Novel α-Arylnitriles Synthesis via Ni-Catalyzed Cross-coupling of α-Bromonitriles with Arylboronic Acids under Mild Conditions

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1. General Methods

All reactions and manipulations were performed in a nitrogen-filled glove box or using standard Schlenk techniques, Column chromatography was performed using EM silica gel 60 (230-400 mesh). ^{1}H NMR and ^{13}C NMR were recorded on Mercury 300 MHz. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. All ^{1}H NMR experiments were reported in parts per million (ppm) downfield of TMS. All ^{13}C NMR spectra were reported in ppm and were obtained with ^{1}H decoupling. Gas chromatographic analyses were preformed on Varian GC 2000 gas chromatography instrument with a FID detector and naphthalene was added as internal standard. HRMS was recorded on MicroMass GC-TOF (EI). Unless otherwise noted, all chemicals were obtained directly from commercial source. K_3PO_4 was obtained by the oven dry of $K_3PO_4 \cdot 3H_2O$ at 600 ^{0}C overnight. 2-Bromobutanenitrile and 2-bromopentanenitrile were obtained following the literature procedure from the corresponding commercially available 2-bromocarboxylic acids.[1-3] Ethyl 2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate was obtained following the literature report.[4]

2. General procedure for the arylation of α-Bromonitrile compounds

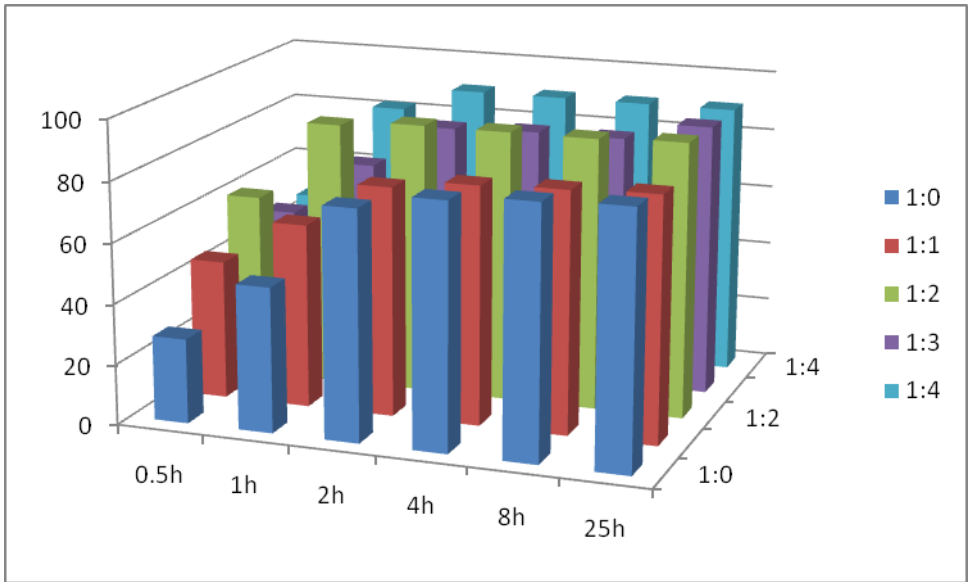
Method A In a glove box, 1.0 mmol $ArB(OH)_2$, 0.05 mmol $Ni(PPh_3)_4$ and 2.0 mmol K_3PO_4 are combined in a schlenk tube. The tube was fitted with a rubber septum and removed from the glove box. Then the tube was backfilled with Nitrogen, 0.5 mmol α-bromonitrile and 2 mL toluene were injected in the tube. The resulting solution kept stirring for 3 h at 80 ^{o}C, and then the suspension solution was diluted by ethyl acetate (3*5 mL), the organic layers were combined, and dried over sodium sulfate. The pure product was obtained by flash column chromatography.

Method B In a glove box (as K_3PO_4 is quite deliquescent under air condition, it is stored in the glovebox), 1.0 mmol $ArB(OH)_2$, 0.025mmol $Ni(acac)_2$, 0.05 mmol PPh_3 and 3.0 mmol K_3PO_4 (636.9 mg, 3.0 mmol) are combined in a schlenk tube. The tube

was fitted with a rubber septum and removed from the glove box. Then the tube was backfilled with Nitrogen, 0.5 mmol α-bromonitrile and 1 ml toluene were injected in the tube. The resulting solution kept stirring for 3 h at 80 ^{o}C, and then the suspension solution was diluted by ethyl acetate (3*5 mL), the organic layers were combined, and dried over sodium sulfate. The pure product was obtained by flash column chromatography.

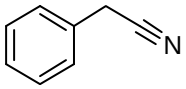
3. Data for Figure 2.

Effect of PPh_3	**$Ni(acac)_2$: PPh_3 (5 mol% $Ni(acac)_2$)**					**Reaction time**
	1:0	**1:1**	**1:2**	**1:3**	**1:4**	
GC Yield [%]	*28*	*46*	*61*	*49*	*48*	**0.5 h**
	48	*61*	*88*	*68*	*82*	**1 h**
	76	*76*	*90*	*83*	*90*	**2 h**
	81	*79*	*90*	*84*	*90*	**4 h**
	83	*80*	*90*	*84*	*90*	**8 h**
	84	*81*	*91*	*90*	*90*	**25 h**

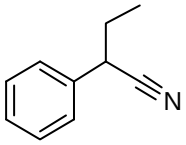


4. Analytical data

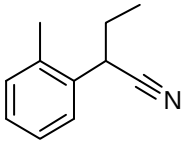
Table 1



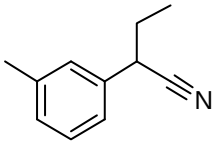
2-phenylacetonitrile (Table 1, Entry 1)[5] Method A was followed using $PhB(OH)_2$ (121.9 mg, 1.0 mmol), 2-bromoacetonitrile (60 mg, 0.5 mmol), $Ni(PPh_3)_4$ (55.4 mg, 0.05 mmol), K_3PO_4 (424.6 mg, 2.0 mmol). The GC yield was 67%. MS (EI) m/z: 128.0, 117.0, 89.0, 45.1.



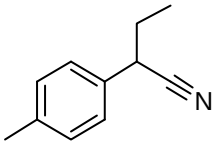
2-phenylbutanenitrile (Table 1, Entry 2)[6] Method A was followed using $PhB(OH)_2$ (121.9 mg, 1.0 mmol), 2-bromonbutanenitrile (74mg, 0.5 mmol), $Ni(PPh_3)_4$ (55.4 mg, 0.05 mmol), K_3PO_4 (424.6 mg, 2.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 76% of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.26 (m, 5H), 3.74 (t, *J* = 7.2 Hz, 1H), 2.00 - 1.88 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.98, 129.25, 128.24, 127.53, 121.03, 39.13, 29.47, 11.73. MS (EI) m/z: 144.8, 116.9, 89.0, 63.0.



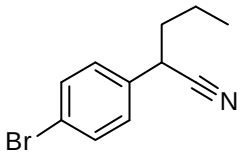
2-*o*-tolybutanenitrile (Table 1, Entry 3)[7] Method A was followed using *o*-tolylboronic acid (204.5 mg, 1.5 mmol), 2-bromonbutanenitrile (148 mg, 1.0 mmol), $Ni(PPh_3)_4$ (110.8 mg, 0.1 mmol), K_3PO_4 (424.6 mg, 2.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 75% of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 1H), 7.23 – 7.03 (m, 3H), 3.80 (t, *J* = 7.9, 1H), 2.25 (s, 3H), 1.91 – 1.71 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.16, 134.35, 130.10, 128.27, 127.69, 126.99, 121.31, 36.00, 28.06, 19.35, 12.07. MS (EI): 158.8, 129.9, 103.0, 77.0.



2-*m*-tolybutanenitrile (Table 1， Entry 4) Method A was followed using *m*-tolylboronic acid（204.5 mg, 1.5 mmol), 2-bromonbutanenitrile (148 mg, 1.0 mmol), $Ni(PPh_3)_4$ (110.8 mg, 0.1 mmol), K_3PO_4 (424.6 mg, 2.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 81% of the desired product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.5 Hz, 1H), 7.06 – 7.02 (m, 3H), 3.61 (t, *J* = 7.2 Hz, 1H), 2.28 (s, 3H), 1.92 – 1.75 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.48, 133.32, 126.52, 126.39, 125.61, 122.01, 118.57, 36.50, 26.90, 19.05, 9.21. MS (EI) m/z: 159.0, 130.1, 103.0, 91.2. HRMS (EI) calcd for $C_{11}H_{13}N$ $[M]^+$: 159.1048; found: 159.1046.



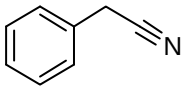
2-*p*-tolylbutanenitrile (Table 1, Entry 5)[8] Method A was followed using *p*-tolylboronic acid (204.5 mg, 1.5 mmol), 2-bromonbutanenitrile (148 mg, 1.0 mmol), $Ni(PPh_3)_4$ (110.8 mg, 0.1 mmol), K_3PO_4 (424.6 mg, 2.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 78% of the desired product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.14 – 7.08 (m, 4H), 3.61 (t, *J* = 7.2 Hz, 1H), 2.26 (s, 3H), 1.85 – 1.76 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.01, 132.98, 129.89, 127.40, 121.20, 38.75, 29.47, 21.30, 11.73. MS (EI) m/z: 158.8, 130.0, 103.0, 77.0.



