Supporting Information

N-Methylimidazole-Catalyzed Synthesis of Carbamates from Hydroxamic Acids via the Lossen Rearrangement

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Supporting Information Contents:

General Procedures

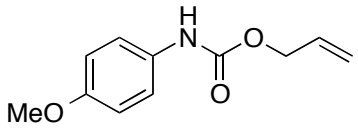
All commercially available reagents were purchased and used without further purification, unless otherwise stated. Air and moisture sensitive reactions were done under nitrogen atmosphere employing flame-dried glassware. Commercially available solvents (> 99.0% purity) were used for column chromatography without any further purification. Proton and carbon NMR spectra were recorded on a 500 MHz or 400 MHz spectrometer. Proton chemical shifts are reported in ppm (δ) relative to residual $CHCl_3$ (δ 7.26 ppm). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), doublet of doublets (dd), doublet of doublets of doublets (ddd), triplet (t), quartet (q), quintet (p), sextet (h), multiplet (m), apparent singlet (app. s), apparent doublet (app. d)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.06 ppm). Unless otherwise noted, all NMR spectra were acquired at ambient temperature. Infrared spectra (thin film) were recorded on a FT-IR, v_{max} (cm^{-1}) and are partially reported. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 Å F254 precoated plates (0.25 mm thickness). The following visualization methods were used for monitoring reactions and column chromatography: UV absorption by fluorescence quenching; Ninhydrin spray (Ninhydrin: acetic acid: *n*-butanol/ 0.6g:6mL:200mL) or PMA stain (phosphomolybdic acid, H_2SO_4). Flash column chromatography was performed using Flash Silica Gel (32-63 micron). Mass spectrometry data were collected using a Ultra high performance LC/MS, which was was performed on a UPLC/MS instrument equipped with a reverse-phase C18 column (1.7 µm particle size, 2.1 x 50 mm), dual atmospheric pressure chemical ionization (API)/electrospray (ESI) mass spectrometry detector, and photodiode array detector.

General procedure for the synthesis of hydroxamic acid precursors[1,2]:

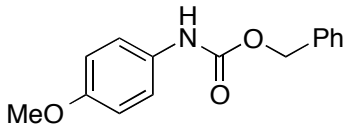
Carboxylic acid (6 mmol, 1 equiv.) and 1,1'-Carbonyldiimidazole (1.2 equiv.) were dissolved in CH_3CN (20 mL) and the resulting solution was stirred at 20 ˚C for 60 minutes. Then a solution of NH_2OH (50 wt. % in H_2O, 2 mL) was added to the flask and the reaction mixture was continued to stir at 23 ˚C . After 14 h of reaction, the crude reaction mixture was diluted with 5% $KHSO_{4(aq)}$ (60 mL) and extracted with EtOAc (3 x 60 mL). The combined organic layer was washed with water, saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated to yield the crude product. The crude material was recrystallized using ethyl acetate and hexanes to obtain the desired product in pure form.

General procedure for conversion of isocyanate to carbamate:

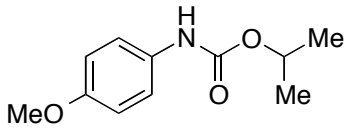
Isocyanate (0.4 mmol, 1 equiv.) was added to a solution of alcohol (0.8 mmol, 2 equiv.) and NMI (0.04 mmol, 0.1 equiv.) in CH_3CN (1 mL). Once the reaction was complete, as analyzed by TLC, the crude reaction mixture was purified using silica column chromatography (eluent: 100% hexanes to 10% EtOAc/hexanes) to yield the desired product.



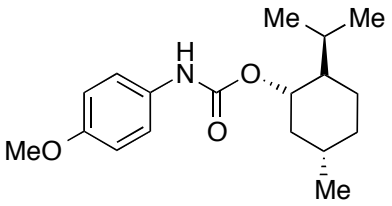
Allyl 4-methoxyphenylcarbamate (9): white solid, 41 mg, 95%. R_f: 0.36 (20% EtOAc/hexanes). **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 2H), 6.92 – 6.82 (m, 2H), 6.61 (s, 1H), 5.99 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.38 (m, 1H), 5.28 (m, 1H), 4.68 (dt, *J* = 5.7, 1.3 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 156.0, 153.7, 132.6, 130.9, 120.7, 118.0, 114.2, 65.7, 55.5. **IR:** (cast film, cm^{-1}) 3318, 2952, 2837, 1698, 1600, 1511, 1413, 1211. **LC-MS:** (ESI) calculated for $C_{11}H_{14}NO_3$ $[M+H]^+$ 208.10, observed 208.11.



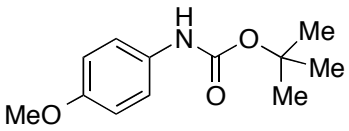
Benzyl (4-methoxyphenyl)carbamate (10): white solid, 53 mg, 99%. R_f: 0.34 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 7H), 6.87 – 6.82 (m, 2H), 6.66 (s, 1H), 5.19 (s, 2H), 3.78 (s, 3H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 156.0, 153.8, 136.2, 130.8, 128.6, 128.5, 128.3, 120.7, 114.3, 66.9, 55.5. **IR:** (cast film, cm^{-1}) 3305, 3061, 2967, 2842, 1698, 1599, 1526, 1519, 1413, 1236. **LC-MS:** (ESI) calculated for $C_{15}H_{16}NO_3$ $[M+H]^+$ 258.11, observed 258.11.



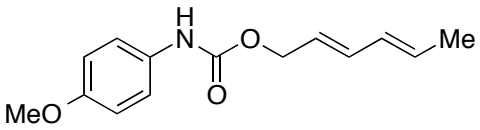
Isopropyl (4-methoxyphenyl)carbamate (11): white solid, 38 mg, 87%. R_f: 0.40 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 2H), 6.86 – 6.79 (m, 2H), 6.47 (s, 1H), 5.09 – 4.87 (m, 1H), 3.75 (s, 3H), 1.26 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 155.8, 153.7, 131.2, 120.6, 114.2, 68.6, 55.5, 22.1. **IR:** (cast film, cm^{-1}) 3315, 2980, 1694, 1600, 1513, 1165, 1413, 1220, 1176. **LC-MS:** (ESI) calculated for $C_{11}H_{16}NO_3$ $[M+H]^+$ 210.11, observed 210.13.



