Highly Chemoselective Reduction of Amides (Primary, Secondary, Tertiary) to Alcohols using SmI_2/amine/H_2O under Mild Conditions

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Supplementary Information

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List of Known Compounds/General Methods

All compounds reported in the manuscript have been described in the literature or are commercially available. Amides were purchased from commercial suppliers or prepared by standard methods.[1-13] Samarium(II) iodide was prepared by standard methods and titrated prior to use.[14-18] All experiments involving SmI_2 were performed using standard techniques under argon or nitrogen atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from Na/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR, and/or GC-MS analysis and comparison with authentic samples. All yields refer to yields determined by ^{1}H NMR using an internal standard unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 300, 400 and 500 MHz (^{1}H NMR) and 75, 100 and 125 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.27 and 77.2 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (J) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; br s, broad singlet. GC-MS chromatography was performed using Agilent 7890A GC System and Agilent 5975C inert XL EI/CI MSD with Triple Axis Detector equipped with Agilent HP-5MS column (19091S-433) (length 30 m, internal diameter 0.25 mm, film 0.25 μm) using helium as the carrier gas, flow rate of 1 mL/min, initial oven temperature of 40 °C or 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 25 °C/min ramp after 50 °C hold for 3 min to a final temperature of 300 °C, then hold at 300 °C for 5 min (splitlesss mode of injection, total run time of 18 min). All flash chromatography was performed using silica gel, 60 Å, 230−400 mesh. TLC analysis was carried out on aluminium sheets coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Experimental for characterization purposes. ^{1}H NMR, ^{13}C NMR, IR and HRMS data are reported for all new compounds.

Experimental Procedures and Characterization Data

General procedure for the reduction of amides. An oven-dried vial equipped with a stir bar was charged with an amide substrate (neat), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, typically 8 equiv) was added followed by Et_3N (typically, 72 equiv) and H_2O (typically, 72 equiv) with vigorous stirring, which resulted in the formation of a characteristic dark brown color of the SmI_2–Et_3N–H_2O complex, and the reaction mixture was stirred for the indicated time. In some cases, a solution of amide substrate (1.0 equiv, stock solution in THF, 1.0 mL) was added to the preformed samarium(II) iodide/amine/H_2O complex, and the reaction mixture was stirred for the indicated time. The excess of Sm(II) was oxidized by bubbling air through the reaction mixture, and the reaction mixture was diluted with CH_2Cl_2 (30 mL) and NaOH (1 *N*, 10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL), the organic layers were combined, dried over Na_2SO_4, filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 400 or 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples. Unless stated otherwise, the crude product was purified by chromatography on silica gel. Routinely, LC/MS analysis was used as a complementary method of analysis to confirm the product distribution. In all examples reported in the manuscript the observed C–N/C–O cleavage selectivity was >95:5. Note that reactions involving samarium(II) can typically be followed by visual observation of the color changes of the respective reaction mixtures. In the case of Sm(II)/amine/H_2O complexes, the color changes from Sm^{II} (dark brown) to Sm^{III} (dark to light green: oxidized, solvated; then white and yellow: fully oxidized, characteristic of SmI_2X).

Representative procedure for the reduction of amides. Table 2, entry 1. An oven-dried 100 mL round-bottomed flask equipped with a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (6 equiv, THF solution, 0.080 M) was added followed by Et_3N (36 equiv) and H_2O (36 equiv) with vigorous stirring, which resulted in the formation of a characteristic dark brown color of the SmI_2–Et_3N–H_2O complex. A solution of decanamide (1.0 equiv, 1.0 mmol, stock solution in THF, 5.0 mL) was added to the preformed samarium(II) iodide/amine/H_2O complex, and the reaction mixture was stirred for 18 h. The excess of SmI_2 was oxidized by bubbling air through

the reaction mixture. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and NaOH (50 mL, 1 *N*). The aqueous layer was extracted with CH_2Cl_2 (2 x 100 mL), organic layers were combined, dried over Na_2SO_4, filtered and concentrated. Analysis of the crude reaction mixture showed >98% conversion and >98:2 selectivity. Purification by chromatography afforded decan-1-ol in 95% yield. Characterization data are included in the section below.

*Characterization Data for Amides **1a-1o** (Table 1).*

3-Phenylpropanamide (1a). Table 1, Entry 1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (t, *J* = 7.5 Hz, 2 H), 2.84 (t, *J* = 7.5 Hz, 2 H), 5.76 (br, 1 H), 6.26 (br, 1 H), 7.08-7.12 (m, 3 H), 7.16-7.20 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4, 37.5, 126.3, 128.3, 128.6, 140.7, 175.5.

***N*-Butyl-3-phenylpropanamide (1b). Table 1, Entry 2.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.0 Hz, 3 H), 1.13-1.21 (m, 2 H), 1.29-1.35 (m, 2 H), 2.39 (t, *J* = 7.5 Hz, 2 H), 2.87 (t, *J* = 8.5 Hz, 2 H), 3.09-3.13 (m, 2 H), 5.79 (br, 1 H), 7.09-7.13 (m, 3 H), 7.16-7.21 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 20.0, 31.6, 31.9, 38.4, 39.3, 126.2, 128.4, 128.5, 140.9, 172.4.

***N*-Dodecyl-3-phenylpropanamide (1c). Table 1, Entry 3.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.9 Hz, 3 H), 1.13-1.36 (m, 18 H), 1.37-1.48 (m, 2 H), 2.47 (t, *J* = 7.5 Hz, 2 H), 2.98 (t, *J* = 7.8 Hz, 2 H), 3.21 (q, *J* = 6.9 Hz, 2 H), 5.42 (br, 1 H), 7.17-7.24 (m, 3 H), 7.26-7.33 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 26.9, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 29.7, 31.8, 31.9, 38.6, 39.6, 126.2, 128.4, 128.5, 140.9, 172.0.

***N*-Phenyl-3-phenylpropanamide (1d). Table 1, Entry 4.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.54 (t, *J* = 7.0 Hz, 2 H), 2.93 (t, *J* = 7.5 Hz, 2 H), 6.99 (t, *J* = 7.0 Hz, 1 H), 7.09-7.13 (m, 3 H), 7.15-7.21 (m, 4 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.45 (br, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.6, 39.4, 120.1, 124.4, 126.4, 128.4, 128.7, 130.0, 137.8, 140.7, 170.8.

***N*,*N*-Diethyl-3-phenylpropanamide (1e). Table 1, Entry 5.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (t, *J* = 6.5 Hz, 3 H), 1.03 (t, *J* = 7.0 Hz, 3 H), 2.52 (t, *J* = 8.0 Hz, 2 H), 2.91 (t, *J* = 7.5 Hz, 2 H), 3.14 (q, *J* = 7.5 Hz, 2 H), 3.30 (q, *J* = 7.0 Hz, 2 H), 7.09-7.16 (m, 3 H), 7.19-7.23 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.1, 14.3, 31.7, 35.1, 40.2, 41.9, 126.1, 128.5, 128.5, 141.6, 171.3.

1-(Azetidin-1-yl)-3-phenylpropan-1-one (1f). Table 1, Entry 6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99-2.06 (m, 2 H), 2.22 (t, *J* = 7.5 Hz, 2 H), 2.82 (t, *J* = 7.5 Hz, 2 H), 3.78 (t, *J* = 7.5 Hz, 2 H),

3.86 (t, *J* = 7.5 Hz, 2 H), 7.06-7.11 (m, 3 H), 7.15-7.19 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9, 31.1, 33.1, 47.7, 49.9, 126.1, 128.3, 128.4, 141.2, 172.1.

3-Phenyl-1-(pyrrolidin-1-yl)propan-1-one (1g). Table 1, Entry 7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.79-1.92 (m, 4 H), 2.58 (t, *J* = 7.5 Hz, 2 H), 3.0 (t, *J* = 8.0 Hz, 2 H), 3.30 (t, *J* = 7.0 Hz, 2 H), 3.47 (t, *J* = 7.0 Hz, 2 H), 7.19-7.26 (m, 3 H), 7.28-7.32 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.4, 26.1, 31.2, 36.8, 45.7, 46.6, 126.1, 128.5, 128.5, 141.5, 170.9.

3-Phenyl-1-(piperidin-1-yl)propan-1-one (1h). Table 1, Entry 8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34-1.39 (m, 2 H), 1.41-1.46 (m, 2 H), 1.50-1.56 (m, 2 H), 2.54 (t, *J* = 8.0 Hz, 2 H), 2.89 (t, *J* = 7.5 Hz, 2 H), 3.25 (t, *J* = 6.0 Hz, 2 H), 3.48 (t, *J* = 5.5 Hz, 2 H), 7.09-7.15 (m, 3 H), 7.19-7.23 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.5, 25.6, 26.4, 31.6, 35.2, 42.7, 46.6, 126.1, 128.5, 128.5, 141.5, 170.4.

***N*-Methoxy-*N*-methyl-3-phenylpropanamide (1i). Table 1, Entry 9.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.75 (t, *J* = 7.8 Hz, 2 H), 2.97 (t, *J* = 7.5 Hz, 2 H), 3.17 (s, 3 H), 3.58 (s, 3 H), 7.16-7.33 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.7, 32.2, 33.8, 61.2, 126.1, 128.5, 128.5, 141.4, 173.6.

1-Morpholino-3-phenylpropan-1-one (1j). Table 1, Entry 10. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.63 (t, *J* = 7.5 Hz, 2 H), 3.00 (t, *J* = 8.0 Hz, 2 H), 3.37 (t, *J* = 5.0 Hz, 2 H), 3.52 (t, *J* = 5.0 Hz, 2 H), 3.61-3.67 (m, 4 H), 7.21-7.25 (m, 3 H), 7.29-7.33 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.5, 34.8, 42.0, 46.0, 66.5, 66.9, 126.3, 128.5, 128.6, 141.1, 170.9.

***N*-((1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl)-*N*-methyl-3-phenylpropanamide (1k). Table 1, Entry 11.** ^{1}H NMR (300 MHz, $CDCl_3$) (rotamers, 67:33) δ 0.93 (d, *J* = 6.9 Hz, 3 H, minor), 1.08 (d, *J* = 6.3 Hz, 3 H, major), 2.41-2.81 (m, 4 H), 2.78 (s, 3 H, major), 2.94 (s, 3 H, minor), 2.81-3.02 (m, 4 H), 3.48 (br, 1 H, minor), 3.92-4.03 (m, 1 H, minor), 4.41 (br, 1 H, major), 4.46-4.64 (m, 3 H), 7.11-7.43 (m, 20 H); ^{13}C NMR (75 MHz, $CDCl_3$) (rotamers) δ 14.5, 15.4, 27.0, 31.2, 31.6, 32.3, 35.5, 36.2, 58.0, 58.4, 75.5, 76.4, 126.1, 126.2, 126.6, 127.0, 127.7, 128.3, 128.4, 128.5, 128.5, 128.5, 128.7, 141.3, 141.6, 141.7, 142.4, 173.4, 174.2.

(*S*)-4-Benzyl-3-(3-phenylpropanoyl)oxazolidin-2-one (1l). Table 1, Entry 12. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.78 (dd, *J* = 9.6, 13.5 Hz, 1 H), 2.98-3.13 (m, 2 H), 3.21-3.42 (m, 3 H), 4.11-4.24 (m, 2 H), 4.65-4.73 (m, 1 H), 7.18-7.39 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.3, 37.2, 37.9, 55.1, 66.2, 126.3, 127.4, 128.5, 128.6, 129.0, 129.5, 135.2, 140.5, 153.5, 172.4.

***N*-Benzyl-3-phenylpropanamide (1m). Table 1, Entry 13.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 (t, *J* = 7.5 Hz, 2 H), 3.01 (t, *J* = 7.5 Hz, 2 H), 4.41 (d, *J* = 5.7 Hz, 2 H), 5.77 (br, 1 H), 7.14-7.35 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.7, 38.5, 43.6, 126.3, 127.5, 127.8, 128.4, 128.6, 128.7, 138.2, 140.8, 171.9.

1-(Indolin-1-yl)-3-phenylpropan-1-one (1n). Table 1, Entry 14. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.76 (t, *J* = 7.2 Hz, 2 H), 3.11 (t, *J* = 8.1 Hz, 2 H), 3.17 (t, *J* = 8.4 Hz, 2 H), 3.99 (t, *J* = 8.4 Hz, 2 H), 7.04 (t, *J* = 6.6 Hz, 1 H), 7.13-7.37 (m, 7 H), 8.30 (d, *J* = 8.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.0, 30.8, 37.9, 48.0, 117.1, 123.6, 124.5, 126.2, 127.6, 128.5, 128.6, 131.1, 141.3, 143.0, 170.4.

***N*,*N*-Diisopropyl-3-phenylpropanamide (1o). Table 1, Entry 15.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (d, *J* = 6.5 Hz, 6 H), 1.23 (d, *J* = 7.0 Hz, 6 H), 2.42 (t, *J* = 8.0 Hz, 2 H), 2.80 (t, *J* = 8.0 Hz, 2 H), 3.18-3.43 (m, 1 H), 3.72-3.81 (m, 1 H), 7.01-7.08 (m, 3 H), 7.11-7.15 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 31.7, 37.2, 45.7, 126.0, 128.5, 128.5, 141.7, 171.0.

*Characterization Data for Amides **3a-3o** (Table 2).*

Decanamide (3a). Table 2, Entry 1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.5 Hz, 3 H), 1.13-1.29 (m, 12 H), 1.52-1.59 (m, 2 H), 2.15 (t, *J* = 7.5 Hz, 2 H), 5.52 (br, 1 H), 5.93 (br, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.6, 29.3, 29.3, 29.4, 29.5, 31.9, 36.0, 176.1.

***N*-Butyldecanamide (3b). Table 2, Entry 2.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.0 Hz, 3 H), 0.84 (t, *J* = 7.0 Hz, 3 H), 1.14-1.31 (m, 14 H), 1.37-1.44 (m, 2 H), 1.51-1.58 (m, 2 H), 2.10 (t, *J* = 7.5 Hz, 2 H), 3.13-3.17 (m, 2 H), 6.40 (br, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 14.0, 20.1, 22.6, 25.9, 29.2, 29.3, 29.4, 29.4, 31.7, 31.8, 36.7, 39.1, 173.4.

***trans*-4-Pentylcyclohexanecarboxamide (3c). Table 2, Entry 3.** ^{1}H NMR (300 MHz, $CDCl_3$) (82:18 mixture of cis/trans isomers) δ 0.89 (t, *J* = 7.2 Hz, 3 H), 0.84-0.99 (m, 2 H), 1.12-1.36 (m, 9 H), 1.44 (qd, *J* = 3.0, 12.3 Hz, 2 H), 1.79-1.88 (m, 2 H), 1.90-1.98 (m, 2 H), 2.10 (tt, *J* = 3.6, 12.3 Hz, 1 H), 5.55 (br, 1 H), 5.76 (br, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 26.5, 29.7, 32.2, 32.5, 37.0, 37.2, 45.1, 178.9.

Adamantane-1-carboxamide (3d). Table 2, Entry 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59-1.71 (m, 6 H), 1.78-1.82 (m, 6 H), 1.94-2.01 (m, 3 H), 5.66 (br, 1 H), 6.23 (br, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 36.4, 39.3, 40.6, 181.5.

***N,N*-Diethyladamantane-1-carboxamide (3e). Table 2, Entry 5.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.0 Hz, 6 H), 1.61-1.68 (m, 6 H), 1.90-1.94 (m, 6 H), 1.94-1.98 (m, 3 H), 3.27-3.43 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 28.6, 36.7, 39.1, 41.7, 41.8, 176.0.

4-Methoxybenzamide (3f). Table 2, Entry 6. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 3 H), 5.93 (br, 2 H), 6.96 (d, *J* = 8.7 Hz, 2 H), 7.81 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.5, 113.8, 125.4, 129.3, 162.7, 168.9.

***N*-Butyl-4-methoxybenzamide (3g). Table 2, Entry 7.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.5 Hz, 3 H), 1.24-1.37 (m, 2 H), 1.46-1.57 (m, 2 H), 3.34 (q, *J* = 6.0 Hz, 2 H), 3.76 (s, 3 H), 6.81 (d, *J* = 8.7 Hz, 2 H), 6.94 (t, *J* = 4.5 Hz, 1 H), 7.74 (t, *J* = 9.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 20.2, 31.8, 39.8, 55.3, 113.5, 127.1, 128.8, 161.9, 167.3.

***N,N*-Diethyl-4-methoxybenzamide (3h). Table 2, Entry 8.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09-1.26 (m, 6 H), 3.13-3.62 (m, 4 H), 3.82 (s, 3 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 39.6, 43.0, 55.3, 113.7, 128.2, 129.5, 160.3, 171.2.

Undec-10-enamide (3t-SI). Table SI-9, Entry 2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16-1.32 (m, 10 H), 1.51-1.58 (m, 2 H), 1.93-1.99 (m, 2 H), 2.13 (t, *J* = 7.5 Hz, 2 H), 4.83-4.94 (m, 2 H), 5.69-5.77 (m, 1 H), 5.84 (br, 1 H), 6.36 (br, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.6, 28.9, 29.1, 29.2, 29.3, 29.3, 33.8, 36.0, 114.2, 139.2, 176.5.

***N*-Butyl-2-phenylacetamide (3j). Table 2, Entry 10.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.79 (t, *J* = 7.5 Hz, 3 H), 1.14-1.22 (m, 2 H), 1.29-1.34 (m, 2 H), 3.12 (q, *J* = 6.0 Hz, 2 H), 3.47 (s, 2 H), 5.55 (br, 1 H), 7.16-7.22 (m, 3 H), 7.24-7.28 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 20.0, 31.5, 39.4, 43.8, 127.2, 128.9, 129.4, 135.2, 170.9.

2-(4-Fluorophenyl)acetamide (3k). Table 2, Entry 11. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.48 (s, 2 H), 5.33 (br, 1 H), 5.63 (br, 1 H), 6.98 (t, *J* = 9.0 Hz, 2 H), 7.18 (dd, *J* = 5.0, 8.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.3, 115.9 (d, J^2 = 20.8 Hz), 130.5 (d, J^4 = 3.6 Hz), 130.9 (d, J^3 = 8.1 Hz), 162.2 (d, J^1 = 244.6 Hz), 173.2; ^{19}F (470.6 MHz, $CDCl_3$) δ -115.0.

2-(4-Chlorophenyl)acetamide (3l). Table 2, Entry 12. ^{1}H NMR (500 MHz, $CD_3C(O)CD_3$) δ 3.52 (s, 2 H), 6.29 (br, 1 H), 6.87 (br, 1 H), 7.32-7.37 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.5, 129.1, 131.8, 132.7, 136.4, 172.5.

2-(4-Bromophenyl)acetamide (3m). Table 2, Entry 13. ^{1}H NMR (300 MHz, $CD_3C(O)CD_3$) δ 3.49 (s, 2 H), 6.33 (br, 1 H), 6.91 (br, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CD_3C(O)CD_3$) δ 42.5, 120.7, 132.1, 132.2, 136.8, 172.4.

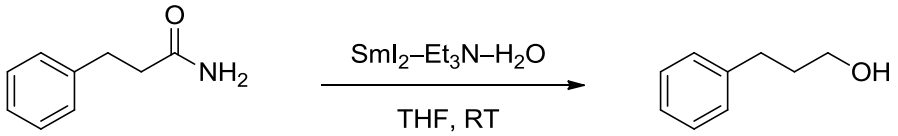
2-(4-(Trifluoromethyl)phenyl)acetamide (3n). Table 2, Entry 14. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 2 H), 5.35 (br, 1 H), 5.67 (br, 1 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.55 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.8, 122.2, 125.9 (q, J^3 = 3.8 Hz), 129.4 (q, J^2 = 31.6 Hz) 129.7, 138.7, 172.2; ^{19}F (470.6 MHz, $CDCl_3$) δ -62.6.

***N*-Butyl-2-(4-methoxyphenyl)acetamide (3o). Table 2, Entry 15.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (t, *J* = 7.5 Hz, 3 H), 1.13-1.21 (m, 2 H), 1.28-1.35 (m, 2 H), 3.10 (q, *J* = 7.0 Hz, 2 H), 3.38 (s, 2 H), 3.69 (s, 3 H), 5.84 (br, 1 H), 6.77 (d, *J* = 8.5 Hz, 2 H), 7.07 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 20.0, 31.5, 39.4, 42.8, 55.2, 114.3, 127.2, 130.4, 158.7, 171.4.

Amides **3p-3r** were purchased from commercial suppliers (**3p**, CAS: 879-37-8; **3q**, CAS: 16564-43-5; **3r**, CAS: 29122-68-7).

*Reduction of Amides **1a-1o** to Alcohols using SmI_2 (Table 1).*

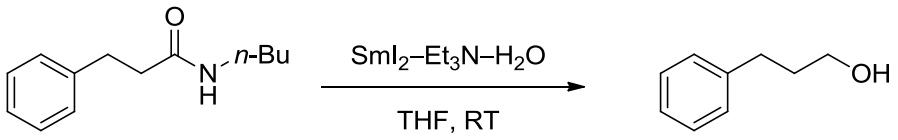
3-Phenylpropanamide (Table 1, entry 1)



1a **2a**

According to the general procedure, the reaction of 3-phenylpropanamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 3 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 82% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

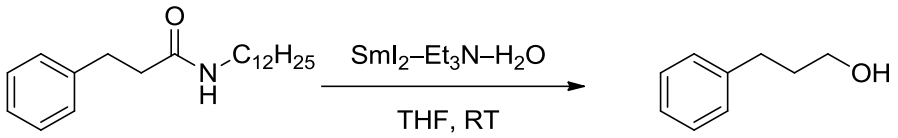
***N*-Butyl-3-phenylpropanamide** (Table 1, entry 2)



1b **2a**

According to the general procedure, the reaction of *N*-butyl-3-phenylpropanamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 3 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 89% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

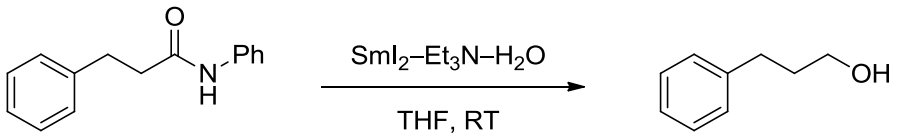
***N*-Dodecyl-3-phenylpropanamide** (Table 1, entry 3)



1c **2a**

According to the general procedure, the reaction of *N*-dodecyl-3-phenylpropanamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.080 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 88% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8. In addition, dodecan-1-amine was formed in 99% yield, demonstrating that the present reaction can be used for the synthesis of amines from amide precursors. See also examples below in the "Additional Experiments" section. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.9 Hz, 3 H), 1.18-1.37 (m, 18 H), 1.41-1.54 (m, 2 H), 2.22 (br, 2 H), 2.72 (t, *J* = 7.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 26.9, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9, 33.2, 42.0.

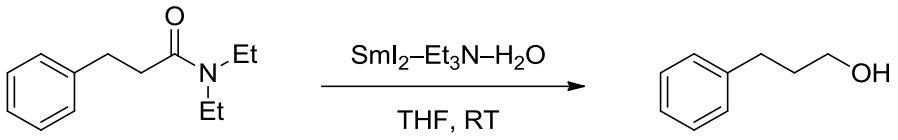
***N*-Phenyl-3-phenylpropanamide** (Table 1, entry 4)



1d **2a**

According to the general procedure, the reaction of *N*-phenyl-3-phenylpropanamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 3 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 84% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

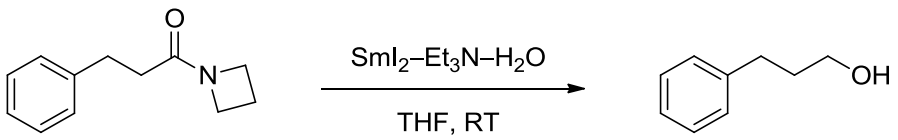
***N,N*-Diethyl-3-phenylpropanamide** (Table 1, entry 5)



1e **2a**

According to the general procedure, the reaction of *N*,*N*-diethyl-3-phenylpropanamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 82% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

1-(Azetidin-1-yl)-3-phenylpropan-1-one (Table 1, entry 6)

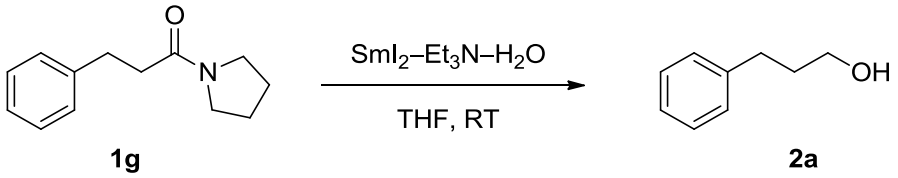


1f **2a**

According to the general procedure, the reaction of 1-(azetidin-1-yl)-3-phenylpropan-1-one (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2

mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 98% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

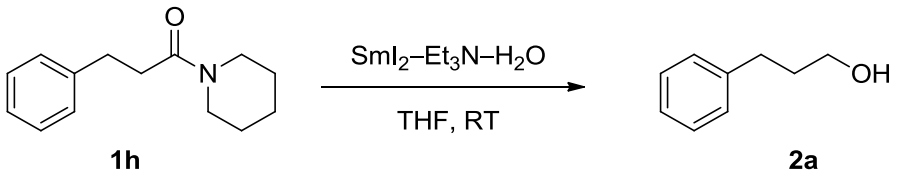
3-Phenyl-1-(pyrrolidin-1-yl)propan-1-one (Table 1, entry 7)



1g **2a**

According to the general procedure, the reaction of 3-phenyl-1-(pyrrolidin-1-yl)propan-1-one (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 90% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

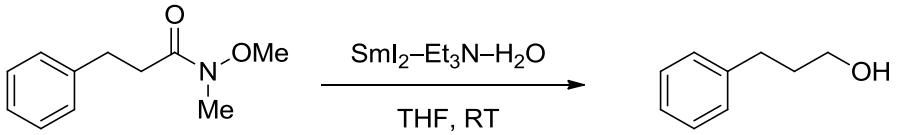
3-Phenyl-1-(piperidin-1-yl)propan-1-one (Table 1, entry 8)



1h **2a**

According to the general procedure, the reaction of 3-phenyl-1-(piperidin-1-yl)propan-1-one (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 81% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

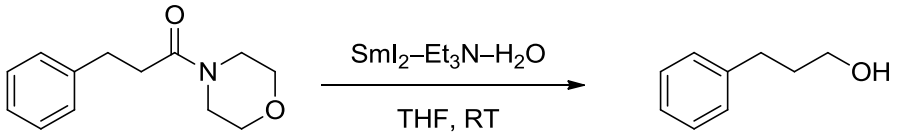
***N*-Methoxy-*N*-methyl-3-phenylpropanamide** (Table 1, entry 9)



1i **2a**

According to the general procedure, the reaction of *N*-methoxy-*N*-methyl-3-phenylpropanamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 97% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8. The reaction of **1i** (0.10 mmol) with limiting SmI_2 (0.20 mmol, 0.10 M in THF), water (2.4 mmol) and triethylamine (2.4 mmol) afforded the corresponding *N*-methyl-3-phenylpropanamide in 49% yield (57% conversion), suggesting that the reduction of **1i** proceeds via sequential N–O cleavage/amide reduction.

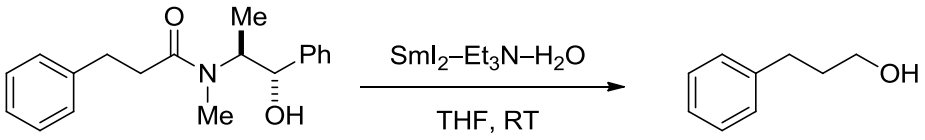
1-Morpholino-3-phenylpropan-1-one (Table 1, entry 10)



1j **2a**

According to the general procedure, the reaction of 1-morpholino-3-phenylpropan-1-one (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.080 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 83% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

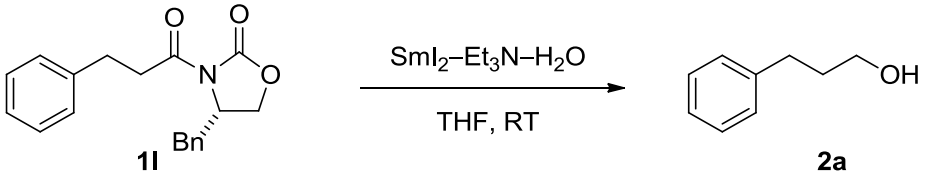
***N*-((1*S*,2*S*)-1-Hydroxy-1-phenylpropan-2-yl)-*N*-methyl-3-phenylpropanamide** (Table 1, entry 11)



1k **2a**

According to the general procedure, the reaction of *N*-((1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl)-*N*-methyl-3-phenylpropanamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.080 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 79% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

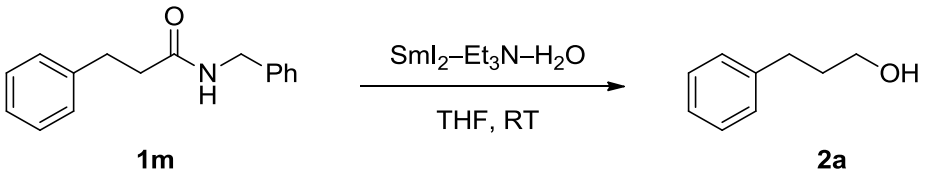
(*S*)-4-Benzyl-3-(3-phenylpropanoyl)oxazolidin-2-one (Table 1, entry 12)



1l **2a**

According to the general procedure, the reaction of (*S*)-4-benzyl-3-(3-phenylpropanoyl)oxazolidin-2-one (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 81% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

***N*-Benzyl-3-phenylpropanamide** (Table 1, entry 13)

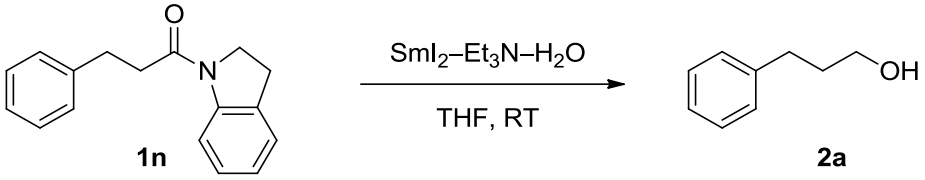


1m **2a**

According to the general procedure, the reaction of *N*-benzyl-3-phenylpropanamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.087 M), water (7.2 mmol) and triethylamine (7.2 mmol) for

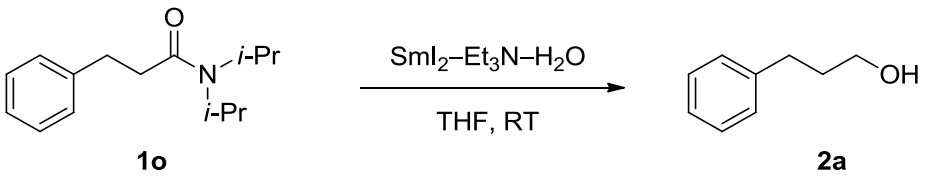
18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 92% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8. The reaction of **1m** (0.10 mmol) with limiting SmI_2 (0.20 mmol, 0.10 M in THF), water (2.4 mmol) and triethylamine (2.4 mmol) afforded the corresponding 3-phenylpropan-1-ol **2a** in 24% yield (3-phenylpropanamide not detected), suggesting that the reduction of **1m** proceeds via direct amide reduction or that the reduction of 3-phenylpropanamide is faster than the N–Bn bond cleavage.

1-(Indolin-1-yl)-3-phenylpropan-1-one (Table 1, entry 14)



According to the general procedure, the reaction of 1-(indolin-1-yl)-3-phenylpropan-1-one (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 99% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

***N,N*-Diisopropyl-3-phenylpropanamide** (Table 1, entry 15)

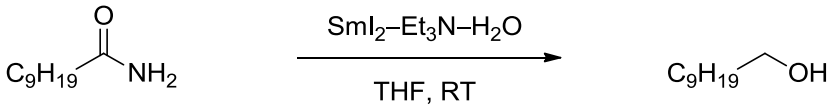


According to the general procedure, an oven-dried vial containing a stir bar was charged with samarium(II) iodide (THF solution, 0.80 mmol, 0.080 M), Et_3N (7.2 mmol) and water (7.2 equiv) with vigorous stirring, which resulted in the formation of a characteristic dark brown

color of the SmI_2–Et_3N–H_2O complex. A solution of *N*,*N*-diisopropyl-3-phenylpropanamide (0.10 mmol in THF, 1.0 mL) was added and the reaction mixture was stirred for 18 h at room temperature. After the standard work-up as described above, the sample was analyzed by ^{1}H NMR and GC-MS to obtain conversion and yield using internal standard: conversion <5%; yield of recovered starting material: >95%, indicating that the chemoselective reduction of amides **1a-1n** in the presence of hindered amides **1o** can be readily achieved.

*Reduction of Amides **3a-3o** to Alcohols using SmI_2 (Table 2).*

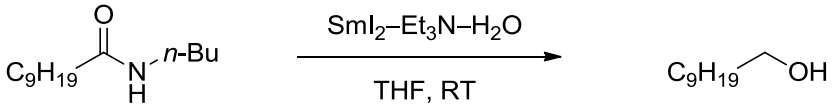
Decanamide (Table 2, entry 1)



3a **4a**

According to the general procedure, the reaction of decanamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 91% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 (t, *J* = 6.9 Hz, 3 H), 1.15-1.33 (m, 15 H), 1.47-1.53 (m, 2 H), 3.57 (t, *J* = 6.6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.8, 29.3, 29.5, 29.6, 29.7, 31.9, 32.8, 63.1.

***N*-Butyldecanamide** (Table 2, entry 2)

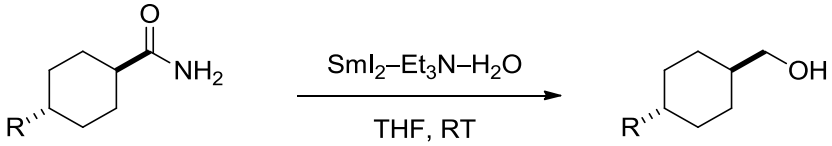


3b **4a**

According to the general procedure, the reaction of *N*-butyldecanamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 76% yield. C–N/C–O bond cleavage selectivity >95:5. Spectroscopic properties matched those described above. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 (t, *J* = 6.9 Hz, 3 H), 1.15-

1.33 (m, 15 H), 1.47-1.53 (m, 2 H), 3.57 (t, *J* = 6.6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.8, 29.3, 29.5, 29.6, 29.7, 31.9, 32.8, 63.1.

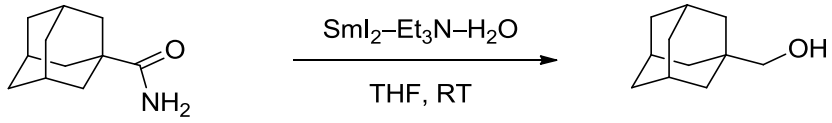
***trans*-4-Pentylcyclohexanecarboxamide** (Table 2, entry 3)



3c, R = *n*-C_5H_{11} **4c**

According to the general procedure, the reaction of *trans*-4-pentylcyclohexanecarboxamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 95% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75-0.91 (m, 7 H), 1.02-1.27 (m, 10 H), 1.38 (br, 1 H), 1.71 (d, *J* = 8.7 Hz, 4 H), 3.37 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 26.6, 29.5, 32.2, 32.7, 37.4, 37.8, 40.7, 68.8.

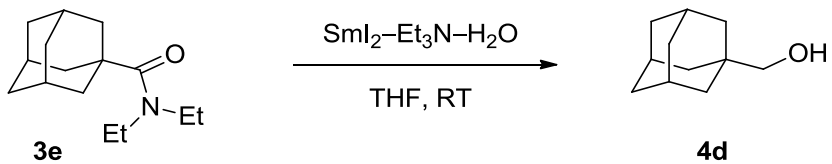
Adamantane-1-carboxamide (Table 2, entry 4)



3d **4d**

According to the general procedure, the reaction of adamantane-1-carboxamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 86% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (br, 1 H), 1.43-1.46 (m, 6 H), 1.55-1.70 (m, 6 H), 1.90-1.95 (m, 3 H), 3.13 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.2, 34.5, 37.2, 39.0, 73.9.

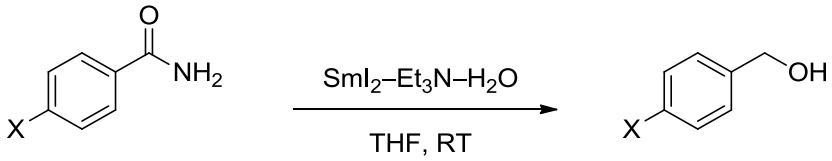
***N,N*-Diethyladamantane-1-carboxamide** (Table 2, entry 5)



3e **4d**

According to the general procedure, the reaction of *N*,*N*-diethyladamantane-1-carboxamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.080 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 75% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (br, 1 H), 1.43-1.46 (m, 6 H), 1.55-1.70 (m, 6 H), 1.90-1.95 (m, 3 H), 3.13 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.2, 34.5, 37.2, 39.0, 73.9.

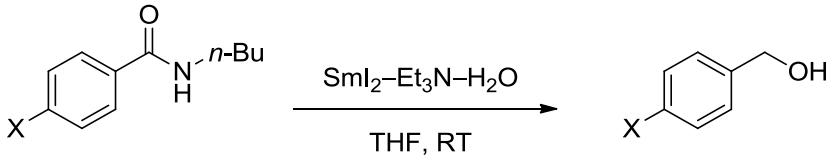
4-Methoxybenzamide (Table 2, entry 6)



3f, X = OMe **4f**

According to the general procedure, the reaction of 4-methoxybenzamide (0.10 mmol), samarium(II) iodide (0.60 mmol, 0.087 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 93% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57 (br, 1 H), 3.74 (s, 3 H), 4.54 (s, 2 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 7.22 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 65.1, 114.0, 128.7, 133.2, 159.3.

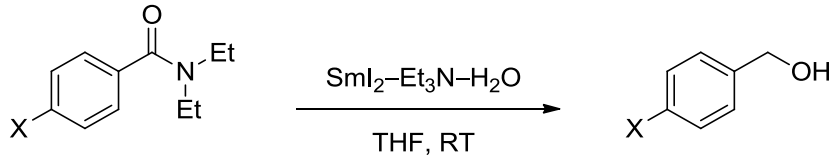
***N*-Butyl-4-methoxybenzamide** (Table 2, entry 7)



3g, X = OMe **4f**

According to the general procedure, the reaction of *N*-butyl-4-methoxybenzamide (0.10 mmol), samarium(II) iodide (0.60 mmol, 0.087 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 82% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57 (br, 1 H), 3.74 (s, 3 H), 4.54 (s, 2 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 7.22 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 65.1, 114.0, 128.7, 133.2, 159.3.

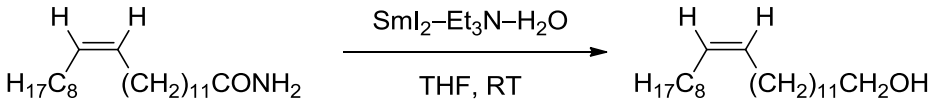
***N,N*-Diethyl-4-methoxybenzamide** (Table 2, entry 8)



3h, X = OMe **4f**

According to the general procedure, the reaction of *N*,*N*-diethyl-4-methoxybenzamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 84% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57 (br, 1 H), 3.74 (s, 3 H), 4.54 (s, 2 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 7.22 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 65.1, 114.0, 128.7, 133.2, 159.3.

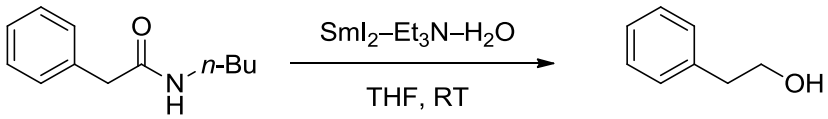
***cis*-13-Docosenoamide** (Table 2, entry 9)



3i **4i**

According to the general procedure, the reaction of *cis*-13-docosenoamide (CAS: 112-84-5) (0.10 mmol), samarium(II) iodide (0.60 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 94% yield. C–N/C–O bond cleavage >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3 H), 1.21-1.43 (m, 31 H), 1.52-1.64 (m, 2 H), 1.97-2.08 (m, 4 H), 3.66 (t, *J* = 6.9 Hz, 2 H), 5.31-5.42 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 25.8, 27.2, 29.3, 29.3, 29.5, 29.5, 29.6, 29.6, 29.6, 29.7, 29.8, 31.9, 32.8, 63.1, 129.9, 129.9.

***N*-Butyl-2-phenylacetamide** (Table 2, entry 10)

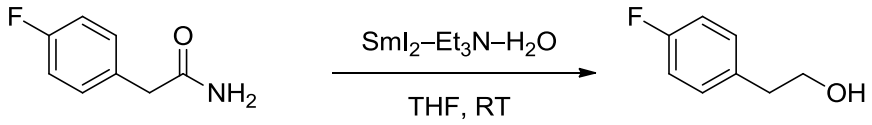


3j **4j**

According to the general procedure, the reaction of *N*-butyl-2-phenylacetamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.087 M), water (7.2 mmol) and triethylamine (7.2 mmol) for

18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 96% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (br, 1 H), 2.90 (t, *J* = 6.6 Hz, 2 H), 3.89 (t, *J* = 6.6 Hz, 2 H), 7.22-7.29 (m, 3 H), 7.31-7.38 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.2, 63.7, 126.5, 128.6, 129.1, 138.5.

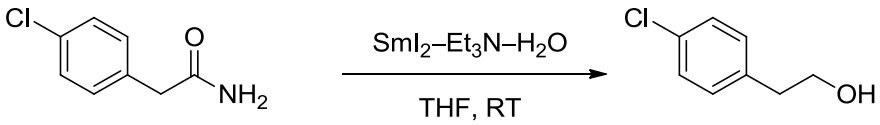
2-(4-Fluorophenyl)acetamide (Table 2, entry 11)



3k **4k**

According to the general procedure, the reaction of 2-(4-fluorophenyl)acetamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.087 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 94% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (br, 1 H), 2.77 (t, *J* = 6.6 Hz, 2 H), 3.77 (t, *J* = 6.6 Hz, 2 H), 6.93 (t, *J* = 8.7 Hz, 2 H), 7.12 (dd, *J* = 5.7, 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.3, 63.5, 115.4 (d, J^2 = 21.2 Hz), 130.4 (d, J^3 = 7.7 Hz), 134.2 (d, J^4 = 3.2 Hz), 161.7 (d, J^1 = 242.8 Hz); ^{19}F (376 MHz, $CDCl_3$) δ -116.8.

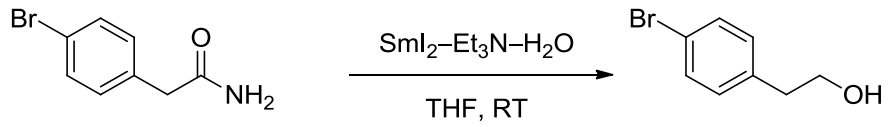
2-(4-Chlorophenyl)acetamide (Table 2, entry 12)



3l **4l**

According to the general procedure, the reaction of 2-(4-chlorophenyl)acetamide (0.10 mmol), samarium(II) iodide (0.40 mmol, 0.10 M), water (3.6 mmol) and triethylamine (3.6 mmol), preformed Sm(II) complex, for 1 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 85% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (br, 1 H), 2.86 (t, *J* = 6.6 Hz, 2 H), 3.87 (t, *J* = 6.6 Hz, 2 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.5, 63.5, 128.7, 130.4, 132.3, 137.0.

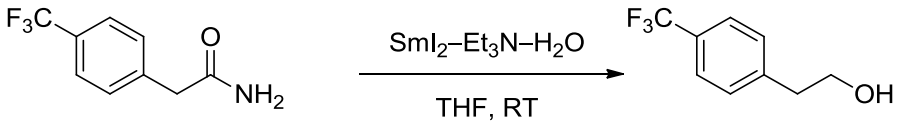
2-(4-Bromophenyl)acetamide (Table 2, entry 13)



3m **4m**

According to the general procedure, the reaction of 2-(4-bromophenyl)acetamide (0.10 mmol), samarium(II) iodide (0.40 mmol, 0.10 M), water (3.6 mmol) and triethylamine (3.6 mmol), preformed Sm(II) complex, for 1 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 63% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (br, 1 H), 2.85 (t, *J* = 6.6 Hz, 2 H), 3.87 (t, *J* = 6.6 Hz, 2 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.6, 63.4, 120.4, 130.8, 131.6, 137.6.

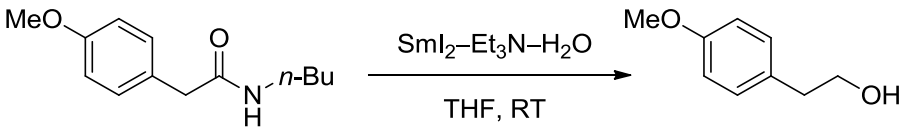
2-(4-(Trifluoromethyl)phenyl)acetamide (Table 2, entry 14)



3n **4n**

According to the general procedure, the reaction of 2-(4-(trifluoromethyl)phenyl)acetamide (0.10 mmol), samarium(II) iodide (0.40 mmol, 0.10 M), water (3.6 mmol) and triethylamine (3.6 mmol), preformed Sm(II) complex, for 1 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 73% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (br, 1 H), 2.95 (t, *J* = 6.6 Hz, 2 H), 3.92 (t, *J* = 6.6 Hz, 2 H), 7.37 (d, *J* = 8.1 Hz, 2 H), 7.59 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.9, 63.2, 122.5, 125.5 (q, J^3 = 3.8 Hz), 129.3 (q, J^2 = 32.5 Hz), 129.4, 142.8; ^{19}F (376 MHz, $CDCl_3$) δ -62.4.

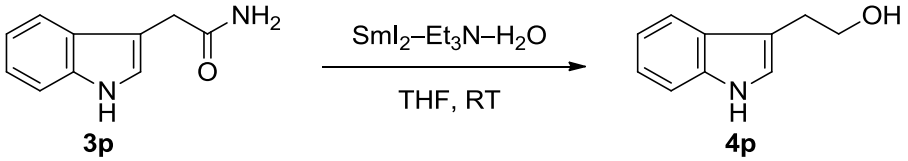
***N*-Butyl-2-(4-methoxyphenyl)acetamide** (Table 2, entry 15)



3o **4o**

According to the general procedure, the reaction of *N*-butyl-2-(4-methoxyphenyl)acetamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.087 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 91% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (br, 1 H), 2.84 (t, *J* = 6.6 Hz, 2 H), 3.82 (s, 3 H), 3.85 (t, *J* = 6.6 Hz, 2 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 7.17 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.3, 55.3, 63.8, 114.1, 130.0, 130.4, 158.3.

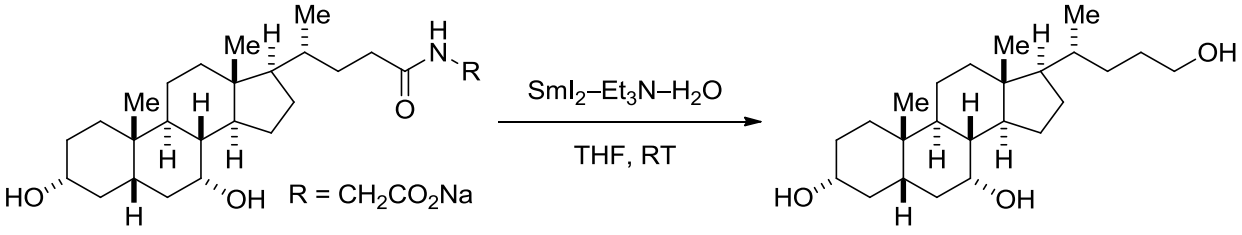
2-(1*H*-Indol-3-yl)acetamide (Table 2, entry 16)



3p **4p**

According to the general procedure, the reaction of 2-(1*H*-indol-3-yl)acetamide (0.10 mmol), samarium(II) iodide (0.40 mmol, 0.10 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 82% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (br, 1 H), 2.97 (t, *J* = 6.3 Hz, 2 H), 3.84 (t, *J* = 6.3 Hz, 2 H), 7.01 (d, *J* = 1.5 Hz, 1 H), 7.06 (t, *J* = 7.0 Hz, 1 H), 7.14 (t, *J* = 7.5 Hz, 1 H), 7.30 (d, *J* = 8.2 Hz, 1 H), 7.56 (d, *J* = 7.9 Hz, 1 H), 7.99 (br, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.8, 62.6, 111.3, 112.3, 118.9, 119.5, 122.3, 122.5, 127.4, 136.5.

Glycochenodeoxycholic acid sodium salt, CAS: 16564-43-5 (Table 2, entry 16)

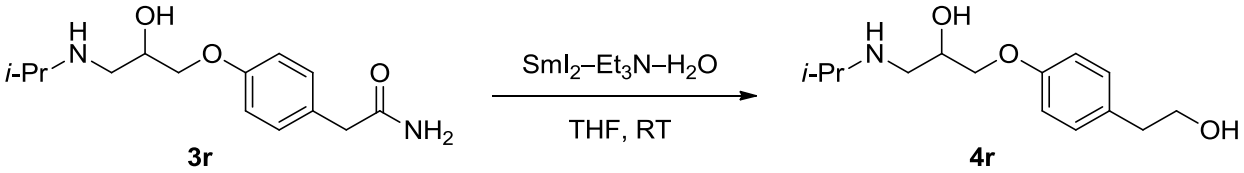


3q **4q**

According to the general procedure, the reaction of glycochenodeoxycholic acid sodium salt (0.10 mmol), samarium(II) iodide (1.50 mmol, 0.080 M), water (9.0 mmol) and triethylamine (9.0 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and

chromatography the title compound in 79% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.60 (s, 3 H), 0.84 (s, 3 H), 0.87 (d, *J* = 6.4 Hz, 3 H), 0.86-0.96 (m, 1 H), 0.98-1.14 (m, 4 H), 1.17-1.47 (m, 14 H), 1.51-1.68 (m, 4 H), 1.72-1.86 (m, 3 H), 1.88-1.95 (m, 2 H), 2.14 (q, *J* = 11.2 Hz, 1 H), 3.35-3.44 (m, 1 H), 3.55 (td, *J* = 2.0, 6.4 Hz, 2 H), 3.76-3.81 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.8, 18.6, 20.6, 22.8, 23.7, 28.3, 29.4, 30.7, 31.9, 32.9, 34.6, 35.1, 35.3, 35.6, 39.5, 39.7, 39.9, 41.5, 42.7, 50.5, 56.0, 63.6, 68.6, 72.0.

2-(4-(2-Hydroxy-3-(isopropylamino)propoxy)phenyl)acetamide, Atenolol, CAS: 29122-68-7 (Table 2, entry 16)



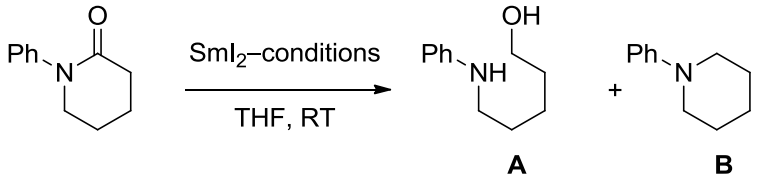
3r **4r**

According to the general procedure, the reaction of 2-(4-(2-hydroxy-3-(isopropylamino)propoxy)phenyl)acetamide (0.10 mmol), samarium(II) iodide (0.45 mmol, 0.087 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (0.1 *N*) the title compound in 61% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.09 (d, *J* = 6.0 Hz, 6 H), 2.54-2.77 (m, 4 H), 2.74 (t, *J* = 6.5 Hz, 2 H), 2.83-2.91 (m, 2 H), 3.75 (t, *J* = 6.5 Hz, 2 H), 3.86-3.93 (m, 2 H), 4.02-4.07 (m, 1 H), 6.79 (d, *J* = 8.5 Hz, 2 H), 7.07 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.4, 22.4, 38.3, 49.1, 49.4, 63.8, 68.0, 70.4, 114.7, 130.1, 130.9, 157.3.

Optimization Experiments using 1-Phenylpiperidin-2-one

To determine the effect of reaction conditions on the reduction of unactivated amides using Sm(II), 1-phenylpiperidin-2-one was selected as a model test substrate. (1) According to the literature precedent,[19] cyclic amides should be more reactive towards Sm(II) due to anomeric stabilization of the radical anion. (2) Carbinolamine intermediates resulting from the reduction of cyclic amides are well-known to show higher stability relative to acyclic amides,[20] which should facilitate determining the effect of reaction conditions on partitioning of the C–N/C–O cleavage.

Table SI-1. Optimization Studies in the Reduction of Unactivated Amides using SmI_2.[a]

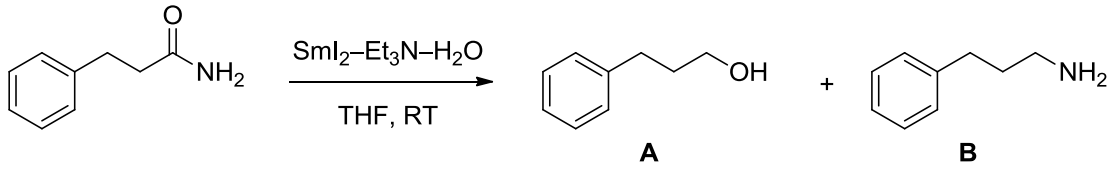


entry	amine	ROH	amine (equiv)	ROH (equiv)	time[b] (h)	conv.[c] (%)	**A:B**[d]	yield[c] (%)
1	-	H_2O	-	200	18	<5	-	-
2	Et_3N	-	12	-	18	<5	-	-
3	Et_3N	H_2O	12	18	18	85	89:11	85
4	Et_3N	$(HOCH_2)_2$	12	9	18	94	82:18	94
5	Et_3N	MeOH	12	18	18	12	82:18	12
6	Et_3N	TFE	12	18	18	6	78:22	6
7	Et_3N	AcOH	12	18	18	5	43:57	5
8	*N*-Me-morpholine	H_2O	12	18	18	87	84:16	87
9	pyrrolidine	H_2O	12	18	18	>95	97:3	>95
10	piperidine	H_2O	12	18	18	>95	95:5	>95
11	morpholine	H_2O	12	18	18	>95	94:6	>95
12	*n*-$BuNH_2$	H_2O	12	18	18	>95	95:5	>95
13	Et_3N	H_2O	36	36	18	>95	92:8	>95
14	Et_3N	H_2O	72	72	18	>95	92:8	88
15[e]	Et_3N	H_2O	60	60	18	>95	97:3	>95

[a]Conditions: SmI_2 (6 equiv), amine, ROH, THF, room temperature. All reactions carried out using standard Schlenk techniques. SmI_2 (freshly prepared from Sm and ICH_2CH_2I) was used. [b]Quenched with air after the indicated time. [c]Determined by ^1H NMR. [d]Refers to the combined yield of **A** and **B**. Conversion = (100-SM). [e]SmI_2 (10 equiv) was used.