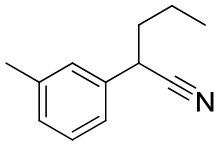
2-(4-bromophenyl)pentanenitrile (Table 1, Entry 6)[9] Method A was followed using 4-bromophenylboronic acid (301.2 mg, 1.5 mmol), 2-bromopentanenitrile (162.0 mg, 1.0 mmol), $Ni(PPh_3)_4$ (110.8 mg, 0.1 mmol), K_3PO_4 (424.6 mg, 2.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 86% of the desired product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* =

8.4 Hz, 2H), 3.67 (t, J = 8.3 Hz, 1H), 1.91 – 1.63 (m, 2H), 1.49 – 1.28 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.27, 132.41, 129.18, 122.23, 120.63, 37.93, 36.89, 20.46, 13.64. MS (EI) m/z: 238.9, 237.0, 197.0, 195.1, 116.1. HRMS (EI) calcd for $C_{11}H_{12}BrN$ $[M]^+$: 237.0153; found: 237.0157.

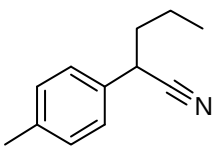
Table 2



2-phenylacetonitrile (Table 2, Entry 1)[5] Method B was followed using $PhB(OH)_2$ (121.9 mg, 1.0 mmol), 2-bromoacetonitrile (60 mg, 0.5 mmol), $Ni(acac)_2$ (6.4 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and K_3PO_4 (636.9 mg, 3.0 mmol). The GC yield was 68%. MS (EI) m/z: 128.0, 117.0, 89.0, 45.1.

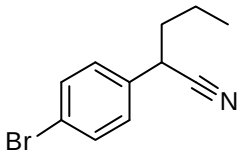


2-*m*-tolylpentanenitrile (Table 2, Entry 2) Method B was followed using *m*-tolylboronic acid (136.3 mg, 1.0 mmol), 2-bromopentanenitrile (81.0 mg, 0.5 mmol), $Ni(acac)_2$ (6.4 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and K_3PO_4 (636.9 mg, 3.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 81% of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 6.95 (m, 4H), 3.66 (t, J = 8.5, 1H), 2.28 (s, 3H), 1.93 – 1.64 (m, 2H), 1.47 – 1.41 (m, 2H), 0.97 – 0.79 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.07, 136.18, 129.12, 128.94, 128.14, 124.54, 121.32, 38.16, 37.33, 21.64, 20.59, 13.70. MS (EI) m/z: 172.8, 131.0, 104.0, 91.1. HRMS (EI) calcd for $C_{12}H_{15}N$ $[M]^+$: 173.1204; found: 173.1198.

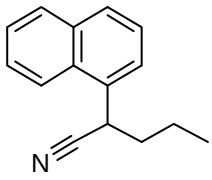


2-*p*-tolylpentanenitrile (Table 2, Entry 3)[10] Method B was followed using *p*-tolylboronic acid (136.3 mg, 1.0 mmol), 2-bromopentanenitrile (81.0 mg, 0.5

mmol), $Ni(acac)_2$ (6.4 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and K_3PO_4 (636.9 mg, 3.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 88% of the desired product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.11 (m, 4H), 3.66 (t, *J* = 8.3, 1H), 2.26 (s, 3H), 1.88 – 1.63 (m, 2H), 1.50 – 1.32 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.97, 133.25, 129.90, 127.34, 121.35, 38.15, 36.99, 21.30, 20.52, 13.68. MS (EI) m/z: 173.0, 131.0, 116.1, 91.2, 77.2.

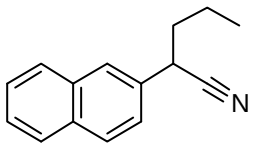


2-(4-bromophenyl)pentanenitrile (Table 2, Entry 4) Method B was followed using 4-bromophenylboronic acid (200.8 mg, 1.0 mmol), 2-bromopentanenitrile (81.0mg, 0.5 mmol), $Ni(acac)_2$ (6.4 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and K_3PO_4 (636.9 mg, 3.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 89% of the desired product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.67 (t, *J* = 8.3 Hz, 1H), 1.91 – 1.63 (m, 2H), 1.49 – 1.28 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.27, 132.41, 129.18, 122.23, 120.63, 37.93, 36.89, 20.46, 13.64. MS (EI) m/z: 238.9, 237.0, 197.0, 195.1, 116.1. HRMS (EI) calcd for $C_{11}H_{12}BrN$ $[M]^+$: 237.0153; found: 237.0157.



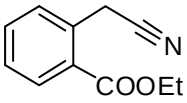
2-(naphthalene-1-yl)pentanenitrile (Table 2, Entry 5)[11] Method B was followed using naphthalene-1-ylboronic acid (172.0 mg, 1.0 mmol), 2-bromopentanenitrile (81.0 mg, 0.5 mmol), $Ni(acac)_2$ (6.4 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and K_3PO_4 (636.9 mg, 3.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 75% of the desired product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.55 (m, 4H), 7.41 - 7.37 (m, 2H), 7.27 (d, *J* = 8.5 Hz, 1H), 3.81 (t, *J* = 6.0 Hz,

1H), 1.85 – 1.76 (m, 2H), 1.45 – 1.38 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.54, 133.01, 129.26, 128.08, 127.98, 126.94, 126.69, 126.52, 125.08, 121.23, 37.98, 37.53, 20.59, 13.72. MS (EI) m/z: 209.0, 166.2, 139.2, 115.2.

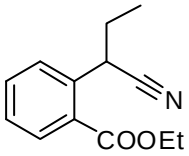


2-(naphehalen-2-yl)pentanenitrile (Table 2, Entry 6) Method B was followed using naphthalene-2-ylboronic acid (172.0 mg, 1.0 mmol), 2-bromopentanenitrile (81.0 mg, 0.5 mmol), $Ni(acac)_2$ (6.4 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and K_3PO_4 (636.9 mg, 3.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 86% of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 4H), 7.37 – 7.34 (m, 2H), 7.26 – 7.23 (m, 1H), 3.78 (t, J = 8.5 Hz, 1H), 1.82 – 1.75 (m, 2H), 1.52 – 1.26 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.56, 133.01, 129.26, 128.09, 127.99, 126.95, 126.70, 126.52, 125.09, 121.25, 37.97, 37.52, 20.60, 13.73. MS (EI) m/z: 209.0, 167.2, 139.2, 115.2. HRMS (EI) calcd for $C_{15}H_{15}N$ $[M]^+$: 209.1204; found: 209.1210.

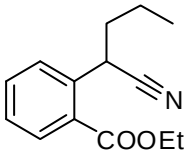
Table 3



Ethyl 2-(cyanomethyl)benzoate (Table 3, Entry 1)[12] Method B was followed using ethyl 2-(5,5-dimethyl-1,3,2-dioxabotinan-2-yl)benzoate (262.1 mg, 1.0 mmol), 2-bromoacetonitrile (60.0 mg, 0.5 mmol), $Ni(acac)_2$ (6.4 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and K_3PO_4 (636.9 mg, 3.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 63% of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 4.0 Hz, 2H), 7.44 (dd, J = 8.0, 4.0 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 4.23 (s, 2H), 1.42 (t, J = 7.1 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 166.54, 133.25, 132.14, 131.75, 130.38, 128.85, 128.55, 118.23, 61.65, 23.48, 14.47. MS (EI) m/z: 188.9, 161.1, 144.5, 133.1, 116.1, 89.0.



Ethyl 2-(1-cyanopropyl)benzoate (Table 3, Entry 2) Method B was followed using ethyl 2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoat (262.1 mg, 1.0 mmol), 2-bromobutanenitrile (74.0 mg, 0.5 mmol), $Ni(acac)_2$ (6.4 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and K_3PO_4 (636.9 mg, 3.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 95% of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 4.98 (dd, *J* = 8.9, 5.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.00 – 1.70 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.75, 138.09, 133.07, 131.62, 129.21, 128.25, 128.13, 121.58, 61.60, 35.90, 29.71, 14.46, 12.09. MS (EI) m/z: 217.1, 202.1, 174.1, 156.0, 115.1. HRMS (EI) calcd for $C_{13}H_{15}NO_2$ $[M]^+$: 217.1103; found: 217.1105.



Ethyl 2-(l-cyanobutyl)benzoate (Table 3, Entry 3) Method B was followed using ethyl 2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (262.1 mg, 1.0 mmol), 2-bromopentanenitrile (81.0 mg, 0.5 mmol), $Ni(acac)_2$ (6.4 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and K_3PO_4 (636.9 mg, 3.0 mmol). The reaction mixture was purified by silica gel chromatography to afford 87% of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 5.12 (dd, *J* = 8.1, 6.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.98 – 1.75 (m, 2H), 1.66 – 1.57 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.77, 138.37, 133.11, 131.57, 129.20, 128.22, 128.08, 121.73, 61.61, 38.31, 34.18, 20.98, 14.47, 13.69. MS (EI) m/z: 232.0, 202.0, 174.1, 156.1. HRMS (EI) calcd for $C_{14}H_{17}NO_2$ $[M]^+$: 231.1259; found: 231.1256.

5. References

(1) Boschi, F.; Camps, P.; Comes-Franchini, M.; Munoz-Torrero, D.; Ricci, A.; Sanchez, L. *Tetrahedron: Asymmetry* **2005**, *16*, 3739.

