Supporting Information

Rhodium(III)-catalyzed aromatic C–H cyanation with dimethylmalononitrile as a cyanating agent

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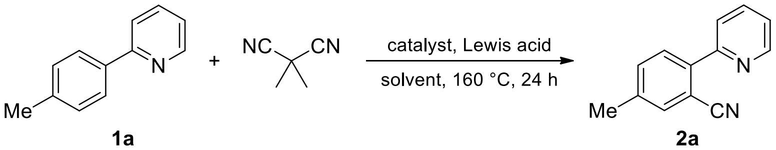
1. General Information

All reactions were carried out under air atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm down field (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectras was recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on a GC-TOF mass spectrometry. TLC was carried out on SiO_2 (silica gel $60F_{254}$, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silicagel 60, 200-300 meth).

The starting materials **1a**, **1b**, **1g**, **1i**, **1l**, **3a**, **3i**, **3j**, and **3l** are commercially available. **1c**−**1f**, **1h**−**1o**, **3b**−**3h**, and **3k** were synthesized according the previous literatures.[1]

2. Catalysts Screening

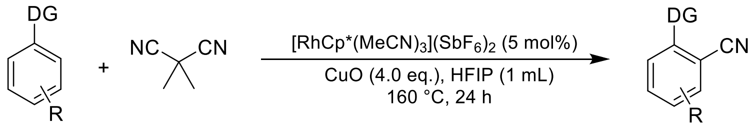
Table S1. Optimization study of catalysts



entry	catalyst	Lewis acid	solvent	Yield (%)^b
1	$[RhCl(COD)]_2$	none	HFIP	NR^c
2	$[Rh(OAc)_2]_2$	none	HFIP	NR^c
3	$RhCl(PPh_3)_3$	none	HFIP	NR^c
4	$RhCl_3 \cdot 3H_2O$	none	HFIP	NR^c
5	$[RuCl_2(p\text{-cymene})]_2$	none	HFIP	NR^c
6	$Pd(OAc)_2$	none	HFIP	NR^c
7	$Mn(CO)_5Br$	none	HFIP	NR^c

^{a}Reaction conditions: 2-(*p*-tolyl)pyridine (**1a**, 0.2 mmol, 33.8 mg), dimethylmalononitrile (DMMN, 0.4 mmol, 37.6 mg), catalyst (10 mol%) and Lewis acid (4.0 eq.) in solvent (1.0 mL) at 160 ^{o}C for 24 h. ^{b}Determined by ^{1}H NMR analysis of the crude reaction mixture using dibromomethane as an internal standard. ^{c}No reaction was observed, and starting materials were recovered.

3. General Procedure for the Catalytic Aromatic C−H Bond Direct Cyanation

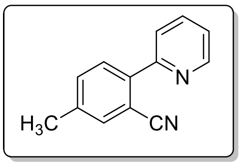


1 or **3** **2** or **4**

A reaction flask was charged with a mixture of arene substrate (**1** or **3**) (0.2 mmol), dimethylmalononitrile (0.4 mmol, 2.0 equiv.), $[RhCp^*(MeCN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol, 5.0 mol%), CuO (63.6 mg, 0.8 mmol, 4.0 equiv.), and HFIP (1.0 mL). The reaction mixture was stirred at 160 °C for 24 h, and then was cooled to room temperature. The resultant mixture was evaporated under a reduced pressure to remove the solvent. The residue obtained was filtered through a short silica gel column with ethyl acetate to remove rhodium residue and CuO. The product **2** or **4** was then purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5:1).

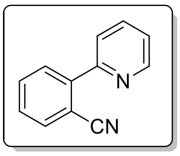
4. Characterization Data for All Compounds

5-Methyl-2-(pyridin-2-yl)benzonitrile (2a)[2]



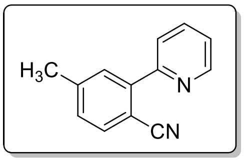
Colorless solid (32.2 mg, 83% yield), mp 63−64 °C, (lit.[2] mp 63–64 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.76 (d, J = 8.0 Hz, 1H), 7.82−7.80 (m, 1H), 7.77−7.73 (m, 2H), 7.60 (s, 1H), 7.50−7.48 (m, 1H), 7.35−7.31 (m, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 150.0, 140.8, 139.2, 136.9, 134.5, 133.9, 130.0, 123.2, 123.1, 119.0, 110.9, 21.0.

2-(Pyridin-2-yl)benzonitrile (2b)[2]



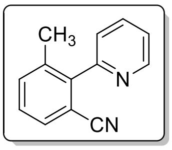
Pale yellow oil (28.5 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.77 (d, J = 4.0 Hz, 1H), 7.86−7.77 (m, 4H), 7.71−7.67 (m, 1H), 7.53−7.49 (m, 1H), 7.38−7.34 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3, 150.0, 143.5, 137.0, 134.2, 132.9, 130.1, 128.9, 123.5, 123.4, 118.8, 111.1.

4-Methyl-2-(pyridin-2-yl)benzonitrile (2c)[3]



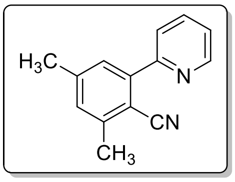
Colorless oil (34.3 mg, 88% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.77 (d, J = 4.0 Hz, 1H), 7.85−7.78 (m, 2H), 7.69−7.67 (m, 2H), 7.36−7.30 (m, 2H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 150.0, 143.9, 143.4, 136.9, 134.1, 130.8, 129.6, 123.4, 123.3, 119.1, 108.1, 21.9.

3-Methyl-2-(pyridin-2-yl)benzonitrile (2d)[2]



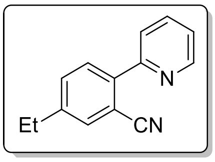
Colorless oil (22.9 mg, 58% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.76 (d, J = 4.0 Hz, 1H), 7.86−7.82 (m, 1H), 7.60 (d, J = 4.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.43−7.35 (m, 3H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.2, 149.9, 143.7, 137.9, 136.8, 134.9, 130.7, 128.6, 124.7, 123.2, 118.3, 112.8, 20.2.

2,4-Dimethyl-6-(pyridin-2-yl)benzonitrile (2e)[4]



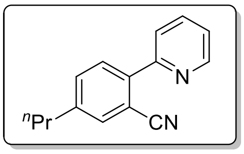
Yellow oil (23.3 mg, 56% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.75 (d, J = 8.0 Hz, 1H), 7.82−7.80 (m, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.42 (s, 1H), 7.36−7.33 (m, 1H), 7.19 (s, 1H), 2.60 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.1, 149.9, 144.0, 143.3, 143.2, 136.9, 131.0, 128.3, 123.6, 123.3, 118.0, 108.6, 21.8, 21.1.

5-Ethyl-2-(pyridin-2-yl)benzonitrile (2f)[5]



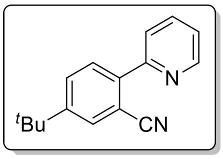
Colorless oil (26.5 mg, 64% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.76 (d, J = 4.0 Hz, 1H), 7.84−7.75 (m, 3H), 7.62 (s, 1H), 7.52−7.50 (m, 1H), 7.34−7.31 (m, 1H), 2.74 (q, J = 8.0, 2H), 1.29 (t, J = 8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 150.0, 145.4, 141.0, 136.9, 133.5, 132.8, 130.1, 123.2, 119.1, 111.0, 28.3, 15.2.

5-Propyl-2-(pyridin-2-yl)benzonitrile (2g)



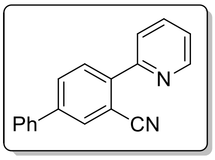
Colorless oil (26.6 mg, 60% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.76 (d, J = 4.0 Hz, 1H), 7.83−7.75 (m, 3H), 7.60 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.34−7.31 (m, 1H), 2.67 (t, J = 8.0 Hz, 2H), 1.71−1.66 (m, 2H), 0.96 (t, J = 8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 150.0, 143.9, 141.0, 136.9, 134.1, 133.3, 130.0, 123.2, 119.1, 110.9, 37.3, 24.2, 13.7; IR (neat): 2928, 2225, 1606, 1557, 1464, 1429, 1328, 1152, 1128, 1073, 1013, 835 (cm^{-1}); HRMS (EI) calcd for $C_{15}H_{14}N_2$: 222.1157 $[M]^+$; found: 222.1164.

5-(*tert*-Butyl)-2-(pyridin-2-yl)benzonitrile (2h)[3]



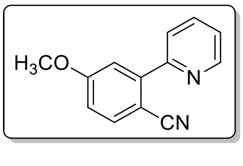
Colorless solid (32.2 mg, 68% yield), mp 69−71 °C, (lit.[3] mp 68–71 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.76 (d, J = 4.0 Hz, 1H), 7.84−7.75 (m, 4H), 7.72−7.70 (m, 1H), 7.34−7.31 (m, 1H), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3, 152.4, 150.0, 140.7, 136.9, 131.2, 130.3, 129.8, 123.2, 123.1, 119.4, 110.7, 34.9, 31.1.

4-(Pyridin-2-yl)-[1, 1'-biphenyl]-3-carbonitrile (2i)[2]



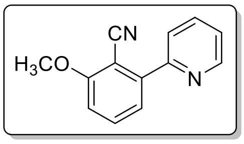
Colorless oil (30.4 mg, 60% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.80 (d, J = 4.0 Hz, 1H), 8.01 (s, 1H), 7.94−7.83 (m, 4H), 7.63−7.61 (m, 2H), 7.52−7.35 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.0, 150.1, 142.1, 142.0, 138.4, 137.0, 132.7, 131.5, 130.6, 129.3, 128.7, 127.2, 123.5, 123.3, 118.9, 111.6.

4-Methoxy-2-(pyridin-2-yl)benzonitrile (2j)[5]



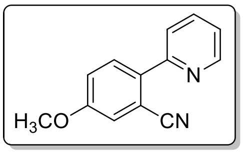
Colorless oil (29.2 mg, 70% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.77 (d, J = 4.0 Hz, 1H), 7.84−7.80 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.37−7.36 (m, 2H), 7.02−6.99 (m, 1H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 163.0, 155.3, 150.0, 145.7, 137.0, 135.8, 123.6, 123.5, 119.2, 115.3, 115.2, 102.8, 55.8.

2-Methoxy-6-(pyridin-2-yl)benzonitrile (2j′)



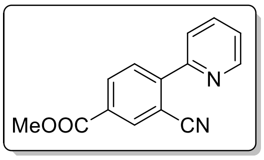
Colorless oil (5.0 mg, 12% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 8.75 (d, *J* = 4.0 Hz, 1H), 7.83−7.75 (m, 2H), 7.63−7.59 (m 1H), 7.38−7.32 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 162.4, 155.4, 150.0, 145.4, 136.8, 134.0, 123.7, 123.5, 122.0, 116.0, 111.0, 100.8, 56.5; IR (neat): 2947, 2221, 1589, 1573, 1496, 1423, 1349, 1313, 1241, 1034, 849, 783 (cm^{-1}); HRMS (EI) calcd for $C_{13}H_{10}N_2$: 210.0793 $[M]^+$; found: 210.0799.

5-Methoxy-2-(pyridin-2-yl)benzonitrile (2k)[2]



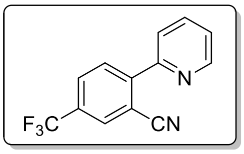
Colorless solid (37.1 mg, 88% yield), mp 101−102 ºC, (lit.[2] mp 99–100 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 8.75 (d, *J* = 4.0 Hz, 1H), 7.83−7.74 (m, 3H), 7.33−7.20 (m, 3H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 159.7, 155.1, 149.9, 136.9, 136.1, 131.5, 123.0, 122.9, 119.5, 118.8, 118.6, 111.8, 55.9.

Methyl 3-cyano-4-(pyridin-2-yl)benzoate (2l)[3]



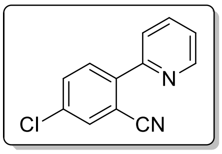
Colorless solid (28.2 mg, 59% yield), mp 105−106 ºC, (lit.[3] mp 107–108 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 8.80 (d, *J* = 4.0 Hz, 1H), 8.46 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.89−7.82 (m, 2H), 7.42−7.39 (m, 1H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 165.1, 154.3, 150.3, 147.1, 137.1, 135.5, 133.7, 130.8, 130.4, 124.1, 123.6, 118.0, 111.6, 52.9.

2-(Pyridin-2-yl)-5-(trifluoromethyl)benzonitrile (2m)[5]



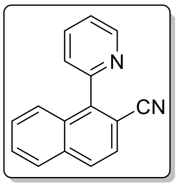
Colorless solid (28.8 mg, 58% yield), mp 65−67 ºC, (lit.[5] mp 70–72 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.82 (d, J = 4.0 Hz, 1H), 8.07 (s, 1H), 8.03−8.01 (m, 1H), 7.95−7.83 (m, 3H), 7.44−7.41 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 153.9, 150.4, 146.6, 137.2, 131.2 (q, $^3J_{C\text{-}F}$ = 5.0 Hz), 130.9, 129.6 (q, $^2J_{C\text{-}F}$ = 3.8 Hz), 124.4, 124.2, 122.6 (d, $^1J_{C\text{-}F}$ = 176.2 Hz), 117.5, 112.0.

5-Chloro-2-(pyridin-2-yl)benzonitrile (2n)[6]



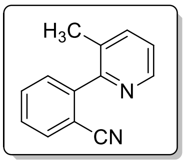
Colorless solid (18.4 mg, 43% yield), mp 165−167 ºC, (lit.[6] mp 165–166 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.77 (d, J = 4.0 Hz, 1H), 7.87−7.78 (m, 4H), 7.68−7.66 (m, 1H), 7.39−7.36 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 154.2, 150.2, 142.0, 137.1, 135.1, 133.7, 133.3, 131.4, 123.7, 123.2, 117.6, 112.5.

1-(Pyridin-2-yl)-2-naphthonitrile (2o)[2]



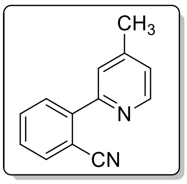
Colorless solid (21.2 mg, 46% yield), mp 156−157 ºC, (lit.[2] mp 156–157 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.86 (d, J = 4.0 Hz, 1H), 7.97−7.89 (m, 3H), 7.70 (d, J = 8.0 Hz, 2H), 7.64−7.58 (m, 2H), 7.54−7.50 (m, 1H), 7.45 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 155.3, 150.1, 144.5, 136.8, 135.1, 131.2, 129.5, 128.9, 128.4, 128.0, 126.9, 126.8, 125.7, 123.6, 118.6, 109.8.

2-(3-Methylpyridin-2-yl)benzonitrile (4a)[2]



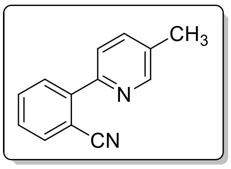
Colorless oil (23.4 mg, 60% yield). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.57 (d, J = 4.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.70−7.66 (m, 2H), 7.53−7.49 (m, 2H), 7.29 (dd, J = 8.0, 4.0 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 155.6, 147.2, 144.4, 138.7, 133.1, 132.7, 131.8, 130.1, 128.5, 123.7, 118.0, 112.6, 19.2.

2-(4-Methylpyridin-2-yl)benzonitrile (4b)[7]



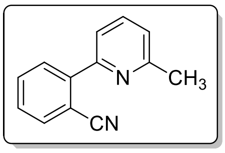
Colorless oil (23.4 mg, 60% yield). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.61 (d, J = 4.0 Hz, 1H), 7.80 (m, 2H), 7.67 (m, 1H), 7.58 (s, 1H), 7.49 (m, 1H), 7.18 (d, J = 8.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 155.3, 149.7, 148.2, 143.7, 134.2, 132.9, 130.1, 128.7, 124.4, 124.3, 118.8, 111.2, 21.3.

2-(5-Methylpyridin-2-yl)benzonitrile (4c)[5]



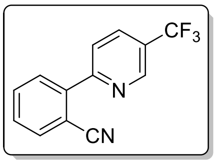
Colorless oil (30.4 mg, 78% yield). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.60 (s, 1H), 7.80 (dd, J = 16.0, 8.0 Hz, 2H), 7.69−7.63 (m, 3H), 7.48 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 152.6, 150.5, 143.6, 137.4, 134.2, 133.3, 132.9, 129.9, 128.6, 122.8, 119.0, 111.0, 18.4.

2-(6-Methylpyridin-2-yl)benzonitrile (4d)



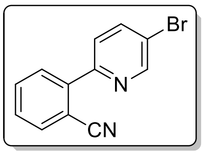
Colorless oil (22.2 mg, 57% yield). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.83−7.77 (m, 2H), 7.73−7.65 (m, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.50−7.46 (m, 1H), 7.21 (d, J = 8.0 Hz, 1H), 2.66 (s, 3H), ^{13}C NMR (CDCl$_3$, 100 MHz) δ 159.0, 154.7, 143.9, 137.2, 134.3, 132.9, 130.0, 128.7, 123.1, 120.3, 118.9, 111.3, 24.6; IR (neat): 2922, 2220, 1587, 1575, 1462, 1422,1263, 1196, 1132, 1076, 1021, 769 (cm^{-1}); HRMS (EI) calcd for $C_{13}H_{10}N_2$: 194.0844 [M]$^+$; found: 194.0841.

2-(5-(Trifluoromethyl)pyridin-2-yl)benzonitrile (4e)



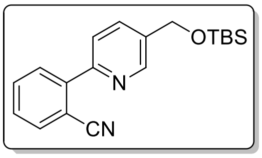
Colorless solid (39.7 mg, 80% yield), mp 99−101 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 9.04 (s, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.86 (dd, J = 20.0, 8.0 Hz, 2H), 7.76−7.73 (m, 1H), 7.60−7.56 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 158.6, 146.9 (q, $^4J_{C\text{-}F}$ = 4.0 Hz), 142.0, 134.5, 134.3 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 133.2, 130.3, 129.8, 126.2 (q, $^2J_{C\text{-}F}$ = 34.0 Hz), 123.5 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 123.0, 118.4, 111.3; IR (KBr): 2917, 2227, 1606, 1541, 1473, 1387,1337, 1175, 1131, 1085, 1015, 860 (cm^{-1}); HRMS (EI) calcd for $C_{13}H_7N_2F_3$: 248.0561 [M]$^+$; found: 248.0569.

2-(5-Bromopyridin-2-yl)benzonitrile (4f)



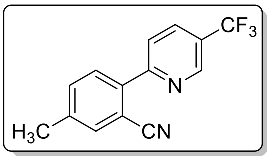
Colorless solid (23.3 mg, 45% yield), mp 106−108 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.83 (s, 1H), 7.98−7.96 (m, 1H), 7.84−7.80 (m, 2H), 7.72−7.69 (m, 2H), 7.55−7.51 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 153.6, 151.1, 142.3, 139.5, 134.3, 133.0, 129.8, 129.1, 124.3, 121.0, 118.5, 110.9; IR (KBr): 2923, 2223, 1603, 1531, 1456, 1363, 1328, 1167, 1131, 1091, 1005, 831 (cm^{-1}); HRMS (EI) calcd for $C_{12}H_7BrN_2$: 257.9793 and 259.9772 [M]$^+$; found: 257.9796 and 259.9779.

2-(5-(((*tert*-Butyldimethylsilyl)oxy)methyl)pyridin-2-yl)benzonitrile (4g)



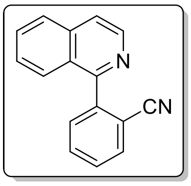
Colorless oil (43.5 mg, 67% yield). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.71 (s, 1H), 7.84−7.74 (m, 4H), 7.69−7.65 (m, 1H), 7.50−7.46 (m, 1H), 4.83 (s, 2H), 0.95 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 154.0, 148.0, 143.5, 136.6, 134.7, 134.2, 132.9, 130.0, 128.7, 122.9, 118.9, 111.1, 62.6, 26.0, 18.4, -5.2; IR (neat): 2923, 2224, 1597, 1561, 1471, 1361, 1257, 1097, 1022, 1006, 839, 777 (cm^{-1}); HRMS (EI) calcd for $C_{13}H_{10}N_2$: 324.1658 [M]$^+$; found: 324.1650.

5-Methyl-2-(5-(trifluoromethyl)pyridin-2-yl)benzonitrile (4h)



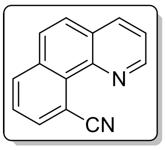
Colorless solid (47.5 mg, 84% yield), mp 78−80 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 9.02 (s, 1H), 8.08−8.05 (m, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.64 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 158.6, 146.9 (q, $^4J_{C\text{-}F}$ = 4.0 Hz), 140.4, 139.2, 134.8, 134.2 (q, ${}^{3}J_{C\text{-}F}$ = 4.0 Hz), 134.0, 130.1, 125.9 (q, ${}^{2}J_{C\text{-}F}$ = 33.0 Hz), 123.5 (q, ${}^{1}J_{C\text{-}F}$ = 271.0 Hz), 122.8, 118.6, 111.0, 21.0; IR (KBr): 2923, 2227, 1603, 1531, 1479, 1385, 1328, 1167, 1131, 1081, 1015, 829 (cm^{-1}); HRMS (EI) calcd for $C_{14}H_{9}N_{2}F_{3}$: 262.0718 [M]$^{+}$; found: 262.0714.

2-(Isoquinolin-1-yl)benzonitrile (4i)[2]



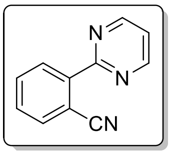
Yellow solid (21.3 mg, 46% yield), mp 126−127 ºC, (lit.[2] mp 124–125 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.68 (d, J = 4.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.77−7.71 (m, 4H), 7.67−7.66 (m, 1H), 7.62−7.54 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 157.1, 143.1, 142.3, 136.8, 133.6, 132.5, 131.0, 130.6, 129.0, 127.9, 127.4, 126.9, 126.6, 121.4, 117.9, 113.3.

Benzo[*h*]quinoline-10-carbonitrile (4j)[3]



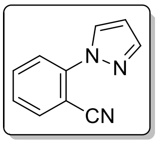
Colorless solid (24.1 mg, 59% yield), mp 139−141 ºC, (lit.[3] mp 138–140 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 9.14 (d, J = 4.0 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.16−8.11 (m, 2H), 7.84−7.71 (m, 2H), 7.73 (m, 1H), 7.63 (dd, J = 8.0, 4.0 Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 148.6, 144.6, 136.4, 135.8, 134.2, 132.9, 130.9, 127.5, 127.4, 127.2, 127.1, 123.2, 120.9, 109.1.

2-(Pyrimidin-2-yl)benzonitrile (4k)[2]



Colorless solid (16.3 mg, 45% yield), mp 136−138 ºC, (lit.[2] mp 136–137 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.92 (d, J = 4.0 Hz, 2H), 8.39−8.36 (m, 1H), 7.87−7.85 (m, 1H), 7.73−7.71 (m, 1H), 7.60−7.58 (m, 1H), 7.35−7.33 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 163.0, 157.5, 140.4, 135.2, 132.7, 130.6, 130.4, 120.3, 119.1, 111.9.

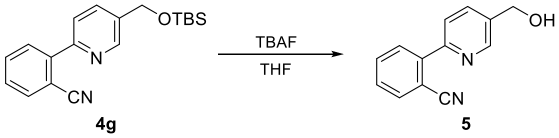
2-(1*H*-Pyrazol-1-yl)benzonitrile (4l)[3]



Colorless oil (19.1 mg, 56% yield). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.14 (d, J = 4.0 Hz, 1H), 7.82−7.77 (m, 3H), 7.73−7.69 (m, 1H), 7.45−7.41 (m, 1H), 6.55 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 142.4, 142.1, 134.6, 134.1, 129.6, 127.4, 124.4, 117.1, 108.6, 105.4.

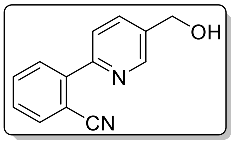
5. Synthesis of 2-(5-(Hydroxymethyl)pyridin-2-yl)benzonitrile (5) and Rh(III) Complex 6

(1) Synthesis of 2-(5-(Hydroxymethyl)pyridin-2-yl)benzonitrile (5)



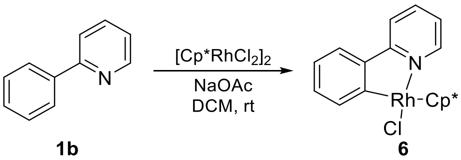
A mixture of **4g** (64.9 mg, 0.2 mmol) and TBAF (0.3 mL, 0.3 mmol) in THF (2 mL) was stirred at room temperature for 5 h. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 2:1) to give 39.2 mg (93%) of **5** as a white solid.

2-(5-(Hydroxymethyl)pyridin-2-yl)benzonitrile (5)[8]



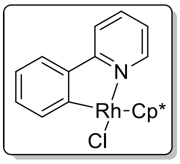
White solid (39.2 mg, 93% yield), mp 151−153 ºC, (lit.[8] mp 152–153 °C). ^{1}H NMR (DMSO, 400 MHz) δ 8.68 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.92−7.87 (m, 2H), 7.83−7.79 (m, 2H), 7.65−7.61 (m, 1H), 5.46−5.43 (m, 1H), 4.63 (d, J = 8.0 Hz, 2H); ^{13}C NMR (DMSO, 100 MHz) δ 153.8, 148.4, 143.2, 138.1, 136.0, 134.8, 133.7, 130.2, 129.6, 123.1, 119.1, 110.6, 60.9.

