Supporting Information

Direct Electrosynthesis of Aromatic Nitriles from Methylarenes with Hydroxylamine as a Nitrogen Source

Hong Zeng, Ming-Qiu-Hao Fu, Zhi Guan* and Yan-Hong He*

Key Laboratory of Applied Chemistry of Chongqing Municipality, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

* Corresponding authors: Prof. Dr. Zhi Guan: guanzhi@swu.edu.cn; Prof. Dr. Yan-Hong He: heyh@swu.edu.cn

Contents

1. General methods

The instruments for electrolysis used were ElectraSyn 2.0 Pro Package (IKA) and MAISHENG DC Power. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light and vanillic aldehyde or phosphomolybdic acid as visualizing agents. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^{1}H NMR spectra, ^{19}F NMR spectra and ^{13}C NMR spectra were respectively recorded on 600 MHz, 565 MHz, and 151 MHz NMR spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard, and coupling constants (*J*) were reported in Hz. High-resolution mass spectra were obtained by using ESI ionization sources (quadrupole time-of-flight mass spectrometer, Bruker Impact II, Bremen, Germany). Cyclic voltammograms were obtained on a CHI 700E potentiostat (CH Instruments, Inc.).

Abbreviations: HFIP = hexafluoroisopropanol, MeOH = methanol, DMA = *N*,*N*-dimethylaniline, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, EA = ethyl acetate, DCE = dichloroethane, DCM = dichloromethane, THF = Tetrahydrofuran, MeCN = acetonitrile, TEMPO = 2,2,6,6-tetramethylpiperidinooxy, *m*CPBA = 3-chloroperoxybenzoic acid, NHPI = N-Hydroxyphthalimide, FTO = F-doped tin oxide, N.D. = not detected, N.R. = no reaction.

2. Electrochemical reaction setup

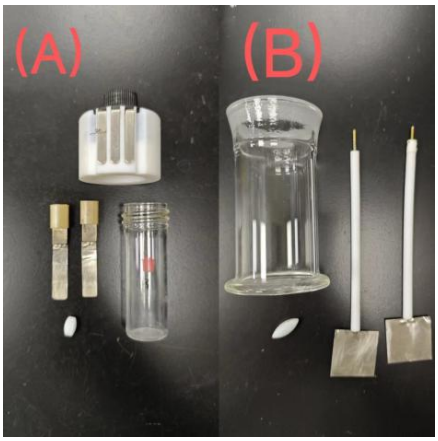


Figure S1. Electrochemical setup.

(A): IKA ElectraSyn Electrode Starter Kit, platinum plates (52 mm x 8 mm x 0.2 mm), 10 mL reaction vessel (for general procedure for the electrochemical synthesis of products **3**). (B): A cylindrical bottle with a diameter of 5 cm and a height of 10 cm as reaction vessel, Pt sheet (30 mm x 30 mm x 0.2 mm) (for gram-scale preparation of product **3a**).

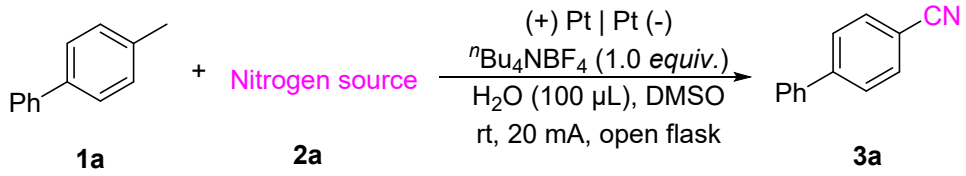
Divided cell experiments:

Figure S2. Electrochemical setup used for divided cell experiments.

Pt sheet (10 mm x 10 mm x 0.1 mm). The reaction vessel: an H-type divided electrolytic cell (10 mL + 10 mL) separated by a hydrogen ion-permeable membrane (Dupont N-117).

3. Reaction optimization

Table S1. Nitrogen source screening [a]

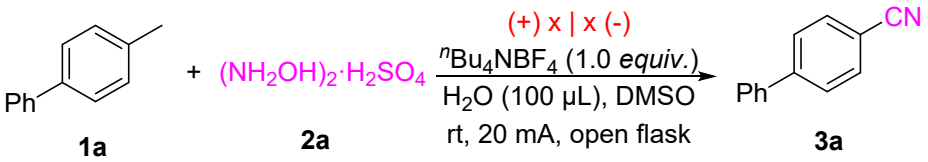


1a **2a** **3a**

Entry	Nitrogen source	Yield (%)[b]
1	NH_2OH•HCl	N.D.
2	**$(NH_2OH)_2$•H_2SO_4**	**30**
3	NH_4I	N.D.
4	NH_4OAc	N.D.
5	HMDS	N.D.

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 *equiv.*), **2a** (0.6 mmol, 2.0 *equiv.*), ^{n}Bu$_4$NBF$_4$ (0.3 mmol, 1.0 *equiv.*), H_2O (100 μL), DMSO (5 mL), constant current of = 20 mA, room temperature, 6 h, in an undivided electrolytic cell. [b] Isolated yield.

Table S2. Electrode screening [a]

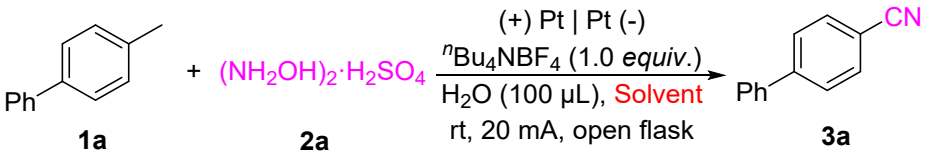


1a **2a** **3a**

Entry	Electrode material	Yield (%)[b]
1	(+) Pt sheet | Ni foam (-)	15
2	(+) Pt sheet | Cu foam (-)	16
3	(+) Pt sheet | C plate (-)	11
4	(+) C plate | C plate (-)	6
5	(+) C plate | Pt sheet (-)	12
6	(+) C plate | Cu foam (-)	N.D.
7	(+) C plate | SS plate (-)	trace
8	(+) C plate | Ni foam (-)	trace
9	(+) FTO plate | Pt sheet (-)	N.R.
10	(+) Glassy C plate | Glassy C plate (-)	trace
11	(+) Glassy C plate | Ni foam (-)	trace
12	**(+) Pt sheet | Pt sheet (-)**	**30**

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 *equiv.*), **2a** (0.6 mmol, 2.0 *equiv.*), $^{n}Bu_4NBF_4$ (0.3 mmol, 1.0 *equiv.*), H_2O (100 μL), DMSO (5 mL), constant current = 20 mA, room temperature, 5-8 h, in an undivided electrolytic cell. [b] Isolated yield.

Table S3. Solvent screening [a]



Entry	Solvent	Yield (%)[b]
1	DMSO	30
2	DMF	N.D.
3	DMA	N.D.
4	DCM	12
5	DCE	25
6	MeOH	N.D.
7	NMP	N.D.
8	HFIP	15
9	MeCN	trace
10	EA	N.D.
11	THF	N.D.
12	acetone	N.D.
13	**DMSO/DCE (4:1)**	**50**
14	DMSO/DCE (3:2）	44
15	DMSO/DCE (1:1)	21
16	DMSO/DCE (2:3)	13

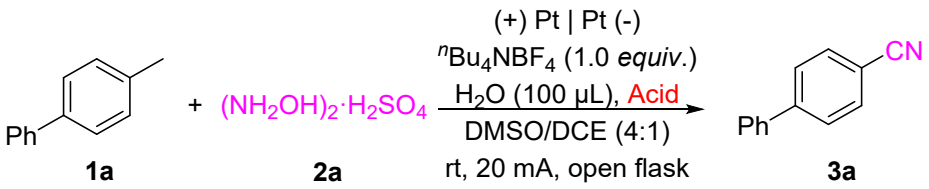
[a] Reaction conditions: **1a** (0.3 mmol, 1.0 *equiv.*), **2a** (0.6 mmol, 2.0 *equiv.*), $^{n}Bu_4NBF_4$ (0.3 mmol, 1.0 *equiv.*), H_2O (100 μL), solvent (5 mL), constant current = 20 mA, room temperature, 5-10 h, in an undivided electrolytic cell. [b] Isolated yield.

Table S4 Electrolyte screening [a]

Entry	Electrolyte	Yield (%)[b]
1	**$^{n}Bu_4NBF_4$**	**50**
2	$^{n}Et_4NBF_4$	34
3	$^{n}Et_4NPF_6$	40
4	$^{n}Bu_4NPF_6$	33
5	$NaBF_4$	30
6	$LiBF_4$	N.D.
7	$NaClO_4$	27
8	$LiClO_4$	25
9	$^{n}Et_4NClO_4$	22
10	$^{n}Bu_4NClO_4$	21
11	KPF_6	30
15	NaI	N.D.
13	$^{n}Bu_4NI$	N.D.
14	$^{n}Bu_4NCl$	N.D.
15	$^{n}Bu_4PCl$	N.D.
16	$^{n}Bu_4NOAc$	trace
17	$^{n}Bu_4NTfOH$	15
18	$^{n}Bu_4NTsOH$	12

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 *equiv.*), **2a** (0.6 mmol, 2.0 *equiv.*), Electrolyte (0.3 mmol, 1.0 *equiv.*), H_2O (100 μL), DMSO/DCE (4:1 v/v, 5 mL), constant current = 20 mA, room temperature, 5-9 h, in an undivided electrolytic cell. [b] Isolated yield.

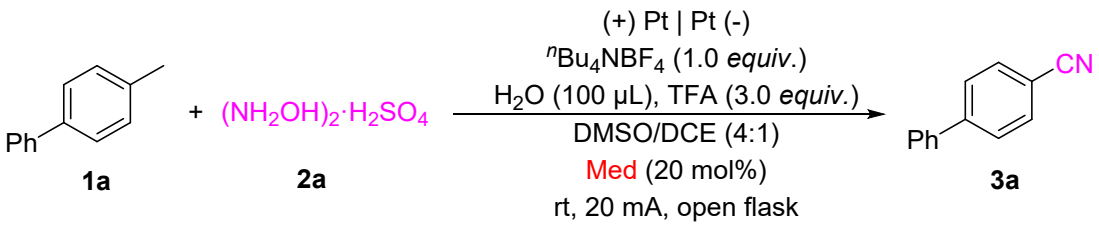
Table S5. Acid screening [a]



Entry	Acid (*equiv.*)	Yield (%)[b]
1	--	trace
2	TFA (1.0)	45
3	TFA (2.0)	59
4	**TFA (3.0)**	**65**
5	TFA (4.0)	64
6	AcOH (3.0)	30
7	PhCOOH (3.0)	N.D.
8	$B(OH)_3$ (3.0)	27
8	BF_3•Et_2O (3.0)	28

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 *equiv.*), **2a** (0.6 mmol, 2.0 *equiv.*), $^nBu_4NBF_4$ (0.3 mmol, 1.0 *equiv.*), H_2O (100 μL), DMSO/DCE (4:1 v/v, 5 mL), constant current = 20 mA, room temperature, 5-12 h, in an undivided electrolytic cell. [b] Isolated yield.

Table S6. Mediator screening [a]

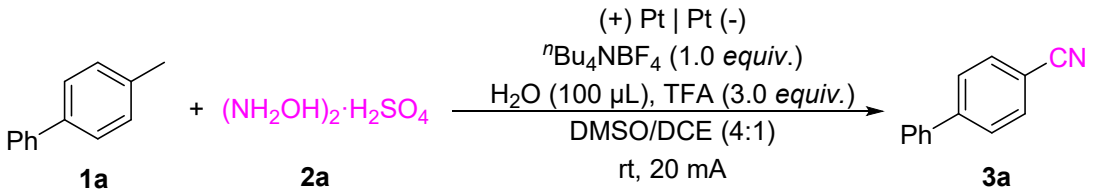


Entry	Mediator	Yield (%)[b]
1	Cp_2Fe	45
2	TEMPO	34
3	BHT	40
4	Ph_3P	33
5	NHPI	30

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 *equiv.*), **2a** (0.6 mmol, 2.0 *equiv.*), $^nBu_4NBF_4$ (0.3 mmol, 1.0 *equiv.*), TFA (0.9 mmol, 3.0 *equiv.*), H_2O (100 μL), DMSO/DCE (4:1 v/v, 5 mL),

constant current = 20 mA, room temperature, 6 h, in an undivided electrolytic cell. [b] Isolated yield.

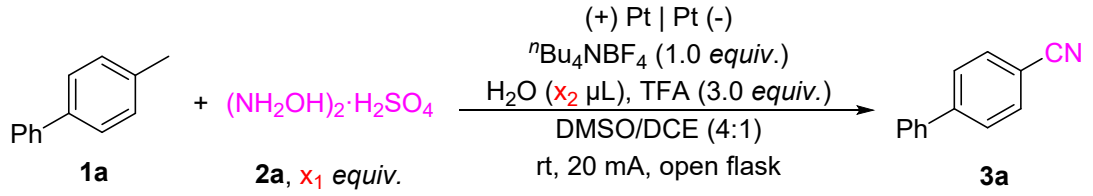
Table S7. Screening of reaction temperature and atmosphere [a]



Entry	Temperature (°C)/ atmosphere	Yield (%)[b]
1	10, open flask	55
2	**rt, open flask**	**65**
3	40, open flask	60
4	rt, O_2	48
5	rt, Ar	50

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 *equiv.*), **2a** (0.6 mmol, 2.0 *equiv.*), $^{n}Bu_4NBF_4$ (0.3 mmol, 1.0 *equiv.*), TFA (0.9 mmol, 3.0 *equiv.*), H_2O (100 μL), DMSO/DCE (4:1 v/v, 5 mL), constant current = 20 mA, 6-12 h, in an undivided electrolytic cell. [b] Isolated yield.

Table S8. Screening of hydroxylamine and water amounts [a]

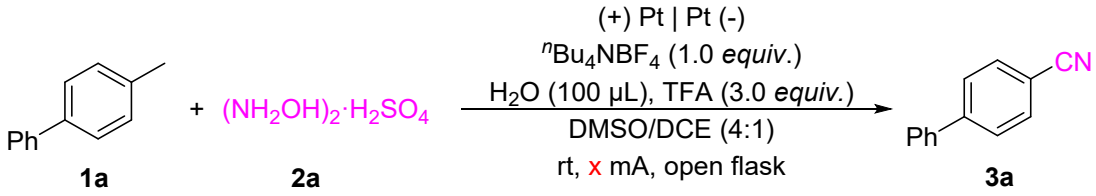


Entry	**2a** (*equiv.*)	H_2O (μL)	Yield (%)[b]
1	2.0	100	65
2	3.0	50	58
3	**3.0**	**100**	**72**
4	3.0	150	70
5	4.0	150	71

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 *equiv.*), **2a** (x_1 *equiv.*), $^{n}Bu_4NBF_4$ (0.3 mmol, 1.0 *equiv.*), TFA (0.9 mmol, 3.0 *equiv.*), H_2O (x_2 μL), DMSO/DCE (4:1 v/v, 5 mL), constant current

= 20 mA, room temperature, 6-12 h, in an undivided electrolytic cell. [b] Isolated yield.

Table S9. Screening of current [a]

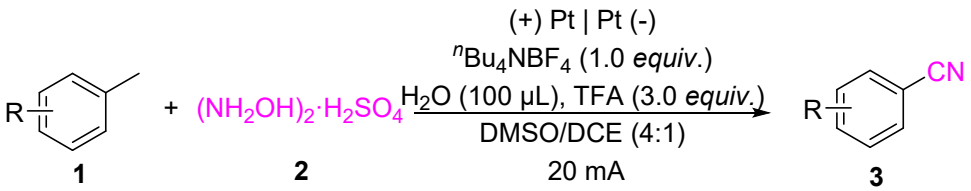


1a **2a** **3a**

Entry	Current (mA)	Yield (%)[b]
1	10	45
2	15	53
3	**20**	**72**
4	25	60

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 *equiv.*), **2a** (0.9 mmol, 3.0 *equiv.*), ^{n}Bu$_4$NBF$_4$ (0.3 mmol, 1.0 *equiv.*), TFA (0.9 mmol, 3.0 *equiv.*), H$_2$O (100 μL), DMSO/DCE (4:1 v/v, 5 mL), constant current, room temperature, 6-12 h, in an undivided electrolytic cell. [b] Isolated yield.

4. General procedure for the electrochemical synthesis of products 3



1 **2** **3**

To a 10 mL standard IKA vessel were added methylarene (**1**) (0.3 mmol, 1.0 *equiv.*), hydroxyl ammonium sulfate (**2**) (0.9 mmol, 3.0 *equiv.*), ^{n}Bu$_4$NBF$_4$ (0.3 mmol, 1.0 *equiv.*), H$_2$O (100 μL), TFA (0.9 mmol, 3.0 *equiv.*), DMSO/DCE (4:1 v/v, 5 mL) and a magnetic stirring bar. Both the anode and cathode are platinum sheets measuring 52 mm x 8 mm x 0.2 mm (the electrodes were immersed 1 cm in the reaction solution). The constant current (20 mA) electrolysis was then performed at room temperature under air atmosphere with vigorous stirring (600 rpm). Upon completion, the reaction mixture was poured into 30 mL H$_2$O and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with 30 mL brine and dried over anhydrous Na$_2$SO$_4$. Then, the solvent was removed under reduced

pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with ethyl acetate/petroleum ether) to afford the desired product **3**.

5. Mechanistic investigation

5.1. Control experiments

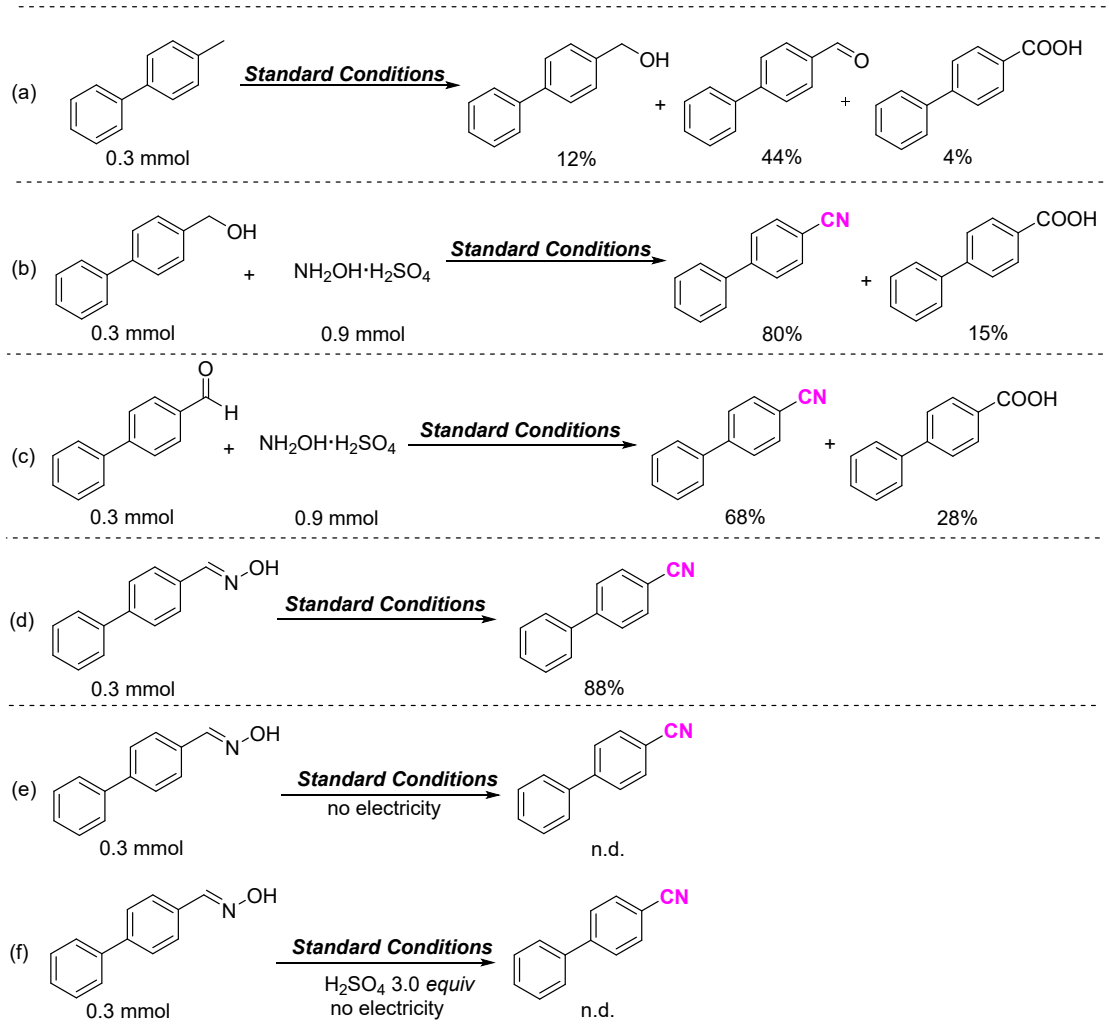


Figure S3. Control experiments.

(a) For the reaction shown in Figure S3a: To a 10 mL standard IKA vessel were added 4-methylbiphenyl (0.3 mmol, 1.0 *equiv.*), $^{n}Bu_4NBF_4$ (0.3 mmol, 1.0 *equiv.*), H_2O (100 μL), TFA (0.9 mmol, 3.0 *equiv.*), DMSO/DCE (4:1 v/v, 5 mL) and a magnetic stirring bar. Both the anode and cathode are platinum sheets measuring 52 mm x 8 mm x 0.2 mm (the electrodes were immersed 1 cm in the reaction solution). The constant current (20 mA) electrolysis was then

performed at room temperature under air atmosphere with vigorous stirring (600 rpm). Upon completion, the reaction mixture was poured into 30 mL H_2O and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with ethyl acetate/petroleum ether).

(b) For the reaction shown in Figure S3b: Replace 4-methylbiphenyl with 4-biphenylmethanol, add hydroxyl ammonium sulfate (0.9 mmol, 3.0 *equiv.*), while keeping the other experimental procedures consistent with those described in (a).

(c) For the reaction shown in Figure S3c: Replace 4-methylbiphenyl with 4-biphenylcarbaldehyde, add hydroxyl ammonium sulfate (0.9 mmol, 3.0 *equiv.*), while keeping the other experimental procedures consistent with those described in (a).

(d) For the reaction shown in Figure S3d: Replace 4-methylbiphenyl and hydroxyl ammonium sulfate with 4-biphenylcarbaldehyde oxime, while keeping the other experimental procedures consistent with those described in (a).

(e) For the reaction shown in Figure S3e: Follow the same procedure as described for (d), but without applying an electrical current.

(f) For the reaction shown in Figure S3f: The reaction was conducted according to the procedure shown in (e), with the addition of 3 equivalents of H_2SO_4.

5.2. Cyclic voltammetry experiments

The cyclic voltammetry experiments were carried out with a computer-controlled electrochemical analyzer for electrochemical measurements. The solution of interest was sparged with argon for 5 minutes before data collection with the CHI 700E potentiostat (CH Instruments, Inc.). The experiment was performed in a three-electrode cell with CH_3CN (10 mL) as the solvent, $^{n}Bu_4NBF_4$ (0.05 M) as the supporting electrolyte, and the concentration of the tested compounds (**1a**, **2a**, **3a**, **4**, **12**, **13** was 2.0 mM.) The scan speed was 100 mV/s. The oxidation potential ranges investigated were 0 V to +3.0 V *vs.* Ag/AgCl (saturated aqueous

KCl). CV plotting convention is IUPAC.

Working electrode: The working electrode was a 3 mm diameter glassy carbon working electrode. Polished with 0.05 μm aluminum oxide and then sonicated in distilled water and ethanol before measurements.

Reference electrode: The reference electrode was Ag/AgCl (saturated aqueous KCl) that was washed with water and ethanol before measurements.

Counter electrode: The counter electrode was a platinum wire that was polished with 0.05 μm aluminum oxide and then sonicated in distilled water and ethanol before measurements.

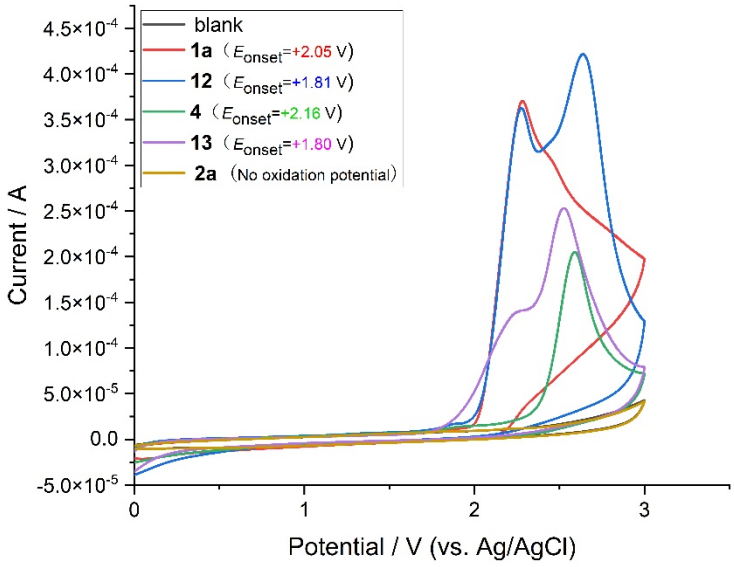


Figure S4.1 Cyclic voltammogram of **1a**, **2a**, **4**, **12** and **13** in an electrolyte of $^{n}Bu_4NBF_4$ (0.05 M) in MeCN from 0 to +3.0 V.

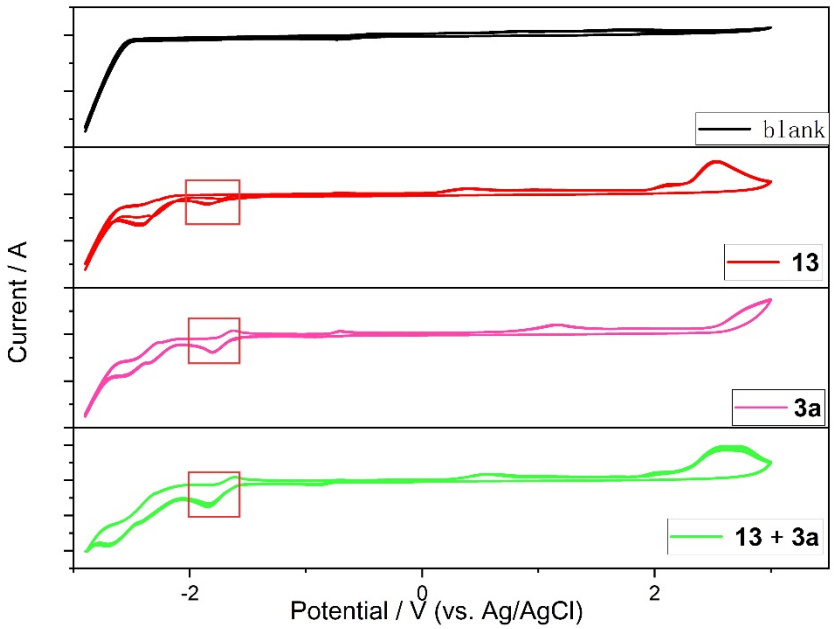


Figure S4.2 Cyclic voltammogram of **13**, **3a**, **13**+**3a** in an electrolyte of $^{n}Bu_4NBF_6$ (0.05 M) in MeCN from -3.0 V to +3.0 V (three scans).

5.3. Radical trapping experiments

Under standard conditions, TEMPO (3.0 *equiv.* to **1a**) or BHT (3.0 *equiv.* to **1a**) was added to the model reaction system at the beginning of the reaction. The reaction was monitored by TLC. After 6 h, a small amount of reaction mixture was taken out for high-resolution mass spectrometry (HRMS) measurement.

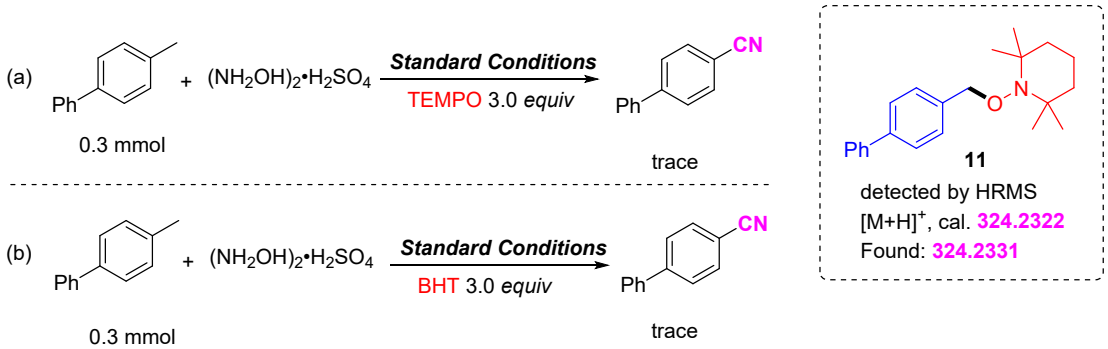


Figure S5. Radical validation experiments.

5.4. Divided cell experiments

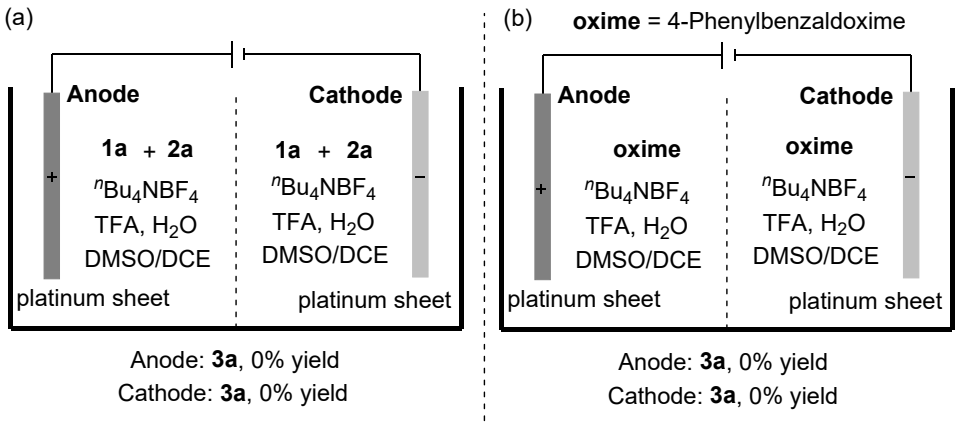


Figure S6. Divided cell experiments.

For the experiment shown in Figure S6a: To the left and right parts of the H-type divided electrolytic cell were added **1a** (0.3 mmol, 1.0 *equiv.*), **2a** (0.9 mmol, 3.0 *equiv.*), electrolyte ^{n}Bu$_4$NBF$_4$ (0.3 mmol, 1.0 *equiv.*), H$_2$O (100 μL), TFA (0.9 mmol, 3.0 *equiv.*), 5 mL DMSO/DCE (4:1 v/v) and a magnetic stirrer bar. Platinum plates (10 mm x 8 mm x 0.2 mm) were used as the anode and cathode. The constant current (20 mA) electrolysis was then performed at room temperature under air atmosphere with vigorous stirring (600 rpm) for 20 h. Through TLC detection, no target product **3a** was detected at either the anode or the cathode.

For the experiment shown in Figure S6b: To the left and right parts of the H-type divided electrolytic cell were added 4-phenylbenzaldoxime (0.3 mmol, 1.0 *equiv.*), electrolyte ^{n}Bu$_4$NBF$_4$ (0.3 mmol, 1.0 *equiv.*), H$_2$O (100 μL), TFA (0.9 mmol, 3.0 *equiv.*), 5 mL DMSO/DCE (4:1 v/v) and a magnetic stirrer bar. Platinum plates (10 mm x 8 mm x 0.2 mm) were used as the anode and cathode. The constant current (20 mA) electrolysis was then performed at room temperature under air atmosphere with vigorous stirring (600 rpm) for 10 h. Through TLC detection, no target product **3a** was detected at either the anode or the cathode.

