

Supporting Information

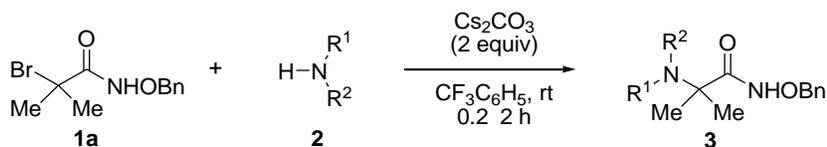
Rapid access to hindered α -amino acid derivatives and benzodiazepin-3-ones from aza-oxyallyl cations

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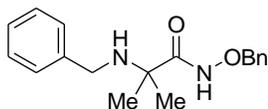
1. General Information. Organic solvents were distilled prior to use. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63. Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Developed chromatograms were visualized by fluorescence quenching and with anisaldehyde stain. ^1H and ^{13}C NMR spectra were recorded (400 MHz for ^1H and 100 MHz for ^{13}C), and were internally referenced to residual protic solvent signals. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on an FT IR spectrometer and are reported in wave numbers. High-resolution mass spectroscopy (HRMS) was performed by electron impact (EI). The crystal structure was determined by single-crystal diffractometer at the Western Seoul Center of Korea Basic Science Institute. α -Halohydroxamates¹ and 2-aminophenyl α,β -unsaturated carbonyl compounds² were prepared according to literature.

2. General Procedure I for the α -Amination of α -Haloamides (Scheme 2).

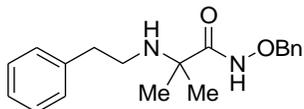


To a solution of α -Bromhydroxamate **1a** (0.30 mmol), and alkylamine **2** (0.60 mmol) in trifluorotoluene (0.6 mL) was added Cs_2CO_3 (0.60 mmol) at room temperature. The reaction mixture was stirred at same temperature until α -halohydroxamate **1** was complete consumed, as determined by TLC. Then, the resulting mixture was filtered through the plug of celite and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as eluent to afford desired product **3**.

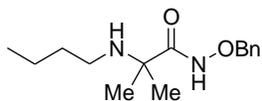
Procedure for a 1 mmol scale synthesis of 3a. To a solution of α -bromhydroxamate **1a** (272 mg, 1.0 mmol), and benzylamine **2a** (0.22 mL, 2.0 mmol) in trifluorotoluene (5 mL) was added Cs_2CO_3 (652 mg, 2.0 mmol) at room temperature. The reaction mixture was stirred at same temperature for 20 min. Then, the resulting mixture was filtered through the plug of celite and concentrated in vacuo. The crude residue was purified by flash column chromatography (EtOAc : hexanes = 1:1) to afford desired product **3a** (169 mg, 60% yield) as colorless gum.

2-(Benzylamino)-N-(benzyloxy)-2-methylpropanamide (3a)

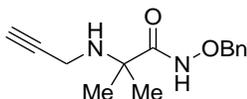
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 1:1, 55 mg, yield 61%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.61 (s, 2H), 7.41 (dd, $J = 7.0, 2.4$ Hz, 2H), 7.38–7.31 (m, 3H), 7.29–7.23 (m, 3H), 7.12–7.01 (m, 2H), 4.94 (s, 2H), 3.56 (s, 2H), 1.39 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 139.7, 135.6, 129.2, 128.9, 128.8, 128.7, 128.0, 127.3, 78.0, 59.1, 48.1, 25.9; IR (neat) 3329, 2922, 2851, 1677, 1495, 1454, 1380, 1359, 1291, 1273, 1260, 1190, 1113, 1030 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$: 298.1681 Found: 298.1703.

N-(Benzyloxy)-2-methyl-2-(phenethylamino)propanamide (3b)

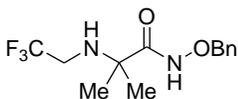
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 3:7, 42 mg, yield 45%), White solid; m.p. 63–64 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.27 (s, 2H), 7.40–7.32 (m, 5H), 7.25 (dq, $J = 21.4, 7.1$ Hz, 3H), 7.12 (d, $J = 6.9$ Hz, 2H), 4.78 (s, 2H), 2.69 (t, $J = 6.6$ Hz, 2H), 2.58 (t, $J = 6.6$ Hz, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 139.7, 135.5, 129.2, 128.8 (two peaks overlapping), 128.7, 128.6, 126.4, 77.8, 58.6, 45.0, 36.9, 25.7; IR (neat) 3315, 3300, 2922, 2865, 1669, 1496, 1466, 1448, 1375, 1354, 1197, 1151, 1089, 1050, 1031 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2$: 312.1838 Found: 312.1827.

N-(Benzyloxy)-2-(butylamino)-2-methylpropanamide (3c)

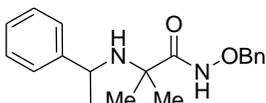
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 1:1 to 3:1, 42 mg, yield 53%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.46–7.30 (m, 5H), 4.92 (s, 2H), 2.36 (t, $J = 6.6$ Hz, 2H), 1.28 (s, 6H), 1.25–1.18 (m, 4H), 0.85 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 135.6, 129.2, 128.8, 128.7, 77.9, 58.7, 43.5, 33.0, 25.8, 20.4, 14.1; IR (neat) 3234, 2958, 2928, 2871, 1656, 1496, 1455, 1377, 1360, 1261, 1210, 1186, 1083, 1028 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}_2$: 264.1838 Found: 264.1819.

***N*-(Benzyloxy)-2-methyl-2-(prop-2-ynylamino)propanamide (3d)**

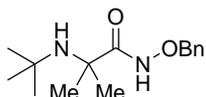
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 1:1, 38 mg, yield 51%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.57 (s, 1H), 7.35 (dd, $J = 26.0, 19.1$ Hz, 5H), 4.91 (s, 2H), 3.22 (s, 2H), 2.20 (s, 1H), 1.54 (d, $J = 46.2$ Hz, 1H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 135.3, 129.3, 128.8, 128.7, 82.0, 78.0, 71.8, 58.9, 33.1, 25.5; IR (neat) 3329, 2971, 2927, 2216, 1655, 1601, 1494, 1451, 1372, 1328, 1208, 1174, 1080, 1024 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2$: 246.1368 Found: 246.1355.

***2*-(2,2,2-Trifluoroethylamino)-*N*-(benzyloxy)-2-methylpropanamide (3e)**

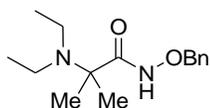
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 3:7, 34 mg, yield 39%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.38 (s, 1H), 7.37 (dd, $J = 8.1, 5.0$ Hz, 5H), 4.93 (s, 2H), 2.94 (q, $J = 8.9$ Hz, 2H), 1.42 (s, 1H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.3, 135.1, 129.2, 128.9, 128.7, 125.1 (q, $J^1 = 266.9$ Hz), 78.0, 58.6, 45.7 (q, $J^2 = 31.8$ Hz), 25.7; IR (neat) 3290, 2976, 2929, 1660, 1483, 1455, 1379, 1364, 1208, 1177, 1081, 1039, 1029 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{13}\text{H}_{17}\text{F}_3\text{N}_2\text{O}_2$: 290.1242 Found: 290.1272.

***2*-(1-Phenylethylamino)-*N*-(benzyloxy)-2-methylpropanamide (3f)**

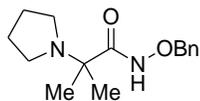
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 2:3, 51 mg, yield 54%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.44 (s, 1H), 7.38 (s, 5H), 7.25 (dq, $J = 12.1, 7.3$ Hz, 5H), 4.83 (dd, $J = 30.2, 11.1$ Hz, 2H), 3.79 (d, $J = 6.6$ Hz, 1H), 1.25 (s, 6H), 1.22 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.4, 147.2, 135.5, 129.2, 128.7, 128.6 (two peaks overlapping), 126.9, 126.1, 77.8, 59.2, 53.8, 27.5, 26.3, 25.2; IR (neat) 3235, 2980, 2935, 1655, 1496, 1456, 1400, 1382, 1365, 1298, 1270, 1129, 1038, 1029 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2$: 312.1838 Found: 312.1830.

2-(tert-Butylamino)-N-(benzyloxy)-2-methylpropanamide (3g)

Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 1:1 to 3:2, 38 mg, yield 48%), White solid; m.p. 91-93 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.51–7.30 (m, 5H), 4.92 (s, 2H), 1.37 (s, 6H), 1.08 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 176.3, 135.7, 129.2, 128.7, 128.6, 77.8, 58.2, 51.9, 31.7, 28.8; IR (neat) 3286, 3145, 2919, 1603, 1588, 1526, 1450, 1418, 1384, 1318, 1300, 1259, 1241, 1195, 1175, 1149, 1086, 1048, 1017 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₅H₂₄N₂O₂: 264.1838 Found: 264.1820.

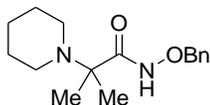
N-(Benzyloxy)-2-(diethylamino)-2-methylpropanamide (3h)

Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 3:7, 21 mg, yield 26%), Colorless gum; ¹H NMR (400 MHz, CDCl₃) δ 9.52 (s, 1H), 7.38 (dtd, *J* = 13.8, 7.2, 4.1 Hz, 5H), 4.93 (s, 2H), 2.42 (q, *J* = 7.1 Hz, 4H), 1.25 (s, 1H), 1.25 (d, *J* = 5.4 Hz, 6H), 0.90 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 175.4, 135.7, 129.2, 128.7 (two peaks overlapping), 77.9, 65.0, 43.7, 22.2, 15.6; IR (neat) 3285, 2972, 2930, 2871, 1679, 1479, 1457, 1387, 1358, 1296, 1211, 1162, 1138, 1041, 1027 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₅H₂₄N₂O₂: 264.1838 Found: 264.1811.

N-(Benzyloxy)-2-methyl-2-(pyrrolidin-1-yl)propanamide (3i)

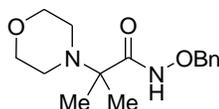
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 4:1, 20 mg, yield 25%), Colorless gum; ¹H NMR (400 MHz, CDCl₃) δ 9.43 (s, 1H), 7.39 (dd, *J* = 18.5, 6.8 Hz, 5H), 4.93 (s, 2H), 2.55–2.42 (m, 4H), 1.55–1.68 (m, 4H), 1.23 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 135.7, 129.3, 128.8, 128.7, 78.02, 61.1, 46.5, 23.5, 21.0; IR (neat) 3273, 2971, 2932, 2856, 1674, 1599, 1454, 1379, 1362, 1251, 1197, 1117, 1081, 1040 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₁₅H₂₂N₂O₂: 262.1681 Found: 262.1664.

N-(Benzyloxy)-2-methyl-2-(piperidin-1-yl)propanamide (3j)



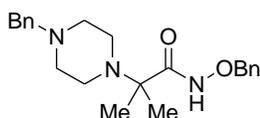
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 1:1, 27 mg, yield 33%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.52 (s, 1H), 7.46–7.32 (m, 5H), 4.93 (s, 2H), 2.45–2.25 (m, 4H), 1.45–1.31 (m, 6H), 1.18 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.9, 135.7, 129.2, 128.7, 128.7, 77.9, 64.0, 48.0, 26.7, 24.7, 20.9; IR (neat) 3275, 2979, 2933, 3809, 1681, 1471, 1354, 1441, 1387, 1363, 1277, 1198, 1108, 1033 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_2$: 276.1838 Found: 276.1819.

N-(Benzyloxy)-2-methyl-2-morpholinopropanamide (3k)



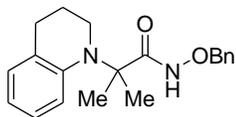
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 1:1, 33 mg, yield 40%), White solid; m.p. 68–70 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.39 (s, 1H), 7.53–7.30 (m, 5H), 4.95 (s, 2H), 3.61–3.33 (m, 4H), 2.53–2.25 (m, 4H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 135.6, 129.1, 128.9, 128.8, 77.8, 67.4, 63.6, 47.3, 20.6; IR (neat) 3329, 2963, 2851, 2825, 1677, 1495, 1454, 1380, 1359, 1291, 1273, 1260, 1190, 1113, 1030 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_3$: 278.1630 Found: 278.1612.

N-(Benzyloxy)-2-(4-benzylpiperazin-1-yl)-2-methylpropanamide (3l)



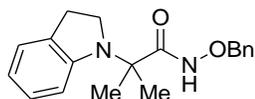
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 1:1, 38 mg, yield 34%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.43 (s, 1H), 7.50–7.21 (m, 10H), 4.92 (s, 2H), 3.42 (s, 2H), 2.51–2.38 (m, 4H), 2.37–2.10 (m, 4H), 1.18 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.1, 137.8, 135.7, 129.4, 129.2, 128.8 (two peaks overlapping), 128.4, 127.3, 77.9, 63.4, 63.0, 53.6, 46.6, 20.9; IR (neat) 3353, 3281, 2933, 2813, 2768, 1677, 1454, 1361, 1350, 1294, 1199, 1130, 1041, 1011 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{22}\text{H}_{29}\text{N}_3\text{O}_2$: 367.2260 Found: 367.2238.

N-(Benzyloxy)-2-(3,4-dihydroquinolin-1(2H)-yl)-2-methylpropanamide (3m)



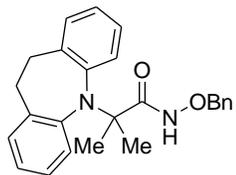
Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 1:4, 48 mg, yield 49%), White solid; m.p. 77-79 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.94 (s, 1H), 7.33–7.24 (m, 3H), 7.17 (d, $J = 5.4$ Hz, 2H), 7.03 (dd, $J = 12.0, 7.3$ Hz, 2H), 6.74 (t, $J = 7.3$ Hz, 1H), 6.65 (d, $J = 8.3$ Hz, 1H), 4.79 (s, 2H), 3.27–3.07 (m, 2H), 2.72 (t, $J = 6.5$ Hz, 2H), 2.01–1.84 (m, 2H), 1.50 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.8, 143.9, 135.1, 129.7, 129.5, 128.8, 128.6, 126.5 (two peaks overlapping), 118.8, 115.9, 78.0, 62.3, 43.4, 28.3, 23.7, 23.6; IR (neat) 3248, 2983, 2934, 2844, 1661, 1602, 1493, 1453, 1364, 1308, 1286, 1253, 1196, 1104, 1044, 1026 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$: 324.1838 Found: 324.1825.

N-(Benzyloxy)-2-(indolin-1-yl)-2-methylpropanamide (3n)



Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 1:4, 56 mg, yield 60%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.24 (s, 1H), 7.41–7.26 (m, 5H), 7.10 (d, $J = 7.2$ Hz, 1H), 7.02 (t, $J = 7.6$ Hz, 1H), 6.75 (t, $J = 7.3$ Hz, 1H), 6.45 (d, $J = 7.9$ Hz, 1H), 4.89 (s, 2H), 3.31 (t, $J = 8.1$ Hz, 2H), 2.89 (t, $J = 8.0$ Hz, 2H), 1.38 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 148.6, 135.2, 131.5, 129.5, 128.7, 128.5, 127.0, 124.7, 119.5, 111.3, 78.1, 60.6, 48.6, 28.1, 21.5; IR (neat) 3365, 3244, 2982, 2937, 2846, 1670, 1605, 1484, 1471, 1456, 1363, 1249, 1233, 1215, 1172, 1043 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$: 310.1681 Found: 310.1680.

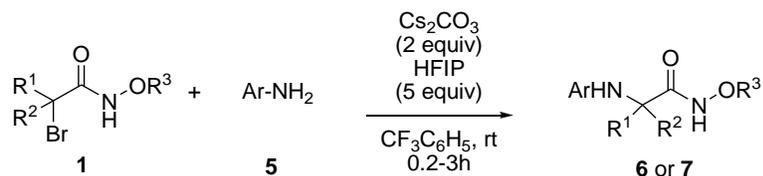
1-(O-Benzyloxyamino)-2-{2-azatricyclo[9.4.0.0^{3,8}]pentadeca-1(11),3(8),4,6,12,14-hexaen-2-yl}-2-methyl-1-propanone (3o)



Synthesized by the general procedure I; flash chromatography (EtOAc : hexane = 3:17, 41mg, yield 35%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.05 (s, 1H), 7.48–7.37 (m, 5H), 7.23 (d, $J = 7.6$ Hz, 2H), 7.12–6.92 (m, 6H), 4.92 (s, 2H), 3.35–3.18 (m, 2H), 2.86–2.63 (m, 2H), 1.41 (s, 6H); ^{13}C NMR (100 MHz,

CDCl₃) δ 175.1, 145.6, 137.4, 135.7, 130.2, 129.3, 128.9, 128.8, 128.6, 128.4, 126.9, 126.5, 125.1, 77.8, 64.5, 32.4, 27.6; IR (neat) 3241, 2983, 2825, 1659, 1599, 1483, 1453, 1364m 1317, 1257, 1232, 1215, 1173, 1105, 1026 cm⁻¹; HRMS (EI) m/z calcd for [M]⁺ C₂₅H₂₆N₂O₂: 386.1994 Found: 386.1989.

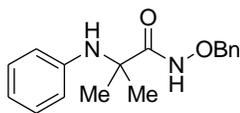
3. General Procedure II for the α -Amination of α -Haloamides (Scheme 3 and 4).



To a solution of α -halohydroxamate **1** (0.30 mmol), aniline **5** (0.45 mmol), and HFIP (1.5 mmol) in trifluorotoluene (0.6 mL) was added Cs₂CO₃ (0.60 mmol) at 0 °C. The reaction mixture was stirred at room temperature until α -halohydroxamate **1** was completely consumed, as determined by TLC. Then, the resulting mixture was filtered through the plug of celite and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as eluent to afford desired product **6** or **7**.

Procedure for a 1 mmol scale synthesis of 6a. To a solution of α -bromohydroxamate **1a** (272 mg, 1.0 mmol), aniline **5a** (0.14 mL, 1.5 mmol), and HFIP (0.52 mL, 5.0 mmol) in trifluorotoluene (5 mL) was added Cs₂CO₃ (652 mg, 2.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 15 min. Then, the resulting mixture was filtered through the plug of celite and concentrated in vacuo. The crude residue was purified by flash column chromatography with (EtOAc : hexanes = 3:7) to afford desired product **6a** (253 mg, 89% yield) as white solid.

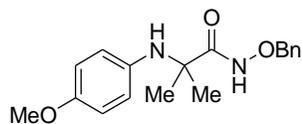
***N*-(Benzyloxy)-2-methyl-2-(phenylamino)propanamide (6a)**



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 77 mg, yield 91%), White solid; m.p. 125-157 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.28 (s, 1H), 7.35–7.28 (m, 5H), 7.15 (dd, J = 8.4, 7.5 Hz, 2H), 6.80 (t, J = 7.4 Hz, 1H), 6.62–6.48 (m, 2H), 4.88 (s, 2H), 3.72 (s, 1H), 1.48 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 144.3, 135.1, 129.4, 129.2, 128.7, 128.5, 119.3, 116.0, 78.1, 57.4, 26.1;

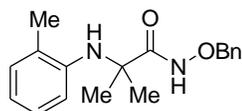
IR (neat) 3349, 3329, 2924, 2874, 1677, 1599, 1497, 1453, 1378, 1258, 1213, 1059, 1023 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2$: 284.1525 Found: 284.1498.

2-(4-Methoxyphenylamino)-*N*-(benzyloxy)-2-methylpropanamide (6b)



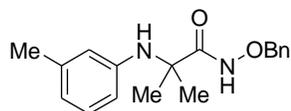
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:17 to 3:7, 73 mg, yield 77%), White solid; m.p. 128-130 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.41 (s, 1H), 7.41–7.28 (m, 5H), 6.78–6.66 (m, 2H), 6.56–6.44 (m, 2H), 4.91 (s, 2H), 3.72 (s, 3H), 3.45 (s, 1H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.2, 153.4, 138.0, 135.2, 129.3, 128.7, 128.5, 117.8, 114.6, 78.0, 57.9, 55.6, 26.1; IR (neat) 3348, 3332, 2980, 2940, 2873, 1671, 1515, 1439, 1320, 1255, 1237, 1210, 1159, 1107, 1035 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_3$: 314.1630 Found: 314.1621.

2-(*o*-Tolylamino)-*N*-(benzyloxy)-2-methylpropanamide (6c)



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 81 mg, yield 91%), White solid; m.p. 123-125 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.25 (s, 1H), 7.36–7.25 (m, 5H), 7.06 (t, J = 8.3 Hz, 2H), 6.73 (td, J = 7.4, 0.8 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 4.86 (s, 2H), 3.58 (s, 1H), 2.12 (s, 3H), 1.51 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 142.3, 135.1, 130.7, 129.4, 128.7, 128.5, 126.9, 123.4, 118.9, 114.2, 78.1, 57.3, 26.4, 17.7; IR (neat) 3425, 3244, 2941, 1887, 1656, 1605, 1587, 1507, 1457, 1378, 1314, 1261, 1217, 1184, 1113, 1040 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$: 298.1681 Found: 298.1657.

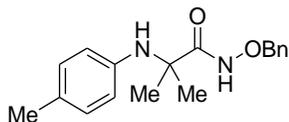
2-(*m*-Tolylamino)-*N*-(benzyloxy)-2-methylpropanamide (6d)



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 85 mg, yield 95%), White solid; m.p. 69-71 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) 9.31 (s, 1H), 7.39–7.26 (m, 5H), 7.04 (t, J = 7.7 Hz, 1H), 6.62 (d, J = 7.5 Hz, 1H), 6.45–6.30 (m, 2H), 4.87 (s, 2H), 3.71 (s, 1H), 2.25 (s, 3H), 1.47 (s, 6H);

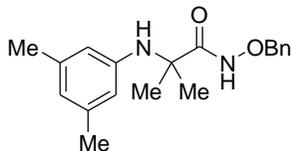
^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 144.4, 139.0, 135.1, 129.4, 129.1, 128.7, 128.5, 120.2, 116.7, 113.1, 78.0, 57.4, 26.1, 21.6.; IR (neat) 3379, 3343, 2976, 2923, 2873, 1691, 1605, 1586, 1490, 1455, 1378, 1318, 1263, 1214, 1171, 1056 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$: 298.1681 Found: 298.1682.

2-(*p*-Tolylamino)-*N*-(benzyloxy)-2-methylpropanamide (6e)



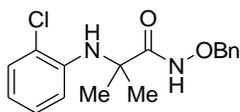
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 1:4, 74 mg, yield 83%), White solid; m.p. 145-147 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.34 (s, 1H), 7.39–7.30 (m, 5H), 6.98 (d, J = 8.1 Hz, 2H), 6.48 (d, J = 8.2 Hz, 2H), 4.90 (s, 2H), 3.62 (s, 1H), 2.25 (s, 3H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 141.9, 135.2, 129.7, 129.4, 128.7 (two peaks overlapping), 128.5, 116.2, 78.0, 57.6, 26.1, 20.4; IR (neat) 3354, 3304, 2973, 2922, 2867, 1673, 1617, 1515, 1454, 1376, 1301, 1258, 1207, 1057 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$: 298.1681 Found: 298.1665.

2-(3,5-Dimethylphenylamino)-*N*-(benzyloxy)-2-methylpropanamide (6f)



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 76 mg, yield 81%), White solid; m.p. 108-110 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.30 (s, 1H), 7.42–7.29 (m, 5H), 6.47 (s, 1H), 6.20 (s, 2H), 4.88 (s, 2H), 3.60 (s, 1H), 2.21 (s, 6H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 144.4, 138.9, 135.1, 129.4, 128.7, 128.5, 121.3, 113.9, 78.0, 57.4, 26.2, 21.5; IR (neat) 3375, 3245, 2935, 2918, 2862, 1651, 1599, 1536, 1479, 1381, 1343, 1228, 1182, 1034 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2$: 312.1838 Found: 312.1861.

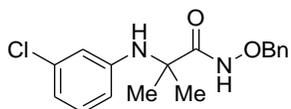
2-(2-Chlorophenylamino)-*N*-(benzyloxy)-2-methylpropanamide (6g)



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 84mg, yield 88%), White solid; m.p. 151-153 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) 9.21 (s, 1H), 7.34–7.29 (m, 5H), 7.27 (dd, J =

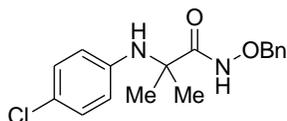
8.0, 1.5 Hz, 1H), 7.10–7.03 (m, 1H), 6.72 (td, $J = 7.9, 1.4$ Hz, 1H), 6.58 (dd, $J = 8.2, 1.3$ Hz, 1H), 4.88 (s, 2H), 4.40 (s, 1H), 1.51 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 140.4, 135.0, 129.5, 129.4, 128.8, 128.6, 127.5, 120.8, 119.5, 115.4, 78.1, 57.4, 26.1; IR (neat) 3401, 3243, 2925, 1659, 1594, 1501, 1476, 1453, 1378, 1319, 1260, 1209, 1132, 1035 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{17}\text{H}_{19}\text{ClN}_2\text{O}_2$: 318.1135 Found: 318.1156.

2-(3-Chlorophenylamino)-*N*-(benzyloxy)-2-methylpropanamide (6h)



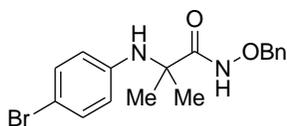
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 94 mg, yield 98%), White solid; m.p. 87–89 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.23 (s, 1H), 7.35–7.29 (m, 5H), 7.05 (t, $J = 8.0$ Hz, 1H), 6.76 (dd, $J = 7.9, 1.2$ Hz, 1H), 6.57 (s, 1H), 6.41 (d, $J = 8.1$ Hz, 1H), 4.87 (s, 2H), 3.93 (s, 1H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.4, 145.6, 134.9, 134.8, 130.2, 129.4, 128.8, 128.6, 119.2, 115.8, 113.8, 78.2, 57.4, 26.0; IR (neat) 3339, 3323, 2940, 1663, 1597, 1511, 1479, 1454, 1440, 1377, 1311, 1249, 1210, 1163, 1037 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{17}\text{H}_{19}\text{ClN}_2\text{O}_2$: 318.1135 Found: 318.1116.

2-(4-Chlorophenylamino)-*N*-(benzyloxy)-2-methylpropanamide (6i)



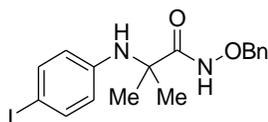
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 87 mg, yield 91%), White solid; m.p. 134–136 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.21 (s, 1H), 7.35–7.30 (m, 5H), 7.09 (d, $J = 8.5$ Hz, 2H), 6.46 (d, $J = 8.7$ Hz, 2H), 4.89 (s, 2H), 3.75 (s, 1H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 142.9, 135.0, 129.3, 129.0, 128.8, 128.6, 124.2, 117.0, 78.1, 57.5, 26.0; IR (neat) 3368, 3234, 2940, 2871, 1648, 1597, 1516, 1490, 1455, 1385, 1352, 1298, 1258, 1215, 1181, 1092, 1035 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{17}\text{H}_{19}\text{ClN}_2\text{O}_2$: 318.1135 Found: 318.1155.

2-(4-Bromophenylamino)-*N*-(benzyloxy)-2-methylpropanamide (6j)



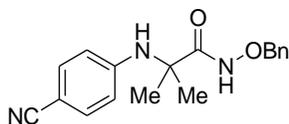
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 97mg, yield 89%), White solid; m.p. 147-149 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.13 (s, 1H), 7.36–7.31 (m, 5H), 7.24 (d, J = 8.9 Hz, 2H), 6.41 (d, J = 8.9 Hz, 2H), 4.90 (s, 2H), 3.66 (s, 1H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.4, 143.3, 135.0, 132.0, 129.3, 128.8, 128.6, 117.5, 111.4, 78.1, 57.5, 26.0; IR (neat) 3363, 3328, 2994, 2878, 1665, 1592, 1507, 1487, 1381, 1315, 1253, 1215, 1045 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{17}\text{H}_{19}\text{BrN}_2\text{O}_2$: 362.0630 Found: 362.0619.

2-(4-Iodophenylamino)-*N*-(benzyloxy)-2-methylpropanamide (6k)



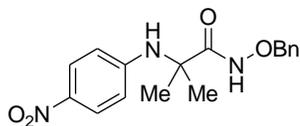
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 101 mg, yield 82%), White solid; m.p. 171-173 °C; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{acetone-d}_6$) δ 10.44 (s, 1H), 7.43–7.27 (m, 7H), 6.41 (d, J = 8.9 Hz, 2H), 5.29 (s, 1H), 4.83 (s, 2H), 1.44 (s, 6H); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{acetone-d}_6$) δ 172.0, 145.7, 137.3 (two peaks overlapping), 136.2, 129.0, 128.2 (two peaks overlapping), 117.4, 77.1, 56.5, 25.1; IR (neat) 3363, 3316, 3252, 2979, 2932, 2876, 1672, 1651, 1589, 1512, 1485, 1445, 1384, 1295, 1258, 1213, 1047, 1035 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{17}\text{H}_{19}\text{IN}_2\text{O}_2$: 410.0491 Found: 410.0477.

2-(4-Cyanophenylamino)-*N*-(benzyloxy)-2-methylpropanamide (6l)



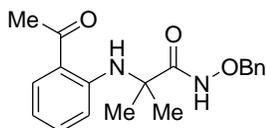
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 2:3, 74 mg, yield 80%), White solid; m.p. 177-179 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.02 (s, 1H), 7.39 (d, J = 8.8 Hz, 2H), 7.31 (ddd, J = 6.9, 5.3, 2.7 Hz, 5H), 6.52 (d, J = 8.8 Hz, 2H), 4.88 (s, 2H), 4.34 (s, 1H), 1.52 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 148.0, 134.8, 133.5, 129.2, 128.9, 128.6, 119.7, 115.2, 101.1, 78.1, 57.4, 26.0; IR (neat) 3343, 3288, 2995, 2212, 1664, 1606, 1524, 1474, 1457, 1334, 1273, 1209, 1174, 1040 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_2$: 309.1477 Found: 309.1460.

2-(4-Nitrophenylamino)-*N*-(benzyloxy)-2-methylpropanamide (6m)



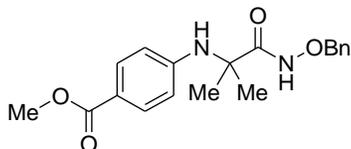
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 2:3, 64 mg, yield 65%), White solid; m.p. 164-167 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.00 (s, 1H), 8.00 (d, J = 8.1 Hz, 2H), 7.38–7.27 (m, 5H), 6.50 (d, J = 8.4 Hz, 2H), 4.89 (d, J = 4.8 Hz, 2H), 4.64 (s, 1H), 1.54 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 150.0, 139.5, 134.8, 129.2, 128.9, 128.6, 125.9, 114.1, 78.2, 57.6, 26.0; IR (neat) 3246, 2976, 2922, 1666, 1597, 1494, 1462, 1383, 1302, 1279, 1212, 1186, 1109, 1036 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_4$: 329.1376 Found: 329.1350.

2-(2-Acetylphenylamino)-N-(benzyloxy)-2-methylpropanamide (6n)



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 83 mg, yield 85%), White solid; m.p. 114-116 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.81 (s, 1H), 8.94 (s, 1H), 7.57 (dd, J = 8.1, 1.3 Hz, 1H), 7.28–7.14 (m, 6H), 6.66–6.56 (m, 1H), 6.47 (d, J = 8.4 Hz, 1H), 4.80 (s, 2H), 2.13 (s, 3H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.4, 172.6, 148.1, 135.3, 134.8, 132.9, 129.4, 128.6, 128.4, 118.7, 115.9, 115.0, 77.9, 56.4, 27.4, 26.2; IR (neat) 3284, 3204, 2989, 2927, 1685, 1624, 1575, 1519, 1499, 1452, 1421, 1334, 1251, 1208, 1171, 1029 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_3$: 326.1630 Found: 326.1627.

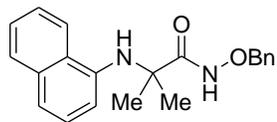
Methyl 4-(2-(benzyloxycarbonyl)propan-2-ylamino)benzoate (6o)



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7 to 2:3, 84 mg, yield 82%), White solid; m.p. 170-172 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.11 (s, 1H), 7.83 (d, J = 8.6 Hz, 2H), 7.34–7.24 (m, 5H), 6.52 (d, J = 8.7 Hz, 2H), 4.87 (s, 2H), 4.21 (s, 1H), 3.85 (s, 3H), 1.52 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.1, 167.0, 148.4, 134.9, 131.2, 129.3, 128.8, 128.6, 120.5, 114.6, 78.1, 57.4, 51.8,

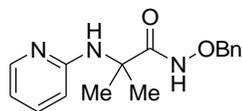
26.1; IR (neat) 3347, 3308, 2984, 2940, 1703, 1680, 1606, 1522, 1436, 1316, 1299, 1213, 1187, 1110, 1039 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_4$: 342.1580 Found: 342.1560.

***N*-(Benzyloxy)-2-methyl-2-(naphthalen-2-ylamino)propanamide (6p)**



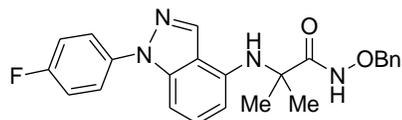
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 89 mg, yield 89%), White solid; m.p. 139-141 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.25 (s, 1H), 7.80 (dd, J = 6.4, 2.9 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.50–7.39 (m, 2H), 7.33–7.16 (m, 7H), 6.54 (d, J = 6.9 Hz, 1H), 4.83 (s, 2H), 4.49 (s, 1H), 1.60 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.9, 139.0, 135.0, 134.5, 129.4, 129.1, 128.7, 128.5, 126.1, 125.9, 125.3, 124.0, 119.5, 119.2, 109.2, 78.1, 57.5, 26.2; IR (neat) 3378, 3254, 2933, 2858, 1648, 1579, 1537, 1454, 1409, 1384, 1346, 1284, 1229, 1178, 1085, 1032 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$: 334.1681 Found: 334.1689.

***N*-(Benzyloxy)-2-methyl-2-(pyridin-2-ylamino)propanamide (6q)**



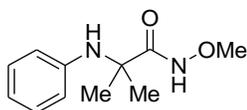
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 1:1, 68 mg, yield 79%), White solid; m.p. 135-137 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.96 (s, 1H), 7.95 (dd, J = 5.0, 1.0 Hz, 1H), 7.37 (ddd, J = 8.5, 7.3, 1.9 Hz, 1H), 7.33–7.25 (m, 5H), 6.60 (ddd, J = 7.2, 5.1, 0.8 Hz, 1H), 6.37 (d, J = 8.4 Hz, 1H), 4.87 (s, 2H), 4.62 (s, 1H), 1.52 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 156.4, 147.5, 137.4, 135.6, 129.3, 128.5, 128.4, 114.2, 109.7, 77.7, 56.9, 26.0; IR (neat) 3359, 3285, 2975, 2926, 1683, 1598, 1513, 1482, 1455, 1417, 1334, 1292, 1213, 1148, 1057 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_2$: 285.1477 Found: 285.1457.

2-(1-(4-Fluorophenyl)-1H-indazol-4-ylamino)-*N*-(benzyloxy)-2-methylpropanamide (6r)



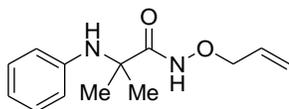
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 1:4 to 1:1, 88mg, yield 70%), White solid; m.p. 165-168 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.41 (s, 1H), 8.02 (s, 1H), 7.66–7.57 (m, 2H), 7.28–7.16 (m, 8H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.22 (d, *J* = 7.6 Hz, 1H), 4.85 (s, 2H), 4.44 (s, 1H), 1.60 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 172.5, 162.4, 160.0, 140.2, 137.9, 136.3, 136.2, 135.0, 131.8, 129.4, 128.7 (two peaks overlapping), 128.5, 124.7, 124.6, 116.4, 116.2, 116.1, 104.3, 100.7, 78.1, 57.5, 26.1; IR (neat) 3312, 3113, 2934, 1667, 1603, 1591, 1512, 1452, 1415, 1366, 1296, 1218, 1169, 1101, 1078, 1009 cm⁻¹; HRMS (EI) *m/z* calcd for [M]⁺ C₂₄H₂₃FN₄O₂: 418.1805 Found: 418.1812.

***N*-Methoxy-2-methyl-2-(phenylamino)propanamide (7a)**



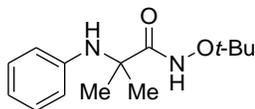
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 2:3, 53 mg, yield 85%), White solid; m.p. 120-122 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.42 (s, 1H), 7.18 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 2H), 3.83 (s, 1H), 3.73 (s, 3H), 1.52 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 173.0, 144.3, 129.2, 119.3, 115.9, 64.0, 57.4, 26.0; IR (neat) 3374, 3310, 2929, 1682, 1603, 1498, 1445, 1384, 1316, 1262, 1209, 1187, 1059 cm⁻¹; HRMS (EI) *m/z* calcd for [M]⁺ C₁₁H₁₆N₂O₂: 208.1212 Found: 208.1183.

***N*-(Allyloxy)-2-methyl-2-(phenylamino)propanamide (7b)**



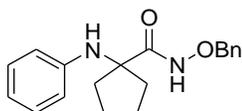
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 59 mg, yield 84%), White solid; m.p. 102-105 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.37 (s, 1H), 7.16 (t, *J* = 7.9 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 2H), 6.06–5.79 (m, 1H), 5.25 (dd, *J* = 14.0, 1.8 Hz, 2H), 4.37 (d, *J* = 6.5 Hz, 2H), 3.81 (s, 1H), 1.50 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 144.4, 132.2, 129.1, 120.8, 119.3, 116.0, 76.8, 57.5, 26.1; IR (neat) 3367, 3319, 2991, 2922, 2866, 1680, 1603, 1525, 1499, 1454, 1377, 1317, 1262, 1213, 1185, 1103, 1054 cm⁻¹; HRMS (EI) *m/z* calcd for [M]⁺ C₁₃H₁₈N₂O₂: 234.1368 Found: 234.1354.

***N*-tert-Butoxy-2-methyl-2-(phenylamino)propanamide (7c)**



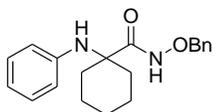
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 73 mg, yield 98%), White solid; m.p. 160-161 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.98 (s, 1H), 7.18 (t, $J = 7.8$ Hz, 2H), 6.81 (t, $J = 7.3$ Hz, 1H), 6.63 (d, $J = 7.8$ Hz, 2H), 3.86 (s, 1H), 1.54 (s, 6H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.2, 144.5, 129.2, 119.3, 116.0, 82.4, 77.3, 57.7, 26.4, 26.3; IR (neat) 3374, 3310, 2929, 1682, 1603, 1524, 1498, 1445, 1384, 1366, 1316, 1262, 1209, 1187, 1059 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_2$: 250.1681 Found: 250.1660.

***N*-(Benzyloxy)-1-(phenylamino)cyclopentanecarboxamide (7e)**



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 83 mg, yield 89%), White solid; m.p. 124-127 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.28 (s, 1H), 7.36–7.25 (m, 5H), 7.16 (dd, $J = 8.3, 7.5$ Hz, 2H), 6.79 (t, $J = 7.4$ Hz, 1H), 6.52 (d, $J = 7.7$ Hz, 2H), 4.85 (s, 2H), 3.77 (s, 1H), 2.35 (dd, $J = 13.3, 6.6$ Hz, 2H), 1.79 (dd, $J = 16.6, 11.4$ Hz, 4H), 1.74–1.55 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 144.4, 135.1, 129.4, 129.2, 128.7, 128.5, 119.1, 115.4, 78.1, 67.5, 37.3, 24.7; IR (neat) 3386, 3304, 2955, 2873, 1669, 1602, 1520, 1495, 1455, 1344, 1294, 1266, 1228, 1185, 1048, 1028 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$: 310.1681 Found: 310.1688.

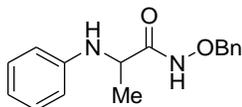
***N*-(Benzyloxy)-1-(phenylamino)cyclohexanecarboxamide (7f)**



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 1:4, 76 mg, yield 78%), White solid; m.p. 137-139 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.32 (s, 1H), 7.40–7.28 (m, 5H), 7.16 (dd, $J = 8.4, 7.5$ Hz, 2H), 6.80 (t, $J = 7.4$ Hz, 1H), 6.66–6.50 (m, 2H), 4.89 (s, 2H), 3.84 (s, 1H), 2.08–1.87 (m, 4H), 1.70–1.51 (m, 3H), 1.40–1.19 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 143.7, 135.2, 129.4, 129.2, 128.7, 128.5, 119.3, 116.2, 78.0, 59.6, 31.4, 25.0, 20.8; IR (neat) 3379, 3259, 2938, 2855, 1645, 1599,

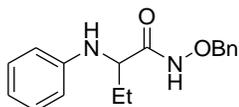
1515, 1494, 1452, 1359, 1320, 1289, 1259, 1170, 1099, 1016 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$: 324.1838 Found: 324.1825.

***N*-(Benzyloxy)-2-(phenylamino)propanamide (7g)**



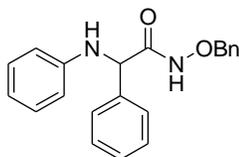
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:7, 49 mg, yield 60%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.07 (s, 1H), 7.29–7.08 (m, 7H), 6.74 (t, $J = 7.2$ Hz, 1H), 6.49 (d, $J = 7.9$ Hz, 2H), 4.77 (dd, $J = 29.3, 11.2$ Hz, 2H), 3.76 (d, $J = 6.5$ Hz, 2H), 1.40 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.1, 146.2, 134.8, 129.5, 128.8, 128.6, 119.3, 113.7, 78.3, 54.1, 19.7; IR (neat) 3355, 3183, 3029, 2927, 1688, 1643, 1601, 1525, 1498, 1453, 1359, 1324, 1298, 1184, 1079, 1024 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2$: 270.1368 Found: 270.1348.

***N*-(Benzyloxy)-2-(phenylamino)butanamide (7h)**



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 1:4 to 3:7, 60mg, yield 70%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.21 (s, 1H), 7.44–7.27 (m, 5H), 7.21 (t, $J = 7.5$ Hz, 2H), 6.83 (t, $J = 7.2$ Hz, 1H), 6.62 (d, $J = 7.8$ Hz, 2H), 4.86 (dd, $J = 24.8, 11.2$ Hz, 2H), 3.90 (s, 1H), 3.71 (s, 1H), 2.02–1.70 (m, 2H), 1.04 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 146.6, 134.9, 129.5 (two peaks overlapping), 128.8, 128.6, 119.2, 113.7, 78.4, 59.6, 26.7, 10.4; IR (neat) 3292, 3149, 2963, 1673, 1643, 1601, 1520, 1495, 1335, 1263, 1233, 1178, 1146, 1068, 1014 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2$: 284.1525 Found: 284.1501.

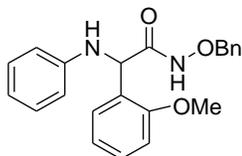
***N*-(Benzyloxy)-2-phenyl-2-(phenylamino)acetamide (7i)**



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:17, 83 mg, yield 83%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.07 (s, 1H), 7.44–7.12 (m, 12H), 6.88–6.56 (m, 3H), 4.96–

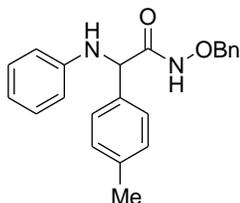
4.64 (m, 3H), 4.47 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 146.2, 137.9, 134.8, 129.5, 129.4, 129.2, 128.8, 128.7, 128.6, 127.4, 119.2, 113.8, 78.3, 62.5; IR (neat) 3367, 3184, 3030, 1660, 1600, 1501, 1454, 1431, 1352, 1314, 1213, 1180, 1133, 1028 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_2$: 332.1525 Found: 332.1536.

***N*-(Benzyloxy)-2-(2-methoxyphenyl)-2-(phenylamino)acetamide (7j)**

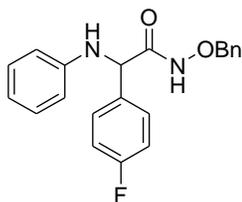


Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 1:4, 85mg, yield 78%), White solid; m.p. 163-168 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.98 (s, 1H), 7.33 (dd, J = 7.6, 1.6 Hz, 1H), 7.26–7.14 (m, 4H), 7.09 (d, J = 6.4 Hz, 2H), 7.00 (t, J = 7.9 Hz, 2H), 6.85 (t, J = 7.2 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 6.58 (t, J = 7.3 Hz, 1H), 6.37 (d, J = 7.9 Hz, 2H), 5.12 (s, 2H), 4.79–4.68 (m, 2H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 155.8, 145.9, 135.1, 129.3, 129.2 (two peaks overlapping), 128.7 (two peaks overlapping), 127.5, 126.2, 121.9, 117.9, 113.3, 110.9, 78.0, 55.5, 53.1; IR (neat) 3392, 3240, 2924, 1657, 1601, 1493, 1462, 1428, 1312, 1240, 1124, 1051, 1019 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_3$: 362.1630 Found: 362.1602.

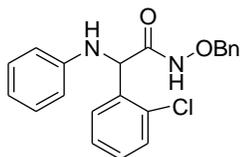
***N*-(Benzyloxy)-2-(phenylamino)-2-*p*-tolylacetamide (7k)**



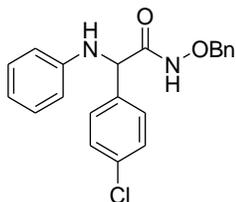
Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 3:17, 71mg, yield 68%), White solid; m.p. 128-131 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.12 (s, 1H), 7.37–7.10 (m, 12H), 6.78 (t, J = 7.1 Hz, 1H), 6.58 (d, J = 7.7 Hz, 2H), 4.91–4.67 (m, 3H), 4.42 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 146.3, 138.6, 135.0, 134.8, 129.9, 129.5, 129.4, 128.8, 128.6, 127.2, 119.1, 113.8, 78.3, 62.2, 21.2; IR (neat) 3384, 3155, 2986, 1674, 1602, 1504, 1432, 1361, 1313, 1270, 1232, 1183, 1132, 1080, 1021 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2$: 346.1681 Found: 346.1682.

***N*-(Benzyloxy)-2-(4-fluorophenyl)-2-(phenylamino)acetamide (7l)**

Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 1:4, 81 mg, yield 77%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.40 (s, 1H), 7.41–7.27 (m, 5H), 7.25–7.14 (m, 4H), 7.00 (t, $J = 8.6$ Hz, 2H), 6.82 (t, $J = 7.0$ Hz, 1H), 6.58 (d, $J = 7.9$ Hz, 2H), 4.90–4.73 (m, 3H), 4.49 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.4, 162.8 (d, $J^1 = 247.8$ Hz), 145.9, 134.7, 133.7 (d, $J^2 = 3.1$ Hz), 129.4, 129.2, 129.1, 128.9, 128.6, 119.4, 116.1 (d, $J^2 = 21.6$ Hz), 113.8, 78.3, 61.5; IR (neat) 3401, 3176, 3030, 1659, 1601, 1502, 1432, 1352, 1312, 1222, 1158, 1094, 1025 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{19}\text{FN}_2\text{O}_2$: 350.1431 Found: 350.1419.

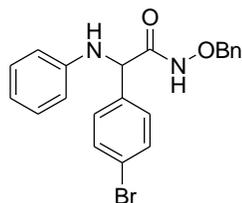
***1*-(*O*-Benzyloxyamino)-2-anilino-2-(*o*-chlorophenyl)-1-ethanone (7m)**

Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 1:4, 68 mg, yield 62%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 8.75 (s, 1H), 7.51–7.41 (m, 1H), 7.37–7.21 (m, 8H), 7.12 (t, $J = 7.7$ Hz, 2H), 6.72 (t, $J = 7.3$ Hz, 1H), 6.52 (d, $J = 7.5$ Hz, 2H), 5.27 (s, 1H), 5.04–4.72 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.7, 145.6, 135.7, 134.6, 133.1, 129.9, 129.8, 129.4 (two peaks overlapping), 128.9, 128.7, 128.6, 128.0, 118.7, 113.5, 78.4, 56.7; IR (neat) 3360, 3203, 1030, 1688, 1601, 1502, 1469, 1434, 1351, 1311, 1248, 1214, 1180, 1037 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{19}\text{ClN}_2\text{O}_2$: 366.1135 Found: 366.1149.

***1*-(*O*-Benzyloxyamino)-2-anilino-2-(*p*-chlorophenyl)-1-ethanone (7n)**

Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 1:4, 87 mg, yield 79%), White solid; m.p. 113-115 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.10 (s, 1H), 7.36–7.15 (m, 12H), 6.82 (t, J = 6.5 Hz, 1H), 6.58 (d, J = 7.9 Hz, 2H), 4.92–4.67 (m, 3H), 4.47 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 145.9, 136.4, 134.6, 129.4 (three peaks overlapping), 129.4, 129.2, 128.9, 128.6, 119.4, 113.8 (two peaks overlapping), 78.3, 61.6; IR (neat) 3383, 3170, 2923, 1669, 1600, 1500, 1486, 1454, 1399, 1346, 1311, 1156, 1091, 1007 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{19}\text{ClN}_2\text{O}_2$: 366.1135 Found: 366.1133.

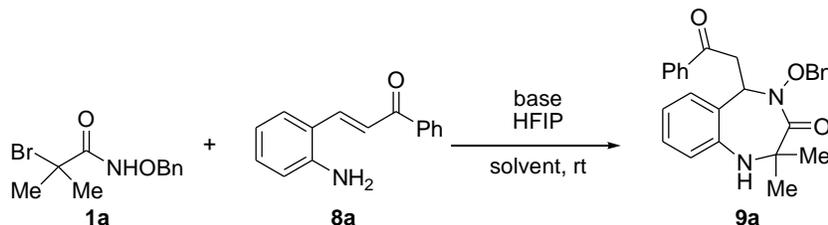
1-(*O*-Benzyloxyamino)-2-anilino-2-(*p*-bromophenyl)-1-ethanone (7o)



Synthesized by the general procedure II; flash chromatography (EtOAc : hexane = 1:4, 94 mg, yield 76%), White solid; m.p. 62-64 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.42 (s, 1H), 7.40 (d, J = 7.7 Hz, 2H), 7.32–7.10 (m, 9H), 6.78 (t, J = 6.5 Hz, 1H), 6.53 (d, J = 7.7 Hz, 2H), 4.84–4.65 (m, 8.9 Hz, 3H), 4.52 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 145.8, 137.0, 134.6, 132.3, 129.4 (two peaks overlapping), 129.0, 128.6, 122.7, 119.4, 113.9 (two peaks overlapping), 78.3, 61.3; IR (neat) 3171, 1924, 1658, 1601, 1485, 1454, 1432, 1403, 1311, 1288, 1210, 1155, 1100, 1071, 1025 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{19}\text{BrN}_2\text{O}_2$: 410.0630 Found: 410.0618.

4. Optimization of [4+3] Cycloaddition of 2-Aminophenyl α,β -Unsaturated Carbonyls with α -Bromohydroxamates.

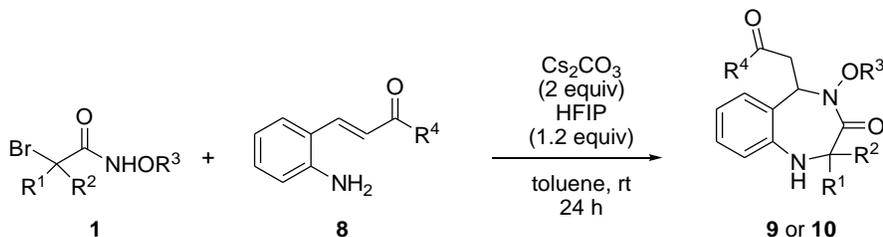
Table 1. Optimization of [4+3] Cycloaddition of α -bromohydroxamate **1a with 2-Aminophenyl α,β -Unsaturated Phenylketone **8a**^a**



entry	base	HFIP (eq)	solvent	time (h)	yield (%) ^b
1	Cs ₂ CO ₃	0	CF ₃ C ₆ H ₅	24	26
2	Cs ₂ CO ₃	5	CF ₃ C ₆ H ₅	24	87
3	Cs ₂ CO ₃	5	CH ₃ CN	24	22
4	Cs ₂ CO ₃	5	THF	24	25
5	Cs ₂ CO ₃	5	Toluene	24	85
6	Cs₂CO₃	1.2	Toluene	24	84
7	Cs ₂ CO ₃	1.2	<i>o</i> -xylene	24	60
8	Cs ₂ CO ₃	1.2	<i>p</i> -xylene	24	61
9	Cs ₂ CO ₃	0.2	Toluene	24	45
10	Na ₂ CO ₃	1.2	Toluene	24	39
11	K ₂ CO ₃	1.2	Toluene	24	34
12	Et ₃ N	1.2	Toluene	24	48
13	DBU	1.2	Toluene	24	29

^aThe reactions were carried out in solvent (0.1 M) with **1a** (0.15 mmol), **8a** (0.10 mmol), base (0.2 mmol) and HFIP. ^bIsolated yield.

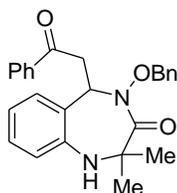
5. General Procedure III for the [4+3] Cycloaddition of 2-Aminophenyl α,β -Unsaturated Ketones with α -Bromohydroxamates (Scheme 5 and 6).



To a solution of α -halohydroxamate **1** (0.15 mmol), 2-aminophenyl α,β -unsaturated carbonyls **8** (0.10 mmol), and HFIP (0.12 mmol) in toluene (1 mL) was added Cs_2CO_3 (0.20 mmol) at 0 °C. The reaction mixture was stirred at room temperature until 2-aminophenyl α,β -unsaturated carbonyls **8** was completely consumed, as determined by TLC. Then, the resulting mixture was filtered through the plug of celite and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as eluent to afford desired product **9** or **10**.

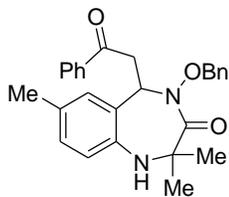
Procedure for a 1 mmol scale synthesis of 9a. To a solution of α -halohydroxamate **1** (408 mg, 1.5 mmol), 2-aminophenyl α,β -unsaturated phenylketone **8a** (233 mg, 1.0 mmol), and HFIP (0.13 mL, 1.2 mmol) in toluene (10 mL) was added Cs_2CO_3 (652 mg, 2.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 24 h. Then, the resulting mixture was filtered through the plug of celite and concentrated in vacuo. The crude residue was purified by flash column chromatography with (EtOAc : hexanes = 1:3) to afford desired product **6a** (340 mg, 82% yield) as white solid.

4-(Benzyloxy)-2,2-dimethyl-5-phenacyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9a)



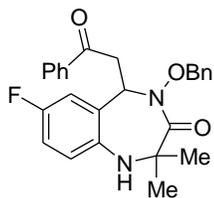
Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 3:7, 35 mg, yield 84%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 7.3 Hz, 2H), 7.57–7.29 (m, 8H), 7.11 (td, J = 7.6, 1.4 Hz, 1H), 6.98 (d, J = 6.5 Hz, 1H), 6.89 (t, J = 7.1 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 5.06 (dd, J = 9.9, 3.1 Hz, 1H), 4.96 (q, J = 10.5 Hz, 2H), 4.31 (dd, J = 16.8, 9.9 Hz, 1H), 3.50 (dd, J = 16.8, 3.1 Hz, 1H), 3.11 (s, 1H), 1.69 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 173.2, 144.1, 136.7, 135.4, 133.2, 130.6 (two peaks overlapping), 130.1, 129.3, 128.8, 128.6, 128.5, 128.1, 123.1, 122.9, 76.0, 64.6, 62.9, 41.9, 29.8, 28.1; IR (neat) 3314, 3031, 2967, 2927, 1681, 1644, 1597, 1490, 1449, 1409, 1356, 1323, 1284, 1230, 1200, 1177, 1111, 1080 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_3$: 414.1943 Found: 414.1920.

4-(Benzyloxy)-2,2,7-trimethyl-5-phenacyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9b)



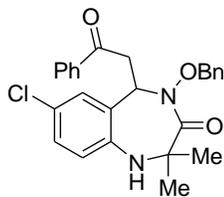
Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 29 mg, yield 69%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 7.5$ Hz, 2H), 7.57–7.29 (m, 8H), 6.90 (d, $J = 7.3$ Hz, 1H), 6.73 (s, 1H), 6.62 (d, $J = 7.7$ Hz, 1H), 5.06–4.86 (m, 3H), 4.33 (dd, $J = 16.8, 9.7$ Hz, 1H), 3.50 (dd, $J = 16.7, 2.1$ Hz, 1H), 3.07 (s, 1H), 2.21 (s, 3H), 1.67 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.7, 173.2, 141.5, 136.8, 135.4, 133.1, 132.6, 131.1, 130.6, 130.2, 129.7, 128.7, 128.6, 128.5, 128.1, 122.9, 76.0, 64.7, 62.9, 42.1, 29.8, 28.0, 20.7; IR (neat) 3316, 2969, 2924, 2870, 1735, 1681, 1639, 1598, 1509, 1449, 1373, 1318, 1244, 1210, 1128, 1045 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_3$: 428.2100 Found: 428.2116.

4-(Benzyloxy)-7-fluoro-2,2-dimethyl-5-phenacyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9c)



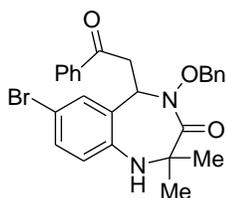
Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 3:7, 27mg, yield 62%), White solid; m.p. 155-157 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.3$ Hz, 2H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.42–7.33 (m, 7H), 6.81 (td, $J = 8.3, 2.8$ Hz, 1H), 6.66 (dt, $J = 8.7, 4.2$ Hz, 2H), 5.06–4.88 (m, 3H), 4.33 (dd, $J = 17.1, 10.0$ Hz, 1H), 3.49 (dd, $J = 17.1, 3.0$ Hz, 1H), 3.04 (s, 1H), 1.67 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.4, 173.2, 158.6 (d, $J^1 = 242.3$ Hz), 140.0 (d, $J^1 = 2.6$ Hz), 136.6, 135.3, 133.3, 132.5 (d, $J^3 = 7.8$ Hz), 130.3, 129.0, 128.7 (two peaks overlapping), 128.1, 124.1 (d, $J^3 = 8.0$ Hz), 117.5 (d, $J^2 = 23.2$ Hz), 115.8 (d, $J^2 = 22.3$ Hz), 76.2, 64.3, 63.0, 41.8, 29.8, 28.0; IR (neat) 3318, 2965, 2919, 2852, 1672, 1651, 1496, 1448, 1401, 1352, 1319, 1261, 1207, 1150, 1061 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{26}\text{H}_{25}\text{FN}_2\text{O}_3$: 432.1849 Found: 432.1838.

4-(Benzyloxy)-7-chloro-2,2-dimethyl-5-phenacyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9d)



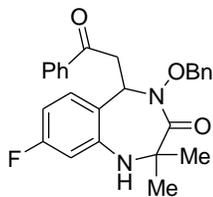
Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 34mg, yield 75%), White solid; m.p. 126-128 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.85–7.76 (m, 2H), 7.55–7.47 (m, 1H), 7.42–7.31 (m, 7H), 7.07 (dd, $J = 8.2, 2.4$ Hz, 1H), 6.84 (d, $J = 2.4$ Hz, 1H), 6.65 (d, $J = 8.3$ Hz, 1H), 4.93 (ddd, $J = 11.4, 9.9, 6.9$ Hz, 3H), 4.28 (dd, $J = 17.1, 9.9$ Hz, 1H), 3.50 (dd, $J = 17.1, 3.1$ Hz, 1H), 3.07 (s, 1H), 1.68 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.2, 172.9, 142.7, 136.6, 135.2, 133.3, 132.2, 130.5, 130.3, 129.1, 129.1, 128.8, 128.6, 128.1 (two peaks overlapping), 124.1, 76.2, 64.2, 63.0, 41.6, 29.7, 28.2; IR (neat) 3317, 2980, 2919, 2864, 1672, 1650, 1595, 1489, 1449, 1396, 1355, 1309, 1259, 1195, 1180, 1126, 1057 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{26}\text{H}_{25}\text{ClN}_2\text{O}_3$: 448.1554 Found: 448.1532.

4-(Benzyloxy)-7-bromo-2,2-dimethyl-5-phenacyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9e)



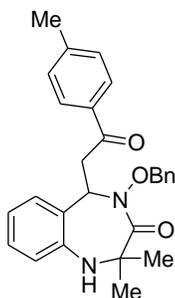
Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4 to 3:7, 40mg, yield 82%), White solid; m.p. 58-61 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.83–7.74 (m, 2H), 7.50 (dd, $J = 10.5, 4.2$ Hz, 1H), 7.41–7.31 (m, 7H), 7.20 (dd, $J = 8.2, 2.3$ Hz, 1H), 6.95 (d, $J = 2.2$ Hz, 1H), 6.60 (d, $J = 8.2$ Hz, 1H), 4.92 (ddd, $J = 13.3, 11.5, 7.0$ Hz, 3H), 4.26 (dd, $J = 17.1, 9.8$ Hz, 1H), 3.50 (dd, $J = 17.1, 3.2$ Hz, 1H), 3.14 (d, $J = 23.4$ Hz, 1H), 1.67 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.2, 172.8, 143.2, 136.6, 135.2, 133.3 (two peaks overlapping), 132.5, 132.1, 130.3, 129.1, 128.7, 128.6, 128.0, 124.4, 115.6, 76.2, 64.1, 62.9, 41.6, 29.7, 28.3; IR (neat) 3309, 2967, 2926, 2873, 1681, 1643, 1634, 1597, 1487, 1448, 1393, 1393, 1302, 1283, 1259, 1196, 1176, 1051 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{26}\text{H}_{25}\text{BrN}_2\text{O}_3$: 492.1049 Found: 492.1032.

