Supplemental Information

Giese Reaction of Alkyl Bromides using Amine Carboxyboranes

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1. General Experimental

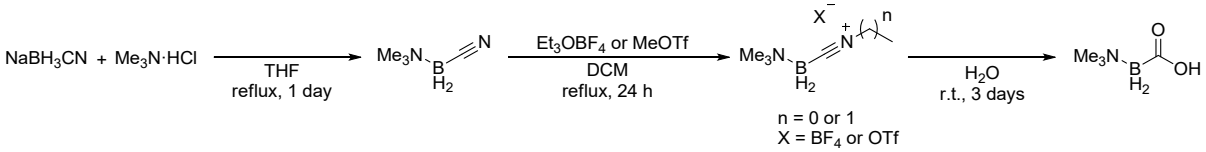
All chemicals and solvents were used without further purifications. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on Bruker Avance III-400 spectrometer. The chemical shifts reported in ppm relative to residual solvent $CDCl_3$, CD_3CN, C_6D_6 or added TMS as an internal reference. Splitting patterns are designated as follows: br; broad, s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, dt; doublet of triplet, td; triplet of doublet, dd; doublet of doublet. Flash chromatography was carried out on Merck silica 60 (230-400 mesh ASTM). Analytical thin-layer chromatography (TLC) was performed on E. Merck precoated silica gel 60 F_{254} plates. Mass spectral data were obtained from the Korea Basic Science Institute (Daegu). Blue light LEDs were purchased from Kessil (A160WE, PR 160 440 nm)

2. Experimental Methods

General Procedure: All experiments were performed in flame-dried glassware using argon as a protective gas. Solvents were transferred by using a syringe and were introduced into the vial through a rubber septum. All reactions were monitored by thin-layer chromatography (TLC). NMR yield was measured with dibromomethane or 1,3,5-trimethoxybenzene as an internal standard and isolated yield was obtained by flash chromatography using silica gel.

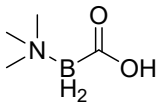
General Procedure for synthesis of carboxyborane

Synthesis of trimethylamine carboxyborane



Trimethylamine carboxyborane was prepared using a modified procedure from the literature[1], in which $NaBH_3CN$ was reacted under reflux with trimethylammonium hydrochloride (1.0 equiv.) in THF until the evolution of H_2 gas ceased. The resulting product was purified by extraction with CH_2Cl_2/H_2O, then reacted with Et_3OBF_4 or MeOTf (1.1 equiv.) in CH_2Cl_2 under reflux. After the reaction, solvent was removed under reduced pressure. The resulting product was dissolved in H_2O, then the reaction solution was stirred for 3 days. The carboxyborane was extracted with CH_2Cl_2/H_2O and recrystallized in CH_2Cl_2/Hx.

Trimethylamine carboxyborane (1a)



1H NMR (400 MHz, CDCl3) δ 2.75 (s, 9H), 2.00 (p, *J* = 198.2, 95.7 Hz, 2H).

^{11}B NMR (128 MHz, $CDCl_3$) δ -10.02 (t, *J* = 99.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 52.3. (one peak is missing)

HRMS (FAB) m/z:[M]+ calcd. For $C_4H_{12}BNO_2$ 117.0961; Found 117.0962

Isolated yield: 6.78 g, 58% (3 steps for 100 mmol scale)

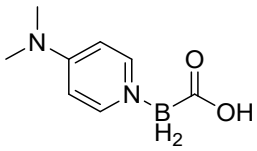
Amine exchange of carboxyborane

Other carboxyboranes were prepared as follows.

Procedure 1) Trimethylamine carboxyborane (1.0 mmol) was dissolved in corresponding amine (1.0 mL), protected from the atmosphere by purged with Ar gas, and maintained at 65 °C for 24 hours. The product was purified by recrystallization in DCM/Hx.

Procedure 2) Trimethylamine carboxyborane (1.0 mmol) and corresponding amine (2.2 equiv.) were dissolved in THF (4.0 mL), protected from the atmosphere by purged with Ar gas, and maintained at 65 °C for 24 hours. The product was purified by recrystallization in DCM/Hx or column chromatography on silica gel.

DMAP-carboxyborane (1b)



DMAP-carboxyborane was synthesized according to procedure 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 6.8 Hz, 2H), 6.59 – 6.53 (m, 2H), 3.13 (s, 4H).

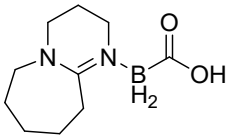
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 106.6, 39.7. (Two peaks are missing)

^{11}B NMR (128 MHz, $CDCl_3$) δ -12.57 (t, J = 92.7 Hz).

HRMS (FAB) m/z:[M]+ calcd. For $C_8H_{13}BN_2O_2$ 180.1070; Found 180.1150

Isolated yield: 171 mg, 95%

DBU-carboxyborane (1c)



DBU-carboxyborane was synthesized according to procedure 1.

^{1}H NMR (400 MHz, CDCl3) δ 7.91 (s, 1H), 3.39 (dd, J = 7.7, 4.4 Hz, 4H), 3.33 (t, J = 6.1 Hz, 2H), 2.91 – 2.79 (m, 2H), 1.96 (p, J = 6.0 Hz, 2H), 1.67 (dtt, J = 9.6, 7.0, 4.1 Hz, 6H).

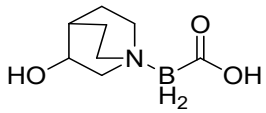
^{11}B NMR (128 MHz, $CDCl_3$) δ -15.31 (t, J = 96.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 54.0, 49.1, 48.5, 30.4, 29.0, 27.2, 23.4, 21.2. (One peak is missing)

HRMS (FAB) m/z:[M]+ calcd. For $C_{10}H_{19}BN_2O_2$ 210.1540; Found 211.1620

Isolated yield: 187 mg, 89%

3-Quinuclidinol-carboxyborane (1d)



3-Quinuclidinol-carboxyborane was synthesized according to procedure 2.

^{1}H NMR (400 MHz, CD3CN) δ 7.67 (s, 1H), 4.02 – 3.94 (m, 1H), 3.35 (ddd, *J* = 13.9, 8.4, 2.8 Hz, 1H), 3.22 (d, *J* = 3.5 Hz, 1H), 3.15 (dddd, *J* = 13.2, 10.6, 6.4, 2.7 Hz, 1H), 3.10 – 3.01 (m, 1H), 3.01 – 2.91 (m, 1H), 2.87 (dt, *J* = 13.8, 2.9 Hz, 1H), 2.06 (ddddd, *J* = 13.0, 10.7, 4.7, 3.6, 2.6 Hz, 1H), 1.97 (dd, *J* = 5.2, 2.5 Hz, 1H), 1.82 (ddt, *J* = 13.1, 10.3, 4.4 Hz, 1H), 1.70 – 1.53 (m, 2H).

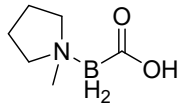
^{13}C NMR (101 MHz, CD_3CN) δ 61.6, 52.5, 51.5, 28.4, 23.1, 18.7. (One peak is missing)

^{11}B NMR (128 MHz, CD_3CN) δ -11.66 (t, *J* = 98.2 Hz).

HRMS (FAB) m/z:[M]+ calcd. For $C_8H_{16}BNO_3$ 185.1223; Found 186.1303

Isolated yield: 166 mg, 90%

N-methyl pyrrolidine-carboxyborane (1e)



N-methyl pyrrolidine-carboxyborane was synthesized according to procedure 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 – 3.25 (m, 2H), 2.98 (dtd, *J* = 13.3, 5.5, 4.9, 1.7 Hz, 2H), 2.78 (s, 3H), 2.11 – 1.95 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 61.6, 48.5, 22.5. (One peak is missing)

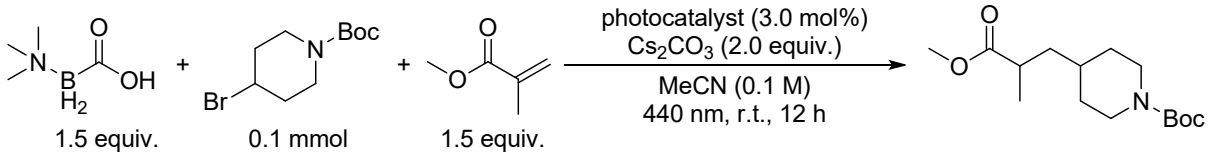
^{11}B NMR (128 MHz, $CDCl_3$) δ -11.18 (t, *J* = 99.5 Hz).

HRMS (FAB) m/z:[M]+ calcd. For $C_6H_{14}BNO_2$ 143.1118; Found 143.1120

Isolated yield: 107 mg, 75%

3. Optimization of Reaction conditions

Table S1. Photocatalyst Screening

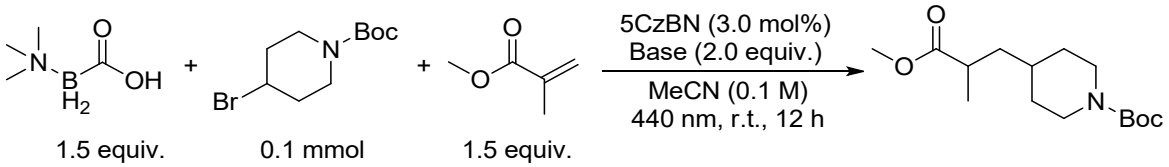


Entry	Potocatalyst	Yield (%) [a]
1	Mes-Acr-$Me^{+}ClO_4^{-}$	9
2	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	37

3	$[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$	53
4	$Ir(ppy)_3$	48
5	5CzBN	64
6	4CzIPN	75

[a] Yield was determined by ^1H NMR using dibromomethane.

Table S2. Base Screening

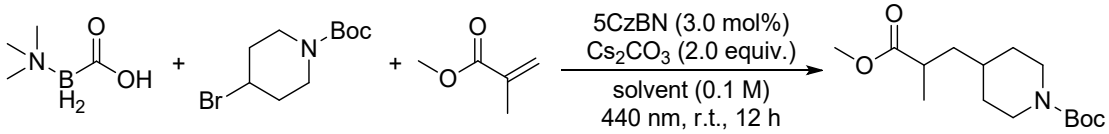


1.5 equiv. 0.1 mmol 1.5 equiv.

Entry	Base	Yield (%)[a]
1	Cs_2CO_3	64
2	K_2CO_3	56
3	Na_2CO_3	6
4	K_2HPO_4	7
5	BTMG	67
6	CsF	57

[a]Yield was determined by ^1H NMR using dibromomethane.

Table S3. Solvent Screening

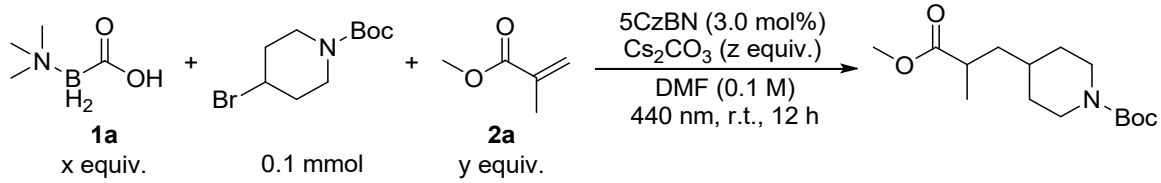


1.5 equiv. 0.1 mmol 1.5 equiv.

Entry	Solvent	Yield (%)[a]
1	MeCN	64
2	DMSO	45
3	DMF	83
4	MeCN/H_2O 1:1	30
5	MeCN/H_2O 9:1	69
6	toluene	40
7	$PhCF_3$	49
8	tBuCN	55

[a]Yield determined by ^1H NMR using dibromomethane.

Table S4. Equivalent Screening

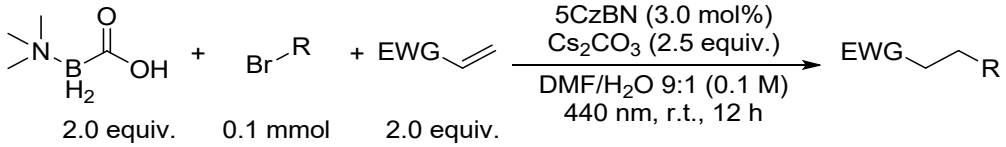


Entry	Equiv. of **1a**	Equiv. of **2a**	Equiv. of Cs_2CO_3	Yield (%)[a]
1	1.5	1.5	2.0	83
2	1.5	2.0	2.0	77
3	1.5	2.5	2.0	73
4	2.0	1.5	2.5	89
5	2.0	2.0	2.5	97
6	2.0	2.5	2.5	81
7	2.5	1.5	3.0	76
8	2.5	2.0	3.0	96
9	3.0	2.0	3.5	98
10	3.0	2.5	3.5	99

[a] Yield determined by ^{1}H NMR using dibromomethane.

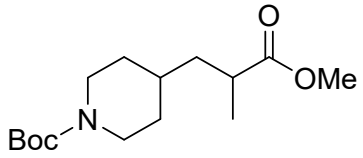
4. Substrate scope

General Procedure for Giese Reaction of Alkyl Bromide by XAT using Carboxyborane



A 4 mL vial was placed under Ar. The carboxyborane (0.2 mmol, 2.0 equiv.), alkyl bromide (0.1 mmol, 1.0 equiv.), 5CzBN (3.0 mol%), and Cs_2CO_3 (0.25 mmol, 2.5 equiv.) were added followed by DMF/H_2O 9:1 mixture as a solvent (1.0 mL), appropriate Michael acceptor (2.0 mmol, 2.0 equiv.). The reaction was then stirred at room temperature under the irradiation of 440 nm blue LEDs for 12 h. After the reaction, the reaction mixture was diluted with H_2O and Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. The solvent was removed under the vacuo and the residue was purified by column chromatography on silica gel to provide the corresponding products.

tert-butyl 4-(3-methoxy-2-methyl-3-oxopropyl)piperidine-1-carboxylate (3a)



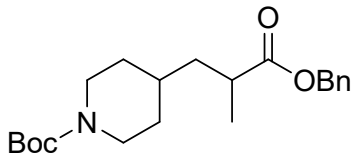
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (s, 2H), 3.66 (s, 3H), 2.63 (q, J = 11.0, 9.1 Hz, 2H), 2.53 (dq, J = 8.6, 6.8 Hz, 1H), 1.71 – 1.54 (m, 3H), 1.43 (s, 9H), 1.31 – 1.21 (m, 2H), 1.13 (d, J = 7.0 Hz, 3H), 1.05 (qt, J = 12.2, 4.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 155.0, 79.4, 51.7, 44.0, 40.7, 36.7, 34.0, 32.1, 28.6, 17.8.

The spectroscopic characterization matched with data reported in the literature.[2]

Isolated yield: 25.7 mg, 90%

tert-butyl 4-(3-(benzyloxy)-2-methyl-3-oxopropyl)piperidine-1-carboxylate (3b)



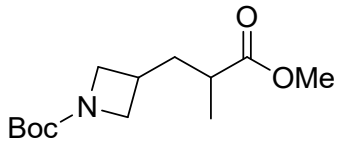
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 5.18 – 5.06 (dd, 2H), 4.02 (s, 2H), 2.66 – 2.38 (m, 3H), 1.69 – 1.52 (m, 3H), 1.44 (s, 9H), 1.35 – 1.28 (m, 2H), 1.16 (d, J = 6.9 Hz, 3H), 1.06 – 0.99 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 154.9, 136.3, 128.7, 128.4, 79.4, 66.2, 44.0, 40.8, 36.9, 34.0, 32.3, 32.0, 28.6, 17.9. (one peak is missing)

The spectroscopic characterization matched with data reported in the literature.[3]

Isolated yield: 21.7 mg, 62%

tert-butyl 3-(3-methoxy-2-methyl-3-oxopropyl)azetidine-1-carboxylate (3c)



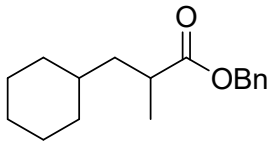
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (dt, *J* = 11.1, 8.3 Hz, 2H), 3.66 (s, 3H), 3.51 (dt, *J* = 8.5, 6.0 Hz, 2H), 2.57 – 2.46 (m, 1H), 2.45 – 2.34 (m, 1H), 1.95 (dt, *J* = 13.7, 7.7 Hz, 1H), 1.70 (ddd, *J* = 14.0, 8.2, 6.1 Hz, 1H), 1.42 (s, 8H), 1.14 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 156.5, 79.4, 54.6, 51.8, 38.5, 37.8, 28.5, 27.3, 17.3.

The spectroscopic characterization matched with data reported in the literature.[4]

Isolated yield: 20.0 mg, 78%

benzyl 3-cyclohexyl-2-methylpropanoate (3d)



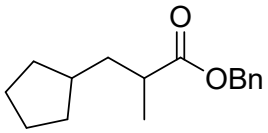
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.11 (dd, 2H), 2.65 – 2.55 (m, 1H), 1.76 – 1.56 (m, 6H), 1.30 – 1.05 (m, 8H), 0.90 – 0.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 136.5, 128.7, 128.2, 66.1, 41.8, 37.1, 35.5, 33.4, 33.3, 26.7, 26.4, 17.8.

The spectroscopic characterization matched with data reported in the literature.[5]

Isolated yield: 21.4mg, 82%

benzyl 3-cyclopentyl-2-methylpropanoate (3e)



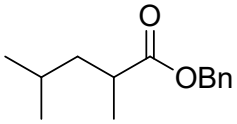
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 5.12 (s, 2H), 2.60 – 2.47 (m, 1H), 1.82 – 1.66 (m, 4H), 1.66 – 1.52 (m, 2H), 1.52 – 1.35 (m, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.12 – 0.99 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 136.4, 128.7, 128.2, 128.2, 66.1, 40.4, 39.1, 38.1, 32.8, 32.7, 25.2, 25.2, 17.7.

HRMS (FAB) m/z: [M]+ calcd. For $C_{16}H_{22}O_2$ 246.1620; Found 246.1618

Isolated yield: 13.5 mg, 55%

benzyl 2,4-dimethylpentanoate (3f)



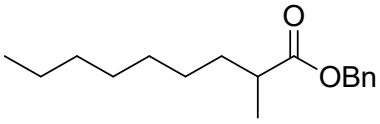
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.11 (s, 2H), 2.64 – 2.51 (m, 1H), 1.66 – 1.50 (m, 2H), 1.29 – 1.19 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 136.4, 128.7, 128.2, 128.2, 66.1, 43.1, 37.8, 26.0, 22.6, 22.6, 17.6.

The spectroscopic characterization matched with data reported in the literature.[6]

Isolated yield: 9.4 mg, 43%

benzyl 2-methylnonanoate (3g)



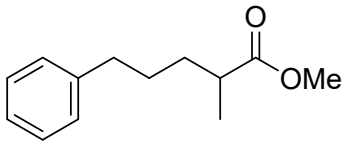
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 5.12 (s, 2H), 2.49 (dq, *J* = 13.9, 7.0 Hz, 1H), 1.74 – 1.61 (m, 1H), 1.49 – 1.36 (m, 1H), 1.35 – 1.18 (m, 10H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 136.5, 128.7, 128.2, 128.2, 66.1, 39.7, 34.0, 31.9, 29.6, 29.3, 27.3, 22.8, 17.2, 14.2.

HRMS (FAB) m/z: [M]+ calcd. For $C_{17}H_{26}O_2$ 262.1933; Found 262.1935

Isolated yield: 16.3 mg, 62%

methyl 2-methyl-5-phenylpentanoate(3h)



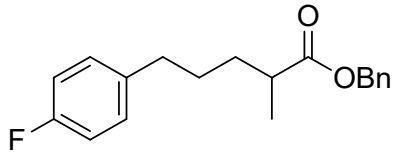
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 7.13 – 7.07 (m, 3H), 3.59 (s, 3H), 2.56 – 2.50 (m, 2H), 2.45 – 2.34 (m, 1H), 1.68 – 1.49 (m, 3H), 1.43 – 1.33 (m, 1H), 1.07 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 142.3, 128.5, 128.4, 125.9, 51.6, 39.5, 35.9, 33.6, 29.2, 17.2.

The spectroscopic characterization matched with data reported in the literature.[7]

Isolated yield: 13.0 mg, 63%

benzyl 5-(4-fluorophenyl)-2-methylpentanoate (3i)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 7.09 – 7.03 (m, 2H), 6.97 – 6.90 (m, 2H), 5.11 (d, *J* = 1.4 Hz, 2H), 2.58 – 2.53 (m, 2H), 2.52 – 2.46 (m, 1H), 1.76 – 1.64 (m, 1H), 1.64 – 1.50 (m, 2H), 1.51 – 1.43 (m, 1H), 1.17 (d, *J* = 7.0 Hz, 3H).

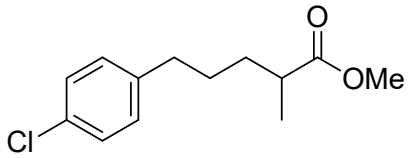
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 161.4 (d), 137.8 (d), 136.3, 129.8 (d), 128.68, 128.29, 128.25, 115.1 (d), 66.2, 39.5, 35.0, 33.4, 29.2, 17.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.92 (ddd, *J* = 14.3, 8.9, 5.4 Hz).

HRMS (FAB) m/z: [M]+ calcd. For $C_{19}H_{21}FO_2$ 300.15; Found 300.1523

Isolated yield: 12.9 mg, 43%

methyl 5-(4-chlorophenyl)-2-methylpentanoate (3j)



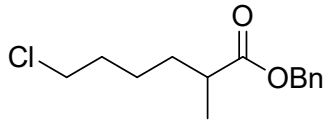
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.10 – 7.06 (m, 2H), 3.66 (s, 3H), 2.62 – 2.54 (m, 2H), 2.52 – 2.40 (m, 1H), 1.73 – 1.63 (m, 1H), 1.63 – 1.54 (m, 2H), 1.48 – 1.38 (m, 1H), 1.14 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 140.7, 131.6, 129.8, 128.5, 51.7, 39.5, 35.2, 33.4, 29.1, 17.3.

HRMS (FAB) m/z: [M]+ calcd. For $C_{13}H_{17}ClO_2$ 240.0917; Found 240.0919

Isolated yield: 14.9 mg, 62%

benzyl 6-chloro-2-methylhexanoate (3k)



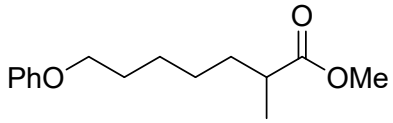
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 5.12 (d, *J* = 1.0 Hz, 2H), 3.49 (t, *J* = 6.7 Hz, 2H), 2.50 (dq, *J* = 13.1, 7.0 Hz, 1H), 1.79 – 1.65 (m, 3H), 1.49 – 1.36 (m, 3H), 1.18 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 136.3, 128.7, 128.3, 128.3, 66.2, 44.9, 39.6, 33.1, 32.6, 24.7, 17.2.

HRMS (FAB) m/z: [M]+ calcd. For $C_{14}H_{19}ClO_2$ 254.1074; Found 254.1076

Isolated yield: 15.0 mg, 59%

methyl 2-methyl-6-phenoxyhexanoate (3l)



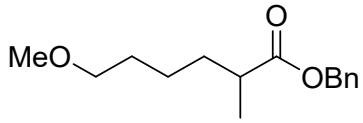
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 2H), 6.88 – 6.83 (m, 1H), 6.83 – 6.78 (m, 2H), 3.87 (t, *J* = 6.5 Hz, 2H), 3.59 (s, 3H), 2.43 – 2.33 (m, 1H), 1.75 – 1.55 (m, 3H), 1.44 – 1.24 (m, 55H), 1.08 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 159.2, 129.5, 120.6, 114.6, 67.8, 51.6, 39.5, 33.9, 29.3, 27.2, 26.1, 17.2.

HRMS (FAB) m/z: [M]+ calcd. For $C_{15}H_{22}O_3$ 250.1569; Found 250.1569

Isolated yield: 18.3 mg, 77%

benzyl 6-methoxy-2-methylhexanoate (3m)



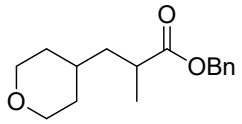
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.11 (s, 2H), 3.33 (t, *J* = 6.6 Hz, 2H), 3.31 (s, 3H), 2.54 – 2.44 (m, 1H), 1.70 (dddd, *J* = 15.7, 7.4, 3.9, 1.6 Hz, 1H), 1.55 (dtd, *J* = 8.3, 6.9, 6.1 Hz, 2H), 1.50 – 1.38 (m, 1H), 1.38 – 1.27 (m, 2H), 1.17 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 136.4, 128.7, 128.2, 128.2, 72.7, 66.1, 58.7, 39.7, 33.7, 29.6, 24.0, 17.1.

HRMS (FAB) m/z: [M]+ calcd. For $C_{15}H_{22}O_3$ 250.16; Found 250.1566

Isolated yield: 13.8 mg, 55%

benzyl 2-methyl-3-(tetrahydro-2H-pyran-4-yl)propanoate (3n)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 5.12 (dd, *J* = 12.3 Hz, 2H), 3.93 – 3.87 (m, 2H), 3.27 (tdd, *J* = 11.8, 6.8, 2.1 Hz, 2H), 2.60 (ddt, *J* = 13.0, 8.8, 6.9 Hz, 1H), 1.67 (ddd, *J* = 13.5, 8.9, 5.9 Hz, 1H), 1.61 (ddd, *J* = 8.5, 3.8, 1.6 Hz, 1H), 1.50 – 1.36 (m, 2H), 1.34 – 1.27 (m, 1H), 1.27 – 1.18 (m, 2H), 1.17 (d, *J* = 6.9 Hz, 3H).

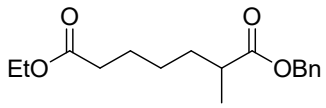
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 136.3, 128.7, 128.4, 68.0, 66.2, 41.2, 36.7, 33.2, 33.0, 17.8.

HRMS (FAB) m/z: [M]+ calcd. For $C_{16}H_{22}O_3$ 262.16; Found 262.1571

The spectroscopic characterization matched with data reported in the literature.[8]

Isolated yield: 18.1 mg, 69%

1-benzyl 7-ethyl 2-methylheptanedioate (3o)



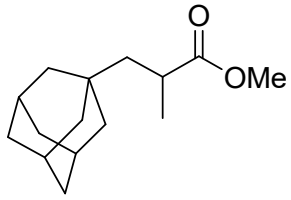
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.11 (s, 2H), 4.11 (dd, *J* = 7.1 Hz, 2H), 2.54 – 2.43 (m, 1H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.74 – 1.64 (m, 2H), 1.64 – 1.56 (m, 2H), 1.50 – 1.39 (m, 1H), 1.35 – 1.27 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 4H), 1.16 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 173.7, 136.3, 128.7, 128.3, 128.2, 66.2, 60.3, 39.5, 34.3, 33.5, 26.8, 24.9, 17.1, 14.4.

HRMS (FAB) m/z: [M]+ calcd. For $C_{17}H_{24}O_4$ 292.1675; Found 293.1753

Isolated yield: 17.4 mg, 60%

methyl 3-((1s,3s)-adamantan-1-yl)-2-methylpropanoate (3p)



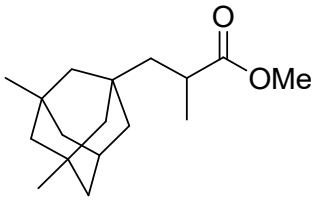
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.55 (dqd, *J* = 9.1, 7.1, 3.2 Hz, 1H), 1.92 (p, *J* = 3.2 Hz, 3H), 1.77 – 1.63 (m, 5H), 1.65 – 1.55 (m, 3H), 1.49 (dq, *J* = 12.1, 2.6 Hz, 3H), 1.39 (dq, *J* = 12.2, 2.6 Hz, 3H), 1.13 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 51.7, 48.7, 42.4, 37.2, 34.3, 32.8, 28.8, 20.6.

HRMS (FAB) m/z: [M]+ calcd. For $C_{15}H_{24}O_2$ 236.1776; Found 236.1778

Isolated yield: 14.0 mg, 59%

methyl 3-((1S,3R)-3,5-dimethyladamantan-1-yl)-2-methylpropanoate (3q)



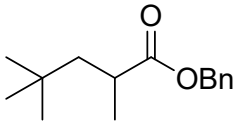
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 2.55 (dqd, *J* = 9.0, 7.0, 3.2 Hz, 1H), 2.00 (dq, *J* = 6.3, 3.2 Hz, 1H), 1.75 (dd, *J* = 14.2, 9.2 Hz, 1H), 1.35 – 1.17 (m, 6H), 1.13 (d, *J* = 7.1 Hz, 4H), 1.12 – 1.01 (m, 4H), 1.03 – 0.94 (m, 2H), 0.78 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 51.7, 51.3, 48.9, 48.7, 48.0, 43.4, 43.4, 40.9, 34.5, 34.5, 31.3, 30.8, 29.8, 20.6.

HRMS (FAB) m/z: [M]+ calcd. For $C_{17}H_{28}O_2$ 264.21; Found 264.2090

Isolated yield : 19.3 mg, 73%

benzyl 2,4,4-trimethylpentanoate (3r)



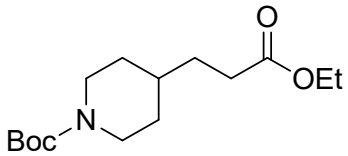
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.10 (s, 2H), 2.56 (dqd, *J* = 9.1, 7.1, 3.2 Hz, 1H), 1.88 (dd, *J* = 14.1, 9.1 Hz, 1H), 1.23 – 1.14 (m, 4H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 136.3, 128.7, 128.3, 128.3, 66.3, 48.0, 36.4, 30.9, 29.6, 20.5.

The spectroscopic characterization matched with data reported in the literature.[9]

Isolated yield: 7.5 mg, 32%

tert-butyl 4-(3-ethoxy-3-oxopropyl)piperidine-1-carboxylate (3s)



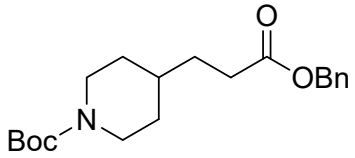
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 – 4.01 (m, 4H), 2.71 – 2.60 (m, 2H), 2.31 (t, *J* = 7.7 Hz, 2H), 1.69 – 1.53 (m, 4H), 1.44 (s, 8H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.08 (qd, *J* = 12.3, 4.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 155.0, 79.4, 60.5, 44.0, 35.7, 32.0, 31.7, 31.6, 28.6, 14.4.

The spectroscopic characterization matched with data reported in the literature.[2]

Isolated yield: 12.1 mg, 42%

tert-butyl 4-(3-(benzyloxy)-3-oxopropyl)piperidine-1-carboxylate (3t)



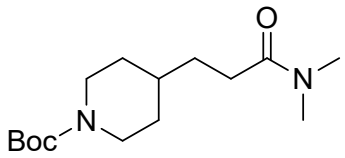
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 5.11 (s, 2H), 4.06 (s, 2H), 2.63 (t, *J* = 12.7 Hz, 2H), 2.38 (t, *J* = 7.7 Hz, 2H), 1.62 (dq, *J* = 14.8, 7.7 Hz, 4H), 1.45 (s, 9H), 1.37 (ddt, *J* = 11.4, 7.6, 3.9 Hz, 1H), 1.07 (qd, *J* = 12.4, 4.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 155.0, 136.2, 128.7, 128.4, 79.4, 66.4, 44.0, 35.6, 31.9, 31.7, 31.5, 28.6.

The spectroscopic characterization matched with data reported in the literature.[2]

Isolated yield: 18.9 mg, 36%

tert-butyl 4-(3-(dimethylamino)-3-oxopropyl)piperidine-1-carboxylate (3u)



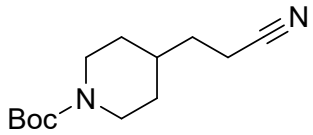
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 – 3.99 (m, 2H), 2.96 (d, *J* = 22.7 Hz, 6H), 2.66 (t, 2H), 2.31 (t, *J* = 7.7 Hz, 2H), 1.76 – 1.62 (m, 2H), 1.57 (q, *J* = 7.3 Hz, 2H), 1.43 (s, 10H), 1.09 (qd, *J* = 12.5, 4.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 155.0, 79.3, 44.0, 37.4, 35.7, 35.5, 32.1, 31.7, 30.4, 28.6.

HRMS (FAB) m/z: [M]+ calcd. For $C_{15}H_{28}N_2O_3$ 284.2100; Found 284.2099

Isolated yield: 17.1 mg, 60%

tert-butyl 4-(2-cyanoethyl)piperidine-1-carboxylate (3v)



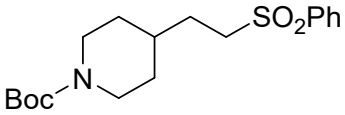
^{1}H NMR (400 MHz, CDCl3) δ 4.11 (s, 2H), 2.69 (t, *J* = 12.9 Hz, 2H), 2.38 (t, *J* = 7.0 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.63 – 1.58 (m, 2H), 1.45 (s, 9H), 1.11 (tdd, *J* = 12.7, 10.9, 4.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 119.7, 79.6, 43.7, 35.1, 31.9, 31.6, 28.6, 14.7.

The spectroscopic characterization matched with data reported in the literature.[2]

Isolated yield: 11.2 mg, 47%

tert-butyl 4-(2-(phenylsulfonyl)ethyl)piperidine-1-carboxylate (3w)



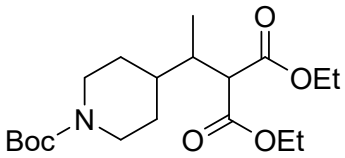
^{1}H NMR (400 MHz, CDCl3) δ 7.94 – 7.87 (m, 2H), 7.71 – 7.62 (m, 1H), 7.58 (dd, *J* = 8.2, 6.9 Hz, 2H), 4.06 (s, 2H), 3.14 – 3.05 (m, 2H), 2.62 (t, *J* = 12.8 Hz, 2H), 1.73 – 1.62 (m, 2H), 1.63 – 1.55 (m, 2H), 1.48 (ddt, *J* = 11.5, 7.7, 3.9 Hz, 1H), 1.43 (s, 9H), 1.06 (qd, *J* = 12.4, 4.4 Hz, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 154.8, 139.2, 133.9, 129.4, 128.1, 79.5, 54.0, 43.8, 35.0, 31.7, 29.0, 28.5.

The spectroscopic characterization matched with data reported in the literature.[2]

Isolated yield: 10.5 mg, 30%

diethyl 2-(1-(1-(tert-butoxycarbonyl)piperidin-4-yl)ethyl)malonate (3x)



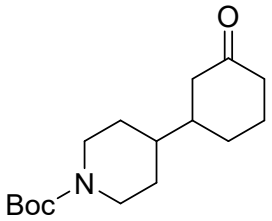
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 – 4.09 (m, 6H), 3.40 (d, *J* = 8.7 Hz, 1H), 2.72 – 2.47 (m, 2H), 2.22 (m, *J* = 8.6, 6.8, 4.4, 1.9 Hz, 1H), 1.63 – 1.53 (m, 2H), 1.47 (s, 1H), 1.45 (s, 9H), 1.27 (m, *J* = 7.1, 0.6 Hz, 7H), 1.15 (m, *J* = 12.7, 4.9 Hz, 1H), 0.92 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 169.2, 154.9, 79.5, 61.5, 55.5, 44.1, 38.9, 37.9, 30.5, 28.6, 14.3, 13.2

The spectroscopic characterization matched with data reported in the literature.[2]

Isolated yield: 7.6 mg, 20%

tert-butyl 4-(3-oxocyclohexyl)piperidine-1-carboxylate (3y)

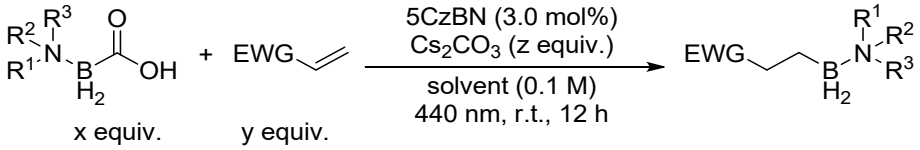


^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (s, 2H), 2.63 (t, *J* = 12.9 Hz, 2H), 2.43 – 2.33 (m, 2H), 2.32 – 2.19 (m, 1H), 2.11 – 2.01 (m, 2H), 1.90 (d, *J* = 13.3 Hz, 1H), 1.62 (pd, *J* = 13.3, 12.1, 5.9 Hz, 4H), 1.45 (s, 9H), 1.42 – 1.08 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.98, 154.94, 79.54, 45.54, 43.95, 41.63, 41.24, 29.84, 29.21, 28.61, 28.42, 25.46.

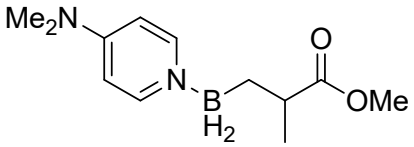
Isolated yield: 11.5 mg, 41%

General Procedure for Giese Reaction of Boryl Radical



A 4 mL vial was placed under Ar. The carboxyborane (2.0-3.0 equiv.), 5CzBN (3.0 mol%) and Cs_2CO_3 (2.5-3.5 equiv.) were added, followed by DMA or MeCN as a solvent (1.0 mL), appropriate Michael acceptor (0.1 mmol, 1.0 equiv.). The reaction was then stirred at room temperature under the irradiation of 440 nm blue LEDs for 12 h. The solvent was removed under the vacuo, and the residue was purified by column chromatography on alumina grade III to provide the corresponding products.

methyl 3-boraneyl-2-methylpropanoate DMAP complex (4b)



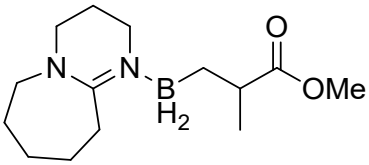
^{1}H NMR (400 MHz, C_6D_6) δ 8.02 – 7.96 (m, 2H), 5.60 – 5.56 (m, 2H), 3.53 (s, 3H), 2.88 (dt, *J* = 7.8, 6.8 Hz, 1H), 1.96 (s, 6H), 1.64 (s, 1H), 1.62 (d, *J* = 6.8 Hz, 3H), 1.36 (tt, *J* = 13.3, 5.4 Hz, 1H).

^{13}C NMR (101 MHz, C_6D_6) δ 179.8, 154.4, 146.5, 106.3, 50.7, 40.3, 38.3, 20.0. (one peak is missing)

^{11}B NMR (128 MHz, C_6D_6) δ -6.39 (t, *J* = 105.9 Hz).

Isolated yield: 18.3 mg, 78%

methyl 3-boraneyl-2-methylpropanoate DBU complex (4c)



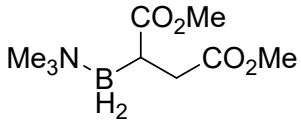
^{1}H NMR (400 MHz, C_6D_6) δ 3.56 (s, 3H), 3.22 (td, *J* = 5.4, 2.2 Hz, 2H), 2.93 (dp, *J* = 8.1, 6.7 Hz, 1H), 2.75 (pt, *J* = 8.5, 4.7 Hz, 2H), 2.35 (ddd, *J* = 7.1, 3.0, 1.2 Hz, 2H), 2.29 – 2.21 (m, 2H), 1.65 (d, *J* = 6.8 Hz, 3H), 1.43 – 1.27 (m, 5H), 1.23 – 1.02 (m, 5H), 0.90 – 0.81 (m, 2H).

^{13}C NMR (101 MHz, C_6D_6) δ 180.2, 164.7, 52.8, 50.6, 48.4, 47.7, 40.5, 29.9, 29.0, 27.3, 24.4, 21.5, 20.0. (one peak is missing)

^{11}B NMR (128 MHz, C_6D_6) δ -9.69 (t, *J* = 97.5 Hz).

Isolated yield: 24.8 mg, 93%

dimethyl 2-trimethylamine-boranylsuccinate (4f)



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (d, *J* = 4.8 Hz, 6H), 2.75 (dd, *J* = 17.3, 10.4 Hz, 1H), 2.62 (s, 9H), 2.38 – 2.26 (m, 1H), 2.20 (d, *J* = 10.5 Hz, 1H).

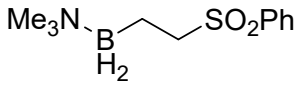
^{13}C NMR (101 MHz, $CDCl_3$) δ 181.4, 175.0, 52.5, 52.0, 51.5, 51.0, 36.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ -1.79 (t).

The spectroscopic characterization matched with data reported in the literature.[10]

Isolated yield: 14.5 mg, 67%

((2-trimethylamine-boranylethyl)sulfonyl)benzene (4g)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.62 – 7.55 (m, 1H), 7.55 – 7.46 (m, 2H), 3.02 – 2.94 (m, 2H), 2.54 (s, 9H), 0.86 – 0.74 (m, 2H).

