SUPPORTING INFORMATION

Cu-Catalyzed Regioselective Borylcyanation of 1,3-Dienes

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■ **General.** Infrared (IR) spectra were recorded on a BRUKER TENSOR 27 FT-IR spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on an Agilent 400 MHz spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz). ^{13}C NMR spectra were recorded on an Agilent 100 MHz spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.00 pm). EI-HRMS and ESI-HRMS spectra were obtained on a Waters Micromass G1540N/GCT Premier and a Thermo Fisher Scientific LTQ FT Ultra, respectively. Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques. Anhydrous tetrahydrofuran (Energy Chemical Co.Ltd.) were used without further purification. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher Scientific) in air.

■ **Reagents and Ligands:**

Copper chloride: purchased from Strem Chemicals Inc. and used as received.

Ligand (4a-4h): purchased from Tokyo Chemical Industry Co., Ltd. or Sino compound Co., Ltd. and used as received.

Lithium tert-butoxide: purchased from Tokyo Chemical Industry Co., Ltd. and used as received.

Bis(pinacolato)diboron: purchased from Dalian AllyChem Co.Ltd. and purified by recrystallization in *n*-pentane.

4A molecular sieve: purchased from Energy Chemical Co.Ltd. and dried over by oven.

Tetrahydrofuran and Dichloromethane: purchased from Adamas Reagent, Ltd. and used as received.

Sodium perborate tetrahydrate: purchased from Energy Chemical Co.Ltd. and used as received.

1-Substituted 1,3-dienes: prepared according to a previous reported procedure.[1,2]

2-Substituted 1,3-dienes: prepared according to a previous reported procedure.[3]

1,2-Disubstituted 1,3-dienes: prepared according to a previous reported procedure.[4]

1,3-Disubstituted 1,3-dienes: prepared according to a previous reported procedure.[5]

1,1-Disubstituted 1,3-dienes: prepared with the wittig reaction between acetopheno ne and allyl phosphorus ylide.

NCTS: prepared according to a previous reported procedure.[6]

Diisobutylaluminium hydride: purchased from Adamas Reagent, Ltd. and used as received.

Nickel(II) chloride hexahydrate: purchased from Tokyo Chemical Industry Co., Ltd. and used as received.

Sodium borohydride: purchased from Energy Chemical Co.Ltd. and used as received.

Di-tert-butyl decarbonate: purchased from Energy Chemical Co.Ltd. and used as received.

Methanol: purchased from Adamas Reagent, Ltd. and used as received.

Furan: purchased from Tokyo Chemical Industry Co., Ltd. and distilled by CaH_2.

N-Bromosuccinimide: purchased from Tokyo Chemical Industry Co., Ltd. and purified by recrystallization in water.

Vinylmagnesium bromide: purchased from Energy Chemical Co.Ltd. and used as received.

■ General Experimental Procedure for Cu-Catalyzed Regioselective Borylcyanation of 1,3-dienes.

In a N_2-filled glove-box, an oven-dried vial (8 mL, 61 × 16.6 mm) with a magnetic stir bar was charged with phosphine ligand **4h** (5.8 mg, 0.01 mmol, 5 mol %), CuCl (1.0 mg, 0.01 mmol, 5 mol%), LiO*t*-Bu (24.0 mg, 0.30 mmol, 1.5 equiv) and tetrahydrofuran (thf, 2 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (76.2 mg, 0.30 mmol, 1.5 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 20 min under an atmosphere of N_2. Diene **1a** (26.0 mg, 0.20 mmol, 1.0 equiv) and **2** (81.7 mg, 0.30 mmol, 1.5 equiv) were added. The resulting solution was allowed to stir at 22 °C for 14 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et_2O (3 × 2 mL). The filtrate was concentrated in vacuo to provide yellow oil. The crude was dissolved in tetrahydrofuran (thf, 1.0 mL), $NaBO_3$•$4H_2O$ (123.1 mg, 0.80 mmol, 4.0 equiv) and H_2O (1 mL) were added. The resulting mixture was allowed to stir at 22 °C for 3 h. The aqueous layer was washed with Et_2O (3 × 2 mL). The combined organic layers were concentrated *in vacuo* to provide colorless oil, which was purified by silica gel chromatography (dichloromethane : diethyl ether = 30:1) to afford **3a** (26.0 mg, 75% yield) as colorless oil.

■ Characterization of product.

(*E*)-2-(Hydroxymethyl)-4-phenylbut-3-enenitrile (3a). IR (neat): 3440 (br), 2921 (w), 2844 (w), 2249 (w), 1645 (w), 1490 (w), 1450 (w), 1398 (w), 1369 (w), 1288 (w), 1182 (w), 1048 (s), 968 (s), 858 (w), 749 (s), 693 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40-7.28 (m, 5H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.06 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.88 (d, *J* = 5.6 Hz, 2H), 3.66-3.61 (m, 1H), 2.67 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 135.4, 135.3, 128.7, 128.5, 126.6, 119.0, 118.8, 63.3, 38.0; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{11}H_{12}ON$:174.0913 m/z, found: 174.0914 m/z.

(*E*)-4-(4-Fluorophenyl)-2-(hydroxymethyl)but-3-enenitrile (3b). IR (neat): 3422 (br), 2945 (w), 2886 (w), 2247 (w), 1600 (m), 1507 (s), 1467 (w), 1413 (w), 1299 (w), 1226 (s), 1159 (m), 1056 (s), 966 (s), 852 (m), 812 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37-7.34 (m, 2H), 7.05-7.00 (m, 2H), 6.76 (d, *J* = 16.0 Hz, 1H), 5.98 (dd, *J* = 16.0, 6.4 Hz, 1H), 3.89-3.87 (m, 2H), 3.66-3.61 (m, 1H), 2.57 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.7 (d, *J* = 247.0 Hz), 134.2, 131.5 (d, *J* = 3.3 Hz), 128.2 (d, *J* = 8.1 Hz), 118.8 (d, *J* = 2.3 Hz), 118.7, 115.7 (d, *J* = 21.7 Hz), 63.3, 38.0; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -112.8; **HRMS (ESI$^+$) [M-H]$^+$:** Calcd for $C_{11}H_9ONF$:190.0674 m/z, found: 190.0675 m/z.

(*E*)-4-(4-(Dimethylamino)phenyl)-2-(hydroxymethyl)but-3-enenitrile (3c). IR (neat): 3391 (br), 2918 (w), 2803 (w), 2240 (w), 1646 (w), 1609 (s), 1519 (s), 1477 (w), 1350 (s), 1223 (w), 1164 (w), 1055 (m), 968 (w), 812 (s), 749 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.70-6.66 (m, 3H), 5.80 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.83 (d, *J* = 6.0 Hz, 2H), 3.60-3.56 (m, 1H), 2.97 (s, 6H); **^{13}C NMR (100**

MHz, $CDCl_3$): δ 150.6, 135.4, 127.7, 123.5, 119.2, 114.0, 112.2, 63.6, 40.3, 38.1; **HRMS (ESI^+) $[M+H]^+$:** Calcd for $C_{13}H_{17}ON_2$: 217.1335 m/z, found: 217.1337 m/z.

(*E*)-2-(Hydroxymethyl)-4-(4-methoxyphenyl)but-3-enenitrile (3d). IR (neat): 3243 (br), 2917 (w), 2838 (w), 2243 (w), 1602 (s), 1508 (s), 1423 (m), 1247 (s), 1175 (s), 1058 (s), 1028 (s), 970 (s), 848 (m), 807 (s), 747 (w) cm^{-1}; **^1H NMR (400 MHz, $CDCl_3$):** δ 7.32 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 16.0 Hz, 1H), 5.90 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.85 (d, *J* = 6.0 Hz, 2H), 3.81 (s, 3H), 3.63-3.58 (m, 1H), 2.61 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.8, 134.8, 128.1, 127.9, 119.0, 116.7, 114.1, 63.4, 55.3, 38.0; **HRMS (ESI^+) $[M+H]^+$:** Calcd for $C_{12}H_{14}O_2N$: 204.1019 m/z, found: 204.1021 m/z.

(*E*)-2-(Hydroxymethyl)-4-(2-methoxyphenyl)but-3-enenitrile (3e). IR (neat): 3421 (br), 2940 (w), 2885 (w), 2837 (w), 2245 (w), 1596 (w), 1488 (m), 1461 (m), 1436 (w), 1242 (s), 1052 (s), 1023 (s), 970 (s), 750 (s), 694 (w) cm^{-1}; **^1H NMR (400 MHz, $CDCl_3$):** δ 7.38 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29-7.24 (m, 1H), 7.07 (d, *J* = 16.0 Hz, 1H), 6.95-6.91 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.11 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.88-3.85 (m, 5H), 3.65-3.60 (m, 1H), 2.55 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.9, 130.8, 129.6, 127.5, 124.3, 120.6, 119.8, 119.0, 110.9, 63.4, 55.4, 38.5; **HRMS (ESI^+) $[M+H]^+$:** Calcd for $C_{12}H_{14}O_2N$: 204.1019 m/z, found: 204.1021 m/z.

(*E*)-2-(Hydroxymethyl)-4-(o-tolyl)but-3-enenitrile (3f). IR (neat): 3420 (br), 3032 (w), 2922 (w), 2246 (w), 1603 (w), 1458 (w), 1336 (w), 1261 (w), 1171 (w), 1056 (s), 965 (s), 881 (w), 775 (s), 692 (s), 646 (w) cm^{-1}; **^1H NMR (400 MHz, $CDCl_3$):** δ 7.26-7.18 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.04 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.90-3.87 (m, 2H), 3.66-3.61 (m, 1H), 2.39-2.32 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.3, 135.5, 135.2, 129.3, 128.6, 127.3, 123.7, 118.9, 118.8, 63.3, 38.1, 21.3; **HRMS (ESI^+) $[M-H]^+$:** Calcd for $C_{12}H_{12}ON$: 186.0924 m/z, found:186.0929 m/z.

(*E*)-2-(Hydroxymethyl)-4-(3-methoxyphenyl)but-3-enenitrile (3g). IR (neat): 3421 (br), 2942 (w), 2886 (w), 2836 (w), 2246 (w), 1599 (m), 1489 (m), 1460 (m), 1431 (m), 1287 (s), 1193 (s), 1044 (s), 965 (s), 775 (s), 687 (s) cm^{-1}; **^1H NMR (400 MHz, $CDCl_3$):** δ 7.28-7.24 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.93-6.90 (m, 1H), 6.85 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.05 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.90-3.87 (m, 2H), 3.82 (s, 3H), 3.66-3.61 (m, 1H), 2.46-2.43 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.8, 136.7, 135.3, 129.7, 119.4, 119.2, 118.7, 114.2, 111.9, 63.3, 55.3, 38.0; **HRMS (ESI^+) $[M-H]^+$:** Calcd for $C_{12}H_{12}O_2N$: 202.0874 m/z, found: 202.0878 m/z.

(*E*)-2-(Hydroxymethyl)-4-(naphthalen-2-yl)but-3-enenitrile (3h). IR (neat): 3433 (br), 3053 (w), 2920 (w), 2882 (w), 2249 (w), 1594 (w), 1464 (w), 1175 (m), 1052 (s), 966 (s), 898 (w), 866 (w), 814 (s), 750 (s), 627 (w) cm^{-1}; **^1H NMR (400 MHz, $CDCl_3$):** δ 7.82-7.79 (m, 3H), 7.76 (s, 1H), 7.56 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.51-7.46 (m, 2H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 6.4 Hz, 1H), 3.92 (d, *J* = 5.6 Hz, 2H), 3.71-3.66 (m, 1H), 2.50 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 135.4, 133.3, 133.2,

132.7, 128.4, 128.1, 127.7, 127.2, 126.5, 126.4, 123.1, 119.3, 118.8, 63.3, 38.1; **HRMS (ESI$^+$) [M-H]$^+$:** Calcd for $C_{15}H_{12}ON$: 222.0924 m/z, found: 222.0923 m/z.

(*E*)-4-(Furan-3-yl)-2-(hydroxymethyl)but-3-enenitrile (3i). IR (neat): 3458 (br), 2921 (w), 2851 (w), 2245 (w), 1737 (w), 1636 (w), 1464 (w), 1424 (w), 1347 (w), 1179 (w), 1104 (w), 1016 (w), 968 (w), 769 (w), 704 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (s, 1H), 7.41-7.36 (m, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.53-6.49 (m, 1H), 5.78 (dd, *J* = 16.0, 6.4 Hz, 1H), 3.86 (d, *J* = 5.6 Hz, 2H), 3.62-3.57 (m, 1H), 2.23 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.9, 141.4, 125.3, 122.6, 118.8, 118.5, 107.2, 63.3, 37.9; **HRMS (ESI$^+$) [M-H]$^+$:** Calcd for $C_9H_8O_2N$: 162.0561 m/z, found: 162.0562 m/z.

(*E*)-2-(Hydroxymethyl)-4-(thiophen-3-yl)but-3-enenitrile (3j). IR (neat): 3409 (br), 3099 (w), 2940 (w), 2884 (w), 2245 (w), 1651 (w), 1465 (w), 1413 (w), 1244 (w), 1159 (w), 1054 (s), 962 (s), 864 (w), 769 (s), 693 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30-7.28 (m, 1H), 7.23 (d, *J* = 1.6 Hz, 1H), 7.19 (d, *J* = 4.8 Hz, 1H), 6.79 (d, *J* = 15.6 Hz, 1H), 5.90 (dd, *J* = 15.6, 6.4 Hz, 1H), 3.88-3.80 (m, 2H), 3.62-3.57 (m, 1H), 2.95 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 137.9, 129.3, 126.5, 124.6, 123.7, 118.9, 118.8, 63.1, 37.9; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_9H_{10}ONS$: 180.0478 m/z, found: 180.0479 m/z.

(*E*)-Tert-butyl 3-(3-cyano-4-hydroxybut-1-en-1-yl)-1H-pyrrole-1-carboxylate (3k). IR (neat): 3408 (br), 2979 (w), 2247 (w), 1714 (m), 1480 (w), 1392 (w), 1366 (w), 1302 (w), 1253 (w), 1149 (m), 1063 (w), 972 (w), 865 (w), 749 (s), 665 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.21-7.18 (m, 2H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.32 (s, 1H), 5.76 (dd, *J* = 16.0, 6.4 Hz, 1H), 3.82 (d, *J* = 5.6 Hz, 2H), 3.60-3.55 (m, 1H), 2.88 (s, 1H), 1.58 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 148.5, 127.6, 123.9, 121.2, 119.0, 118.9, 117.3, 109.0, 84.1, 63.3, 38.0, 27.9; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{14}H_{19}O_3N_2$: 263.1390 m/z, found: 263.1393 m/z.

(*E*)-4-Cyclohexyl-2-(hydroxymethyl)but-3-enenitrile (3l). IR (neat): 3413 (br), 2923 (s), 2850 (m), 2246 (w), 1660 (w), 1447 (m), 1407 (w), 1374 (w), 1309 (w) 1259 (w), 1057 (s), 969 (s), 889 (w), 841 (w), 695 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.86 (dd, *J* = 15.6, 6.8 Hz, 1H), 5.27 (dd, *J* = 15.6, 6.4 Hz, 1H), 3.78-3.71 (m, 2H), 3.43-3.38 (m, 1H), 2.35 (s, 1H), 2.04-1.95 (m, 1H), 1.78-1.63 (m, 5H), 1.31-1.02 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.1, 119.3, 117.2, 63.4, 40.4, 37.9, 32.4, 32.4, 25.9, 25.8; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{11}H_{18}ON$: 180.1383 m/z, found:180.1384 m/z.

2-(Hydroxymethyl)-3-methylbut-3-enenitrile (5a). IR (neat): 3419 (br), 3089 (w), 2978 (w), 2946 (w), 2890 (w), 2247 (w), 1651 (w), 1449 (w), 1379 (w), 1068 (s), 1045 (s), 907 (s), 710 (w), 575 (w), 425 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.15 (s, 1H), 5.11 (s, 1H), 3.84 (d, *J* = 6.0 Hz, 2H), 3.40 (t, *J* = 6.0 Hz, 1H), 2.44 (s, 1H), 1.85 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 135.9, 118.9, 116.8, 61.8, 42.3, 20.4; **HRMS (EI$^+$) [M]$^+$:** Calcd for: C_6H_9ON: 111.0682 m/z, found: 111.0680 m/z.

2-(Hydroxymethyl)-7-methyl-3-methyleneoct-6-enenitrile (5b). IR (neat): 3424 (br), 3088 (w), 2966 (w), 2915 (w), 2857 (w), 2246 (w), 1648 (w), 1440 (w), 1377 (w), 1185 (w), 1066 (s), 1045 (s) 907 (s), 827 (m), 751 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.24 (s, 1H), 5.13 (s, 1H), 5.07 (t, *J* = 6.0 Hz, 1H), 3.86-3.78 (m, 2H), 3.40 (t, *J* = 6.0 Hz, 1H), 2.43 (s, 1H), 2.21-2.02 (m, 4H), 1.68 (s, 3H), 1.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.8, 132.9, 122.7, 119.2, 115.5, 62.2, 41.4, 33.9, 26.1, 25.6, 17.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{11}H_{18}ON$: 180.1383 m/z, found:180.1383 m/z.

5-(3,3-Dimethyloxiran-2-yl)-2-(hydroxymethyl)-3-methylenepentanenitrile (5c). IR (neat): 3422 (br), 3091 (w), 2964 (w), 2928 (w), 2884 (w), 2245 (w), 1648 (w), 1454 (w), 1380 (m), 1251 (w), 1114 (m), 1069 (s), 910 (s), 867 (m), 820 (w), 798 (w), 733 (w), 675 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.27-5.25 (m, 1H), 5.16 (s, 1H), 3.89-3.77 (m, 2H), 3.45-3.38 (m, 1H), 3.11 (s, 1H), 2.77-2.73 (m, 1H), 2.39-2.20 (m, 2H), 1.87-1.76 (m, 1H), 1.69-1.59 (m, 1H), 1.30 (s, 3H), 1.27 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.4, 139.2, 119.1, 119.0, 116.2, 115.9, 63.7, 63.6, 62.3, 62.2, 58.9, 58.8, 41.5, 41.1, 31.1, 30.9, 26.9, 26.8, 24.7, 18.7; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{11}H_{21}O_2N_2$: 213.1598 m/z, found: 213.1595 m/z.

2-(Hydroxymethyl)-3-methylene-5-(2,2,5,5-tetramethyl-1,3-dioxolan-4-yl)pentanenitrile (5d). IR (neat): 3447 (br), 2980 (w), 2934 (w), 2875 (w), 2247 (w), 1649 (w), 1459 (w), 1372 (m), 1216 (m), 1111 (m), 1065 (m), 1001 (s), 909 (s), 855 (m), 823 (w), 730 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.28-5.27 (m, 1H), 5.15 (s, 1H), 3.85 (d, *J* = 6.0 Hz, 2H), 3.69-3.67 (m, 1H), 3.44-3.40 (m, 1H), 2.79 (s, 1H), 2.44-2.11 (m, 2H), 1.74-1.52 (m, 2H), 1.40 (s, 3H), 1.31 (s, 3H), 1.24 (s, 3H), 1.09 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.6, 139.5, 119.1, 115.8, 115.7, 106.9, 82.5, 82.4, 80.2, 80.1, 62.2, 41.6, 41.4, 31.4, 31.3, 28.4, 27.2, 27.1, 26.8, 25.9, 25.8, 24.8, 22.9; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{14}H_{24}O_3N$: 254.1751 m/z, found: 254.1750 m/z.

2-(Hydroxymethyl)-6-((4-methoxybenzyl)oxy)-3-methylenehexanenitrile (5e). IR (neat): 3426 (br), 3001 (w), 2936 (w), 2860 (w), 2245 (w), 1611 (w), 1512 (m), 1362 (w), 1300 (w), 1245 (s), 1174 (m), 1031 (s), 909 (s), 818 (m), 729 (s), 646 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.23 (s, 1H), 5.11 (s, 1H), 4.42 (s, 2H), 3.80 (s, 3H), 3.80-3.73 (m, 2H), 3.48 (t, *J* = 6.0 Hz, 2H), 3.36 (t, *J* = 6.0 Hz, 1H), 2.79 (s, 1H), 2.27-2.08 (m, 2H), 1.82-1.74 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.2, 139.7, 130.1, 129.4, 119.2, 115.4, 113.7, 72.6, 68.9, 62.1, 55.2, 41.3, 30.6, 27.5; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{16}H_{25}O_3N_2$: 293.1860 m/z, found: 293.1865 m/z.

6-((Tert-butyldimethylsilyl)oxy)-2-(hydroxymethyl)-3-methylenehexanenitrile (5f). IR (neat): 3429 (br), 2952 (w), 2929 (w), 2885 (w), 2856 (w), 2246 (w), 1649 (w), 1502 (w), 1253 (m), 1100 (m), 909 (w), 833 (s), 774 (s), 732 (w), 662 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.26 (s, 1H), 5.13 (s, 1H), 3.88-3.80 (m, 2H), 3.64 (t, *J* = 6.0 Hz, 2H), 3.42 (t, *J* = 6.0 Hz, 1H), 2.52 (s, 1H), 2.27-2.10 (m, 2H), 1.74-1.67 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.8, 119.2, 115.5,

62.2, 62.0, 41.4, 30.4, 30.1, 25.9, 18.3, -5.4; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{14}H_{28}O_2NSi$: 270.1884 m/z, found: 270.1877 m/z.

Tert-butyl 5-cyano-6-hydroxy-4-methylenehexanoate (5g). IR (neat): 3467 (br), 2979 (w), 2933 (w), 2250 (w), 1718 (m), 1650 (w), 1391 (w), 1253 (w), 1147 (s), 1067 (w), 980 (w), 910 (s), 844 (w), 729 (s), 647 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.26 (s, 1H), 5.08 (s, 1H), 3.88 (d, *J* = 5.6 Hz, 2H), 3.40 (t, *J* = 6.0 Hz, 1H), 3.22 (s, 1H), 2.50 (t, *J* = 6.8 Hz, 2H), 2.44-2.29 (m, 2H), 1.42 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 172.4, 139.1, 118.8, 115.4, 81.3, 62.2, 41.6, 32.8, 28.0, 27.8; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{12}H_{23}O_3N_2$: 243.1703 m/z, found: 243.1694 m/z.

2-(Hydroxymethyl)-3-phenylbut-3-enenitrile (5h). (3.5:1 mixture of two regioisomers). **IR (neat):** 3427 (br), 2937 (w), 2886 (w), 2248 (w), 1630 (w), 1493 (w), 1410 (w), 1187 (w), 1064 (s), 1029 (s), 915 (m), 772 (m), 700 (s), 621 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48-7.31 (m, 5H), 6.08-5.45 (m, 2H), 4.07-3.68 (m, 3H), 2.83-2.66 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.8, 137.8, 135.6, 133.9, 129.1, 128.8, 128.6, 128.5, 126.5, 126.3, 119.9, 119.5, 119.2, 117.8, 68.2, 62.5, 53.2, 40.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{11}H_{12}ON$: 174.0913 m/z, found: 174.0913 m/z.

(*E*)-2-(Hydroxymethyl)-3-methyl-4-phenylbut-3-enenitrile (6a). IR (neat): 3417 (br), 3027 (w), 2945 (w), 2886 (w), 2246 (w), 1490 (w), 1443 (m), 1381 (w), 1041 (s), 921 (w), 867 (w), 748 (s), 699 (s), 571 (w), 513 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39-7.32 (m, 2H), 7.29-7.23 (m, 3H), 6.64 (s, 1H), 3.95-3.88 (m, 2H), 3.53 (t, *J* = 6.4 Hz, 1H), 2.70 (s, 1H), 1.97 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.2, 130.9, 128.8, 128.5, 128.2, 127.2, 119.1, 62.2, 44.5, 16.2; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{12}H_{14}ON$: 188.1070 m/z, found: 188.1072 m/z.

(*E*)-2-(Hydroxymethyl)-3-methyl-4-(o-tolyl)but-3-enenitrile (6b). IR (neat): 3417 (br), 3024 (w), 2920 (w), 2887 (w), 2244 (w), 1601 (w), 1443 (w), 1244 (w), 1168 (w), 1043 (s), 913 (w), 785 (s), 742 (m), 697 (s), 514 (w), 441 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.28-7.22 (m, 1H), 7.11-7.05 (m, 3H), 6.61 (s, 1H), 3.96-3.88 (m, 2H), 3.53 (t, *J* = 6.4 Hz, 1H), 2.54 (s, 1H), 2.36 (s, 3H), 1.98 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 137.9, 136.1, 131.1, 129.6, 128.3, 128.2, 128.0, 125.9, 119.0, 62.3, 44.5, 21.4, 16.2; **HRMS (EI$^+$) [M]$^+$:** Calcd for: $C_{13}H_{15}ON$: 201.1154 m/z, found: 201.1150 m/z.

(*E*)-4-(2-Bromophenyl)-2-(hydroxymethyl)-3-methylbut-3-enenitrile (6c). IR (neat): 3424 (br), 2938 (w), 2887 (w), 2246 (w), 1653 (w), 1463 (m), 1431 (m), 1386 (w), 1268 (w), 1024 (s), 850 (w), 749 (s), 666 (w), 524 (w), 444 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.33-7.27 (m, 1H), 7.22 (d, *J* = 6.4 Hz, 1H), 7.18-7.12 (m, 1H), 6.61 (s, 1H), 4.00-3.90 (m, 2H), 3.58 (t, *J* = 6.4 Hz, 1H), 2.55 (s, 1H), 1.83 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.5, 132.5, 130.7, 130.5, 130.4, 129.0, 127.1, 123.8, 118.7, 62.1, 43.5, 15.9; **HRMS (EI$^+$) [M]$^+$:** Calcd for: $C_{12}H_{12}ONBr$: 265.0102 m/z, found: 265.0100 m/z.

(*E*)-4-(4-Bromophenyl)-2-(hydroxymethyl)-3-methylbut-3-enenitrile (6d). IR (neat): 3417 (br), 2941 (w), 2885 (w), 2245 (w), 1650 (w), 1586 (w), 1482 (m), 1398 (w), 1308 (w), 1066 (s), 1007 (s), 872 (m), 811 (m), 662 (w), 509 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.56 (s, 1H), 3.92 (d, *J* = 6.0 Hz, 2H), 3.52 (t, *J* = 6.4 Hz, 1H), 2.57 (s, 1H), 1.94 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 135.0, 131.4, 130.5, 129.8, 129.5, 121.2, 118.9, 62.12, 44.4, 16.3; **HRMS (EI$^+$) [M]$^+$:** Calcd for: $C_{12}H_{12}ONBr$: 265.0102 m/z, found: 265.0090 m/z.

(*E*)-4-(4-Fluorophenyl)-2-(hydroxymethyl)-3-methylbut-3-enenitrile (6e). IR (neat): 3419 (br), 2946 (w), 2888 (w), 2246 (w), 1599 (m), 1506 (s), 1443 (w), 1404 (w), 1224 (s), 1159 (m), 1044 (s), 873 (m), 828 (s), 669 (w), 522 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.24-7.18 (m, 2H), 7.07-7.00 (m, 2H), 6.58 (s, 1H), 3.94-3.87 (m, 2H), 3.52 (t, *J* = 6.4 Hz, 1H), 2.90 (s, 1H), 1.93 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.7 (d, *J* = 246.1 Hz), 132.2 (d, *J* = 3.4 Hz), 130.5 (d, *J* = 8.0 Hz), 129.8 (d, *J* = 2.3 Hz), 128.6 (d, *J* = 1.5 Hz), 119.1, 115.2 (d, *J* = 21.5 Hz), 62.2, 44.4, 16.1; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -114.3; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{12}H_{13}ONF$: 206.0976 m/z, found: 206.0976 m/z.

(*E*)-2-(Hydroxymethyl)-3-methyl-4-(3-(trifluoromethyl)phenyl)but-3-enenitrile (6f). IR (neat): 3431 (br), 2941 (w), 2248 (w), 1442 (w), 1326 (s), 1208 (w), 1164 (m), 1121 (s), 1069 (s), 909 (m), 802 (m), 701 (m), 657 (w), 576 (w), 519 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55-7.40 (m, 4H), 6.67 (s, 1H), 3.98-3.91 (m, 2H), 3.56 (t, *J* = 6.4 Hz, 1H), 2.79 (s, 1H), 1.96 (d, *J* = 0.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.9, 132.1, 130.7, 130.6 (q, *J* = 32.0 Hz), 129.4, 128.8, 125.5 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 271.0 Hz), 123.9 (q, *J* = 3.8 Hz), 118.9, 62.2, 44.4, 16.2; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.7; **HRMS (ESI$^+$) [M-H]$^+$:** Calcd for $C_{13}H_{11}ONF_3$: 254.0798 m/z, found: 254.0797 m/z.

(*E*)-4-(3-Chlorophenyl)-2-(hydroxymethyl)-3-methylbut-3-enenitrile (6g). IR (neat): 3418 (br), 2939 (w), 2888 (w), 2246 (w), 1654 (w), 1592 (w), 1564 (m), 1471 (m), 1417 (m), 1214 (w), 1043 (s), 891 (m), 781 (s), 683 (s), 442 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.32-7.22 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.59 (s, 1H), 3.98-3.89 (m, 2H), 3.53 (t, *J* = 6.4 Hz, 1H), 2.44 (s, 1H), 1.96 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.0, 134.1, 130.1, 129.6, 129.5, 128.8, 127.3, 127.0, 118.8, 62.2, 44.3, 16.3; **HRMS (EI$^+$) [M]$^+$:** Calcd for: $C_{12}H_{12}ONCl$: 221.0607 m/z, found: 221.0611 m/z.

(*E*)-Methyl 3-(3-cyano-4-hydroxy-2-methylbut-1-en-1-yl)benzoate (6h). IR (neat): 3466 (br), 2950 (w), 2887 (w), 2245 (w), 1713 (s), 1438 (m), 1287 (s), 1208 (s), 1108 (m), 1044 (m), 920 (w), 859 (w), 750 (s), 707 (w), 535 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.94-7.88 (m, 2H), 7.44-7.39 (m, 2H), 6.65 (s, 1H), 3.97-3.91 (m, 2H), 3.91 (s, 3H), 3.55 (t, *J* = 6.4 Hz, 1H), 2.90 (t, *J* = 5.6 Hz, 1H), 1.96 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.0, 136.5, 133.3, 130.1, 130.0, 129.9, 129.8, 128.4, 128.3, 118.9, 62.2, 52.2, 44.3, 16.2; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{14}H_{19}O_3N_2$: 263.1390 m/z, found: 263.1391 m/z.

(*E*)-2-(Hydroxymethyl)-4-(3-methoxyphenyl)-3-methylbut-3-enenitrile (6i). IR (neat): 3449 (br), 2942 (w), 2839 (w), 2245 (w), 1583 (m), 1483 (m), 1376 (w), 1263 (m), 1160 (m), 1040 (s), 882 (m), 782 (m), 693 (m), 559 (w), 513 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30-7.24 (m, 1H), 6.87-6.78 (m, 3H), 6.62 (s, 1H), 3.96-3.89 (m, 2H), 3.81 (s, 3H), 3.53 (t, *J* = 6.4 Hz, 1H), 2.40 (s, 1H), 1.98 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.4, 137.5, 130.8, 129.3, 128.8, 121.3, 119.0, 114.5, 112.7, 62.2, 55.2, 44.4, 16.3; **HRMS (EI$^+$) [M]$^+$:** Calcd for: $C_{13}H_{15}O_2N$: 217.1103 m/z, found: 217.1098 m/z.

(*E*)-2-(Hydroxymethyl)-3-methyl-4-(thiophen-3-yl)but-3-enenitrile (6j). IR (neat): 3446 (br), 3095 (w), 2943 (w), 2890 (w), 2245 (w), 1448 (w), 1391 (m), 1342 (w), 1183 (m), 1062 (s), 1020 (s), 878 (m), 771 (s), 629 (m), 532 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.31 (dd, *J* = 5.2, 3.2 Hz, 1H), 7.21 (d, *J* = 1.6 Hz, 1H), 7.10 (d, *J* = 5.2 Hz, 1H), 6.58 (s, 1H), 3.92-3.85 (m, 2H), 3.51 (t, *J* = 6.4 Hz, 1H), 2.60 (s, 1H), 2.02 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 137.2, 128.3, 127.4, 125.4, 125.1, 123.9, 119.0, 62.2, 44.5, 16.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{10}H_{12}ONS$: 194.0634 m/z, found: 194.0635 m/z.

(*E*)-4-(Furan-2-yl)-2-(hydroxymethyl)-3-methylbut-3-enenitrile (6k). IR (neat): 3443 (br), 2923 (s), 2855 (m), 2216 (w), 1712 (m), 1659 (m), 1442 (m), 1389 (m), 1255 (w), 1059 (s), 1015 (s), 801 (w), 747 (w), 597 (w), 567 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 (d, *J* = 1.6 Hz, 1H), 6.42 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.40 (s, 1H), 6.34 (d, *J* = 3.2 Hz, 1H), 3.92-3.85 (m, 2H), 3.49 (t, *J* = 6.4 Hz, 1H), 2.43 (s, 1H), 2.12 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.5, 142.1, 126.2, 119.2, 118.8, 111.3, 110.6, 62.2, 44.6, 16.8; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{10}H_{12}O_2N$: 178.0863 m/z, found: 178.0864 m/z.

(*E*)-2-(Hydroxymethyl)-3-methyl-4-(thiophen-2-yl)but-3-enenitrile (6l). IR (neat): 3445 (br), 3101 (w), 2943 (w), 2890 (w), 2242 (w), 1638 (w), 1399 (m), 1182 (m), 1059 (s), 1014 (s), 881 (m), 848 (m), 817 (m), 703 (s), 563 (s), 525 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.31 (d, *J* = 4.8 Hz, 1H), 7.06-7.02 (m, 2H), 6.74 (s, 1H), 3.90-3.83 (m, 2H), 3.51 (t, *J* = 6.4 Hz, 1H), 2.88 (t, *J* = 6.0 Hz, 1H), 2.08 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.0, 128.4, 126.9, 126.0, 126.0, 123.9, 118.9, 62.1, 44.7, 16.9; **HRMS (ESI$^+$) [M-H]$^+$:** Calcd for $C_{10}H_{10}ONS$: 192.0489 m/z, found: 192.0488 m/z.

(*E*)-Tert-butyl2-(3-cyano-4-hydroxy-2-methylbut-1-en-1-yl)-1H-pyrrole-1-carboxylate (6m). IR (neat): 3359 (br), 2925 (m), 2854 (w), 2248 (w), 1731 (m), 1665 (m), 1462 (w), 1369 (w), 1325 (m), 1153 (s), 1064 (w), 1023 (w), 842 (w), 768 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.23-7.20 (m, 1H), 6.80 (s, 1H), 6.21-6.14 (m, 2H), 3.94-3.83 (m, 2H), 3.51 (t, *J* = 6.4 Hz, 1H), 3.06 (s, 1H), 1.95 (s, 3H), 1.57 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.2, 129.9, 127.6, 122.6, 121.5, 118.7, 114.7, 110.7, 84.2, 61.9, 43.5, 27.9, 16.3; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{15}H_{21}O_3N_2$: 277.1547 m/z, found: 277.1549 m/z.

(*E*)-2-Methyl-4-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2 yl)methyl)but-3-enenitrile (7a). IR (neat): 2978 (w), 2933 (w), 2236 (w), 1450 (w),

1362 (s), 1333 (s), 1253 (w), 1215 (w), 1139 (s), 1074 (w), 966 (s), 878 (w), 845 (s), 748 (s), 693 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42-7.29 (m, 4H), 7.29-7.23 (m, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.16 (d, *J* = 16.0 Hz, 1H), 1.62 (s, 3H), 1.42 (s, 2H), 1.25 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.0, 131.0, 129.3, 128.6, 127.9, 126.5, 123.6, 83.7, 36.2, 27.5, 24.8, 24.7; **HRMS (ESI$^+$) $[M+NH_4]^+$:** Calcd for $C_{18}H_{28}O_2N_2B$: 314.2275 m/z, found: 314.2274 m/z.

(*E*)-2-(Hydroxymethyl)-4-(4-methoxyphenyl)-2-methylbut-3-enenitrile (7b). IR (neat): 3442 (br), 2936 (w), 2877 (w), 2837 (w), 2239 (w), 1606 (s), 1510 (s), 1420 (m), 1246 (s), 1175 (s), 1053 (s), 1030 (s), 966 (s), 849 (w), 809 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 16.0 Hz, 1H), 5.81 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 3.69 (d, *J* = 4.0 Hz, 2H), 2.44 (s, 1H), 1.52 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.7, 132.4, 128.1, 127.9, 123.5, 121.8, 114.1, 68.5, 55.3, 42.8, 21.9; **HRMS (ESI$^+$) $[M+H]^+$:** Calcd for $C_{13}H_{16}O_2N$: 218.1176 m/z, found: 218.1177 m/z.

(*E*)-2-(Hydroxymethyl)-4-(3-methoxyphenyl)-2-methylbut-3-enenitrile (7c). IR (neat): 3448 (br), 2938 (w), 2877 (w), 2837 (w), 2241 (w), 1599 (m), 1581 (m), 1489 (m), 1458 (m), 1265 (m), 1159 (m), 1047 (s), 966 (m), 932 (w), 777 (m), 688 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.27-7.22 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.93-6.91 (m, 1H), 6.83 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.82 (d, *J* = 16.0 Hz, 1H), 5.96 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 3.70 (d, *J* = 4.0 Hz, 2H), 2.68 (s, 1H), 1.52 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.8, 136.8, 132.8, 129.7, 126.2, 121.6, 119.2, 114.1, 111.9, 68.3, 55.2, 42.8, 21.8; **HRMS (ESI$^+$) $[M+H]^+$:** Calcd for $C_{13}H_{16}O_2N$: 218.1176 m/z, found: 218.1177 m/z.

(*E*)-4-(3-Fluorophenyl)-2-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (7d). IR (neat): 2979 (w), 2931 (w), 2236 (w), 1611 (w), 1583 (m), 1446 (w), 1362 (s), 1334 (s), 1267 (m), 1217 (m), 1139 (s), 965 (s), 875 (m), 845 (s), 778 (s), 683 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33-7.25 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 10.0 Hz, 1H), 6.99-6.92 (m, 1H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.17 (d, *J* = 16.0 Hz, 1H), 1.61 (s, 3H), 1.41 (s, 2H), 1.25 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.0 (d, *J* = 244.3 Hz), 138.4 (d, *J* = 7.7 Hz), 132.4, 130.1 (d, *J* = 8.3 Hz), 128.4 (d, *J* = 2.7 Hz), 123.4, 122.5 (d, *J* = 2.7 Hz), 114.7 (d, *J* = 21.3 Hz), 112.9 (d, *J* = 21.8 Hz), 83.8, 36.3, 27.4, 24.8, 24.7; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -113.3; **HRMS (ESI$^+$) $[M+NH_4]^+$:** Calcd for $C_{18}H_{27}O_2N_2BF$: 332.2180 m/z, found: 332.2181 m/z.

(*E*)-4-(3-Chlorophenyl)-2-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (7e). IR (neat): 2978 (w), 2933 (w), 2236 (w), 1594 (w), 1565 (w), 1473 (w), 1362 (s), 1334 (s), 1213 (m), 1139 (s), 966 (s), 878 (m), 845 (s), 779 (s), 684 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36 (s, 1H), 7.27-7.20 (m, 3H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.17 (d, *J* = 16.0 Hz, 1H), 1.60 (s, 3H), 1.40 (s, 2H), 1.24 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 137.9, 134.5, 132.6, 129.8, 128.1, 127.8, 126.3,

124.9, 123.3, 83.8, 36.3, 27.4, 24.8, 24.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{18}H_{24}O_2NBCl$: 331.1619 m/z, found: 331.1615 m/z.

(*E*)-2-Methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(3-(trifluoromethyl)phenyl)but-3-enenitrile (7f). IR (neat): 2980 (w), 2935 (w), 2237 (w), 1446 (w), 1365 (m), 1332 (s), 1260 (w), 1204 (w), 1165 (m), 1127 (s), 968 (m), 876 (m), 846 (m), 797 (s), 698 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63 (s, 1H), 7.55-7.49 (m, 2H), 7.48-7.41 (m, 1H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 1.62 (s, 3H), 1.42 (s, 2H), 1.25 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.9, 133.1, 131.0 (q, *J* = 32.2 Hz), 129.9, 129.1, 128.1, 124.4 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 270.9 Hz), 123.3, 123.0 (q, *J* = 3.8 Hz), 83.8, 36.3, 27.4, 24.8, 24.7; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.9; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{19}H_{27}O_2N_2BF_3$: 382.2149 m/z, found: 382.2148 m/z.

(*E*)-Methyl 3-(3-cyano-4-hydroxy-3-methylbut-1-en-1-yl)benzoate (7g). IR (neat): 3474 (br), 2920 (w), 2874 (w), 2240 (w), 1700 (s), 1588 (w), 1432 (m), 1295 (s), 1205 (s), 1107 (s), 1083 (s), 968 (s), 808 (w), 746 (s), 647 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06 (s, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.42-7.36 (m, 1H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.07 (d, *J* = 16.0 Hz, 1H), 3.91 (s, 3H), 3.73 (d, *J* = 4.8 Hz, 2H), 2.85 (s, 1H), 1.53 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.8, 135.8, 131.8, 131.3, 130.5, 129.2, 128.8, 127.4, 127.3, 121.5, 68.3, 52.2, 42.9, 21.8; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{14}H_{16}O_3N$: 246.1125 m/z, found: 246.1127 m/z.

(*E*)-3-(3-Cyano-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)-N-methoxy-N-methylbenzamide (7h). IR (neat): 2977 (w), 2934 (w), 2235 (w), 1642 (m), 1601 (w), 1579 (w), 1362 (s), 1259 (w), 1218 (w), 1140 (s), 968 (m), 877 (w), 846 (m), 799 (s), 735 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.37-7.31 (m, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 3.53 (s, 3H), 3.34 (s, 3H), 1.59 (s, 3H), 1.38 (s, 2H), 1.22 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.5, 135.9, 134.4, 132.0, 128.6, 128.5, 128.3, 127.4, 126.1, 123.4, 83.7, 61.0, 36.2, 27.4, 24.7, 24.6; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{21}H_{30}O_4N_2B$: 384.2329 m/z, found: 384.2331 m/z.

(*E*)-4-(2-Fluorophenyl)-2-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (7i). IR (neat): 2979 (w), 2934 (w), 2206 (w), 1488 (w), 1455 (w), 1365 (s), 1337 (m), 1260 (w), 1226 (m), 1141 (s), 1096 (m), 969 (m), 846 (m), 799 (m), 757 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42-7.37 (m, 1H), 7.25-7.19 (m, 1H), 7.12-7.07 (m, 1H), 7.06-7.00 (m, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 1.62 (s, 3H), 1.41 (s, 2H), 1.24 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.3 (d, *J* = 248.9 Hz), 133.7 (d, *J* = 6.0 Hz), 129.2 (d, *J* = 8.4 Hz), 127.9 (d, *J* = 3.7 Hz), 124.1 (d, *J* = 3.6 Hz), 123.8 (d, *J* = 12.0 Hz), 123.4, 122.4 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 22.0 Hz), 83.7, 36.5, 27.3, 24.7, 24.6; **^{19}F NMR (376 MHz, $CDCl_3$):** δ-117.0; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{18}H_{27}O_2N_2BF$: 332.2180 m/z, found: 332.2181 m/z.

(*E*)-2-(Hydroxymethyl)-4-(2-methoxyphenyl)-2-methylbut-3-enenitrile (7j). IR (neat): 3433 (br), 2938 (w), 2878 (w), 2838 (w), 2241 (w), 1644 (w), 1489 (m), 1462 (m), 1438 (w), 1293 (w), 1244 (s), 1180 (w), 1051 (s), 1025 (m), 971 (m), 752 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29-7.23 (m, 1H), 7.14 (d, *J* = 16.0 Hz, 1H), 6.95-6.90 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.03 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H), 3.70 (d, *J* = 2.8 Hz, 2H), 2.66 (s, 1H), 1.53 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.9, 129.4, 128.1, 127.3, 126.5, 124.3, 121.8, 120.5, 110.8, 68.5, 55.3, 43.0, 21.8; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{13}H_{16}O_2N$: 218.1176 m/z, found: 218.1177 m/z.

(*E*)-2-Methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(o-tolyl)but-3-enenitrile (7k). IR (neat): 2965 (w), 2142 (w), 1459 (w), 1365 (w), 1336 (w), 1260 (m), 1218 (w), 1140 (w), 1091 (m), 969 (w), 846 (w), 798 (s), 751 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41-7.36 (m, 1H), 7.21-7.13 (m, 3H), 6.99 (d, *J* = 16.0 Hz, 1H), 6.03 (d, *J* = 16.0 Hz, 1H), 2.38 (s, 3H), 1.63 (s, 3H), 1.43 (s, 2H), 1.26 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 135.8, 135.2, 132.6, 130.3, 127.7, 127.3, 126.0, 125.8, 123.6, 83.7, 36.4, 27.6, 24.8, 24.7, 19.7; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{19}H_{30}O_2N_2B$: 328.2431 m/z, found: 328.2433 m/z.

(*E*)-2-Methyl-4-(naphthalen-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (7l). IR (neat): 2978 (w), 2926 (w), 2238 (w), 1465 (w), 1447 (w), 1364 (s), 1322 (s), 1213 (m), 1142 (s), 1101 (w), 1042 (w), 965 (s), 846 (m), 816 (s), 745 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84-7.78 (m, 3H), 7.76 (s, 1H), 7.57 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.51-7.43 (m, 2H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 1.66 (s, 3H), 1.47 (s, 2H), 1.26 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 133.5, 133.4, 133.0, 131.3, 129.5, 128.3, 128.0, 127.6, 126.8, 126.3, 126.0, 123.6, 123.4, 83.8, 36.4, 27.6, 24.8, 24.7; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{22}H_{30}O_2N_2B$: 364.2431 m/z, found: 364.2435 m/z.

(*E*)-5-Hydroxy-2-methyl-2-phenylpent-3-enenitrile (8a). IR (neat): 3410 (br), 2927 (w), 2857 (w), 2239 (w), 1663 (w), 1600 (w), 1492 (w), 1448 (m), 1310 (w), 1088 (m), 1017 (m), 969 (s), 763 (s), 696 (s), 519 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48-7.42 (m, 2H), 7.42-7.35 (m, 2H), 7.35-7.29 (m, 1H), 6.08 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.86 (d, *J* = 15.6 Hz, 1H), 4.23 (d, *J* = 3.6 Hz, 2H), 1.83 (s, 3H), 1.66 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.6, 131.1, 130.4, 129.0, 128.0, 125.8, 122.0, 62.3, 43.5, 27.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{12}H_{14}ON$: 188.1070 m/z, found: 188.1070 m/z.

(*E*)-5-Hydroxy-2-(4-methoxyphenyl)-2-methylpent-3-enenitrile (8b). IR (neat): 3424 (br), 2931 (w), 2841 (w), 2238 (w), 1608 (w), 1509 (s), 1455 (m), 1302 (m), 1250 (s), 1181 (m), 1090 (w), 1023 (s), 970 (m), 830 (s), 539 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.04 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.82 (d, *J* = 15.6 Hz, 1H), 4.24-4.18 (m, 2H), 3.80 (s, 3H), 1.82 (s, 1H), 1.79 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.2, 131.5, 131.4, 130.1, 127.1, 122.2, 114.2, 62.2, 55.3, 42.7, 27.1; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{13}H_{19}O_2N_2$: 235.1441 m/z, found: 235.1441 m/z.

(*E*)-5-Hydroxy-2-methyl-2-(3-(trifluoromethyl)phenyl)pent-3-enenitrile (8c). IR (neat): 3412 (br), 2990 (w), 2935 (w), 2871 (w), 2243 (w), 1442 (w), 1381 (w), 1325 (s), 1166 (m), 1123 (s), 1073 (m), 1014 (w), 803 (m), 697 (m), 527 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70-7.65 (m, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.56-7.50 (m, 1H), 6.12 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.87 (d, *J* = 15.6 Hz, 1H), 4.29-4.23 (m, 2H), 1.86 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 140.8, 131.5 (q, *J* = 32.5 Hz), 131.4, 130.0, 129.6, 129.5, 125.1 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 270.8 Hz), 122.6 (q, *J* = 3.9 Hz), 121.4, 62.1, 43.4, 27.1; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.6; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{13}H_{13}ONF_3$: 256.0944 m/z, found: 256.0944 m/z.

(*E*)-2-(3-Chlorophenyl)-5-hydroxy-2-methylpent-3-enenitrile (8d). IR (neat): 3415 (br), 2986 (w), 2928 (w), 2864 (w), 2241 (w), 1585 (m), 1470 (m), 1416 (m), 1205 (w), 1085 (m), 969 (s), 879 (m), 785 (s), 690 (s), 441 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43-7.39 (m, 1H), 7.37-7.29 (m, 3H), 6.09 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.84 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.28-4.23 (m, 2H), 1.82 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 141.6, 135.0, 131.1, 130.3, 130.2, 128.4, 126.2, 124.2, 121.5, 62.2, 43.3, 27.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{12}H_{13}ONCl$: 222.0680 m/z, found: 222.0680 m/z.

(*E*)-5-Hydroxy-2-methyl-2-(o-tolyl)pent-3-enenitrile (8e). IR (neat): 3406 (br), 2984 (w), 2930 (w), 2867 (w), 2237 (w), 1454 (m), 1378 (w), 1222 (w), 1085 (m), 1020 (m), 970 (s), 763 (s), 727 (s), 544 (w), 454 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.44-7.40 (m, 1H), 7.36-7.26 (m, 3H), 6.07 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.82 (d, *J* = 15.6 Hz, 1H), 4.27 (d, *J* = 4.8 Hz, 2H), 2.58 (s, 3H), 2.10 (s, 1H), 1.97 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 137.1, 135.8, 132.5, 130.7, 130.6, 128.4, 126.4, 125.5, 121.9, 62.1, 41.7, 27.0, 21.0; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{13}H_{19}ON_2$: 219.1492 m/z, found: 219.1492 m/z.

(*E*)-2-(Benzofuran-2-yl)-5-hydroxy-2-methylpent-3-enenitrile (8f). IR (neat): 3418 (br), 2930 (w), 2867 (w), 2238 (w), 1585 (w), 1451 (m), 1306 (w), 1251 (m), 1166 (m), 1080 (m), 1012 (m), 969 (m), 810 (m), 746 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.34-7.28 (m, 1H), 7.27-7.22 (m, 1H), 6.71 (d, *J* = 0.8 Hz, 1H), 6.20 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.92 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.26 (d, *J* = 4.4 Hz, 2H), 1.90 (s, 3H), 1.87 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.1, 153.9, 132.1, 127.5, 127.4, 124.8, 123.2, 121.2, 119.7, 111.4, 103.6, 62.0, 39.8, 25.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{14}H_{14}O_2N$: 228.1019 m/z, found: 228.1019 m/z.

(*E*)-2-(Benzo[b]thiophen-2-yl)-5-hydroxy-2-methylpent-3-enenitrile (8g). IR (neat): 3409 (br), 2925 (w), 2862 (w), 2232 (w), 1661 (w), 1443 (m), 1304 (w), 1161 (w), 1071 (w), 1009 (m), 966 (m), 829 (m), 748 (s), 435 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.39-7.30 (m, 3H), 6.19 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.93 (dt, *J* = 15.4, 1.6 Hz, 1H), 4.25 (d, *J* = 3.6 Hz, 2H), 1.99 (s, 1H), 1.94 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.1, 139.4, 139.0, 131.3, 129.9,

124.9, 124.7, 123.8, 122.3, 121.9, 120.8, 62.0, 41.2, 28.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{14}H_{14}ONS$: 224.0791 m/z, found: 224.0790 m/z.

(*E*)-Tert-butyl 3-(2-cyano-5-hydroxypent-3-en-2-yl)-1H-indole-1-carboxylate (8h). IR (neat): 3436 (br), 2981 (w), 2933 (w), 2864 (w), 2240 (w), 1731 (s), 1452 (m), 1368 (s), 1245 (m), 1150 (s), 1106 (m), 1022 (w), 849 (m), 743 (s), 472 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.37-7.30 (m, 1H), 7.28-7.21 (m, 1H), 6.13 (dt, *J* = 15.2, 4.8 Hz, 1H), 5.86 (d, *J* = 15.2 Hz, 1H), 4.16 (d, *J* = 3.2 Hz, 2H), 2.69 (s, 1H), 1.90 (s, 3H), 1.67 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.3, 135.8, 131.3, 129.1, 127.1, 124.7, 122.7, 122.6, 121.1, 120.0, 119.0, 115.3, 84.3, 61.7, 37.3, 27.9, 25.8; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{19}H_{23}O_3N_2$: 327.1703 m/z, found: 327.1703 m/z.

(*E*)-2-Cyclohexyl-5-hydroxy-2-methylpent-3-enenitrile (8i). IR (neat): 3427 (br), 2927 (s), 2855 (m), 2237 (w), 1665 (w), 1450 (m), 1375 (w), 1312 (w), 1269 (w), 1093 (m), 1015 (m), 971 (s), 893 (s), 803 (w), 516 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.00 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.49 (d, *J* = 15.6 Hz, 1H), 4.19 (d, *J* = 4.4 Hz, 2H), 1.93-1.62 (m, 6H), 1.43-1.31 (m, 4H), 1.28-1.00 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 130.5, 130.3, 122.1, 62.3, 45.5, 43.9, 28.3, 27.9, 26.1, 25.8, 23.5; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{12}H_{23}ON_2$: 211.1805 m/z, found: 211.1805 m/z.

(*E*)-2-(3-Hydroxyprop-1-en-1-yl)-2,6-dimethylhept-5-enenitrile (8j). IR (neat): 3424 (br), 2972 (m), 2923 (m), 2861 (m), 2238 (w), 1668 (w), 1601 (w), 1448 (m), 1378 (m), 1212 (w), 1094 (m), 1018 (m), 970 (s), 831 (w), 752 (w), 541 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.03 (d, *J* = 15.6, 4.8 Hz, 1H), 5.51 (d, *J* = 15.6 Hz, 1H), 5.06 (t, *J* = 6.4 Hz, 1H), 4.24-4.15 (m, 2H), 2.19-2.00 (m, 2H), 1.78-1.49 (m, 9H), 1.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 132.9, 130.7, 130.4, 122.5, 122.3, 62.2, 40.1, 39.3, 26.0, 25.6, 23.9, 17.6; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{12}H_{20}ON$: 194.1539 m/z, found: 194.1539 m/z.

(*E*)-4-(3-Hydroxyprop-1-en-1-yl)chroman-4-carbonitrile (8k). IR (neat): 3423 (br), 2929 (m), 2875 (m), 2238 (w), 1718 (w), 1580 (w), 1485 (m), 1449 (m), 1285 (w), 1258 (w), 1222 (s), 1096 (m), 1046 (m), 968 (m), 756 (s), 492 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.26-7.17 (m, 2H), 6.97-6.88 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.12 (dt, *J* = 15.2, 4.4 Hz, 1H), 5.71 (d, *J* = 15.2 Hz, 1H), 4.38-4.17 (m, 4H), 2.43-2.33 (m, 1H), 2.26-2.13 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 153.5, 133.2, 130.1, 129.4, 129.3, 121.2, 121.1, 118.6, 117.7, 62.2, 61.8, 39.6, 33.6; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{13}H_{17}O_2N_2$: 233.1285 m/z, found: 233.1285 m/z.

(*E*)-5-Hydroxy-2-isopropyl-2-phenylpent-3-enenitrile (8l). IR (neat): 3416 (br), 2969 (m), 2929 (w), 2873 (w), 2241 (w), 1662 (w), 1598 (w), 1493 (w), 1456 (m), 1384 (w), 1092 (m), 1010 (m), 969 (m), 757 (m), 700 (s), 525 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46-7.41 (m, 2H), 7.40-7.34 (m, 2H), 7.32-7.27 (m, 1H), 6.11 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.89 (d, *J* = 15.6 Hz, 1H), 4.24-4.13 (m, 2H), 2.34-2.23 (m, 1H), 1.75 (s, 1H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):**

δ 139.0 131.1, 129.5, 128.9, 127.7, 125.9, 119.4, 62.2, 55.9, 37.1, 18.4, 18.3; **HRMS (ESI$^+$) [M+NH$_4$]$^+$:** Calcd for $C_{14}H_{21}ON_2$: 233.1648 m/z, found: 233.1648 m/z.

(*E*)-2-(3-Hydroxyprop-1-en-1-yl)-2,6-dimethylhept-5-enal (9). IR (neat): 3385 (br), 2970 (w), 2931 (w), 2874 (w), 1709 (m), 1451 (w), 1375 (m), 1310 (w), 1256 (w), 1225 (w), 1154 (w), 1022 (s), 980 (m), 802 (w), 583 (w) cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 9.31 (s, 1H), 5.71-5.56 (m, 2H), 5.01 (t, *J* = 5.6 Hz, 1H), 4.10 (d, *J* = 3.2 Hz, 2H), 2.57 (s, 1H), 1.96-1.75 (m, 2H), 1.66-1.48 (m, 8H), 1.14 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$):** δ 202.8, 132.3, 131.5, 131.1, 123.5, 63.1, 51.6, 35.7, 25.5, 22.5, 18.0, 17.5; **HRMS (ESI$^+$) [M+NH$_4$]$^+$:** Calcd for $C_{12}H_{24}O_2N$: 214.1802 m/z, found: 214.1801 m/z.

