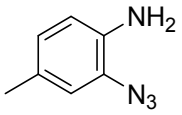
Entry	**1a** (equiv)	Lewis acid (mol %)	Solvent	T (^{o}C)	Yield[b]
1	1.0	none	CH_3CN	20	0
2	2	CuI (10)	CH_3CN	20	67
3	2	CuBr (10)	CH_3CN	20	59
4	2	CuCl (10)	CH_3CN	20	57
5	2	CuOAc(10)	CH_3CN	20	52
6	2	$Fe(ClO_4)_3$ (10)	CH_3CN	20	0
7	2	$Zn(ClO_4)_2 \cdot 6H_2O$ (10)	CH_3CN	20	0
8	2	ZnI_2 (10)	CH_3CN	20	63
9	2	$ZnCl_2$ (10)	CH_3CN	20	57
10	2	$CuCl_2$ (10)	CH_3CN	20	45
11	2	$CuSO_4$ (10)	CH_3CN	20	57
12	2	$Cu(OAc)_2$ (10)	CH_3CN	20	72
13	2	$Cu(OAc)_2$ (10)	CH_2Cl_2	20	69
14	2	$Cu(OAc)_2$ (10)	THF	20	79
15	2	$Cu(OAc)_2$ (10)	MeOH	20	0
16	2	$Cu(OAc)_2$ (20)	THF	20	85
17	2	$Cu(OAc)_2$ (20)	THF	30	86
18	1.0	$Cu(OAc)_2$ (20)	THF	20	57[c]
	0.5	$Cu(OAc)_2$ (20)	THF	20	37[d]
19	2	$Sc(OTf)_3$(20)	THF	20	13
20	2	Cu(OTf)·1/2Ph(20)	THF	20	62
21	2	$Ni(OAc)_2$ (20)	THF	20	21
22	2	$MgSO_4$ (20)	THF	20	25
23	2	$FeCl_3$ (20)	THF	20	10
24	2	$AlCl_3$ (20)	THF	20	trace
25	2	$ZnSO_4$ ((20)	THF	20	39

[a] Reagent **2** (0.3 mmol), 4-methyl aniline, catalyst, solvent, temperature and indicated solvents under N_2. [b] Isolated yield. [c] with 14% diazidation product [d] with 26% diazidation product

Coution:

Because of the hazard of azidobenziodoxolone, it is required to perform the experiment carefully when azidobenziodoxolone is used. The azidobenziodoxolone is stable and safe in solvent. However, the solids of starting materials are forbidden to be mixed together in the beginning of the experiment. Otherwise, decomposition may take place. First, the starting materials should be dissolved in solvents, respectively. Then, the materials can be mixed together in solvent and the reaction is allowed to begin.

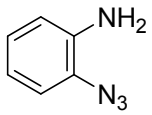
2-azido-4-methylaniline(3a)



3a

Experimental procedure(3a)： compound **4 (**86.7 mg, 0.3 mmol) and $Cu(OAc)_2$ (12.1 mg, 0.06 mmol) were added to THF (2.0 ml) in a 10 ml tube under air, followed by addition of aniline(64.2 mg, 0.6 mmol). The formed mixture was stirred at room temperature under air for 12 h. The solution was then diluted with ethyl acetate (20 mL), and washed with saturated aqueous $NaHCO_3$ and separated. The organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* to afford a crude product. The crude product was purified by column chromatography on silica gel to afford 66.1 mg (85%) brown liquid of the product. **IR:** (KBr) 3459, 3369, 2115, 1620, 1515, 1381, 810 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 6.85 (s, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 6.61(d, *J* = 8.0 Hz, 1 H), 3.68 (br s, 2 H), 2.28 (s, 3 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 135.6, 128.8, 126.2, 125.1, 118.8, 116.1, 20.1; HRMS (ESI) *m/z* Calcd for $C_7H_8N_4$ $(M + H)^+$ 149.0749, found 149.0756.

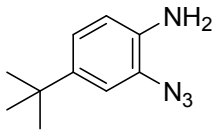
2-Azidoaniline(3b)



3b

The reaction was performed according to the procedure for **3a**. Yield 72% (reported 27%[12]). A brown solid. **IR**: (KBr) 3734, 3669, 2110, 1616, 1456, 1305, 872 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 7.9, 0.8 Hz, 1 H), 6.96 (td, *J* = 7.7, 1.0 Hz, 1 H), 6.80 (td, *J* = 7.8, 1.2 Hz, 1 H), 6.70 (dd, *J* = 7.9, 1.0 Hz, 1 H), 3.81 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 138.1, 125.6, 125.2, 119.1, 118.4, 115.9; HRMS (ESI) *m/z* Calcd for $C_6H_6N_4$ $(M + H)^+$ 135.0592, found 135.0584.

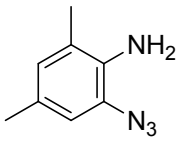
2-azido-4-(tert-butyl)aniline(3c)



3c

The reaction was performed according to the procedure for **3a**. Yield 88% (reported 30%[12]). A brown solid. **IR**: (KBr) 3469, 3373, 2111, 1620, 1515, 1365, 815 cm^{-1};**^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 2.1 Hz, 1 H), 6.96 (dd, *J* = 8.2, 2.0 Hz, 1 H), 6.61 (d, *J* = 8.3 Hz, 1 H), 3.67 (br s, 2 H), 1.28 (s, 9 H) ; **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 142.5, 135.7, 124.6, 122.7, 115.8, 115.3, 34.3, 31.5; HRMS (ESI) *m/z* Calcd for $C_{10}H_{14}N_4$ $(M + H)^+$ 191.1218, found 191.1227.

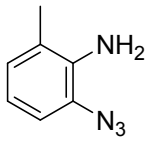
2-azido-4,6-dimethylaniline(3d)



3d

The reaction was performed according to the procedure for **3a**. Yield 86% (reported 68%[12]). A brown solid. **IR**: (KBr) 3421, 3322, 2108, 1632, 1498, 1318, 1265, 833 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 6.74 (s, 1 H), 6.70 (s, 1 H), 3.62 (br s, 2 H), 2.26 (s, 3 H), 2.14 (s, 3 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 133.8, 128.0, 127.6, 124.7, 123.6, 116.3, 20.5, 17.3; HRMS (ESI) *m/z* Calcd for $C_8H_{10}N_4$ $(M + H)^+$ 163.0905, found 163.0918.

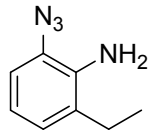
2-azido-6-methylaniline(3e)



3e

The reaction was performed according to the procedure for **3a**. Yield 53%. A brown liquid. **IR**: (KBr) 3446, 3334, 2127, 1618, 1447, 1388, 814 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.0 Hz, 1 H), 6.87 (d, *J* = 7.6 Hz, 1 H), 6.74 (t, *J* = 7.7 Hz, 1 H), 3.77 (br s, 2 H), 2.17 (s, 3 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 136.4, 126.8, 124.8, 123.5, 118.4, 116.0, 17.3; HRMS (ESI) *m/z* Calcd for $C_7H_8N_4$ $(M + H)^+$ 149.0749, found 149.0738.

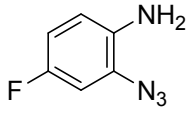
2-azido-6-ethylaniline(3f)



3f

The reaction was performed according to the procedure for **3a**. Yield 46%. A brown liquid. **IR**: (KBr) 3452, 3328, 2127, 1621, 1443, 1382, 822 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 6.95 (d, *J* = 7.9 Hz, 1 H), 6.90 (d, *J* = 7.5 Hz, 1 H), 6.79 (t, *J* = 7.7 Hz, 1 H), 3.81 (br s, 2 H), 2.52 (q, *J* = 7.5 Hz, 2 H), 1.26 (t, *J* = 7.5 Hz, 3 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 135.8, 129.2, 125.0, 124.7, 118.6,115.9, 24.1, 12.8; HRMS (ESI) *m/z* Calcd for $C_7H_8N_4$ $(M + H)^+$ 163.0905, found 163.0928.

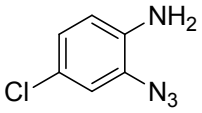
2-azido-4-fluoroaniline(3g)



3g

The reaction was performed according to the procedure for **3a**. Yield 54%. A brown solid. **IR**: (KBr) 3454, 3375, 2125, 1588, 1513, 1310, 1258, 932 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 6.78 (dd, *J* = 8.8, 2.6 Hz, 1 H), 6.68 (td, *J* = 8.7, 2.7 Hz, 1 H), 6.62 (dd, *J* = 8.7, 5.2 Hz, 1 H), 3.66 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 156.2 (d, *J* = 238.8 Hz), 134.4, 126.1 (d, *J* = 8.3 Hz), 116.5 (d, *J* = 8.8 Hz), 112.3 (d, *J* = 23 Hz), 105.7 (d, J = 26.1 Hz); HRMS (ESI) *m/z* Calcd for $C_6H_5FN_4$ $(M + H)^+$ 153.0498, found 153.0493; Anal. Calcd for $C_6H_5FN_4$: C, 47.37; H, 3.31; F, 12.49; N, 36.83. Found: C, 47.56; H, 3.43; F, 12.87; N, 37.02.

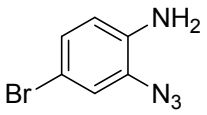
2-azido-4-chloroaniline(3h)



3h

The reaction was performed according to the procedure for **3a**. Yield 66%. A brown solid. **IR**: (KBr) 3738, 3668, 2113, 1615, 1452, 872 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 2.2 Hz, 1 H), 6.91 (dd, *J* = 8.5, 2.2 Hz, 1 H), 6.59 (d, *J* = 8.4 Hz, 1 H), 3.80 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 136.8, 126.2, 125.5, 123.2, 118.3, 116.5; HRMS (ESI) *m/z* Calcd for $C_6H_5ClN_4$ $(M + H)^+$ 169.0203, found 169.0208; Anal. Calcd for $C_6H_5ClN_4$: C, 42.75; H, 2.99; Cl, 21.03; N, 33.23. Found: C, 42.93; H, 3.18; Cl, 21.87; N, 33.61.

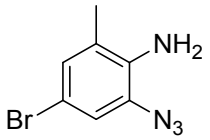
2-azido-4-bromoaniline(3i)



3i

The reaction was performed according to the procedure for **3a**. Yield 75%. A brown solid. **IR**: (KBr) 3734, 3669, 2117, 1618, 1447, 1388, 863 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.11 (s, 1 H), 7.02 (dd, *J* = 8.4, 1.5 Hz, 1 H), 6.54 (d, *J* = 8.5 Hz, 1 H), 3.82 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 137.3, 128.4, 126.5, 121.0, 116.9, 109.8; HRMS (ESI) *m/z* Calcd for $C_6H_5BrN_4$ $(M + H)^+$ 212.9698, found 212.9689. Anal. Calcd for $C_6H_5BrN_4$: C, 33.83; H, 2.37; Br, 37.51; N, 26.30. Found: C, 33.95; H, 2.62; Br, 37.76; N, 26.42.

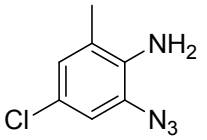
2-azido-4-bromo-6-methylaniline(3j)



3j

The reaction was performed according to the procedure for **3a.** Yield 60%. A brown solid. **IR**: (KBr) 3734, 3669, 2117, 1608, 1462, 1380, 845 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.01 (d, *J* = 1.9 Hz, 1 H), 6.97 (d, *J* = 1.32 Hz, 1 H), 3.75 (br s, 2 H), 2.12 (s, 3 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 135.5, 129.4, 126.0, 125.1, 118.6, 109.3, 17.2; HRMS (ESI) *m/z* Calcd for $C_7H_7BrN_4$ $(M + H)^+$ 226.9854, found 226.9861.

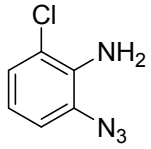
2-azido-4-chloro-6-methylaniline(3k)



3k

The reaction was performed according to the procedure for **3a**. Yield 68%. A brown solid. **IR**: (KBr) 3734, 3669, 2117, 1628, 1480, 1388, 842 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 6.88 (d, *J* = 2.1 Hz, 1 H), 6.84-6.83 (m, 1 H), 3.74 (br s, 2 H), 2.12 (s, 3 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 135.0, 126.5, 125.7, 124.7, 122.5, 115.8, 17.3; HRMS (ESI) *m/z* Calcd for $C_7H_7ClN_4$ $(M + H)^+$ 183.0359, found 183.0362.

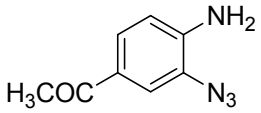
2-azido-6-chloroaniline(3l)



3l

The reaction was performed according to the procedure for **3a**. Yield 50%. A brown liquid. **IR**: (KBr) 3734, 3669, 2117, 1634, 1457, 745 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.05 (dd, *J* = 8.1, 1.1 Hz, 1 H), 6.94 (dd, *J* = 8.0, 1.0 Hz, 1 H), 6.71 (t, *J* = 8.1 Hz, 1 H), 4.20 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 135.3, 126.1, 125.5, 119.7, 118.2, 116.6; HRMS (ESI) *m/z* Calcd for $C_6H_5ClN_4$ $(M + H)^+$ 169.0203, found 169.0201.

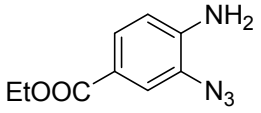
1-(4-amino-3-azidophenyl)ethanone(3m)



3m

The reaction was performed according to the procedure for **3a** at 40 °C. Yield 55% (reported 45%[12]). A brown solid. **IR**: (KBr) 3449, 3342, 2128, 1662, 1620, 1587, 1322, 1245, 886, 815 cm^{-1};; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.9 Hz, 1 H), 7.56 (dd, *J* = 8.3, 1.8 Hz, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 4.47 (br s, 2 H), 2.51(s, 3 H) ; **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 195.9, 142.9, 128.1, 127.4, 125.0, 118.5, 113.9, 26.1; HRMS (ESI) *m/z* Calcd for $C_8H_8N_4O$ $(M + H)^+$ 177.0698, found 177.0694.

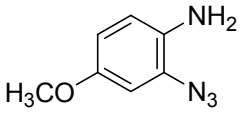
ethyl 4-amino-3-azidobenzoate(3n)



3n

The reaction was performed according to the procedure for **3a** at 40 °C. Yield 43%. A brown solid. **IR**: (KBr) 3478, 3356, 2118, 1685, 1619, 1428, 1372, 805 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 1.7 Hz, 1 H), 7.65 (dd, *J* = 8.3, 1.7 Hz, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 4.25 (br s, 2 H), 1.37 (t, *J* =7.1 Hz, 3 H) ; **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 166.0, 142.4, 127.8, 124.6, 120.6, 119.8, 114.2, 60.7, 14.4; HRMS (ESI) *m/z* Calcd for $C_9H_{10}N_4O_2$ $(M + H)^+$ 207.0804, found 207.0815.

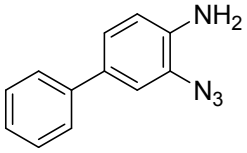
2-azido-4-methoxyaniline(3o)



3o

The reaction was performed according to the procedure for **3a**. Yield 47% (reported 23%[12]). A brown solid. **IR**: (KBr) 3742, 3280, 2113, 1592, 1521, 1453, 1249, 1245,1040, 826 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 6.65 (d, *J* = 8.7 Hz, 1 H), 6.62 (d, *J* = 2.7, 1 H), 6.55 (dd, *J* = 8.6, 2.7 Hz, 1 H), 3.76 (s, 3 H), 3.52 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 153.2, 131.8, 126.1, 117.0, 111.2, 104.6, 55.9; HRMS (ESI) *m/z* Calcd for $C_7H_8N_4O$ $(M + H)^+$ 165.0698, found 165.0692.

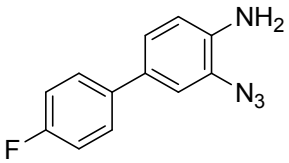
3-azido-[1,1'-biphenyl]-4-amine(3p)



3p

The reaction was performed according to the procedure for **3a**. Yield 71%. A brown solid. **IR**: (KBr) 3449, 3668, 2127, 1618, 1448, 872 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.9, 1.2 Hz, 2 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.32 (d, *J* = 1.9 Hz, 1 H), 7.27 (dd, *J* = 8.2, 2.0 Hz, 1 H), 6.80 (d, *J* = 8.2 Hz, 1 H), 3.92 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 140.5, 137.6, 132.5, 128.9, 126.8, 126.5, 125.5, 124.5, 116.9, 116.2; HRMS (ESI) *m/z* Calcd for $C_{12}H_{10}N_4$ $(M + H)^+$ 211.0905, found 211.0906.

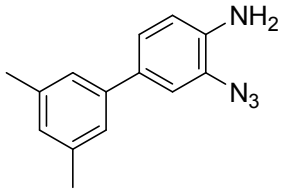
3-azido-4'-fluoro-[1,1'-biphenyl]-4-amine(3q)



3q

The reaction was performed according to the procedure for **3a**. Yield 78%. A brown solid. **IR**: (KBr) 3475, 3378, 2109, 1604, 1509, 1467, 1231, 880, 846, 833 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2 H), 7.15 (d, *J* = 1.9 Hz, 1 H), 7.11 (dd, *J* = 8.2, 2.0 Hz, 1 H), 7.07 (td, *J* = 8.7, 2.1 Hz, 2 H), 6.71 (d, *J* = 8.2 Hz, 1 H), 3.84 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 163.1, 161.2, 137.6, 136.6 (d, *J* = 2.8 Hz), 131.5, 128.0 (d, *J* = 8.3 Hz), 125.5, 124.3, 116.8, 116.1, 115.7, 115.6; HRMS (ESI) *m/z* Calcd for $C_{12}H_9FN_4$ $(M + H)^+$ 229..0811, found 229.0806.

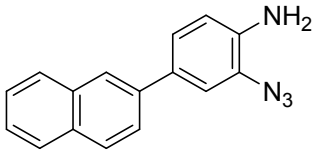
3-azido-3',5'-dimethyl-[1,1'-biphenyl]-4-amine(3r)



3r

The reaction was performed according to the procedure for **3a**. Yield 72%. A brown solid. **IR**: (KBr) 3453, 3368, 2107, 1618, 1447, 1378, 872, 832, 689 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 1.9 Hz, 1 H), 7.15 (dd, *J* = 8.2, 2.0 Hz, 1 H), 7.11 (s, 2 H), 6.92 (s, 1 H), 6.66 (d, *J* = 8.2 Hz, 1 H), 3.78 (br s, 2 H), 2.34 (s, 6 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 140.5, 138.4, 137.5, 132.8, 128.6, 125.4, 124.5, 117.0, 116.2, 21.5; HRMS (ESI) *m/z* Calcd for $C_{14}H_{14}N_4$ $(M + H)^+$ 239.1218, found 239.1210.

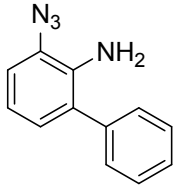
2-azido-4-(naphthalen-2-yl)aniline(3s)



3s

The reaction was performed according to the procedure for **3a**. Yield 80%. A brown solid. **IR**: (KBr) 3471, 3365, 2119, 1608, 1456, 810 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 0.8 Hz, 1 H), 7.79 (t, *J* = 8.4 Hz, 3 H), 7.60 (dd, *J* = 8.6, 1.7 Hz, 1 H), 7.45-7.38 (m, 2 H), 7.29 (d, *J* = 1.9 Hz, 1 H), 7.24 (dd, *J* = 8.1, 1.8 Hz, 1 H), 6.65 (d, *J* = 8.2 Hz, 1 H), 3.80 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 137.8, 133.9, 132.5, 132.3, 128.6, 128.4, 128.2, 127.8, 126.4, 125.8, 125.6, 125.2, 124.8, 124.7, 117.1, 116.3; HRMS (ESI) *m/z* Calcd for $C_{16}H_{12}N_4$ $(M + H)^+$ 261.1062, found 261.1056.

