Supporting Information for

$Cu(NO_3)_2 \cdot 3H_2O$-Mediated Cyanation of Aryl Iodides and Bromides using DMF as a Single Surrogate of Cyanide

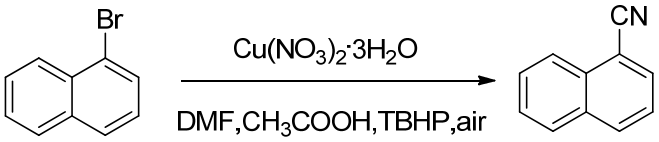
Lianpeng Zhang, Ping Lu*, and Yanguang Wang*
Department of Chemistry, Zhejiang University, Hangzhou, 310027, P. R. China
Email:pinglu@zju.edu.cn; orgwyg@zju.edu.cn, Fax: (+86) 571-87952543

Table of Contents

1. General

Unless stated otherwise, reactions were conducted in flame-dried glassware. Commercially available reagents and solvents were used as received. 300-400 Mesh silica gel was used for flash column chromatography. Visualization on TLC was achieved by the use of UV light (254 nm). 400 MHz and 100 MHz were used for the record of ^{1}H NMR and ^{13}C NMR spectra. Chemical shifts (δ ppm) were reported in parts per million referring to either the internal standard of TMS or the residue of the deuterated solvents. Splitting pattern was described as follows: s for singlet, d for doublet, t for triplet, q for quartet, and m for multiplet. Coupling constants were reported in Hz. The high-resolution mass spectrum (HRMS) was recorded on GCT premier instrument.

2. Optimization of the 1-Bromonaphthalene



3d **2f**

Entry	[Cu] (equiv)	HOAc (equiv)	TBHP (equiv)	Temp (^{o}C)	Time (h)	Yield (%)[b]
1	$Cu(NO_3)_2$•$3H_2O$(1.2)	4	2	140	48	54
2	$Cu(NO_3)_2$•$3H_2O$(1.2)	8	2	140	48	38
3	$Cu(NO_3)_2$•$3H_2O$(1.2)	4	4	140	48	48
4	$Cu(NO_3)_2$•$3H_2O$(1.2)	4	2	140	48	87(85[c])
5	$Cu(NO_3)_2$•$3H_2O$(1.2)	4	2	140	48	40
6	$Cu(NO_3)_2$•$3H_2O$(1.2)	4	2	130	48	31

[a] *Reaction conditions:* 1-Bromonaphthalene(**3d**) (0.5 mmol, 0.1035g) in DMF (3.0 mL) was stirred under air. [b] Determined by GC analysis .[c] Yield of isolated product after column chromatography on silica gel.

3. Typical Procedure of Cu-Mediated Cyanation with DMF

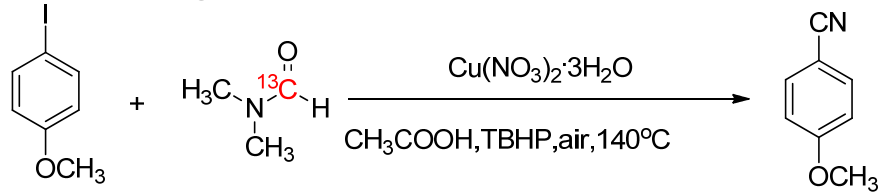
3.1 Cu-Mediated Cyanation of Aryl Iodide

An oven-dried 25 mL eggplant-shaped bottle equipped with a magnetic stir bar was charged with $Cu(NO_3)_2 \cdot 3H_2O$ (0.6 mmol, 1.2 equiv), aryl iodide (0.5 mmol), CH_3COOH (4.0 equiv), t-BuOOH (2.0 equiv, 70% aq.) and DMF (3.0 mL). The bottle was left at 120-140 ^oC (oil bath temperature) for about 40-48 h (checked by TLC). After the aryl iodide was completely consumed, the reaction mixture was then cooled to room temperature, and quenched by adding 10 mL water and extracted with DCM (3×10 mL). After the organic layer was washed with saturated salt water, it was filtrated and concentrated under reduced pressure. The residue was purified by column chromatography to afford the cyanated product.

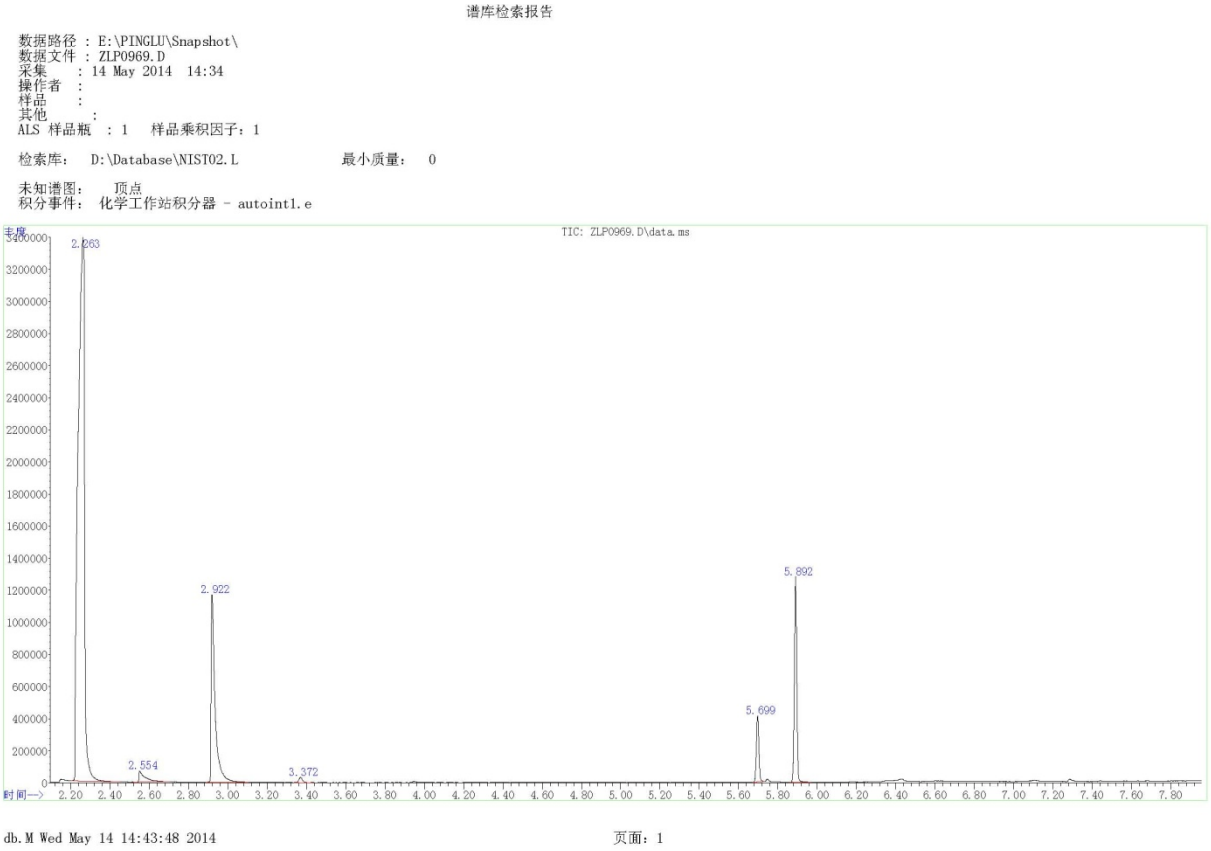
3.2 Cu-Mediated Cyanation of Aryl Bromide

An oven-dried 25 mL eggplant-shaped bottle equipped with a magnetic stir bar was charged with $Cu(NO_3)_2 \cdot 3H_2O$ (0.75 mmol, 1.5 equiv), aryl bromide (0.5 mmol), CH_3COOH (4.0 equiv), t-BuOOH (2.0 equiv,70% aq.) and DMF (3.0 mL). The bottle was left at 130-140 ^oC (oil bath temperature) for about 40-48 h (checked by TLC). After the aryl bromide completely consumed, the reaction mixture was then cooled to room temperature, and quenched by adding 10 mL water and extracted with DCM (3×10 mL). After the organic layer was washed with saturated salt water, it was filtrated and concentrated under reduced pressure. The residue was purified by column chromatography to afford the cyanated product.

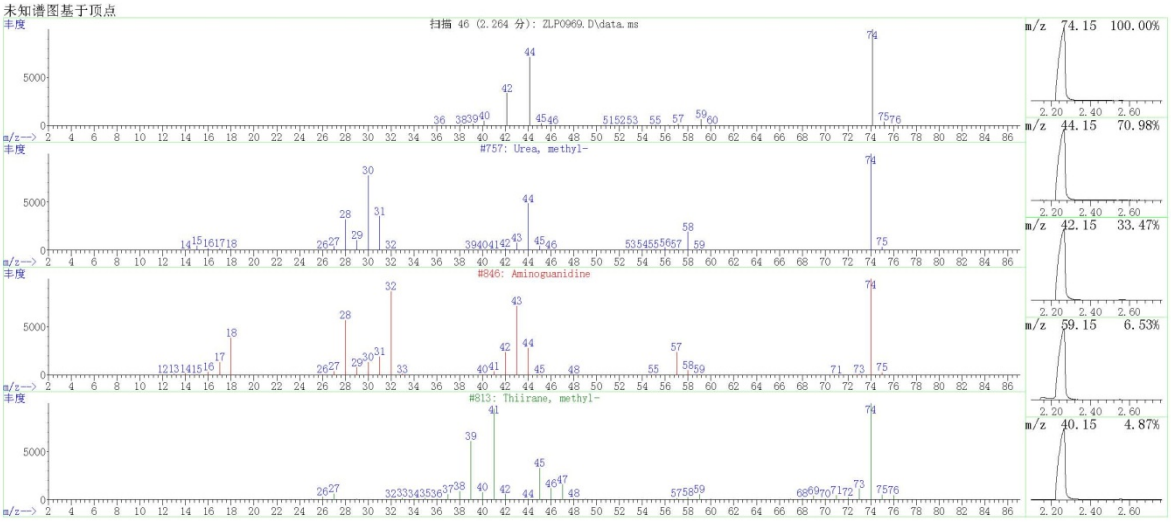
4. Experiment using DMF with Carbon-13 Labeled on Its Carbonyl



An oven-dried 25 mL eggplant-shaped bottle equipped with a magnetic stir bar was charged with Cu（NO_3）$_2$•3H_2O (0.12 mmol, 1.2 equiv), 1-iodo-4-methoxybenzene (0.1 mmol), CH_3COOH (4.0 equiv), t-BuOOH (2.0 equiv, 70% aq.) and DMF with carbon-13 labeled on its carbonyl (0.25 mL). The bottle was left at 140 ^oC (oil bath temperature) for about 40 h. Then took 20μL from the reaction mixture to do GC-MS.



未知谱图基于顶点

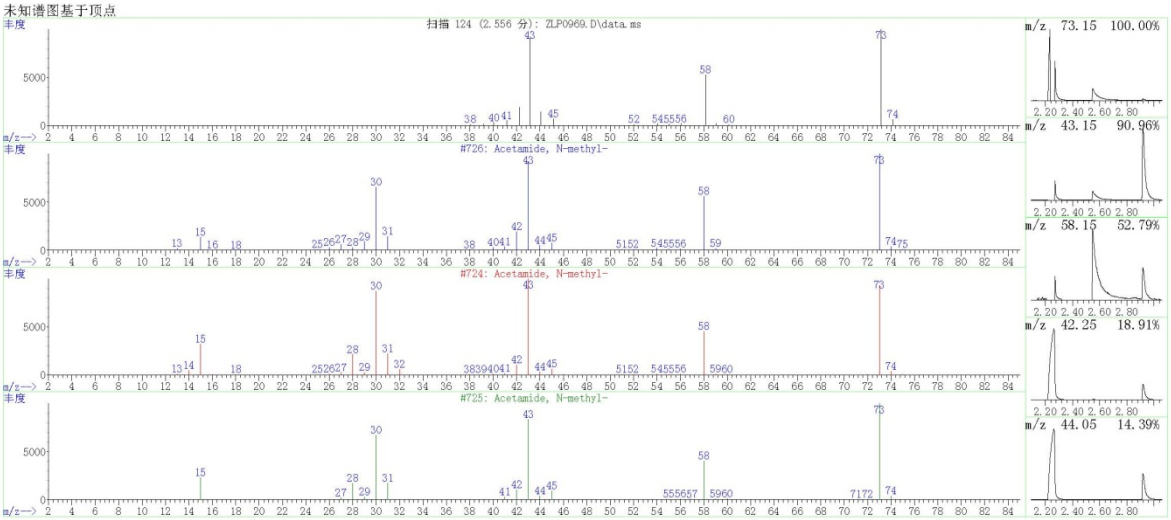


Data File: E:\PINGLU\Snapshot\ZLP0969.D
样品:

峰编号: 1 2.264 分钟处 面积: 77275410 面积 % 70.25

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Urea, methyl-	757	000598-50-5	7
2 Aminoguanidine	846	000079-17-4	5
3 Thiirane, methyl-	813	001072-43-1	5

未知谱图基于顶点

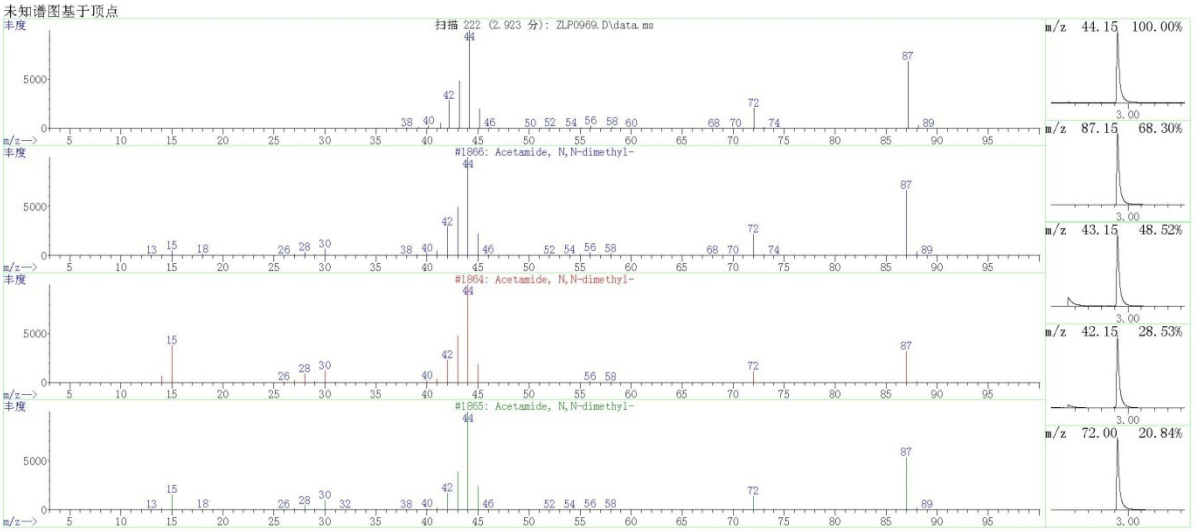


Data File: E:\PINGLU\Snapshot\ZLP0969.D
样品:

峰编号: 2 2.556 分钟处 面积: 1552970 面积 % 1.41

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Acetamide, N-methyl-	726	000079-16-3	86
2 Acetamide, N-methyl-	724	000079-16-3	80
3 Acetamide, N-methyl-	725	000079-16-3	72

未知谱图基于顶点

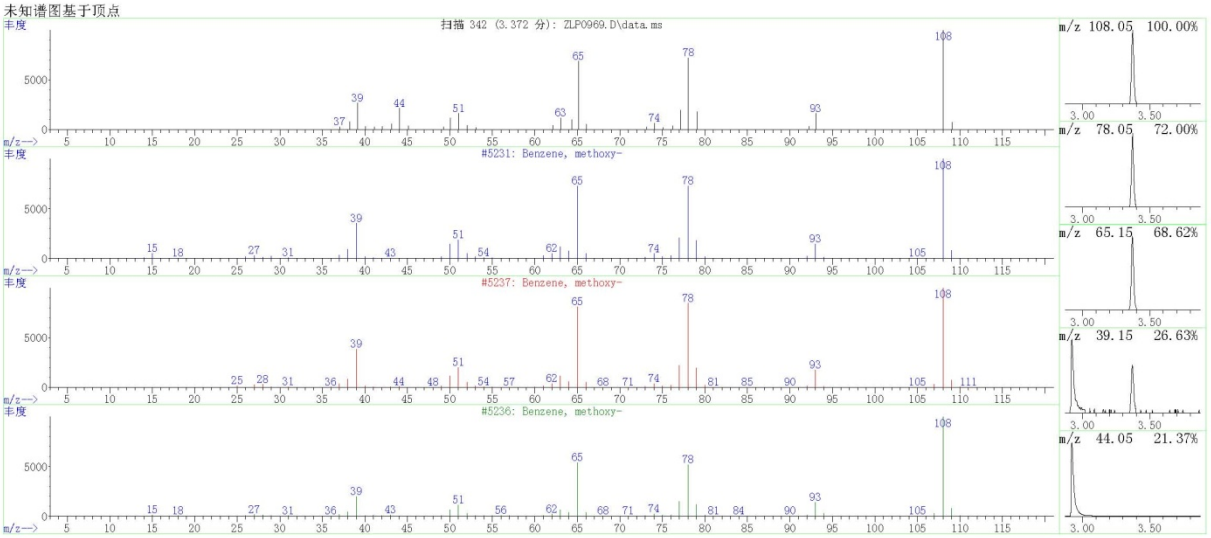


Data File: E:\PINGLU\Snapshot\ZLP0969.D
样品:

峰编号: 3 2.923 分钟处 面积: 16495471 面积 % 15.00

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Acetamide, N,N-dimethyl-	1866	000127-19-5	91
2 Acetamide, N,N-dimethyl-	1864	000127-19-5	83
3 Acetamide, N,N-dimethyl-	1865	000127-19-5	78

未知谱图基于顶点

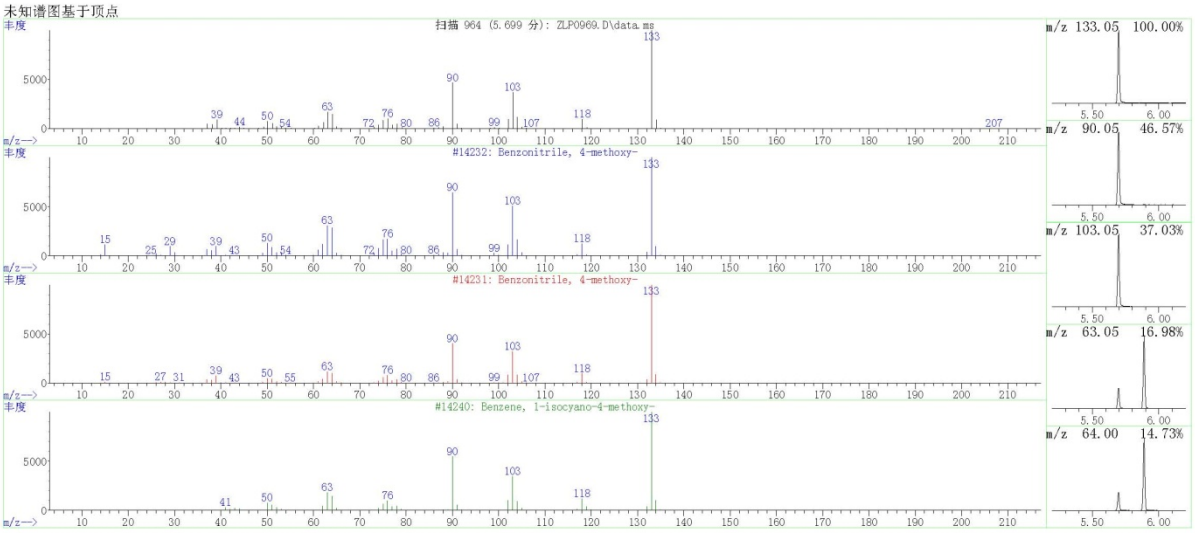


Data File: E:\PINGLU\Snapshot\ZLP0969.D
样品:

峰编号: 4 3.372 分钟处 面积: 395527 面积 % 0.36

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Benzene, methoxy-	5231	000100-66-3	97
2 Benzene, methoxy-	5237	000100-66-3	96
3 Benzene, methoxy-	5236	000100-66-3	90

未知谱图基于顶点

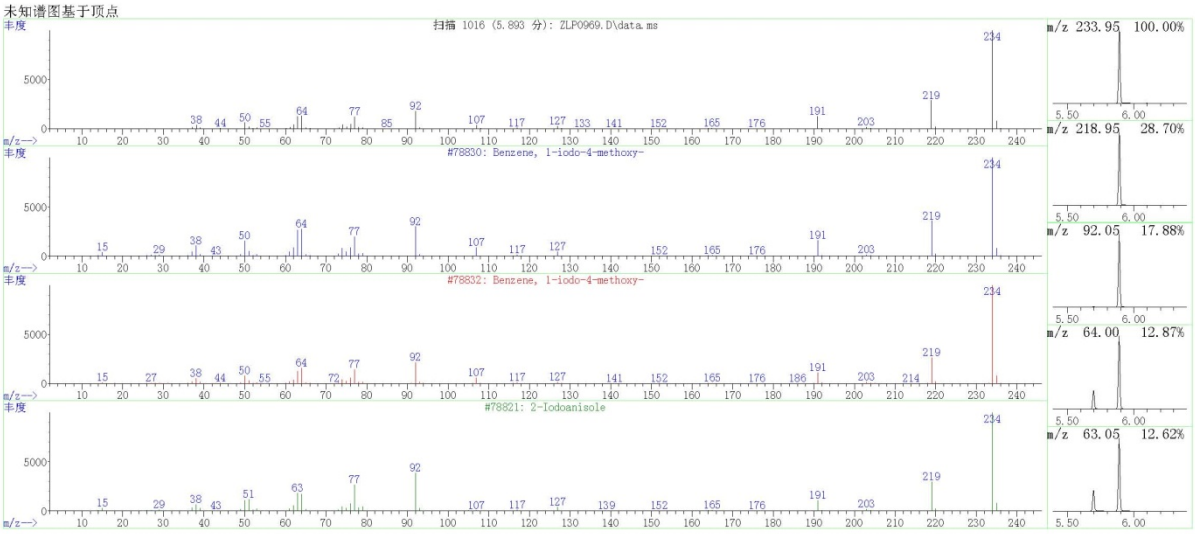


Data File: E:\PINGLU\Snapshot\ZLP0969.D
样品:

峰编号: 5 5.699 分钟处 面积: 3578349 面积 % 3.25

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Benzonitrile, 4-methoxy-	14232	000874-90-8	97
2 Benzonitrile, 4-methoxy-	14231	000874-90-8	97
3 Benzene, 1-isocyano-4-methoxy-	14240	010349-38-9	96

未知谱图基于顶点



Data File: E:\PINGLU\Snapshot\ZLP0969.D
样品:

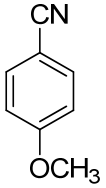
峰编号: 6 5.893 分钟处 面积: 10697943 面积 % 9.73

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Benzene, 1-iodo-4-methoxy-	78830	000696-62-8	97
2 Benzene, 1-iodo-4-methoxy-	78832	000696-62-8	96
3 2-Iodoanisole	78821	000529-28-2	95

.

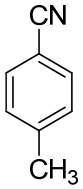
5. NMR data for the products

4-Methoxybenzonitrile (**2a**)[1]



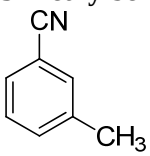
White solid, m.p. 57-58 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 9.2 Hz, 2H), 6.95 (d, J = 9.2Hz, 2H), 3.85 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 134.3, 119.5, 115.1, 104.3, 55.9.

4-Methylbenzonitrile (**2b**)



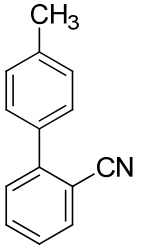
White solid, m.p. 27-29 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 132.3, 130.1, 119.5, 109.6, 22.1.

3-Methylbenzonitrile (**2c**)



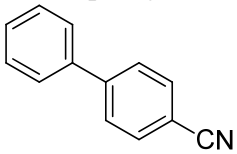
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 2H), 7.41 (d, J = 7.7 Hz, 1H), 7.38-7.32 (m, 1H), 2.39 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 134.0, 132.8, 129.6, 129.3, 119.4, 112.6, 21.5.

4'-Methyl-[1,1'-biphenyl]-2-carbonitrile (**2d**)



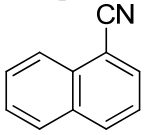
White solid,52-53 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 7.6, 1.0 Hz, 1H), 7.49 (dd, J = 7.6, 1.3 Hz, 1H), 7.38 (dd, J = 7.9, 0.7 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.30 (dd, J = 7.6, 1.2 Hz, 1H), 7.18 (d, J = 7.9 Hz, 2H), 2.30 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 138.9, 135.5, 133.9, 133.0, 130.2, 129.7, 128.8, 127.5, 119.1, 111.4, 21.5.

[1,1'-Biphenyl]-4-carbonitrile (**2e**)[2]



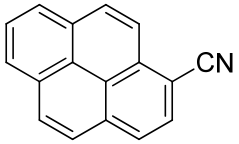
White solid, m.p. 83-84 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 7.4 Hz, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 139.5, 132.9, 129.4, 129.0, 128.1, 127.6, 119.3, 111.2.

1-Naphthonitrile (**2f**)[1]



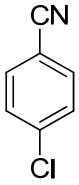
White solid, m.p. 55-56 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J =8.0 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.70 (dd, J = 8.4, 7.0 Hz, 1H), 7.62 (dd, J = 8.4, 7.0 Hz, 1H), 7.52 (dd, J = 8.4, 7.0 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 133.3, 133.0, 132.7, 129.0, 128.9, 127.9, 125.5, 125.3, 118.1, 110.5.

Pyrene-1-carbonitrile (**2g**)



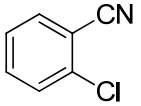
White solid,152-154°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 9.0 Hz, 1H), 8.25 (d, J = 7.6 Hz, 2H), 8.17 (dd, J = 13.1, 5.9 Hz, 3H), 8.07 (t, J = 7.6 Hz, 2H), 8.00 (d, J = 9.0 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 133.1, 131.0, 130.72, 130.69, 129.8, 127.3, 127.24, 127.21, 127.1, 124.6, 124.14, 124.12, 123.7, 119.1, 105.8.

4-Chlorobenzonitrile (**2h**)[3]



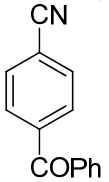
White solid, m.p. 90-91 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 133.7, 130.1, 118.3, 111.2.

2-Chlorobenzonitrile (**2i**)



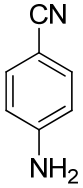
White solid, m.p. 44-45 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.8 Hz, 1H), 7.59-7.49 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 134.3, 134.2, 130.4, 127.5, 116.3, 113.7.

4-Benzoylbenzonitrile (**2j**) [1]



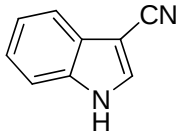
White solid, m.p. 110-112 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J =8.8 Hz, 2H), 7.81-7.75 (m, 4H), 7.64 (dd, J = 7.6, 7.2 Hz, 1H), 7.52 (dd, J = 8.0, 7.2 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 141.6, 136.7, 133.7, 132.5, 130.6, 130.4, 129.0, 118.4, 116.0.

4-Aminobenzonitrile (**2k**)



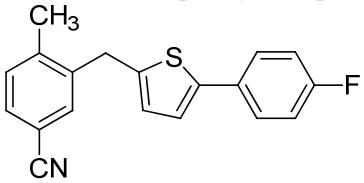
Yellow solid, m.p. 84-85 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 8.6 Hz, 2H), 4.17 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 134.2, 120.4, 114.8, 100.6.

1H-Indole-3-carbonitrile (**2l**)[4]



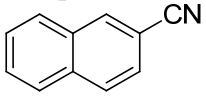
Yellow solid, m.p. 178-180 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.89 (d, J =7.6 Hz, 1H), 7.75 (s, 1H), 7.49 (d, J = 7.2 Hz, 1H), 7.35 (td, J = 7.2Hz, 1.2 Hz, 1H), 7.31 (td, J = 7.2 Hz, 1.2Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 132.2, 127.3, 124.7, 122.7, 120.0, 116.2, 112.4, 87.8.

3-((5-(4-Fluorophenyl)thiophen-2-yl)methyl)-4-methylbenzonitrile (**2m**)



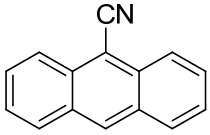
Gray solid, m.p. 97-99 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 4H), 7.27 (d, J = 7.6 Hz, 1H), 7.05-7.01 (m, 3H), 6.68 (s, 1H), 4.13 (s, 2H), 2.39 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 ($J_{C\text{-}F}$ = 245.6 Hz), 142.6 ($J_{C\text{-}F}$ = 5.0 Hz), 141.4, 140.0, 133.0, 131.5, 130.9, 130.9 ($J_{C\text{-}F}$ = 3.3 Hz), 127.6 ($J_{C\text{-}F}$ = 8.0 Hz), 126.9, 123.1, 119.4, 116.2($J_{C\text{-}F}$ = 21.6 Hz), 110.4, 33.9, 20.2. HRMS: Calcd. for $C_{19}H_{14}FNS.[M]^+$, 307.0831; found, 307.0832.

2-Naphthonitrile (**2n**)



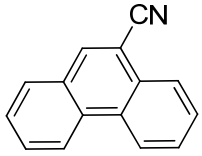
White solid, m.p. 68-70 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.93-7.89(m, 3H), 7.65-7.60 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 134.5, 132.6, 129.5, 129.4, 128.8, 128.4, 128.0, 126.7, 119.6, 109.7.

Anthracene-9-carbonitrile (**2o**) [1]



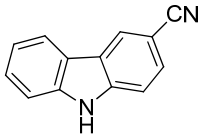
White solid, m.p. 177-178 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.38 (d, J = 8.6 Hz, 2H), 8.04 (d, J = 8.6 Hz, 2H), 7.69 (t, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 133.0, 130.9, 129.3, 129.2, 126.7, 125.6, 117.6, 105.7.

Phenanthrene-9-carbonitrile (**2p**)



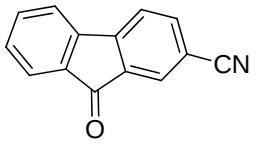
White solid,108-109 ^{o}C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68-8.64 (m, 2H), 8.29-8.26 (m, 1H), 8.20 (s, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.81-7.72 (m, 3H), 7.67 (t, J = 7.6 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 131.9, 130.2, 130.1, 129.9, 129.7, 129.0, 128.4, 128.3, 127.9, 126.3, 123.3, 123.1, 118.2, 109.6.

9H-Carbazole-3-carbonitrile (**2q**)



White solid, 180-181 ^{o}C.
^{1}H NMR (400 MHz, DMSO) δ 11.91 (s, 1H), 8.85(s, 1H), 8.27 (d, J = 7.8 Hz, 1H), 7.78 (dd, J = 8.4, 1.6 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H).^{13}C NMR (100 MHz, DMSO) δ 142.6, 141.2, 129.5, 127.9, 126.5, 123.6, 122.5, 121.9, 121.5, 120.8, 113.0, 112.5, 101.1.

9-Oxo-9H-fluorene-2-carbonitrile (**2r**)

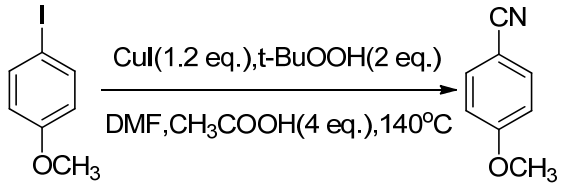


Yellow solid, 171-172 ^{o}C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.3 Hz, 1H), 7.69 -7.55 (m, 3H), 7.42 (t, J = 7.1 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 148.4, 143.0, 138.8, 135.7, 134.9, 134.5, 131.2, 127.8, 125.3, 121.8, 121.3, 118.4, 113.0.

6. Detection of Cyanide Anion (CN^-) by Indicator Paper

Picrate paper was prepared by wetting filter paper with a solution of 5.0 g of sodium bicarbonate and 0.5 g picric acid in 100 mL water. After drying the paper, it was cut into strips for use. An oven-dried 25 mL eggplant-shaped bottle equipped with a magnetic stir bar was charged with $Cu(NO_3)_2 \cdot 3H_2O$ (0.6 mmol), aryl bromide (0.5 mmol), CH_3COOH (2.0 mmol), t-BuOOH (1.0 equiv,70% aq.) and DMF (3.0 mL). The bottle was left at 140 ^oC (oil bath temperature) for 3 h, then the solution was cooled to 80 ^oC, Tartaric acid (0.2 g) and the reaction mixture (1.5 mL) were added into a flask. A sealed plastic vial, with a number of holes and a strip inside, was placed above the reaction mixture. The flask was heated in the water bath under 80 ^oC for 1h. The strip turned red indicating the existence of CN^-.[6]

7. GC tracking of the reaction process of 1-Iodo-4-methoxybenzene



1a **2a**

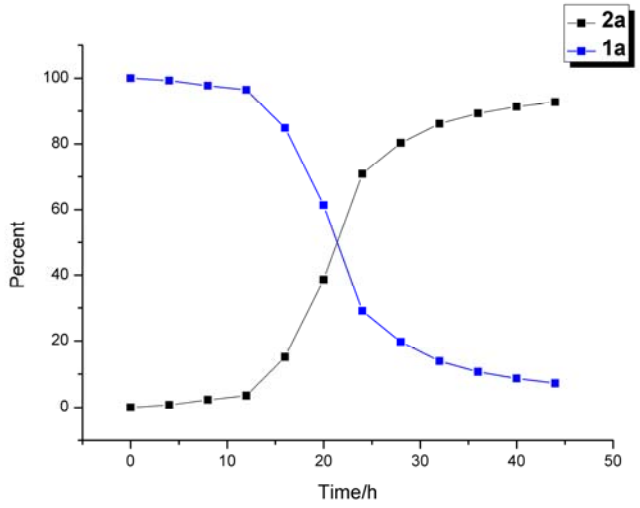
A flame-dried 25 mL eggplant-shaped bottle equipped with a magnetic stir bar was charged with $Cu(NO_3)_2 \cdot 3H_2O$ (0.6 mmol,1.2 equiv) and **2a** (0.5 mmol), CH_3COOH (4.0 equiv), t-BuOOH (2.0 equiv, 70% aq.) and DMF (3.0 mL). The bottle was left at 140 °C (oil bath temperature). Every once in ia whle, we took 10μl sample from the reaction mixture and the samples were analyzed by GC.