Tert-butyl (4-(4-(dimethylamino)phenyl)-2-(hydroxymethyl)butyl)carbamate (10). IR (neat): 3348 (br), 2972 (w), 2925 (w), 2878 (w), 2798 (w), 1682 (s), 1614 (w), 1515 (s), 1248 (m), 1163 (s), 1040 (w), 893 (w), 808 (s), 550 (w), 519 (w) cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.05 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 4.96 (t, *J* = 5.6 Hz, 1H), 3.65-3.55 (m, 1H), 3.49-3.38 (m, 1H), 3.34-3.23 (m, 1H), 3.17-3.06 (m, 1H), 2.90 (s, 6H), 2.64-2.48 (m, 2H), 1.65-1.53 (m, 2H), 1.53-1.38 (m, 10H); **^{13}C NMR (100 MHz, CDCl$_3$):** δ 157.4, 149.0, 130.2, 128.8, 113.0, 79.6, 62.2, 40.8, 40.7, 40.6, 32.1, 30.5, 28.3; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{18}H_{31}O_3N_2$: 323.2329 m/z, found: 323.2332 m/z.

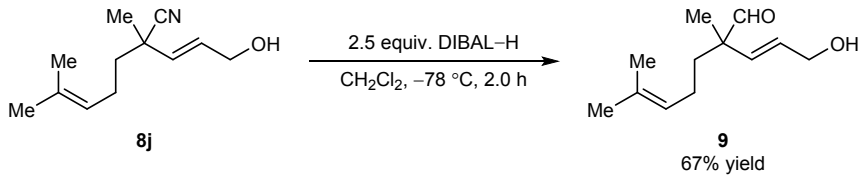
(*E*)-Tert-butyl(4-(3-chlorophenyl)-2-(hydroxymethyl)-3-methylbut-3-en-1-yl)carbamate (11). IR (neat): 3352 (br), 2974 (w), 2929 (w), 2878 (w), 1685 (s), 1592 (w), 1510 (s), 1249 (m), 1164 (s), 1031 (m), 891 (w), 857 (w), 774 (m), 687 (m), 531 (w) cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.26-7.14 (m, 3H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.25 (s, 1H), 4.83 (s, 1H), 3.77-3.63 (m, 2H), 3.43-3.25 (m, 2H), 3.02 (s, 1H), 2.49-2.38 (m, 1H), 1.84 (s, 3H), 1.43 (s, 9H); **^{13}C NMR (100 MHz, CDCl$_3$):** δ 156.8, 139.4, 138.4, 133.8, 129.3, 128.9, 127.1, 126.4, 79.8, 62.1, 51.4, 40.0, 28.3, 16.4; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{17}H_{25}O_3NCl$: 326.1517 m/z, found: 326.1518 m/z.

(*E*)-2-(Furan-2-ylmethyl)-2-methyl-4-phenylbut-3-enenitrile (12). IR (neat):3029 (w), 2982 (w), 2931 (w), 2237 (w), 1716 (w), 1498 (w), 1451 (w), 1205 (w), 1148 (w), 1076 (w), 1013 (m), 966 (m), 808 (w), 742 (s), 694 (m) cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.41-7.26 (m, 6H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.37-6.27 (m, 2H), 6.03 (d, *J* = 16.0 Hz, 1H), 3.08 (s, 2H), 1.55 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$):** δ 149.6, 142.3, 135.8, 131.1, 128.7, 128.6, 128.2, 126.7, 122.2, 110.6, 109.2, 40.2, 39.0, 25.4; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{16}H_{16}ON$: 238.1226 m/z, found: 238.1225 m/z.

(*E*)-2-Methyl-2-styrylpent-4-enenitrile (13). IR (neat):3074 (w), 3026 (w), 2980 (w), 2930 (w), 2236 (w), 1642 (w), 1599 (w), 1447 (m), 1295 (w), 965 (s), 922 (s), 747 (s), 691 (s), 604 (m), 564 (m) cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.46-7.26 (m, 5H), 6.80 (d, *J* = 16.0 Hz, 1H), 5.99 (d, *J* = 16.0 Hz, 1H), 5.94-5.80 (m, 1H), 5.31-5.20 (m, 2H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.54 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$):** δ 135.6, 131.5, 130.8, 128.8, 128.6, 128.0, 126.4, 122.1, 120.1, 44.5, 39.6, 25.3; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{14}H_{16}N$: 198.1277 m/z, found: 198.1276 m/z.

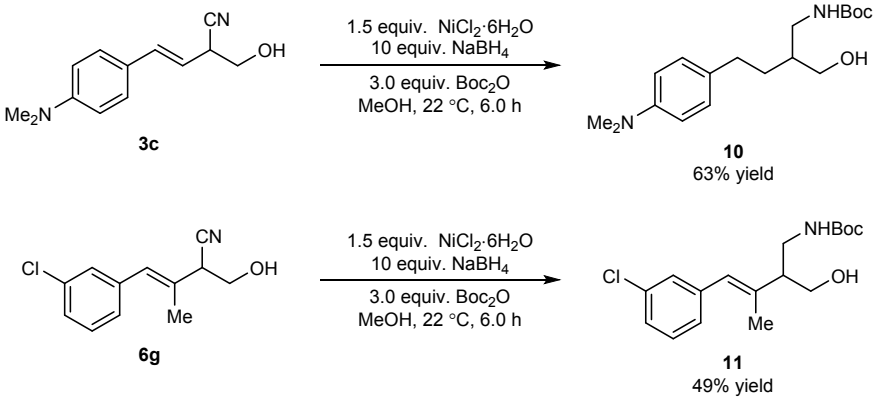
4-(Hydroxymethyl)-2,2,9-trimethyl-5-methylene-3-oxodec-8-enenitrile(S1). IR (neat): 3435 (br), 2965 (w), 2927 (w), 2239 (w), 1723 (s), 1641 (w),1461 (w), 1382 (w), 1260 (w), 1087 (m), 1039 (s), 910 (w), 799 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.13-5.04 (m, 2H), 4.83 (s, 1H), 3.95-3.86 (m, 2H), 3.65 (d, J = 8.4 Hz, 1H), 2.37-2.13 (m, 4H), 2.00 (s, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.52 (s, 3H), 1.50 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.2, 141.9, 132.4, 123.2, 121.9, 114.8, 63.1, 58.6, 43.9, 35.6, 25.9, 25.6, 24.9, 24.6, 17.7; **HRMS (ESI$^+$) $[M+H]^+$:** Calcd for $C_{15}H_{24}NO_2$: 250.1802 m/z, found: 250.1802 m/z.

■ **Representative Experimental Procedure for Reduction of CN to Aldehyde.**



To a solution of **8j** (135.8 mg, 0.7 mmol) in DCM at –78 °C was added DIBAL-H (1.75 mL, 1.75 mmol, 1.0 M in hexanes) dropwise. The reaction mixture was allowed to stir for 2.0 h and then quenched with a saturated aqueous solution of potassium sodium tartrate. The reaction mixture was diluted with Et_2O. The layers were separated and the aqueous layer was washed with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. Purification by column chromatography on silica gel, gave the desired product **9** (91.7 mg, 67% yield) as colorless oil.

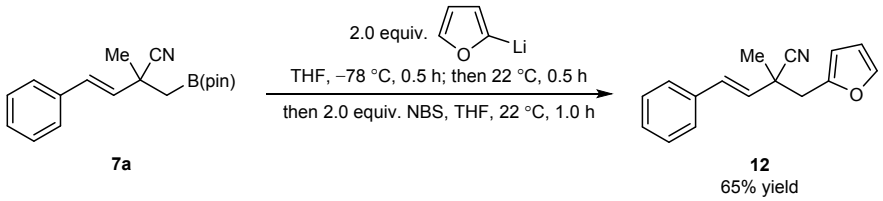
■ **Representative Experimental Procedure for Reduction of the Nitrile Moiety to the Protected Amines.**



To a solution of **3c** (69.1 mg, 0.32 mmol), $NiCl_2$•$6H_2O$ (114.1 mg, 0.48 mmol) and Boc_2O (209.5 mg, 0.96 mmol) in MeOH at 0 °C was added $NaBH_4$ (121.1 mg, 3.20 mmol) portion. The mixture was allowed to stir for 6h at r.t. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl. diluted with Et_2O. The layers were separated and the aqueous layer was washed with Et_2O. The combined organic

layers were dried over $MgSO_4$, filtered and concentrated under vacuum. Purification by column chromatography on silica gel, gave the desired product **10** (64.8 mg, 63% yield) as colorless oil.

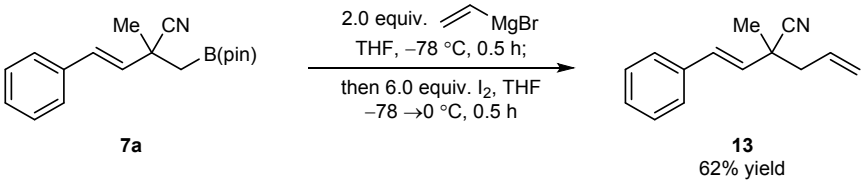
■ **Representative Experimental Procedure for Functionalization of C-B(pin) bond to C-furan.**



7a **12**
65% yield

A solution of furan (73 ul, 1.0 mmol) in THF was cooled to -78 °C and treated with *n*-BuLi (400 μL, 1.0 mmol, 2.5 M in hexanes). The cooling bath was removed and the mixture was allowed to stir at room temperature for 1 h. The mixture was cooled to –78 °C and the boronic ester **7a** (149 mg, 0.5 mmol) was added dropwise as a solution in THF. The mixture was stirred at -78 °C for 1 h. Then a solution of *N*-bromosuccinimide (NBS, 178 mg, 1.0 mmol) in THF was added dropwise. After 1 h at -78 °C, a saturated aqueous solution of $Na_2S_2O_3$ was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et_2O and water. The layers were separated and the aqueous layer was washed with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. Purification by column chromatography on silica gel, gave the desired product **12** (80.8 mg, 65% yield) as colorless oil.

■ **Representative Experimental Procedure for Functionalization of C-B(pin) bond to C-vinyl.**

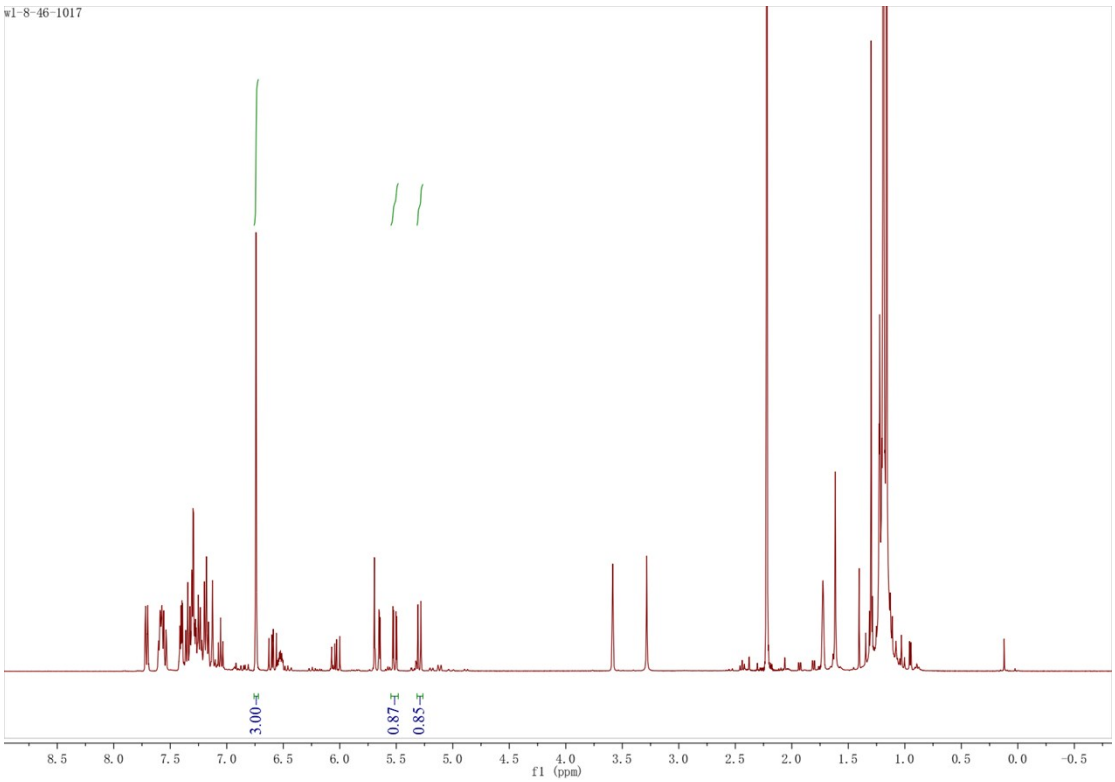


7a **13**
62% yield

To a solution of boronic ester **7a** (161.4 mg, 0.54 mmol) in THF at –78 °C was added vinylmagnesium bromide (3.24 mL, 3.24 mmol, 1 M in THF) dropwise. The mixture was allowed to stir for 30 min at -78 °C. Then a solution of I_2 (822.3 mg, 3.24 mmol) in MeOH was added dropwise, and the reaction mixture was allowed to stir for a further 30 min and then allowed to warm to 0°C. 5% $Na_2S_2O_3$ was added and the solvents was removed from the reaction mixture in vacuo. The mixture was washed with Et_2O, the organic layers were combined, washed with brine, dried ($MgSO_4$), concentrated and purified by column chromatography to give the desired product **13** (66.4 mg, 62%) as colorless oil.

■ **Representative Experimental Procedure for Equivalent Cu-B(pin) Addition to 1,3-dienes (s2).**

In a N_2-filled glove-box, an oven-dried vial (8 mL, 61 × 16.6 mm) with a magnetic stir bar was charged with phosphine ligand **4h** (57.9 mg, 0.1 mmol, 1.0 equiv), CuCl (10 mg, 0.1 mmol, 1.0 equiv), LiO*t*-Bu (8.0 mg, 0.10 mmol, 1.0 equiv) and *d*8-tetrahydrofuran (*d*8-thf, 1 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (25.4 mg, 0.10 mmol, 1.0 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 20 min under an atmosphere of N_2. Diene **s2** (20.9 mg, 0.10 mmol, 1.0 equiv) were added. The resulting solution was allowed to stir at 22 °C for 1 h. Then 1,35-trimethylbenzene (12.0mg, 0.1mmol) was added as internal standard. The reaction was monitored by ^{1}H NMR and 0.85 mmol diene **s2** remains with <5% conversion. The reason why such type of substrates was unreactive is that Cu–B(pin) addition did not occur.



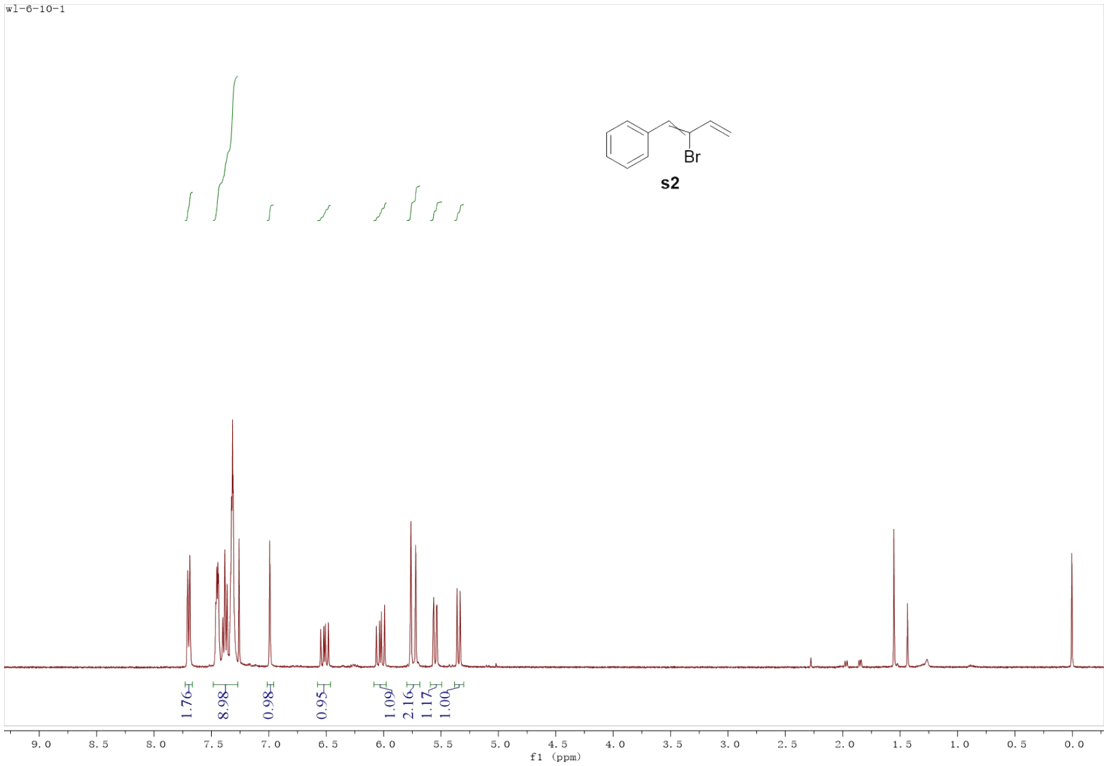
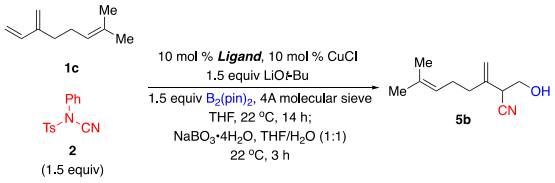
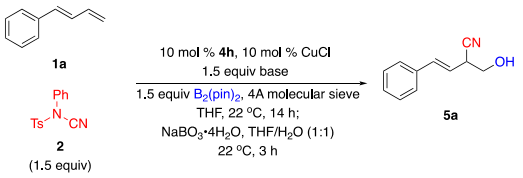


Table S1. Ligand Screen



Entry	Ligand	Yield (%)
1	**4a**	55
2	**4b**	40
3	**4c**	51
4	**4d**	41
5	**4e**	66
6	**4f**	75
7	**4g**	27
8	**4h**	34

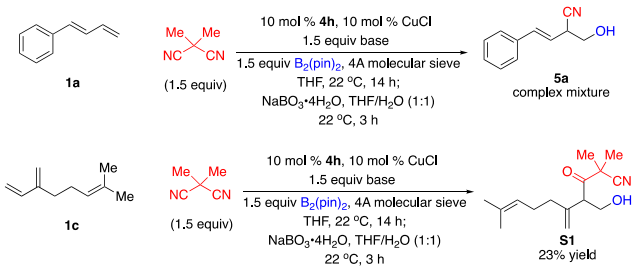
Table S2. Screen of Bases



Entry	base	Yield (%)
1	K_2CO_3	23
2	K_3PO_4	15
3	LiO*t*-Bu	75
4	NaO*t*-Bu	36
5	KO*t*-Bu	32

Screening of bases indicated that the reaction with LiO*t*-Bu provided highest yield. Low conversions of **1a** in the cases of reactions with K_2CO_3 and K_3PO_4 were observed, whereas stronger bases led to messy reactions, maybe due to decomposition of the product.

Scheme S1. Reaction with DMMN



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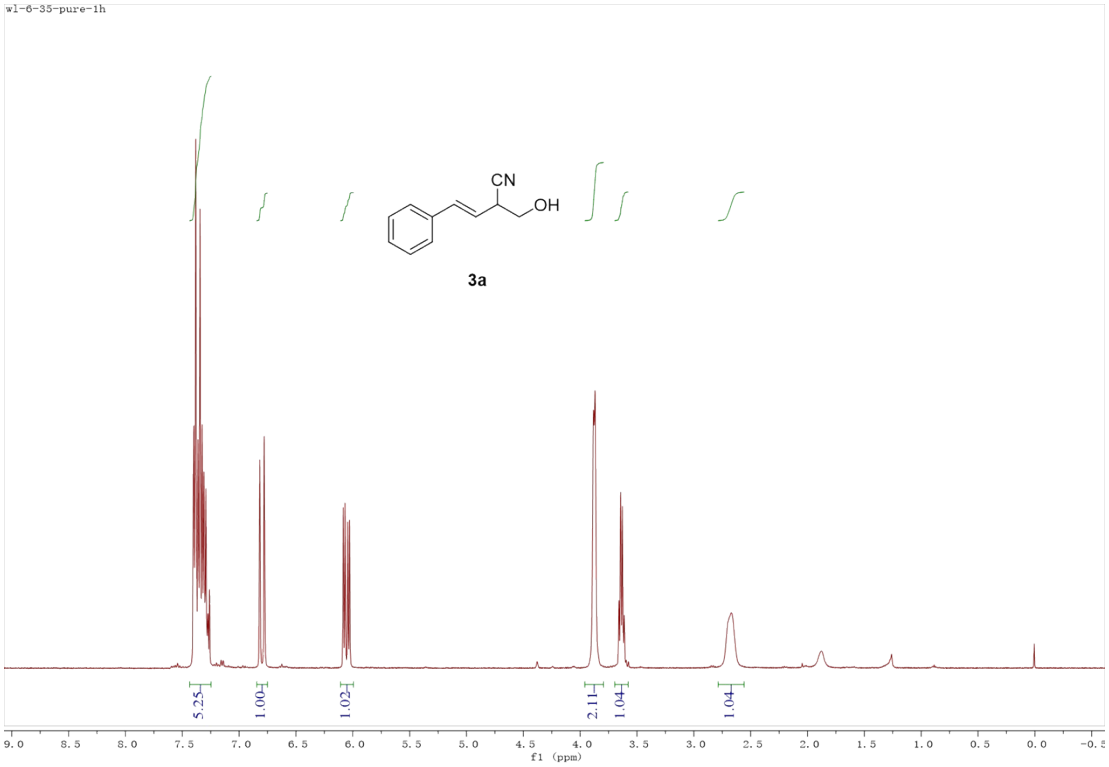
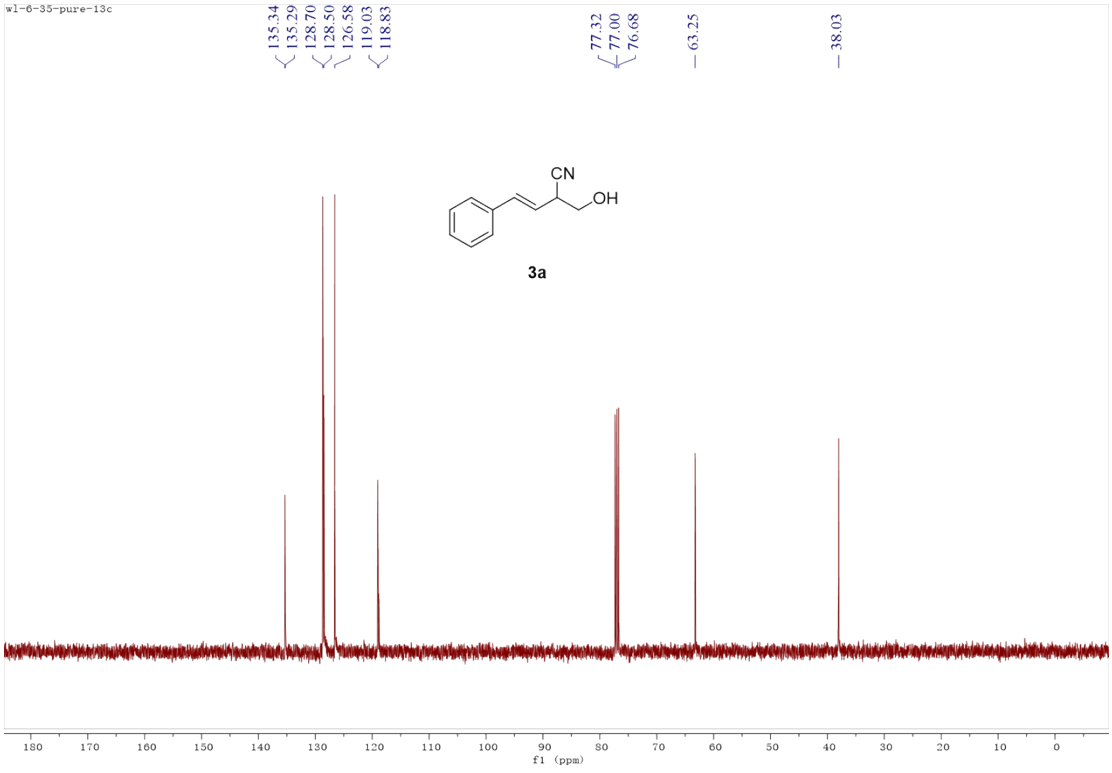
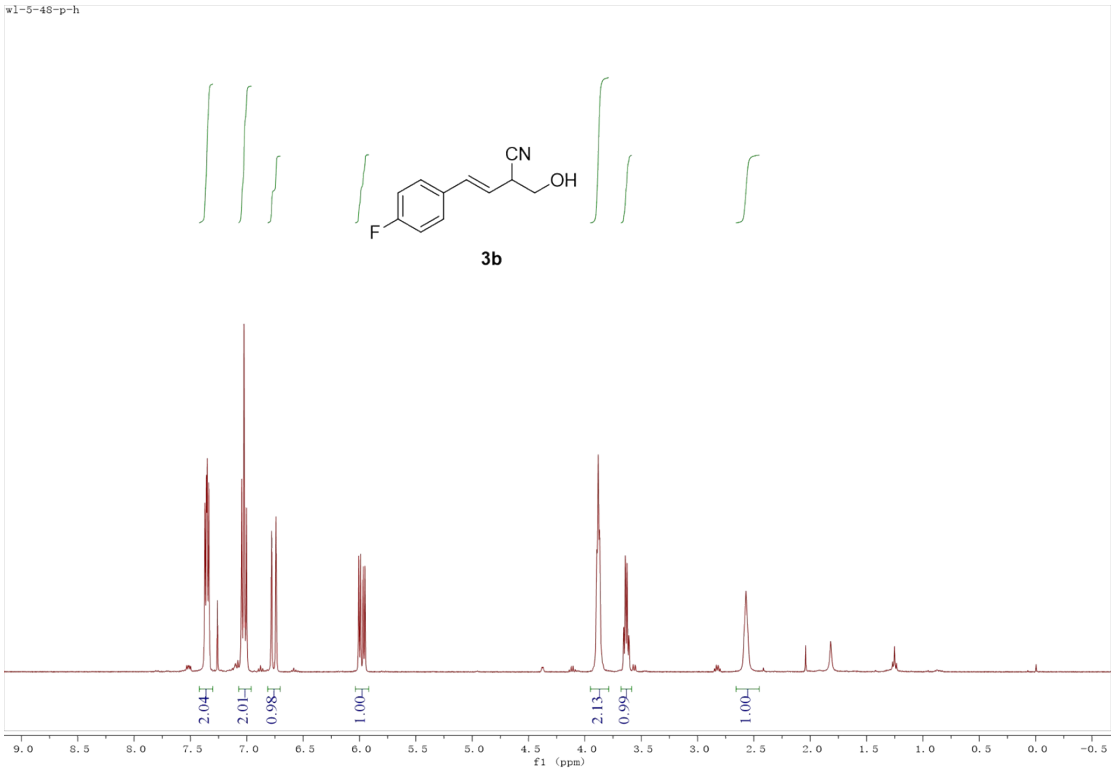
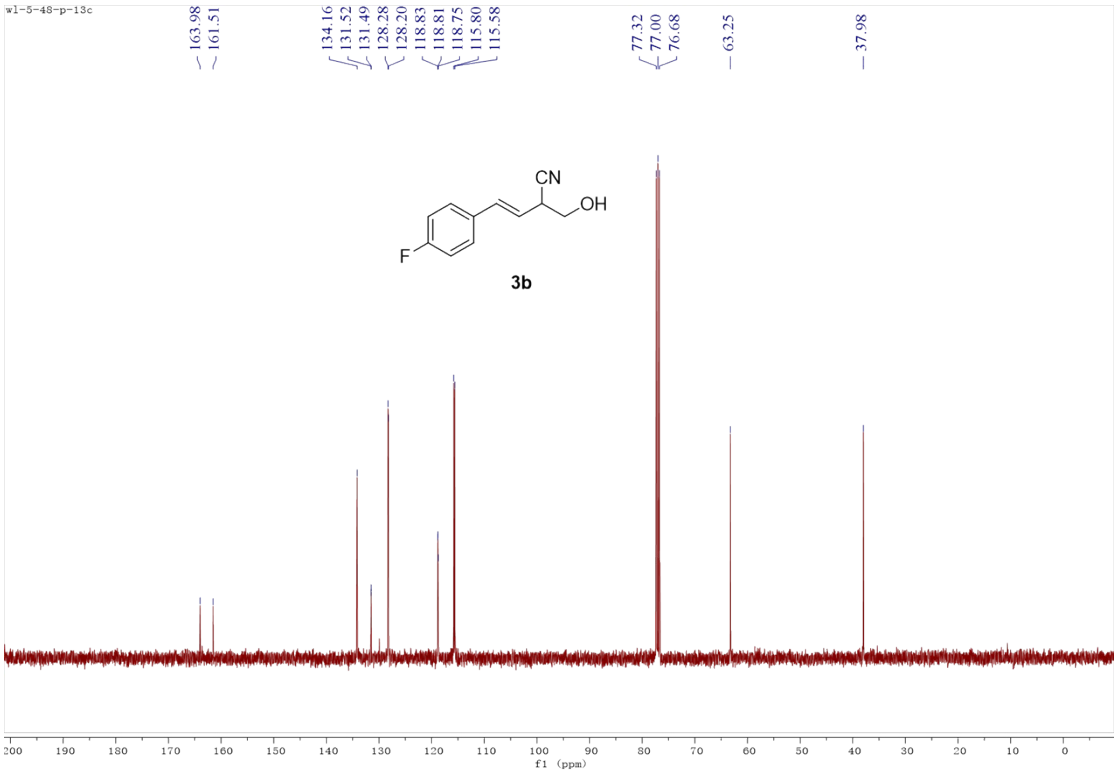
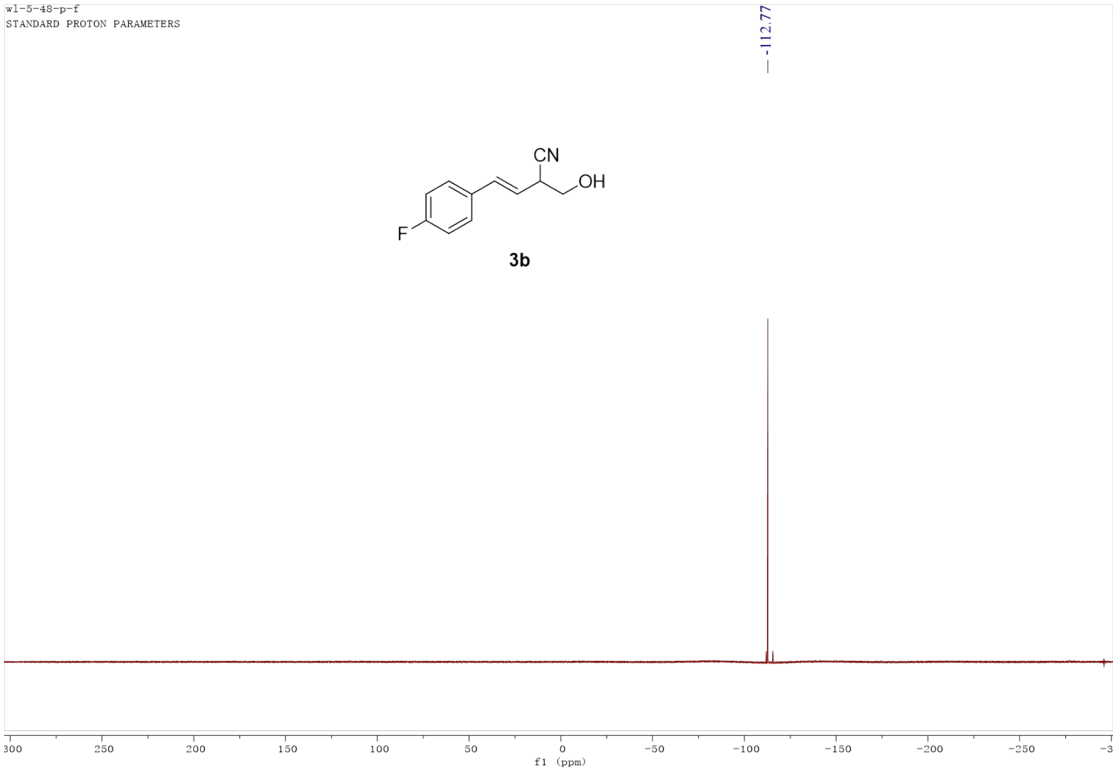
NMR Spectra

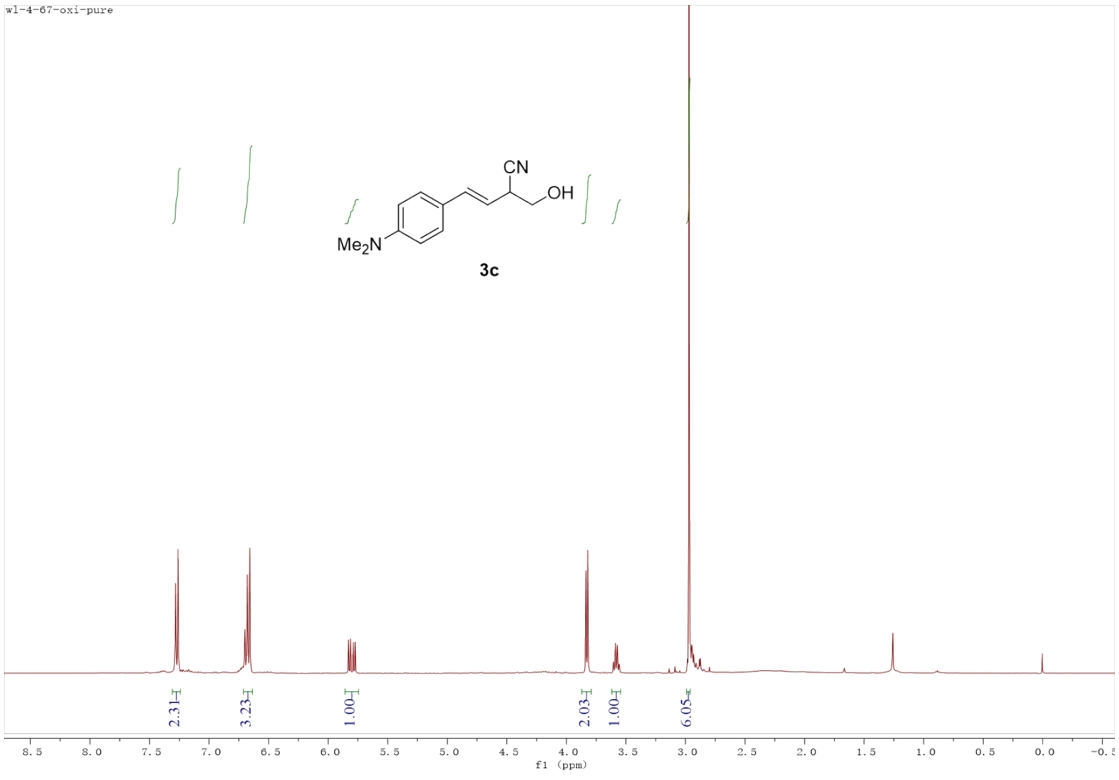

wl-6-35-pure-1h
CN
OH
3a
5.25
1.00
1.02
2.11
1.04
1.04
f1 (ppm)

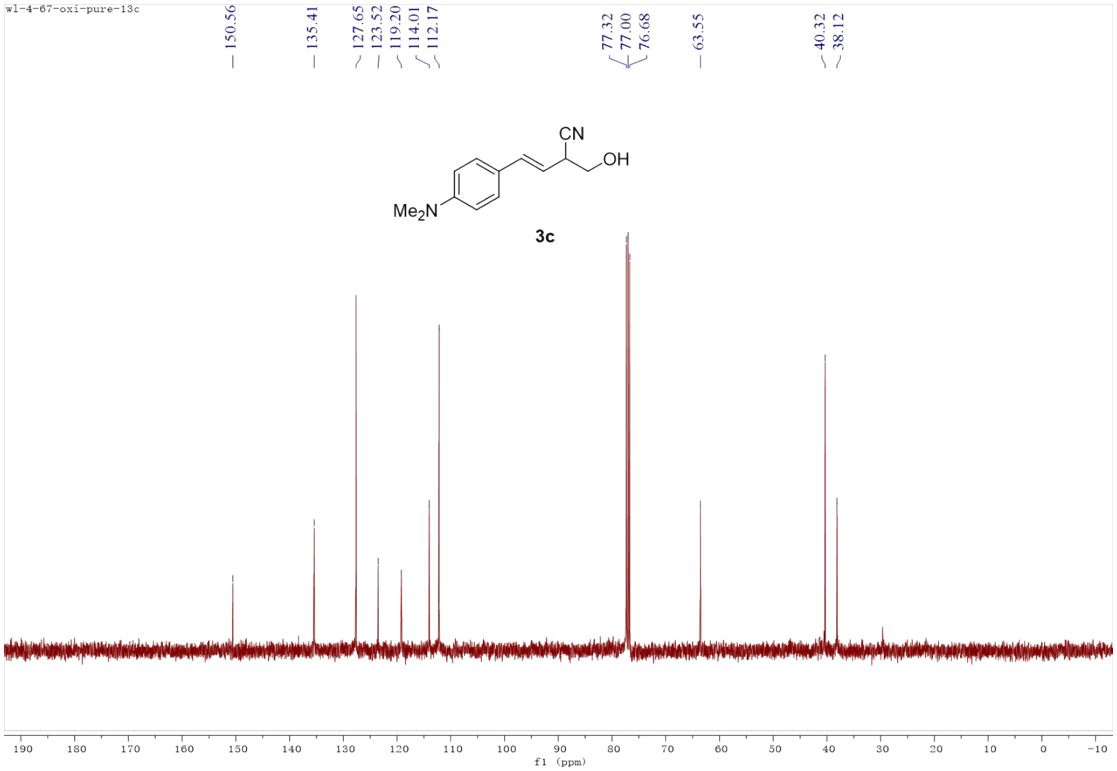

wl-6-35-pure-13c
135.34
135.29
128.70
128.50
126.58
119.03
118.83
77.32
77.00
76.68
63.25
38.03
CN
OH
3a
f1 (ppm)

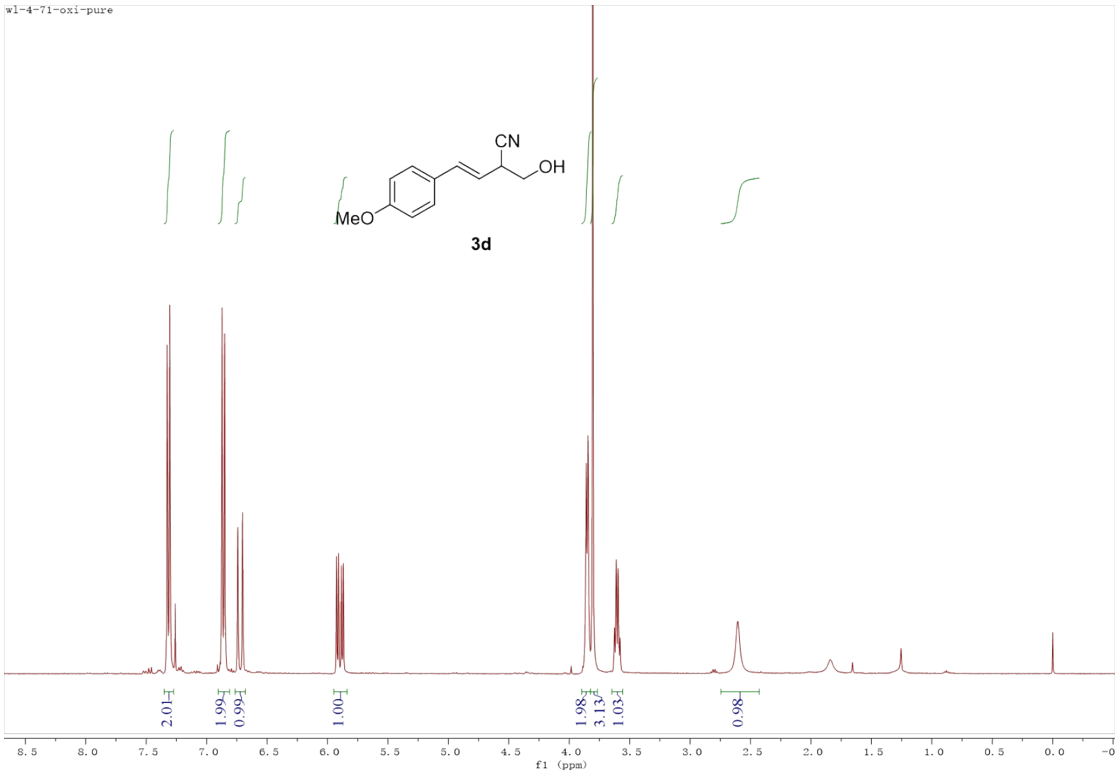

wl-5-48-p-h
CN
OH
F
3b
2.04
2.01
0.98
1.00
2.13
0.99
1.00
f1 (ppm)

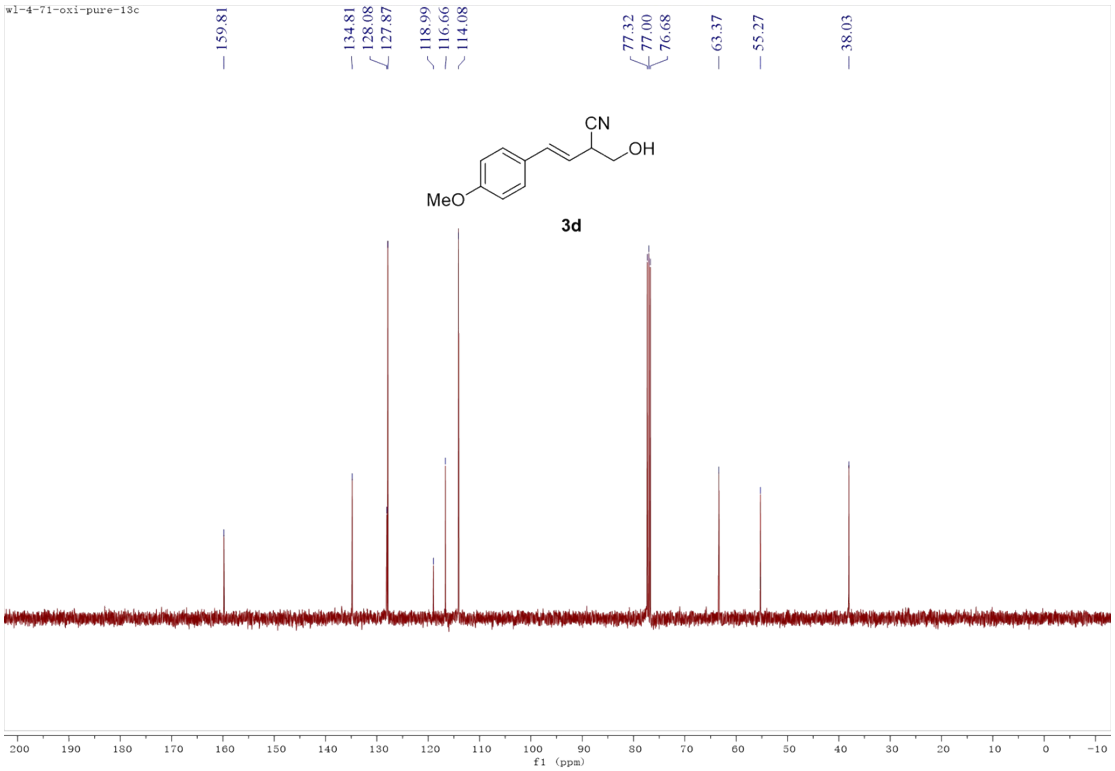

wl-5-48-p-13c
163.98
161.51
134.16
131.52
131.49
128.28
128.20
118.83
118.81
118.75
115.80
115.58
77.32
77.00
76.68
63.25
37.98
CN
OH
F
3b
f1 (ppm)

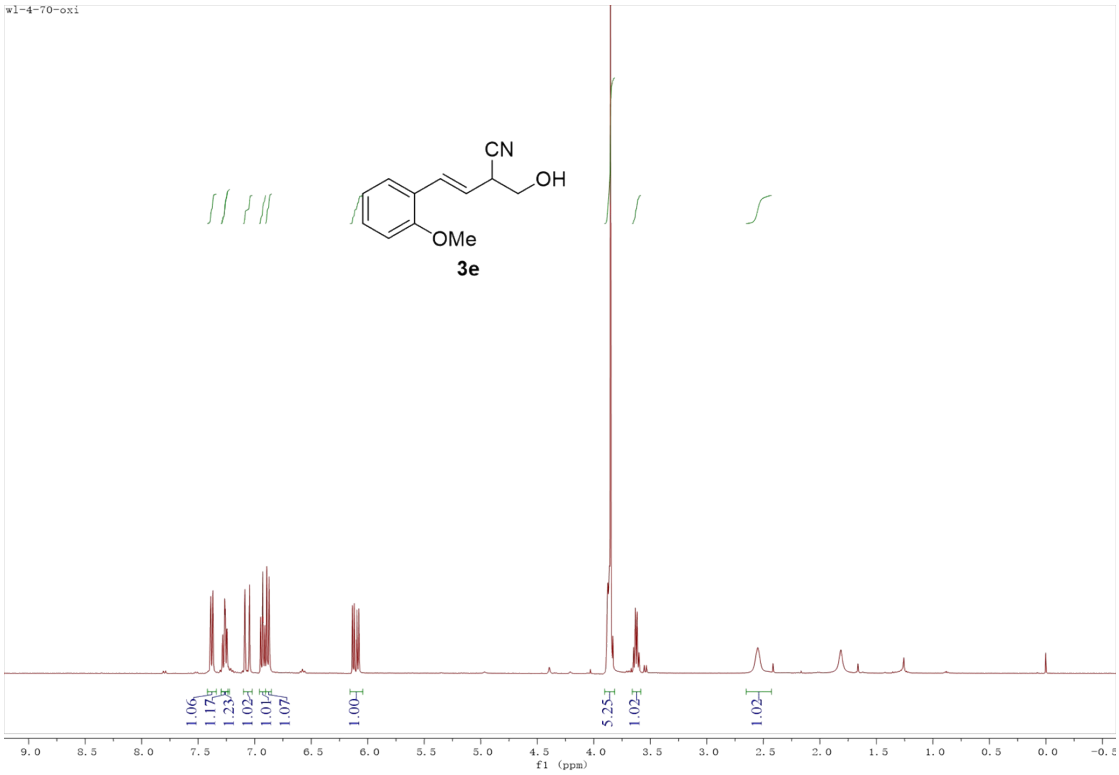

wl-5-48-p-f
STANDARD PROTON PARAMETERS
-112.77
CN
OH
F
3b
f1 (ppm)

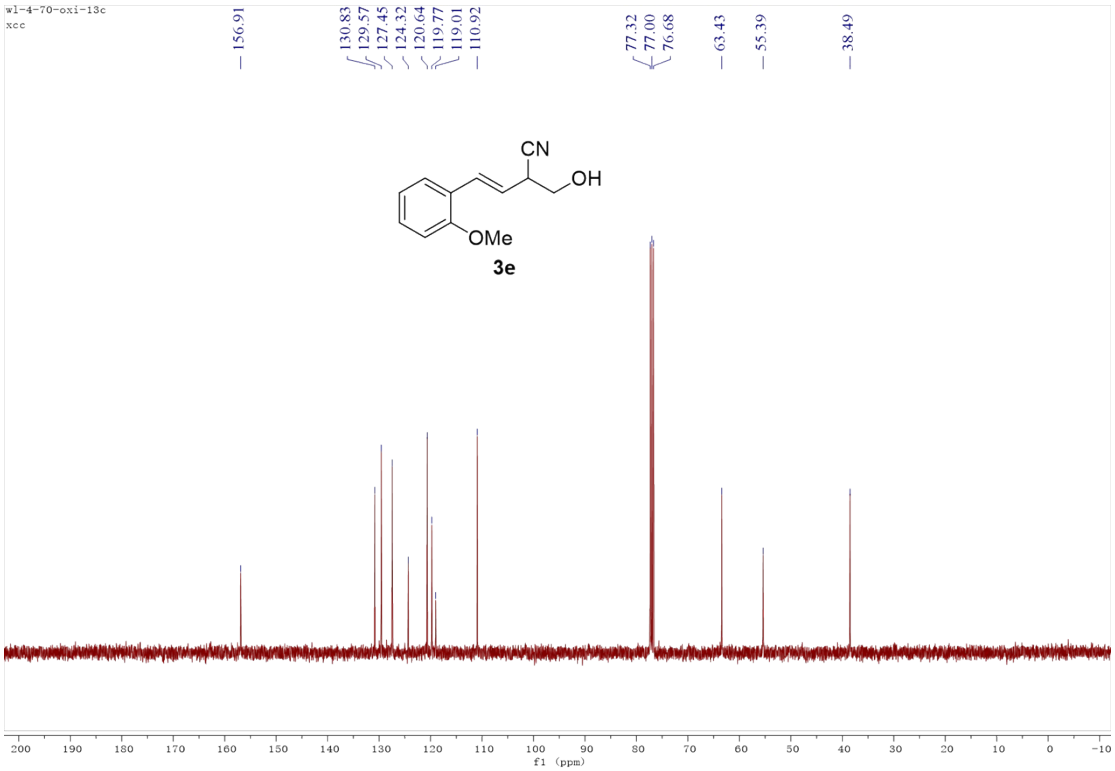

wl-4-67-oxi-pure
CN
OH
Me2N
3c
2.31
3.23
1.00
2.03
1.00
6.05
f1 (ppm)

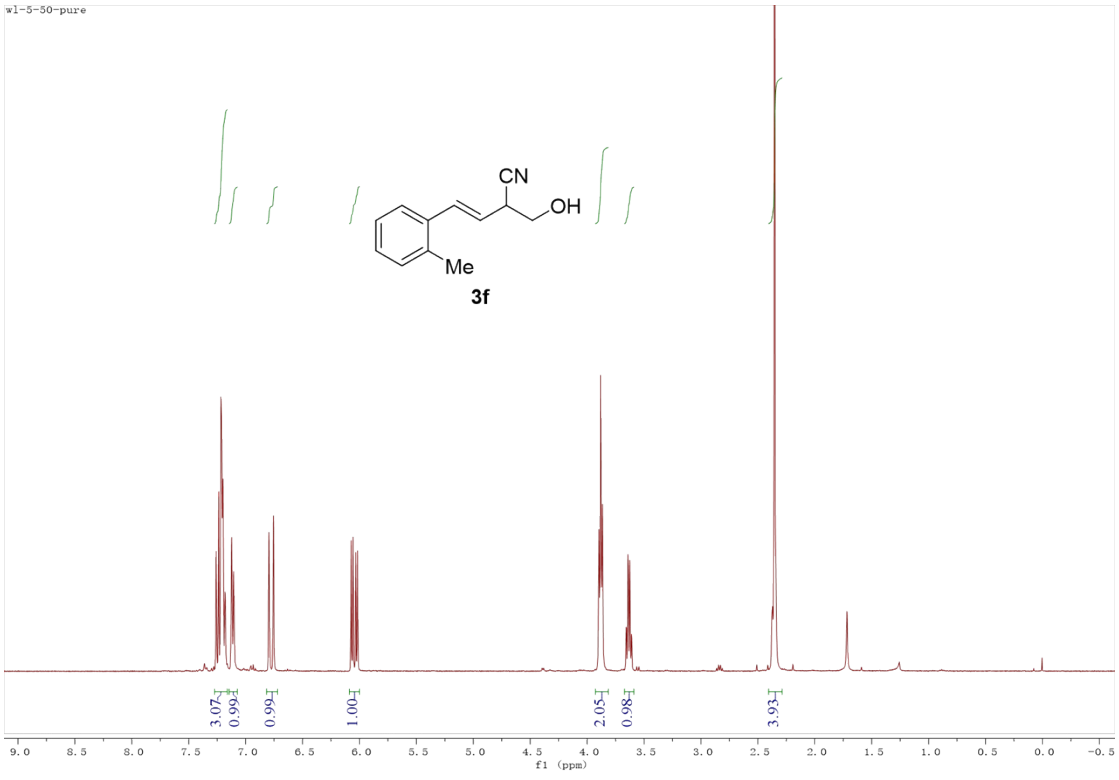

wl-4-67-oxi-pure-13c
150.56
135.41
127.65
123.52
119.20
114.01
112.17
77.32
77.00
76.68
63.55
40.32
38.12
CN
OH
Me2N
3c
f1 (ppm)

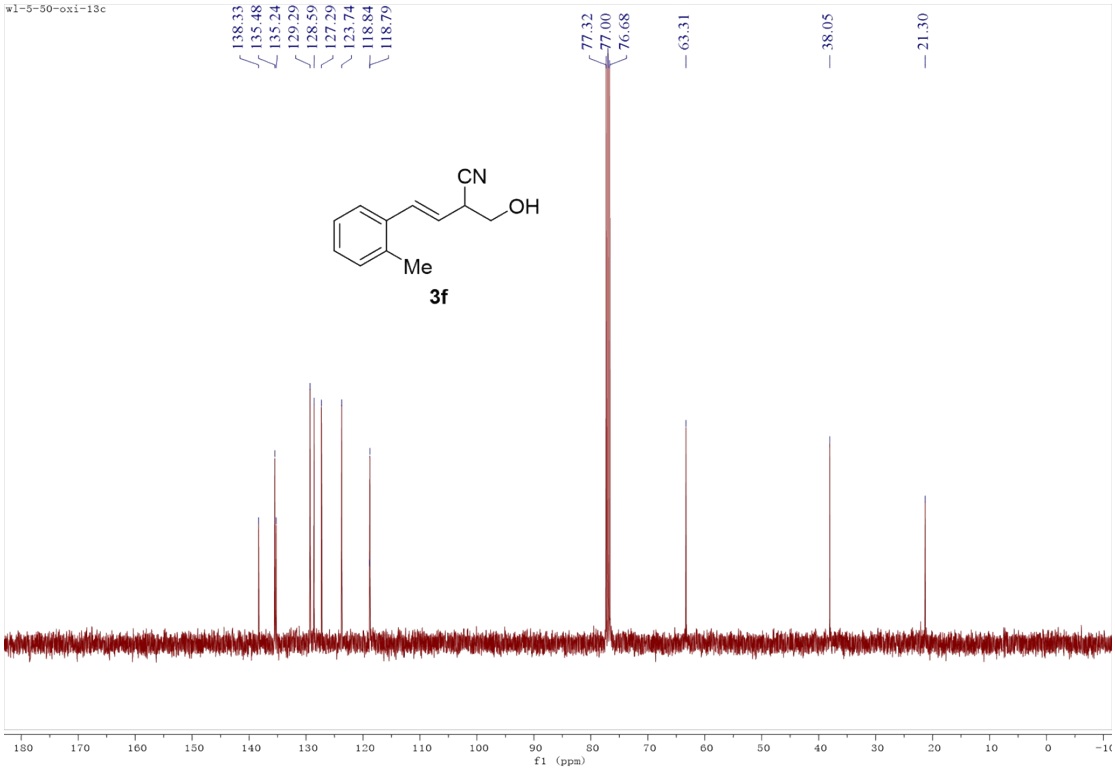

wl-4-71-oxi-pure
CN
OH
MeO
3d
2.01
1.99
0.99
1.00
1.98
3.13
1.03
0.98
f1 (ppm)

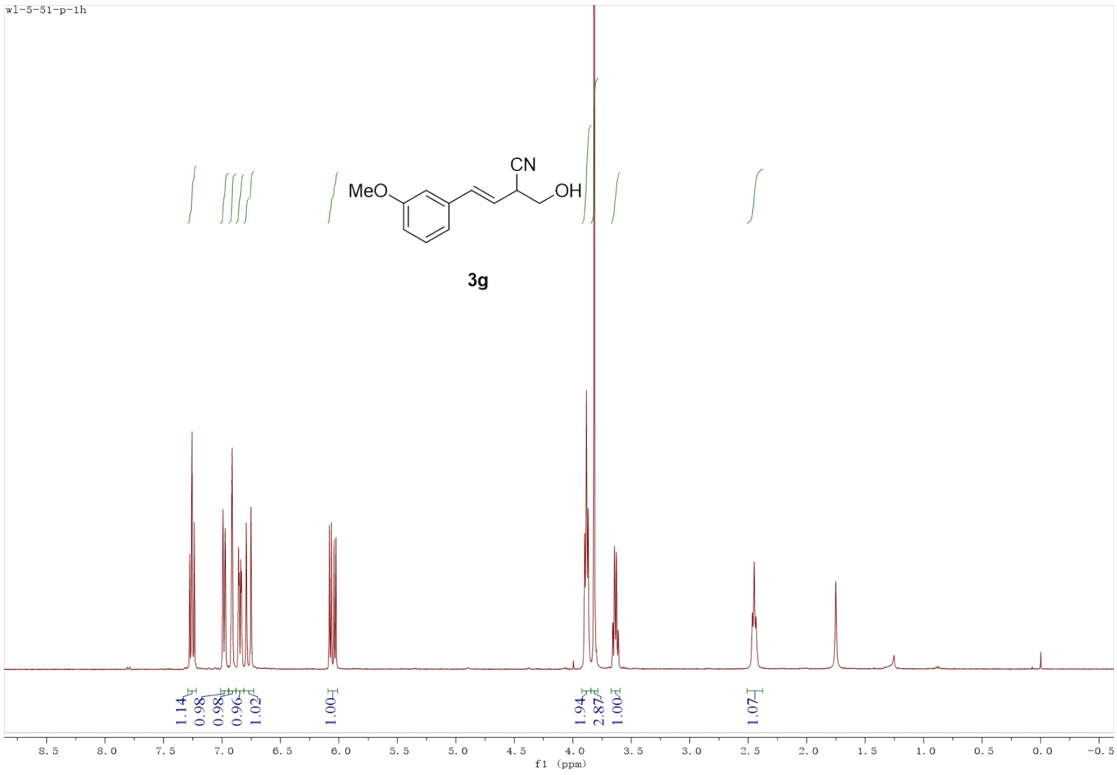

wl-4-71-oxi-pure-13c
159.81
134.81
128.08
127.87
118.99
116.66
114.08
77.32
77.00
76.68
63.37
55.27
38.03
CN
OH
MeO
3d
f1 (ppm)