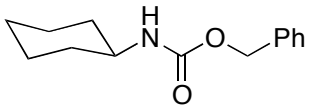
(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl (4-methoxyphenyl)carbamate (12): white solid, 44 mg, 69%. R_f: 0.55 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 2H), 6.87 – 6.82 (m, 2H), 6.47 (s, 1H), 4.64 (dd, *J* = 10.4, 7.1 Hz, 1H), 3.78 (s, 3H), 2.11 (d, *J* = 11.7 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.72 – 1.63 (m, 3H), 1.56 – 1.46 (m, 1H), 1.36 (t, *J* = 11.5 Hz, 1H), 1.14 – 0.95 (m, 2H), 0.93 – 0.88 (m, 6H), 0.88 – 0.82 (m, 1H), 0.81 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 155.8, 131.3, 120.4, 114.2, 74.9, 55.5, 47.4, 41.4, 34.3, 31.4, 26.3, 23.5, 22.1, 20.8, 16.5. **IR:** (cast film, cm^{-1}) 3335, 2953, 2923, 2868, 1693, 1525, 1512, 1413, 1219, 1175. **LC-MS:** (ESI) calculated for $C_{18}H_{28}NO_3$ $[M+H]^+$ 306.21, observed 306.21.



***Tert*-butyl (4-methoxyphenyl)carbamate (13):** white solid, 8 mg, 17%. R_f: 0.45 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 6.88 – 6.80 (m, 2H), 6.40 (s, 1H), 3.77 (s, 3H), 1.51 (s, 9H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 155.9, 153.4, 131.6, 120.7, 114.4, 80.4, 55.7, 28.6. **IR:** (cast film, cm^{-1}) 3363, 2988, 2971, 1692, 1598, 1518, 1412, 1234, 1158. **LC-MS:** (ESI) calculated for $C_{12}H_{18}NO_3$ $[M+H]^+$ 224.13, observed 224.12.



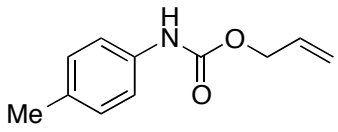
(2*E*,4*E*)-hexa-2,4-dien-1-yl (4-methoxyphenyl)carbamate (14): white solid, 46 mg, 90%. R_f: 0.40 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.53 (s, 1H), 6.28 (dd, *J* = 15.2, 10.5 Hz, 1H), 6.12 – 6.01 (m, 1H), 5.76 (dd, *J* = 15.0, 6.8 Hz, 1H), 5.71 – 5.61 (m, 1H), 4.65 (d, *J* = 6.6 Hz, 2H), 3.78 (s, 3H), 1.77 (dd, *J* = 6.7, 0.7 Hz, 2H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 156.0, 153.7, 134.9, 131.5, 130.9, 130.5, 124.0, 120.7, 114.3, 65.6, 55.5, 18.2. **IR:** (cast film, cm^{-1}) 3315, 2912, 2854, 2837, 1695, 1597, 1535, 1512, 1418, 1223. **LC-MS:** (ESI) calculated for $C_{14}H_{18}NO_3$ $[M+H]^+$ 248.13, observed 248.14.



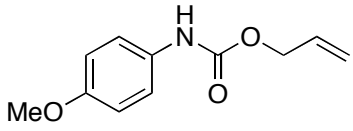
Benzyl cyclohexylcarbamate (16): white solid, 53 mg, 55%. R_f: 0.45 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 5H), 5.08 (s, 2H), 4.68 (s, 1H), 3.59 – 3.43 (m, 1H), 1.94 (d, *J* = 10.0 Hz, 2H), 1.75 – 1.64 (m, 2H), 1.59 (dd, *J* = 9.2, 3.8 Hz, 1H), 1.40 – 1.24 (m, 2H), 1.26 – 1.06 (m, 3H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 155.6, 136.7, 128.5, 128.2, 128.1, 66.5, 49.9, 33.4, 25.5, 24.8. **IR:** (cast film, cm^{-1}) 3316, 2932, 2854, 1684, 1538, 1452, 1310, 1249, 1233. **LC-MS:** (ESI) calculated for $C_{14}H_{20}NO_2$ $[M+H]^+$ 234.15, observed 234.17.

General procedure for the Lossen rearrangement:

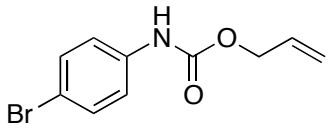
Hydroxamic acid (0.6 mmol, 1 equiv.) and 4-NsCl (0.66 mmol, 1.1 equiv.) were cooled to 0 ˚C and then THF (5 mL) and DIPEA (1.5 mmol, 2.5 equiv.) were added to the flask. After stirring the reaction mixture for 2 h at 0 ˚C, NMI (0.12 mmol, 0.2 equiv.) and allyl alcohol (3 mmol, 5 equiv.) were added to the flask. The reaction mixture was allowed to stir at 23 ˚C until all isocyanate was consumed, as indicated by TLC analysis (6 – 8 hrs) (Note: For compounds **23** - **28**, reaction was allowed to stir at 35 ˚C for 12 h). Once the reaction was done, crude reaction mixture was purified using silica column chromatography to yield the product (eluent: 100% hexanes to 10% EtOAc/hexanes).



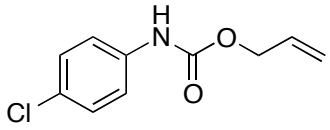
Allyl-*p*-tolylcarbamate (17): white solid, 105 mg, 83%. $\mathbf{R_f}$: 0.48 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.1 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.56 (s, 1H), 5.89 (ddt, *J* = 16.6, 11.1, 5.7 Hz, 1H), 5.28 (m, 1H), 5.18 (m, 1H), 4.58 (dt, *J* = 5.3, 1.3 Hz, 2H), 2.23 (s, 3H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 153.4, 135.2, 133.1, 132.5, 129.8, 129.6, 118.8, 118.2, 65.8, 20.8. **IR:** (cast film, cm^{-1}) 3318, 2923, 1703, 1599, 1529, 1408, 1315, 1223, 1208. **LC-MS:** (ESI) calculated for $C_{11}H_{14}NO_2$ $[M+H]^+$ 192.10, observed 192.11.



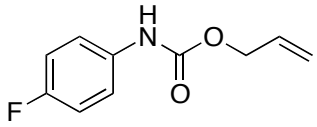
Allyl-4-methoxyphenylcarbamate (9): white solid, 112 mg, 97%. $\mathbf{R_f}$: 0.36 (20% EtOAc/hexanes). **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 2H), 6.92 – 6.82 (m, 2H), 6.61 (s, 1H), 5.99 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.38 (m, 1H), 5.28 (m, 1H), 4.68 (dt, *J* = 5.7, 1.3 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 156.0, 153.7, 132.6, 130.9, 120.7, 118.0, 114.2, 65.7, 55.5. **IR:** (cast film, cm^{-1}) 3318, 2952, 2837, 1698, 1600, 1511, 1413, 1211. **LC-MS:** (ESI) calculated for $C_{11}H_{14}NO_3$ $[M+H]^+$ 208.10, observed 208.17.