4-(Benzyloxy)-8-fluoro-2,2-dimethyl-5-phenacyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9f)

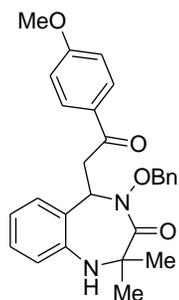


Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 33mg, yield 77%), White solid; m.p. 127-129 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.84–7.72 (m, 2H), 7.50 (ddd, $J = 6.9, 4.0, 1.3$ Hz, 1H), 7.44–7.31 (m, 7H), 6.88 (dd, $J = 8.4, 6.2$ Hz, 1H), 6.57 (td, $J = 8.4, 2.5$ Hz, 1H), 6.45 (dd, $J = 9.2, 2.5$ Hz, 1H), 5.01–4.86 (m, 3H), 4.26 (dd, $J = 16.9, 10.1$ Hz, 1H), 3.47 (dd, $J = 16.9, 3.0$ Hz, 1H), 1.68 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 173.0, 163.0 (d, $J^1 = 248.1$ Hz), 145.8 (d, $J^2 = 9.2$ Hz), 136.7, 135.4, 133.3, 132.2 (d, $J^2 = 9.7$ Hz), 130.2, 128.9, 128.7, 128.6, 128.1, 126.4 (d, $J^3 = 3.0$ Hz), 109.9 (d, $J^4 = 1.8$ Hz), 109.7, 76.1, 64.0, 63.1, 41.7, 29.7, 28.2; IR (neat) 3309, 3029, 2923, 2850, 1680, 1634, 1610, 1503, 1493, 1450, 1378, 1254, 1275, 1233, 1180, 1110, 1047 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{26}\text{H}_{15}\text{FN}_2\text{O}_3$: 432.1849 Found: 432.1852.

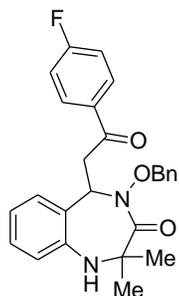
4-(Benzyloxy)-2,2-dimethyl-5-[(*p*-toluoyl)methyl]-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9g)



Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 33 mg, yield 78%), White solid; m.p. 117-119 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.2$ Hz, 2H), 7.46–7.31 (m, 5H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.11 (td, $J = 7.6, 1.6$ Hz, 1H), 6.98 (dd, $J = 7.5, 1.4$ Hz, 1H), 6.89 (td, $J = 7.5, 1.1$ Hz, 1H), 6.72 (d, $J = 7.7$ Hz, 1H), 5.06 (dd, $J = 9.9, 3.1$ Hz, 1H), 4.96 (q, $J = 10.4$ Hz, 2H), 4.28 (dd, $J = 16.8, 9.9$ Hz, 1H), 3.49 (dd, $J = 16.7, 3.2$ Hz, 1H), 3.11 (s, 1H), 2.36 (s, 3H), 1.69 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 173.2, 144.1, 144.0, 135.4, 134.4, 130.7, 130.6, 130.1, 129.3, 129.2, 128.8, 128.6, 128.2, 123.1, 122.9, 76.0, 64.7, 62.9, 41.8, 29.9, 28.1, 21.7; IR (neat) 3322, 2965, 2922, 2865, 1681, 1667, 1645, 11602, 1493, 1455, 1407, 1325, 1292, 1232, 1199, 1179, 1112, 1059, 1038 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_3$: 428.2100 Found: 428.2093.

5-[(*p*-Anisoyl)methyl]-4-(benzyloxy)-2,2-dimethyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9h)

Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 3:7, 35 mg, yield 80%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.9$ Hz, 2H), 7.48–7.30 (m, 5H), 7.10 (td, $J = 7.6$, 1.4 Hz, 1H), 6.98 (dd, $J = 7.5$, 1.2 Hz, 1H), 6.88 (t, $J = 7.1$ Hz, 1H), 6.83 (d, $J = 8.9$ Hz, 2H), 6.73 (d, $J = 7.6$ Hz, 1H), 5.05 (dd, $J = 9.9$, 3.1 Hz, 1H), 4.96 (q, $J = 10.4$ Hz, 2H), 4.26 (dd, $J = 16.5$, 9.9 Hz, 1H), 3.82 (s, 3H), 3.46 (dd, $J = 16.5$, 3.2 Hz, 1H), 3.19 (s, 1H), 1.69 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.2, 173.2, 163.5, 144.1, 135.4, 130.7, 130.6, 130.4, 130.1, 130.0, 129.3, 128.8, 128.6, 123.1, 122.9, 113.7, 76.0, 64.8, 62.9, 55.5, 41.6, 29.9, 28.1; IR (neat) 3316, 2965, 2926, 2855, 1644, 1597, 1574, 1510, 1492, 1456, 1417, 1356, 1318, 1257, 1202, 1166, 1112, 1026 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_4$: 444.2049 Found: 444.2043.

4-(Benzyloxy)-5-[(*p*-fluorobenzoyl)methyl]-2,2-dimethyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9i)

Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 41mg, yield 97%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.86–7.75 (m, 2H), 7.48–.29 (m, 5H), 7.12 (td, $J = 7.5$, 1.5 Hz, 1H), 7.02 (t, $J = 8.6$ Hz, 2H), 6.95 (dd, $J = 7.5$, 1.3 Hz, 1H), 6.89 (td, $J = 7.4$, 0.9 Hz, 1H), 6.73 (d, $J = 7.6$ Hz, 1H), 5.03–4.92 (m, 3H), 4.27 (dd, $J = 16.6$, 9.8 Hz, 1H), 3.46 (dd, $J = 16.6$, 3.1 Hz, 1H), 3.13 (s, 1H), 1.69 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.1, 173.2, 165.8 (d, $J^1 = 254.9$ Hz), 144.1, 135.4, 133.3 (d, $J^4 = 3.0$ Hz), 130.8, 130.7, 130.6, 130.4, 130.1, 129.4, 128.9, 128.7, 123.0 (d, $J^2 = 27.6$ Hz), 115.6 (d, $J^3 = 21.9$ Hz), 76.1, 64.8, 62.9, 41.8, 29.8, 28.1; IR (neat) 1725, 1681, 1642, 1597, 1508, 1457,

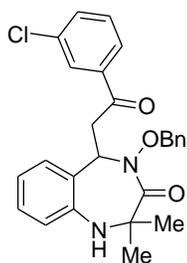
1408, 1323, 1285, 1230, 1177, 1112 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$: $\text{C}_{26}\text{H}_{25}\text{FN}_2\text{O}_3$: 432.1849 Found: 432.1855.

4-(Benzyloxy)-5-[(*p*-chlorobenzoyl)methyl]-2,2-dimethyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9j)



Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 38 mg, yield 84%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.75–7.66 (m, 2H), 7.46–7.30 (m, 7H), 7.12 (td, $J = 7.5$, 1.7 Hz, 1H), 6.94 (dd, $J = 7.5$, 1.5 Hz, 1H), 6.89 (td, $J = 7.4$, 0.9 Hz, 1H), 6.73 (d, $J = 7.6$ Hz, 1H), 5.00–4.91 (m, 3H), 4.25 (dd, $J = 16.6$, 9.8 Hz, 1H), 3.45 (dd, $J = 16.6$, 3.2 Hz, 1H), 3.15 (s, 1H), 1.69 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.5, 173.2, 144.1, 139.6, 135.4, 135.1, 130.6, 130.4, 130.1, 129.5, 129.4, 128.9, (two peaks overlapping), 128.7, 123.2, 122.9, 76.1, 64.8, 63.0, 41.9, 29.9, 28.1; IR (neat) 3316, 2967, 2926, 2871, 1682, 1642, 1588, 1488, 1456, 1399, 1323, 1286, 1200, 1176, 1112, 1096 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{26}\text{H}_{25}\text{ClN}_2\text{O}_3$: 448.1554 Found: 448.1526.

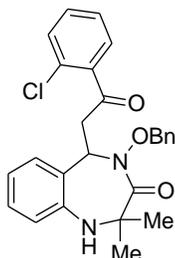
4-(Benzyloxy)-5-[(*m*-chlorobenzoyl)methyl]-2,2-dimethyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9k)



Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:1, 34 mg, yield 75%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (t, $J = 1.8$ Hz, 1H), 7.68–7.60 (m, 1H), 7.54–7.28 (m, 7H), 7.12 (td, $J = 7.6$, 1.8 Hz, 1H), 6.99–6.83 (m, 2H), 6.74 (d, $J = 7.5$ Hz, 1H), 5.04–4.88 (m, 3H), 4.23 (dd, $J = 16.6$, 9.8 Hz, 1H), 3.45 (dd, $J = 16.6$, 3.3 Hz, 1H), 3.13 (s, 1H), 1.69 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.5, 173.2, 144.1, 138.3, 135.4, 134.9, 133.1, 130.6, 130.3, 130.2, 129.9, 129.5, 128.9, 128.7, 128.3, 126.2, 123.2, 122.9, 76.1, 64.8, 63.0, 42.0, 29.8, 28.1; IR (neat) 1682, 1644, 1598, 1571,

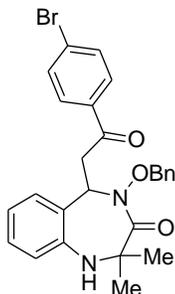
1488, 1456, 1415, 1321, 1288, 1199, 1177, 1112 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{26}\text{H}_{25}\text{ClN}_2\text{O}_3$: 448.1554 Found: 448.1532.

4-(Benzyloxy)-5-[(*o*-chlorobenzoyl)methyl]-2,2-dimethyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9l)



Flash chromatography (ethyl acetate : hexane = 1:4, 34 mg, yield 77%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (dt, $J = 6.3, 3.7$ Hz, 2H), 7.39–7.28 (m, 5H), 7.21–7.05 (m, 3H), 6.90 (d, $J = 4.3$ Hz, 2H), 6.72 (d, $J = 7.7$ Hz, 1H), 5.01–4.95 (m, 3H), 4.25 (dd, $J = 16.7, 9.8$ Hz, 1H), 3.49 (dd, $J = 16.7, 3.7$ Hz, 1H), 3.10 (s, 1H), 1.63 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.6, 173.1, 144.3, 138.9, 135.3, 131.8, 131.0, 130.5, 130.4, 130.3, 130.2, 129.4, 129.0, 128.9, 128.7, 126.8, 123.1, 122.8, 76.1, 64.6, 62.9, 46.0, 29.8, 28.1; IR (neat) 3316, 2968, 2926, 2872, 1693, 1640, 1591, 1490, 1457, 1433, 1408, 1318, 1229, 1200, 1131, 1111, 1072 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{26}\text{H}_{25}\text{ClN}_2\text{O}_3$: 448.1554 Found: 448.1564.

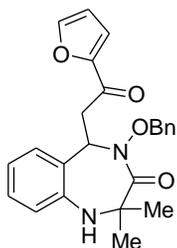
4-(Benzyloxy)-5-[(*p*-bromobenzoyl)methyl]-2,2-dimethyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9m)



Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 39 mg, yield 80%), White solid; m.p. 109–111 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.66–7.58 (m, 2H), 7.53–7.46 (m, 2H), 7.38 (ddd, $J = 31.3, 5.7, 3.3$ Hz, 5H), 7.12 (td, $J = 7.5, 1.7$ Hz, 1H), 6.91 (dtd, $J = 8.4, 7.5, 1.2$ Hz, 2H), 6.73 (d, $J = 7.5$ Hz, 1H), 5.04–4.89 (m, 3H), 4.24 (dd, $J = 16.6, 9.8$ Hz, 1H), 3.45 (dd, $J = 16.6, 3.2$ Hz, 1H), 3.17 (s, 1H), 1.68 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.7, 173.2, 144.1, 135.5, 135.3, 131.8, 130.5, 130.4, 130.1, 129.6, 129.4, 128.9, 128.7, 128.3, 123.2, 122.9, 76.1, 64.7, 62.9, 41.8, 29.8, 28.1; IR

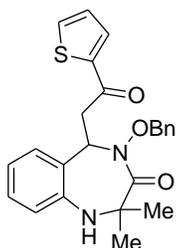
(neat) 3329, 2922, 2851, 1677, 1495, 1454, 1380, 1359, 1291, 1273, 1260, 1190, 1113, 1030 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{26}\text{H}_{25}\text{BrN}_2\text{O}_3$: 492.1049 Found: 492.1046.

4-(Benzyloxy)-5-[(2-furoyl)methyl]-2,2-dimethyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9n)



Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 3:7 to 7:13), 32 mg, yield 80%), White solid; m.p. 124-126 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (dd, $J = 1.7, 0.7$ Hz, 1H), 7.46–7.39 (m, 2H), 7.37–7.31 (m, 3H), 7.11 (ddd, $J = 7.7, 6.9, 2.1$ Hz, 1H), 7.02 (dd, $J = 3.6, 0.7$ Hz, 1H), 6.89 (dt, $J = 6.9, 3.2$ Hz, 2H), 6.74 (d, $J = 7.4$ Hz, 1H), 6.41 (dd, $J = 3.6, 1.7$ Hz, 1H), 5.05–4.90 (m, 3H), 4.03 (dd, $J = 16.0, 9.5$ Hz, 1H), 3.43 (dd, $J = 16.0, 3.9$ Hz, 1H), 3.16 (s, 1H), 1.67 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.4, 173.1, 152.6, 146.5, 144.2, 135.3, 130.4, 130.3, 130.1, 129.4, 128.8, 128.6, 123.2, 122.9, 117.5, 112.2, 76.0, 64.5, 62.9, 42.0, 29.8, 28.1; IR (neat) 3317, 2967, 2927, 2871, 1666, 1660, 1644, 1599, 1567, 1492, 1464, 1409, 1392, 1320, 1295, 1261, 1202, 1176, 1112, 1058 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_4$: 404.1736 Found: 404.1748.

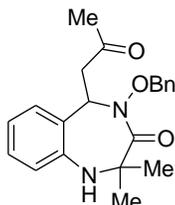
4-(Benzyloxy)-5-[(2-thenoyl)methyl]-2,2-dimethyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9o)



Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 3:7, 33 mg, yield 78%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.59–7.50 (m, 2H), 7.47–7.40 (m, 2H), 7.39–7.31 (m, 3H), 7.11 (td, $J = 7.6, 1.9$ Hz, 1H), 7.01 (dd, $J = 4.9, 3.8$ Hz, 1H), 6.94–6.84 (m, 2H), 6.73 (d, $J = 7.5$ Hz, 1H), 5.01–4.92 (m, 3H), 4.18 (dd, $J = 16.0, 9.8$ Hz, 1H), 3.48 (dd, $J = 16.0, 3.6$ Hz, 1H), 3.12 (s, 1H), 1.68 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.5, 173.2, 144.3, 144.2, 135.3, 133.9, 132.2, 130.5, 130.3, 130.1, 129.4, 128.9, 128.7, 128.1, 123.2, 122.9, 76.1, 64.9, 62.9, 42.5, 29.8, 28.1; IR (neat) 3317,

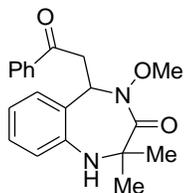
2967, 2926, 2859, 1643, 1598, 1518, 1491, 1456, 1412, 1357, 1318, 1289, 1235, 1201, 176, 1125, 1082 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_3\text{S}$: 420.1508 Found: 420.1534.

5-Acetyl-4-(benzyloxy)-2,2-dimethyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (9p)

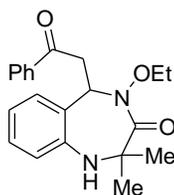


Synthesized by the general procedure III; flash chromatography (EtOAc : hexane : dichloromethane = 1:4:5, 22 mg, yield 62%), White solid; m.p. 58-61 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.45–7.32 (m, 5H), 7.16 (ddd, $J = 7.7, 6.7, 2.3$ Hz, 1H), 6.98–6.89 (m, 2H), 6.76 (d, $J = 7.4$ Hz, 1H), 4.92 (q, $J = 10.4$ Hz, 2H), 4.84 (dd, $J = 9.6, 3.5$ Hz, 1H), 3.64 (dd, $J = 16.8, 9.6$ Hz, 1H), 3.06 (s, 1H), 3.04 (dd, $J = 16.9, 3.4$ Hz, 1H), 1.90 (s, 3H), 1.64 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 206.3, 173.0, 144.1, 135.4, 130.7, 130.4, 130.1, 129.4, 128.9, 128.7, 123.2, 122.9, 76.0, 64.0, 62.9, 46.8, 30.6, 29.8, 28.1; IR (neat) 3316, 2968, 2927, 2873, 1709, 1637, 1598, 1490, 1456, 1409, 1358, 1259, 1202, 1158, 1113, 1022 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_3$: 352.1787 Found: 352.1783.

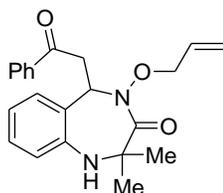
4-Methoxy-2,2-dimethyl-5-phenacyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (10a)



Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 3:7, 17 mg, yield 51%), White solid; m.p. 154-156 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.4$ Hz, 2H), 7.51 (t, $J = 7.3$ Hz, 1H), 7.46–7.34 (m, 3H), 7.15 (td, $J = 7.4, 0.9$ Hz, 1H), 6.99 (t, $J = 7.3$ Hz, 1H), 6.76 (d, $J = 7.6$ Hz, 1H), 5.29 (dd, $J = 9.7, 3.1$ Hz, 1H), 4.39 (dd, $J = 16.9, 9.7$ Hz, 1H), 3.79 (s, 3H), 3.60 (dd, $J = 16.8, 3.2$ Hz, 1H), 3.15 (s, 1H), 1.67 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.8, 172.8, 144.2, 136.9, 133.3, 131.0, 130.5, 129.5, 128.6, 128.1, 123.4, 123.1, 63.1, 62.8, 61.5, 42.2, 30.0, 28.0; IR (neat) 3316, 2963, 2921, 2852, 1669, 1647, 1597, 1494, 1449, 1409, 1357, 1324, 1262, 1197, 1160, 1130, 1058, 1025 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_3$: 338.1630 Found: 338.1632.

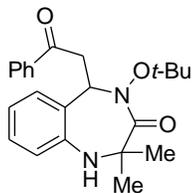
4-Ethoxy-2,2-dimethyl-5-phenacyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (10b)

Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 22 mg, yield 64%), White solid; m.p. 136-138 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.6$ Hz, 2H), 7.50 (t, $J = 7.3$ Hz, 1H), 7.45–7.34 (m, 3H), 7.15 (t, $J = 7.5$ Hz, 1H), 6.98 (t, $J = 7.4$ Hz, 1H), 6.76 (d, $J = 7.6$ Hz, 1H), 5.26 (dd, $J = 9.7, 2.9$ Hz, 1H), 4.42 (dd, $J = 16.8, 9.8$ Hz, 1H), 4.12–3.93 (m, 2H), 3.62 (dd, $J = 16.8, 3.0$ Hz, 1H), 3.18 (s, 1H), 1.67 (s, 3H), 1.28 (t, $J = 7.0$ Hz, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.8, 173.0, 144.3, 136.8, 133.3, 130.9, 130.6, 129.4, 128.6, 128.1, 123.3, 123.1, 69.4, 63.9, 62.8, 42.1, 29.9, 28.2, 13.7; IR (neat) 3319, 2957, 2921, 2851, 1650, 1596, 1578, 1494, 1449, 1415, 1377, 1358, 1309, 1289, 1230, 1160, 1112, 1058 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_3$: 352.1787 Found: 352.1768.

4-(Allyloxy)-2,2-dimethyl-5-phenacyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (10c)

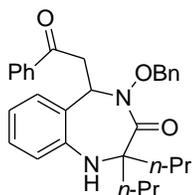
Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 25 mg, yield 71%), White solid; m.p. 117-119 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.2$ Hz, 2H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.43–7.35 (m, 3H), 7.15 (td, $J = 7.6, 1.3$ Hz, 1H), 7.05–6.94 (m, 1H), 6.76 (d, $J = 7.6$ Hz, 1H), 6.11–5.99 (m, 1H), 5.36–5.20 (m, 3H), 4.56–4.34 (m, 3H), 3.62 (dd, $J = 16.9, 3.1$ Hz, 1H), 3.21 (s, 1H), 1.67 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.8, 173.2, 144.3, 136.8, 133.3, 132.3, 130.7, 130.7, 129.4, 128.6, 128.1, 123.3, 123.0, 120.9, 75.2, 64.3, 62.9, 42.0, 29.8, 28.2; IR (neat) 3312, 2968, 2926, 2865, 1736, 1689, 1639, 1597, 1491, 1449, 1374, 1357, 1324, 1232, 1200, 1179, 1111, 1039 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_3$: 364.1787 Found: 364.1780.

2,2-Dimethyl-5-phenacyl-4-tert-butoxy-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (10d)



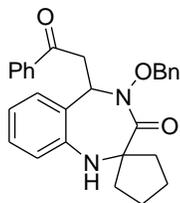
Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 26 mg, yield 69%), White solid; m.p. 143-146 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.5$ Hz, 2H), 7.50 (t, $J = 7.3$ Hz, 1H), 7.45–7.31 (m, 3H), 7.16 (dd, $J = 11.0, 4.1$ Hz, 1H), 6.98 (t, $J = 7.3$ Hz, 1H), 6.76 (d, $J = 7.6$ Hz, 1H), 5.19 (dd, $J = 10.2, 2.4$ Hz, 1H), 4.45 (dd, $J = 16.7, 10.4$ Hz, 1H), 3.60 (dd, $J = 16.8, 2.5$ Hz, 1H), 3.24 (s, 1H), 1.67 (s, 3H), 1.31 (s, 9H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.1, 177.3, 144.5, 136.8, 133.2, 131.3 (two peaks overlapping), 129.3, 128.6, 128.1, 122.9, 122.4, 83.1, 77.5, 77.2, 76.8, 66.6, 62.8, 40.7, 29.2 (two peaks overlapping), 27.3; IR (neat) 3341, 2967, 2923, 2853, 1672, 1596, 1579, 1493, 1450, 1379, 1264, 1320, 1305, 1226, 1179, 1112, 1101, 1058 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_3$: 380.2100 Found: 380.2108.

4-(Benzyloxy)-5-phenacyl-2,2-dipropyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one (10e)



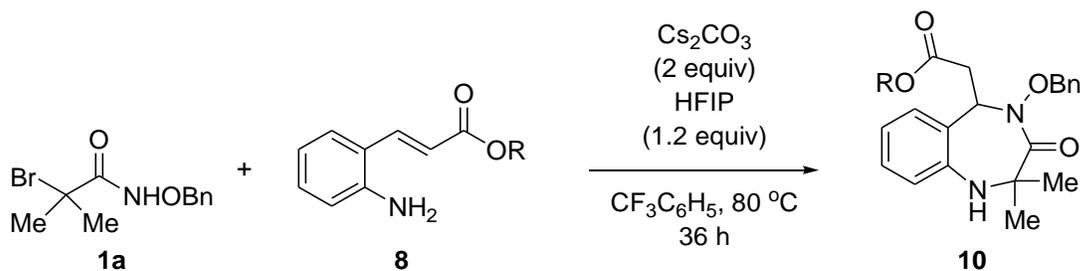
Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:9, 37 mg, yield 79%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.80–7.73 (m, 2H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.45–7.31 (m, 7H), 7.09 (td, $J = 7.6, 1.5$ Hz, 1H), 6.93 (dd, $J = 7.5, 1.3$ Hz, 1H), 6.84 (dd, $J = 10.8, 4.1$ Hz, 1H), 6.72 (d, $J = 7.5$ Hz, 1H), 5.05 (dd, $J = 10.0, 3.0$ Hz, 1H), 4.97 (q, $J = 10.5$ Hz, 2H), 4.34 (dd, $J = 16.6, 10.0$ Hz, 1H), 3.50 (dd, $J = 16.6, 3.0$ Hz, 1H), 3.25 (s, 1H), 2.33–2.23 (m, 1H), 1.89–1.75 (m, 1H), 1.63–1.40 (m, 4H), 1.32–1.19 (m, 2H), 1.03 (t, $J = 7.1$ Hz, 3H), 0.76 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.5, 172.4, 144.2, 136.7, 135.2, 133.1, 130.5, 130.0 (two peaks overlapping), 129.2, 128.7, 128.6, 128.5, 127.9, 122.5, 122.3, 76.2, 69.2, 64.5, 42.4, 42.3, 42.2, 18.1, 16.4, 14.7, 14.3; IR (neat) 3314, 2958, 2927, 2871, 1682, 1633, 1597, 1488, 1448, 1410, 1352, 1326, 1281, 1260, 1218, 1202, 1158, 1080, 1036 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_3$: 470.2569 Found: 470.2549.

4-(Benzyloxy)-5-phenacyl-4,5-dihydro-1H-spiro[1,4-benzodiazepine-2,1'-cyclopentan]-3-one (10f)



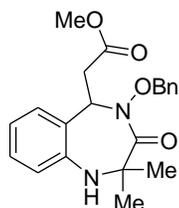
Synthesized by the general procedure III; flash chromatography (EtOAc : hexane = 1:4, 17 mg, yield 38%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 7.5$ Hz, 2H), 7.49 (t, $J = 7.3$ Hz, 1H), 7.45–7.32 (m, 7H), 7.11 (t, $J = 7.5$ Hz, 1H), 6.98 (d, $J = 6.7$ Hz, 1H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.69 (d, $J = 7.6$ Hz, 1H), 5.06 (dd, $J = 9.8, 3.1$ Hz, 1H), 4.95 (dt, $J = 19.6, 9.8$ Hz, 2H), 4.28 (dd, $J = 16.8, 9.8$ Hz, 1H), 3.56 (dd, $J = 16.8, 3.1$ Hz, 1H), 3.20 (s, 1H), 2.92–2.82 (m, 1H), 2.04–1.93 (m, 1H), 1.91–1.77 (m, 3H), 1.75–1.49 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 173.2, 144.0, 136.7, 135.3, 133.1, 130.7, 130.5, 130.0, 129.2, 128.7, 128.5, (two peaks overlapping), 128.0, 122.9, 122.5, 75.9, 73.2, 64.5, 42.0, 39.6, 37.6, 24.1, 24.0; IR (neat) 3327, 2955, 2924, 2872, 1681, 1634, 1597, 1485, 1449, 1408, 1328, 1260, 1180, 1118, 1017 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_3$: 440.2100 Found: 440.2081.

6. General Procedure IV for the [4+3] Cycloaddition of 2-Aminophenyl α,β -Unsaturated Esters with α -Bromohydroxamates.



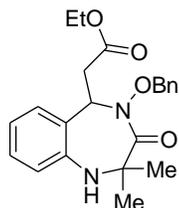
To a solution of α -halohydroxamate **1** (0.15 mmol), 2-aminophenyl α,β -unsaturated esters **8** (0.10 mmol), and HFIP (0.12 mmol) in trifluorotoluene (1 mL) was added Cs_2CO_3 (0.20 mmol) at 0 °C. After stirring at room temperature for 1 h, the reaction mixture was stirred at 80 °C for 36 h. Then, the resulting mixture was allowed to room temperature and filtered through the plug of celite and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as eluent to afford desired product **10**.

Methyl [4-(benzyloxy)-2,2-dimethyl-3-oxo-1,2,4,5-tetrahydro-1,4-benzodiazepin-5-yl]acetate (10g)



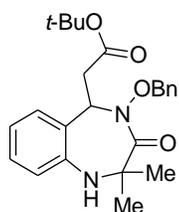
Synthesized by the general procedure IV; flash chromatography (EtOAc : hexane = 1:4, 26 mg, yield 71%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.49–7.33 (m, 5H), 7.17 (t, $J = 7.2$ Hz, 1H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.85 (d, $J = 7.2$ Hz, 1H), 6.77 (d, $J = 7.7$ Hz, 1H), 4.95 (q, $J = 10.4$ Hz, 2H), 4.77 (dd, $J = 9.7, 4.4$ Hz, 1H), 3.47 (d, $J = 11.5$ Hz, 3H), 3.43 (dd, $J = 15.3, 9.8$ Hz, 1H), 3.10 (s, 1H), 3.07 (dd, $J = 15.3, 4.3$ Hz, 1H), 1.63 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.9, 171.3, 144.3, 135.3, 130.1 (two peaks overlapped), 130.0, 129.6, 128.9, 128.7, 123.1, 123.0, 76.1, 65.3, 62.9, 51.7, 37.7, 29.8, 28.1; IR (neat) 1733, 1641, 1599, 1492, 1456, 1436, 1413, 1376, 1357, 1288, 1229, 1200, 1157, 1111, 1082 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_4$: 368.1736 Found: 368.1714.

Ethyl [4-(benzyloxy)-2,2-dimethyl-3-oxo-1,2,4,5-tetrahydro-1,4-benzodiazepin-5-yl]acetate (10h)



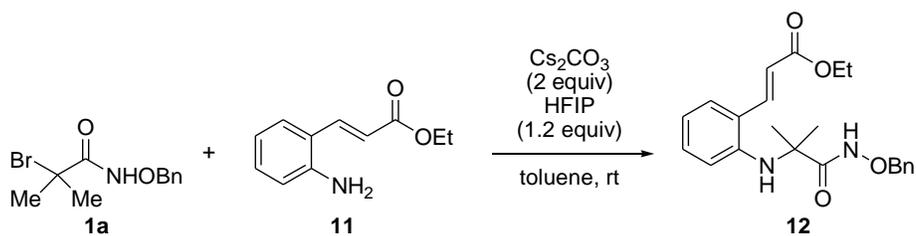
Synthesized by the general procedure IV; flash chromatography (EtOAc : hexane = 1:4 to 3:7, 31 mg, yield 82%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.49–7.32 (m, 5H), 7.17 (dd, $J = 11.0, 4.1$ Hz, 1H), 6.90 (t, $J = 7.3$ Hz, 1H), 6.83 (d, $J = 7.2$ Hz, 1H), 6.77 (d, $J = 7.7$ Hz, 1H), 4.95 (q, $J = 10.5$ Hz, 2H), 4.76 (dd, $J = 9.9, 4.3$ Hz, 1H), 4.03–3.84 (m, 2H), 3.43 (dd, $J = 15.1, 10.0$ Hz, 1H), 3.07 (s, 1H), 3.05 (dd, $J = 15.1, 4.3$ Hz, 1H), 1.63 (s, 3H), 1.21 (s, 3H), 1.07 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.9, 170.8, 144.4, 135.4, 130.1 (two peaks overlapping), 130.0, 129.5, 128.8, 128.6, 123.0, 123.0, 76.1, 65.3, 62.9, 60.5, 37.9, 29.8, 28.1, 14.1; IR (neat) 3316, 2976, 2928, 2872, 1729, 1640, 1599, 1492, 1456, 1413, 1371, 1317, 1288, 1251, 1229, 1200, 1155, 1111, 1036 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4$: 382.1893 Found: 382.1868.

***tert*-Butyl [4-(benzyloxy)-2,2-dimethyl-3-oxo-1,2,4,5-tetrahydro-1,4-benzodiazepin-5-yl]acetate (10i)**



Synthesized by the general procedure IV; flash chromatography (EtOAc : hexane = 1:9 to 1:4, 28 mg, yield 69%), Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 7.51–7.30 (m, 5H), 7.16 (dd, $J = 7.4, 6.7$ Hz, 1H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.80 (d, $J = 7.3$ Hz, 1H), 6.76 (d, $J = 7.7$ Hz, 1H), 4.95 (q, $J = 10.5$ Hz, 2H), 4.70 (dd, $J = 10.1, 4.4$ Hz, 1H), 3.35 (dd, $J = 14.5, 10.2$ Hz, 1H), 3.08 (s, 1H), 2.97 (dd, $J = 14.5, 4.4$ Hz, 1H), 1.63 (s, 3H), 1.25 (s, 9H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 169.9, 144.5, 135.5, 130.1 (three peaks overlapped), 129.4, 128.8, 128.6, 122.9, 122.8, 80.7, 76.1, 65.6, 62.9, 39.2, 29.8, 28.1, 28.0; IR (neat) 3318, 2951, 2927, 2872, 1733, 1641, 1599, 1492, 1456, 1436, 1376, 1357, 1320, 1288, 1229, 1200, 1157, 1111, 1048 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_4$: 410.2206 Found: 410.2212.

7. Procedure for the α -Substitution of 2-Aminophenyl α,β -Unsaturated Ethylester **11** with α -Bromohydroxamate **1a**

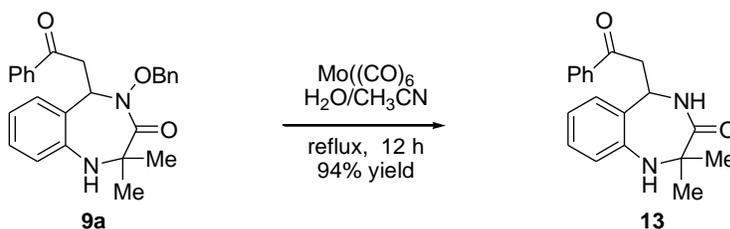


To a solution of α -bromohydroxamate **1a** (0.15 mmol), 2-aminophenyl α,β -unsaturated ethylester **11** (0.10 mmol), and HFIP (0.22 mmol) in toluene (1 mL) was added Cs_2CO_3 (0.60 mmol) at 0 °C. After stirring at room temperature for 24 h, the reaction mixture was filtered through the plug of celite and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as eluent to afford desired product **12** (31 mg, 80% yield).

Ethyl (*E*)-3- $\{o$ -[2-(*O*-benzyloxyamino)-1,1-dimethyl-2-oxoethylamino]phenyl}acrylate, Colorless gum; ^1H NMR (400 MHz, CDCl_3) δ 9.06 (s, 1H), 7.71 (d, $J = 15.6$ Hz, 1H), 7.38 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.35–7.27 (m, 5H), 7.24–7.17 (m, 1H), 6.82 (t, $J = 7.5$ Hz, 1H), 6.57 (d, $J = 8.0$ Hz, 1H), 6.32 (d, $J = 15.6$ Hz, 1H), 4.88 (d, $J = 9.3$ Hz, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 4.01 (s, 1H), 1.54 (s, 6H), 1.34 (t, $J = 7.1$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 167.0, 142.6, 139.2, 134.9, 131.0, 129.4, 128.8, 128.6, 128.4, 121.9, 120.1, 119.4, 115.4, 78.1, 60.7, 57.6, 26.3, 14.3; IR (neat) 3253, 2981, 2930, 1682, 1622, 1601, 1578, 1505, 1455, 1383, 1366, 1316, 1263, 1212, 1159, 1095, 1033 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4$: 382.1893 Found: 382.1866.

7. Procedure for the N–O Bond Cleavage of **9a**

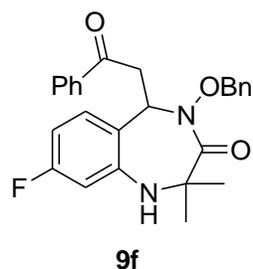
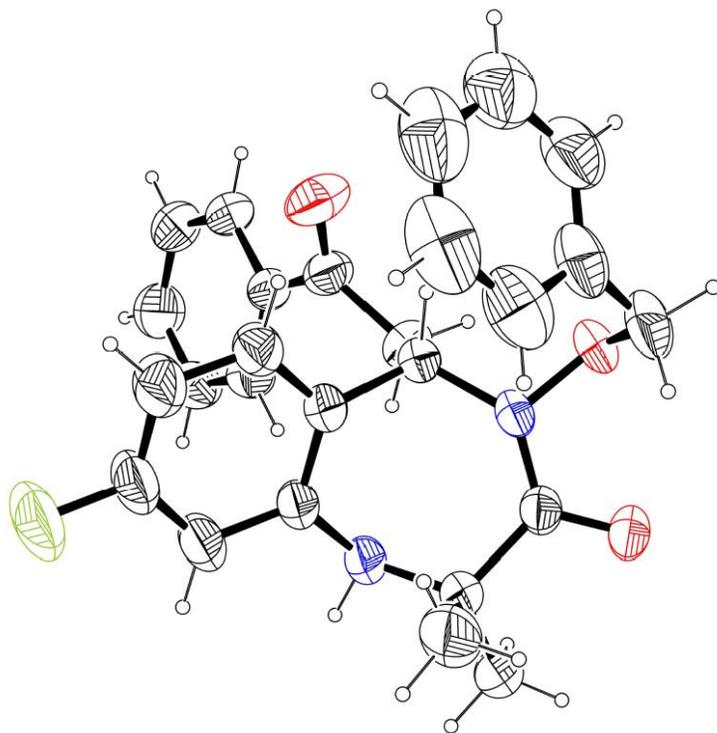


To a solution of compound **9a** (41 mg, 0.10 mmol in CH_3CN (0.5 mL) and H_2O (0.5 mL) was added $\text{Mo}(\text{CO})_6$ (32 mg, 0.12 mmol) at room temperature. After stirring at reflux for 12 h. Then, the resulting mixture was allowed to room temperature and filtered through the plug of celite and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as eluent to afford desired product **13** (29 mg, 94% yield).

2,2-Dimethyl-5-phenacyl-1,2,4,5-tetrahydro-1,4-benzodiazepin-3-one, White solid; m.p. 223-225 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 7.4$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.21 (dd, $J = 16.4, 7.8$ Hz, 2H), 7.03 (t, $J = 7.3$ Hz, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.57 (d, $J = 6.2$ Hz, 1H), 4.98–4.78 (m, 1H), 4.37 (dd, $J = 18.0, 9.4$ Hz, 1H), 3.31 (dd, $J = 18.0, 3.5$ Hz, 1H), 3.17 (brs, 1H), 1.55 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.6, 177.2, 145.2, 136.7, 133.5, 133.4, 129.1, 128.8, 128.3, 128.2, 123.7, 123.5, 61.8, 53.5, 44.7, 29.9, 28.2; IR (neat) 3335, 3186, 3054, 2972, 1732, 1651, 1580, 1457, 1400, 1373, 1343, 1279, 1180, 1159, 1105, 1042, 1017, 1001 cm^{-1} ; HRMS (EI) m/z calcd for $[\text{M}]^+$ $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$: 308.1525 Found: 308.1525.

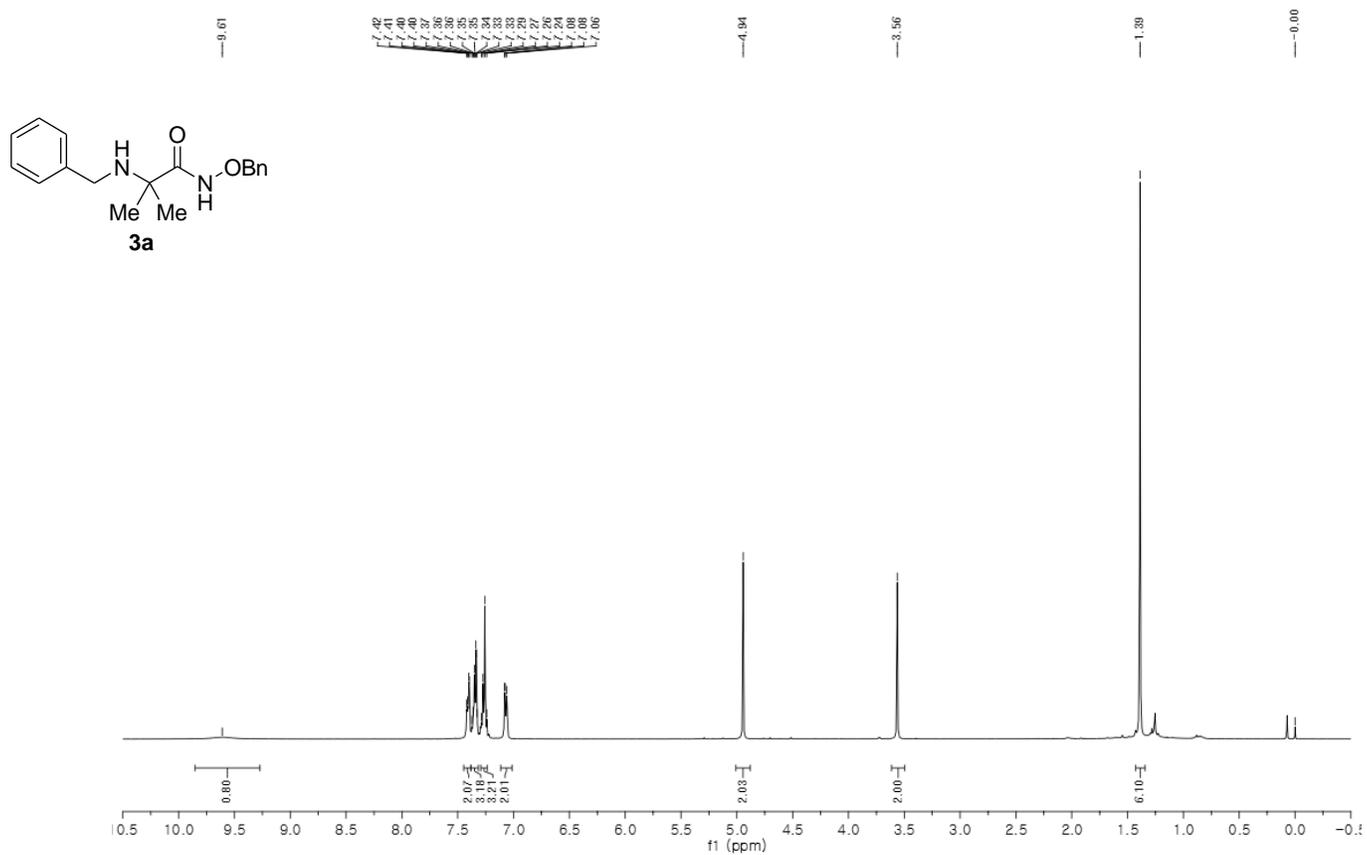
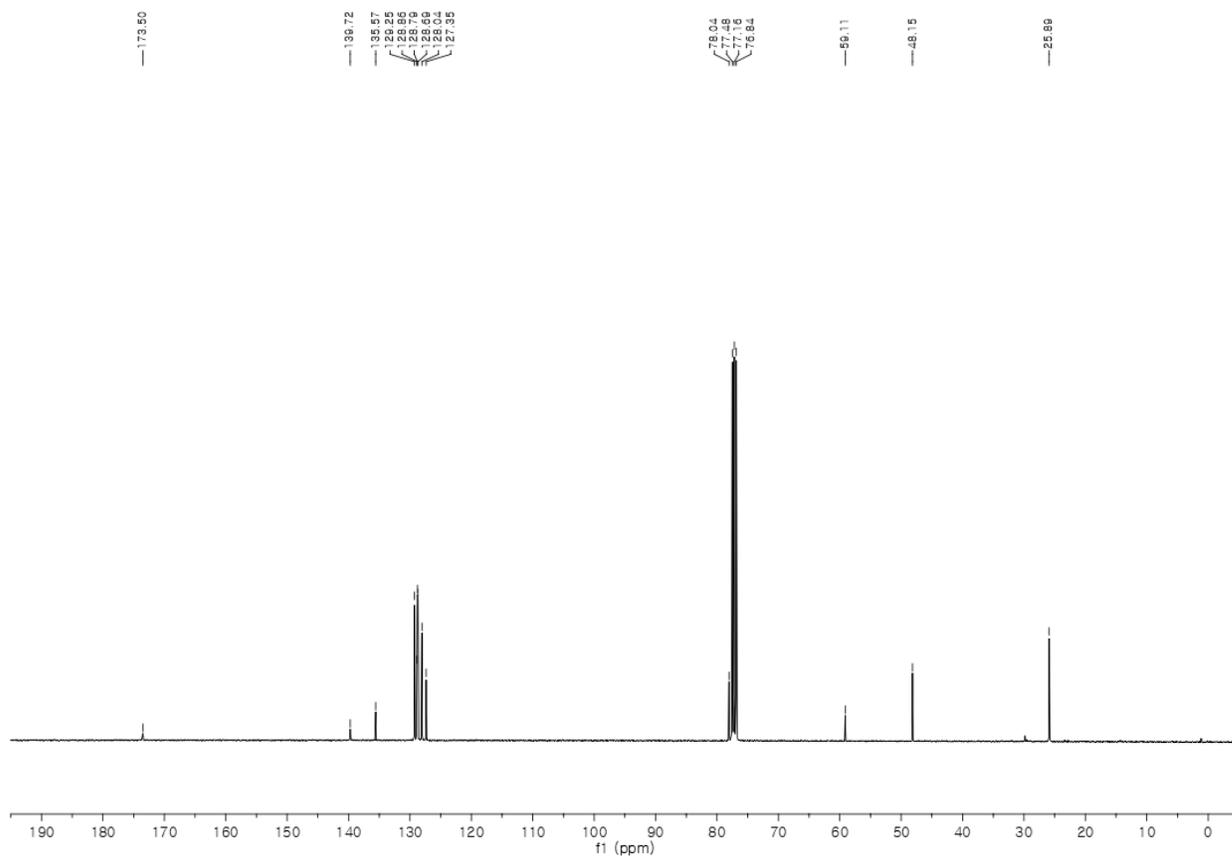
- (1) (a) Jeffrey, C. S.; Barnes, K.; Eickhoff, J.; Carson, C. *J. Am. Chem. Soc.* **2011**, *133*, 7688. (b) DiPoto, M. C.; Wu, J. *Org. Lett.* **2018**, *20*, 499. (c) Murata, Y.; Takeuchi, K.; Nishikata, T. *Tetrahedron* **2019**, *75*, 2726; d) Mirhashemi, F. Amrollahi, M. A. *Tetrahedron Lett.* **2018**, *15*, 2661.
- (2) (a) Jia, Z.-X.; Luo, Y.-C.; Wang, Y.; Chen, L.; Xu, P.-F.; Wang, B. *Chem. Eur. J.* **2012**, *18*, 12958. (b) Park, D. Y.; Lee, S. Y.; Jeon, J.; Cheon, C.-H. *J. Org. Chem.* **2018**, *83*, 12486.

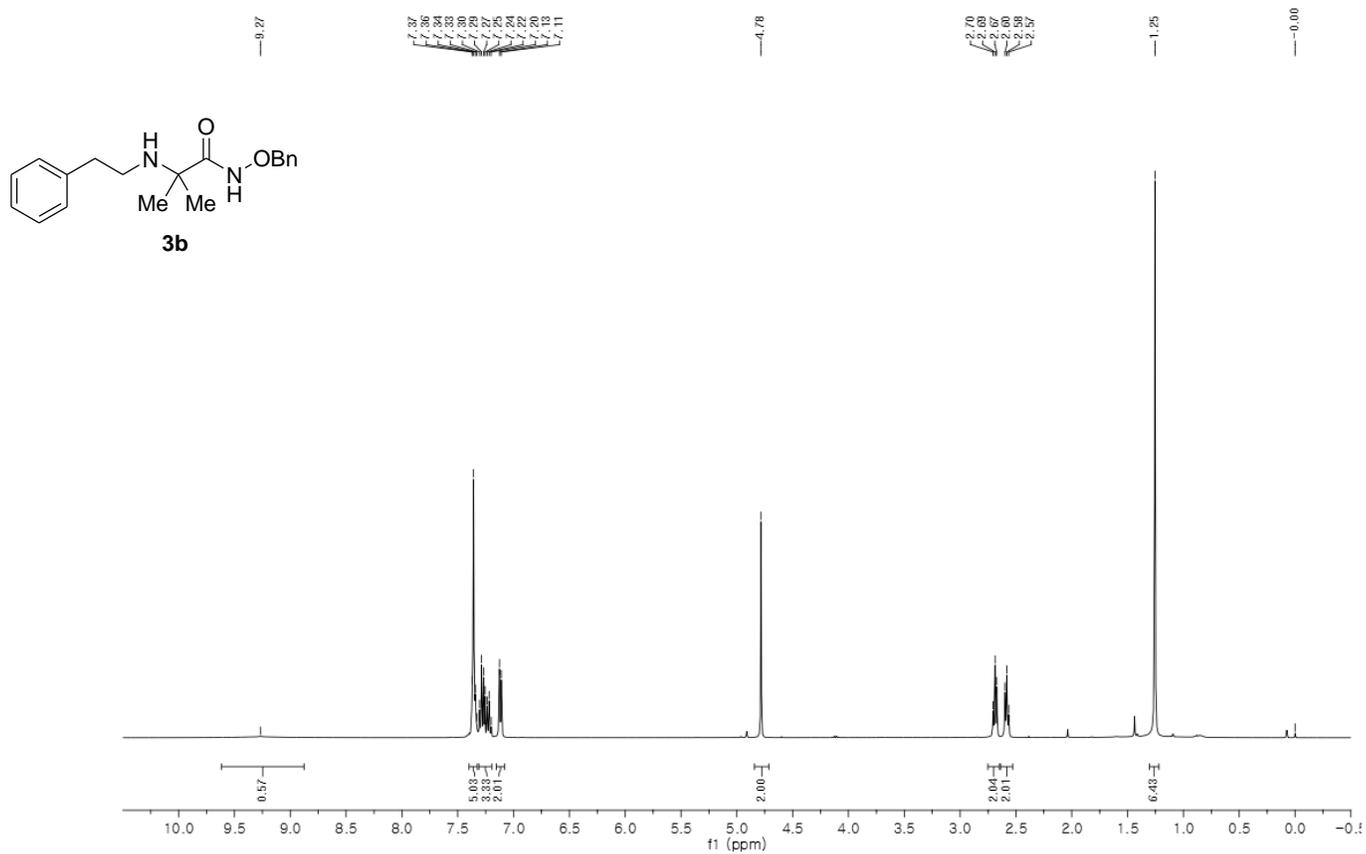
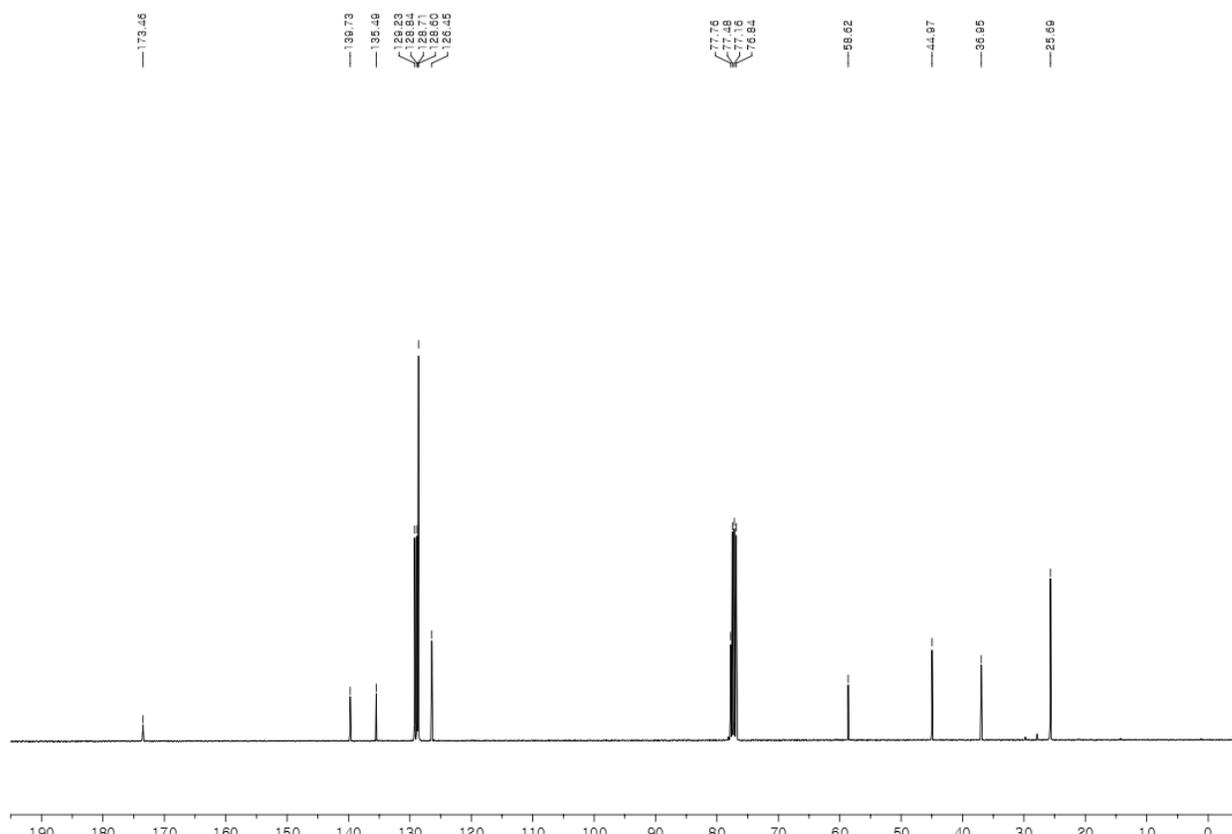
Crystallography Data for Compound 9f

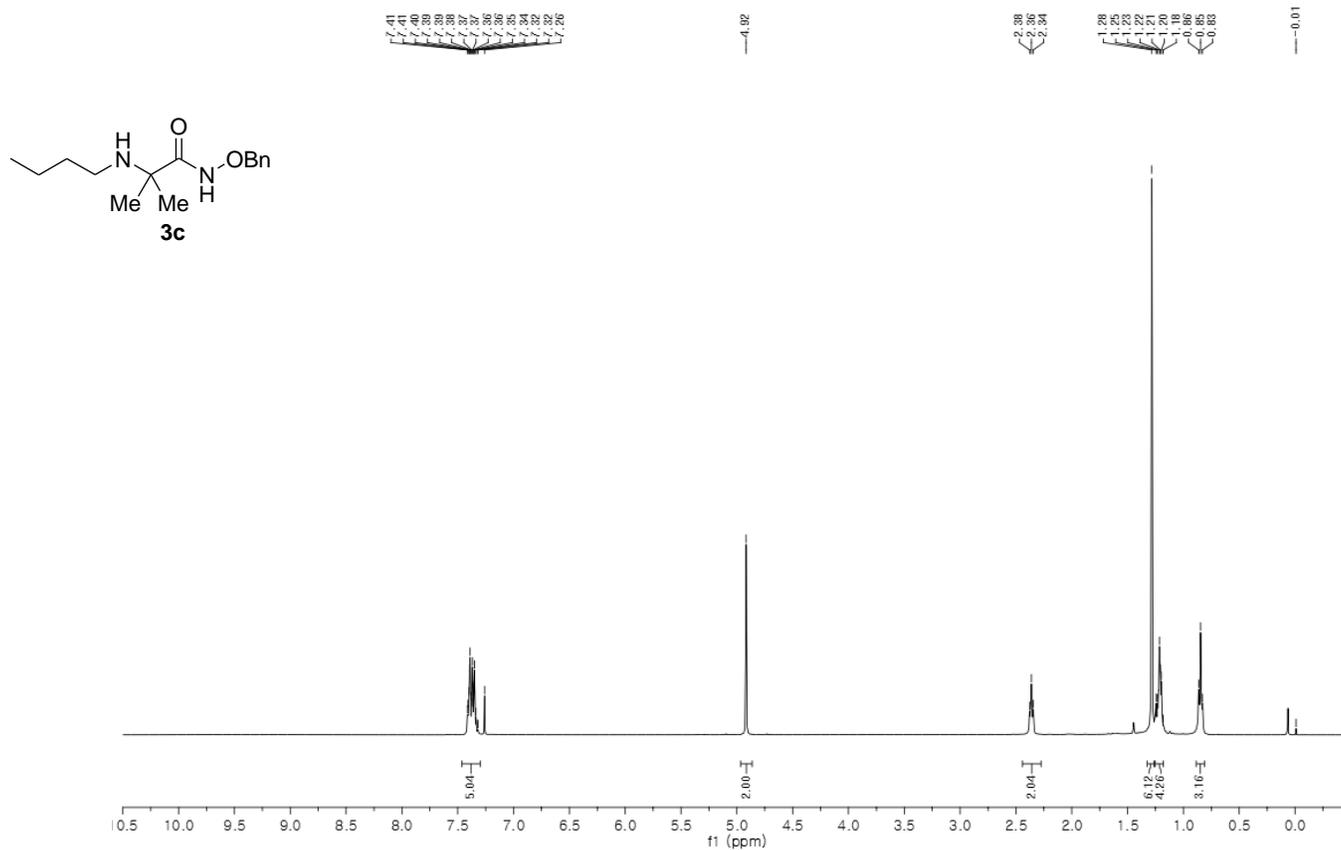
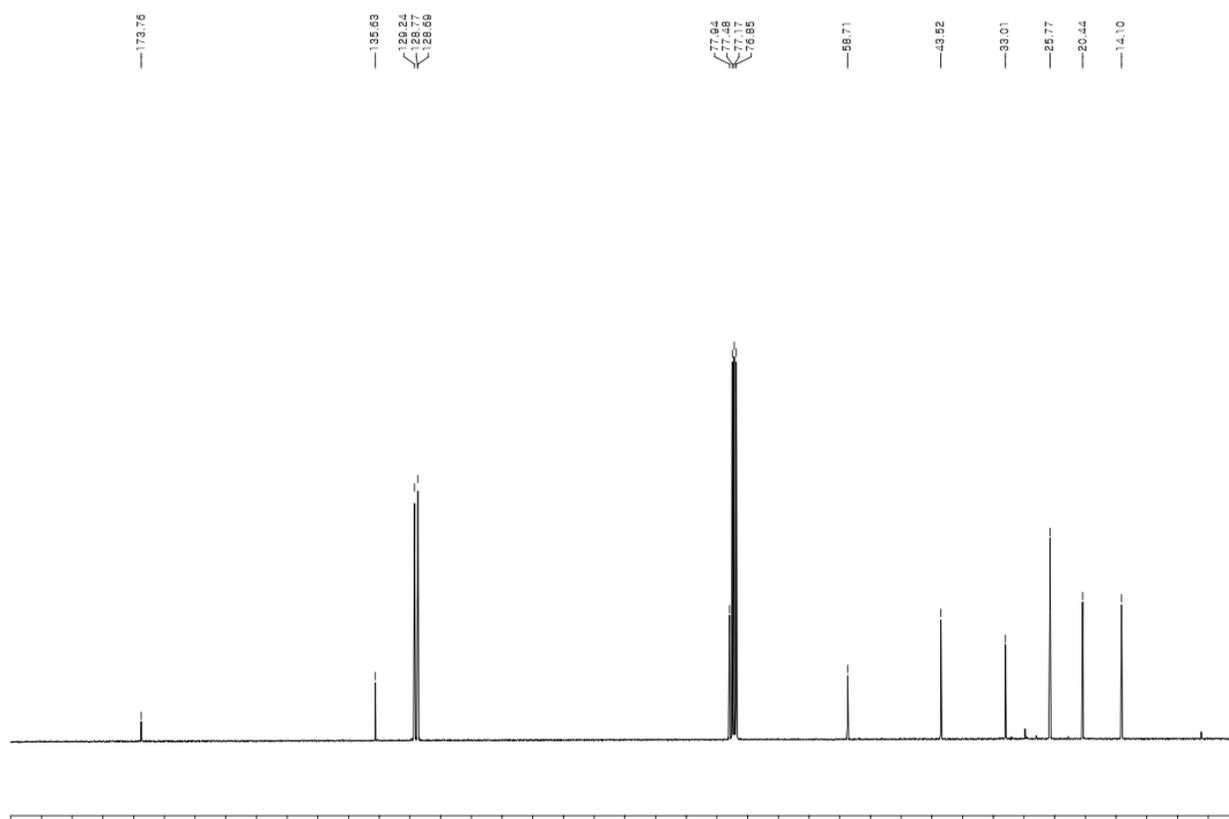


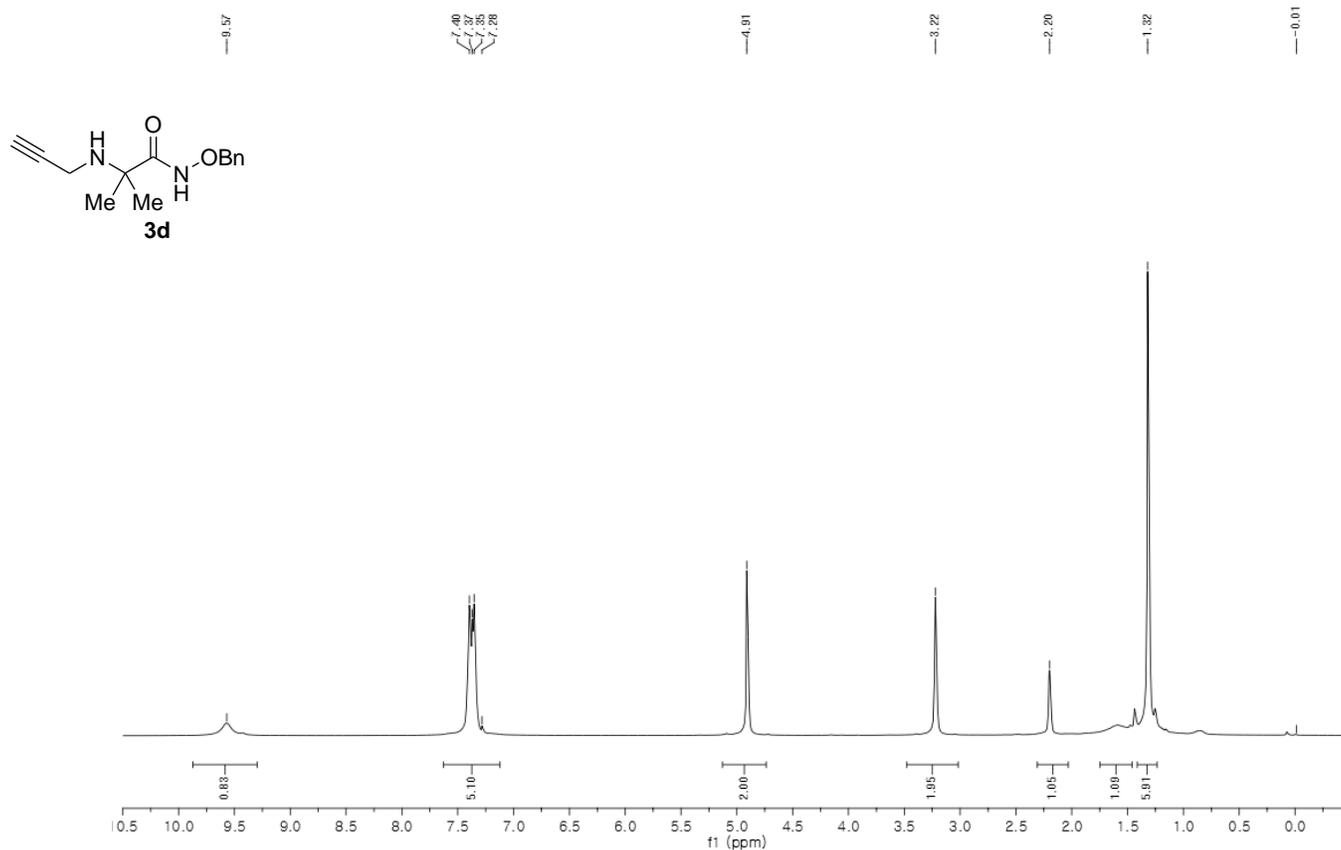
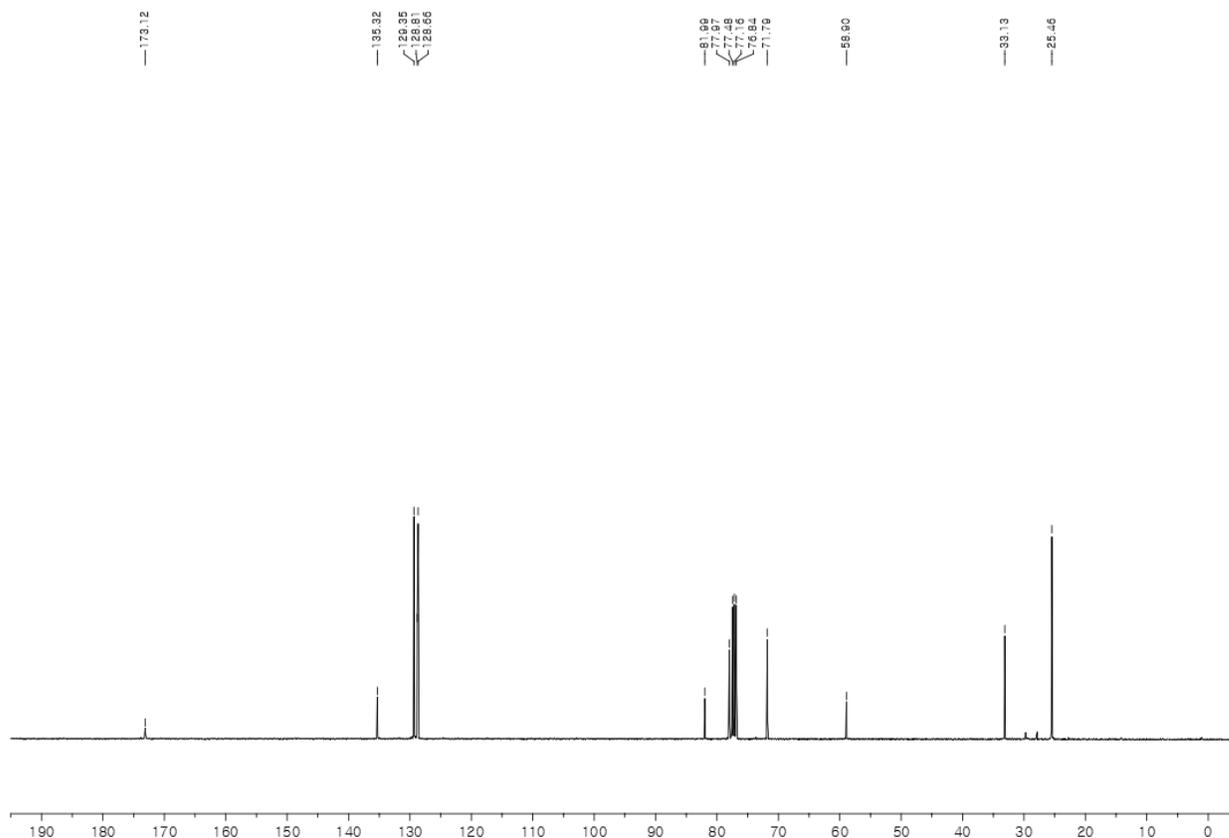
Identification code	KGU-19-11	
Empirical formula	C ₂₆ H ₂₅ F N ₂ O ₃	
Formula weight	432.48	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 11.450(2) Å	α = 90°.
	b = 17.545(4) Å	β = 98.014(7)°.
	c = 11.655(2) Å	γ = 90°.
Volume	2318.4(8) Å ³	
Z	4	
Density (calculated)	1.239 Mg/m ³	
Absorption coefficient	0.087 mm ⁻¹	
F(000)	912	
Crystal size	0.280 x 0.200 x 0.120 mm ³	
Theta range for data collection	2.112 to 28.418°.	

