Electronic Supplementary Material (ESI) for ChemComm.

Copper-catalyzed aerobic conversion of C=O bond of ketones to C≡N bond using ammonium salt as nitrogen source

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Supporting Information

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1. General information

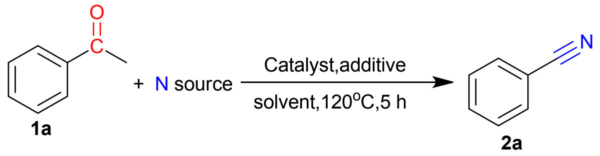
Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification. All products were characterized by GC-MS, ^{1}H NMR and ^{13}C NMR. Mass spectra were measured on a mass instrument (EI). ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 101 MHz in $CDCl_3$ or DMSO-d_6 using TMS as internal standard. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quintet), and m (multiplet), and coupling constants (*J*) are reported in hertz. The yield of benzonitrile and conversion of acetophenone were detected by gas phase chromatography, using a RTX-5 capillary column and a frame ionization detector (FID).

2. Typical procedure for the synthesis of nitriles from ketones

A Schlenk tube was charged with ketones **1** or **3** (1.0 mmol), $Cu(OAc)_2$ (54 mg, 0.3 mmol), TBAI (111 mg, 0.3 mmol) , $(NH_4)_2CO_3$(157 mg, 1.0 mmol), and DMSO (3.0 mL), and the reaction mixture was stirred at 120°C under oxygen atmosphere for 5 h. After cooling to room temperature, the solution was then diluted with ethyl acetate (3×10 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated under vacuum and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to obtain the desired product **2**.

3. Optimization of reaction conditions

Table S1. Screening of Reaction Conditions.[a]

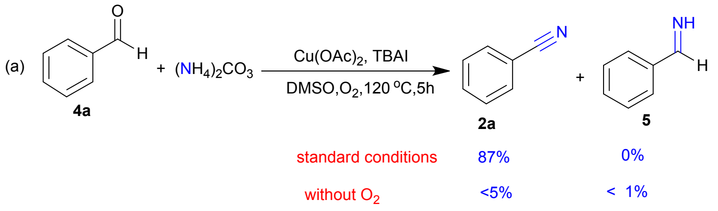


Entry	Catalyst	N source	Additive	Solvent	Conv.(%)[b]	Yield(%)[b]
1	CuI	$(NH_4)_2CO_3$		DMSO	87	47
2	CuBr	$(NH_4)_2CO_3$		DMSO	83	35
3	CuCl	$(NH_4)_2CO_3$		DMSO	84	38
4	$CuBr_2$	$(NH_4)_2CO_3$		DMSO	80	42
5	$CuCl_2$	$(NH_4)_2CO_3$		DMSO	82	39
6	$Cu(acac)_2$	$(NH_4)_2CO_3$		DMSO	68	25
7	CuO	$(NH_4)_2CO_3$		DMSO	86	27
8	Cu_2O	$(NH_4)_2CO_3$		DMSO	89	43
9	$Cu(OAc)_2\cdot H_2O$	$(NH_4)_2CO_3$		DMSO	96	58
10	**$Cu(OAc)_2$**	**$(NH_4)_2CO_3$**		**DMSO**	**>99**	**69**
11	$Cu(TFA)_2$	$(NH_4)_2CO_3$		DMSO	>99	52
12[c]	Other metals	$(NH_4)_2CO_3$		DMSO	<10	0
13	$Cu(OAc)_2$	$(NH_4)_2CO_3$		DMF	>99	60
14	$Cu(OAc)_2$	$(NH_4)_2CO_3$		Toluene	82	42
15	$Cu(OAc)_2$	$(NH_4)_2CO_3$		DCE	65	27
16	$Cu(OAc)_2$	$(NH_4)_2CO_3$		NMP	>99	52
17	$Cu(OAc)_2$	$(NH_4)_2CO_3$		DMA	>99	57

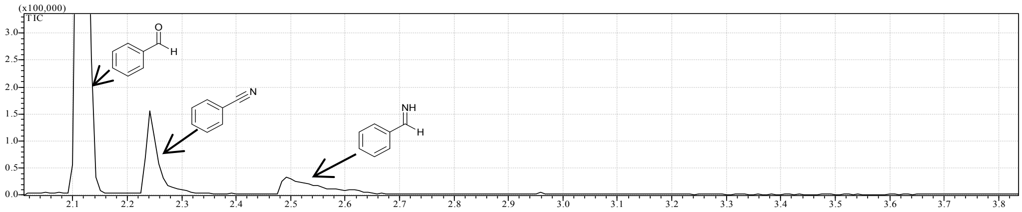
18	$Cu(OAc)_2$	NH_4HCO_3		DMSO	>99	62
19	$Cu(OAc)_2$	urea		DMSO	96	10
20	$Cu(OAc)_2$	NH_4I		DMSO	98	12
21	$Cu(OAc)_2$	$NH_3 \cdot H_2O$		DMSO	>99	52
22	$Cu(OAc)_2$	$HCOONH_4$		DMSO	98	36
23	$Cu(OAc)_2$	$(NH_4)_2CO_3$	pyridine	DMSO	>99	70
24	$Cu(OAc)_2$	$(NH_4)_2CO_3$	TEMPO	DMSO	>99	71
25	$Cu(OAc)_2$	$(NH_4)_2CO_3$	HAcO	DMSO	>99	36
26	**$Cu(OAc)_2$**	**$(NH_4)_2CO_3$**	**TBAI**	**DMSO**	**>99**	**80**
27	$Cu(OAc)_2$	$(NH_4)_2CO_3$	TBAB	DMSO	>99	78
28	$Cu(OAc)_2$	$(NH_4)_2CO_3$	TBAF	DMSO	>99	75
29	$Cu(OAc)_2$	$(NH_4)_2CO_3$	TBAHS	DMSO	>99	36
30[d]	$Cu(OAc)_2$	$(NH_4)_2CO_3$	TBAI	DMSO	>99	68
31[e]	$Cu(OAc)_2$	$(NH_4)_2CO_3$	TBAI	DMSO	>99	75
32[f]	$Cu(OAc)_2$	$(NH_4)_2CO_3$	TBAI	DMSO	>99	77
33[g]	$Cu(OAc)_2$	$(NH_4)_2CO_3$	TBAI	DMSO	>99	71
34[h]	$Cu(OAc)_2$	$(NH_4)_2CO_3$	TBAI	DMSO	50	40
35[i]	$Cu(OAc)_2$	$(NH_4)_2CO_3$	TBAI	DMSO	0	0
36	$Cu(OAc)_2$	—		DMSO	80	0
37	—	$(NH_4)_2CO_3$		DMSO	0	0

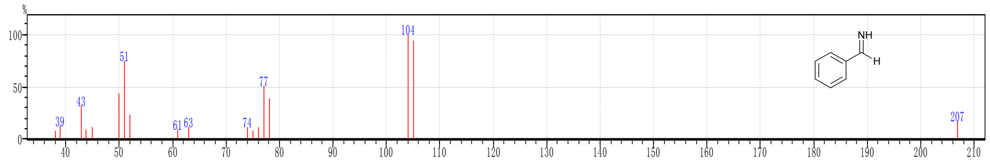
[a]Unless otherwise noted, the reaction conditions: **1a** (1.0 mmol), N source (1.0 equiv), catalyst (0.3mmol, 30mol%), additive (0.3mmol, 30mol%), solvent (3.0 mL), 120°C for 5 h. [b]Determined by GC analysis using bromobenzene as an internal standard. [c]Other metals: $FeCl_2$, $FeCl_3$, $Ni(OAc)_2$, $MnCl_2 \cdot 6H_2O$, and $AgNO_3$, respectively. [d]$(NH_4)_2CO_3$ (0.6 equiv). [e]$(NH_4)_2CO_3$ (2.0 equiv). [f]110 °C, [g]130 °C. [h]Under air atmosphere. [i]Under nitrogen atmosphere.

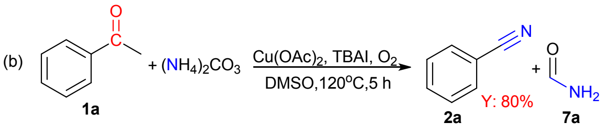
4. The detection of benzaldimine and cleavage fragment by GC-MS

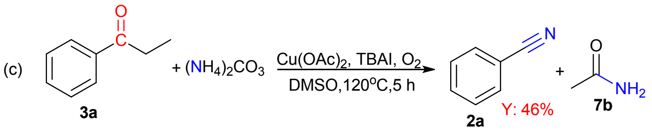


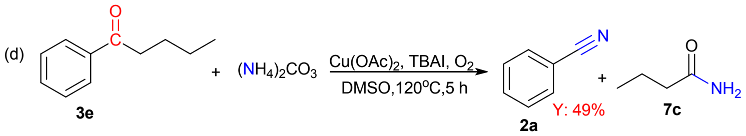
In order to verify if imines can be formed from aldehydes in the presence of ammonium salts, benzaldehyde was chosen to reacte with $(NH_4)_2CO_3$ under N_2 atmosphere. Not only trace (<5%) of benzonitrile was obtained, but also trace amount (<1%) of the corresponding benzaldimine (**5**) could be determined by GC-MS.



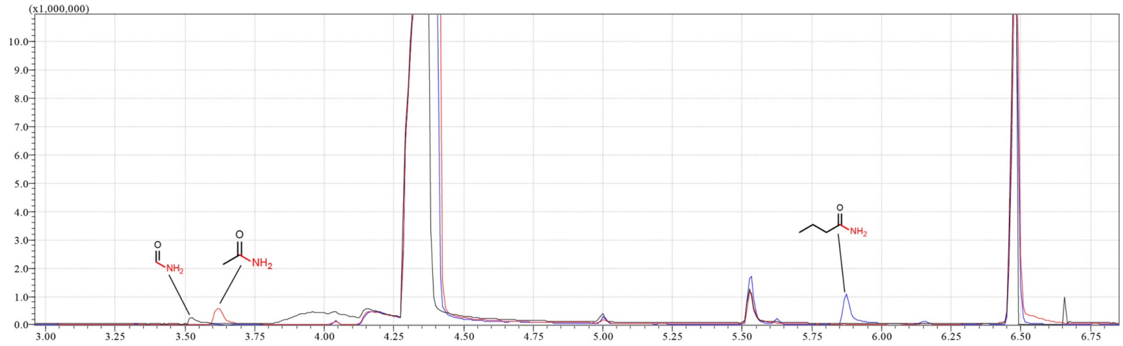


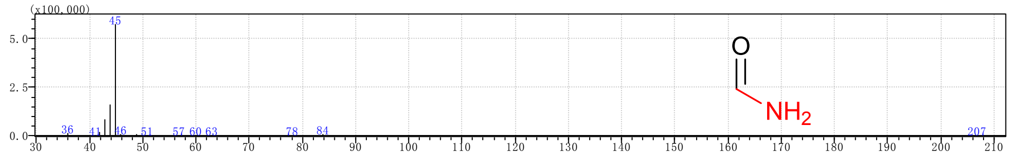


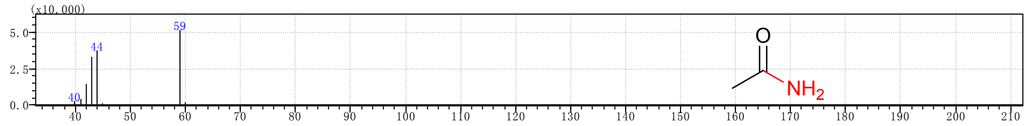


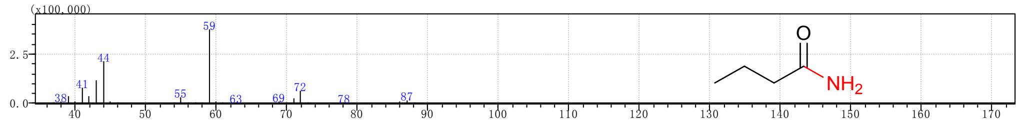


In order to identify the fragment of the ketones, substrate acetophenone (**1a**), propiophenone (**3a**) and valerophenone (**3e**) were tested under the standard conditions. As expected, apart from the generation of benzonitrile (**2a**), trace amount of formamide (**7a**), acetamide (**7b**) and *n*-butyramide (**7c**) could be detected by GC-MS, respectively.

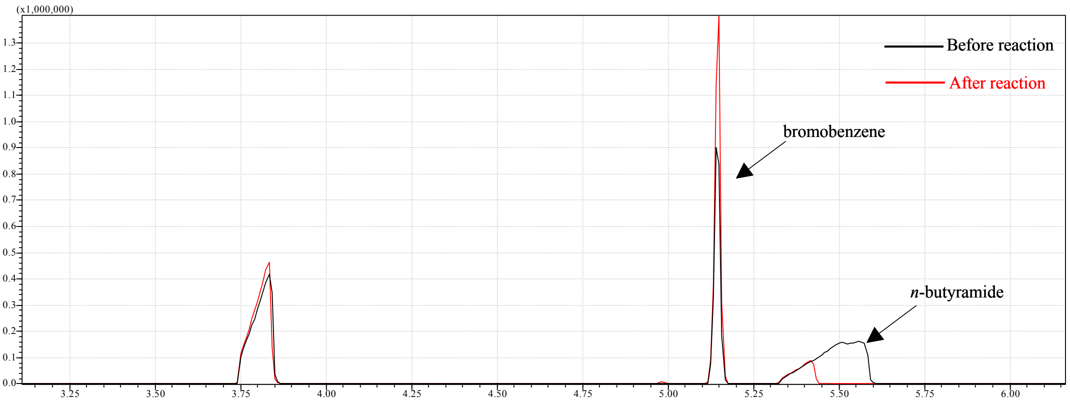






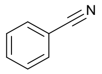


In order to explain why only trace amount of amide was detected for **1a**, **3a** and **3e**, *n*-butyramide was used as the substrate under the standard conditions to test the stability of the aliphatic amides under the copper/O_2 catalyst system. The amount of the *n*-butyramide was quantified by GC using bromobenzene as the internal standard before and after the reaction (the spectrum of GC were shown as below). Before reaction, the *n*-butyramide was quantified as 87 mg (the ratio of the peak area of *n*-butyramide to bromobenzene was 236136/284648). After reaction, the *n*-butyramide was quantified as 32 mg (the ratio of the peak area of *n*-butyramide to bromobenzene was 128214/425740).Which revealed that the amount of *n*-butyramide was declined dramatically after reaction. These results implied the aliphatic amides may be unstable under the copper/O_2 catalyst system, so only trace amount of formamide, acetamide and *n*-butyramide could be detected by GC-MS, but 40% yield of benzamide could be isolated from 1,2-diphenylethanone (**3i**).



5. Characterization data of products

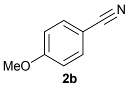
(1) **Benzonitrile (2a).**



2a

Following general procedure, **2a** was obtained from **1a, 3a, 3e, 3i, 4a, 6, 7 and 8** in 80% (82 mg), 46% (47 mg), 49% (50 mg), 62% (64 mg), 87% (90 mg), 92%(95 mg), 61%(63 mg) and 86% (89 mg) yield as colorless oil, respectively (the yield was detected by GC using bromobenzene as internal standard). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.67–7.58 (m, 3H), 7.50–7.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 132.8, 132.1, 129.2, 118.9, 112.4; LRMS (EI 70 ev): *m/z* (%): 103 (M^+, 100); Known compound.[1]

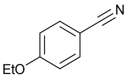
(2) **4-Methoxybenzonitrile (2b).**



2b

Following general procedure, **2b** was obtained from **1b, 3b, 3f** in 90% (119 mg), 48% (64 mg) and 59% (78 mg) yield as colorless solid, respectively. ^{1}H NMR ($CDCl_3$, 400 MHz): δ =7.59 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 162.9, 134.0, 119.3, 114.8, 104.0, 55.6; LRMS (EI 70 ev): *m/z* (%): 133 (M^+, 100); Known compound.[1]

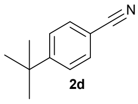
(3) **4-Ethoxybenzonitrile (2c).**



2c

Following general procedure, **2c** was obtained from **1c** in 88% (129 mg) yield as colorless solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.57 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 162.3, 134.0, 119.3, 115.2, 103.6, 64.0, 14.6; LRMS (EI 70 ev): *m/z* (%): 147 (M^+, 100); Known compound.[2]

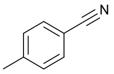
(4) **4-*Tert*-butylbenzonitrile (2d).**



2d

Following general procedure, **2d** was obtained from **1d** in 80% (127 mg) yield as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.59 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 156.7, 132.0, 126.2, 119.2, 109.3, 35.3, 31.0; LRMS (EI 70 ev): *m/z* (%): 159 (M^+, 100); Known compound.[1]

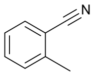
(5) **4-Methylbenzonitrile (2e) .**



2e

Following general procedure, **2e** was obtained from **1e** and **3c** in 86% (101 mg) and 45% (53 mg) yield as colorless oil, respectively. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.54 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 142.7, 131.0, 128.8, 118.2, 108.3, 20.8; LRMS (EI 70 ev): *m/z* (%): 117 (M^+, 100); Known compound.[1]

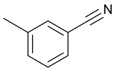
(6) **2-Methylbenzonitrile (2f).**



2f

Following general procedure, **2f** was obtained from **1f** in 68% (79 mg) yield as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.59 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.24 (m, 2H), 2.55 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 141.9, 132.7, 132.5, 130.2, 126.2, 118.2, 112.8, 20.5; LRMS (EI 70 ev): *m/z* (%): 117 (M^+, 100); Known compound.[3]

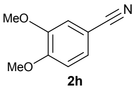
(7) **3-Methylbenzonitrile (2g).**



2g

Following general procedure, **2g** was obtained from **1g** in 75% (84 mg) yield as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.46 (s, 2H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.32 (m, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 139.2, 133.7, 132.5, 129.3, 129.0, 119.1, 112.2, 21.2; LRMS (EI 70 ev): *m/z* (%): 117 (M^+, 100); Known compound.[4]