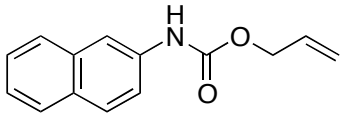
Allyl-(4-bromophenyl)carbamate (18): an off-white solid, 110 mg, 72%. $\mathbf{R_f}$: 0.42 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.32 – 7.24 (m, 2H), 6.75 (s, 1H), 5.95 (ddt, *J* = 16.2, 10.5, 5.7 Hz, 1H), 5.36 (m, 1H), 5.26 (m, 1H), 4.66 (dt, *J* = 5.7, 1.3 Hz, 2H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 153.05, 136.90, 132.20, 131.96, 120.24, 118.44, 116.00, 66.01. **IR:** (cast film, cm^{-1}) 3310.4, 1695.3, 1591.5, 1544.8, 1374.5. **LC-MS:** (ESI) calculated for $C_{10}H_{11}BrNO_2$ $[M+H]^+$ 256.00, observed 256.10.



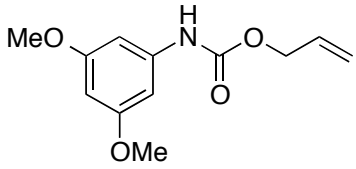
Allyl-(4-chlorophenyl)carbamate (19): pale yellow solid, 92 mg, 75%. R_f: 0.41 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 (dt, *J* = 5.5, 2.5 Hz, 2H), 6.74 (s, 1H), 5.95 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.35 (m, 1H), 5.26 (m, 1H), 4.65 (dt, *J* = 5.7, 1.3 Hz, 2H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 153.1, 136.4, 132.2, 129.1, 128.5, 119.9, 118.5, 66.0. **IR:** (cast film, cm^{-1}) 3303, 1696, 1602, 1592, 1535, 1402, 1240. **LC-MS:** (ESI) calculated for $C_{10}H_{11}ClNO_2$ $[M+H]^+$ 212.05, observed 212.05.



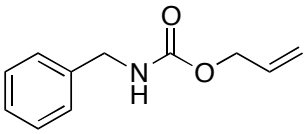
Allyl-(4-fluorophenyl)carbamate (20): white solid, 69 mg, 59%. R_f: 0.24 (20% EtOAc/hexanes). **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 4.2 Hz, 2H), 6.97 – 6.87 (m, 2H), 6.64 (s, 1H), 5.89 (ddt, *J* = 17.0, 10.5, 5.7 Hz, 1H), 5.34 – 5.23 (m, 1H), 5.19 (m, 1H), 4.59 (dt, *J* = 5.7, 1.3 Hz, 2H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 159.1 (d, *J* = 243 Hz), 153.4, 133.8, 132.4, 120.5, 118.4, 115.7 (d, *J* = 22 Hz), 66.0. **^{19}F NMR:** (376 MHz, $CDCl_3$) δ -119.4 (s). **IR:** (cast film, cm^{-1}) 3315, 1701, 1614, 1533, 1508, 1409, 1205. **LC-MS:** (ESI) calculated for $C_{10}H_{11}FNO_2$ $[M+H]^+$ 196.08, observed 196.09.



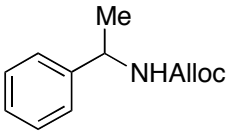
Allyl-naphthalen-2-ylcarbamate (21): white solid, 115 mg, 85%. R_f: 0.38 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.77 (dd, *J* = 8.1, 5.6 Hz, 3H), 7.45 (ddd, *J* = 8.2, 6.8, 1.1 Hz, 1H), 7.42 – 7.36 (m, 2H), 6.91 (s, 1H), 6.01 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.40 (m, 1H), 5.29 (m, 1H), 4.72 (dt, *J* = 5.7, 1.3 Hz, 2H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 153.4, 135.2, 133.9, 132.4, 130.2, 128.9, 127.6, 127.4, 126.6, 124.7, 119.2, 118.4, 114.9, 66.0. **IR:** (cast film, cm^{-1}) 3320, 1701, 1633, 1605, 1537, 1502, 1208. **LC-MS:** (ESI) calculated for $C_{14}H_{14}NO_2$ $[M+H]^+$ 228.10, observed 228.11.



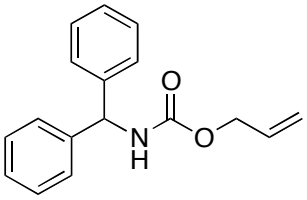
Allyl-(3,5-dimethoxyphenyl)carbamate (22): white solid, 124 mg, 87%. R_f: 0.27 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 6.80 (s, 1H), 6.63 (app. s, 2H), 6.19 (t, *J* = 2.2 Hz, 1H), 5.95 (ddt, *J* = 16.1, 10.6, 5.7 Hz, 1H), 5.35 (m, 1H), 5.25 (m, 1H), 4.65 (dt, *J* = 5.7, 1.3 Hz, 2H), 3.75 (s, 6H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 161.1, 153.1, 139.6, 132.4, 118.2, 96.9, 95.8, 65.8, 55.3. **IR:** (cast film, cm^{-1}) 3325, 2941, 1707, 1648, 1600, 1542, 1454, 1419, 1202. **LC-MS:** (ESI) calculated for $C_{12}H_{16}NO_4$ $[M+H]^+$ 238.11, observed 238.11.



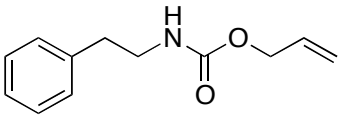
Allyl-benzylcarbamate (23): white solid, 94 mg, 74%. R_f: 0.32 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 5.99 – 5.87 (m, 1H), 5.31 (app. d, *J* = 17.2 Hz, 1H), 5.26 – 4.80 (m, 2H), 4.60 (app. d, *J* = 5.5 Hz, 2H), 4.38 (app. d, *J* = 5.9 Hz, 2H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 138.5, 132.9, 128.7, 127.5, 117.8, 65.7, 45.1. **IR:** (cast film, cm^{-1}) 3321, 3030, 1694, 1519, 1496, 1236. **LC-MS:** (ESI) calculated for $C_{11}H_{14}NO_2$ $[M+H]^+$ 192.10, observed 192.10.