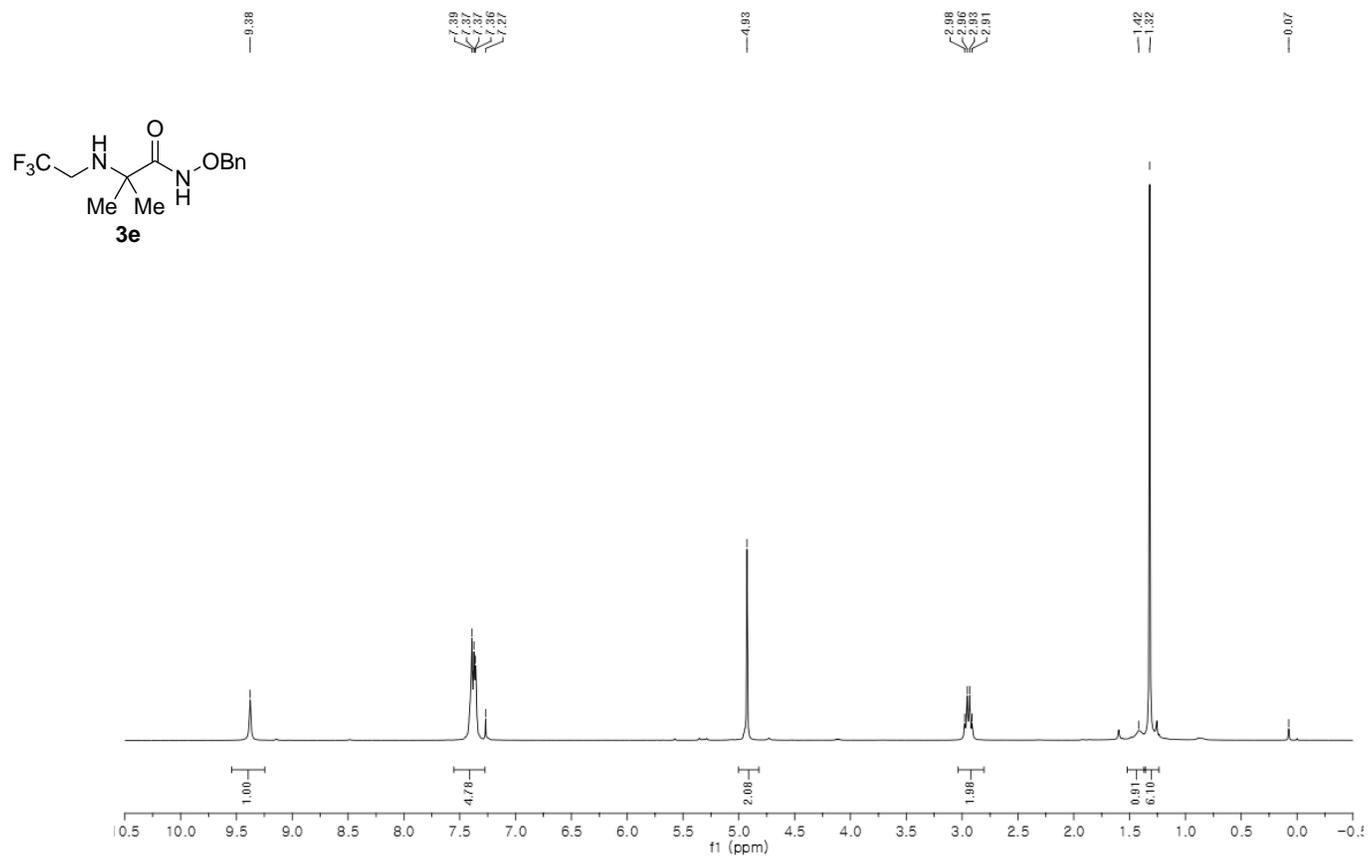
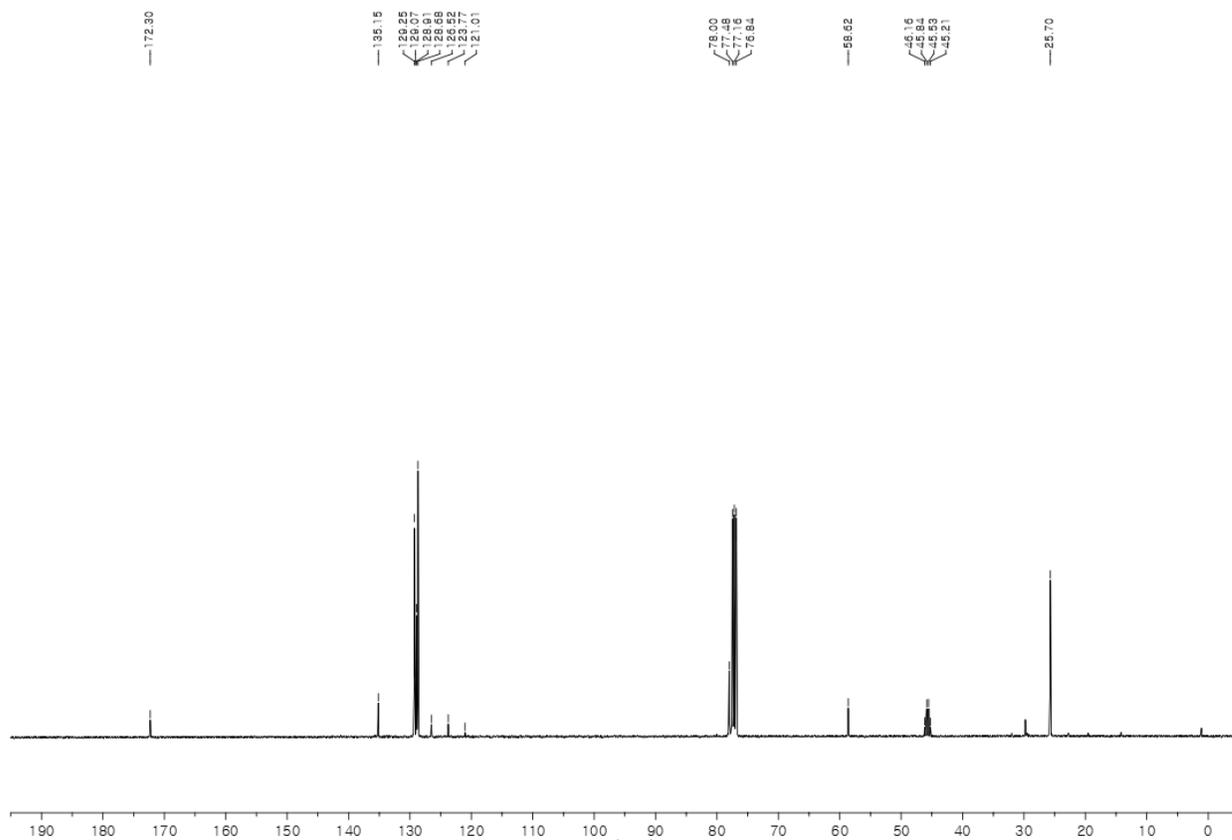
Index ranges	-15<=h<=15, -23<=k<=23, -15<=l<=15
Reflections collected	74595
Independent reflections	5791 [R(int) = 0.0580]
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7059
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5791 / 0 / 295
Goodness-of-fit on F ²	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1192
R indices (all data)	R1 = 0.0869, wR2 = 0.1487
Extinction coefficient	n/a
Largest diff. peak and hole	0.309 and -0.344 e.Å ⁻³

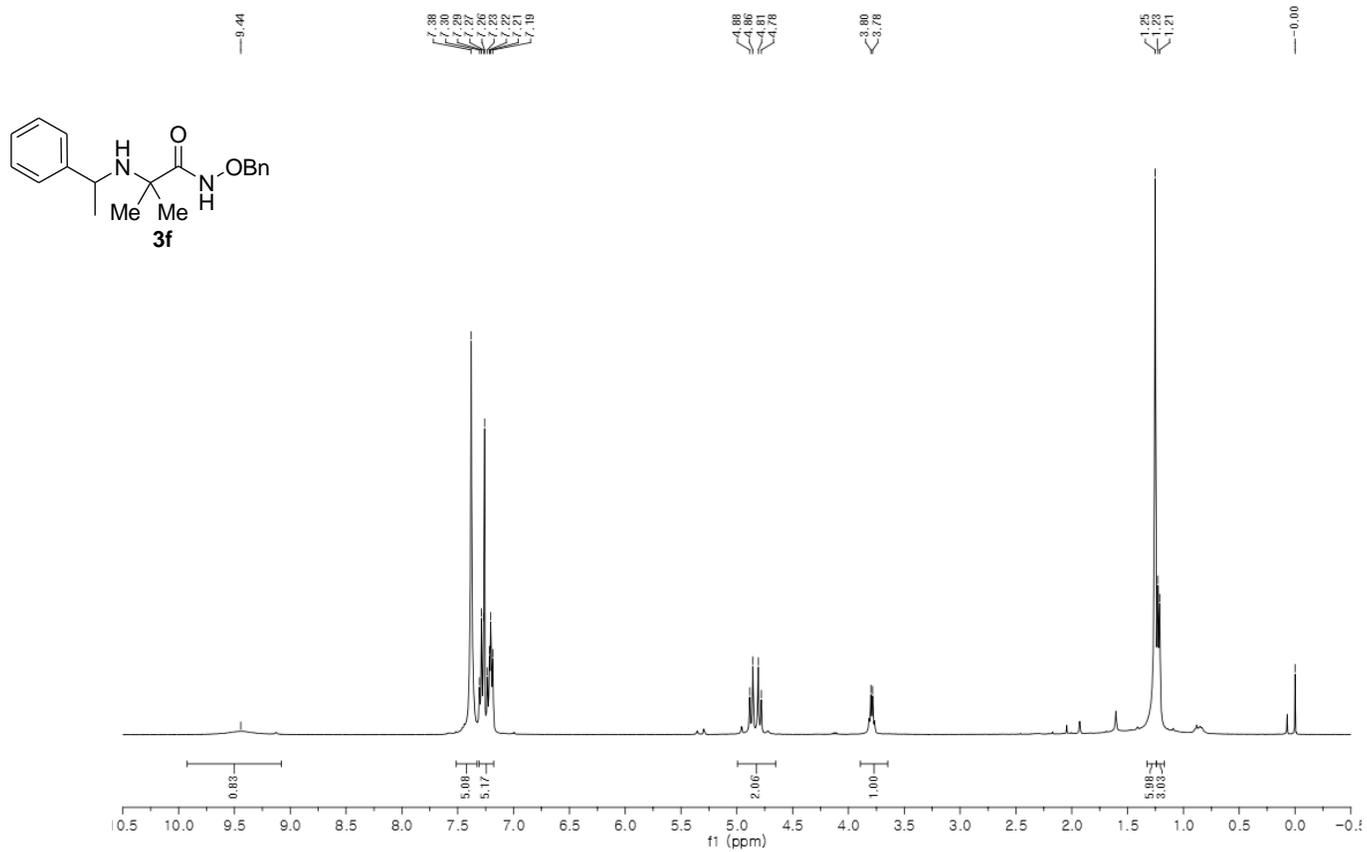
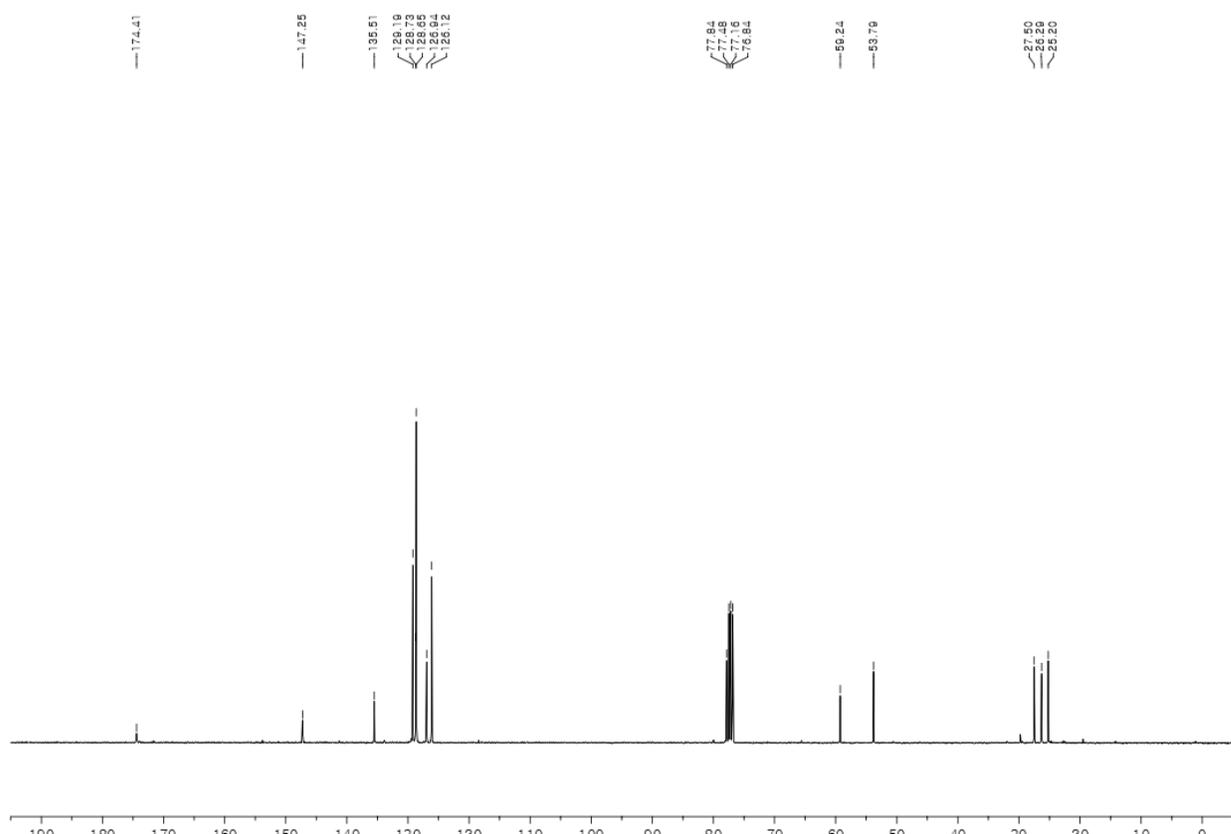
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

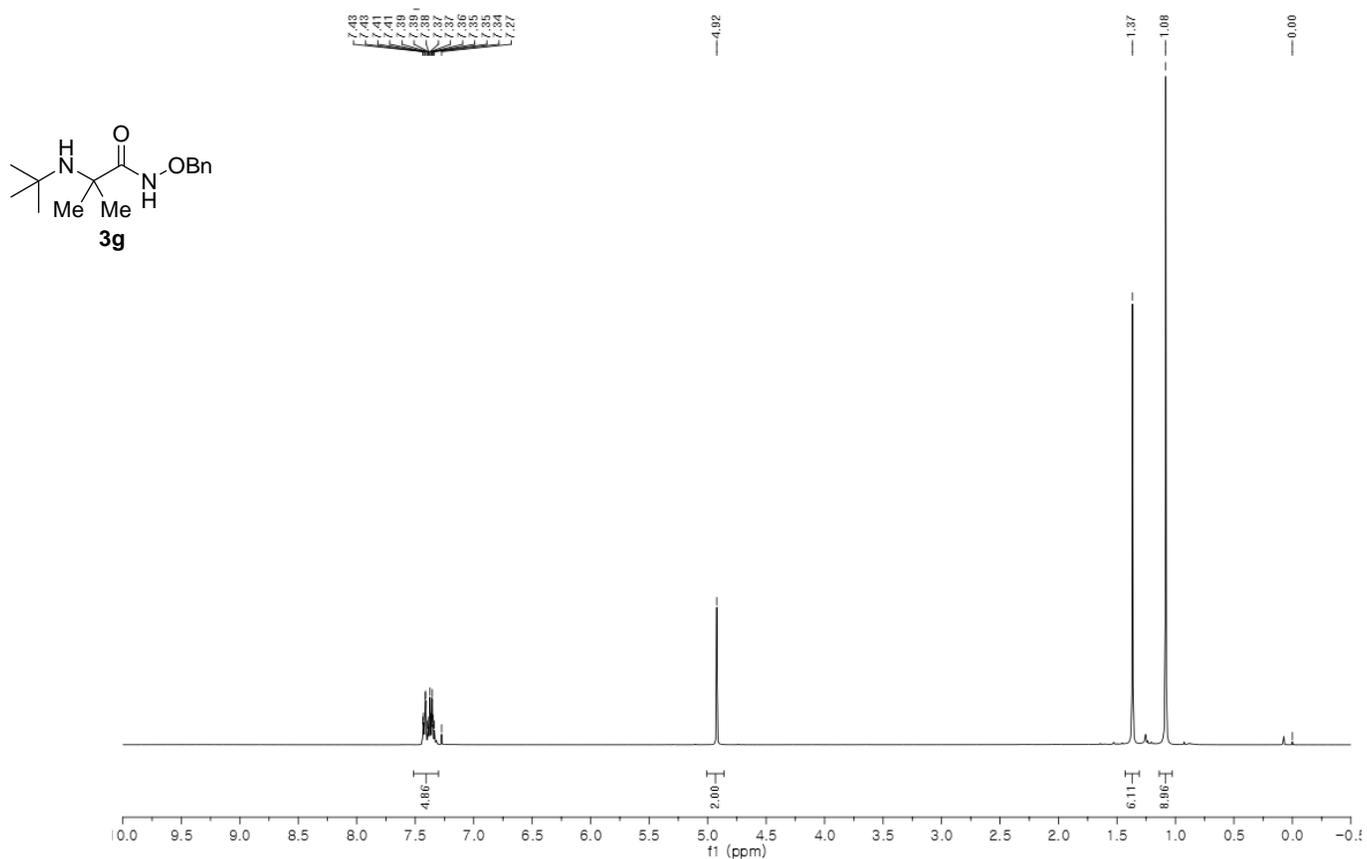
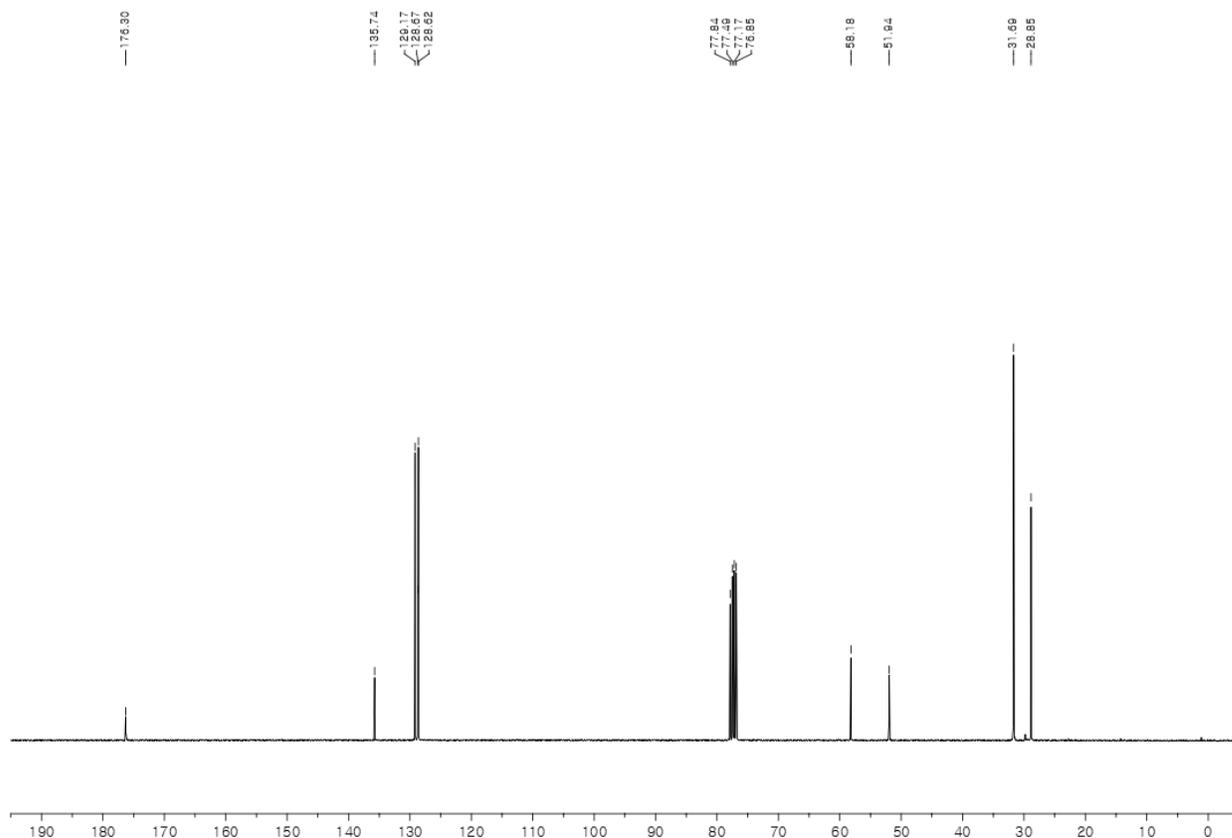
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

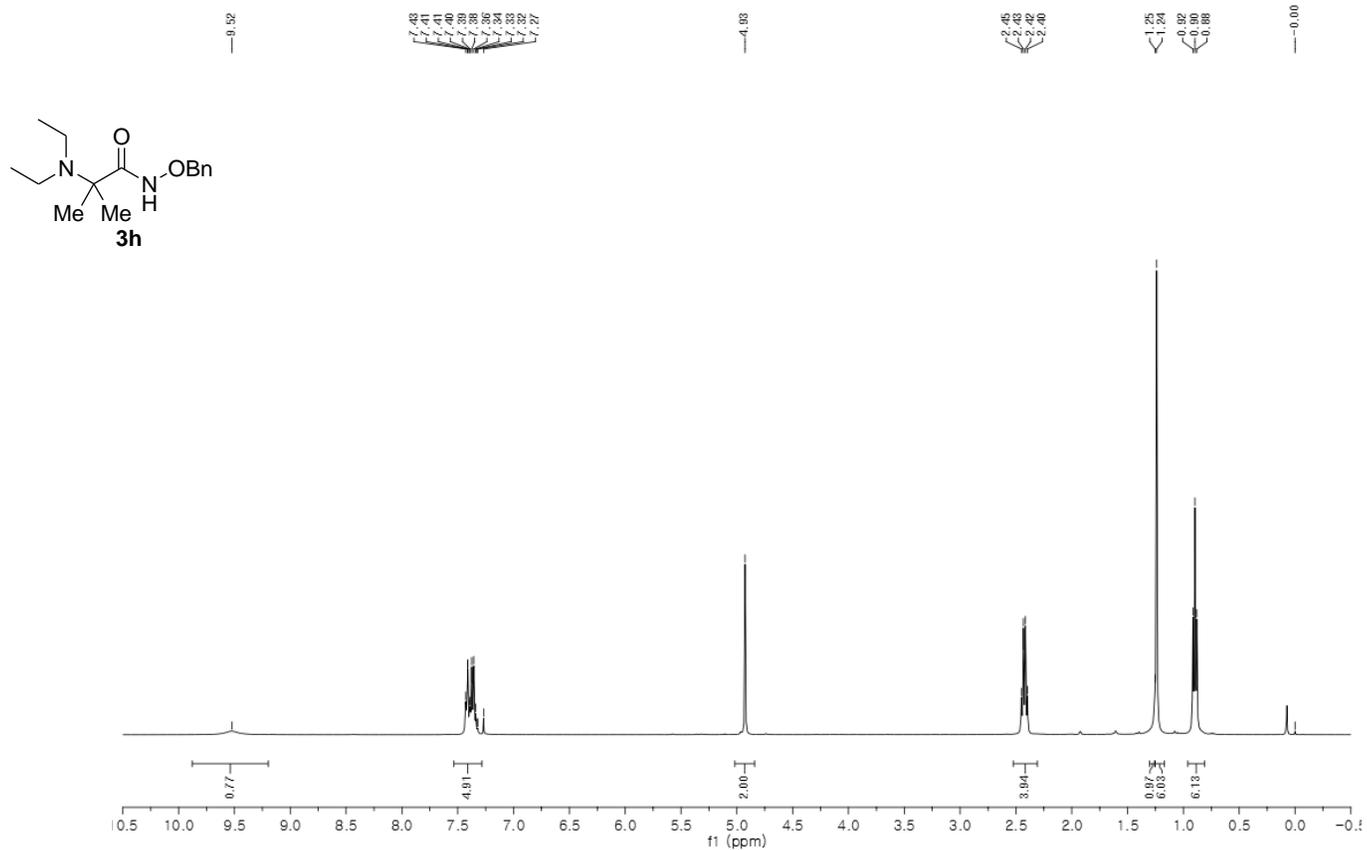
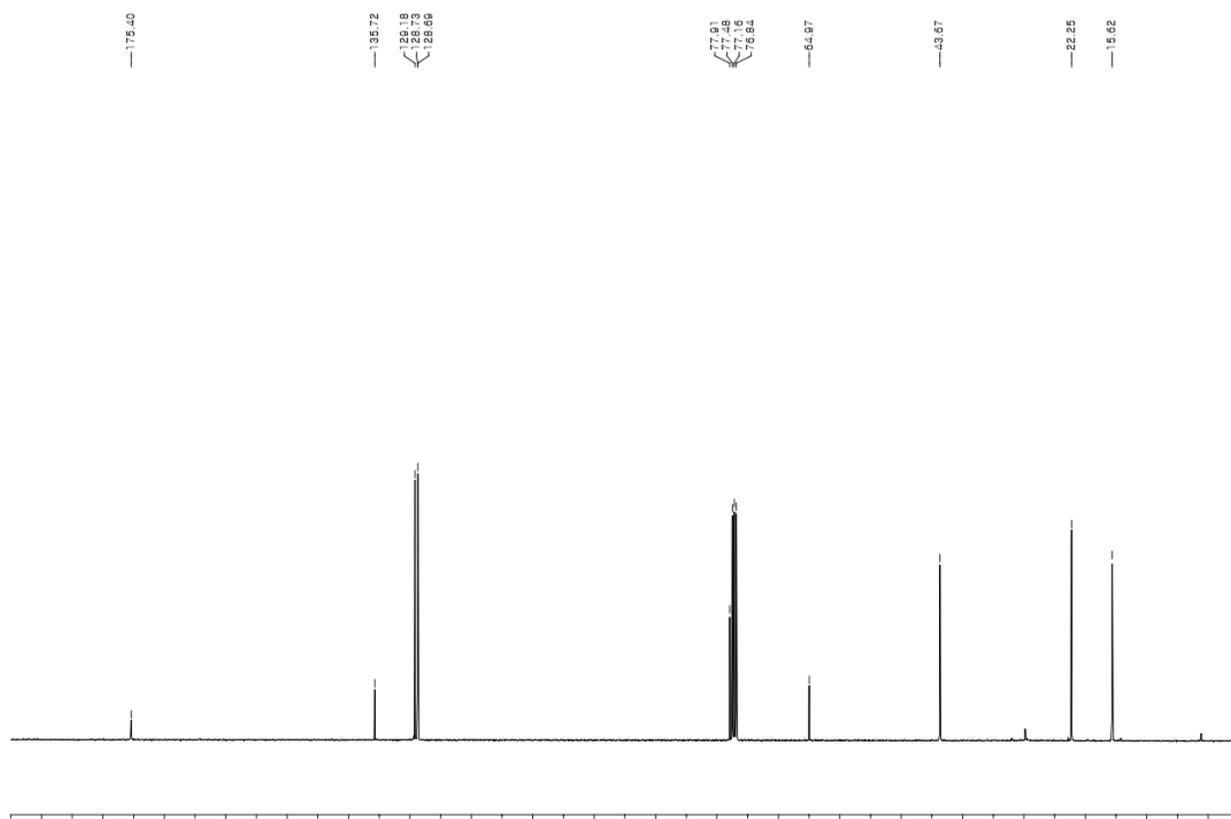
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

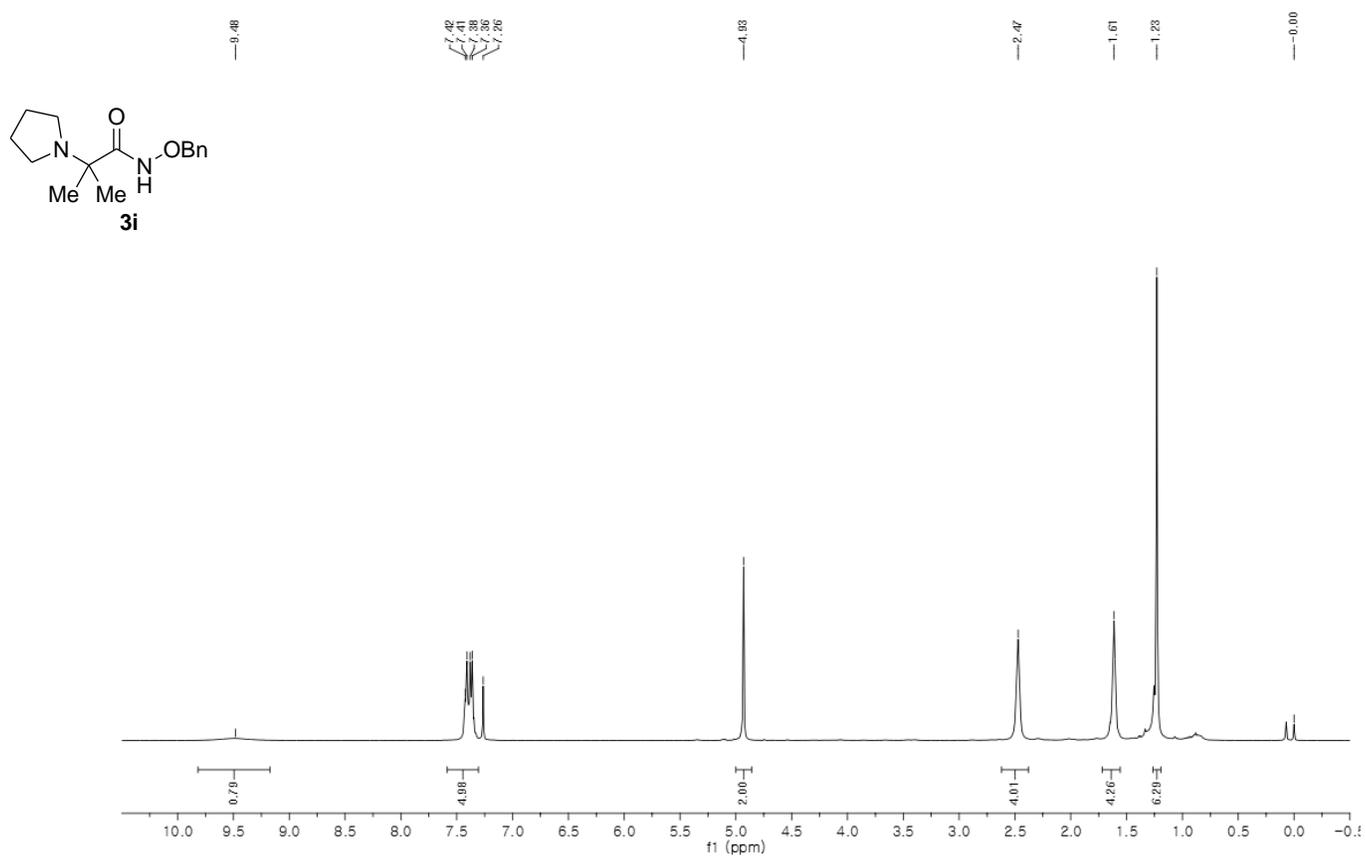
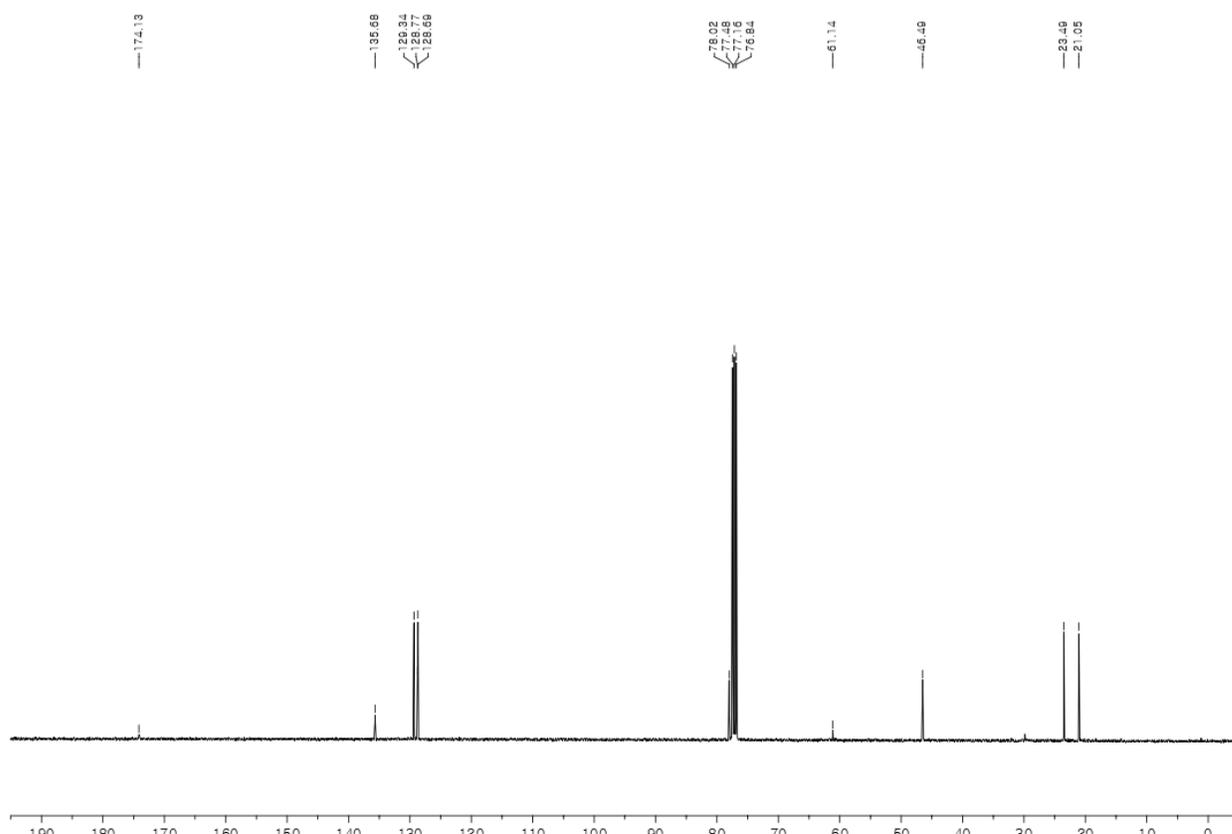
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

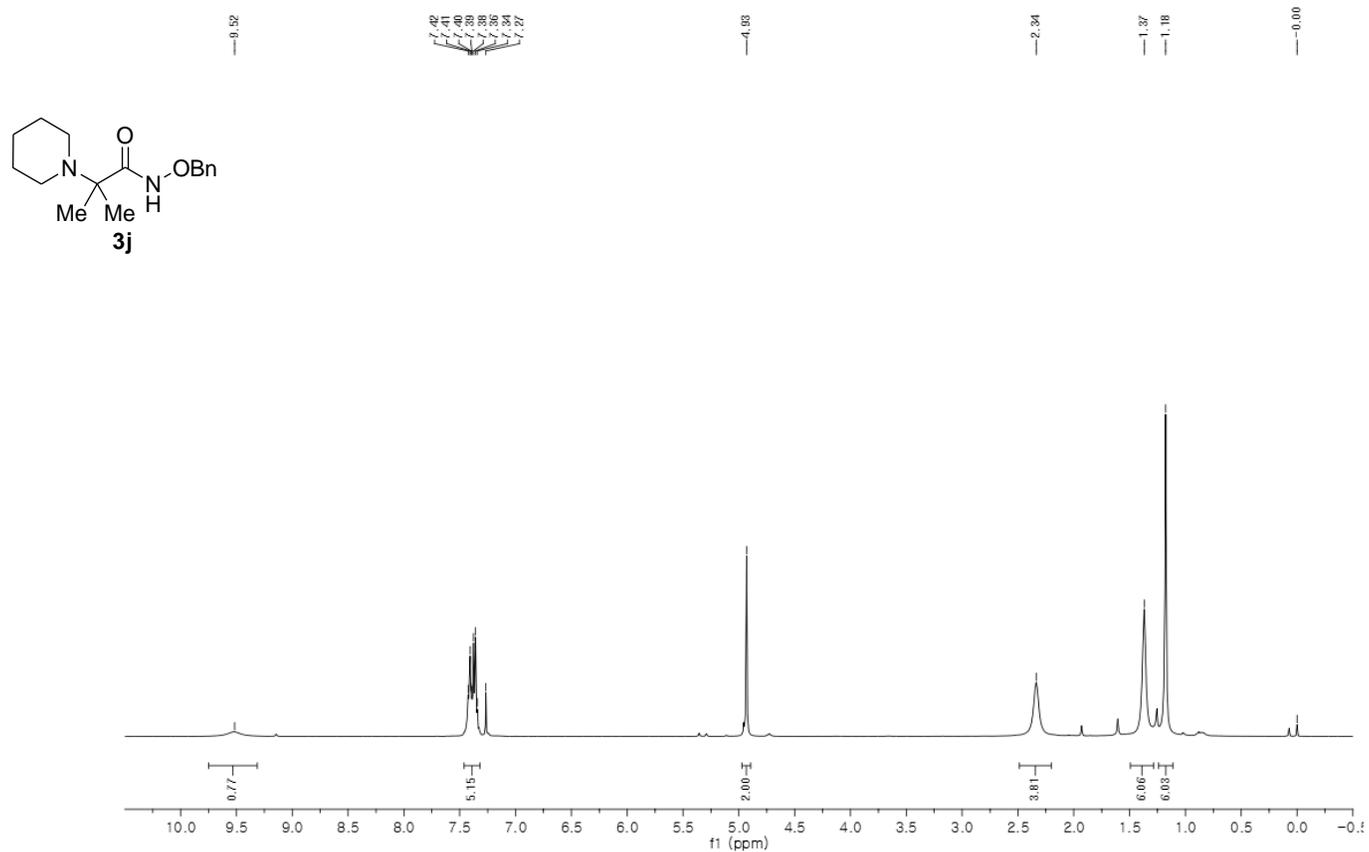
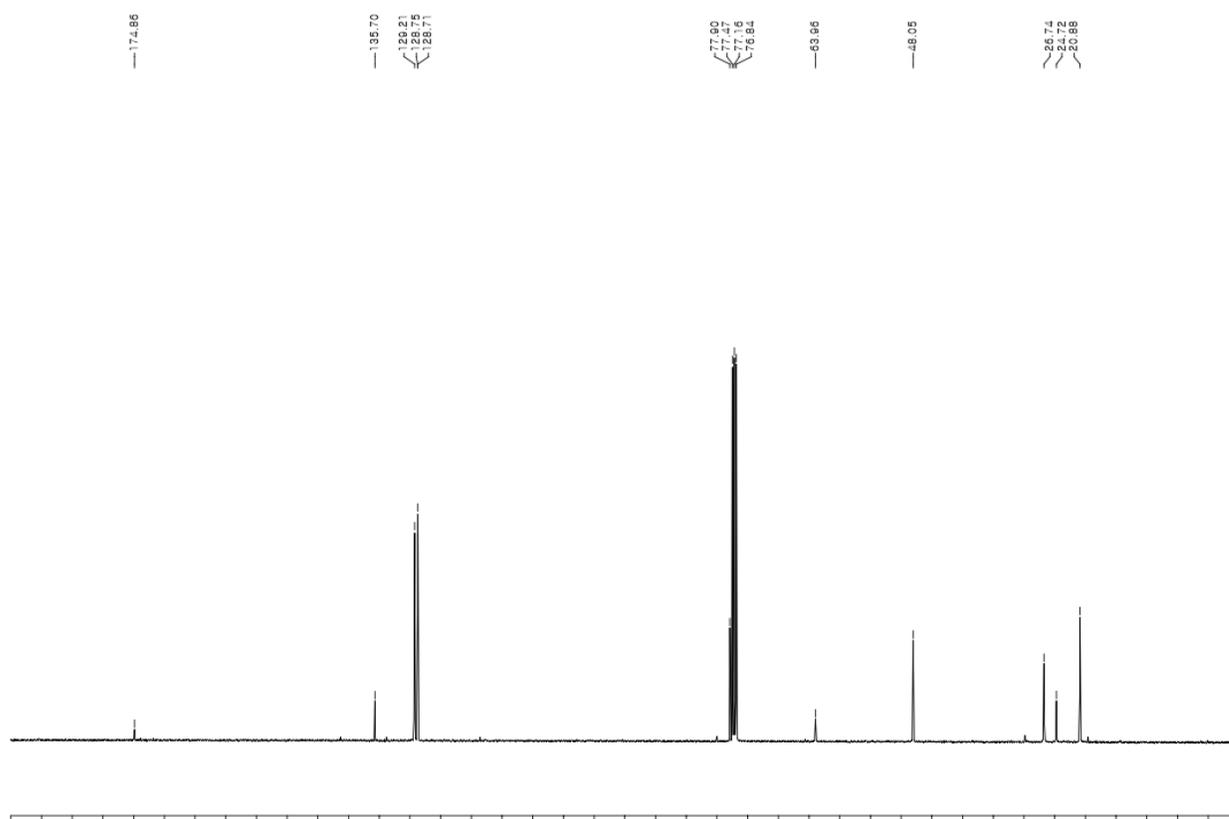
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

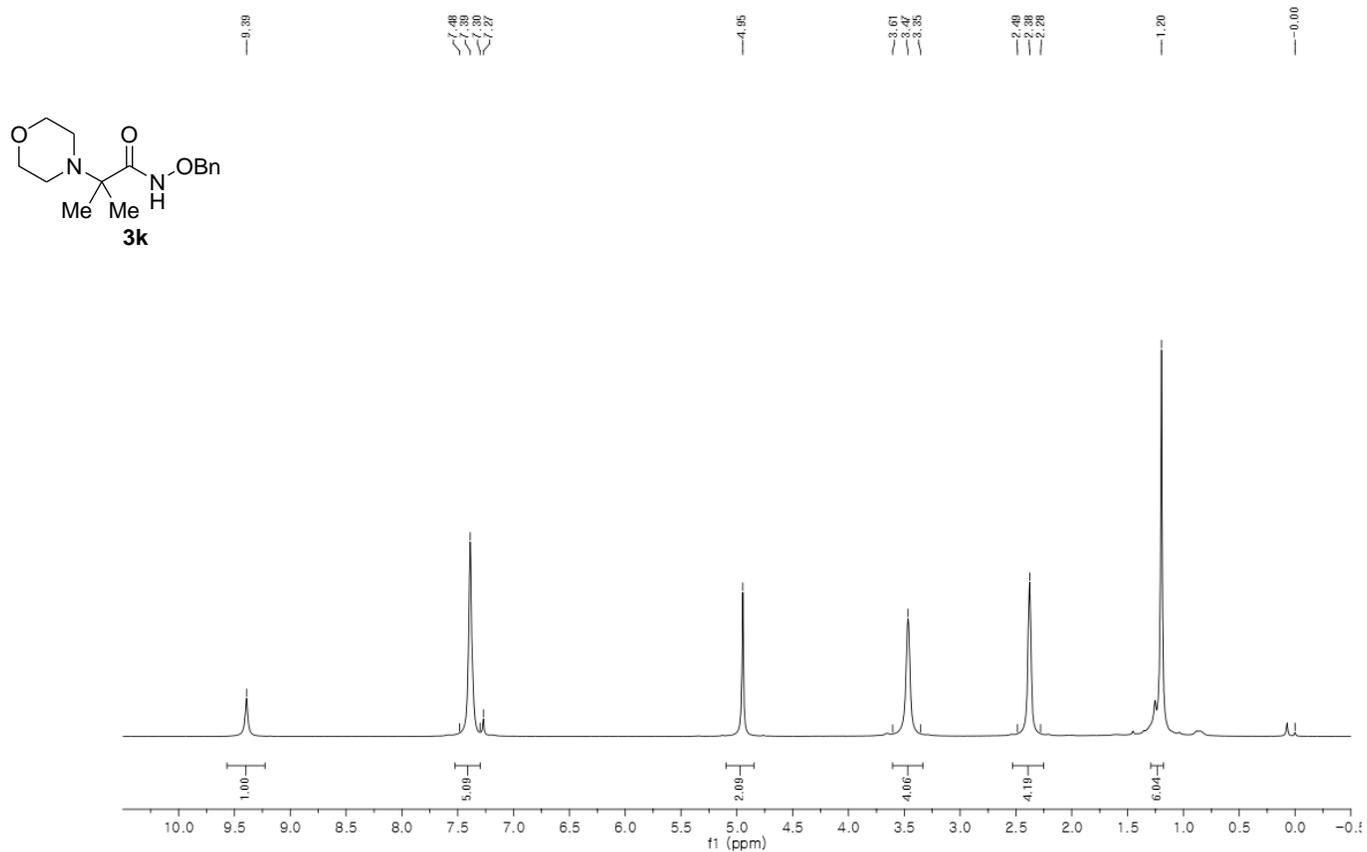
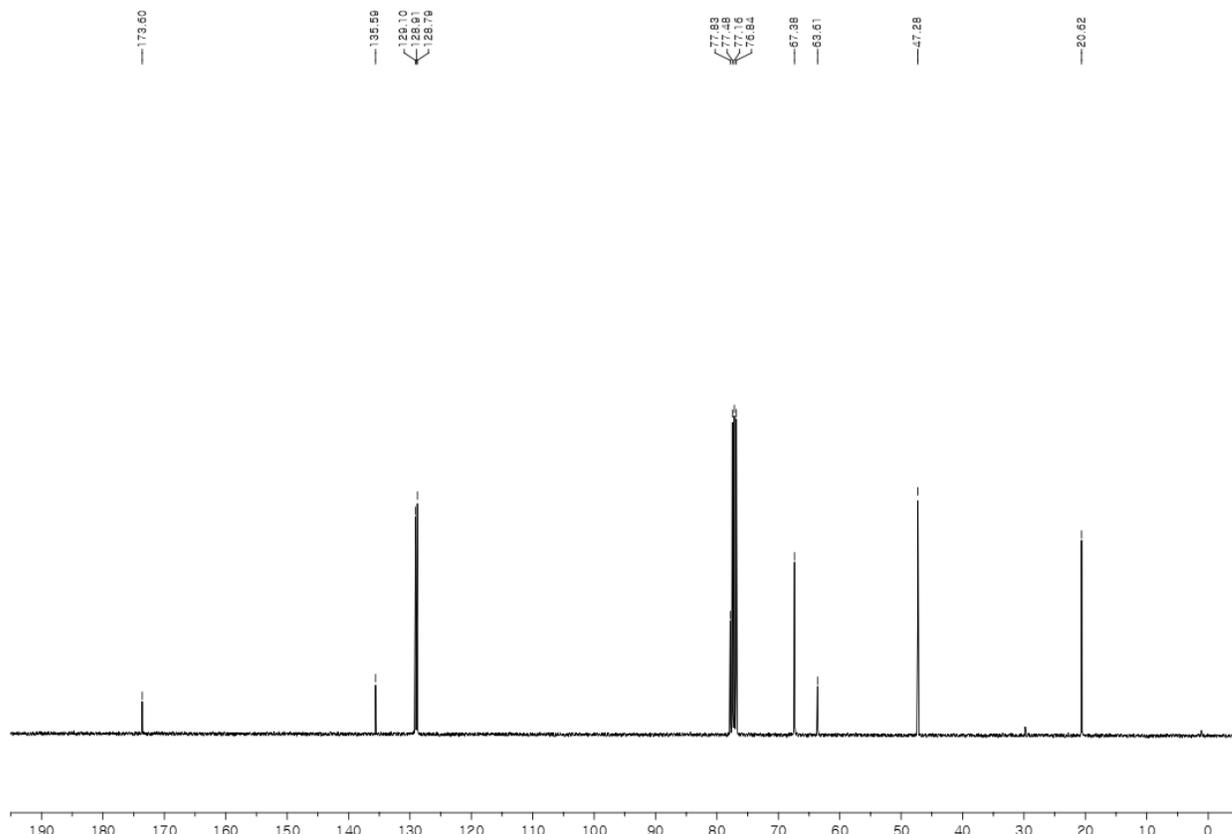
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

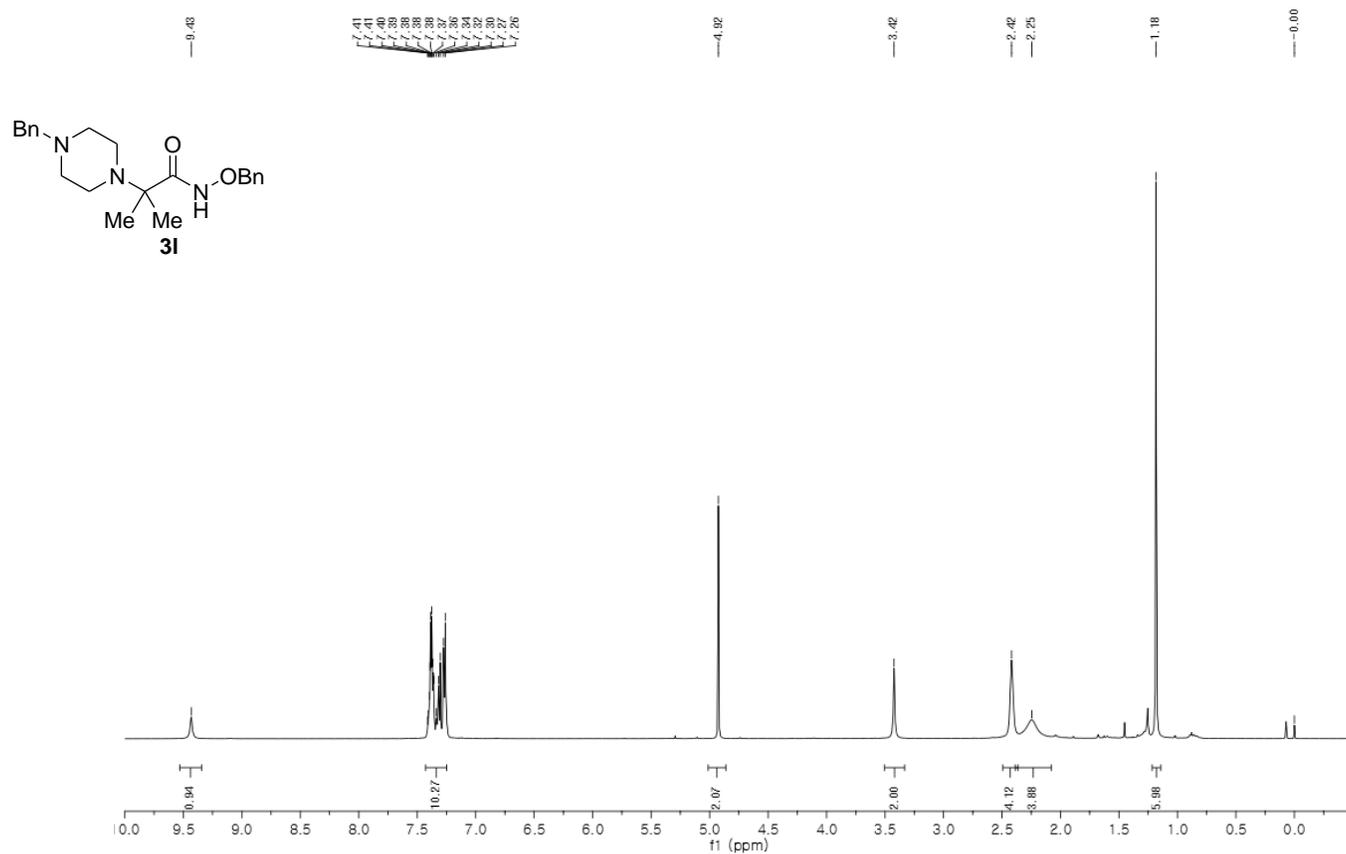
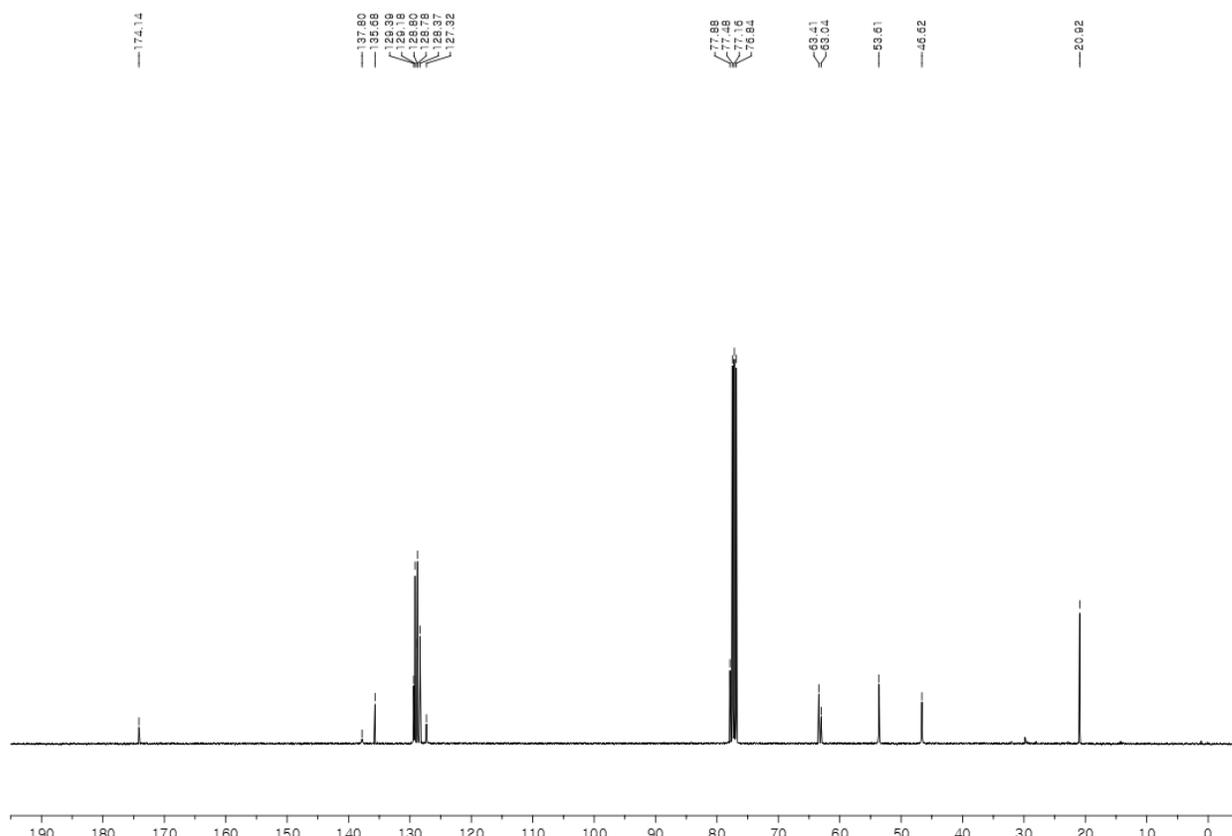
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