5.5. KIE experiments

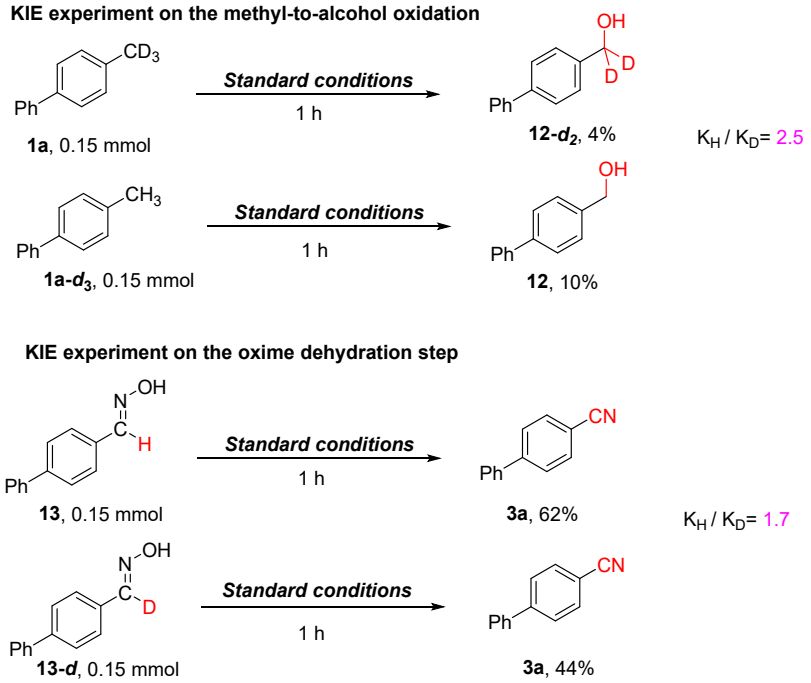


Figure S7. KIE experiments

Parallel KIE experiments

(a) Methyl-to-alcohol oxidation: 4-Methyl-1,1'-biphenyl (0.15 mmol) and its deuterated analogue 4-(methyl-d_3)-1,1'-biphenyl (0.15 mmol) were each placed in separate 10 mL IKA reaction vials. After electrolysis under standard conditions (without hydroxylamine) for 1 h, the mixtures were purified. The non-deuterated substrate afforded [1,1'-biphenyl]-4-methanol in 10% yield, while the deuterated substrate gave the corresponding deuterated alcohol in 4% yield, leading to a K_H/K_D value of 2.5.

(b) Oxime dehydration: [1,1'-Biphenyl]-4-carbaldehyde oxime (0.15 mmol) and its benzylic-deuterated analogue [1,1'-biphenyl]-4-carbaldehyde-*d* oxime-1-*d* (0.15 mmol) were each placed in separate 10 mL IKA reaction vials. After electrolysis under standard conditionsfor 1 h, the mixtures were purified. The non-deuterated substrate afforded [1,1'-biphenyl]-4-carbonitrile in 62% yield, while the deuterated substrate gave the corresponding product in 44% yield. Because the reaction proceeded to relatively high conversion, the raw yield ratio (1.4) does not directly equal k_H/k_D. Therefore, the KIE was calculated using the first-order kinetic correction formula: $k_H/k_D = \ln(1-C_H)/\ln(1-C_D) = \ln(0.38)/\ln(0.56) = 1.7$.

5.6. ^{18}O-labeling experiment

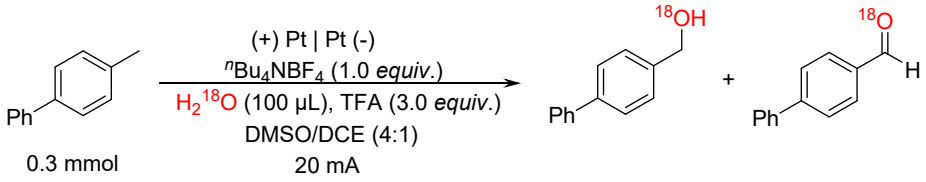


Figure S8.1 ^{18}O-labeling experiment

To a 10 mL standard IKA vessel were added 4-methylbiphenyl (0.3 mmol, 1.0 *equiv.*), ^{n}Bu$_4$NBF$_4$ (0.3 mmol, 1.0 *equiv.*), H$_2$^{18}O (100 μL), TFA (0.9 mmol, 3.0 *equiv.*), DMSO/DCE (4:1 v/v, 5 mL), and a magnetic stirring bar. Both the anode and cathode were platinum sheets measuring 52 mm × 8 mm × 0.2 mm (the electrodes were immersed 1 cm into the reaction solution). Constant current electrolysis (20 mA) was then performed at room temperature under air atmosphere with vigorous stirring (600 r/min) for 6 hours. After purification, the product was analyzed by HRMS.

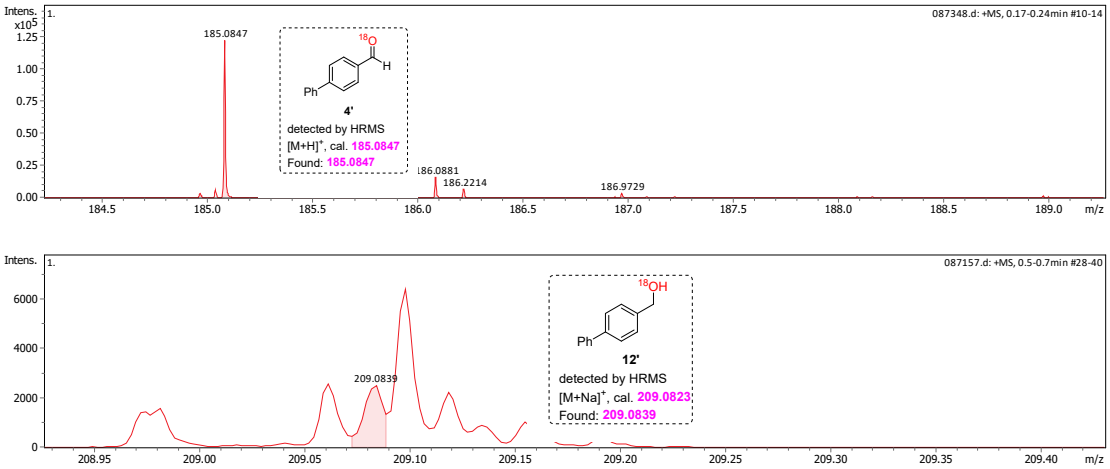
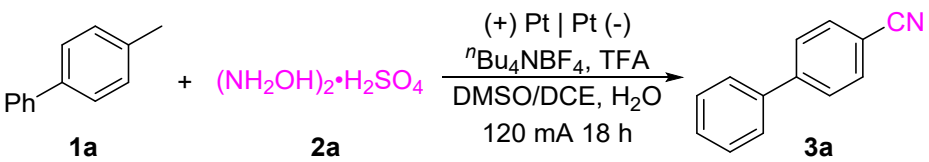


Figure S8.2 ^{18}O-labeling experiment (HRMS)

6. Synthetic applications

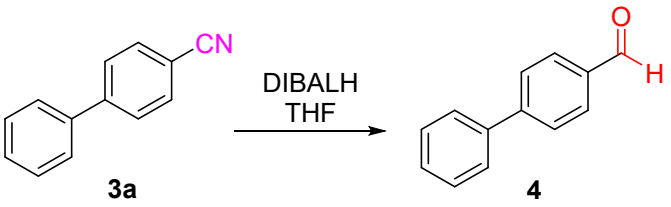
6.1. Gram-scale preparation of product 3a



A mixture of 4-methylbiphenyl (**1a**) (10.0 mmol, 1.0 *equiv.*), hydroxylamine sulfate (**2a**)

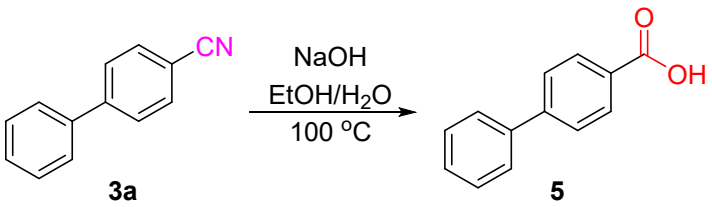
(15.0 mmol, 1.5 *equiv.*), TFA (15.0 mmol, 1.5 *equiv.*), H_2O (3.0 mL), $^nBu_4NBF_4$ (3.0 mmol, 0.3 *equiv.*), DMSO/DCE (4:1, 40.0 mL), and a magnetic stir bar was added to a cylindrical vessel (5 cm diameter × 10 cm height). Two platinum plates (30 mm × 30 mm × 0.2 mm) were employed as the cathode and anode. Constant-current electrolysis (120 mA) was performed at room temperature under an air atmosphere with vigorous stirring (600 rpm). Upon completion, the reaction mixture was poured into 100 mL of H_2O and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with 30 mL of saturated NaCl solution and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The resulting crude product was purified by silica gel column chromatography (eluted with petroleum ether) to afford the desired product **3a** (1.11 g, 62% yield).

6.2. Derivatization and synthesis of bioactive intermediate compounds

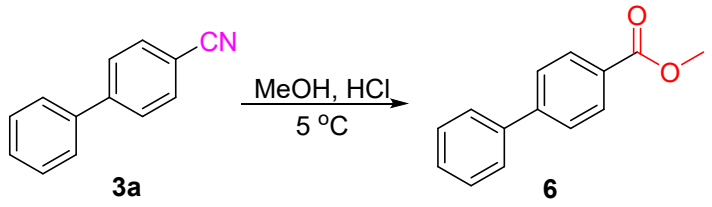


A 50 mL flask equipped with a magnetic stir bar was charged and purged with argon. morpholine (0.22 mL, 2.55 mmol) and tetrahydrofuran (5.0 mL) were added, and the reaction system was cooled to 0 °C by immersion in an ice bath. diisobutylaluminum hydride (DIBALH, 2.5 mL of 1.0 M solution in hexane, 2.5 mmol) was slowly added dropwise over 2 minutes, and the mixture was stirred at this temperature for 30 minutes. To the stirring mixture was introduced 4-cyanobiphenyl **3a** (0.5 mmol), followed by continuous stirring at 25 °C for 60 minutes. Upon completion of the reaction, the mixture was quenched with aqueous hydrochloric acid (5.0 mL). Diethyl ether (10.0 mL) was subsequently added, and stirring was maintained until the organic layer clarified. The reaction mixture was then poured into 30 mL of H_2O and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with saturated NaCl solution (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum ether), affording 4-biphenylcarbaldehyde **4** as the desired product in

80% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.05 (s, 1H), 7.95 (d, *J* = 7.9 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.39 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 192.0, 147.2, 139.7, 135.2, 130.3, 129.0, 128.5, 127.7, 127.39. The spectral data is identical to those reported previously[1].

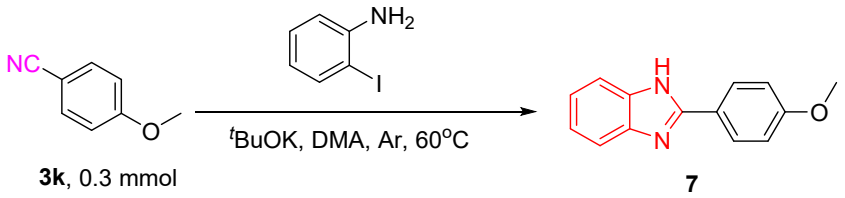


A mixture of 4-cyanobiphenyl **3a** (1.0 mmol), NaOH (0.1 mmol), and EtOH/H_2O (0.5 mL) was charged into a 50 mL flask equipped with a magnetic stir bar. The reaction mixture was stirred at 110 °C (external temperature) for 15 hours. Upon completion, the mixture was poured into 30 mL of H_2O and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with saturated NaCl solution (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum ether), yielding 4-biphenylcarboxylic acid **5** as a white solid in 62% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.01 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.77 – 7.72 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.6, 144.8, 139.5, 130.4, 130.1, 129.5, 128.7, 127.4, 127.3. The spectral data is identical to those reported previously[2].



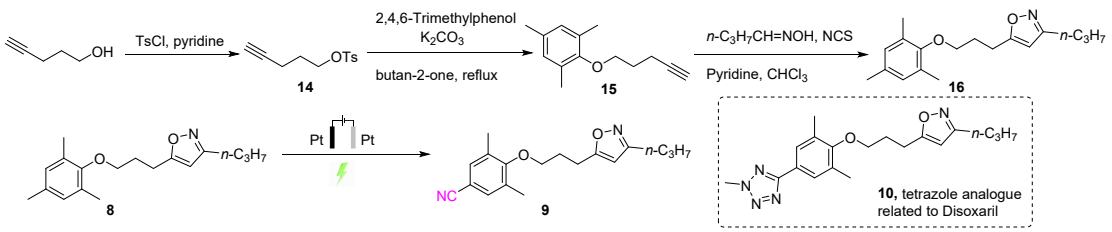
A mixture of 4-cyanobiphenyl **3a** (1.0 mmol) and methanol (3.0 mL) was charged into a 50 mL flask. The mixture was cooled to 5 °C using an ice bath. An HCl solution was added dropwise to the methanolic solution until the required amount (3.0 mmol HCl) was achieved. The resulting mixture was allowed to react at 5 °C for 24 hours. Upon completion, the reaction mixture was poured into 30 mL of H_2O and extracted with ethyl acetate (3 × 30 mL). The

combined organic layers were washed with saturated NaCl solution (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum ether), yielding methyl 4-biphenylcarboxylate **6** as a white solid in 70% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.12 – 8.08 (m, 2H), 7.68 – 7.64 (m, 2H), 7.64 – 7.60 (m, 2H), 7.46 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.41 – 7.36 (m, 1H), 3.93 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.0, 145.7, 140.0, 130.1, 128.9, 128.9, 128.2, 127.3, 127.1, 52.1. The spectral data is identical to those reported previously[3].



3k, 0.3 mmol **7**

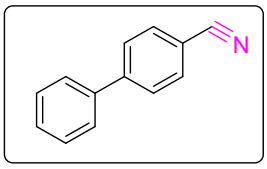
4-Methoxybenzonitrile **3k** (0.3 mmol) and potassium *tert*-butoxide (0.6 mmol, 2.0 *equiv*) were placed in a 5 mL round-bottom flask and dissolved in DMA (1 mL) to afford solution A, which was set aside. In a separate 5 mL round-bottom flask, 2-iodoaniline (0.6 mmol, 2.0 *equiv*) was added. The flask was evacuated and backfilled with argon, and the contents were heated to 60 °C. Solution A was then added to the reaction mixture, and stirring was continued at 60 °C for 20 h. The reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was poured into water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with saturated aqueous sodium chloride solution (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the product **7** as a white solid in 34% yield. **7**: ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.78 (s, 1H), 8.19 – 8.15 (m, 2H), 7.71 – 7.49 (m, 2H), 7.22 (s, 2H), 7.18 – 7.13 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.1, 151.8, 144.4, 135.4, 128.5, 123.2, 122.5, 121.9, 119.0, 114.8, 111.5, 55.8. The spectral data is identical to those reported previously[17][18].



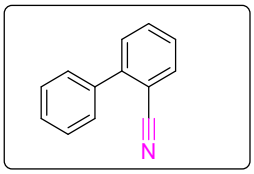
Following reported procedures,[19] compounds **14**, **15**, and **16** were synthesized starting from pent-4-yn-1-ol.

Compound **8** (0.3 mmol) and **2a** (0.9 mmol, 3.0 *equiv.*) were subjected to electrolysis under standard conditions. The reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was poured into water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with saturated aqueous sodium chloride solution (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 10:1) to afford the product **9** (22.5 mg)as a yellow solid in 38% yield. **15**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.71 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.08 (t, *J* = 6.1 Hz, 2H), 2.38 (s, 3H), 2.19 (td, *J* = 6.9, 2.7 Hz, 2H), 1.83 – 1.75 (m, 3H). **16**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.74 (s, 2H), 3.76 (t, *J* = 6.1 Hz, 2H), 2.40 (td, *J* = 7.1, 2.6 Hz, 2H), 2.16 (d, *J* = 5.9 Hz, 9H), 1.96 – 1.88 (m, 3H). **8**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.73 (s, 2H), 5.80 (s, 1H), 3.70 (t, *J* = 6.1 Hz, 2H), 2.92 (t, *J* = 7.7 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.15 (d, *J* = 5.4 Hz, 9H), 2.09 (s, 2H), 1.60 (d, *J* = 7.5 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **9**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 0.6 Hz, 2H), 5.88 (s, 1H), 3.83 (t, *J* = 6.1 Hz, 2H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.63 – 2.58 (m, 2H), 2.26 (s, 6H), 2.23 – 2.19 (m, 2H), 1.69 – 1.64 (m, 2H), 0.98 – 0.95 (m, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.9, 163.0, 158.6, 131.8, 131.5, 118.0, 106.4, 99.8, 69.8, 27.2, 27.0, 22.3, 20.6, 15.2, 12.7. The spectral data is identical to those reported previously[19].

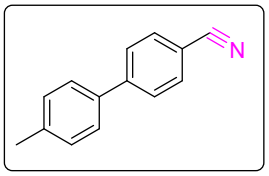
7. Characterization data of products



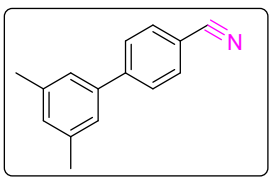
[1,1'-biphenyl]-4-carbonitrile (3a)[4]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 38.7 mg, 72% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.58 (dd, *J* = 7.3, 1.7 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.45 – 7.39 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.7, 139.2, 132.6, 129.1, 128.7, 127.7, 127.2, 118.9, 111.1.



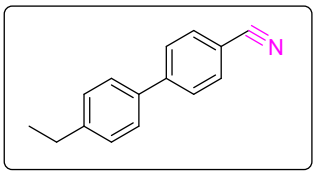
[1,1'-biphenyl]-2-carbonitrile (3b)[4]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 26.9 mg, 50% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.64 (td, *J* = 7.7, 1.4 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.53 – 7.47 (m, 3H), 7.47 – 7.40 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.5, 138.2, 133.8, 132.8, 130.1, 128.8, 128.7, 128.7, 127.6, 118.7, 111.3.



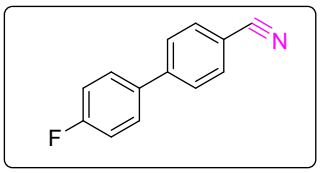
4'-methyl-[1,1'-biphenyl]-4-carbonitrile (3c)[4]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 41.1 mg, 71% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.6, 138.8, 136.3, 132.6, 129.9, 127.5, 127.1, 119.0, 110.6, 21.2.



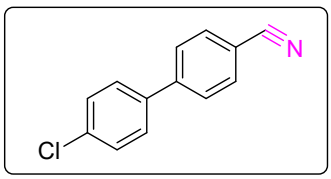
3',5'-dimethyl-[1,1'-biphenyl]-4-carbonitrile (3d)[4]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 43.5 mg, 70% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 – 7.61 (m, 4H), 7.18 (s, 2H), 7.05 (s, 1H), 2.38 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.0, 139.2, 138.7, 132.5, 130.3, 127.7, 125.12, 119.0, 110.7, 21.4.



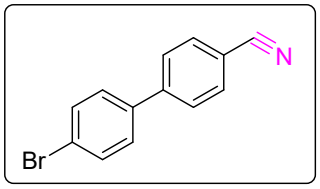
4'-ethyl-[1,1'-biphenyl]-4-carbonitrile (3e)[5]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 25.0 mg, 40% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.7 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.6, 145.1, 136.5, 132.6, 128.7, 127.5, 127.2, 119.0, 110.6, 28.6, 15.5.



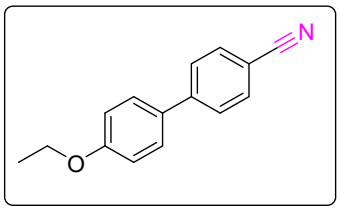
4'-fluoro-[1,1'-biphenyl]-4-carbonitrile (3f)[6]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 43.1 mg, 73% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.56 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.17 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.2 (d, *J* = 249.1 Hz), 162.4, 144.6, 135.3 (d, *J* = 3.0 Hz), 129.0 (d, *J* = 7.6 Hz), 127.6, 118.8, 116.1 (d, *J* = 22.7 Hz), 111.0. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.2.



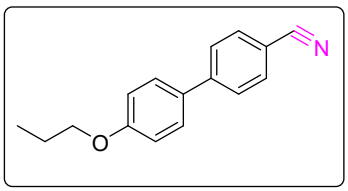
4'-chloro-[1,1'-biphenyl]-4-carbonitrile (3g)[6]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 44.1 mg, 69% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.4, 137.6, 135.0, 132.7, 129.3, 128.5, 127.6, 118.7, 111.3.



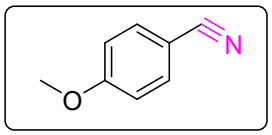
4'-bromo-[1,1'-biphenyl]-4-carbonitrile (3h)[7]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 50.1 mg, 65% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.70 (m, 2H), 7.67 – 7.63 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.4, 138.1, 132.7, 132.3, 128.8, 127.6, 123.2, 118.7, 111.4.



4'-ethoxy-[1,1'-biphenyl]-4-carbonitrile (3i)[8]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 41.5 mg, 62% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.61 (m, 4H), 7.52 (dd, *J* = 9.0, 2.5 Hz, 2H), 6.98 (dt, *J* = 9.1, 2.7 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.6, 145.3, 132.6, 131.3, 128.3, 127.1, 119.1, 115.1, 110.1, 63.7, 14.8.

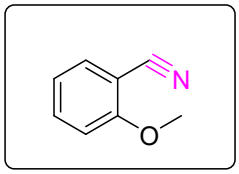


4'-propoxy-[1,1'-biphenyl]-4-carbonitrile (3j)[9]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 44.8 mg, 63% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.58 – 7.48 (m, 2H), 7.05 – 6.93 (m, 2H), 3.97 (t, *J* = 6.5 Hz, 2H), 1.84 (h, *J* = 7.1 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.9, 145.3, 132.6, 131.3, 128.3, 127.1, 119.1, 115.2, 110.1, 69.7, 22.6, 10.5.

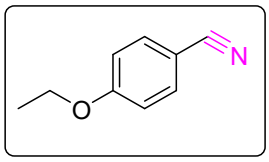


4-methoxybenzonitrile (3k)[10]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 18.4 mg, 46% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 7.6, 4.8 Hz, 2H), 7.04 – 6.85

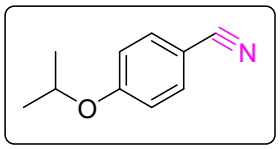
(m, 2H), 3.86 (d, *J* = 3.3 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.9, 134.0, 119.2, 114.8, 104.0, 55.6.



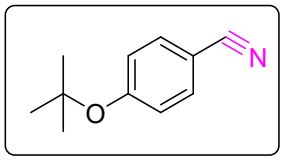
2-methoxybenzonitrile (3l)[11]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 9.9 mg, 25% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (t, *J* = 7.6 Hz, 2H), 7.04 – 6.96 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.2, 134.4, 133.7, 120.8, 116.5, 111.3, 101.8, 56.0.



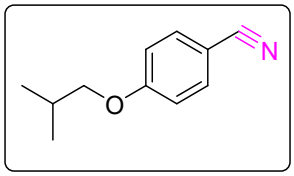
4-ethoxybenzonitrile (3m)[10]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 19.8 mg, 45% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.3, 134.0, 119.3, 115.2, 103.7, 63.9, 14.6.



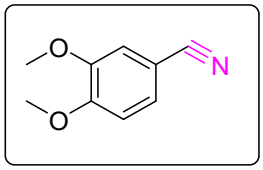
4-isopropoxybenzonitrile (3n)[10]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 20.3 mg, 42% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.61 (h, *J* = 6.1 Hz, 1H), 1.36 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.4, 134.0, 119.4, 116.1, 103.4, 70.4, 21.8.



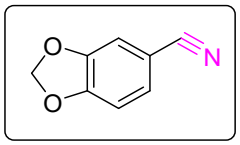
4-(tert-butoxy)benzonitrile (3o)[10]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 20.5 mg, 39% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 1.42 (d, *J* = 1.1 Hz, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.9, 133.4, 123.0, 119.1, 105.7, 80.2, 28.8.



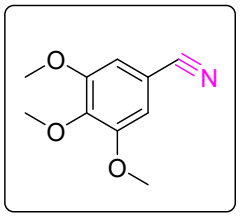
4-isobutoxybenzonitrile (3p)[10]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 22.1 mg, 42% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 – 7.55 (m, 2H), 6.95 – 6.92 (m, 2H), 3.76 (d, *J* = 6.5 Hz, 2H), 2.10 (dp, *J* = 13.3, 6.7 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.6, 134.0, 119.4, 115.2, 103.6, 74.7, 28.1, 19.1.



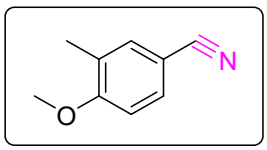
3,4-dimethoxybenzonitrile (3q)[11]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 18.6 mg, 38% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 1H), 7.08 (t, *J* = 3.1 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 3.91 (dd, *J* = 19.6, 4.3 Hz, 6H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.9, 149.2, 126.4, 119.2, 114.0, 111.3, 103.9, 56.1, 56.1.



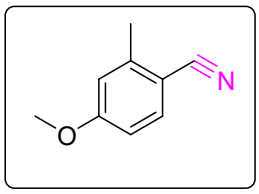
benzo[d][1,3]dioxole-5-carbonitrile (3r)[11]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 18.0 mg, 41% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.04 (d, *J* = 1.8 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.07 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.5, 148.1, 128.2, 118.9, 111.4, 109.1, 105.0, 102.2.



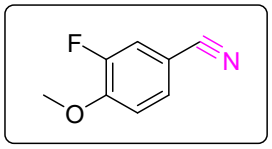
3,4,5-trimethoxybenzonitrile (3s)[12]: Rf = 0.25 (Petroleum ether/EtOAc, 10:1). 17.9 mg, 31% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.87 (s, 2H), 3.90 (s, 3H), 3.88 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.6, 142.5, 118.9, 109.5, 106.7, 61.0, 56.4.



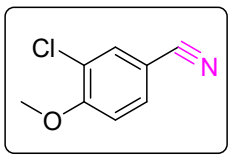
4-methoxy-3-methylbenzonitrile (3t)[13]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 18.1 mg, 41% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.41 – 7.38 (m, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.1, 133.9, 132.0, 128.2, 110.1, 103.4, 55.6, 16.0.



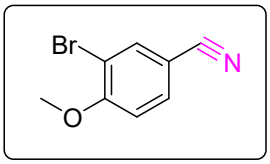
4-methoxy-2-methylbenzonitrile (3u)[13]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 13.2 mg, 30% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 8.0, 4.2 Hz, 1H), 6.85 – 6.72 (m, 2H), 3.83 (d, *J* = 3.6 Hz, 3H), 2.50 (d, *J* = 3.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.8, 144.1, 134.2, 118.5, 115.7, 112.1, 104.5, 55.5, 20.7.



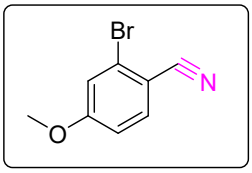
3-fluoro-4-methoxybenzonitrile (3v)[14]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 23.1 mg, 54% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 (dt, *J* = 8.5, 1.6 Hz, 1H), 7.36 (dt, *J* = 10.6, 1.5 Hz, 1H), 7.03 (t, *J* = 8.4 Hz, 1H), 3.96 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.9 (d, *J* = 9.1 Hz), 151.8 (d, *J* = 250.6 Hz), 129.7 (d, *J* = 3.0 Hz), 119.6 (d, *J* = 21.1 Hz), 118.0 (d, *J* = 3.0 Hz), 113.6 (d, *J* = 3.0 Hz), 104.0 (d, *J* = 7.6 Hz), 56.4. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -132.0.



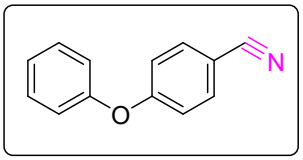
3-chloro-4-methoxybenzonitrile (3w)[15]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 25.5 mg, 51% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 2.1 Hz, 1H), 7.56 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.6, 133.6, 132.5, 123.6, 117.9, 112.2, 104.8, 56.5.



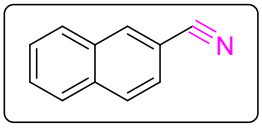
3-bromo-4-methoxybenzonitrile (3x)[16]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 28.5 mg, 45% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 2.5 Hz, 1H), 7.60 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 136.7, 133.2, 117.7, 112.3, 111.9, 105.3, 56.6.



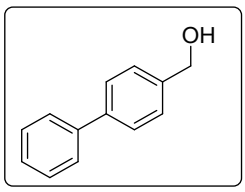
2-bromo-4-methoxybenzonitrile (3y)[16]: Rf = 0.25 (Petroleum ether/EtOAc, 20:1). 27.8 mg, 44% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 6.91 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.2, 135.3, 126.5, 118.7, 117.6, 114.0, 107.5, 56.0.



4-phenoxybenzonitrile (3z)[12]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 31.0 mg, 53% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.7, 154.9, 134.1, 130.3, 125.2, 120.4, 118.8, 118.0, 105.9.



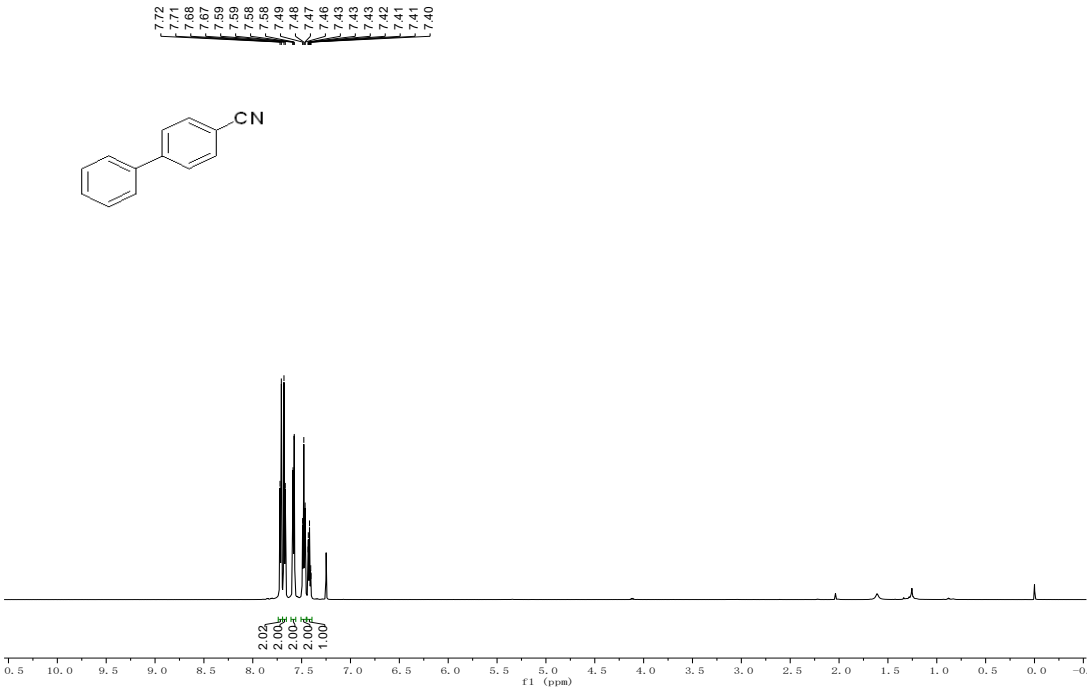
2-naphthonitrile (3aa)[10]: Rf = 0.25 (Petroleum ether/EtOAc, 30:1). 128.9 mg, 60% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.90 – 7.83 (m, 3H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.58 (dd, *J* = 12.2, 7.9 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 134.7, 134.1, 132.3, 129.2, 129.1, 128.4, 128.1, 127.7, 126.3, 119.3, 109.4.