(8) **3,4-Dimethoxybenzonitrile (2h).**

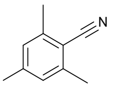


2h

Following general procedure, **2h** was obtained from **1h** in 89% (145 mg) yield as white solid. ^{1}H NMR

($CDCl_3$, 400 MHz): δ = 7.29 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.08 (d, *J* = 1.8 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 152.9, 149.2, 126.5, 119.2, 113.9, 111.2, 103.8, 56.1; LRMS (EI 70 ev): *m/z* (%): 163 (M^+, 100); Known compound.[2]

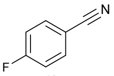
(9) **2,4,6-Trimethylbenzonitrile (2i).**



2i

Following general procedure, **2i** was obtained from **1i** in 71% (103 mg) yield as white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.93 (d, *J* = 0.4 Hz, 2H), 2.48 (s, 6H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 142.8, 142.0, 128.2, 117.8, 110.6, 21.6, 20.6; LRMS (EI 70 ev): *m/z* (%): 145 (M^+, 100); Known compound.[1]

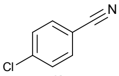
(10) **4-Fluorobenzonitrile (2j).**



2j

Following general procedure, **2j** was obtained from **1j** and **3g** in 65% (79 mg) and 49% (59 mg) yield as colorless solid, respectively. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.69 (dd, *J* = 8.7, 5.2 Hz, 2H), 7.19 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 165.0 (d, *J* = 256.5 Hz), 134.6 (d, *J* = 9.3 Hz), 118.0, 116.8 (d, *J* = 22.7 Hz), 108.5 (d, *J* = 3.7 Hz); LRMS (EI 70 ev): *m/z* (%): 121 (M^+, 100); Known compound.[5]

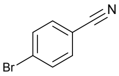
(11) **4-Chlorobenzonitrile (2k).**



2k

Following general procedure, **2k** was obtained from **1k** and **3c** in 85% (117 mg) and 49% (67 mg) yield as colorless solid, respectively. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.61 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 139.5, 133.3, 129.6, 117.8, 110.7; LRMS (EI 70 ev): *m/z* (%): 137 (M^+, 100); Known compound.[1]

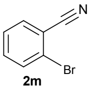
(12) **4-Bromobenzonitrile (2l).**



2l

Following general procedure, **2l** was obtained from **1l** in 77% (141 mg) yield as yellow solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.64 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 133.4, 132.7, 128.0, 118.1, 111.3; LRMS (EI 70 ev): *m/z* (%):183 (M^+, 100), 181 (95); Known compound.[1]

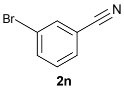
(13) **2-Bromobenzonitrile (2m).**



2m

Following general procedure, **2m** was obtained from **1m** in 70% (127 mg) yield as colorless solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.69 (ddd, *J* = 10.9, 7.9, 1.8 Hz, 2H), 7.51 – 7.39 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 134.3, 133.9, 133.2, 127.6, 125.4, 117.2, 115.9; LRMS (EI 70 ev): *m/z* (%):183 (M^+, 100), 181 (95); Known compound.[1]

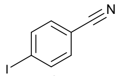
(14) **3-Bromobenzonitrile (2n).**



2n

Following general procedure, **2n** was obtained from **1n** in 72% (130 mg) yield as colorless solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 136.1, 134.7, 130.7, 130.6, 122.9, 117.3, 114.2. LRMS (EI 70 ev): *m/z* (%):183 (M^+, 100), 181 (95); Known compound.[1]

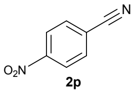
(15) **4-iodobenzonitrile (2o).**



2o

Following general procedure, **2o** was obtained from **1o** in 82% (188 mg) yield as white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 138.5, 133.2, 118.3, 111.8, 100.4; LRMS (EI 70 ev): *m/z* (%): 229 (M^+, 100); Known compound.[1]

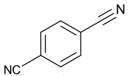
(16) **4-Nitrobenzonitrile (2p).**



2p

Following general procedure, **2p** was obtained from **1p** in 75% (111 mg) yield as colorless solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.37 (d, *J* = 8.3 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 150.1, 133.5, 124.3, 118.4, 116.8; LRMS (EI 70 ev): *m/z* (%): 148 (M^+, 100); Known compound.[1]

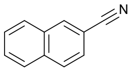
(17) **1,4-Benzenedicarbonitrile (2q).**



2q

Following general procedure, **2q** was obtained from **1q** in 49% (63 mg) yield as white solid; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 8.10 (s, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz,): δ = 133.7, 118.0, 116.2; LRMS (EI 70 ev): *m/z* (%): 128 (M^+, 100); Known compound.[6]

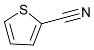
(18) **2-Naphthonitrile (2r).**



2r

Following general procedure, **2r** was obtained from **1r** in 63% (96 mg) yield as yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.23 (s, 1H), 7.90 (t, *J* = 8.4 Hz, 3H), 7.69 – 7.56 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 134.6, 134.2, 132.2, 129.2, 129.0, 128.4, 128.1, 127.7, 126.3, 119.3, 109.4; LRMS (EI 70 ev): *m/z* (%): 153 (M^+, 100); Known compound.[1]

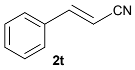
(19) **Thiophene-2-carbonitrile (2s).**



2s

Following general procedure, **2s** was obtained from **1s** in 59% (64 mg) yield as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.67 – 7.60 (m, 2H), 7.15 (dd, *J* = 5.0, 3.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 137.5, 132.7, 127.7, 114.3, 109.9; LRMS (EI 70 ev): *m/z* (%): 10 (M^+, 100); Known compound.[7]

(20) **3-Phenyl-acrylonitrile (2t).**

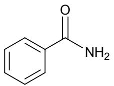


2t

Following general procedure, **2t** was obtained from **3h** in 35% (46 mg) yield as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48 – 7.33 (m, 6H), 5.87 (d, *J* = 16.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ =

150.6, 133.5, 131.3, 129.2, 127.4, 118.2, 96.4 ; LRMS (EI 70 ev): *m/z* (%): 129 (M^+, 100); Known compound.[3]

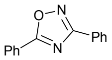
(21) **Benzamide (3d).**



3d

Following general procedure, **3d** was obtained from **3i** and **4b** in 40% (48 mg) and 48% (58 mg) yield as white solid, respectively. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.82 (d, J = 8.6 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 6.21 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz,): δ = 169.7, 133.2, 132.0, 128.7, 127.4; LRMS (EI 70 ev): *m/z* (%): 121 (M^+, 100); Known compound.[8]

(22) **3,5-diphenyl-1,2,4-oxadiazole (10).**



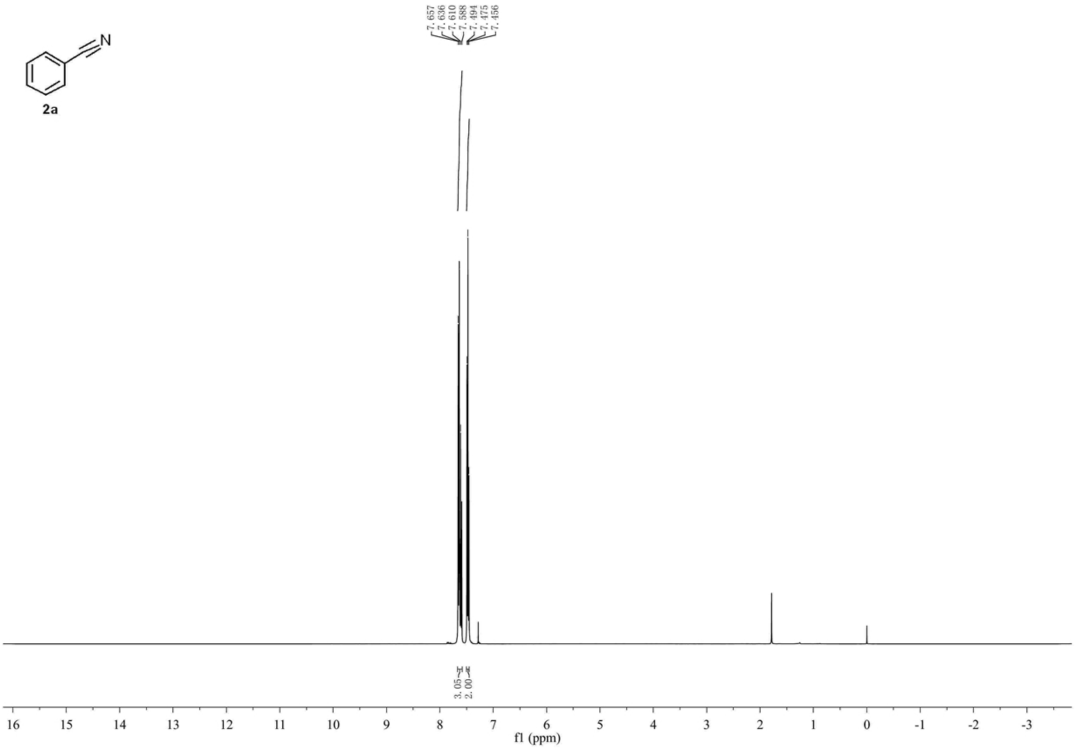
10

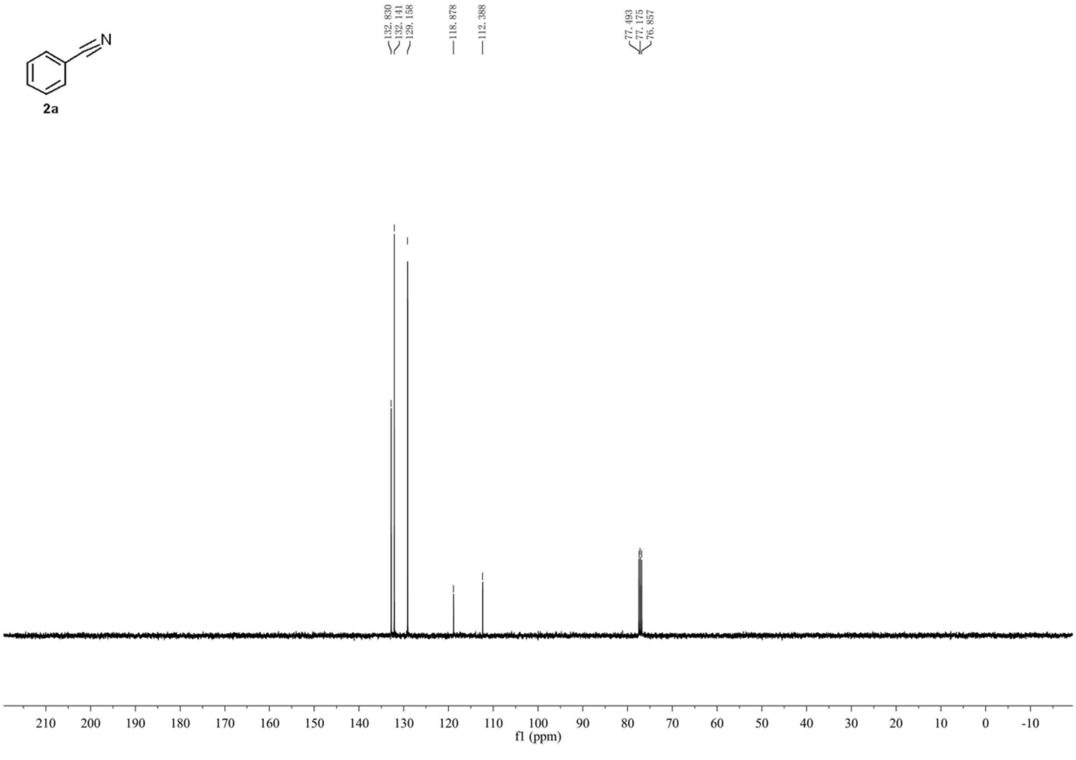
Following general procedure, **10** was obtained from **9** in 42% (47 mg) yield as white solid. ^{1}H NMR (400 MHz, CDCl3): δ = 8.23 (d, J = 7.3 Hz, 2H), 8.18 (dd, J = 6.6, 2.7 Hz, 2H), 7.60 (d, J = 7.2 Hz, 1H), 7.58 – 7.50 (m, 5H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 175.7, 169.0, 132.8, 131.2, 129.1, 128.9, 128.2, 127.6, 127.0, 124.3; LRMS (EI 70 ev): *m/z* (%): 222 (M^+, 100); Known compound.[9]

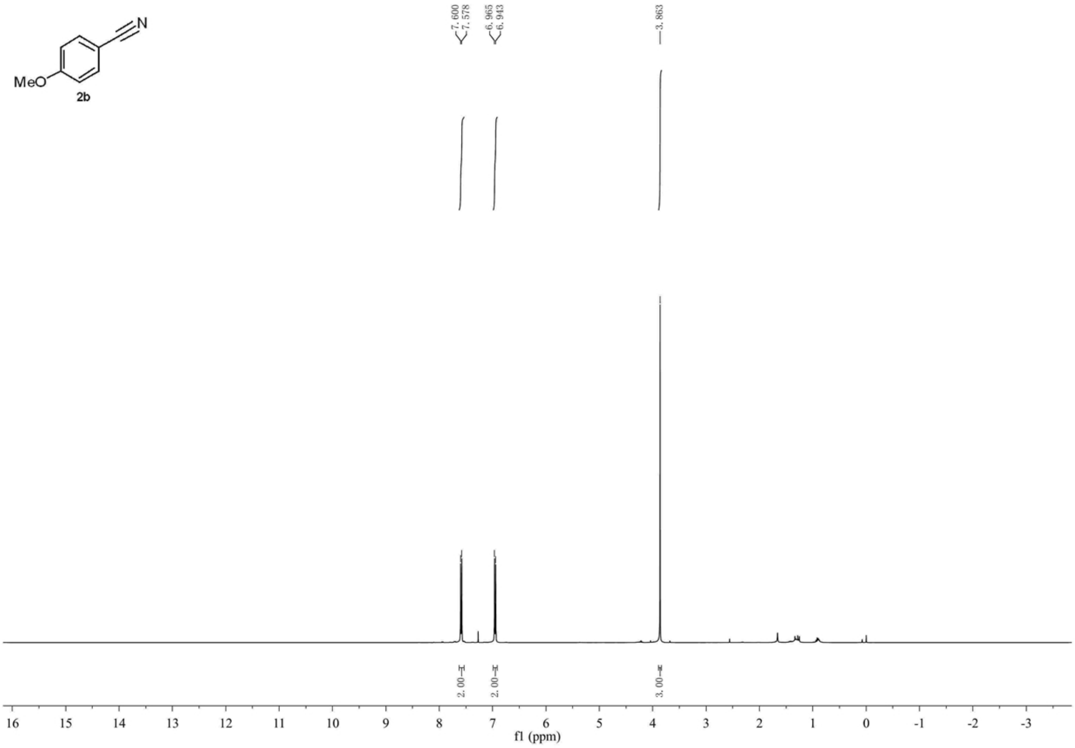
Reference

1. J. H. Xu, Q. Jiang and C. C. Guo, *The Journal of organic chemistry*, 2013, **78**, 11881-11886.
2. W. Zhou, L. Zhang and N. Jiao, *Angew Chem Int Ed Engl*, 2009, **48**, 7094-7097.
3. J. Kim and S. S. Stahl, *ACS catalysis*, 2013, **3**, 1652-1656.
4. L. Zhang, P. Lu and Y. Wang, *Chemical Communications*, 2015, **51**, 2840-2843.
5. L. Gu and C. Jin, *Chemical Communications*, 2015.
6. D. Azarifar and Z. Najminejad, *Journal of the Iranian Chemical Society*, 2014, **12**, 107-111.
7. T. Shen, T. Wang, C. Qin and N. Jiao, *Angew Chem Int Ed Engl*, 2013, **52**, 6677-6680.
8. C. Tang and N. Jiao, *Angew Chem Int Ed Engl*, 2014, **53**, 6528-6532.
9. A. Yoshimura, K. R. Middleton, A. D. Todora, B. J. Kastern, S. R. Koski, A. V. Maskaev and V. V. Zhdankin, *Organic letters*, 2013, **15**, 4010-4013.