Table S1 The percent of **4a** and **2n**:

Components / Time(h)	**1a**	**2a**
0	100	0
4	99.2828	0.7172
8	97.7194	2.2806
12	96.4866	3.5134
16	84.8828	15.1172
20	61.3572	38.6428
24	29.0984	70.9016
28	19.6821	80.3179
32	13.851	86.149
36	10.686	89.314
40	8.6641	91.3359
44	7.2348	92.7652

GC conditions: Column: RTX-5, Length 30.0 m, Film Thickness 0.25 μm, Inner Diameter 0.25 mm ID

Figure S1 $Cu(NO_3)_2 \cdot 3H_2O$-mediated cyanation of **1a** using DMF



8. References

1 Q.Wen, J. Jin, B. Hu, P. Lu, Y. Wang, *RSC Adv.*, 2012, **2**, 6167.

2 D. Qiu, L. Jin, Z. Zheng, H. Meng, F. Mo, X. Wang, Y. Zhang, J. Wang, *J. Org. Chem.*, 2013, **78**, 1923.

3 J. Kim, J. Choi, K. Shin, S. Chang, *J. Am. Chem. Soc.*, 2012, **134**, 2528.

4 L. Zhang, Q. Wen, J. Jin, C. Wang, P. Lu, Y. Wang, *Tetrahedron*, 2013, **69**, 4236.

5 V. Chandrasekhar, R. S. Narayanan, *Tetrahedron Lett.*, 2011, **52**, 3527.

6 (a) J. Kim, J. Choi, K. Shin and S. Chang, *J. Am. Chem. Soc.*, 2012, **134**, 2528; (b) G. Zhang, X. Ren, J. Chen, M. Hu, and J. Cheng, *Org. Lett.*, 2011, **13**, 5004.