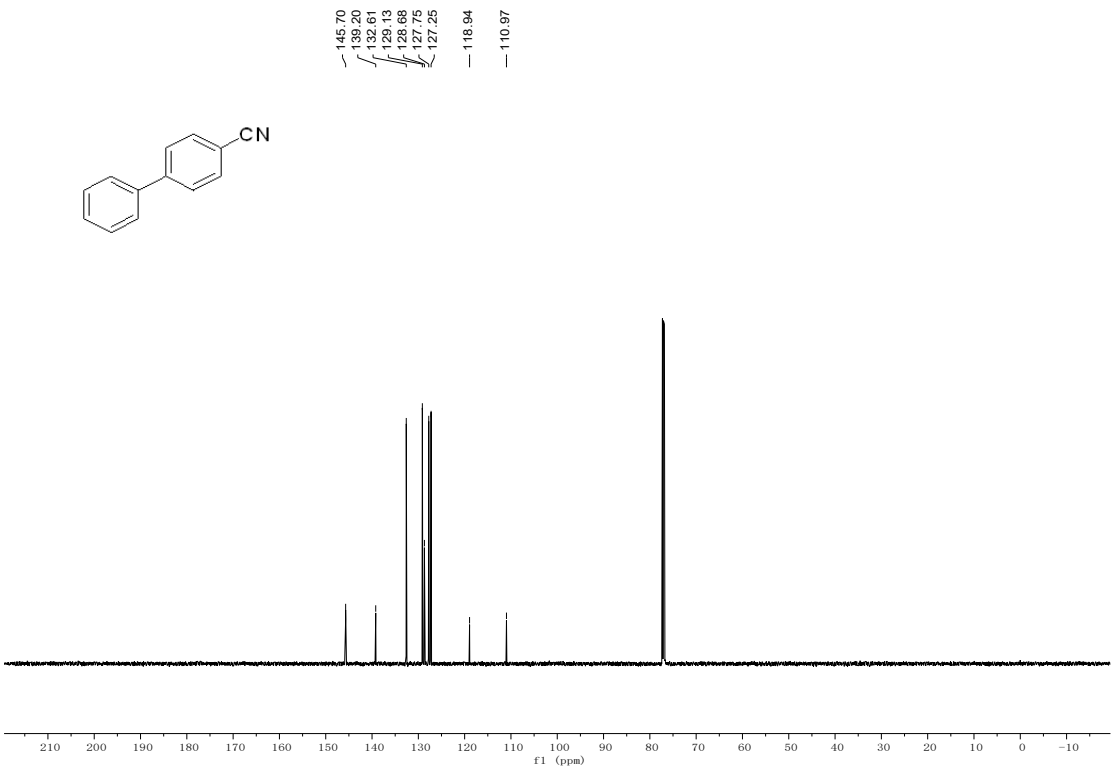
[1,1'-biphenyl]-4-ylmethanol (12)[10]: Rf = 0.25 (Petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.1 Hz, 4H), 7.51 – 7.46 (m, 4H), 7.40 (td, *J* = 7.2, 1.3 Hz, 1H), 4.76 (s, 2H), 1.99 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.9, 140.7, 139.9, 128.8, 127.5, 127.4, 127.3, 127.1, 65.1.

8. NMR spectra of products

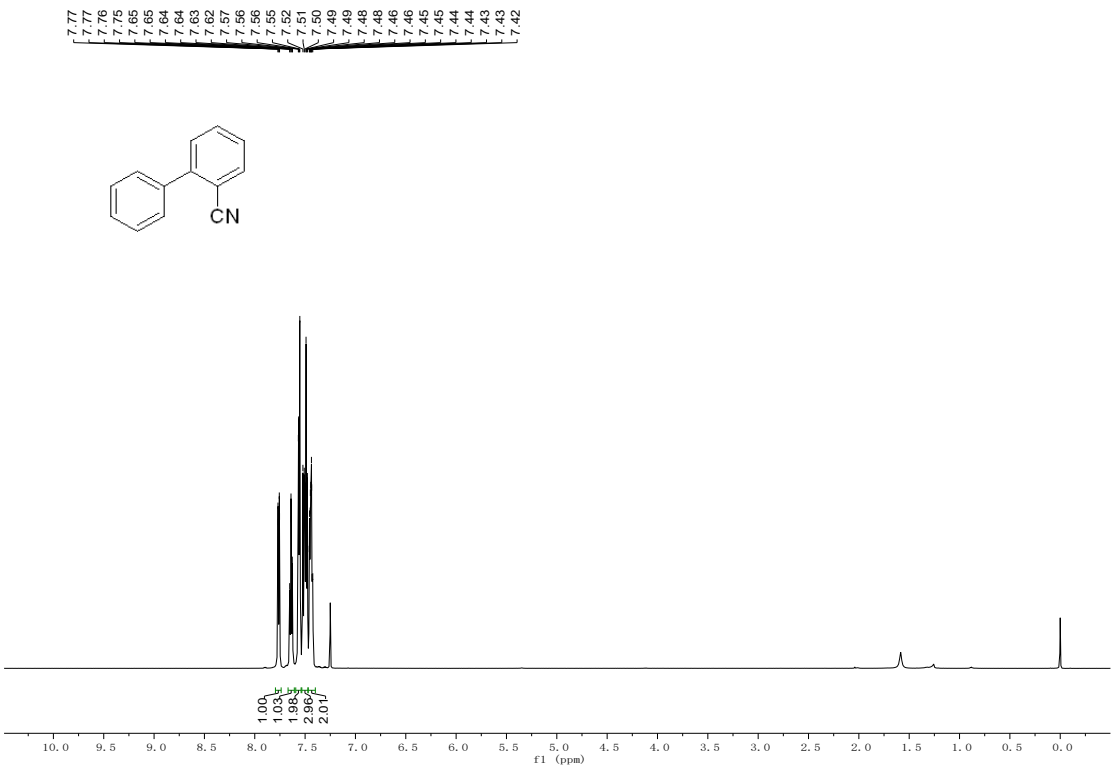
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3a



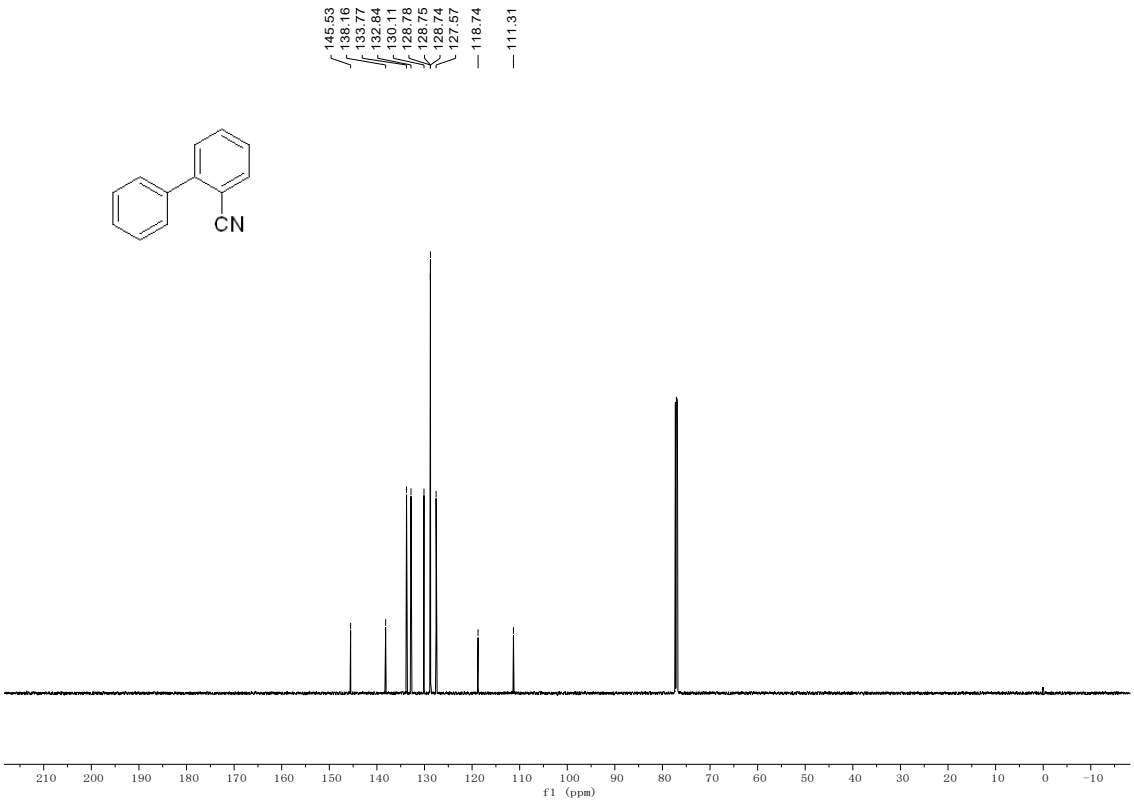
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3a



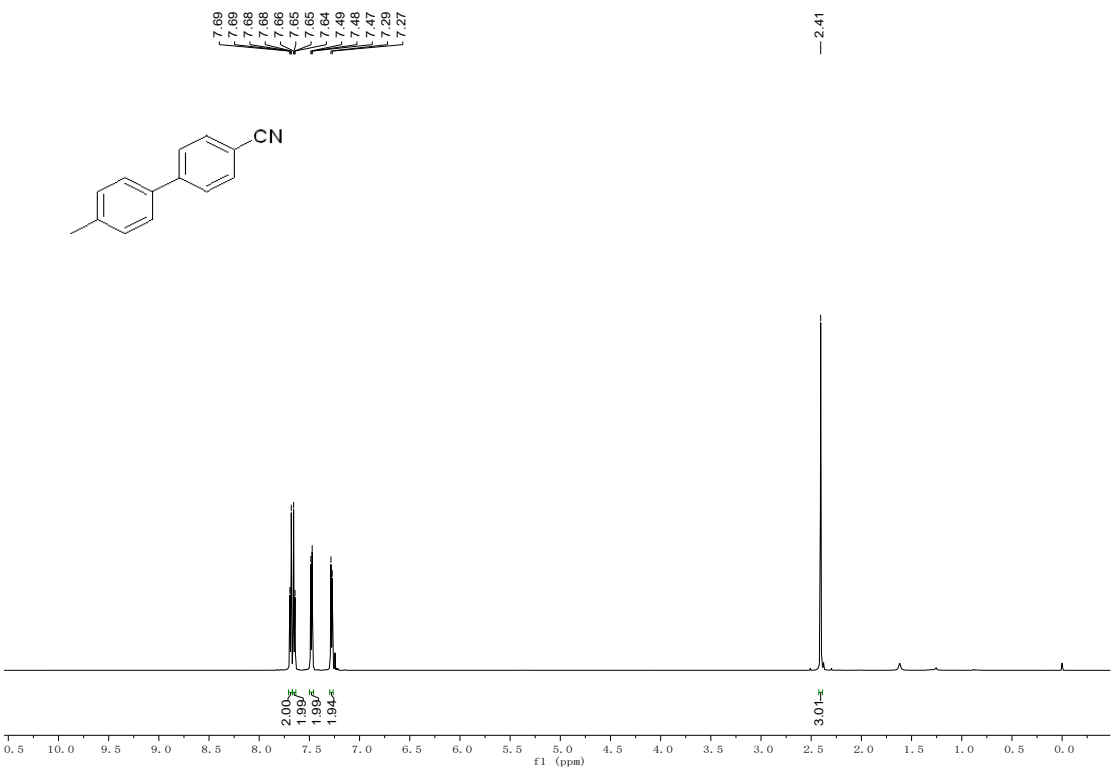
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3b



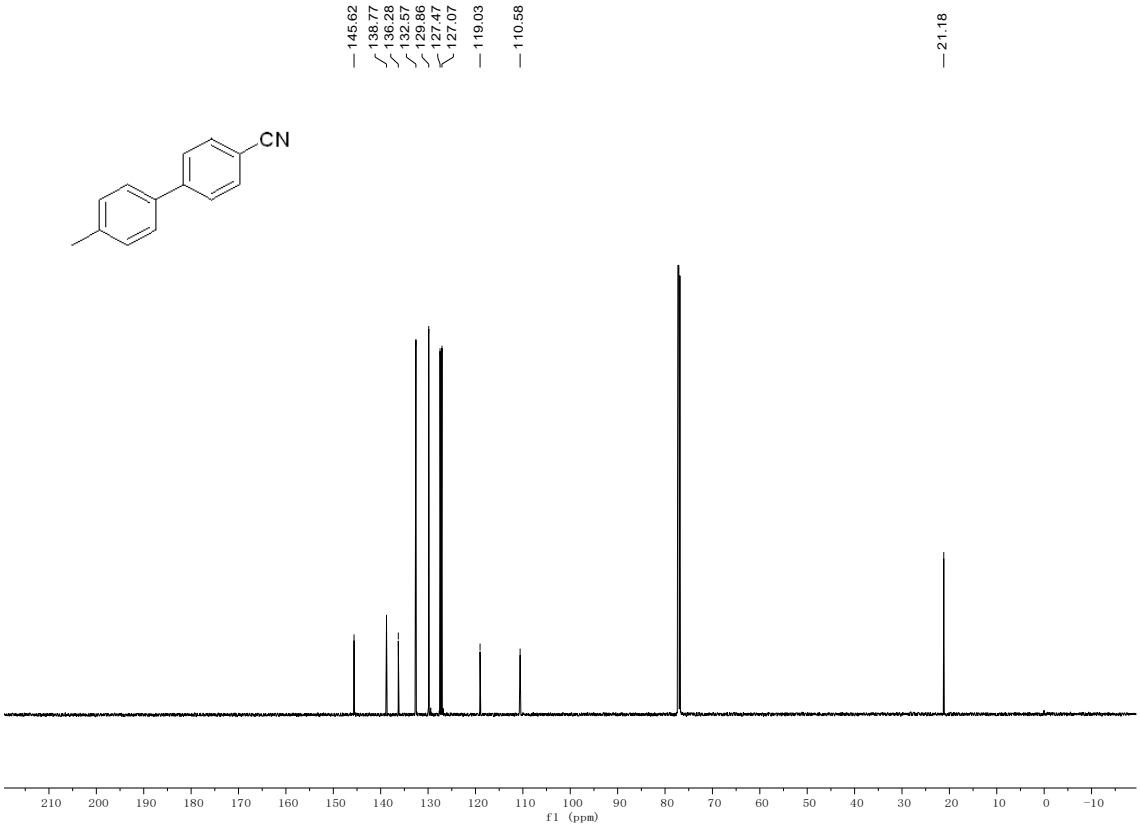
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3b



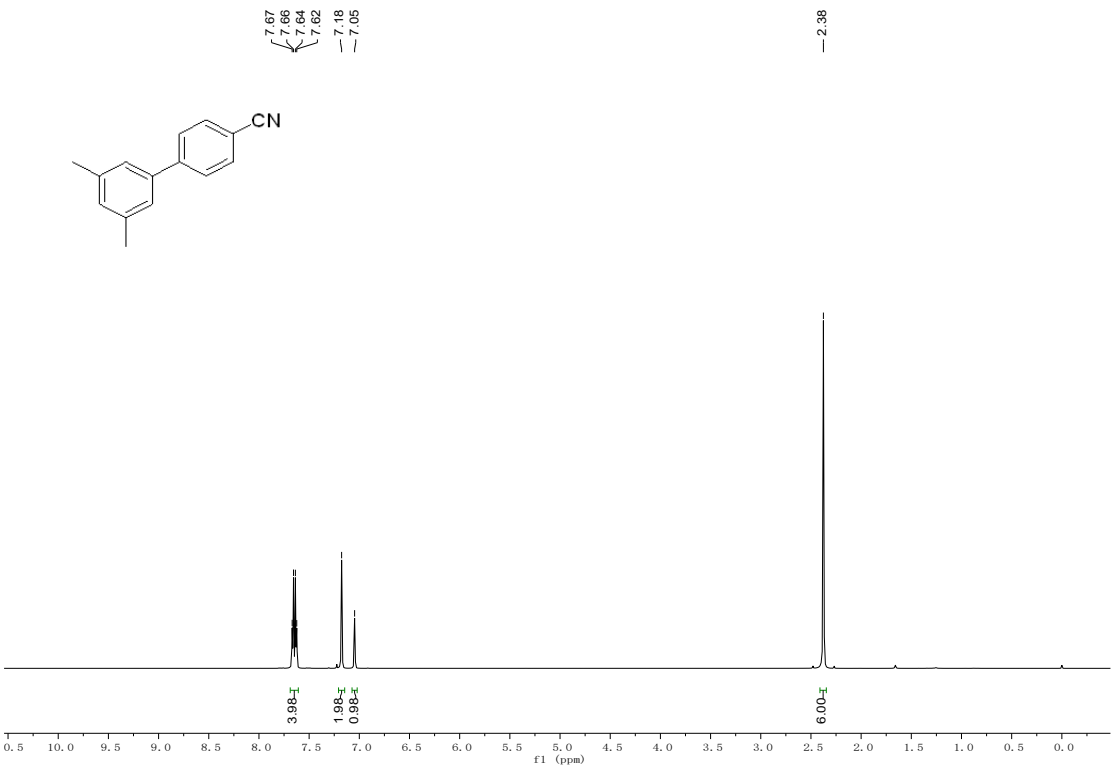
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3c



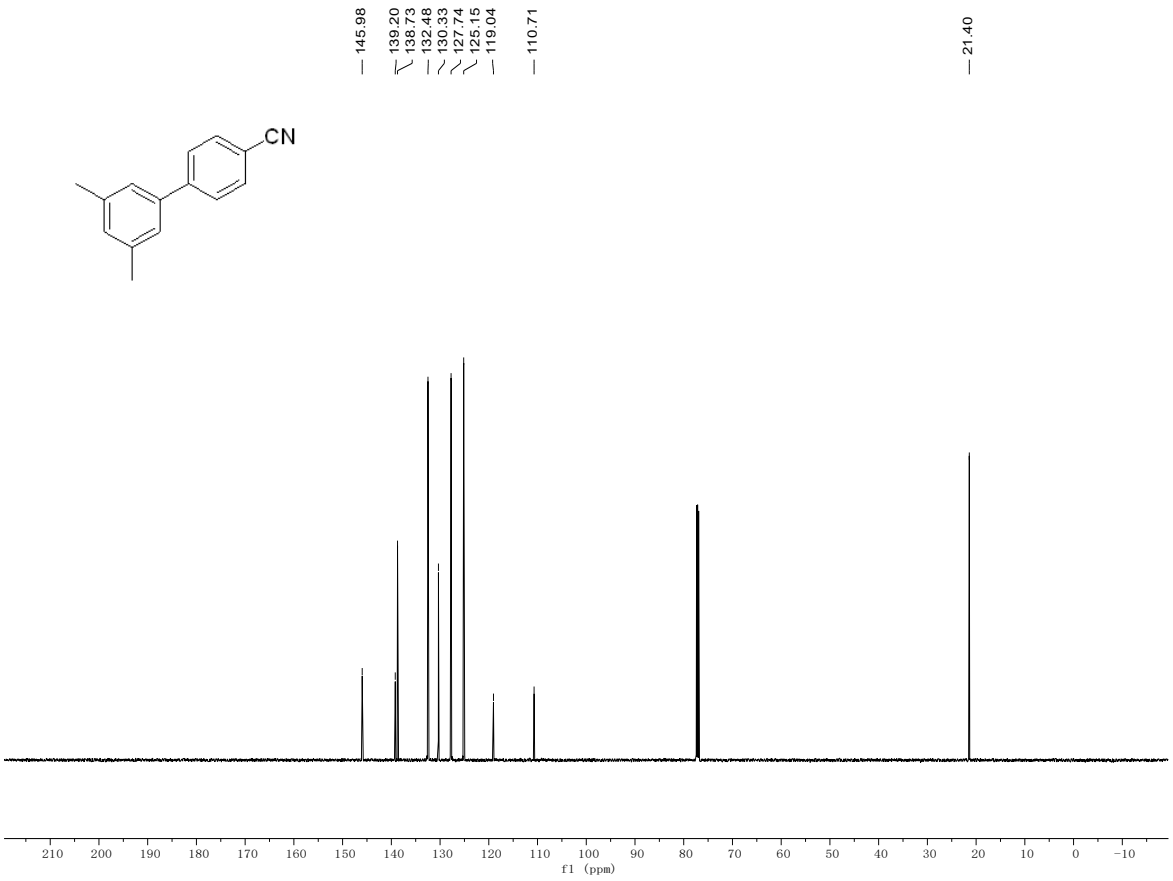
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3c



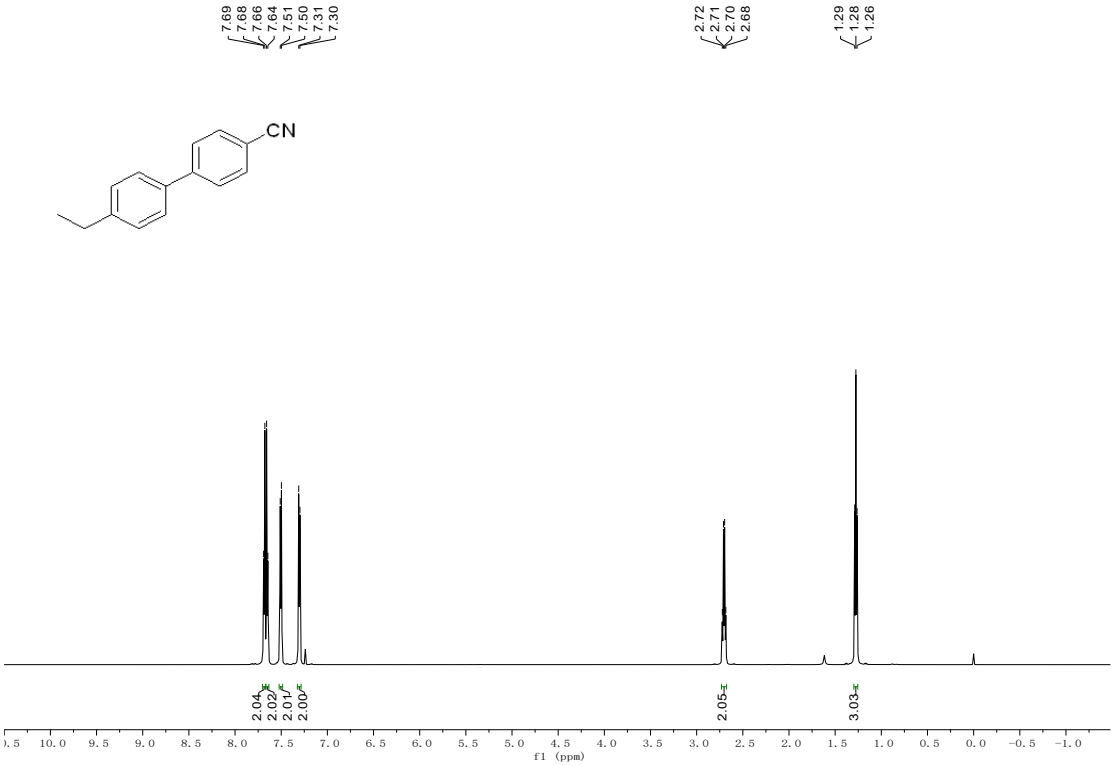
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3d



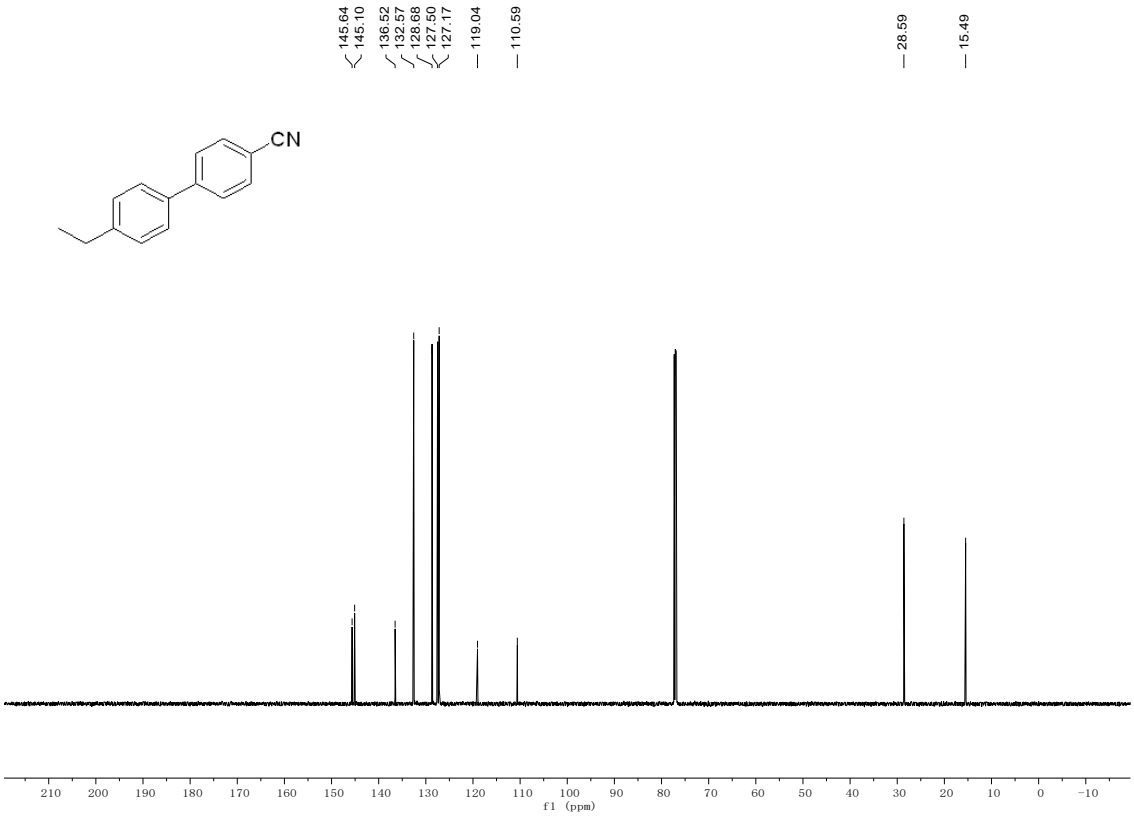
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of 3d



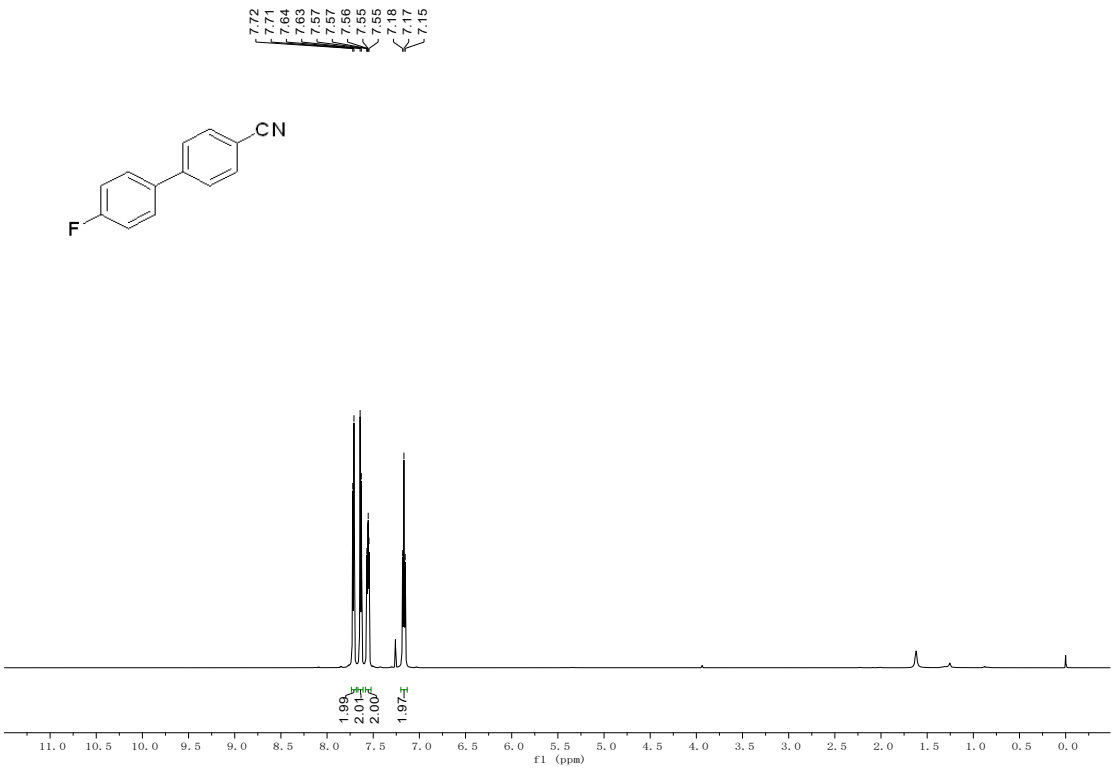
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3e



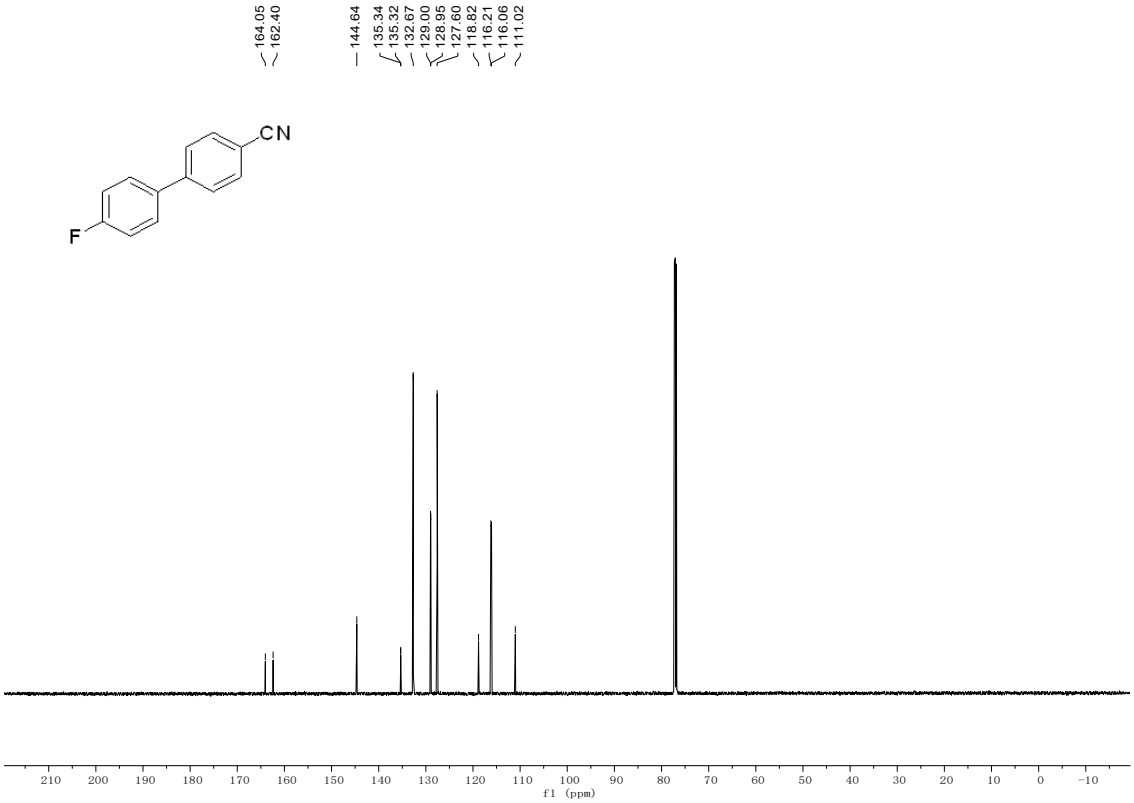
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3e