6. NMR Spectra of Products



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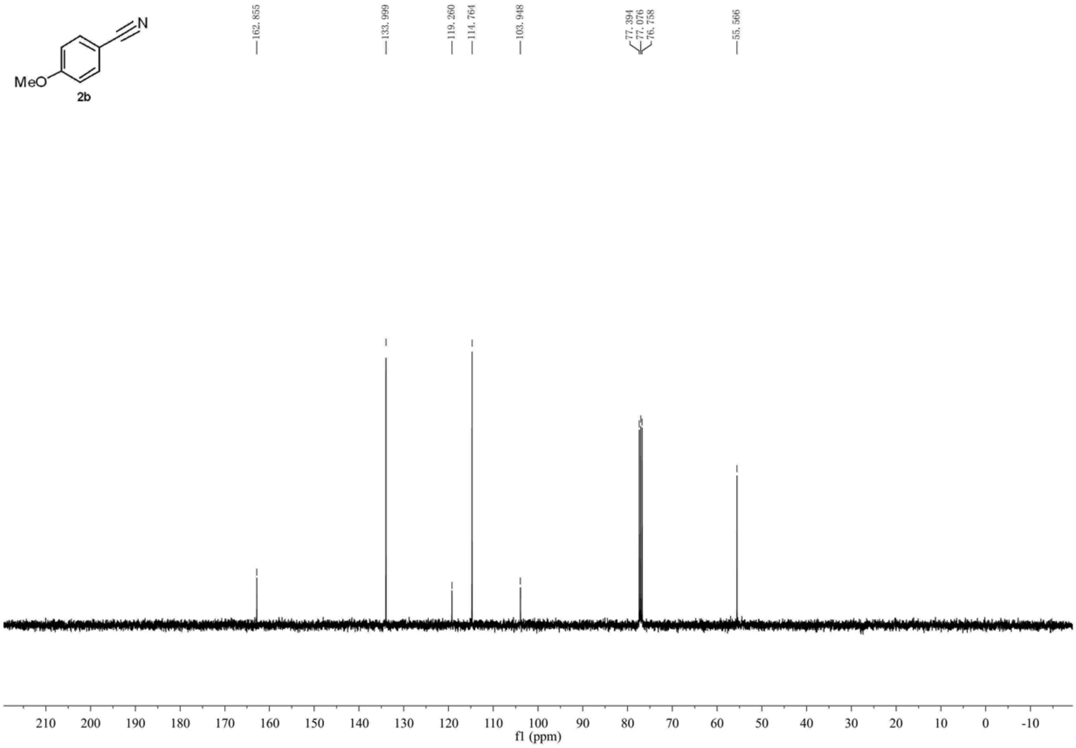
7.600
7.578
6.965
6.943
3.863
2.00
2.00
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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N
2b
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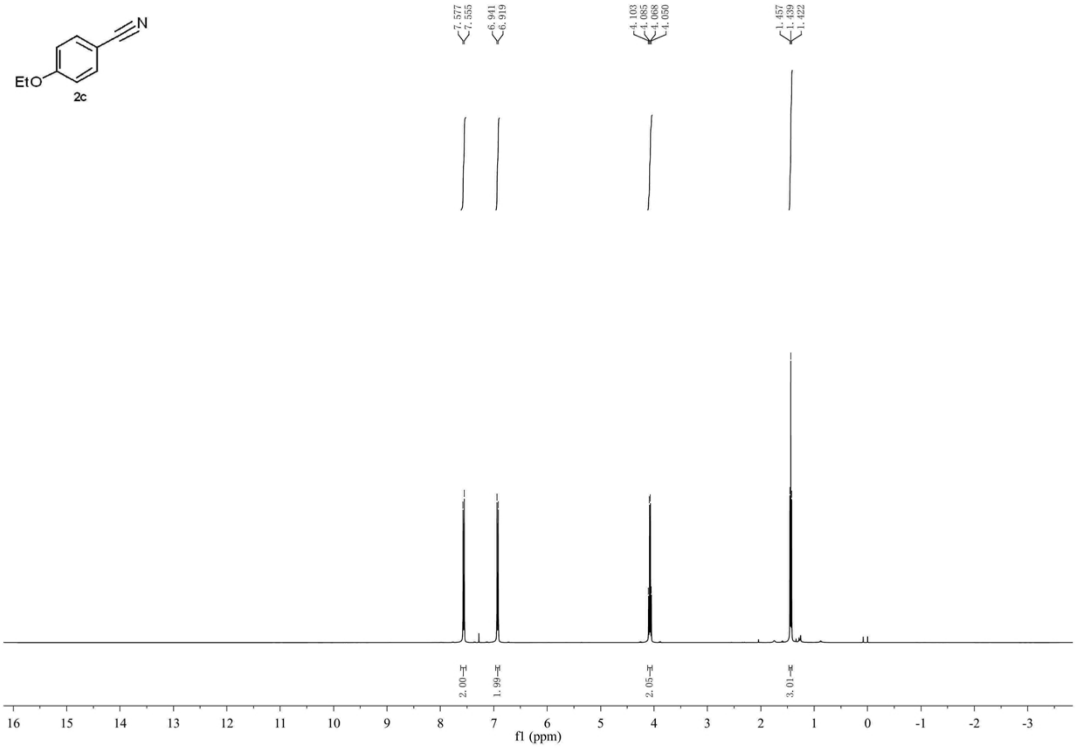
133.999
119.260
114.764
103.948
77.394
77.076
76.758
55.566
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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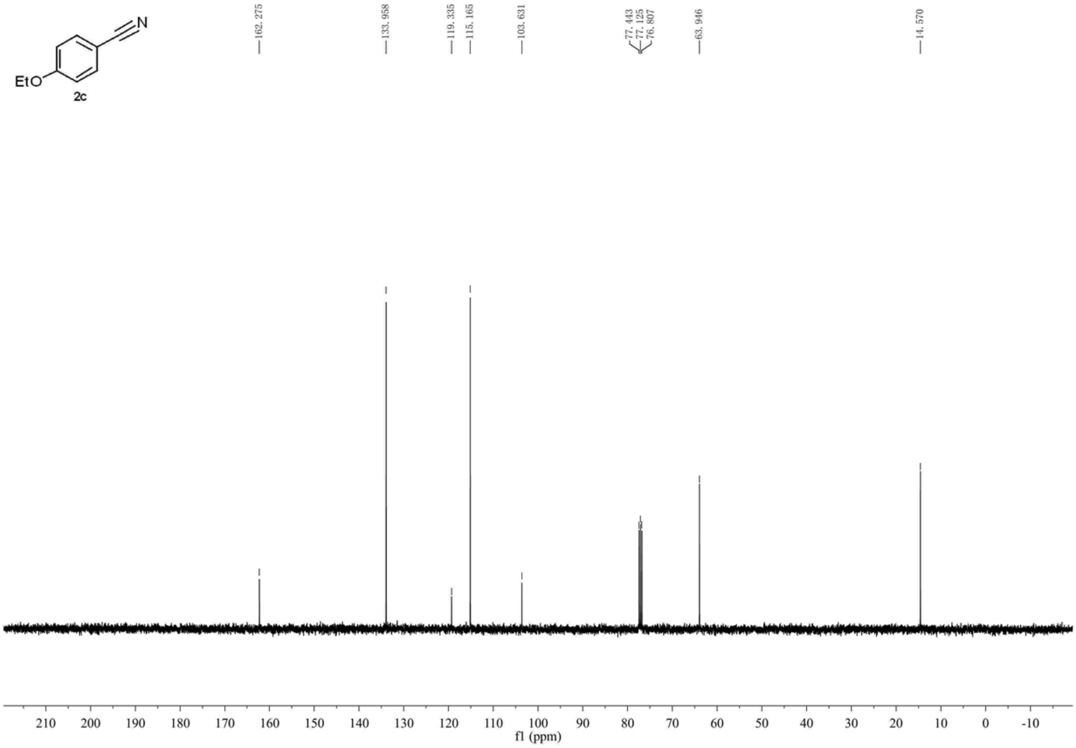
7.555
6.941
6.919
4.103
4.085
4.068
4.050
1.457
1.439
1.422
2.00
1.99
2.05
3.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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133.958
119.335
115.165
103.631
77.443
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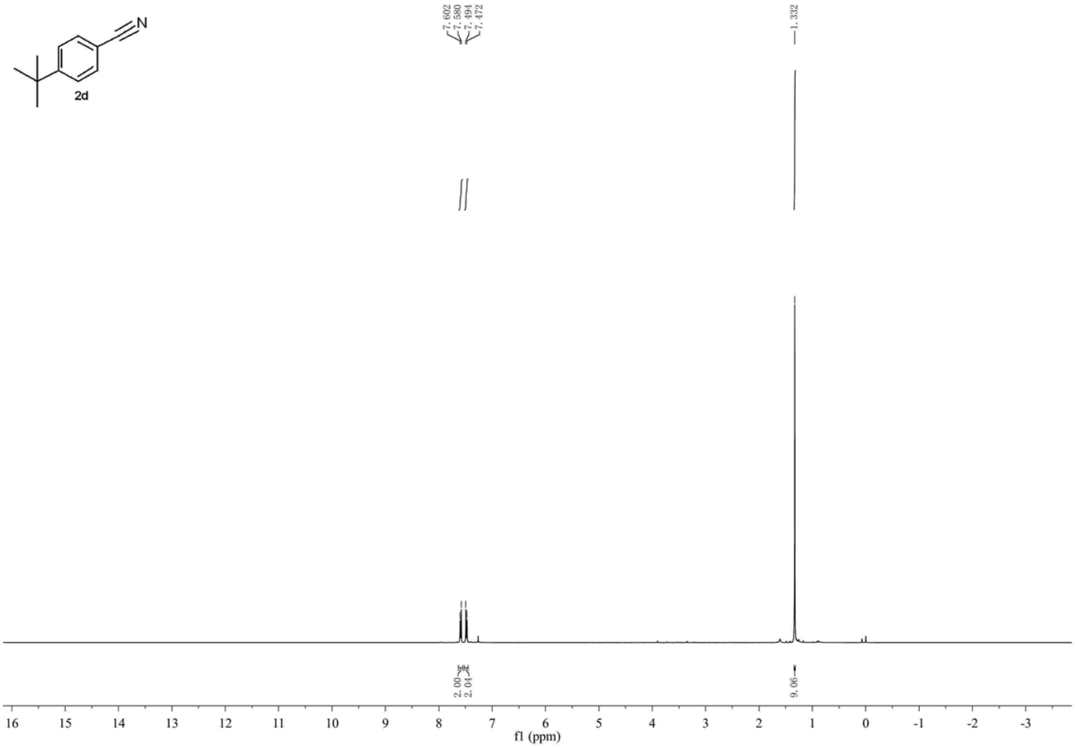
76.807
63.946
14.570
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.580
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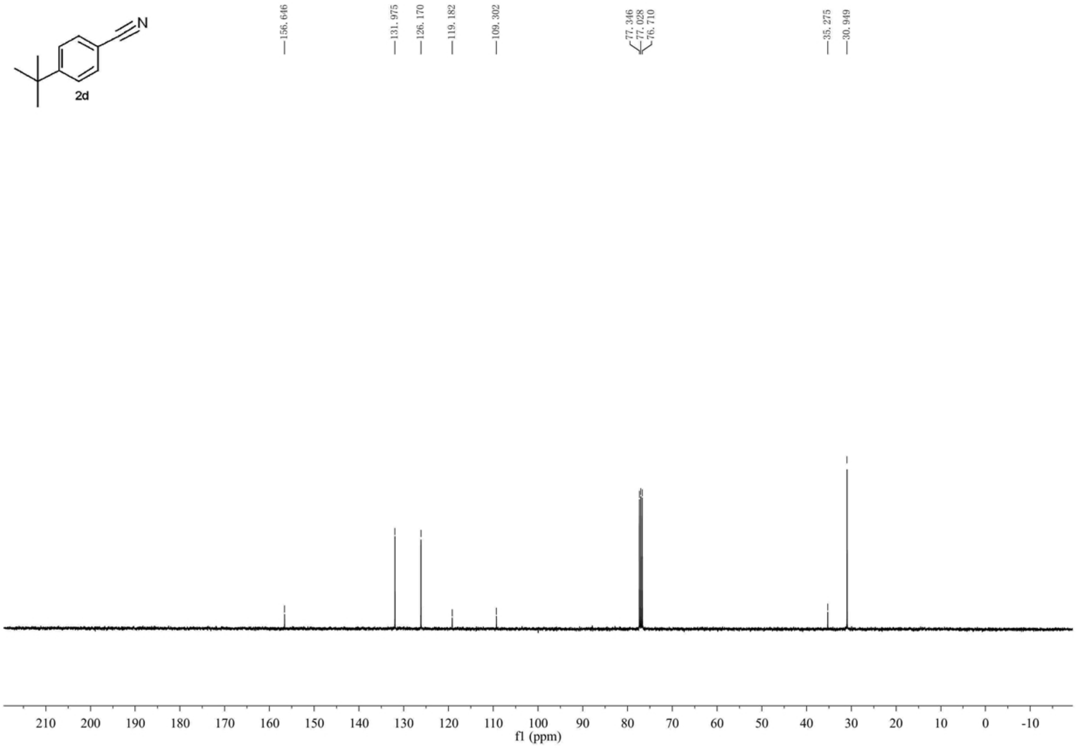
7.472
1.332
2.00
2.01
9.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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2d
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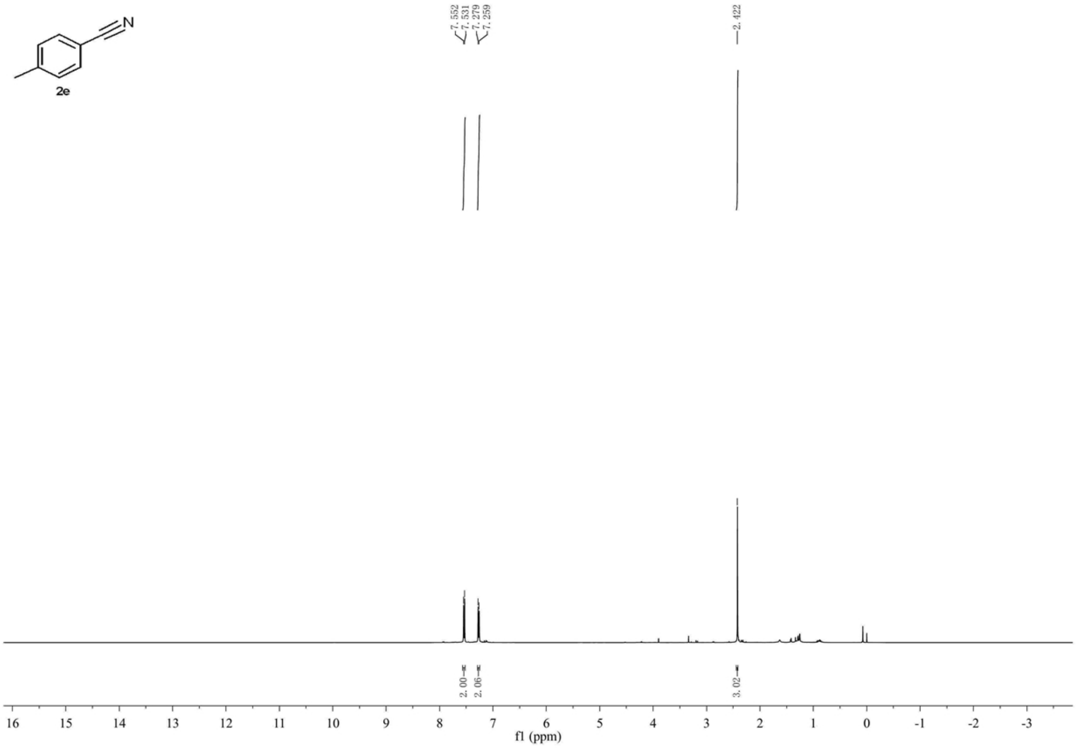
131.975
126.170
119.182
109.302
77.346
77.028
76.710
35.275
30.949
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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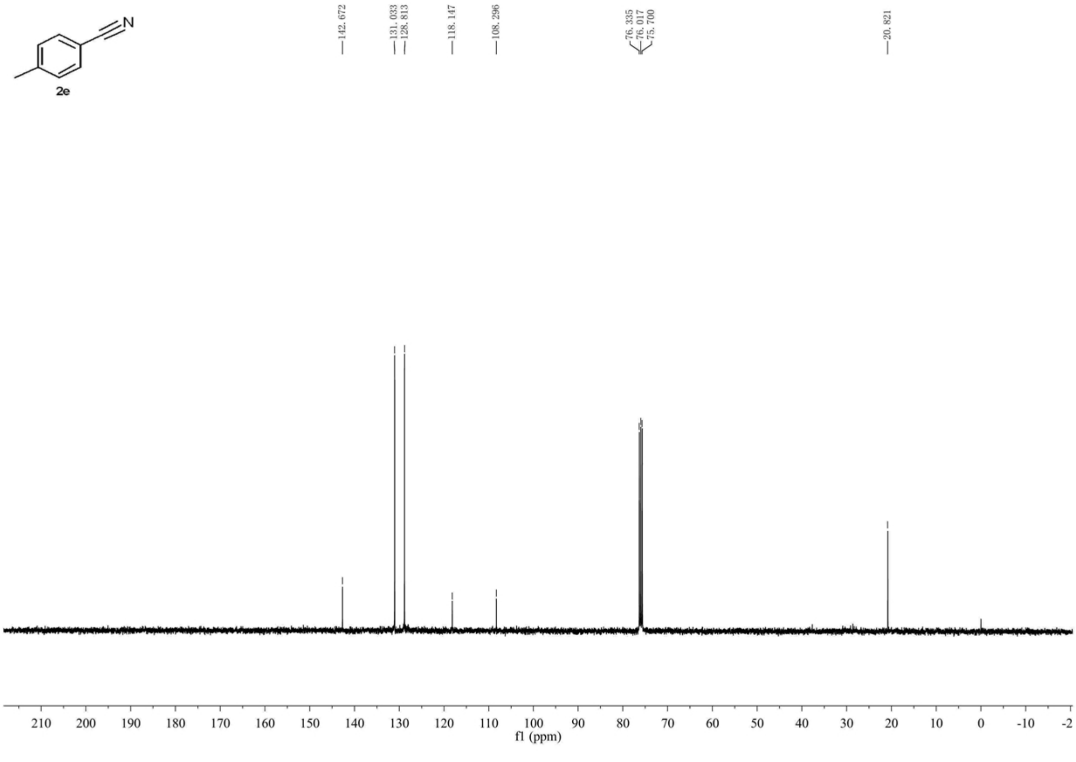
7.531
7.279
7.259
2.422
2.00
2.06
3.02
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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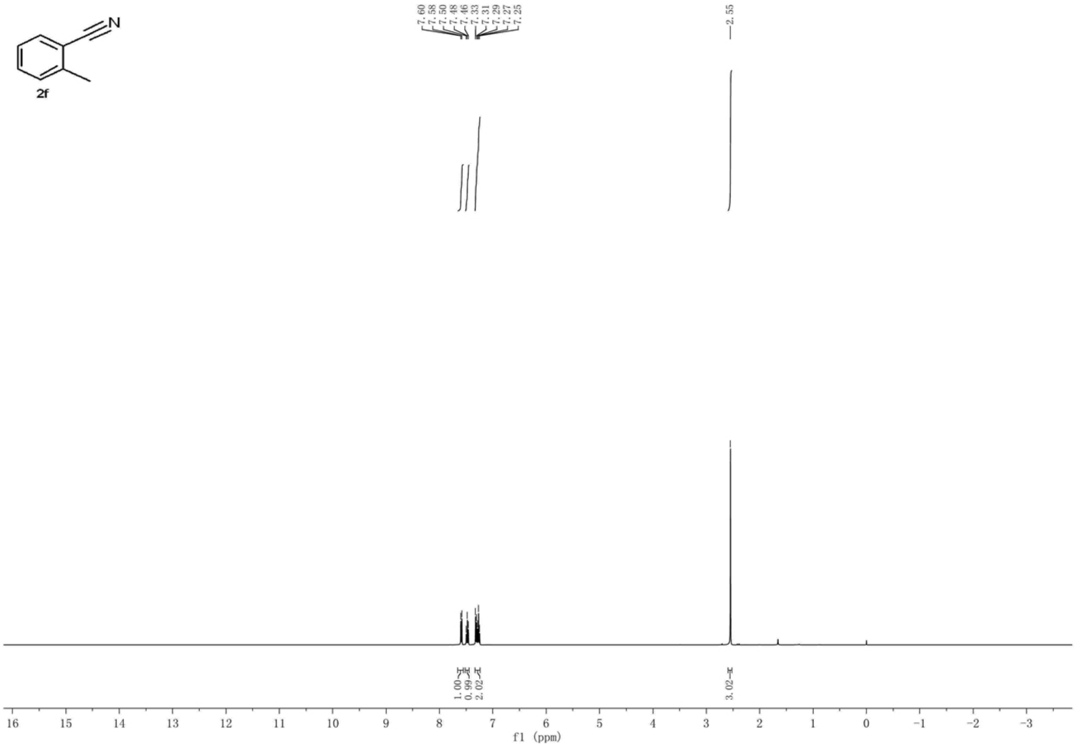
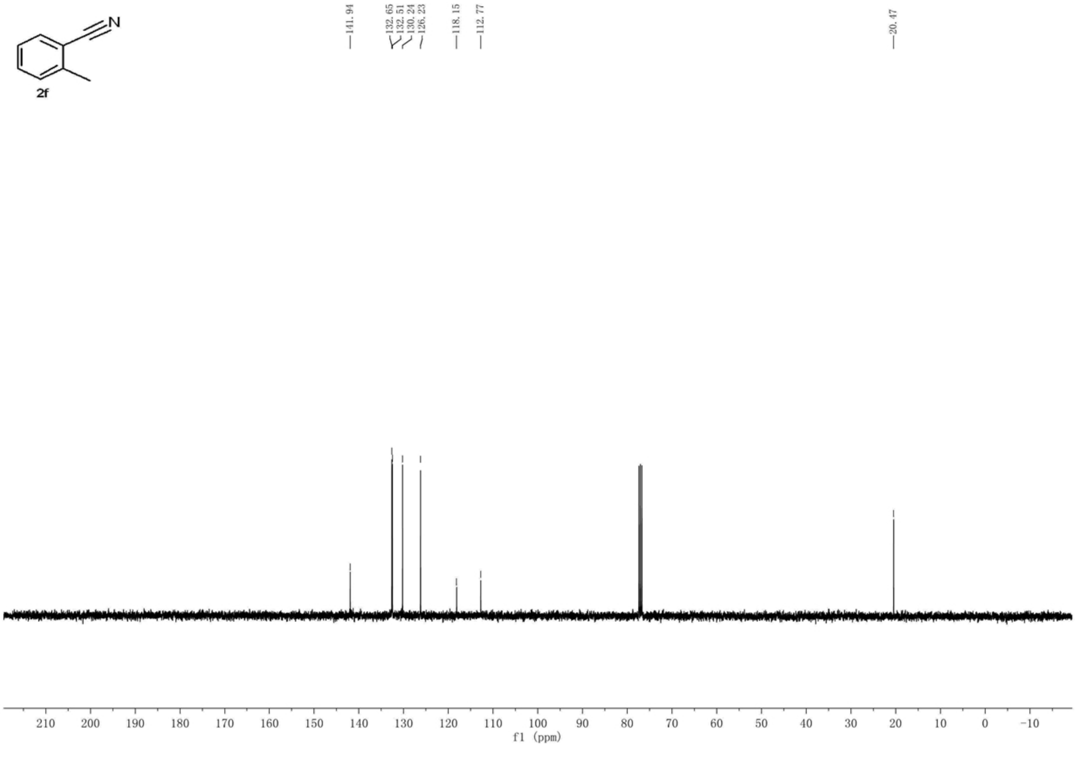
76.335
76.017
75.700
20.821
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