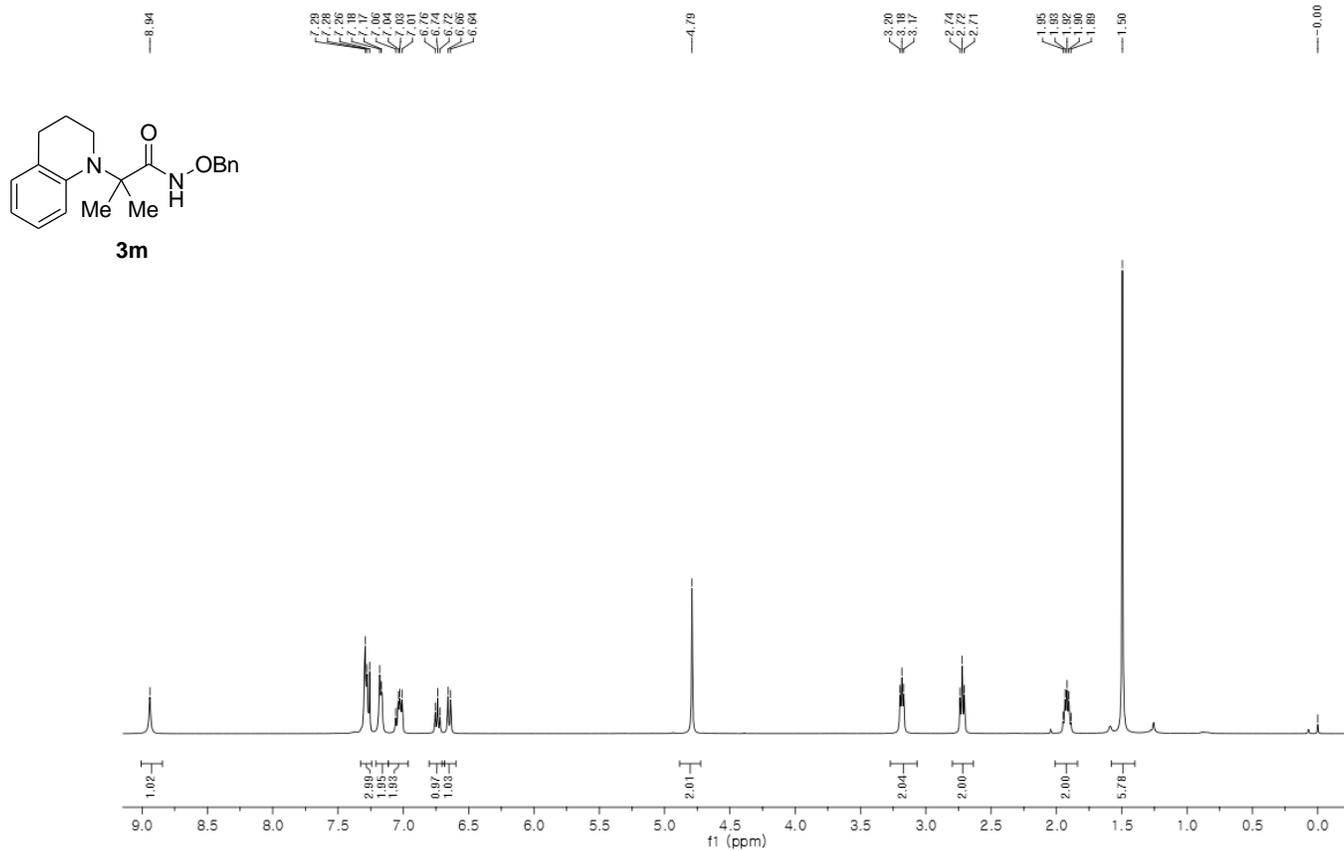
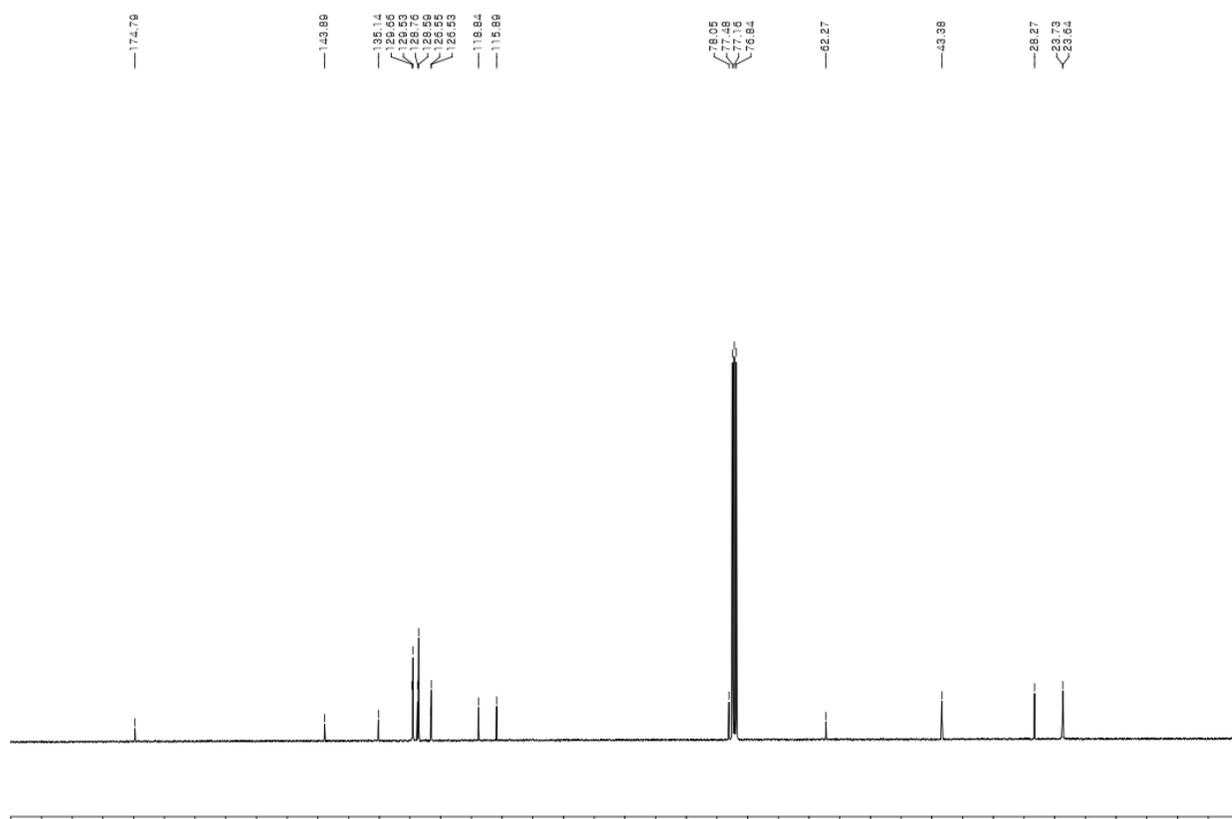
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

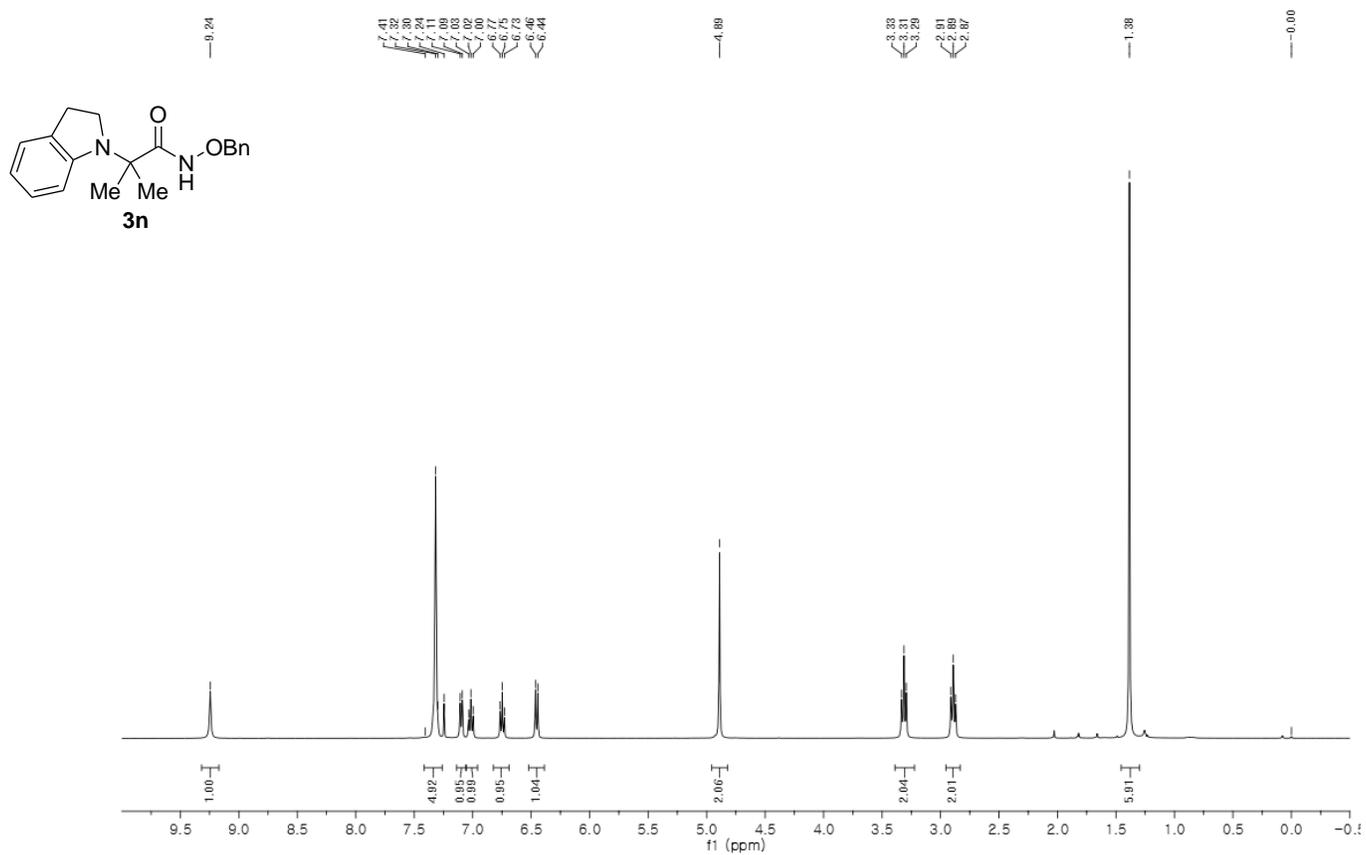
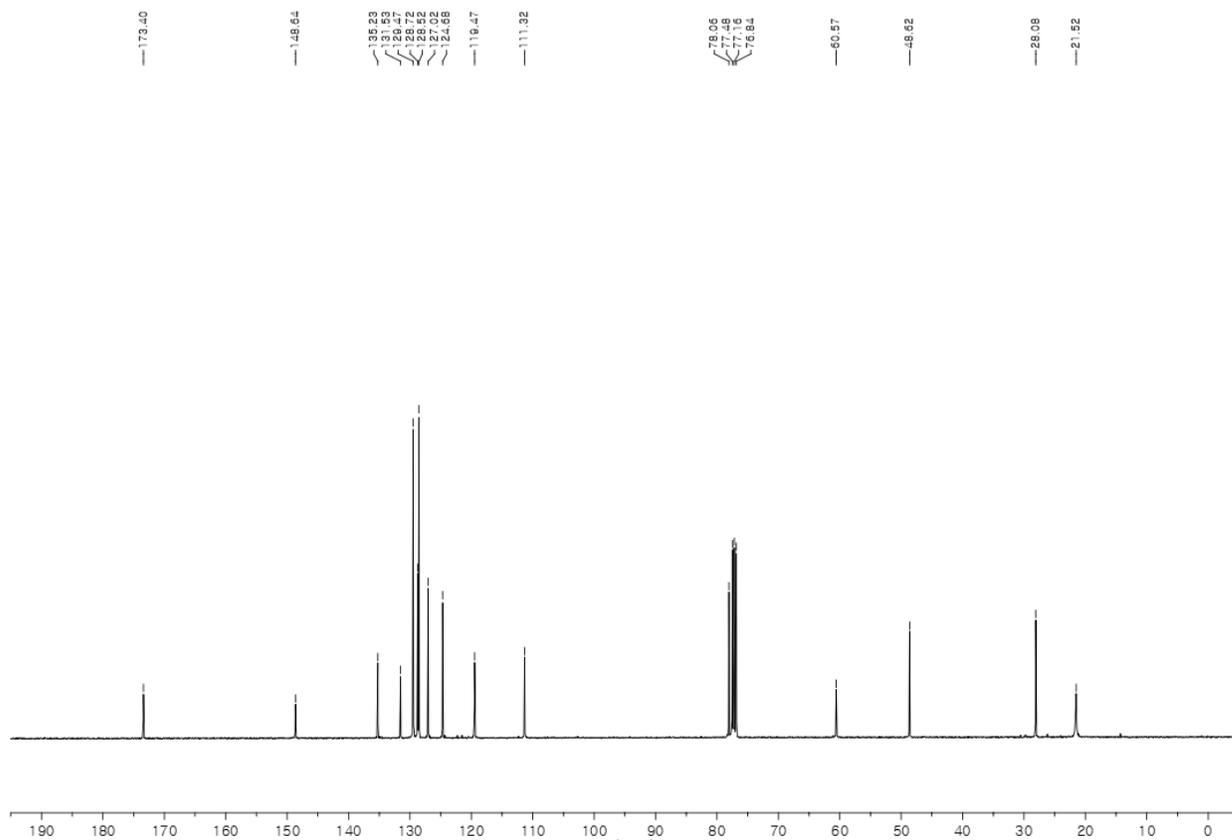
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

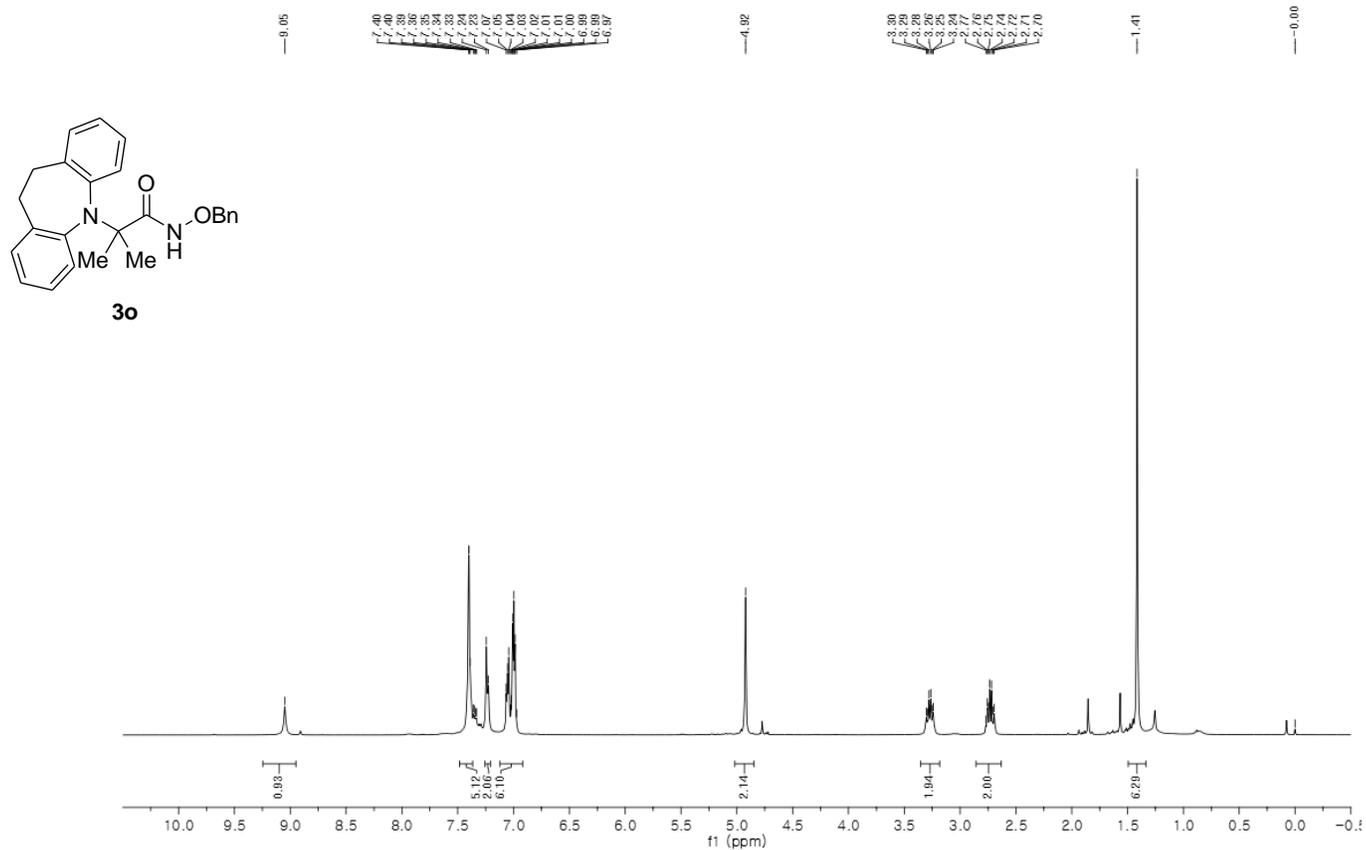
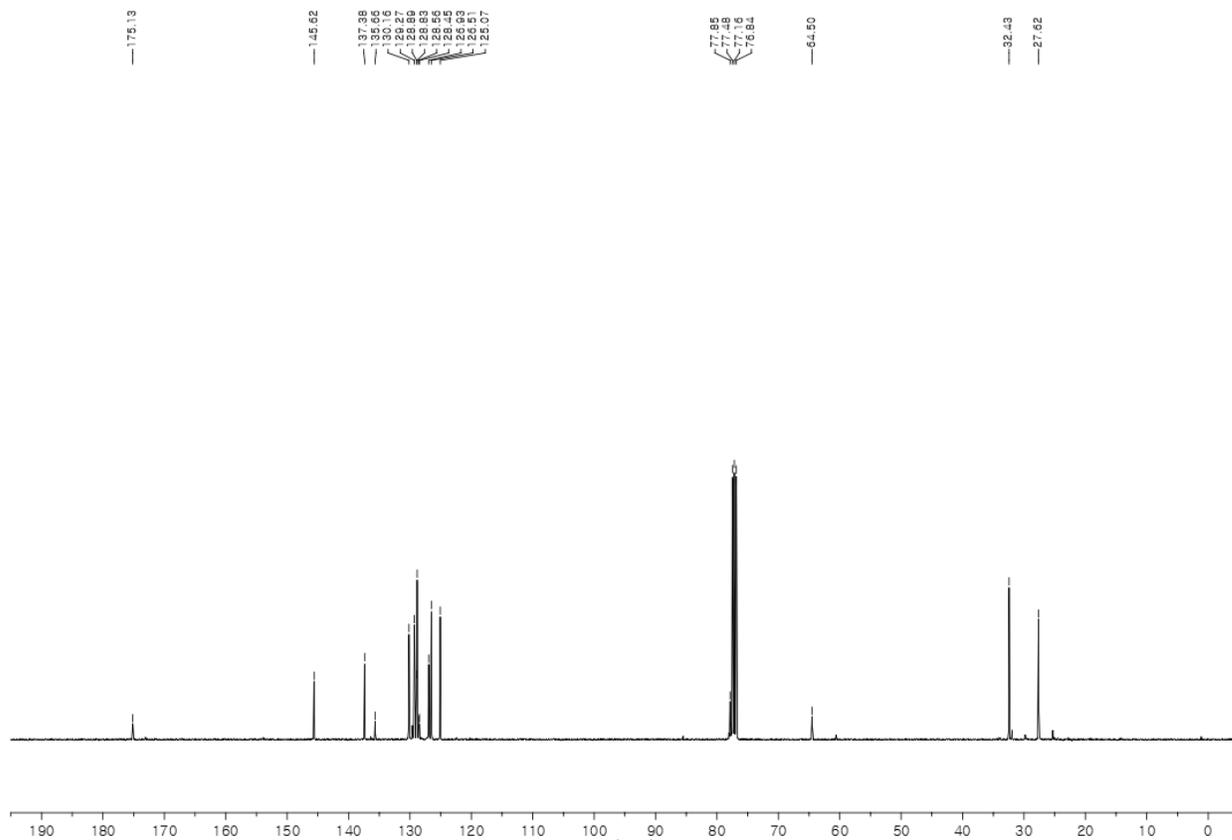
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

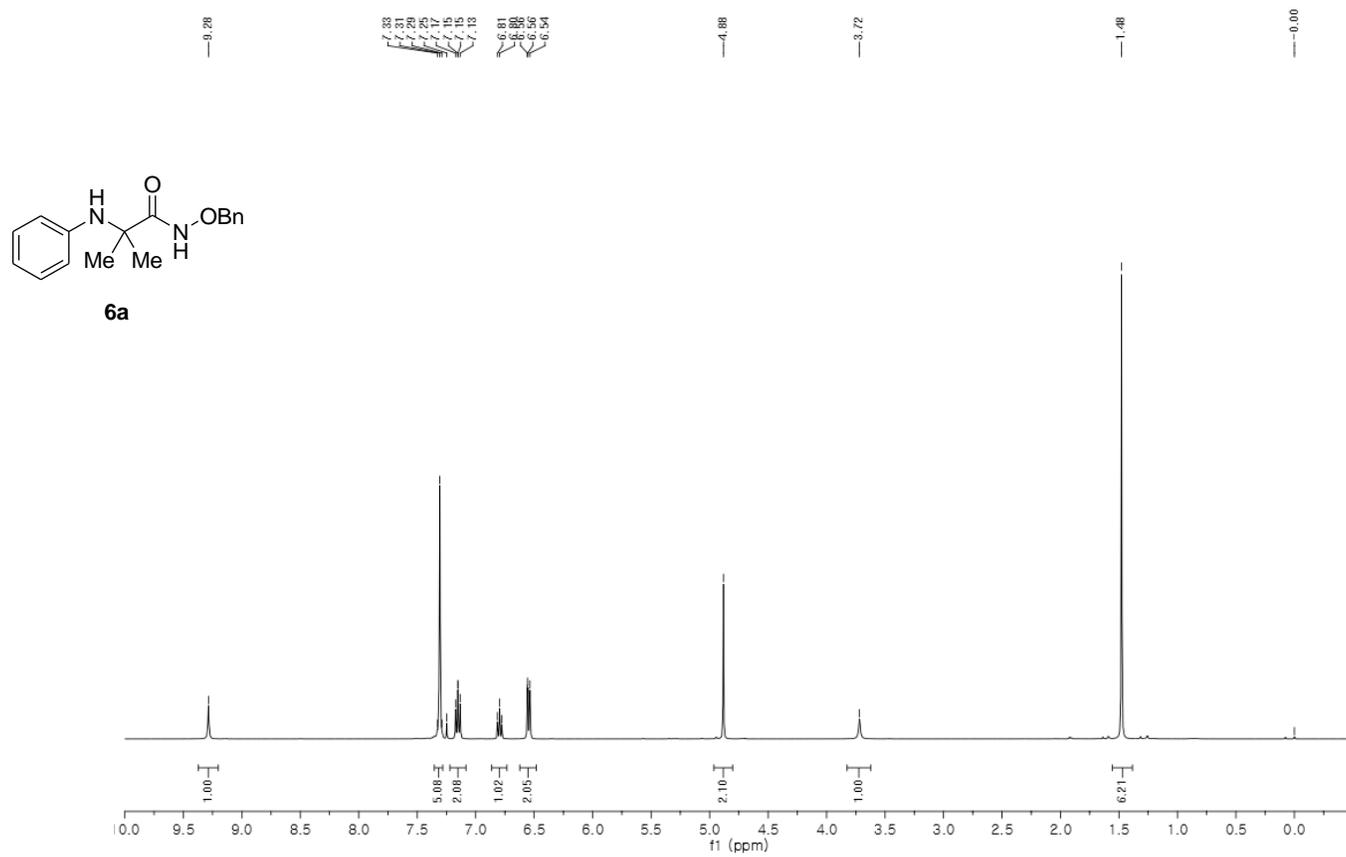
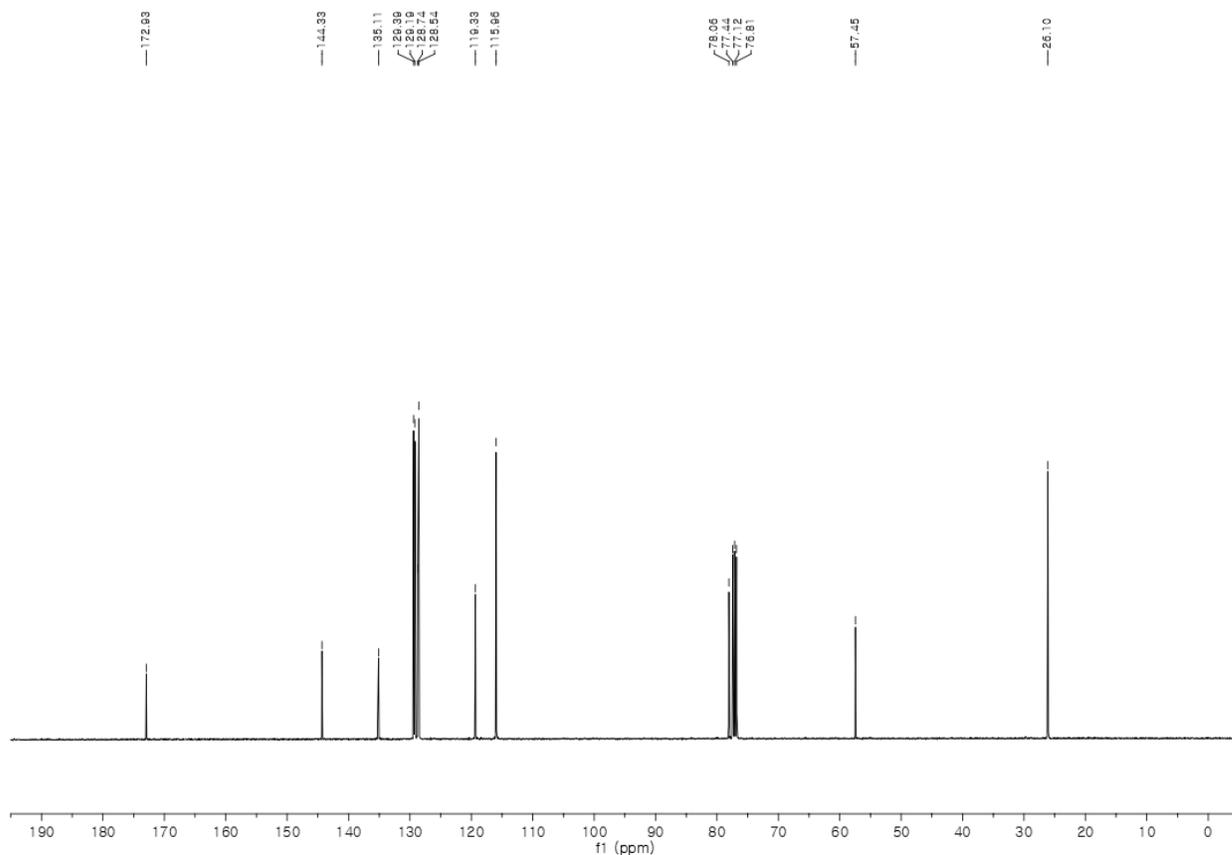
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

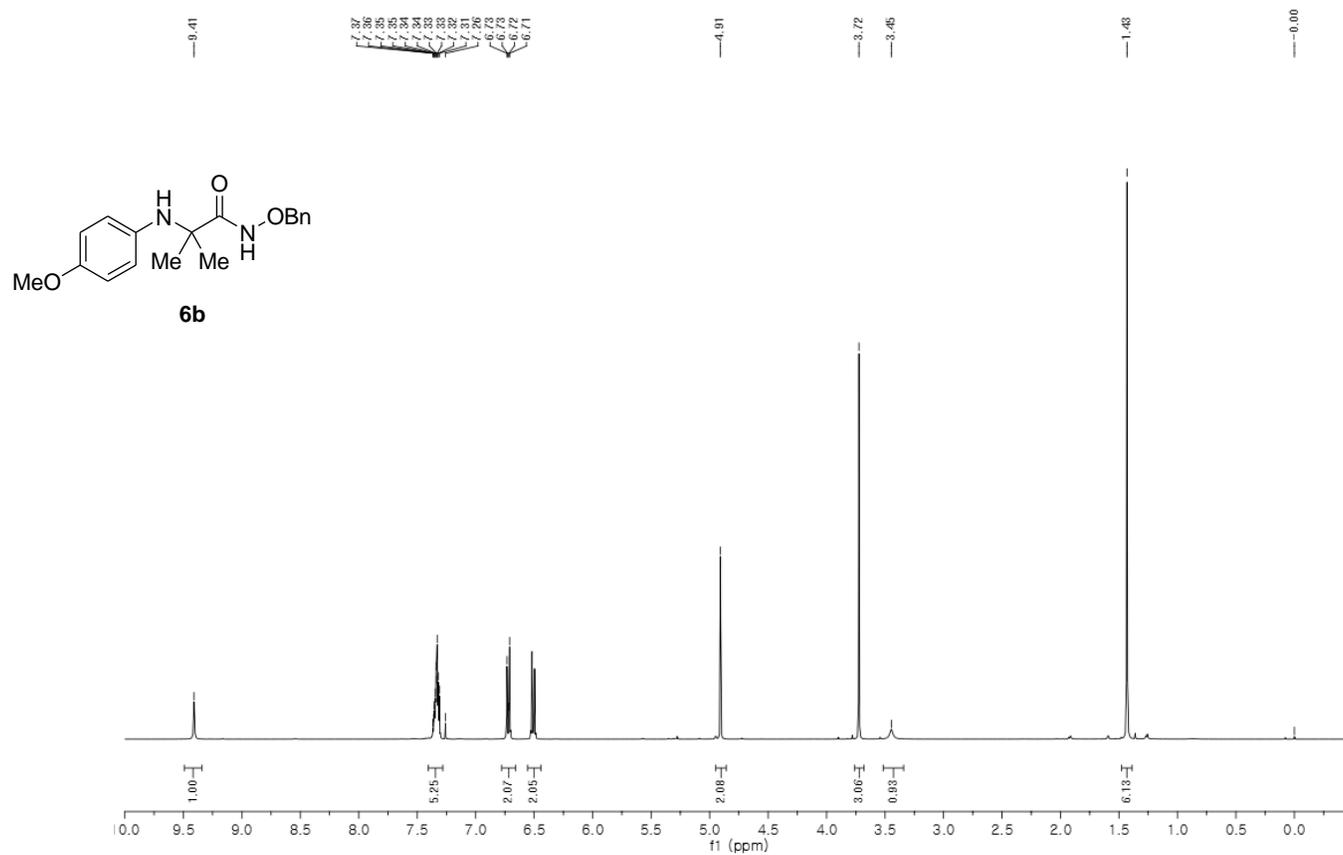
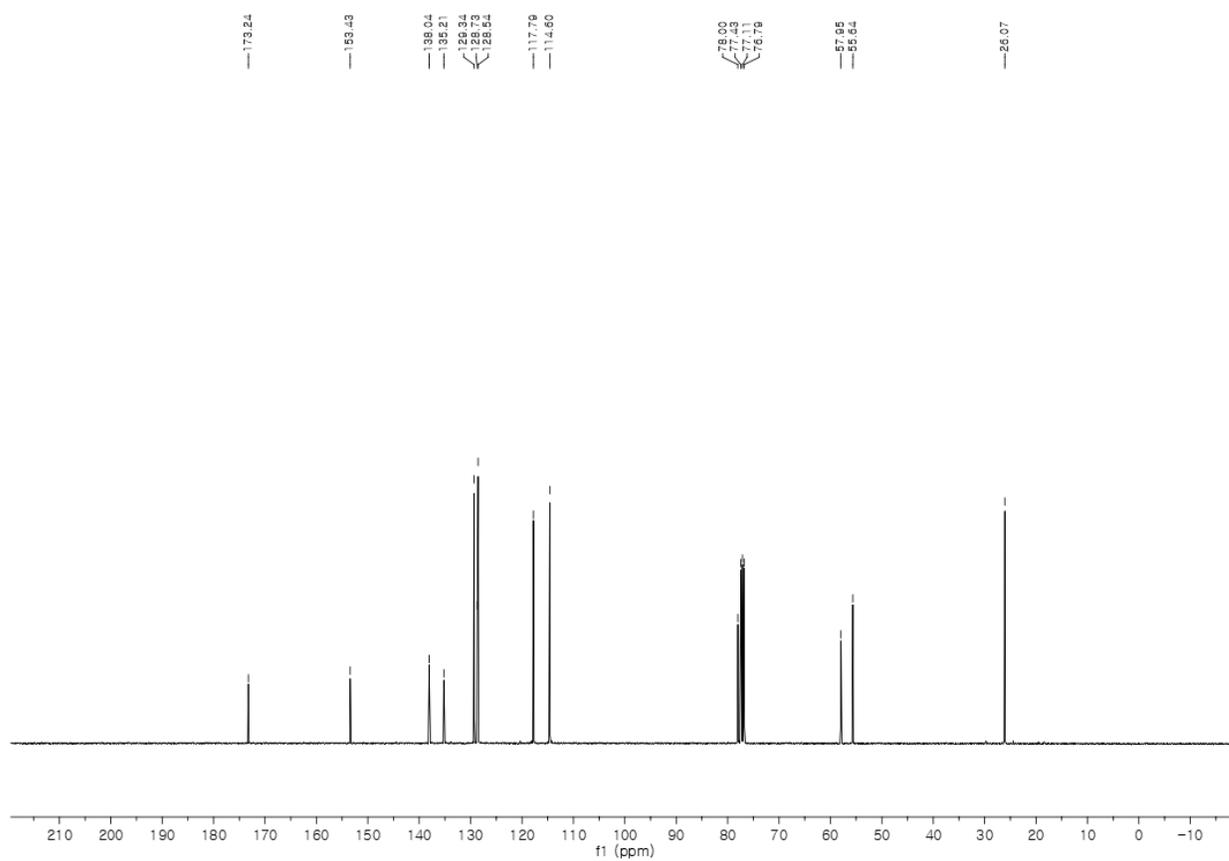
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

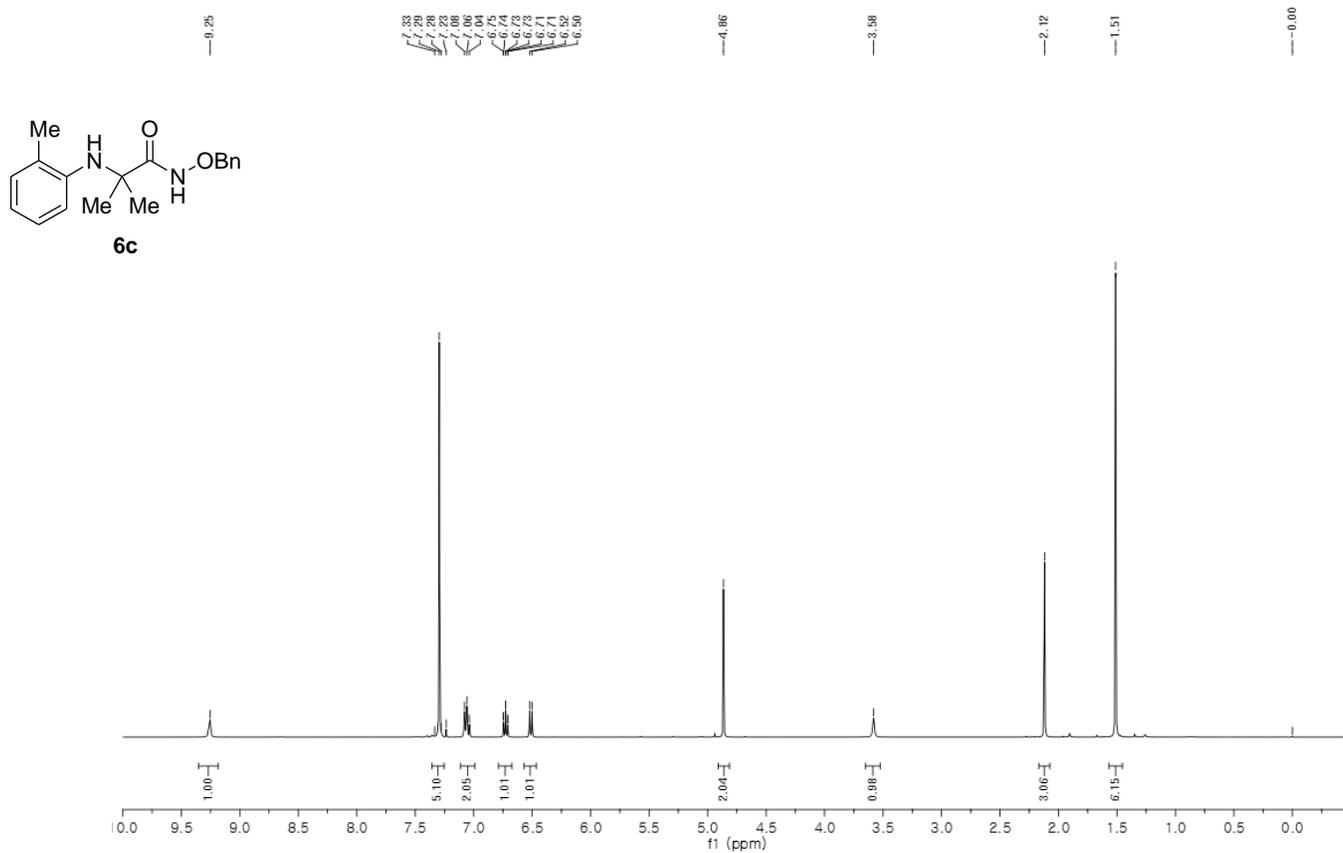
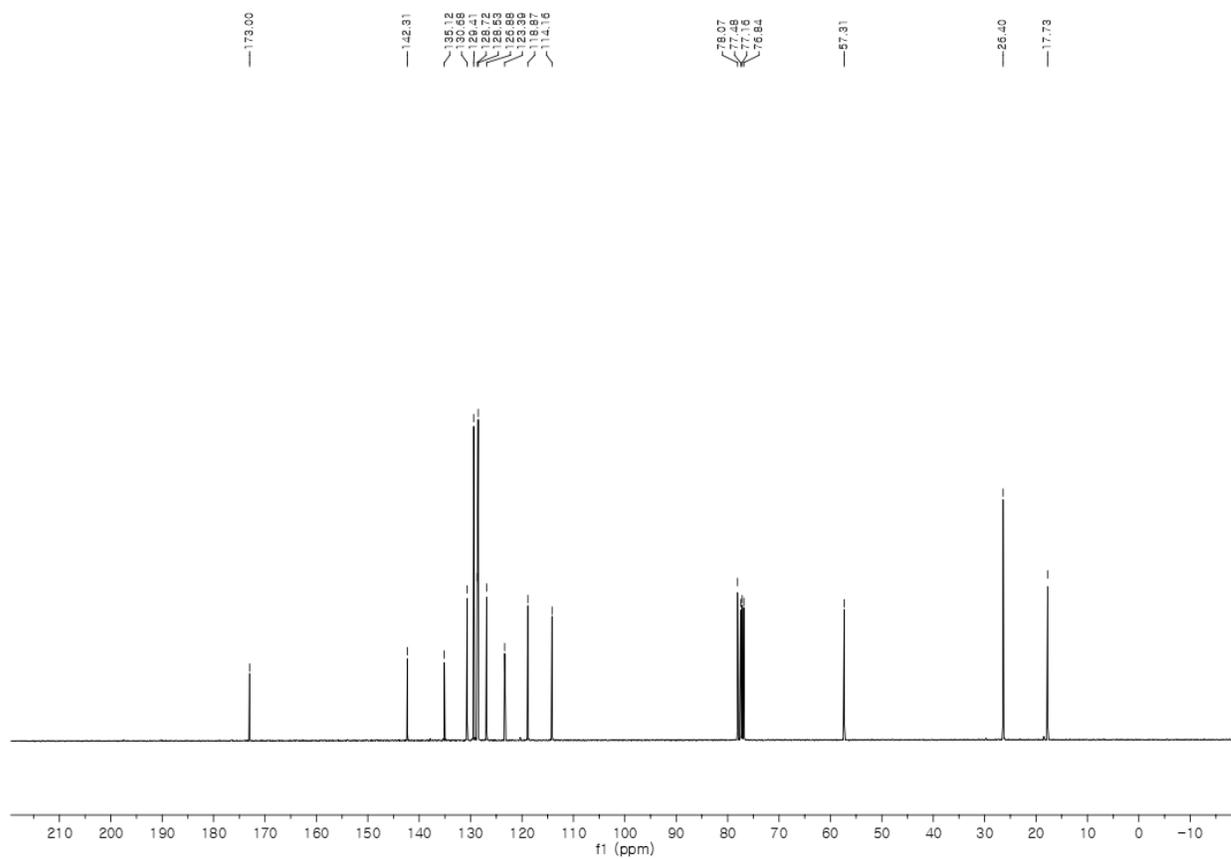
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

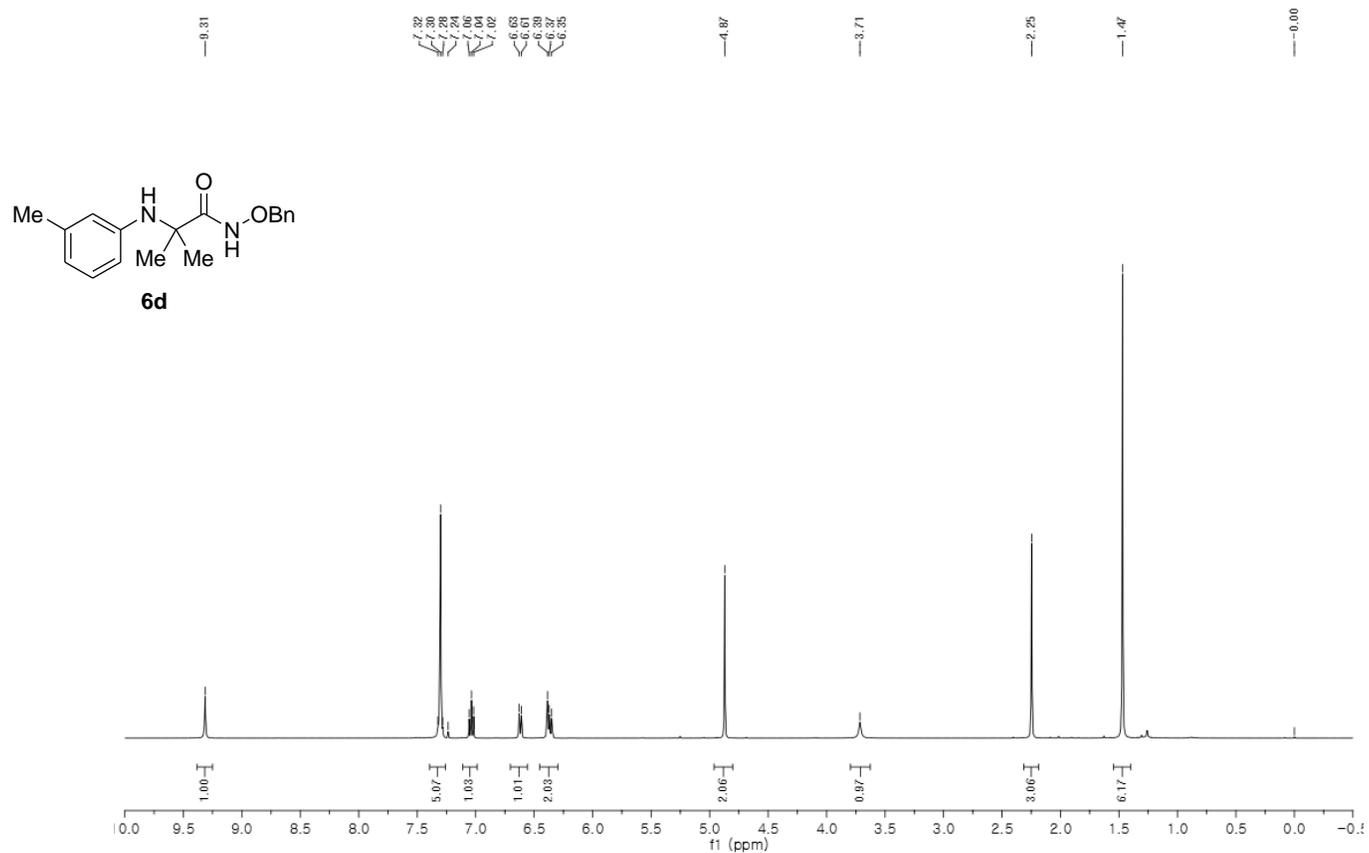
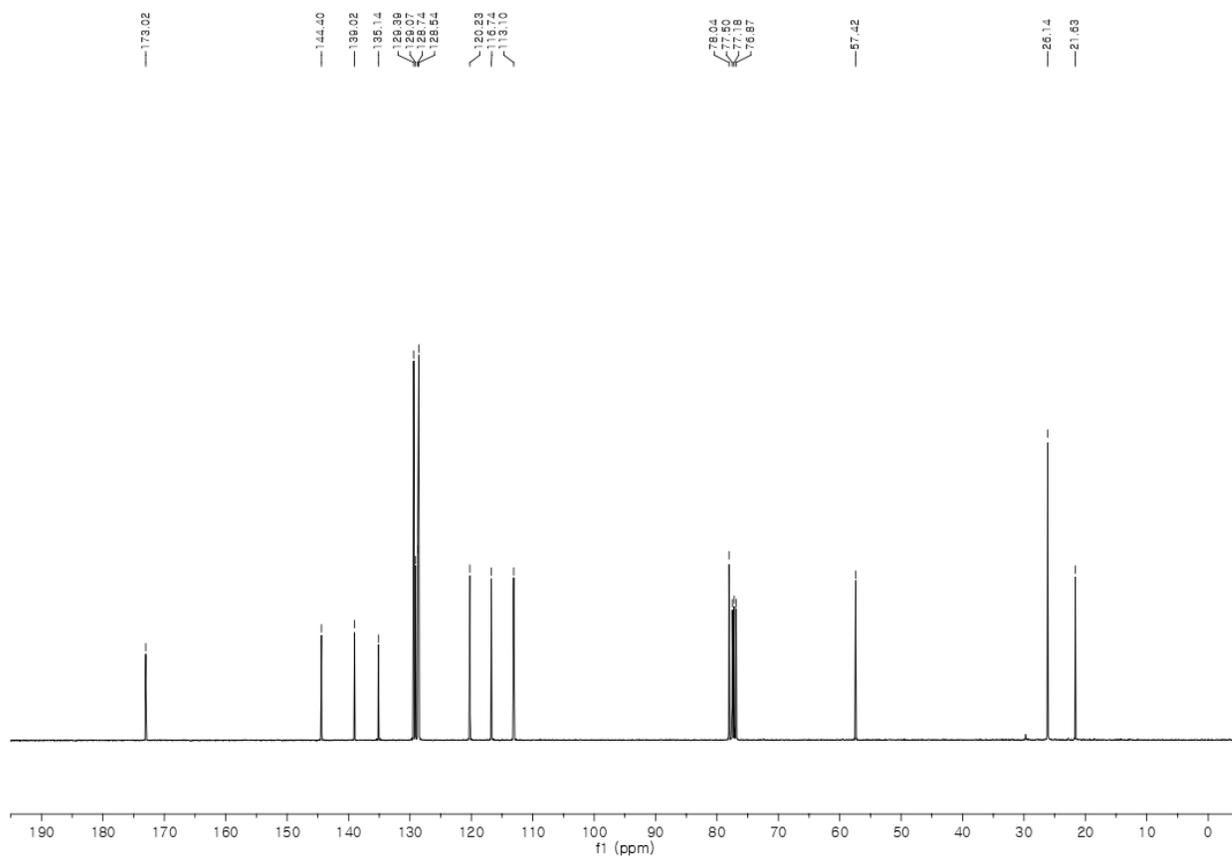
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

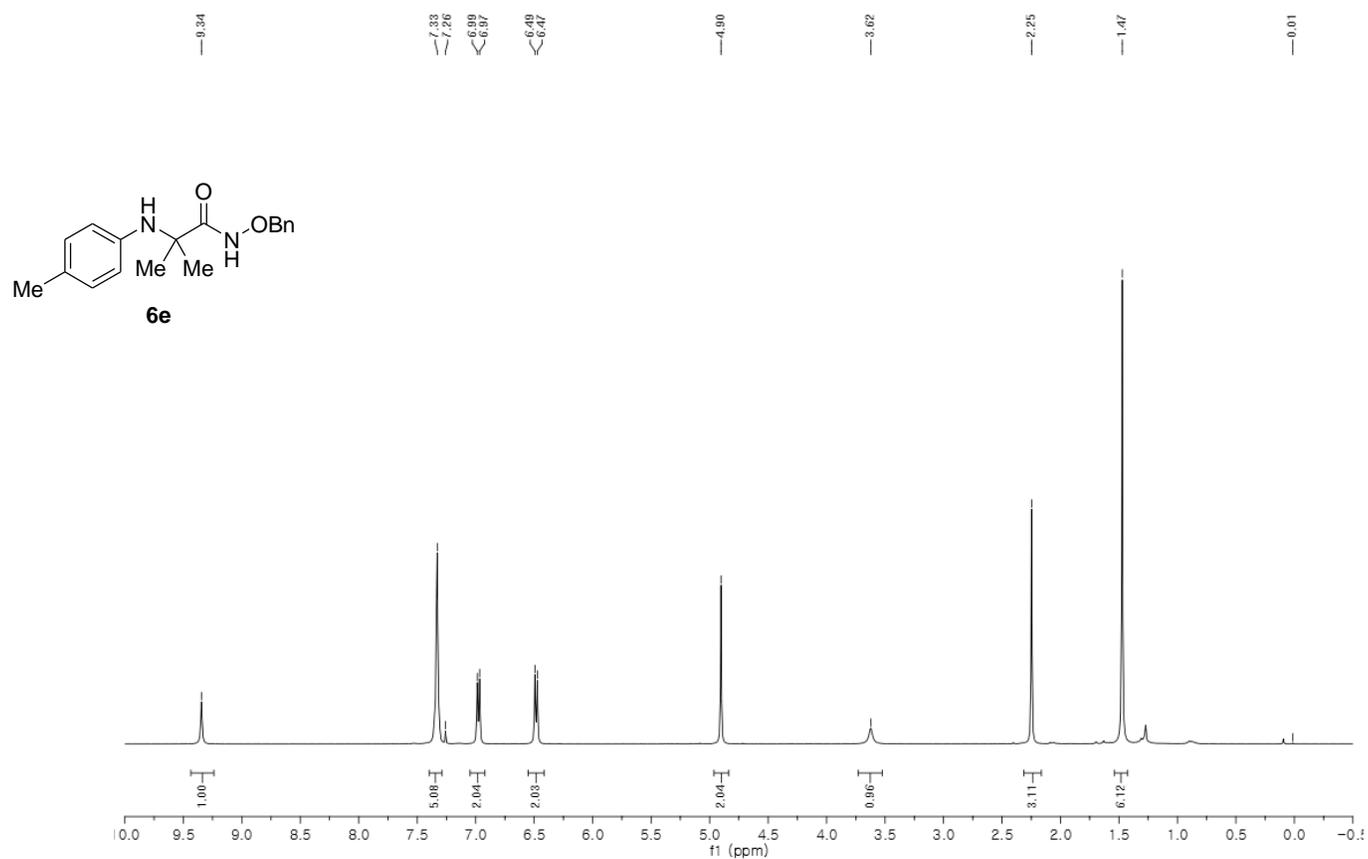
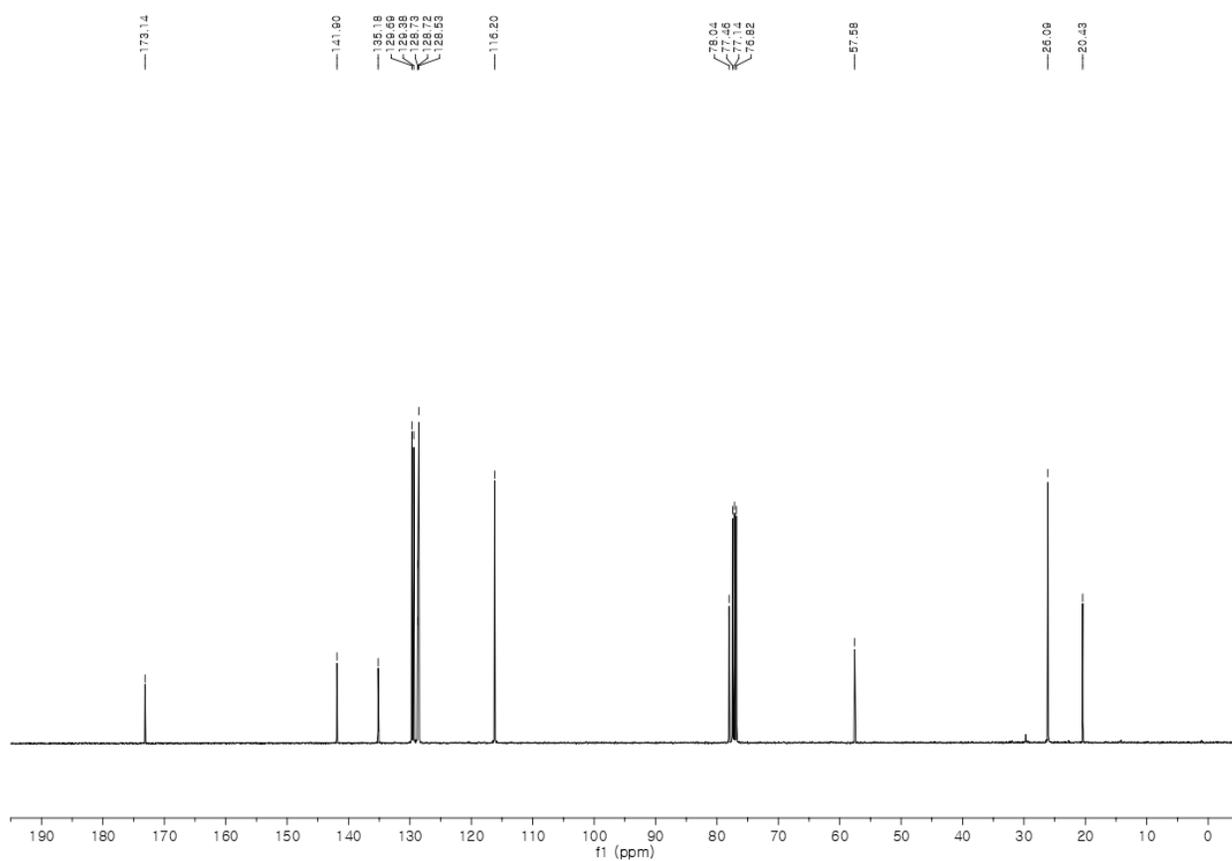
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

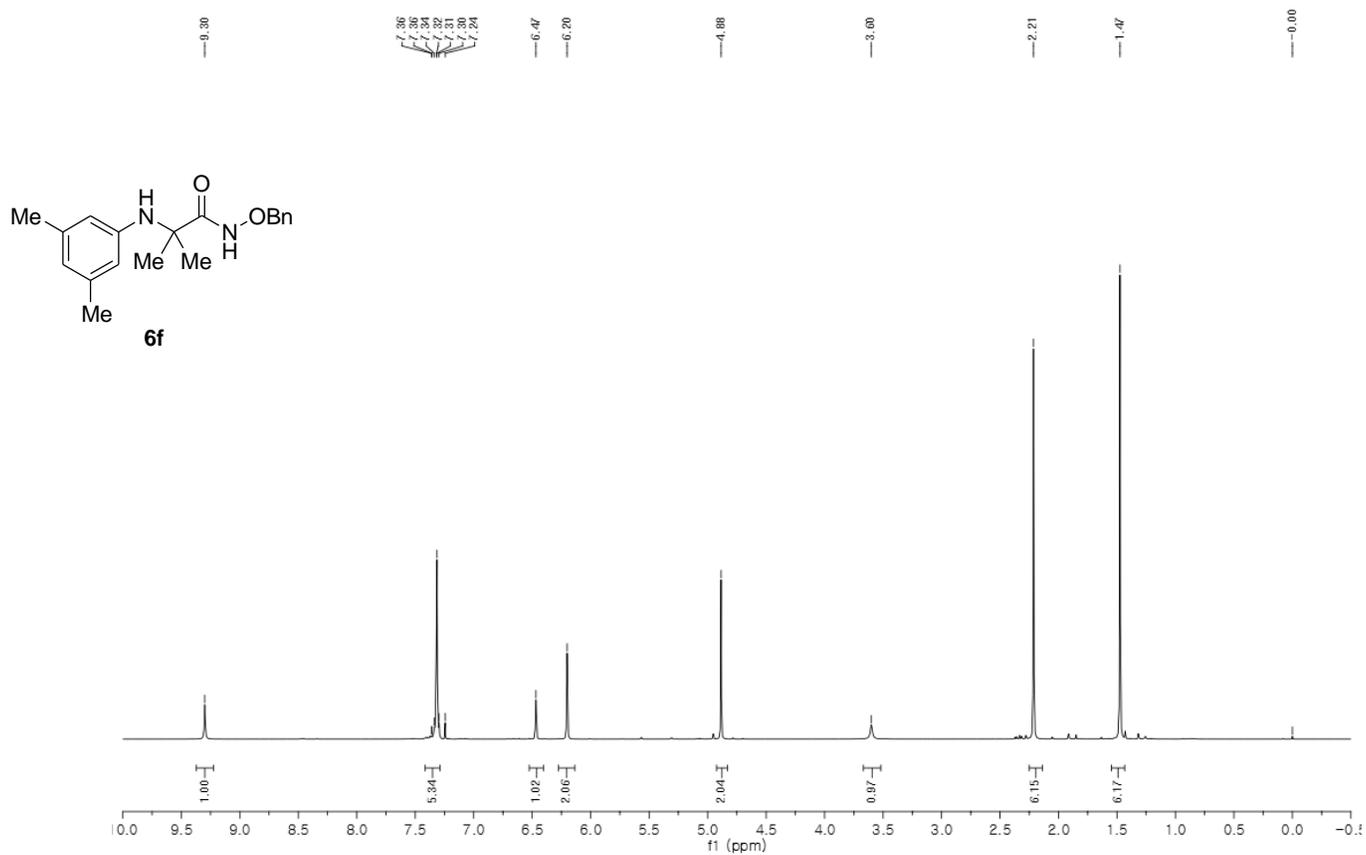
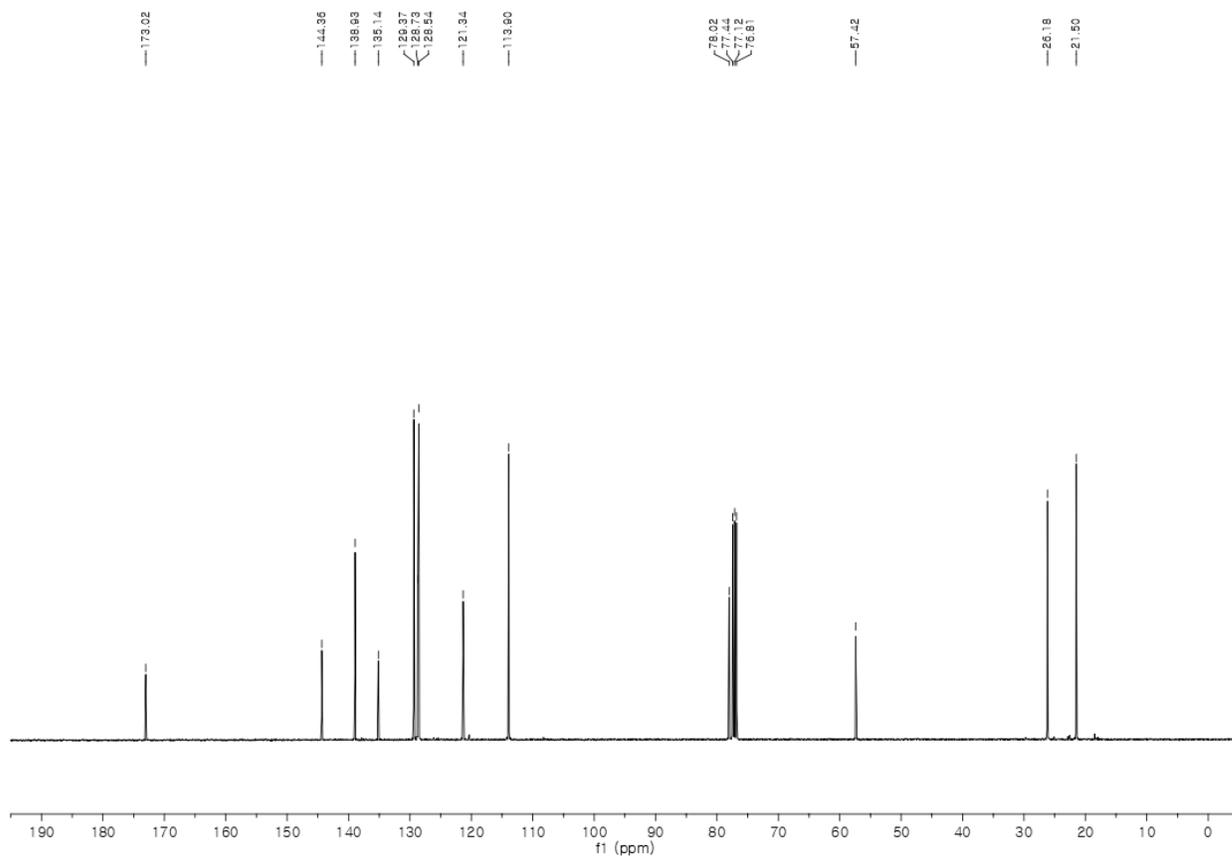
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