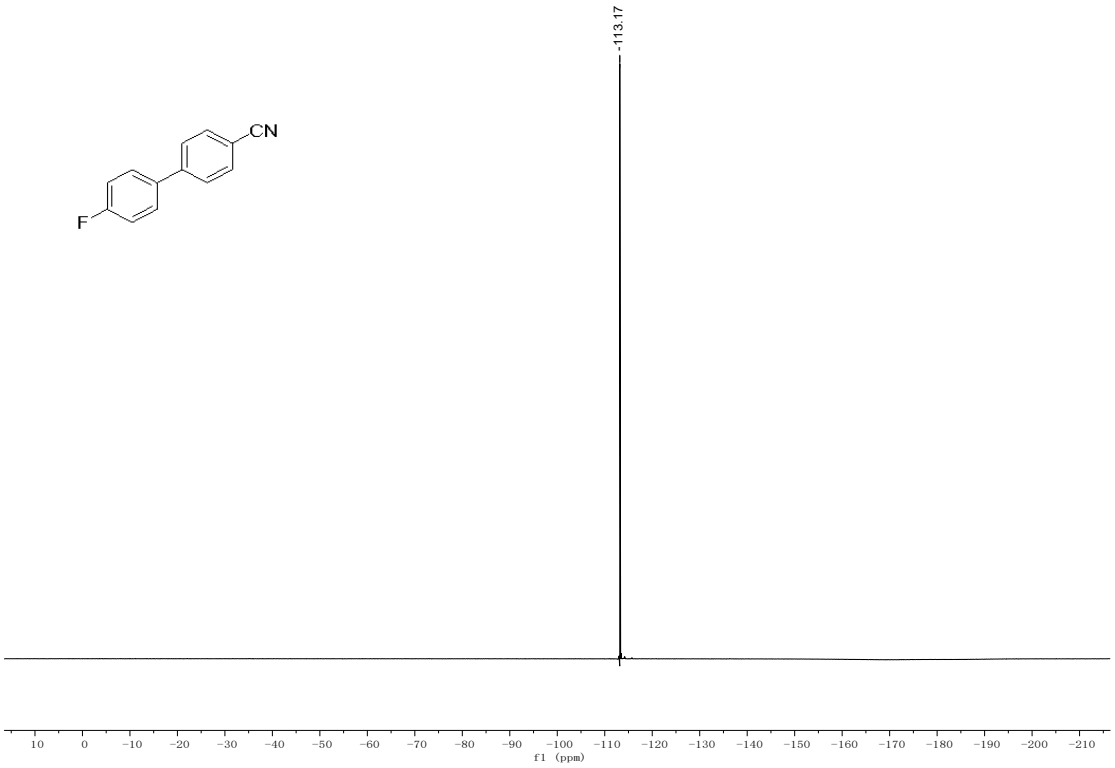
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3f



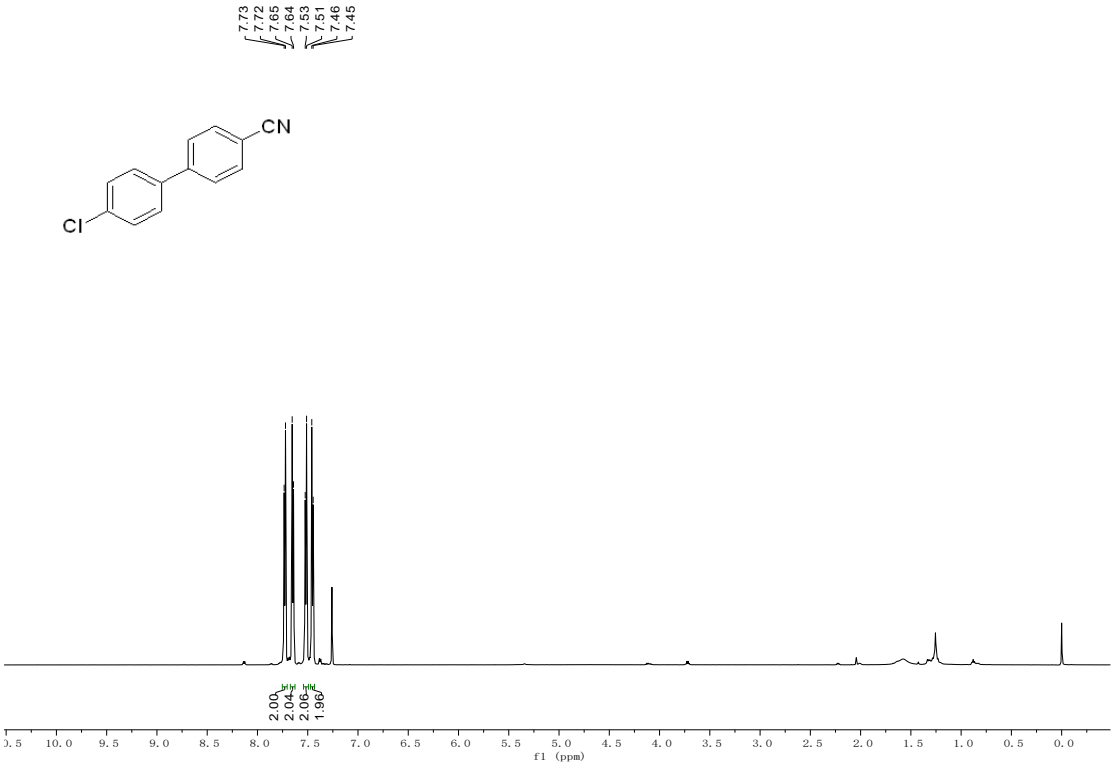
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3f



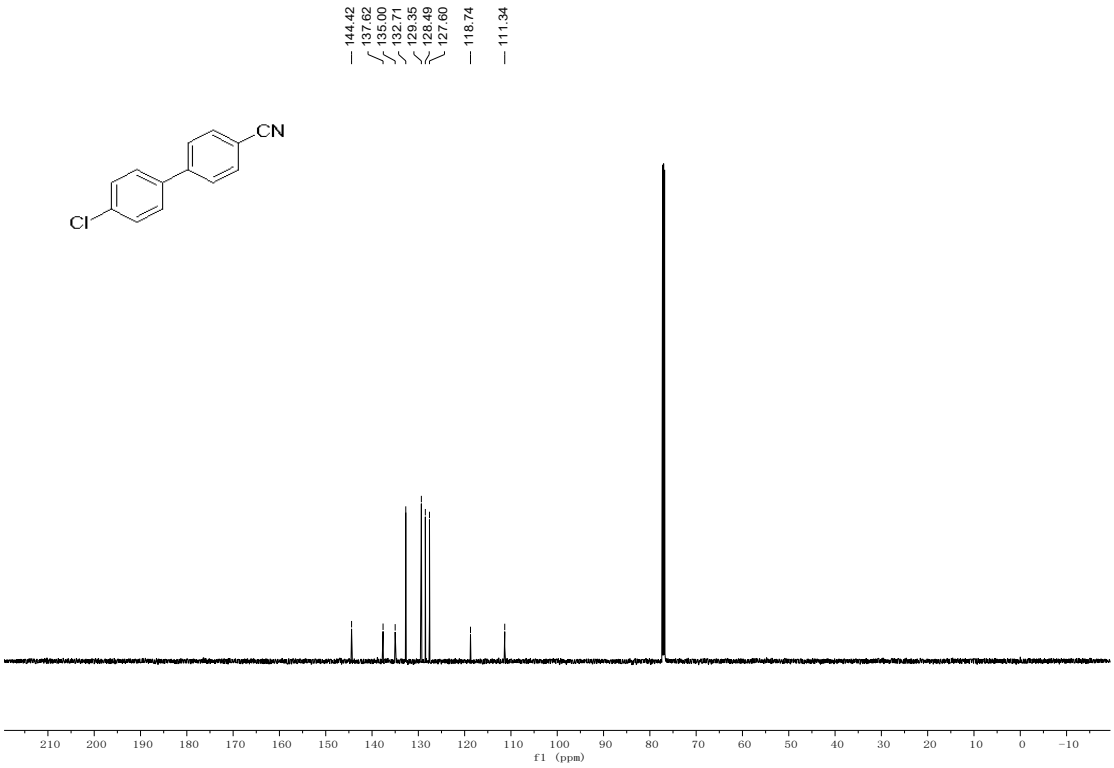
^{19}F-NMR Spectrum (565 MHz, $CDCl_3$) of 3f



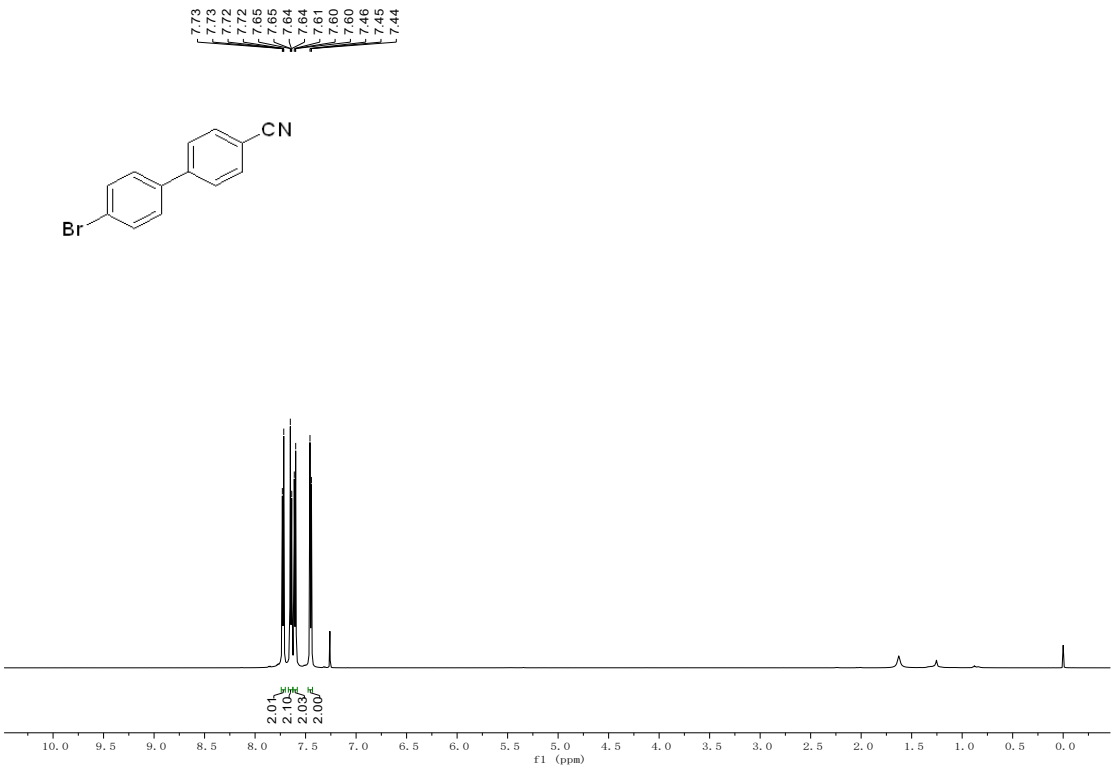
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3g



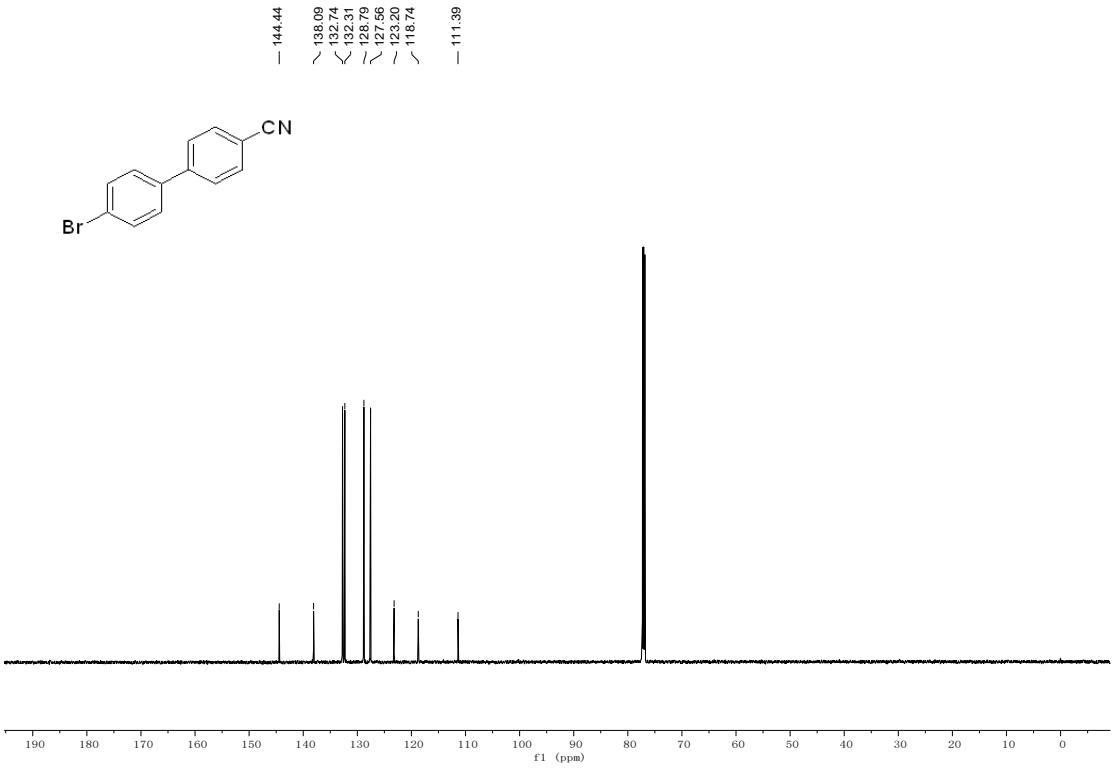
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3g



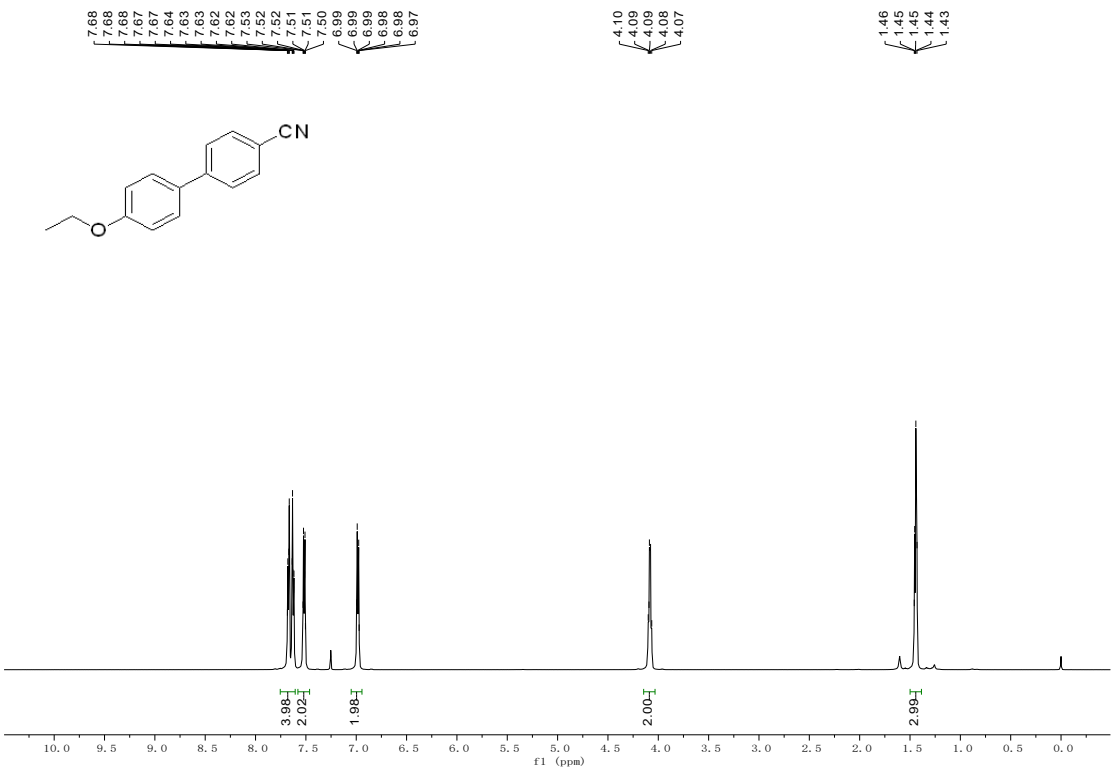
[1]H-NMR Spectrum (600MHz, DMSO) of 3h



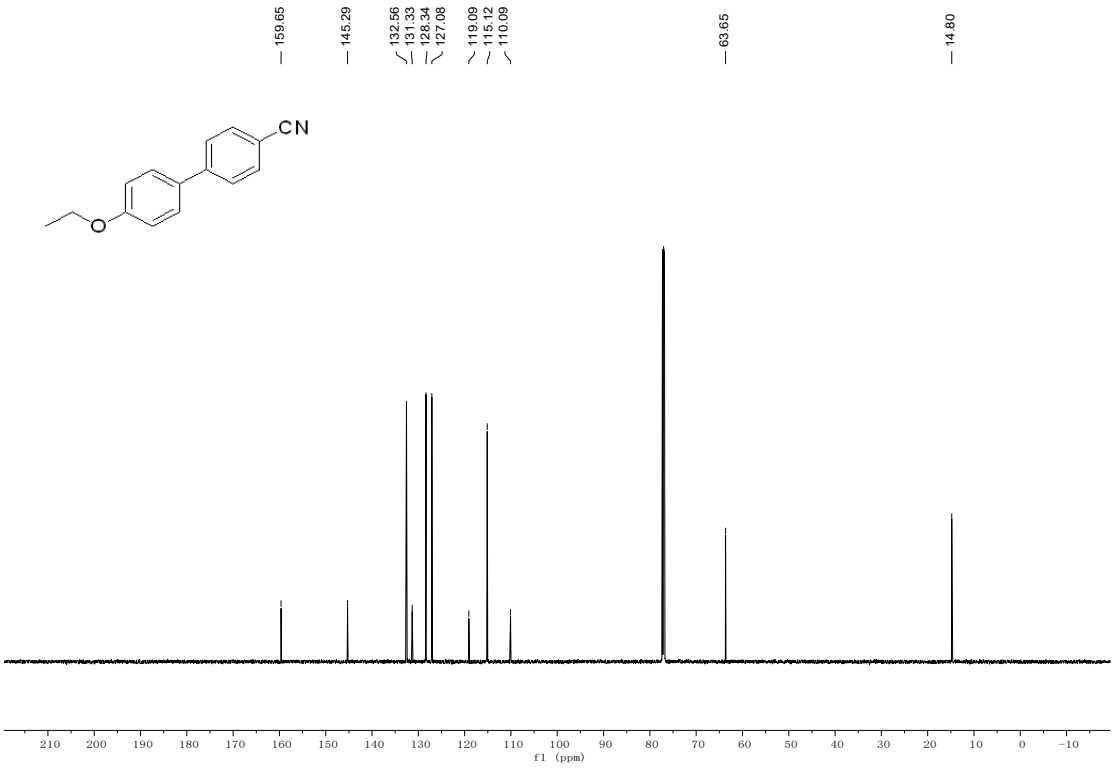
[13]C-NMR Spectrum (151MHz, DMSO) of 3h



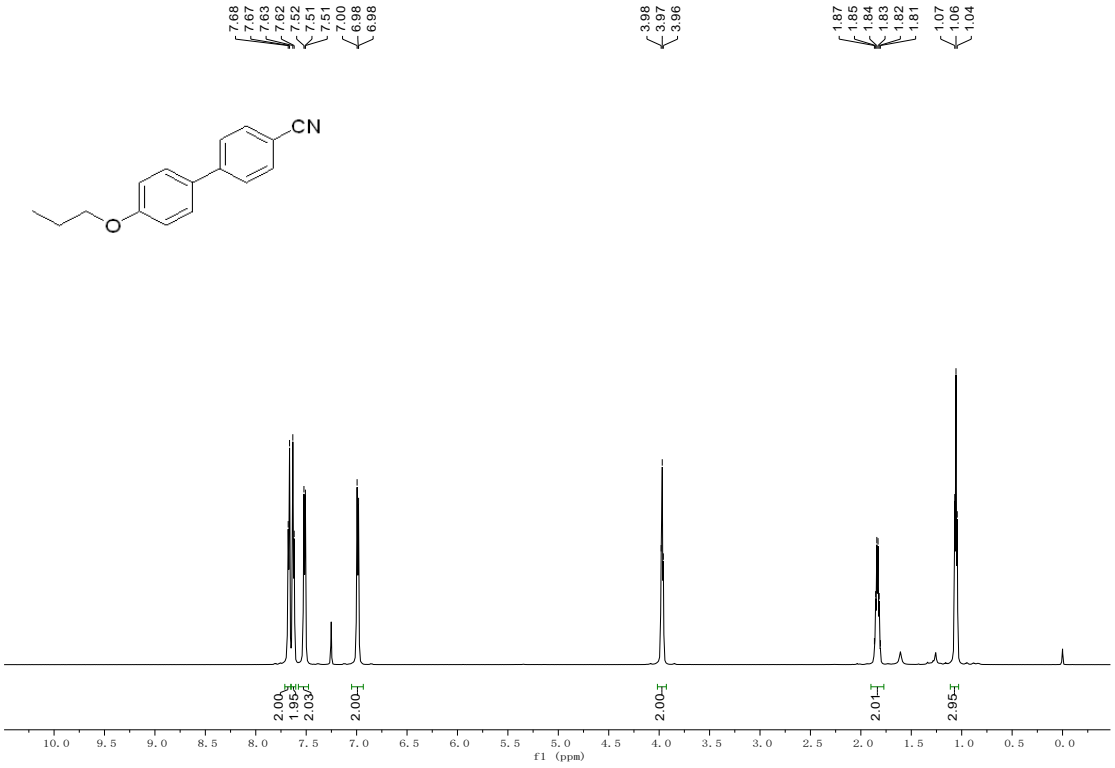
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3i



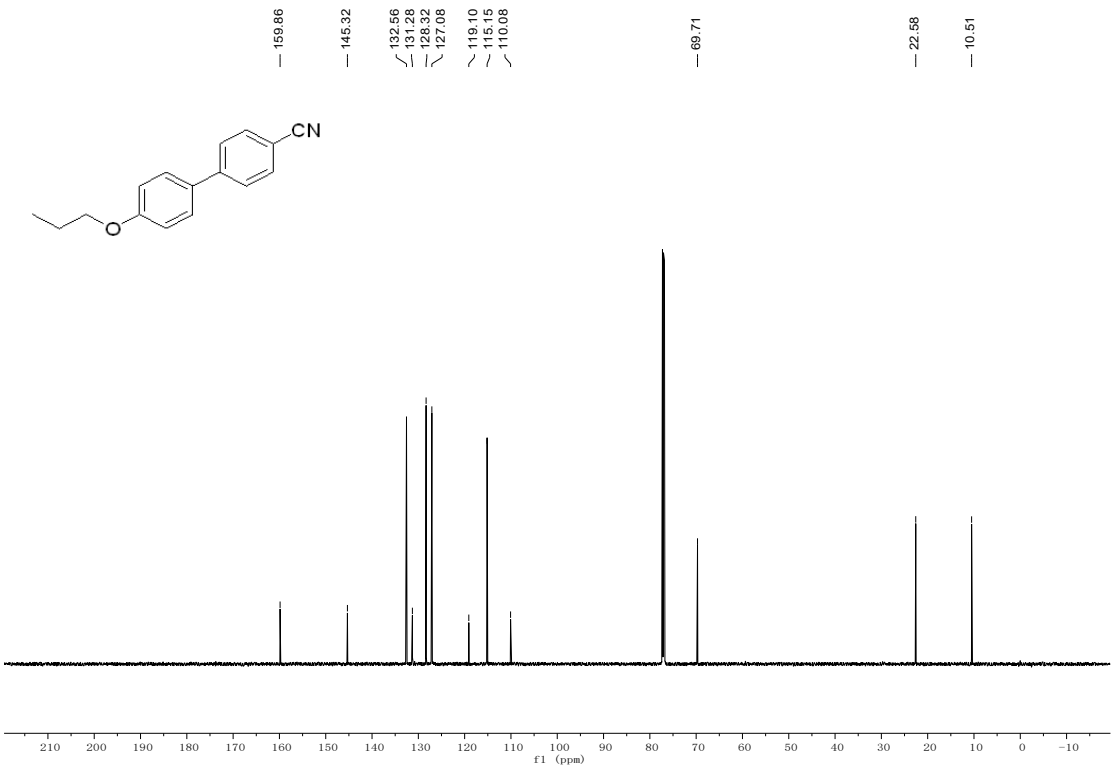
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3i



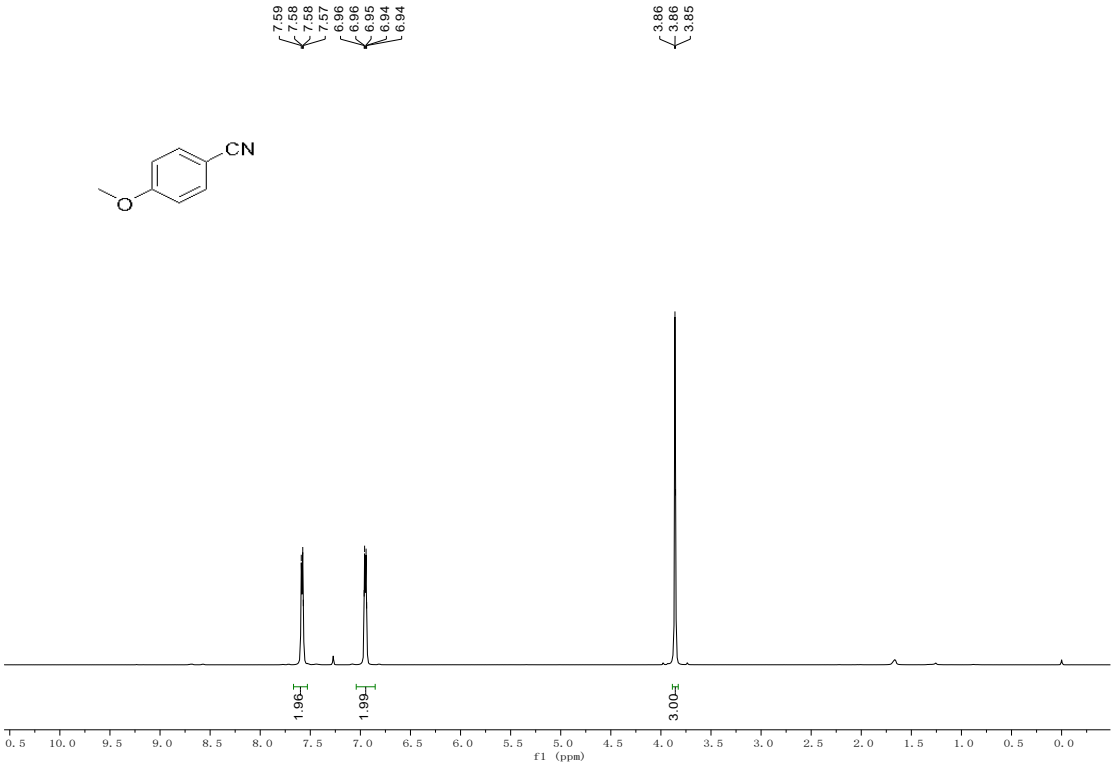
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3j



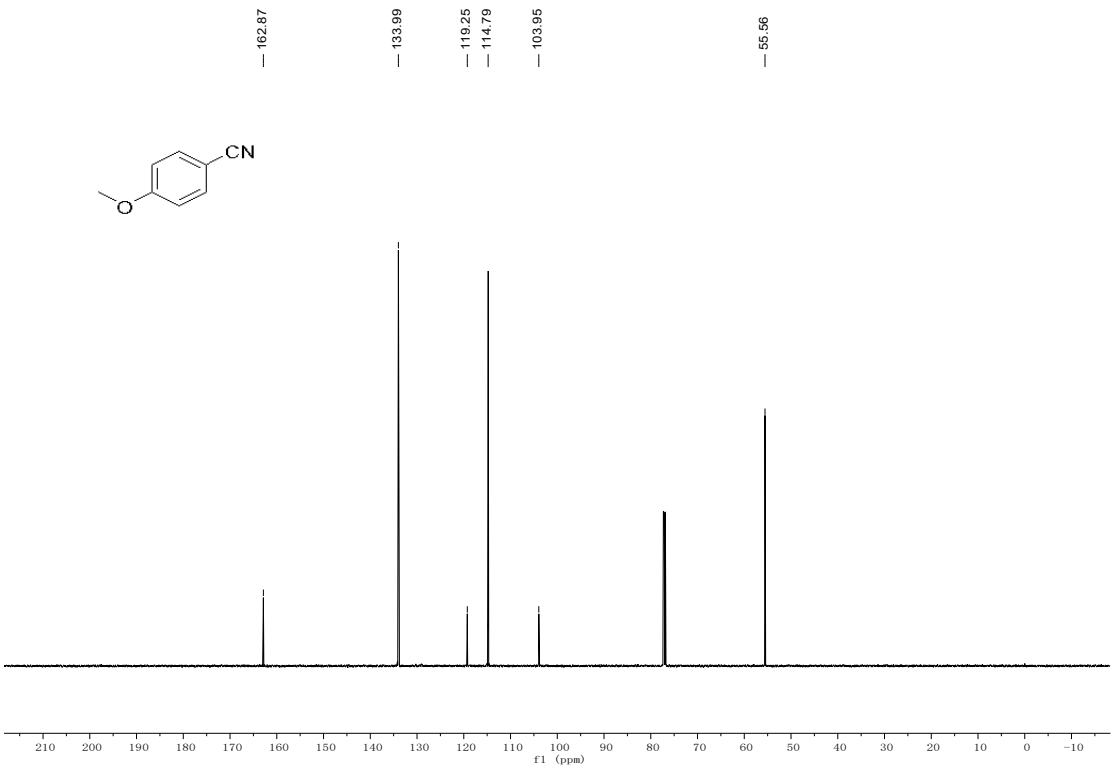
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3j



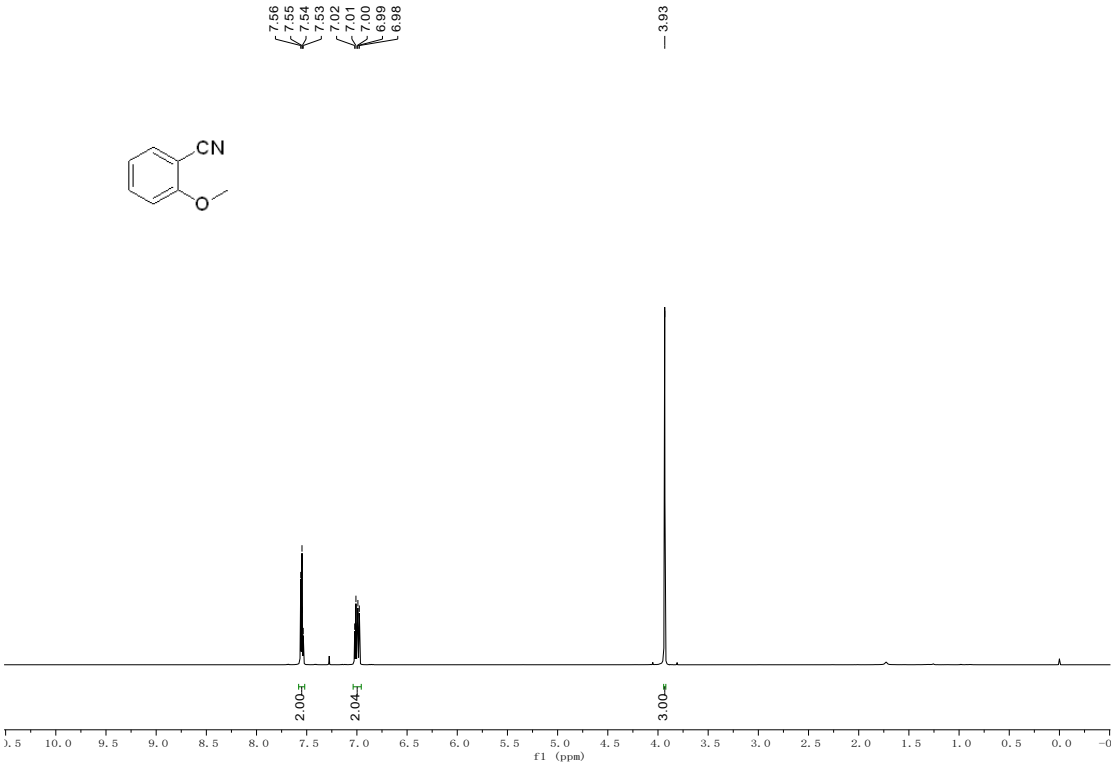
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3k