N
2f
7.60
7.58
7.50
7.48
7.46
7.33
7.31
7.29
7.27
7.25
2.55
1.00
0.99
2.02
3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


N
2f
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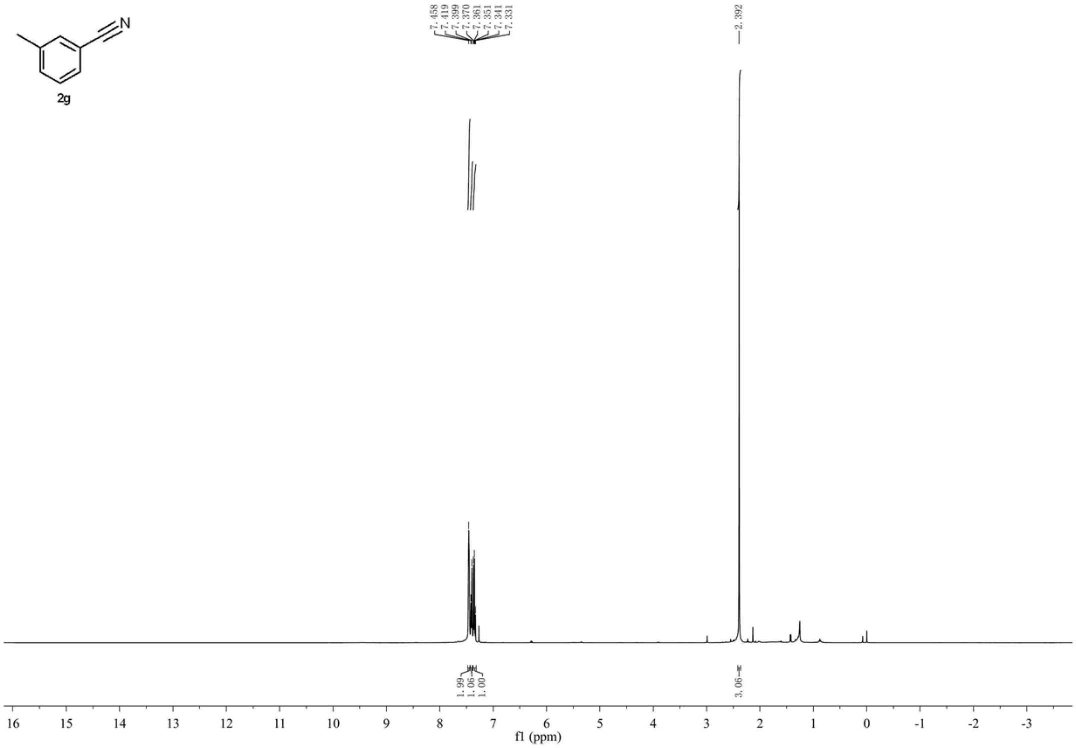
132.65
132.51
130.24
126.23
118.15
112.77
20.47
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


2g
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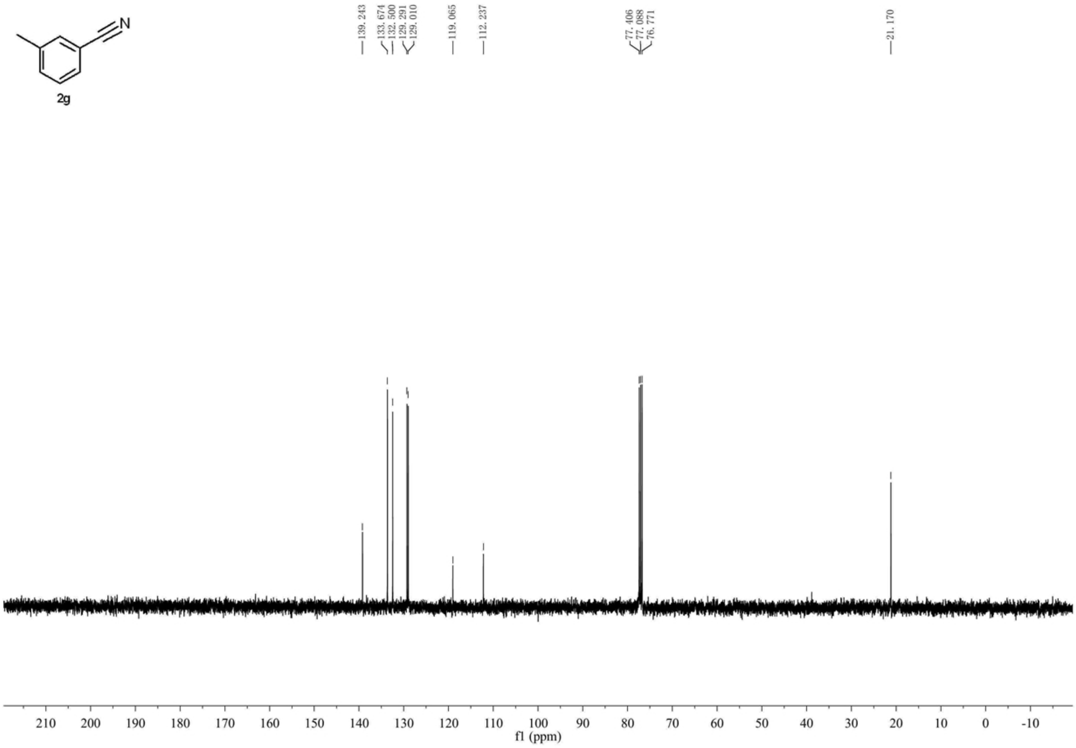
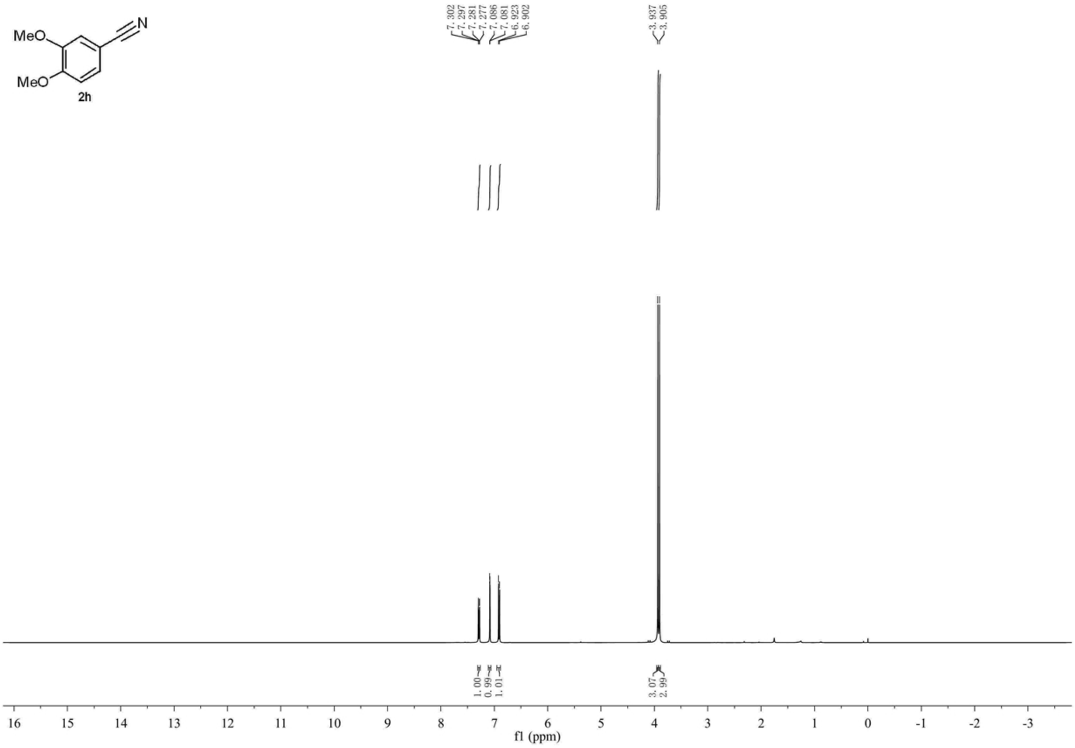
7.419
7.399
7.370
7.361
7.351
7.341
7.331
2.392
1.99
1.06
1.00
3.06
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


2g
139.243
133.674
132.500
129.291
129.010
119.065
112.237
77.406
77.088
76.771
21.170
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
MeO
N
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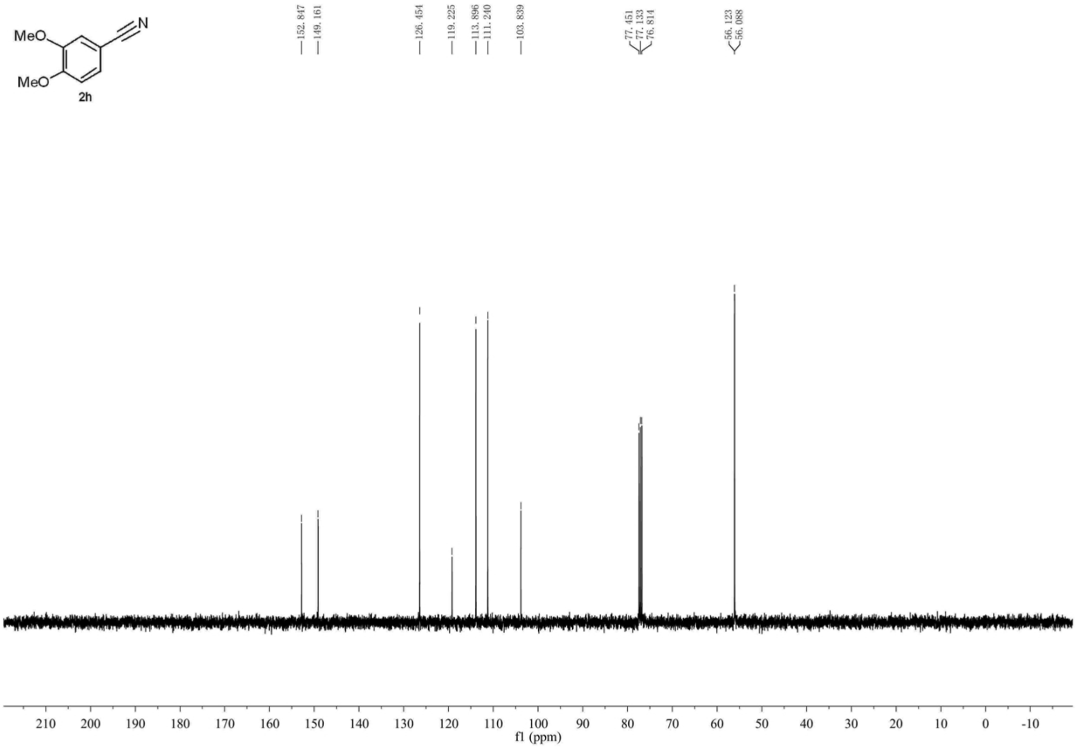
7.281
7.277
7.086
7.081
6.923
6.902
3.937
3.905
1.00
0.99
1.01
3.07
2.99
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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119.225
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77.451
77.133
76.814
56.123
56.088
210
200
190
180
170
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140
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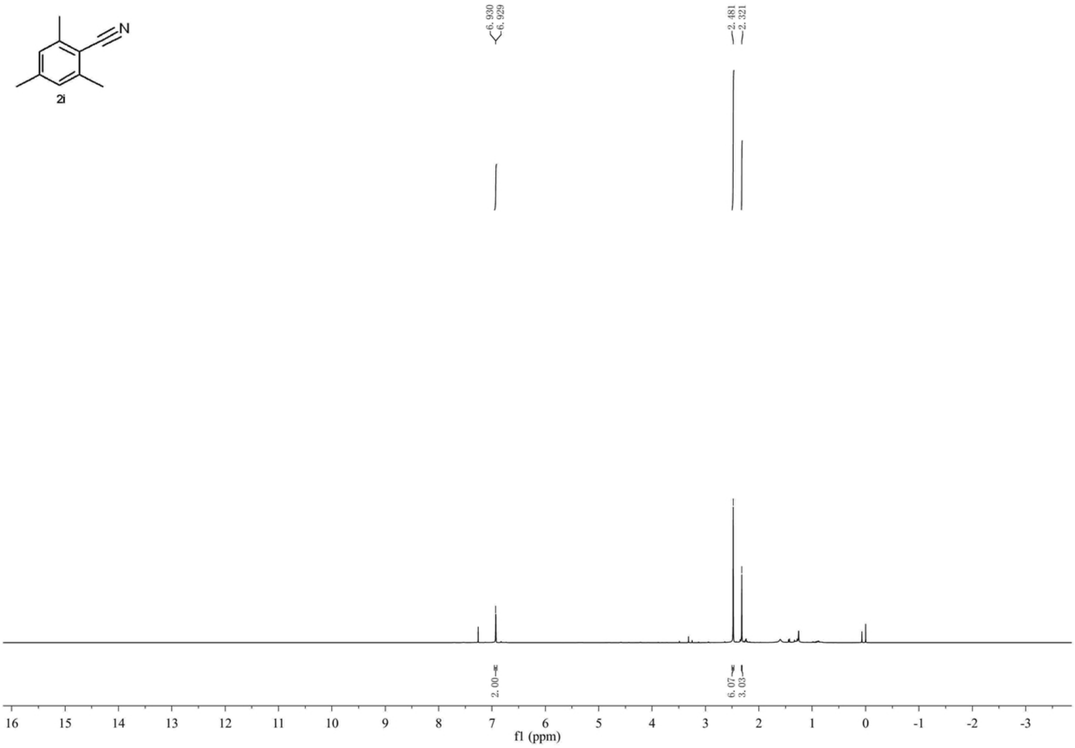
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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2i
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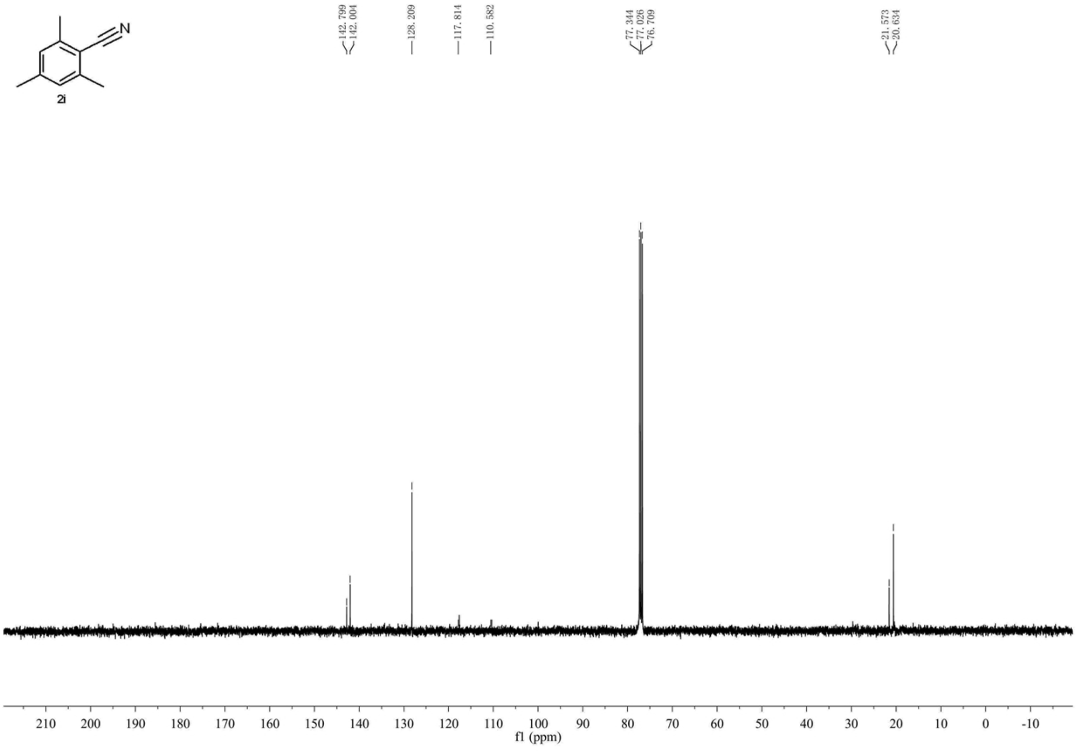
6.07
3.03
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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200
190
180
170
160
150
140
130
120
110
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80
70
60
50
40
30
20
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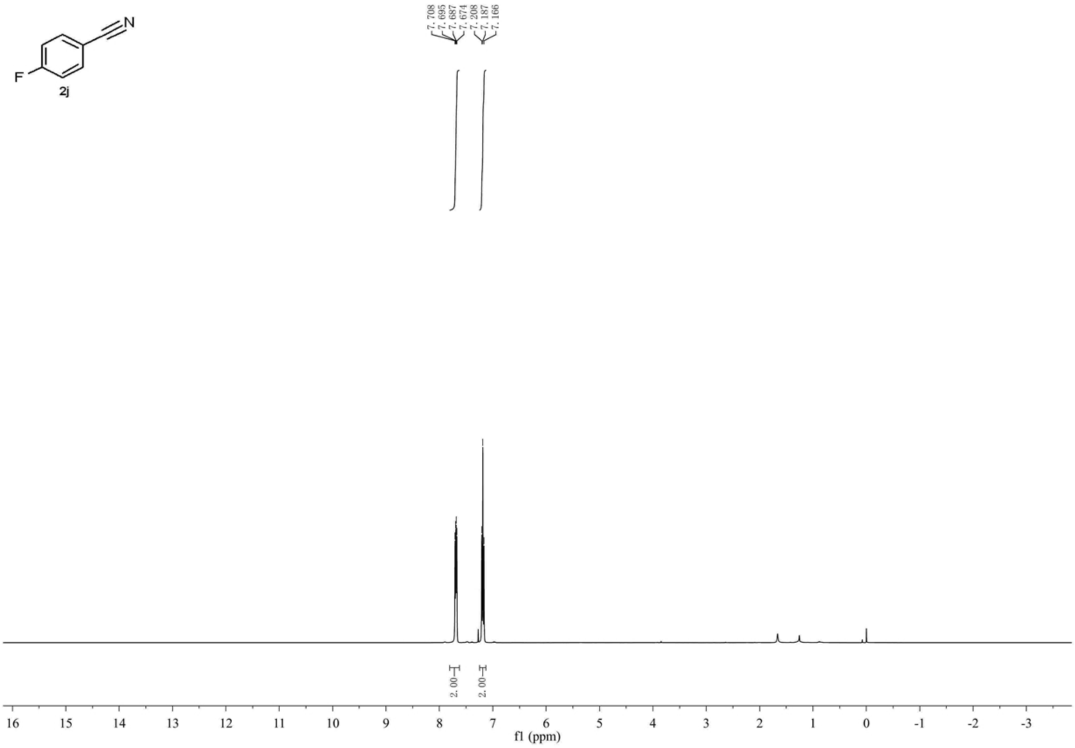
0
-10
f1 (ppm)