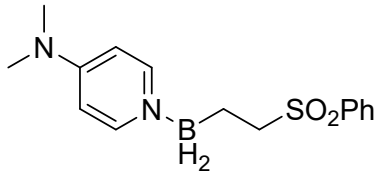
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 133.1, 129.1, 128.1, 57.0, 52.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ -2.79 (t).

The spectroscopic characterization matched with data reported in the literature.[10]

Isolated yield: 20.7 mg, 86%

((DMAP-boranylethyl)sulfonyl)benzene (4h)



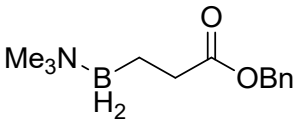
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.91 – 7.83 (m, 2H), 7.60 – 7.54 (m, 1H), 7.50 (dd, *J* = 8.2, 6.7 Hz, 2H), 6.52 – 6.46 (m, 2H), 3.10 (s, 6H), 2.99 – 2.91 (m, 2H), 0.84 (tq, *J* = 9.9, 5.1, 4.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 146.2, 139.9, 132.9, 129.6, 128.9, 128.4, 106.7, 57.9, 39.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.68.

Isolated yield: 13.7 mg, 45%

benzyl 3-bornaeylpropanoate trimethylamine complex (4a)



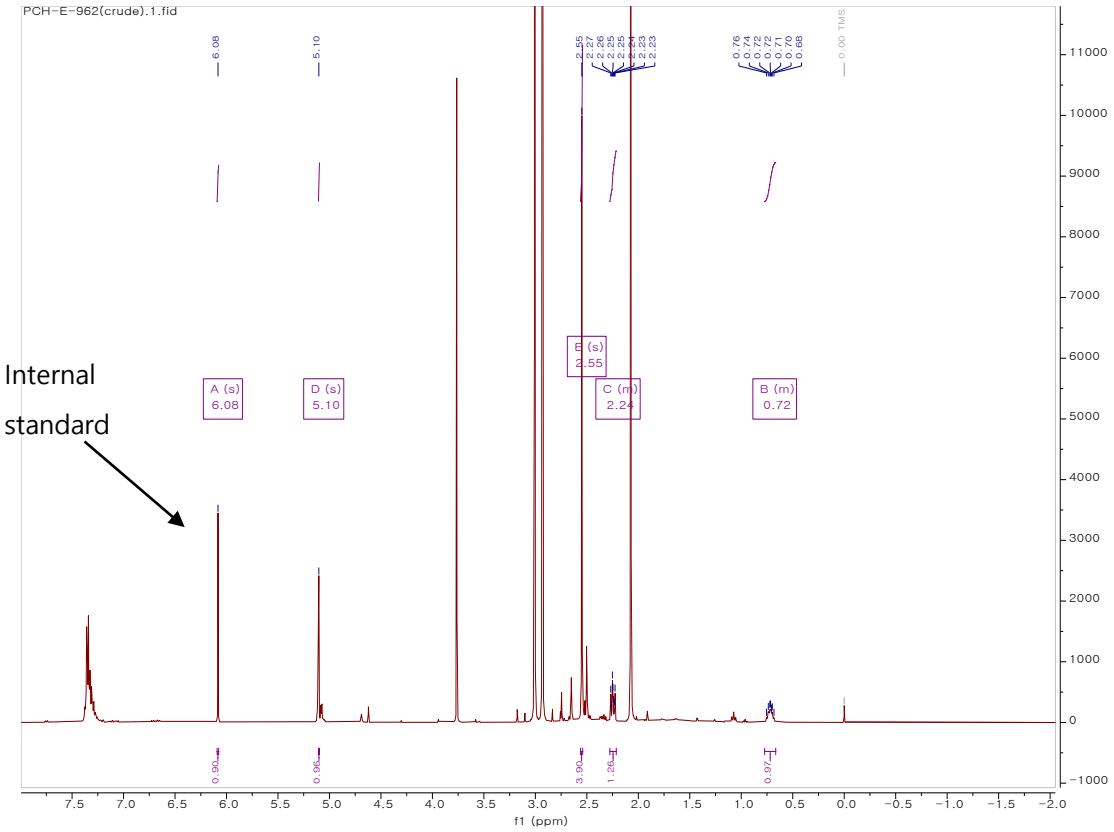
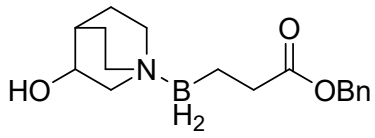


Figure S1. Crude ^{1}H NMR spectroscopy of **4a**

benzyl 3-bornaeylpropanoate 3-quinuclidinol complex (4d)



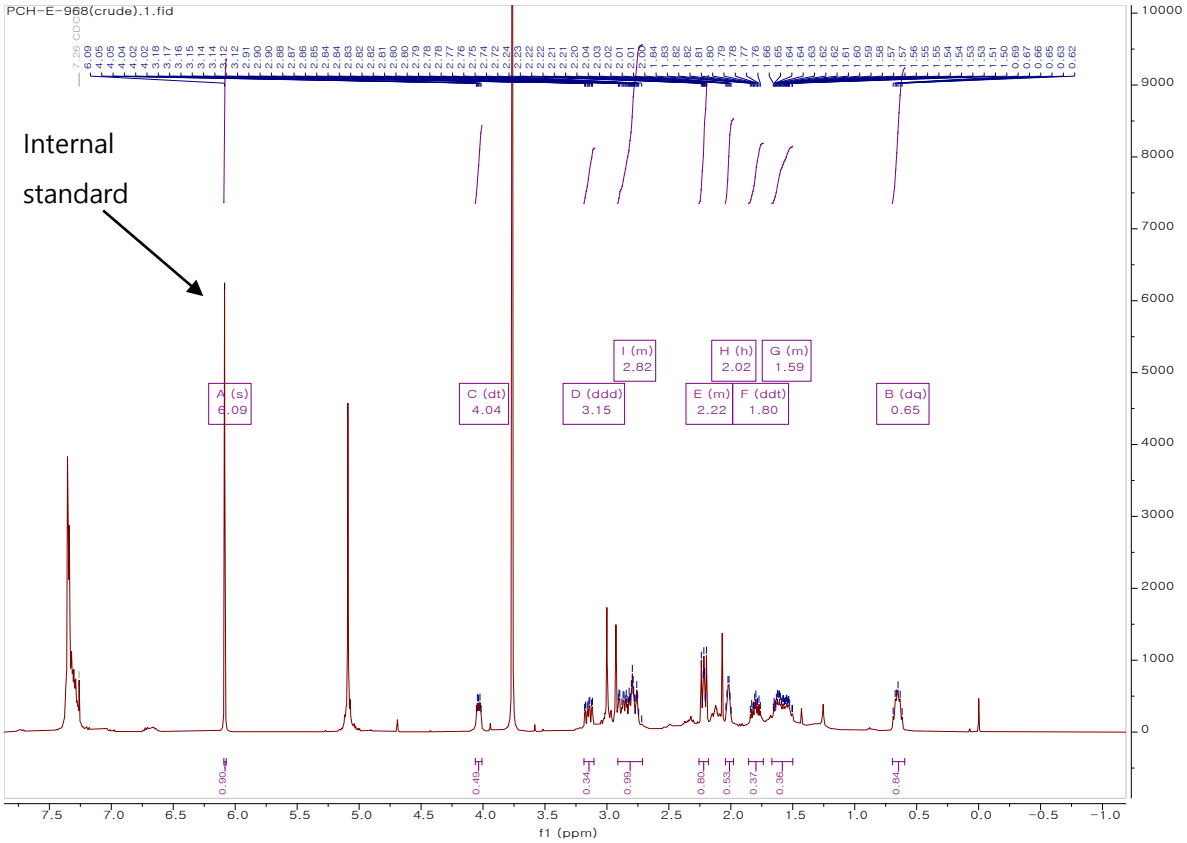
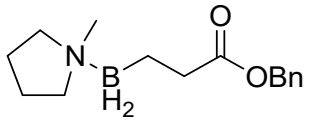


Figure S2. Crude ^{1}H NMR spectroscopy of **4d**

benzyl 3-bornaeylpropanoate N-methyl pyrrolidine complex (4e)



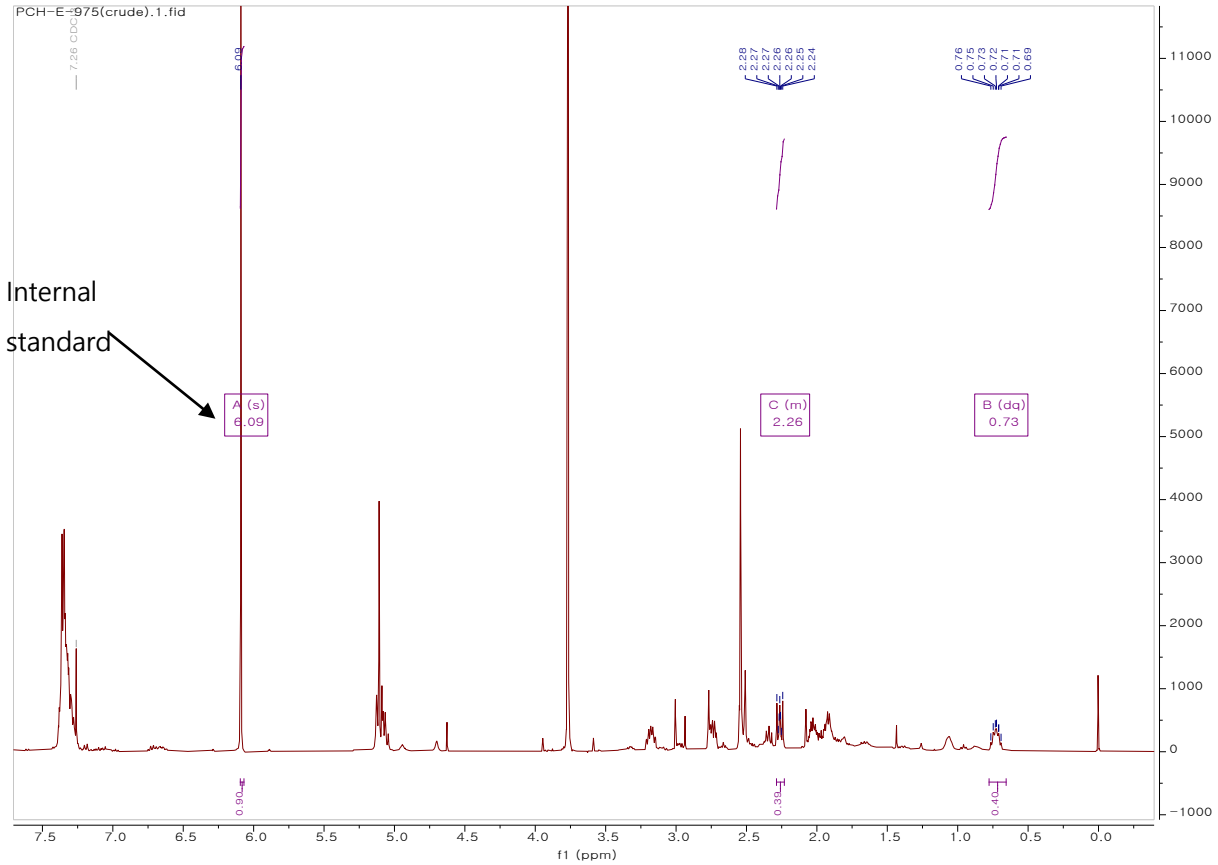
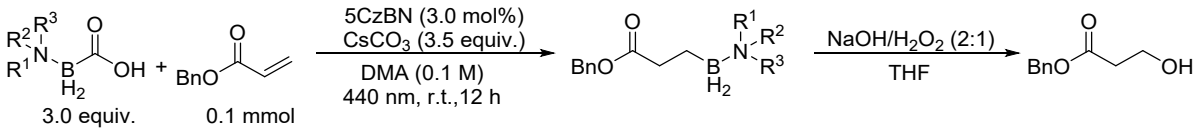


Figure S3. Crude ^{1}H NMR spectroscopy of **4e**

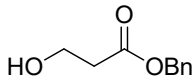
4a, **4d**, and **4e** converted to benzyl 3-hydroxypropanoate **5** by oxidation.

General Procedure for oxidation of C-B bond



After the Giese reaction of boryl radical, DMA was removed by extraction with Et_2O and water. The crude reaction mixture was dissolved in THF (2.0 mL). The reaction solution was cooled to 0 °C and an aqueous solution of 2 M NaOH and 30% H_2O_2 (2:1 v/v, 6 mL) was added dropwise. The solution was stirred vigorously for 2 h. Then it was warmed to room temperature and diluted with water and EtOAc. The layers were separated, the organic layer was washed with Brine and the combined aqueous layers were extracted with EtOAc. The organic layers were combined, dried over $MgSO_4$, and concentrated under vacuum. The solvent was removed under the vacuo and the residue was purified by column chromatography on silica gel to provide the corresponding products.

benzyl 3-hydroxypropanoate (5)

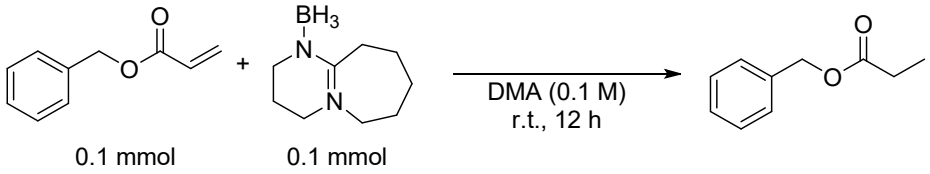


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 5.16 (s, 2H), 3.89 (t, J = 5.6 Hz, 2H), 2.63 (t, J = 5.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 135.8, 128.8, 128.5, 128.4, 66.7, 58.4, 37.0.

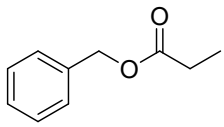
HRMS (FAB) m/z:[M]+ calcd. For $C_{10}H_{12}O_3$ 180.0786; Found 180.0788

Reduction of benzylacrylate by DBU-BH_3



A 4 mL vial was placed under Ar. The DBU-BH_3 (0.1 mmol, 1.0 equiv.) was added followed by DMA as a solvent (1.0 mL), and benzyl acrylate (1.0 mmol, 1.0 equiv.). The reaction was then stirred at room temperature for 12 h. After the reaction, the reaction mixture was diluted with H_2O and Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. The solvent was removed under the vacuo and the residue was purified by column chromatography on silica gel to provide the corresponding products.

benzyl propionate



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 5.12 (s, 2H), 2.39 (q, J = 7.6 Hz, 2H), 1.16 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 136.3, 128.7, 128.3, 66.0, 27.8, 9.3.

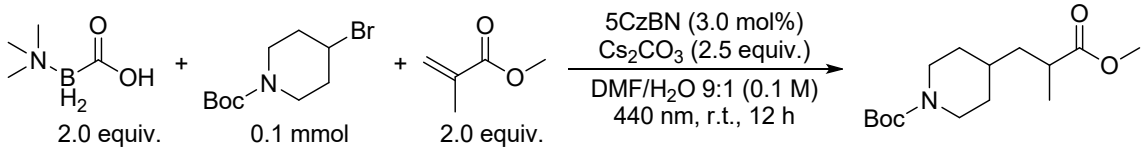
The spectroscopic characterization matched with data reported in the literature.[11]

Isolated yield: 7.7 mg, 47%

5. Mechanism Study

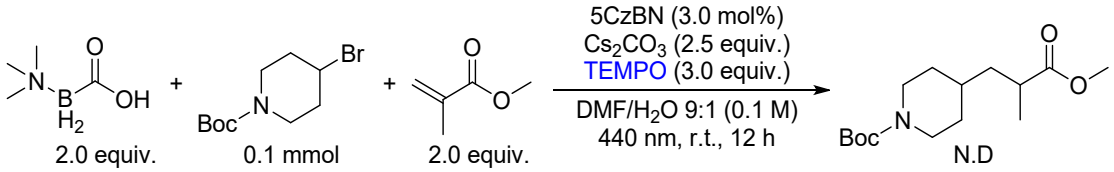
Table S5. Control Experiments

Entry	Photocatalyst	Carboxyborane	Base	Light	Yield (%) [a]
1	-	1a	Cs_2CO_3	440 nm	NR
2	5CzBN	-	Cs_2CO_3	440 nm	NR
3	5CzBN	1a	-	440 nm	NR
4	5CzBN	1a	Cs_2CO_3	-	NR



[a] Yield determined by 1H NMR using dibromomethane, NR = no reaction.

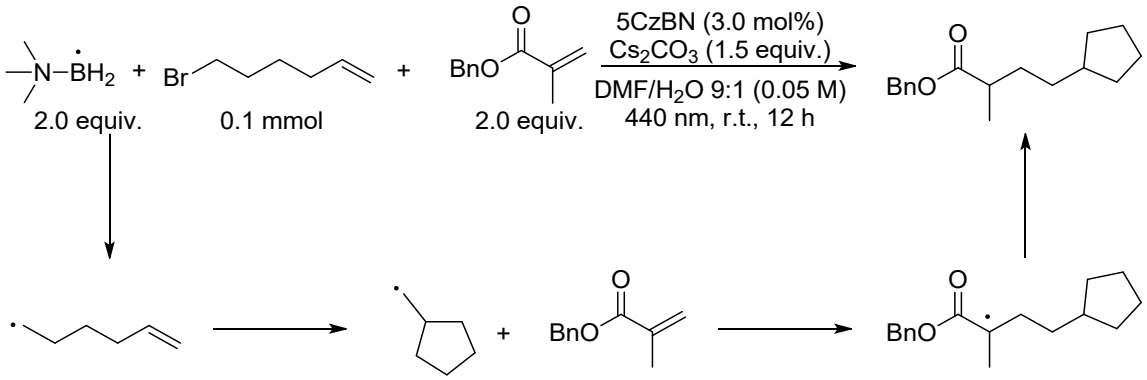
Radical inhibition experiment



A 4 mL vial was placed under Ar. Carboxyborane (**1a**) (0.2 mmol, 2.0 equiv.), *N*-boc-bromopiperidine (0.1 mmol, 1.0 equiv.), 5CzBN (3.0 mol%), TEMPO (0.3 mmol, 3.0 equiv.), and Cs_2CO_3 (0.25 mmol, 2.5 equiv.) were added followed by DMF/H_2O 9:1 mixture as a solvent (1.0 mL), appropriate methyl methacrylate (**2a**) (2.0 mmol, 2.0 equiv.). The reaction was then stirred at room temperature under the irradiation of 440 nm blue LEDs for 12 h. The solvent was removed under the vacuo then, reaction was monitored by TLC and crude NMR.

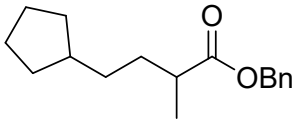
When TEMPO (3.0 equiv.) was introduced into the model reactions under the standard reaction conditions, no desired product was observed according to both TLC and NMR analysis. This result indicated that a free radical process was involved.

Scheme S1. Radical clock experiment



A 4 mL vial was placed under Ar. Carboxyborane (**1a**) (0.2 mmol, 2.0 equiv.), 5CzBN (3.0 mol%), and Cs_2CO_3 (0.25 mmol, 2.5 equiv.) were added followed by DMF/H_2O 9:1 mixture as a solvent (2.0 mL), 6-bromo-1-hexene (0.1 mmol, 1.0 equiv.), and methyl methacrylate (**2a**) (2.0 mmol, 2.0 equiv.). The reaction was then stirred at room temperature under the irradiation of 440 nm blue LEDs for 12 h. The solvent was removed under the vacuo and the residue was purified by column chromatography on silica gel to provide the corresponding products.

benzyl 4-cyclopentyl-2-methylbutanoate (3z)



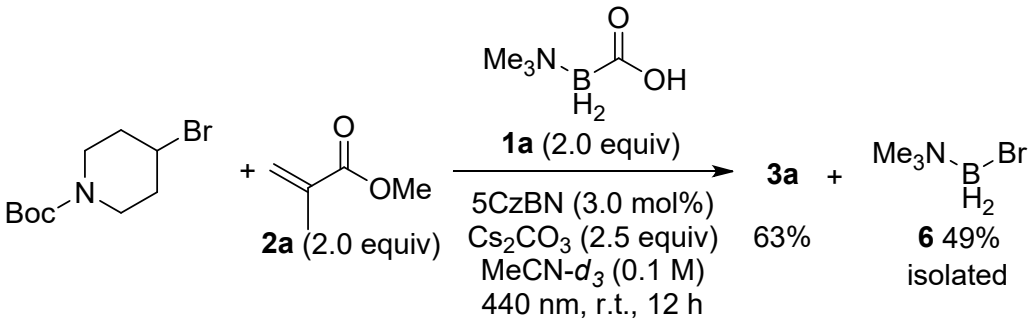
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.12 (s, 2H), 2.47 (h, *J* = 7.0 Hz, 1H), 1.69 (dtdd, *J* = 13.3, 9.7, 6.2, 4.7 Hz, 4H), 1.60 – 1.37 (m, 5H), 1.31 – 1.22 (m, 2H), 1.16 (d, *J* = 7.0 Hz, 3H), 1.09 – 0.96 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 136.5, 128.7, 128.2, 66.1, 40.1, 39.9, 33.8, 33.1, 32.8, 32.7, 25.3, 17.2. (One peak is missing)

The spectroscopic characterization matched with data reported in the literature.[12]

Isolated yield: 14.2 mg, 55%

Isolation of Byproduct: Probing Boryl Radical-Mediated XAT



A 4 mL vial was placed under Ar. Carboxyborane (**1a**) (0.2 mmol, 2.0 equiv.), *N*-boc-bromopiperidine (0.1 mmol, 1.0 equiv.), 5CzBN (3.0 mol%), and Cs_2CO_3 (0.25 mmol, 2.5 equiv.) were added followed by MeCN-d_3 as a solvent (1.0 mL), appropriate methyl methacrylate (**2a**) (2.0 mmol, 2.0 equiv.). The reaction was then stirred at

room temperature under the irradiation of 440 nm blue LEDs for 12 h. The solvent was removed under the vacuo and the residue was purified by column chromatography on silica gel to provide the corresponding products.

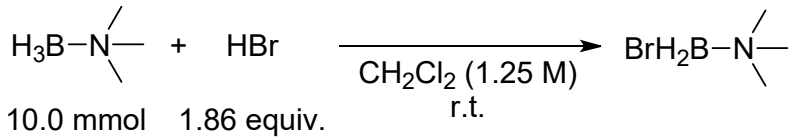
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 9H).

^{11}B NMR (128 MHz, $CDCl_3$) δ -2.49 (t, J = 127.7 Hz).

Isolated yield: 7.5 mg, 49%

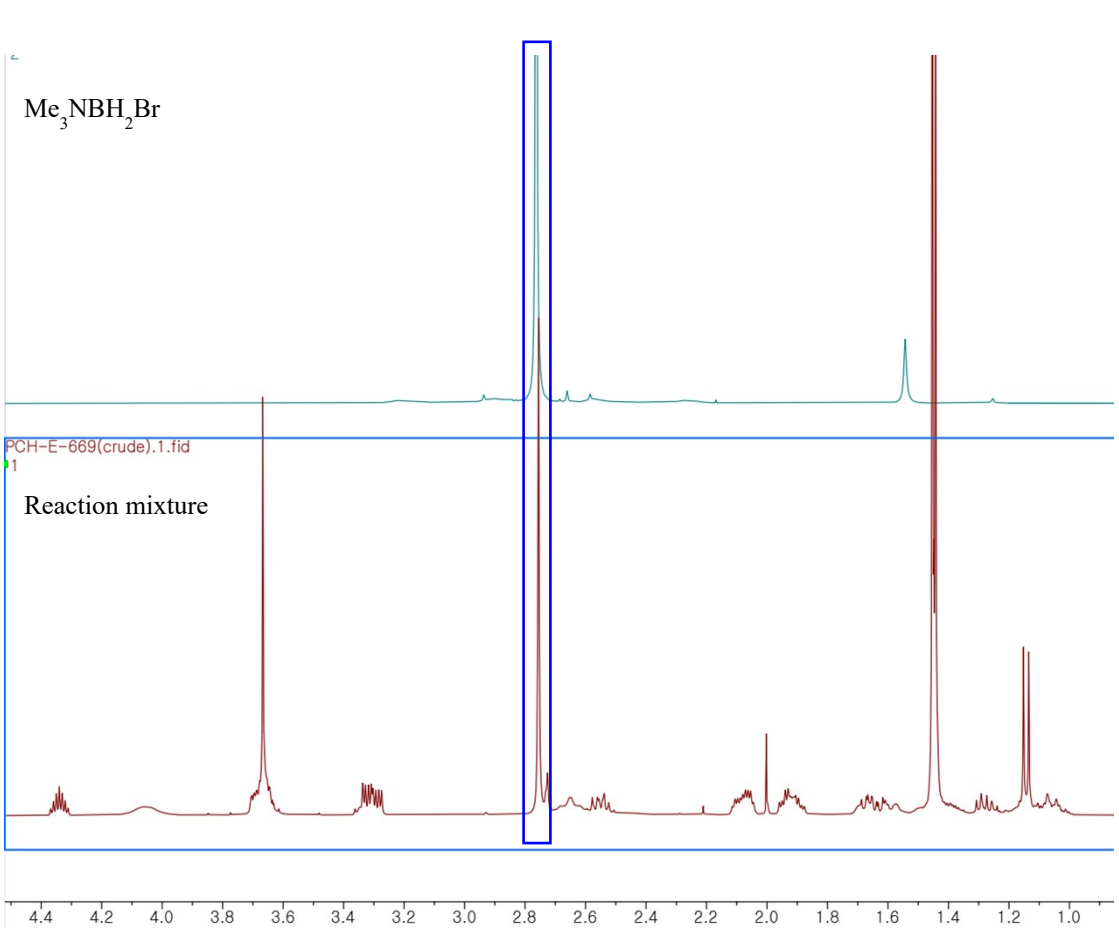
To obtain evidence of the XAT between the amine-boryl radical and the alkyl bromides, we synthesized Me_3NBH_2Br (**6**) and confirmed its formation by comparing crude NMR of reaction mixture and isolation.

Preparation of Me_3NBH_2Br[13]



A 20 mL vial was placed under Ar. Trimethylamine-borane (729 mg, 10.0 mmol) was partially dissolved in 8.0 mL of CH_2Cl_2. Hydrogen bromide (48%, 2.1 mL, 1.86 equiv.) was added and then the reaction mixture was stirred at room temperature till gas evolution ceases. After the reaction, the solvent was removed under the vacuo, and the residue was purified by column chromatography on silica gel to provide the corresponding products.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 9H). ^{11}B NMR (128 MHz, $CDCl_3$) δ -2.49 (t, J = 127.7 Hz).



We have then, compared the crude NMR spectrum of reaction mixture and Me_3NBH_2Br.

Figure S4. [1]H-NMR spectroscopy studies probing boryl radical mediated XAT

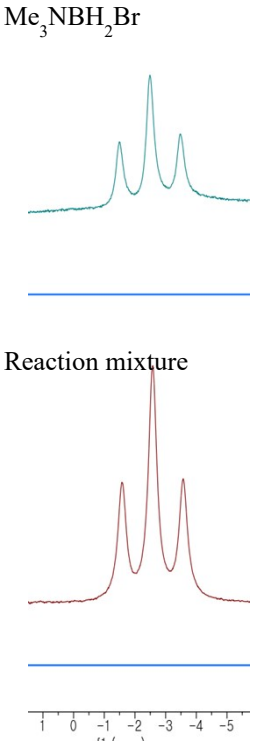
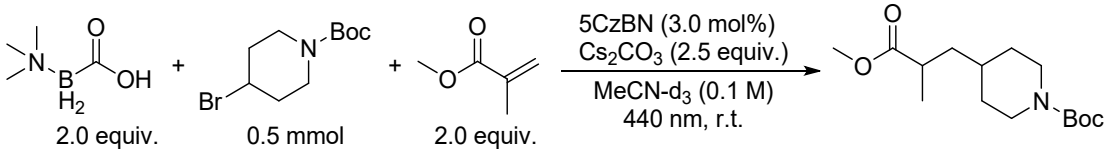


Figure S5. [11]B-NMR spectroscopy studies probing boryl radical mediated XAT

Light on/off experiments



To a 10 mL Schlenk flask equipped with a magnetic stir bar was added *N*-Boc-4-bromo piperidine (0.5 mmol, 1.0 equiv.), trimethylamine carboxyborane (**1a**) (1.0 mmol, 2.0 equiv.), 5CzBN (3.0 mol%), Cs_2CO_3 (1.25 mmol, 2.5 equiv.), and 1,3,5-trimethoxybenzene (0.2 mmol, 0.4 equiv.) as an internal standard. Dry MeCN-d_3 (5.0 mL) was added, after that the methyl methacrylate (**1a**) (1.0 mmol, 2.0 equiv.) was added. The reaction solution was stirred under the irradiation of 440 nm at room temperature. After being stirred for 0.5 h, 0.5 mL sample of the reaction mixture was taken with a syringe and measured by ^{1}H NMR. The Schlenk flask was wrapped in tin foil and stirred for 0.5 h, then 0.5 mL sample of the reaction mixture was taken with a syringe and measured by ^{1}H NMR. Repeating this process.

These experiments revealed that the reaction was completely halted in the absence of light and resumed once illumination was restored, indicating that light is essential for the reaction to proceed. Although it was not possible

to entirely exclude the possibility of a radical-chain mechanism, the findings suggested that any such chain-propagation would be short-lived.

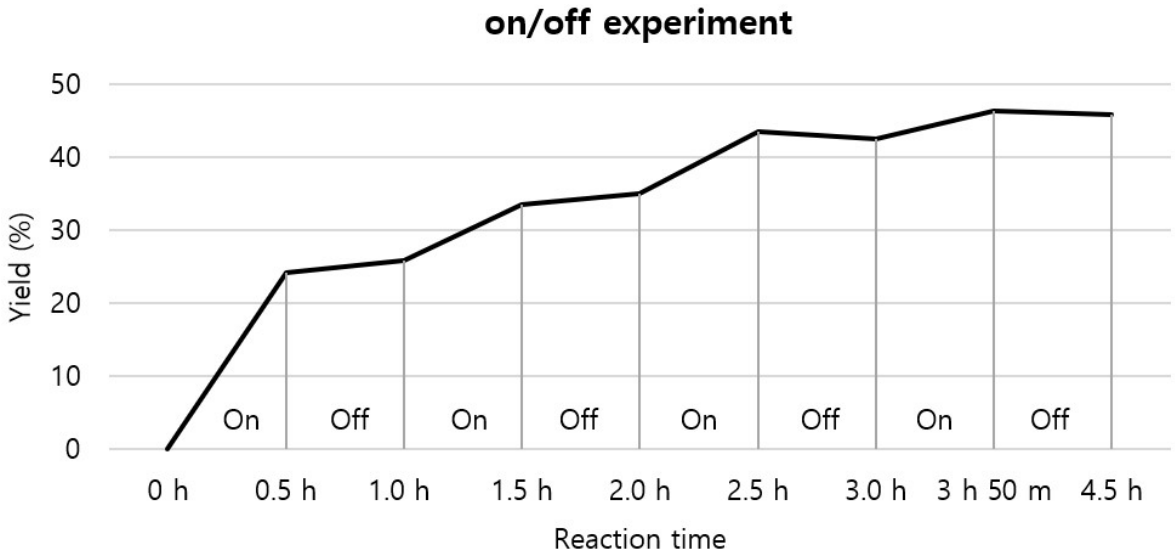


Figure S6. on/off experiment

Stern-Volmer quenching experiments

Stern-Volmer quenching experiments were conducted using a 3.0×10^{-5} M solution of 5CzBN in MeCN and variable quencher concentrations.

The excitation wavelength was 390 nm, and the fluorescence wavelength was 523 nm.

Trimethylamine carboxyborane (**1a**) and tetrabutylammonium hydroxide were used as carboxyborane and base, respectively.

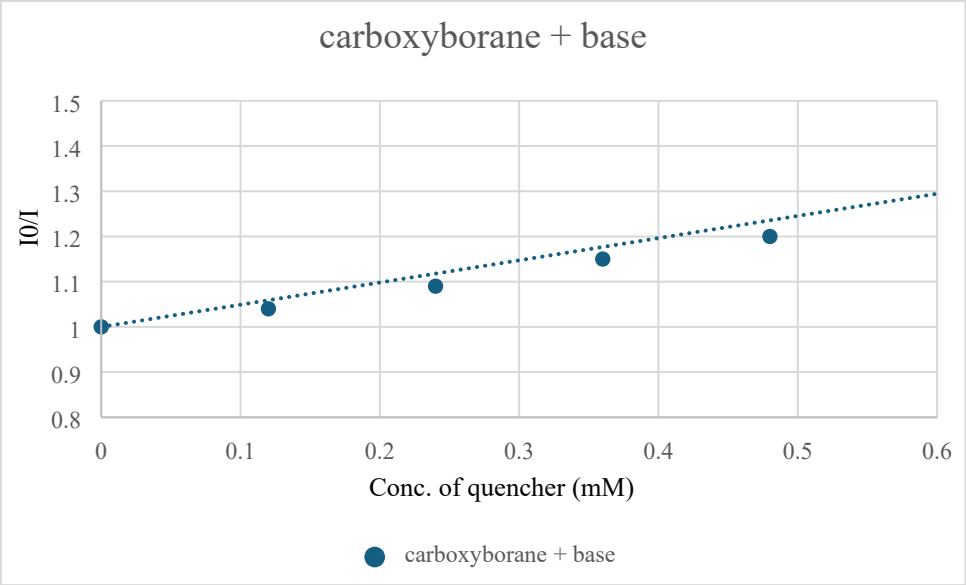


Figure S7. Fluorescence quenching study of carboxyborane + base

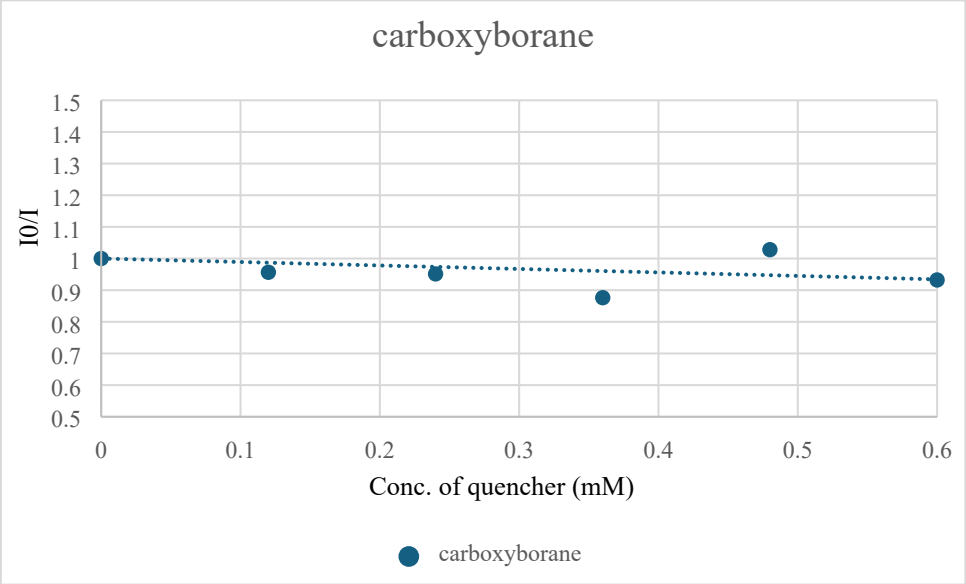


Figure S8. Fluorescence quenching study of carboxyborane

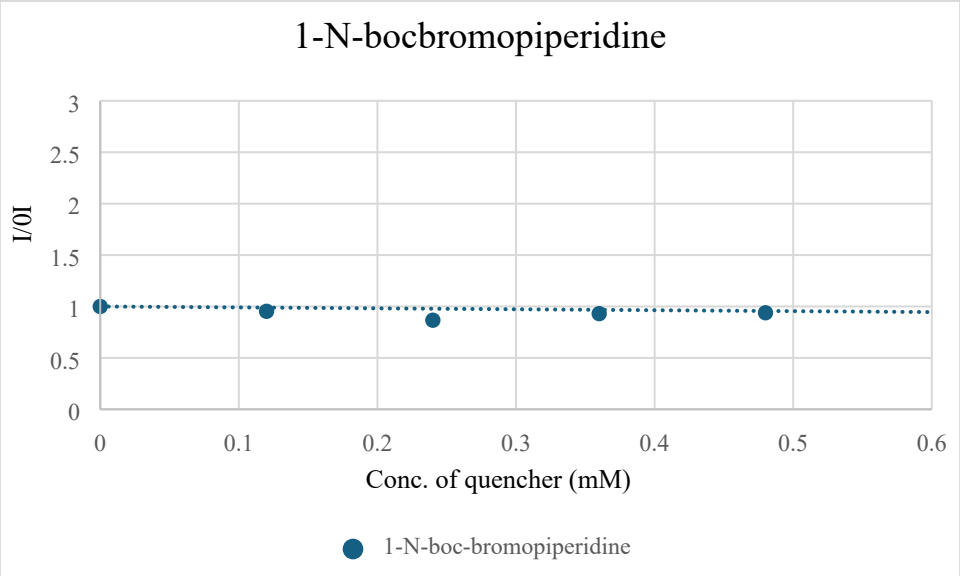


Figure. S9. Fluorescence quenching study of 1-N-boc bromopiperidine

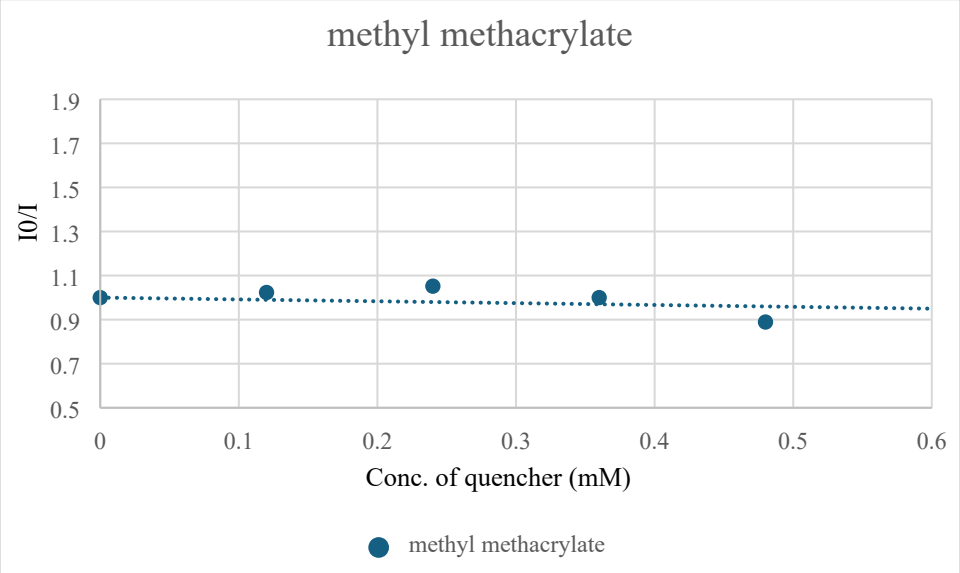


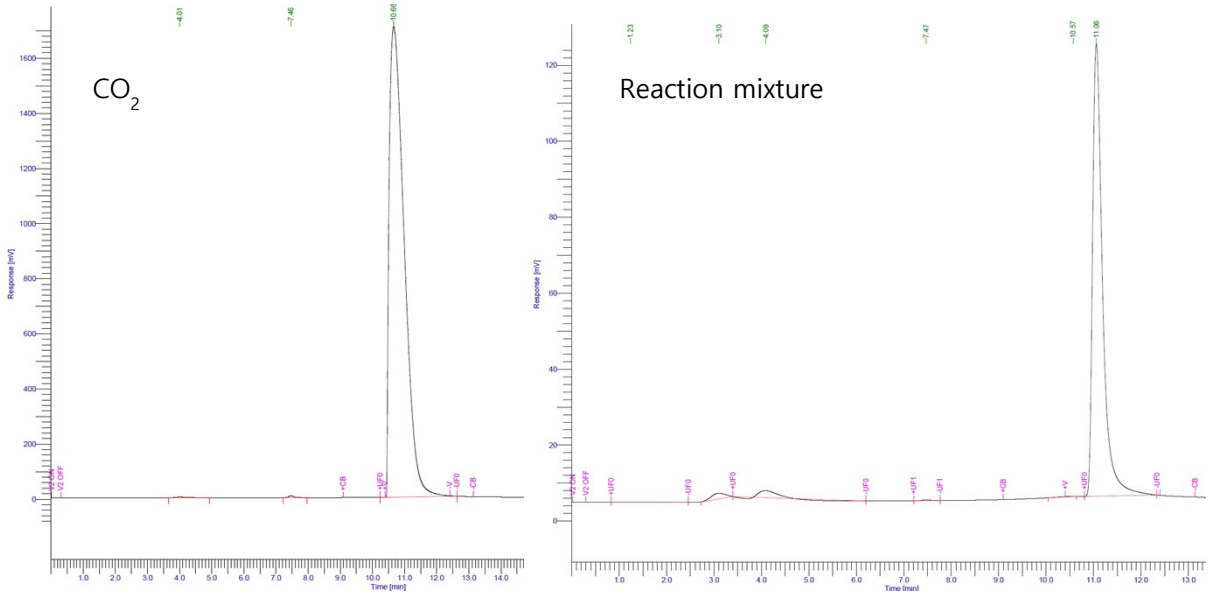
Figure S10. Fluorescence quenching study of methyl methacrylate

Detection of CO_2

To obtain evidence of the release of CO_2 gas during the reaction, we detected CO_2 from gas phase of the reaction mixture by using gas chromatography (GC). GC analyses were performed on a PerkinElmer Clarus GC equipped with packed column (ShinCarbon ST 100/120, 2m 1mmID 1/16OD Silico).

ss

Sample	Detection time (min)
CO_2	10.659
Reaction mixture	11.059



6. Cyclic voltammetry (CV) measurements

6-1. Reagent

Tetrabutylammonium perchlorate (TBAP, $CH_3CH_2CH_2CH_2)_4N(ClO_4)$), anhydrous acetonitrile (CH_3CN) were obtained from Sigma Aldrich (St. Louis, MO, USA) and without further purification. TBAP was dried at 120 ℃ overnight in a vacuum oven.

