Supporting Information

Copper-Catalyzed Amination of α-C(sp^3)–H Bond in Inactivated Ethers to Synthesis α-Aminonitriles

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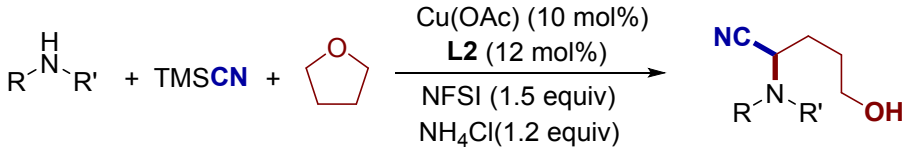
Table of Contents

1. General Information

Reactions were performed in oven-dried glassware using syringe-septum cap techniques under nitrogen atmosphere. All commercially obtained compounds were used as received. Solvents were purified as described in "Purification of Laboratory Chemicals". Thin layer chromatography was performed on GF254 plates (0.25 mm layer thickness). Flash chromatography was performed with 300–400 mesh silica gels. Visualization was accomplished with UV light (254 nm) and phosphomolybdic acid. ^{1}H, ^{13}C NMR spectra were recorded using a Bruker AM-400NMR spectrometer at room temperature. The chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 ppm for 1H) $CDCl_3$ (77.0 ppm for ^{13}C), CD_3OD (3.34 ppm for ^{1}H), CD_3OD (49.86 ppm for ^{13}C). HRMS (EI) were recorded on a Waters AutoSpec Premier P776 spectrometer.

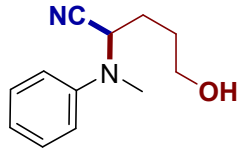
2. General Procedure for Copper-Catalyzed Functionlization



An oven-dried round-bottom flask equipped with a magnetic stirring bar under a nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), Cu(OAc) catalyst (0.02 mmol, 0.1 equiv.), and ether (1 mL). The reaction mixture was allowed to stir at room temperature for 15 min. Then, NH_4Cl (0.24 mmol, 1.2 equiv.), NFSI (0.3 mmol, 1.5 equiv.), TMSCN (0.6 mmol, 3 equiv.), and substrate (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 8 h. The resulting solution was diluted with ethyl acetate and washed with brine. After dried over anhydrous Na_2SO_4, the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford the product.

3. Product Characterization

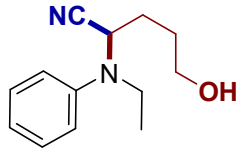
5-Hydroxy-2-(methyl(phenyl)amino)pentanenitrile (2a)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (39.1 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.7 Hz, 2H), 6.99 – 6.92 (m, 3H), 4.56 (t, J = 7.9 Hz, 1H), 3.77 – 3.63 (m, 2H), 2.89 (s, 3H), 2.09 – 1.98 (m, 3H), 1.79 – 1.70 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.19, 129.34, 120.96, 117.86, 116.80, 61.71, 54.01, 34.24, 28.55, 28.52; HRMS (EI) exact mass calculated for $C_{12}H_{16}N_2O$: 204.1263, found *m/z* 204.1265.

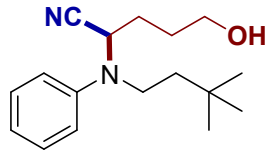
2-(Ethyl(phenyl)amino)-5-hydroxypentanenitrile (2b)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (41.6 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.32 (m, 2H), 7.04 – 6.96 (m, 3H), 4.39 (t, J = 7.8 Hz, 1H), 3.78 – 3.68 (m, 2H), 3.34 (q, J = 7.1 Hz, 2H), 2.08 – 1.96 (m, 2H), 1.84 – 1.73 (m, 2H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.01, 129.32, 121.70, 118.95, 118.85, 98.34, 67.35, 61.77, 53.70, 43.46, 33.18, 29.00, 28.83, 23.33, 13.47; HRMS (EI) exact mass calculated for $C_{13}H_{18}N_2O$: 218.1419, found *m/z* 218.1415.

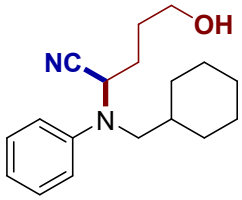
2-((3,3-Dimethylbutyl)(phenyl)amino)-5-hydroxypentanenitrile (2c)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (46.6 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.32 (m, 2H), 6.96 – 7.00 (m, 3H), 4.39 (t, J = 7.8 Hz, 1H), 3.83 – 3.63 (m, 2H), 3.40 – 3.16 (m, 2H), 2.00 (dd, J = 14.9, 7.3 Hz, 2H), 1.73 - 1.80 (m, 2H), 1.52 – 1.59 (m, 1H), 1.45 – 1.33 (m, 1H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.41, 129.40, 121.66, 118.83, 61.95, 54.26, 45.44, 41.18, 29.99, 29.35, 29.08, 28.95; HRMS (EI) exact mass calculated for $C_{17}H_{26}N_2O$: 274.2045, found *m/z* 274.2040.

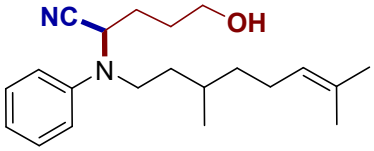
2-((Cyclohexylmethyl)(phenyl)amino)-5-hydroxypentanenitrile (2d)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (46.7 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 3H), 4.28 (t, *J* = 7.9 Hz, 1H), 3.70 (t, *J* = 5.6 Hz, 2H), 3.12 (dd, *J* = 13.6, 5.8 Hz, 1H), 2.89 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.87 -20.5 (m, 2H), 1. 59 – 1.85(m, 8H), 1.49 (ddd, *J* = 11.3, 5.9, 2.9 Hz, 1H), 1.12 (dd, *J* = 14.8, 5.9 Hz, 3H), 0.99 – 0.80 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.98, 129.22, 122.56, 120.89, 118.62, 61.89, 56.43, 55.97, 35.43, 31.38, 31.23, 28.86, 28.85, 25.89, 25.79; HRMS (EI) exact mass calculated for $C_{18}H_{26}N_2O$: 286.2045, found *m/z* 286.2043.

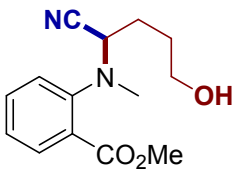
2-((3,7-Dimethyloct-6-en-1-yl)(phenyl)amino)-5-hydroxypentanenitrile (2e)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (51.0 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.9 Hz, 2H), 7.12 – 6.92 (m, 3H), 5.05 - 5.09 (m, 1H), 4.36 (td, *J* = 7.8, 3.0 Hz, 1H), 3.81 – 3.56 (m, 2H), 3.39 – 3.14 (m, 2H), 2.05 – 1.85 (m, 4H), 1.82 – 1.55 (m, 10H), 1.54 – 1.10 (m, 4H), 0.93 (dd, *J* = 6.3, 3.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.43, 147.33, 131.33, 129.32, 124.53, 122.00, 121.95, 119.50, 119.42, 118.80, 118.74, 61.89, 54.45, 54.42, 47.63, 47.49, 36.95, 36.83, 34.84, 34.76, 30.66, 30.61, 29.01, 28.89, 25.70, 25.40, 19.59, 19.49, 17.63; HRMS (EI) exact mass calculated for $C_{21}H_{32}N_2O$: 328.2515, found *m/z* 328.2521.

Methyl 2-((1-cyano-4-hydroxybutyl)(methyl)amino)benzoate (2f)

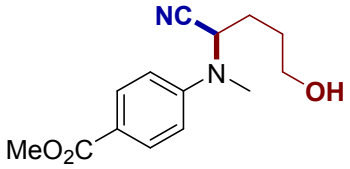


Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (48.2 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.53 – 7.44 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.33 (dd, *J* = 9.1, 6.6 Hz, 1H), 3.87 (s, 3H), 3.69 (t, *J* = 5.9 Hz, 2H), 2.82 (s, 3H), 2.30 (brs, 1H), 2.21 – 1.91 (m, 2H), 1.86 – 1.62 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.71, 150.66, 132.84, 131.15,

126.24, 124.06, 122.07, 118.04, 61.33, 57.29, 52.32, 36.60, 28.42, 28.28; HRMS (EI) exact mass calculated for $C_{14}H_{18}N_2O_3$: 262.1317, found *m/z* 262.1324.

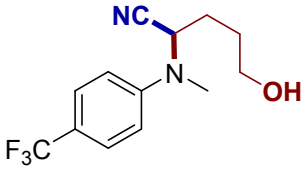
Methyl 4-((1-cyano-4-hydroxybutyl)(methyl)amino)benzoate (2g)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (47.2 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.83 (t, *J* = 7.9 Hz, 1H), 3.86 (s, 3H), 3.70 (dd, *J* = 11.6, 5.7 Hz, 2H), 2.98 (s, 3H), 2.17 – 1.94 (m, 3H), 1.75 – 1.60 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.00, 152.05, 131.43, 120.70, 117.74, 113.44, 61.67, 51.84, 51.75, 33.63, 28.61, 28.20;HRMS (EI) exact mass calculated for $C_{14}H_{18}N_2O_3$: 262.1317, found *m/z* 262.1322.

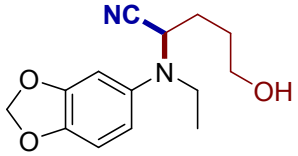
5-Hydroxy-2-(methyl(4-(trifluoromethyl)phenyl)amino)pentanenitrile (2h)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (35.2 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.76 (t, *J* = 7.9 Hz, 1H), 3.82 – 3.61 (m, 2H), 2.97 (s, 3H), 2.22 – 1.97 (m, 2H), 1.87 (s, 1H), 1.77 – 1.65 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.15, 126.73 (q, *J* = 3.8 Hz), 124.53 (q, *J* = 270.8 Hz), 121.51 (q, *J* = 32.9 Hz), 114.45, 61.75, 52.28, 33.76, 28.60, 28.19; HRMS (EI) exact mass calculated for $C_{13}H_{15}F_3N_2O$: 272.1136, found *m/z* 272.1130.

2-(Benzo[d][1,3]dioxol-5-yl(ethyl)amino)-5-hydroxypentanenitrile (2i)

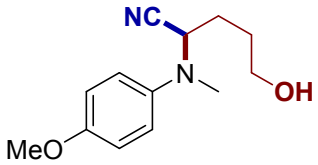


Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as light-yellow oil (35.9 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 – 6.76 (m, 2H), 6.64 (dd, *J* = 8.2, 2.3 Hz, 1H), 5.95 (s, 2H), 4.04 (t, *J* = 7.7 Hz, 1H), 3.77 – 3.62 (m, 2H), 3.23 – 3.05 (m, 2H),

2.03 – 1.71 (m, 4H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 148.19, 144.72, 141.52, 118.73, 116.98, 108.24, 105.38, 101.29, 61.98, 56.51, 45.63, 29.17, 29.11, 13.42; HRMS (EI) exact mass calculated for $C_{14}H_{18}N_2O_3$: 262.1317, found *m/z* 262.1316.

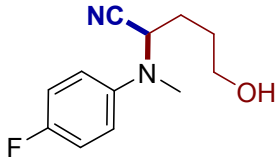
5-Hydroxy-2-((4-methoxyphenyl)(methyl)amino)pentanenitrile (2j)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as light-yellow oil (33.1 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 8.9 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 4.25 (t, J = 7.9 Hz, 1H), 3.77 (s, 3H), 3.70 (dd, J = 9.6, 5.7 Hz, 2H), 2.80 (s, 3H), 1.98 (dd, J = 15.1, 7.5 Hz, 2H), 1.76 (dt, J = 13.0, 6.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.36, 143.19, 120.96, 117.81, 114.54, 61.81, 56.63, 55.48, 35.98, 28.80, 28.73; HRMS (EI) exact mass calculated for $C_{13}H_{18}N_2O_2$: 234.1368, found *m/z* 234.1363.

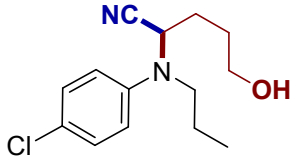
2-((4-Fluorophenyl)(methyl)amino)-5-hydroxypentanenitrile (2k)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (35.8 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (dd, J = 16.2, 6.1 Hz, 4H), 4.29 (t, J = 7.3 Hz, 1H), 3.61 (s, 2H), 2.74 (d, J = 1.3 Hz, 3H), 2.20 (s, 1H), 1.92 (dd, J = 14.5, 6.8 Hz, 2H), 1.76 – 1.56 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.08 (d, J = 241.2 Hz), 145.75 (d, J = 2.5 Hz), 119.81 (d, J = 7.9 Hz), 117.62 , 115.83 (d, J = 22.4 Hz), 61.64 , 55.64 , 35.19 , 28.56 , 28.47 ; HRMS (EI) exact mass calculated for $C_{12}H_{15}FN_2O$: 222.1168, found *m/z* 222.1172.

2-((4-Chlorophenyl)(propyl)amino)-5-hydroxypentanenitrile (2l)

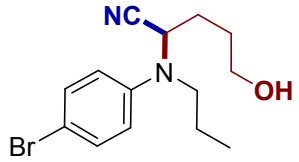


Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (49.5 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.16 (m, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.32 (t, J = 7.9 Hz, 1H), 3.70 (dt, J = 9.6, 5.4 Hz, 2H), 3.27 – 3.01 (m,2H), 1.97 (dd, J = 15.3, 7.6 Hz, 2H), 1.85 (s, 1H), 1.73 (dt, J = 12.9, 6.4 Hz, 2H), 1.64 – 1.38 (m, 2H),

0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.98, 129.32, 127.04, 120.68, 118.59, 61.81, 54.45, 51.25, 28.96, 28.72, 20.99, 11.43; HRMS (EI) exact mass calculated for $C_{14}H_{19}ClN_2O$: 266.1186, found *m/z* 266.1184.

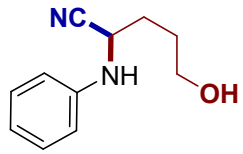
2-((4-Bromophenyl)(propyl)amino)-5-hydroxypentanenitrile (2m)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as light-yellow oil (56.4 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.9 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 4.35 (t, J = 7.9 Hz, 1H), 3.74 – 3.55 (m, 2H), 3.26 – 3.05 (m, 2H), 2.14 (s, 1H), 1.96 (dd, J = 15.3, 7.7 Hz, 2H), 1.75 – 1.67 (m, 2H), 1.65 – 1.41 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.26, 132.08, 120.37, 118.47, 113.93, 61.56, 53.93, 50.84, 28.76, 28.52, 20.82, 11.28; HRMS (EI) exact mass calculated for $C_{14}H_{19}BrN_2O$: 310.0681, found *m/z* 310.0683.

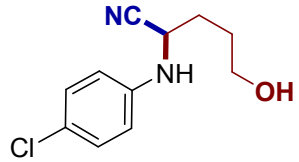
5-Hydroxy-2-(phenylamino)pentanenitrile (2n)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (27.3 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 7.9 Hz, 2H), 6.87 (t, J = 7.4 Hz, 1H), 6.72 (d, J = 7.9 Hz, 2H), 4.31 (q, J = 6.6 Hz, 1H), 3.99 (d, J = 7.7 Hz, 1H), 3.76 (t, J = 5.9 Hz, 2H), 2.09 (q, J = 7.1 Hz, 2H), 1.87 (ddt, J = 13.4, 8.7, 4.5 Hz, 2H), 1.75 – 1.62 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.92, 129.57, 120.06, 119.58, 114.12, 61.81, 45.80, 30.43, 28.44; HRMS (EI) exact mass calculated for $C_{11}H_{14}N_2O$: 190.1106, found *m/z* 190.1104.

2-((4-Chlorophenyl)amino)-5-hydroxypentanenitrile (2o)

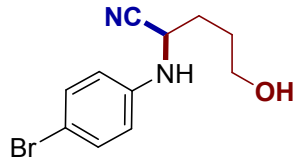


Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless crystal (34.0 mg, 76%). Mp:84.2-86.2 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 5.9 Hz, 2H), 6.62 (d, J = 8.7 Hz, 2H), 4.24 (J = 5.8 Hz, 2H), 3.71 (t, J = 5.8 Hz,2H), 2.18 (s, 1H), 2.04 (dd, J = 12.6, 6.3 Hz, 2H), 1.89 – 1.72 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.56, 129.34, 124.58,

119.36, 115.14, 61.57, 45.79, 30.11, 28.26; HRMS (EI) exact mass calculated for $C_{11}H_{13}ClN_2O$: 224.0716, found *m/z* 224.0720.

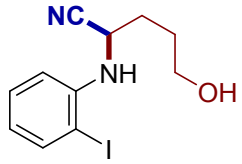
2-((4-Bromophenyl)amino)-5-hydroxypentanenitrile (2p)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as light-yellow oil (38.3 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.27 (d, *J* = 6.3 Hz, 1H), 4.11 (d, *J* = 15.5 Hz, 1H), 3.76 (t, *J* = 5.7 Hz, 2H), 2.12 – 2.04 (m, 2H), 1.95 – 1.77 (m, 2H), 1.64 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.96, 132.30, 119.16, 115.62, 111.91, 61.73, 45.70, 30.27, 28.25; HRMS (EI) exact mass calculated for $C_{11}H_{13}BrN_2O$: 268.0211, found *m/z* 268.0206.

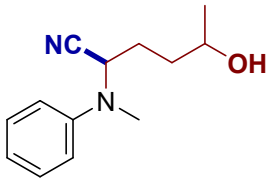
5-Hydroxy-2-((2-iodophenyl)amino)pentanenitrile (2q)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as light-yellow oil (44.0 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.28 (dd, *J* = 14.0, 6.1 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.61 (t, *J* = 7.6 Hz, 1H), 4.35 (dt, *J* = 15.2, 7.9 Hz, 2H), 3.86 – 3.65 (m, 2H), 2.16 (dd, *J* = 14.7, 7.2 Hz, 2H), 1.87 (ddd, *J* = 13.2, 9.5, 4.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.28, 139.50, 129.76, 121.30, 119.05, 112.06, 86.32, 61.65, 45.87, 30.15, 28.39; HRMS (EI) exact mass calculated for $C_{11}H_{13}IN_2O$: 316.0073, found *m/z* 316.0065.

5-Hydroxy-2-(methyl(phenyl)amino)hexanenitrile (2r)

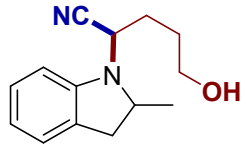


Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (25.6 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 6.97 – 6.90 (m, 3H), 4.58 – 4.52 (m, 1H), 3.84 – 3.87 (m, 1H), 2.88 (s, 3H), 2.15 – 1.94 (m, 2H), 1.86 (brs, 1H), 1.70 – 1.52 (m, 2H), 1.22 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.23, 149.17, 129.33, 129.32, 120.93, 120.85, 117.95, 117.83, 116.76, 116.70, 67.29, 67.19,

54.07, 54.05, 34.79, 34.67, 34.17, 34.16, 28.30, 28.03, 23.87, 23.74; HRMS (EI) exact mass calculated for $C_{13}H_{18}N_2O$: 218.1419, found *m/z* 218.1423.

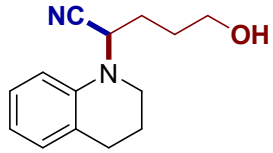
5-Hydroxy-2-(2-methylindolin-1-yl)pentanenitrile (3a)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (37.7 mg, 82%, dr = 5.8:4.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.7 Hz, 2H), 6.79 (dd, *J* = 7.3, 1.9 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 4.41 (t, *J* = 8.1 Hz, 1H, minor diastereomer), 4.24 (t, *J* = 8.1 Hz, 1H, major diastereomer), 3.93 – 3.75 (m, 1H), 3.75 – 3.64 (m, 2H), 3.32 (dd, *J* = 15.7, 9.0 Hz, 1H, minor diastereomer), 3.16 (dd, *J* = 15.4, 8.4 Hz, 1H, major diastereomer), 2.72 – 2.56 (m, 1H), 2.27 – 1.91 (m, 3H), 1.87 – 1.67 (m, 2H), 1.36 (d, *J* = 6.2 Hz, 3H, minor diastereomer), 1.35 (d, *J* = 6.1 Hz, 3H, major diastereomer); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.06 , 148.27 , 129.36 , 129.14 , 127.35 , 127.25 , 124.77 , 124.65 , 119.91 , 119.61 , 118.24 , 118.02 , 109.09 , 108.30 , 61.66 , 61.58 , 59.32 , 59.09 , 50.65 , 47.92 , 37.44 , 36.98 , 29.11 , 28.92 , 28.75 , 28.49 , 21.69 , 18.90 ; HRMS (EI) exact mass calculated for $C_{14}H_{18}N_2O$: 230.1419, found *m/z* 230.1418.

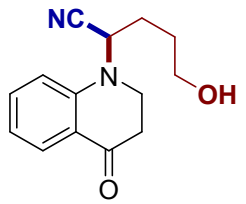
2-(3,4-Dihydroquinolin-1(2H)-yl)-5-hydroxypentanenitrile (3b)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (37.2 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.75 (dd, *J* = 14.1, 7.6 Hz, 15H), 4.56 (t, *J* = 7.9 Hz, 1H), 3.79 – 3.63 (m, 1H), 3.34 – 3.18 (m, 2H), 2.86 – 2.67 (m, 2H), 2.15 – 1.95 (m, 4H), 1.89 (brs, 1H), 1.81 – 1.68 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.64, 129.51, 127.13, 125.31, 118.69, 118.31, 111.94, 61.68, 50.39, 43.95, 28.41, 27.78, 27.64, 21.96； HRMS (EI) exact mass calculated for $C_{14}H_{18}N_2O$: 230.1419, found *m/z* 230.1420.

5-Hydroxy-2-(4-oxo-3,4-dihydroquinolin-1(2H)-yl)pentanenitrile (3c)

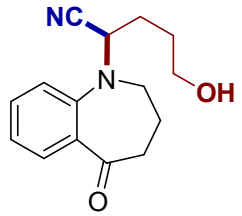


Following the general procedure, column chromatography on silica gel (eluent:

hexanes: EtOAc = 2:1) afforded the title compound as colorless oil (42.3 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.57 – 7.42 (m, 1H), 7.01 – 6.81 (m, 2H), 4.90 (t, *J* = 7.9 Hz, 1H), 3.87 – 3.71 (m, 2H), 3.66 – 3.47 (m, 2H), 2.92 – 2.70 (m, 2H), 2.34 – 2.06 (m, 2H), 1.90 – 1.75 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.79, 149.57, 135.67, 128.99, 121.73, 119.61, 117.34, 112.67, 61.76, 49.35, 44.10, 38.04, 28.18, 27.88.; HRMS (EI) exact mass calculated for $C_{14}H_{16}N_2O_2$: 244.1212, found *m/z* 244.1210.

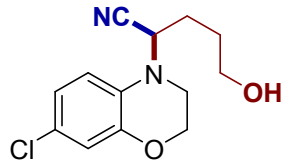
5-Hydroxy-2-(5-oxo-2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)pentanenitrile (3d)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 2:1) afforded the title compound as colorless oil (47.8 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.11 – 6.93 (m, 2H), 4.64 (t, *J* = 7.8 Hz, 1H), 3.82 – 3.63 (m, 2H), 3.58 – 3.39 (m, 1H), 3.19 – 3.01 (m, 1H), 2.95 – 2.78 (m, 1H), 2.78 – 2.66 (m, 1H), 2.26 – 1.99 (m, 5H), 1.86 – 1.71 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.49, 151.00, 133.22, 130.16, 129.36, 121.43, 118.53, 115.88, 61.44, 51.85, 51.07, 40.53, 29.51, 28.64, 28.47; HRMS (EI) exact mass calculated for $C_{15}H_{18}N_2O_2$: 258.1368, found *m/z* 258.1365.

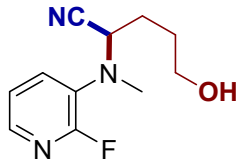
2-(7-Chloro-2,3-dihydro-4H-benzo[b][1,4]oxazin-4-yl)-5-hydroxypentanenitrile (3e)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as light-yellow oil (33.0 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ6.99 – 6.69 (m, 3H), 4.56 (t, *J* = 7.9 Hz, 3H), 3.77 – 3.63 (m, 2H), 2.89 (s, 2H), 2.09 – 1.98 (m, 2H), 1.79 – 1.70 (m, 2H),1.61 (brs, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.83 , 131.42 , 125.19 , 121.35 , 117.47 , 117.38 , 114.30 , 64.36 , 61.81 , 50.34 , 41.93 , 28.22 , 27.59 ; HRMS (EI) exact mass calculated for $C_{13}H_{15}ClN_2O_2$: 266.0822, found *m/z* 266.0819.

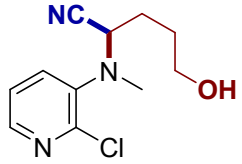
2-((2-Fluoropyridin-3-yl)(methyl)amino)-5-hydroxypentanenitrile (3f)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 2:1) afforded the title compound as light-yellow oil (35.4 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 4.7 Hz, 1H), 7.55 – 7.43 (m, 1H), 7.17 (dd, *J* = 7.0, 5.5 Hz, 1H), 4.44 – 4.32 (m, 1H), 3.73 (t, *J* = 5.6 Hz, 2H), 2.84 (s, 3H), 2.06 (dd, *J* = 15.4, 7.9 Hz, 2H), 1.95 (s, 1H), 1.79 (dt, *J* = 11.3, 6.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.99 (d, *J* = 238.2 Hz), 140.45 (d, *J* = 14.5 Hz), 133.49 (d, *J* = 23.6 Hz), 130.13 (d, *J* = 4.1 Hz), 122.17 (d, *J* = 4.3 Hz), 117.19 , 61.59 , 54.84 (d, *J* = 6.0 Hz), 34.32 , 28.36 , 28.27 ； HRMS (EI) exact mass calculated for $C_{11}H_{14}FN_3O$: 223.1121, found *m/z* 223.1126.

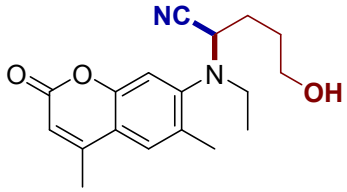
2-((2-Chloropyridin-3-yl)(methyl)amino)-5-hydroxypentanenitrile (3g)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 2:1) afforded the title compound as light-yellow oil (40.8 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 4.4 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.21 (m, 1H), 4.33 (t, *J* = 8.0 Hz, 1H), 3.75 (t, *J* = 5.9 Hz, 2H), 2.85 (s, 3H), 2.42 (s, 1H), 2.15 – 2.04 (m, 2H), 1.89 – 1.78 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.87, 144.72, 144.06, 131.19, 123.24, 117.13, 61.47, 55.51, 35.30, 28.32, 28.23; HRMS (EI) exact mass calculated for $C_{11}H_{14}ClN_3O$: 239.0825, found *m/z* 239.0820.

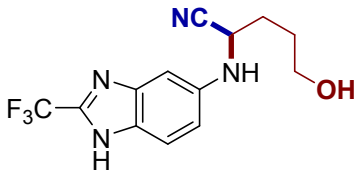
2-((4,6-Dimethyl-2-oxo-2H-chromen-7-yl)(ethyl)amino)-5-hydroxypentane-nitrile (3h)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as yellow oil (58.1 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.32 (d, *J* = 2.1 Hz, 1H), 6.19 (s, 1H), 4.01 (t, *J* = 7.9 Hz, 1H), 3.78 – 3.64 (m, 2H), 3.30 – 3.05 (m, 2H), 2.61 (d, *J* = 34.7 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H), 2.03 (dd, *J* = 13.9, 6.2 Hz, 2H), 1.84 – 1.66 (m, 2H), 1.03 (td, *J* = 6.8, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.02, 152.12, 150.02, 131.63, 126.55, 118.05, 116.87, 113.71, 111.23, 61.32, 55.54, 43.17, 28.54, 28.21, 18.39, 17.79, 12.70; HRMS (EI) exact mass calculated for $C_{18}H_{22}N_2O_3$: 314.1630, found *m/z* 314.1639.

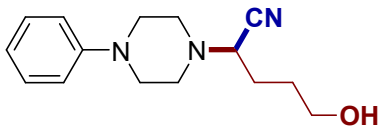
5-Hydroxy-2-((2-(trifluoromethyl)-1H-benzo[d]imidazol-5-yl)amino)pentan-enitrile (3i)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 1:1) afforded the title compound as colorless oil (38.5 mg, 65%).

^{1}H NMR (400 MHz, MeOD) δ 7.57 – 7.49 (m, 1H), 6.91 - 6.92 (m, 2H), 4.48 (t, *J* = 7.3 Hz, 5H), 3.66 (t, *J* = 6.2 Hz, 2H), 2.14 – 2.02 (m, 9H), 1.88 – 1.79 (m, 2H);^{13}C NMR (101 MHz, MeOD) δ 147.04, 141.18 (d, *J* = 39.9 Hz), 125.30, 122.63, 122.05, 119.95, 117.27, 116.78, 62.90, 47.81, 31.75, 30.65; HRMS (EI) exact mass calculated for $C_{13}H_{13}F_3N_4O$: 298.1041, found *m/z* 298.1038.

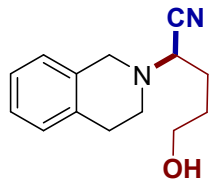
5-Hydroxy-2-(4-phenylpiperazin-1-yl)pentanenitrile (3j)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 2:1) afforded the title compound as colorless oil (31.4 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 2H), 7.00 – 6.80 (m, 3H), 3.79 – 3.53 (m, 3H), 3.41 – 3.12 (m, 4H), 2.99 – 2.84 (m, 2H), 2.77 – 2.63 (m, 2H), 2.61 (brs, 1H), 2.12 – 1.91 (m, 2H), 1.89 – 1.69 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.89, 129.14, 120.22, 116.65, 116.39, 61.91, 57.64, 49.71, 48.94, 29.57, 28.24; HRMS (EI) exact mass calculated for $C_{15}H_{21}N_3O$: 259.1685, found *m/z* 259.1682.