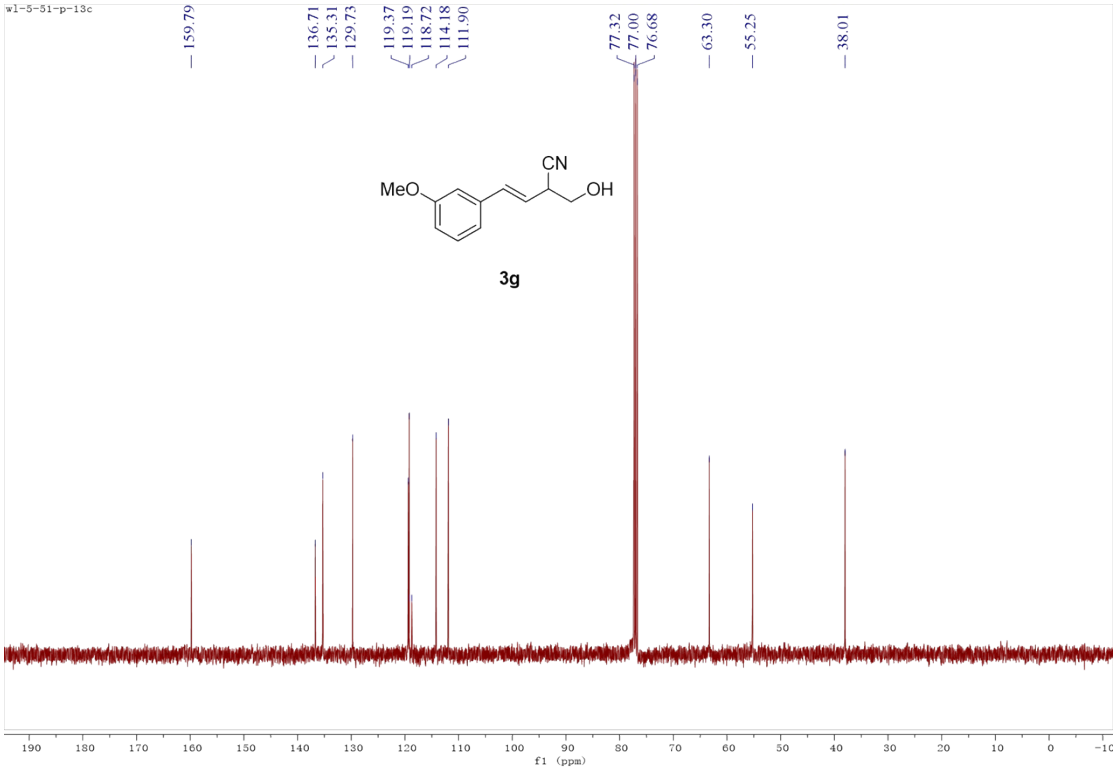

wl-4-70-oxi
CN
OH
OMe
3e
1.06
1.17
1.23
1.02
1.01
1.07
1.00
5.25
1.02
1.02
f1 (ppm)

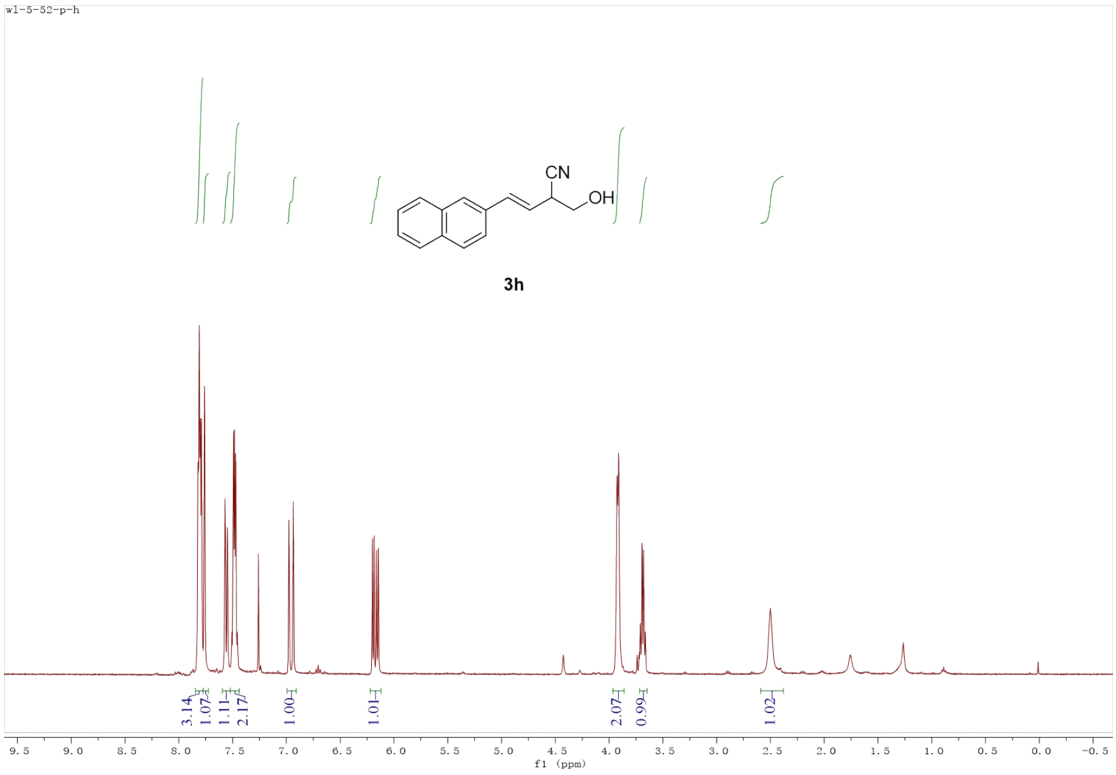

wl-4-70-oxi-13c
xcc
156.91
130.83
129.57
127.45
124.32
120.64
119.77
119.01
110.92
77.32
77.00
76.68
63.43
55.39
38.49
CN
OH
OMe
3e
f1 (ppm)

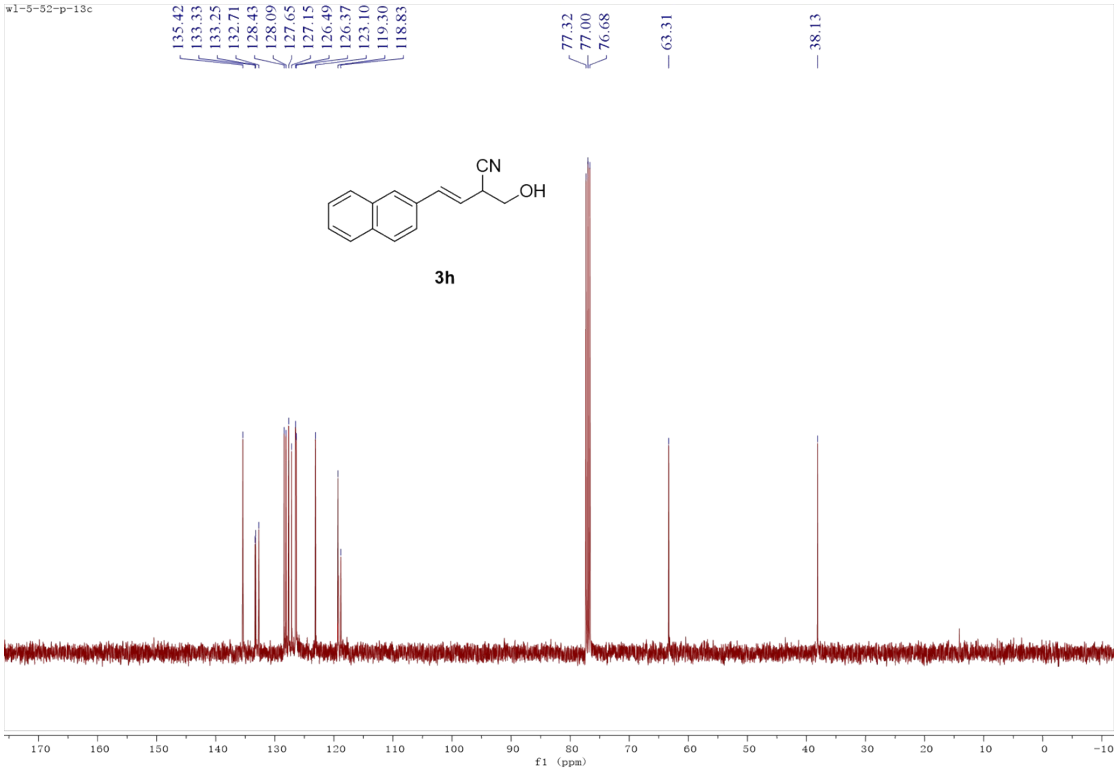

wl-5-50-pure
CN
OH
Me
3f
3.07
0.99
0.99
1.00
2.05
0.98
3.93
f1 (ppm)

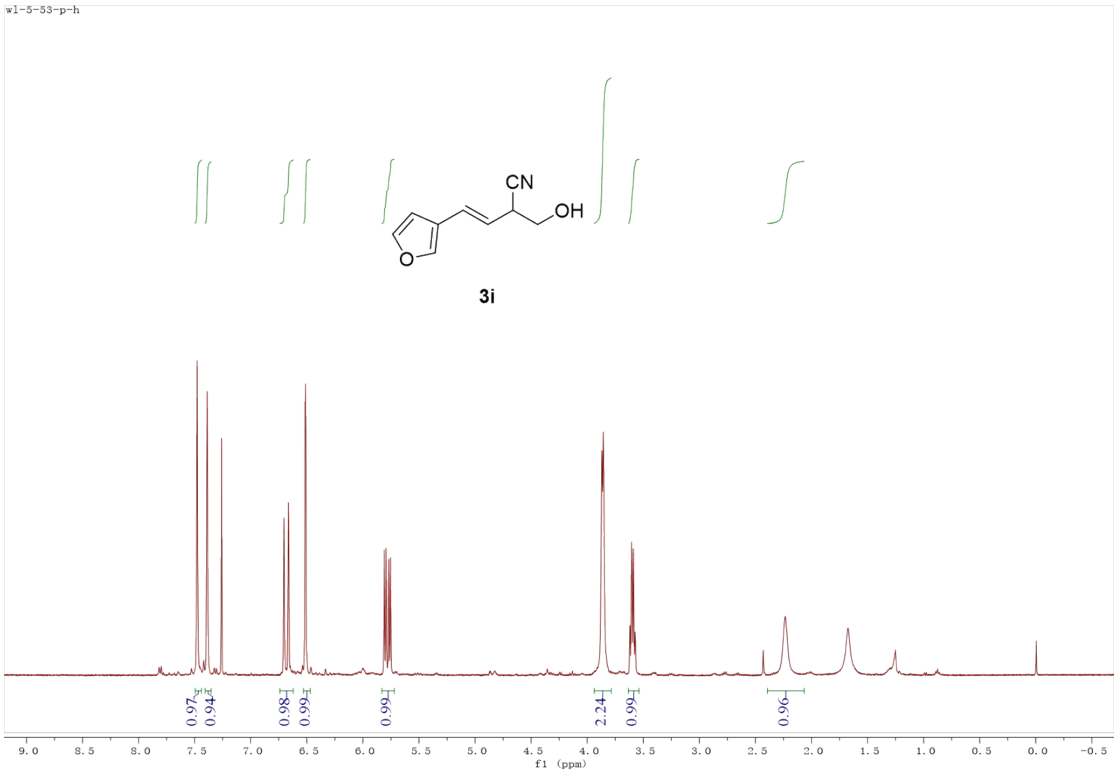

wl-5-50-oxi-13c
138.33
135.48
135.24
129.29
128.59
127.29
123.74
118.84
118.79
77.32
77.00
76.68
63.31
38.05
21.30
CN
OH
Me
3f
f1 (ppm)

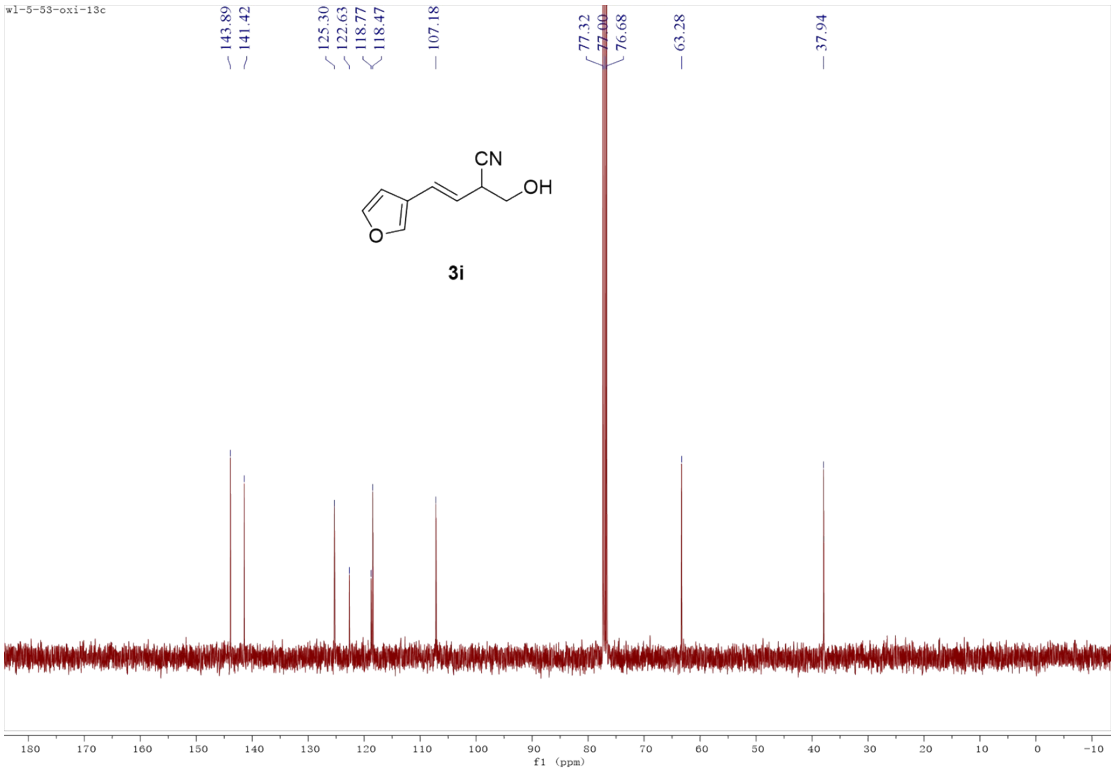

wl-5-51-p-1h
CN
MeO
OH
3g
1.14
0.98
0.98
0.96
1.02
1.00
1.94
2.87
1.00
1.07
f1 (ppm)

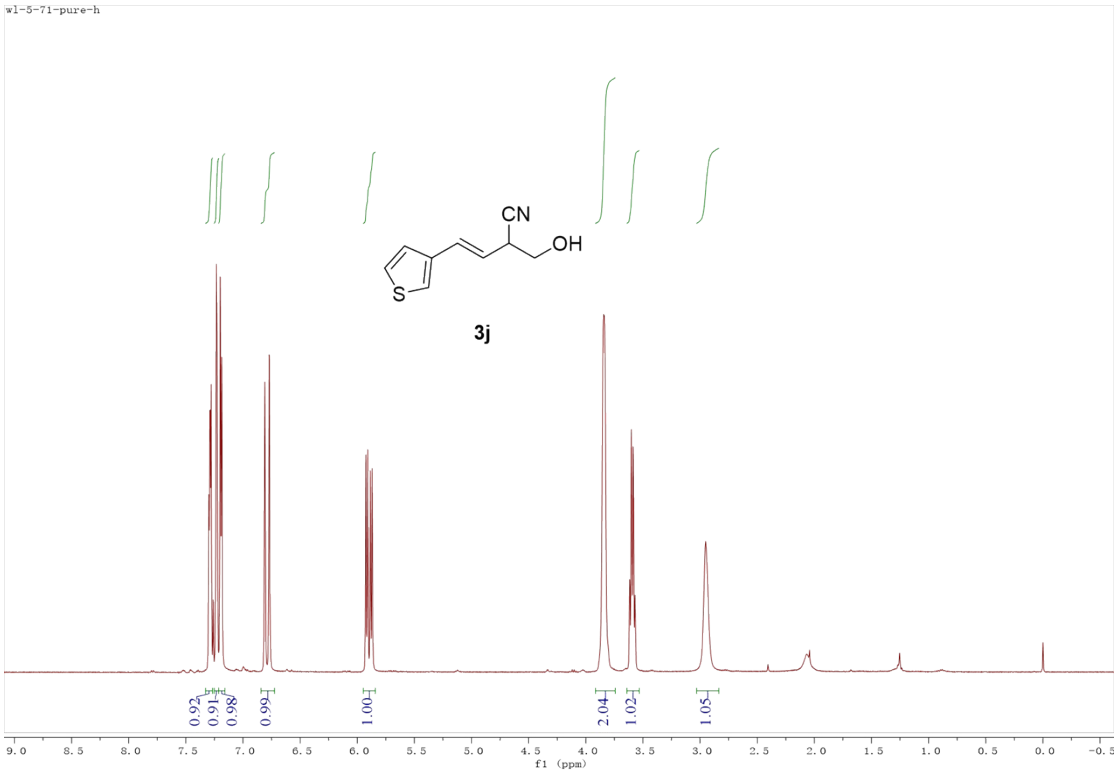

wl-5-51-p-13c
159.79
136.71
135.31
129.73
119.37
119.19
118.72
114.18
111.90
77.32
77.00
76.68
63.30
55.25
38.01
CN
MeO
OH
3g
f1 (ppm)

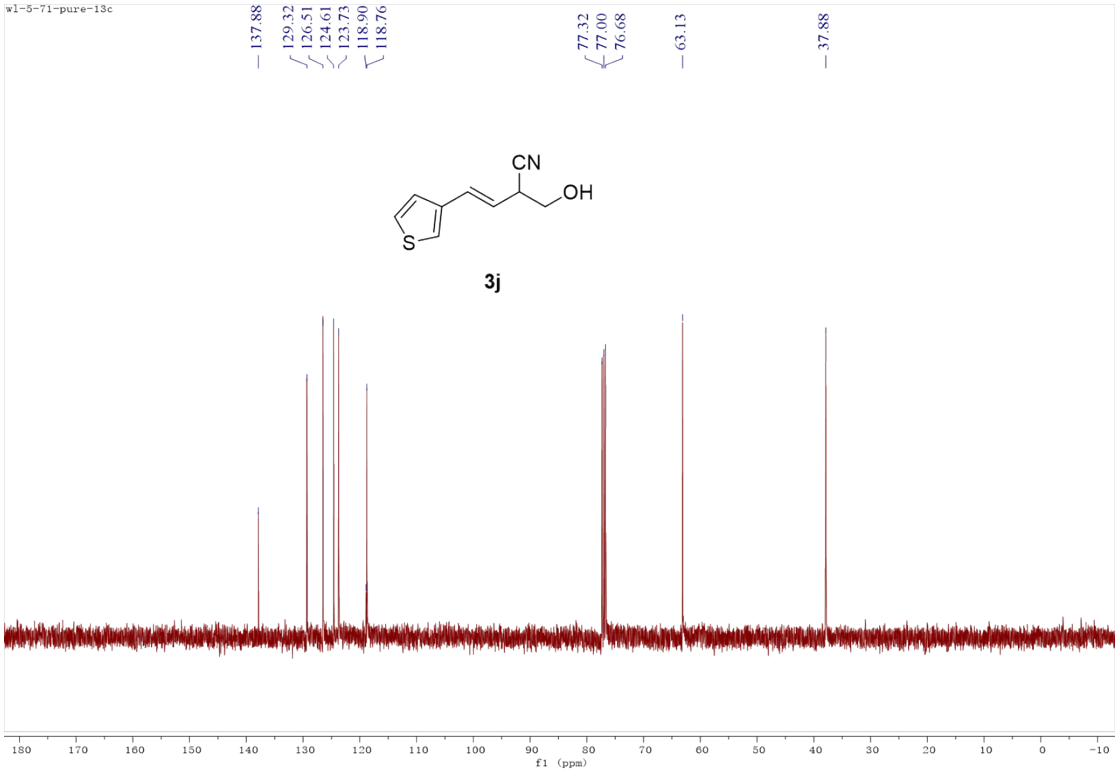

wl-5-52-p-h
CN
OH
3h
3.14
1.07
1.11
2.17
1.00
1.01
2.07
0.99
1.02
f1 (ppm)

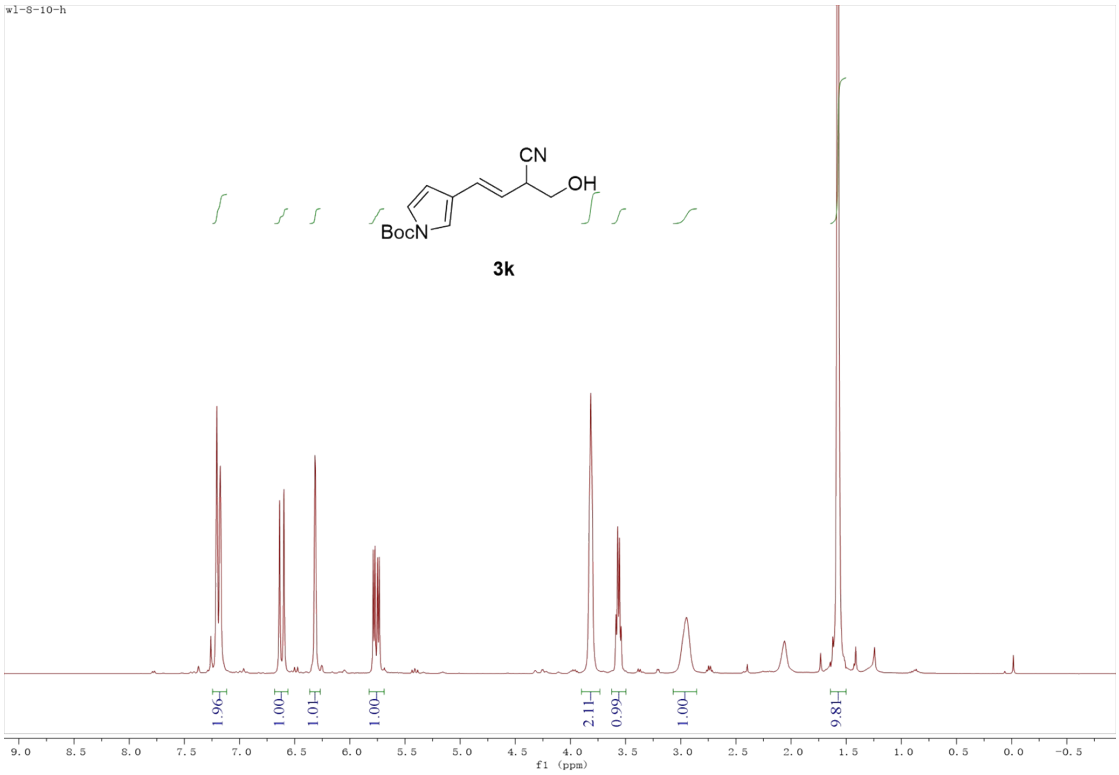

wl-5-52-p-13c
135.42
133.33
133.25
132.71
128.43
128.09
127.65
127.15
126.49
126.37
123.10
119.30
118.83
77.32
77.00
76.68
63.31
38.13
CN
OH
3h
f1 (ppm)

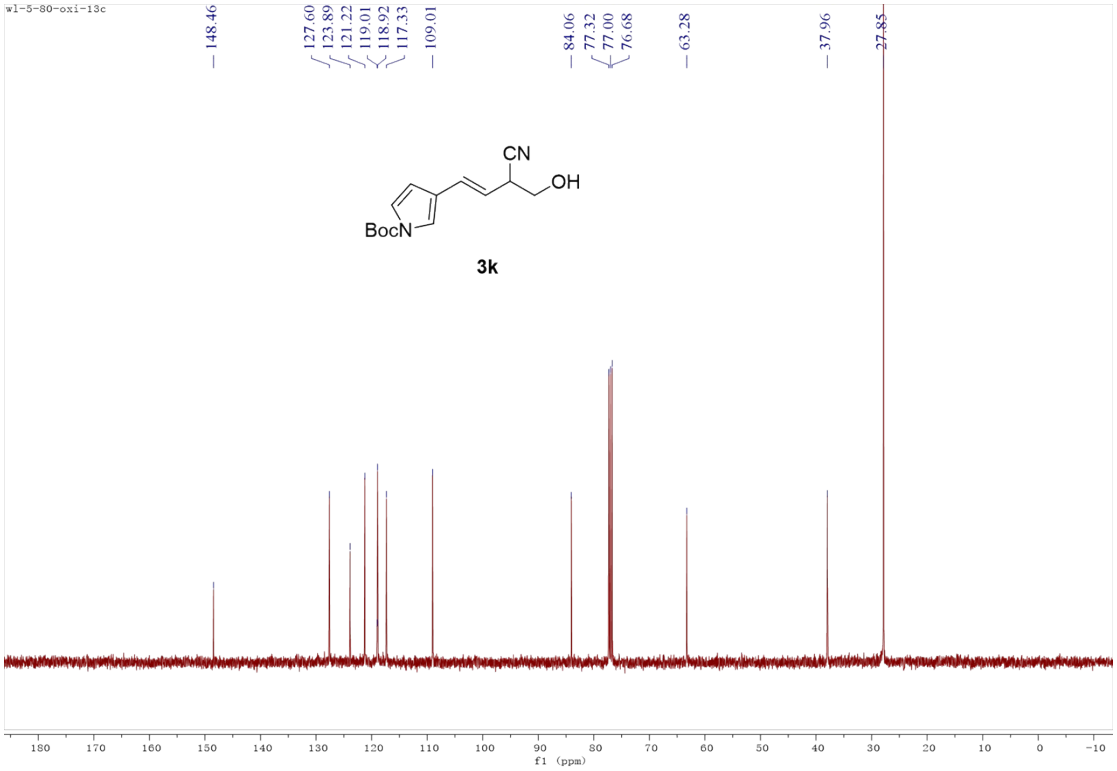

wl-5-53-p-h
CN
OH
O
3i
0.97
0.94
0.98
0.99
0.99
2.24
0.99
0.96
f1 (ppm)

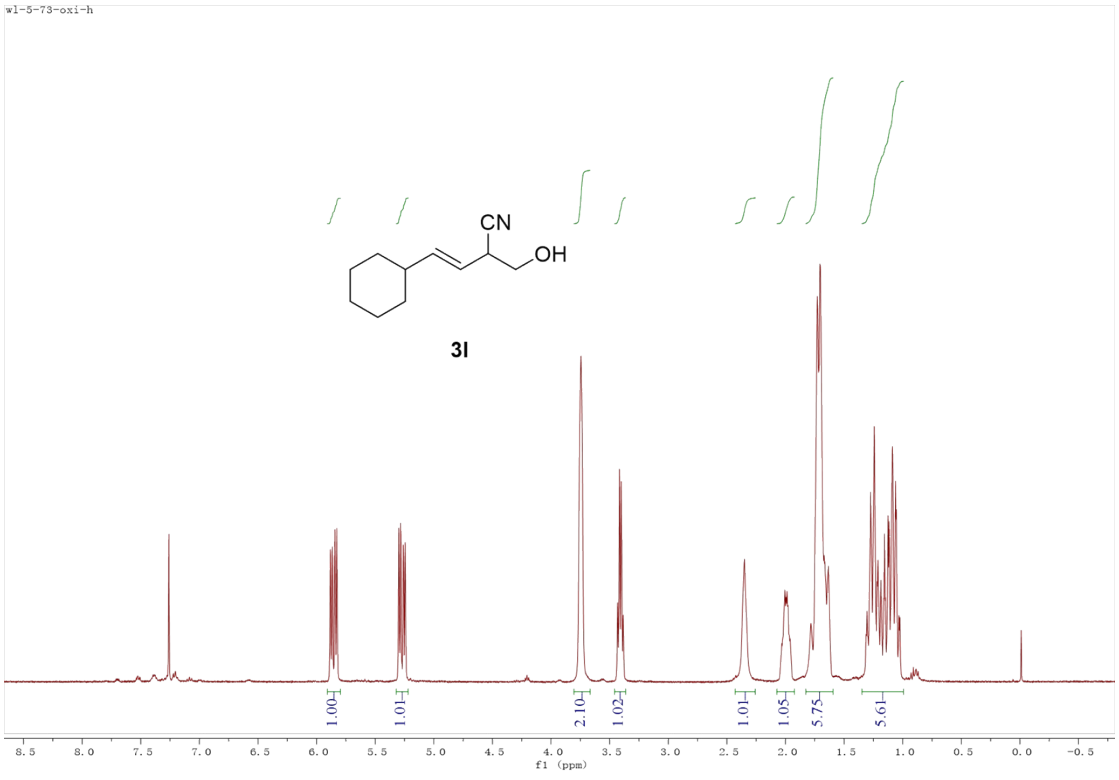

wl-5-53-oxi-13c
143.89
141.42
125.30
122.63
118.77
118.47
107.18
77.32
77.00
76.68
63.28
37.94
CN
OH
O
3i
f1 (ppm)

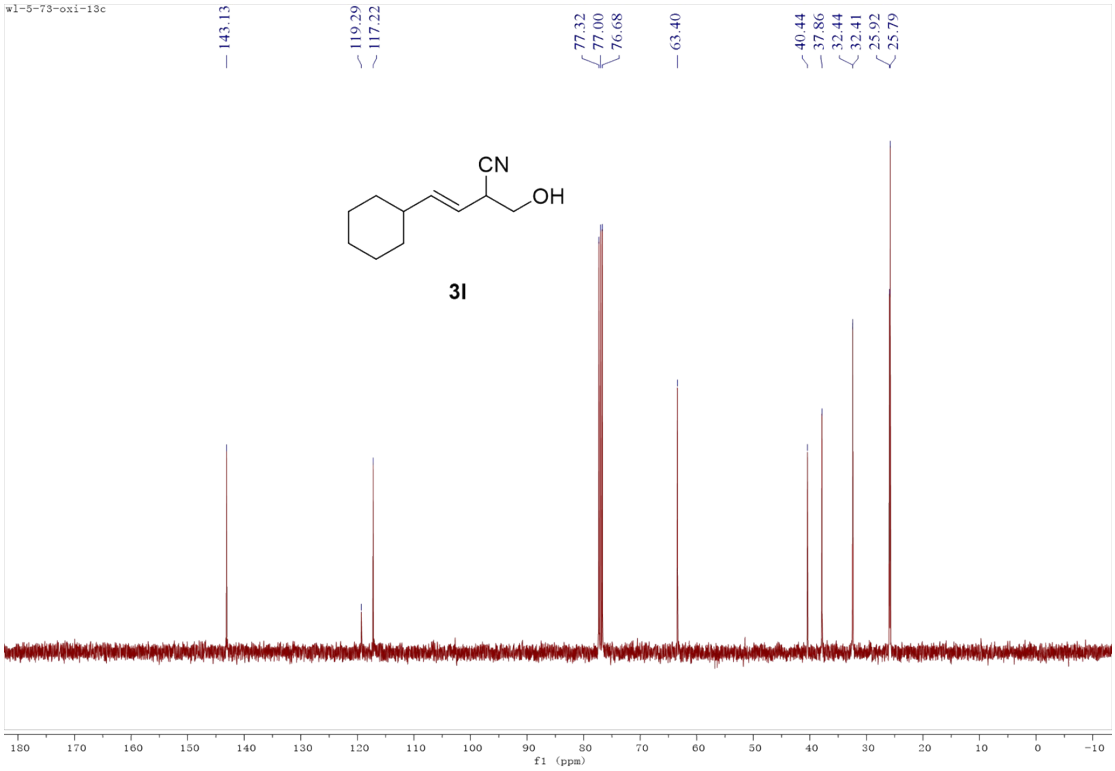

wl-5-71-pure-h
CN
OH
S
3j
0.92
0.91
0.98
0.99
1.00
2.04
1.02
1.05
f1 (ppm)

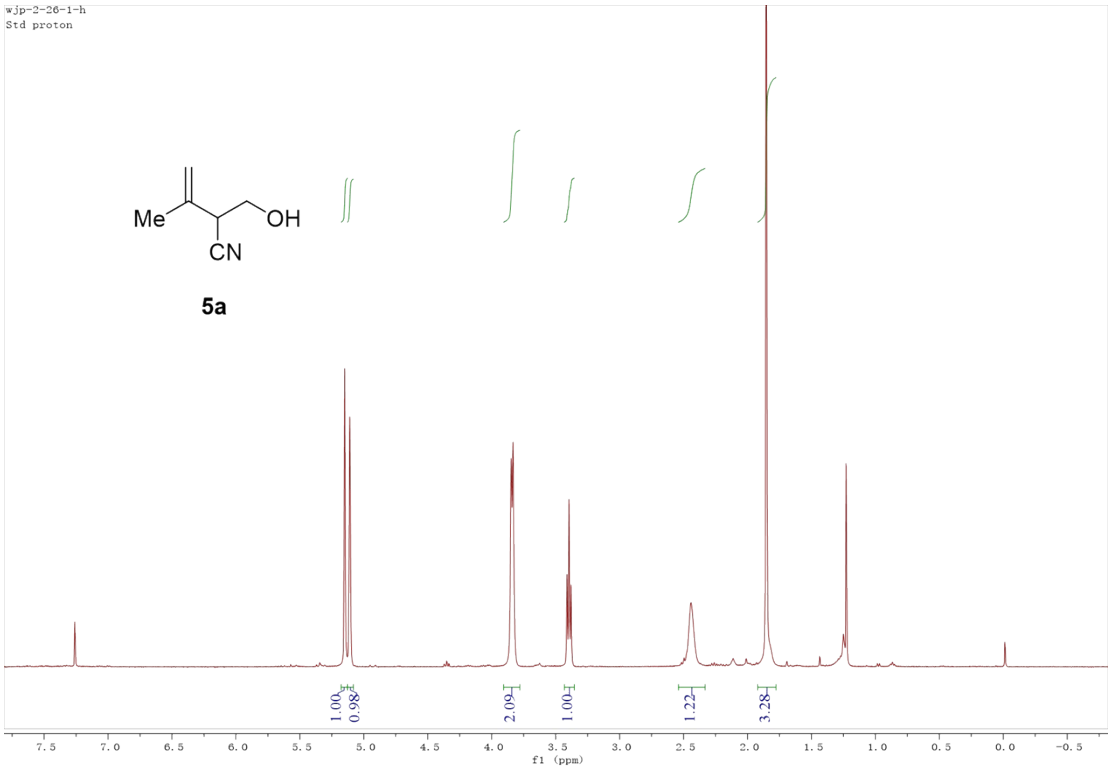

wl-5-71-pure-13c
137.88
129.32
126.51
124.61
123.73
118.90
118.76
77.32
77.00
76.68
63.13
37.88
CN
OH
S
3j
f1 (ppm)

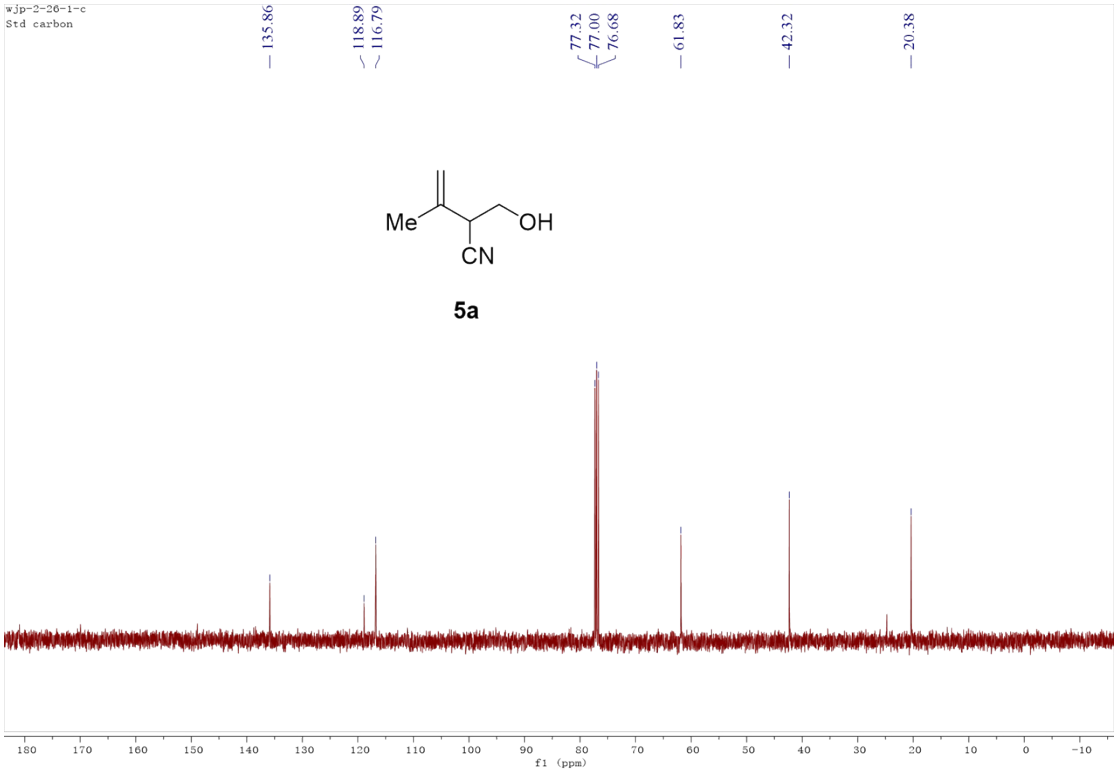

wl-8-10-h
CN
OH
BocN
3k
1.96
1.00
1.01
1.00
2.11
0.99
1.00
9.81
f1 (ppm)


wl-5-80-oxi-13c
148.46
127.60
123.89
121.22
119.01
118.92
117.33
109.01
84.06
77.32
77.00
76.68
63.28
37.96
27.85
CN
OH
BocN
3k
f1 (ppm)

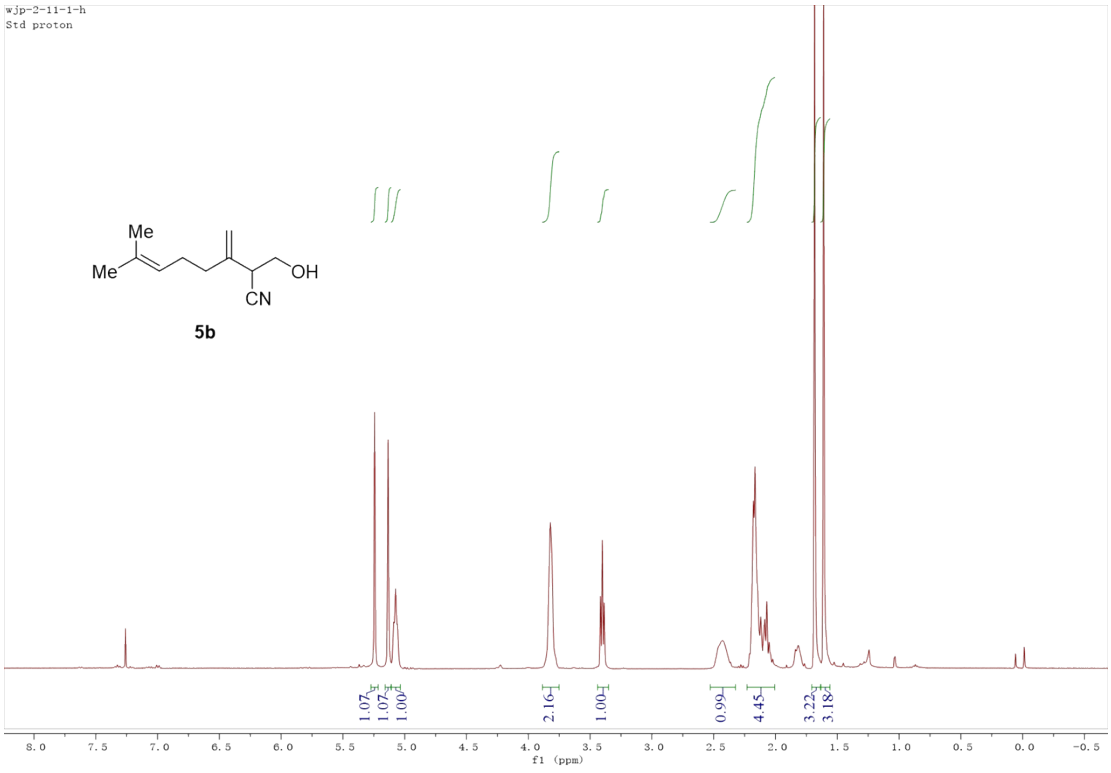

wl-5-73-oxi-h
CN
OH
3l
1.00
1.01
2.10
1.02
1.01
1.05
5.75
5.61
f1 (ppm)


wl-5-73-oxi-13c
143.13
119.29
117.22
77.32
77.00
76.68
63.40
40.44
37.86
32.44
32.41
25.92
25.79
CN
OH
3l
f1 (ppm)

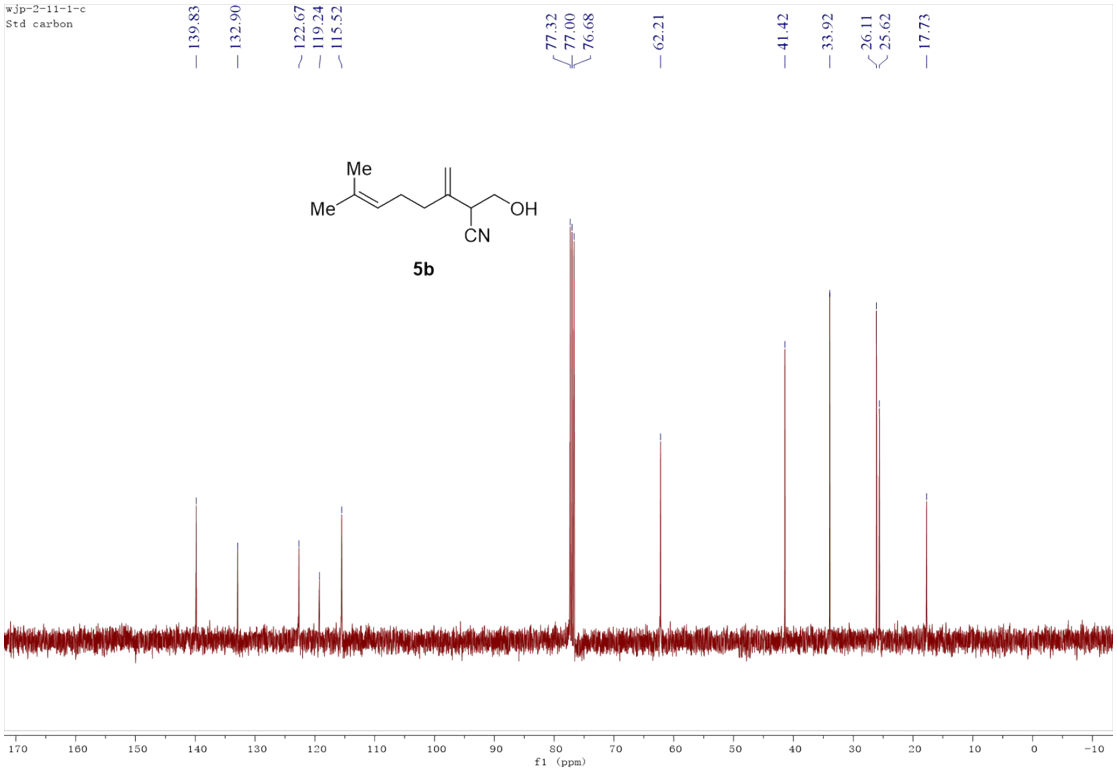

wjp-2-26-1-h
Std proton
Me
OH
CN
5a
1.00
0.98
2.09
1.00
1.22
3.28
f1 (ppm)

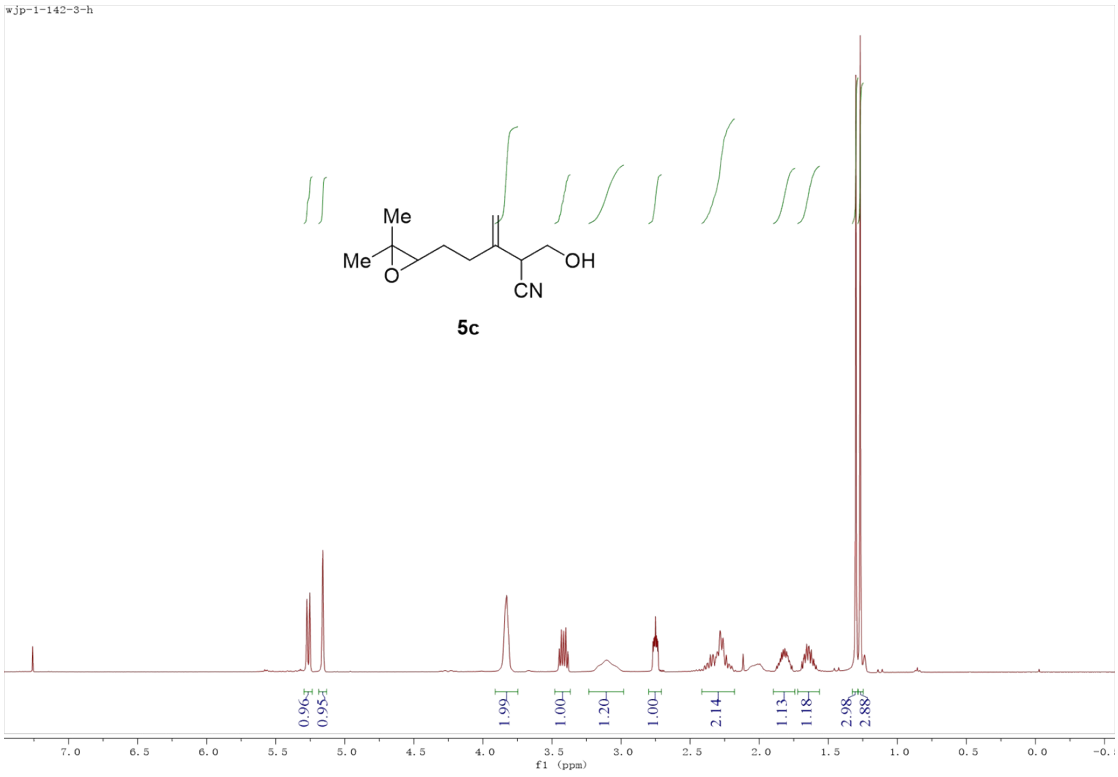

wjp-2-26-1-c
Std carbon
135.86
118.89
116.79
77.32
77.00
76.68
61.83
42.32
20.38
Me
OH
CN
f1 (ppm)

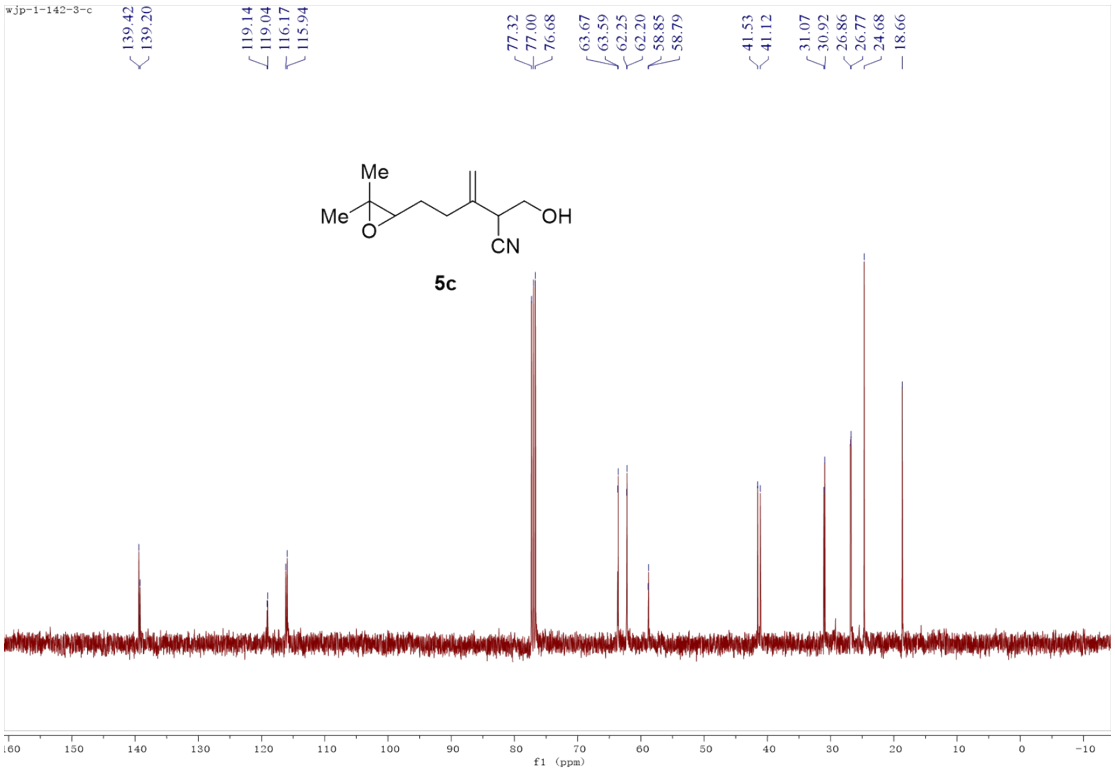
5a

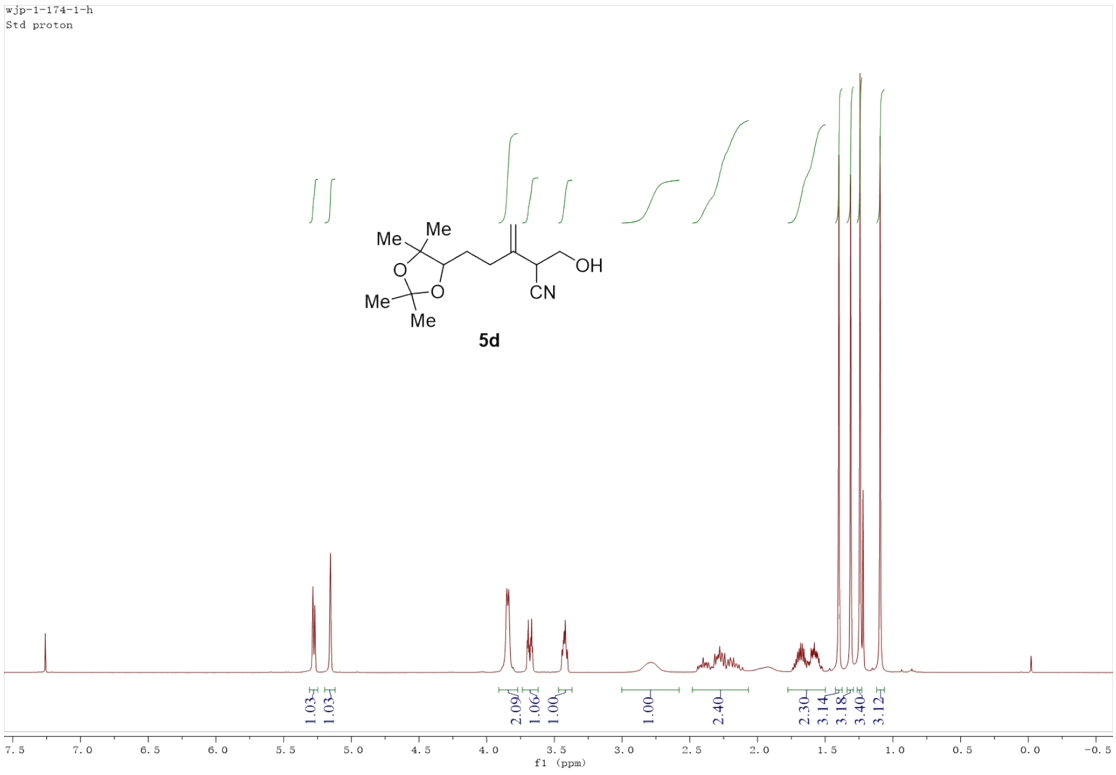

wjp-2-11-1-h
Std proton
Me
Me
OH
CN
1.07
1.07
1.00
2.16
1.00
0.99
4.45
3.22
3.18
f1 (ppm)

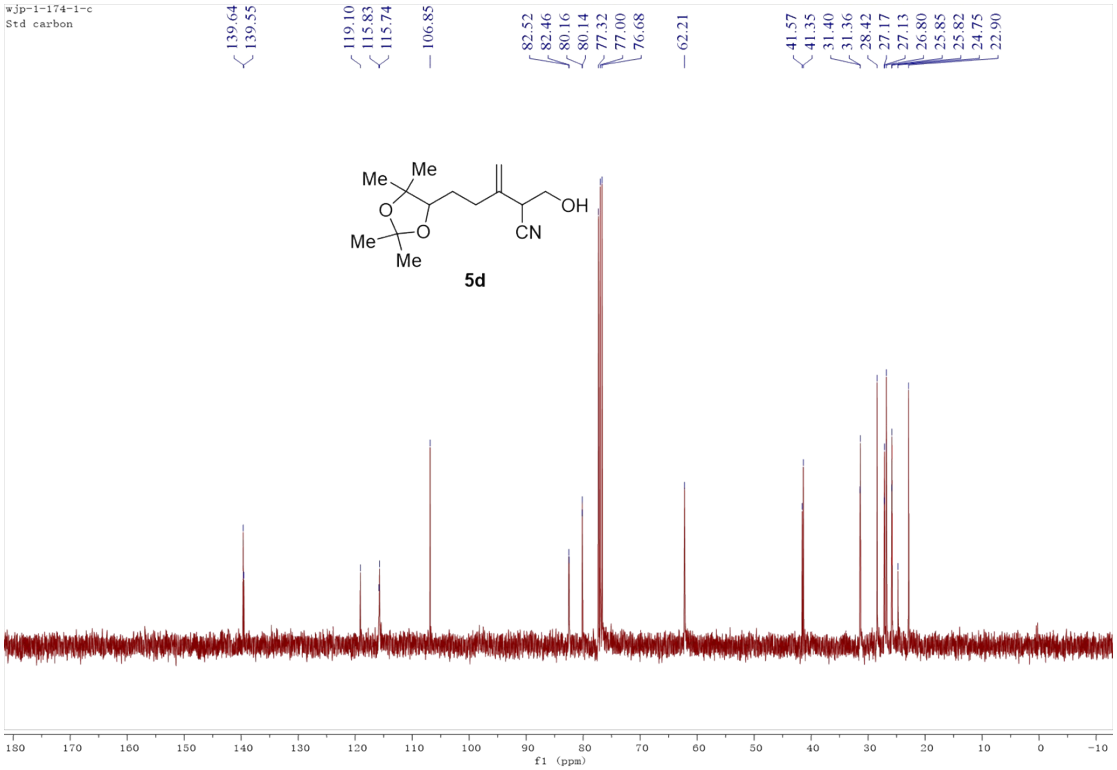
5b

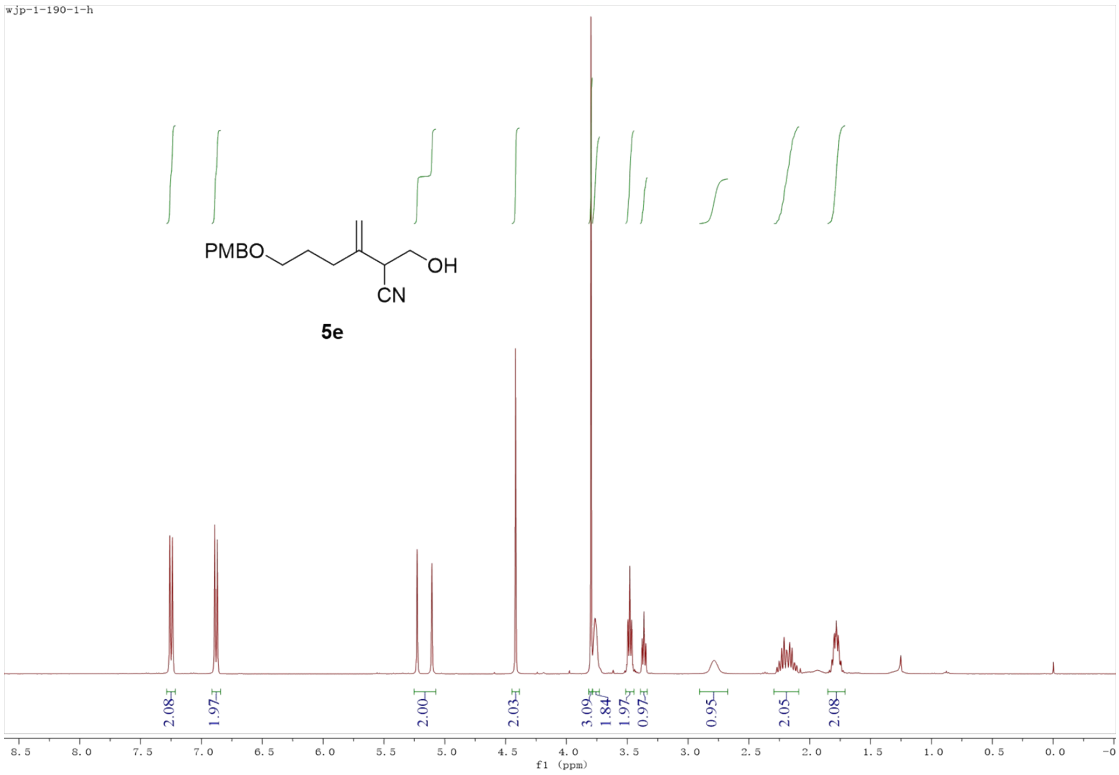

wjp-2-11-1-c
Std carbon
139.83
132.90
122.67
119.24
115.52
77.32
77.00
76.68
62.21
41.42
33.92
26.11
25.62
17.73
Me
Me
OH
CN
5b
f1 (ppm)