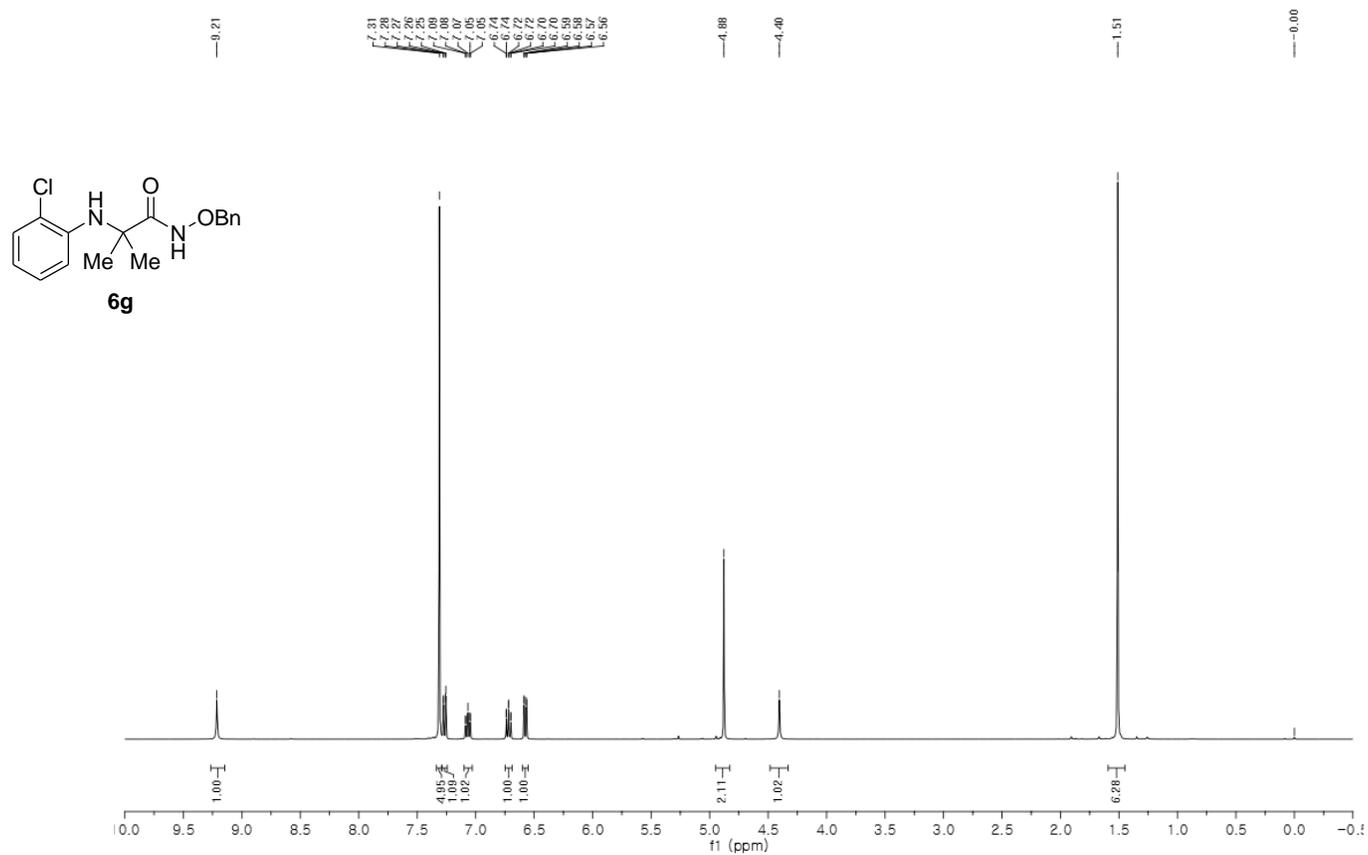
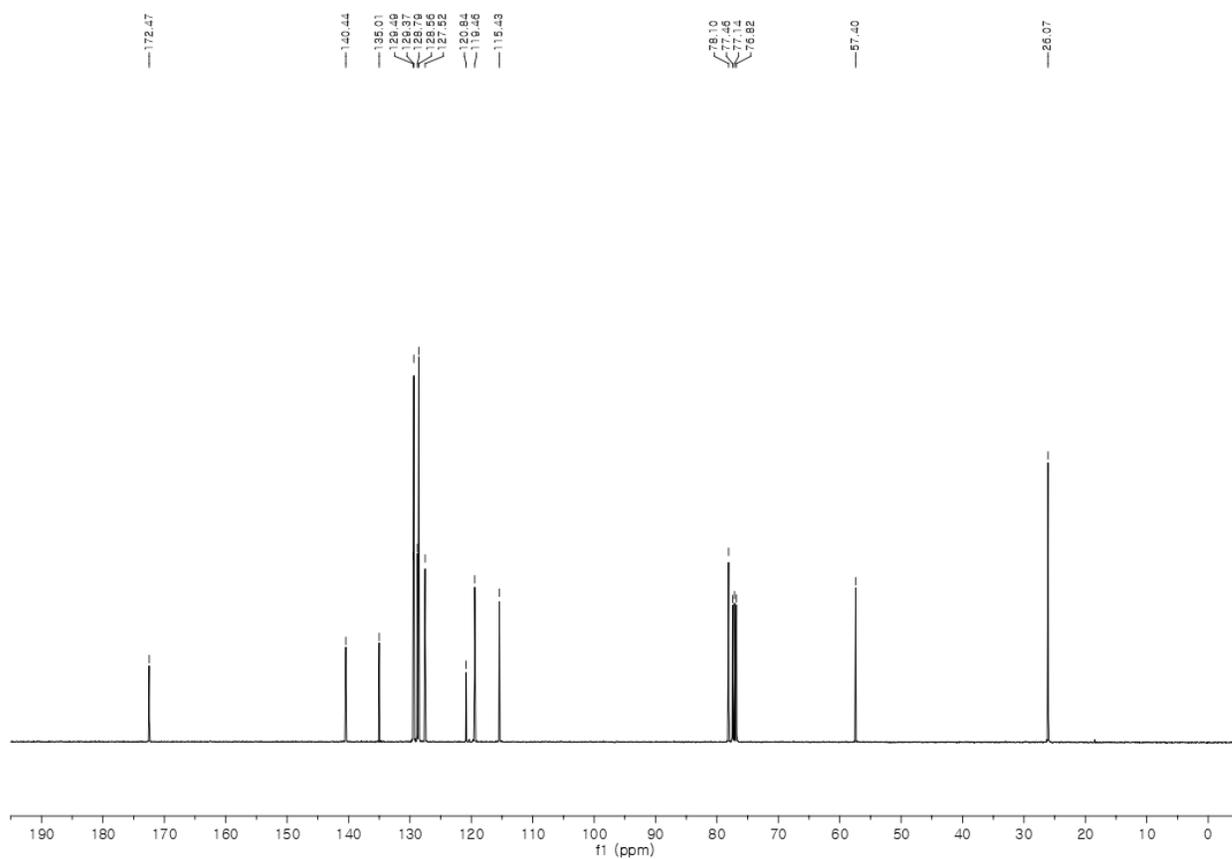
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

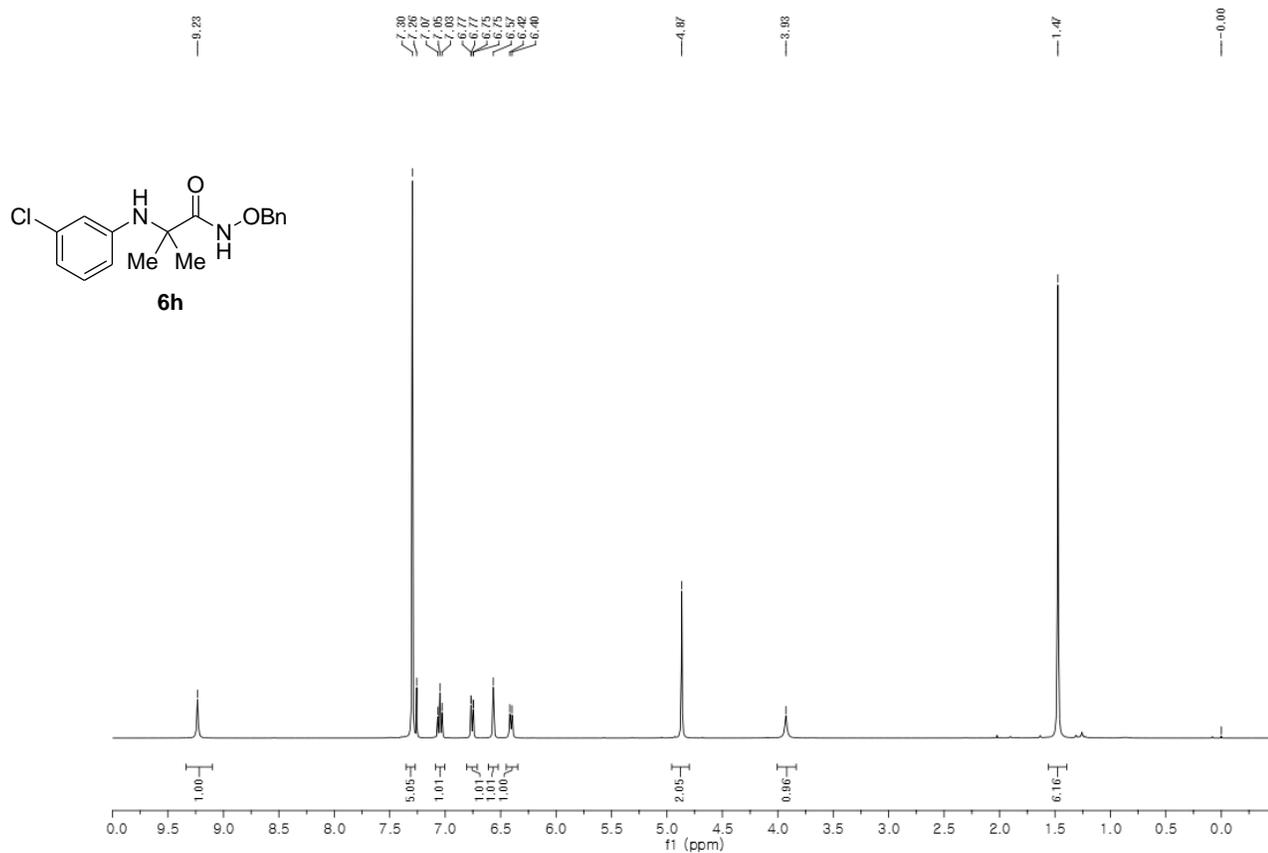
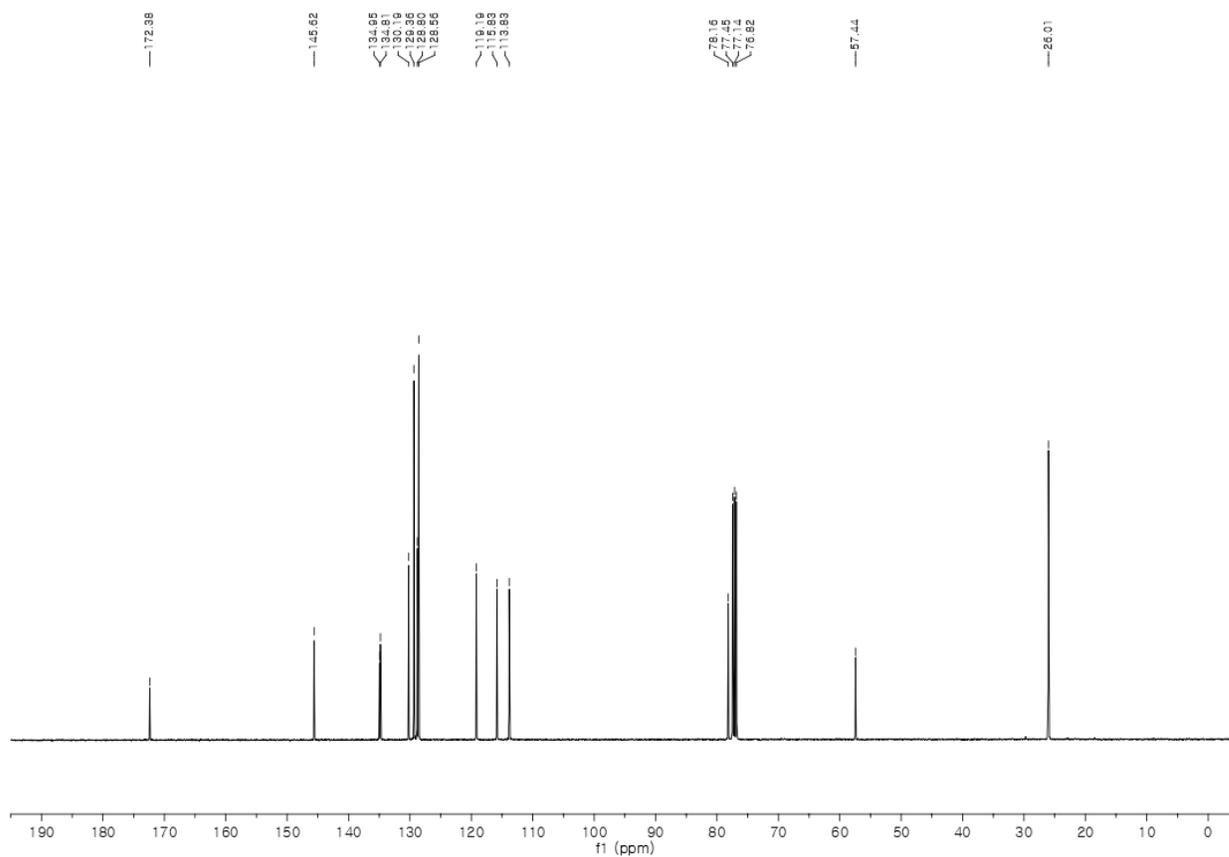
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

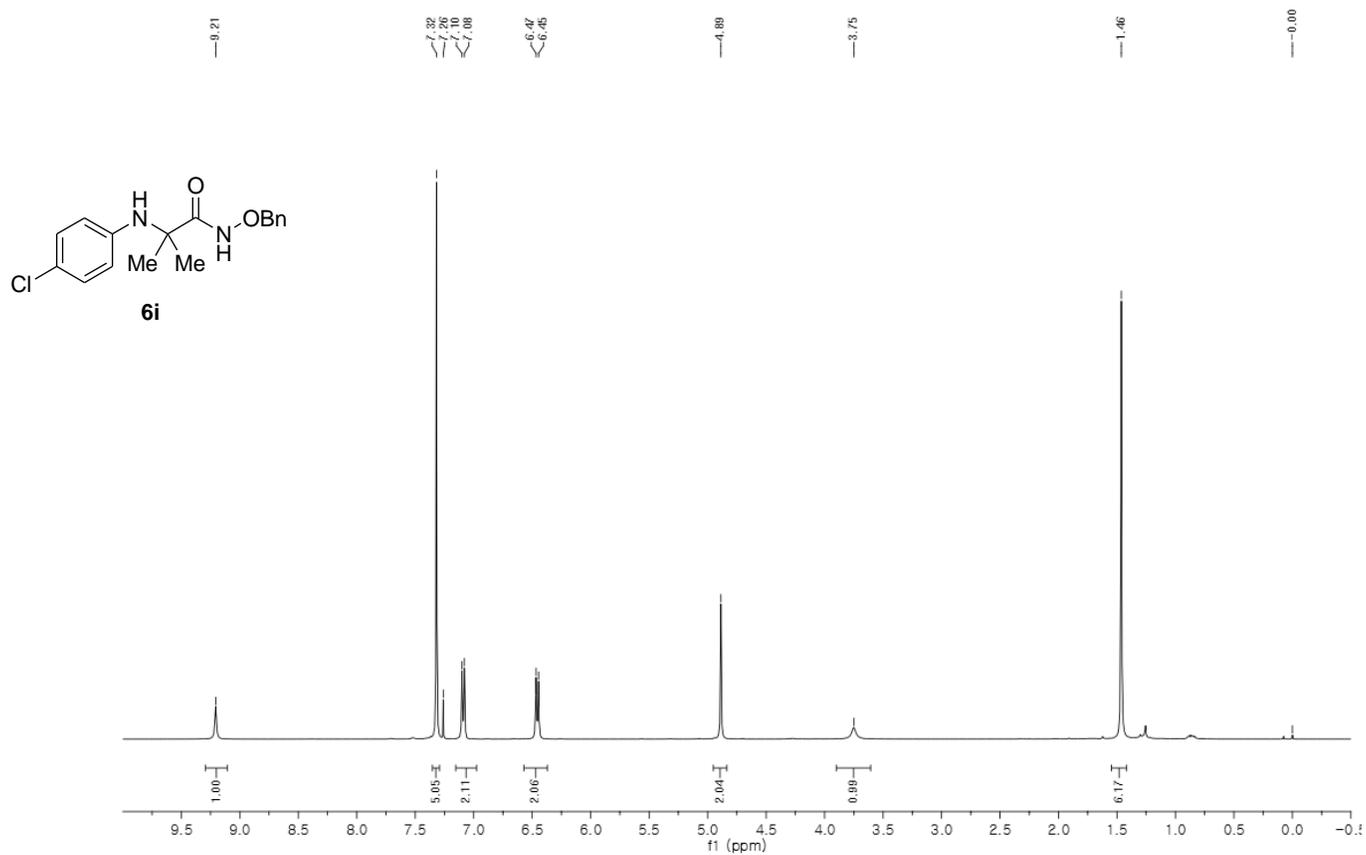
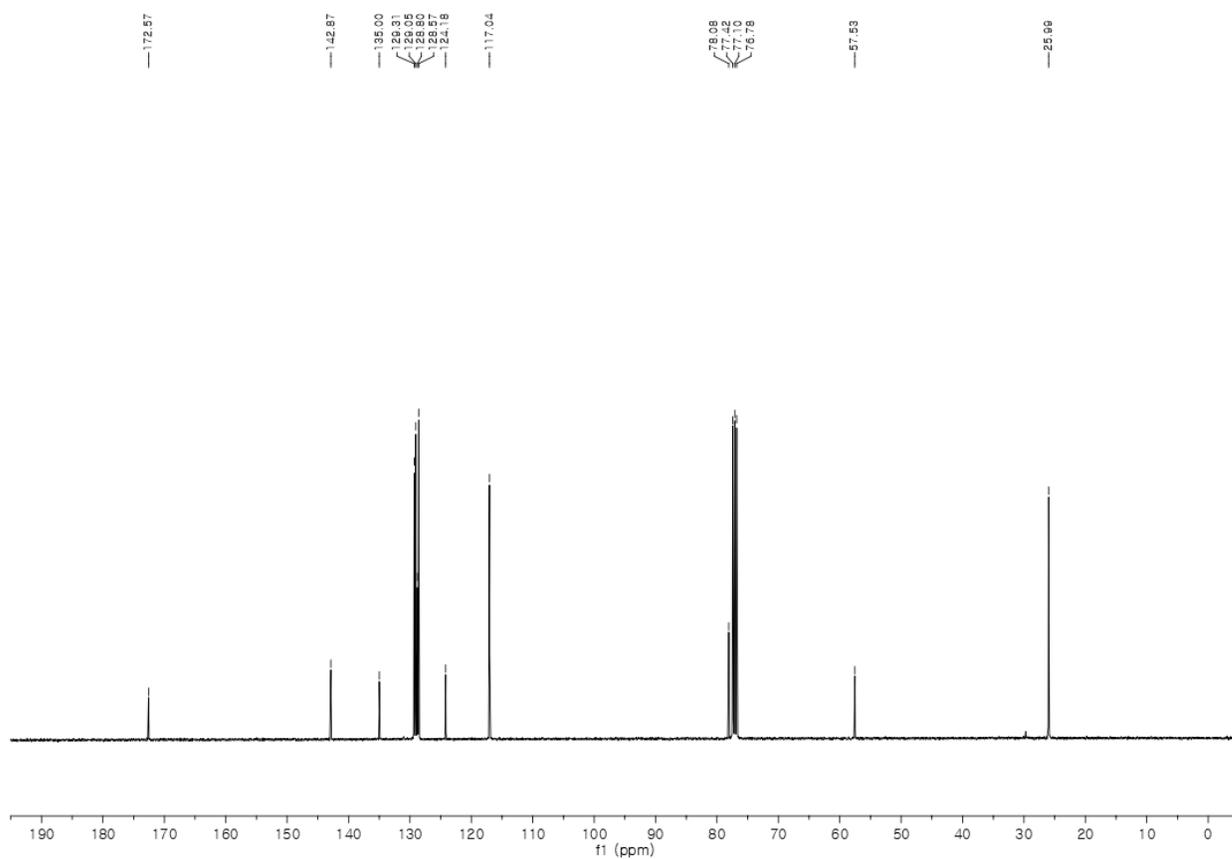
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

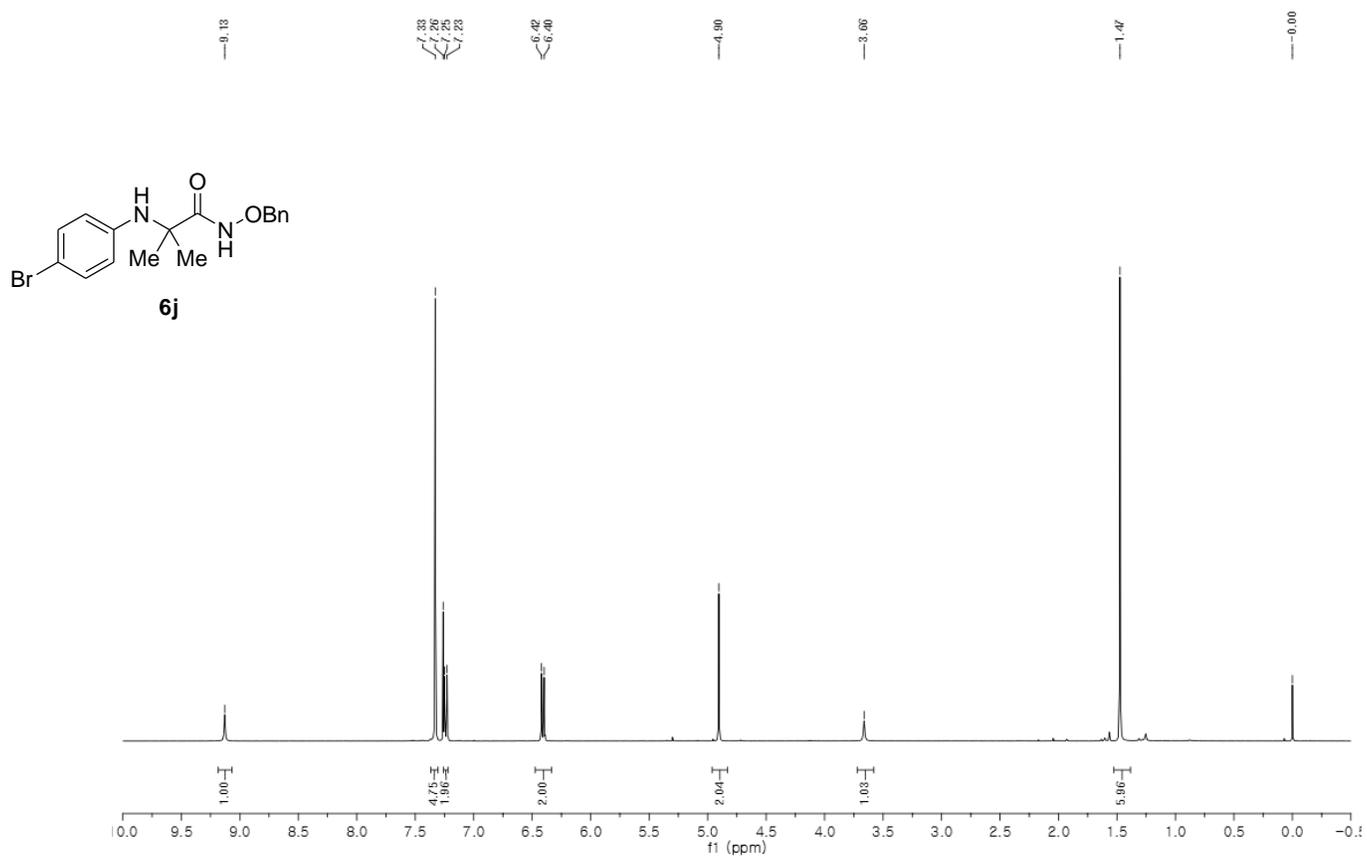
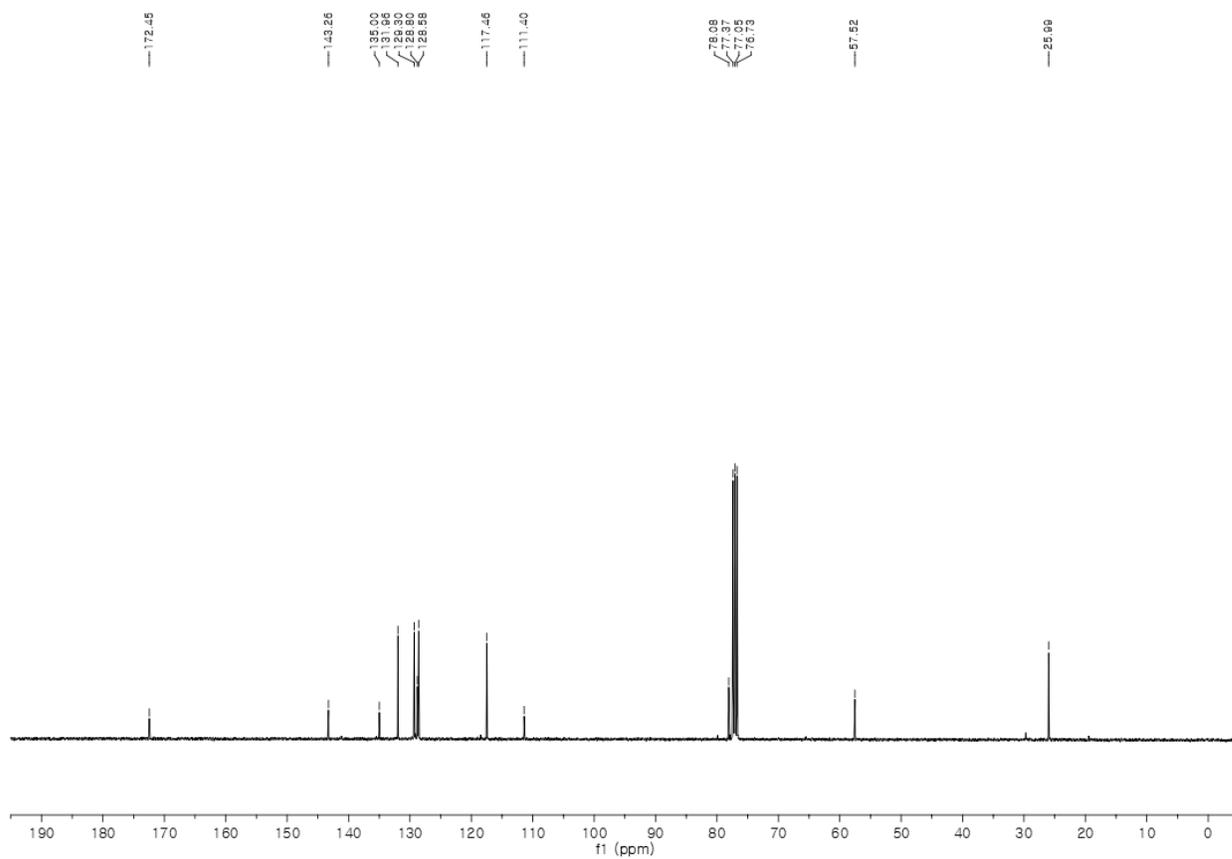
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

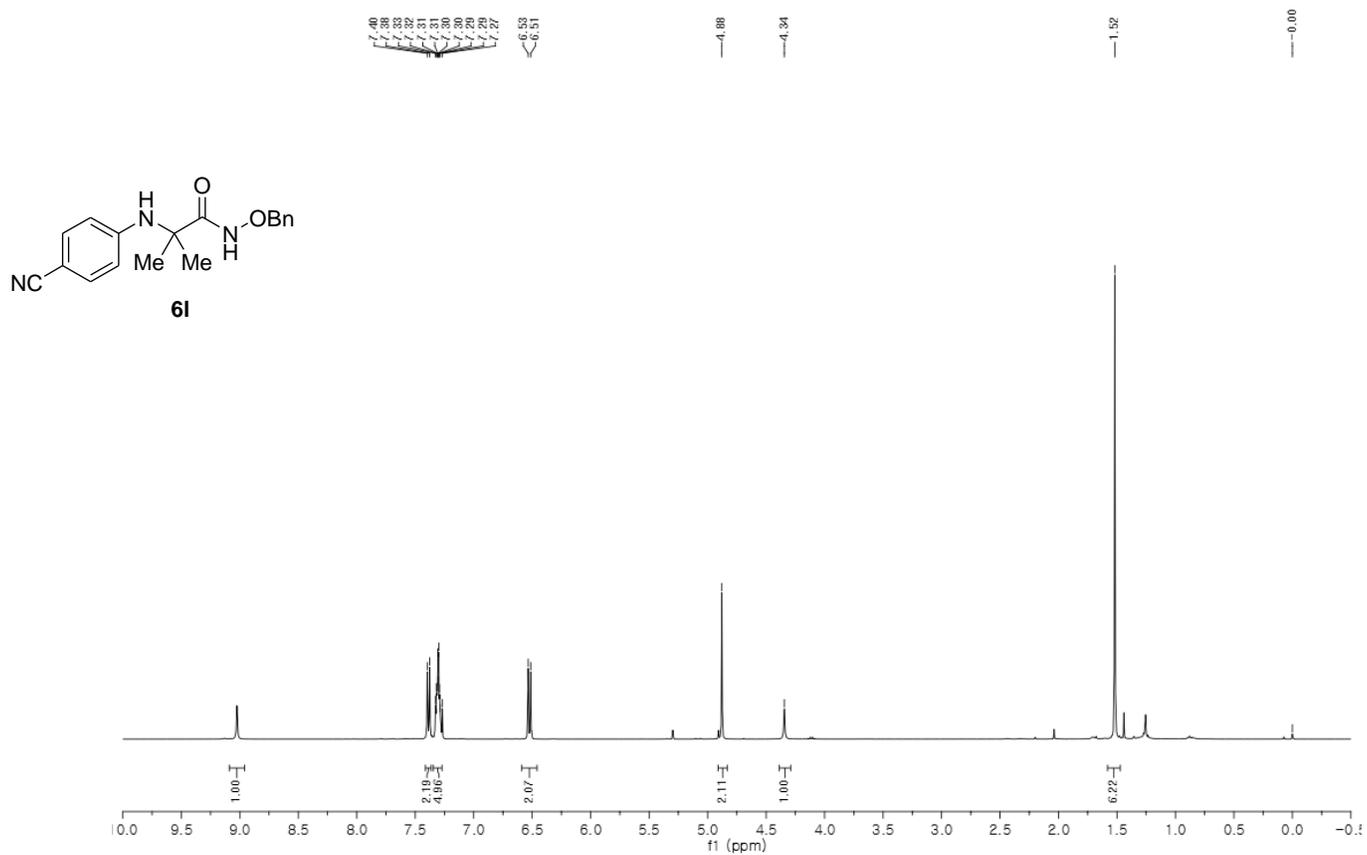
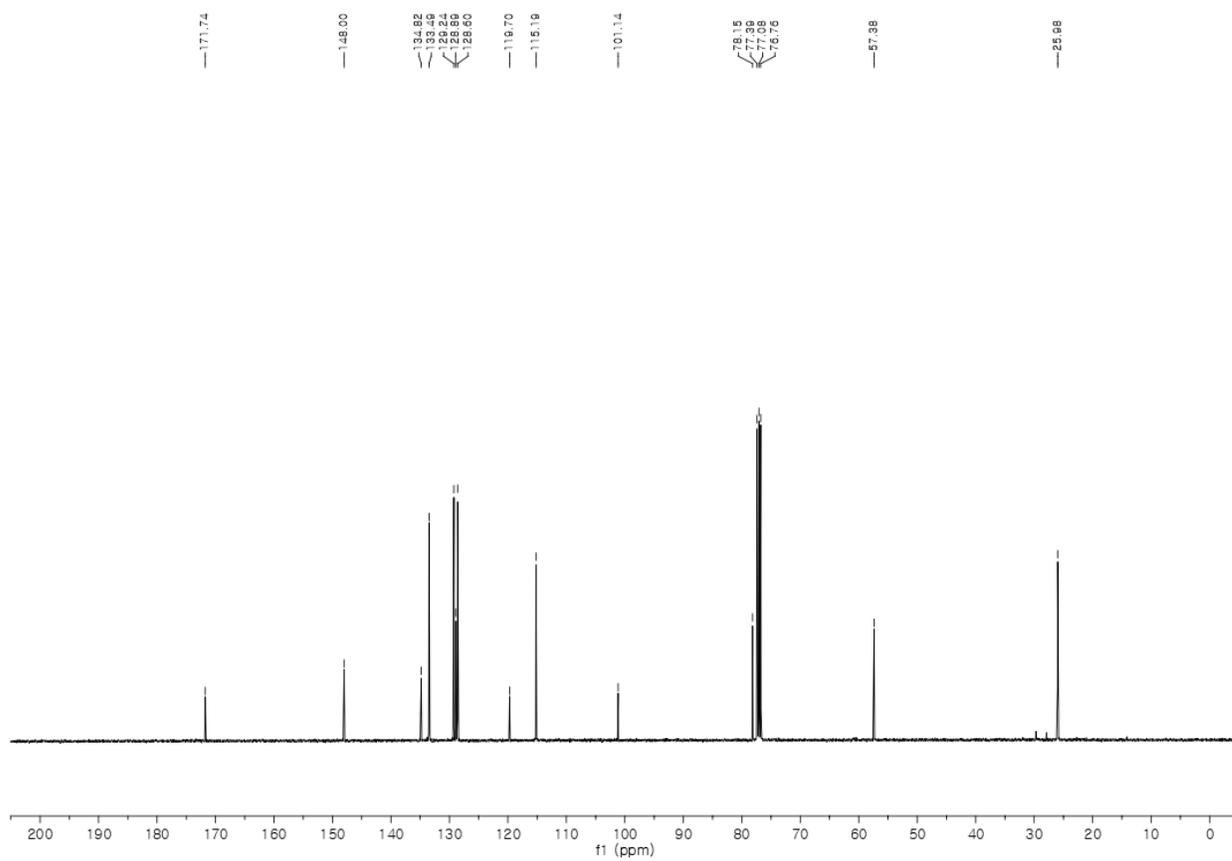
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

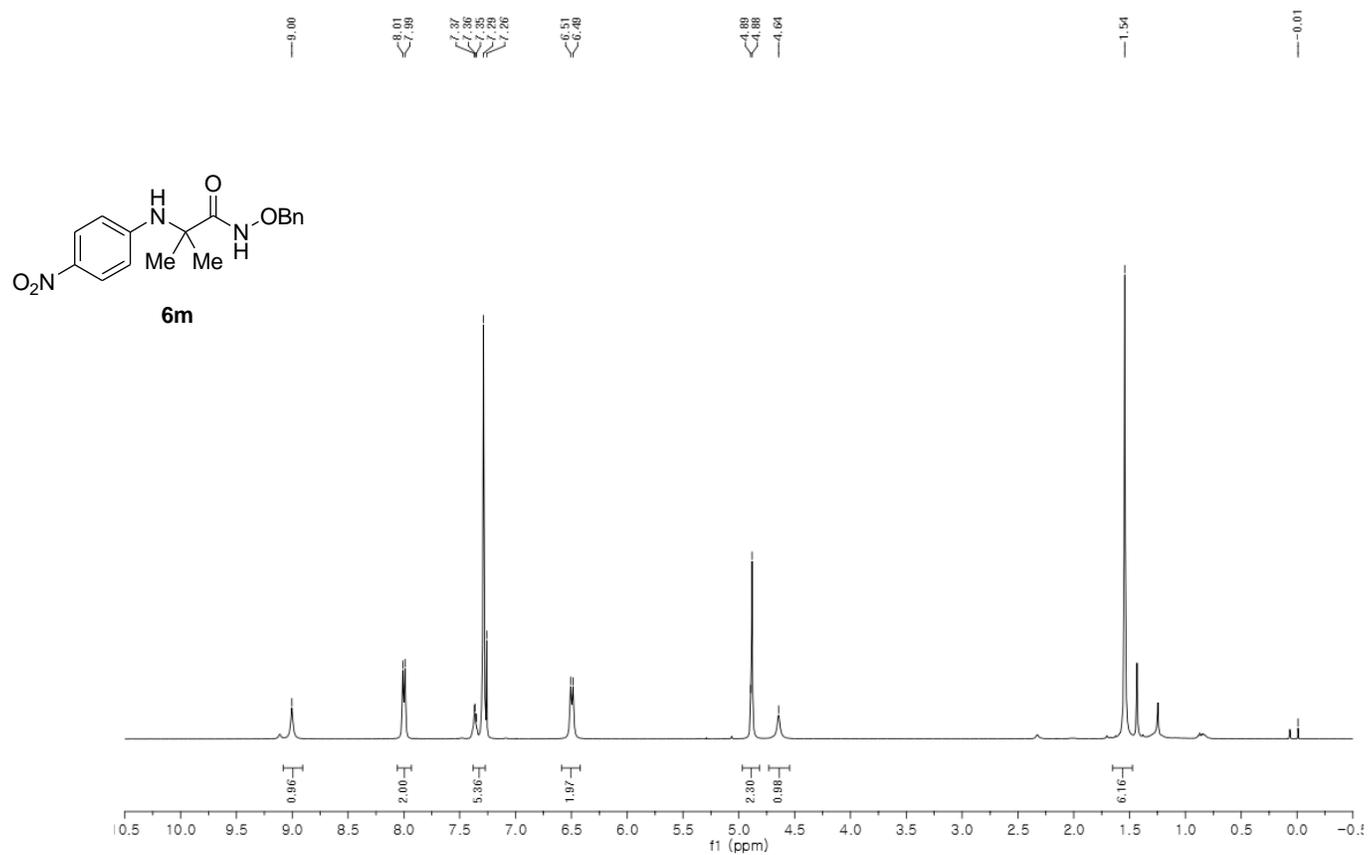
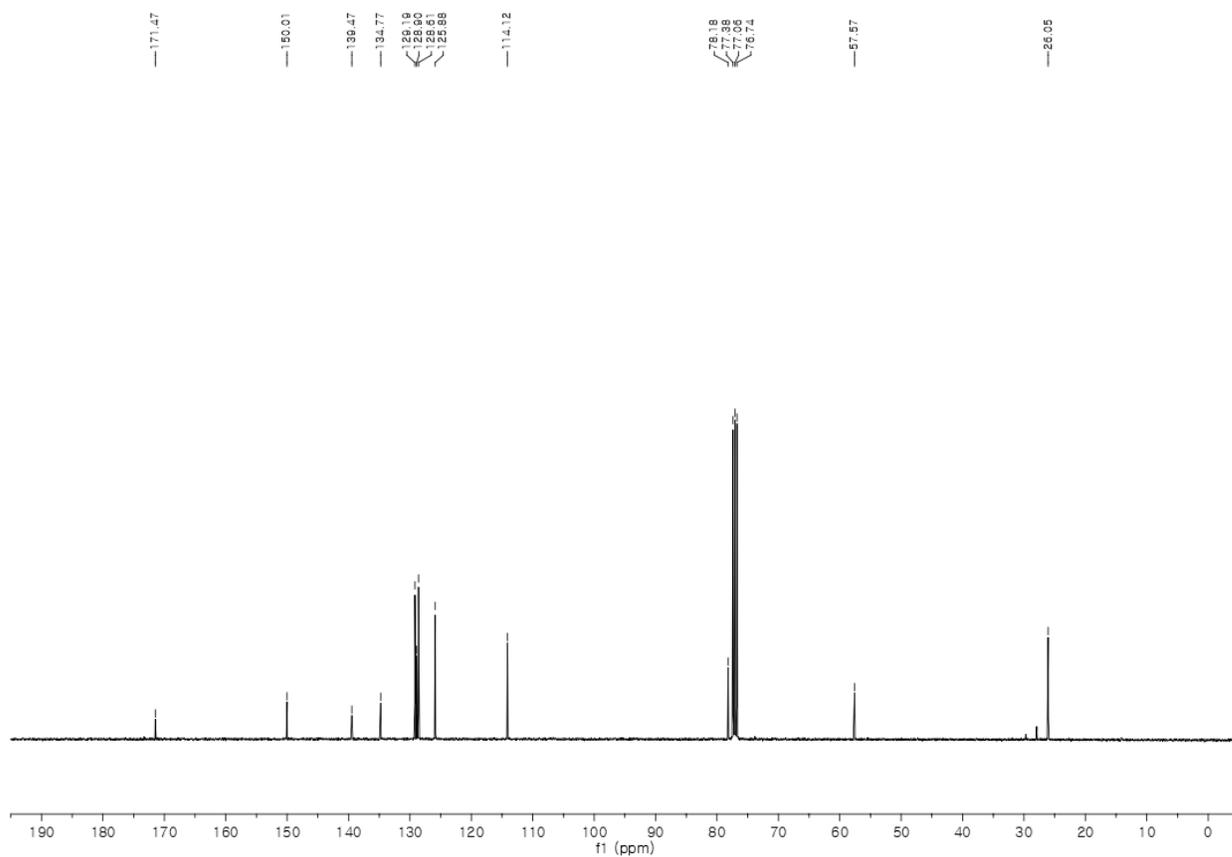
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

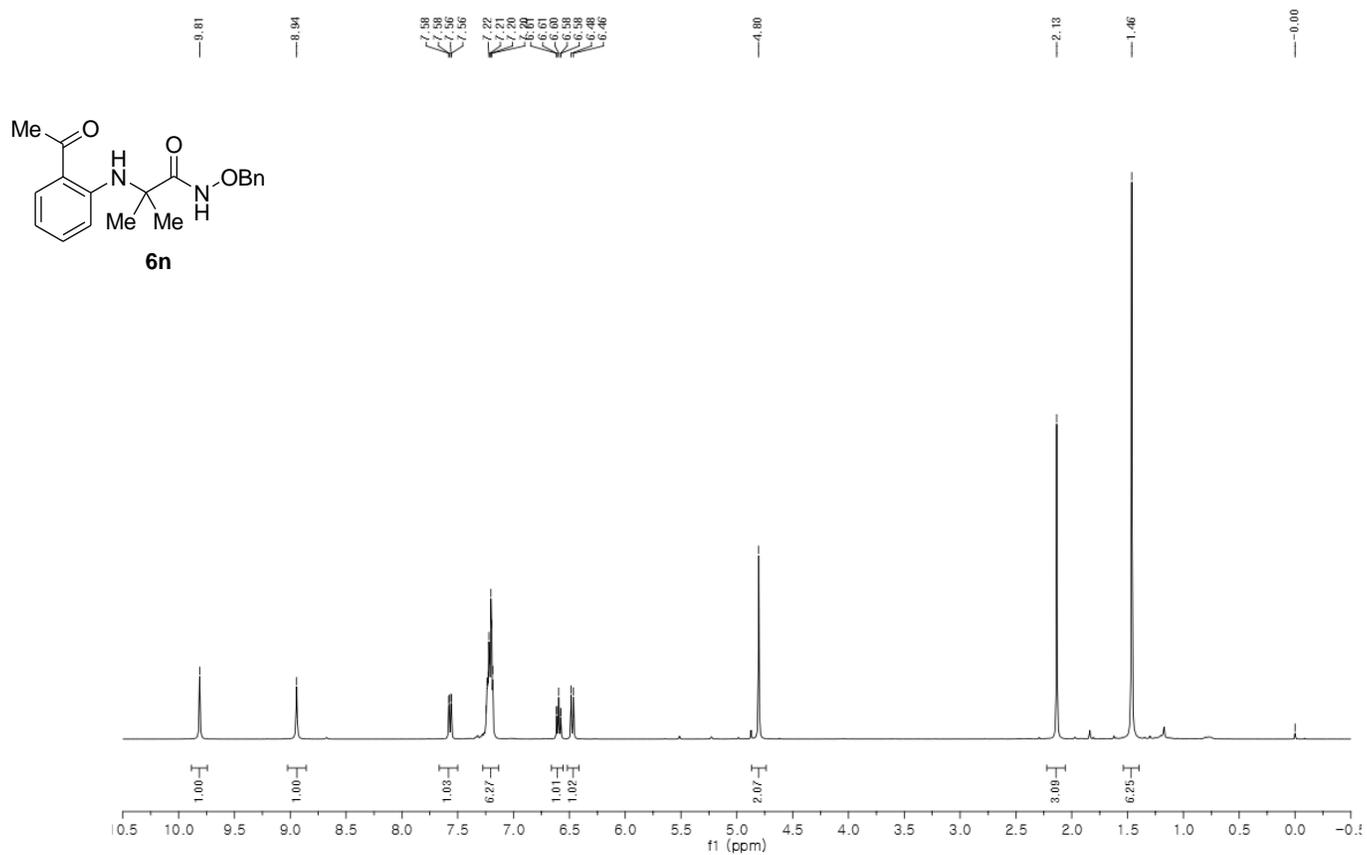
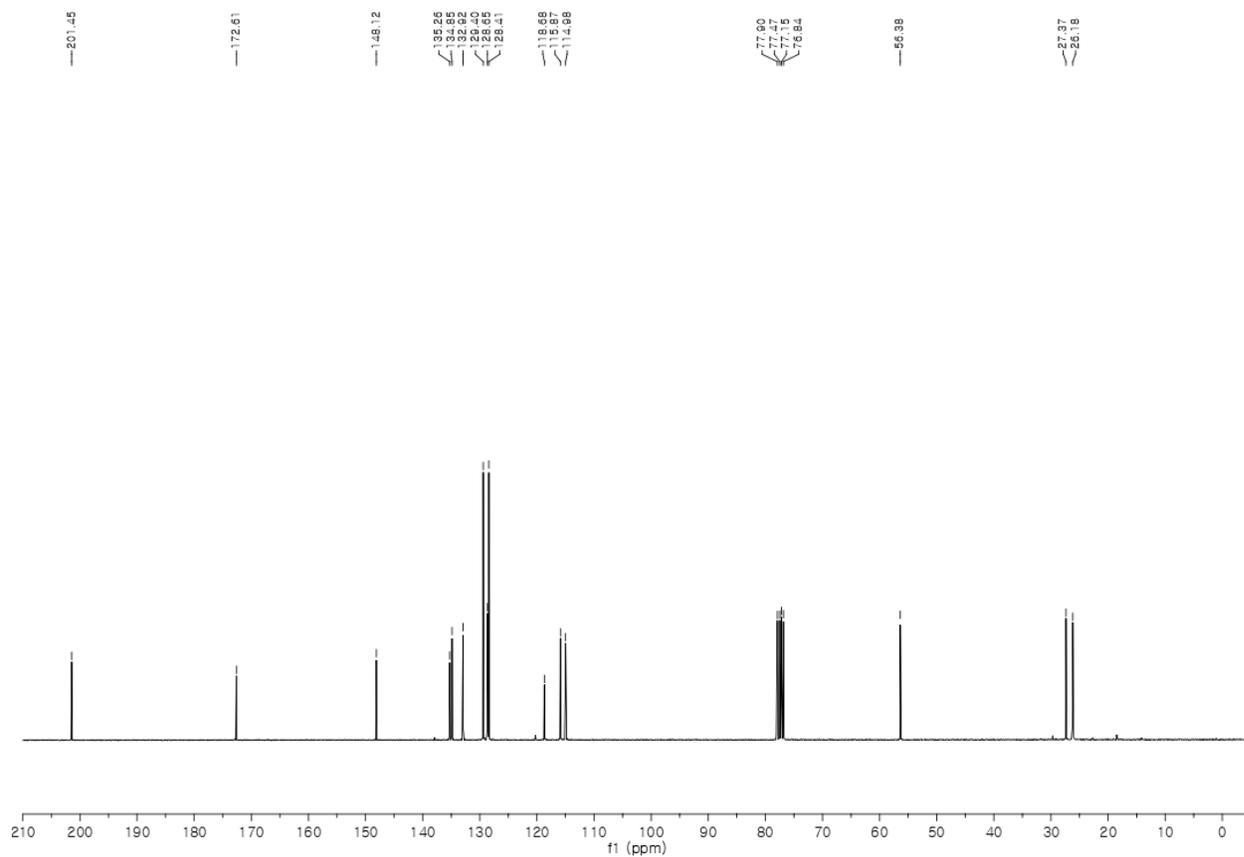
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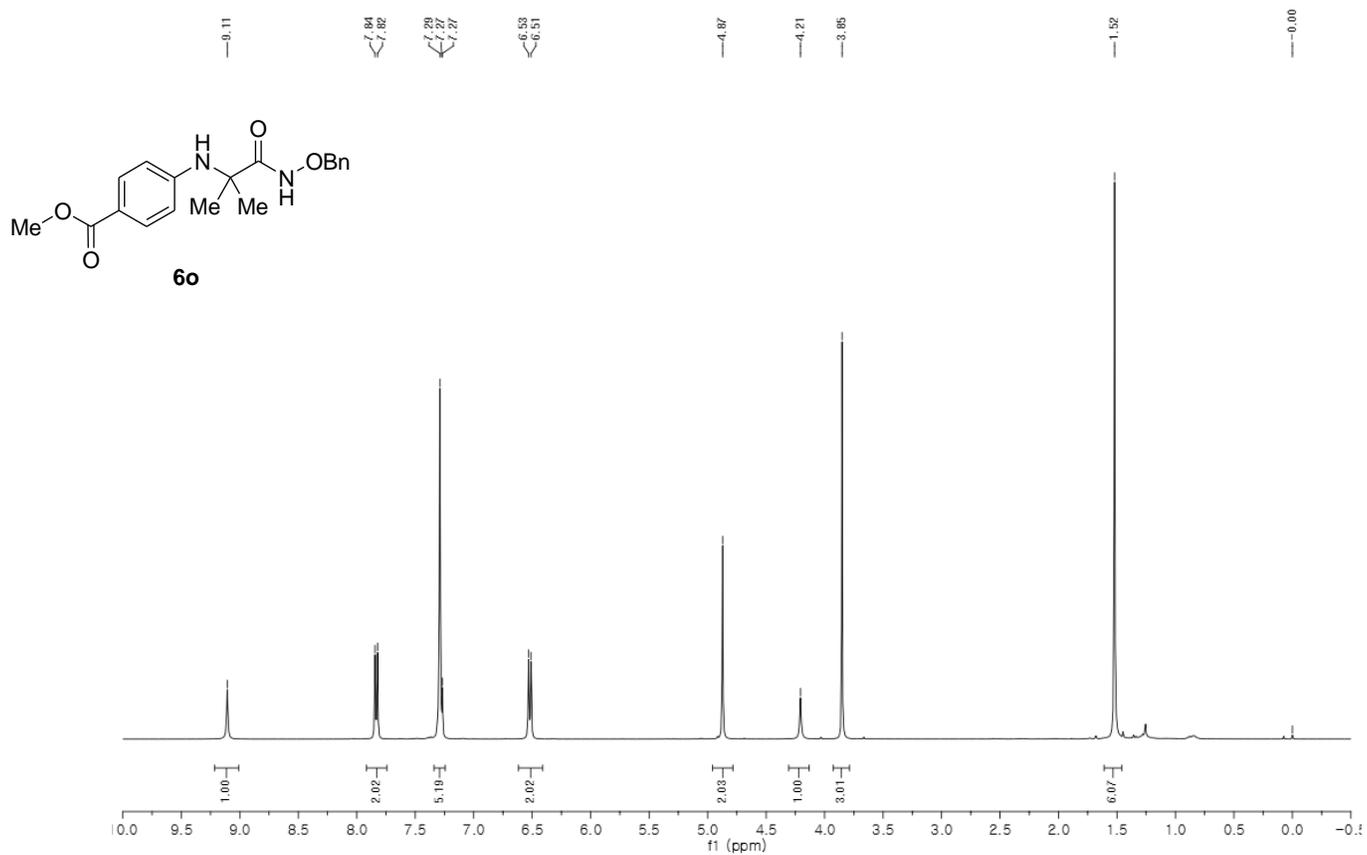
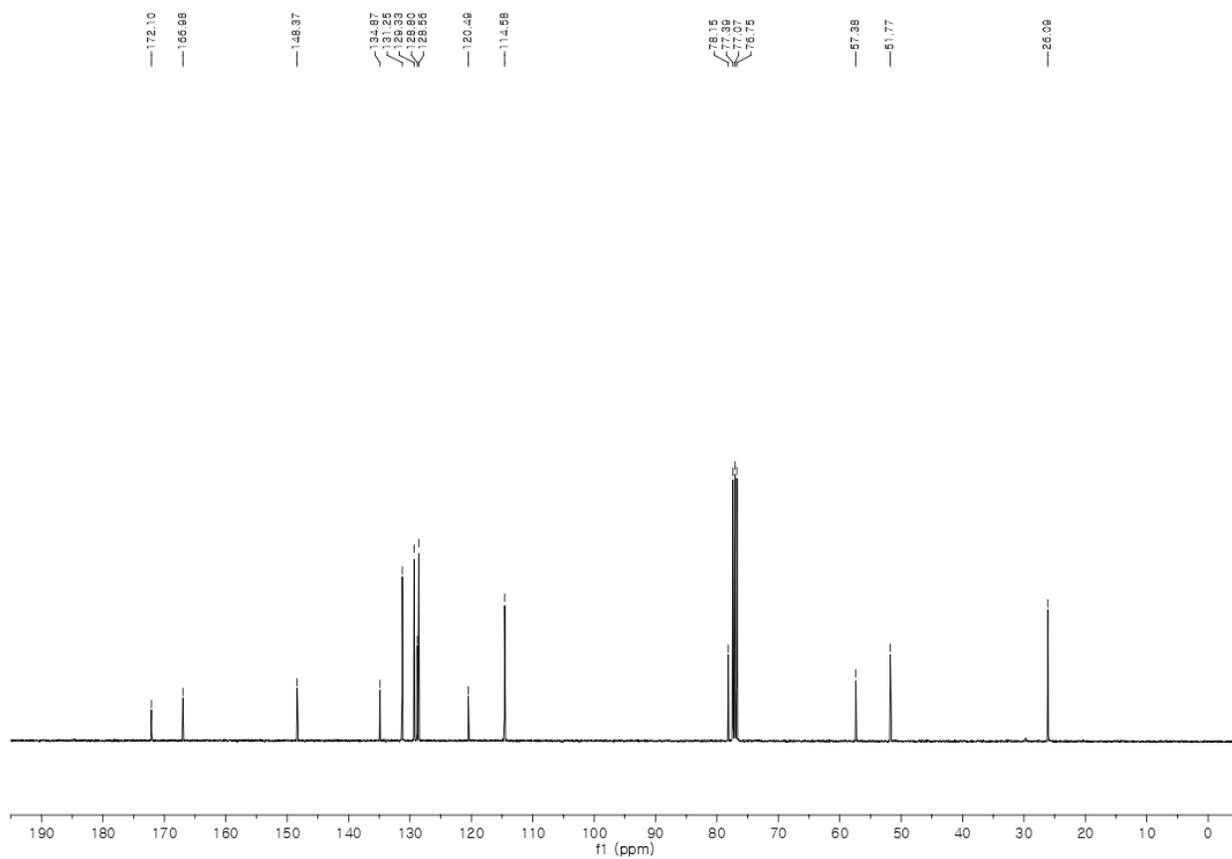
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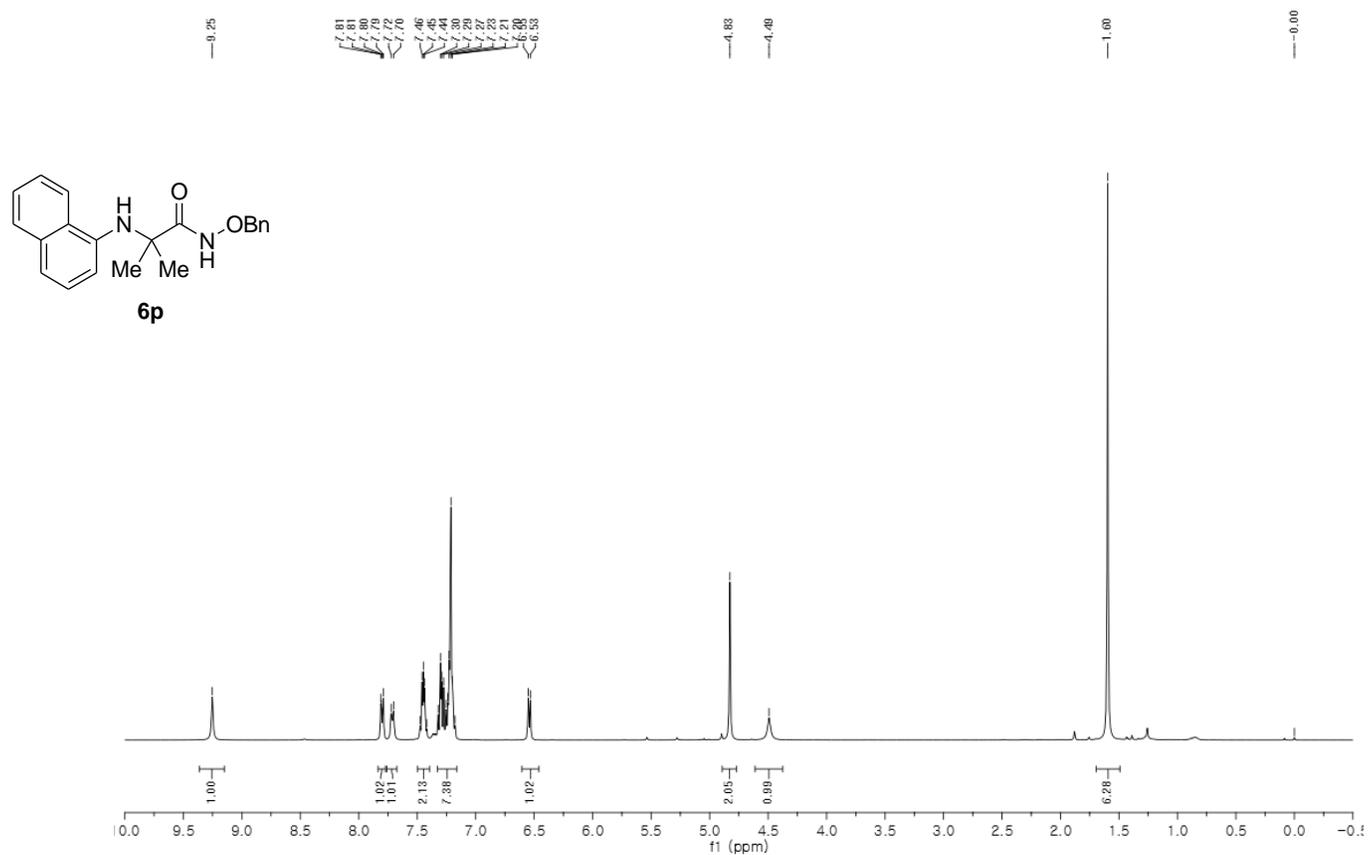
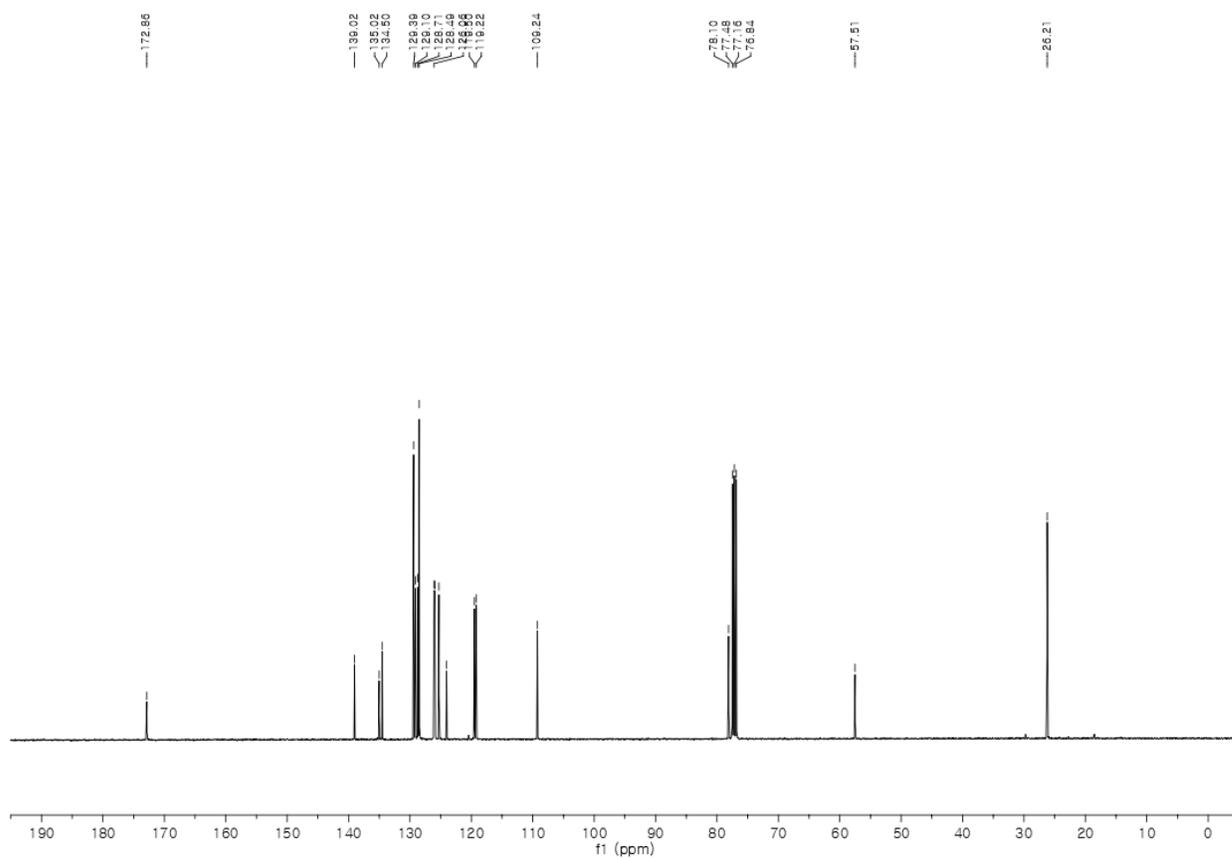
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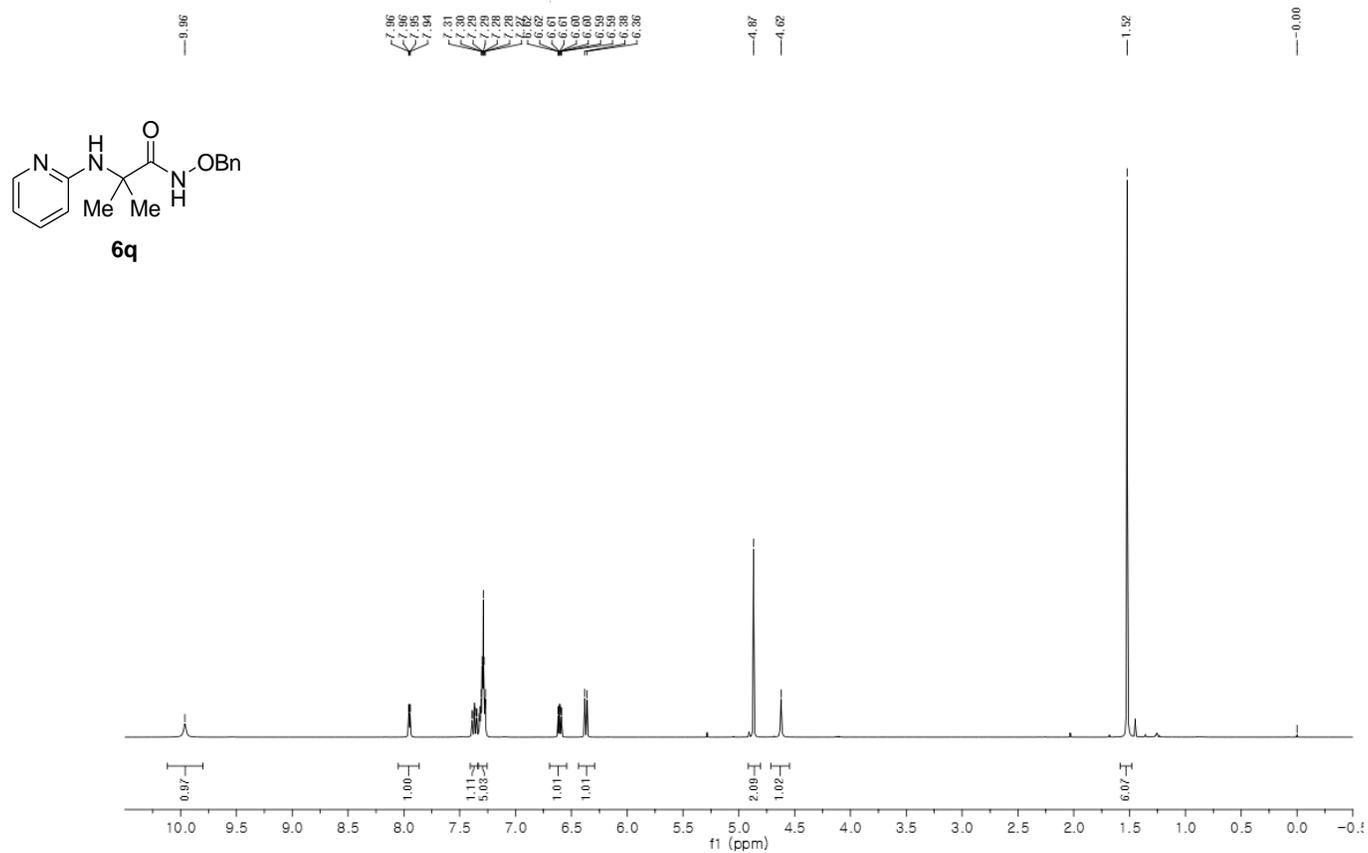
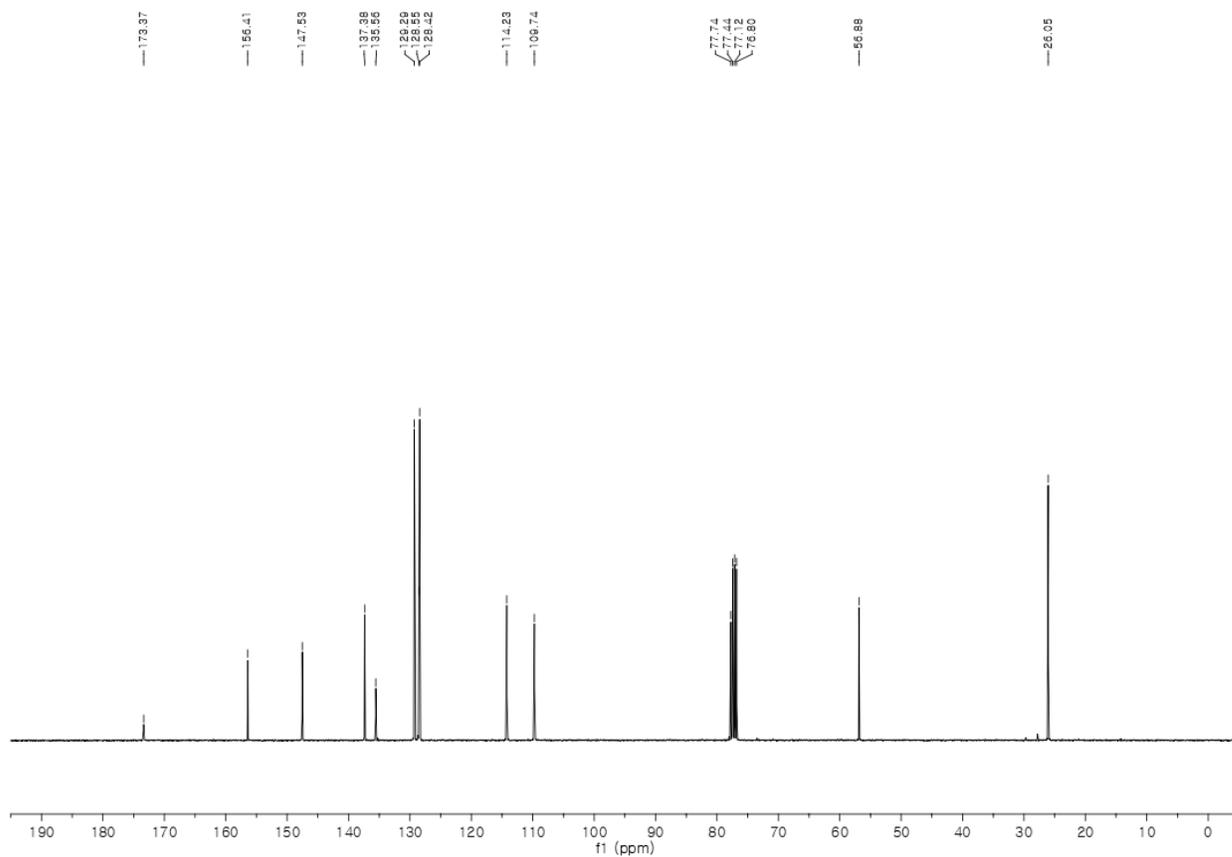
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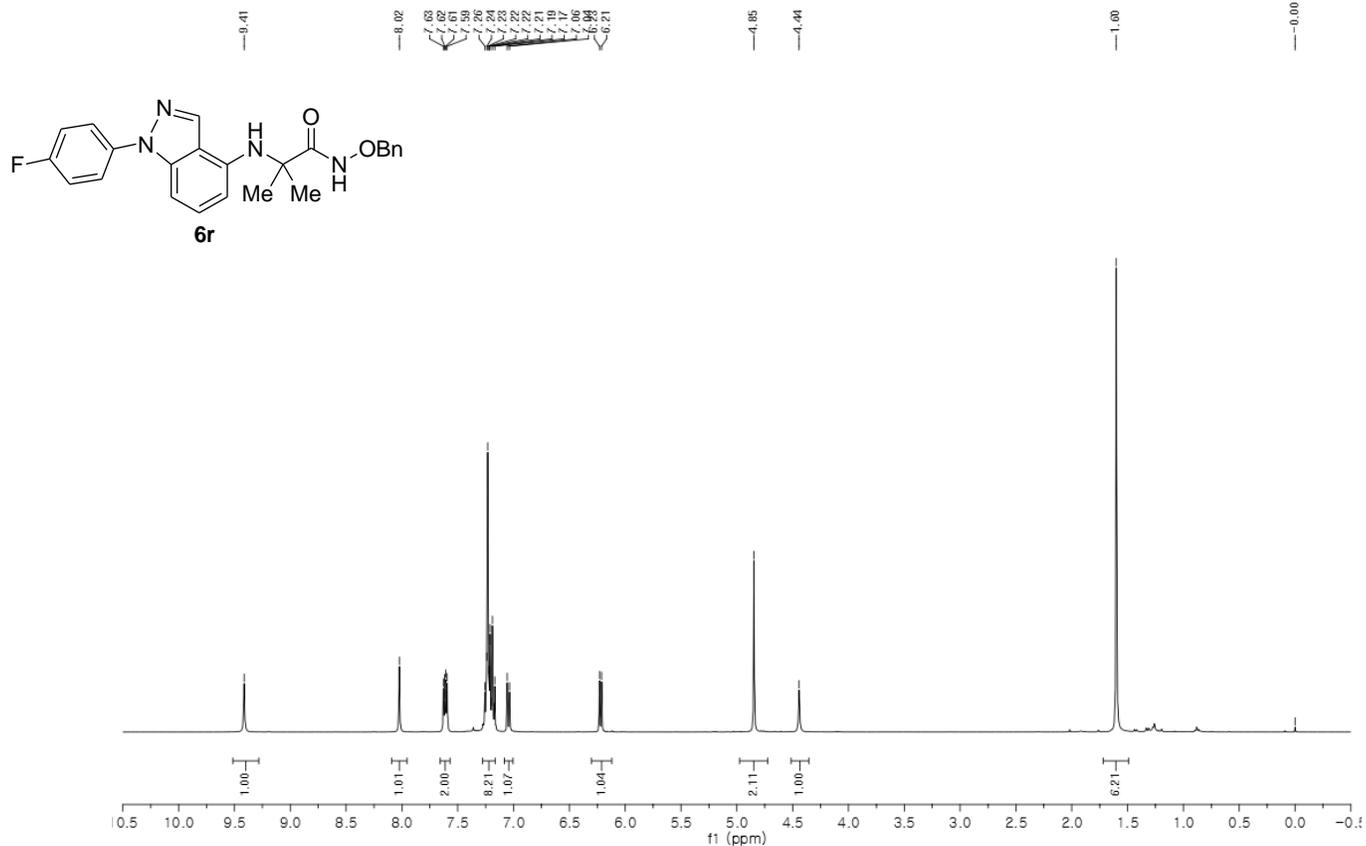
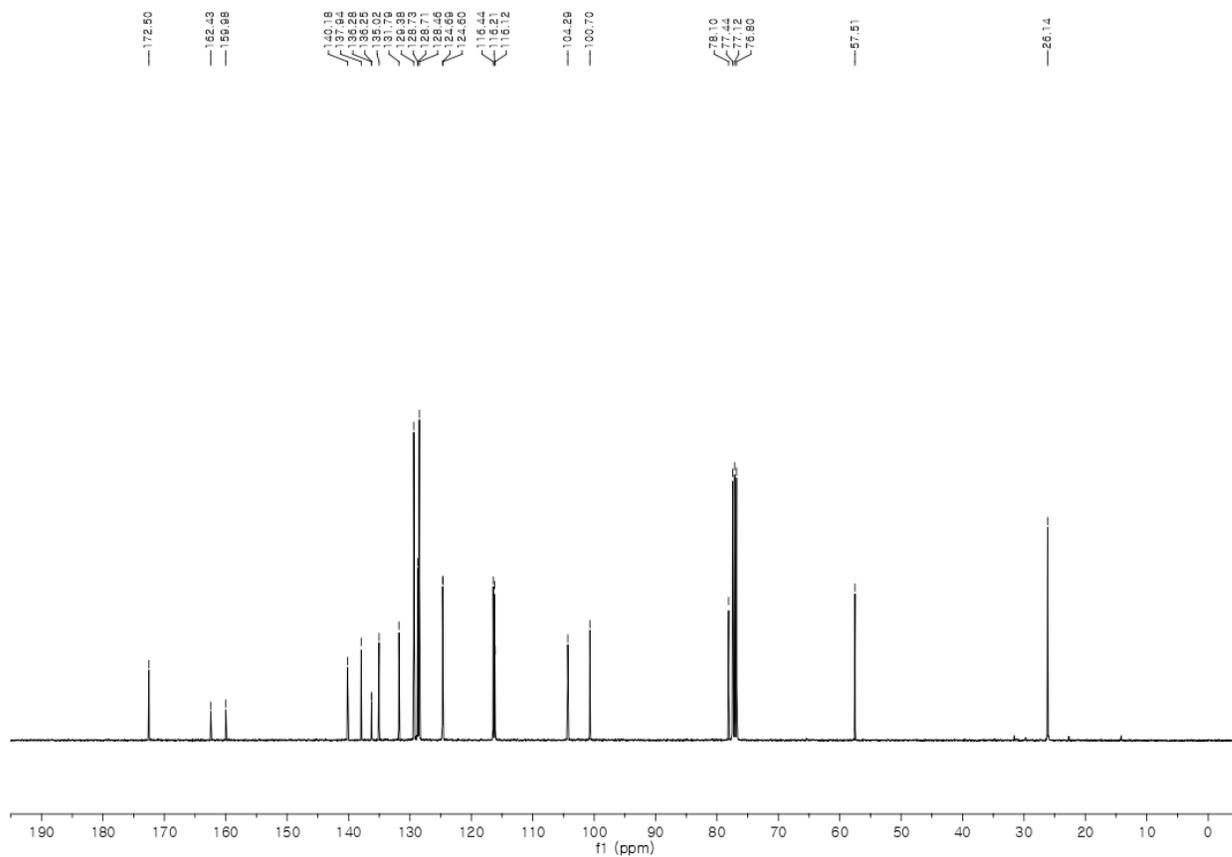
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