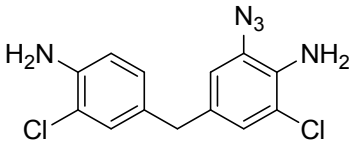
3-azido-[1,1'-biphenyl]-2-amine(3t)



3t

The reaction was performed according to the procedure for **3a**. Yield 64% (reported 68%[12]). A brown solid. **IR**: (KBr) 3472, 3375, 2109, 1621, 1465, 754, 706 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.39-7.38 (m, 4 H), 7.32-7.28 (m, 1 H), 6.98 (dd, *J* = 7.9, 1.3 Hz, 1 H), 6.88 (dd, *J* = 7.6, 1.3 Hz, 1 H), 6.78 (t, *J* = 7.7 Hz, 1 H), 3.87 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 138.9, 135.7, 129.1, 129.0, 128.5, 127.6, 126.9, 125.3, 118.5, 117.5; HRMS (ESI) *m/z* Calcd for $C_{12}H_{10}N_4$ $(M + H)^+$ 211.0905, found 211.0903.

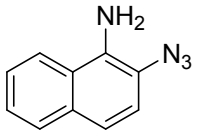
4-(4-amino-3-chlorobenzyl)-2-azido-6-chloroaniline(3u)



3u

The reaction was performed according to the procedure for **3a**. Yield 58%. A brown solid. **IR**: (KBr) 3465, 3368, 2915, 2106, 1610, 1501, 878, 846 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 1.9 Hz, 1 H), 6.86 (dd, *J* = 8.8, 2.0 Hz, 2 H), 6.74 (d, *J* = 1.6 Hz, 1 H), 6.70 (d, *J* = 8.1 Hz, 1 H), 4.09 (br s, 2 H), 3.97 (br s, 2 H), 3.72 (s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 141.3, 133.5, 131.6, 131.5, 129.5, 128.0, 126.1, 125.8, 119.7, 119.4, 117.0, 116.1, 39.7; HRMS (ESI) *m/z* Calcd for $C_{13}H_{11}Cl_2N_5$ $(M + H)^+$ 308.0392, found 308.0394.

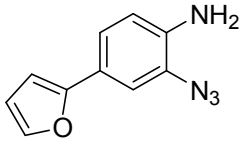
2-azidonaphthalen-1-amine(3v)



3v

The reaction was performed according to the procedure for **3a**. Yield 51%. A brown solid. **IR**: (KBr) 3488, 3325, 2128, 1612, 1572, 1498, 1465, 758 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1 H), 7.73 (d, *J* = 8.3 Hz, 1 H), 7.49-7.41 (m, 2 H), 7.36 (d, *J* = 8.7 Hz, 1 H), 7.24 (d, *J* = 8.7 Hz, 1 H), 4.30 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 132.4, 131.6, 128.7, 125.8, 125.3, 123.8, 120.8, 119.5, 119.1, 117.0; HRMS (ESI) *m/z* Calcd for $C_{10}H_8N_4$ $(M + H)^+$ 185.0749, found 185.0744.

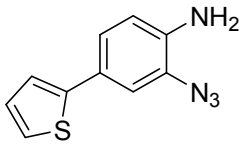
2-azido-4-(furan-2-yl)aniline(3w)



3w

The reaction was performed according to the procedure for **3a**. Yield 31%. A brown solid. **IR**: (KBr) 3459, 3357, 2110, 1636, 1462, 1045, 879, 806 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 1.0 Hz, 1 H), 7.33 (d, *J* = 1.7 Hz, 1 H), 7.25 (dd, *J* = 8.0, 1.7 Hz, 1 H), 6.68 (d, *J* = 8.2 Hz, 1 H), 6.48 (d, *J* = 3.2 Hz, 1 H), 6.44 (dd, *J* = 3.2, 1.8 Hz, 1 H), 3.87 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 153.6, 141.3, 137.5, 125.4, 122.7, 121.6, 115.9, 113.9, 111.6, 103.2; HRMS (ESI) *m/z* Calcd for $C_{10}H_8N_4O$ $(M + H)^+$ 201.0698, found 201.0695.

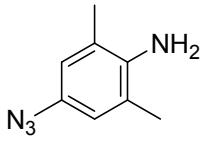
2-azido-4-(thiophen-2-yl)aniline(3x)



3x

The reaction was performed according to the procedure for **3a**. Yield 49%. A brown solid. **IR**: (KBr) 3463, 3362, 2124, 1606, 1465, 1045, 882, 835 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 2.0 Hz, 1 H), 7.22 (dd, *J* = 3.5, 2.0 Hz, 1 H), 7.20 (d, *J* = 1.5 Hz, 1 H), 7.18 (dd, *J* = 3.6, 1.1 Hz, 1 H), 7.06-7.04 (m, 1 H), 6.69 (d, *J* = 8.2 Hz, 1 H), 3.88 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 144.0, 137.7, 128.0, 126.0, 125.5, 123.8, 123.7, 122.0, 116.0, 115.9; HRMS (ESI) *m/z* Calcd for $C_{10}H_8N_4S$ $(M + H)^+$ 217.0476, found 217.0472.

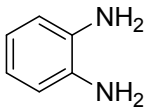
4-azido-2,6-dimethylaniline(3y)



3y

The reaction was performed according to the procedure for **3a**. Yield 36%. A brown liquid. **IR**: (KBr) 3429, 3317, 2114, 1645, 1492, 1316, 1260, 831 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 6.64 (s, 2 H), 3.55 (br s, 2 H), 2.17 (s, 6 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 139.1, 128.1, 122.2, 117.7, 16.7; HRMS (ESI) *m/z* Calcd for $C_8H_{10}N_4$ $(M + H)^+$ 163.0905, found 163.0928.

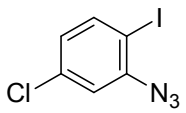
benzene-1,2-diamine(4)



4

To the suspension of 2-azidoaniline (80.4 mg, 0.6 mmol) and NH_4Cl (79.5 mg, 1.5 mmol) in EtOH (3 mL) and water(1 mL), zinc powder (59.2 mg, 0.9 mmol)was added, the mixture was stirred vigorously at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered through a Celite pad and washed with EtOAc. The combined filtrate and washings were concentrated, the residue dissolved in EtOAc (30 mL) and washed with saturated brine solution (30 mL) and water. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography to give 63.5 mg (98%) product. **IR**: (KBr) 3734, 3669, 2117, 1618, 1447, 1388, 872 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 6.74-6.70 (m, 4 H), 3.38 (br s, 4 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 134.7, 120.4, 116.9;

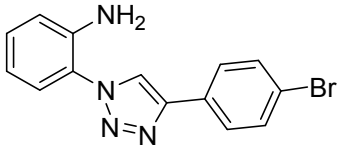
2-azido-4-chloro-1-iodobenzene(5)



5

To a solution of fluoroboric acid (792.2 mg, 5.4mmol) and 2-azido-4-chloroaniline (304.8 mg, 1.8 mmol) in EtOH (3 mL) was added tert-butyl nitrite (50% 370.8 mg, 3.6 mmol) dropwise by syringe. The resulting mixture was stirred at 0 ^{0}C for an hour, filtered, washed with Et_2O. To the resulting suspension of diazonium salt in CH_3CN(8 ml), was added a solution of KI (358.6 mg, 2.16 mmol) in H_2O (3 mL). The reaction mixture was stirred for 15 min then allowed to come to room temperature and stirred for 30 min. After completion, to the reaction mixture was then added saturated aqueous $NaHCO_3$, the crude product was extracted EtOAc and purified by flash chromatography to offer 426.8 mg (85%) product. **IR**: (KBr) 3734, 3669, 2117, 1618, 1447, 1388, 872 cm^{-1};**^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 1 H), 7.09 (d, *J* = 2.2 Hz, 1 H), 6.85 (dd, *J* = 8.4, 2.1 Hz, 1 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 143.0, 140.7, 135.5, 126.6, 118.6, 85.1;

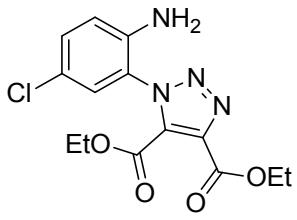
2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)aniline(6)



6

In a 10-mL one-neck round bottle, 2-azidoaniline (67.1 mg, 0.5 mmol) and 1-bromo-4-ethynylbenzene (108.6 mg, 0.6mmol) were suspended in a 1:1.5 mixture of water and *t*-BuOH (1 mL : 1.5 mL). To this was added $CuSO_4 \cdot 5H_2O$(2.5 mg, 0.01 mmol) and sodium ascorbate solution (9.9 mg, 0.05 mmol). The mixture was stirred over night at room temperature, after the reaction was completed (monitored by TLC). The solvent was distilled, water (15 mL) was added, and the mixture was extracted with dichloromethane. The organic layer was separated, washed with brine (10 mL) and saturation $NaHCO_3$ (10 ml), anhydrous Na_2SO_4 dried. The solvent was evaporated to afford crude product, which was further purified by alumina column chromatography to offer 144.5 mg (92 %) product**. IR**: (KBr) 3734, 3669, 2117, 1618, 1447, 1388, 872 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 8.05 (s, 1 H), 7.77 (d, *J* = 8.2 Hz, 2 H), 7.58 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 7.8 Hz, 2 H), 6.90 (d, *J* = 8.3 Hz, 1 H), 6.85 (t, *J* = 7.8 Hz, 1 H), 4.59 (br s, 2 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 146.7, 140.9, 132.1, 130.3, 129.2, 127.4, 124.3, 123.0, 122.4, 120.4, 118.4, 117.7.

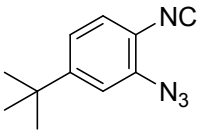
diethyl 1-(2-amino-5-chlorophenyl)-1H-1,2,3-triazole-4,5-dicarboxylate(7)



7

In a 10-mL one-neck round bottle, 2-azido-4-chloroaniline (101.4 mg, 0.6 mmol) and diethyl but-2-ynedioate (204.3 mg, 1.2 mmol) were suspended in a 1:1.5 mixture of water and *t*-BuOH (2 mL : 3 mL). To this was added $CuSO_4 \cdot 5H_2O$(3.1 mg, 0.012 mmol) and sodium ascorbate solution (12.2 mg, 0.06 mmol). The mixture was stirred over night at room temperature, after the reaction was completed (monitored by TLC). The solvent was distilled, water (15 mL) was added, and the mixture was extracted with dichloromethane. The organic layer was separated, washed with brine (10 mL) and saturation $NaHCO_3$ (10 ml), anhydrous Na_2SO_4 dried. The solvent was evaporated to afford crude product, which was further purified by alumina column chromatography to offer 180.5 mg (89%) product**. IR**: (KBr) 3734, 3669, 2117, 1618, 1447, 1388, 872 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 9.54 (s, 1 H), 7.10 (d, *J* = 2.1 Hz, 1 H), 6.99 (dd, *J* = 8.6, 2.1 Hz, 1 H), 6.70 (d, *J* = 8.6 Hz, 1 H), 5.51 (s, 1 H), 4.21(qd, *J* = 7.1, 2.7 Hz, 4 H), 1.30 (t, *J* = 7.2 Hz, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 169.3, 163.5, 151.7, 146.7, 132.3, 130.4, 129.6, 124.9, 122.2, 118.7, 62.2, 60.2, 14.3, 13.8;

2-azido-4-(tert-butyl)-1-isocyanobenzene(8)



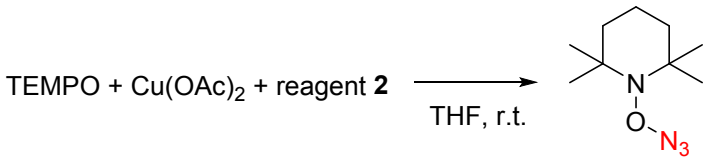
8

To formic acid (1.7 mL, 43.1 mmol) was added acetic anhydride (3.7 mL, 30 mmol) and the mixure was stirred at room temperature. After stirring for 15 min, to the mixture was added dropwise into the solution of 2-azido-4-(tert-butyl)aniline (284.8 mg, 1.5 mmol) in THF (6 mL) and the mixture was stirred at 0 ^{0}C. After the addition was completed, the mixture was warmed to room temperature and stirred for 1h.Then the mixture was treated with saturated solution of $NaHCO_3$ and extracted with EtOAc three times. The extract was dried and concentrated under reduced pressure to give formanilide.To the solution of the formanilide and Et_3N (2 mL) in THF (6 mL) was added $POCl_3$ (0.8 mL) at 0 ^{0}C and stirred at the same temperature. After stirring for 2h, the reaction mixture was basified with saturated aqueous solution of $NaHCO_3$, and extracted with $CHCl_3$. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained residue was purified by silica gel column chromatography to give the product 263.5 mg (88%). **IR**: (KBr) 3734, 3669, 2117, 1618, 1447, 1388, 872 cm^{-1}; **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz, 1 H), 7.18-7.16 (m, 2 H), 1.34 (s, 9 H); **^{13}C NMR**: (126 MHz, $CDCl_3$) δ 168.8, 154.5, 135.9, 127.6, 122.6, 116.2, 115.4, 35.2, 31.0.

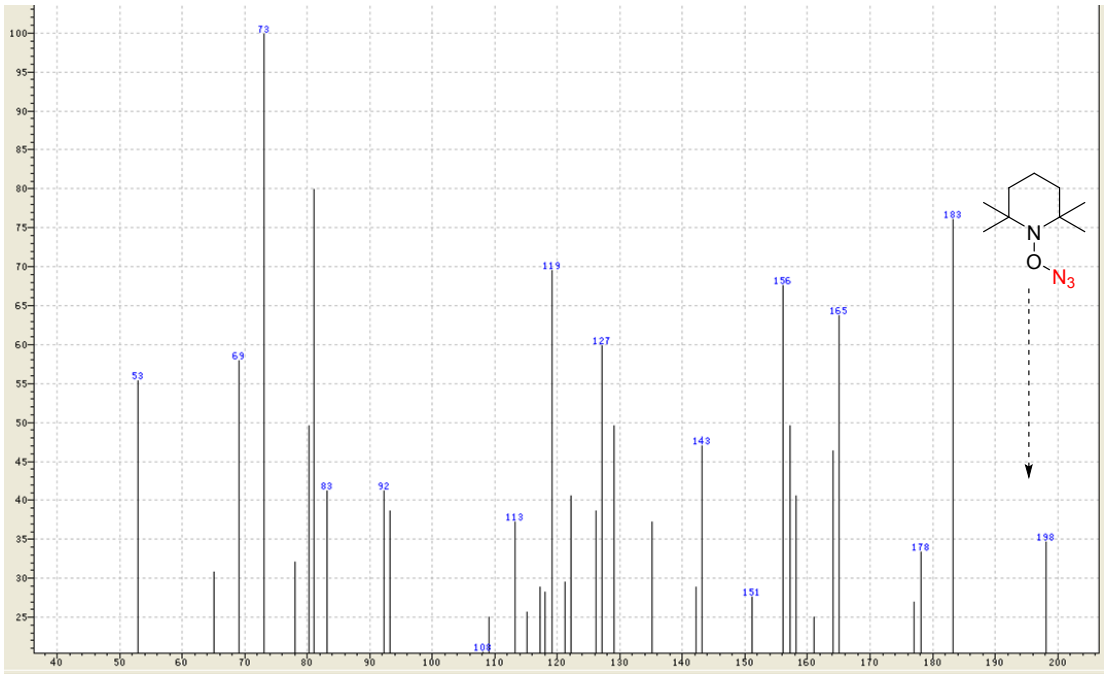
4. Mechanistic Study……..

Experiments of N_3 radical trapped by TEMPO

To a 10 mL Schlenk tube was sequentially added TEMPO (64 mg, 0.4 mmol), reagent **2** (86.4 mg, 0.3 mmol), $Cu(OAc)_2$ (11.9mg, 0.06mmol). The tube was evacuated and filled with argon for three times. THF (2 mL) was added. The reaction mixture was stirred at room temperature for 1 h. The resulting mixture was analyzed by GC-MS measuremnt.



GC-MS anaylsis



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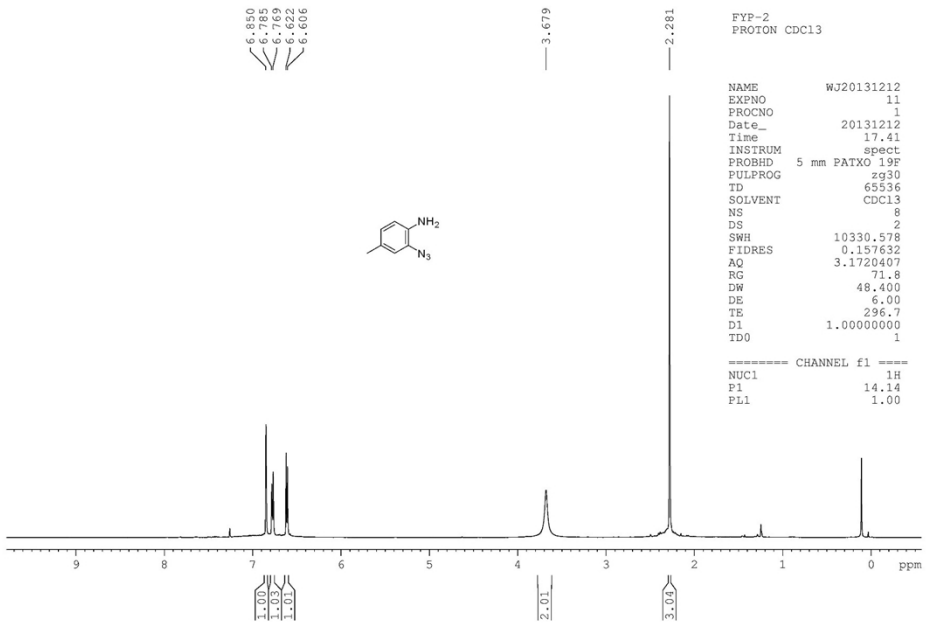
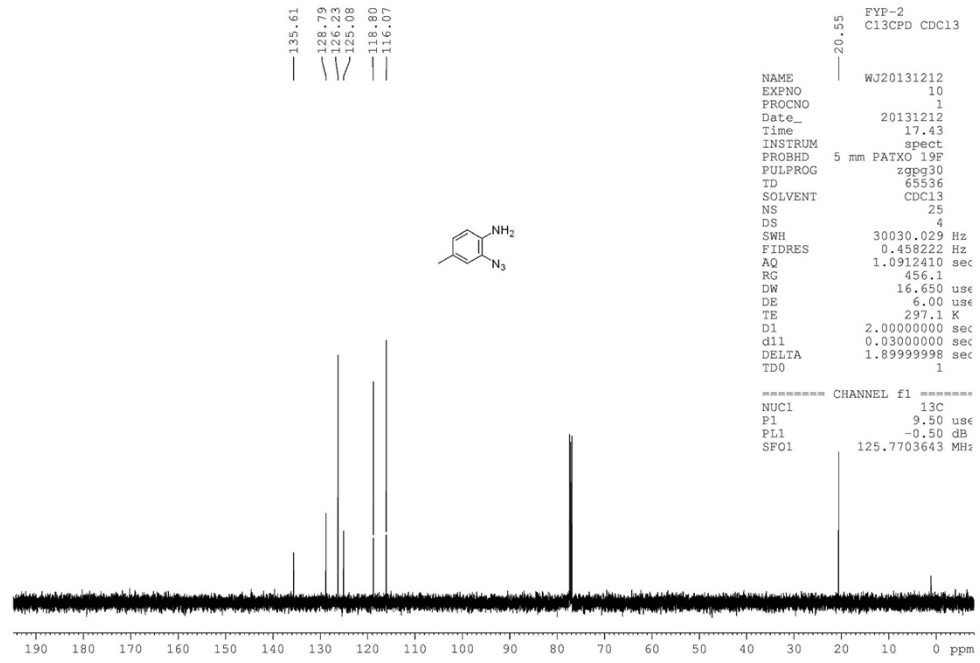
6. Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 3a-3y, 4-8

