Supporting Information for

Copper-Mediated Cyanations of Indoles and Electron-Rich Arenes Using DMF as a Single Surrogate

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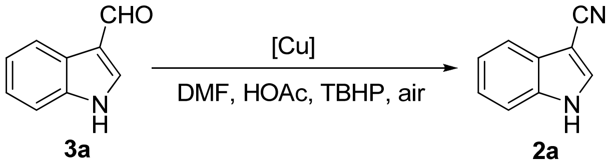
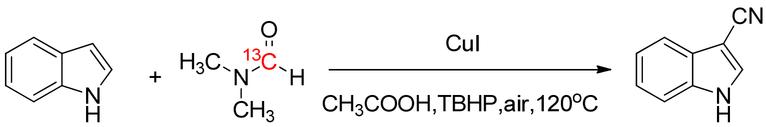
1. Table S1 Screening of the reaction conditions for cyanation of 3a[a]



entry	[Cu] (equiv)	HOAc (equiv)	TBHP (equiv)	Temp (°C)	Yield (%)[b]
1	CuI (1.2)	8	2	130	31
2	CuBr (1.2)	8	2	130	36
3	CuCl (1.2)	8	2	130	25
4	Cu_2O (1.2)	8	2	130	50
5	$CuBr_2$ (1.2)	8	2	130	10
6	$Cu(OAc)_2$ (1.2)	8	2	130	51
7	$CuSO_4$ (1.2)	8	2	130	35
8	$Cu(NO_3)_2{\cdot}3H_2O$ (1.2)	8	2	130	70
9	$CuCl_2{\bullet}2H_2O$ (1.2)	8	2	130	28
10	CuO (1.2)	8	2	130	17
11	$Cu(OTf)_2$ (1.2)	8	2	130	31
12	Cu (1.2)	8	2	130	25
13	$Cu(NO_3)_2{\cdot}3H_2O$ (0.5)	8	2	130	45
14	$Cu(NO_3)_2{\cdot}3H_2O$ (1.0)	8	2	130	74
15	$Cu(NO_3)_2{\cdot}3H_2O$ (1.5)	8	2	130	69
16	$Cu(NO_3)_2{\cdot}3H_2O$ (1.0)	12	2	130	70
17	$Cu(NO_3)_2{\cdot}3H_2O$ (1.0)	4	2	130	51
18	$Cu(NO_3)_2{\cdot}3H_2O$ (1.0)	—	2	130	40
19	$Cu(NO_3)_2{\cdot}3H_2O$ (1.0)	8	3	130	73
20	$Cu(NO_3)_2{\cdot}3H_2O$ (1.0)	8	1	130	46
21	$Cu(NO_3)_2{\cdot}3H_2O$ (1.0)	8	—	130	45
22	$Cu(NO_3)_2{\cdot}3H_2O$ (1.0)	8	2	120	61
23	$Cu(NO_3)_2{\cdot}3H_2O$ (1.0)	8	2	140	70
24	$Cu(NO_3)_2{\cdot}3H_2O$ (1.0)	8	2	130	21[c]

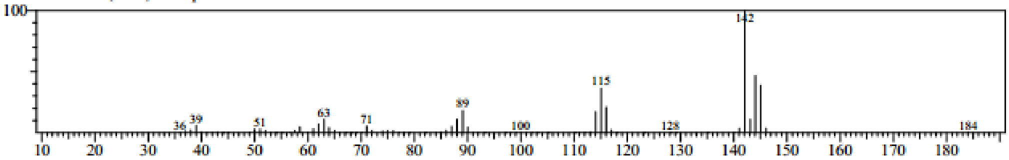
[a] Reaction conditions: **3a** (0.5 mmol), [Cu] source, HOAc, TBHP, DMF (3 mL), air. [b] Yield of isolated product after column chromatography on silica gel. [c] Dry N_2 atmosphere.

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

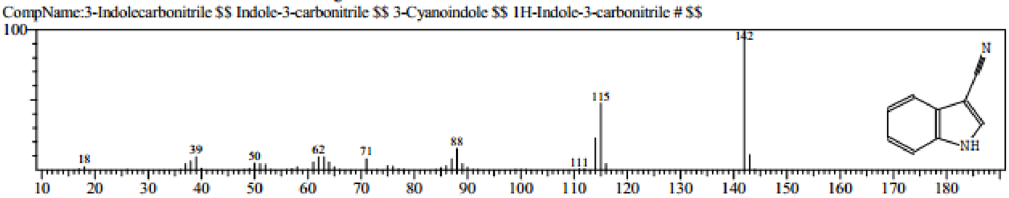


An oven-dried 25 mL eggplant-shaped bottle equipped with a magnetic stir bar was charged with CuI (0.24 mmol, 1.2 equiv), 1H-indole (23.4 mg, 0.2 mmol), HOAc (4.0 equiv), t-BuOOH (2.0 equiv, 70% aq.) and DMF with carbon-13 labeled on its carbonyl (0.25 mL). The bottle was left at 120 °C (oil bath temperature) for 48 h afforded 7.4 mg (26%) of 1H-indole-3-carbonitrile.

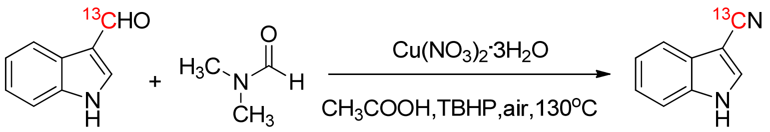
RawMode:Single 5.573(1613) BasePeak:142.10(997971)
BG Mode:5.560(1609) Group 1 - Event 1



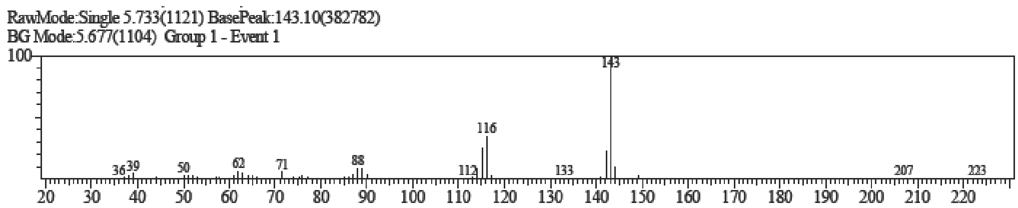
Hit#:1 Entry:11900 Library:NIST05.LIB
SI:82 Formula:C9H6N2 CAS:5457-28-3 MolWeight:142 RetIndex:1509
CompName:3-Indolecarbonitrile $$ Indole-3-carbonitrile $$ 3-Cyanoindole $$ 1H-Indole-3-carbonitrile # $$



3. Experiment using 1H-Indole-3-Carbaldehyde with Carbon-13 Labeled on Its Carbonyl



An oven-dried 25 mL eggplant-shaped bottle equipped with a magnetic stir bar was charged with $Cu(NO_3)_2$•$3H_2O$ (0.24 mmol, 1.2 equiv), 1H-indole-3-carbaldehyde with carbon-13 labeled on its carbonyl (29.2 mg, 0.2 mmol), HOAc (8.0 equiv), t-BuOOH (2.0 equiv, 70% aq.) and DMF (1.2 mL). The bottle was left at 130 ^{o}C (oil bath temperature) for 48 h afforded 9.0 mg (32%) of 1H-indole-3-carbonitrile with carbon-13 labeled on its carbonyl. HRMS m/z (ESI) calcd. for $C_9H_6N_2$. $[M]^+$, 143.0531; found,143.0603.

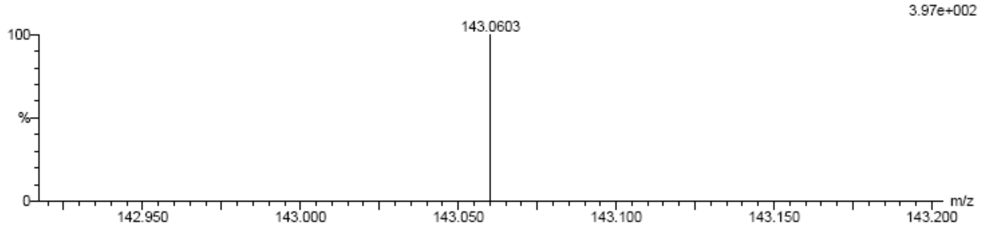


Elemental Composition Report **Page 1**

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

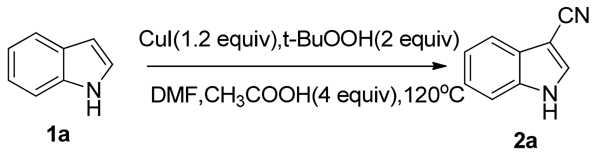
Monoisotopic Mass, Odd and Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-100 N: 0-2

GCT Premier ZJU 30-Jan-2015 zlp143 1041 (4.771)
TOF MS EI+ 3.97e+002



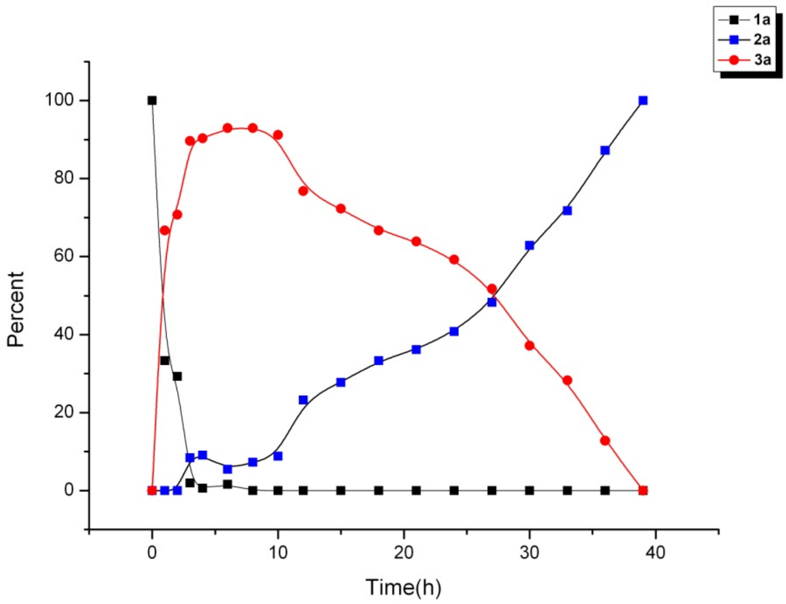
Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
143.0603	143.0609	-0.6	-4.2	7.5	5546181.0	C9 H7 N2

4. HPLC Tracking of the Reaction Process of 1H-Indole



A flame-dried 25 mL eggplant-shaped bottle equipped with a magnetic stir bar was charged with CuI (0.6 mmol,1.2 equiv) and **1a** (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 °C (oil bath temperature). Every once in a while, we took 10μl sample from the reaction mixture and the samples were analyzed by HPLC.

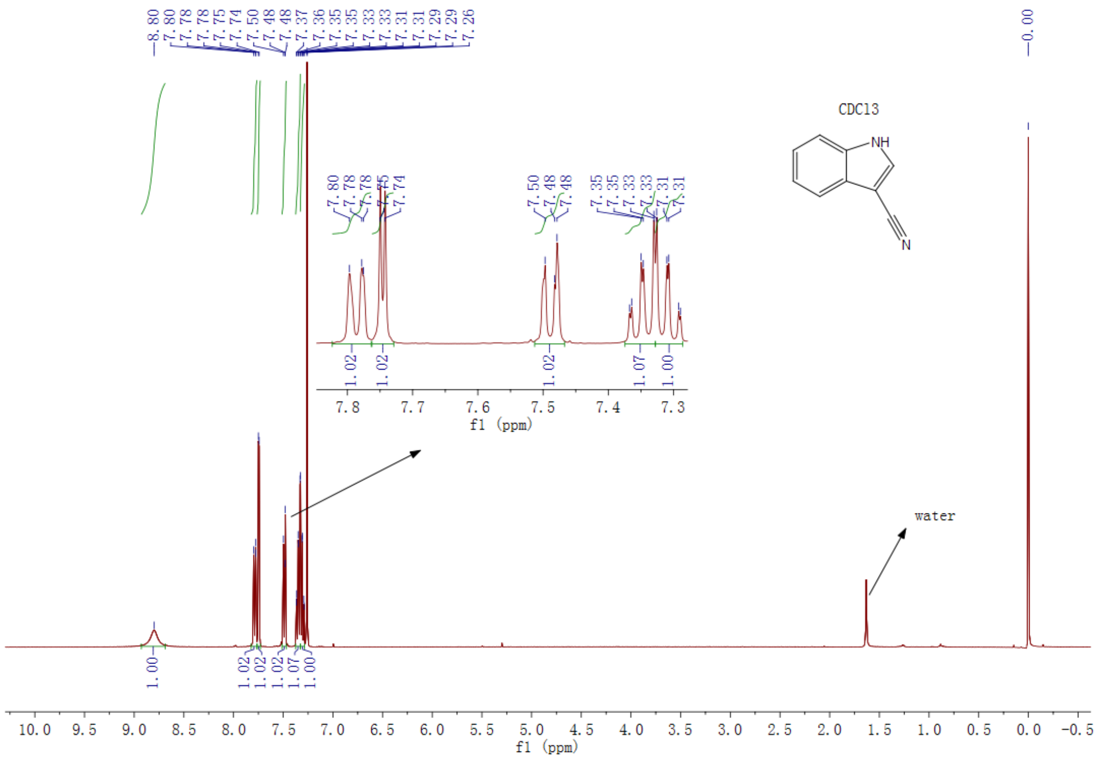
5. Figure S1 CuI-mediated cyanation of 1a using DMF



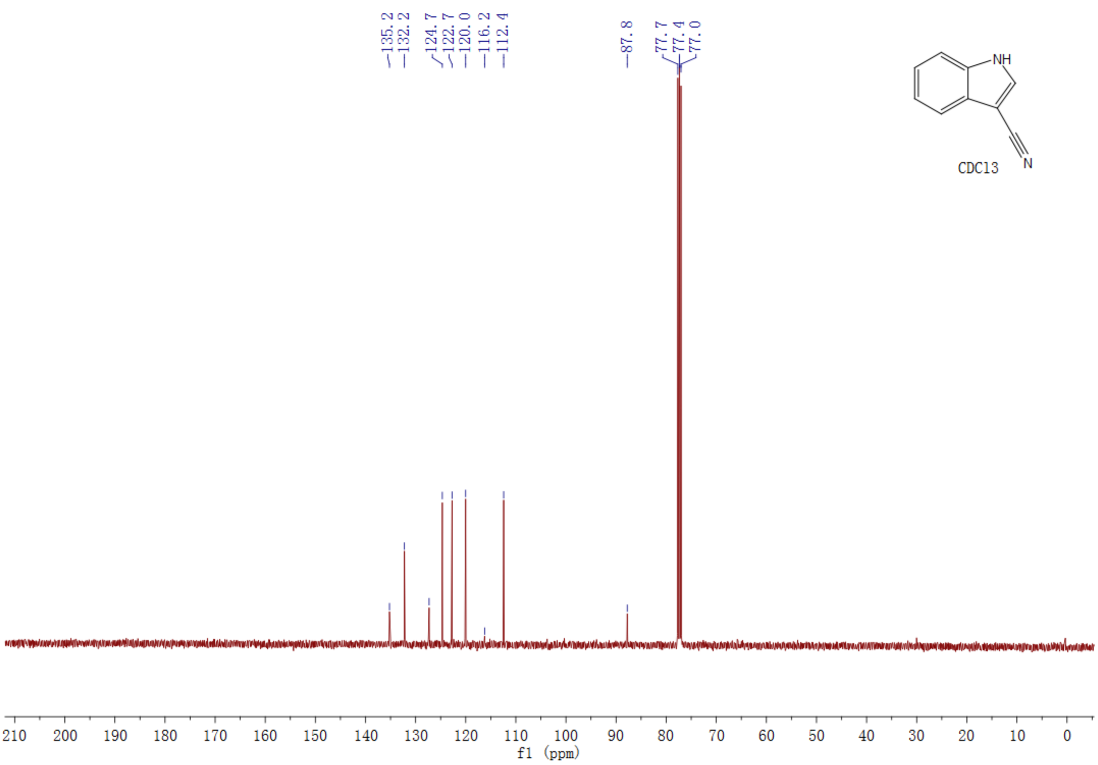
HPLC conditions：MeOH:H_2O = 50:50; UV (254 nm) detector; 0.8 mL/min.