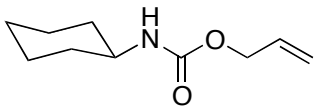
Allyl-(1-phenylethyl)carbamate (24): white solid, 112 mg, 75%. R_f: 0.30 (20% EtOAc/hexanes). **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.37 – 7.13 (m, 5H), 5.89 – 5.85 (m, 1H), 5.29 – 5.24 (m, 2H), 5.17 (app. d, *J* = 10.2 Hz, 1H), 4.85 – 4.82 (m, 2H), 4.58 – 4.48 (m, 1H), 1.45 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ 155.4, 143.5, 132.8, 128.5, 127.2, 125.9, 117.5, 65.4, 50.5, 22.3. **IR:** (cast film, cm^{-1}) 3317, 2974, 2930, 1690, 1528, 1498, 1237. **LC-MS:** (ESI) calculated for $C_{11}H_{14}NO_2$ $[M+H]^+$ 192.10, observed 192.10.



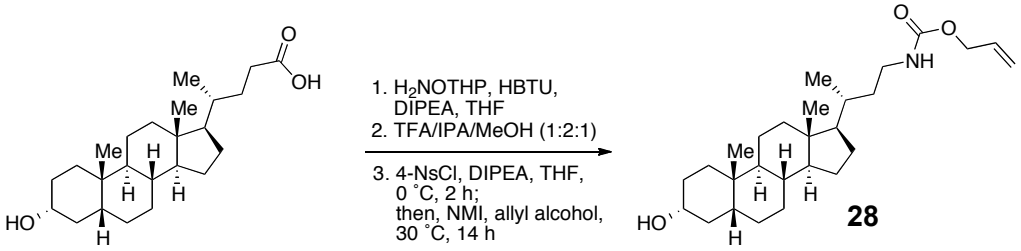
Allyl-benzhydrylcarbamate (25): white solid, 150 mg, 94%. R_f: 0.42 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 6H), 6.0 (m, 1H), 5.95 (m, 1H), 5.46 (s, 1H), 5.34 (m, 1H), 5.25 (m, 1H), 4.62 (dt, *J* = 5.6, 1.4 Hz, 2H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 155.5, 141.7, 132.7, 128.7, 127.5, 127.3, 117.9, 65.8, 58.8. **IR:** (cast film, cm^{-1}) 3282, 3062, 3027, 1714, 1687, 1526, 1494, 1272, 1254. **LC-MS:** (ESI) calculated for $C_{17}H_{19}NO_2$ $[M+H]^+$ 268.13, observed 268.14.



Allyl-phenethylcarbamate (26): white solid, 97 mg, 78%. R_f: 0.29 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.32 – 7.13 (m, 5H), 5.94 – 5.81 (m, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.77 (s, 1H), 4.54 (dt, *J* = 5.3, 1.3 Hz, 2H), 3.43 (dd, *J* = 13.2, 6.7 Hz, 2H), 2.80 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 156.2, 138.8, 133.0. 128.8, 128.6, 126.5, 117.6, 65.5, 42.2, 36.1. **IR:** (cast film, cm^{-1}) 3328, 3027, 2935, 1694, 1519, 1497, 1241. **LC-MS:** (ESI) calculated for $C_{12}H_{16}NO_2$ $[M+H]^+$ 206.12, observed 206.11.



Allyl-cyclohexylcarbamate (27): clear oil, 78 mg, 71%. R_f: 0.39 (20% EtOAc/hexanes). **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 5.91 (ddt, *J* = 16.2, 10.8, 5.5 Hz, 1H), 5.29 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 4.64 (s, 1H), 4.53 (m, 2H), 3.48 (s, 1H), 1.92 (dd, *J* = 12.3, 2.9 Hz, 2H), 1.78 – 1.64 (m, 2H), 1.64 – 1.48 (m, 1H), 1.37 – 1.29 (m, 2H), 1.17 – 1.03 (m, 3H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 155.5, 133.1, 117.6, 65.3, 49.8, 33.4, 25.5, 24.8. **IR:** (cast film, cm^{-1}) 3320, 2930, 2855, 1689, 1529, 1252, 1227. **LC-MS:** (ESI) calculated for $C_{10}H_{19}NO_2$ $[M+H]^+$ 184.13, observed 184.13.



Allyl-((R)-3-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13 dimethylhexadeca hydro-1H-cyclopenta[a]phenanthren-17-yl)butyl)carbamate (28): white solid, 65 mg, 31% (over 3 steps). R_f 0.22 (20% EtOAc/hexanes). **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 5.91 (ddt, *J* = 16.2, 10.8, 5.6 Hz, 1H), 5.29 (m, 1H), 5.20 (m, 1H), 4.65 (s, 1H), 4.55 (dt, *J* = 5.2, 1.3 Hz, 2H), 3.61 (m, 1H), 3.30 – 3.17 (m, 1H), 3.15 – 3.02 (m, 1H), 1.95 (dd, *J* = 12.0, 3.0 Hz, 1H), 1.89 – 1.46 (m, 12H), 1.44 – 0.98 (m, 20H), 0.97 – 0.86 (m, 8H), 0.63 (s, 3H). **^{13}C NMR:** (126 MHz, $CDCl_3$) δ 156.2, 133.1, 117.6, 71.8, 65.4, 56.5, 56.2, 42.8, 42.1, 40.4, 40.2, 38.7, 36.4, 36.1, 35.8, 35.4, 34.6, 33.8, 30.5, 28.4, 27.2, 26.4, 24.2, 23.4, 20.8, 18.6, 12.0. **: IR:** (cast film, cm^{-1}) 3482, 3304, 2931, 2864, 1694, 1544, 1253. **LC-MS:** (ESI) calculated for $C_{27}H_{46}NO_3$ $[M+H]^+$ 432.35, observed 432.36.