Borane carboxylate Tetrabutylammonium salt, 1.0 M in methanol used. The salts were prepared in the vials by stoichiometric neutralization of the acid with tetrabutylammonium hydroxide in methanol in the presence of a 3 Å molecular sieve.

6-2. Cyclic voltammetry (CV) measurements

The electrochemical experiment was performed by using a CHI 660D potentiostat (CH Instruments, Austin, TX, USA). All electrochemical measurements were conducted in the Faraday cage. Sample (5.0 mM) and tetrabutylammonium perchlorate (0.1 M) in anhydrous CH_3CN were used for test solutions. The solutions were purged with N_2 gas for 30 mins. All electrochemical measurements were performed with a three-electrode system at room temperature. Measurements were conducted using a glassy carbon electrode as a working electrode, platinum wire as a counter electrode, and Ag/Ag^+ reference electrode at a scan rate of 0.1 V/s. Ferrocene (+0.4 V vs SCE) was added at the end of the measurements as an internal standard to determine the precise potential scale.

Samples	E_p^{ox} vs.		$E_{p/2}^{ox}$ vs.	
	SCE	Fc/Fc^+	SCE	Fc/Fc^+
$NHC\text{-}BH_3$	1.11 V	0.71 V	0.98 V	0.58 V
$Me_3N\text{-}BH_3$	2.18 V	1.78 V	1.74 V	1.34 V
$DMAP\text{-}BH_3$	0.96 V	0.56 V	0.85 V	0.45 V
$DBU\text{-}BH_3$	1.42 V	1.02 V	1.29 V	0.89 V
$Me_3N\text{-}BH_2COO^-$	1.22 V	0.82 V	1.09 V	0.69 V
$DMAP\text{-}BH_2COO^-$	1.26 V	0.86 V	1.09 V	0.69 V
$DBU\text{-}BH_2COO^-$	1.31 V	0.91 V	1.12 V	0.72 V
$Me_3N\text{-}BH_2COOH$	2.11 V	1.71 V	1.94 V	1.54 V

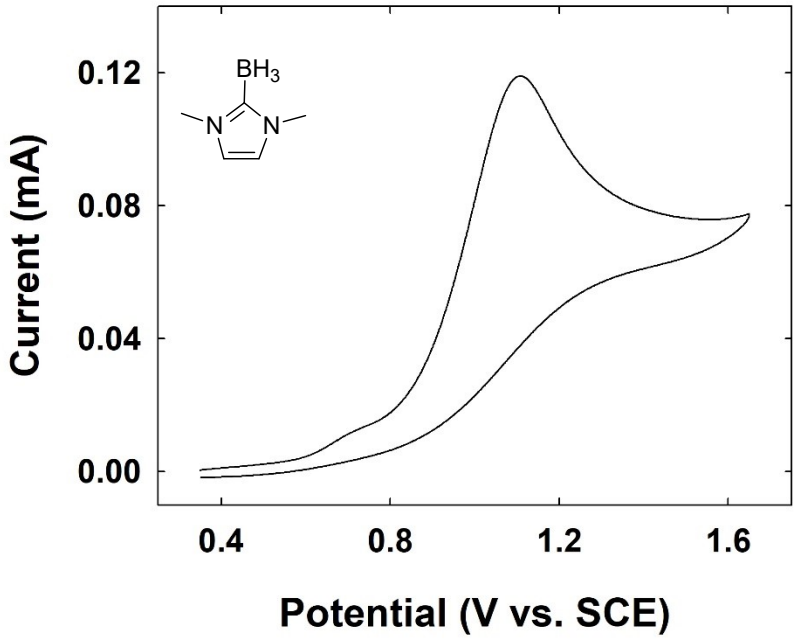


Figure S12. Cyclic voltammetry of NHC-BH_3. $E_{p/2}^{ox}$ = +0.98 V (vs SCE).

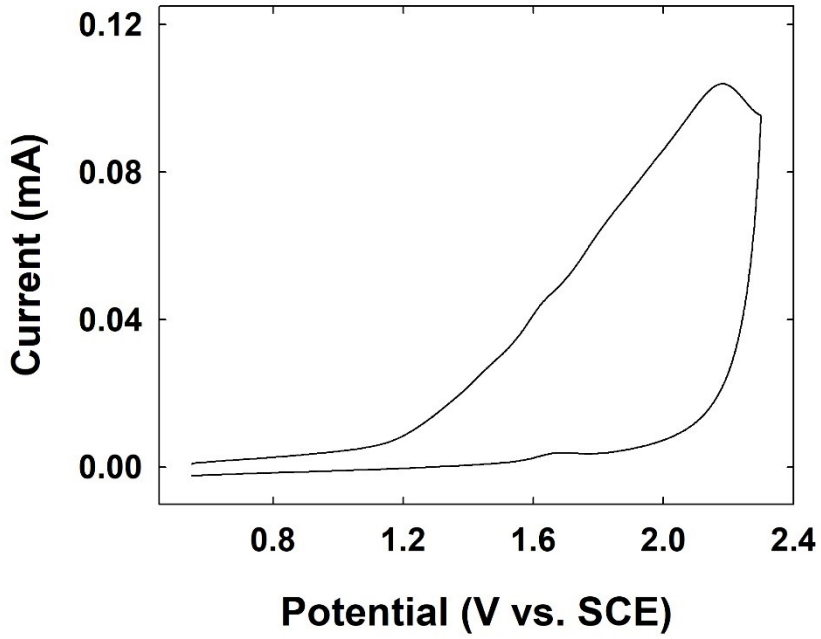


Figure S13. Cyclic voltammetry of Me_3N-BH_3. $E_{p/2}^{ox}$ = +1.74 V (vs SCE).

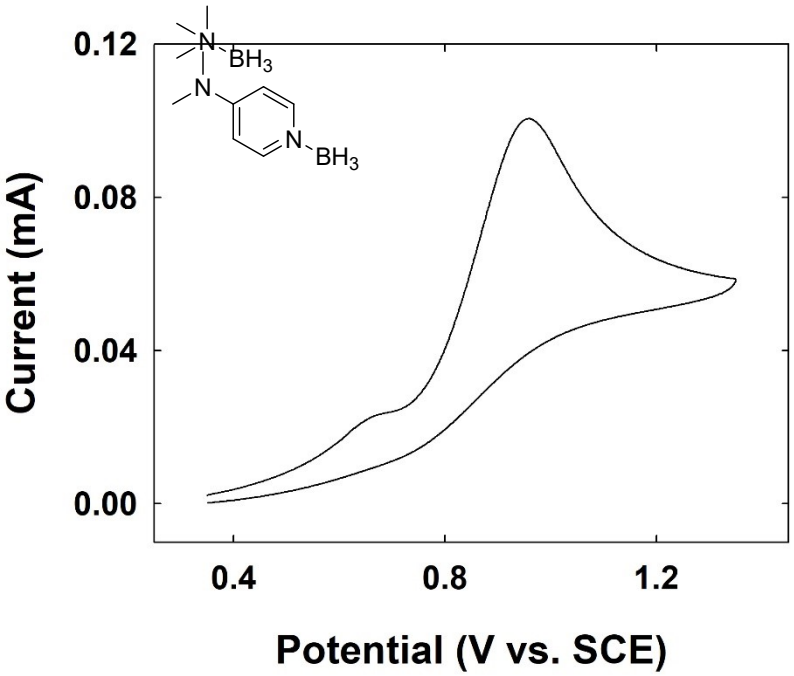


Figure S14. Cyclic voltammetry of DMAP-BH_3. $E_{p/2}^{ox}$ = +0.85 V (vs SCE).

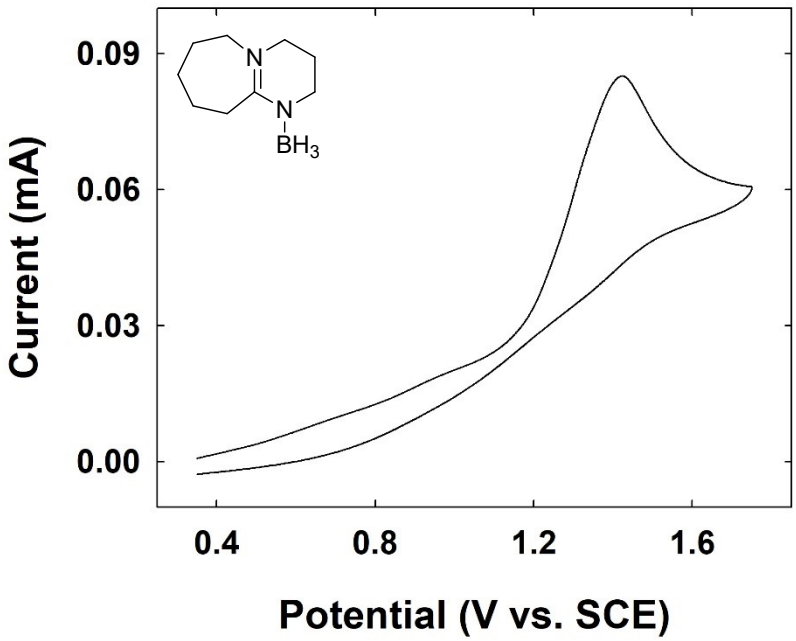
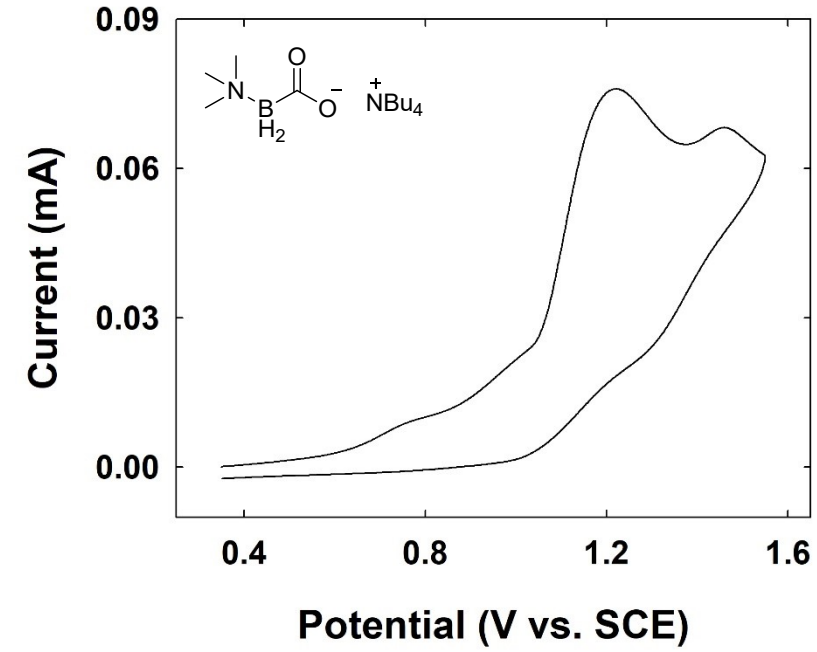


Figure S15. Cyclic voltammetry of DBU-BH_3. $E_{p/2}^{ox}$ = +1.29 V (vs SCE).



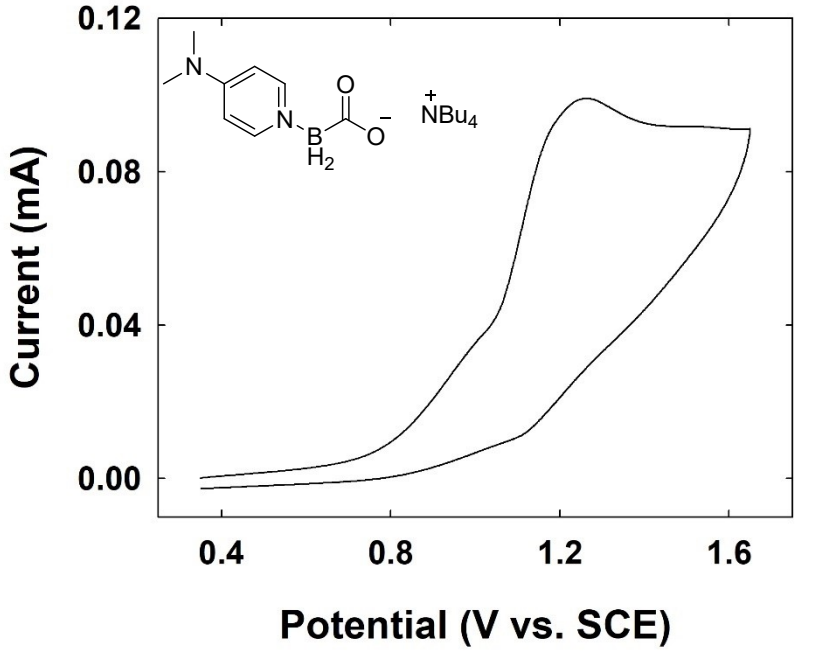


Figure S16. Cyclic voltammetry of Me_3N-BH_2-COO^-. $E_{p/2}^{ox}$ = +1.09 V (vs. SCE).

Figure S17. Cyclic voltammetry of DMAP-BH_2-COO^-. $E_{p/2}^{ox}$ = +1.09 V (vs. SCE).

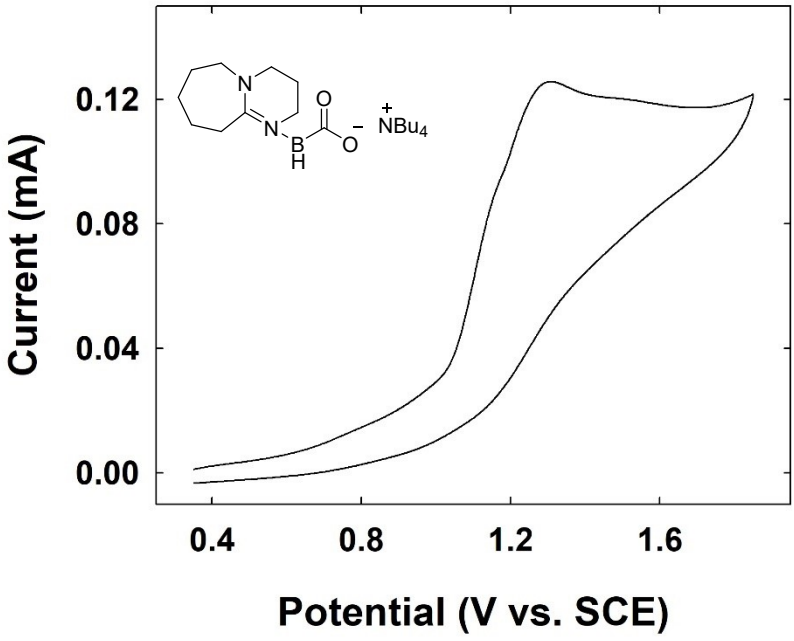


Figure S18. Cyclic voltammetry of DBU-BH_2-COO^-. $E_{p/2}^{ox}$ = +1.12 V (vs. SCE).

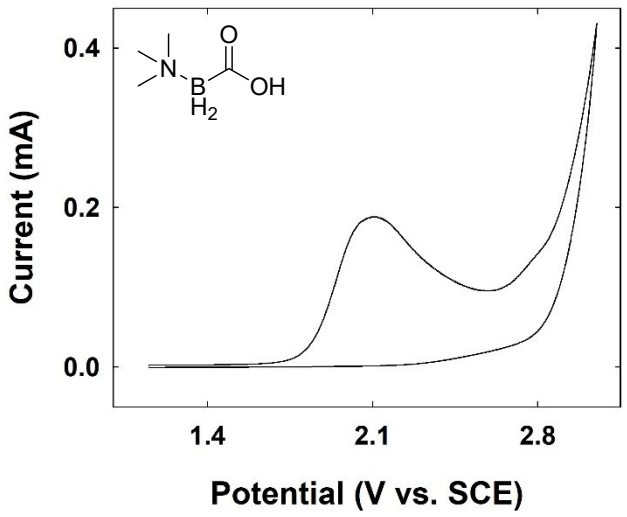


Figure S19. Cyclic voltammetry of of Me_3N-BH_2-COOH. $E_{p/2}^{ox}$ = +1.94 V

7. DFT calculation studies

The spin densities were calculated by the natural bond orbital (NBO) analysis[14] at the UM06-2X-D3/6-31+G(d,p)/SMD(MeCN) level of theory[15–17] using the Gaussian 16 suite of programs.[18]

Spin density of amine-boryl radicals

	$Me_3N-\dot{B}H_2$	DMAP$-\dot{B}H_2$	DBU$-\dot{B}H_2$
spin density on B =	1.026	0.387	0.147

- Cartesian coordinates for Me_3N-BH_2•, **I**

Atom	X	Y	Z
C	0.00008300	0.79069200	1.21258900
C	-1.20851800	-0.83499800	-0.10835800
C	1.20835800	-0.83522400	-0.10837200
H	1.04406000	1.61675300	-1.39905800
H	-1.04376800	1.61695500	-1.39904400
H	0.00002600	0.09142600	2.05494900
H	0.89258000	1.41683400	1.24759500
H	-0.89229400	1.41700100	1.24761100
H	-1.20004200	-1.51199300	0.75053600
H	-1.19841200	-1.40624700	-1.03813300
H	-2.09562400	-0.20105000	-0.07583100
H	2.09558200	-0.20144200	-0.07585700
H	1.19976500	-1.51221400	0.75052400
H	1.19813300	-1.40647400	-1.03814500
B	0.00008900	1.02914800	-1.30281900
N	0.00000200	0.03027100	-0.06945800

- Cartesian coordinates for DMAP-BH_2•, **II**

Atom	X	Y	Z
C	-0.16453500	-1.19960800	-0.06318500
C	-1.52922400	-1.18153300	-0.00339400
N	-2.27717800	-0.00002700	0.02162700
C	-1.52924200	1.18150500	-0.00361700
C	-0.16457600	1.19959800	-0.06337600
C	0.59749700	-0.00002100	-0.10960500
B	-3.70523400	-0.00000500	0.07905900
H	-4.26370200	1.05298700	0.10182200

H	-4.26372800	-1.05298100	0.10201000
N	1.97924400	0.00003200	-0.22538000
C	2.68320500	1.23027700	0.10530700
C	2.68334600	-1.23022400	0.10491400
H	0.31375400	2.17147100	-0.07106600
H	-2.11130100	2.09384800	0.03393800
H	-2.11124300	-2.09389300	0.03434900
H	0.31376800	-2.17150300	-0.07059500
H	3.75047300	1.07521900	-0.05600800
H	2.36334200	2.04683700	-0.54620900
H	2.52357700	1.53248200	1.15217100
H	3.75046900	-1.07538000	-0.05758800
H	2.36274600	-2.04687200	-0.54611800
H	2.52472100	-1.53218500	1.15200500

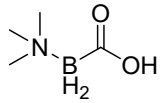
- Cartesian coordinates for DBU-BH_2•, **III**

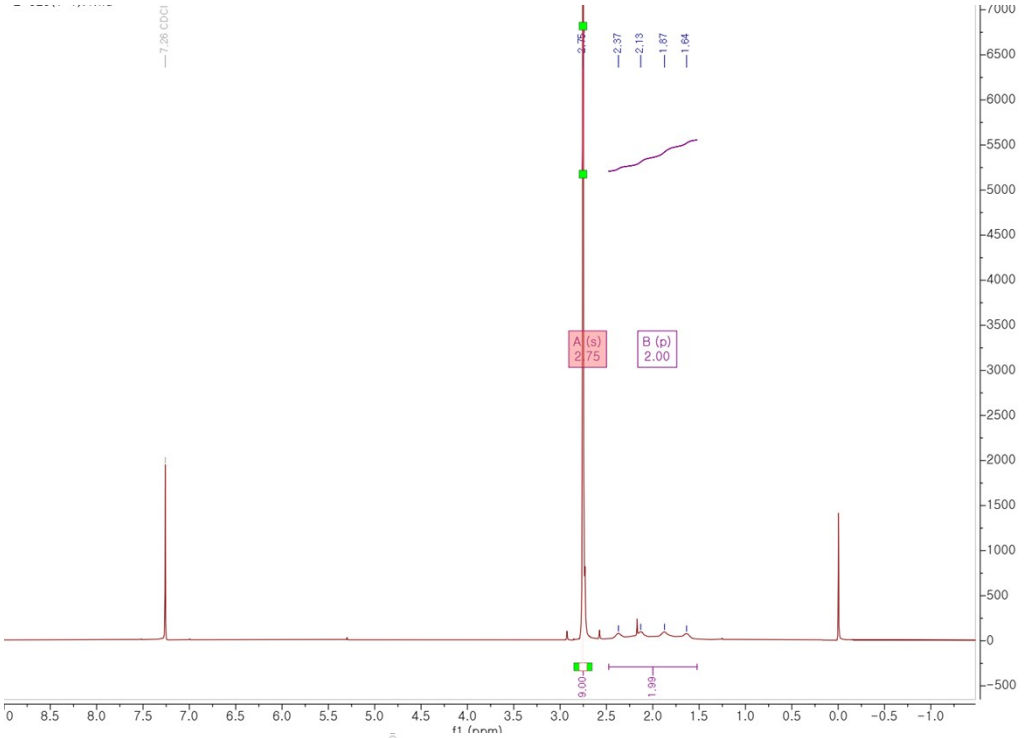
Atom	X	Y	Z
N	0.10122700	-0.79751600	-0.56716900
C	0.26613400	0.51952300	-0.12009800
N	1.61130400	0.95401400	0.01539200
C	2.46002100	0.01839400	0.77258200
C	2.38356000	-1.36364000	0.14351100
C	0.93252700	-1.81391800	0.08513400
C	-1.25632700	-1.25565000	-0.86348900
C	-2.27140500	-1.13871900	0.28335700
C	-2.95681900	0.22732800	0.32419500
C	-2.01890500	1.39748900	0.61325800
C	-0.81649000	1.53505100	-0.34297400
B	2.14735000	2.12898700	-0.52700000
H	1.48051100	2.84266400	-1.21233700
H	3.28687400	2.39504700	-0.28097900
H	3.48099800	0.40209400	0.77349200
H	2.09801300	-0.02572300	1.80868900
H	2.80170500	-1.32518600	-0.86939700
H	2.96835700	-2.07885600	0.72971900
H	0.84042400	-2.74170200	-0.48578400
H	0.56468300	-2.00556200	1.10837900
H	-1.15835800	-2.29976900	-1.17224500

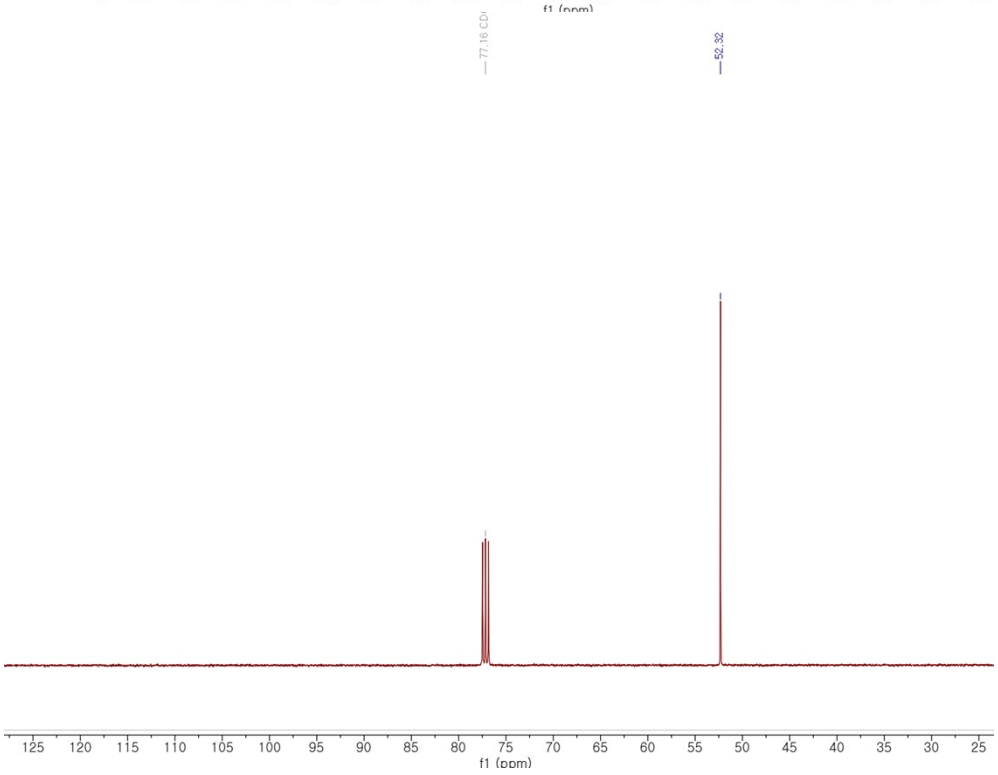
H	-1.63227600	-0.70279300	-1.73282700
H	-1.77151600	-1.35021900	1.23867800
H	-3.03488700	-1.91297100	0.14657800
H	-3.44517900	0.39361200	-0.64662500
H	-3.75332000	0.21721500	1.07763000
H	-2.59743400	2.32792800	0.56351400
H	-1.63474500	1.31709800	1.63883200
H	-1.17546000	1.53240400	-1.38580100
H	-0.37663200	2.51914300	-0.17493200

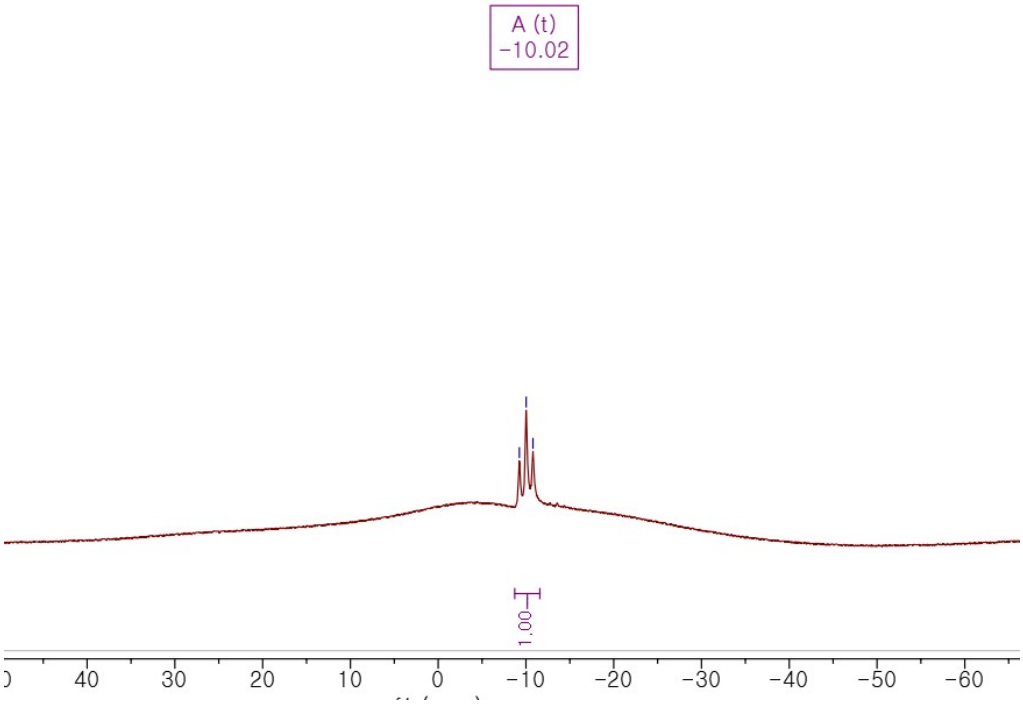
8. NMR spectra

Trimethylamine carboxyborane (1a)

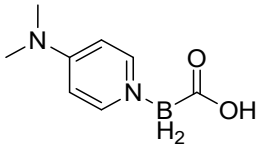


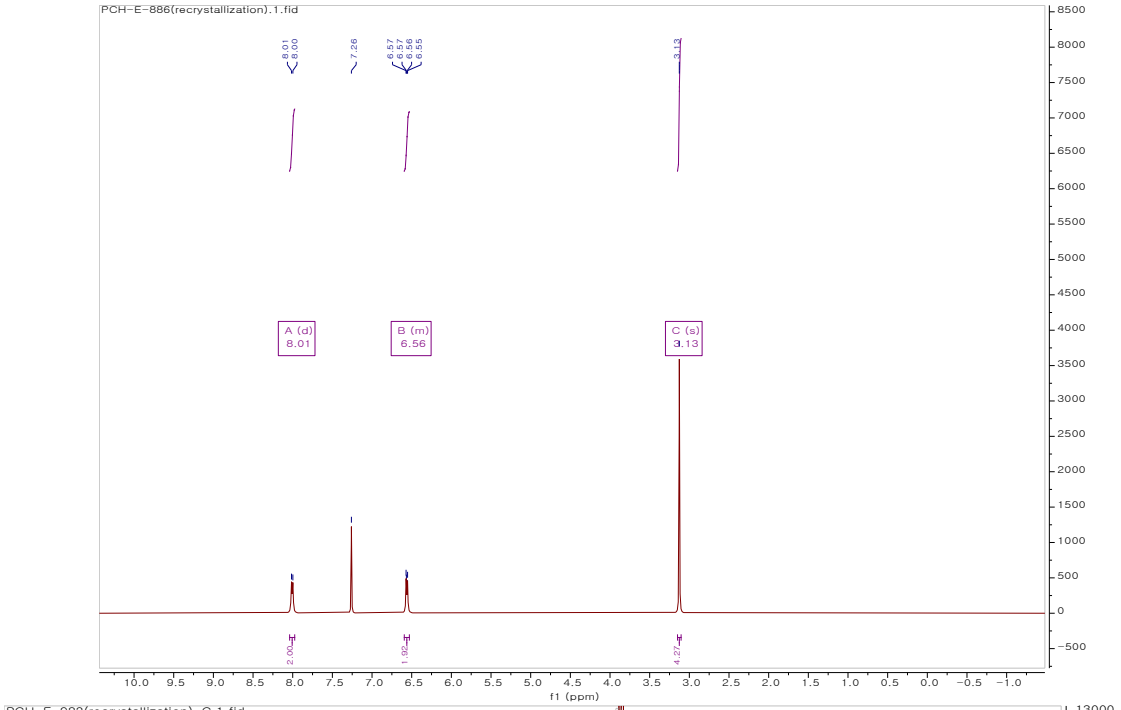


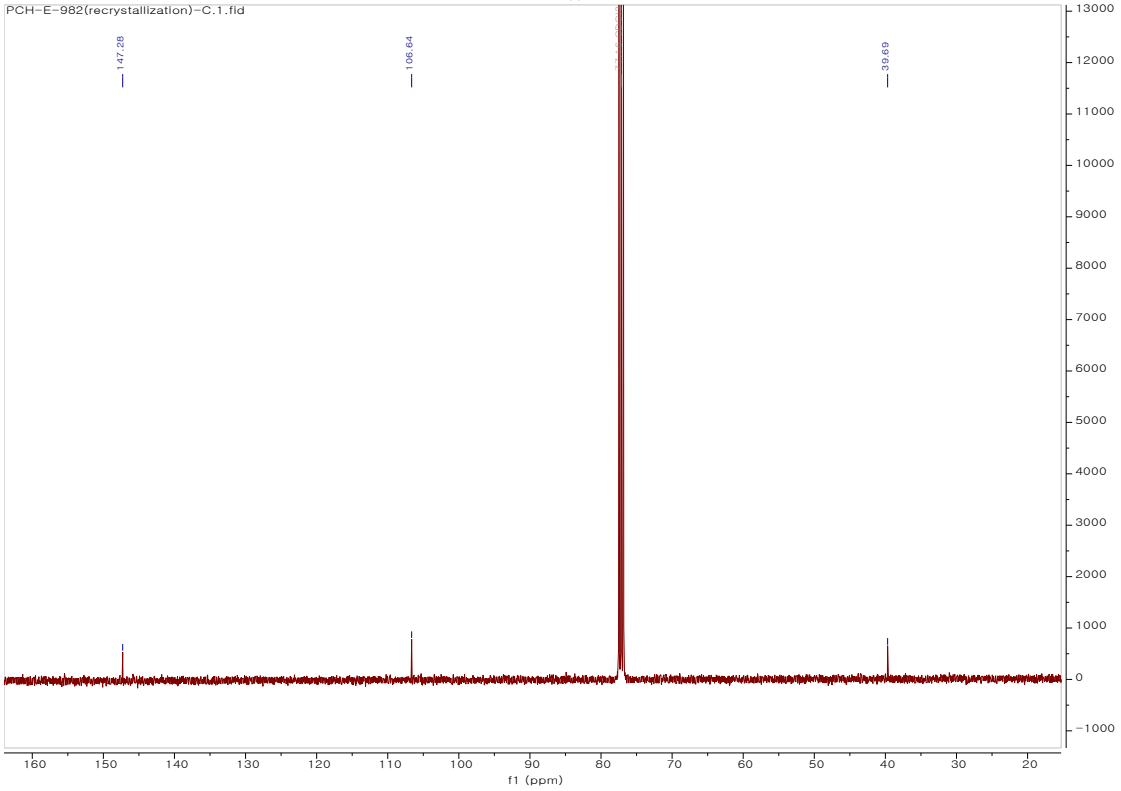


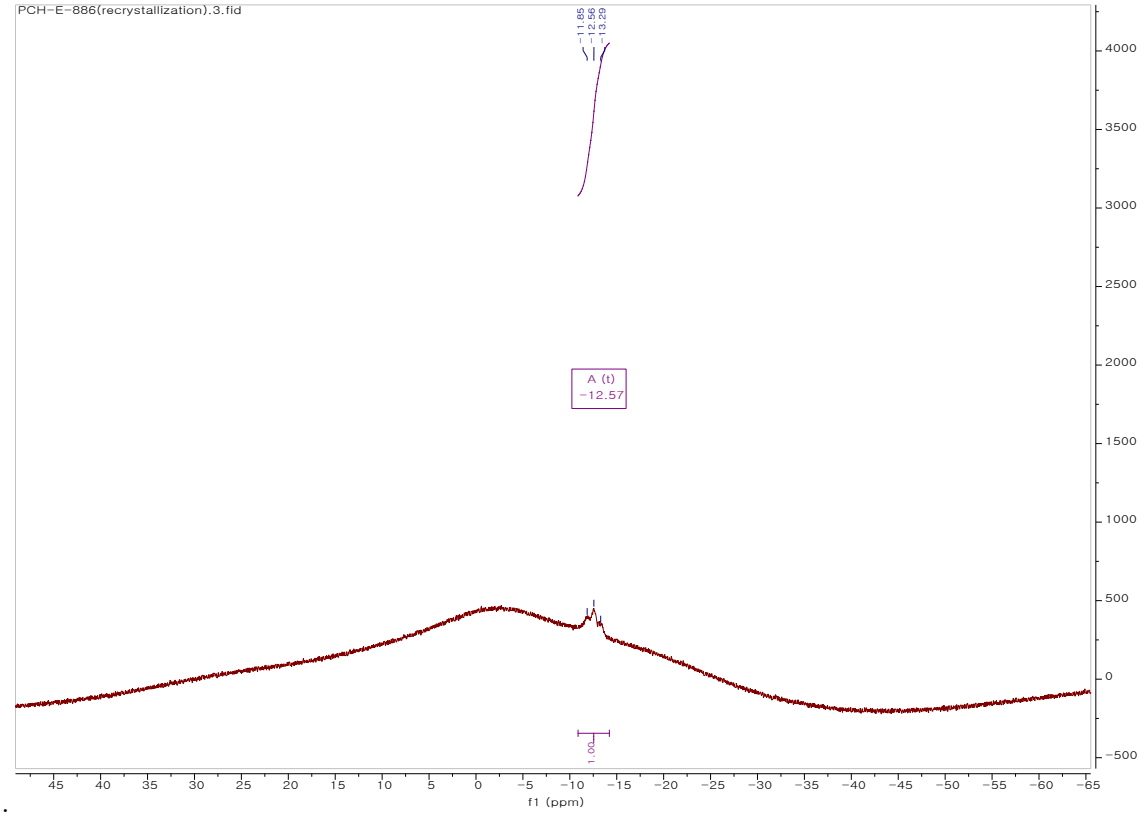

A (t)
-10.02
1.00
40
30
20
10
0
-10
-20
-30
-40
-50
-60

DMAP-carboxyborane (1b)