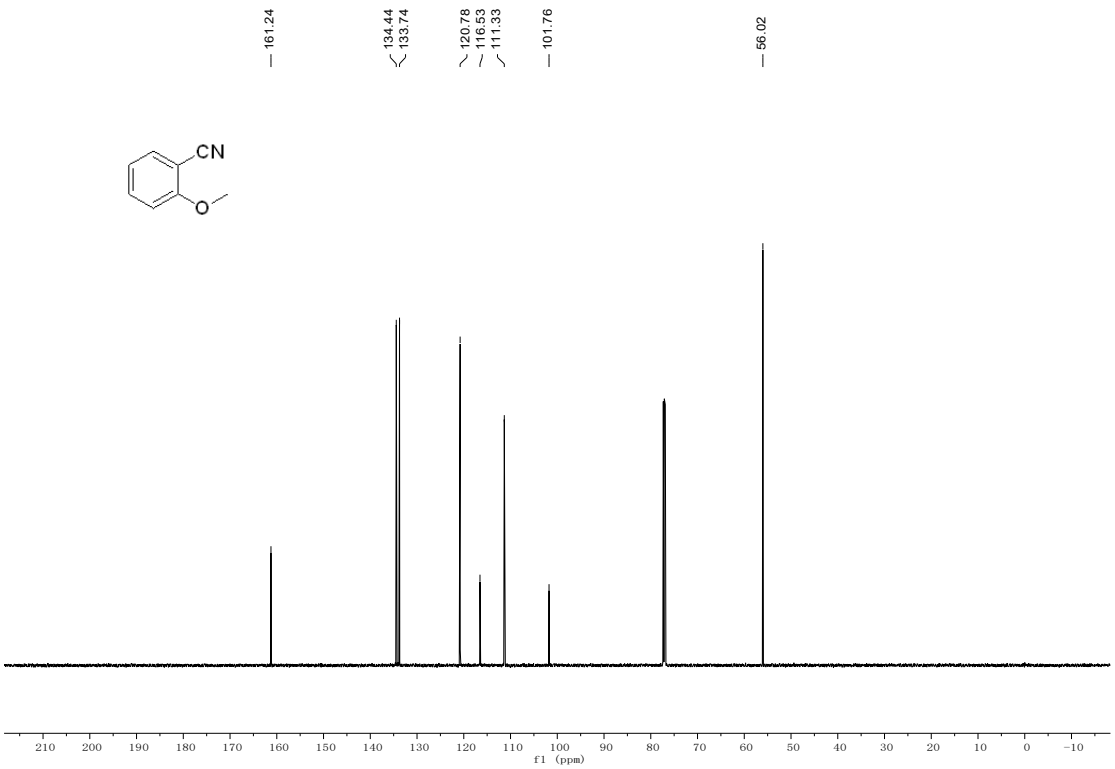
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of 3k



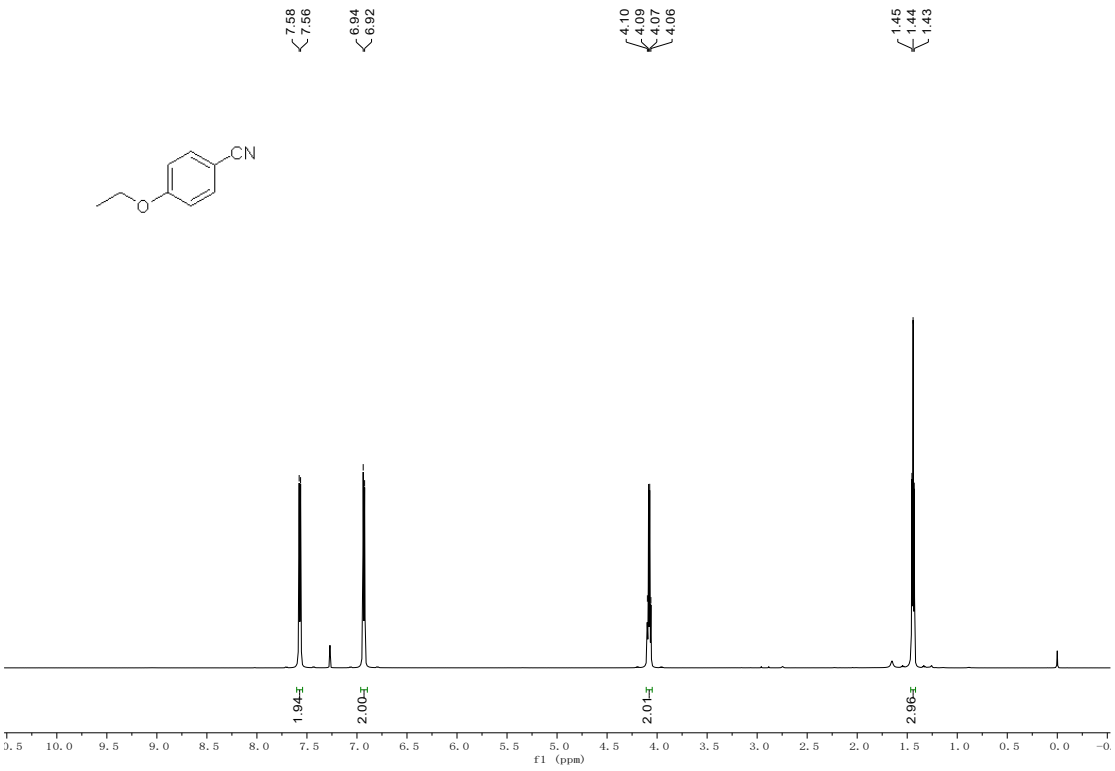
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3l



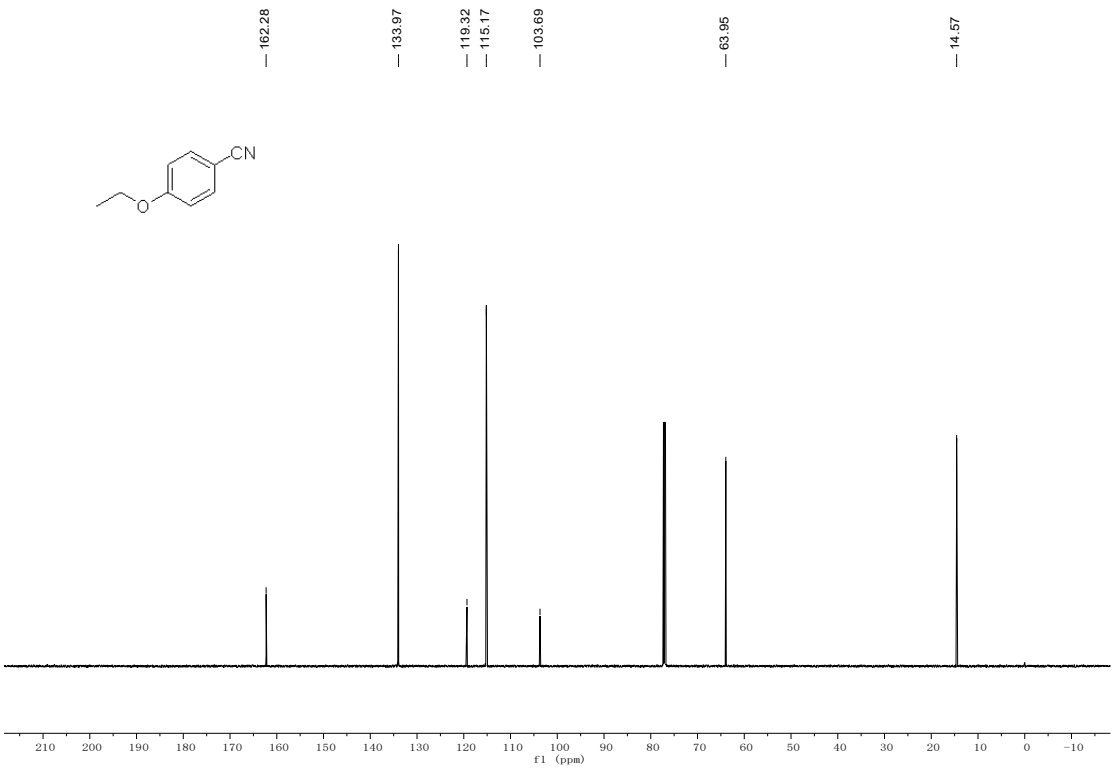
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3l



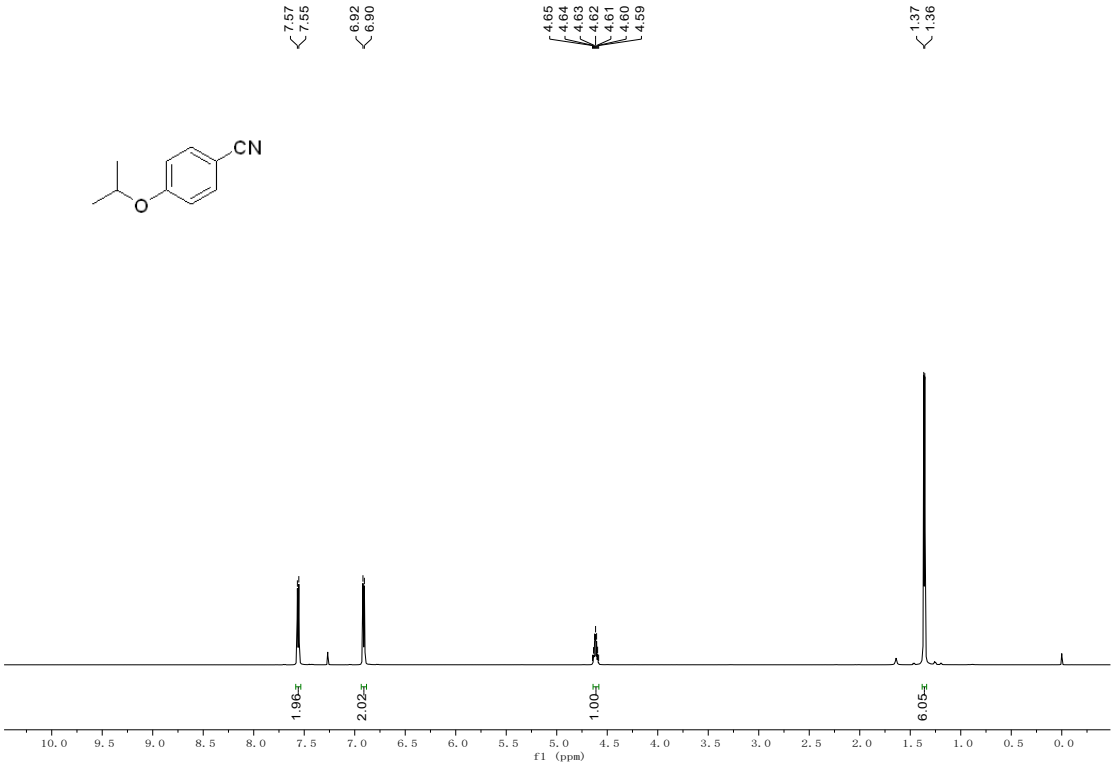
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3m



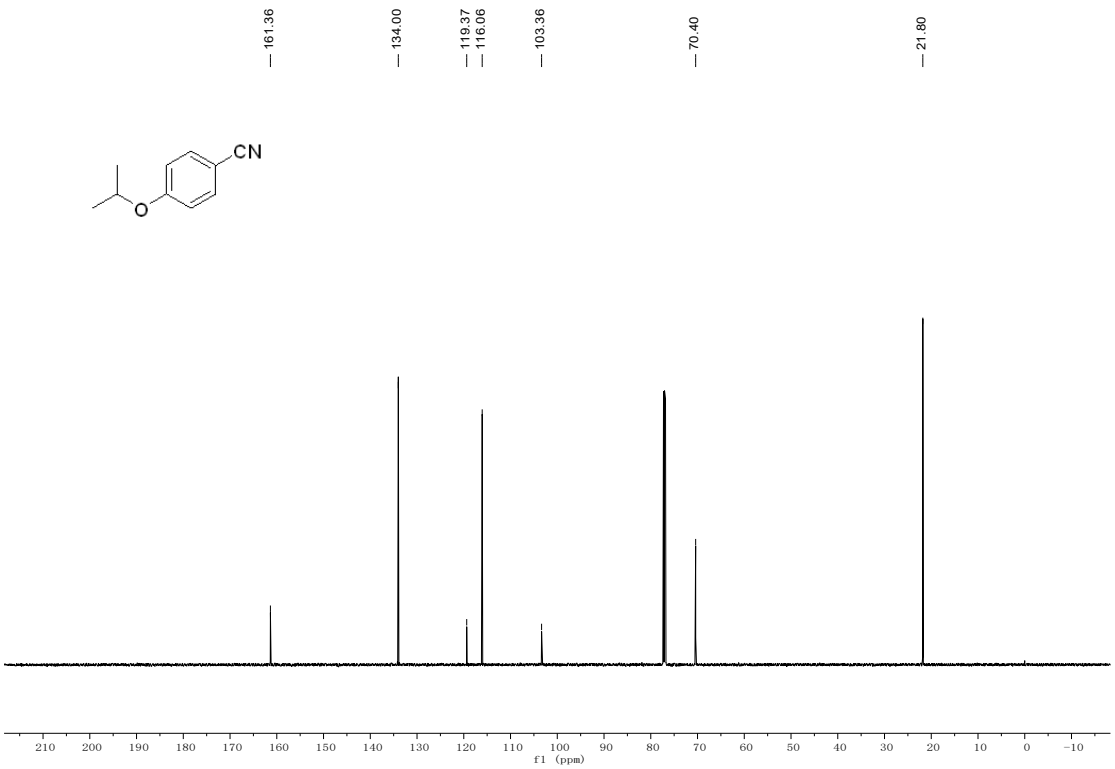
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3m



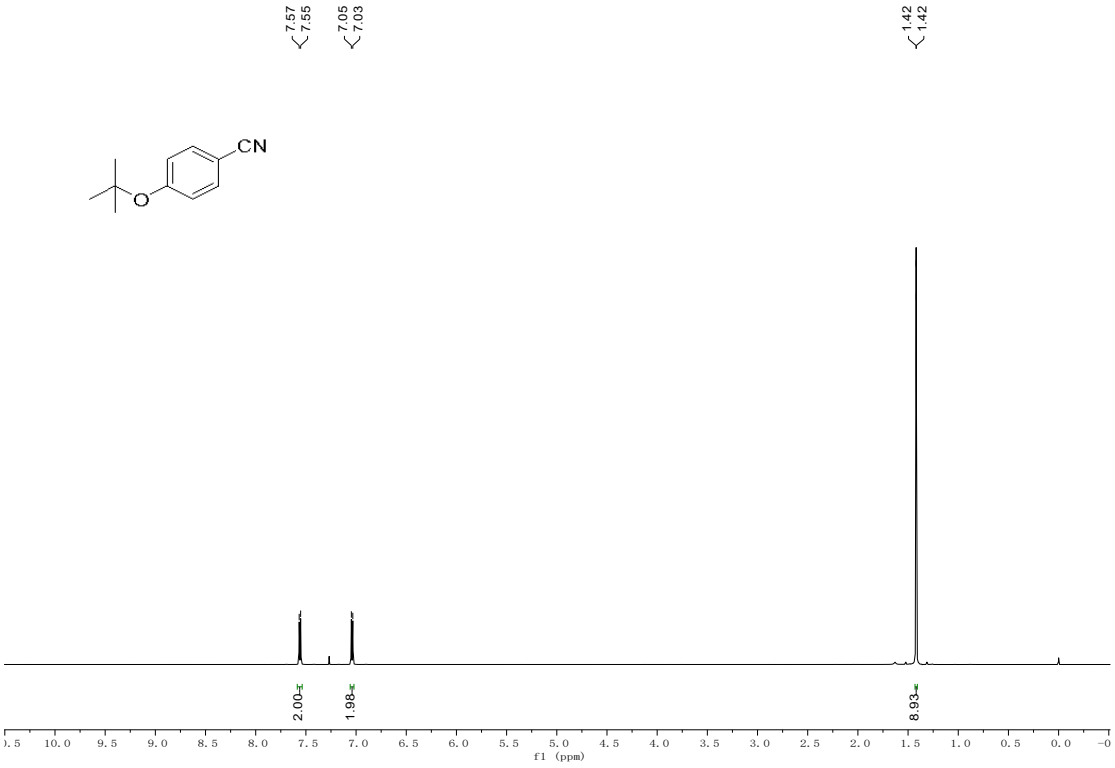
^{1}H-NMR Spectrum (600MHz, $CDCl_3$) of 3n



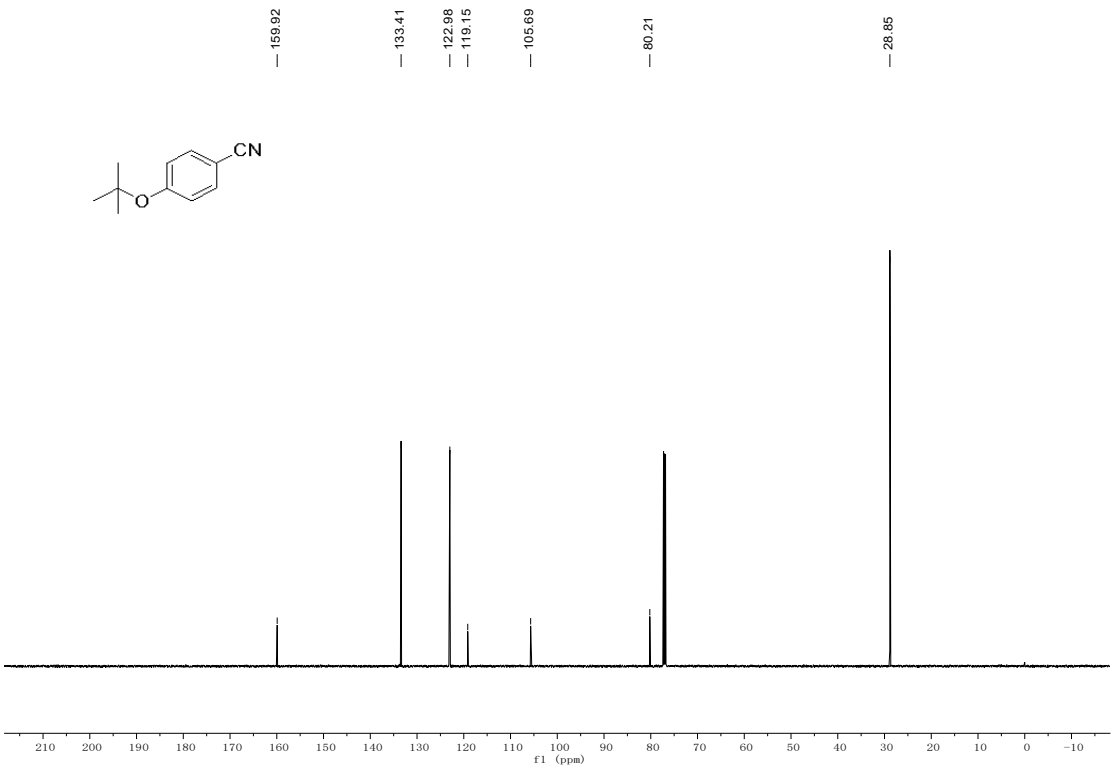
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3n



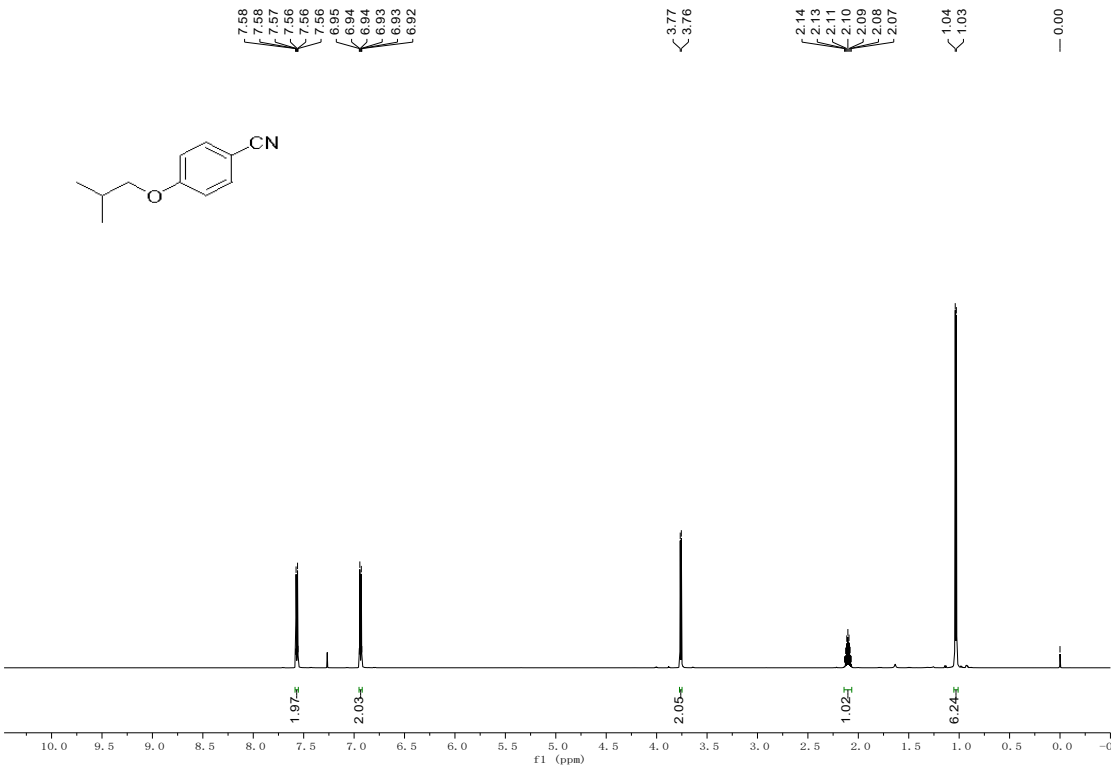
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3o



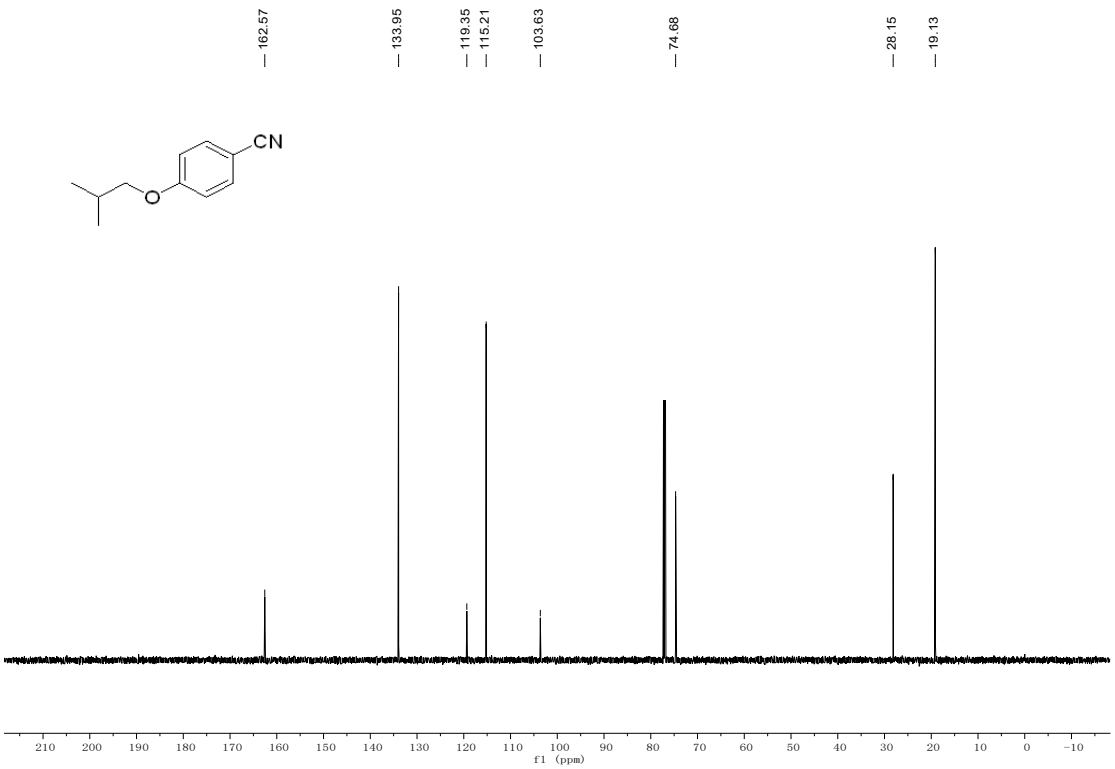
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3o



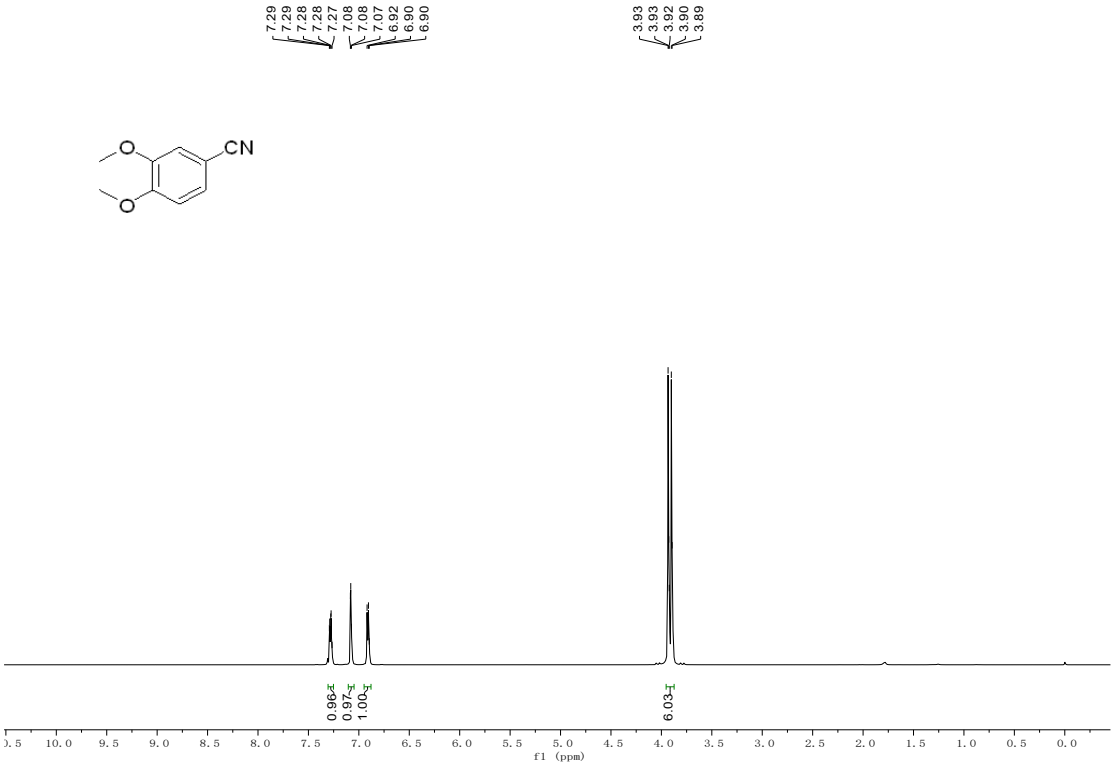
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3p



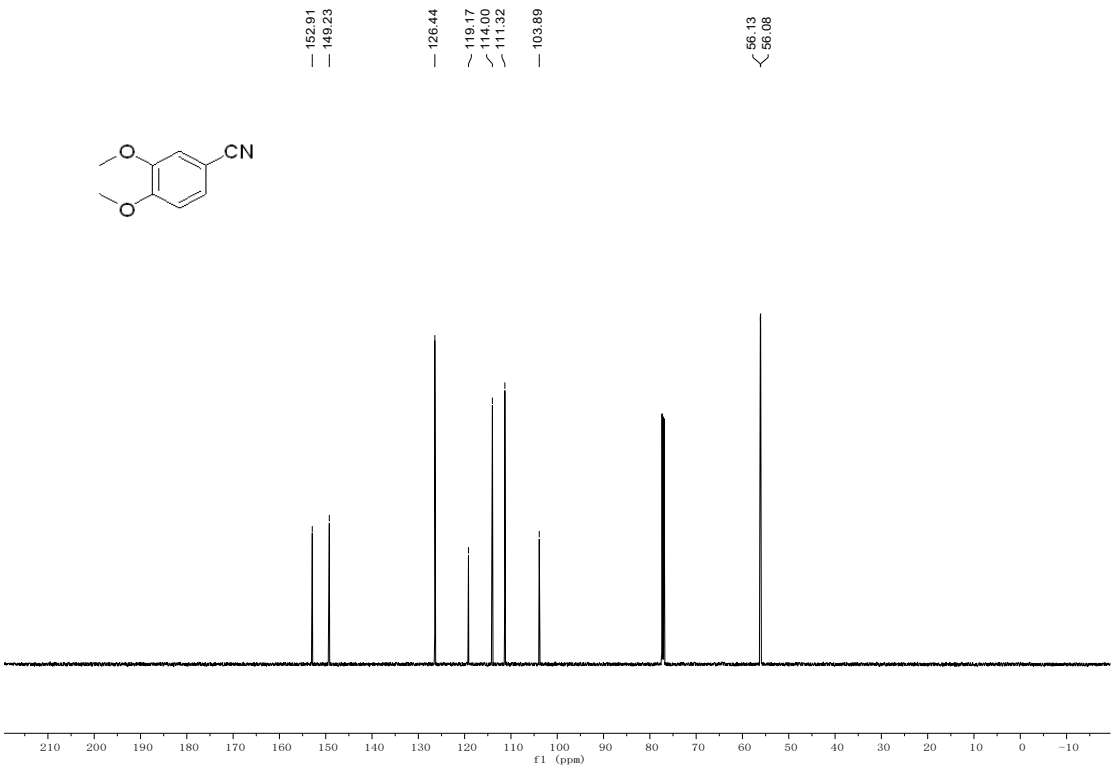
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3p



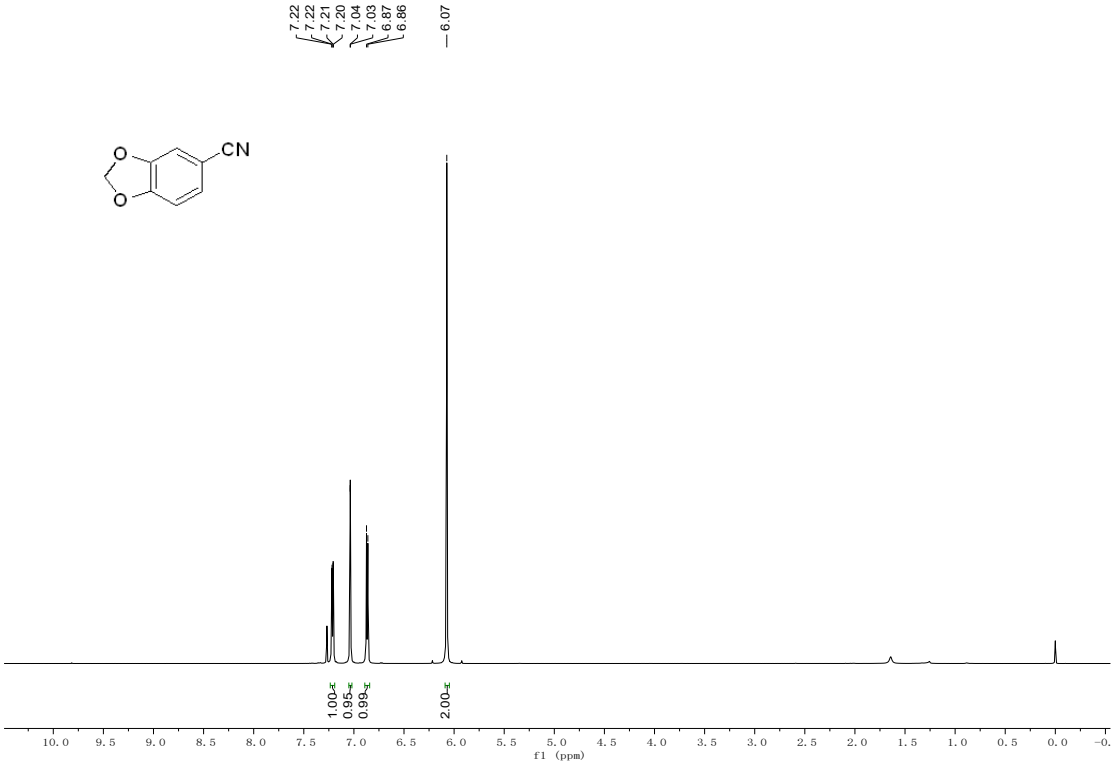
^{1}H-NMR Spectrum (600MHz, $CDCl_3$) of 3q



