Supporting Information

Diboron-catalyzed dehydrative amidation of aromatic carboxylic acids with amines

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1. General comments

GC/MS analyses were performed on Agilent 6850 series network GC system and Agilent 5975C series Mass Selective Detector (EI) [column: HP-5MS capillary column (l = 30 m, d = 0.25 mm, film thickness = 0.25 μm); chromatographic elution: isothermal at 50 °C for 1 min, 50-250 °C at a rate of 20 °C/min, isothermal at 250 °C for 4 min, 250-300 °C at a rate of 20 °C/min, isothermal at 300 °C for 1 min; carrier gas: He (1.5 mL/min, at 27 psi)]. ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on a JEOL ECA-600 (600 MHz for ^{1}H, 150 MHz for ^{13}C), or JEOL ECA-500 (500 MHz for ^{1}H, 125 MHz for ^{13}C) at 27 °C. Chemical shifts are reported as δ in ppm and are internally referenced to tetramethylsilane (TMS, 0.0 ppm for ^{1}H), $CDCl_3$ (77.2 ppm for ^{13}C), or dimethyl sulfoxide-d_6 (DMSO-d_6, 39.5 ppm for ^{13}C). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, bs = broad singlet, dd = double doublet, dq = double quartet, and m = multiplet. High-resolution mass spectra (HRMS) were obtained from Bruker micrOTOF-QII (ESI). Infrared spectroscopy (IR) spectra were recorded on FT-IR6100 (JASCO). Frequencies are given in wave numbers (cm^{-1}) and only selected peaks were reported. Optical rotation values were recorded on Polarimeter P-1010-GT (JASCO). For thin-layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF254 0.25mm) were used and products were observed under UV light or stain in iodine chamber or phosphomolybdic acid solution. HPLC analysis was conducted on a SHIMADZU HPLC system. The products were purified by column chromatography on silica gel 60 (230-400 mesh; Merck). NMR, HRMS, IR, optical rotation analyses were carried out at Chemical Instrumental Center, Research Center for Materials Science, Nagoya University.

2. Materials

Unless otherwise specified, all carboxylic acids, and amines were purchased from commercial suppliers. Tetrakis(dimethylamido)diboron, Bis(pinacolato)diboron, Bis(neopentyl glycolato)diboron, Bis(catecholato)diboron and Bis(hexylene glycolato)-diboron were purchased from Tokyo Chemical Industry (TCI). Boric acid was purchased from Kanto Chemicals. Tetrahydroxydiboron was purchased from Sigma-Aldrich. Toluene-d_8 (C_7D_8, 98%), and Dimethyl sulfoxide-d_6 (DMSO-d_6) were purchased from Kanto Chemicals. Solvents were purchased from Kanto Chemicals. Silica gel (diameter: 40-100 μm) was purchased from Kanto Chemical.

3. Optimization study

List of diboron and boron catalysts for amidation of **1a** with **2a**

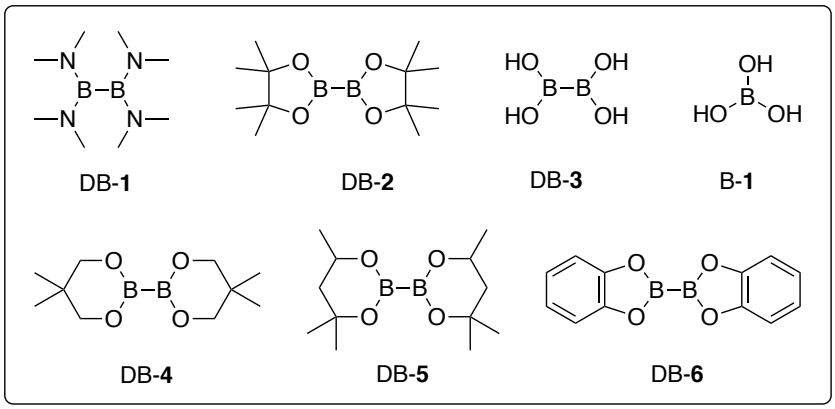
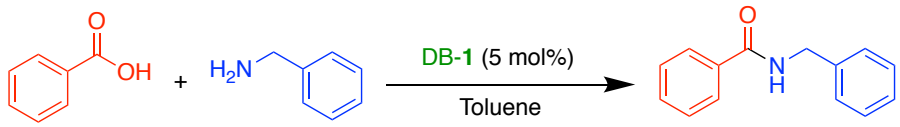


Table S1: Optimization of reaction conditions for tetrakis(dimethylamido)diboron (DB-**1**) catalyzed aryl amide synthesis[a]

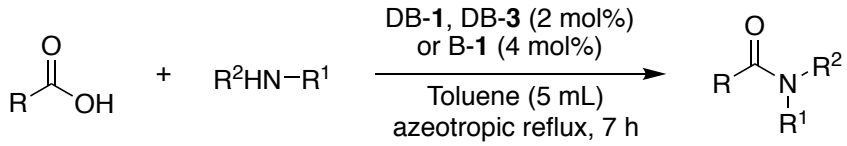


1a (0.5 mmol) **2a** (0.5 mmol) **3aa**

Entry	Toluene (mL)	Temperature (°C)	Cat. DB-**1** (mol%)	Time (h)	Yield[b] (%)
Effect of concentration (Solvent volume)					
1	30	Azeotropic reflux	5	6	53
2	20	Azeotropic reflux	5	6	75
3	15	Azeotropic reflux	5	6	86
4	5	Azeotropic reflux	5	6	95
Effect of Temperature					
5	5	RT	5	6	0
6	5	60	5	6	0
7	5	80	5	6	0
8	5	100	5	6	2
9	5	110	5	6	39
Effect of Catalyst loading					
10	5	Azeotropic reflux	4	6 (3)	91 (71)
11	5	Azeotropic reflux	3	6 (3)	89 (65)
12	5	Azeotropic reflux	2	6 (3)	88 (61)
13	5	Azeotropic reflux	1	6 (3)	86 (44)
Effect of Time					
14	5	Azeotropic reflux	2	4	64
15	5	Azeotropic reflux	2	5	80
16	**5**	**Azeotropic reflux**	**2**	**7**	**98**
17	5	Azeotropic reflux	2	8	98

[a]**Reaction conditions:** Benzoic acid (**1a**, 0.5 mmol), Benzylamine (**2a**, 0.5 mmol), Cat. DB-**1** (5 mol%), under air. Yield in parenthesis is for 3 h. [b]GC Yield (Chlorobenzene used as internal standard).

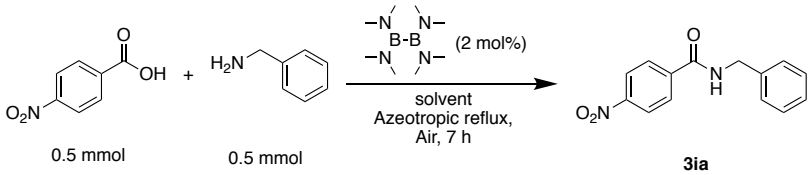
4.1. General procedure for catalytic direct amidation with catalyst DB-**1**, DB-**3**, and B-**1**



An oven dried 20 mL RB flask equipped with magnetic stirring bar was charged with carboxylic acid (0.5 mmol, 1 equiv) and dissolved in 5 mL dry toluene, with subsequent addition of amine (0.5 mmol, 1 equiv) and catalyst (2 mol%). The resulting suspension was stirred at reflux temperature under azeotropic condition for 7 h. After completion, RM was cooled to room temperature. The solvent was evaporated under reduced pressure to dryness and residue was dissolved in ethyl acetate. After the addition of H_2O, the aqueous phase was extracted with EtOAc (3x). The combined organic phases were washed with sat. aq. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-Hexane/EtOAc) to afford the pure products.

Fig. S1 Reaction setup for amidation reaction

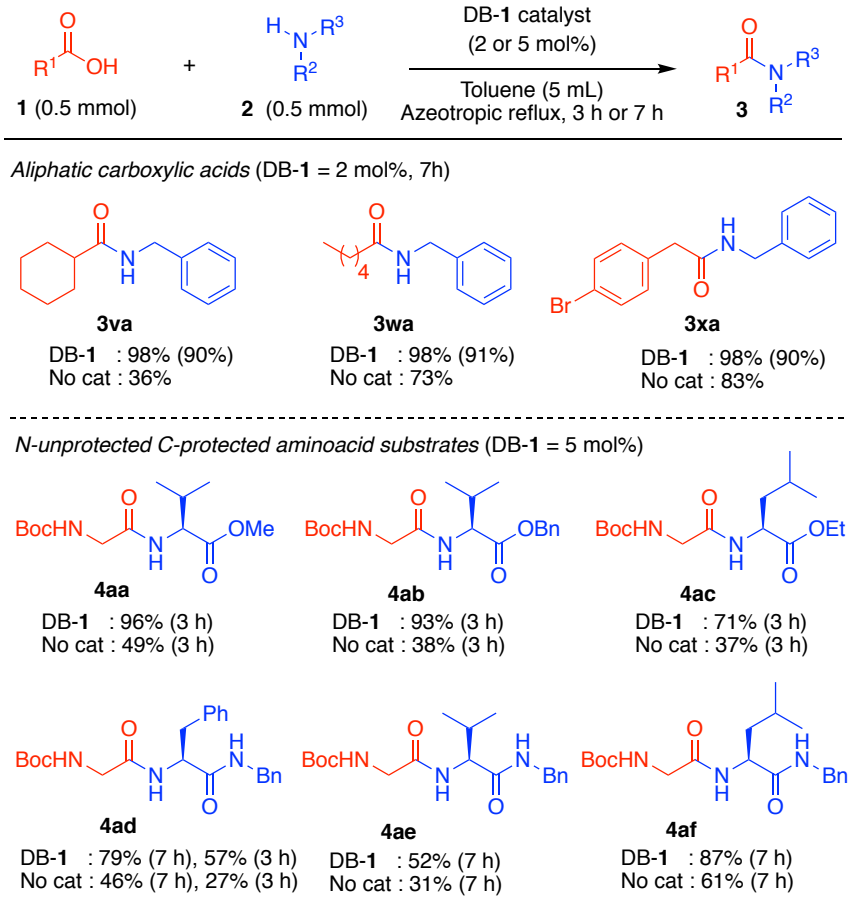
Table S2. Screening of solvents for amidation of 4-nitrobenzoic acid substrate



Entry	Solvent[a]	Yield (%)[b]
1	Toluene	18
2	Chlorobenzene	99
3	Bromobenzene	99
4	Fluorobenzene	0
5	Trifluoromethylbenzene	0
6	Toluene + Chlorobenzene (1:1)	99
7	Toluene + Bromobenzene (1:1)	99
8	Toluene + Fluorobenzene (1:1)	0
9	Toluene + Trifluoromethylbenzene (1:1)	0

[a]Dry solvent [b]GC Yield.

Table S3. Additional substrate scope under the current catalytic system[a,b]

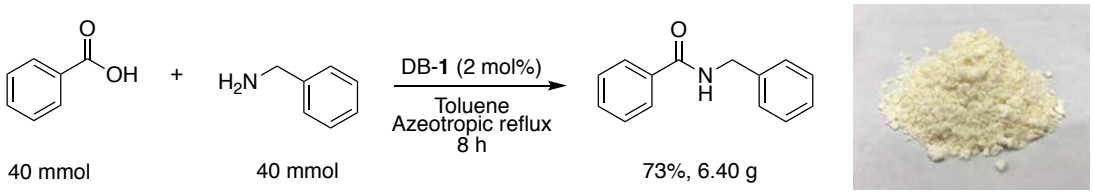


[a]**1** (0.5 mmol), **2** (0.5 mmol), DB-**1** (0, 2 mol% or 5 mol%) in anhydrous toluene (5 mL).

[b]NMR yield using 1,1,2,2-tetrachloroethane as internal standard.

4.2 Application of diboron catalyst for gram scale synthesis of aryl amides

Tetrakis(dimethylamido)diboron (DB-**1**) catalyst shows excellent activity for a gram-scale synthesis of aryl amide under azeotropic reflux conditions.



General procedure for a gram-scale synthesis of aryl amide:

An oven dried, 500 mL round-bottomed flask equipped with magnetic stirring bar was charged with benzoic acid (4.884 g, 40 mmol) and dissolved in dry toluene (200 mL), with subsequent addition of benzylamine (4.286 g, 40 mmol) and Tetrakis(dimethylamido)diboron (0.158 g, 0.8 mmol). The resulting suspension was stirred at reflux temperature under azeotropic conditions for 8 h. After completion, the reaction mixture was cooled to room temperature. The solvent was evaporated under reduced pressure to dryness and residue was dissolved in dichloromethane. After the addition of H_2O, the aqueous phase was extracted with dichloromethane (× 3). The combined organic phases were washed with dilute HCl (0.5 M aqueous solution) followed by a saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and removed under reduced pressure to afford the pure product (**3aa**) in 73% yield (6.40 g, 29.2 mmol). (For 5 mmol-scale reaction, 84% yield of **3aa** was obtained)

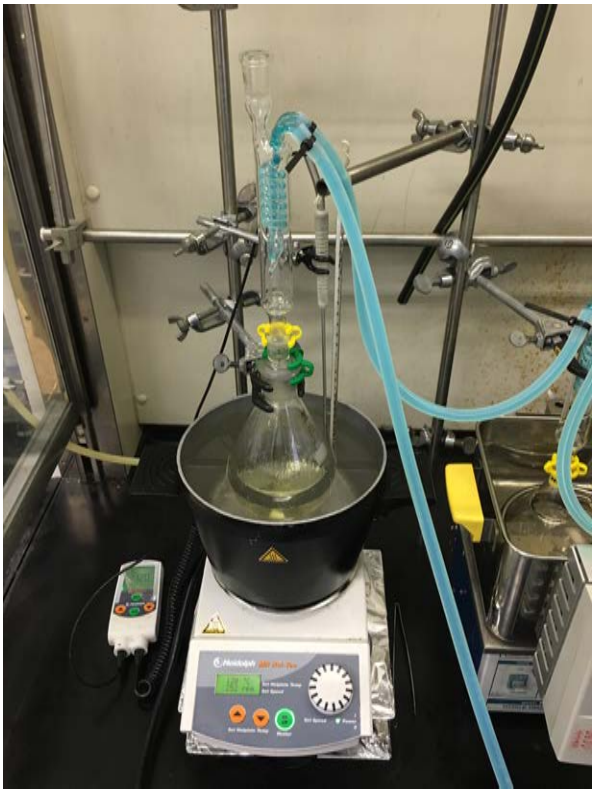
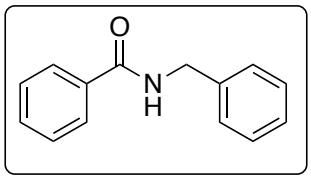


Fig. S2 Reaction set for gram scale amidation

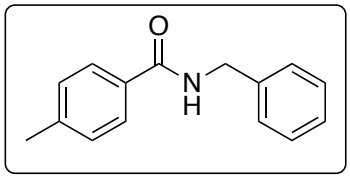
4.3 Characterization data of products (Table 2)

***N*-benzylbenzamide (3aa)**[1]



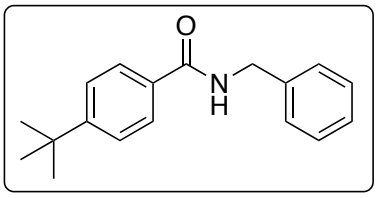
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77-7.80 (m, 2H), 7.46-7.49 (m, 1H), 7.38-7.42 (m, 2H), 7.31-7.34 (m, 4H), 7.25-7.29 (m, 1H), 6.68 (br. s, 1H), 4.60 (d, J = 6.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.5, 138.3, 134.5, 131.7, 128.9, 128.7, 128.0, 127.7, 127.1, 44.2.

***N*-benzyl-4-methylbenzamide (3ba)**[2]



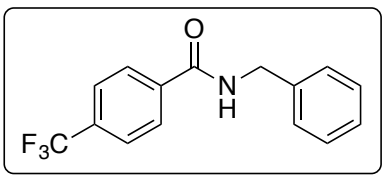
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2H), 7.33-7.35 (m, 4H), 7.29 (td, J = 8.6, 3.9 Hz, 1H), 7.22 (d, J = 8.2 Hz, 2H), 6.44 (s, 1H), 4.63 (d, J = 5.5 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.4, 142.1, 138.4, 131.6, 129.4, 128.9, 128.0, 127.7, 127.1, 44.2, 21.6.

***N*-benzyl-4-(*tert*-butyl)benzamide (3ca)**[4]



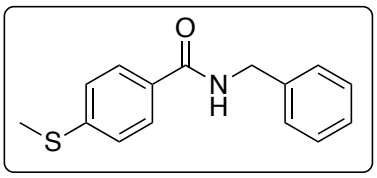
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.33-7.35 (m, 4H), 7.29 (td, J = 8.4, 4.1 Hz, 1H), 7.26 (s, 0H), 6.44 (s, 1H), 4.64 (d, J = 5.5 Hz, 2H), 1.32 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.4, 155.2, 138.5, 131.6, 128.9, 128.0, 127.7, 126.9, 125.7, 44.2, 35.0, 31.3.

***N*-benzyl-4-(trifluoromethyl)benzamide (3da)**[1]



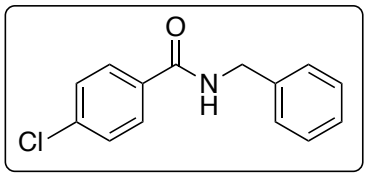
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.26-7.37 (m, 5H), 6.59 (s, 1H), 4.64 (t, J = 2.7 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.2, 137.9, 137.8, 133.8, 133.5, 133.3, 133.1, 129.0, 128.1, 127.9, 127.6, 125.8, 125.8, 124.7, 122.9, 121.1, 44.4.

***N*-benzyl-4-(methylthio)benzamide (3ea)**[5]



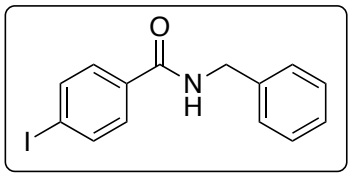
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.32-7.36 (m, 4H), 7.30 (td, J = 8.8, 4.4 Hz, 1H), 7.24-7.26 (m, 3H), 6.37 (s, 1H), 4.64 (d, J = 6.2 Hz, 2H), 2.50 (s, 3H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 166.9, 143.7, 138.3, 130.6, 128.9, 128.1, 127.8, 127.5, 125.6, 44.3, 15.2.

***N*-benzyl-4-chlorobenzamide (3fa)**[1]



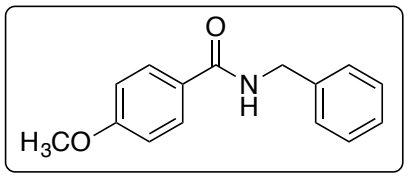
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.9 Hz, 2H), 7.26-7.39 (m, 7H), 6.49 (s, 1H), 4.61 (d, J = 5.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.4, 138.1, 137.9, 132.8, 128.9, 128.5, 128.1, 127.9, 44.4.

***N*-benzyl-4-iodobenzamide (3ga)**[4]



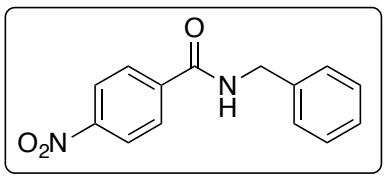
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.9 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.26-7.36 (m, 5H), 6.49 (s, 1H), 4.61 (d, J = 6.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.7, 138.0, 137.9, 133.9, 128.9, 128.7, 128.1, 127.9, 98.6, 44.3.1

***N*-benzyl-4-methoxybenzamide (3ha)**[1]



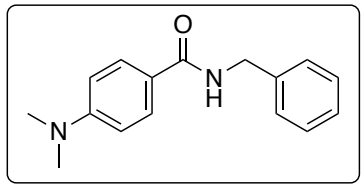
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.33 (dd, J = 25.1, 3.8 Hz, 4H), 7.29 (td, J = 8.6, 4.1 Hz, 1H), 7.26 (s, 0H), 6.91 (td, J = 5.8, 3.4 Hz, 2H), 6.35 (s, 1H), 4.63 (d, J = 5.5 Hz, 2H), 3.84 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.9, 162.4, 138.5, 128.9, 128.1, 127.7, 126.8, 113.9, 55.4, 44.2.

***N*-benzyl-4-nitrobenzamide (3ia)**[1]



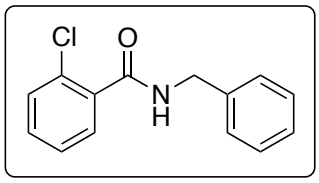
^{1}H NMR (600 MHz, DMSO-d_6) δ 9.39 (d, J = 5.5 Hz, 1H), 8.31-8.34 (m, 2H), 8.13-8.16 (m, 2H), 7.23-7.36 (m, 5H), 4.53 (t, J = 6.9 Hz, 2H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 164.6, 149.0, 139.9, 139.1, 128.8, 128.3, 127.3, 126.9, 123.5, 42.9.

***N*-benzyl-4-(dimethylamino)benzamide (3ja)**[5]



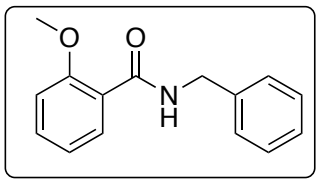
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.75 – 7.56 (m, 2H), 7.30 (d, J = 31.3 Hz, 5H), 6.64 (s, 2H), 6.35 (s, 1H), 4.59 (d, J = 22.0 Hz, 2H), 2.98 (d, J = 20.7 Hz, 6H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 167.4, 152.6, 138.9, 128.8, 128.6, 128.5, 127.9, 127.5, 121.2, 111.2, 44.0, 40.2.

***N*-benzyl-2-chlorobenzamide (3ka)**[6]



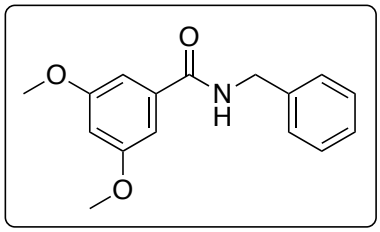
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (dd, J = 7.6, 1.4 Hz, 1H), 7.26-7.39 (m, 8H), 6.54 (s, 1H), 4.65 (d, J = 5.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.5, 137.8, 135.1, 131.5, 130.8, 130.3, 130.3, 128.9, 128.0, 127.8, 127.2, 44.3.

***N*-benzyl-2-methoxybenzamide (3la)**[5]



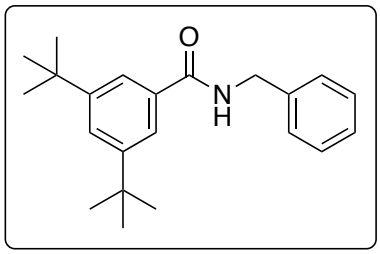
^{1}H NMR (600 MHz, DMSO-d_6) δ 8.69 (t, J = 5.5 Hz, 1H), 7.76 (dd, J = 7.6, 2.1 Hz, 1H), 7.46-7.49 (m, 1H), 7.32-7.35 (m, 4H), 7.24 (td, J = 5.5, 3.4 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 4.51 (d, J = 6.2 Hz, 2H), 3.89 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.1, 156.9, 139.7, 132.1, 130.3, 128.2, 127.0, 126.6, 123.2, 120.4, 111.9, 55.8, 42.5.

***N*-benzyl-3,5-dimethoxybenzamide (3ma)**[2]



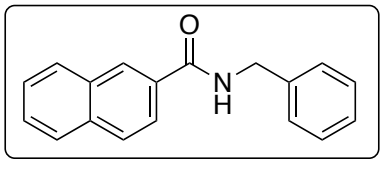
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.36 (m, 4H), 7.28-7.31 (m, 1H), 6.91 (d, J = 2.1 Hz, 2H), 6.57 (t, J = 2.4 Hz, 1H), 6.44 (s, 1H), 4.62 (d, J = 6.2 Hz, 2H), 3.80 (s, 6H); **13C NMR** (151 MHz, $CDCl_3$) δ 167.2, 160.9, 138.1, 136.7, 128.8, 127.9, 127.7, 104.9, 103.6, 77.3, 77.1, 76.9, 55.6, 44.2.

***N*-benzyl-3,5-di-*tert*-butylbenzamide (3na)**[7]



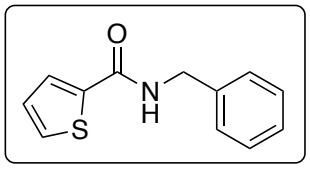
^{1}H NMR (600 MHz, DMSO-d_6) δ 9.03 (t, J = 5.8 Hz, 1H), 7.74 (d, J = 1.8 Hz, 2H), 7.55 (t, J = 1.7 Hz, 1H), 7.33 (t, J = 2.4 Hz, 4H), 7.23-7.25 (m, 1H), 4.49 (d, J = 5.7 Hz, 2H), 1.31 (s, 18H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 166.7, 150.4, 139.9, 133.7, 128.3, 127.3, 126.7, 124.8, 121.4, 42.6, 34.7, 31.2.

***N*-benzyl-2-naphthamide (3oa)**[7]



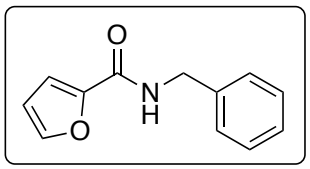
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.83-7.87 (m, 4H), 7.50-7.56 (m, 2H), 7.25-7.39 (m, 5H), 6.68 (s, 1H), 4.69 (d, J = 6.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.5, 138.3, 134.8, 132.7, 131.6, 128.9, 128.9, 128.5, 128.0, 127.8, 127.7, 127.7, 127.5, 126.8, 123.7, 77.3, 77.1, 76.9, 44.3.

***N*-benzylthiophene-2-carboxamide (3pa)**[1]



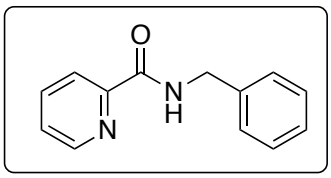
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (t, J = 2.4 Hz, 1H), 7.46-7.47 (m, 1H), 7.35 (d, J = 4.1 Hz, 4H), 7.26-7.31 (m, 1H), 7.06 (dd, J = 5.2, 3.8 Hz, 1H), 6.37 (s, 1H), 4.61 (d, J = 6.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.9, 138.9, 138.2, 130.2, 128.9, 128.3, 128.1, 127.8, 127.8, 44.1.

***N*-benzylfuran-2-carboxamide (3qa)**[1]



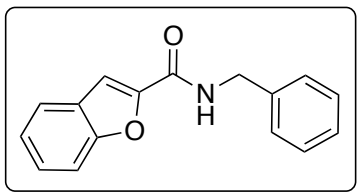
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J = 1.4 Hz, 1H), 7.34 (d, J = 4.8 Hz, 4H), 7.26-7.31 (m, 1H), 7.14 (d, J = 3.3 Hz, 1H), 6.70 (s, 1H), 6.49 (q, J = 1.8 Hz, 1H), 4.61 (d, J = 6.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.4, 148.0, 144.0, 138.1, 128.8, 128.0, 127.7, 114.5, 112.3, 43.3.

***N*-benzylpicolinamide (3ra)**[4]



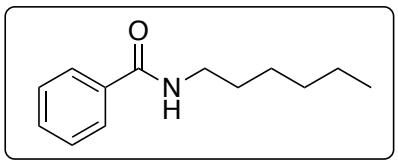
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 6.6 Hz, 2H), 8.23 (t, J = 6.4 Hz, 1H), 7.83 (t, J = 7.8 Hz, 1H), 7.50 – 7.06 (m, 6H), 4.67 (d, J = 6.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.31, 149.92, 148.16, 138.31, 137.43, 128.80, 128.75, 127.92, 127.53, 126.28, 122.42, 77.36, 77.15, 76.95, 43.57.

***N*-benzylbenzofuran-2-carboxamide (3sa)**[8]



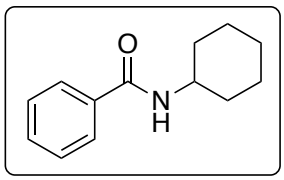
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 0H), 7.51 (s, 0H), 7.46 (d, J = 8.9 Hz, 0H), 7.36-7.42 (m, 1H), 7.26-7.33 (m, 1H), 6.95 (s, 0H), 4.68 (d, J = 5.5 Hz, 0H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.9, 154.8, 148.7, 137.8, 128.9, 128.1, 127.8, 127.7, 127.0, 123.8, 122.8, 111.8, 110.7, 77.3, 77.1, 76.9, 43.5.

***N*-hexylbenzamide (3ab)**[9]



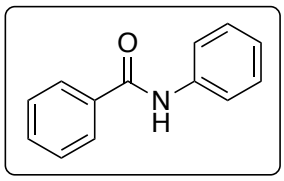
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.77 (m, 2H), 7.46-7.49 (m, 1H), 7.39-7.42 (m, 2H), 6.37 (s, 1H), 3.41-3.47 (m, 2H), 1.57-1.62 (m, 2H), 1.24-1.39 (m, 7H), 0.86-0.92 (m, 3H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 167.7, 134.9, 131.3, 128.6, 126.9, 40.2, 31.6, 29.7, 26.8, 22.7, 14.2, 14.1.

***N*-cyclohexylbenzamide (3ac)**[1]



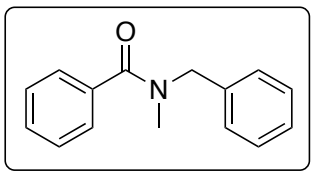
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 6.9 Hz, 2H), 7.40-7.49 (m, 3H), 7.27 (s, 0H), 6.04 (s, 1H), 3.98 (tt, *J* = 10.8, 3.9 Hz, 1H), 2.01-2.04 (m, 2H), 1.73-1.79 (m, 2H), 1.65 (td, *J* = 8.4, 4.4 Hz, 1H), 1.38-1.46 (m, 2H), 1.17-1.27 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.7, 135.2, 131.3, 128.6, 126.9, 48.8, 33.3, 25.7, 25.0.

***N*-phenylbenzamide (3ad)**[1]



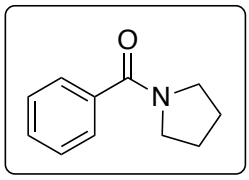
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.25 (s, 1H), 7.95-7.97 (m, 2H), 7.78-7.80 (m, 2H), 7.52-7.60 (m, 3H), 7.34-7.37 (m, 2H), 7.09-7.12 (m, 1H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.6, 139.2, 135.0, 131.5, 128.6, 128.4, 127.6, 123.7, 120.4.

***N*-benzyl-*N*-methylbenzamide (3ae)**[3]



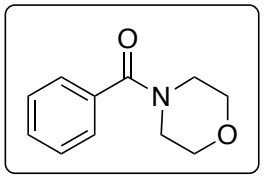
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.17-7.45 (m, 10H), 4.57 (d, *J* = 128.5 Hz, 2H), 2.85 (d, *J* = 44.7 Hz, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 170.6, 170.2, 137.5, 136.9, 136.3, 129.4, 128.6, 128.4, 127.6, 127.3, 127.2, 126.8, 126.7, 126.5, 54.1, 49.8, 36.8, 32.6.

phenyl(pyrrolidin-1-yl)methanone (3af)[10]



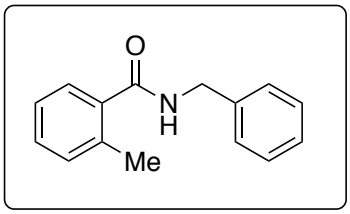
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.41-7.51 (m, 5H), 3.46 (t, *J* = 6.9 Hz, 2H), 3.36 (t, *J* = 6.9 Hz, 2H), 1.77-1.88 (m, 4H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 168.2, 137.3, 129.6, 128.2, 126.9, 48.9, 45.8, 25.9, 23.9.

Morpholino(phenyl)methanone (3ag)[1]



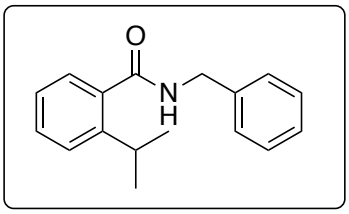
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.38-7.48 (m, 5H), 3.62 (s, 6H), 3.32 (s, 2H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 169.0, 135.6, 129.6, 128.4, 126.9, 66.1, 47.6, 41.9.

***N*-benzyl-2-methylbenzamide (3ta)**[11]



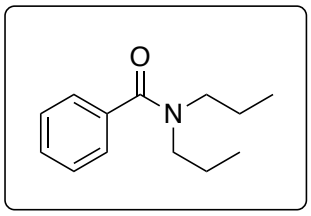
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24-7.49 (m, 7H), 7.13-7.18 (m, 2H), 6.26 (s, 1H), 4.55-4.61 (m, 2H), 2.34-2.47 (m, 3H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 170.0, 138.3, 136.3, 136.2, 131.1, 129.9, 128.8, 127.8, 127.6, 126.7, 125.7, 43.9, 19.9; **HRMS** (ESI) *m/z* calculated for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1226; found: 226.1423.

***N*-benzyl-2-isopropylbenzamide (3ua)**



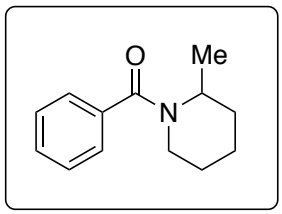
^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.23-7.44 (m, 8H), 7.11-7.13 (m, 1H), 6.25 (s, 1H), 4.42-4.65 (m, 2H), 3.31-3.47 (m, 1H), 1.09-1.24 (m, 6H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 170.4, 146.8, 138.3, 136.1, 130.1, 128.8, 127.9, 127.6, 126.6, 126.1, 125.7, 43.9, 29.9, 24.2; **HRMS** (ESI) *m/z* calculated for $C_{17}H_{20}NO$ $[M+H]^+$: 254.1545; found: 254.1569.

***N,N*-dipropylbenzamide (3ah)**[12]



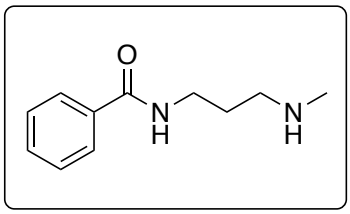
^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.34-7.42 (m, 5H), 3.35-3.55 (m, 2H), 2.97-3.25 (m, 2H), 1.60-1.69 (m, 2H), 1.48 (d, J = 55.0 Hz, 2H), 0.84-1.13 (m, 3H), 0.55-0.84 (m, 3H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 171.8, 137.6, 129.0, 128.4, 126.5, 50.7, 46.3, 21.9, 20.7, 11.5, 11.0; **HRMS** (ESI) *m/z* calculated for $C_{13}H_{20}NO$ $[M+H]^+$: 206.1545; found: 206.1570.

(2-methylpiperidin-1-yl)(phenyl)methanone (3ai)[13]



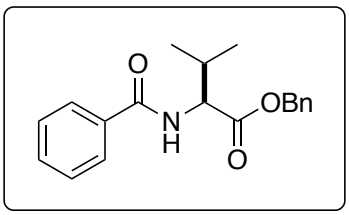
^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.35-7.47 (m, 5H), 3.04 (d, J = 80.4 Hz, 1H), 1.35-1.90 (m, 7H), 1.23-1.35 (m, 4H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 170.5, 137.2, 129.2, 128.5, 126.4, 30.3, 26.1, 18.9, 16.2; **HRMS** (ESI) *m/z* calculated for $C_{13}H_{18}NO$ $[M+H]^+$: 204.1388; found: 204.1413.

***N*-(3-(methylamino)propyl)benzamide (3aj)**[14]



^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.85-7.89 (m, 2H), 7.34-7.43 (m, 8H), 3.65 (t, J = 5.8 Hz, 2H), 3.45-3.51 (m, 2H), 2.87 (d, J = 54.3 Hz, 3H), 1.84 (s, 2H), 1.18 (s, 1H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 167.2, 134.9, 131.1, 128.4, 128.1, 126.9, 77.3, 77.1, 76.9, 51.2, 40.2, 36.4, 27.9; **HRMS** (ESI) *m/z* calculated for $C_{11}H_{17}N_2O$ $[M+Na]^+$: 193.1341; found: 193.1372.

Benzyl benzoyl-L-valinate (3ak)[15]



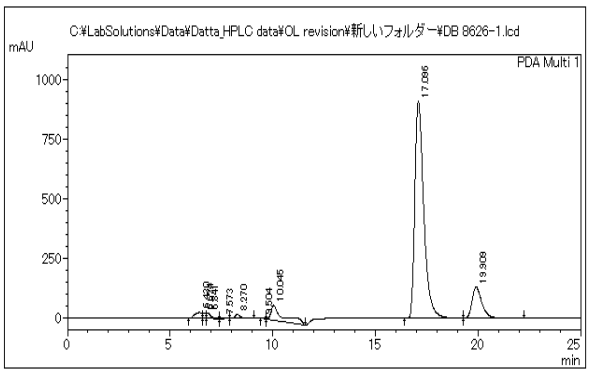
^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.65-7.85 (m, 2H), 7.22-7.42 (m, 8H), 6.62 (d, J = 7.6 Hz, 1H), 5.02-5.27 (m, 2H), 4.70-4.76 (m, 1H), 2.18-2.31 (m, 1H), 0.74-1.01 (m, 6H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 172.0, 167.3, 135.2, 134.2, 131.7, 128.6, 128.5, 128.4, 127.0, 126.9, 67.1, 57.4, 31.7, 19.0, 17.8. $[\alpha]_D^{22}$ = +14.97 (c = 0.67, $CHCl_3$). **HPLC analysis** CHIRALPAK AD-H(ϕ 0.46 cm x 25 cm), *n*-hexane/2-propanol = 8/2, flow rate 0.50 mL/min, detection at 254 nm, *t*R = 17.09 min. (major) and 19.90 min. (minor). Authentic samples were independently prepared from L- and D-amino acids and their mixture was used as reference racemate.

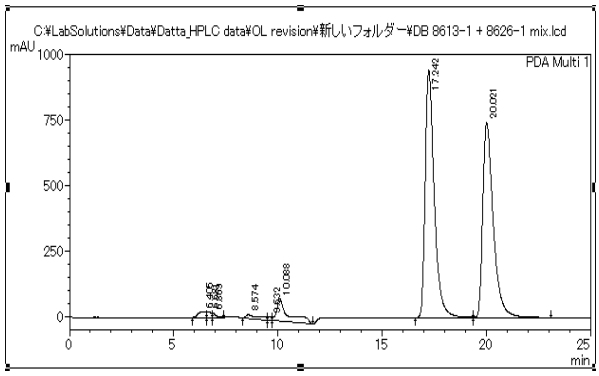
Peak information

Peak name	*t*R (min.)	Area %
(*S*)-**3ak**	17.09	86.20%
(*R*)-**3ak**	19.90	13.80%

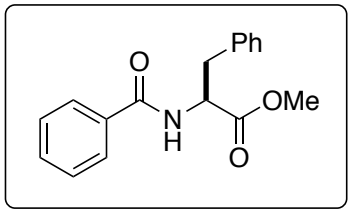
Peak information (mixture ref.)

Peak name	*t*R (min.)	Area %
(*S*)-**3ak**	17.24	52.33%
(*R*)-**3ak**	20.02	47.67%





Methyl benzoyl-L-phenylalaninate (3al)[16]



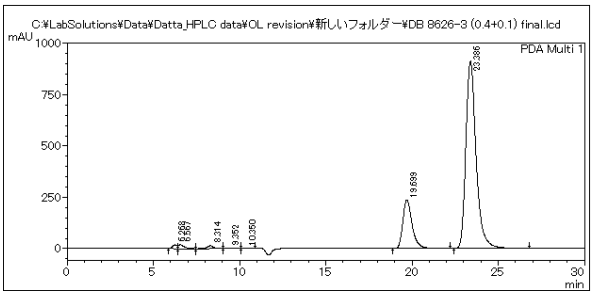
^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.67-7.74 (m, 2H), 7.43-7.51 (m, 1H), 7.30-7.39 (m, 2H), 7.19-7.25 (m, 3H), 7.04-7.16 (m, 2H), 6.53-6.70 (m, 1H), 4.97-5.16 (m, 1H), 3.66-3.75 (m, 3H), 3.16-3.26 (m, 2H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 172.1, 166.9, 135.9, 133.9, 131.8, 129.4, 129.2, 128.7, 128.4, 127.2, 127.1, 53.6, 52.4, 37.9. $[\alpha]_D^{23}$ = +35.1 (*c* = 0.60, $CHCl_3$), (lit. value[16]: +74.4 (*c* 0.58, CH_2Cl_2). **HPLC analysis** CHIRALPAK AD-H(ϕ 0.46 cm x 25 cm), *n*-hexane/2-propanol = 8/2, flow rate 0.50 mL/min, detection at 254 nm, *t*R = 19.69 min. (minor) and 23.38 min. (major). Authentic samples were independently prepared from L- and D-amino acids and their 1:1 mixture was used as reference racemate.