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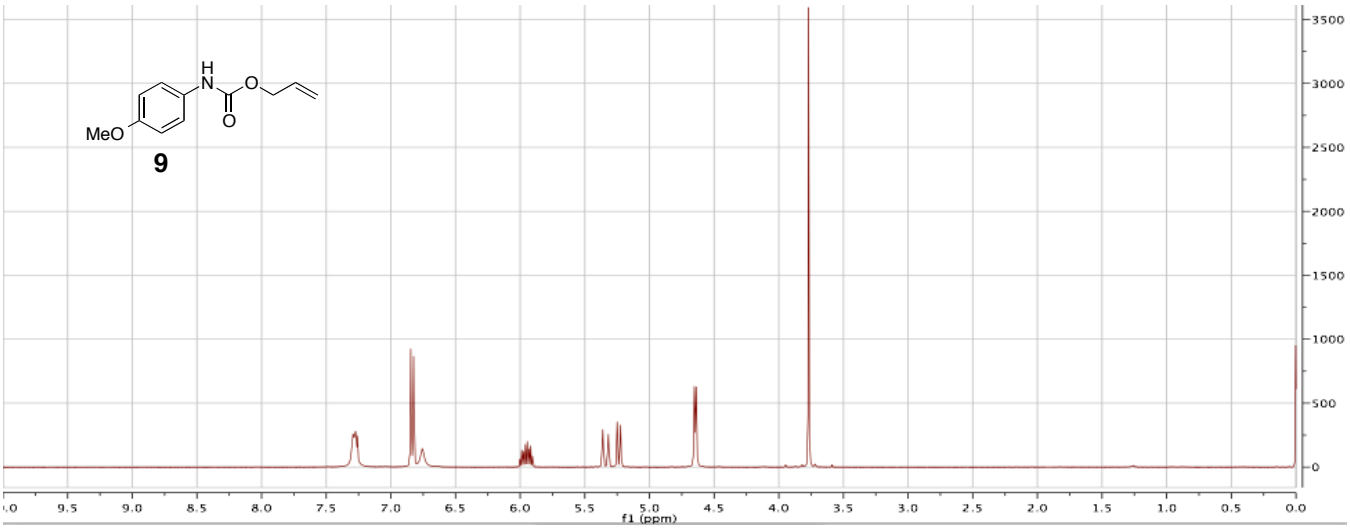
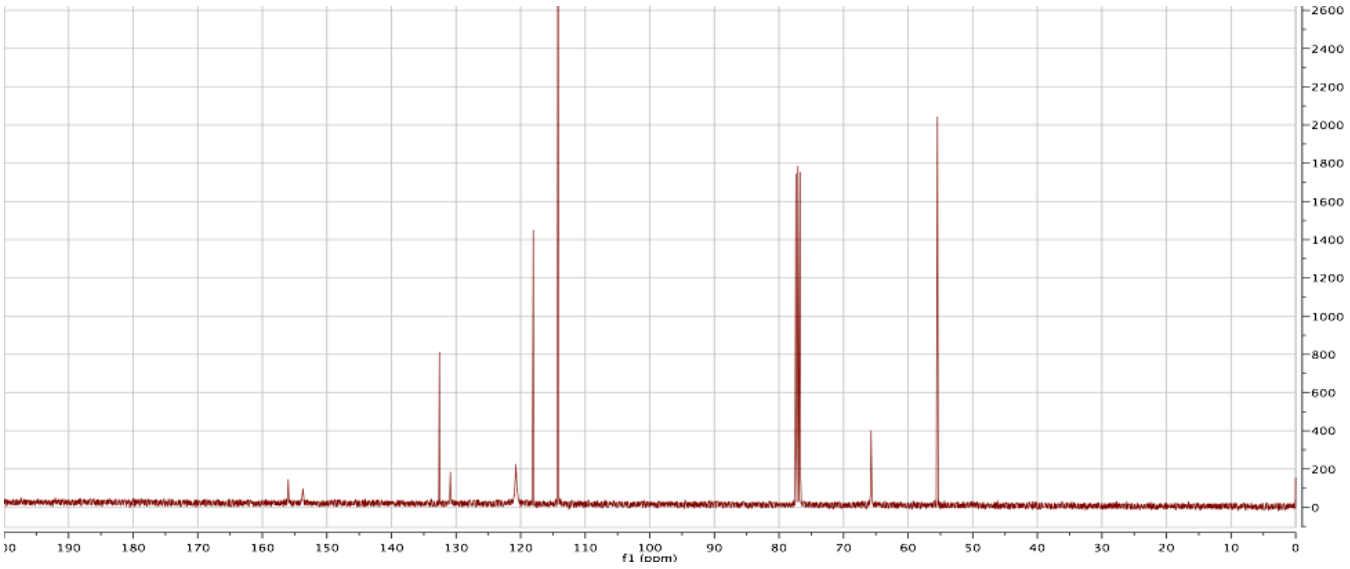
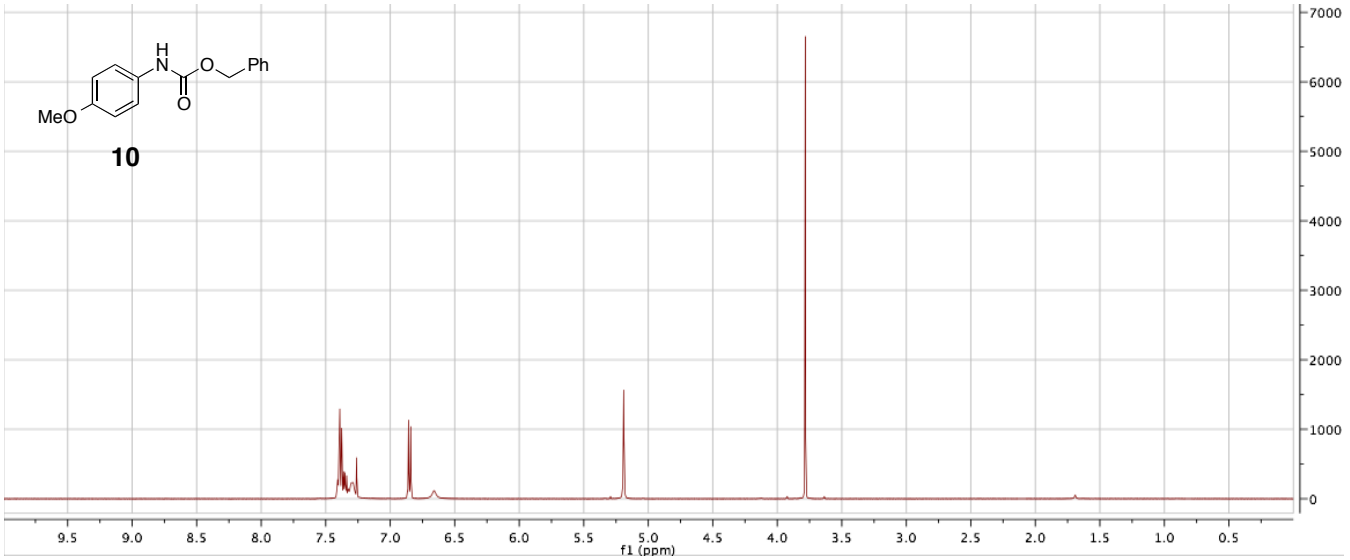
[1] Usachova, N.; Leitis, G.; Jirgensons, A.; Kalvinsh, I. *Synth. Commun.* **2010**, *40*, 927.
[2] Dubé, P.; Nathel, N. F. F.; Vetelino, M.; Couturier, M.; Aboussafy, C. L.; Pichette, S.; Jorgensen, M. L.; Hardink, M. *Org. Lett.* **2009**, *11*, 5622.