(2) Synthesis of Rh(III) Complex 6



Rhodium(III) complex **6** is a known compound, and which was synthesized by following a literature report.[9] $[Cp^*RhCl_2]_2$ (100.0 mg, 0.16 mmol), 2-phenylpyridine (**1b**, 55.8 mg, 0.36mmol), sodium acetate (39.4 mg, 3.0 equiv.), and dichloromethane (DCM, 3 mL) were charged into a Schleck tube under N_2 atmosphere. Then, the mixture was stirred at room temperature for overnight. The resultant mixture was filtered through celite and evaporated to dryness. The product **6** was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 1:1).

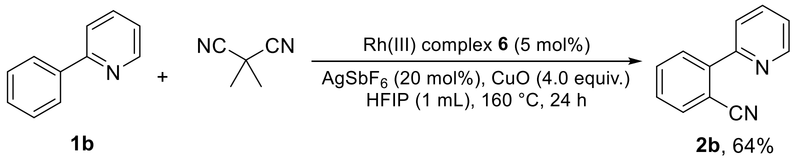
Rh(III) complex 6[9]



Orange solid (123.8 mg, 90% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 8.75 (d, J = 4.0 Hz, 1H), 7.83−7.69 (m, 3H), 7.61 (d, J = 4.0 Hz, 1H), 7.23−7.25 (m, 1H), 7.15−7.05 (m, 2H), 1.63 (s, 15H).

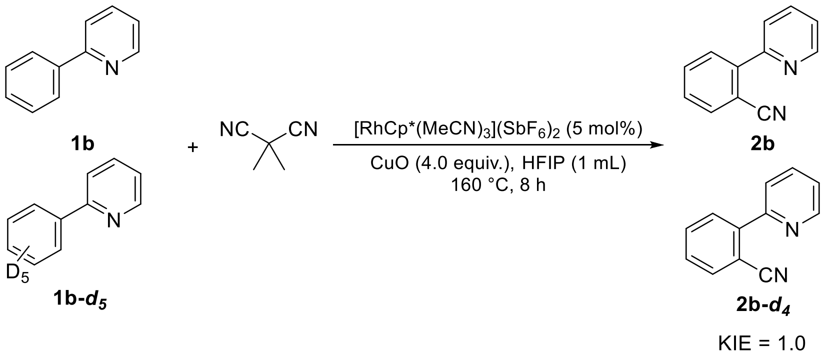
6. Control Experiments

(1) Aromatic C−H bond direct cyanation catalyzed by rhodium(III) complex 6

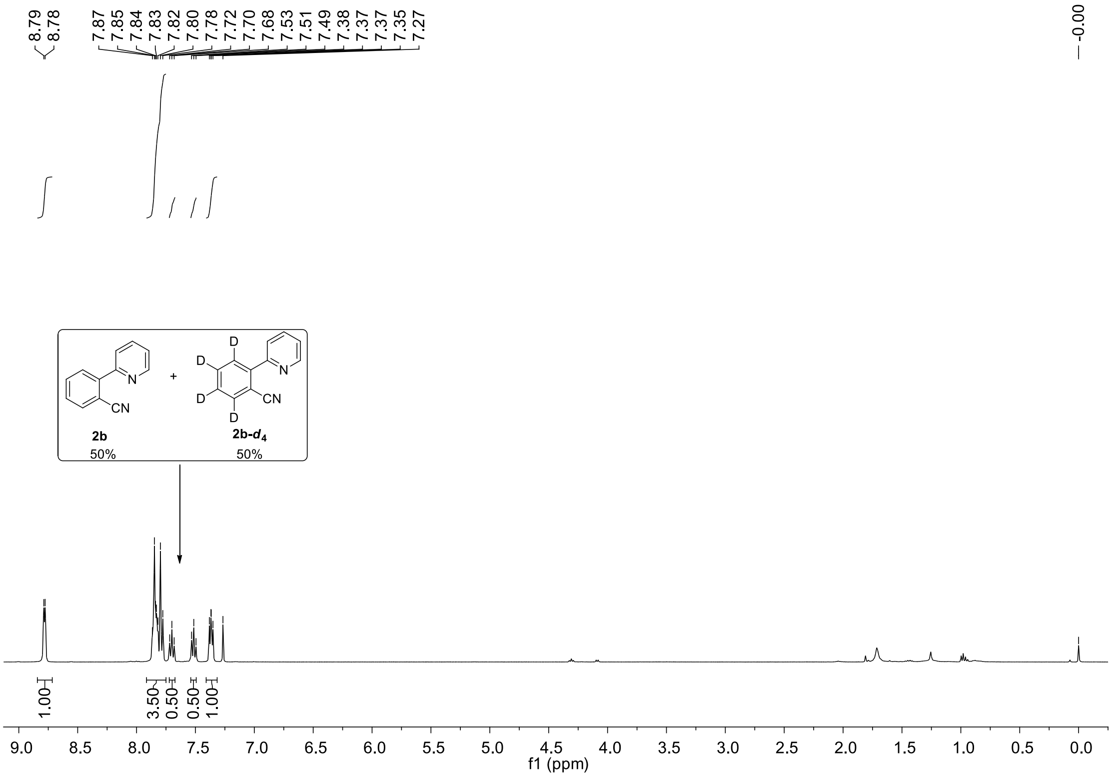


2-Phenylpyridine (**1b**, 0.2 mmol), DMMN (0.4 mmol), rhodium(III) complex **6** (5 mol%), $AgSbF_6$ (20 mol%), CuO (0.8 mmol), and HFIP (1.0 mL) were charged into a Schleck tube. After the reaction mixture was stirred at 160 °C for 24 h, the solvent was removed under reduced pressure. The residue obtained was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5:1) to give product **2b** (23.1 mg, 64%).

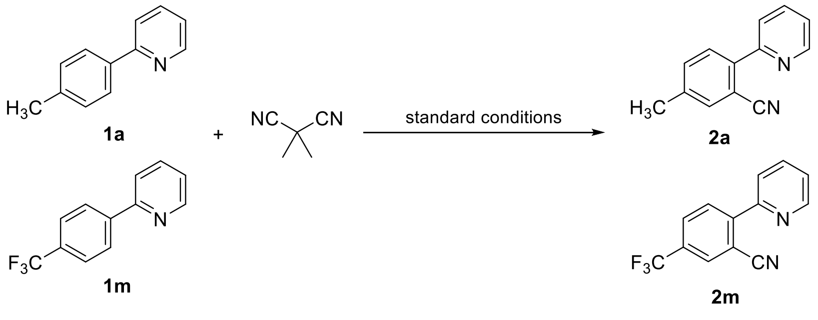
(2) Experiment of deuterium kinetic isotope effect



A reaction flask was charged with a mixture of [RhCp*(MeCN)$_3$](SbF$_6$)$_2$ (5 mol%), CuO (4.0 equiv.), **1b** (0.1 mmol), **1b-*d*$_5$** (0.1 mmol), DMMN (0.4 mmol), and HFIP (1 mL). After the reaction mixture was stirred at 160 °C for 8 h, which was allowed to cool to room temperature. The solvent was removed under reduced pressure, and the residue obtained was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5:1) to give a mixture of products **2b** and **2b-*d*$_5$** (11.0 mg, 30% yield). A 1.0 of KIE was observed by ^{1}H NMR determination.

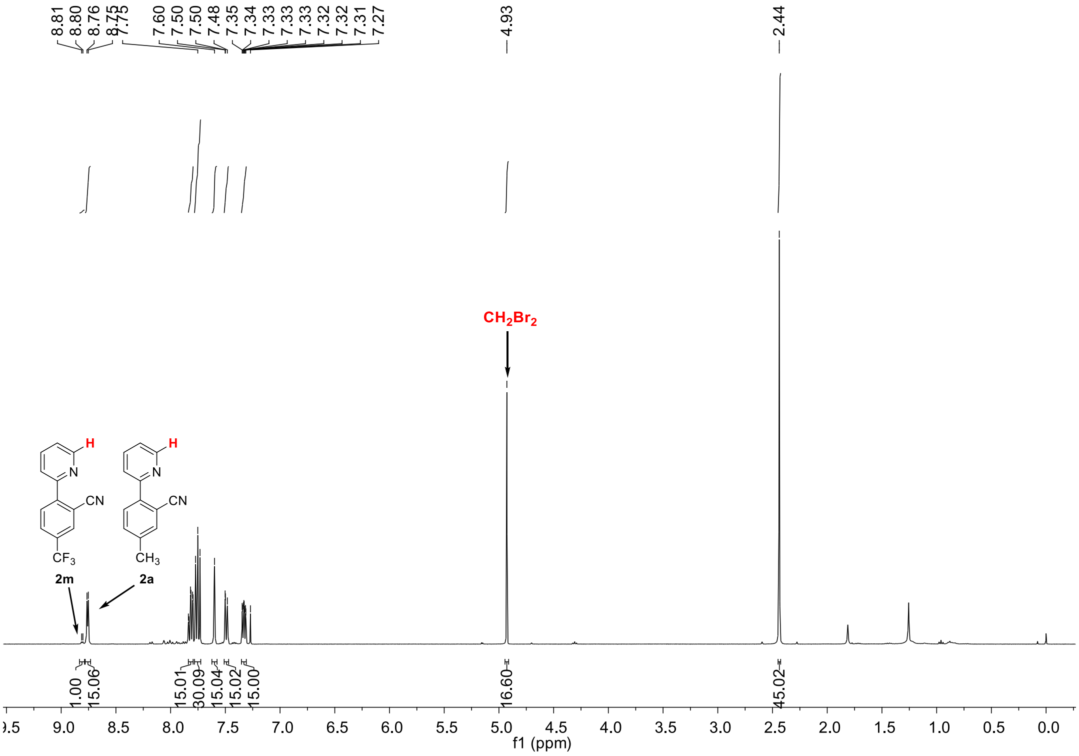


(3) Intermolecular competition experiment between substrates 1a and 1i



2a : **2m** = 15 : 1

A mixture of DMMN (38.7 mg, 0.40 mmol), 2-(*p*-tolyl)pyridine (**1a**, 33.8 mg, 0.2 mmol), 2-[4-(trifluoromethyl)phenyl]pyridine (**1m**, 44.6 mg, 0.2 mmol), [RhCp*(MeCN)$_3$](SbF$_6$)$_2$ (8.3 mg, 5 mol%), CuO (63.6 mg, 4.0 equiv.), and HFIP (1.0 mL) was stirred at 160 °C for 12 h. The solvent was removed under reduced pressure, and the residue obtained was purified by silica gel chromatography to afford a mixture of products **2a** (60% NMR yield) and **2m** (4% NMR yield). A 15:1 ratio of **2a** to **2m** was observed by ^{1}H NMR determination using dibromomethane (11.4 mg) as an internal standard.



7. References

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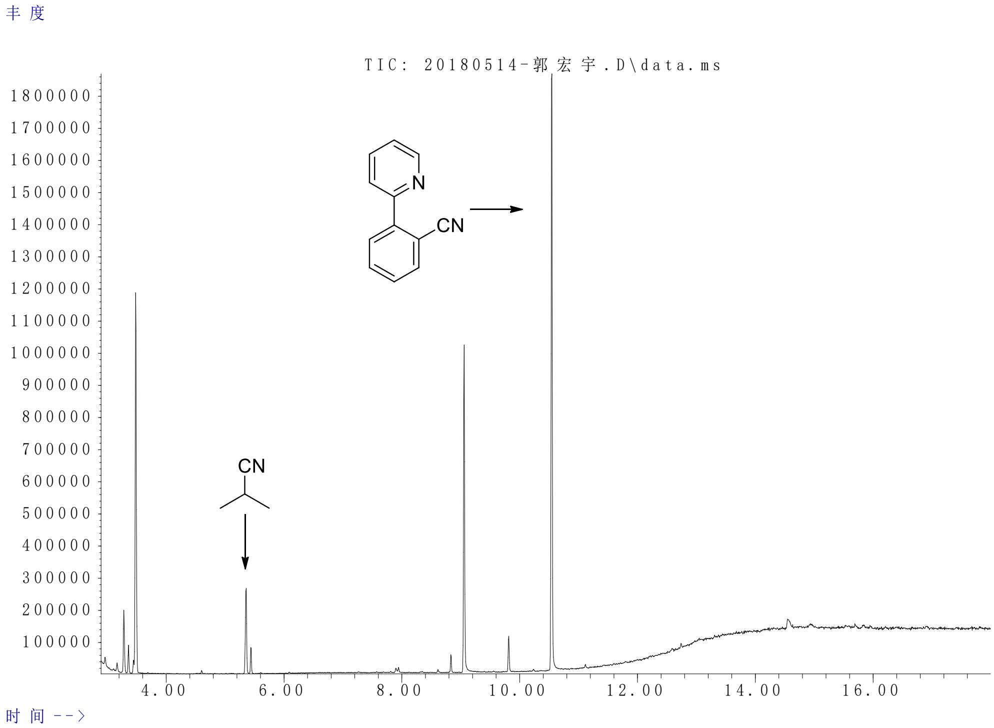
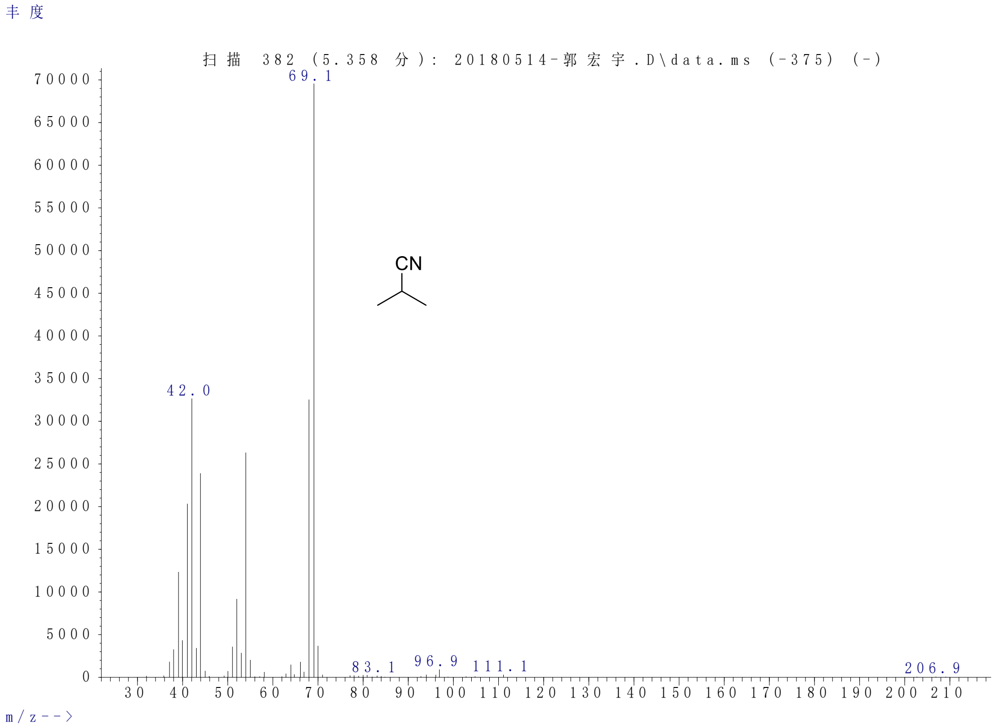
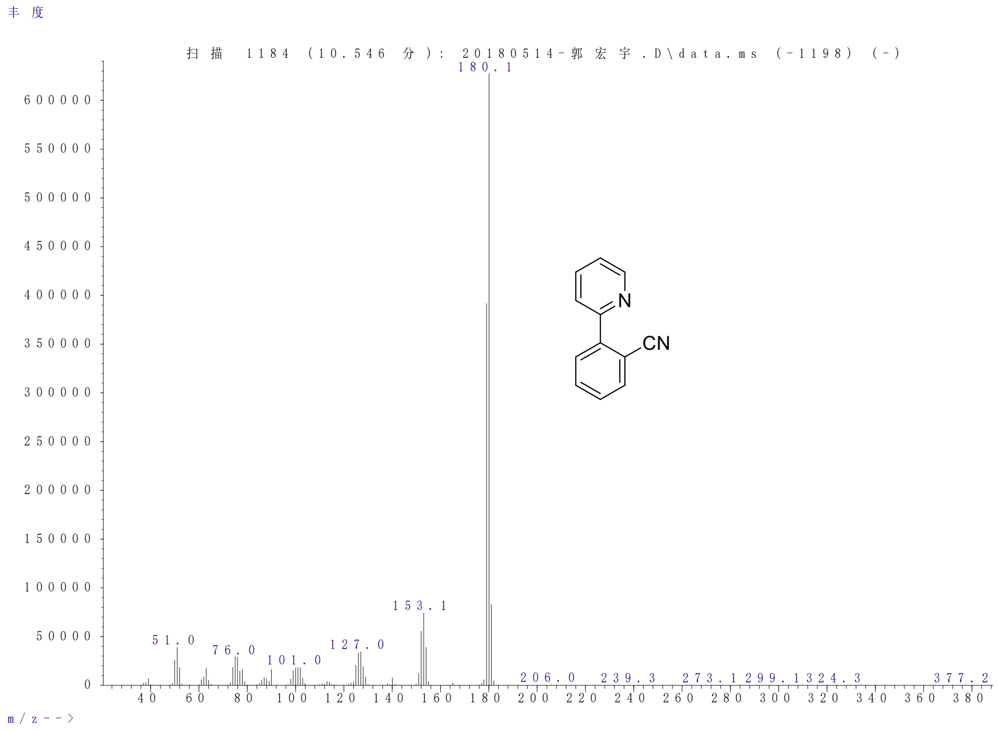
8. GC-MS Spectra of Reaction Mixture

(1) GC spectrum of reaction mixture



(2) MS spectra

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250000
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100000
50000
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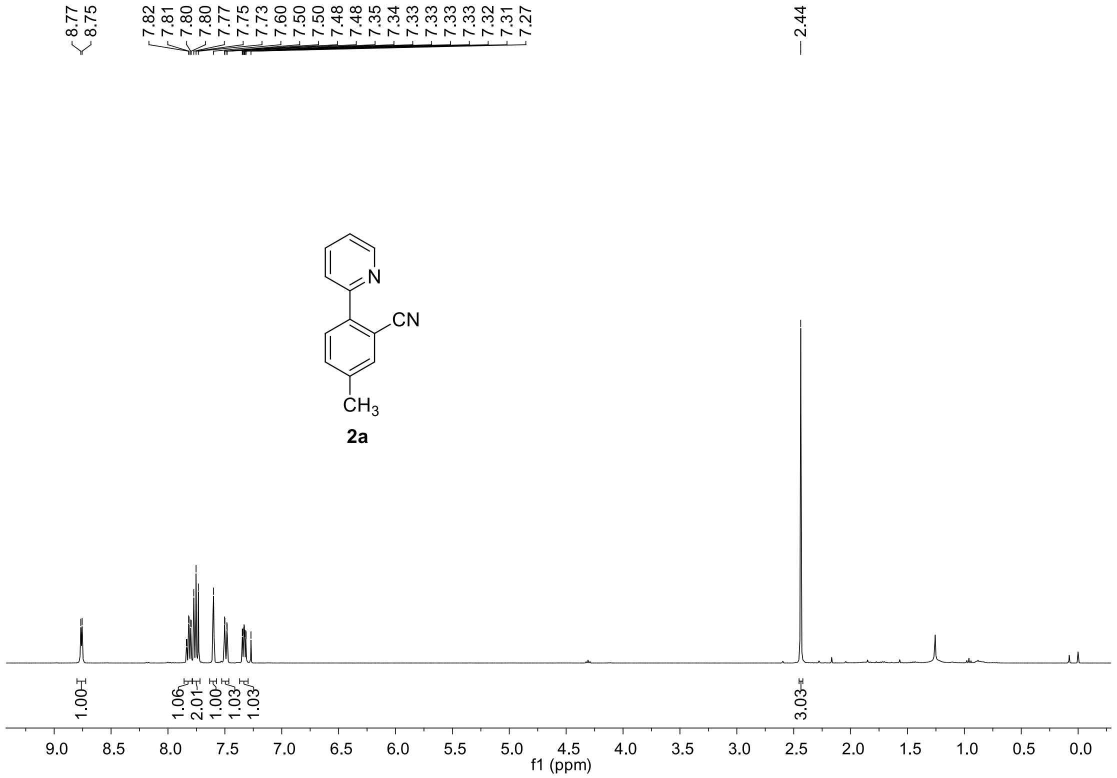
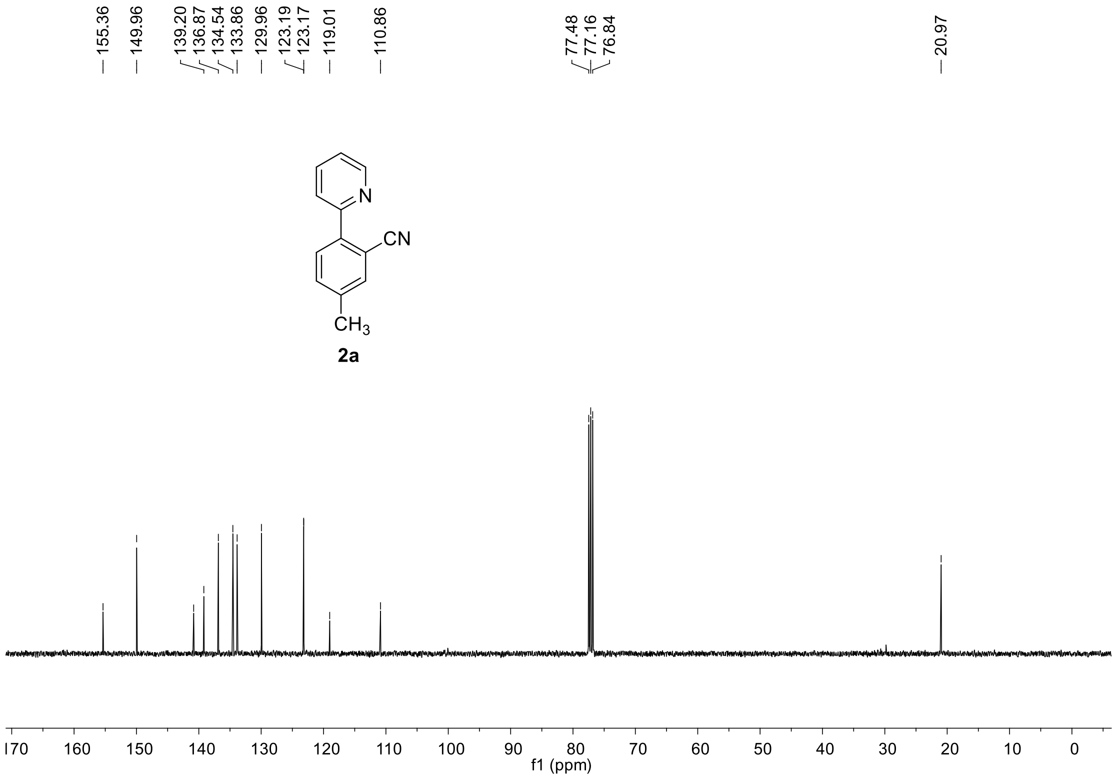
51.0
76.0
101.0
127.0
206.0
239.3
273.1
299.1
324.3
377.2
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380
m/z-->
N
CN