6. Copies of ^{1}H NMR and ^{13}C NMR for All Products

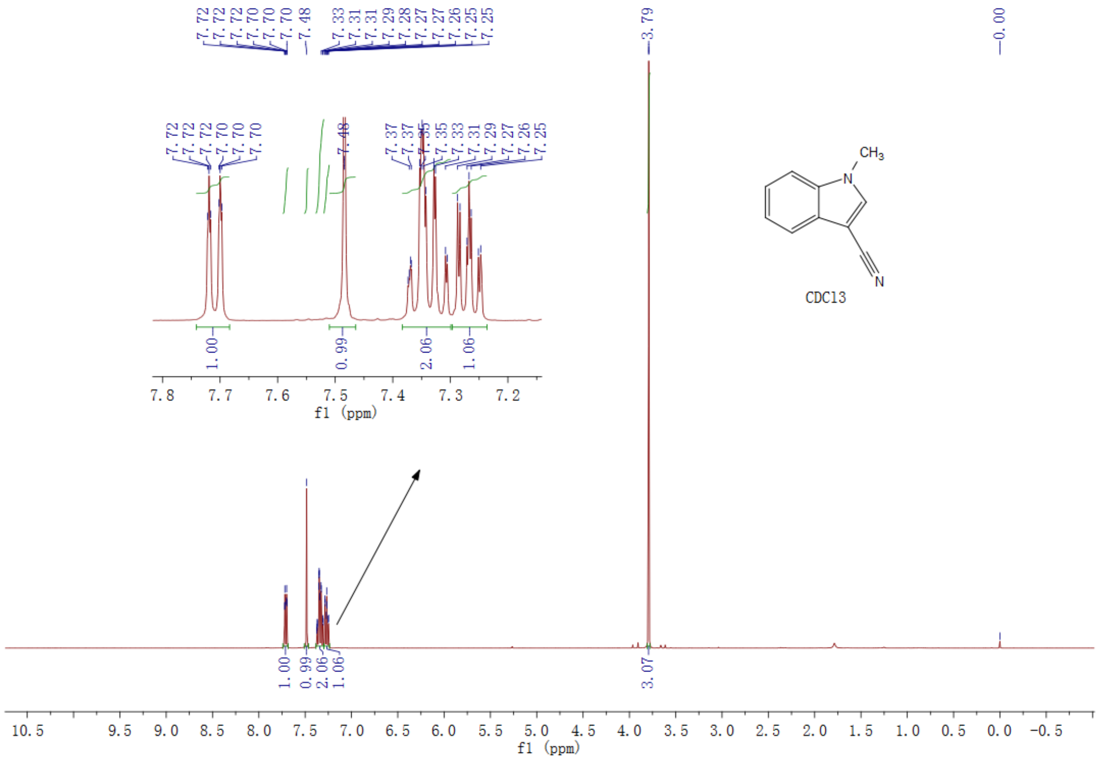
^{1}H-NMR spectrum of **2a**



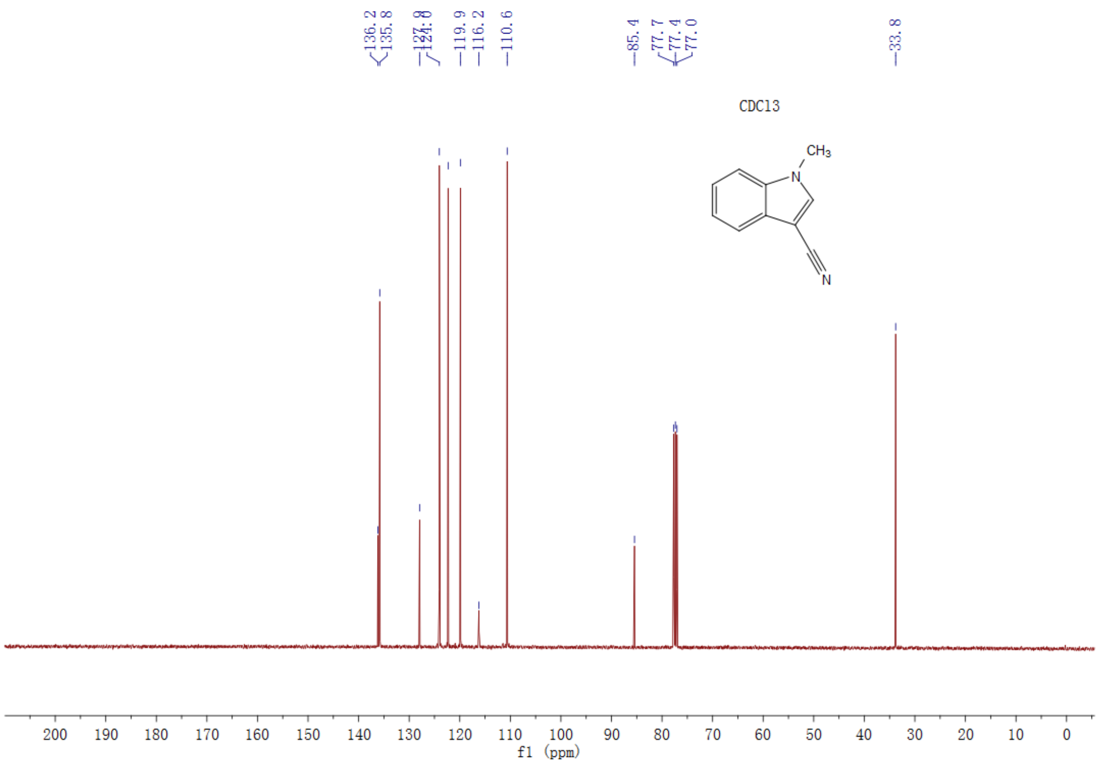
^{13}C-NMR spectrum of **2a**



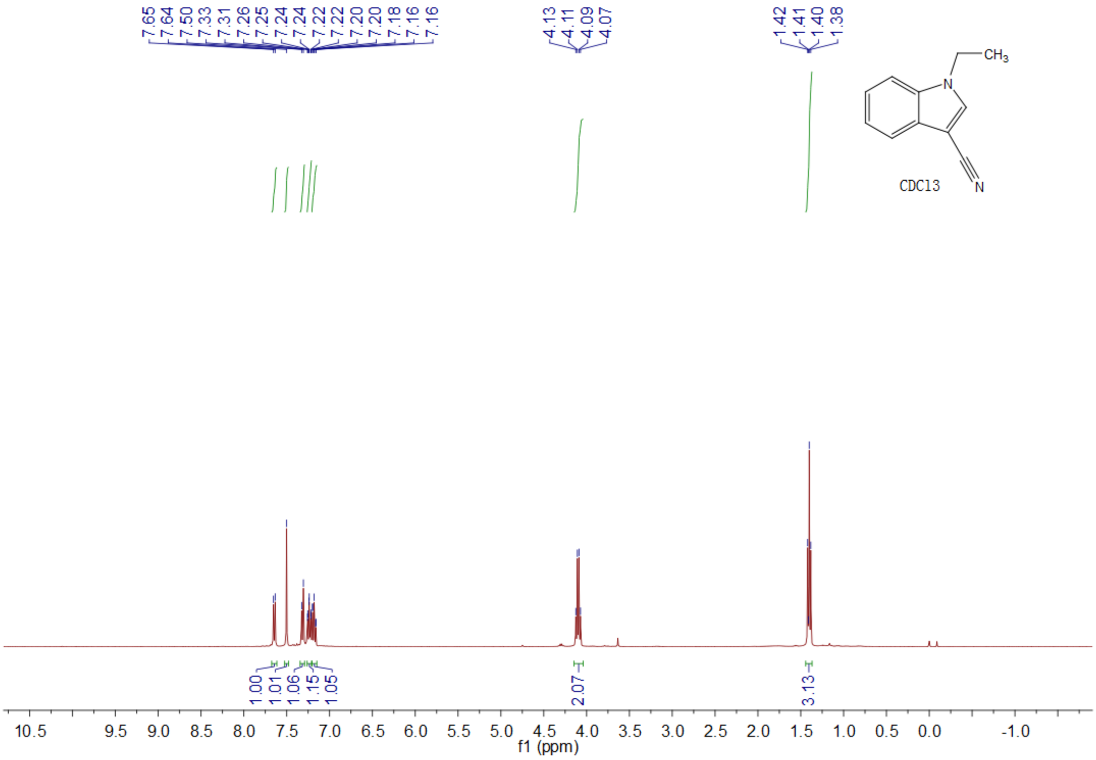
^{1}H-NMR spectrum of **2b**



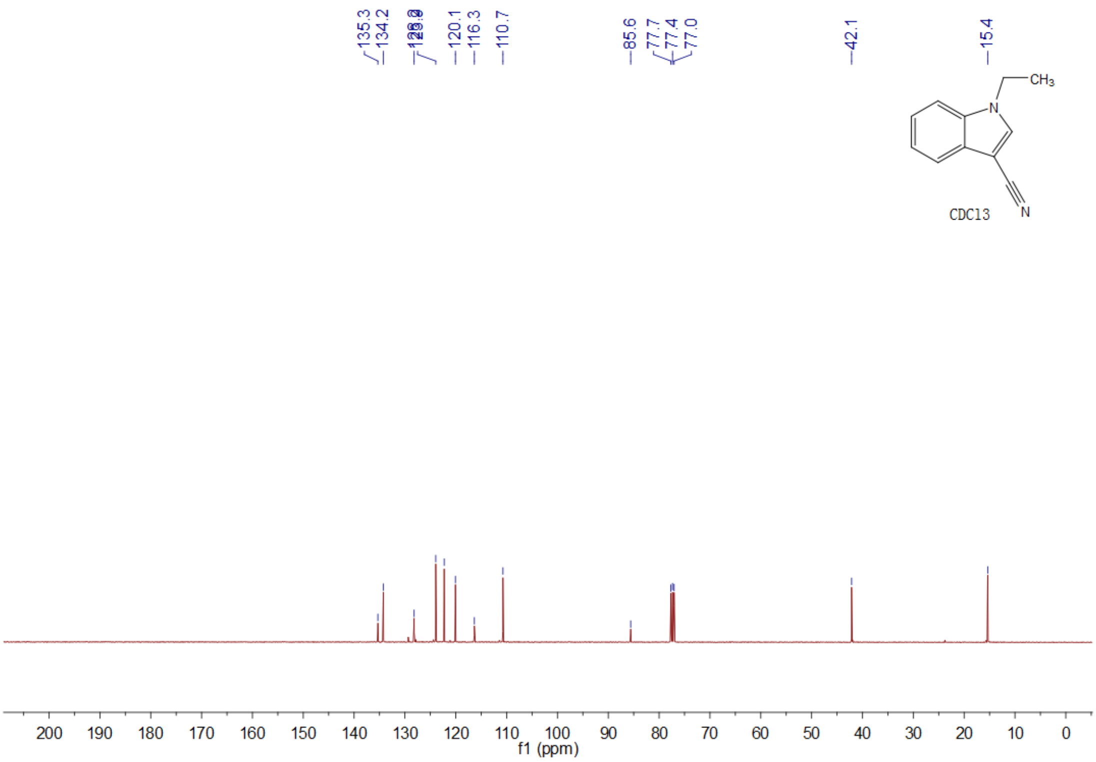
^{13}C-NMR spectrum of **2b**



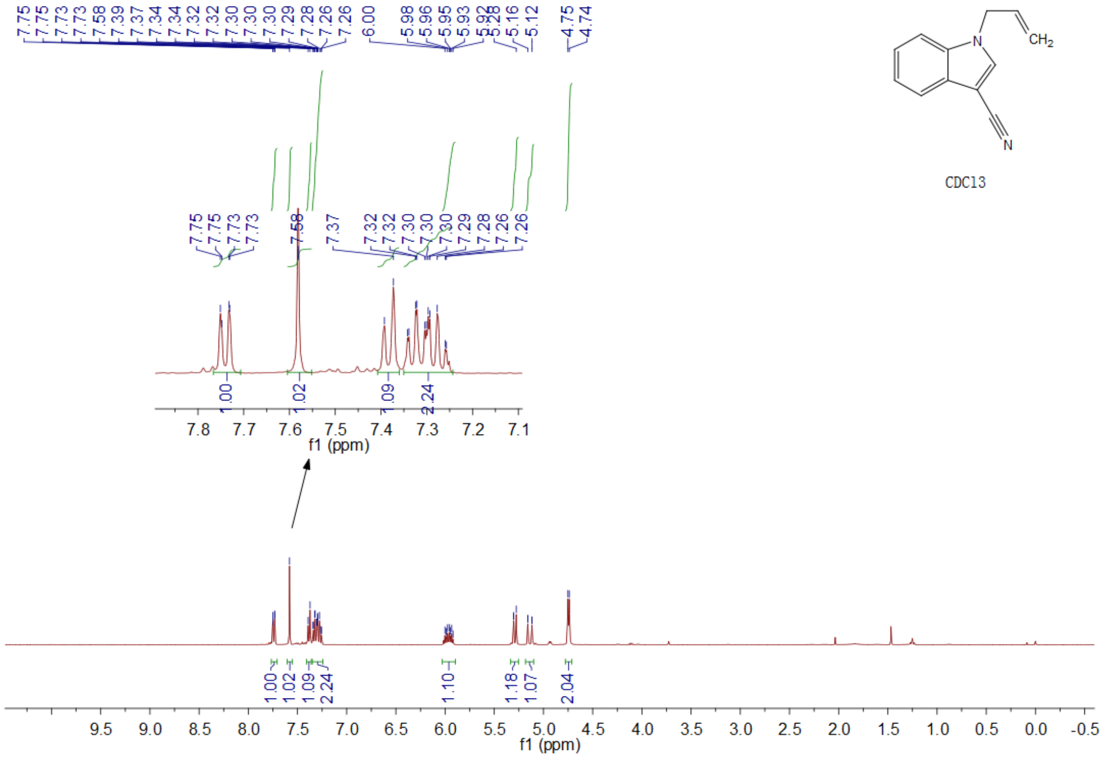
[1]H-NMR spectrum of **2c**



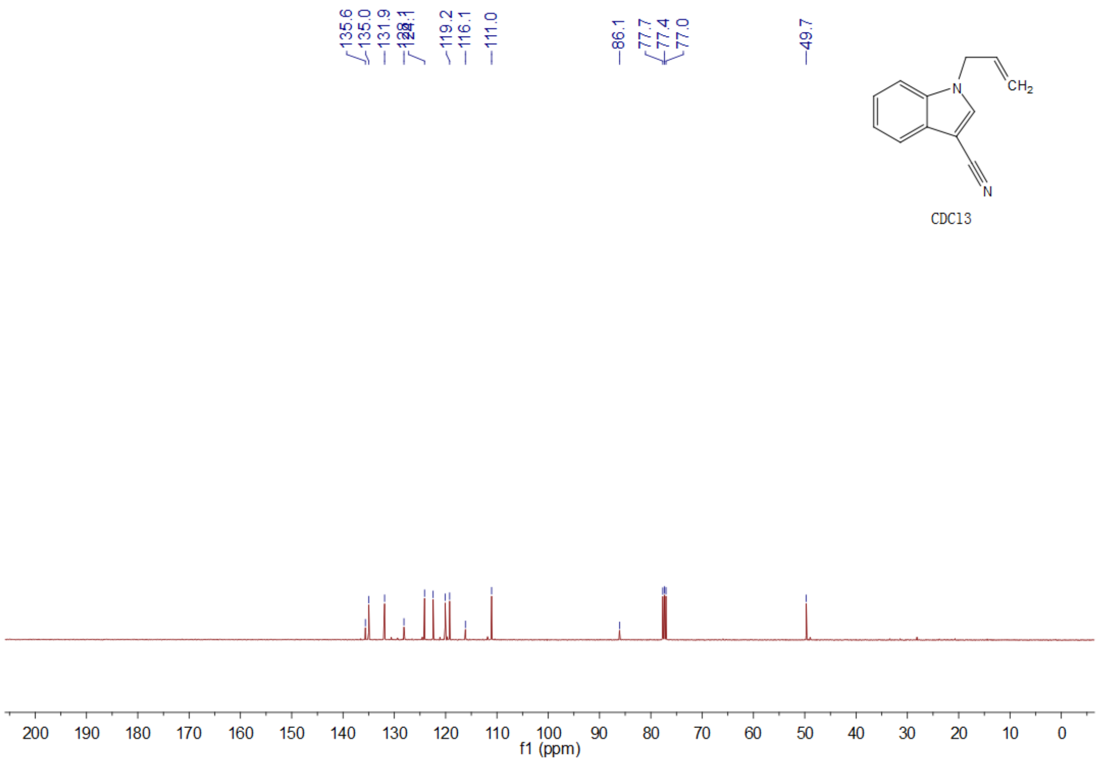
[13]C-NMR spectrum of **2c**



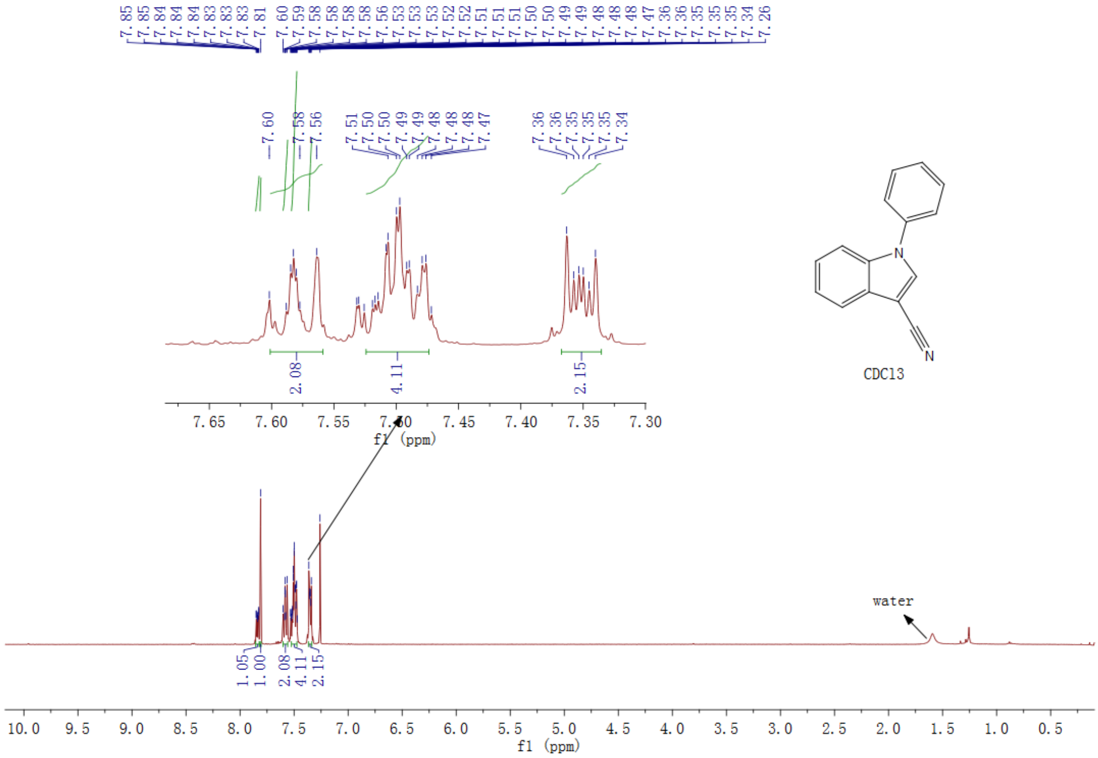
[1]H-NMR spectrum of **2d**



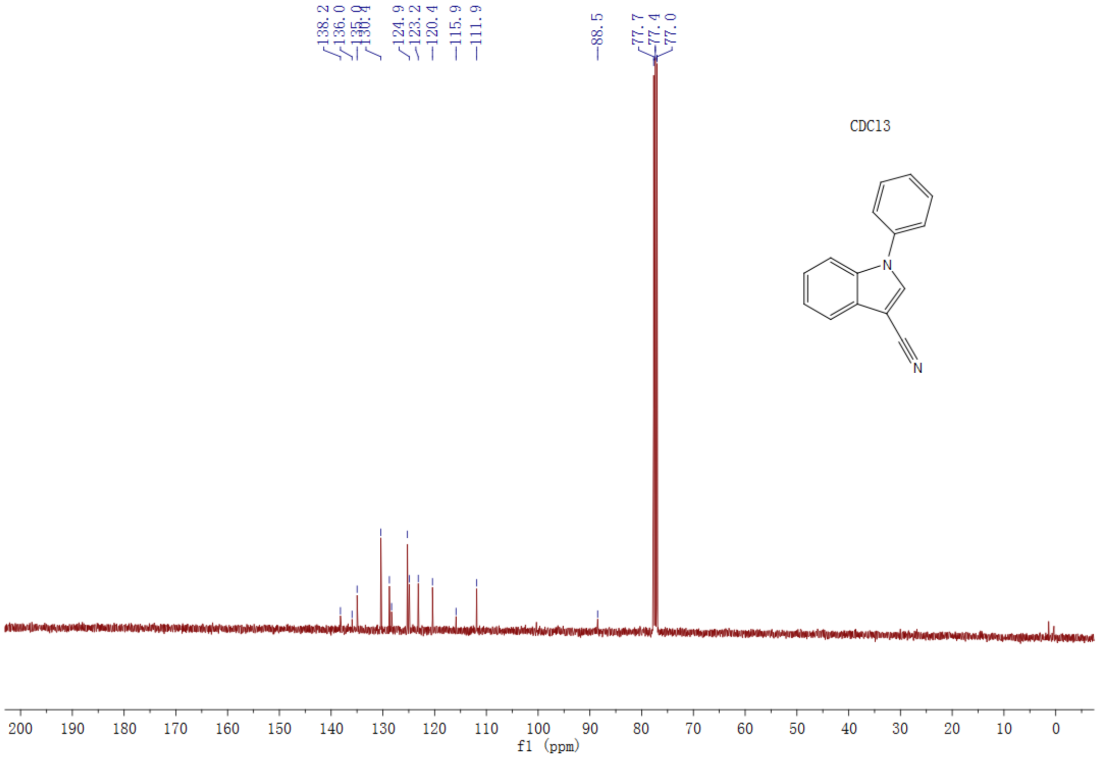
[13]C-NMR spectrum of **2d**



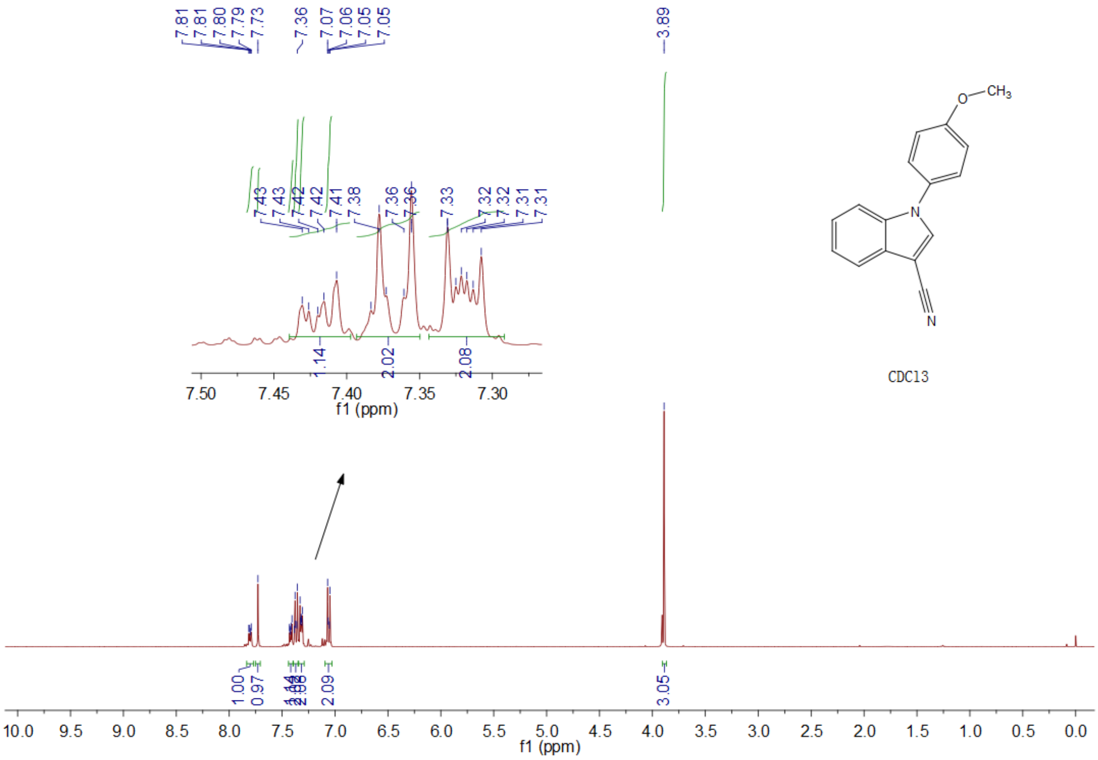
[1]H-NMR spectrum of **2e**



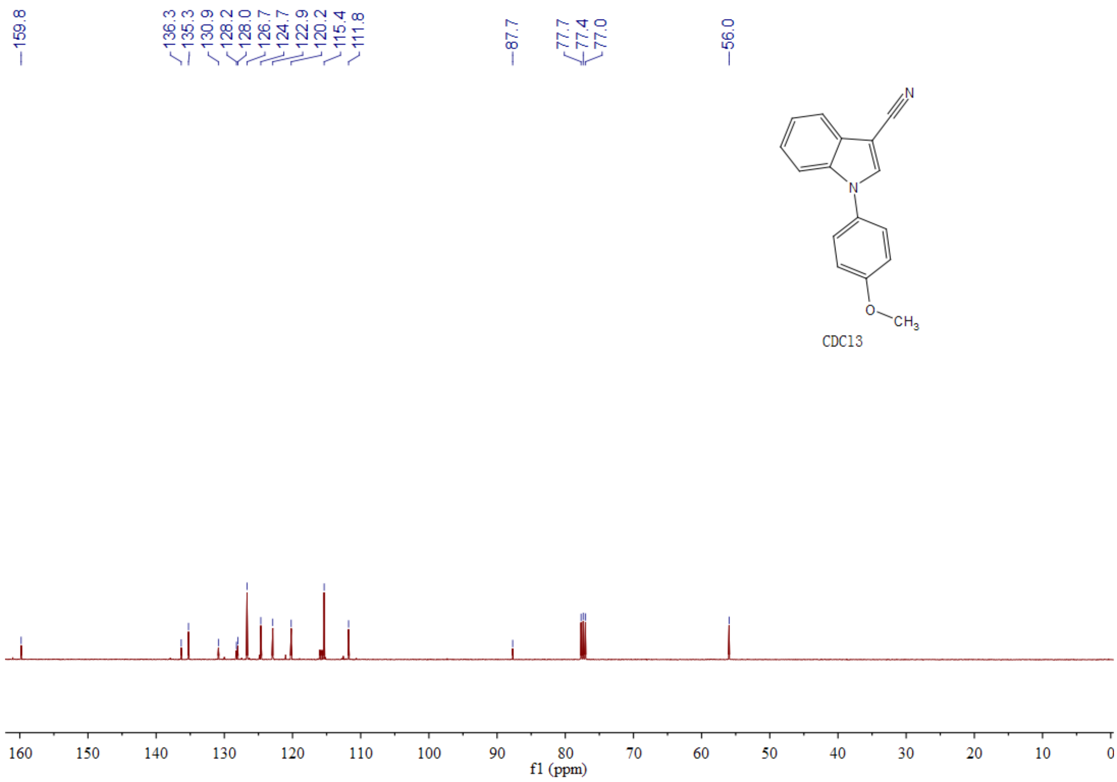
[13]C-NMR spectrum of **2e**



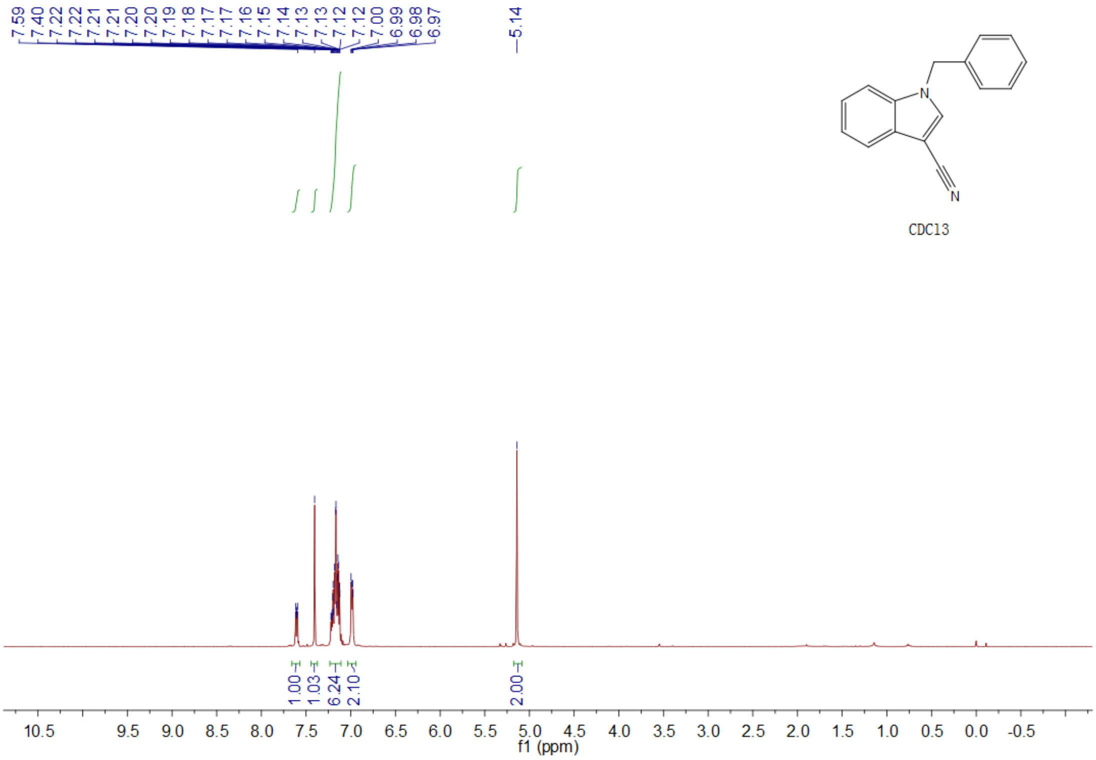
^{1}H-NMR spectrum of **2f**



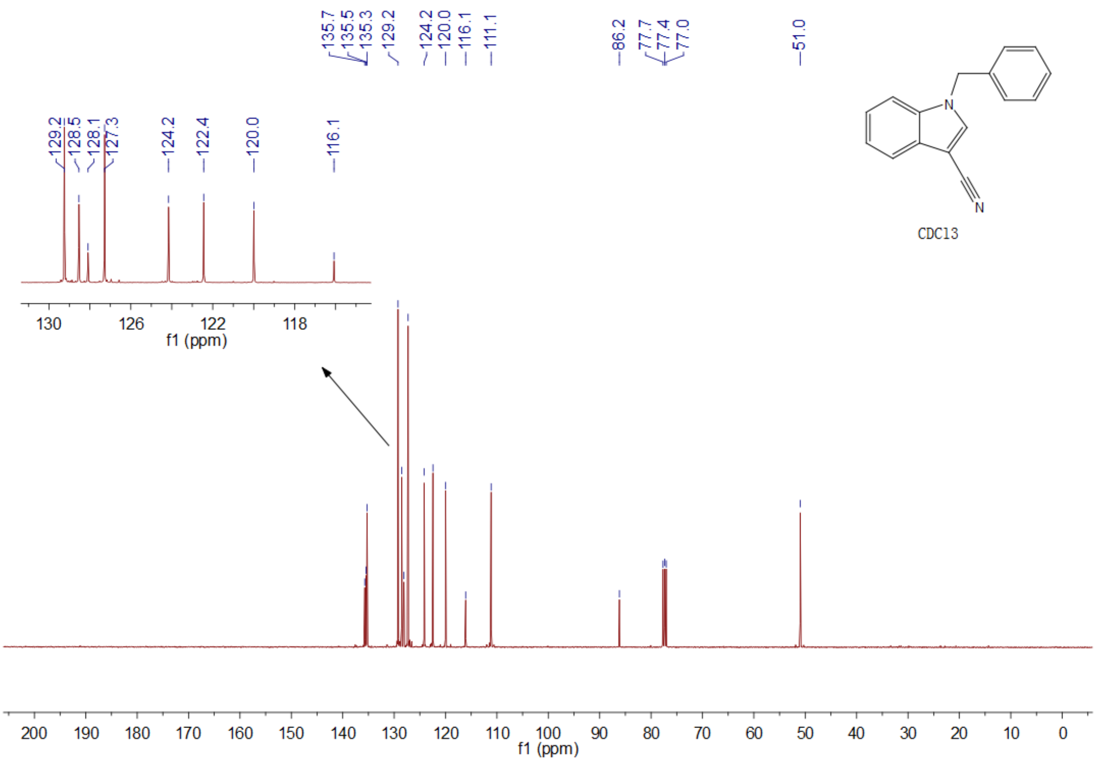
^{13}C-NMR spectrum of **2f**



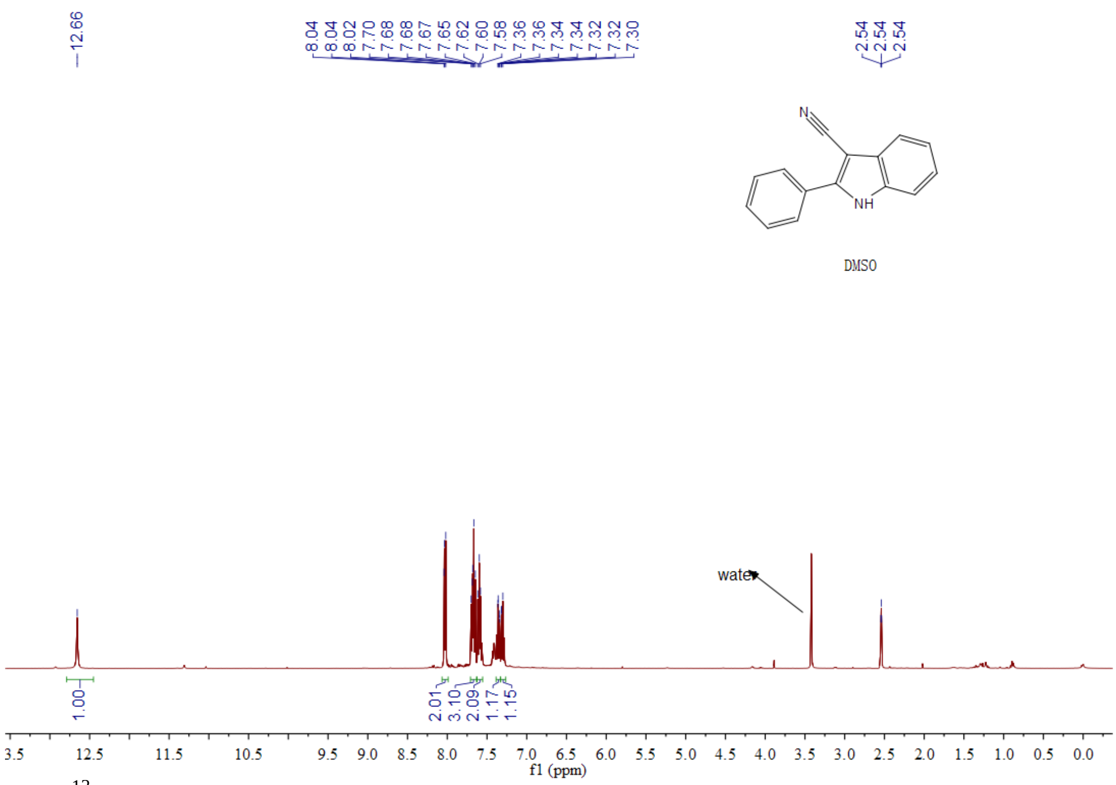
^{1}H-NMR spectrum of **2g**



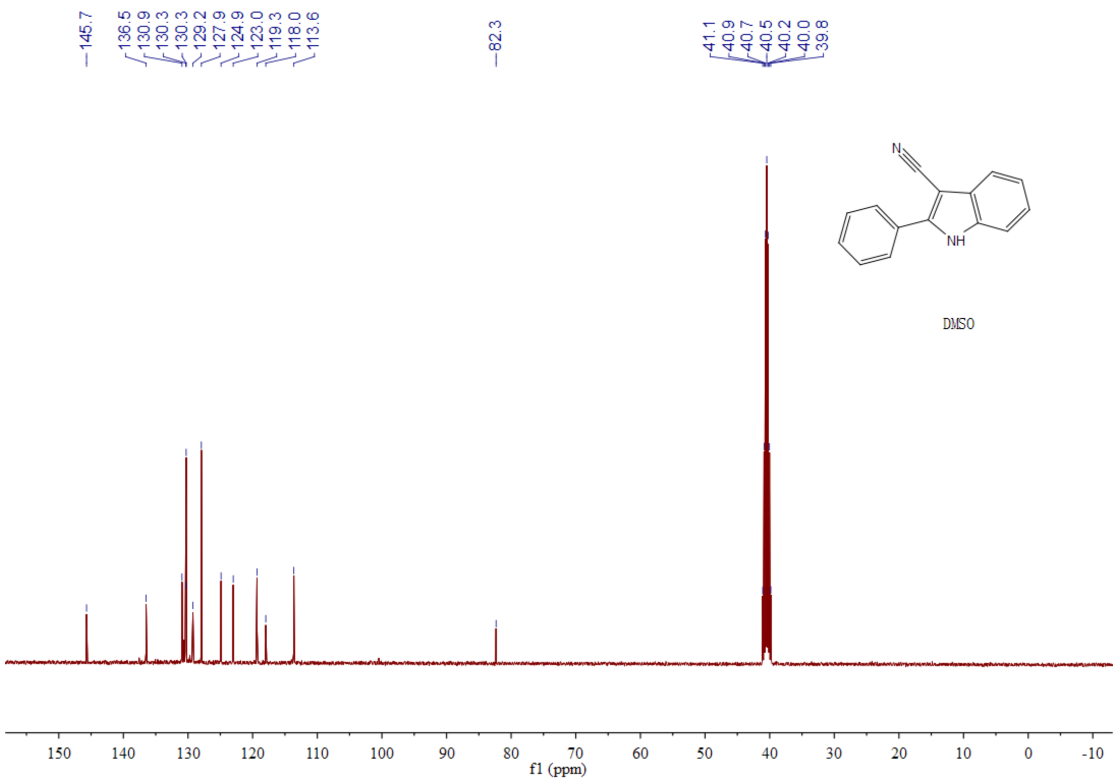
^{13}C-NMR spectrum of **2g**