F
N
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7.187
7.166
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16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
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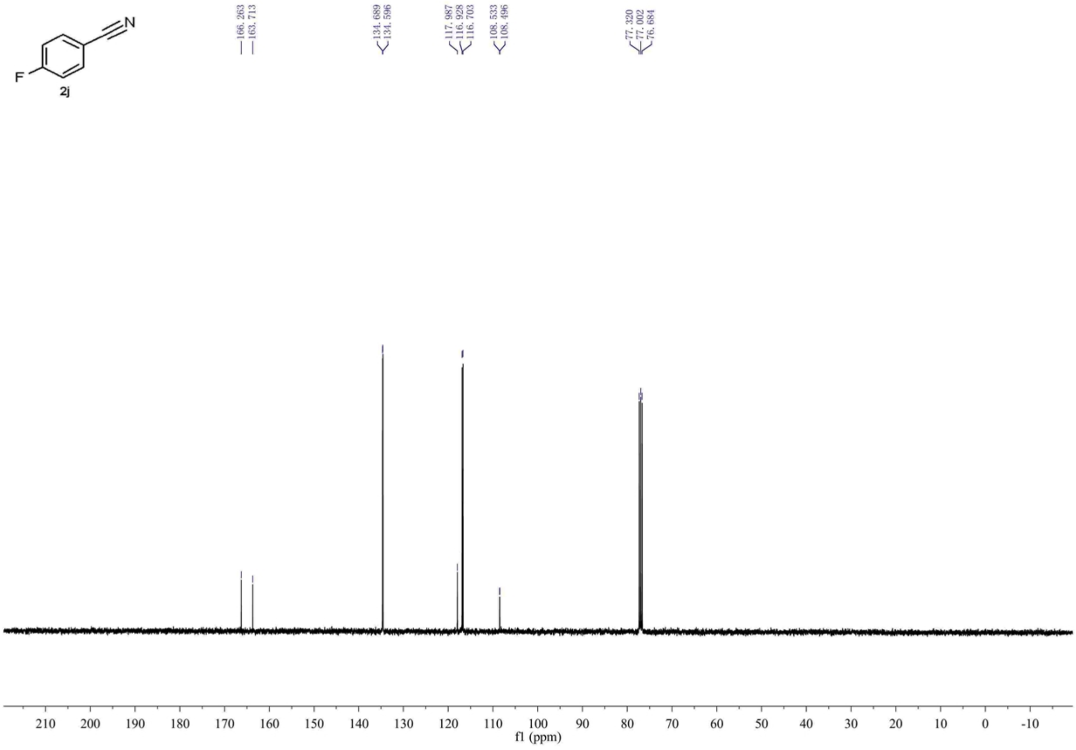
-3
f1 (ppm)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108.533
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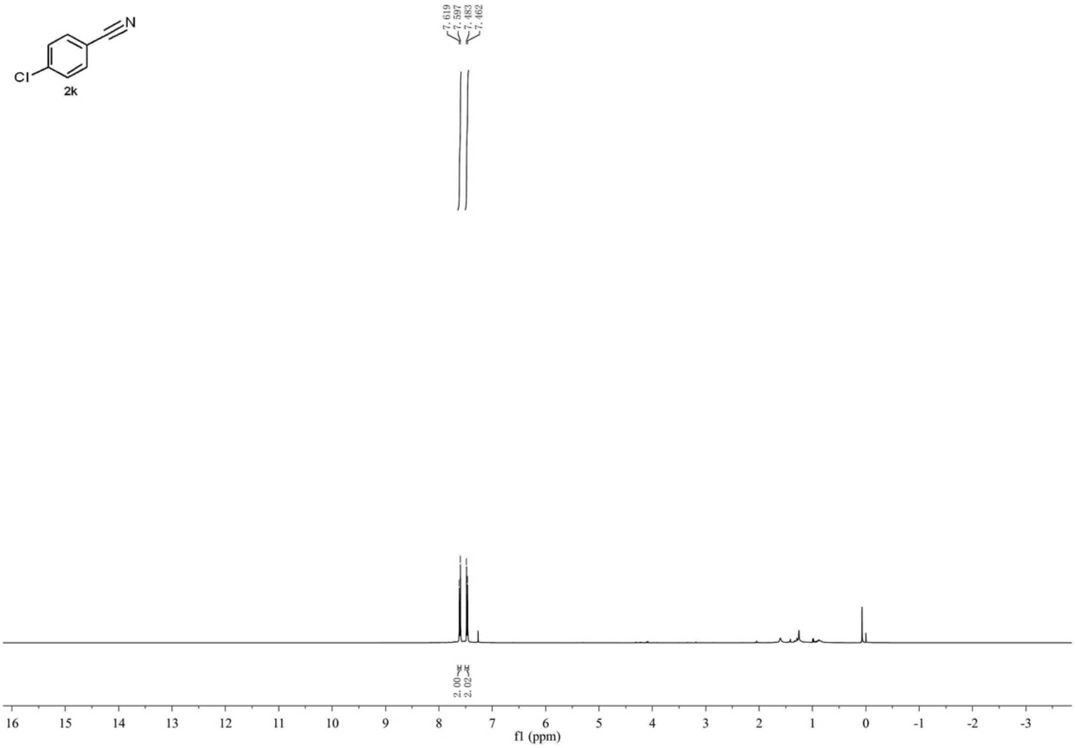
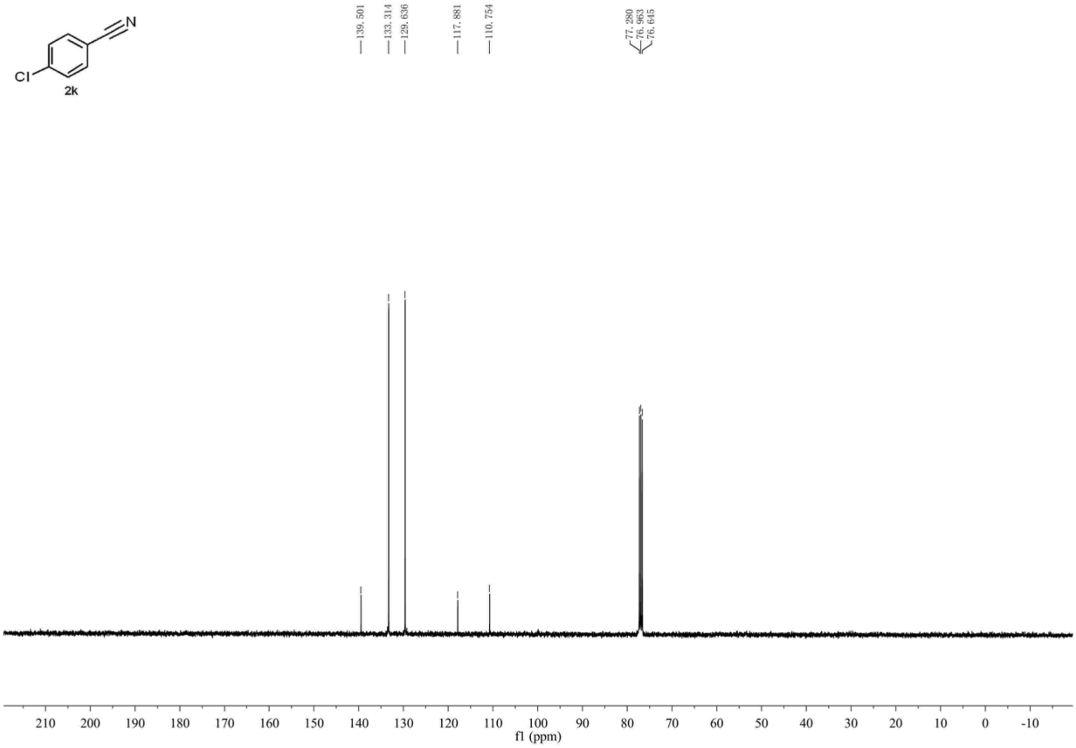
77.320
77.002
76.684
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2k

Cl
N
7.619
7.597
7.483
7.462
2.00
2.02
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)



2k

Cl
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129.636
117.881
110.754
77.280
76.963
76.645
210
200
190
180
170
160
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120
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100
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80
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40
30
20
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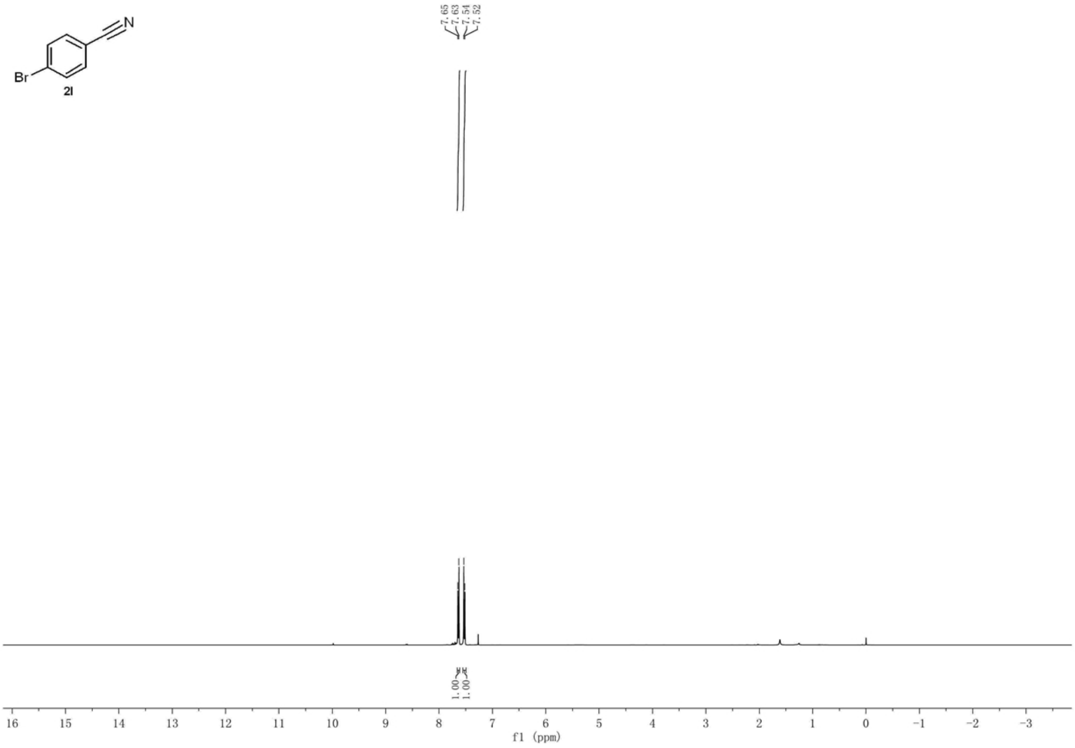
0
-10
f1 (ppm)