9. Copies of ^{1}H and ^{13}C NMR Spectra of Products

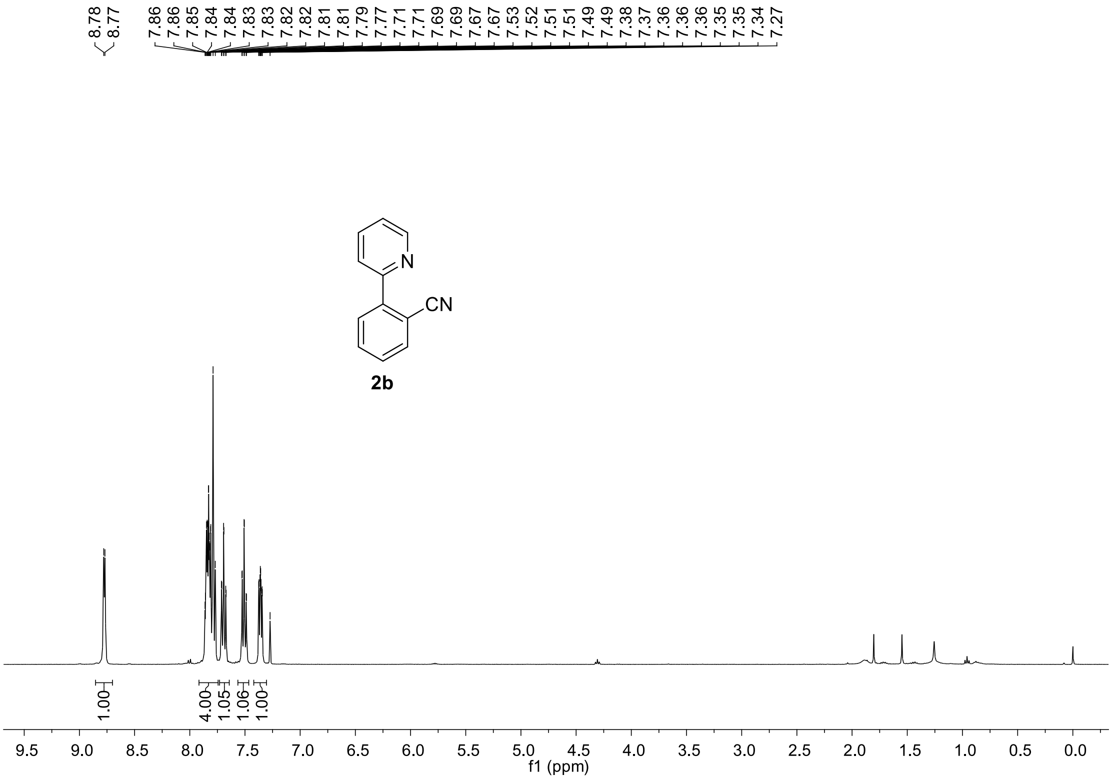
^{1}H NMR, 400 MHz, CDCl$_3$



^{13}C NMR, 100 MHz, CDCl$_3$

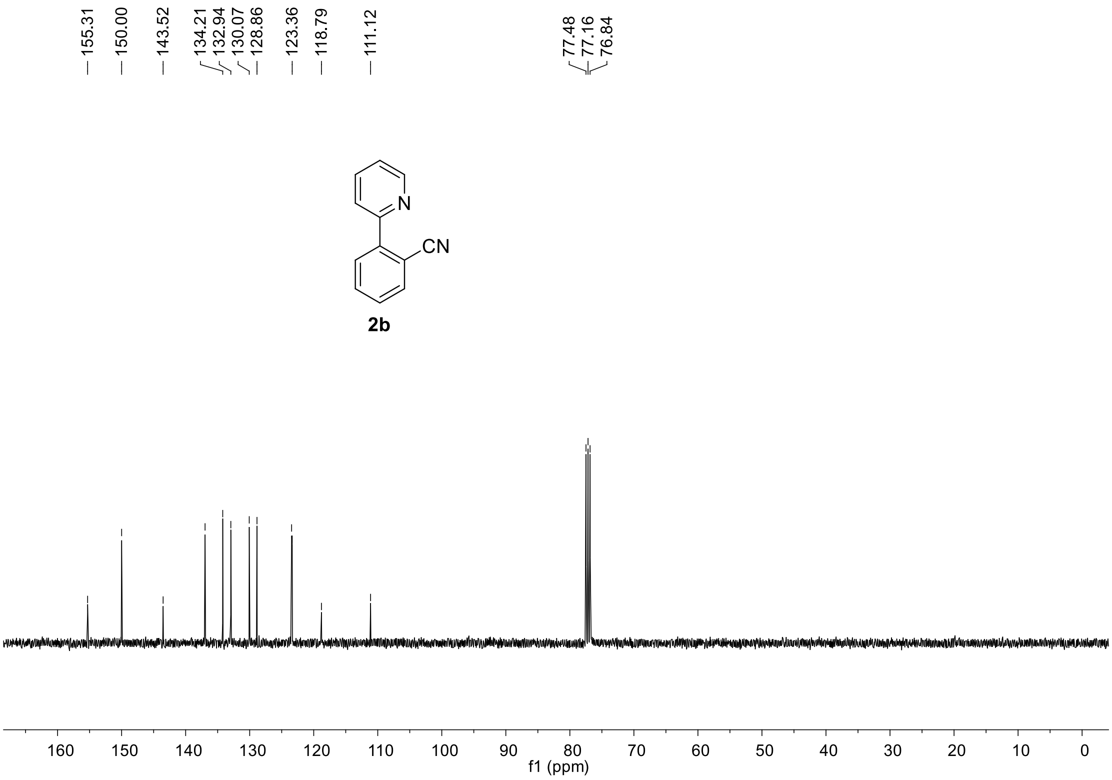


^{1}H NMR, 400 MHz, $CDCl_3$



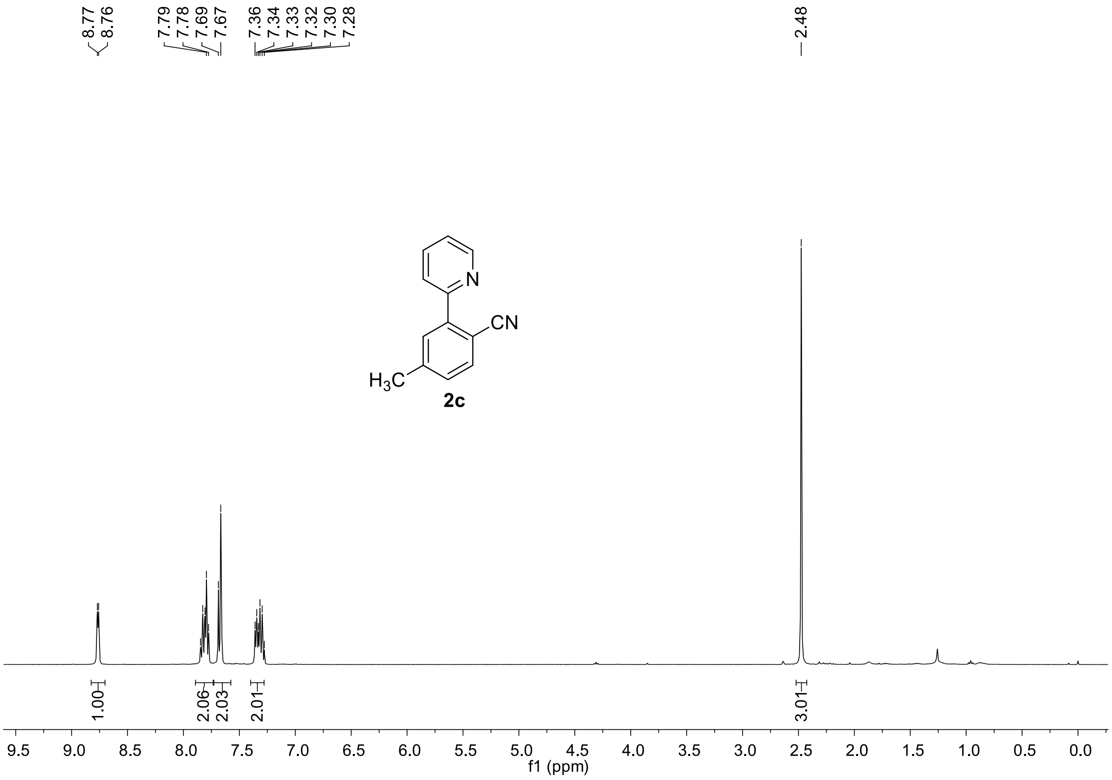
2b

^{13}C NMR, 100 MHz, $CDCl_3$

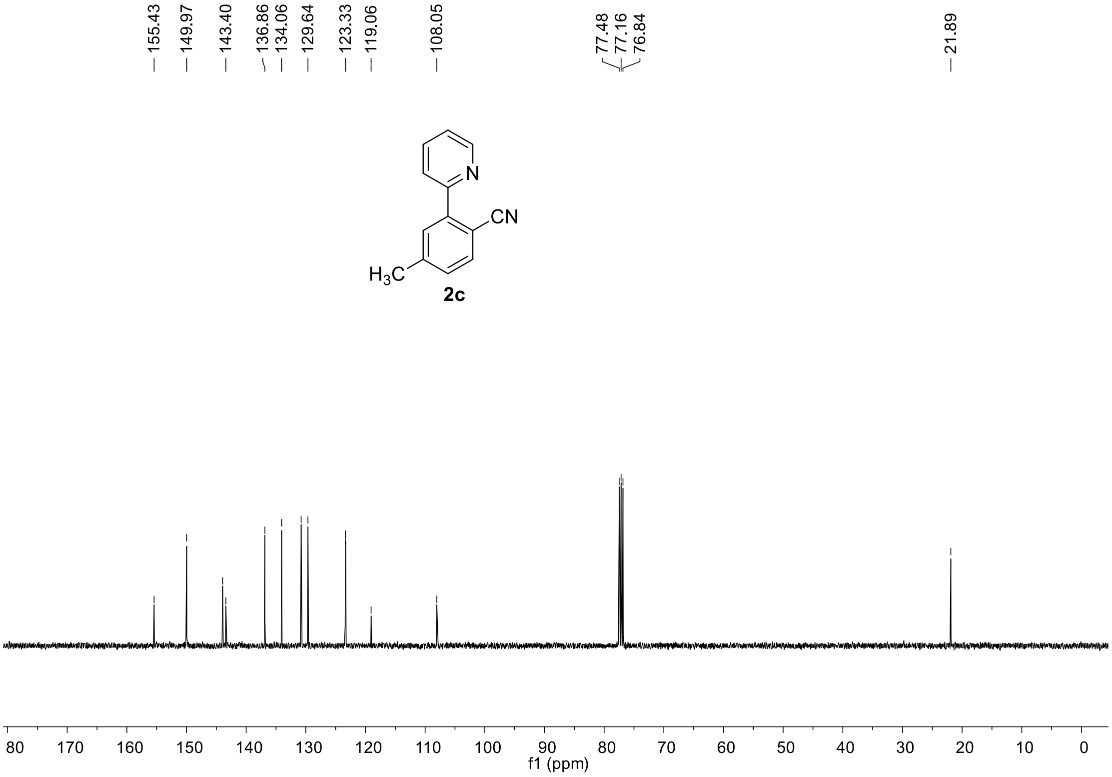


2b

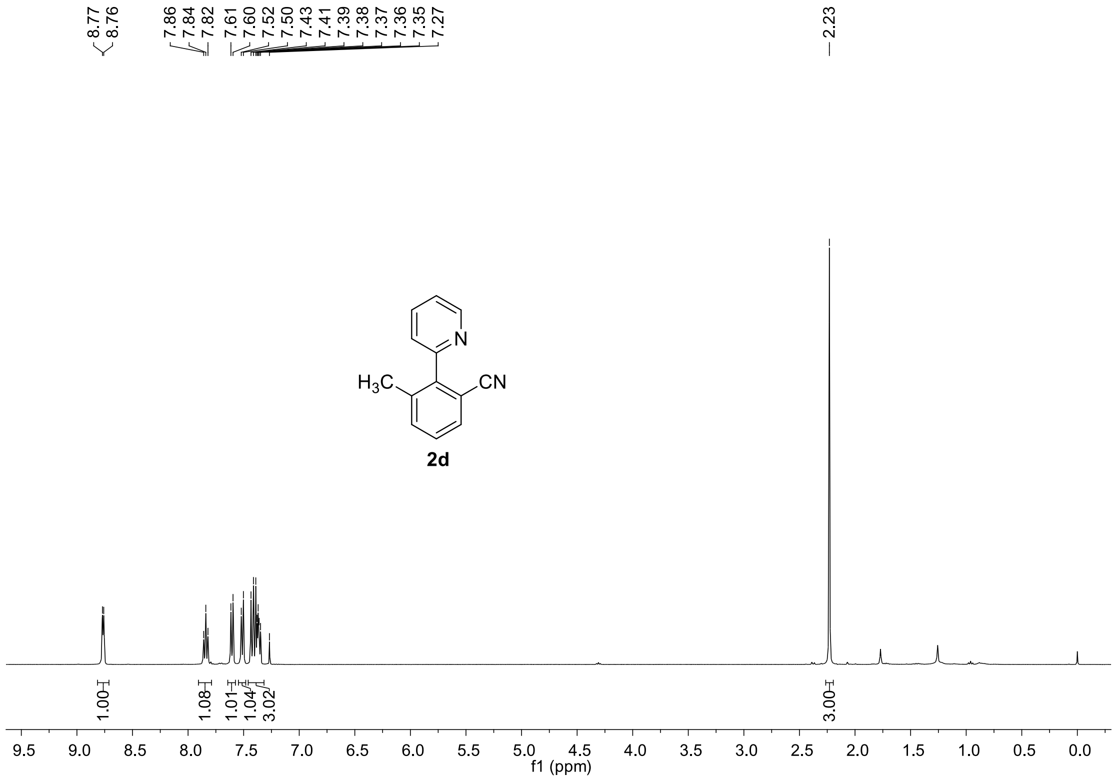
^{1}H NMR, 400 MHz, CDCl$_3$



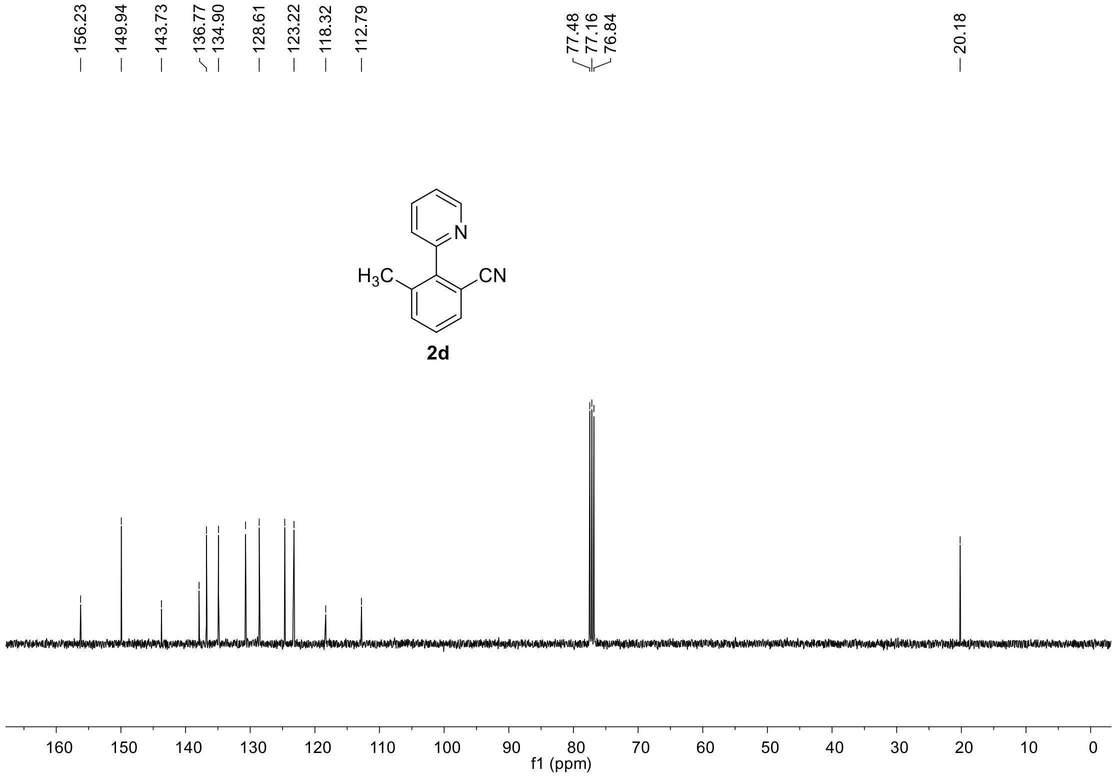
^{13}C NMR, 100 MHz, CDCl$_3$



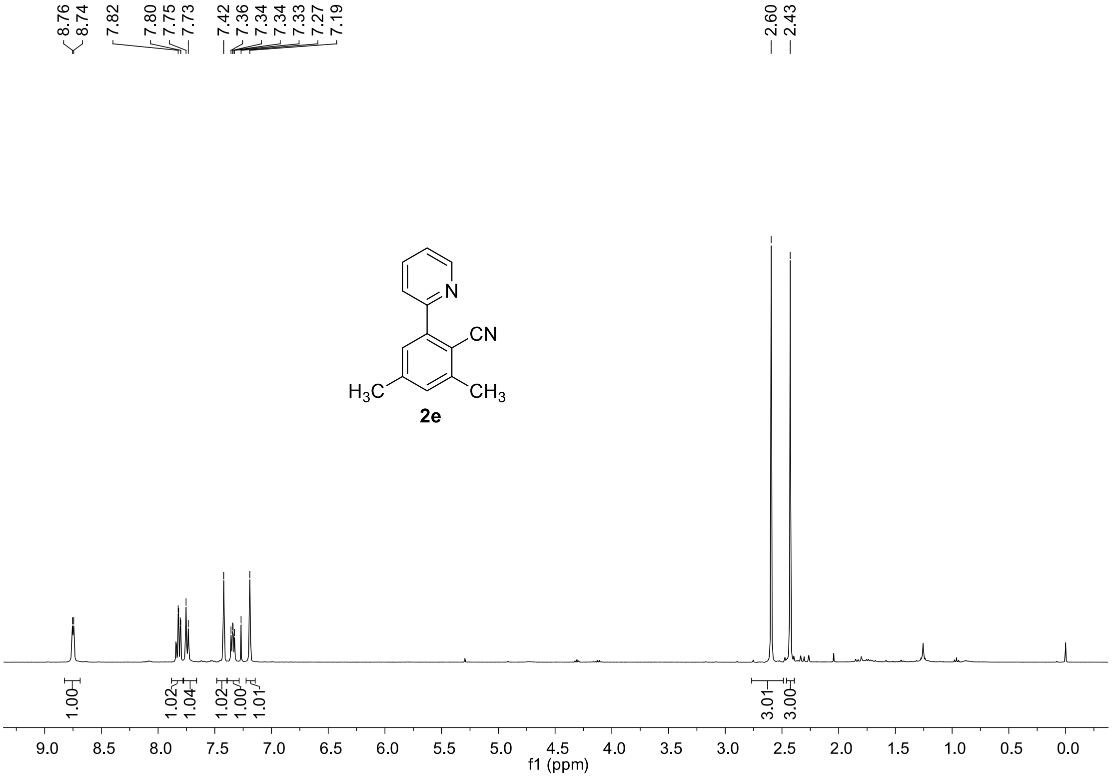
^{1}H NMR, 400 MHz, $CDCl_3$



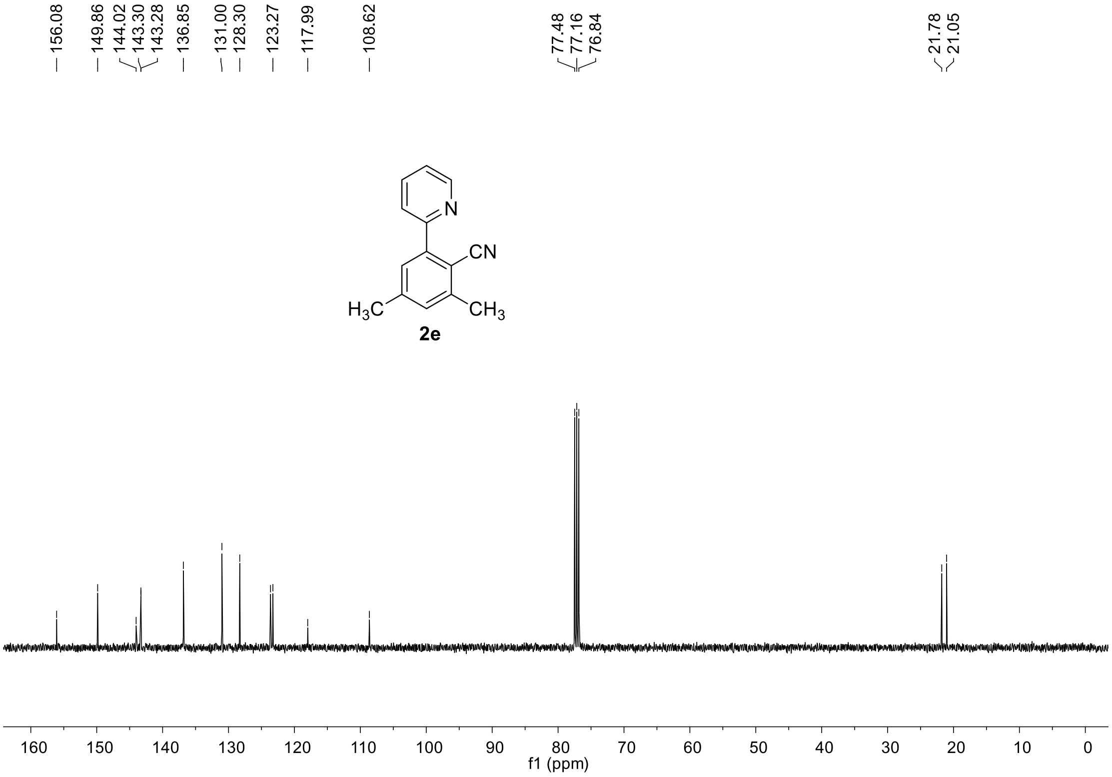
^{13}C NMR, 100 MHz, $CDCl_3$



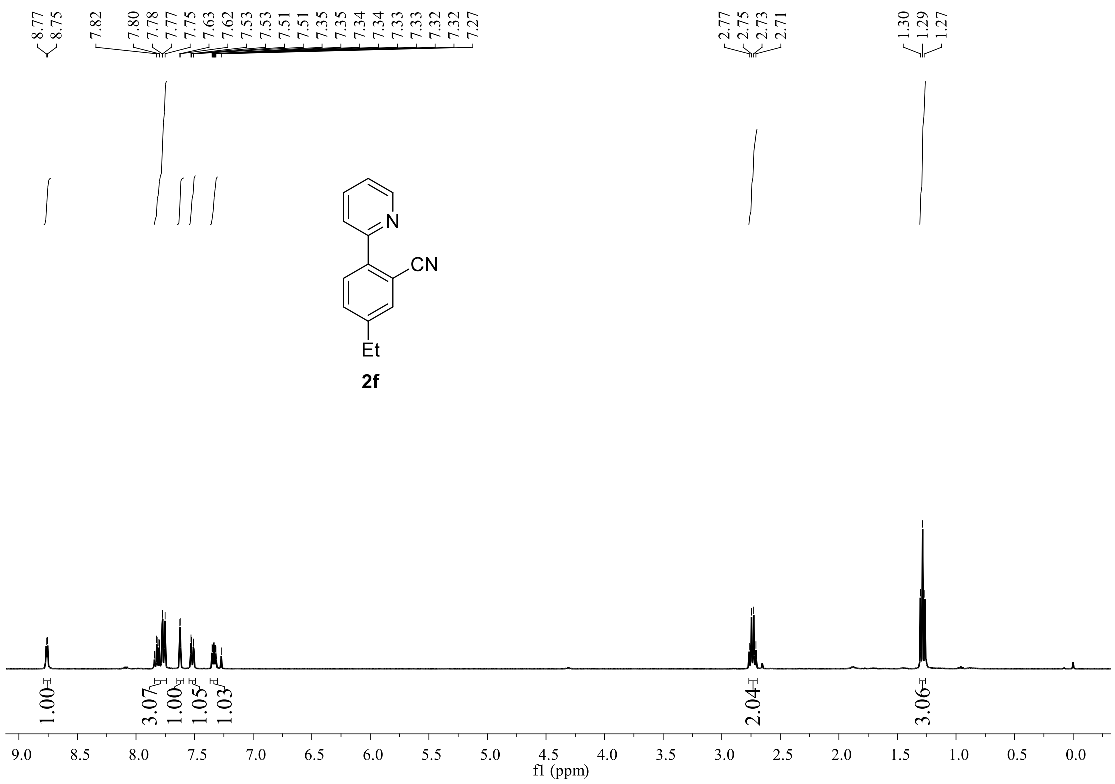
^{1}H NMR, 400 MHz, CDCl$_3$



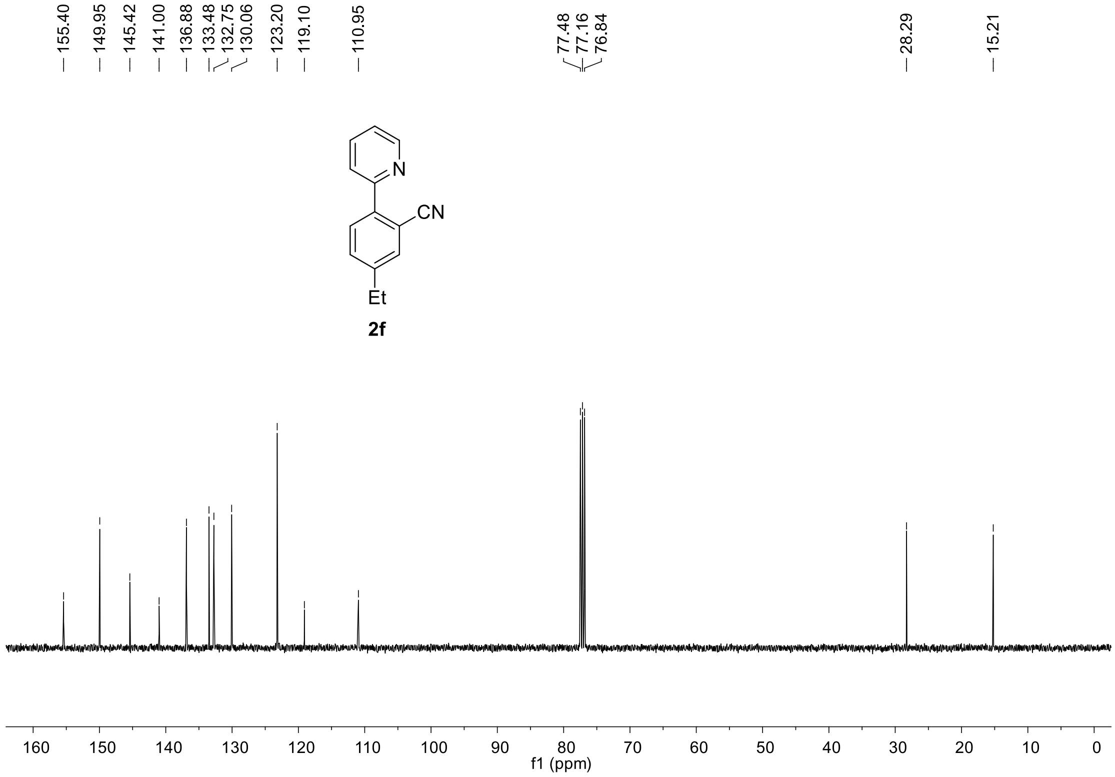
^{13}C NMR, 100 MHz, CDCl$_3$