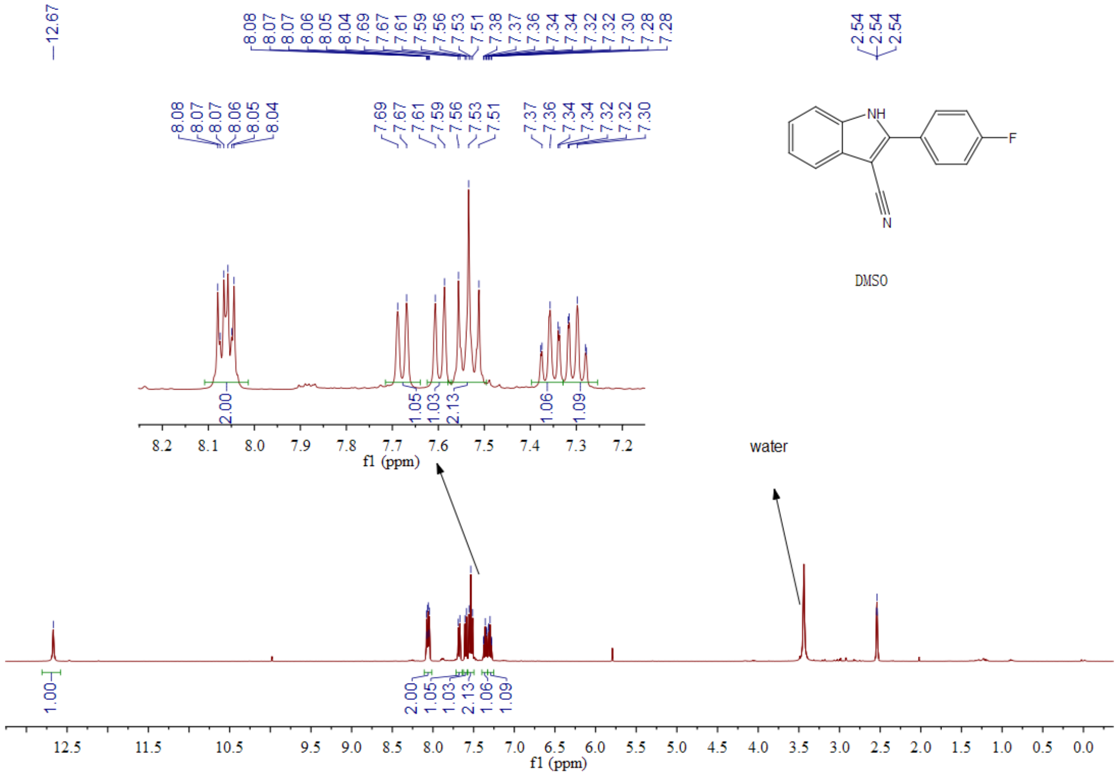
[1]H-NMR spectrum of **2h**



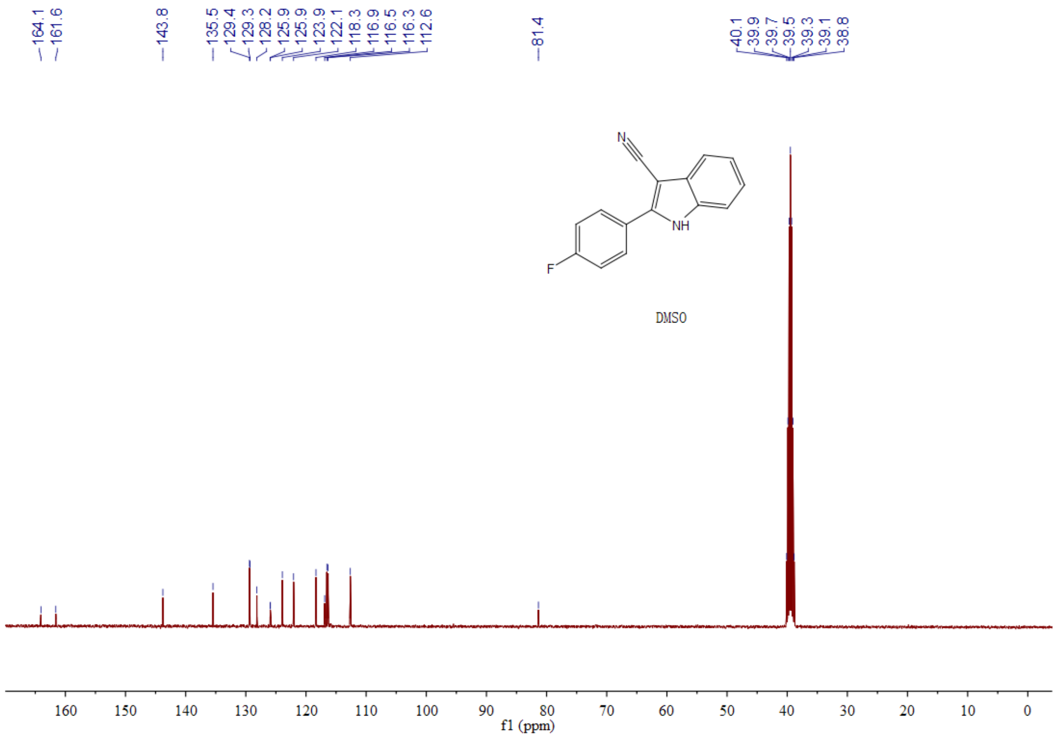
[13]C-NMR spectrum of **2h**



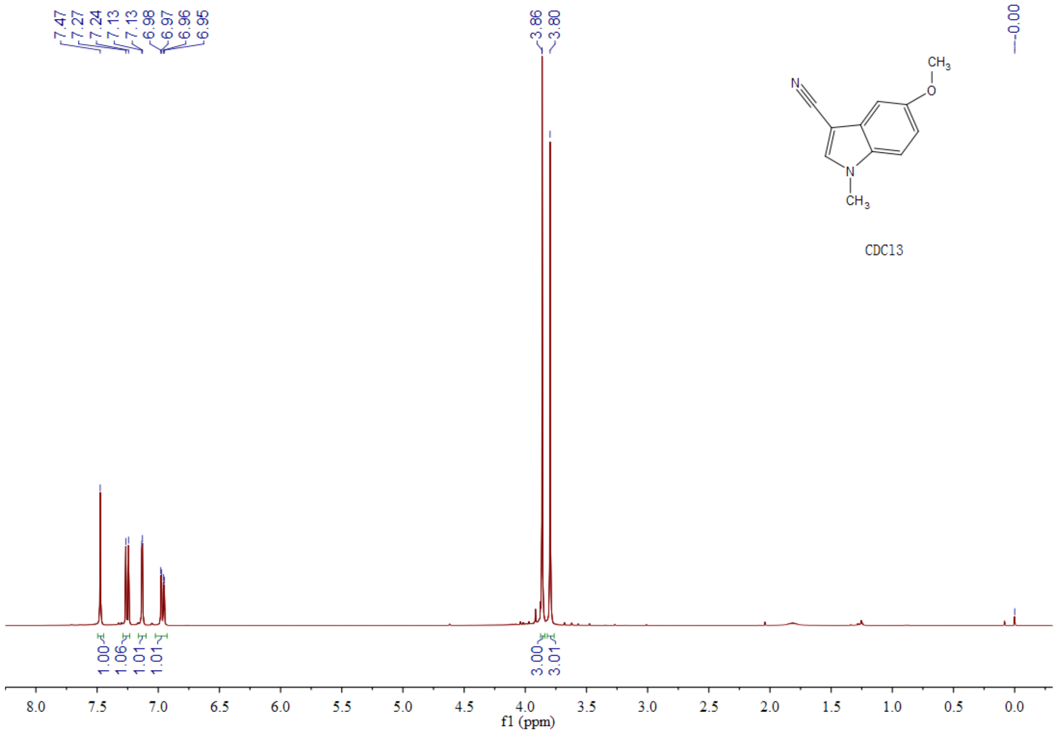
^{1}H-NMR spectrum of **2i**



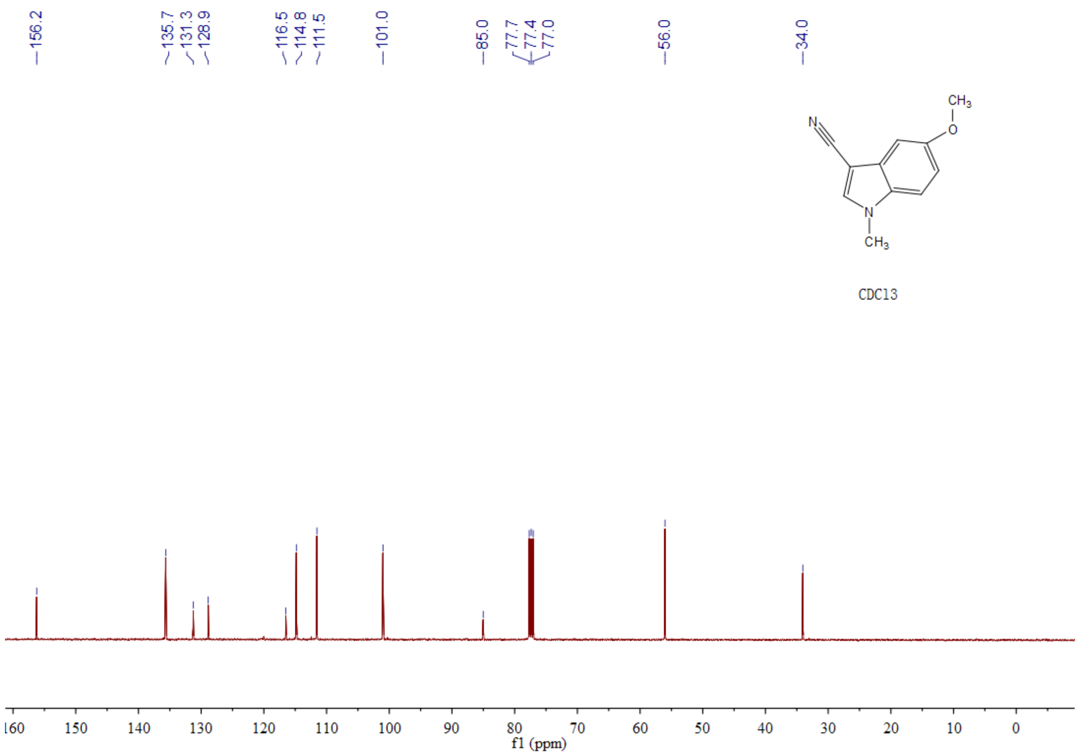
^{13}C-NMR spectrum of **2i**



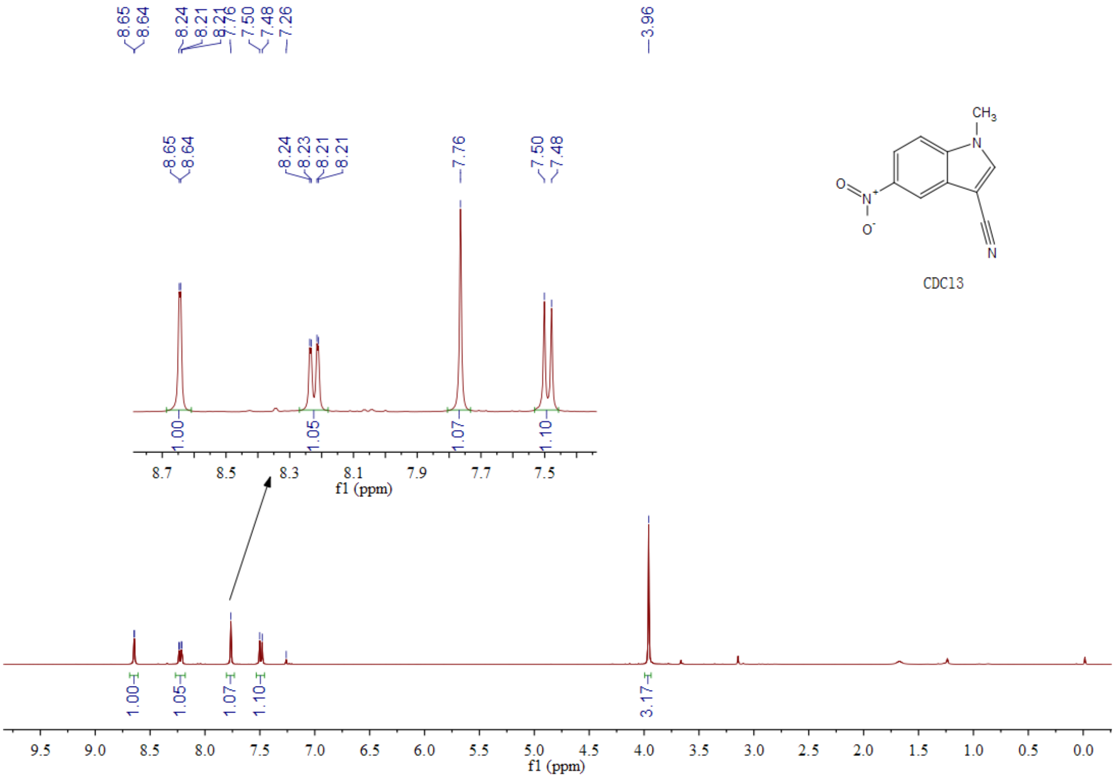
^{1}H-NMR spectrum of **2j**



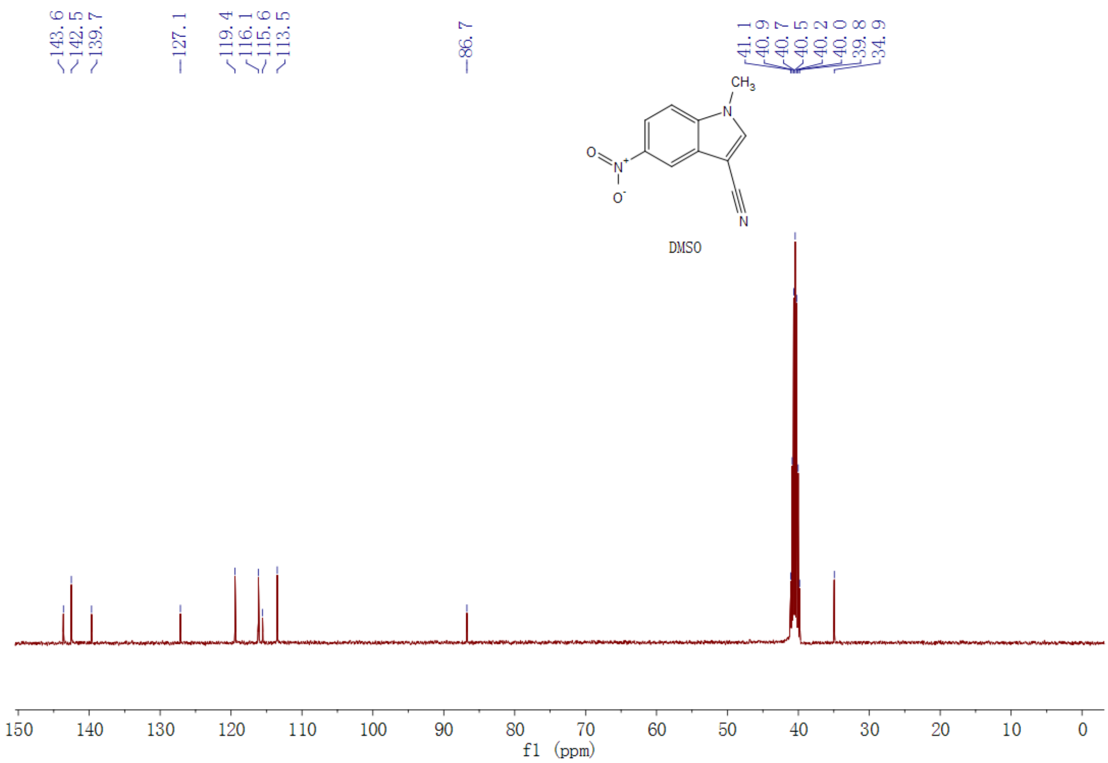
^{13}C-NMR spectrum of **2j**



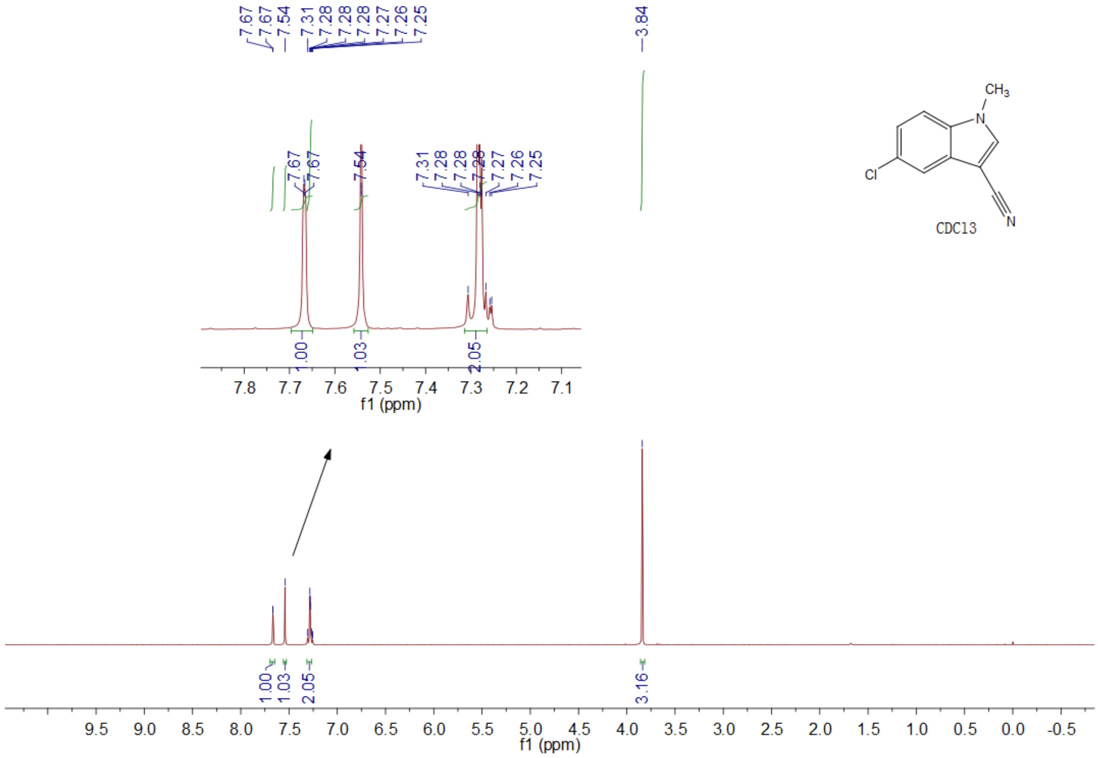
[1]H-NMR spectrum of **2k**



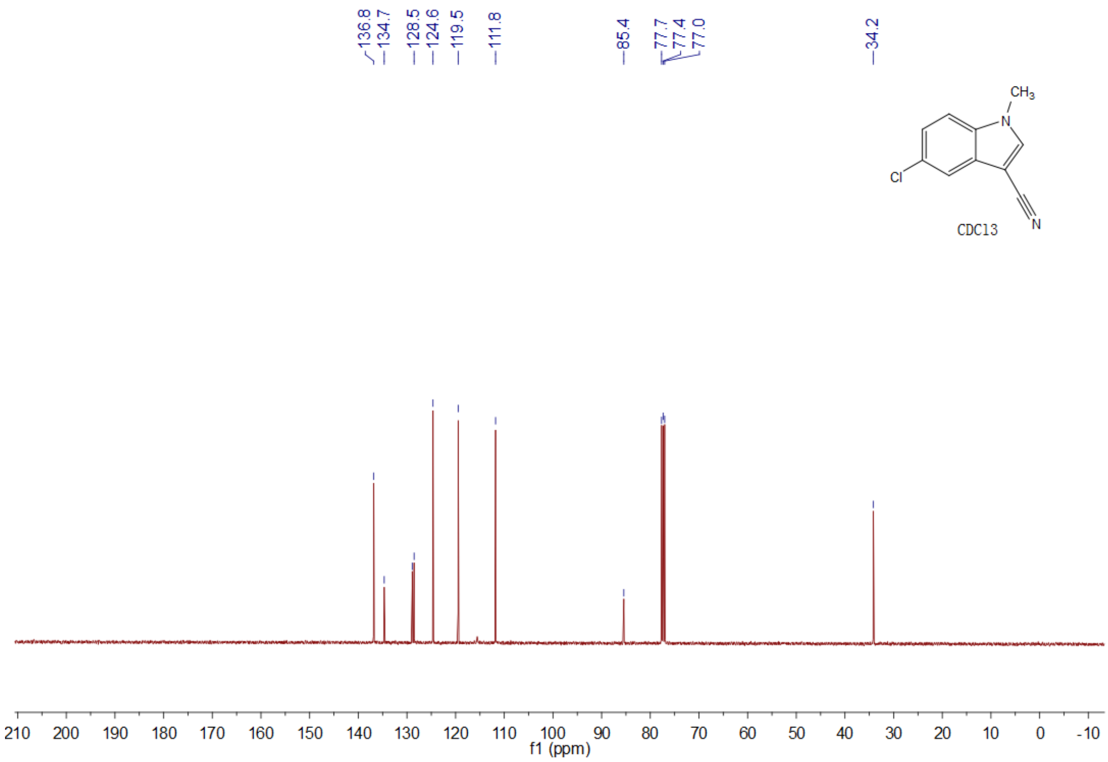
[13]C-NMR spectrum of **2k**



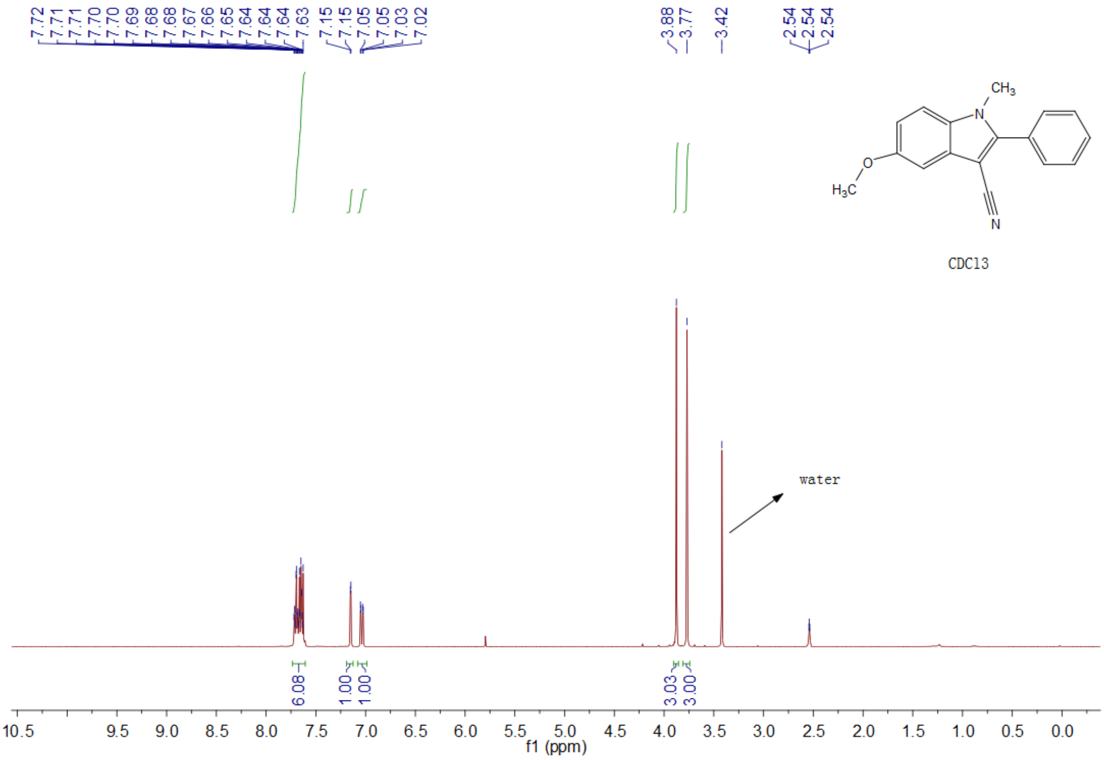
^{1}H-NMR spectrum of **2l**



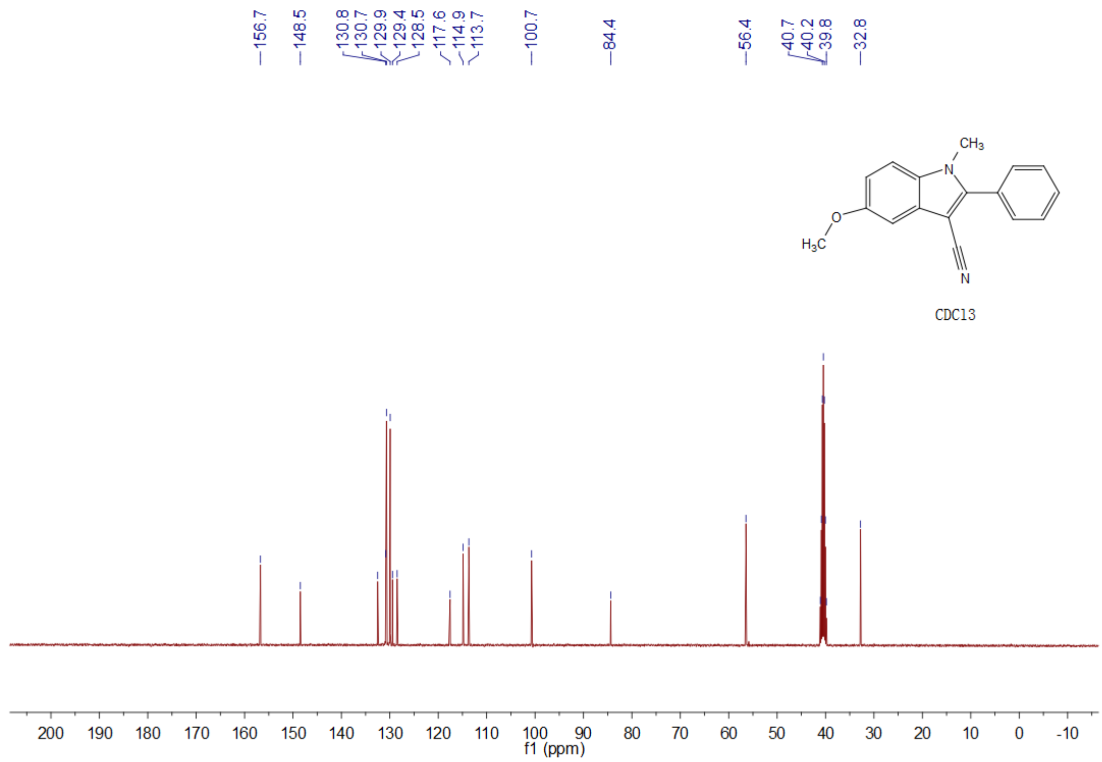
^{13}C-NMR spectrum of **2l**



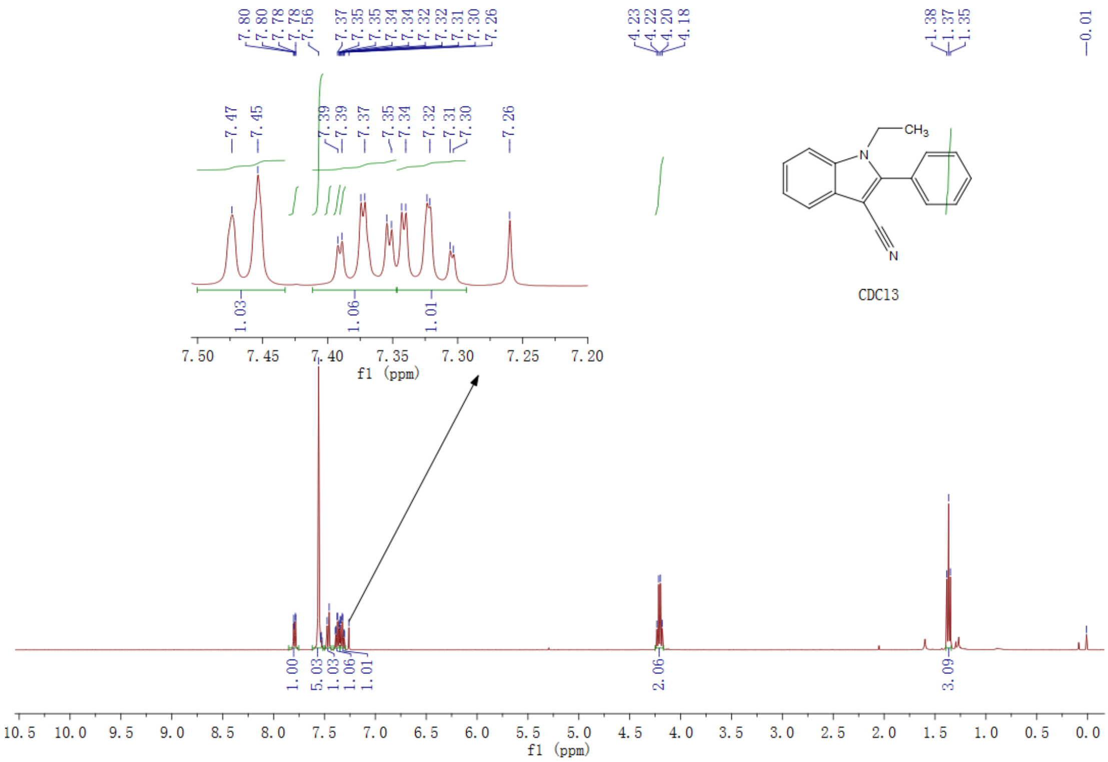
[1]H-NMR spectrum of **2m**



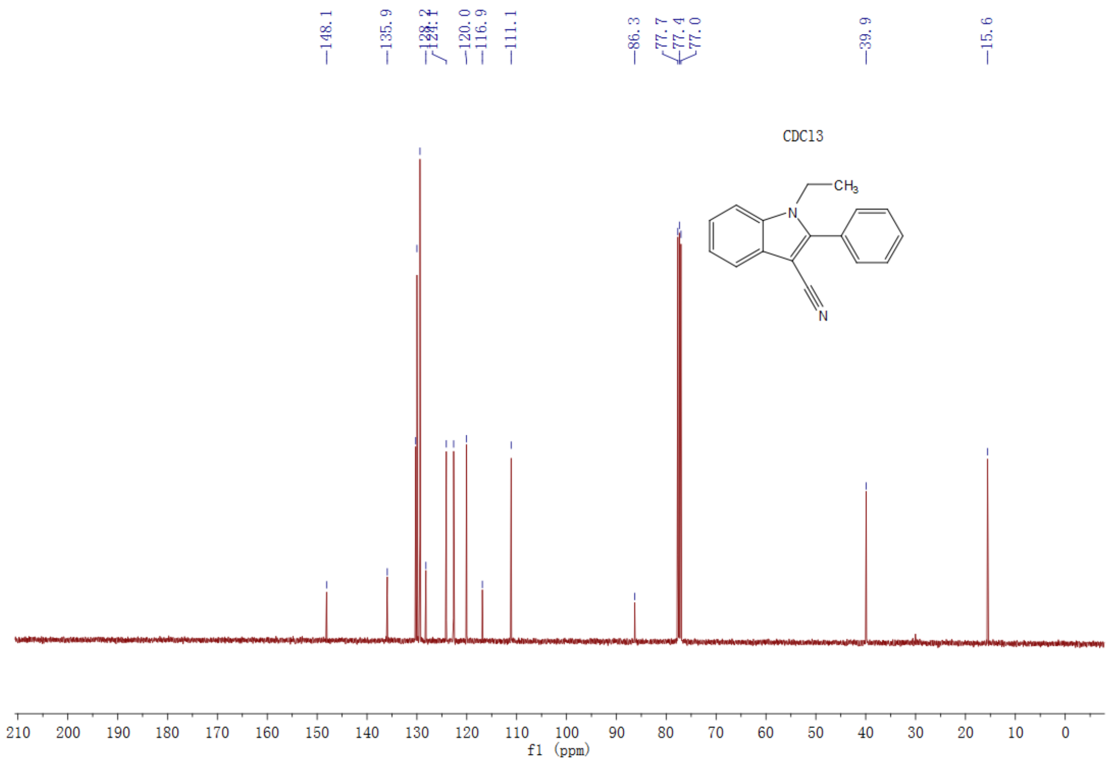
[13]C-NMR spectrum of **2m**



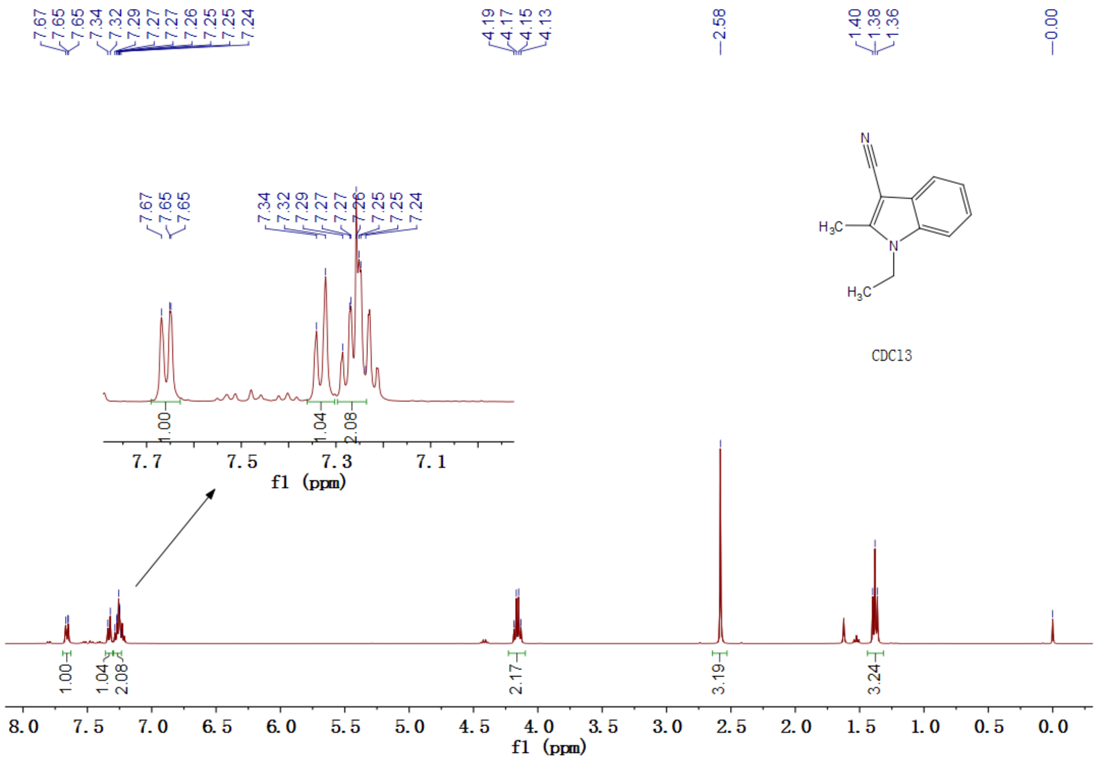
[1]H-NMR spectrum of **2n**



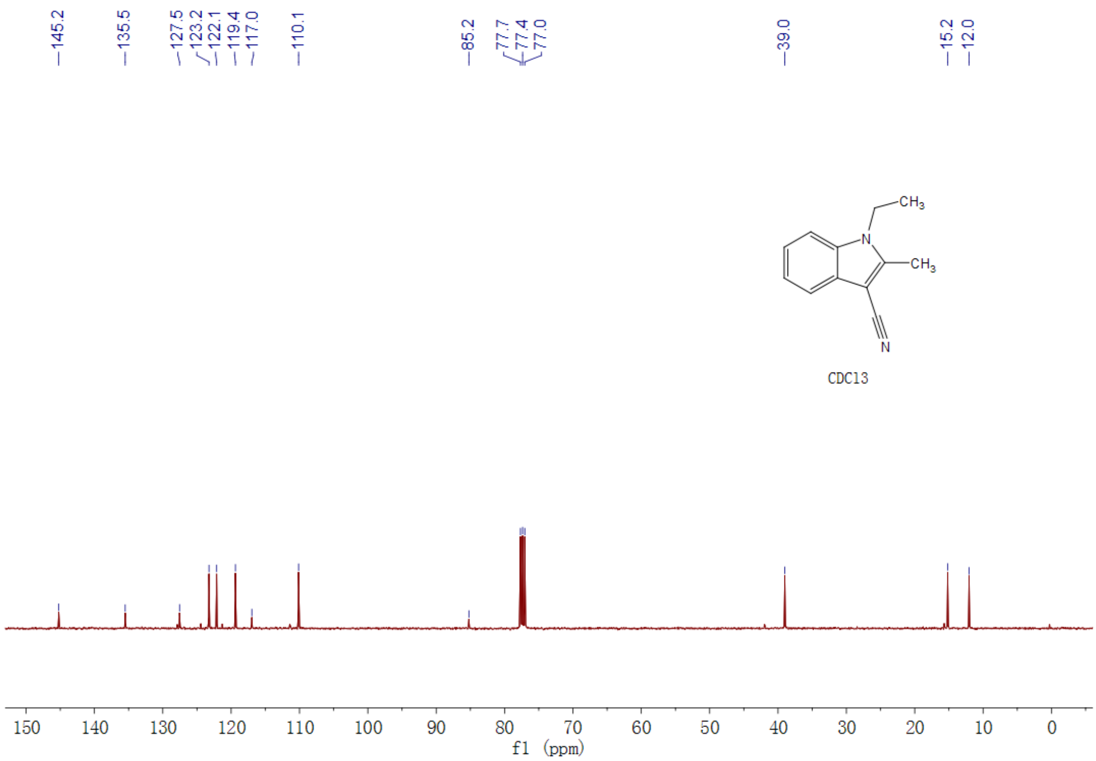
[13]C-NMR spectrum of **2n**



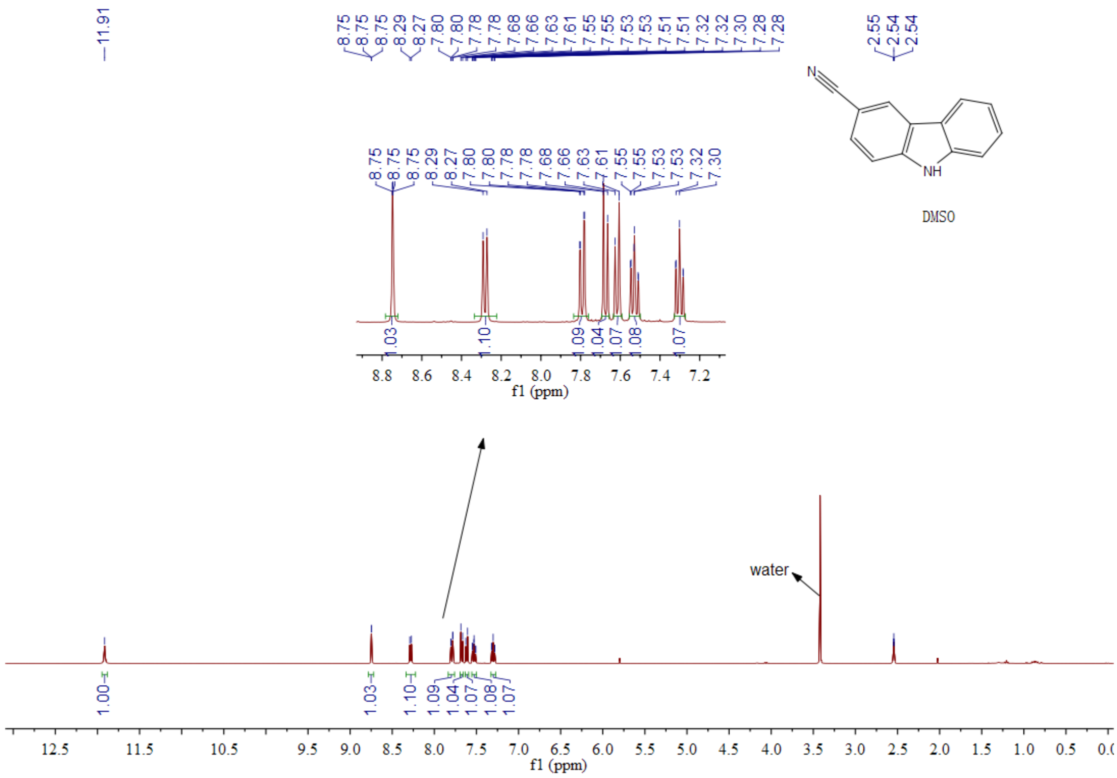
[1]H-NMR spectrum of **2o**