9. Copies of the products ^{1}H NMR and ^{13}C NMR

Figure S2 ^{1}H-NMR spectrum of **2a**

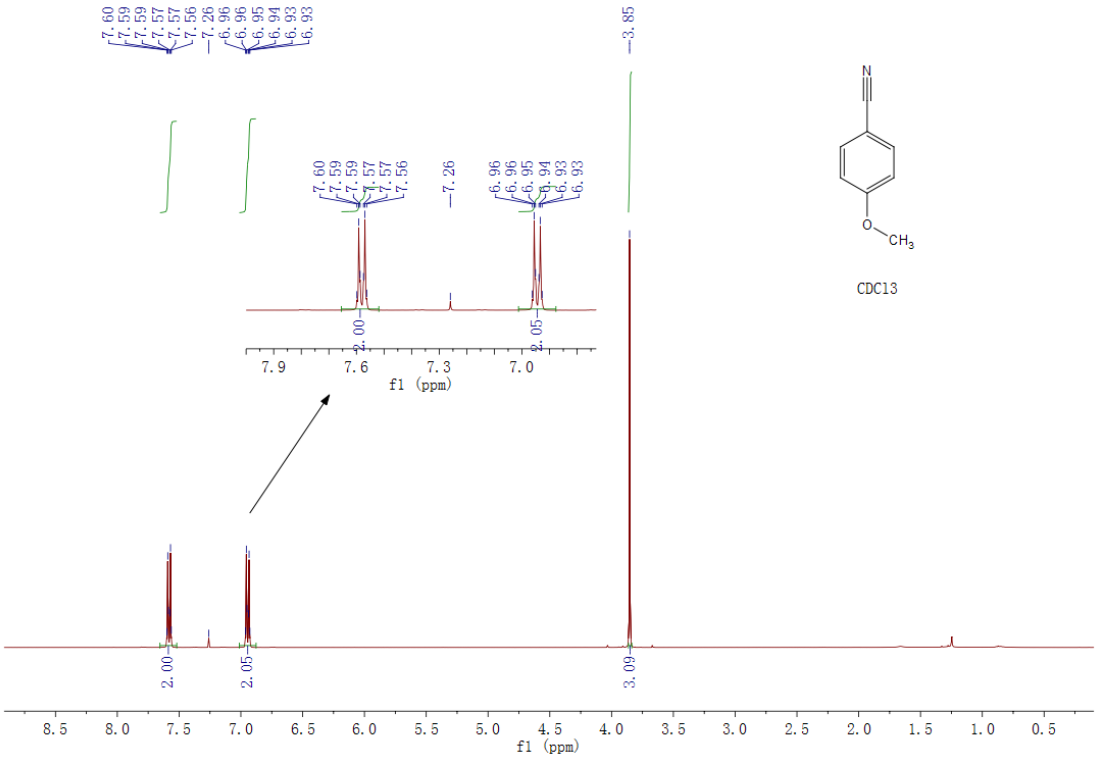


Figure S3 ^{13}C-NMR spectrum of **2a**

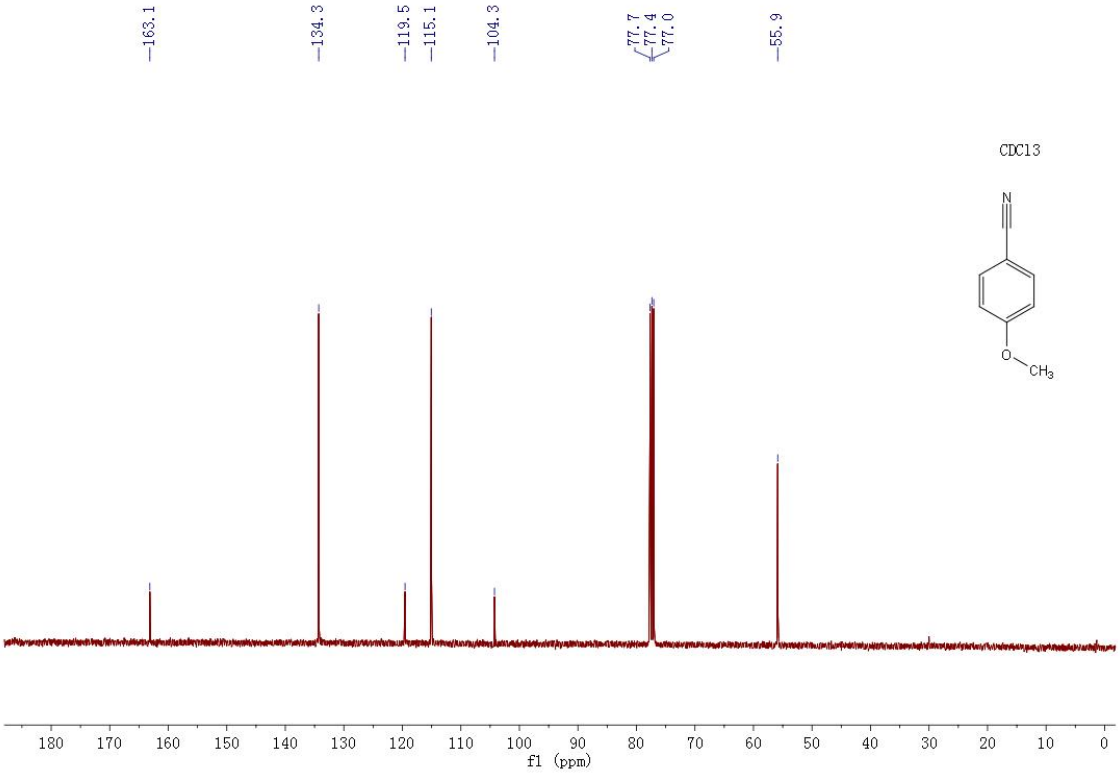


Figure S4 ^{1}H-NMR spectrum of **2b**

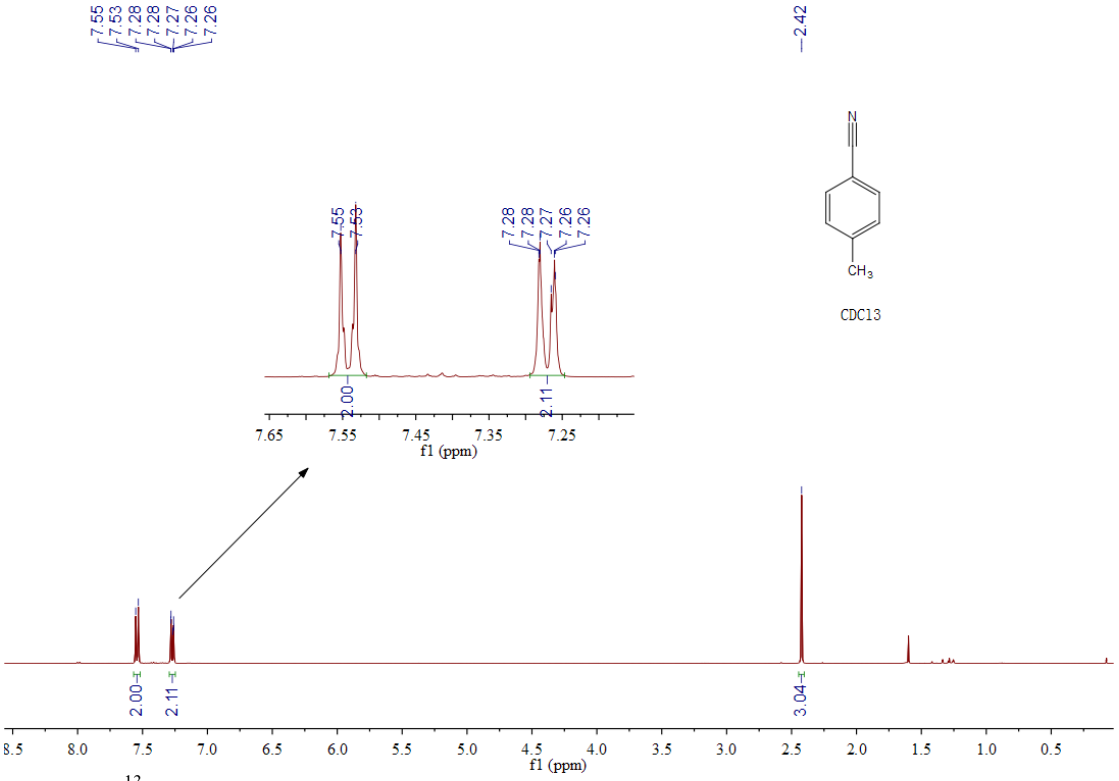


Figure S5 ^{13}C-NMR spectrum of **2b**

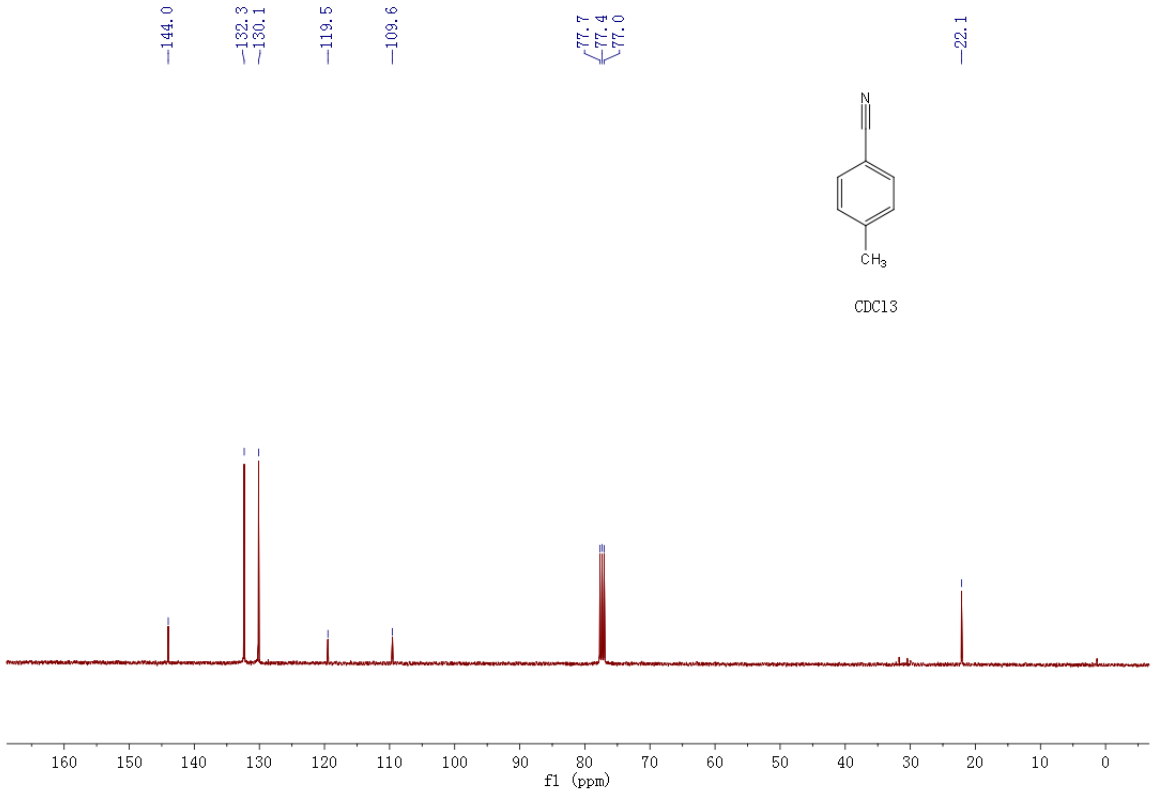


Figure S6 ^{1}H-NMR spectrum of **2c**

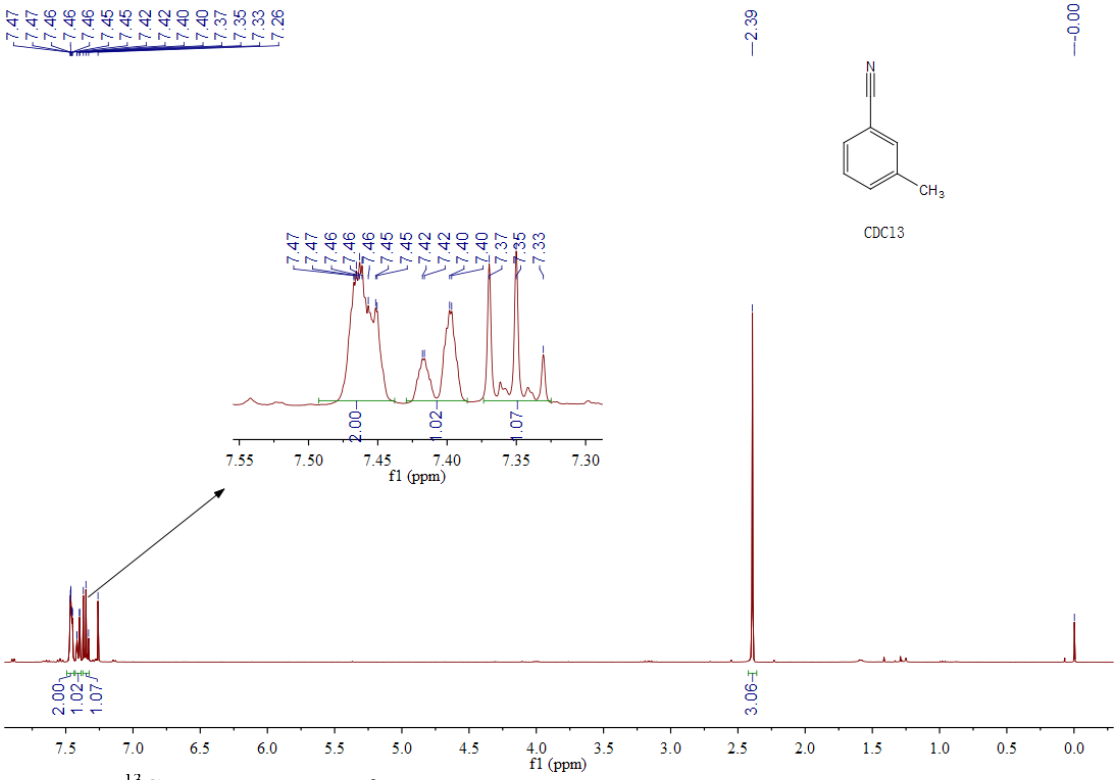


Figure S7 ^{13}C-NMR spectrum of **2c**

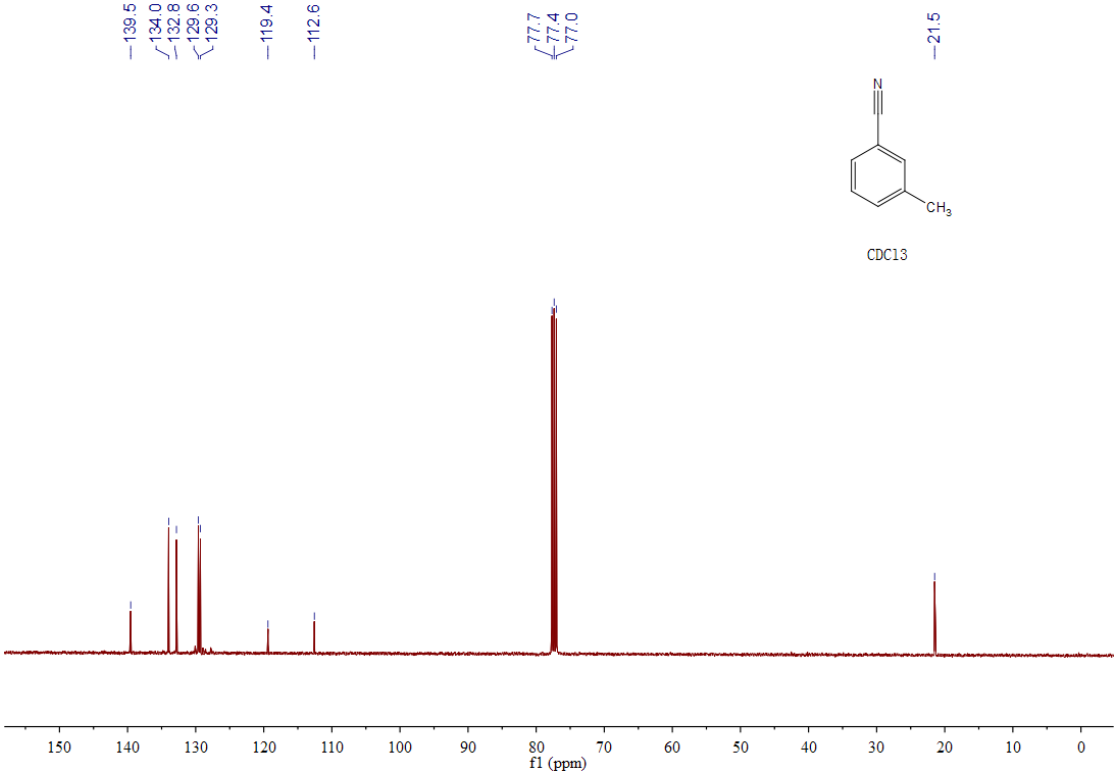


Figure S8 [1]H-NMR spectrum of **2d**

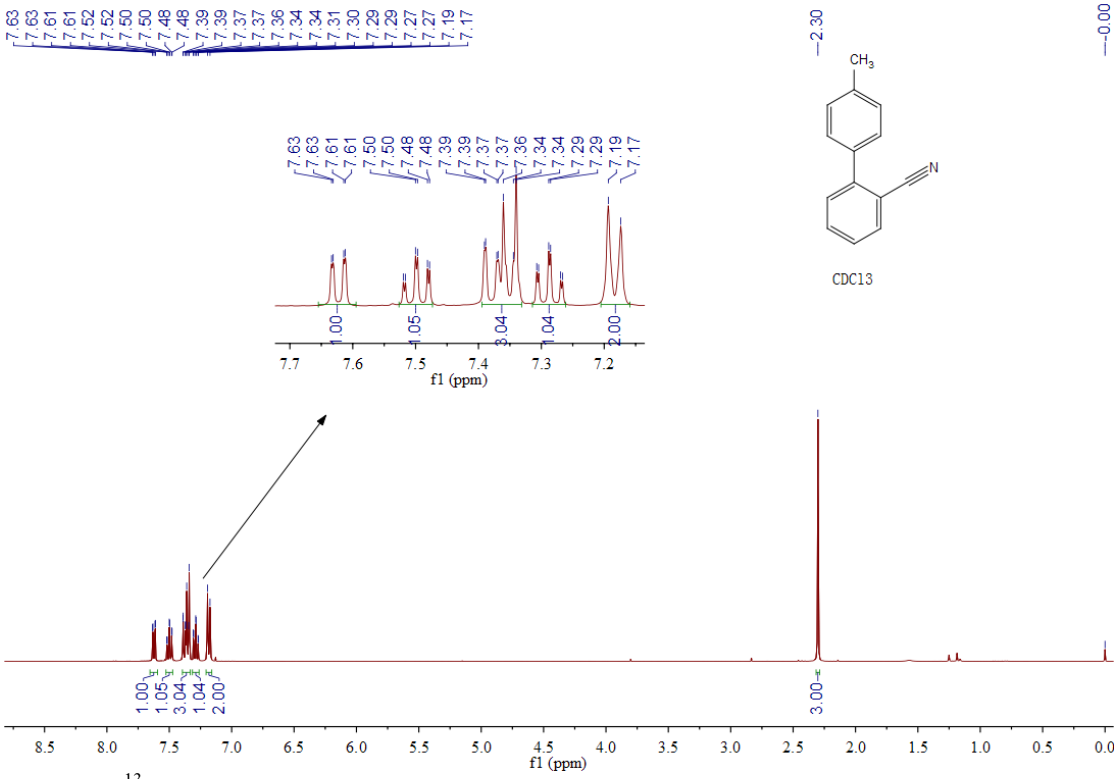


Figure S9 [13]C-NMR spectrum of **2d**

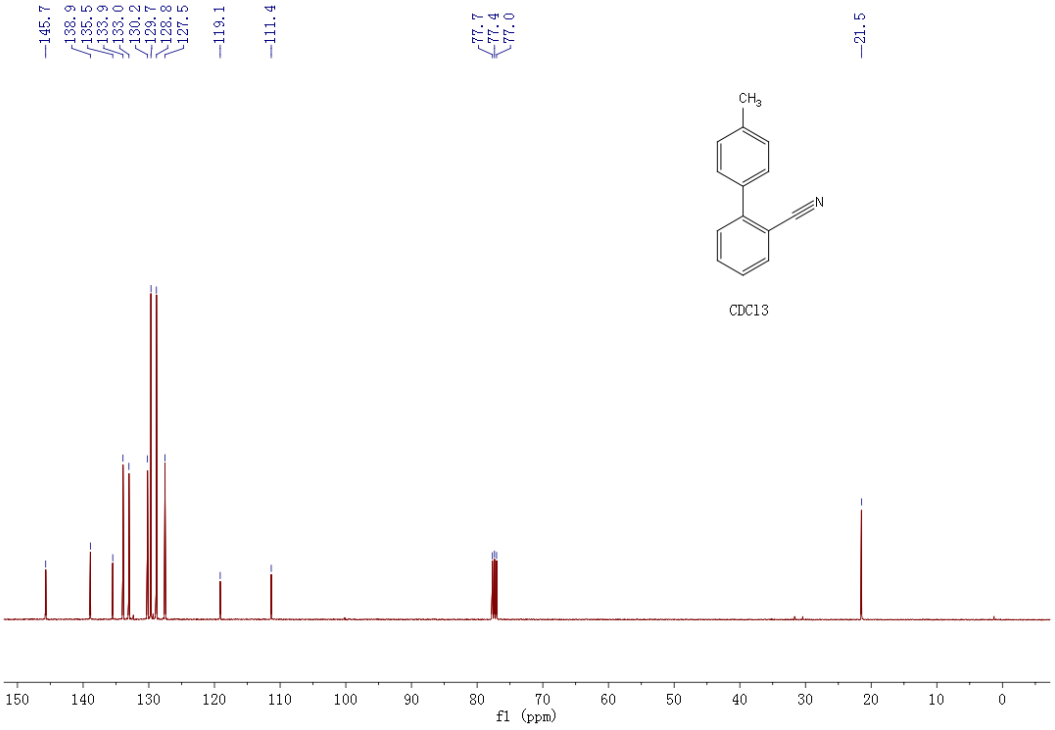