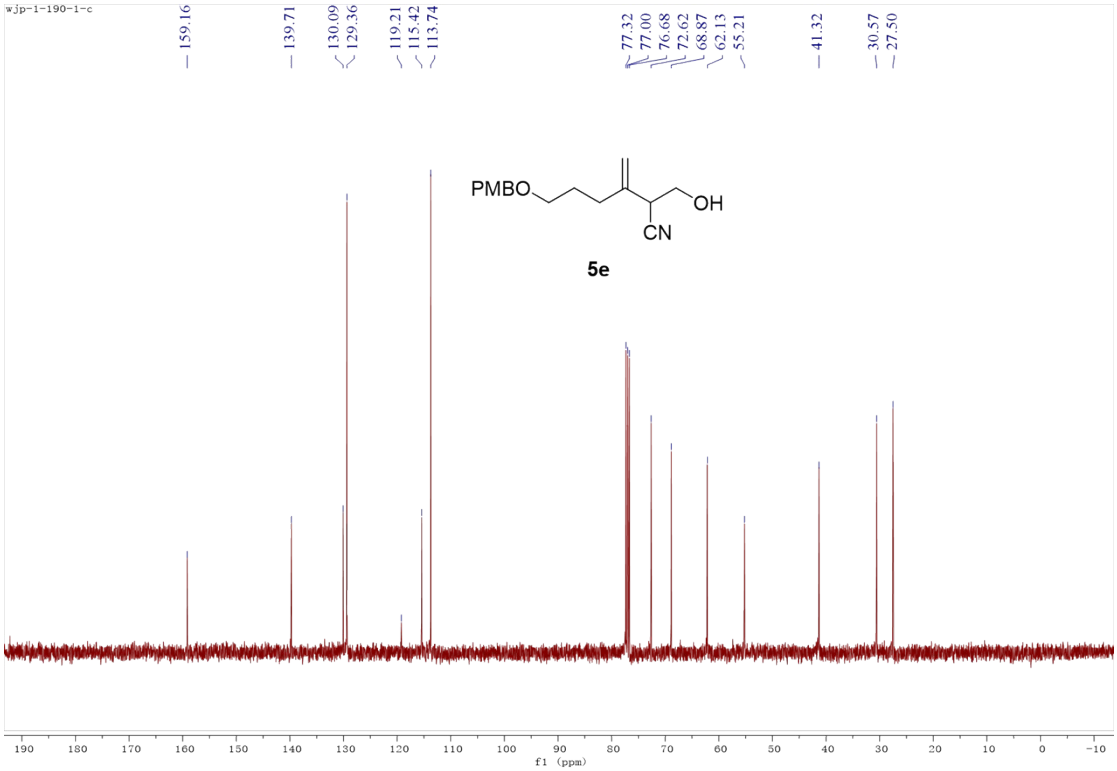

wjp-1-142-3-h
Me
Me
O
OH
CN
5c
0.96
0.95
1.99
1.00
1.20
1.00
2.14
1.13
1.18
2.98
2.88
f1 (ppm)

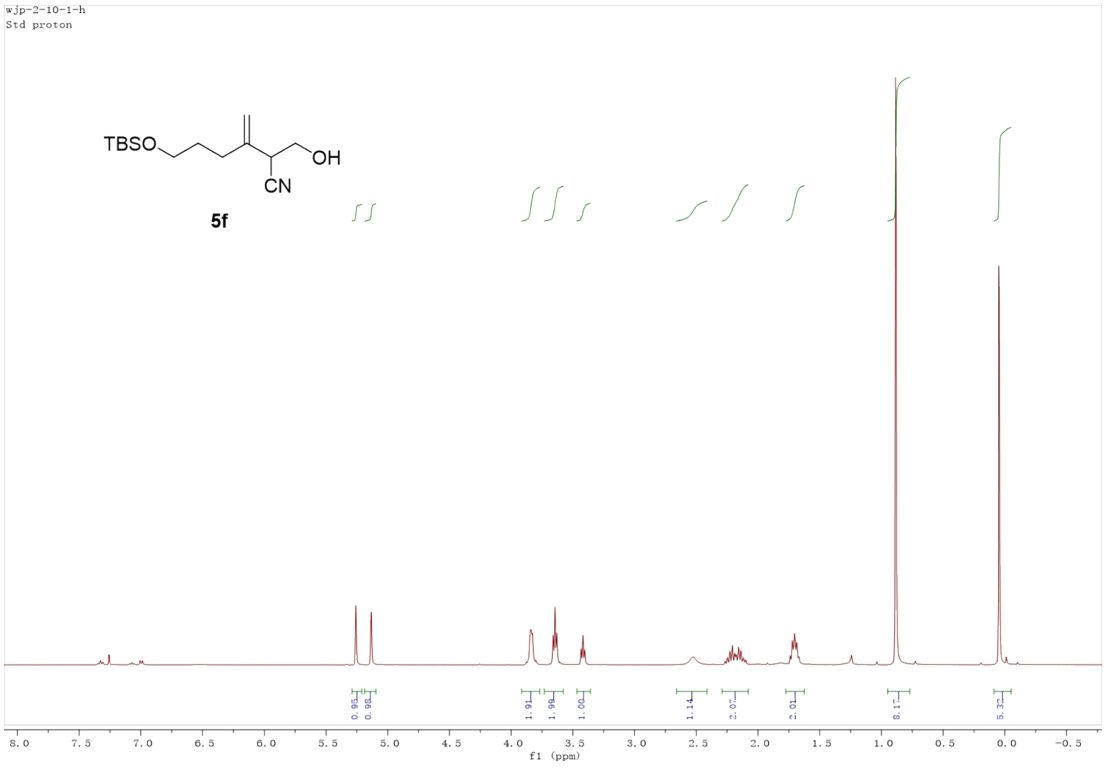

wjp-1-142-3-c
139.42
139.20
119.14
119.04
116.17
115.94
77.32
77.00
76.68
63.67
63.59
62.25
62.20
58.85
58.79
41.53
41.12
31.07
30.92
26.86
26.77
24.68
18.66
Me
Me
O
OH
CN
5c
f1 (ppm)

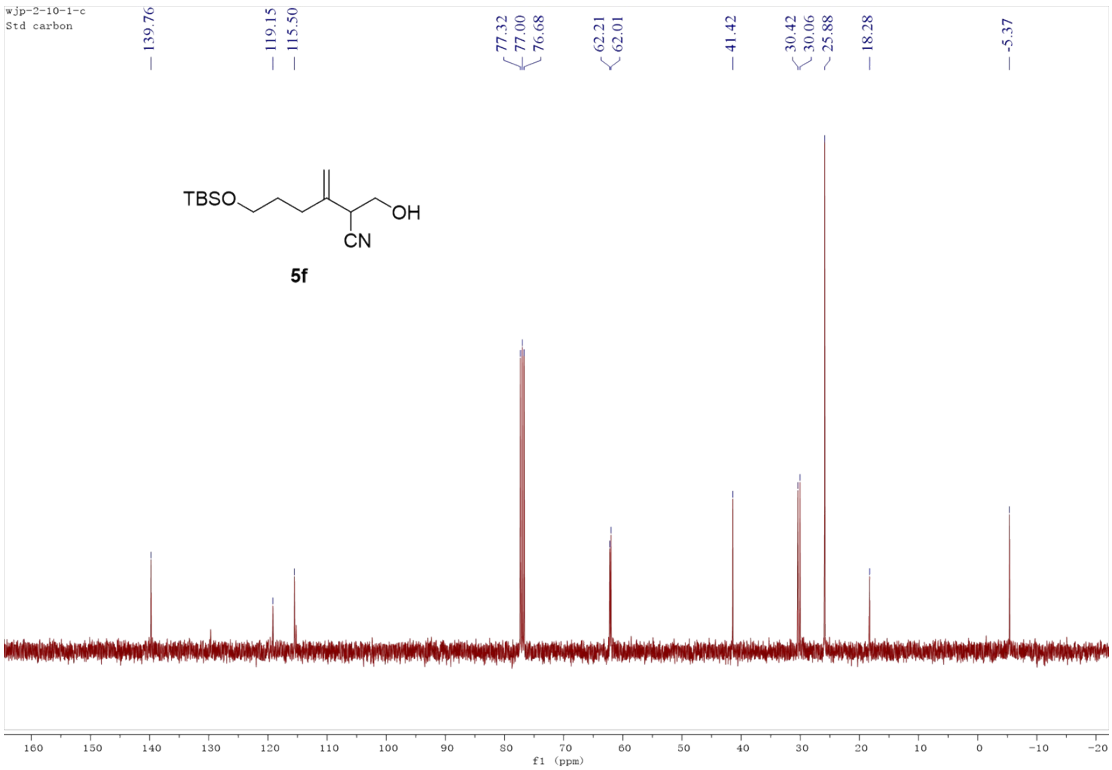

wjp-1-174-1-h
Std proton
Me
Me
O
O
Me
Me
OH
CN
5d
1.03
1.03
2.09
1.06
1.00
1.00
2.40
2.30
3.14
3.18
3.40
3.12
f1 (ppm)

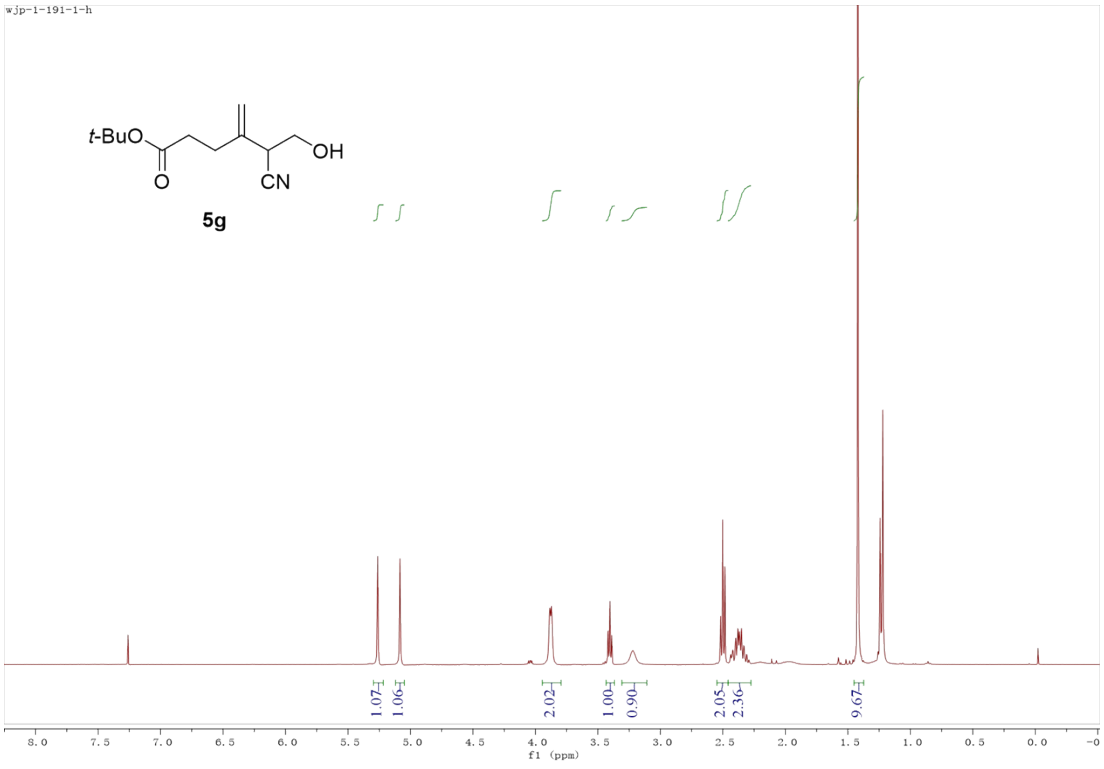

wjp-1-174-1-c
Std carbon
139.64
139.55
119.10
115.83
115.74
106.85
82.52
82.46
80.16
80.14
77.32
77.00
76.68
62.21
41.57
41.35
31.40
31.36
28.42
27.17
27.13
26.80
25.85
25.82
24.75
22.90
Me
Me
O
O
Me
Me
OH
CN
5d
f1 (ppm)

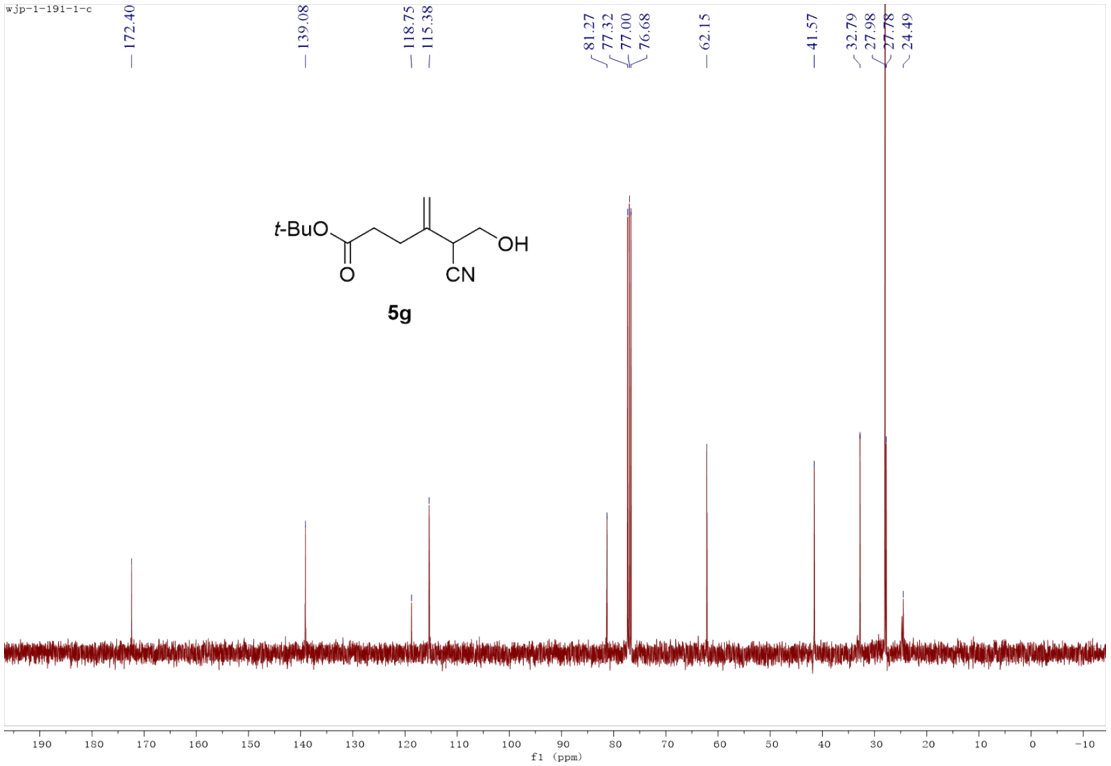

wjp-1-190-1-h
PMBO
OH
CN
5e
2.08
1.97
2.00
2.03
3.09
1.84
1.97
0.97
0.95
2.05
2.08
f1 (ppm)

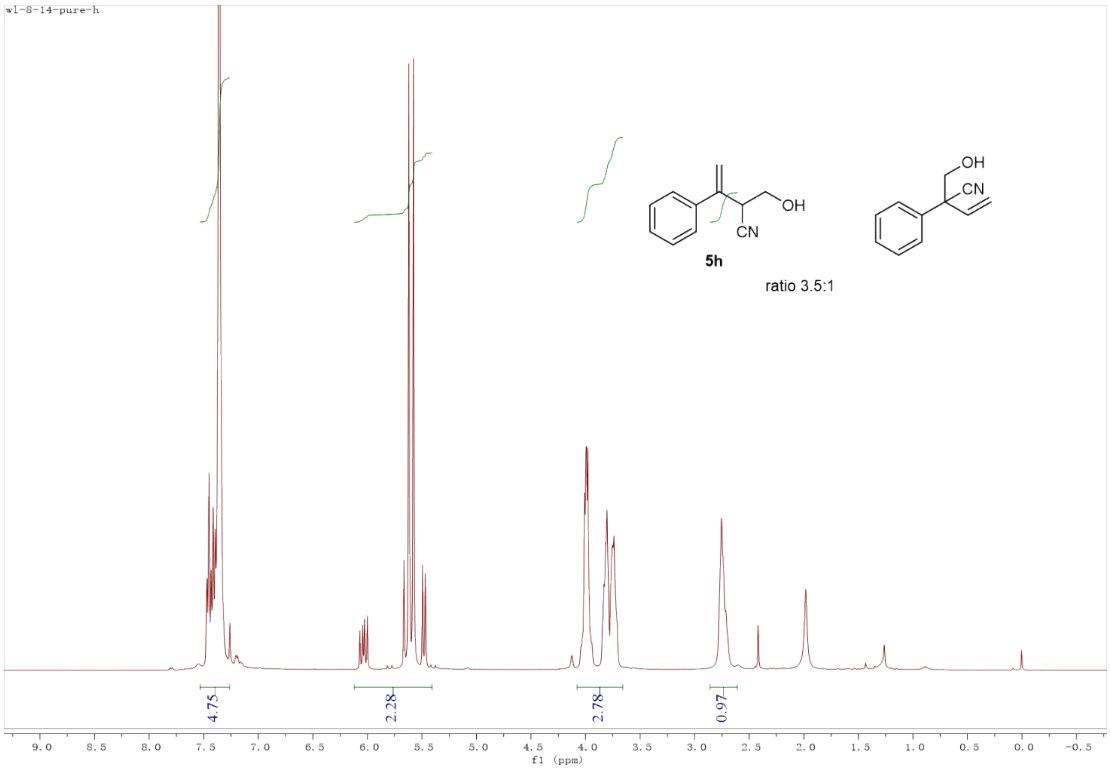

wjp-1-190-1-c
159.16
139.71
130.09
129.36
119.21
115.42
113.74
77.32
77.00
76.68
72.62
68.87
62.13
55.21
41.32
30.57
27.50
PMBO
OH
CN
5e
f1 (ppm)

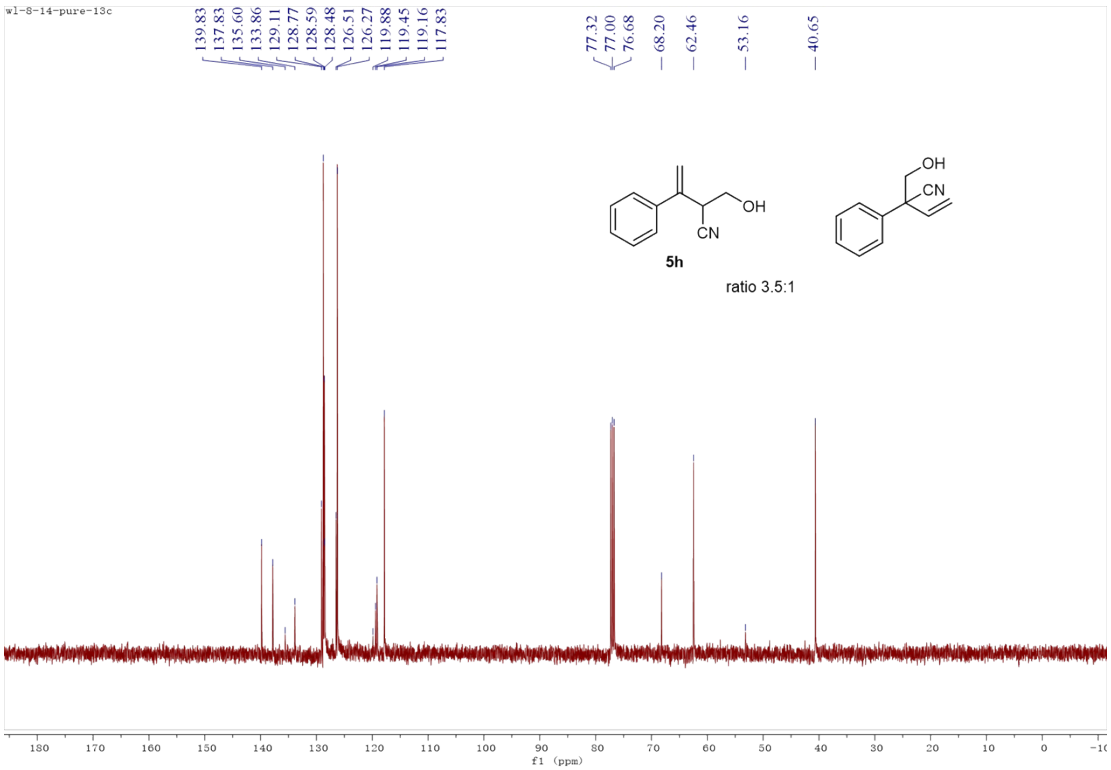

wjp-2-10-1-h
Std proton
TBSO
OH
CN
5f
0.95
0.96
1.91
1.96
1.00
1.14
2.07
2.01
8.17
5.32
f1 (ppm)

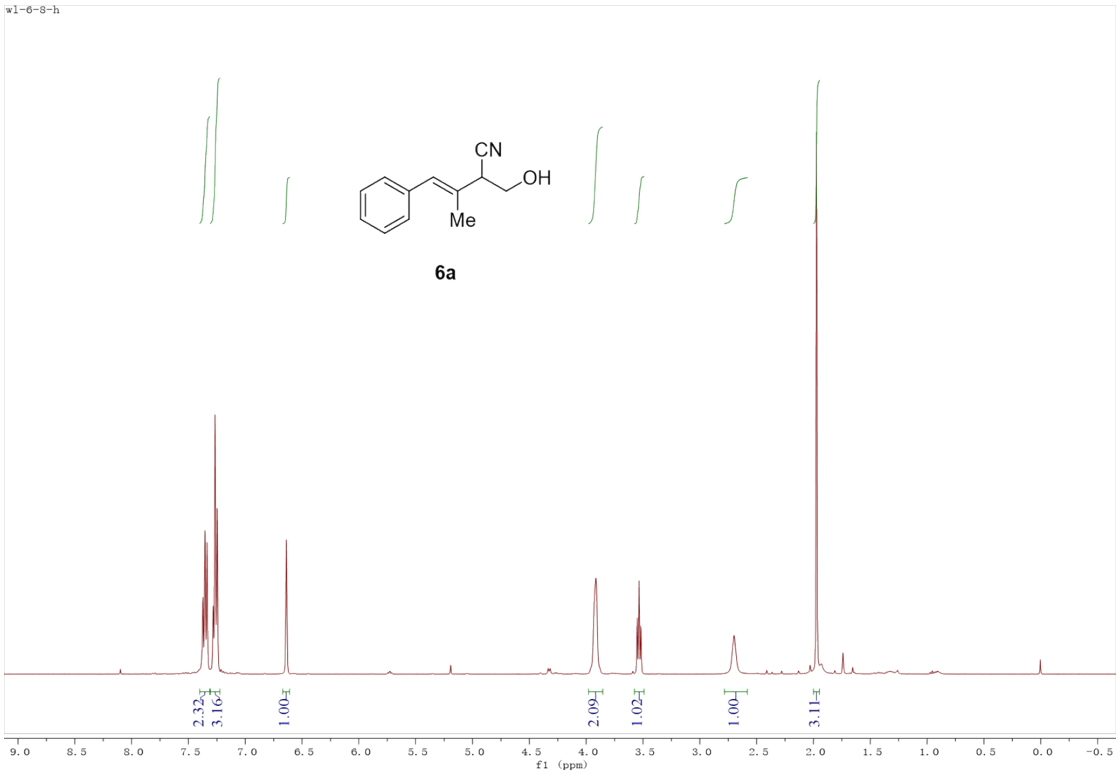

wjp-2-10-1-c
Std carbon
139.76
119.15
115.50
77.32
77.00
76.68
62.21
62.01
41.42
30.42
30.06
25.88
18.28
-5.37
TBSO
OH
CN
5f
f1 (ppm)

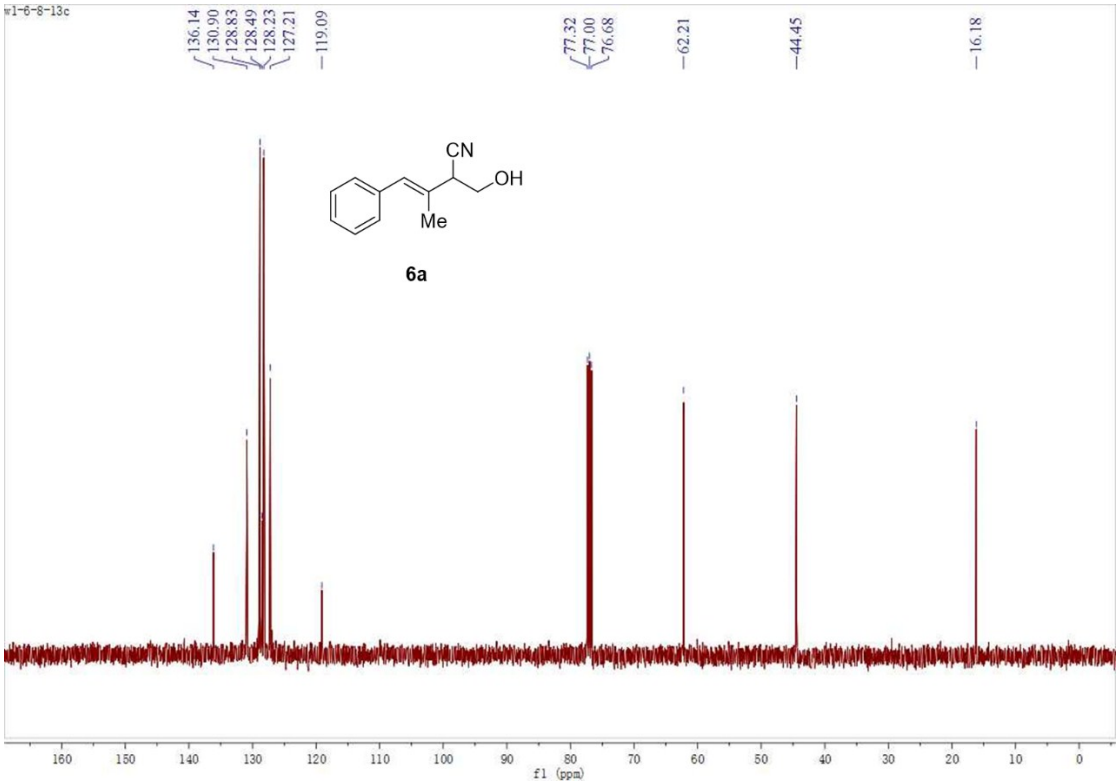

wjp-1-191-1-h
t-BuO
O
OH
CN
5g
1.07
1.06
2.02
1.00
0.90
2.05
2.36
9.67
f1 (ppm)


wjp-1-191-1-c
172.40
139.08
118.75
115.38
81.27
77.32
77.00
76.68
62.15
41.57
32.79
27.98
27.78
24.49
t-BuO
O
OH
CN
5g
f1 (ppm)

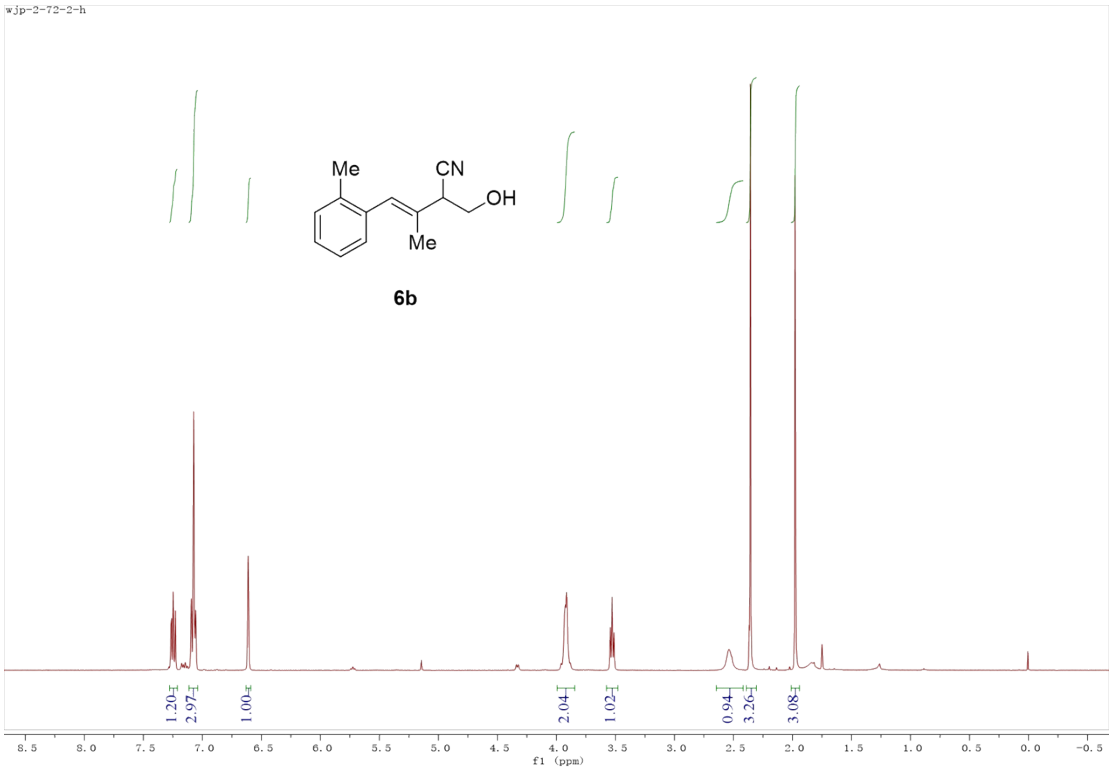

wl-8-14-pure-h
OH
CN
5h
ratio 3.5:1
4.75
2.28
2.78
0.97
f1 (ppm)


wl-8-14-pure-13c
139.83
137.83
135.60
133.86
129.11
128.77
128.59
128.48
126.51
126.27
119.88
119.45
119.16
117.83
77.32
77.00
76.68
68.20
62.46
53.16
40.65
OH
CN
5h
ratio 3.5:1
f1 (ppm)

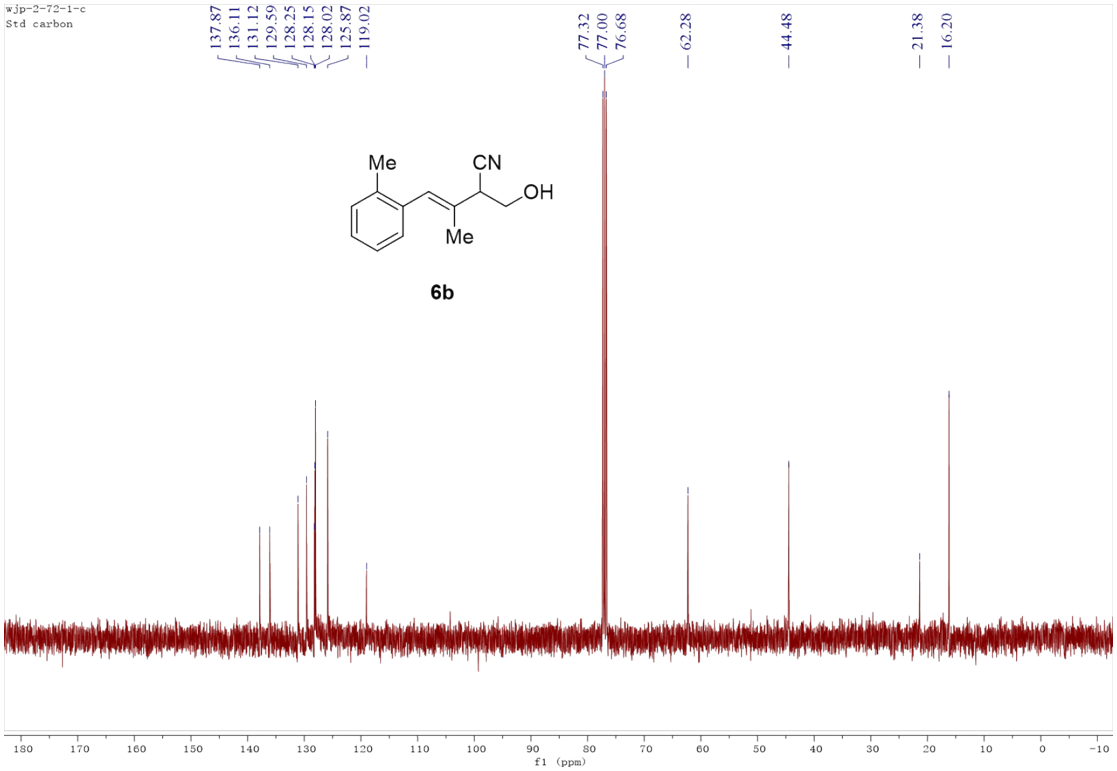

wl-6-8-h
CN
OH
Me
6a
2.32
3.16
1.00
2.09
1.02
1.00
3.11
f1 (ppm)

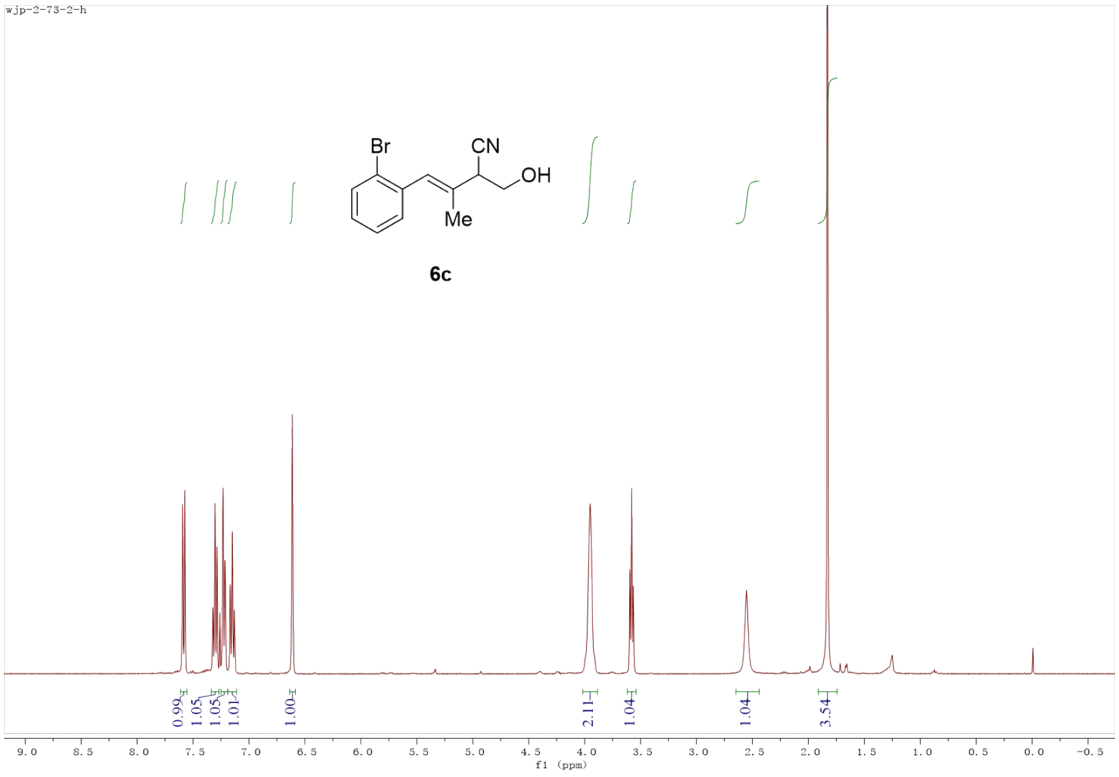

w1-6-8-13c
136.14
130.90
128.83
128.49
128.23
127.21
119.09
77.32
77.00
76.68
62.21
44.45
16.18
CN
OH
Me
f1 (ppm)

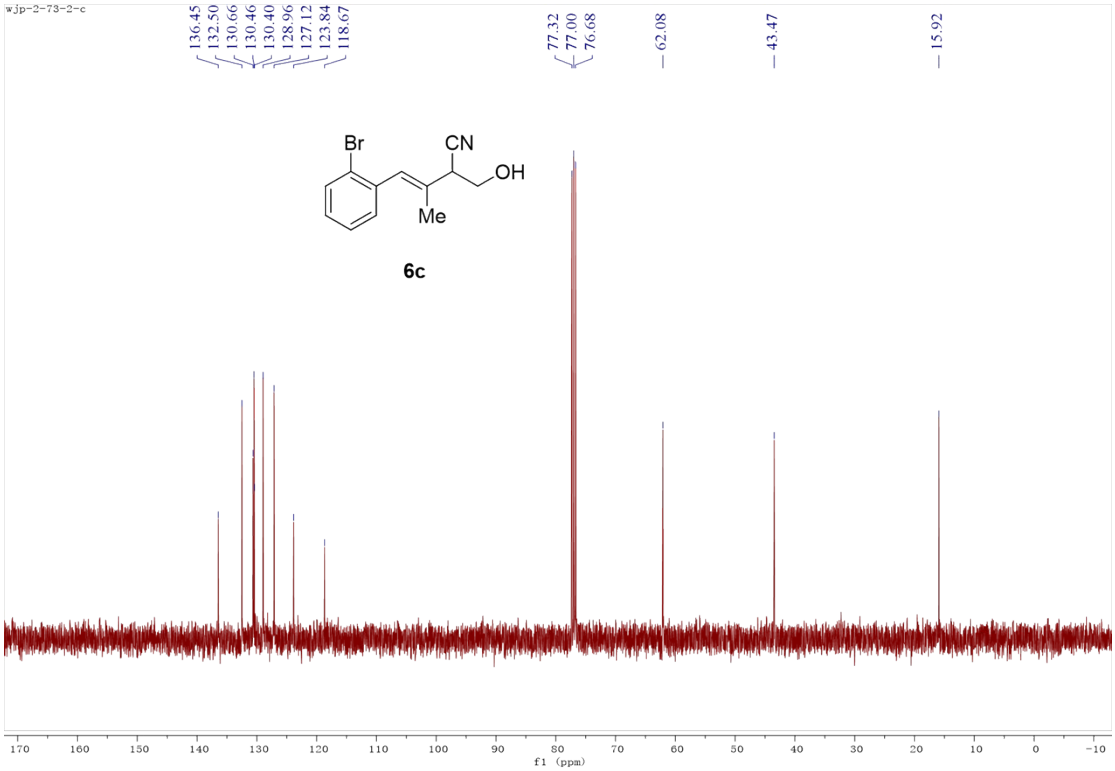
6a

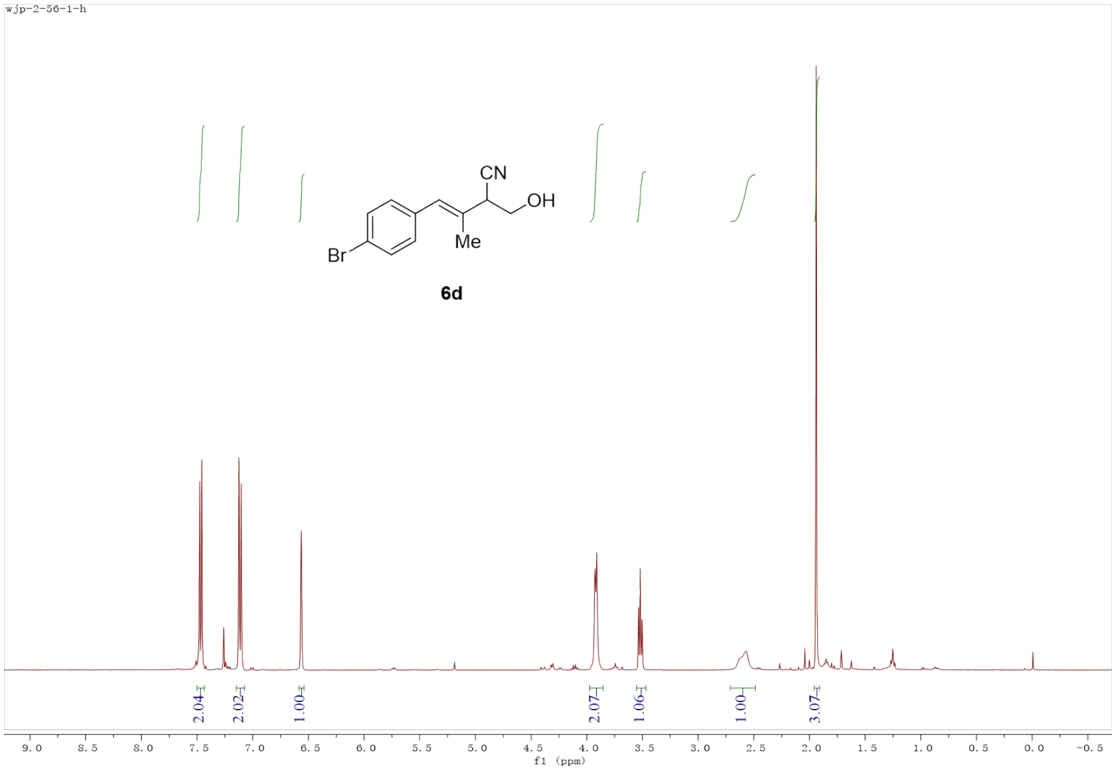

wjp-2-72-2-h
Me
CN
OH
Me
1.20
2.97
1.00
2.04
1.02
0.94
3.26
3.08
f1 (ppm)

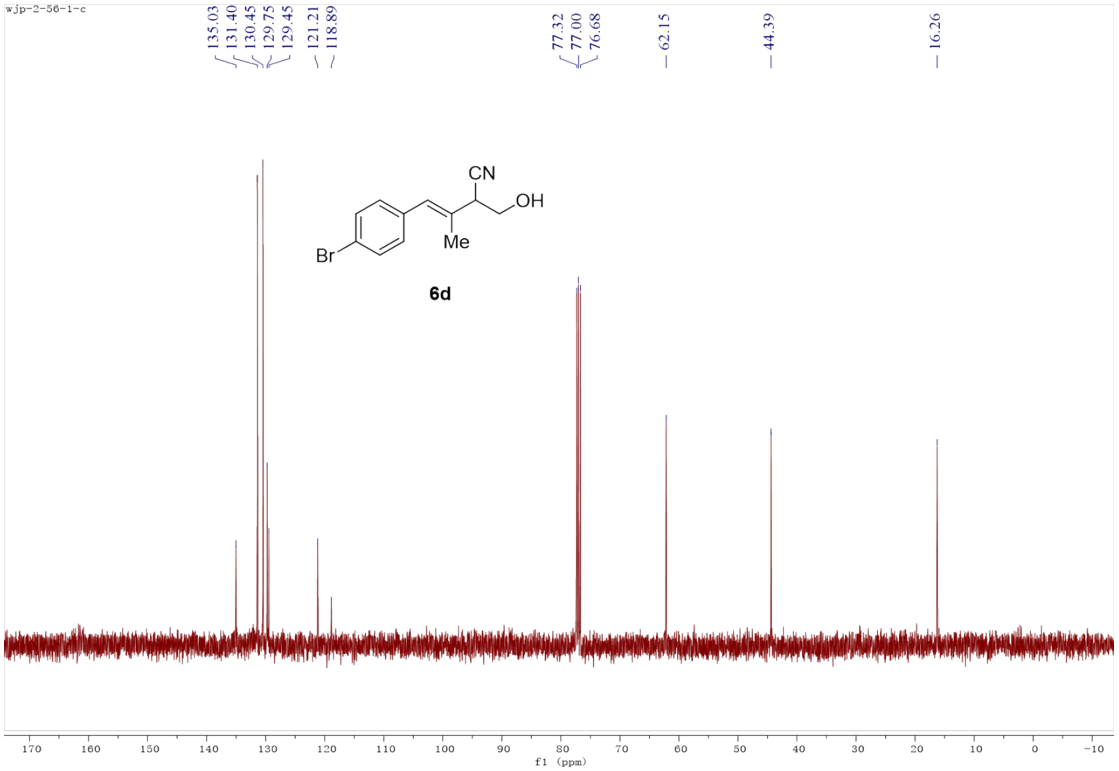
6b

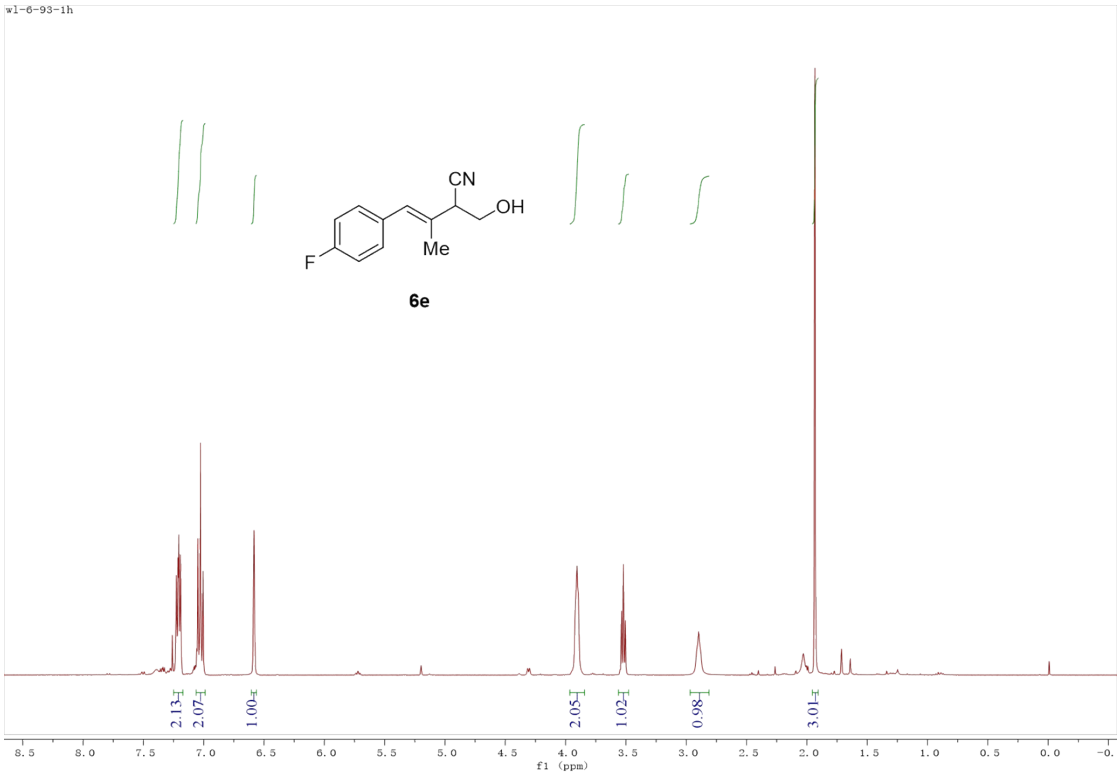

wjp-2-72-1-c
Std carbon
137.87
136.11
131.12
129.59
128.25
128.15
128.02
125.87
119.02
77.32
77.00
76.68
62.28
44.48
21.38
16.20
Me
CN
OH
Me
6b
f1 (ppm)

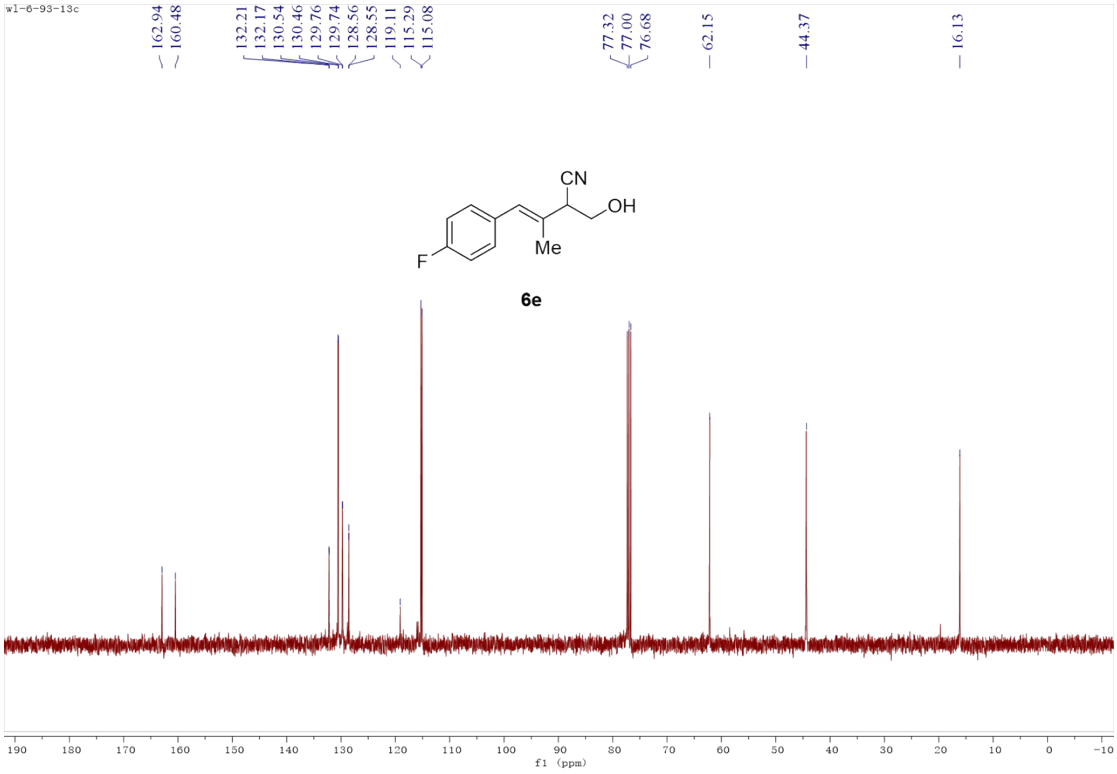

wjp-2-73-2-h
Br
CN
OH
Me
6c
0.99
1.05
1.05
1.01
1.00
2.11
1.04
1.04
3.54
f1 (ppm)

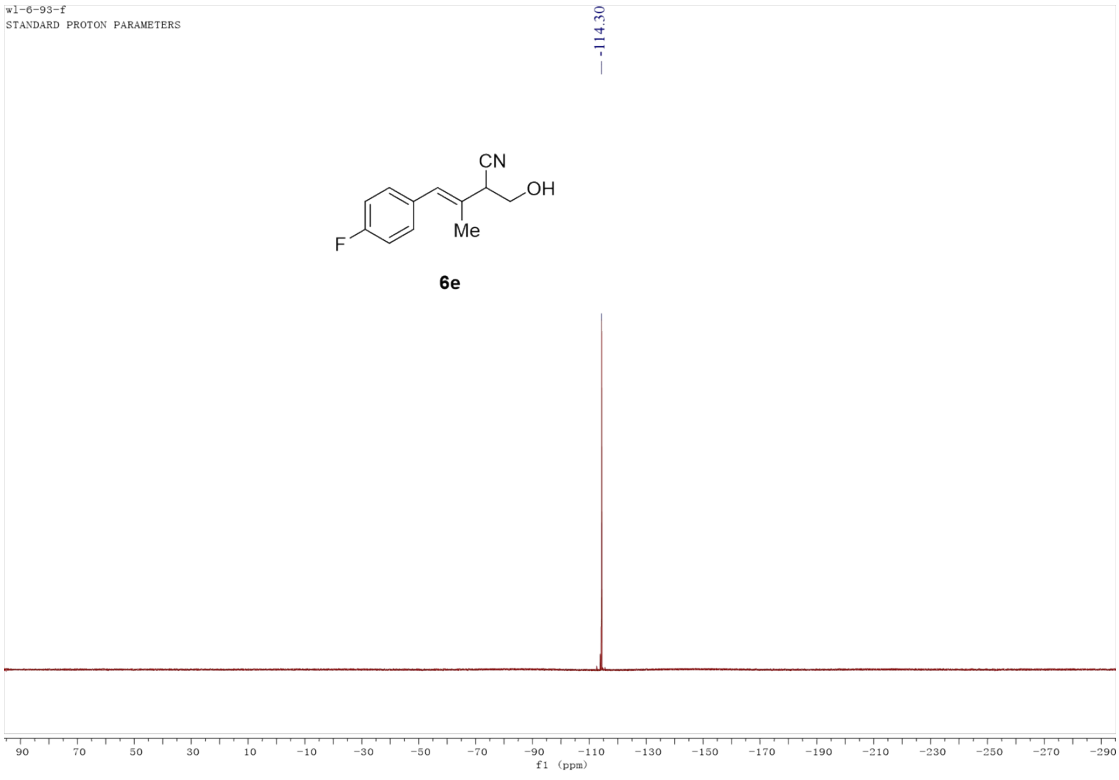

wjp-2-73-2-c
136.45
132.50
130.66
130.46
130.40
128.96
127.12
123.84
118.67
77.32
77.00
76.68
62.08
43.47
15.92
Br
CN
OH
Me
6c
f1 (ppm)

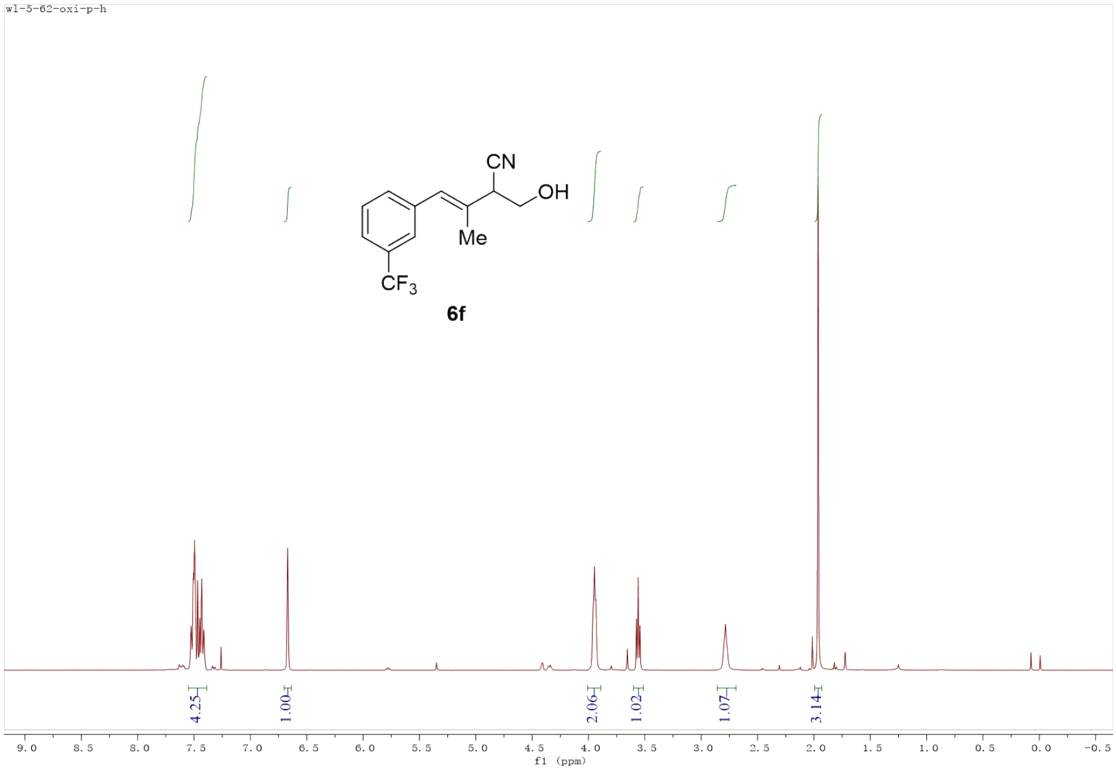

wjp-2-56-1-h
CN
OH
Me
Br
6d
2.04
2.02
1.00
2.07
1.06
1.00
3.07
f1 (ppm)

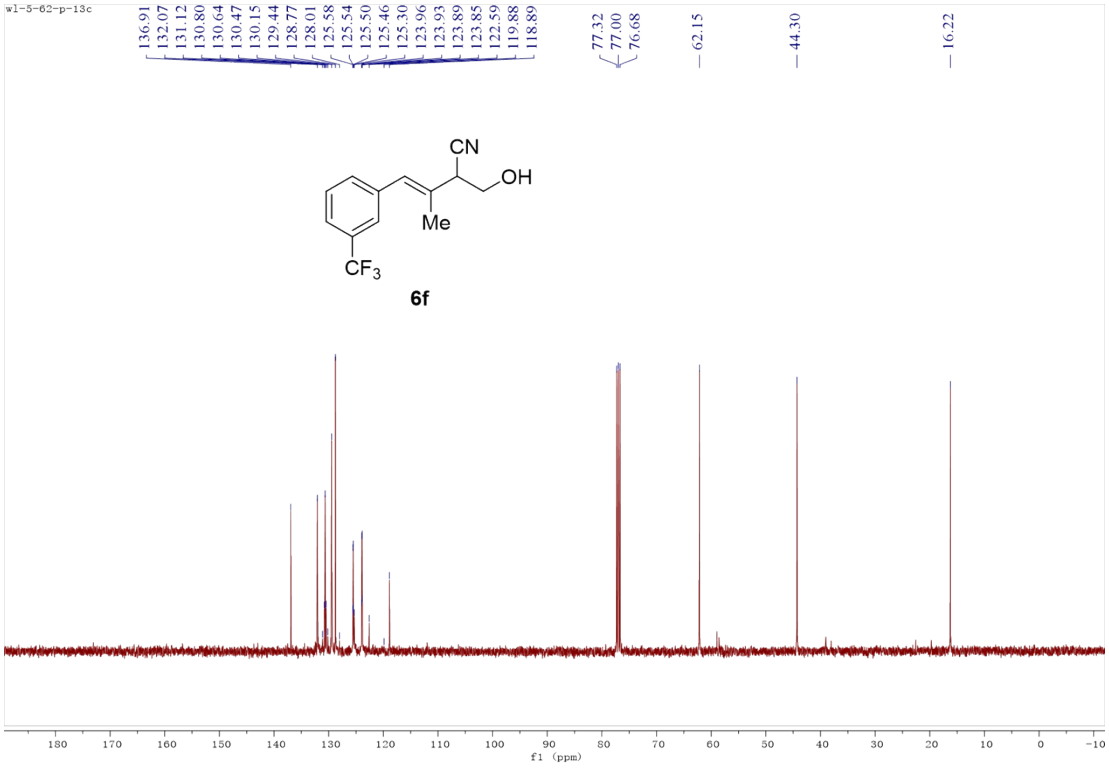

wjp-2-56-1-c
135.03
131.40
130.45
129.75
129.45
121.21
118.89
77.32
77.00
76.68
62.15
44.39
16.26
CN
OH
Me
Br
6d
f1 (ppm)