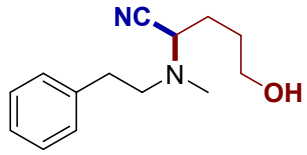
2-(3,4-Dihydroisoquinolin-2(1H)-yl)-5-hydroxypentanenitrile (3k)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 2:1) afforded the title compound as colorless oil (35.0 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.09 (m, 3H), 7.07 – 7.01 (m, 1H), 3.90 (d, *J* = 14.3 Hz, 1H), 3.81 – 3.59 (m, 1H), 3.13 – 2.86 (m, 4H), 2.82 – 2.66 (m, 3H), 2.63 (brs, 1H), 2.17 – 1.94 (m, 2H), 1.88 – 1.65 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.41, 133.08, 128.67, 126.57 ,126.53 , 125.93, 116.84, 61.84, 57.70, 52.29, 47.71, 29.45, 28.99, 28.36; HRMS (EI) exact mass calculated for $C_{14}H_{18}N_2O$: 230.1419, found *m/z* 230.1414.

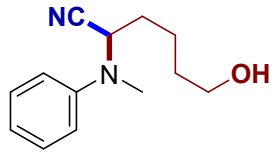
5-Hydroxy-2-(methyl(phenethyl)amino)pentanenitrile (3l)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 2:1) afforded the title compound as colorless oil (28.3 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 14.7, 7.4 Hz, 2H), 7.21 (t, *J* = 9.5 Hz, 3H), 3.71 – 3.43 (m, 3H), 2.86 – 2.75 (m, 3H), 2.73 – 2.58 (m, 1H), 2.39 (s, 3H), 2.01 – 1.78 (m, 1H), 1.74 – 1.54 (m, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.35, 128.74, 128.50, 126.37, 117.13, 61.95, 57.38, 56.74, 38.06, 34.04, 29.51, 28.99; HRMS (EI) exact mass calculated for $C_{14}H_{20}N_2O$: 232.1576, found *m/z* 232.1579.

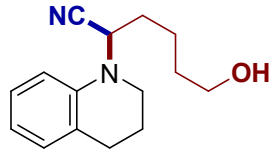
6-Hydroxy-2-(methyl(phenyl)amino)hexanenitrile (3m)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (34.4 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 15.3, 8.0 Hz, 1H), 6.94 (t, *J* = 7.1 Hz, 1H), 4.48 (t, *J* = 7.9 Hz, 1H), 3.68 (s, 1H), 2.90 (s, 1H), 2.14 – 1.90 (m, 1H), 1.61 (dd, *J* = 14.6, 2.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.33 , 129.42 , 120.95 , 117.93 , 116.80 , 62.41 , 54.14 , 34.35 , 31.82 , 31.60 , 29.72 , 22.27 , 19.18; HRMS (EI) exact mass calculated for $C_{13}H_{18}N_2O$: 218.1419, found *m/z* 218.1415.

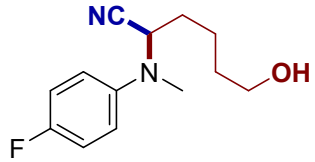
2-(3,4-Dihydroquinolin-1(2H)-yl)-6-hydroxyhexanenitrile (3n)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (36.6 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.82 – 6.65 (m, 2H), 4.66 (t, *J* = 7.8 Hz, 1H), 3.75 – 3.61 (m, 2H), 3.26 (qt, *J* = 11.2, 5.8 Hz, 2H), 2.86 – 2.77 (m, 1H), 2.76 – 2.66 (m, 1H), 2.07 – 1.91 (m, 4H), 1.70 – 1.52 (m, 4H), 1.46 (s, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 143.70 , 129.57 , 127.18 , 125.32 , 118.69 , 118.31 , 111.86 , 62.31 , 50.57 , 44.08 , 31.76 , 30.85 , 27.69 , 22.25 , 22.02 ; HRMS (EI) exact mass calculated for $C_{15}H_{20}N_2O$: 244.1576, found *m/z* 244.1582.

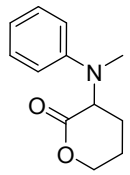
2-((4-Fluorophenyl)(methyl)amino)-6-hydroxyhexanenitrile (3o)



Following the general procedure, column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) afforded the title compound as colorless oil (33.5 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dt, *J* = 13.3, 8.9 Hz, 1H), 4.26 (t, *J* = 7.9 Hz, 1H), 3.65 (t, *J* = 5.6 Hz, 1H), 2.82 (s, 1H), 1.91 (dd, *J* = 14.4, 7.3 Hz, 1H), 1.58 (dd, *J* = 18.2, 5.2 Hz, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 158.15 (d, *J* = 241.1 Hz), 145.93 (d, *J* = 2.4 Hz), 119.88 (d, *J* = 7.9 Hz), 117.73 , 115.94 (d, *J* = 22.4 Hz), 62.27 , 55.84 , 35.35 , 31.76 , 31.57 , 22.28 ; HRMS (EI) exact mass calculated for $C_{13}H_{17}FN_2O$: 236.1325, found *m/z* 236.1321.

3-(Methyl(phenyl)amino)tetrahydro-2H-pyran-2-one(2a')

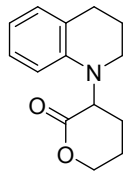


To a solution of 5-hydroxy-2-(methyl(phenyl)amino)pentanenitrile **2a** (0.2 mmol, 1 equiv.) in chlorobenzene (1 mL) was added methanesulfonic acid (1 mL) at 0 °C. Then, the reaction was allowed to stir at 60 °C for 6 hours. After that, saturated aqueous $NaHCO_3$ (5 mL) was added to stirred for 10 min. The aqueous layer was extracted by ethyl acetate (10 mL × 3). The combined organic layers were dried over anhydrous sodium sulfate and concentrated. The residue was purified via chromatography on silica gel (eluent: hexanes: EtOAc = 5:1) to afford the product **2a'** as colorless oil in 86% yield (35.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 2H), 6.86 – 6.73 (m, 3H), 4.56 –

4.27 (m, 3H), 2.92 (s, 3H), 2.30 – 2.17 (m, 1H), 2.17 – 1.98 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.75 , 149.22 , 129.14 , 118.01 , 113.74 , 68.76 , 59.25 , 34.87 , 23.81 , 22.69 , 22.58 ; HRMS (EI) exact mass calculated for $C_{12}H_{15}NO_2$: 205.1102, found m/z 205.1100.

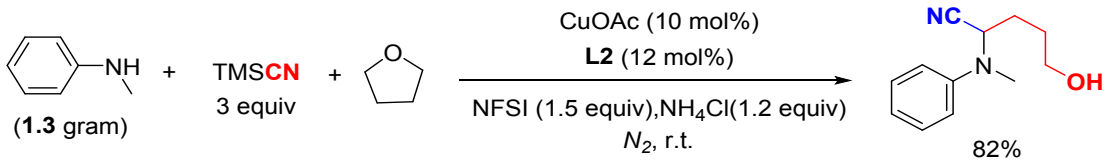
3-(3,4-dihydroquinolin-1(2H)-yl)tetrahydro-2H-pyran-2-one(3b')



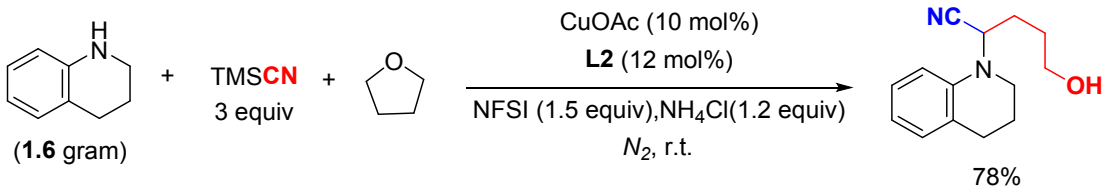
To a solution of 2-(3,4-dihydroquinolin-1(*2H*)-yl)-5-hydroxypentanenitrile **3b'** (0.2 mmol, 1 equiv.) in chlorobenzene (1 mL) was added methanesulfonic acid (1 mL) at 0 °C. Then, the reaction was allowed to stir at 60 °C for 6 hours. After that, saturated aqueous $NaHCO_3$ (5 mL) was added to stir for 10 min. The aqueous layer was extracted by ethyl acetate (10 mL × 3). The combined organic layers were dried over by anhydrous sodium sulfate and concentrated. The residue was purified via chromatography on silica gel (eluent: hexanes: EtOAc = 5:1) to afford the product **3b** as colorless oil in 83% yield (38.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 6.93 (m, 2H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 1H), 4.53 – 4.30 (m, 3H), 3.27 (t, *J* = 5.7 Hz, 2H), 2.86 – 2.69 (m, 2H), 2.28 – 1.90 (m, 6H);^{13}C NMR (101 MHz, $CDCl_3$) δ 170.50, 144.10, 129.49, 126.89 , 123.90 , 116.94 , 110.77 , 68.90 , 57.83 , 46.06 , 28.05 , 23.34 , 22.90 , 22.40 ;HRMS (EI) exact mass calculated for $C_{14}H_{17}NO_2$: 231.1259, found m/z 231.1255.

4. Gram-Scale Experiments

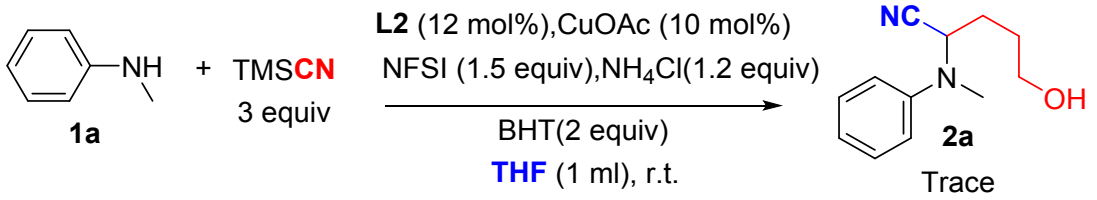


An oven-dried round-bottom flask equipped with a magnetic stirring bar under a nitrogen atmosphere, was charged with Ligand **L2** (0.14 mmol, 0.12 equiv.), Cu(OAc) (0.12 mmol, 0.1 equiv.) and ether (60 mL). The reaction was allowed to stir at room temperature for 15 min. Then, NH_4Cl (1.4 mmol, 1.2 equiv.), NFSI (1.8 mmol, 1.5 equiv.), TMSCN (3.6 mmol, 3 equiv.) and *N*-methylaniline (1.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 8 h. Then, the resulting solution was concentrated and purified by column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) to afford the product as colorless oil in 82% yield (2.04 g, 10.04 mmol).

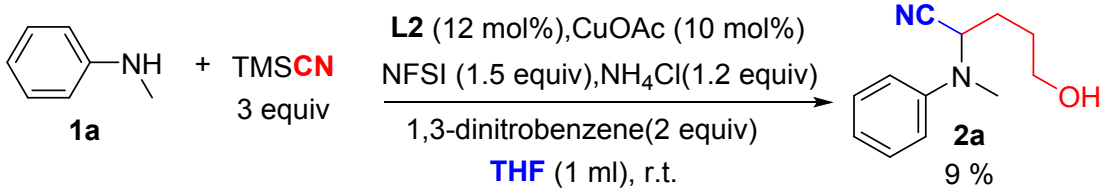


An oven-dried round-bottom flask equipped with a magnetic stirring bar under a nitrogen atmosphere, was charged with Ligand **L2** (0.14 mmol, 0.12 equiv.), Cu(OAc) (0.12 mmol, 0.1 equiv.) and ether (60 mL). The reaction was allowed to stir at room temperature for 15 min. Then, NH_4Cl (1.4 mmol, 1.2 equiv.), NFSI (1.8 mmol, 1.5 equiv.), TMSCN (3.6 mmol, 3 equiv.) and 1,2,3.4-*tetra*-hydroquinoline (1.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 8 h. Then, the resulting solution was concentrated and purified by column chromatography (eluent: hexanes: EtOAc = 3:1) on silica gel to afford the product as colorless oil in 78% yield (2.17 g, 9.42 mmol).

5. Radical Inhibiting Experiments

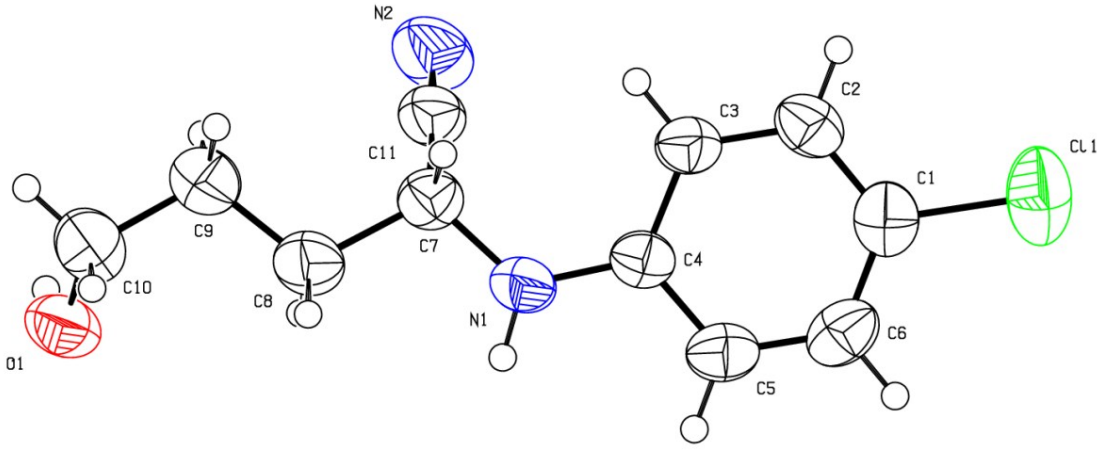


An oven-dried round-bottom flask equipped with a magnetic stirring bar under a nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), Cu(OAc) (0.02 mmol, 0.1 equiv.) and ether (1 mL). The reaction was allowed to stir at room temperature for 15 min. Then, BHT (0.4 mmol, 2 equiv.), NH_4Cl (0.24 mmol, 1.2 equiv.), NFSI (0.3 mmol, 1.5 equiv.), TMSCN (0.6 mmol, 3 equiv.) and *N*-methylaniline (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 8 h. Then, the resulting solution was concentrated and only a trace amount of product was detected.



An oven-dried round-bottom flask equipped with a magnetic stirring bar under a nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), Cu(OAc) (0.02 mmol, 0.1 equiv.) and ether (1 mL). The reaction was allowed to stir at room temperature for 15 min. Then, 1,3-dinitrobenzene (0.4 mmol, 2 equiv.), NH_4Cl (0.24 mmol, 1.2 equiv.), NFSI (0.3 mmol, 1.5 equiv.), TMSCN (0.6 mmol, 3 equiv.) and *N*-methylaniline (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 8 h. Then, the resulting solution was concentrated and purified by column chromatography on silica gel (eluent: hexanes: EtOAc = 3:1) to afford the product in 9% yield (3.7mg, 18.1 μmol).

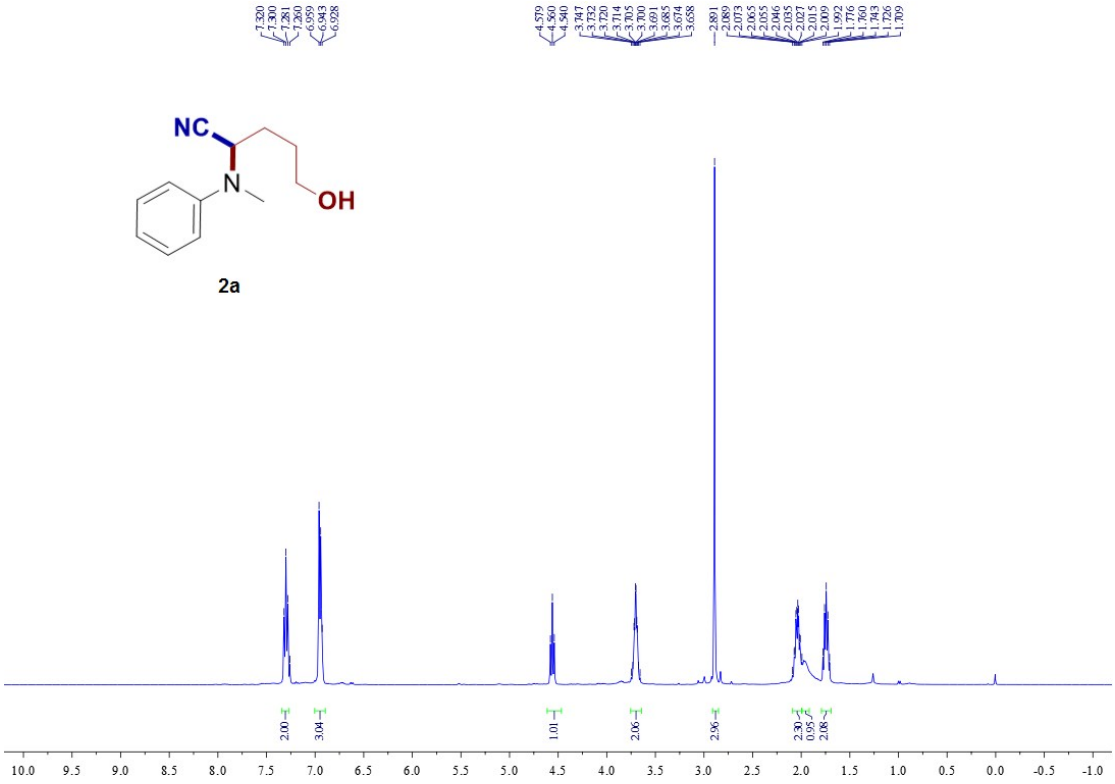
5. X-ray Crystallographic Data of 2o

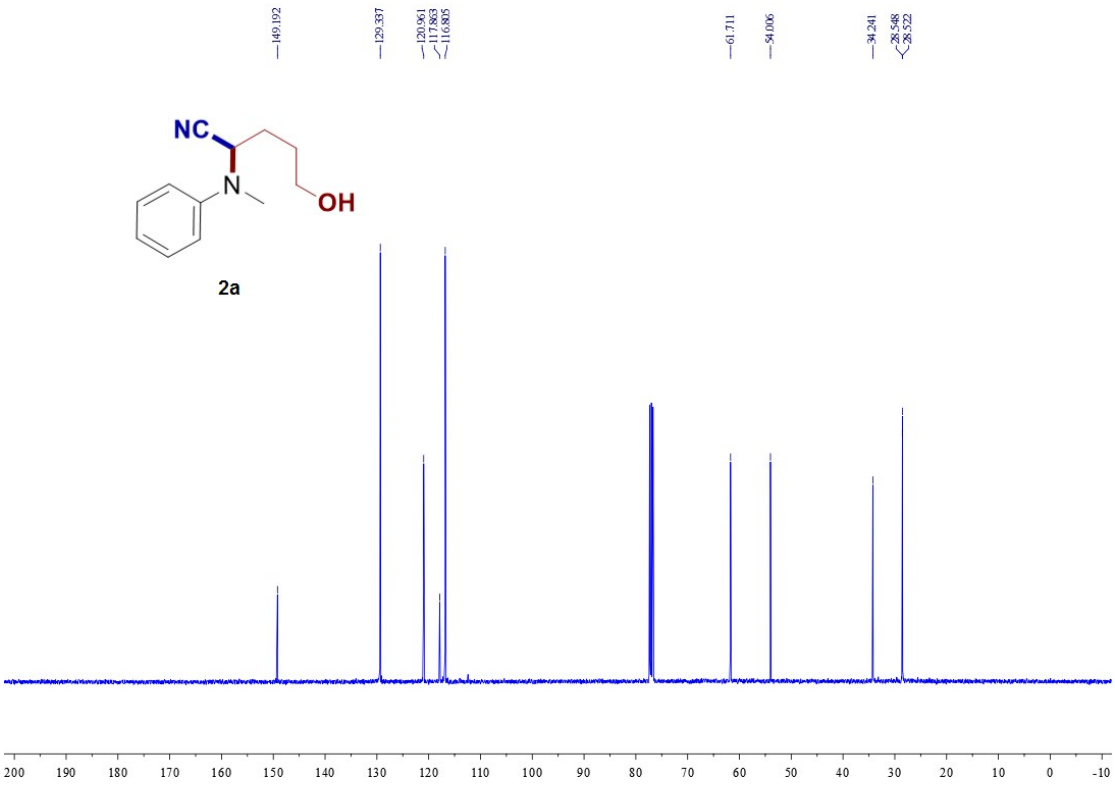


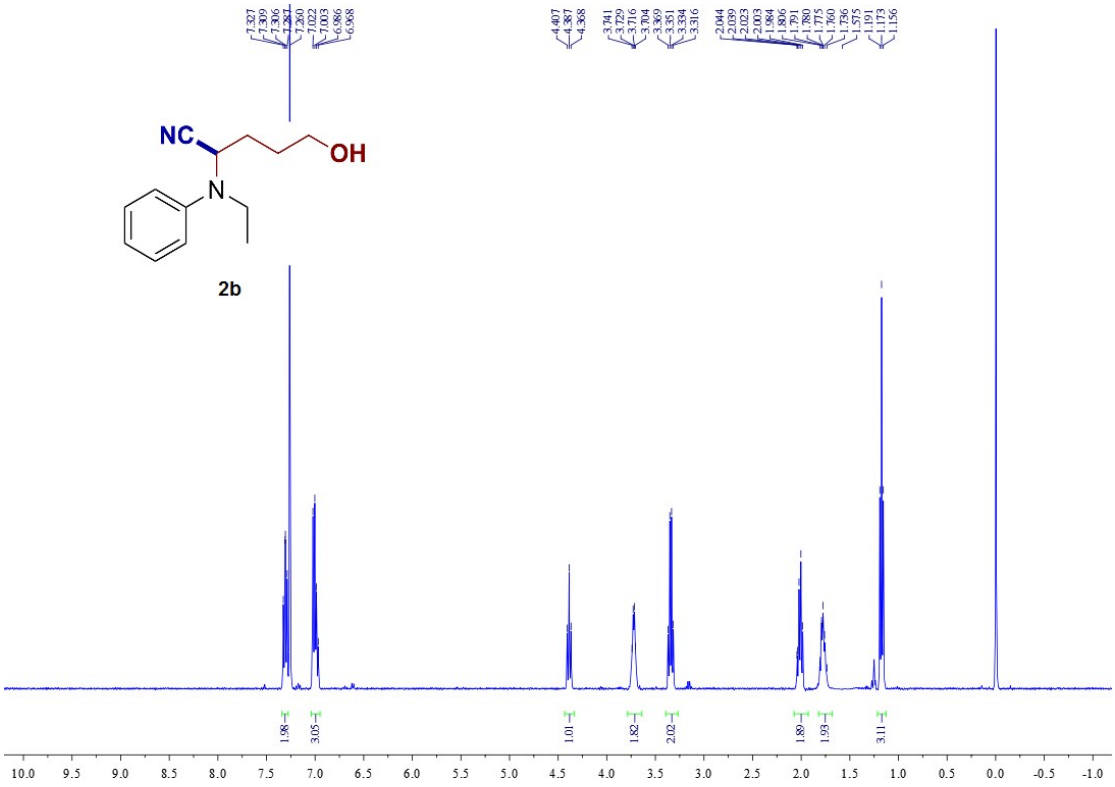
Identification code	2o
Empirical formula	$C_{11}H_{12}ClN_2O$
Formula weight	223.68
Temperature	293(2) K
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.8906(18) Å alpha = 90 deg. b = 8.8166(14) Å beta = 104.338(2) deg. c = 11.2785(17) Å gamma = 90 deg.
Volume	1145.5(3) A^3
Z, Calculated density	4, 1.297 Mg/m^3
Absorption coefficient	0.309 mm^-1
F(000)	468
Crystal size	0.300 x 0.250 x 0.200 mm
Theta range for data collection	1.768 to 25.149 deg.
Limiting indices	-11<=h<=14, -10<=k<=10, -13<=l<=13
Reflections collected / unique	6314 / 2047 [R(int) = 0.0261]
Completeness to theta = 25.149	99.90%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.940 and 0.911
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2047 / 0 / 137
Goodness-of-fit on F^2	0.971
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.1387
R indices (all data)	R1 = 0.0667, wR2 = 0.1588