Figure S10 ^{1}H-NMR spectrum of **2e**

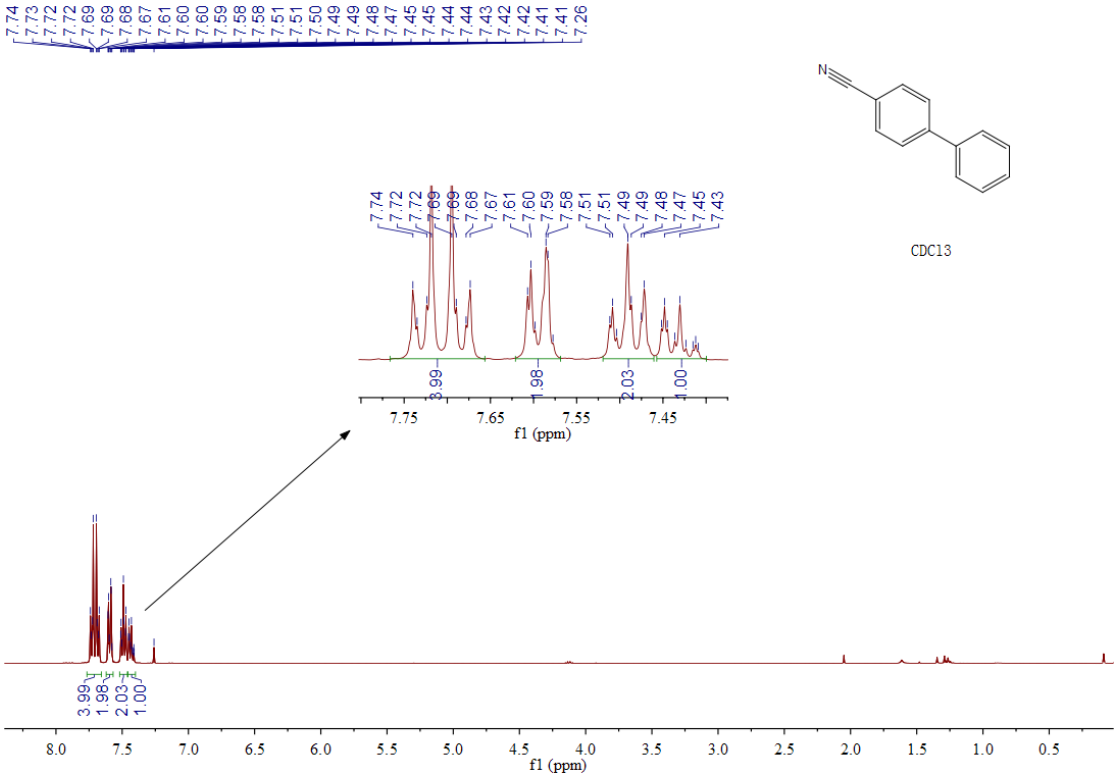


Figure S11 ^{13}C-NMR spectrum of **2e**

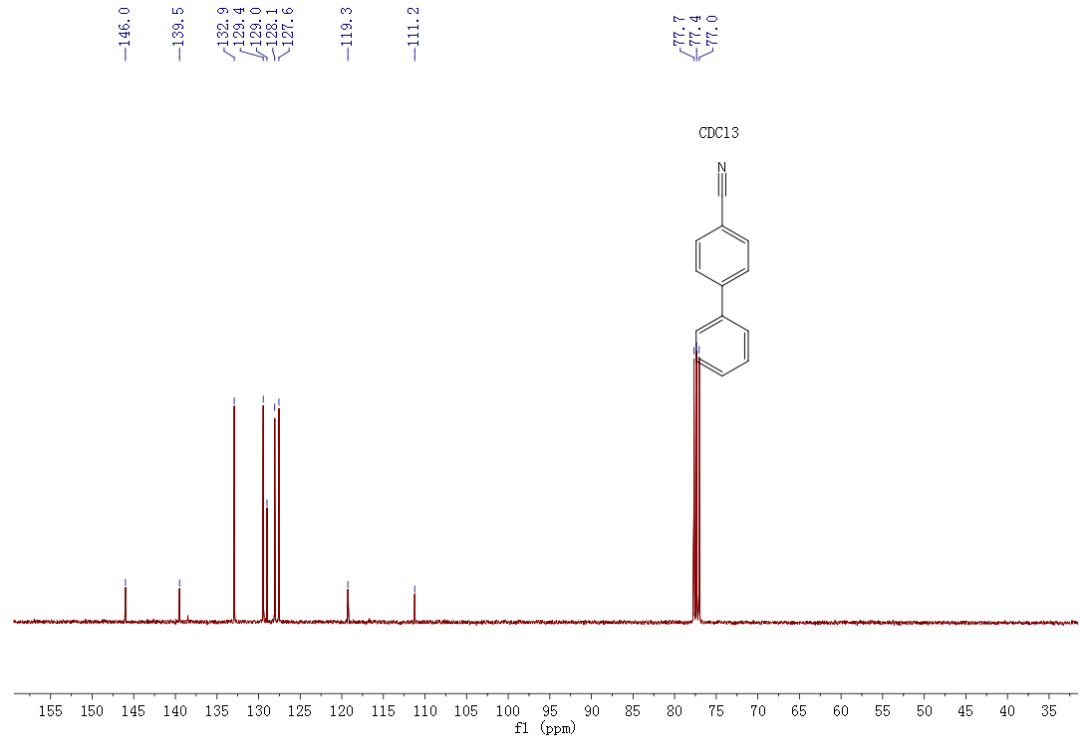


Figure S12 ^{1}H-NMR spectrum of **2f**

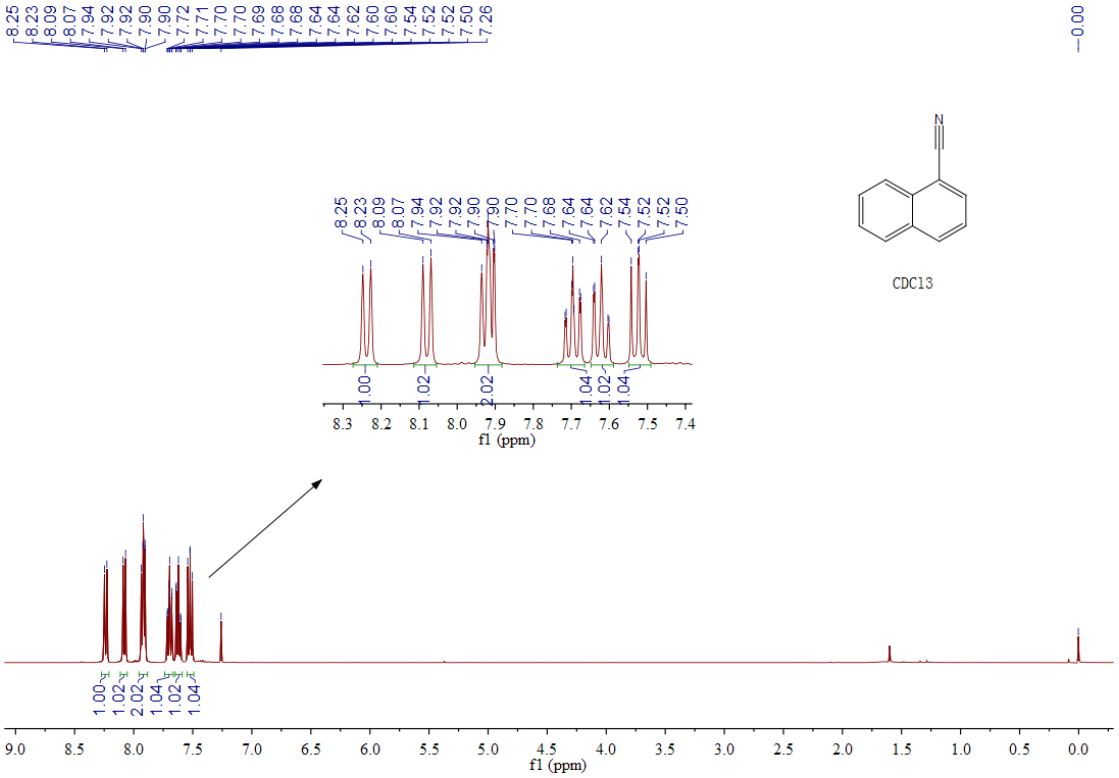


Figure S13 ^{13}C-NMR spectrum of **2f**

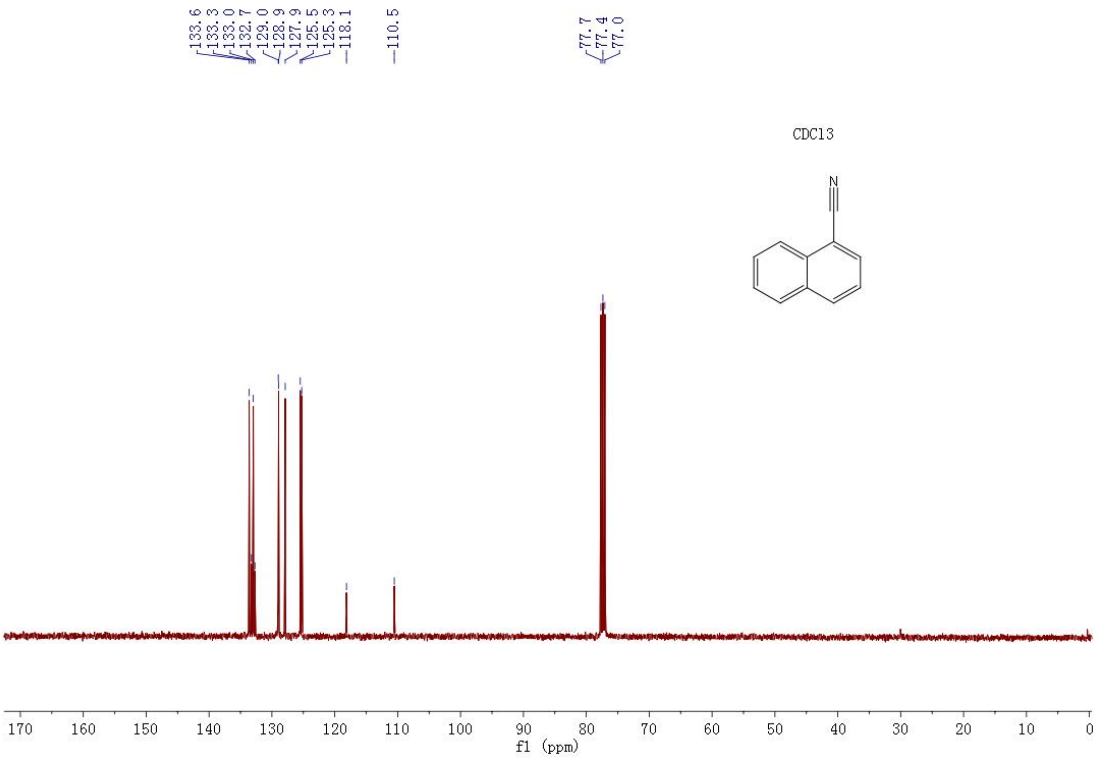


Figure S14 ^{1}H-NMR spectrum of **2g**

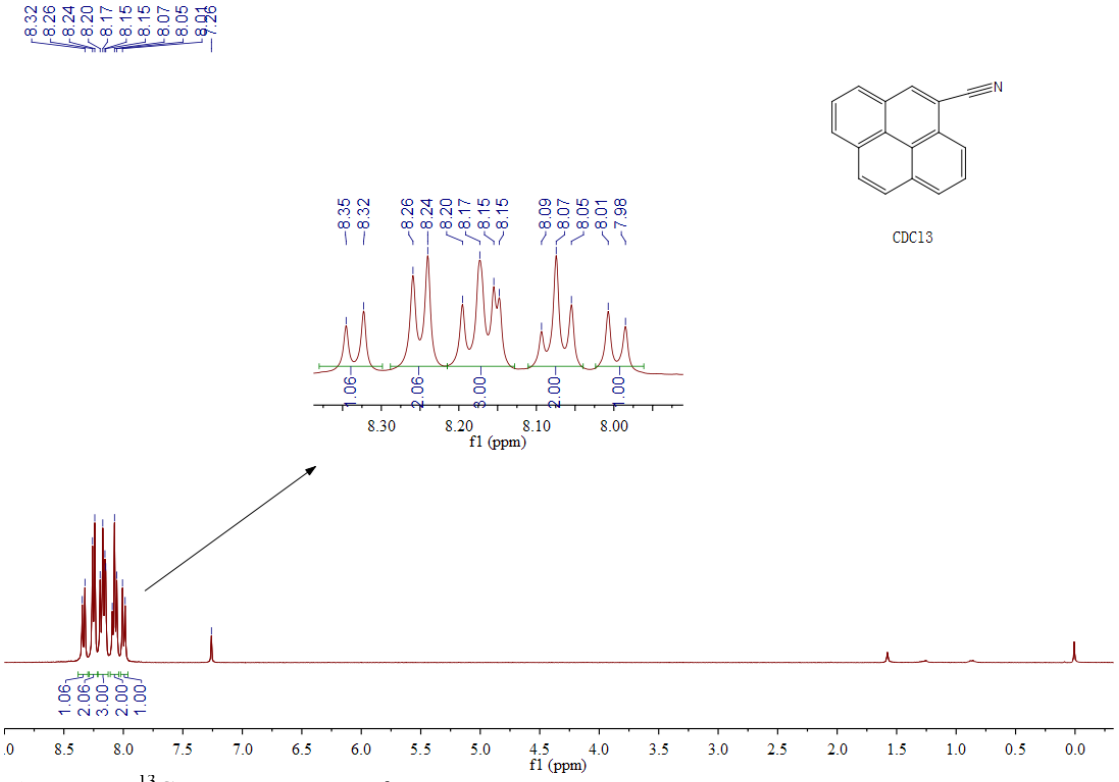


Figure S15 ^{13}C-NMR spectrum of **2g**

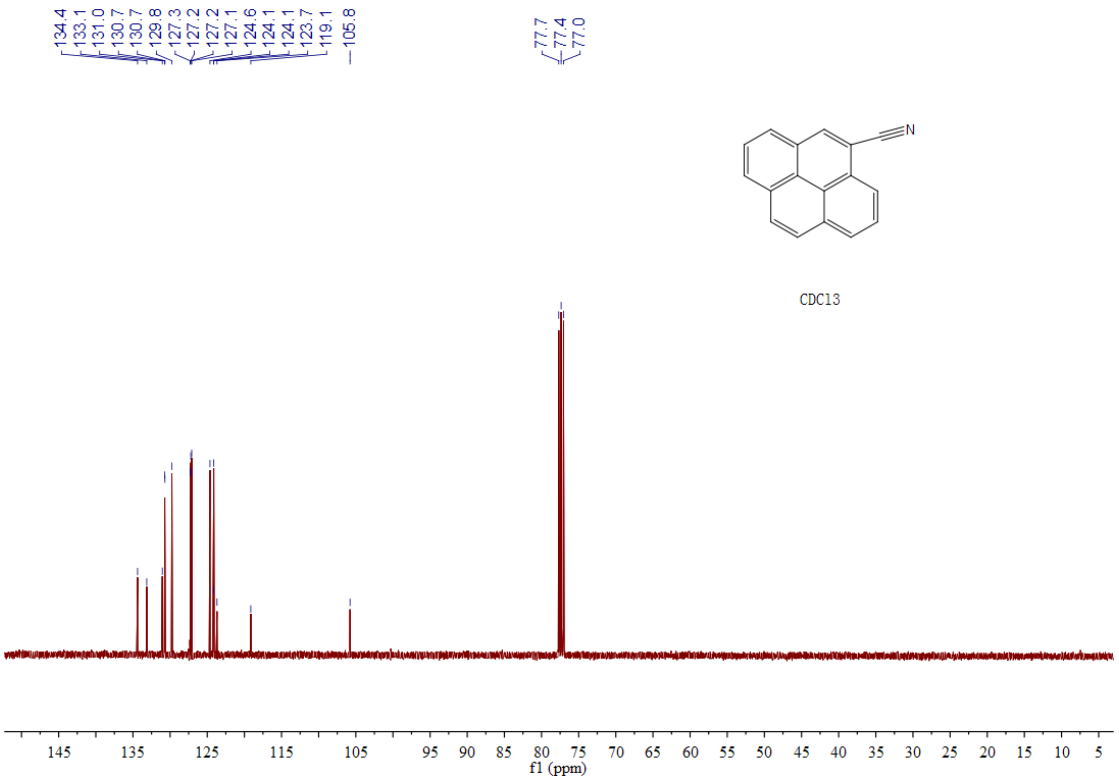


Figure S16 ^{1}H-NMR spectrum of **2h**

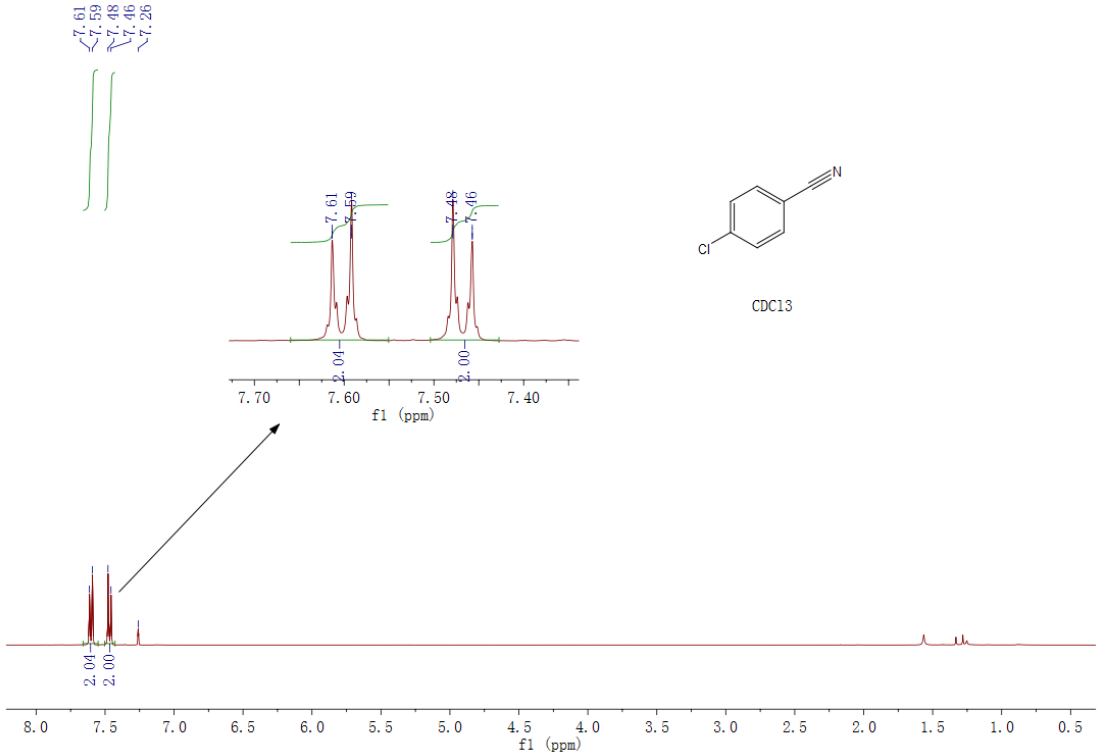


Figure S17 ^{13}C-NMR spectrum of **2h**

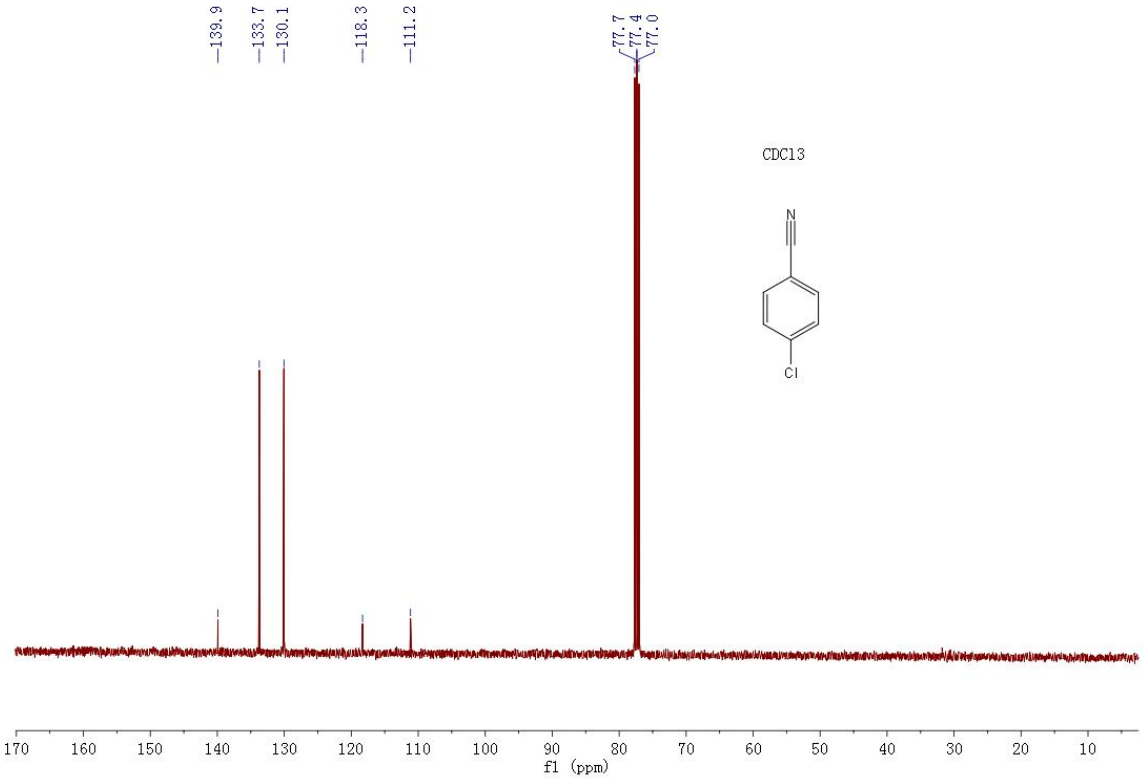