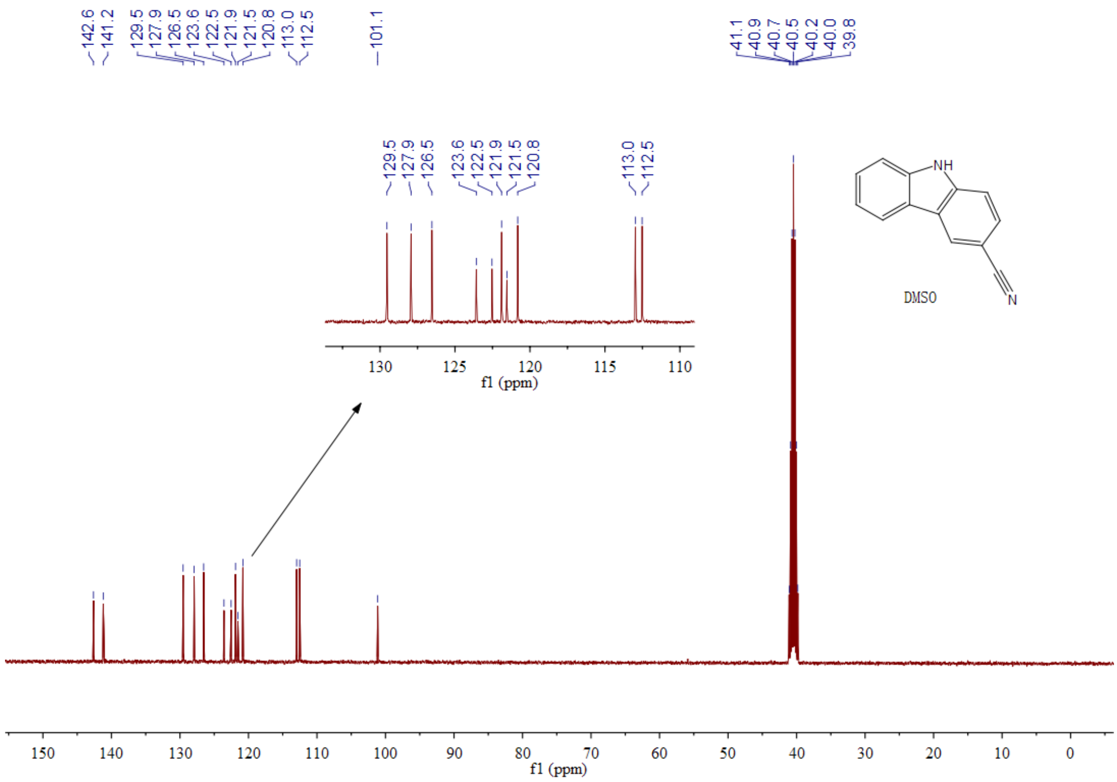
[13]C-NMR spectrum of **2o**



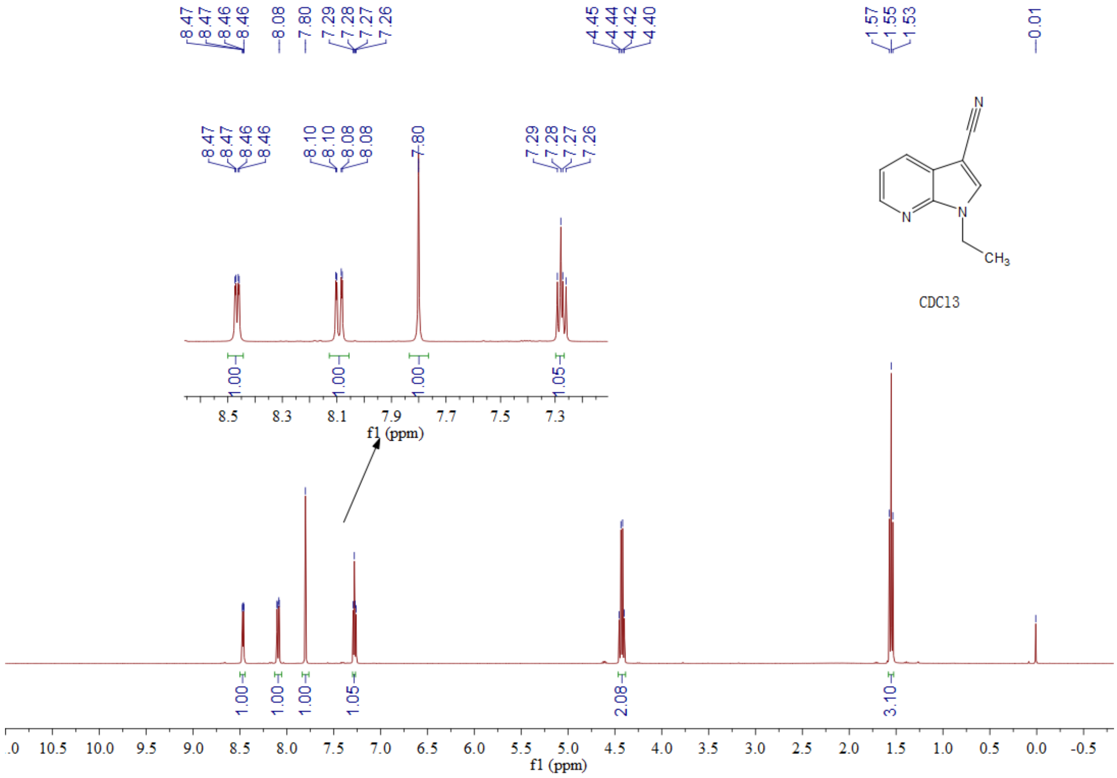
^{1}H-NMR spectrum of **2p**



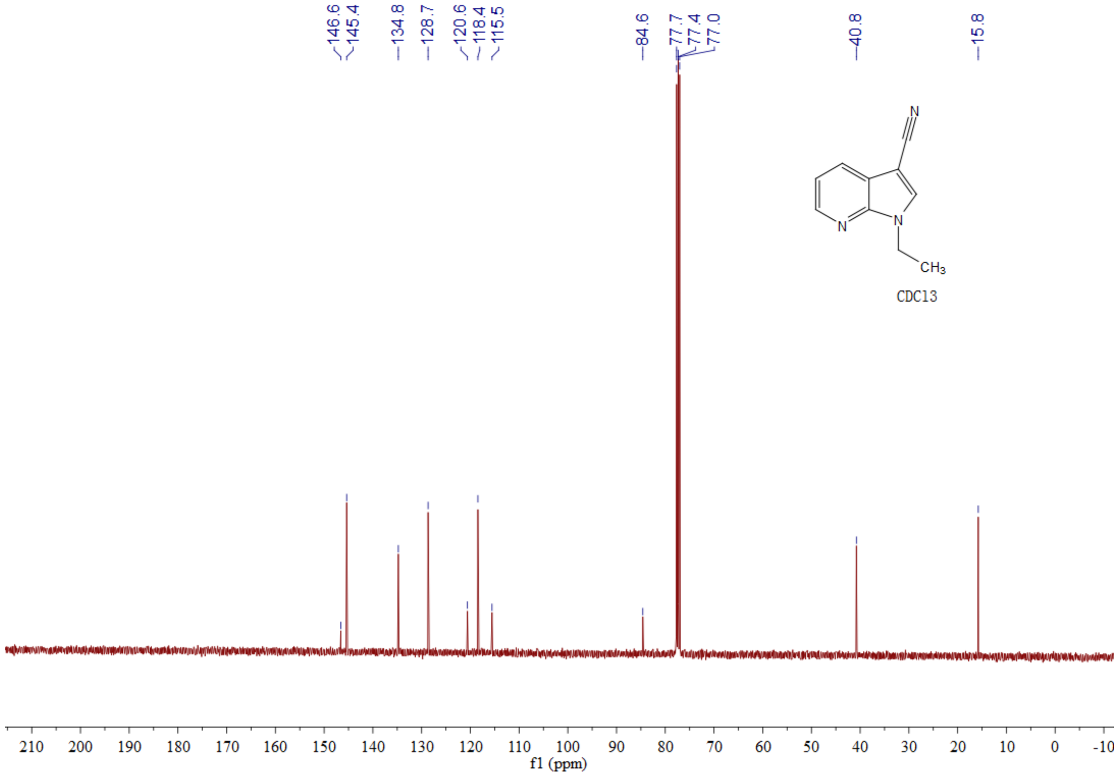
^{13}C-NMR spectrum of **2p**



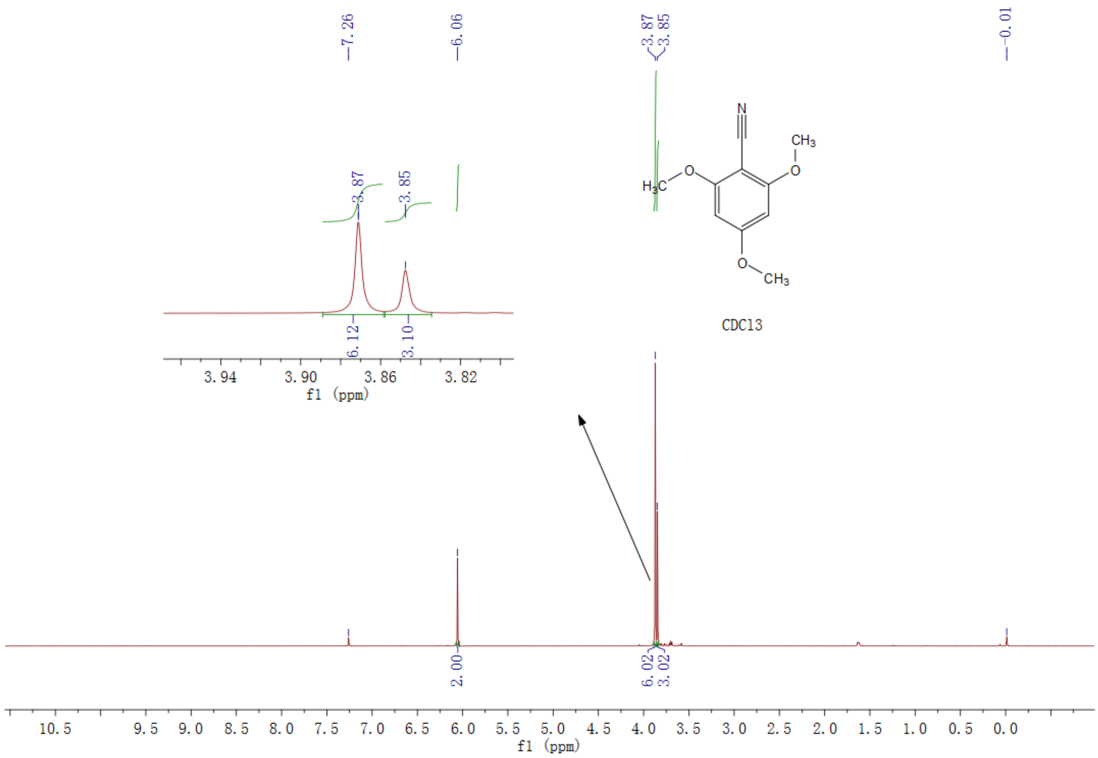
[1]H-NMR spectrum of **2q**



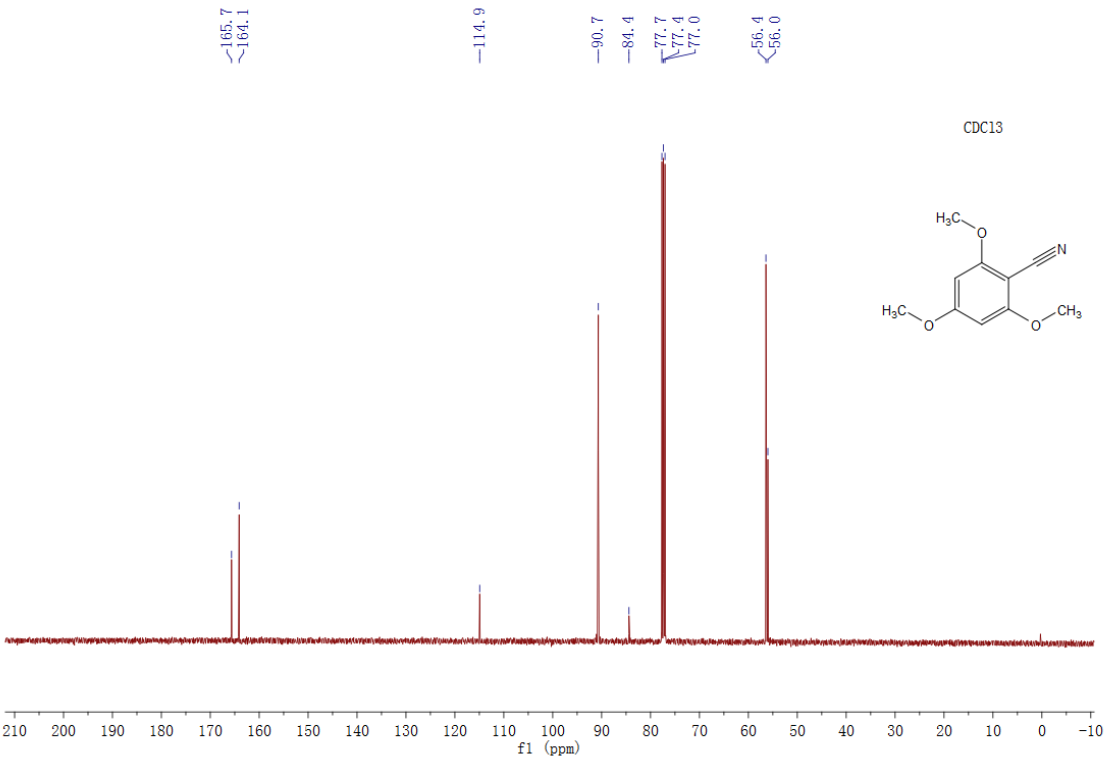
[13]C-NMR spectrum of **2q**



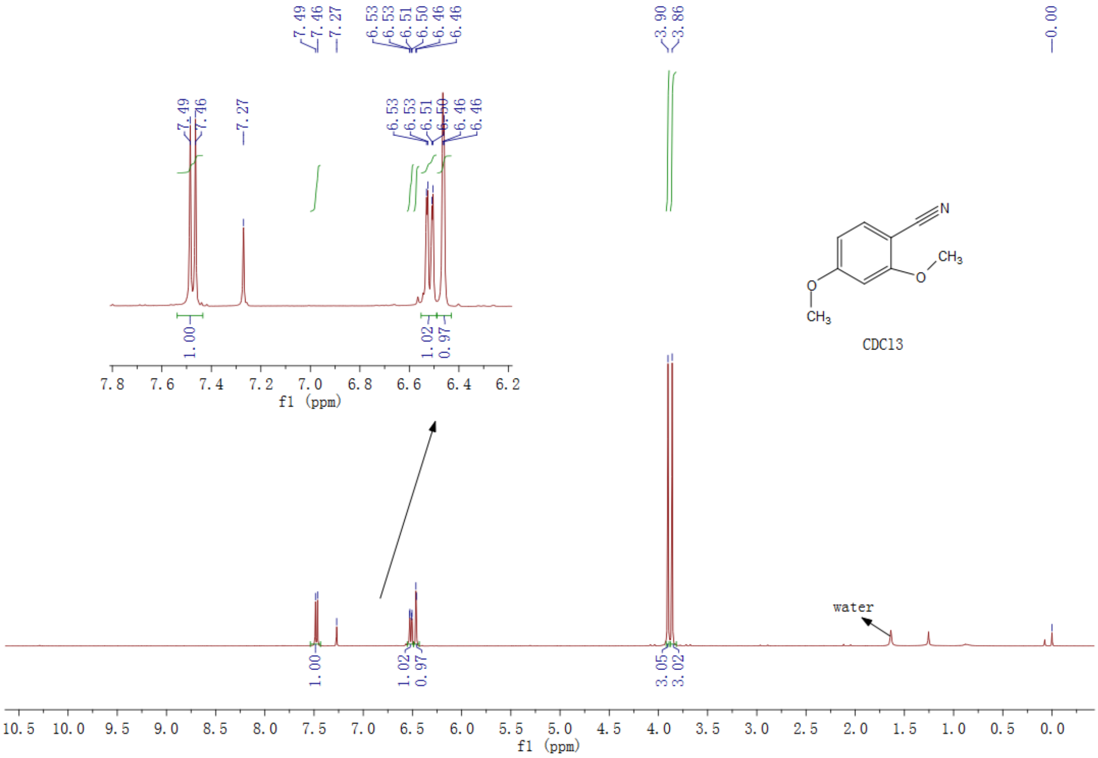
[1]H-NMR spectrum of **2r**



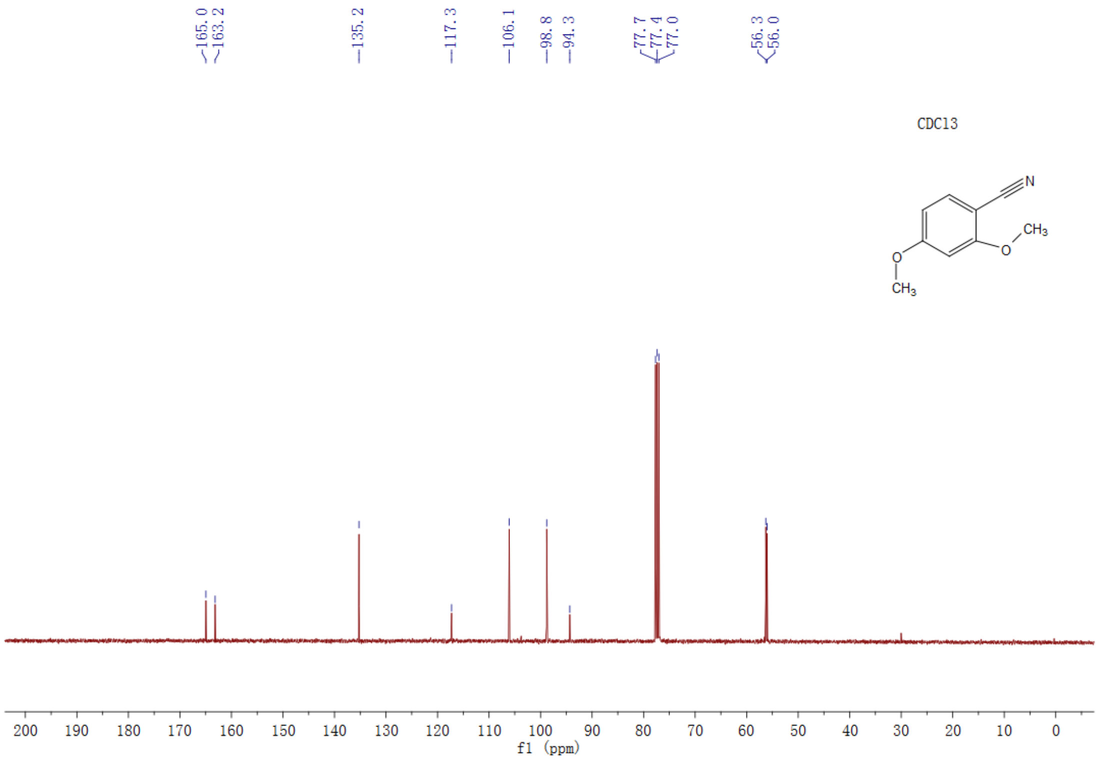
[13]C-NMR spectrum of **2r**



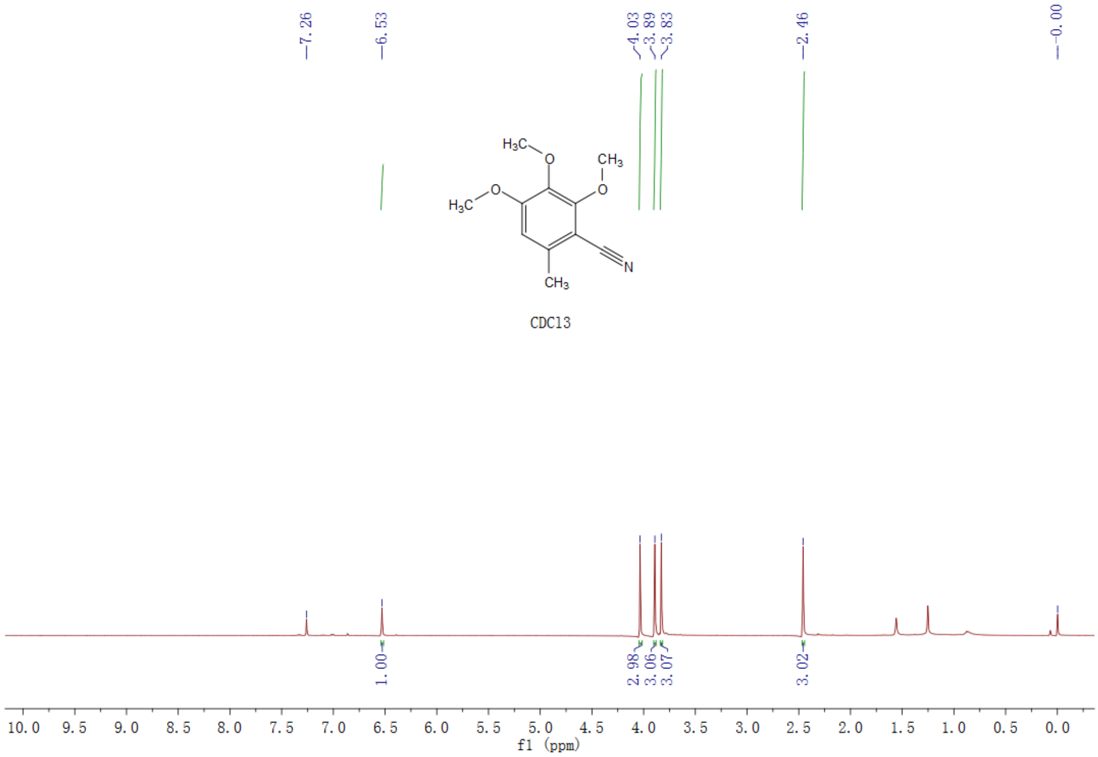
^{1}H-NMR spectrum of **2s**



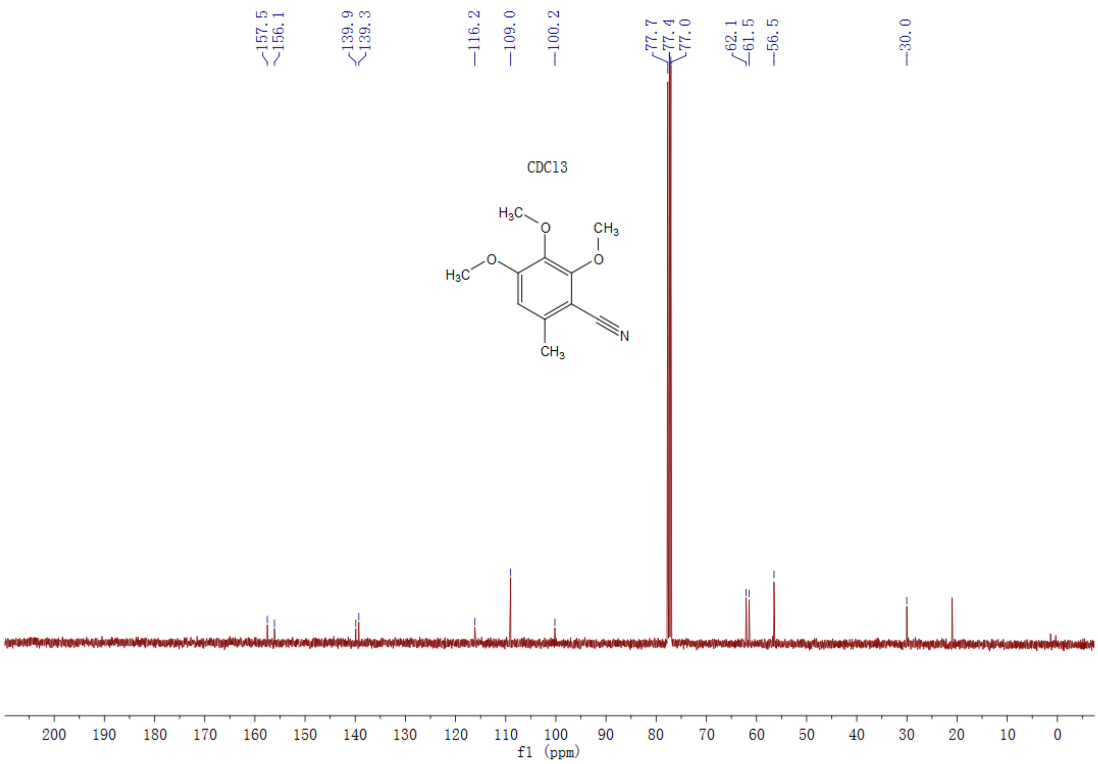
^{13}C-NMR spectrum of **2s**



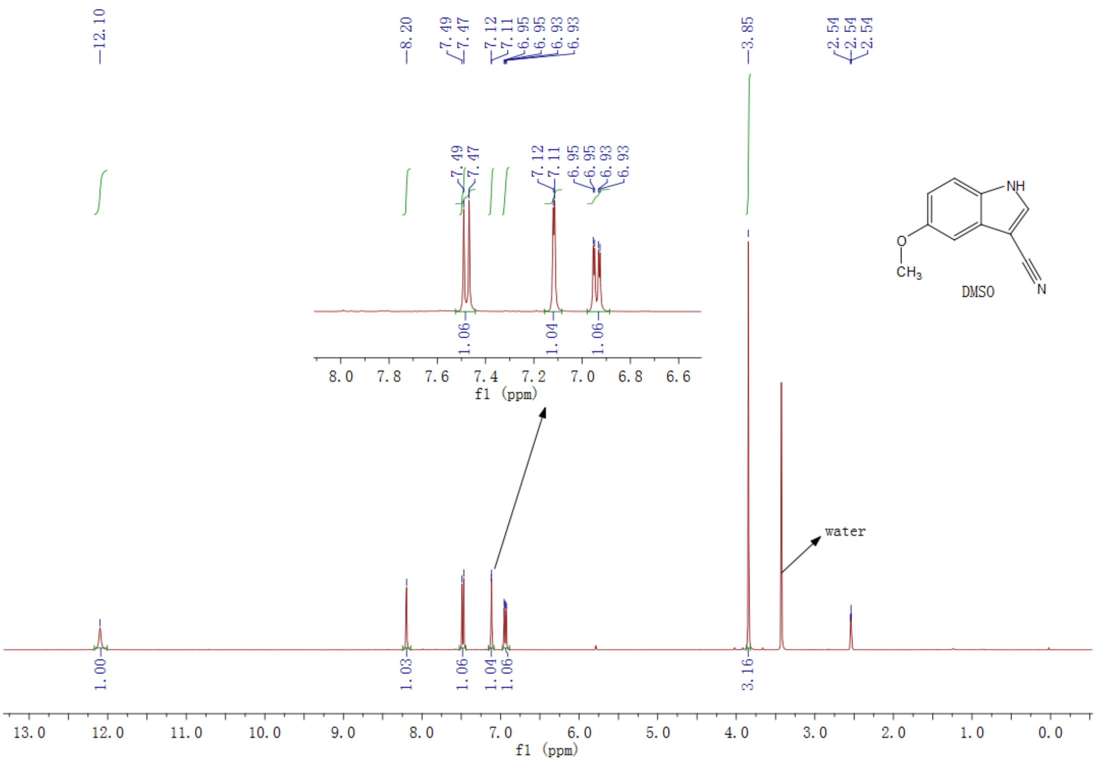
[1]H-NMR spectrum of **2t**



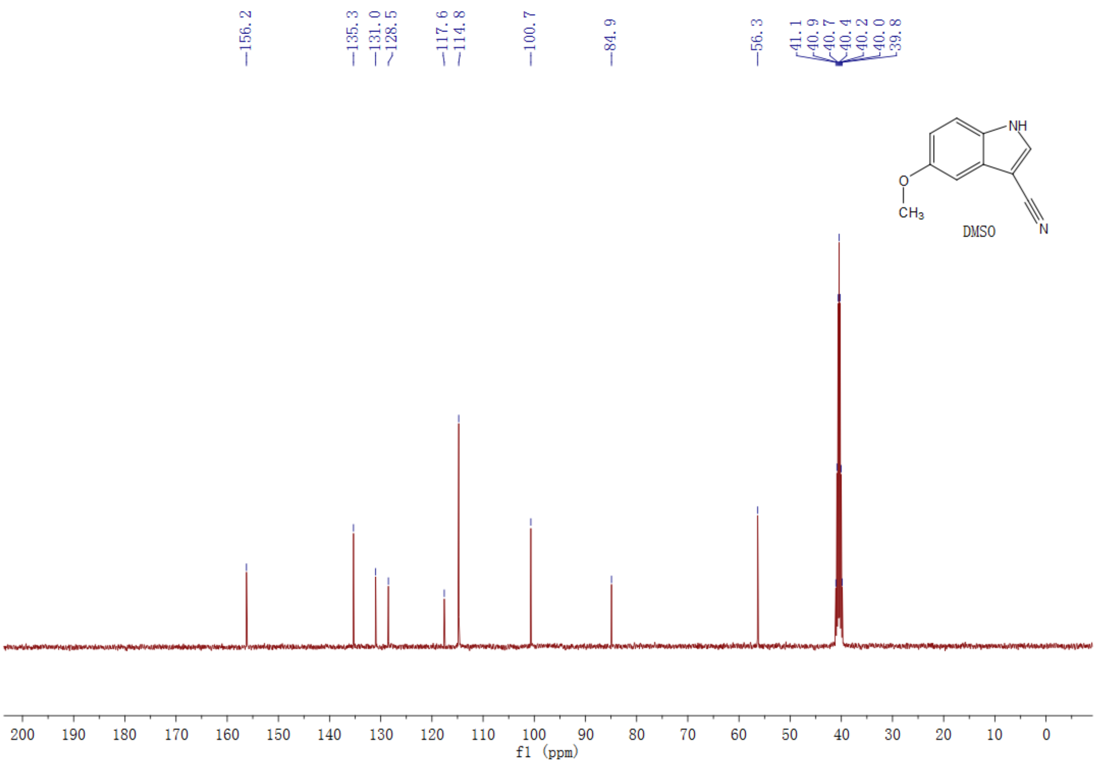
[13]C-NMR spectrum of **2t**



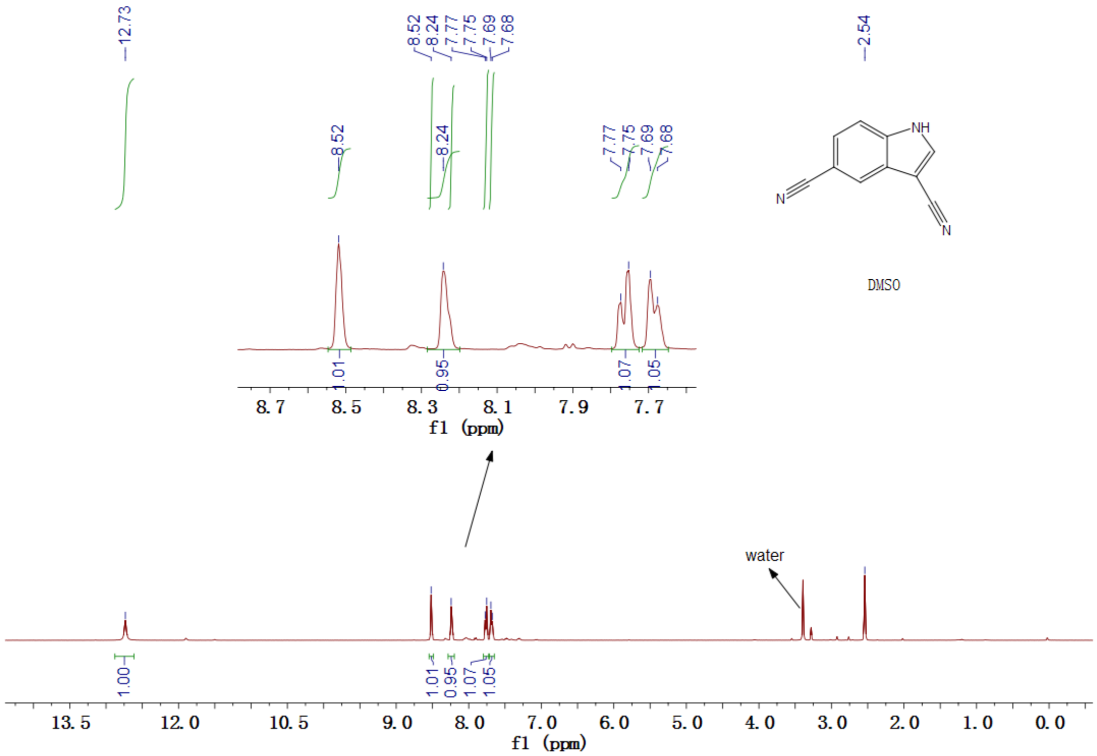
[1]H-NMR spectrum of **2u**



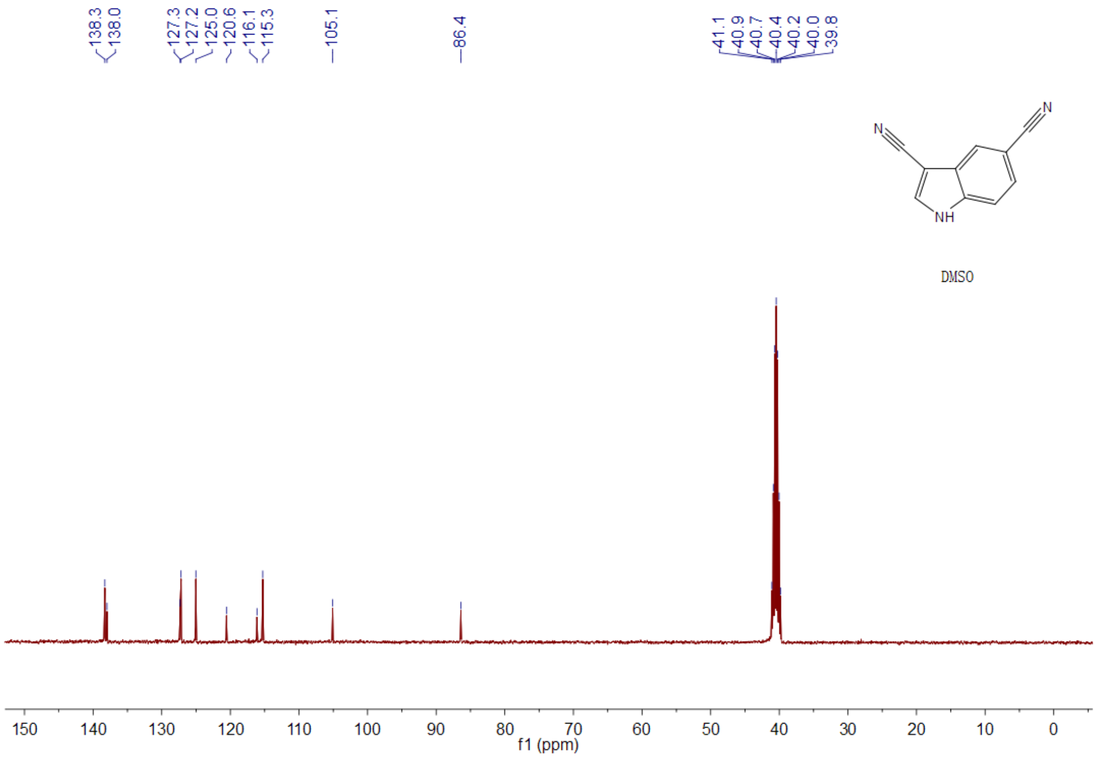
[13]C-NMR spectrum of **2u**



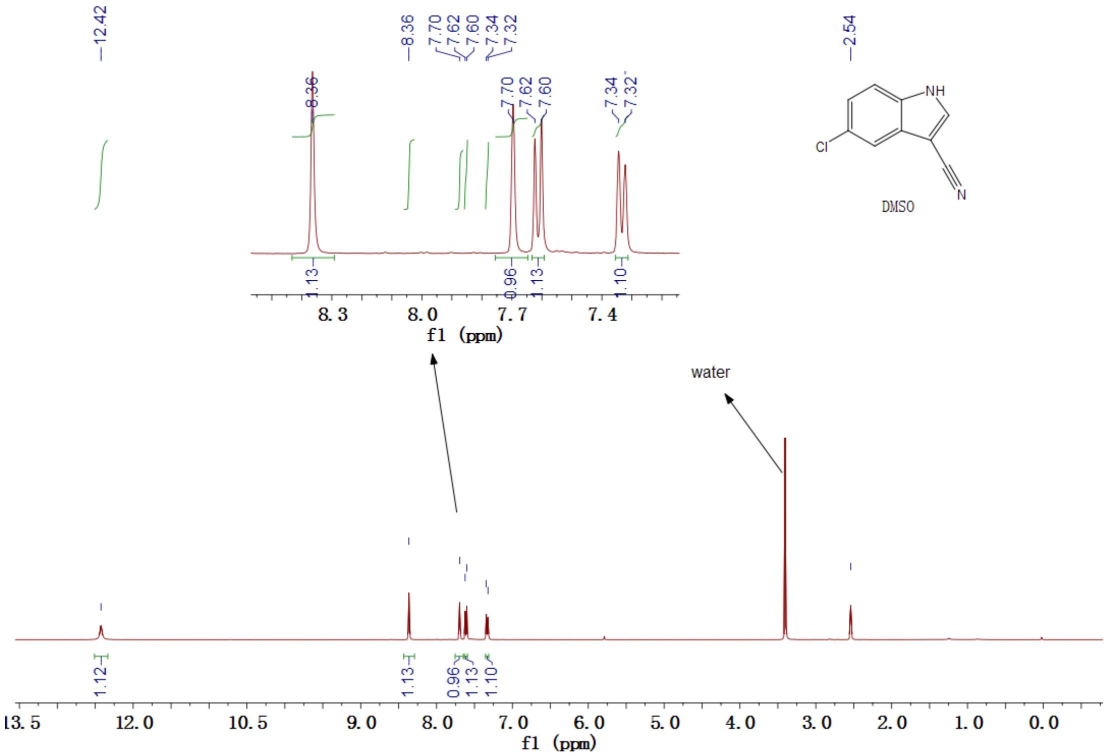
^{1}H-NMR spectrum of **2v**



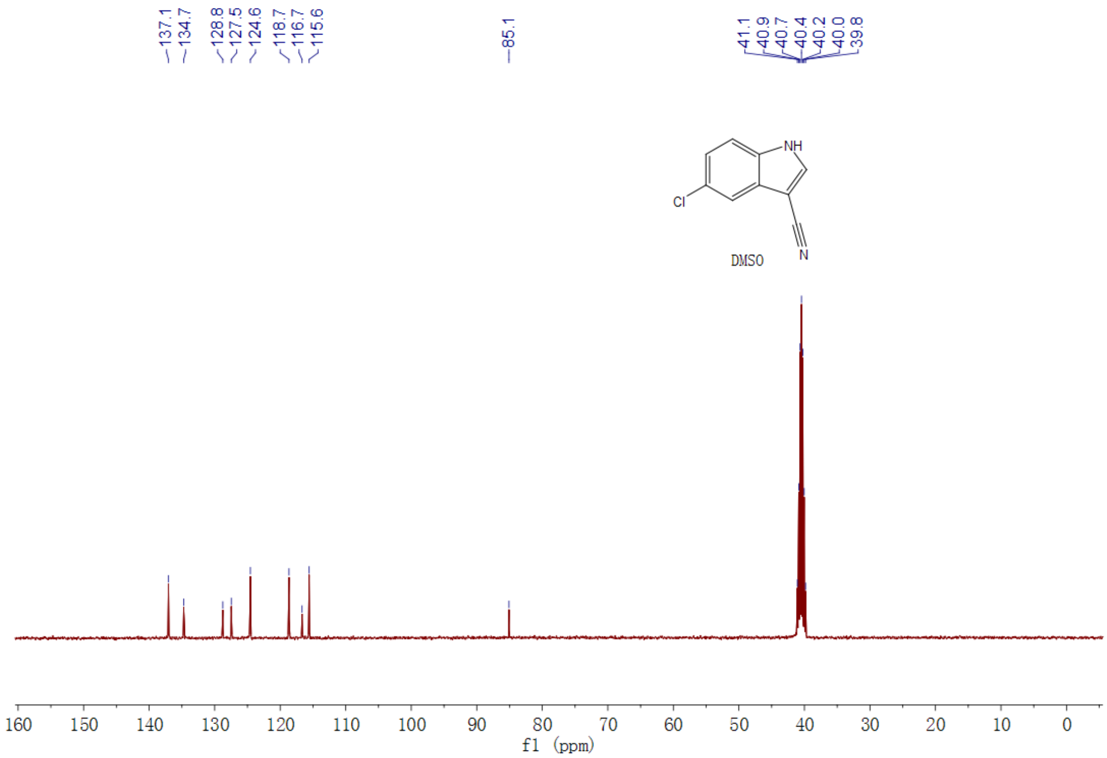
^{13}C-NMR spectrum of **2v**