Extinction coefficient	n/a
Largest diff. peak and hole	0.339 and -0.249 e.Aˆ-3

6. NMR Spectra



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2.013
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1.780
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1.760
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1.575
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1.173
1.156
1.98
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3.11
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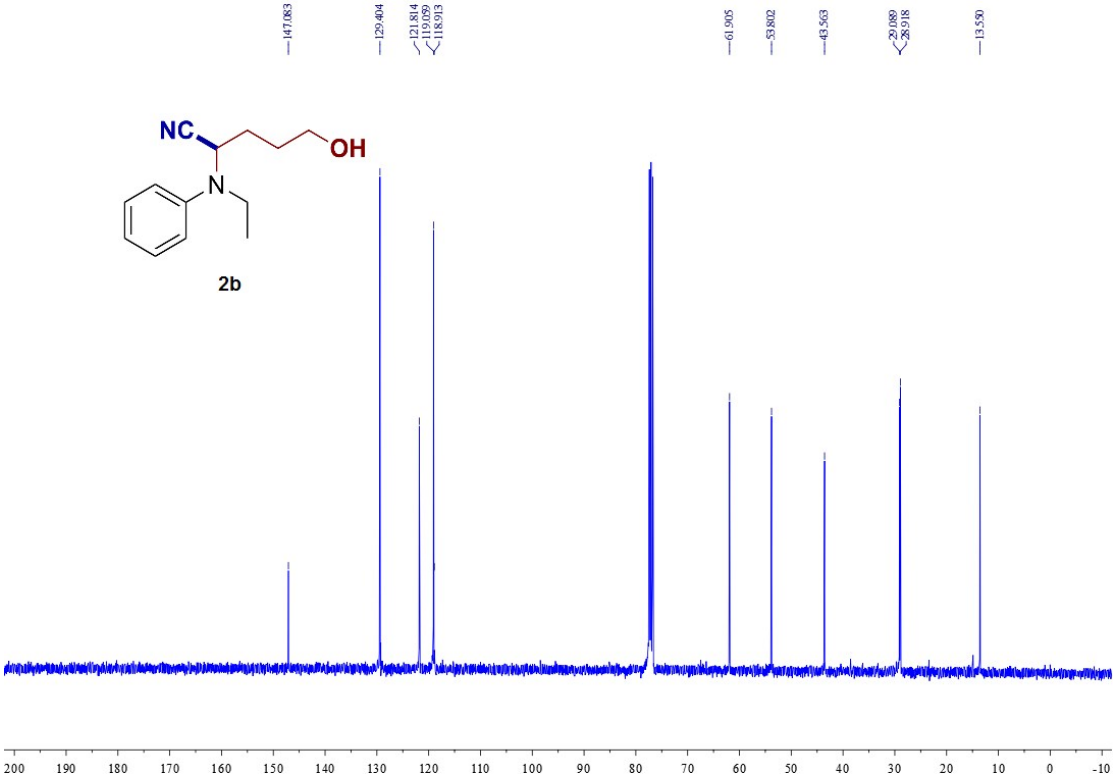
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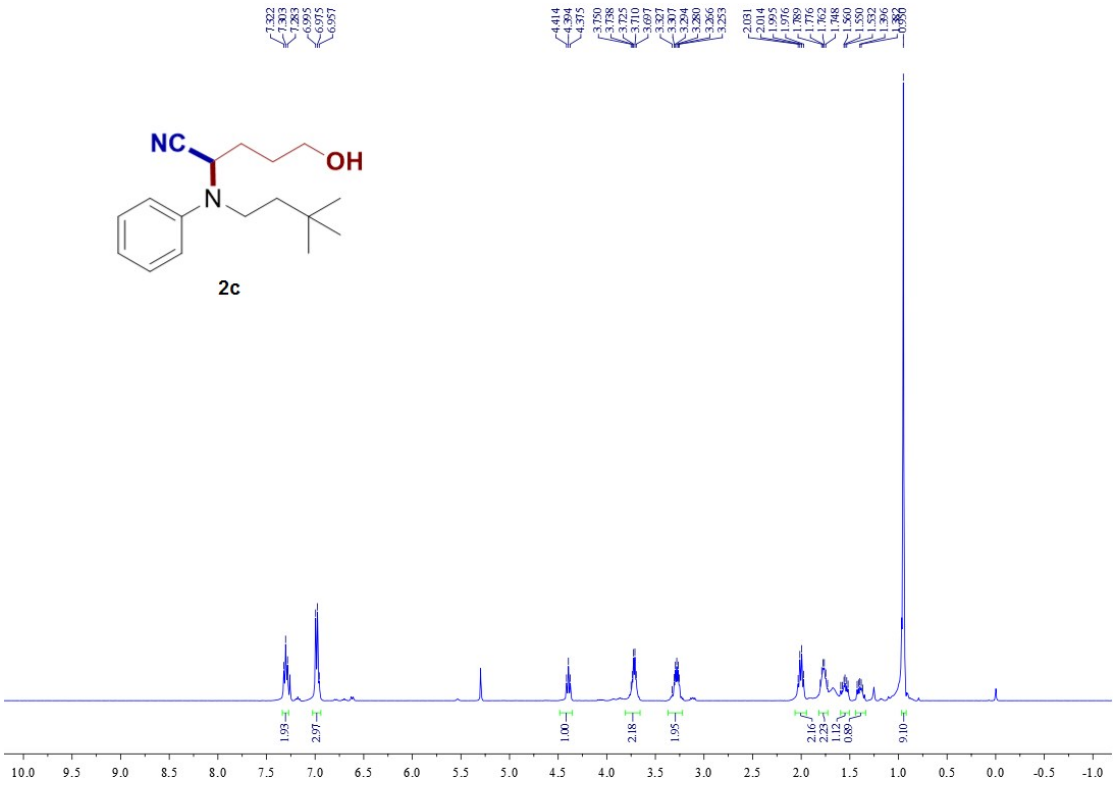
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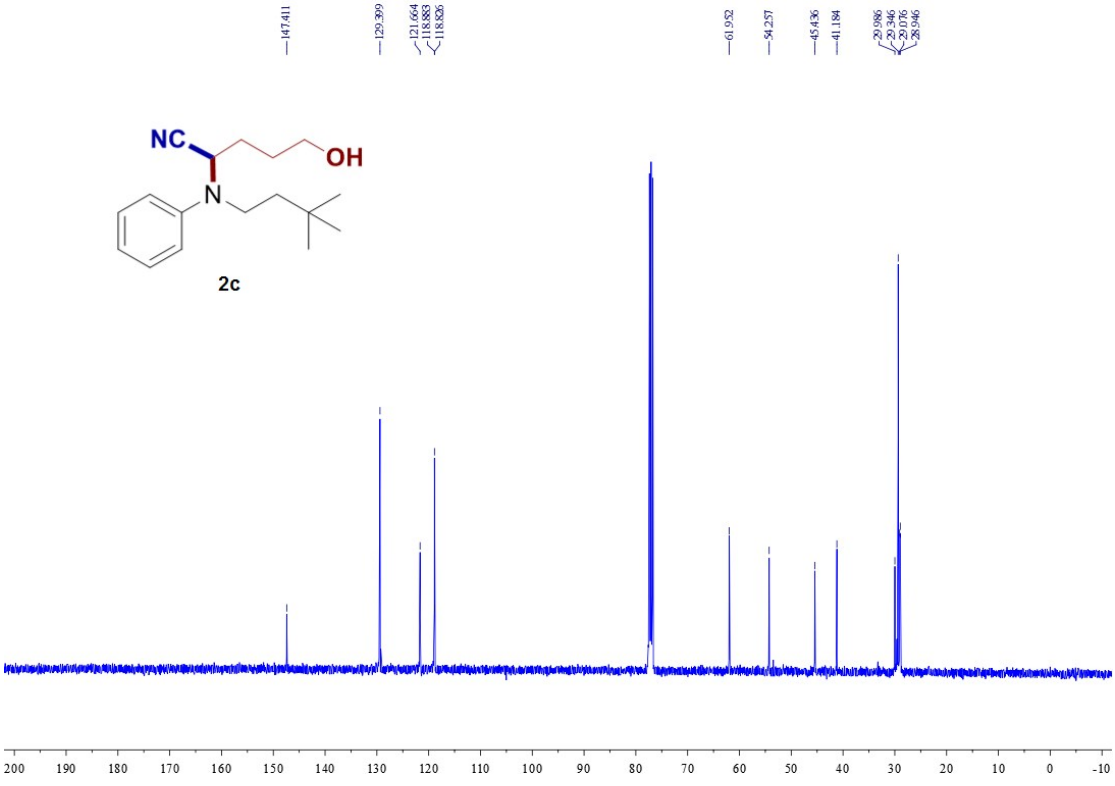
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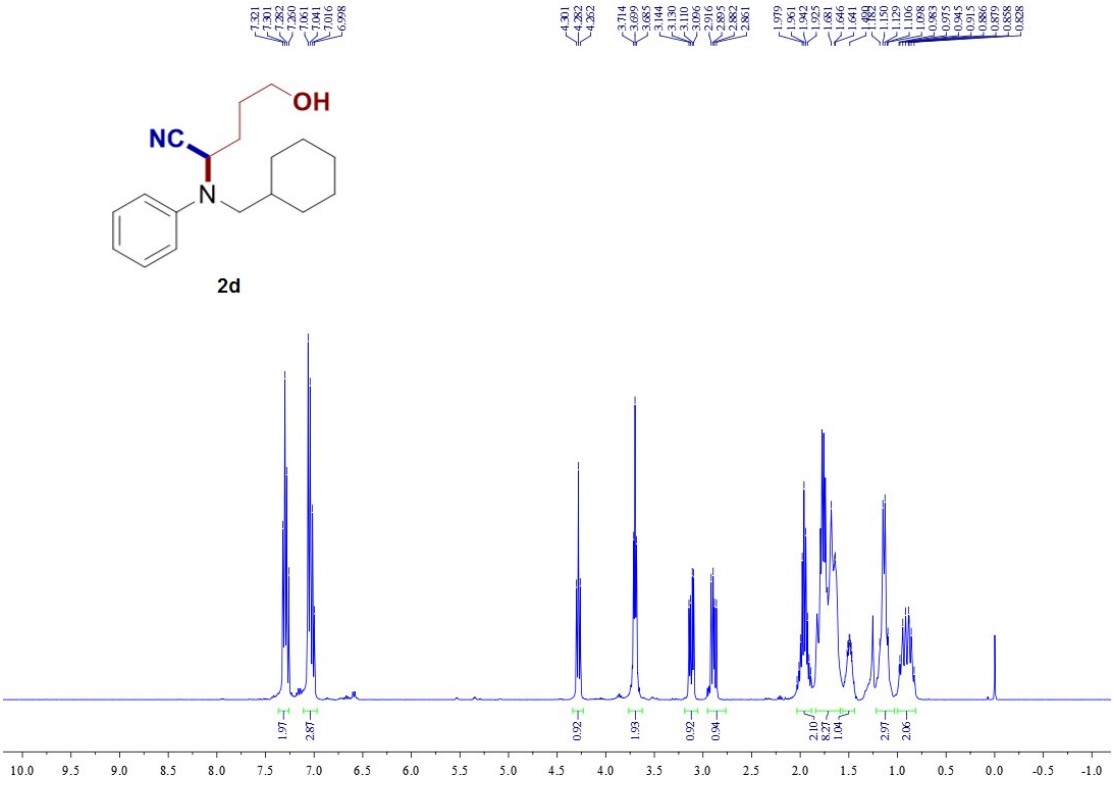
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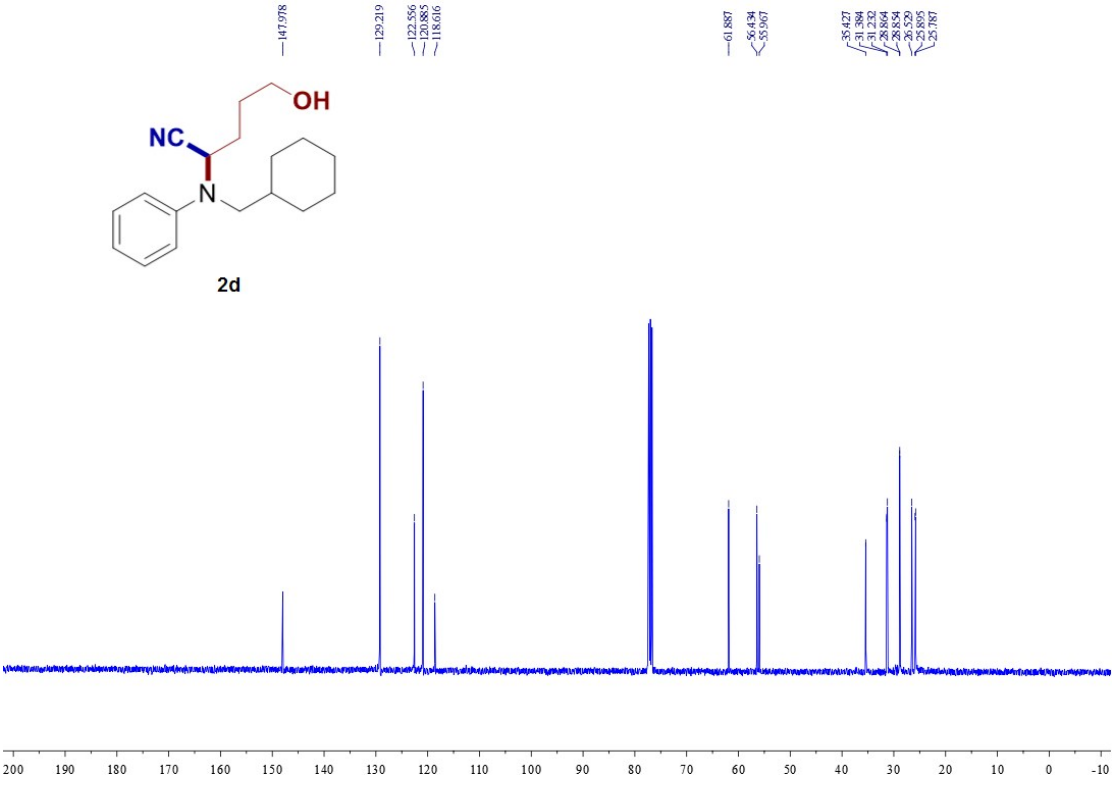
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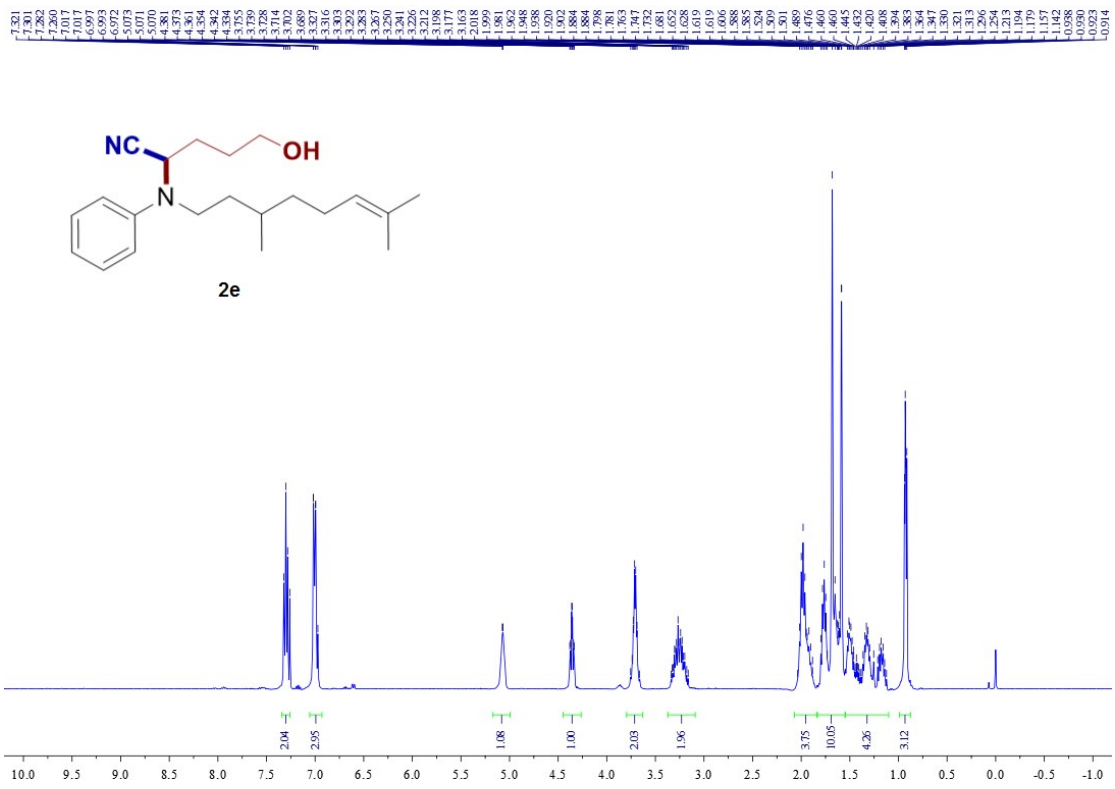
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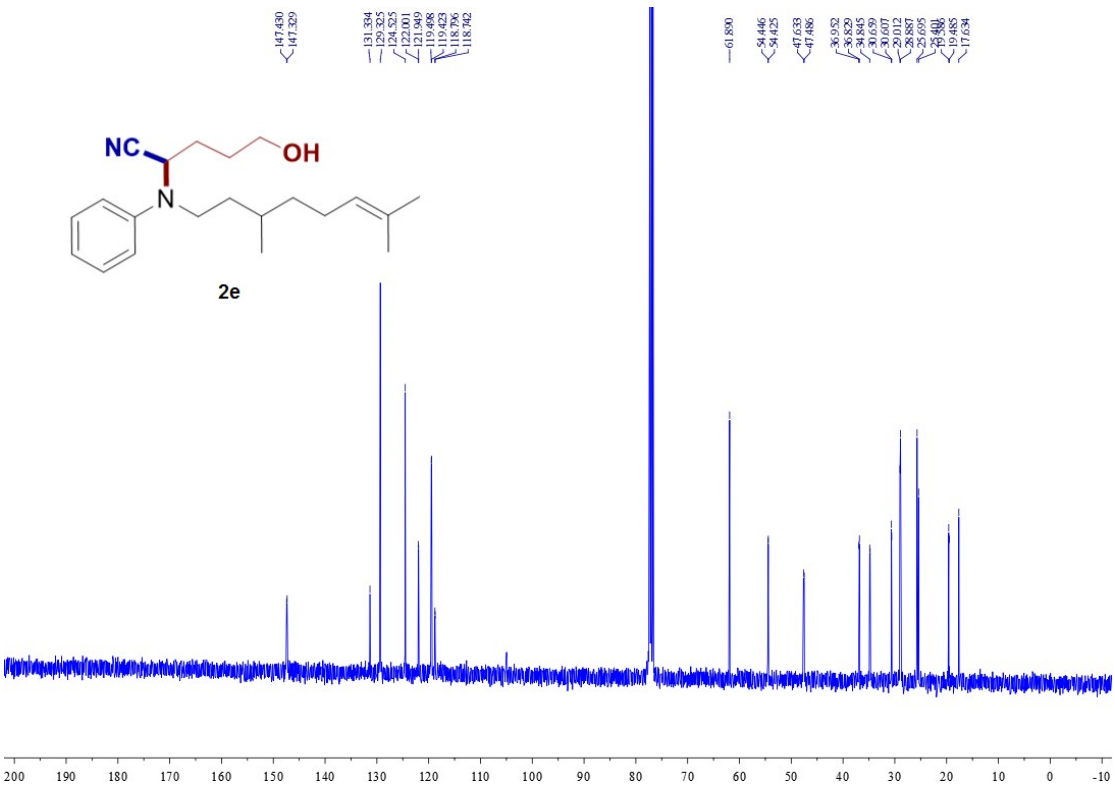
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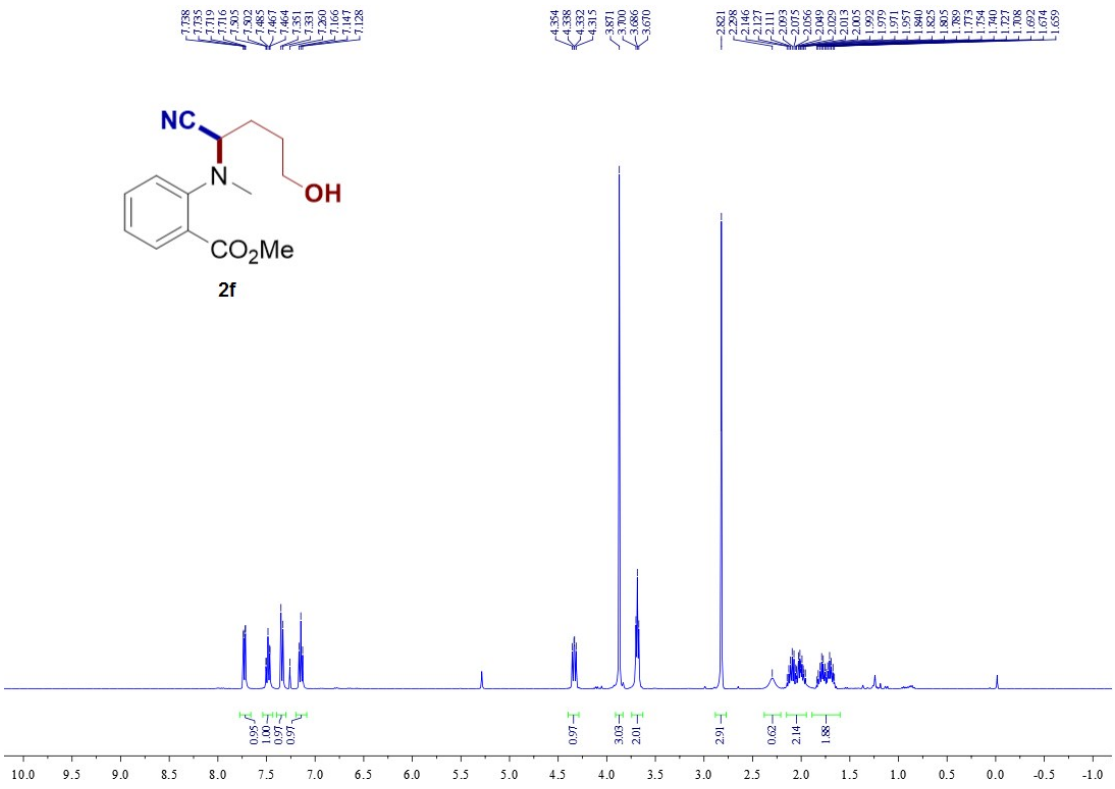
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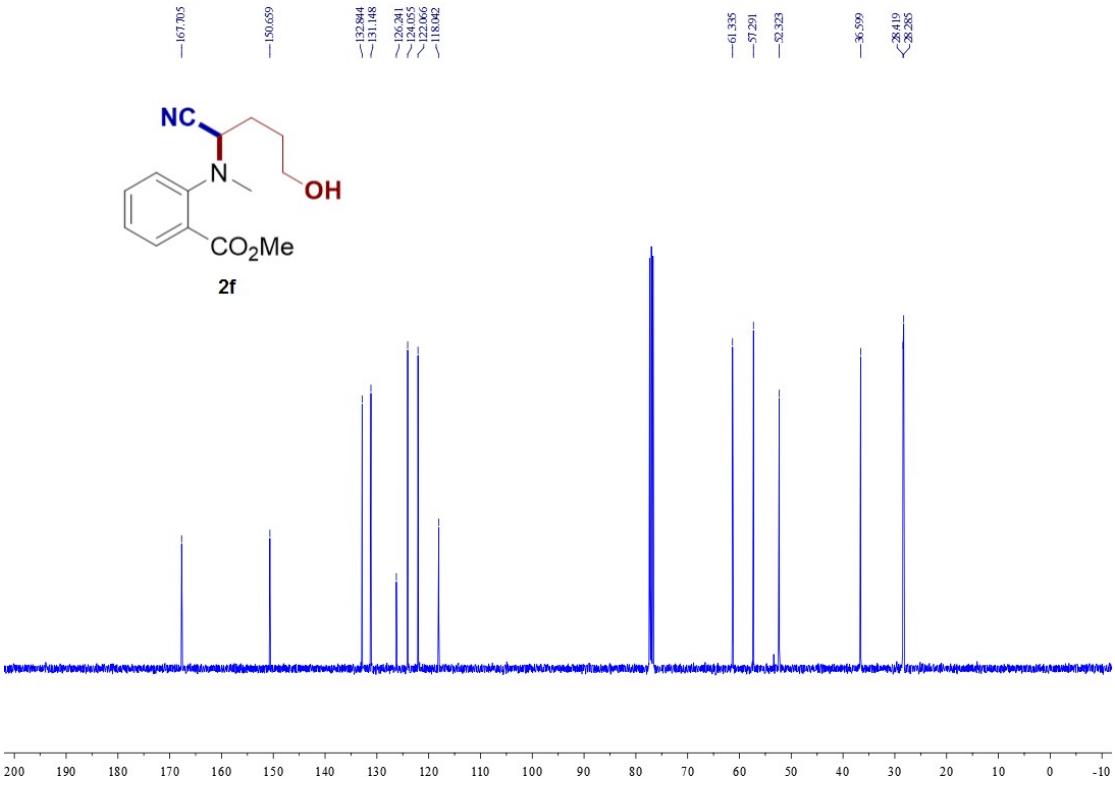
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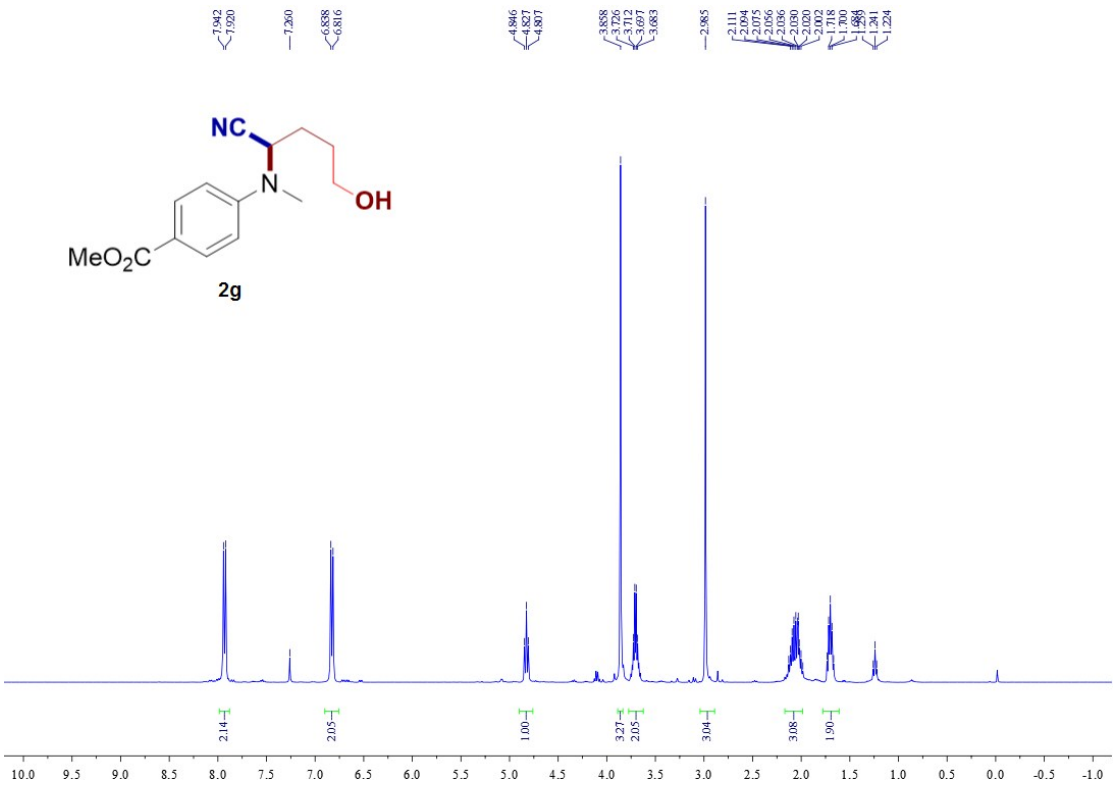
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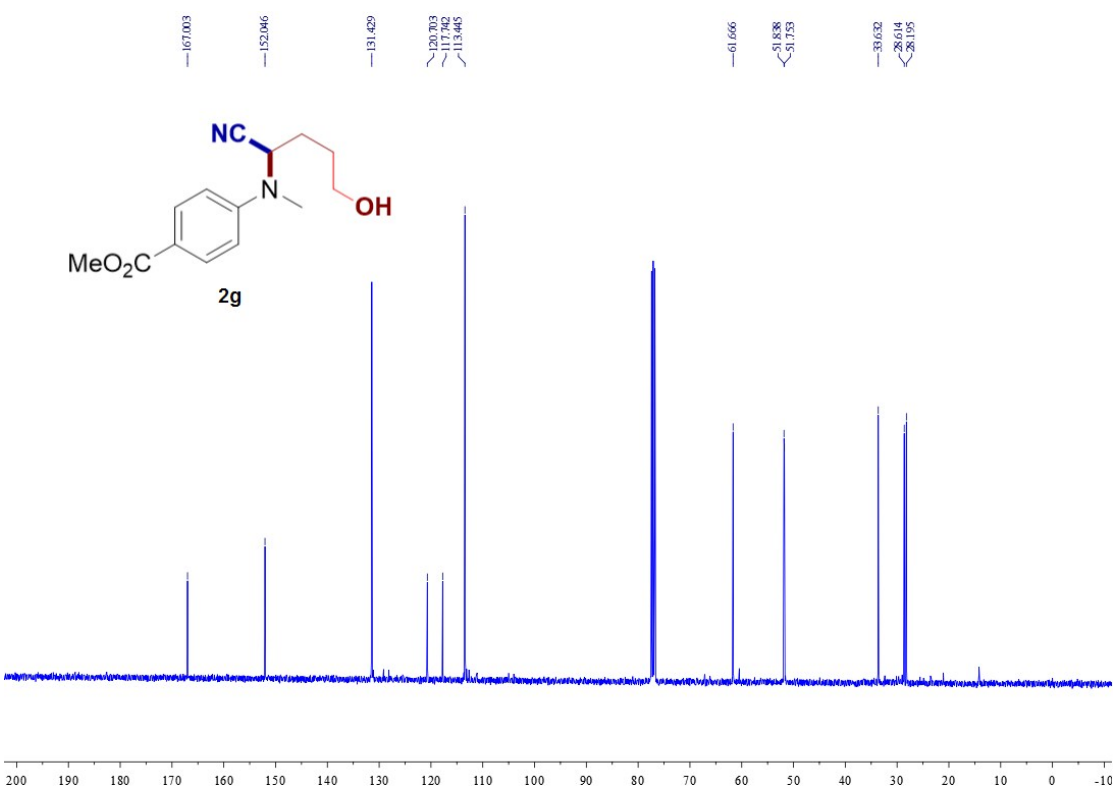
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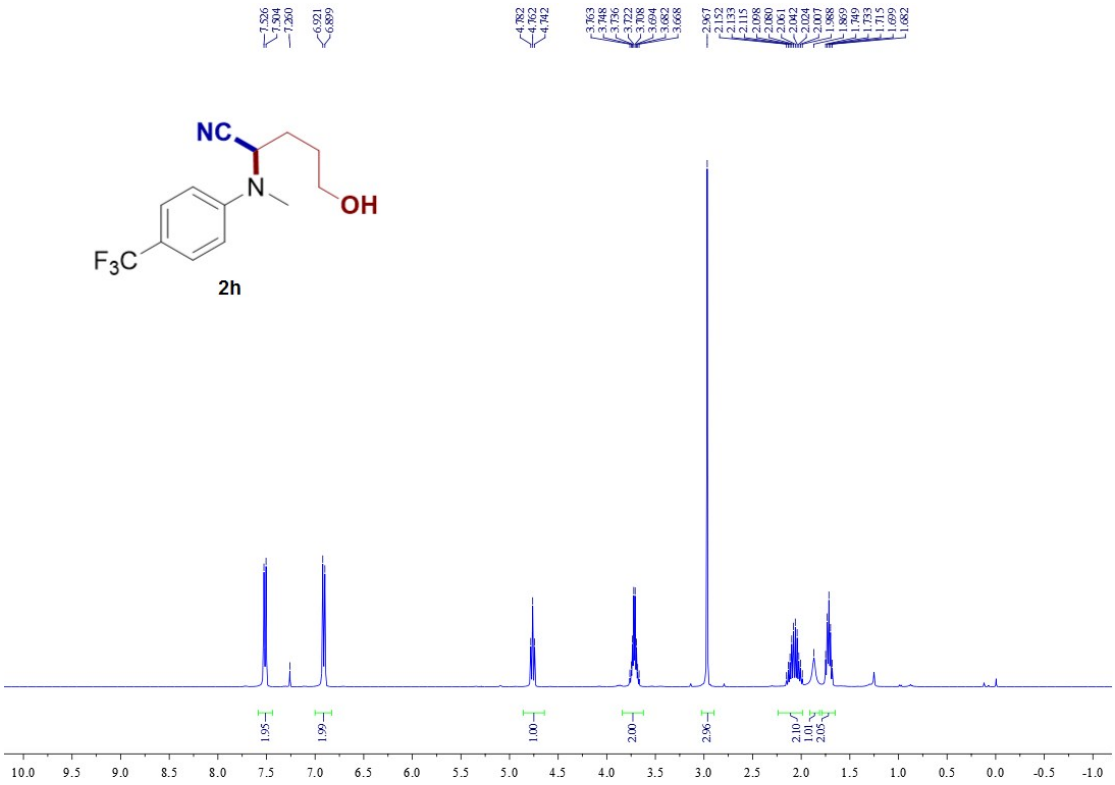
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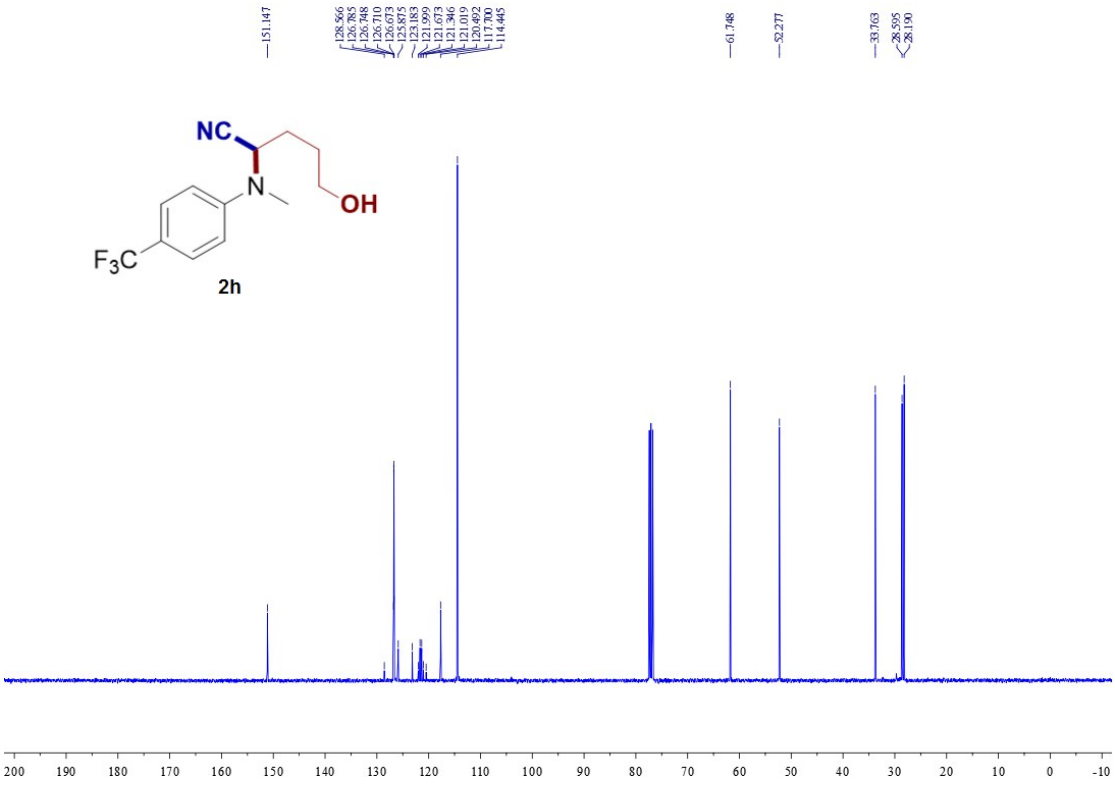
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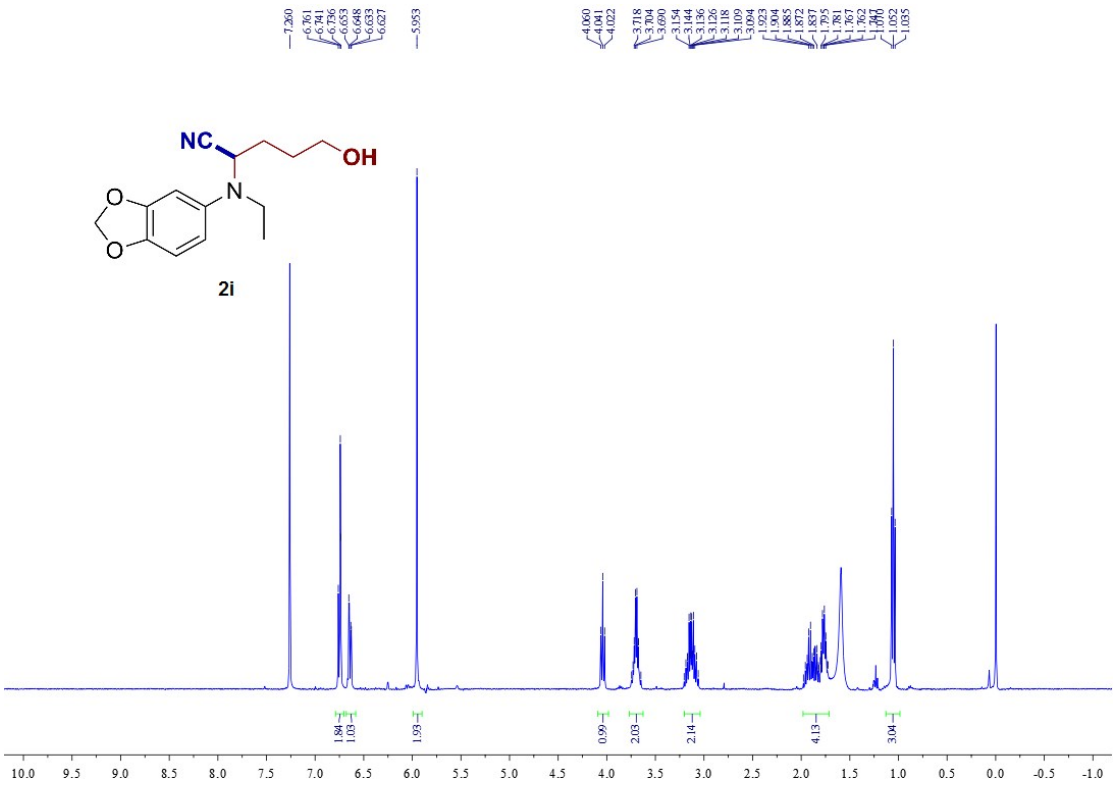