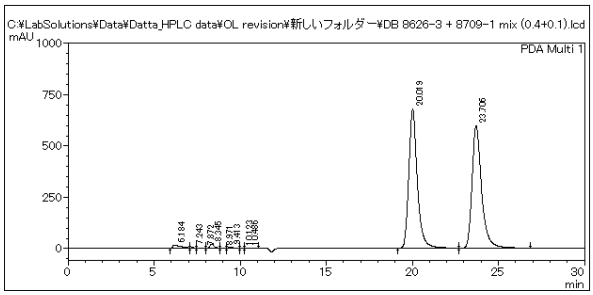
Peak information

Peak name	*t*R (min.)	Area %
(*R*)-**3al**	19.69	19.06%
(*S*)-**3al**	23.38	80.94%

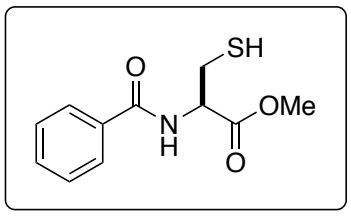
Peak information (mixture ref.)

Peak name	*t*R (min.)	Area %
(*R*)-**3al**	20.01	49.06%
(*S*)-**3al**	23.70	50.84%



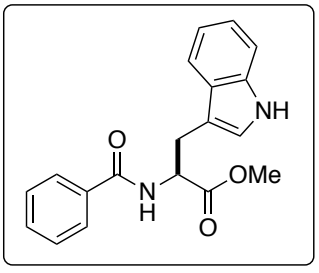


Methyl benzoyl-L-cysteinate (3am)[17]



^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.76 (q, *J* = 7.1 Hz, 2H), 7.33-7.49 (m, 3H), 7.06 (d, *J* = 36.4 Hz, 1H), 4.99-5.01 (m, 1H), 3.41-3.83 (m, 3H), 3.18-3.49 (m, 2H), 1.34-1.97 (m, 1H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 170.9, 167.1, 133.5, 132.0, 128.7, 127.3, 52.9, 52.4, 40.9; **HRMS** (ESI) *m/z* calculated for $C_{11}H_{17}N_2O_3S$ $[M+NH_4]^+$: 257.0954; found: 257.1008. $[\alpha]_D^{22}$ = +38.65 (*c* = 0.40, $CHCl_3$).

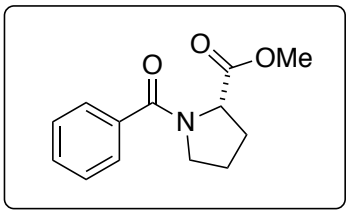
Methyl benzoyl-L-tryptophanate (3an)



^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.66-7.67 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.40-7.46 (m, 1H), 7.31-7.38 (m, 3H), 7.15-7.20 (m, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 2.1 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 5.03-5.15 (m, 1H), 3.62-3.81 (m, 3H), 3.33-3.47 (m, 2H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 172.5,

167.1, 136.3, 133.9, 131.8, 128.6, 127.7, 127.1, 122.9, 122.3, 119.7, 118.6, 111.4, 109.9, 53.6, 52.5, 27.7; **HRMS** (ESI) *m/z* calculated for $C_{19}H_{18}N_2O_3Na$ $[M+Na]^+$: 345.1210; found: 345.2142. $[\alpha]_D^{23}$ = +57.13 (*c* = 0.32, $CHCl_3$).

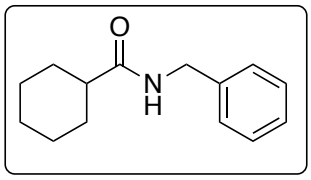
Methyl benzoyl-$_L$-prolinate (3ao)[18]



^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.25-7.51 (m, 5H), 4.67 (d, *J* = 71.5 Hz, 1H), 3.71-3.83 (m, 3H), 3.54 (d, *J* = 59.1 Hz, 2H), 2.22 (d, *J* = 48.8 Hz, 1H), 1.90 (d, *J* = 82.5 Hz, 3H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 172.8, 169.7, 136.2, 130.2, 128.3, 127.3, 59.2, 52.3, 49.9, 29.4, 25.4; **HRMS** (ESI) *m/z* calculated for $C_{13}H_{15}NO_3$ $[M+H]^+$: 234.1125; found: 234.1151. $[\alpha]_D^{22}$ = –37.70 (*c* = 0.80, $CHCl_3$).

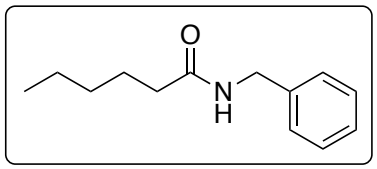
Characterization data of additional substrate products (Table S3)

***N*-benzylcyclohexanecarboxamide (3va)**[1]



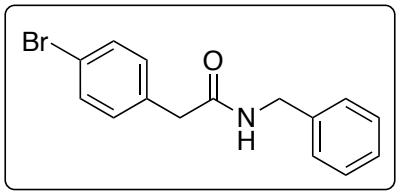
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26-7.34 (m, 5H), 5.72 (s, 1H), 4.44 (d, *J* = 5.5 Hz, 2H), 2.11 (m, 1H), 1.88-1.90 (m, 2H), 1.78-1.81 (m, 2H), 1.64-1.68 (m, 2H), 1.47 (qd, *J* = 12.3, 3.1 Hz, 2H), 1.20-1.30 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.0, 138.7, 128.8, 127.9, 127.6, 45.7, 43.5, 29.9, 25.9.

***N*-benzylhexanamide (3wa)**[19]



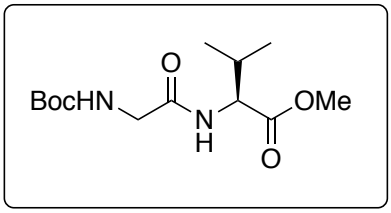
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.33 (m, 2H), 7.23-7.27 (m, 3H), 5.98 (s, 1H), 4.41 (d, *J* = 5.5 Hz, 2H), 2.19 (t, *J* = 7.6 Hz, 2H), 1.62-1.68 (m, 2H), 1.26-1.35 (m, 4H), 0.87-0.91 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.2, 138.6, 128.7, 127.9, 127.5, 43.6, 36.8, 31.6, 25.5, 22.5, 14.0.

***N*-benzyl-2-(4-bromophenyl)acetamide (3xa)**[20]



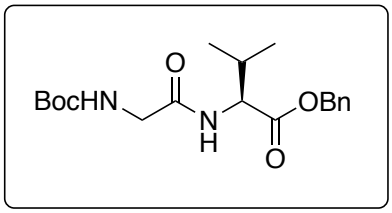
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.24 (dt, *J* = 28.0, 7.2 Hz, 3H), 7.12 (dd, *J* = 26.8, 7.6 Hz, 4H), 5.72 (s, 1H), 4.36 (d, *J* = 6.2 Hz, 2H), 3.50 (s, 2H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 170.3, 138.1, 133.9, 132.2, 131.2, 128.8, 127.7, 127.7, 121.5, 43.8, 43.2.

Methyl (tert-butoxycarbonyl)glycyl-L-valinate (4aa)[21]



Pale yellow oil; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 6.71 (s, 1H), 5.23-5.28 (m, 1H), 4.48 (s, 1H), 3.76 (dd, J = 38.5, 15.1 Hz, 2H), 3.62-3.67 (m, 3H), 2.09-2.20 (m, 1H), 1.38-1.46 (m, 9H), 0.82-0.88 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.3, 169.6, 156.3, 80.3, 57.0, 52.2, 44.5, 31.2, 28.3, 18.9, 17.7; **HRMS** (ESI) m/z calculated for $C_{13}H_{24}N_2NaO_5$ $[M+Na]^+$: 311.1583; found: 311.1581; **IR (cm^{-1})** 3333, 2968, 2934, 2250, 1674, 1518, 1440, 1366, 1249, 1167, 1054, 1024, 916, 864, 730. $[\alpha]_D^{21}$ = +14.2 (c = 0.89, $CHCl_3$); (literature value[14]: $[\alpha]_D^{20}$ = +33.7 (c = 0.92, $CHCl_3$)).

Benzyl (*tert*-butoxycarbonyl)glycyl-L-valinate (4ab)[22]



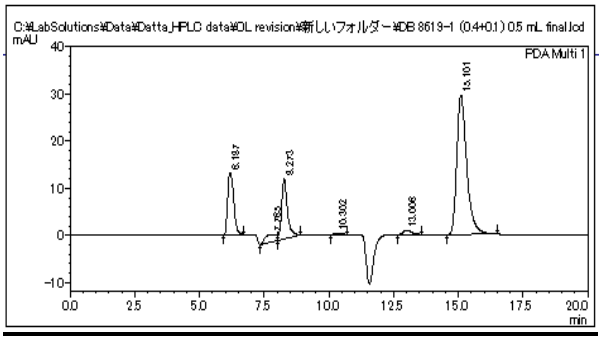
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26-7.31 (m, 5H), 6.55 (s, 1H), 5.06-5.11 (m, 2H), 4.55 (t, J = 4.1 Hz, 1H), 3.75 (ddd, J = 51.0, 16.3, 5.0 Hz, 2H), 2.10-2.15 (m, 1H), 1.39 (s, 9H), 0.85 (d, J = 6.9 Hz, 3H), 0.79 (d, J = 6.9 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7, 168.7, 155.2, 134.3, 127.6, 127.5, 127.4, 79.2, 66.1, 56.0, 43.4, 30.3, 27.3, 18.0, 16.5; **HRMS** (ESI) m/z calculated for $C_{19}H_{28}N_2NaO_5$ $[M+Na]^+$: 387.1896; found: 387.1882; **IR (cm^{-1})** 3324, 2968, 2934, 1722, 1674, 1522, 1453, 1371, 1249, 1167, 1050, 942, 864, 756, 700. $[\alpha]_D^{21}$ = +12.1 (c = 0.72, $CHCl_3$); (literature value[14]: $[\alpha]_D^{20}$ = +11 (c = 0.72, $CHCl_3$)); **HPLC analysis** CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), *n*-hexane/2-propanol = 8/2, flow rate 0.50 mL/min, detection at 220 nm, *t*R = 13.00 min. (minor enantiomer) and 15.10 min. (major enantiomer). Authentic samples were independently prepared from L- and D-amino acids and their 1:1 mixture was used as reference racemate.

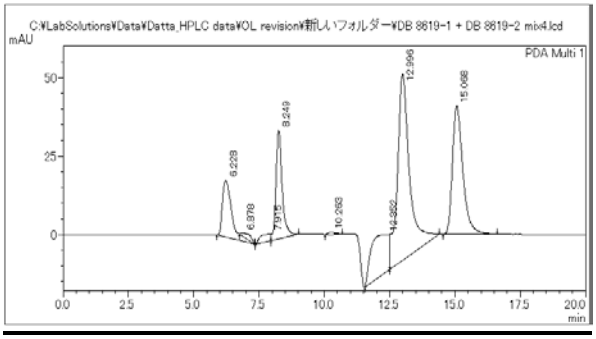
Peak information

Peak name	*t*R (min.)	Area %
(*R*)-**4ab**	13.00	4.80%
(*S*)-**4ab**	15.10	95.20%

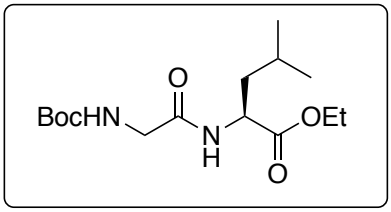
Peak information (mixture ref.)

Peak name	*t*R (min.)	Area %
(*R*)-**4ab**	13.00	53.40%
(*S*)-**4ab**	15.10	46.60%



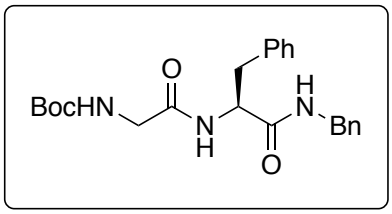


Ethyl (*tert*-butoxycarbonyl)glycyl-$_L$-leucinate (4ac)



Light-brown oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.72 (s, 1H), 5.36 (s, 1H), 4.51 (s, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.66-3.76 (m, 2H), 1.56 (td, J = 12.5, 7.6 Hz, 2H), 1.41-1.48 (m, 1H), 1.38 (d, J = 18.6 Hz, 9H), 1.13-1.20 (m, 3H), 0.84 (t, J = 3.1 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) 172.9, 169.4, 156.1, 80.1, 61.3, 50.7, 44.2, 41.5, 28.3, 24.8, 22.8, 21.9, 14.1; **HRMS** (ESI) m/z calculated for $C_{15}H_{28}N_2NaO_5$ $[M+Na]^+$: 339.1896; found: 339.1913; **IR (cm^{-1})** 3319, 3073, 2960, 2873, 2245, 1674, 1527, 1371, 1249, 1176, 1028, 916, 864, 730. $[\alpha]_D^{22}$ = +2.0 (c = 0.84, $CHCl_3$).

***tert*-Butyl (S)-(2-((1-(benzylamino)-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)-carbamate (4ad)**[23]



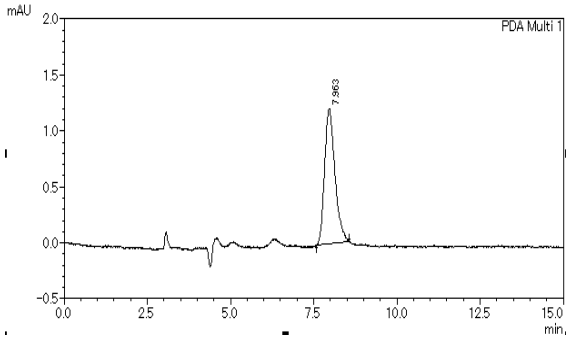
Colorless solid; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.41-8.46 (m, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.02-7.34 (m, 11H), 6.86-6.93 (m, 1H), 4.41-4.54 (m, 1H), 4.10-4.30 (m, 2H), 3.32-3.53 (m, 2H), 2.84-3.01 (m, 1H), 2.78 (dd, J = 13.4, 8.6 Hz, 1H), 1.21-1.31 (m, 9H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 171.3, 169.6, 156.3, 139.5, 138.2, 129.7, 128.7, 128.6, 127.6, 127.2, 126.8, 78.6, 54.5, 43.7, 42.5, 38.3, 28.7; **HRMS** (ESI) m/z calculated for $C_{23}H_{29}N_3NaO_4$ $[M+Na]^+$: 434.2056; found: 434.2026; **IR (cm^{-1})** 3267, 3064, 3029, 2973, 2934, 1696, 1652, 1522, 1449, 1366, 1284, 1167, 1046, 933, 734, 700. $[\alpha]_D^{22}$ = –15.1 (c = 0.40, $CHCl_3$); **HPLC analysis** CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), *n*-hexane/2-propanol = 7/3, flow rate 1.0 mL/min, detection at 220 nm, tR = 6.31 min. (minor enantiomer) and 8.11 min. (major enantiomer). Authentic samples were independently prepared from L- and D-amino acids and their 1:1 mixture was used as reference racemate.

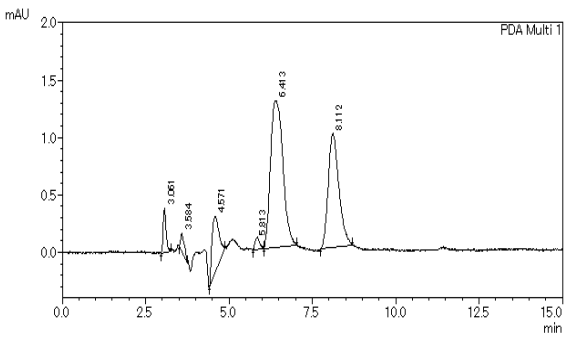
Peak information (4ad)

Peak name	tR (min.)	Area %
(*R*)-**4ad**	6.31	6.293
(*S*)-**4ad**	7.96	93.707

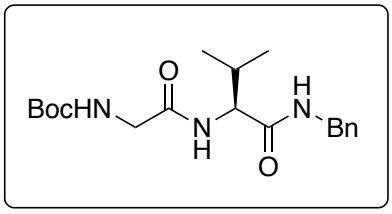
Peak information (mixture ref.)

Peak name	tR (min.)	Area %
(*R*)-**4ad**	6.41	60.341
(*S*)-**4ad**	8.11	39.659



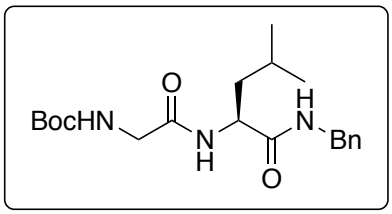


***tert*-Butyl (S)-(2-((1-(benzylamino)-3-methyl-1-oxobutan-2-yl)amino)-2-oxoethyl)-carbamate (4ae)**



Colorless solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17-7.31 (m, 5H), 6.86-7.10 (m, 2H), 5.30 (t, J = 5.8 Hz, 1H), 4.29-4.50 (m, 3H), 3.64-3.89 (m, 2H), 1.99-2.11 (m, 1H), 1.30-1.42 (m, 9H), 0.78-0.90 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.9, 169.8, 138.0, 128.7, 127.8, 127.4, 80.3, 58.6, 44.4, 43.5, 31.0, 28.3, 19.3, 18.0; **HRMS** (ESI) m/z calculated for $C_{19}H_{29}N_3NaO_4$ $[M+Na]^+$: 386.2056; found: 386.2037; **IR (cm^{-1})** 3276, 3081, 2968, 2921, 2782, 1951, 1678, 1543, 1388, 1240, 1162, 1080, 1057, 1024, 942, 868, 747, 695. $[\alpha]_D^{22}$ = -9.5 (c = 0.76, $CHCl_3$).

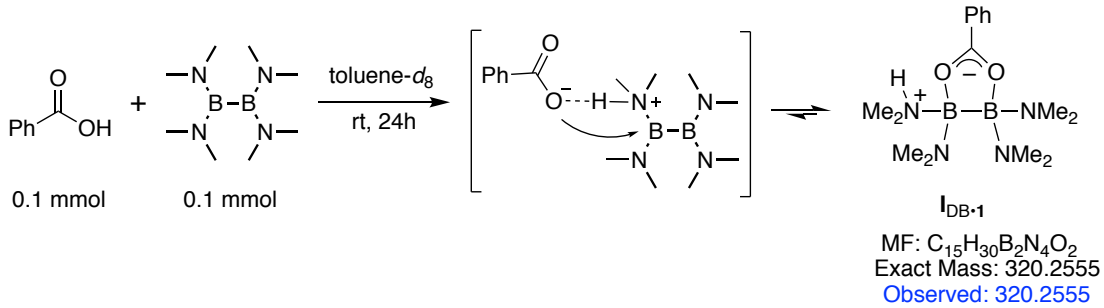
***tert*-Butyl (S)-(2-((1-(benzylamino)-4-methyl-1-oxopentan-2-yl)amino)-2-oxoethyl)-carbamate (4af)**



Colorless solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22-7.32 (m, 6H), 6.86 (s, 1H), 6.73 (s, 1H), 5.22 (s, 1H), 4.51 (dd, J = 14.1, 8.6 Hz, 1H), 4.36-4.43 (m, 2H), 3.70-3.82 (m, 2H), 1.70 (t, J = 6.5 Hz, 1H), 1.55-1.67 (m, 2H), 1.40 (d, J = 28.9 Hz, 9H), 0.85-1.01 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.2, 169.9, 156.2, 138.1, 128.6, 127.6, 127.4, 80.2, 51.8, 44.2, 43.4, 41.3, 28.3, 24.8, 22.9, 22.1; **HRMS** (ESI) m/z calculated for $C_{20}H_{31}N_3NaO_4$ $[M+Na]^+$: 400.2212; found: 400.2210; **IR (cm^{-1})** 3272, 3060, 2960, 1678, 1539, 1453, 1366, 1284, 1245, 1167, 1041, 946, 877, 734, 695. $[\alpha]_D^{22}$ = -28.9 (c = 0.75, $CHCl_3$).

5 Control experiments

5.1 Stoichiometric reaction of benzoic acid with tetrakis(dimethylamido)diboron (DB-**1**)



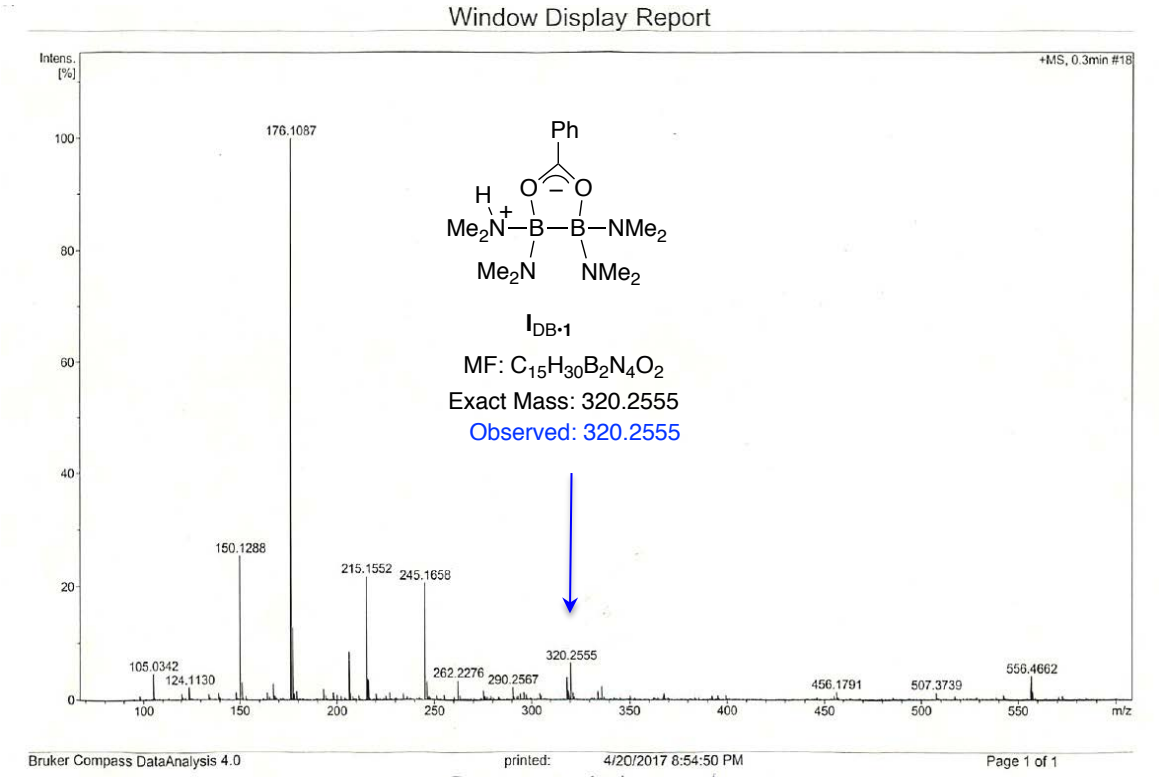
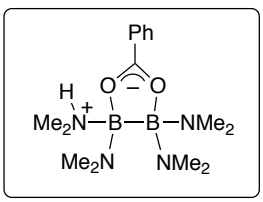


Figure S1. ESI-MS spectrum of the $PhCOO^{-}$•DB-**1** adduct (Tetrakis(dimethylamido)diboron).

^{1}H NMR analysis of stoichiometric reaction of benzoic acid with tetrakis(dimethylamido)diboron (DB-**1**)

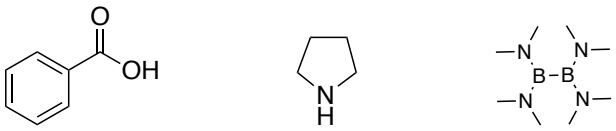


^{1}H-NMR (600 MHz, *Tol-d*$_8$) δ 7.25-7.17 (2H), 7.01-6.94 (3H), 2.88-2.52 (15H), 2.41-2.25 (1H), 2.20-2.09 (9H); **^{11}B NMR** (192 MHz, *Toluene-d*$_8$) 33.32, 20.63, 2.72 (*vide infra*).

5.2 Control experiments for elucidation of favorable diboron-carboxylic acid interaction

^{11}B NMR study of the solution of Benzoic acid, pyrrolidine and tetrakis(dimethylamido)diboron (DB-**1)**

In a dry 5 mL borosilicate vial, were added benzoic acid (12.21 mg, 0.1 mmol), toluene-d_8 (1.0 mL) and tetrakis(dimethylamido)diboron (19.82 mg, 0.1 mmol) and resulting solution was stirred at room temperature for 24 h. The suspension was transferred into a NMR tube and ^{11}B NMR was recorded at rt using $BF_3{\cdot}O(C_2H_5)_2$ as an external standard. (Fig. S2c).



1a **2f** DB-**1**

Fig. S2 shows the NMR spectra of tetrakis(dimethylamido)diboron (DB-**1**) and pyrrolidine (**2f**) or benzoic acid (**1a**) recorded in toluene-d_8. Figures S2a, S2b, S2c, S2d and S2e suggest the followings: 1) ^{11}B NMR spectrum of tetrakis(dimethylamido)diboron (DB-**1**); 2) Pyrrolidine have no affinity to tetrakis(dimethylamido)-diboron; resulting in no tetra-coordination with boron center after stirring DB-**1** with pyrrolidine at rt for 24h (Fig. S2b); 3) Tetrakis(dimethylamido)diboron (DB-**1**) interacts with Benzoic acid (**1a**) giving tetra coordinated species after stirring at rt for 24 h (Fig. S2c); 4) Fig. S2d and S2e represent ^{11}B NMR of reaction mixture of DB-**1**, **1a** and **2f** after stirring at room temperature for 24 h and after reflux (closed vial) for 2.5 h.

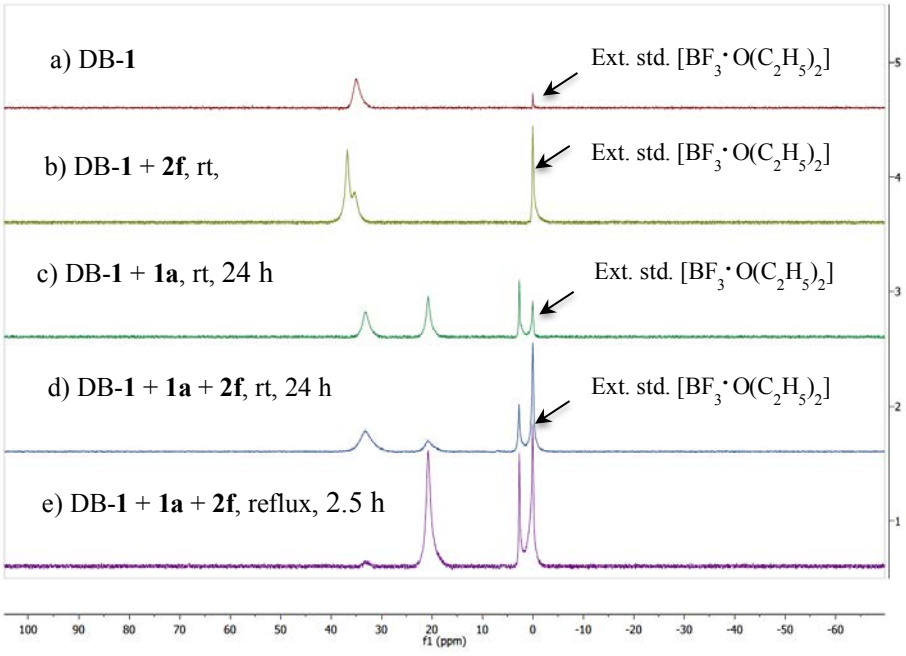


Figure S2. Stacked ^{11}B NMR spectra in toluene-d_8

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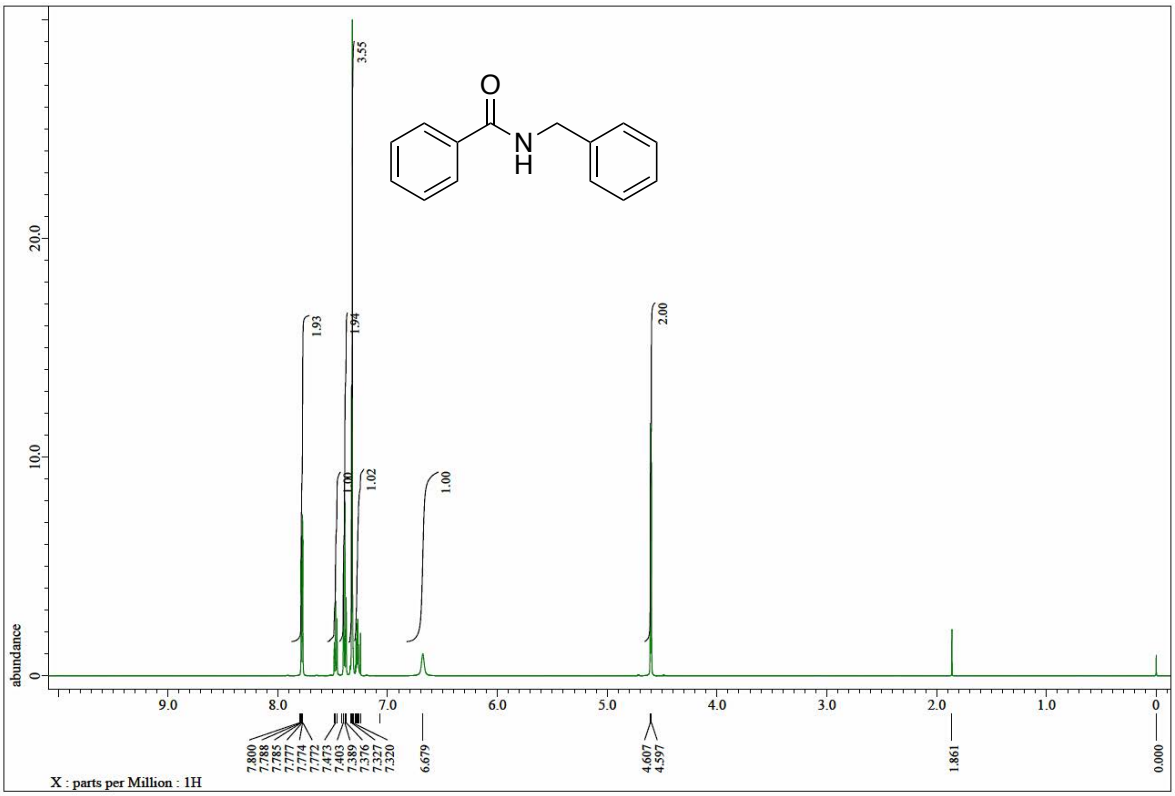
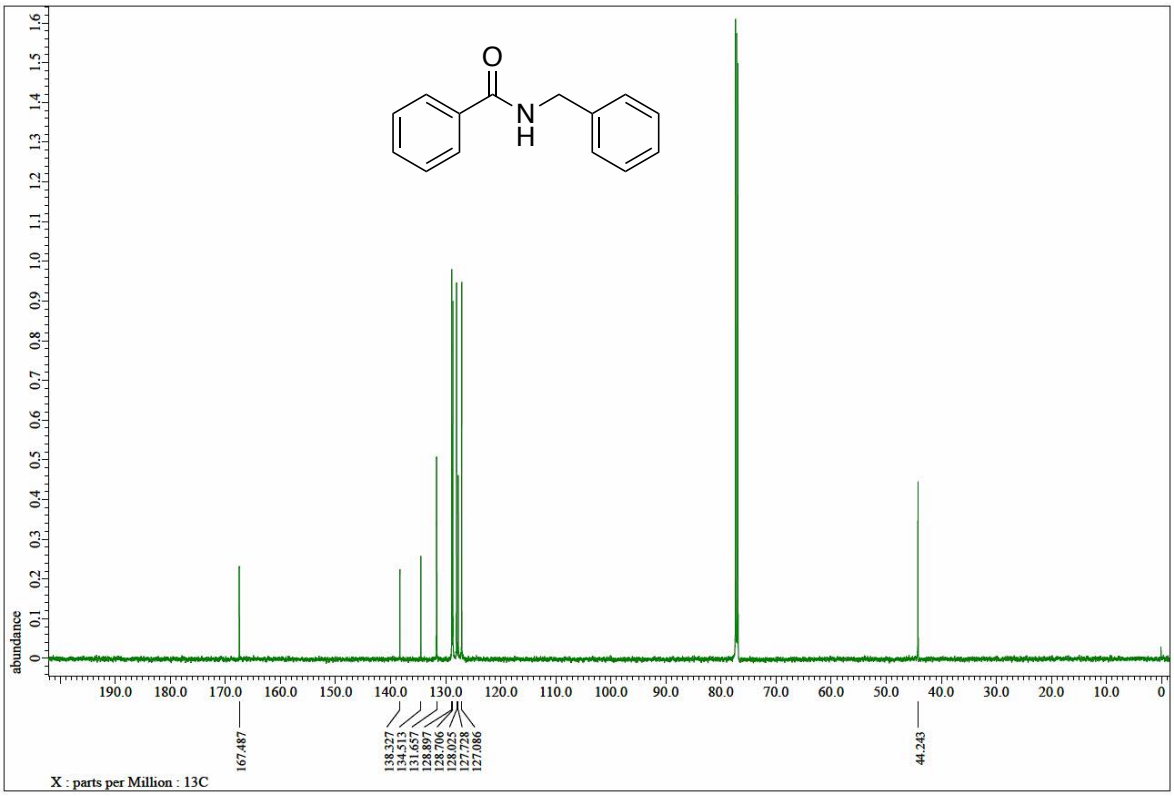
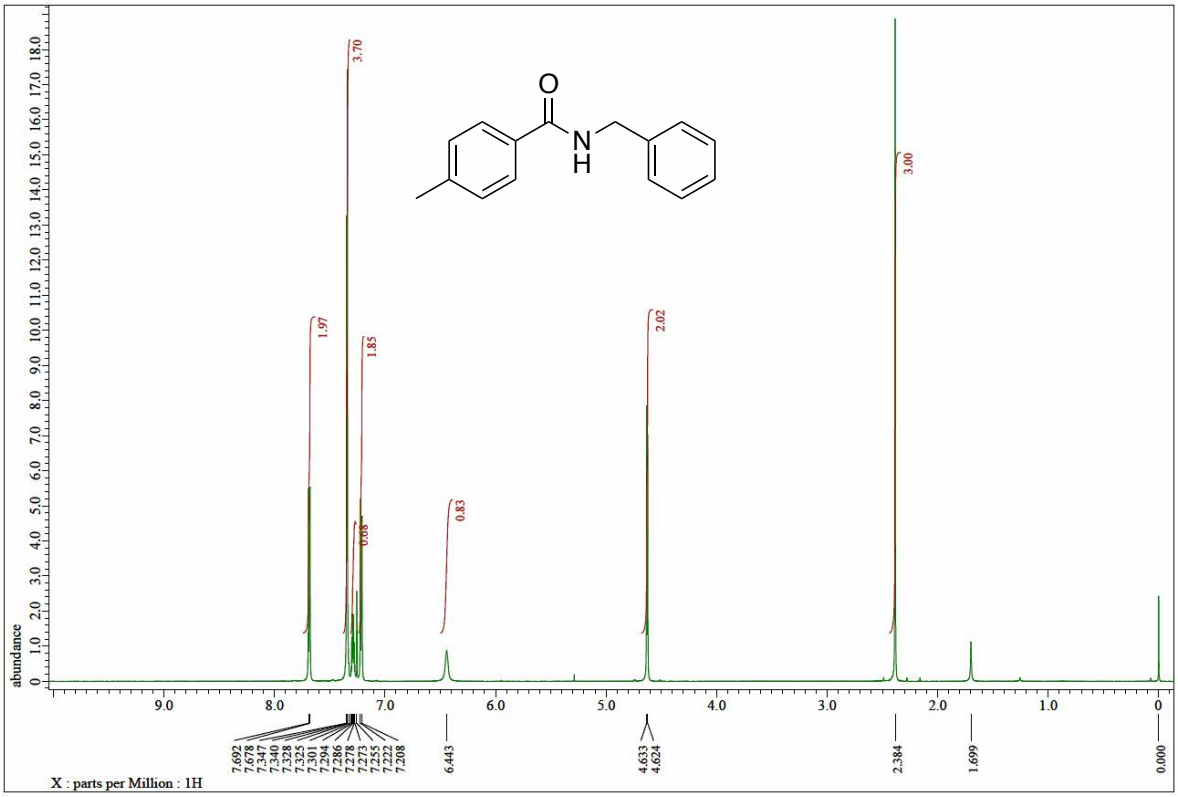
Spectral copies of ^{1}H, ^{13}C NMR of compounds obtained in this study

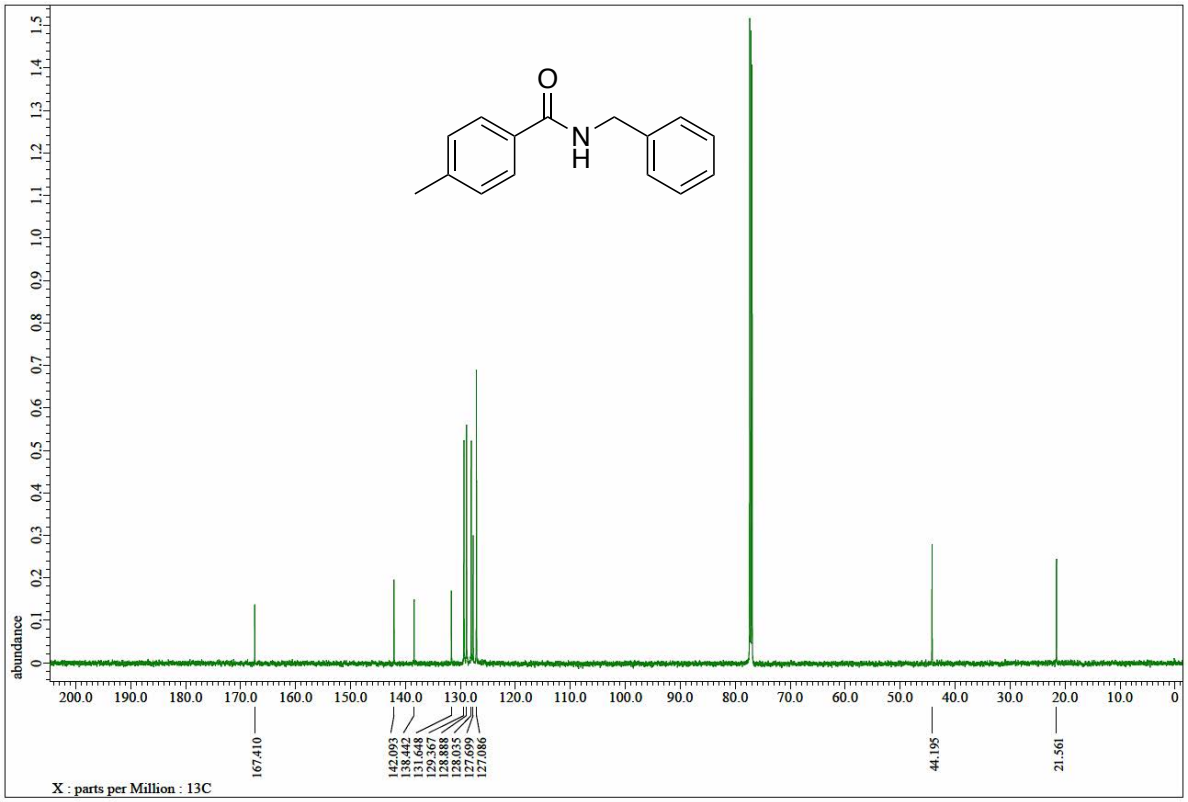
N-benzylbenzamide (3aa)