N
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2l
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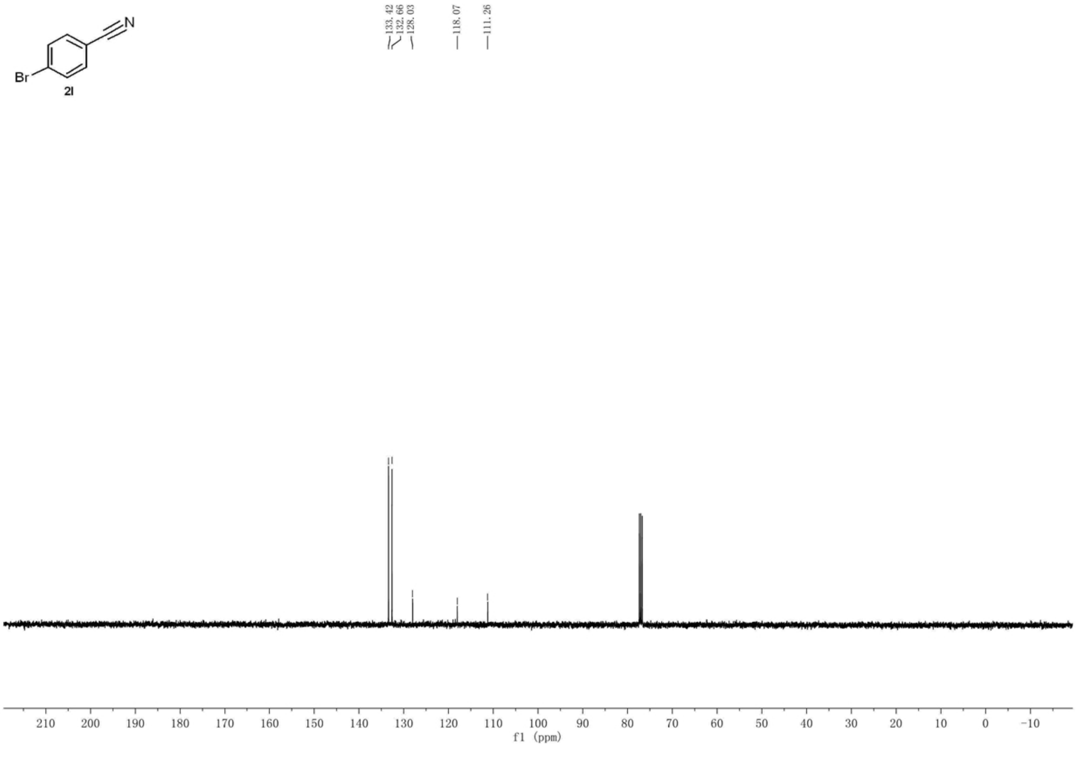
7.63
7.54
7.52
1.00
1.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)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Br
2l
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200
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180
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150
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130
120
110
100
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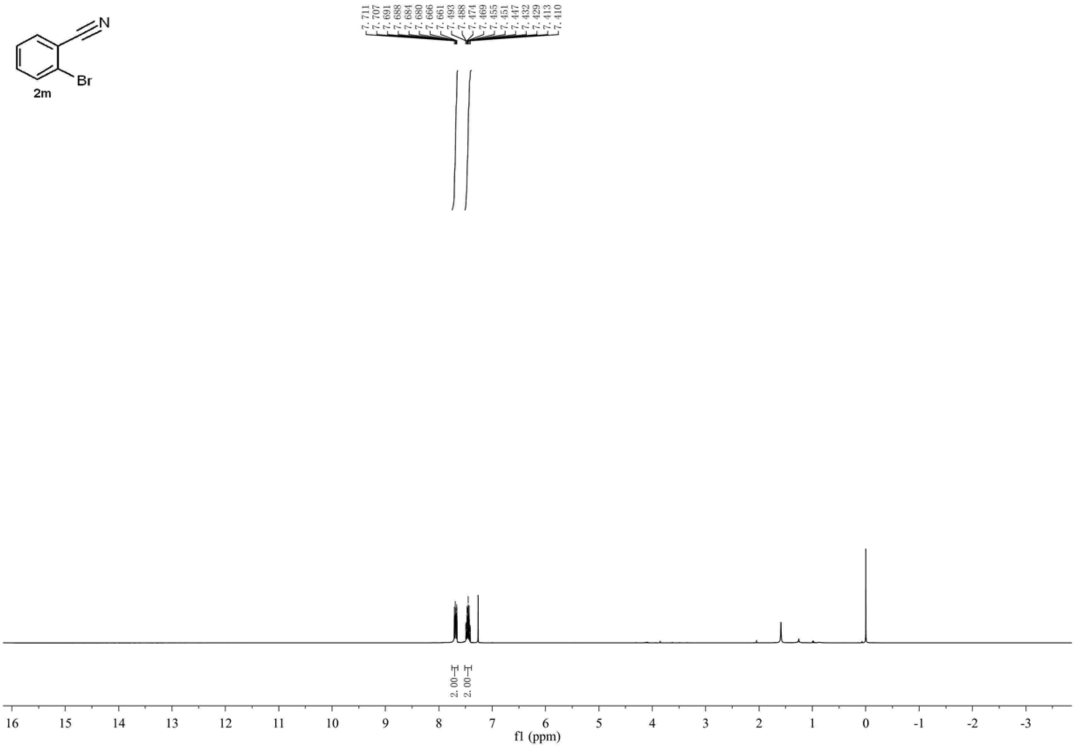
60
50
40
30
20
10
0
−10
f1 (ppm)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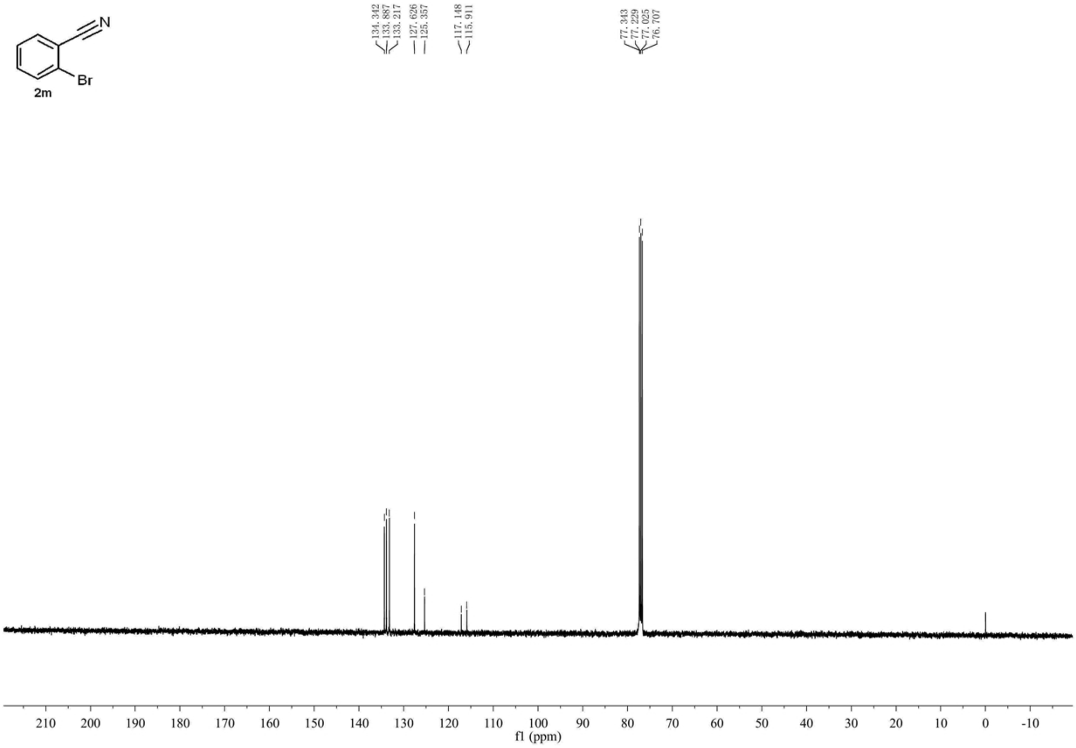
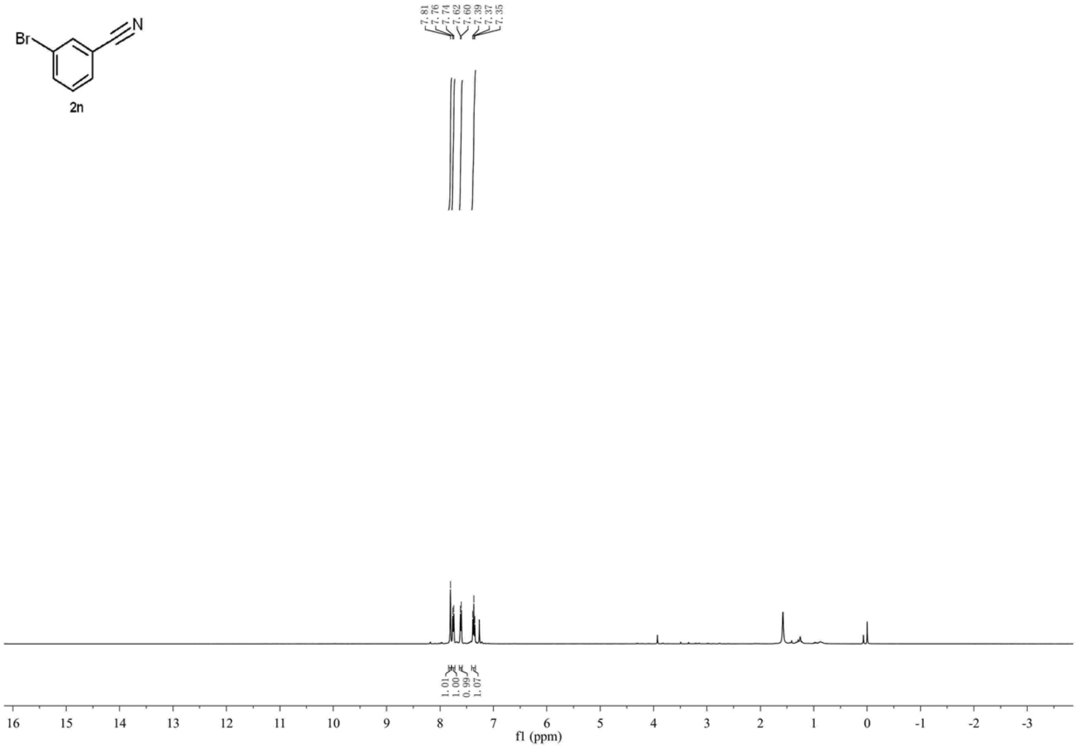
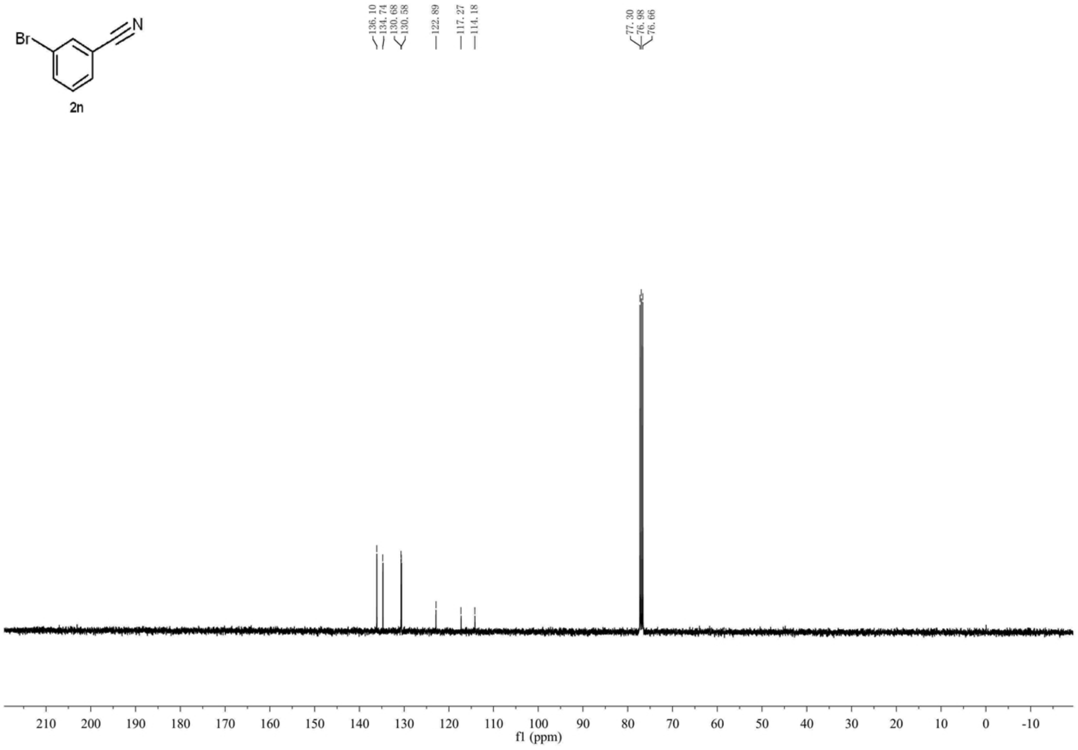
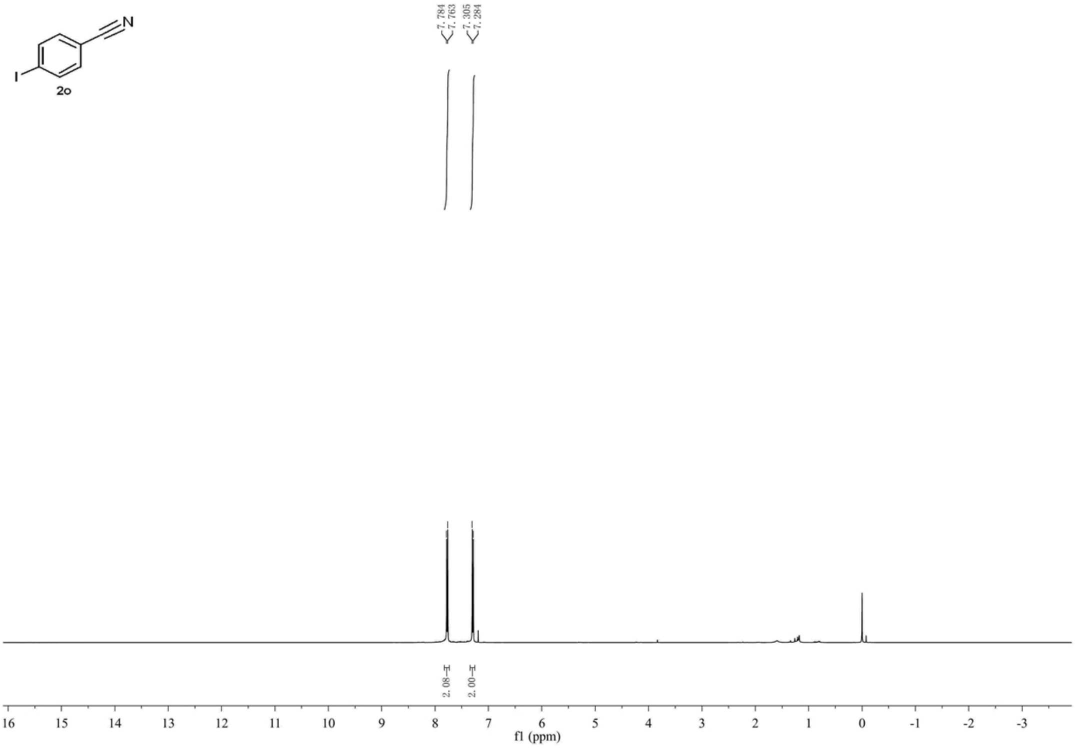
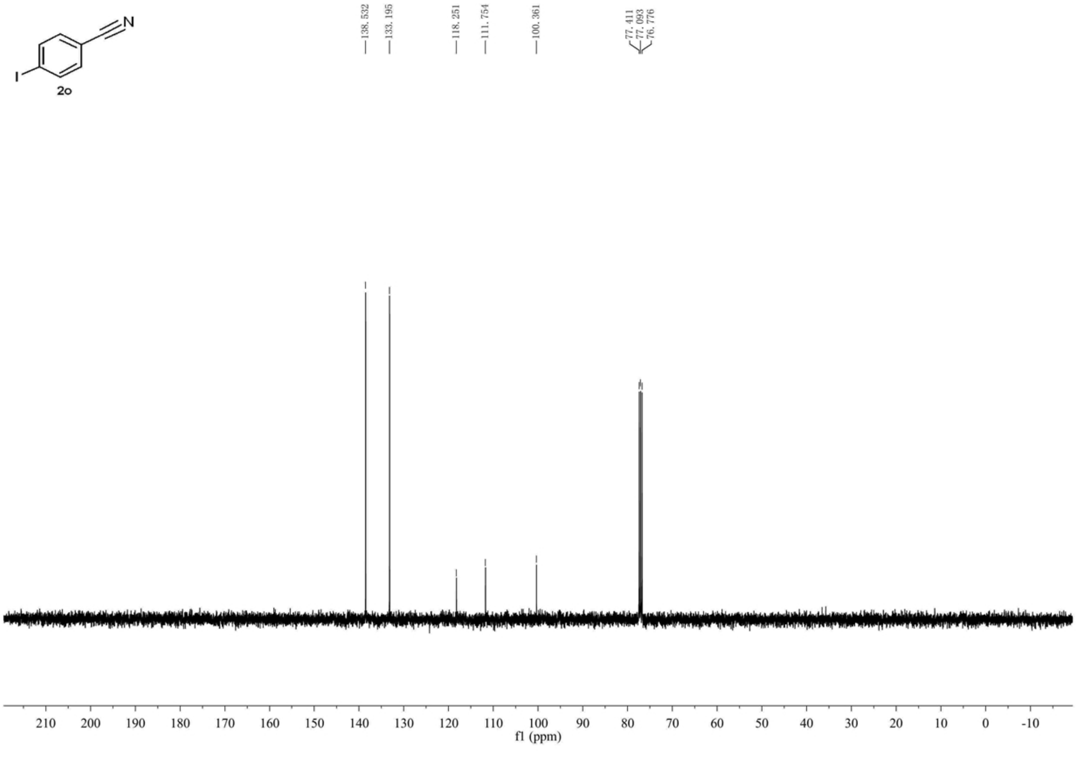
7.474
7.469
7.455
7.451
7.447
7.432
7.429
7.413
7.410
2.00
2.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

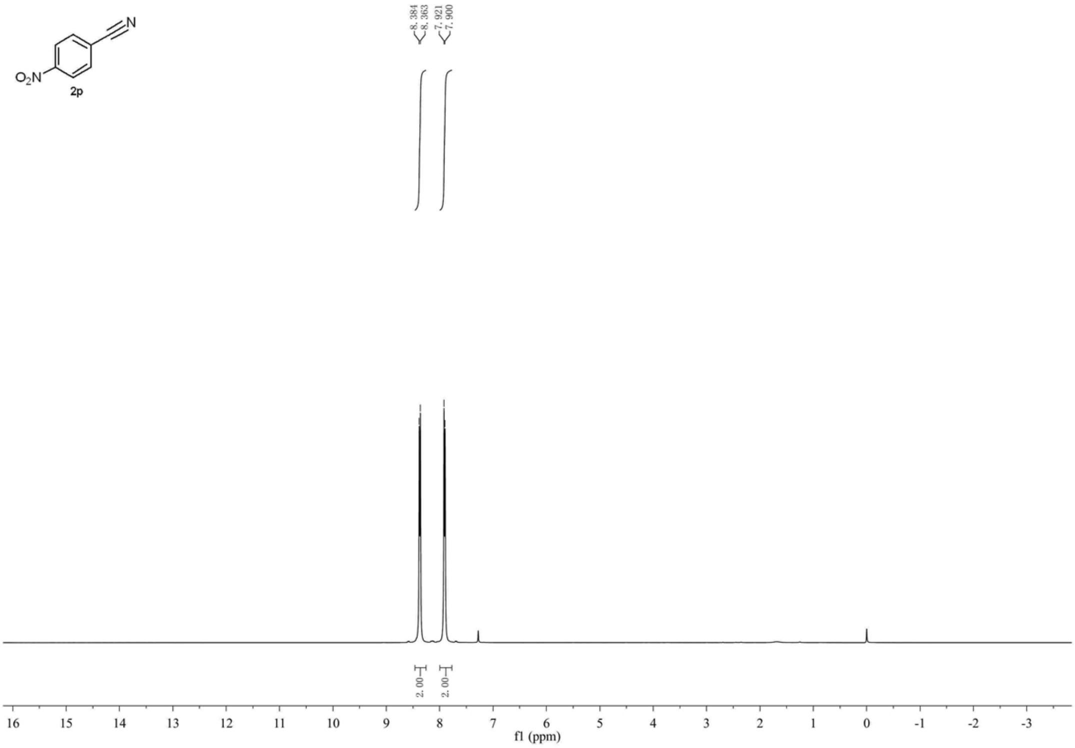

N
Br
2m
134.342
133.887
133.217
127.626
125.357
117.148
115.911
77.343
77.229
77.025
76.707
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Br
N
2n
7.81
7.76
7.74
7.62
7.60
7.39
7.37
7.35
1.01
1.00
0.99
1.07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