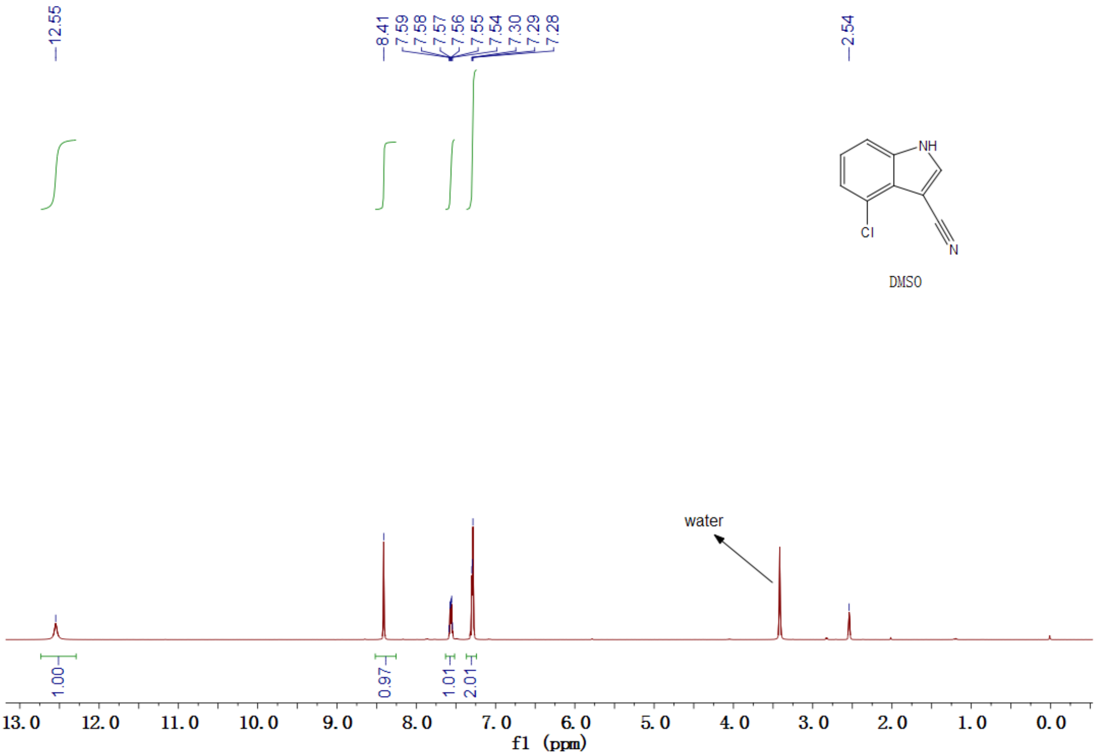
^{1}H-NMR spectrum of **2w**



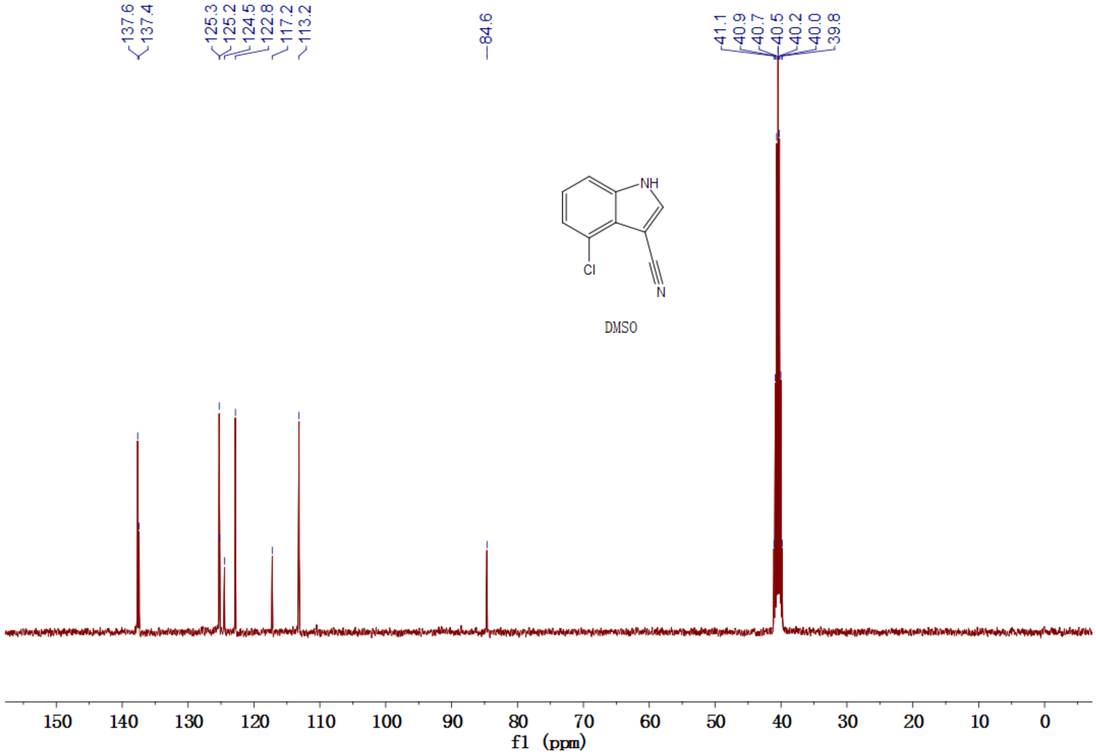
^{13}C-NMR spectrum of **2w**



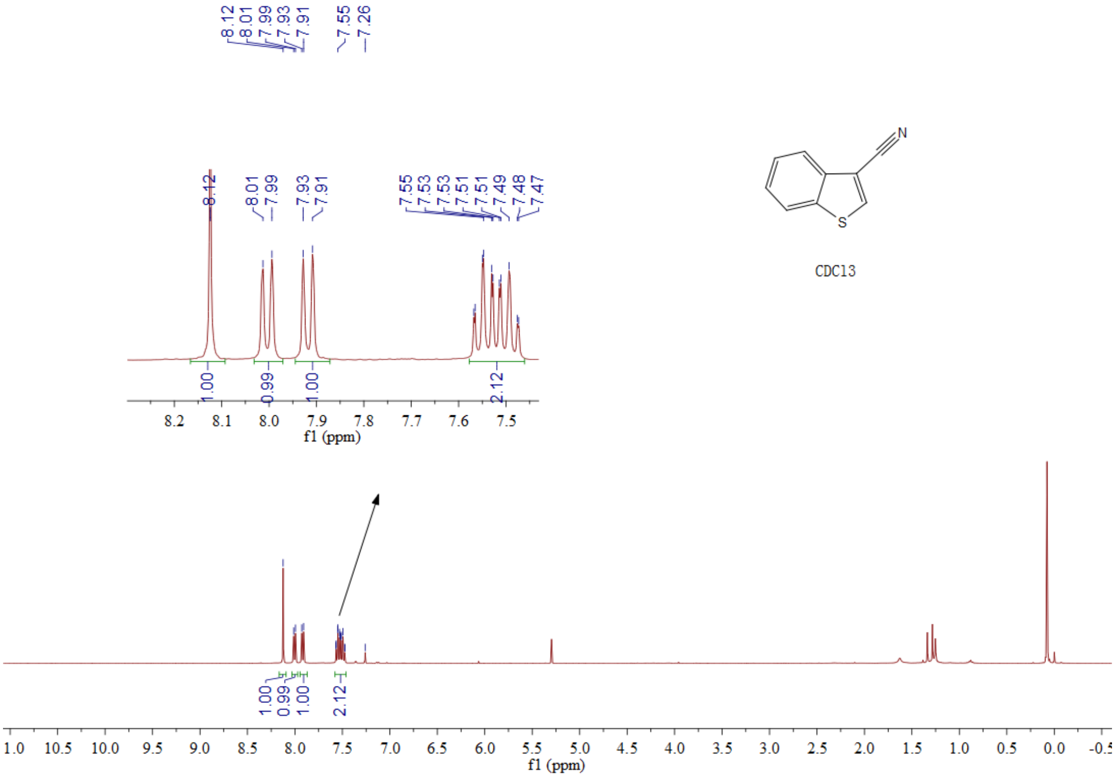
^{1}H-NMR spectrum of **2x**



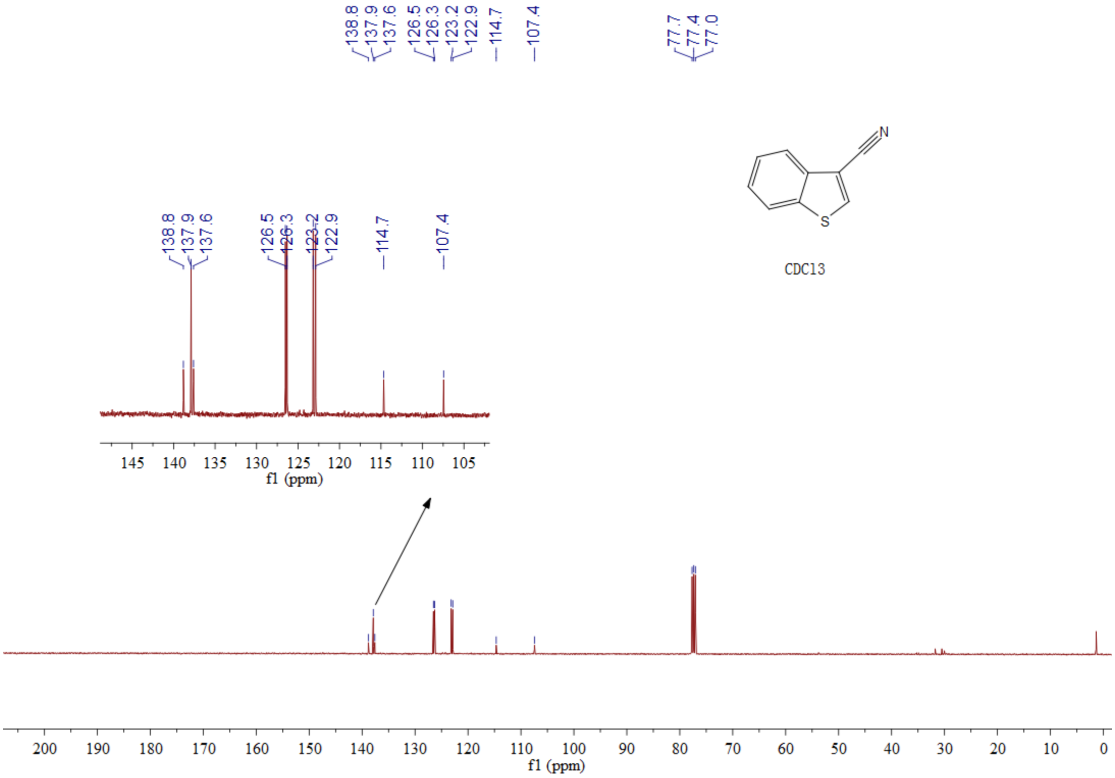
^{13}C-NMR spectrum of **2x**



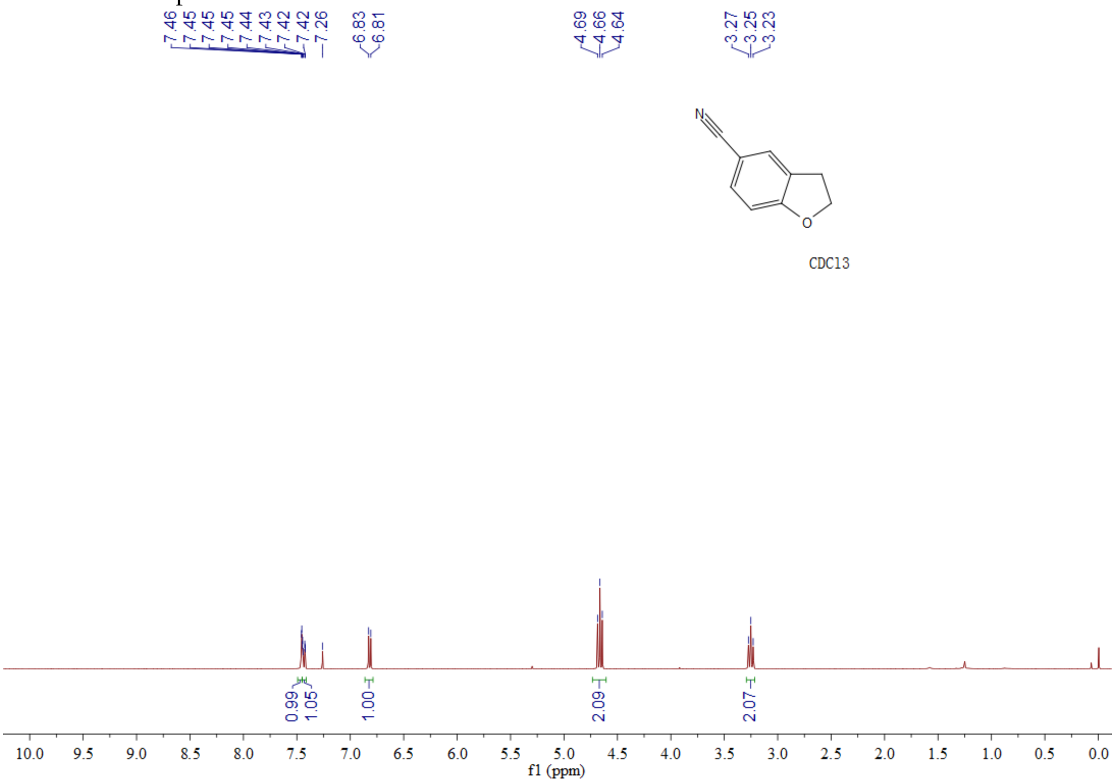
[1]H-NMR spectrum of **2y**



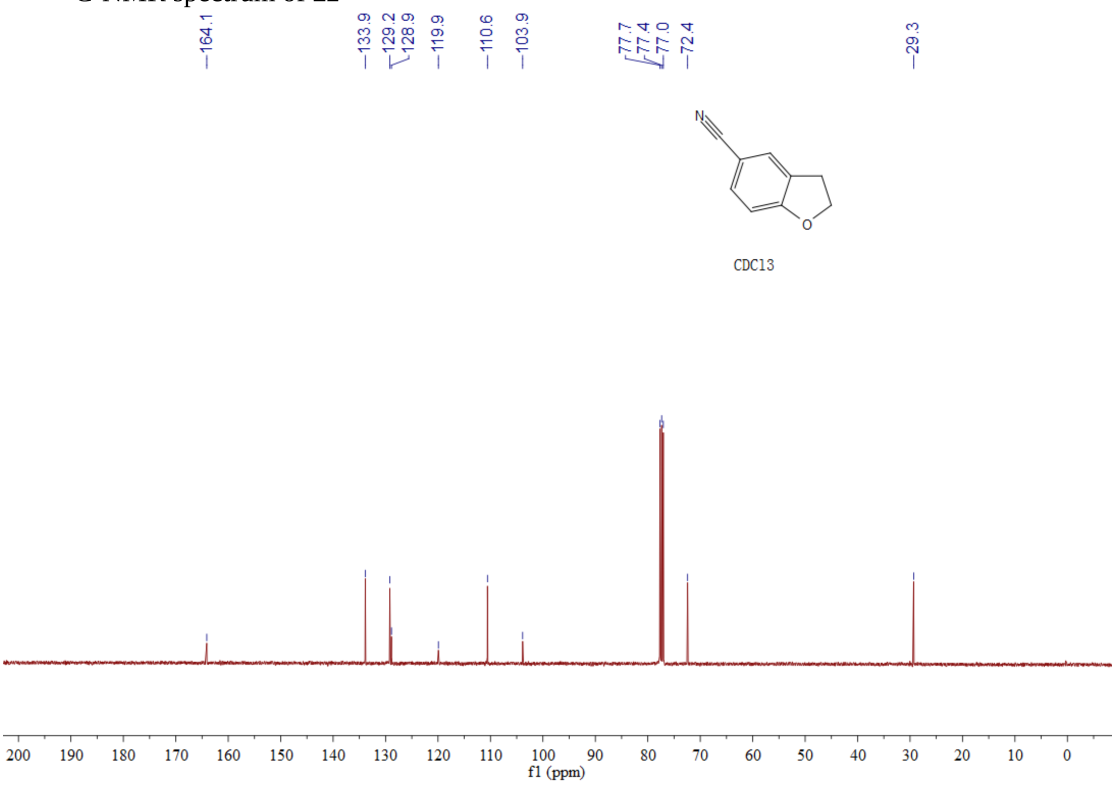
[13]C-NMR spectrum of **2y**



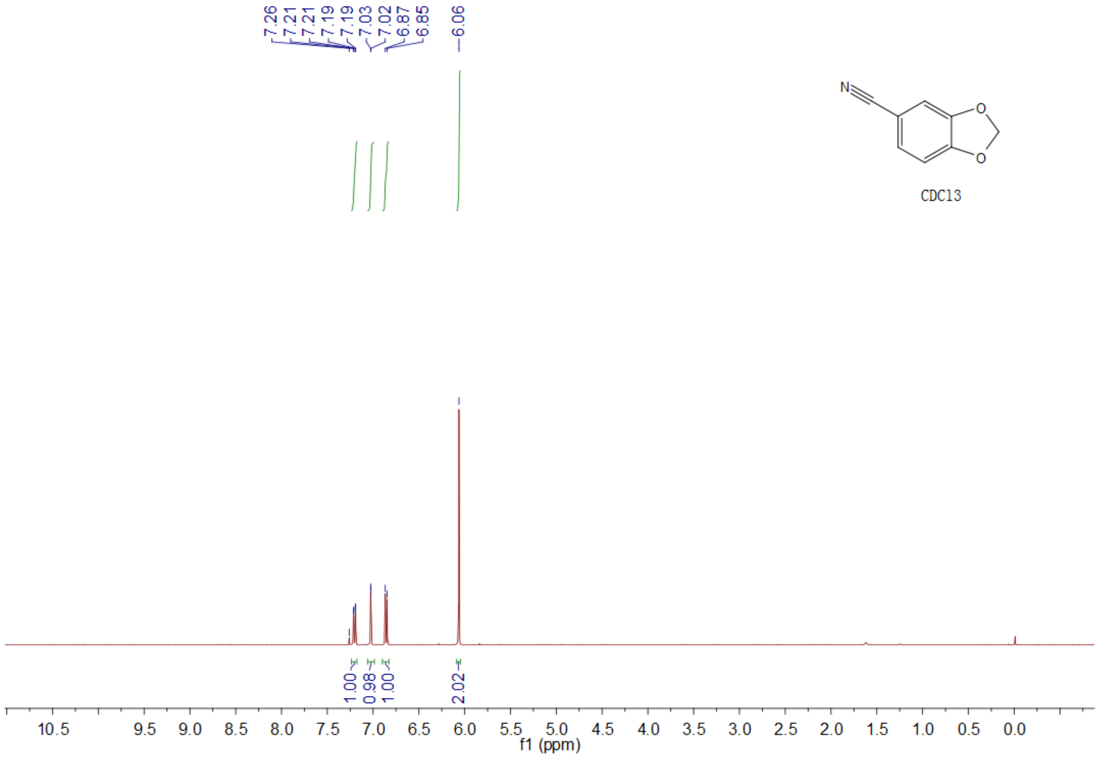
[1]H-NMR spectrum of **2z**



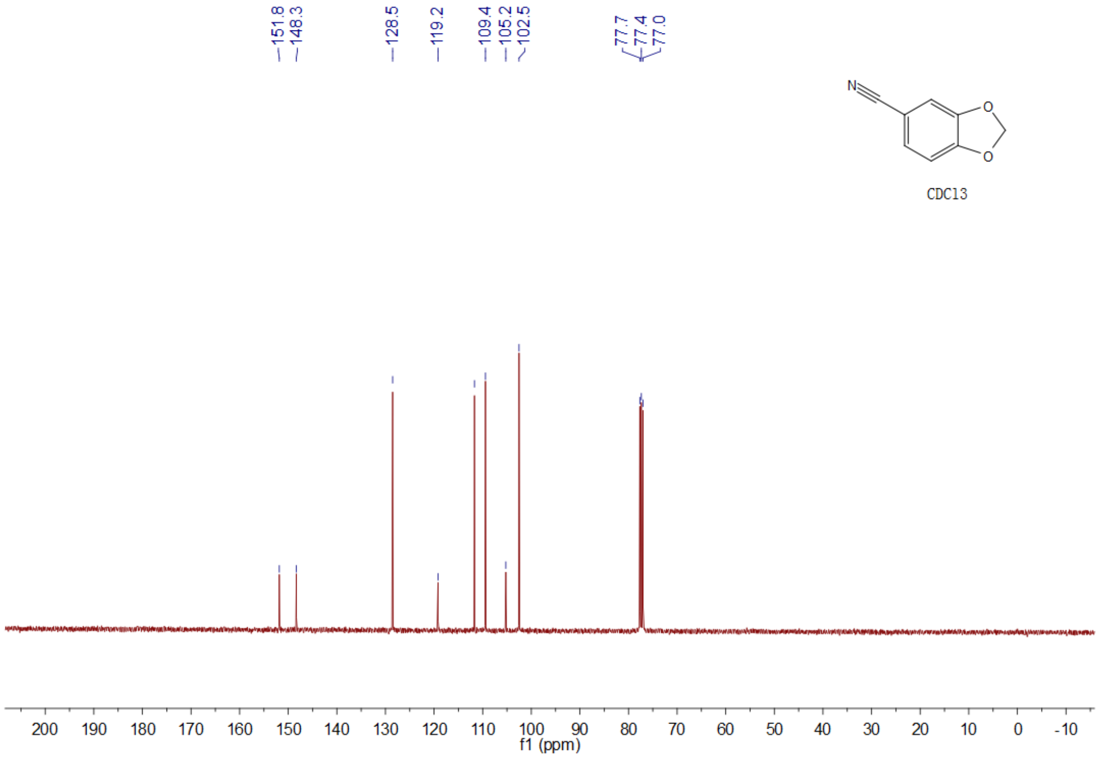
[13]C-NMR spectrum of **2z**



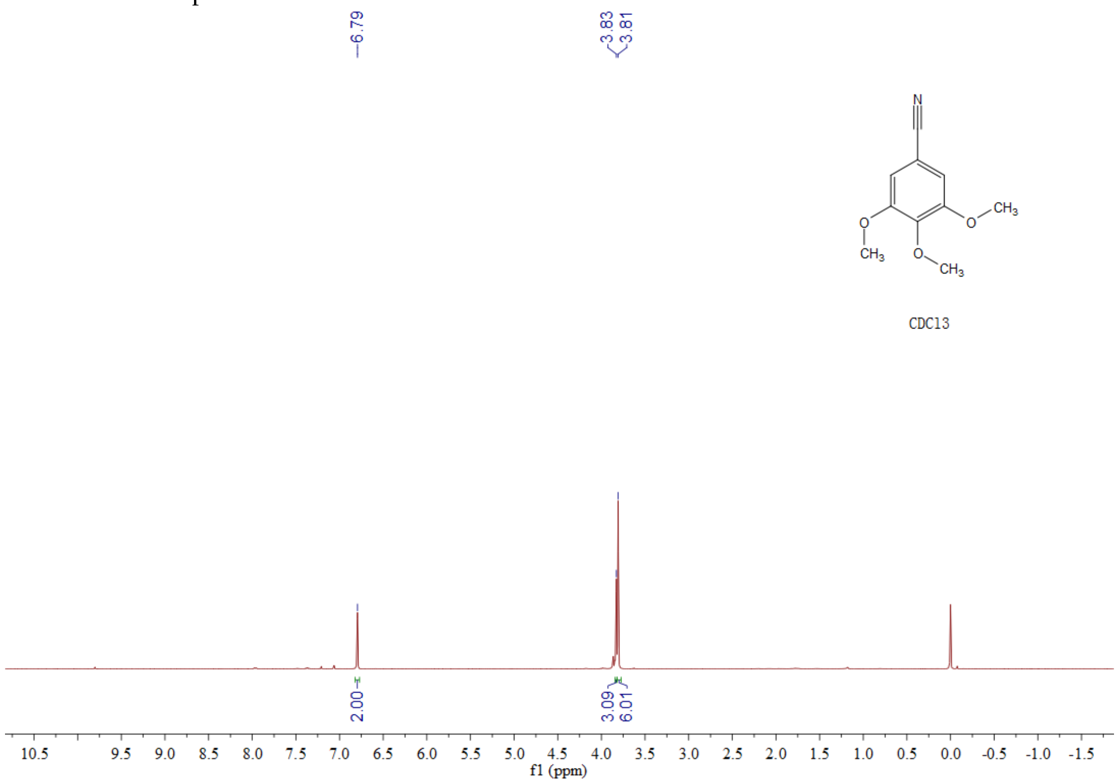
[1]H-NMR spectrum of **2A**



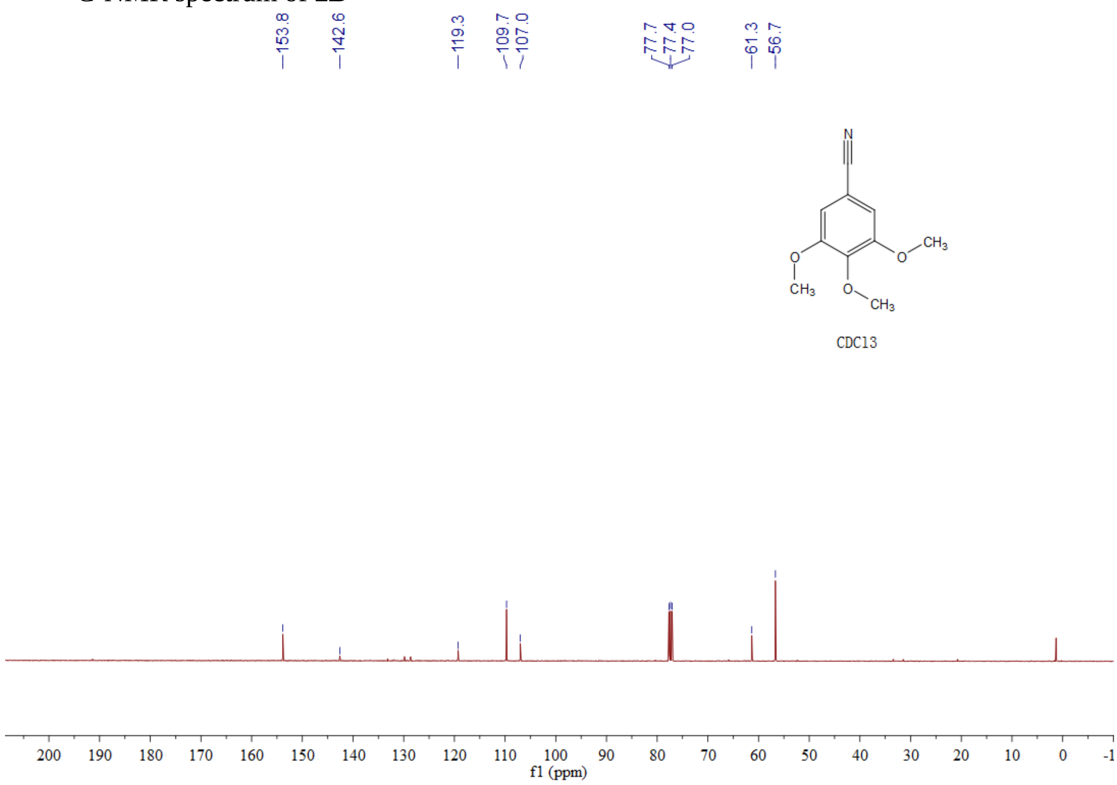
[13]C-NMR spectrum of **2A**



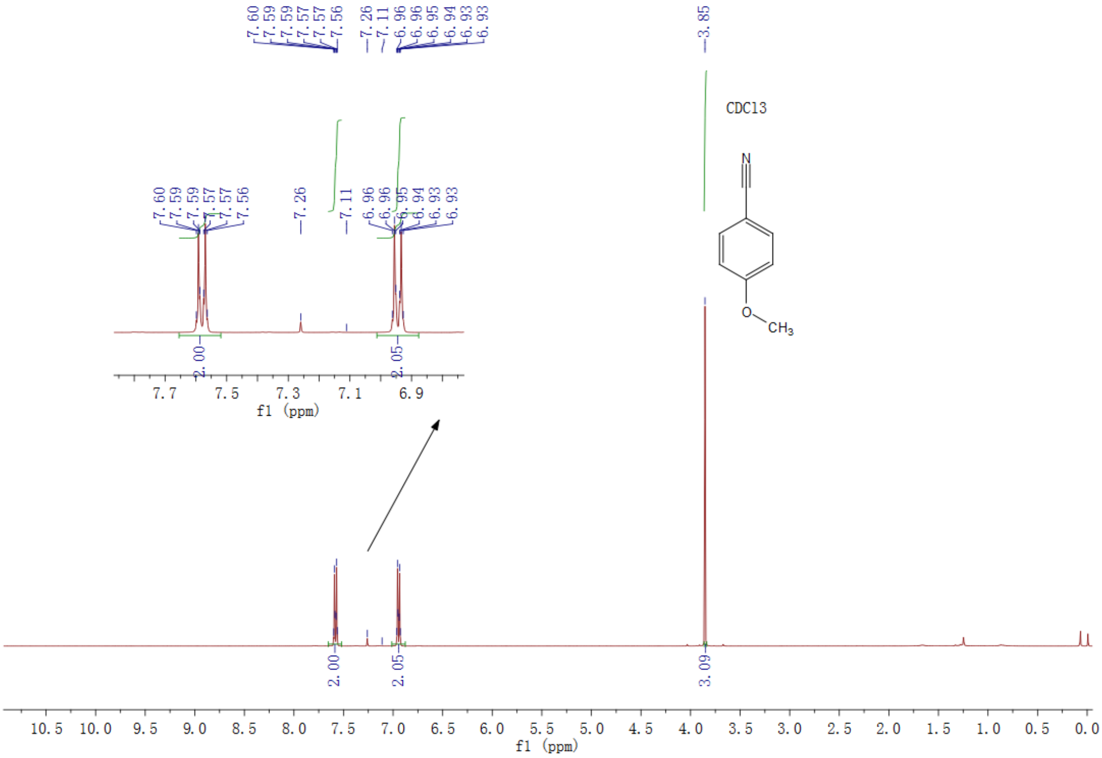
[1]H-NMR spectrum of **2B**



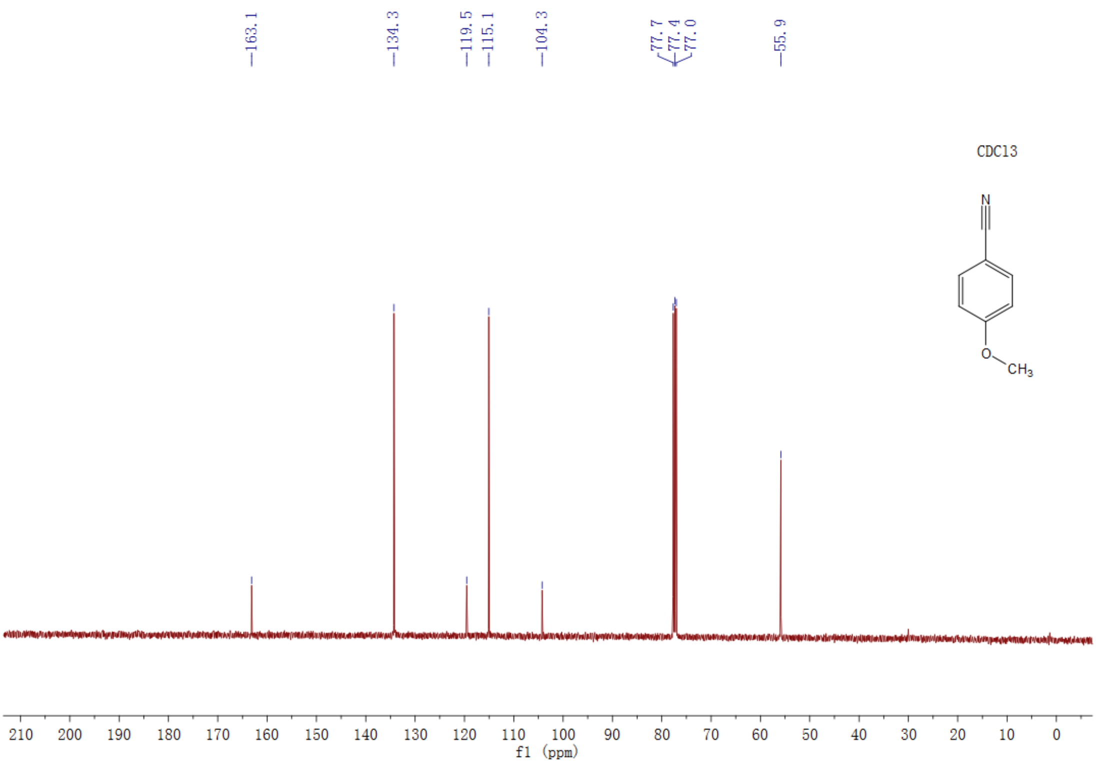
[13]C-NMR spectrum of **2B**



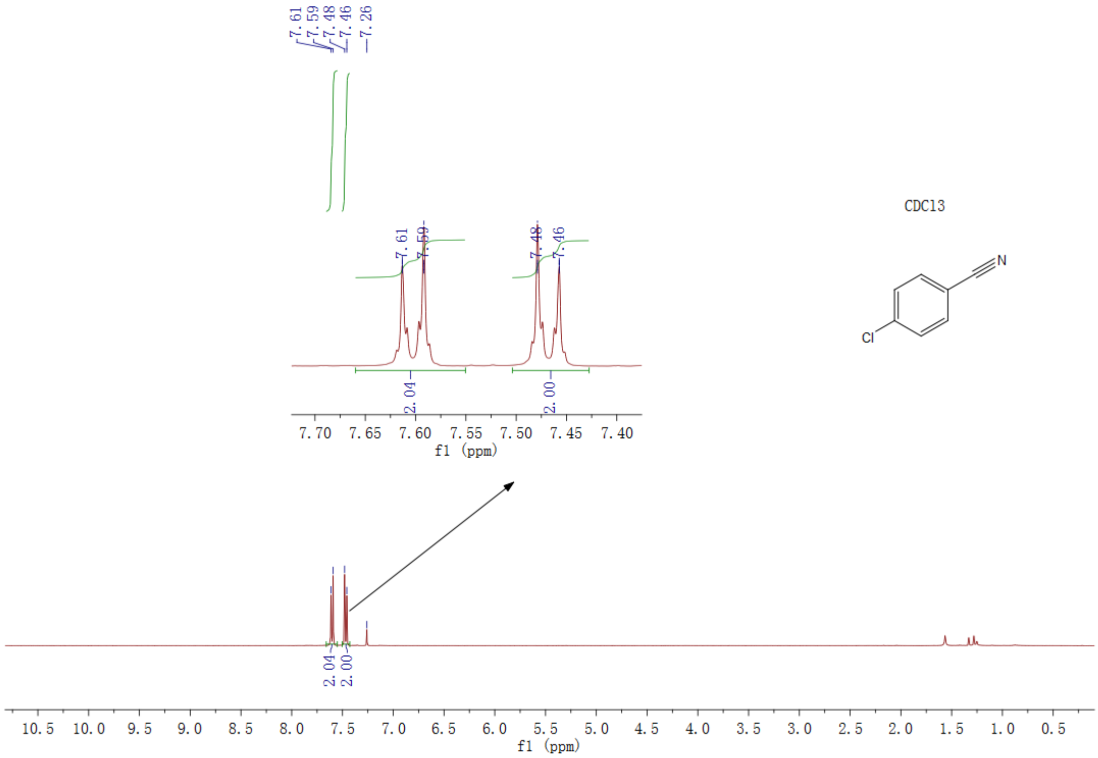
[1]H-NMR spectrum of **2C**



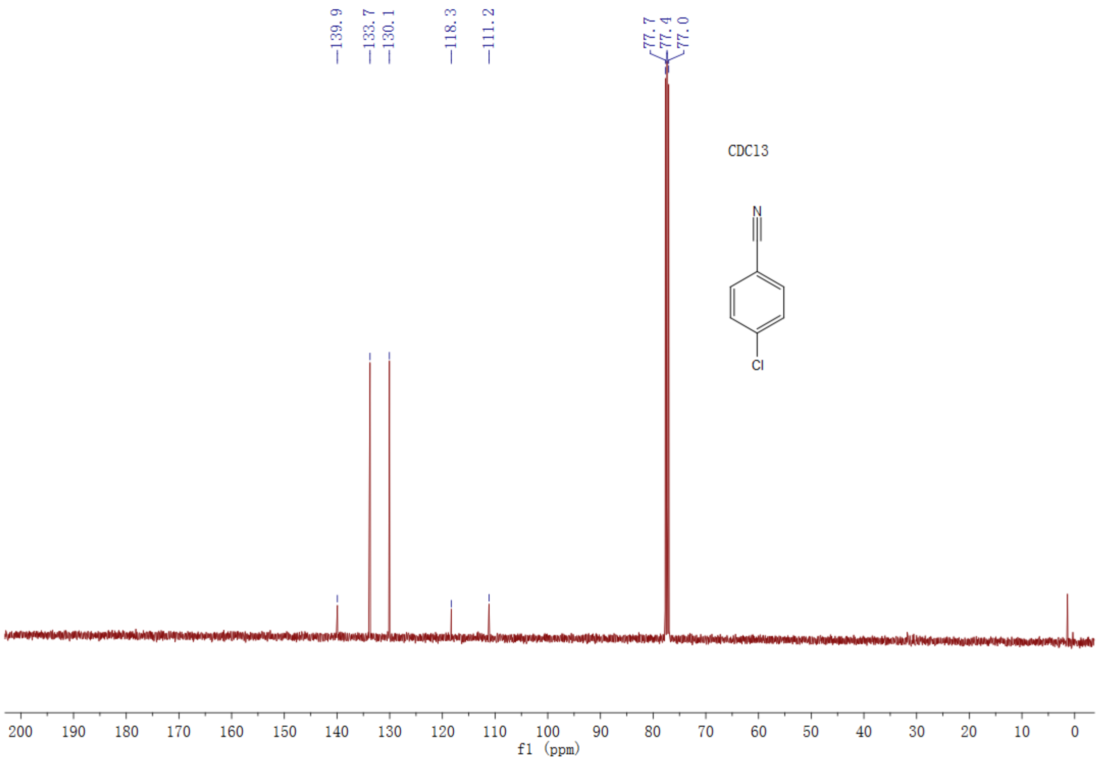
[13]C-NMR spectrum of **2C**



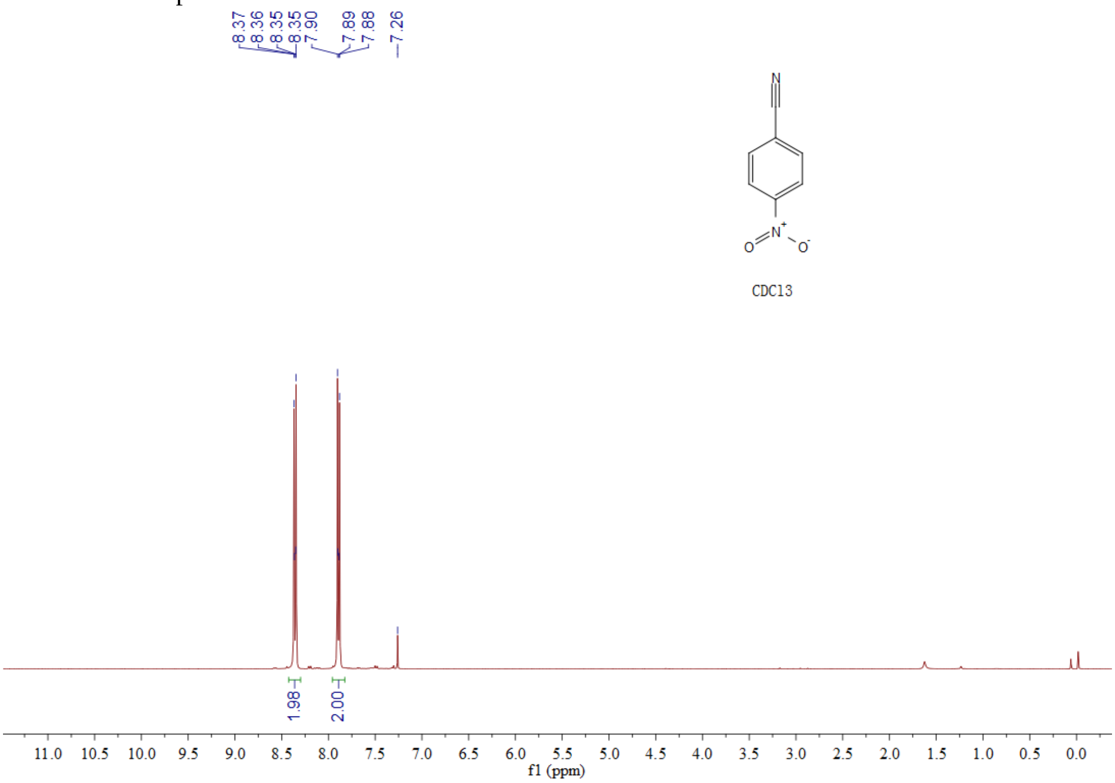