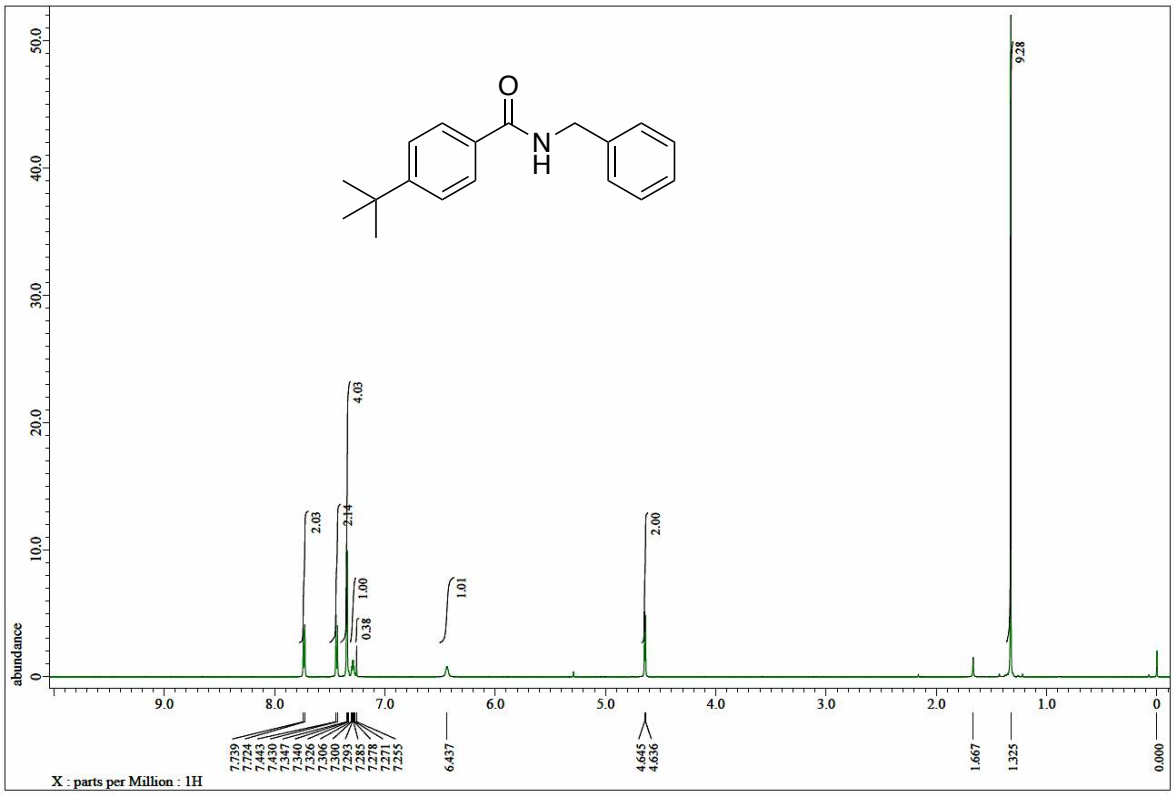


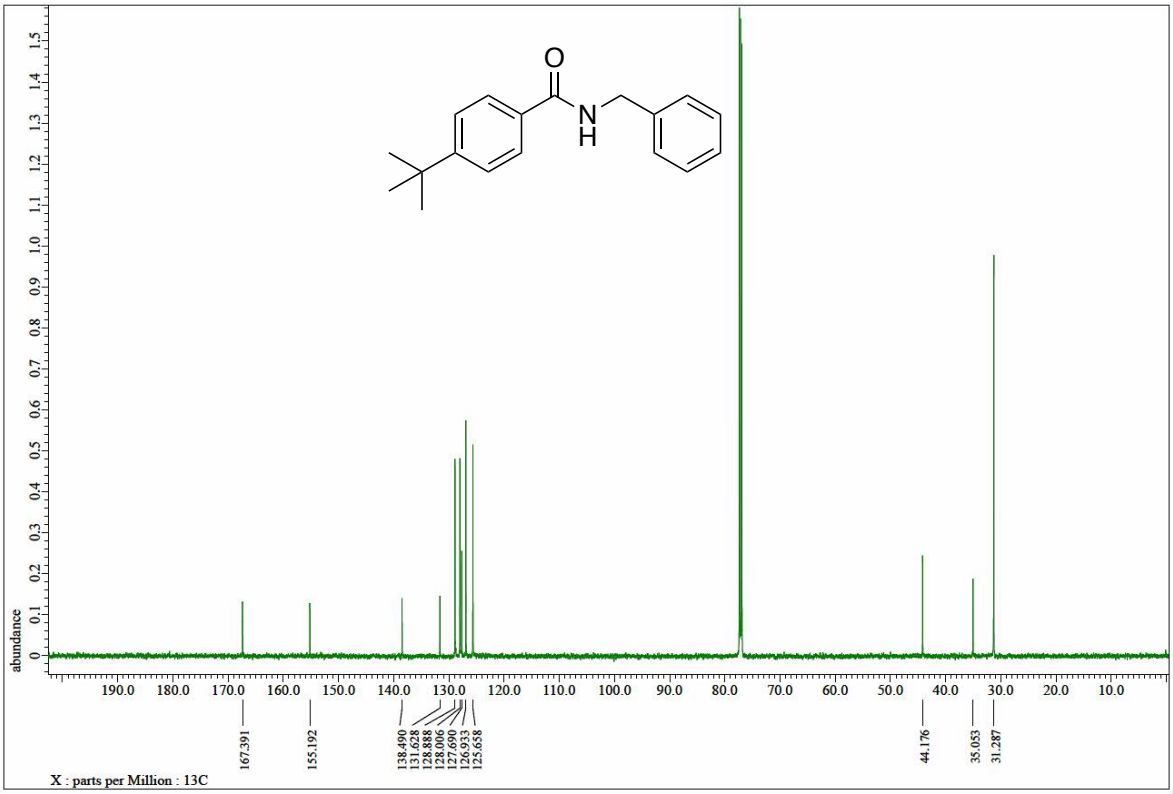
N-benzyl-4-methylbenzamide (3ba)



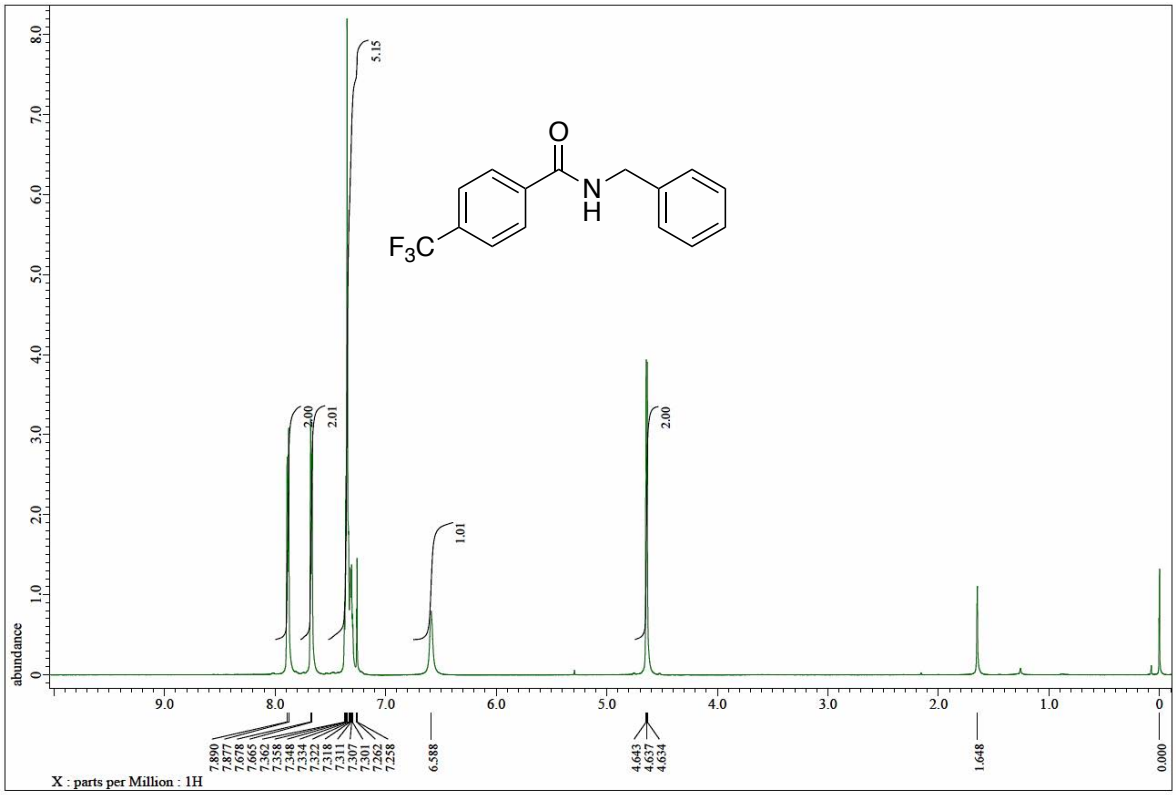


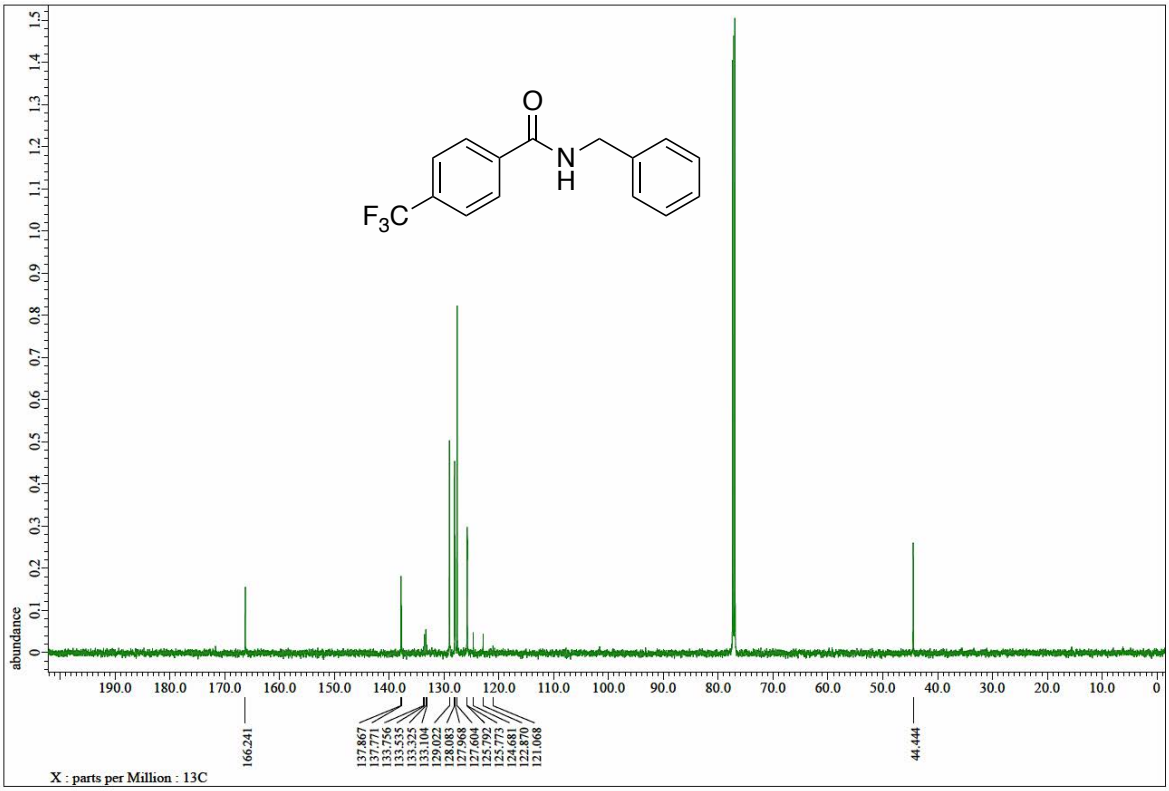
N-benzyl-4-(*tert*-butyl)benzamide (3ca)



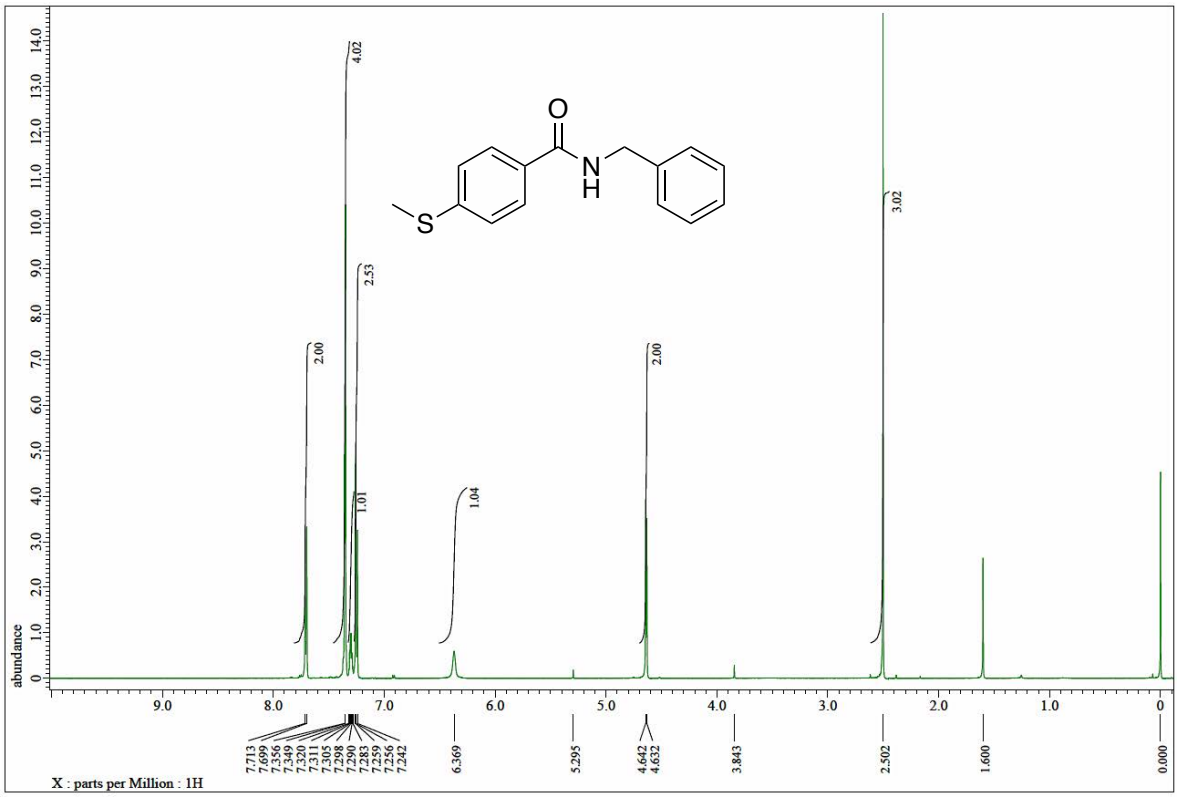


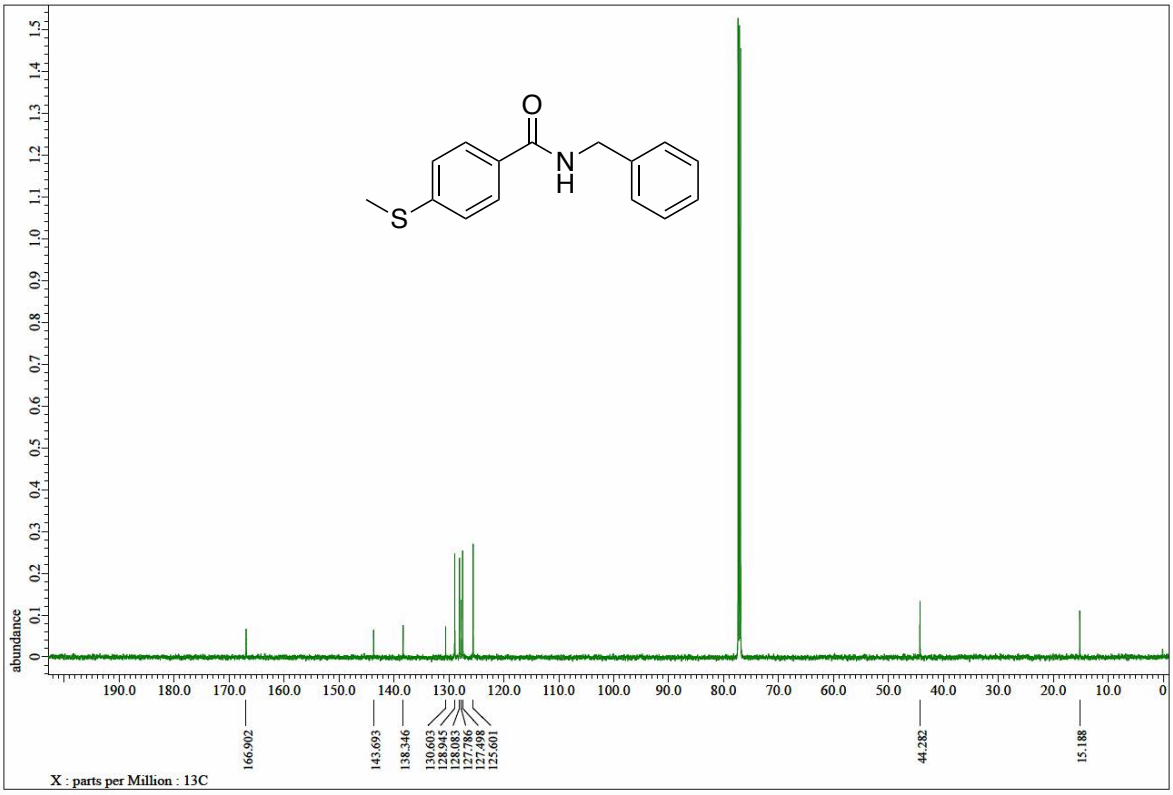
N-benzyl-4-(trifluoromethyl)benzamide (3da)



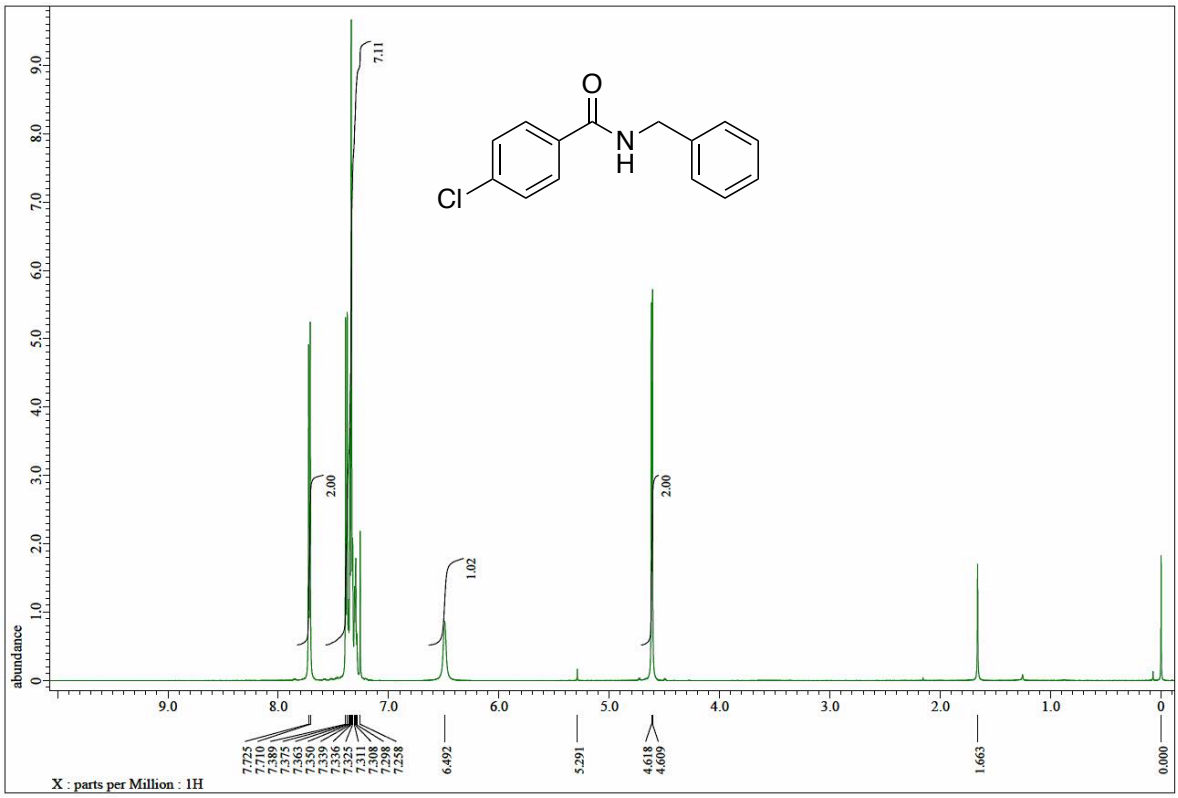


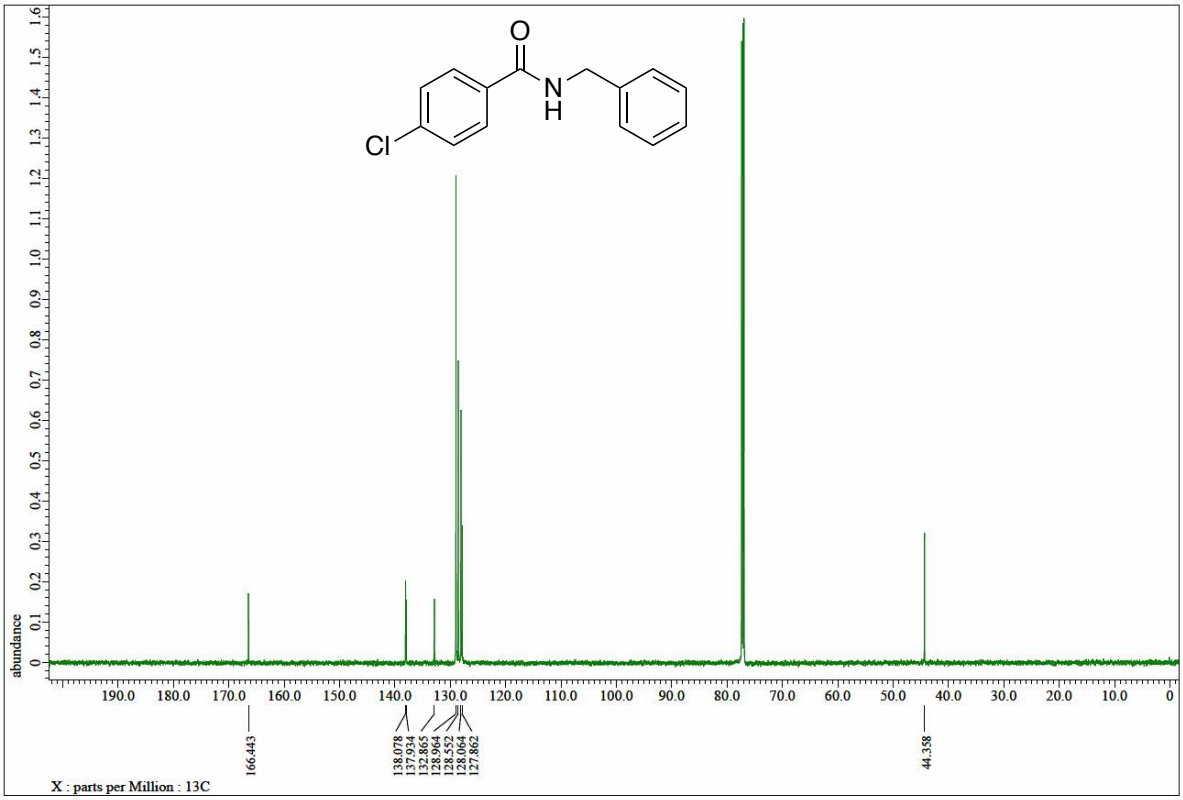
N-benzyl-4-(methylthio)benzamide (3ea)



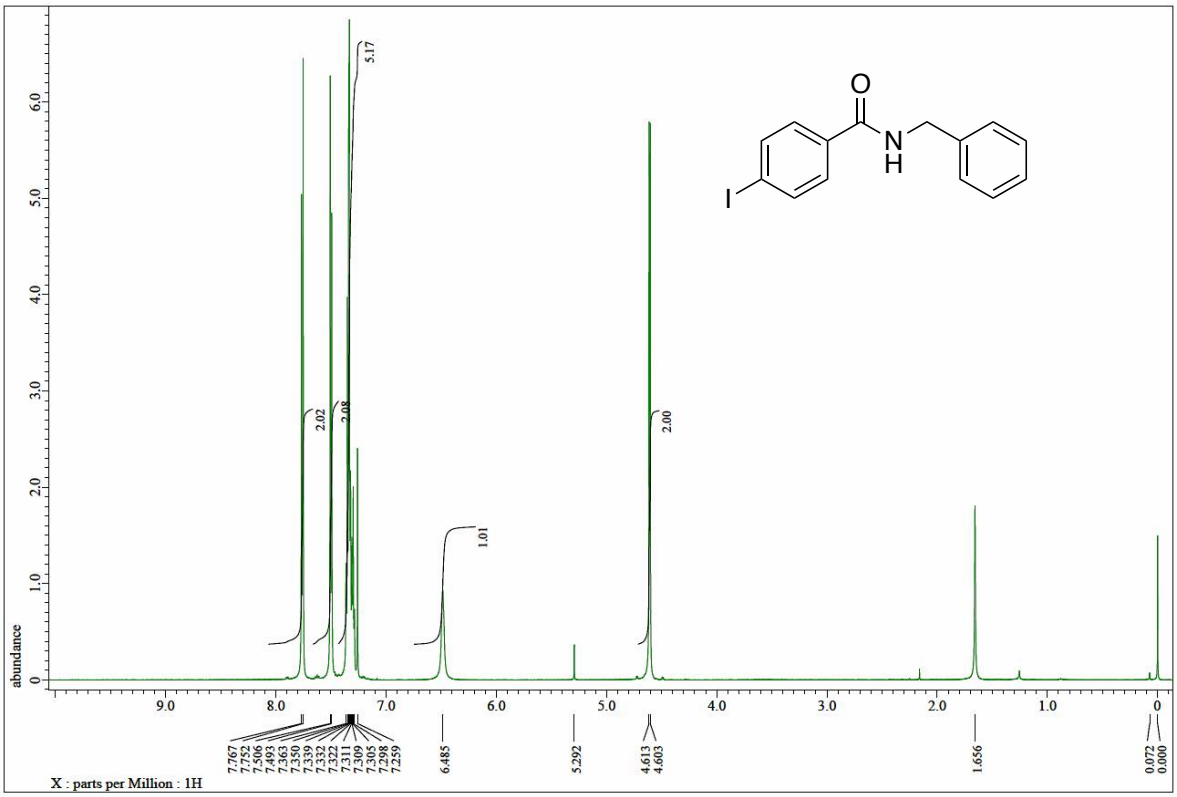


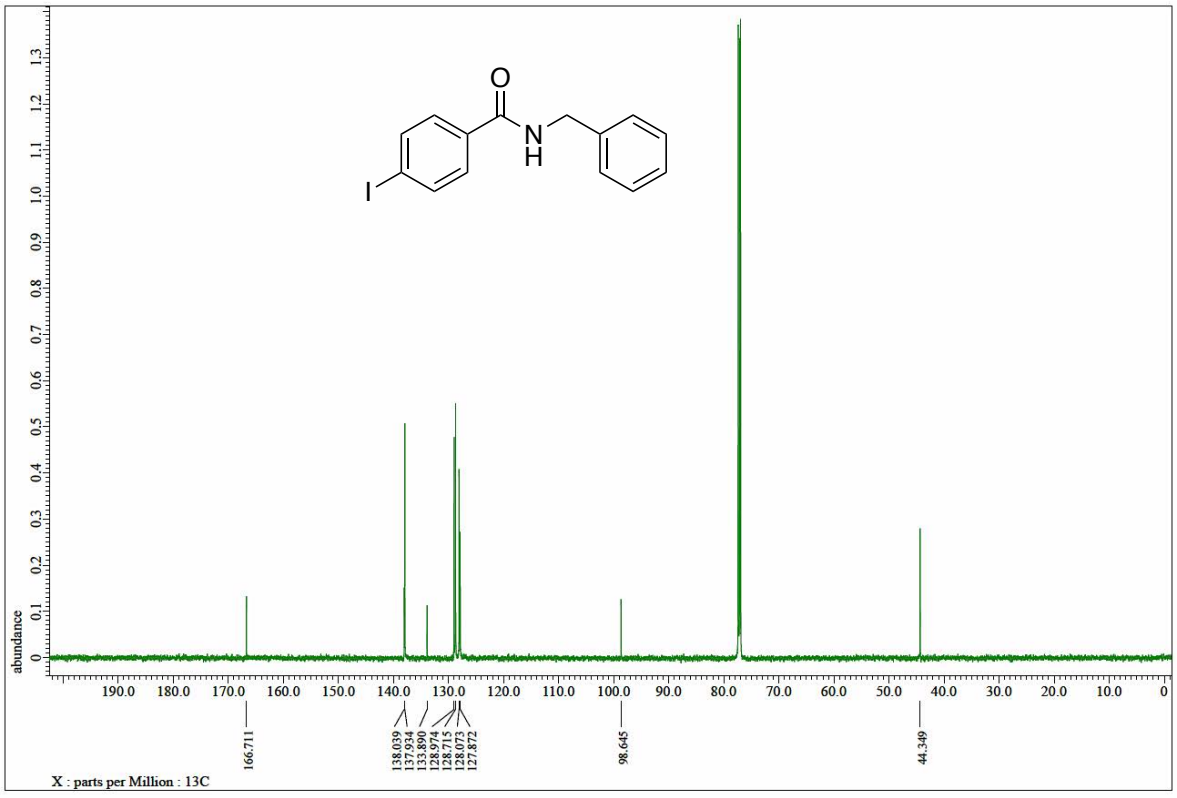
N-benzyl-4-chlorobenzamide (3fa)



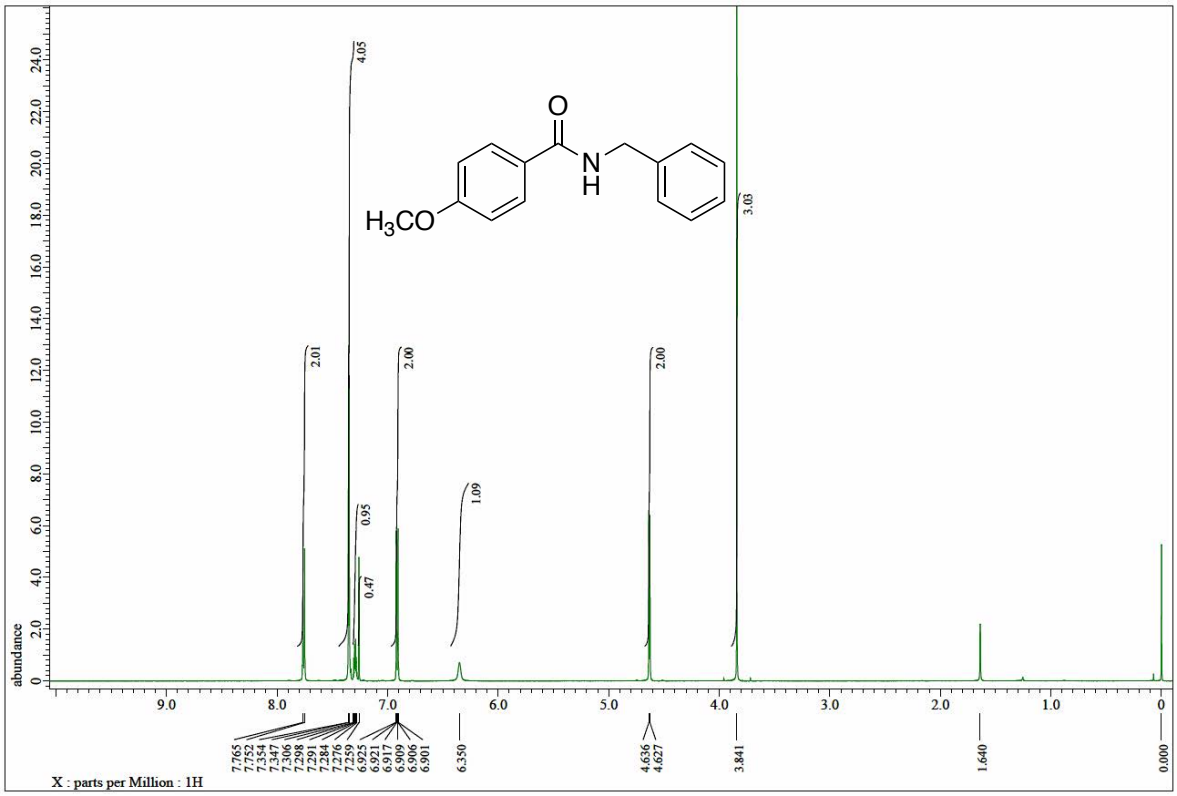


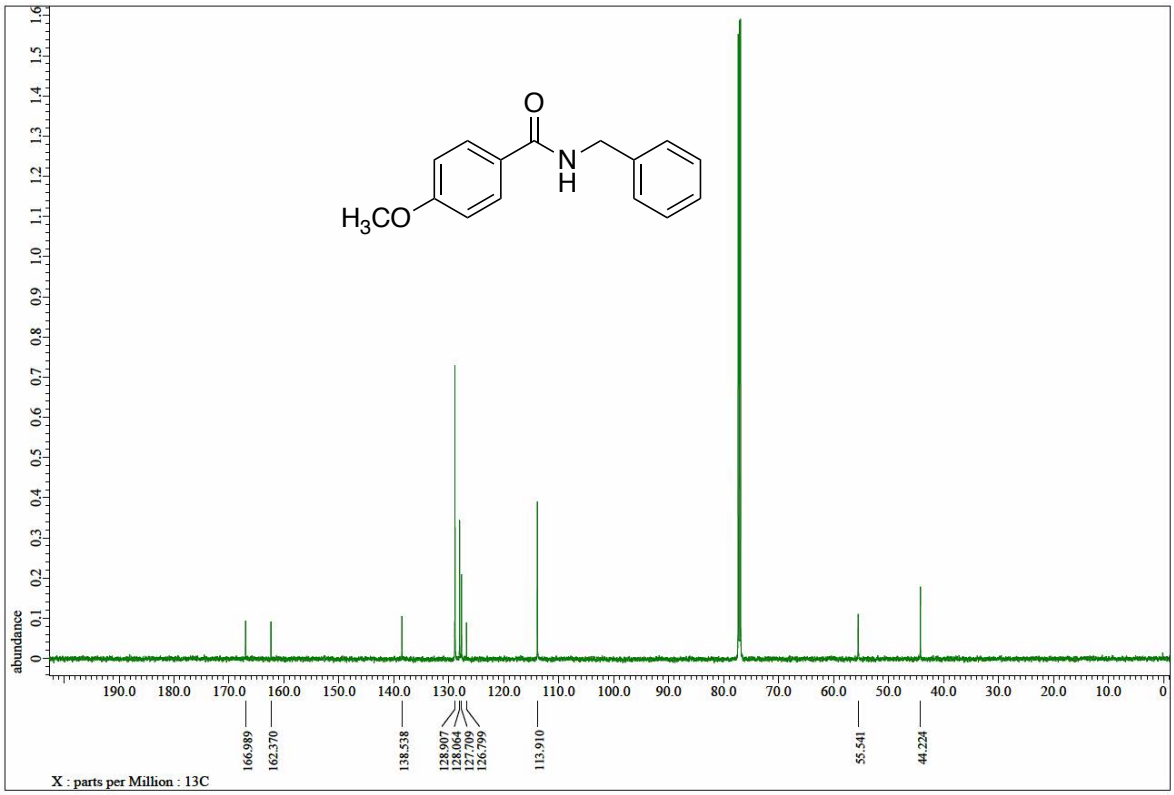
N-benzyl-4-iodobenzamide (3ga)



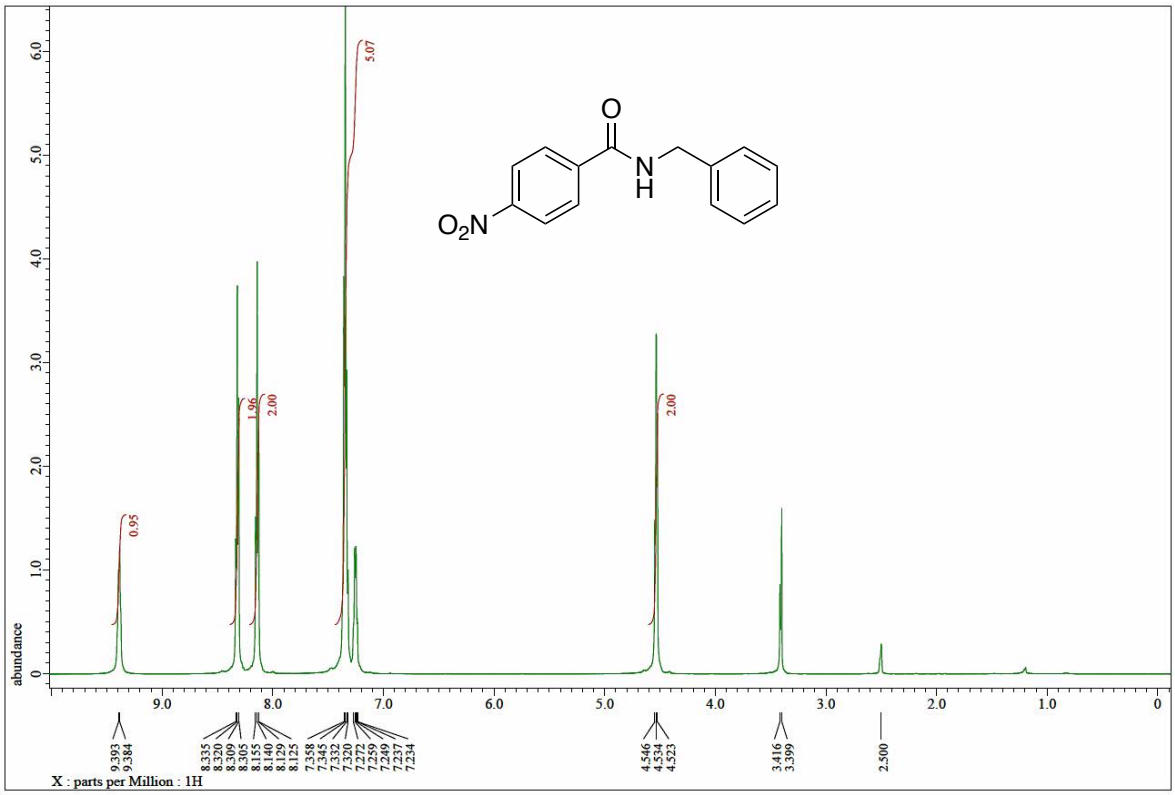


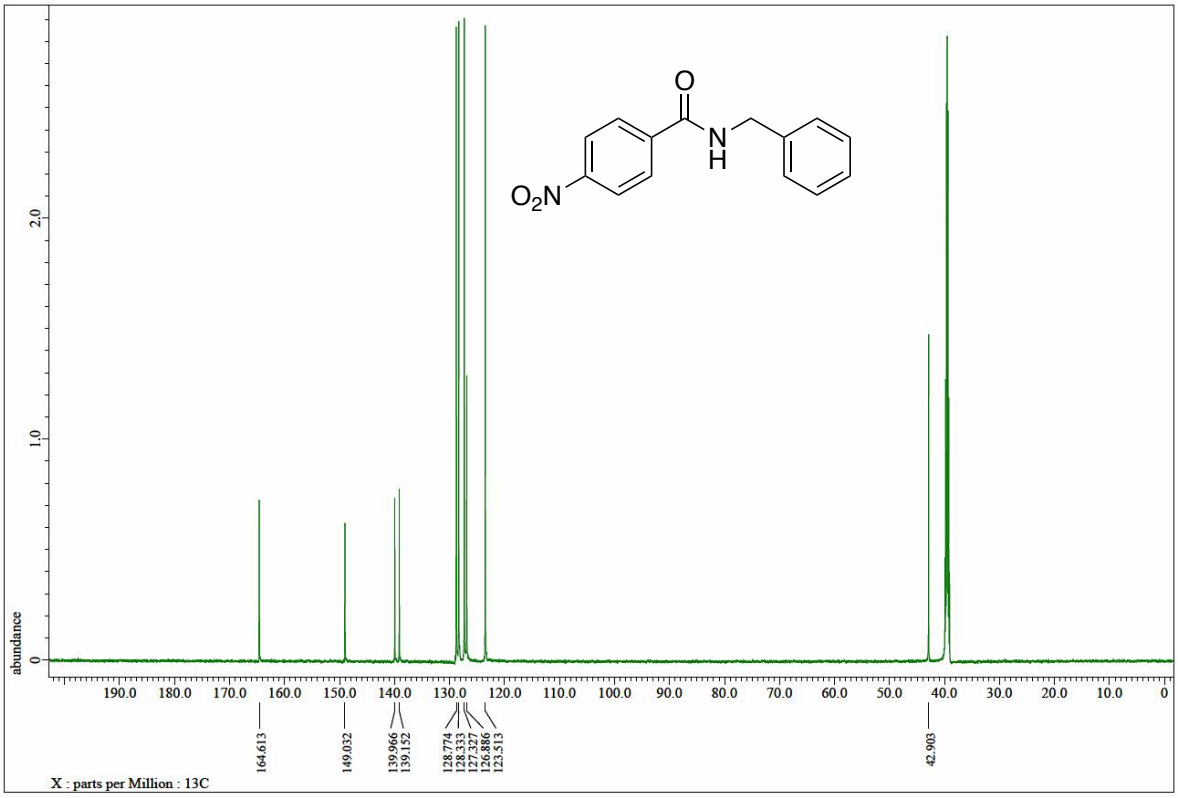
N-benzyl-4-methoxybenzamide (3ha)