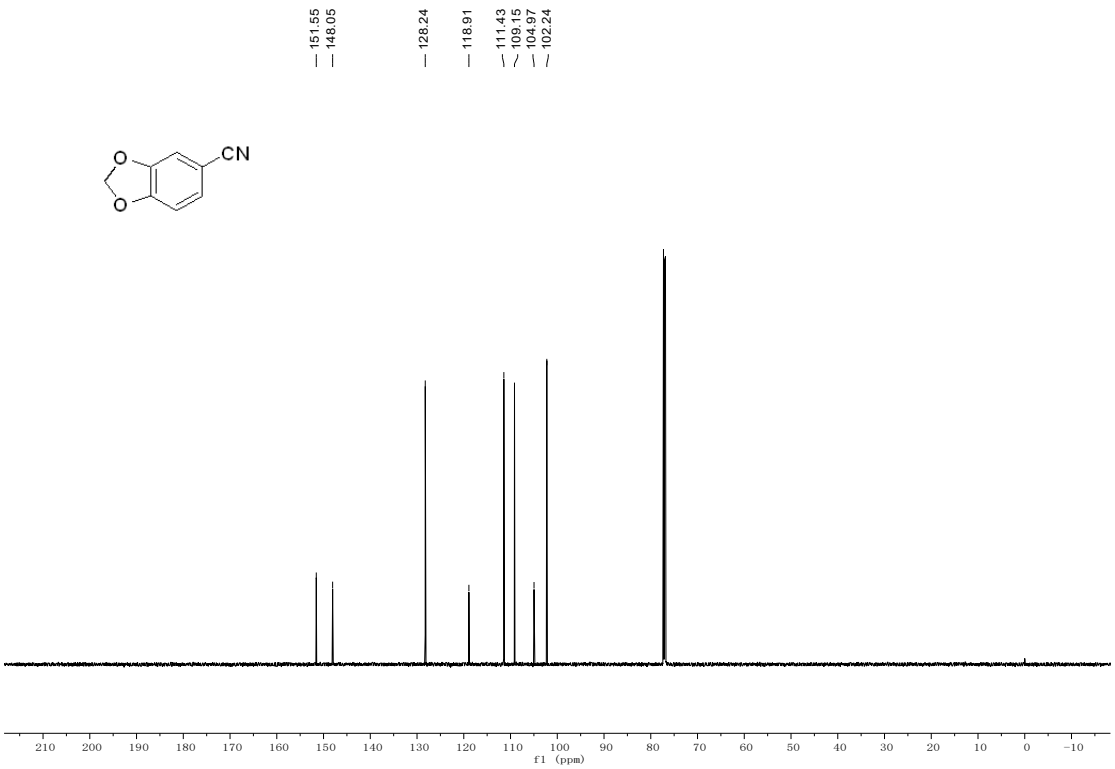
^{13}C-NMR Spectrum (151MHz, DMSO) of 3q



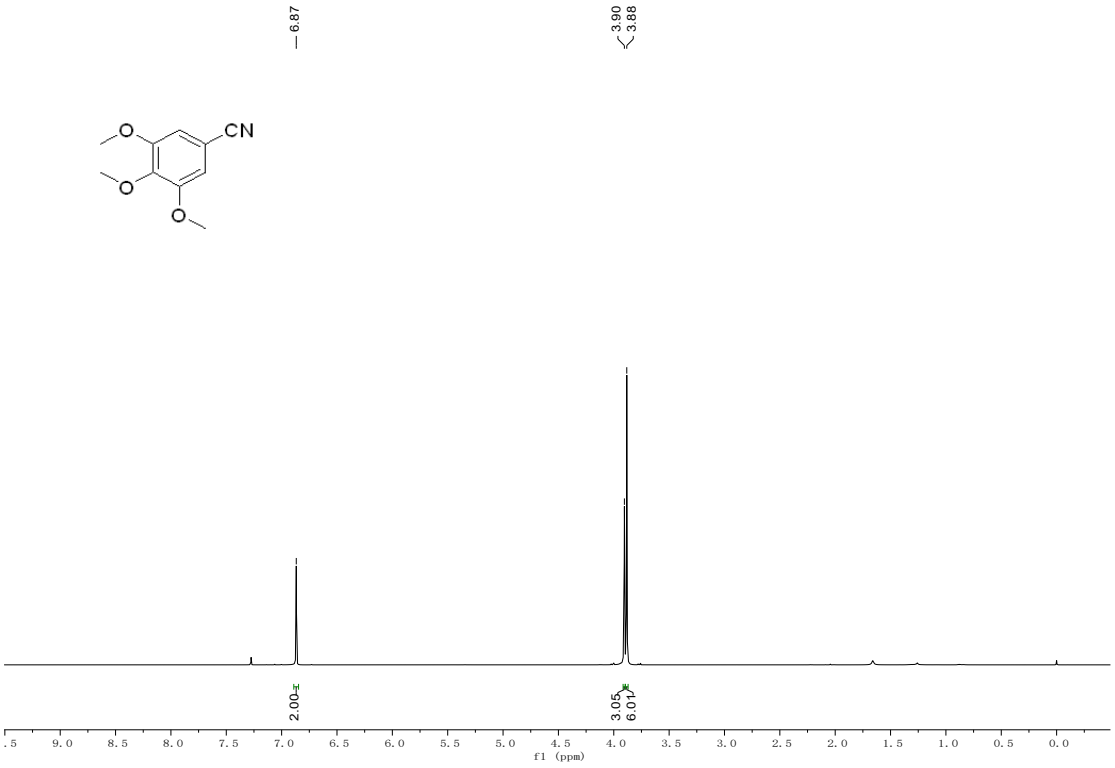
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3r



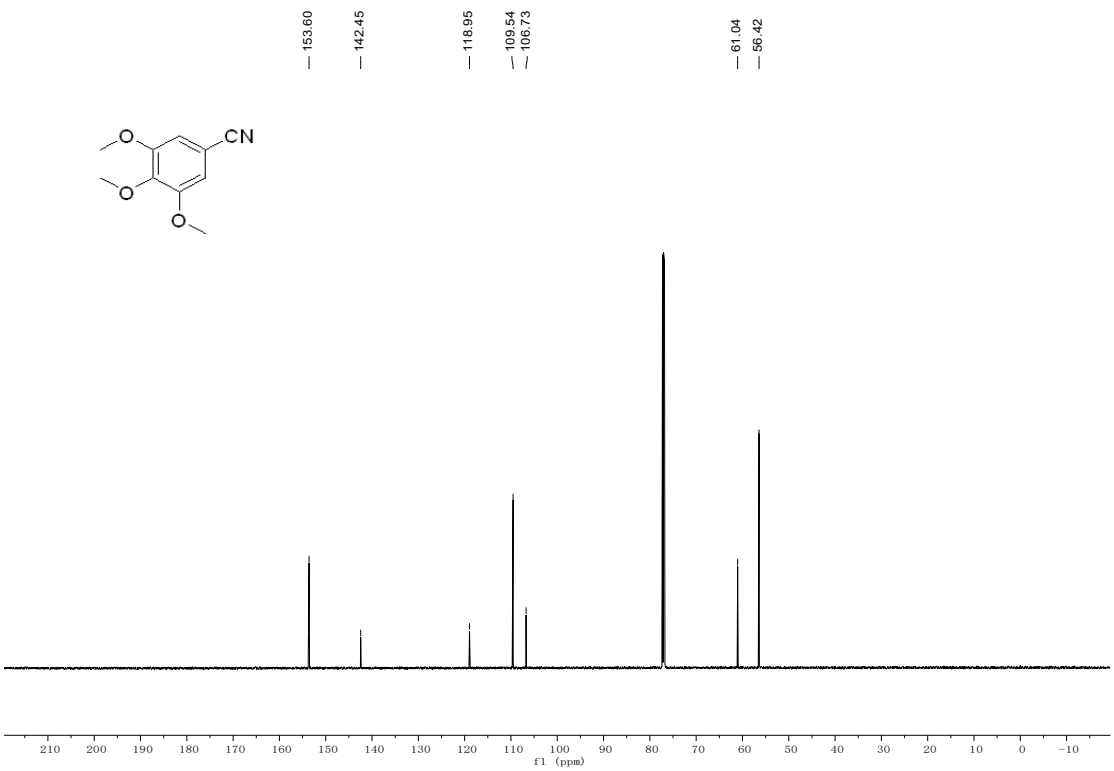
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3r



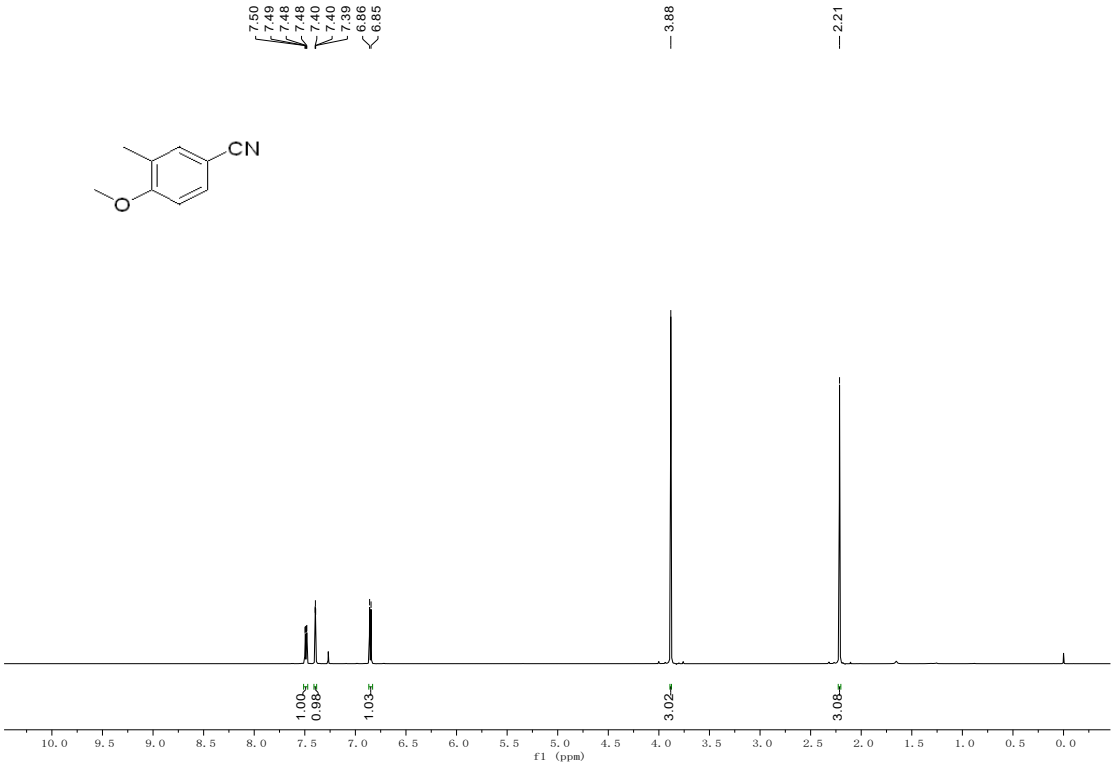
^{1}H-NMR Spectrum (600MHz, $CDCl_3$) of 3s



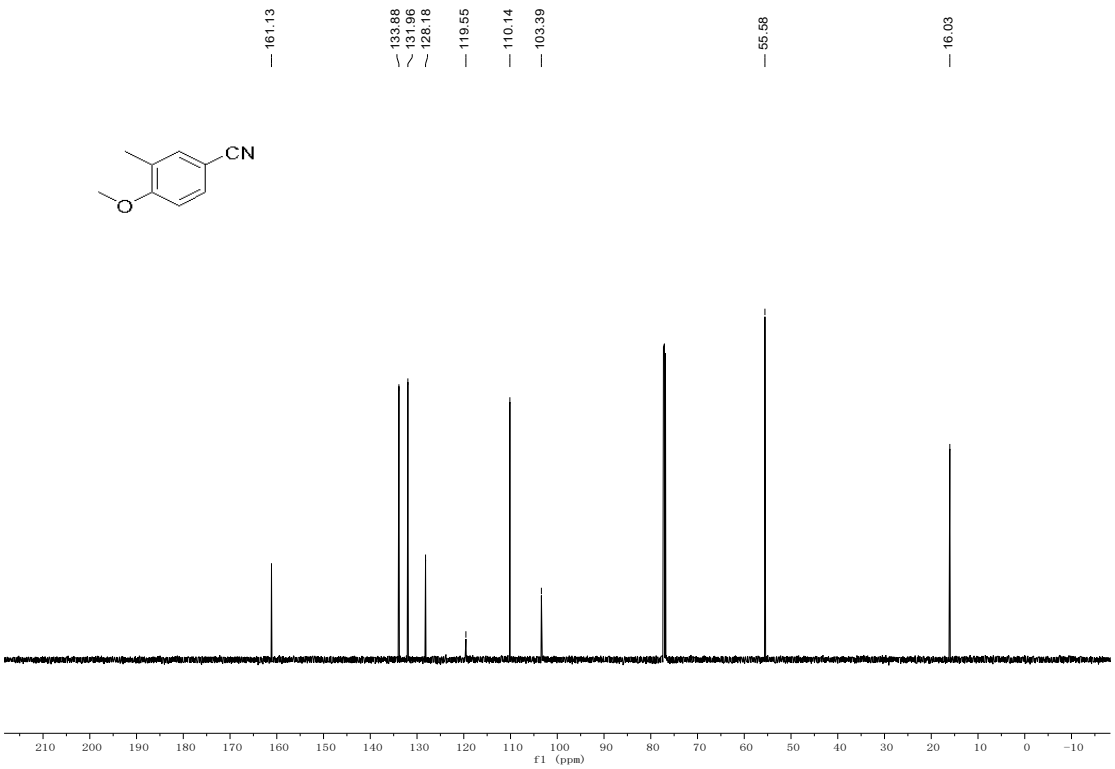
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of 3s



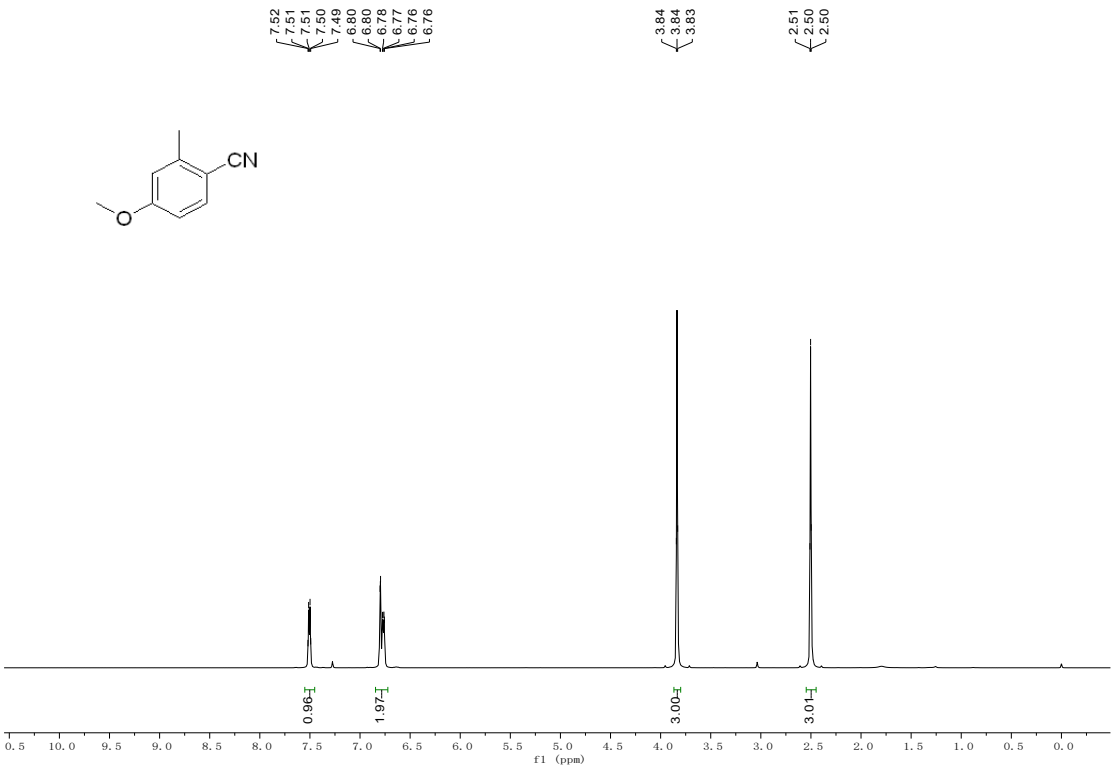
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3t



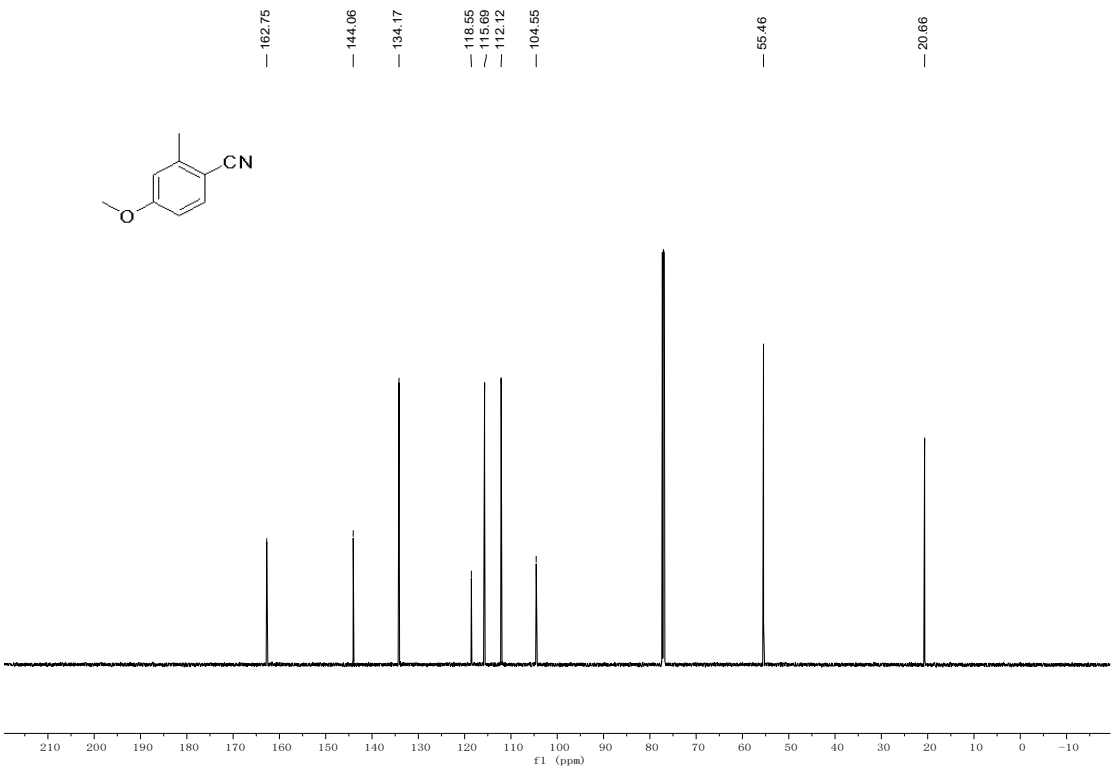
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3t



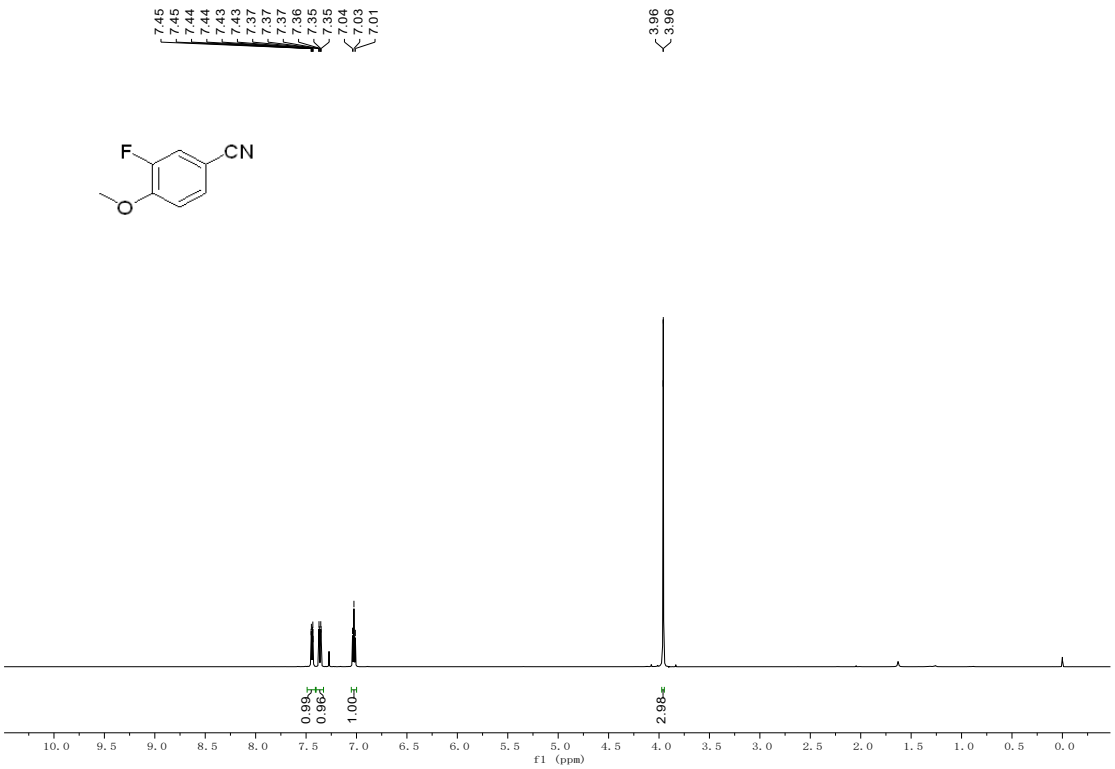
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3u



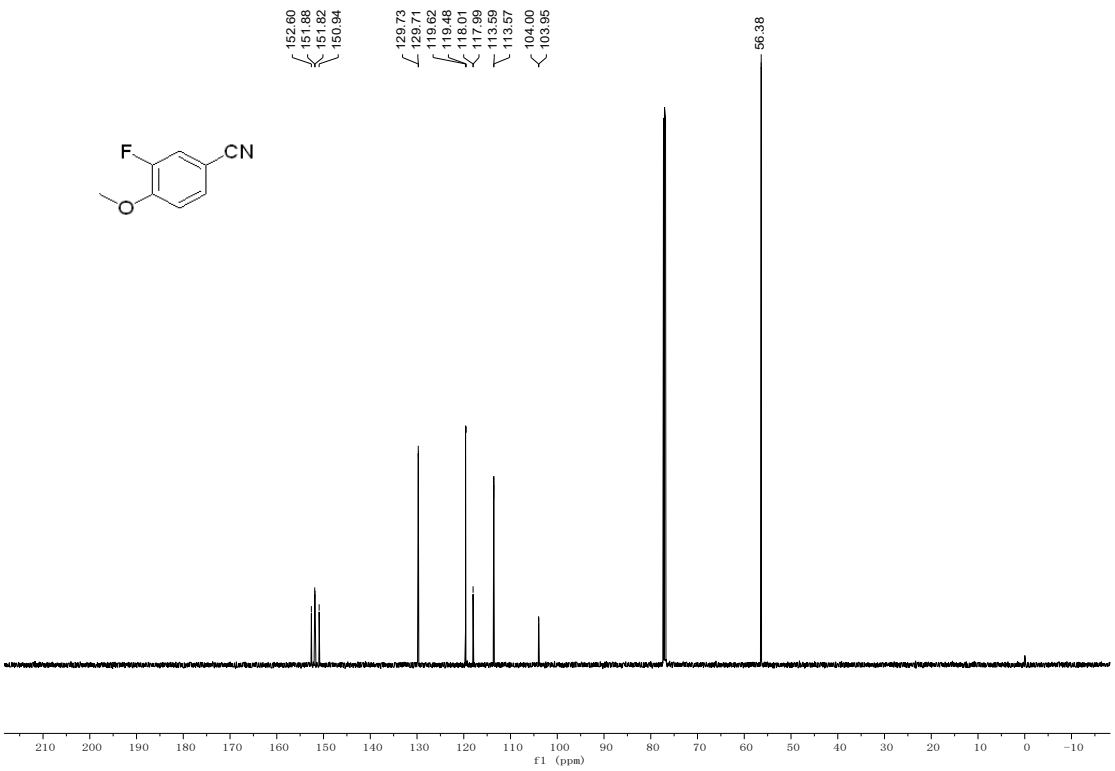
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3u



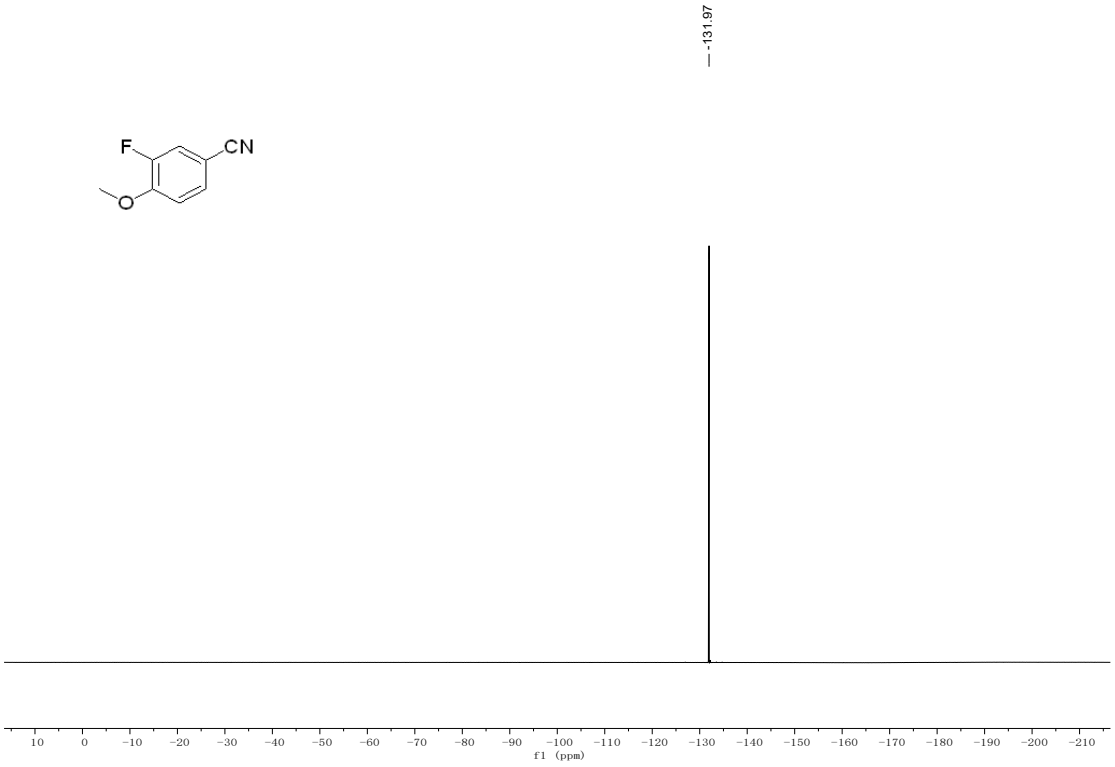
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3v



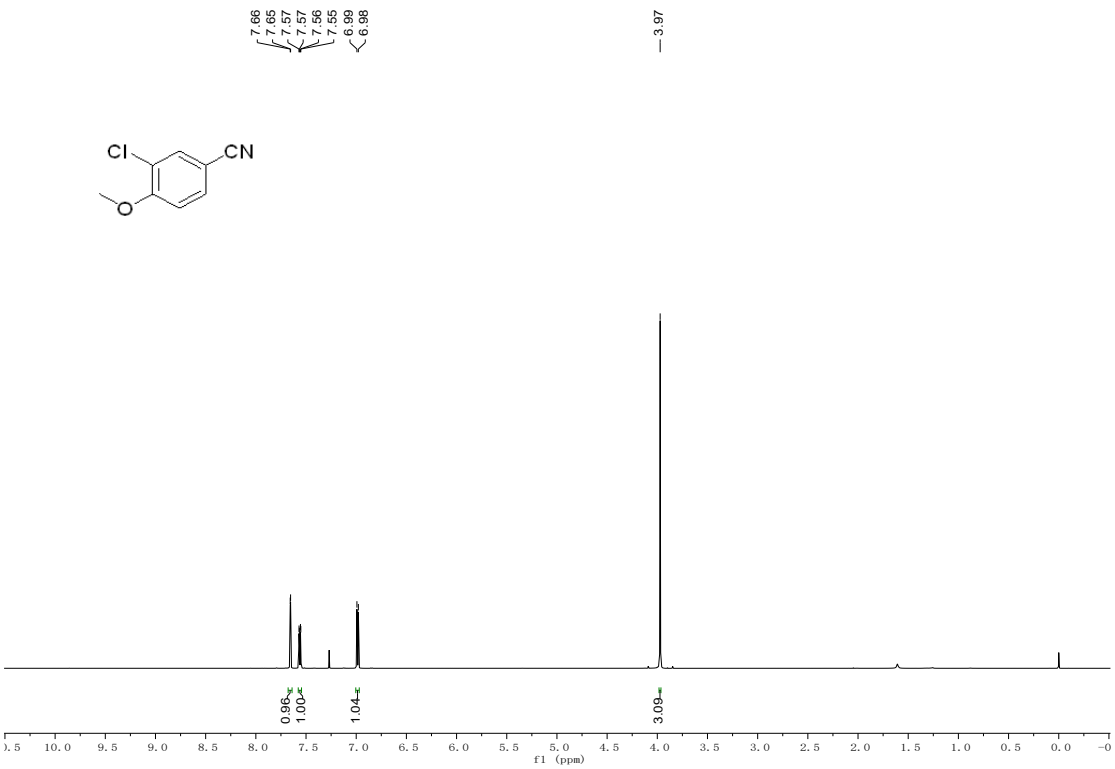
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3v