To determine the key role of additives on the reactivity of the SmI_2-amine-H_2O complex, several control reactions were carried out using 3-phenylpropanamide as a test substrate (Table SI-2). In agreement with the previous studies[21] both additives were found to be critical for the reactivity (Table SI-2, Entries 1-3). Moreover, the use of H_2O, even in high concentrations did not result in a productive reaction (Table SI-2, Entry 4), which is consistent with the previous findings regarding the redox potential of these Sm(II)[22] systems and the ease of reduction of carboxylic acid derivatives via electron transfer.[23]

Table SI-2. Influence of Additives in the Reduction of Unactivated Amides using SmI_2.[a]

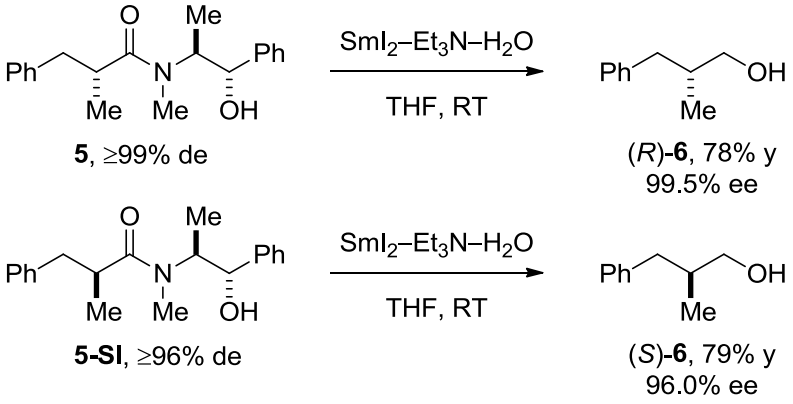


entry	SmI_2 (equiv)	Et_3N (equiv)	H_2O (equiv)	time[b] (h)	conv.[c] (%)	**A:B**[c]	yield[c] (%)
1	6	12	18	18	>95	>95:5	92
2	6	12	-	18	7.5	>95:5	7
3	6	-	18	18	<5	-	<5
4	6	-	800	18	<5	-	<5

[a]Conditions: SmI_2, amine, H_2O, THF, room temperature. All reactions carried out using standard Schlenk techniques. SmI_2 (freshly prepared from Sm and ICH_2CH_2I) was used. [b]Quenched with air after the indicated time. [c]Determined by ^1H NMR. [d]Refers to the combined yield of **A** and **B**. Conversion = (100-SM).

Reduction of Enantioenriched Amides

Scheme SI-1. Reduction of Enantioenriched Pseudoephedrine Amides **5** and **5-SI** to Alcohols using SmI_2–Et_3N–H_2O.

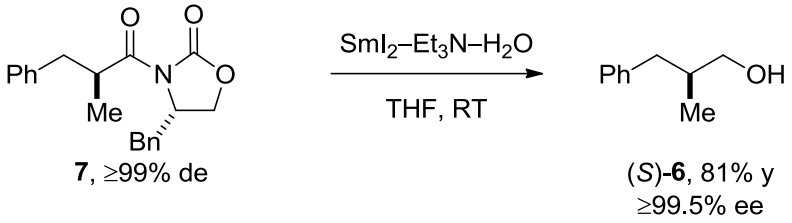


(*R*)-2-Methyl-3-phenylpropan-1-ol (6). According to the general procedure using the preformed Sm(II) complex, (*R*)-*N*-((1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl)-*N*,2-dimethyl-3-phenylpropanamide (0.10 mmol, >99% de),[24] was reacted with samarium(II) iodide (0.80 mmol, 0.080 M, THF solution), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt to afford after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.5 Hz, 3 H), 1.36 (br, 1 H), 1.84-1.93 (m, 1 H), 2.36 (dd, *J* = 8.0, 13.0 Hz, 1 H), 2.69 (dd, *J* = 6.5, 13.5 Hz, 1 H), 3.39-3.49 (m, 2 H), 7.09-7.14 (m, 3 H), 7.19-7.23 (m, 2 H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.5, 37.8, 39.7, 67.7, 125.9, 128.3, 129.2, 140.6. HPLC analysis (chiracel OD-H, hexanes/*i*-PrOH 95/5, 1.0 mL/min, 220 nm) indicated 99.5% ee: t_R (minor) = 8.75 minutes, t_R (major) = 10.39 minutes.

(*S*)-2-Methyl-3-phenylpropan-1-ol (6). According to the general procedure using the preformed Sm(II) complex, (*S*)-*N*-((1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl)-*N*,2-dimethyl-3-phenylpropan amide (0.10 mmol, >96% de)[24] was reacted with SmI_2 (0.80 mmol, 0.080 M, THF solution), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt to afford after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.5 Hz, 3 H), 1.36 (br, 1 H), 1.84-1.93 (m, 1 H), 2.36 (dd, *J* = 8.0, 13.0 Hz, 1 H), 2.69 (dd, *J* = 6.5, 13.5 Hz, 1 H), 3.39-3.49 (m, 2 H), 7.09-7.14 (m, 3 H), 7.19-7.23 (m, 2 H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.5, 37.8, 39.7, 67.7, 125.9, 128.3, 129.2, 140.6.

HPLC analysis (chiracel OD-H, hexanes/*i*-PrOH 95/5, 1.0 mL/min, 220 nm) indicated 96.0% ee: t_R (major) = 9.23 minutes, t_R (minor) = 11.12 minutes.

Scheme SI-2. Reduction of Enantioenriched Amide **7** to Alcohol **6** using SmI_2–Et_3N–H_2O.



7, ≥99% de

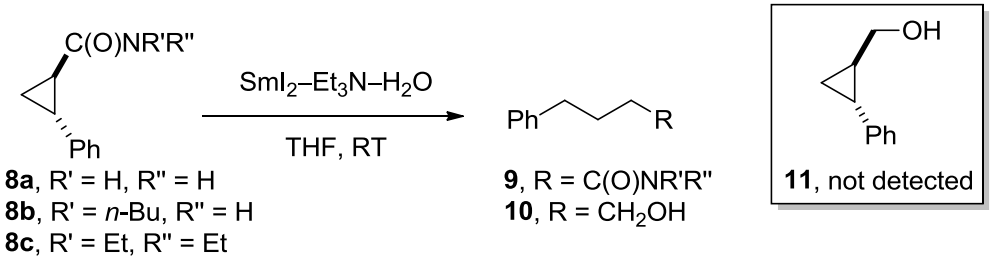
(*S*)-**6**, 81% y
≥99.5% ee

(*S*)-2-Methyl-3-phenylpropan-1-ol (6). According to the general procedure using the preformed Sm(II) complex, (*S*)-4-benzyl-3-((*S*)-2-methyl-3-phenylpropanoyl)oxazolidin-2-one (0.10 mmol, >99% de),[25] was reacted with samarium(II) iodide (0.80 mmol, 0.080 M, THF solution), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt to afford after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.5 Hz, 3 H), 1.36 (br, 1 H), 1.84-1.93 (m, 1 H), 2.36 (dd, *J* = 8.0, 13.0 Hz, 1 H), 2.69 (dd, *J* = 6.5, 13.5 Hz, 1 H), 3.39-3.49 (m, 2 H), 7.09-7.14 (m, 3 H), 7.19-7.23 (m, 2 H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.5, 37.8, 39.7, 67.7, 125.9, 128.3, 129.2, 140.6. HPLC analysis (chiracel OD-H, hexanes/*i*-PrOH 95/5, 1.0 mL/min, 220 nm) indicated >99.5% ee: t_R (major) = 8.27 minutes, t_R (minor) = 10.39 minutes. In addition, the reaction of (*S*)-4-benzyl-3-((*S*)-2-methyl-3-phenylpropanoyl)oxazolidin-2-one (0.10 mmol, >99% de) with samarium(II) iodide (0.80 mmol, 0.080 M, THF solution) and water (20 mmol) for 18 h at rt afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 87% yield. HPLC analysis (chiracel OD-H, hexanes/*i*-PrOH 95/5, 1.0 mL/min, 220 nm) indicated >99.5% ee: t_R (major) = 8.72 minutes, t_R (minor) = 10.41 minutes. Under Sm(II)–H_2O reaction conditions, amide **5** was unreactive. Overall, these results demonstrate that amides bearing alpha-enolizable chiral centers could be readily reduced using the Sm(II)-based methodology, thus providing a valuable alternative to the existing methods for the removal of pseudoephedrine[21] (Scheme SI-1) and oxazolidinone[26-28] (Scheme SI-2) auxiliaries.

Radical Clock Experiments[29-32]

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, typically 0.20-0.80 mmol, 2.0-8.0 equiv, 0.10 M) was added followed by Et_3N (2.4-7.2 mmol) and H_2O (2.4-7.2 mmol) with vigorous stirring, which resulted in the formation of a characteristic dark brown color of the SmI_2–Et_3N–H_2O complex. A solution of amide substrate (0.10 mmol, 1.0 equiv, stock solution in THF, 1.0 mL) was added and the reaction mixture was stirred for the indicated time. The excess of Sm(II) was oxidized by bubbling air through the reaction mixture, and the reaction mixture was diluted with CH_2Cl_2 (30 mL) and NaOH (1 *N*, 10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL), the organic layers were combined, dried over Na_2SO_4, filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

Table SI-3. Summary of the Radical Clock Experiments using SmI_2–Et_3N–H_2O Complexes in the Reductive Opening of Amides **8**.



entry	amide	SmI_2 (equiv)	Et_3N (equiv)	H_2O (equiv)	time[a]	conv.[b] (%)	**9**[b] (%)	**10**[b] (%)	yield[c] (%)
1	**8a**	2	24	24	1 min	54	78	22	54
2	**8b**	2	24	24	1 min	50	85	15	50
3	**8c**	2	24	24	1 min	51	92	8	51
4	**8a**	8	72	72	18 h	>95	<2	>98	99
5	**8b**	8	72	72	18 h	>95	3	97	97
6	**8c**	8	72	72	18 h	>95	59	41	99

All reactions carried out using standard Schlenk techniques. [a]Quenched with air after the indicated time. [b]Determined by ^1H NMR and/or GC-MS of crude reaction mixtures and comparison with authentic samples. [c]Combined yield of **9** and **10**. Conversion = (100-SM). In all entries **11** was not detected (<2.0%).

Rac-(1*R*,2*R*)-2-Phenylcyclopropanecarboxamide (8a). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22-1.26 (m, 1 H), 1.55-1.62 (m, 2 H), 2.43-2.48 (m, 1 H), 5.25 (br, 1 H), 5.50 (br, 1 H), 7.03 (dd, *J* = 1.5, 8.5 Hz, 1 H), 7.13 (tt, *J* = 1.5, 7.5 Hz, 2 H), 7.21 (t, *J* = 7.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.3, 25.7, 25.9, 126.1, 126.4, 128.5, 140.5, 174.3.

Rac-(1*R*,2*R*)-*N*-Butyl-2-phenylcyclopropanecarboxamide (8b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.5 Hz, 3 H), 1.09-1.13 (m, 1 H), 1.22-1.30 (m, 2 H), 1.36-1.43 (m, 2 H), 1.48-1.55 (m, 2 H), 2.35-2.39 (m, 1 H), 3.18 (q, *J* = 7.0 Hz, 2 H), 5.93 (br, 1 H), 6.98 (dd, *J* = 1.5, 7.0 Hz, 2 H), 7.09 (tt, *J* = 1.5, 7.5 Hz, 1 H), 7.17 (t, *J* = 7.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 15.9, 20.1, 24.8, 26.7, 31.8, 39.6, 126.0, 126.2, 128.4, 141.0, 171.9.

Rac-(1*R*,2*R*)-*N*,*N*-Diethyl-2-phenylcyclopropanecarboxamide (8c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11-1.23 (m, 6 H), 1.23-1.29 (m, 1 H), 1.64-1.71 (m, 1 H), 1.92-1.98 (m, 1 H), 2.46-2.58 (m, 1 H), 3.45 (q, *J* = 7.2 Hz, 4 H), 7.14 (dd, *J* = 1.8, 6.9 Hz, 2 H), 7.20 (tt, *J* = 1.5, 7.2 Hz, 1 H), 7.30 (tt, *J* = 1.5, 7.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.3, 14.9, 16.2, 23.3, 25.5, 41.0, 42.2, 126.1, 126.2, 128.5, 141.2, 171.0.

4-Phenylbutanamide (9a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91-2.02 (m, 2 H), 2.21 (t, *J* = 7.2 Hz, 2 H), 2.67 (t, *J* = 7.5 Hz, 2 H), 5.94 (br, 1 H), 6.49 (br, 1 H), 7.16-7.23 (m, 3 H), 7.27-7.24 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.0, 35.1, 35.2, 126.0, 128.5, 128.5, 141.5, 176.1.

***N*-Butyl-4-phenylbutanamide (9b).** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3 H), 1.28-1.41 (m, 2 H), 1.43-1.54 (m, 2 H), 1.93-2.04 (m, 2 H), 2.18 (t, *J* = 6.9 Hz, 2 H), 2.67 (t, *J* = 7.5 Hz, 2 H), 3.25 (q, *J* = 6.9 Hz, 2 H), 5.55 (br, 1 H), 7.17-7.23 (m, 3 H), 7.26-7.33 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 20.1, 27.2, 31.8, 35.2, 36.0, 39.2, 126.0, 128.4, 128.5, 141.6, 172.6.

***N*,*N*-Diethyl-4-phenylbutanamide (9c).** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (t, *J* = 7.2 Hz, 6 H), 1.95-2.06 (m, 2 H), 2.32 (t, *J* = 8.1 Hz, 2 H), 2.69 (t, *J* = 7.8 Hz, 2 H), 3.24 (q, *J* = 7.2 Hz, 2 H), 3.38 (q, *J* = 7.2 Hz, 2 H), 7.16-7.23 (m, 3 H), 7.26-7.32 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 14.3, 26.9, 32.2, 35.4, 40.1, 41.9, 125.8, 128.3, 128.5, 141.9, 171.8.

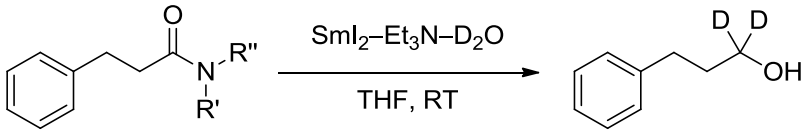
4-Phenylbutan-1-ol (10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44-1.67 (m, 4 H), 1.71 (br, 1 H), 2.56 (t, *J* = 7.8 Hz, 2 H), 3.55 (t, *J* = 6.6 Hz, 2 H), 7.06-7.13 (m, 3 H), 7.16-7.23 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 32.3, 35.7, 62.8, 125.8, 128.3, 128.5, 142.4.

Rac-((1*R*,2*R*)-2-Phenylcyclopropyl)methanol (11). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82-0.91 (m, 2 H), 1.34-1.41 (m, 1 H), 1.65 (br, 1 H), 1.72-1.76 (m, 1 H), 3.49-3.57 (m, 2 H), 6.99 (dd, *J* = 1.5, 7.5 Hz, 2 H), 7.07 (tt, *J* = 1.5, 7.0 Hz, 1 H), 7.18 (t, *J* = 7.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 21.3, 25.3, 66.6, 125.7, 125.9, 128.4, 142.5.

Deuterium Incorporation Studies[33]

General Procedure. According to the general procedure, 3-phenylpropanamide (0.10 mmol), was reacted with samarium(II) iodide (0.8 mmol, 0.085 M, THF solution), D_2O (3.6 mmol) and triethylamine (3.6 mmol) for 18 h at rt to afford 1,1-D^2-3-phenylpropan-1-ol compound in 89% yield, 83.2% D^2 incorporation (determined by ^{1}H NMR, 500 MHz) (Table SI-4, entry 1). In addition, the reaction of *N*-butyl-3-phenylpropanamide (Table SI-4, entry 2) and *N*,*N*-diethyl-3-phenylpropanamide (Table SI-4, entry 3) under the reaction conditions described above afforded the title compound in 92% and 94% yield, respectively, with 94.7% and 96.9% D^2 incorporation, respectively (determined by ^{1}H NMR, 500 MHz). These results are consistent with anions being generated and protonated by H_2O in a series of electron transfer steps and with the formation of a well-defined Sm(II) complex. Moreover, the reaction of decanamide and 2-phenylacetamide under the reaction conditions described above (SmI_2, 0.080 M, THF solution) afforded the corresponding alcohols in 98% and 82% yield, respectively, with 86.0% and 82.5% D^2 incorporation, demonstrating consistent levels of D^2 incorporation can be achieved in the reduction of primary amides using SmI_2–amine–D_2O.

Table SI-4. Determination of D^2 Incorporation in the Reduction of 3-Phenylpropanamides using SmI_2–Et_3N–D_2O.



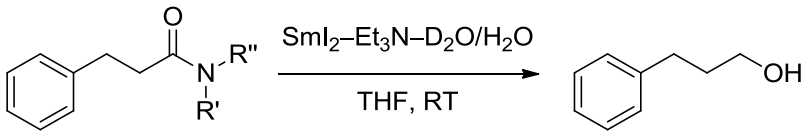
entry	R', R''	SmI_2 (equiv)	Et_3N (equiv)	H_2O (equiv)	time[a] (h)	conv.[b] (%)	yield[b] (%)	D^2 [b] (%)
1	H, H	8	36	36	18	>98	89	83.2
2	*n*-Bu, H	8	36	36	18	>98	92	94.7
3	Et, Et	8	36	36	18	>98	94	96.9

All reactions carried out using standard Schlenk techniques. [a]Quenched with air after the indicated time. [b]Determined by ^{1}H NMR. Conversion = (100-SM).

Kinetic Isotope Studies[34-37]

General Procedure. According to the general procedure, 3-phenylpropanamide (0.10 mmol), was reacted with samarium(II) iodide (0.8 mmol, 0.085 M, THF solution), H_2O/D_2O (1:1, 3.6 mmol) and triethylamine (3.6 mmol) for 18 h at rt to afford 3-phenylpropan-1-ol and 1,1-D^2-3-phenylpropan-1-ol in 95% yield. The amount of each species was determined by ^{1}H NMR (500 MHz, $CDCl_3$,). Kinetic isotope effect, k_H/k_D = 1.37±0.1 (Table SI-5, entry 1). In addition, the reaction of *N*-butyl-3-phenylpropanamide (Table SI-5, entry 2) and *N*,*N*-diethyl-3-phenylpropanamide (Table SI-5, entry 3) under the reaction conditions described above afforded the title compounds in 93% and 96% yield, respectively, k_H/k_D = 1.34±0.1 and k_H/k_D = 1.32±0.1, (determined by ^{1}H NMR, 500 MHz). These results are consistent with proton transfer not being involved in the rate determining step of the reaction.

Table SI-5. Determination of Kinetic Isotope Effect in the Reduction of 3-Phenylpropanamides using SmI_2–Et_3N–D_2O/H_2O.



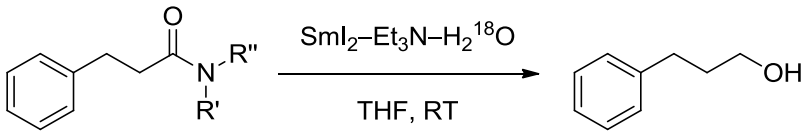
entry	R', R''	SmI_2 (equiv)	Et_3N (equiv)	H_2O (equiv)	time[a] (h)	conv.[b] (%)	yield[b] (%)	k_H/k_D
1	H, H	8	36	36	18	>95	95	1.37±0.1
2	*n*-Bu, H	8	36	36	18	>95	93	1.34±0.1
3	Et, Et	8	36	36	18	>95	96	1.32±0.1

All reactions carried out using standard Schlenk techniques. [a]Quenched with air after the indicated time. [b]Determined by ^{1}H NMR. Conversion = (100-SM).

$H_2{}^{18}O$ Incorporation Studies

General Procedure. According to the general procedure, 3-phenylpropanamide (0.10 mmol), was reacted with samarium(II) iodide (0.8 mmol, 0.085 M, THF solution), $H_2{}^{18}O$ (3.6 mmol) and triethylamine (3.6 mmol) for 18 h at rt to afford -3-phenylpropan-1-ol in 89% yield, 2.59% ^{18}O incorporation (determined by HRMS analysis) (Table SI-6, entry 1). In addition, the reaction of *N*-butyl-3-phenylpropanamide (Table SI-6, entry 2) and *N*,*N*-diethyl-3-phenylpropanamide (Table SI-6, entry 3) under the reaction conditions described above afforded the title compound in 86% and 84% yield, respectively, with 4.19% and 14.20% ^{18}O incorporation (determined by HRMS analysis). These results are consistent with direct electron transfer to the amide carbonyl groups, and show that hydrolysis of the iminium intermediate and/or nucleophilic trapping of aldehyde are not predominant reaction pathways.

Table SI-6. Determination of $H_2{}^{18}O$ Incorporation in the Reduction of 3-Phenylpropanamides using SmI_2–Et_3N–$H_2{}^{18}O$.



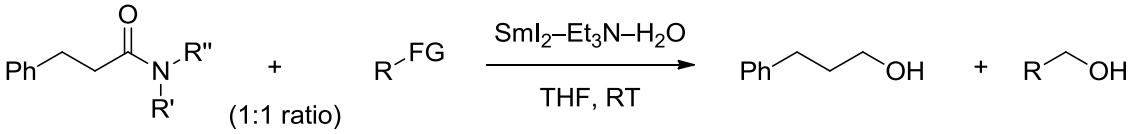
entry	R', R''	SmI_2 (equiv)	Et_3N (equiv)	H_2O (equiv)	time[a] (h)	conv.[b] (%)	yield[b] (%)	^{18}O[c] (%)
1	H, H	8	36	36	18	>95	89	2.59
2	*n*-Bu, H	8	36	36	18	>95	86	4.19
3	Et, Et	8	36	36	18	>95	84	14.20

All reactions carried out using standard Schlenk techniques. [a]Quenched with air after the indicated time. [b]Determined by ^1H NMR. [c]Determined by HRMS. Conversion = (100-SM). HRMS calcd for $C_9H_{12}O_1$ (M^+ + H) 136.0883; HRMS calcd for $C_9H_{12}{}^{18}O_1$ (M^+ + H) 138.0925. Entry 1: found 136.0883; found 138.0929. Entry 2: found 136.0888; found 138.0928. Entry 3: found 136.0888; found 138.0929.

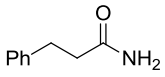
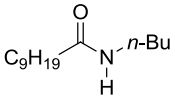
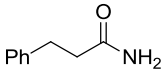
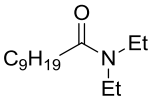
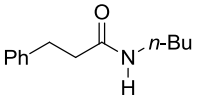
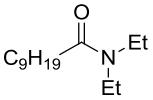
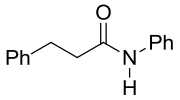
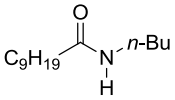
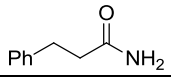
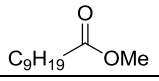
Selectivity Studies

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, typically 0.20 mmol, 2.0 equiv, 0.10 M) was added followed by Et_3N (0.33 mL, 24 equiv) and H_2O (0.043 mL, 24 equiv) with vigorous stirring, which resulted in the formation of a characteristic dark brown color of the SmI_2–Et_3N–H_2O complex. A preformed solution of two substrates (each 0.10 mmol, 1.0 equiv, stock solution in THF) was added and the reaction mixture was stirred until decolorization to white had occurred. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and NaOH (1 *N*, 10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL), the organic layers were combined, dried over Na_2SO_4, filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

Table SI-7. Selectivity Study in the Reduction of Unactivated Amides using SmI_2–amine–H_2O.[a]



Substrate I **Substrate II** **I-red** **II-red**

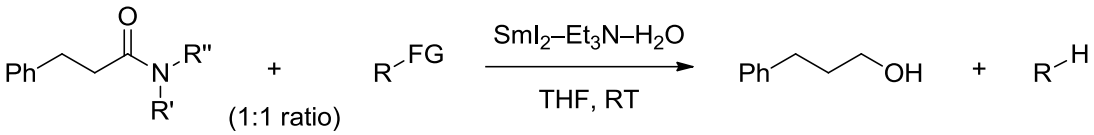
entry	**Substrate I**	**Substrate II**	conv.[b] (**I-red**, %)	conv.[b] (**II-red**, %)	$k_I/k_{R\text{-}FG}$
1			38	<2	>98:2
2			44	<2	>98:2
3			28	2.8	90:10
4			32	<2	>96:4
5			41	<2	>98:2

[a]Conditions: SmI_2 (2 equiv), Et_3N (24 equiv), H_2O (24 equiv), THF, room temperature, 10 s to 1 min. All reactions carried out using standard Schlenk techniques. [b]Determined by ^{1}H NMR (500 MHz) and/or GC-MS. Conversion = (100-SM). In all cases, rapid injection of substrate (THF solution) to the preformed SmI_2–Et_3N–H_2O complex was applied.

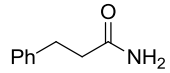
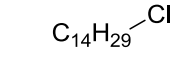
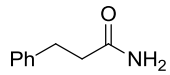
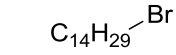
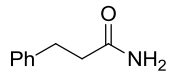
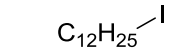
Selectivity Studies – Alkyl Halides

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, typically 0.10 mmol, 1.0 equiv, 0.10 M) was added followed by Et_3N (0.17 mL, 12 equiv) and H_2O (0.022 mL, 12 equiv) with vigorous stirring, which resulted in the formation of a characteristic dark brown color of the SmI_2–Et_3N–H_2O complex. A preformed solution of two substrates (each 0.10 mmol, 1.0 equiv, stock solution in THF) was added and the reaction mixture was stirred until decolorization to white had occurred. A small aliquot (typically, 1.0 mL) was removed from the reaction mixture, diluted with diethyl ether (2 mL) and NaOH (0.1 *N*, 0.25 mL) and analyzed by GC-MS to obtain product distribution using internal standard and comparison with authentic samples. All data represent values corrected for response factors obtained by analyzing known quantities of the starting materials/products. Note that the reduction of alkyl iodides ($E_{1/2}$ = -1.30 V vs. SCE)[38] with SmI_2 is one of the fastest reactions mediated by simple Sm(II)[39] and more complex SmI_2/amine/H_2O systems.[40]

Table SI-8. Selectivity Study in the Reduction of Unactivated Amides using SmI_2–amine–H_2O.[a]



Substrate I **Substrate II** **I-red** **II-red**

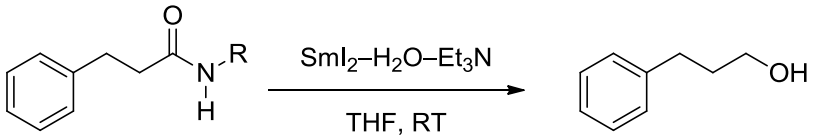
entry	**Substrate I**	**Substrate II**	conv.[b] (**I-red**, %)	conv.[b] (**II-red**, %)	$k_I/k_{R\text{-}FG}$
1			24.7	<2 (<0.1)	>99:1
2			23.3	<2 (0.7)	>97:3
3			24.3	9.7	71.5:28.5

[a]Conditions: SmI_2 (1 equiv), Et_3N (24 equiv), H_2O (24 equiv), THF, room temperature, 10 s to 1 min. All reactions carried out using standard Schlenk techniques. [b]Determined by GC-MS. Conversion = (100-SM). In all cases, rapid injection of substrate (THF solution) to the preformed SmI_2–Et_3N–H_2O complex was applied. GC-MS: Agilent HP-5MS (19091S-433) (length 30 m, internal diameter 0.25 mm, film 0.25 μm), He as the carrier gas, flow rate 1 mL/min, initial oven temp. 50 °C, 25 °C/min ramp, after 50 °C hold for 3 min to 300 °C, then hold at 300 °C for 5 min: retention time: 3-phenylpropanamide: 10.80 min; 3-phenylpropan-1-ol: 9.12 min; 1-chlorotetradecane: 11.43 min; 1-bromotetradecane: 11.89 min; 1-iododododecane: 11.40 min; dodecane: 8.82 min; tetradecane: 9.99 min.

Hammett and Taft Studies[41-43]

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, typically 0.20 mmol, 2.0 equiv, 0.10 M) was added followed by Et_3N (0.33 mL, 24 equiv) and H_2O (0.043 mL, 24 equiv) with vigorous stirring, which resulted in the formation of a characteristic dark brown color of the SmI_2–Et_3N–H_2O complex. A preformed solution of two substrates (each 0.10 mmol, 1.0 equiv, stock solution in THF) was added and the reaction mixture was stirred until decolorization to white had occurred. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and NaOH (1 *N*, 10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL), the organic layers were combined, dried over Na_2SO_4, filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

Chart SI-1. Steric Influence on the Relative Rates in the Reduction of Amides – Taft E_S Correlation Study.[a]



E_S = +0.92

entry	R	k_X/k_{Me}[a]	Taft E_S parameter
1	H	15.3	1.24
2	Me	1.00	0
3	Et	0.77	-0.07
4	*i*-Pr	0.296	-0.47
5	*t*-Bu	0.045	-1.54

[a]Relative reactivity values determined from product distribution by ^1H NMR and/or GC of crude reaction mixtures. Determined from the relative reactivities between $C_9H_{19}C(O)NH$*n*-Bu and $PhCH_2CH_2C(O)NHR$.

Figure SI-1. Taft E_S Correlation Study in the Reduction of N-Alkyl-3-phenylpropanamides.

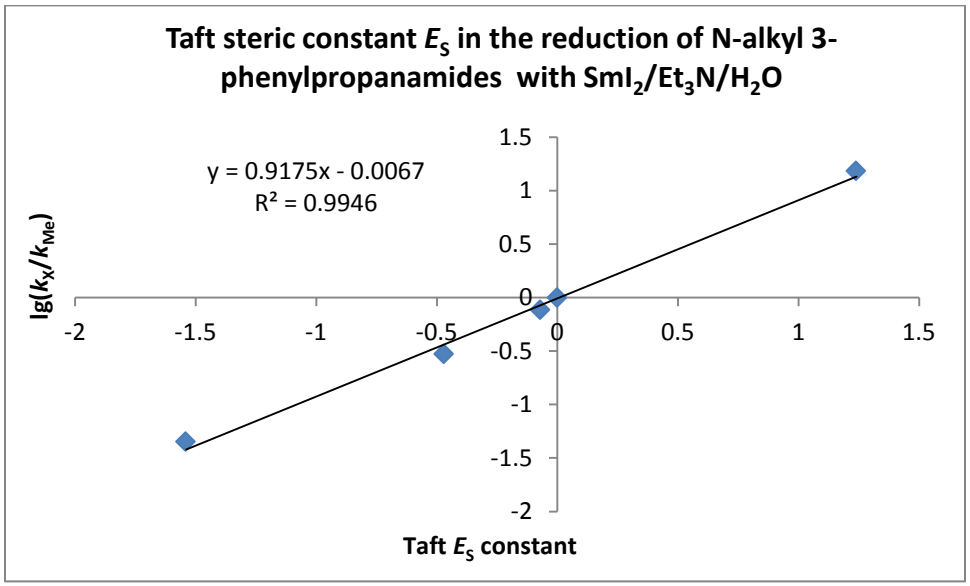
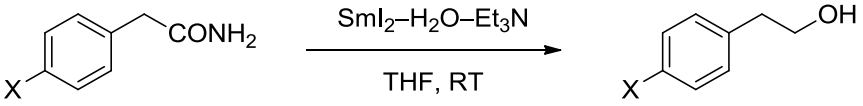


Chart SI-2. Electronic Influence on the Relative Rates in the Reduction of Primary Amides – Hammett Correlation Study.[a]



ρ = +0.52 (vs. σ)
ρ = +0.29 (vs. σ^+)

entry	X	k_X/k_H[a]	Hammett σ constant	Hammett σ^+ constant
1	Cl	1.07	0.23	0.114
2	F	0.94	0.06	-0.073
3	H	1.00	0	0
4	MeO	0.59	-0.27	-0.778

[a]Relative reactivity values determined from product distribution by ^{1}H NMR and/or GC of crude reaction mixtures. The ρ values can be compared with ρ = 0.43 (Hammett σ parameters) and ρ = 0.25 (Hammett σ^+ parameters) for the reduction of 4-phenylacetic methyl esters with $SmI_2/Et_3N/H_2O$.[43]

Figure SI-2. Hammett σ^+ Correlation Study in the Reduction of 4-Substituted 2-Phenylacetamides.

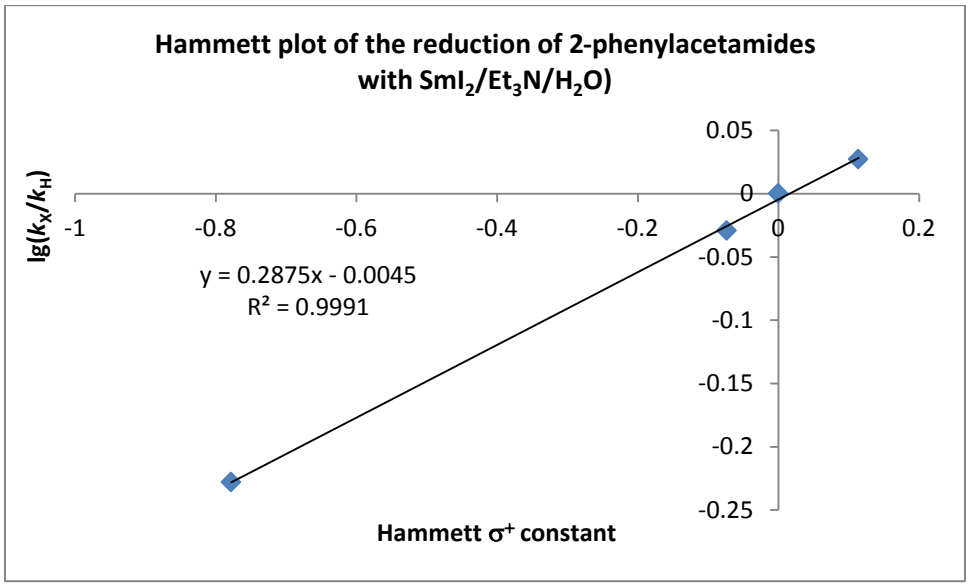
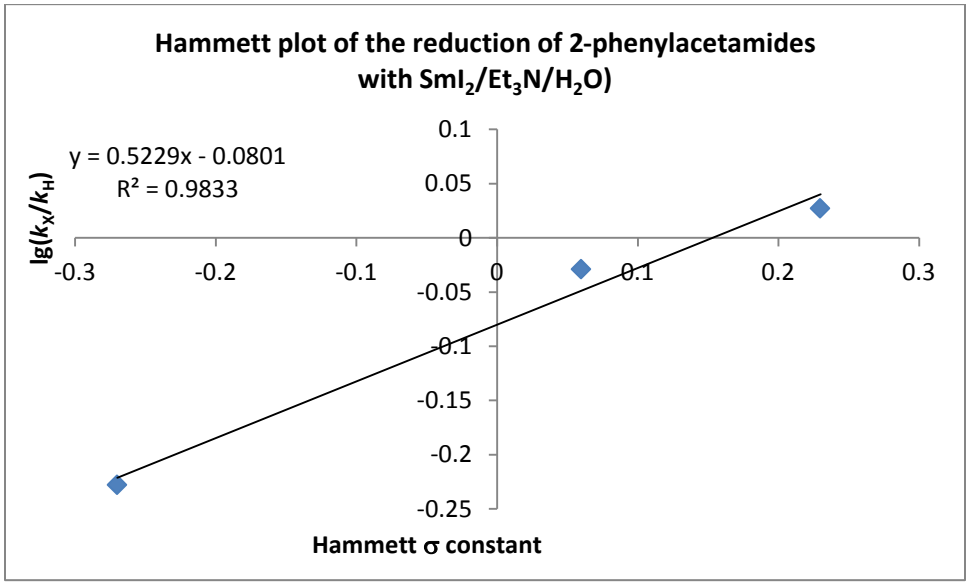


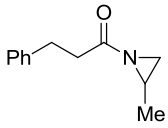
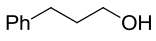
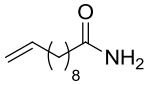
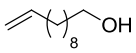
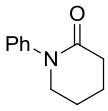
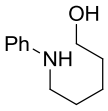
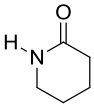
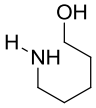
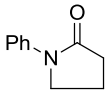
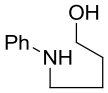
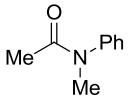
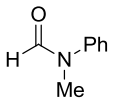
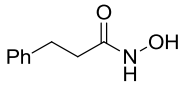
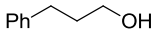
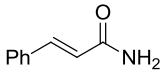
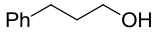
Figure SI-3. Hammett σ Correlation Study in the Reduction of 4-Substituted 2-Phenylacetamides.



Additional Experiments

In addition to the results presented in Tables 1 and 2 in the main manuscript, the reduction of unactivated amides with SmI_2–amine–H_2O can be applied to reduce several other classes of amides, including highly-strained aziridinyl amides, amides containing sensitive cis-olefins, six- and five-membered lactams, formamides, acetamides, hydroxamic acids, and α,β-unsaturated amides (Table SI-9). In all cases excellent C–N/C–O bond cleavage selectivity is observed in these reactions. Overall, these results further highlight that the reduction of unactivated amides using SmI_2–amine–H_2O is characterized by a very broad substrate scope that cannot be achieved using other currently available methods for the reduction of amides to alcohols.[1-13] *Further details and additional substrate scope studies will be reported in a full account of this work.*

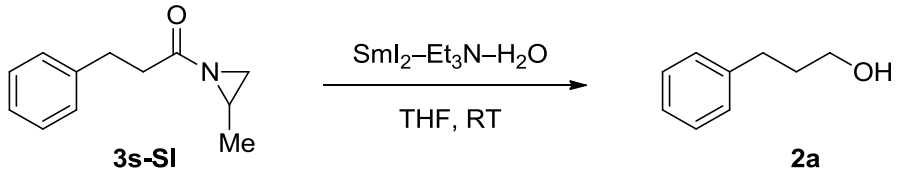
Table SI-9. Reduction of Unactivated Amides using SmI_2–amine–H_2O – Additional Examples.[a]

entry	**3-SI**	amide	**4-SI/2a**	product	yield[b] (%)
1	**3s-SI**		**2a**		95
2	**3t-SI**		**4t-SI**		99
3	**3u-SI**		**4u-SI**		96
4	**3v-SI**		**4v-SI**		95[b]
5	**3w-SI**		**4w-SI**		84
6	**3x-SI**		**4x-SI**		86
7	**3y-SI**		**4x-SI**		80
8	**3z-SI**		**2a**		90
9	**3aa-SI**		**2a**		73

[a]Conditions: SmI_2 (6-12 equiv), Et_3N, H_2O, THF, room temperature. All reactions carried out using standard Schlenk techniques. [b]Conversion determined by GC-MS.

*Reduction of Additional Amides **3-SI** to Alcohols using SmI_2 (Table SI-9).*

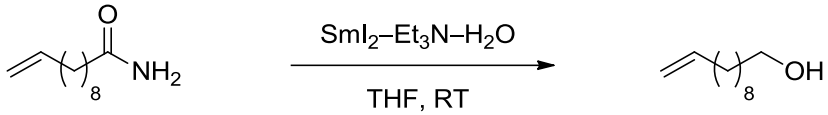
1) 1-(2-Methylaziridin-1-yl)-3-phenylpropan-1-one (Table SI-9, entry 1)



3s-SI **2a**

According to the general procedure, the reaction of 1-(2-methylaziridin-1-yl)-3-phenylpropan-1-one (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 95% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

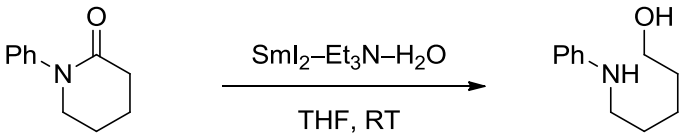
2) Undec-10-enamide (Table SI-9, entry 2)



3t-SI **4t-SI**

According to the general procedure, the reaction of undec-10-enamide (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 99% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06-1.36 (m, 13 H), 1.44-1.55 (m, 2 H), 1.92-2.01 (m, 2 H), 3.57 (t, *J* = 6.6 Hz, 2 H), 4.83-4.96 (m, 2 H), 5.67-5.82 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 28.9, 29.1, 29.4, 29.6, 32.8, 33.8, 63.1, 114.1, 139.2.

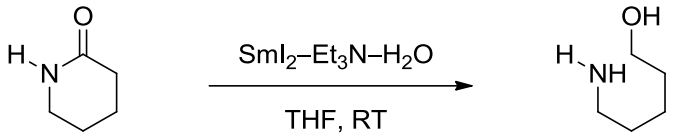
3) 1-Phenylpiperidin-2-one (Table SI-9, entry 3)



3u-SI **4u-SI**

According to the general procedure, the reaction of 1-phenylpiperidin-2-one (0.10 mmol), samarium(II) iodide (1.0 mmol, 0.080 M), water (6.0 mmol) and triethylamine (6.0 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 96% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (br, 1 H), 1.38-1.45 (m, 2 H), 1.52-1.62 (m, 4 H), 3.06 (t, *J* = 7.0 Hz, 2 H), 3.51 (br, 1 H), 3.59 (t, *J* = 6.5 Hz, 2 H), 6.53 (dd, *J* = 1.5, 9.0 Hz, 2 H), 6.62 (tt, *J* = 1.0, 7.5 Hz, 1 H), 7.10 (dd, *J* = 7.0, 8.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.4, 29.3, 32.5, 43.9, 62.8, 112.7, 117.2, 129.3, 148.4.

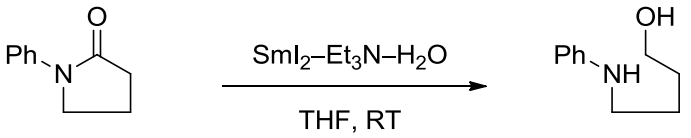
4) Piperidin-2-one (Table SI-9, entry 4)



3v-SI **4v-SI**

According to the general procedure, piperidin-2-one (0.10 mmol) was reacted with samarium(II) iodide (0.80 mmol, 0.080 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt. After the indicated time, the excess of Sm(II) was oxidized by bubbling air through the reaction mixture, a small aliquot (typically, 1.0 mL) was removed from the reaction mixture, diluted with diethyl ether (2 mL) and NaOH (0.1 N, 0.25 mL) and analyzed by GC-MS to obtain product distribution using internal standard and comparison with authentic samples. 5-aminopentan-1-ol > 98% conversion. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29-1.57 (m, 6 H), 2.19 (br, 3 H), 2.66 (t, *J* = 6.9 Hz, 2 H), 3.55 (t, *J* = 6.6 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.1, 32.5, 33.1, 41.9, 61.9.

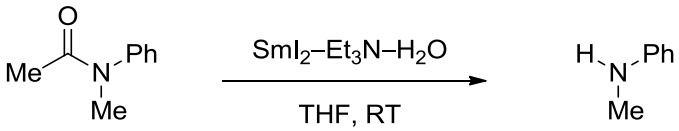
5) 1-Phenylpyrrolidin-2-one (Table SI-9, entry 5)



3w-SI **4w-SI**

According to the general procedure, the reaction of 1-phenylpyrrolidin-2-one (0.10 mmol), samarium(II) iodide (1.2 mmol, 0.087 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 84% yield. C–N/C–O bond cleavage selectivity 85:15. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59-1.68 (m, 4 H), 2.53 (br, 2 H), 3.09 (t, *J* = 7.0 Hz, 2 H), 3.62 (t, *J* = 6.5 Hz, 2 H), 6.56 (dd, *J* = 1.0, 8.5 Hz, 2 H), 6.64 (tt, *J* = 1.0, 7.5 Hz, 1 H), 7.10 (dd, *J* = 7.0, 8.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.1, 30.4, 44.0, 62.7, 113.0, 117.5, 129.3, 148.2.

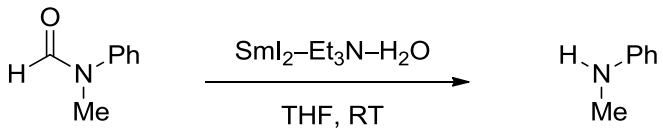
6) *N*-Methyl-*N*-phenylacetamide (Table SI-9, entry 6)



3x-SI **4x-SI**

According to the general procedure, the reaction of *N*-methyl-*N*-phenylacetamide (0.10 mmol), samarium(II) iodide (0.8 mmol, 0.087 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 86% yield. C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.89 (s, 3 H), 3.74 (br, 1 H), 6.68 (dd, *J* = 0.6, 7.8 Hz, 2 H), 6.78 (tt, *J* = 0.9, 7.2 Hz, 1 H), 7.27 (dd, J = 7.2, 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.8, 112.5, 117.3, 129.3, 149.4.

7) *N*-Methyl-*N*-phenylformamide (Table SI-9, entry 7)

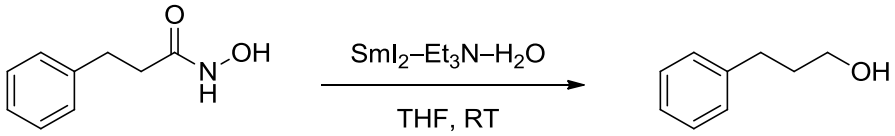


3y-SI **4x-SI**

According to the general procedure, the reaction of *N*-methyl-*N*-phenylformamide (0.10 mmol), samarium(II) iodide (0.8 mmol, 0.087 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 80% yield. C–

N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.89 (s, 3 H), 3.74 (br, 1 H), 6.68 (dd, *J* = 0.6, 7.8 Hz, 2 H), 6.78 (tt, *J* = 0.9, 7.2 Hz, 1 H), 7.27 (dd, J = 7.2, 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.8, 112.5, 117.3, 129.3, 149.4.

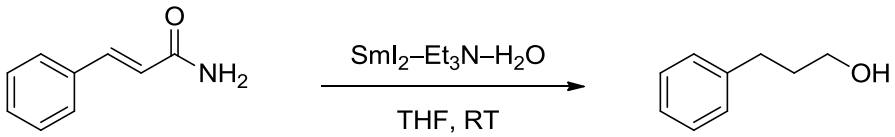
8) *N*-Hydroxy-3-phenylpropanamide (Table SI-9, entry 8)



3z-SI **2a**

According to the general procedure, the reaction of *N*-hydroxy-3-phenylpropanamide (0.10 mmol), samarium(II) iodide (0.8 mmol, 0.085 M), water (7.2 mmol) and triethylamine (7.2 mmol) for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) and chromatography the title compound in 90% yield. C–N/C–O bond cleavage selectivity >95:5. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

9) Cinnamamide (Table SI-9, entry 9)



3aa-SI **2a**

According to the general procedure, the reaction of cinnamamide (0.10 mmol), samarium(II) iodide (0.8 mmol, 0.087 M), water (7.2 mmol) and triethylamine (7.2 mmol), using preformed Sm(II) complex for 18 h at rt, afforded after work-up with CH_2Cl_2/NaOH (1.0 *N*) the title compound in 73% yield. C–N/C–O bond cleavage selectivity >95:5. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). C–N/C–O bond cleavage selectivity >95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 1 H), 1.79-1.87 (m, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 7.09-7.24 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