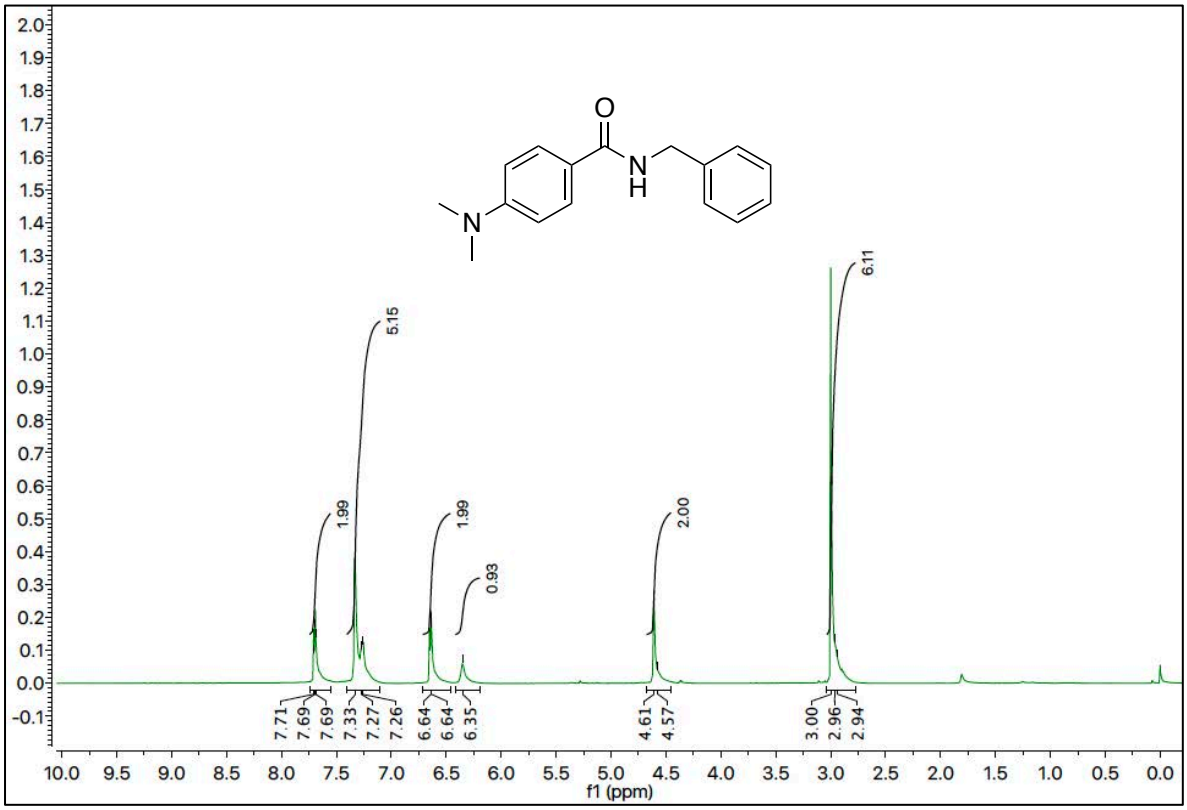


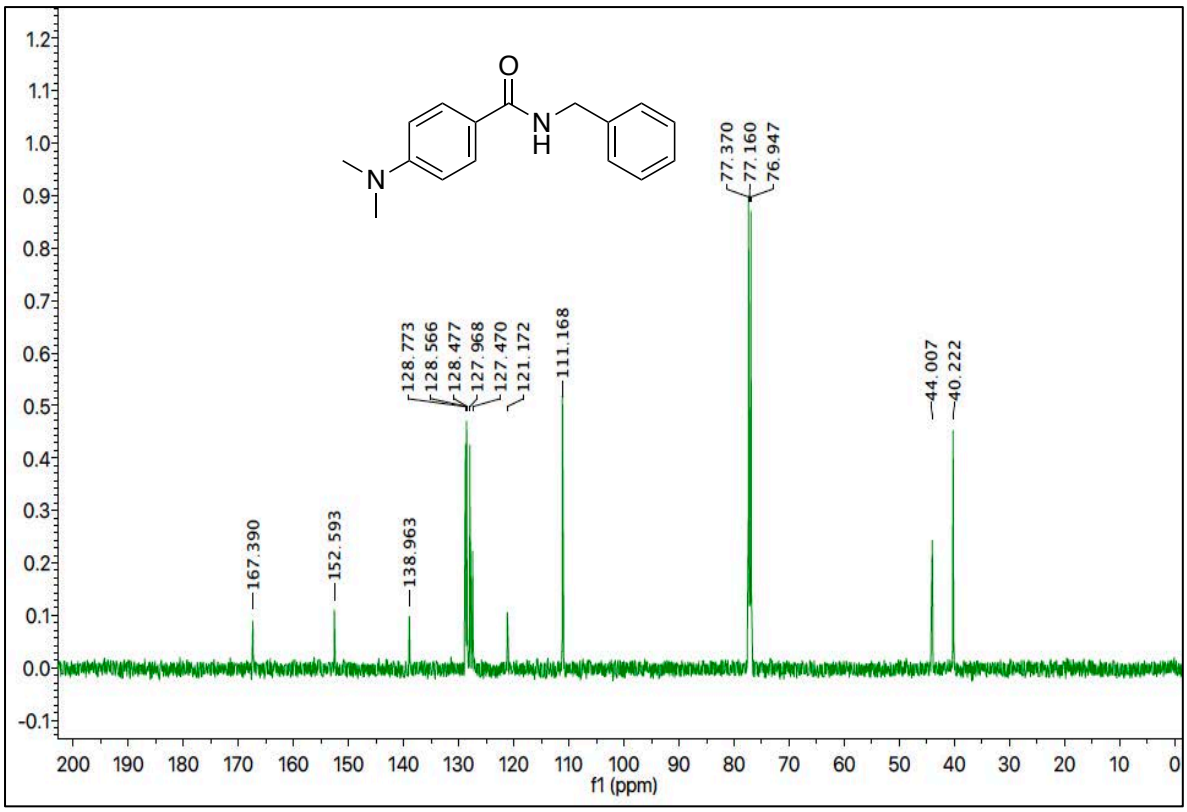
N-benzyl-4-nitrobenzamide (3ia)



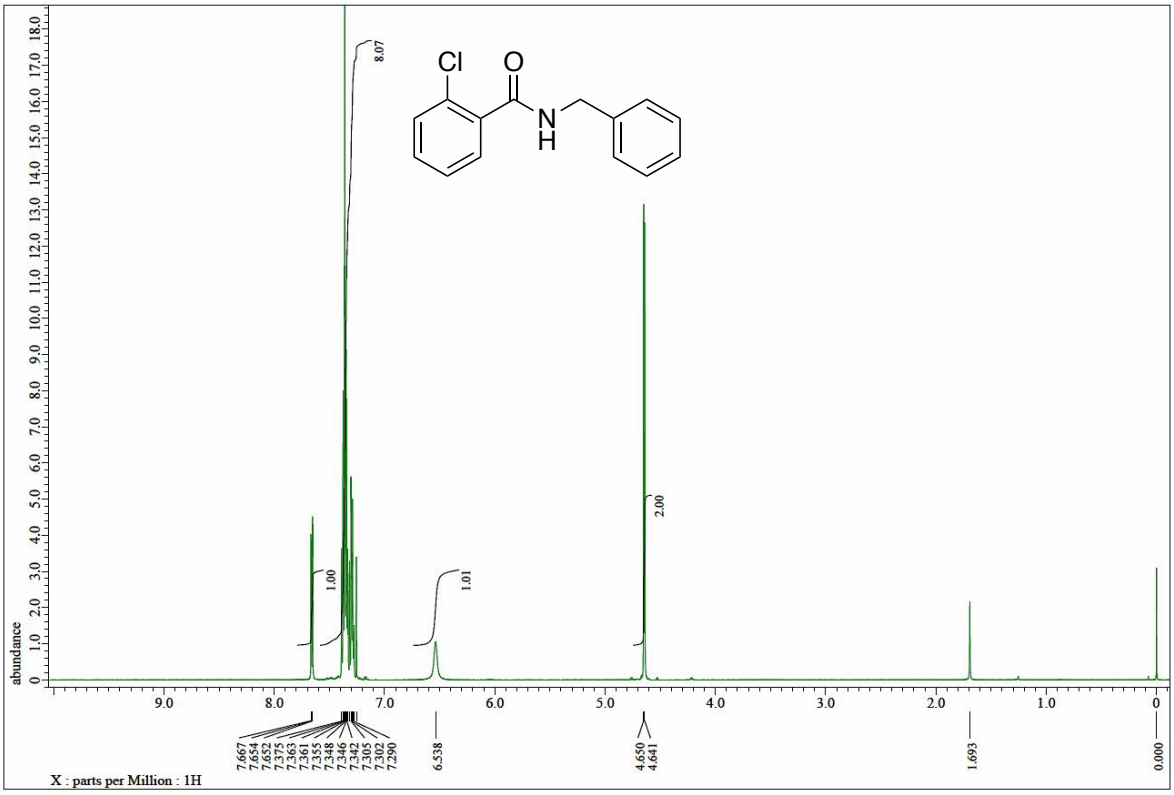


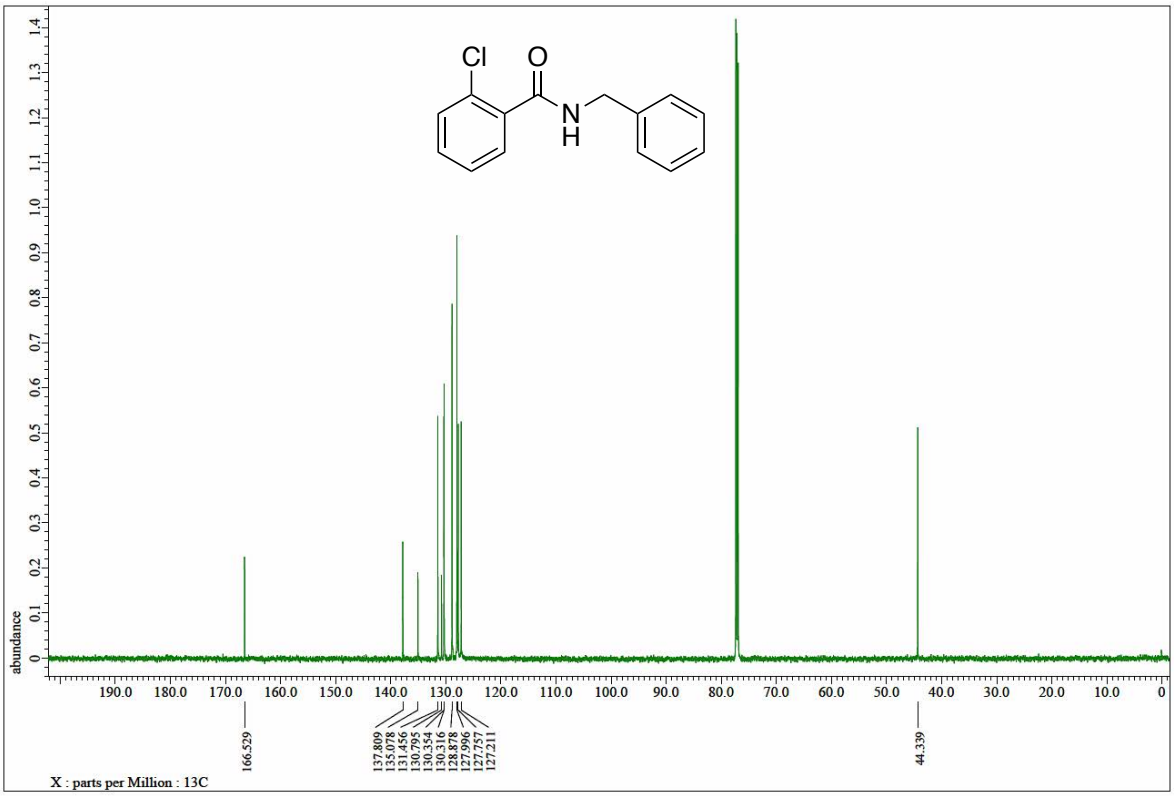
***N*-benzyl-4-(dimethylamino)benzamide (3ja)**



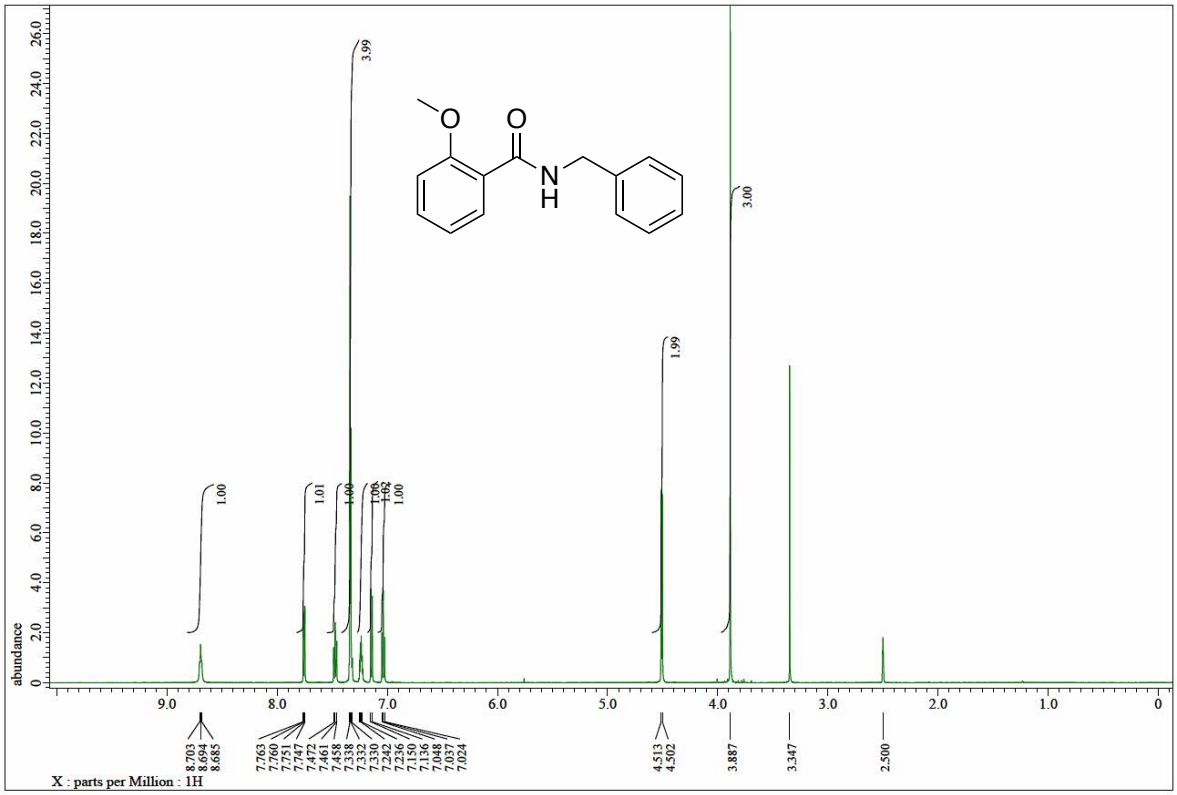


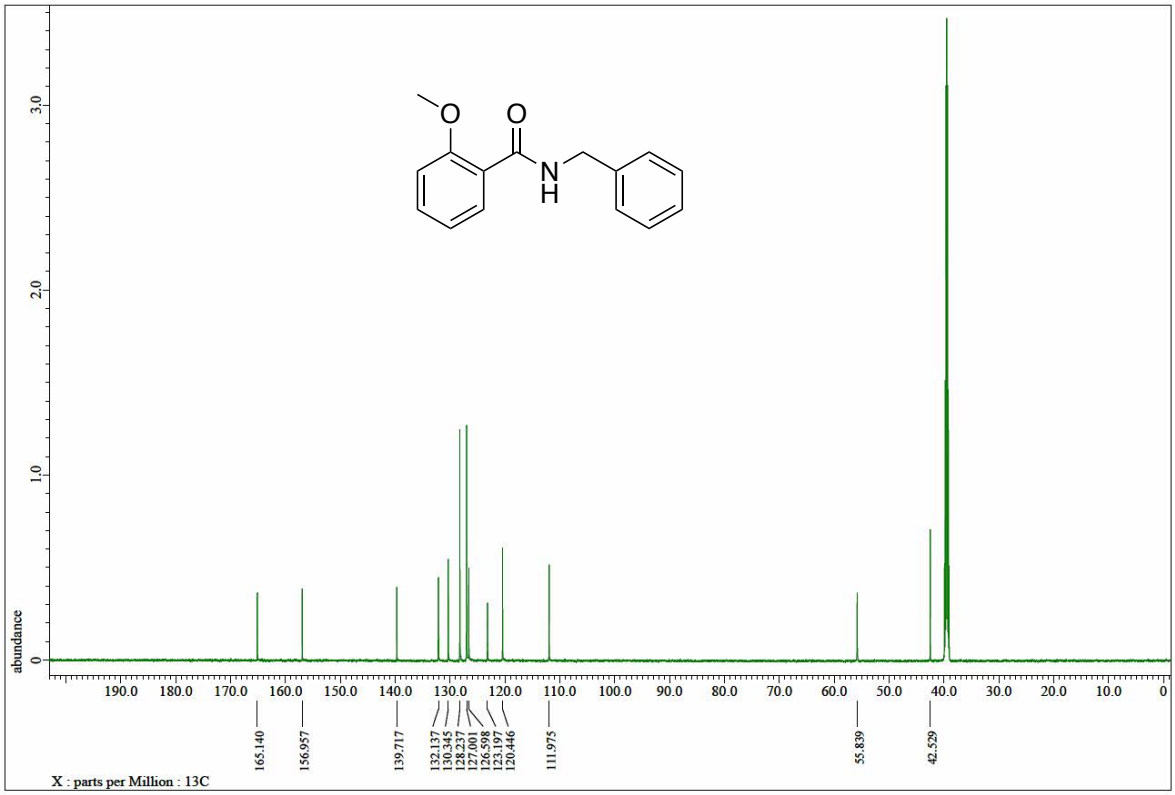
N-benzyl-2-chlorobenzamide (3ka)



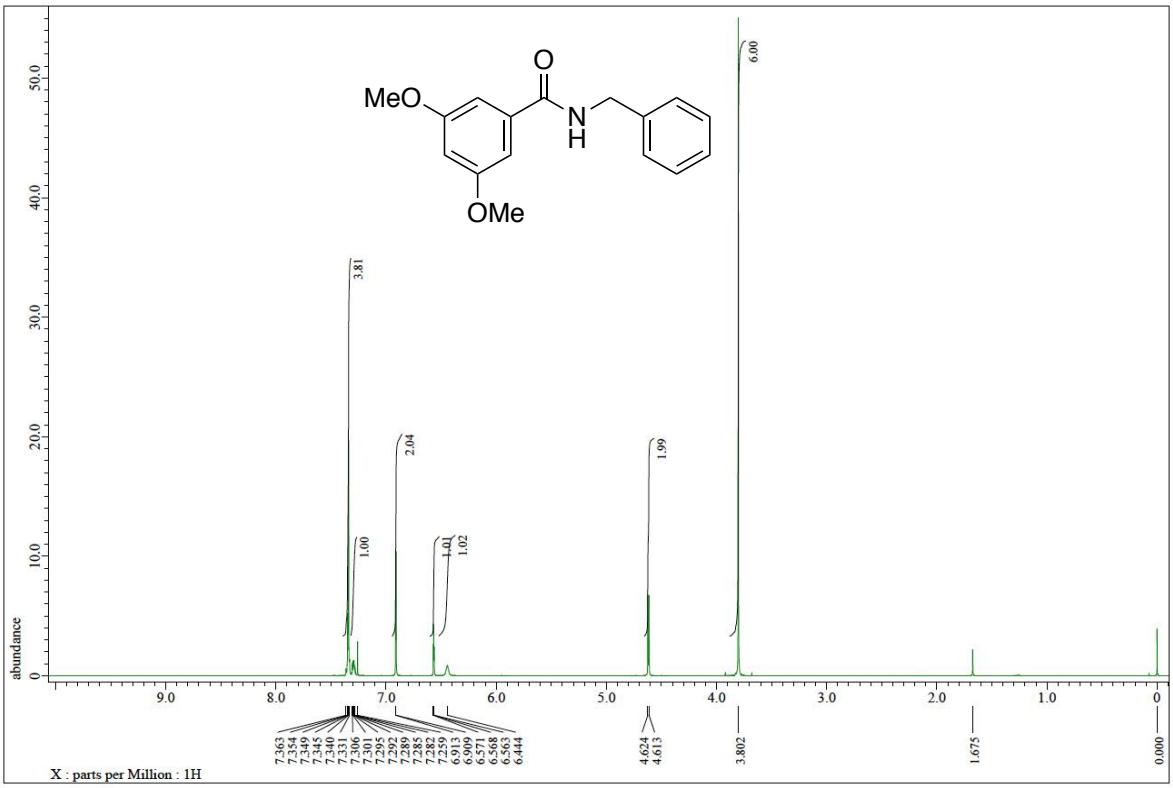


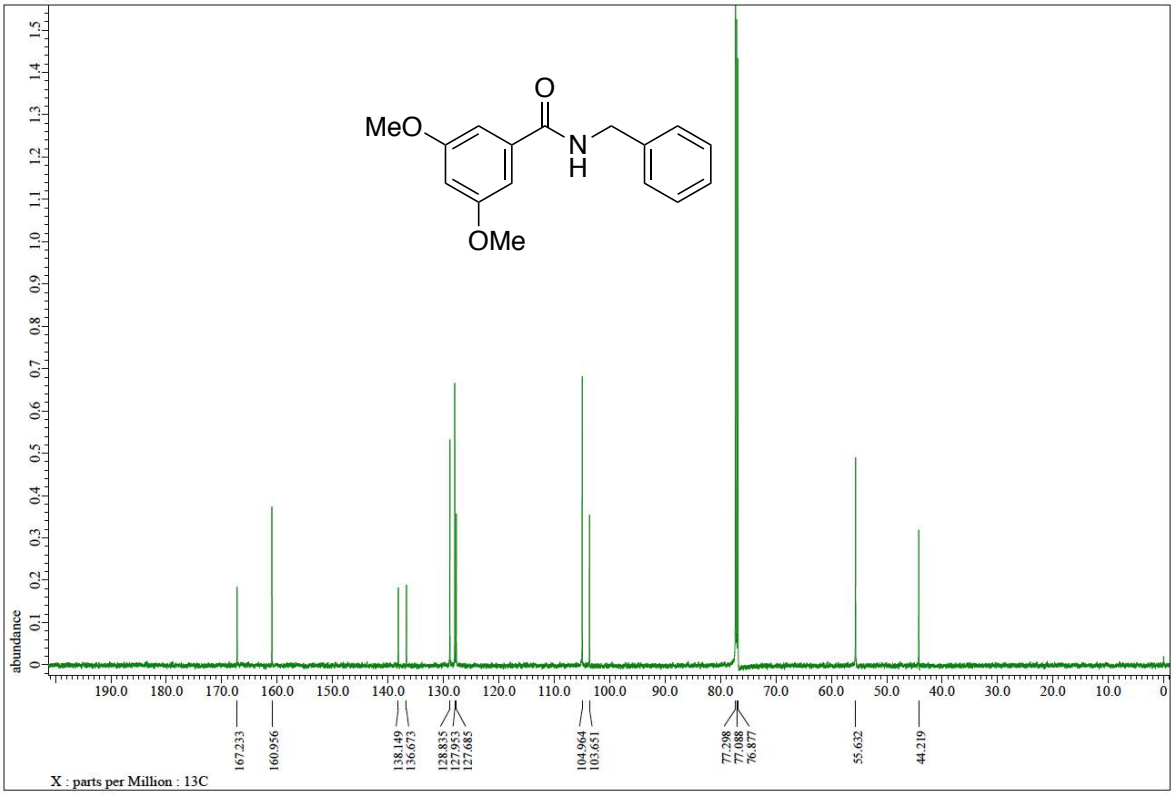
N-benzyl-2-methoxybenzamide (3la)



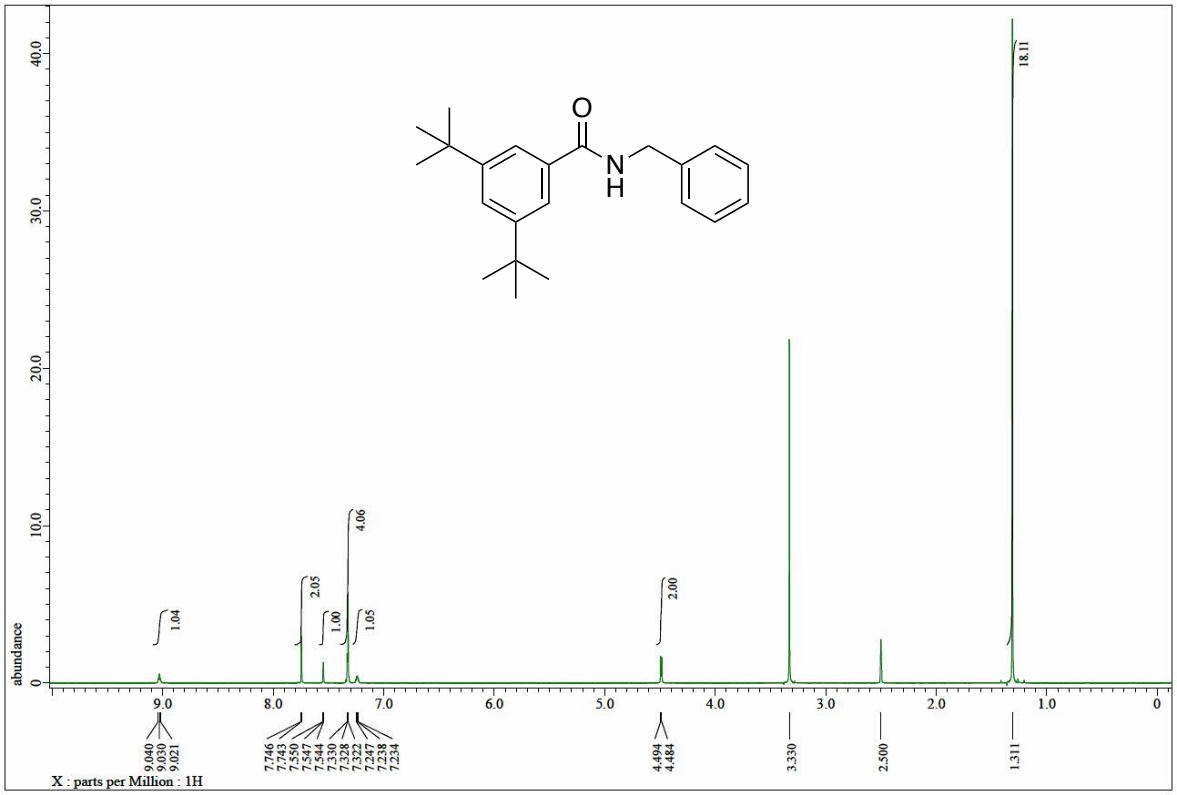


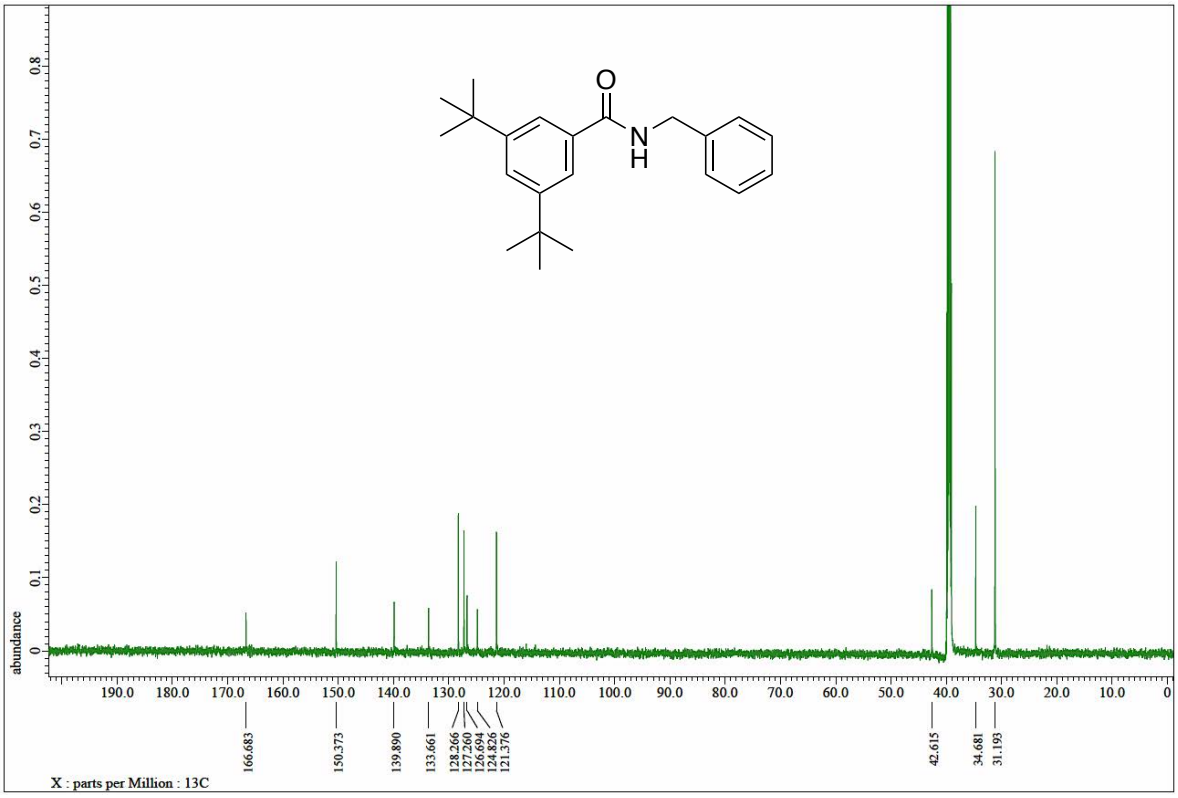
N-benzyl-3,5-dimethoxybenzamide (3ma)



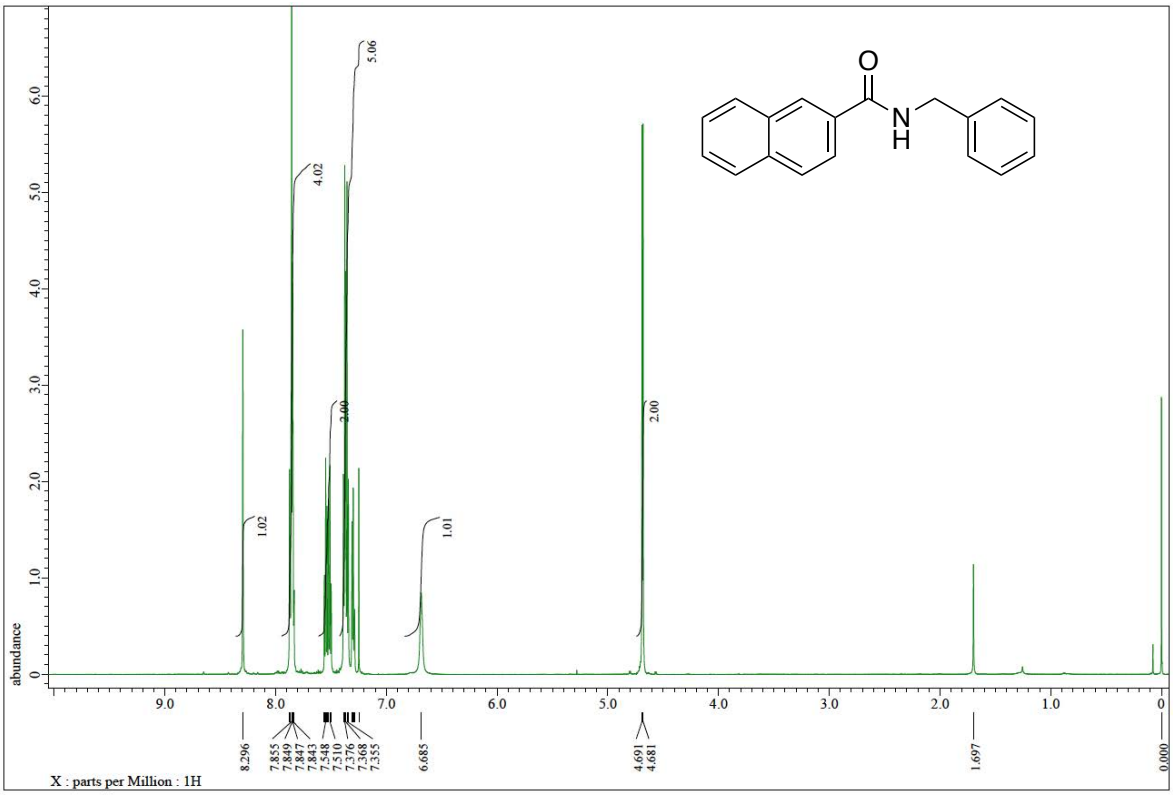


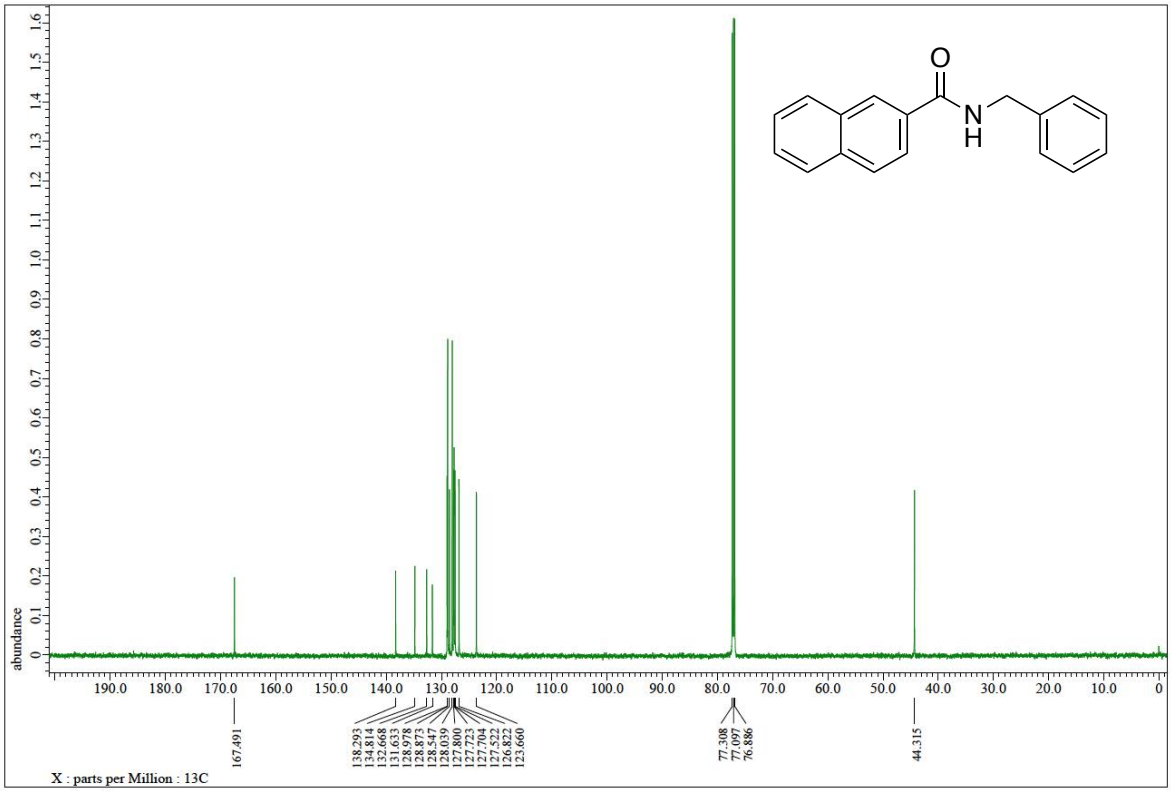
***N*-benzyl-3,5-di-*tert*-butylbenzamide (3na)**



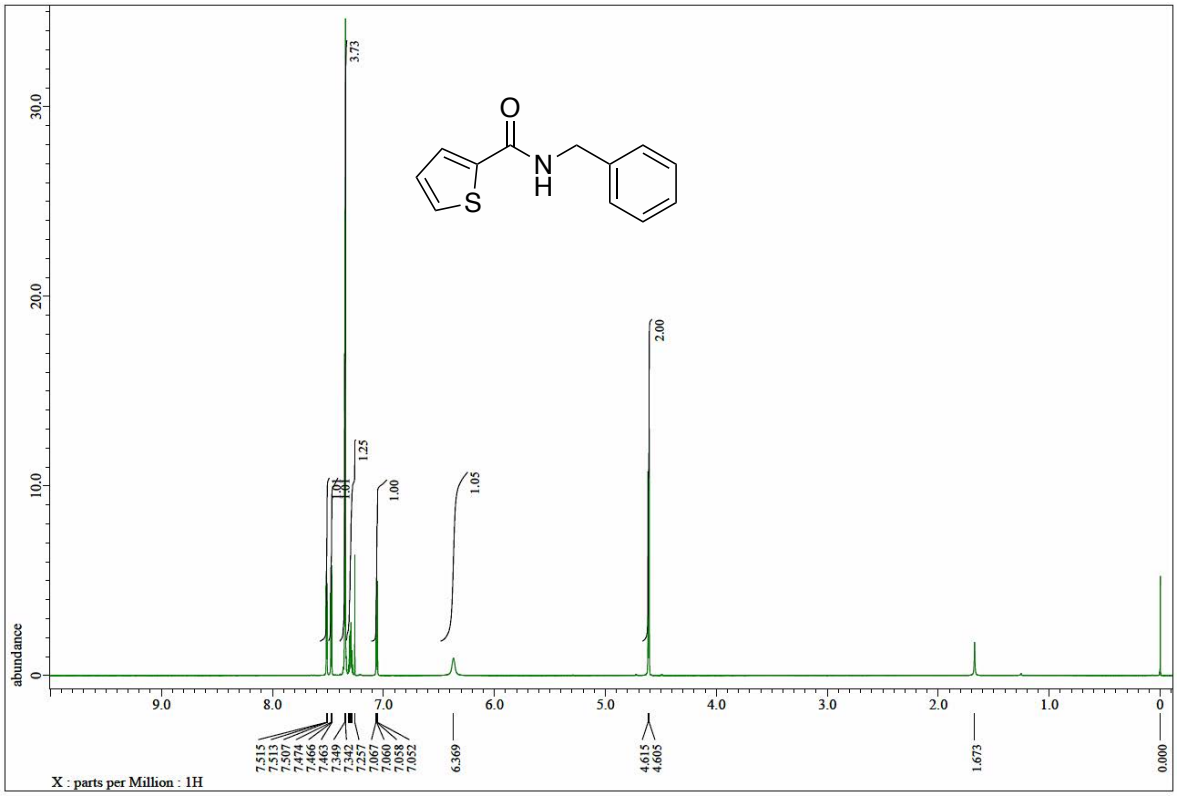


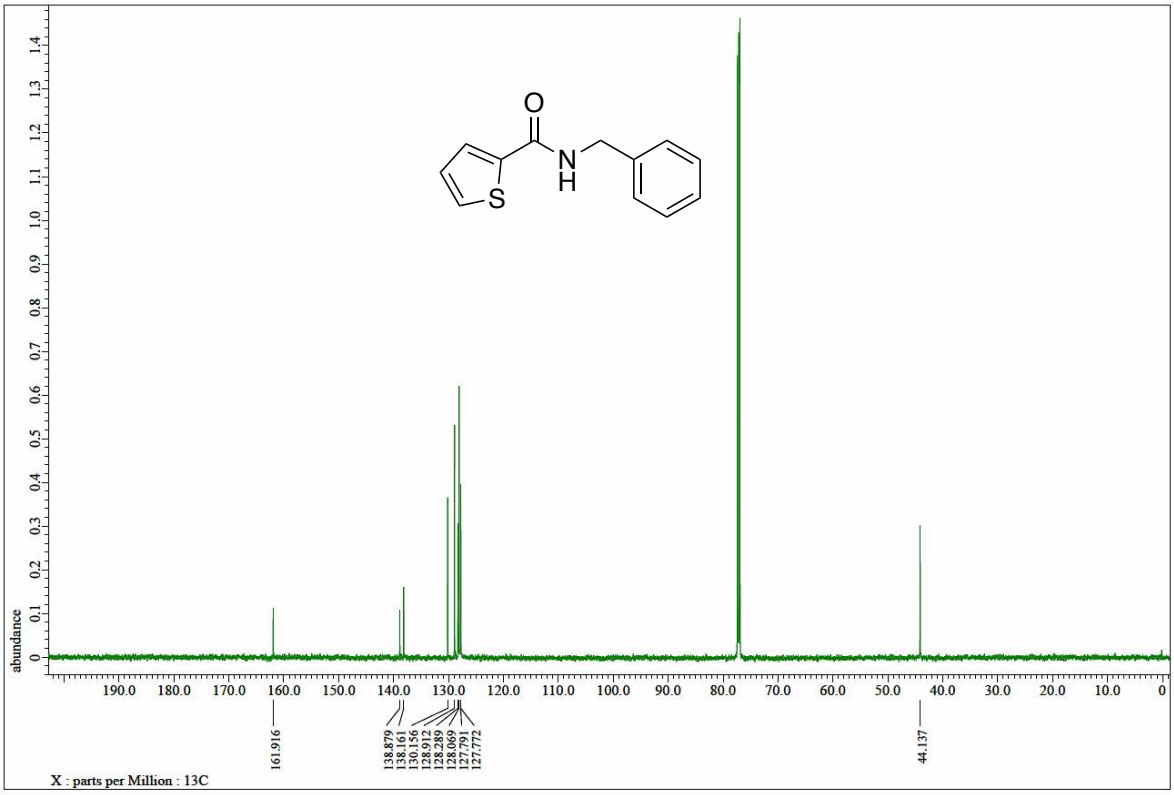
***N*-benzyl-2-naphthamide (3oa)**



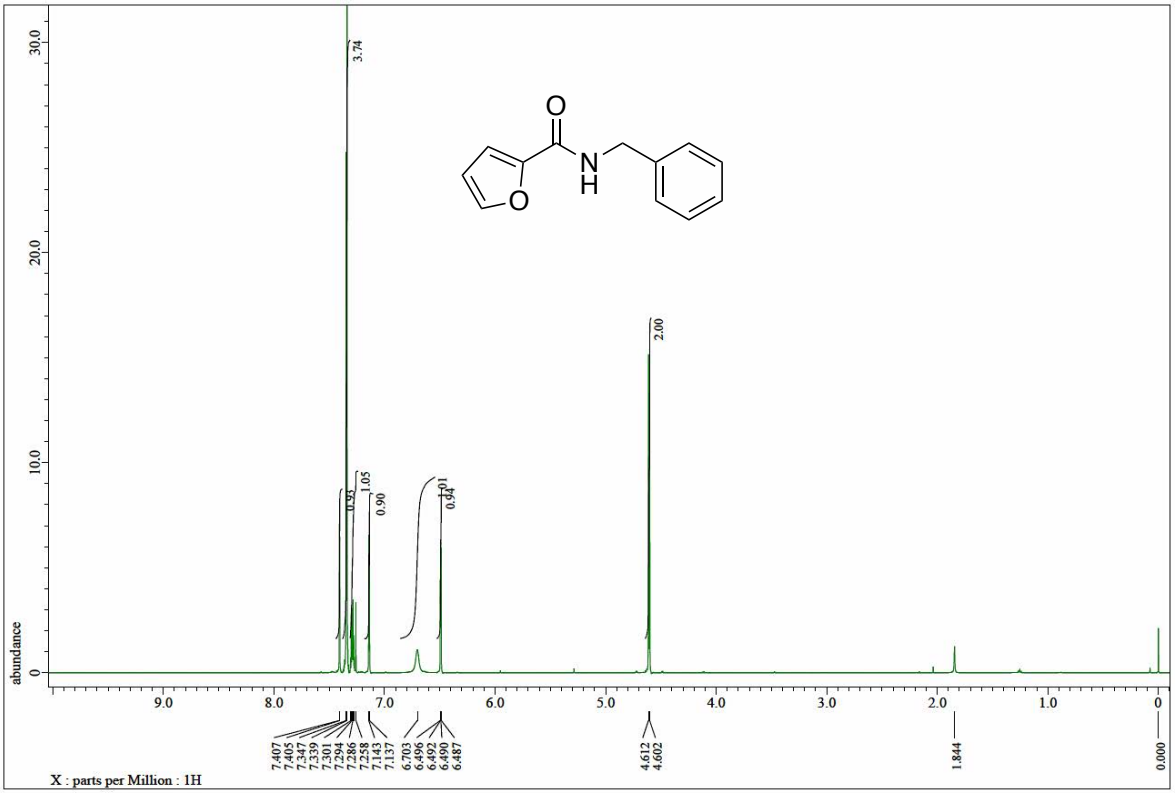


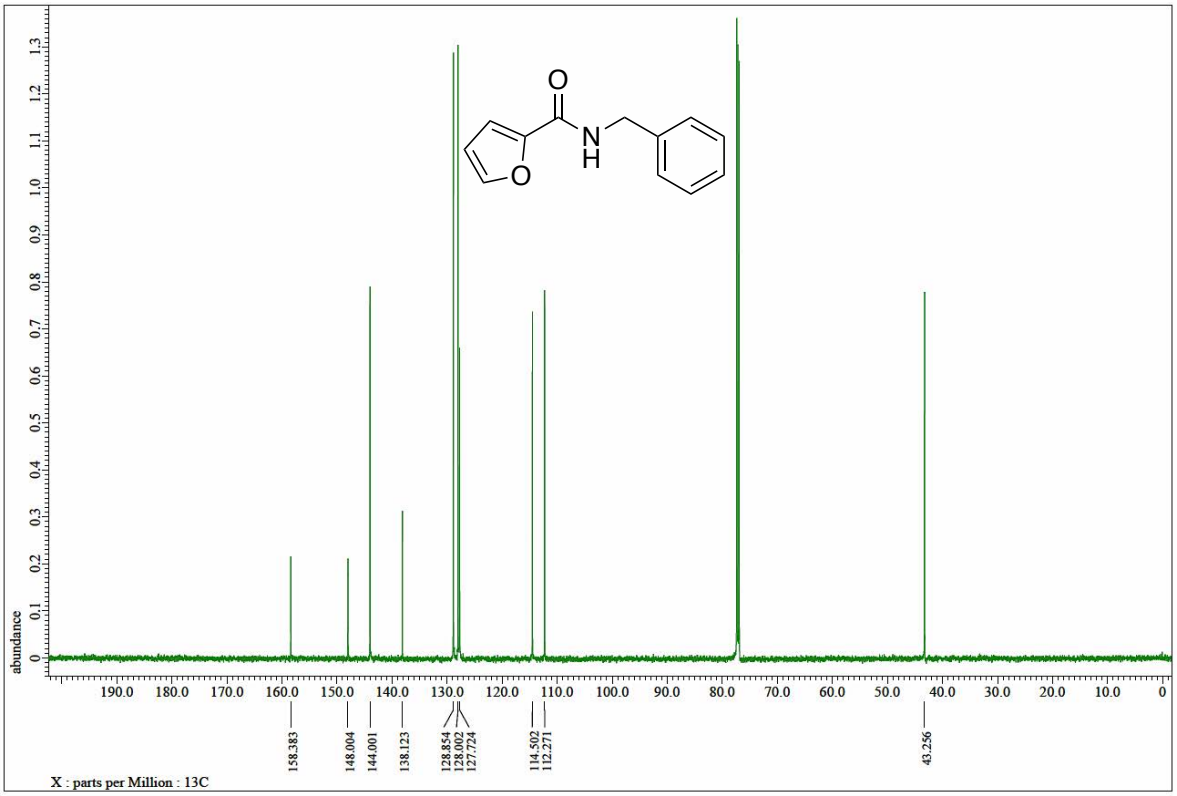
N-benzylthiophene-2-carboxamide (3pa)