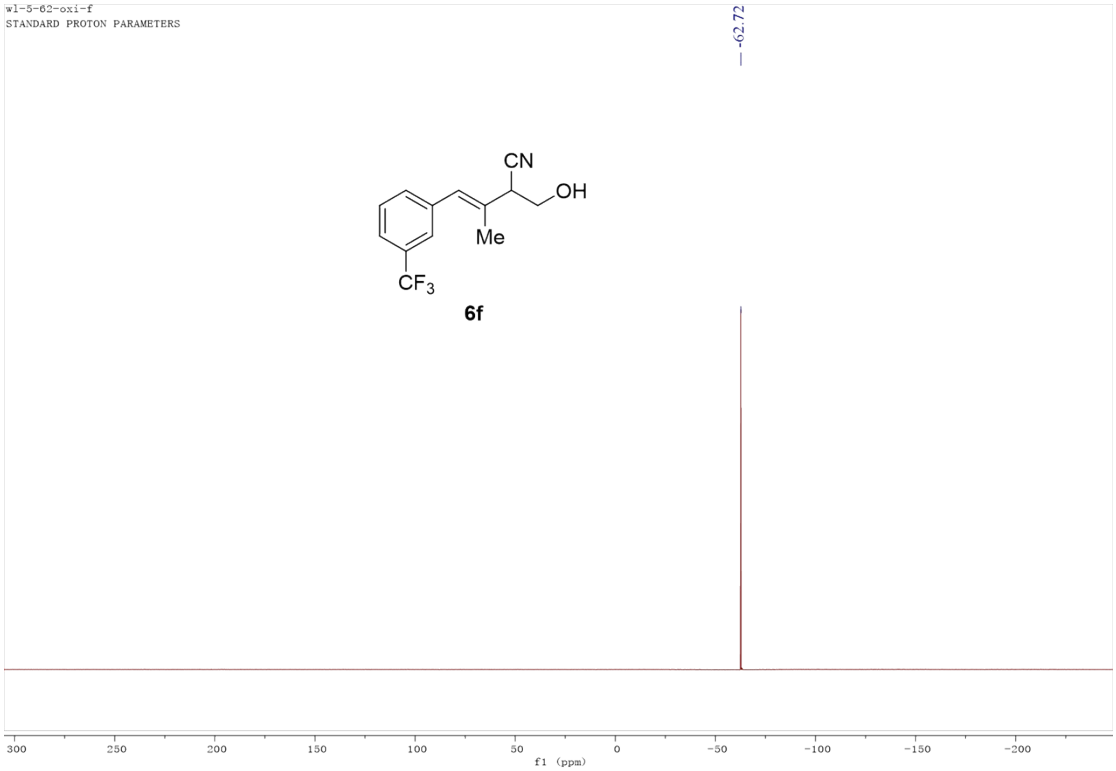

wl-6-93-1h
CN
OH
Me
F
6e
2.13
2.07
1.00
2.05
1.02
0.98
3.01
f1 (ppm)

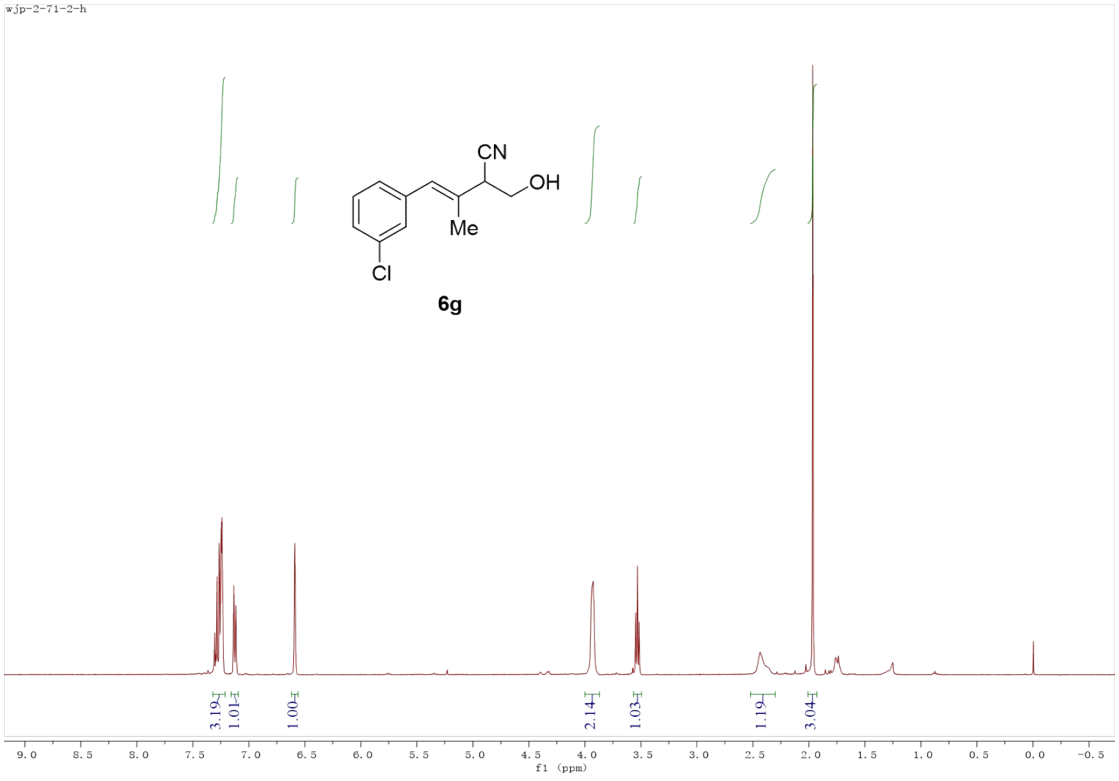

wl-6-93-13c
162.94
160.48
132.21
132.17
130.54
130.46
129.76
129.74
128.56
128.55
119.11
115.29
115.08
77.32
77.00
76.68
62.15
44.37
16.13
CN
OH
Me
F
6e
f1 (ppm)

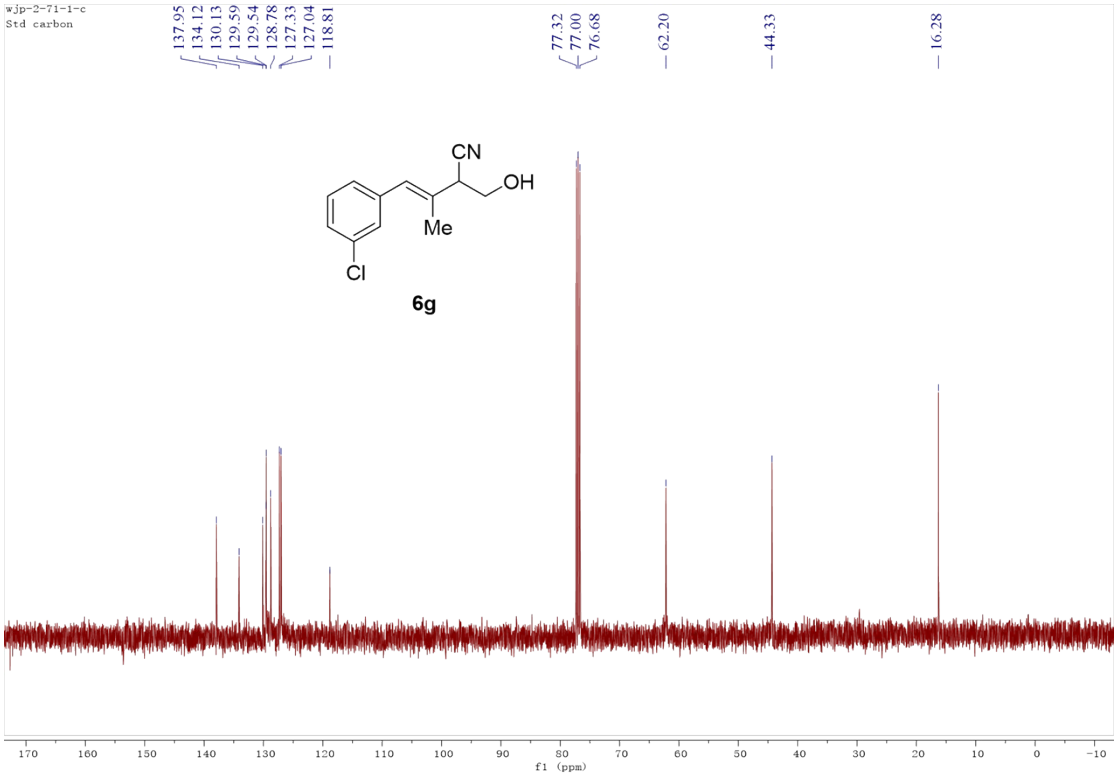

wl-6-93-f
STANDARD PROTON PARAMETERS
-114.30
CN
OH
Me
F
6e
f1 (ppm)

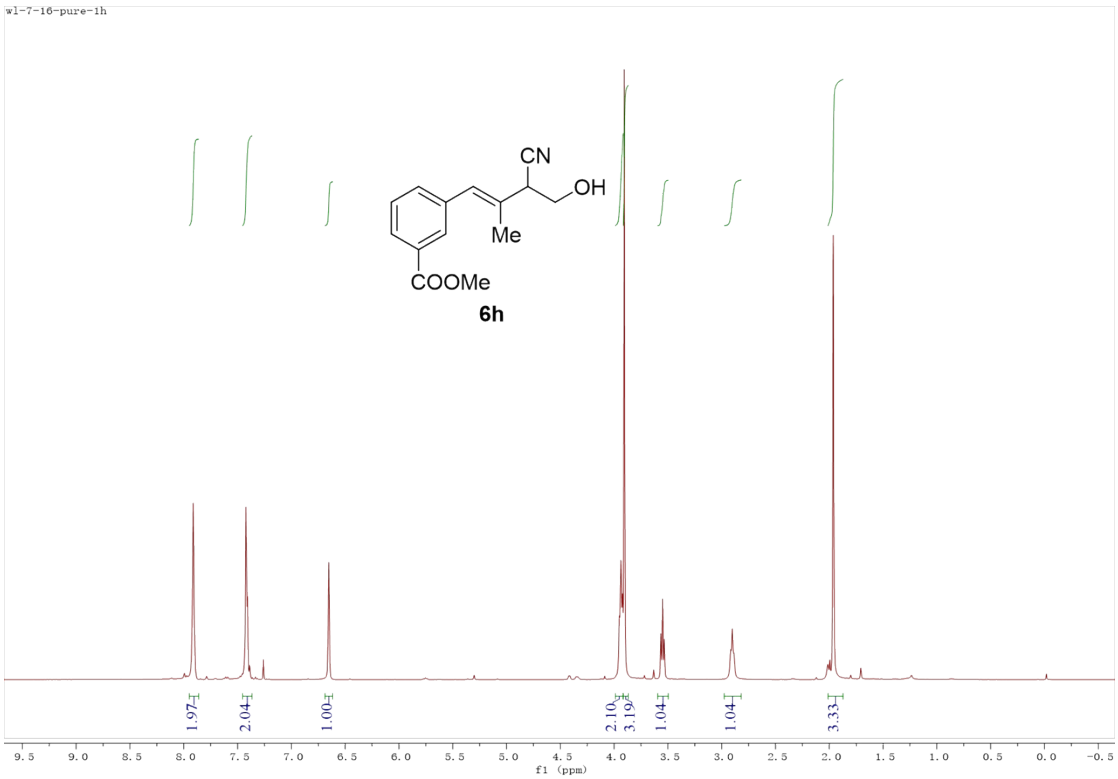

wl-5-62-oxi-p-h
CN
OH
Me
CF3
6f
4.25
1.00
2.06
1.02
1.07
3.14
f1 (ppm)

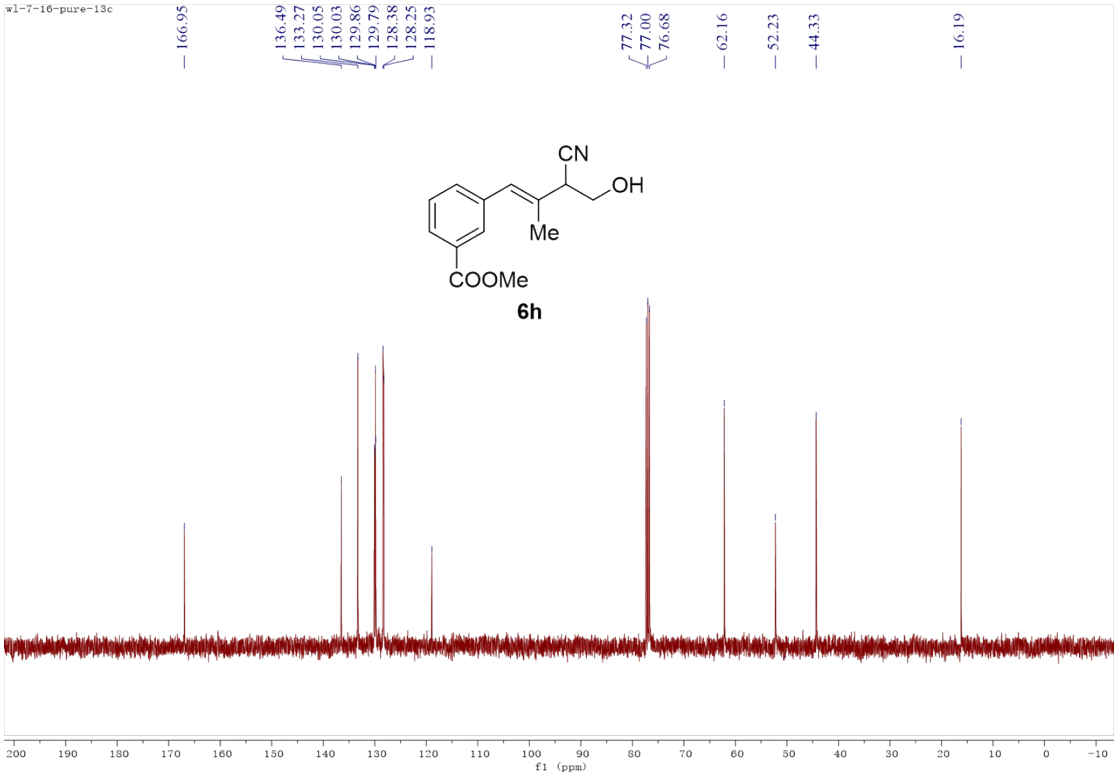

wl-5-62-p-13c
136.91
132.07
131.12
130.80
130.64
130.47
130.15
129.44
128.77
128.01
125.58
125.54
125.50
125.46
125.30
123.96
123.93
123.89
123.85
122.59
119.88
118.89
77.32
77.00
76.68
62.15
44.30
16.22
CN
OH
Me
CF3
6f
f1 (ppm)

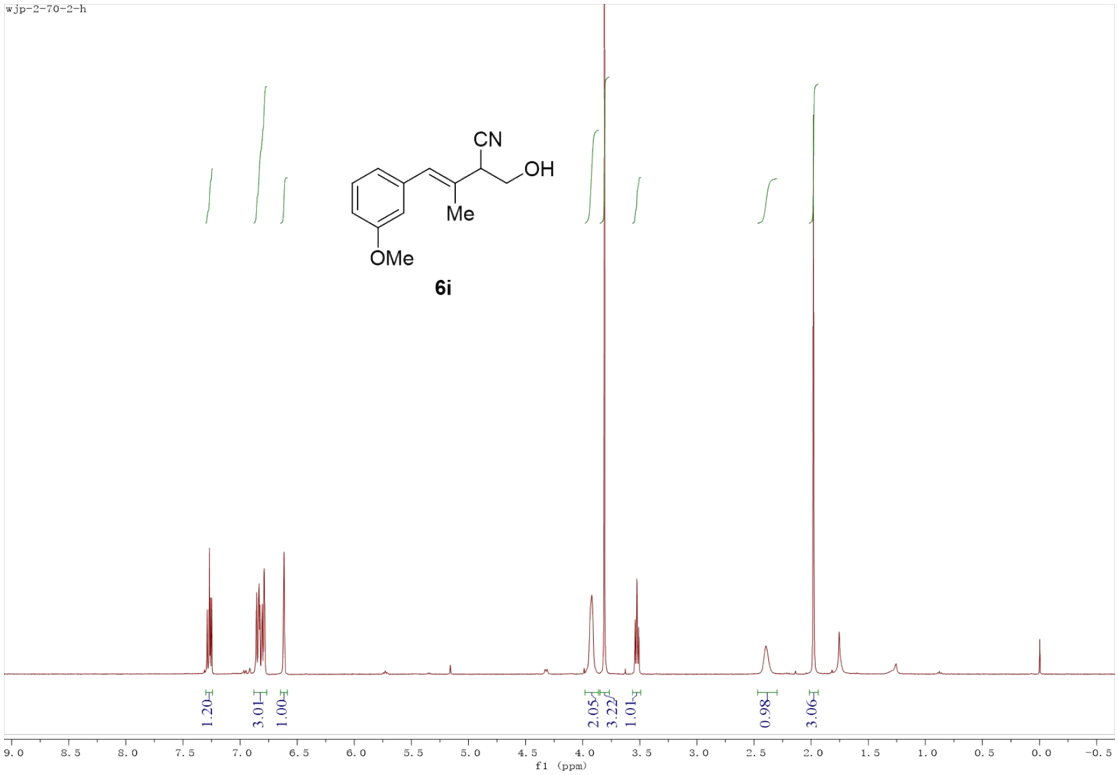

wl-5-62-oxi-f
STANDARD PROTON PARAMETERS
-62.72
CN
OH
Me
CF3
6f
f1 (ppm)

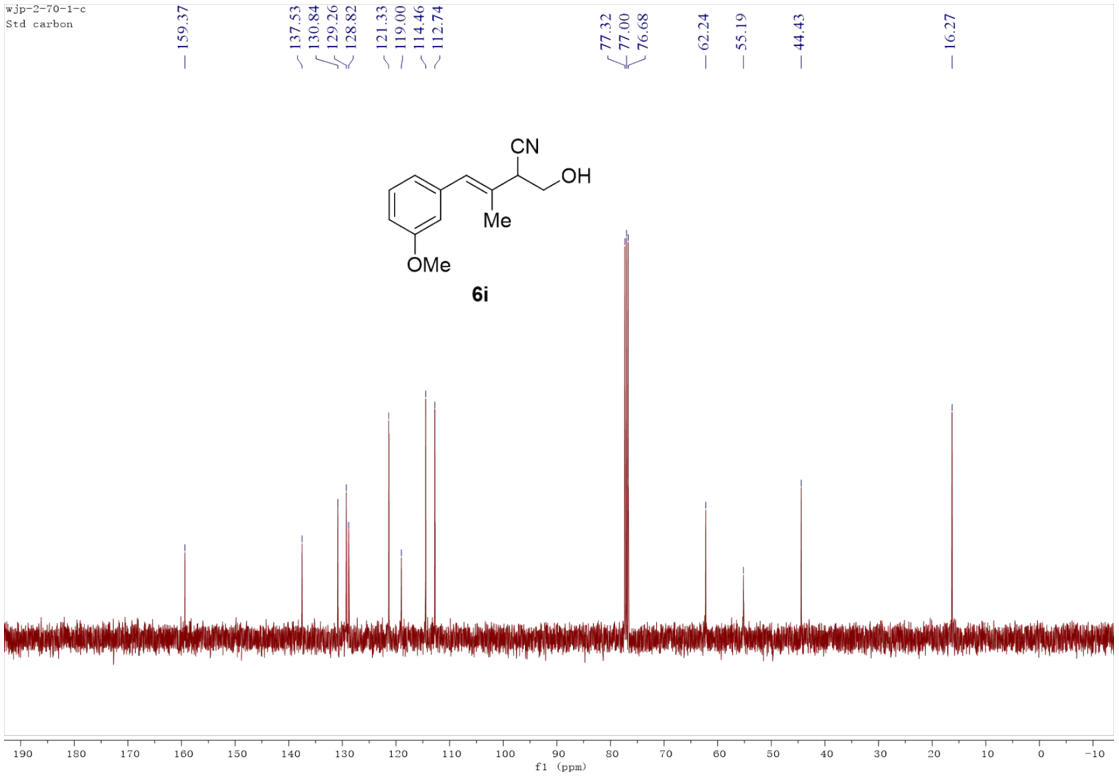

wjp-2-71-2-h
CN
OH
Me
Cl
6g
3.19
1.01
1.00
2.14
1.03
1.19
3.04
f1 (ppm)

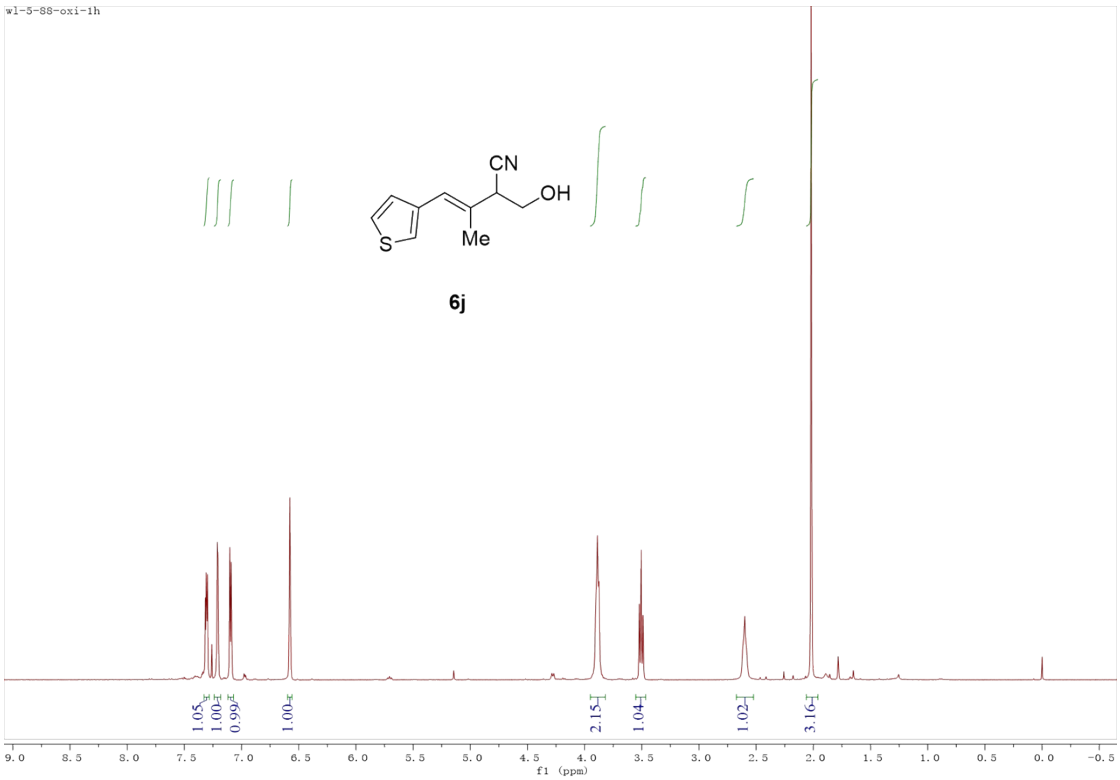

wjp-2-71-1-c
Std carbon
137.95
134.12
130.13
129.59
129.54
128.78
127.33
127.04
118.81
77.32
77.00
76.68
62.20
44.33
16.28
CN
OH
Me
Cl
6g
f1 (ppm)

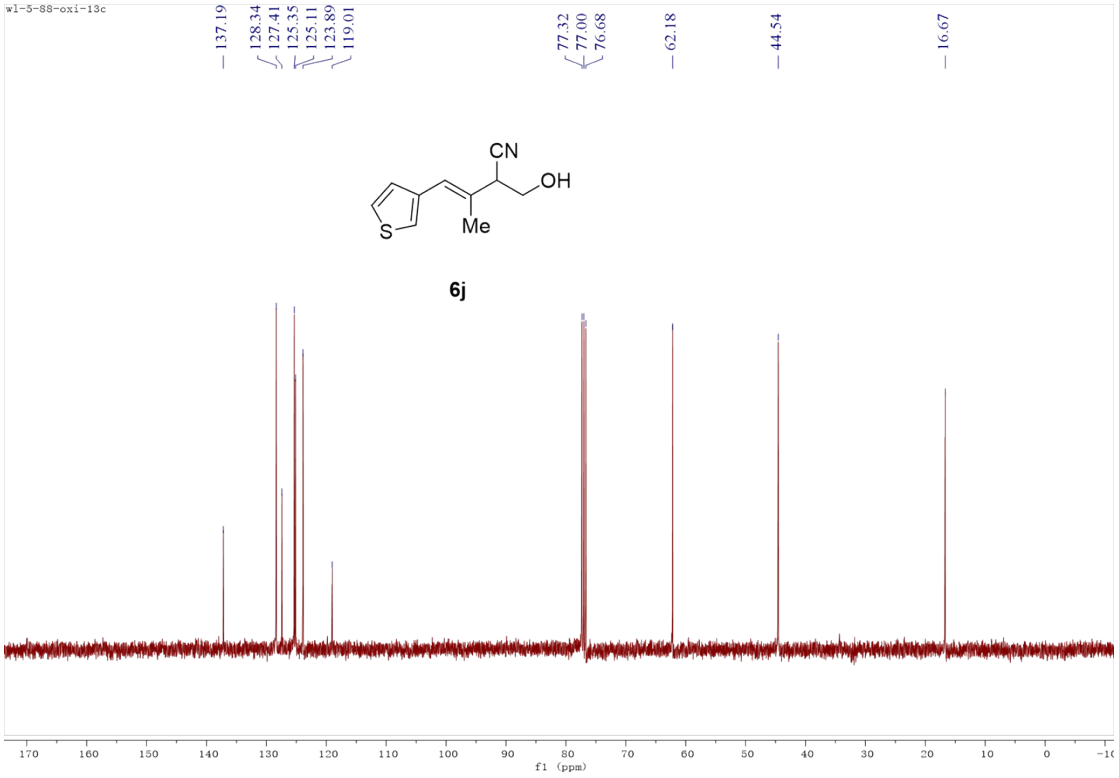

wl-7-16-pure-1h
CN
OH
Me
COOMe
6h
1.97
2.04
1.00
2.10
3.19
1.04
1.04
3.33
f1 (ppm)


wl-7-16-pure-13c
166.95
136.49
133.27
130.05
130.03
129.86
129.79
128.38
128.25
118.93
77.32
77.00
76.68
62.16
52.23
44.33
16.19
CN
OH
Me
COOMe
6h
f1 (ppm)

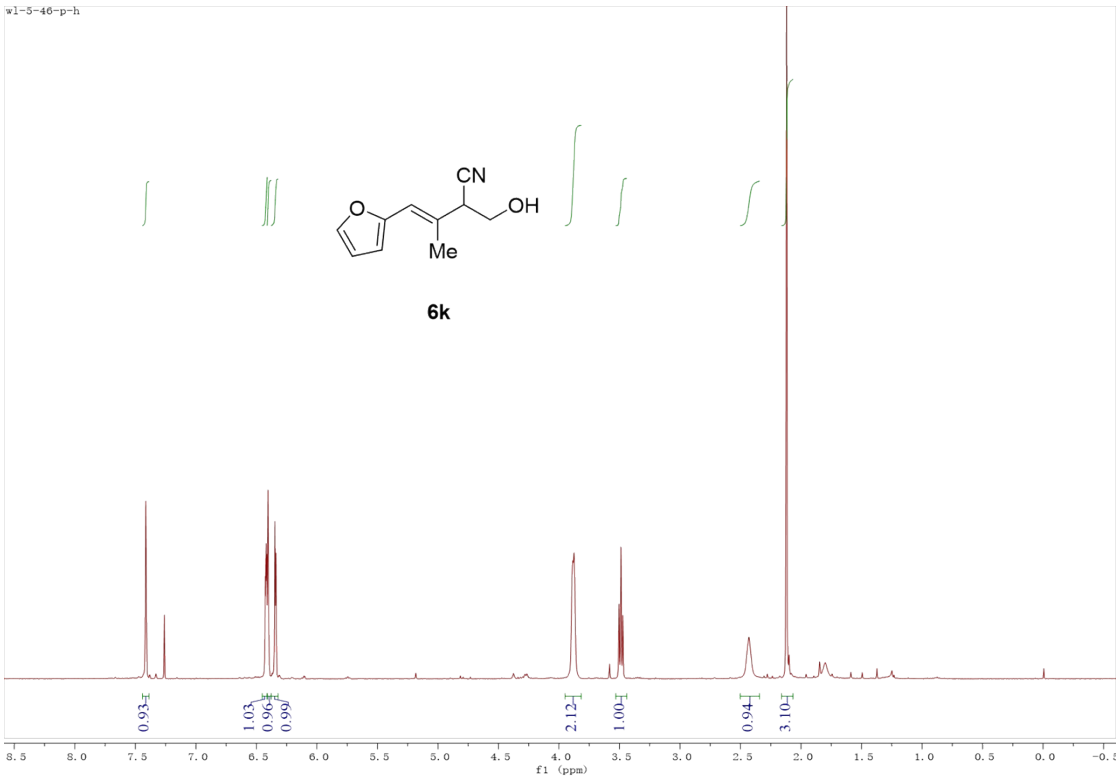

wjp-2-70-2-h
CN
OH
Me
OMe
6i
1.20
3.01
1.00
2.05
3.22
1.01
0.98
3.06
f1 (ppm)


wjp-2-70-1-c
Std carbon
159.37
137.53
130.84
129.26
128.82
121.33
119.00
114.46
112.74
77.32
77.00
76.68
62.24
55.19
44.43
16.27
CN
OH
Me
OMe
6i
f1 (ppm)

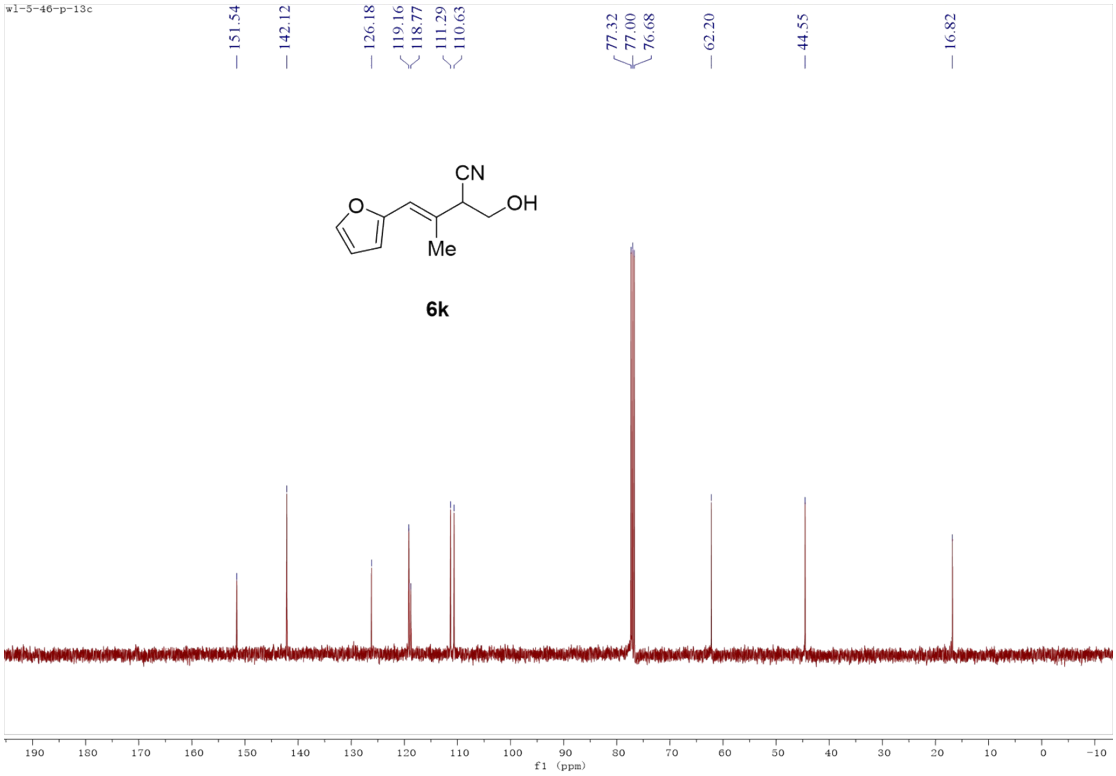

wl-5-88-oxi-1h
CN
OH
Me
S
6j
1.05
1.00
0.99
1.00
2.15
1.04
1.02
3.16
f1 (ppm)


wl-5-88-oxi-13c
137.19
128.34
127.41
125.35
125.11
123.89
119.01
77.32
77.00
76.68
62.18
44.54
16.67
CN
OH
Me
S
f1 (ppm)

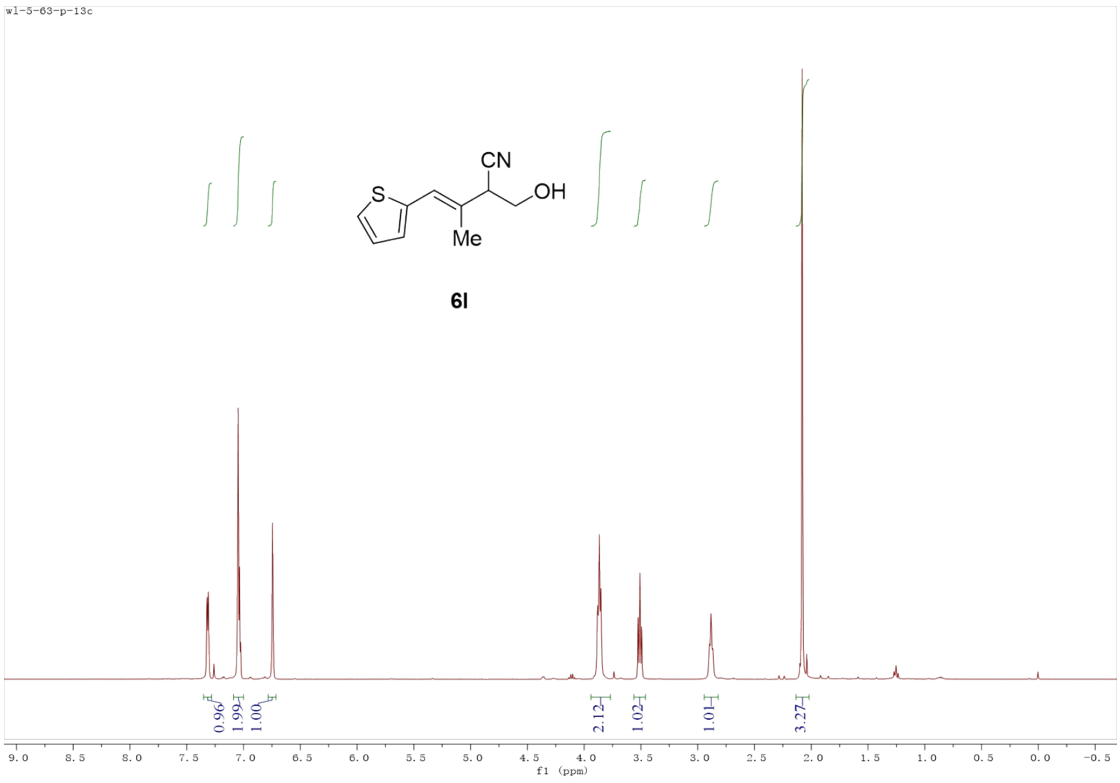
6j


wl-5-46-p-h
CN
OH
Me
O
0.93
1.03
0.96
0.99
2.12
1.00
0.94
3.10
f1 (ppm)

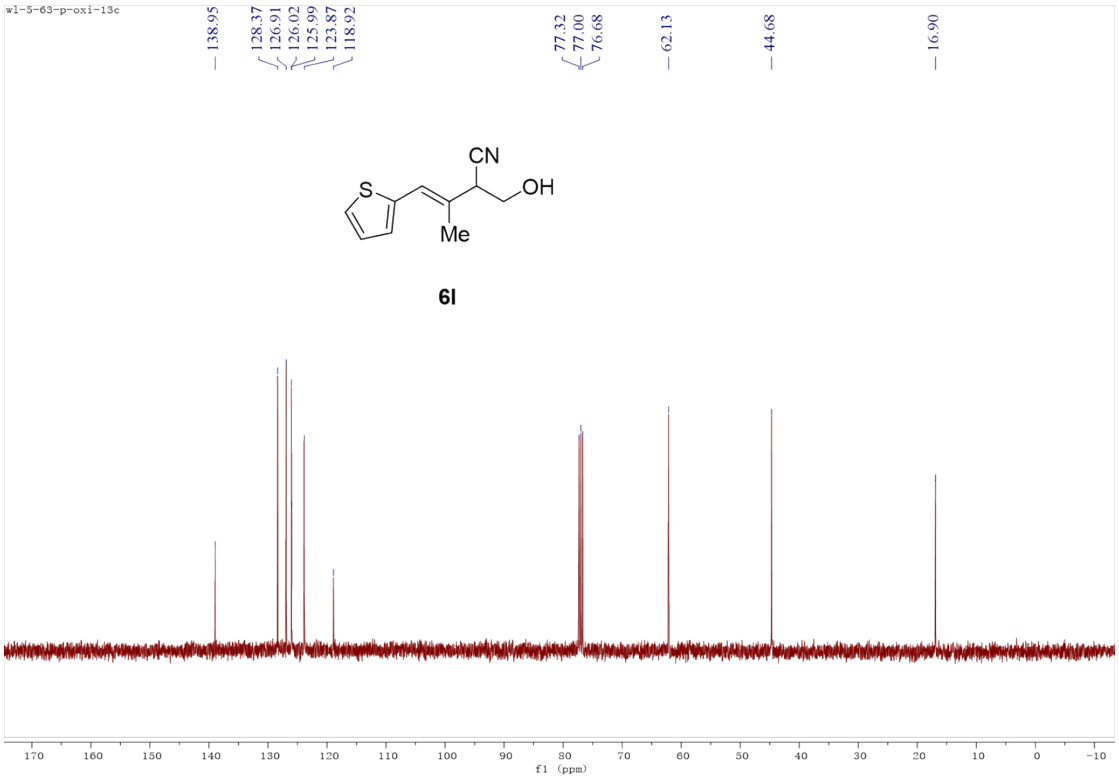
6k


wl-5-46-p-13c
151.54
142.12
126.18
119.16
118.77
111.29
110.63
77.32
77.00
76.68
62.20
44.55
16.82
CN
OH
O
Me
f1 (ppm)

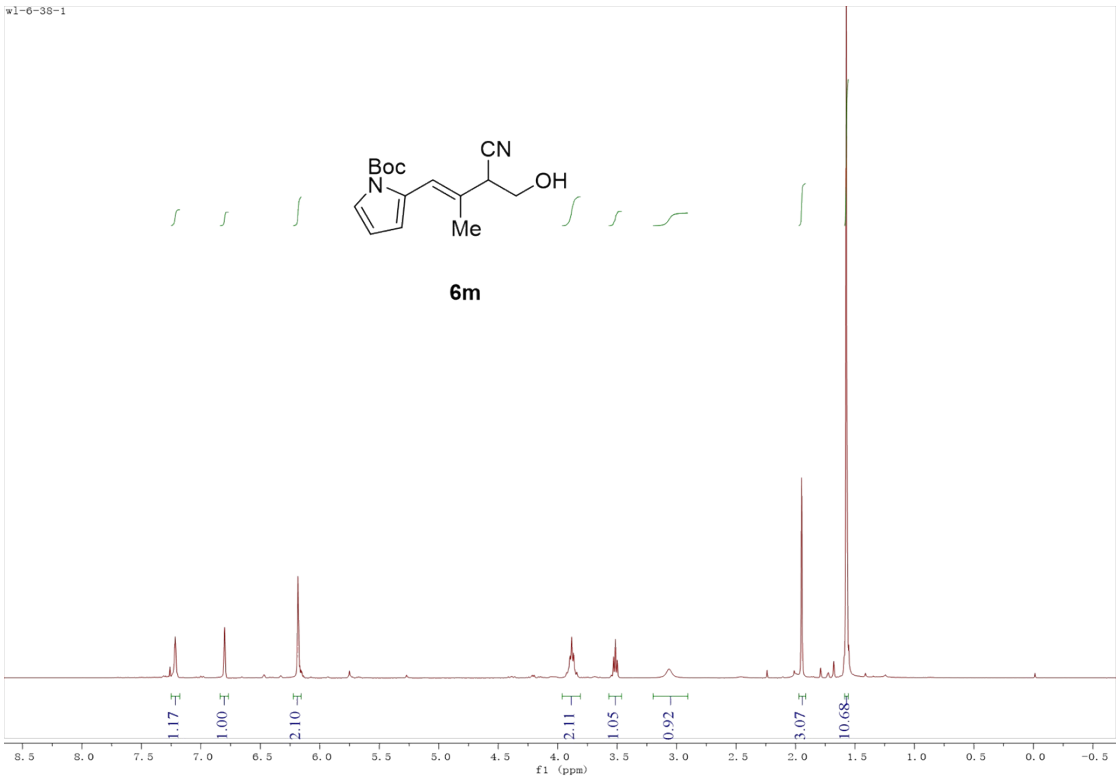
6k


wl-5-63-p-13c
CN
OH
S
Me
0.96
1.99
1.00
2.12
1.02
1.01
3.27
f1 (ppm)

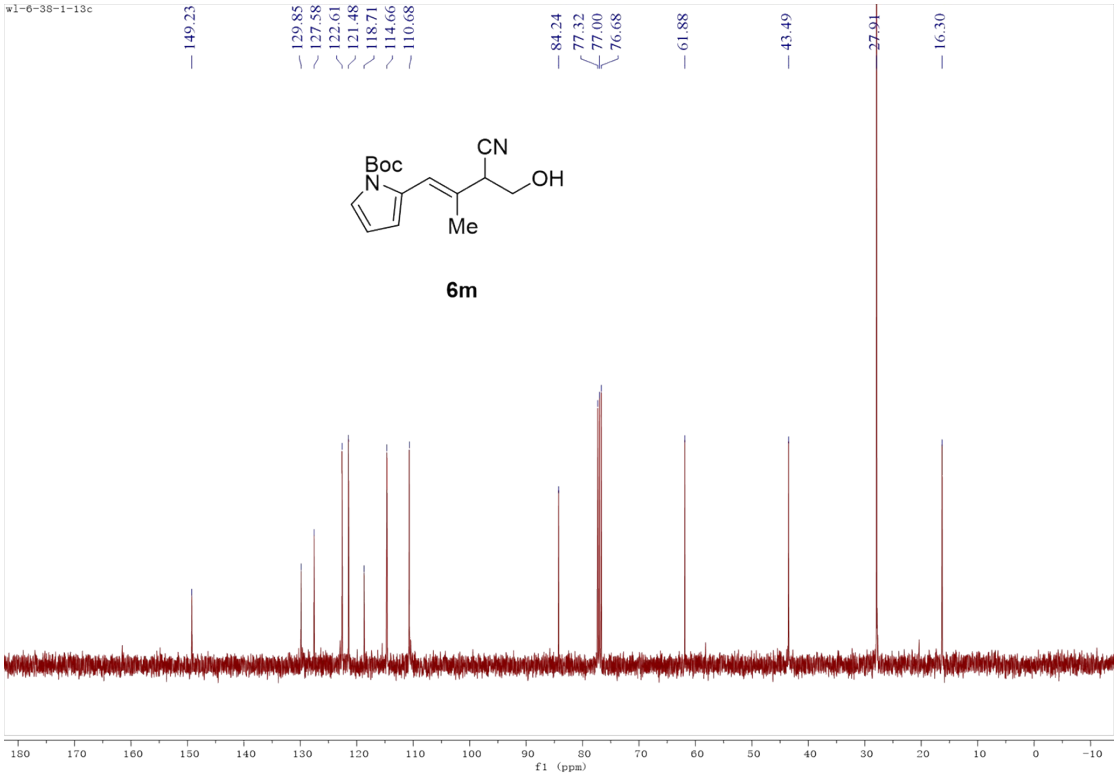
6l


wl-5-63-p-oxi-13c
138.95
128.37
126.91
126.02
125.99
123.87
118.92
77.32
77.00
76.68
62.13
44.68
16.90
CN
OH
S
Me
f1 (ppm)

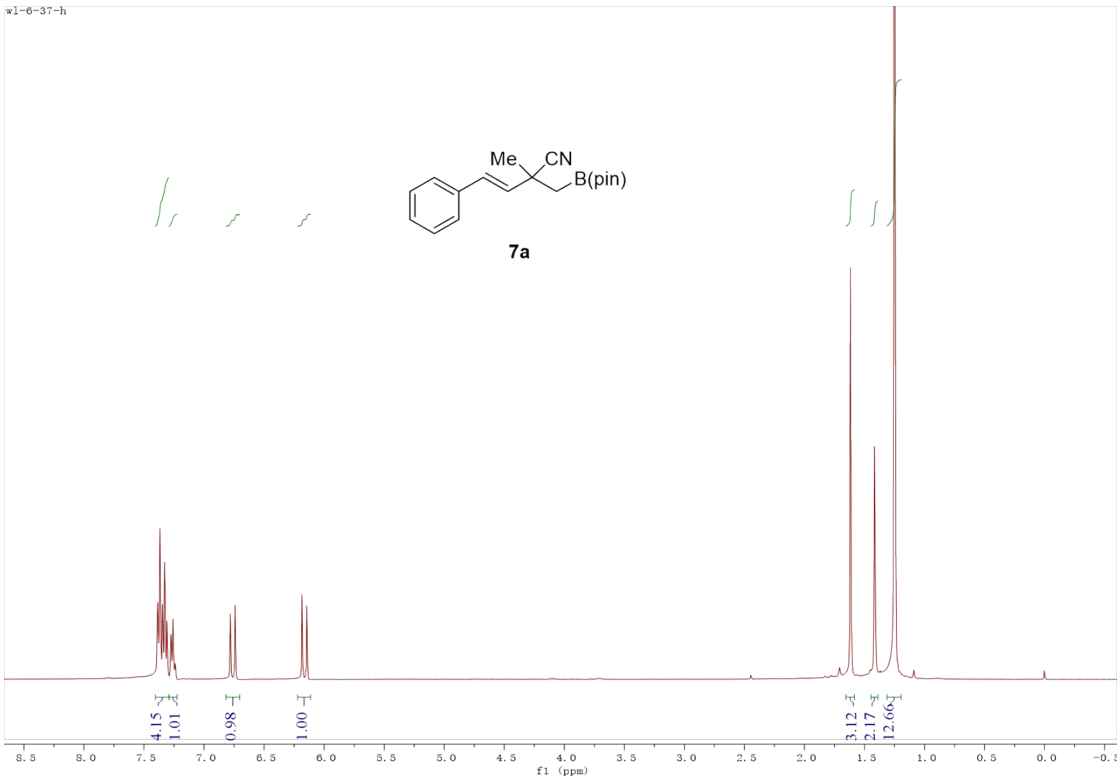
6l


wl-6-38-1
Boc
N
CN
OH
Me
1.17
1.00
2.10
2.11
1.05
0.92
3.07
10.68
f1 (ppm)

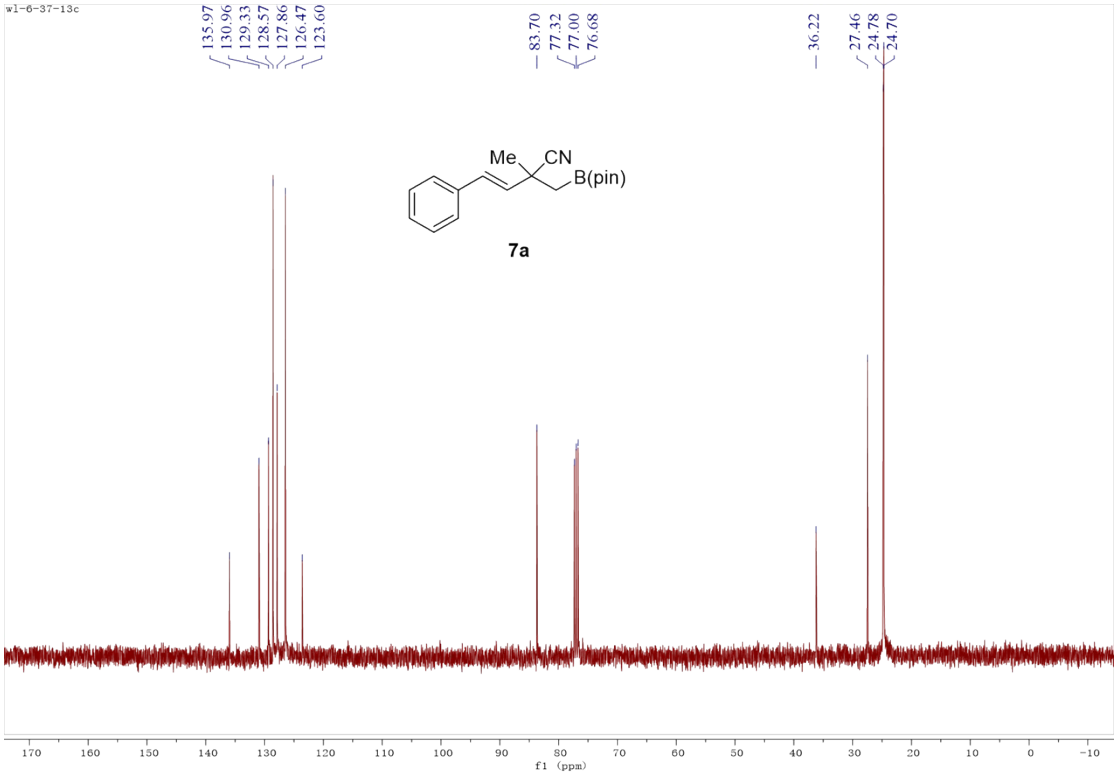
6m

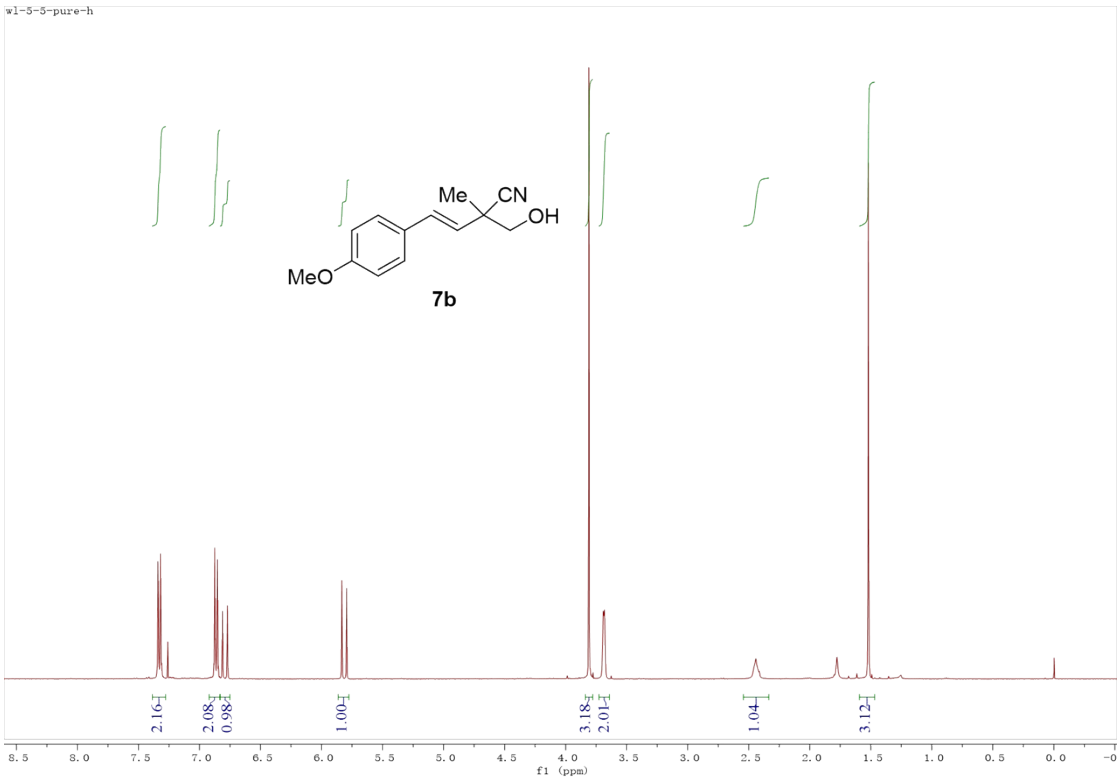

wl-6-38-1-13c
149.23
129.85
127.58
122.61
121.48
118.71
114.66
110.68
84.24
77.32
77.00
76.68
61.88
43.49
27.91
16.30
Boc
N
CN
OH
Me
f1 (ppm)

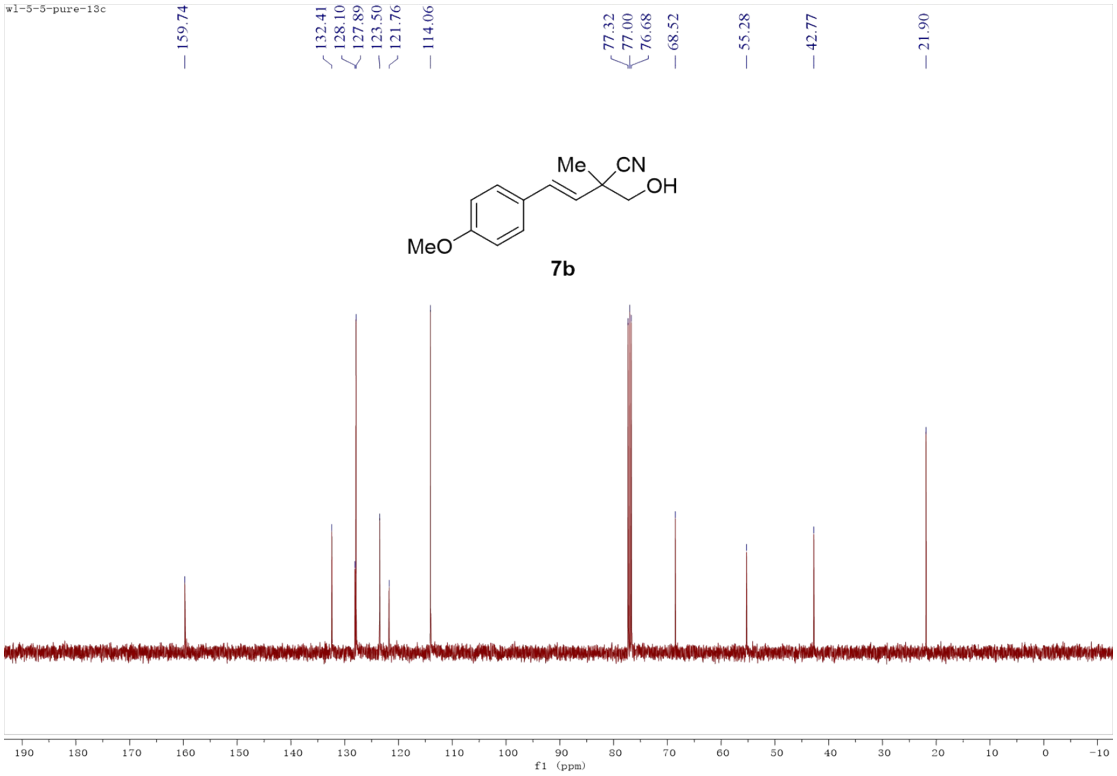
6m

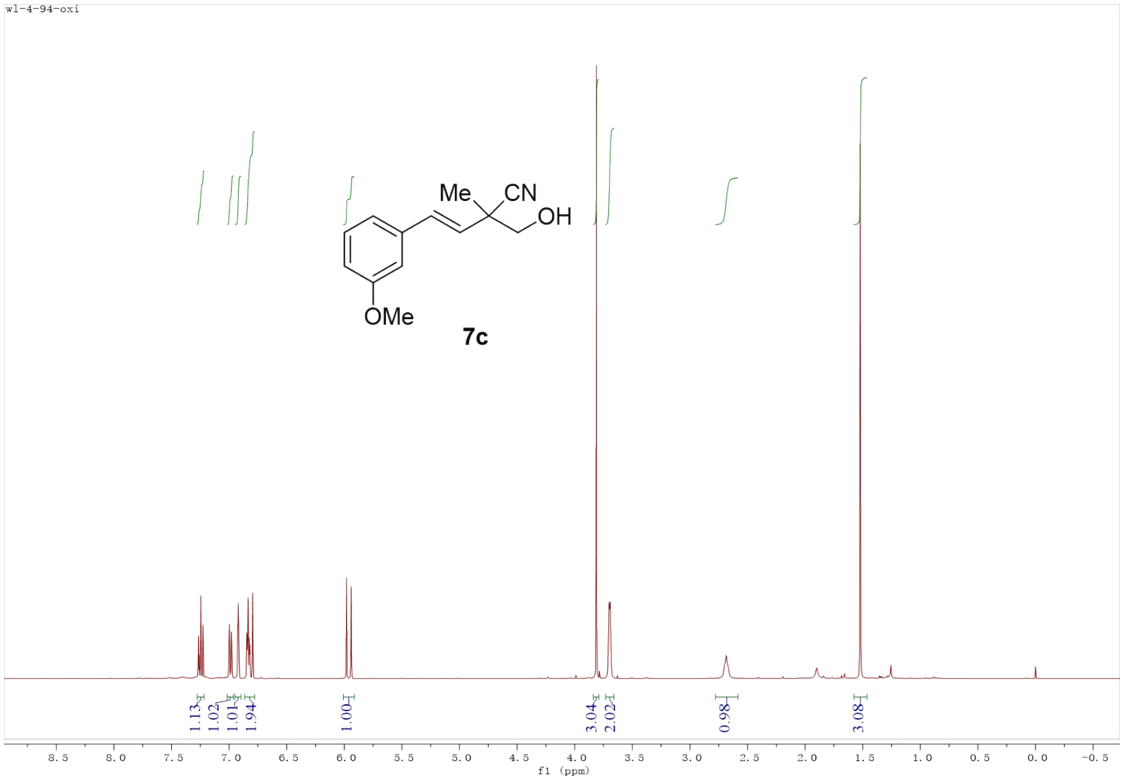

wl-6-37-h
Me
CN
B(pin)
4.15
1.01
0.98
1.00
3.12
2.17
12.66
f1 (ppm)