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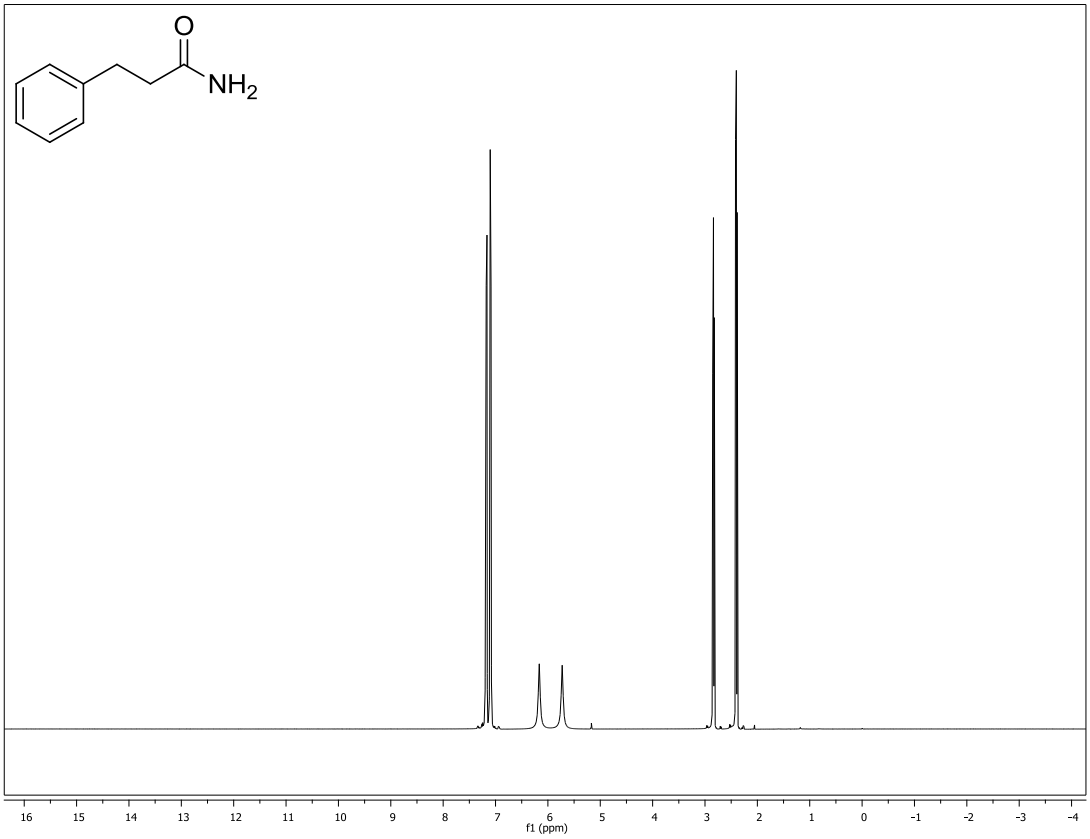
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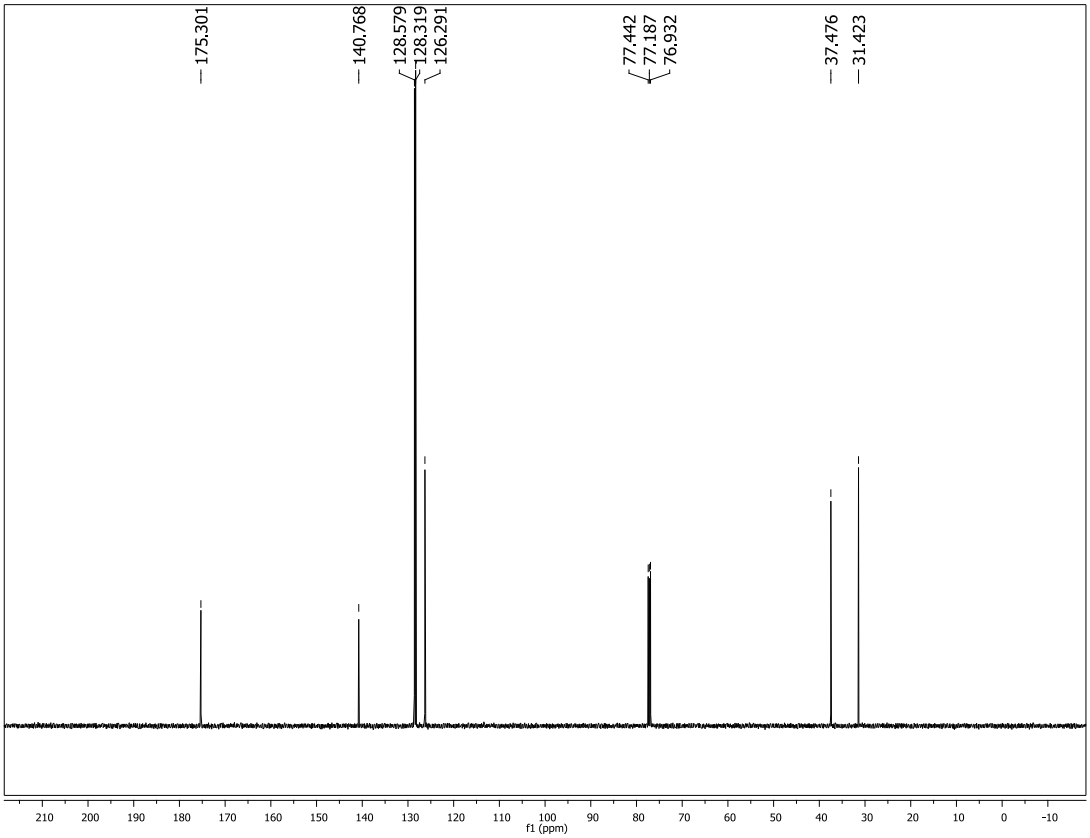
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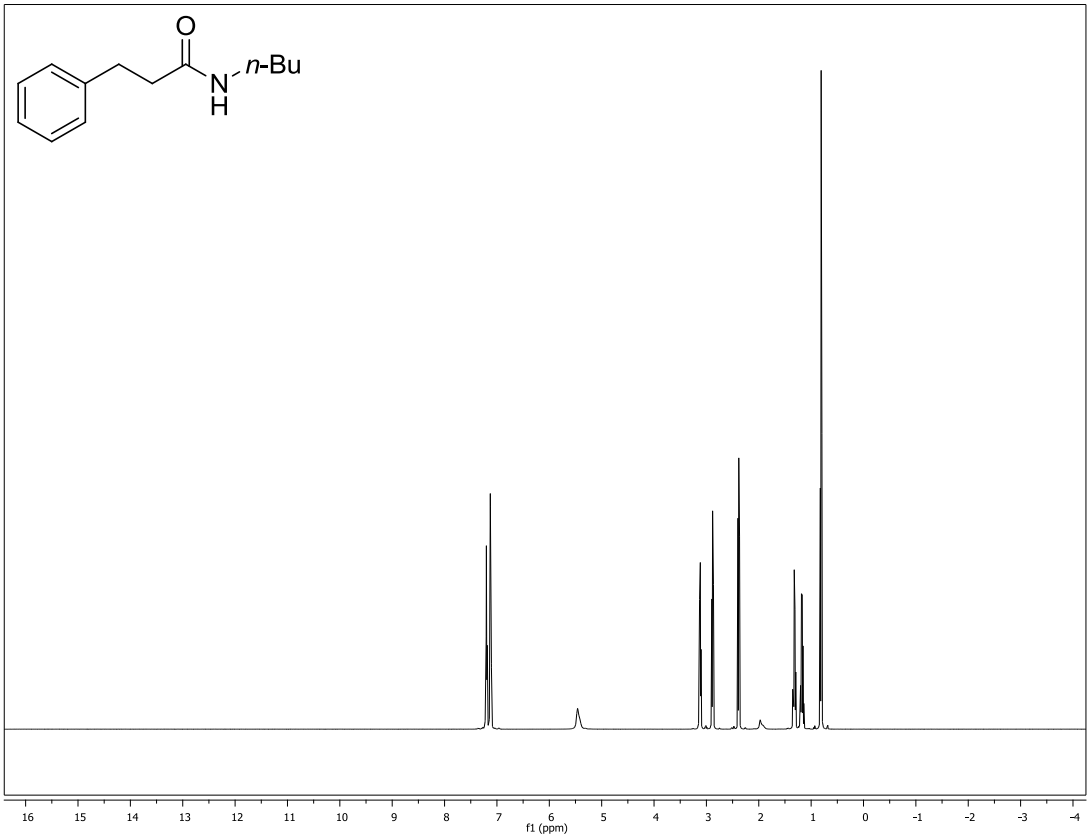
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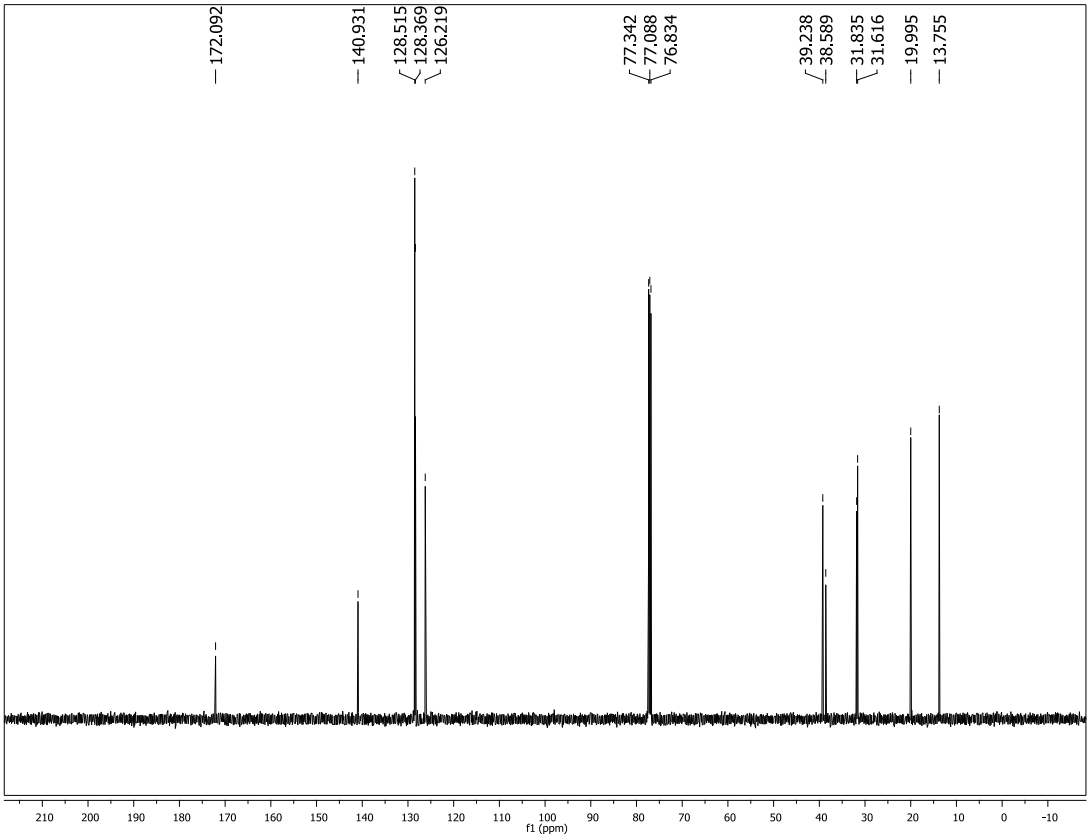
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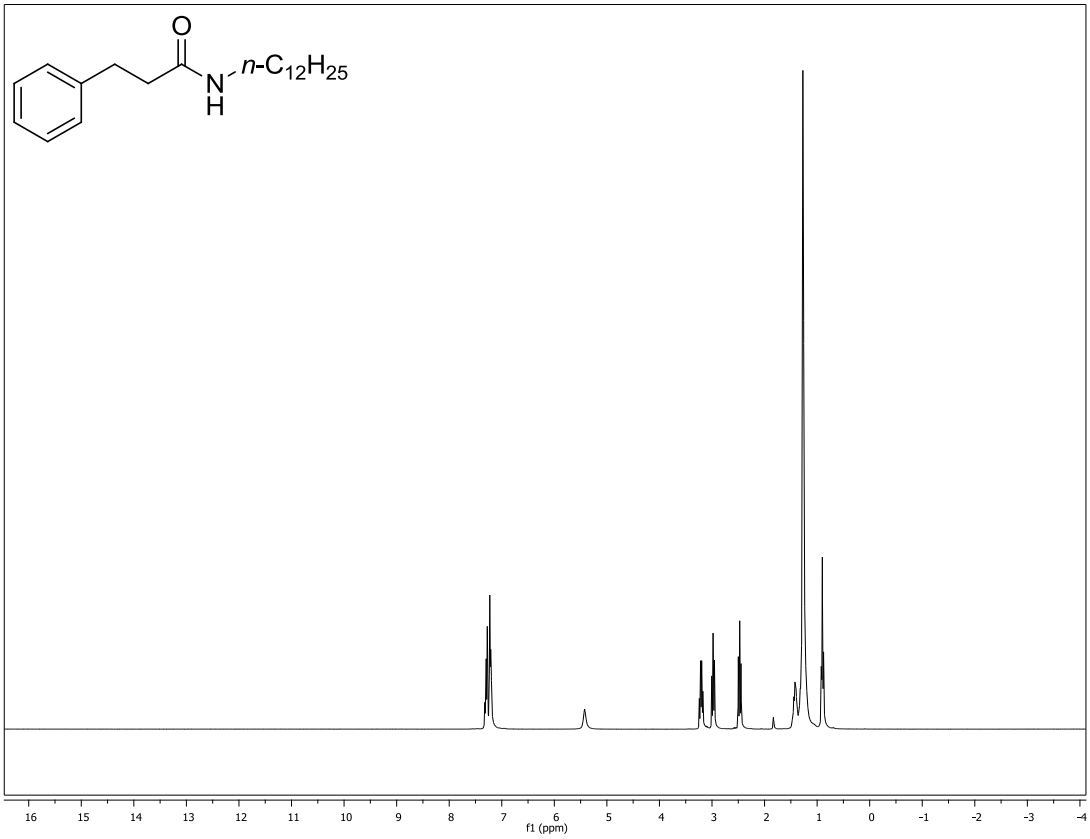
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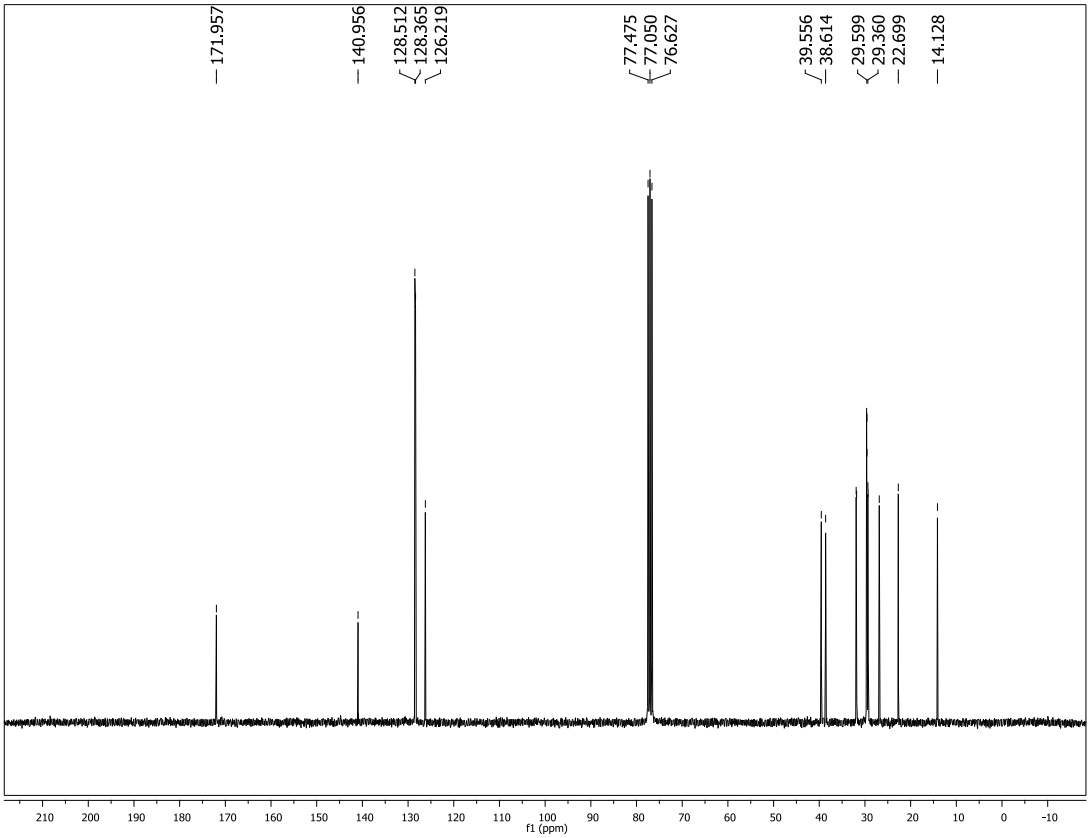
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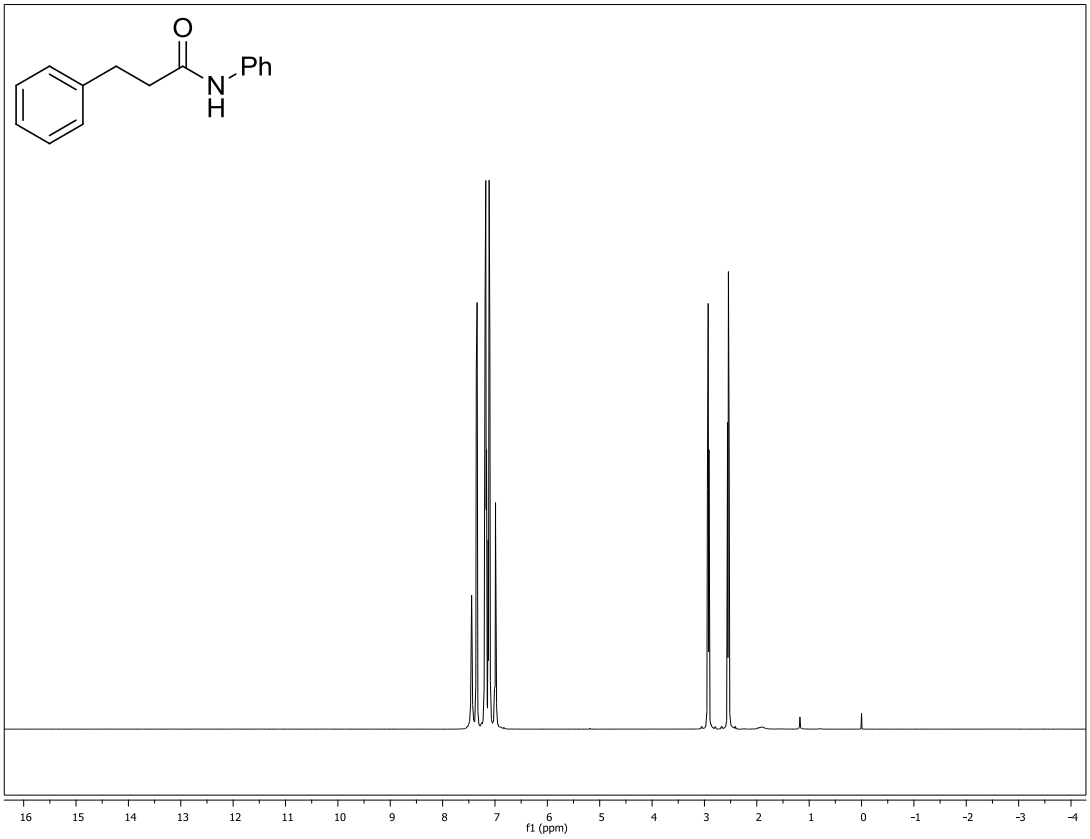
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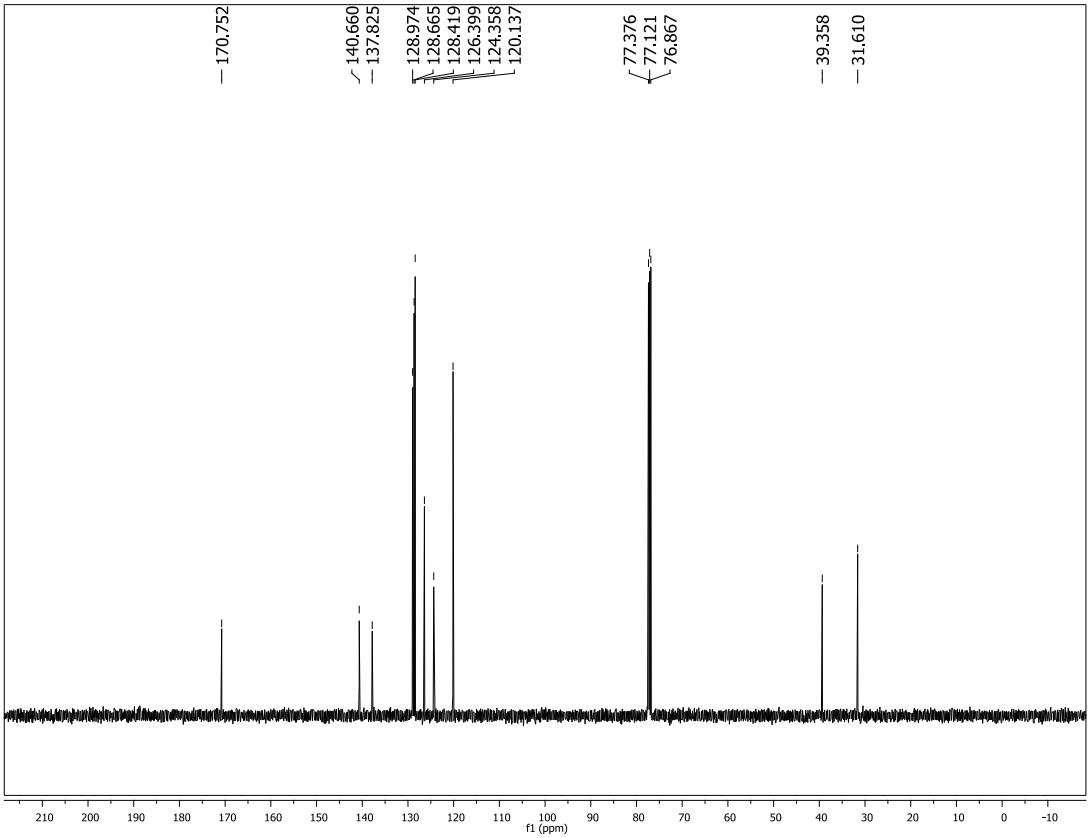
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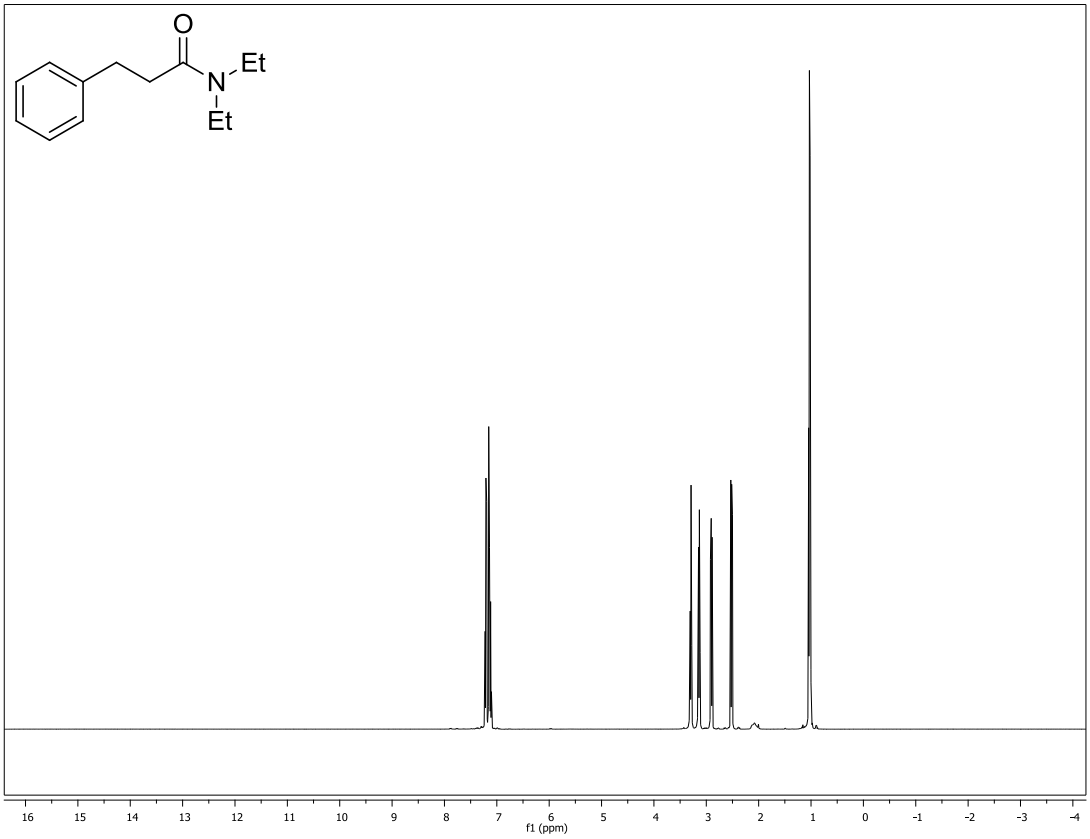
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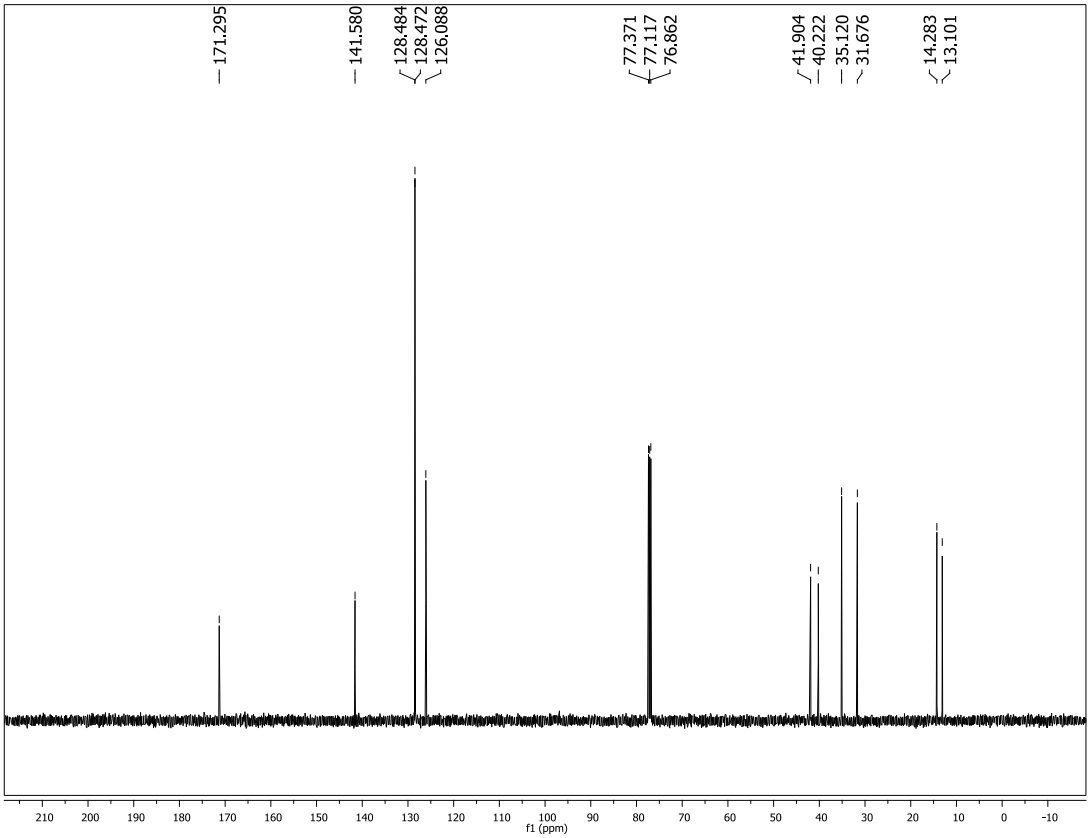
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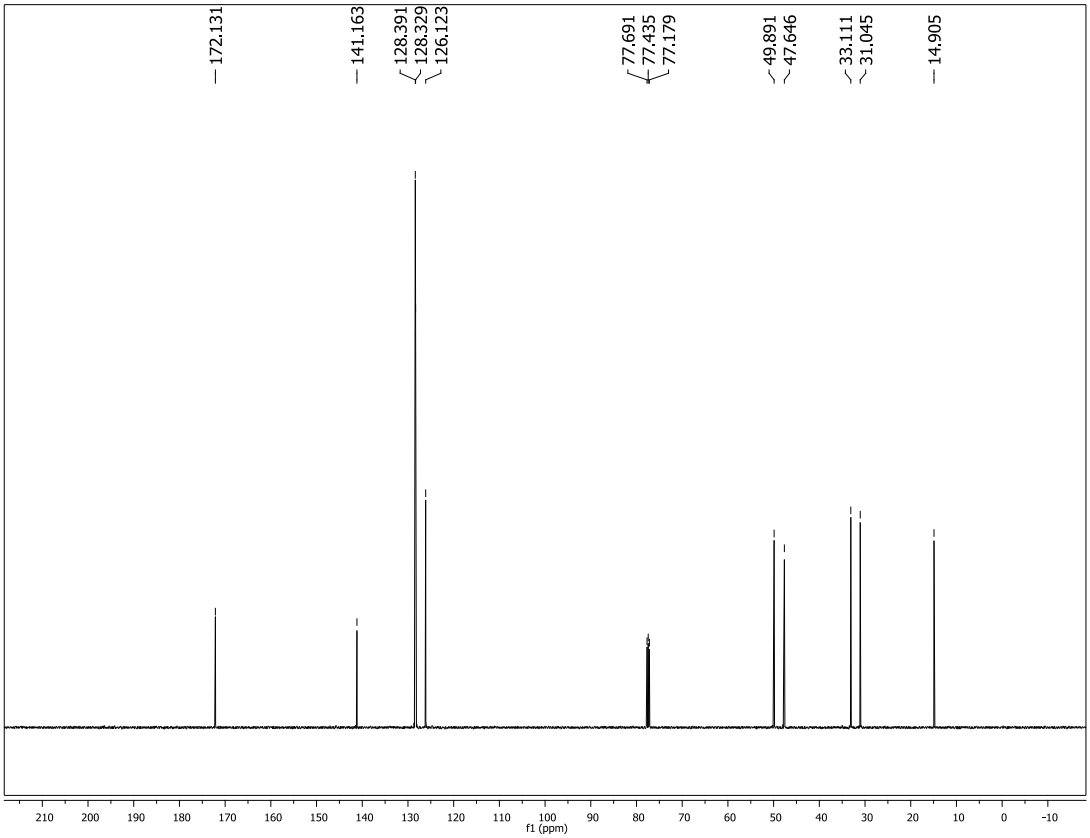
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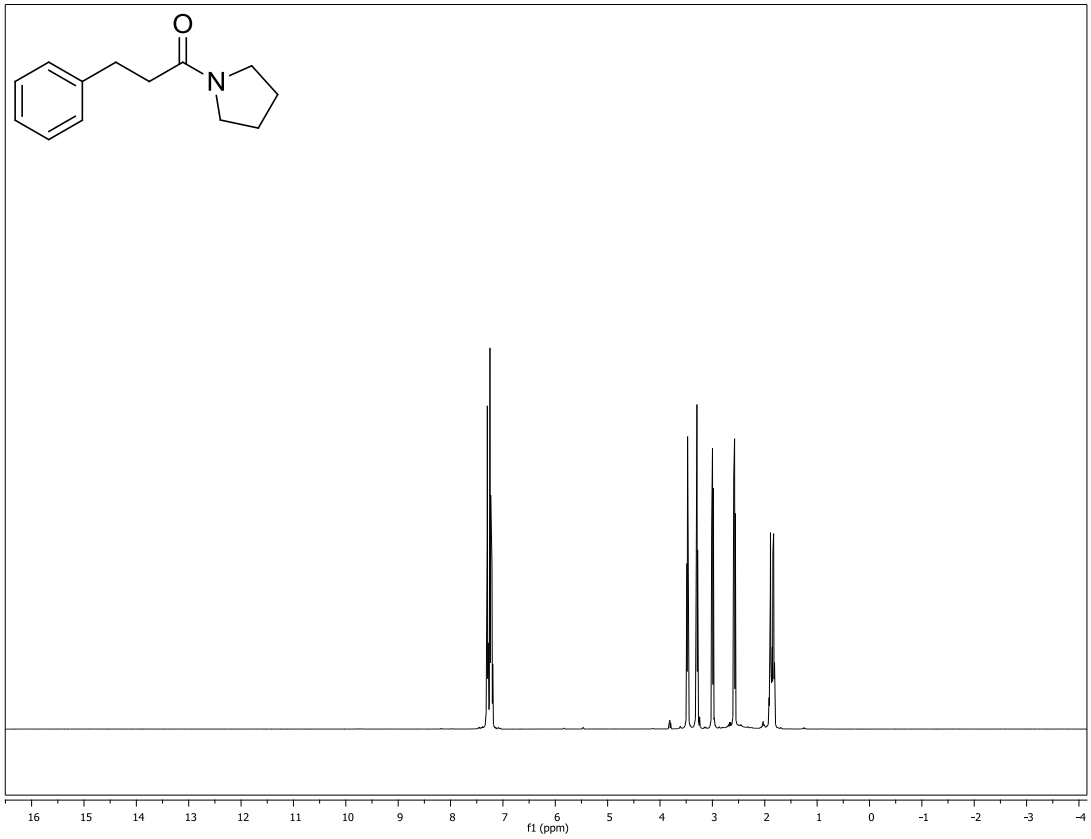
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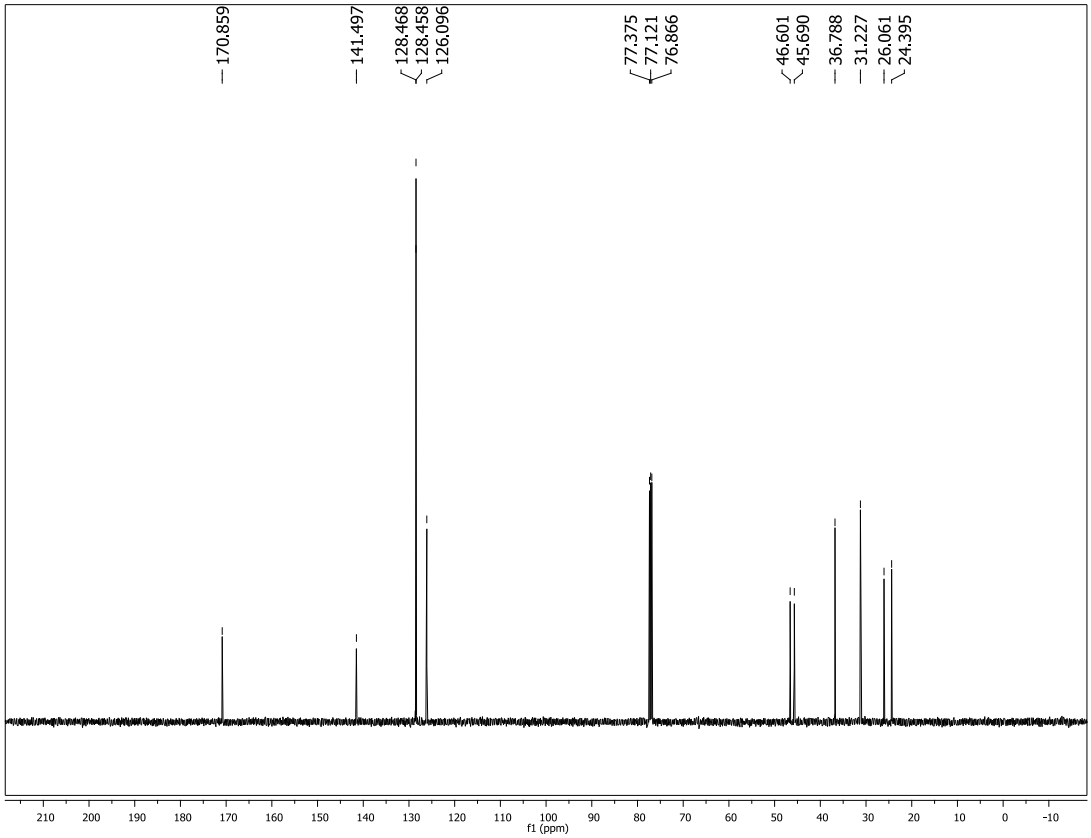
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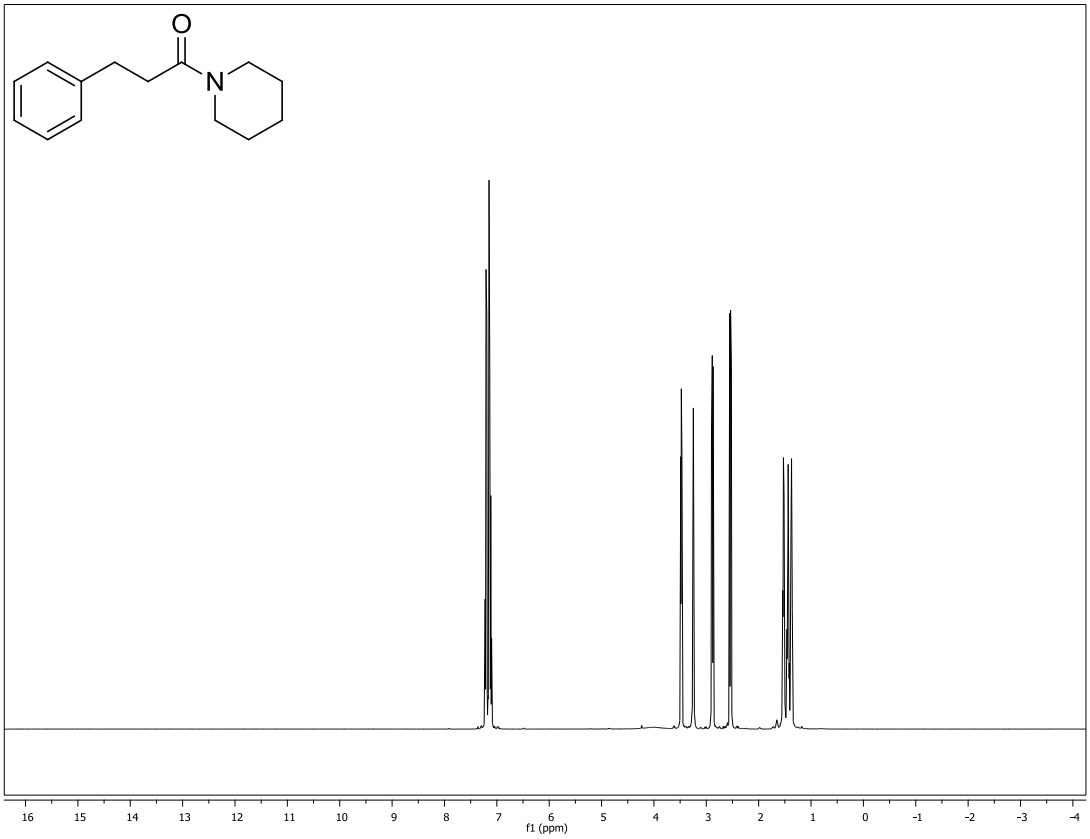
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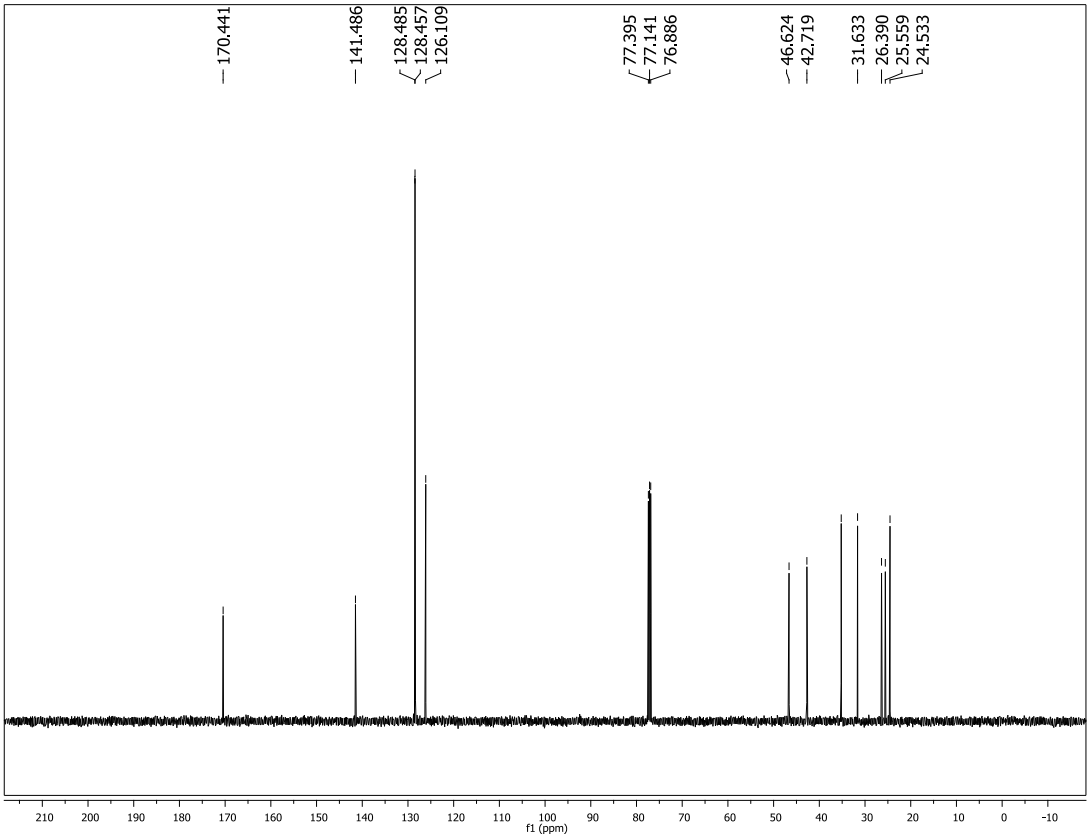
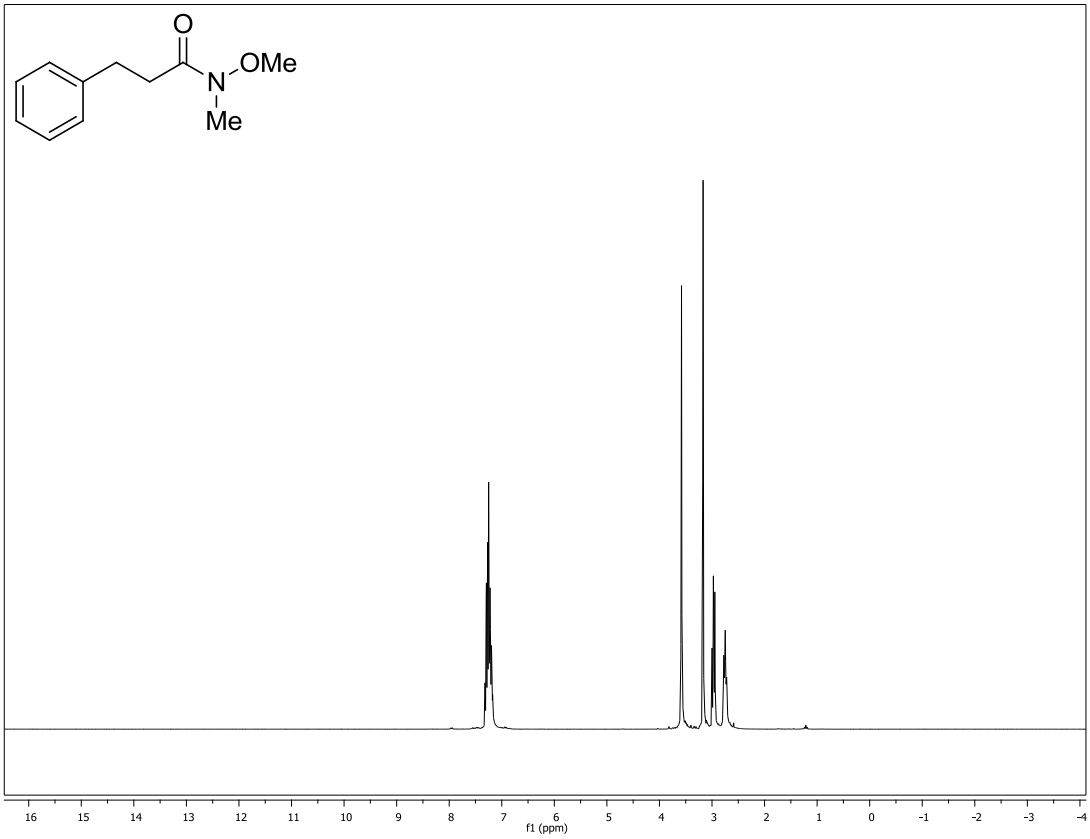
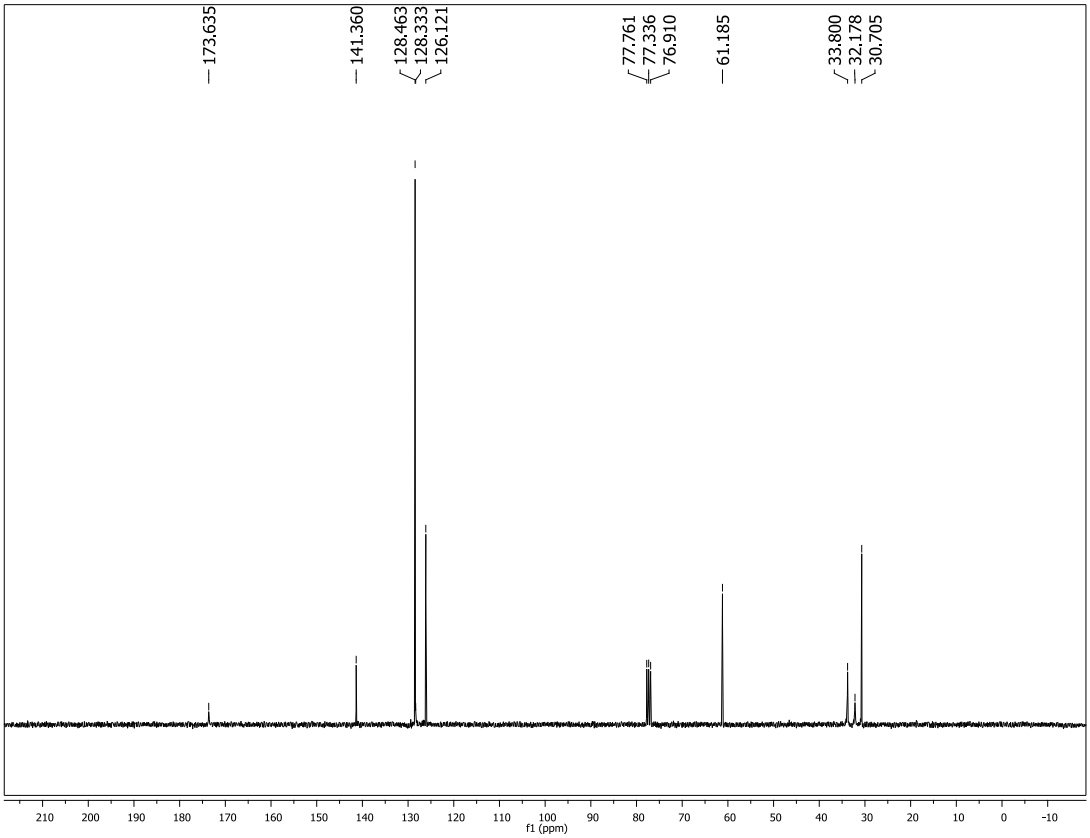
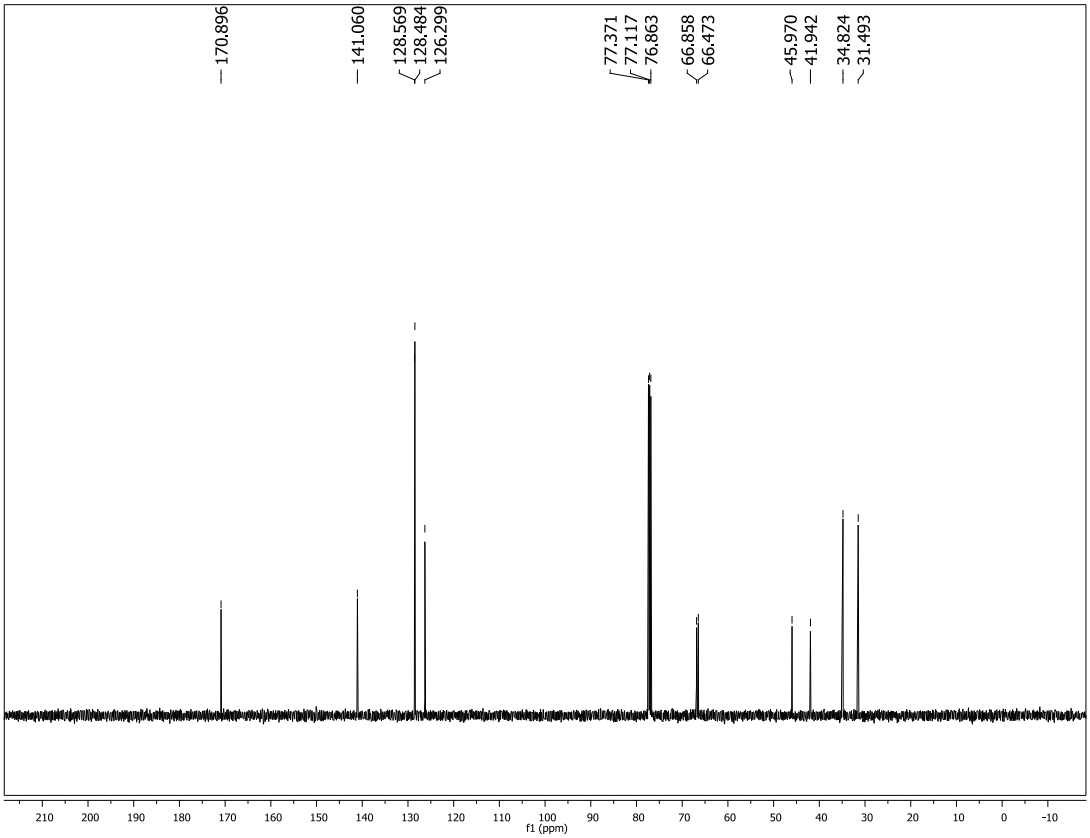
f1 (ppm)

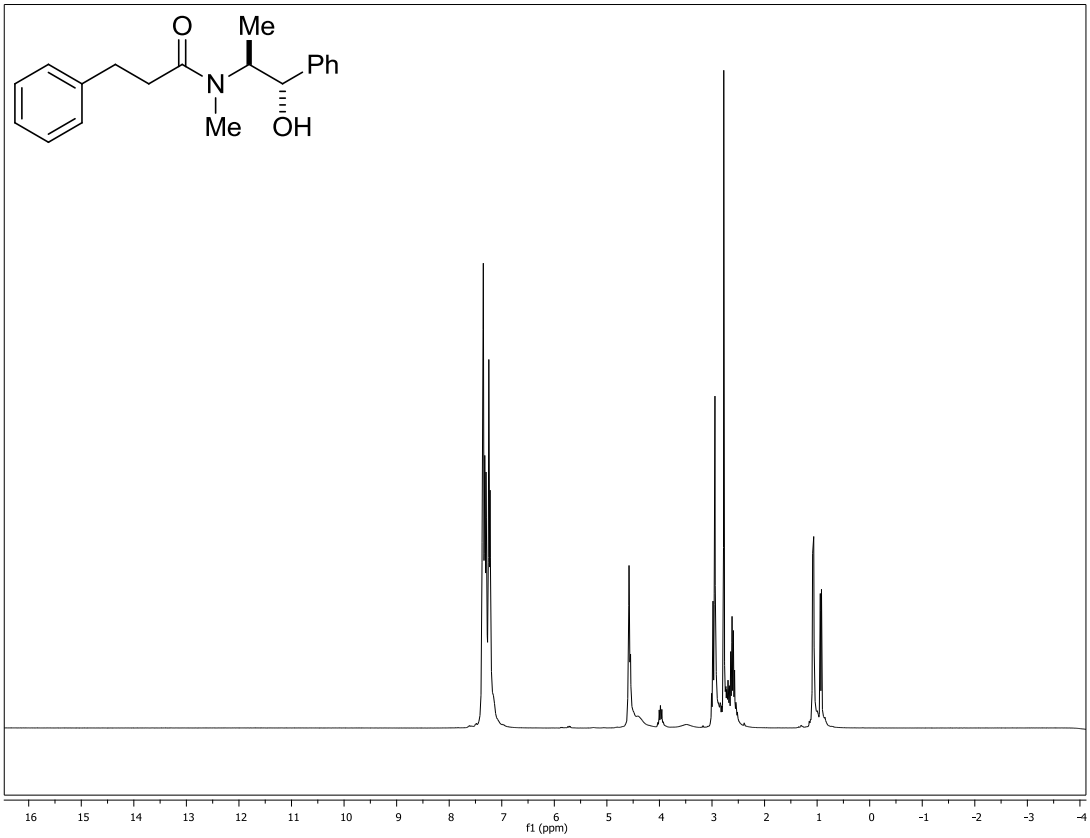

170.441
141.486
128.485
128.457
126.109
77.395
77.141
76.886
46.624
42.719
31.633
26.390
25.559
24.533
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

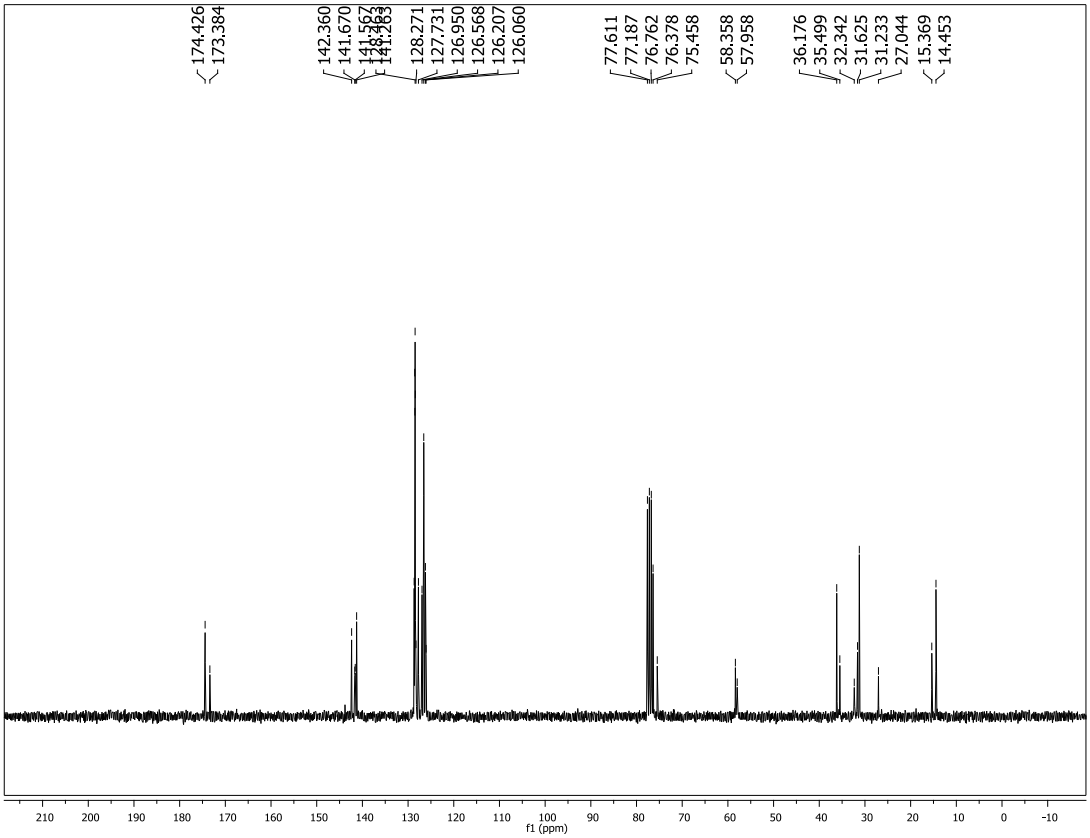

O
N
OMe
Me
f1 (ppm)

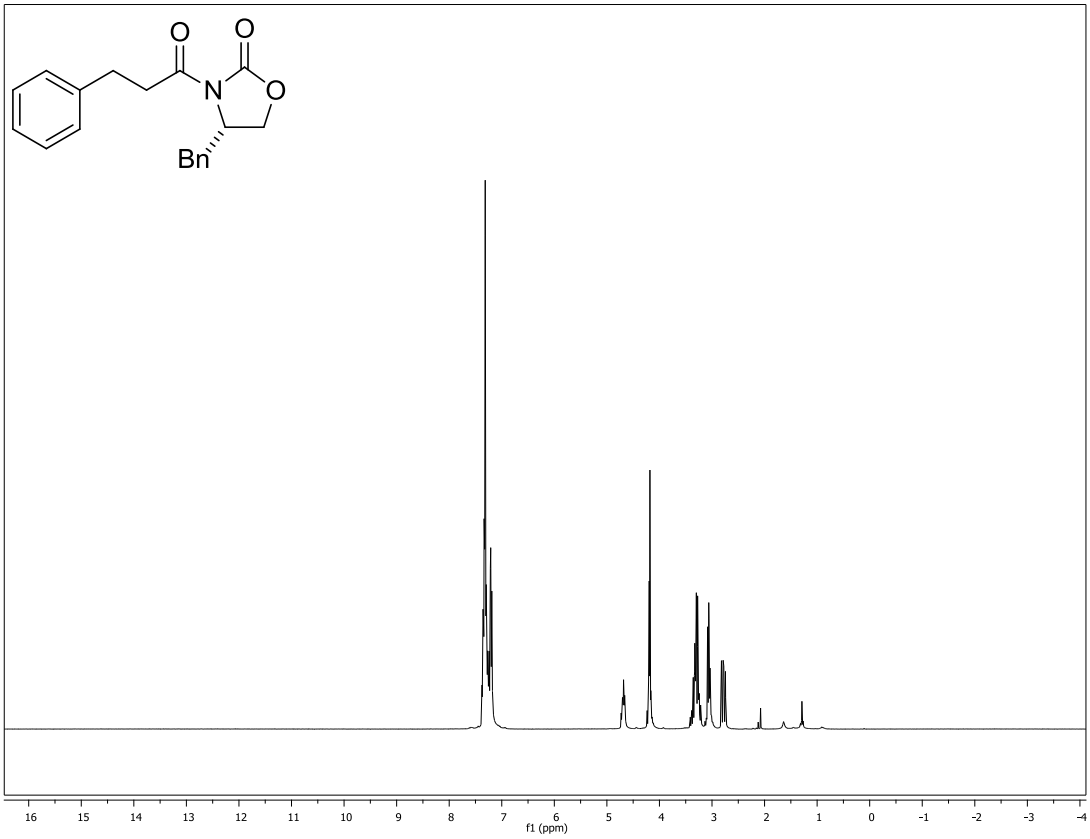

173.635
141.360
128.463
128.333
126.121
77.761
77.336
76.910
61.185
33.800
32.178
30.705
f1 (ppm)