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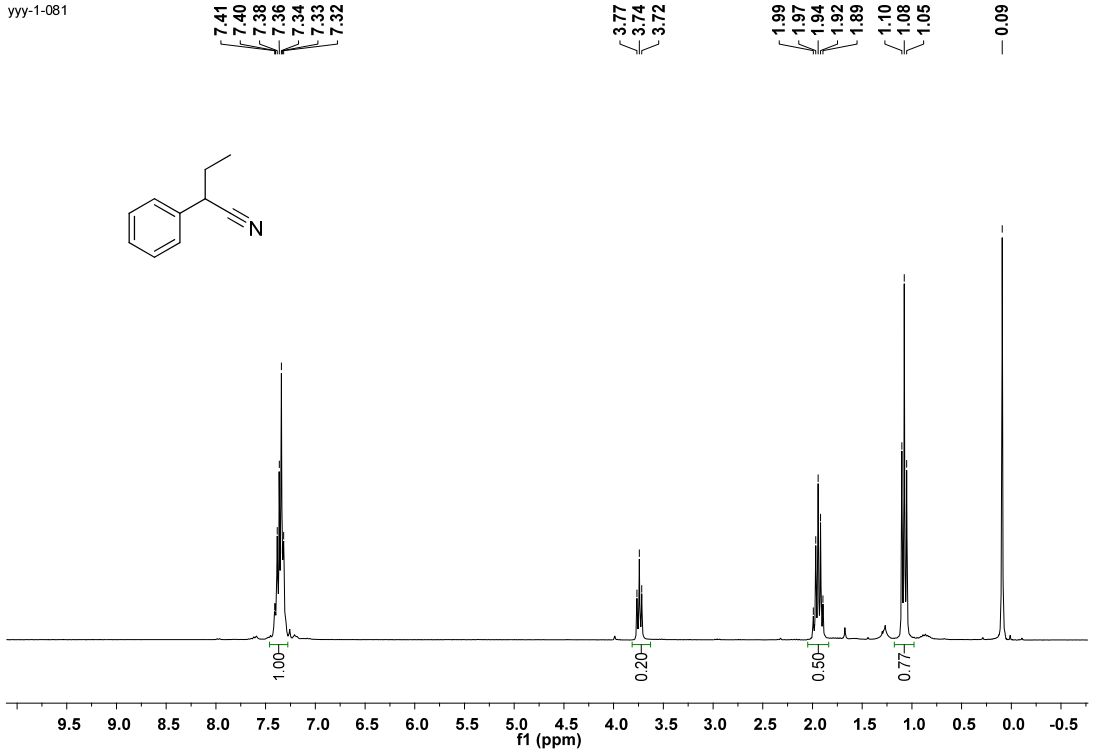
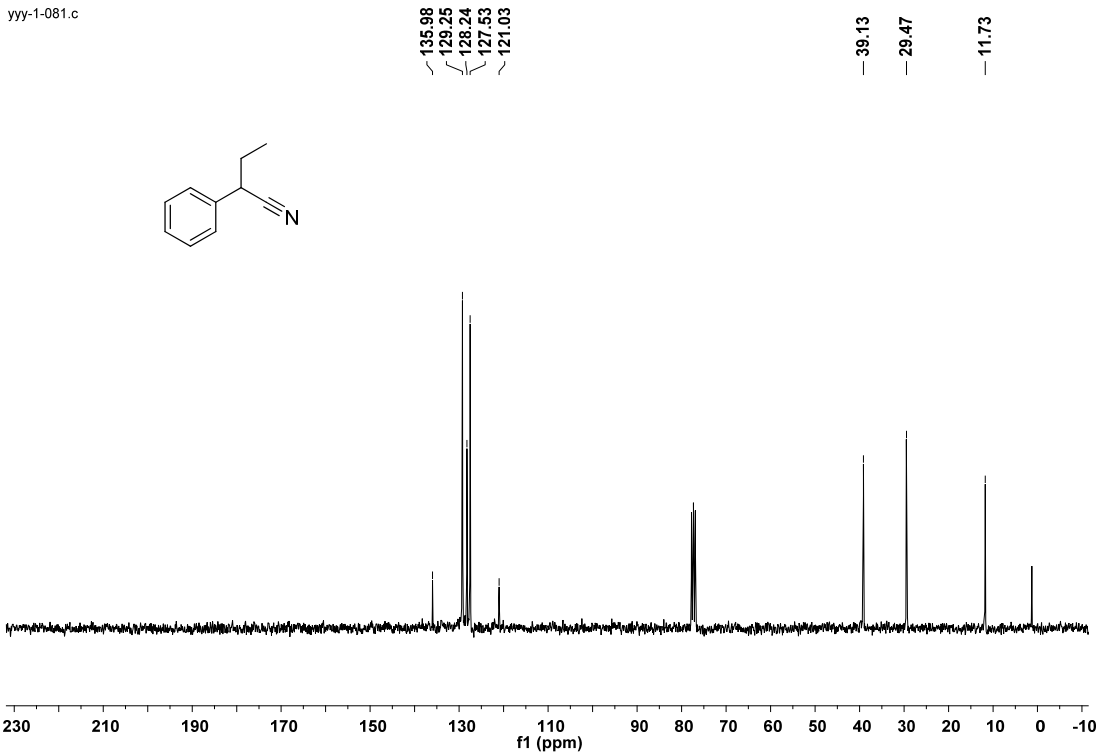
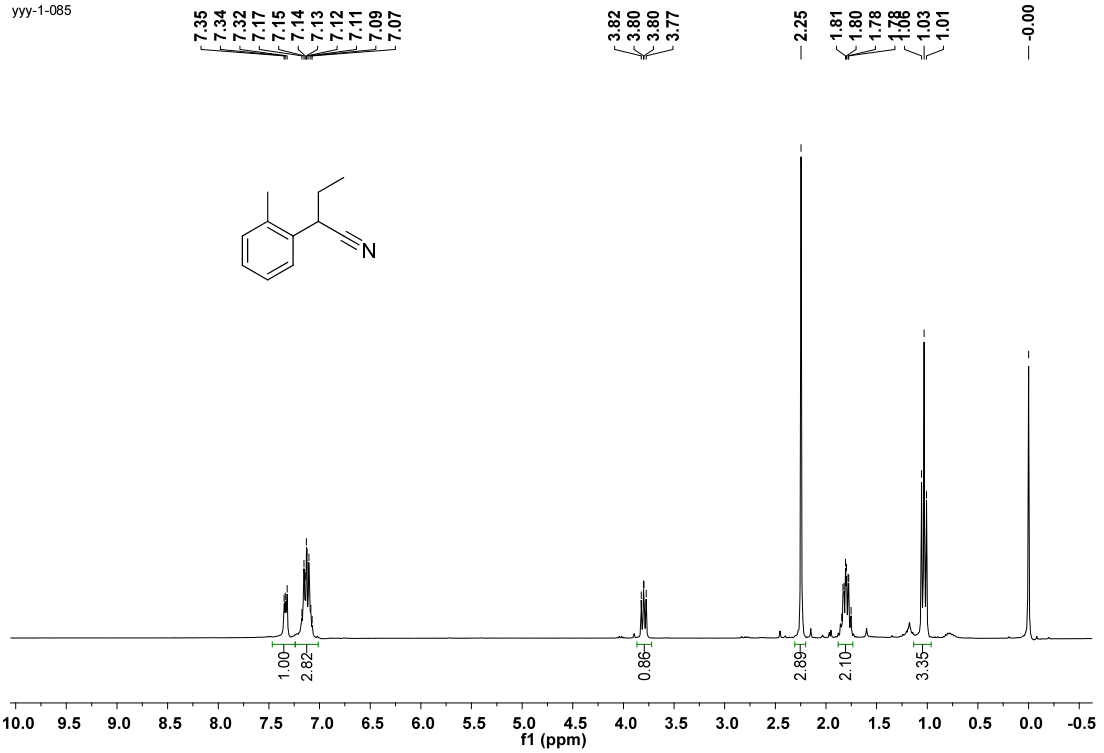
6. NMR Spectra for New Compounds