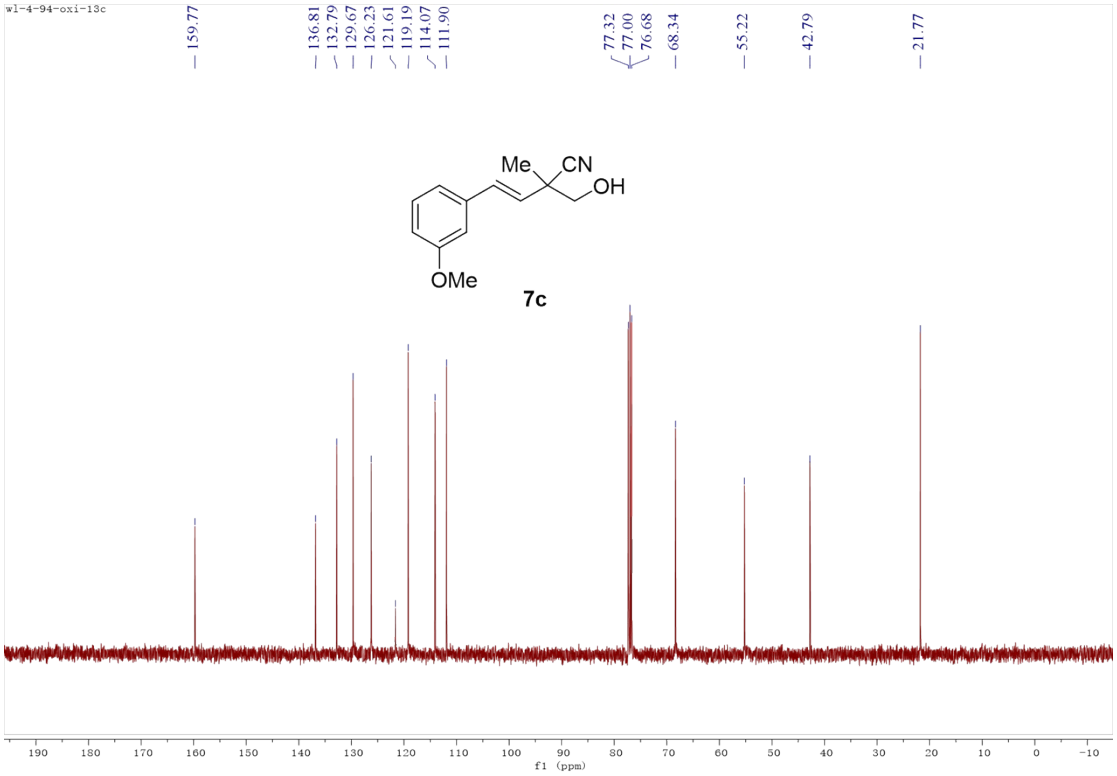
7a

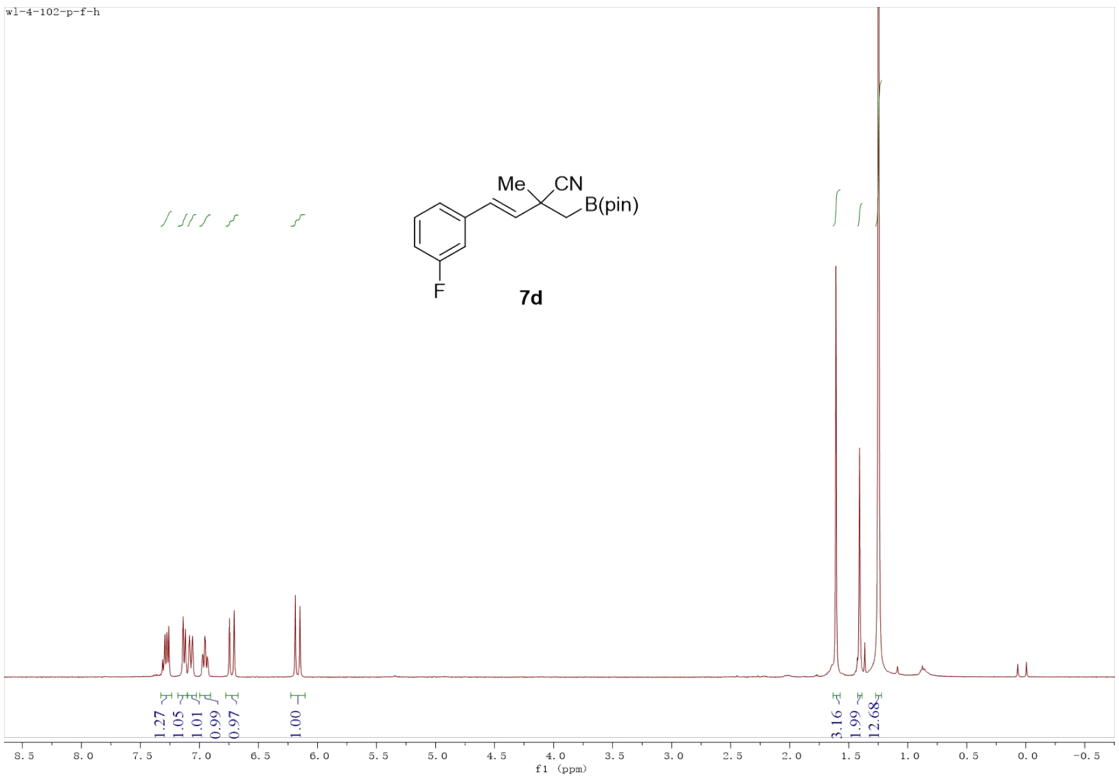

wl-6-37-13c
135.97
130.96
129.33
128.57
127.86
126.47
123.60
83.70
77.32
77.00
76.68
36.22
27.46
24.78
24.70
Me
CN
B(pin)
7a
f1 (ppm)

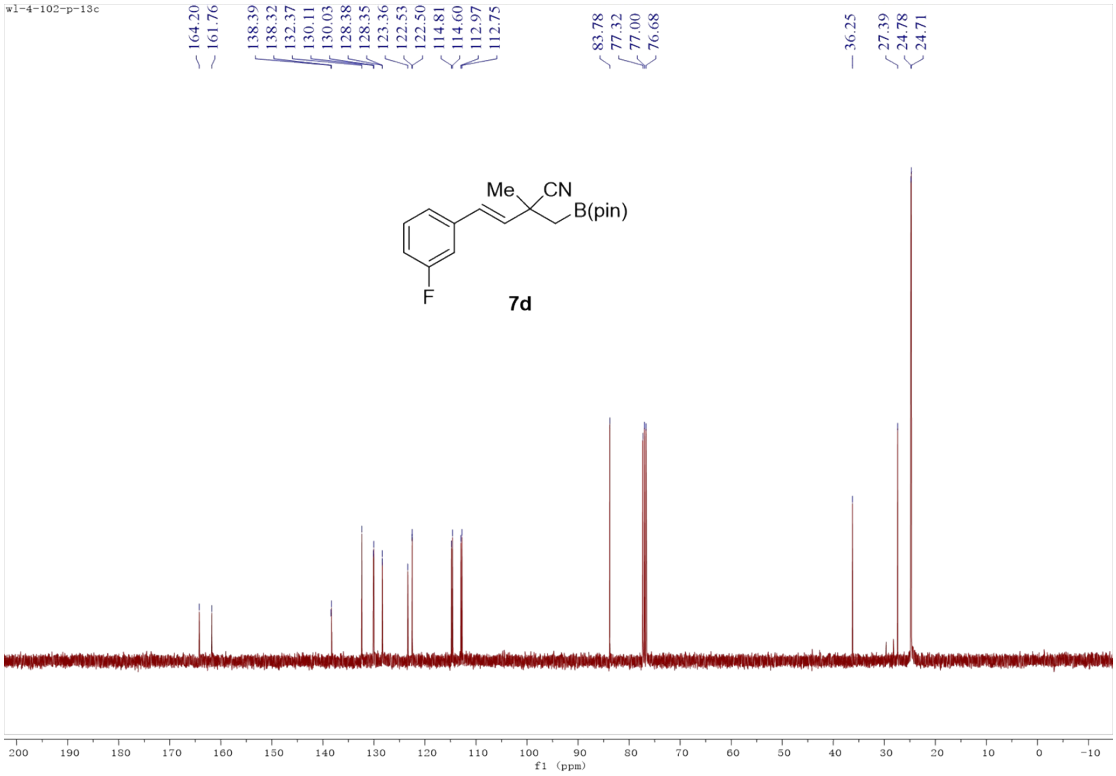

wl-5-5-pure-h
Me
CN
OH
MeO
7b
2.16
2.08
0.98
1.00
3.18
2.01
1.04
3.12
f1 (ppm)

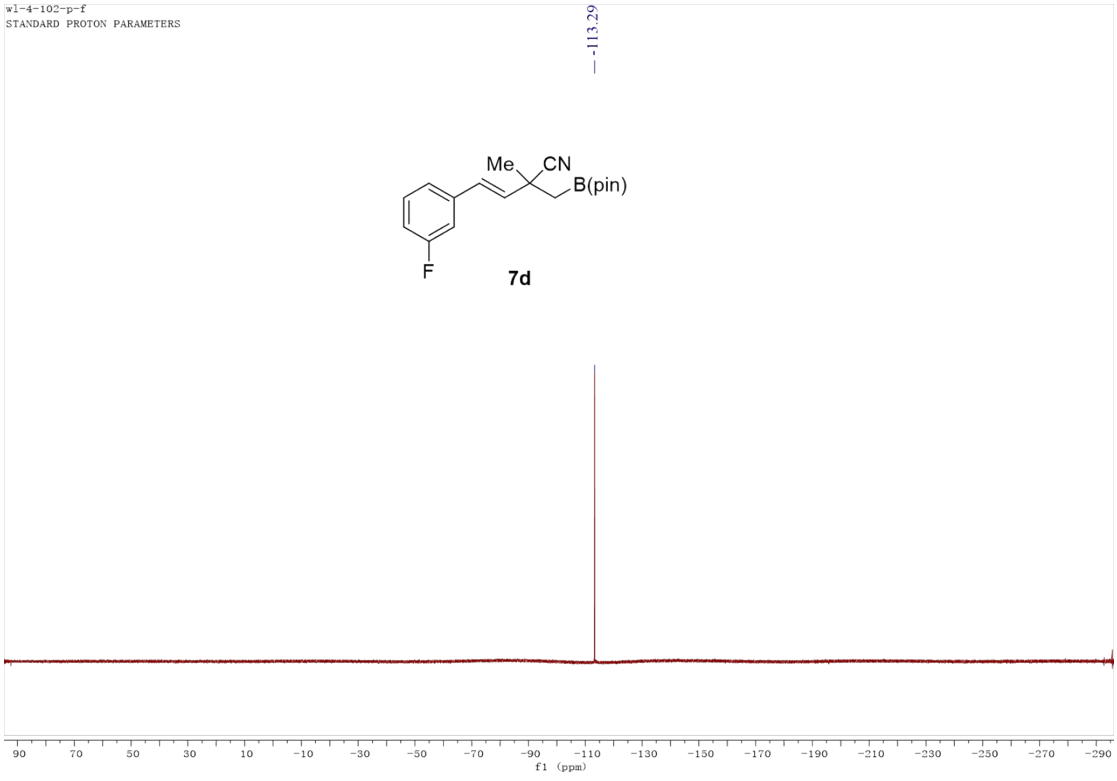

wl-5-5-pure-13c
159.74
132.41
128.10
127.89
123.50
121.76
114.06
77.32
77.00
76.68
68.52
55.28
42.77
21.90
Me
CN
OH
MeO
7b
f1 (ppm)

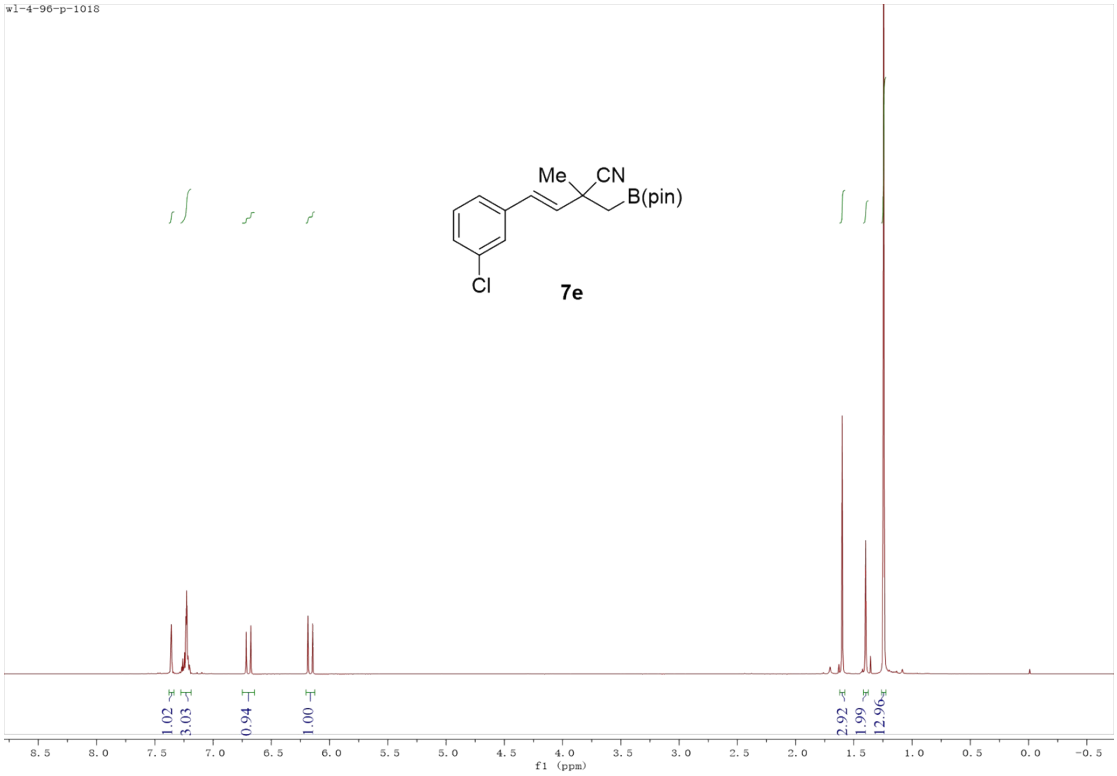

wl-4-94-oxi
Me
CN
OH
OMe
7c
1.13
1.02
1.01
1.94
1.00
3.04
2.02
0.98
3.08
f1 (ppm)

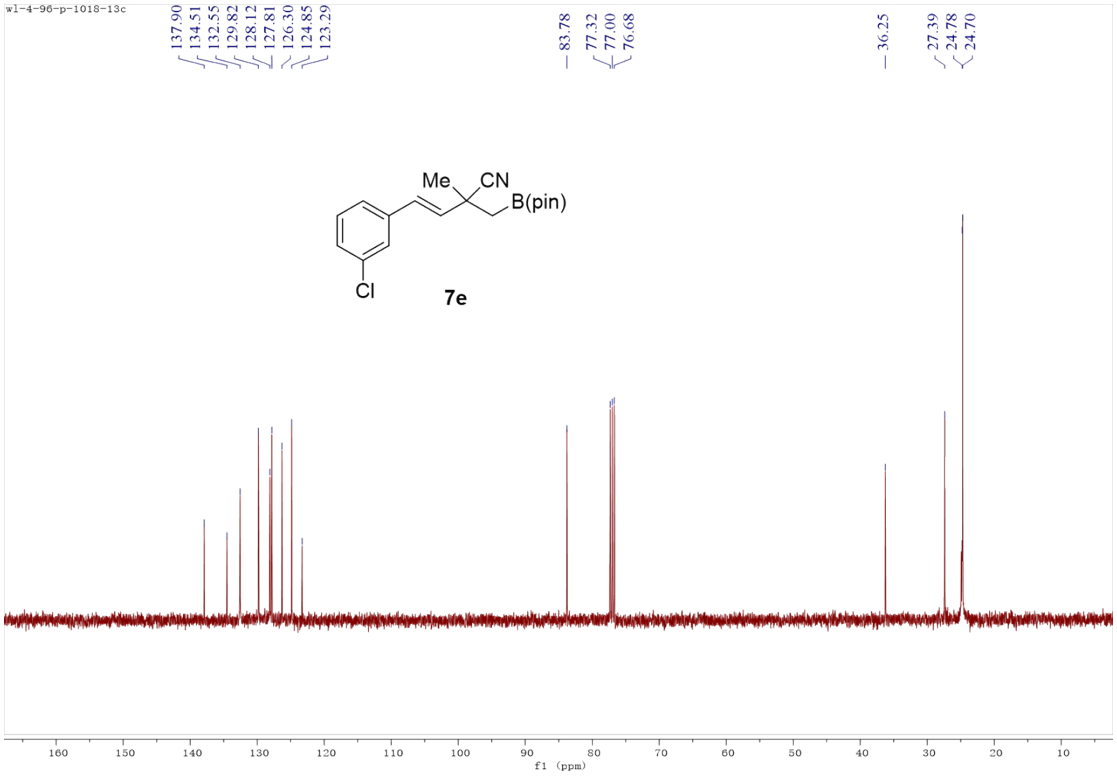

wl-4-94-oxi-13c
159.77
136.81
132.79
129.67
126.23
121.61
119.19
114.07
111.90
77.32
77.00
76.68
68.34
55.22
42.79
21.77
Me
CN
OH
OMe
7c
f1 (ppm)

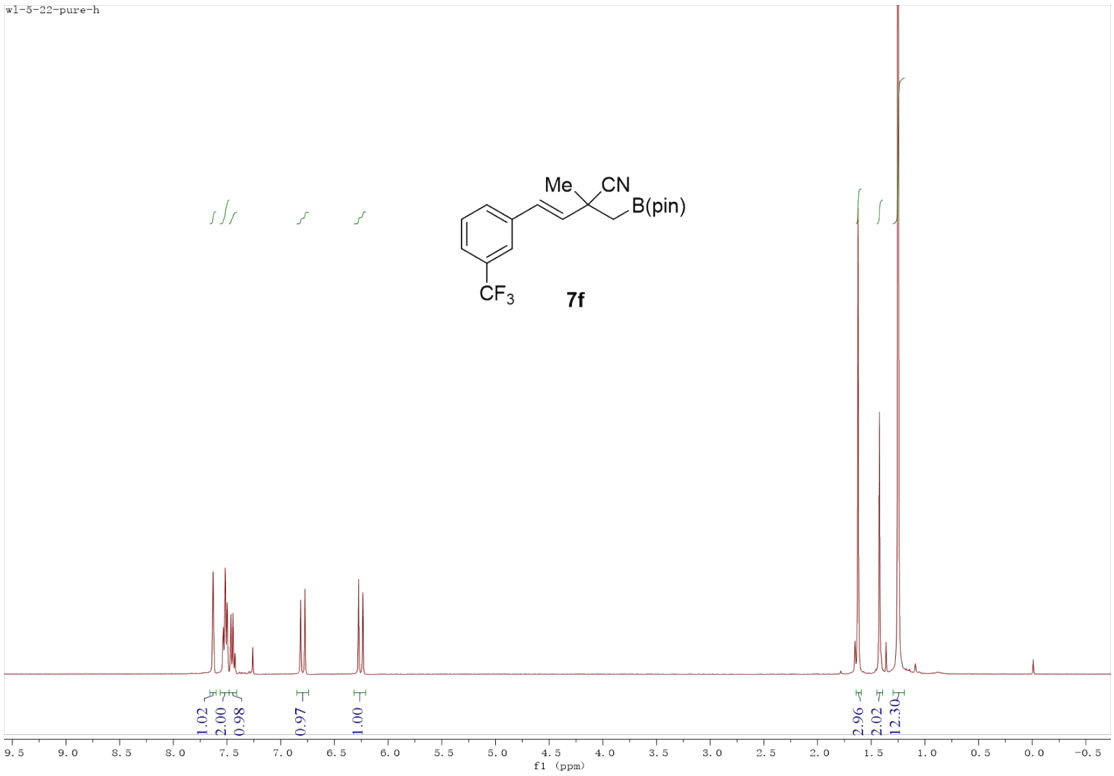

wl-4-102-p-f-h
Me
CN
B(pin)
F
7d
1.27
1.05
1.01
0.99
0.97
1.00
3.16
1.99
12.68
f1 (ppm)

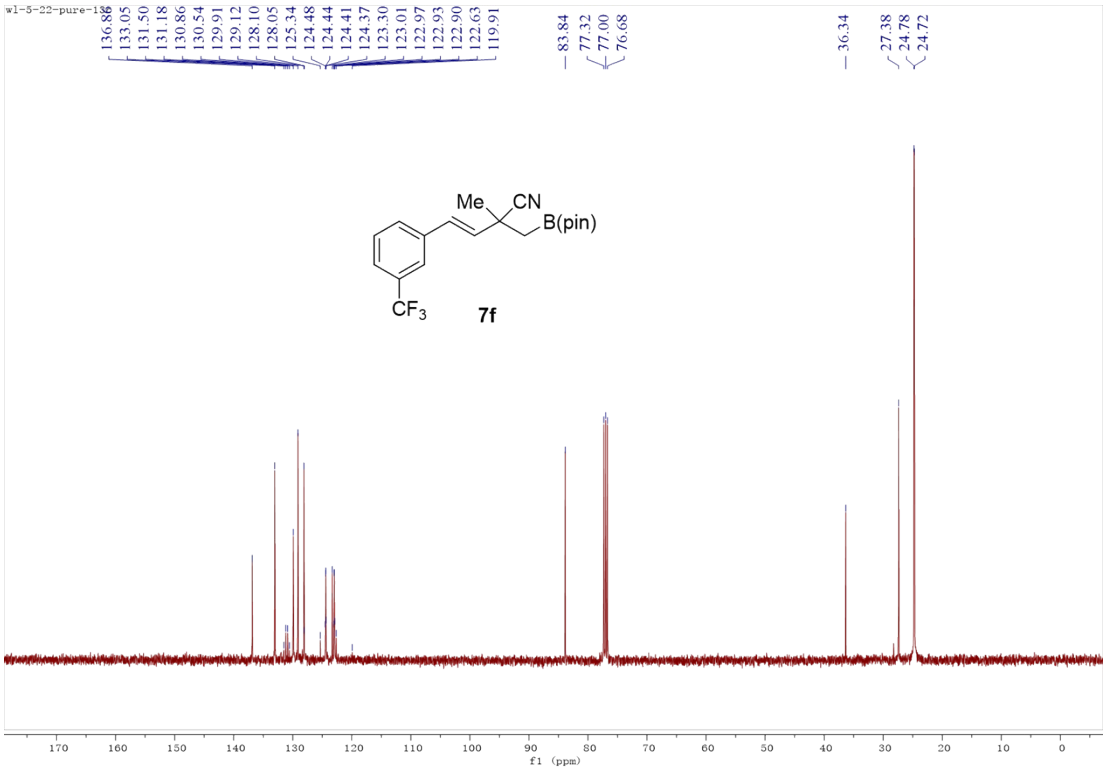

wl-4-102-p-13c
164.20
161.76
138.39
138.32
132.37
130.11
130.03
128.38
128.35
123.36
122.53
122.50
114.81
114.60
112.97
112.75
83.78
77.32
77.00
76.68
36.25
27.39
24.78
24.71
Me
CN
B(pin)
F
7d
f1 (ppm)

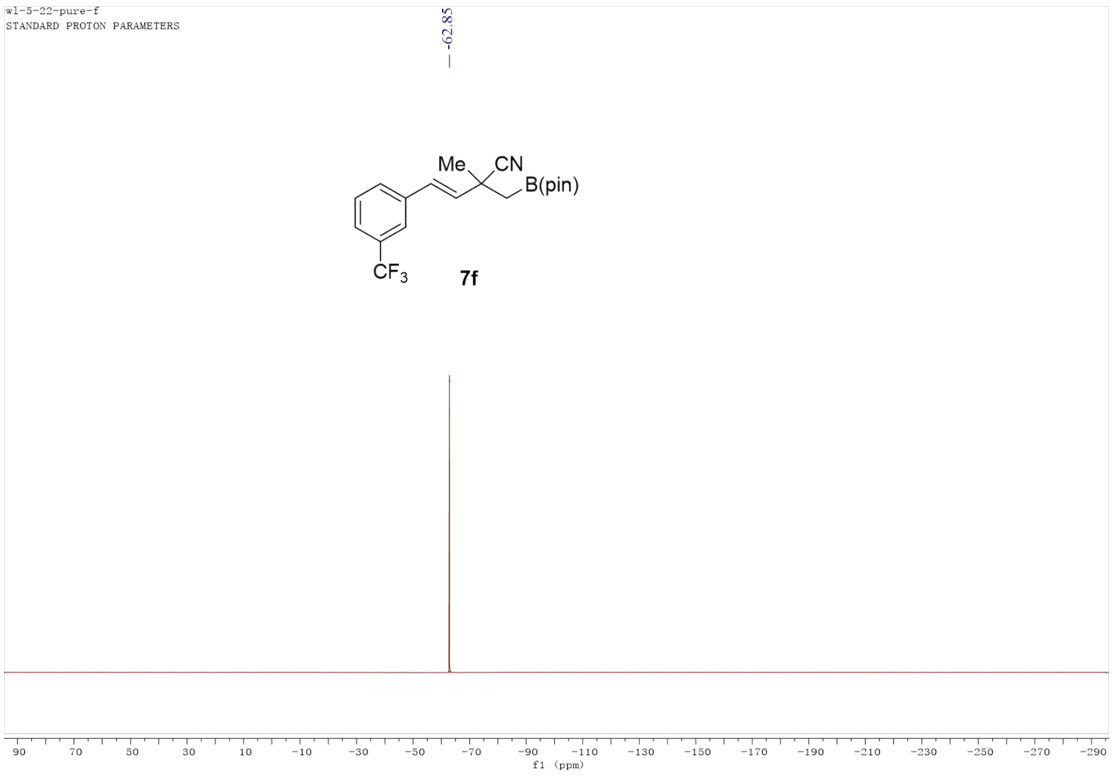

wl-4-102-p-f
STANDARD PROTON PARAMETERS
-113.29
Me
CN
B(pin)
F
7d
f1 (ppm)

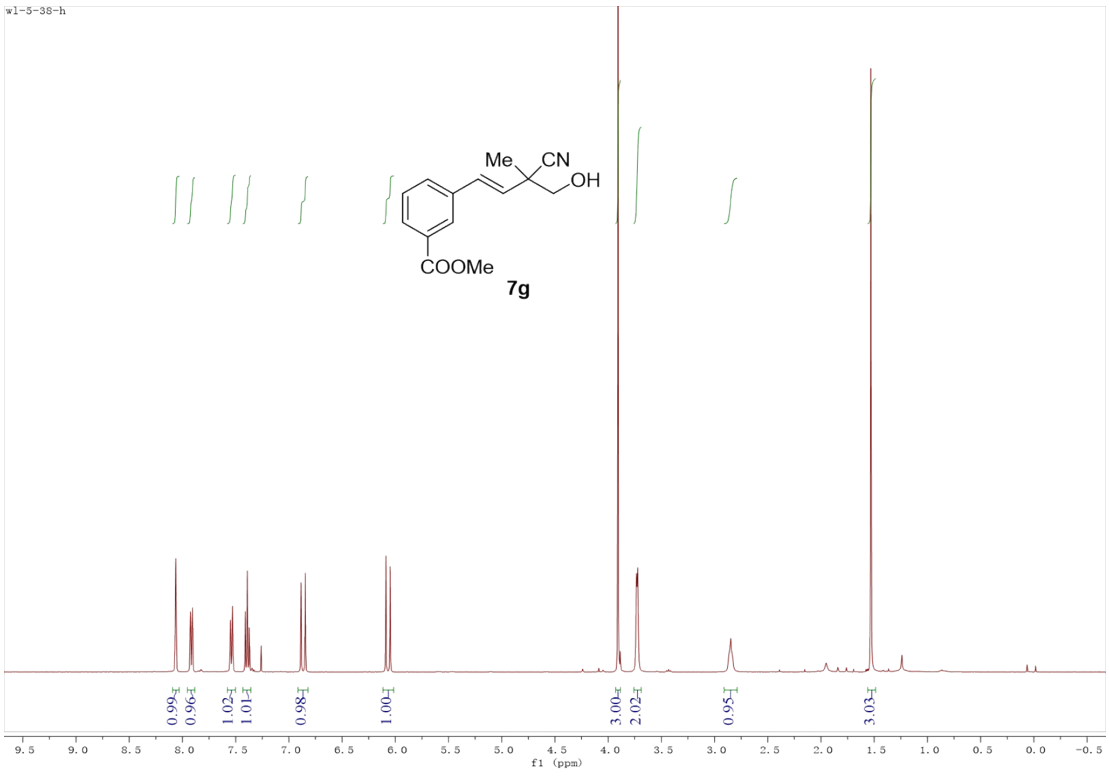

wl-4-96-p-1018
Me
CN
B(pin)
Cl
7e
1.02
3.03
0.94
1.00
2.92
1.99
12.96
f1 (ppm)

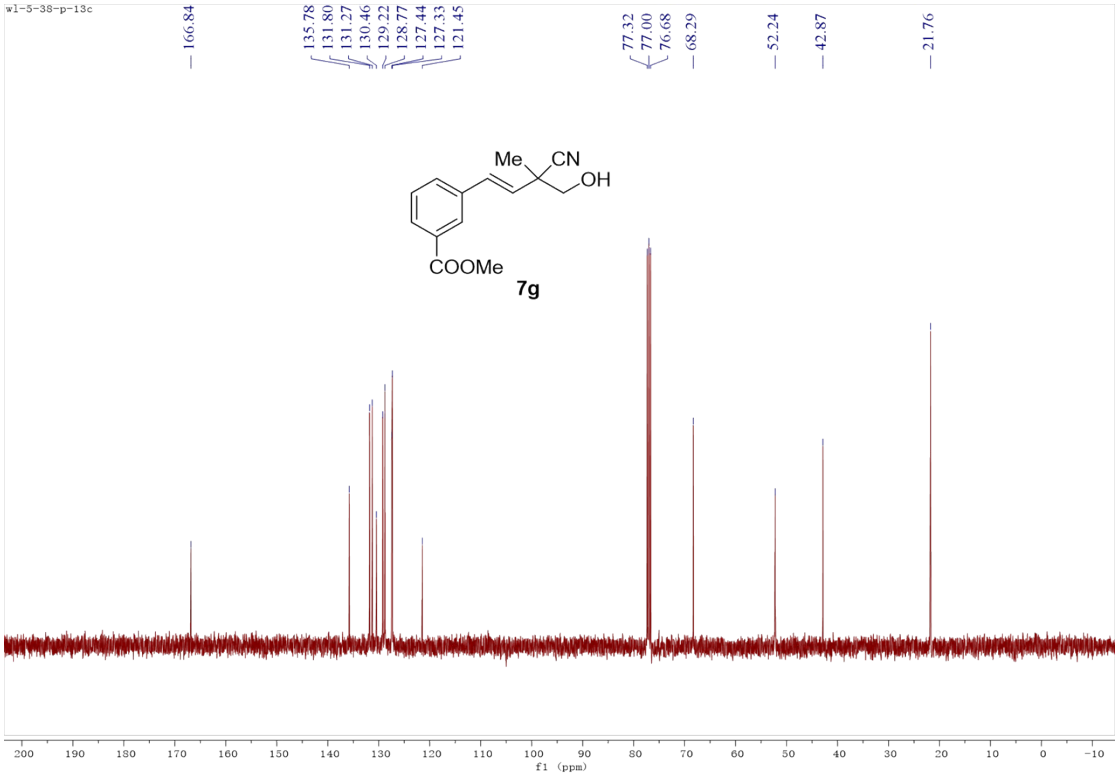

wl-4-96-p-1018-13c
137.90
134.51
132.55
129.82
128.12
127.81
126.30
124.85
123.29
83.78
77.32
77.00
76.68
36.25
27.39
24.78
24.70
Me
CN
B(pin)
Cl
7e
f1 (ppm)

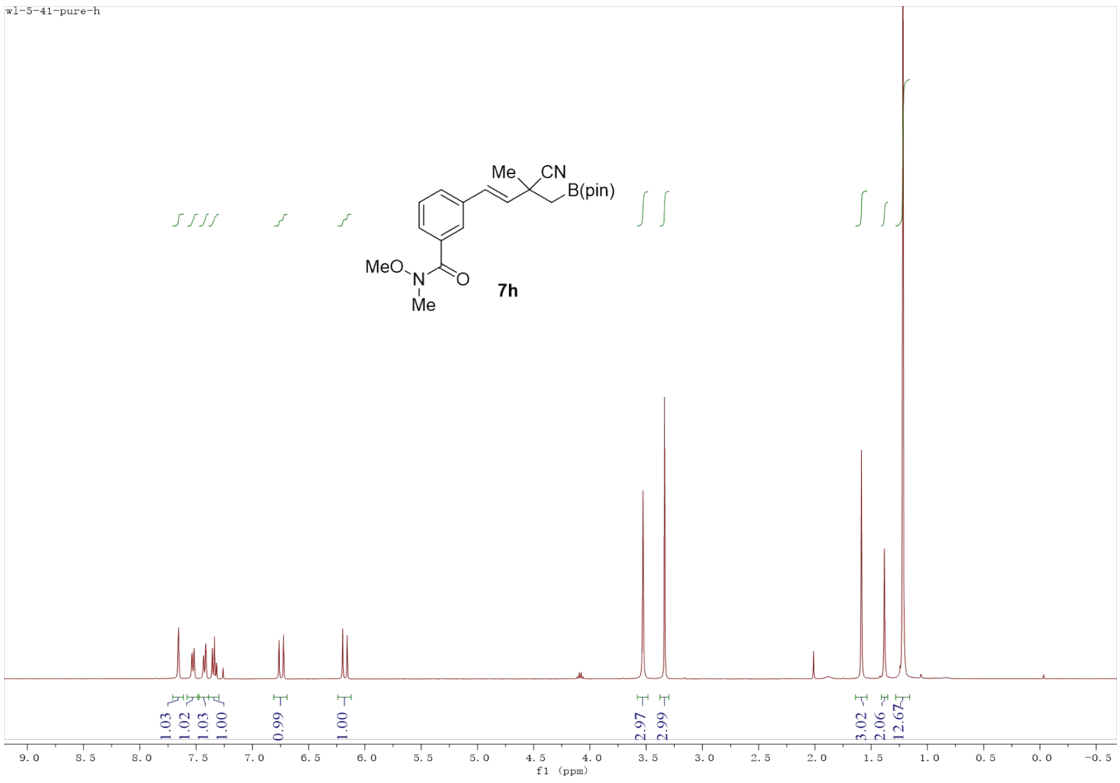

wl-5-22-pure-h
Me
CN
B(pin)
CF3
7f
1.02
2.00
0.98
0.97
1.00
2.96
2.02
12.30
f1 (ppm)

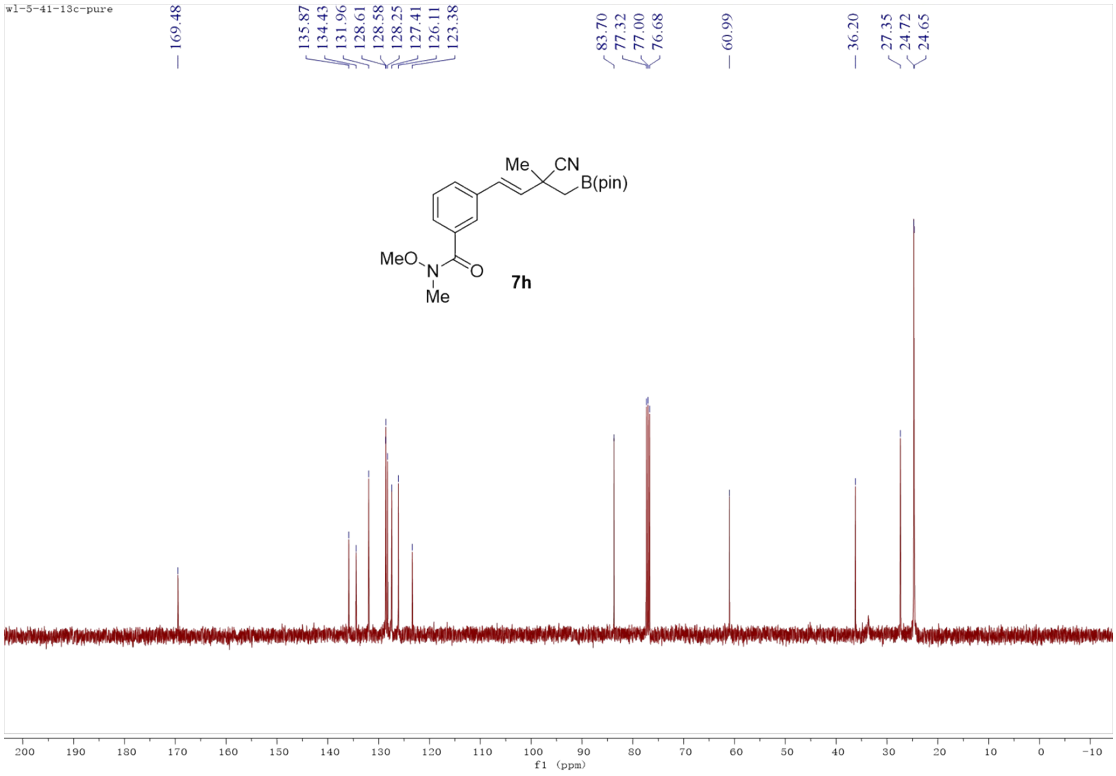

wl-5-22-pure-13
136.86
133.05
131.50
131.18
130.86
130.54
129.91
129.12
128.10
128.05
125.34
124.48
124.44
124.41
124.37
123.30
123.01
122.97
122.93
122.90
122.63
119.91
83.84
77.32
77.00
76.68
36.34
27.38
24.78
24.72
Me
CN
B(pin)
CF3
7f
f1 (ppm)

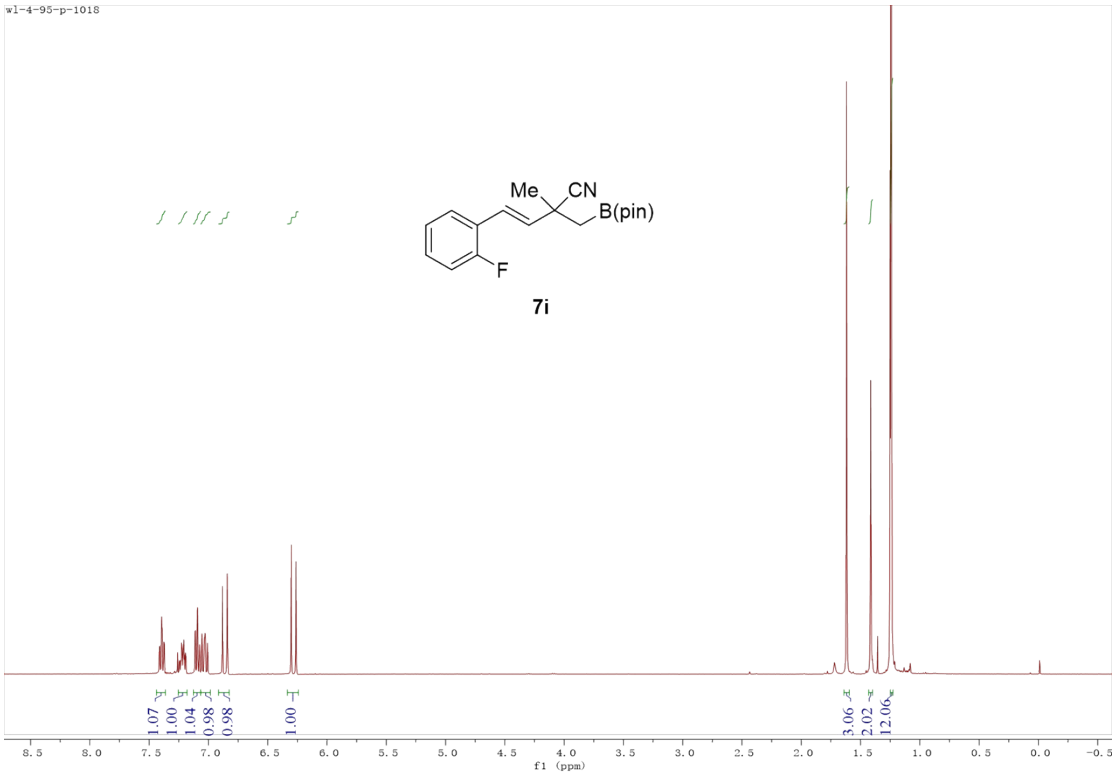

wl-5-22-pure-f
STANDARD PROTON PARAMETERS
-62.85
Me
CN
B(pin)
CF3
7f
f1 (ppm)

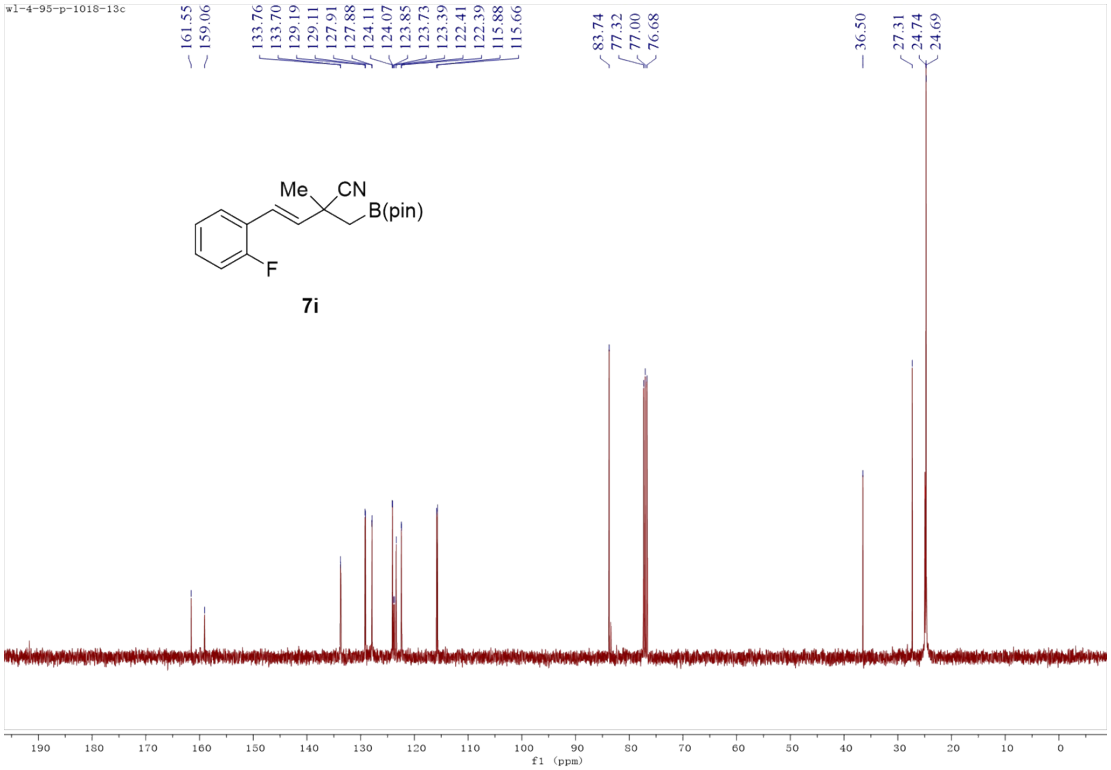

wl-5-38-h
Me
CN
OH
COOMe
7g
0.99
0.96
1.02
1.01
0.98
1.00
3.00
2.02
0.95
3.03
f1 (ppm)

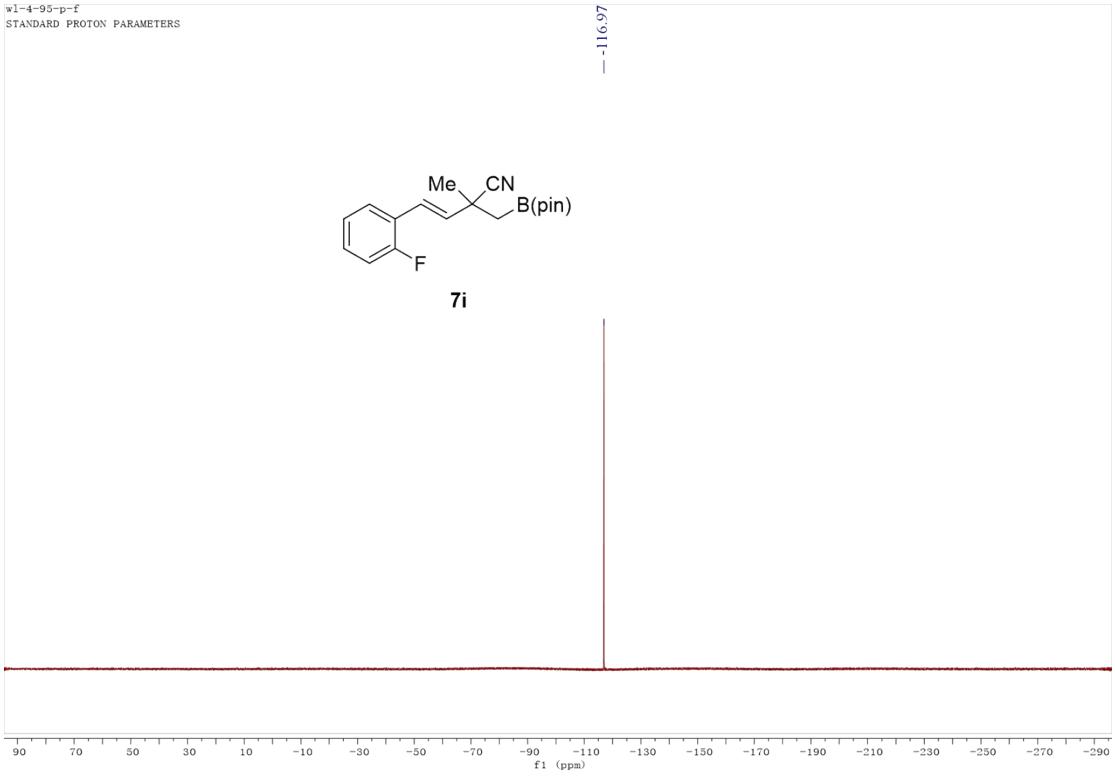

wl-5-38-p-13c
166.84
135.78
131.80
131.27
130.46
129.22
128.77
127.44
127.33
121.45
77.32
77.00
76.68
68.29
52.24
42.87
21.76
Me
CN
OH
COOMe
7g
f1 (ppm)

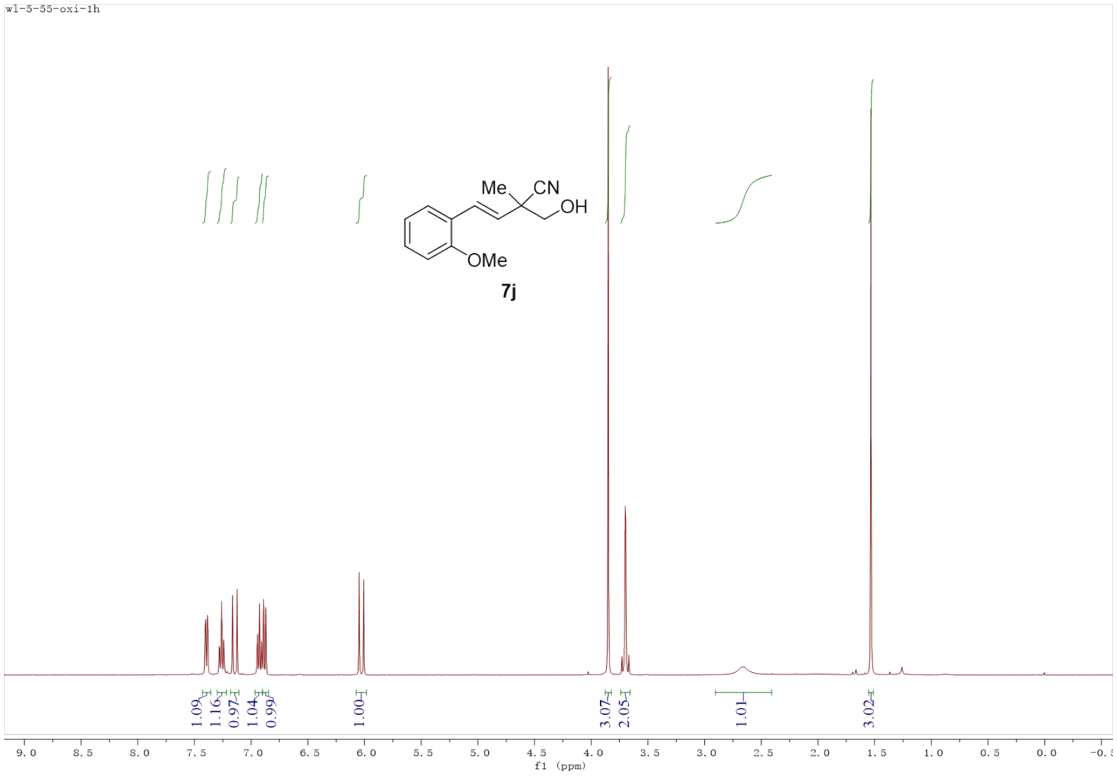

wl-5-41-pure-h
Me
CN
B(pin)
MeO
N
O
Me
7h
1.03
1.02
1.03
1.00
0.99
1.00
2.97
2.99
3.02
2.06
12.67
f1 (ppm)

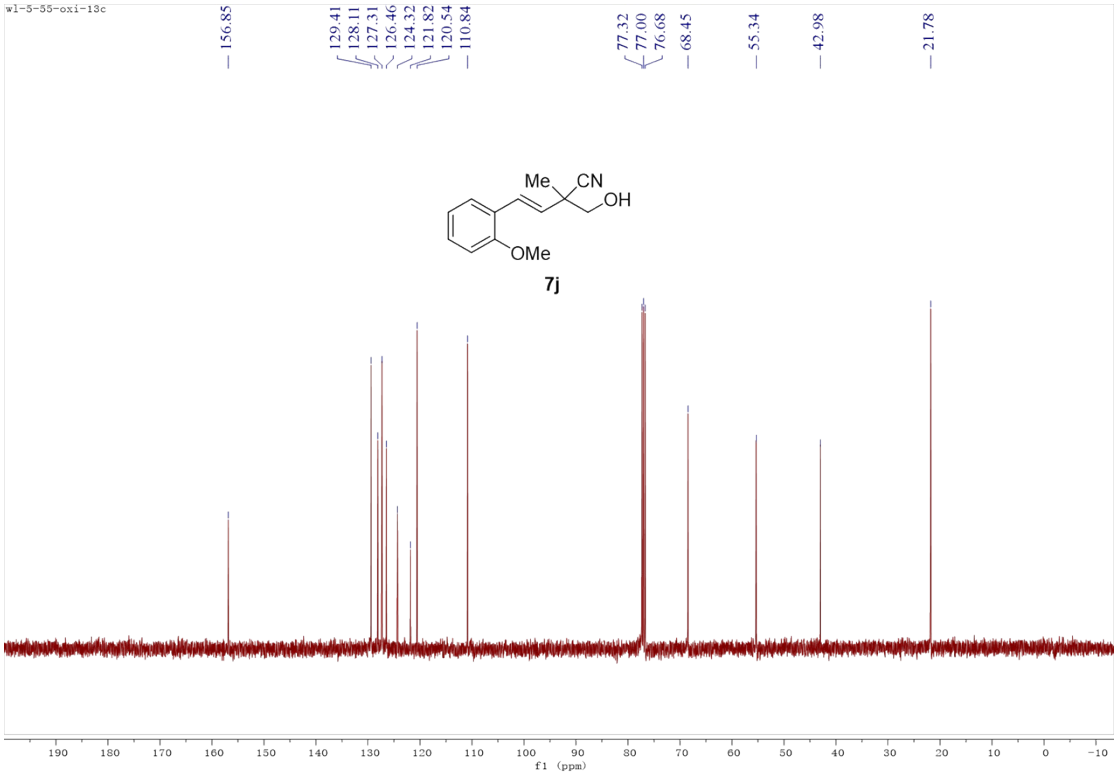

wl-5-41-13c-pure
169.48
135.87
134.43
131.96
128.61
128.58
128.25
127.41
126.11
123.38
83.70
77.32
77.00
76.68
60.99
36.20
27.35
24.72
24.65
Me
CN
B(pin)
MeO
N
O
Me
7h
f1 (ppm)

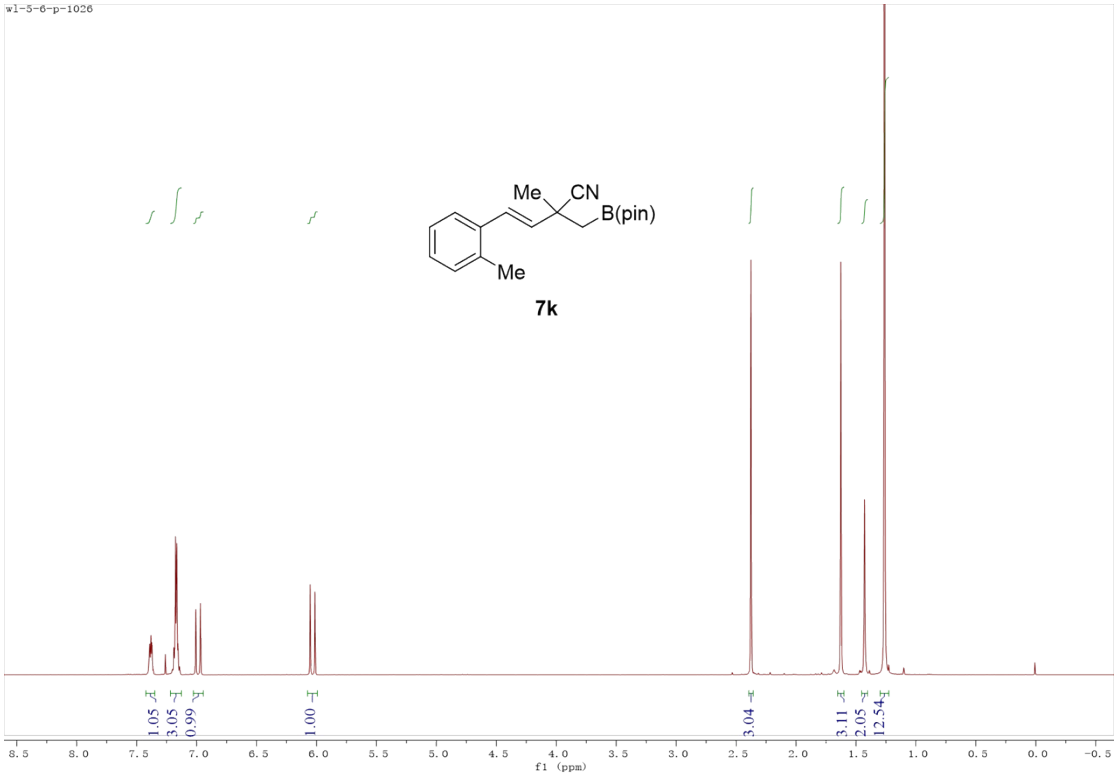

wl-4-95-p-1018
Me
CN
B(pin)
F
7i
1.07
1.00
1.04
0.98
0.98
1.00
3.06
2.02
12.06
f1 (ppm)

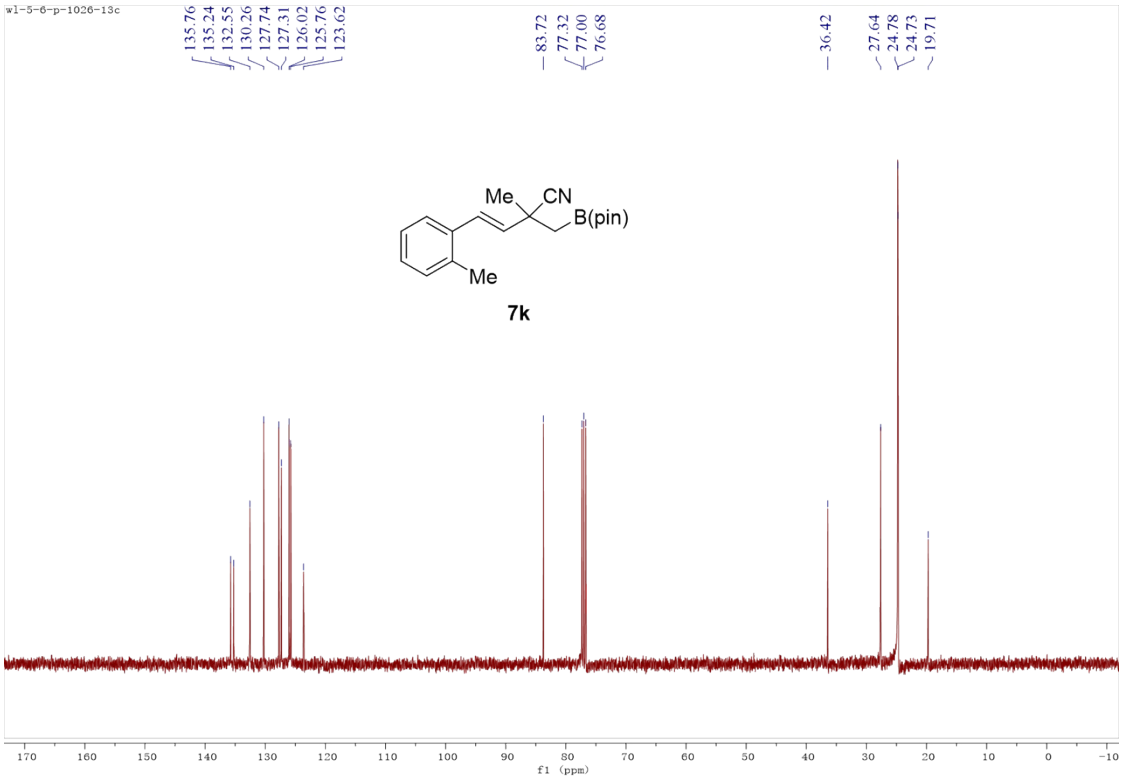

wl-4-95-p-1018-13c
161.55
159.06
133.76
133.70
129.19
129.11
127.91
127.88
124.11
124.07
123.85
123.73
123.39
122.41
122.39
115.88
115.66
83.74
77.32
77.00
76.68
36.50
27.31
24.74
24.69
Me
CN
B(pin)
F
7i
f1 (ppm)