^{1}H-NMR spectrum of **2D**



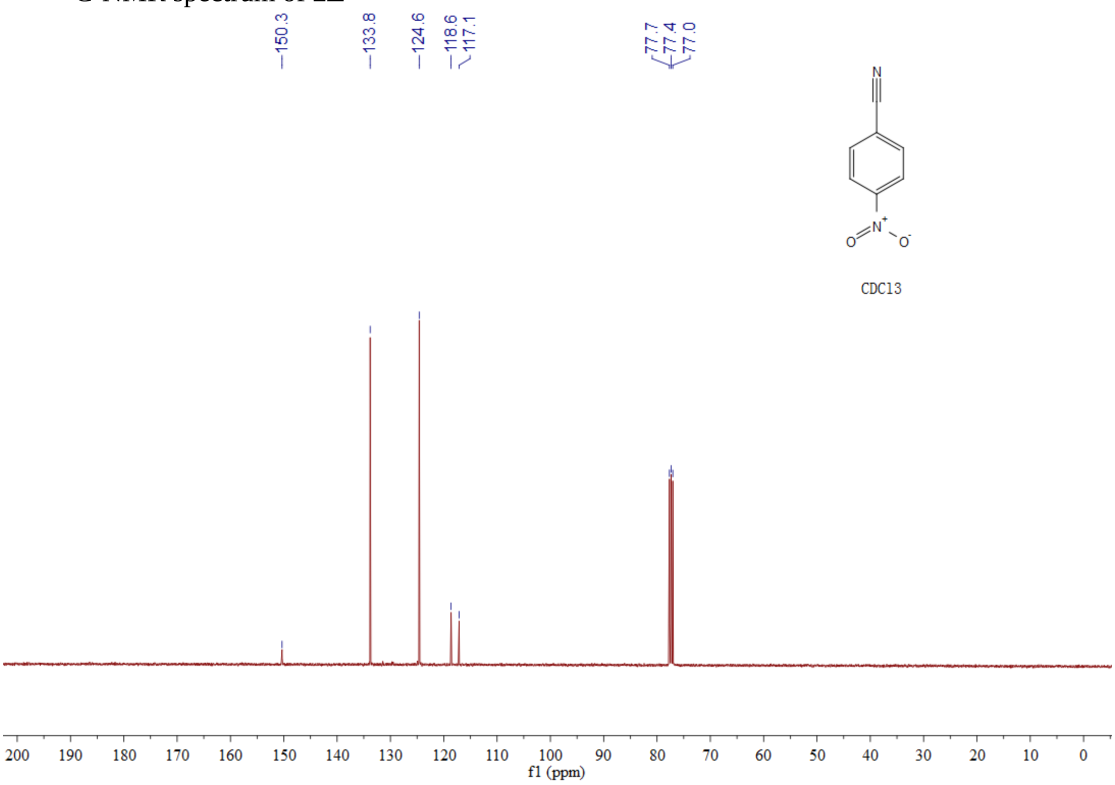
^{13}C-NMR spectrum of **2D**



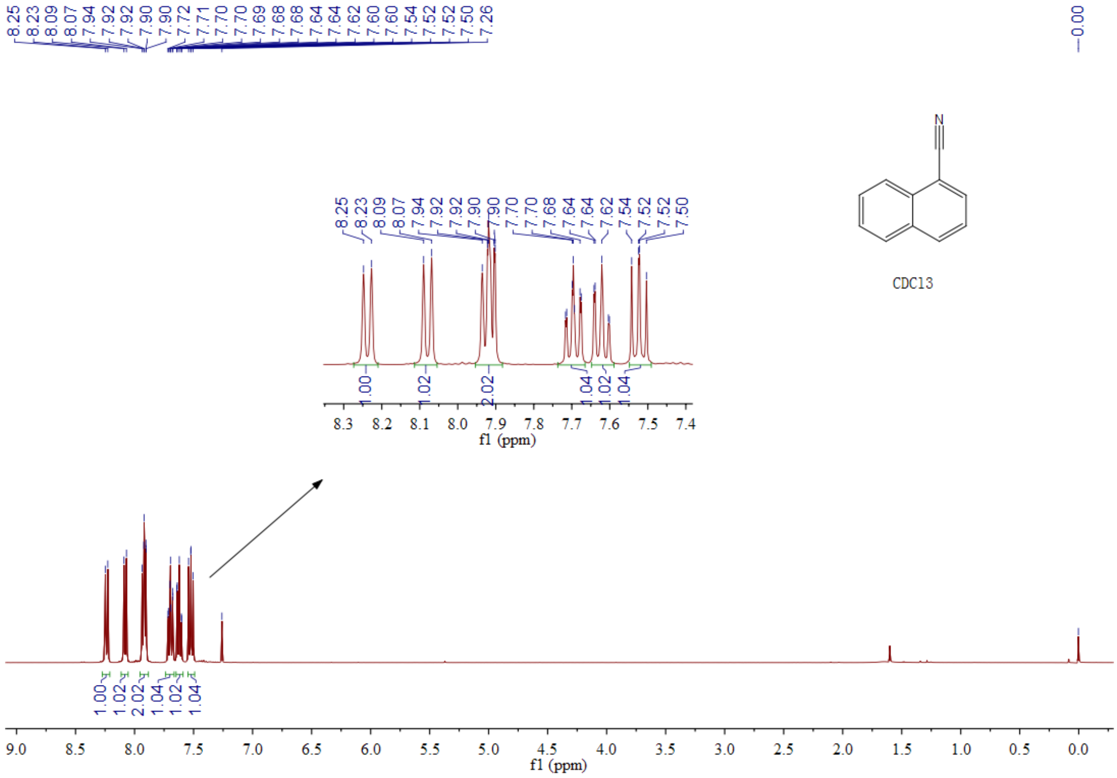
^{1}H-NMR spectrum of **2E**



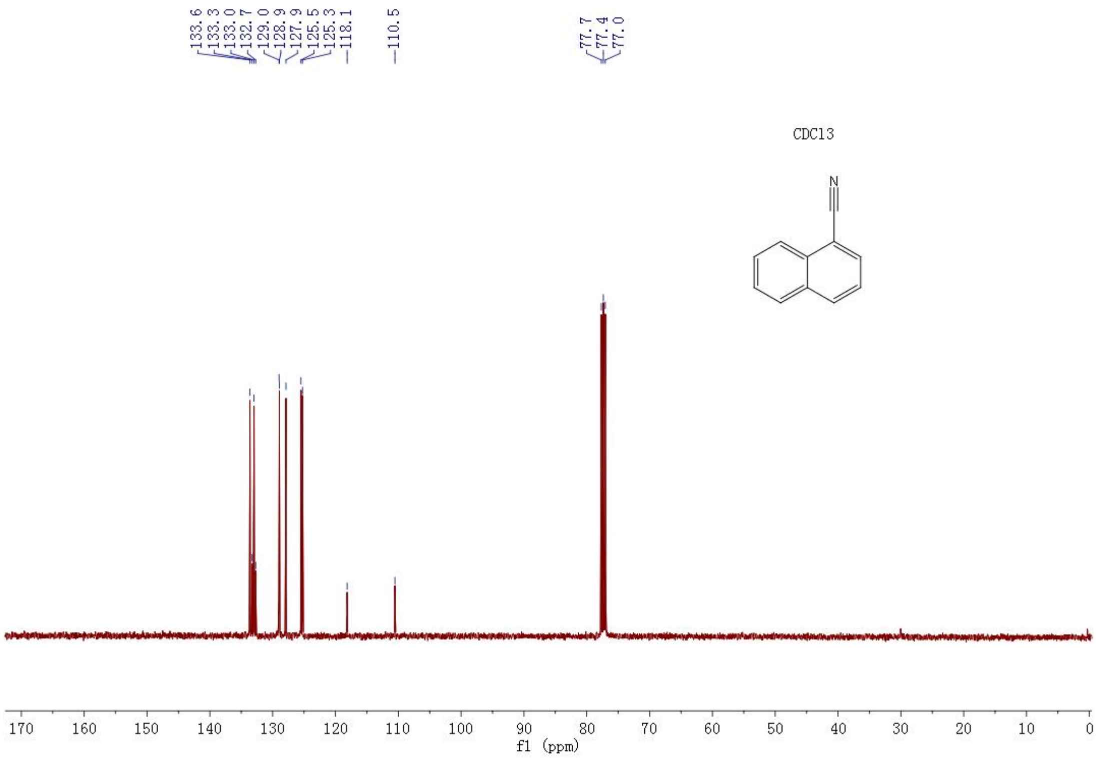
^{13}C-NMR spectrum of **2E**



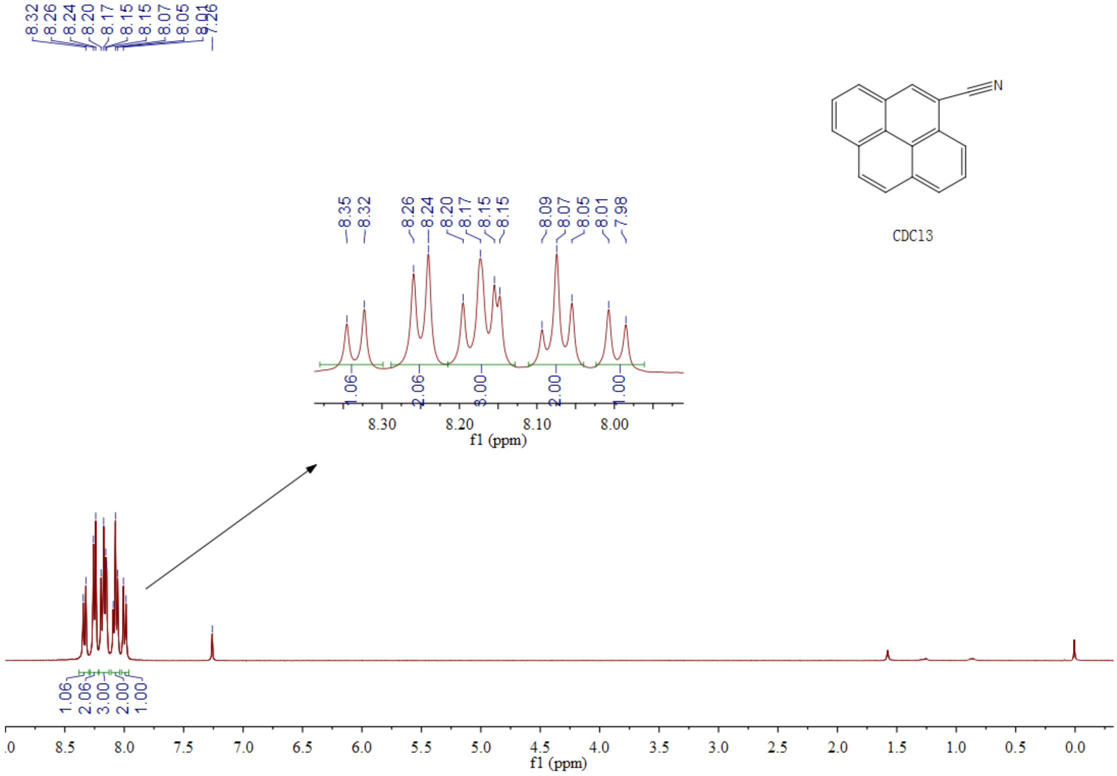
^{1}H-NMR spectrum of **2F**



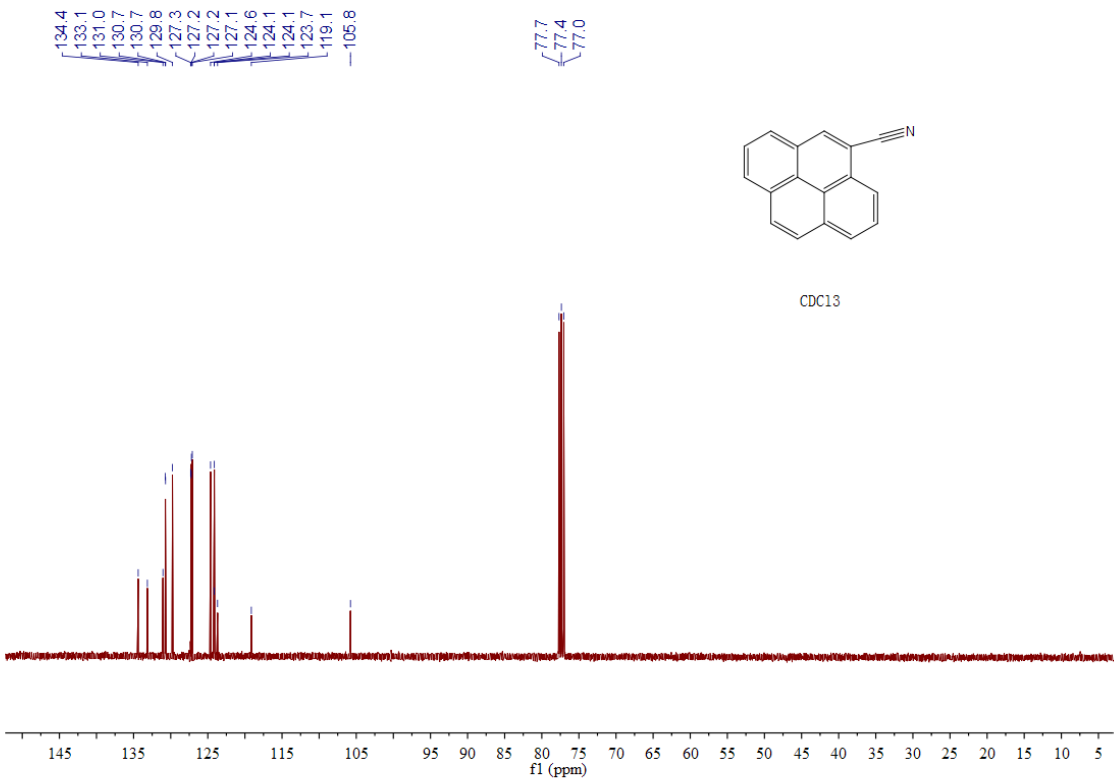
^{13}C-NMR spectrum of **2F**



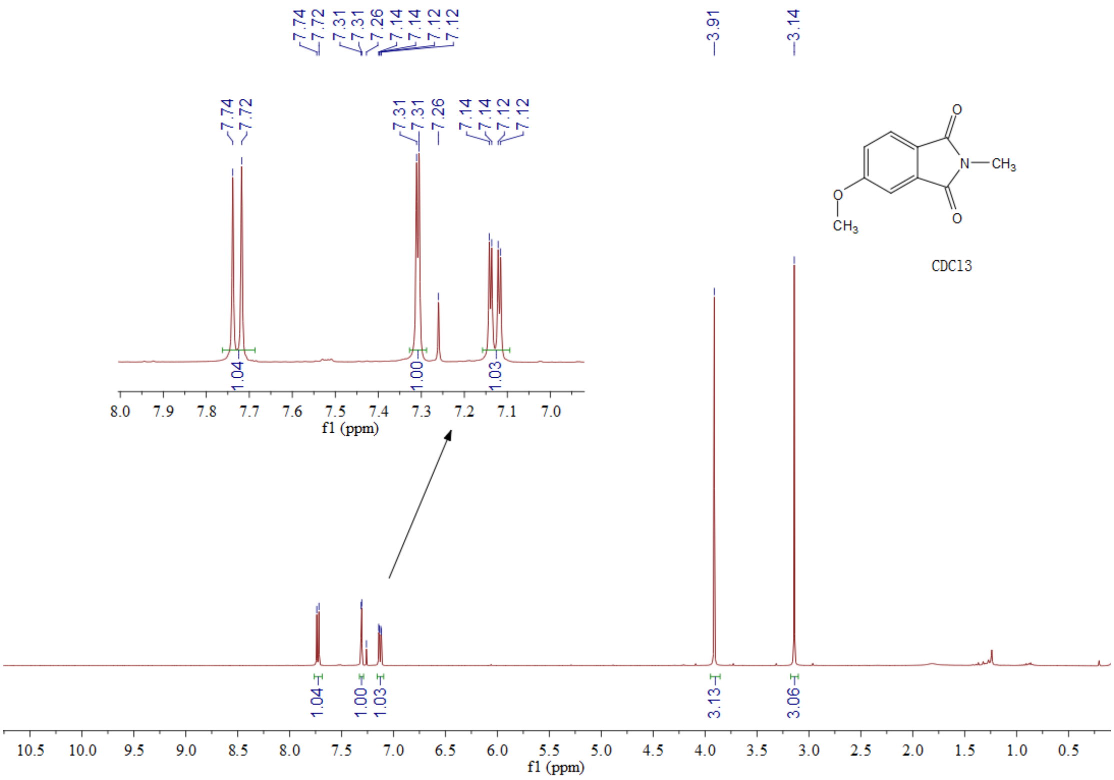
[1]H-NMR spectrum of **2G**



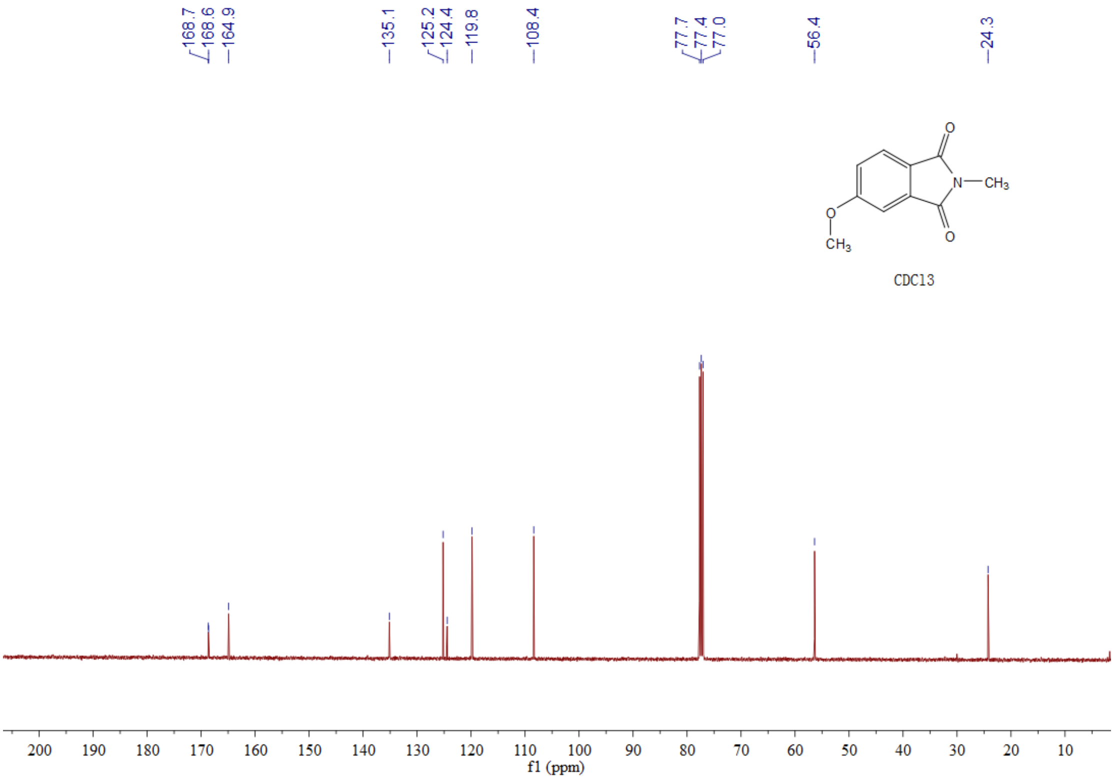
[13]C-NMR spectrum of **2G**



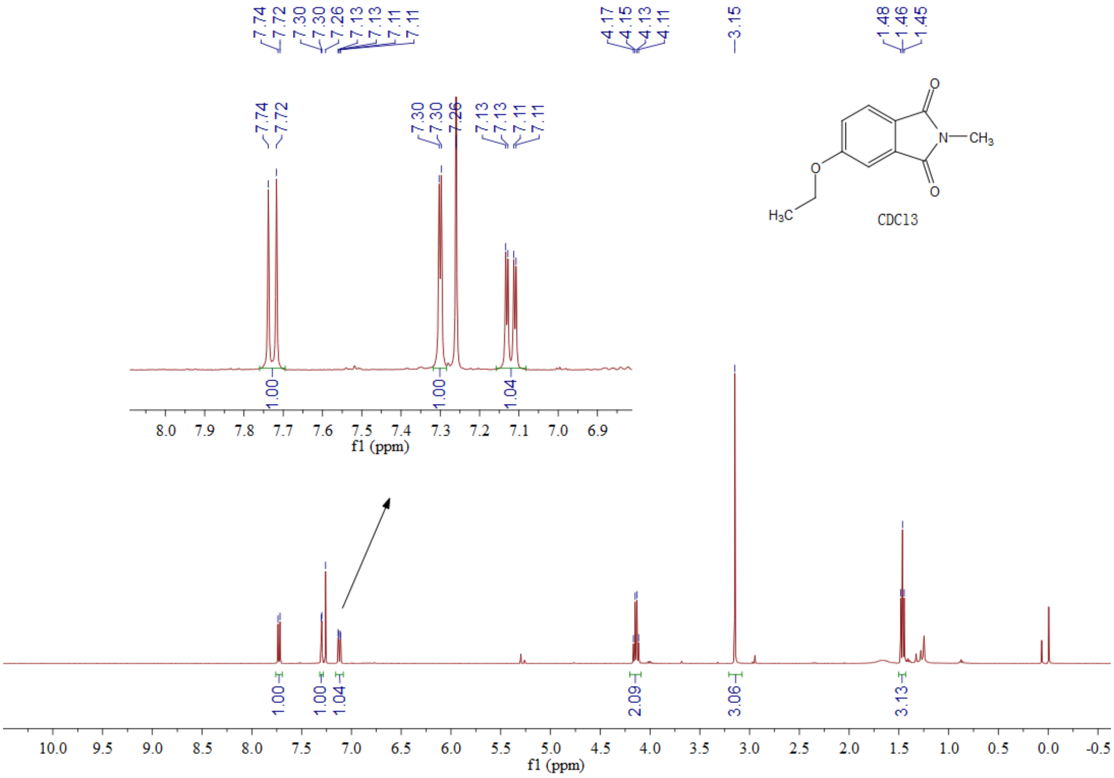
[1]H-NMR spectrum of **5a**



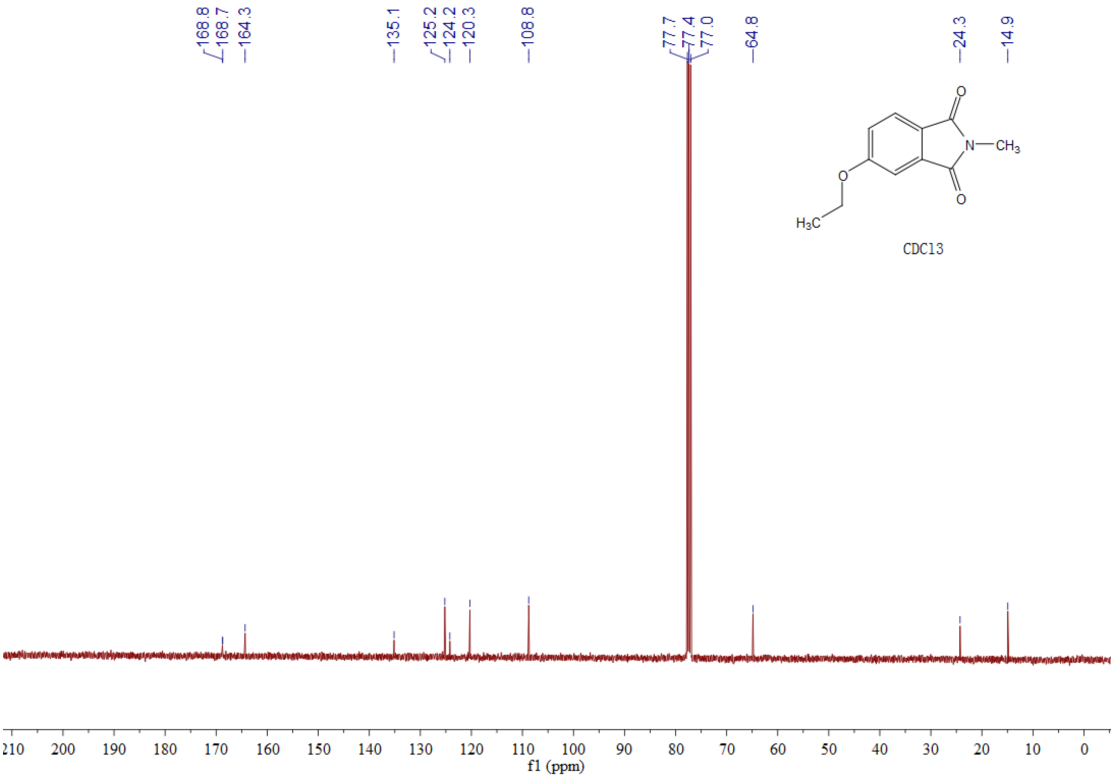
[13]C-NMR spectrum of **5a**



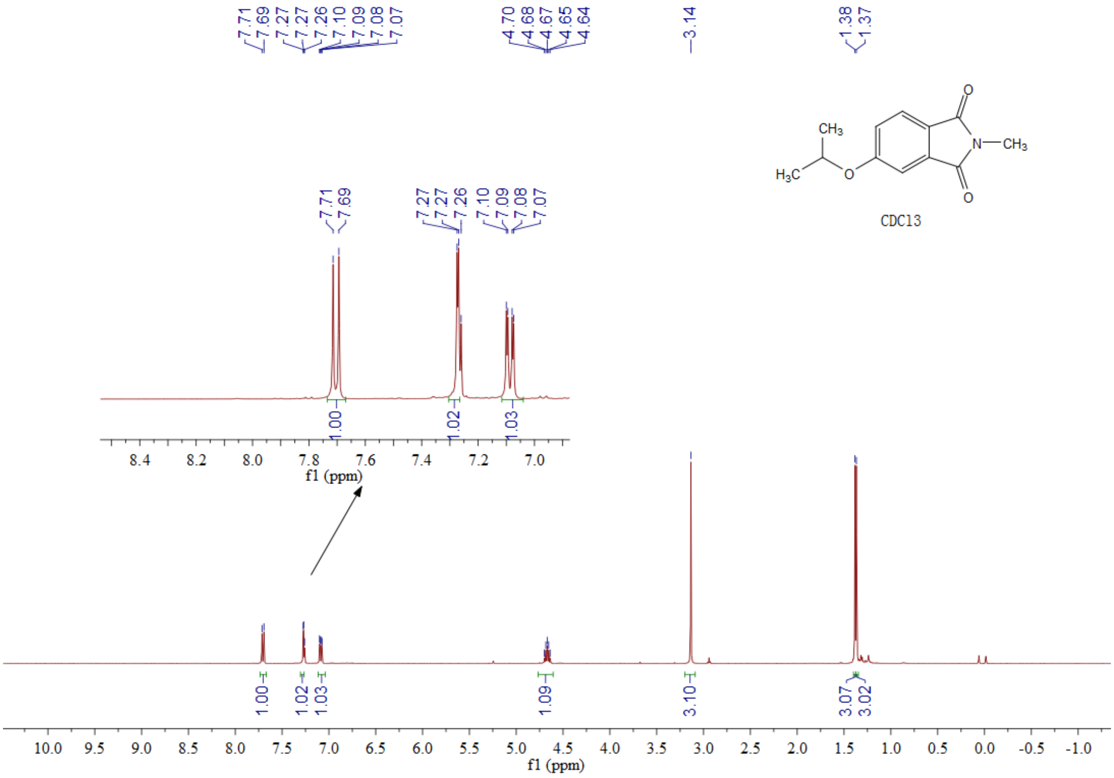
[1]H-NMR spectrum of **5b**



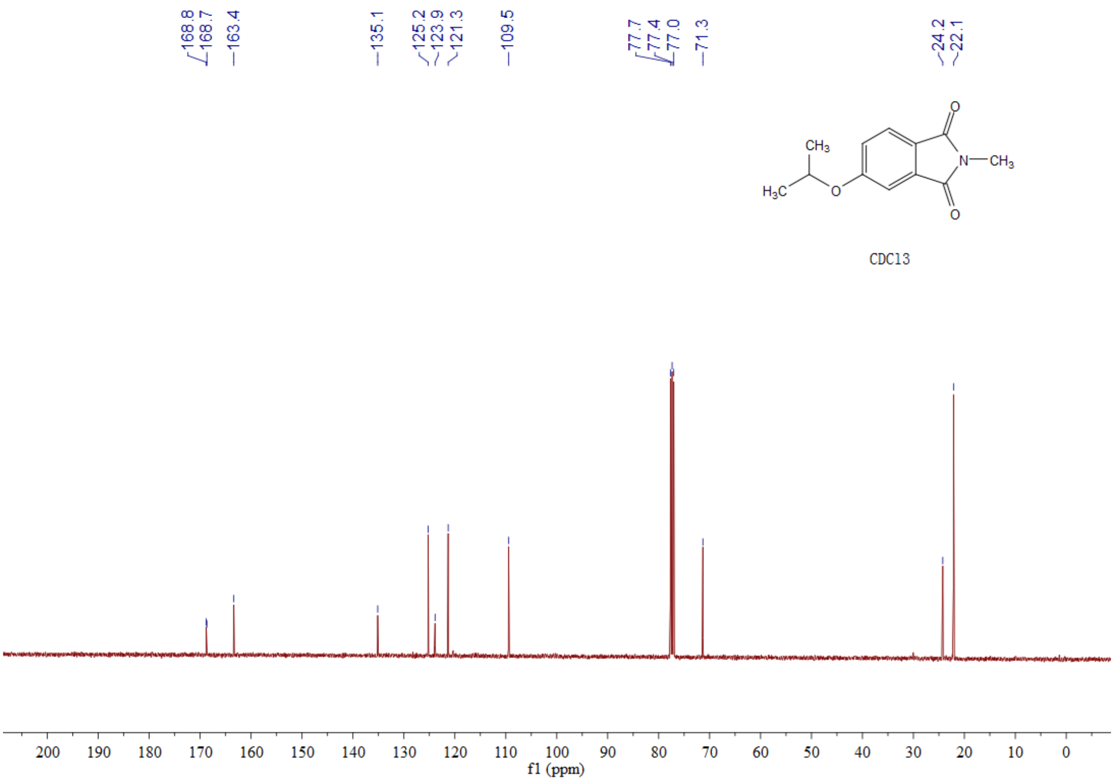
[13]C-NMR spectrum of **5b**



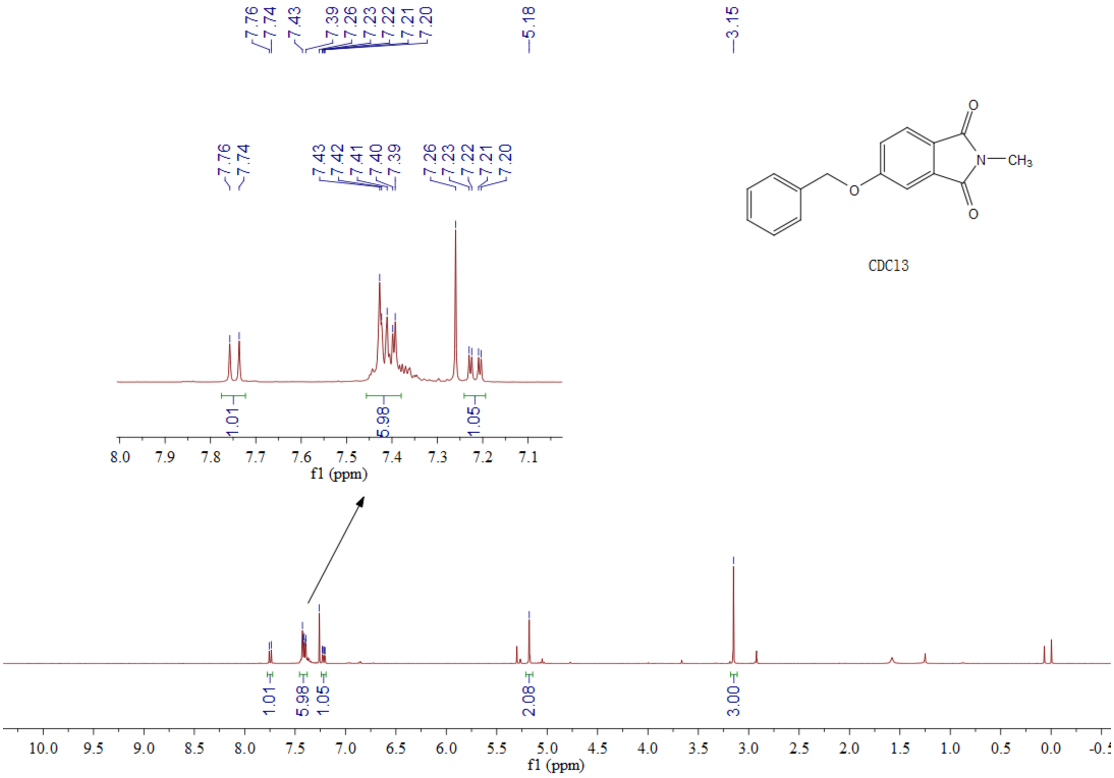
^{1}H-NMR spectrum of **5c**



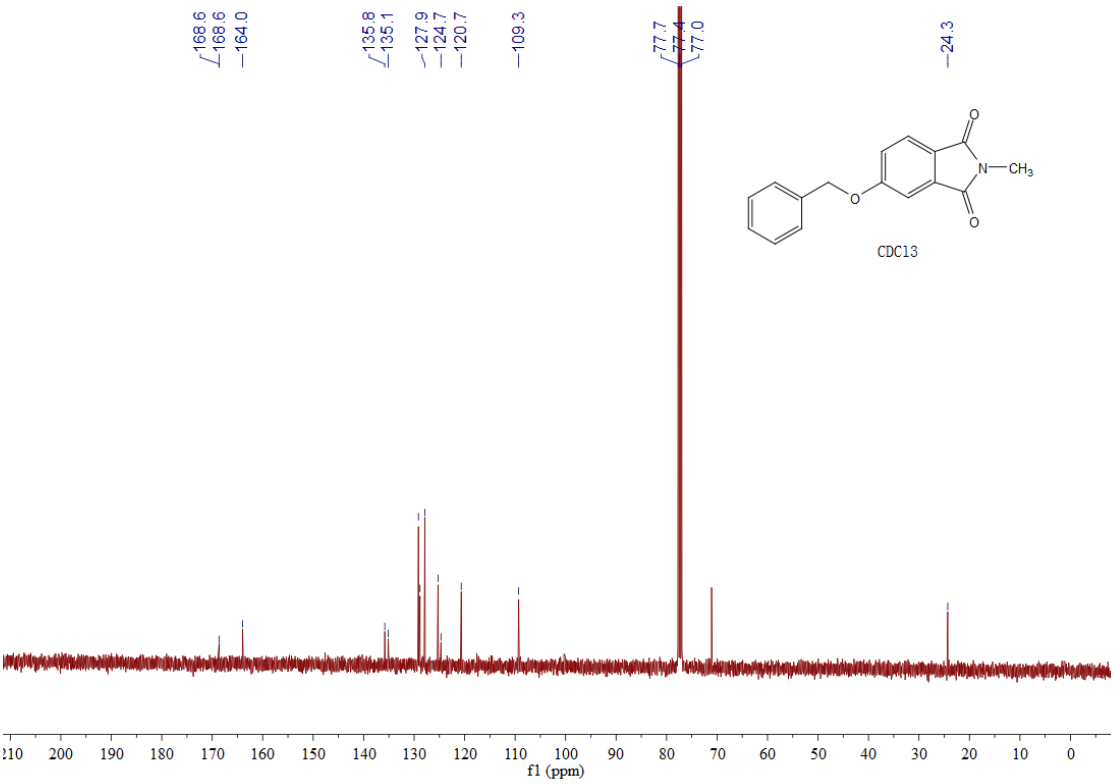
^{13}C-NMR spectrum of **5c**



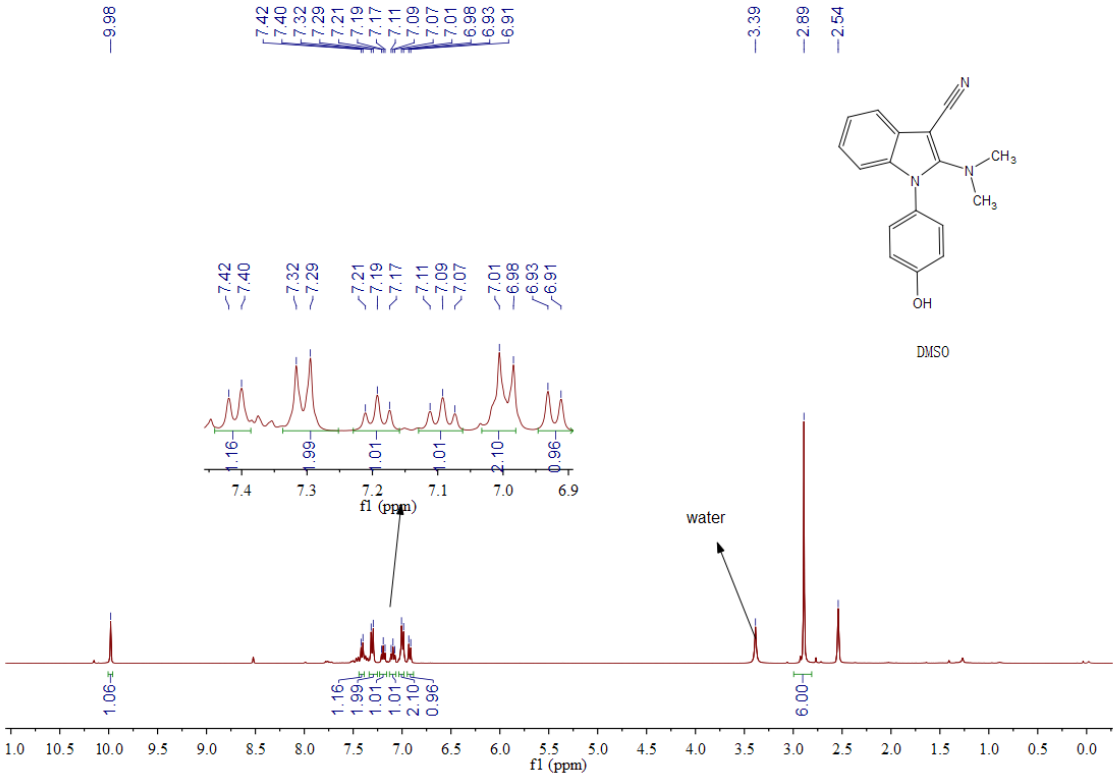
[1]H-NMR spectrum of **5d**



[13]C-NMR spectrum of **5d**