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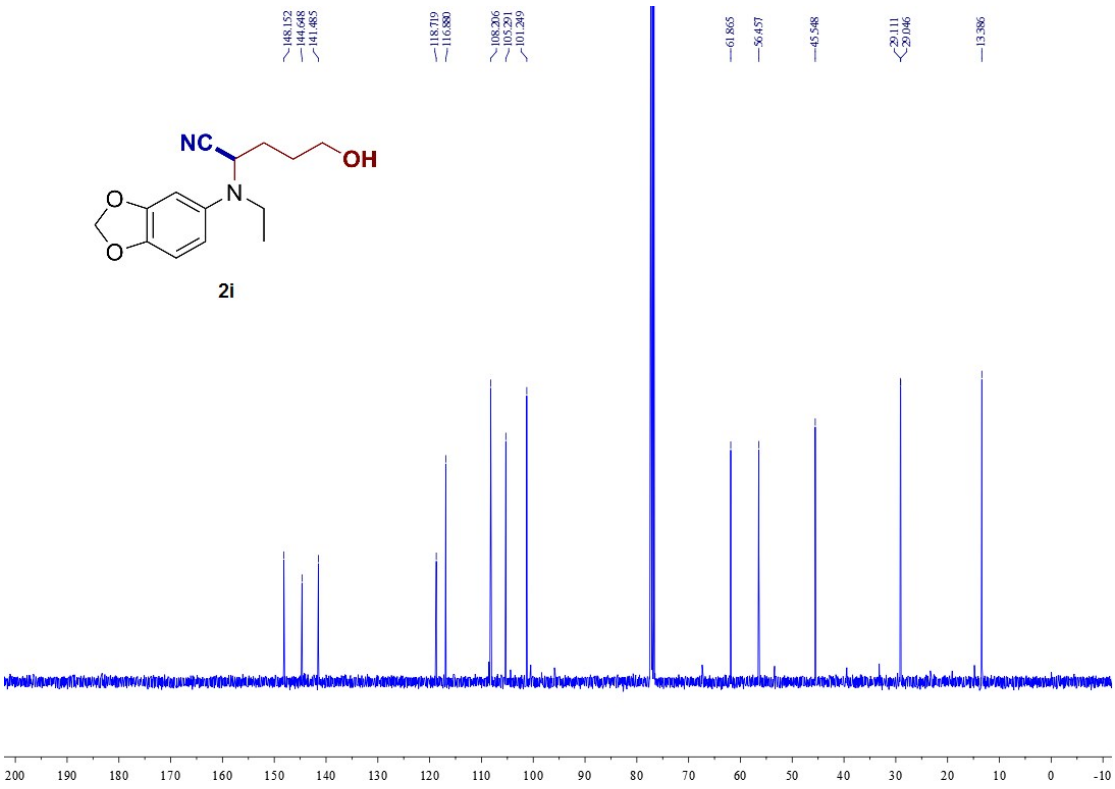
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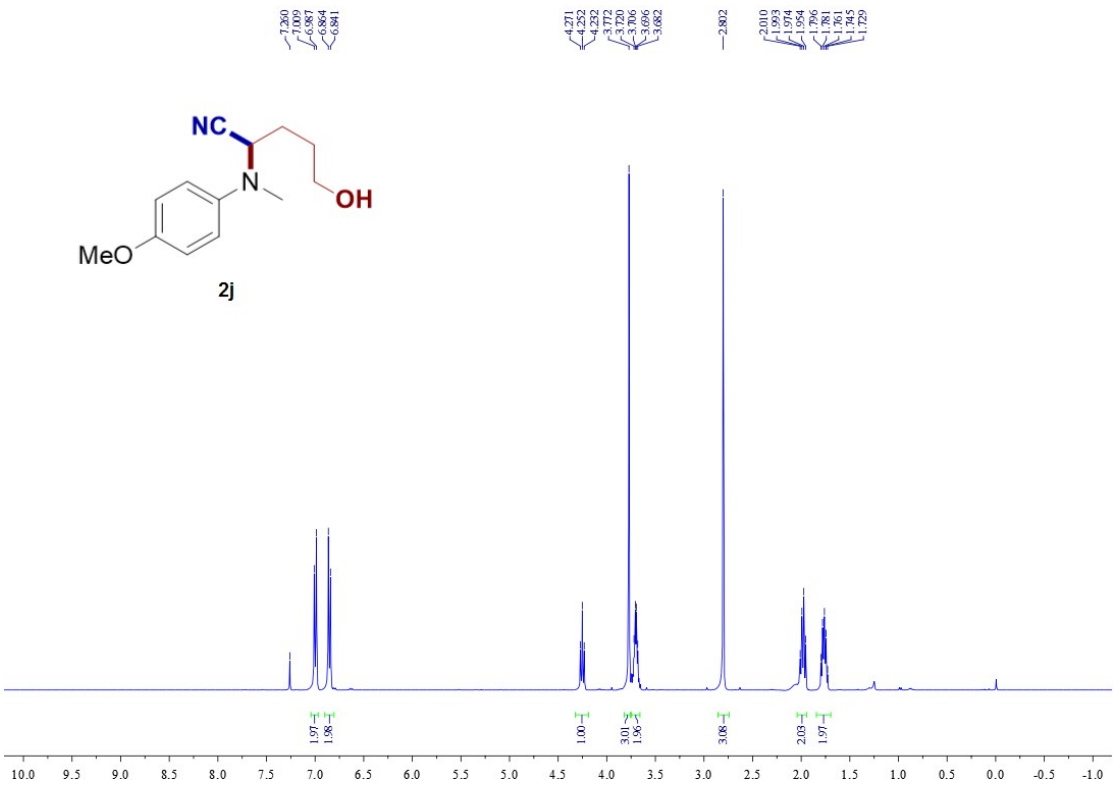
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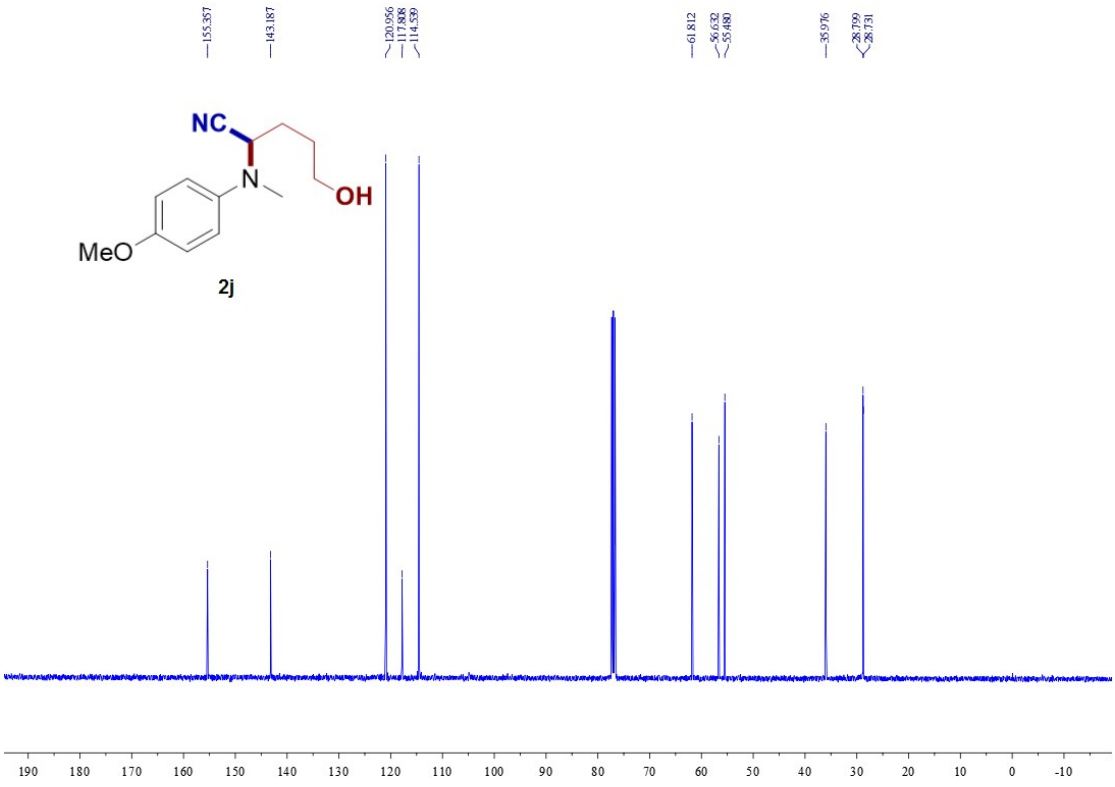
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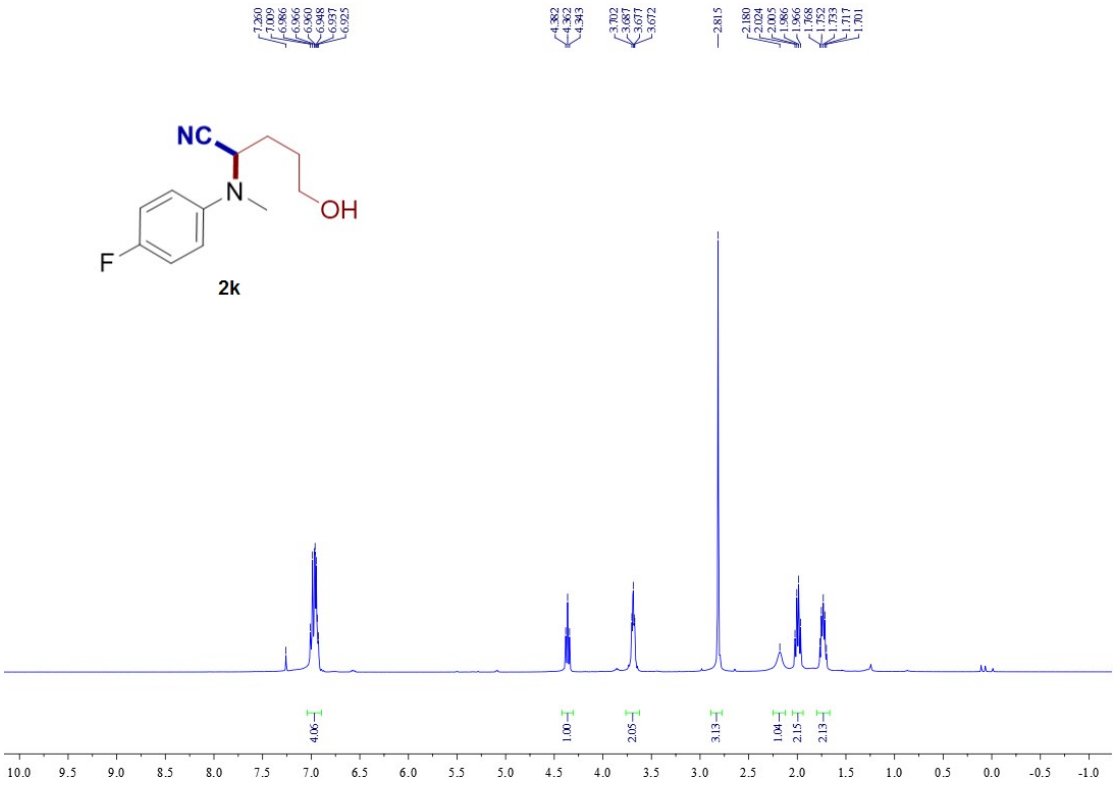
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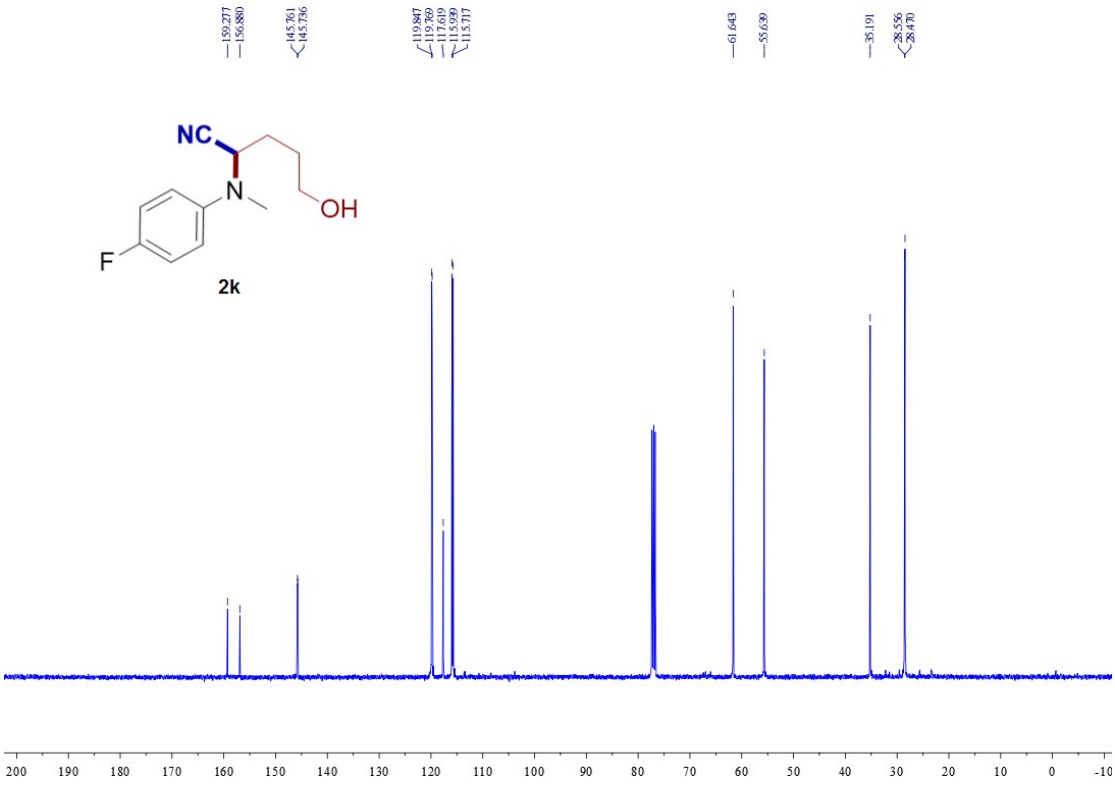
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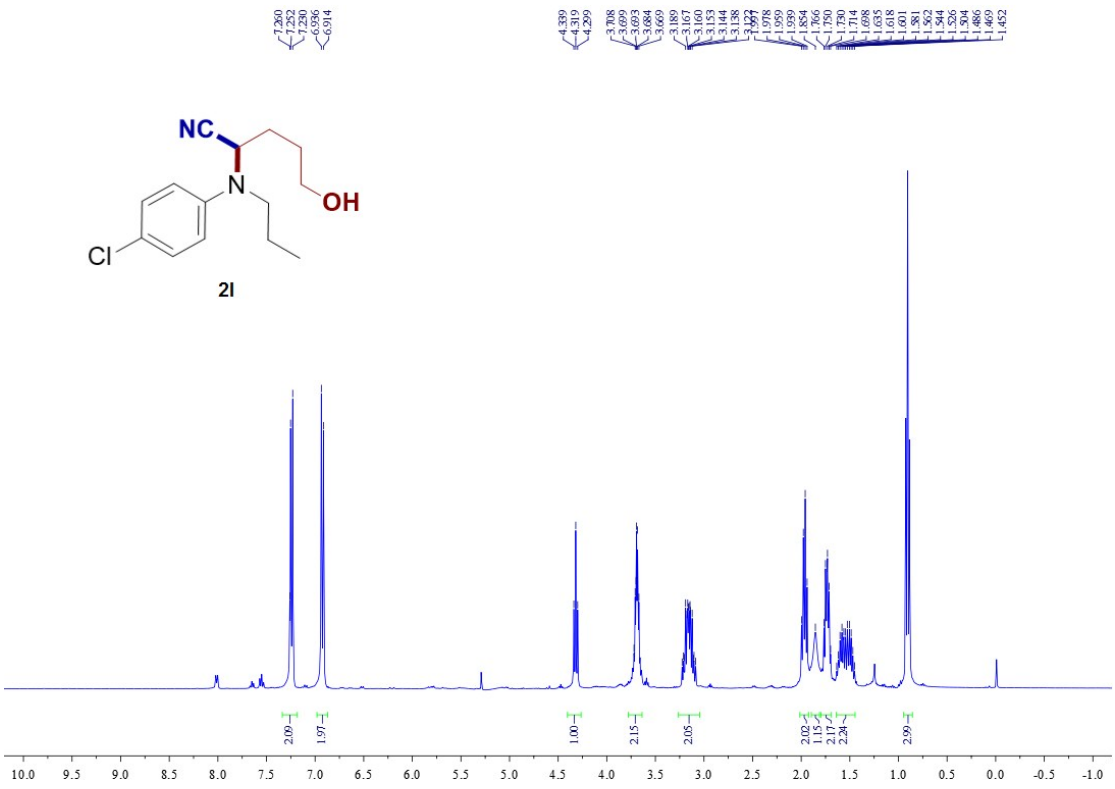
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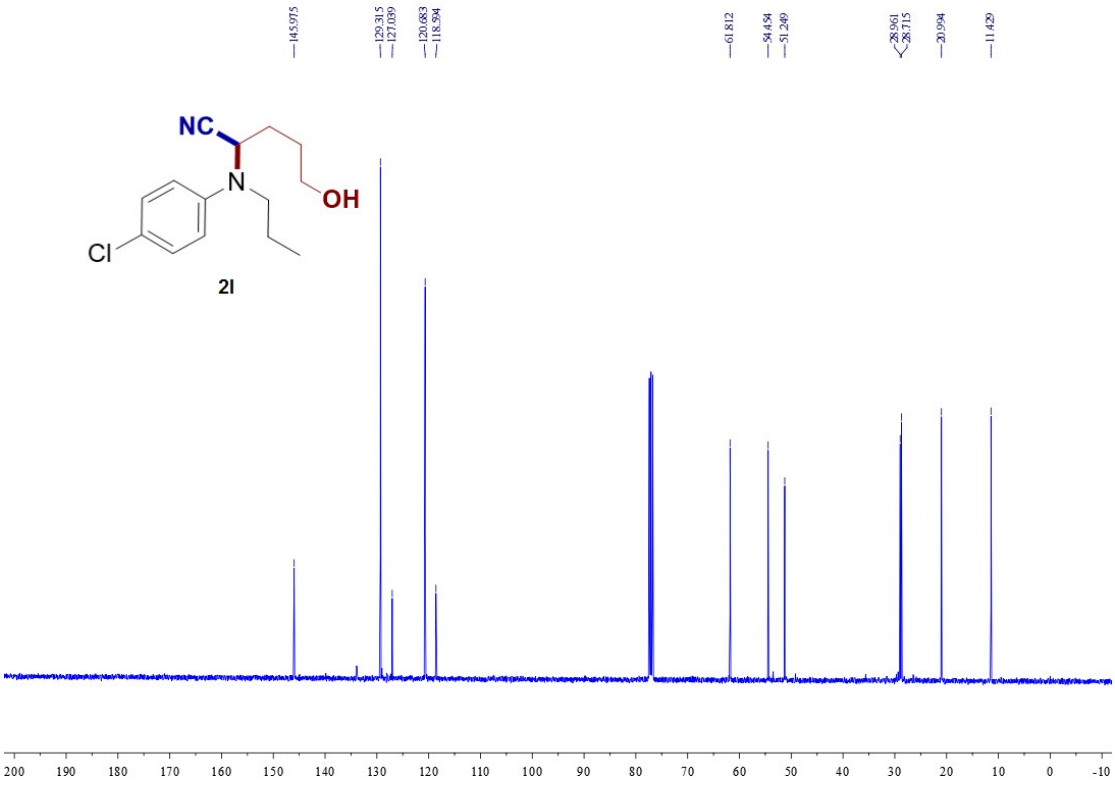
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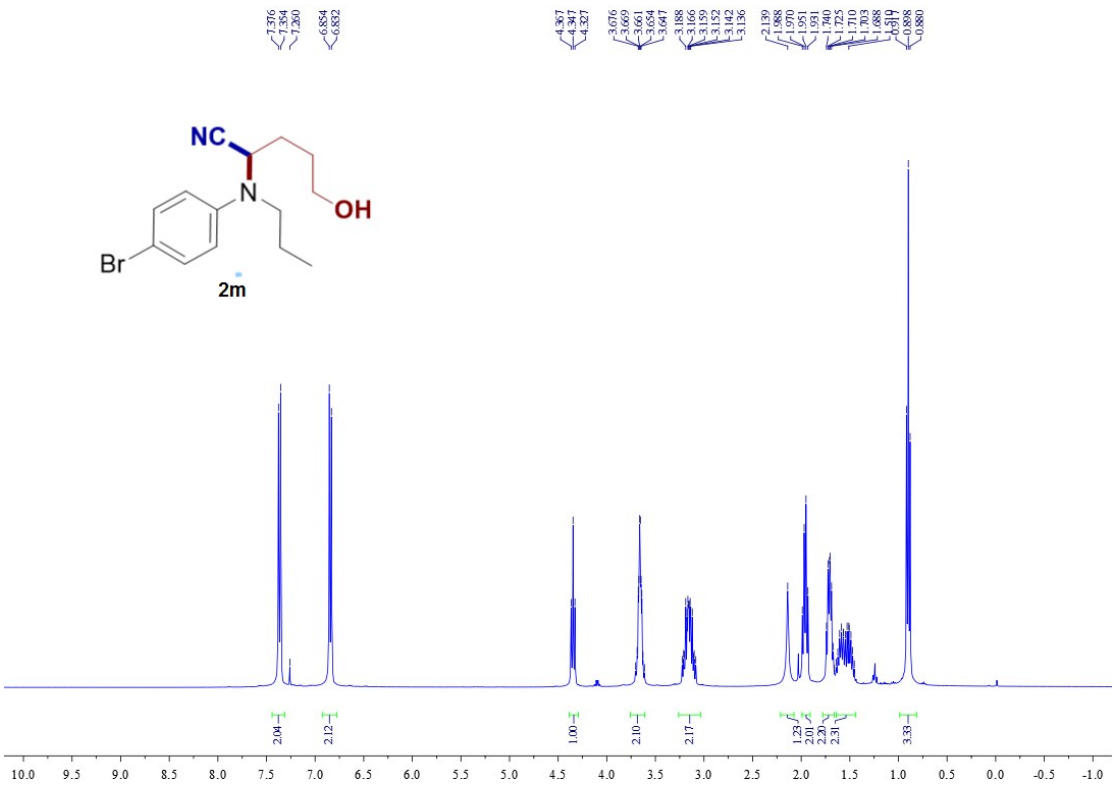
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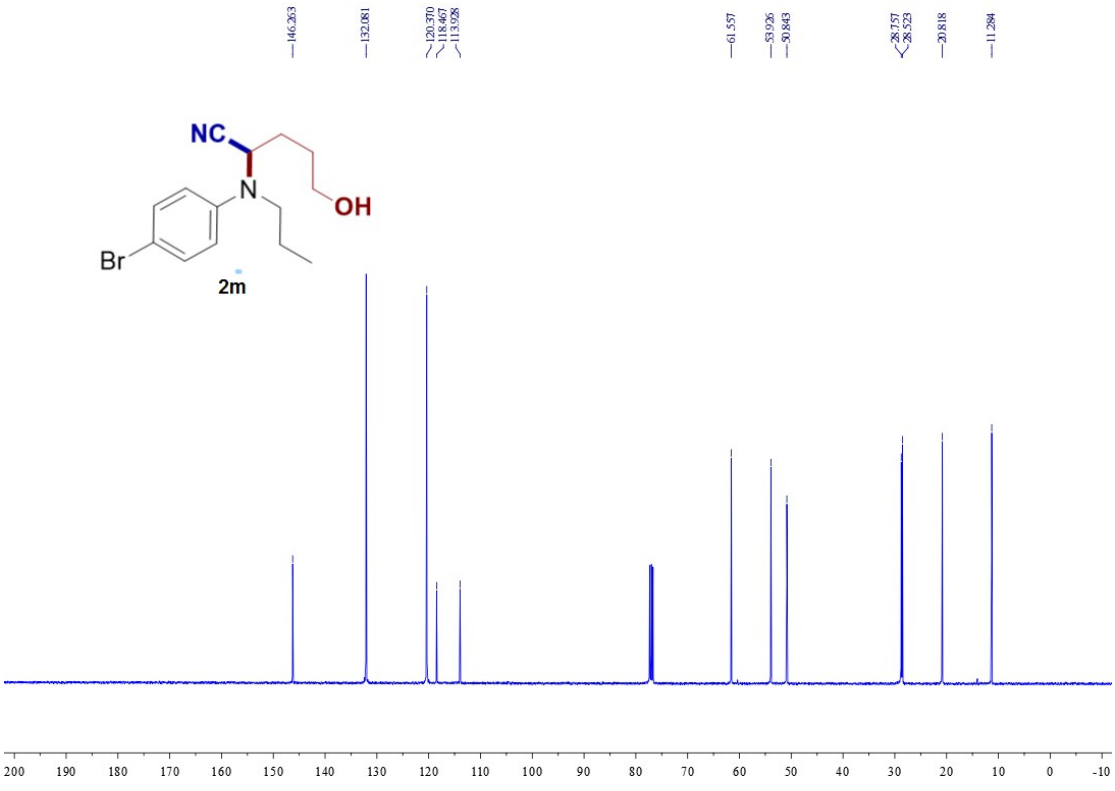
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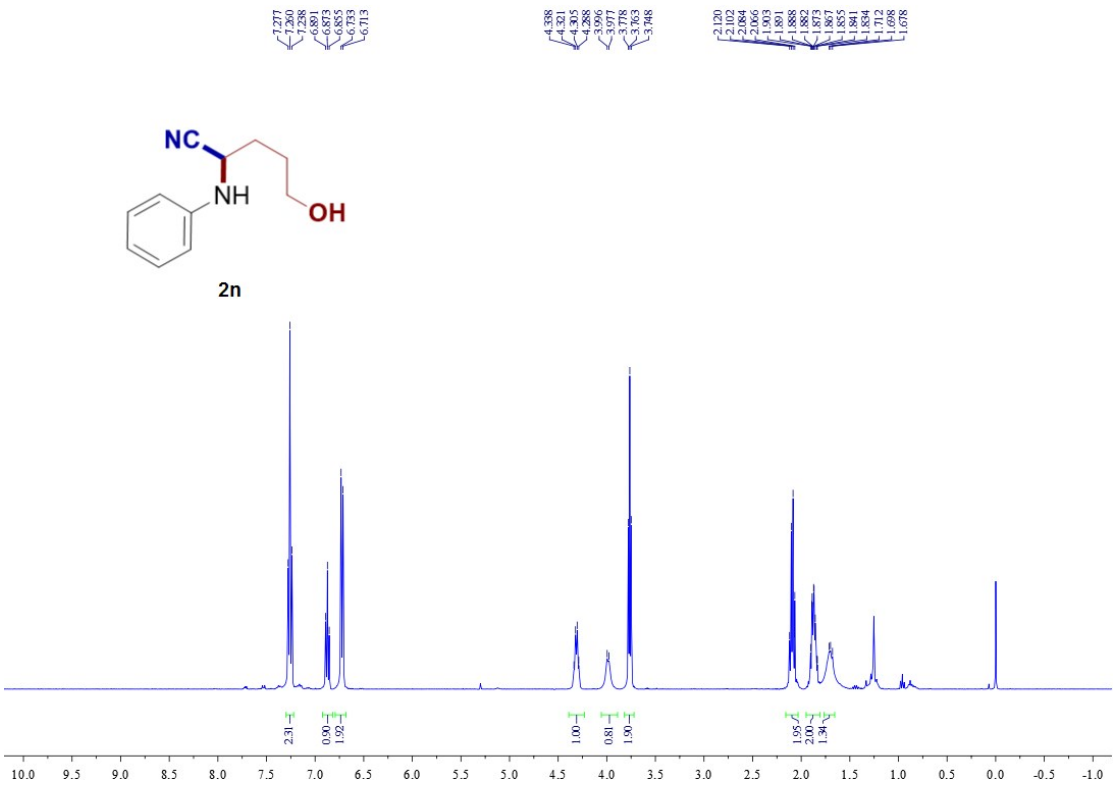
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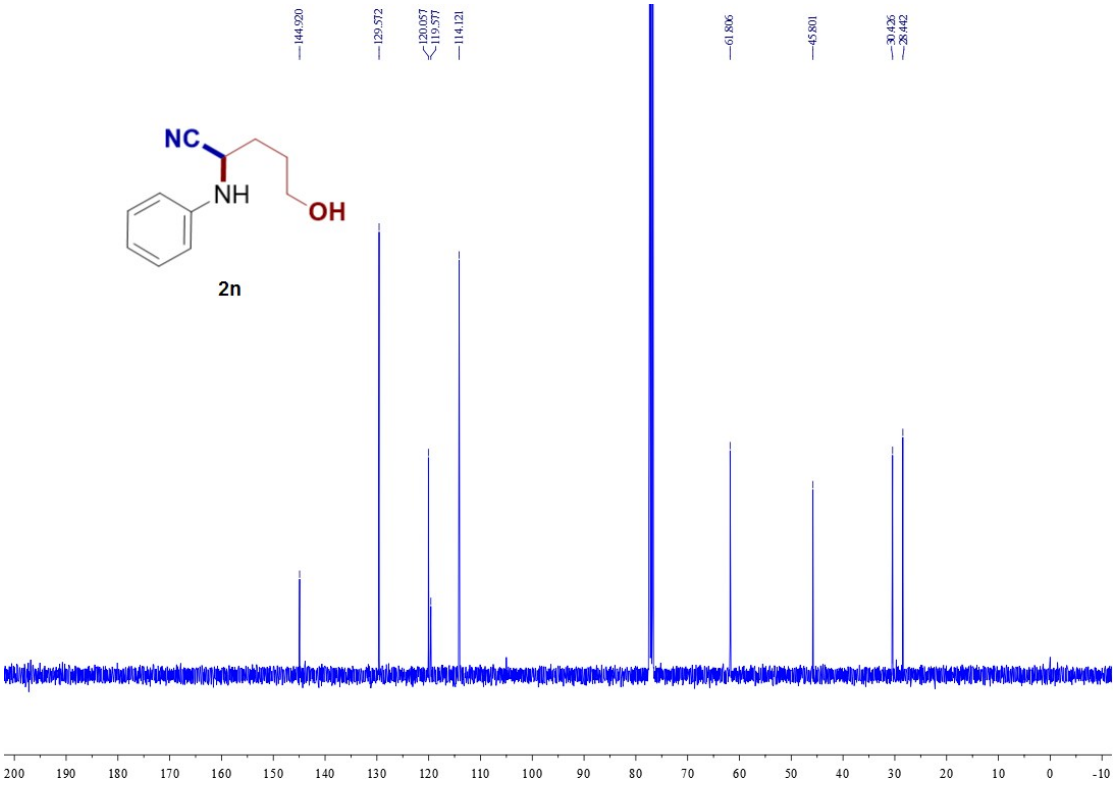
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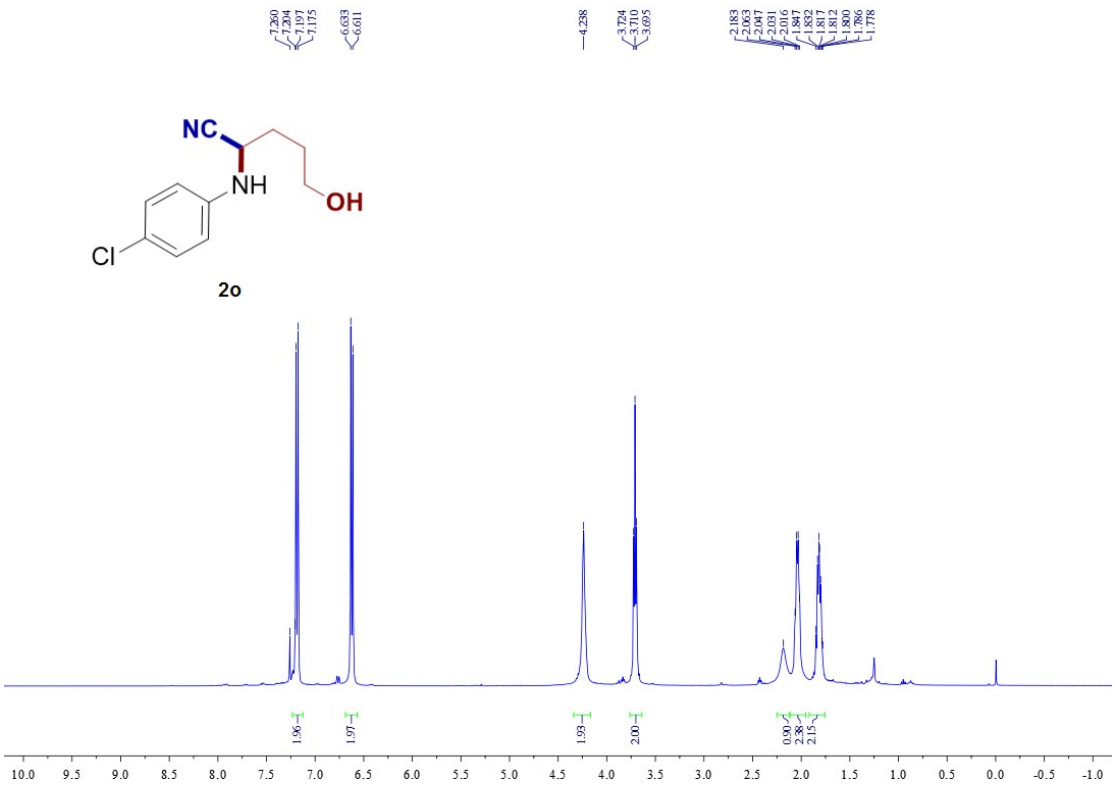
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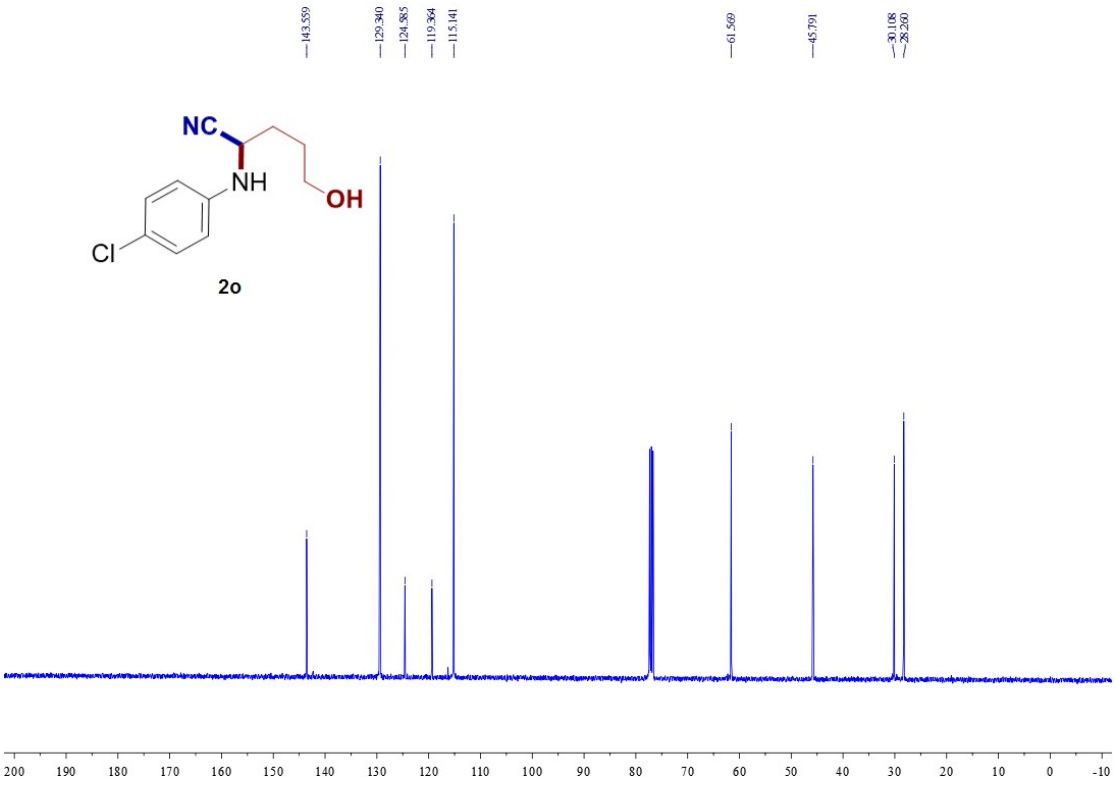
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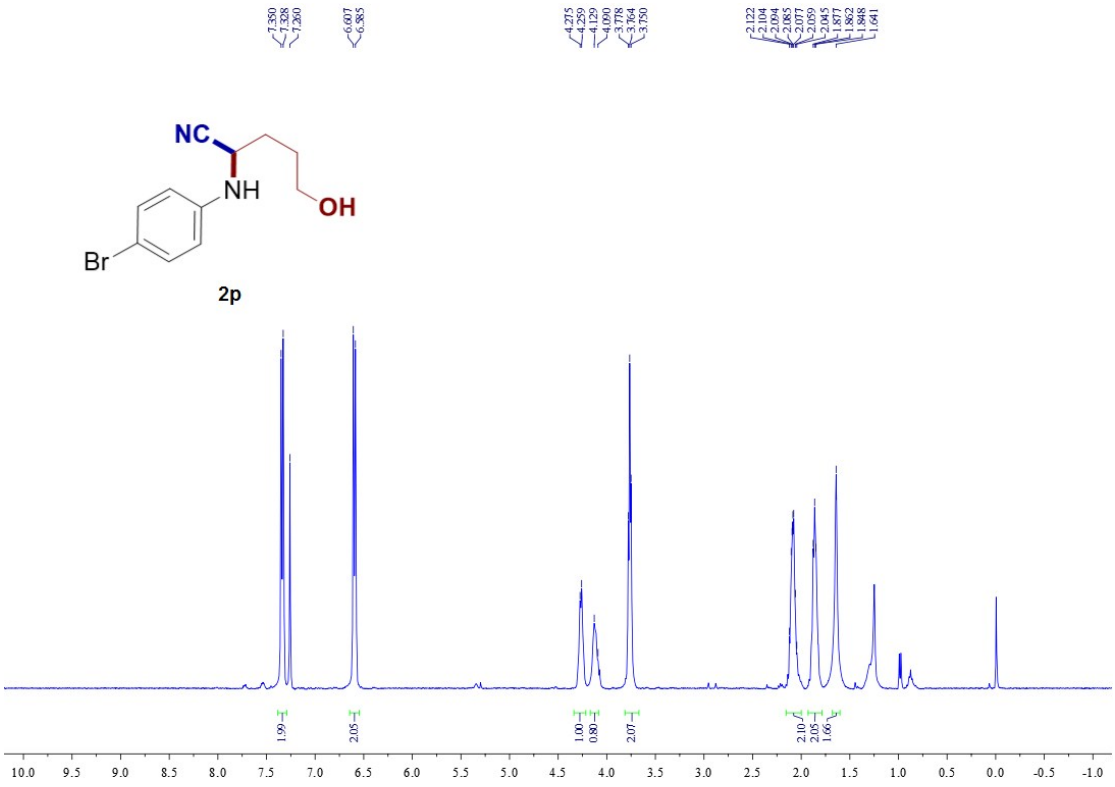
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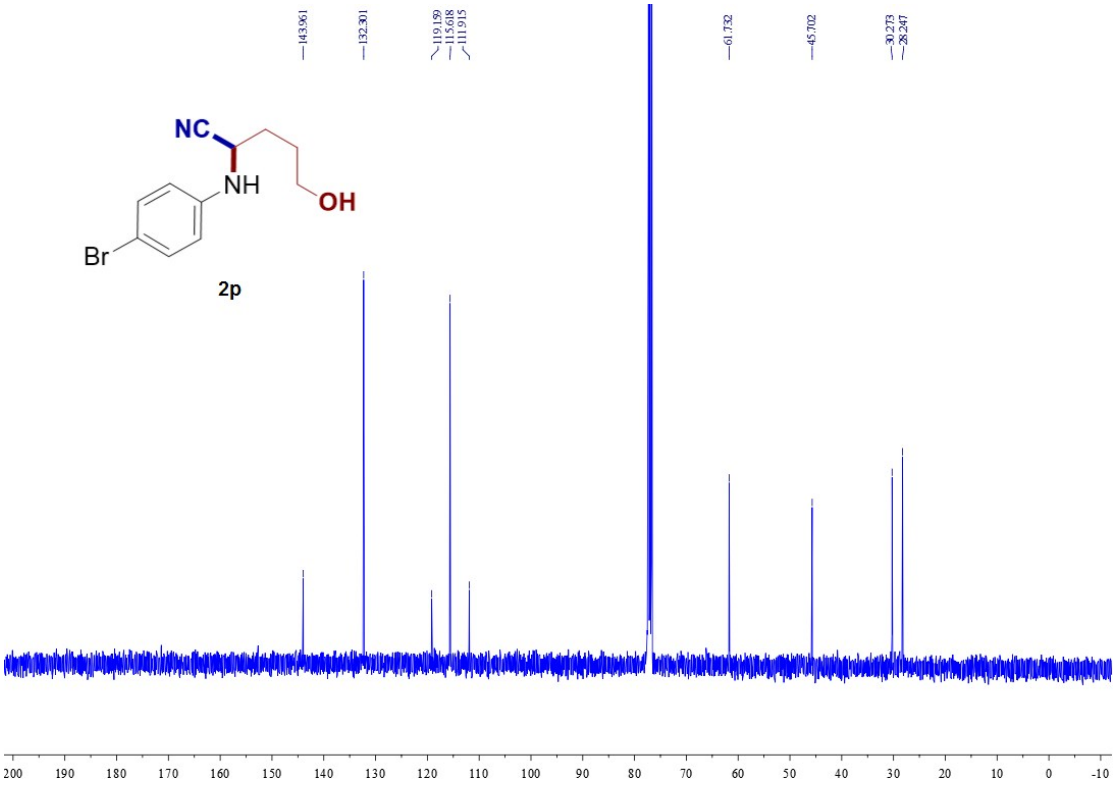
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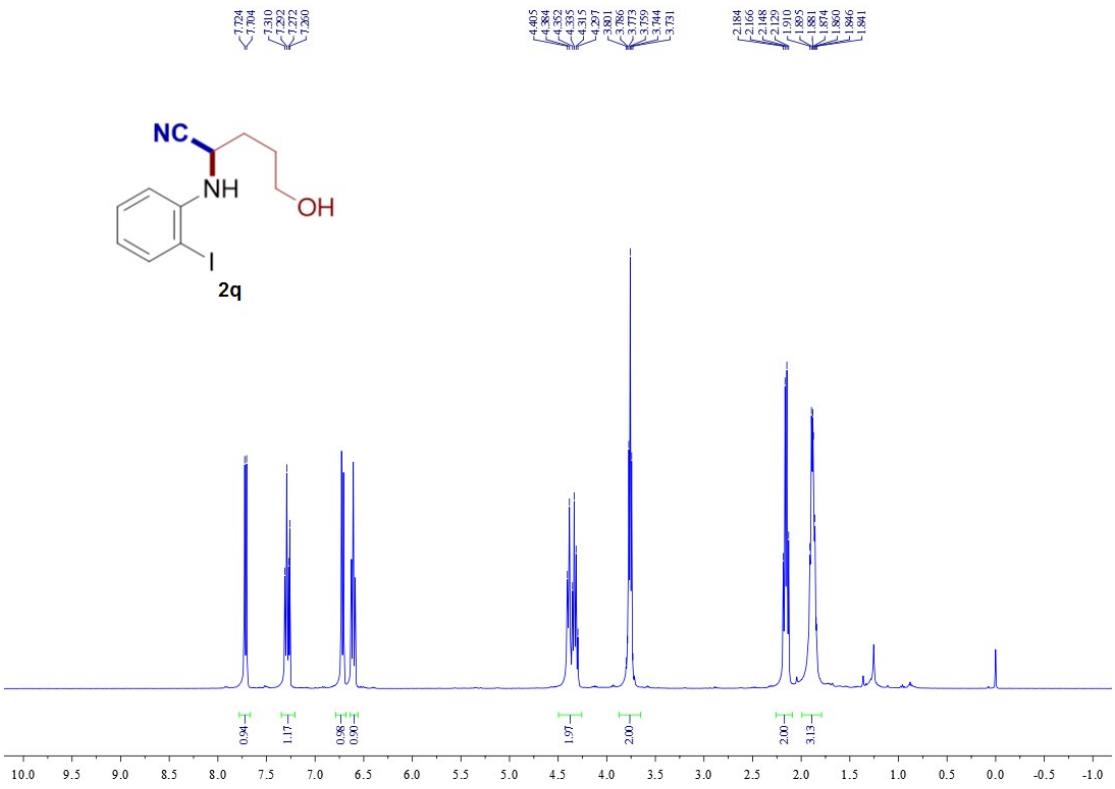
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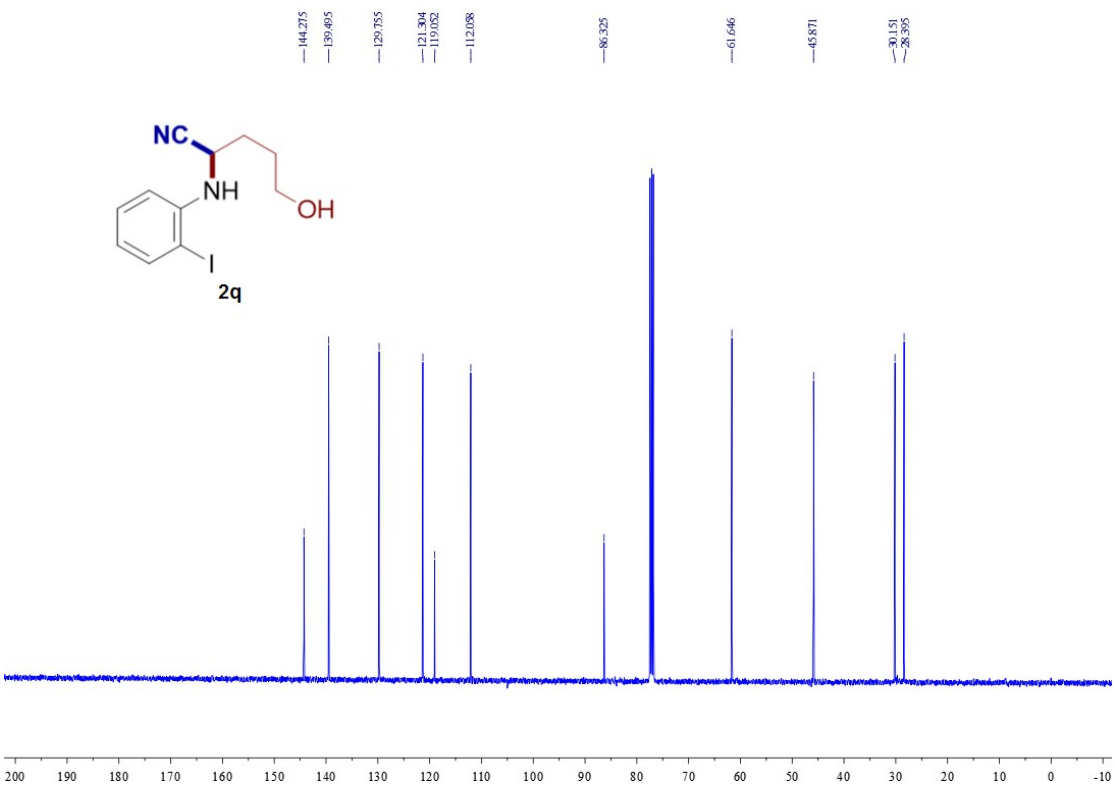
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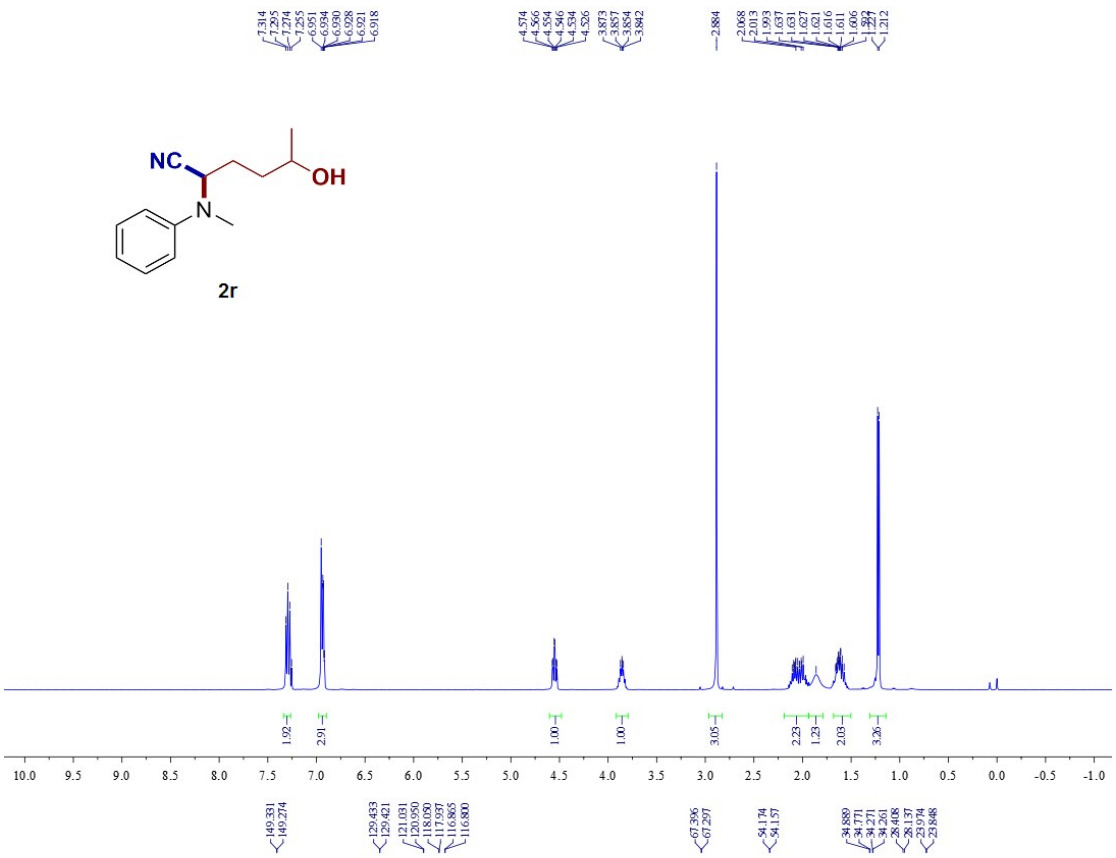
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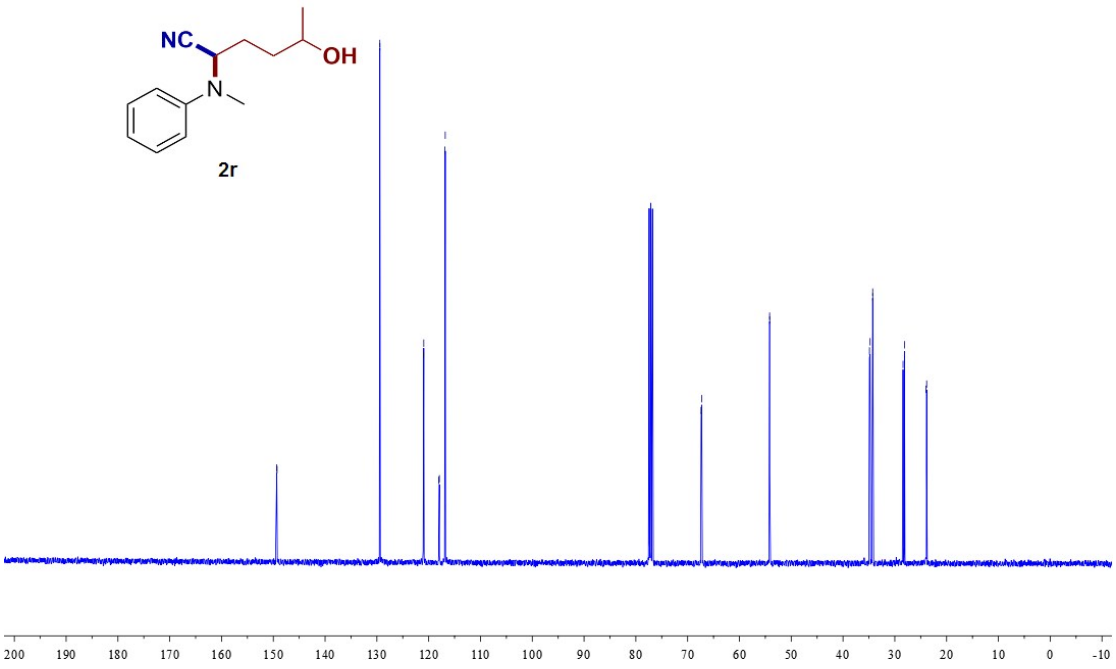