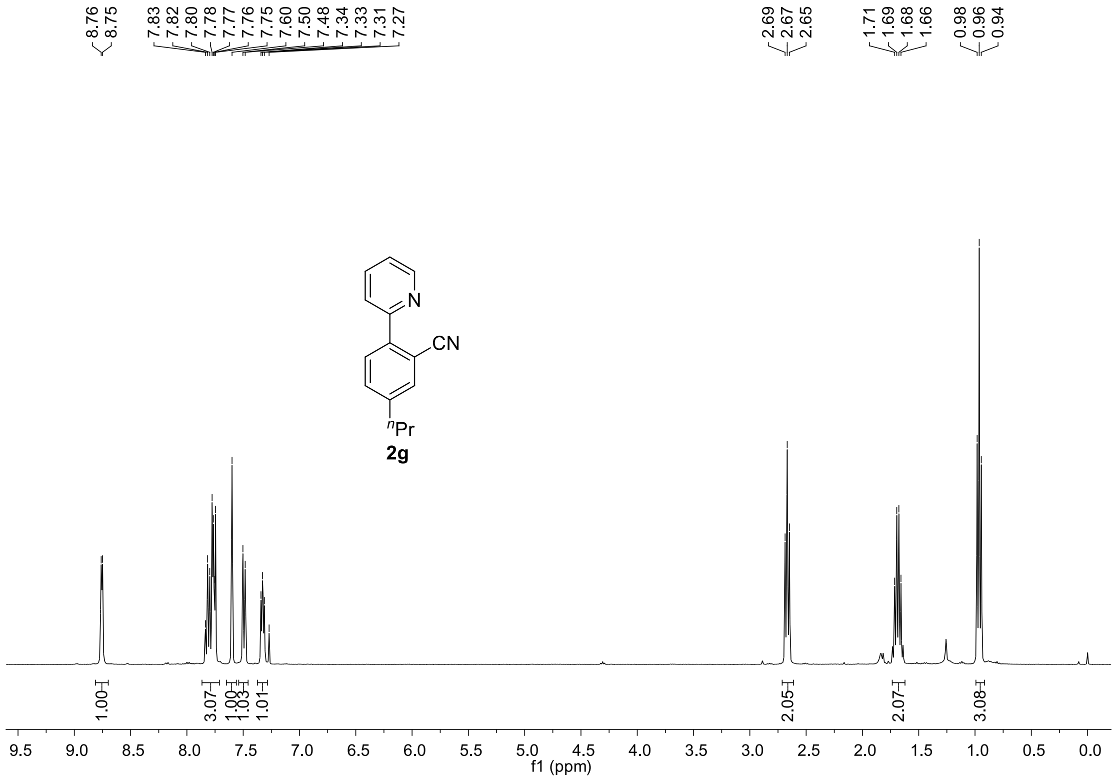
^{1}H NMR, 400 MHz, $CDCl_3$



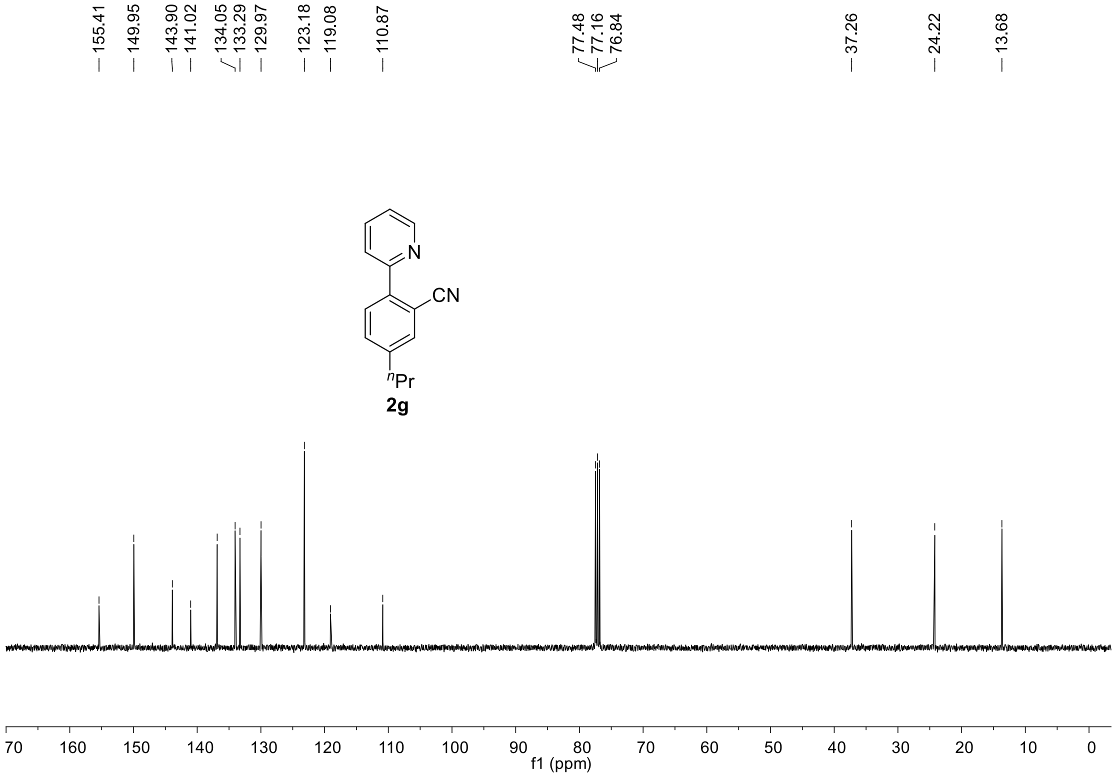
^{13}C NMR, 100 MHz, $CDCl_3$



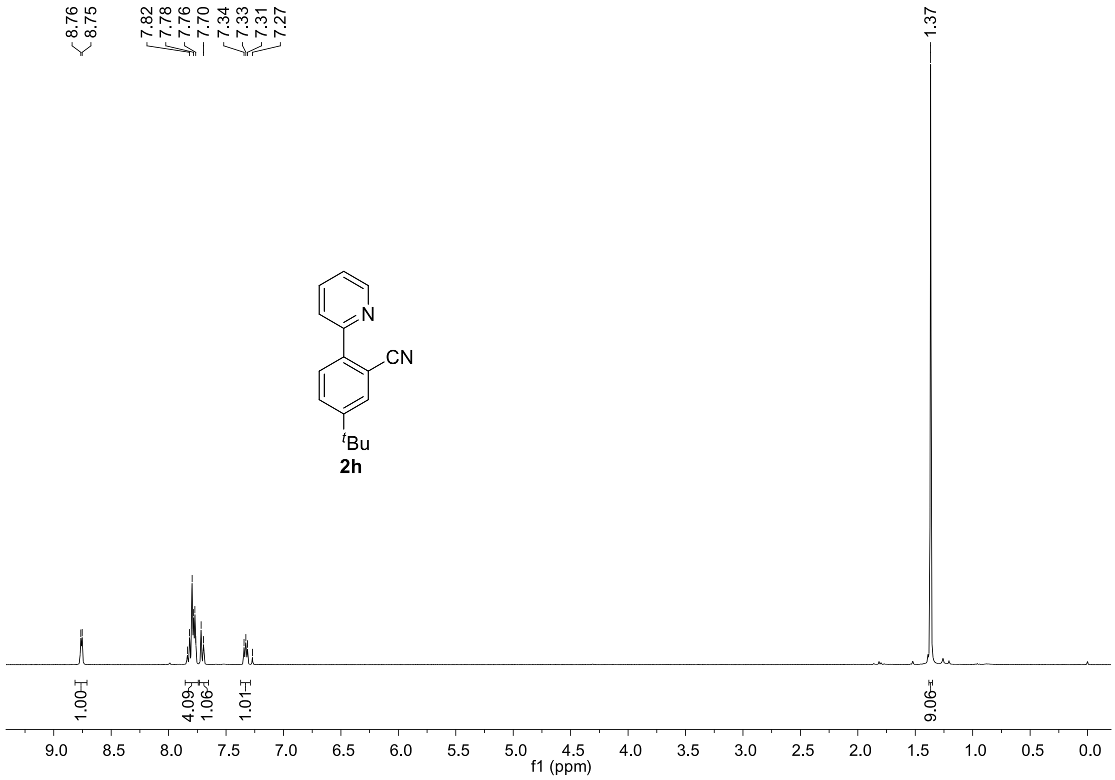
^{1}H NMR, 400 MHz, CDCl$_3$



^{13}C NMR, 100 MHz, CDCl$_3$

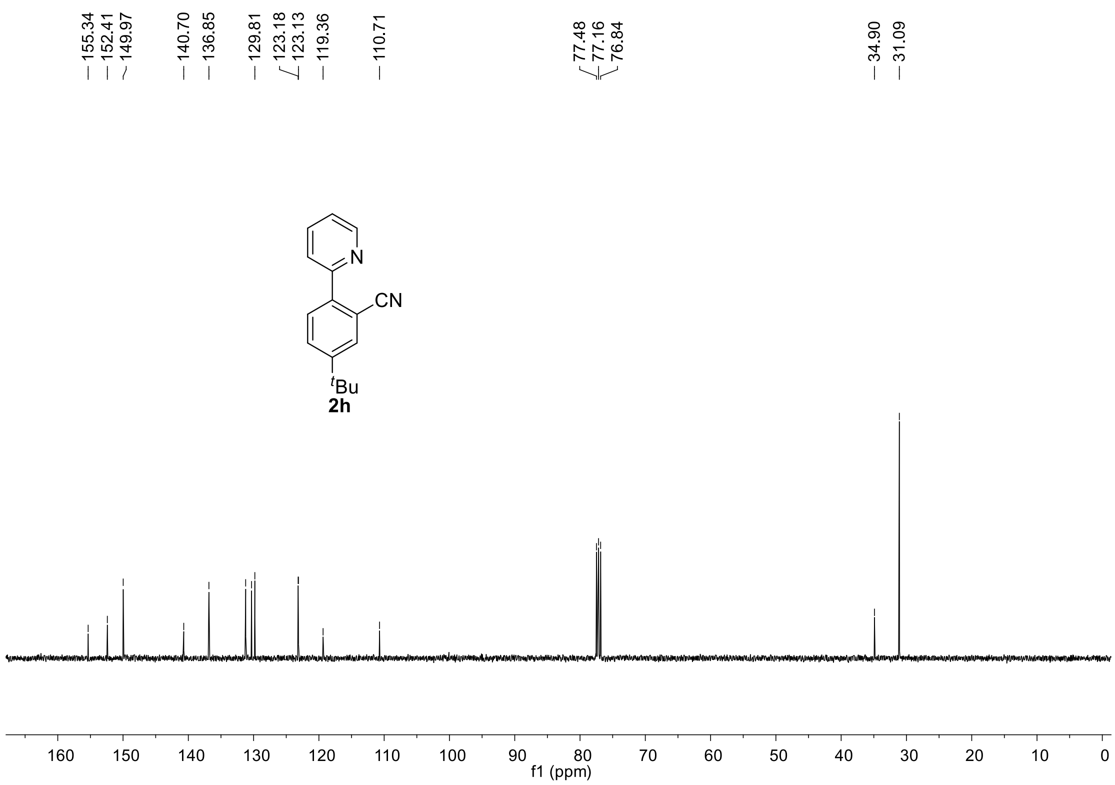


^{1}H NMR, 400 MHz, CDCl$_3$



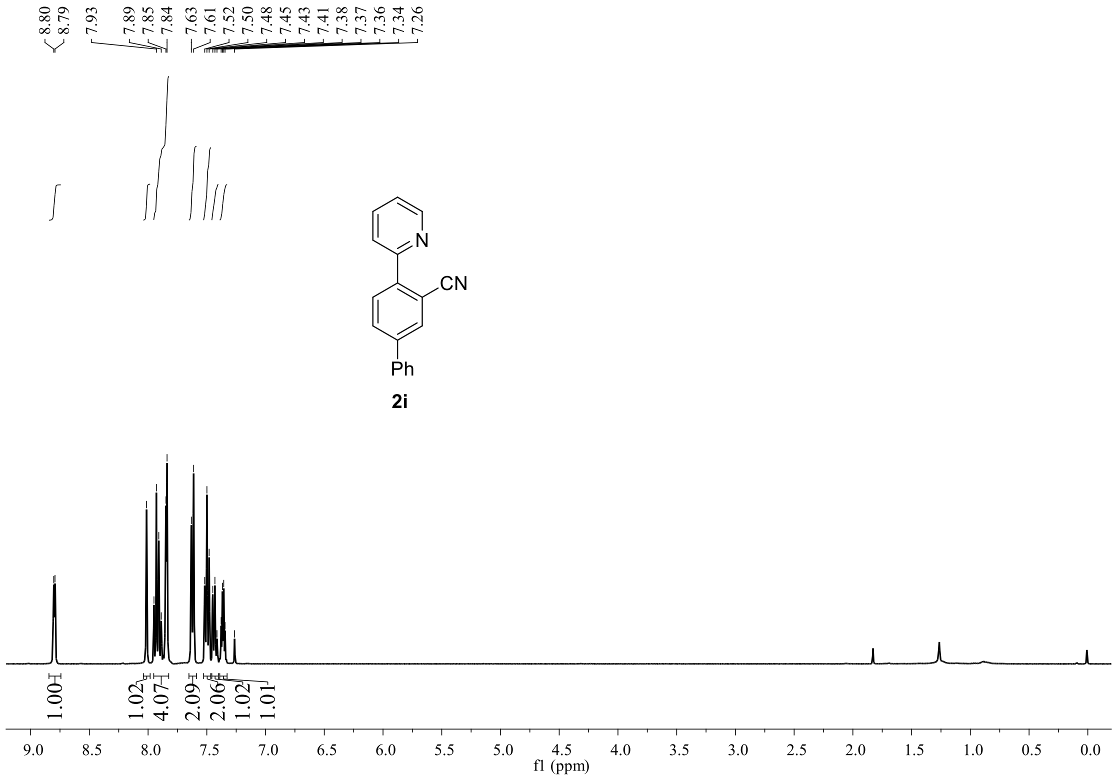
2h

^{13}C NMR, 100 MHz, CDCl$_3$



2h

^{1}H NMR, 400 MHz, CDCl$_3$



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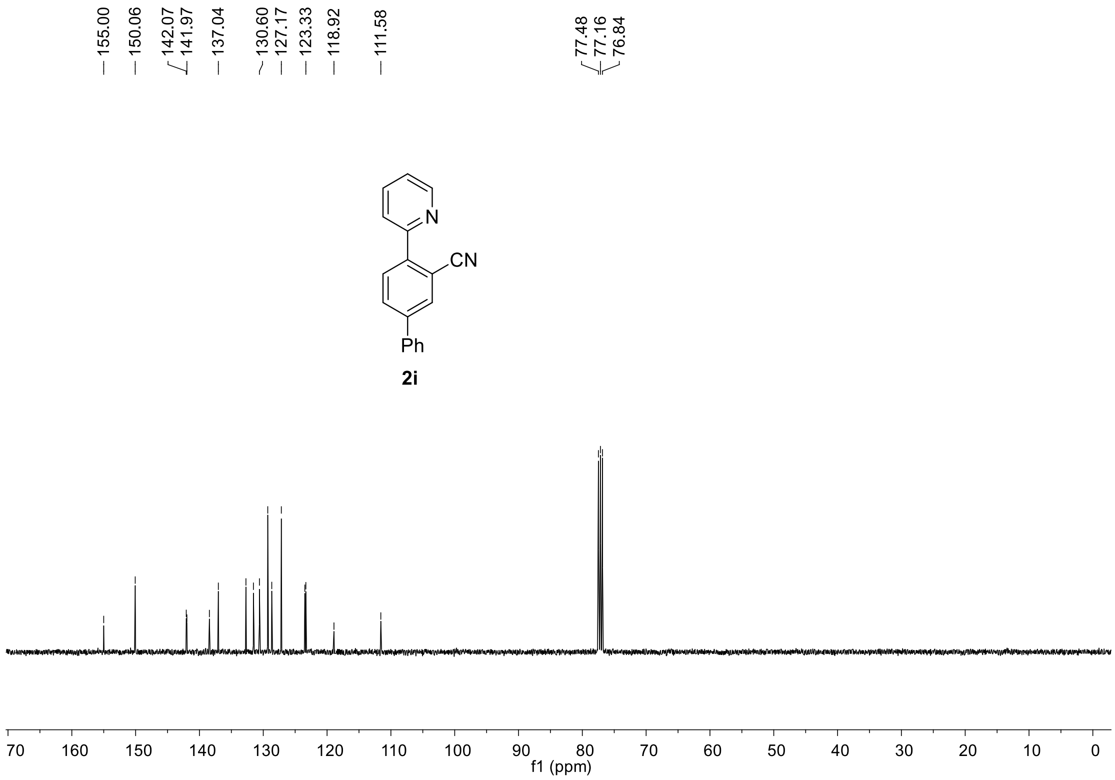

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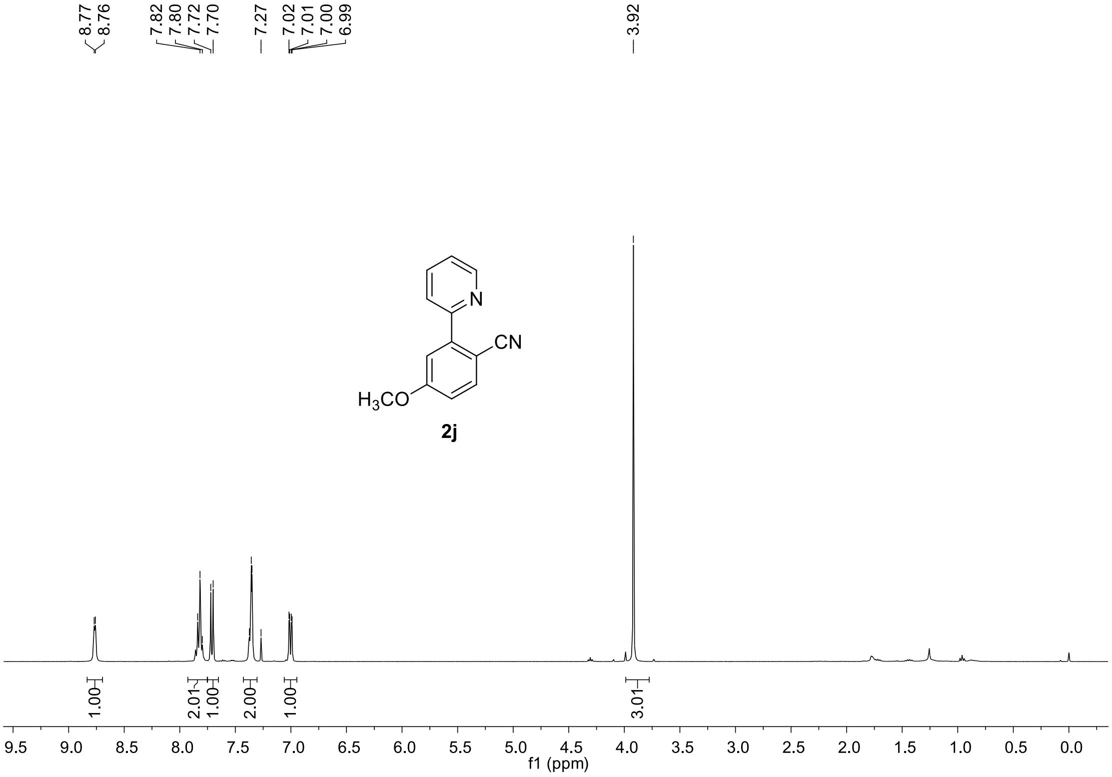

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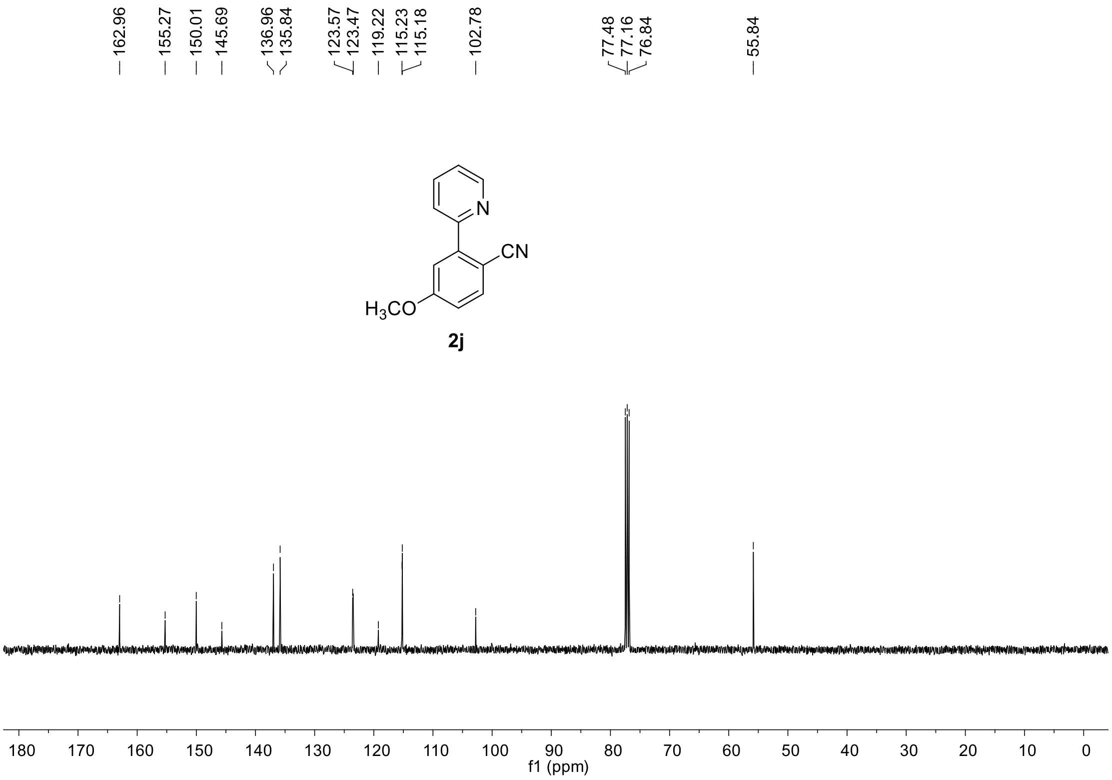

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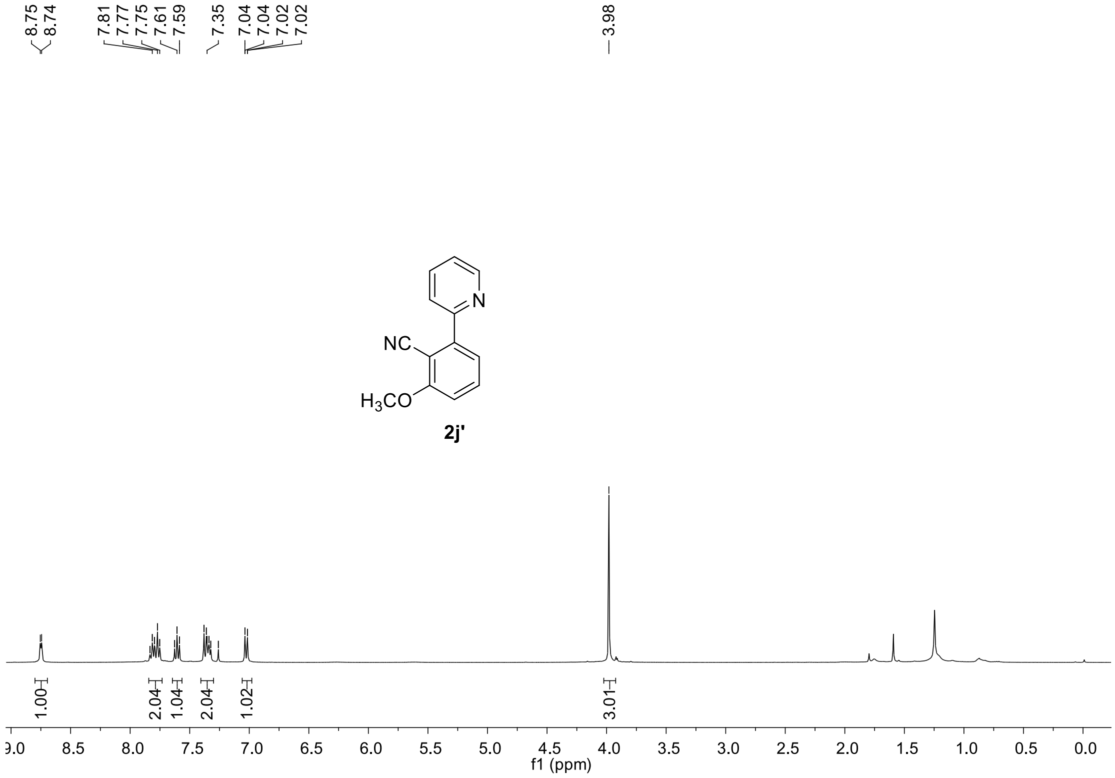