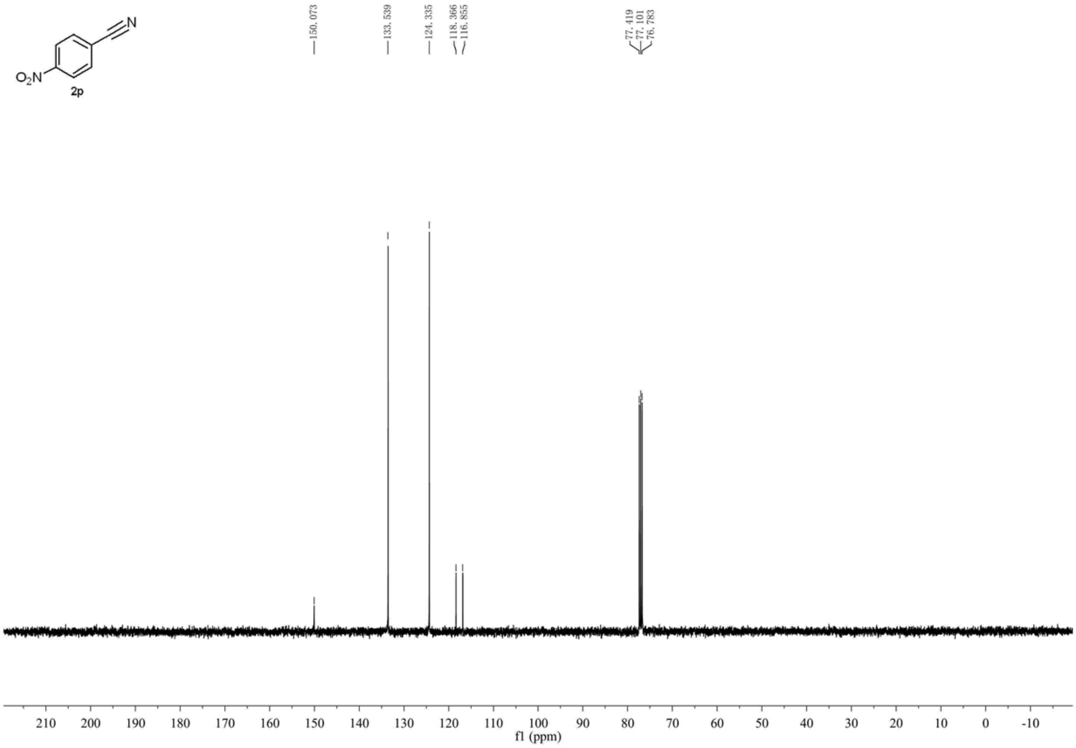

Br
N
2n
136.10
134.74
130.68
130.58
122.89
117.27
114.18
77.30
76.98
76.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


2o
7.784
7.763
7.305
7.284
2.08
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

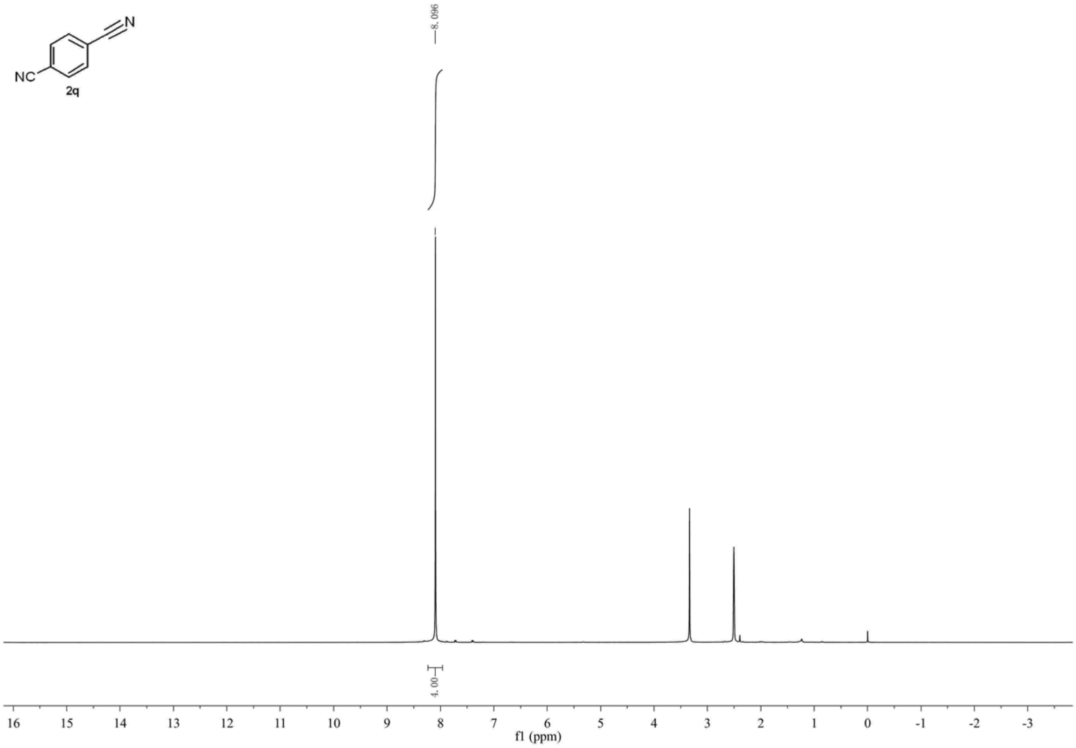

2o
138.532
133.195
118.251
111.754
100.361
77.411
77.093
76.776
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

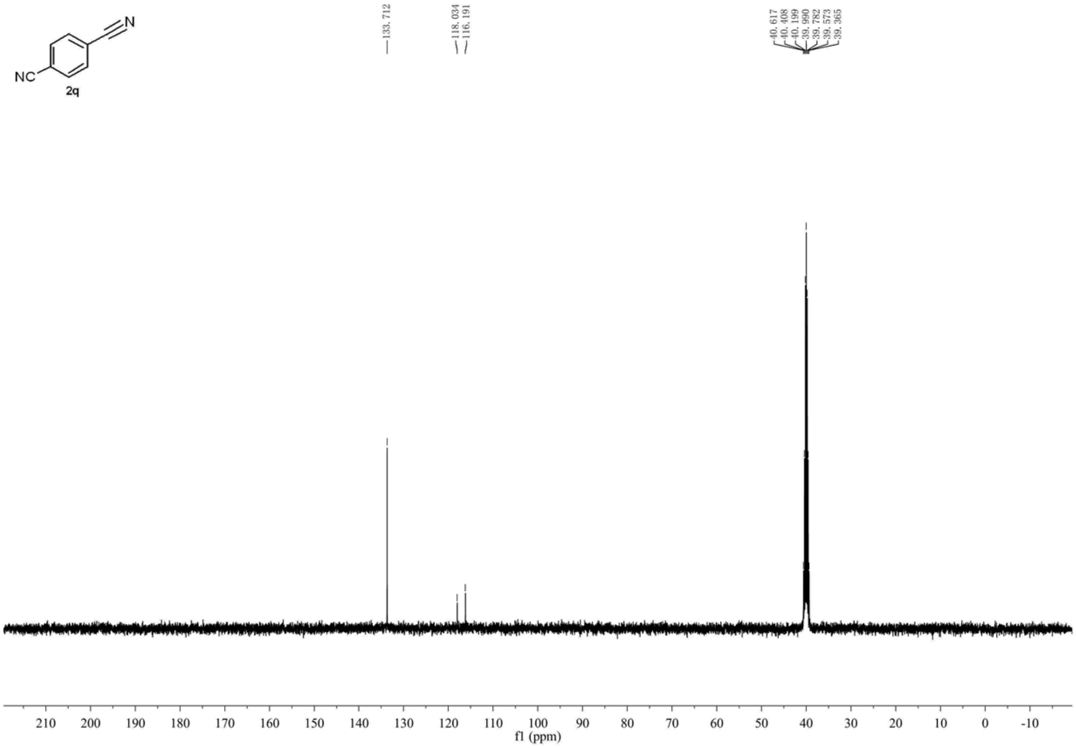


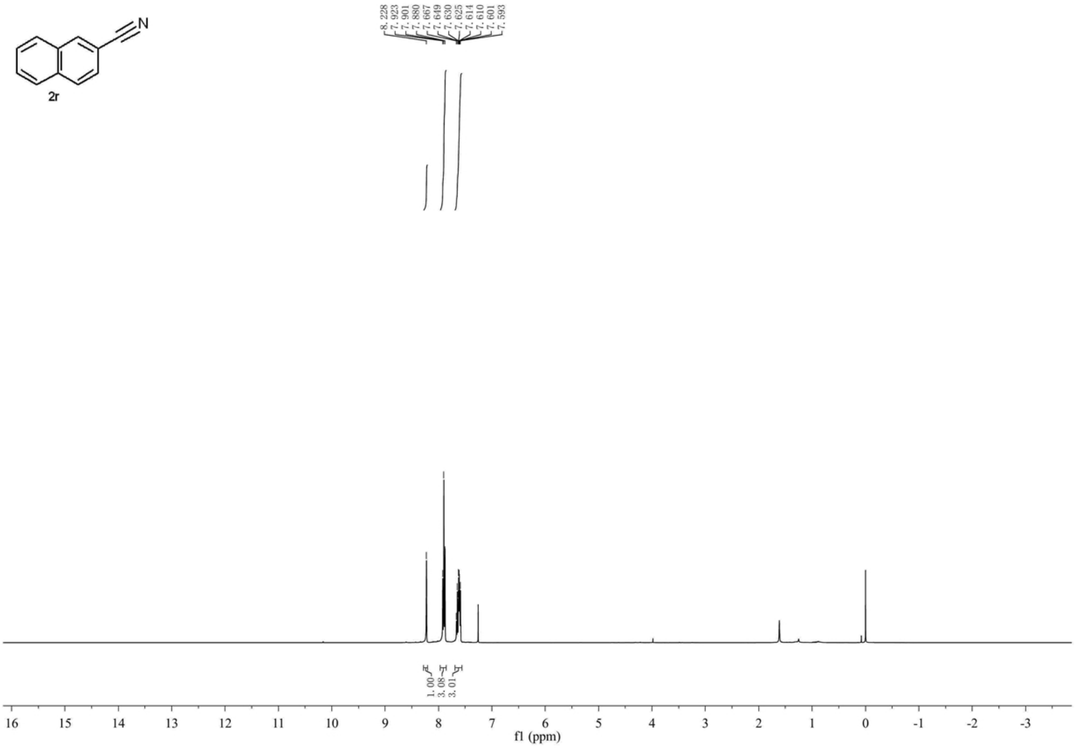
O2N
N
2p
8.384
8.363
7.921
7.900
2.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

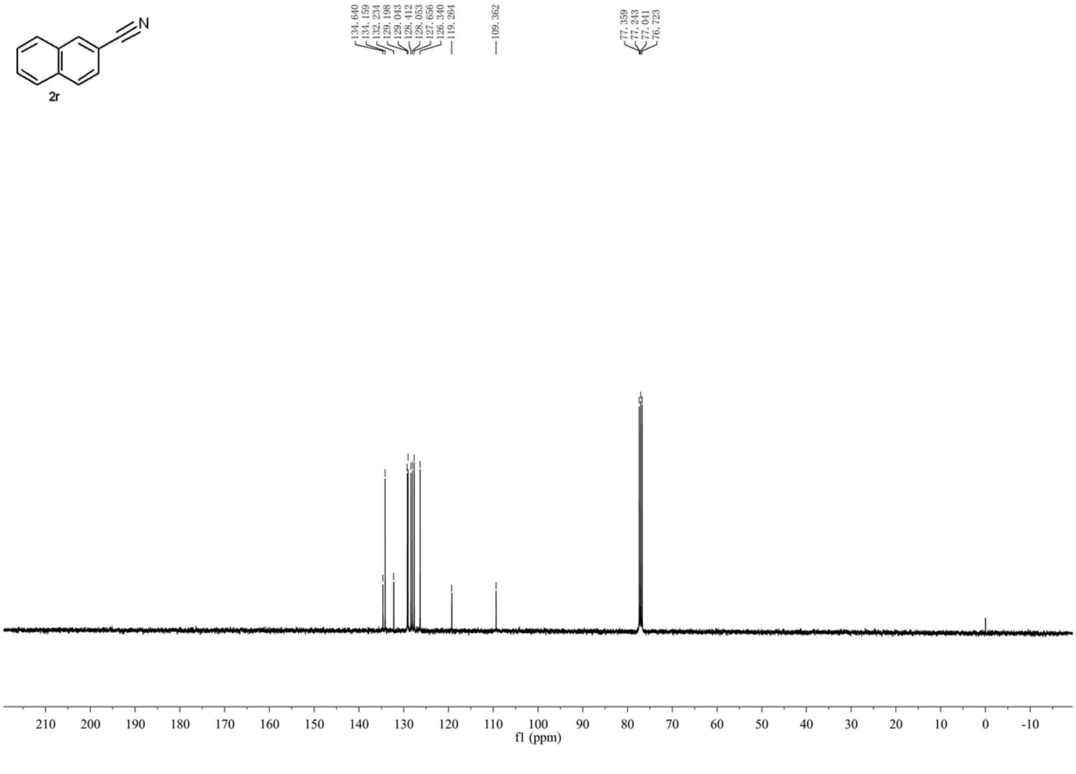


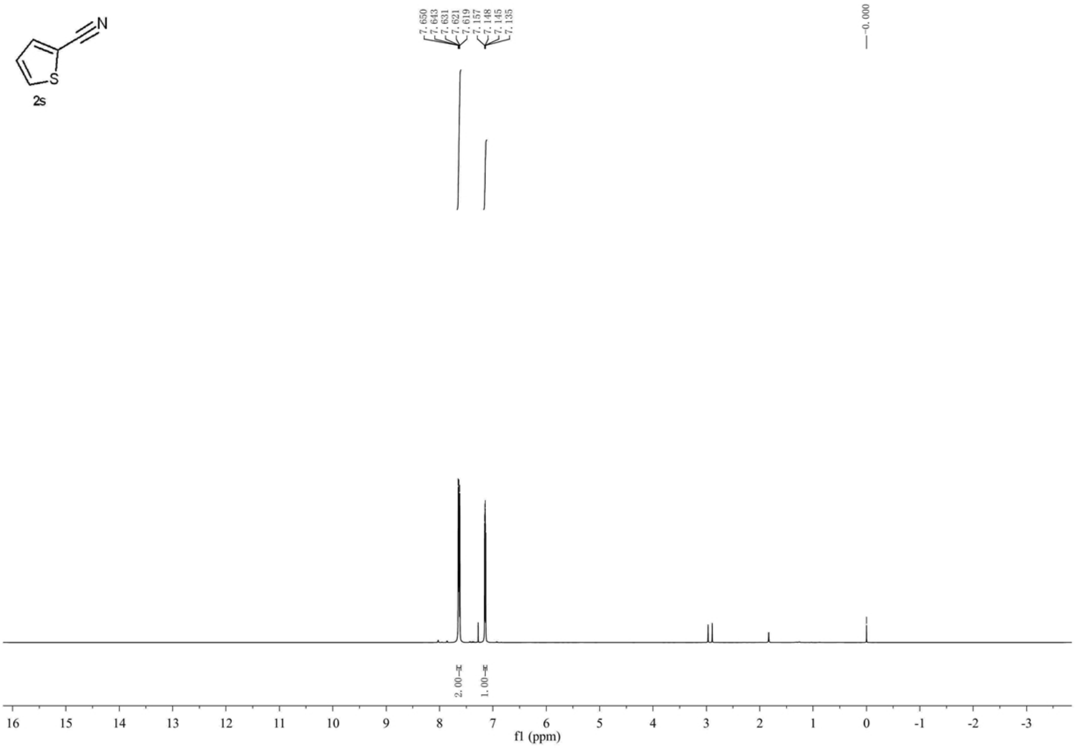
O2N
N
2p
150.073
133.539
124.335
118.366
116.855
77.419
77.101
76.783
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NC
N
2q
8.096
4.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