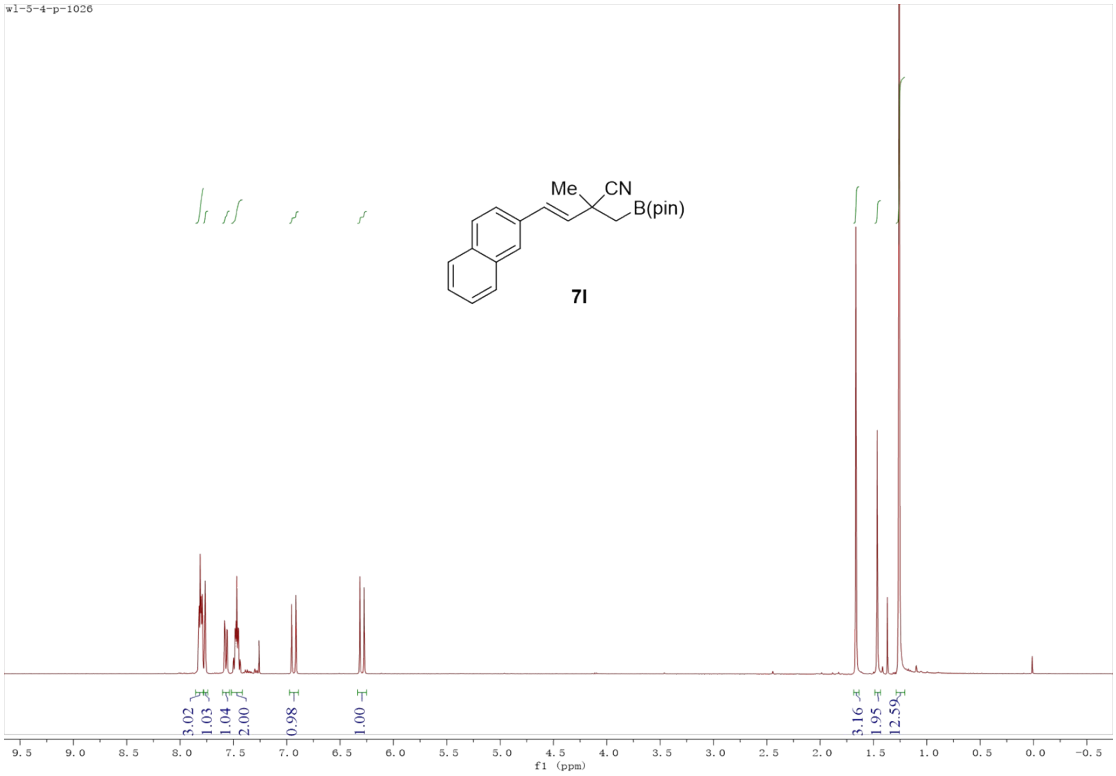

wl-4-95-p-f
STANDARD PROTON PARAMETERS
-116.97
Me
CN
B(pin)
F
7i
f1 (ppm)

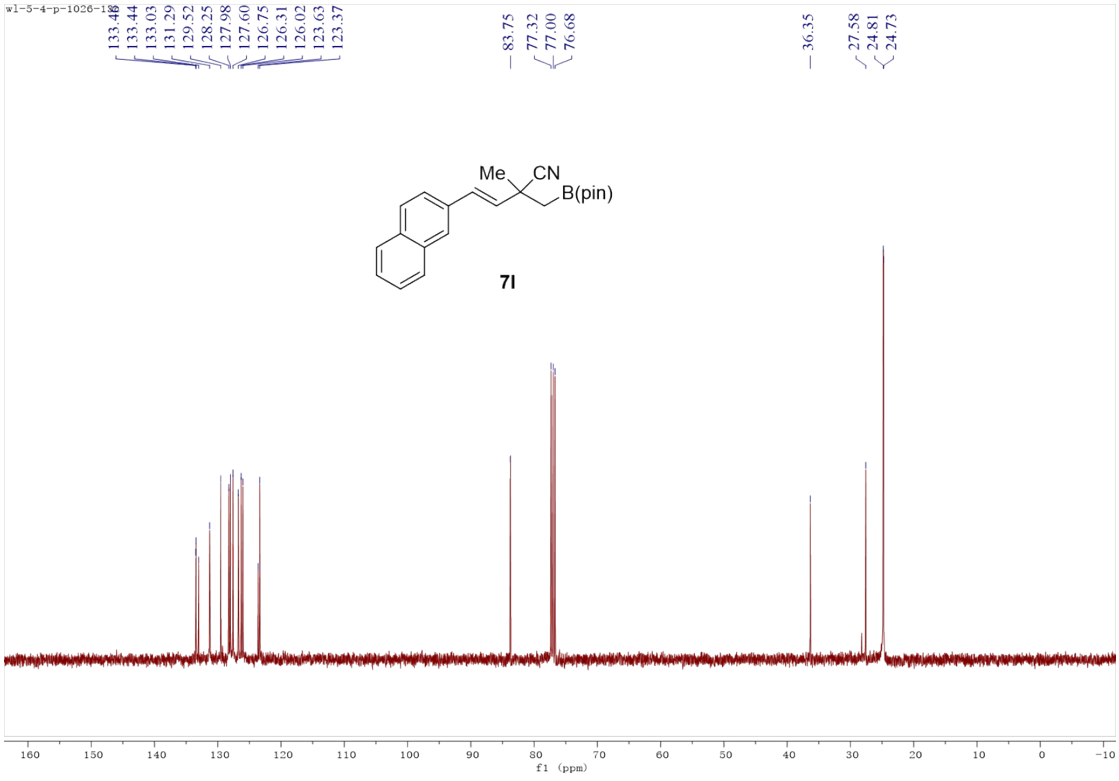

wl-5-55-oxi-1h
Me
CN
OH
OMe
7j
1.09
1.16
0.97
1.04
0.99
1.00
3.07
2.05
1.01
3.02
f1 (ppm)

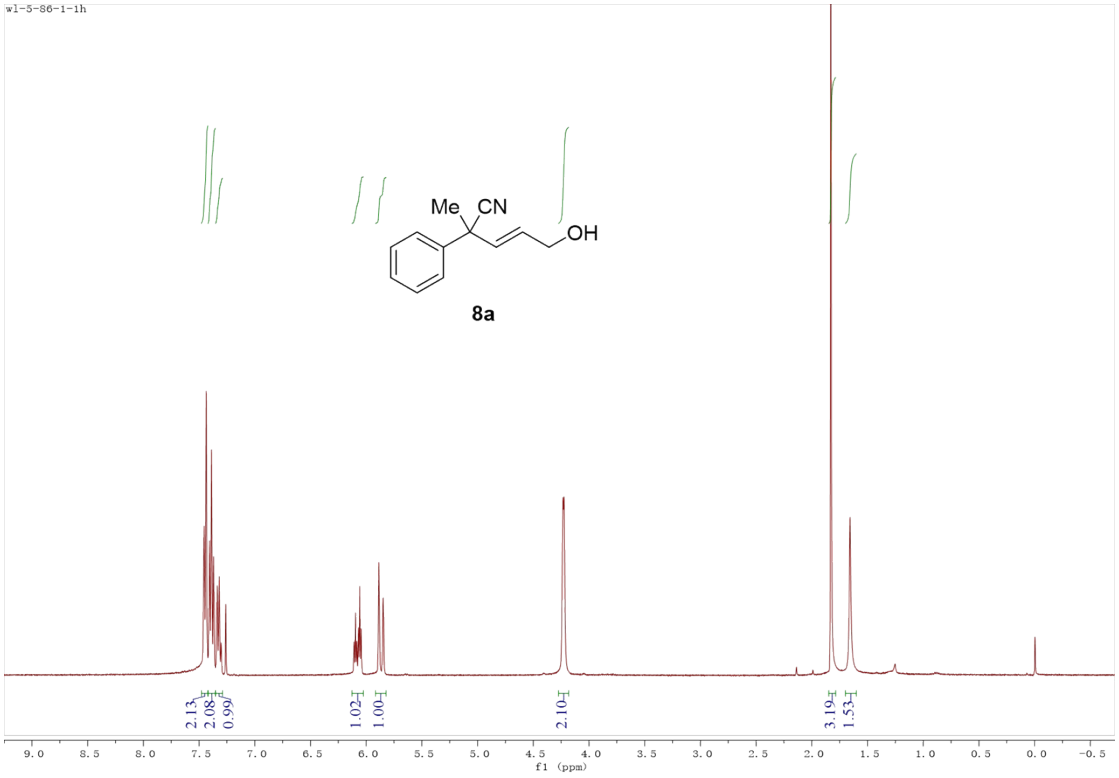

wl-5-55-oxi-13c
156.85
129.41
128.11
127.31
126.46
124.32
121.82
120.54
110.84
77.32
77.00
76.68
68.45
55.34
42.98
21.78
Me
CN
OH
OMe
7j
f1 (ppm)

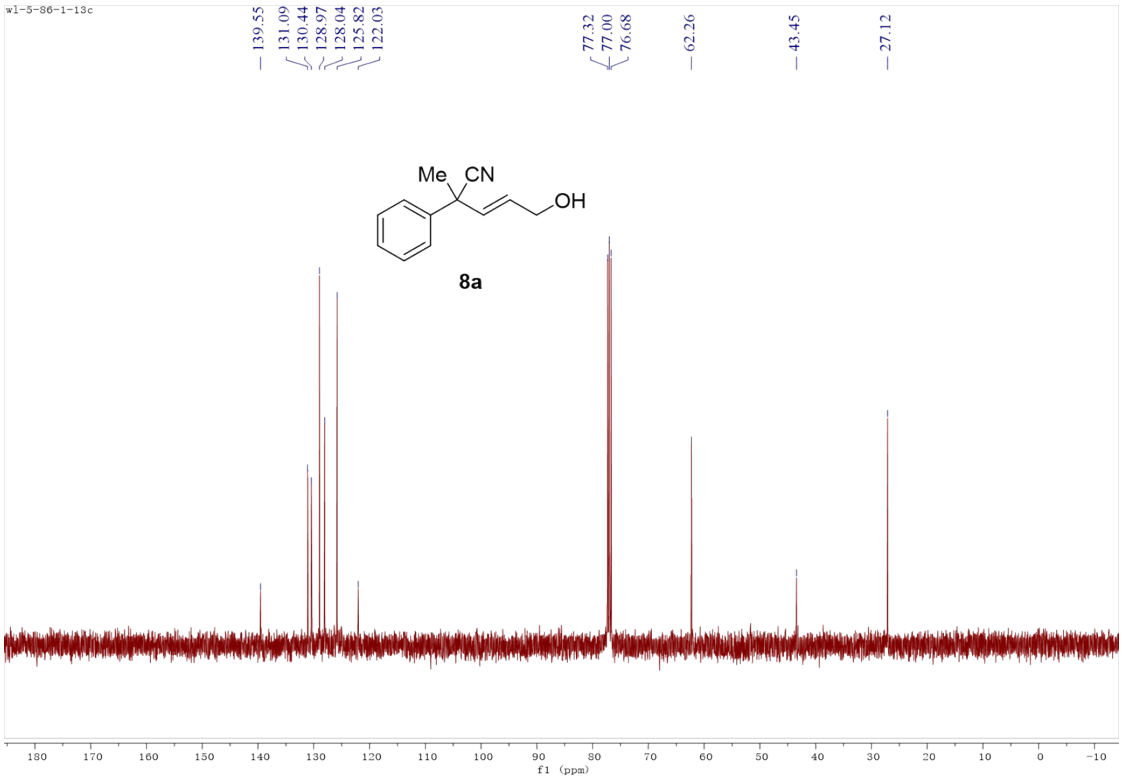

wl-5-6-p-1026
Me
CN
B(pin)
Me
7k
1.05
3.05
0.99
1.00
3.04
3.11
2.05
12.54
f1 (ppm)

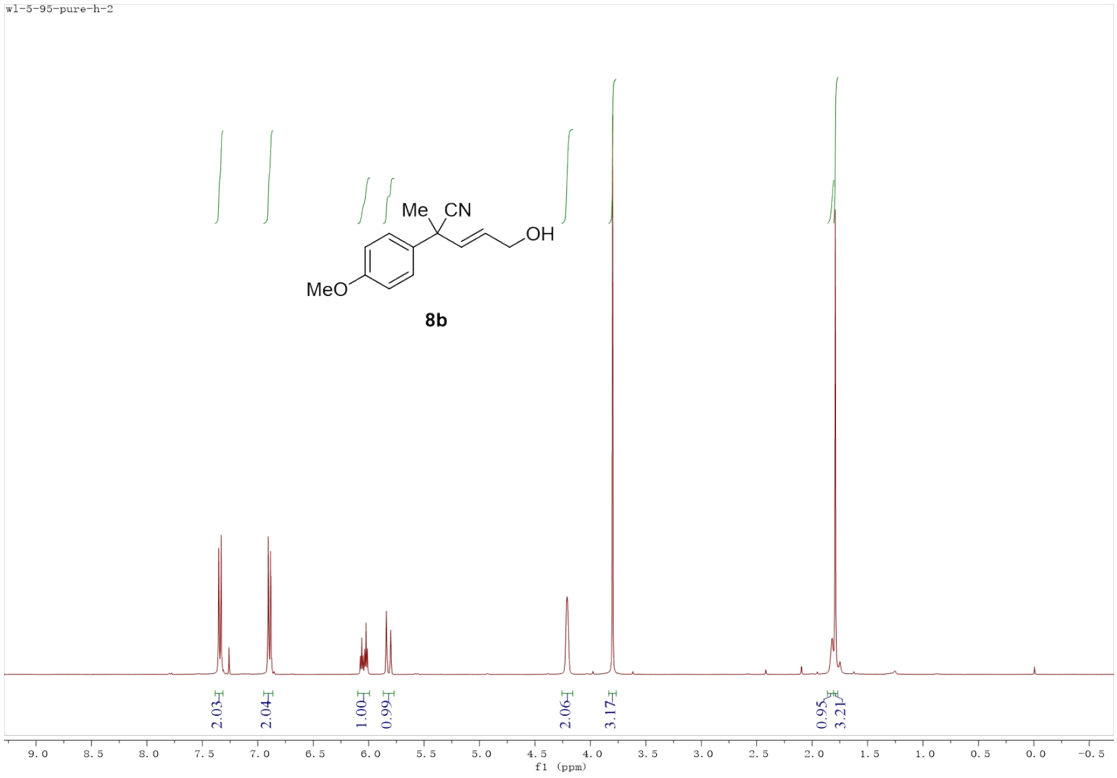

wl-5-6-p-1026-13c
135.76
135.24
132.55
130.26
127.74
127.31
126.02
125.76
123.62
83.72
77.32
77.00
76.68
36.42
27.64
24.78
24.73
19.71
Me
CN
B(pin)
Me
7k
f1 (ppm)

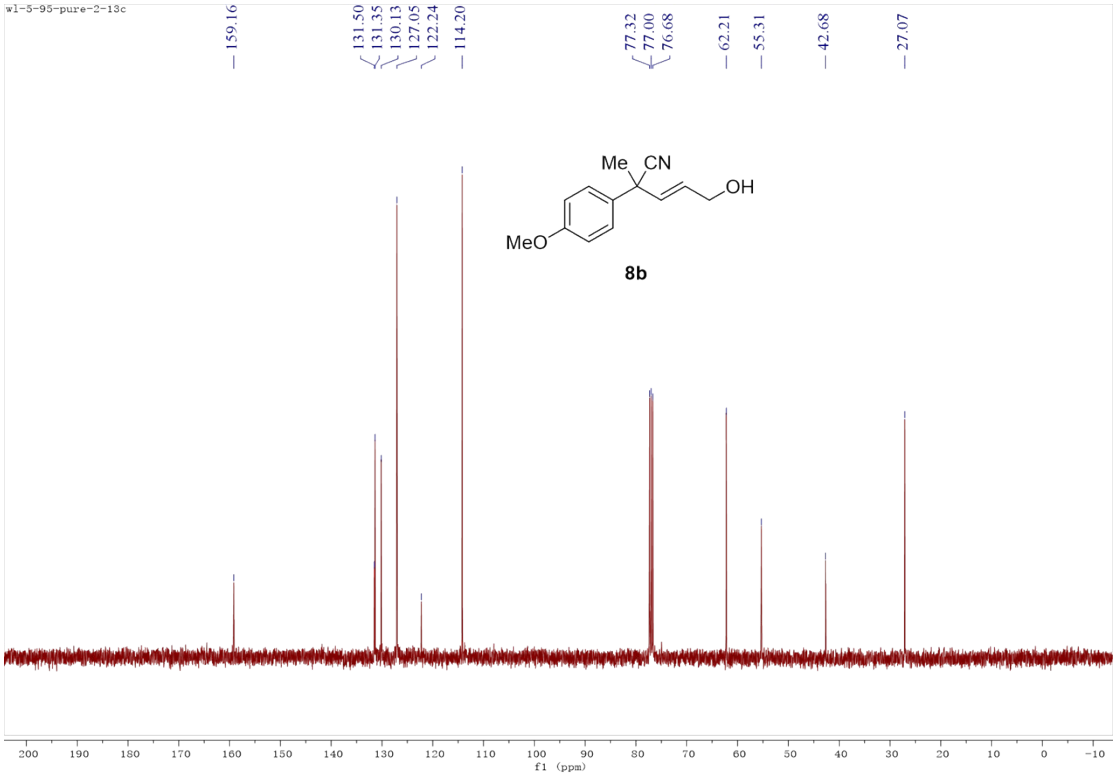

wl-5-4-p-1026
Me
CN
B(pin)
7l
3.02
1.03
1.04
2.00
0.98
1.00
3.16
1.95
12.59
f1 (ppm)

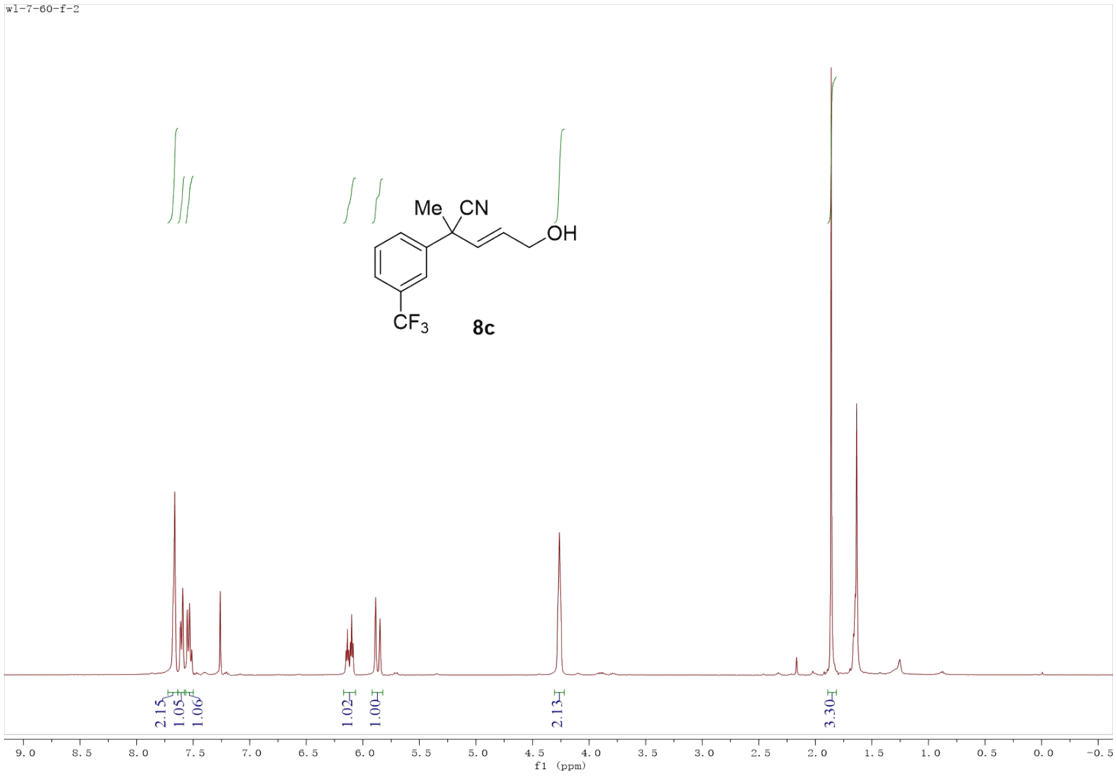

wl-5-4-p-1026-13
133.48
133.44
133.03
131.29
129.52
128.25
127.98
127.60
126.75
126.31
126.02
123.63
123.37
83.75
77.32
77.00
76.68
36.35
27.58
24.81
24.73
Me
CN
B(pin)
7l
f1 (ppm)

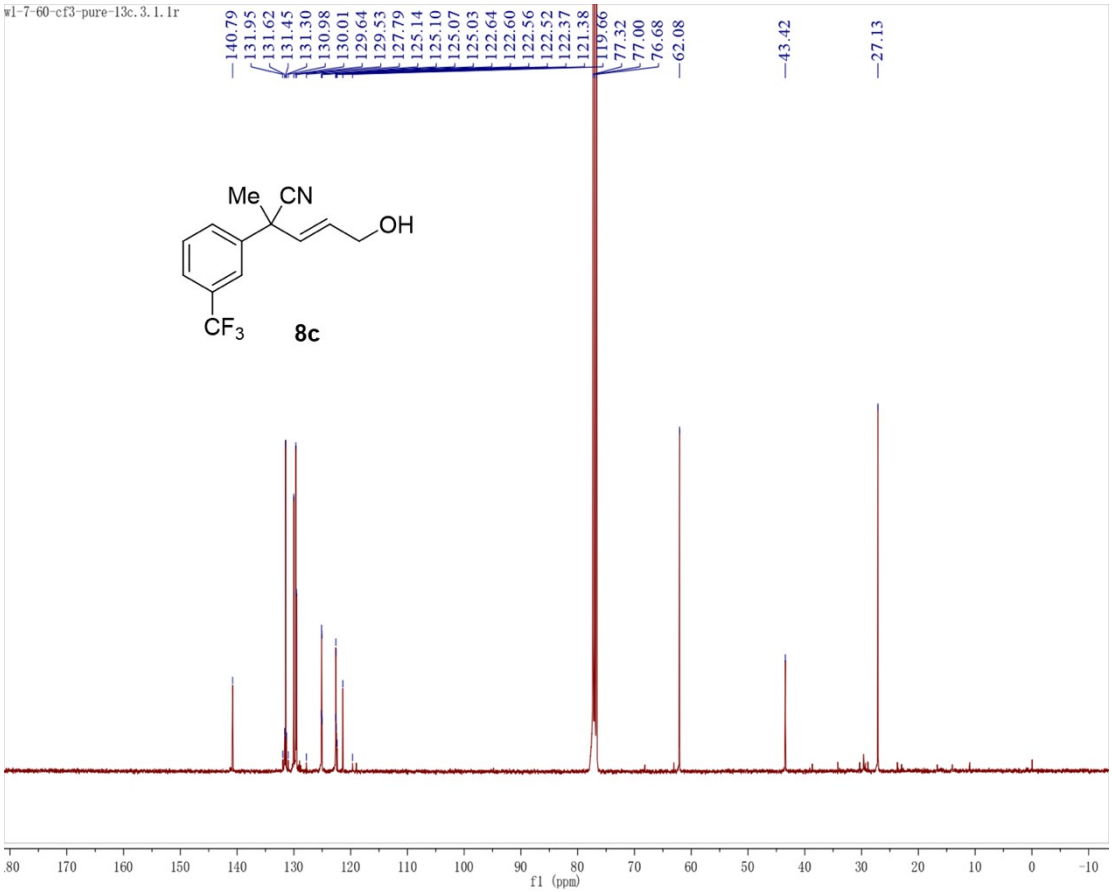

wl-5-86-1-1h
Me
CN
OH
8a
2.13
2.08
0.99
1.02
1.00
2.10
3.19
1.53
f1 (ppm)

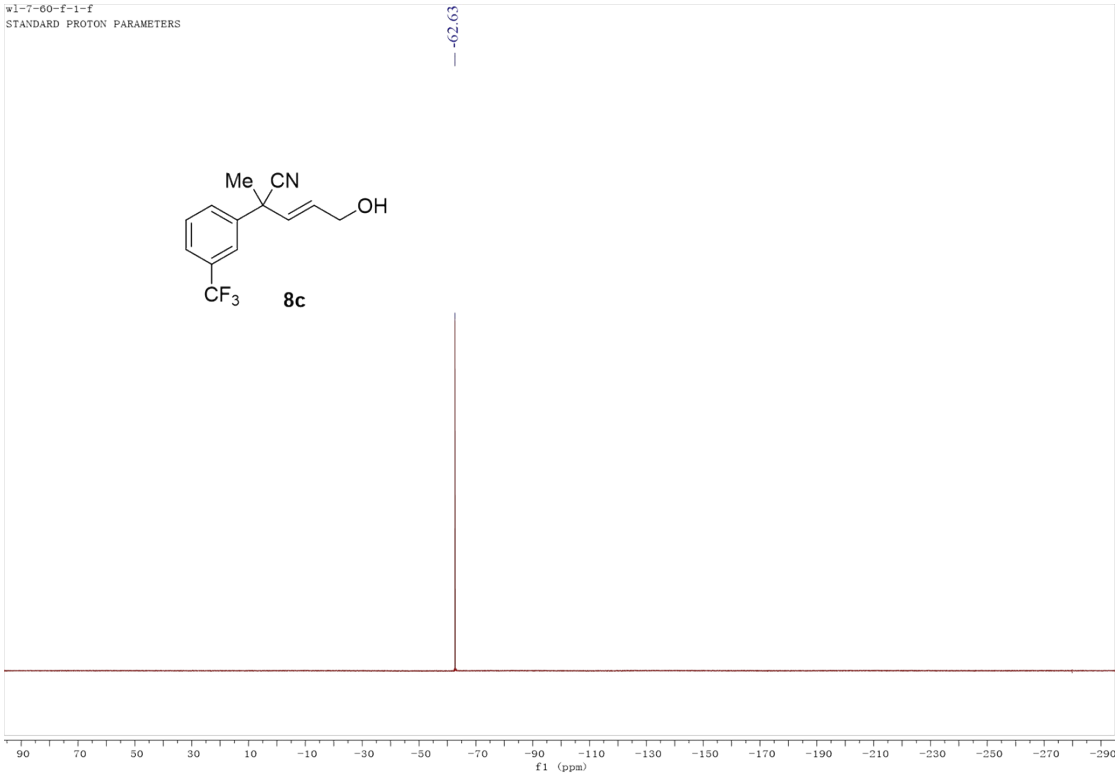

wl-5-86-1-13c
139.55
131.09
130.44
128.97
128.04
125.82
122.03
77.32
77.00
76.68
62.26
43.45
27.12
Me
CN
OH
8a
f1 (ppm)

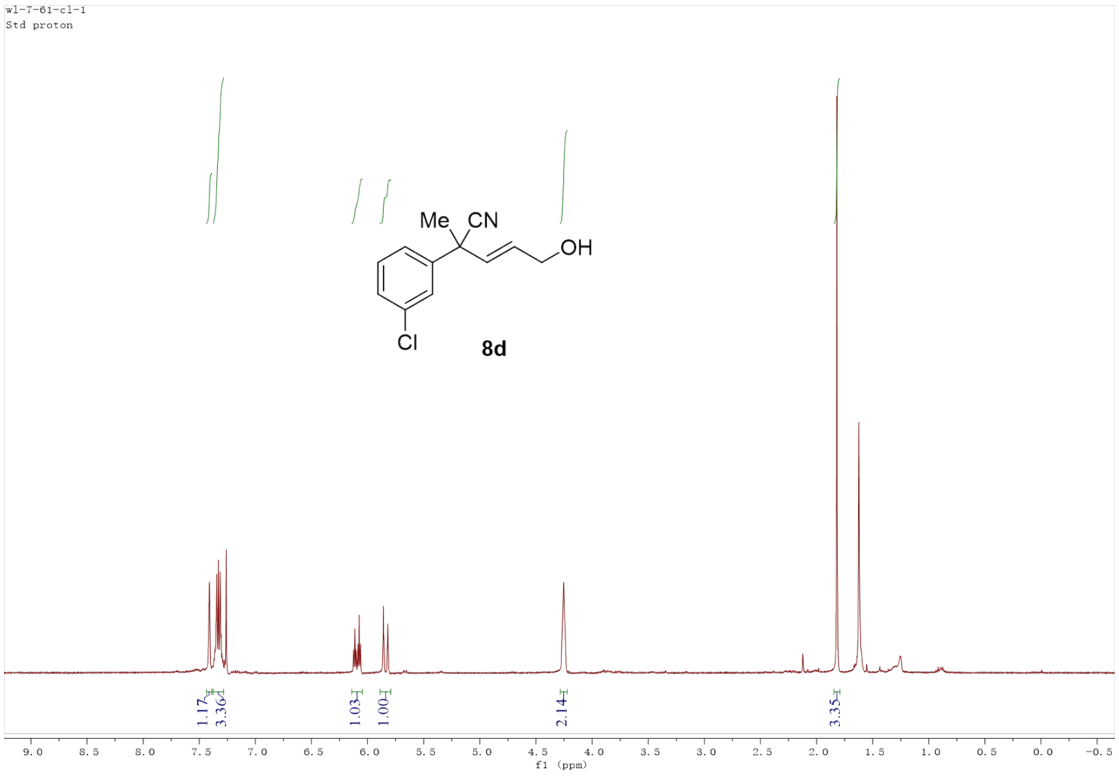

wl-5-95-pure-h-2
Me
CN
OH
MeO
8b
2.03
2.04
1.00
0.99
2.06
3.17
0.95
3.21
f1 (ppm)

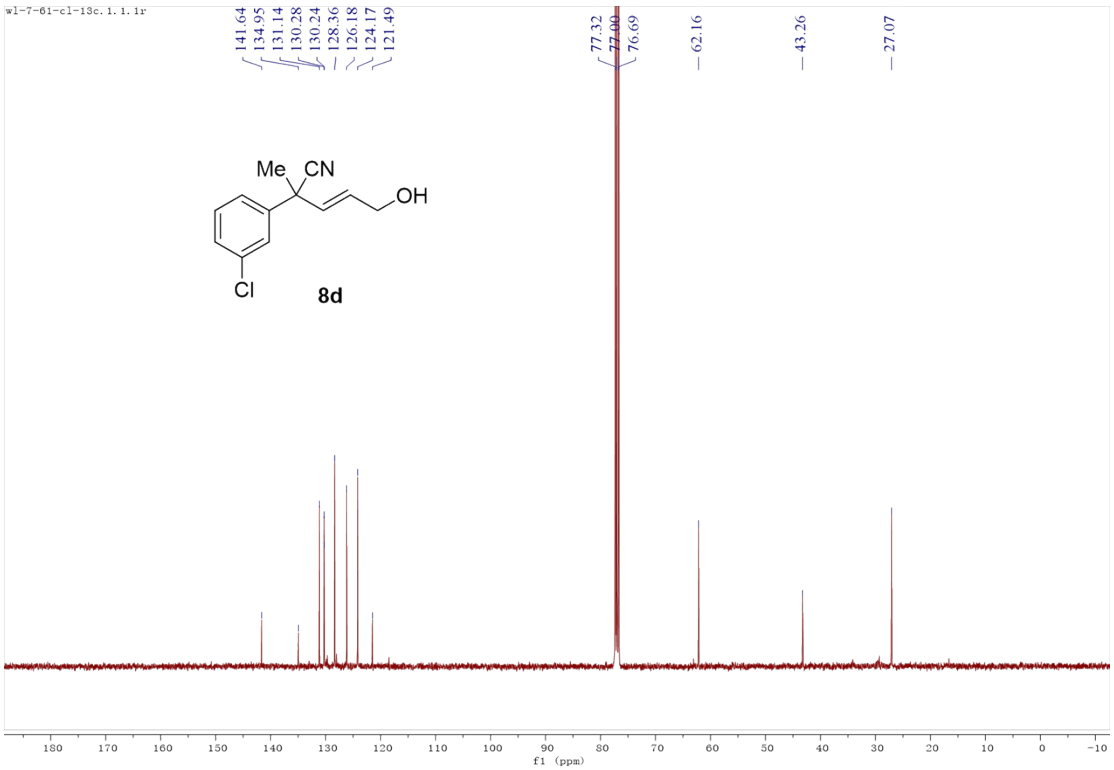

wl-5-95-pure-2-13c
159.16
131.50
131.35
130.13
127.05
122.24
114.20
77.32
77.00
76.68
62.21
55.31
42.68
27.07
Me
CN
OH
MeO
8b
f1 (ppm)

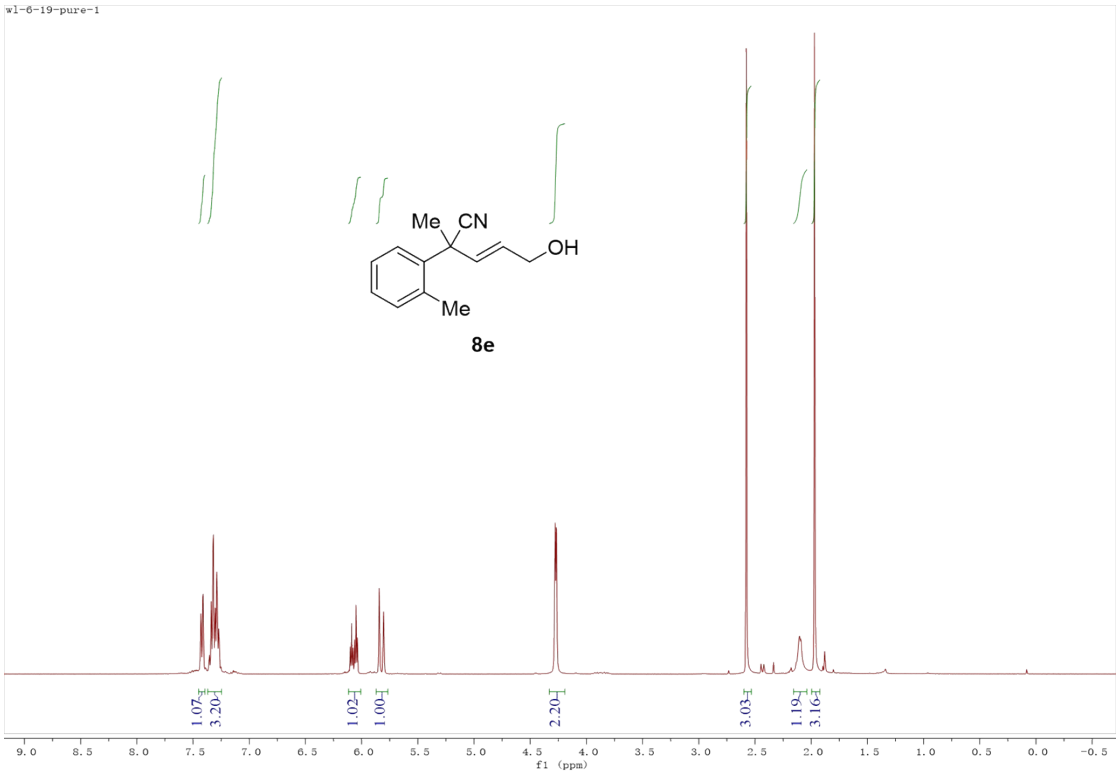

wl-7-60-f-2
Me
CN
OH
CF3
8c
2.15
1.05
1.06
1.02
1.00
2.13
3.30
f1 (ppm)

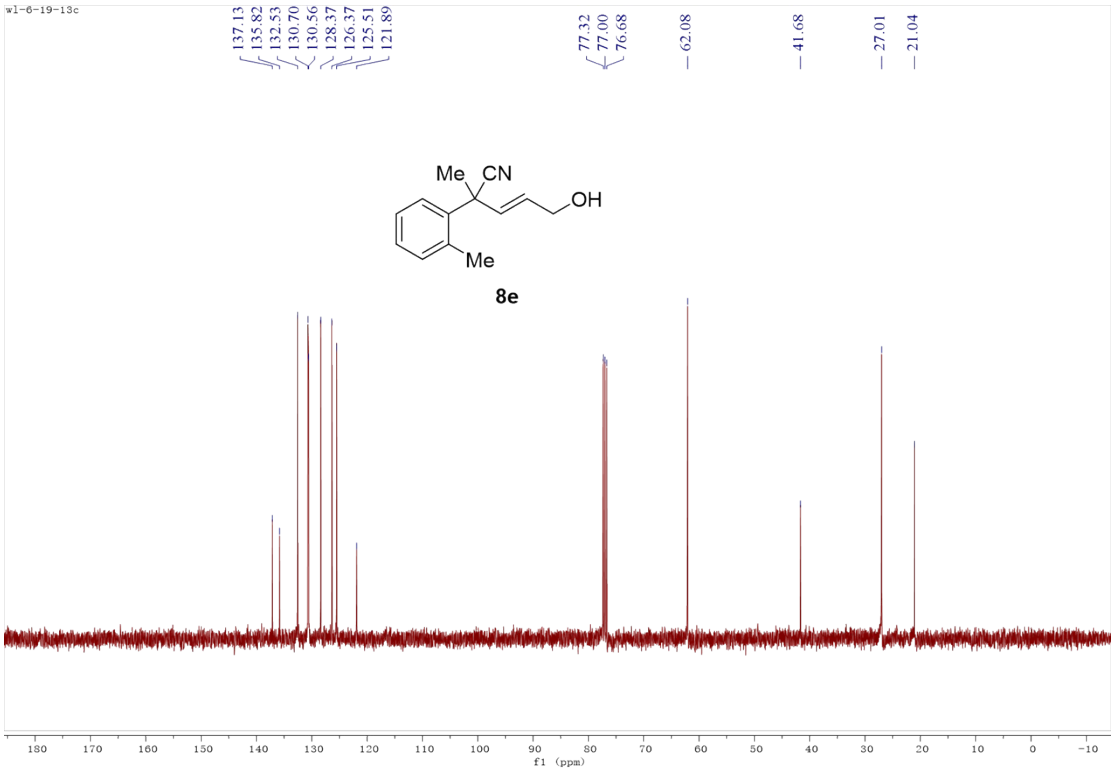

wl-7-60-cf3-pure-13c.3.1.1r
140.79
131.95
131.62
131.45
131.30
130.98
130.01
129.64
129.53
127.79
125.14
125.10
125.07
125.03
122.64
122.60
122.56
122.52
122.37
121.38
119.66
77.32
77.00
76.68
62.08
43.42
27.13
Me
CN
OH
CF3
8c
f1 (ppm)

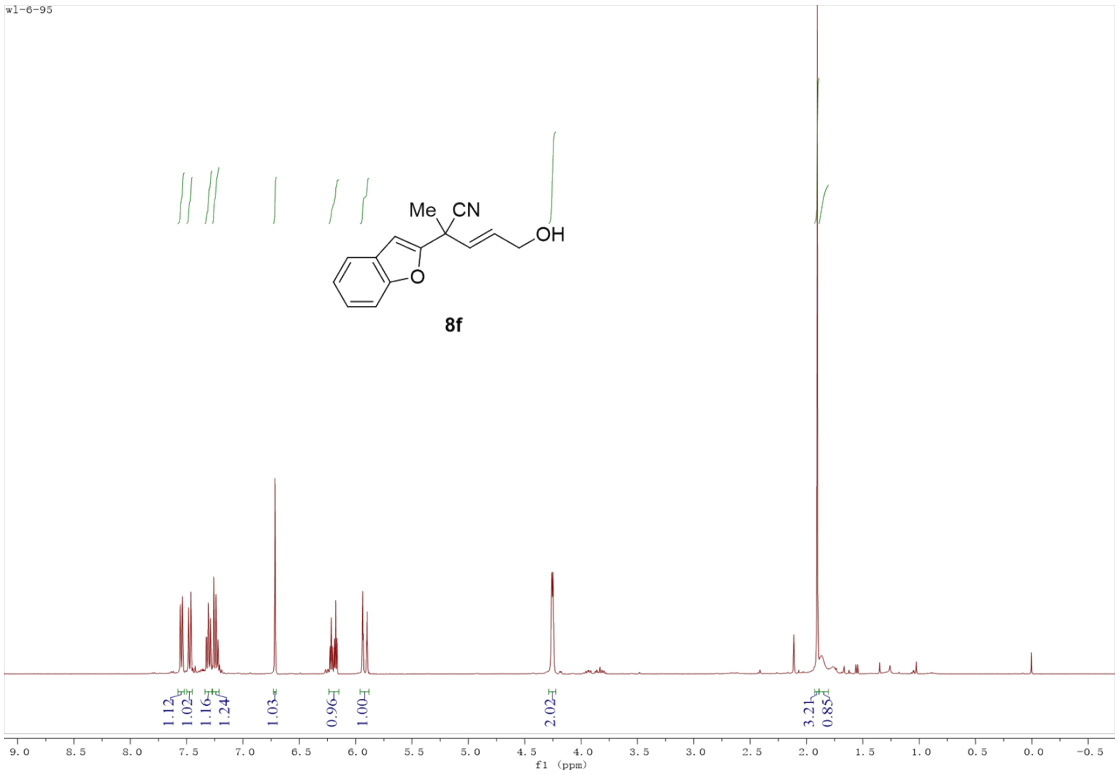

wl-7-60-f-1-f
STANDARD PROTON PARAMETERS
-62.63
Me
CN
OH
CF3
8c
f1 (ppm)

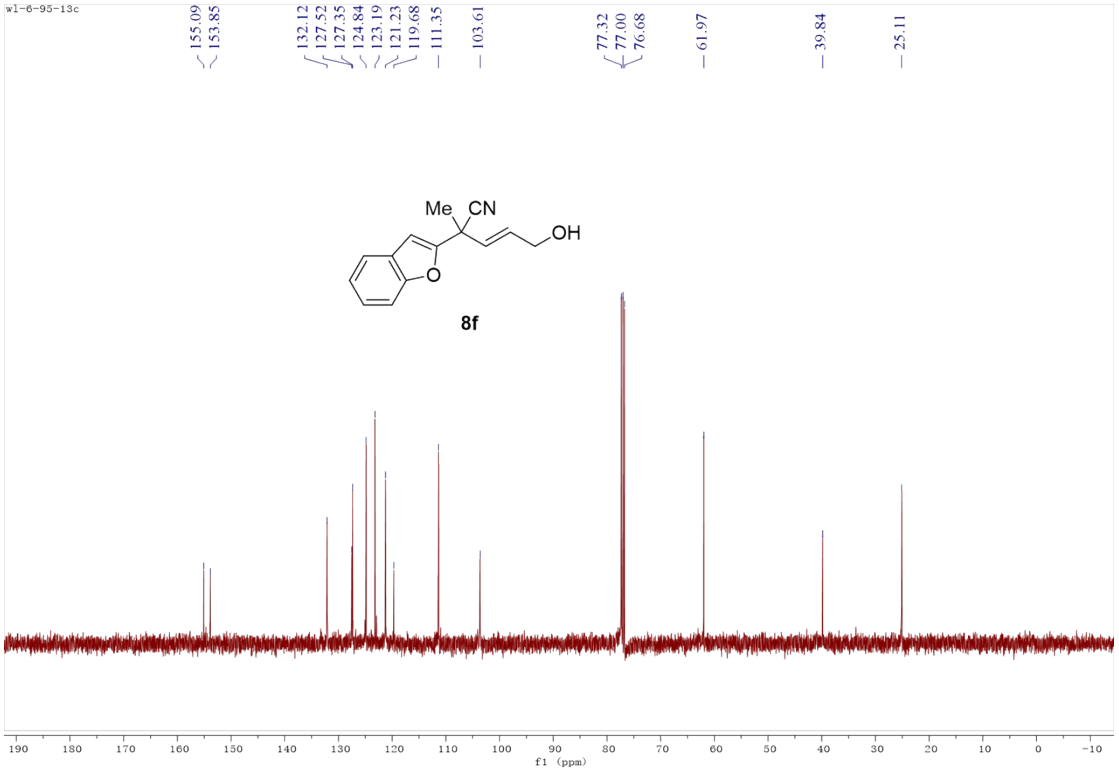

wl-7-61-cl-1
Std proton
Me
CN
OH
Cl
8d
1.17
3.36
1.03
1.00
2.14
3.35
f1 (ppm)

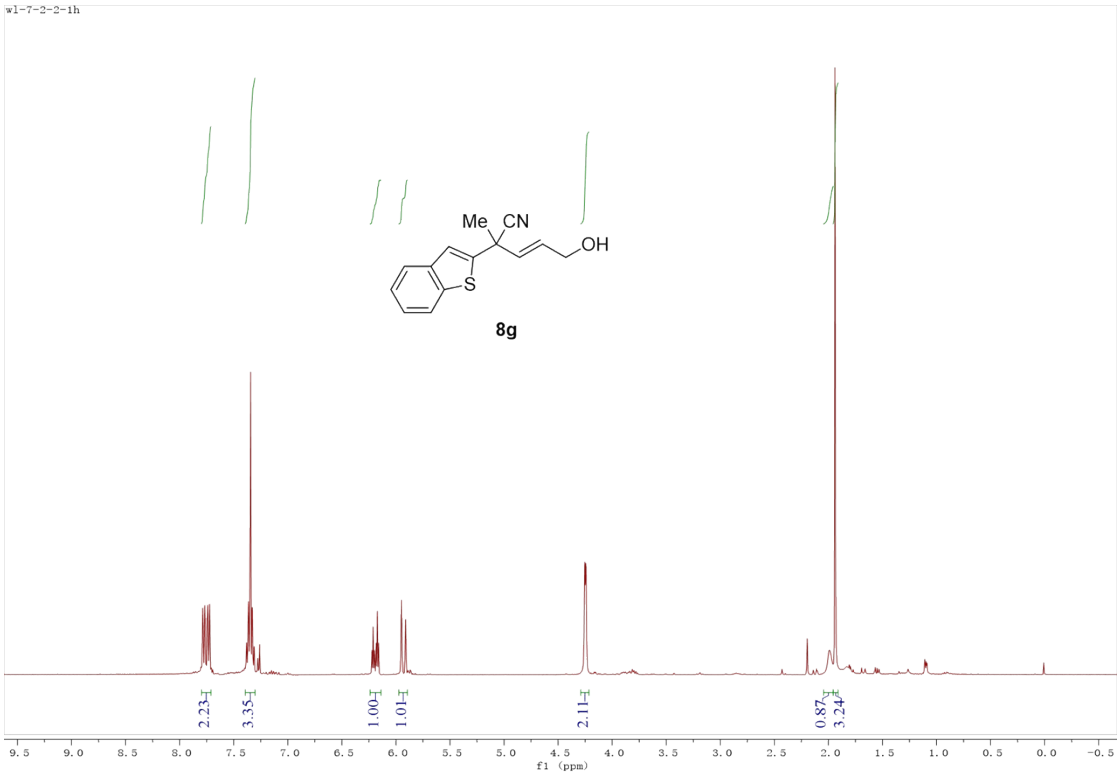

wl-7-61-cl-13c.1.1.1r
141.64
134.95
131.14
130.28
130.24
128.36
126.18
124.17
121.49
77.32
77.00
76.69
62.16
43.26
27.07
Me
CN
OH
Cl
8d
f1 (ppm)

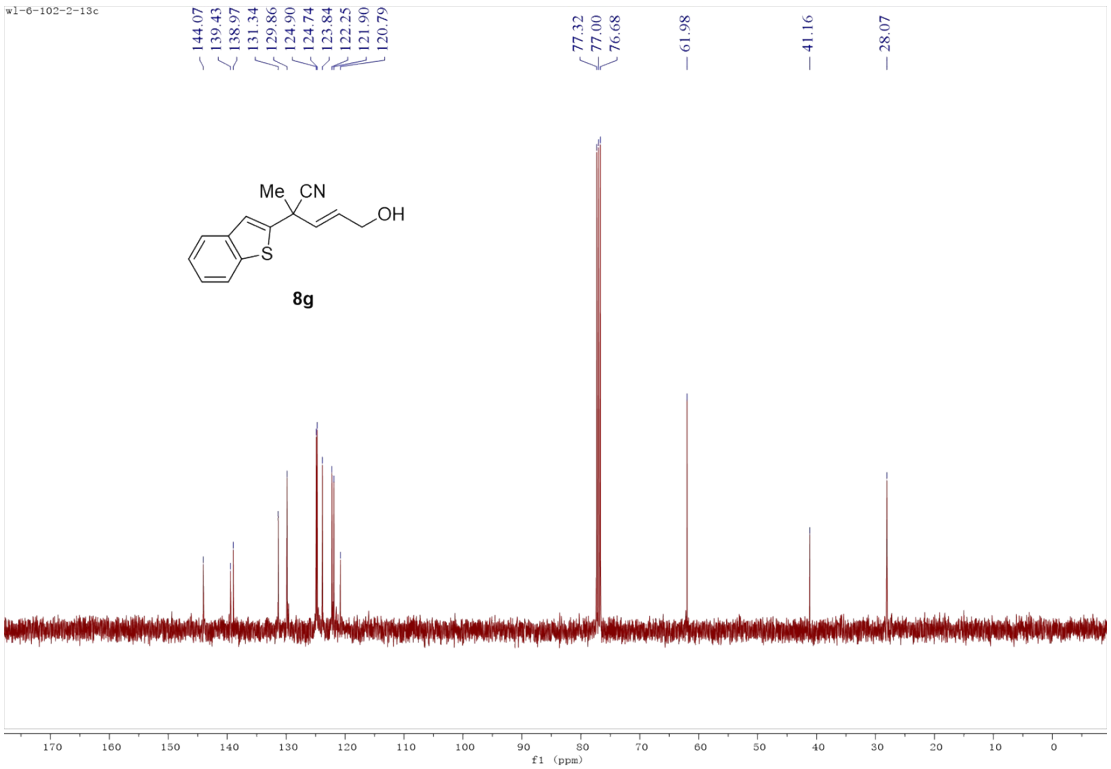

wl-6-19-pure-1
Me
CN
OH
Me
8e
1.07
3.20
1.02
1.00
2.20
3.03
1.19
3.16
f1 (ppm)

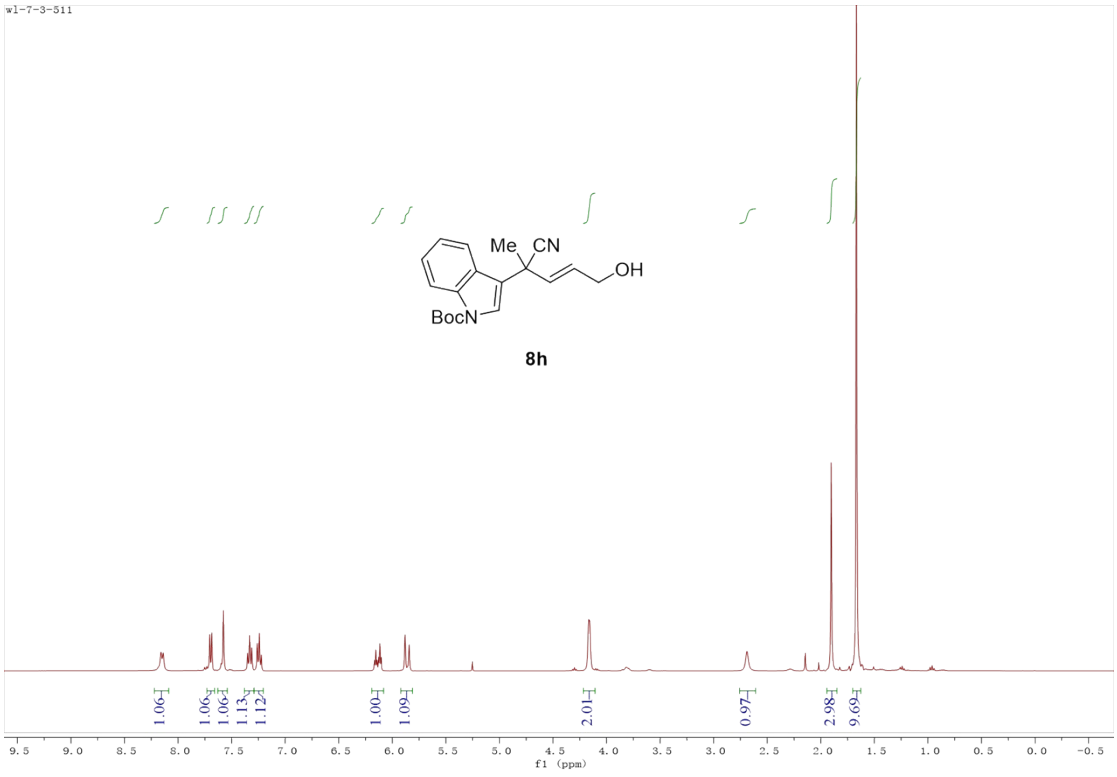

wl-6-19-13c
137.13
135.82
132.53
130.70
130.56
128.37
126.37
125.51
121.89
77.32
77.00
76.68
62.08
41.68
27.01
21.04
Me
CN
OH
Me
8e
f1 (ppm)

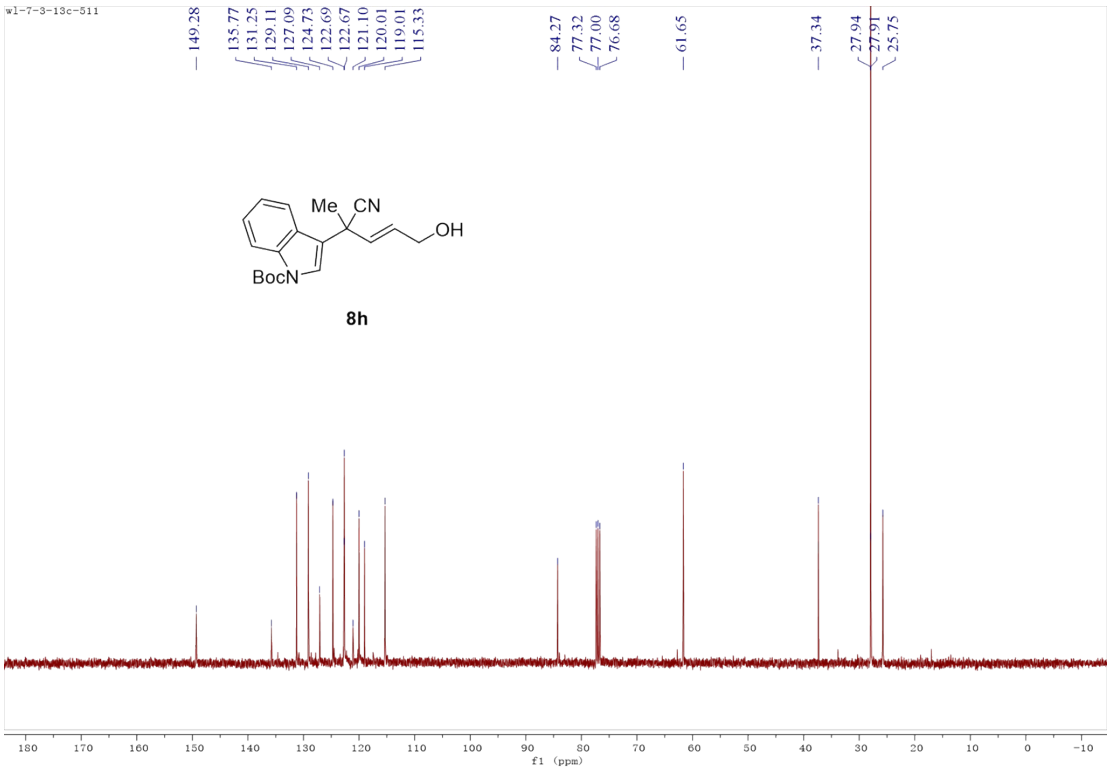

wl-6-95
Me
CN
OH
O
8f
1.12
1.02
1.16
1.24
1.03
0.96
1.00
2.02
3.21
0.85
f1 (ppm)


wl-6-95-13c
155.09
153.85
132.12
127.52
127.35
124.84
123.19
121.23
119.68
111.35
103.61
77.32
77.00
76.68
61.97
39.84
25.11
Me
CN
OH
O
8f
f1 (ppm)