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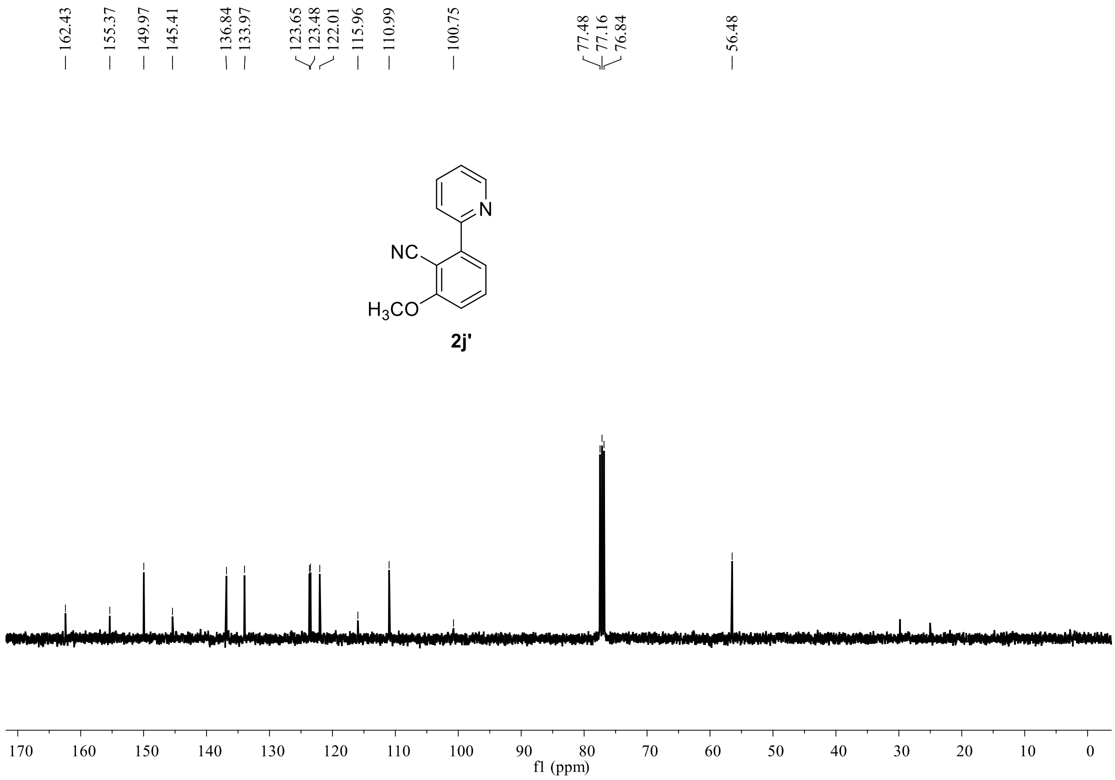

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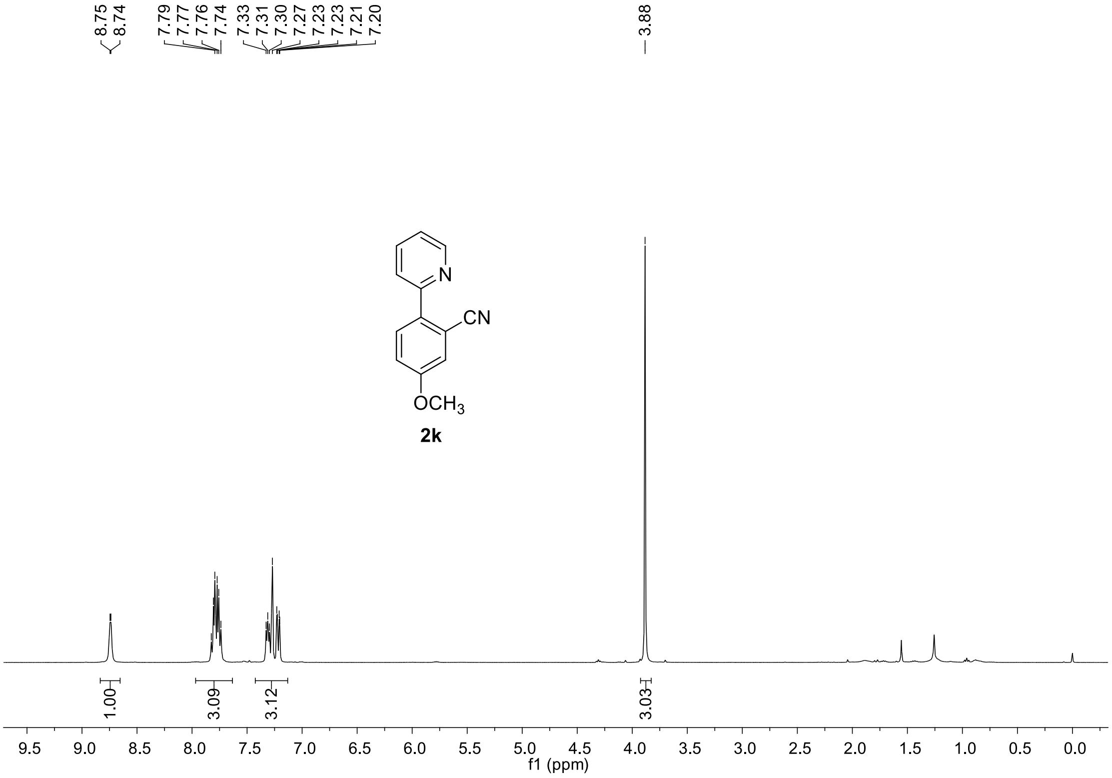

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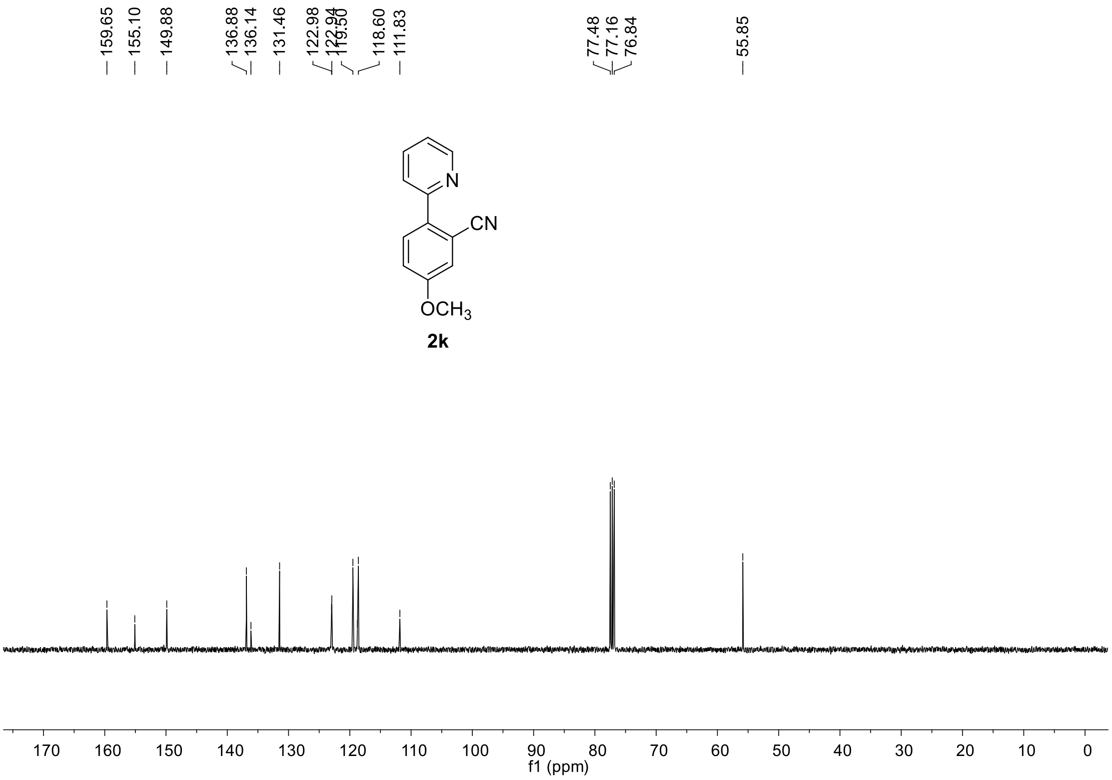

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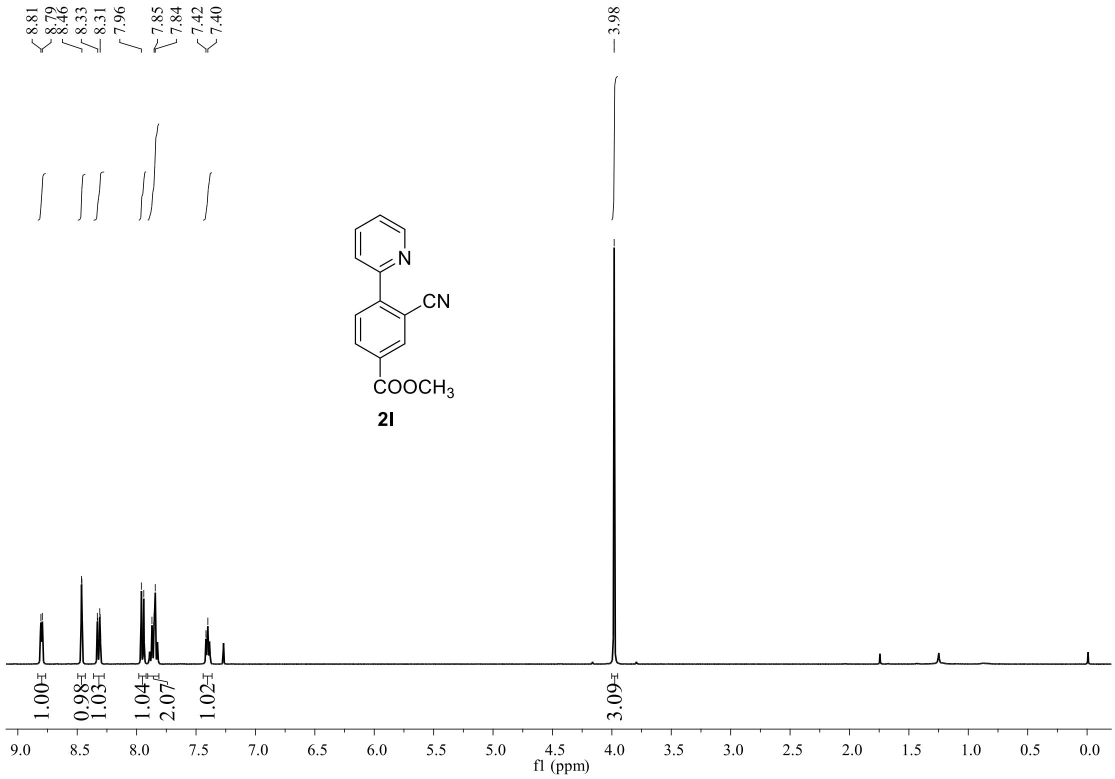

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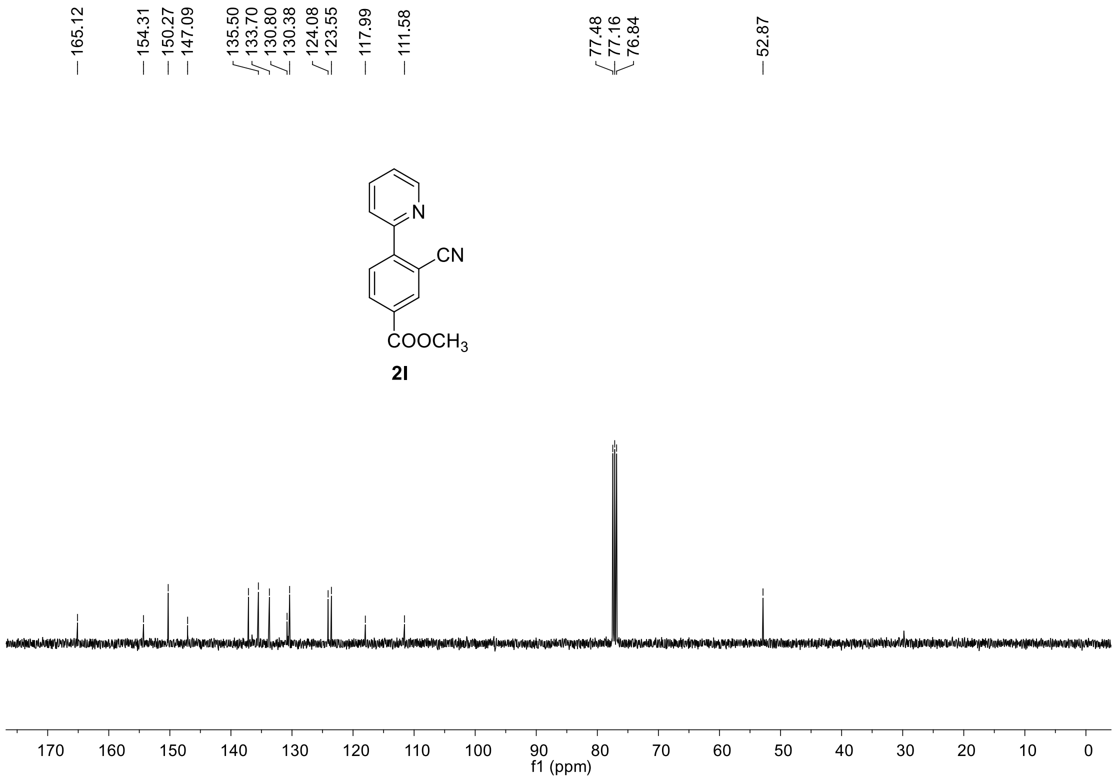

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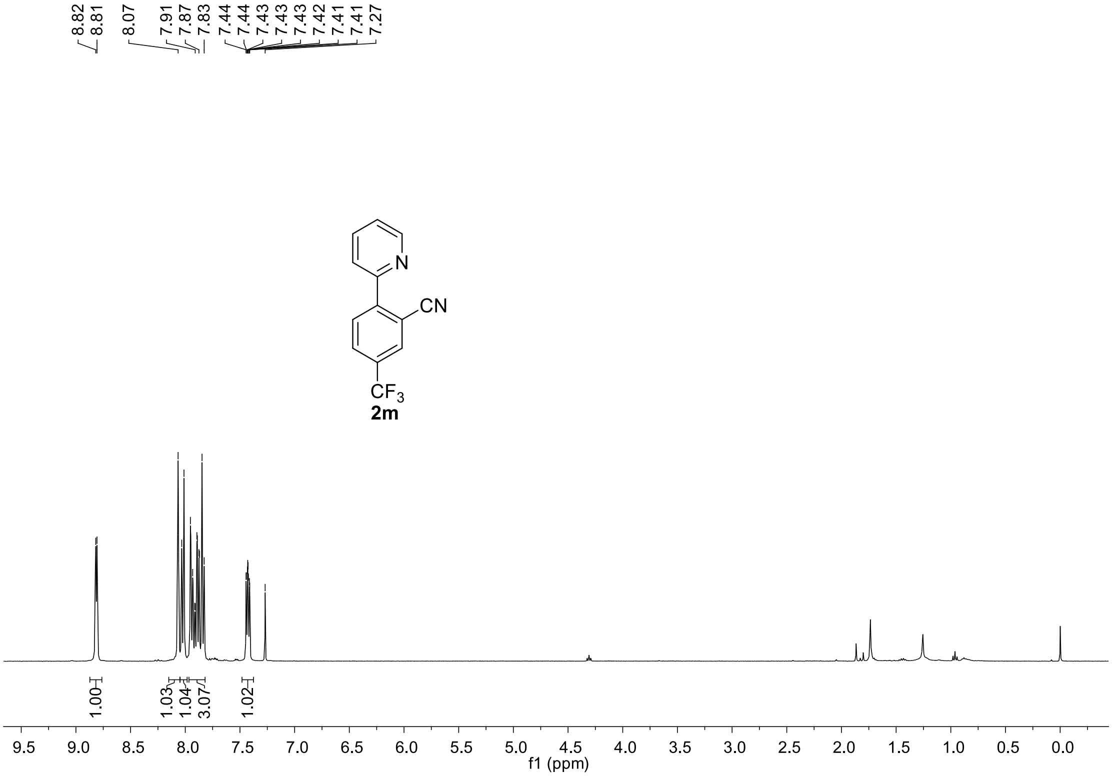

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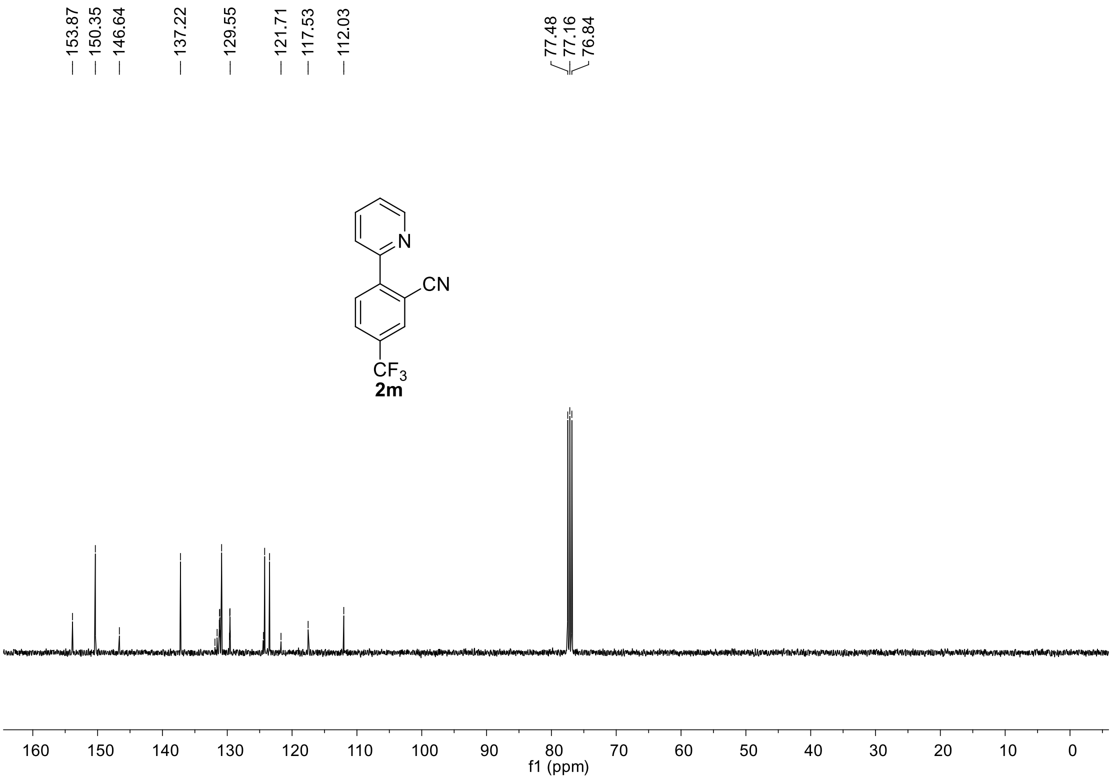

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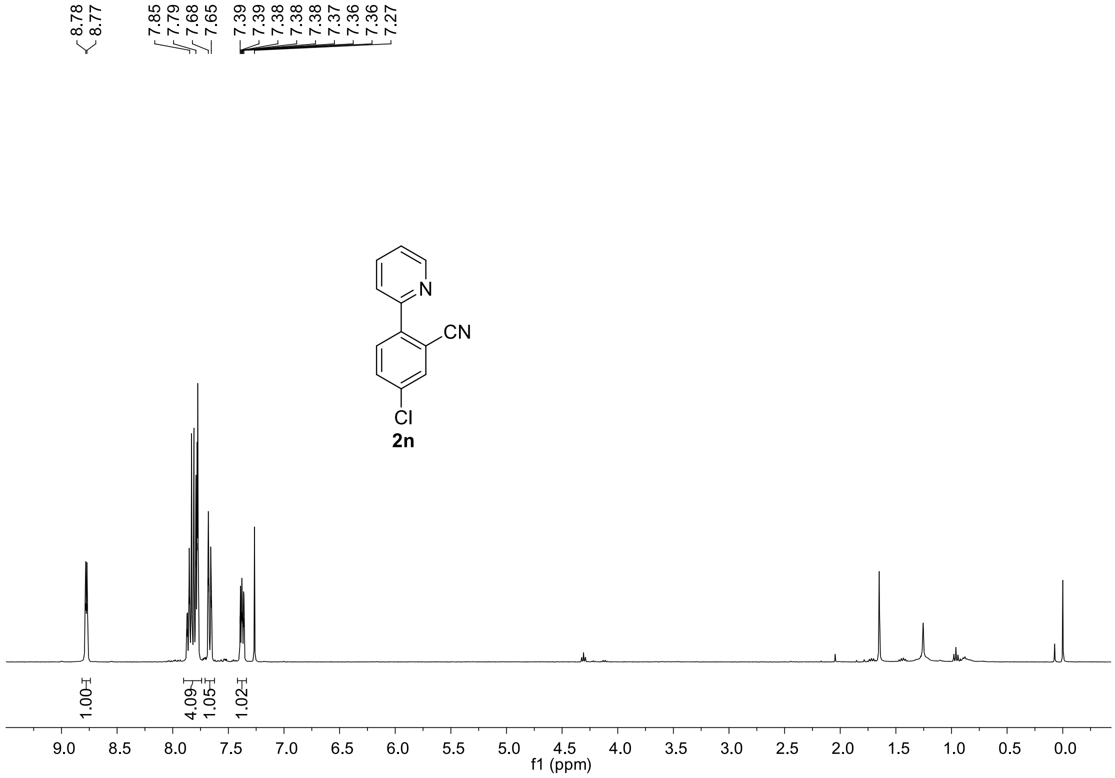

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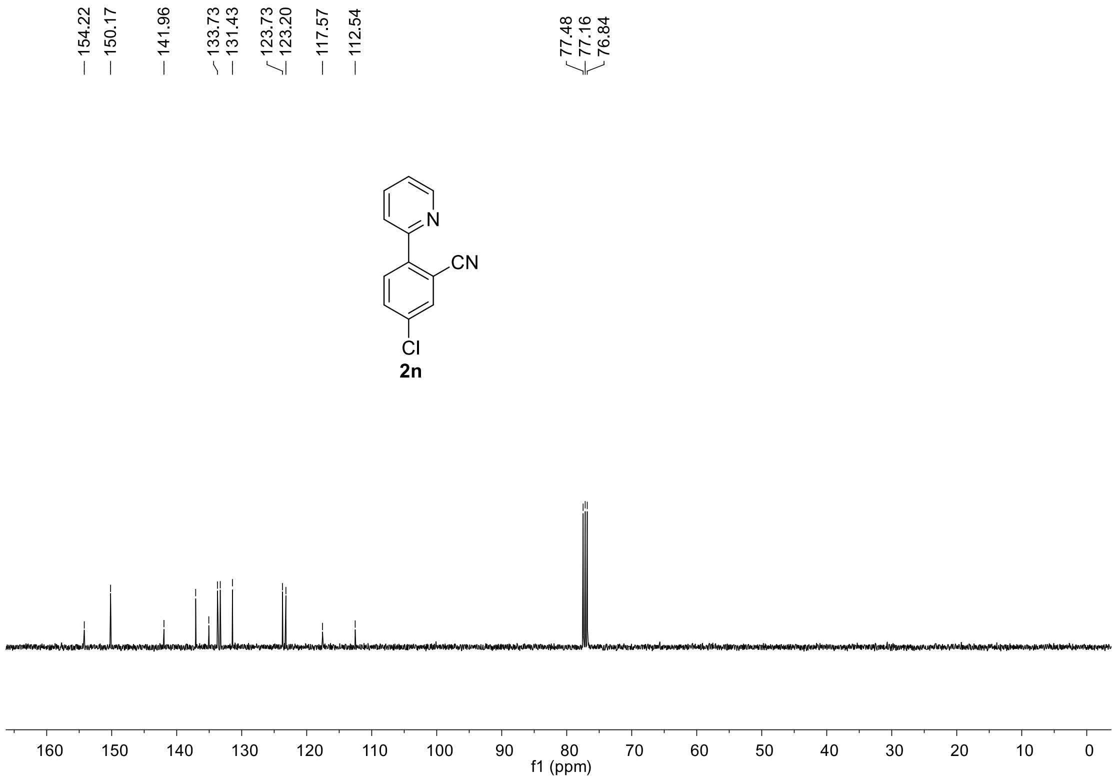

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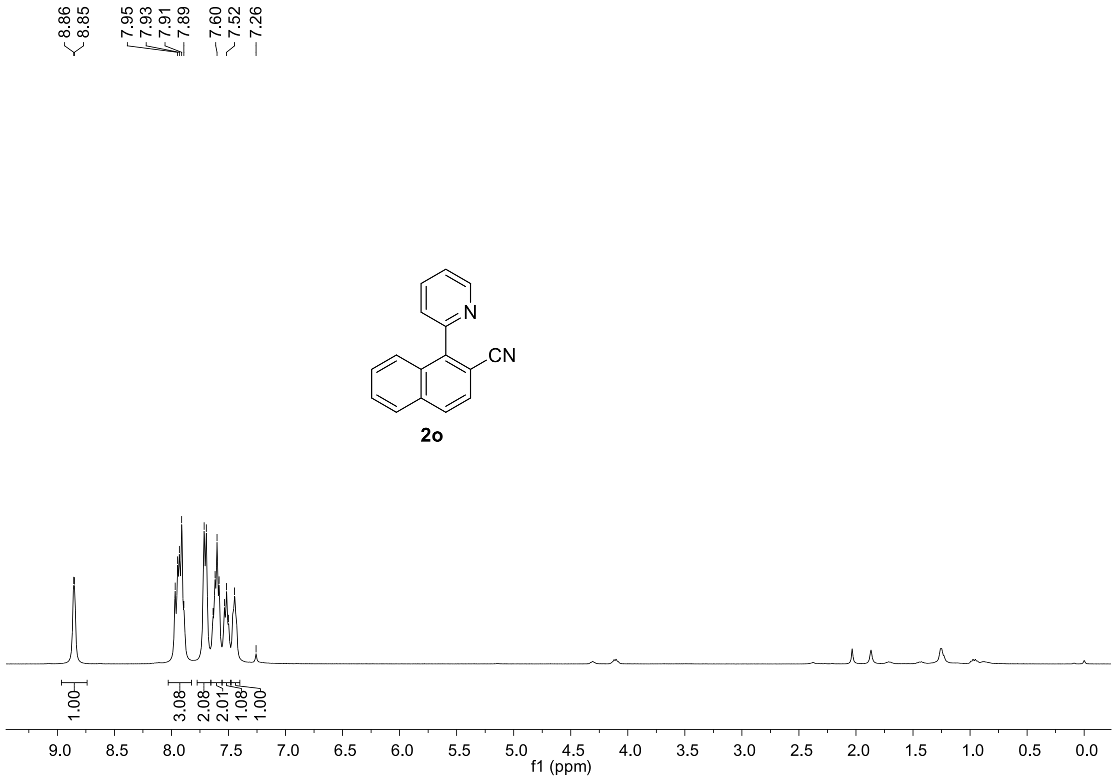