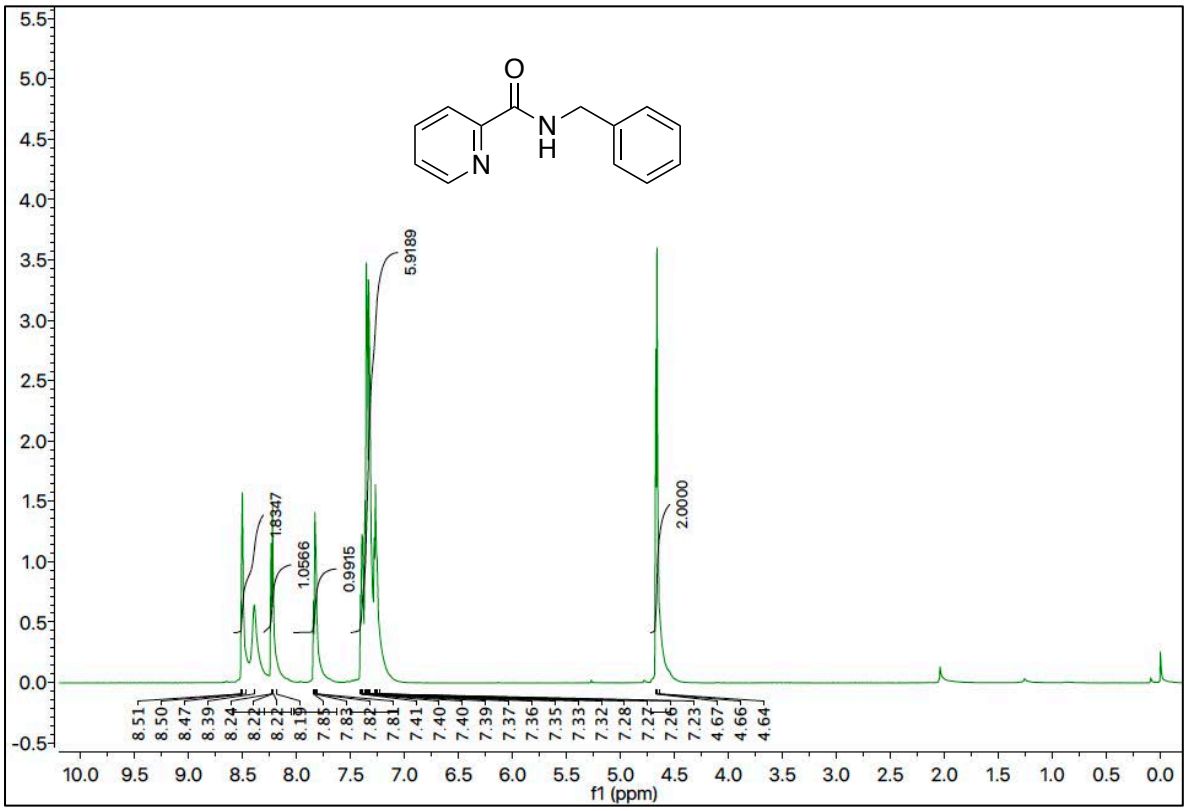


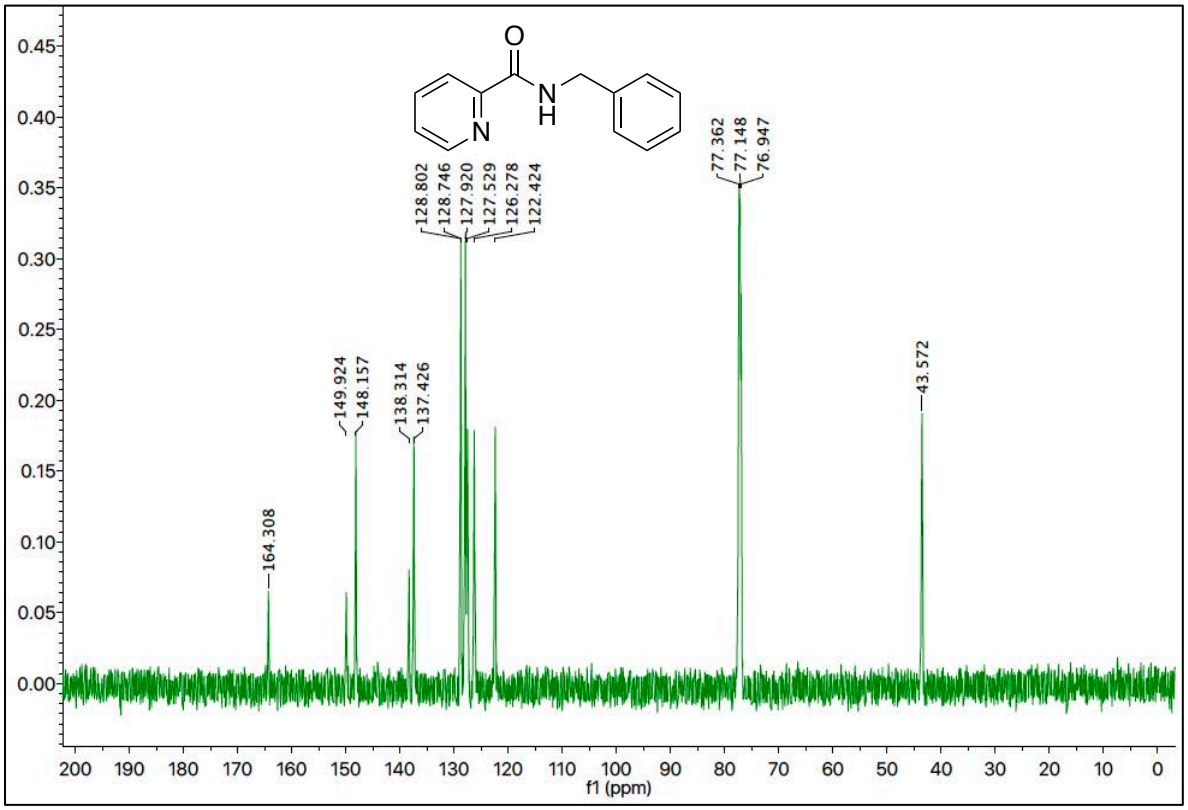
N-benzylfuran-2-carboxamide (3qa)



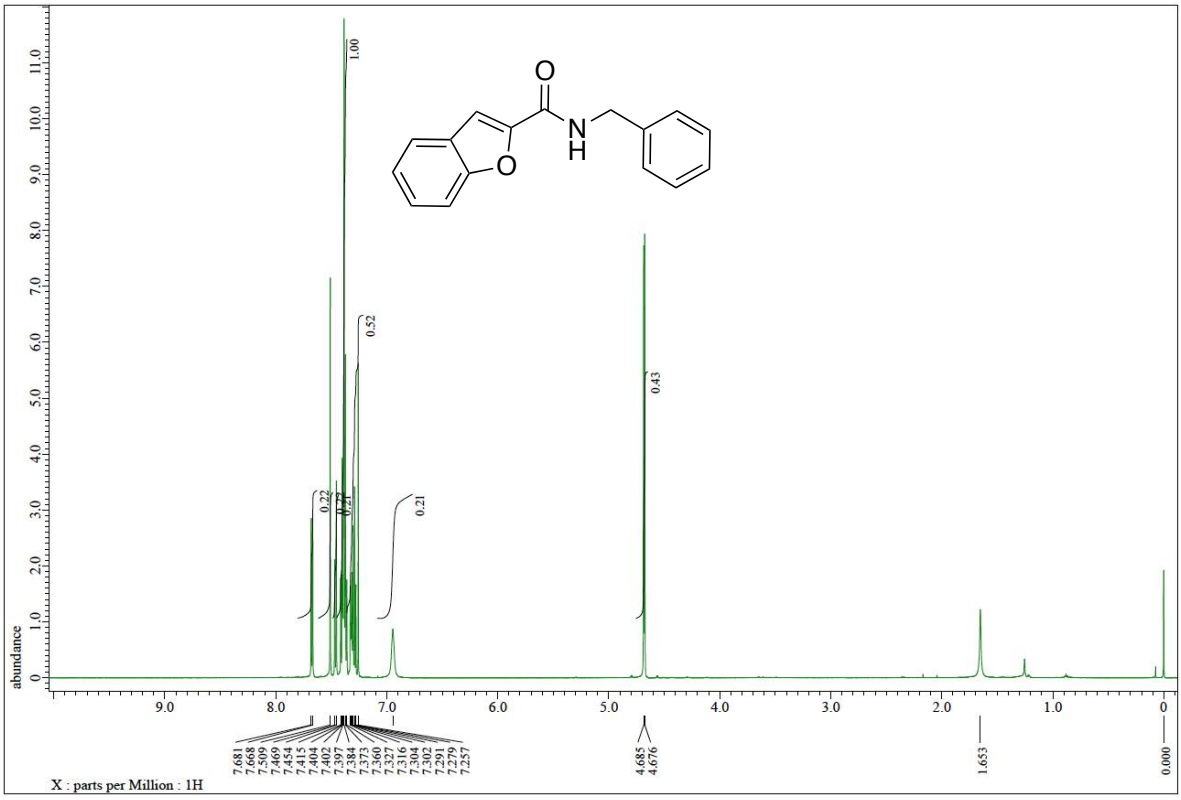


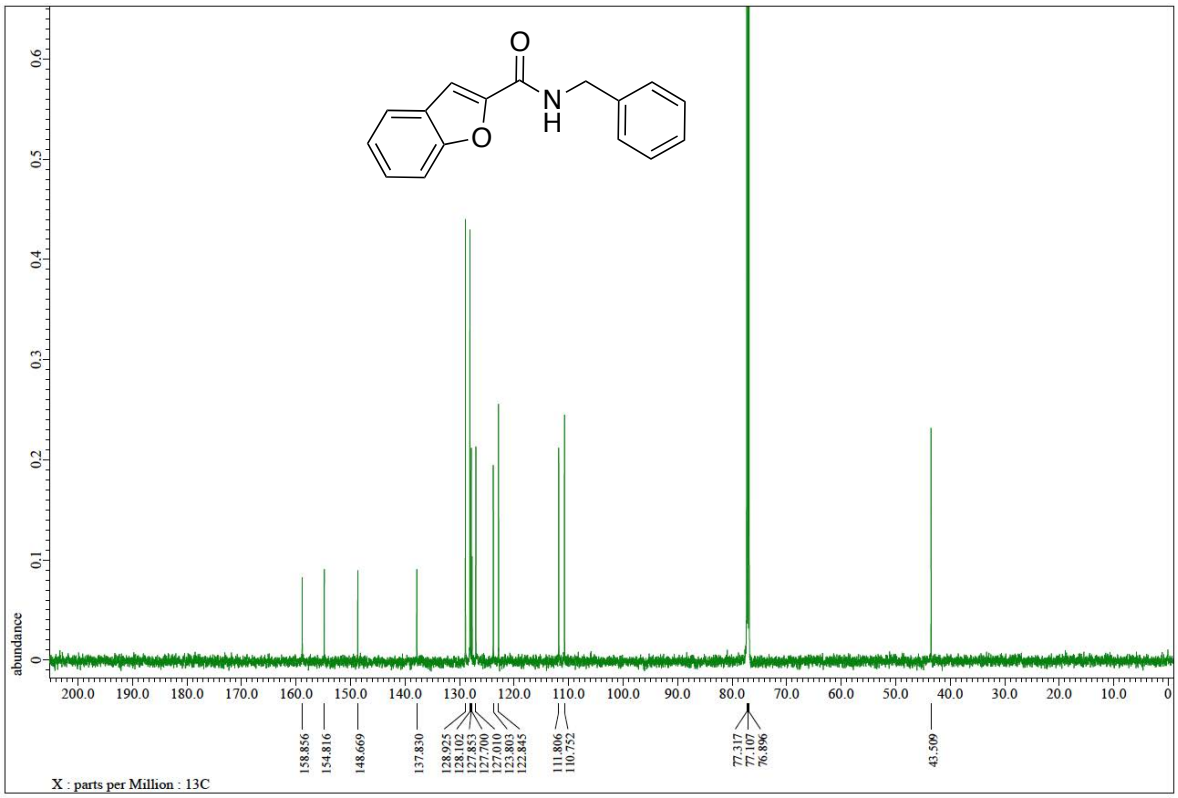
***N*-benzylpicolinamide (3ra)**



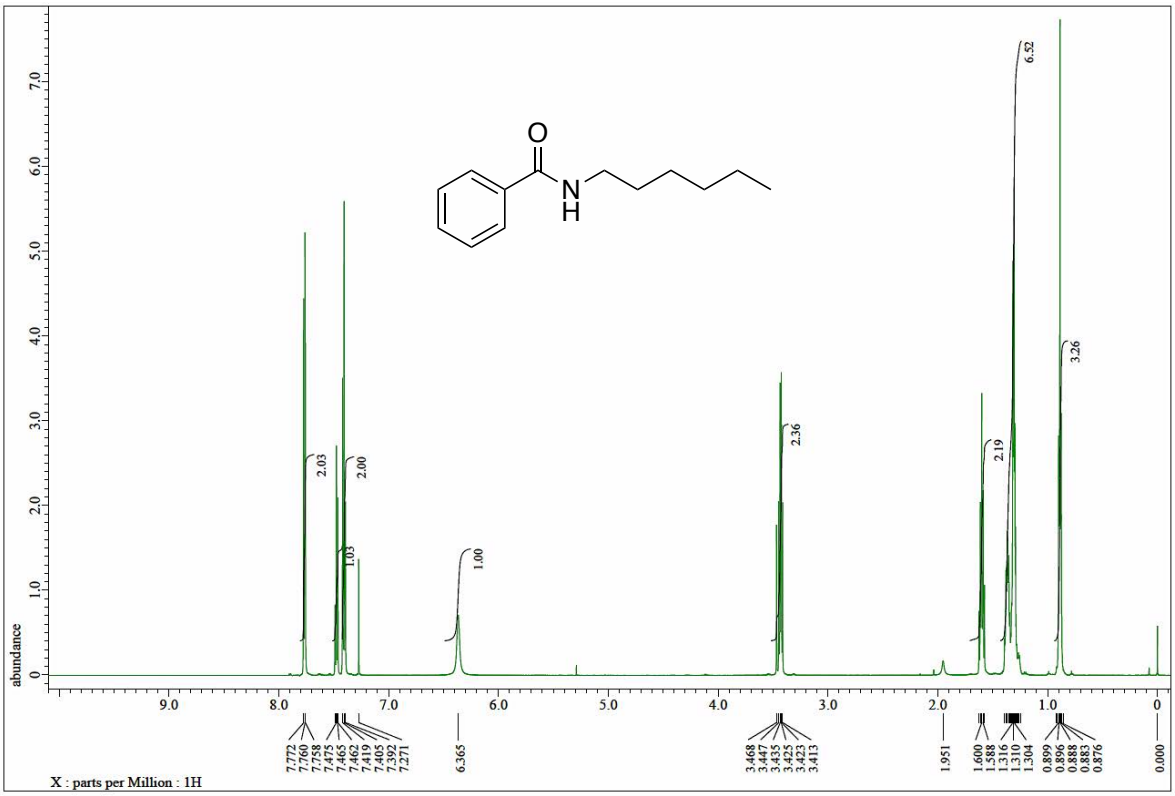


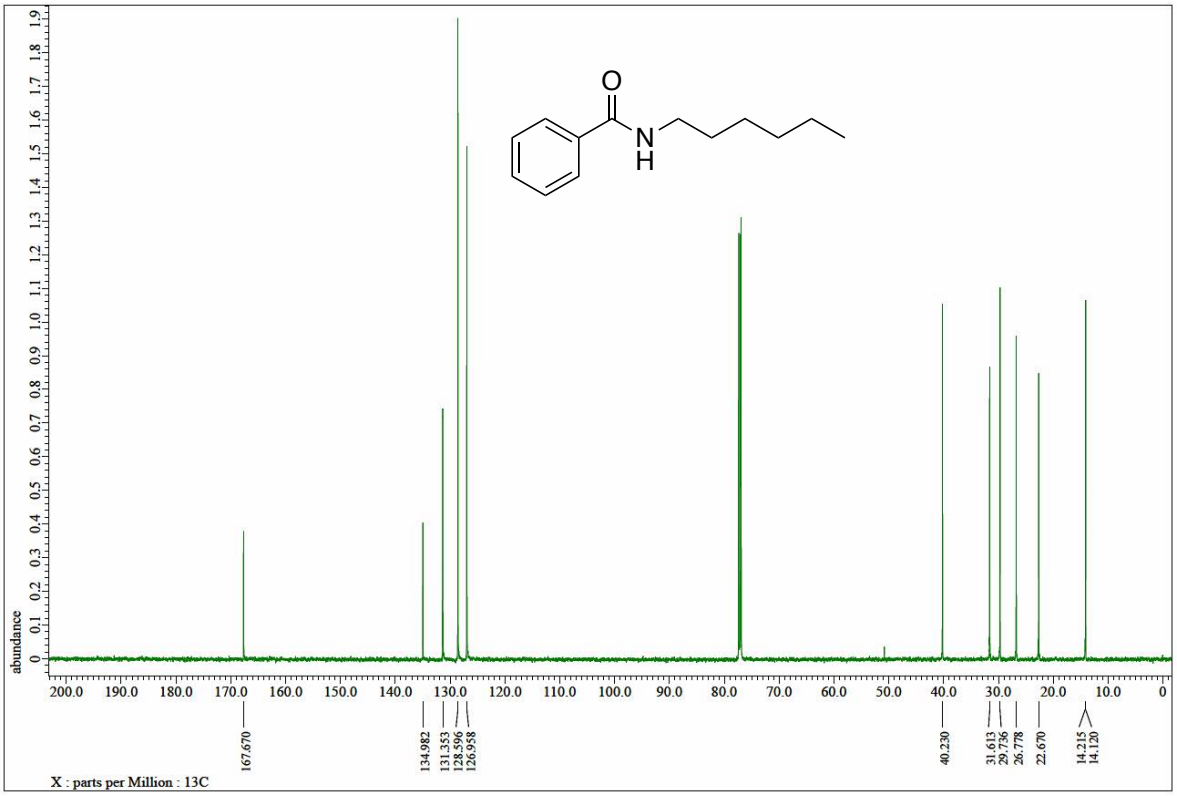
***N*-benzylbenzofuran-2-carboxamide (3sa)**



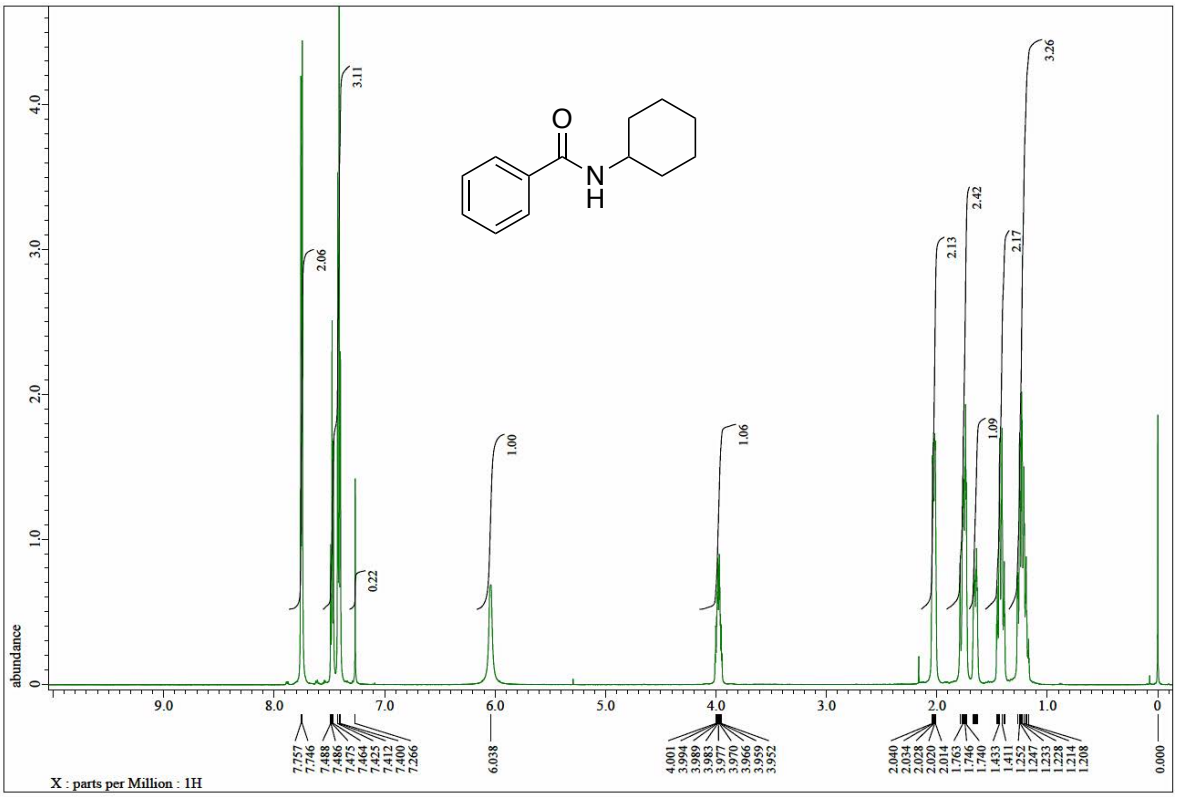


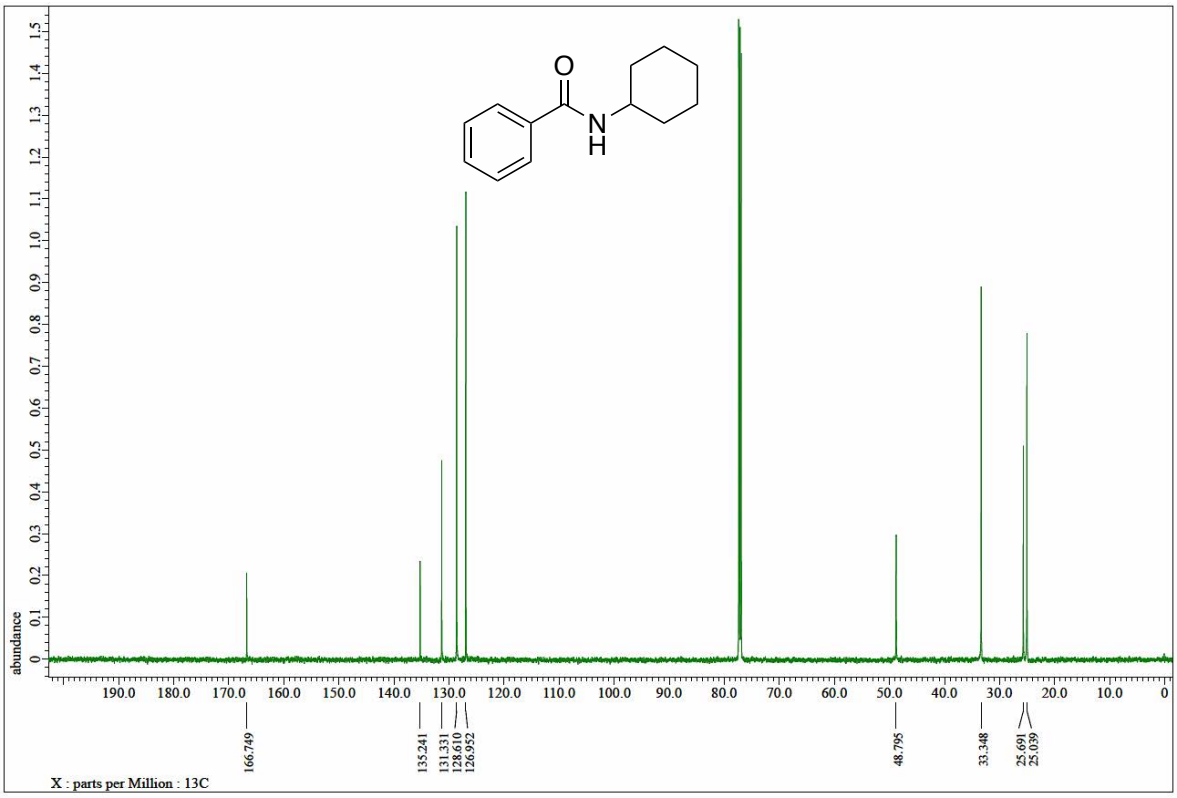
N-hexylbenzamide (3ab)



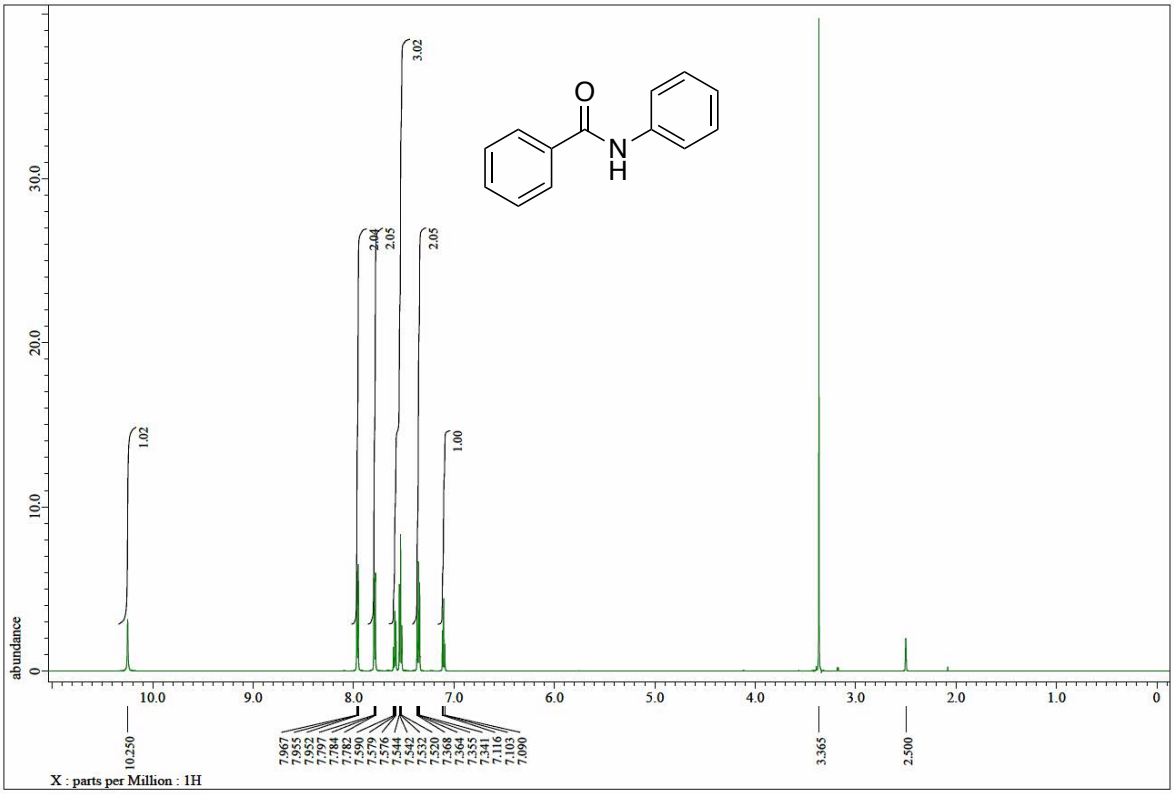


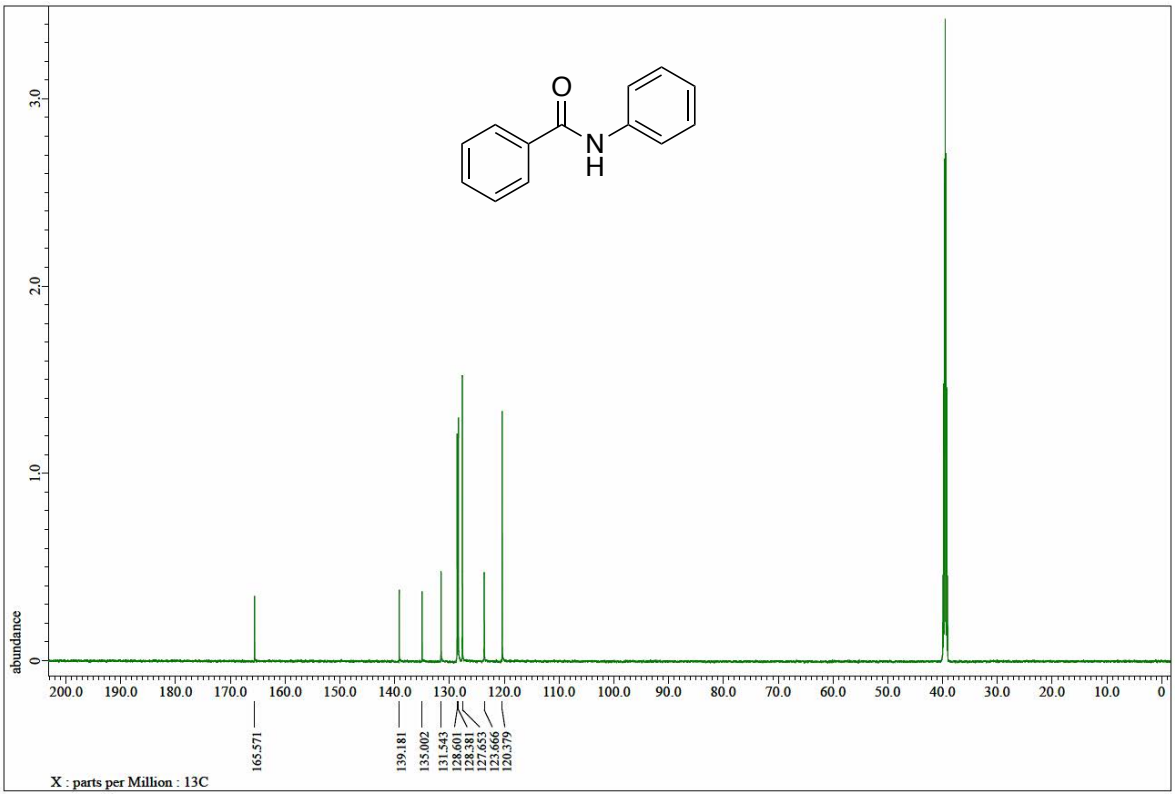
N-cyclohexylbenzamide (3ac)



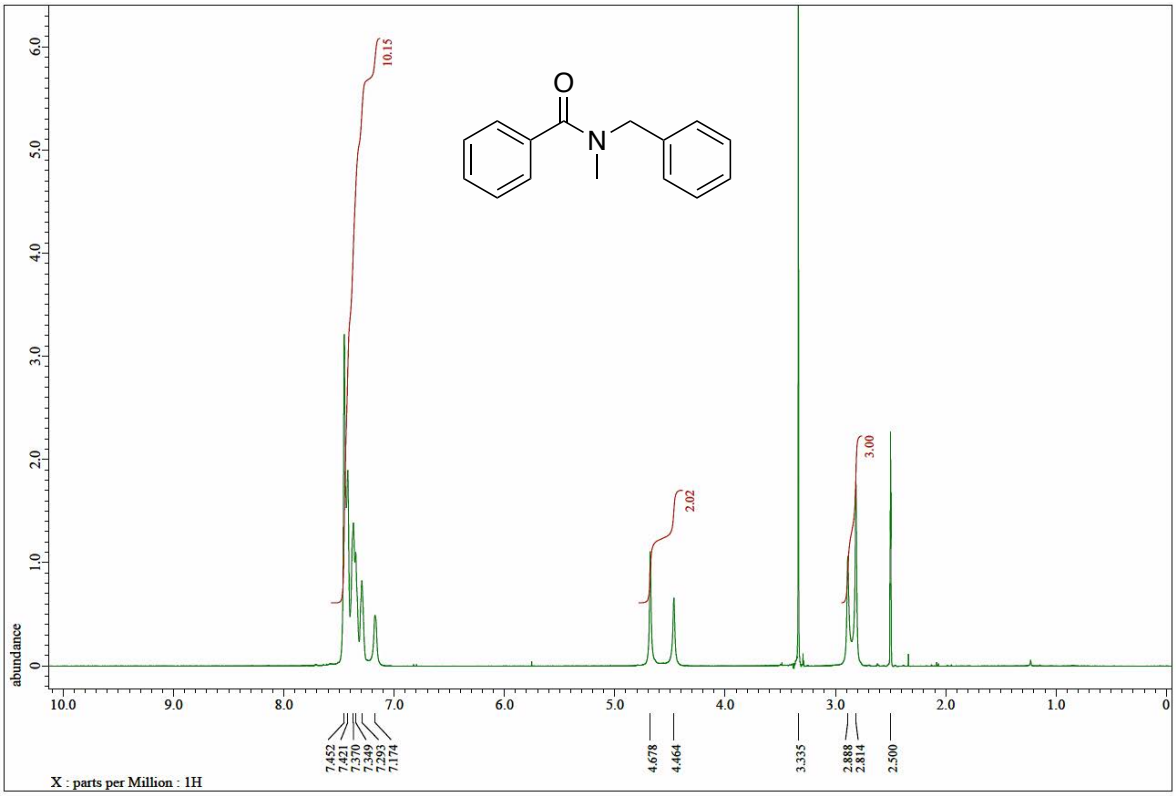


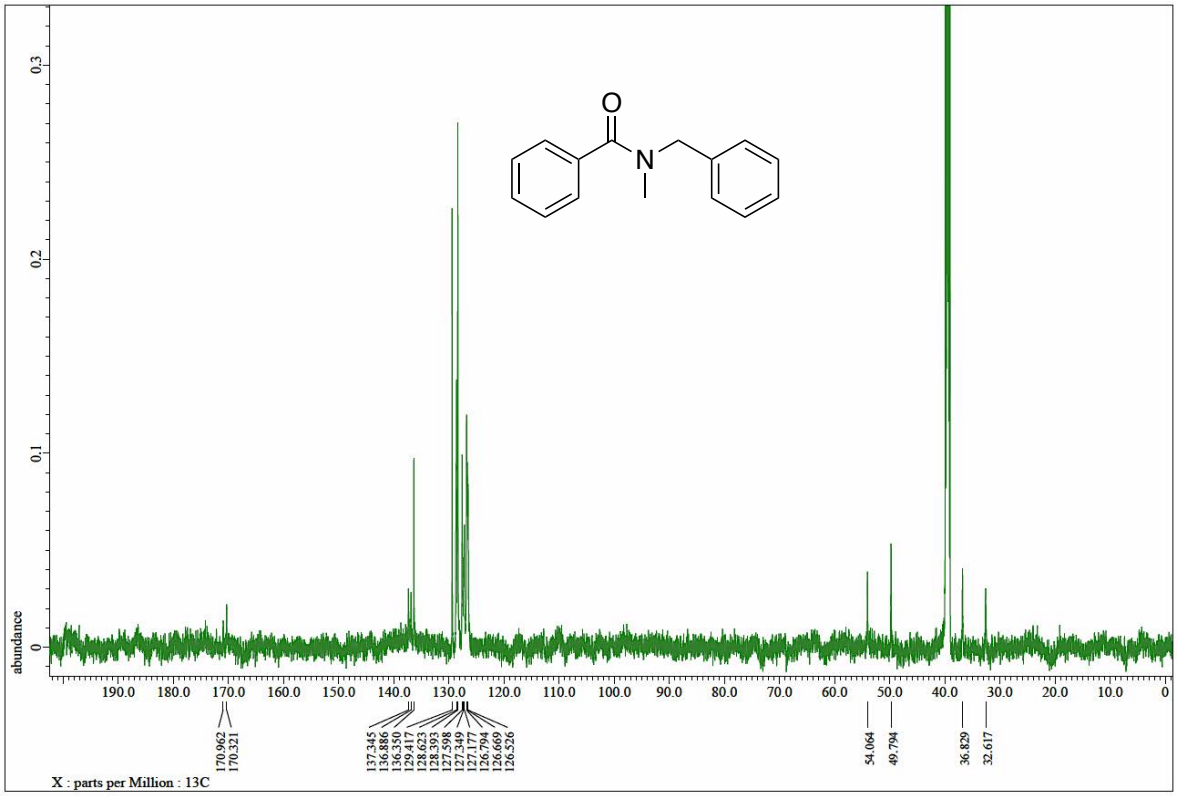
N-phenylbenzamide (3ad)