NMR Spectra



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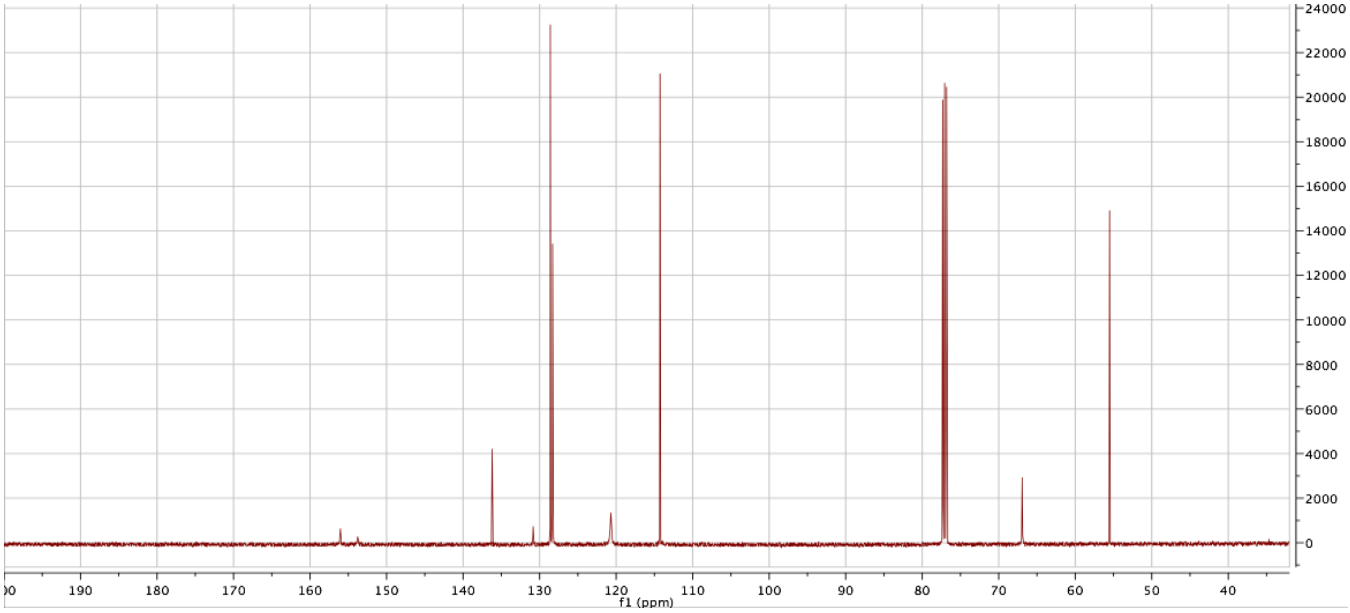
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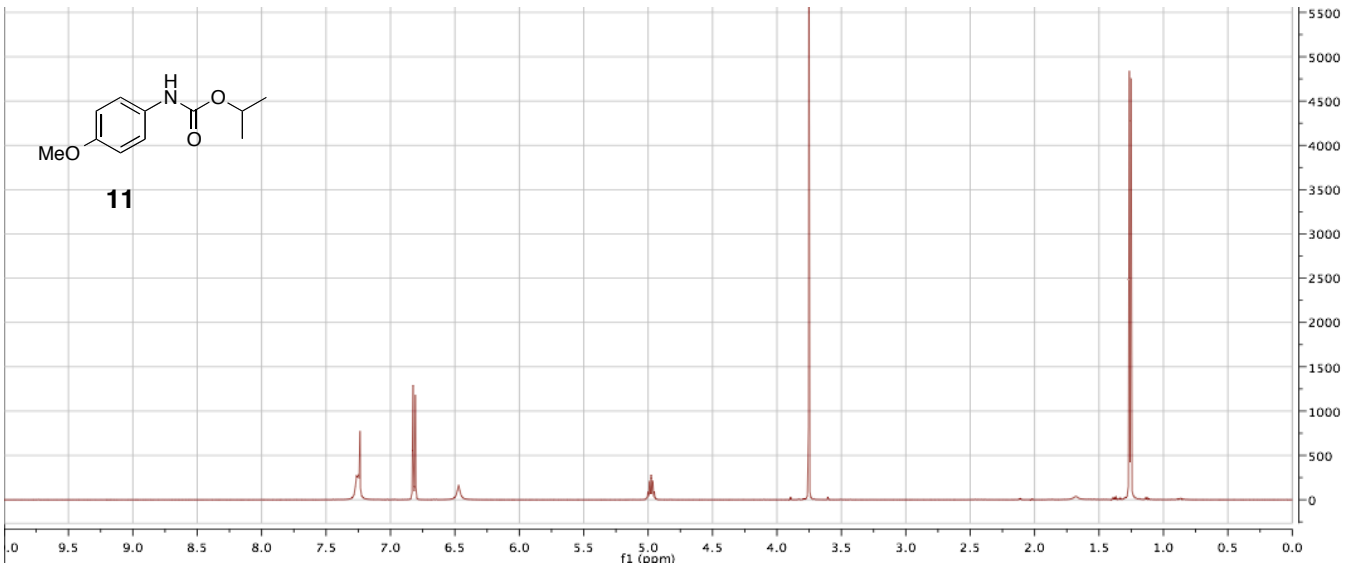
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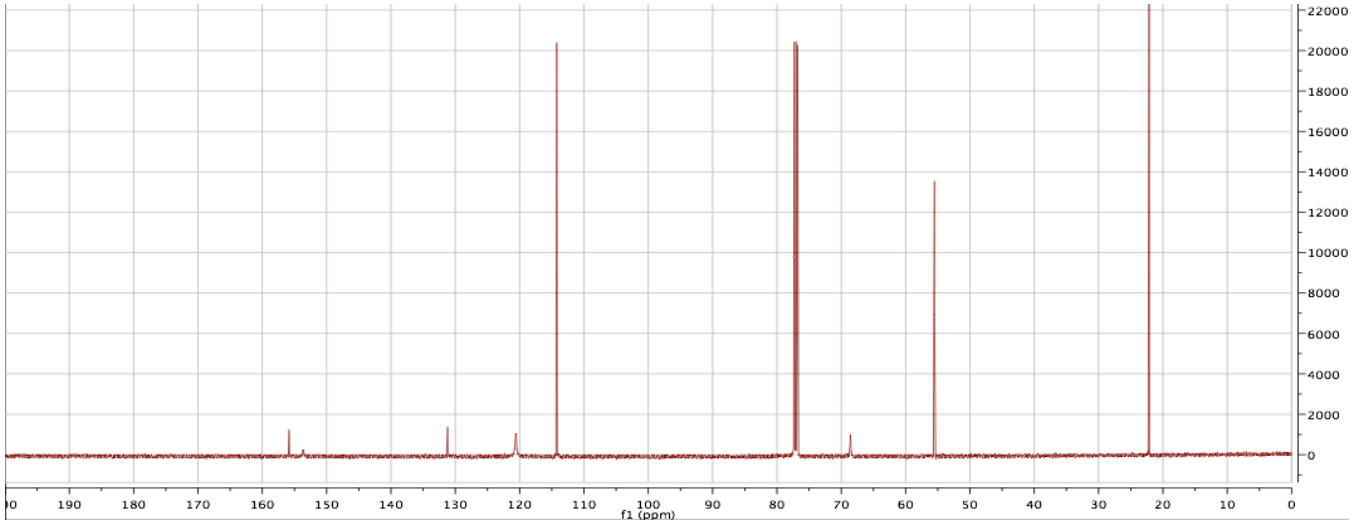