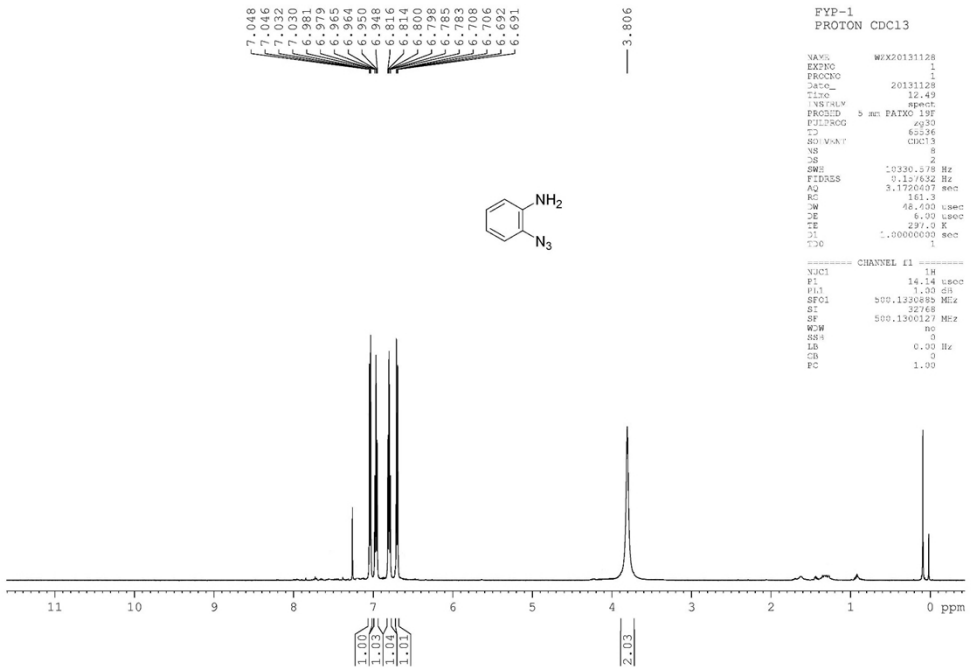
Compound **3a** ^{1}H **NMR**



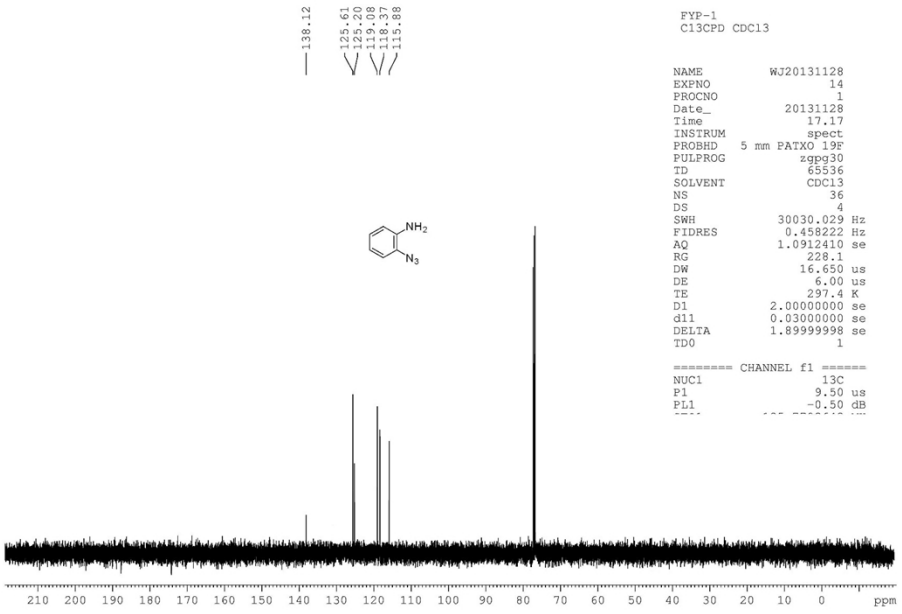
Compound **3a** ^{13}C **NMR**



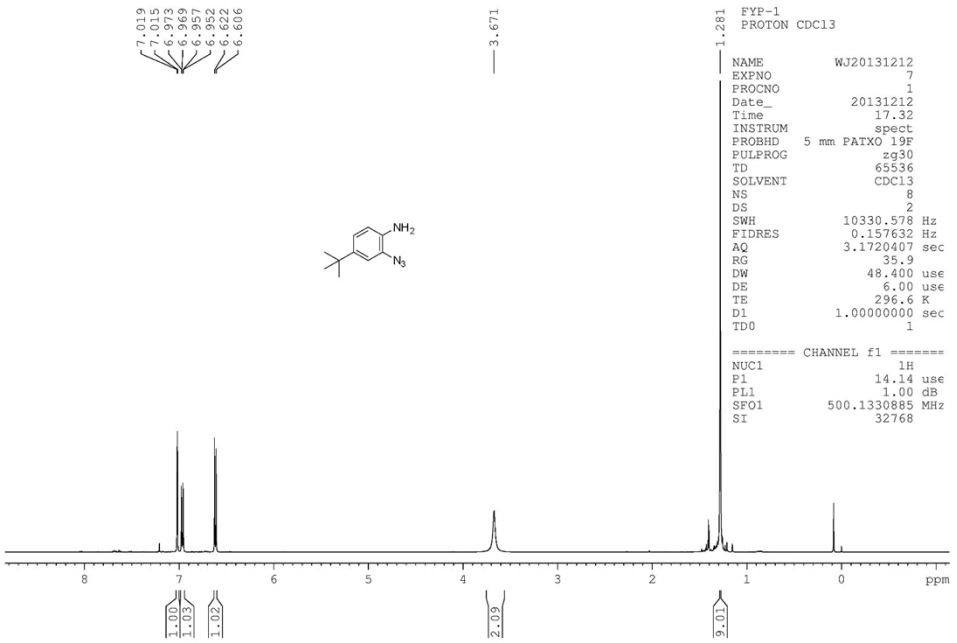
Compound **3b** ^{1}H **NMR**



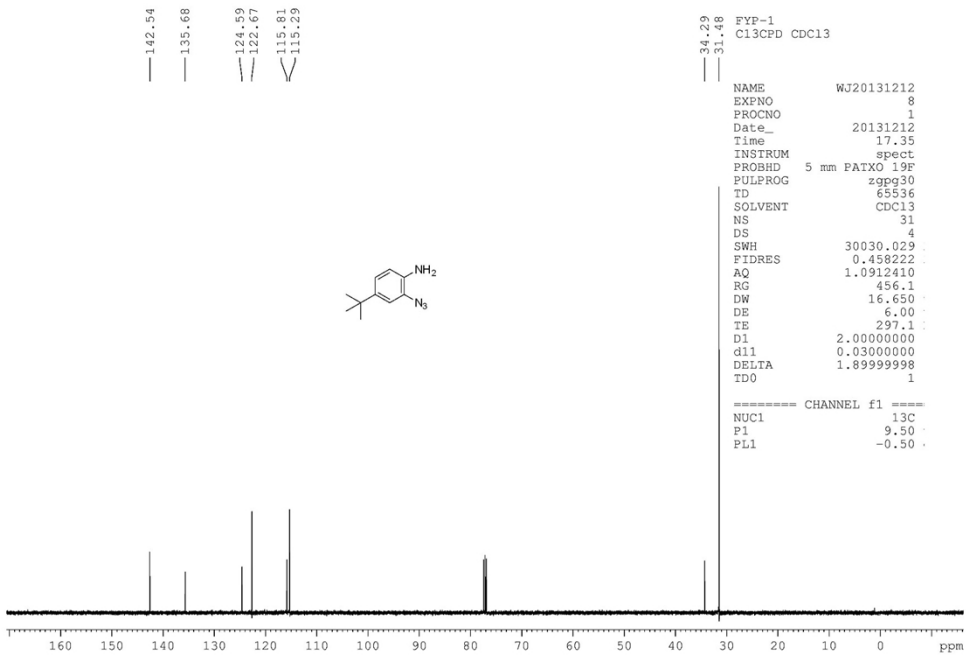
Compound **3b** ^{13}C **NMR**



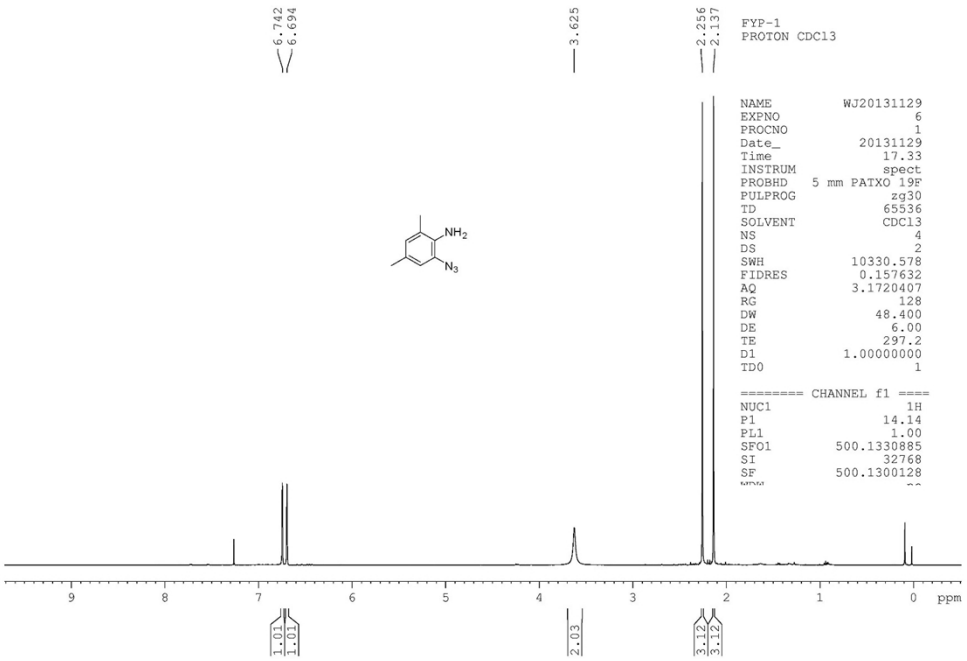
Compound **3c** ^{1}H **NMR**



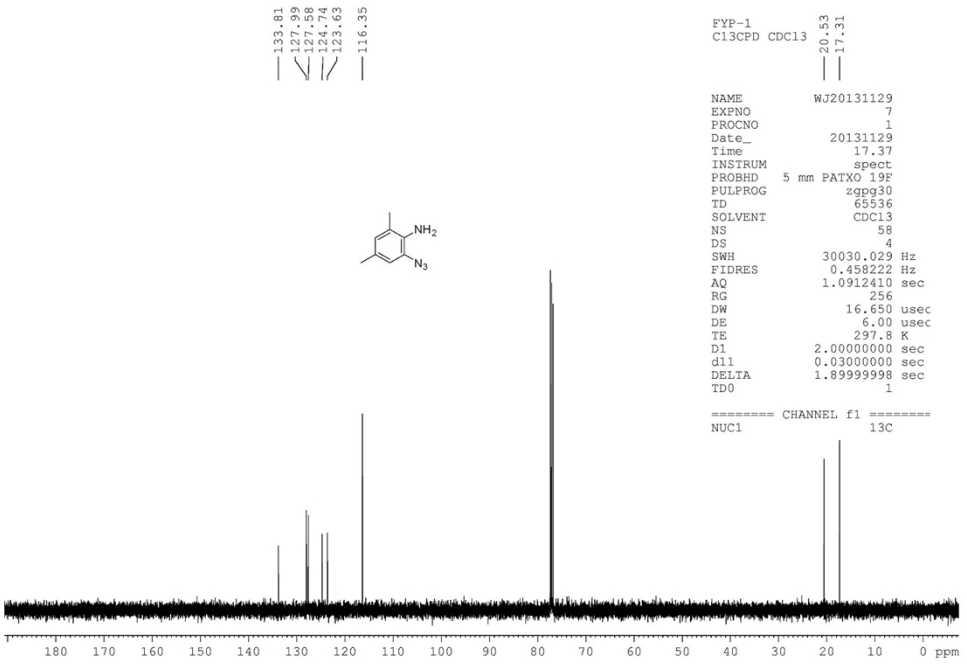
Compound **3c** ^{13}C **NMR**



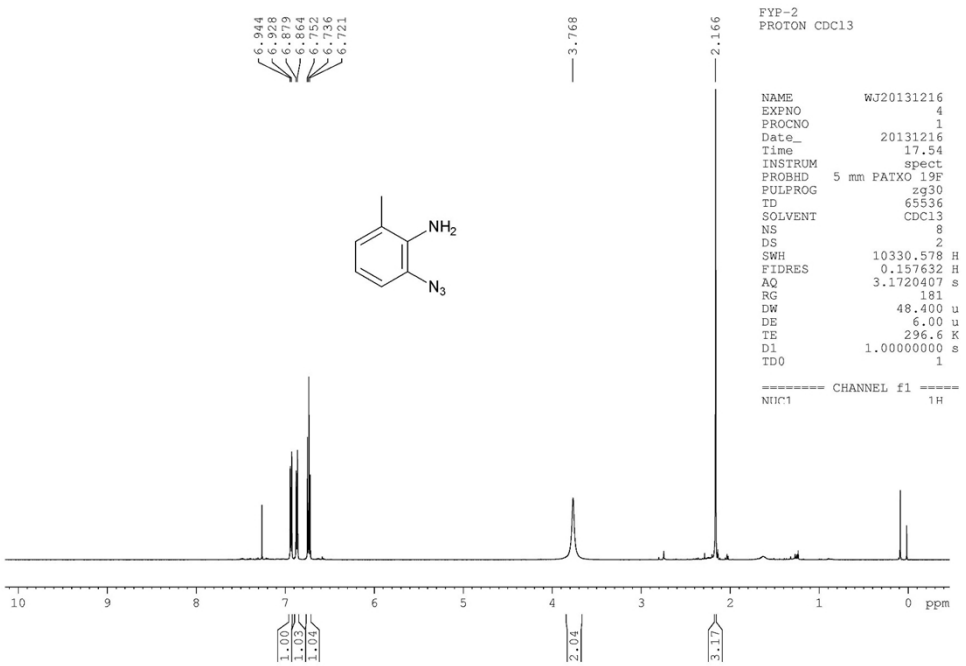
Compound **3d** ^{1}H **NMR**



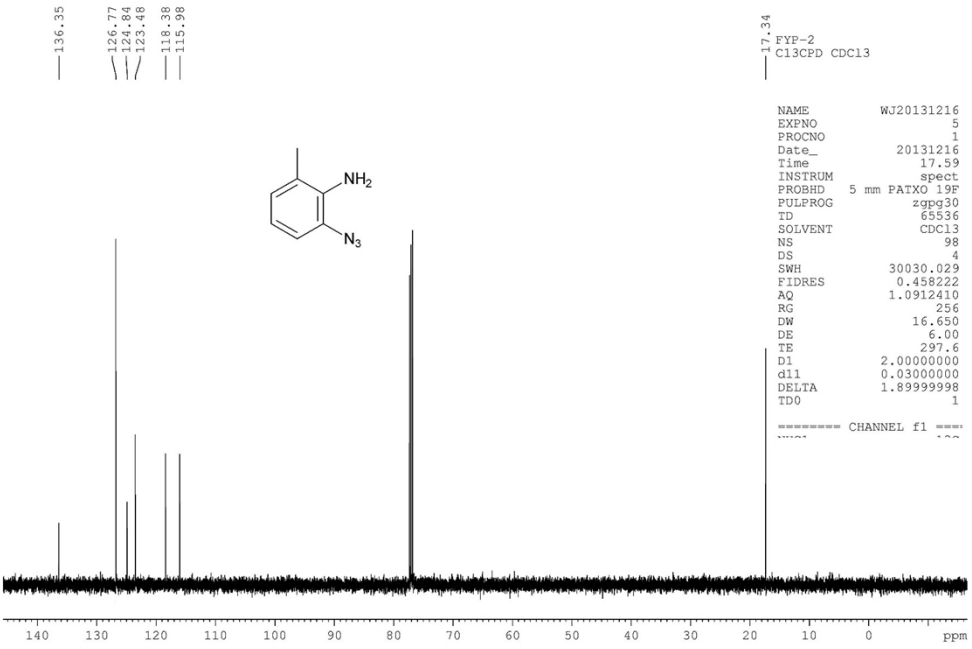
Compound **3d** ^{13}C **NMR**



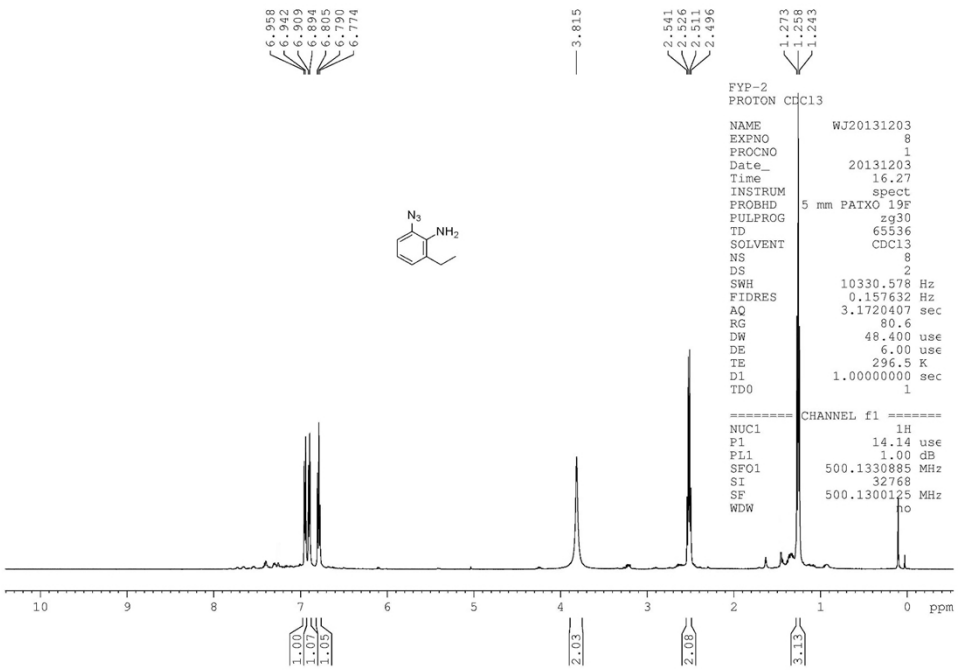
Compound **3e** ^{1}H **NMR**



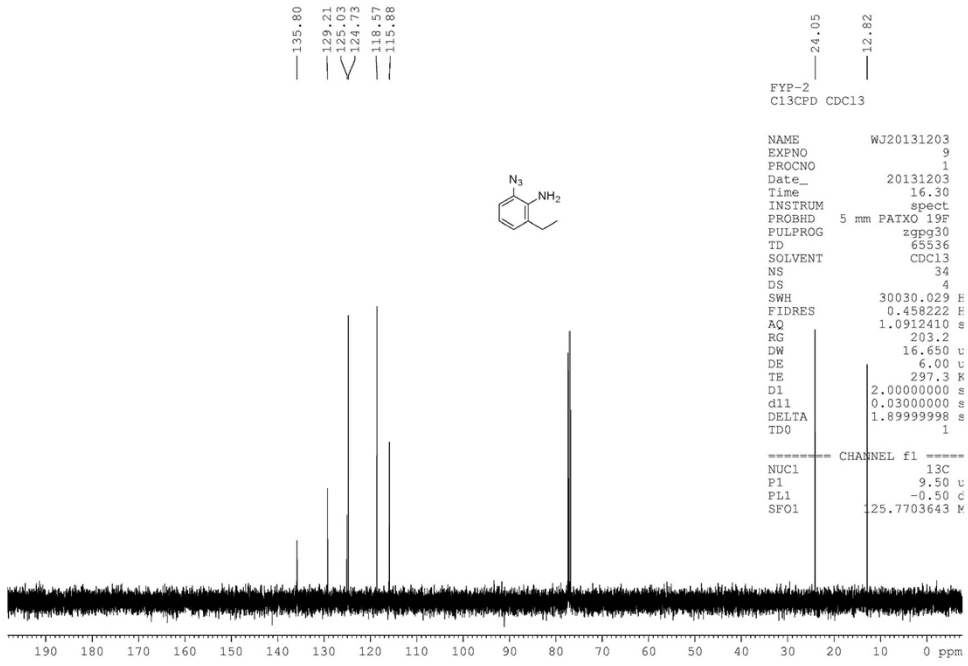