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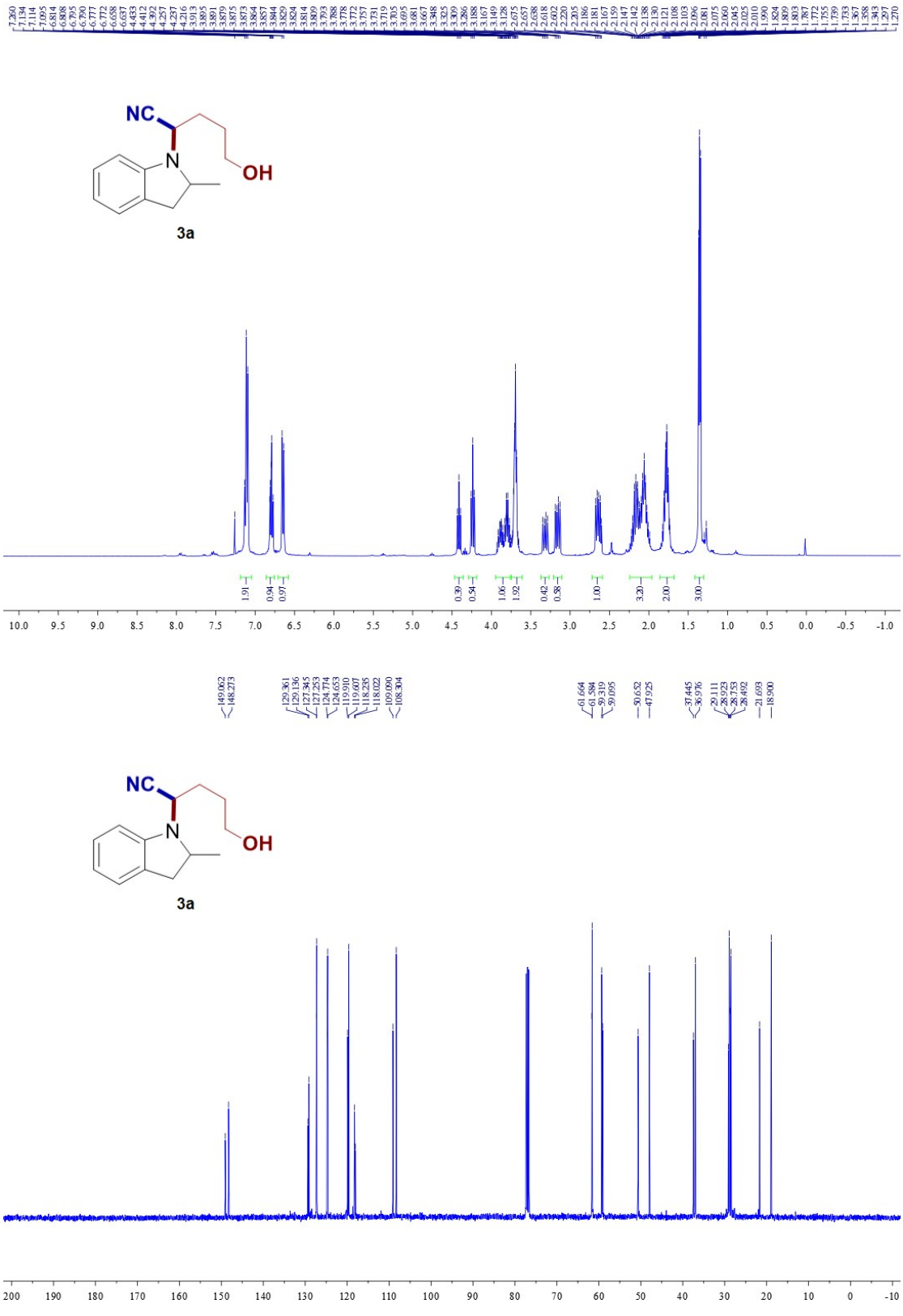
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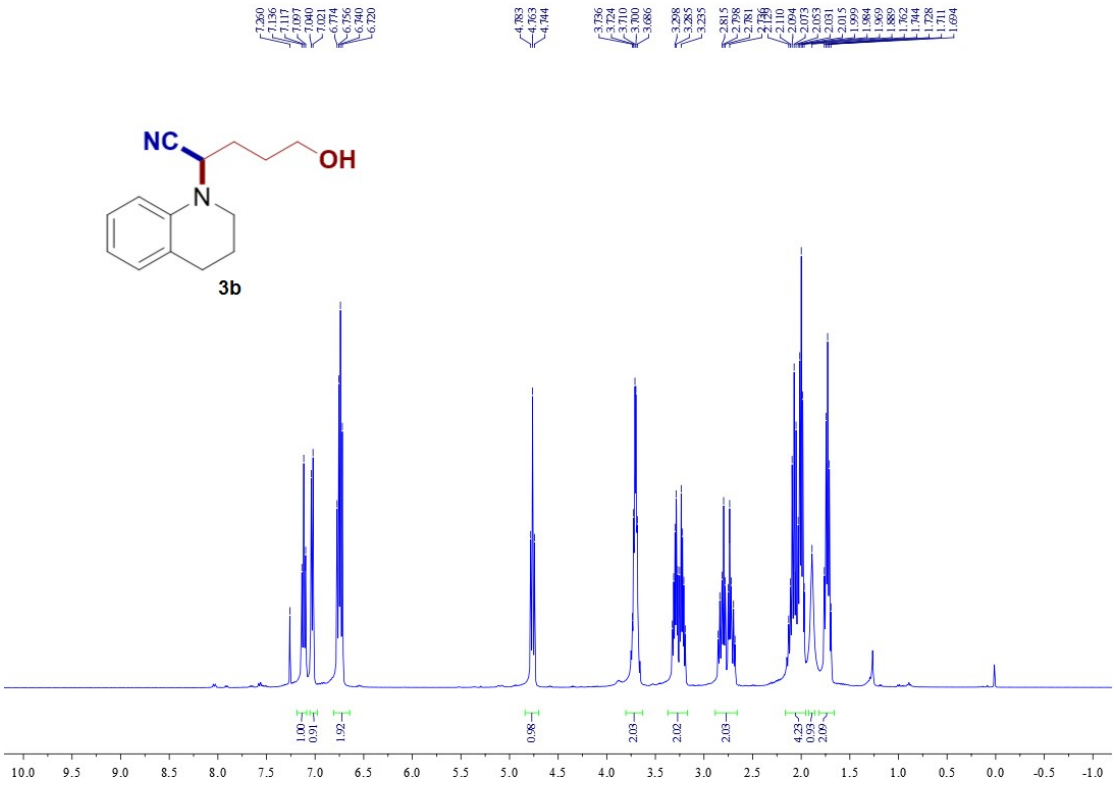
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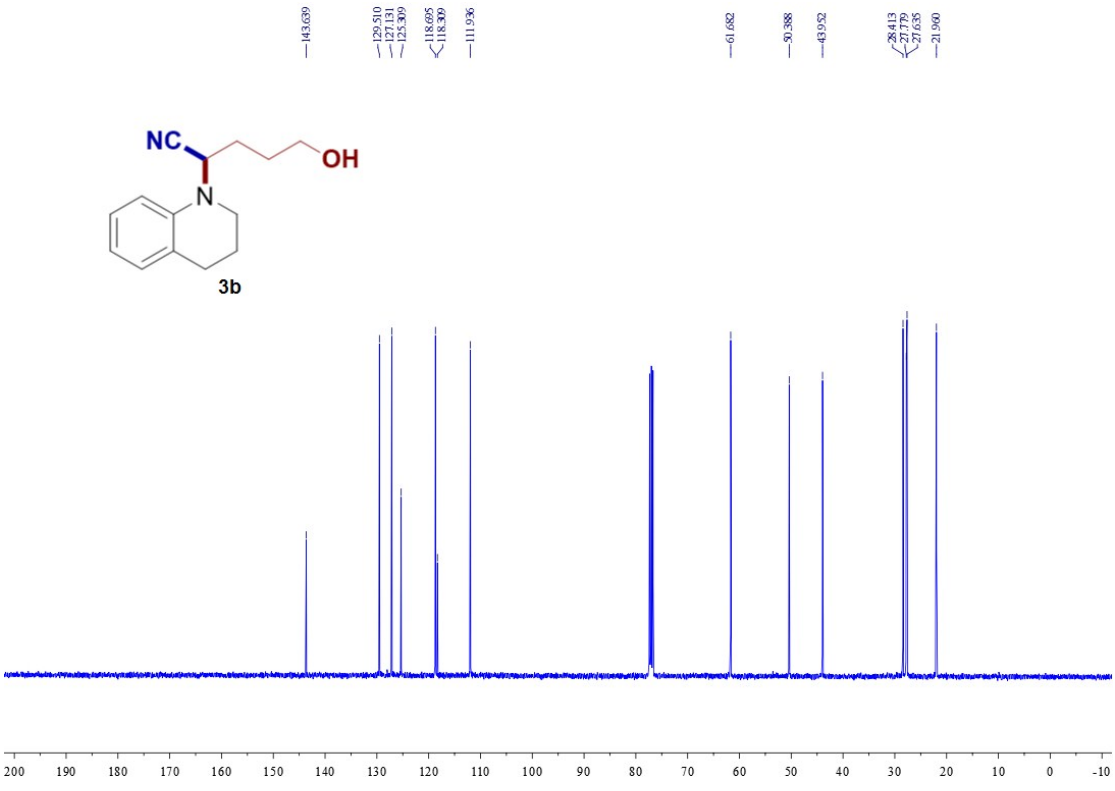
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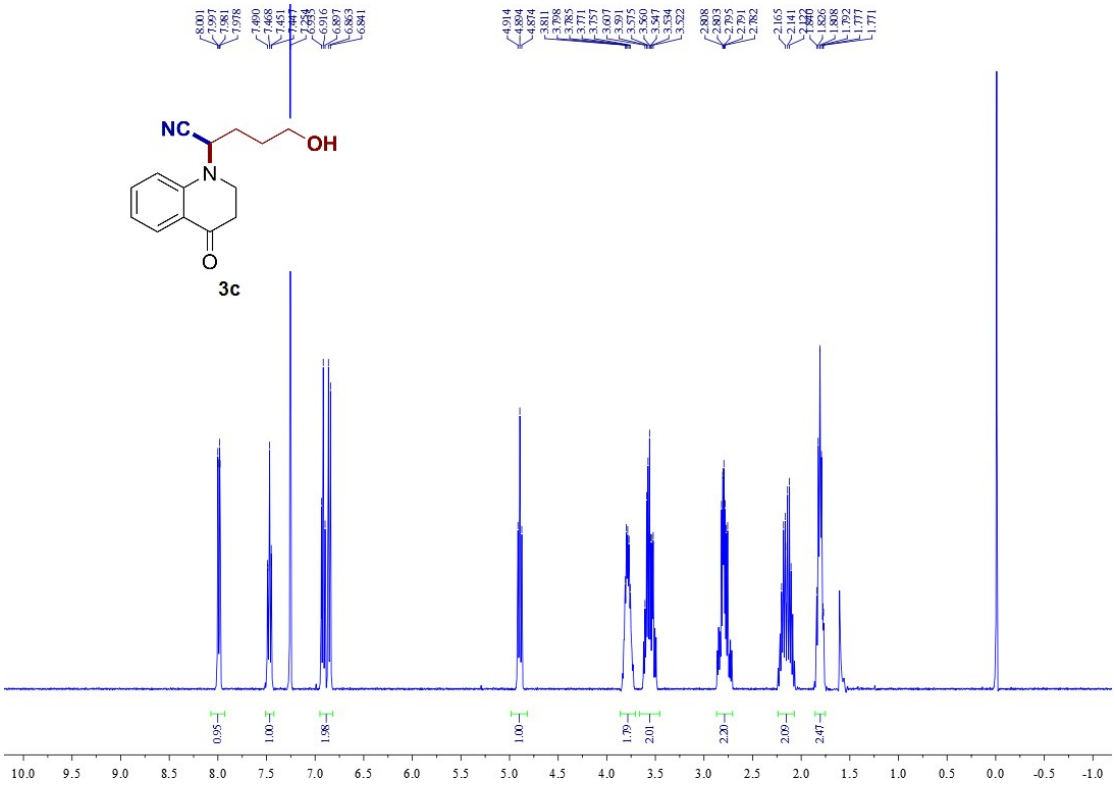
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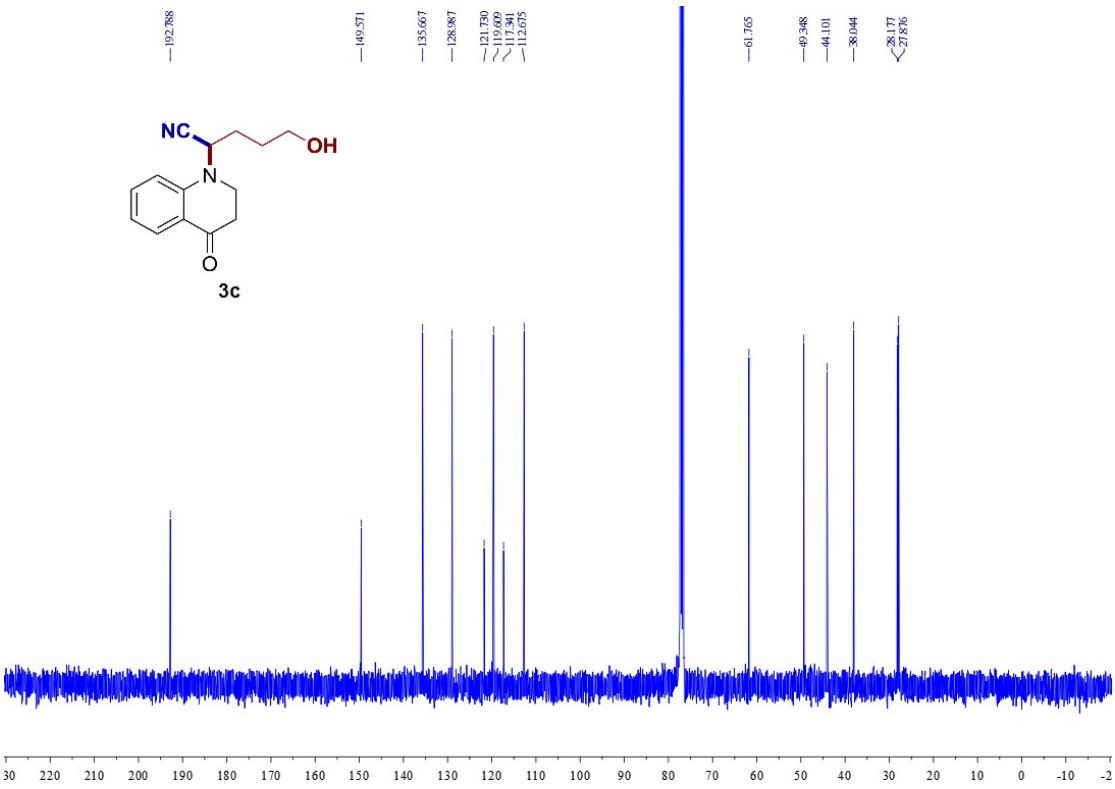
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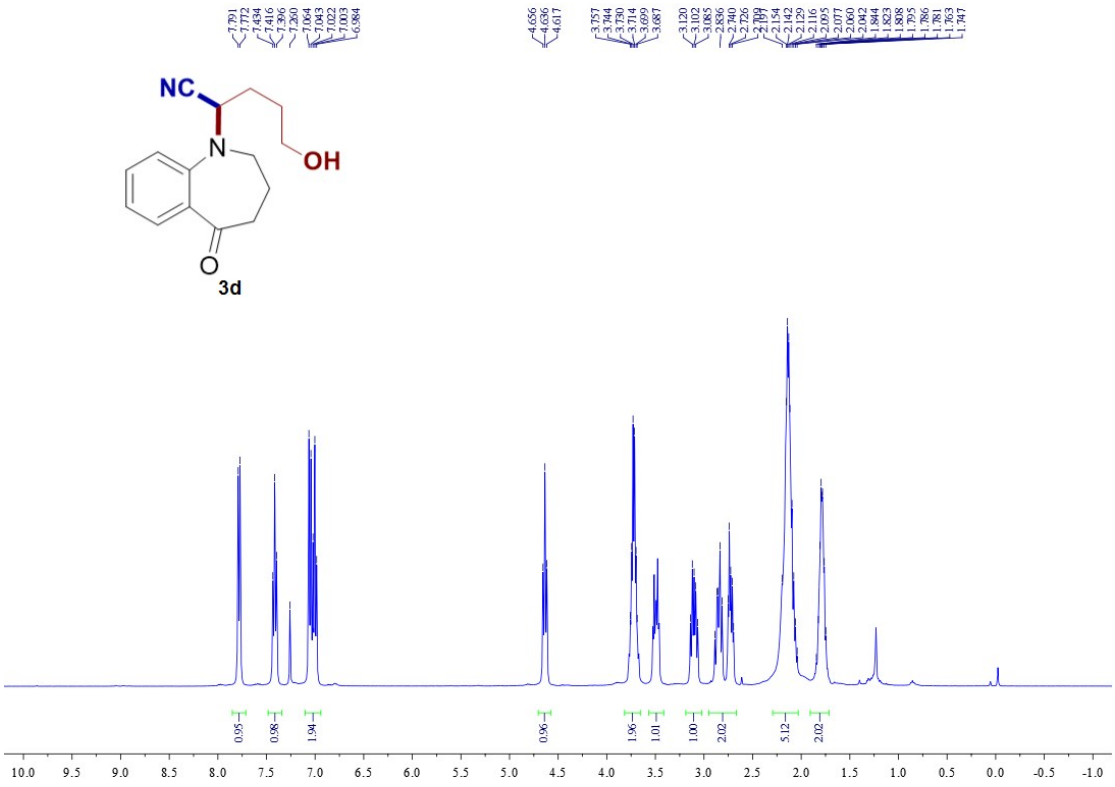
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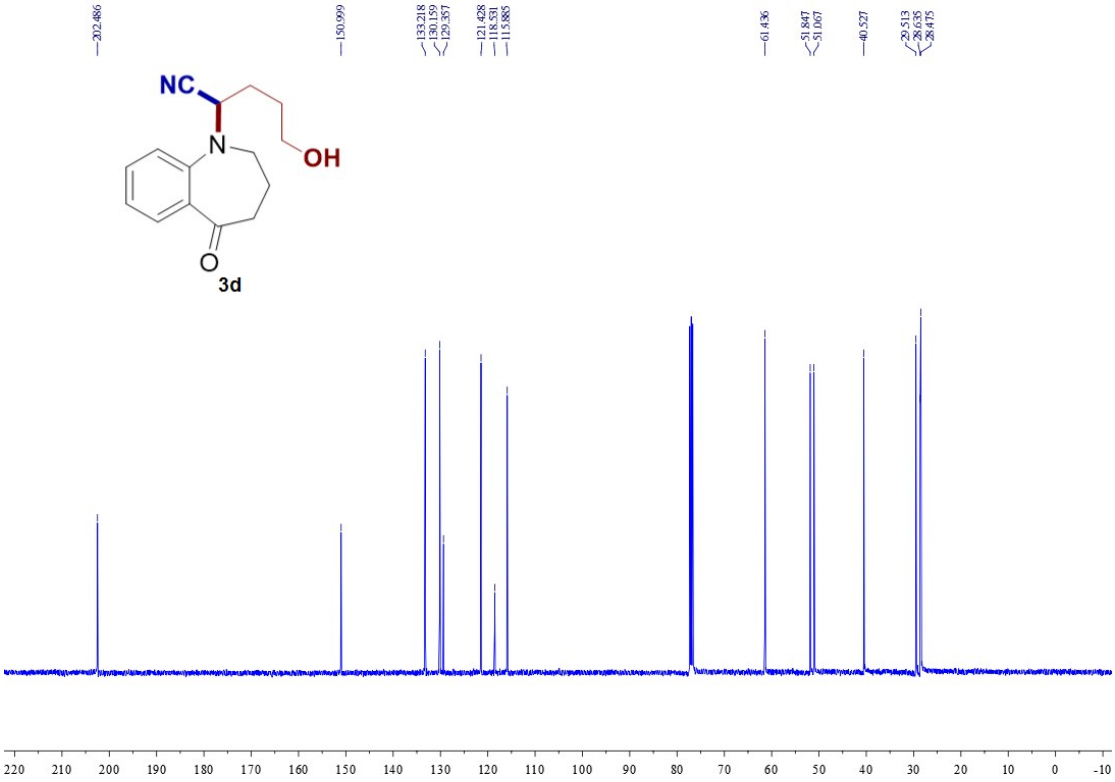
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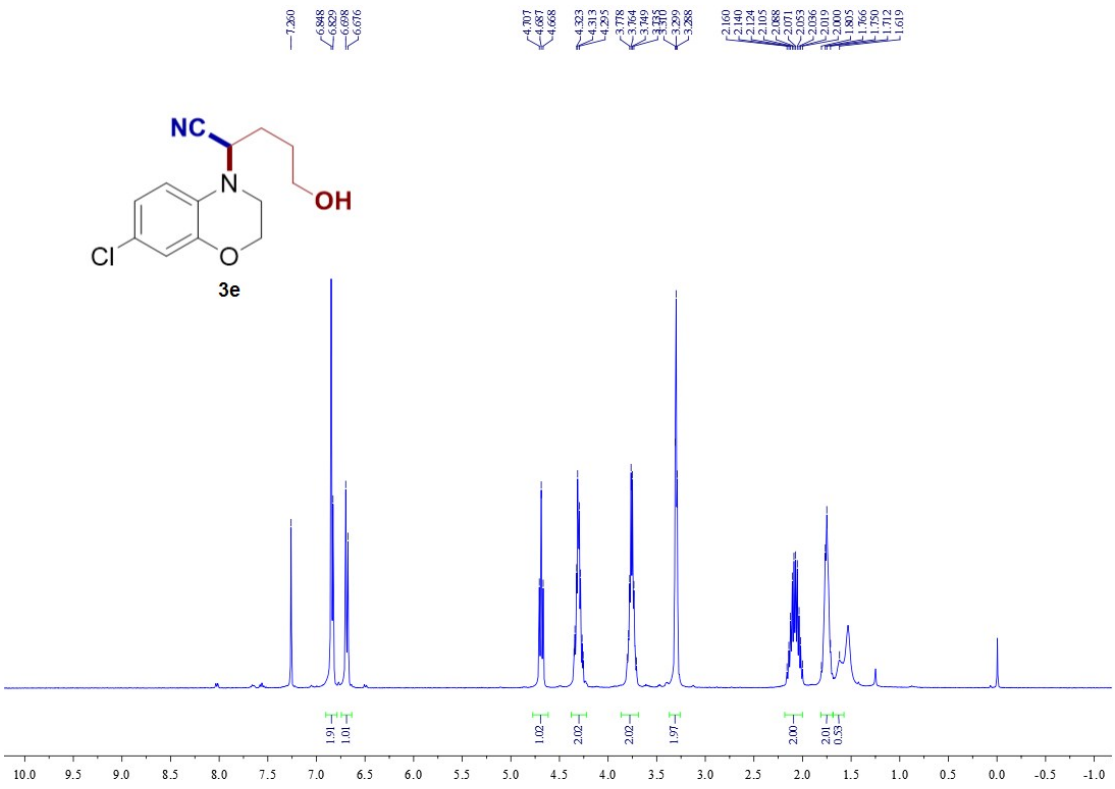
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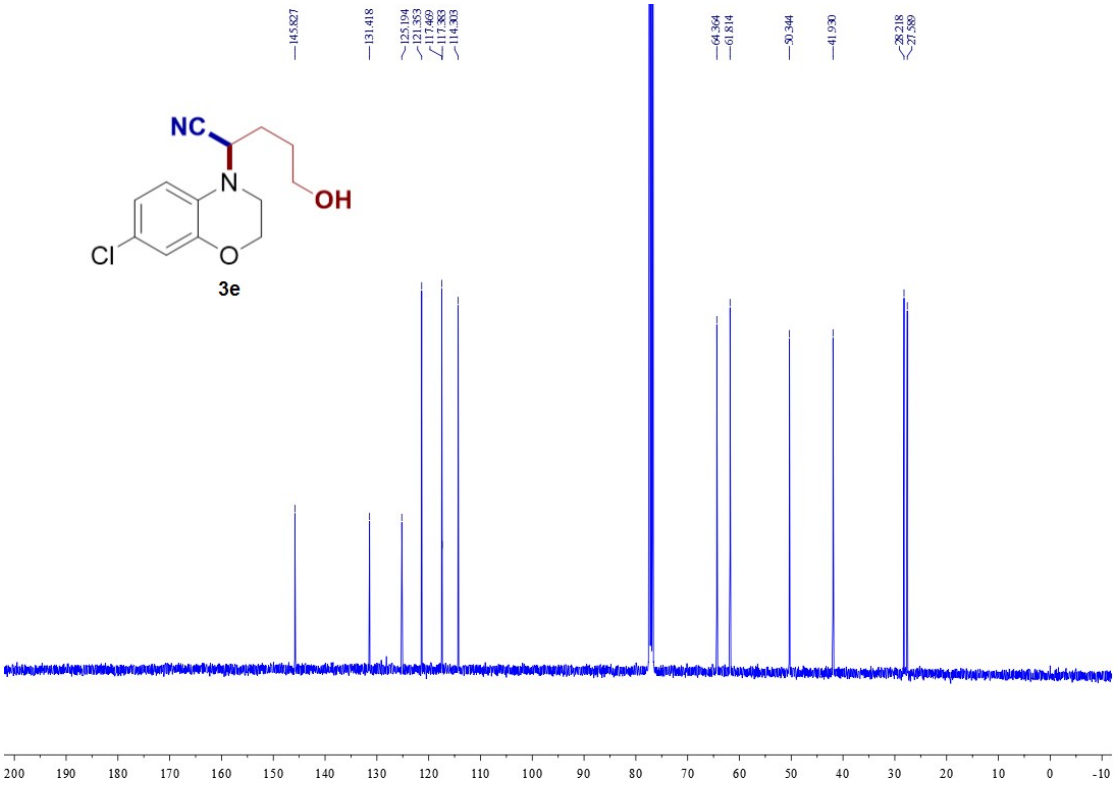
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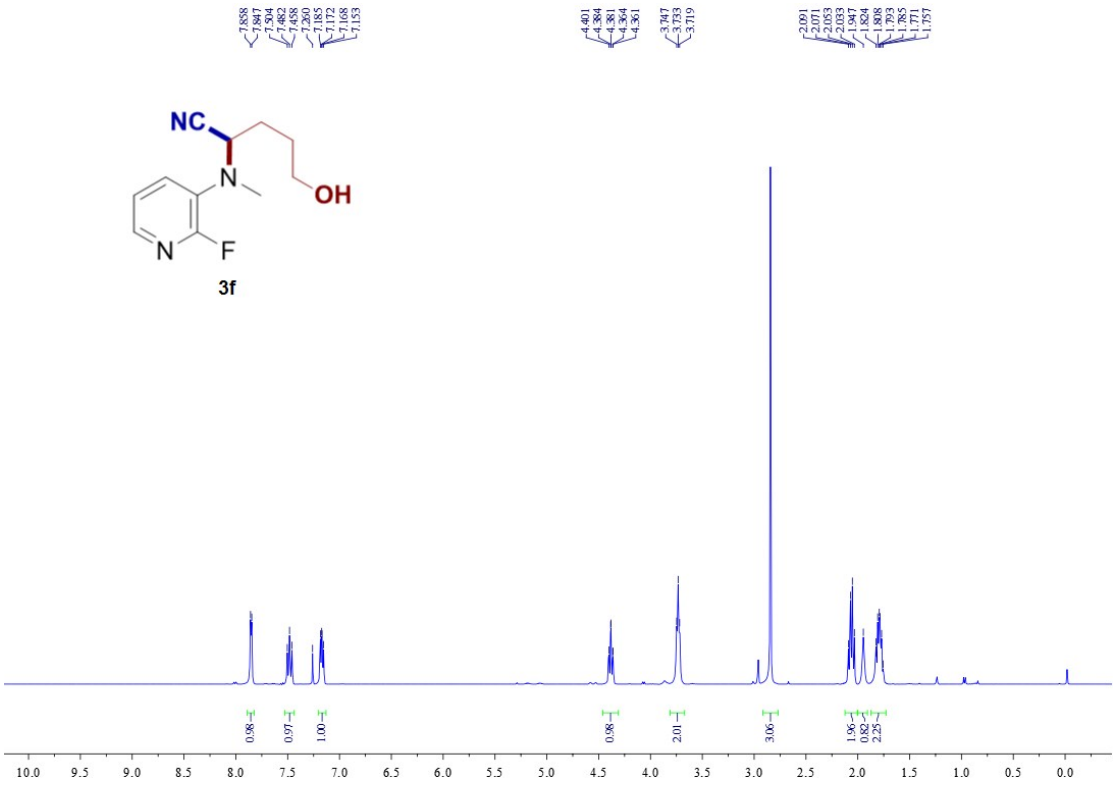
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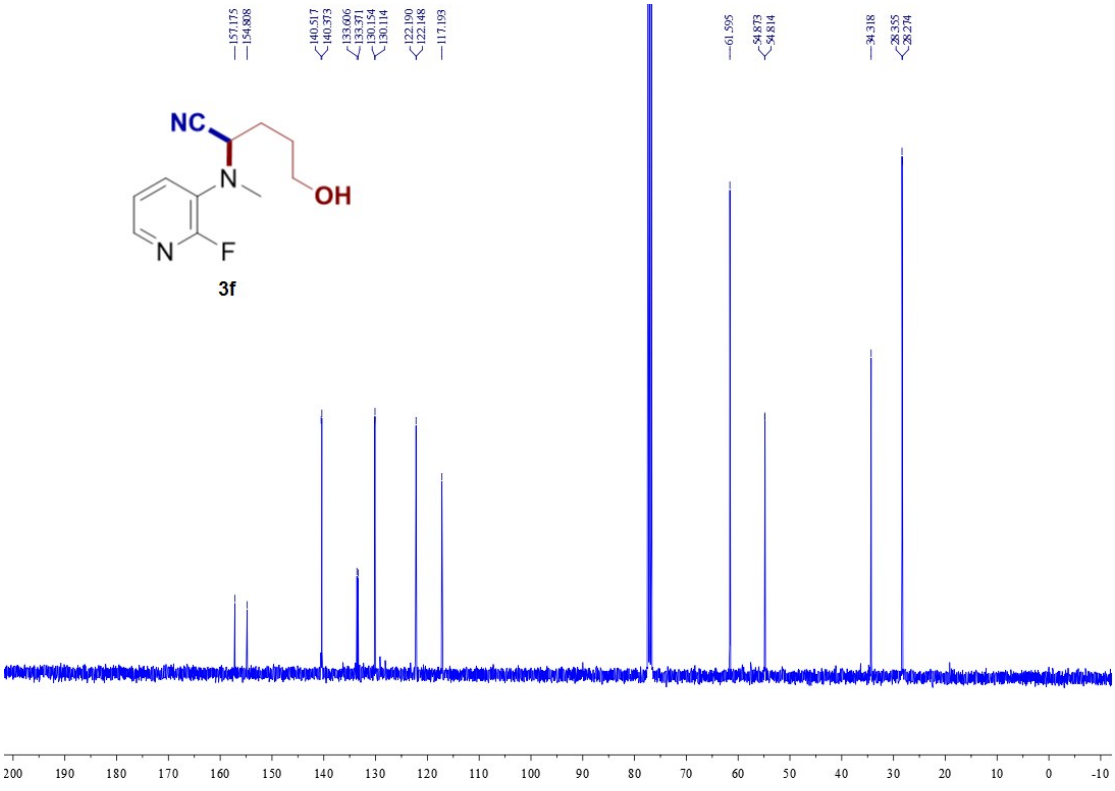
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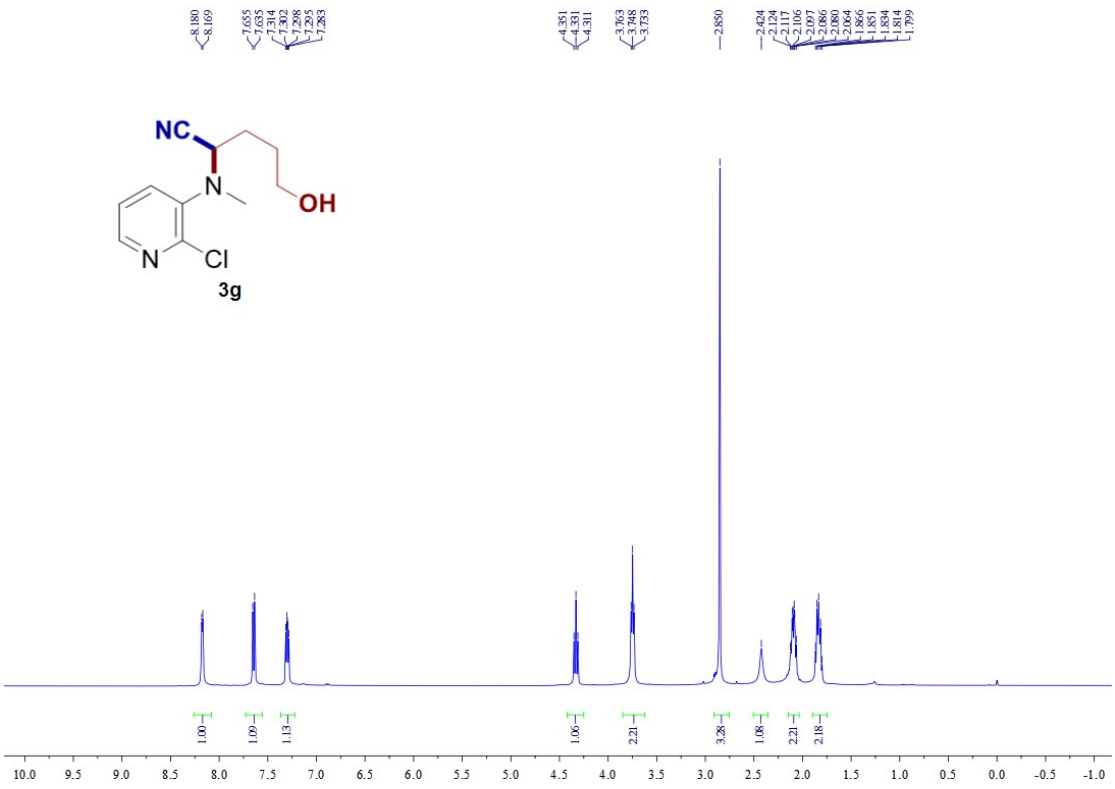
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3.733
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2.106
2.097
2.086
2.080
2.064
1.866
1.851
1.834
1.814
1.799
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N
OH
N
Cl
3g
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1.09
1.13
1.06
2.21
3.28
1.08
2.21
2.18
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8.0
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7.0
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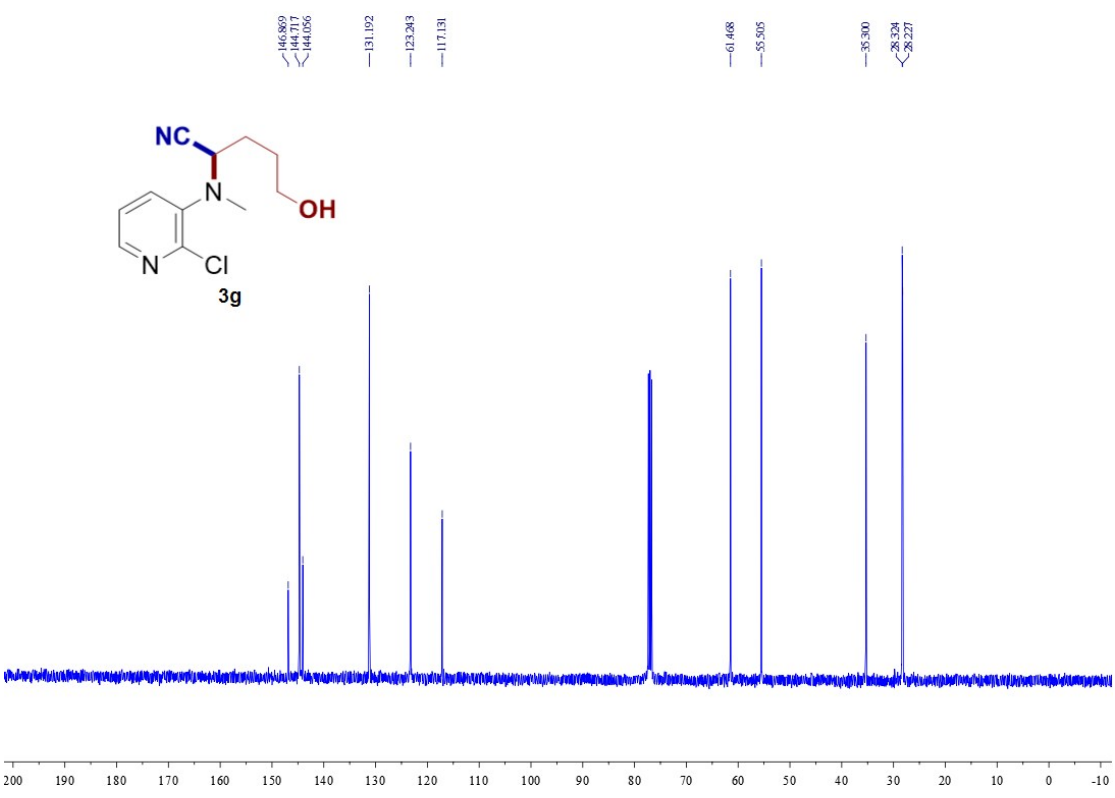
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OH
N
Cl
3g
200