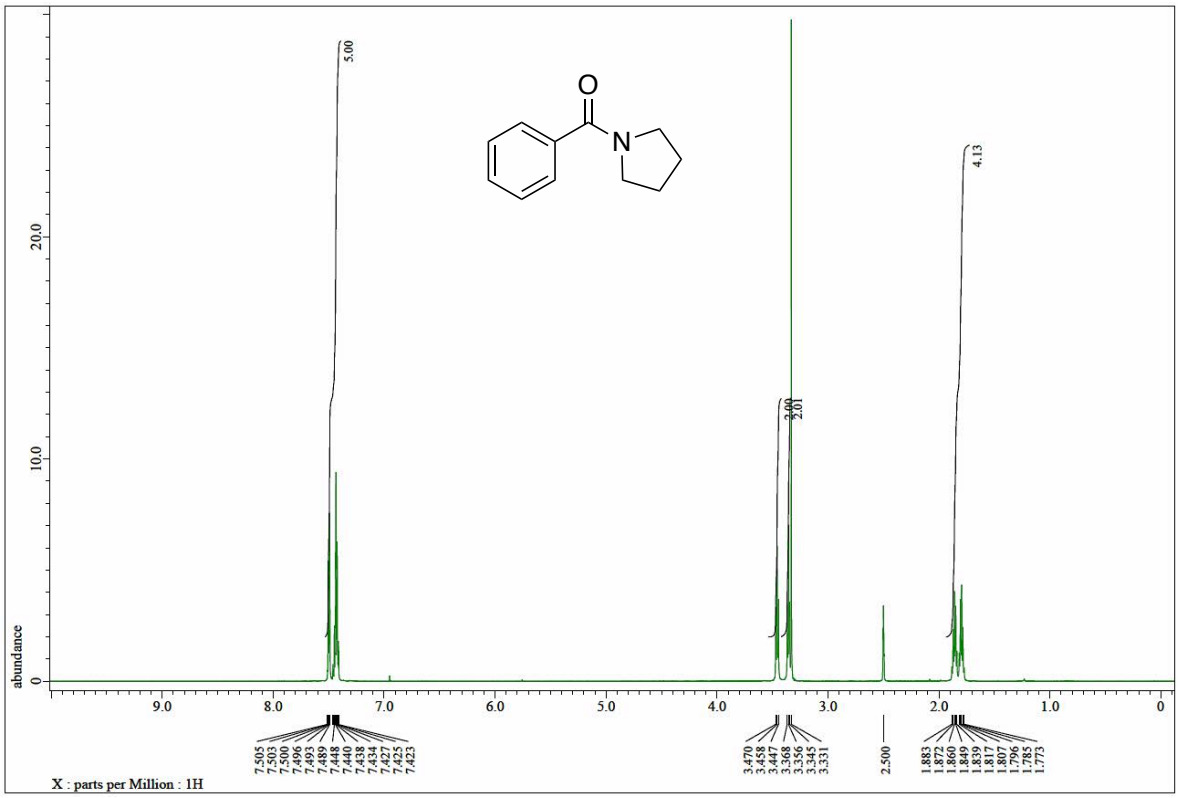


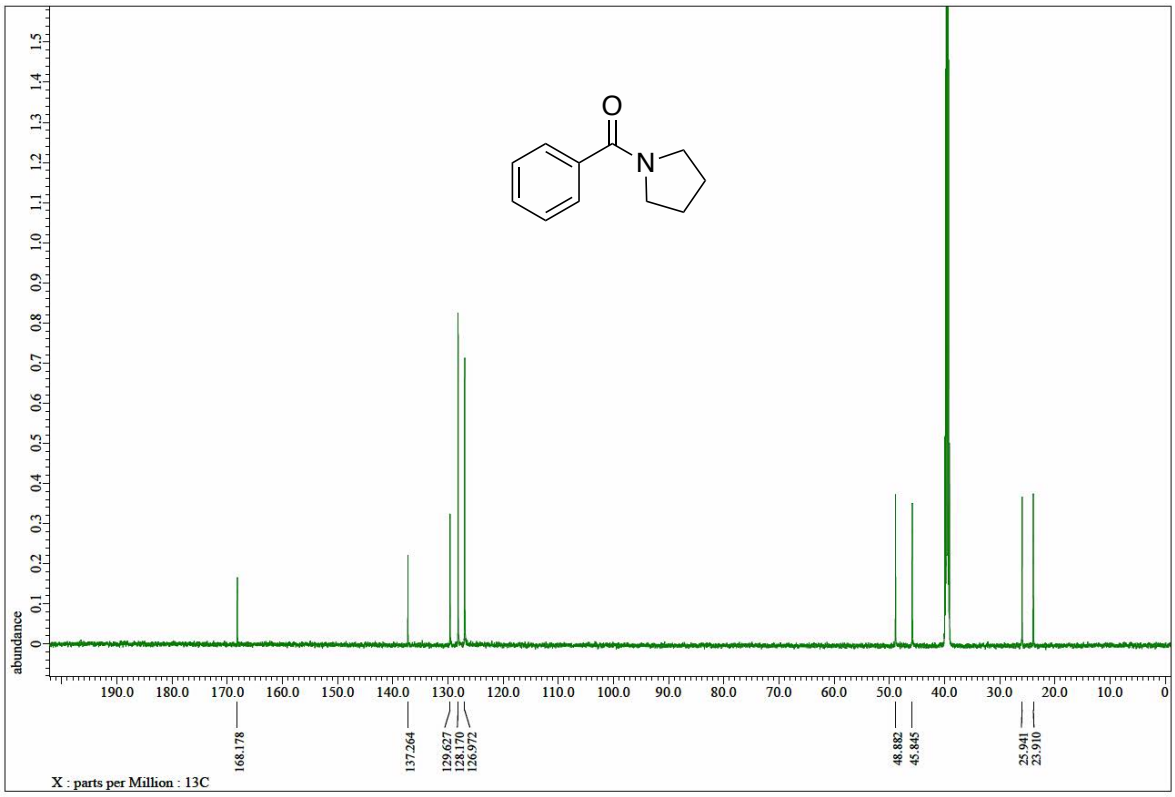
N-benzyl-*N*-methylbenzamide (3ae)



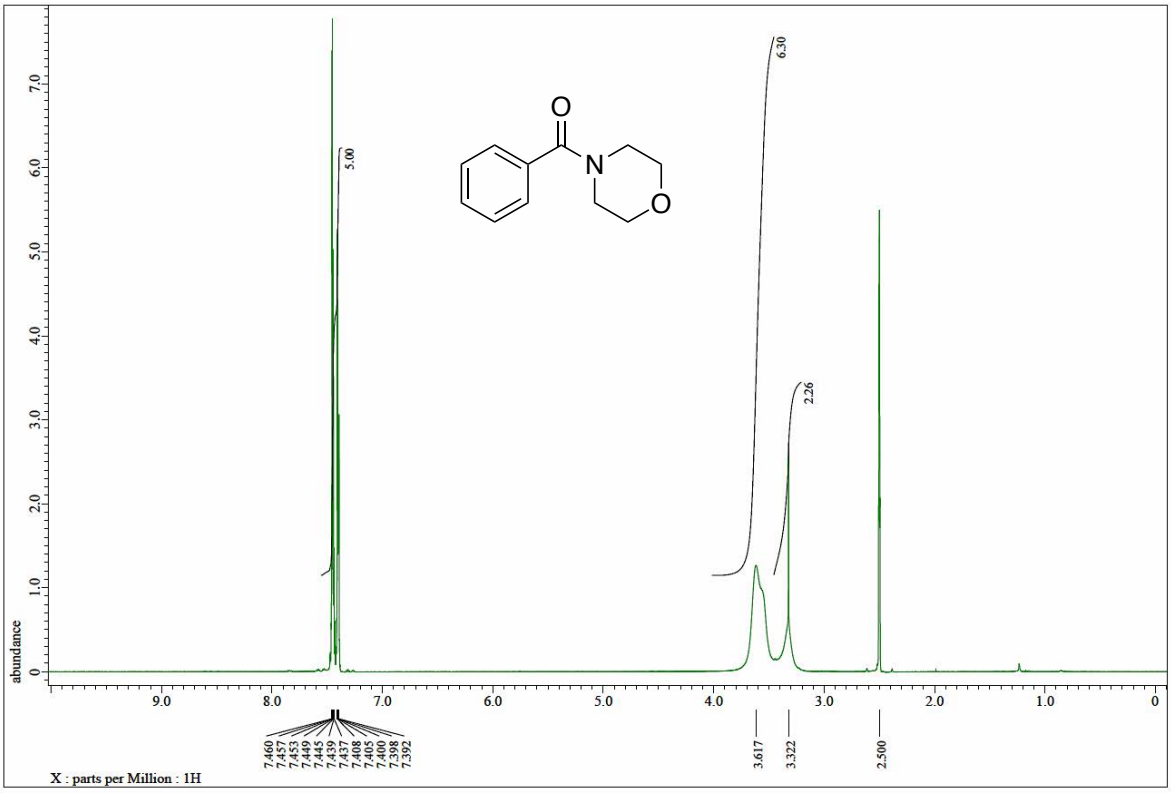


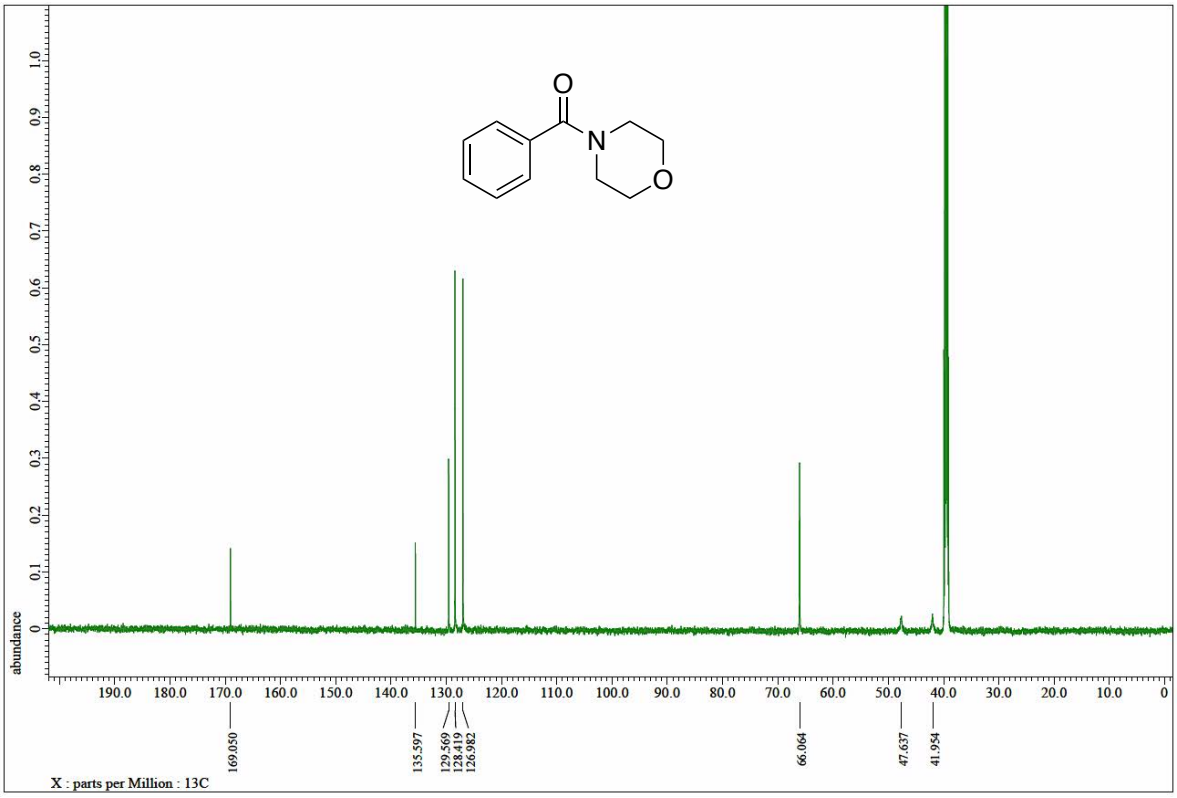
Phenyl(pyrrolidin-1-yl)methanone (3af)



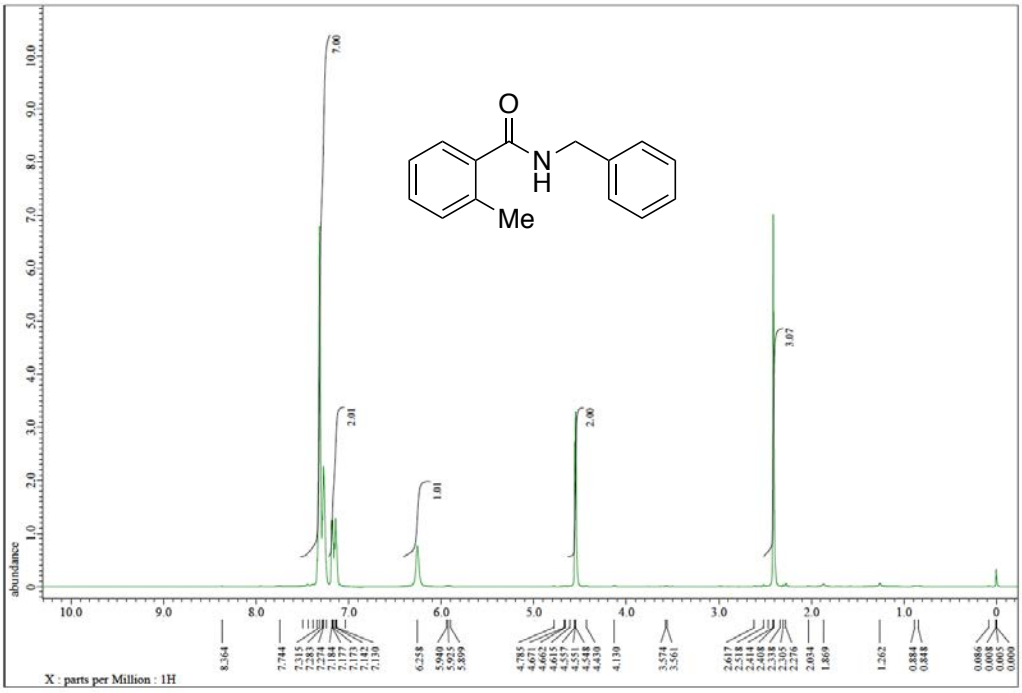


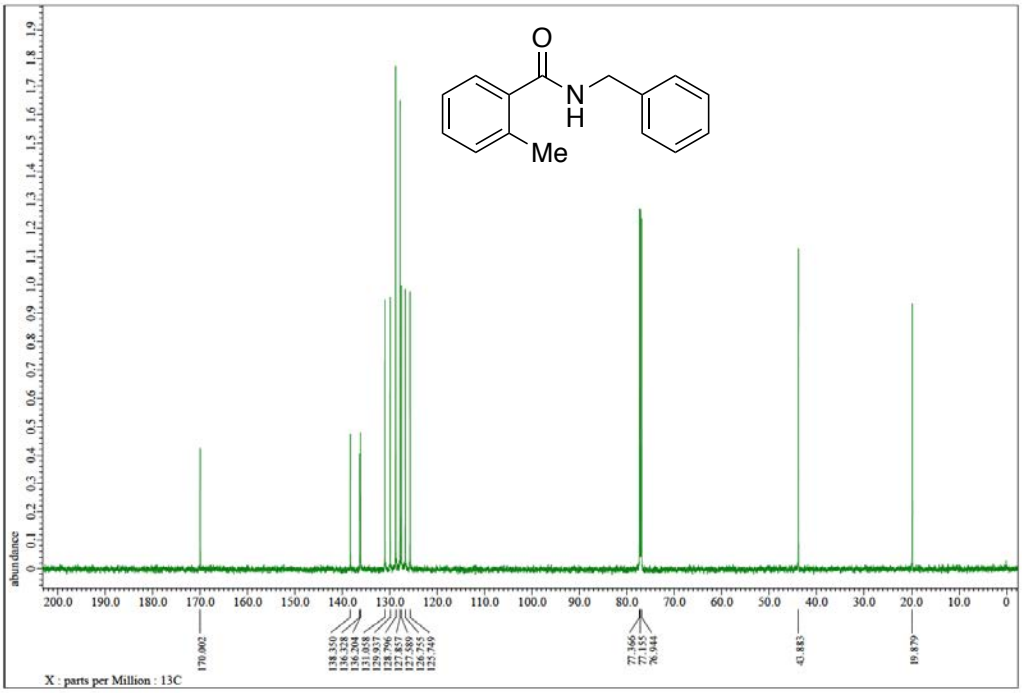
Morpholino(phenyl)methanone (3ag)



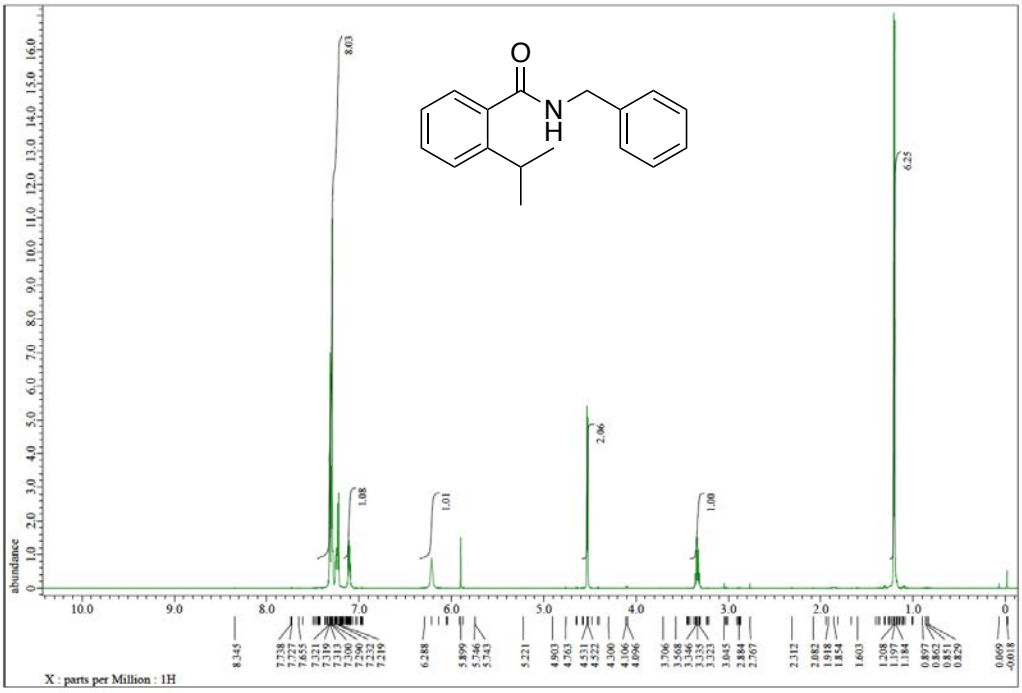


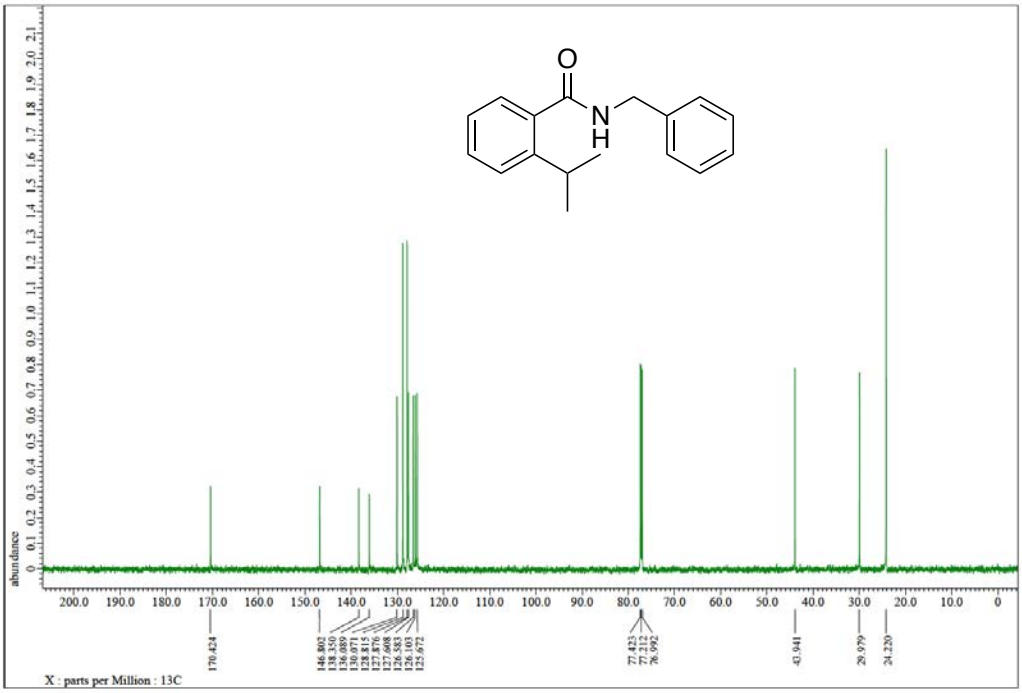
***N*-benzyl-2-methylbenzamide (3ta)**



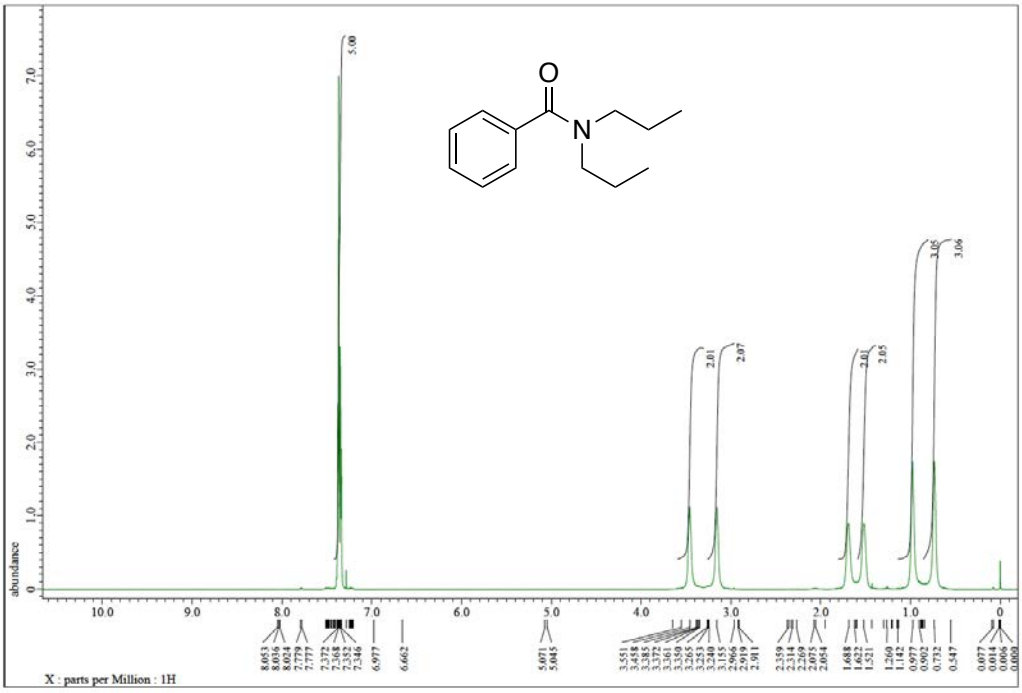


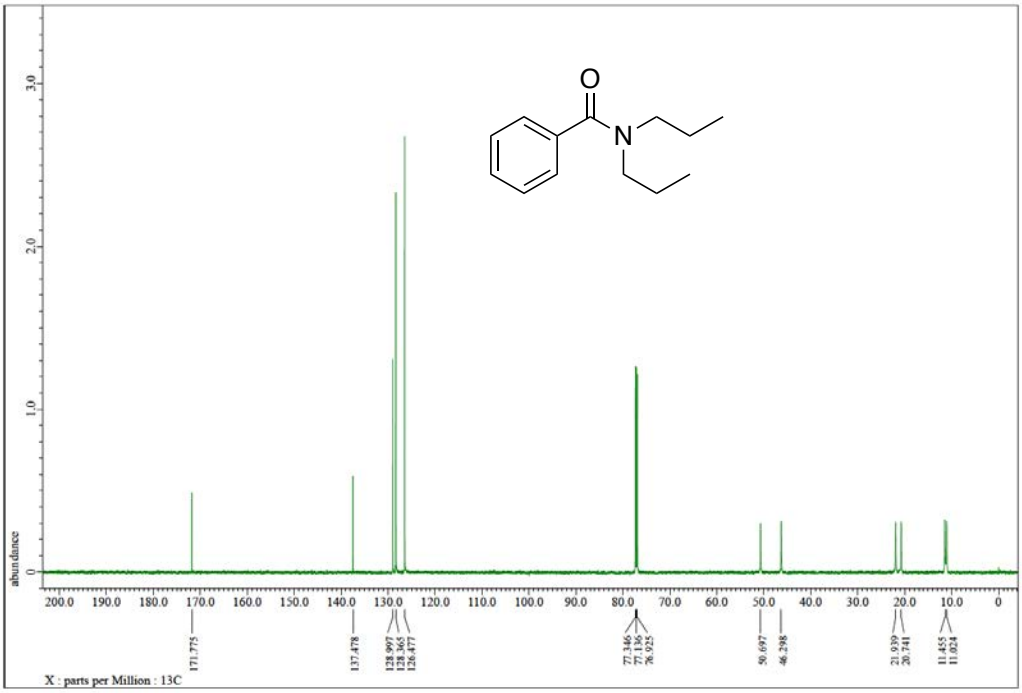
***N*-benzyl-2-isopropylbenzamide (3ua)**



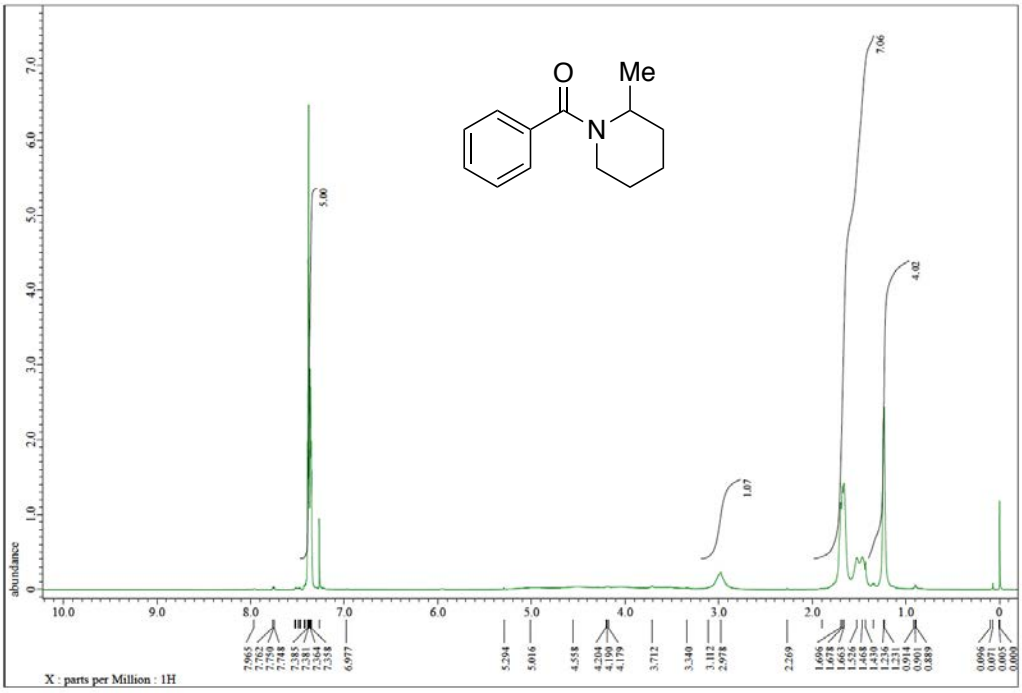


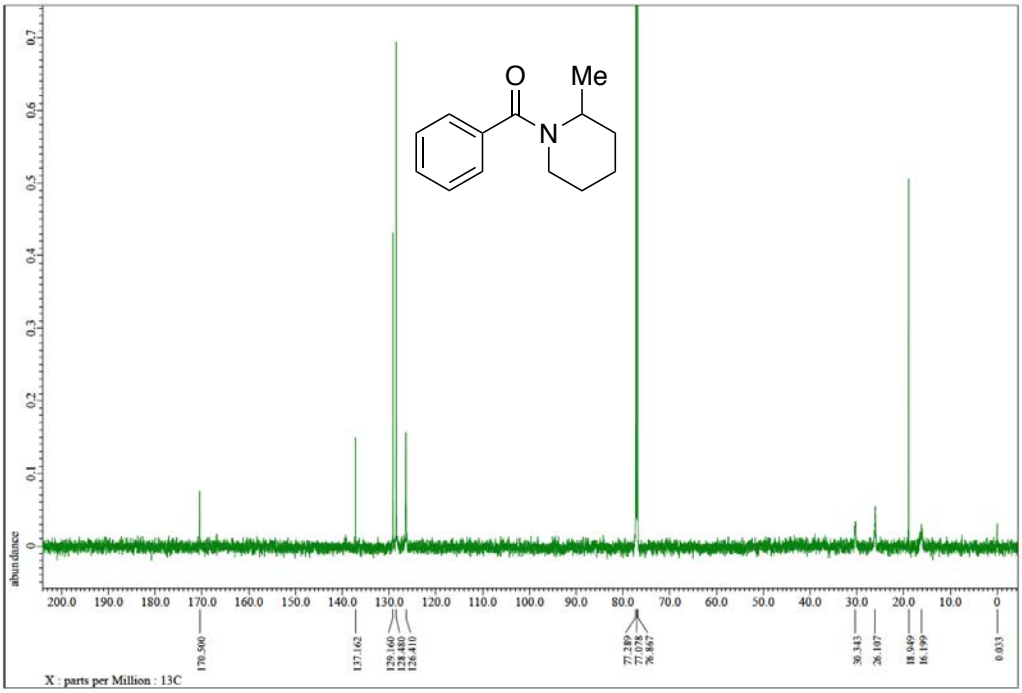
***N,N*-dipropylbenzamide (3ah)**



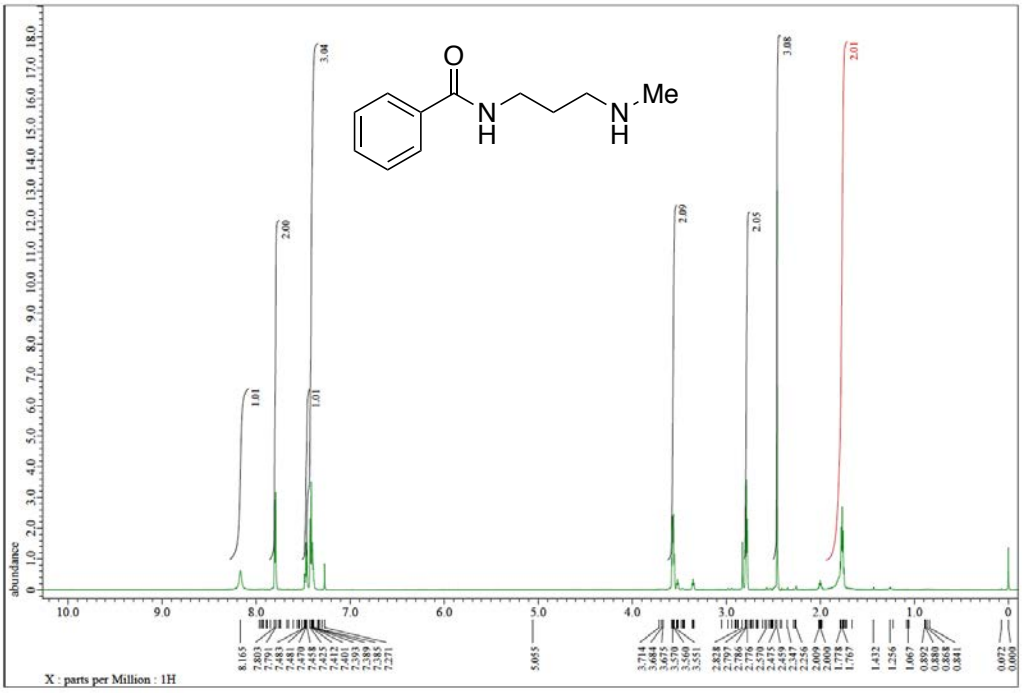


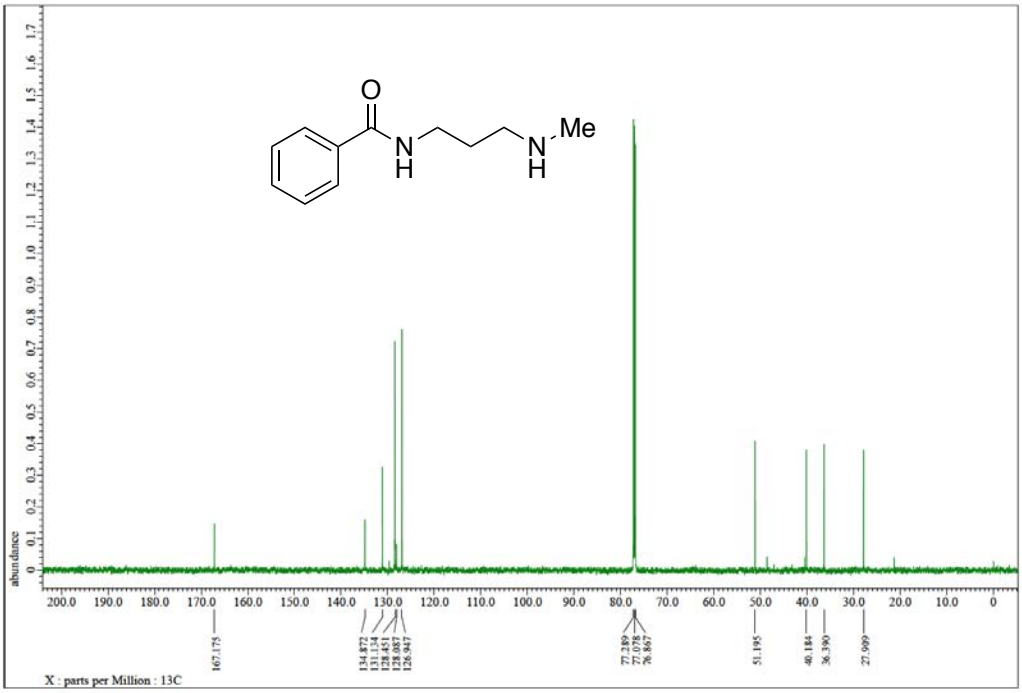
(2-methylpiperidin-1-yl)(phenyl)methanone (3ai)



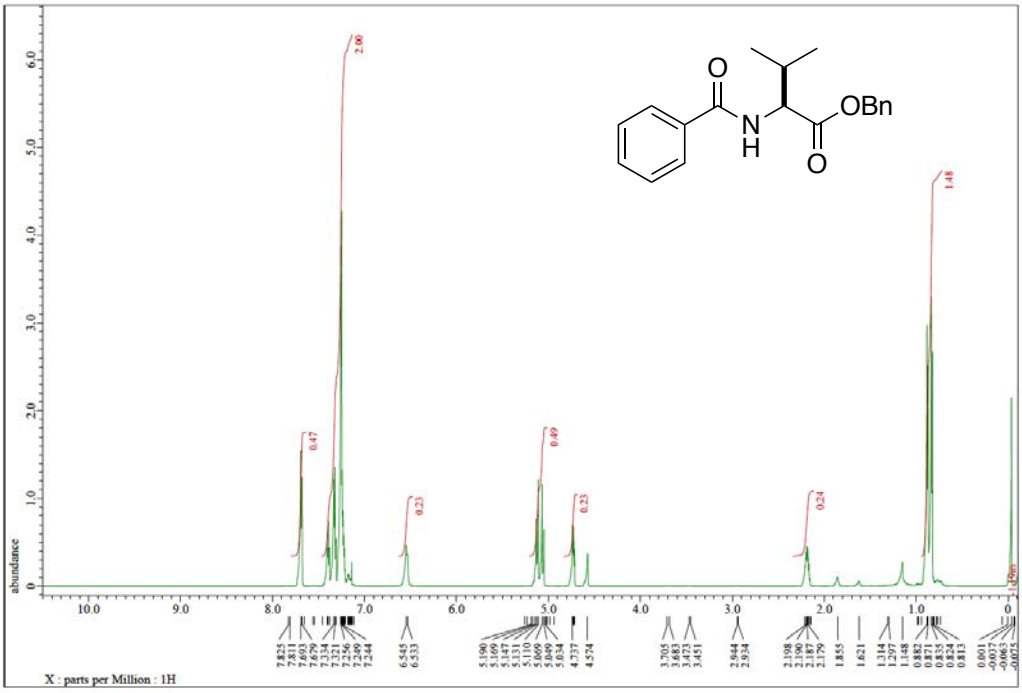


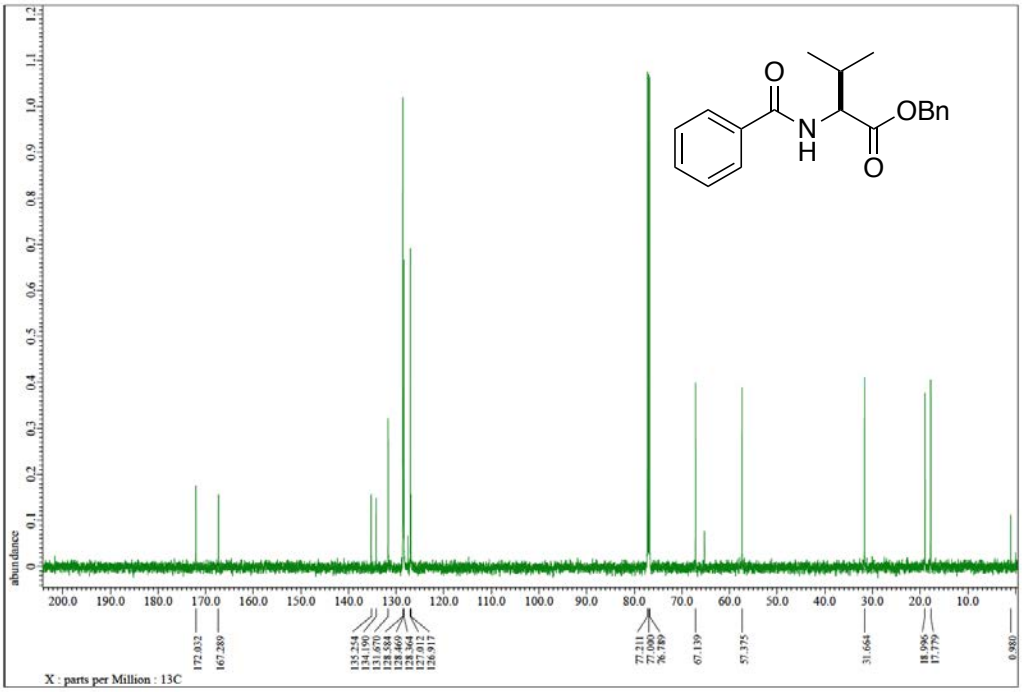
***N*-(3-(methylamino)propyl)benzamide (3aj)**