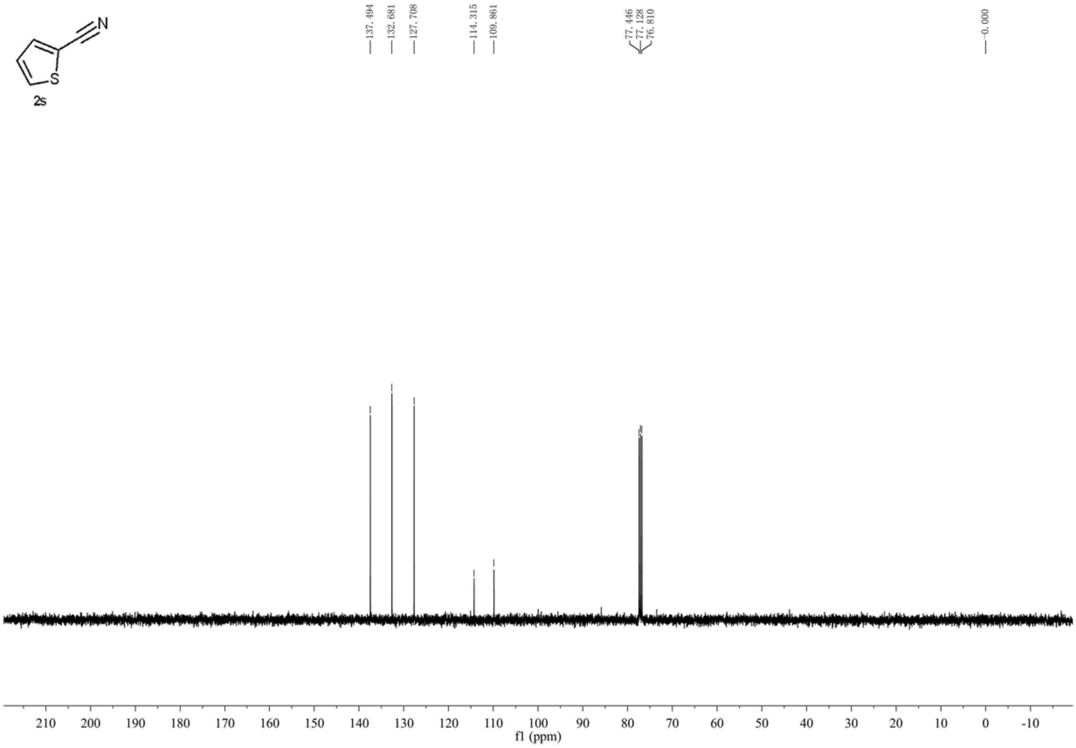

NC
N
2q
133.712
118.034
116.191
40.617
40.408
40.199
39.990
39.782
39.573
39.365
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
2r
8.228
7.923
7.901
7.880
7.667
7.649
7.630
7.625
7.614
7.610
7.601
7.593
1.00
3.08
3.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

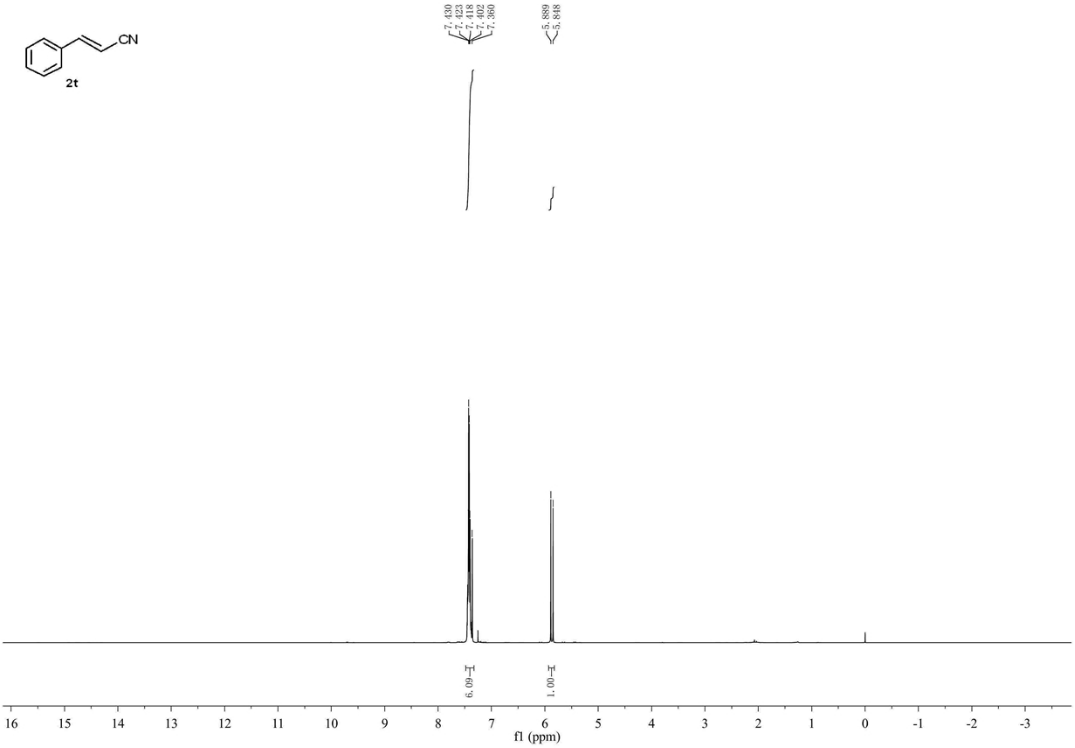

N
2r
134.640
134.159
132.234
129.198
129.043
128.412
128.053
127.656
126.340
119.264
109.362
77.359
77.243
77.041
76.723
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2s
7.650
7.643
7.631
7.621
7.619
7.157
7.148
7.145
7.135
0.000
2.00
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

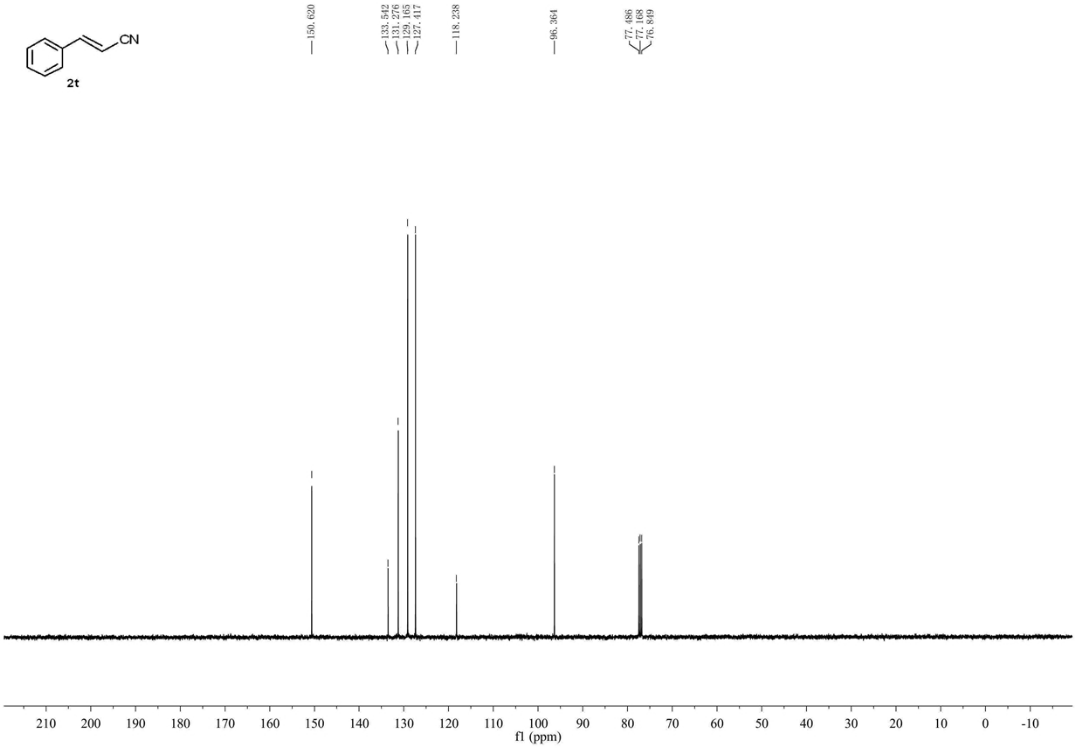


2s
137.494
132.681
127.708
114.315
109.861
77.446
77.128
76.810
0.000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CN

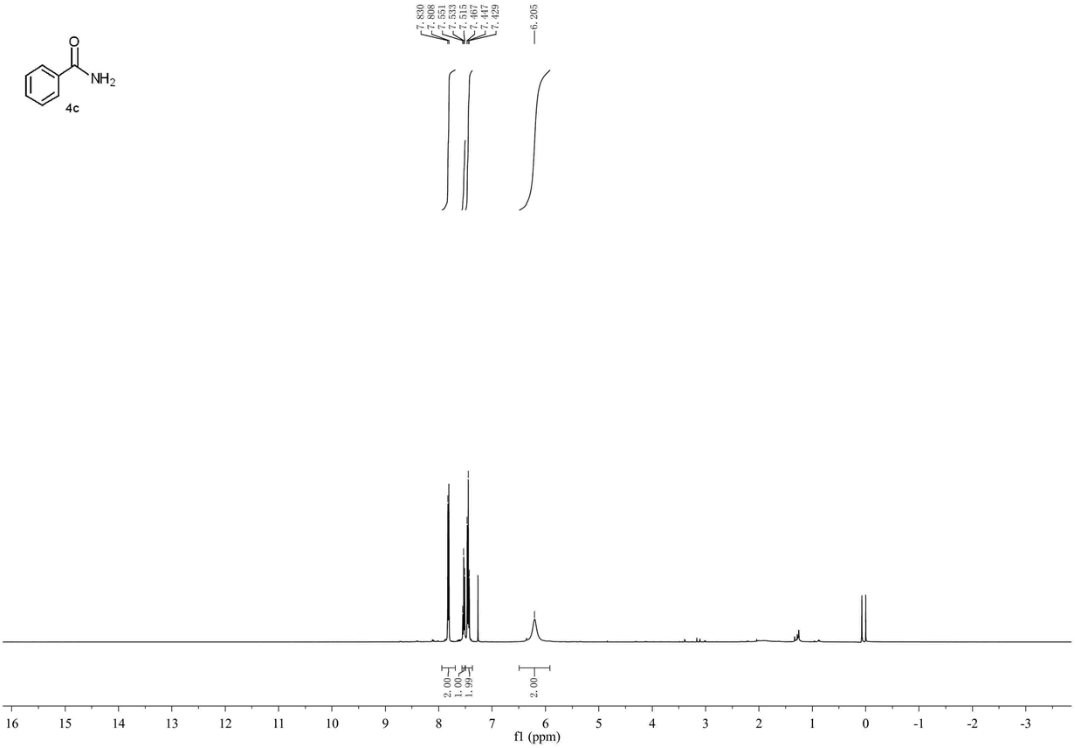
2t

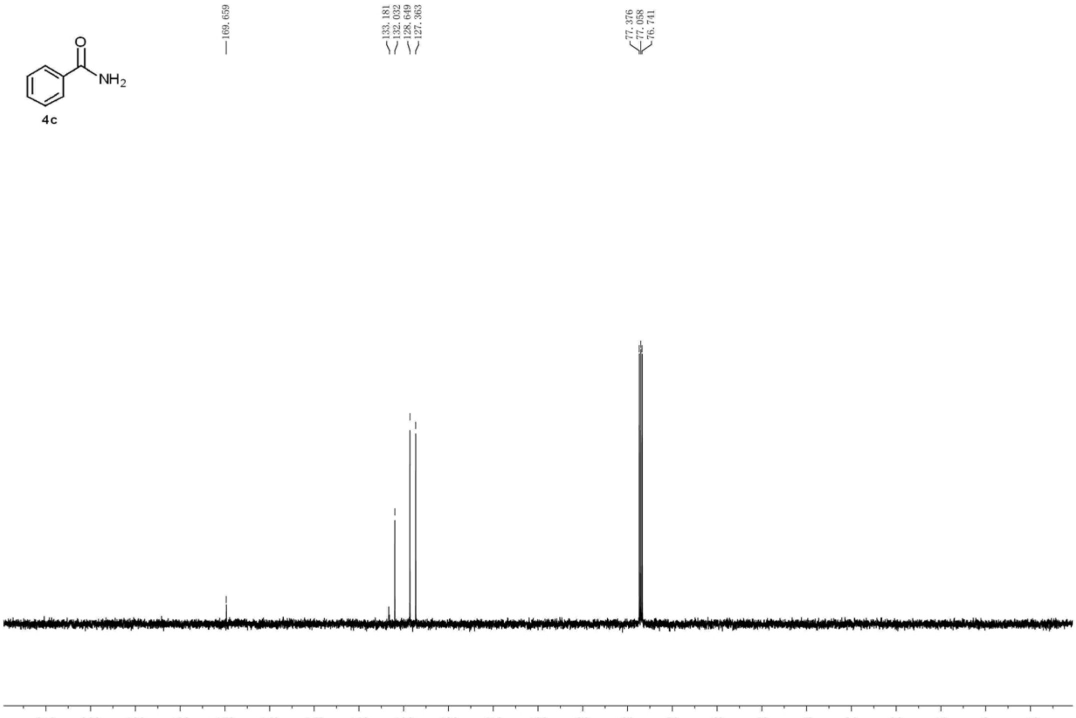
7.430
7.423
7.418
7.402
7.360
5.889
5.848
6.09
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

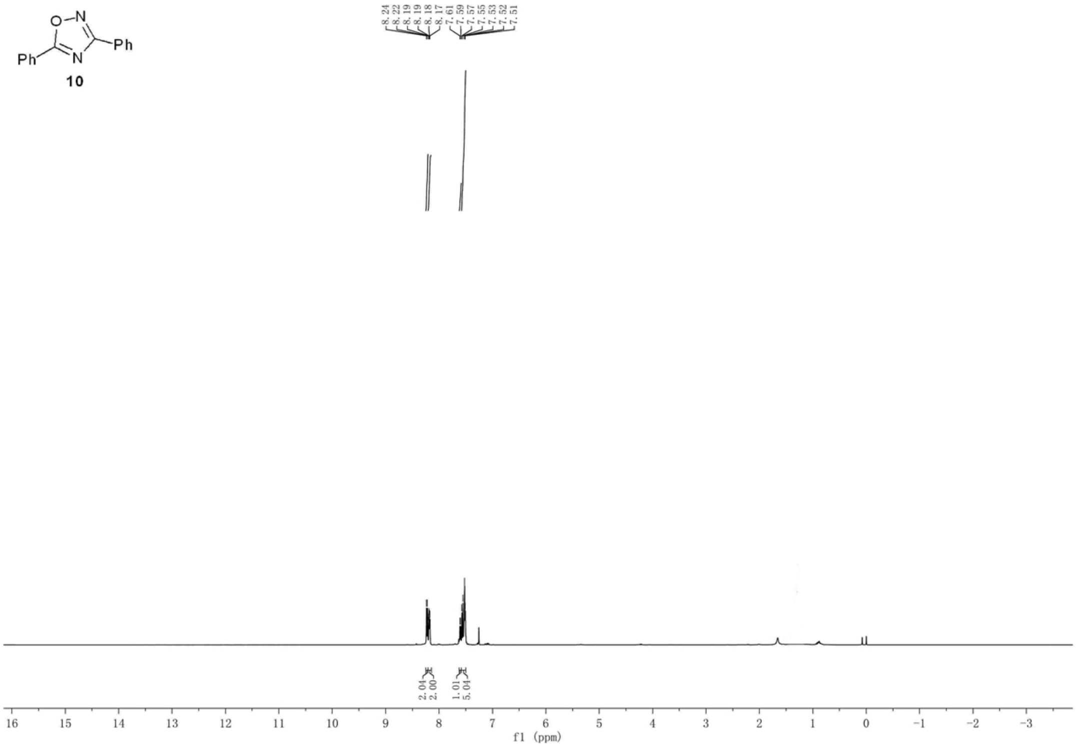

CN

2t

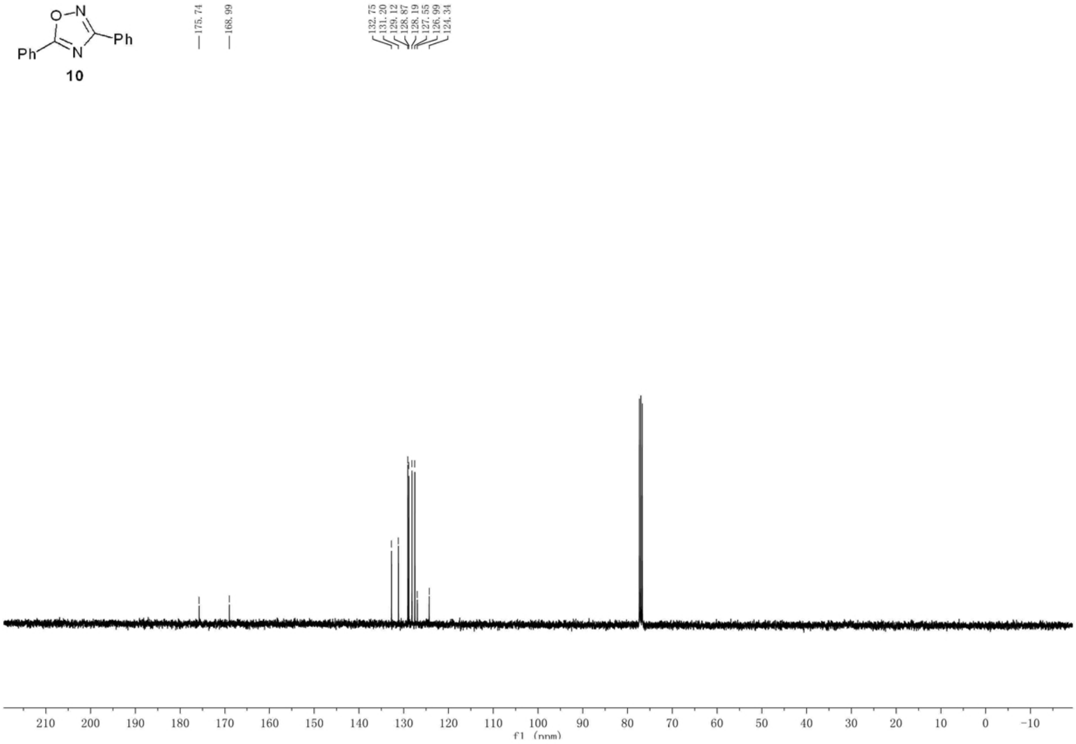
150.620
133.542
131.276
129.165
127.417
118.238
96.364
77.486
77.168
76.849
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
NH2
4c
7.830
7.808
7.551
7.533
7.515
7.467
7.447
7.429
6.205
2.00
1.00
1.99
2.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


O
NH2
4c
169.659
133.181
132.032
128.649
127.363
77.376
77.058
76.741
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O–N
Ph
Ph
N
8.24
8.22
8.19
8.19
8.18
8.17
7.61
7.59
7.57
7.55
7.53
7.52
7.51
2.04
2.00
1.01
5.04
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

10


O–N
Ph
Ph
N
175.74
168.99
132.75
131.20
129.12
128.87
128.19
127.55
126.99
124.34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

10