^{1}H-NMR spectrum of **A**



7. Copies of HRMS for **2l**, **2q**, **2t**, **5c** and **5d**

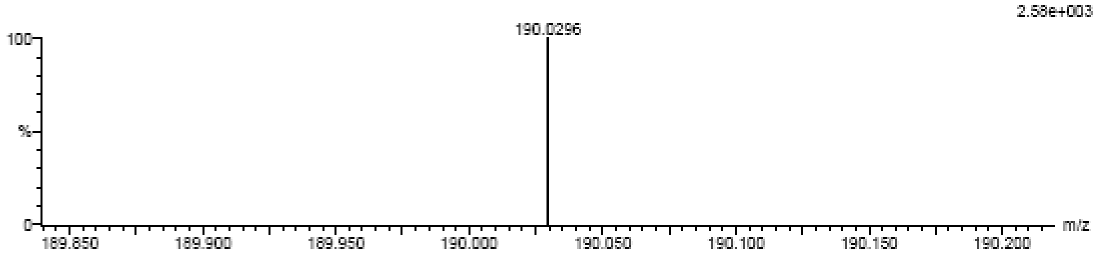
HRMS for **2l**

Elemental Composition Report **Page 1**

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
126 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-100 N: 0-5 O: 0-5 Cl: 1-2

GCT Premier ZJU 23-Apr-2015 zlp2l 524 (2.874)
TOF MS EI+



Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
190.0296	190.0298	-0.2	-1.1	8.0	5547306.0	C10 H7 N2 Cl

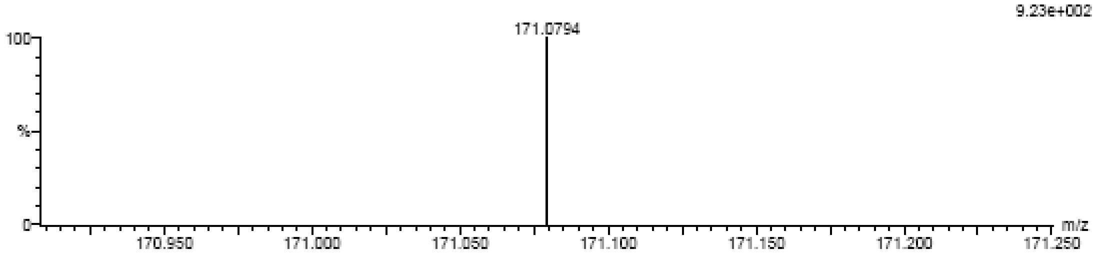
HRMS for **2q**

Elemental Composition Report Page 1

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
87 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-100 N: 0-5 O: 0-5

GCT Premier ZJU 23-Apr-2015 zlp9964 402 (2.427)
TOF MS EI+



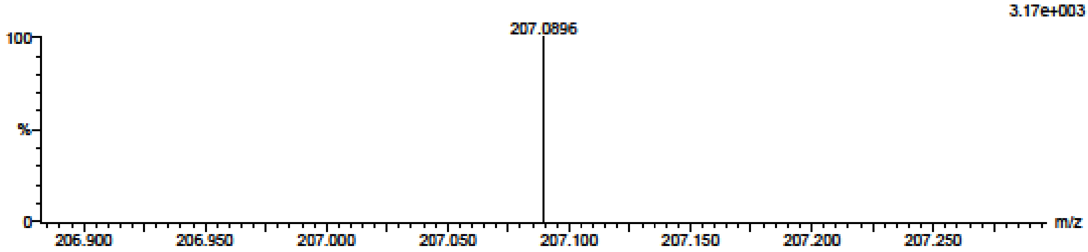
Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
171.0794	171.0796	-0.2	-1.2	8.0	5546448.5	C10 H9 N3

HRMS for **2t**

Elemental Composition Report **Page 1**

Tolerance = 0.5 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