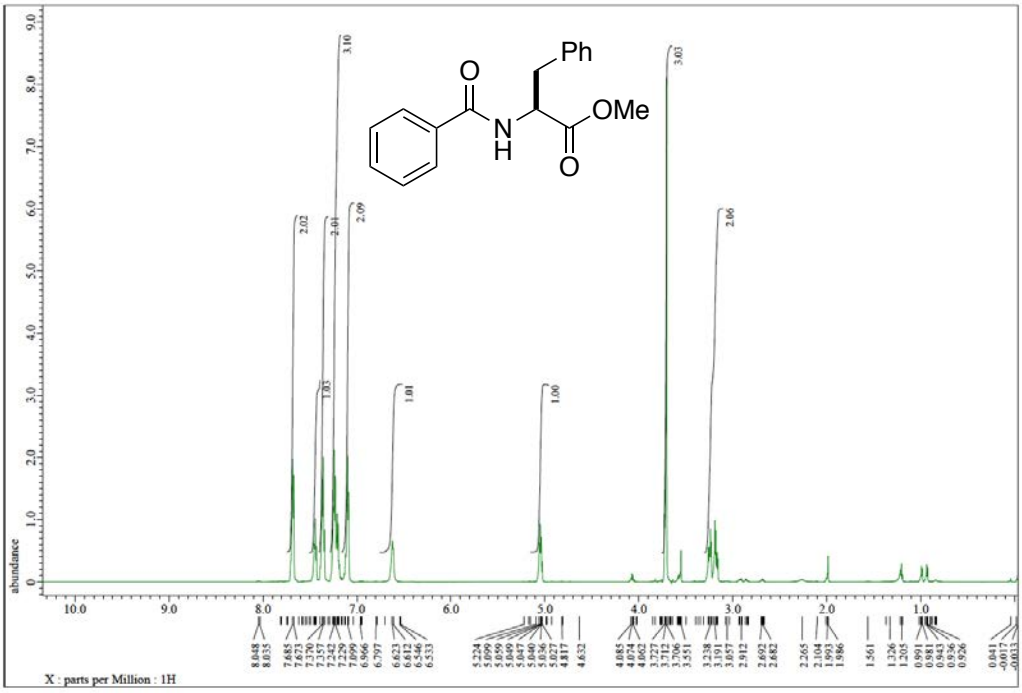


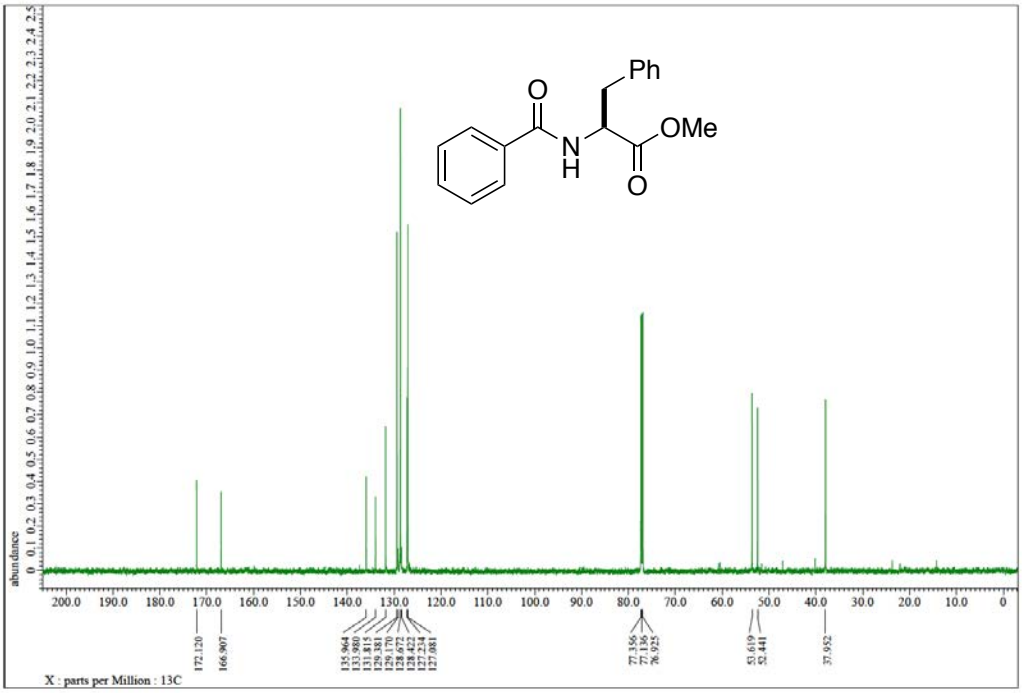
Benzyl benzoyl-$_L$-valinate (3ak)



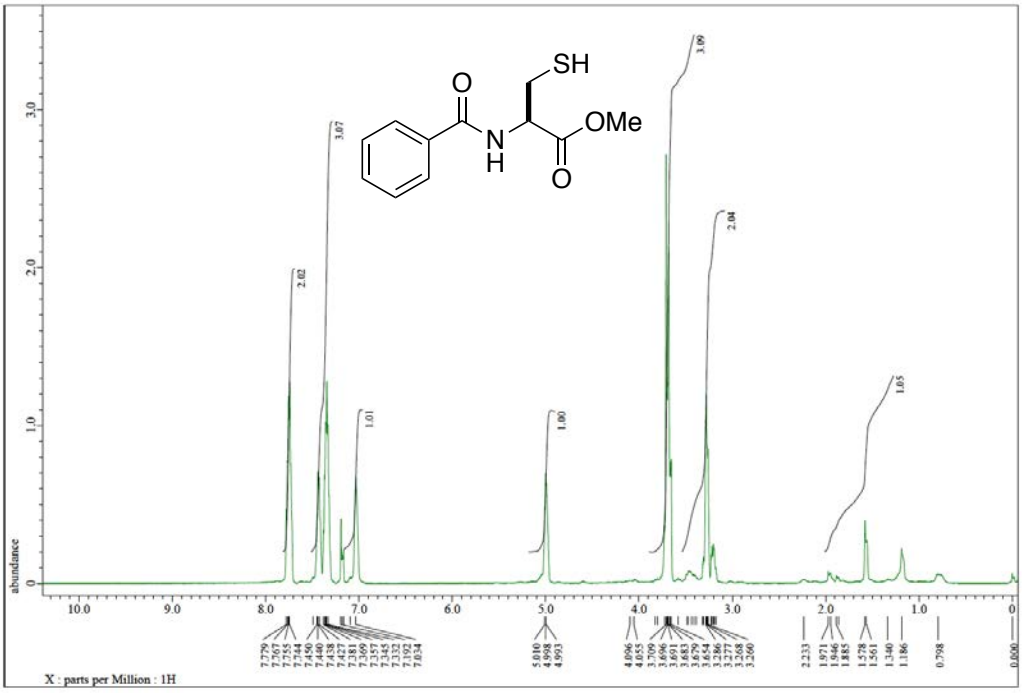


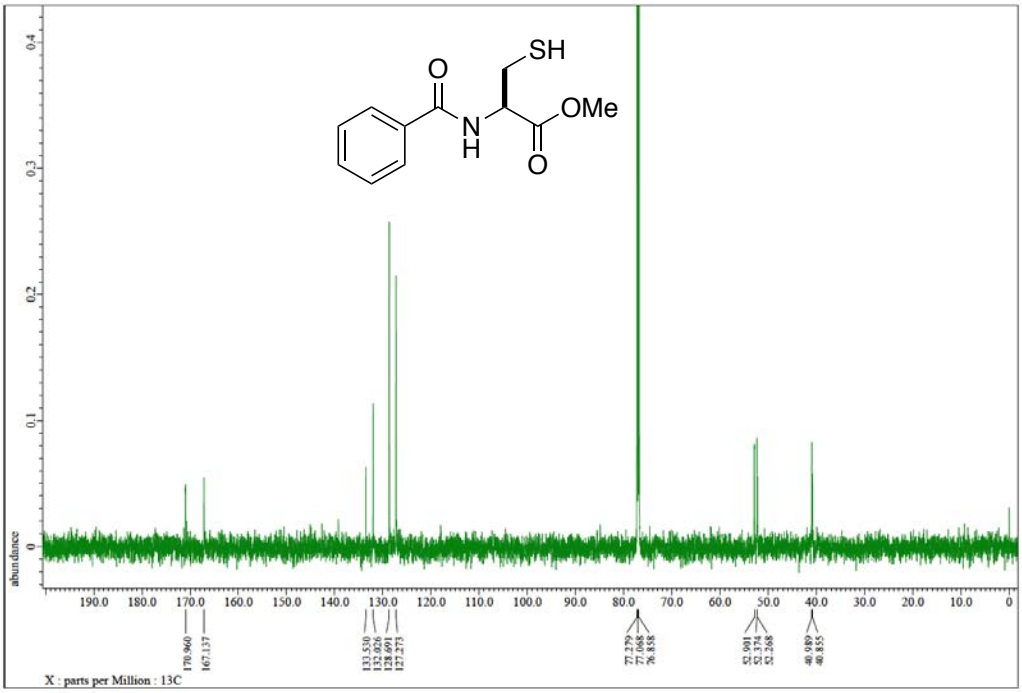
Methyl benzoyl-$_L$-phenylalaninate (3al)



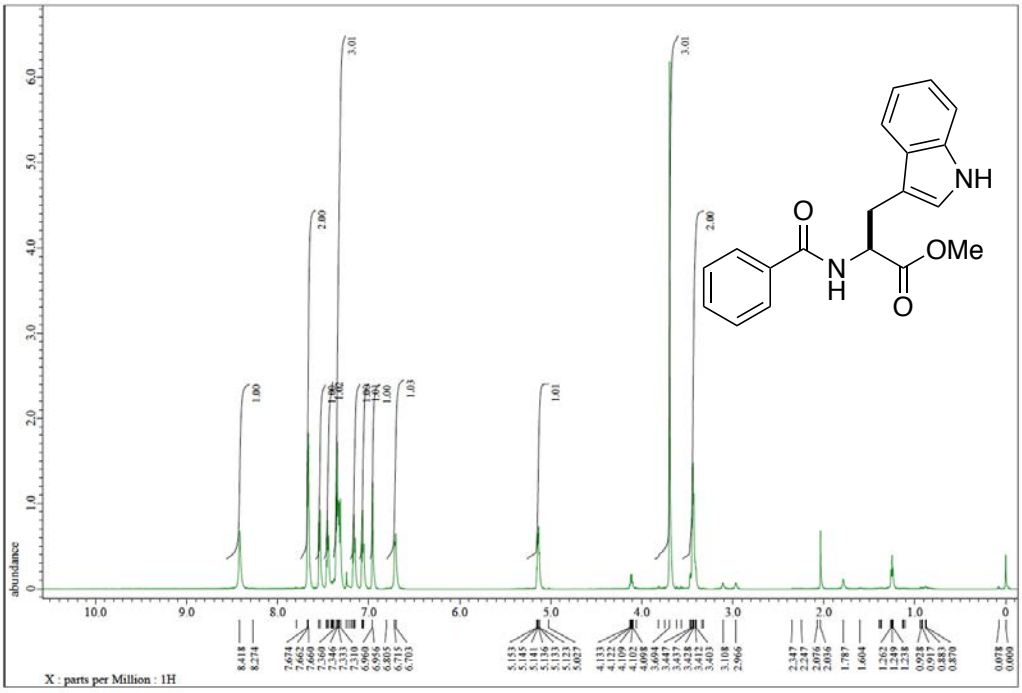


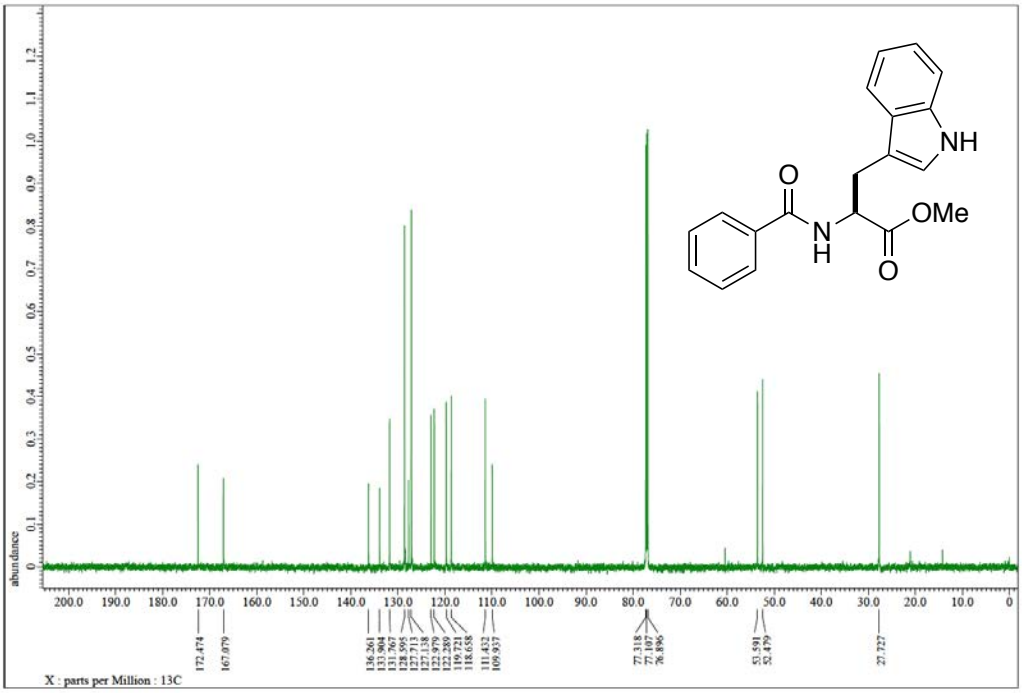
Methyl benzoyl-$_L$-cysteinate (3am)



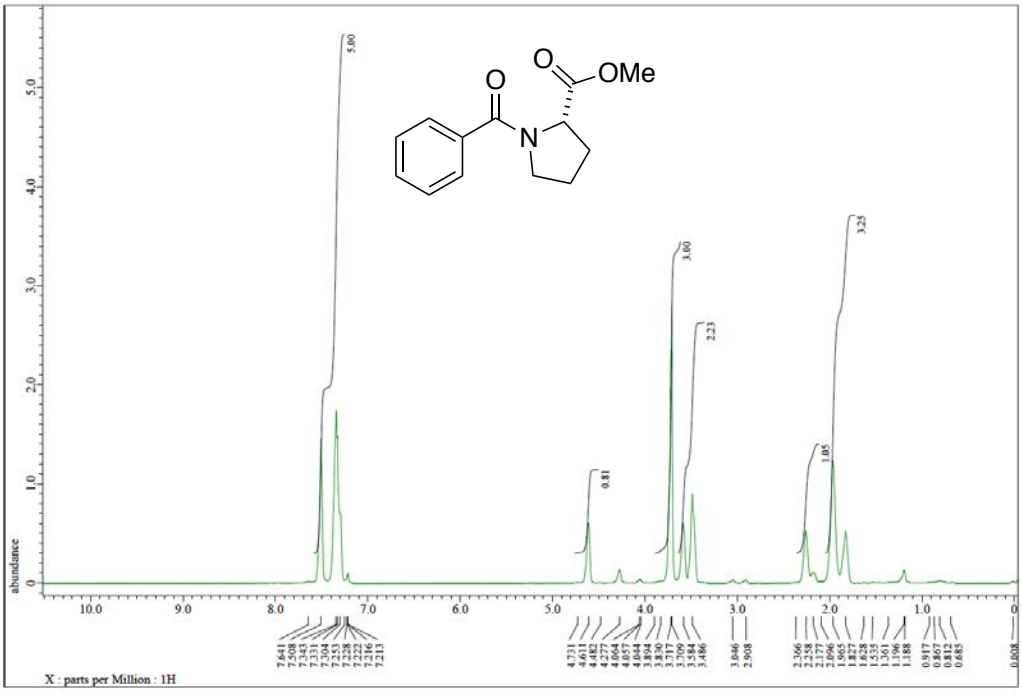


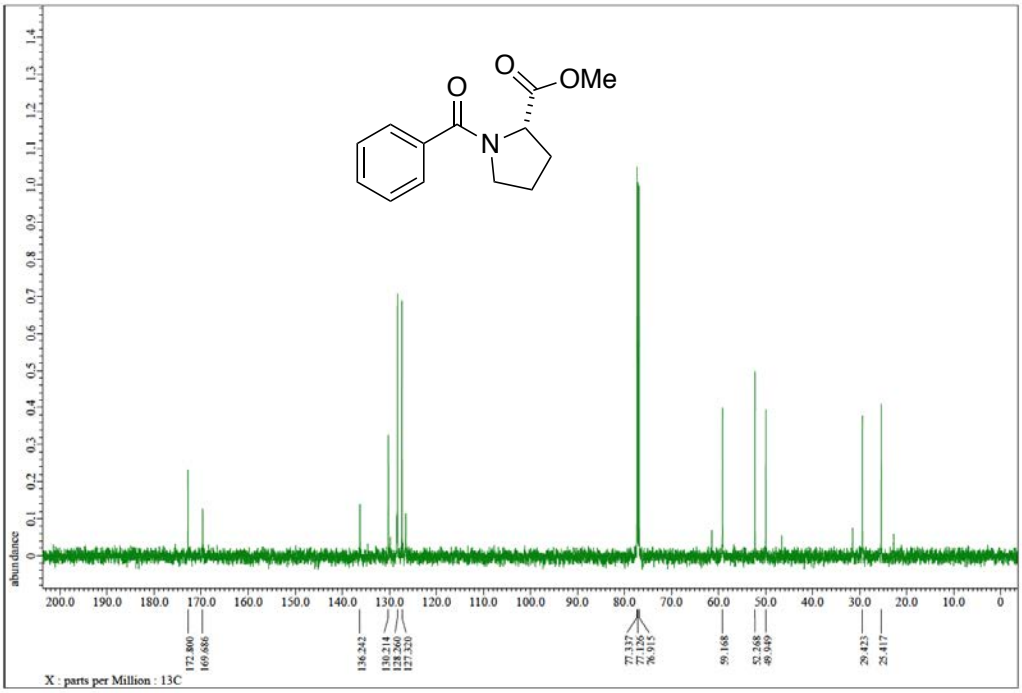
Methyl benzoyl-$_L$-tryptophanate (3an)



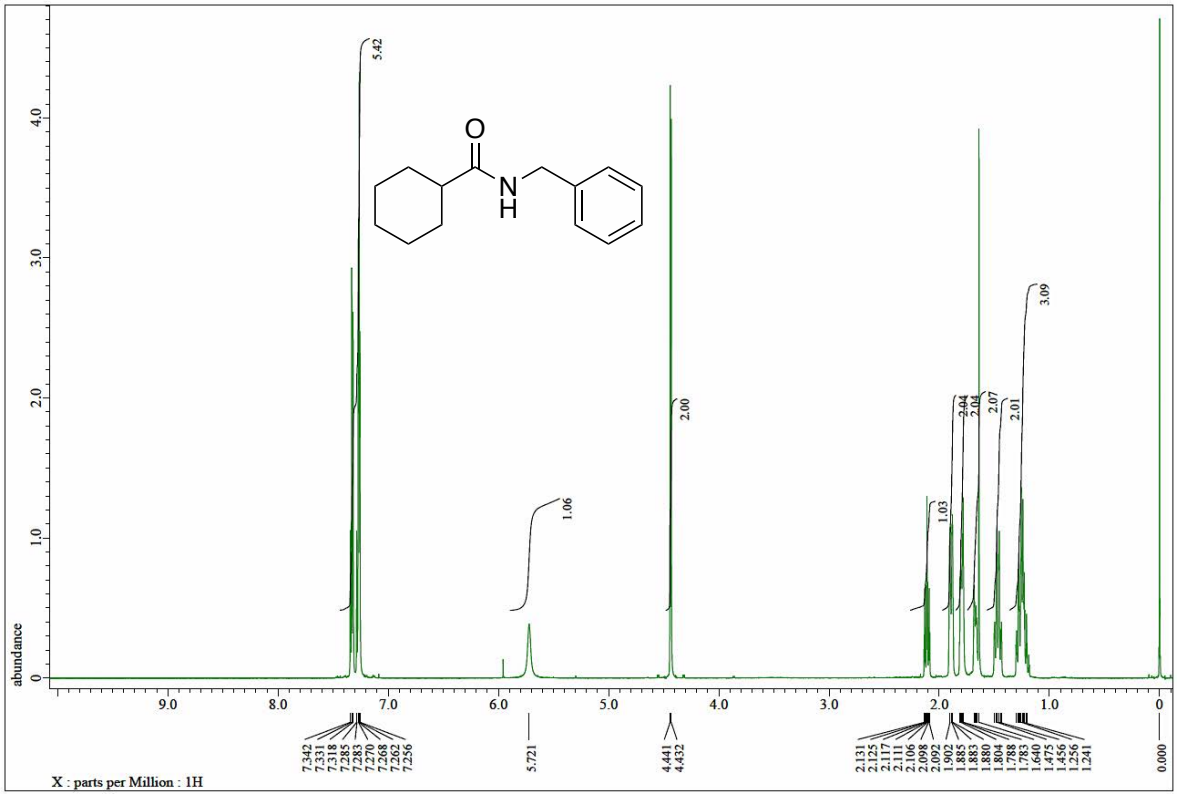


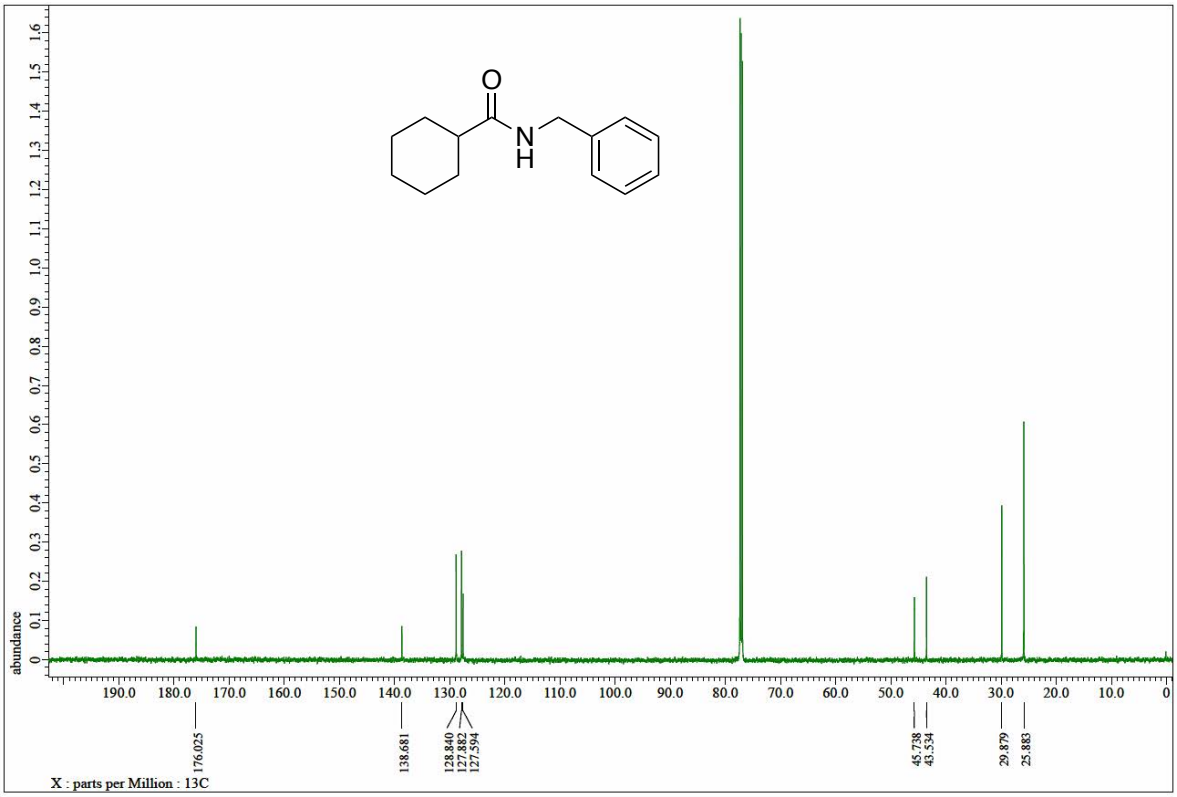
Methyl benzoyl-$_L$-prolinate (3ao)



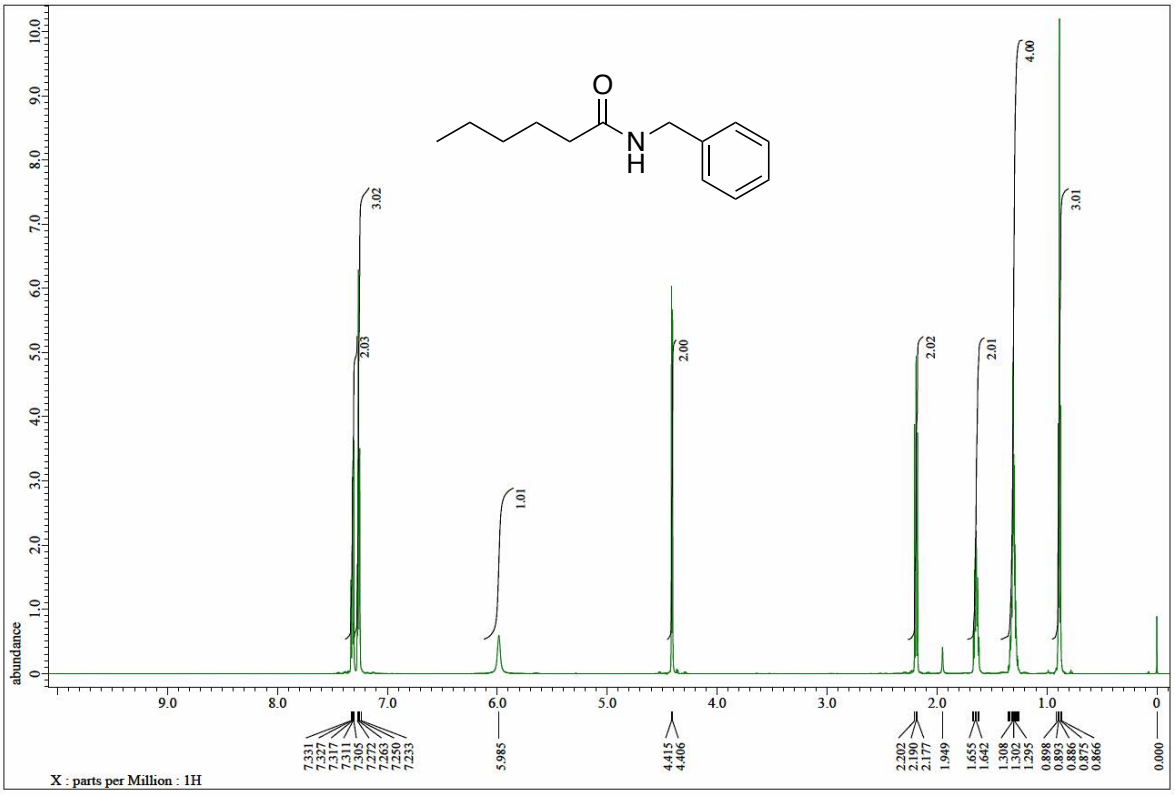


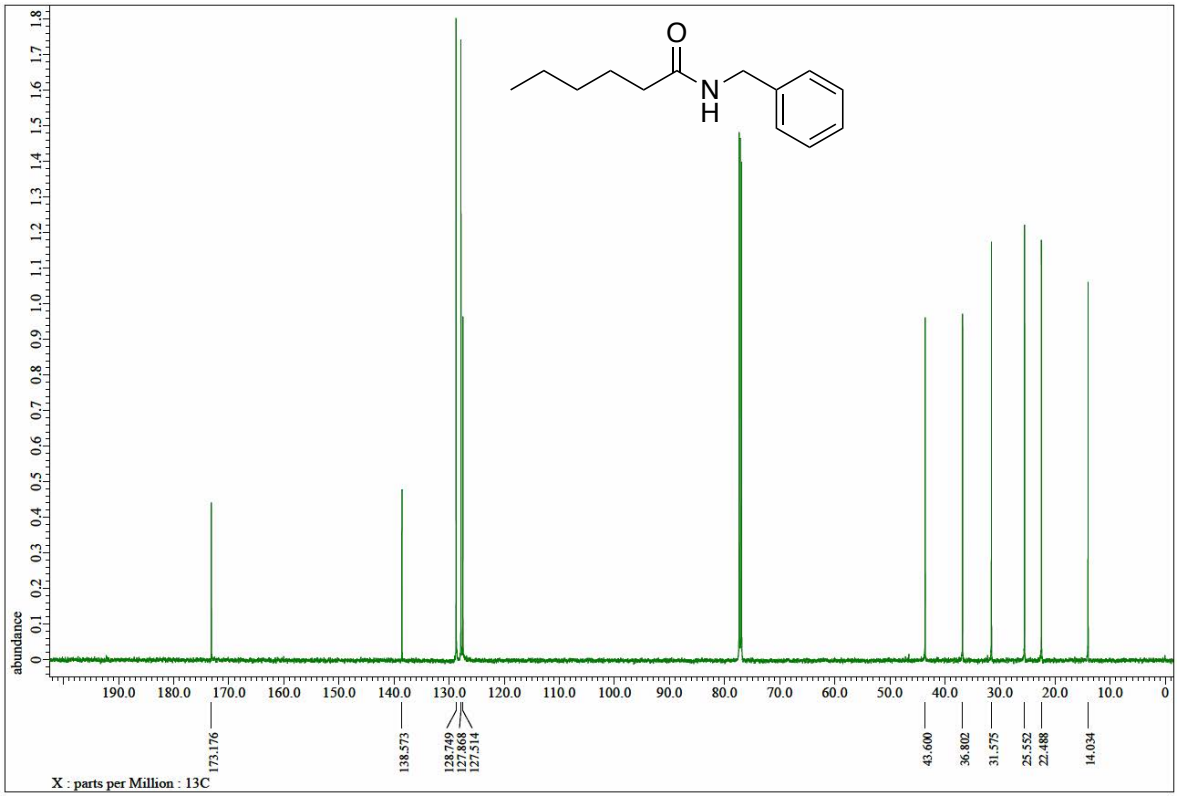
N-benzylcyclohexanecarboxamide (3va)



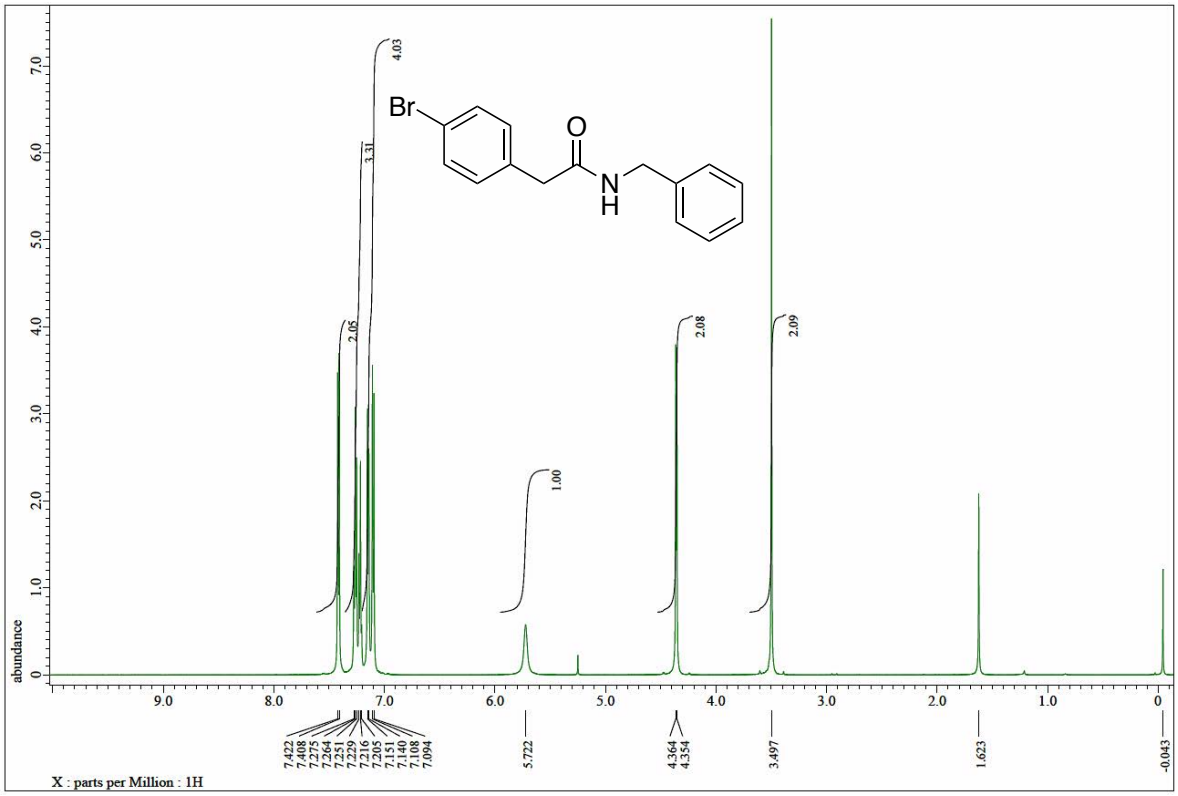


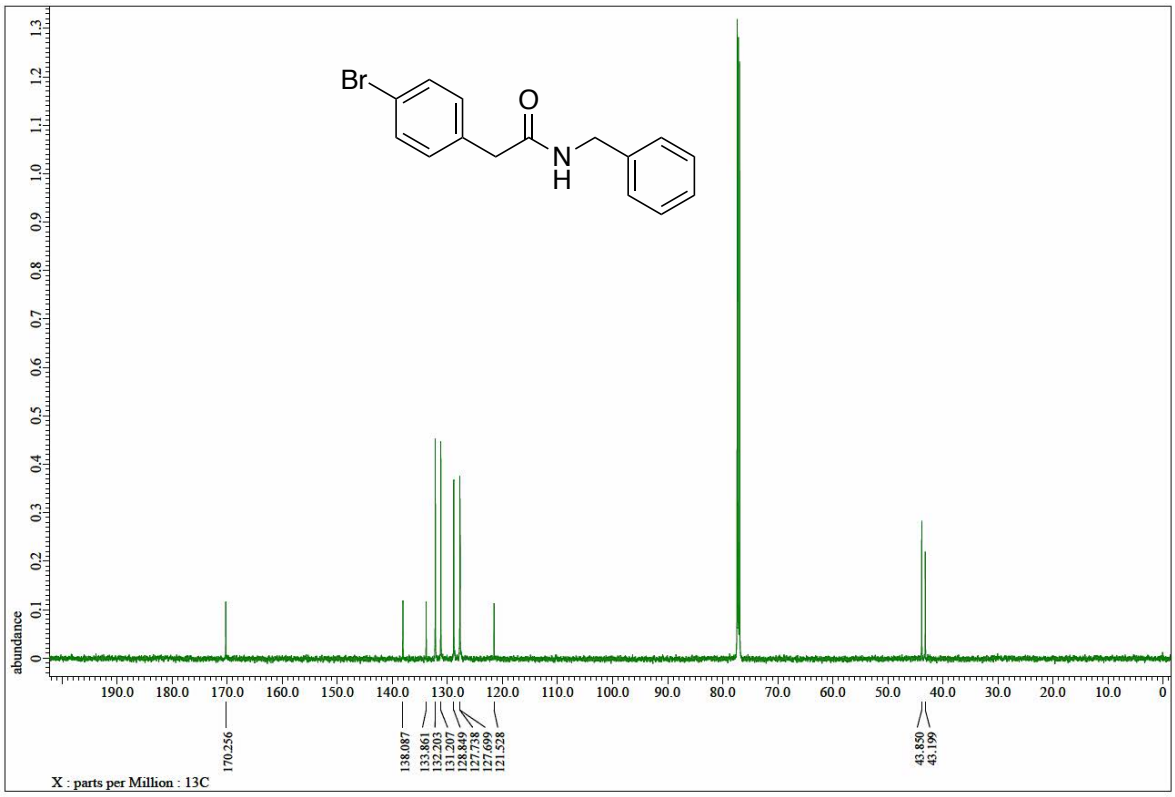
N-benzylhexanamide (3wa)



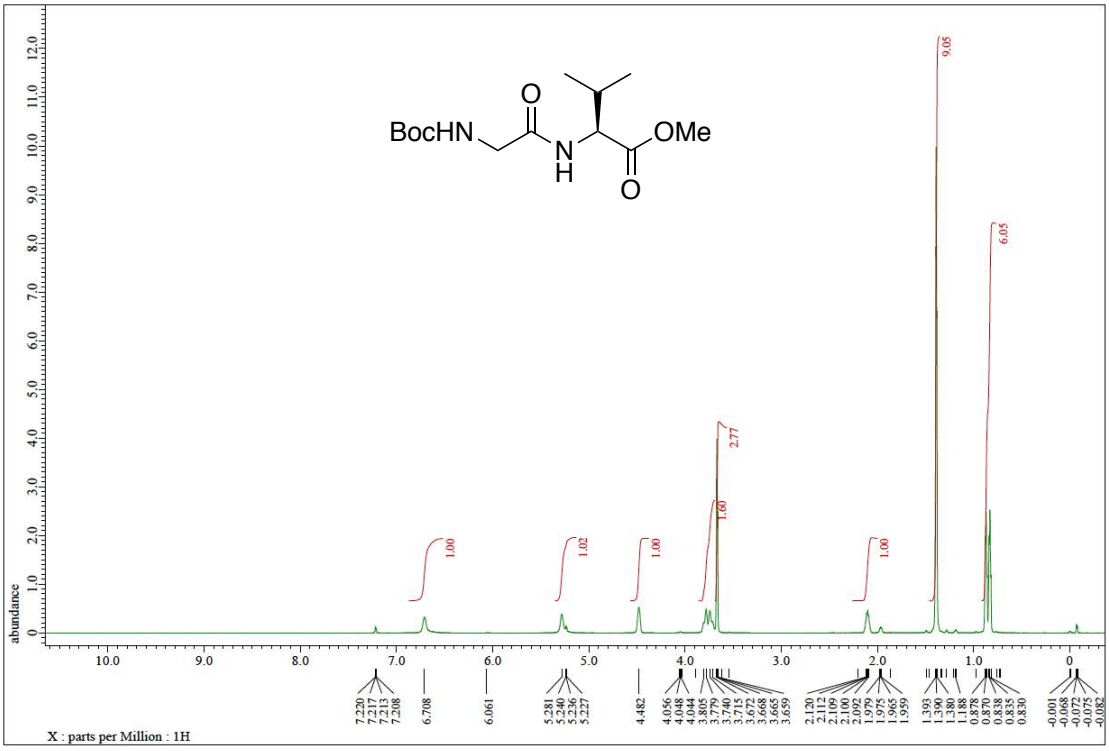


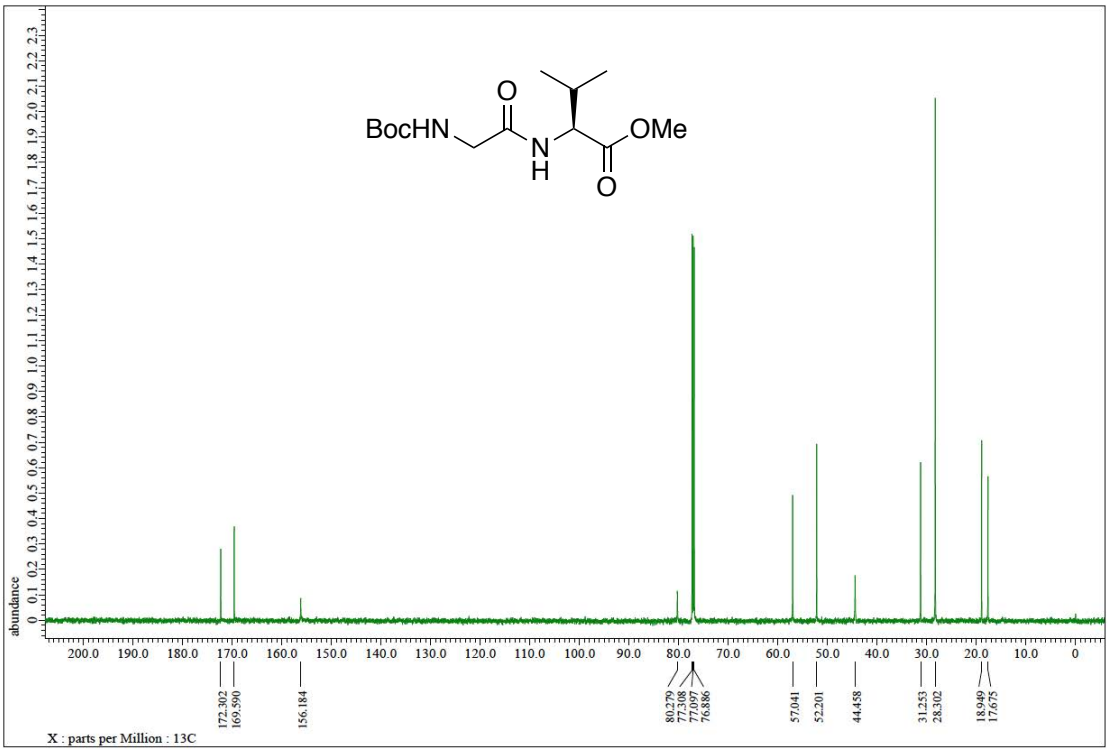
N-benzyl-2-(4-bromophenyl)acetamide (3xa)