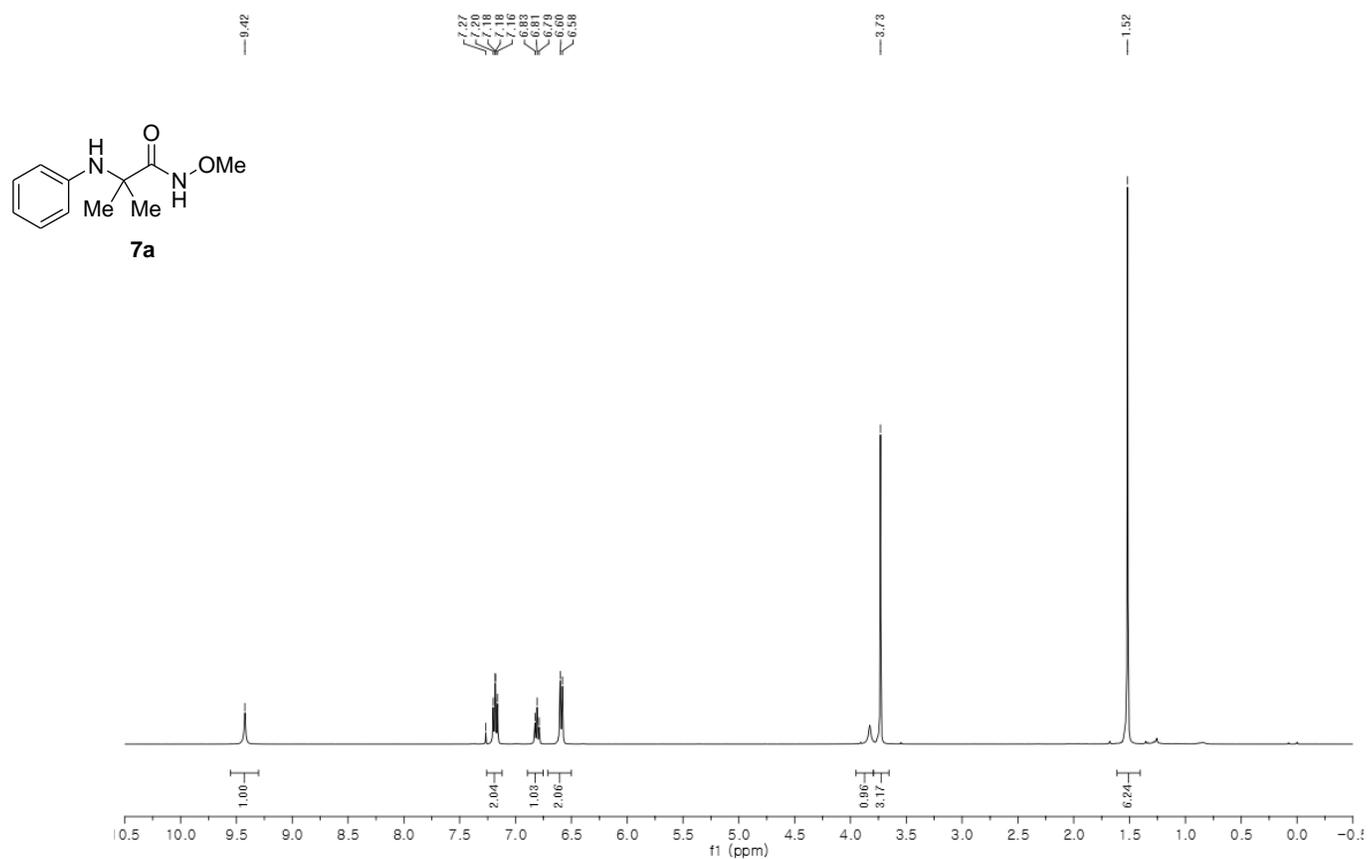
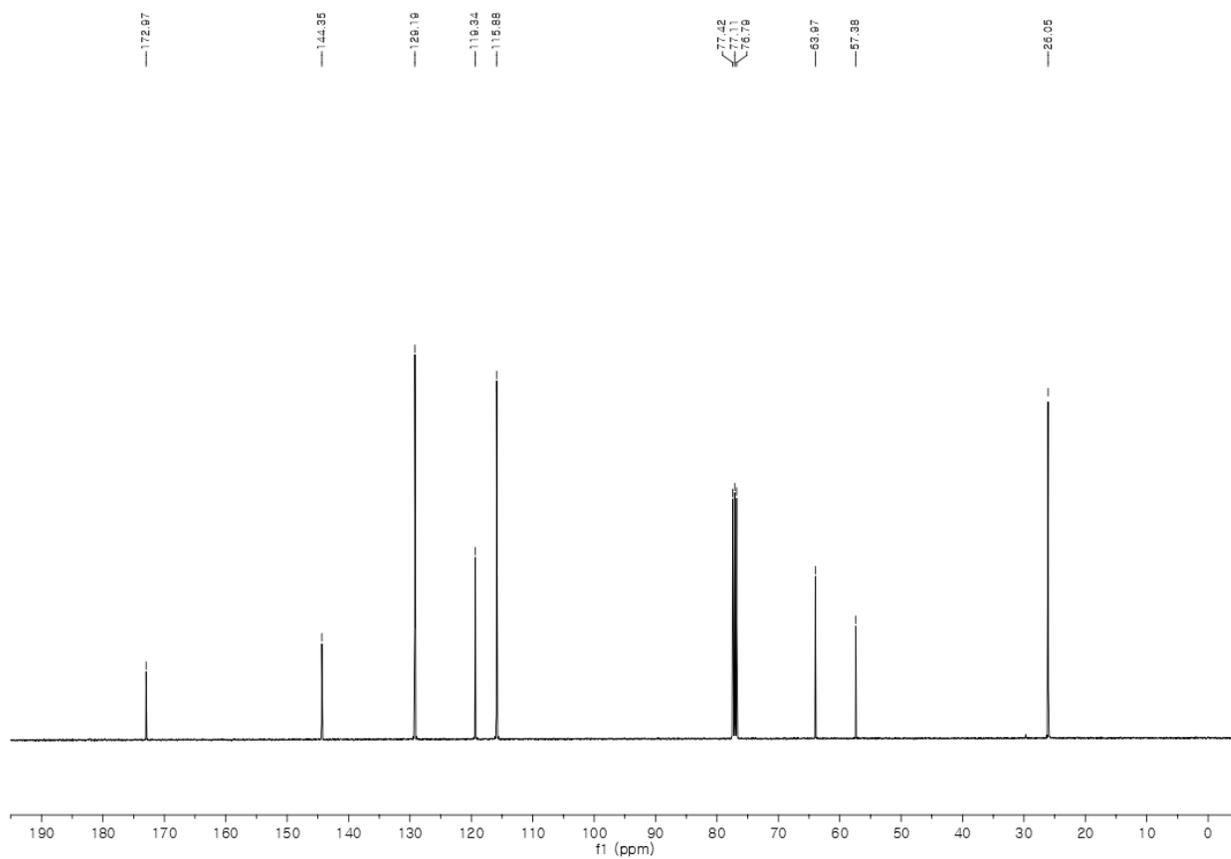
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

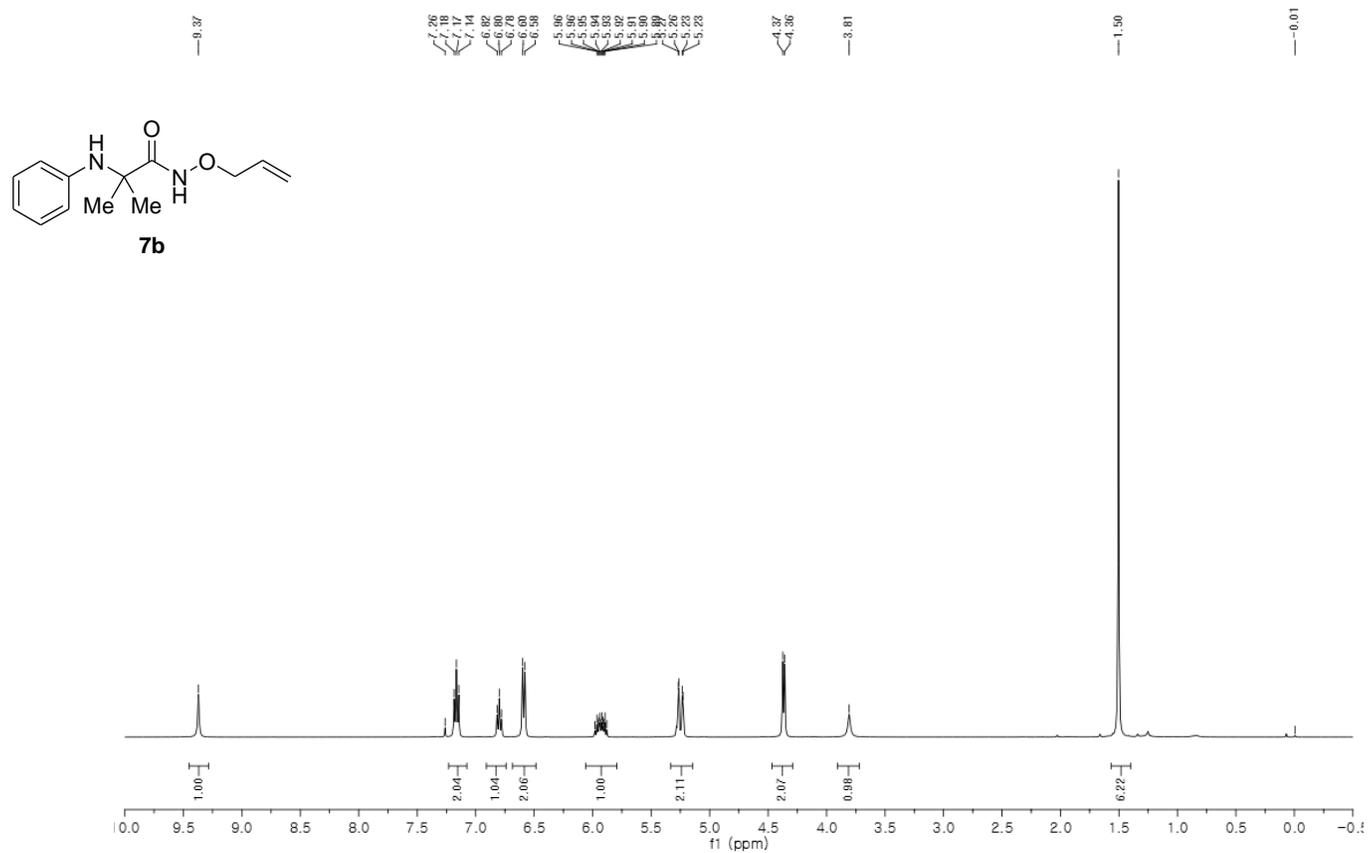
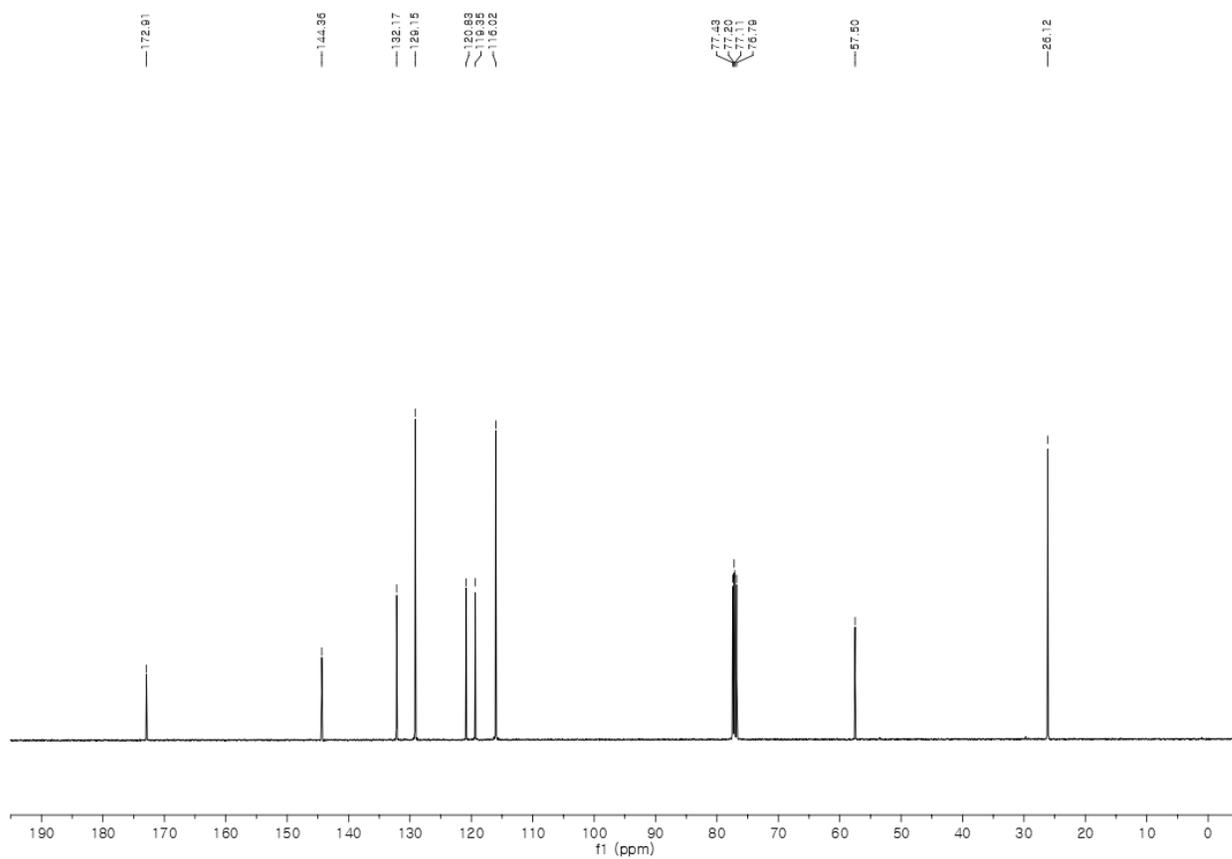
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

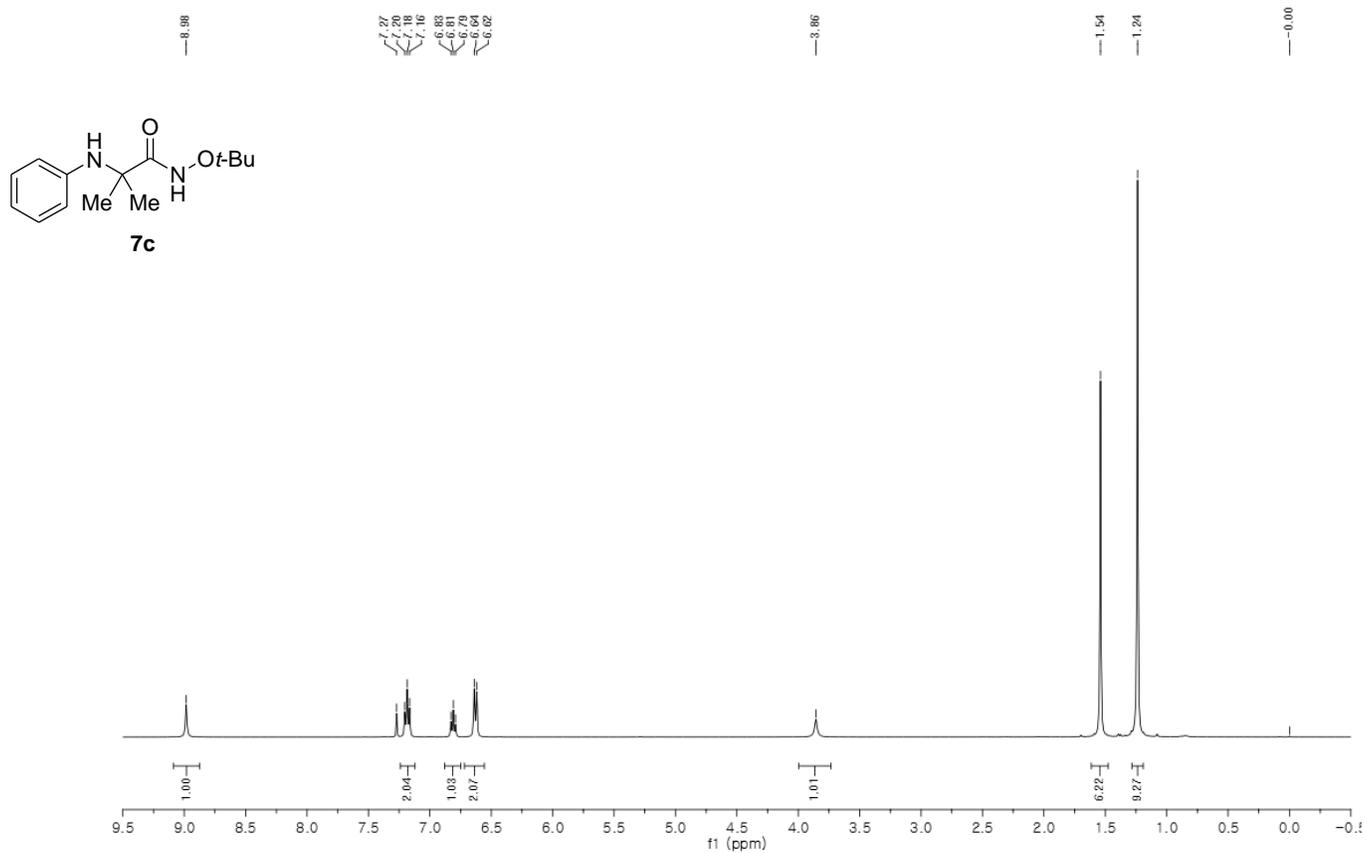
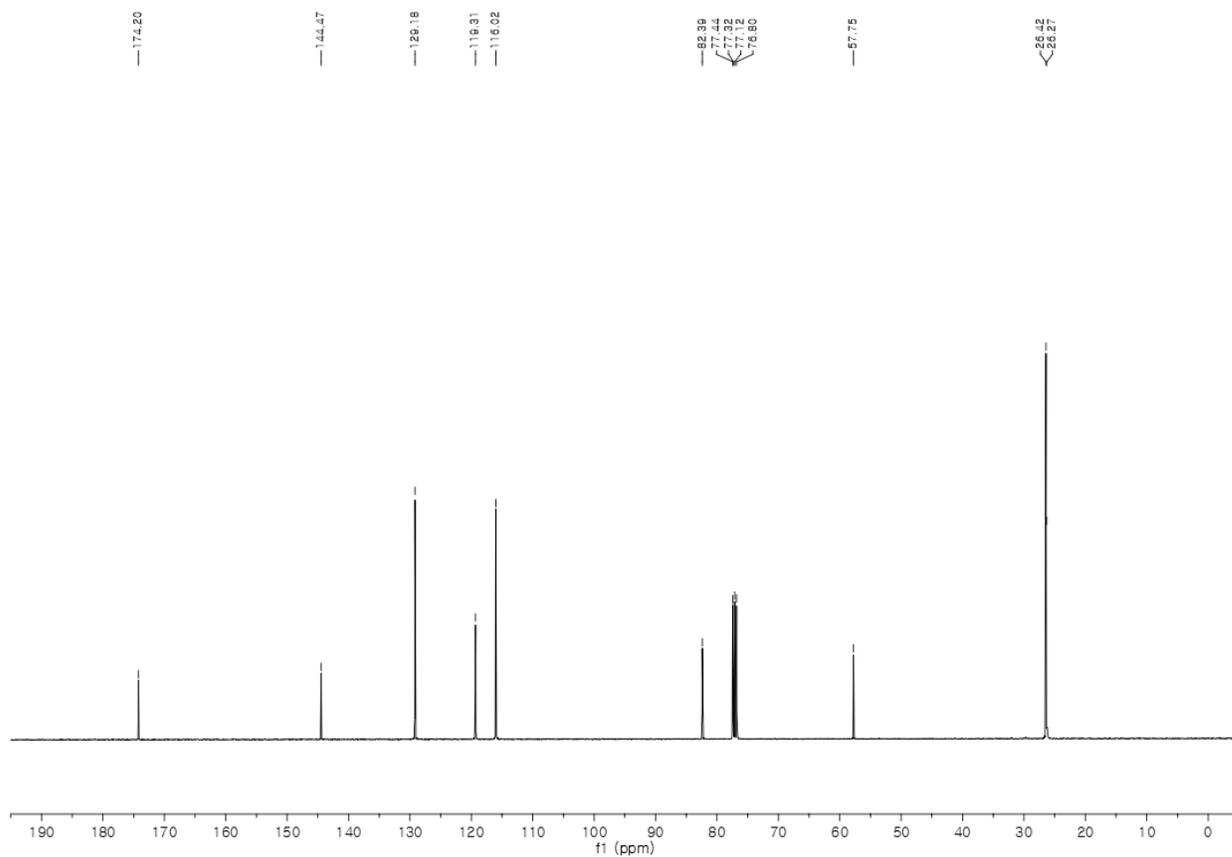
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

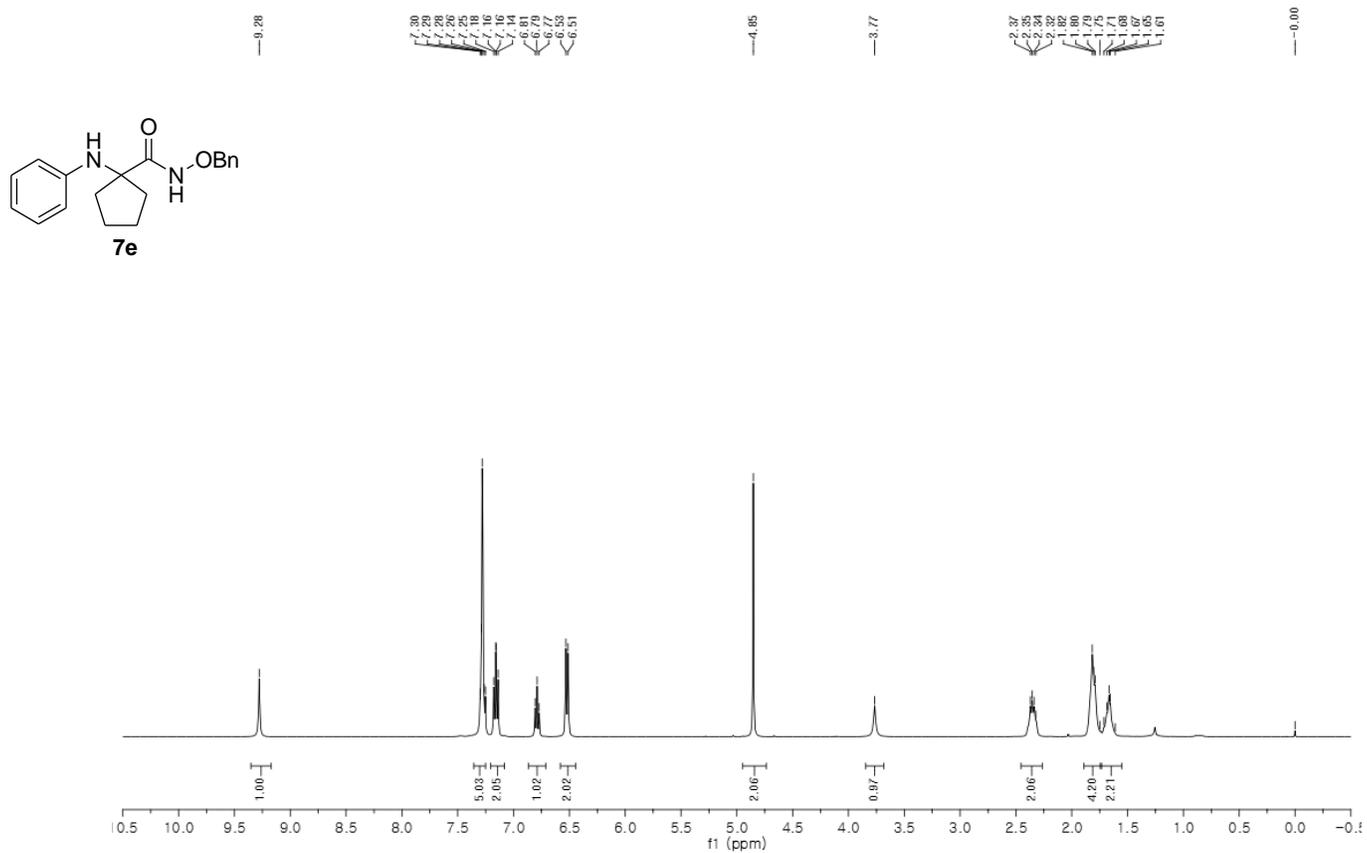
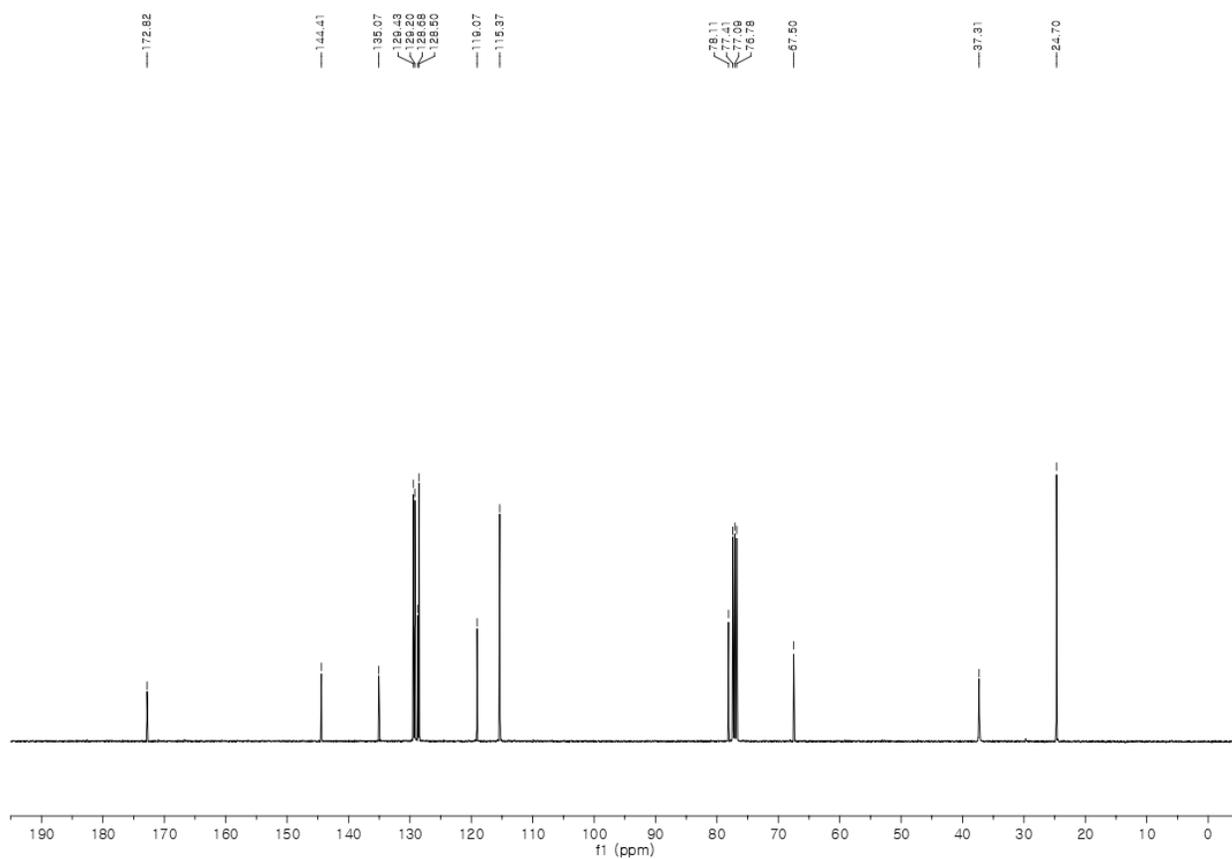
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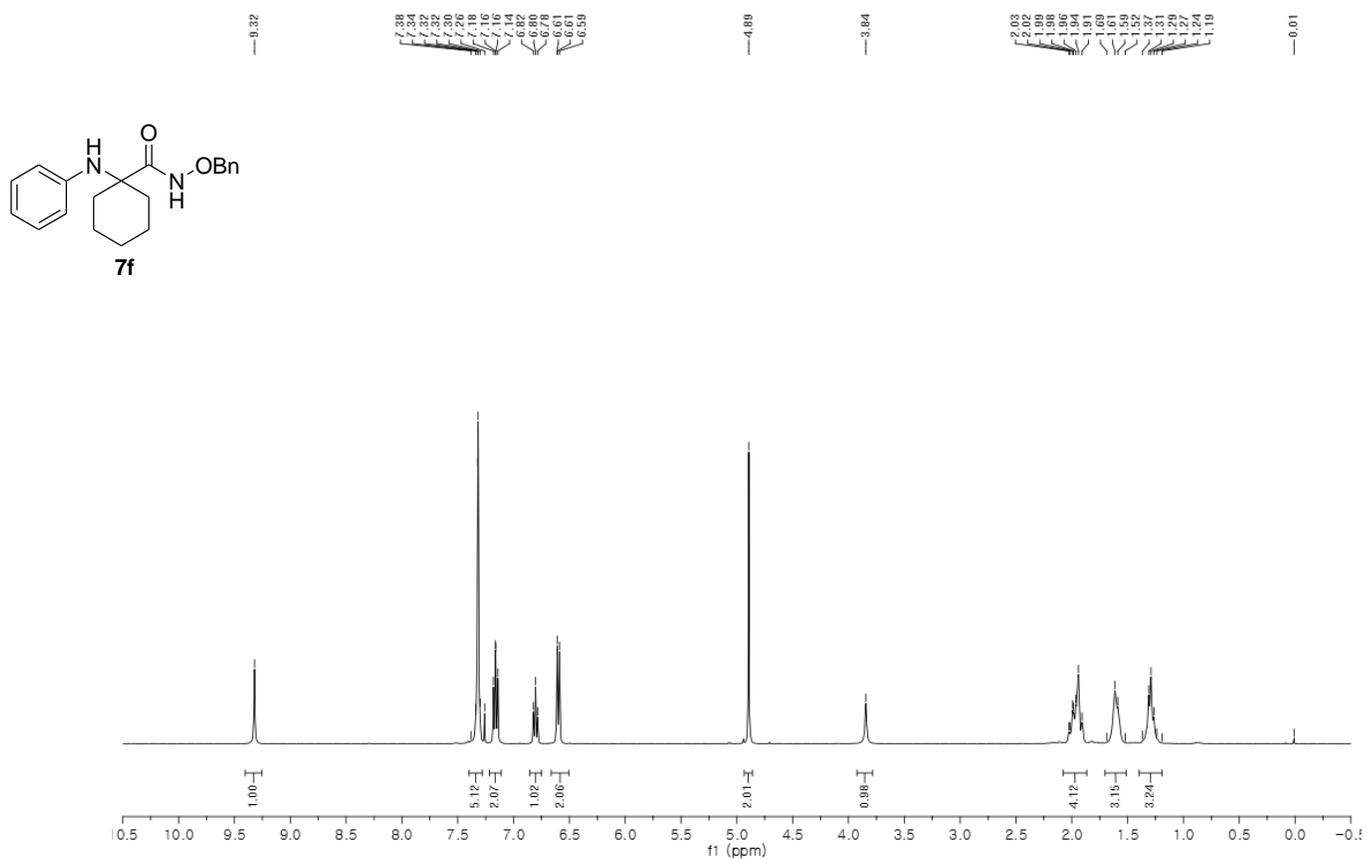
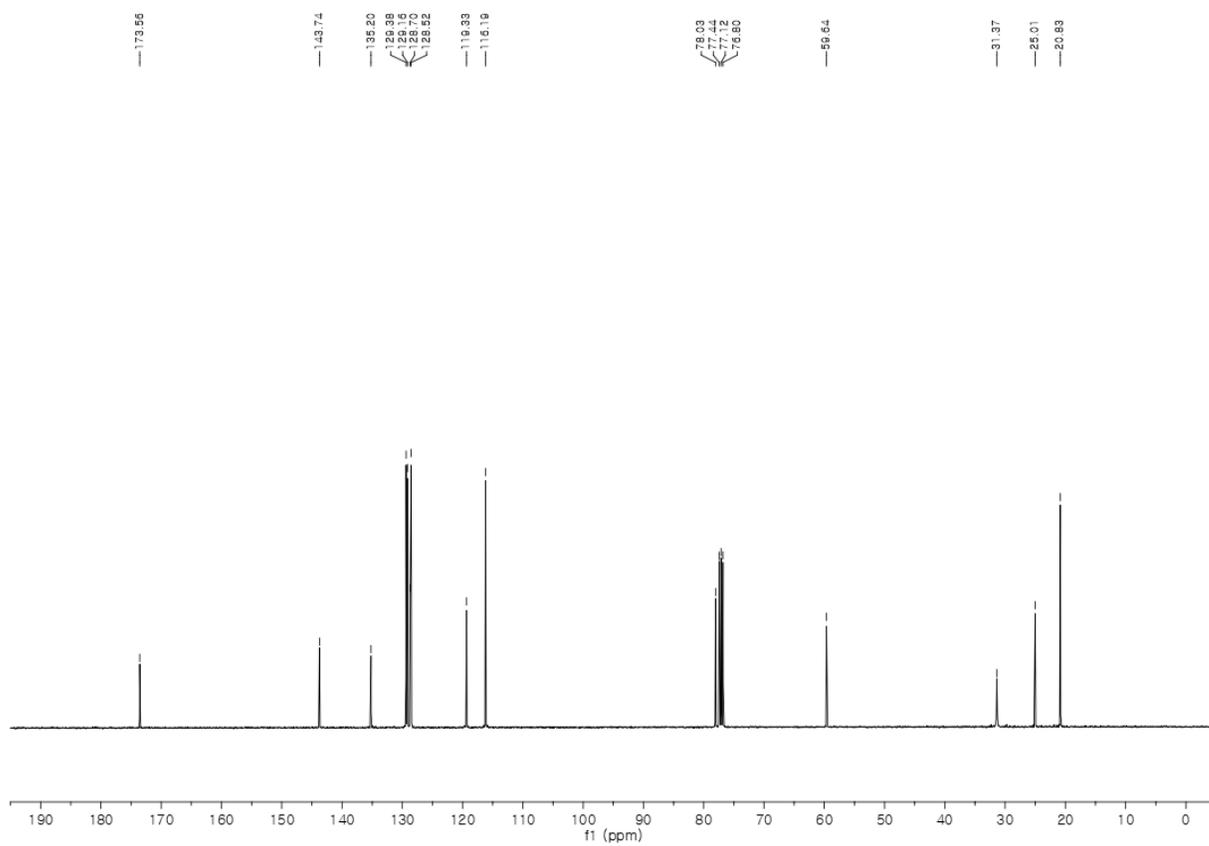
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

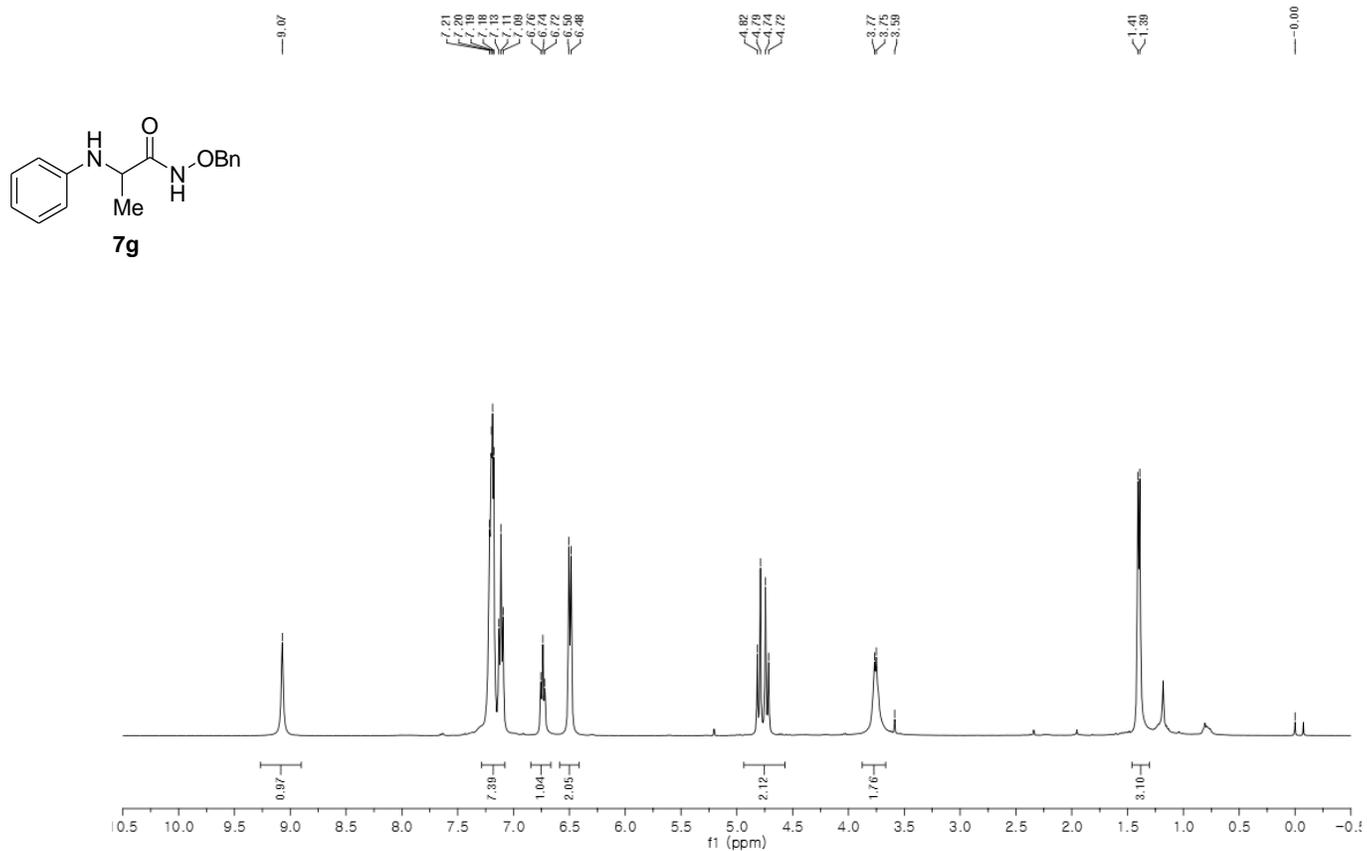
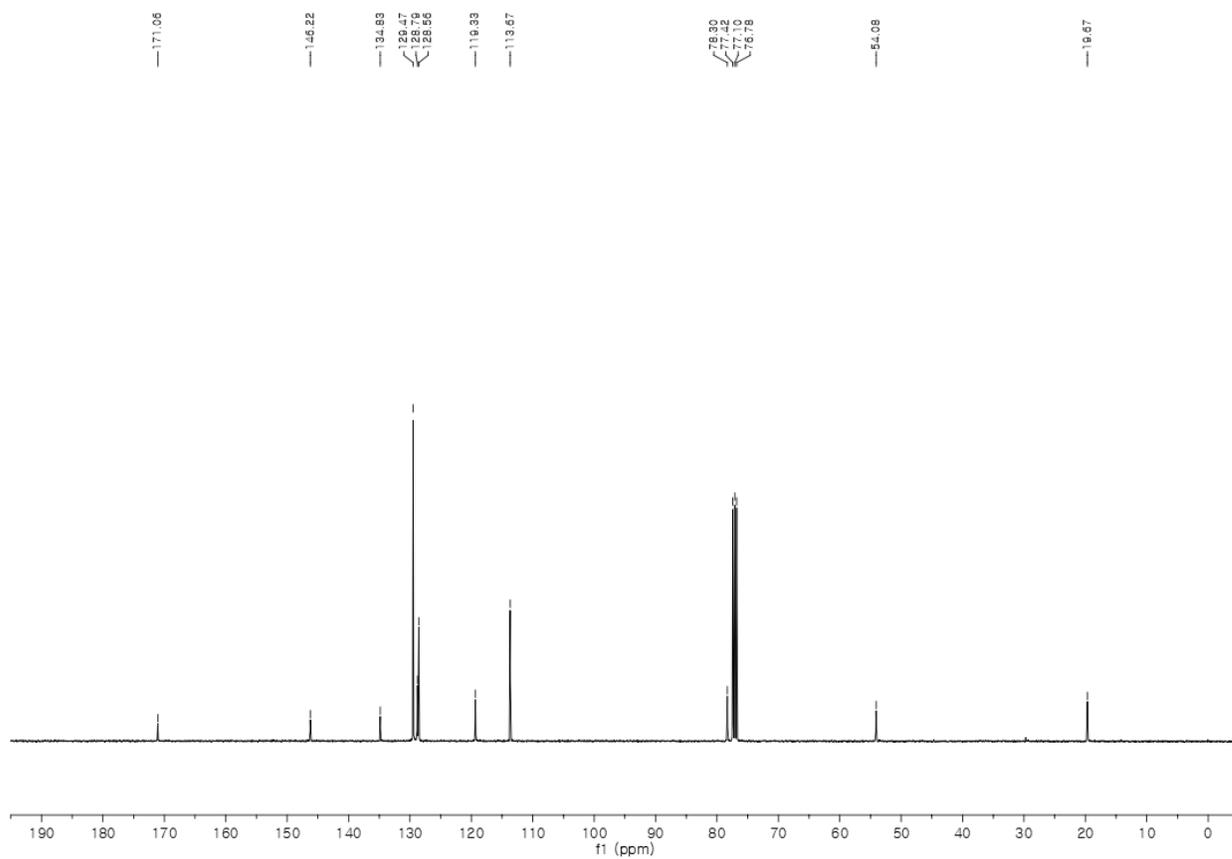
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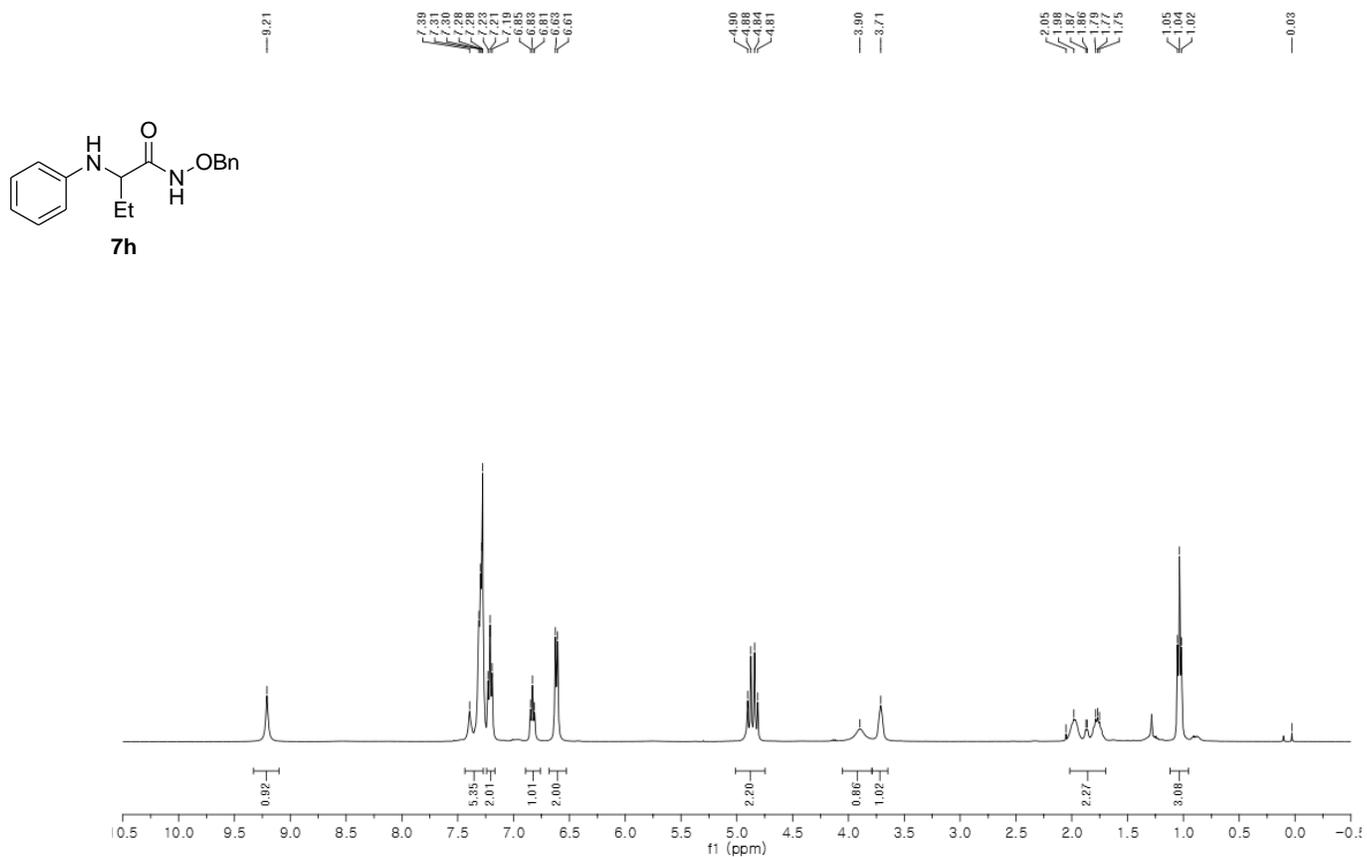
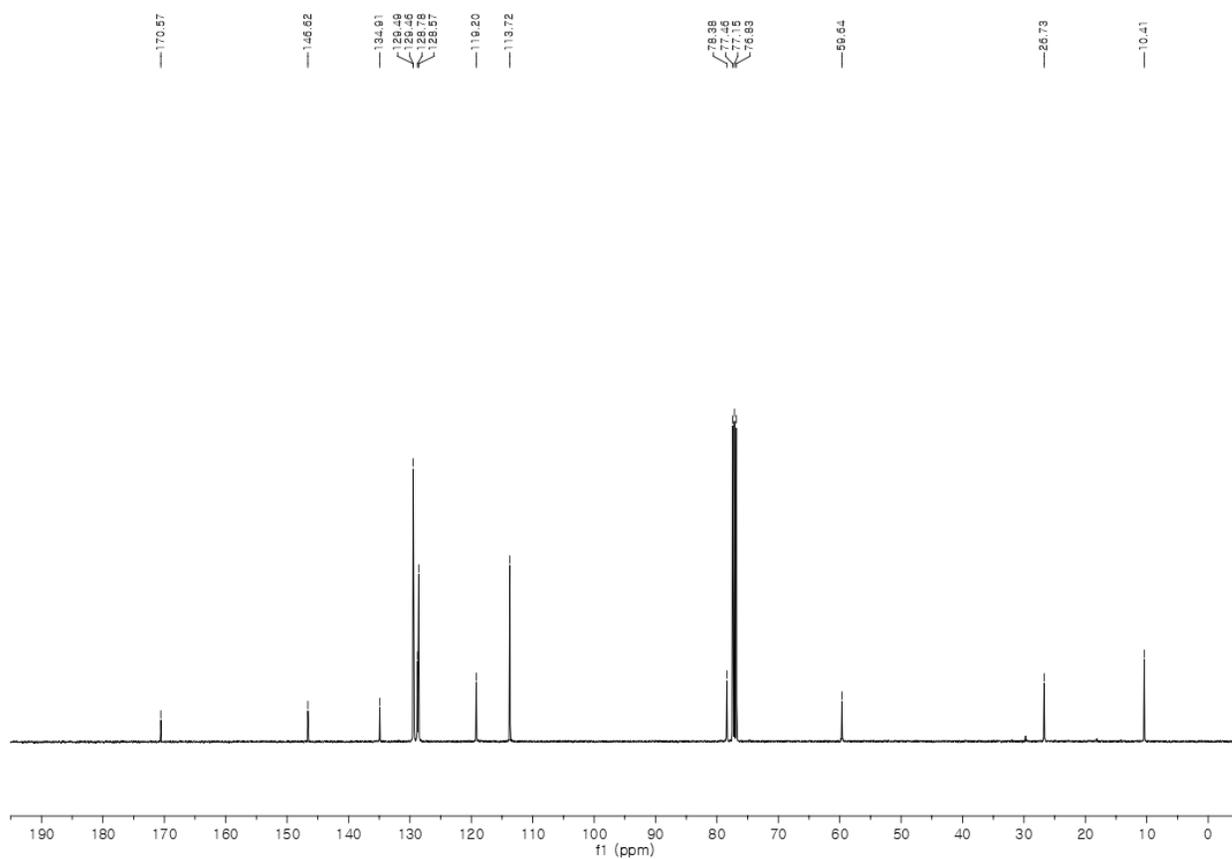
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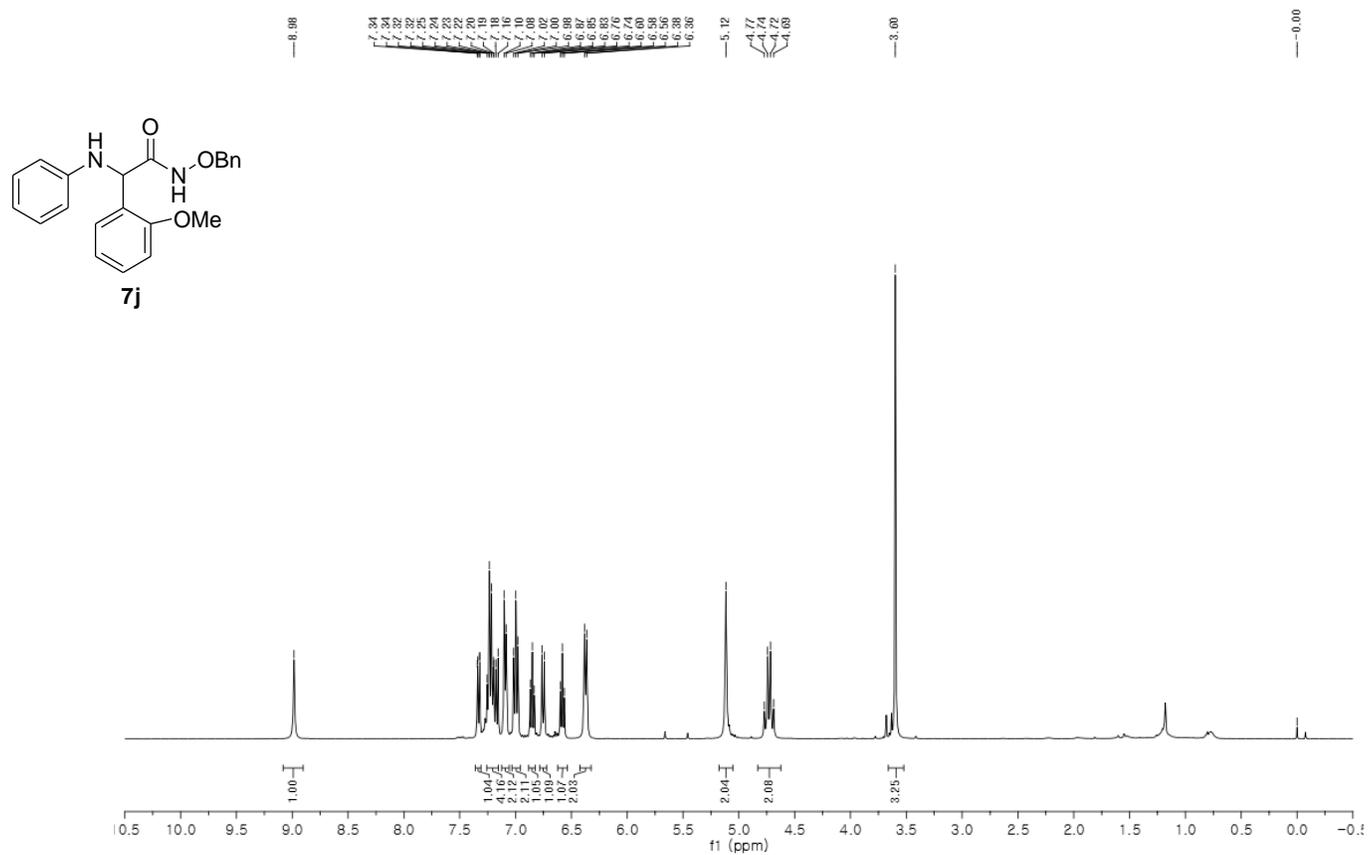
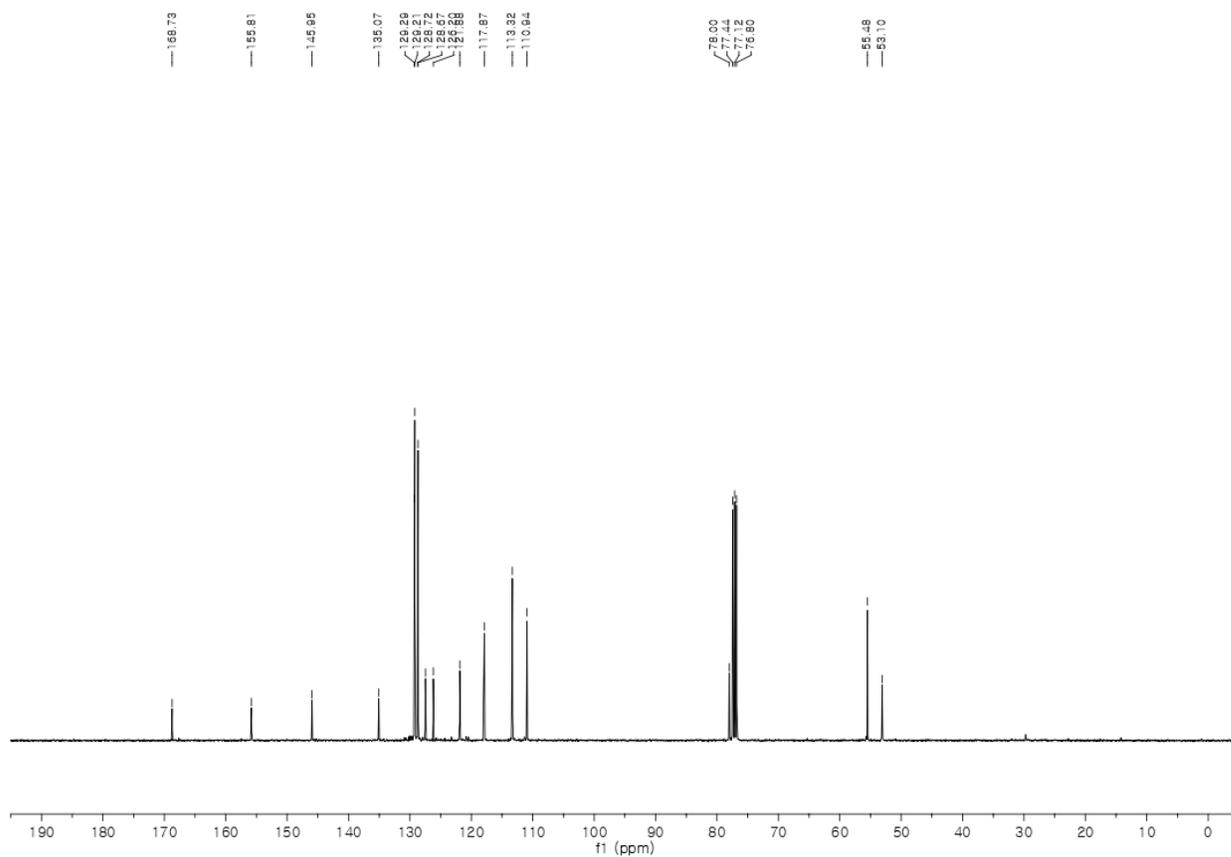
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