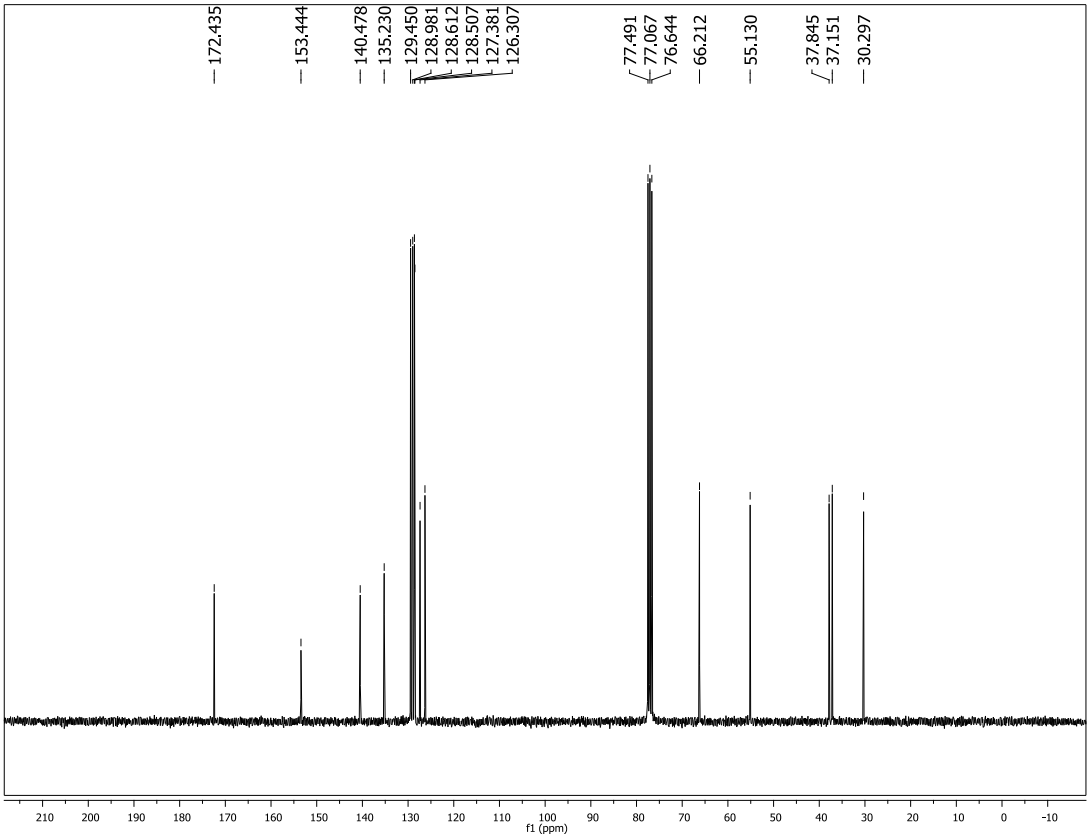

O
N
O
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

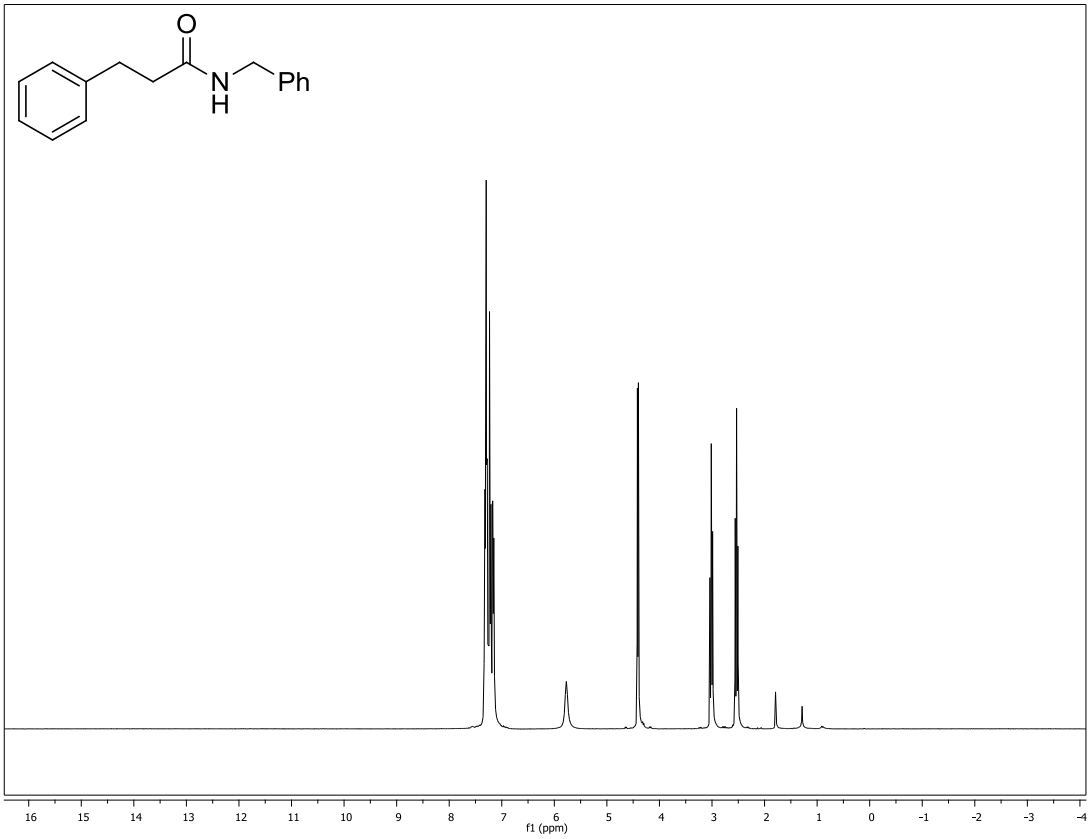

170.896
141.060
128.569
128.484
126.299
77.371
77.117
76.863
66.858
66.473
45.970
41.942
34.824
31.493
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

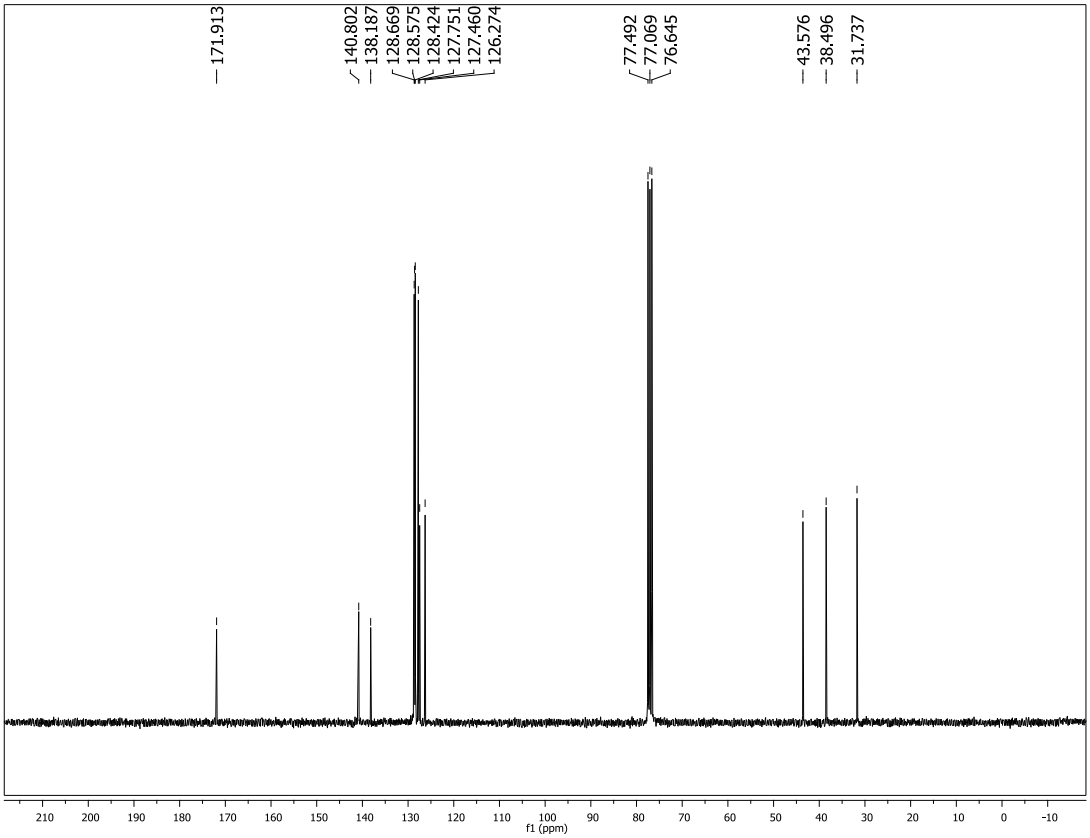

O
Me
N
Ph
Me
OH
f1 (ppm)

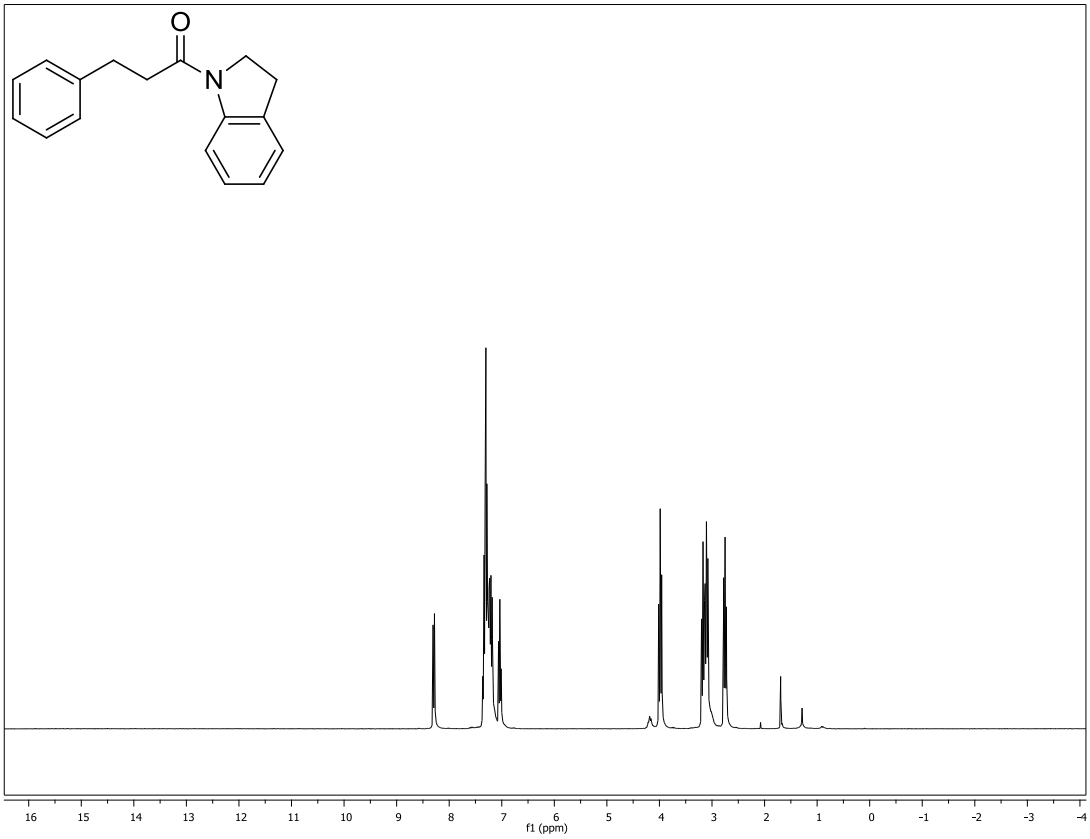

174.426
173.384
142.360
141.670
141.567
141.463
141.283
128.271
127.731
126.950
126.568
126.207
126.060
77.611
77.187
76.762
76.378
75.458
58.358
57.958
36.176
35.499
32.342
31.625
31.233
27.044
15.369
14.453
f1 (ppm)

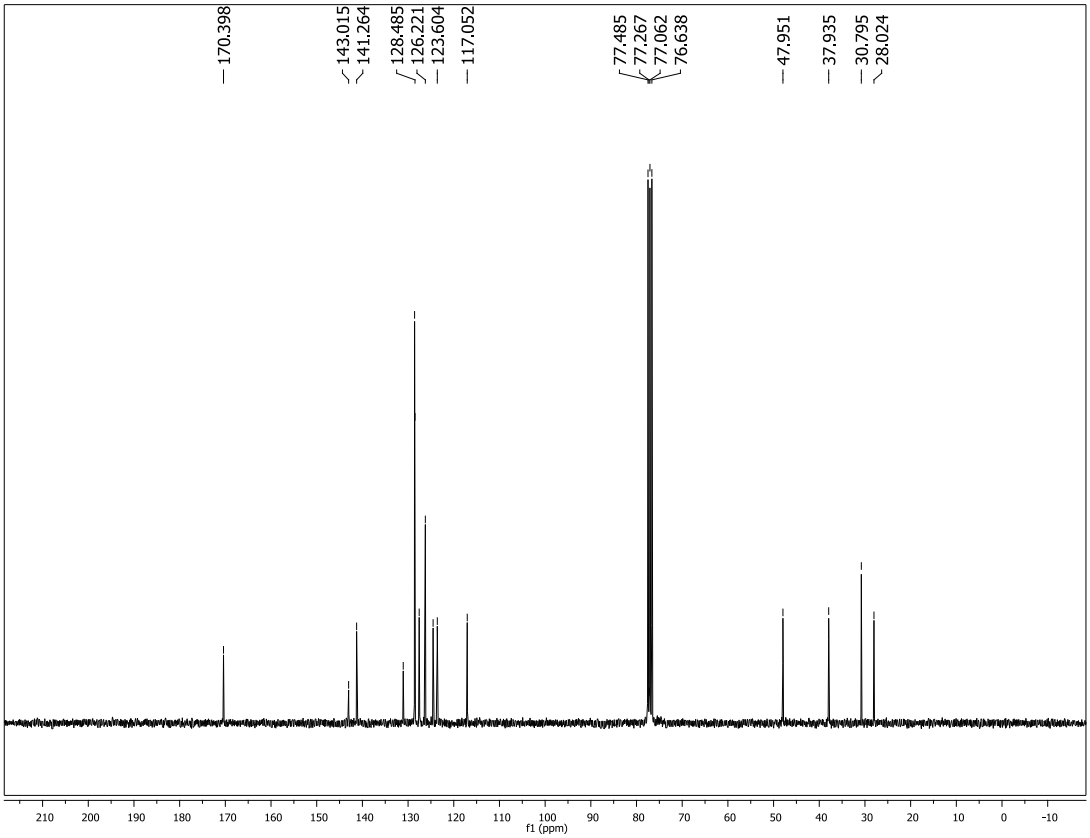

O
O
N
O
Bn
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

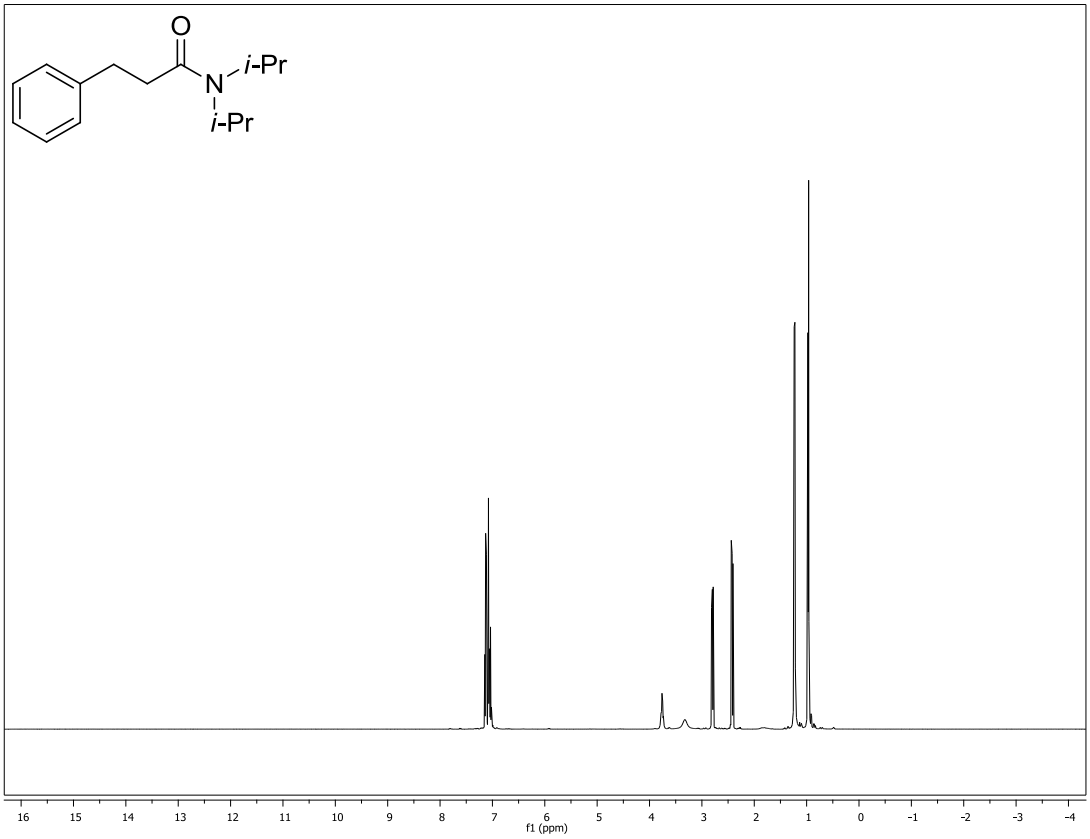

172.435
153.444
140.478
135.230
129.450
128.981
128.612
128.507
127.381
126.307
77.491
77.067
76.644
66.212
55.130
37.845
37.151
30.297
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

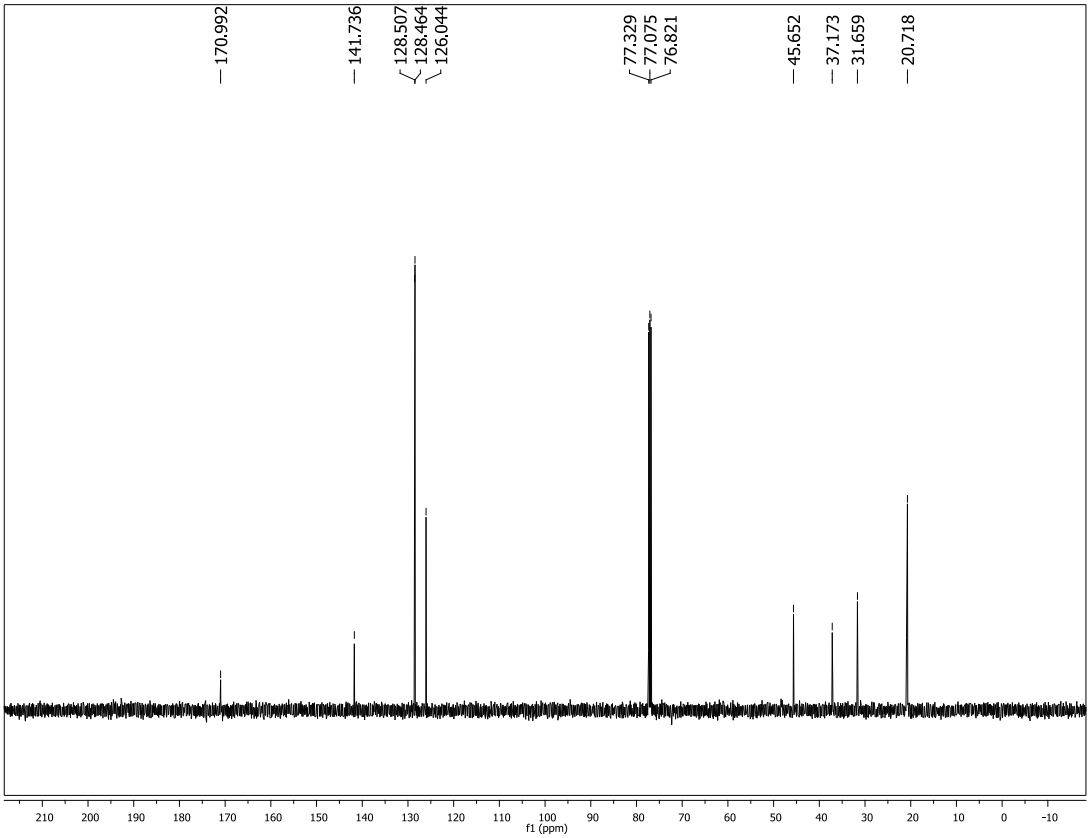

O
N
H
Ph
f1 (ppm)

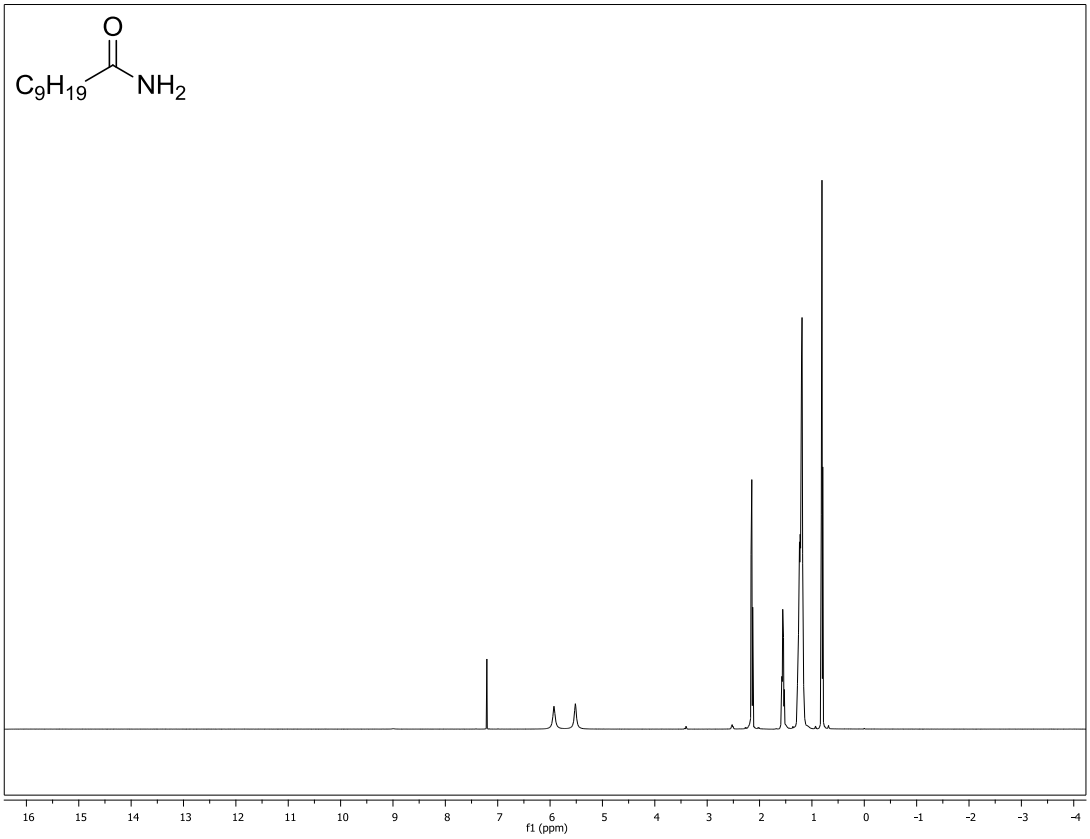

171.913
140.802
138.187
128.669
128.575
128.424
127.751
127.460
126.274
77.492
77.069
76.645
43.576
38.496
31.737
f1 (ppm)

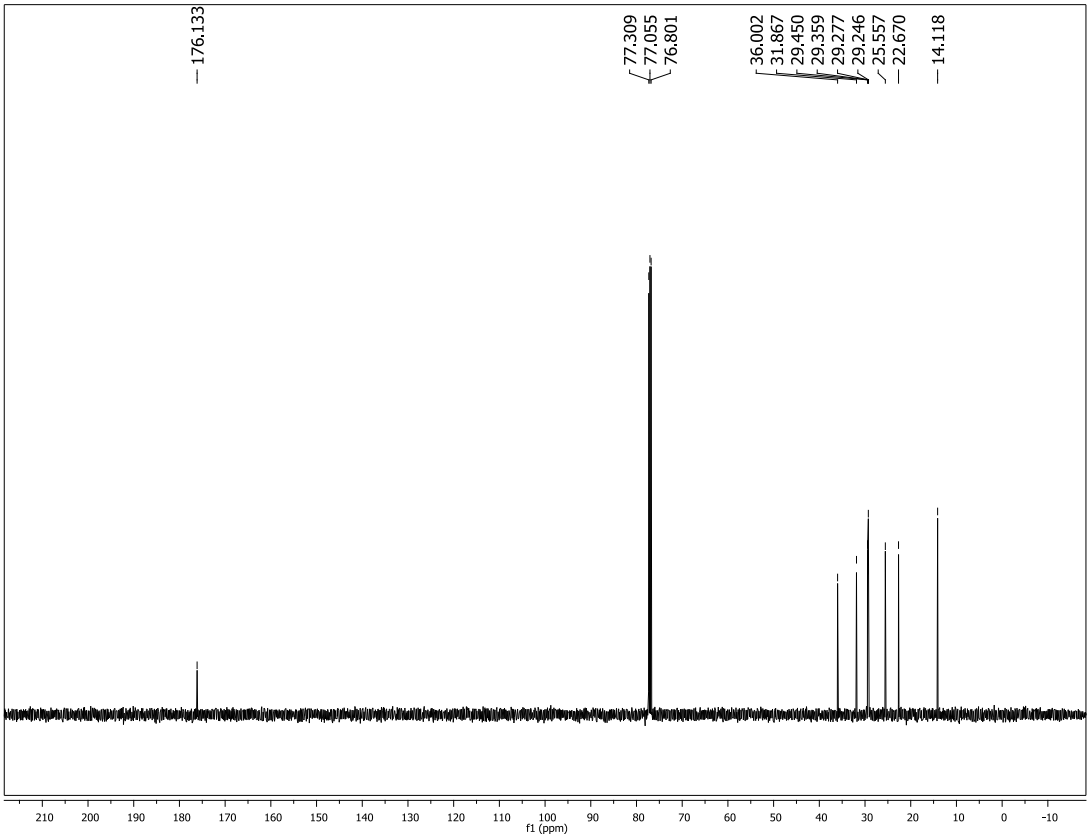

O
N
f1 (ppm)

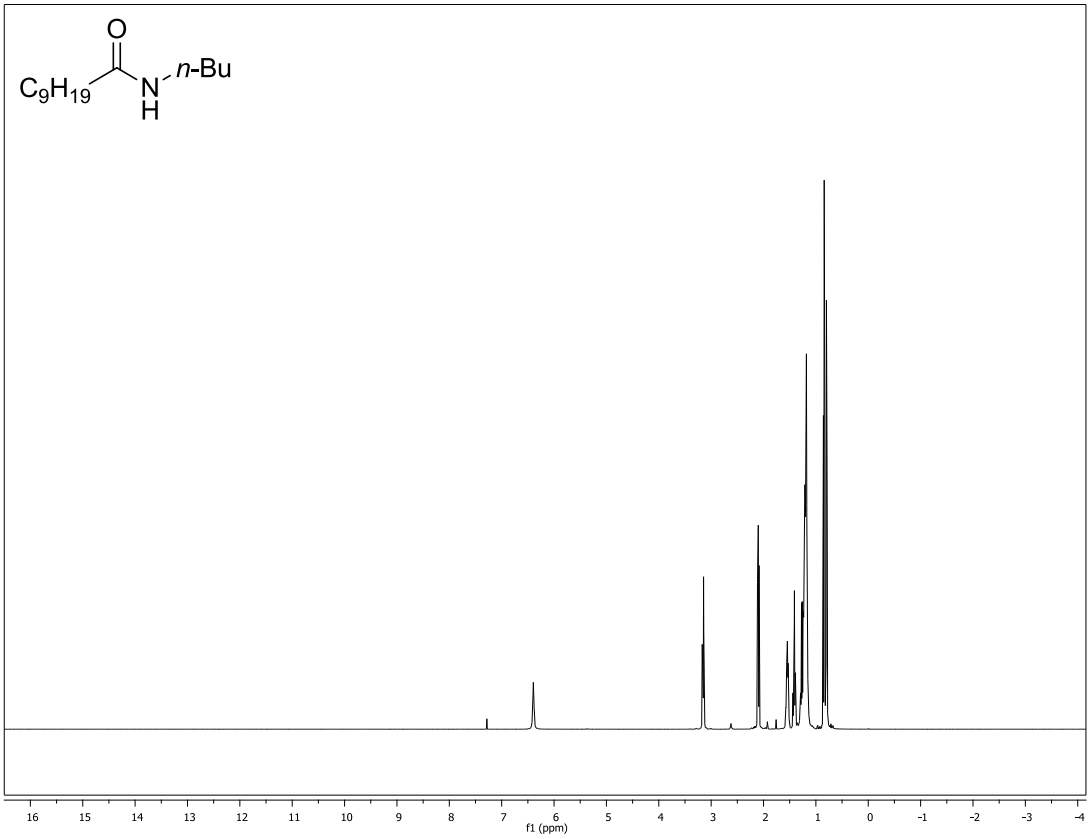

170.398
143.015
141.264
128.485
126.221
123.604
117.052
77.485
77.267
77.062
76.638
47.951
37.935
30.795
28.024
f1 (ppm)

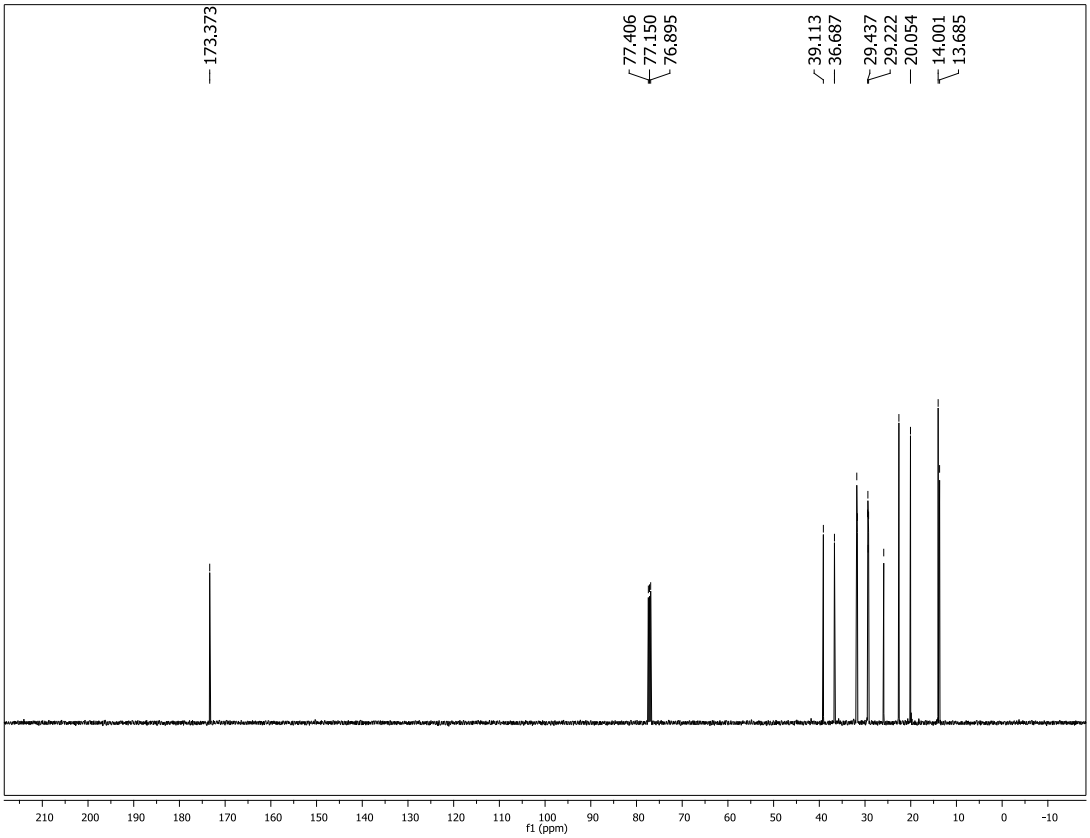

O
N
i-Pr
i-Pr
f1 (ppm)

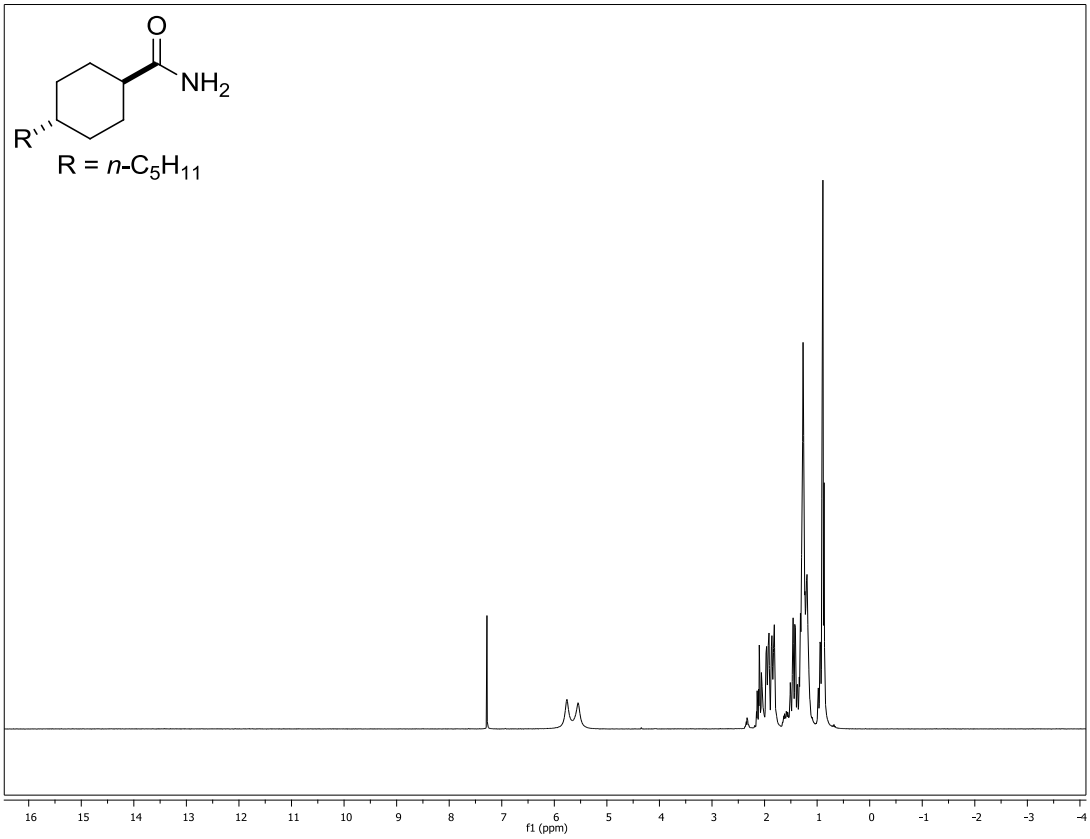

170.992
141.736
128.507
128.464
126.044
77.329
77.075
76.821
45.652
37.173
31.659
20.718
f1 (ppm)

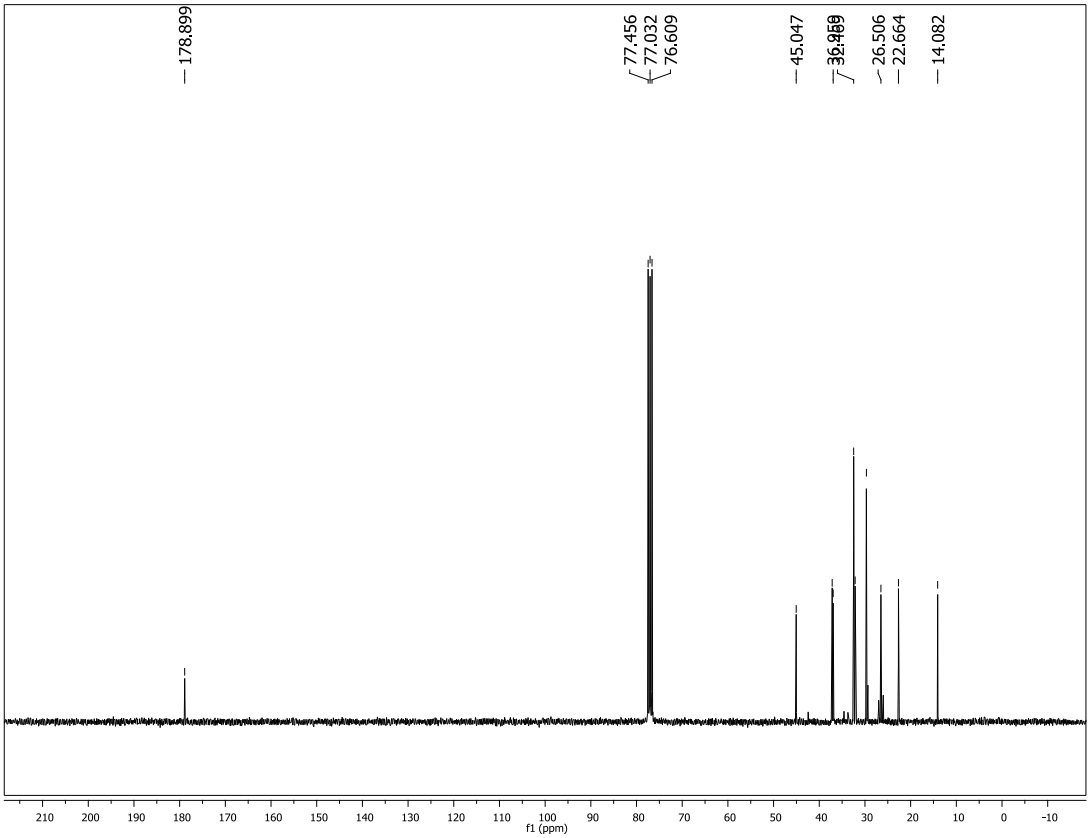

O
C9H19
NH2
f1 (ppm)

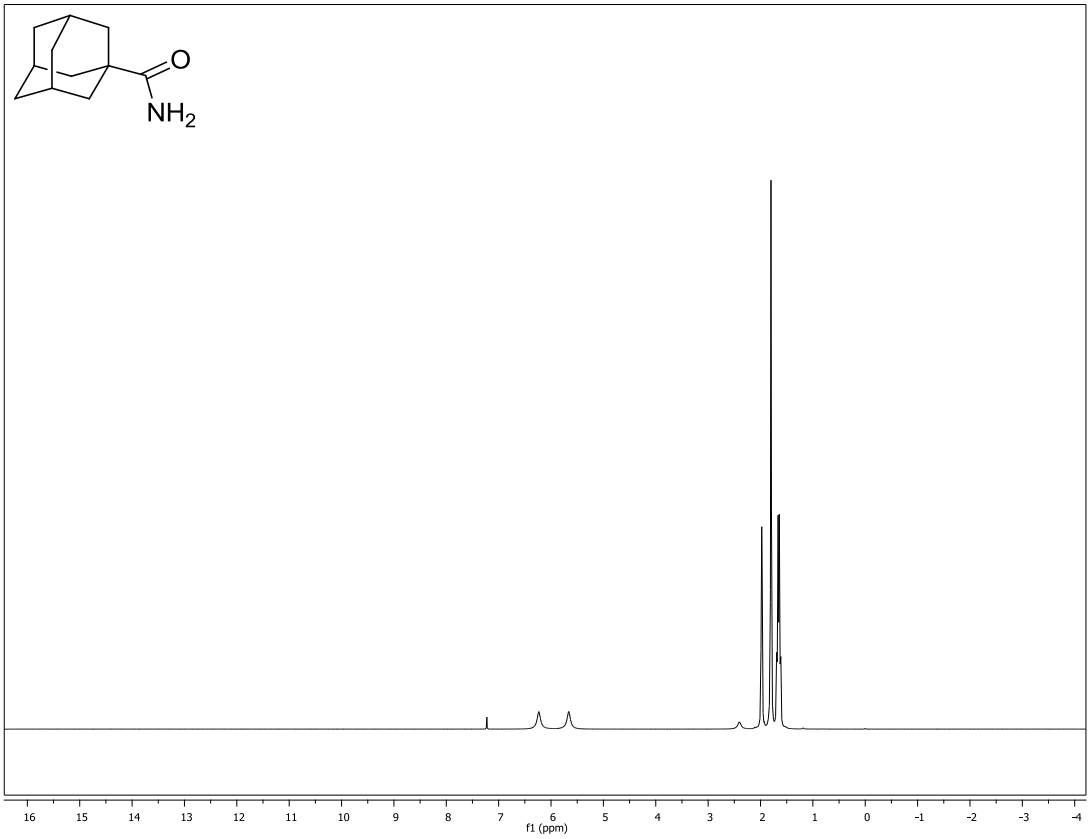

176.133
77.309
77.055
76.801
36.002
31.867
29.450
29.359
29.277
29.246
25.557
22.670
14.118
f1 (ppm)

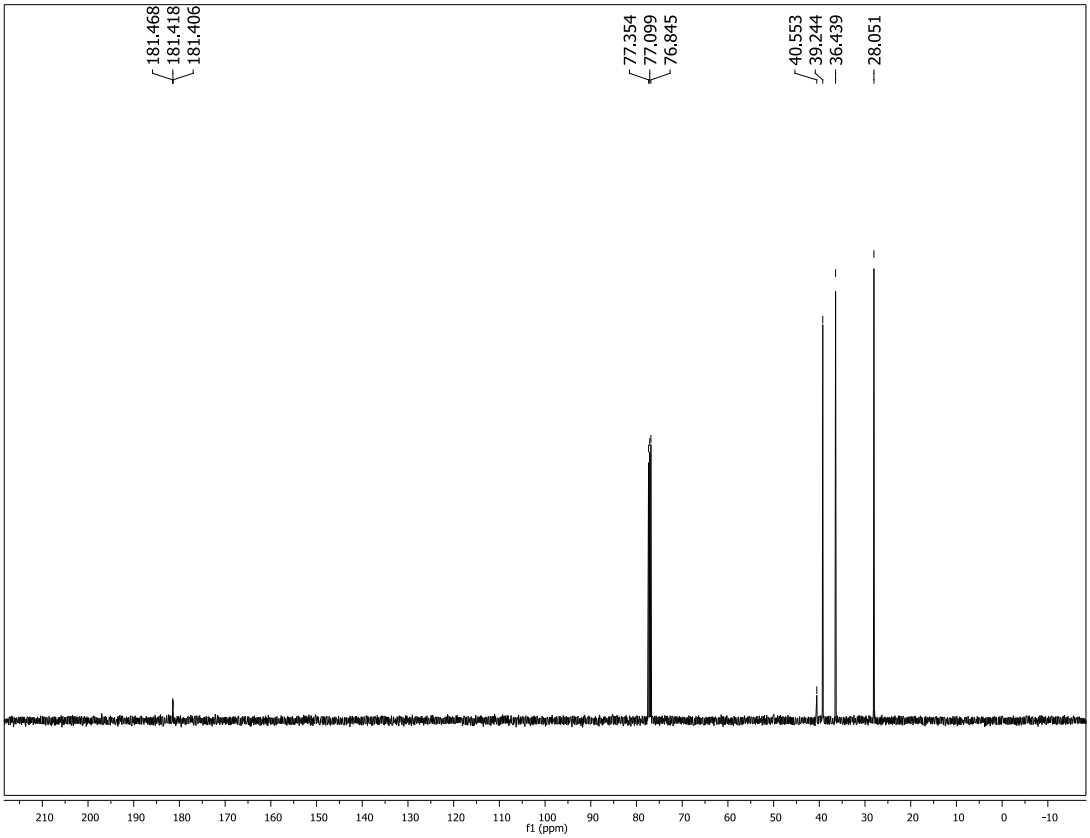

O
C9H19
N
H
n-Bu
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

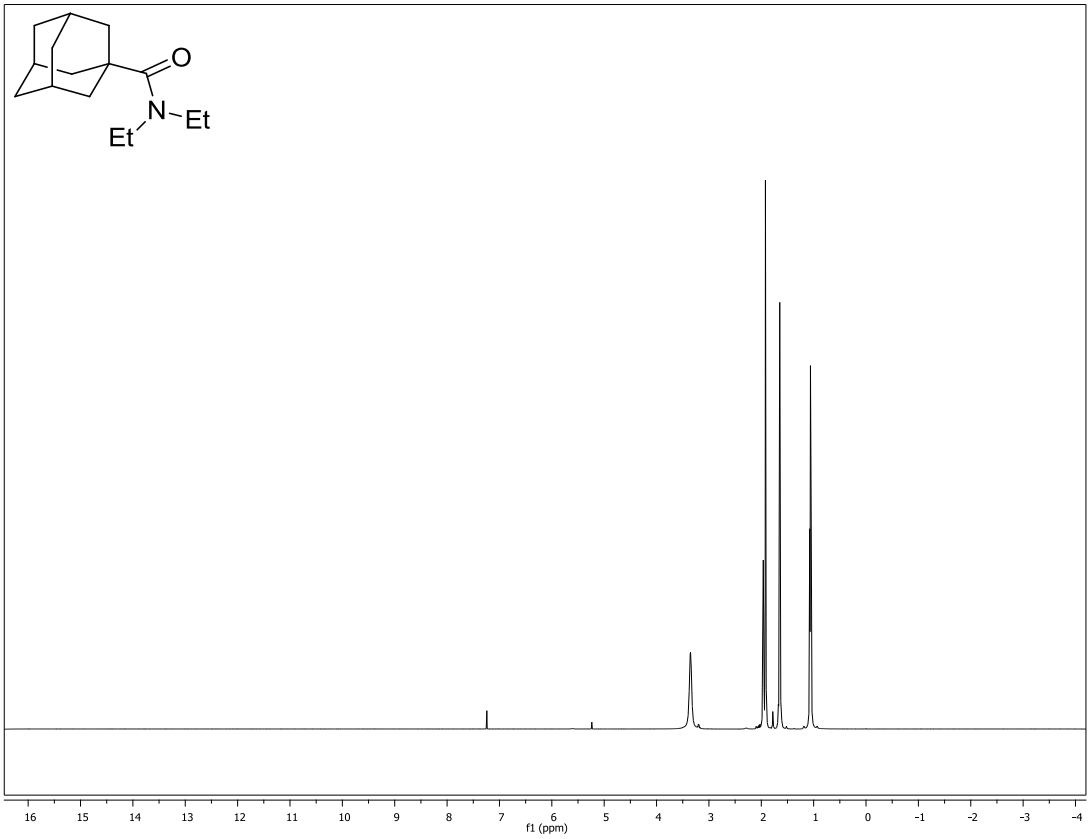

173.373
77.406
77.150
76.895
39.113
36.687
29.437
29.222
20.054
14.001
13.685
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

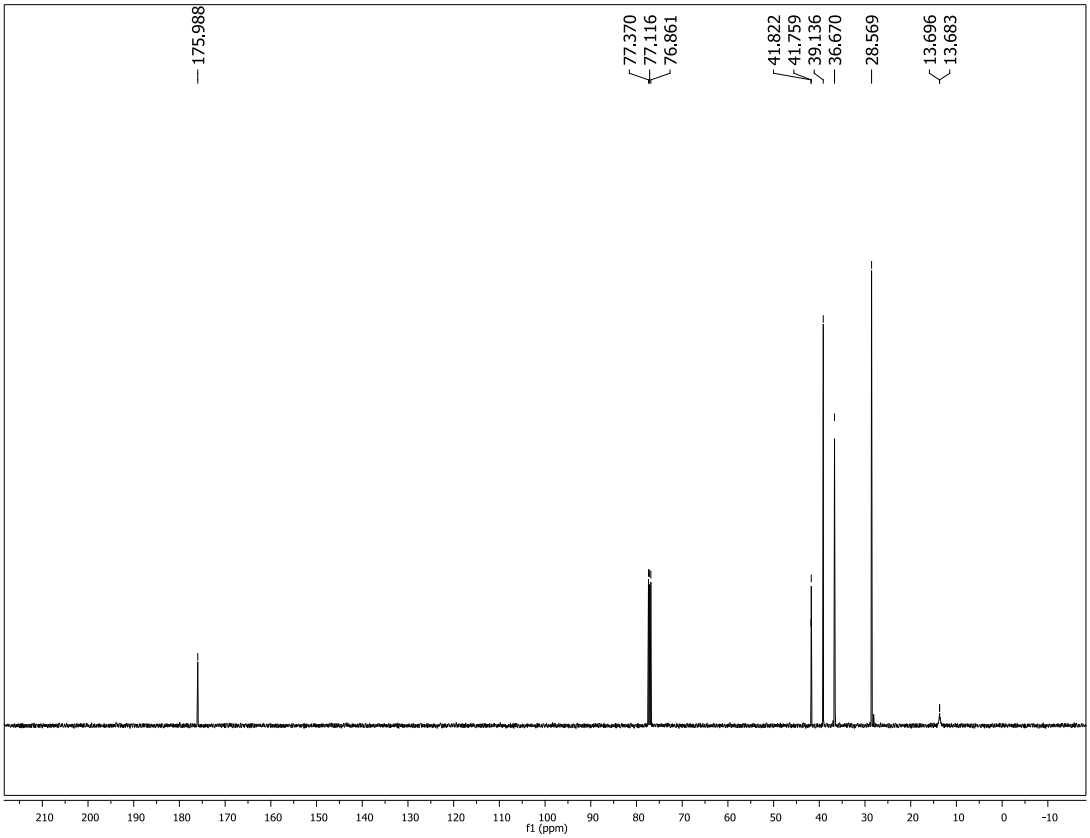

O
NH2
R
R = n-C5H11
f1 (ppm)

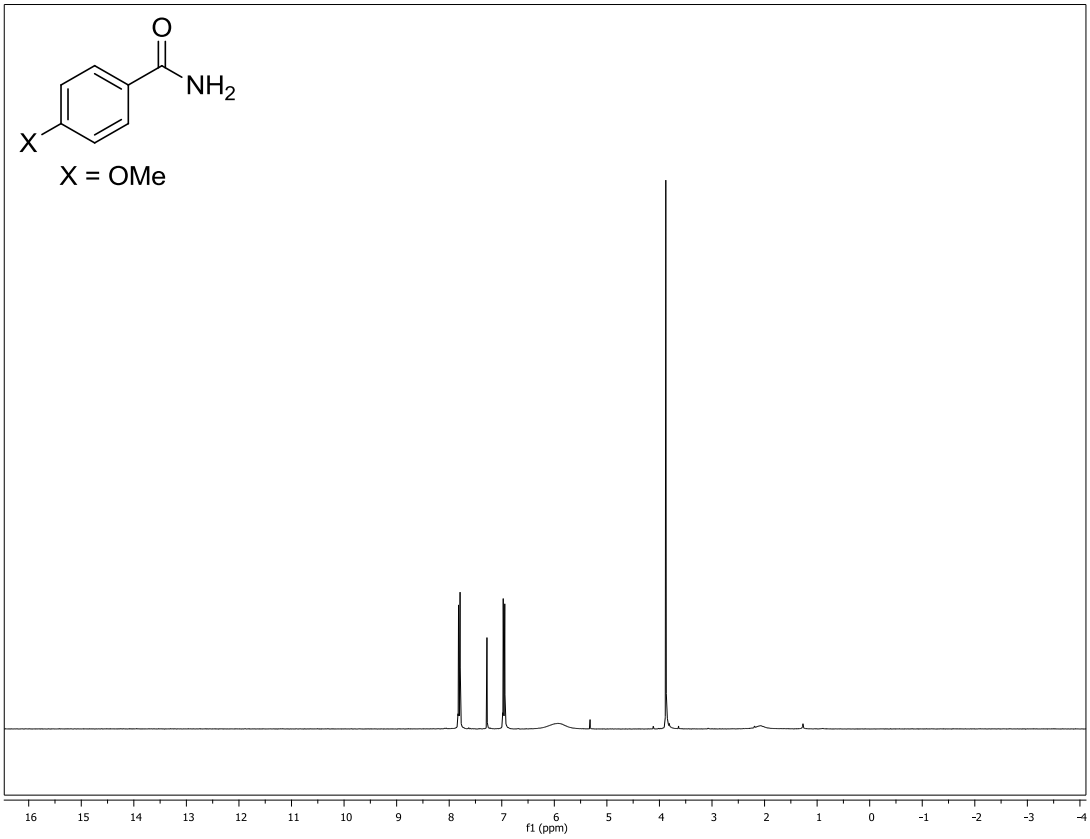

178.899
77.456
77.032
76.609
45.047
36.459
32.469
26.506
22.664
14.082
f1 (ppm)

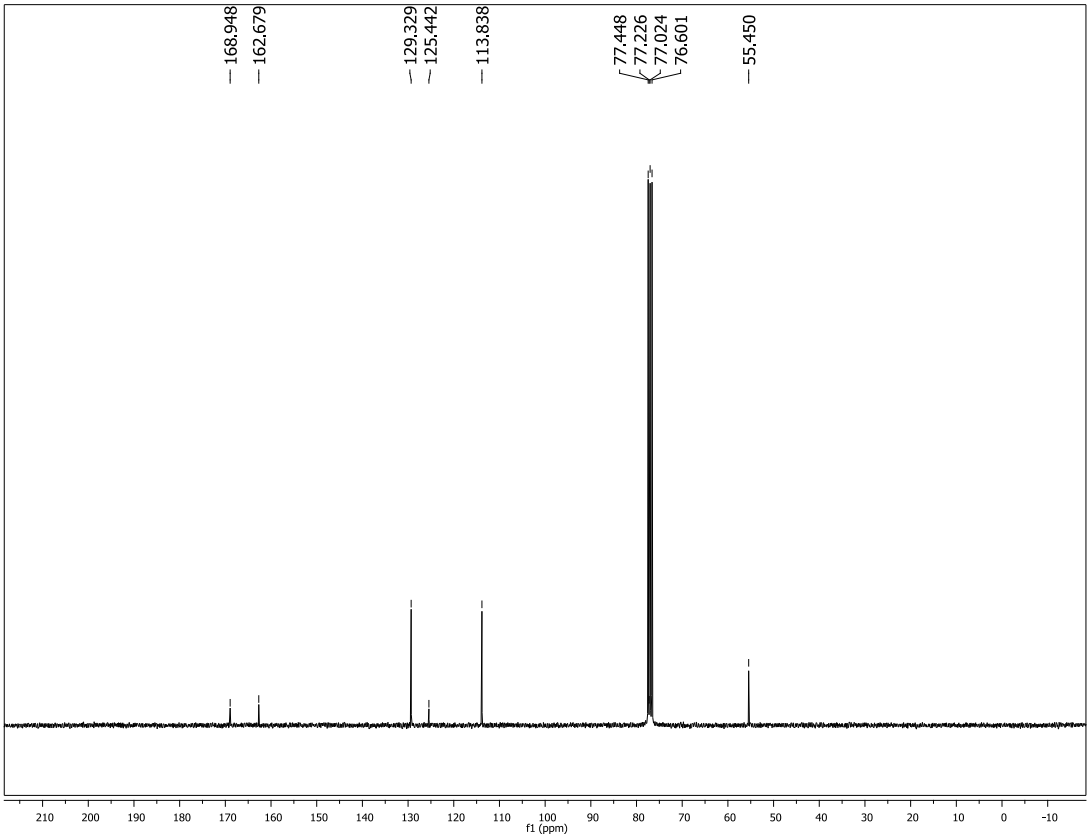

O
NH2
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

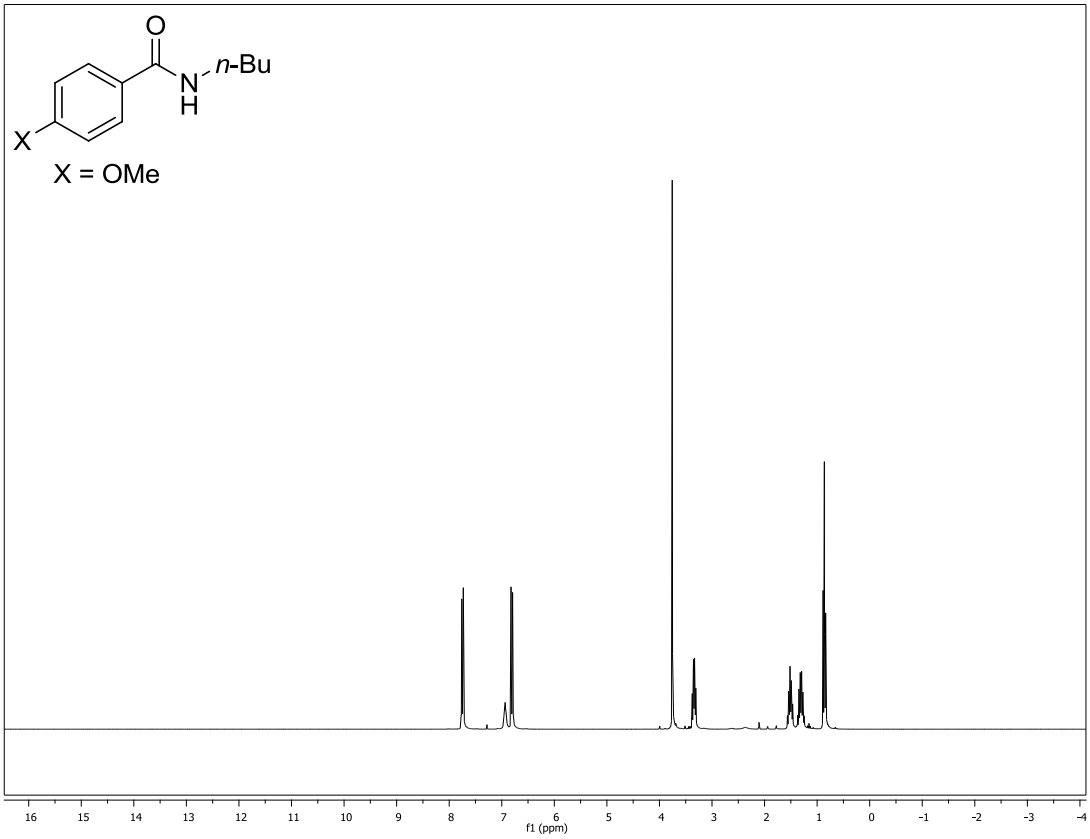

181.468
181.418
181.406
77.354
77.099
76.845
40.553
39.244
36.439
28.051
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