Compound **3e** ^{13}C **NMR**



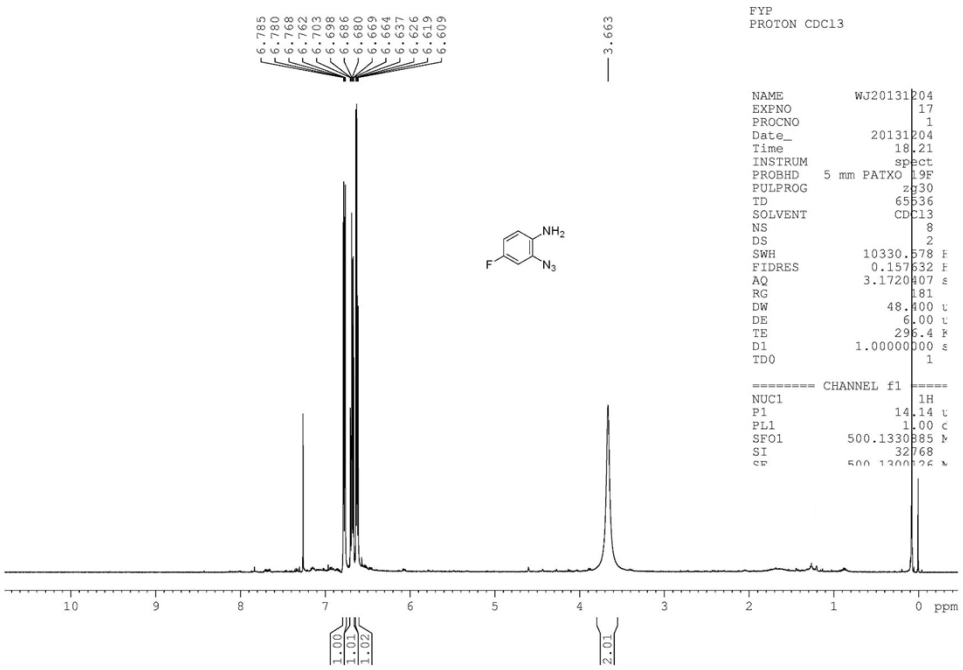
Compound **3f** ^{1}H **NMR**



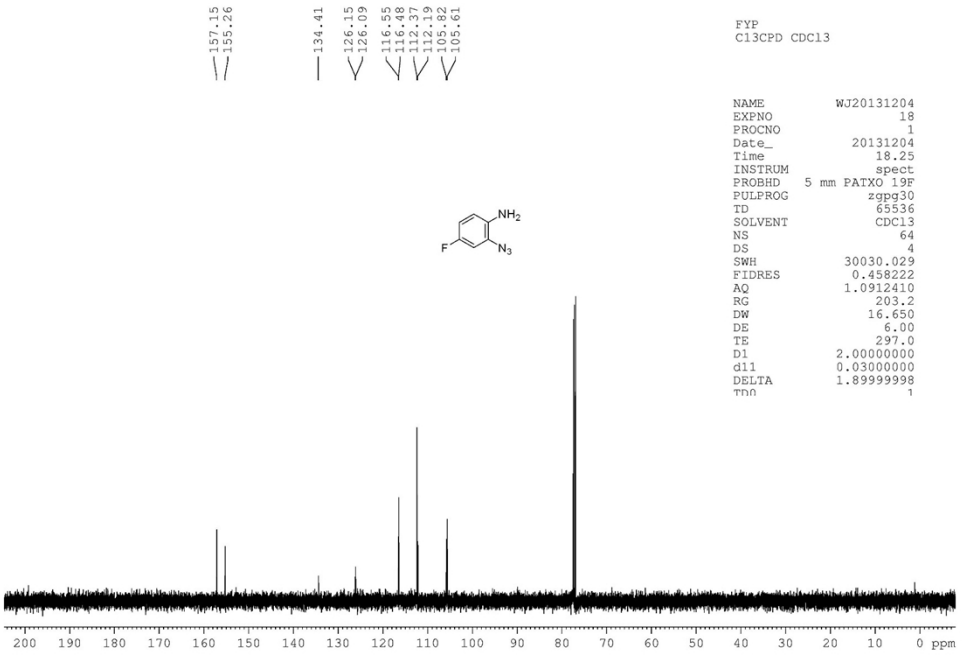
Compound **3f** ^{13}C **NMR**



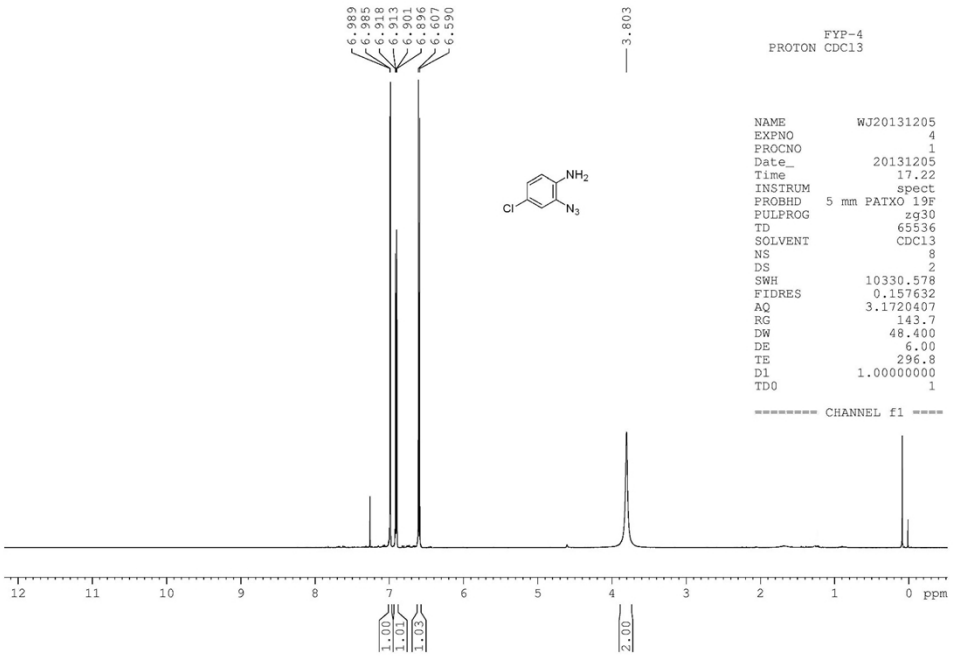
Compound **3g** ^{1}H **NMR**



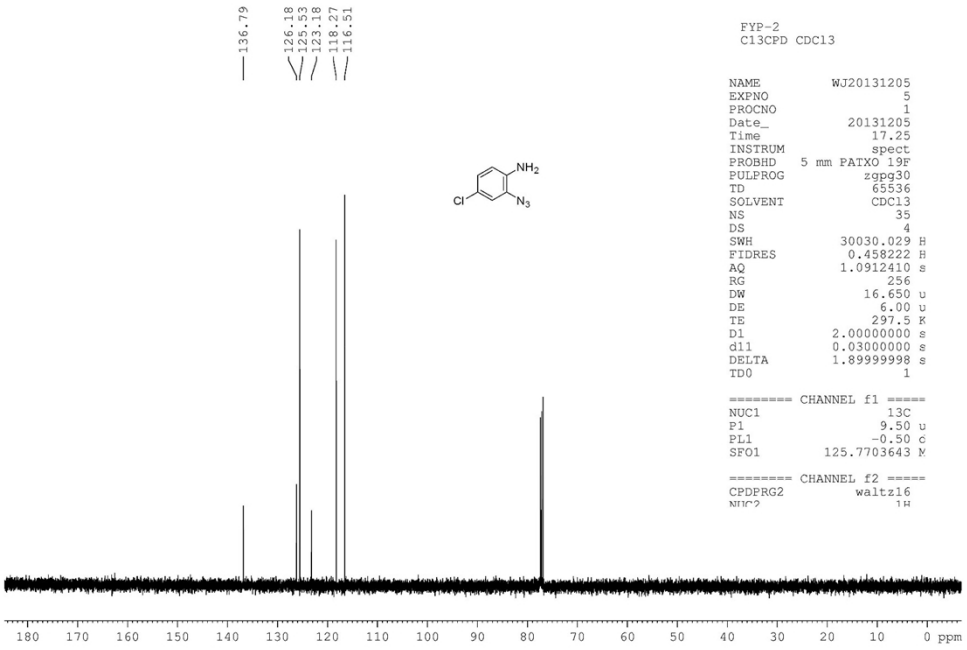
Compound **3g** ^{13}C **NMR**



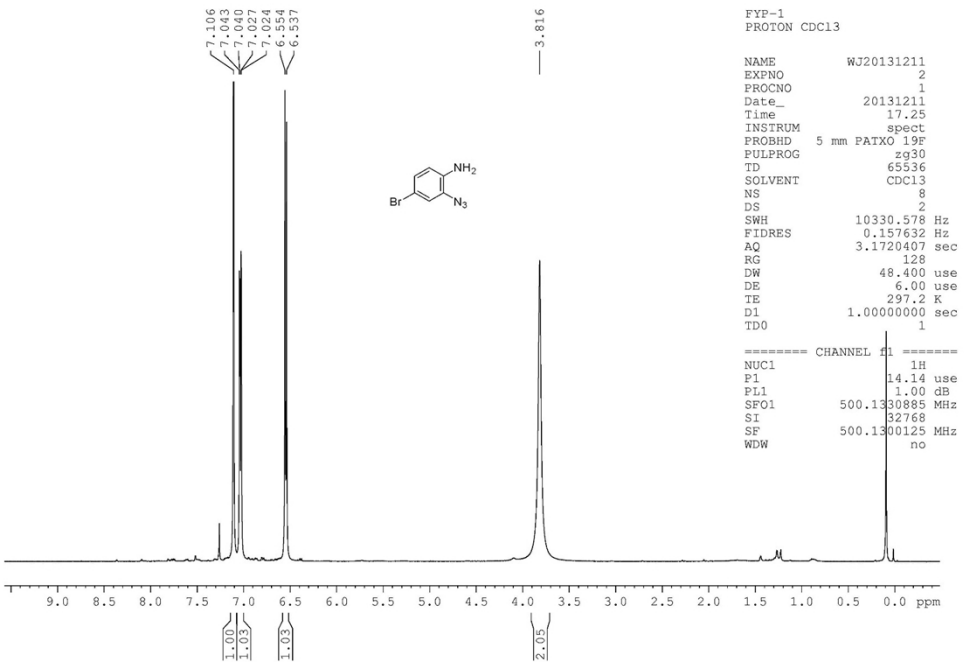
Compound **3h** ^{1}H **NMR**



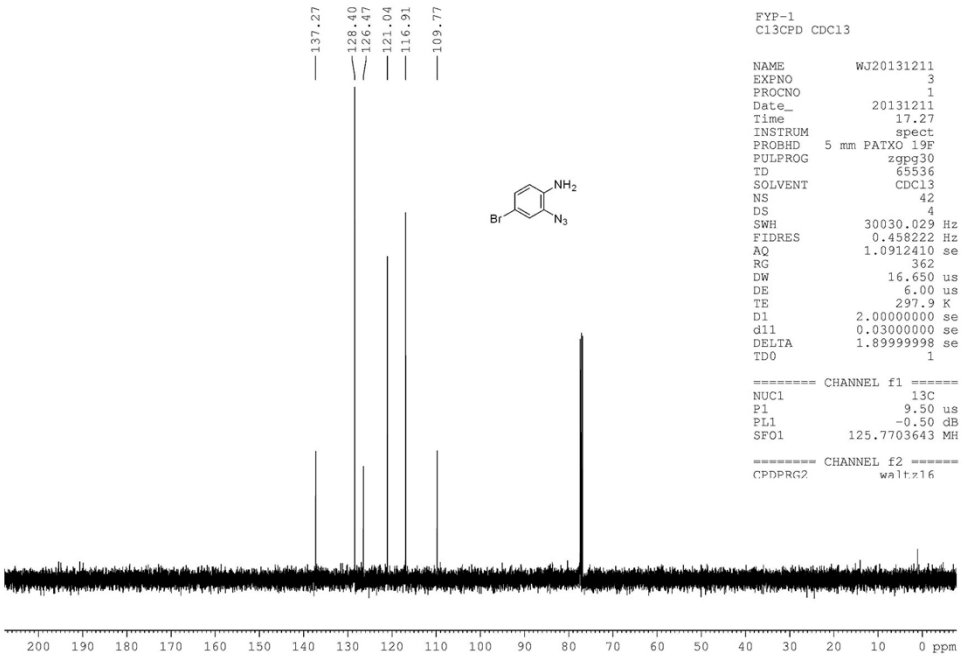
Compound **3h** ^{13}C **NMR**



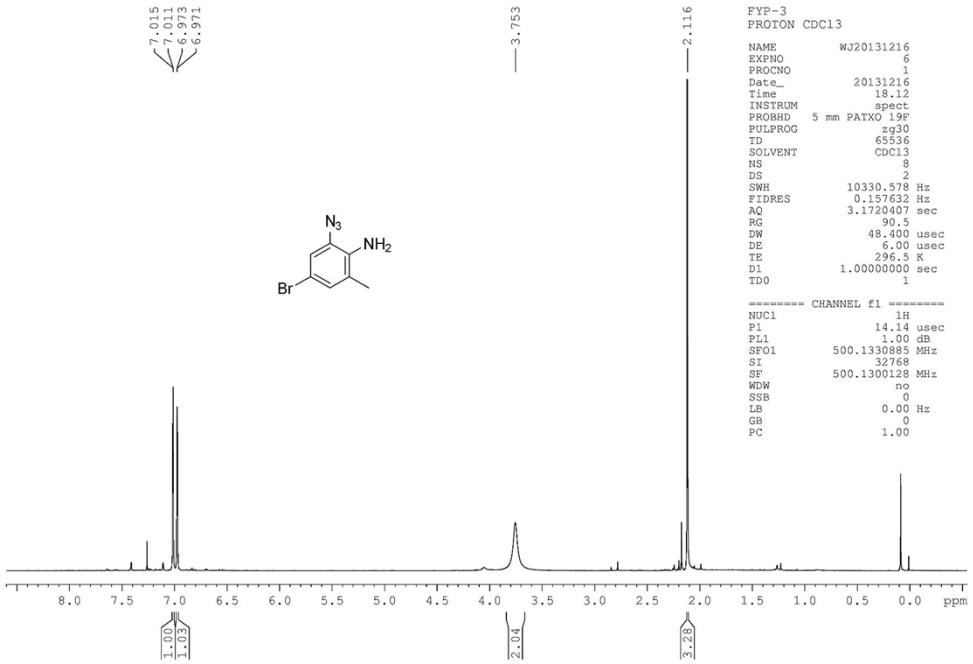
Compound **3i** ^{1}H **NMR**



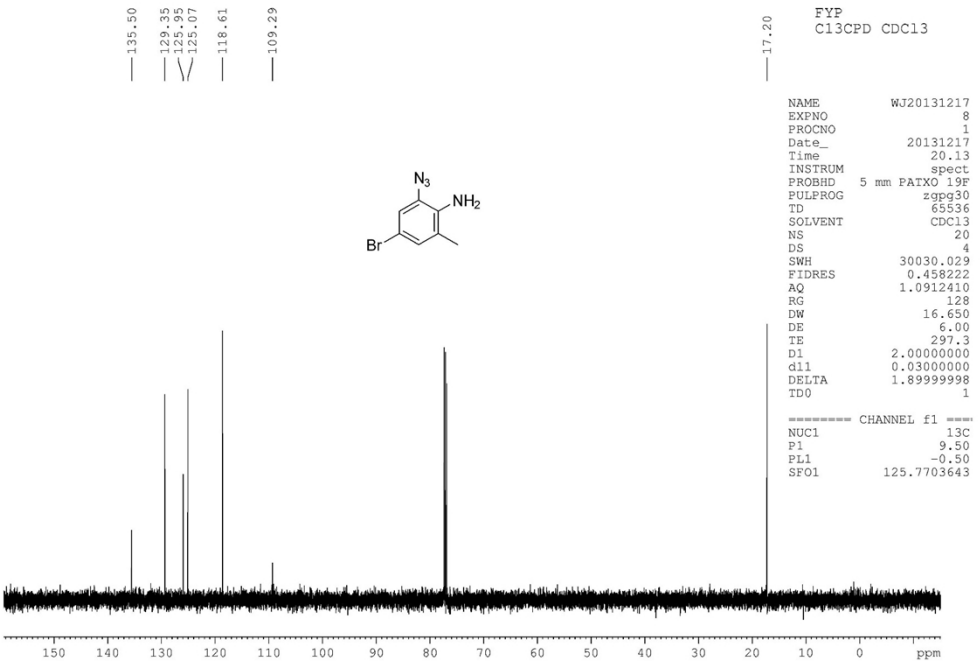
Compound **3i** ^{13}C **NMR**



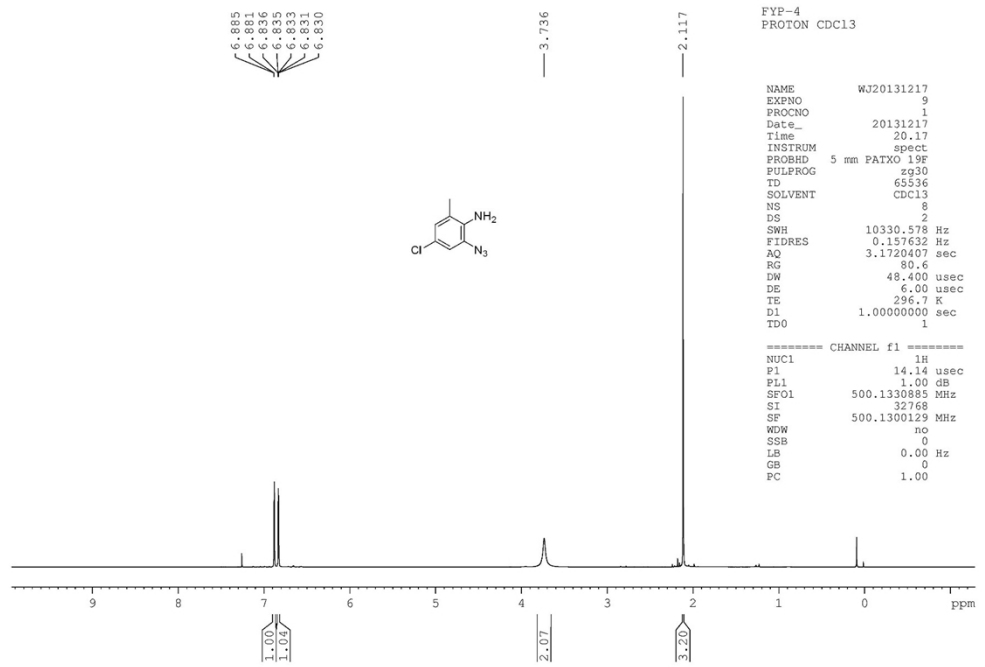
Compound **3j** ^{1}H **NMR**



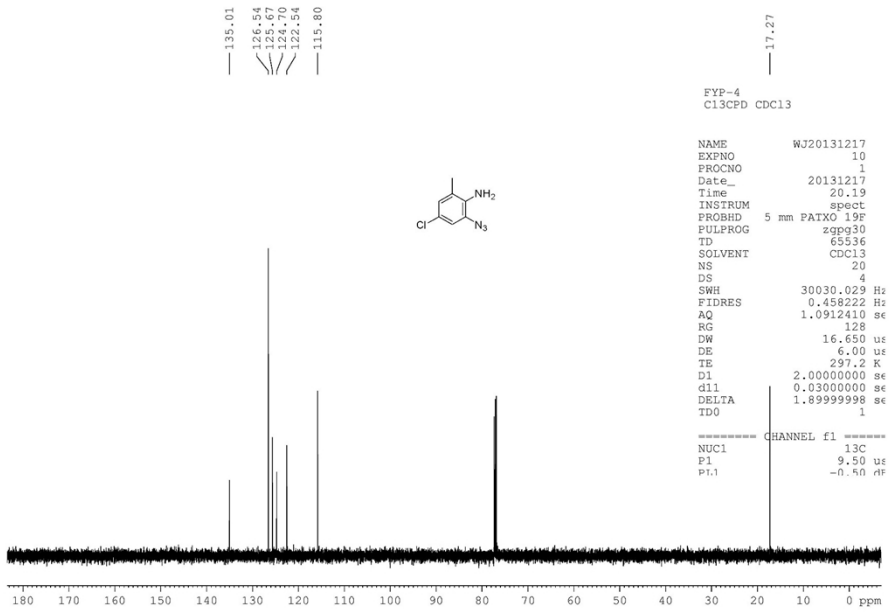