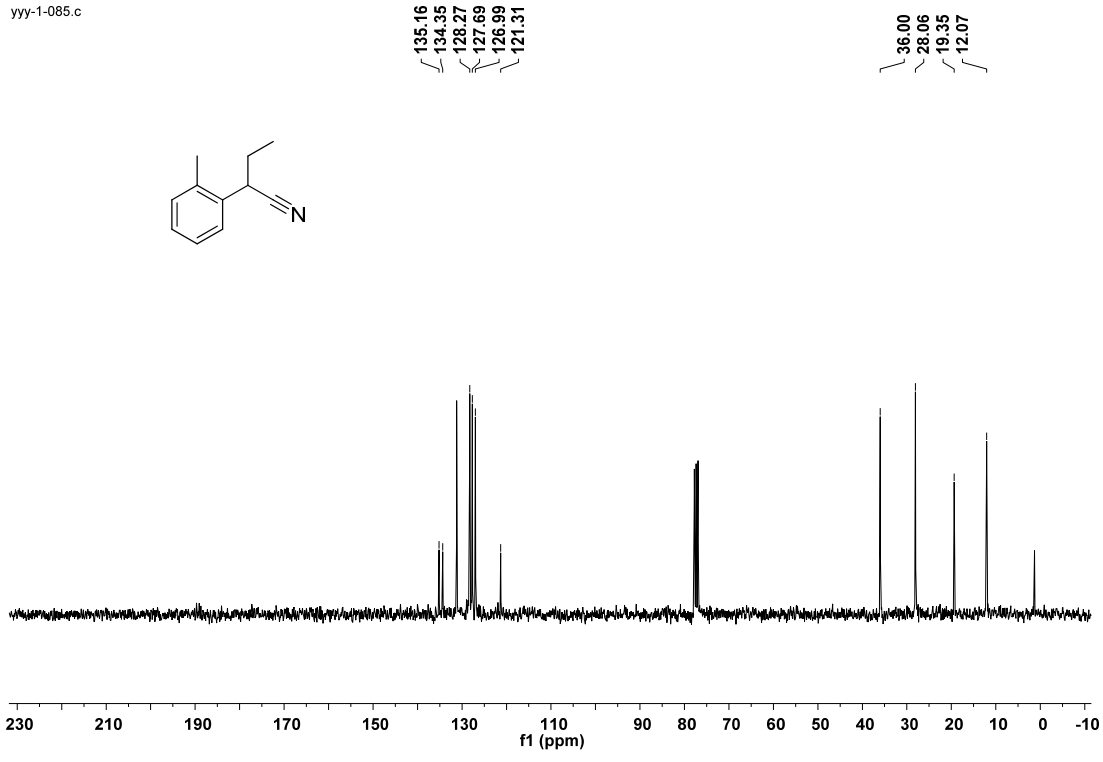
NMR spectra for **Table 1, Entry 2**



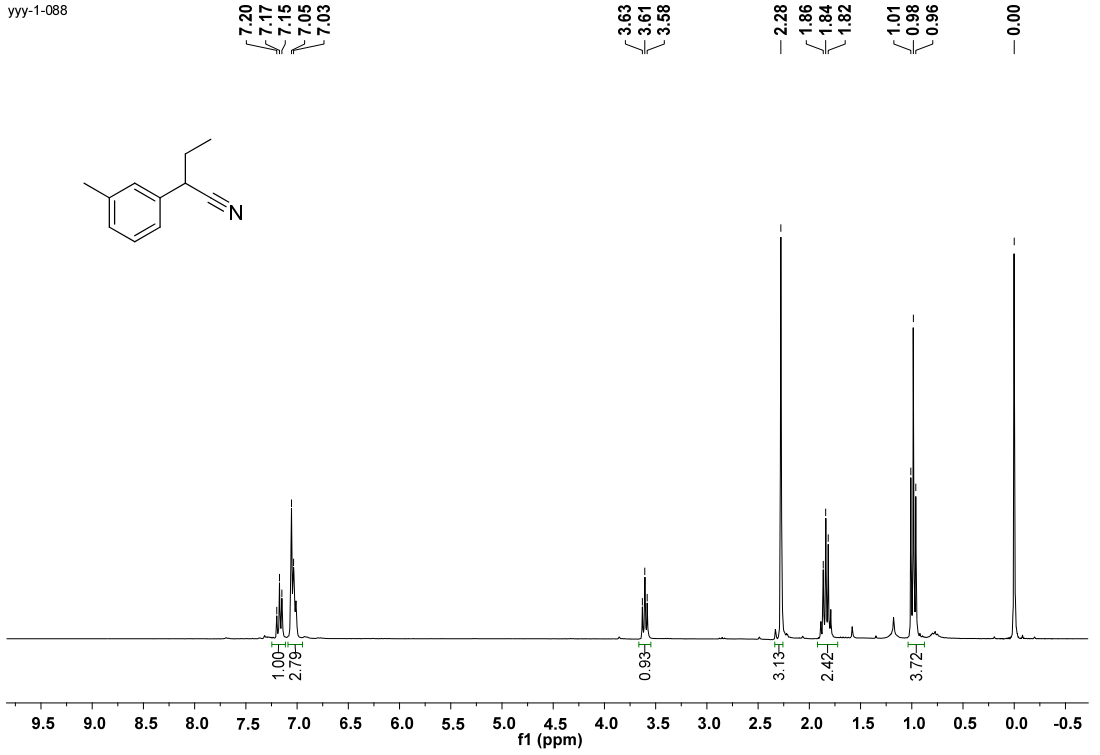


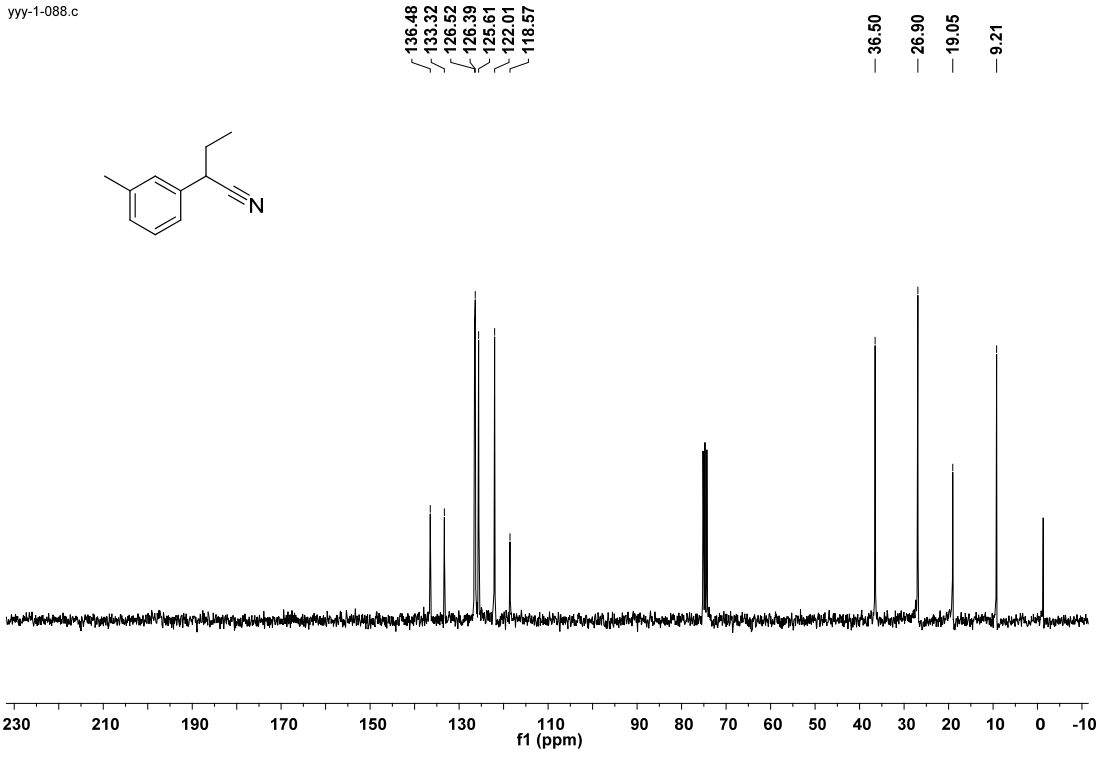
NMR spectra for **Table 1， Entry 3**



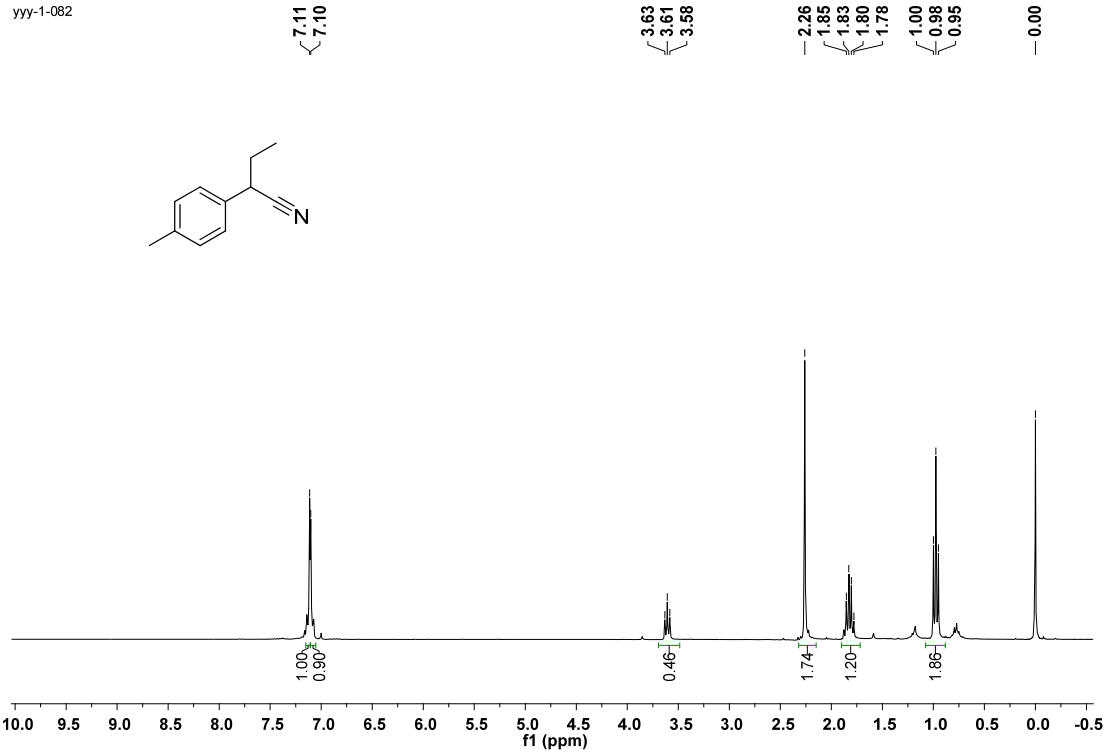


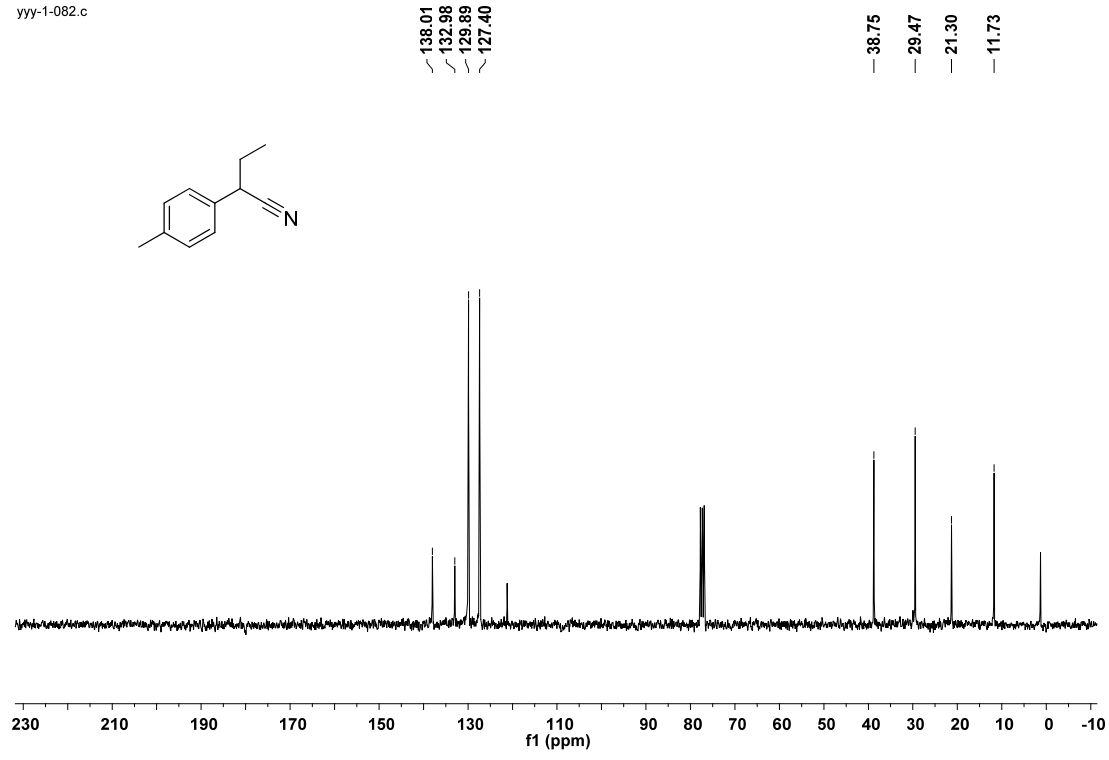