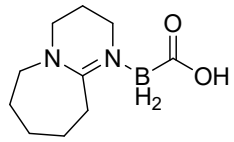


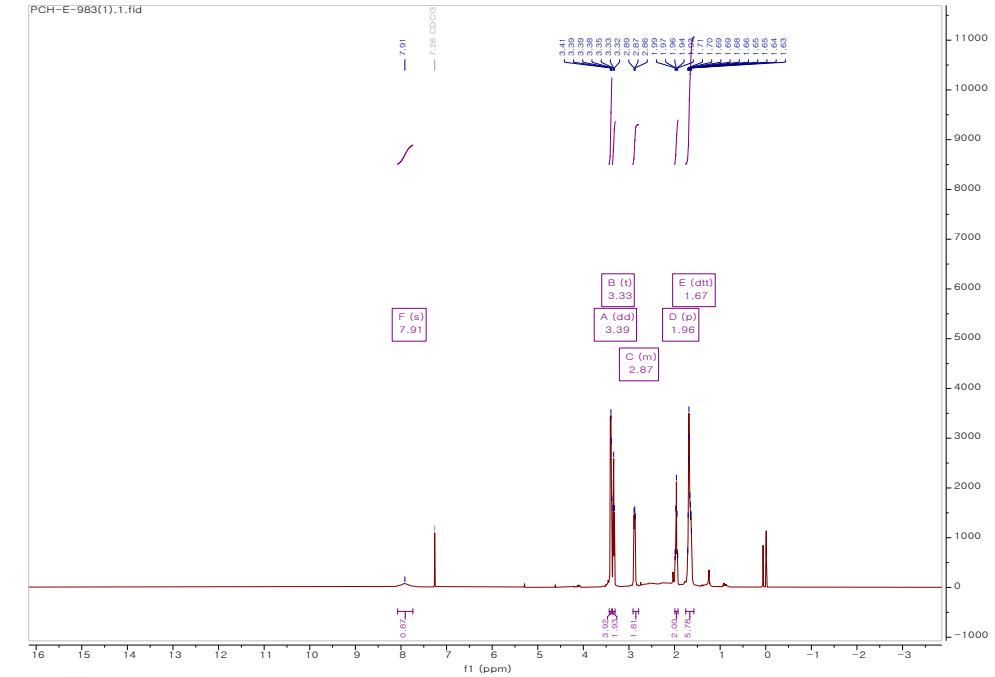


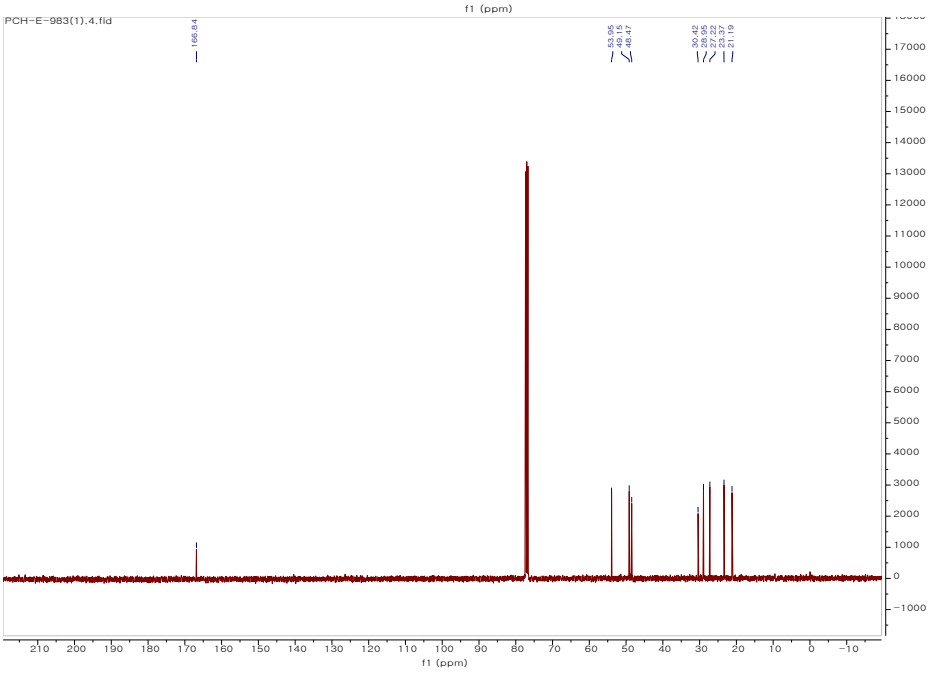


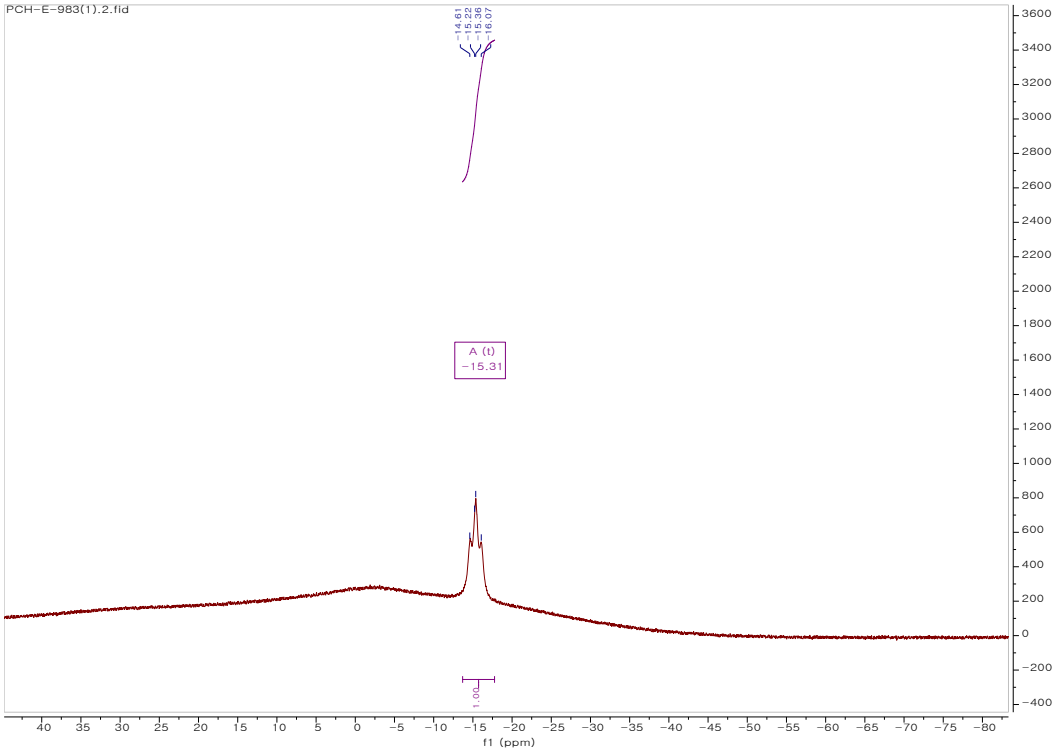

PCH-E-886(recrystallization).3.fid
-11.85
-12.56
-13.29
A (t)
-12.57
1.00
4000
3500
3000
2500
2000
1500
1000
500
0
-500
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65
f1 (ppm)

DBU-carboxyborane (1c)

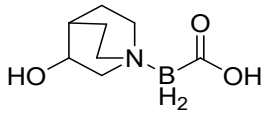


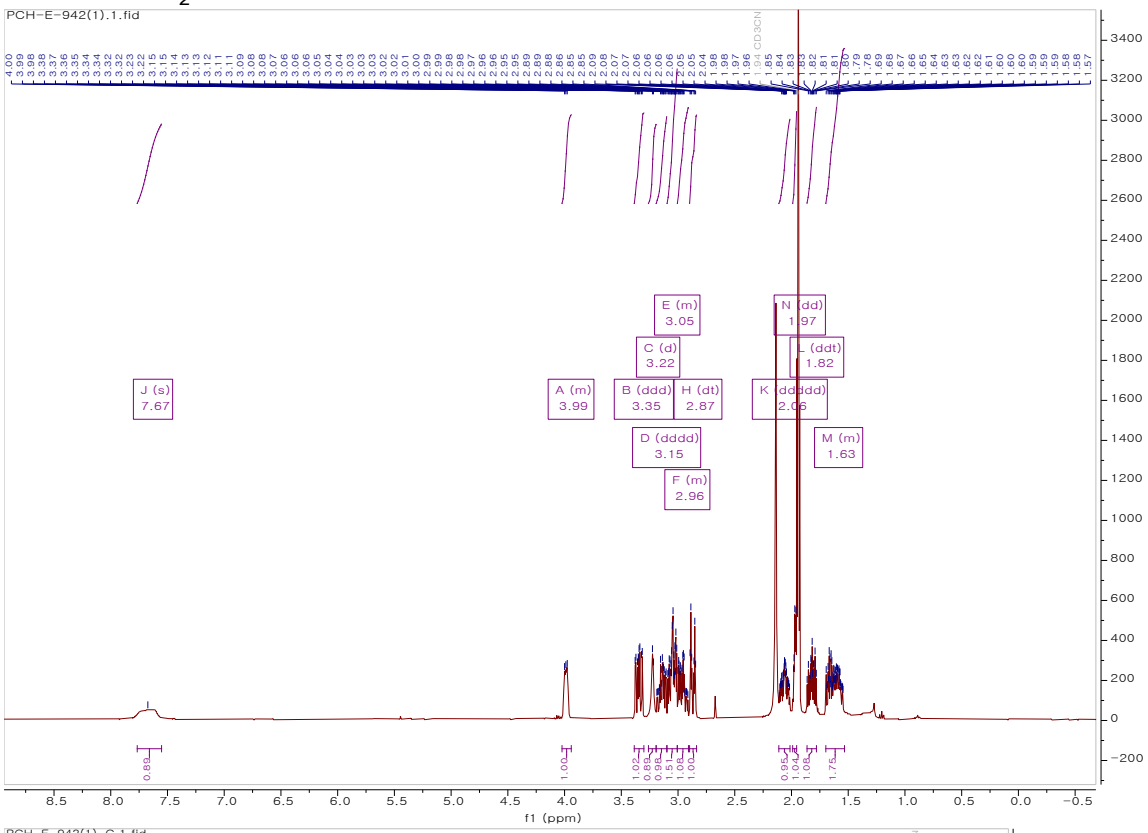


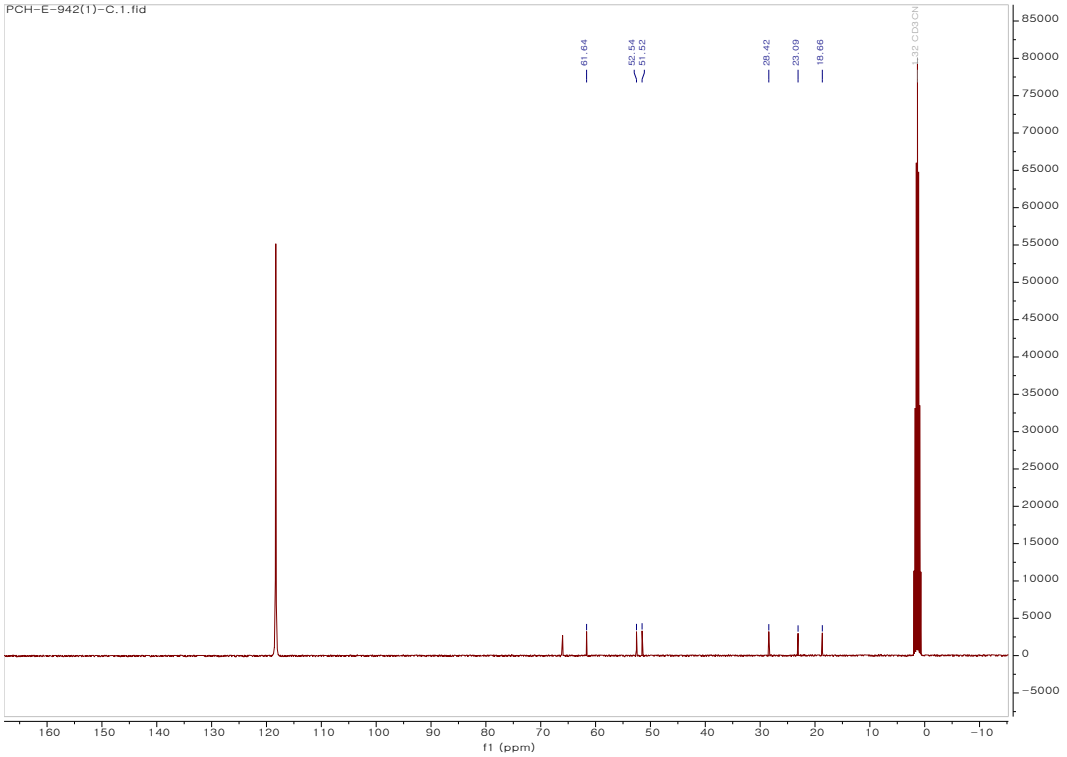


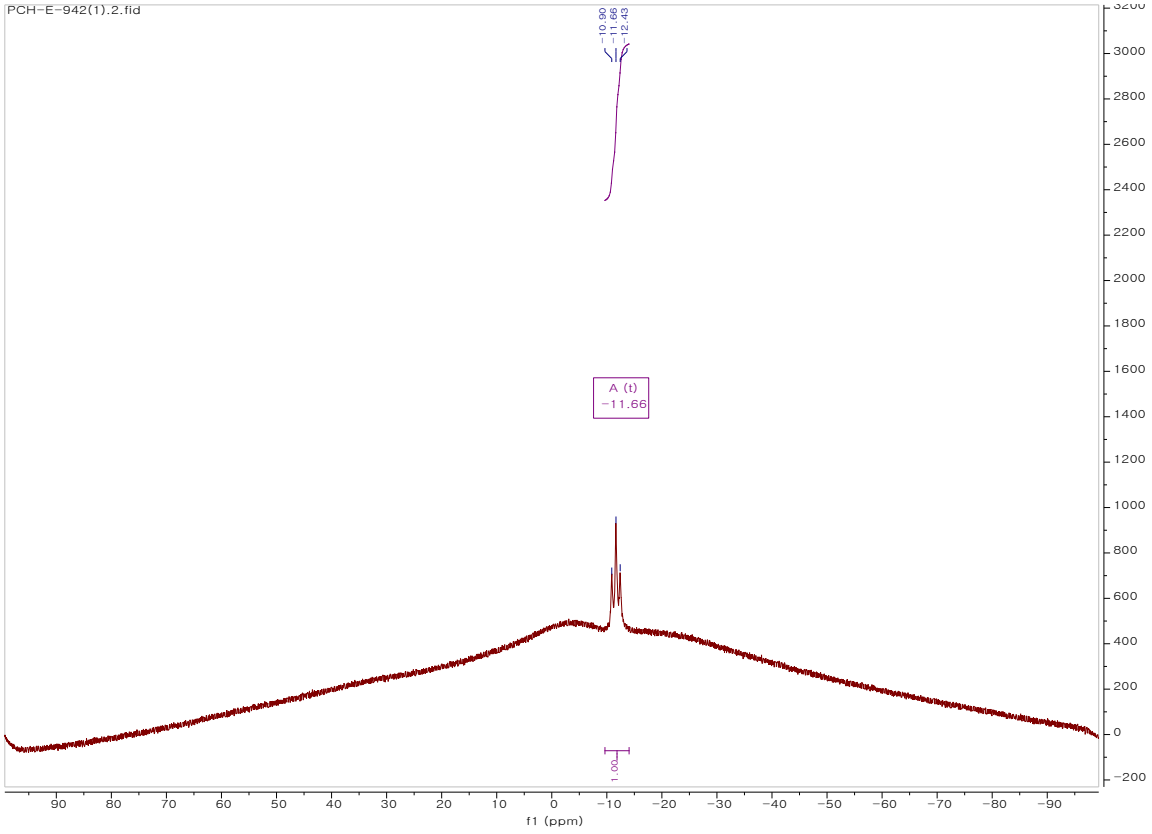

PCH-E-983(1).2.fid
-14.61
-15.22
-15.38
-16.07
A (t)
-15.31
1.00
f1 (ppm)

3-Quinuclidinol-carboxyborane (1d)

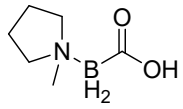


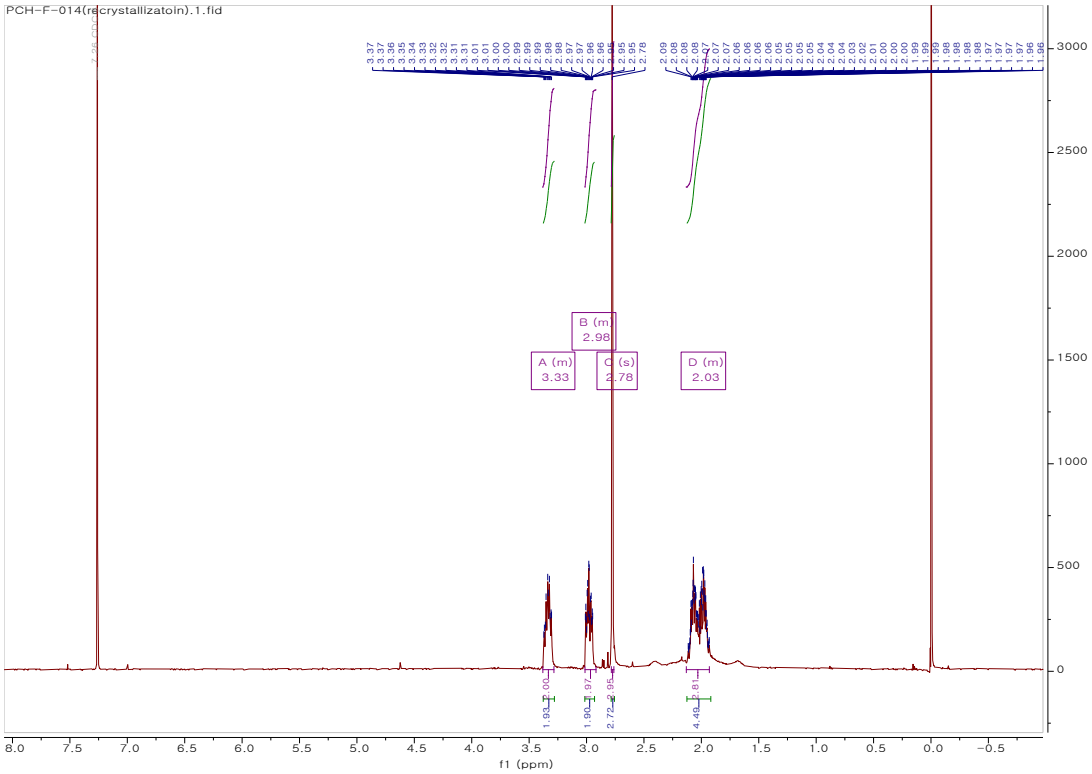


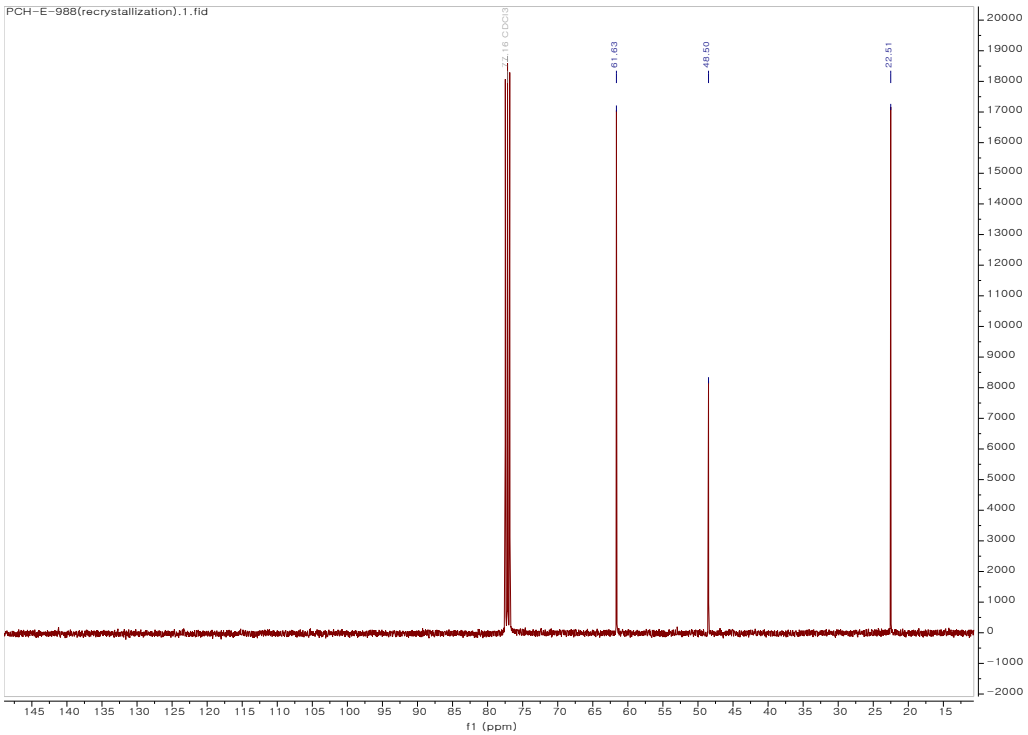



PCH-E-942(1).2.fid
-10.90
-11.66
-12.43
A (t)
-11.66
1.00
f1 (ppm)

N-methyl pyrrolidine-carboxyborane (1e)

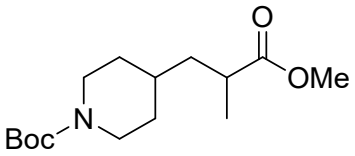


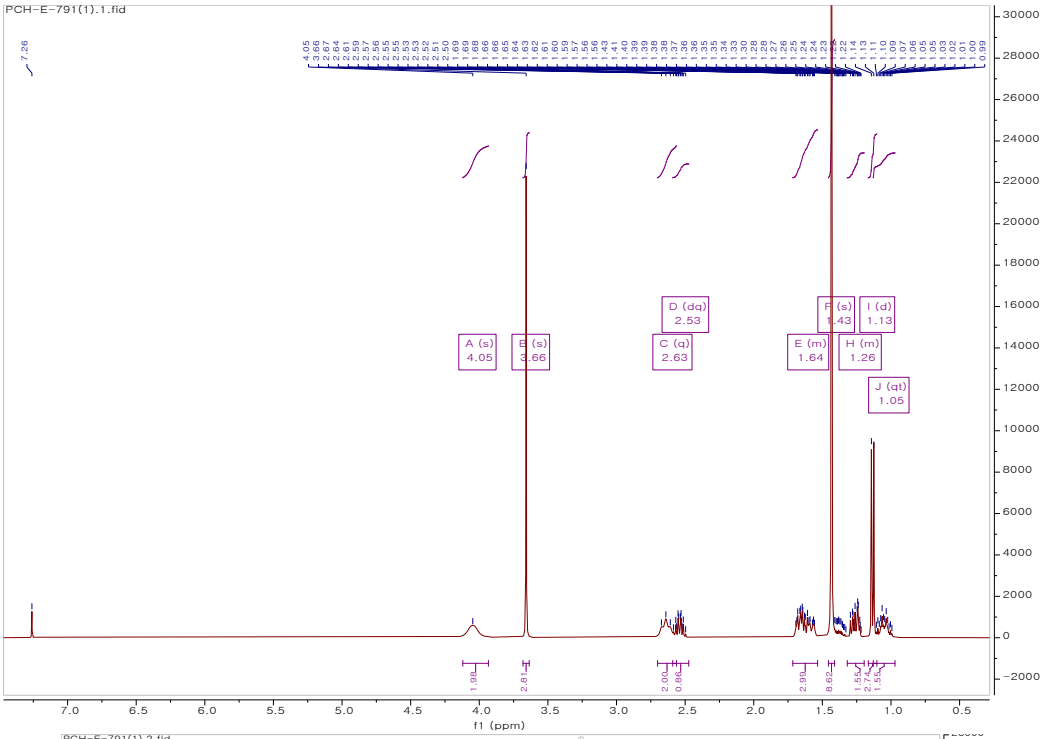


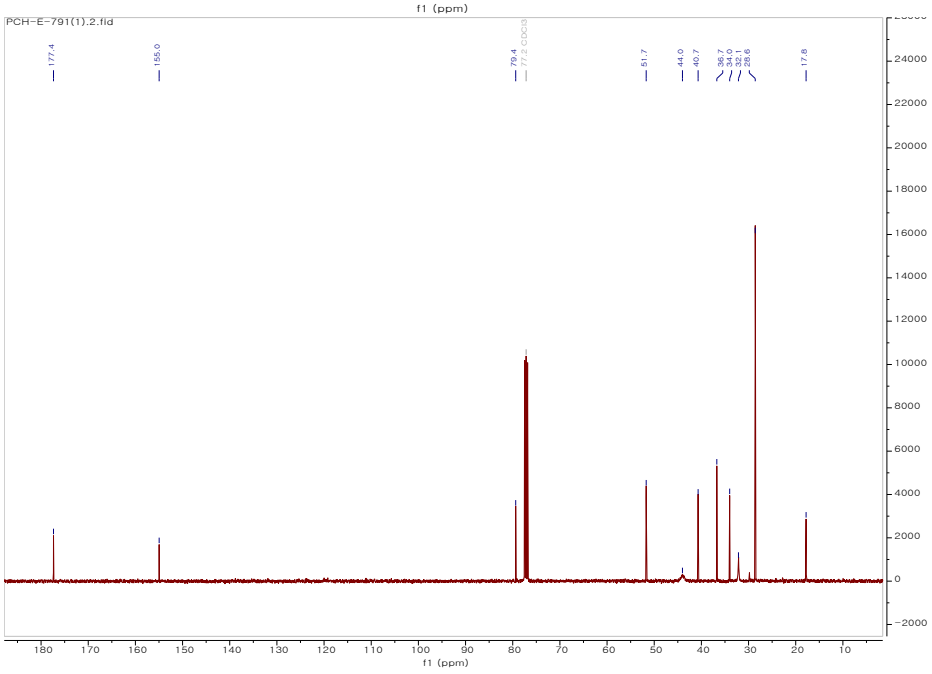



PCH-E-707(crude)-B.1.fid
PCH-E-707(crude)-B
-10.41
-11.19
-11.96
A (t)
-11.18
1.00
f1 (ppm)

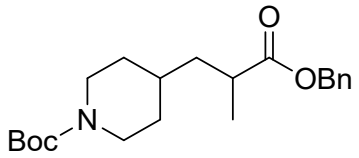
tert-butyl 4-(3-methoxy-2-methyl-3-oxopropyl)piperidine-1-carboxylate (3a)

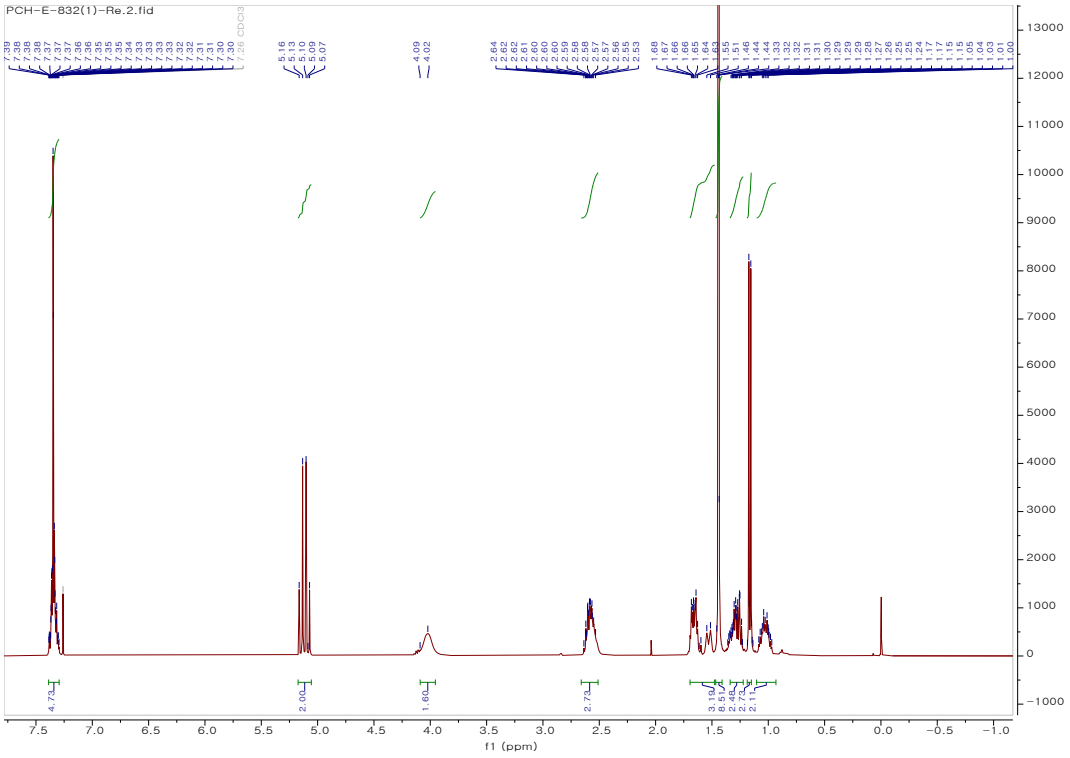


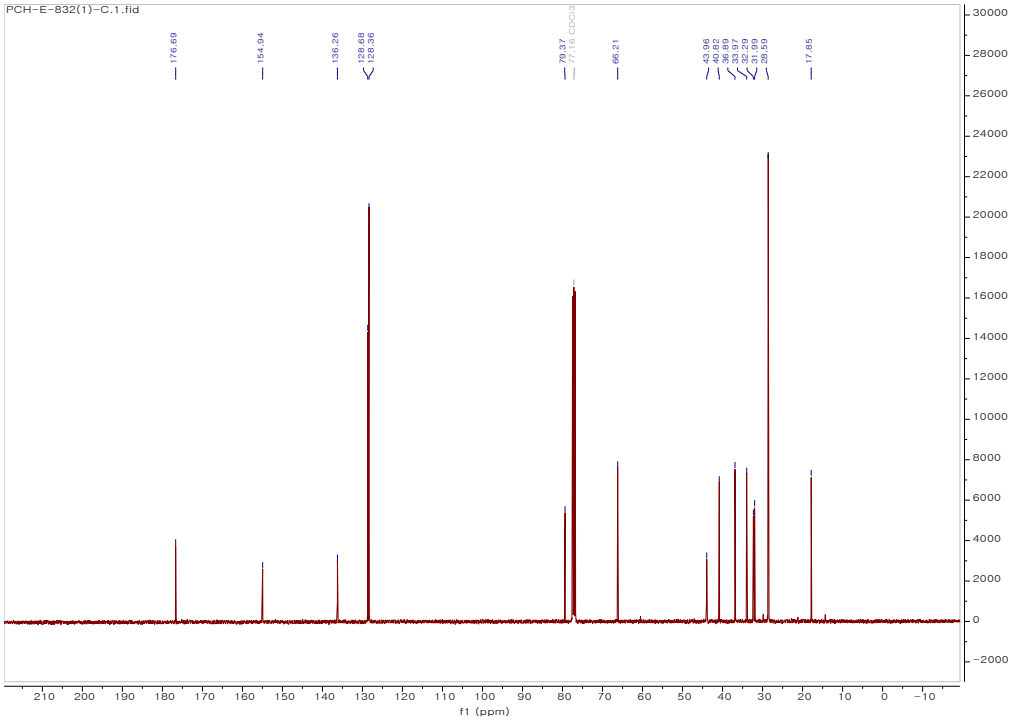




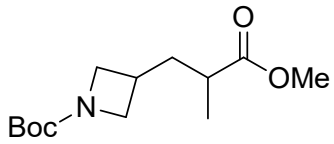
tert-butyl 4-(3-(benzyloxy)-2-methyl-3-oxopropyl)piperidine-1-carboxylate (3b)

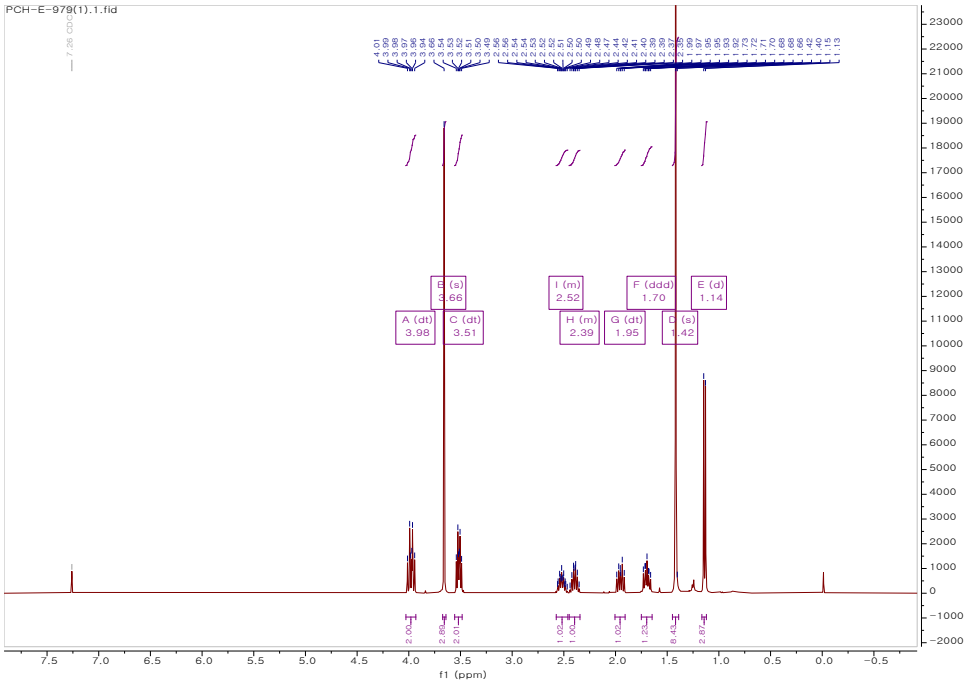


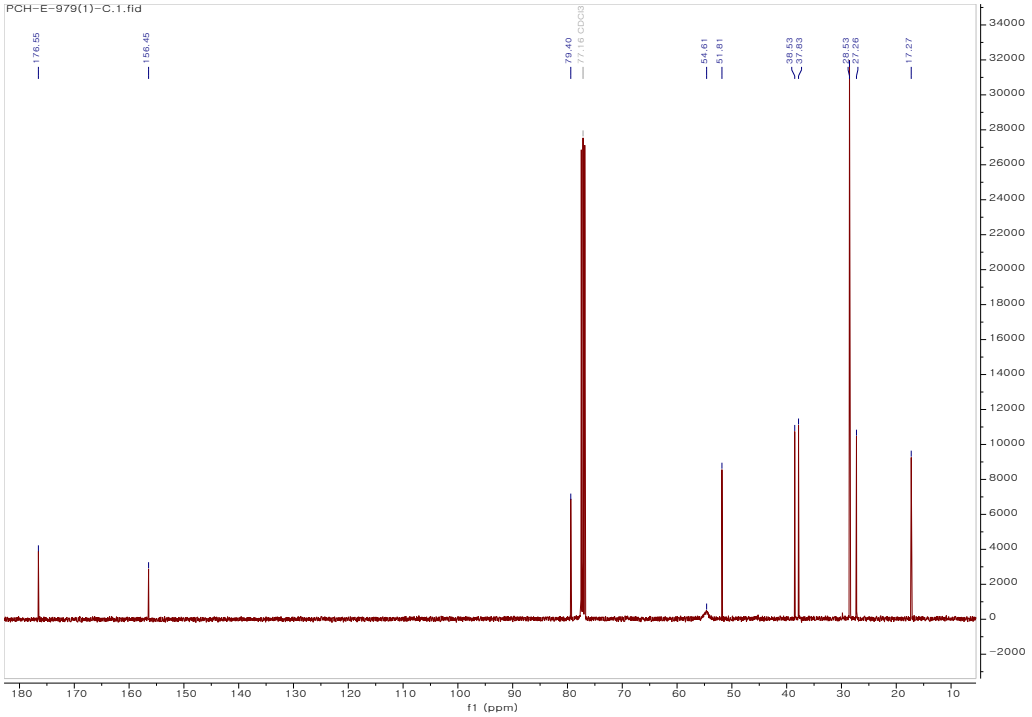




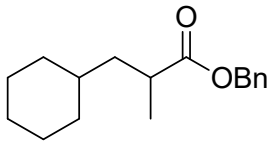
tert-butyl 3-(3-methoxy-2-methyl-3-oxopropyl)azetidine-1-carboxylate (3c)

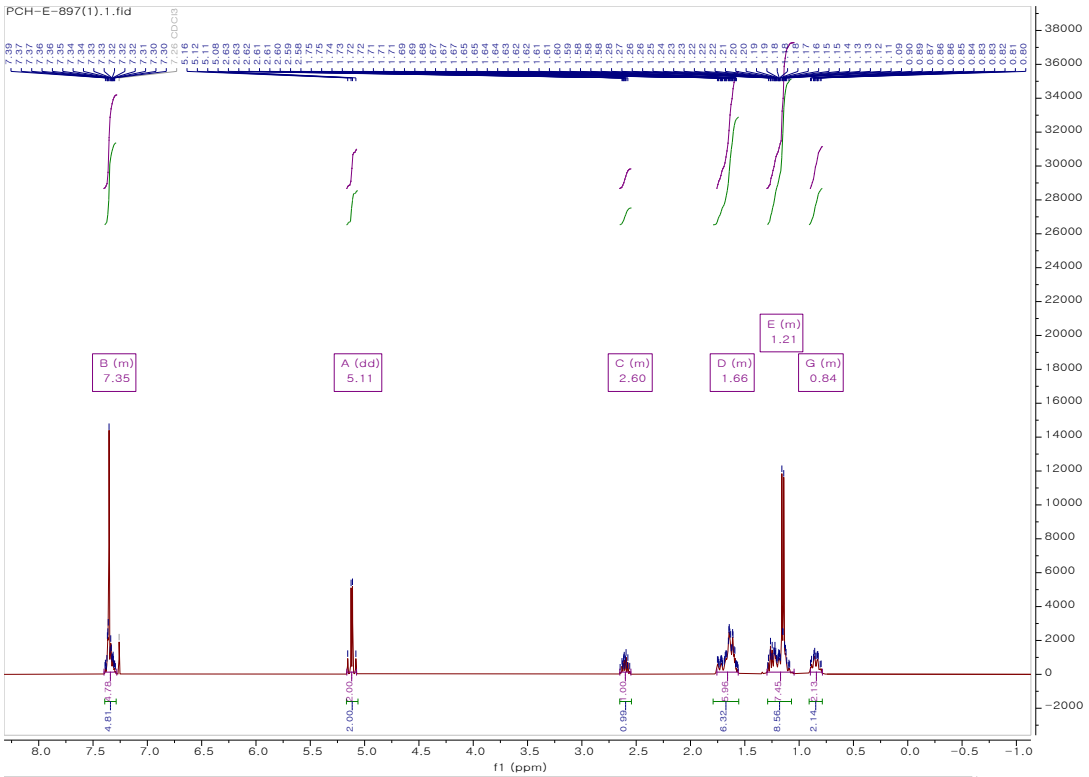


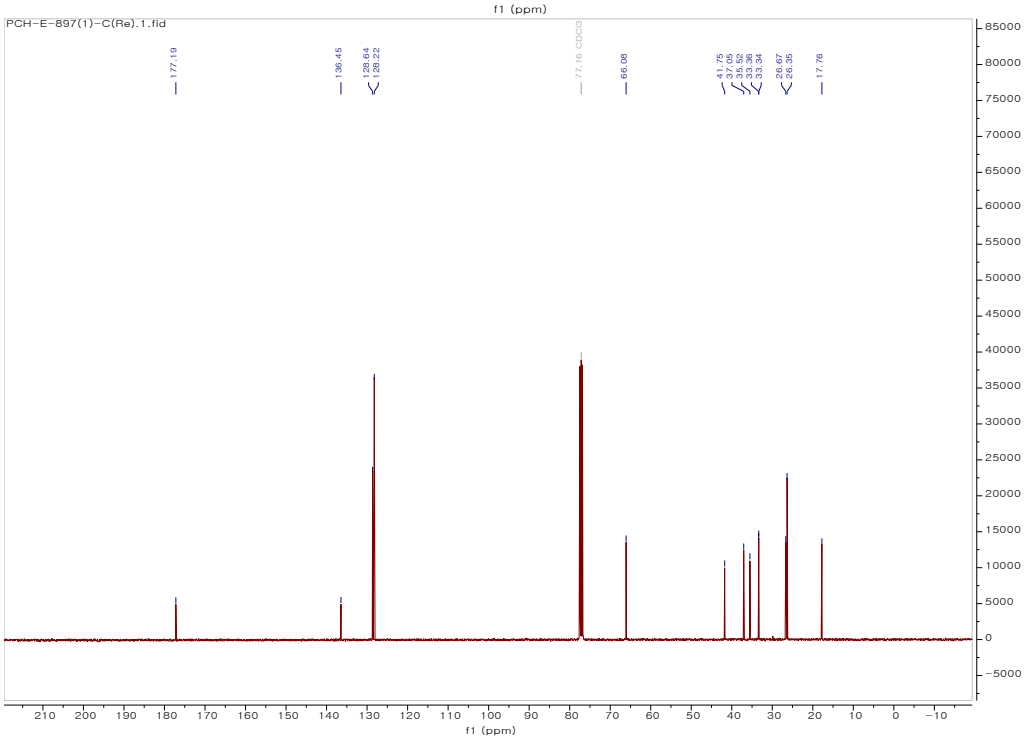




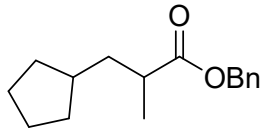
benzyl 3-cyclohexyl-2-methylpropanoate (3d)