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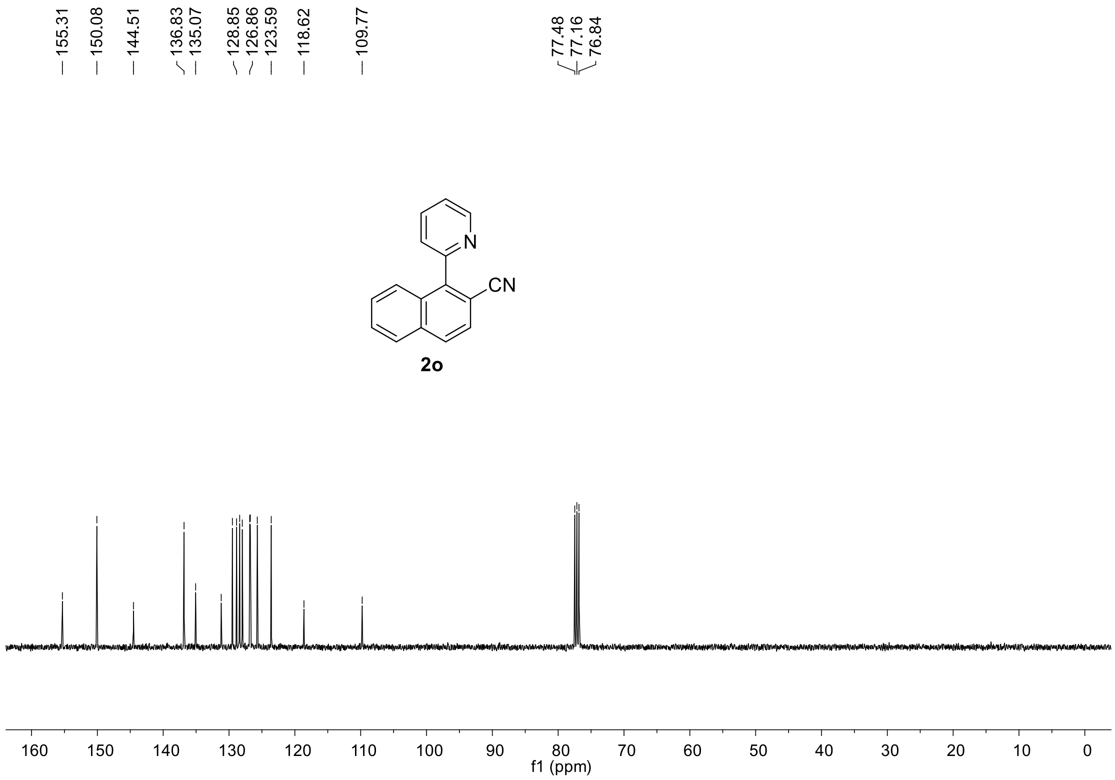

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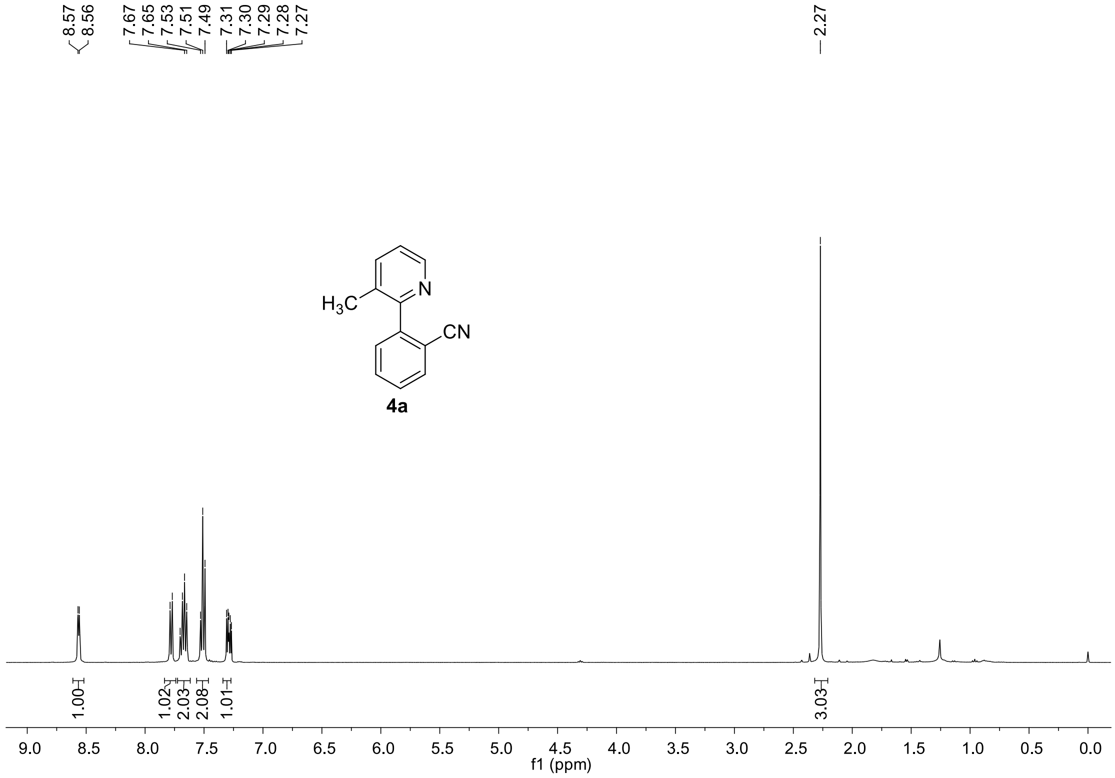

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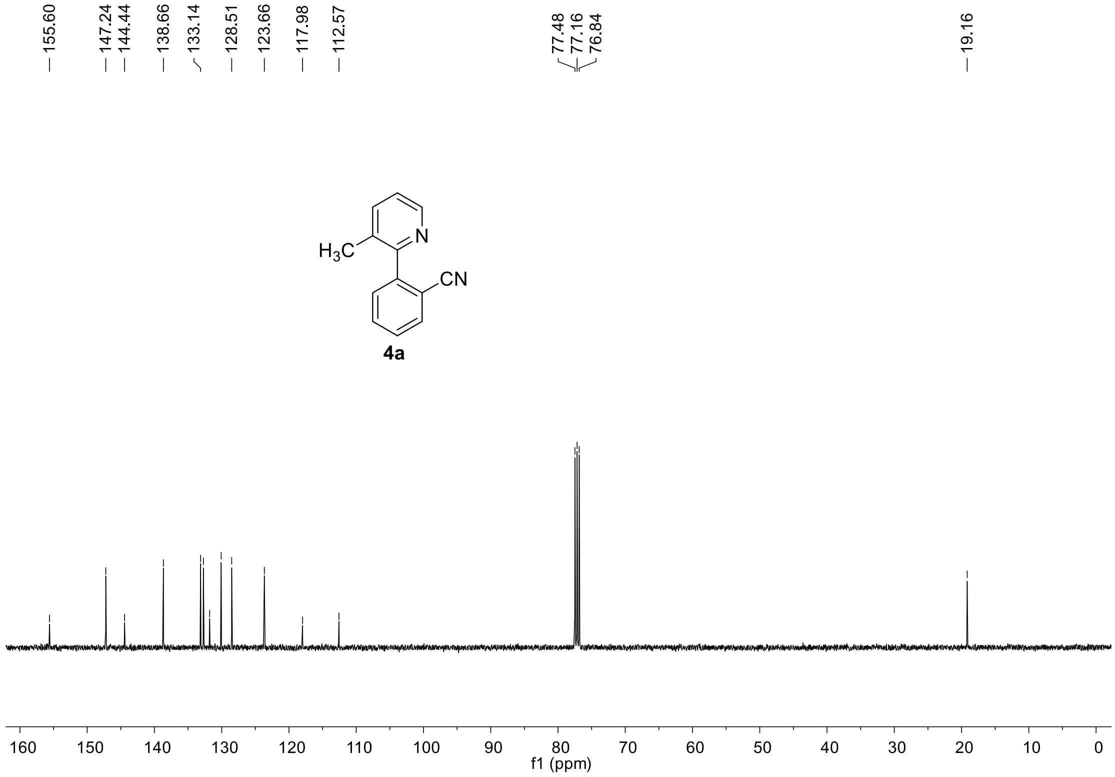

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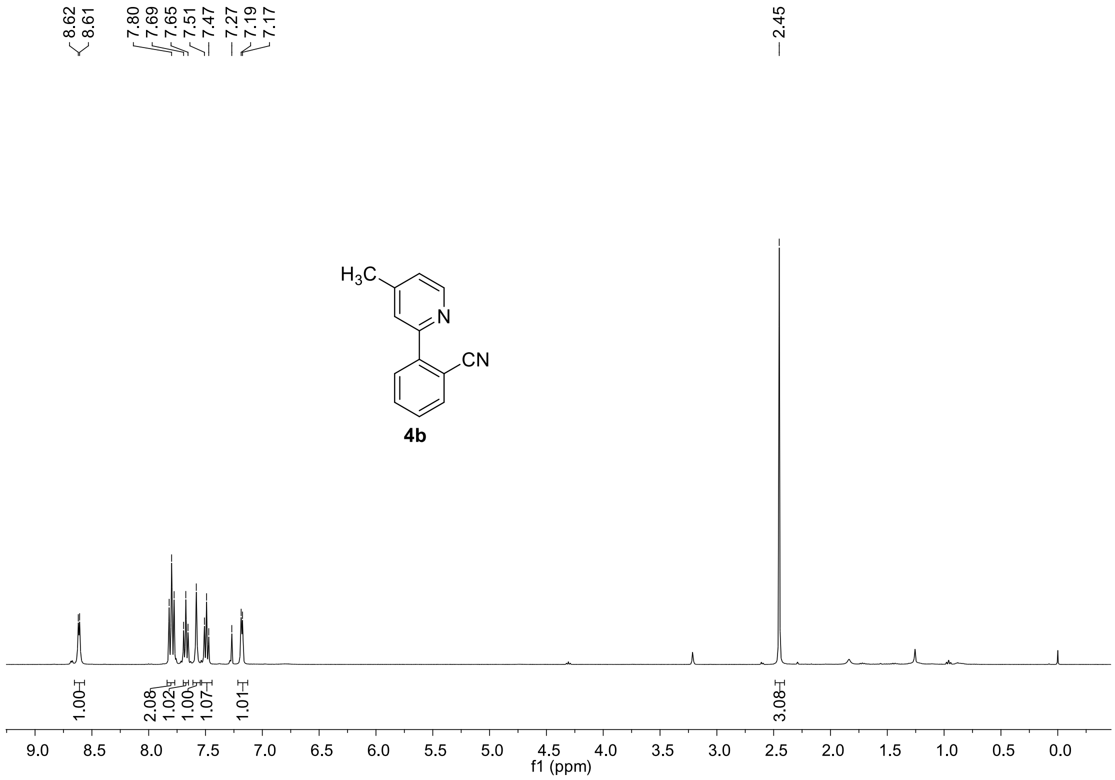

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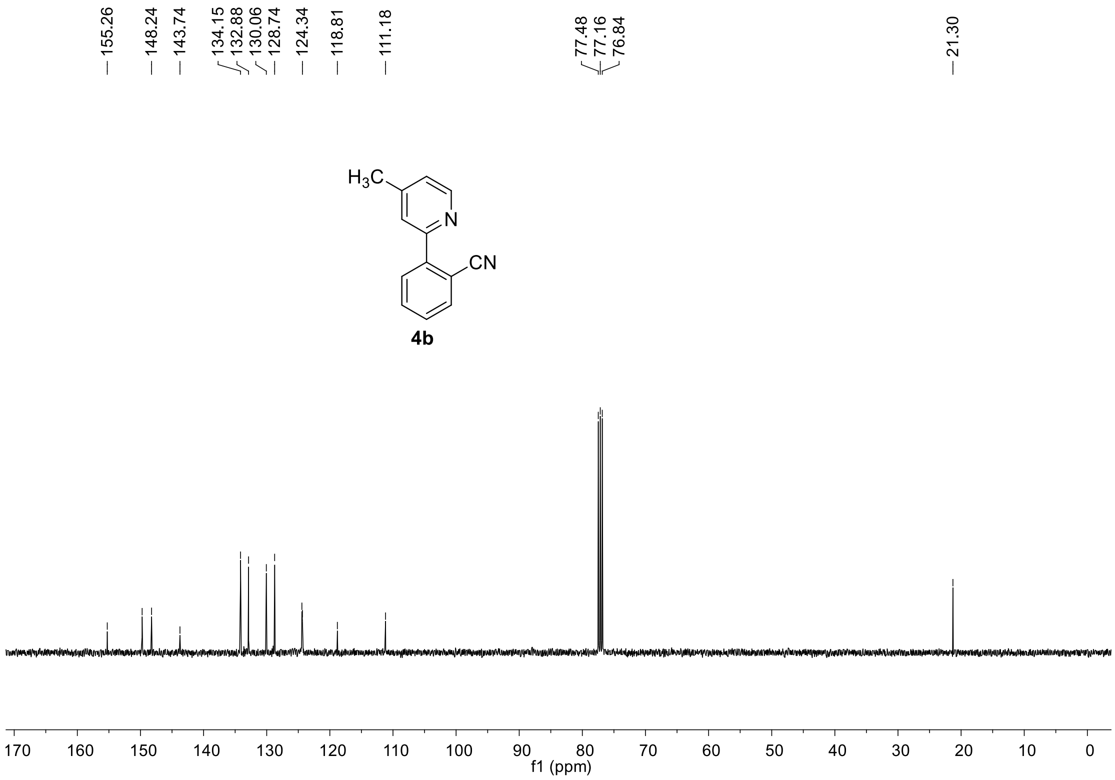

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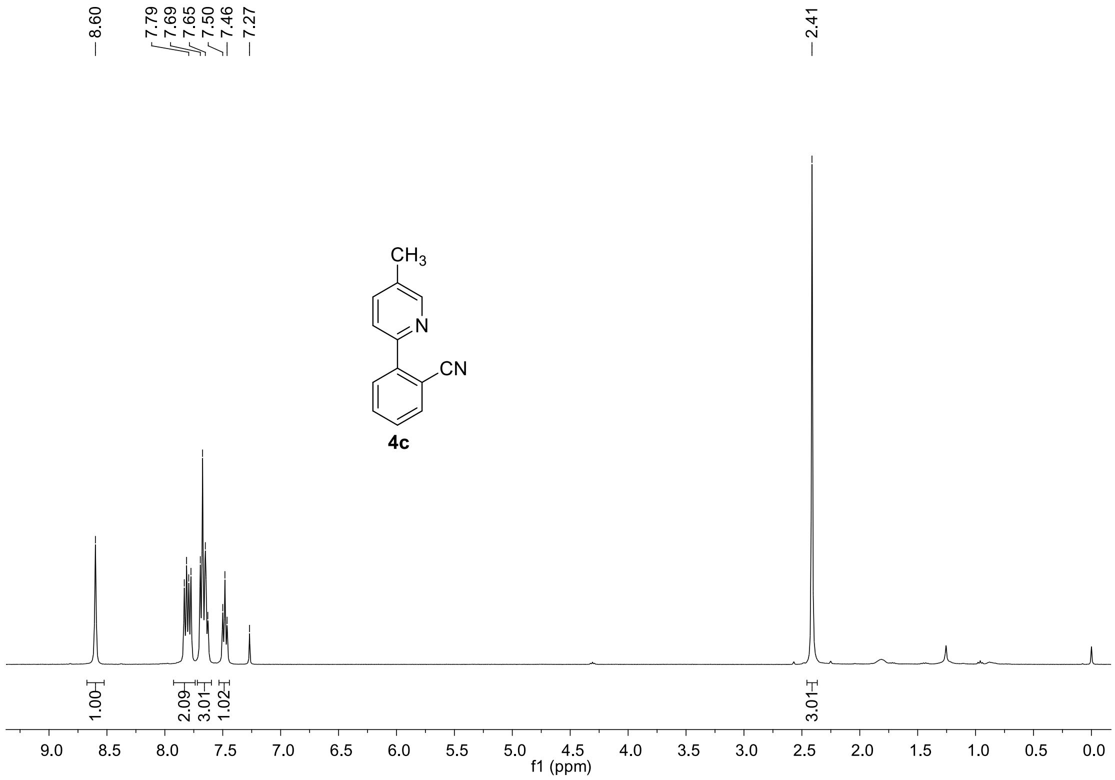

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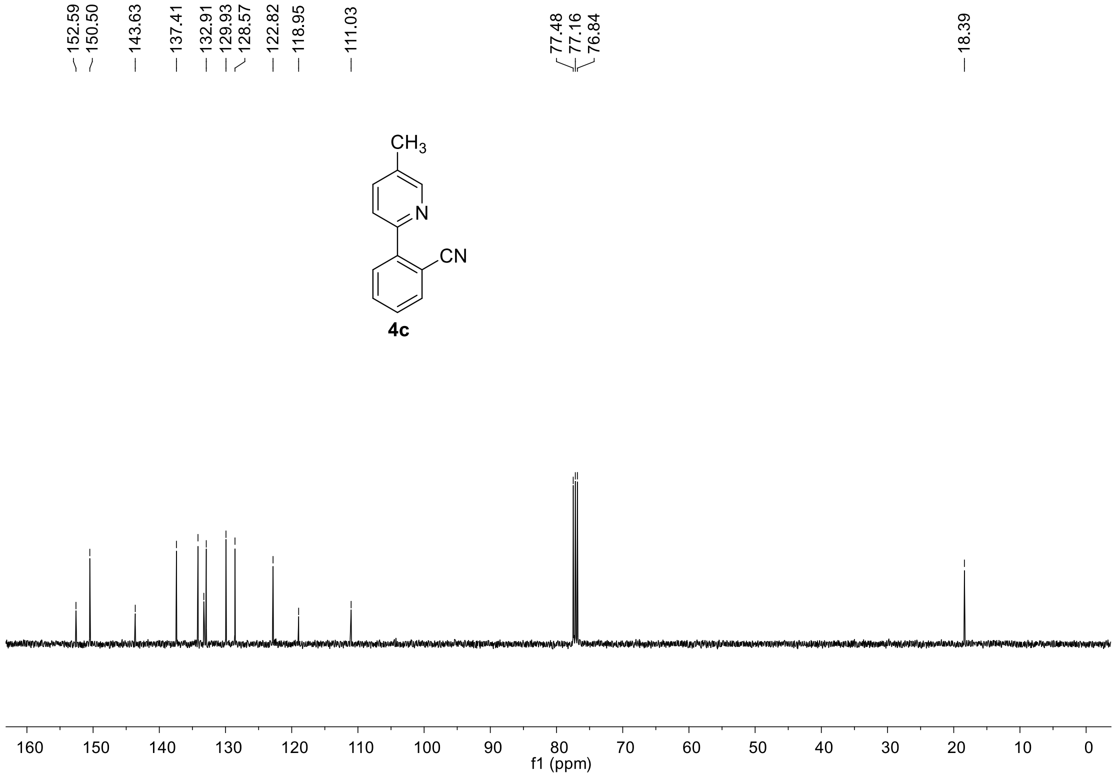

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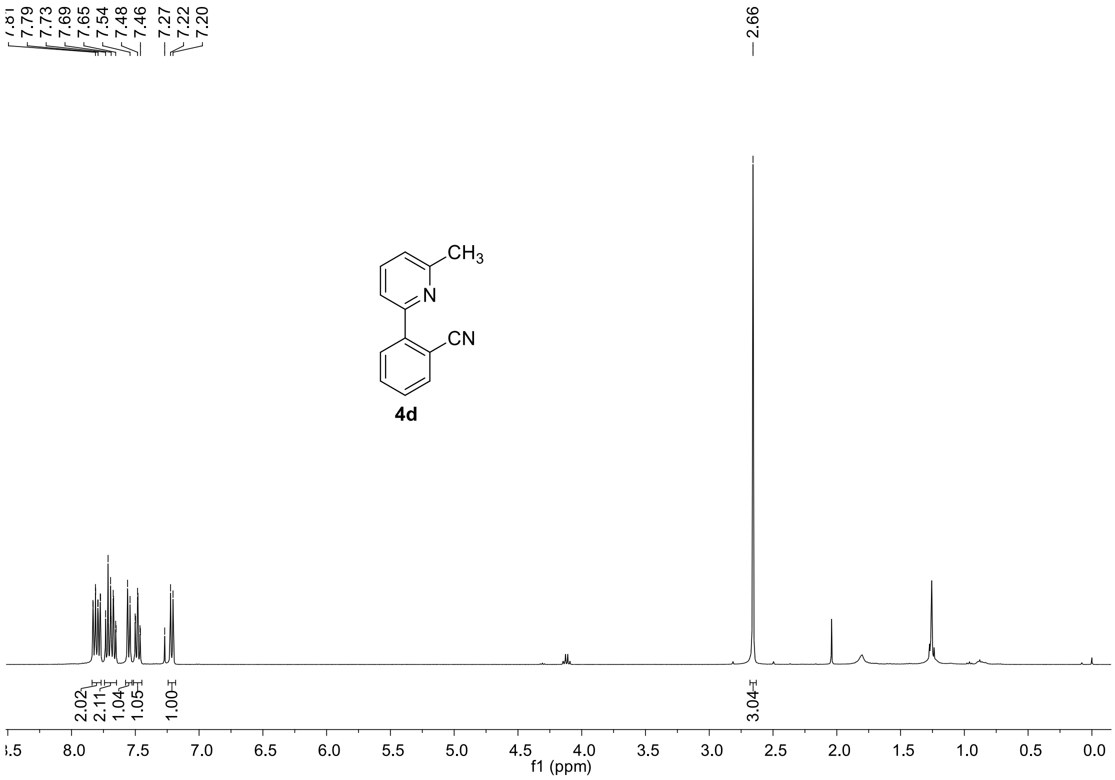

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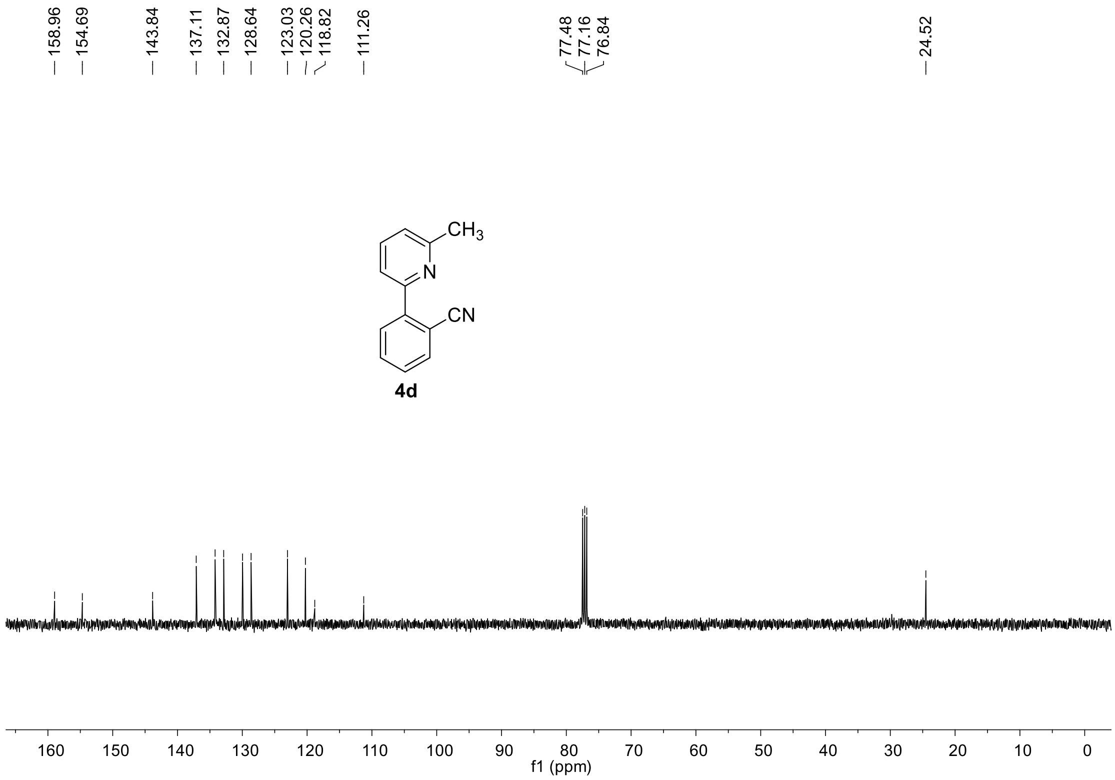