Figure S18 ^{1}H-NMR spectrum of **2i**

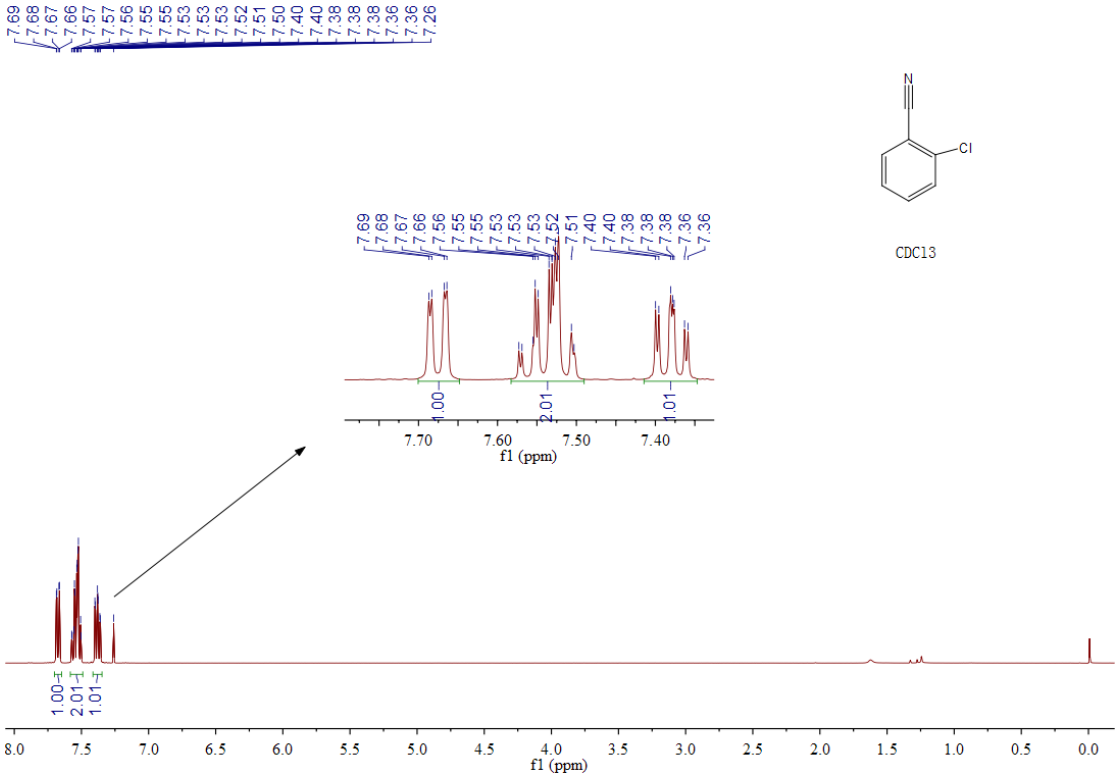


Figure S19 ^{13}C-NMR spectrum of **2i**

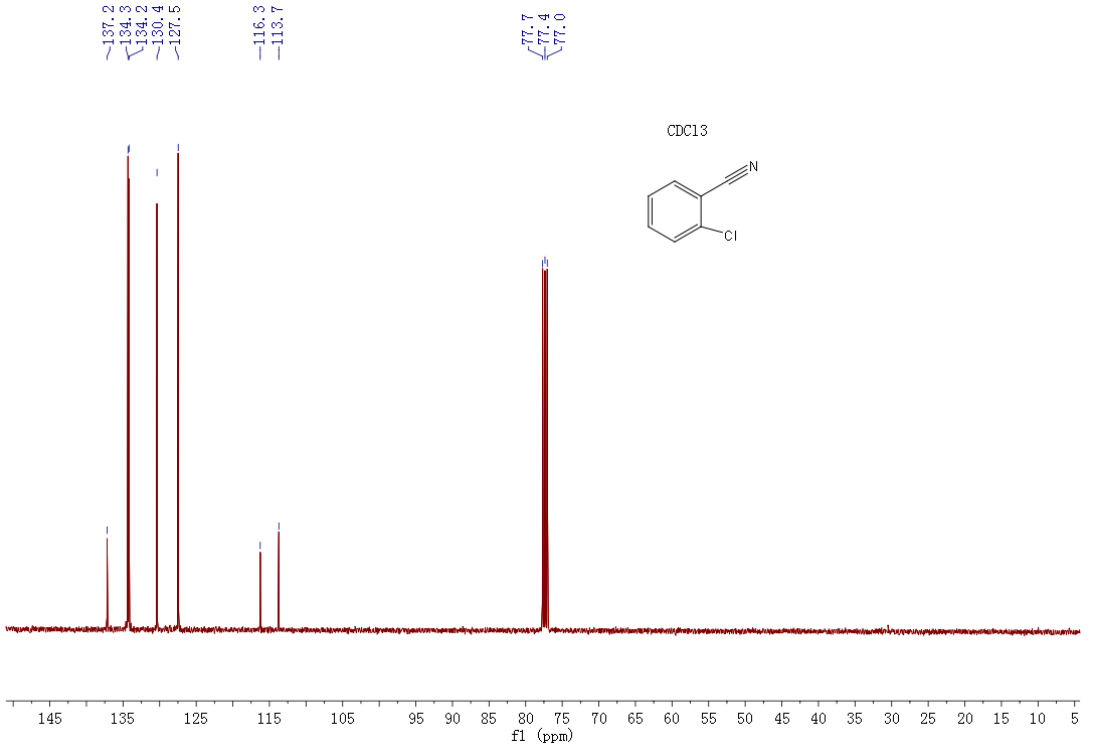


Figure S20 ^{1}H-NMR spectrum of **2j**

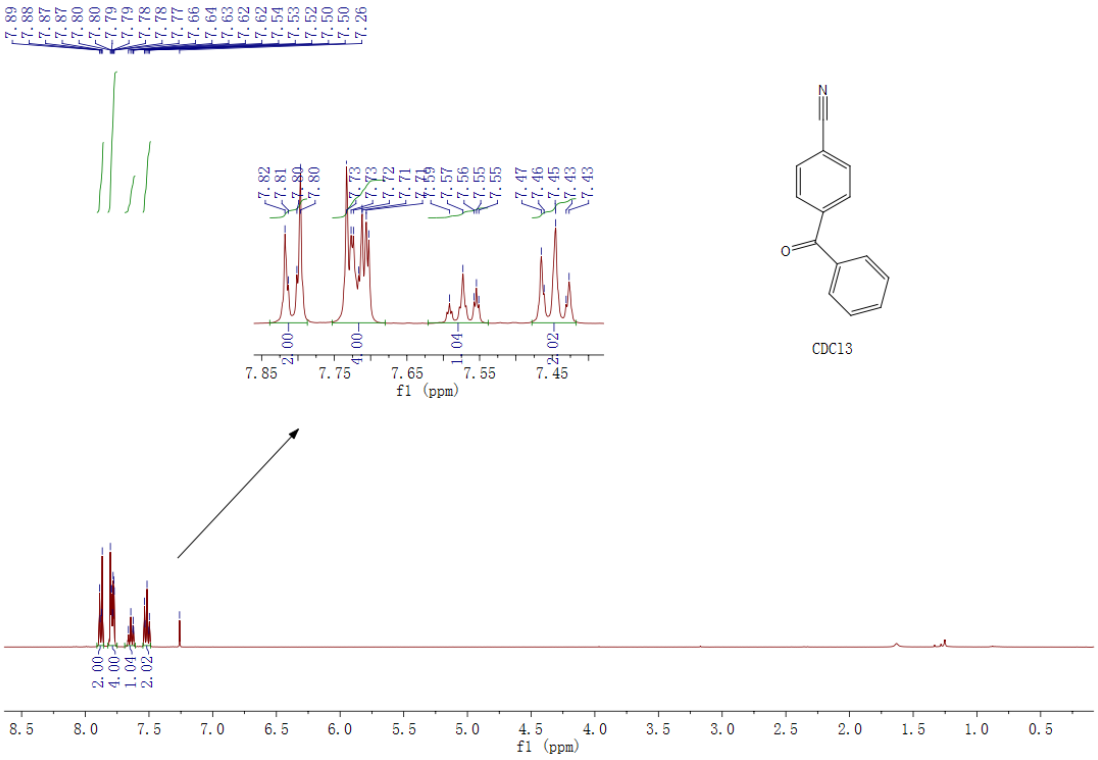


Figure S21 ^{13}C-NMR spectrum of **2j**

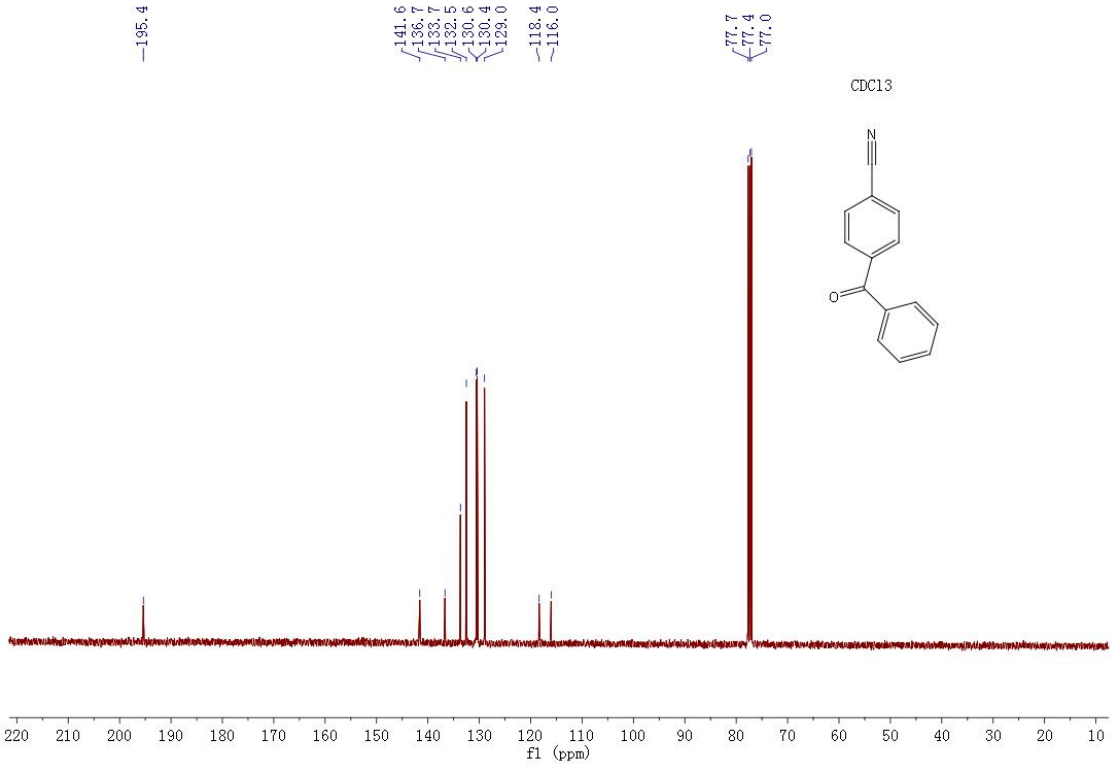


Figure S22 [1]H-NMR spectrum of **2k**

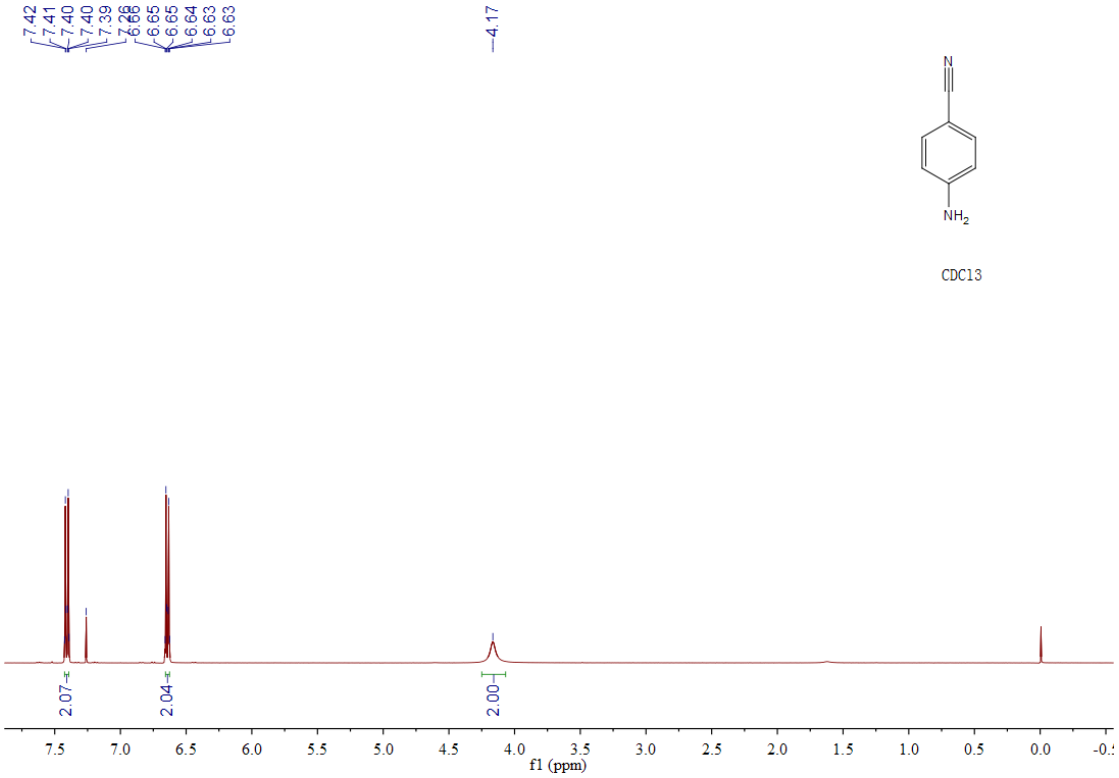


Figure S23 [13]C-NMR spectrum of **2k**

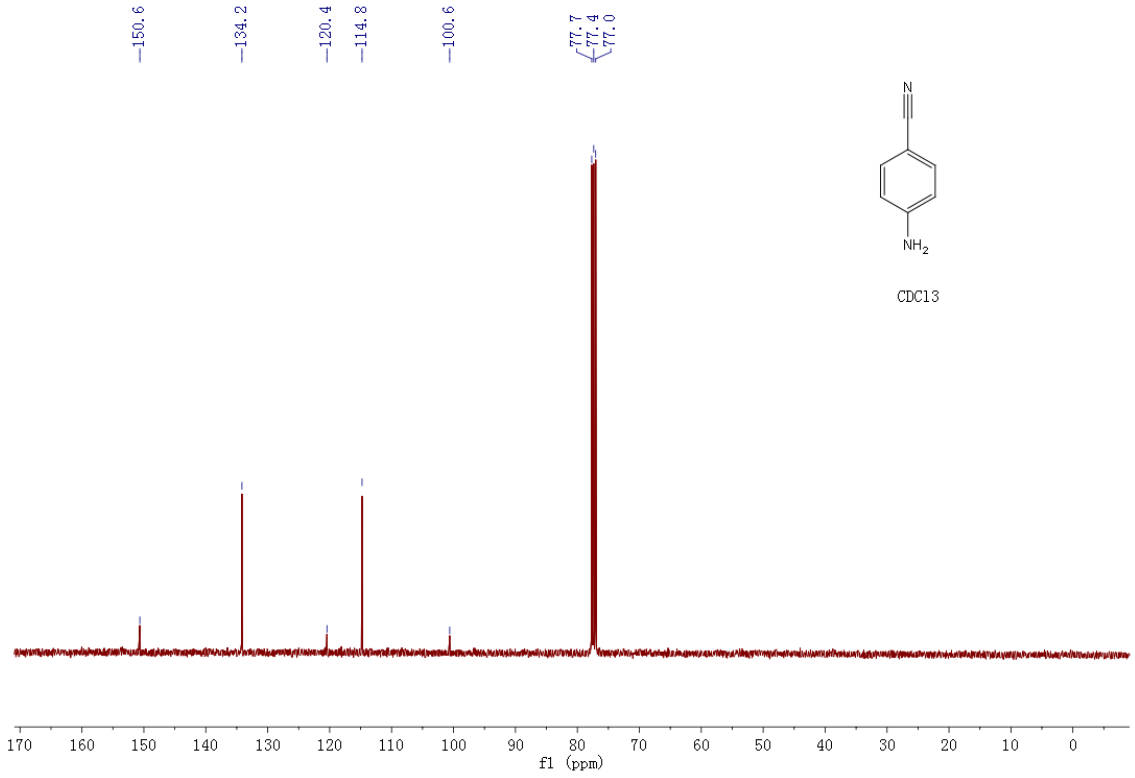


Figure S24 ^{1}H-NMR spectrum of **2l**

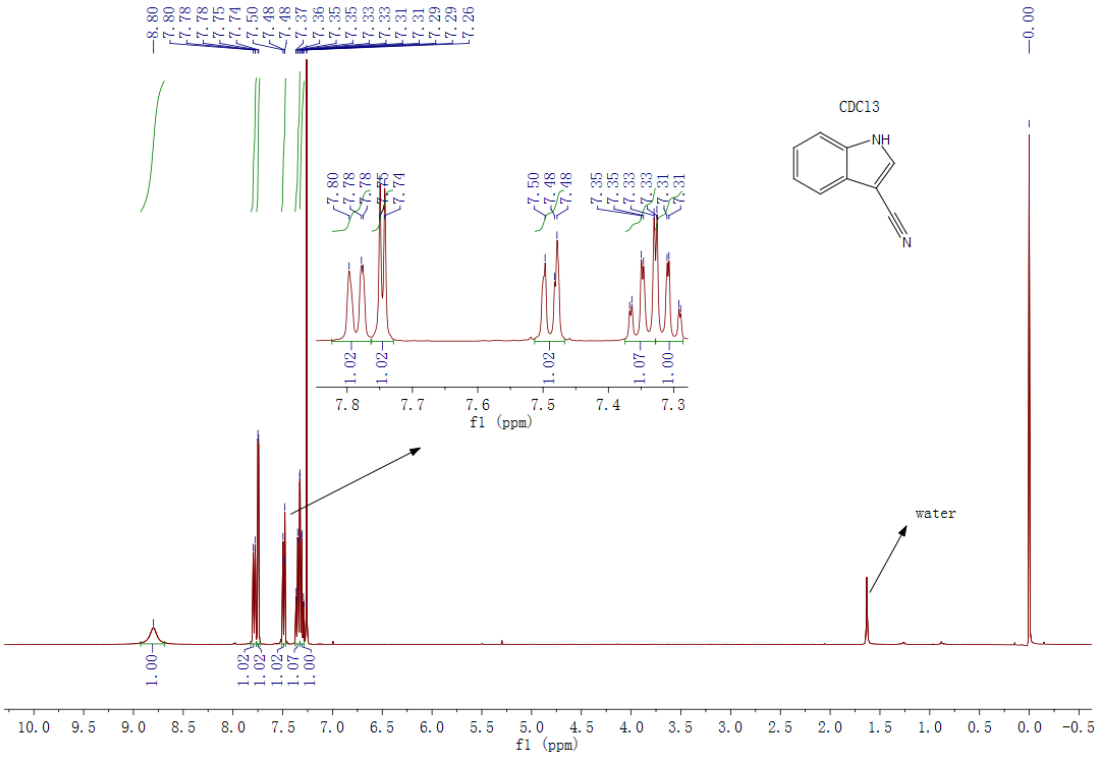


Figure S25 ^{13}C-NMR spectrum of **2l**

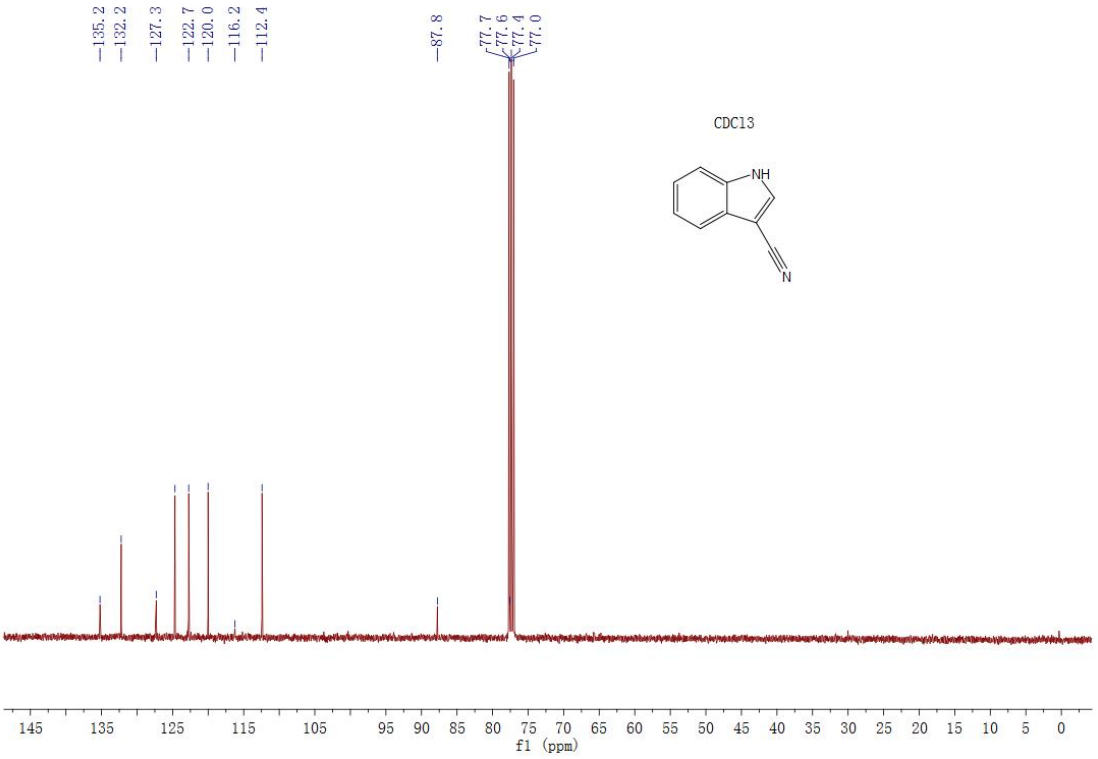


Figure S26 ^{1}H-NMR spectrum of **2m**