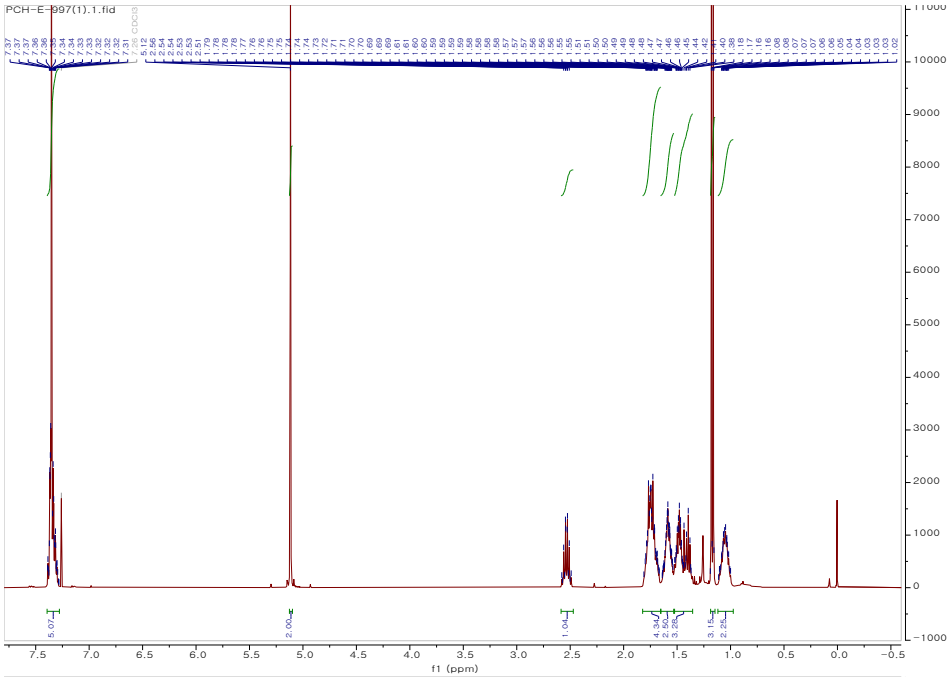


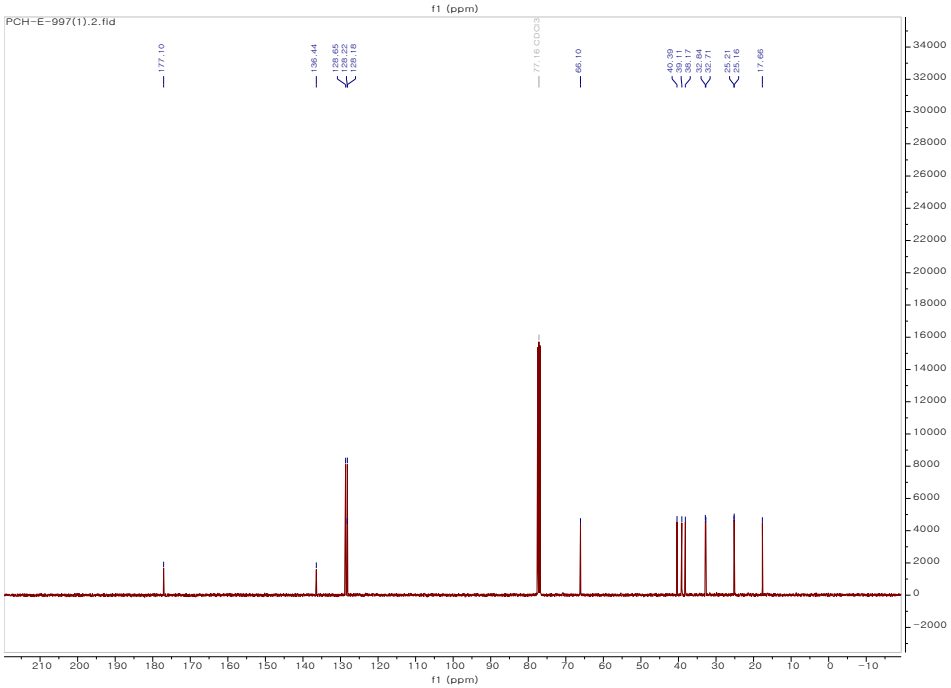




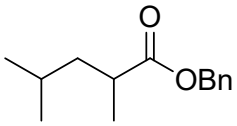
benzyl 3-cyclopentyl-2-methylpropanoate (3e)

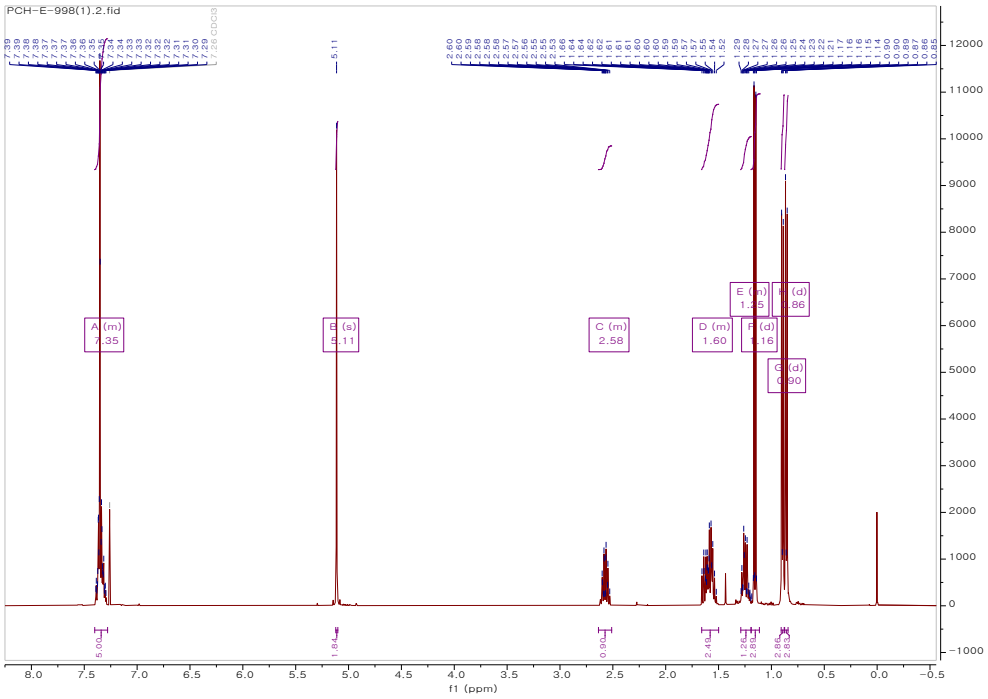


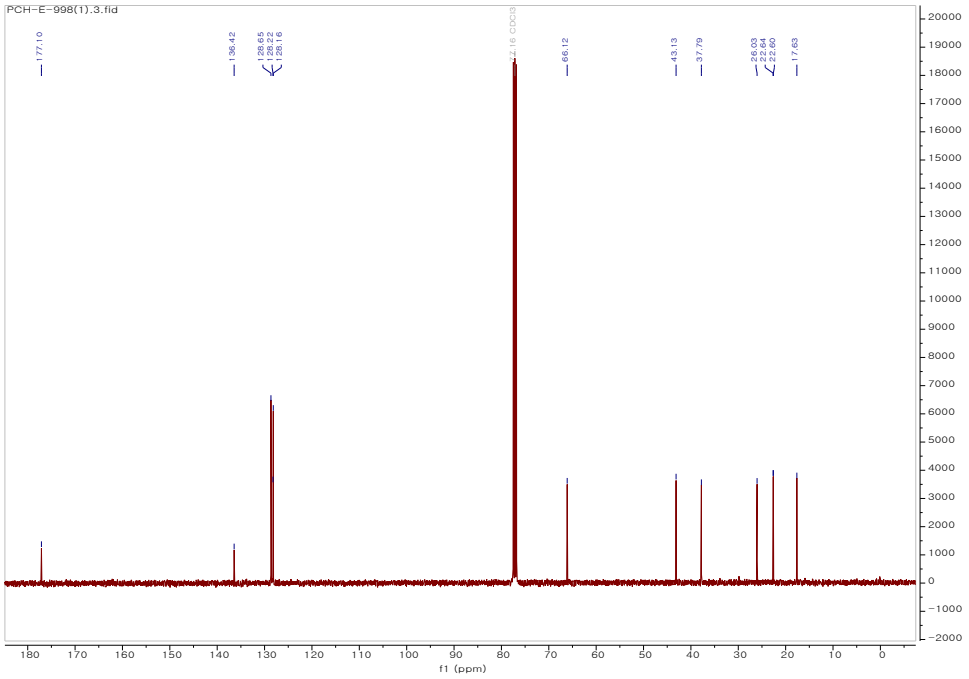




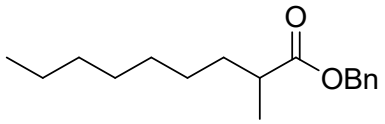
benzyl 2,4-dimethylpentanoate (3f)

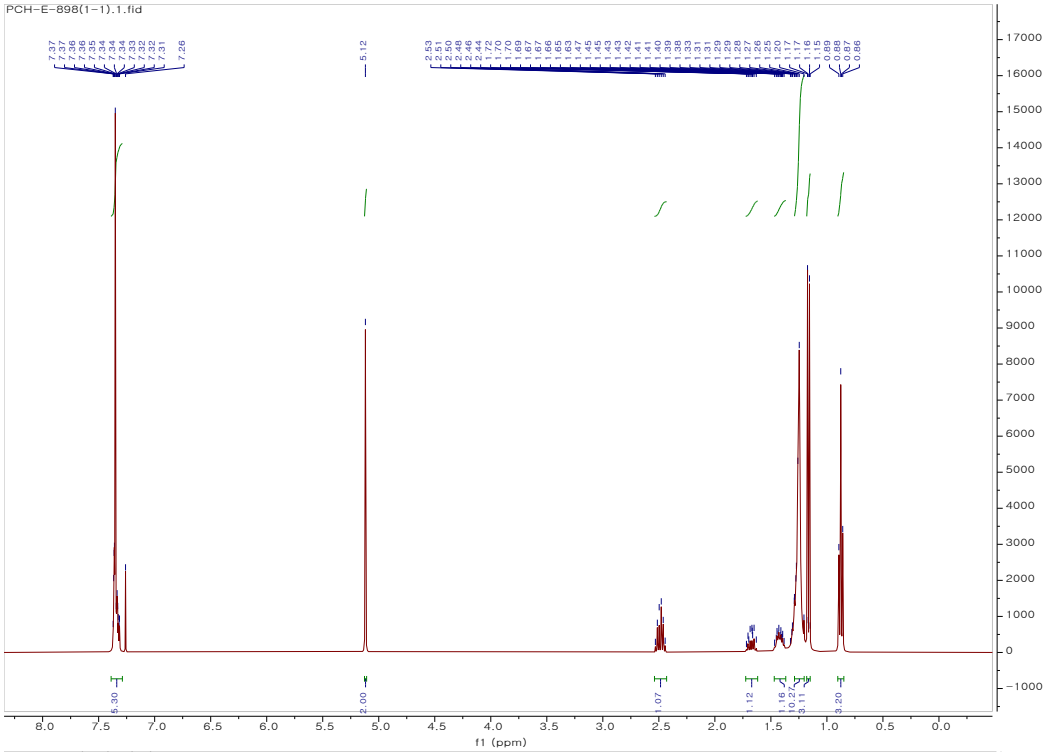


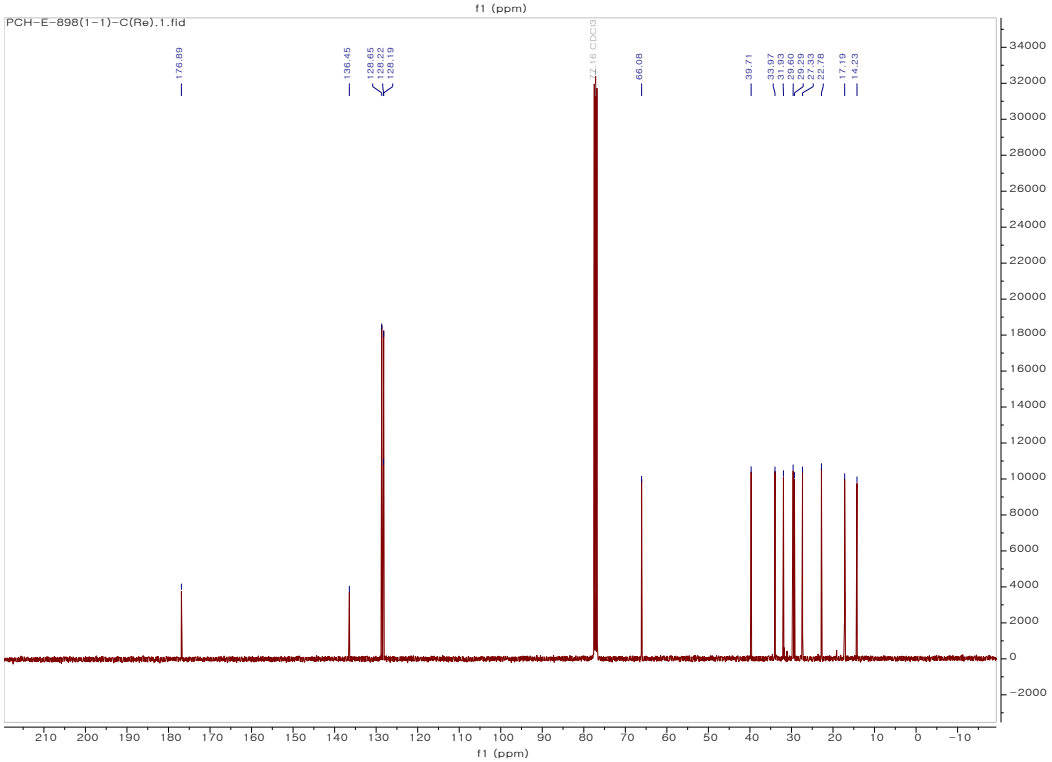




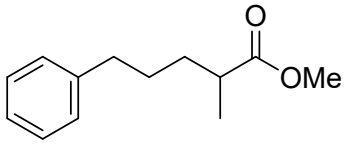
benzyl 2-methylnonanoate (3g)

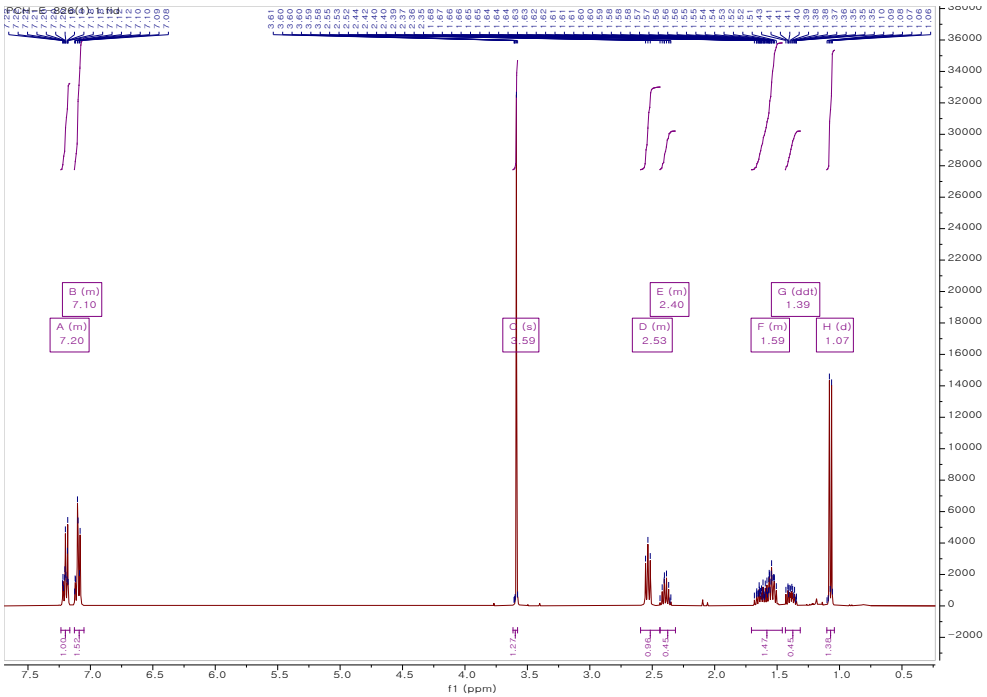


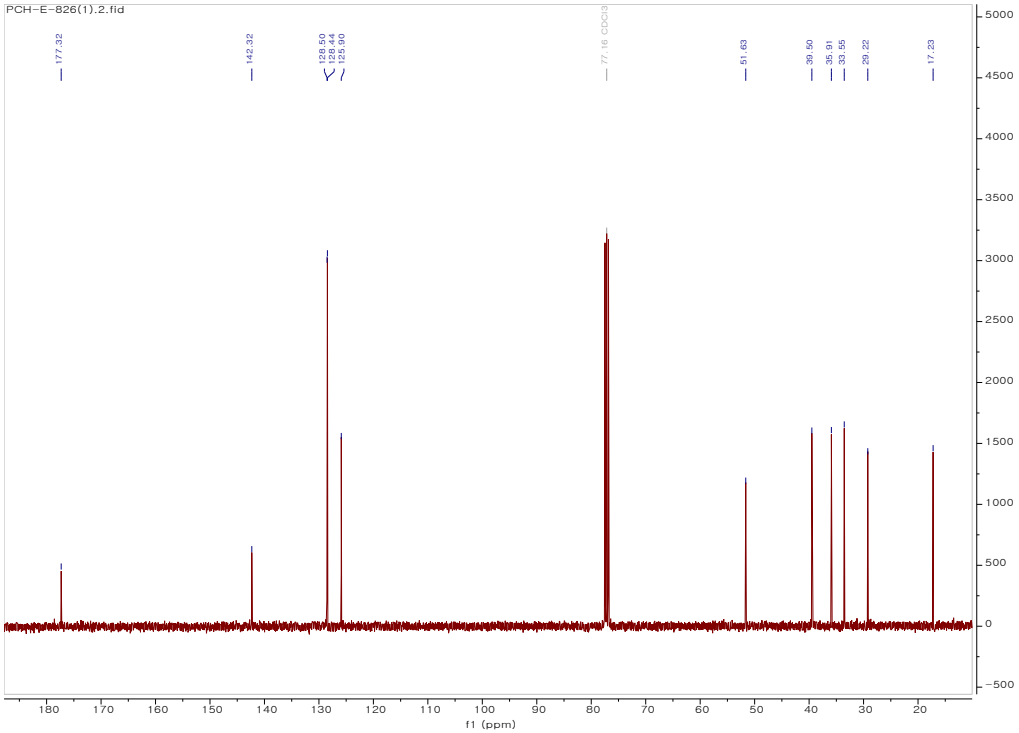




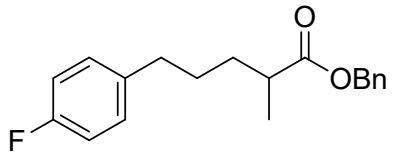
methyl 2-methyl-5-phenylpentanoate (3h)

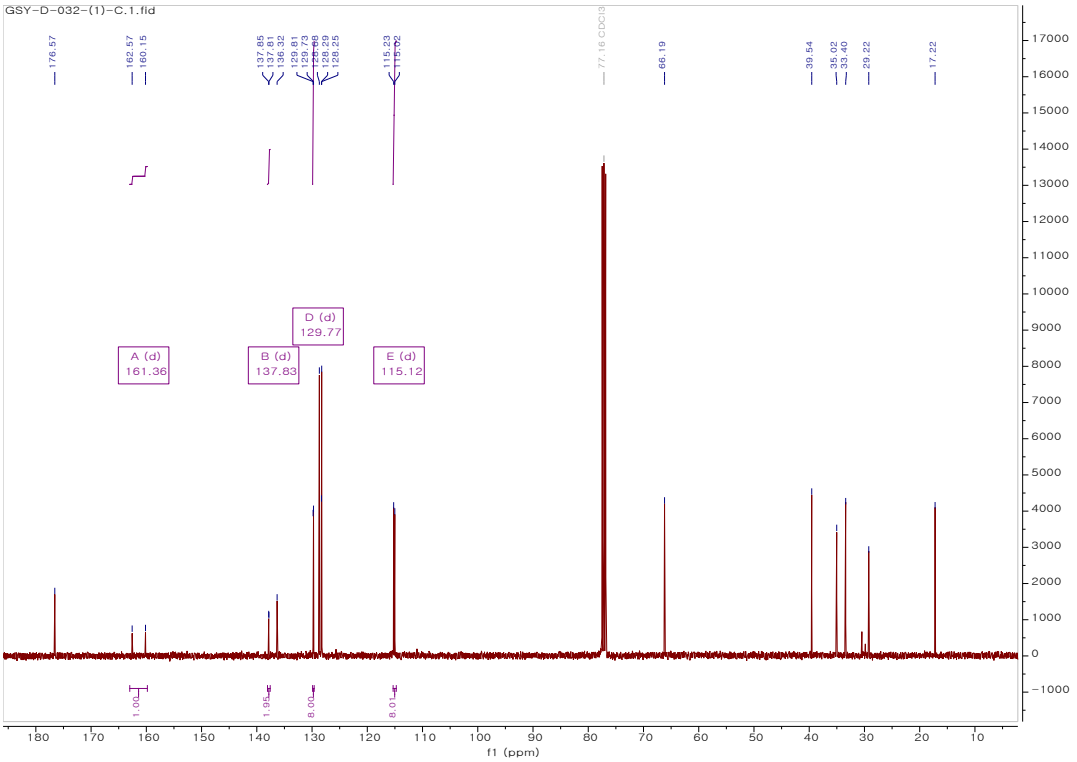


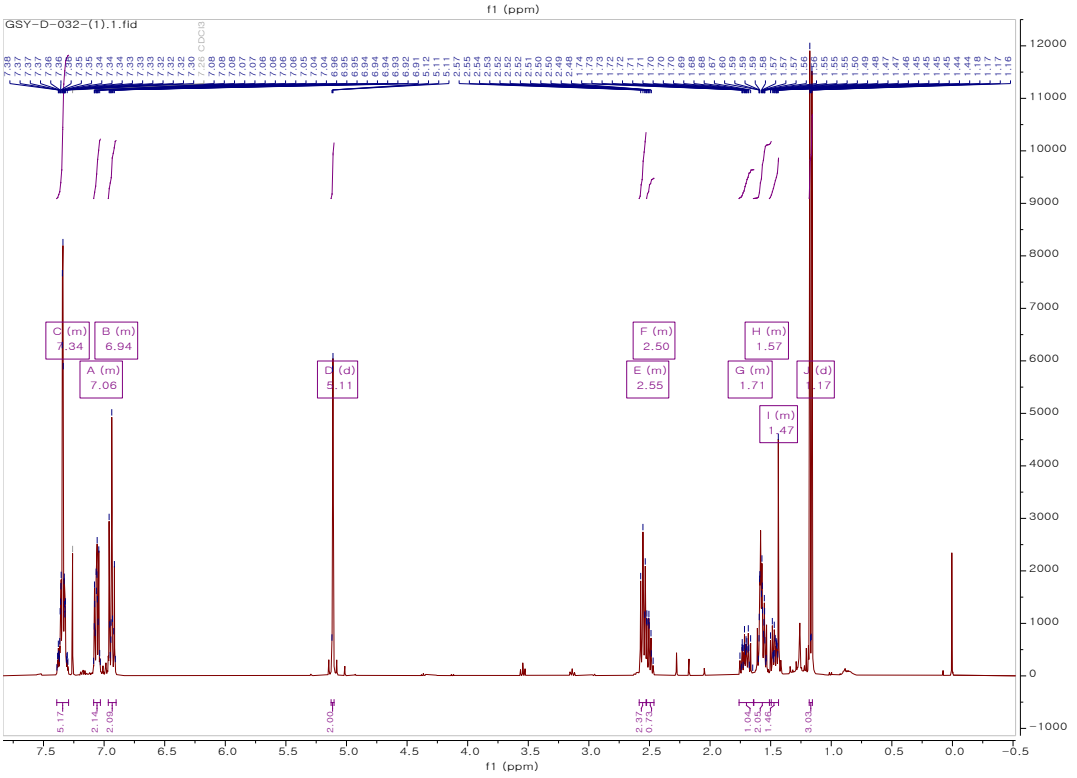


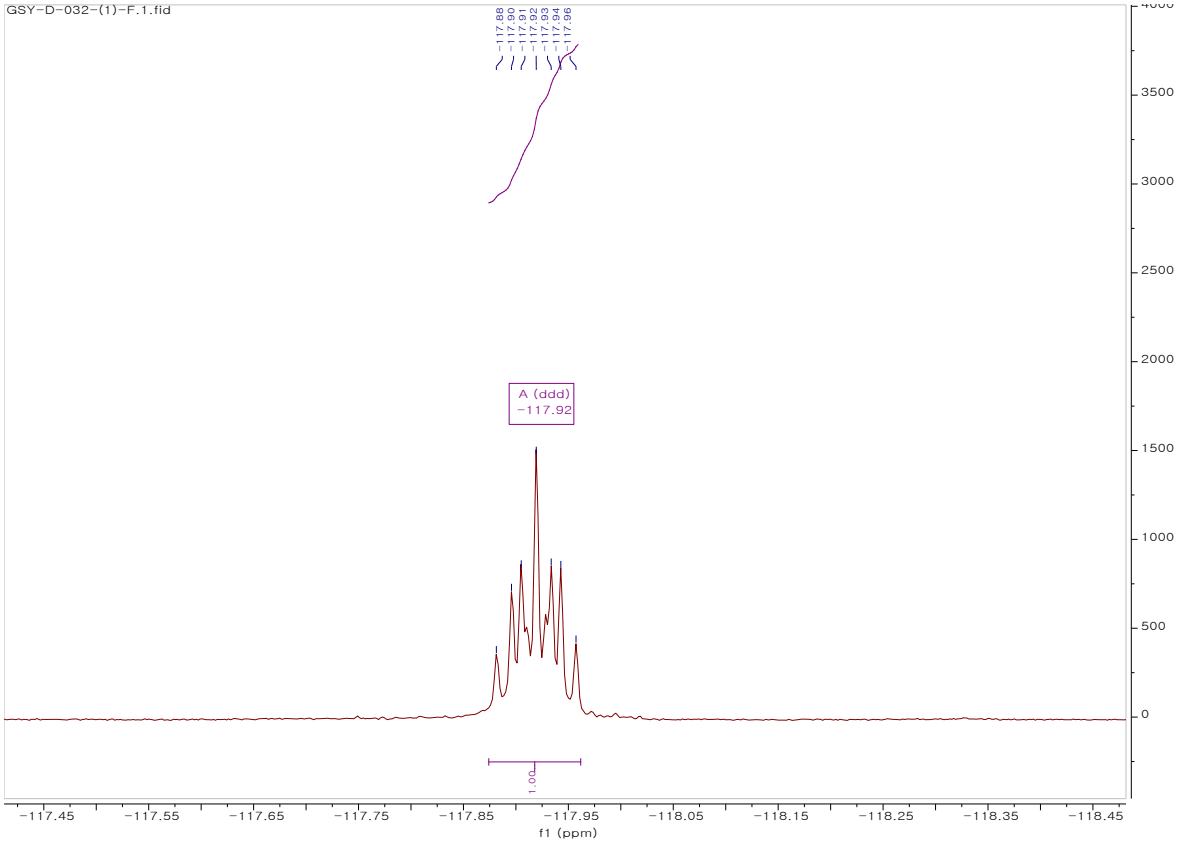


benzyl 5-(4-fluorophenyl)-2-methylpentanoate (3i)

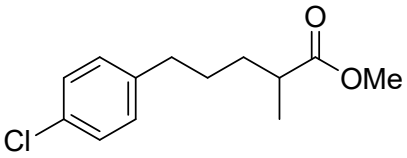


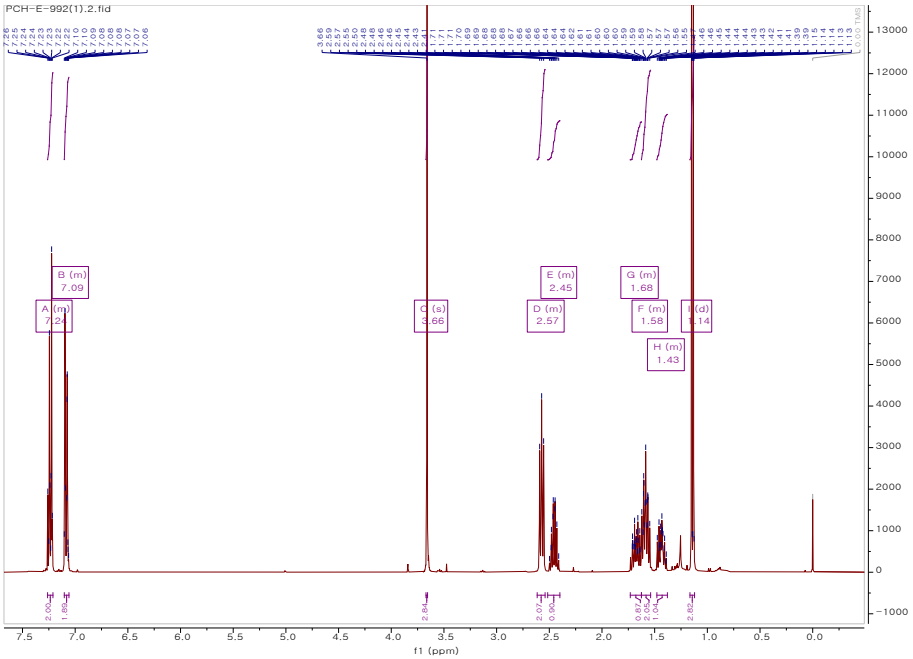


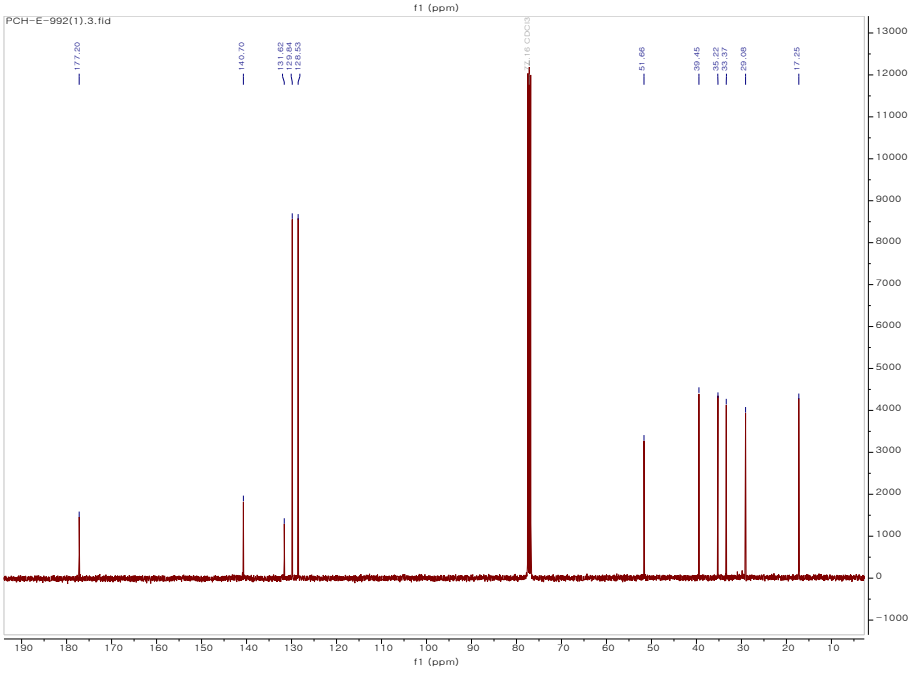



GSY-D-032-(1)-F.1.fid
−117.88
−117.90
−117.91
−117.92
−117.93
−117.94
−117.96
A (ddd)
−117.92
1.00
3500
3000
2500
2000
1500
1000
500
0
−117.45
−117.55
−117.65
−117.75
−117.85
−117.95
−118.05
−118.15
−118.25
−118.35
−118.45
f1 (ppm)

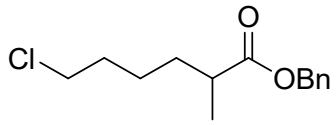
methyl 5-(4-chlorophenyl)-2-methylpentanoate (3j)

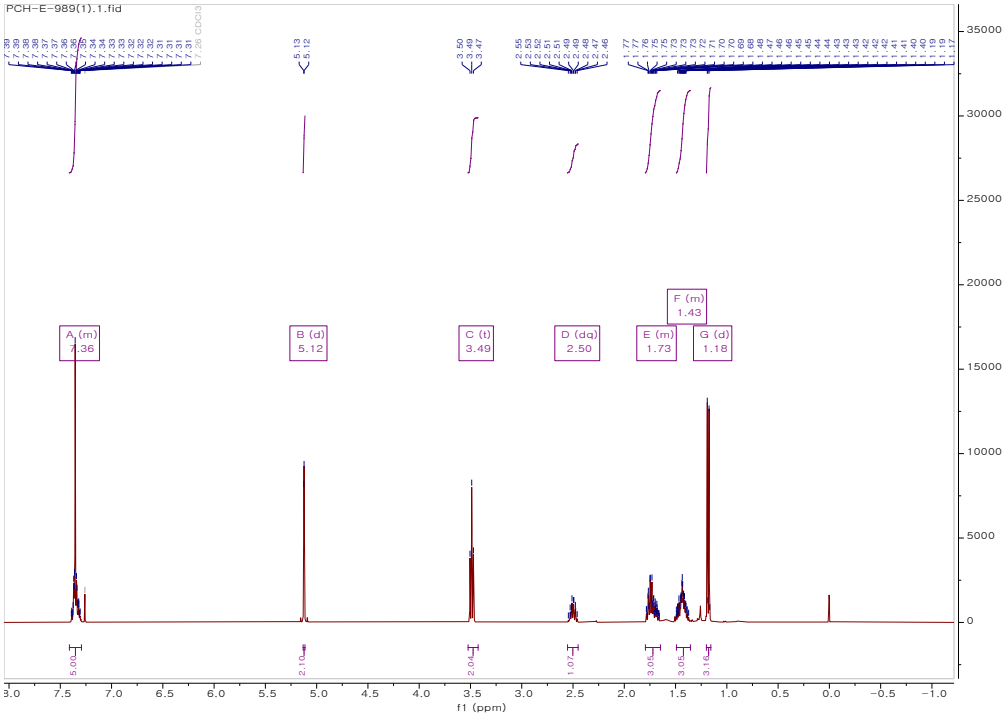


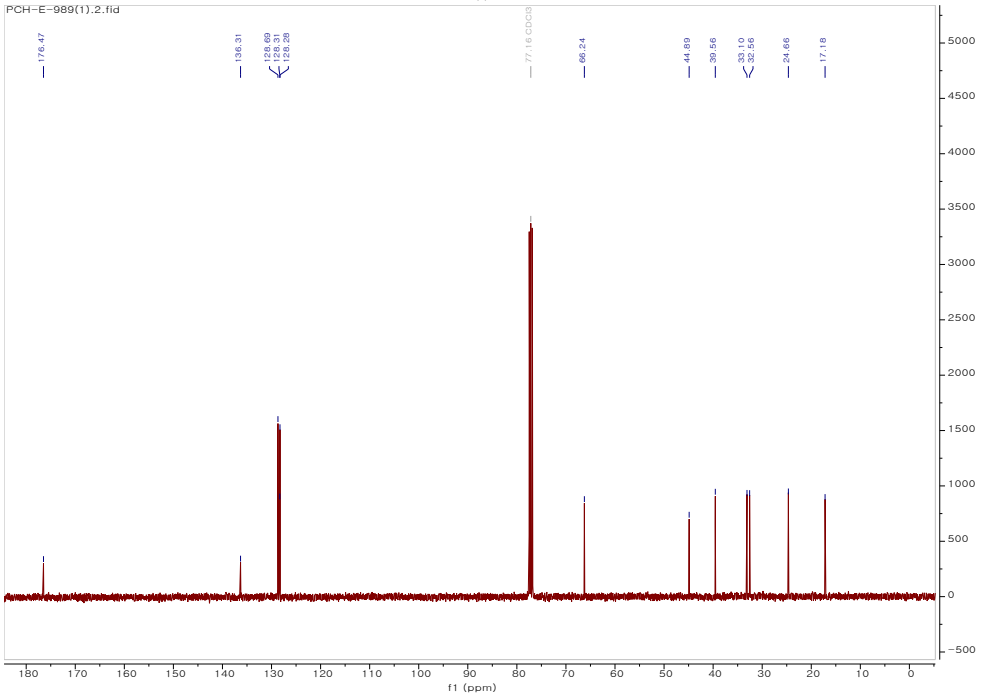




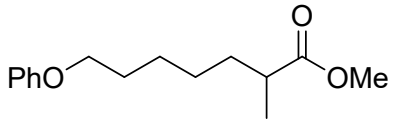
benzyl 6-chloro-2-methylhexanoate (3k)

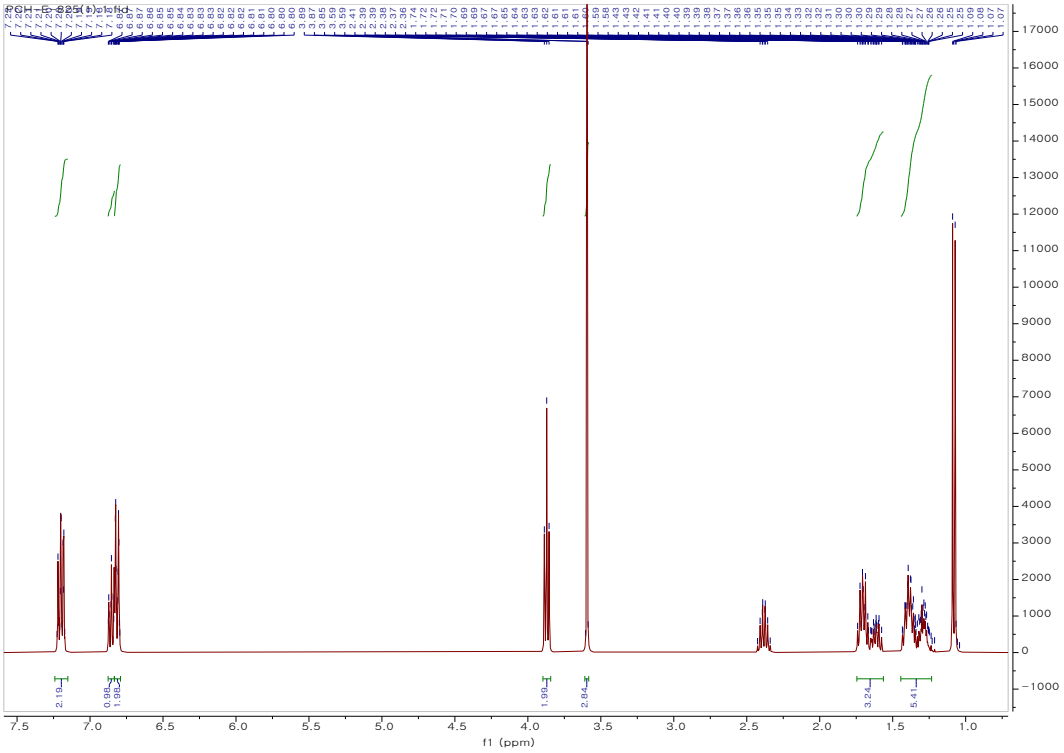


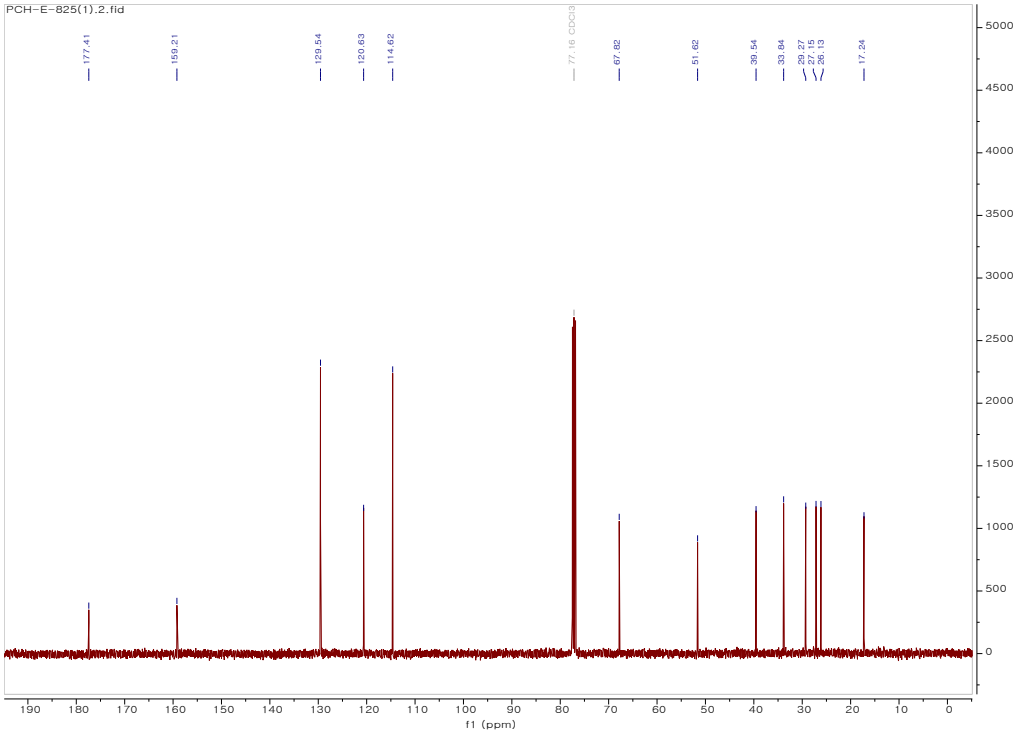




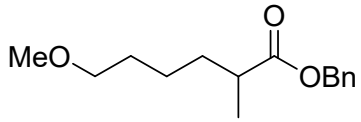
methyl 2-methyl-6-phenoxyhexanoate (3l)