Compound **3j** ^{13}C **NMR**



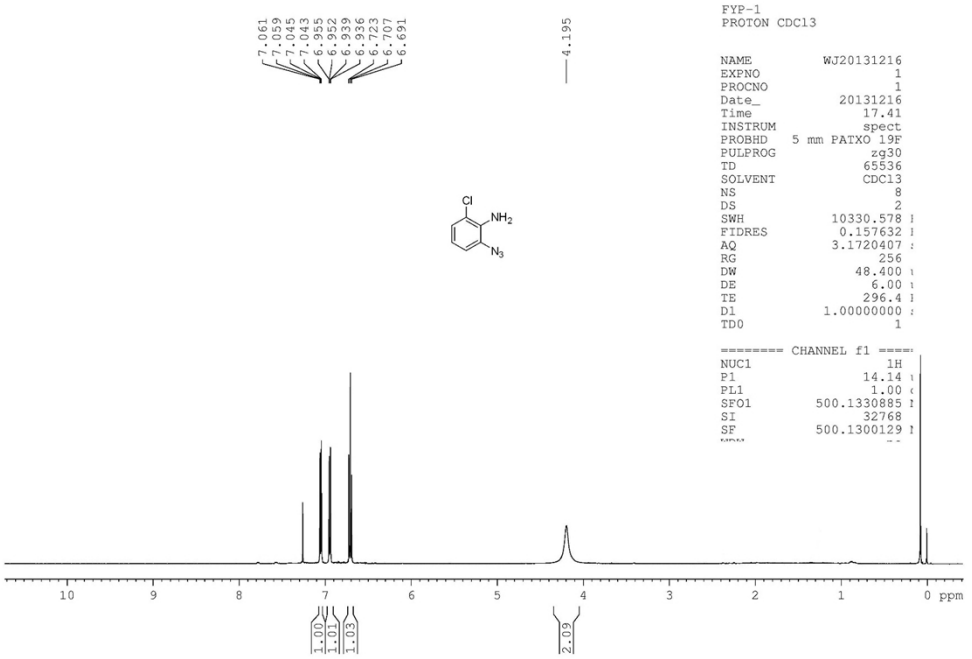
Compound **3k** ^{1}H **NMR**



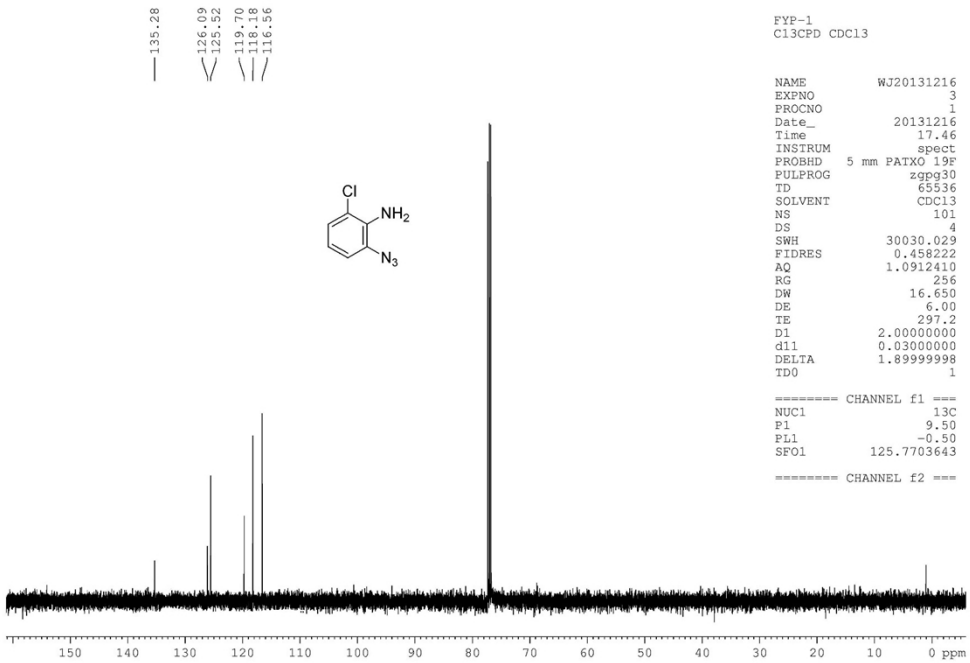
Compound **3k** ^{13}C **NMR**



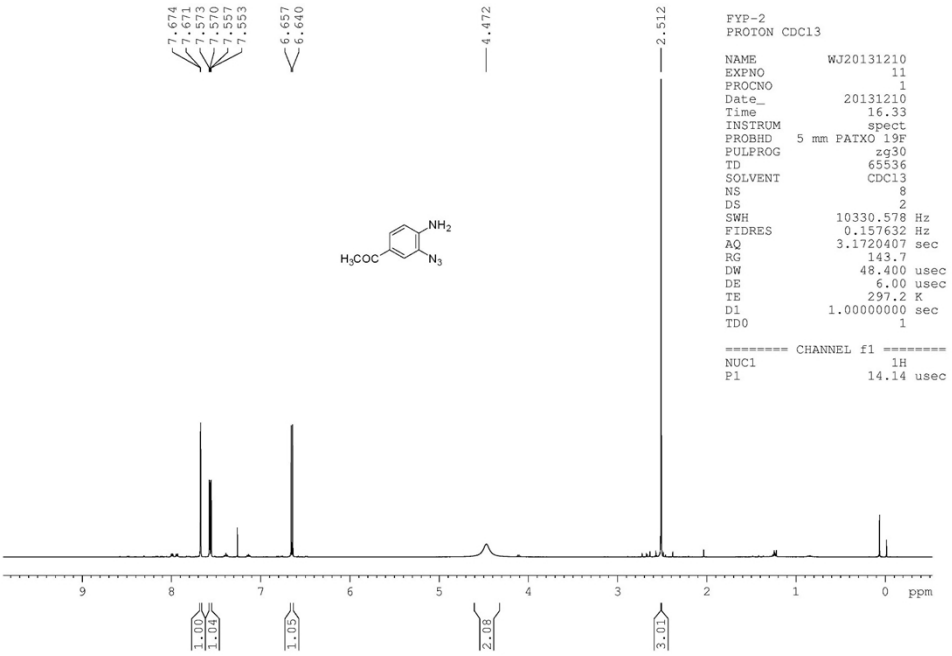
Compound **3l** ^{1}H **NMR**



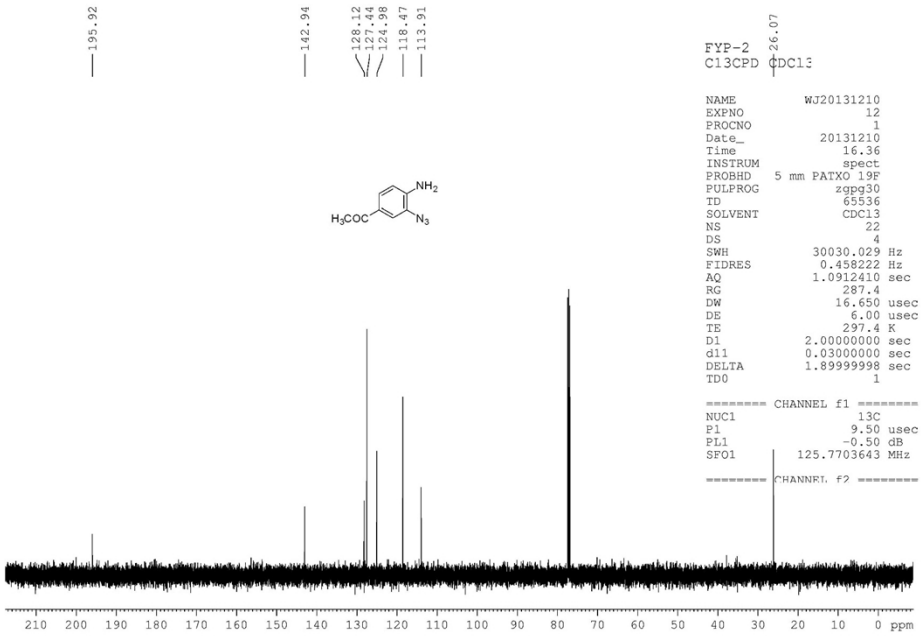
Compound **3l** ^{13}C **NMR**



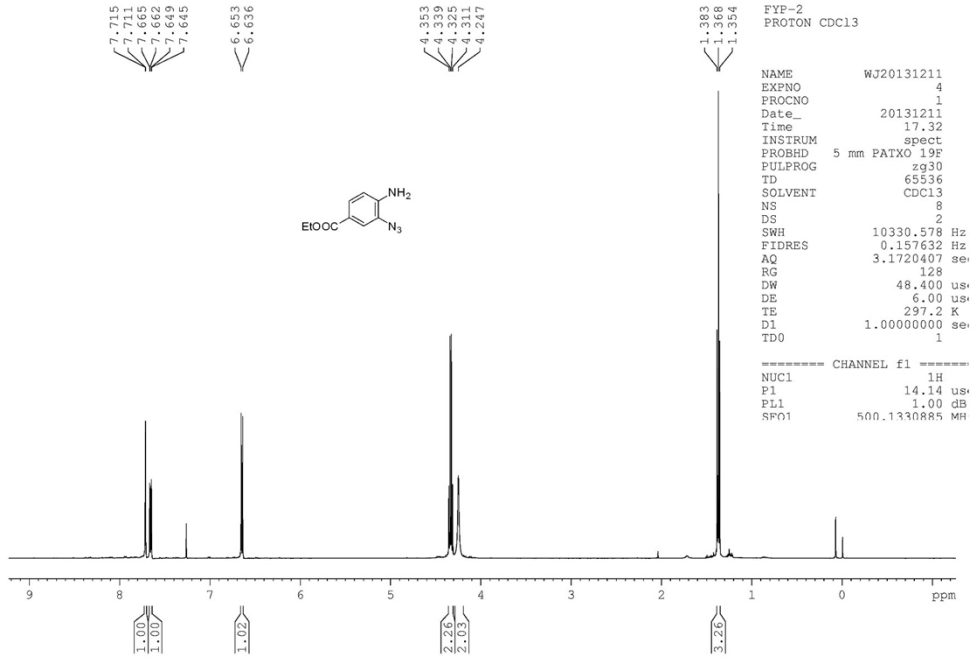
Compound **3m** ^{1}H **NMR**



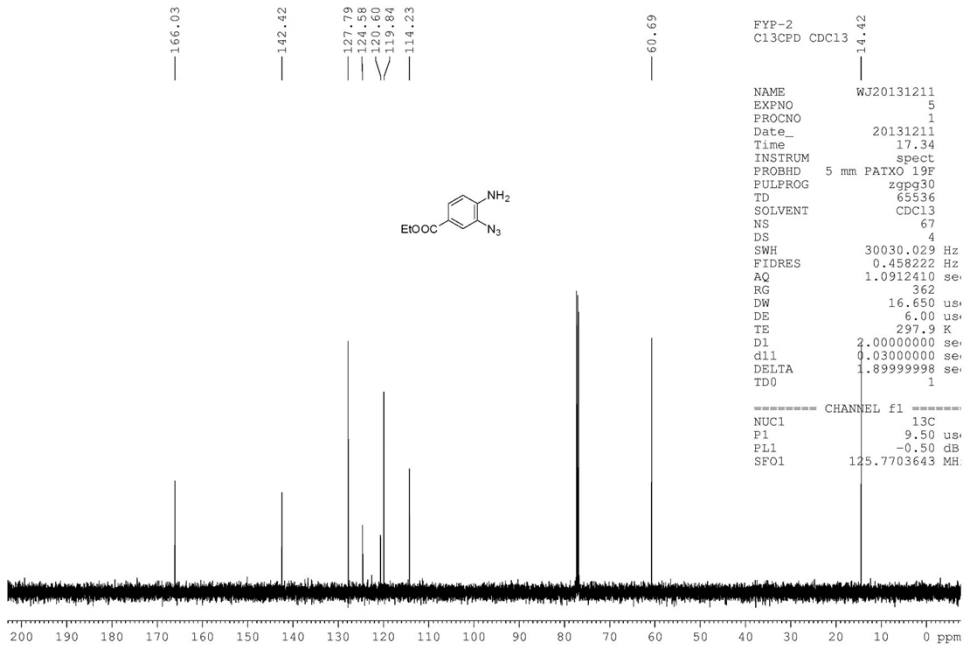
Compound **3m** ^{13}C **NMR**



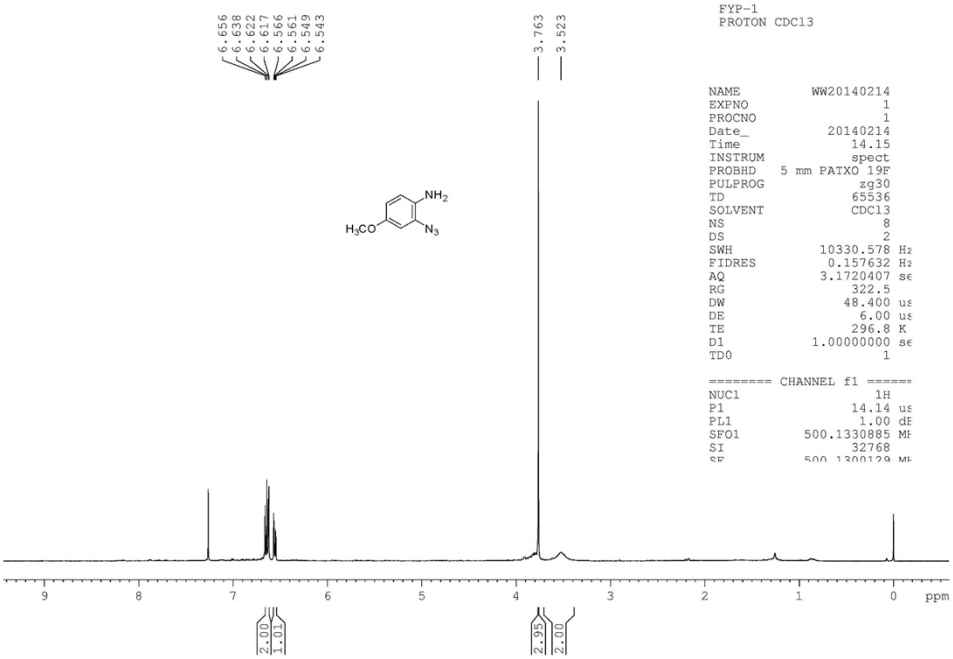
Compound **3n** ^{1}H **NMR**



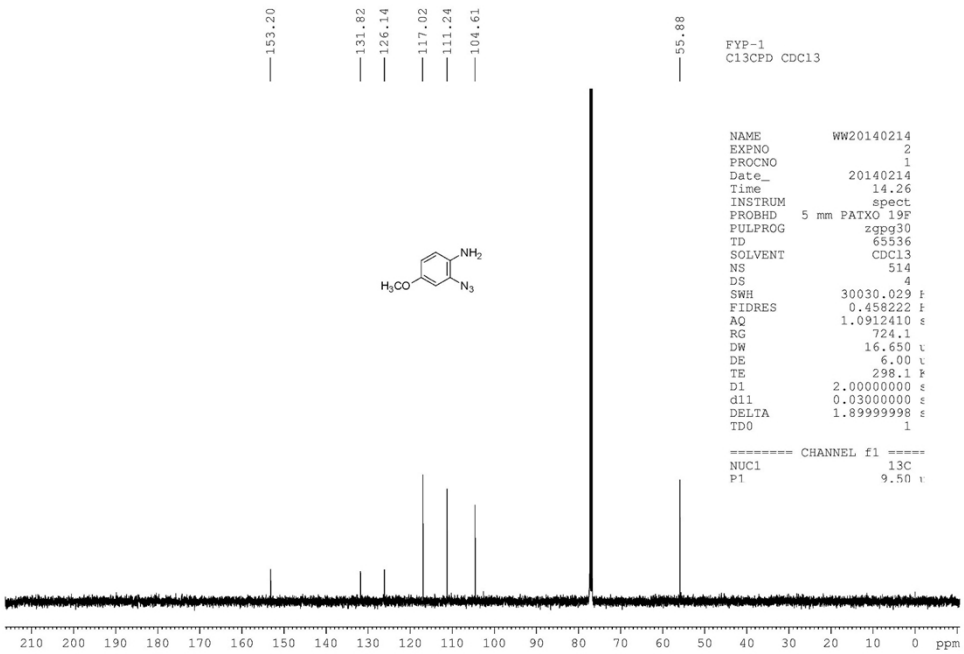
Compound **3n** ^{13}C **NMR**



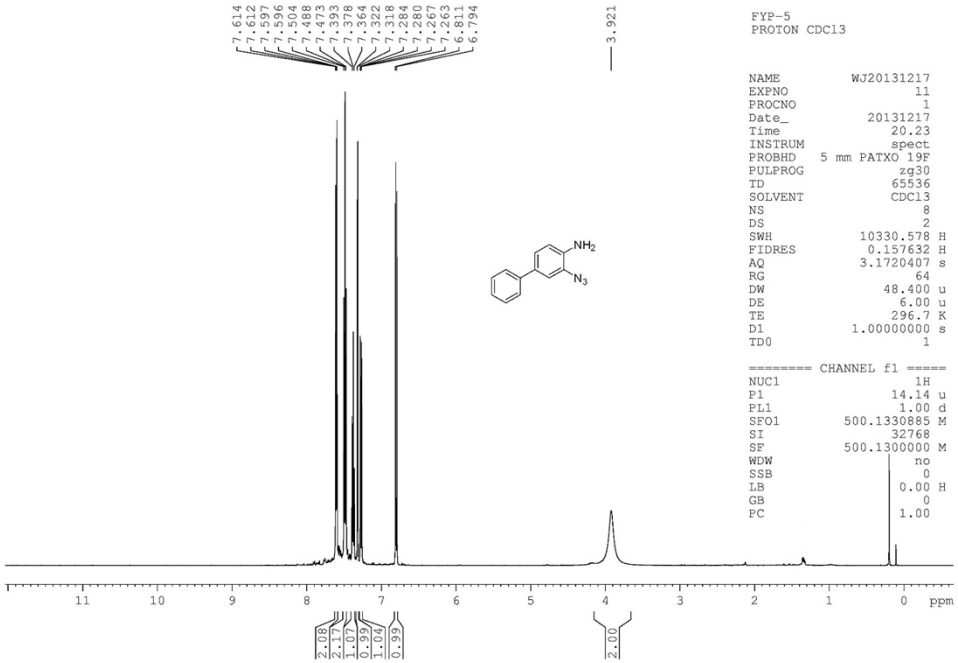
Compound **3o** ^{1}H **NMR**