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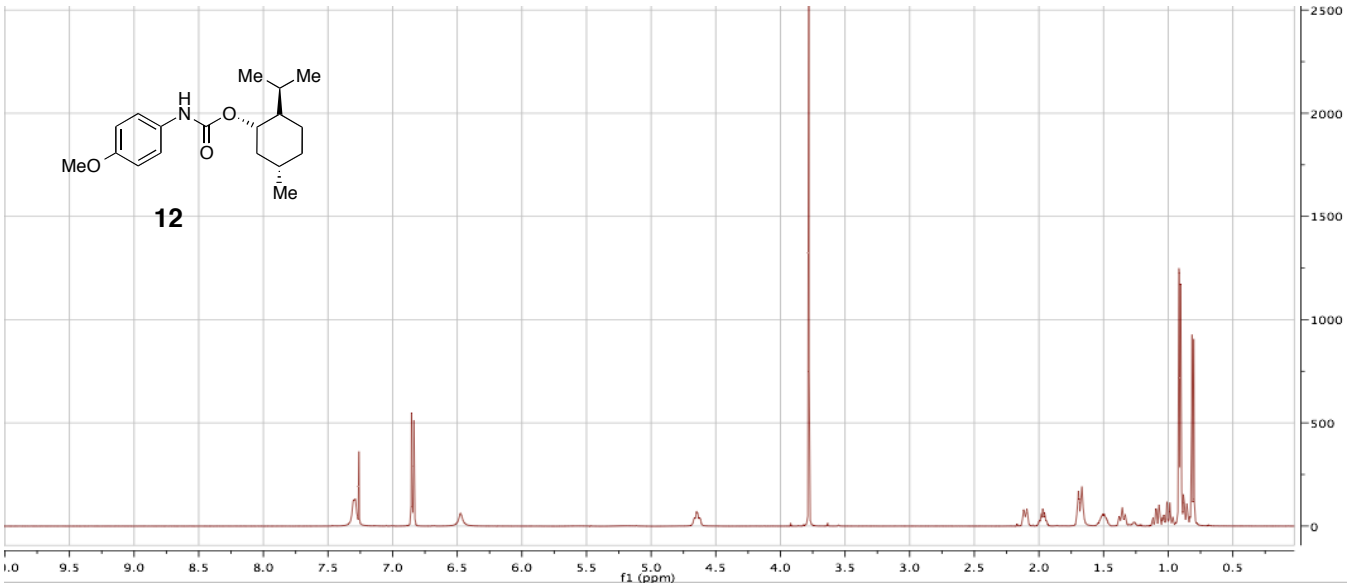
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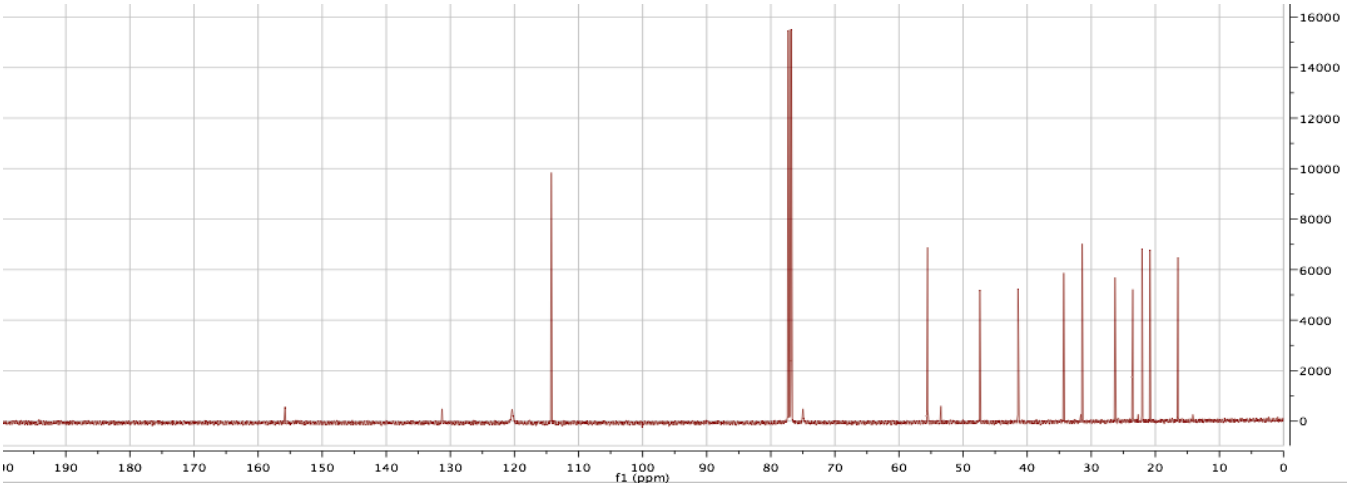
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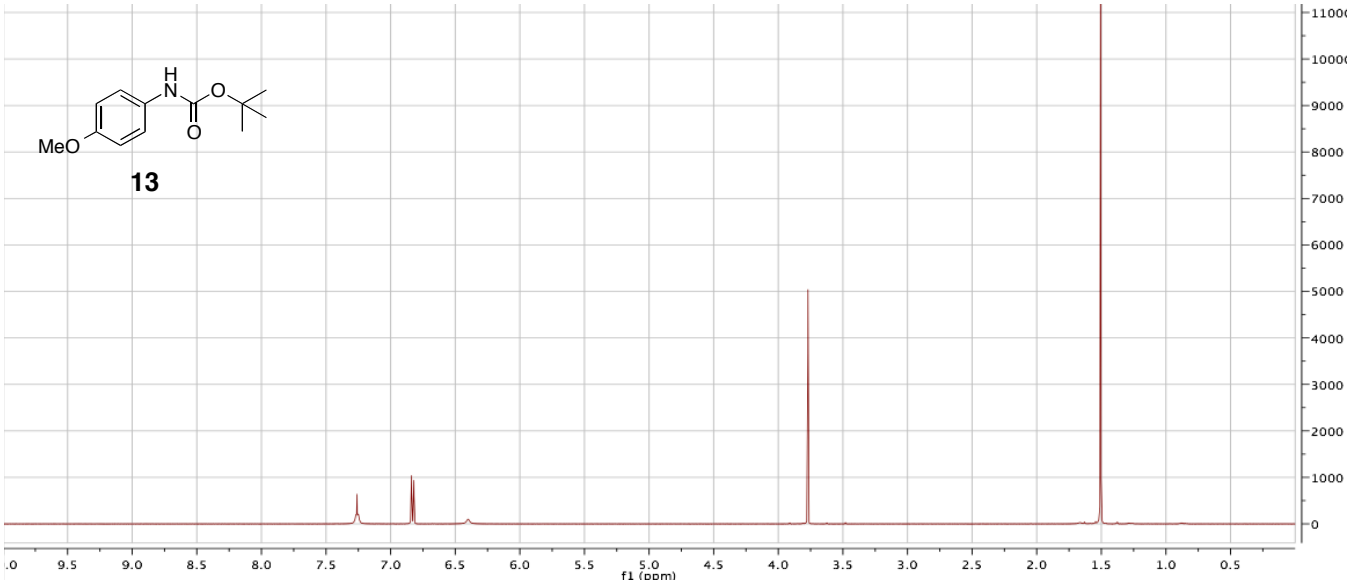