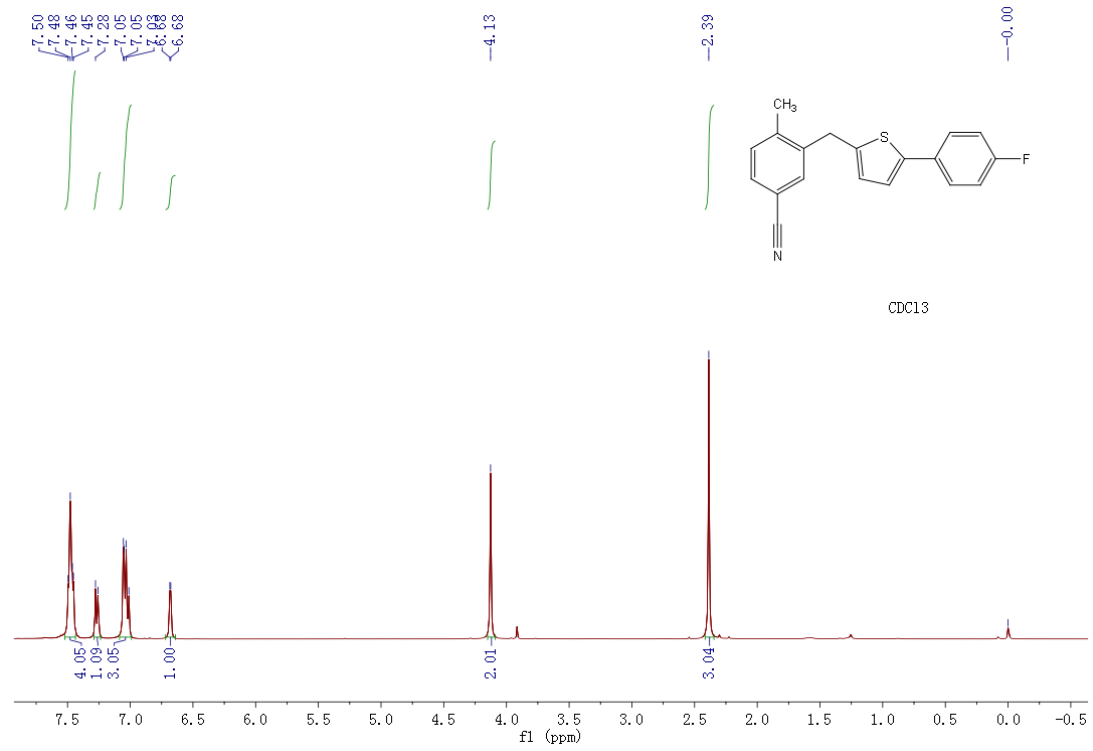


Figure S27 ^{13}C-NMR spectrum of **2m**

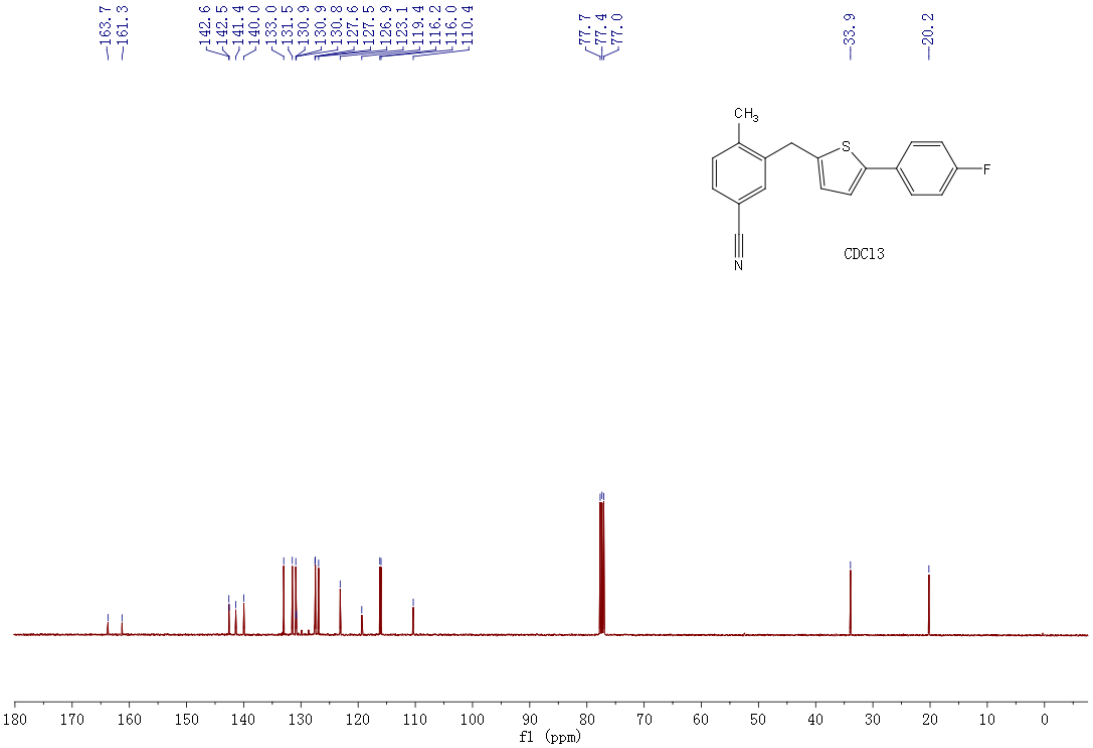


Figure S28 ^{1}H-NMR spectrum of **2n**

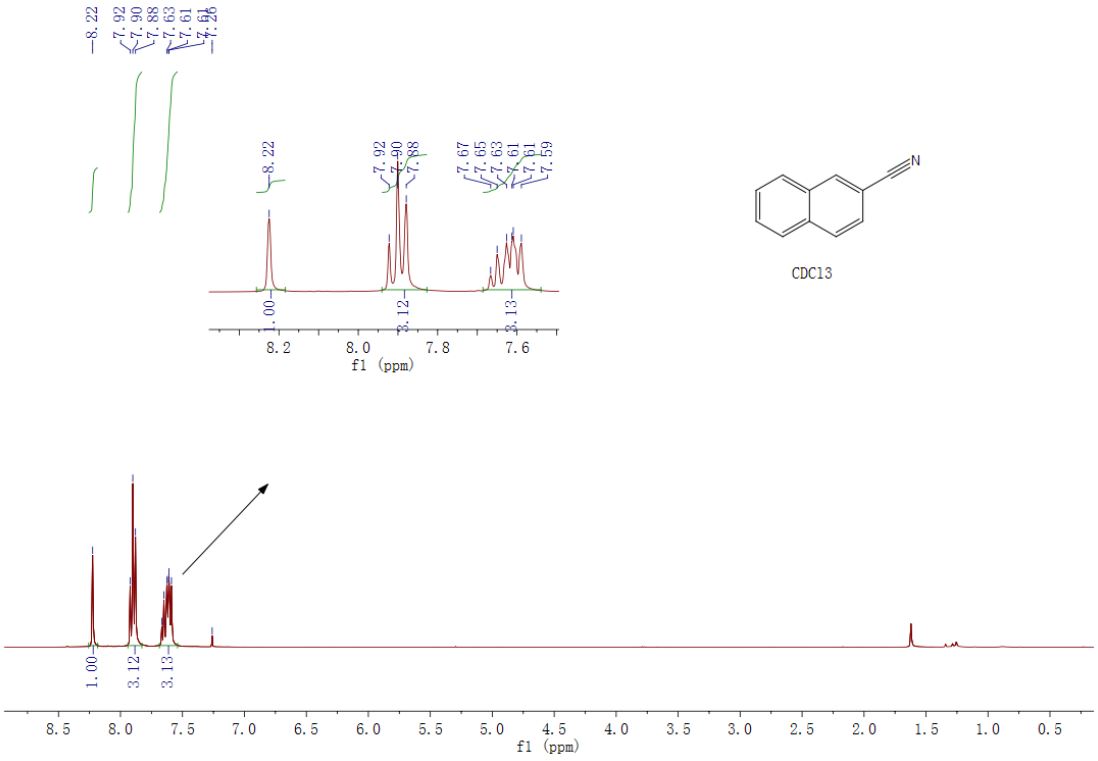


Figure S29 ^{13}C-NMR spectrum of **2n**

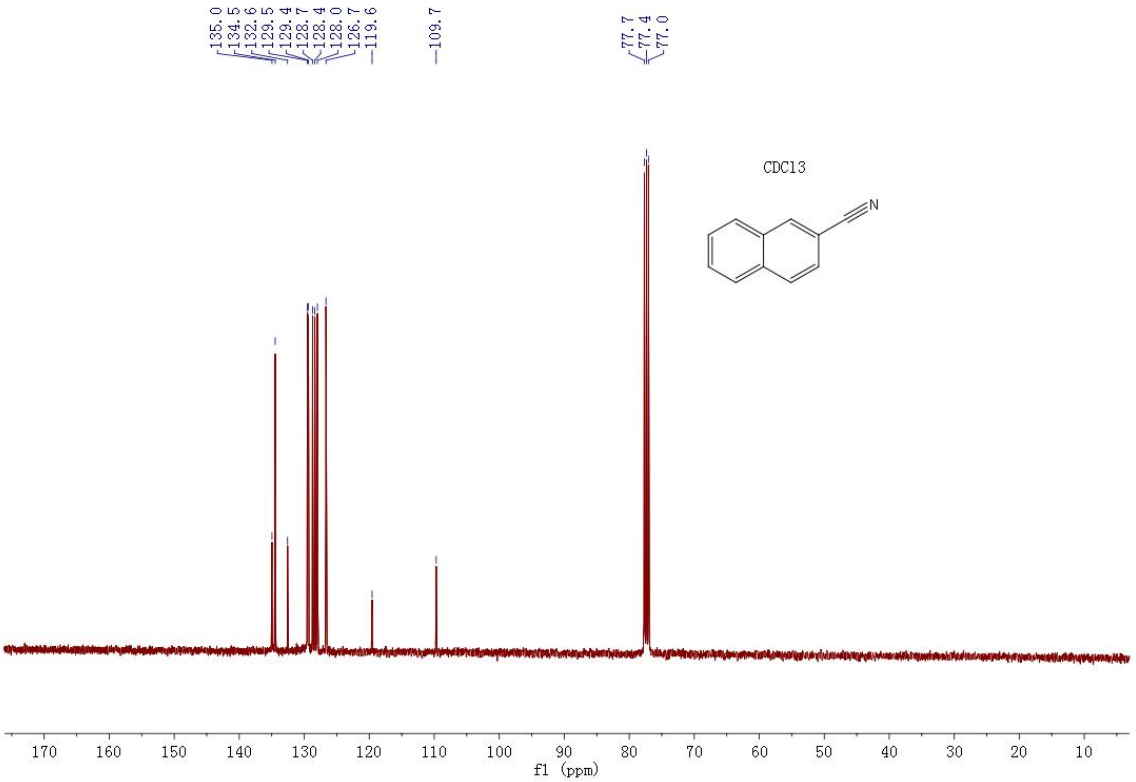


Figure S30 ^{1}H-NMR spectrum of **2o**

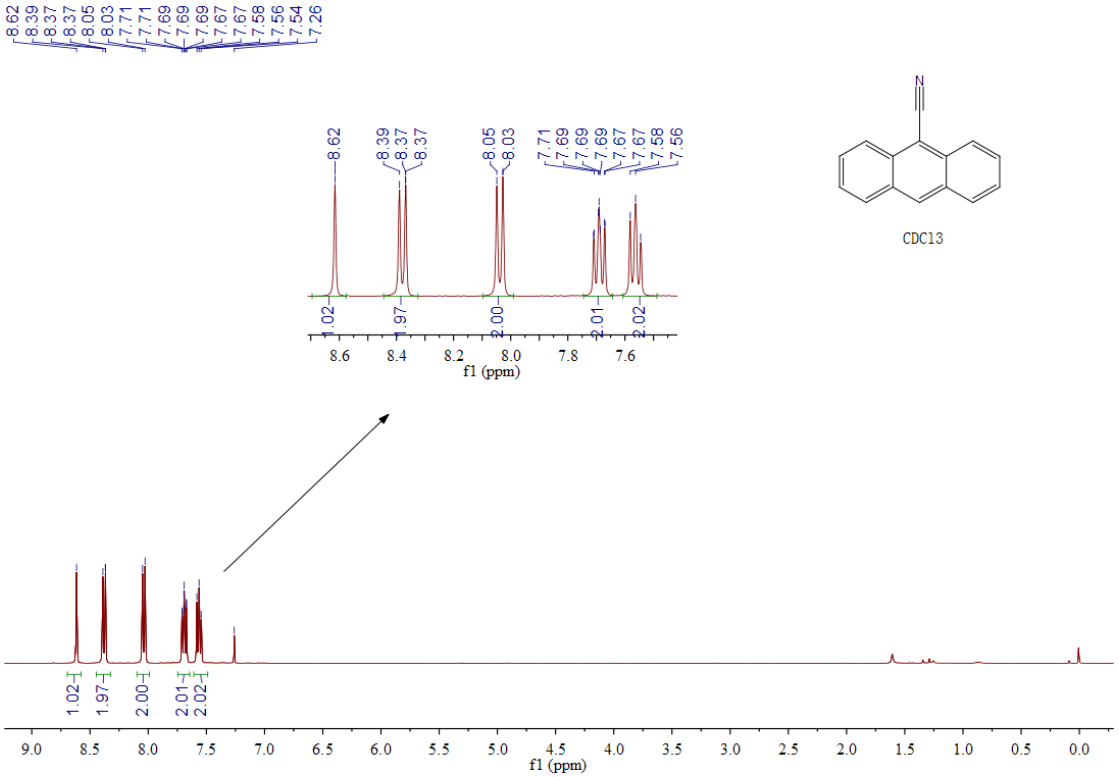


Figure S31 ^{13}C-NMR spectrum of **2o**

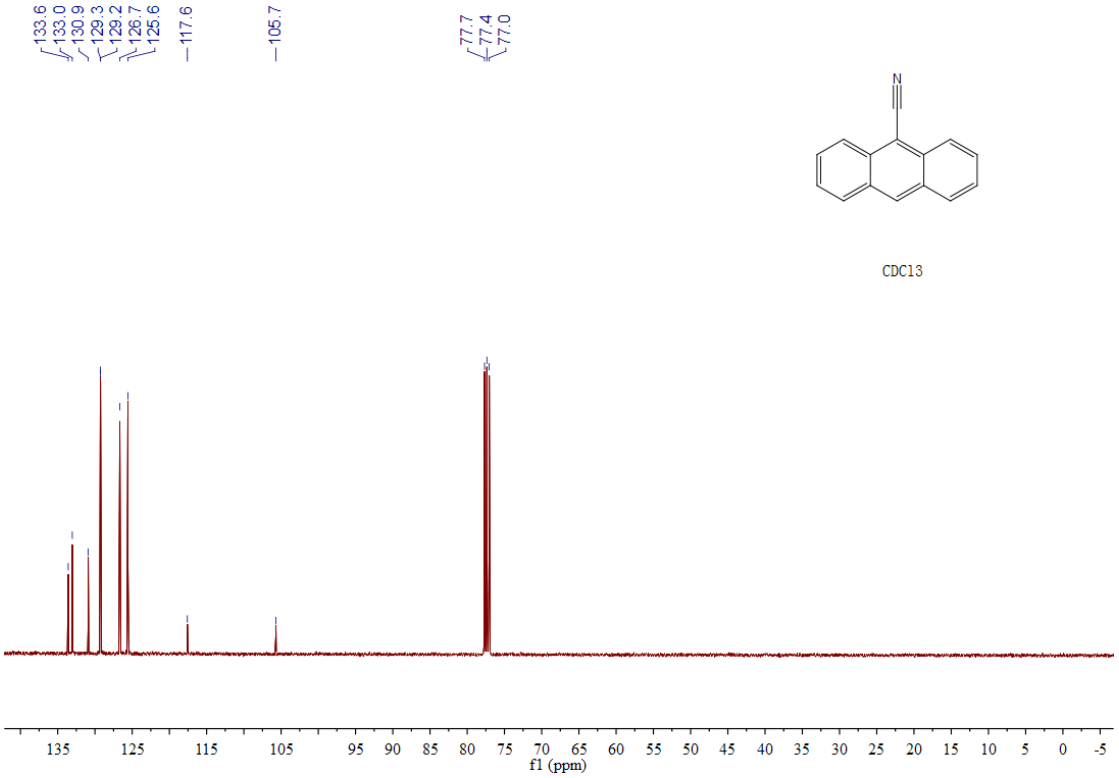


Figure S32 [1]H-NMR spectrum of **2p**

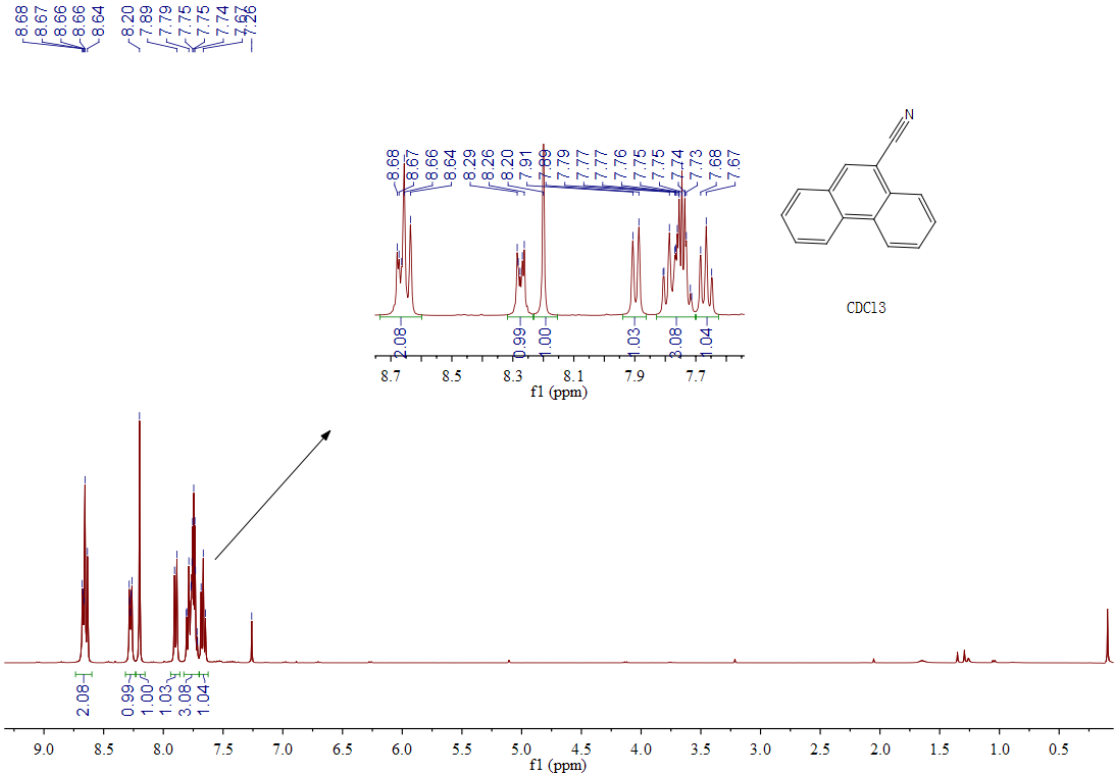


Figure S33 [13]C-NMR spectrum of **2p**

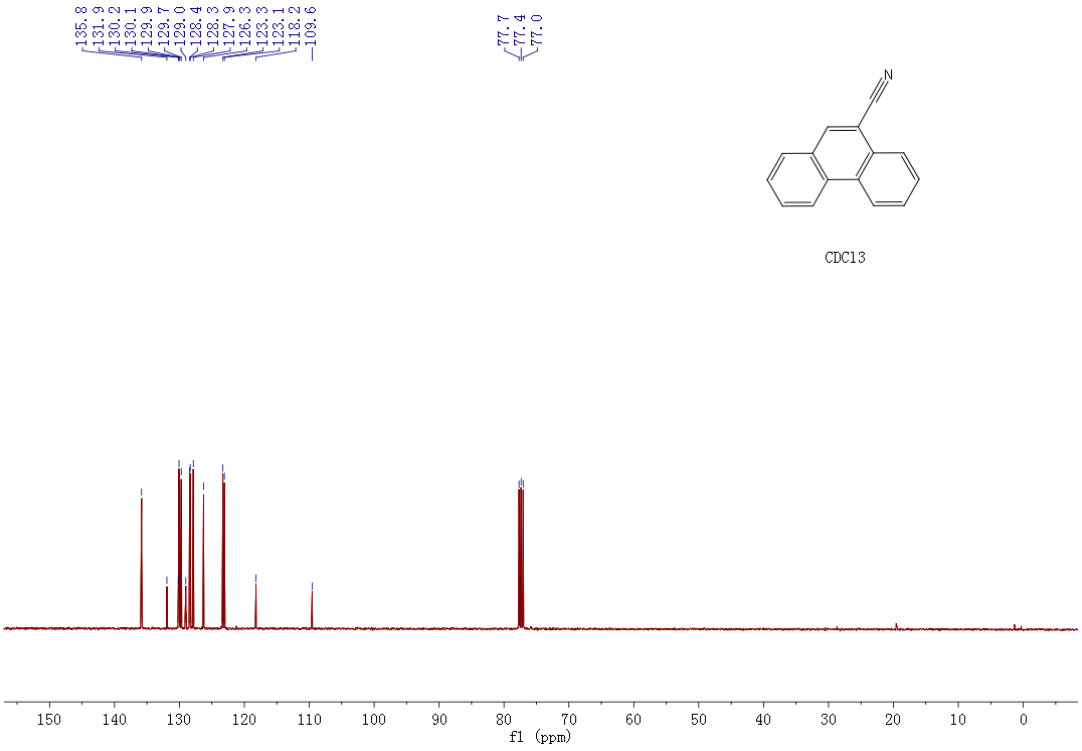


Figure S34 [1]H-NMR spectrum of **2q**