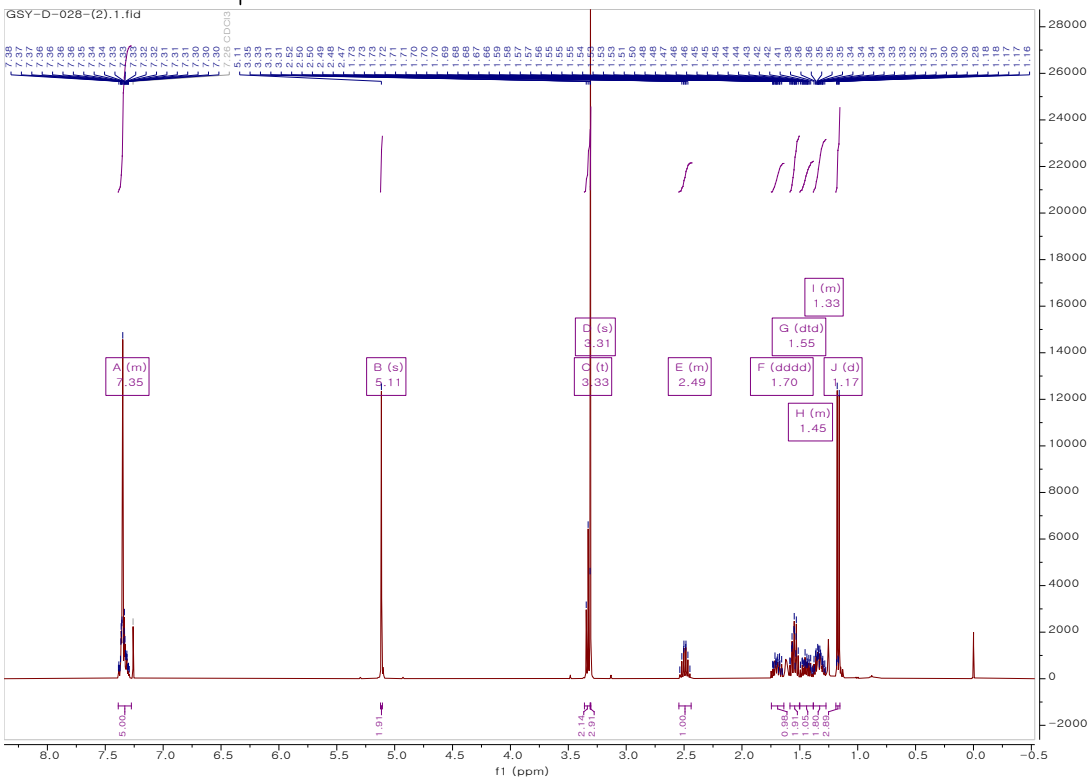


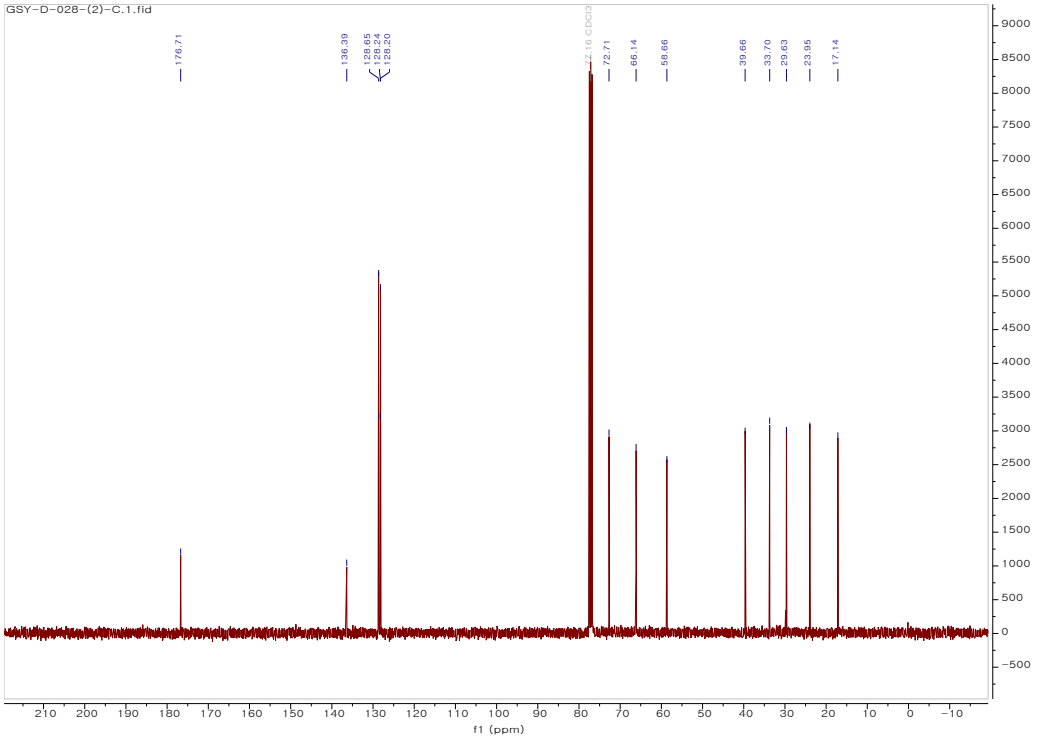




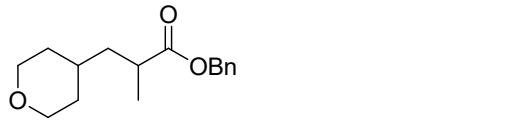
benzyl 6-methoxy-2-methylhexanoate (3m)

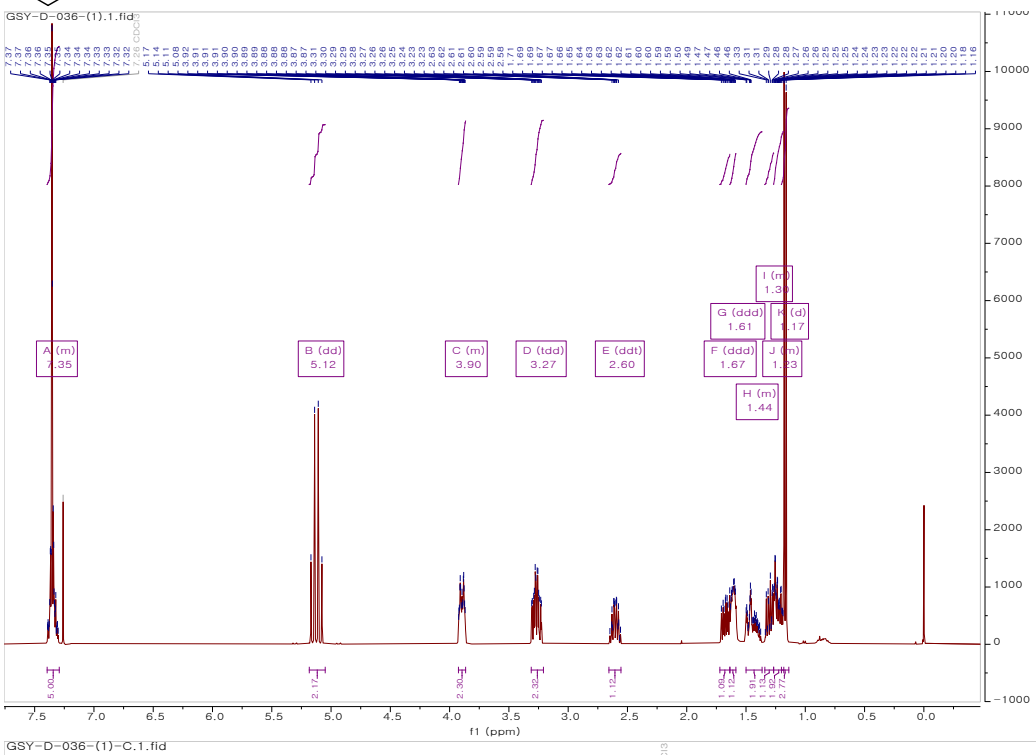


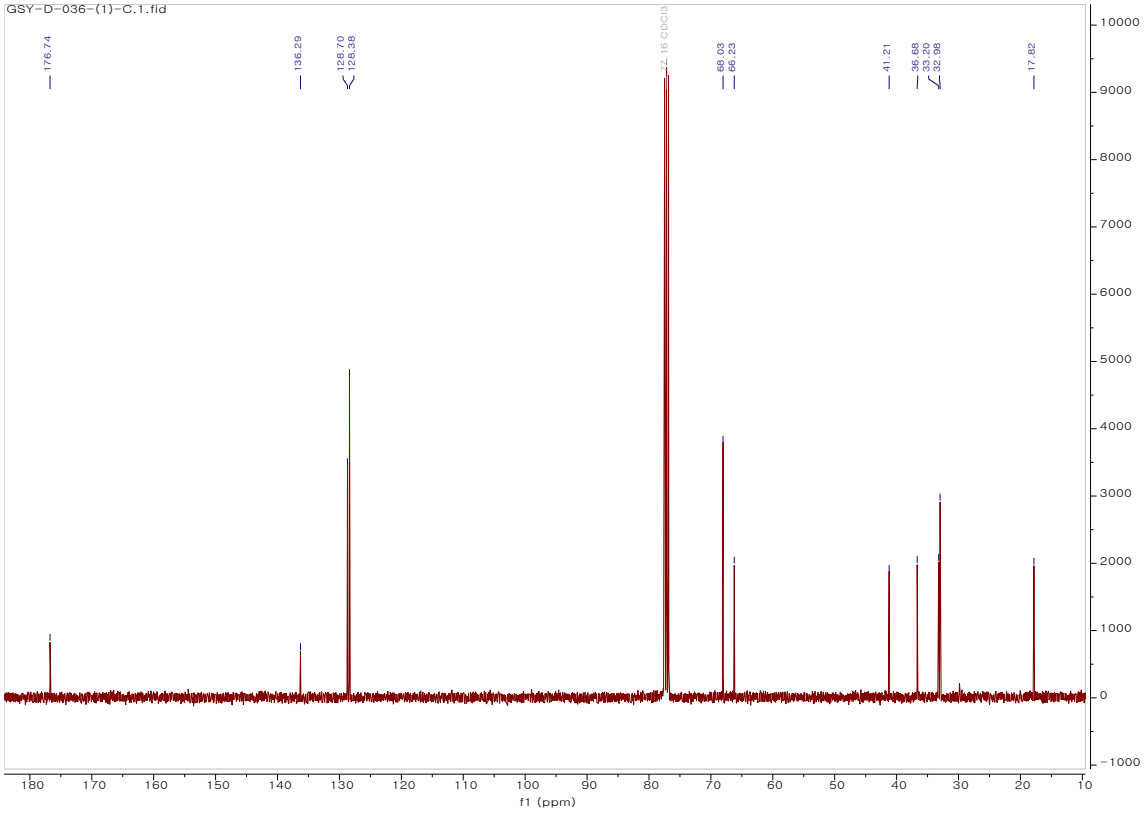




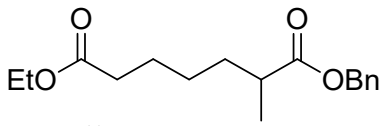
benzyl 2-methyl-3-(tetrahydro-2H-pyran-4-yl)propanoate(3n)

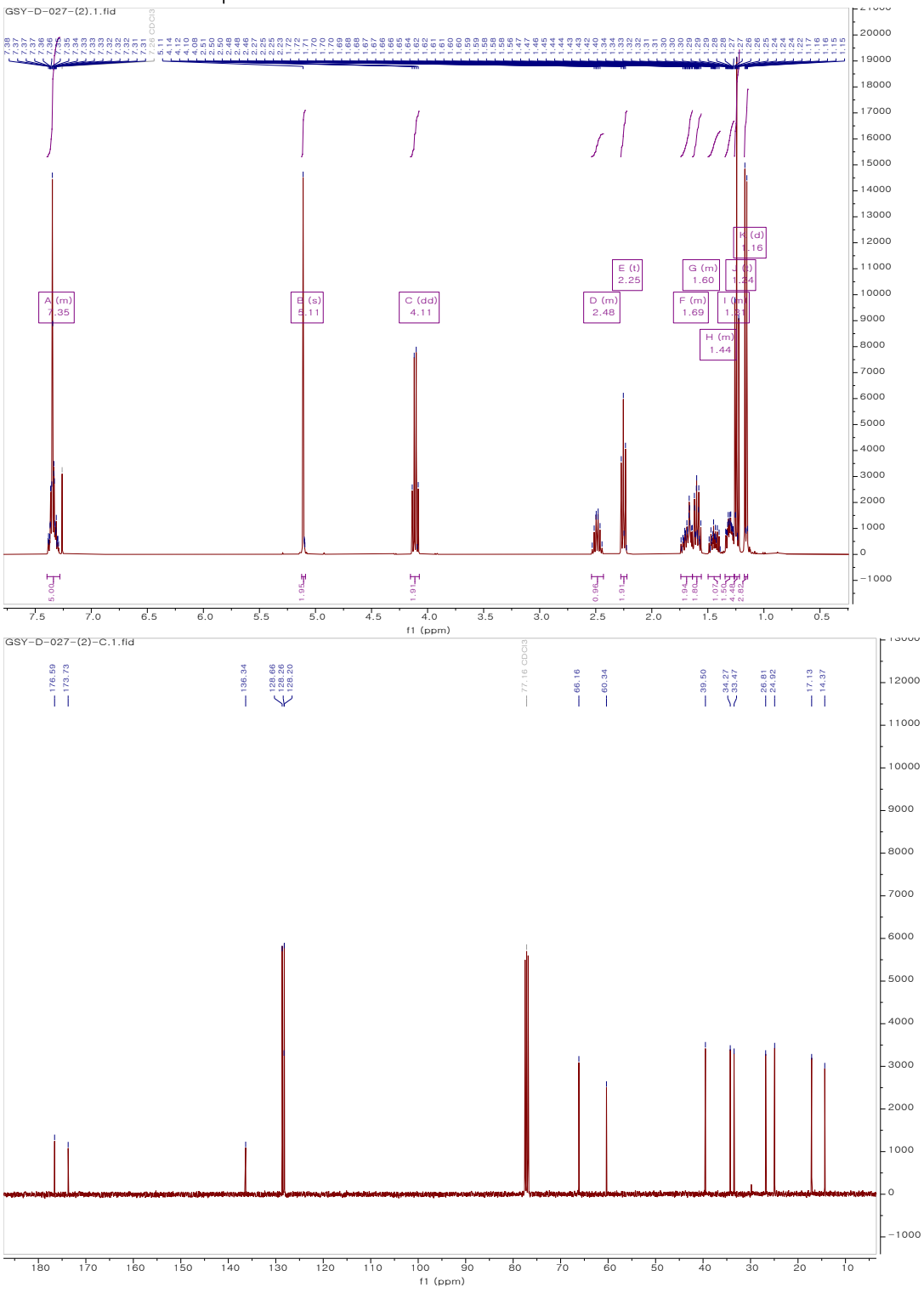




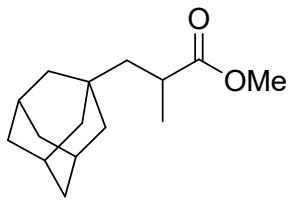


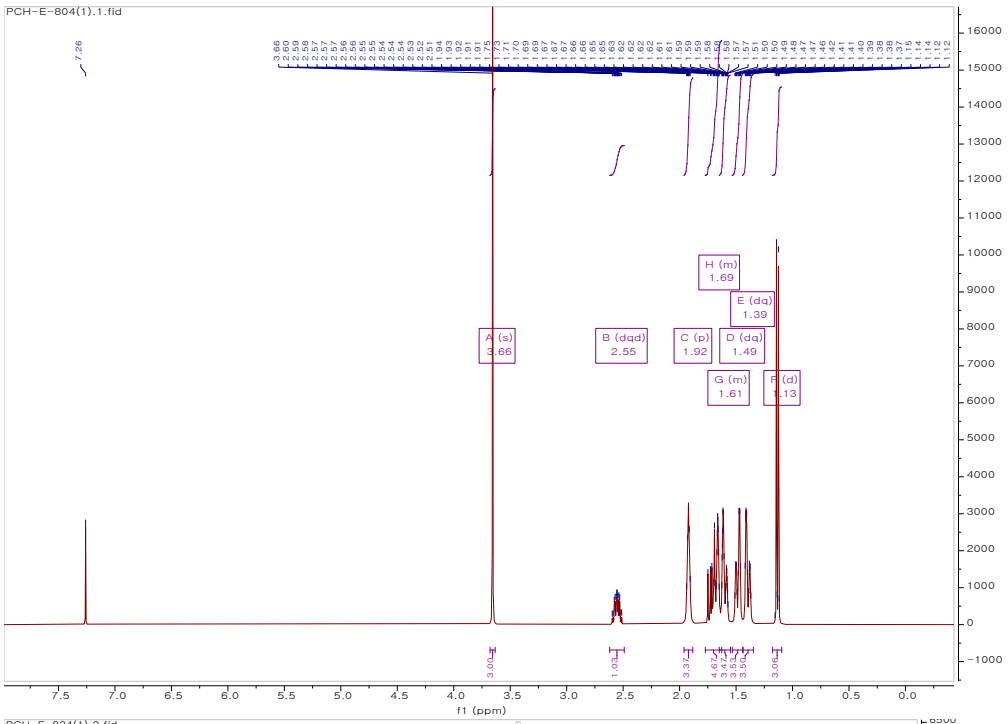
1-benzyl 7-ethyl 2-methylheptanedioate (3o)

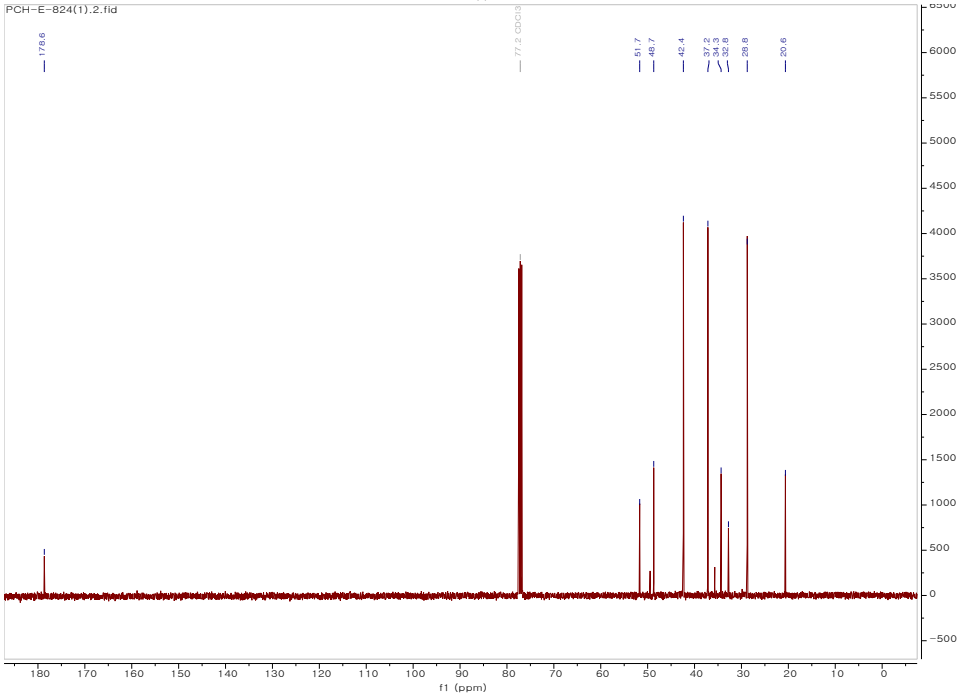




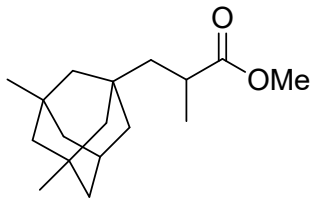
methyl 3-((1s,3s)-adamantan-1-yl)-2-methylpropanoate (3p)

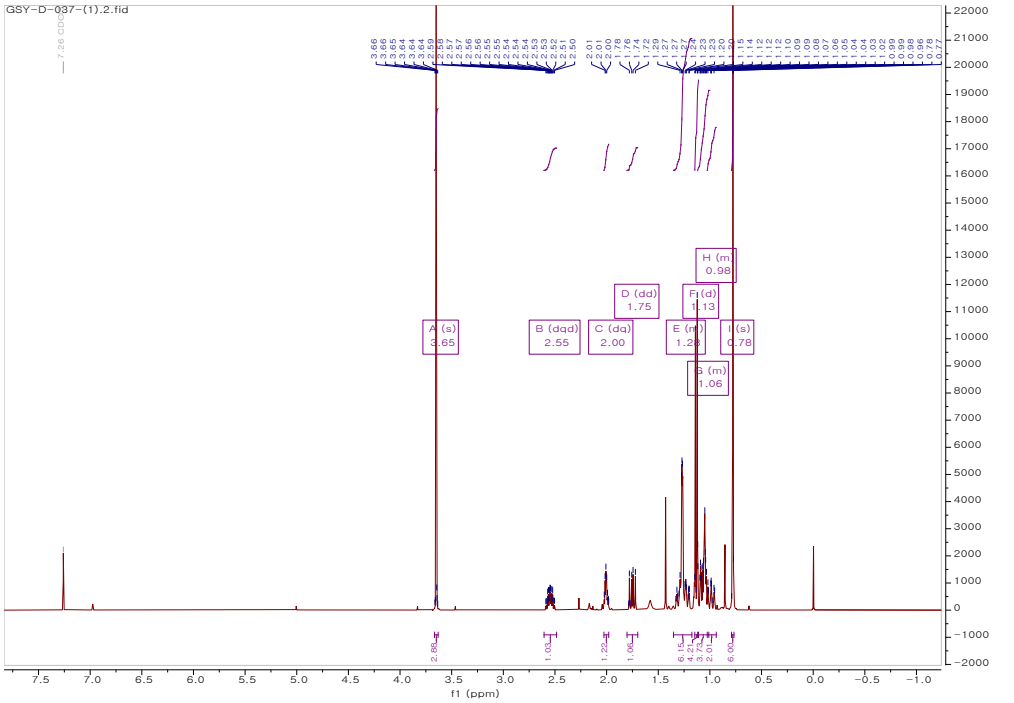

O
OMe

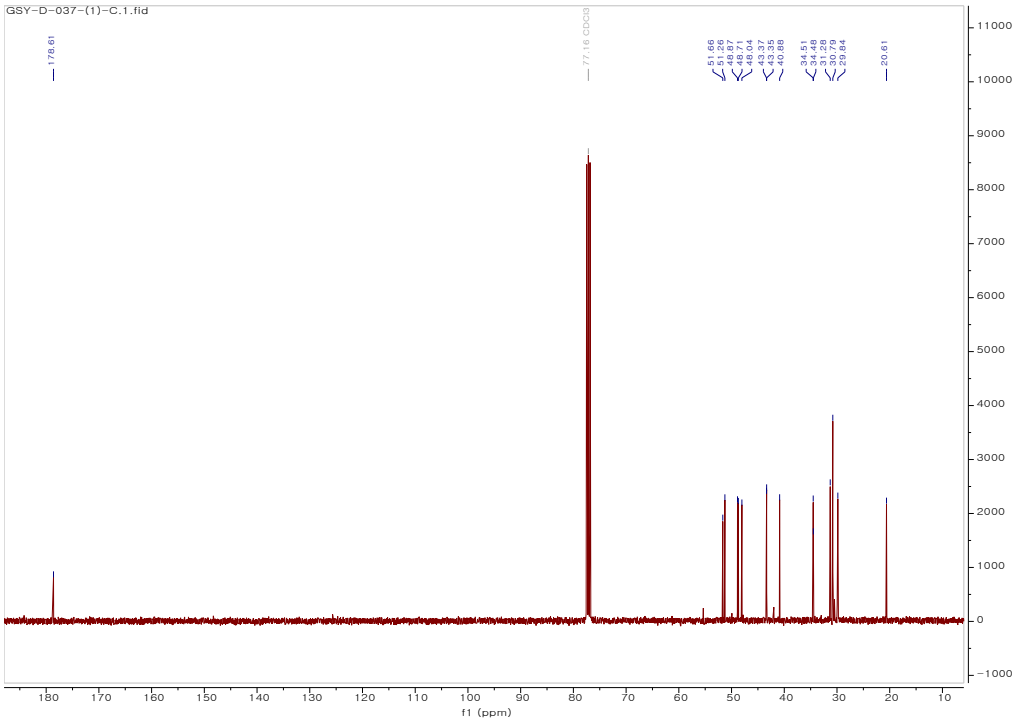

PCH-E-804(1).1.fid
7.26
A (s)
3.66
B (dqd)
2.55
C (p)
1.92
D (dq)
1.49
E (dq)
1.39
H (m)
1.69
G (m)
1.61
F (d)
1.13
f1 (ppm)


PCH-E-824(1).2.fid
178.6
77.2 CDCl3
51.7
48.7
42.4
37.2
34.3
32.8
28.8
20.6
f1 (ppm)

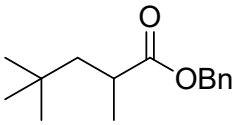
methyl 3-((1S,3R)-3,5-dimethyladamantan-1-yl)-2-methylpropanoate (3q)

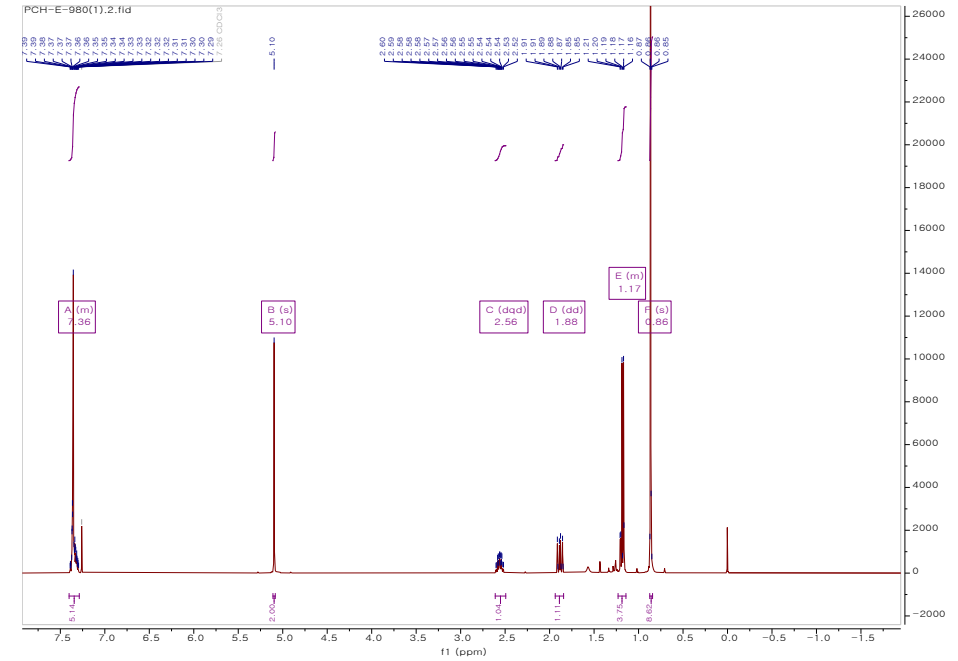


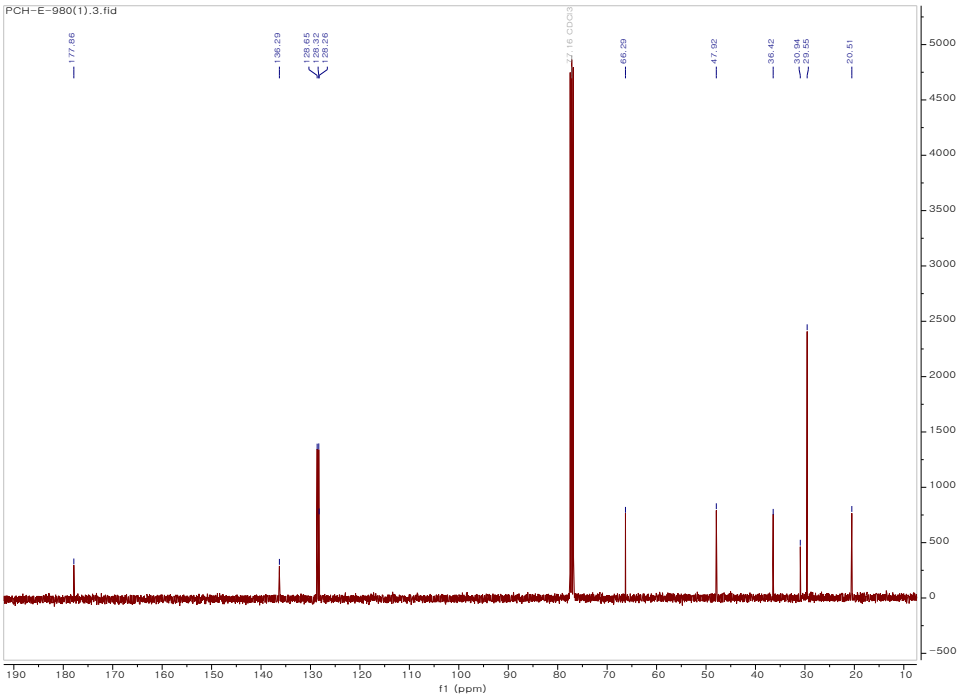




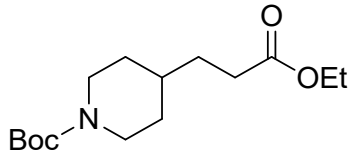
benzyl 2,4,4-trimethylpentanoate (3r)

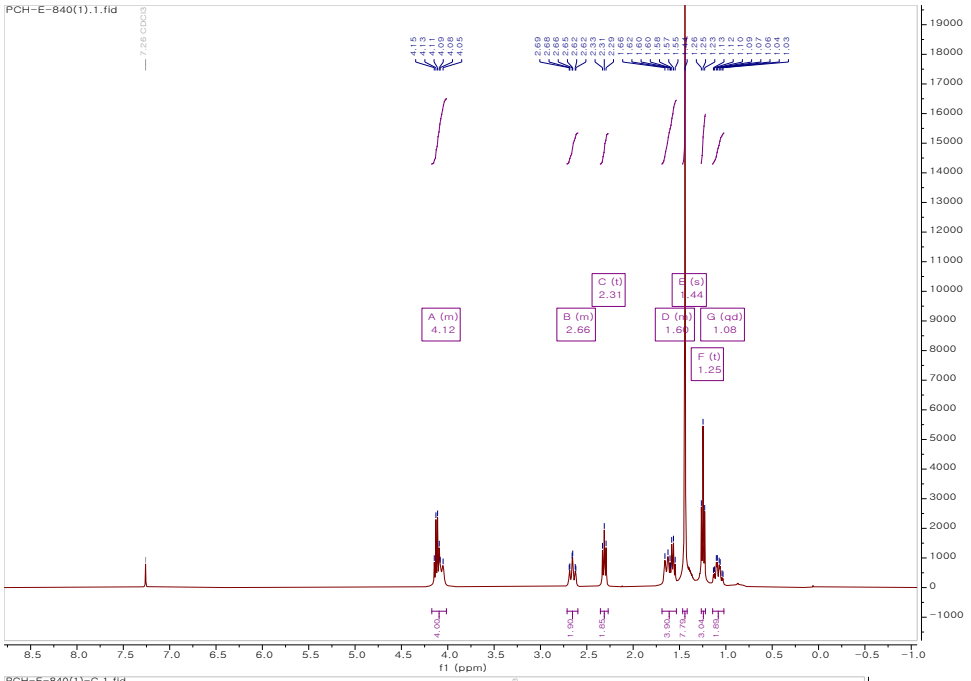


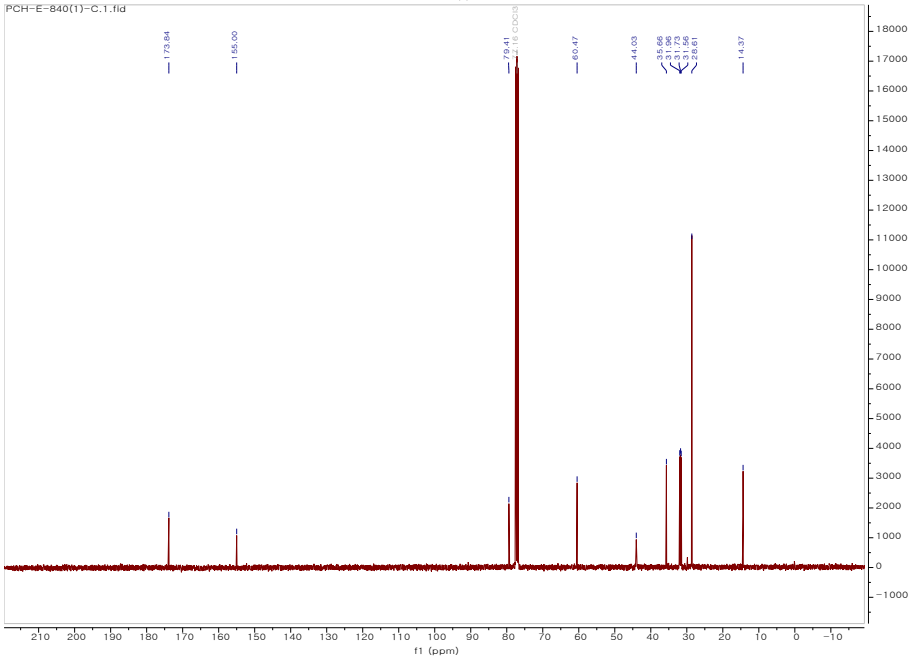




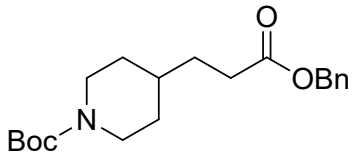
tert-butyl 4-(3-ethoxy-3-oxopropyl)piperidine-1-carboxylate (3s)

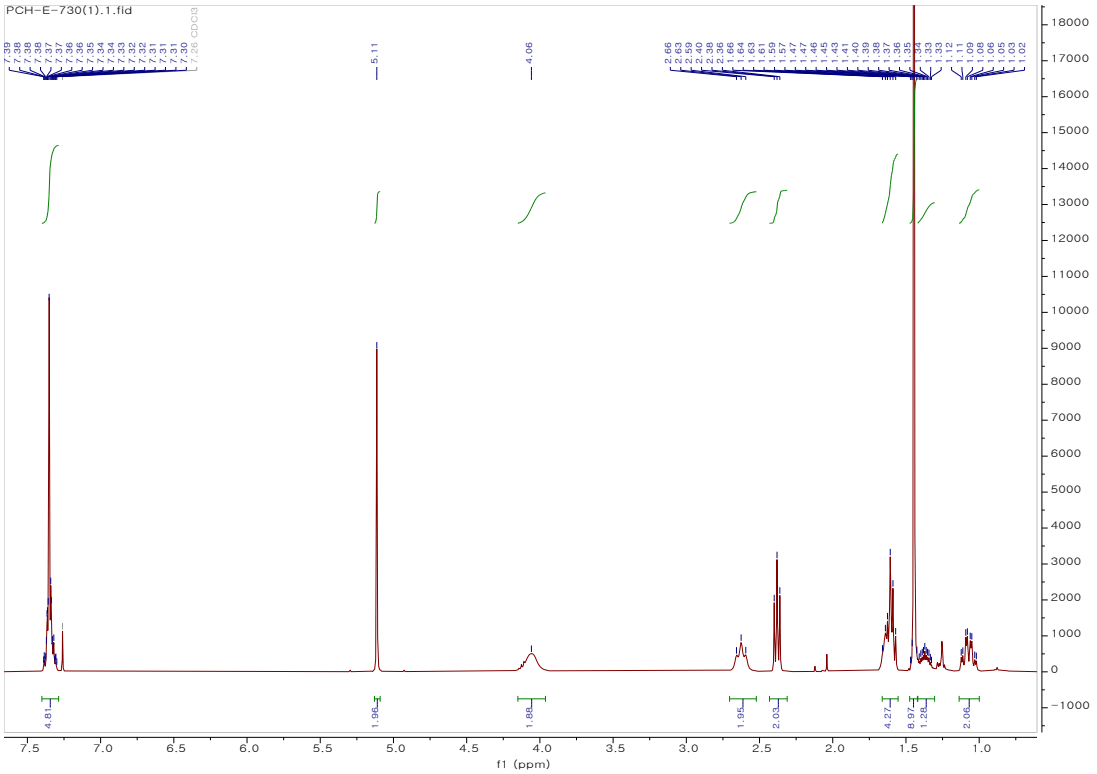


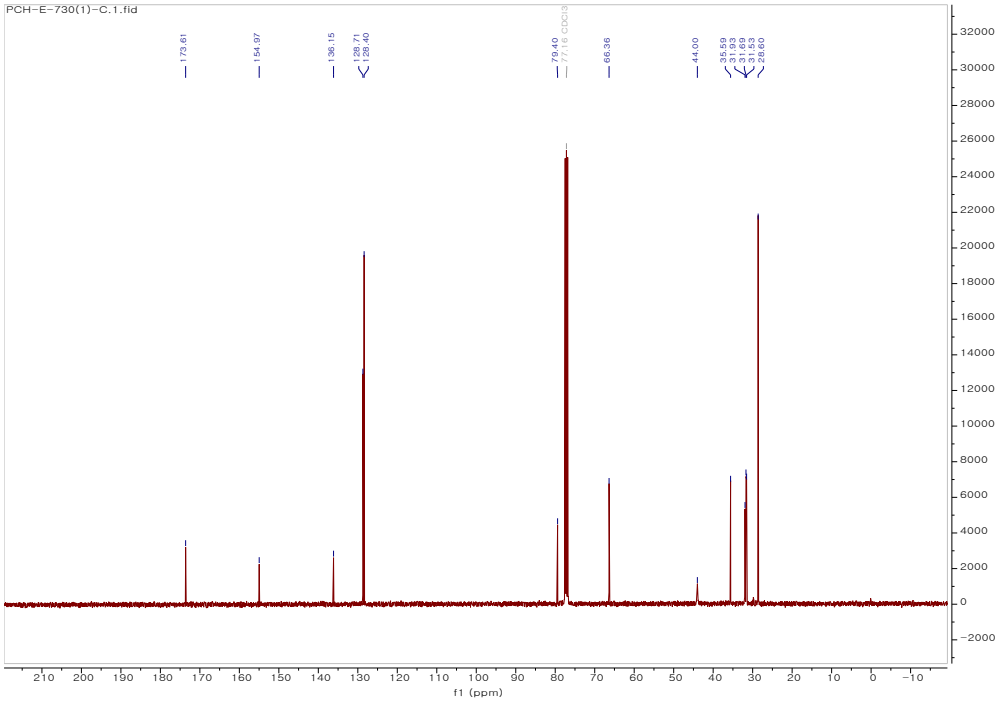




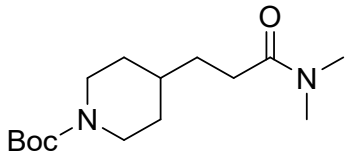
tert-butyl 4-(3-(benzyloxy)-3-oxopropyl)piperidine-1-carboxylate (3t)