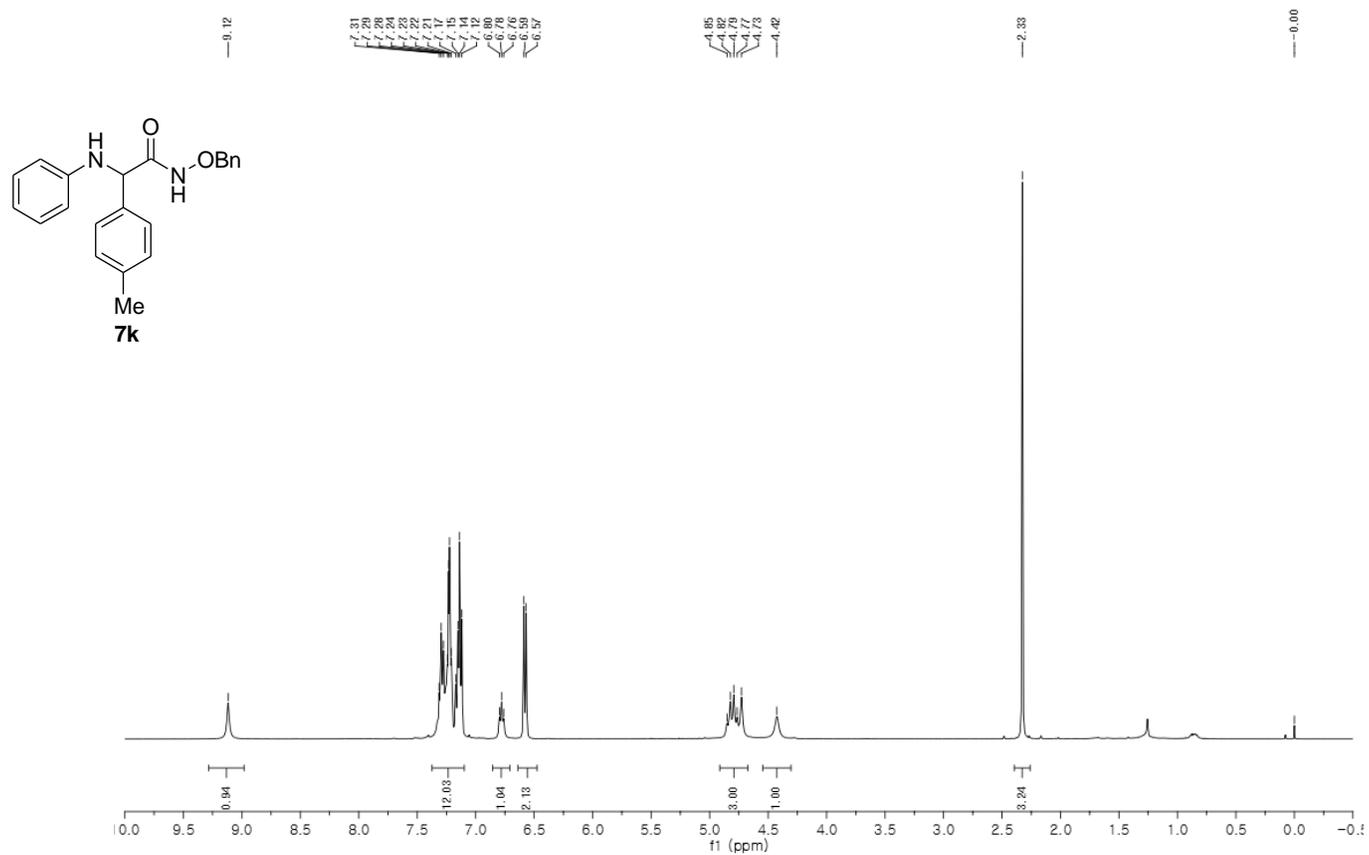
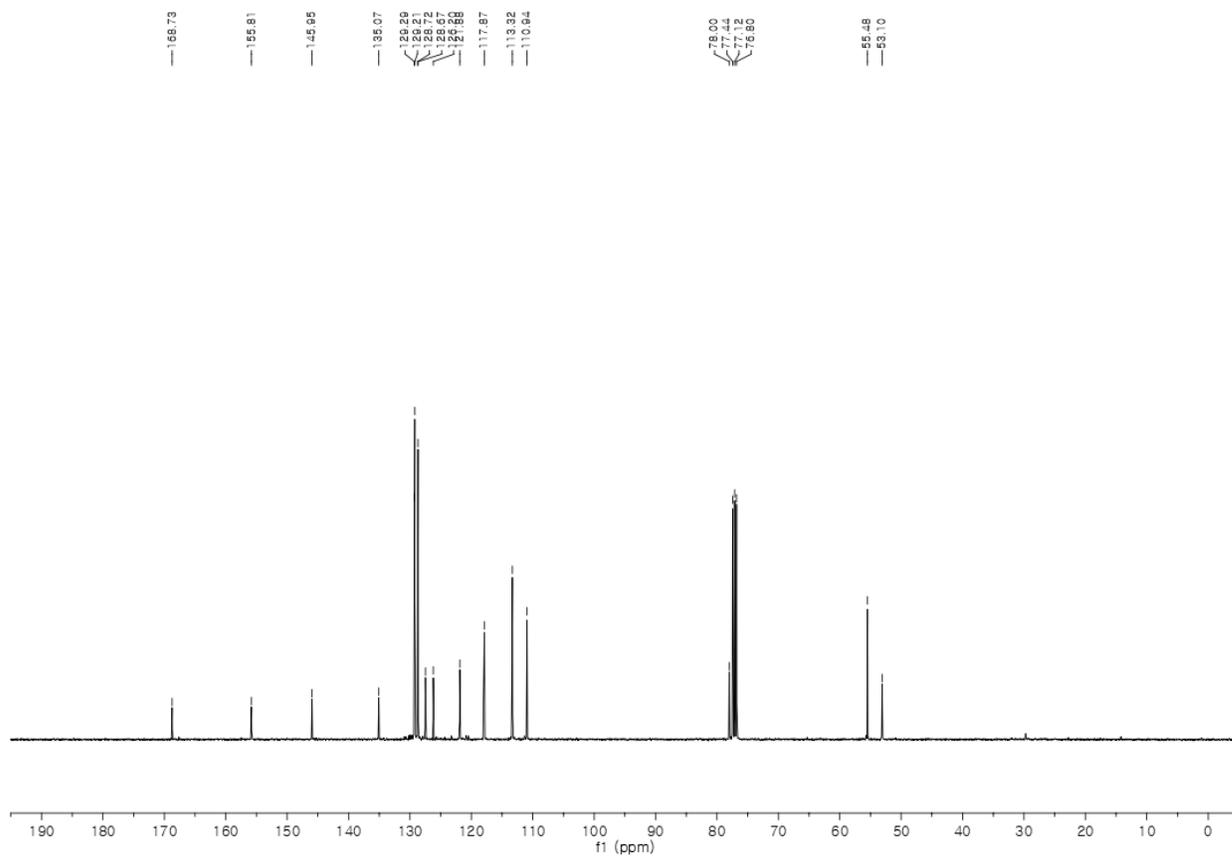
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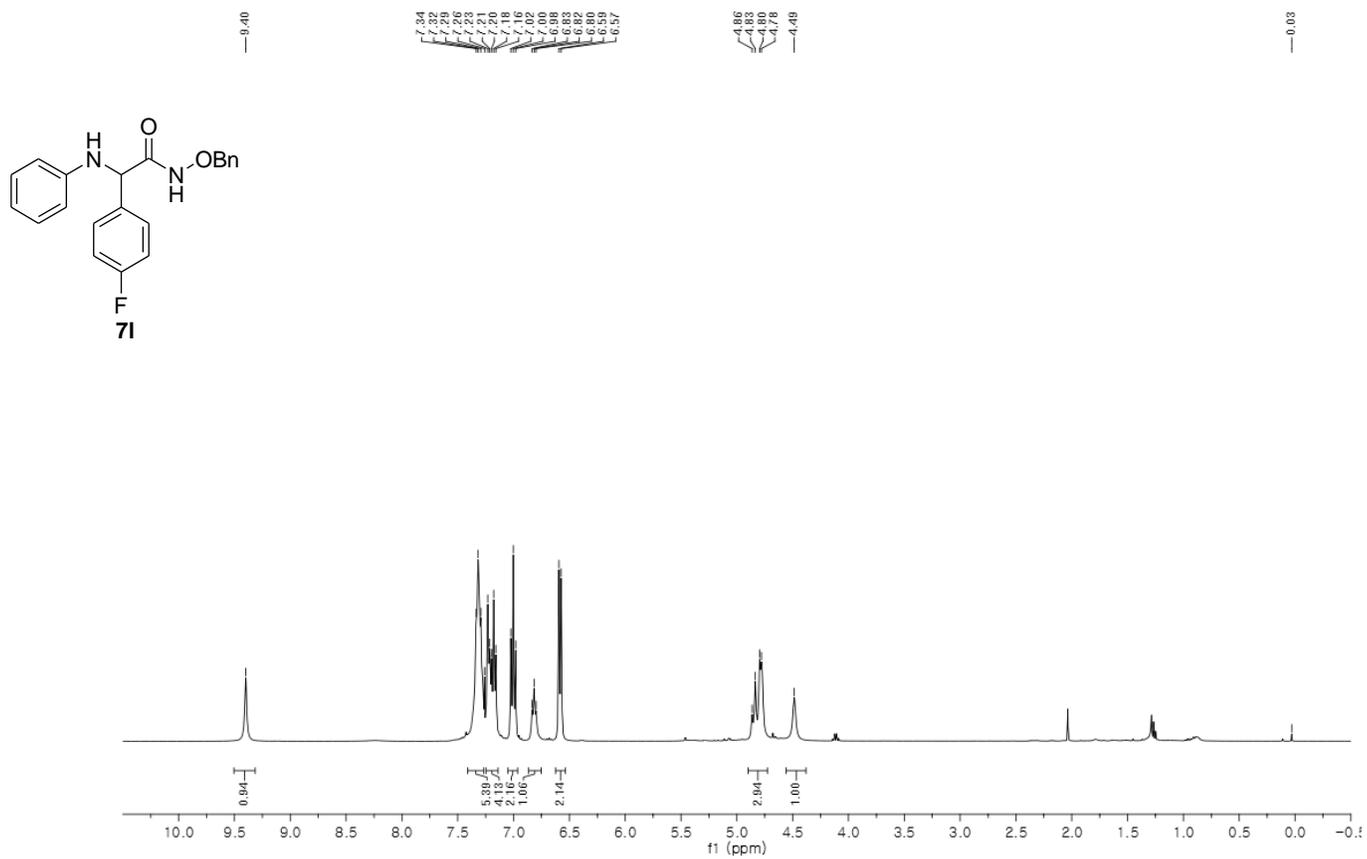
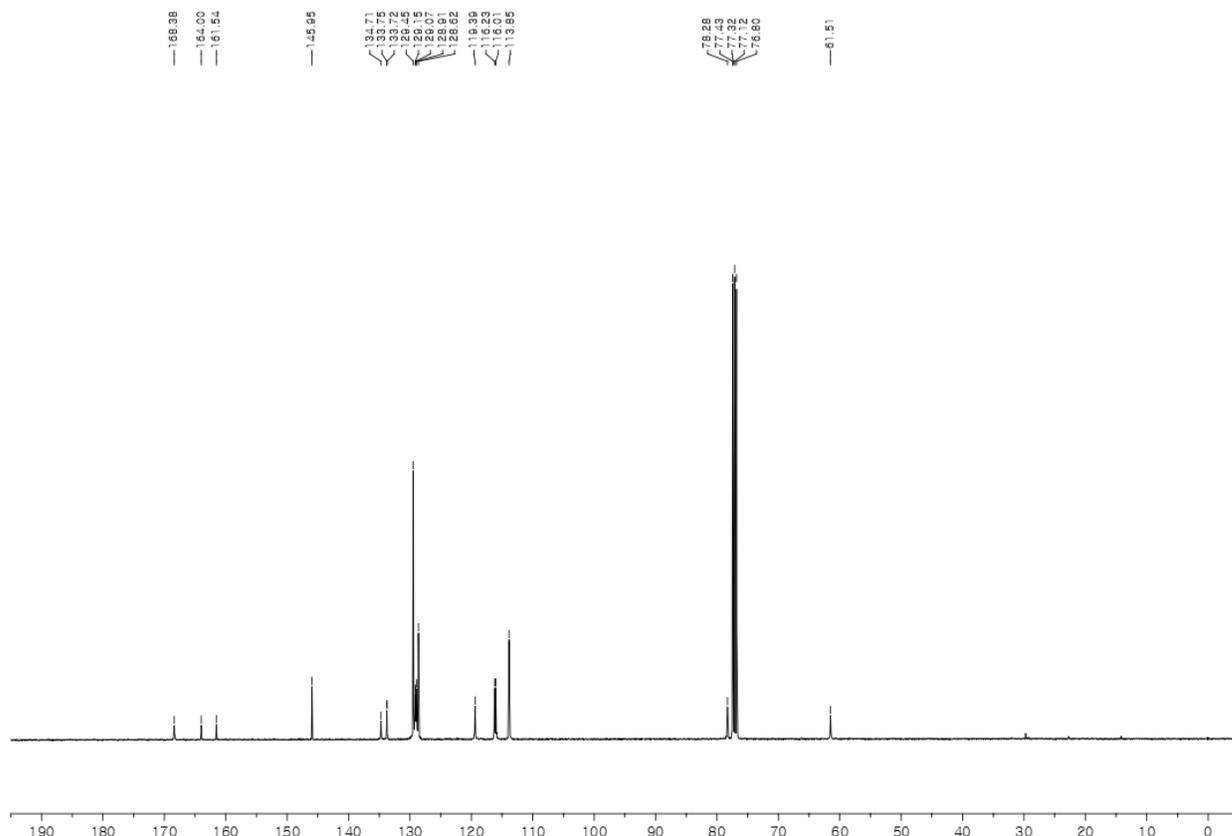
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

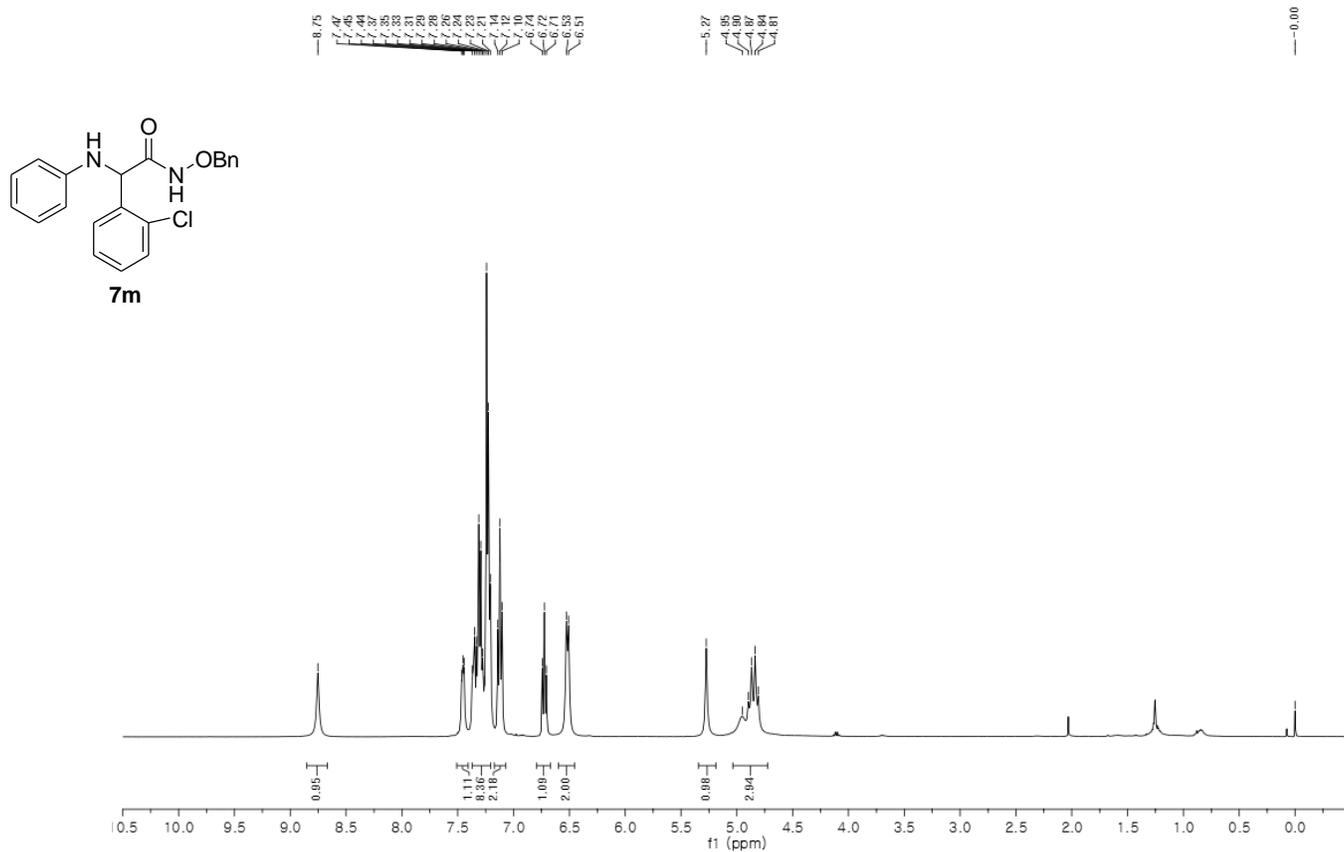
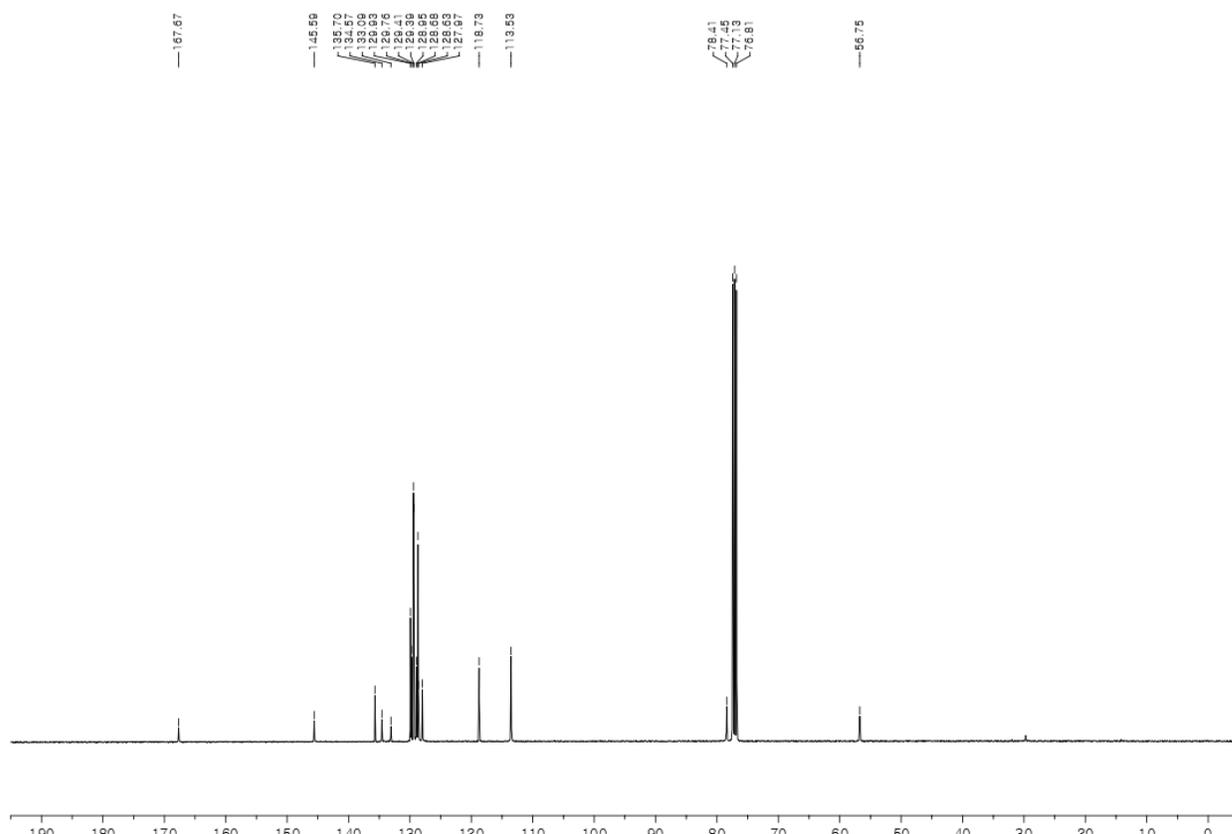
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

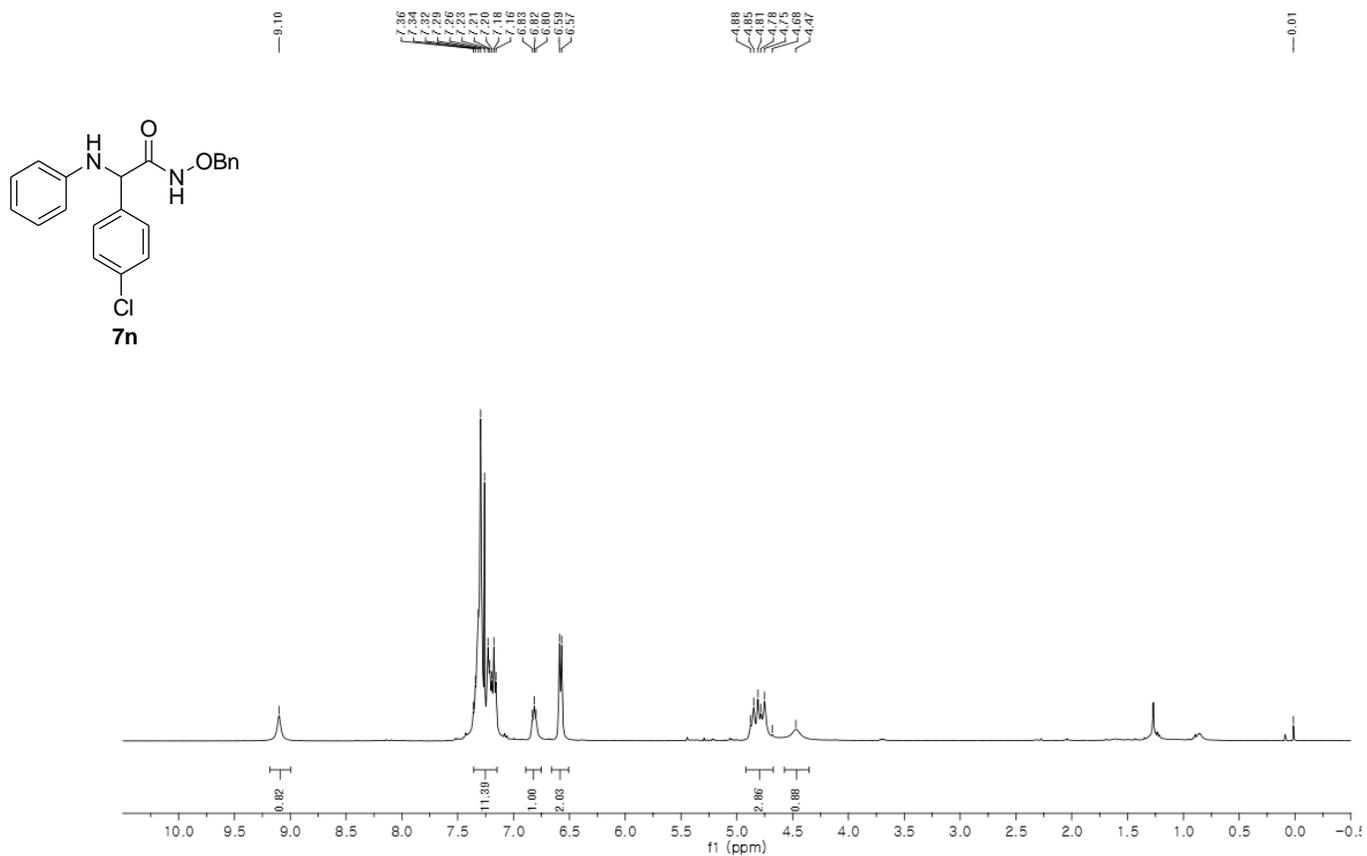
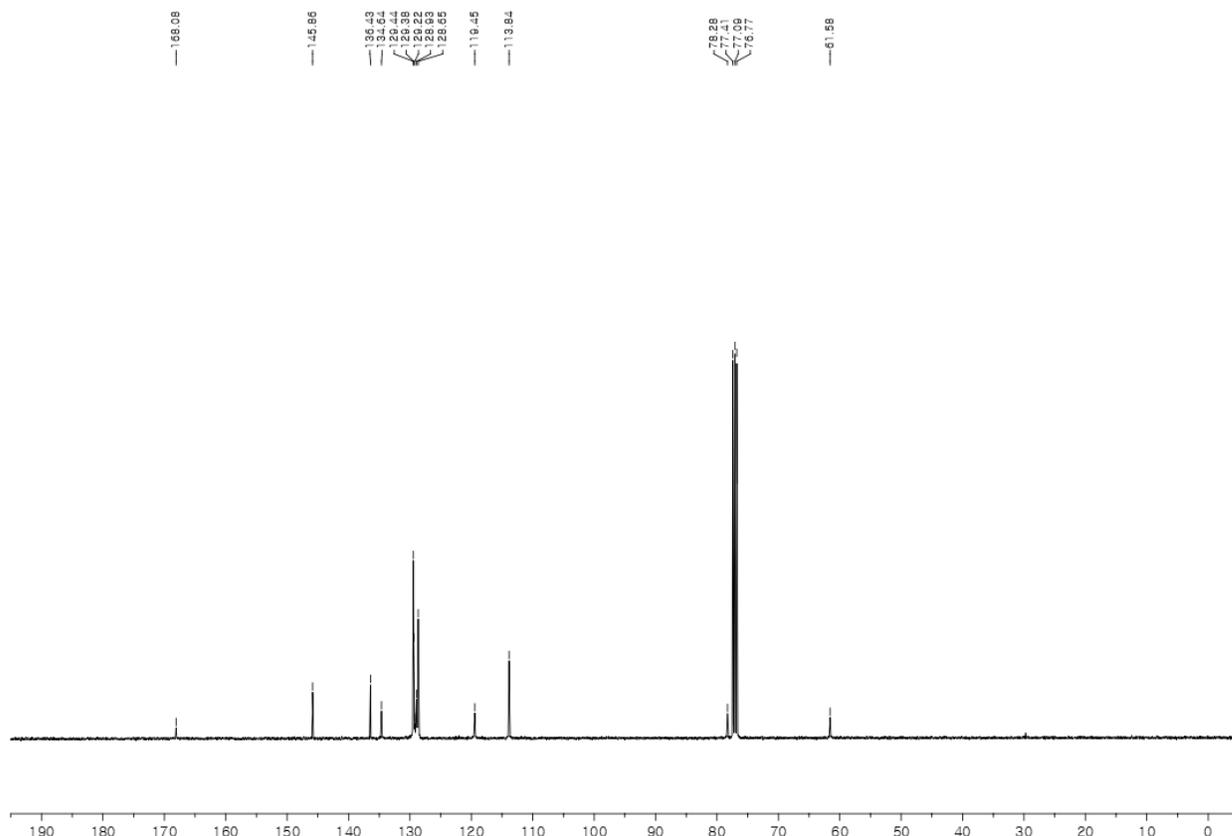
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

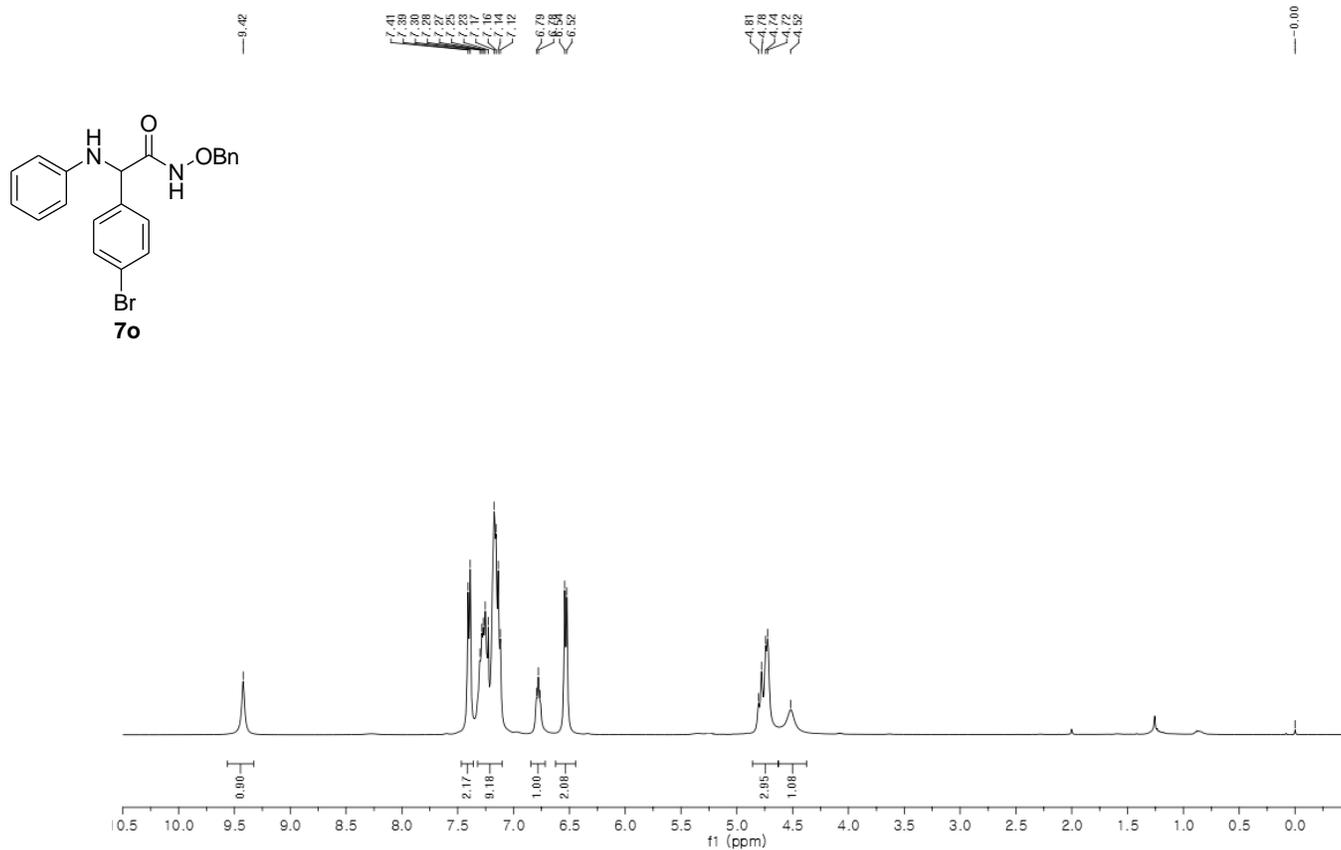
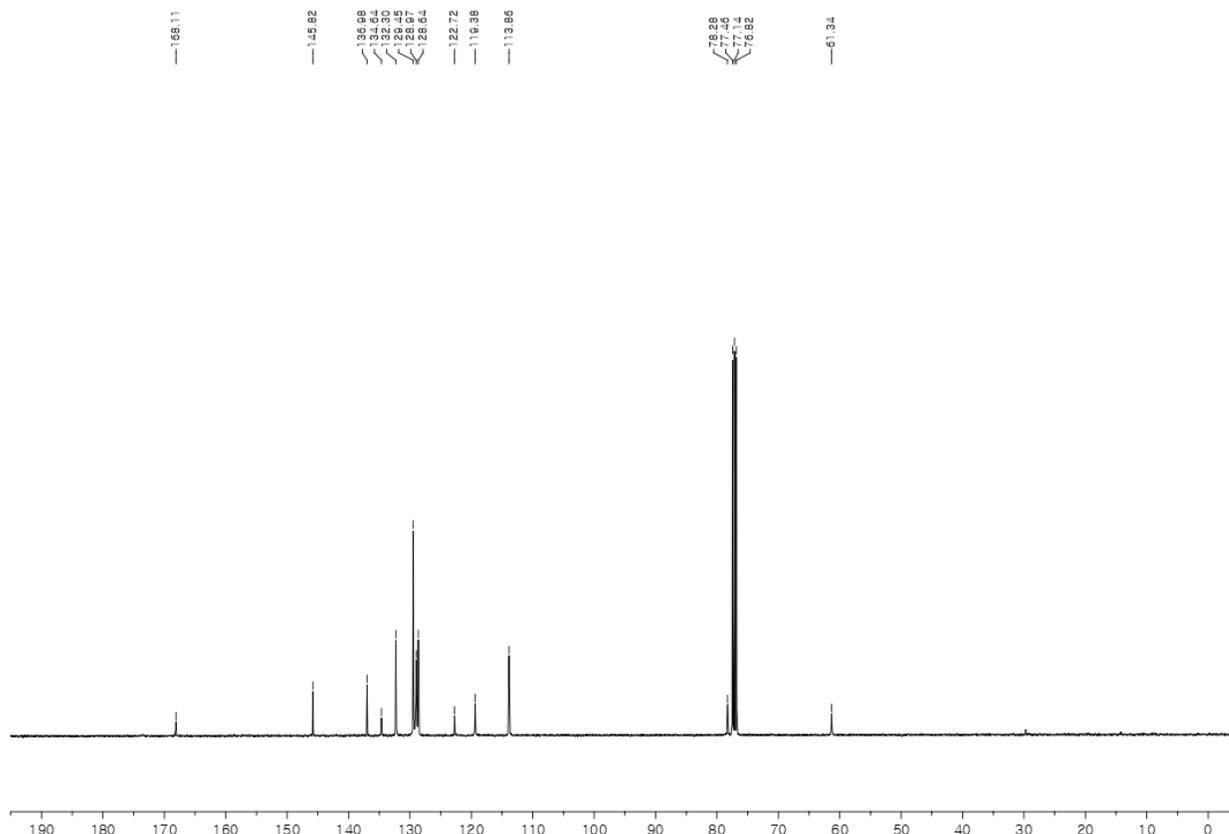
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

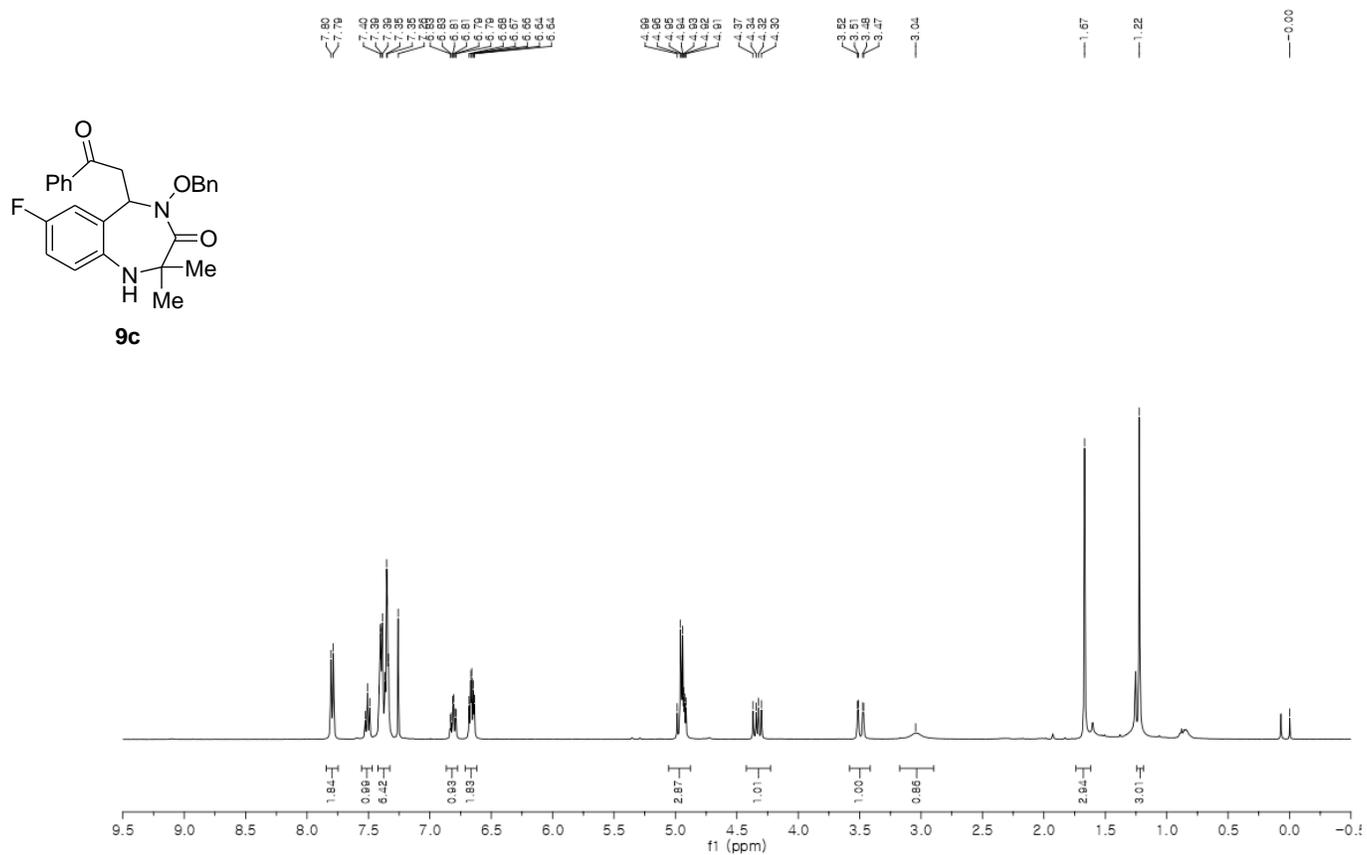
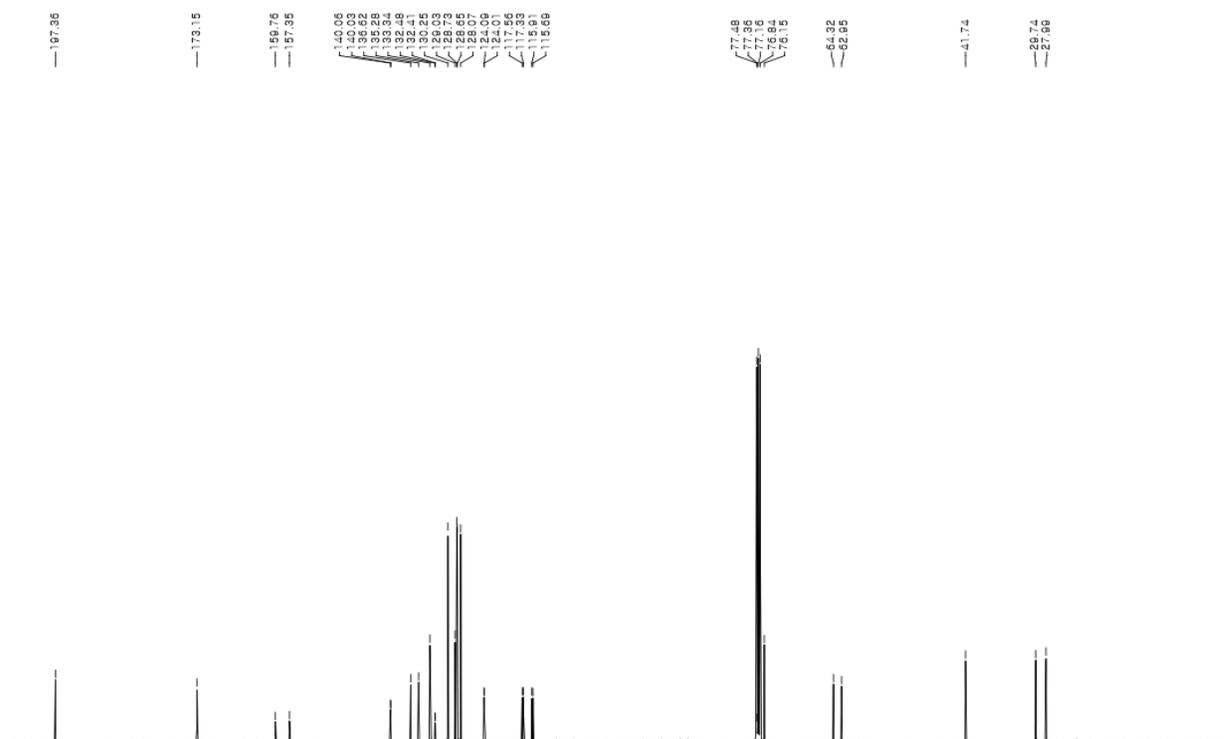
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

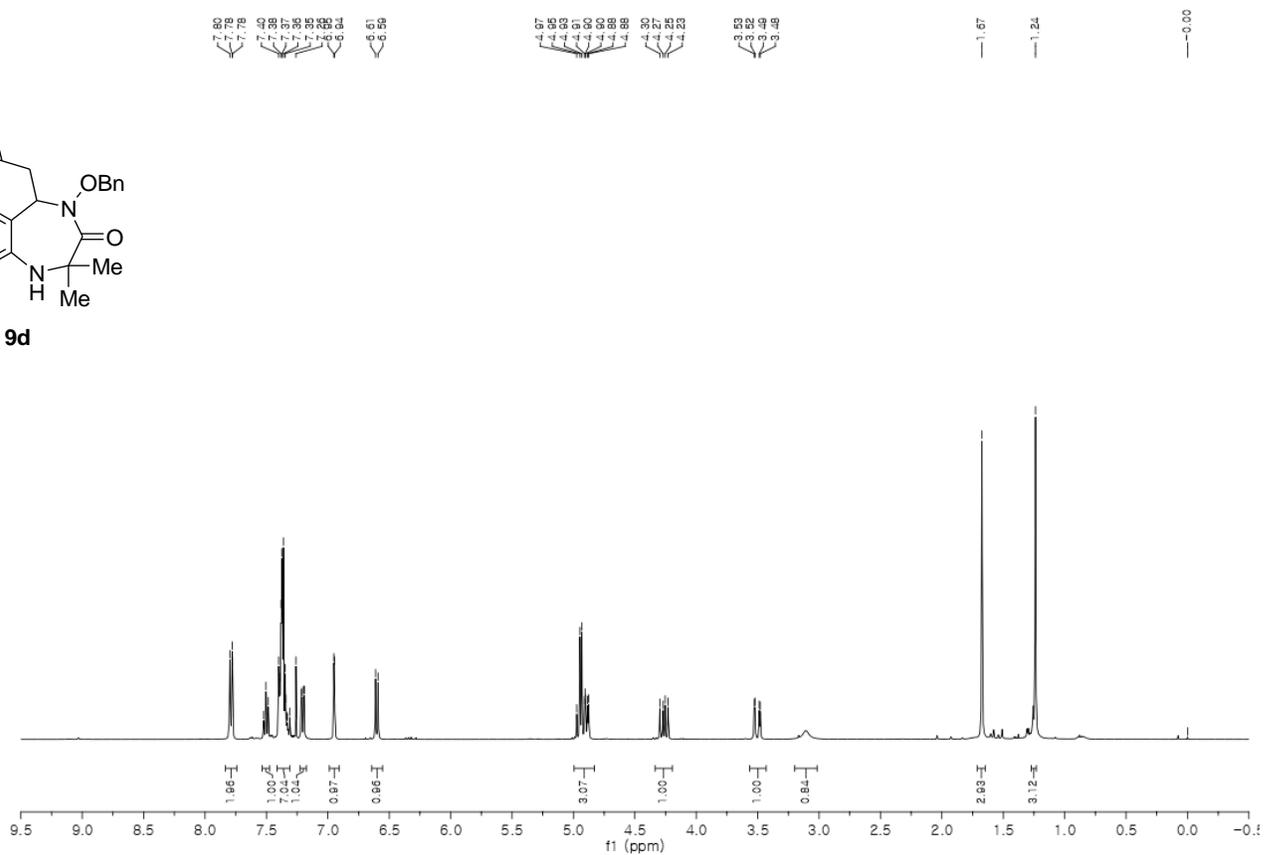
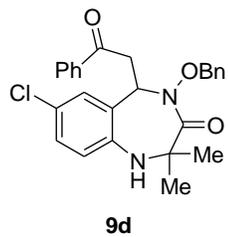
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

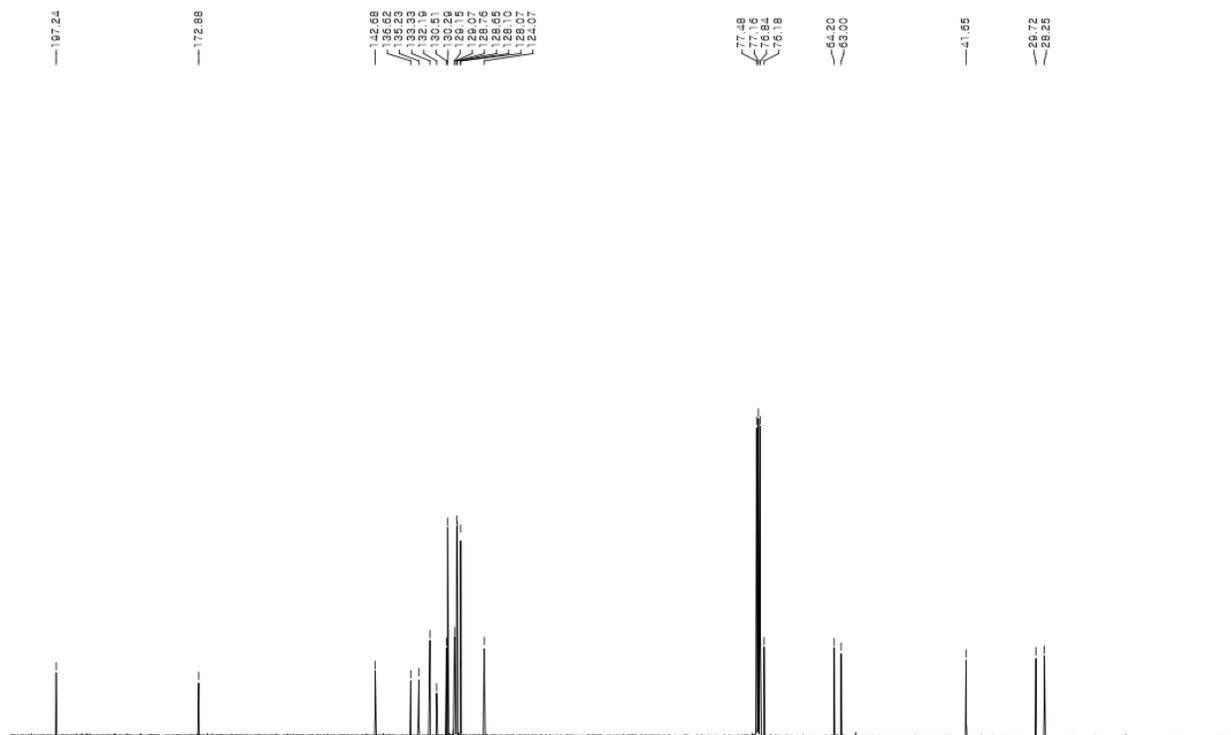
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

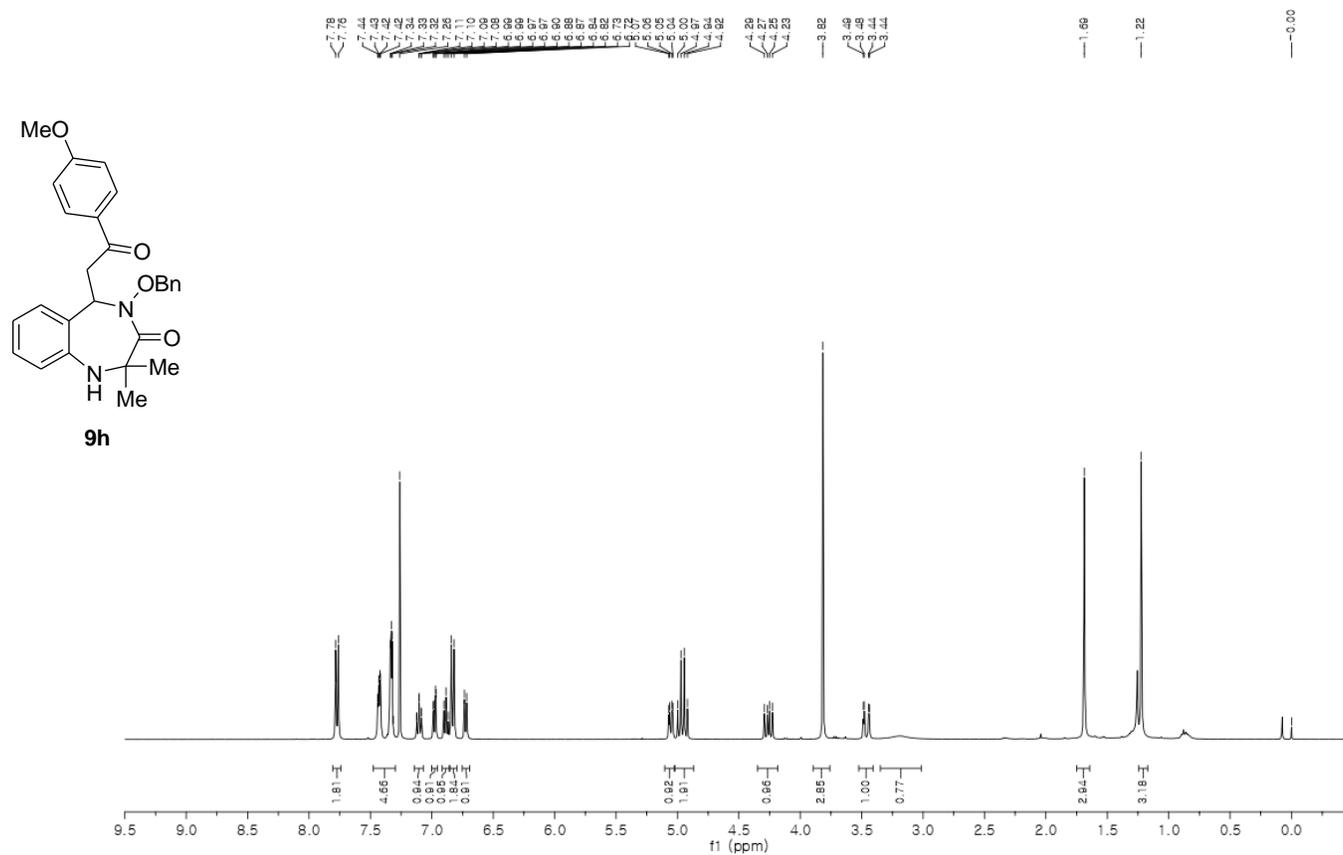
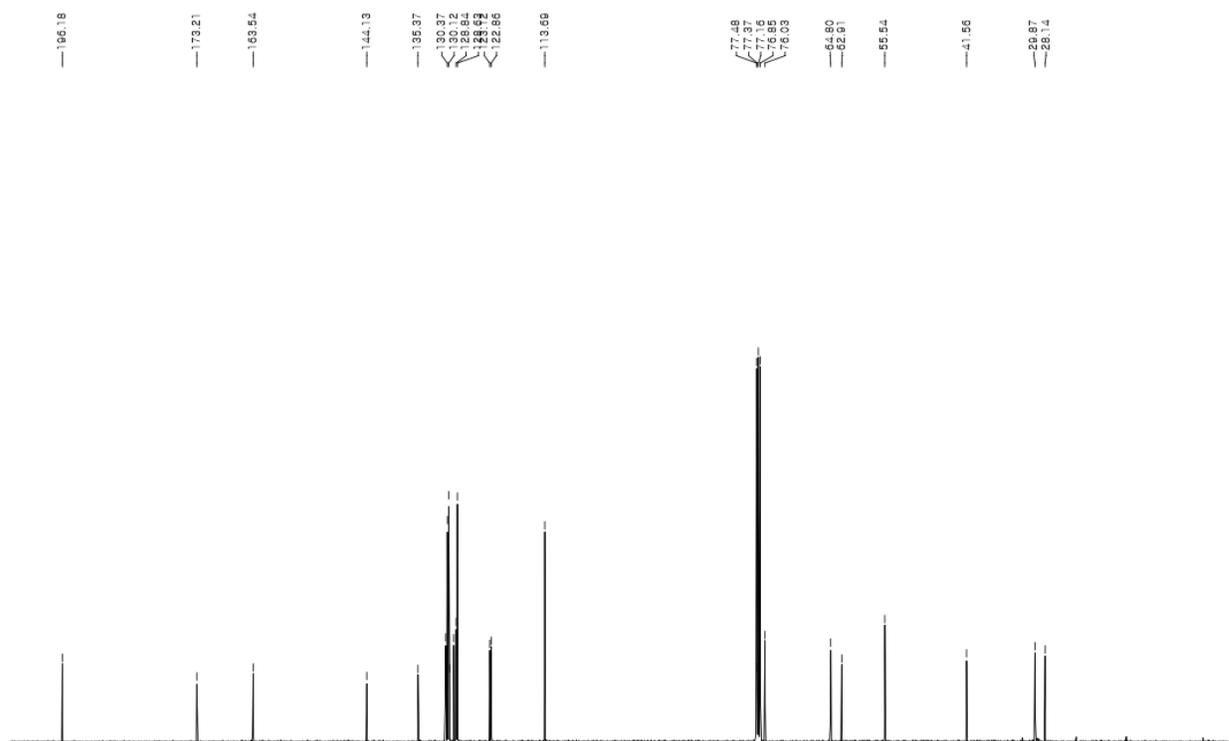
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