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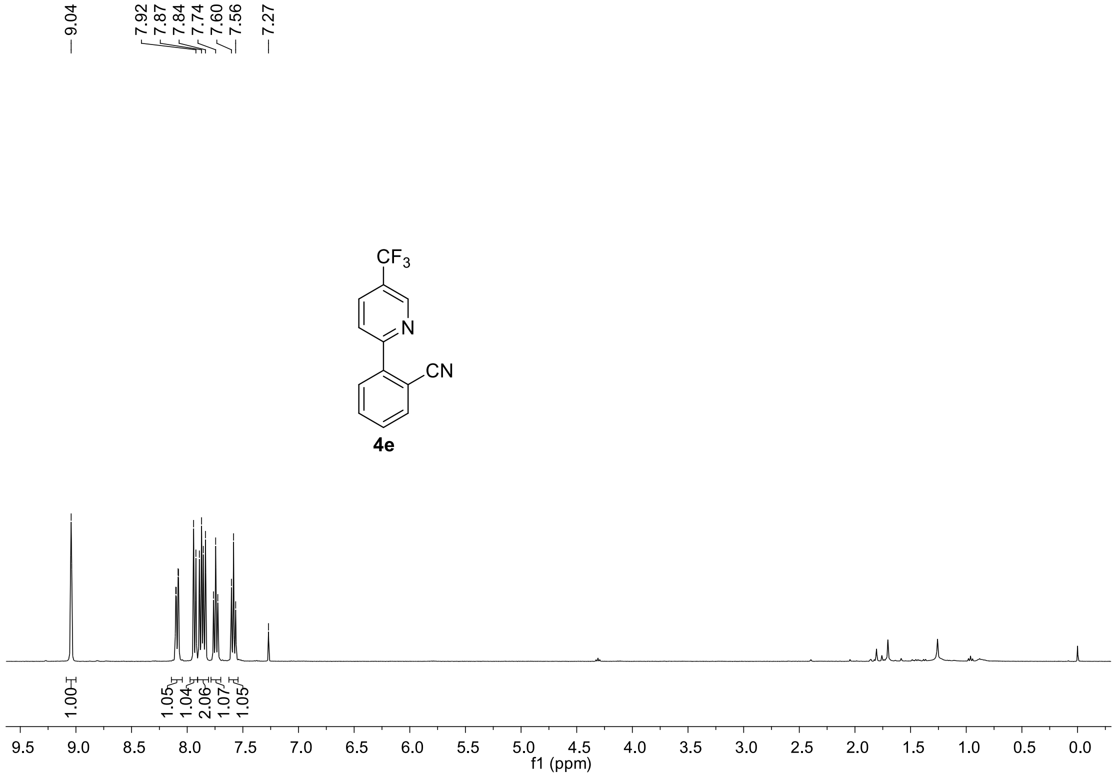

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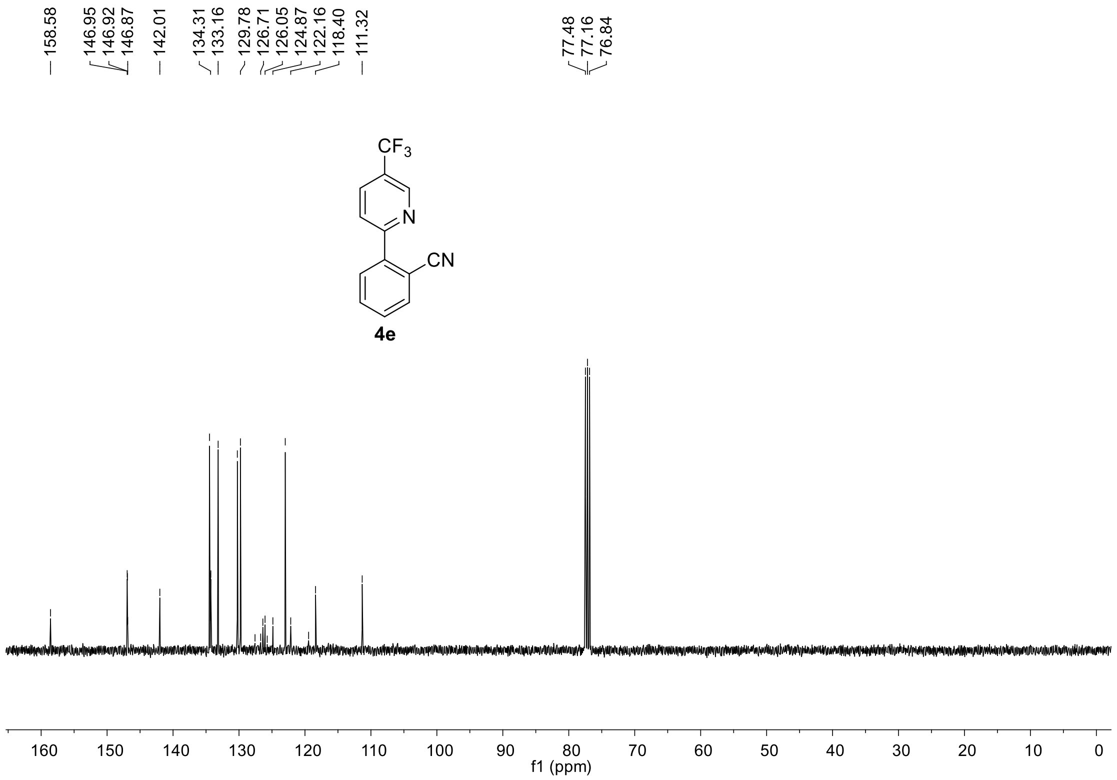

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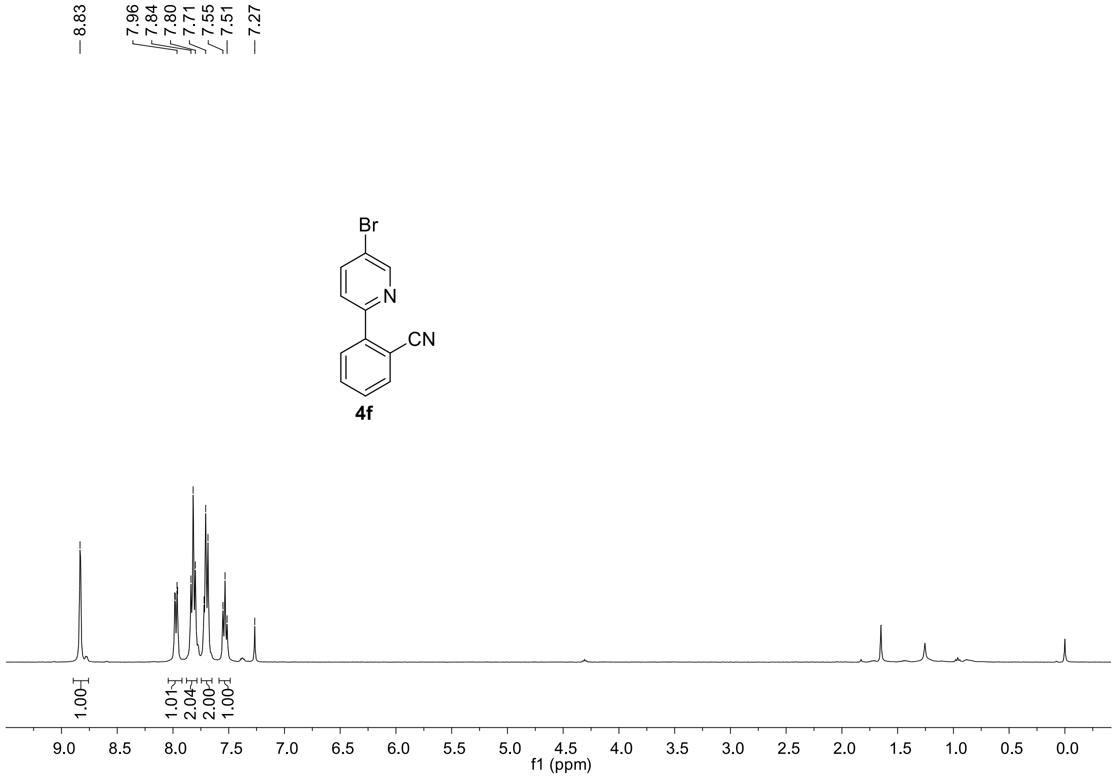

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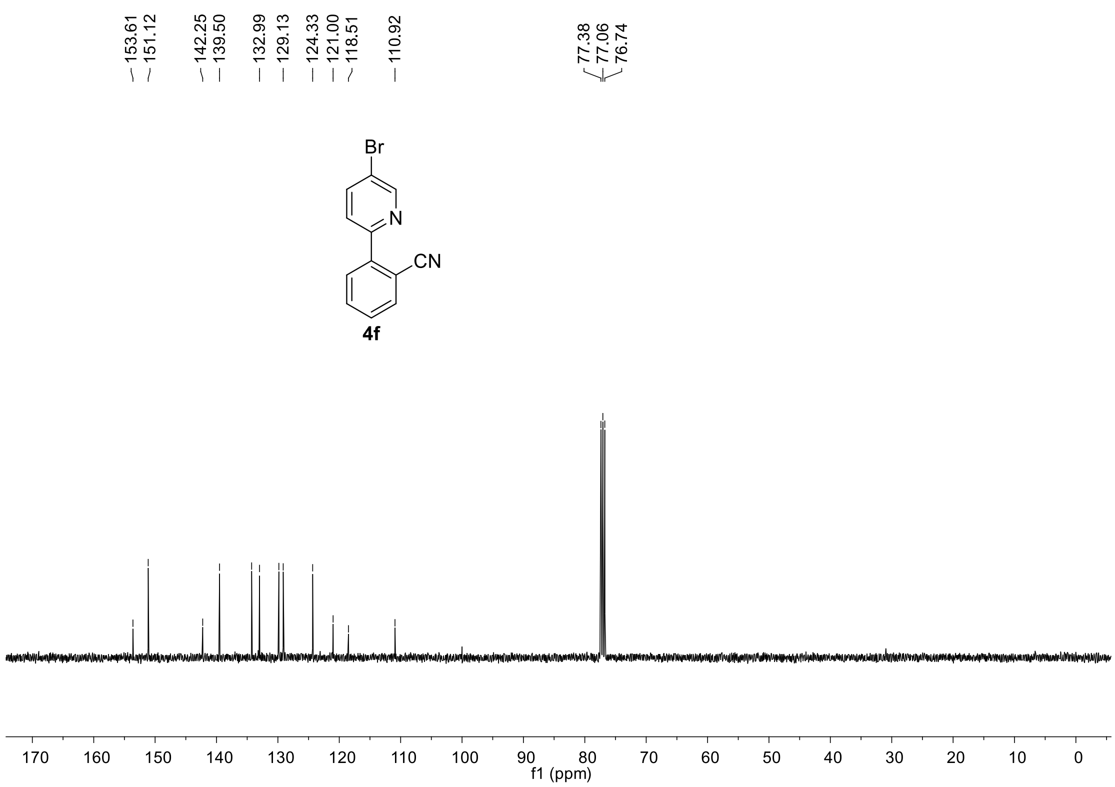

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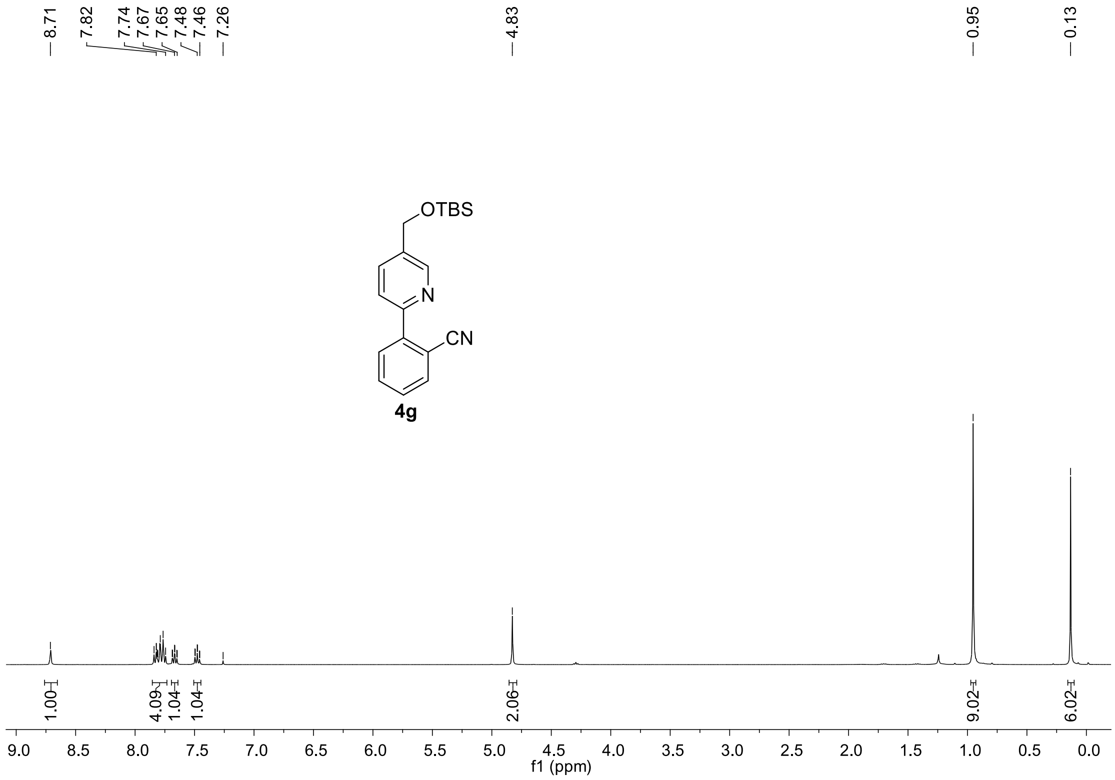

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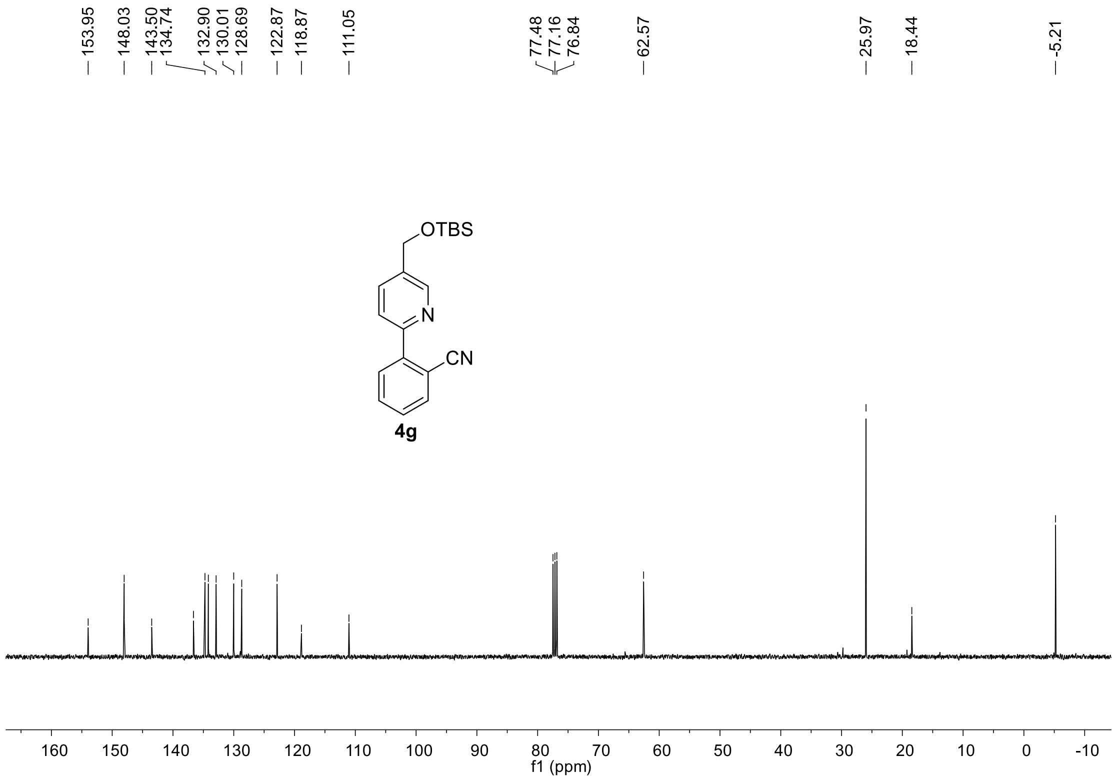

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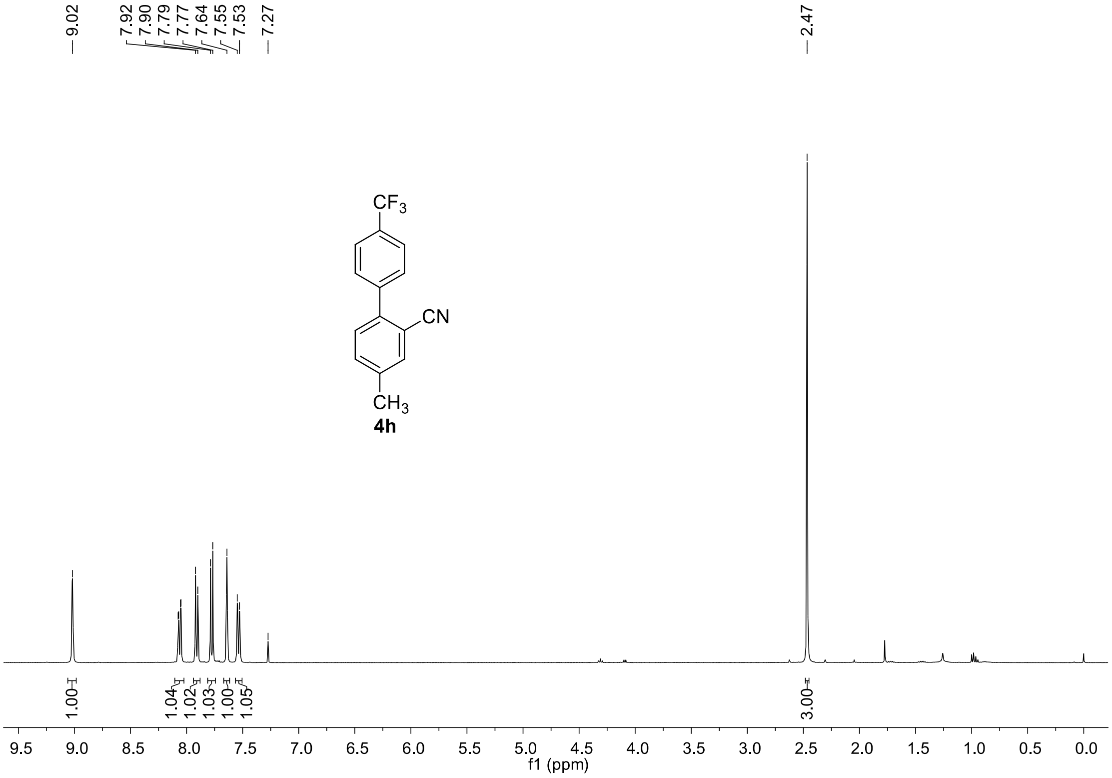

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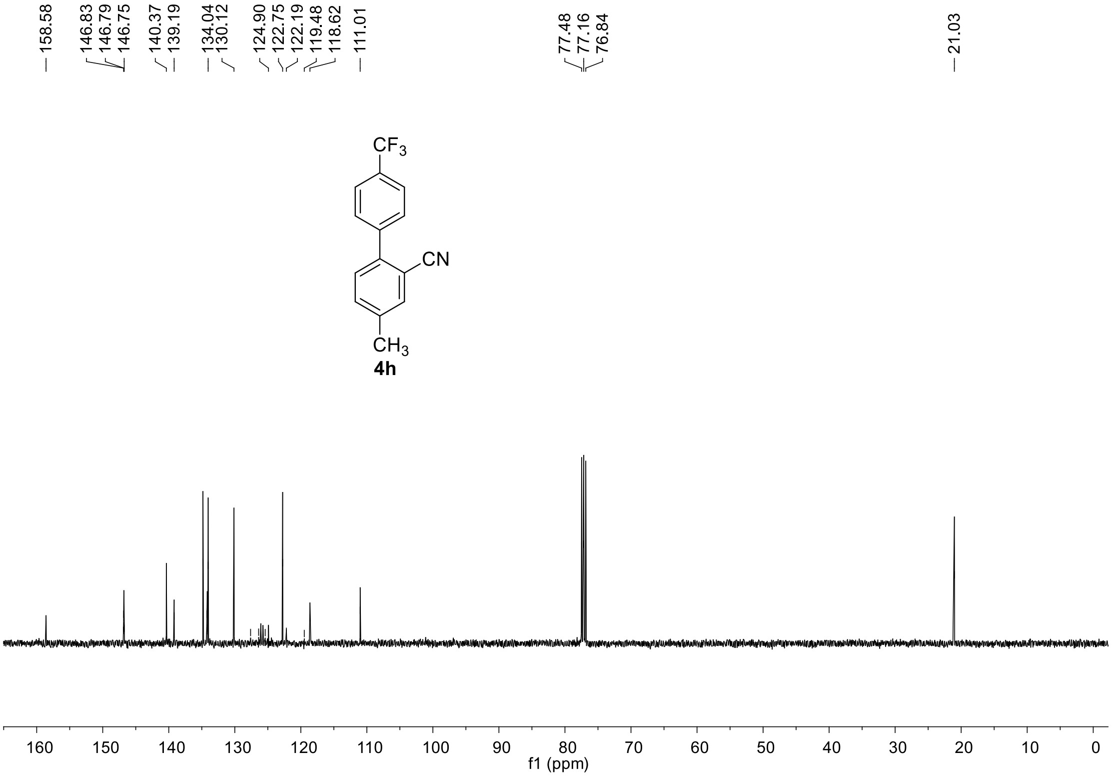

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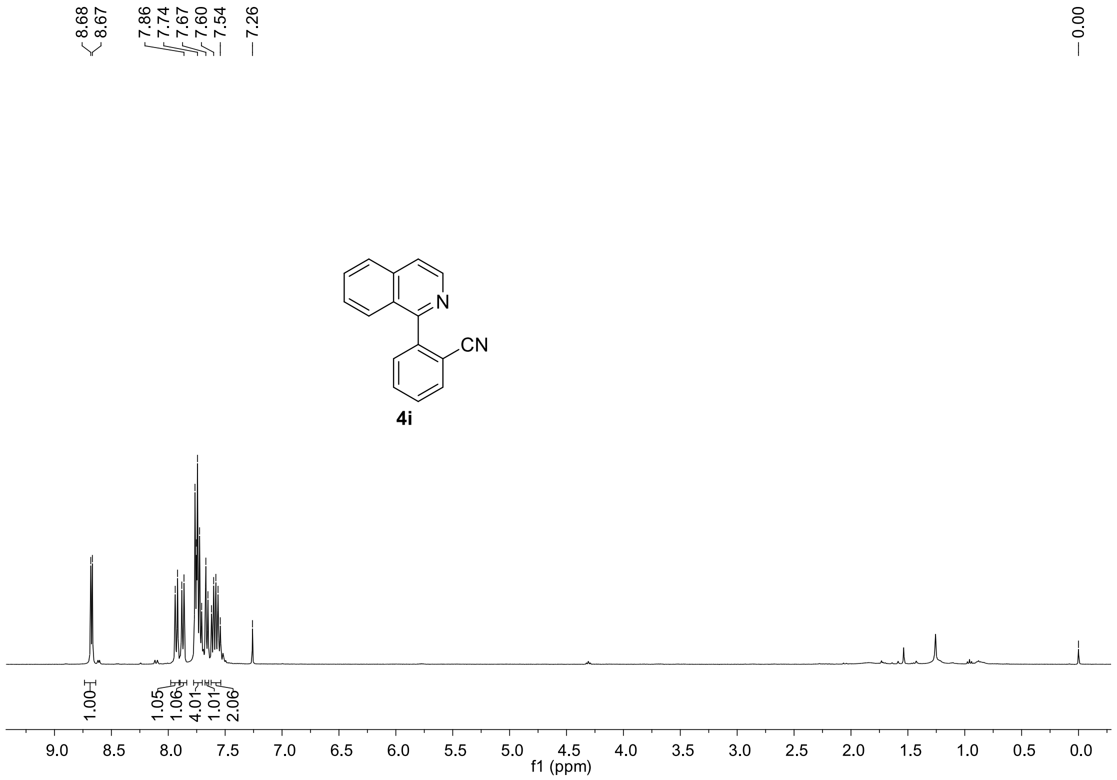

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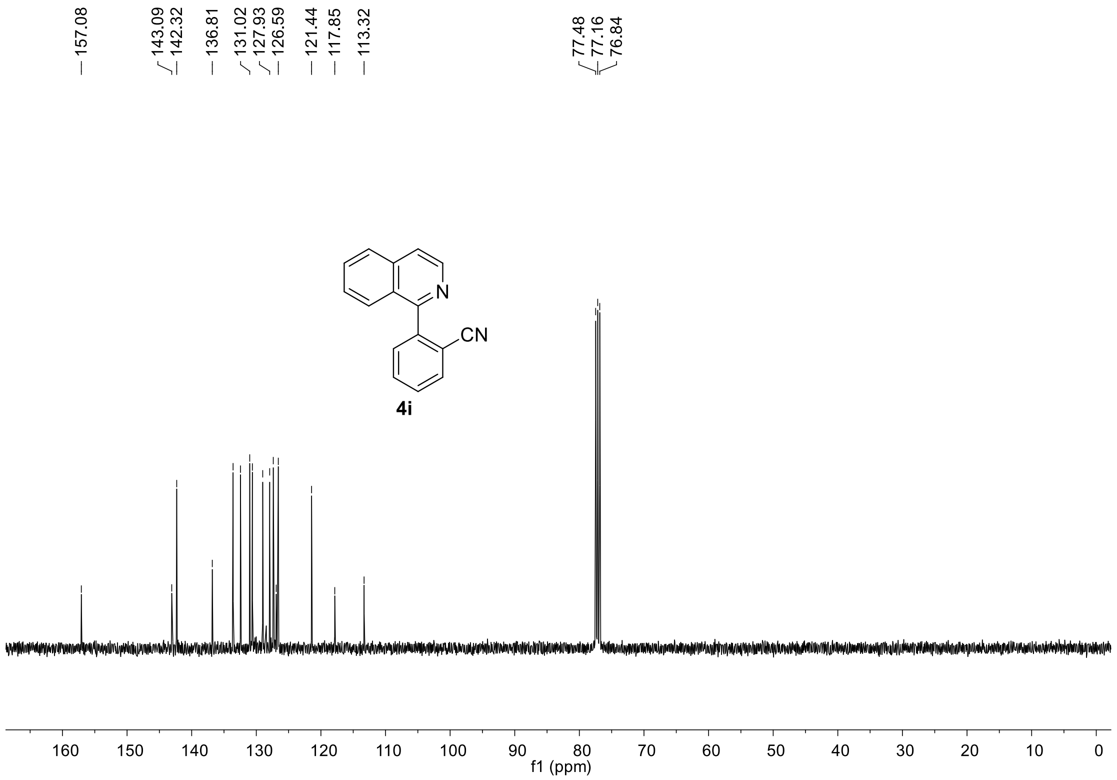