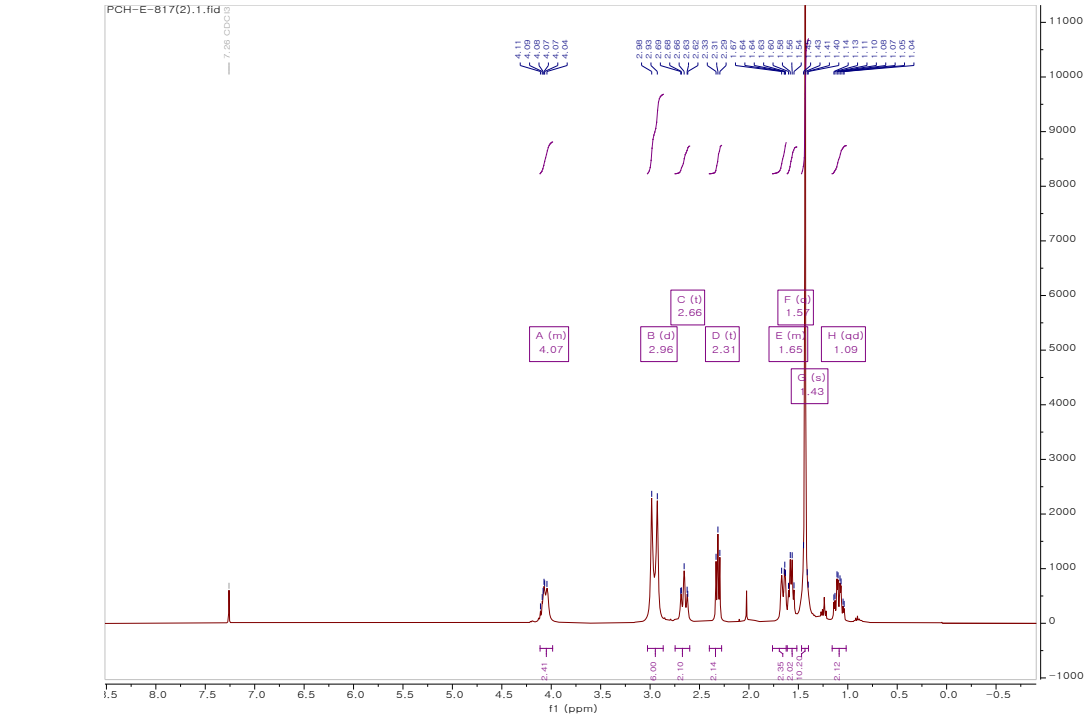


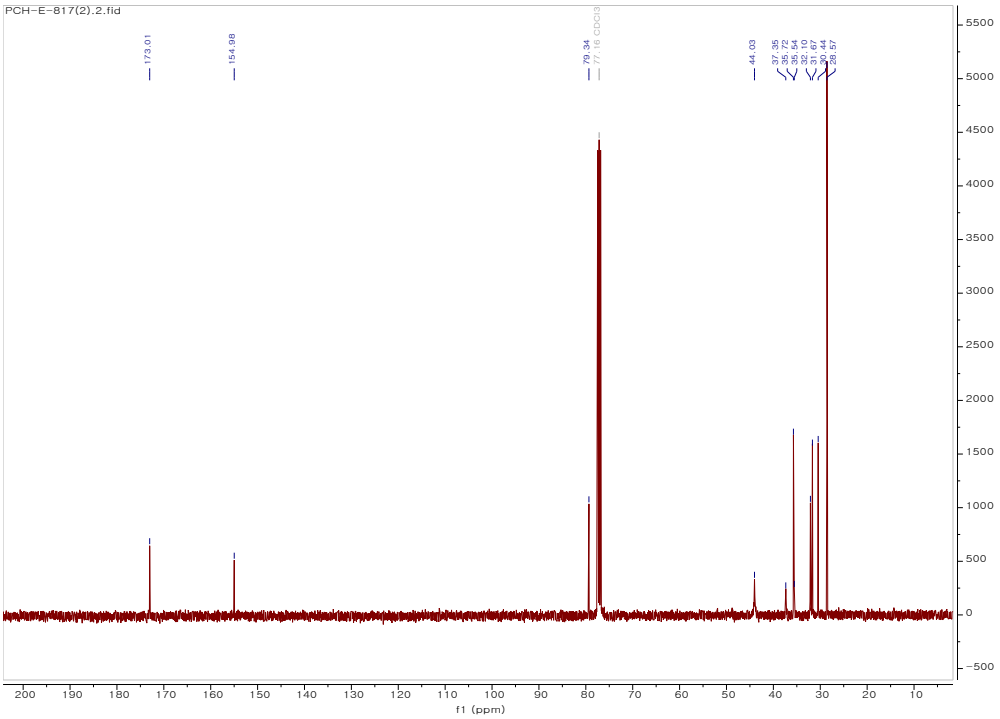




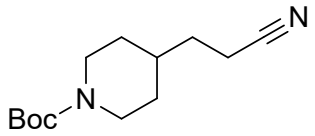
tert-butyl 4-(3-(dimethylamino)-3-oxopropyl)piperidine-1-carboxylate (3u)

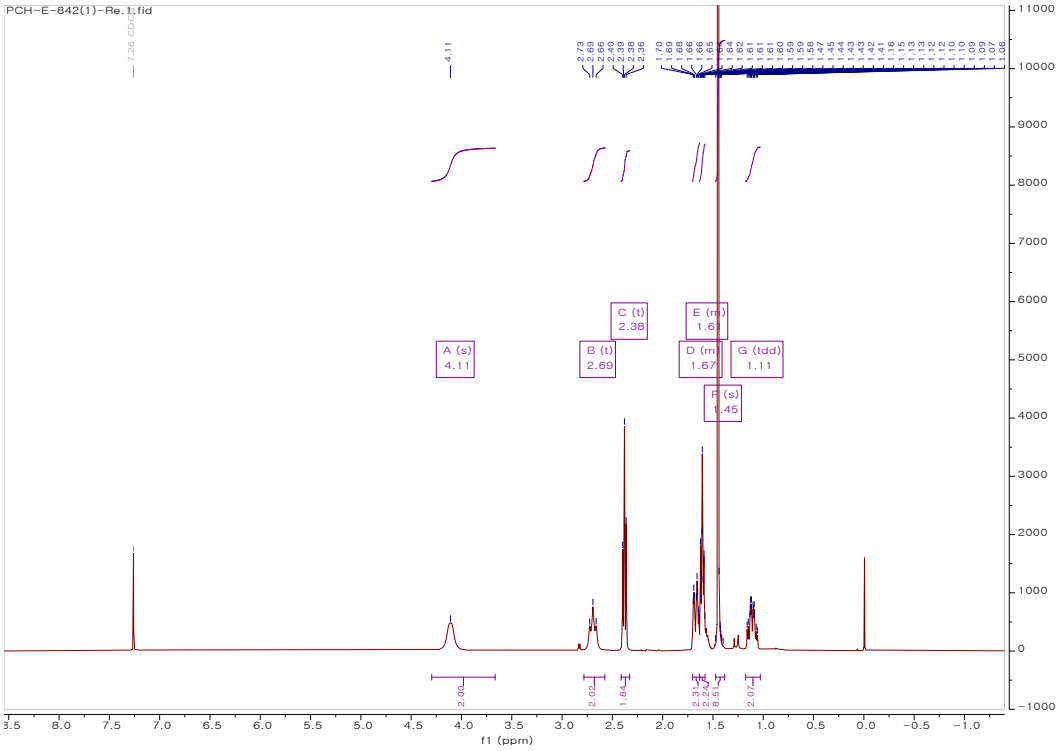


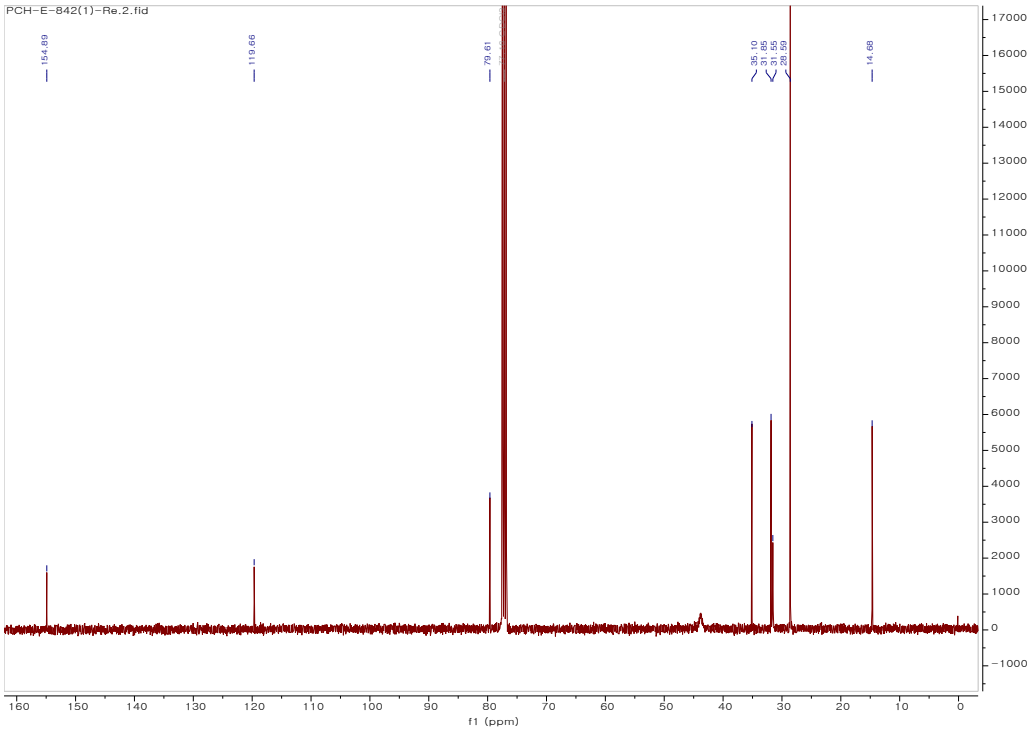




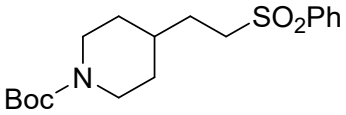
tert-butyl 4-(2-cyanoethyl)piperidine-1-carboxylate (3v)

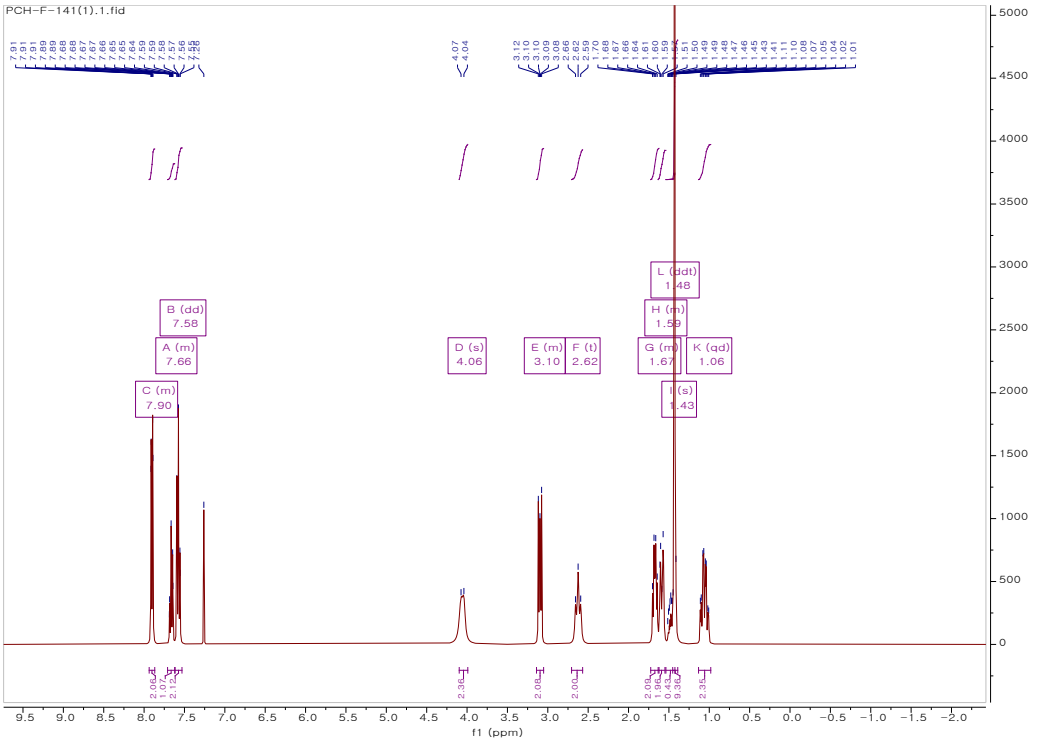


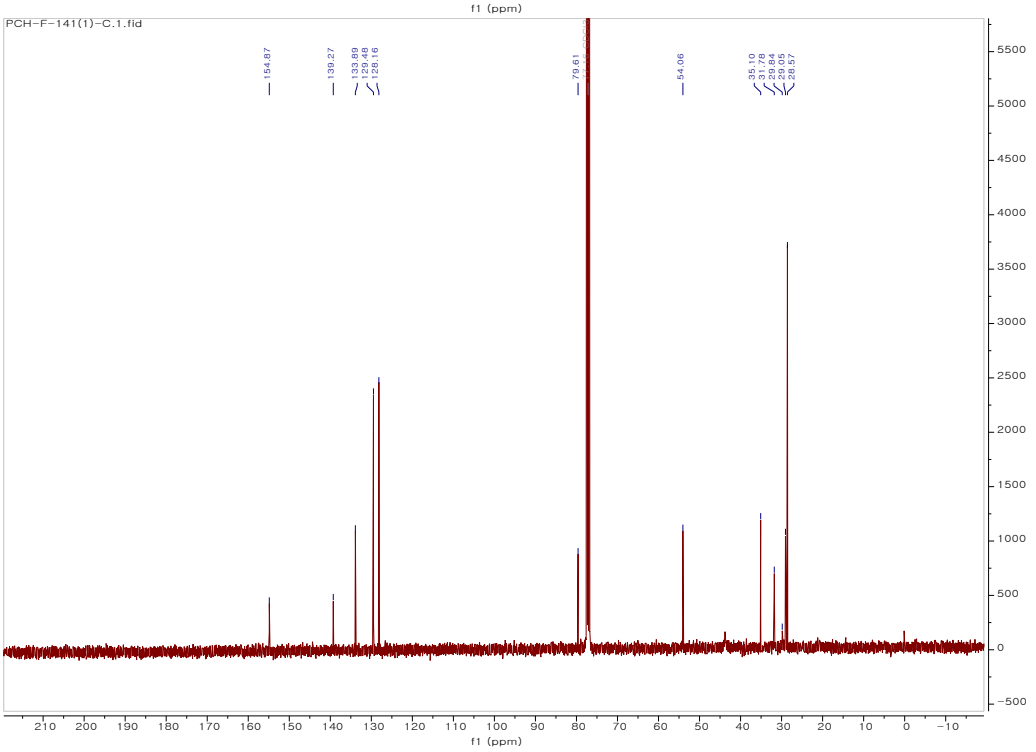




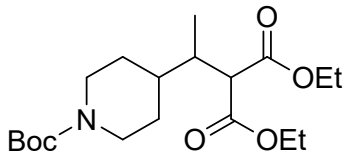
tert-butyl 4-(2-(phenylsulfonyl)ethyl)piperidine-1-carboxylate (3w)

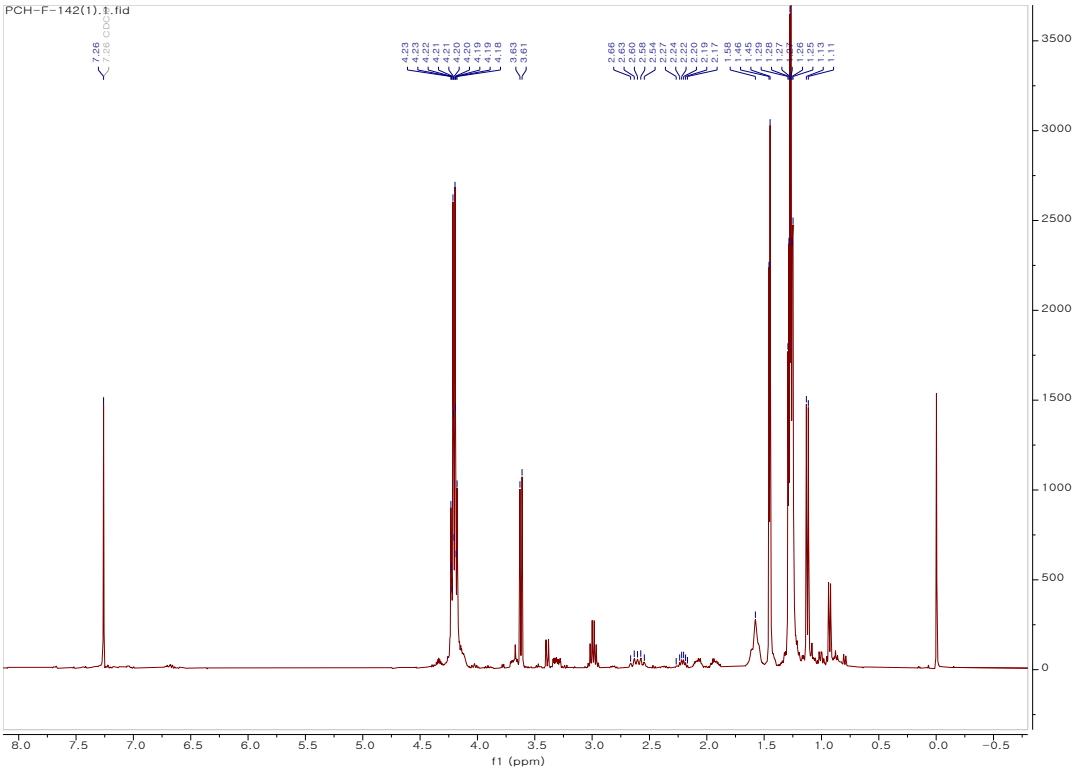


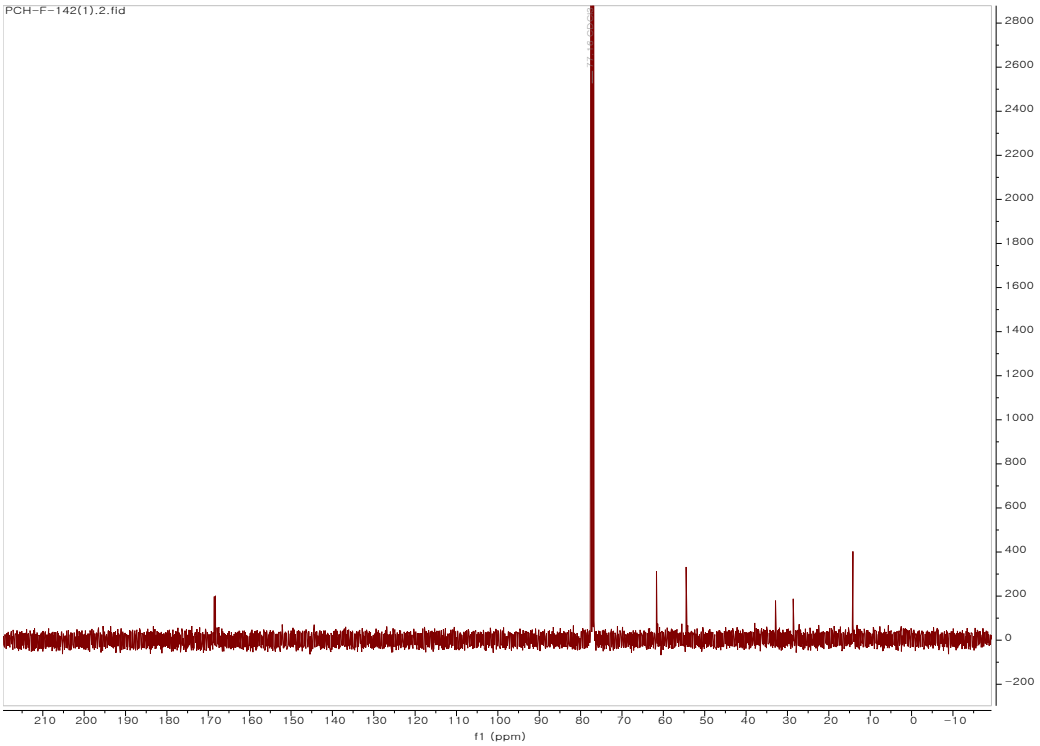




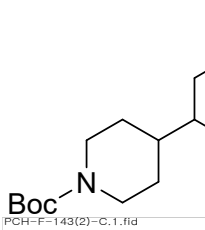
diethyl 2-(1-(1-(tert-butoxycarbonyl)piperidin-4-yl)ethyl)malonate (3x)

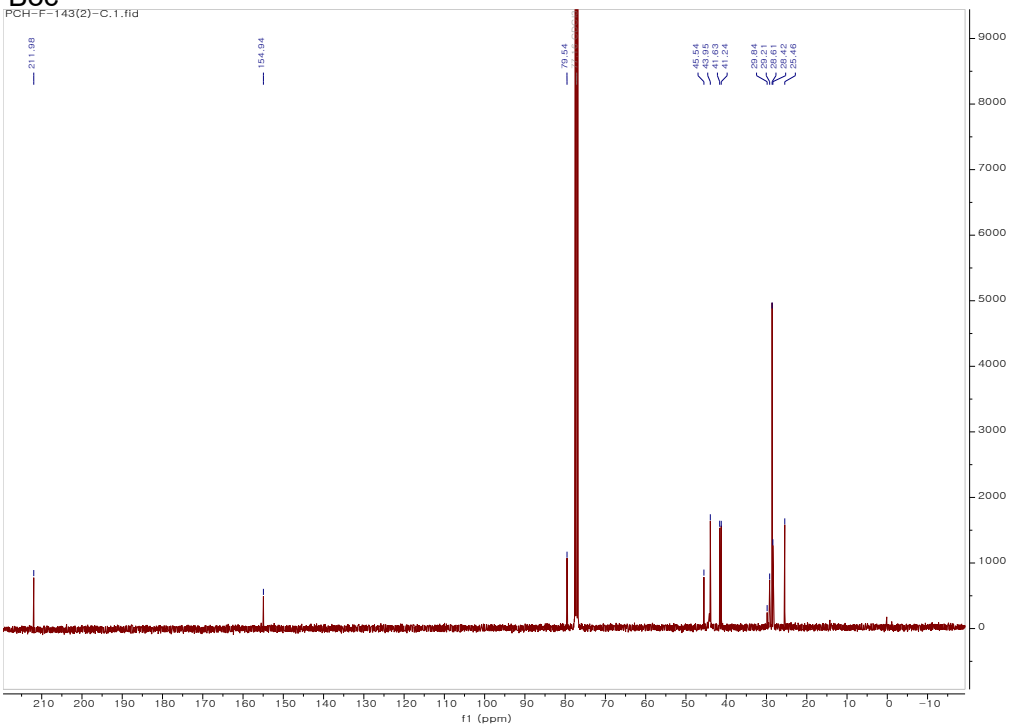


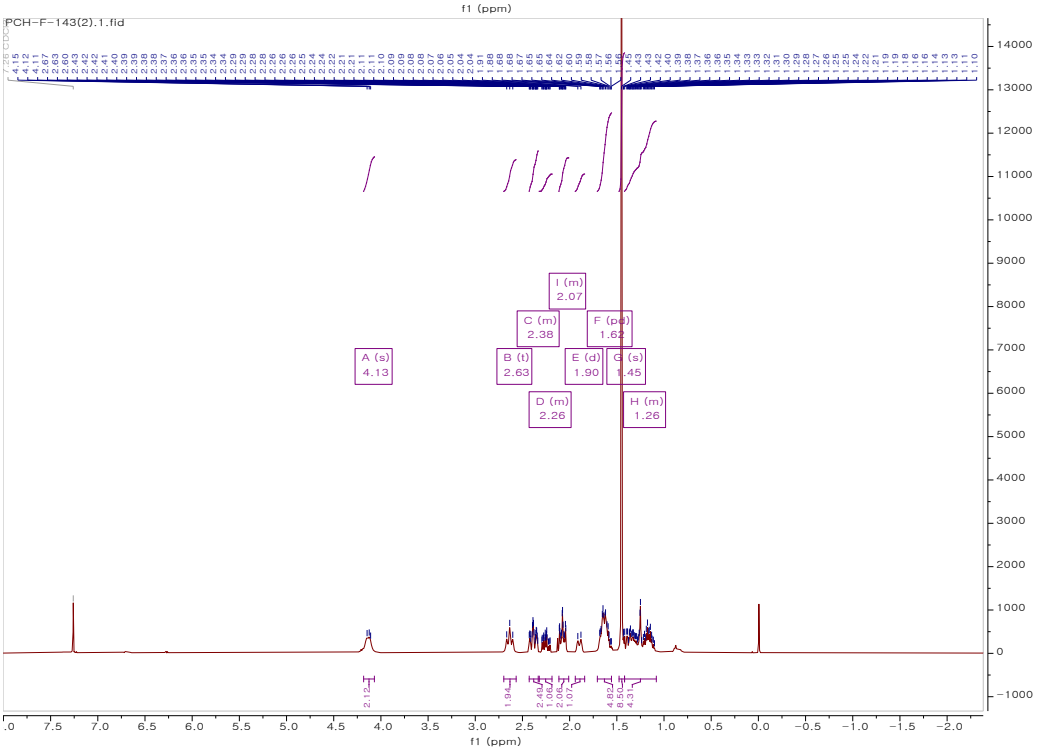




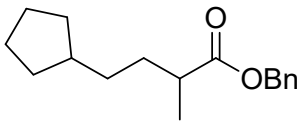
tert-butyl 4-(3-oxocyclohexyl)piperidine-1-carboxylate (3y)

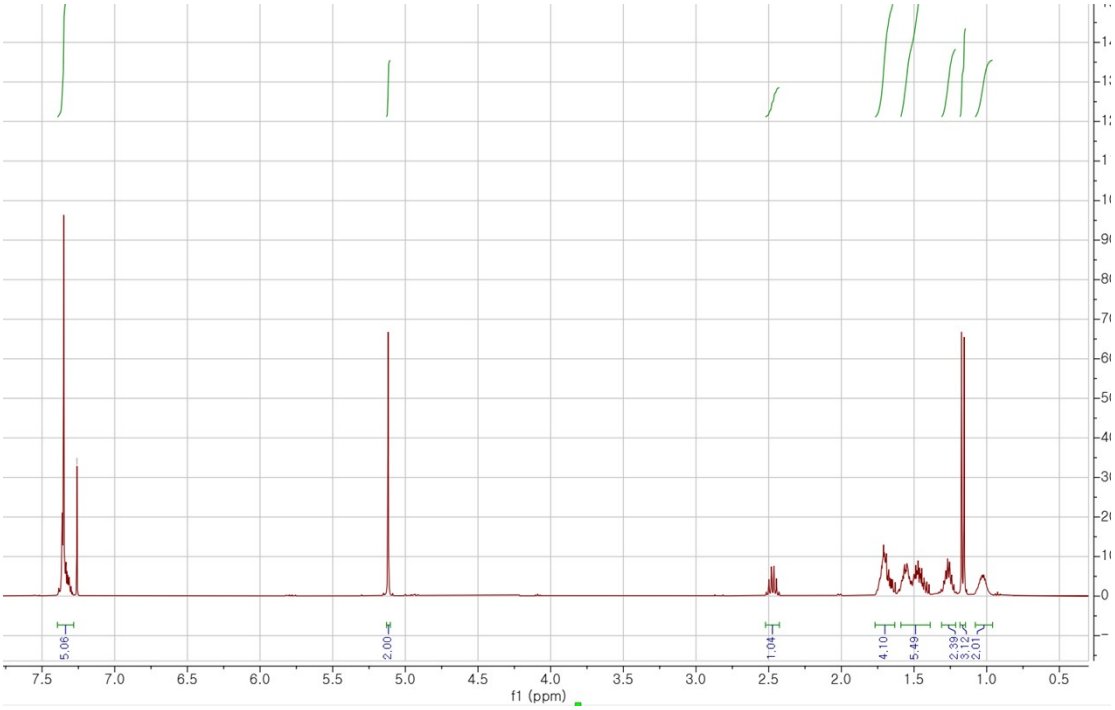


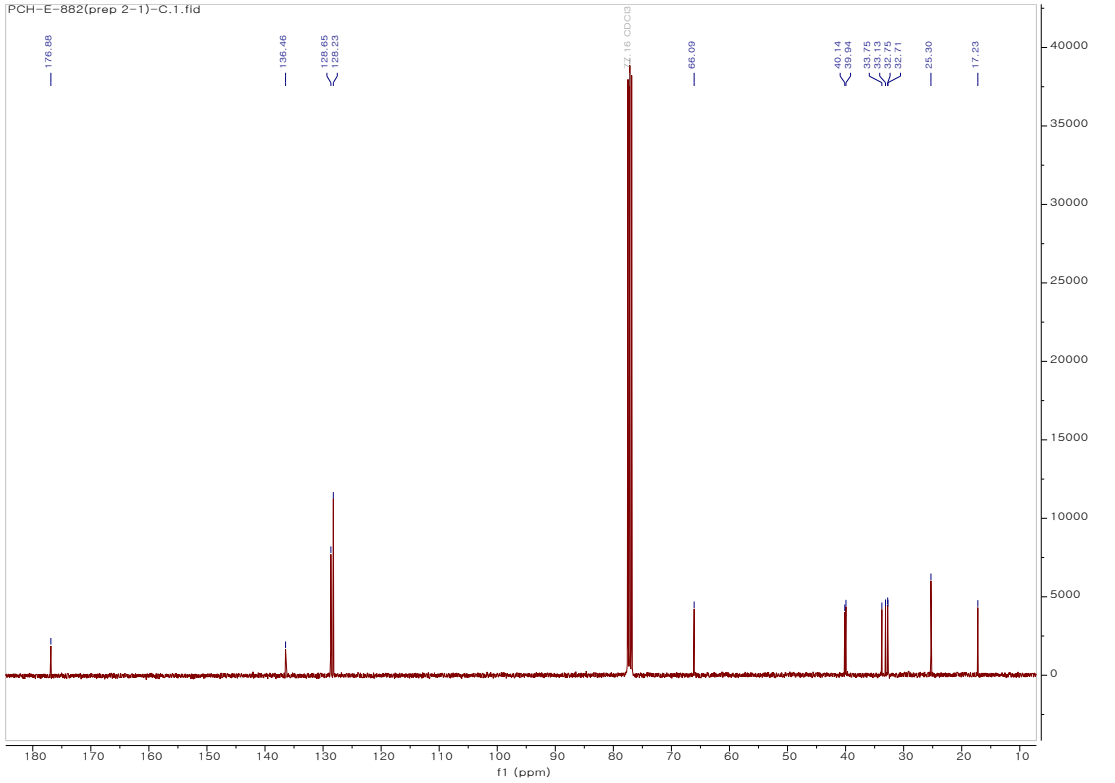




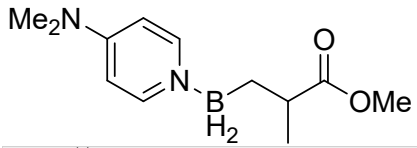
benzyl 4-cyclopentyl-2-methylbutanoate (3z)

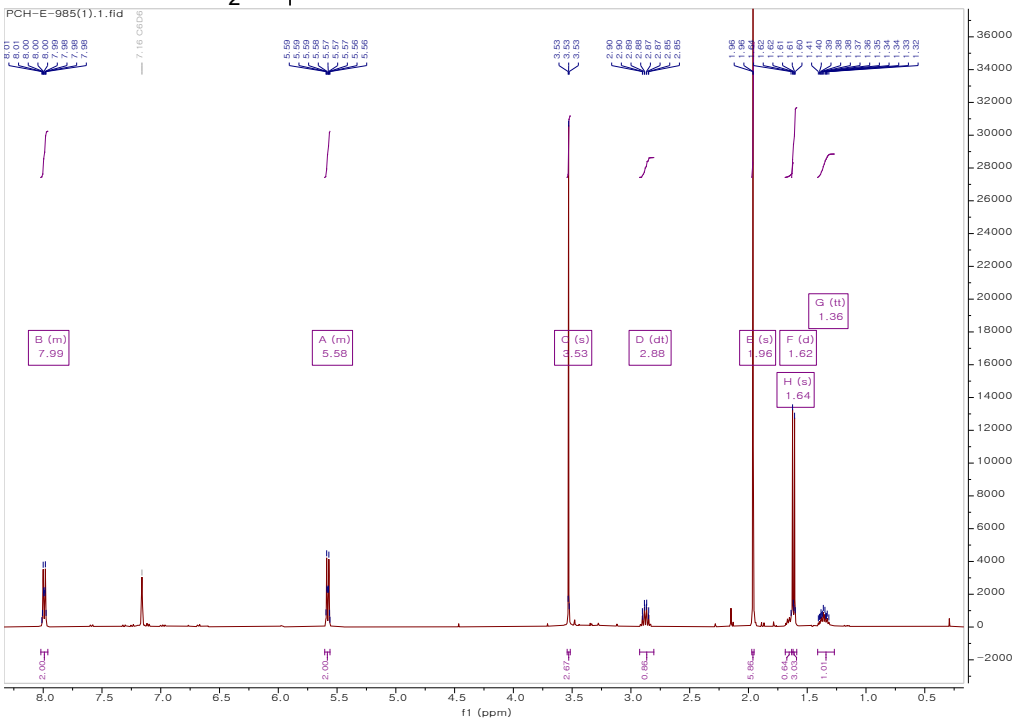


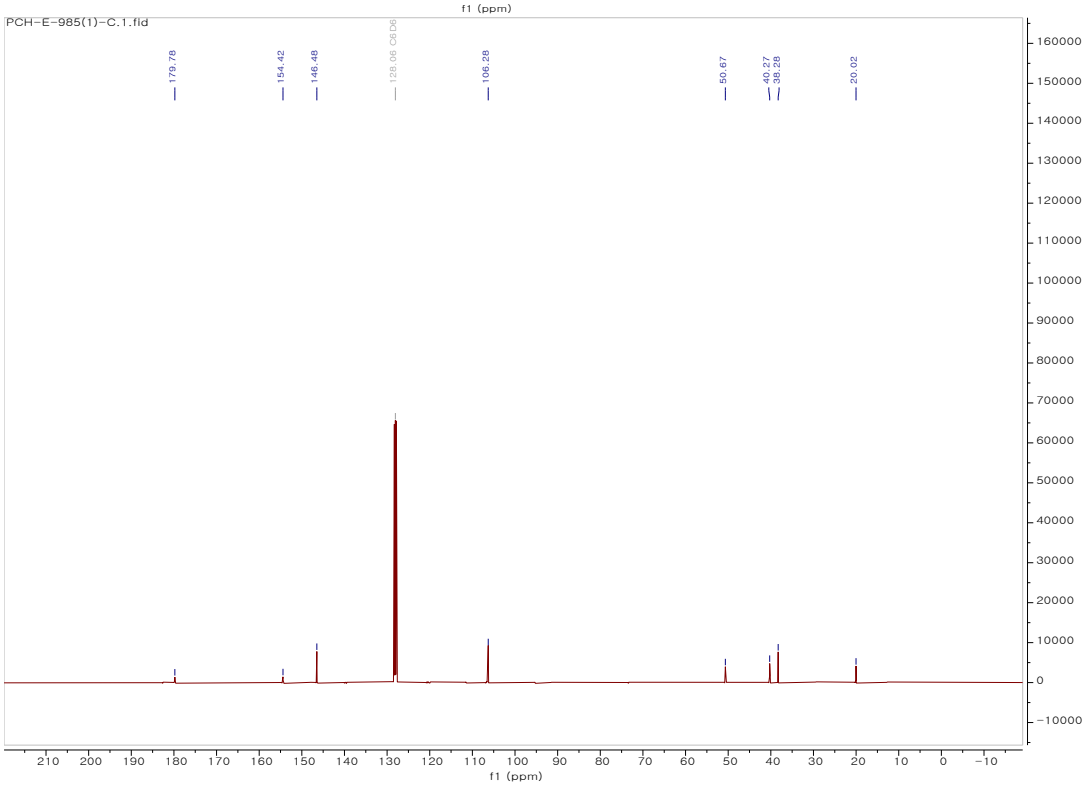


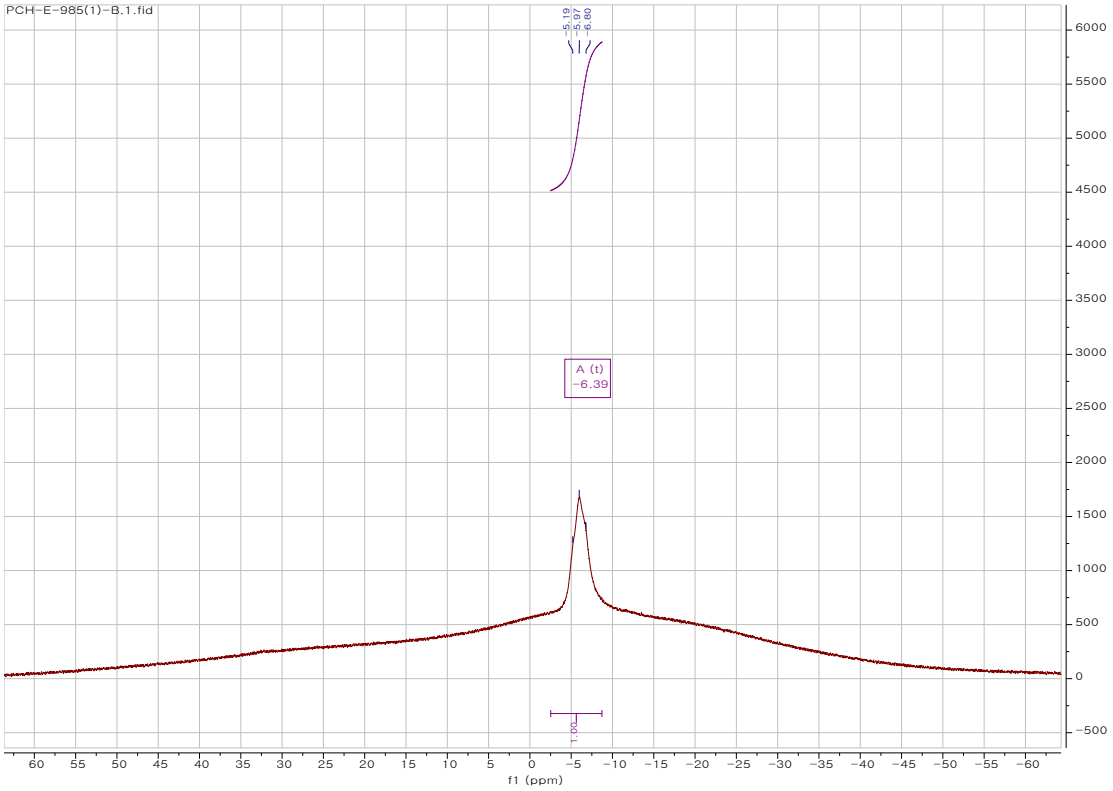


methyl 3-boraneyl-2-methylpropanoate DMAP complex (4b)