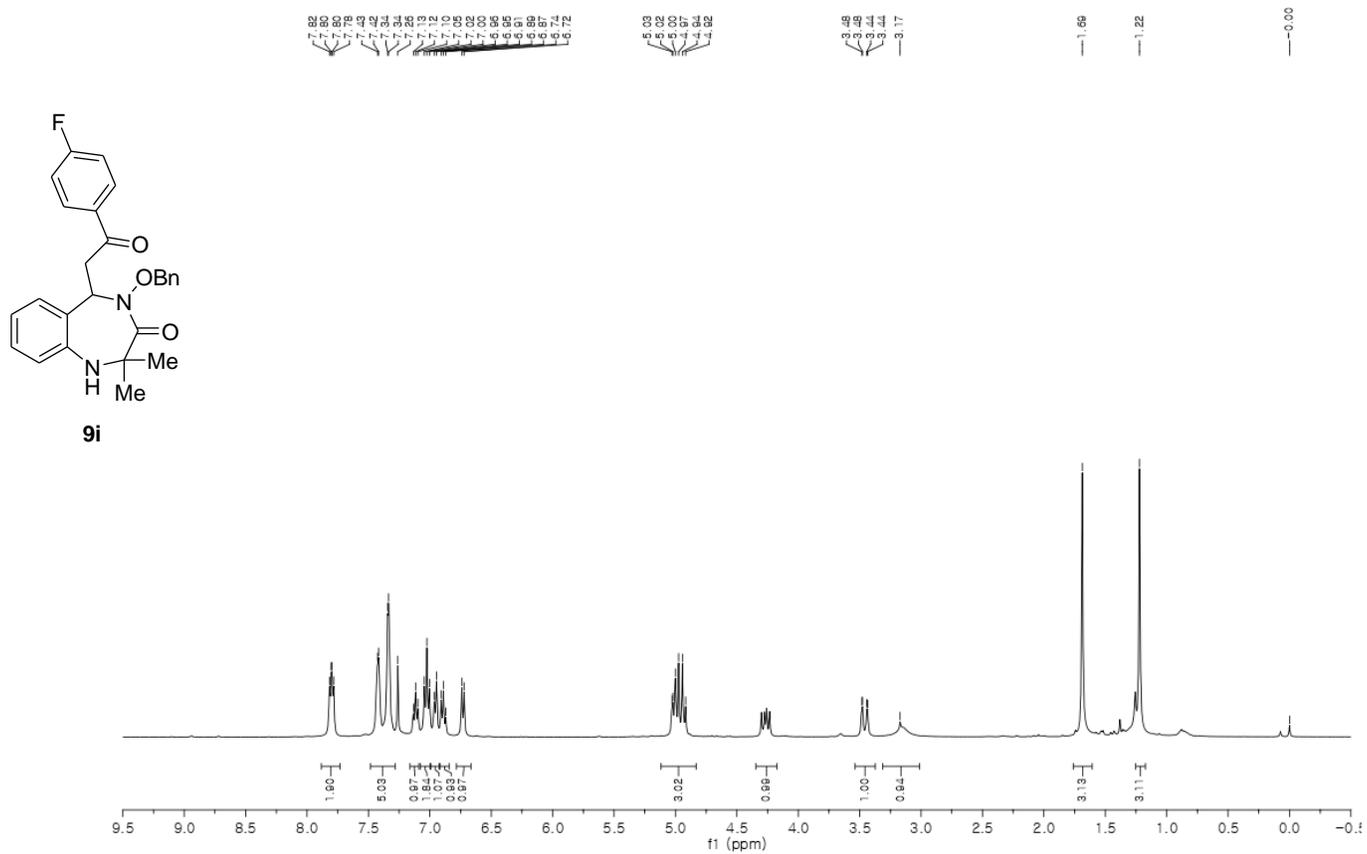
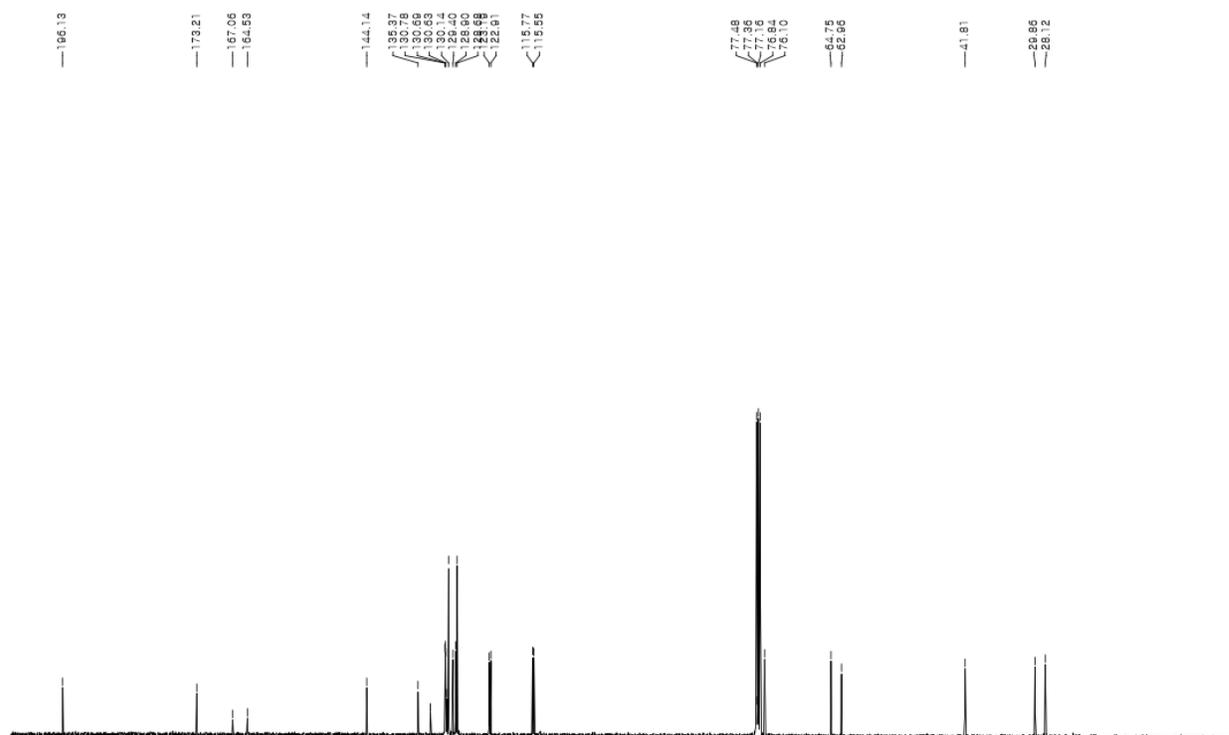
¹H NMR (400 MHz) in CDCl₃

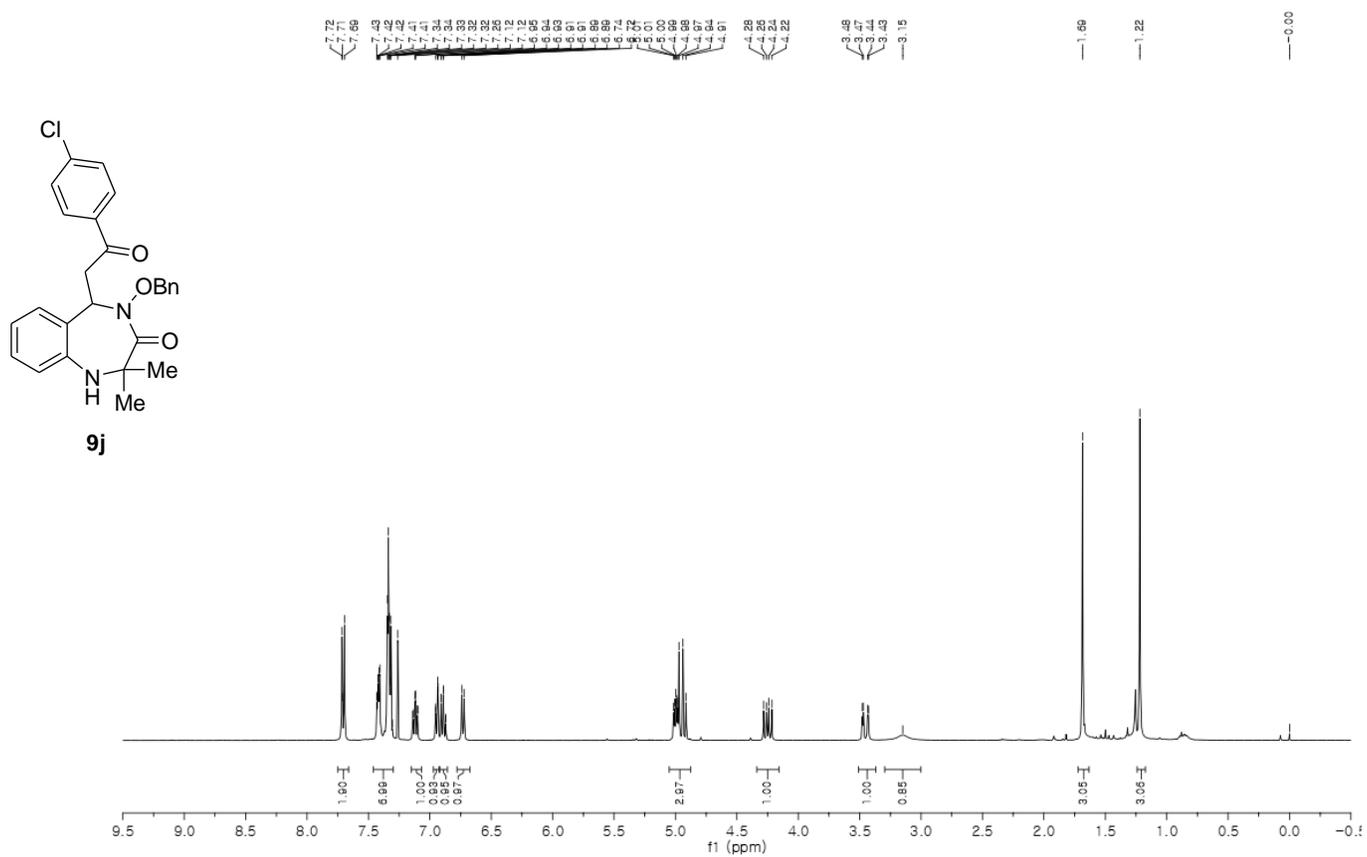
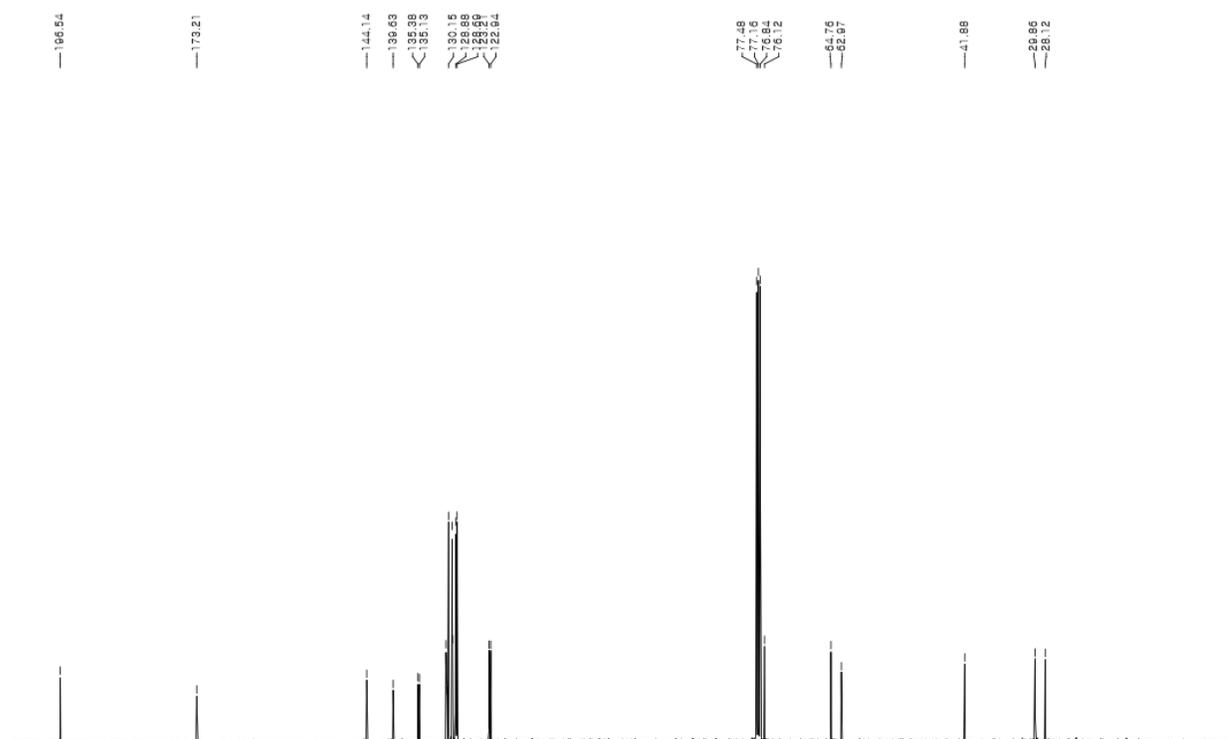


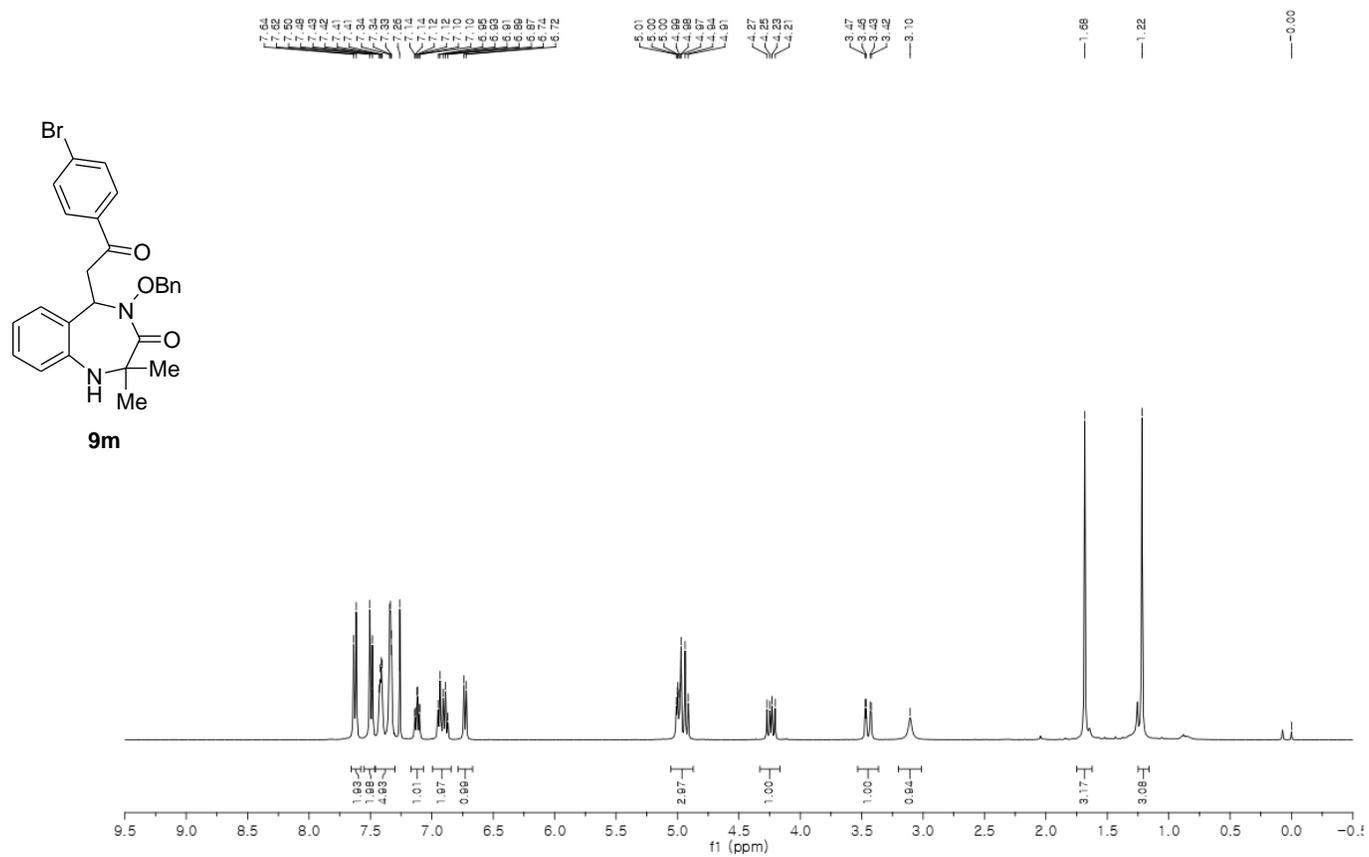
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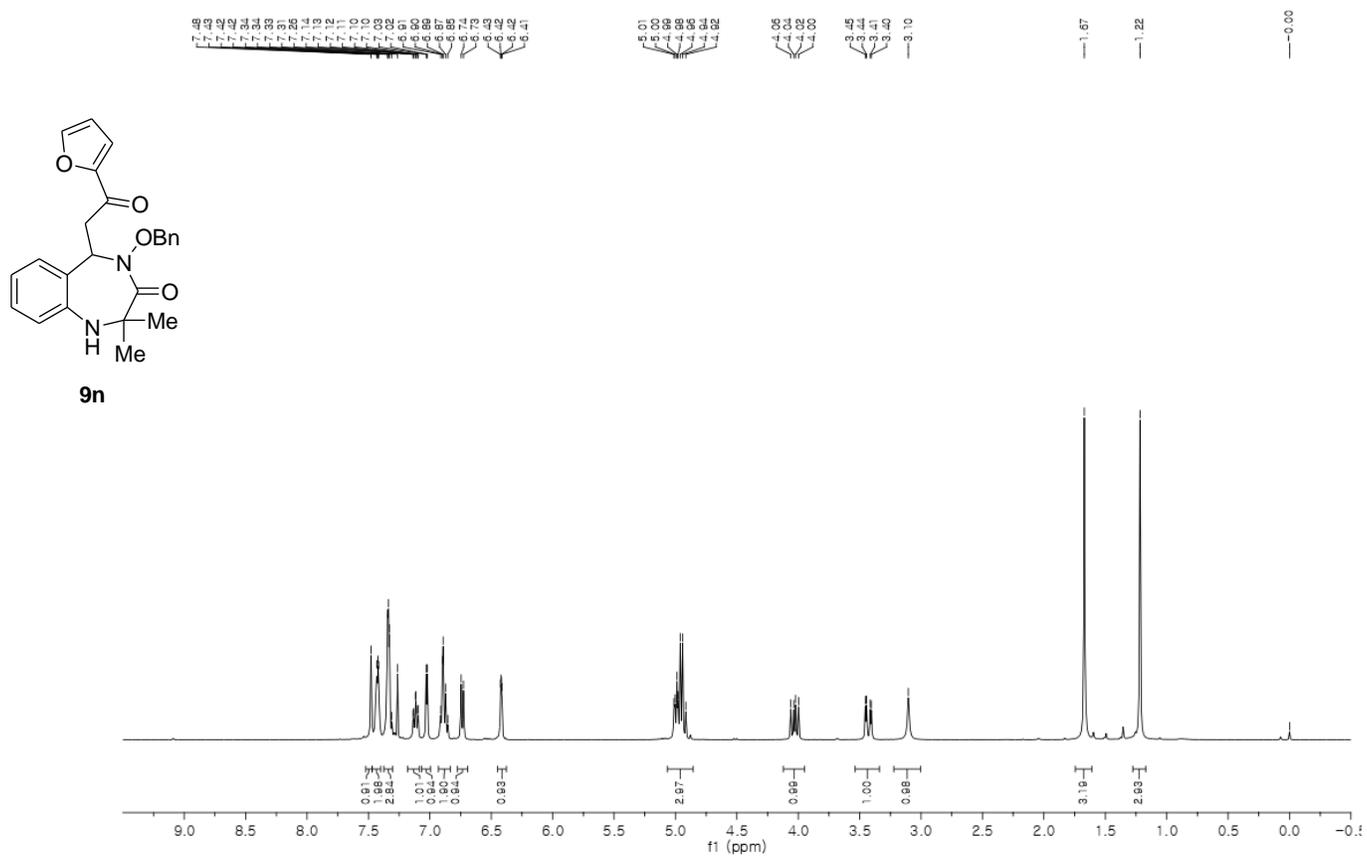
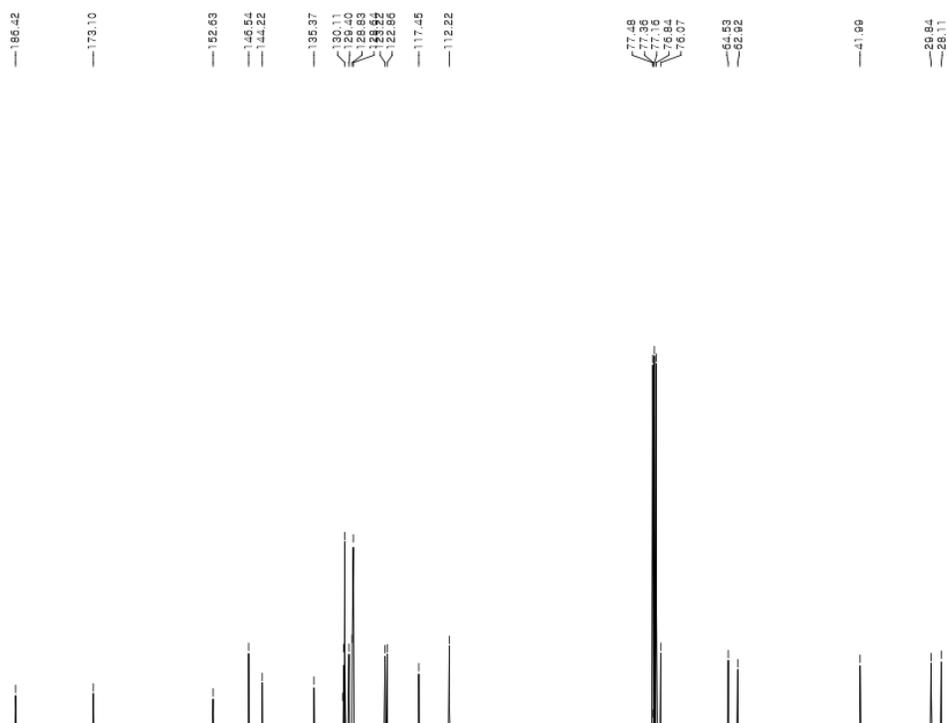


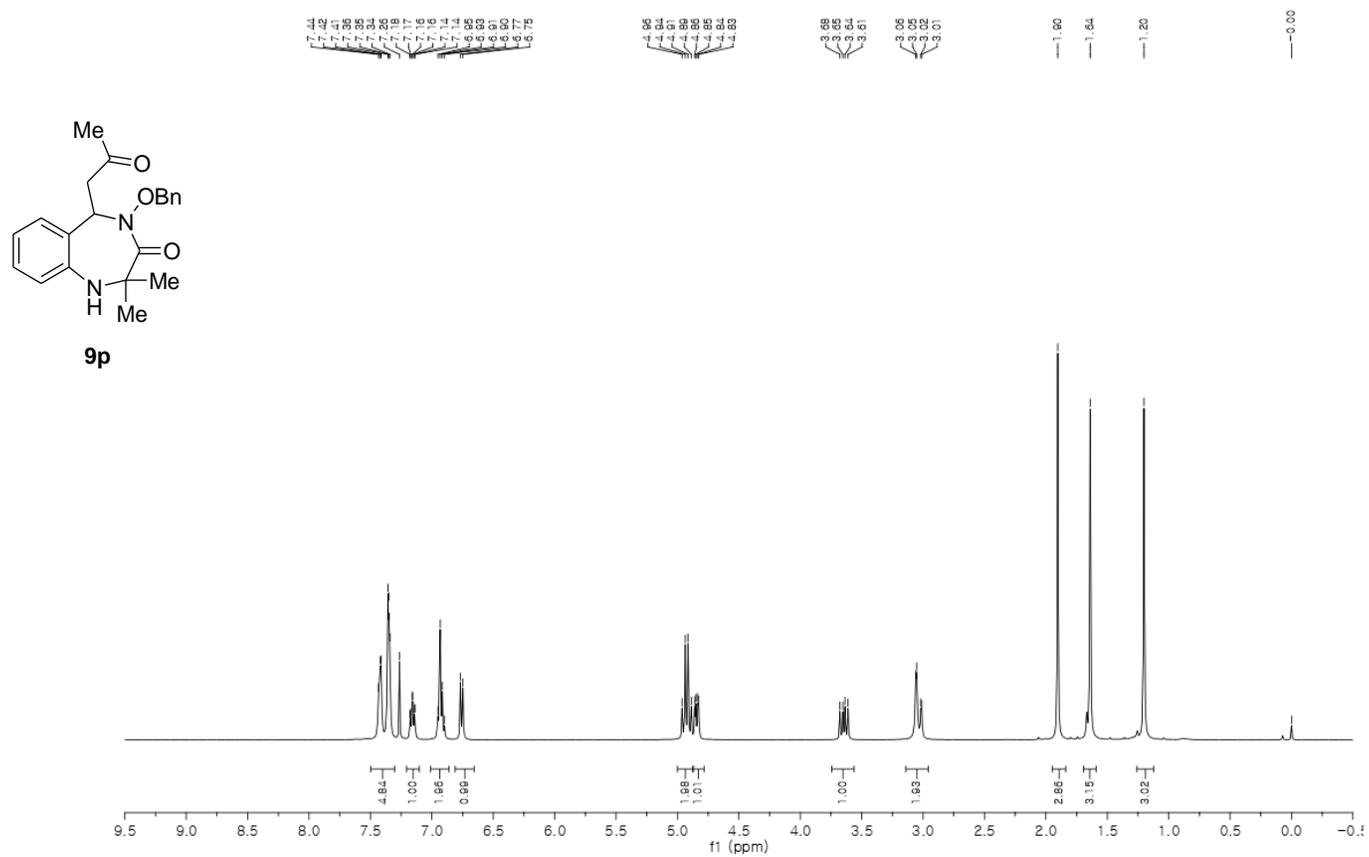
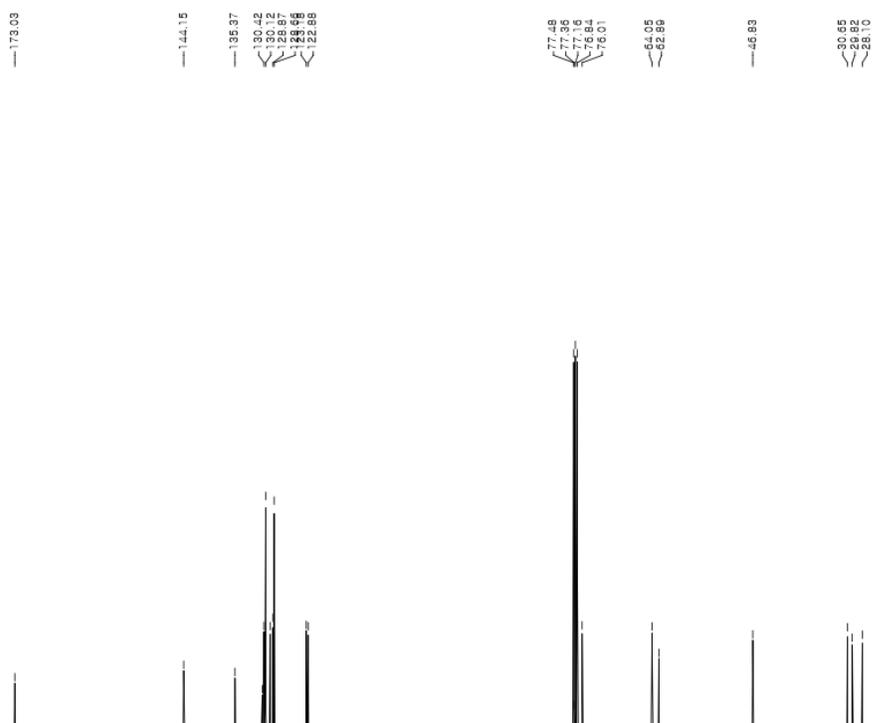
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

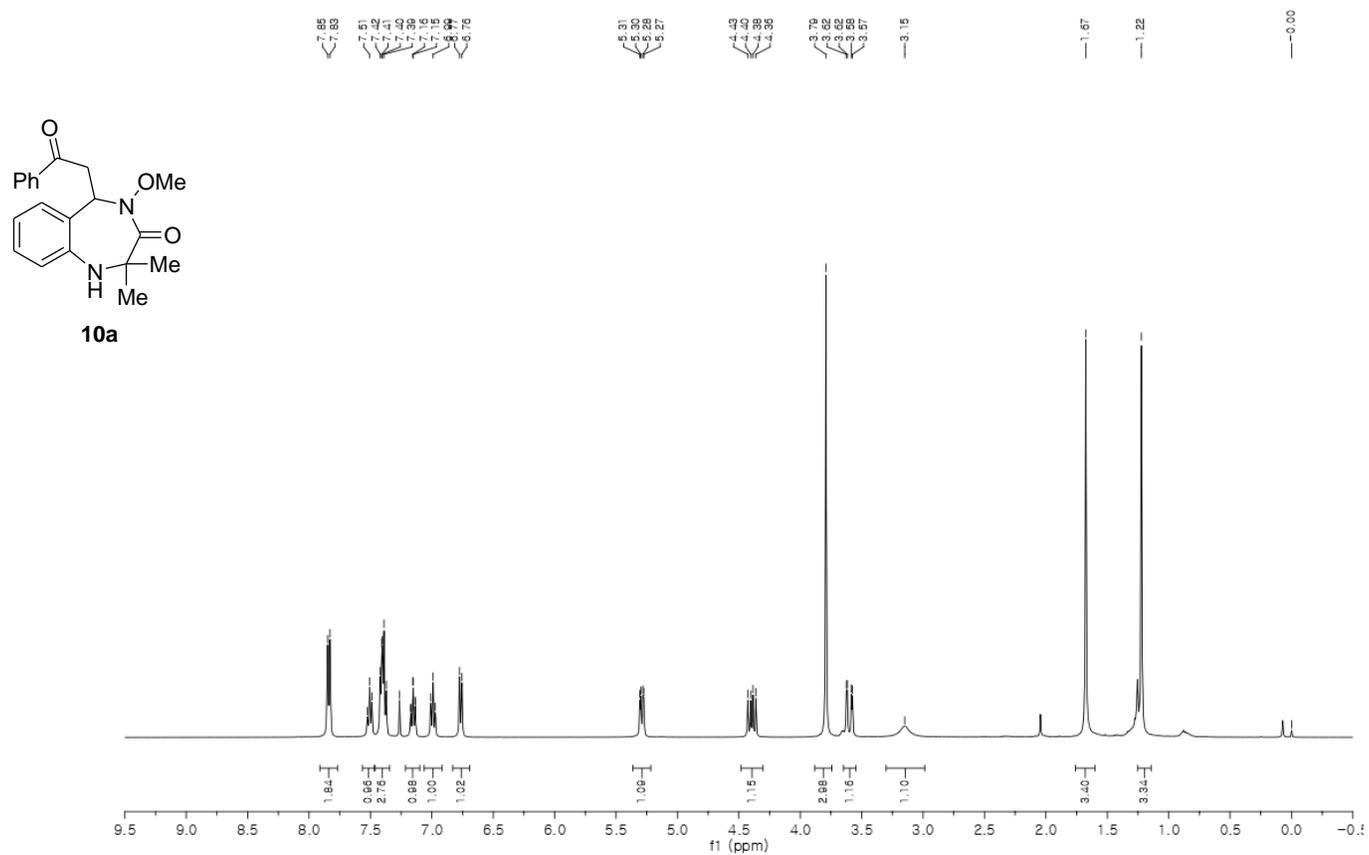
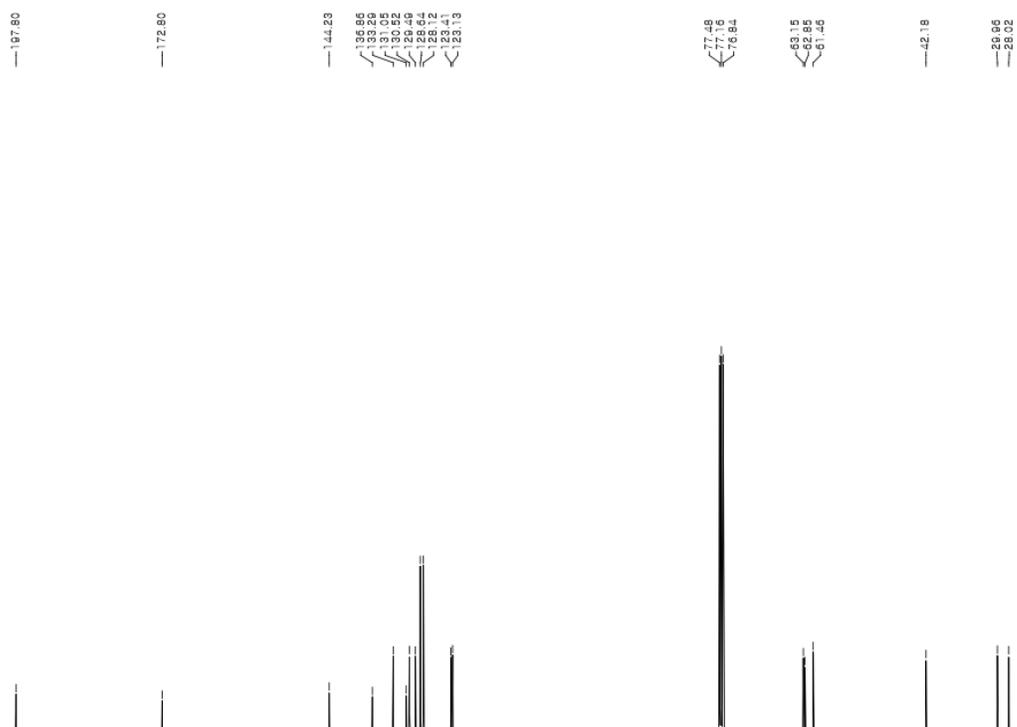
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

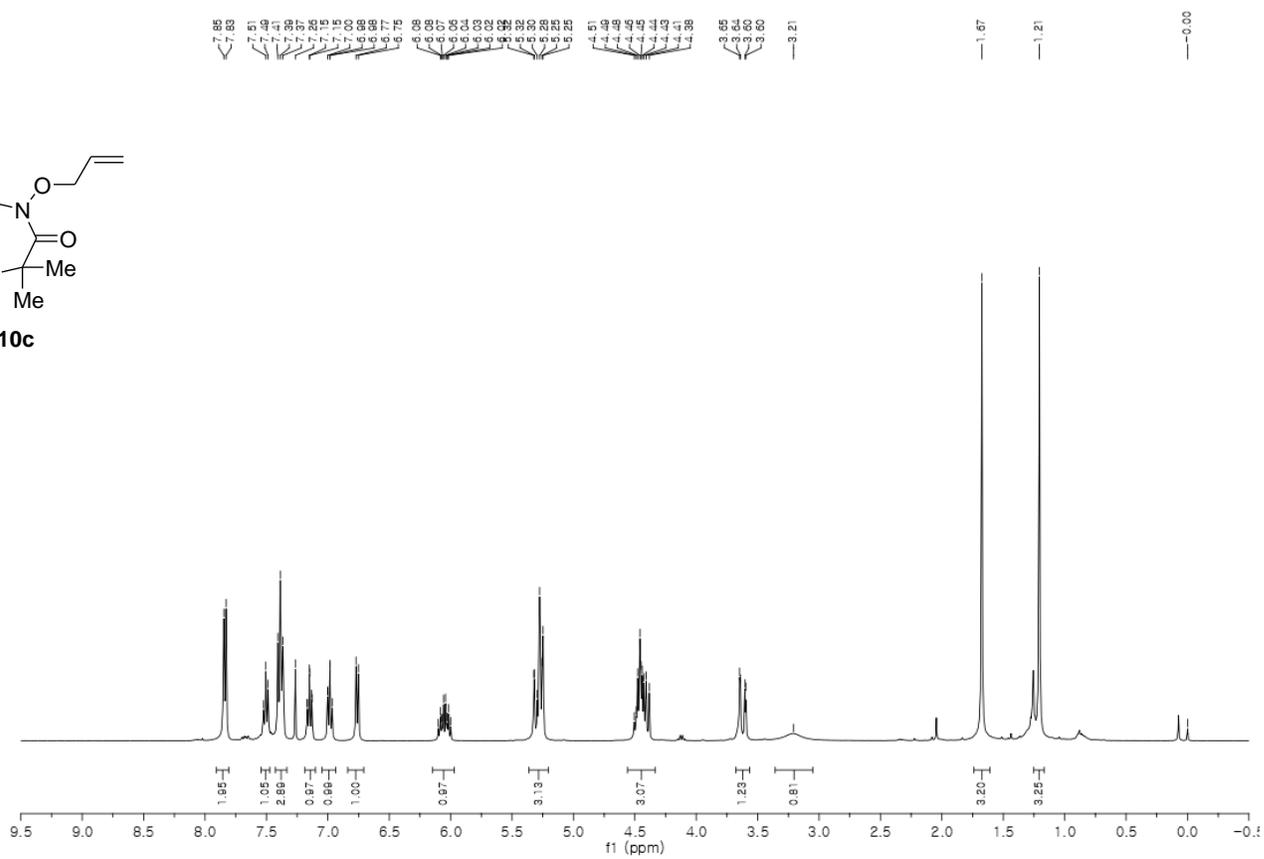
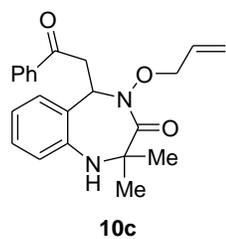
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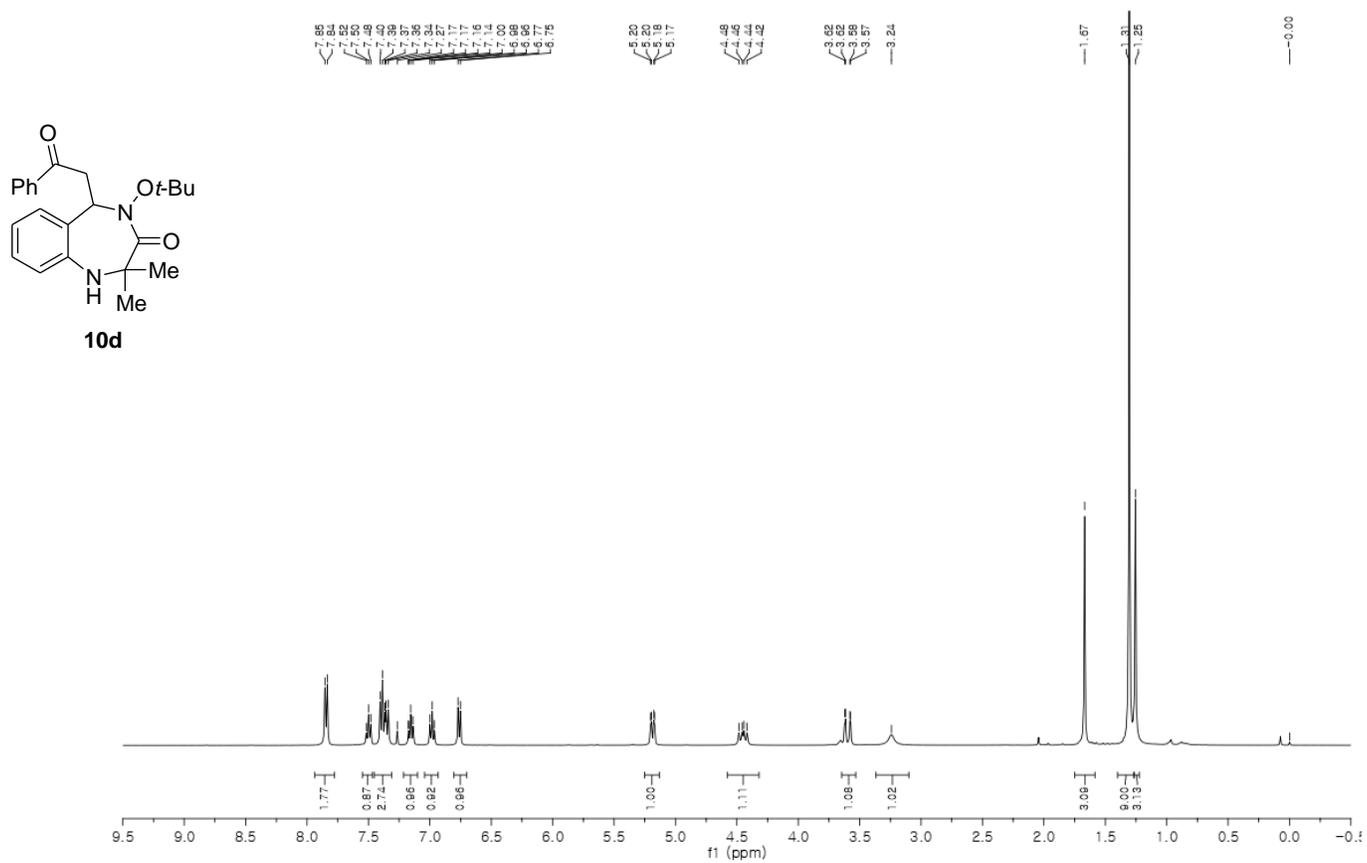
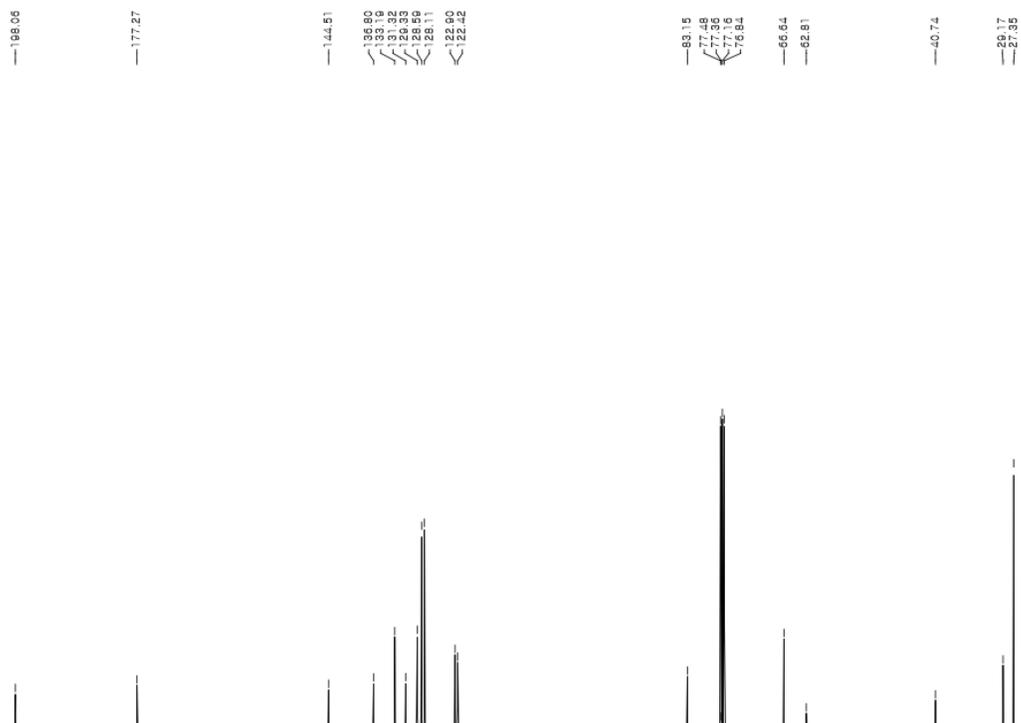
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

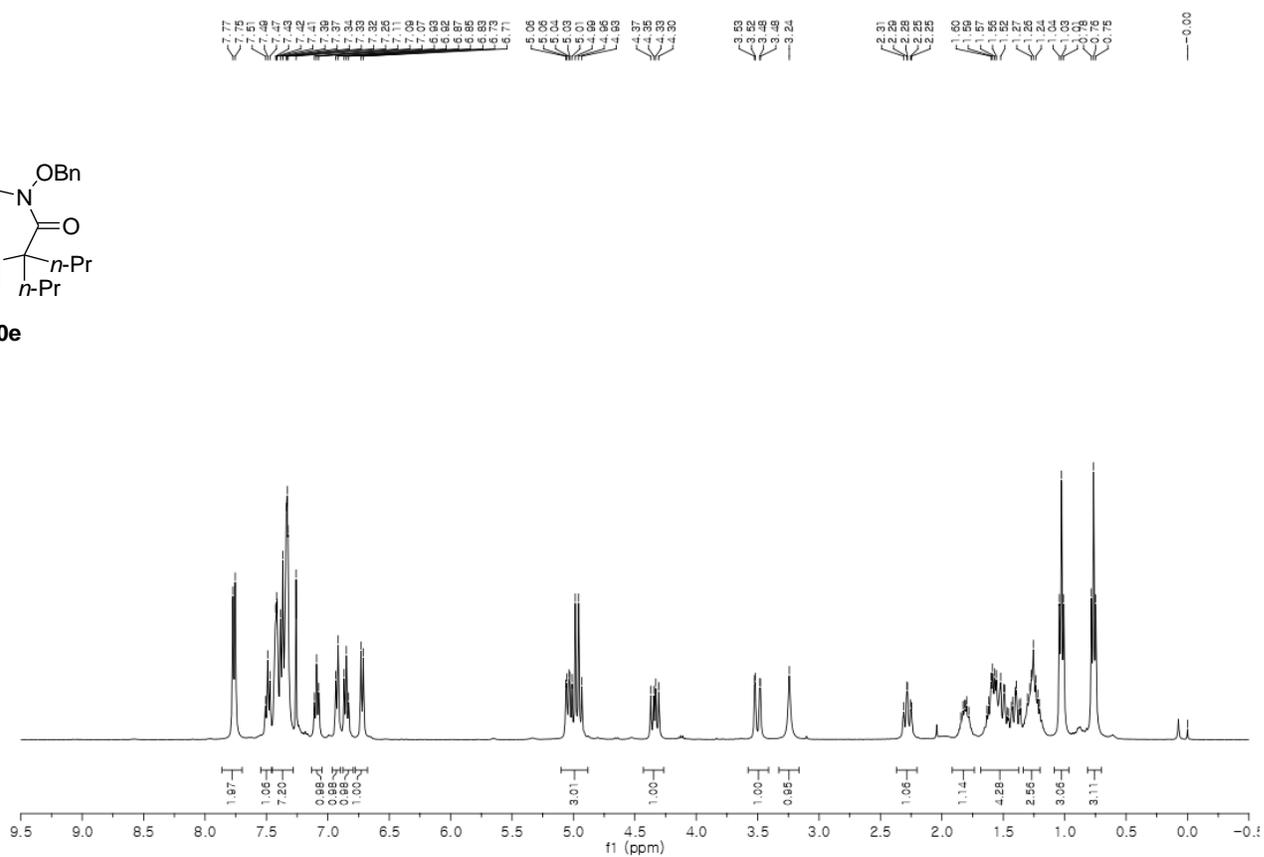
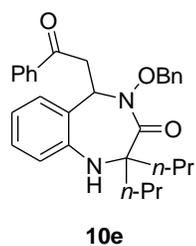
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

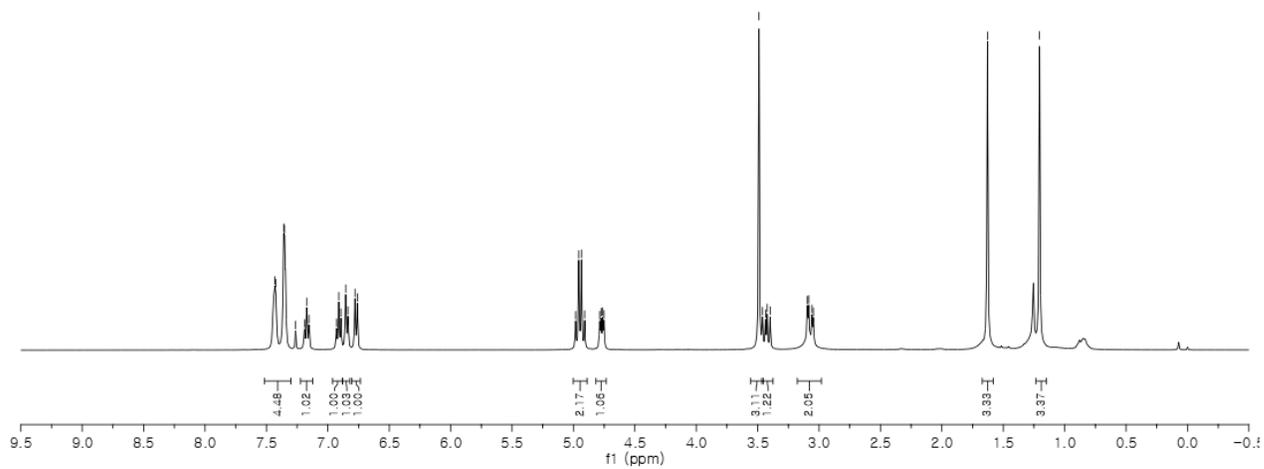
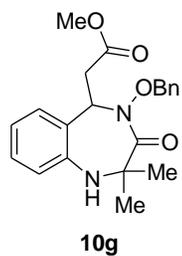
¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

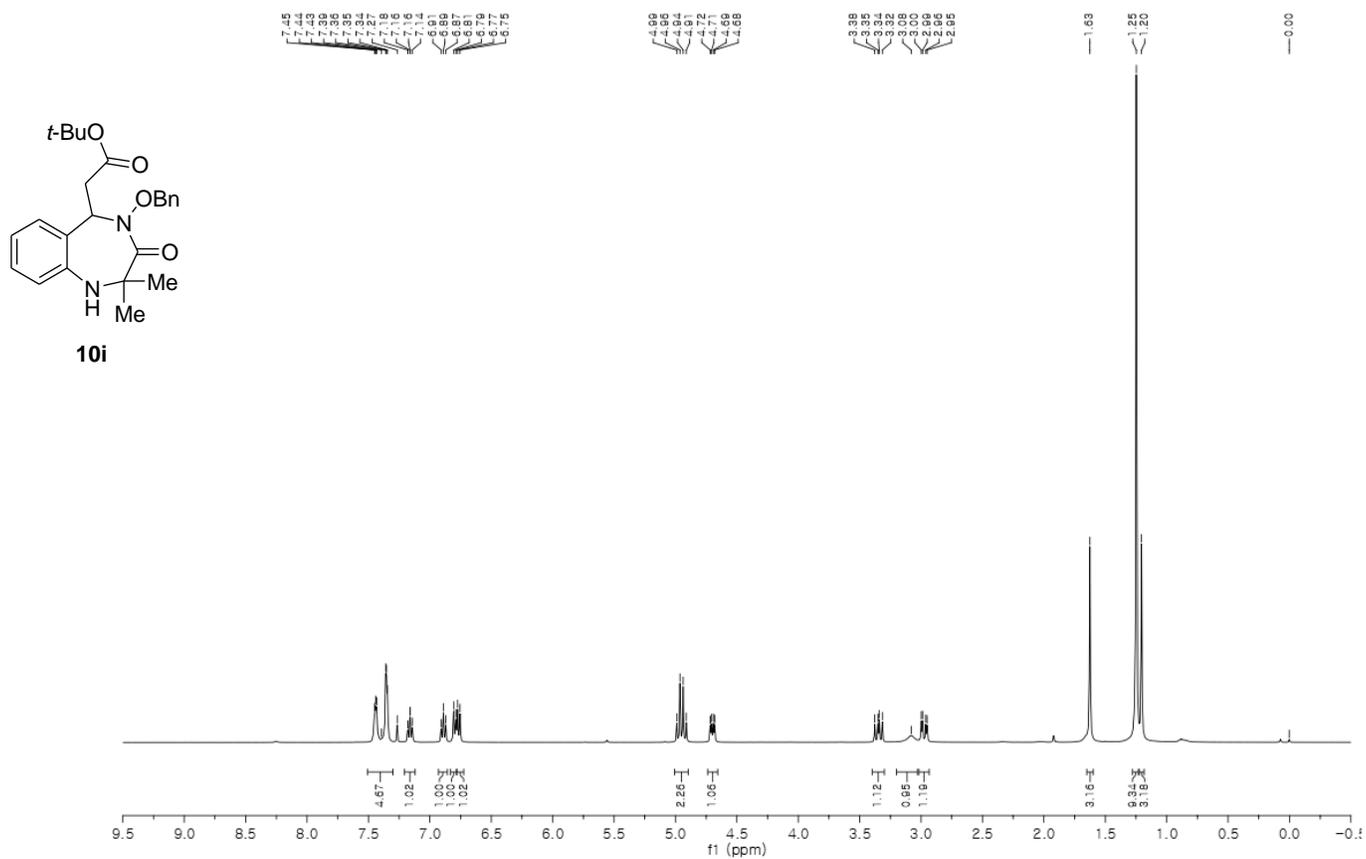
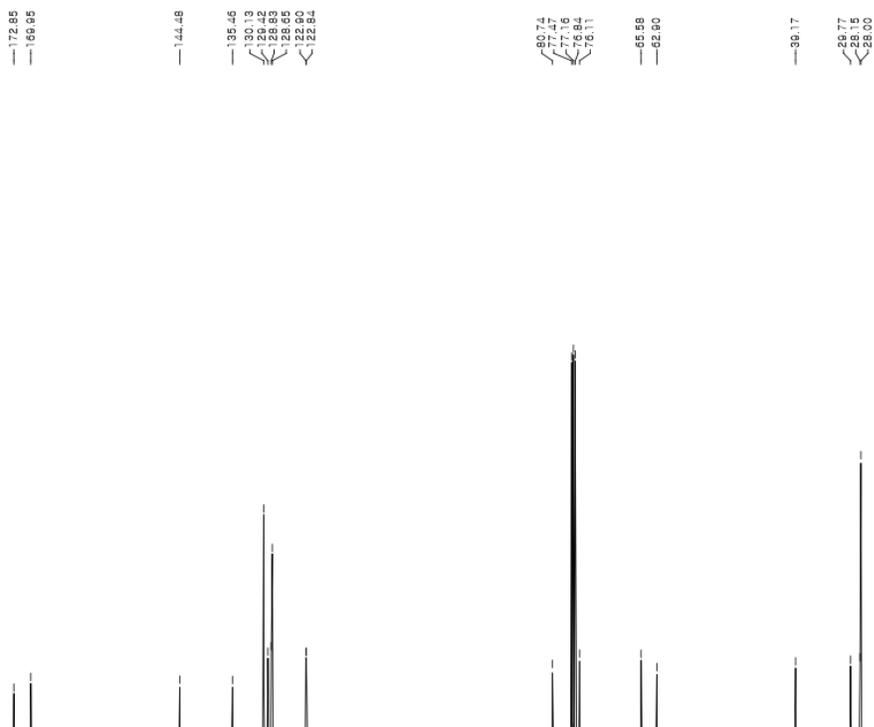
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

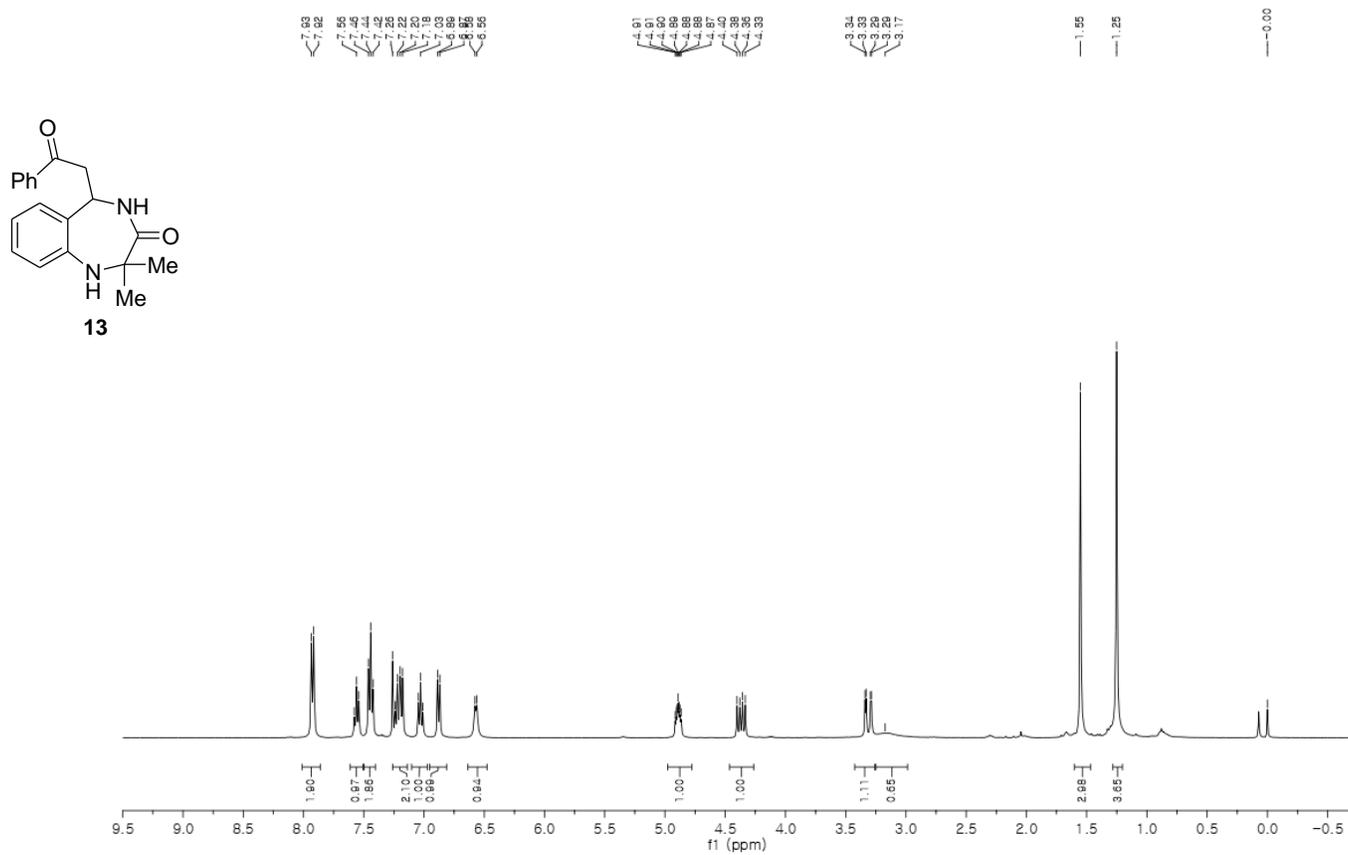
^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**

^1H NMR (400 MHz) in CDCl_3  **^{13}C NMR (100 MHz) in CDCl_3** 

¹H NMR (400 MHz) in CDCl₃**¹³C NMR (100 MHz) in CDCl₃**