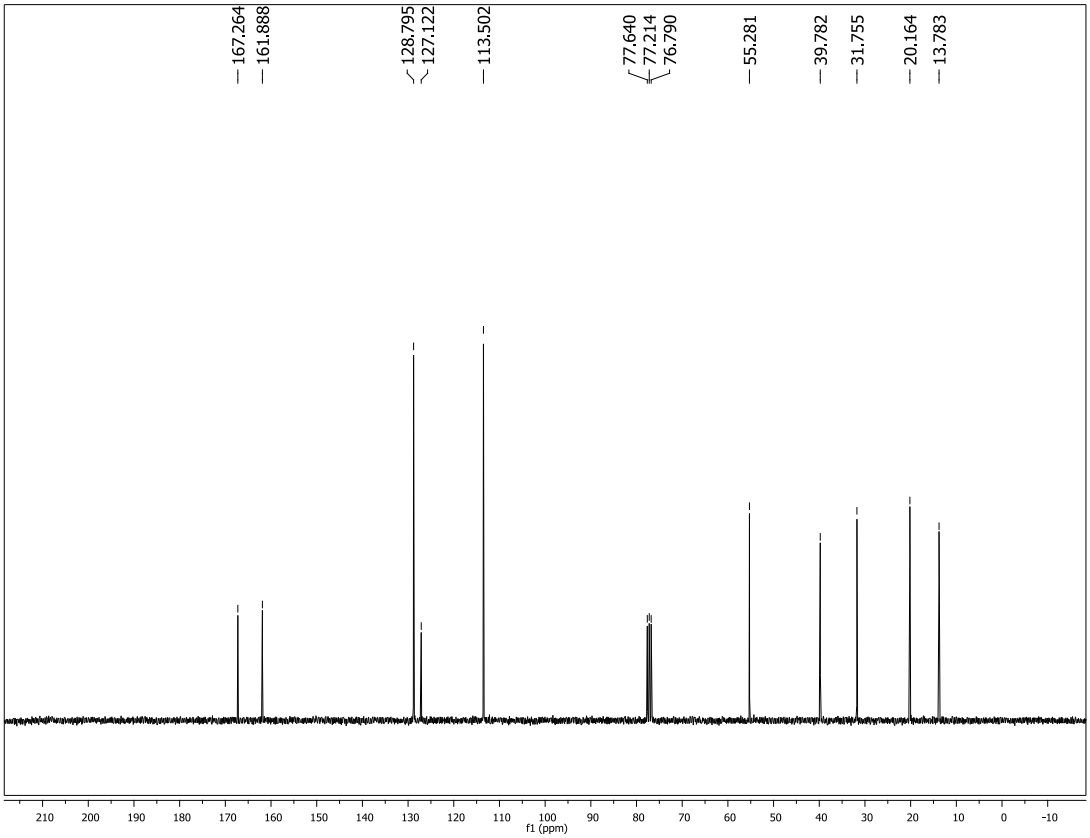

O
N
Et
Et
f1 (ppm)

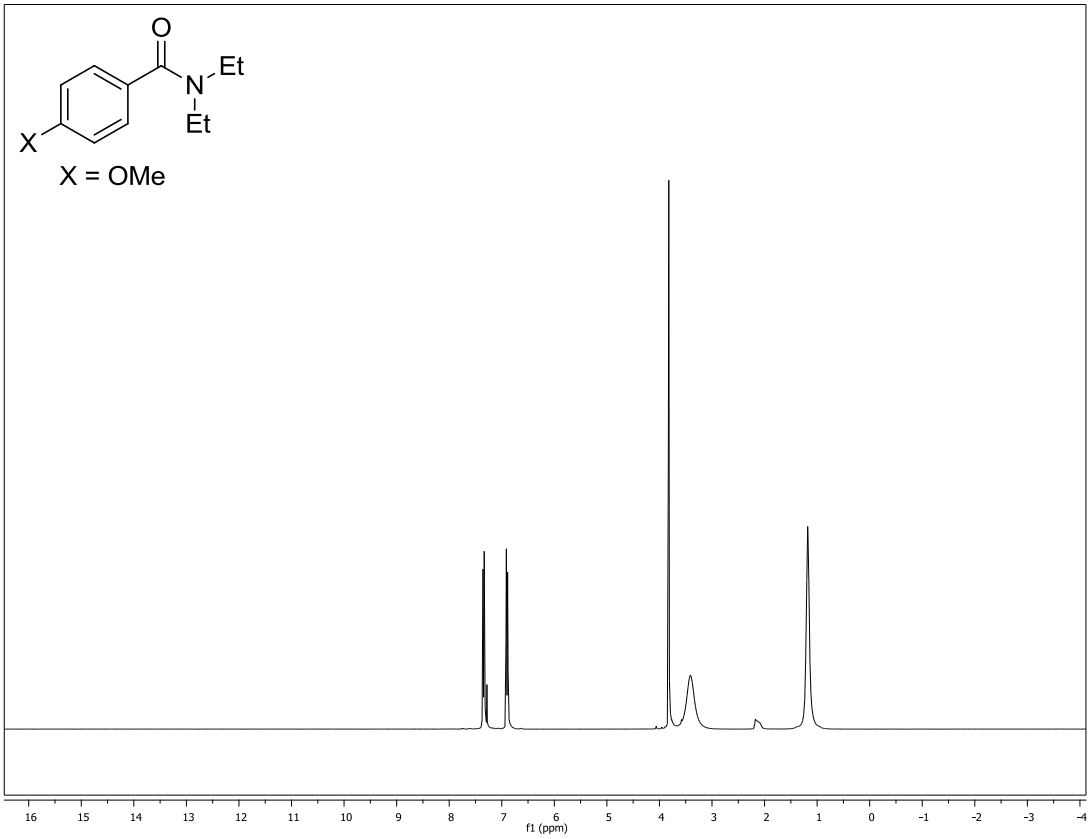

175.988
77.370
77.116
76.861
41.822
41.759
39.136
36.670
28.569
13.696
13.683
f1 (ppm)

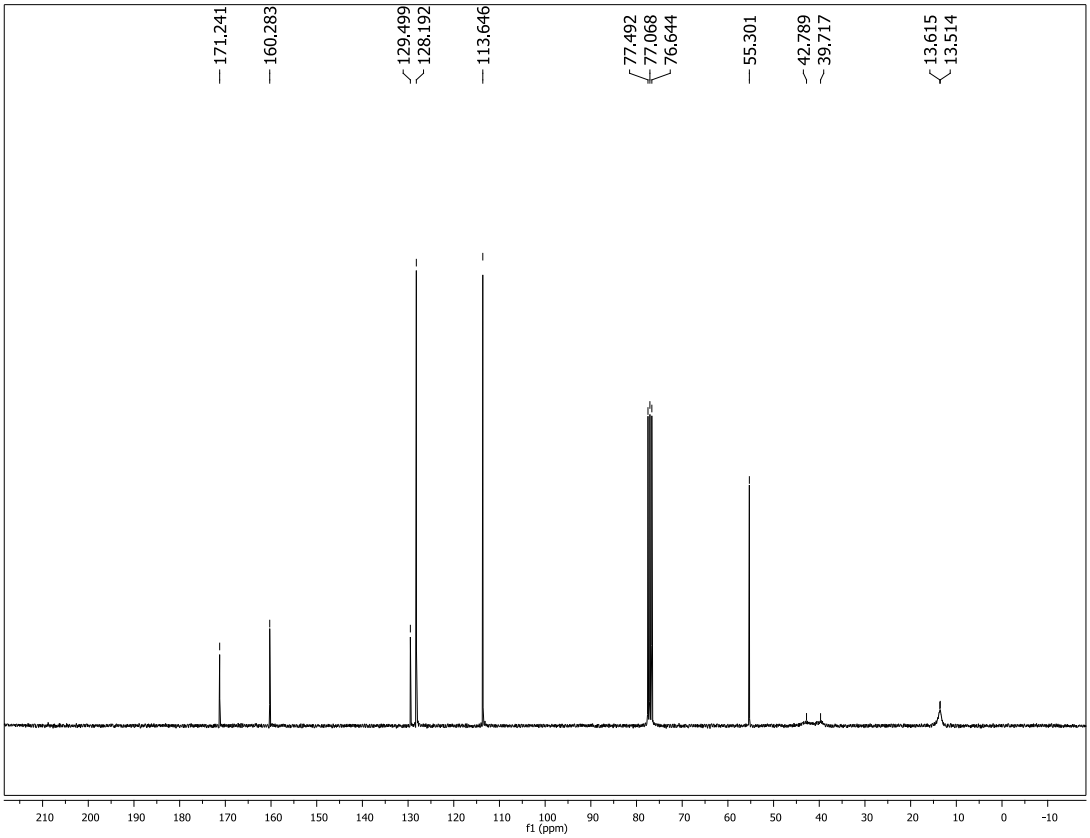

O
NH2
X
X = OMe
f1 (ppm)

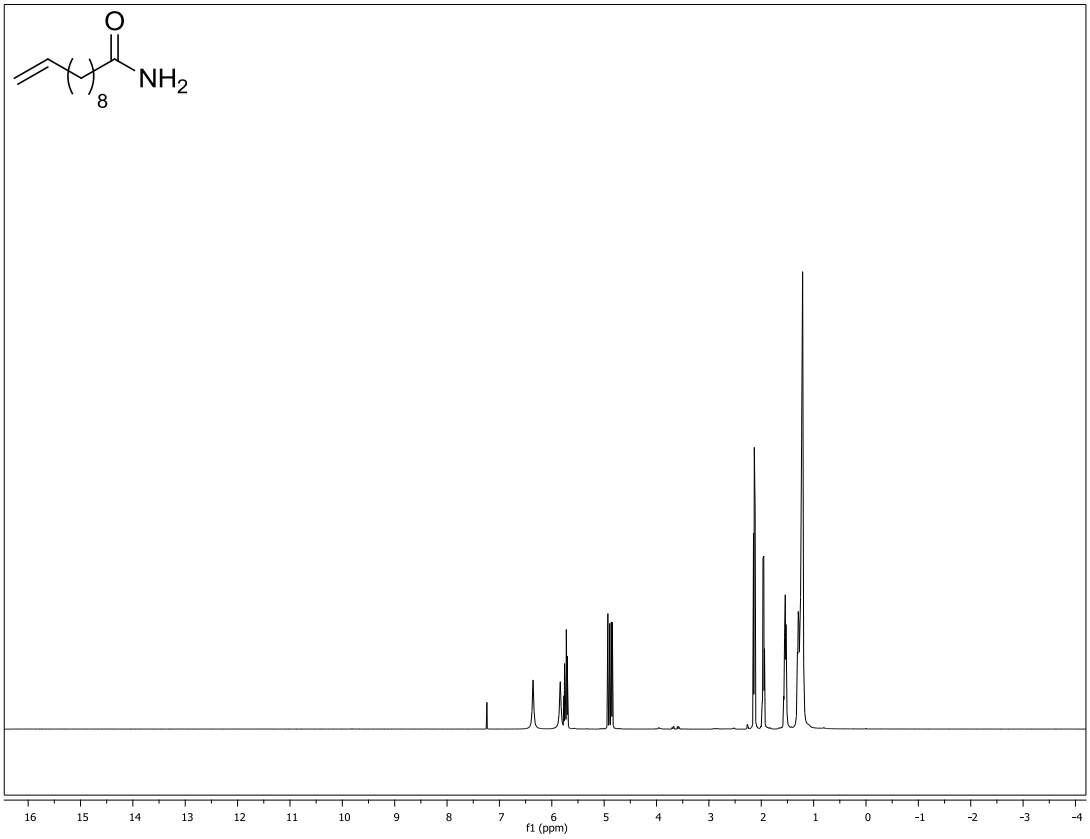

168.948
162.679
129.329
125.442
113.838
77.448
77.226
77.024
76.601
55.450
f1 (ppm)

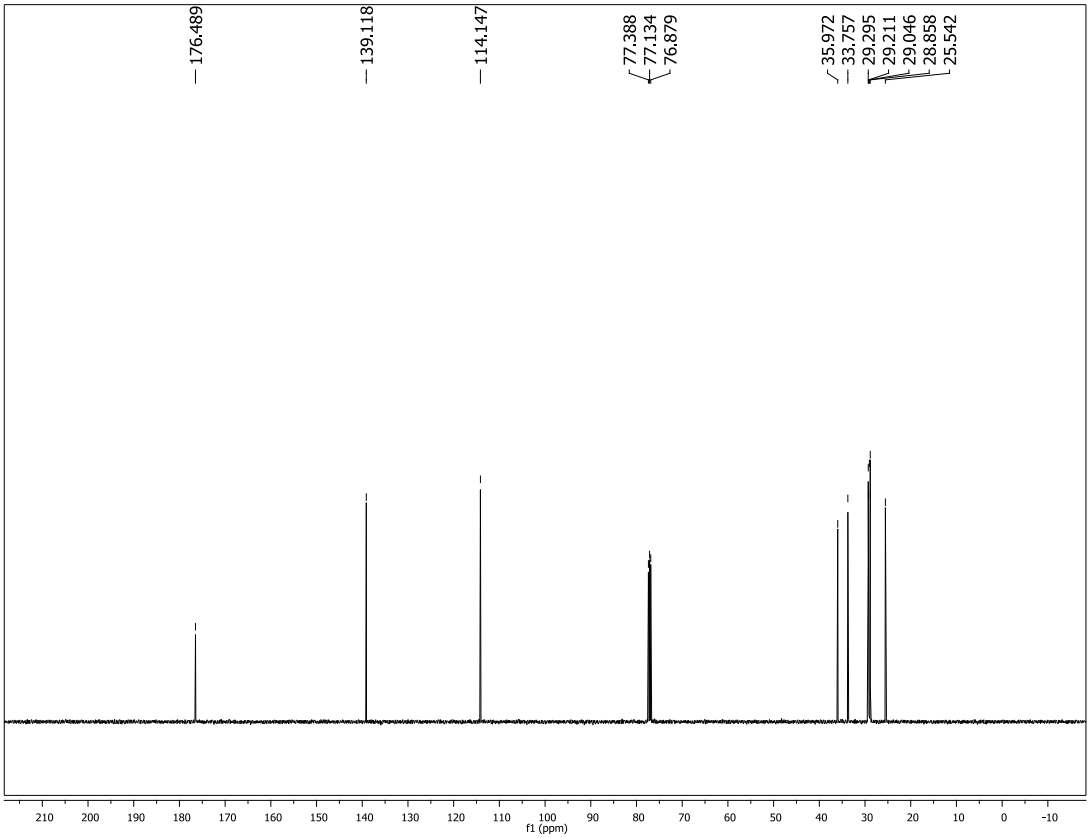

O
N
H
n-Bu
X
X = OMe
f1 (ppm)

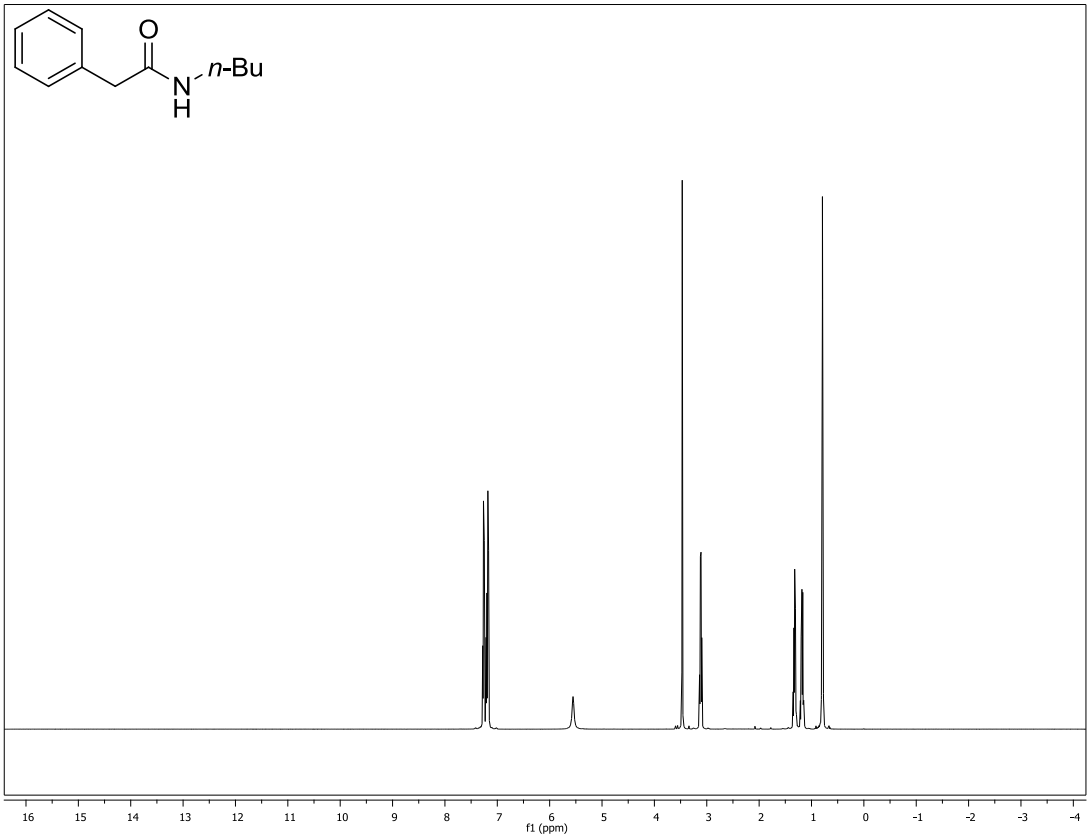

167.264
161.888
128.795
127.122
113.502
77.640
77.214
76.790
55.281
39.782
31.755
20.164
13.783
f1 (ppm)

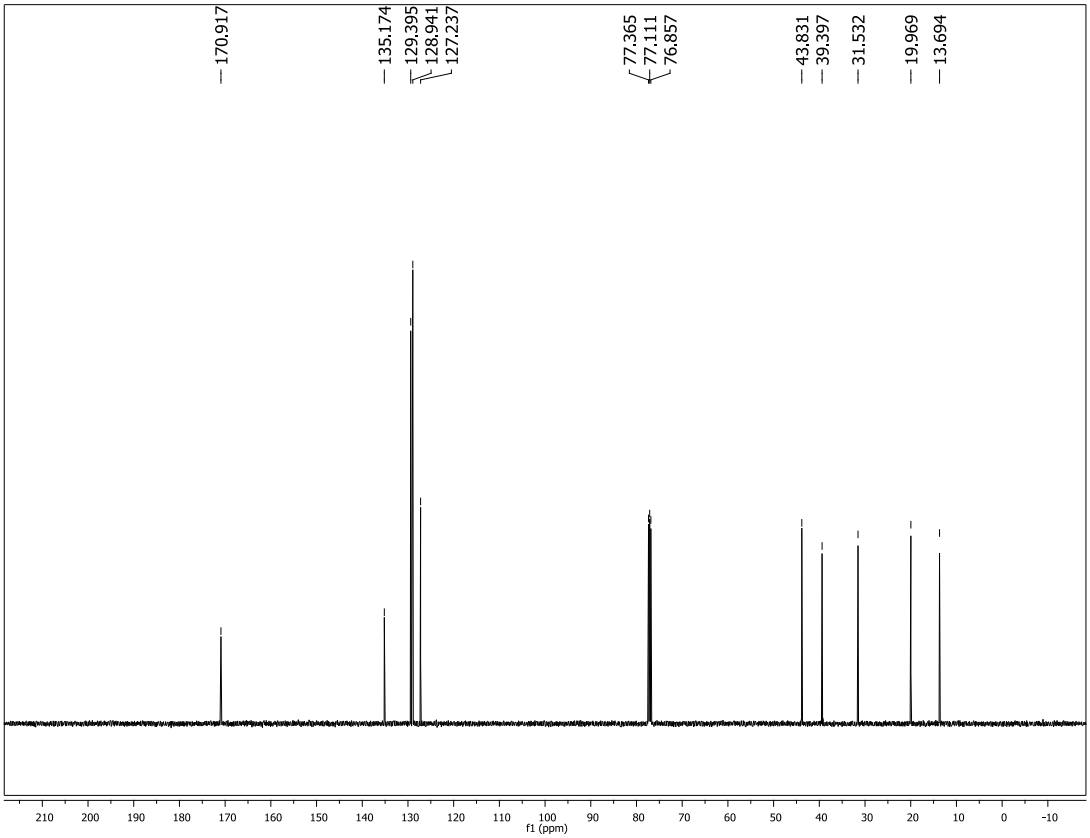

O
N
Et
Et
X
X = OMe
f1 (ppm)

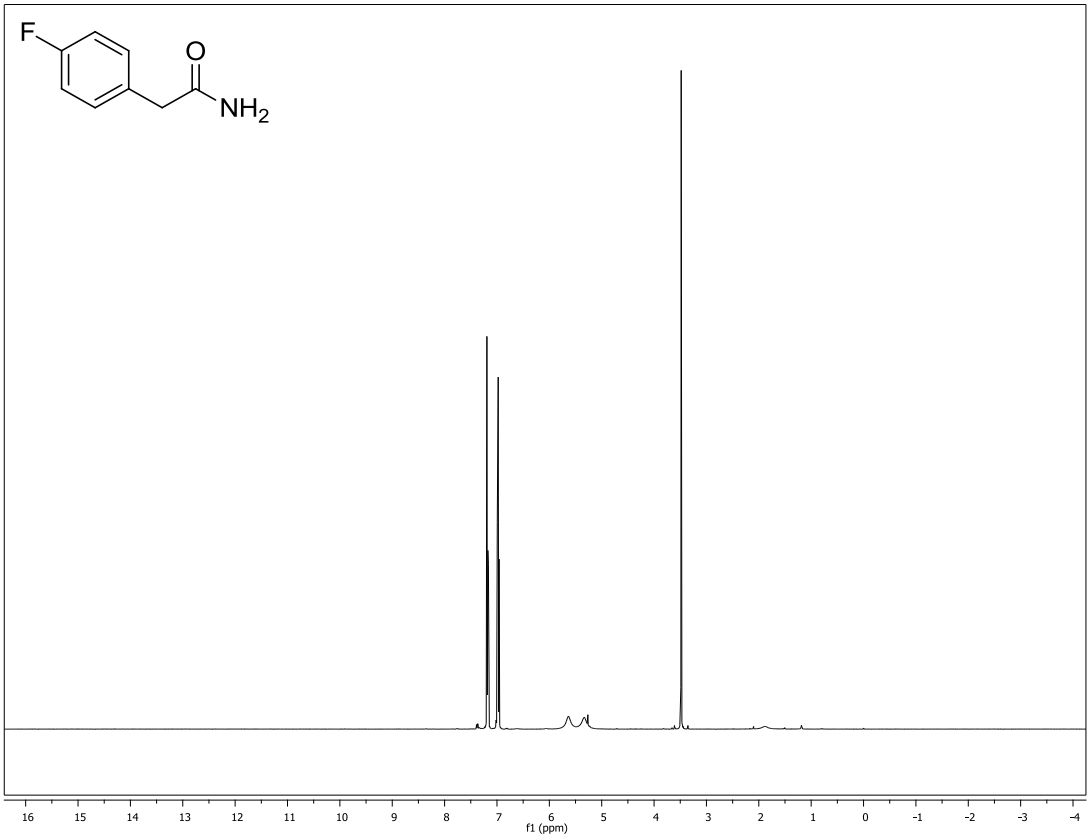

171.241
160.283
129.499
128.192
113.646
77.492
77.068
76.644
55.301
42.789
39.717
13.615
13.514
f1 (ppm)

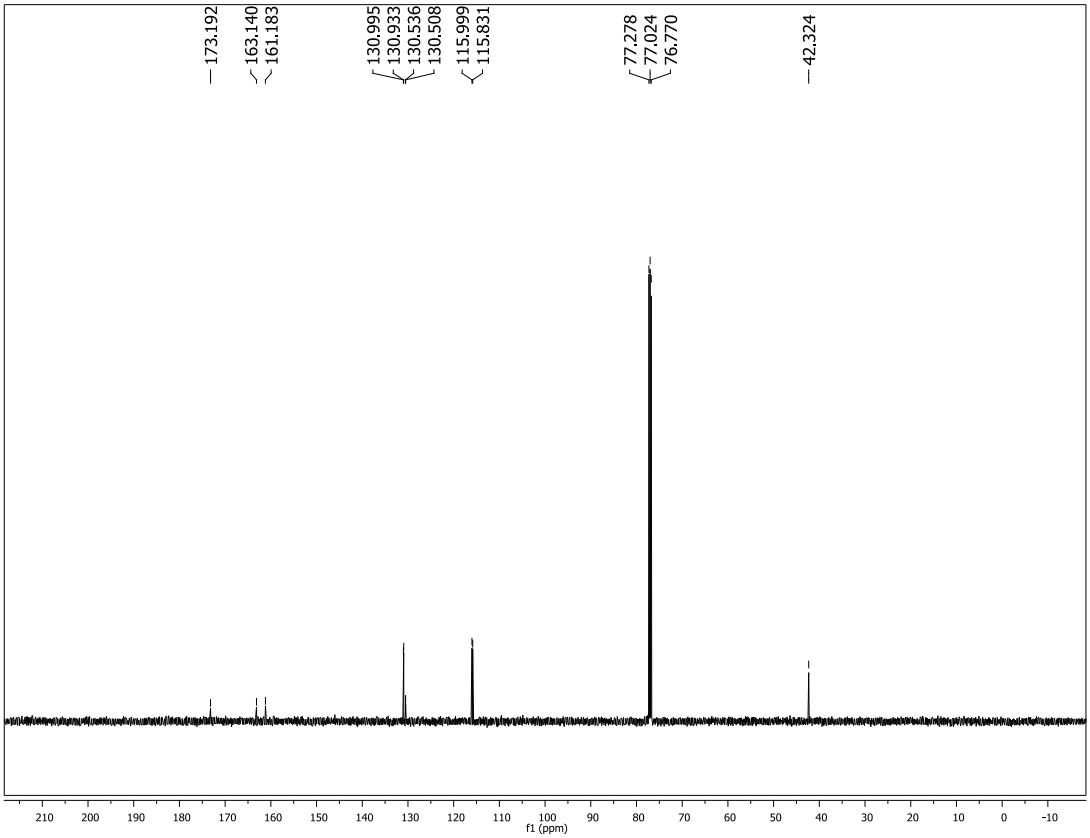

O
NH2
8
f1 (ppm)

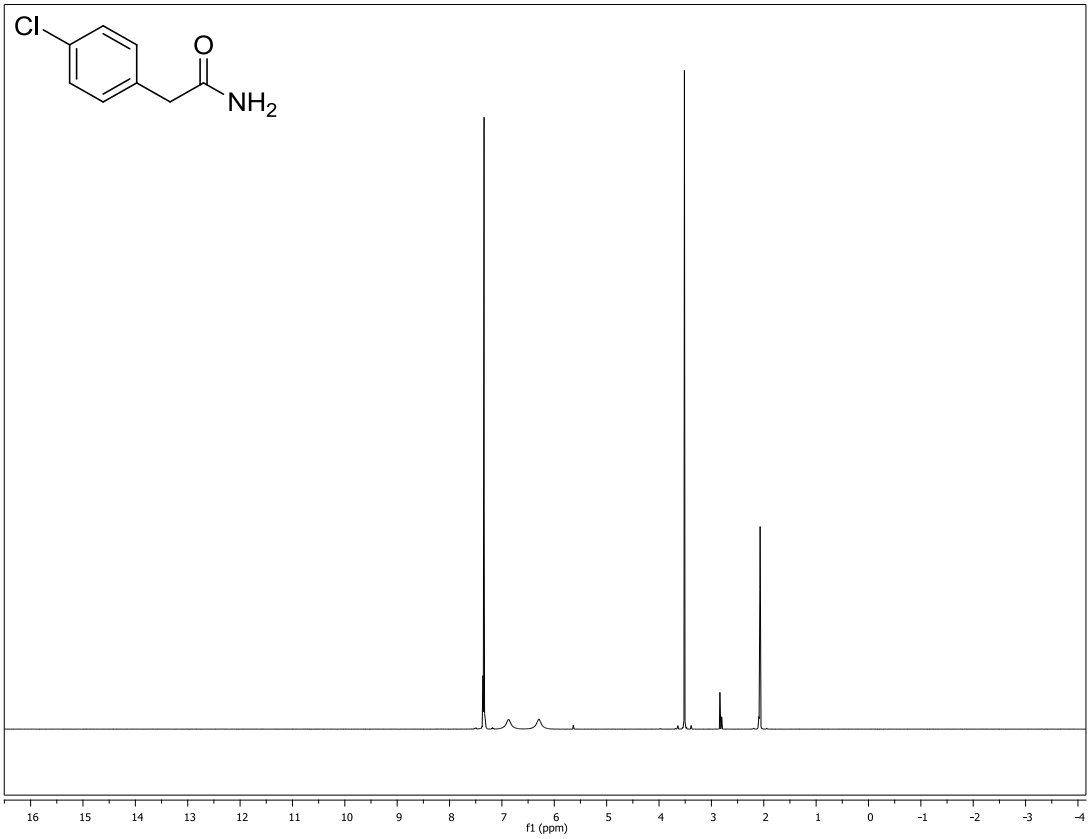

176.489
139.118
114.147
77.388
77.134
76.879
35.972
33.757
29.295
29.211
29.046
28.858
25.542
f1 (ppm)

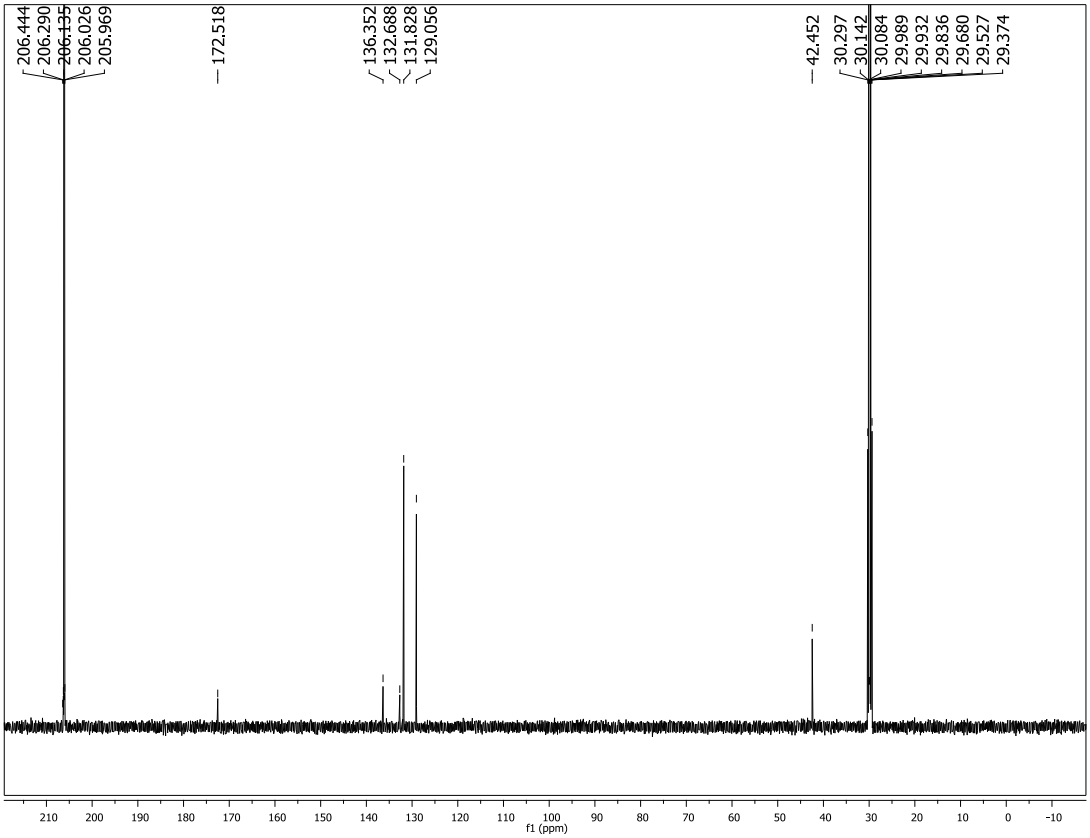

O
N
H
n-Bu
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

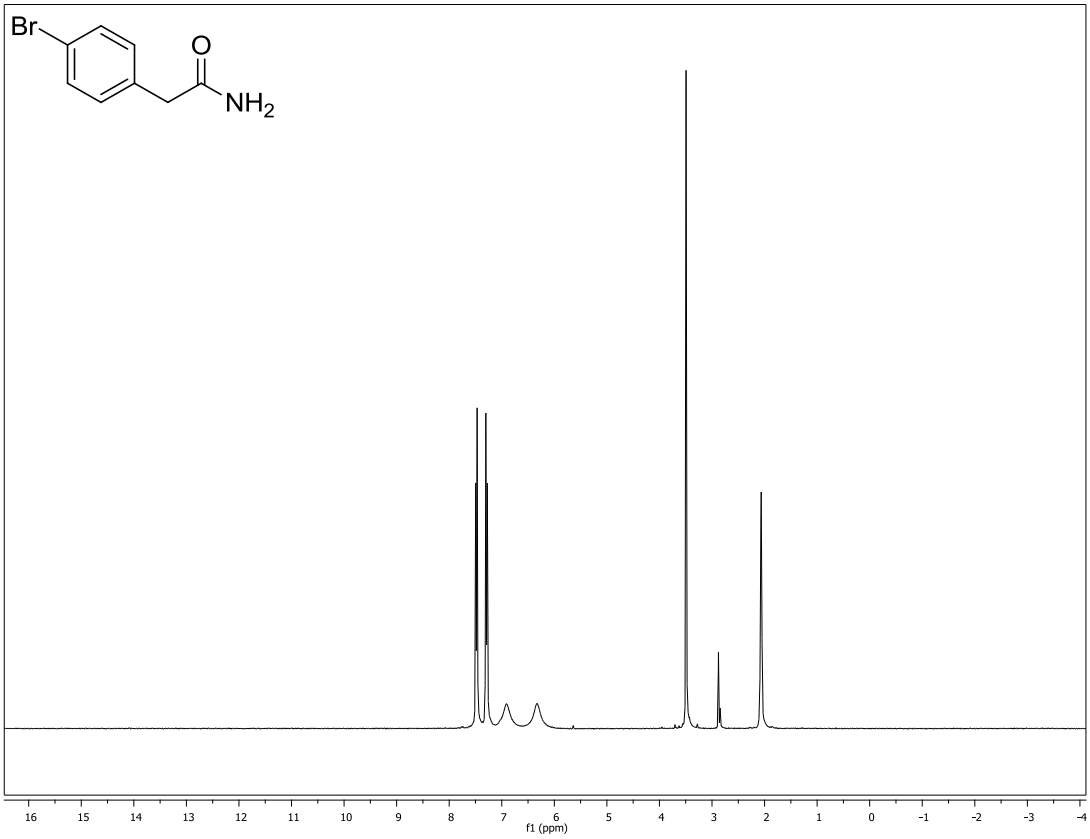

170.917
135.174
129.395
128.941
127.237
77.365
77.111
76.857
43.831
39.397
31.532
19.969
13.694
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

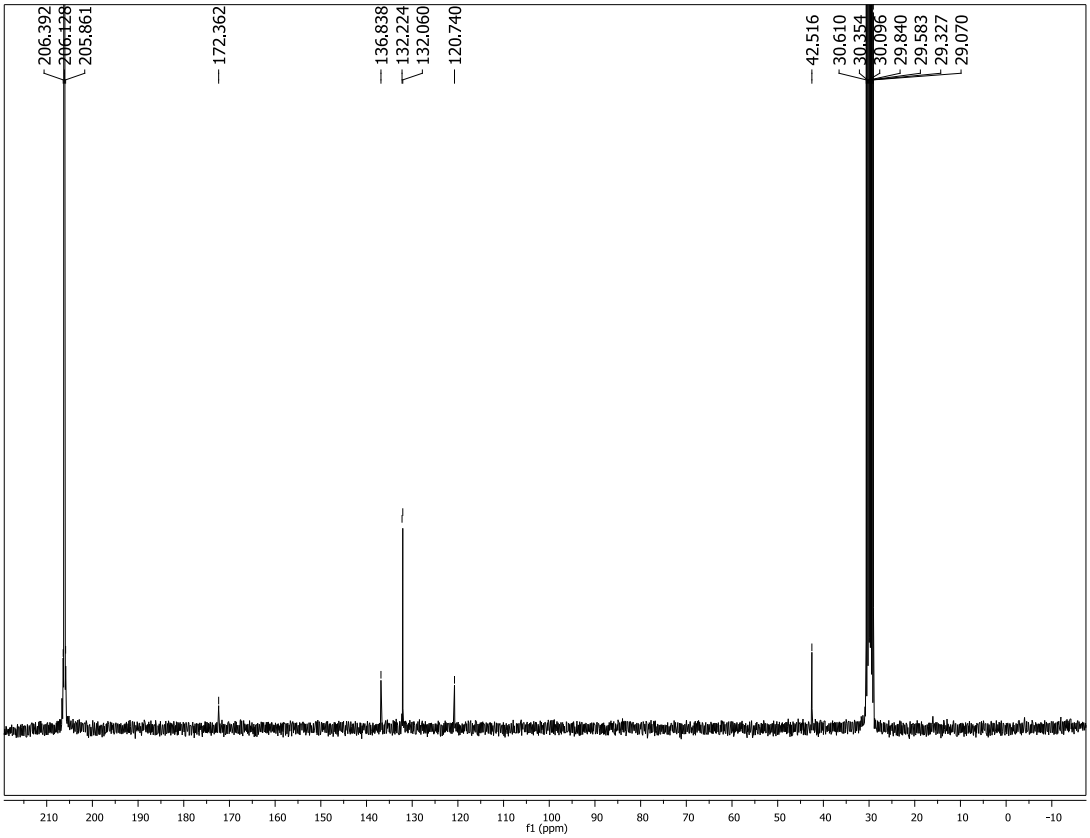

F
O
NH2
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

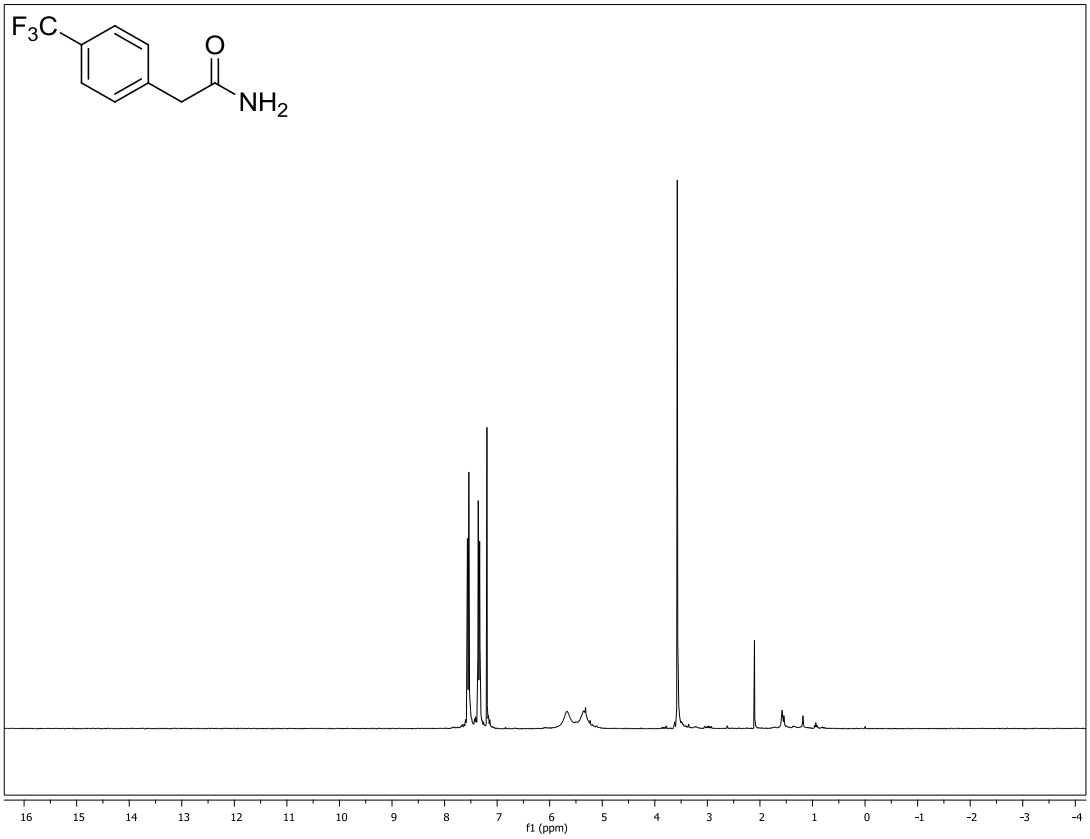

173.192
163.140
161.183
130.995
130.933
130.536
130.508
115.999
115.831
77.278
77.024
76.770
42.324
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

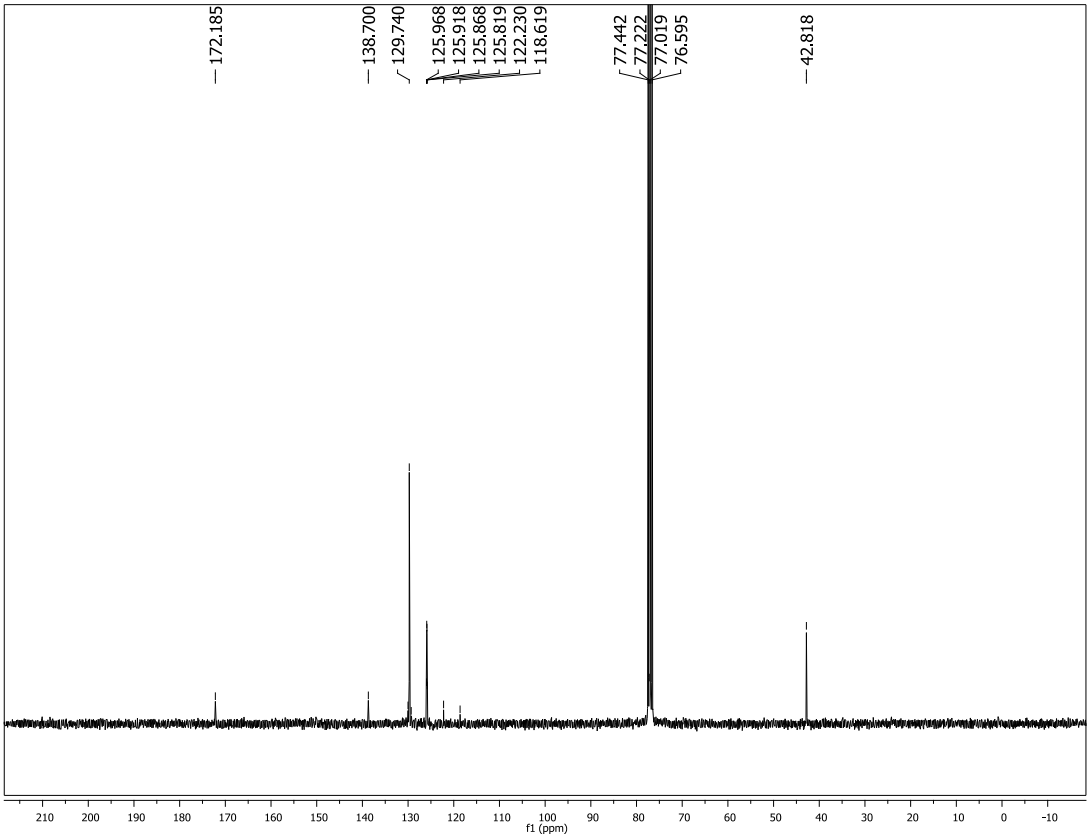

Cl
O
NH2
f1 (ppm)

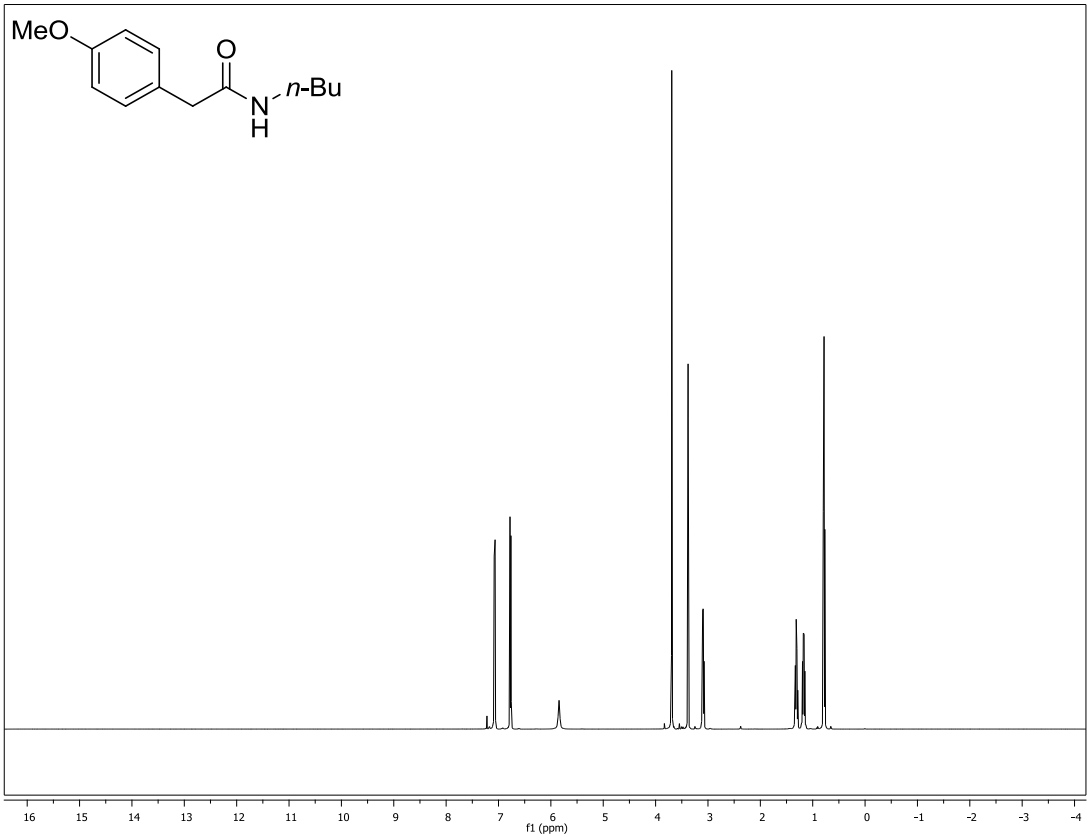

206.444
206.290
206.135
206.026
205.969
172.518
136.352
132.688
131.828
129.056
42.452
30.297
30.142
30.084
29.989
29.932
29.836
29.680
29.527
29.374
f1 (ppm)

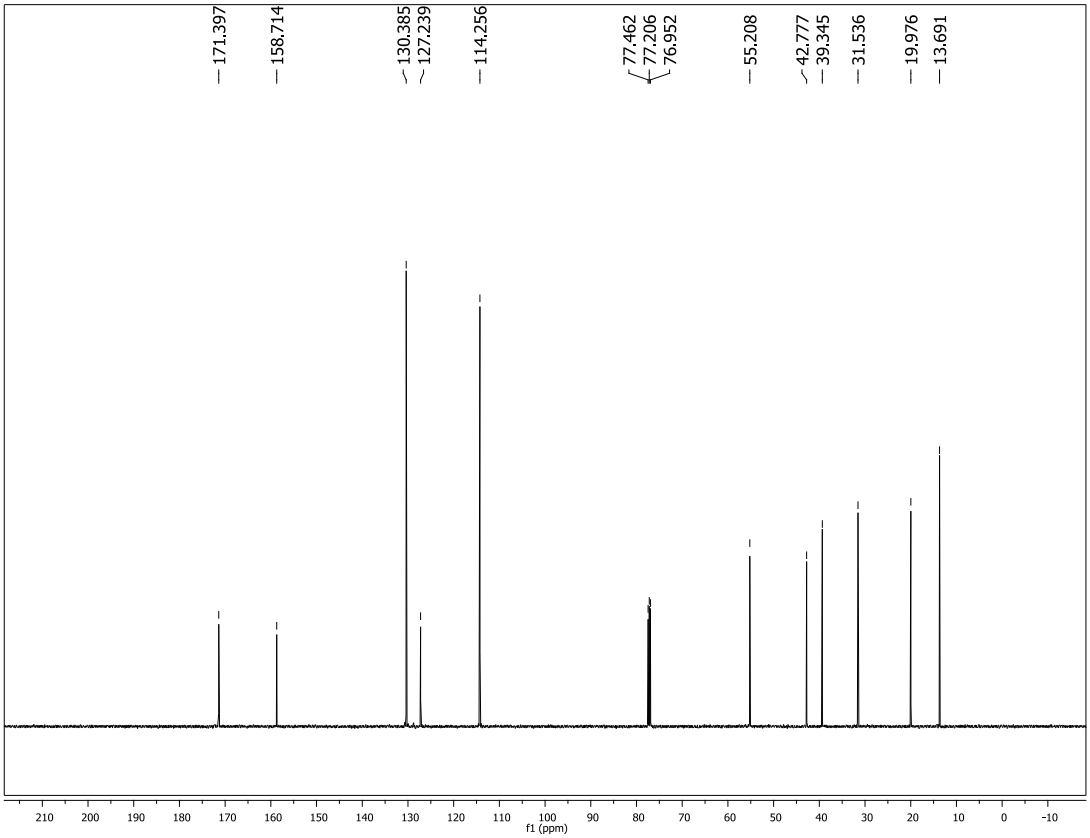

Br
O
NH2
f1 (ppm)

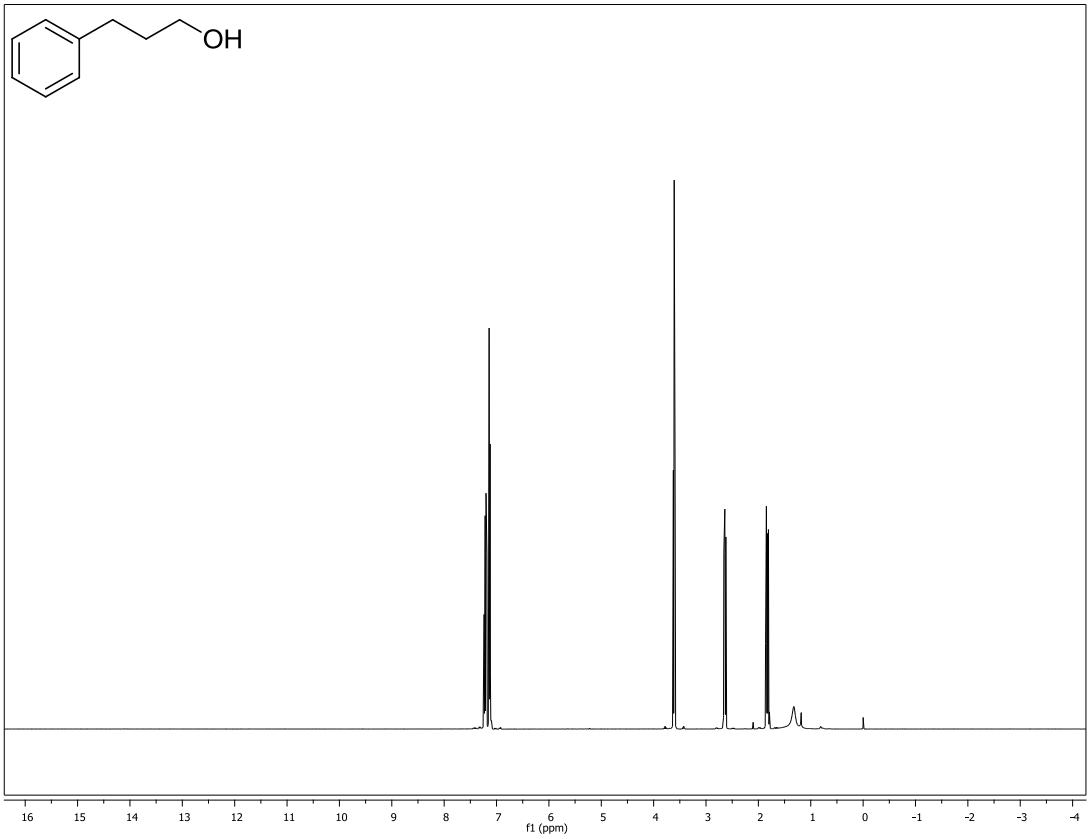

206.392
206.128
205.861
172.362
136.838
132.224
132.060
120.740
42.516
30.610
30.354
30.096
29.840
29.583
29.327
29.070
f1 (ppm)