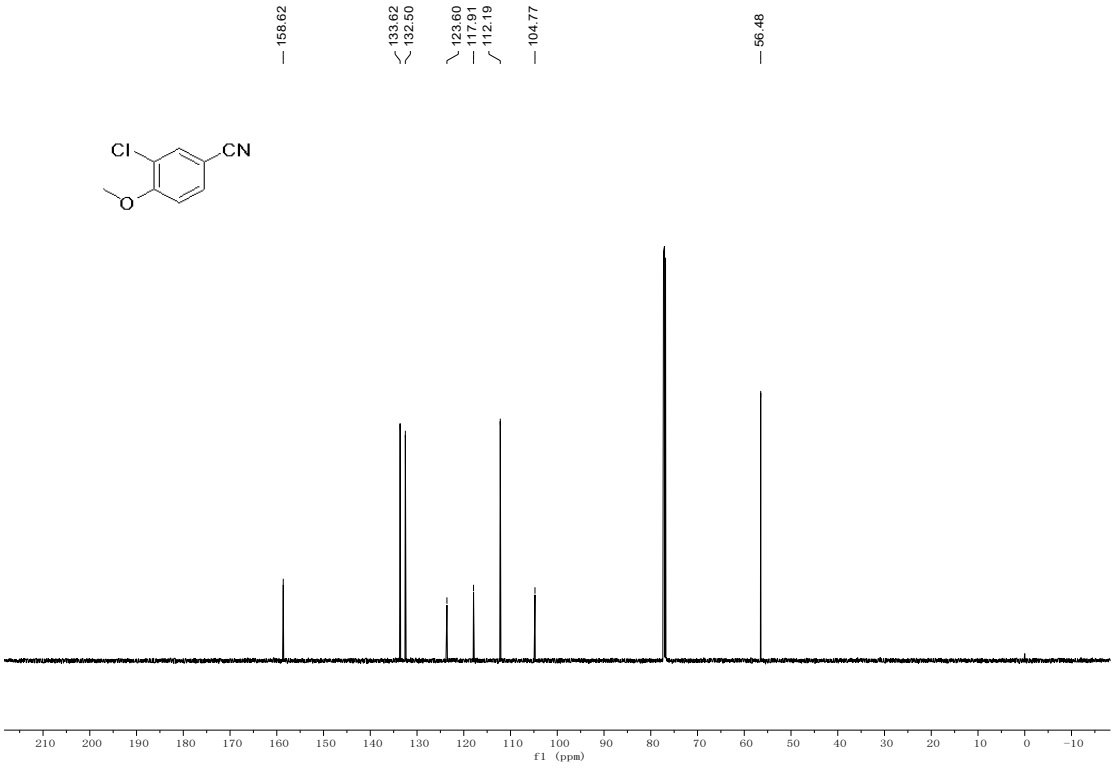
^{19}F-NMR Spectrum (565 MHz, $CDCl_3$) of 3v



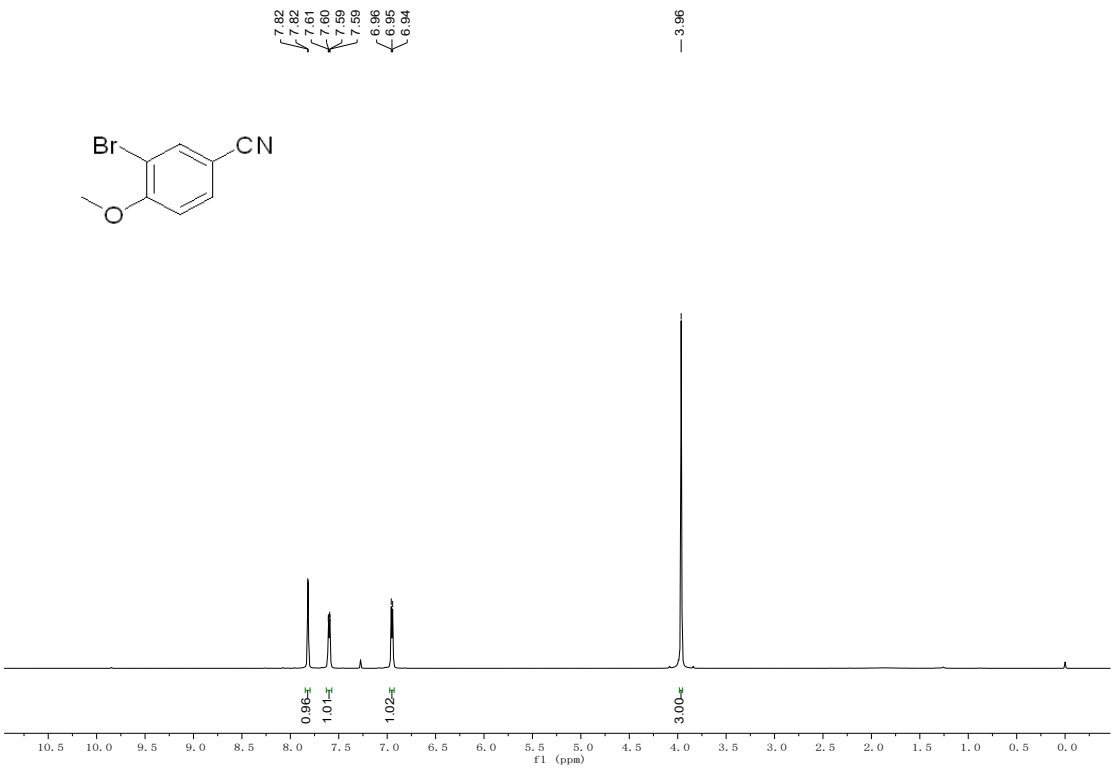
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3w



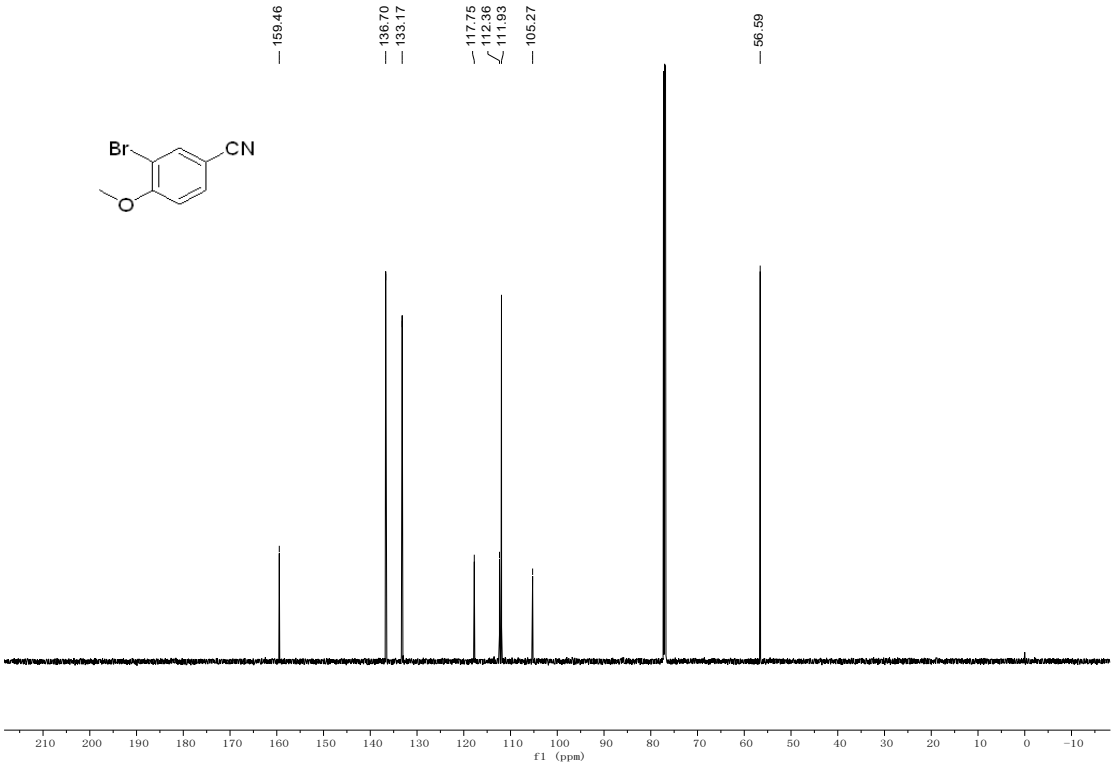
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3w



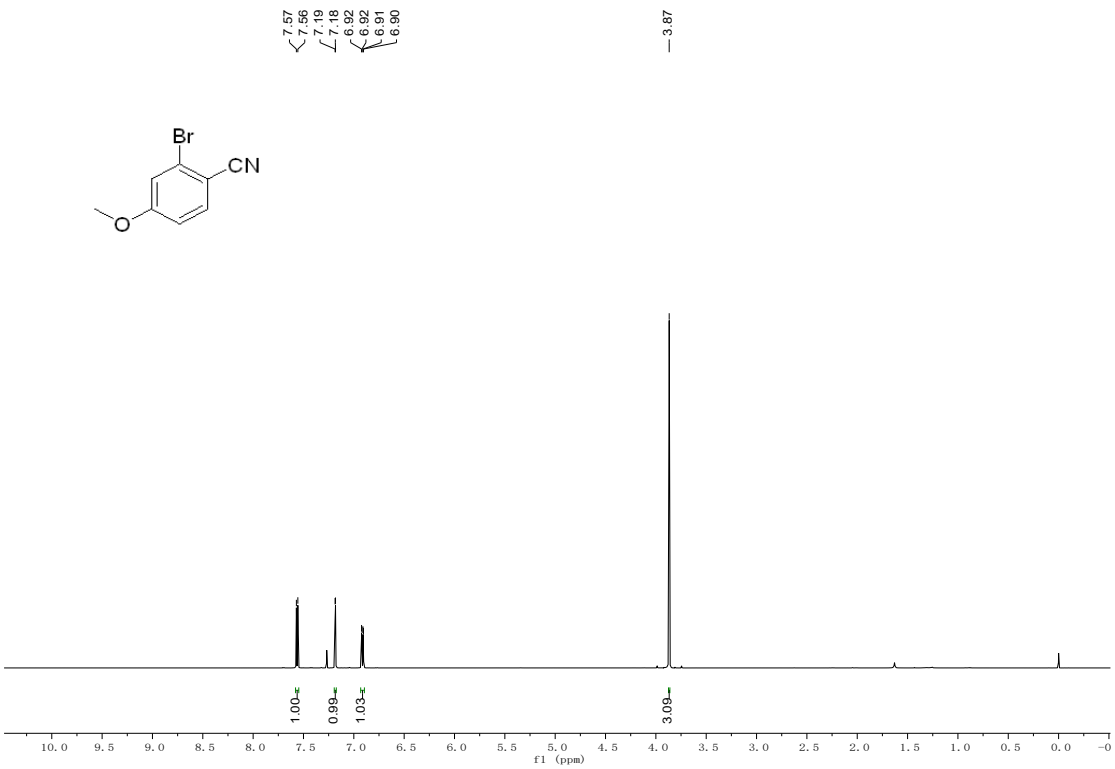
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3x



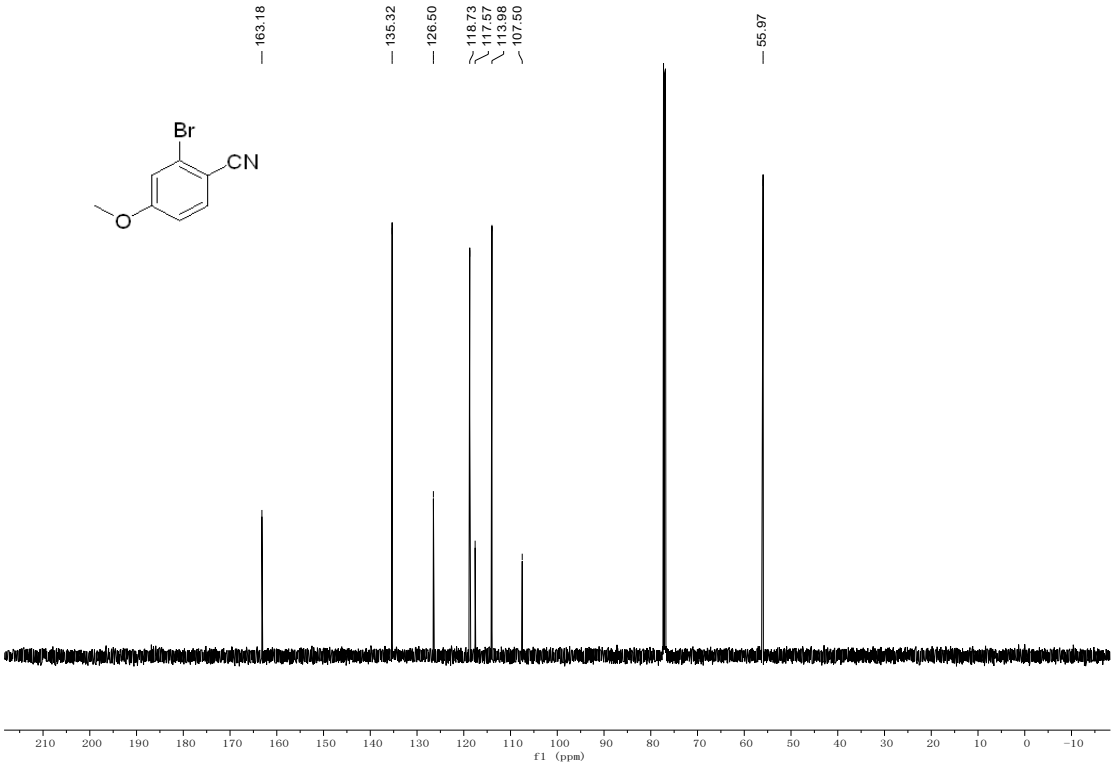
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3x



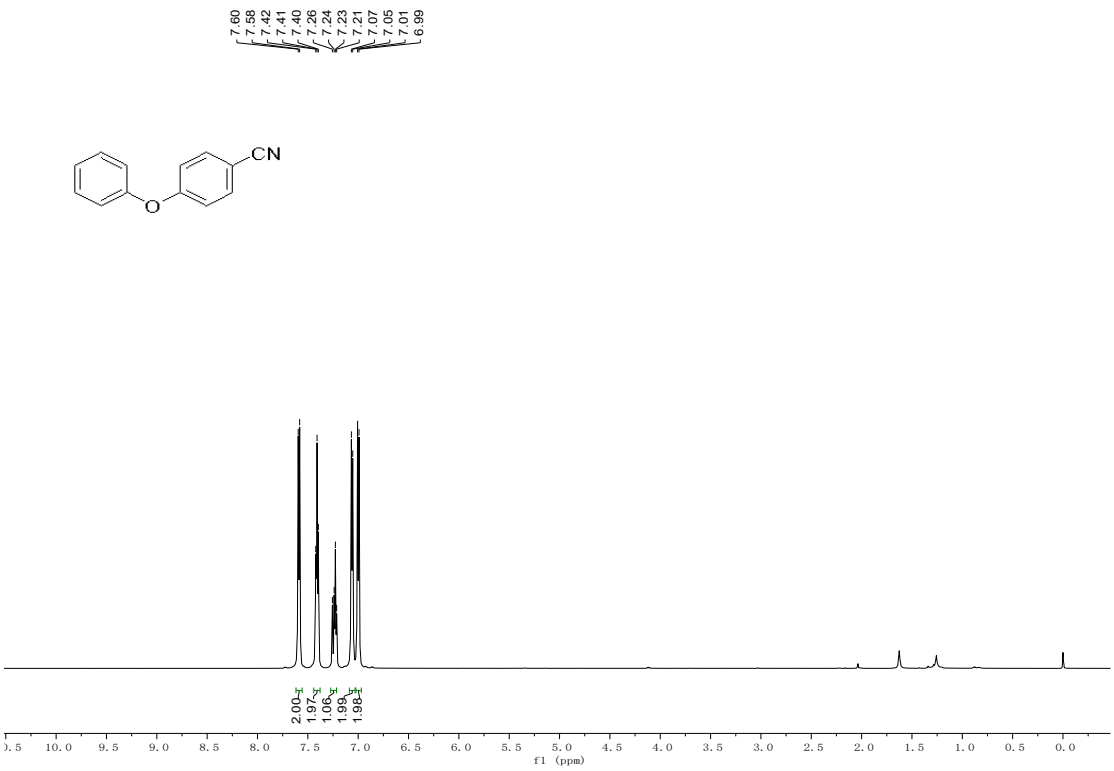
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3y



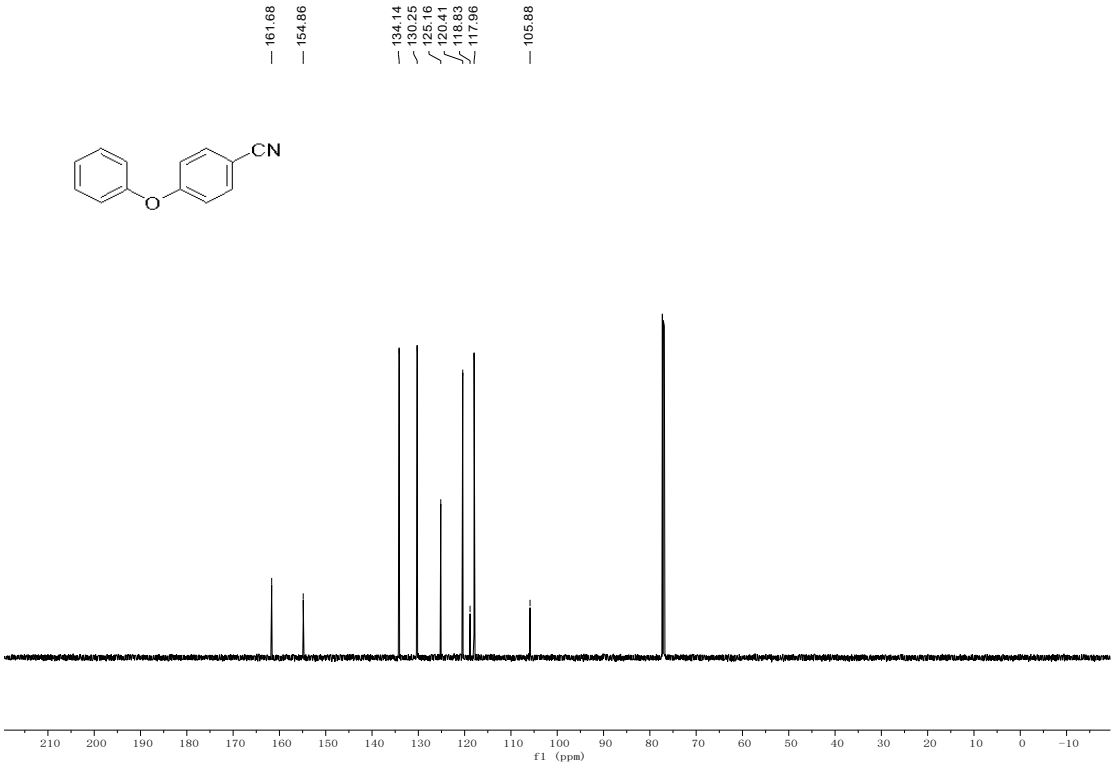
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3y



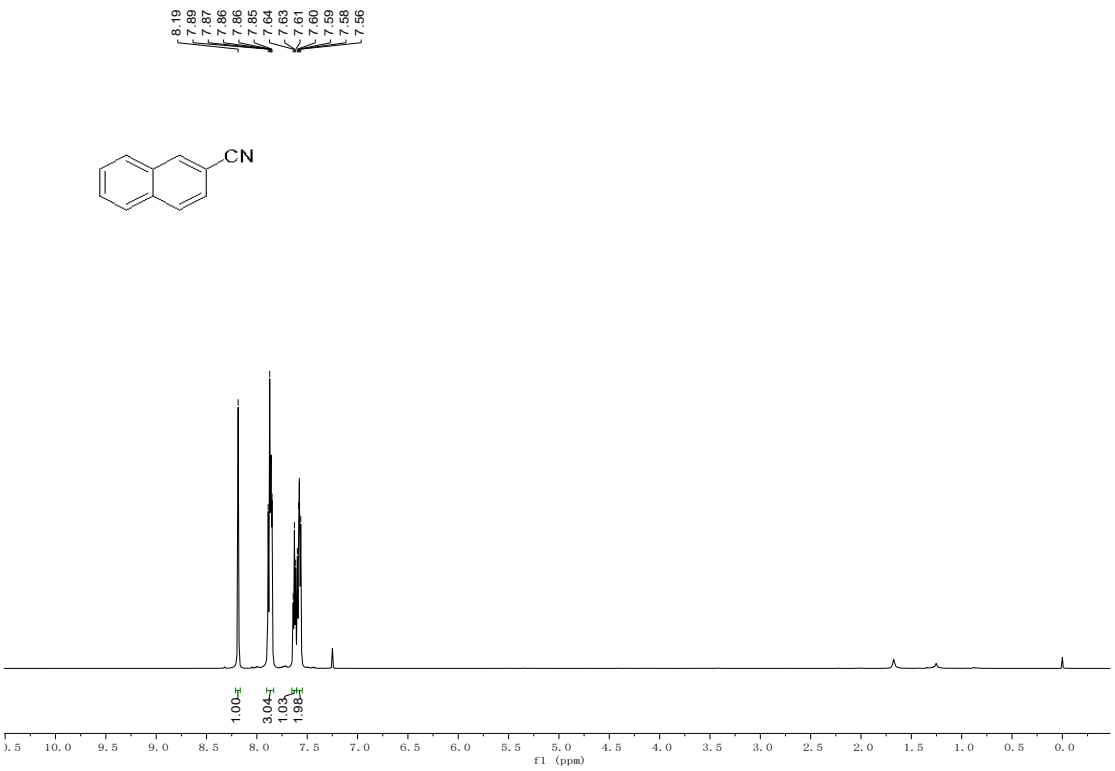
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3z



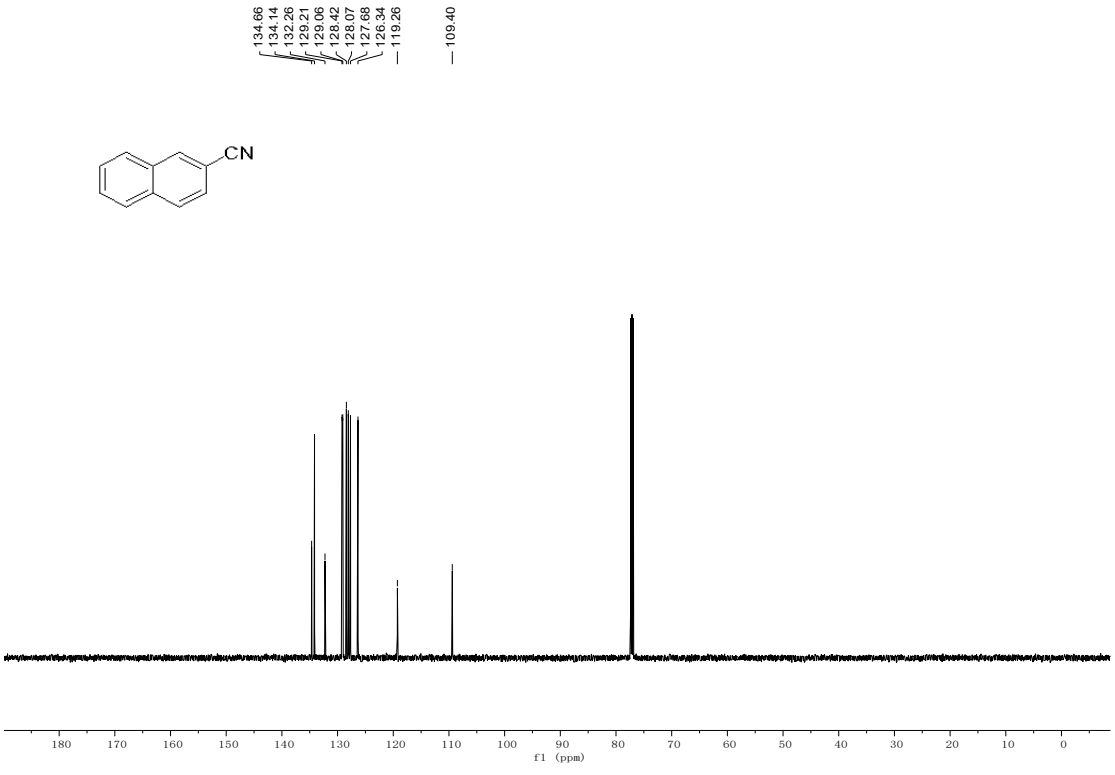
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3z



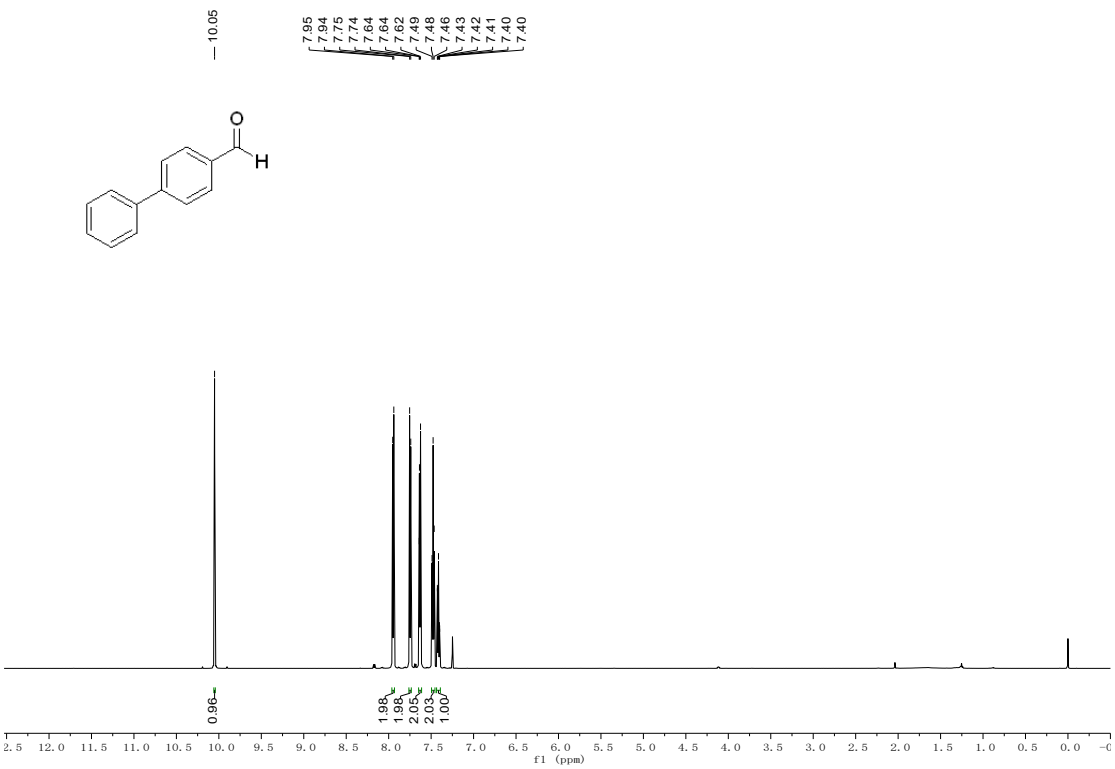
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3aa



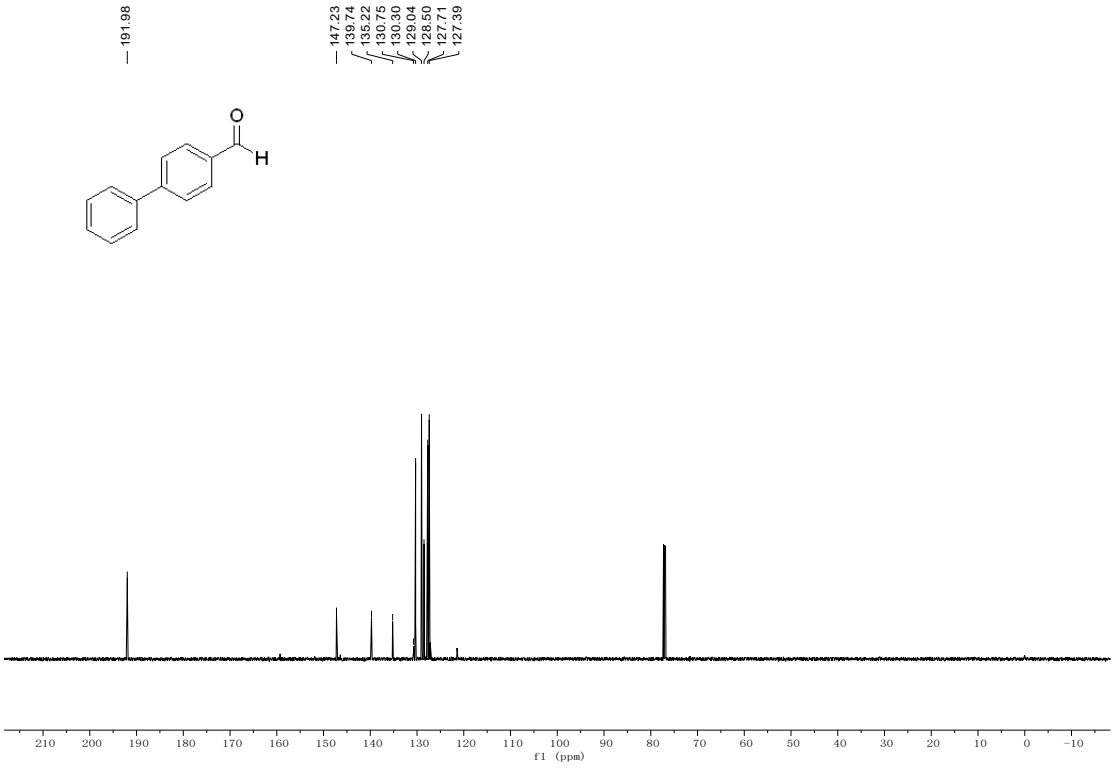
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3aa



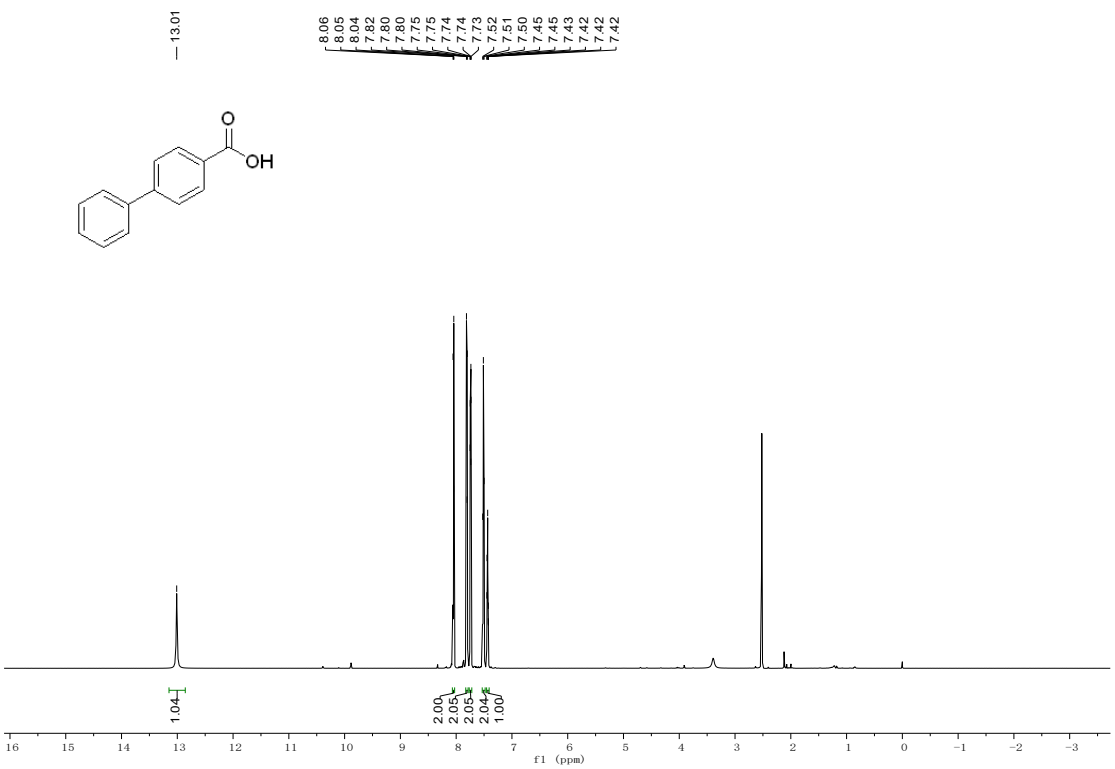
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 4