NMR spectra for **Table 1**， **Entry4**



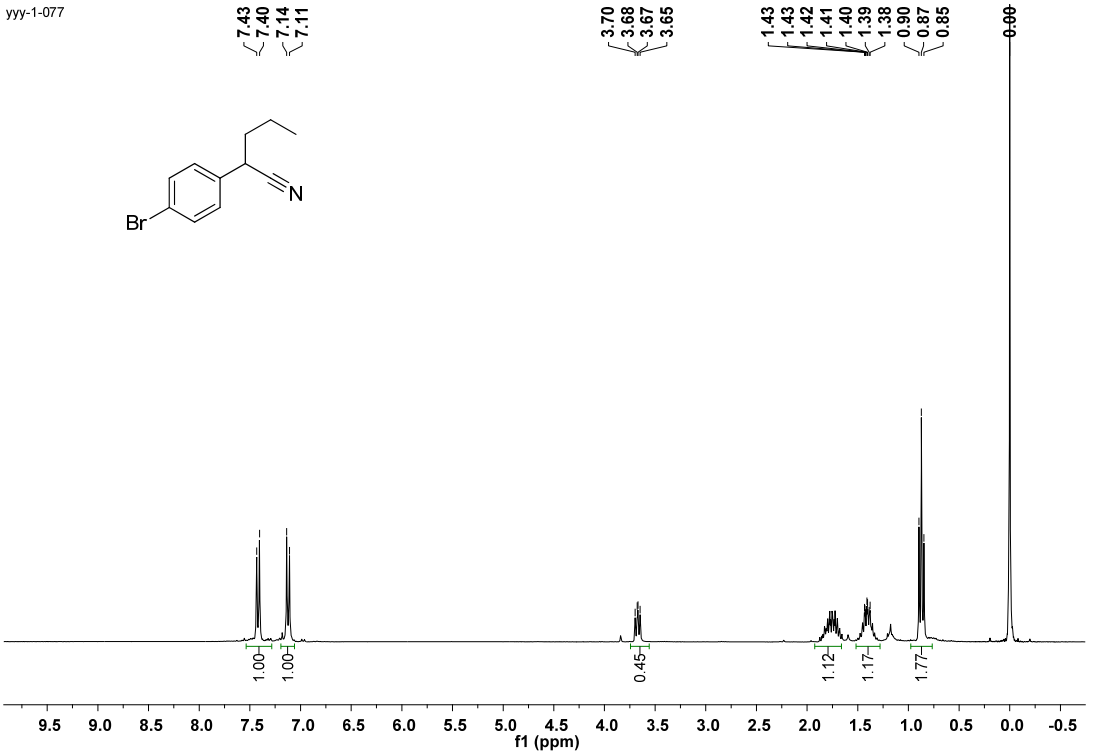


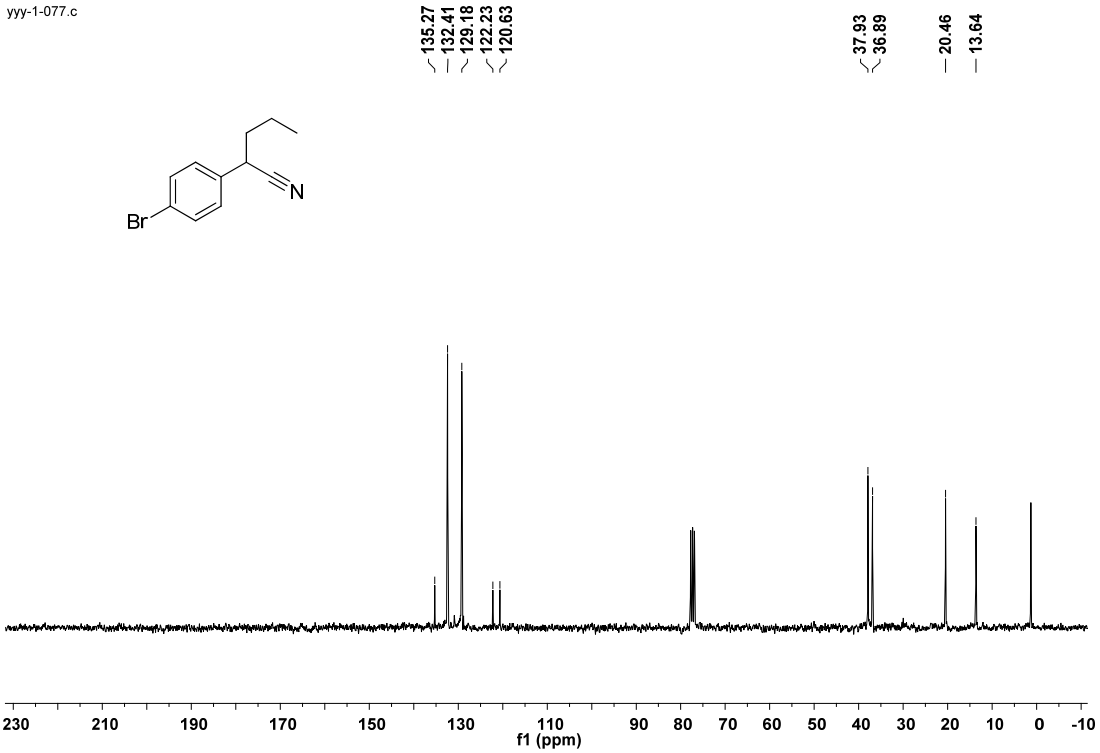
NMR spectra for **Table 1， Entry 5**



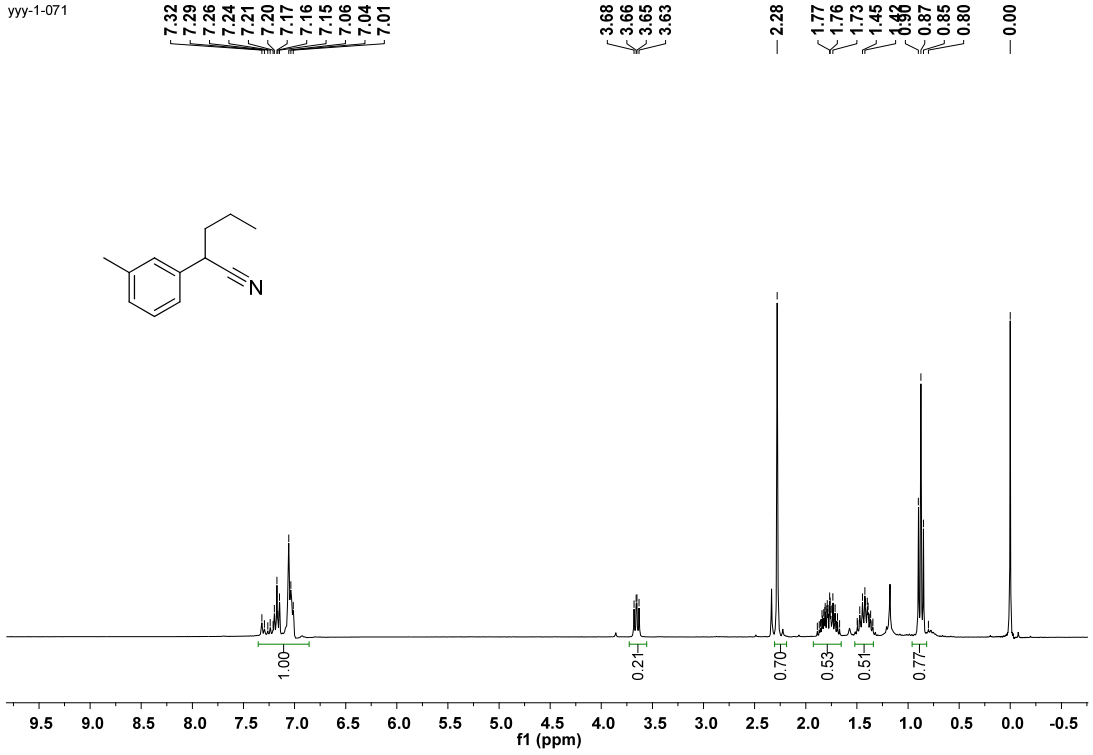


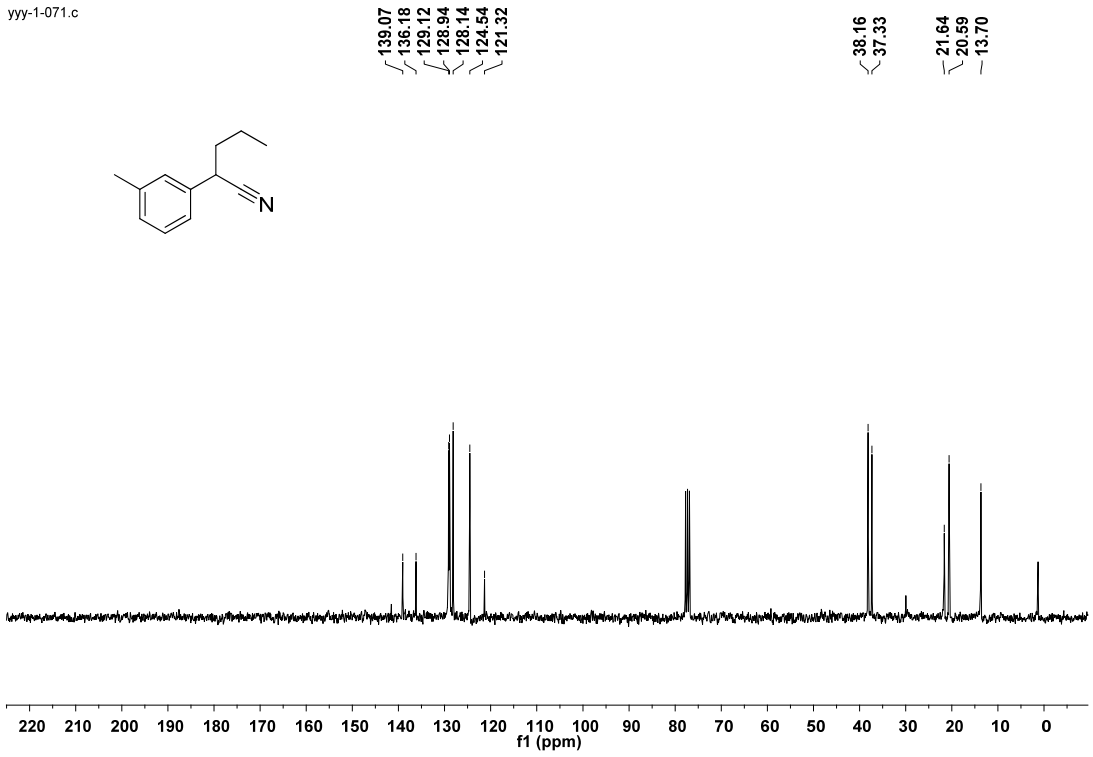
NMR spectra for **Table 1， Entry 6 and Table 2, Entry 5**