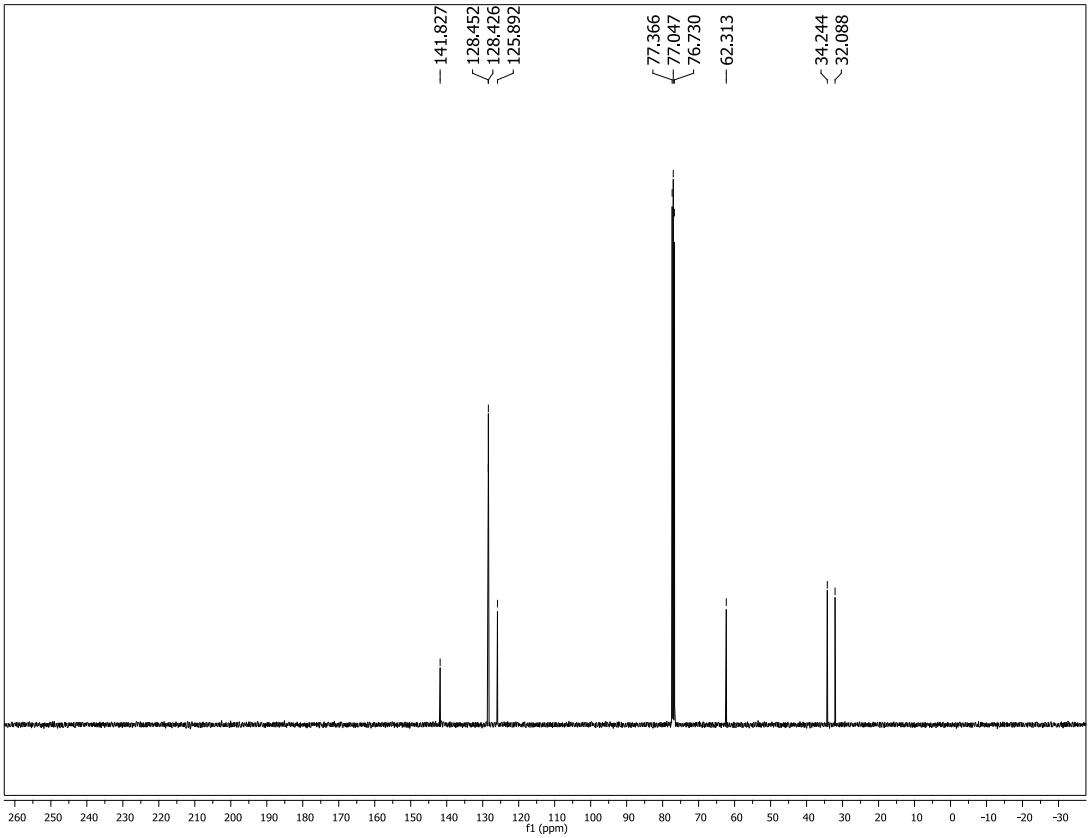

F3C
O
NH2
f1 (ppm)

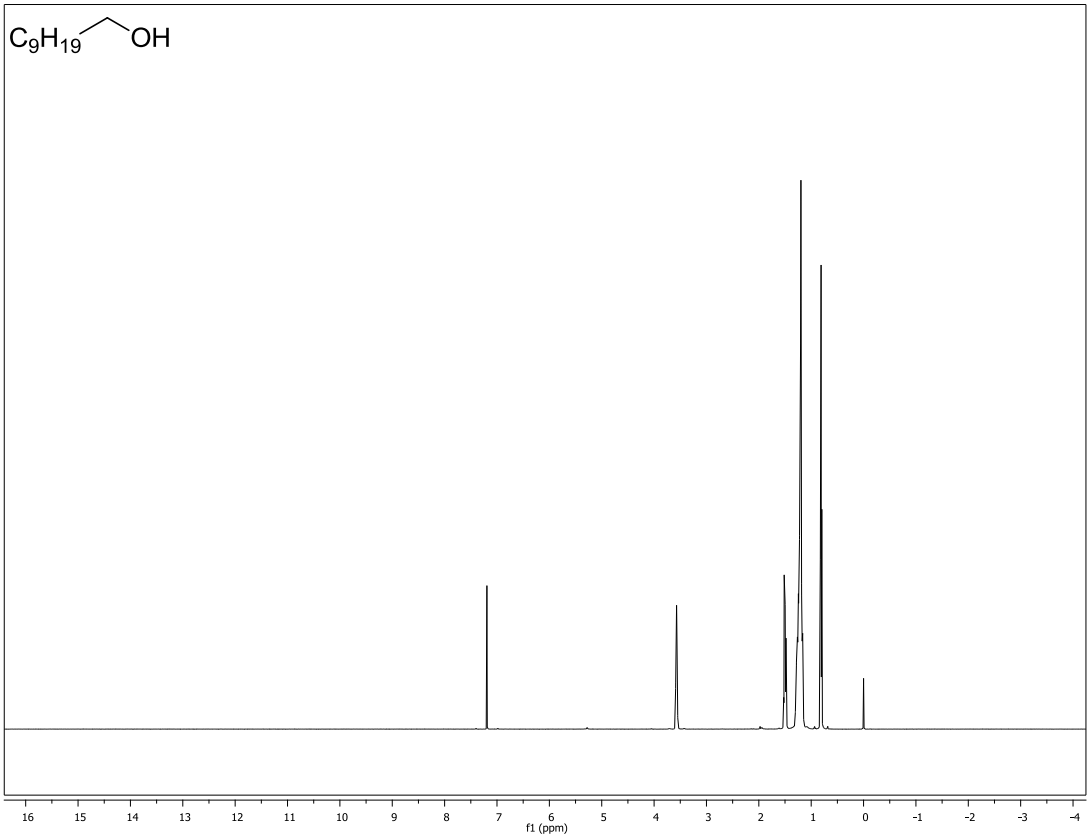

172.185
138.700
129.740
125.968
125.918
125.868
125.819
122.230
118.619
77.442
77.222
77.019
76.595
42.818
f1 (ppm)

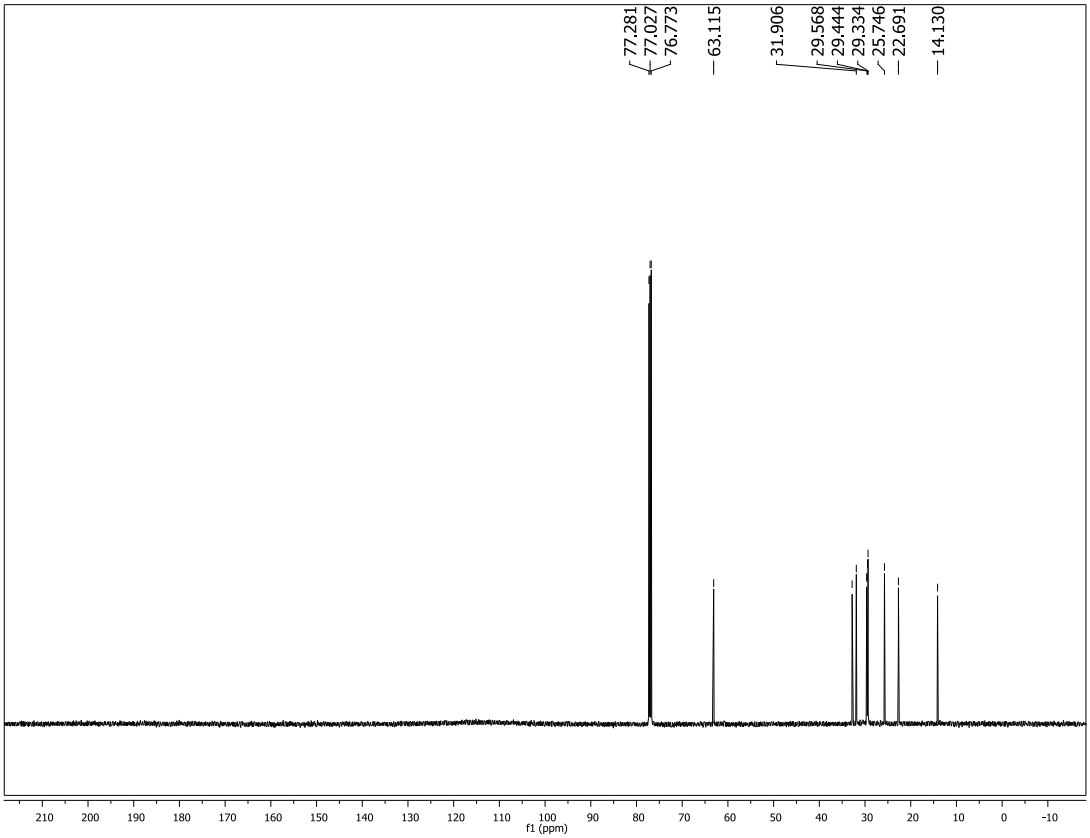

MeO
O
N
H
n-Bu
f1 (ppm)

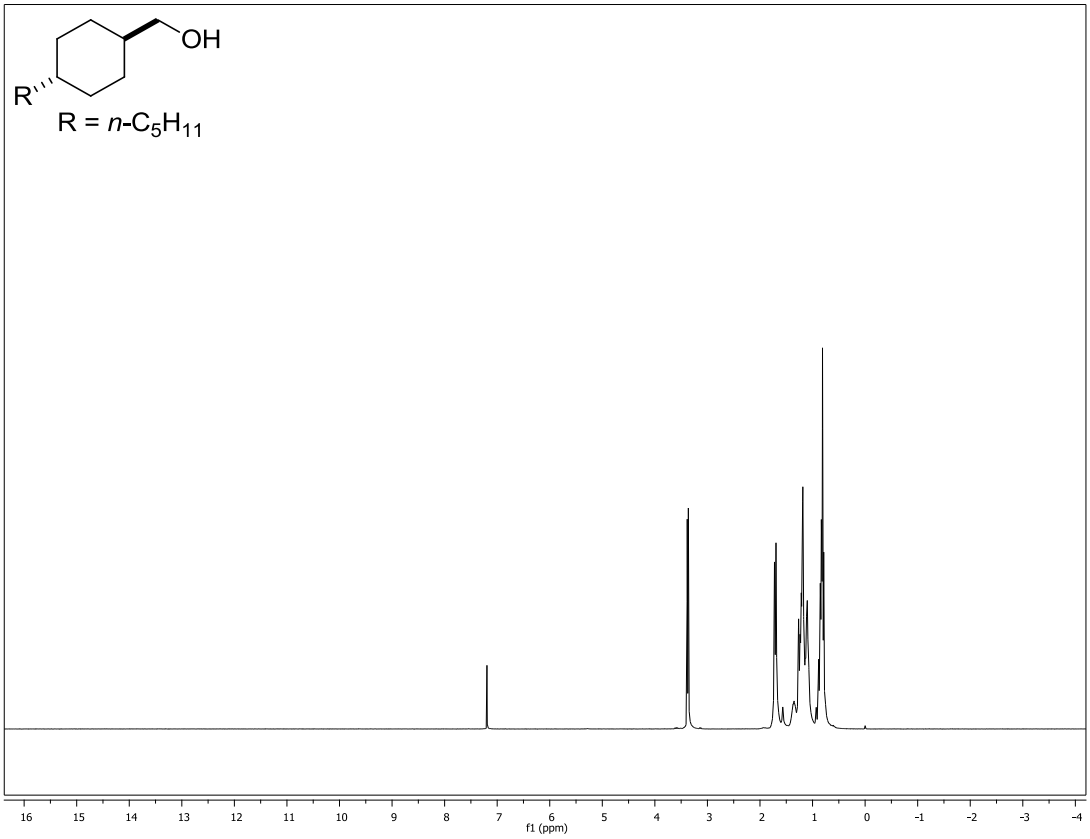

171.397
158.714
130.385
127.239
114.256
77.462
77.206
76.952
55.208
42.777
39.345
31.536
19.976
13.691
f1 (ppm)

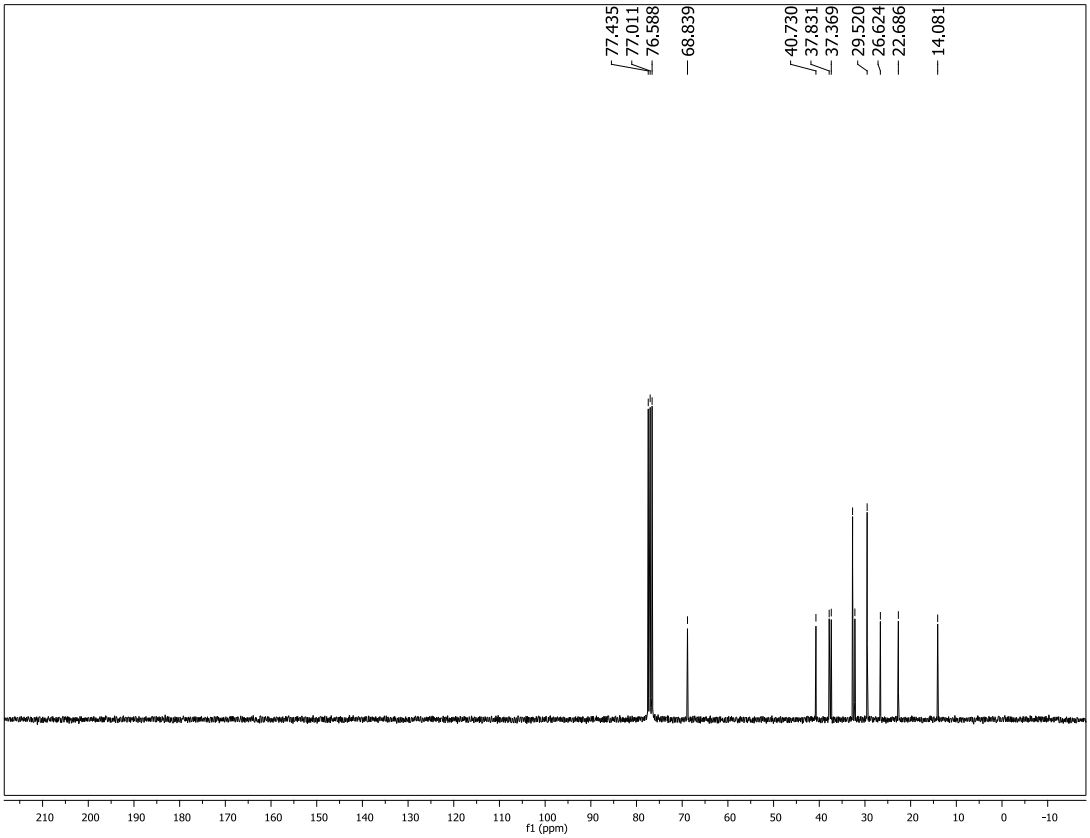

OH
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

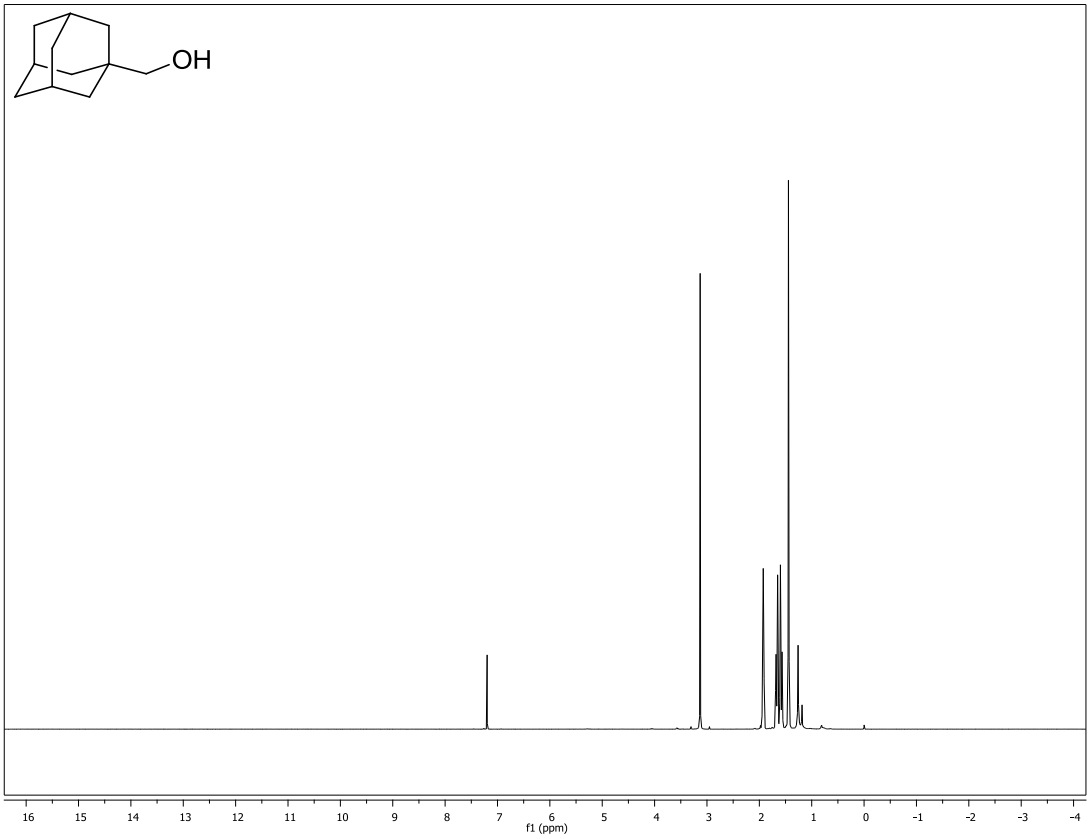

141.827
128.452
128.426
125.892
77.366
77.047
76.730
62.313
34.244
32.088
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

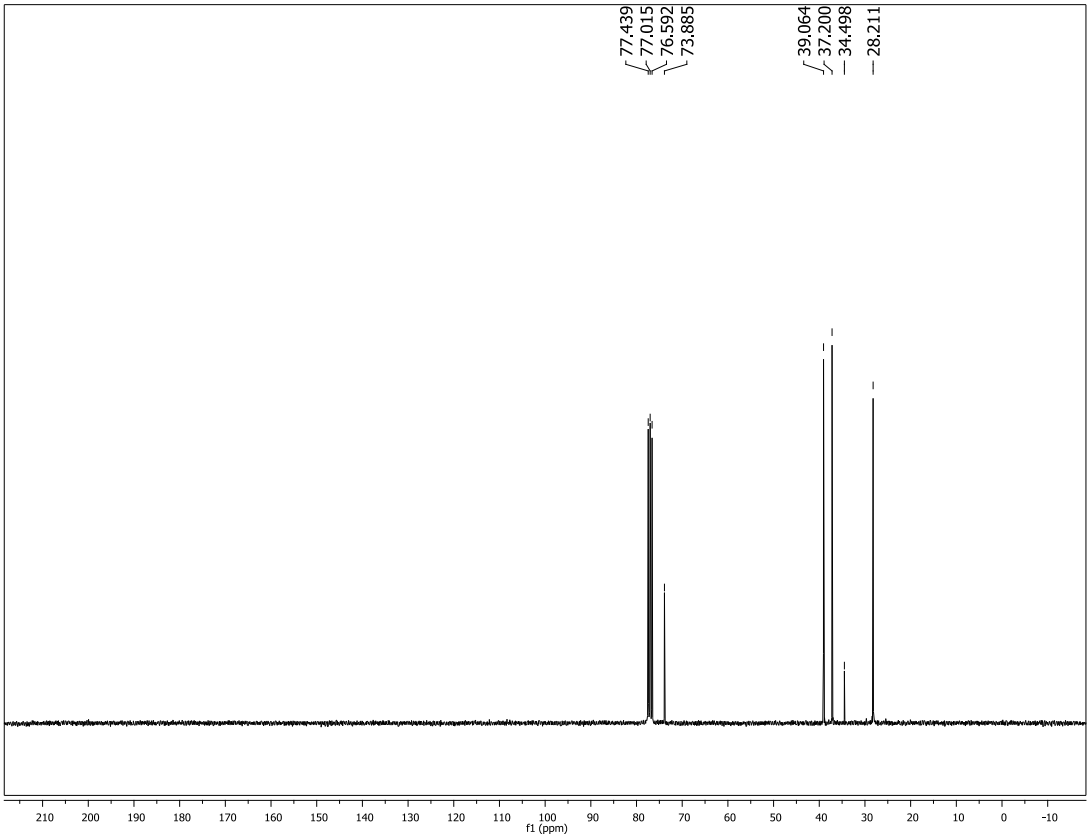

C9H19
OH
f1 (ppm)

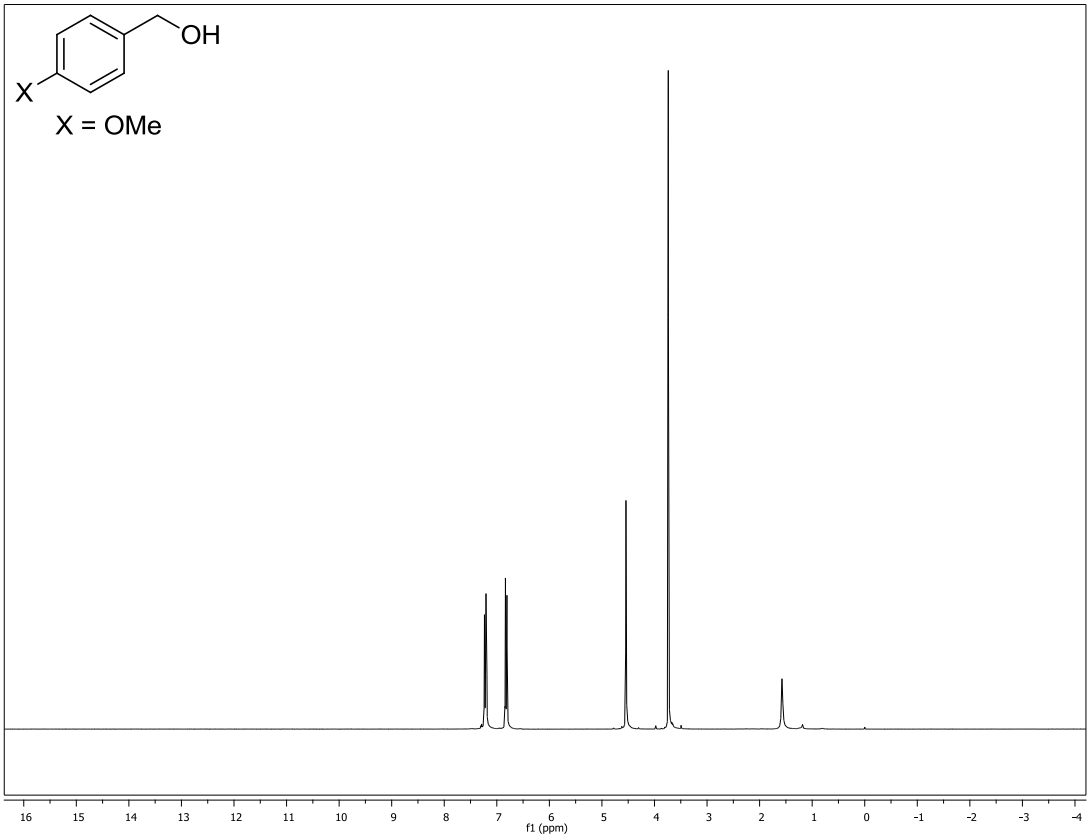

77.281
77.027
76.773
63.115
31.906
29.568
29.444
29.334
25.746
22.691
14.130
f1 (ppm)

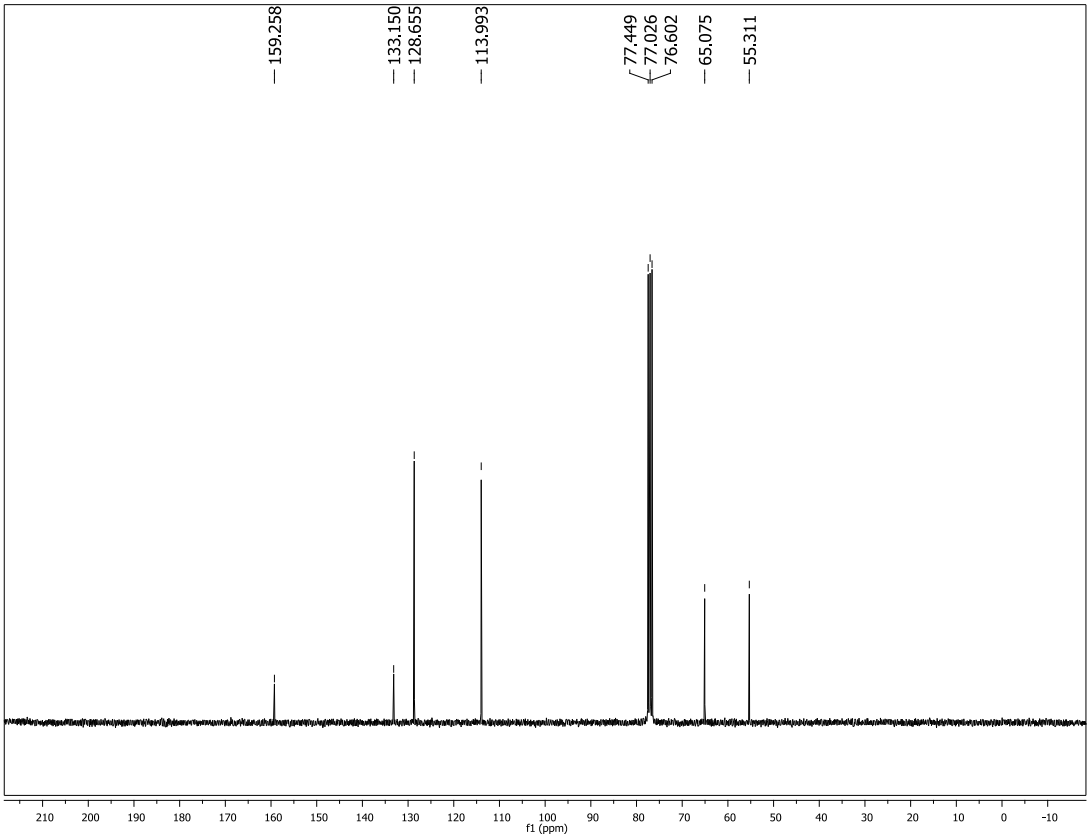

OH
R
R = n-C5H11
f1 (ppm)

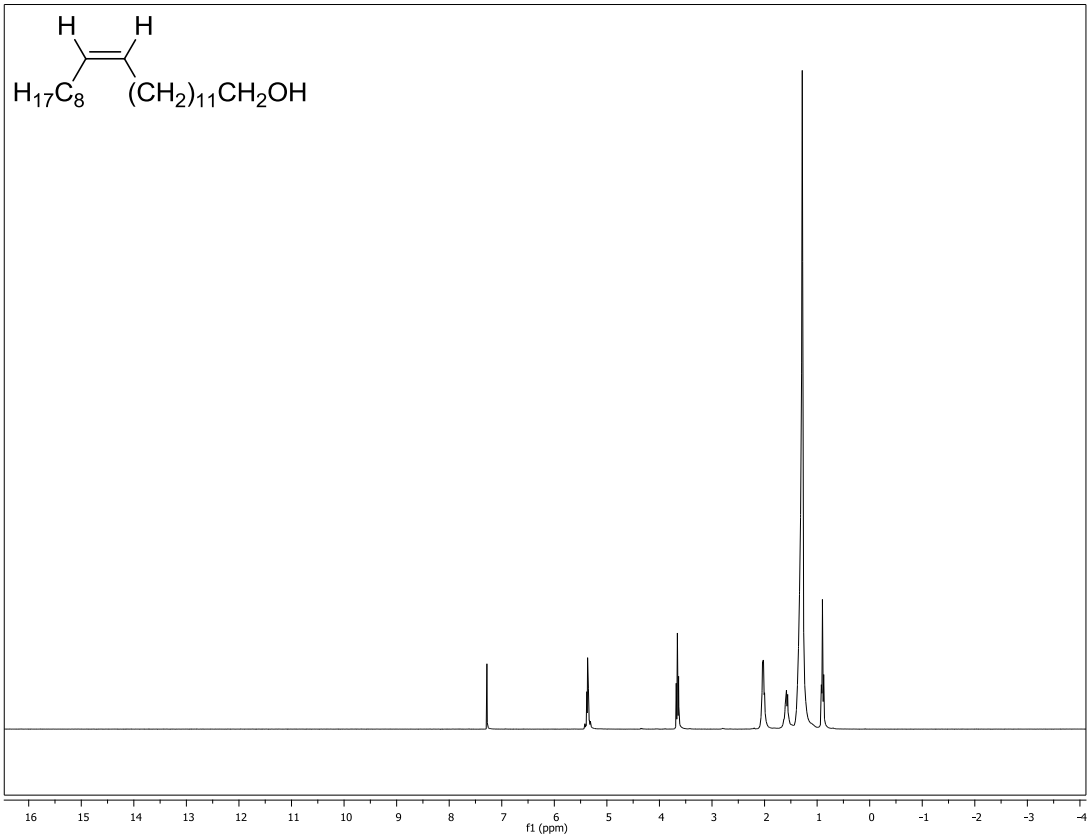

77.435
77.011
76.588
68.839
40.730
37.831
37.369
29.520
26.624
22.686
14.081
f1 (ppm)

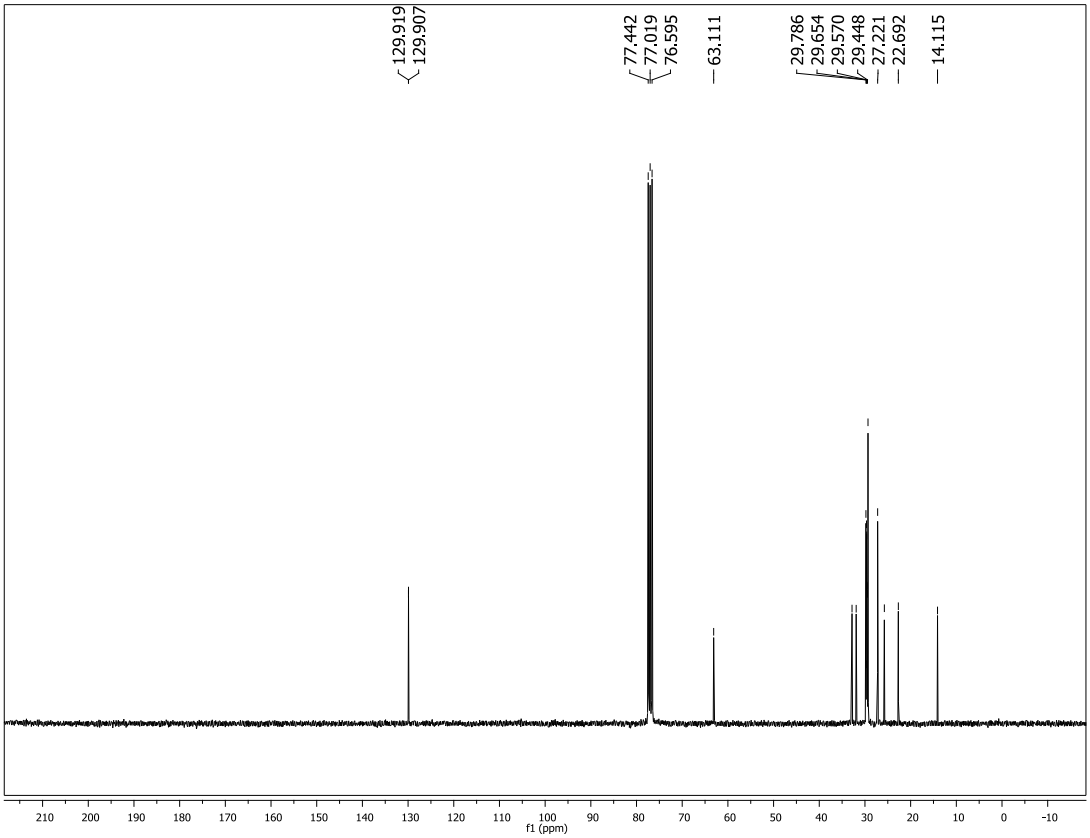

OH
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

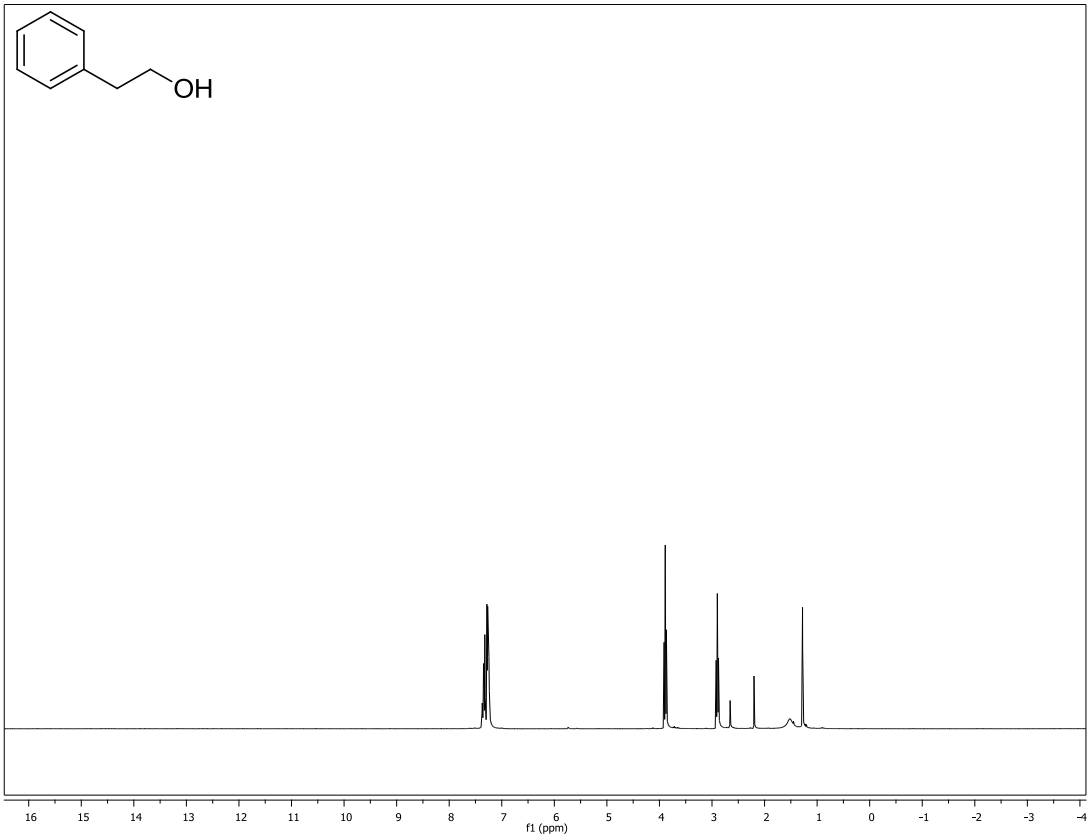

77.439
77.015
76.592
73.885
39.064
37.200
34.498
28.211
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

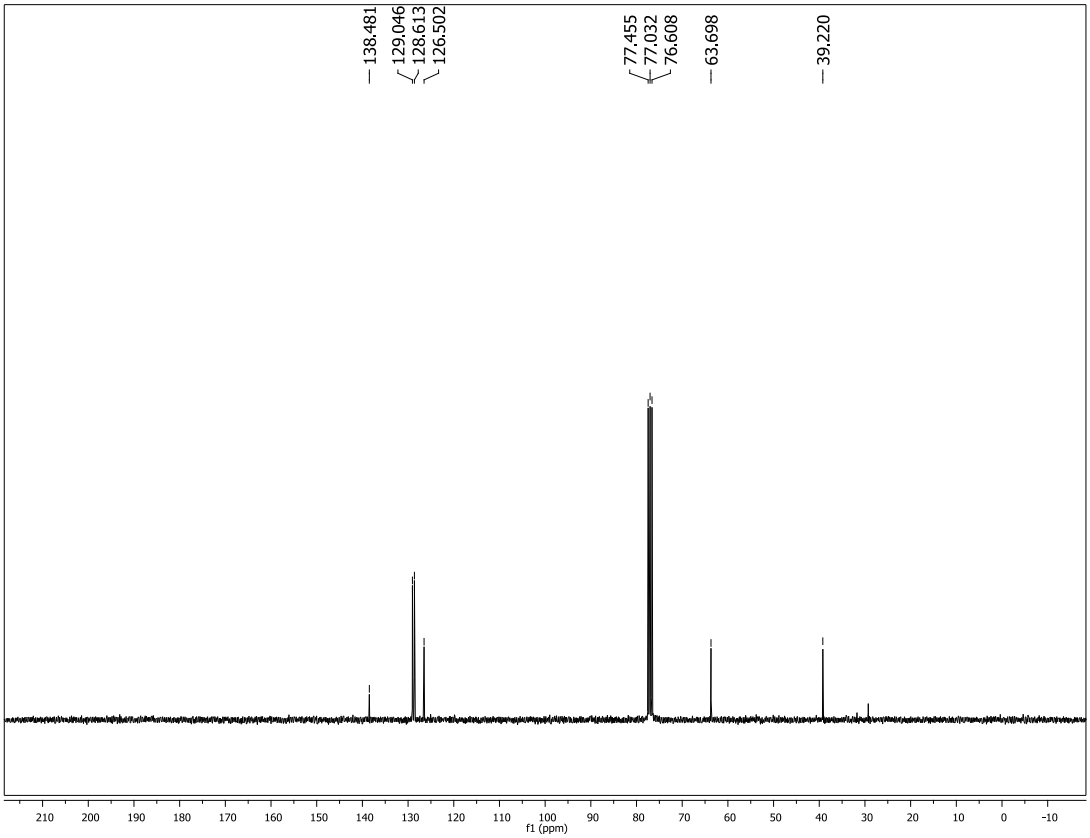

OH
X
X = OMe
f1 (ppm)

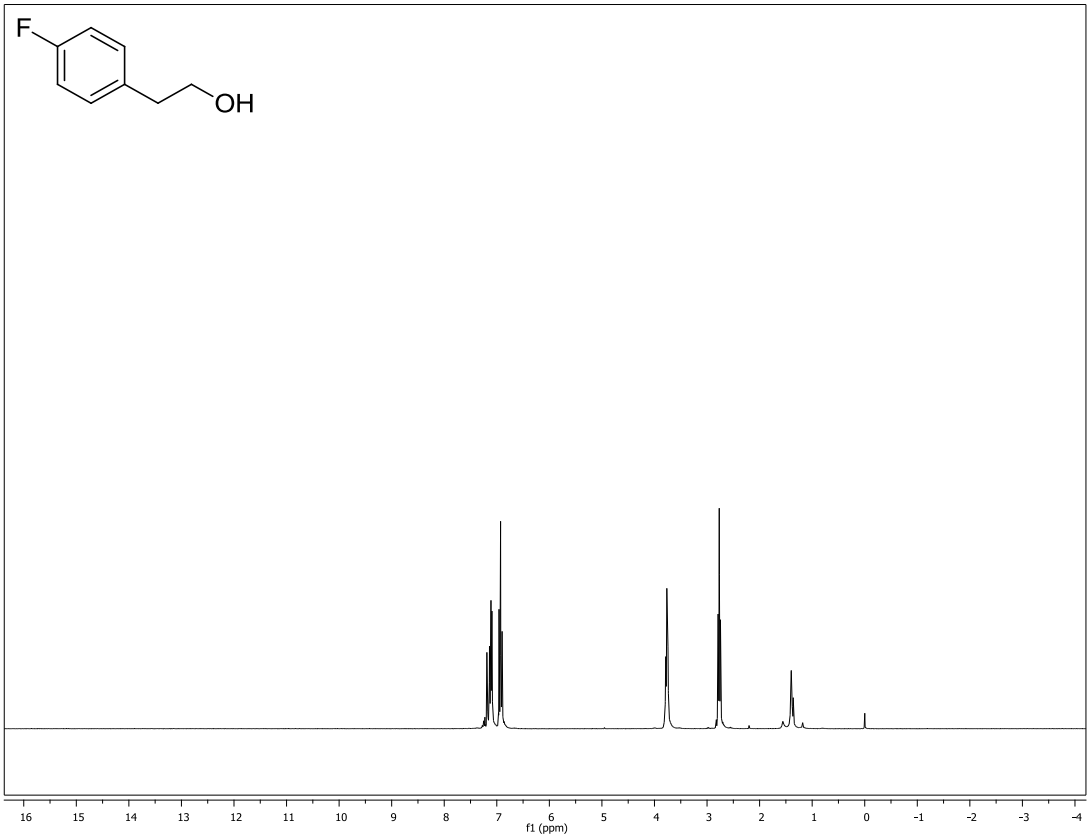

159.258
133.150
128.655
113.993
77.449
77.026
76.602
65.075
55.311
f1 (ppm)

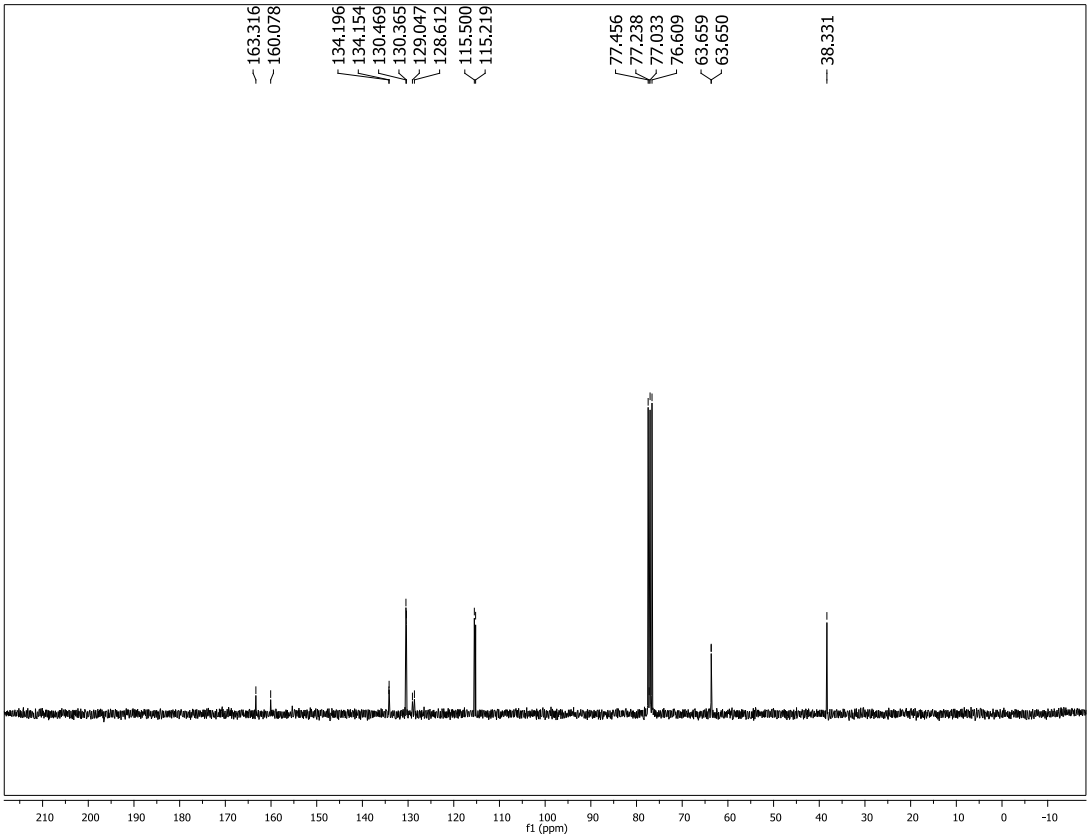

H
H
H17C8
(CH2)11CH2OH
f1 (ppm)

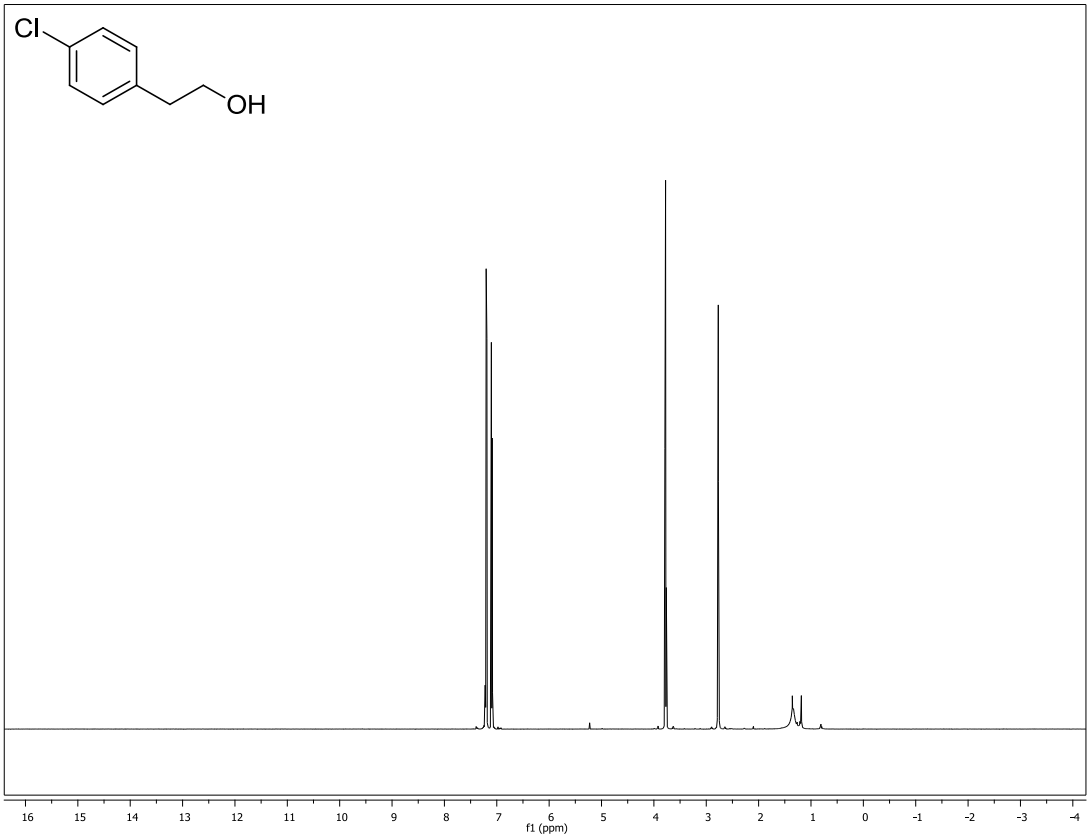

129.919
129.907
77.442
77.019
76.595
63.111
29.786
29.654
29.570
29.448
27.221
22.692
14.115
f1 (ppm)

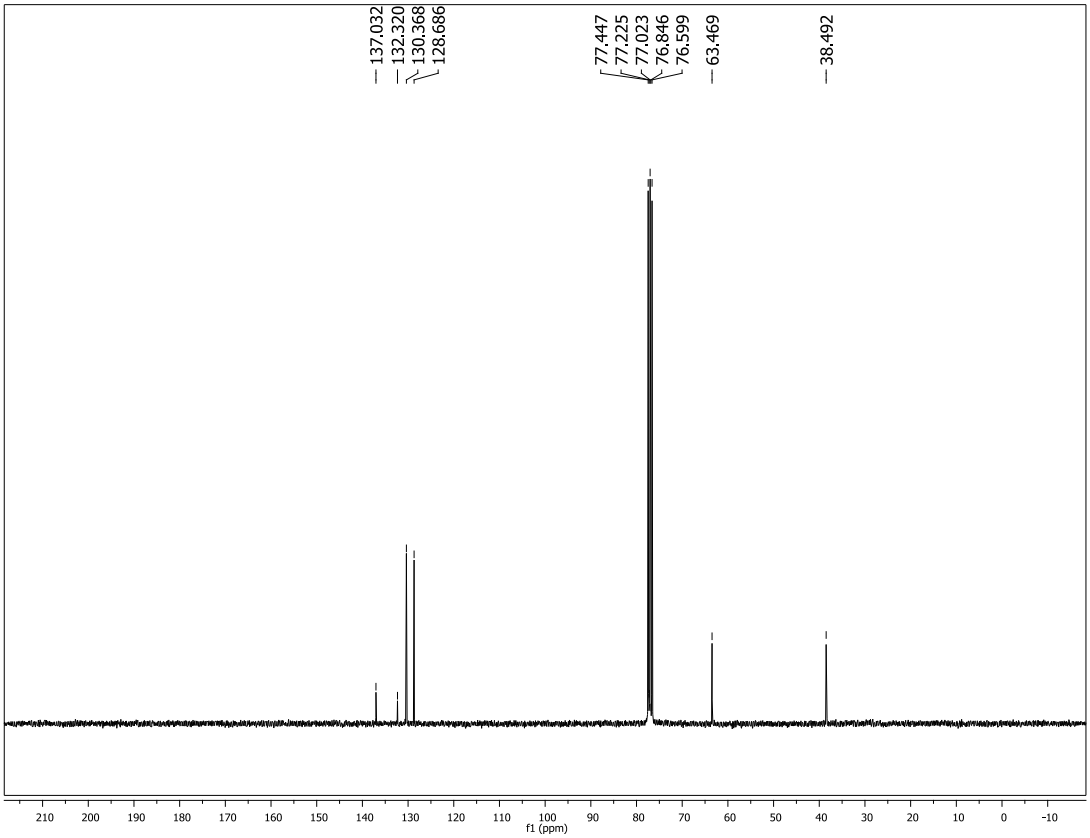

OH
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

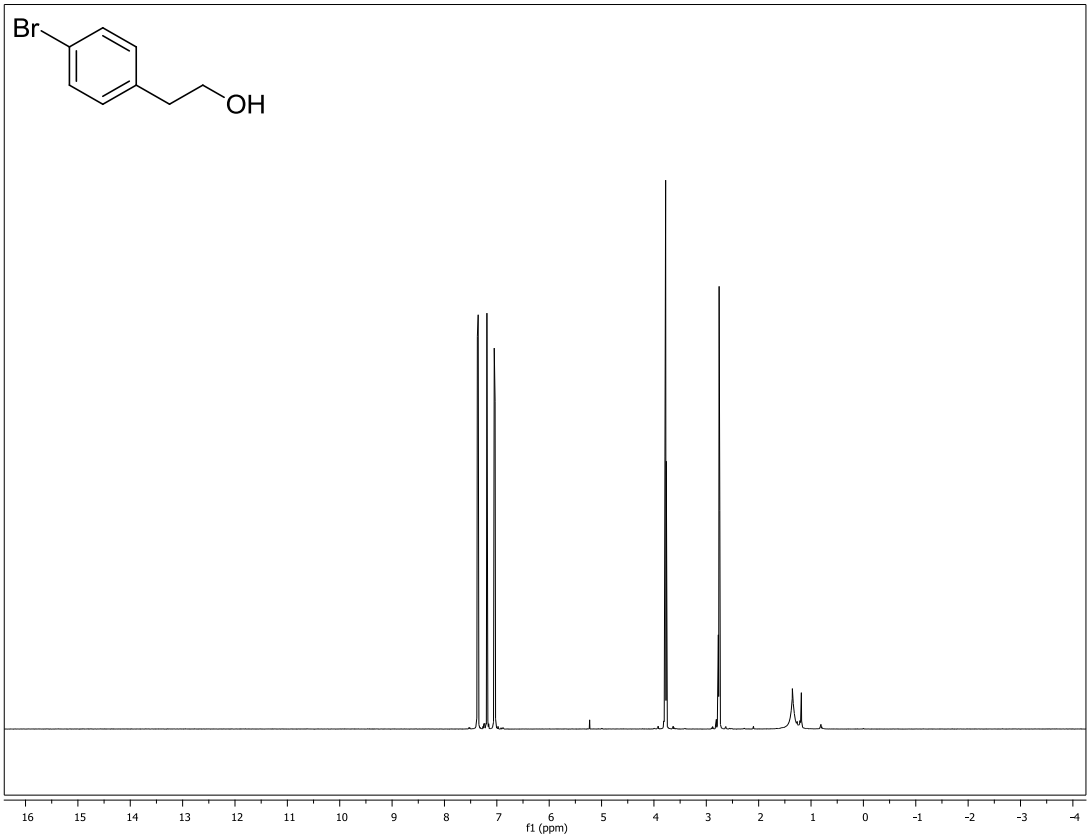

138.481
129.046
128.613
126.502
77.455
77.032
76.608
63.698
39.220
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

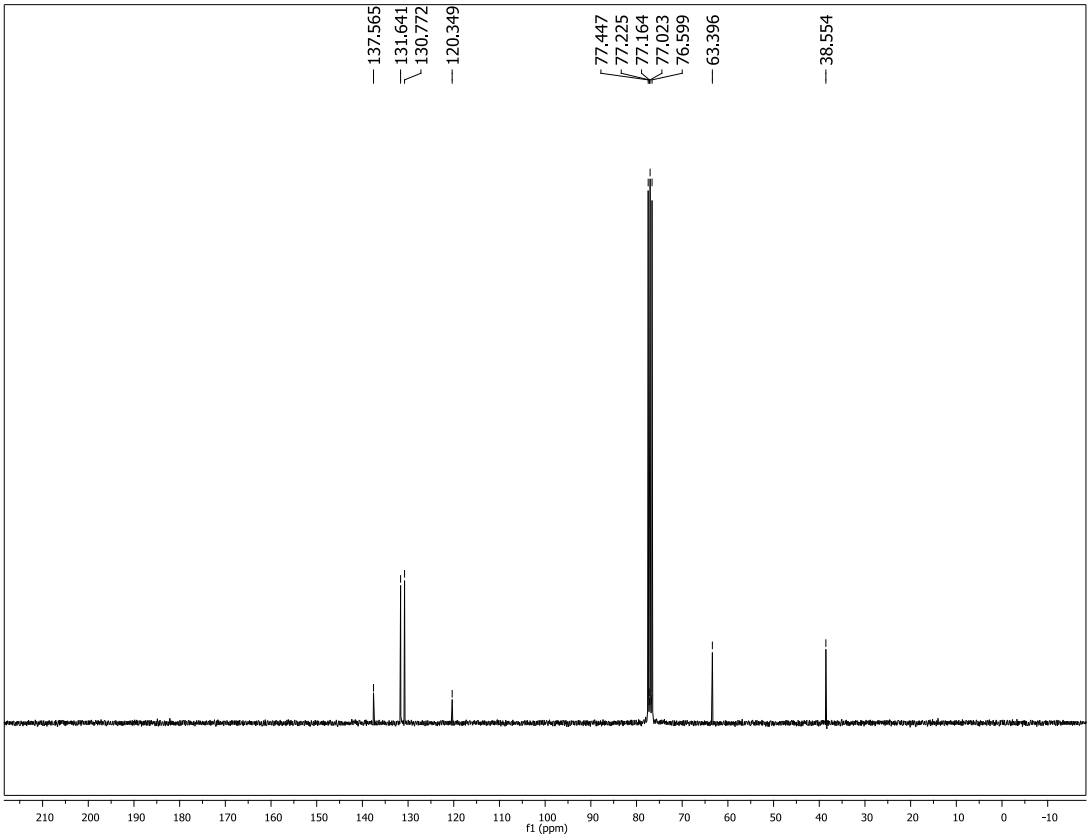

F
OH
f1 (ppm)