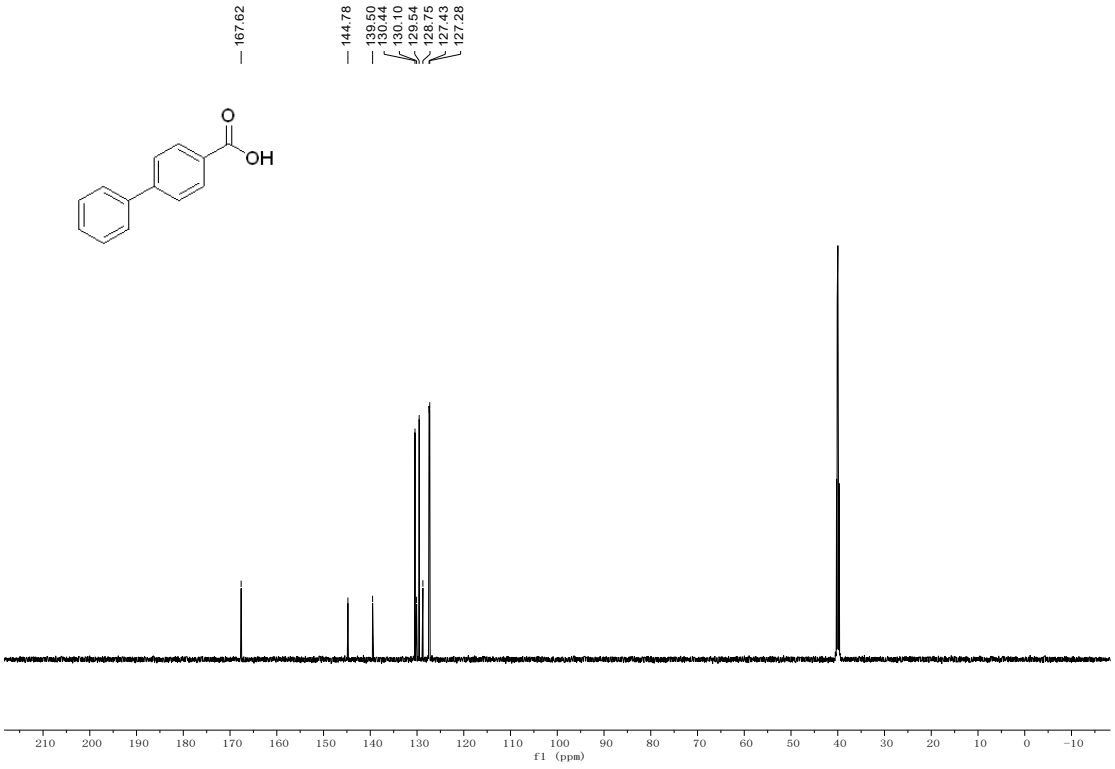
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 4



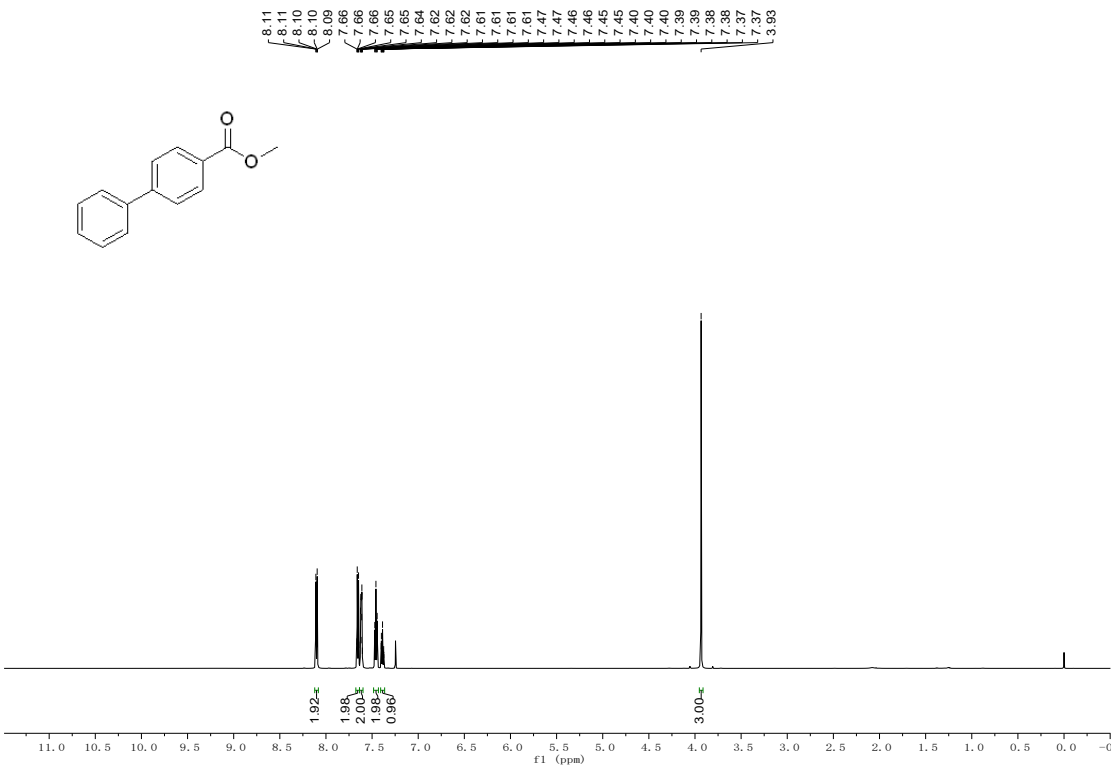
^{1}H-NMR Spectrum (600 MHz, DMSO-d_6) of 5



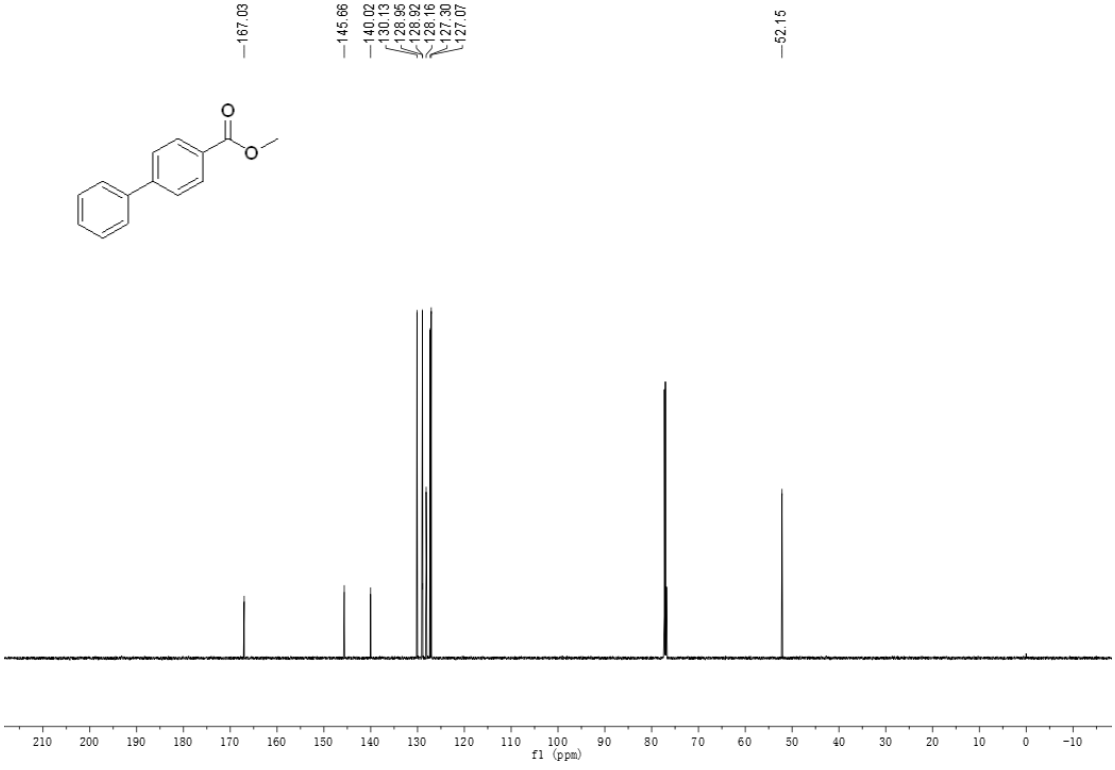
^{13}C-NMR Spectrum (151 MHz, DMSO-d_6) of 5



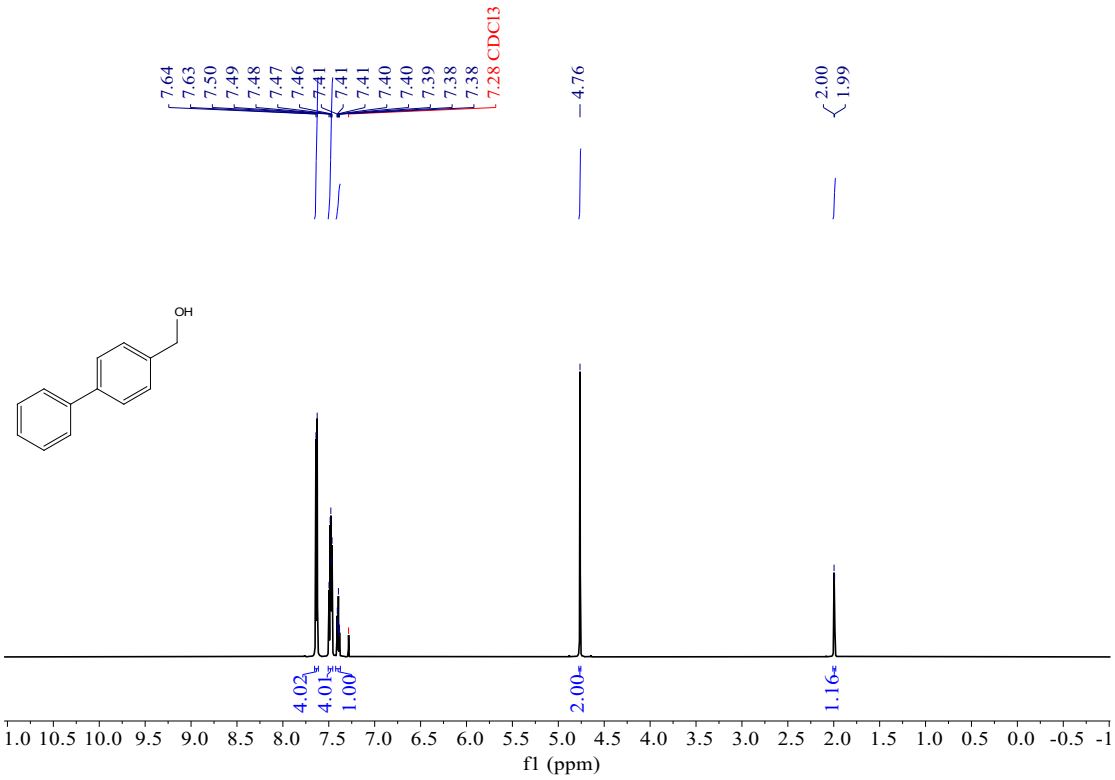
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 6



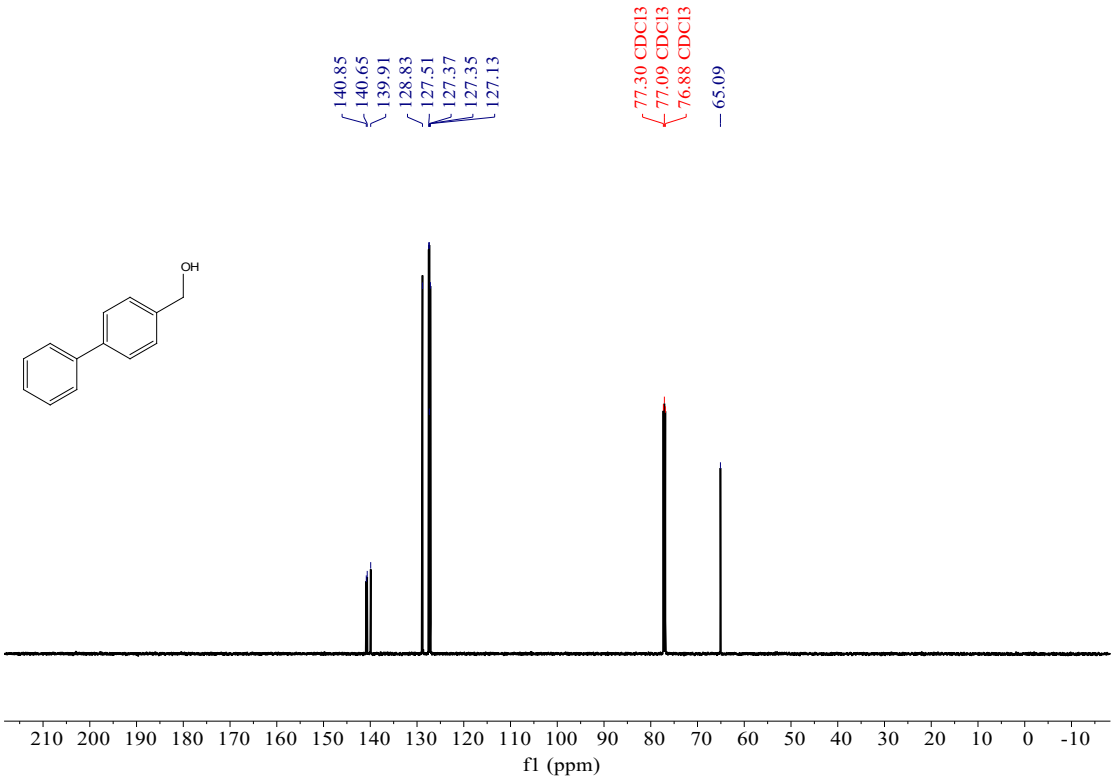
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 6



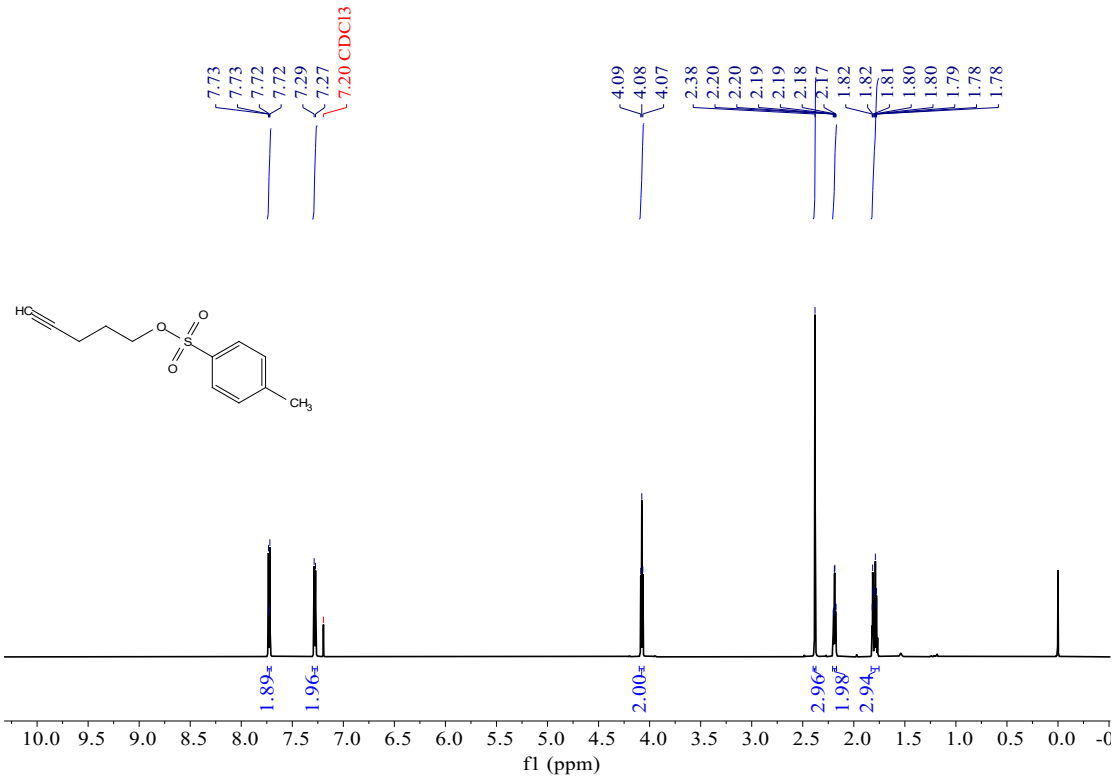
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 12



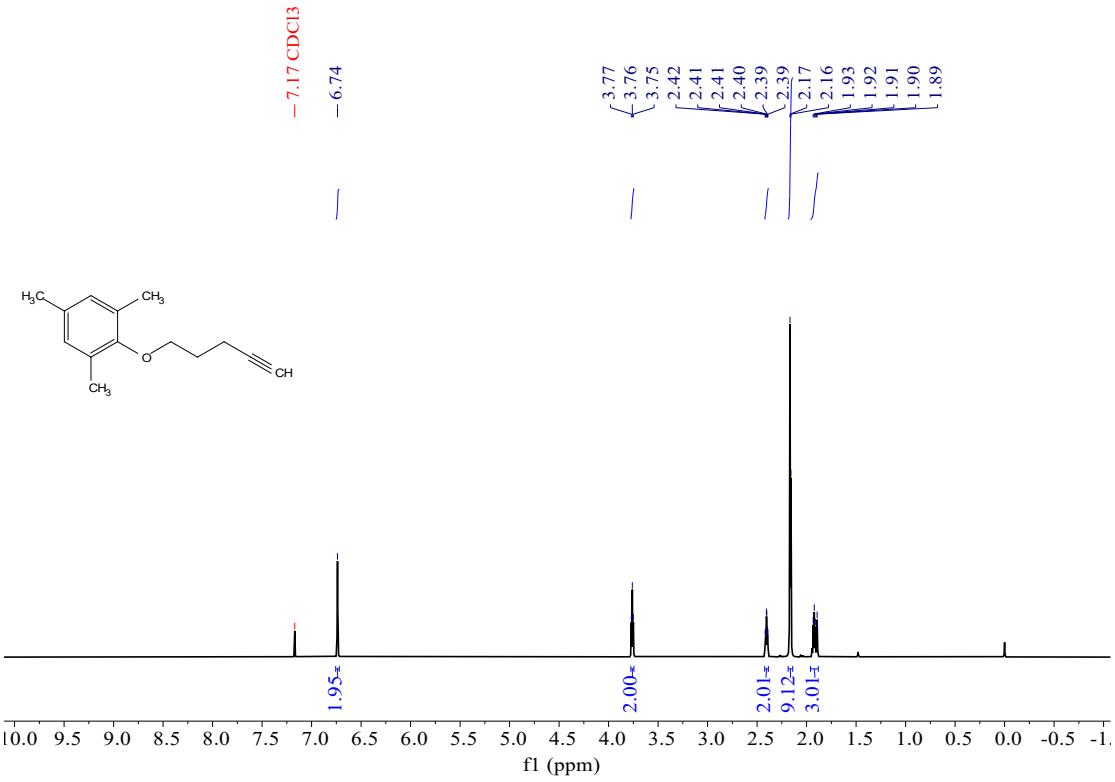
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 12



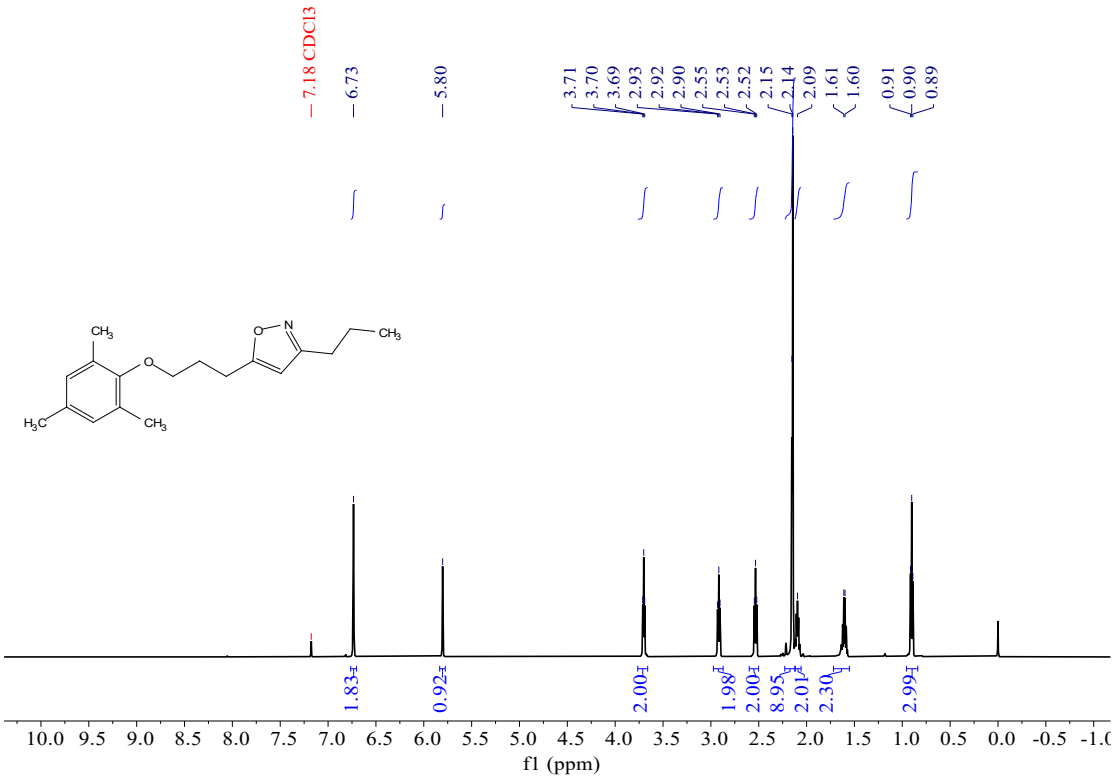
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 15



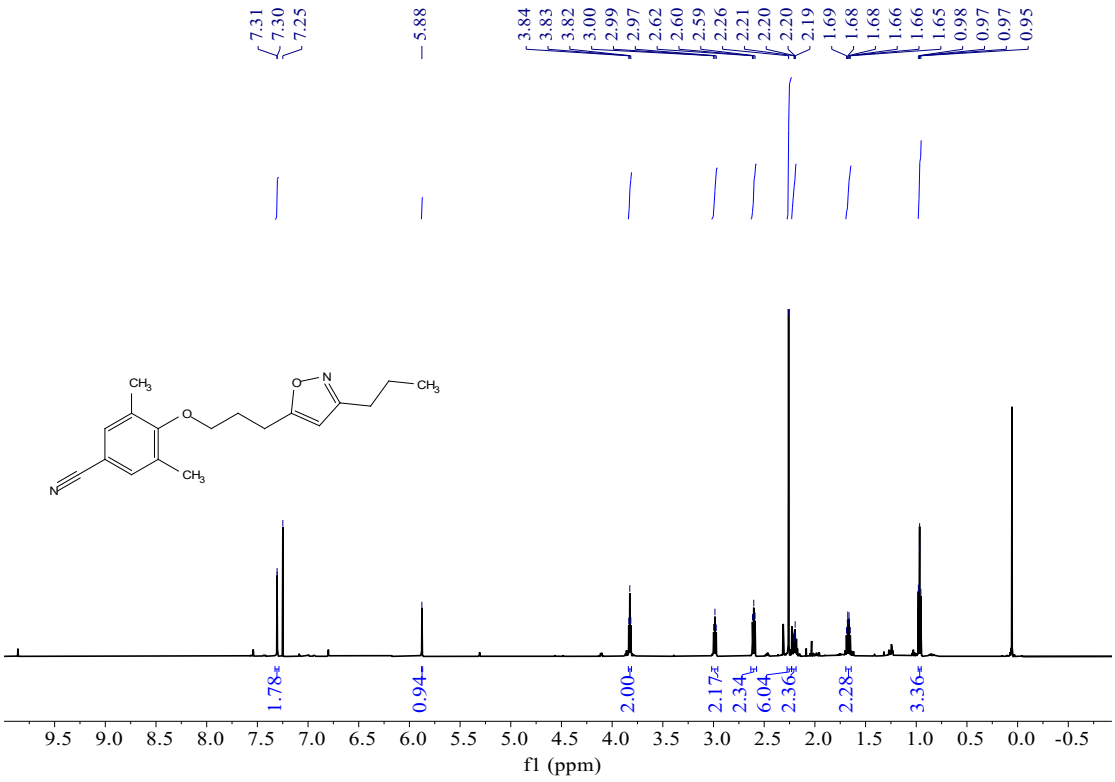
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 16



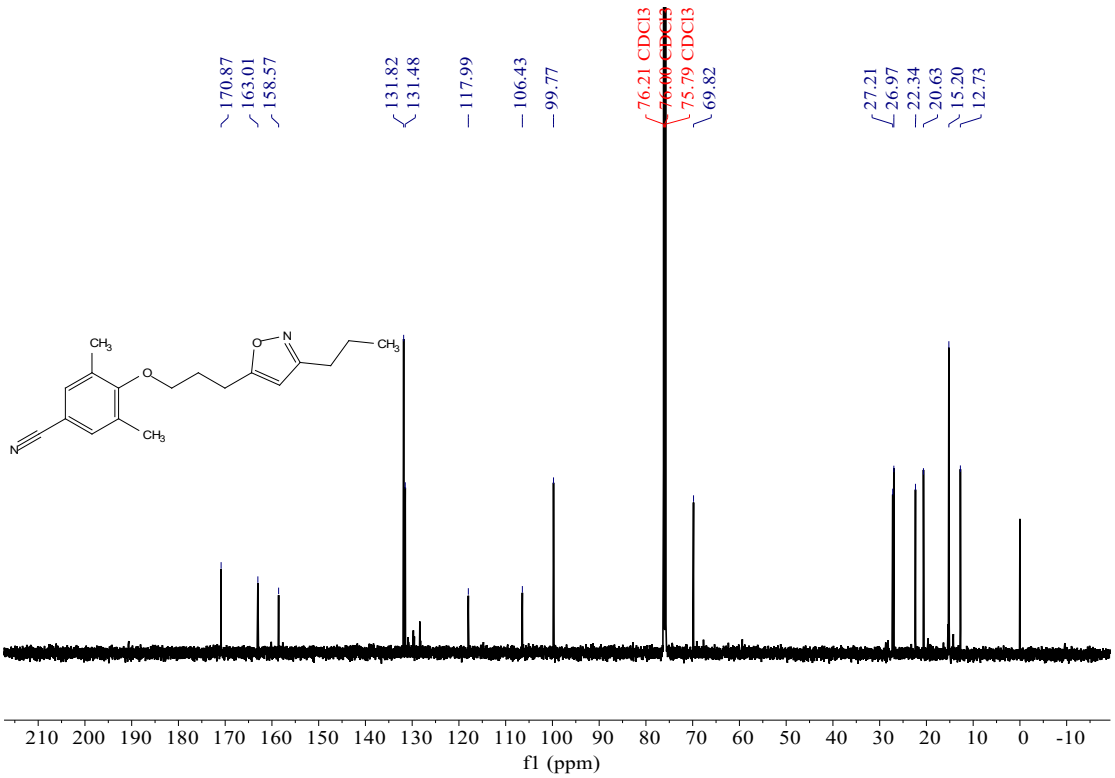
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 8



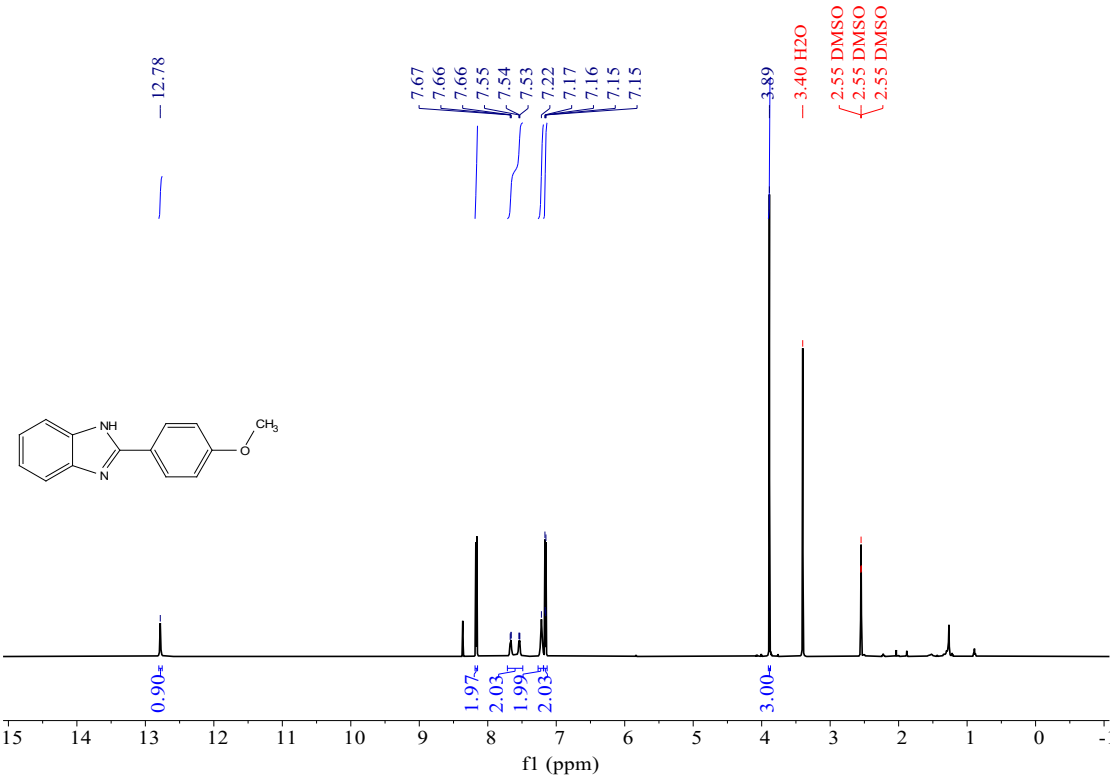
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 9



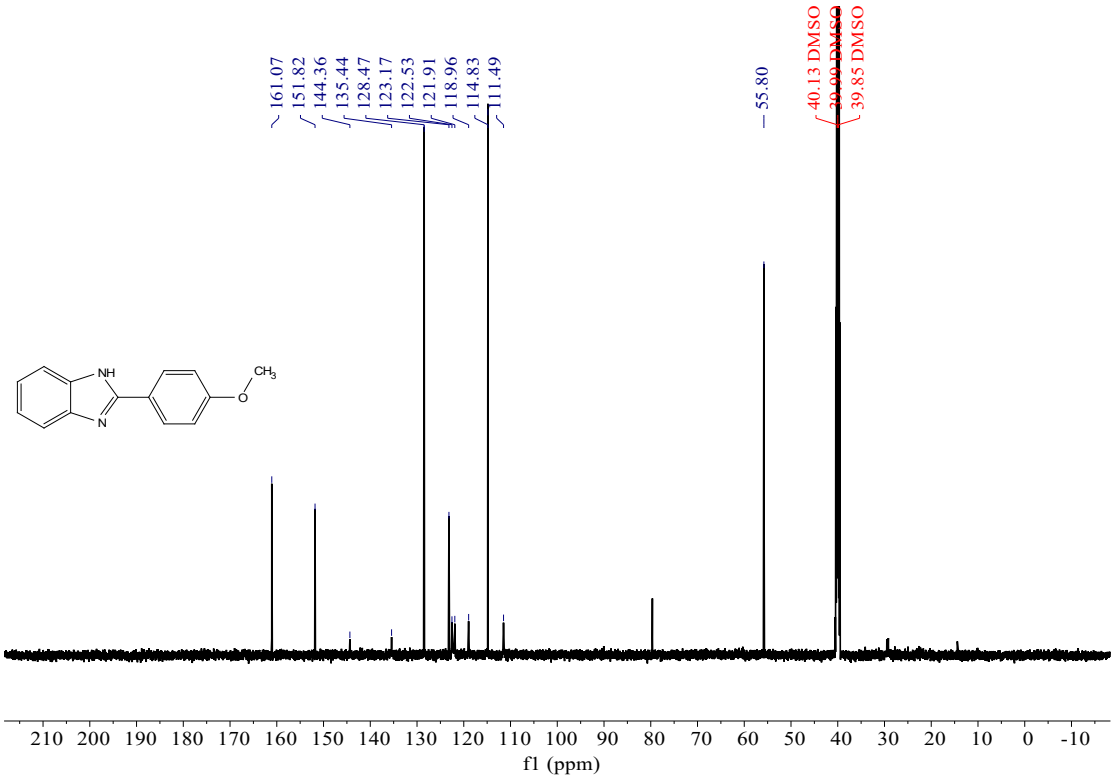
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 9



^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 7



^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 7



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