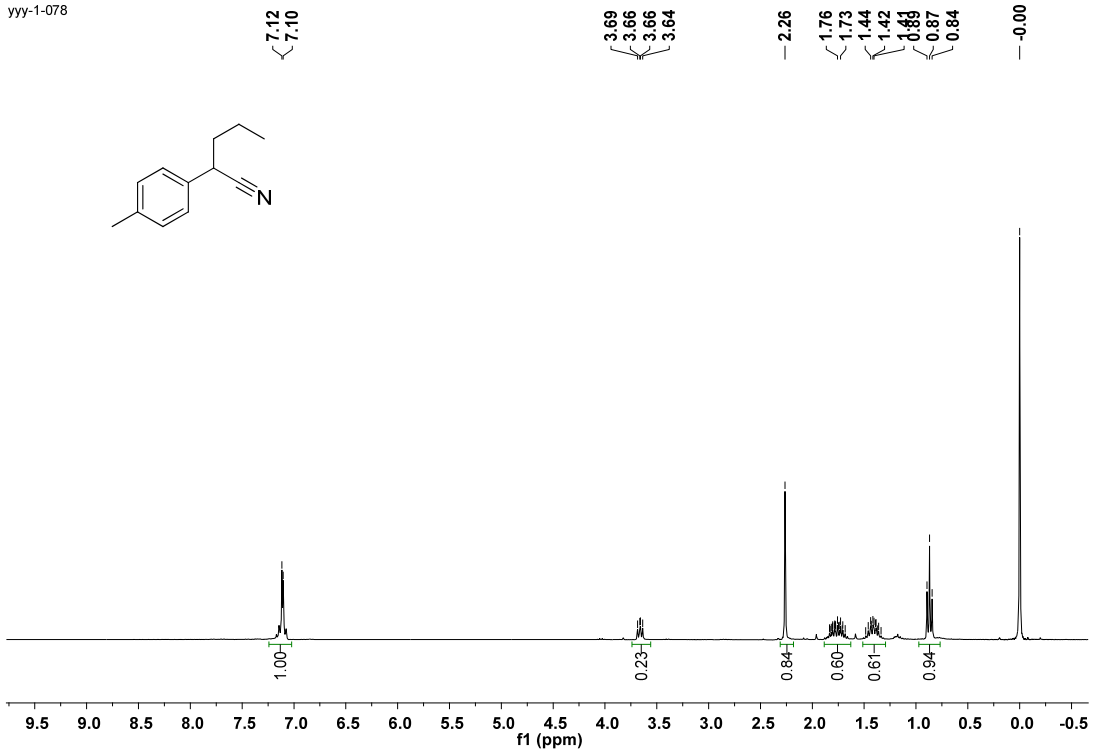


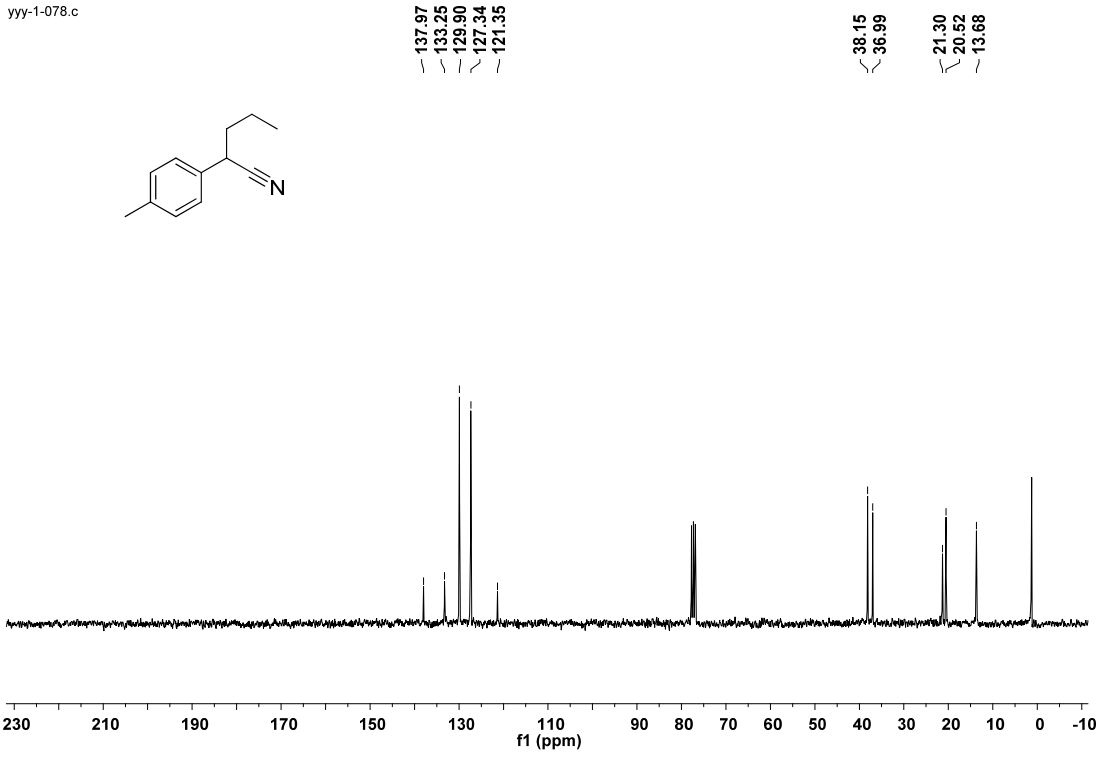
NMR spectra for **Table 2, Entry 2**



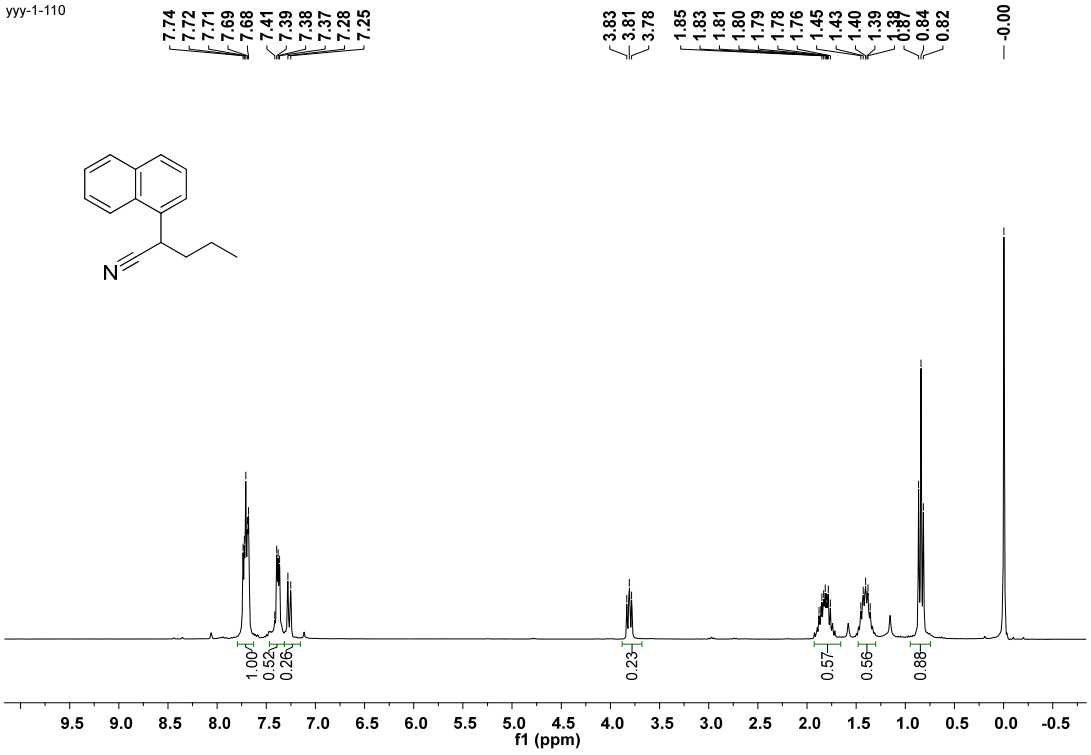


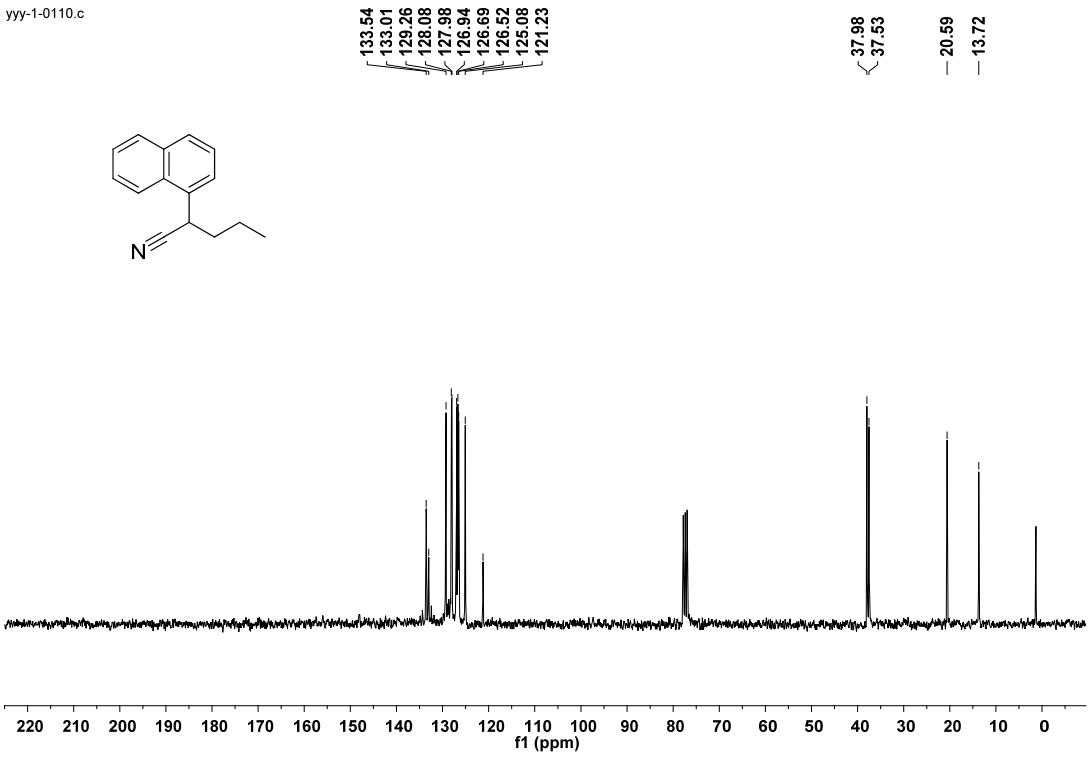
NMR spectra for **Table 2, Entry 3**