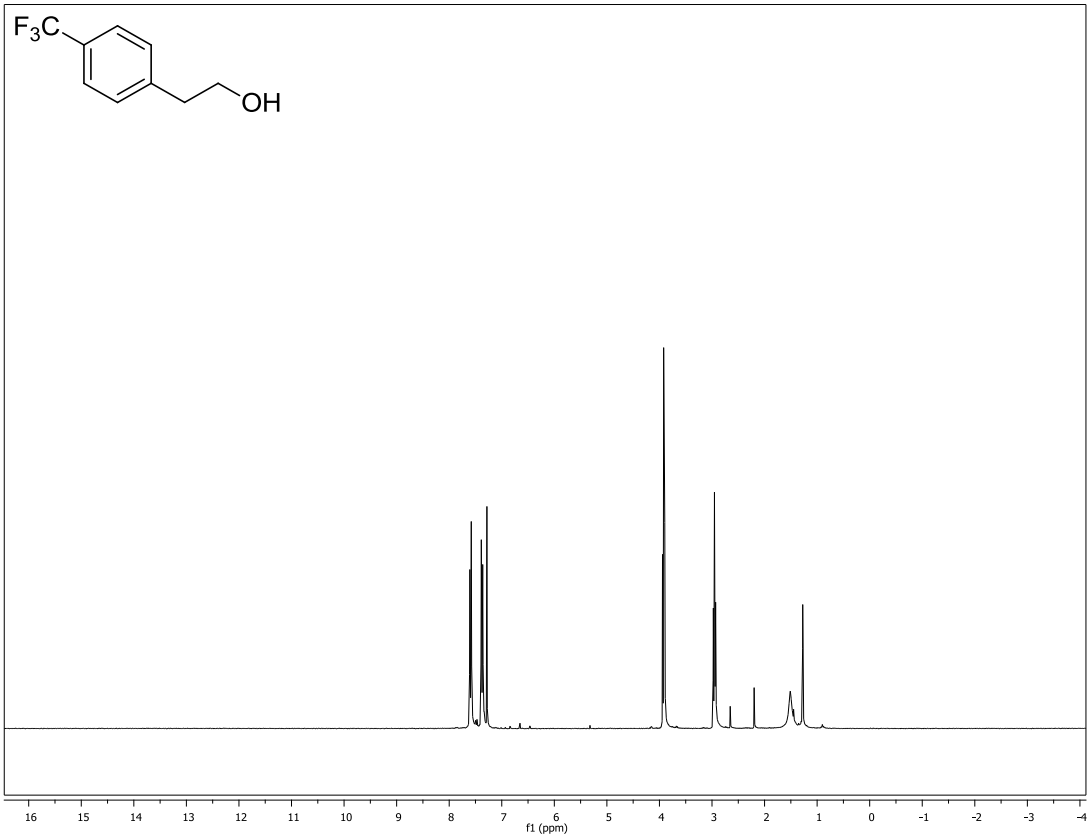

163.316
160.078
134.196
134.154
130.469
130.365
129.047
128.612
115.500
115.219
77.456
77.238
77.033
76.609
63.659
63.650
38.331
f1 (ppm)

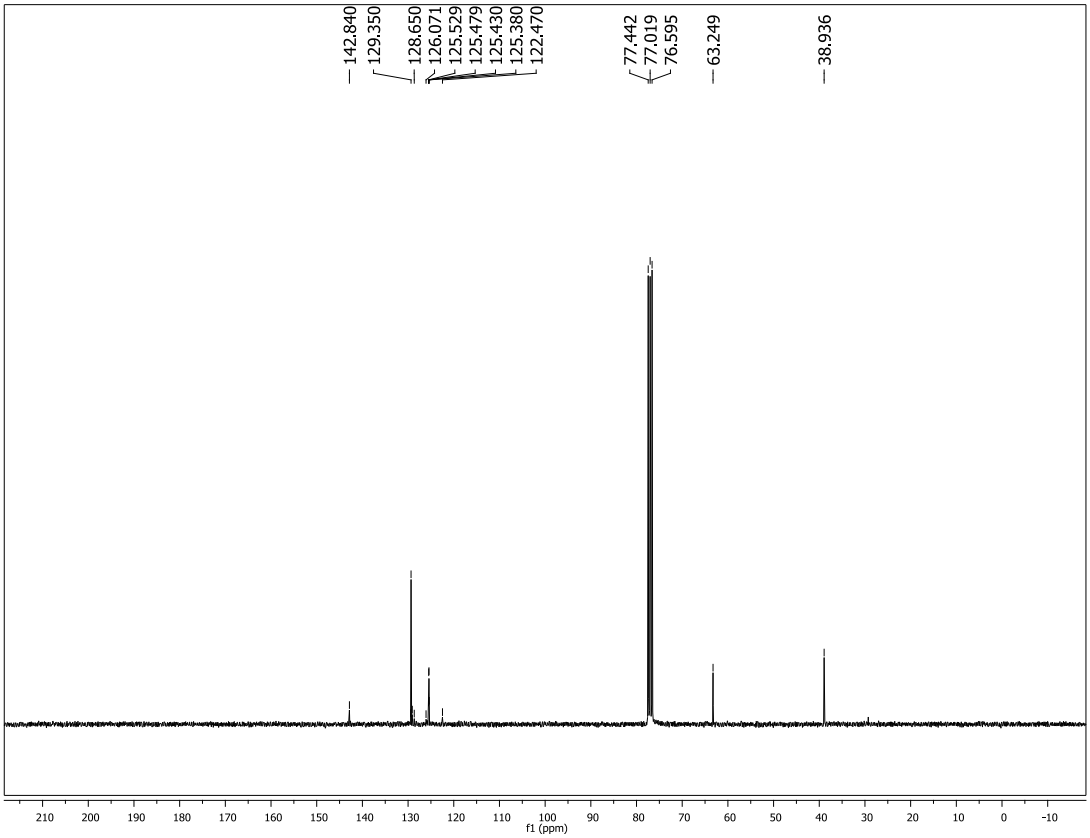

Cl
OH
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

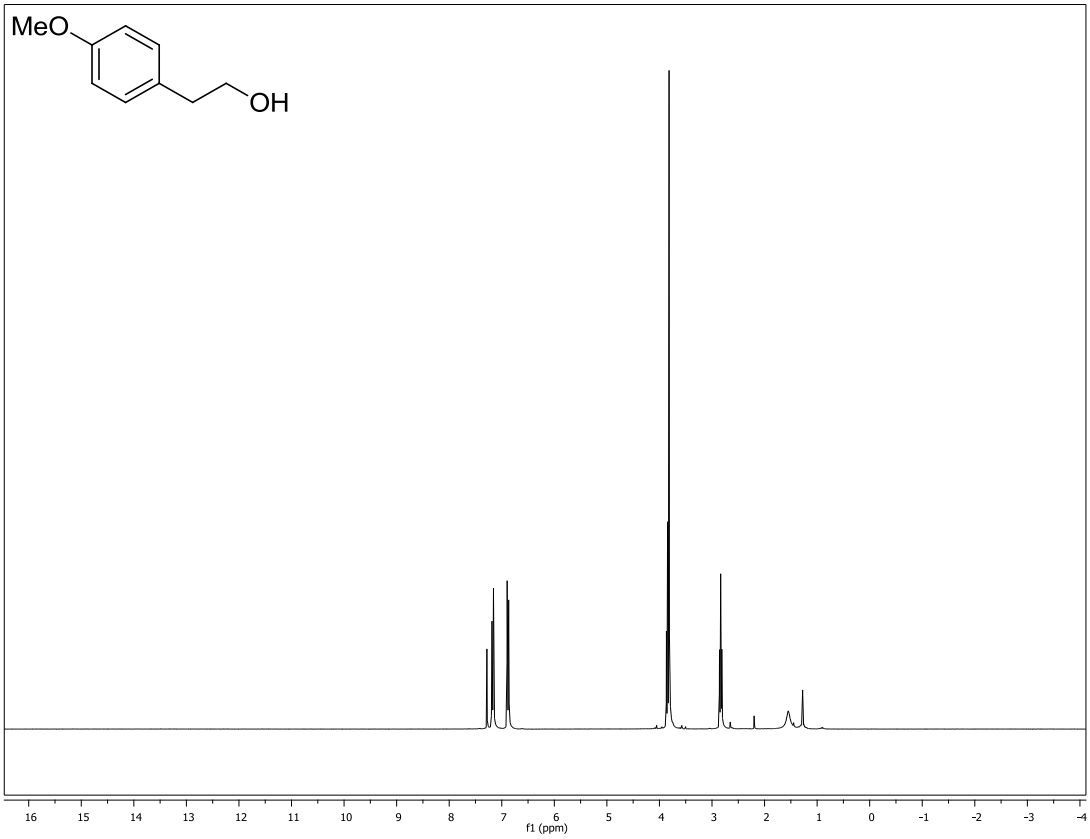

137.032
132.320
130.368
128.686
77.447
77.225
77.023
76.846
76.599
63.469
38.492
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

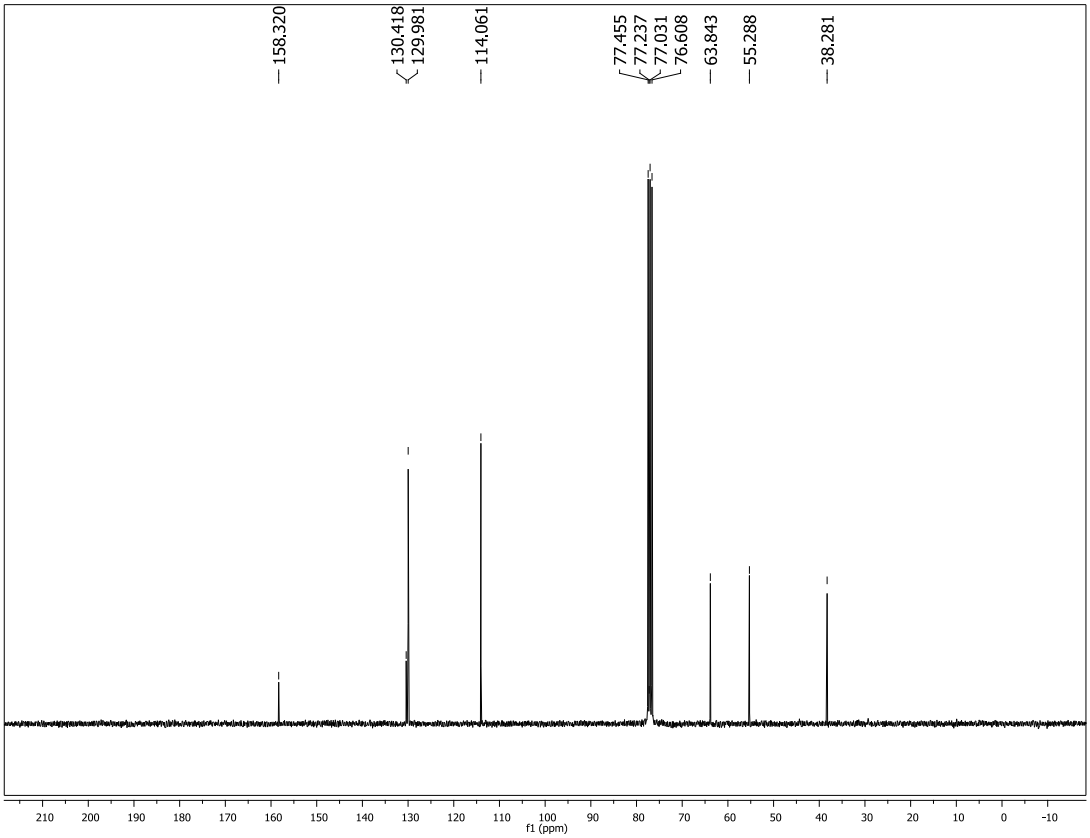

Br
OH
f1 (ppm)

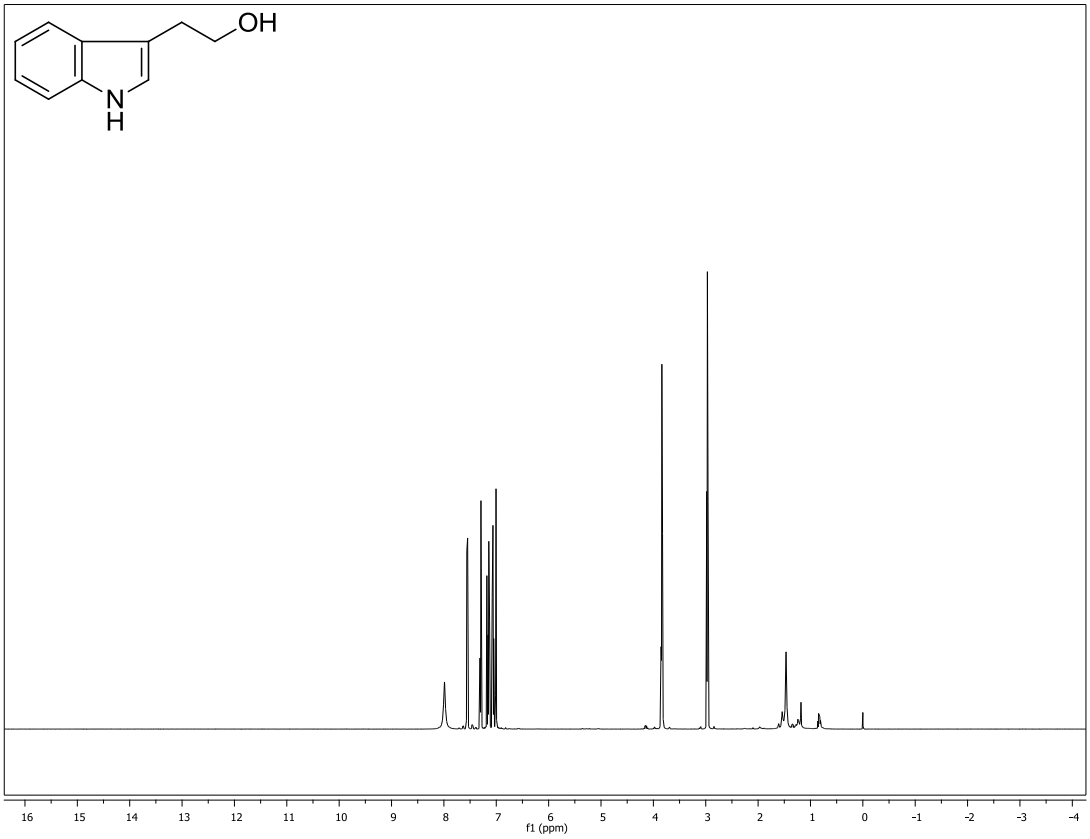

137.565
131.641
130.772
120.349
77.447
77.225
77.164
77.023
76.599
63.396
38.554
f1 (ppm)

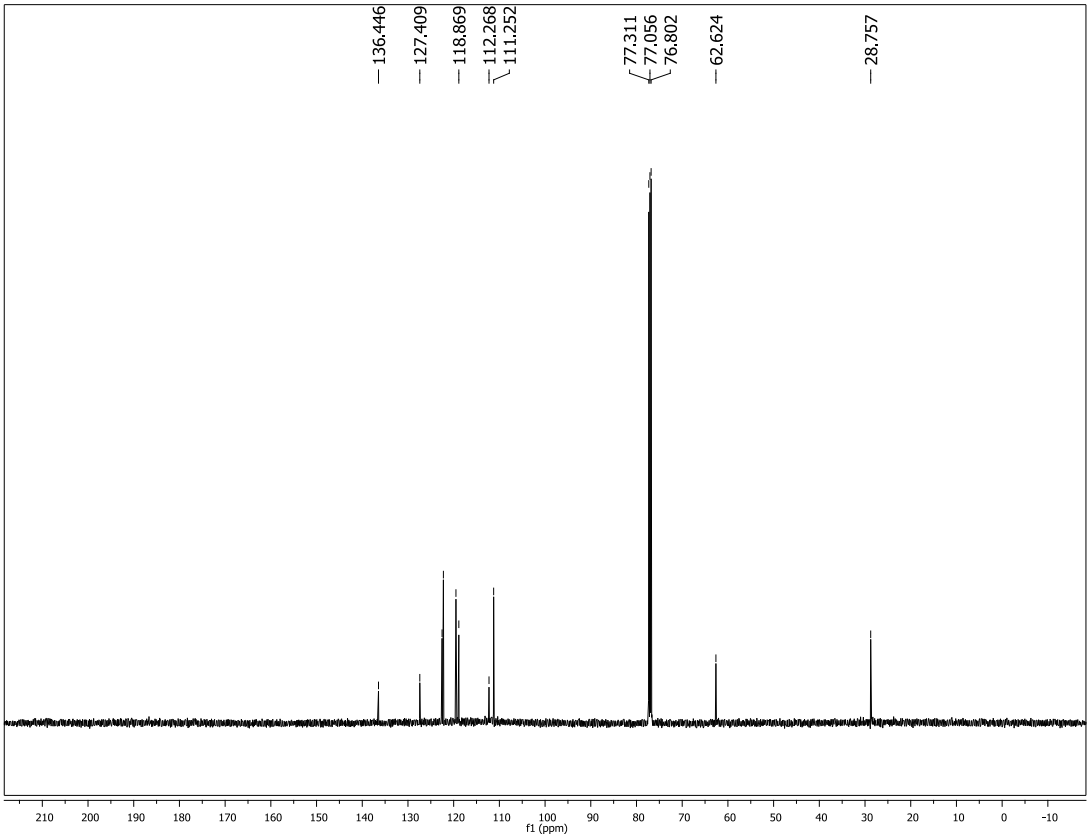

F3C
OH
f1 (ppm)

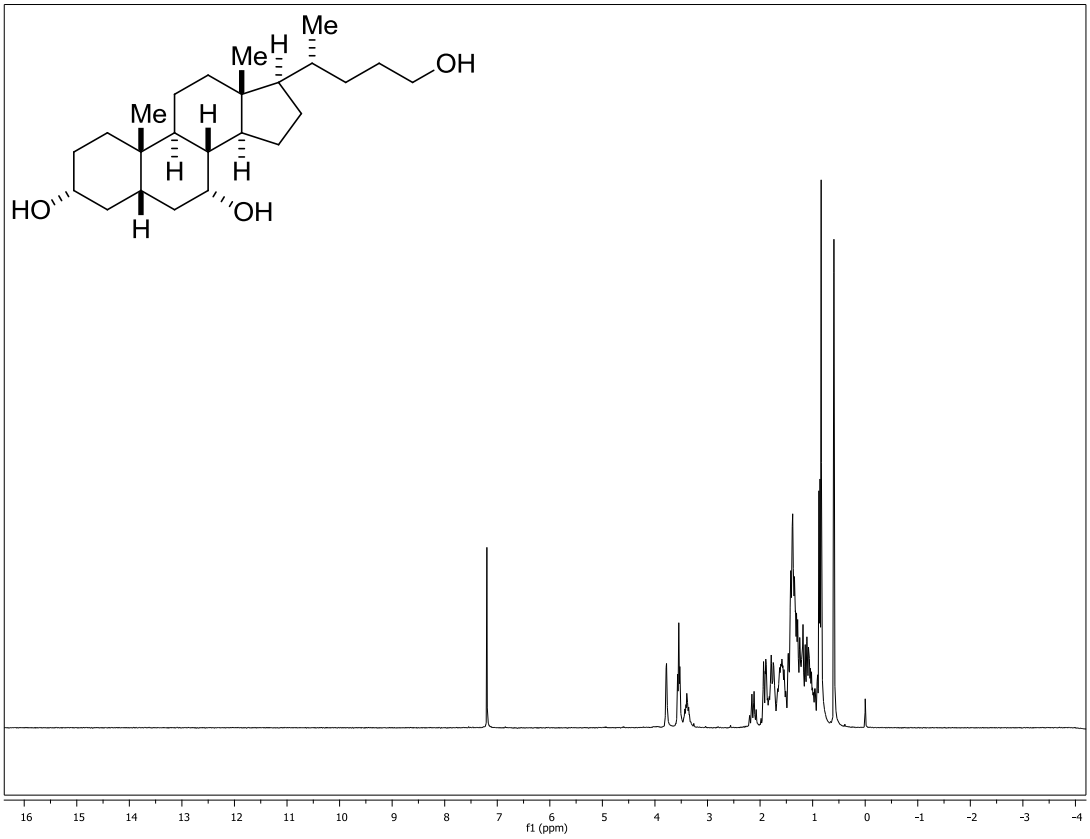

142.840
129.350
128.650
126.071
125.529
125.479
125.430
125.380
122.470
77.442
77.019
76.595
63.249
38.936
f1 (ppm)

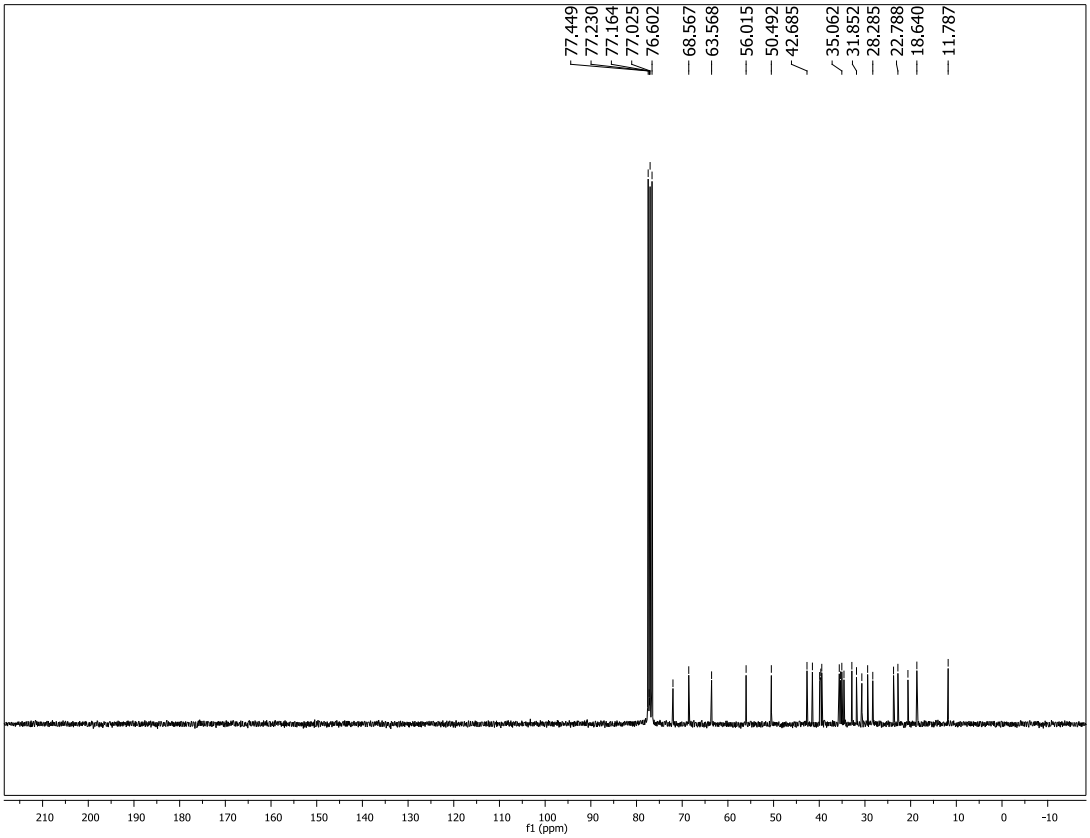

MeO
OH
f1 (ppm)

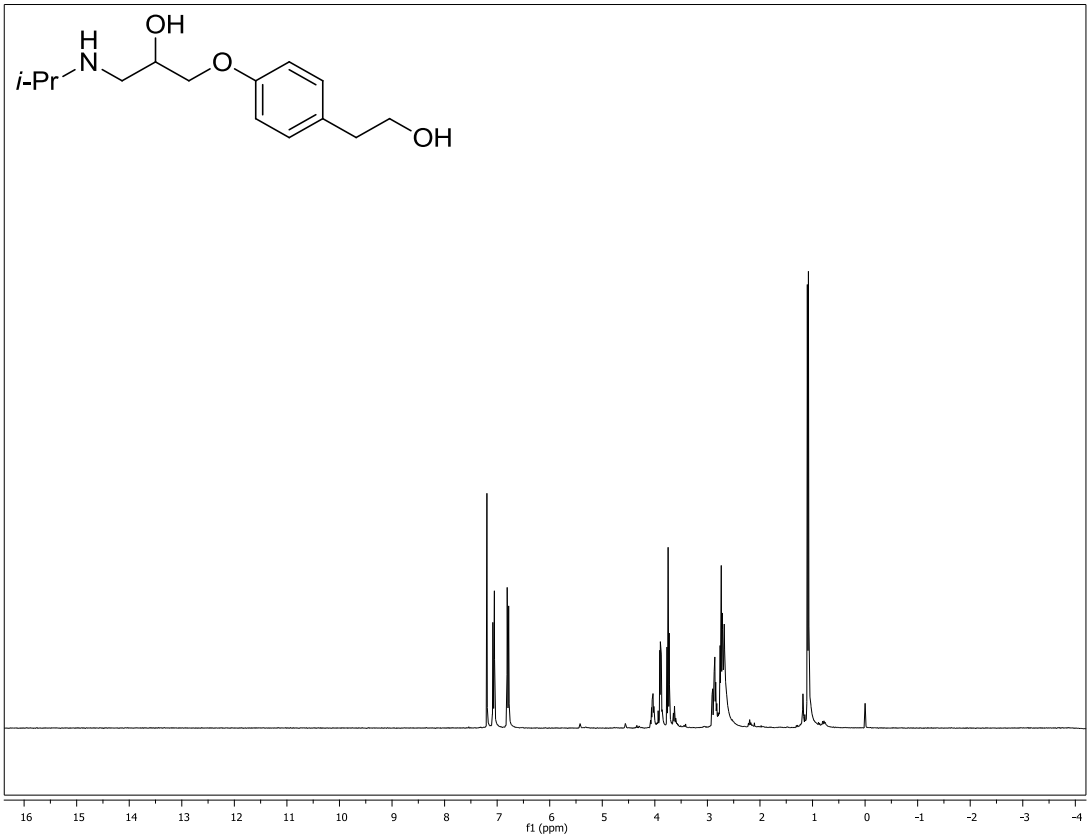

158.320
130.418
129.981
114.061
77.455
77.237
77.031
76.608
63.843
55.288
38.281
f1 (ppm)

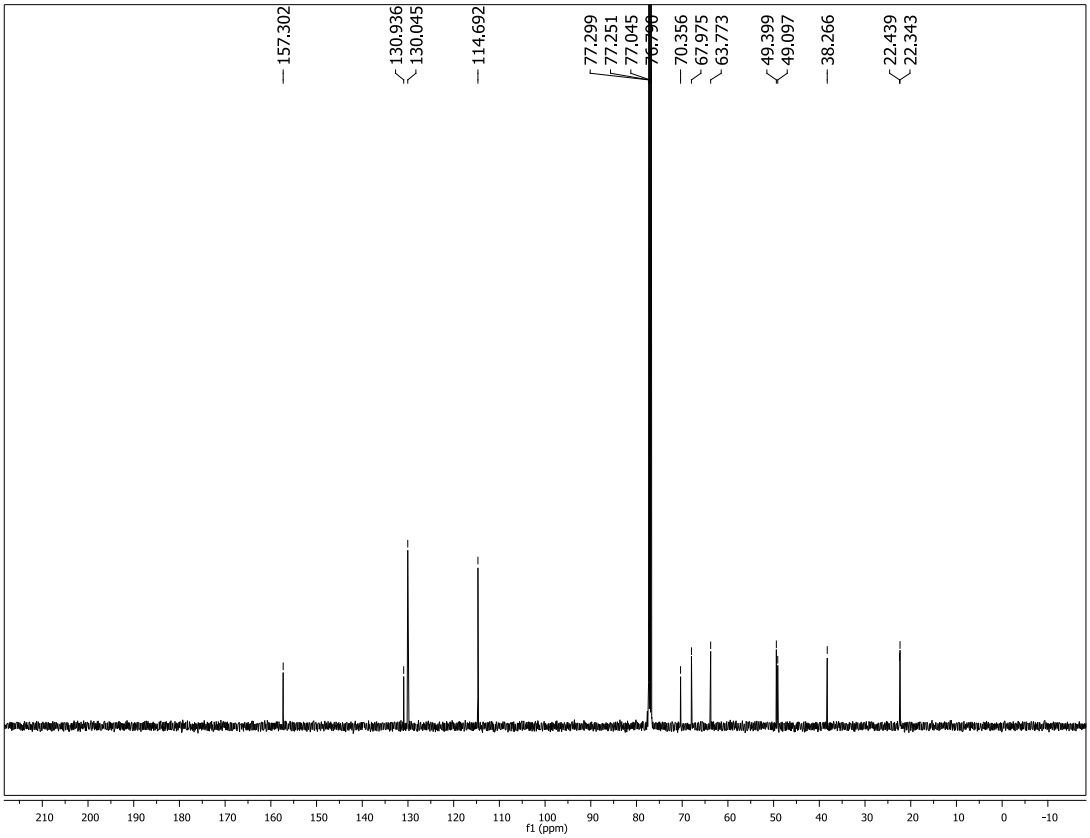

OH
N
H
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

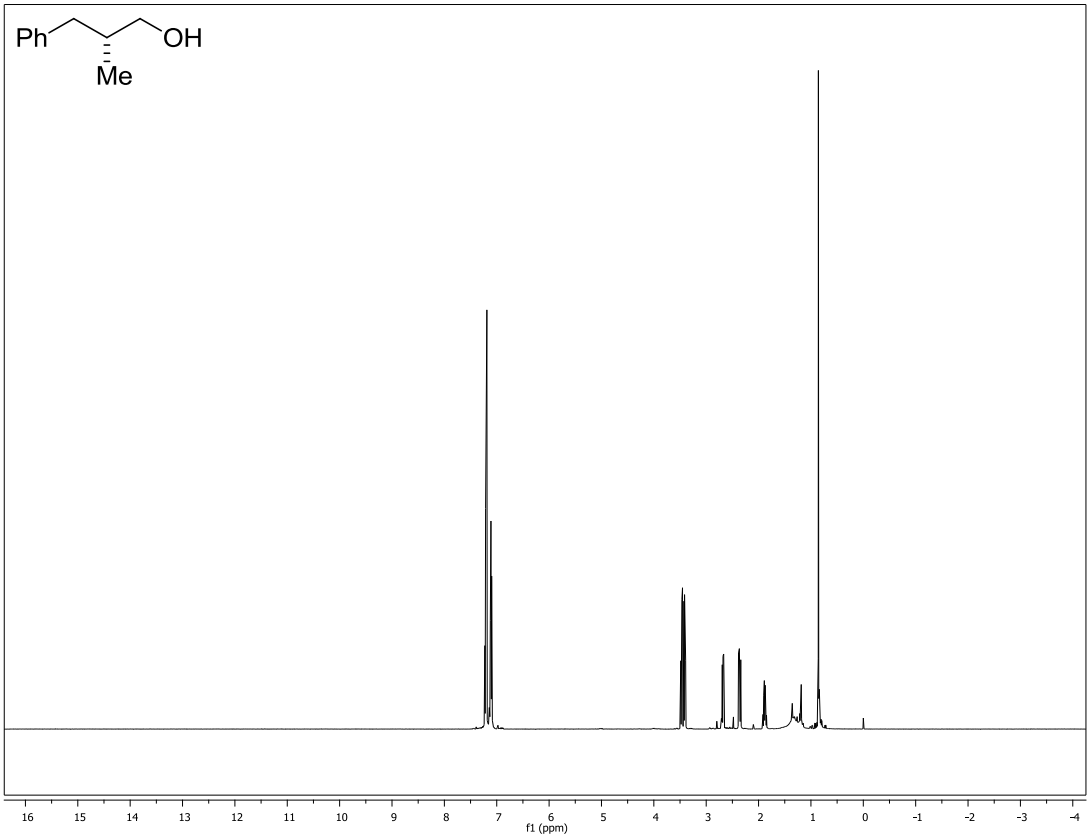

136.446
127.409
118.869
112.268
111.252
77.311
77.056
76.802
62.624
28.757
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

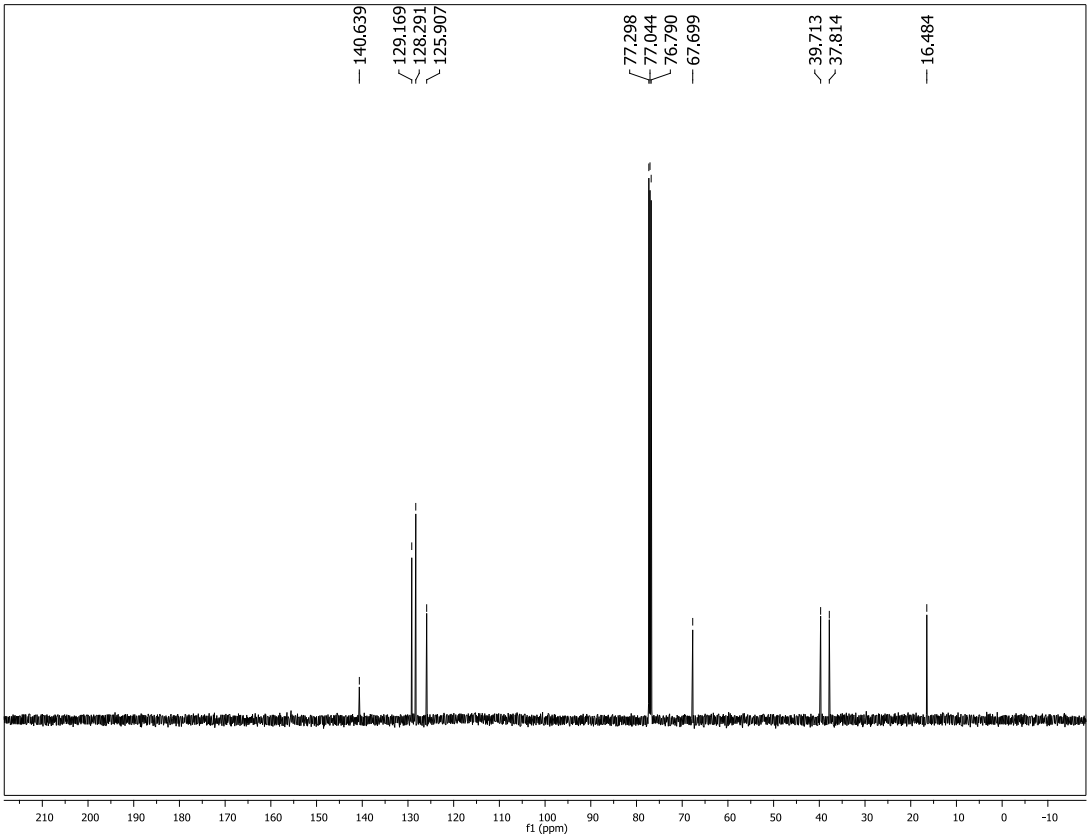

Me
Me
H
OH
Me
H
H
H
HO
OH
H
f1 (ppm)

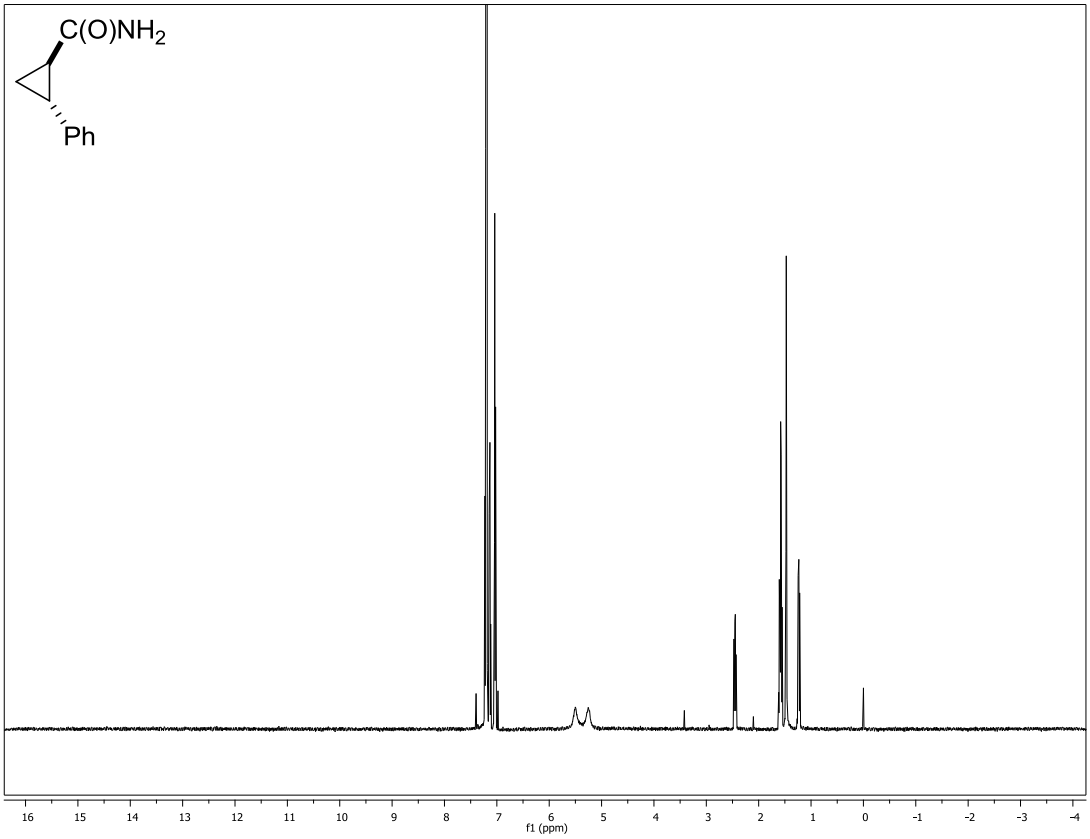

77.449
77.230
77.164
77.025
76.602
68.567
63.568
56.015
50.492
42.685
35.062
31.852
28.285
22.788
18.640
11.787
f1 (ppm)

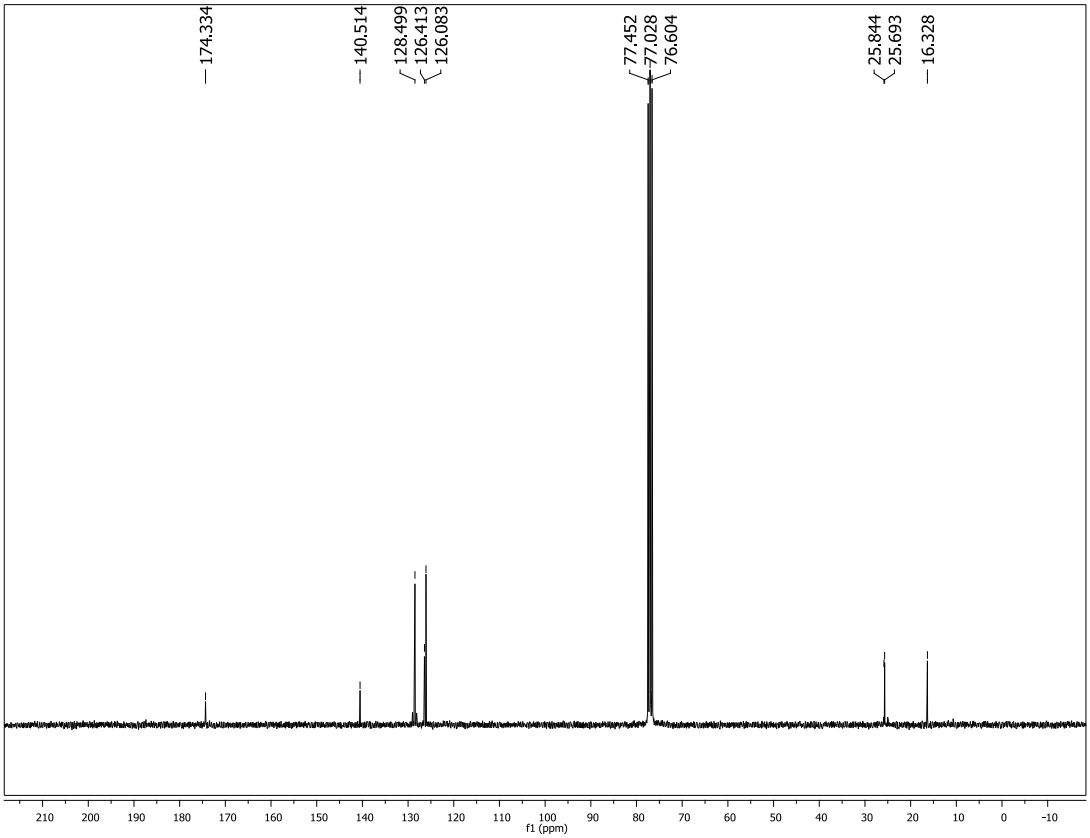

OH
H
N
i-Pr
O
OH
f1 (ppm)

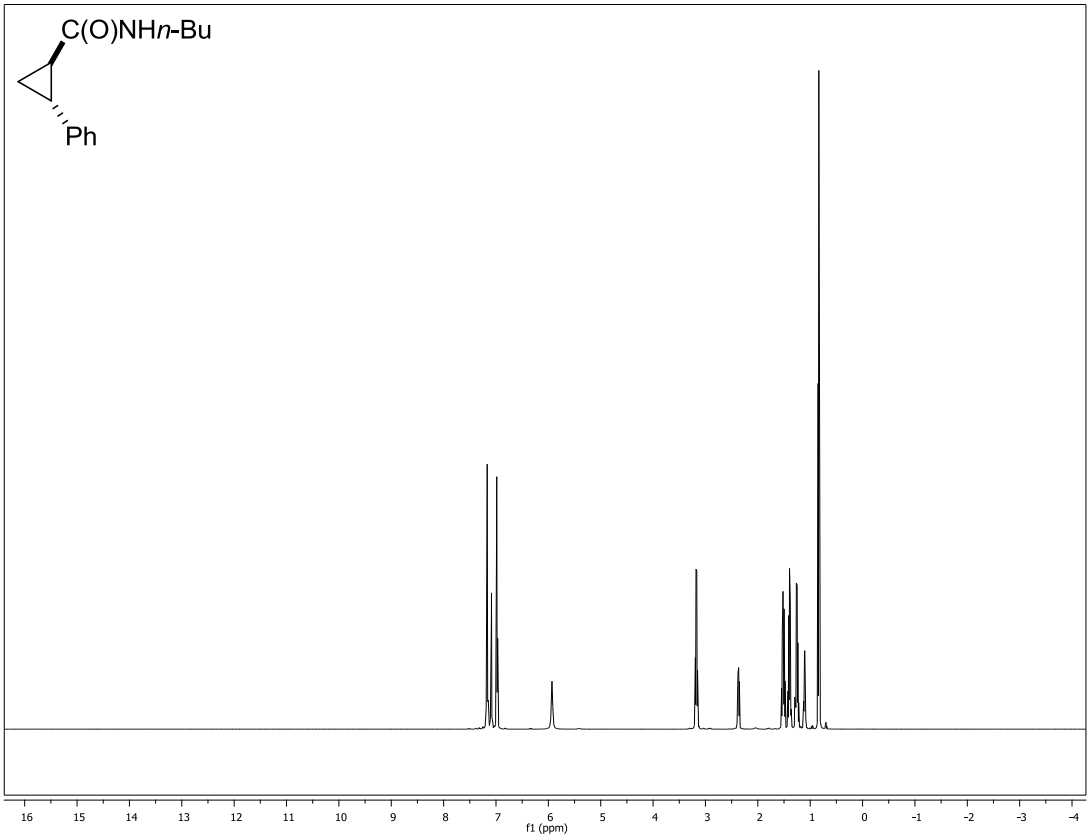

157.302
130.936
130.045
114.692
77.299
77.251
77.045
76.790
70.356
67.975
63.773
49.399
49.097
38.266
22.439
22.343
f1 (ppm)

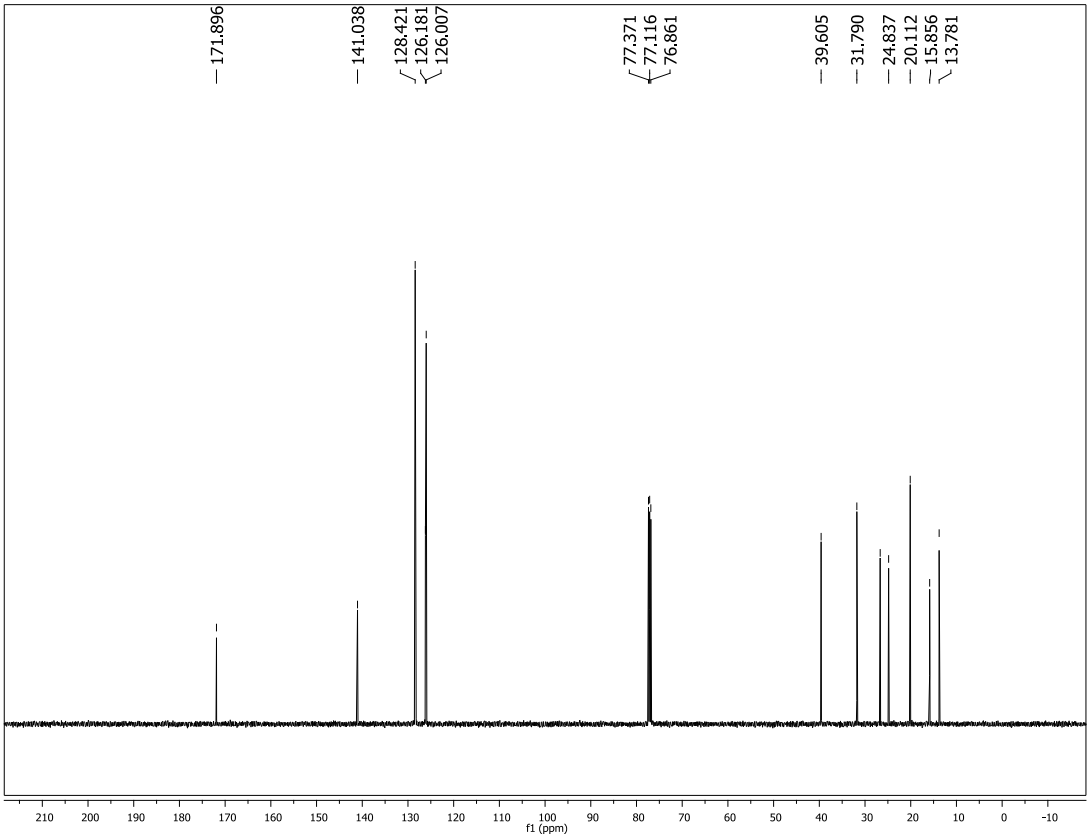

Ph
OH
Me
f1 (ppm)

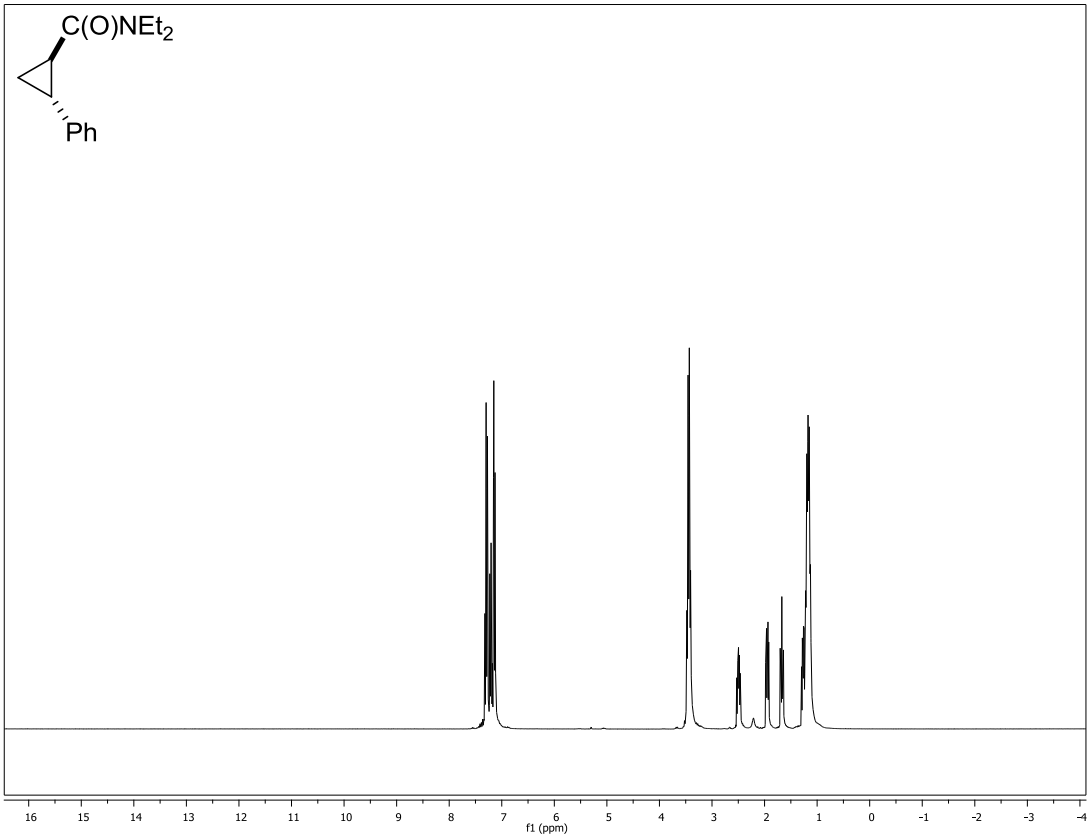

140.639
129.169
128.291
125.907
77.298
77.044
76.790
67.699
39.713
37.814
16.484
f1 (ppm)

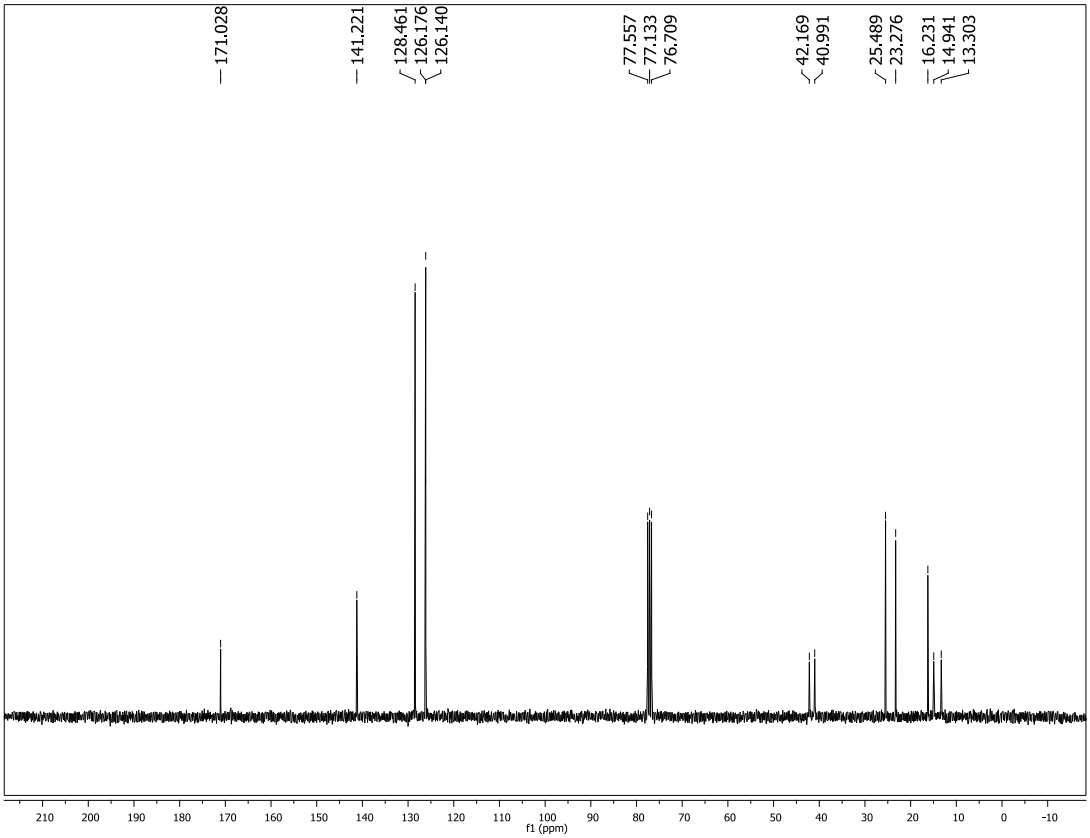

C(O)NH2
Ph
f1 (ppm)