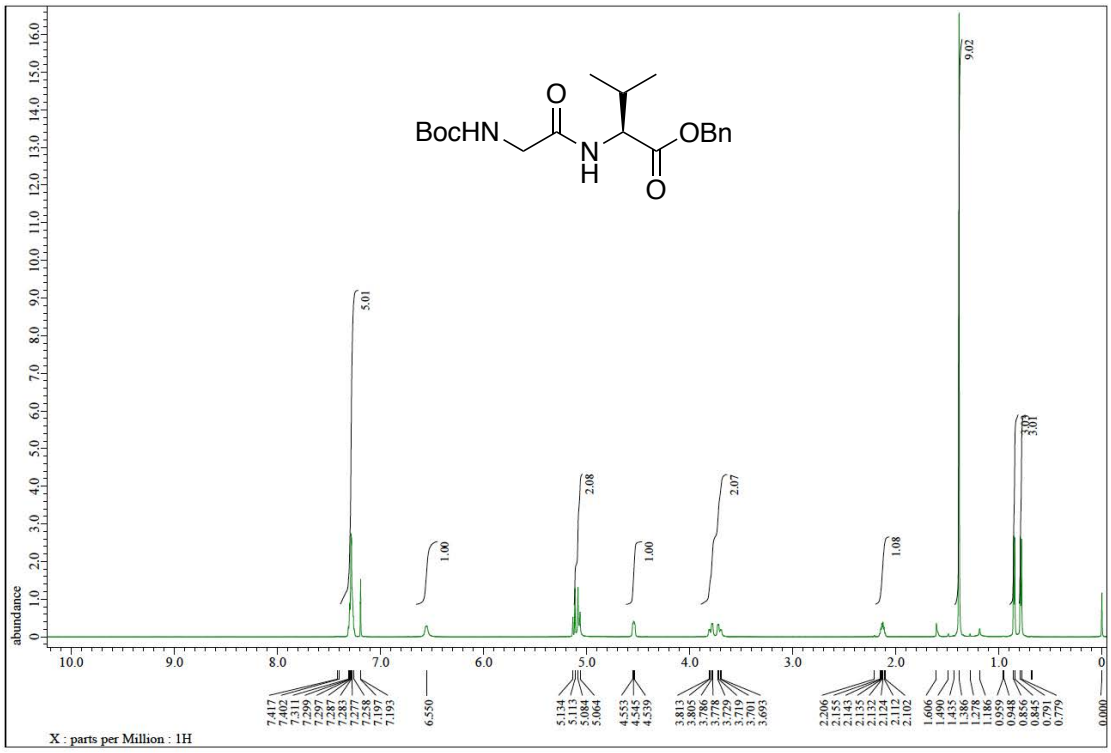


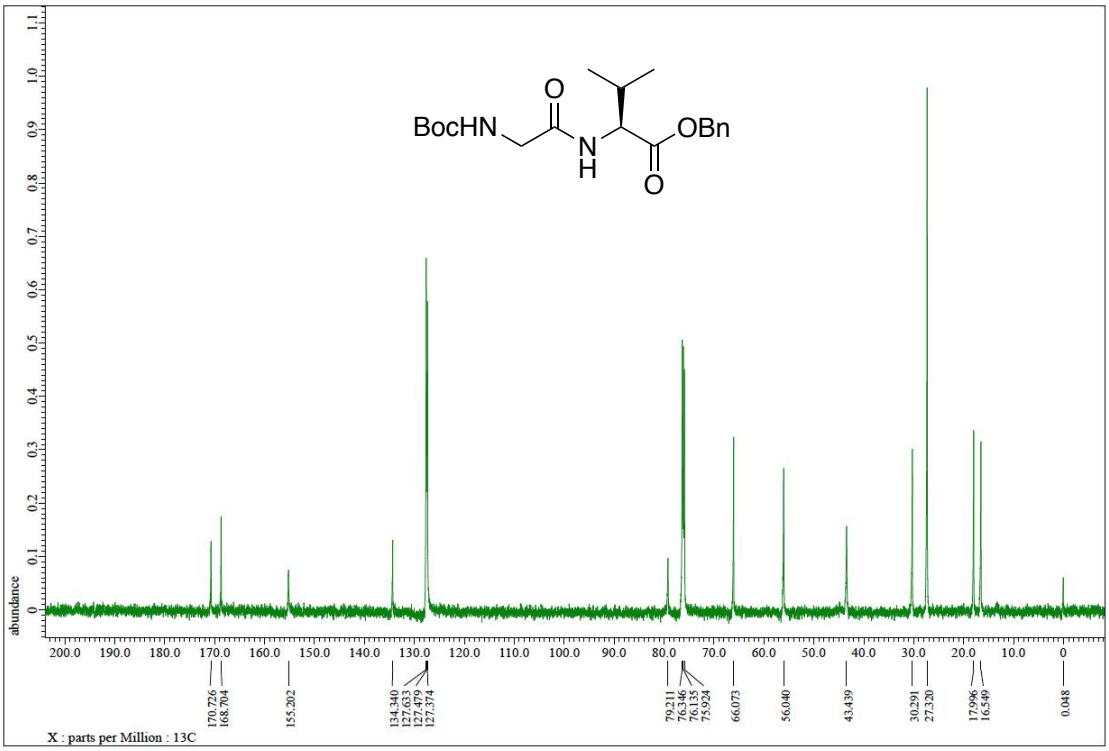
Methyl (tert-butoxycarbonyl)glycyl-$_L$-valinate (4aa)



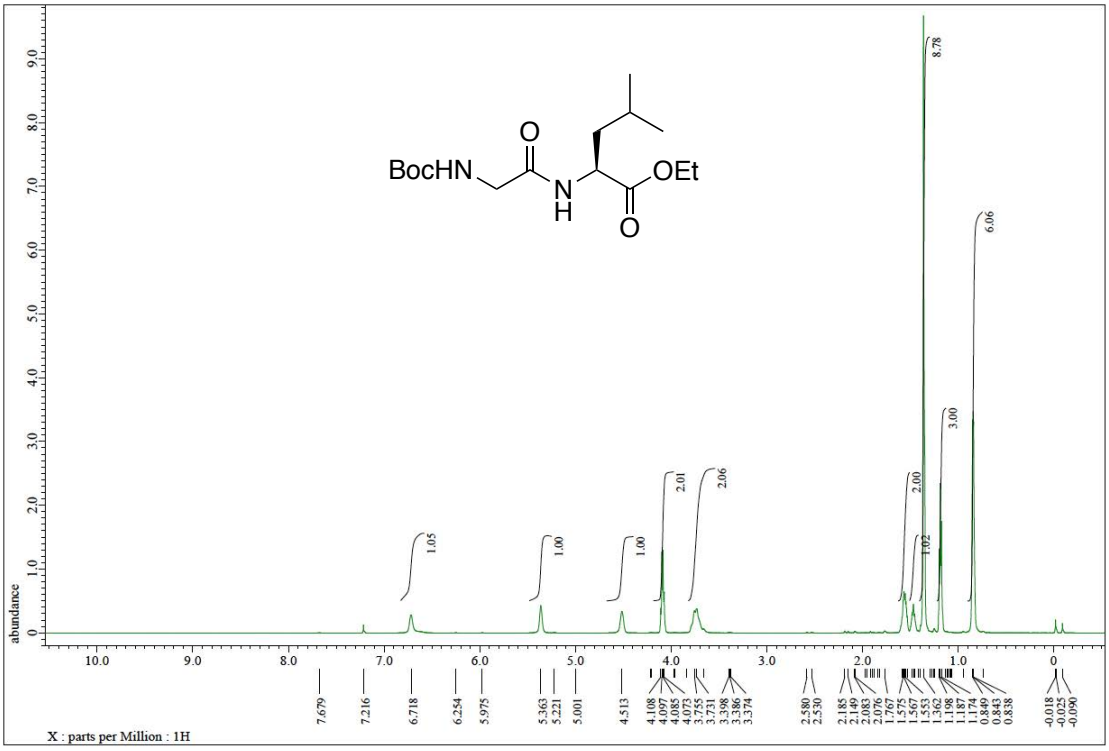


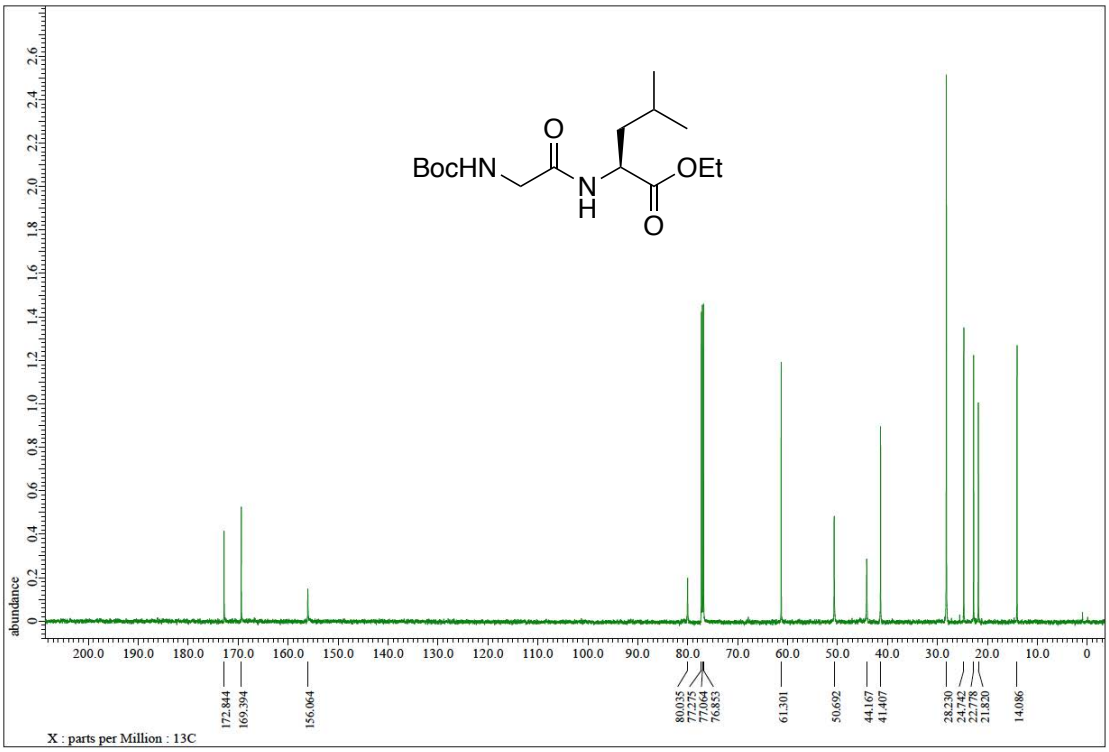
benzyl (tert-butoxycarbonyl)glycyl-$_L$-valinate (4ab)



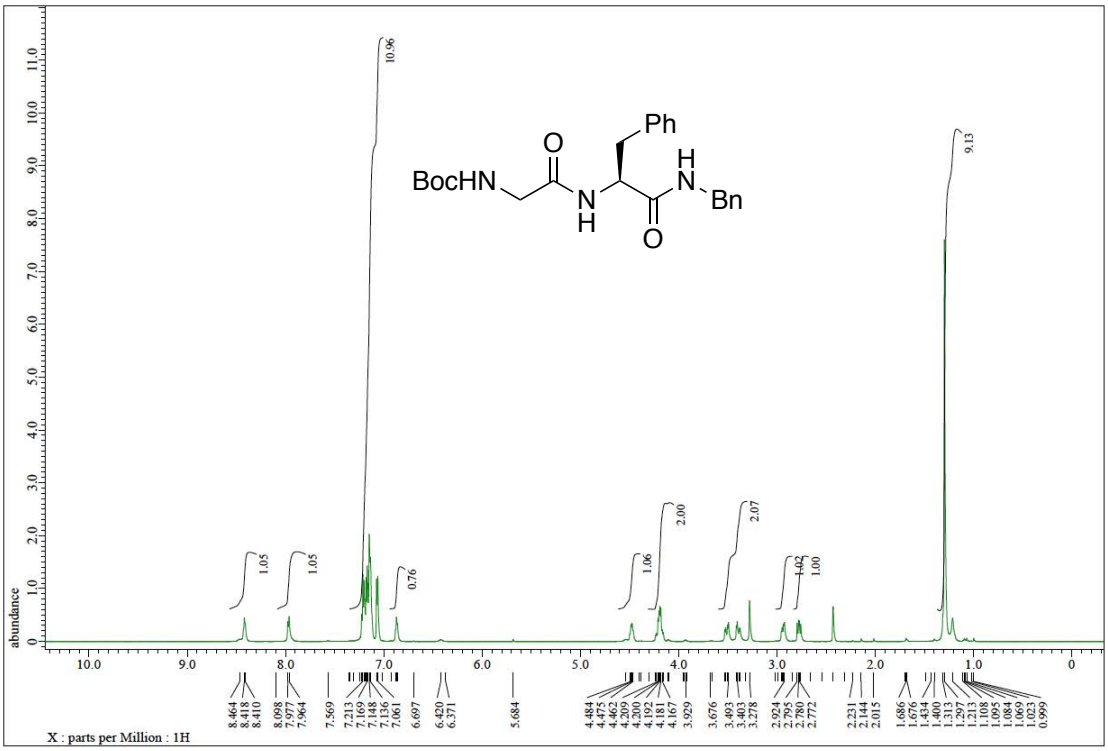


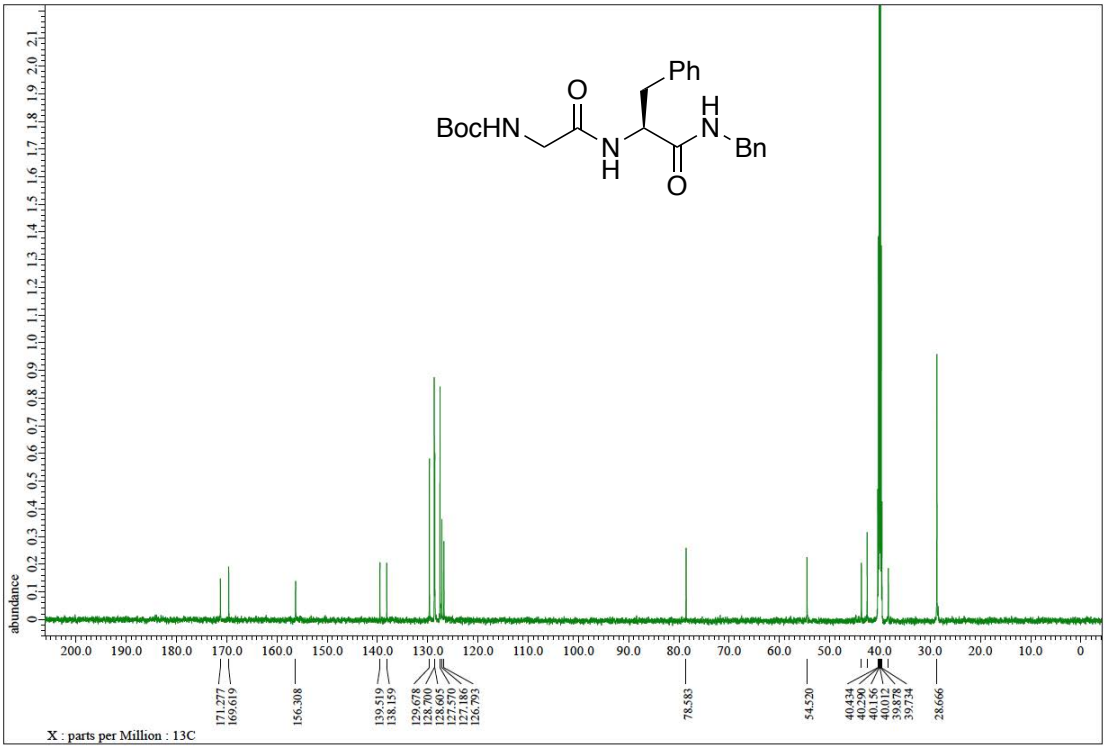
Ethyl (*tert*-butoxycarbonyl)glycyl-$_L$-leucinate (4ac)



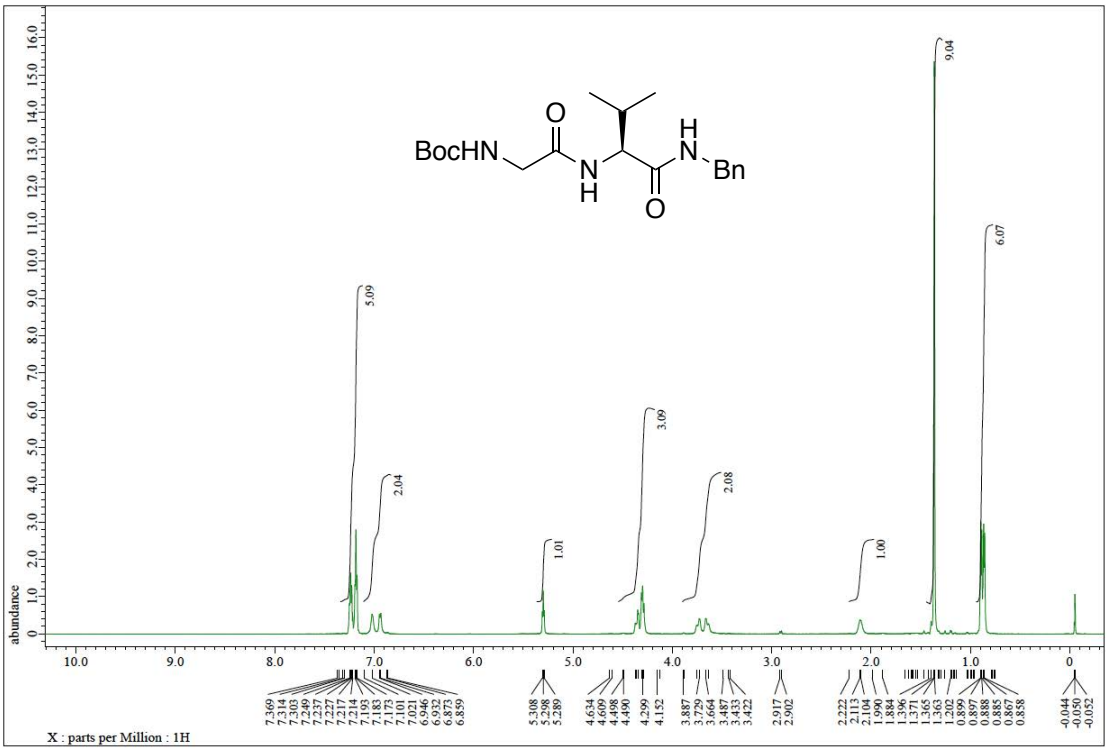


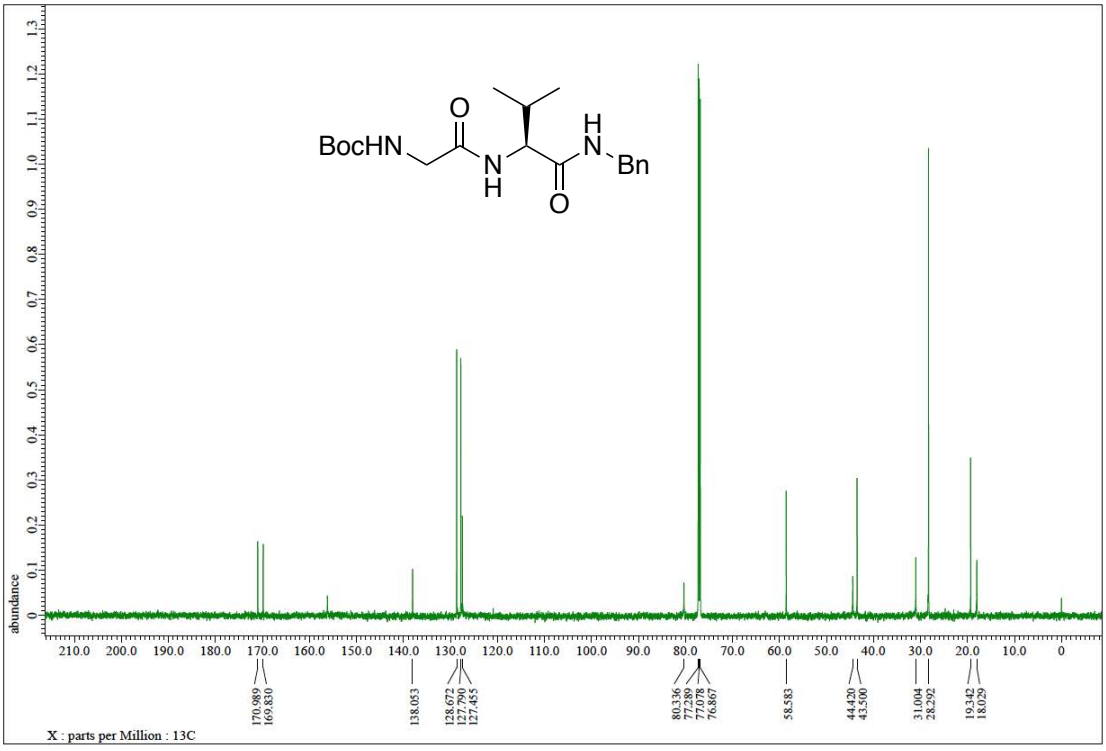
***tert*-Butyl (S)-(2-((1-(benzylamino)-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)-carbamate (4ad)**



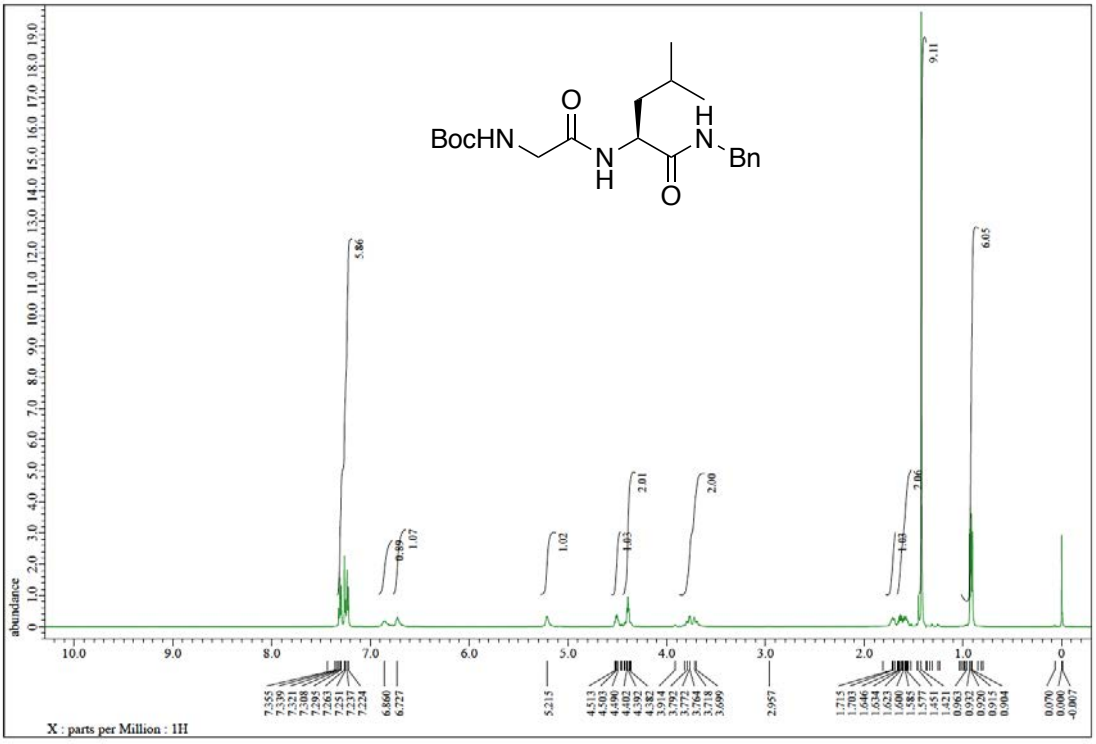


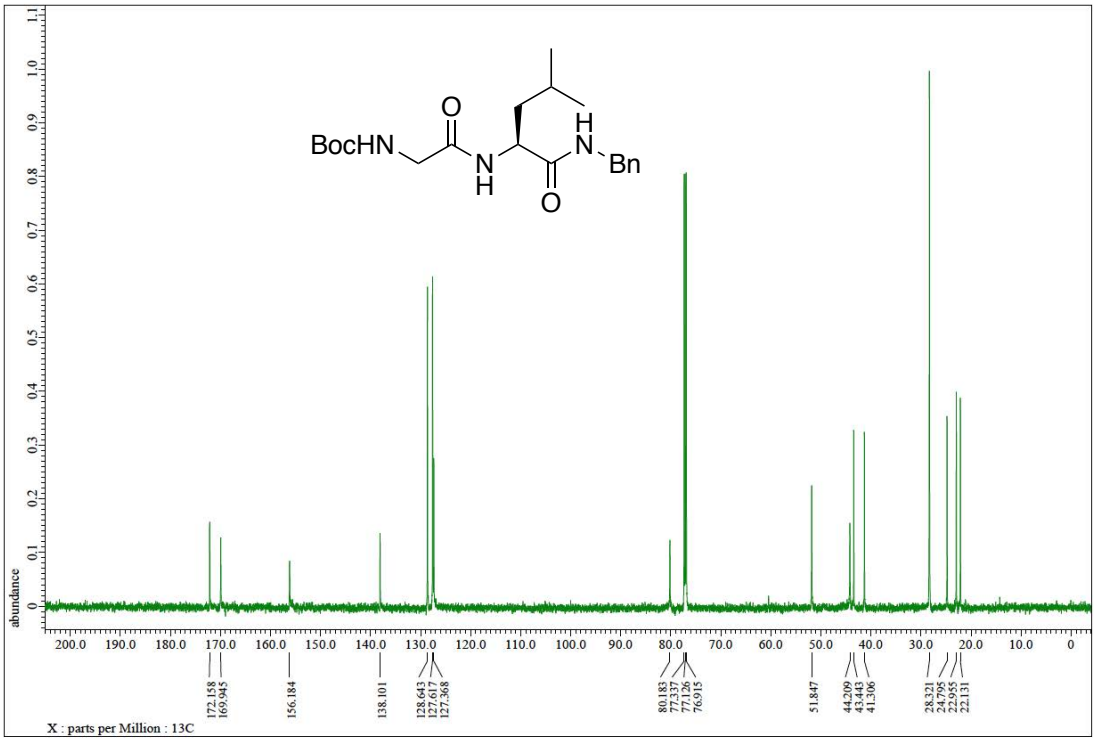
***tert*-Butyl (S)-(2-((1-(benzylamino)-3-methyl-1-oxobutan-2-yl)amino)-2-oxoethyl)-carbamate (4ae)**



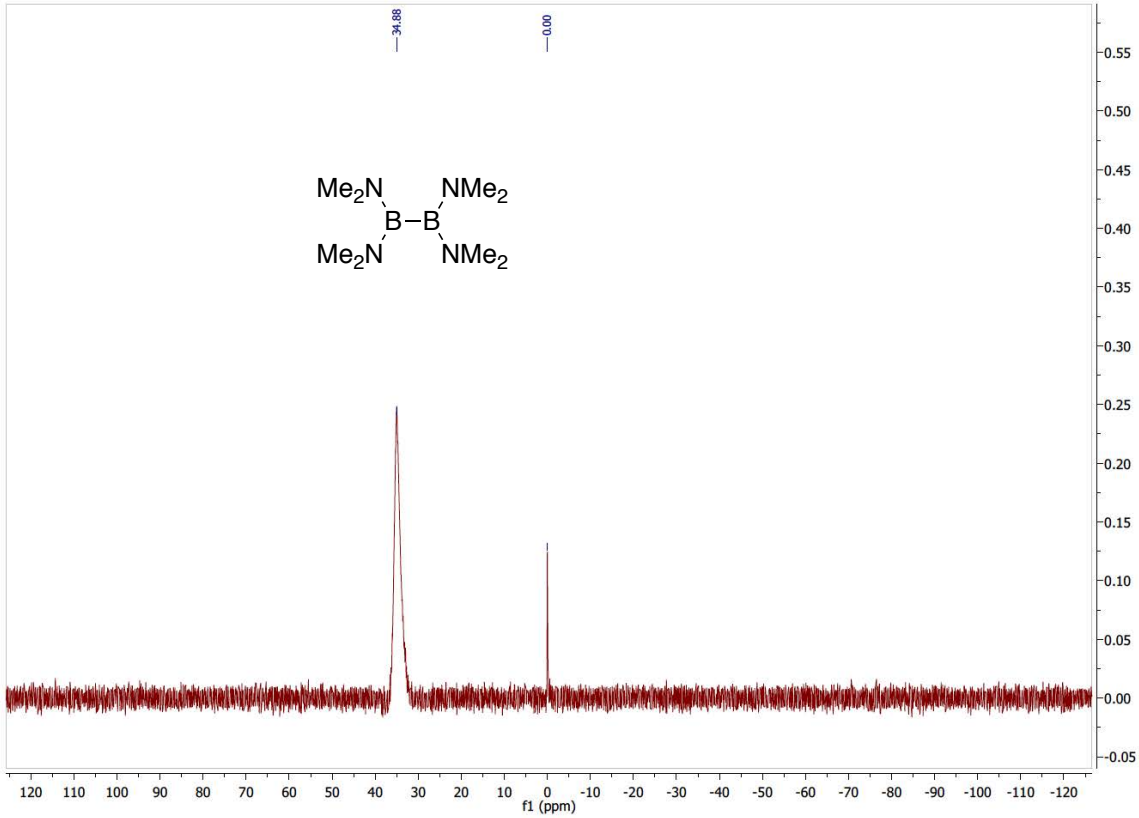


***tert*-butyl (S)-(2-((1-(benzylamino)-4-methyl-1-oxopentan-2-yl)amino)-2-oxoethyl)-carbamate (4af)**

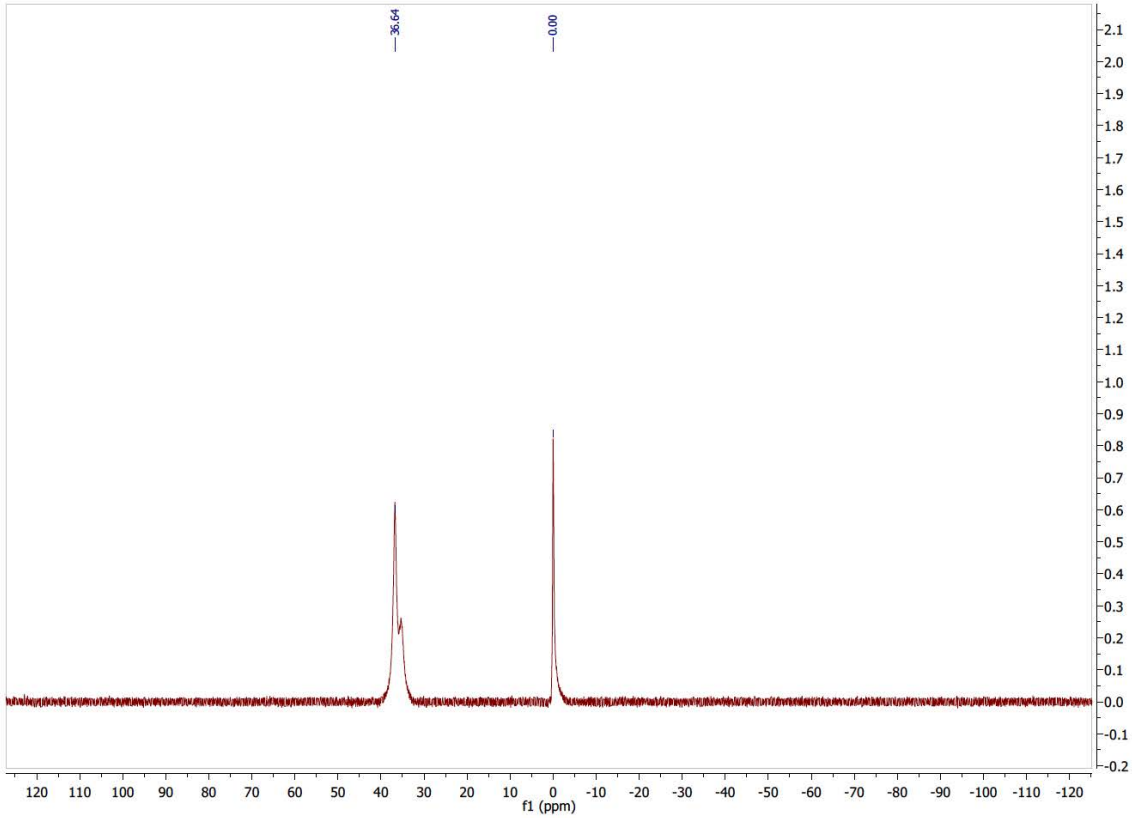




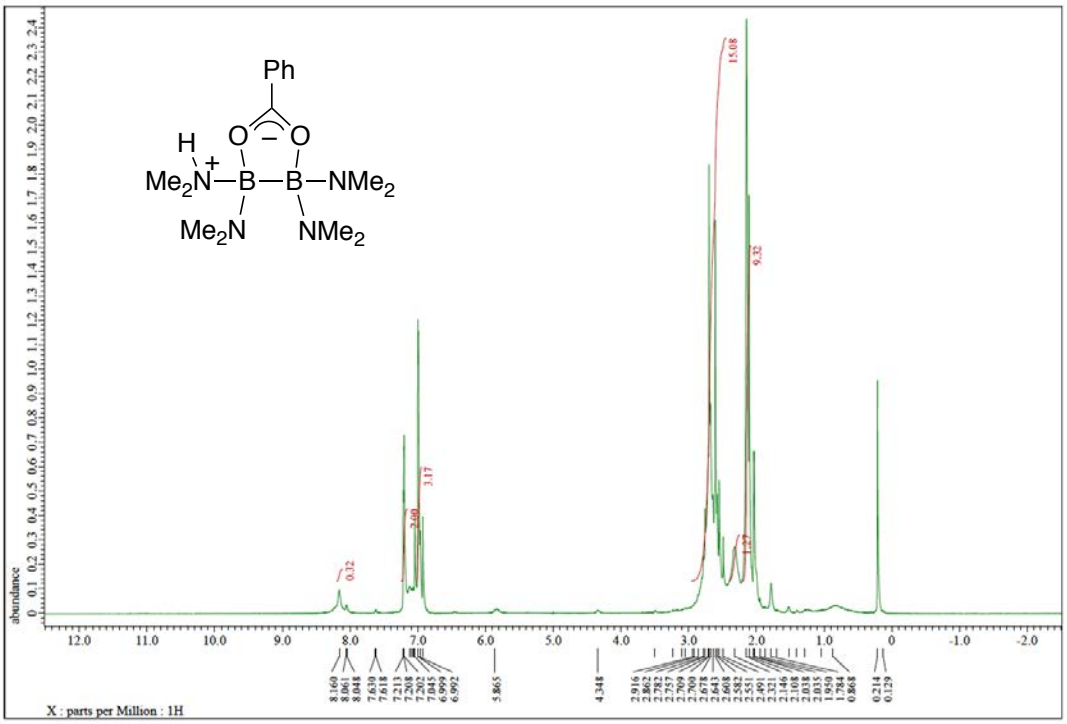
^{11}B NMR: tetrakis(dimethylamido)diboron (DB-**1** catalyst); {Ext. std. [BF_3**.**$O(C_2H5)_2$ = 0.00 ppm}



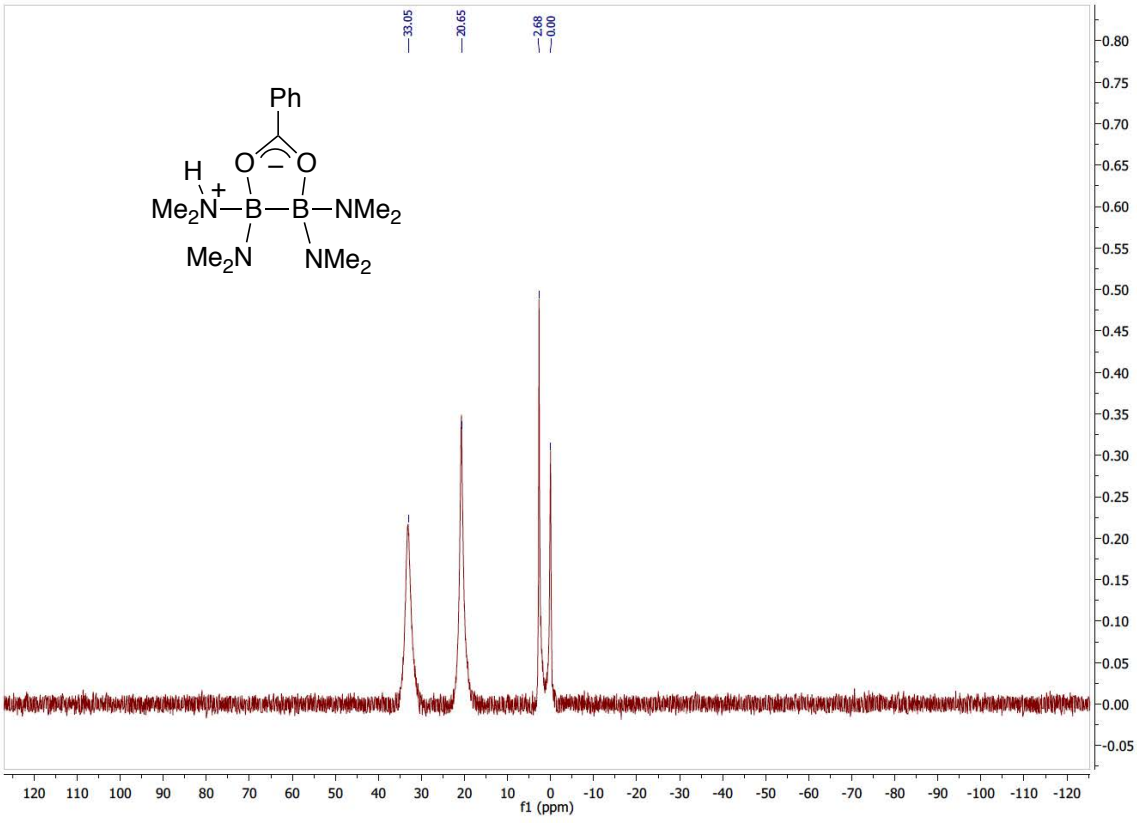
^{11}B NMR: DB-**1** + **2f**, rt, 24 h; {Ext. std. [BF_3**.**$O(C_2H5)_2$ = 0.00 ppm]}



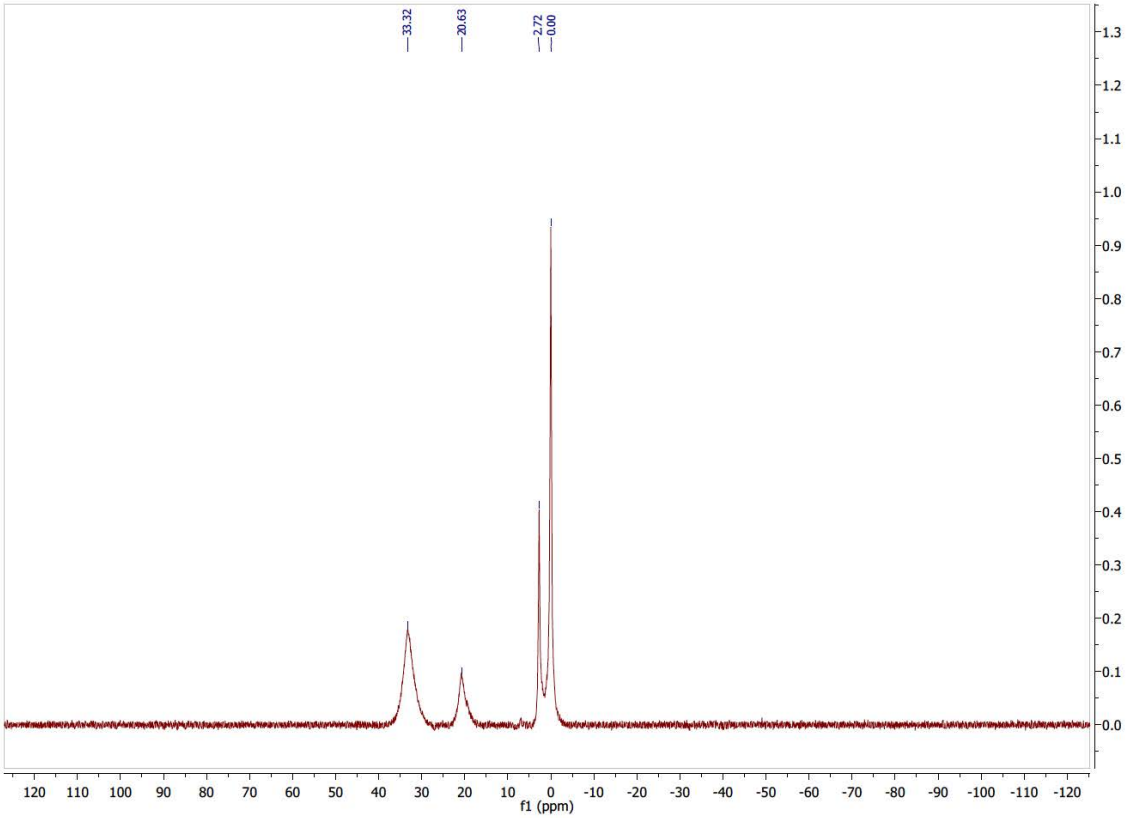
^{1}H NMR: DB-**1** + **1a**, rt, 24 h



^{11}B NMR: DB-**1** + **1a**, rt, 24 h; {Ext. std. [BF_3.$O(C_2H5)_2$ = 0.00 ppm]}



^{11}B NMR: DB-**1** + **1a** + **2f**, rt, 24 h; {Ext. std. [BF_3.$O(C_2H5)_2$ = 0.00 ppm]}



^{11}B NMR: DB-**1** + **1a** + **2f**, reflux, 2.5 h; {Ext. std. [BF_3.$O(C_2H5)_2$ = 0.00 ppm]}