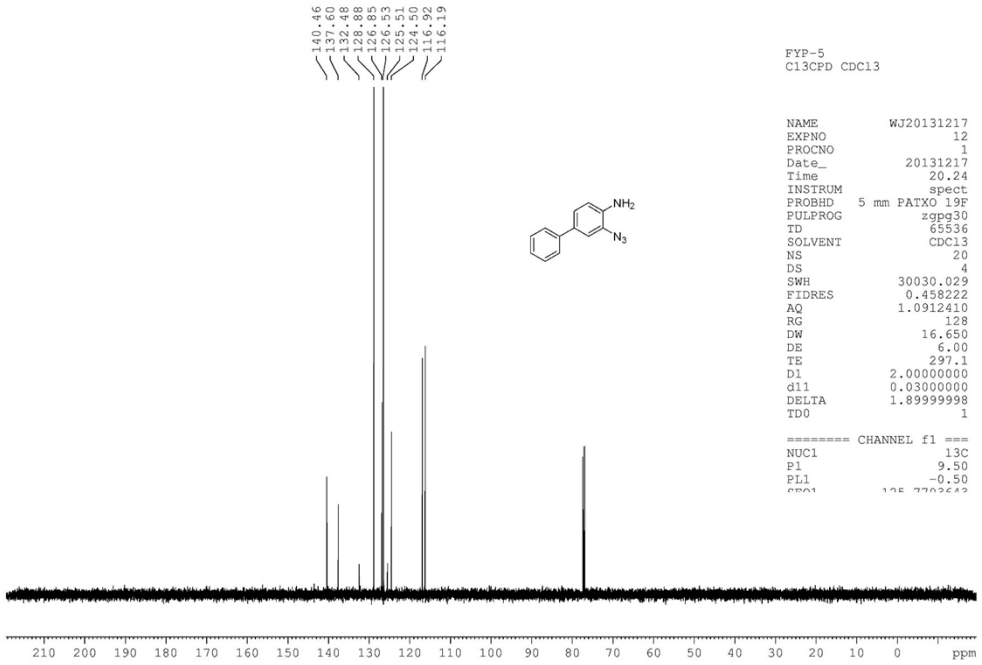
Compound **3o** ^{13}C **NMR**



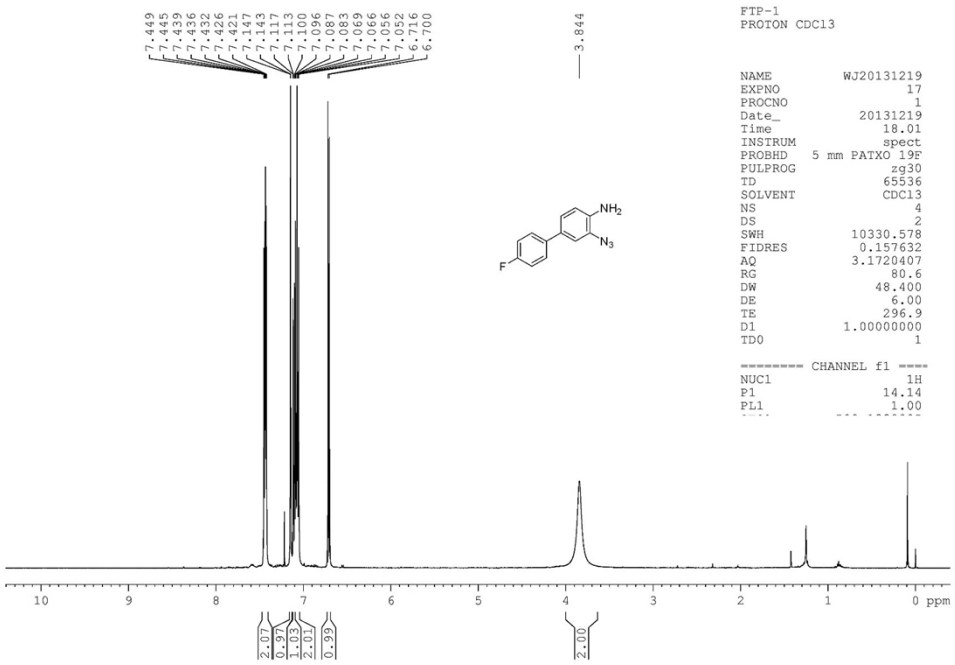
Compound **3p** ^{1}H **NMR**



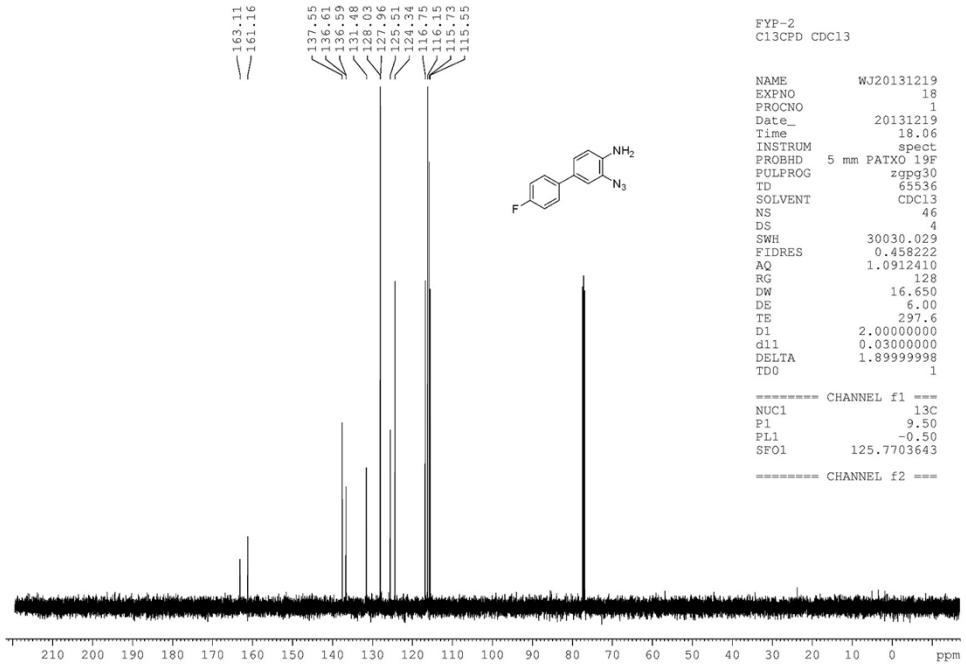
Compound **3p** ^{13}C **NMR**



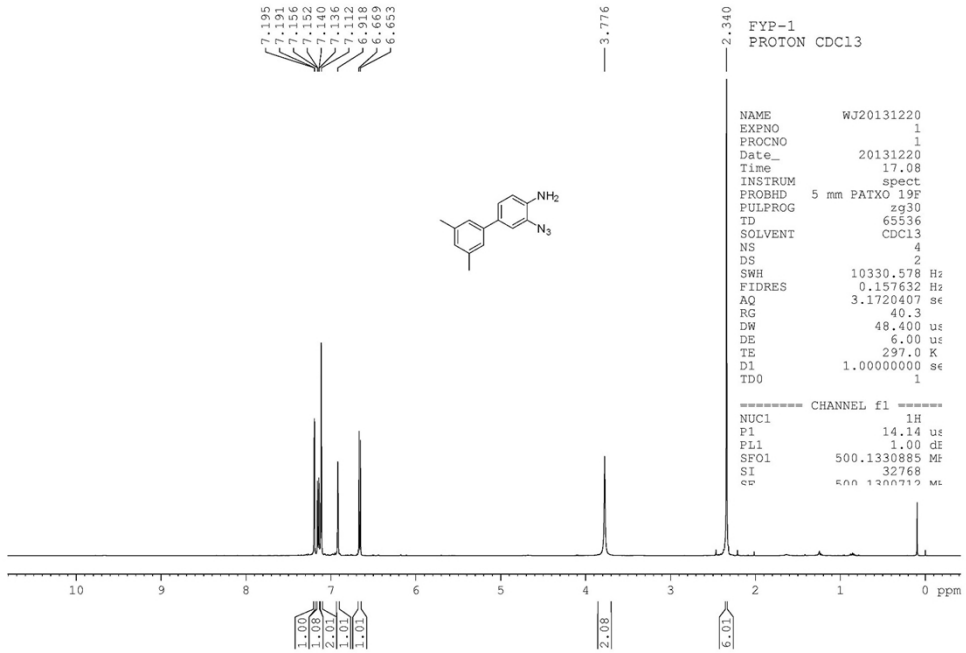
Compound **3q** ^{1}H **NMR**



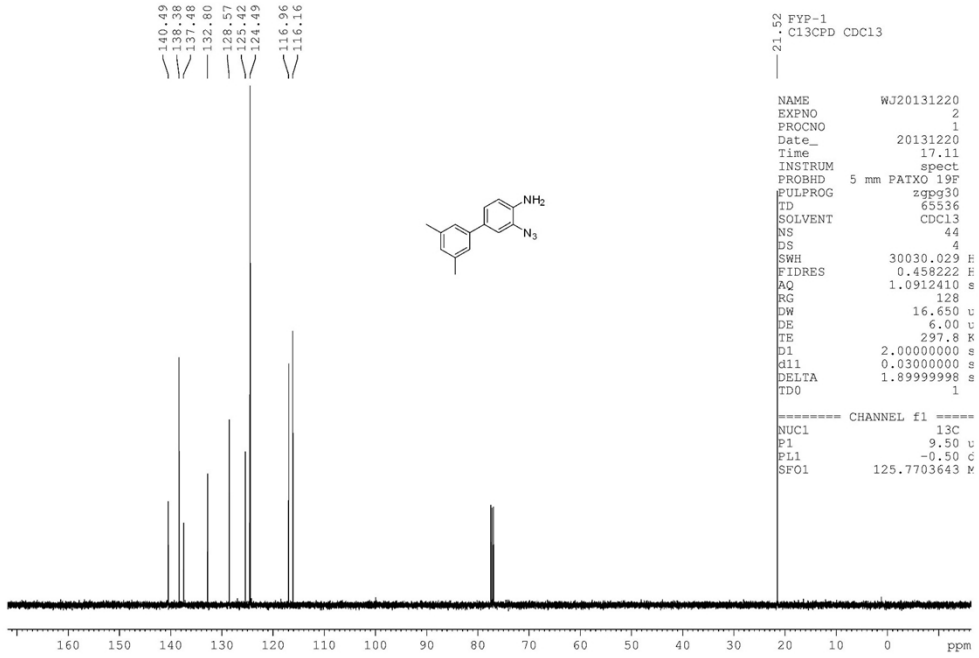
Compound **3q** ^{13}C **NMR**



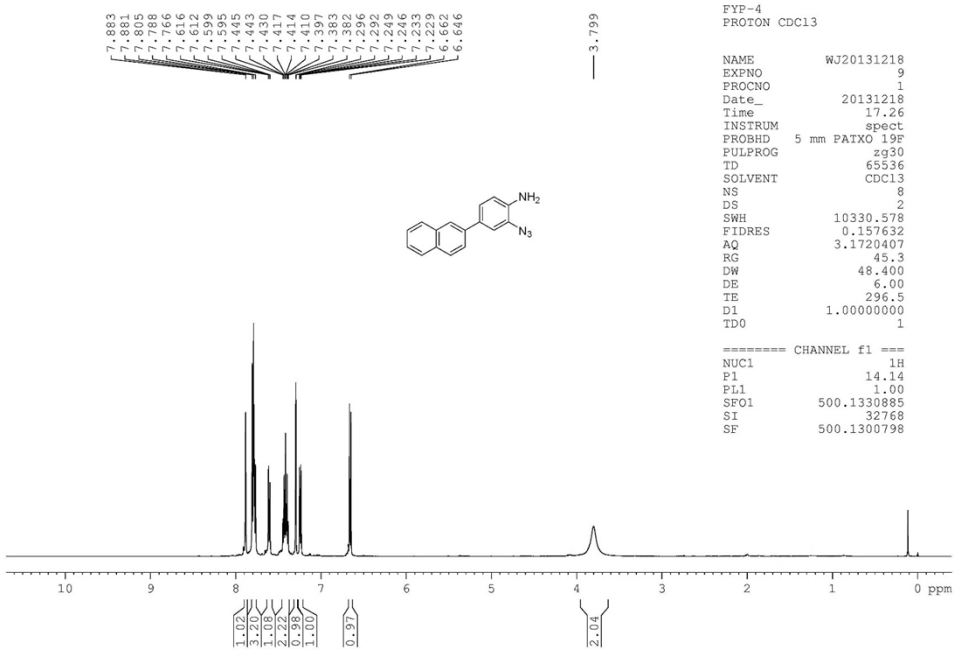
Compound **3r** ^{1}H **NMR**



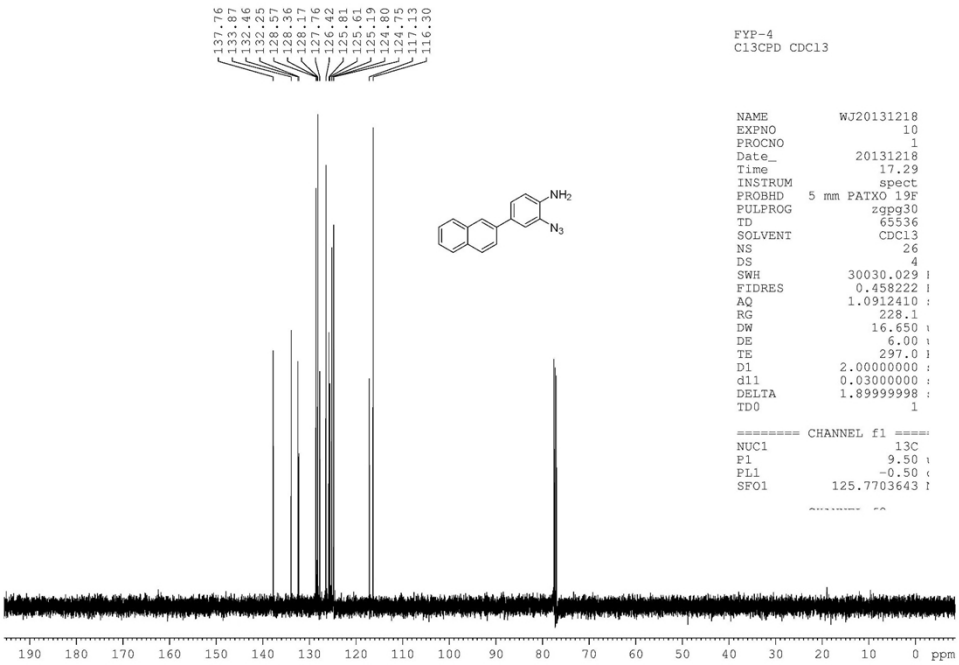
Compound **3r** ^{13}C **NMR**



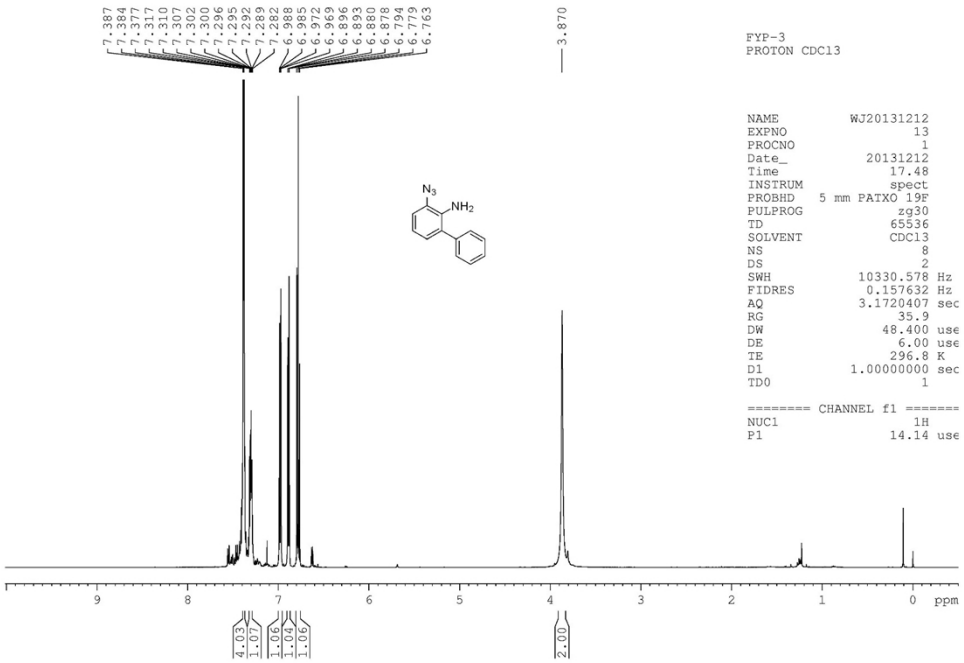
Compound **3s** ^{1}H **NMR**



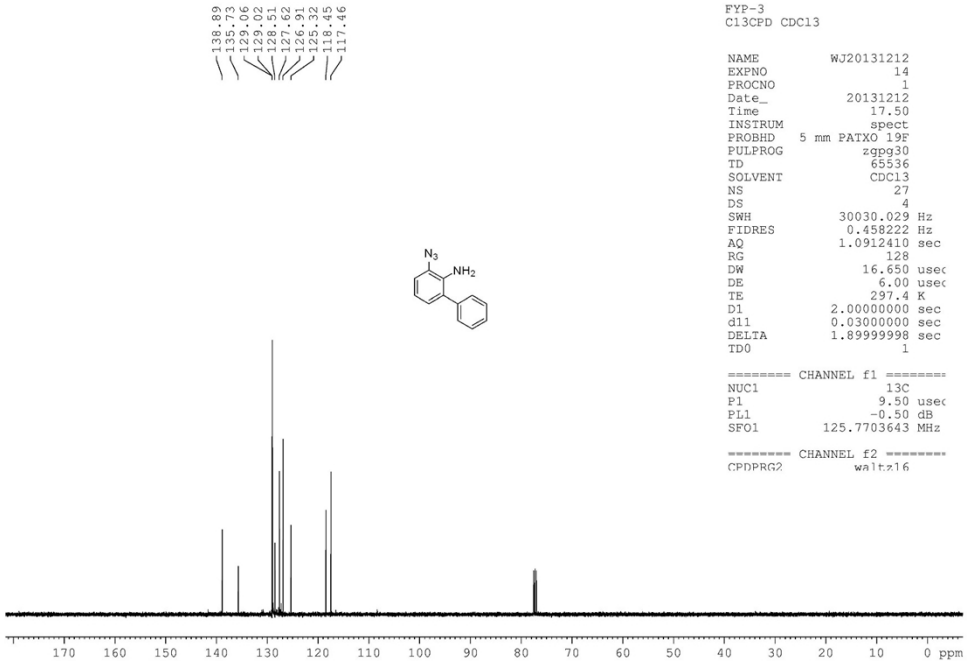
Compound **3s** ^{13}C **NMR**



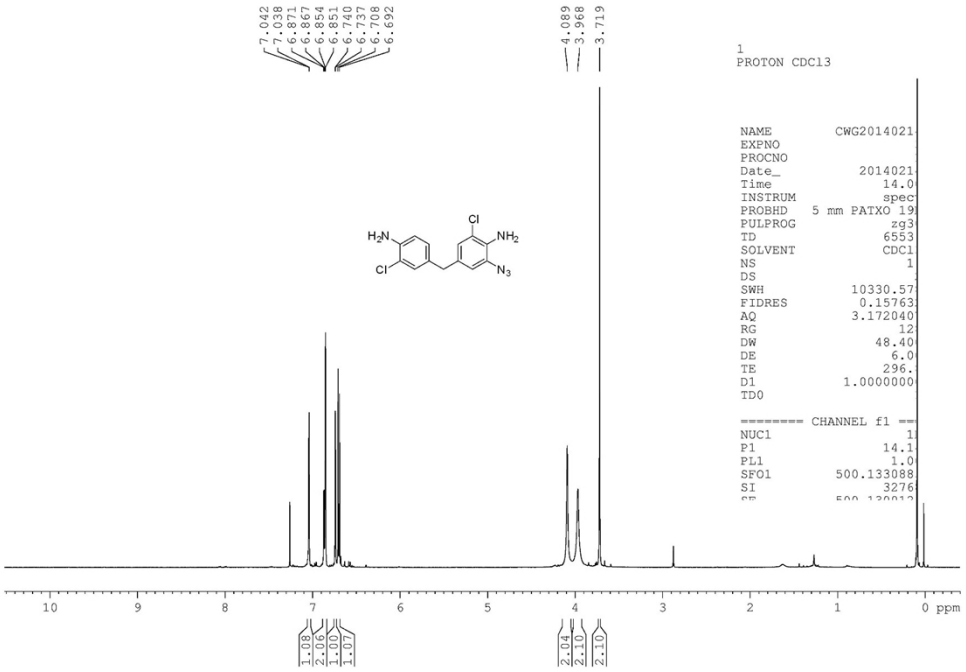
Compound **3t** ^{1}H **NMR**