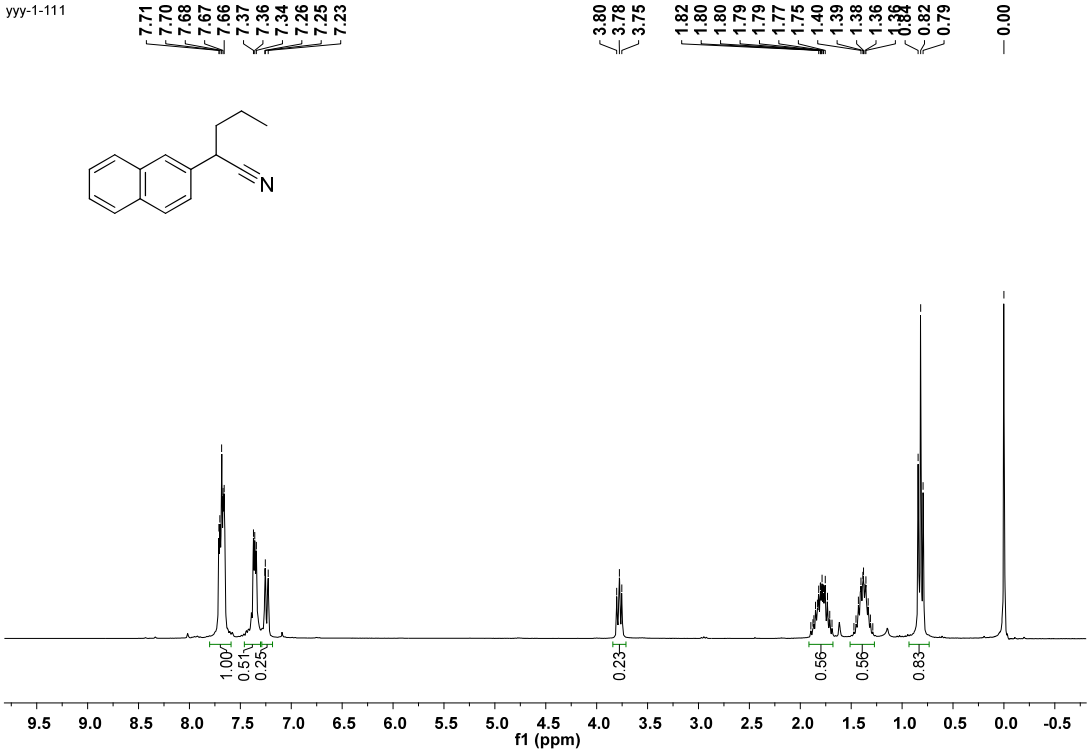


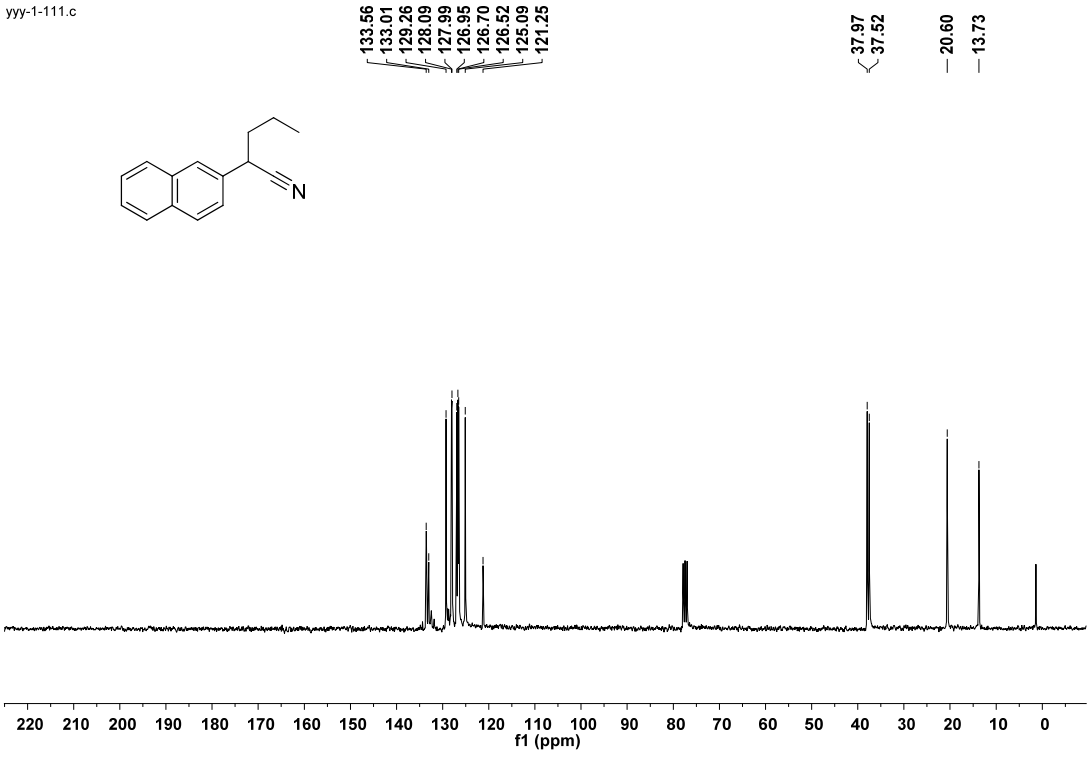
NMR spectra for **Table 2, Entry 5**



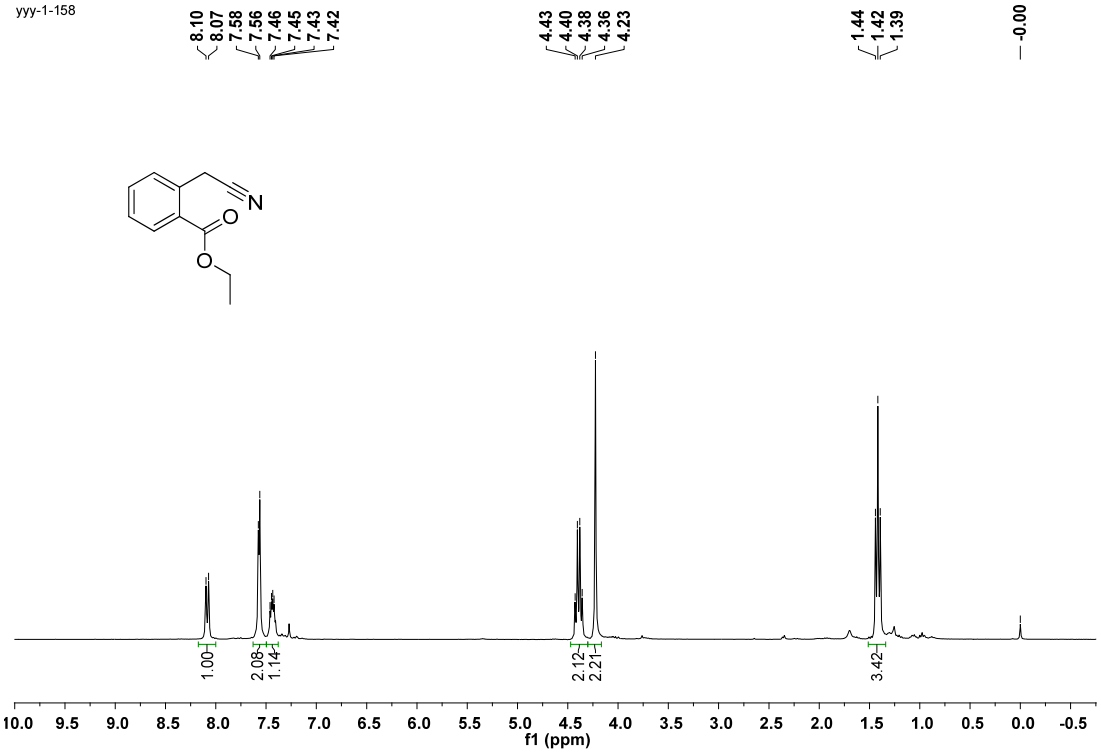


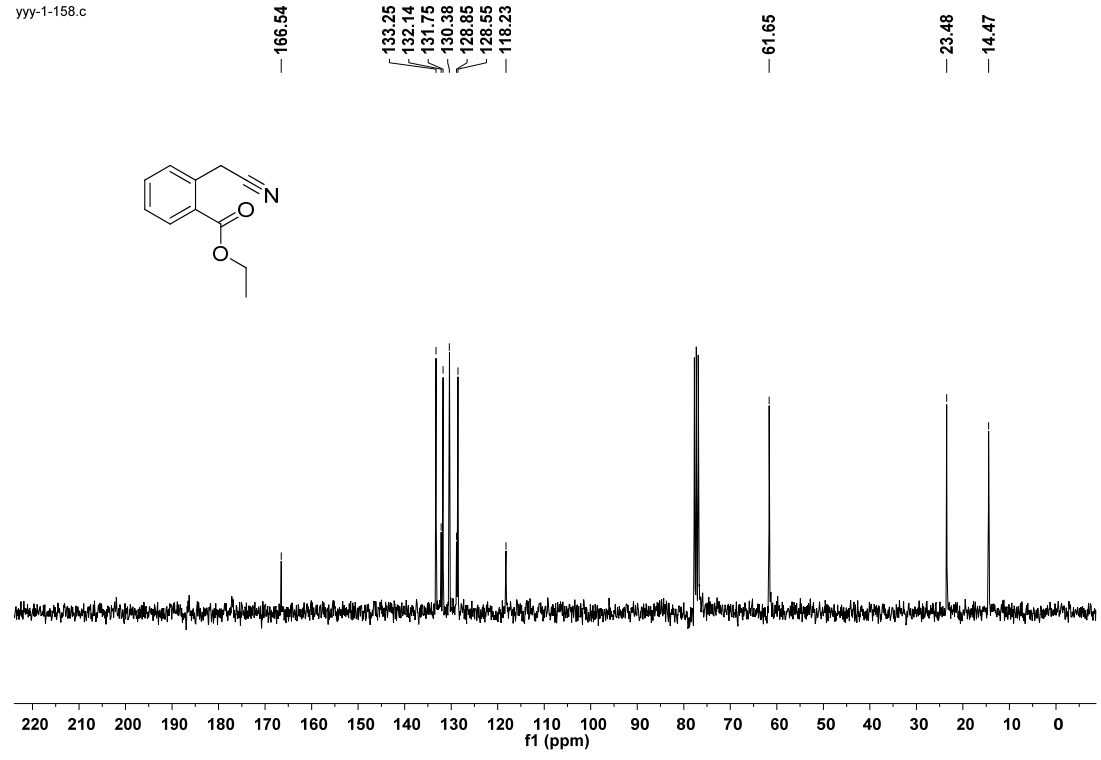