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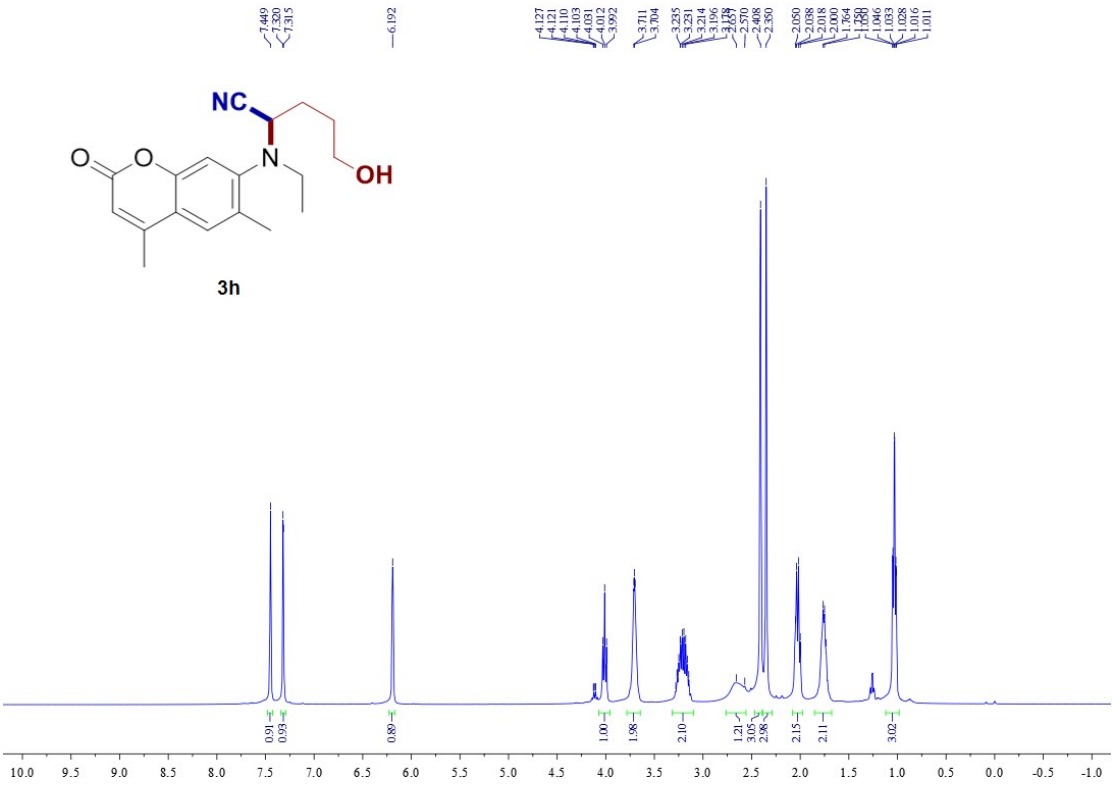
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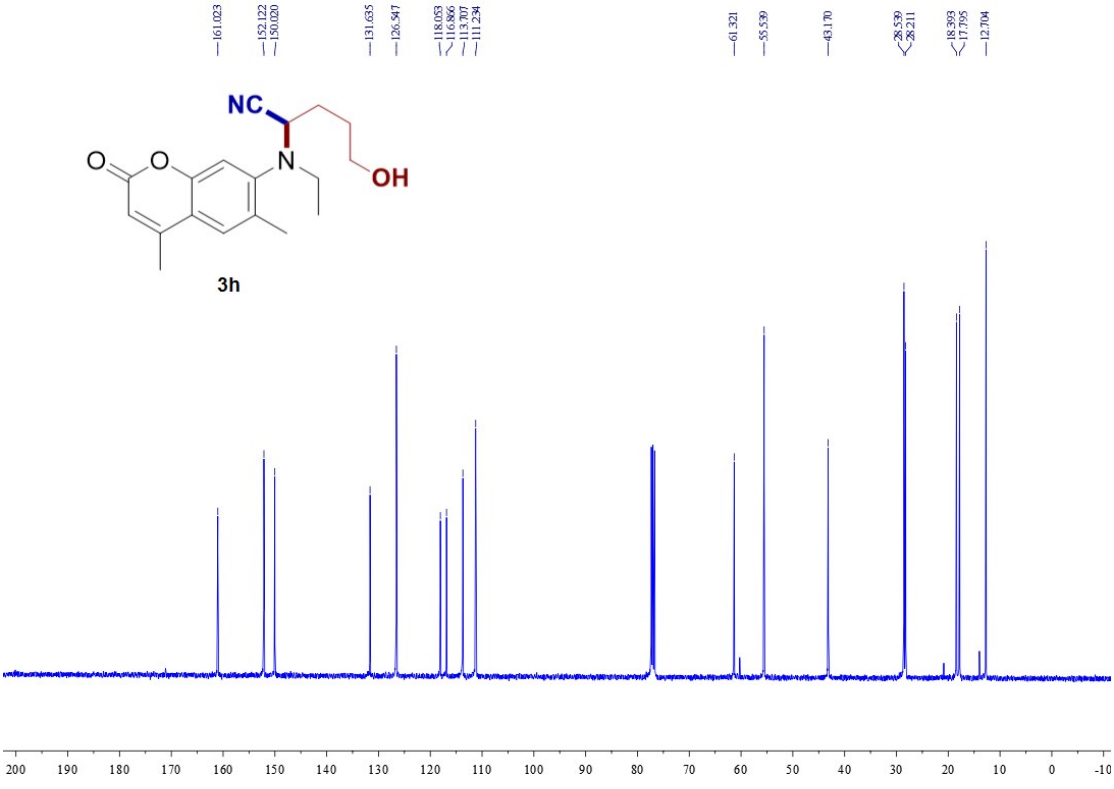
OH
3h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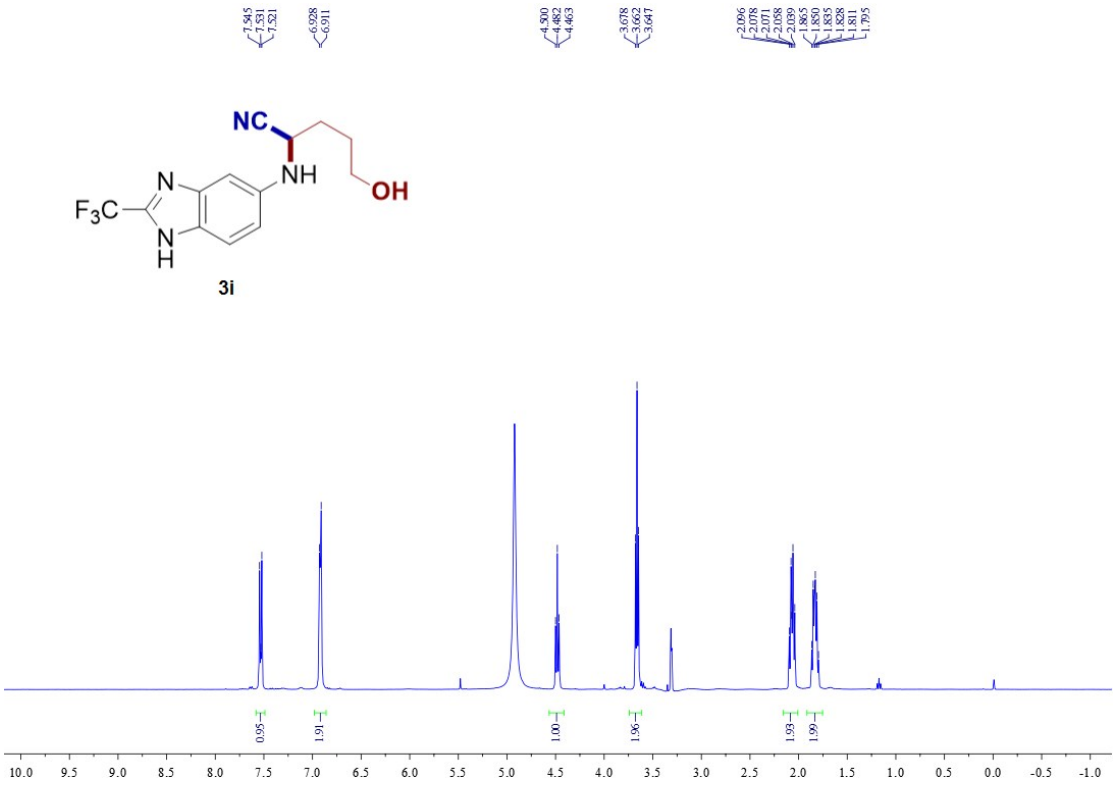
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2.078
2.071
2.058
2.039
1.865
1.850
1.835
1.828
1.811
1.795
NC
NH
OH
N
F3C
N
H
3i
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1.91
1.00
1.96
1.93
1.99
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9.5
9.0
8.5
8.0
7.5
7.0
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6.0
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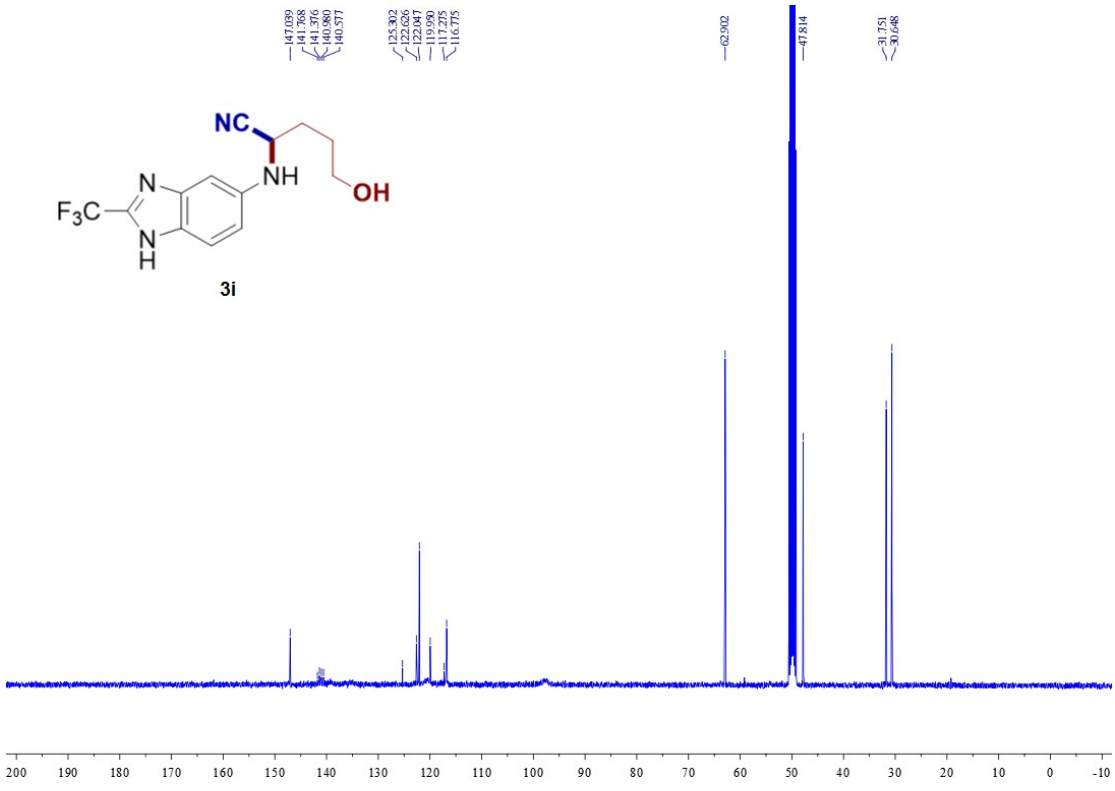
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NC
NH
OH
N
F3C
N
H
3i
200
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100
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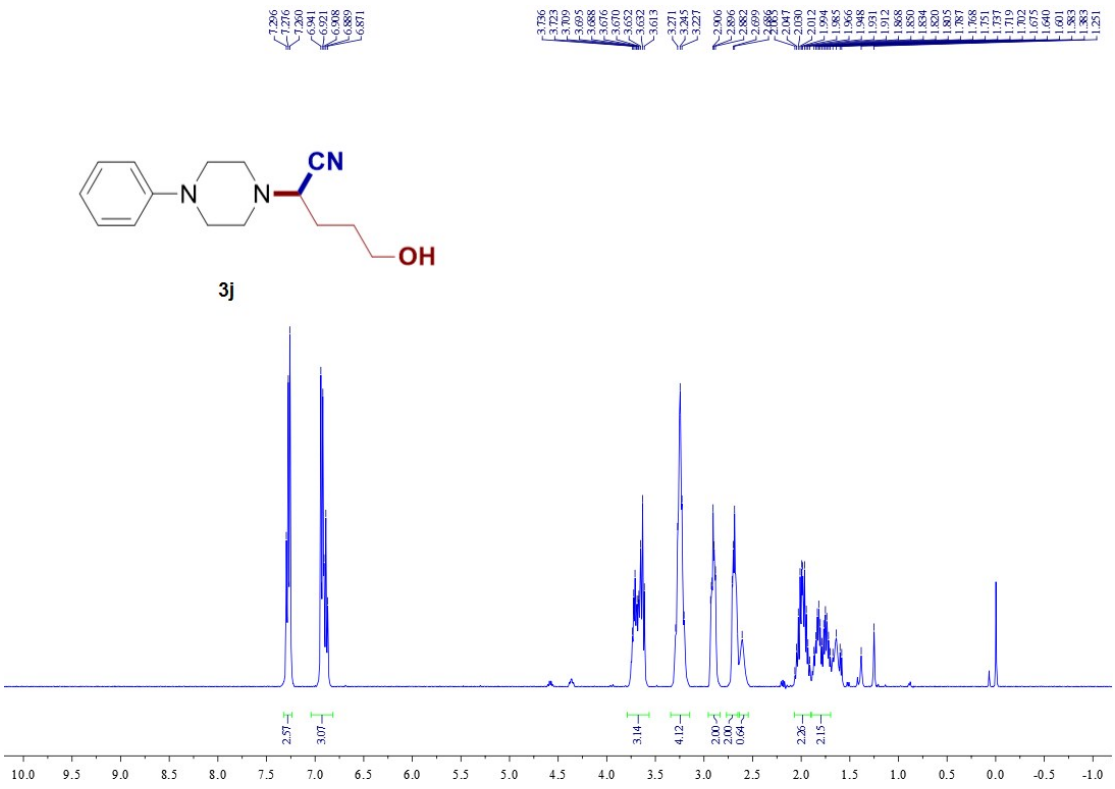
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3.676
3.670
3.652
3.632
3.613
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3.245
3.227
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2.896
2.882
2.690
2.686
2.047
2.030
2.012
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1.966
1.948
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1.912
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1.820
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1.768
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1.719
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1.640
1.601
1.583
1.383
1.251
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N
OH
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3.07
3.14
4.12
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2.00
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2.26