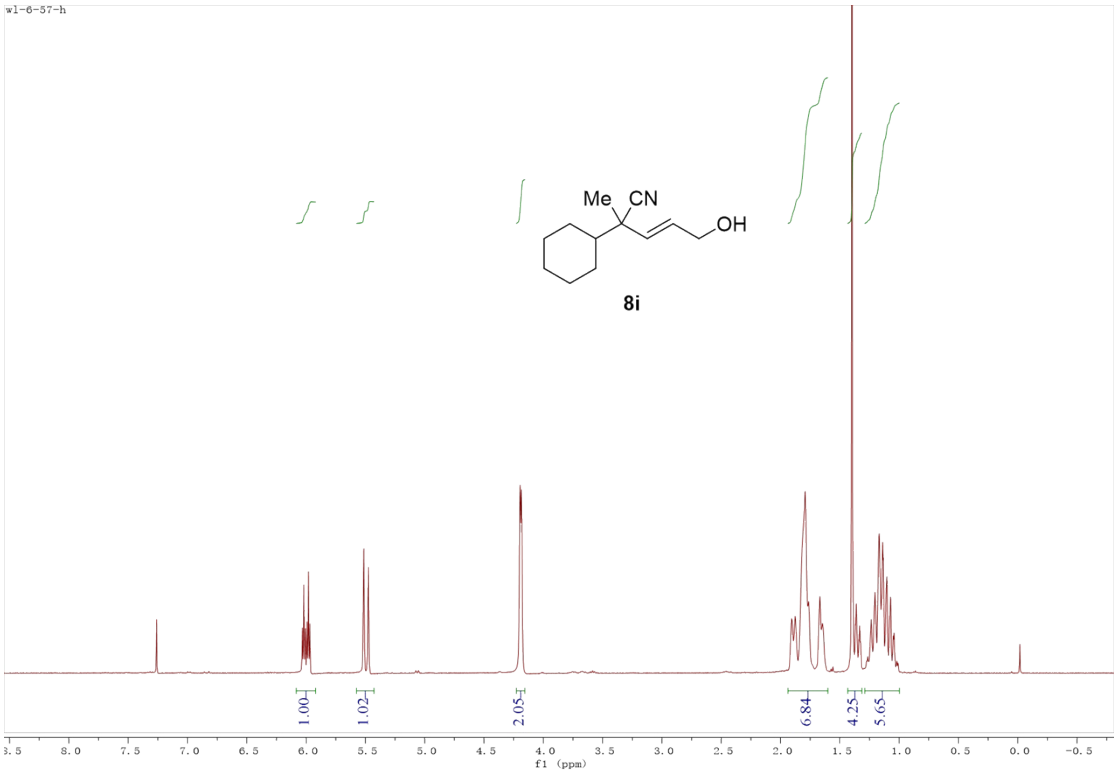

wl-7-2-2-1h
Me
CN
OH
S
8g
2.23
3.35
1.00
1.01
2.11
0.87
3.24
f1 (ppm)


wl-6-102-2-13c
144.07
139.43
138.97
131.34
129.86
124.90
124.74
123.84
122.25
121.90
120.79
77.32
77.00
76.68
61.98
41.16
28.07
Me
CN
OH
S
8g
f1 (ppm)

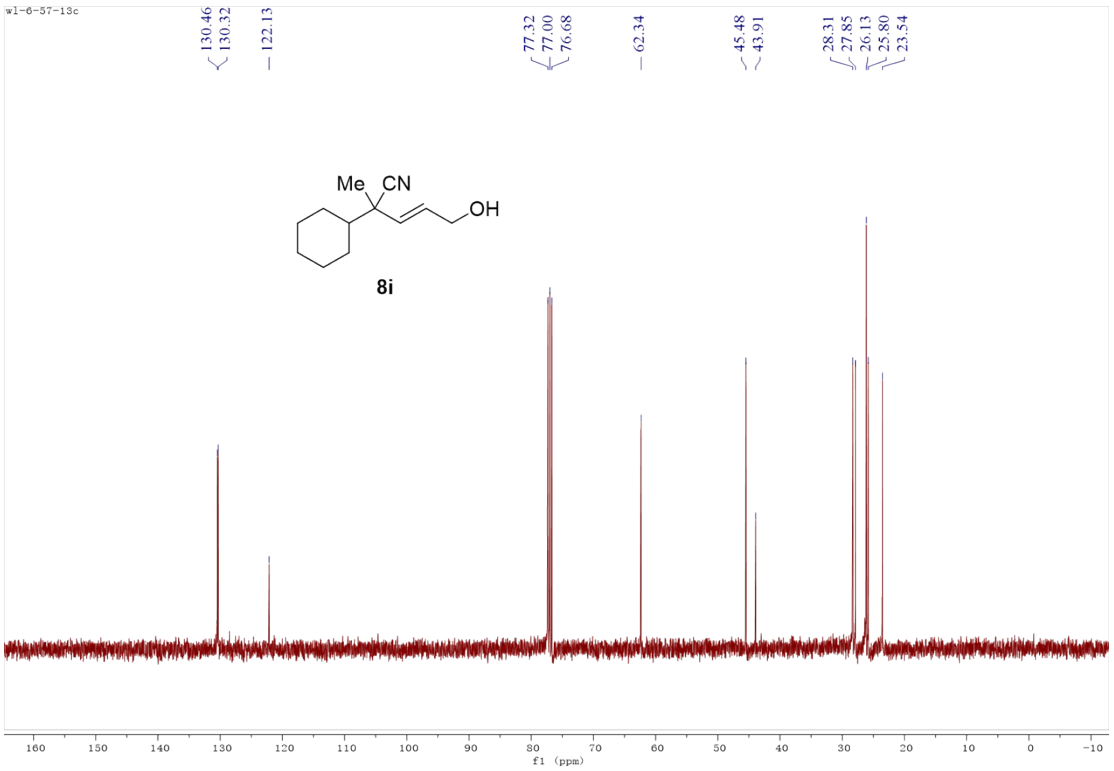

wl-7-3-511
Me
CN
OH
BocN
8h
1.06
1.06
1.06
1.13
1.12
1.00
1.09
2.01
0.97
2.98
9.69
f1 (ppm)

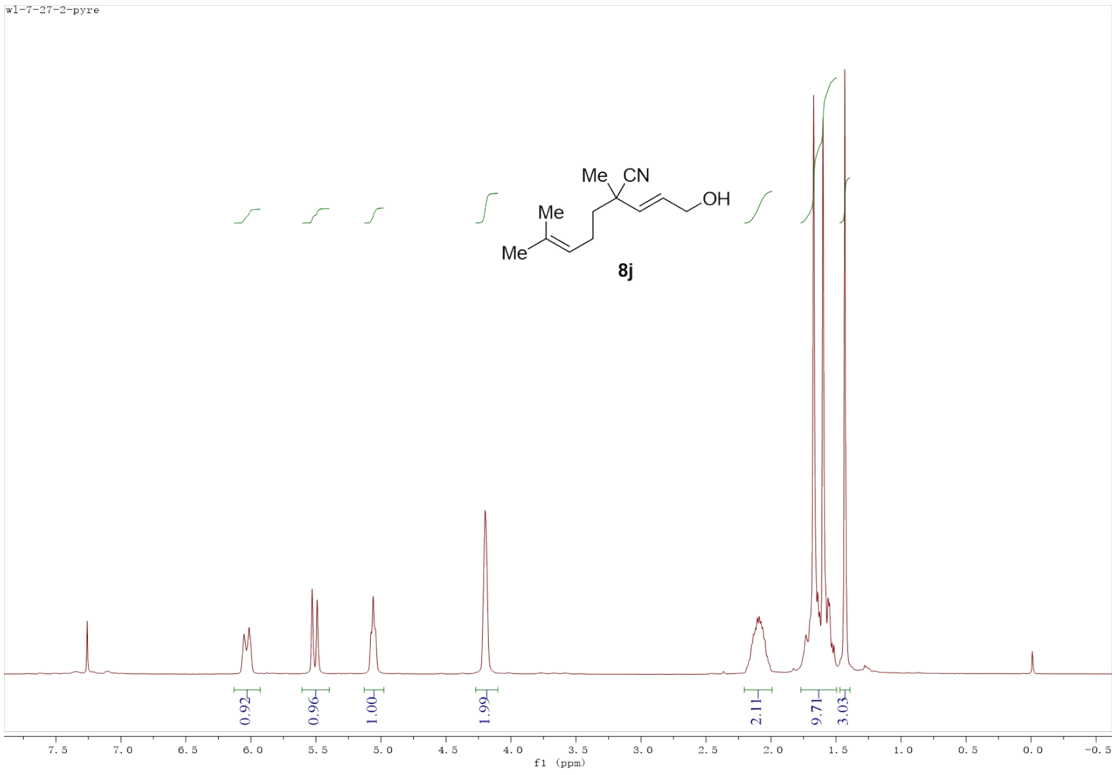

wl-7-3-13c-511
149.28
135.77
131.25
129.11
127.09
124.73
122.69
122.67
121.10
120.01
119.01
115.33
84.27
77.32
77.00
76.68
61.65
37.34
27.94
27.91
25.75
Me
CN
OH
BocN
f1 (ppm)

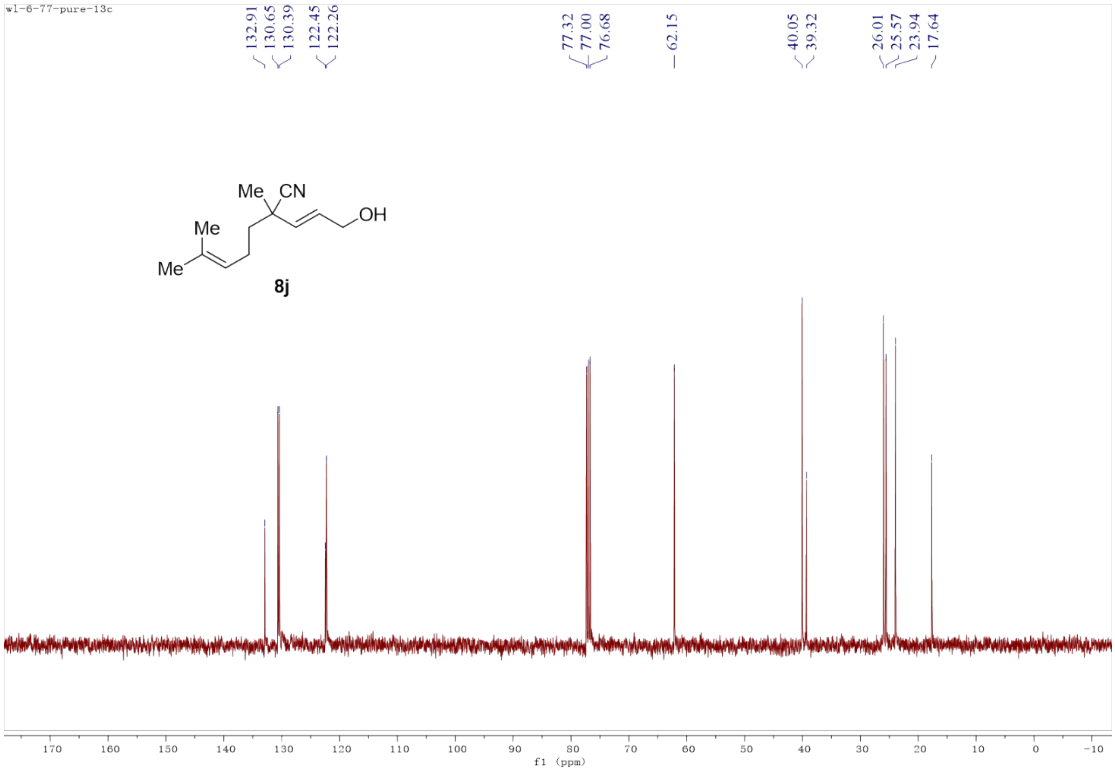
8h

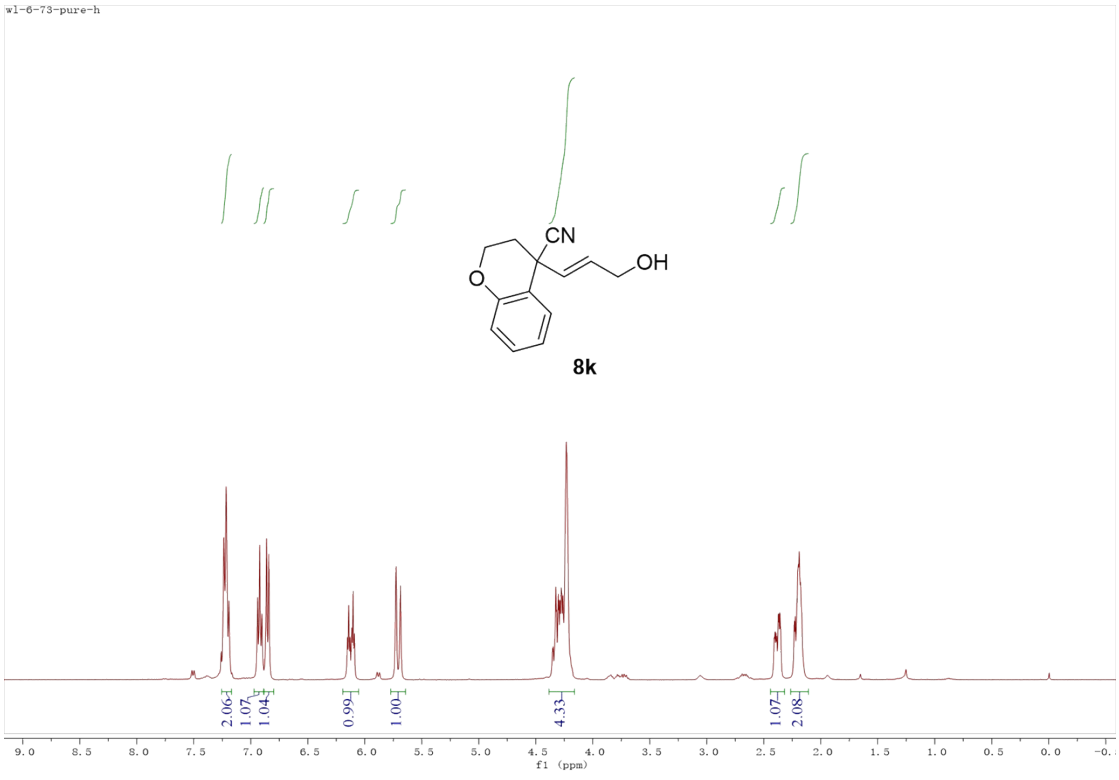

wl-6-57-h
Me
CN
OH
1.00
1.02
2.05
6.84
4.25
5.65
f1 (ppm)

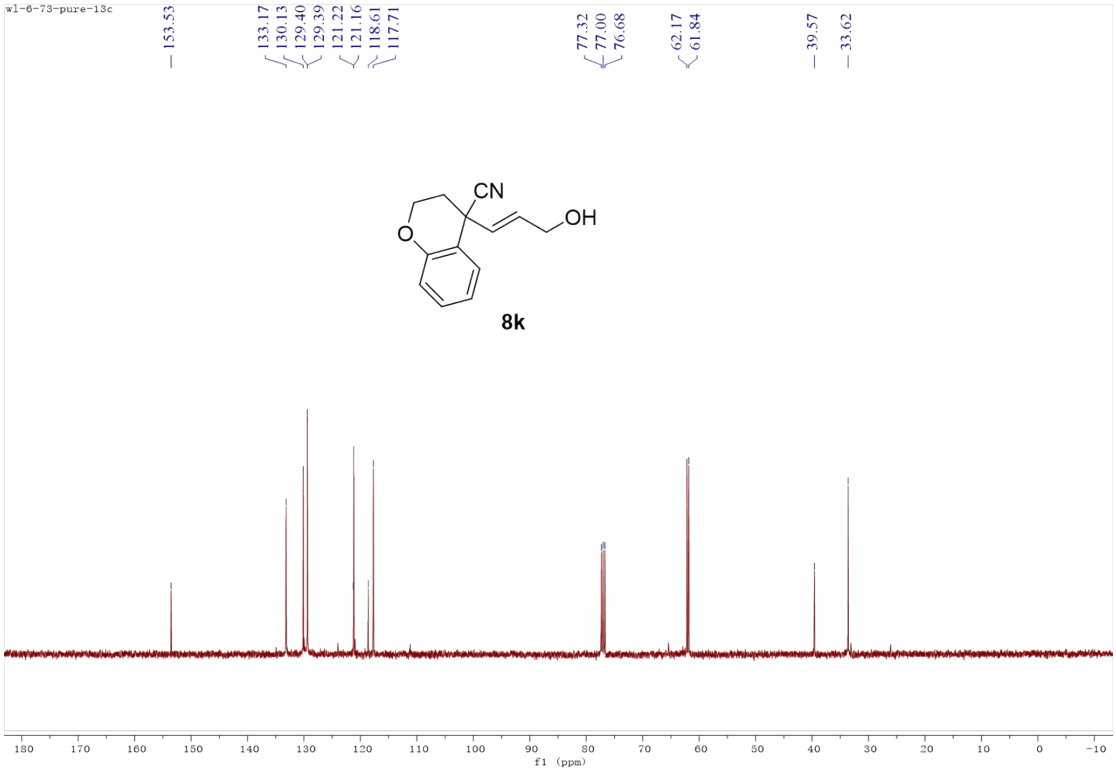
8i

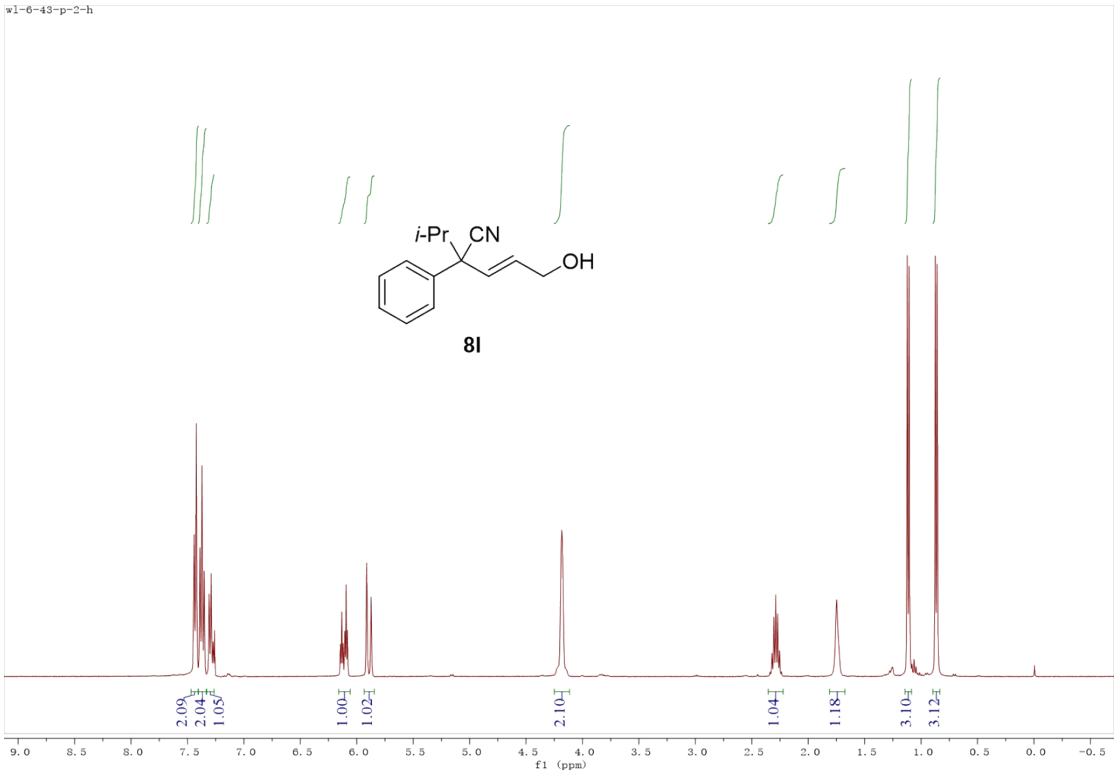

wl-6-57-13c
130.46
130.32
122.13
77.32
77.00
76.68
62.34
45.48
43.91
28.31
27.85
26.13
25.80
23.54
Me
CN
OH
8i
f1 (ppm)

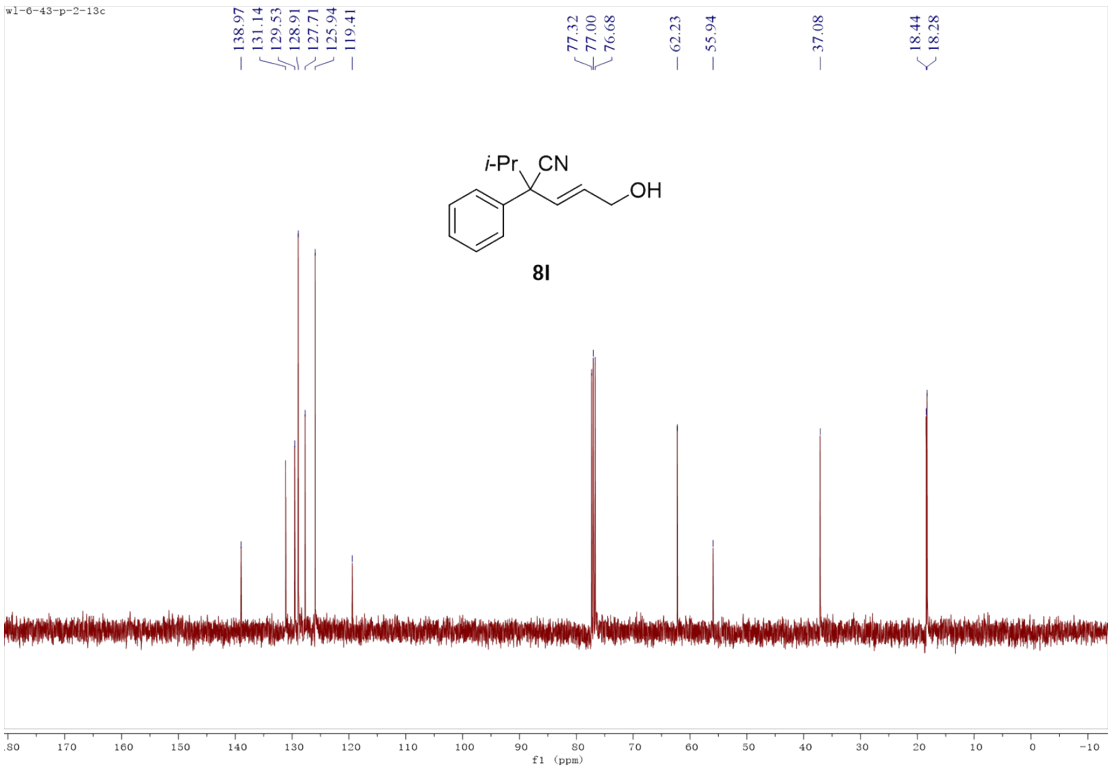

wl-7-27-2-pyre
Me
CN
OH
Me
Me
8j
0.92
0.96
1.00
1.99
2.11
9.71
3.03
f1 (ppm)

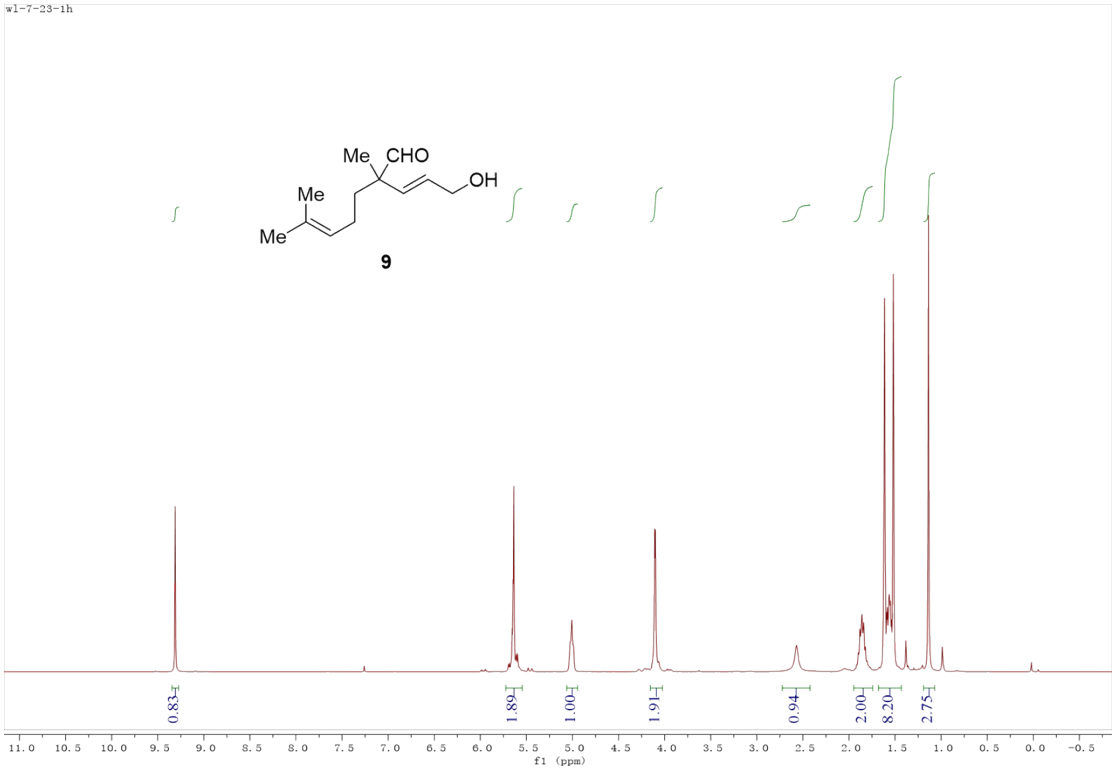

wl-6-77-pure-13c
132.91
130.65
130.39
122.45
122.26
77.32
77.00
76.68
62.15
40.05
39.32
26.01
25.57
23.94
17.64
Me
CN
OH
Me
Me
8j
f1 (ppm)

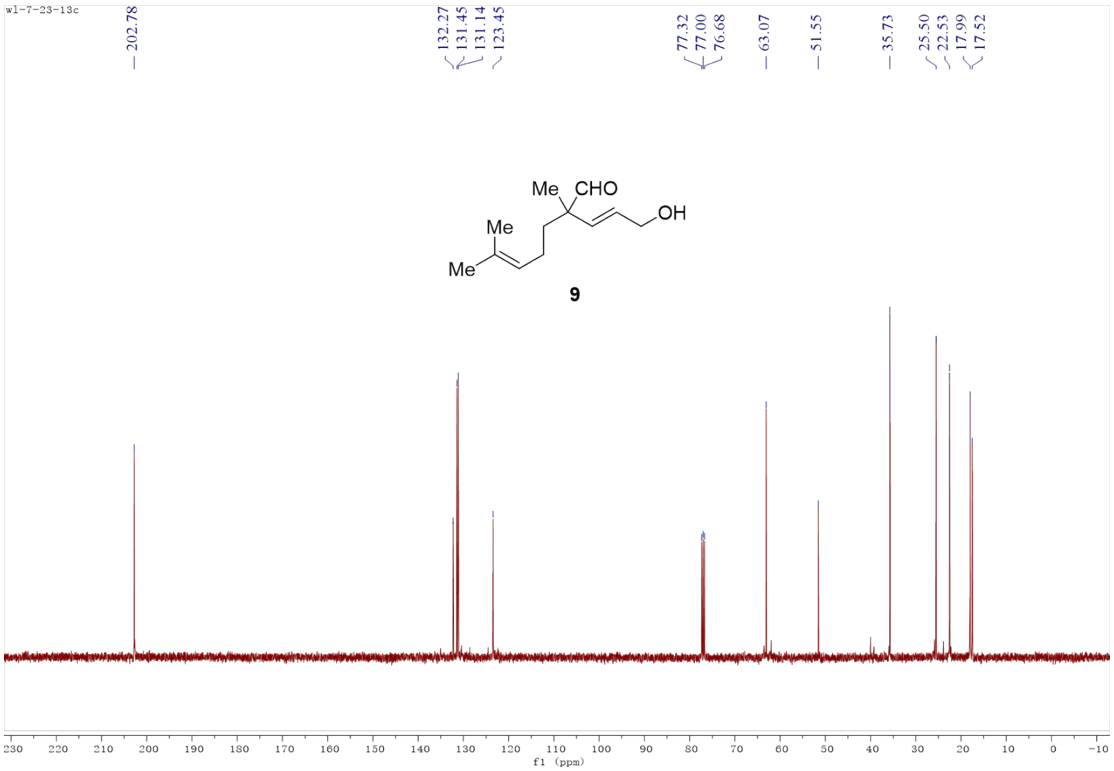

wl-6-73-pure-h
CN
OH
O
8k
2.06
1.07
1.04
0.99
1.00
4.33
1.07
2.08
f1 (ppm)

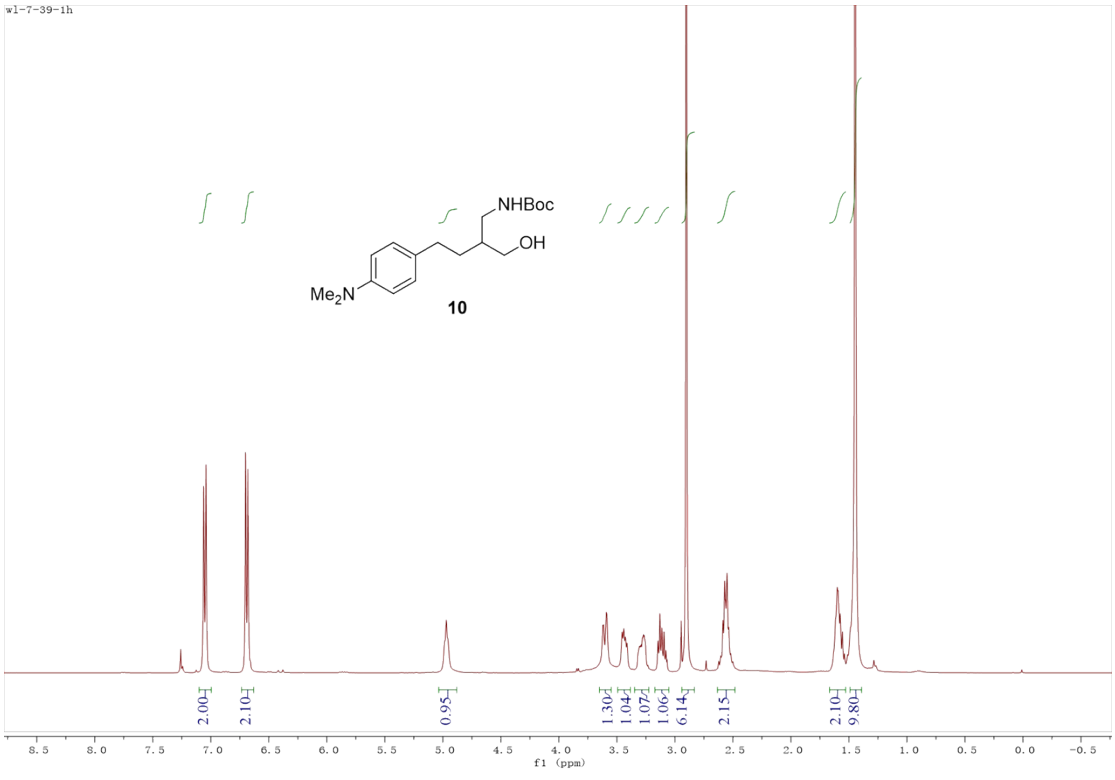

wl-6-73-pure-13c
153.53
133.17
130.13
129.40
129.39
121.22
121.16
118.61
117.71
77.32
77.00
76.68
62.17
61.84
39.57
33.62
CN
OH
O
8k
f1 (ppm)

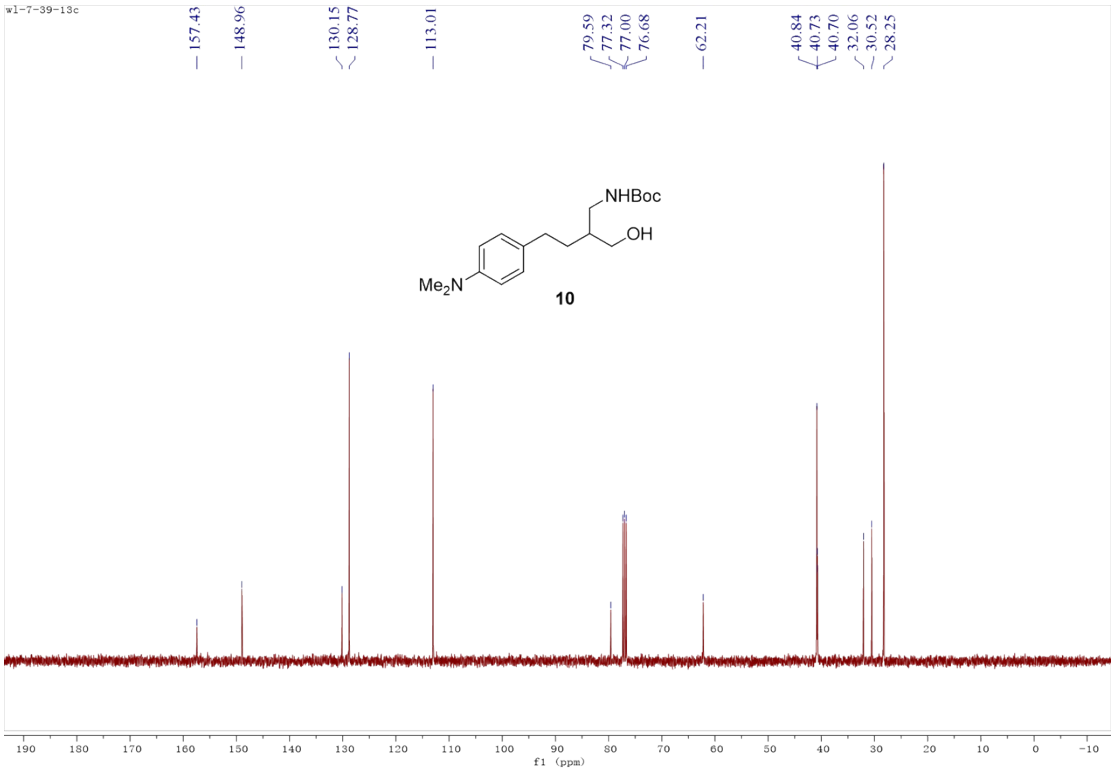

wl-6-43-p-2-h
i-Pr
CN
OH
8l
2.09
2.04
1.05
1.00
1.02
2.10
1.04
1.18
3.10
3.12
f1 (ppm)

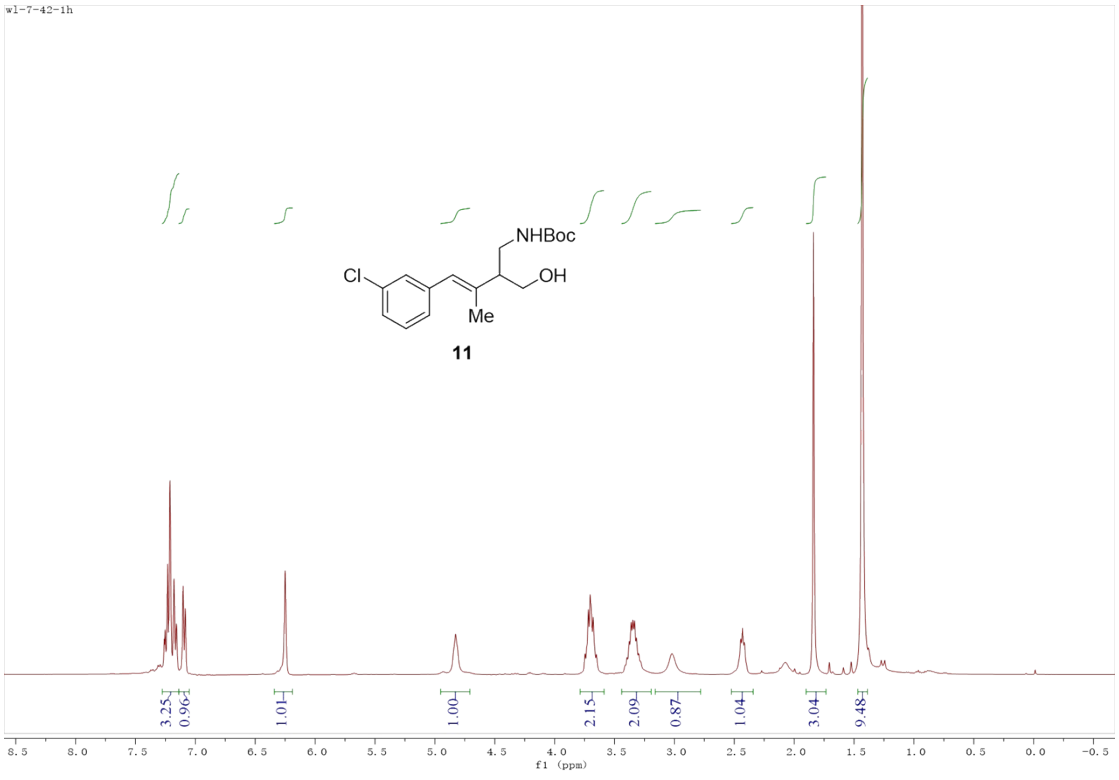

wl-6-43-p-2-13c
138.97
131.14
129.53
128.91
127.71
125.94
119.41
77.32
77.00
76.68
62.23
55.94
37.08
18.44
18.28
i-Pr
CN
OH
8l
f1 (ppm)

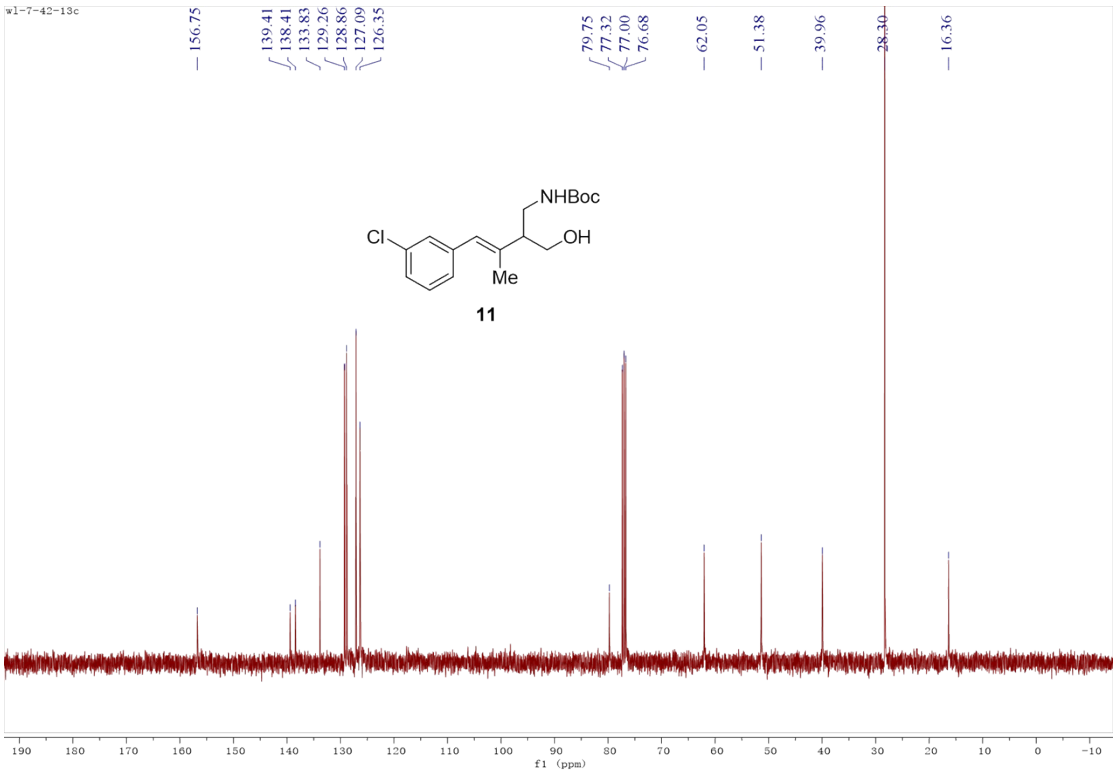

wl-7-23-1h
Me
CHO
OH
Me
Me
9
0.83
1.89
1.00
1.91
0.94
2.00
8.20
2.75
f1 (ppm)

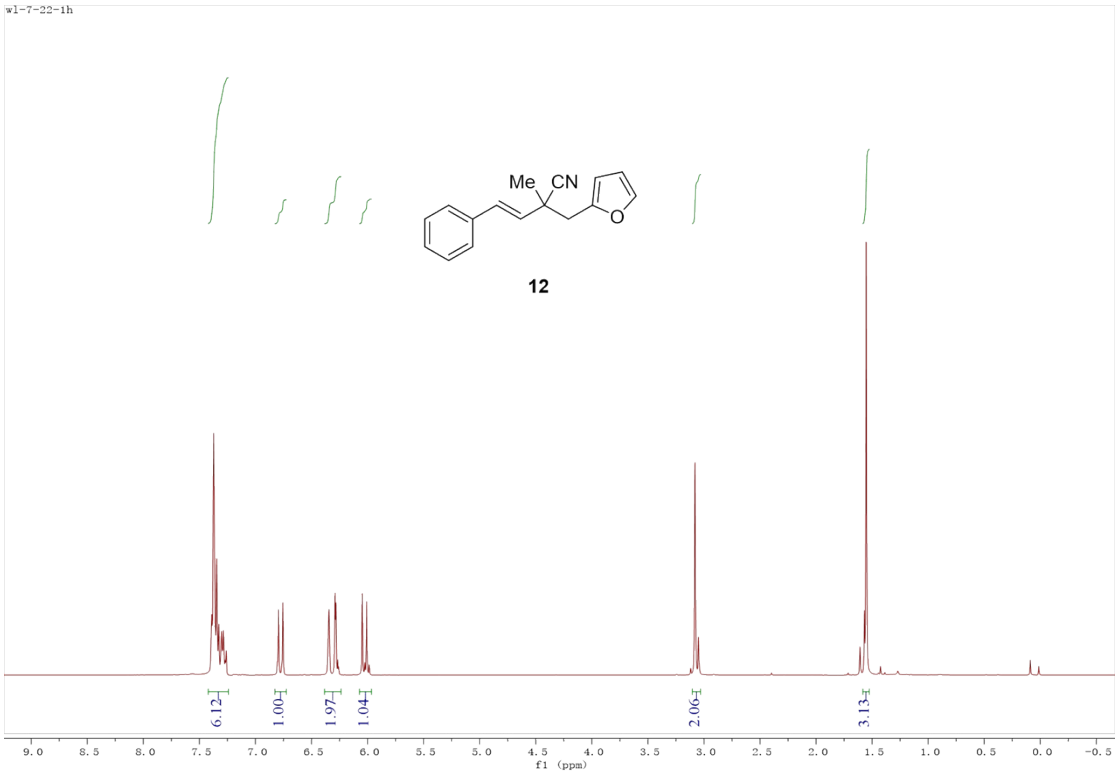

wl-7-23-13c
202.78
132.27
131.45
131.14
123.45
77.32
77.00
76.68
63.07
51.55
35.73
25.50
22.53
17.99
17.52
Me
CHO
OH
Me
Me
9
f1 (ppm)

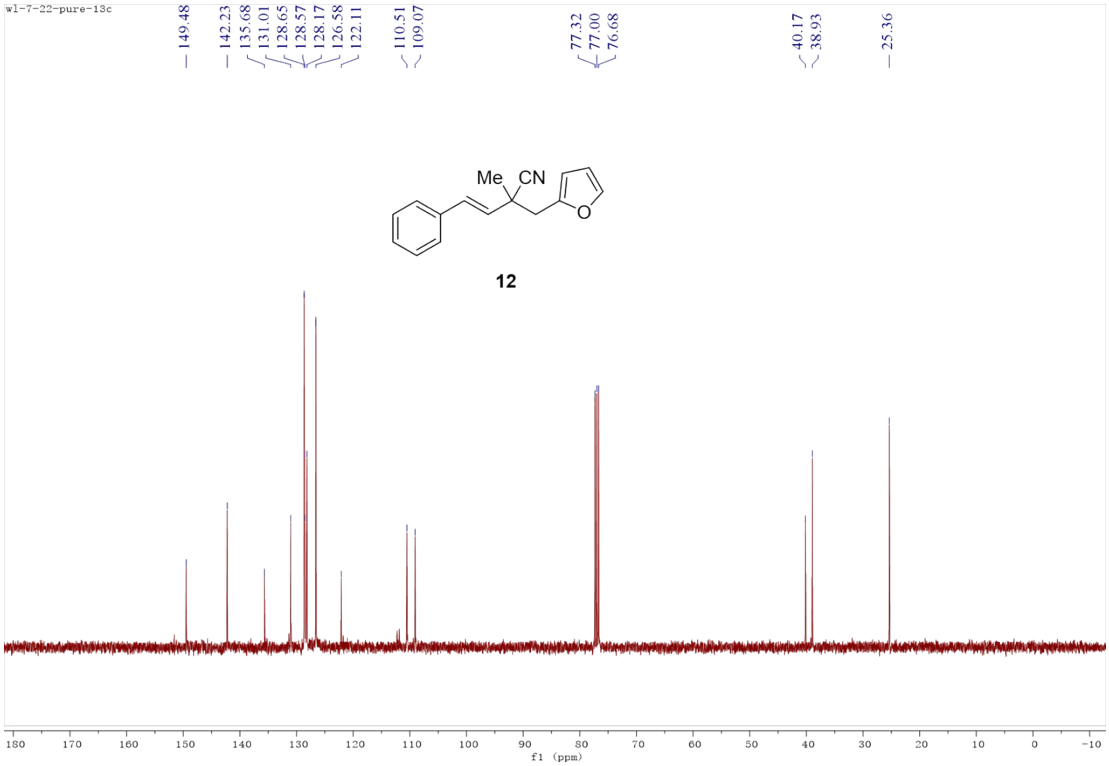

wl-7-39-1h
NHBoc
OH
Me2N
10
2.00
2.10
0.95
1.30
1.04
1.07
1.06
6.14
2.15
2.10
9.80
f1 (ppm)

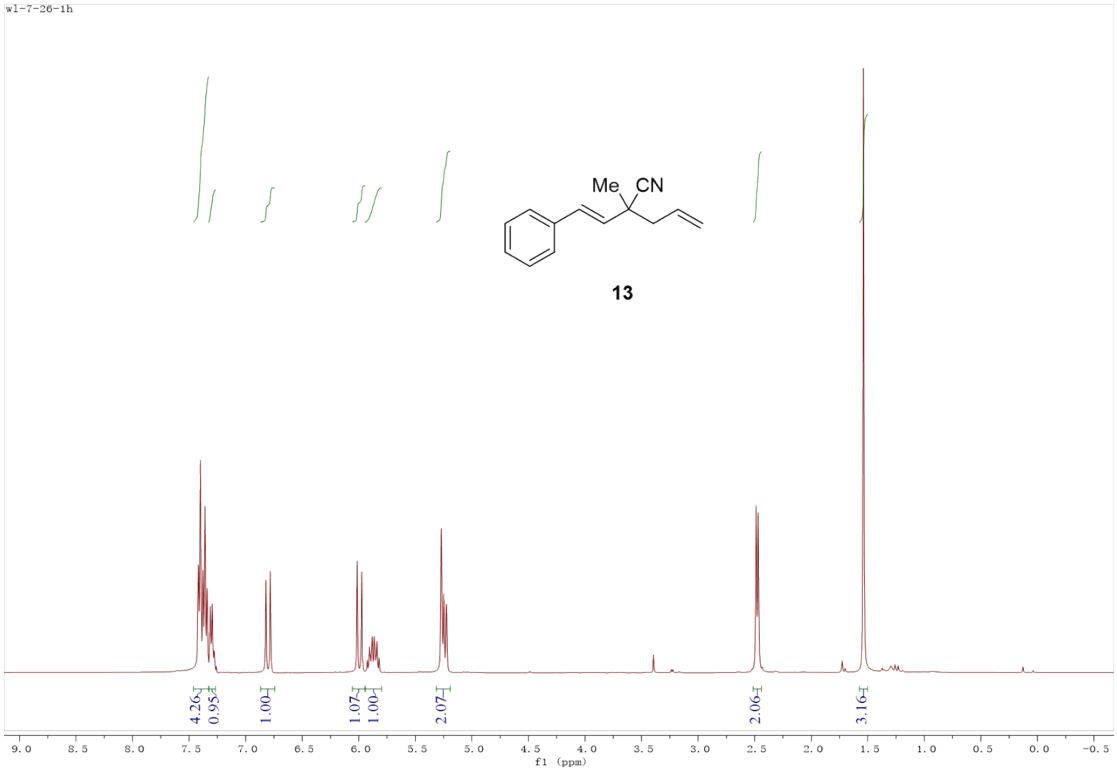

wl-7-39-13c
157.43
148.96
130.15
128.77
113.01
79.59
77.32
77.00
76.68
62.21
40.84
40.73
40.70
32.06
30.52
28.25
NHBoc
OH
Me2N
10
f1 (ppm)

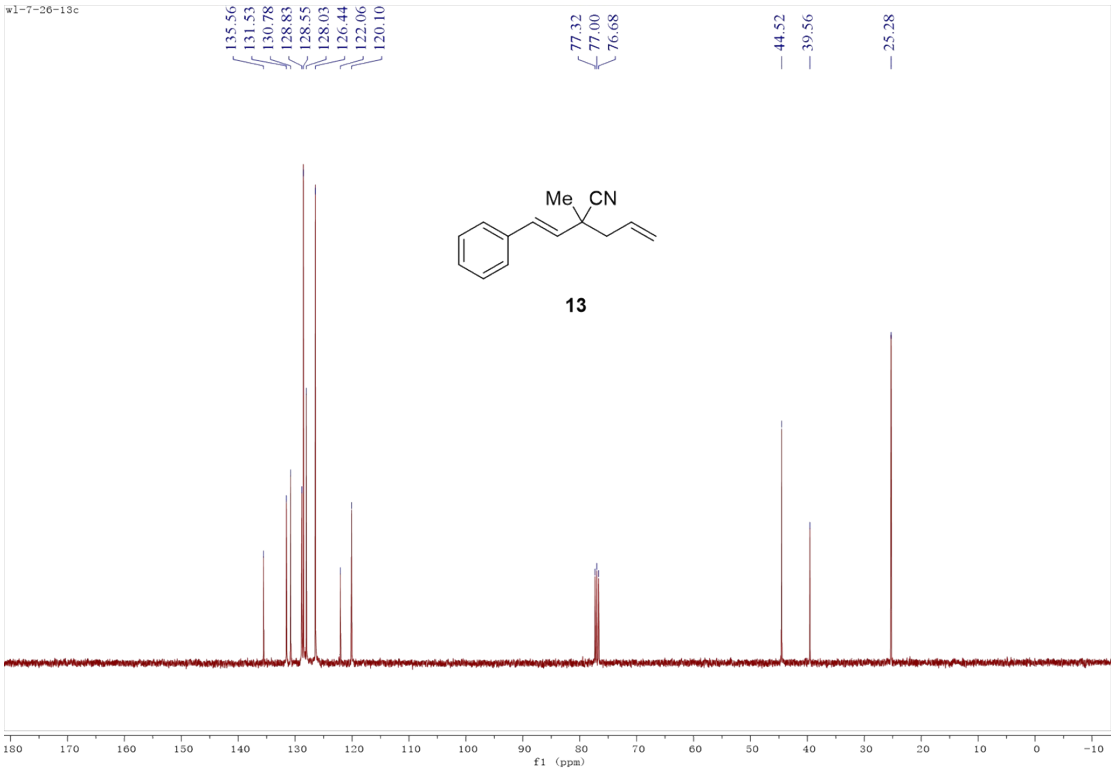

wl-7-42-1h
NHBoc
OH
Cl
Me
11
3.25
0.96
1.01
1.00
2.15
2.09
0.87
1.04
3.04
9.48
f1 (ppm)

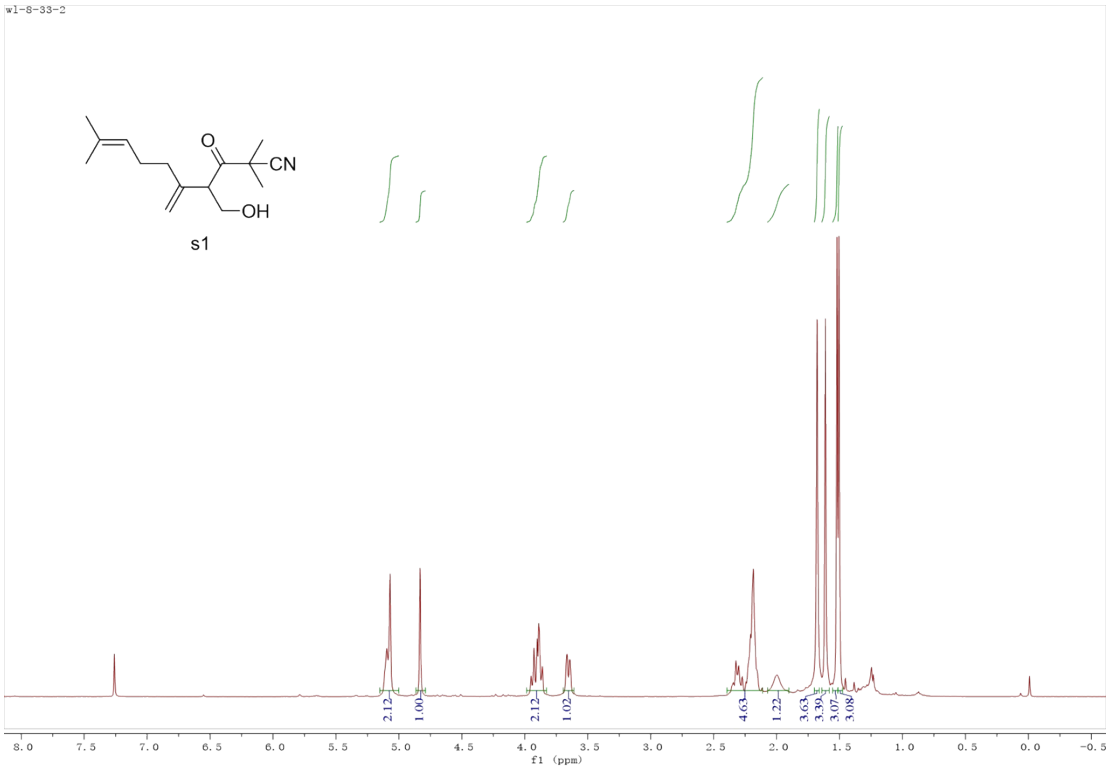

wl-7-42-13c
156.75
139.41
138.41
133.83
129.26
128.86
127.09
126.35
79.75
77.32
77.00
76.68
62.05
51.38
39.96
28.30
16.36
NHBoc
Cl
OH
Me
11
f1 (ppm)

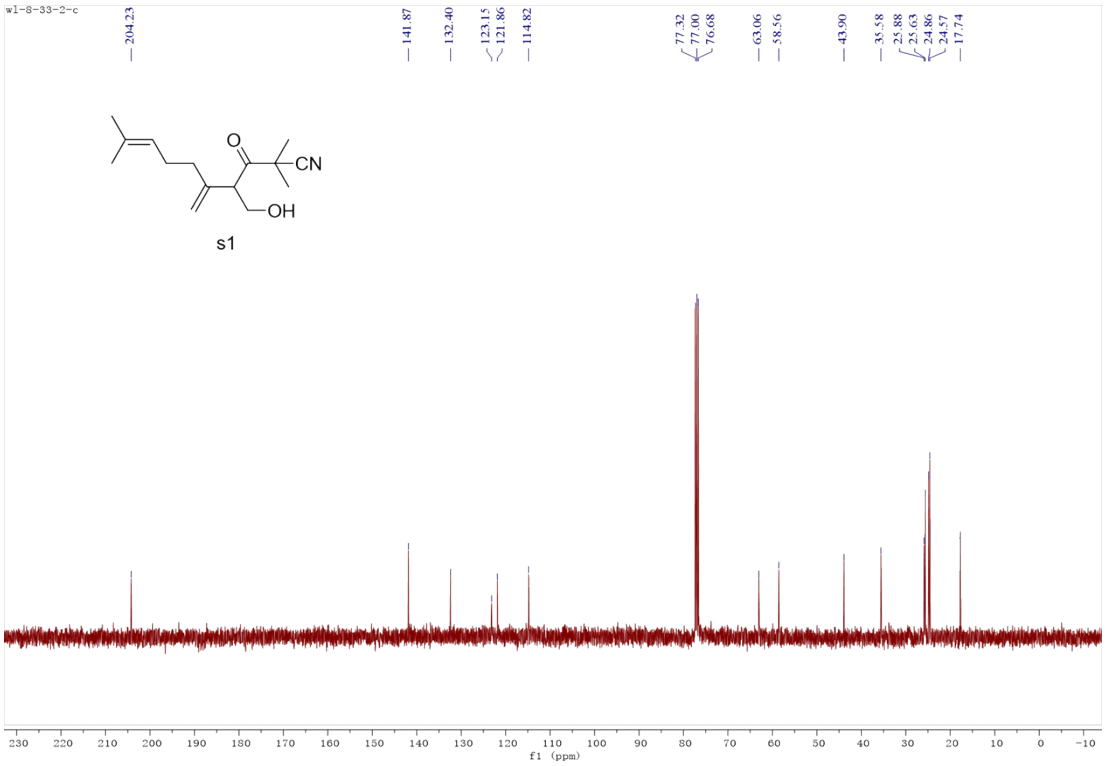

wl-7-22-1h
Me
CN
O
12
6.12
1.00
1.97
1.04
2.06
3.13
f1 (ppm)


wl-7-22-pure-13c
149.48
142.23
135.68
131.01
128.65
128.57
128.17
126.58
122.11
110.51
109.07
77.32
77.00
76.68
40.17
38.93
25.36
Me
CN
O
12
f1 (ppm)


wl-7-26-1h
Me
CN
13
4.26
0.95
1.00
1.07
1.00
2.07
2.06
3.16
f1 (ppm)


wl-7-26-13c
135.56
131.53
130.78
128.83
128.55
128.03
126.44
122.06
120.10
77.32
77.00
76.68
44.52
39.56
25.28
Me
CN
13
f1 (ppm)


wl-8-33-2
O
CN
OH
s1
2.12
1.00
2.12
1.02
4.63
1.22
3.63
3.39
3.07
3.08
f1 (ppm)


wl-8-33-2-c
204.23
141.87
132.40
123.15
121.86
114.82
77.32
77.00
76.68
63.06
58.56
43.90
35.58
25.88
25.63
24.86
24.57
17.74
O
CN
OH
s1
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)