51 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500 H: 0-1000 N: 0-3 O: 0-3
zlp457-2 94 (1.724)
TOF MS EI+



Minimum:				-1.5		
Maximum:		0.5	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
207.0896	207.0895	0.1	0.5	6.0	5547571.5	C11 H13 N O3

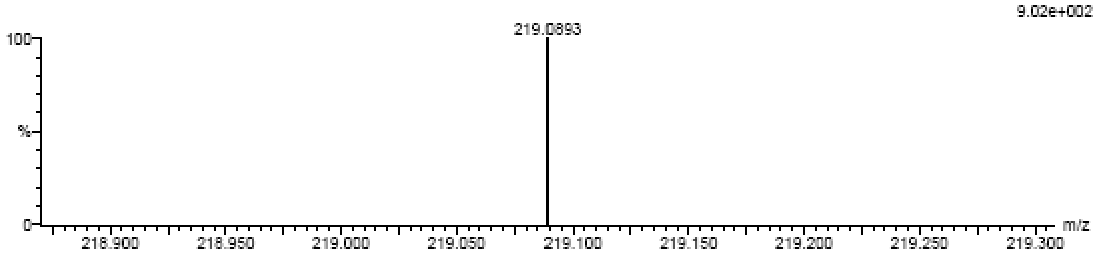
HRMS for **5c**

Elemental Composition Report **Page 1**

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
105 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-100 N: 0-5 O: 0-5

GCT Premier ZJU 23-Apr-2015 zlp9955-2 251 (1.873)
TOF MS EI+



Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
219.0893	219.0895	-0.2	-0.9	7.0	5546445.0	C12 H13 N O3

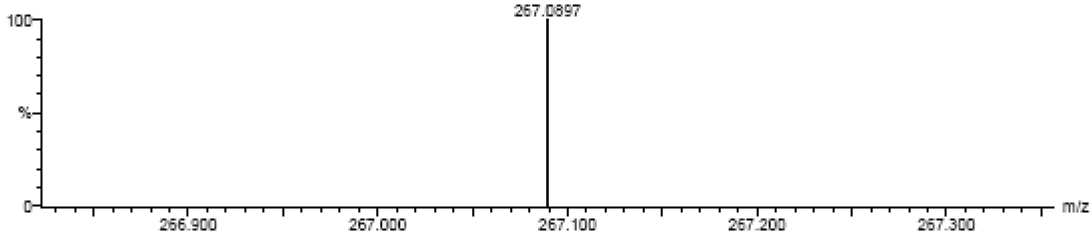
HRMS for **5d**

Elemental Composition Report Page 1

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
128 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-100 N: 0-5 O: 0-5

GCT Premier ZJU 23-Apr-2015 zlp9938-3 597 (3.142) Cm (591:629)
TOF MS EI+



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
Minimum:				-1.5		
Maximum:		1.0	10.0	50.0		
267.0897	267.0895	0.2	0.7	11.0	5547788.0	C16 H13 N O3