2.15
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9.5
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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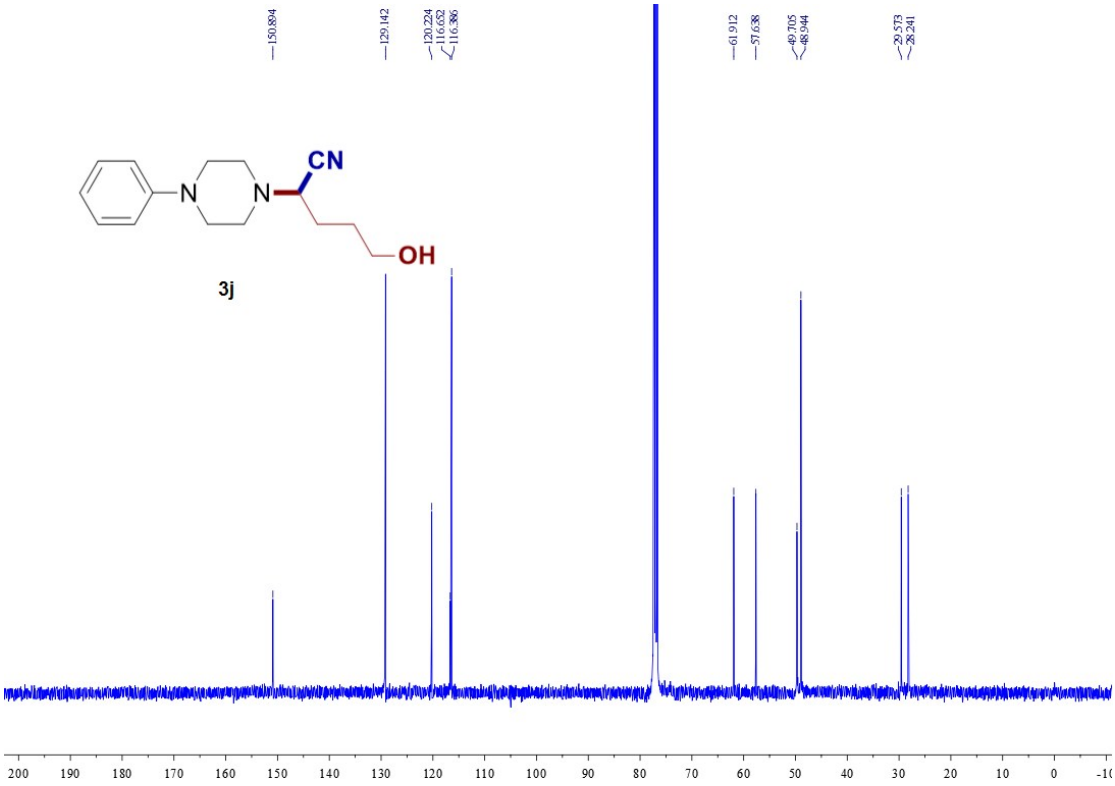
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N
OH
3j
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10
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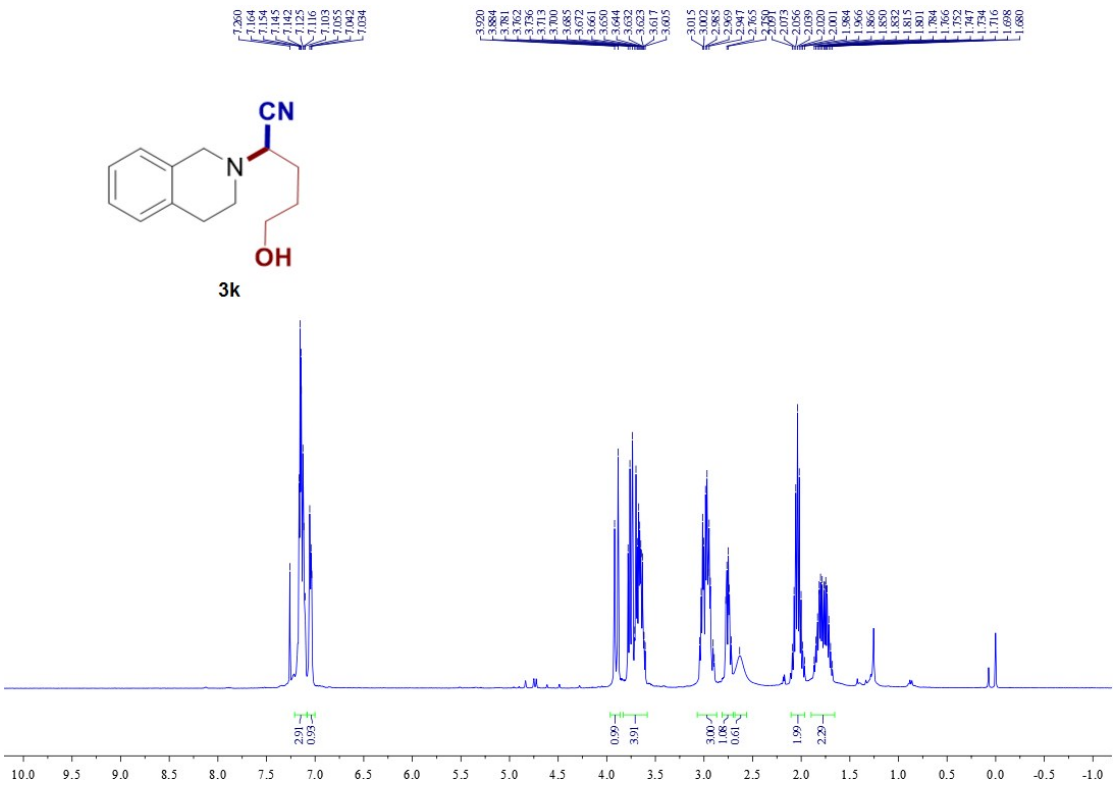
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N
OH
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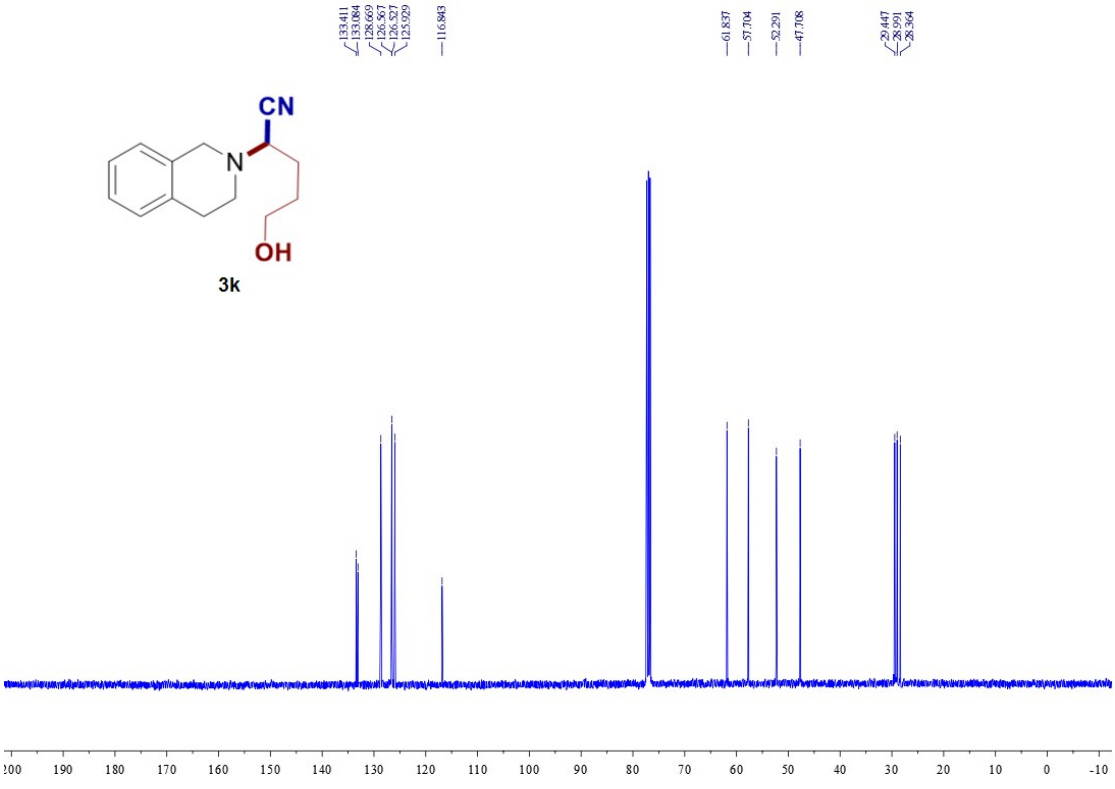
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OH
3k
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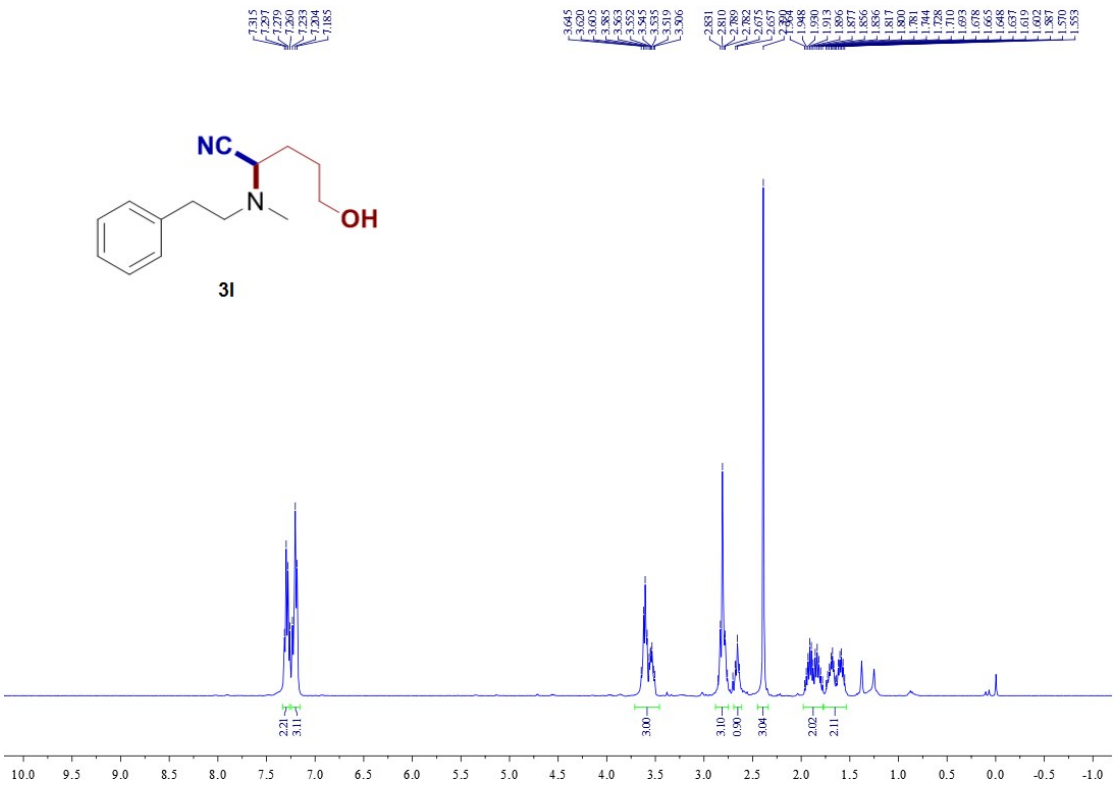
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OH
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7.204
7.185
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3.605
3.585
3.563
3.552
3.545
3.535
3.519
3.506
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2.810
2.789
2.782
2.675
2.657
2.390
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1.913
1.896
1.877
1.856
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1.817
1.800
1.781
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1.587
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3.00
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2.02
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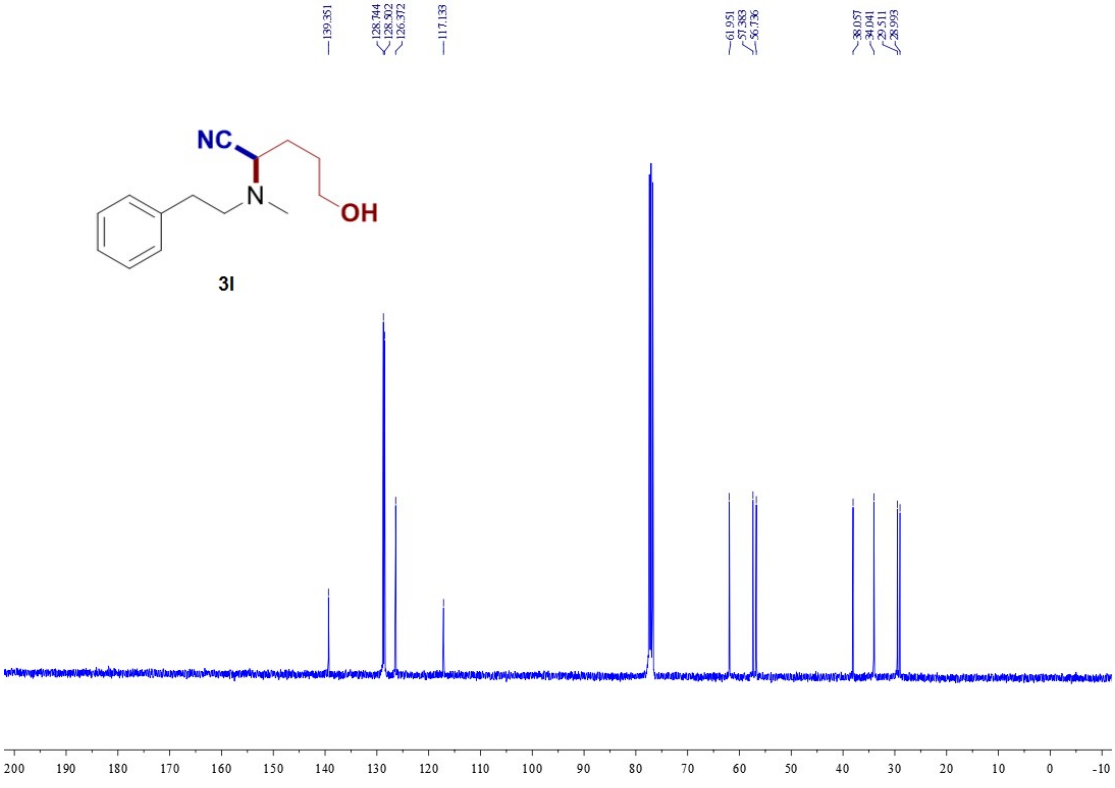
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56.736
38.057
36.044
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200
190
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140
130
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100
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80