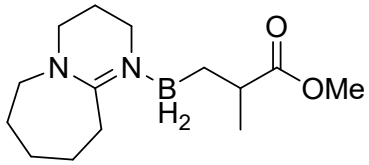


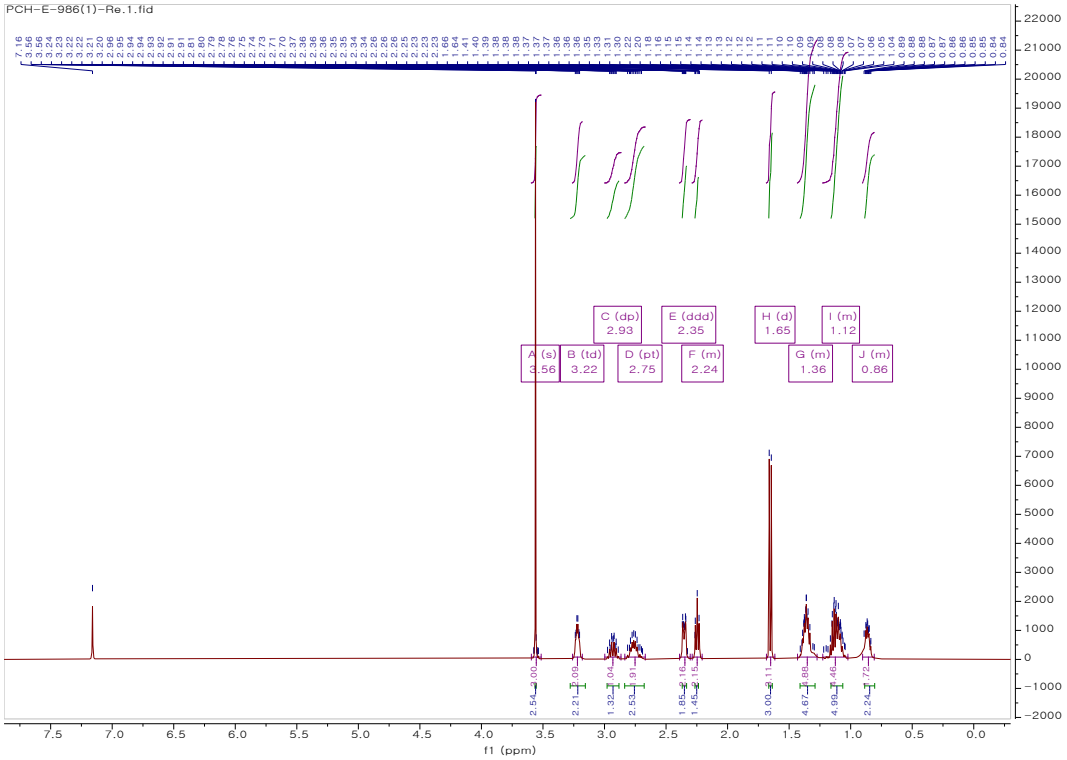


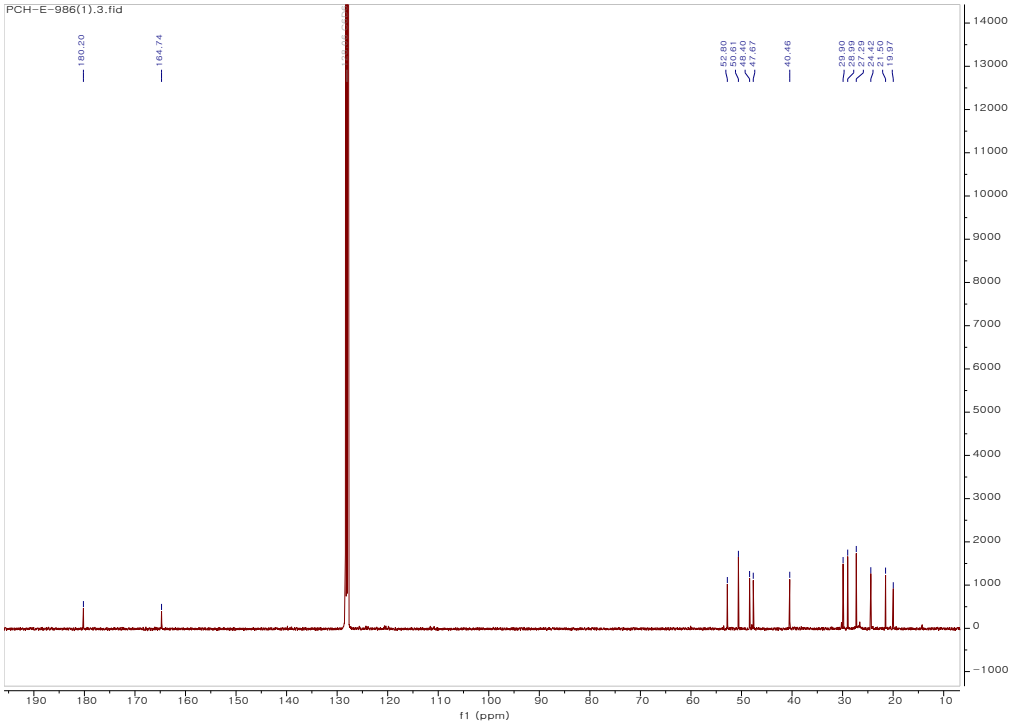


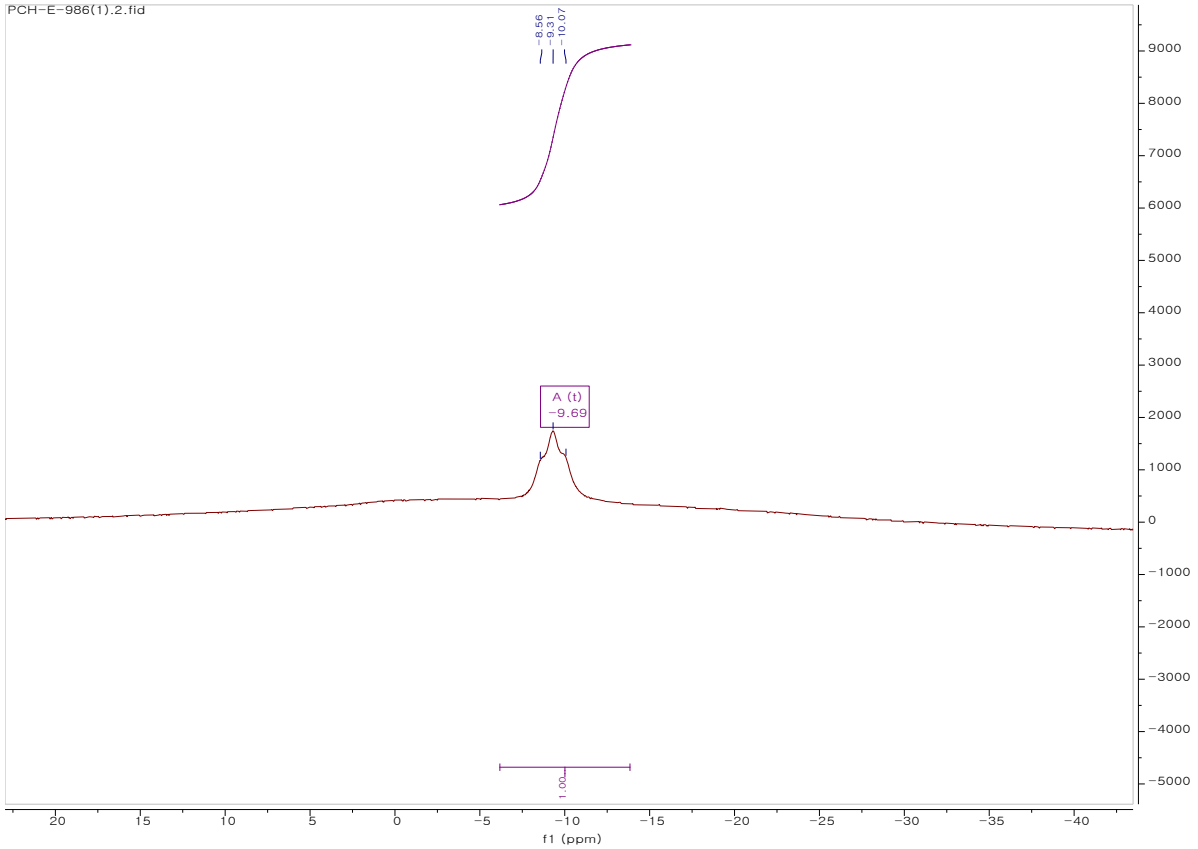

PCH-E-985(1)-B.1.fid
-5.19
-5.97
-6.80
A (t)
-6.39
1.00
f1 (ppm)

methyl 3-boraneyl-2-methylpropanoate DBU complex (4c)

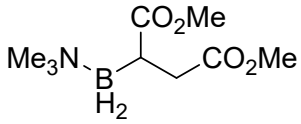


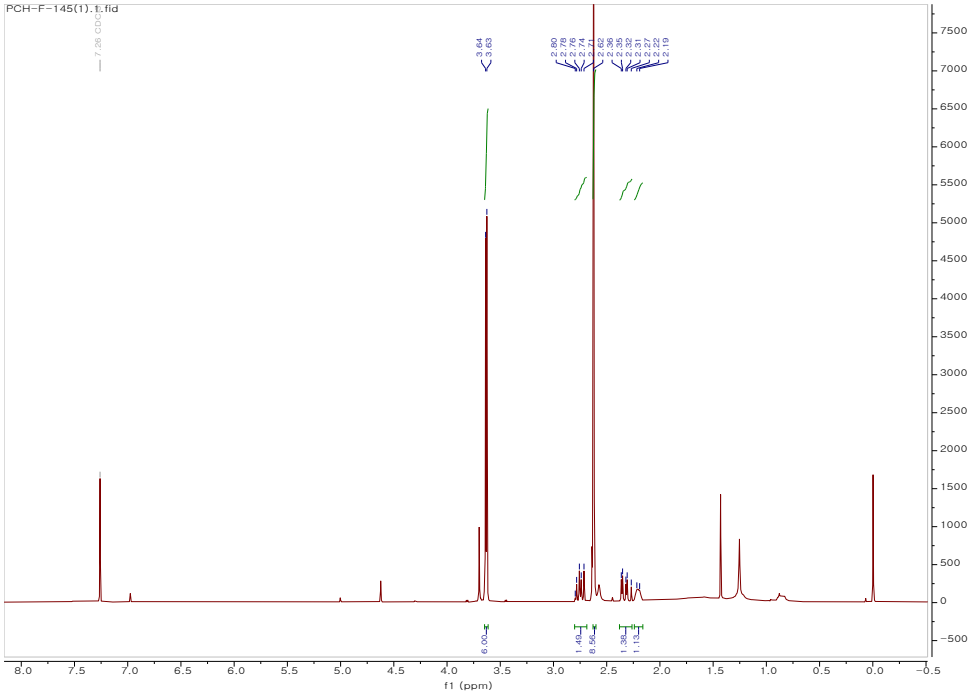


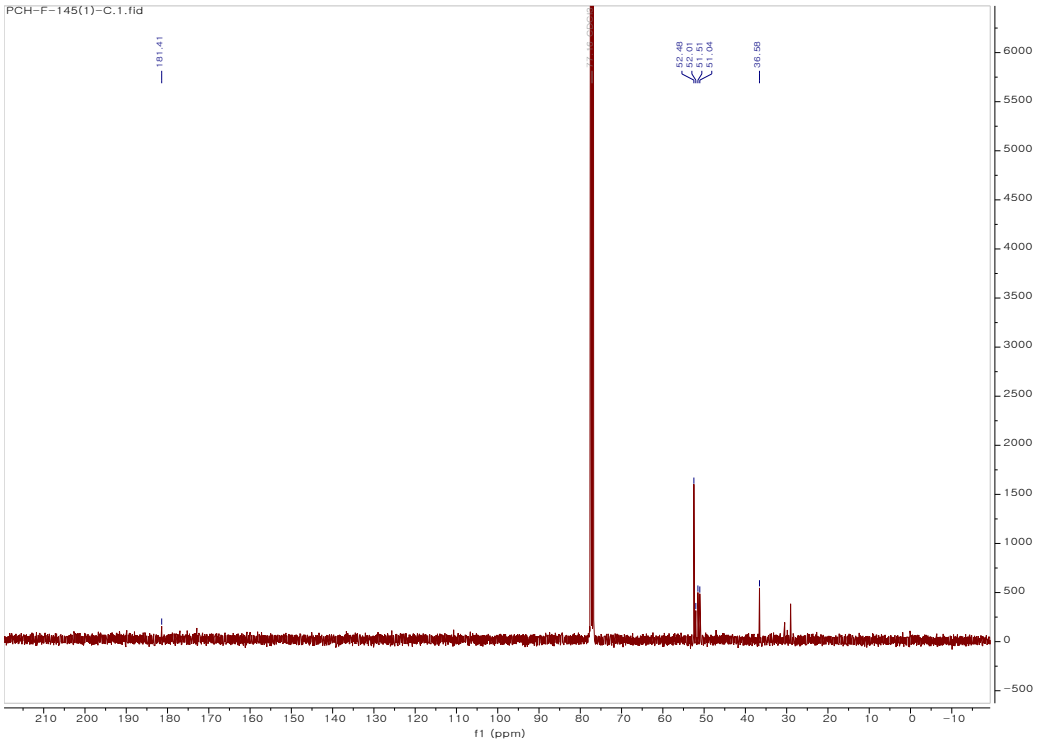


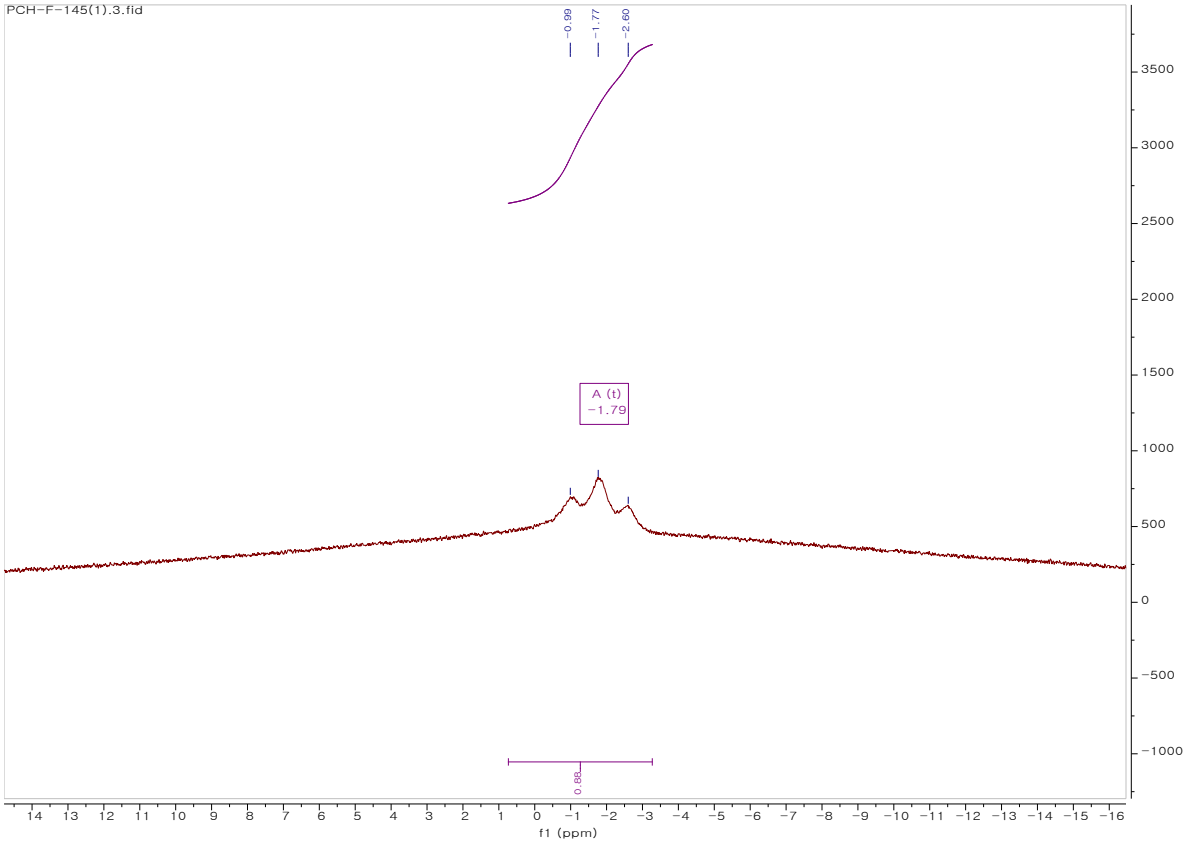

PCH-E-986(1).2.fid
-8.56
-9.31
-10.07
A (t)
-9.69
1.00
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
f1 (ppm)

dimethyl 2-trimethylamine-boranylsuccinate (4f)

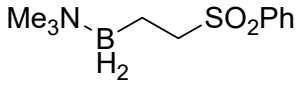


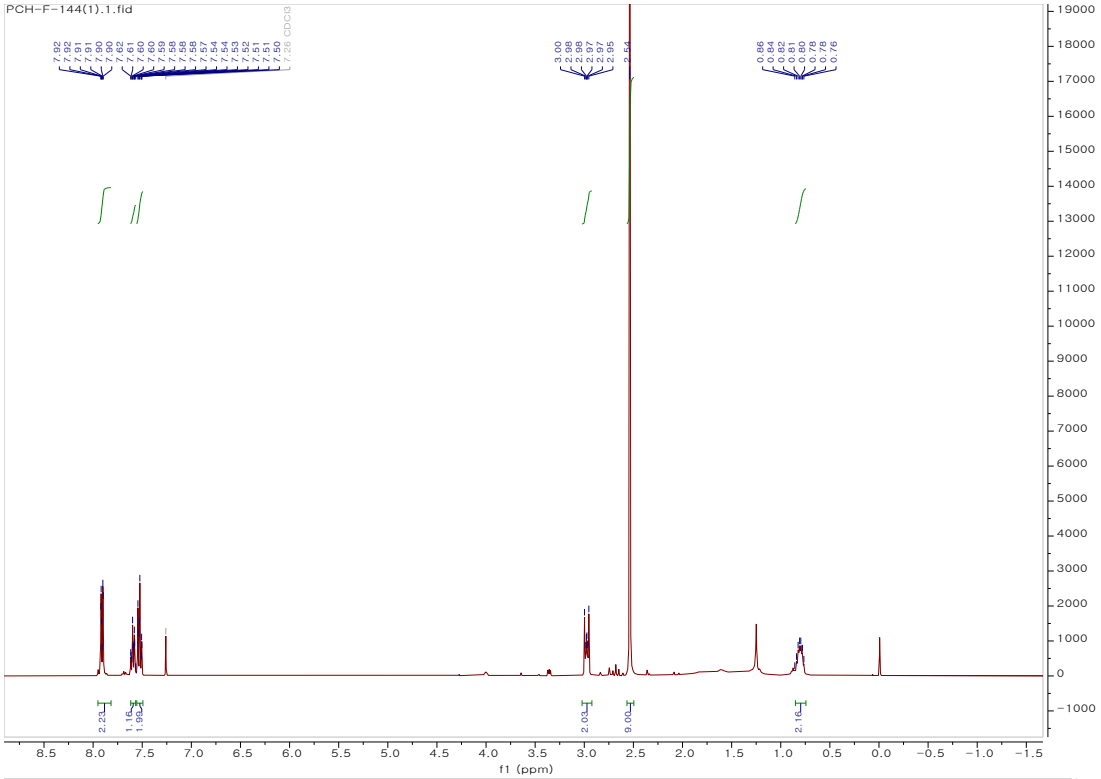


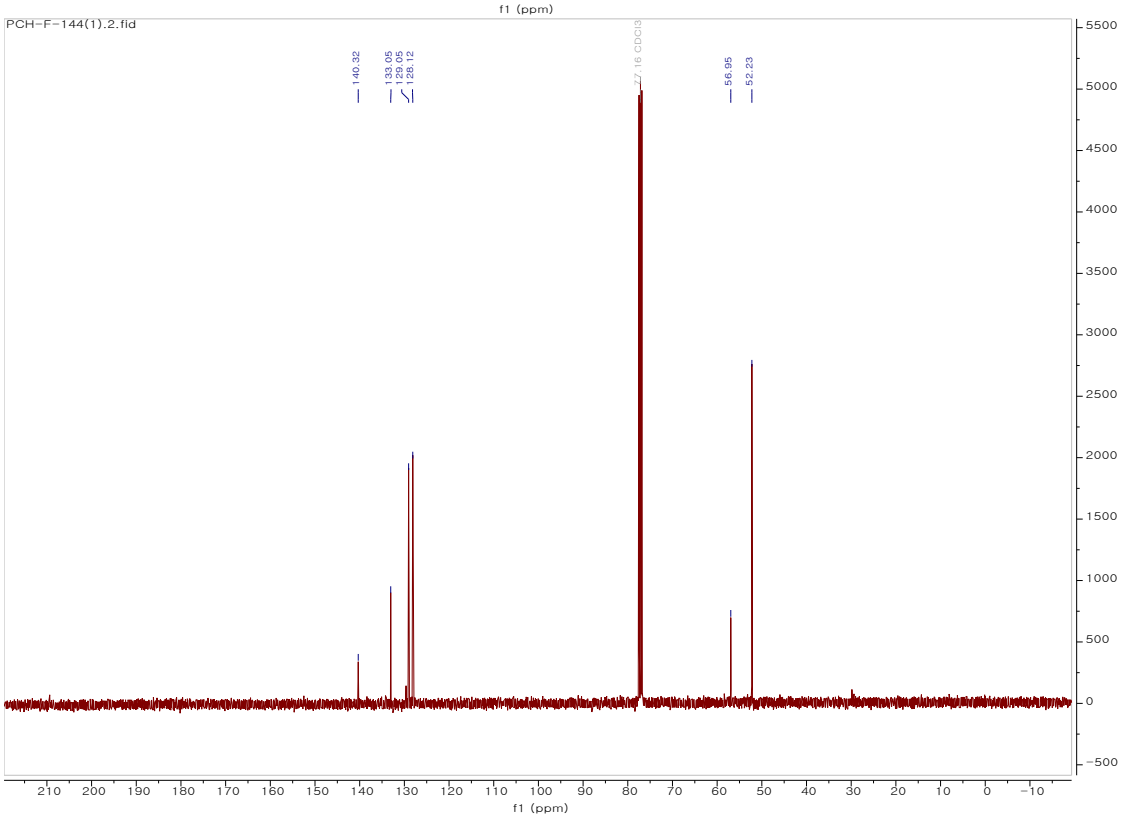


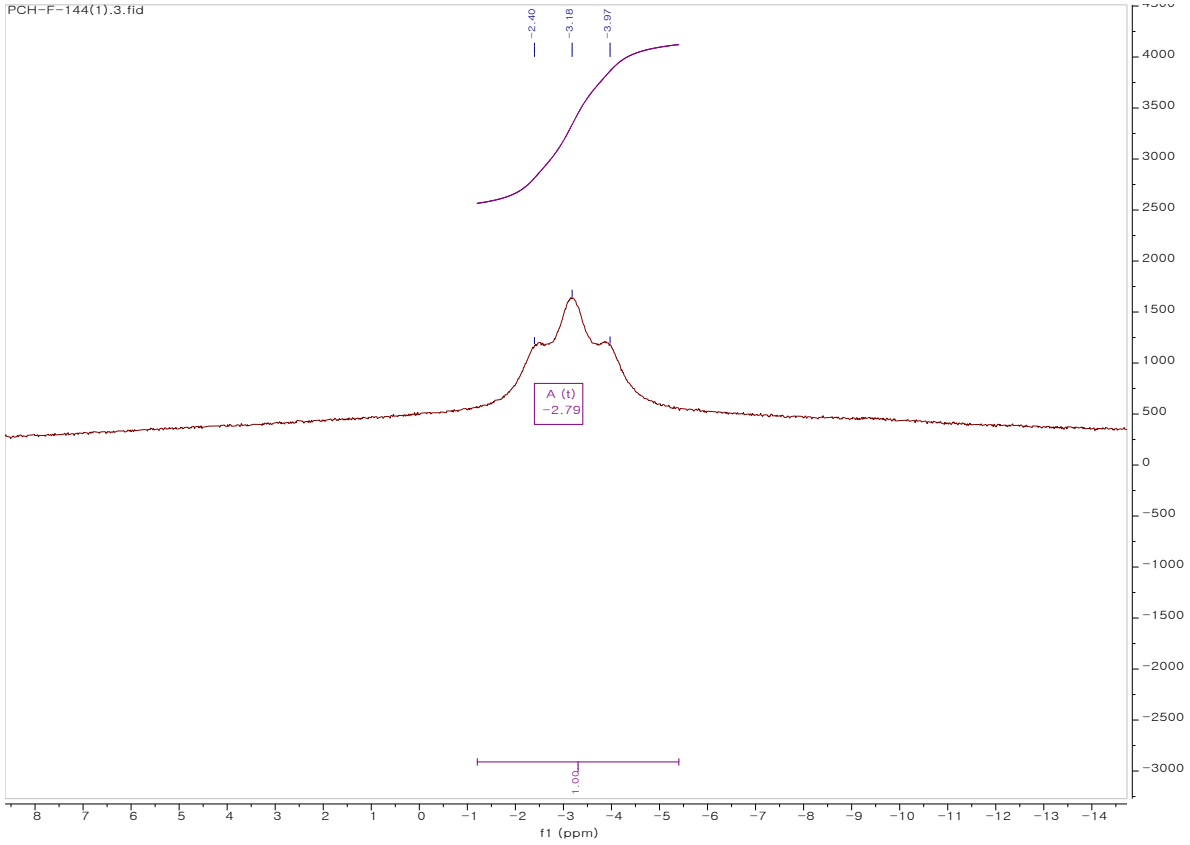

PCH-F-145(1).3.fid
-0.99
-1.77
-2.60
A (t)
-1.79
0.88
f1 (ppm)

((2-trimethylamine-boranylethyl)sulfonyl)benzene (4g)

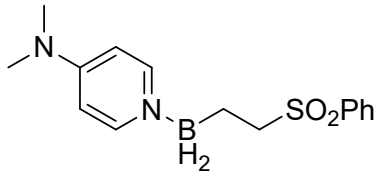


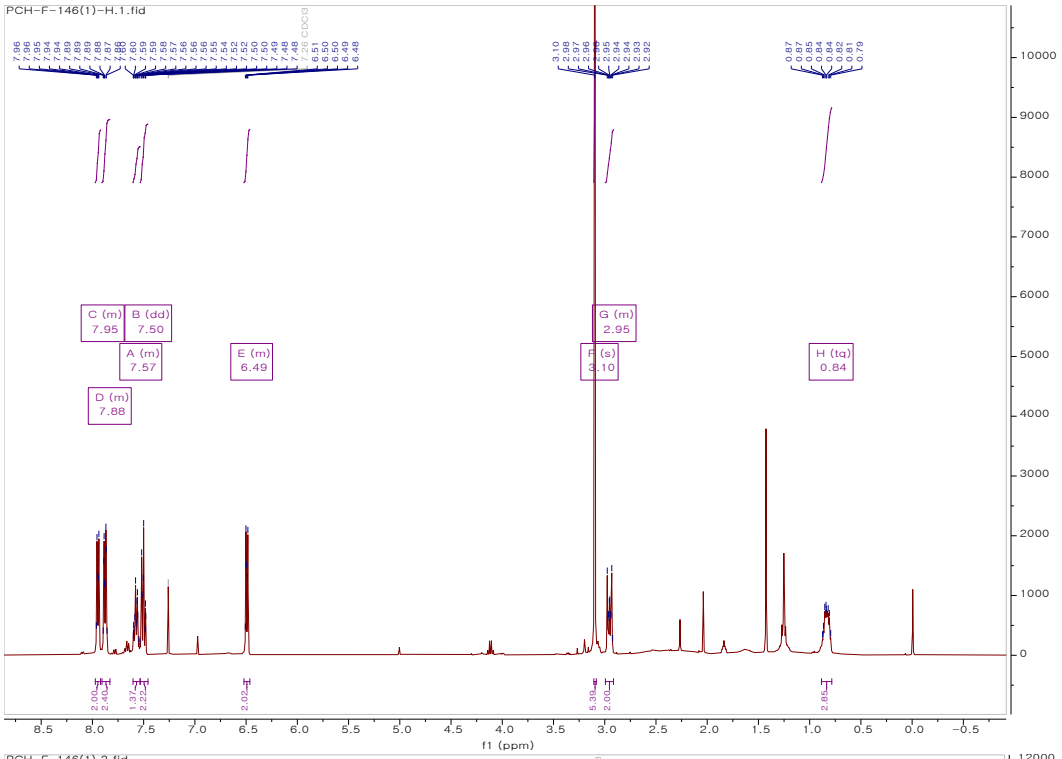


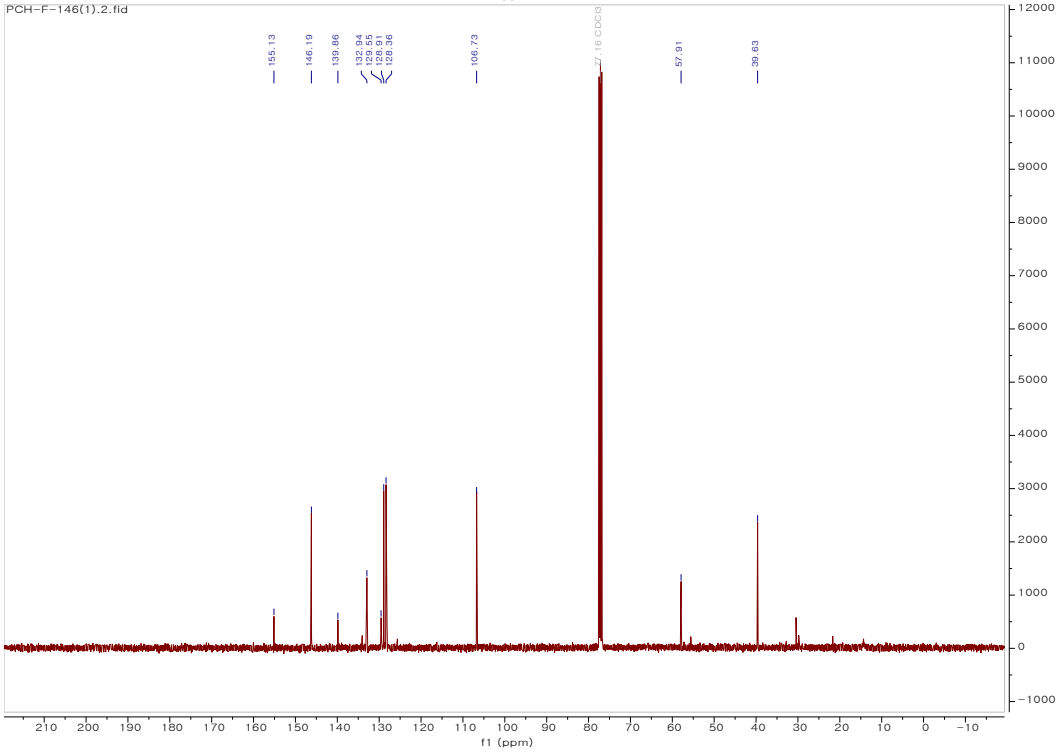


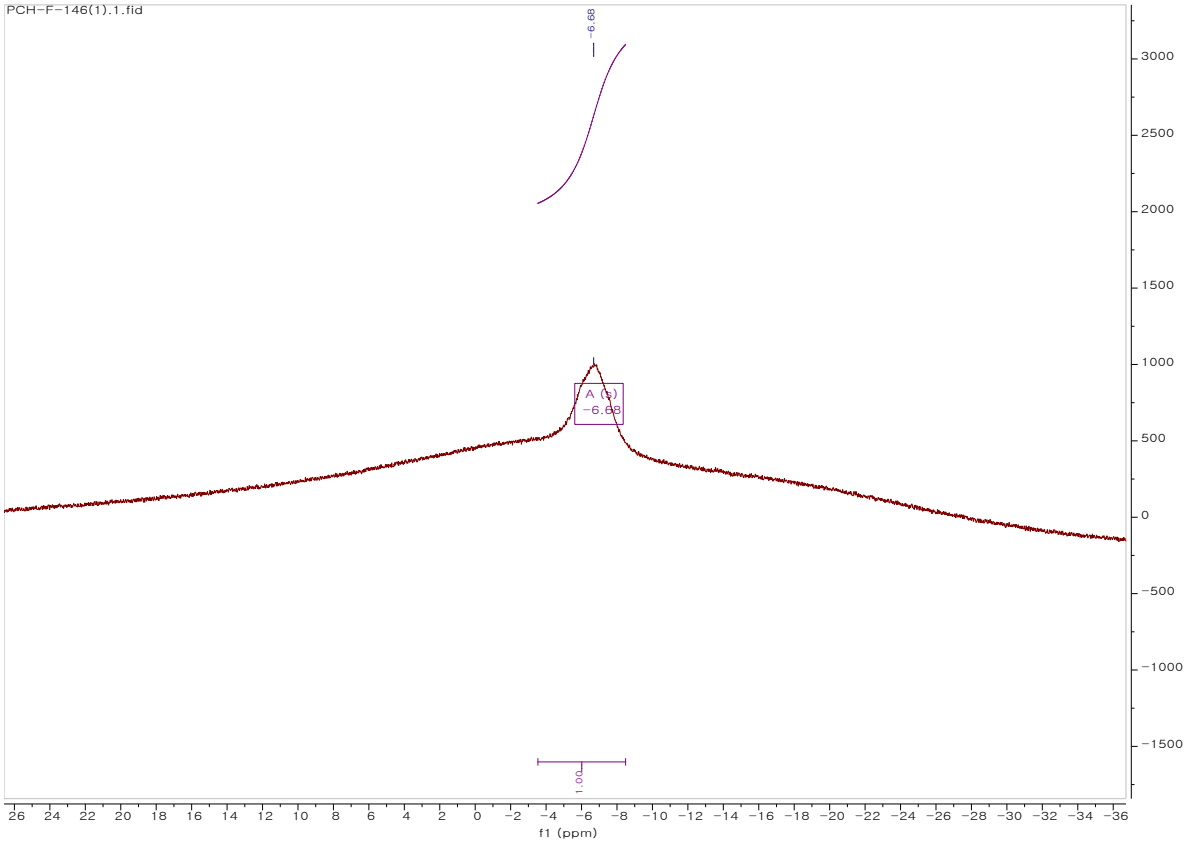

PCH-F-144(1).3.fid
-2.40
-3.18
-3.97
A (t)
-2.79
1.00
f1 (ppm)

((DMAP-boranylethyl)sulfonyl)benzene (4h)

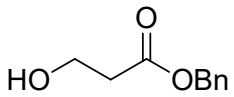


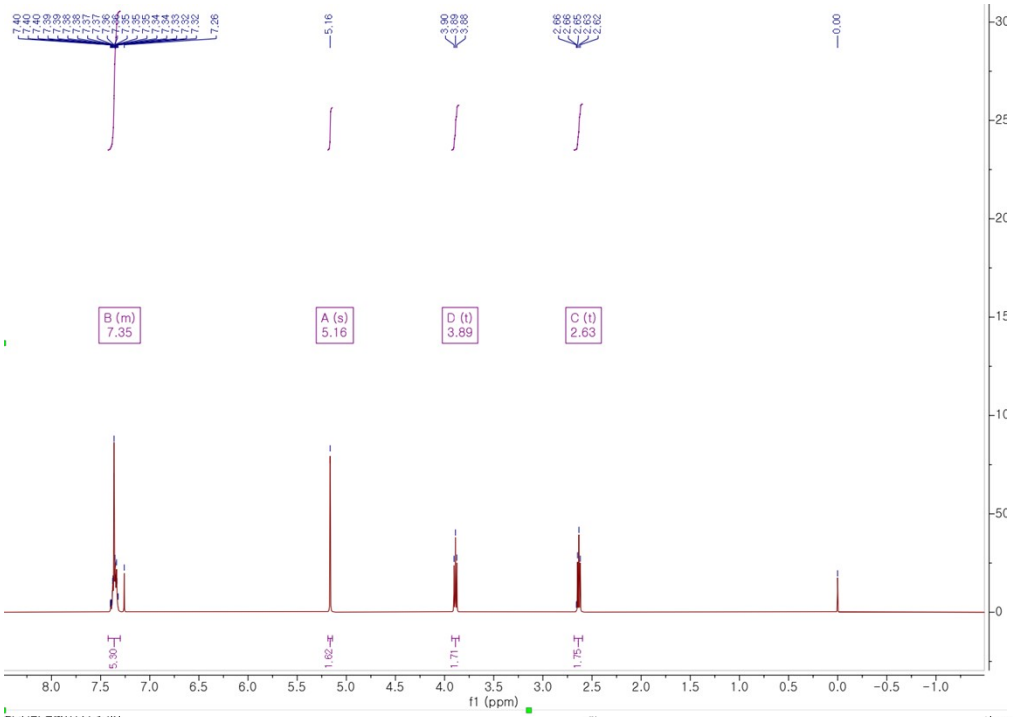


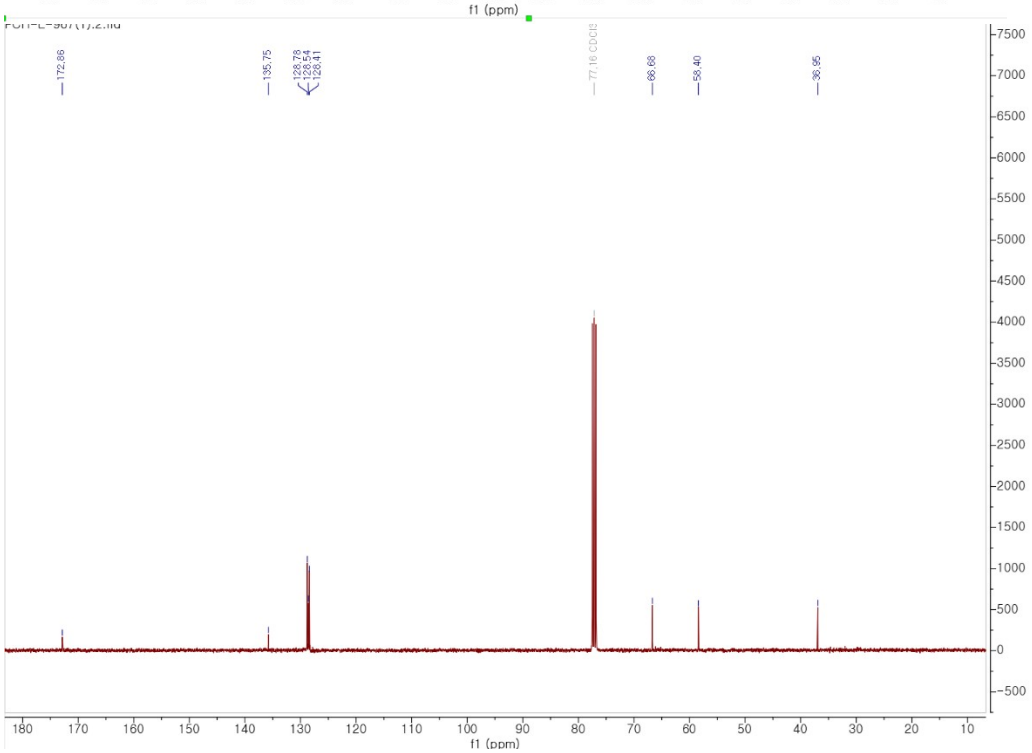



PCH-F-146(1).1.fid
-6.68
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
A (1)
-6.68
1.00
26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34 -36
f1 (ppm)

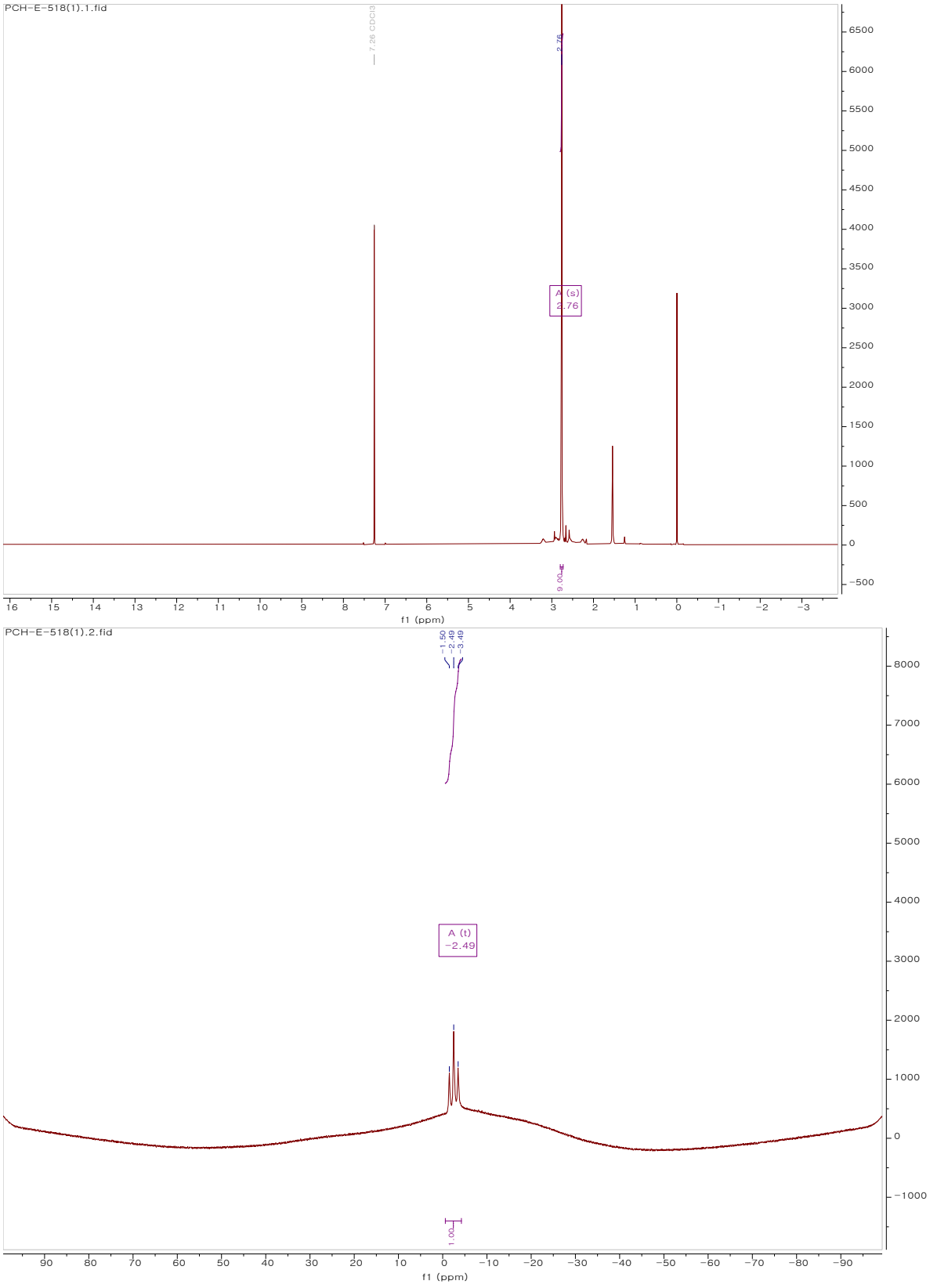
benzyl 3-hydroxypropanoate (5)







Me_3NBH_2Br (6)


PCH-E-518(1).1.fid
7.26 CDCl3
2.76
A (s)
2.76
9.00
f1 (ppm)
PCH-E-518(1).2.fid
1.50
2.49
3.49
A (t)
−2.49
1.00
f1 (ppm)

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