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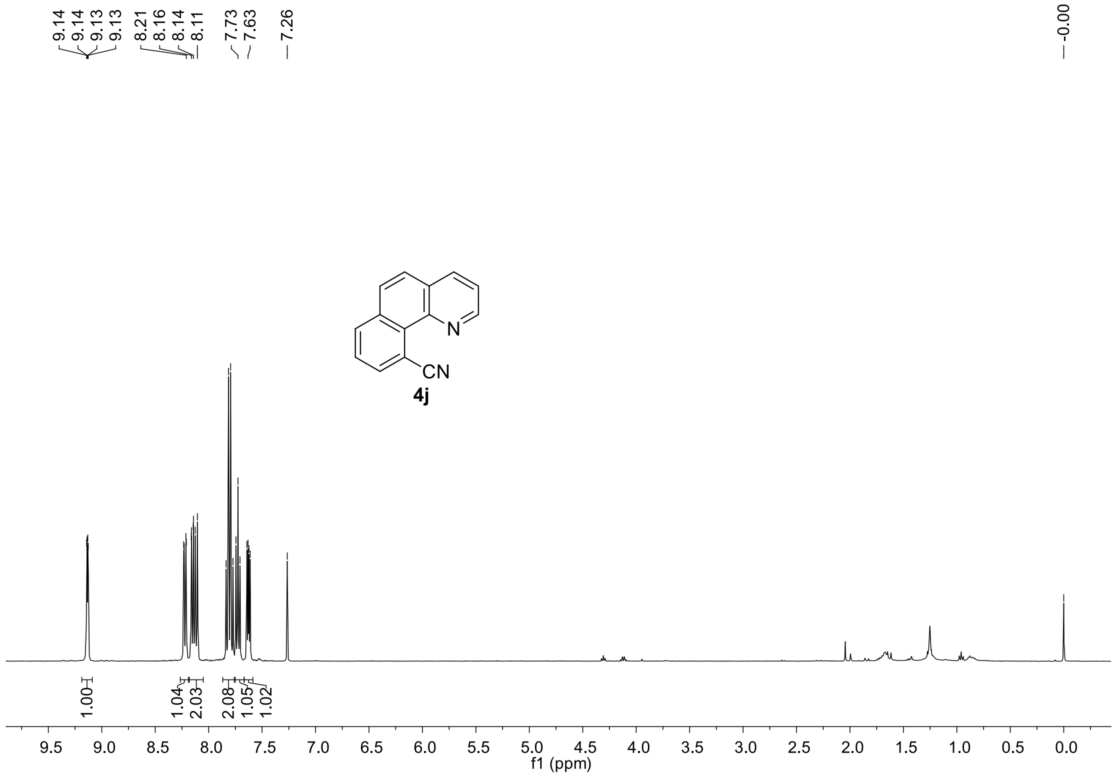

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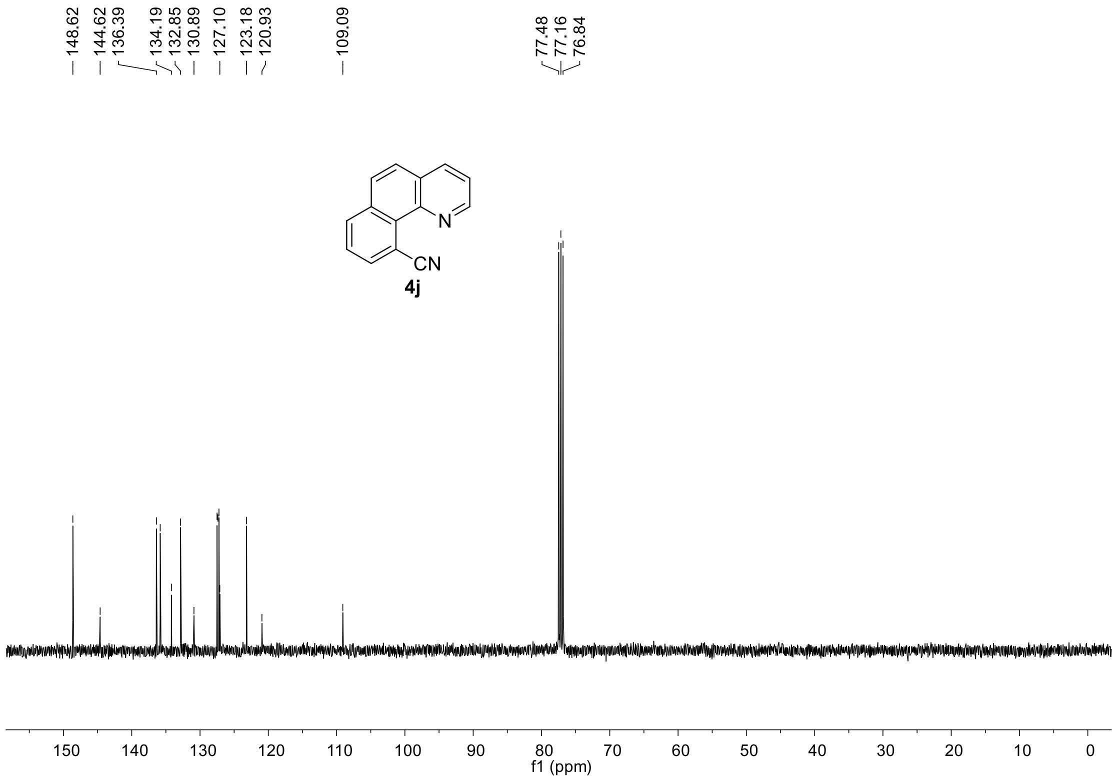

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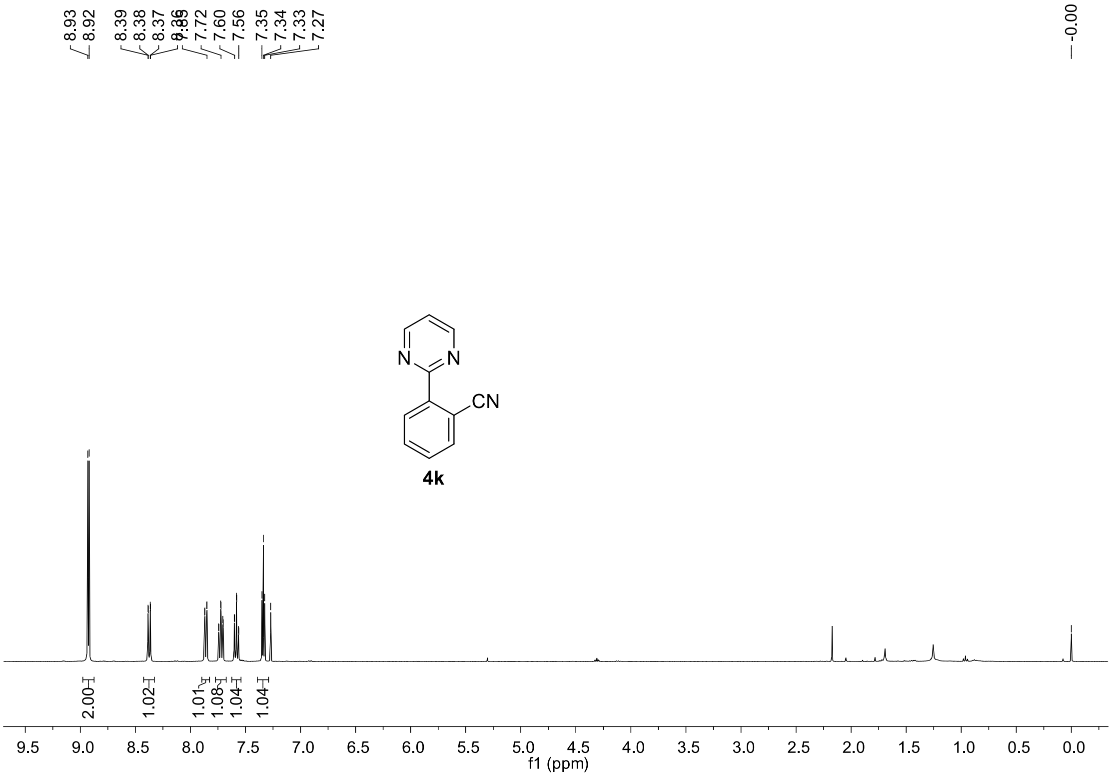

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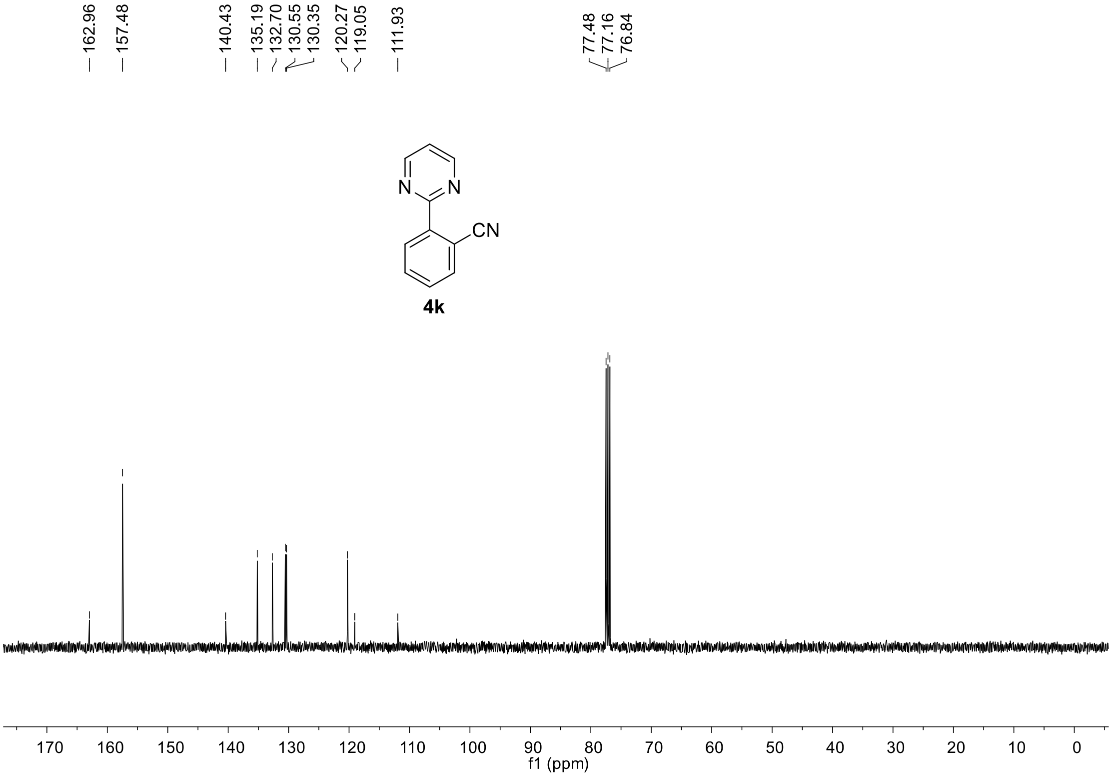

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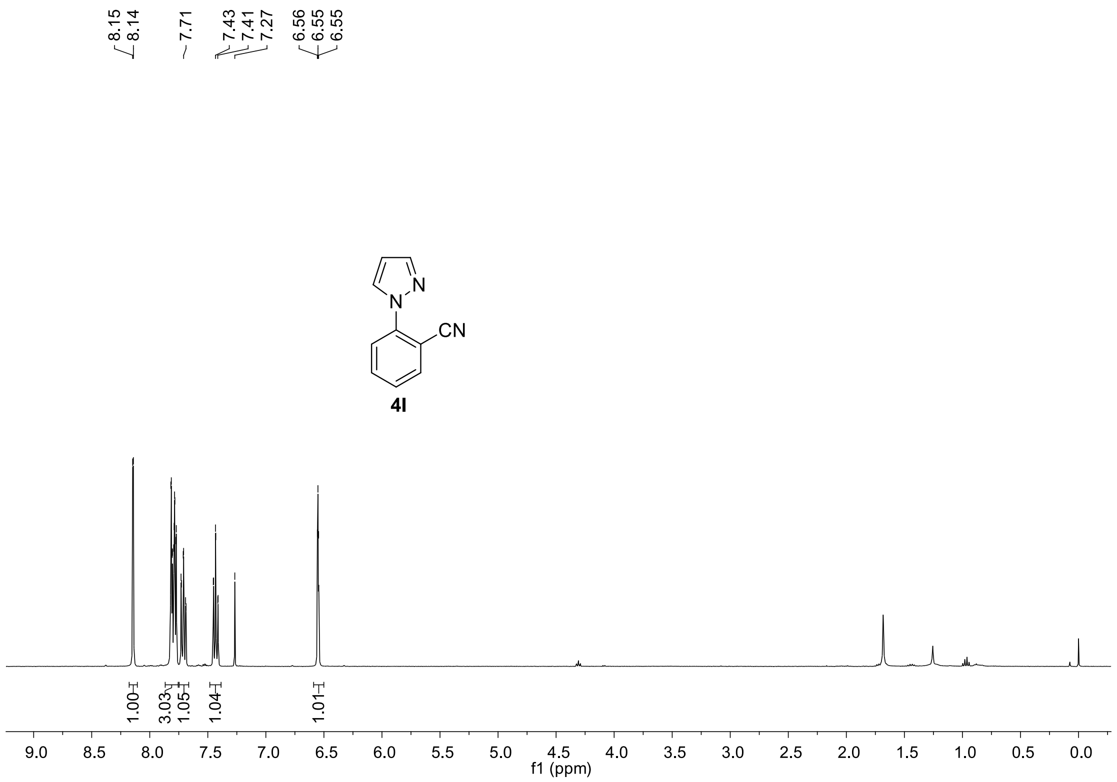

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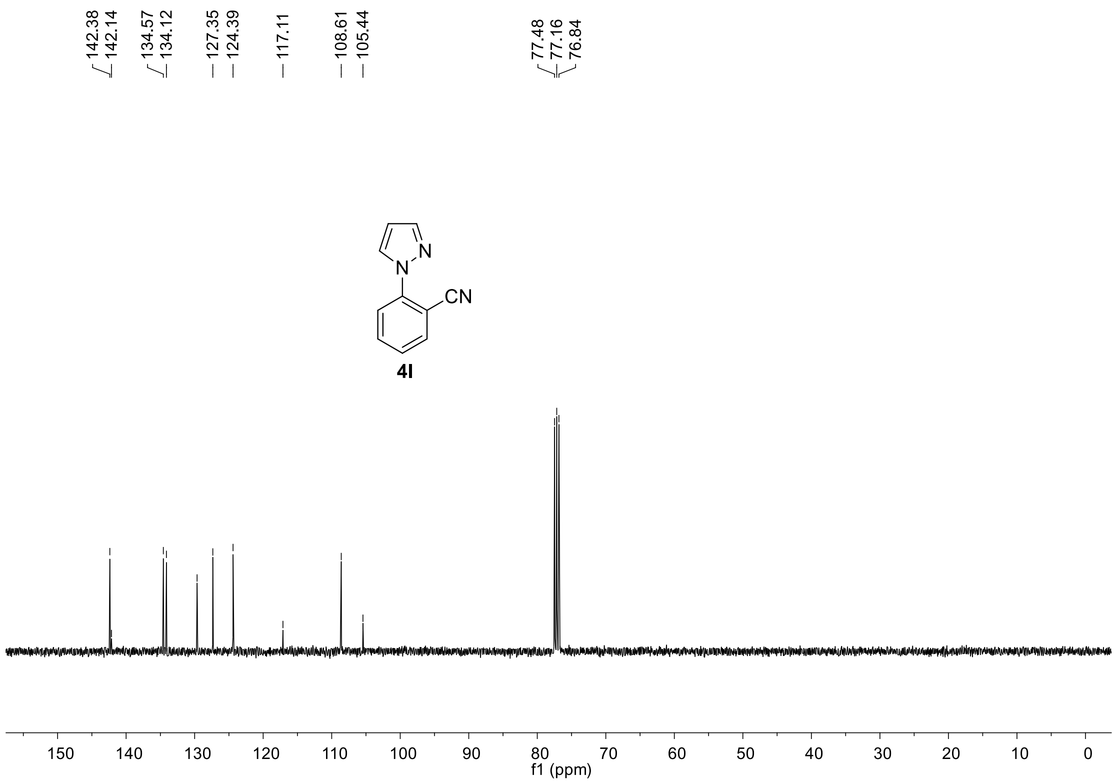

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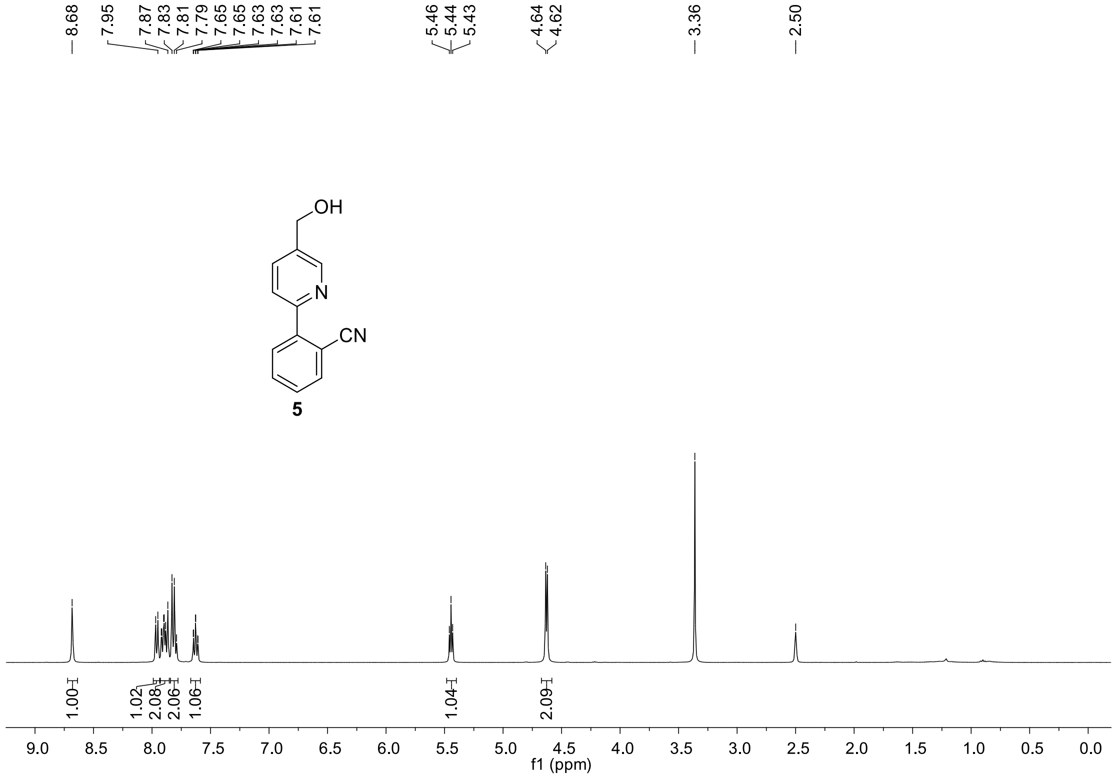

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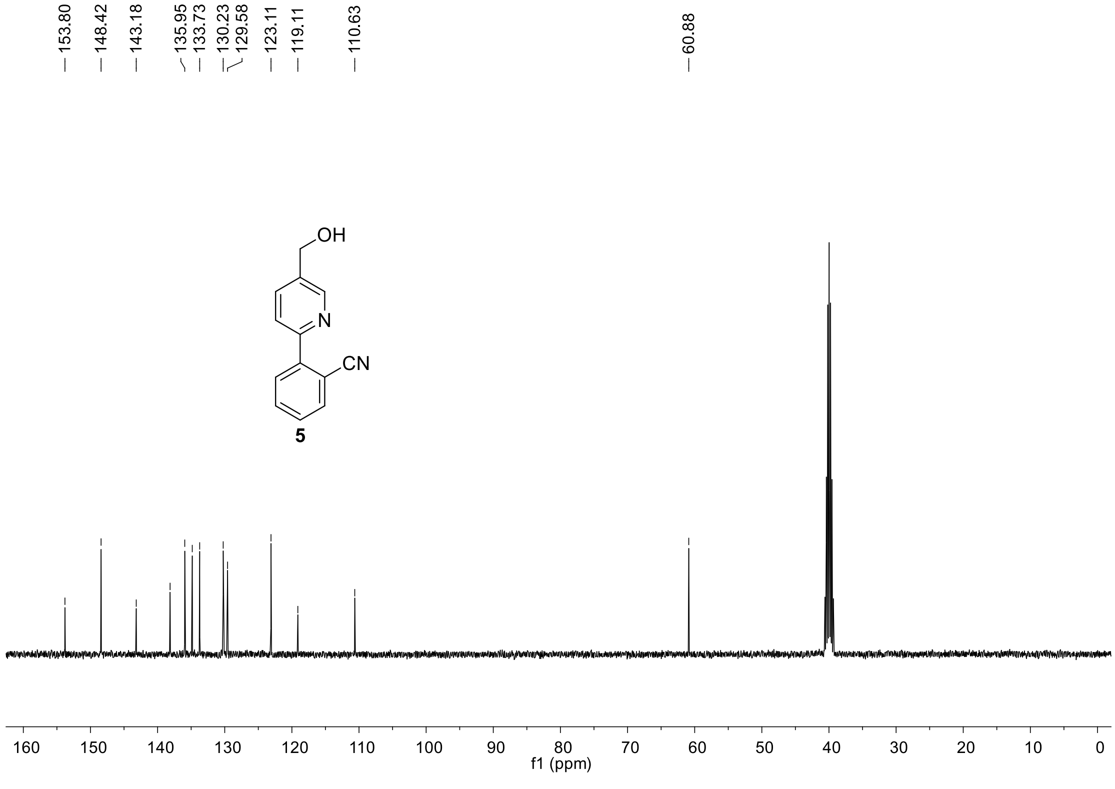

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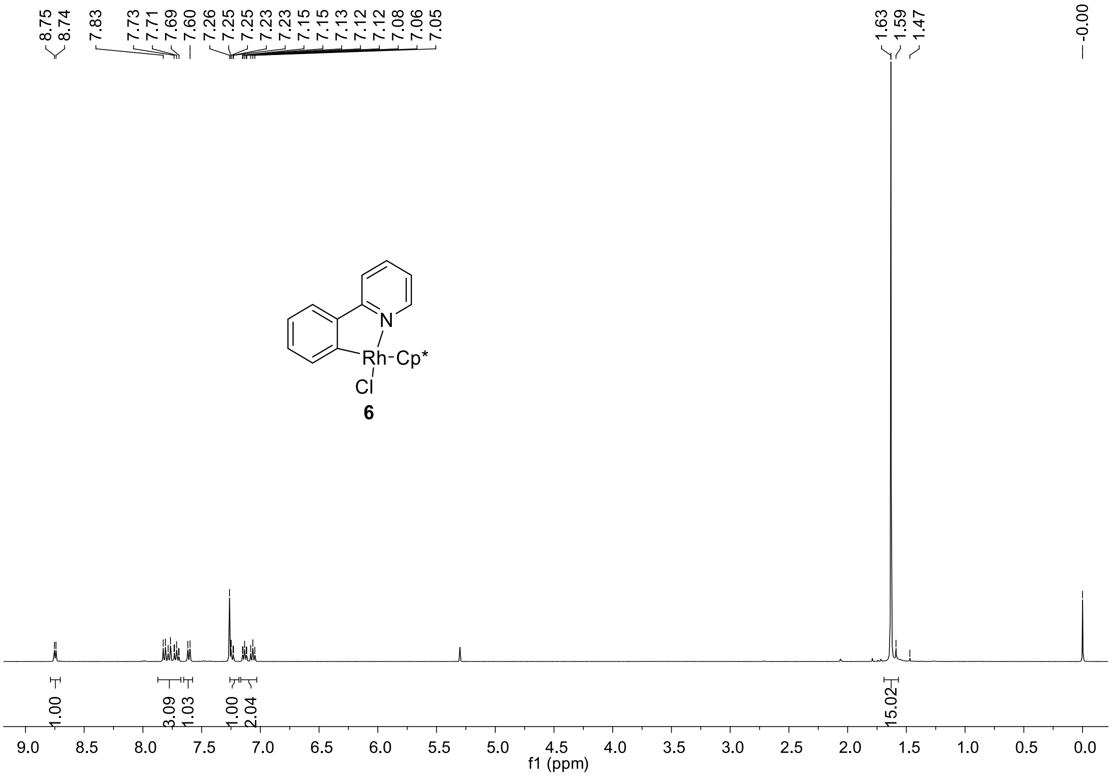

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