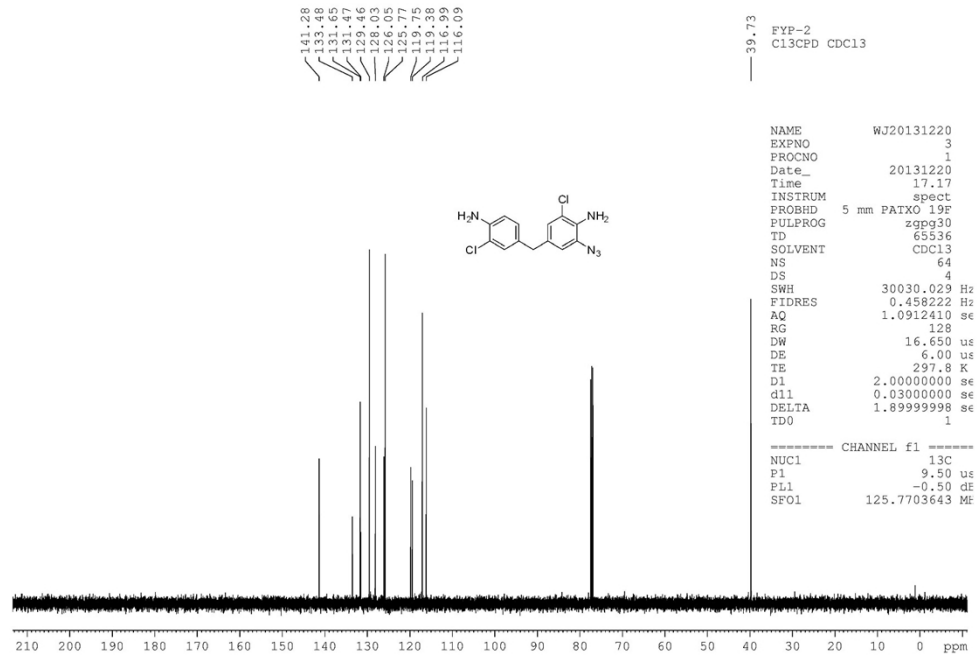
Compound **3t** ^{13}C **NMR**



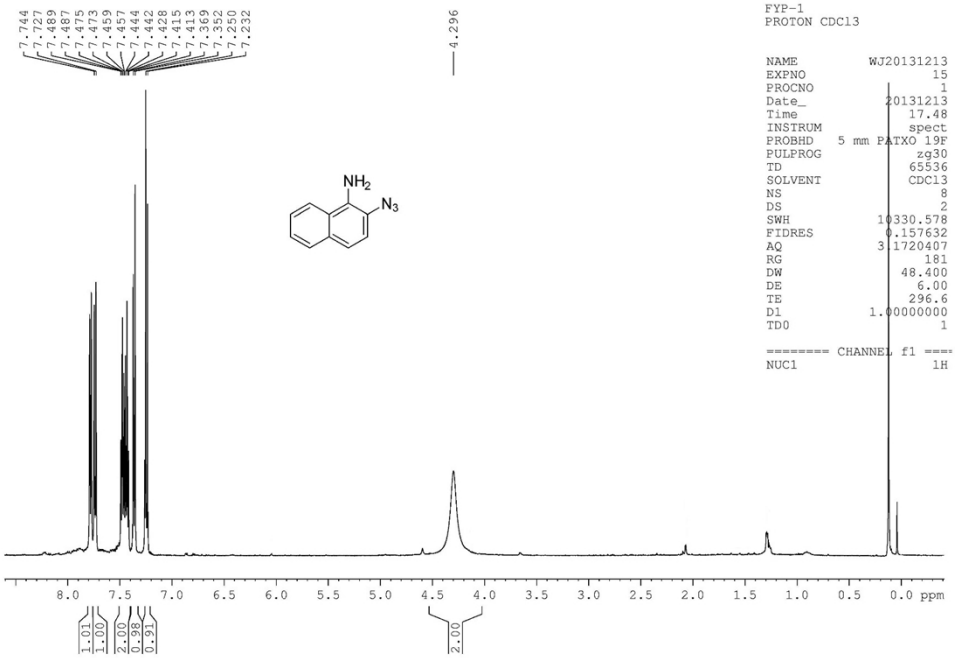
Compound **3u** ^{1}H **NMR**



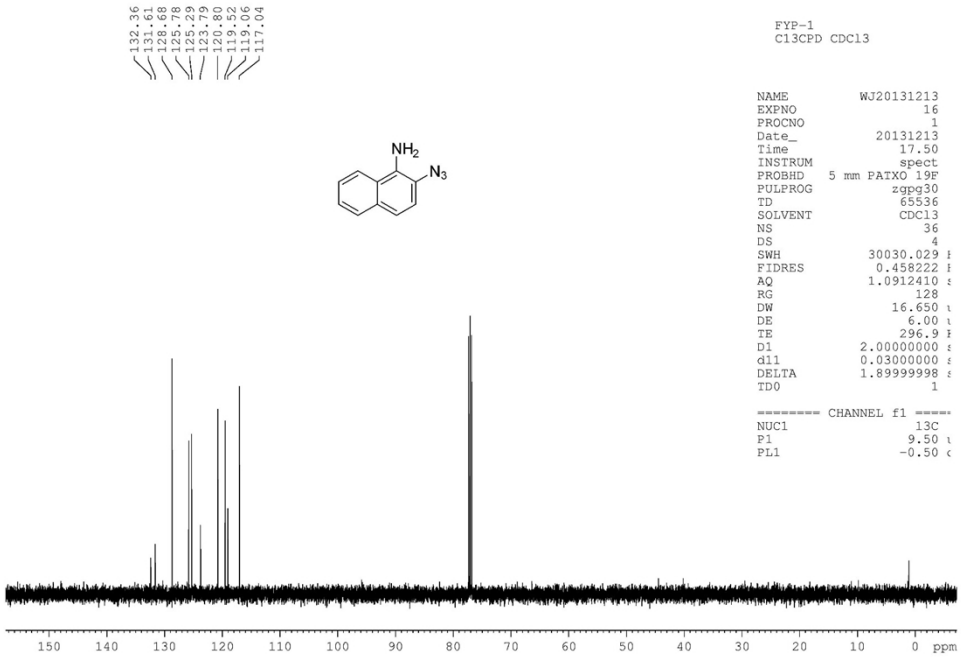
Compound **3u** ^{13}C **NMR**



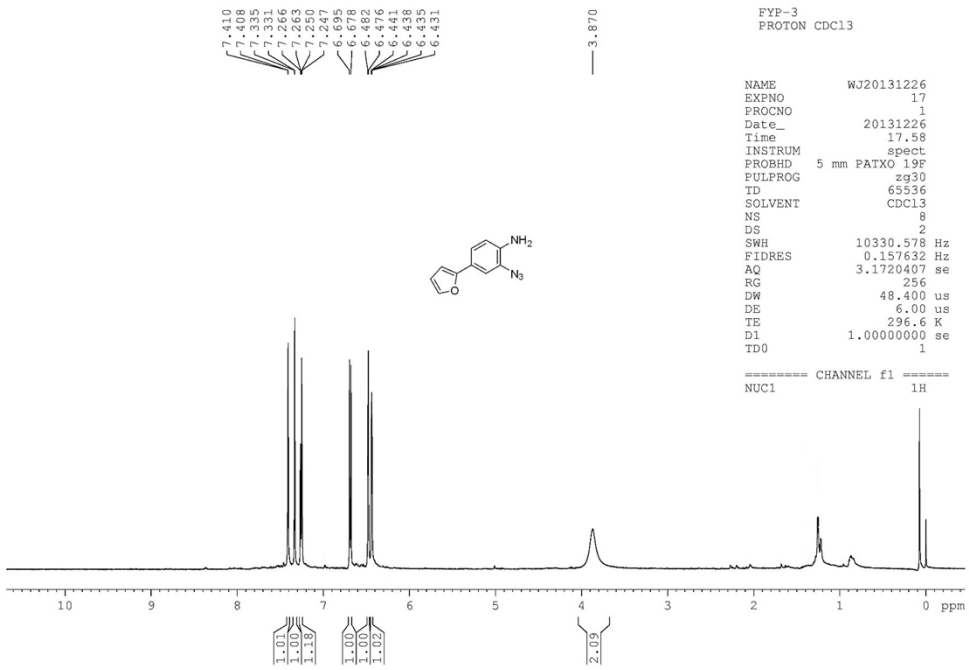
Compound **3v** ^{1}H **NMR**



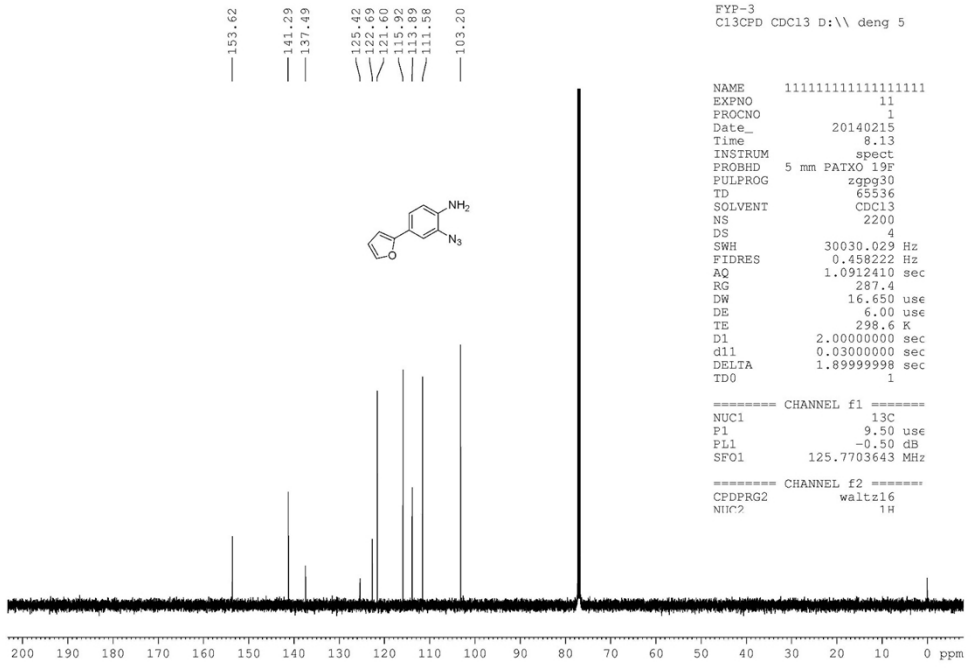
Compound **3v** ^{13}C **NMR**



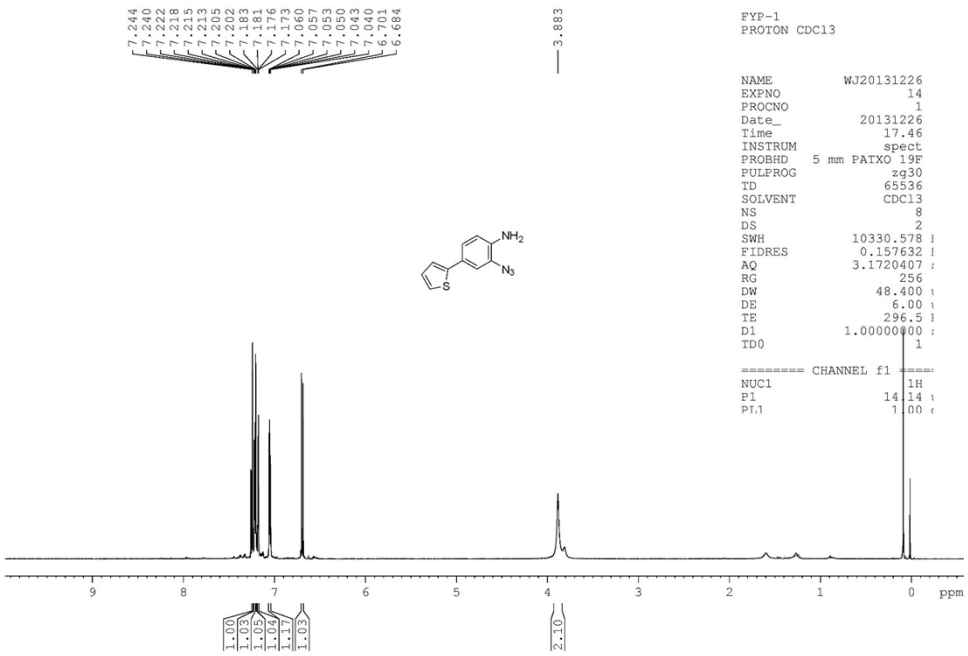
Compound **3w** ^{1}H **NMR**



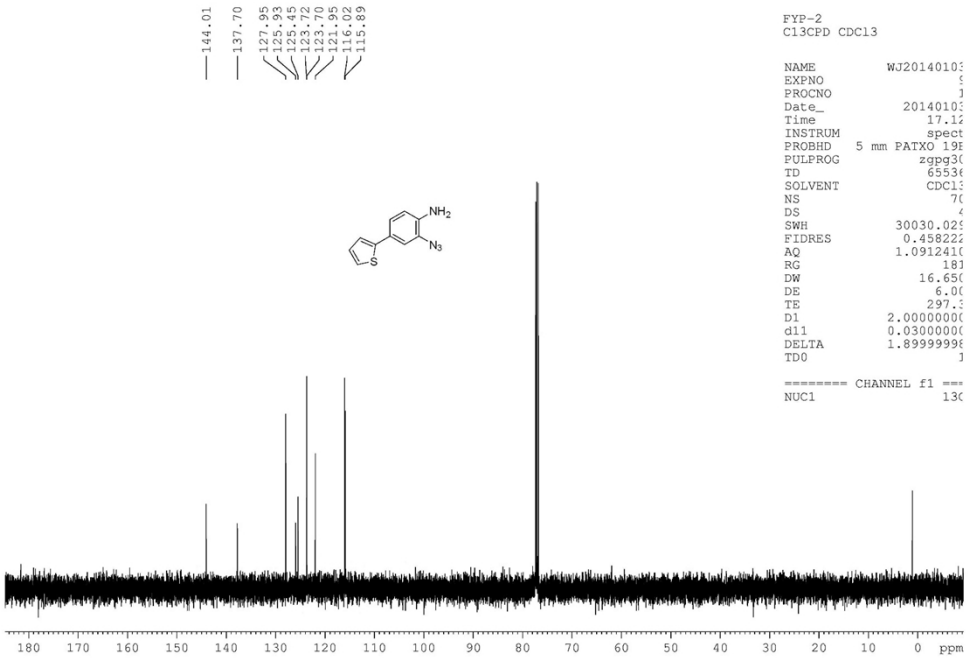
Compound **3w** ^{13}C **NMR**



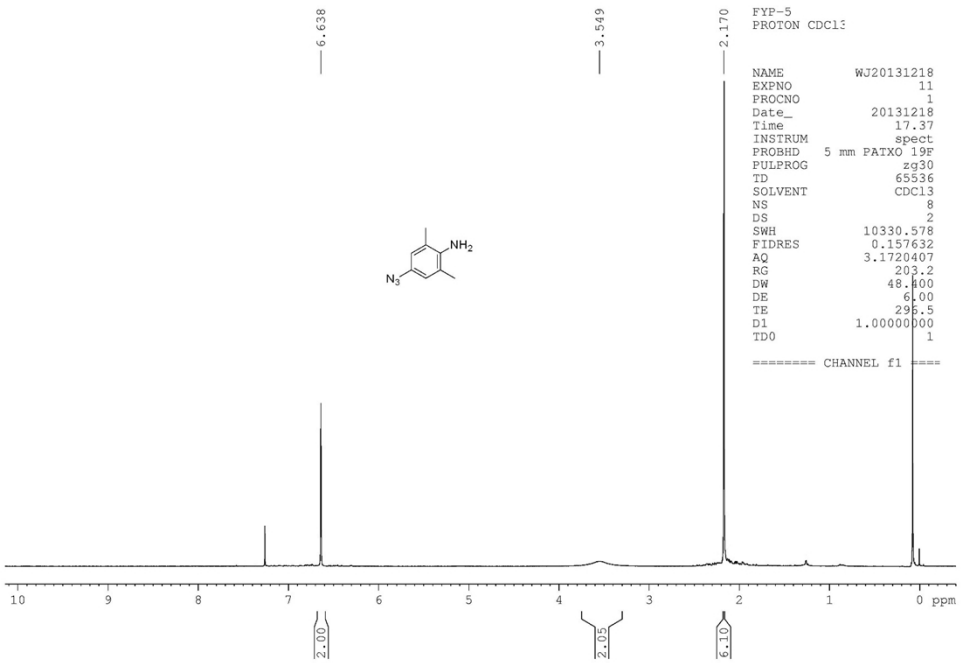
Compound **3x** ^{1}H **NMR**



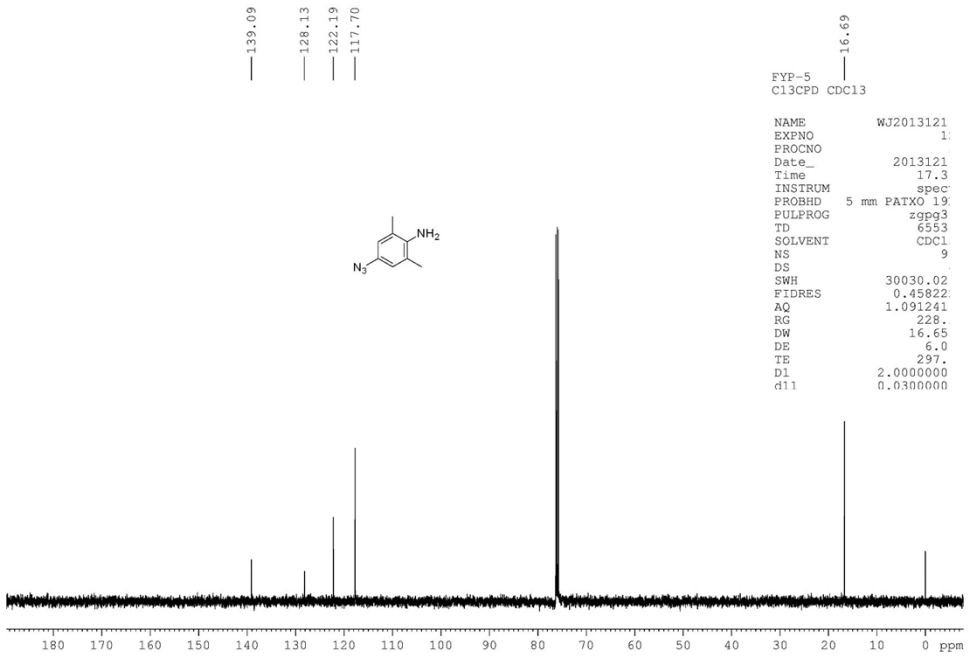
Compound **3x** ^{13}C **NMR**



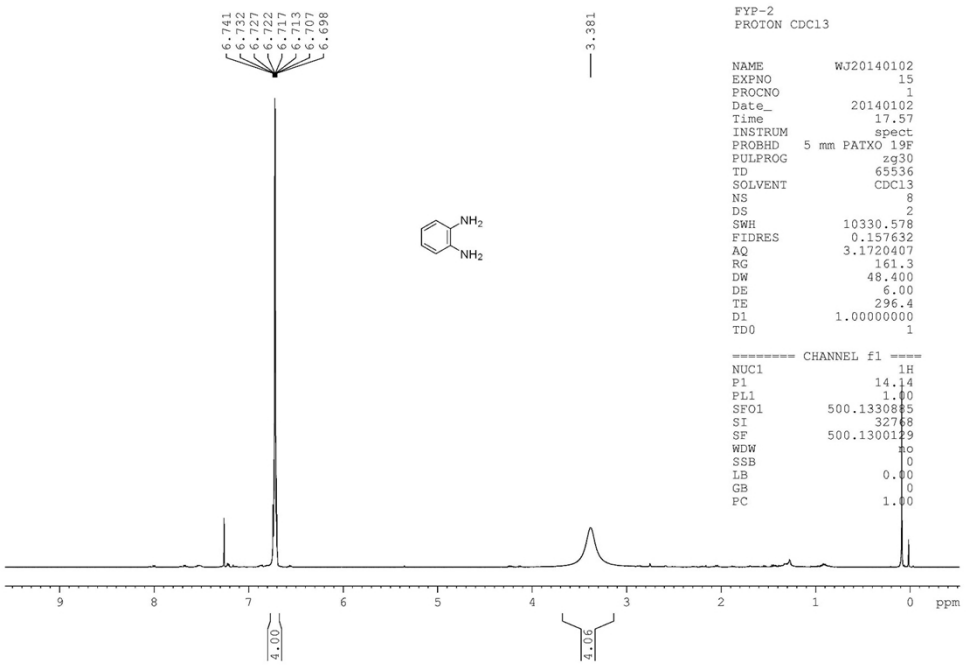