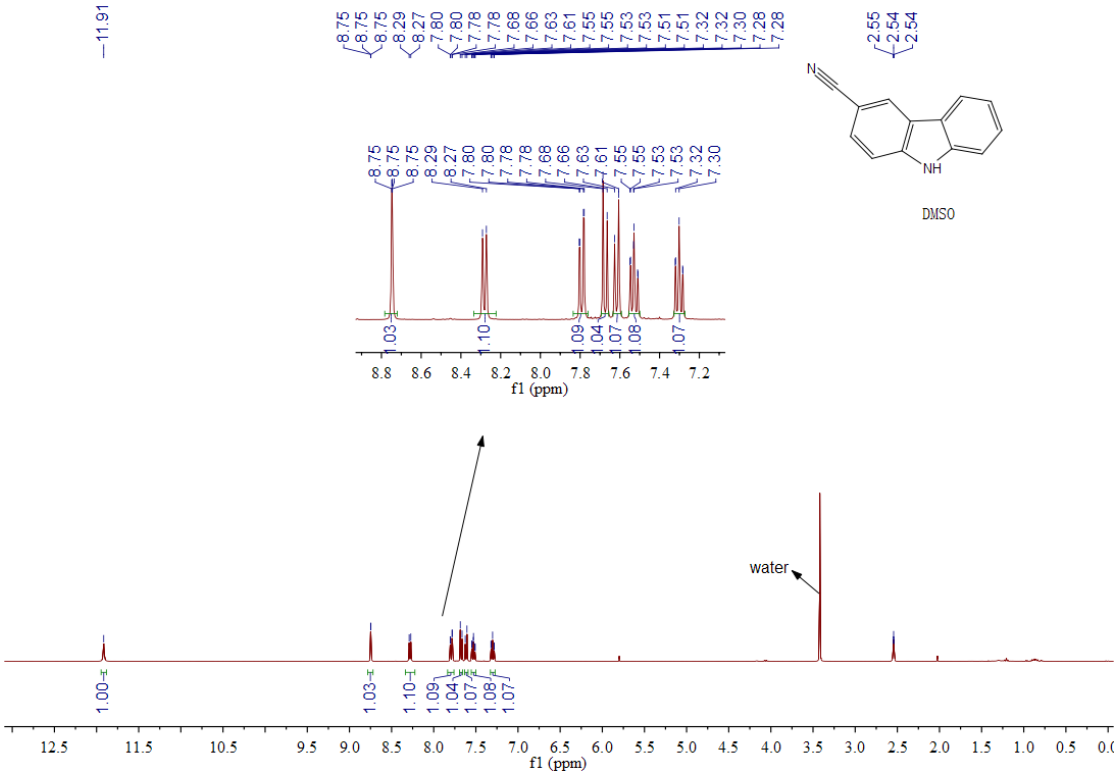


Figure S35 [13]C-NMR spectrum of **2q**

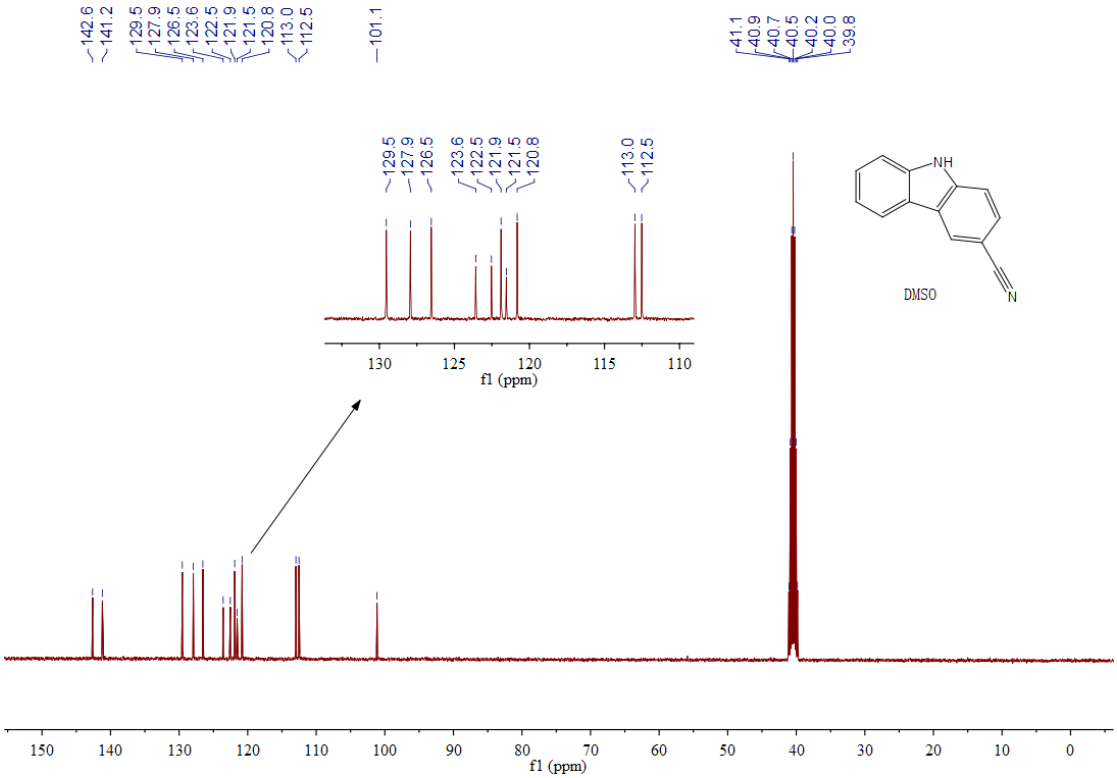


Figure S36 ^{1}H-NMR spectrum of **2r**

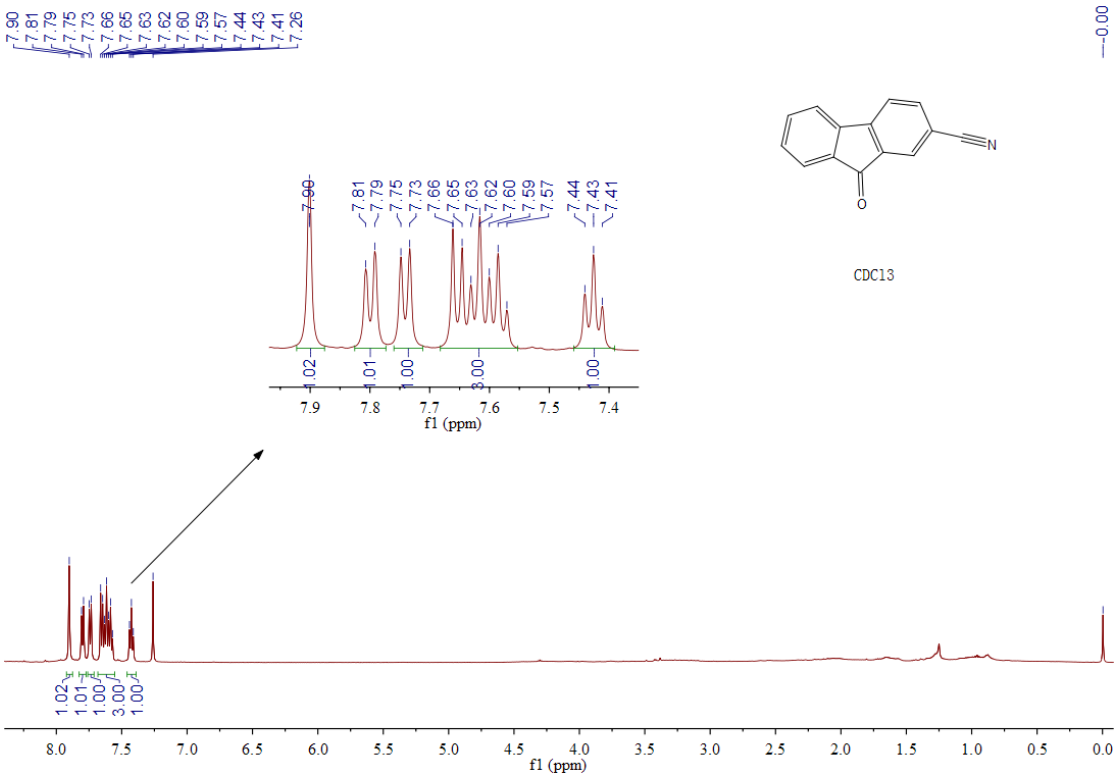


Figure S37 ^{13}C-NMR spectrum of **2r**

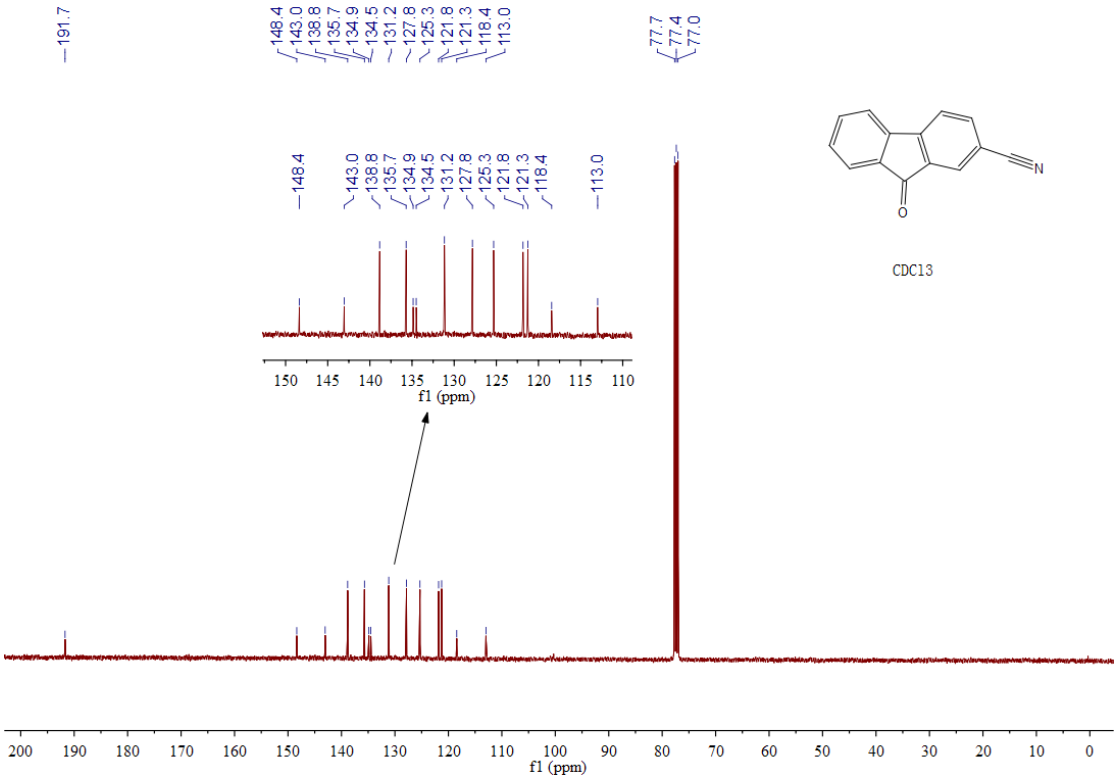


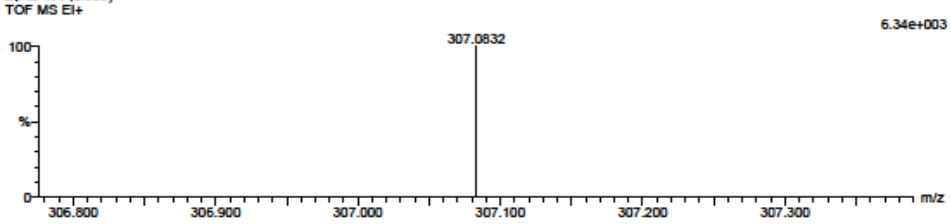
Figure S38 HRMS for **2m**

Elemental Composition Report **Page 1**

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
54 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-200 N: 2-6 S: 1-1 F: 0-2

zip-tz 168 (2.800)
TOF MS EI+



Minimum:				-1.5		
Maximum:		2.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
307.0832	307.0829	0.3	1.0	9.5	5549175.0	C14 H13 N4 S F2