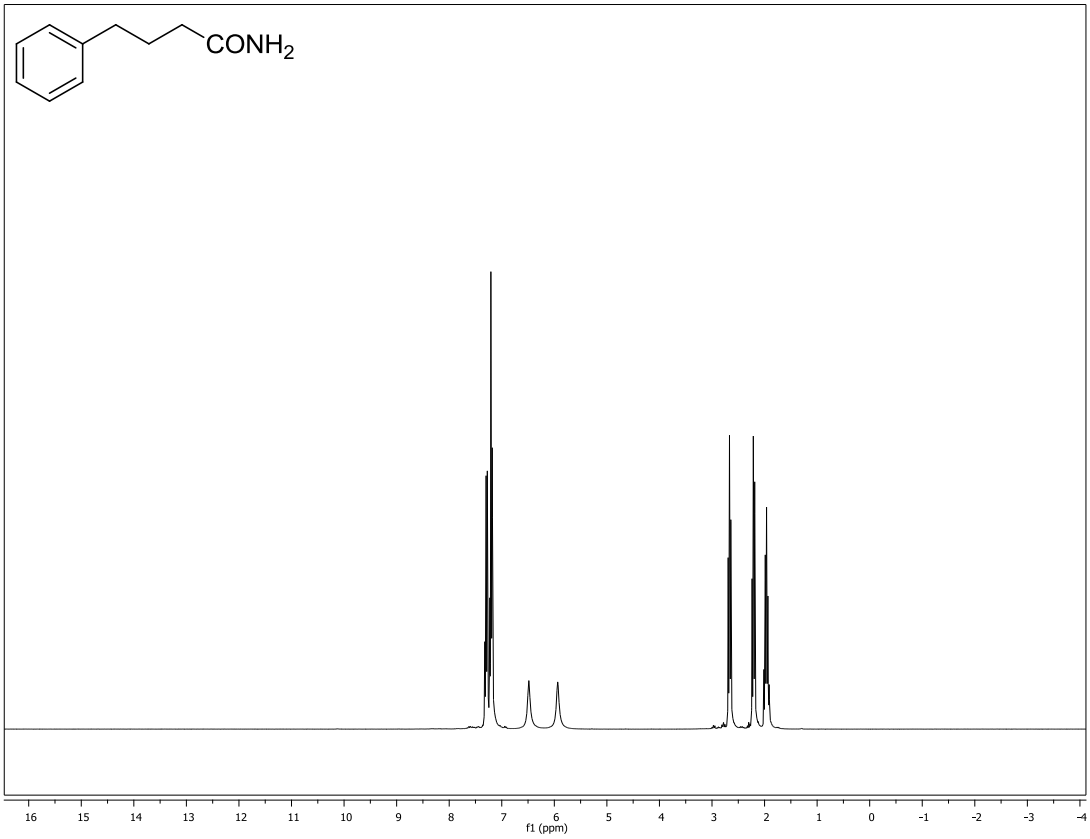

174.334
140.514
128.499
126.413
126.083
77.452
77.028
76.604
25.844
25.693
16.328
f1 (ppm)

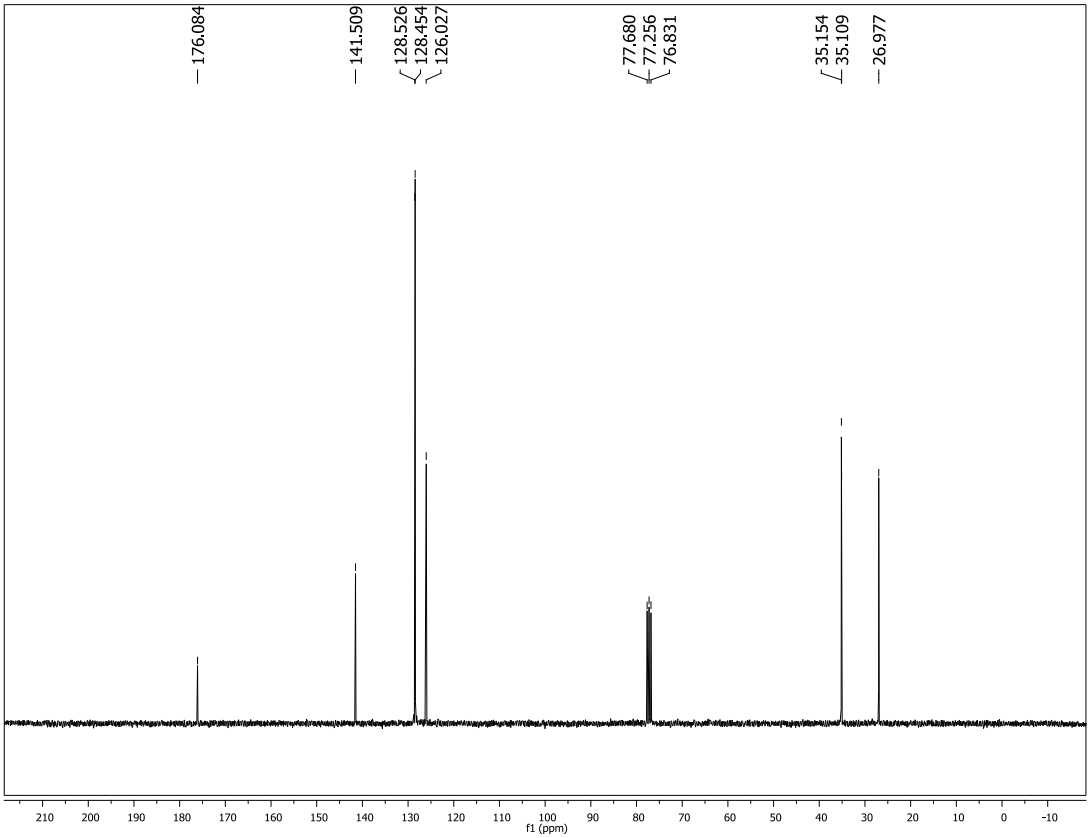

C(O)NHn-Bu
Ph
f1 (ppm)

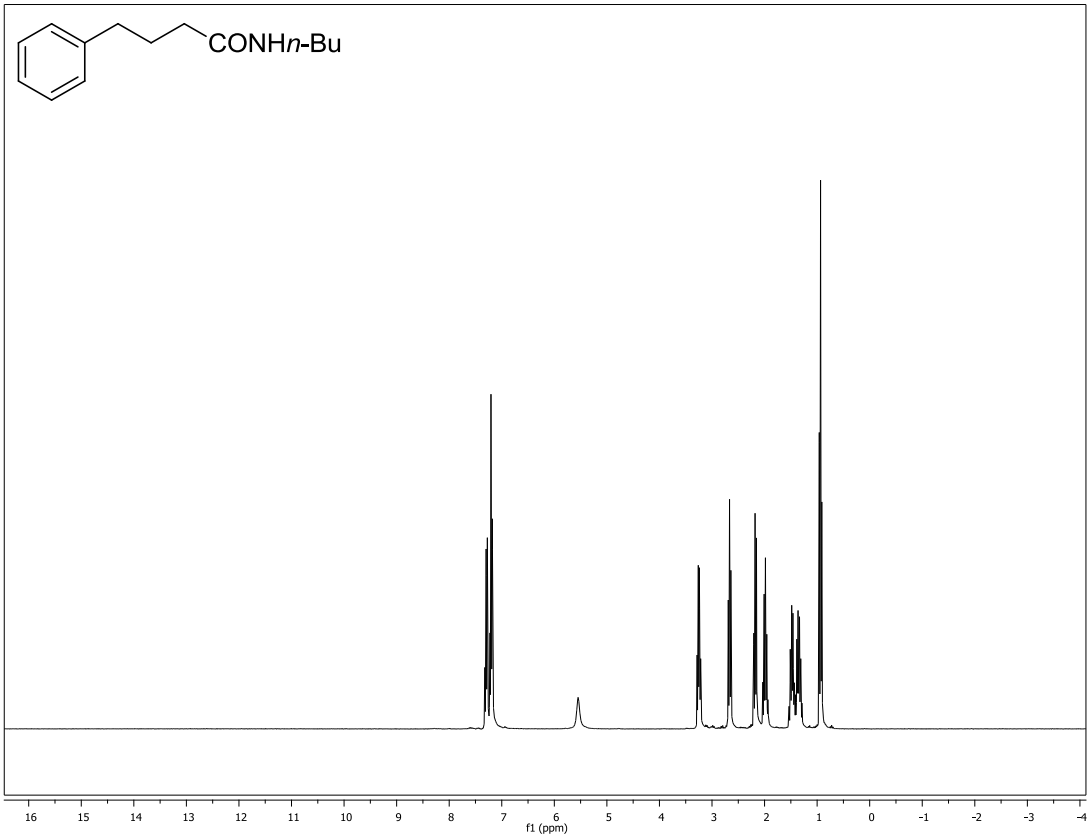

171.896
141.038
128.421
126.181
126.007
77.371
77.116
76.861
39.605
31.790
24.837
20.112
15.856
13.781
f1 (ppm)

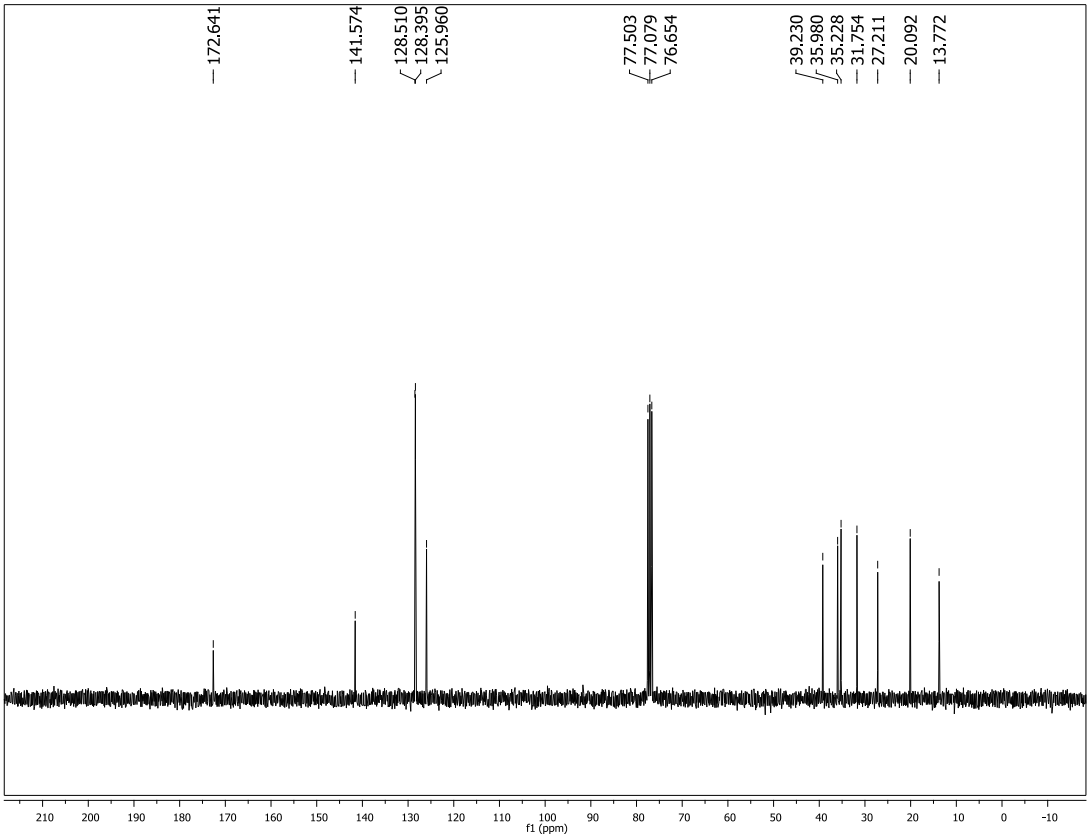

C(O)NEt2
Ph
f1 (ppm)

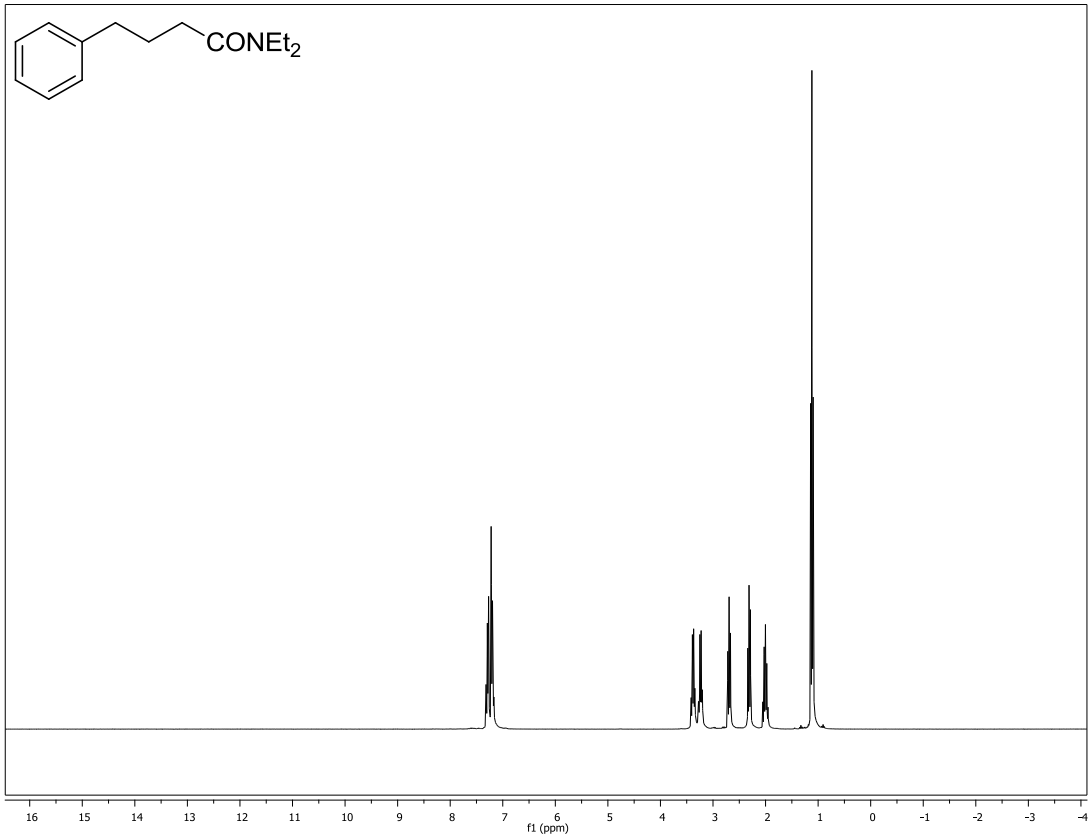

171.028
141.221
128.461
126.176
126.140
77.557
77.133
76.709
42.169
40.991
25.489
23.276
16.231
14.941
13.303
f1 (ppm)

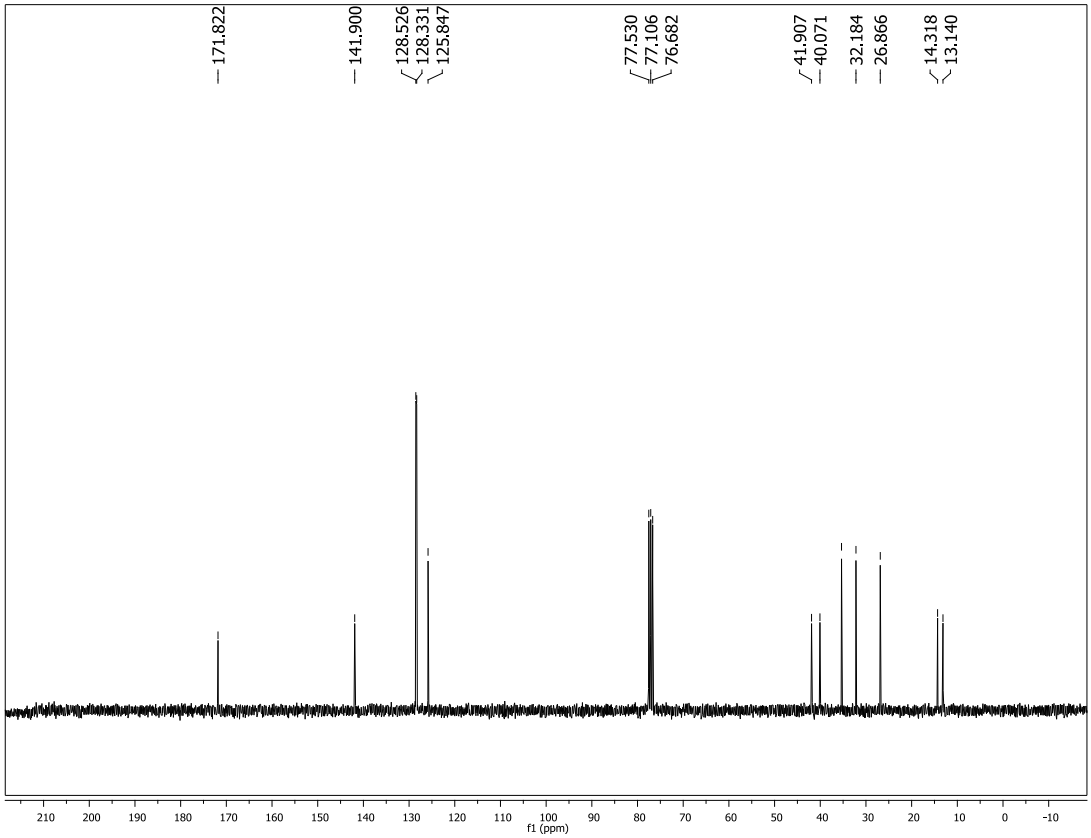

CONH2
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

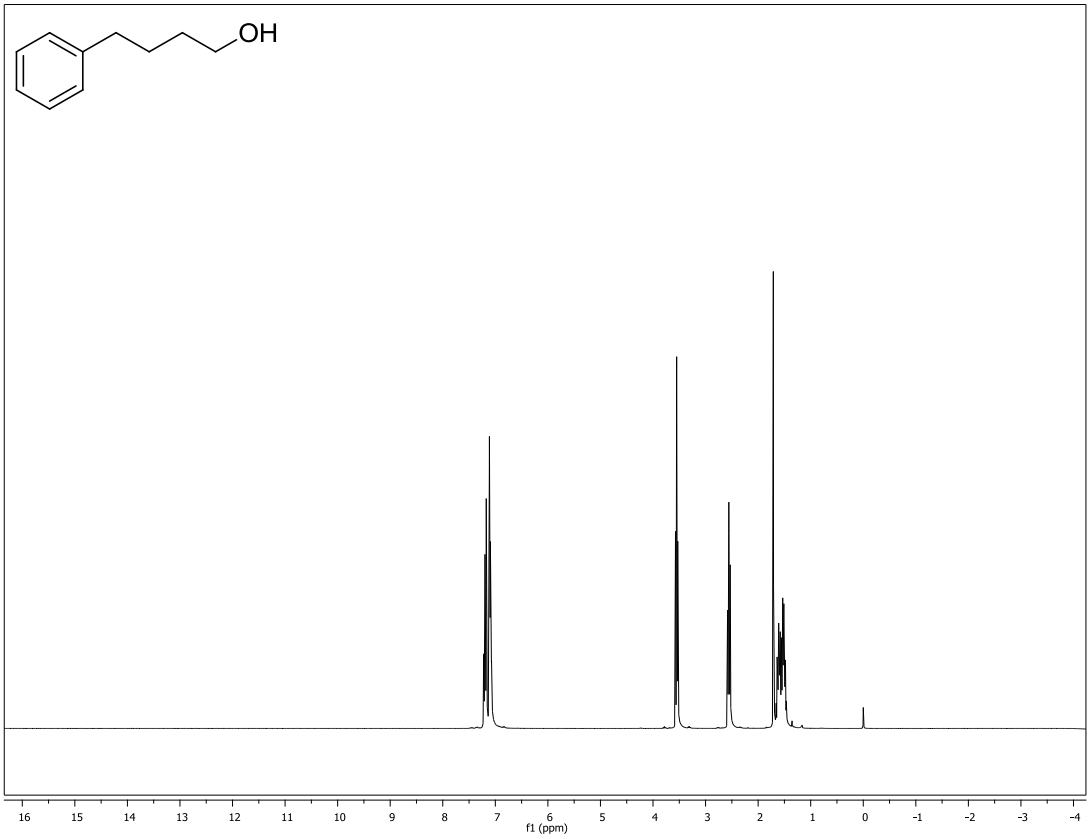

176.084
141.509
128.526
128.454
126.027
77.680
77.256
76.831
35.154
35.109
26.977
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

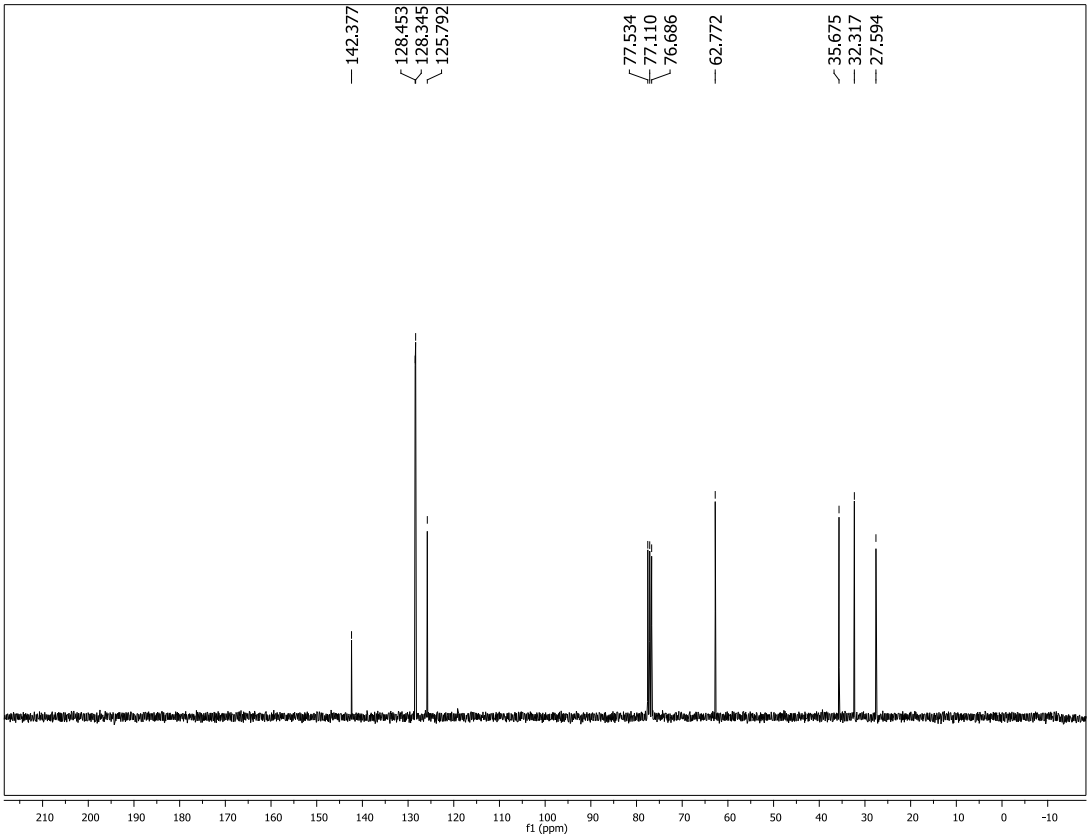

CONHn-Bu
f1 (ppm)

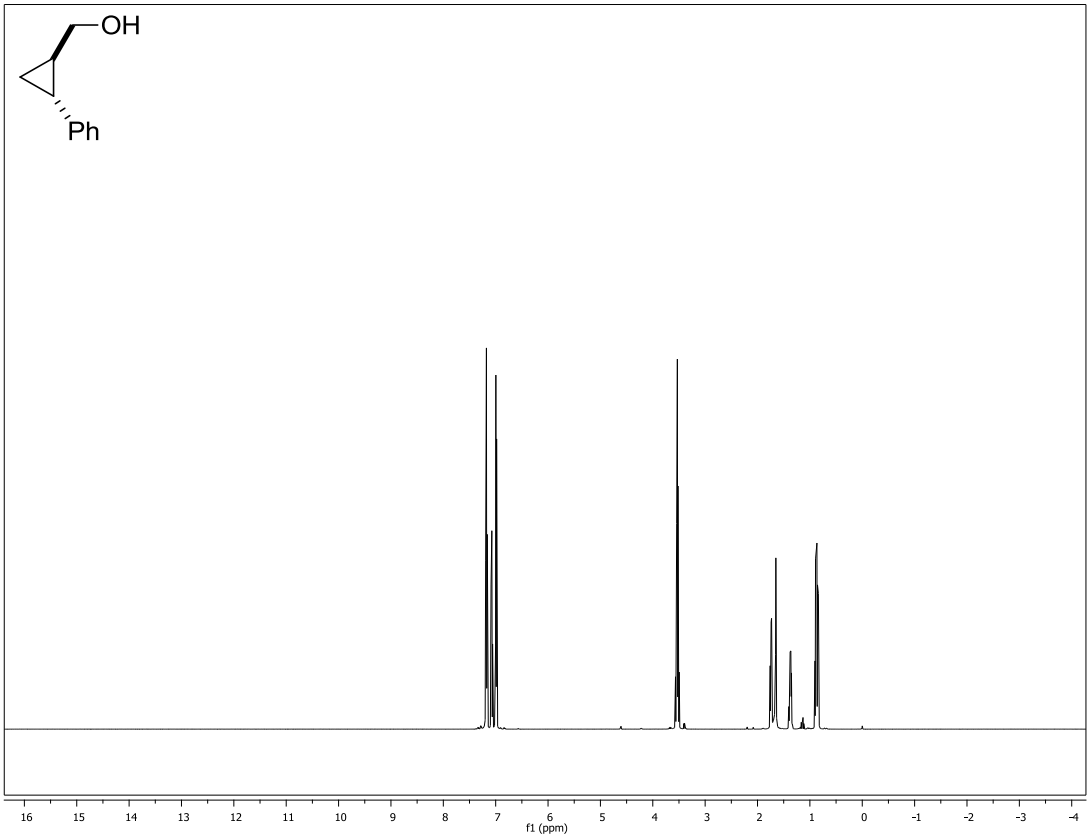

172.641
141.574
128.510
128.395
125.960
77.503
77.079
76.654
39.230
35.980
35.228
31.754
27.211
20.092
13.772
f1 (ppm)

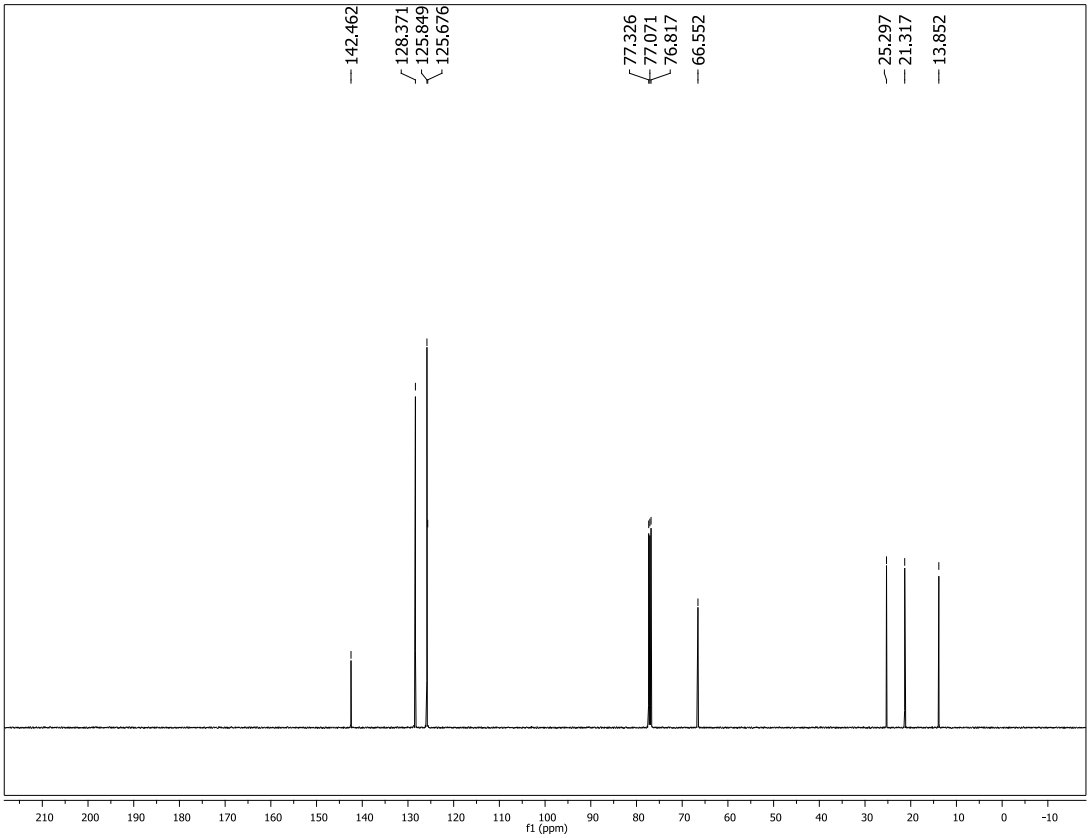

CONEt2
f1 (ppm)

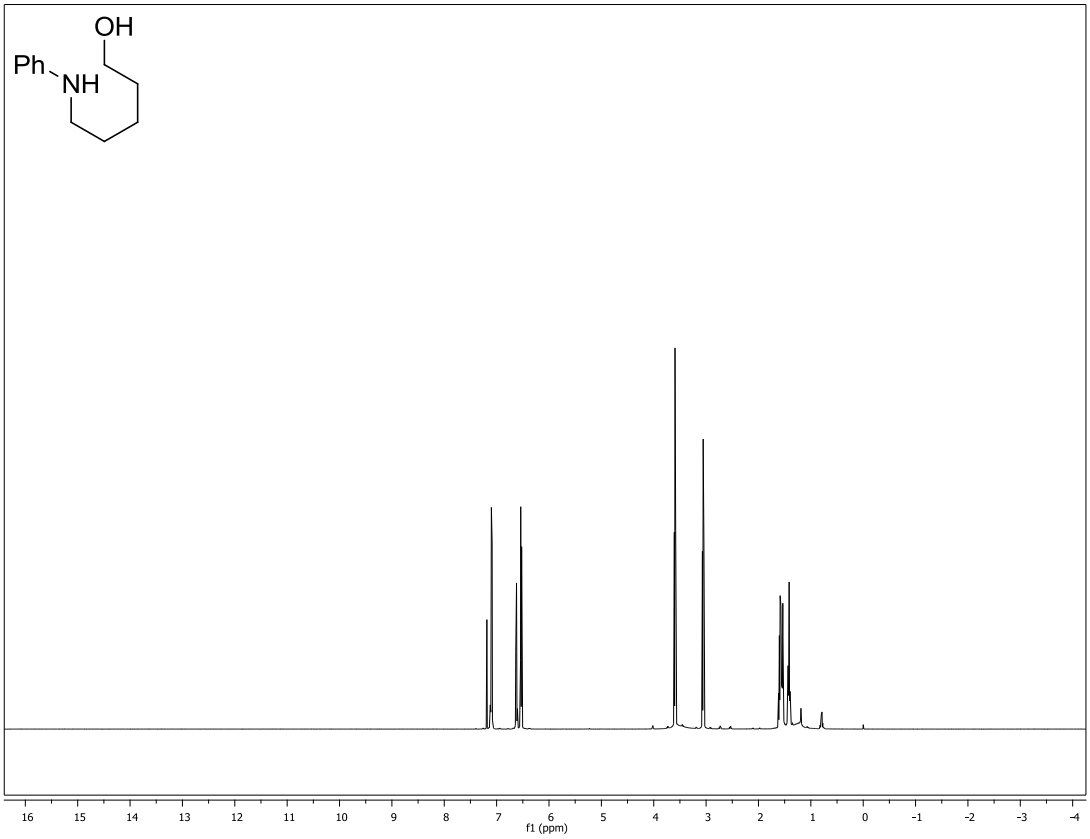

171.822
141.900
128.526
128.331
125.847
77.530
77.106
76.682
41.907
40.071
32.184
26.866
14.318
13.140
f1 (ppm)

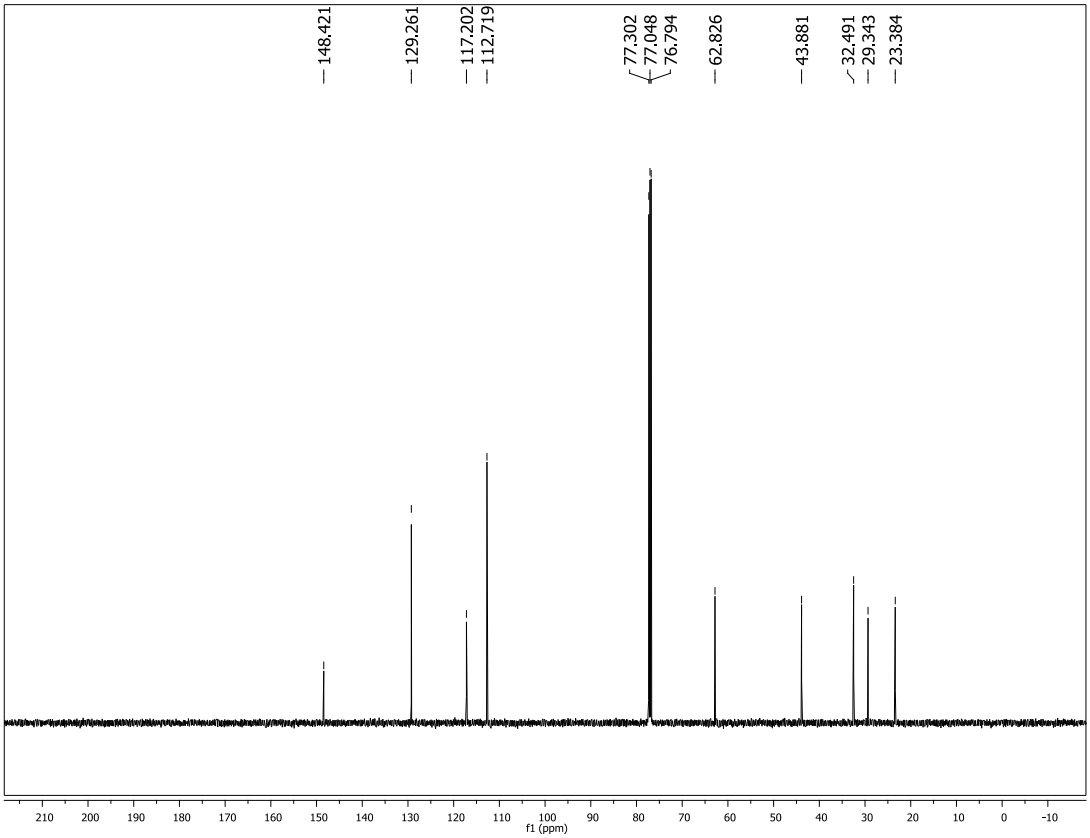

OH
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

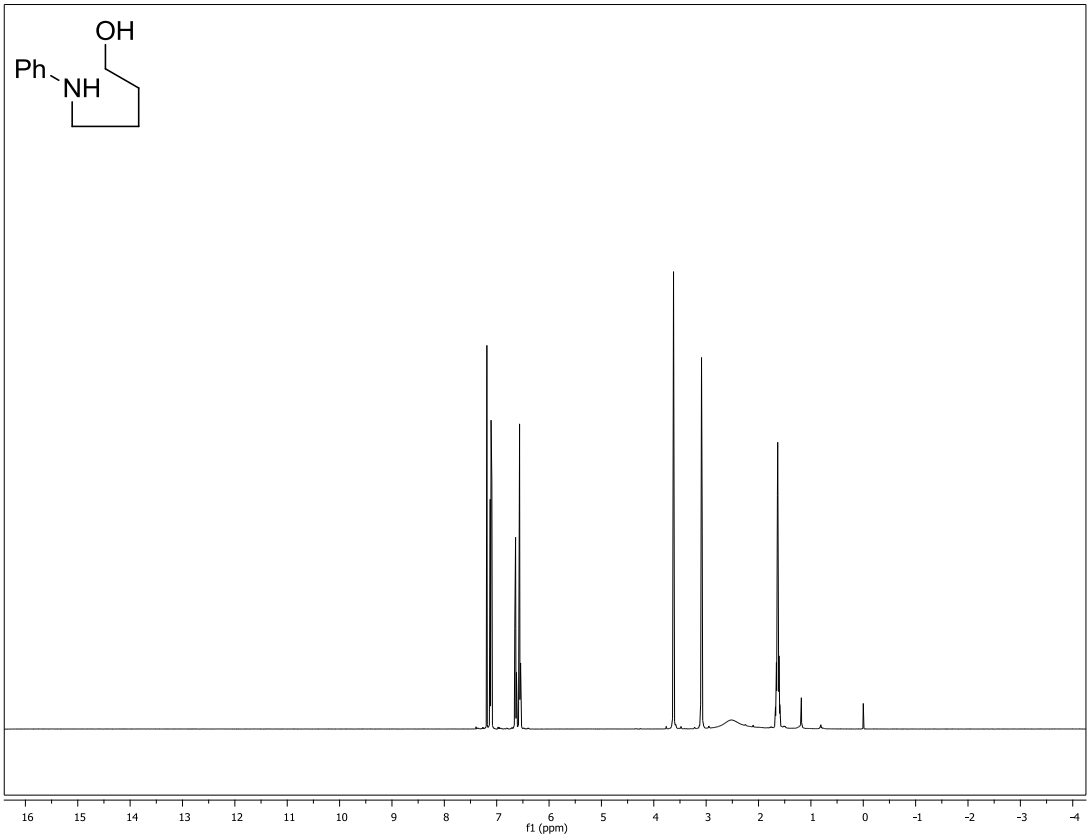

142.377
128.453
128.345
125.792
77.534
77.110
76.686
62.772
35.675
32.317
27.594
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

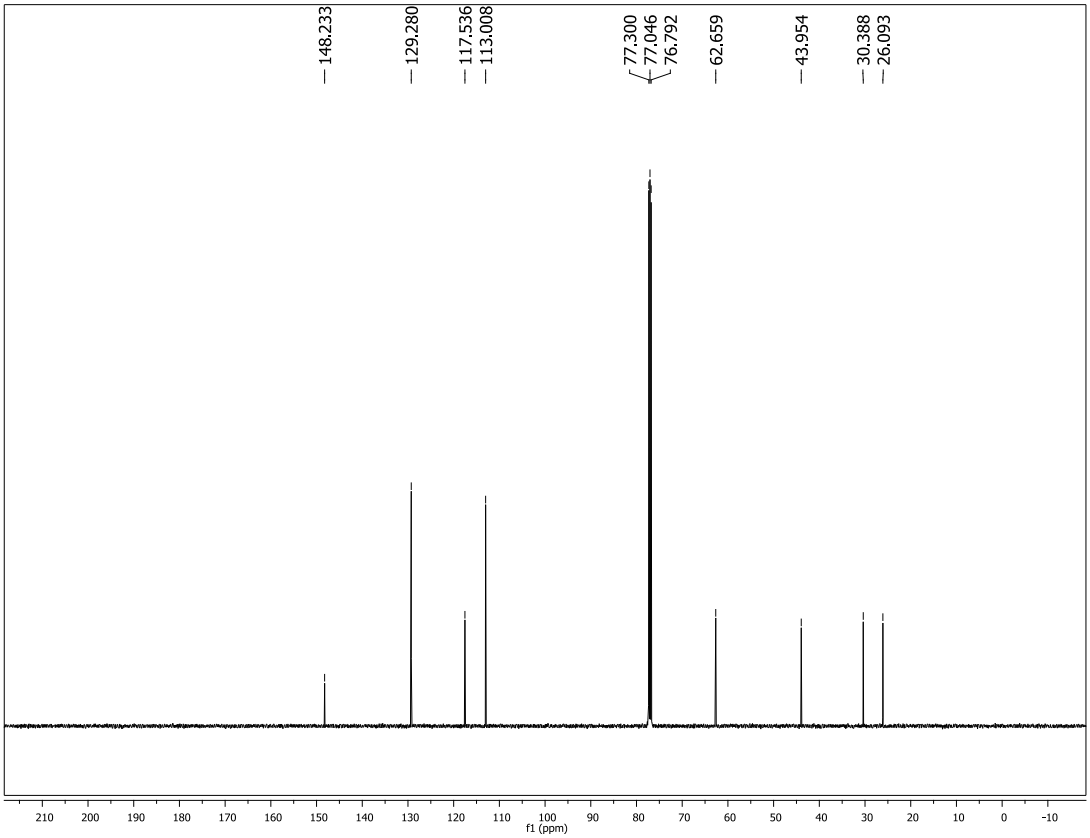

OH
Ph
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

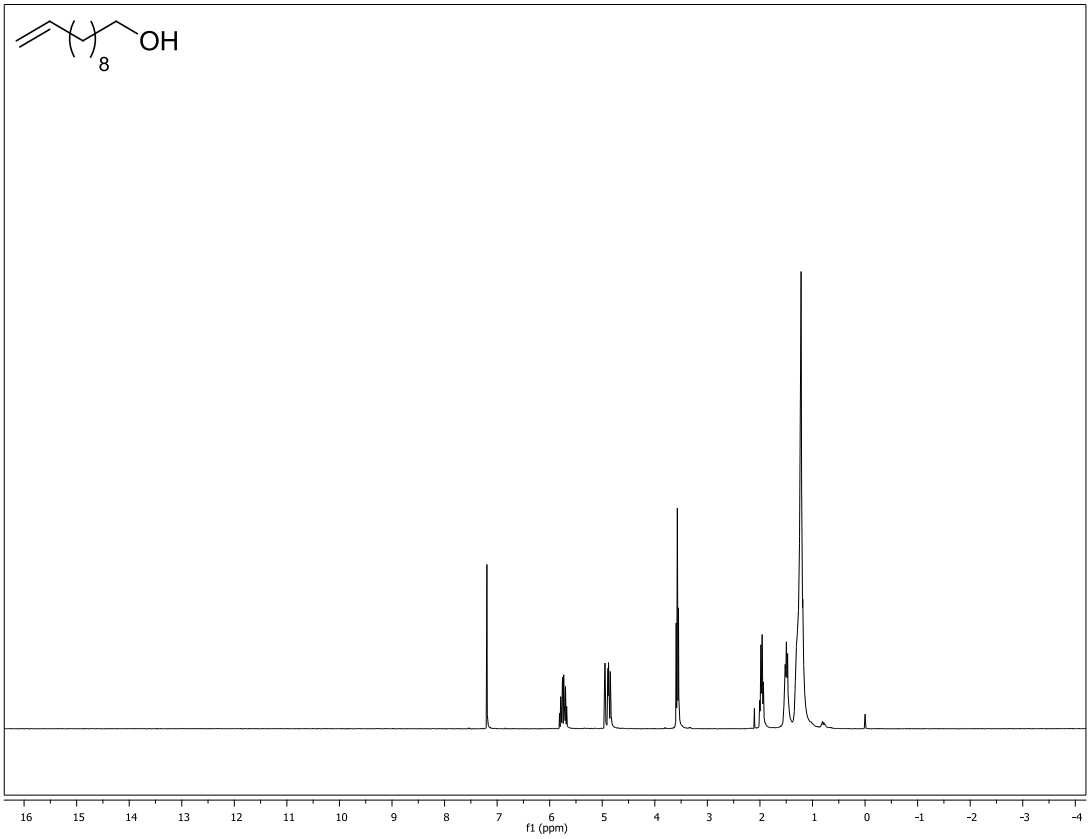

142.462
128.371
125.849
125.676
77.326
77.071
76.817
66.552
25.297
21.317
13.852
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

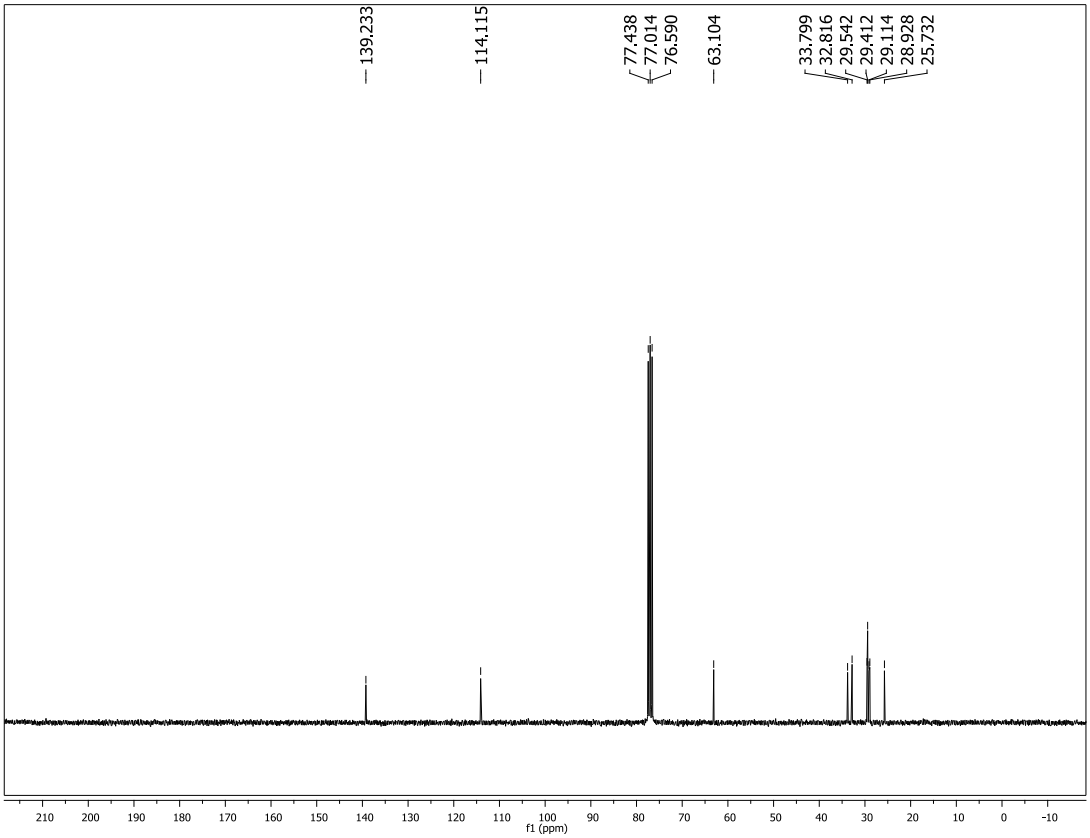

OH
Ph
NH
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


148.421
129.261
117.202
112.719
77.302
77.048
76.794
62.826
43.881
32.491
29.343
23.384
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

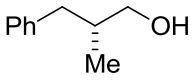

OH
Ph
NH
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


148.233
129.280
117.536
113.008
77.300
77.046
76.792
62.659
43.954
30.388
26.093
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

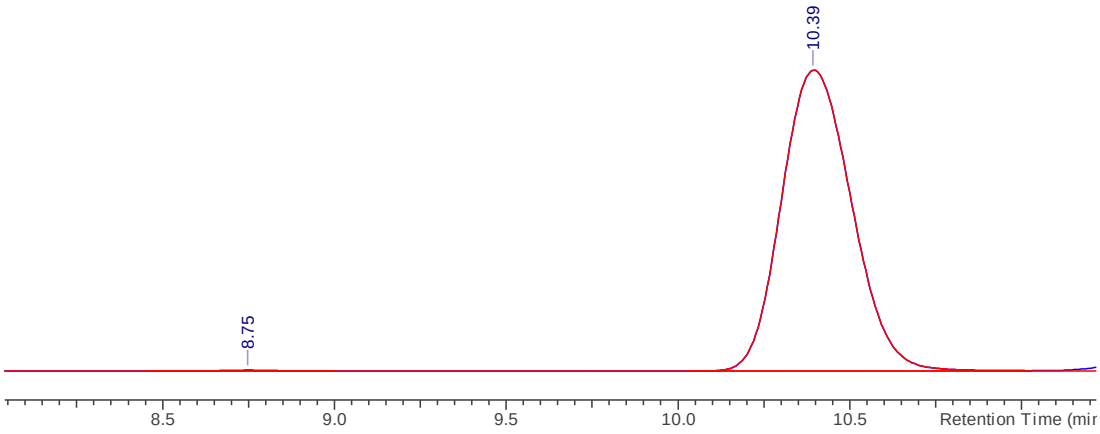

OH
8
f1 (ppm)


139.233
114.115
77.438
77.014
76.590
63.104
33.799
32.816
29.542
29.412
29.114
28.928
25.732
f1 (ppm)

DAD1A.ch

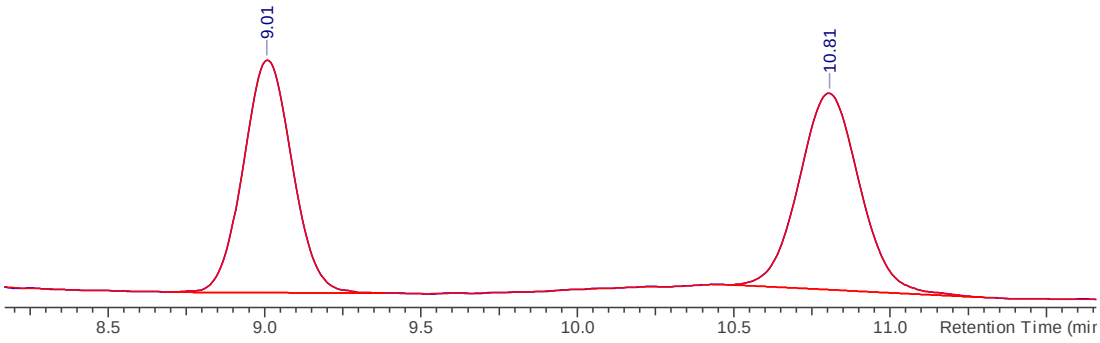


(*R*)-**6**, from **5**
99.5% ee



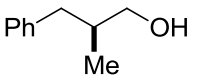
No.	t_R	Peak Area (Y units/ms)	Area Percent	Height
1	8.748	27047.350	0.2618	2499.840
2	10.395	10302975.000	99.738	724258.300

DAD1B.ch



No.	t_R	Peak Area (Y units/ms)	Area Percent	Height
1	9.009	405144.320	49.636	37111.690
2	10.804	411081.510	50.364	30967.040

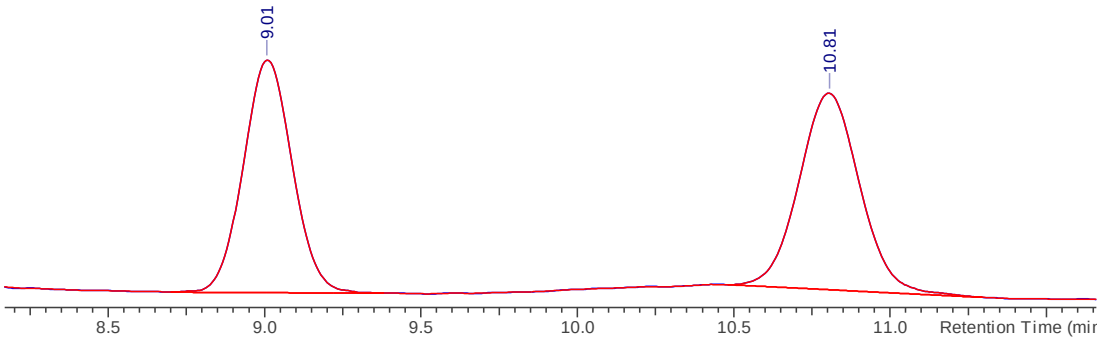
DAD1A.ch



(*S*)-**6**, from **5-SI**
96.0% ee

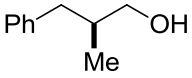
No.	t_R	Peak Area (Y units/ms)	Area Percent	Height
1	9.233	4646565.430	97.987	401524.200
2	11.116	95447.160	2.013	7161.420

DAD1B.ch

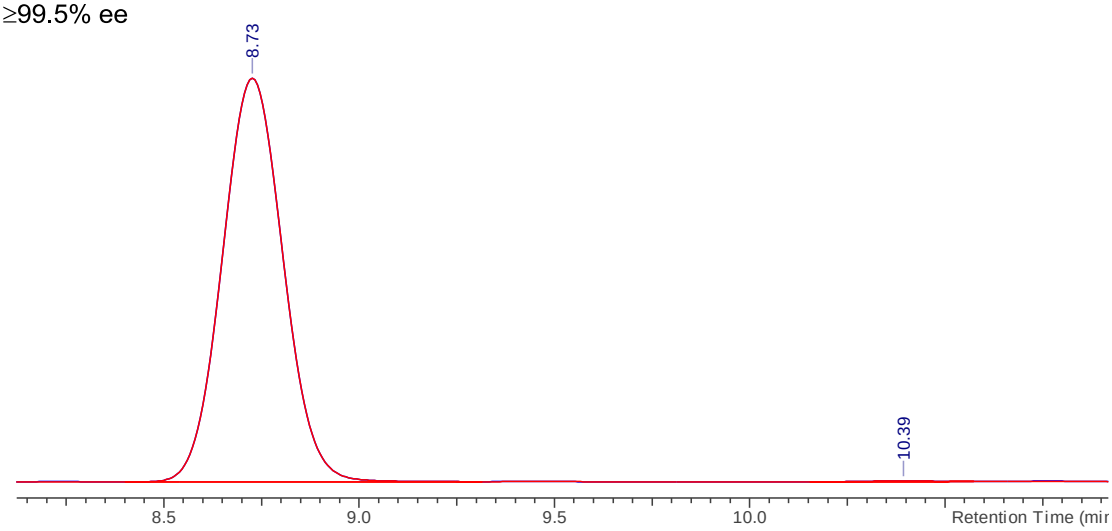


No.	t_R	Peak Area (Y units/ms)	Area Percent	Height
1	9.009	405144.320	49.636	37111.690
2	10.804	411081.510	50.364	30967.040

DAD1A.ch

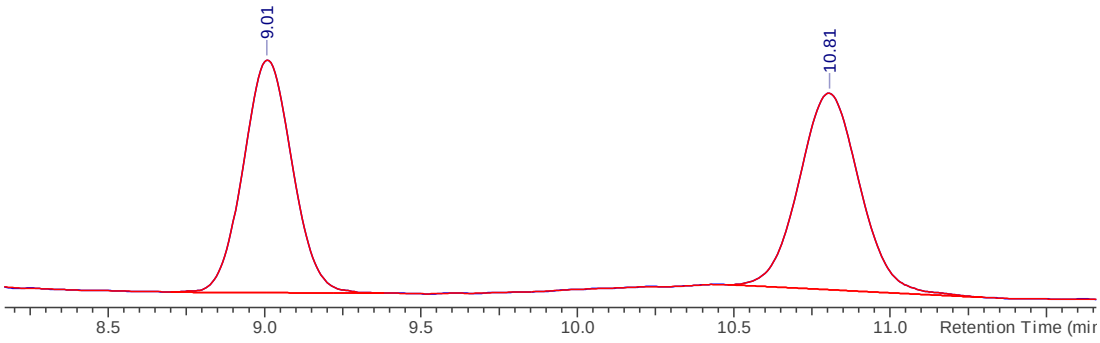


(*S*)-**6**, from **7**
≥99.5% ee



No.	t_R	Peak Area (Y units/ms)	Area Percent	Height
1	8.727	3670707.500	99.696	337265.438
2	10.393	11195.986	0.304	930.083

DAD1B.ch



No.	t_R	Peak Area (Y units/ms)	Area Percent	Height
1	9.009	405144.320	49.636	37111.690
2	10.804	411081.510	50.364	30967.040