Compound **3y** ^{1}H **NMR**



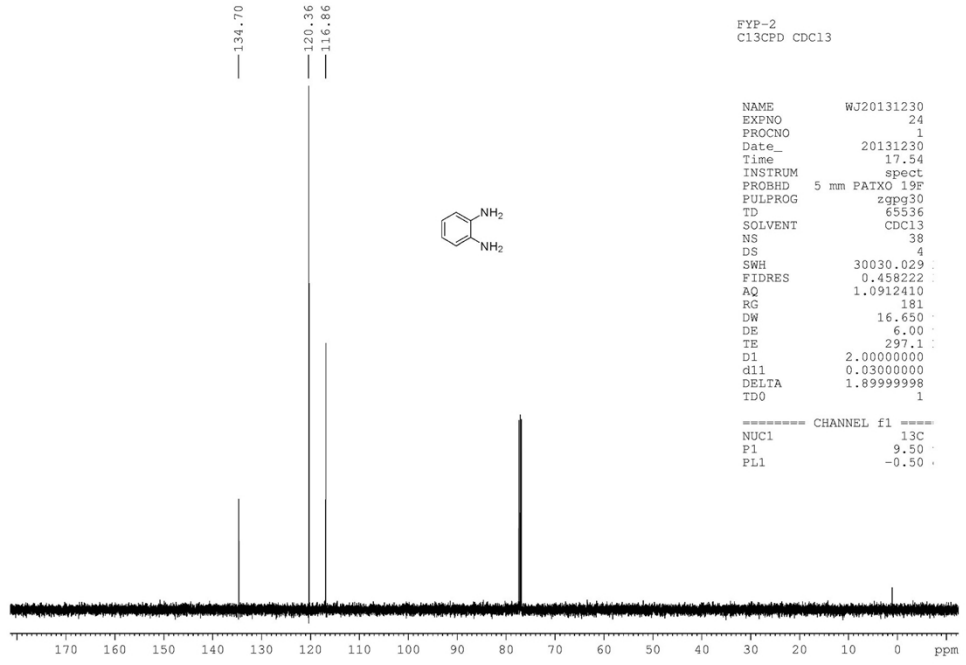
Compound **3y** ^{13}C **NMR**



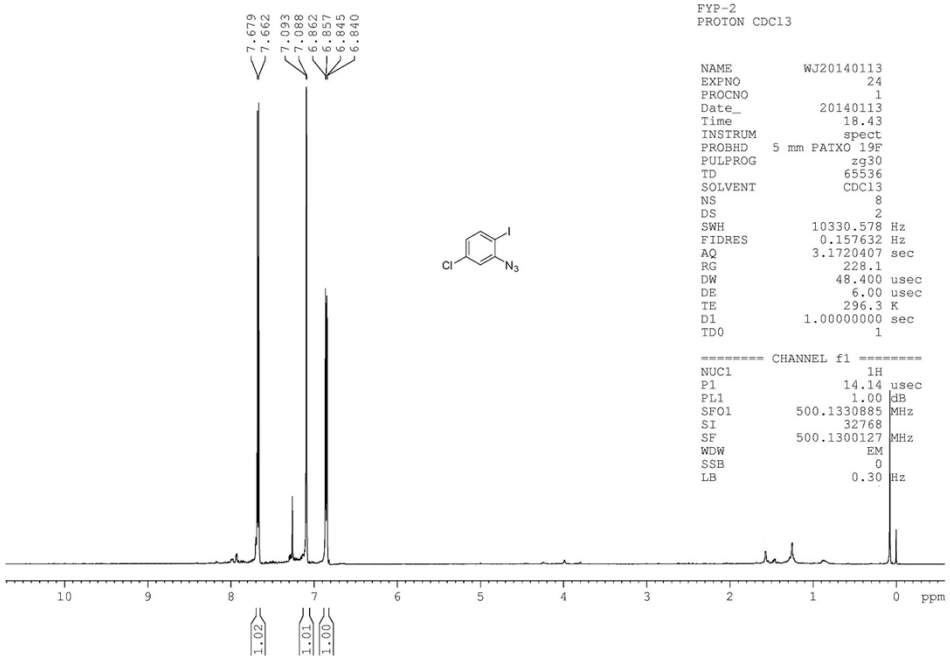
Compound **4** ^{1}H **NMR**



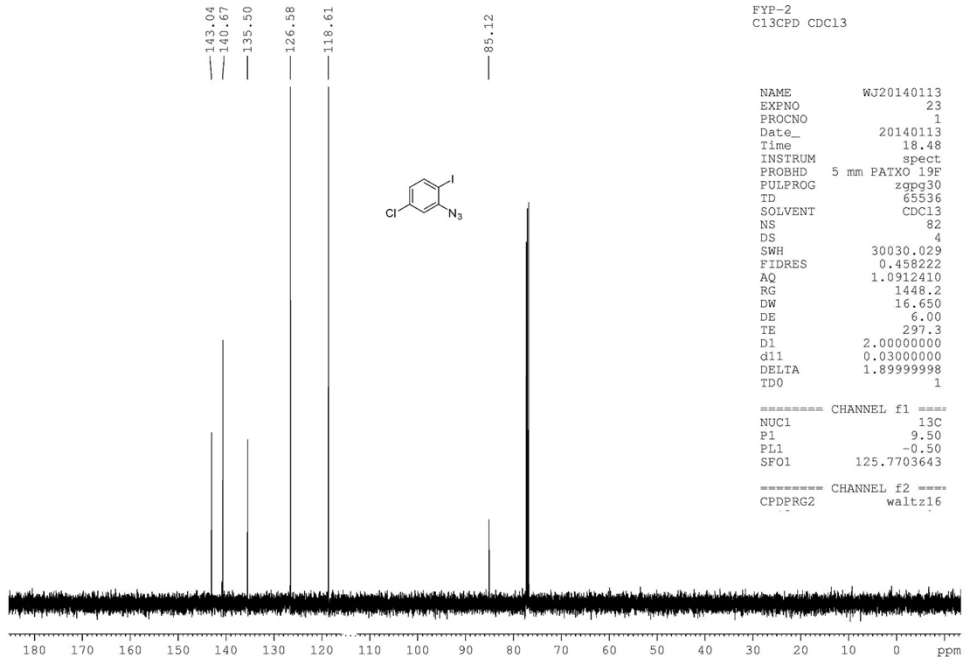
Compound **4** ^{13}C **NMR**



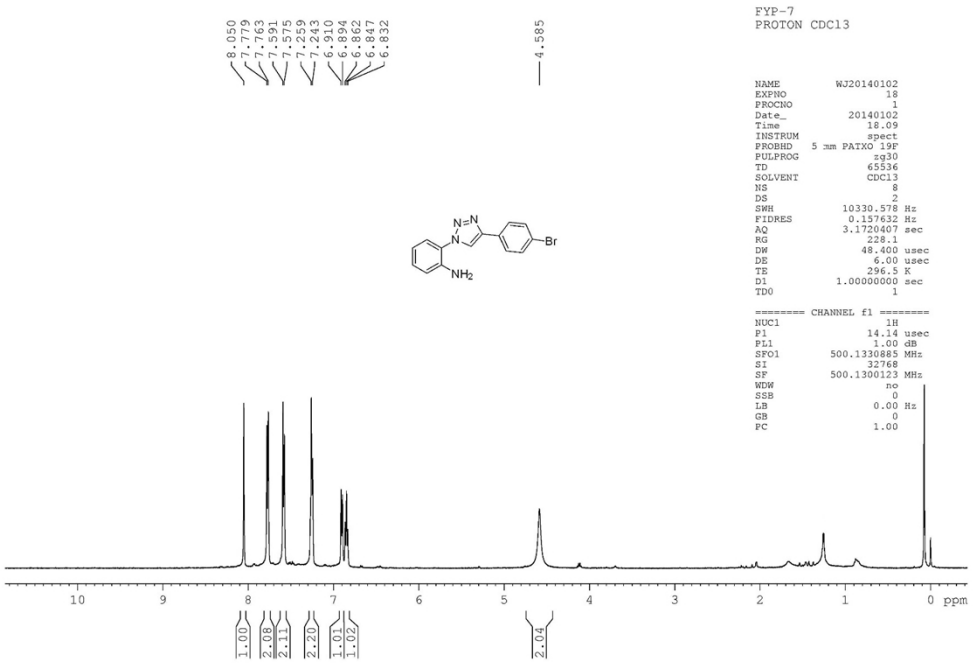
Compound **5** ^{1}H **NMR**



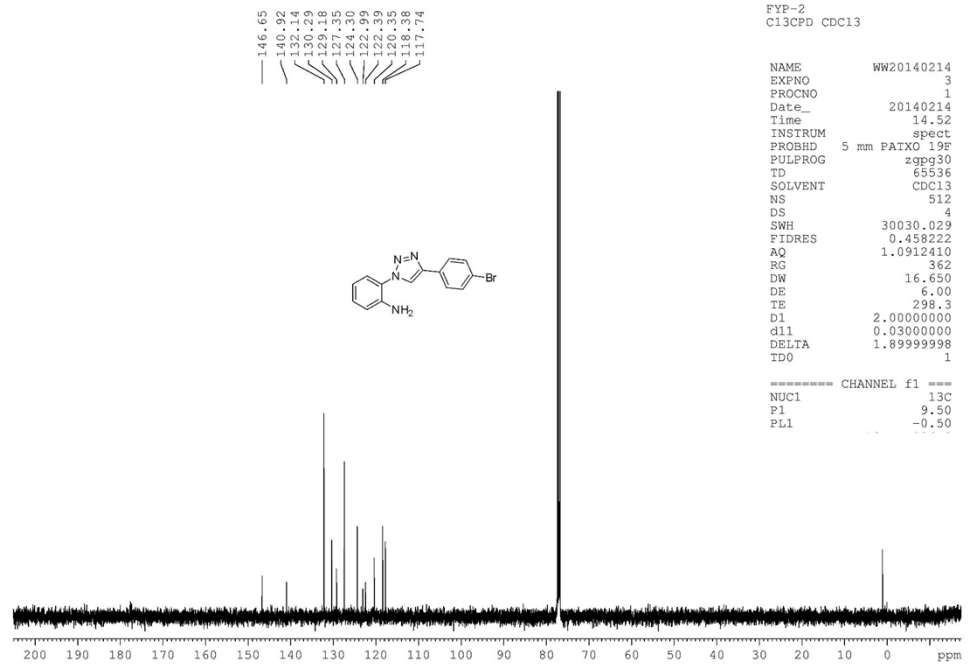
Compound **5** ^{13}C **NMR**



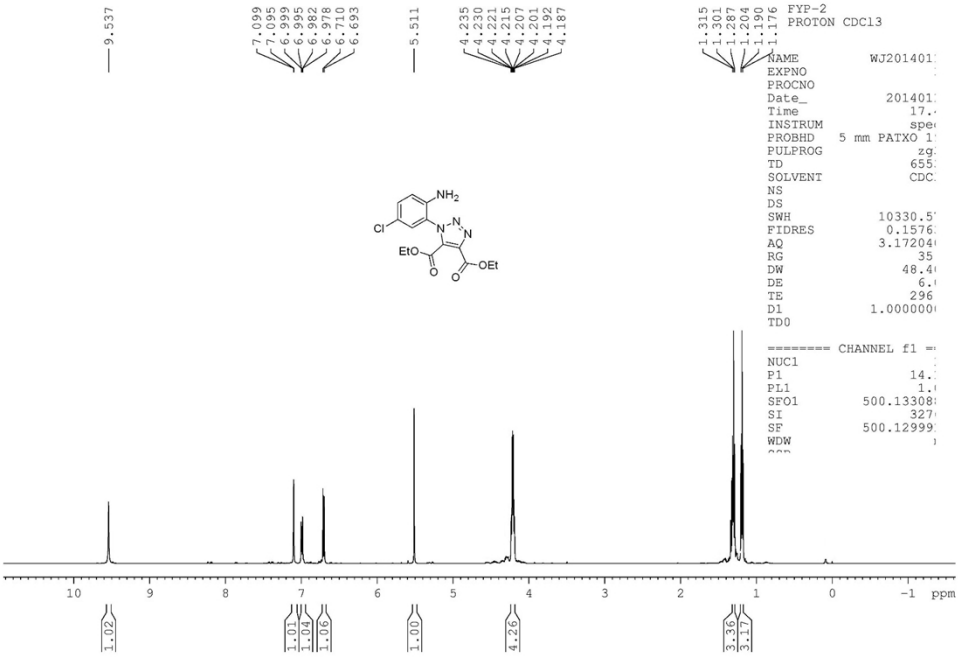
Compound **6** ^{1}H **NMR**



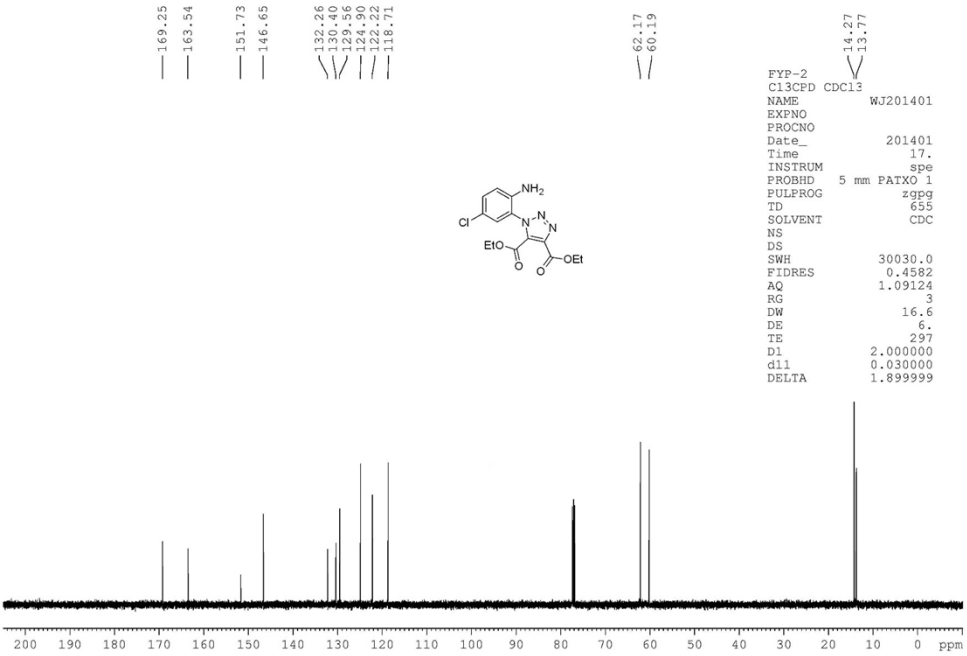
Compound **6** ^{13}C **NMR**



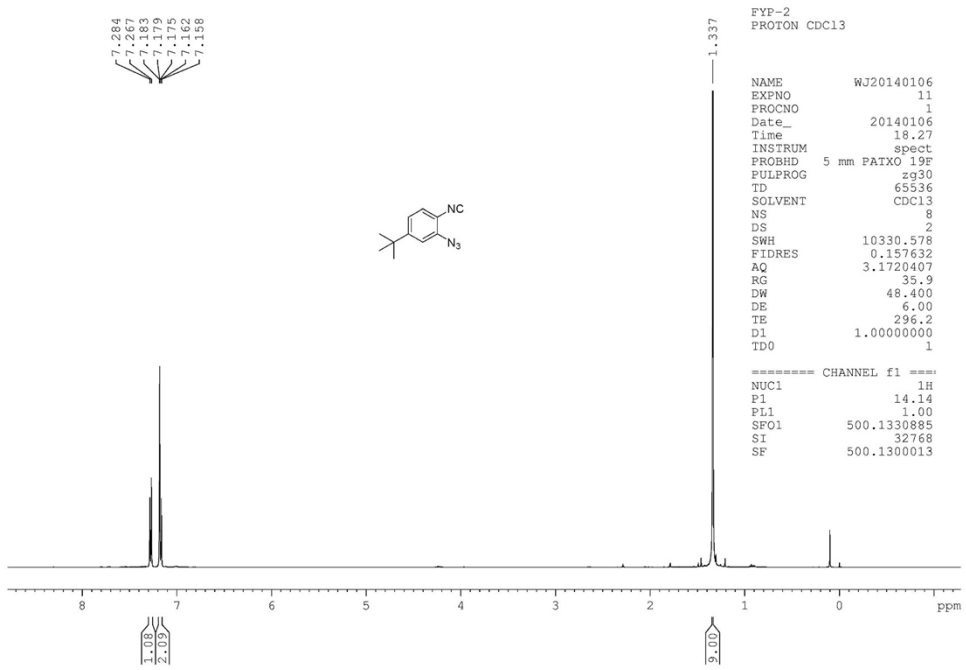
Compound **7** ^{1}H **NMR**



Compound **7** ^{13}C **NMR**



Compound **8** ^{1}H **NMR**



Compound **8** ^{13}C **NMR**