NMR spectra for **Table 2, Entry 6**



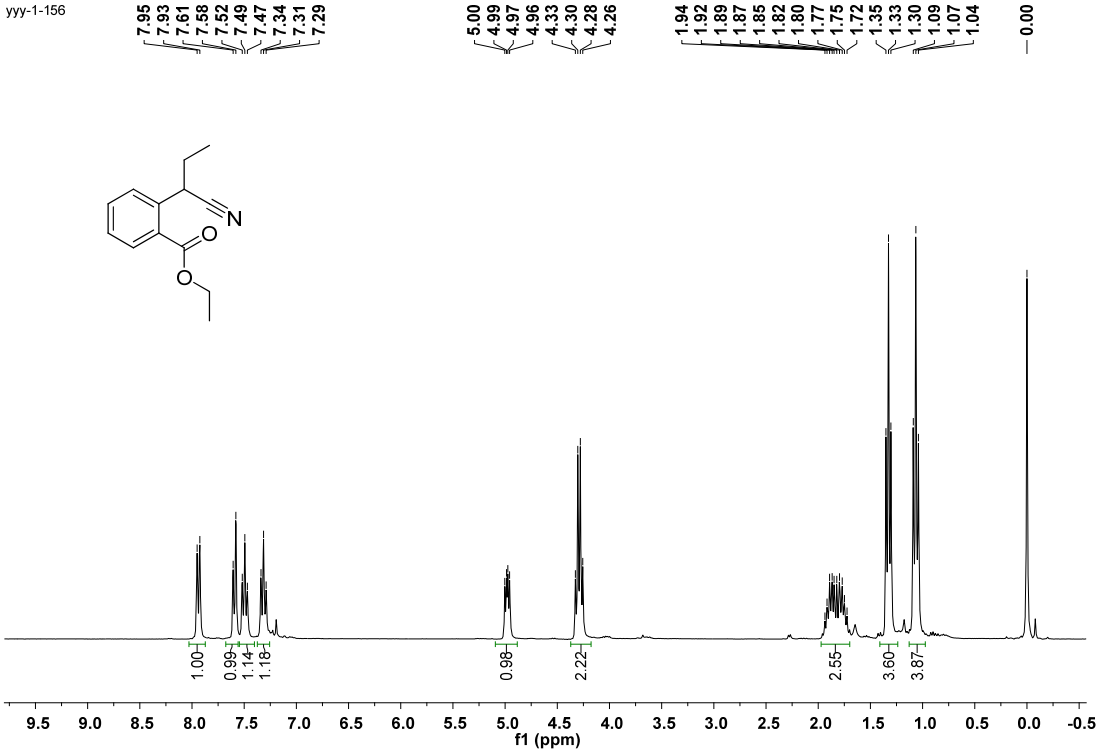


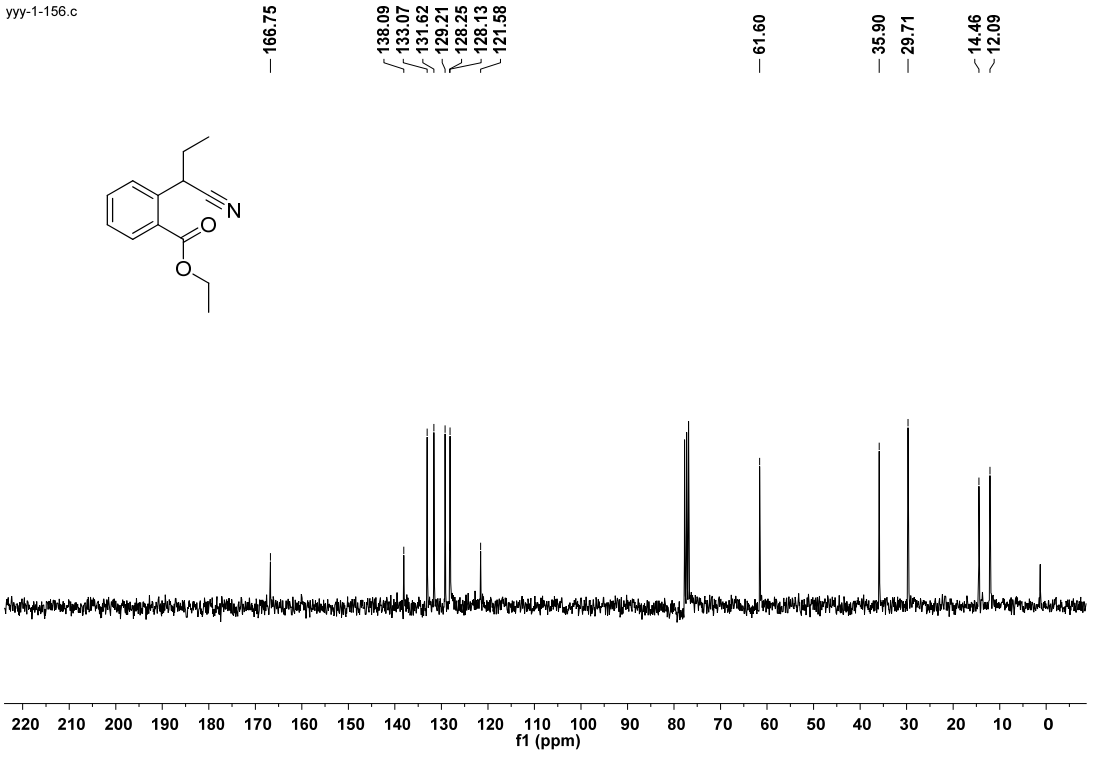
NMR spectra for **Table 3, Entry 1**





NMR spectra for **Table 3, Entry 2**





NMR spectra for **Table 3, Entry 3**