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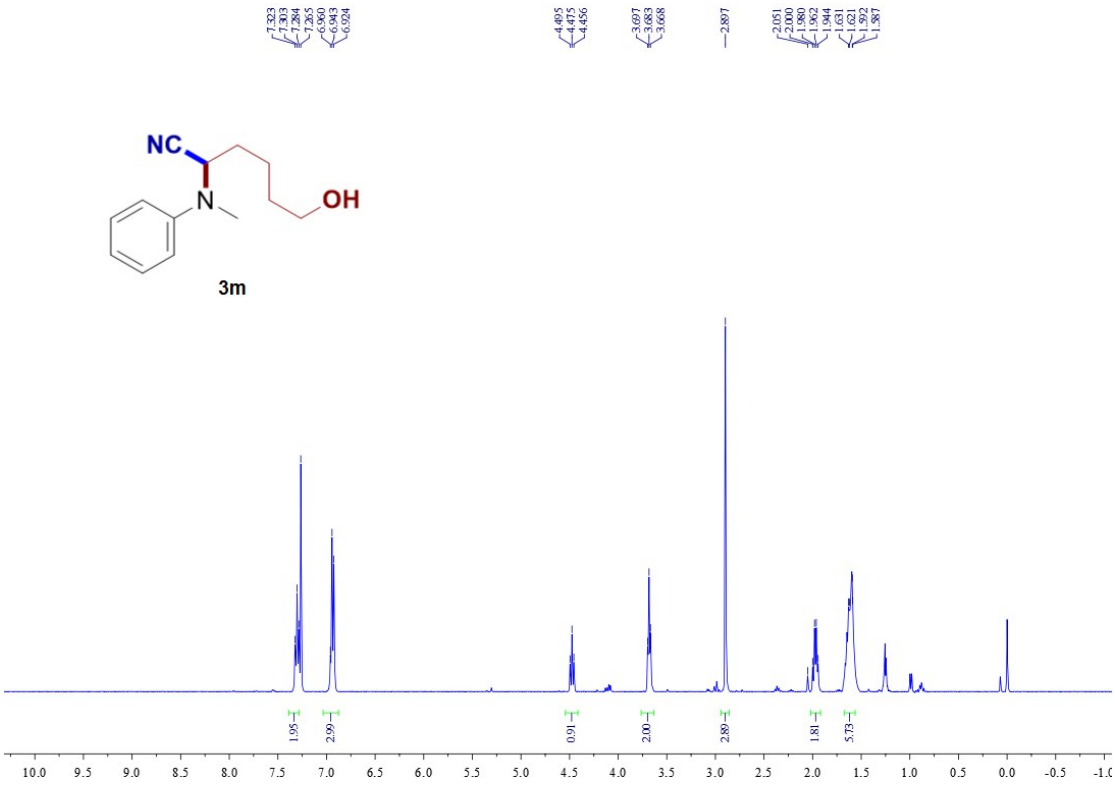
-10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3.668
2.897
2.051
2.000
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1.944
1.631
1.621
1.592
1.587
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N
OH
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7.5
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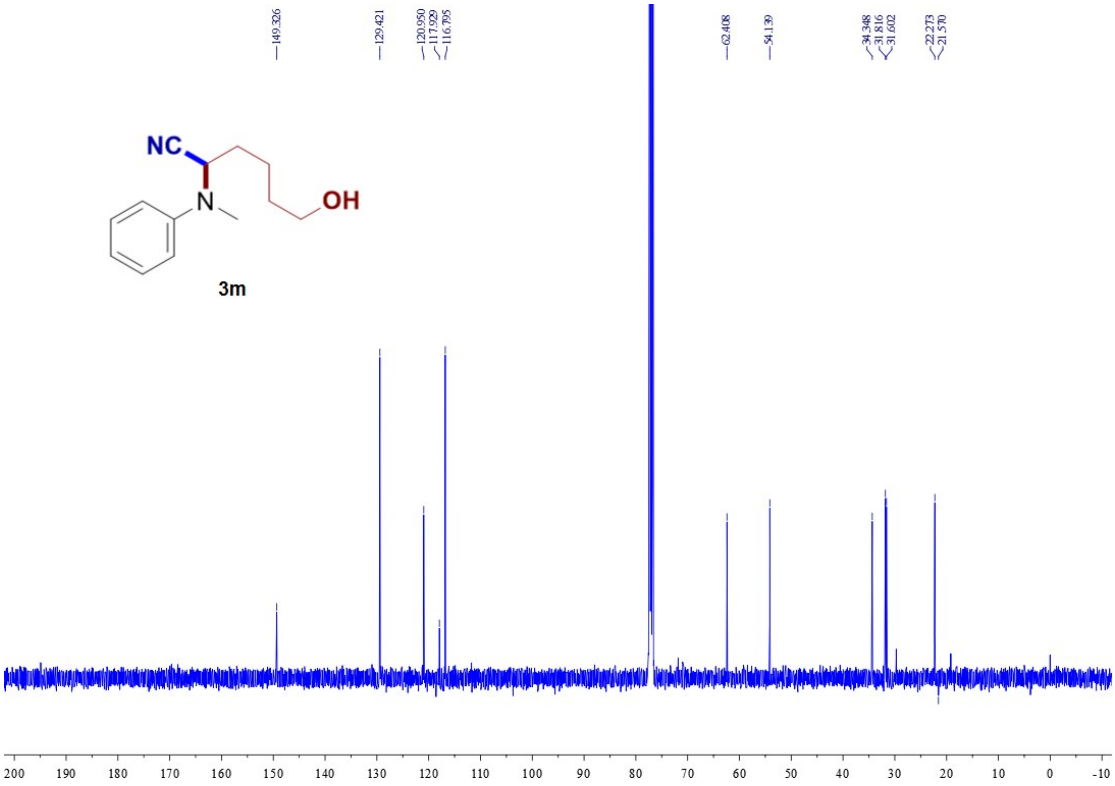
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OH
3m
200
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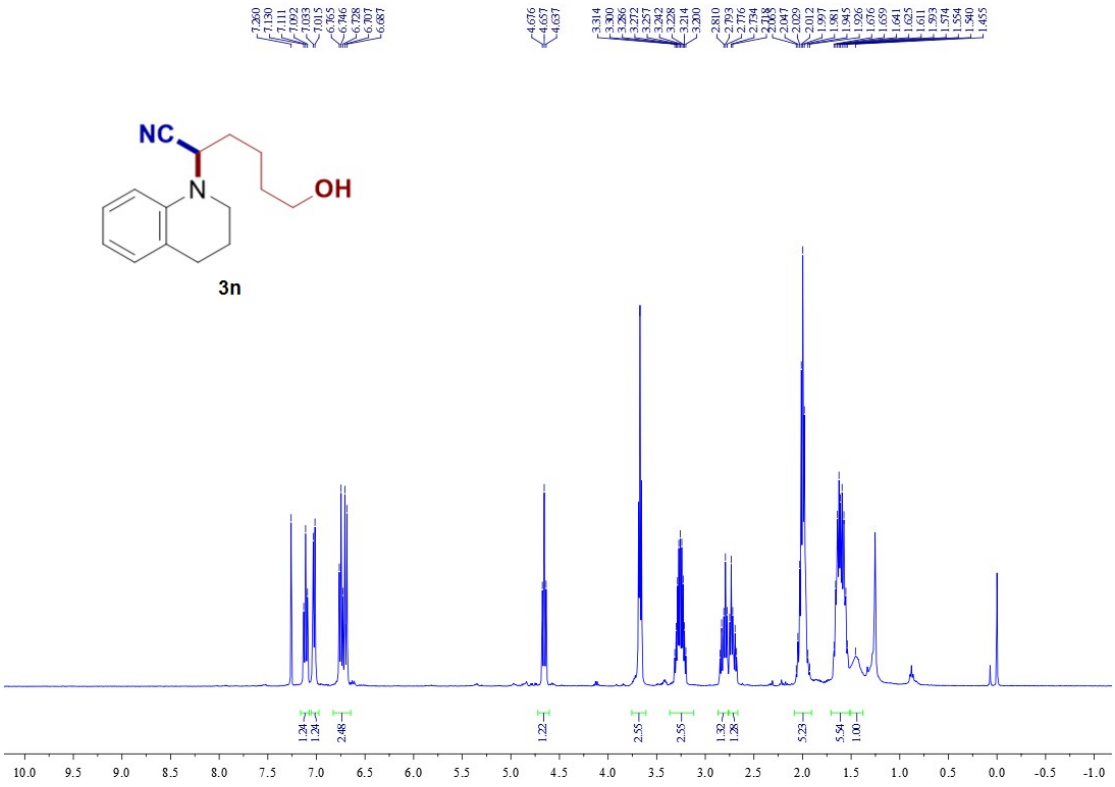
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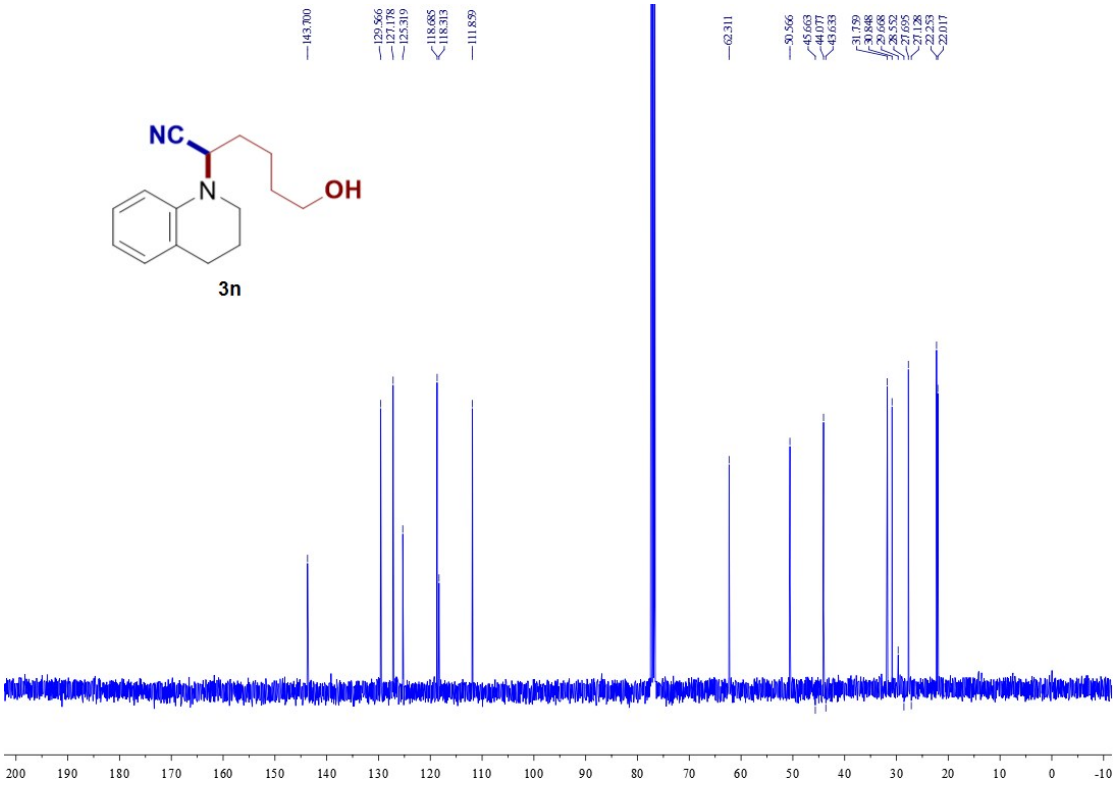
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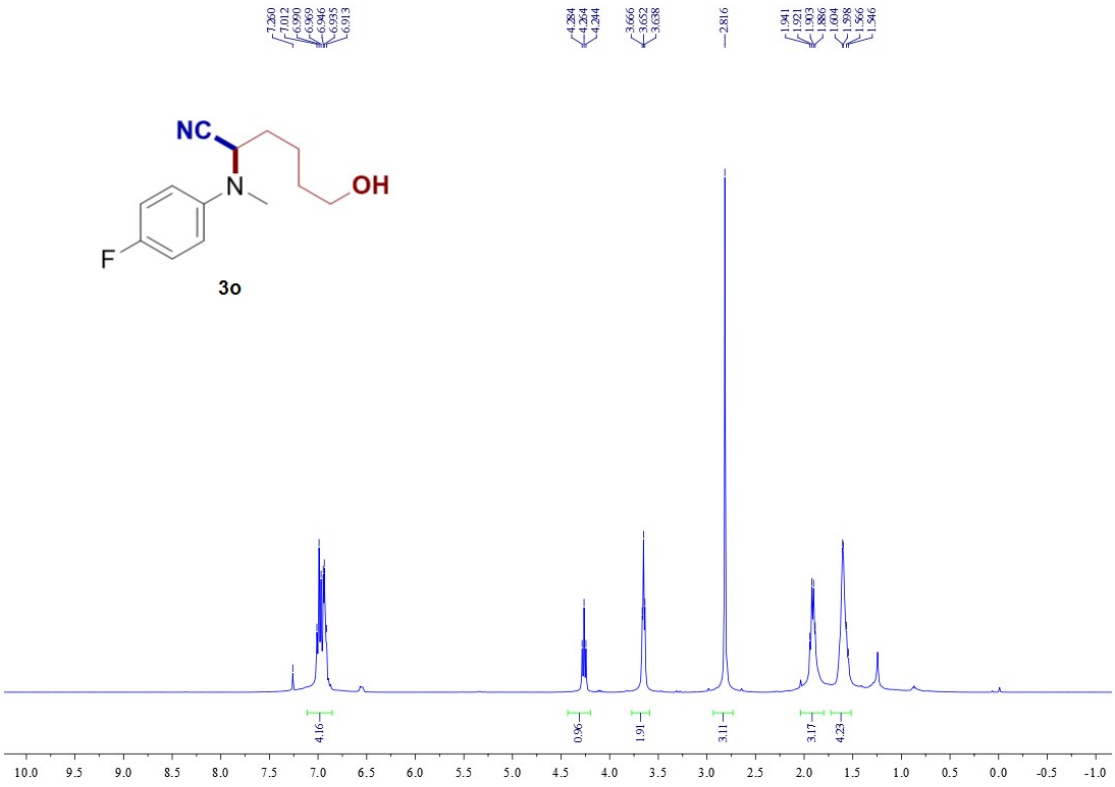
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1.546
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F
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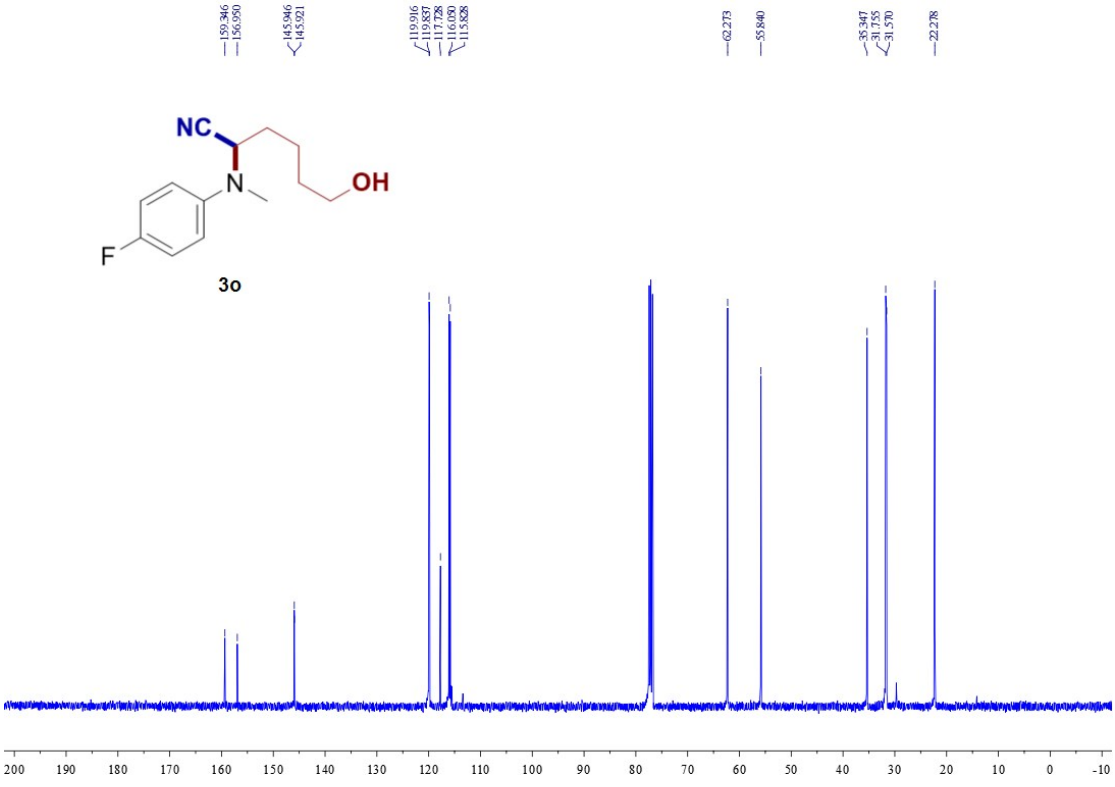
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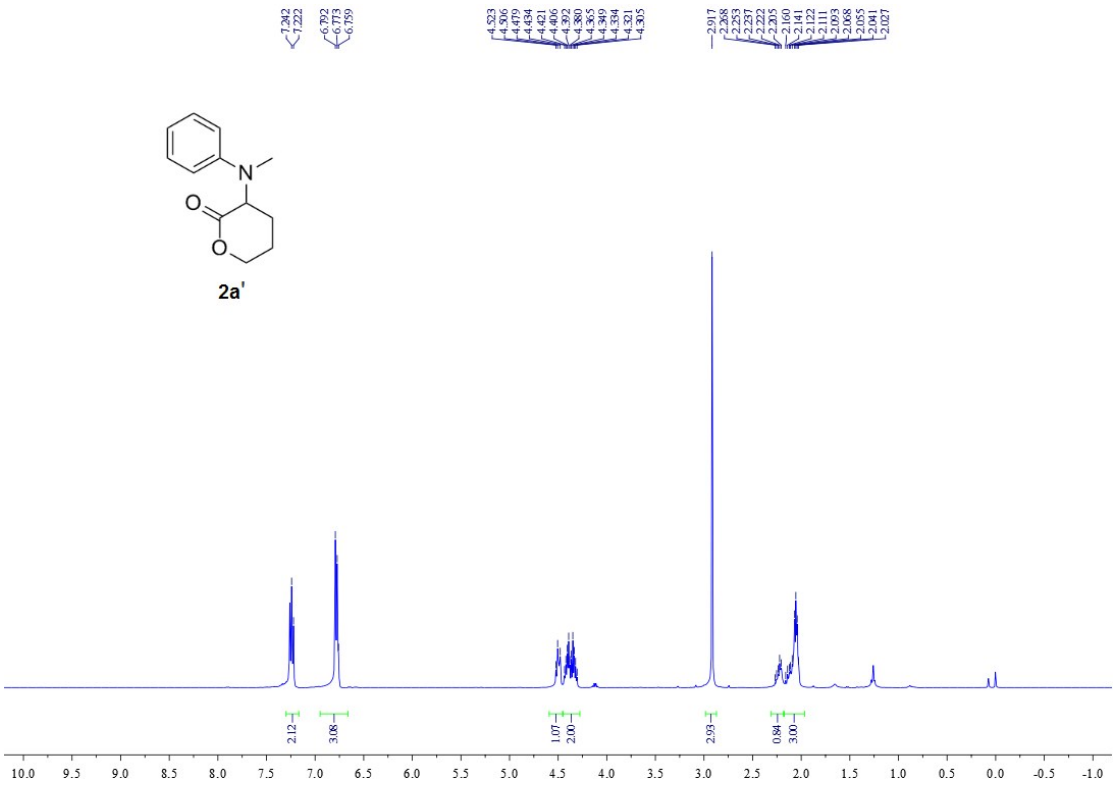
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2.093
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2.041
2.027
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O
O
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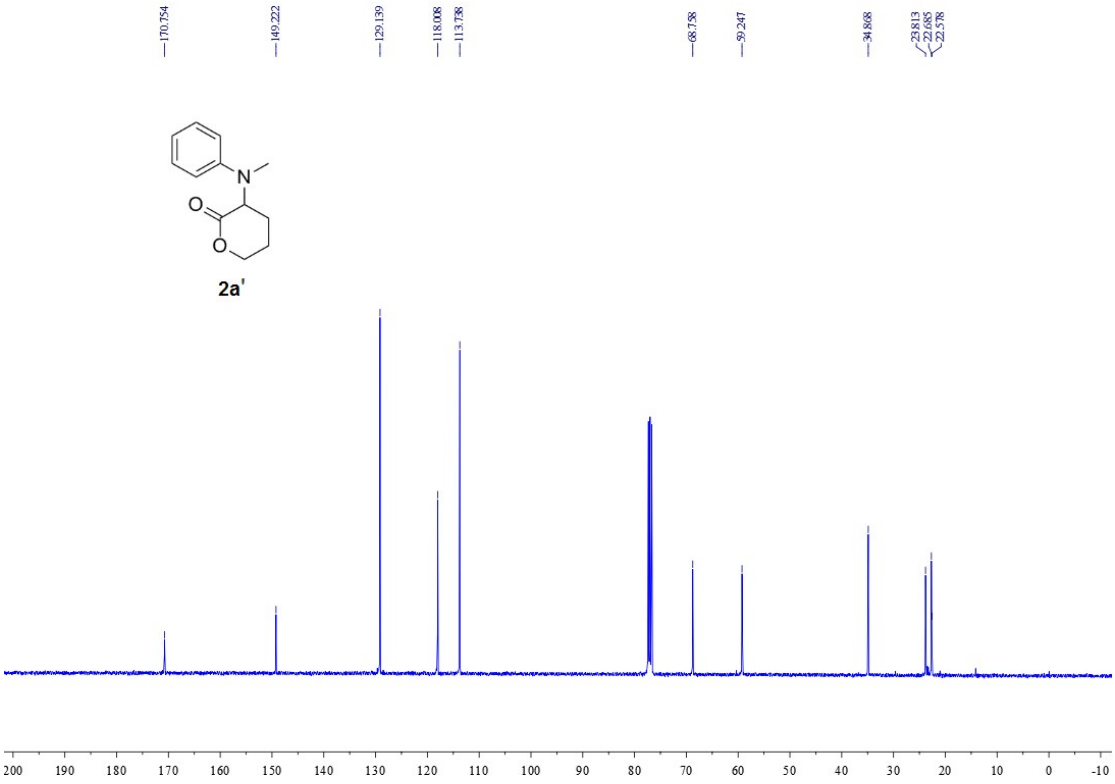
3.08
1.07
2.00
2.93
0.84
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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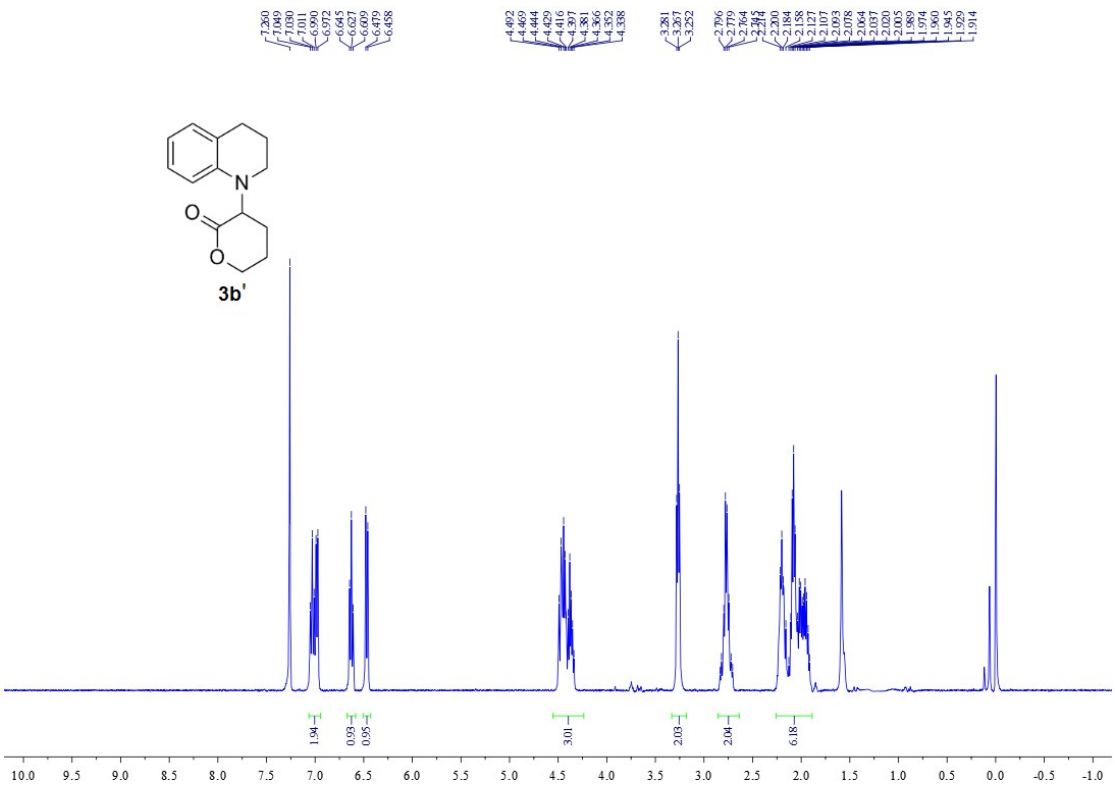
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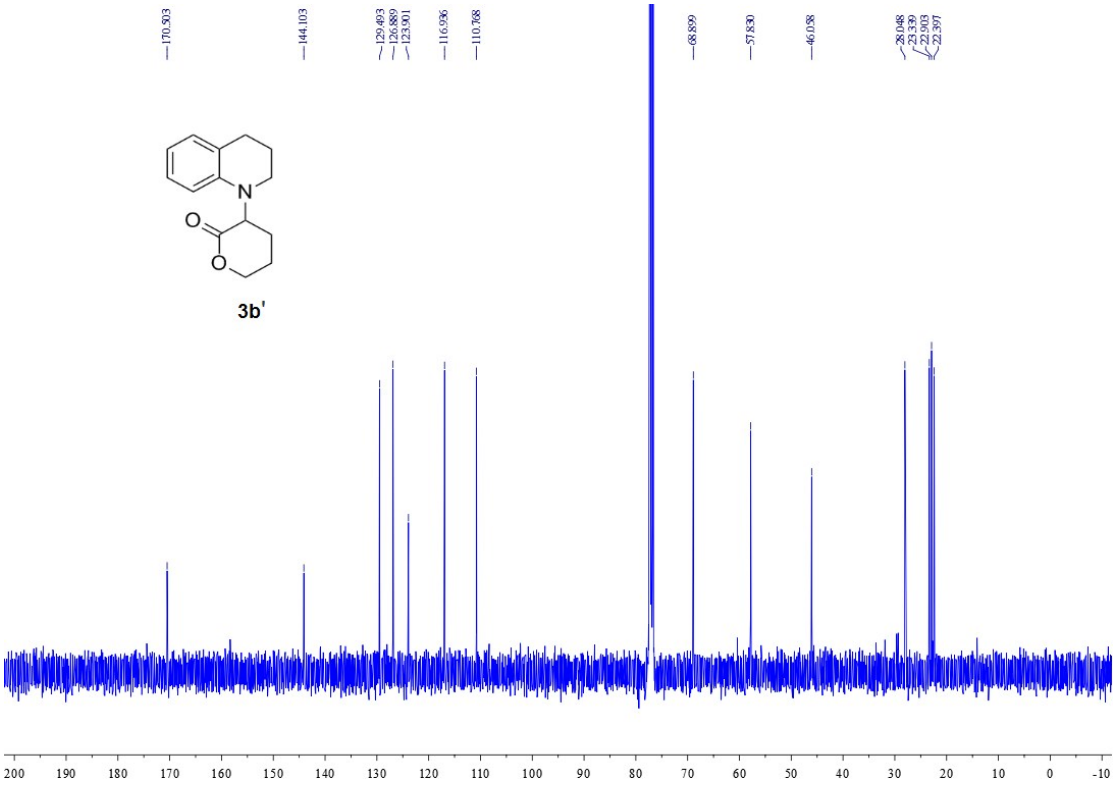
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180
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