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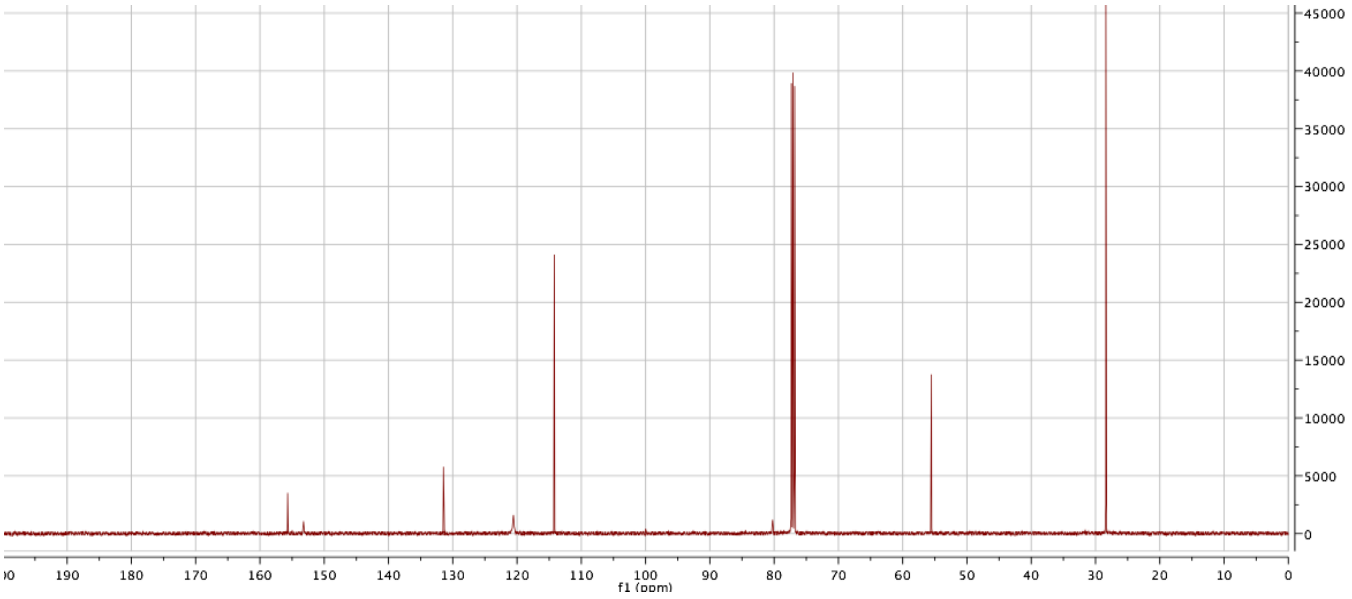
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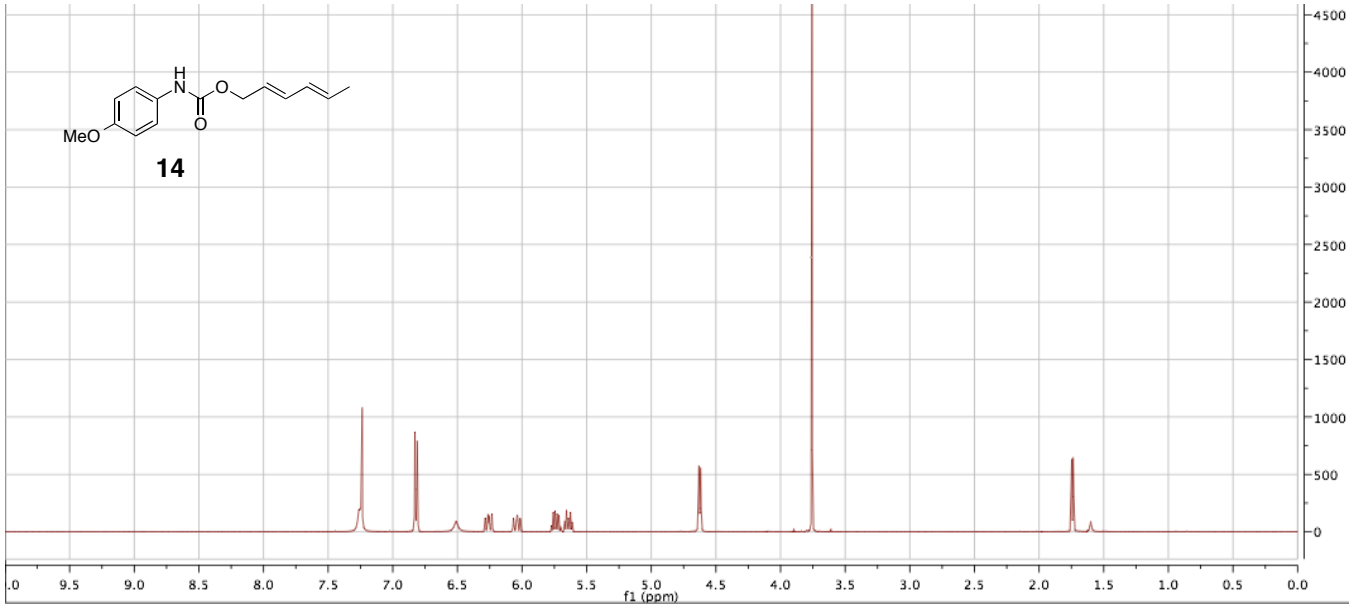
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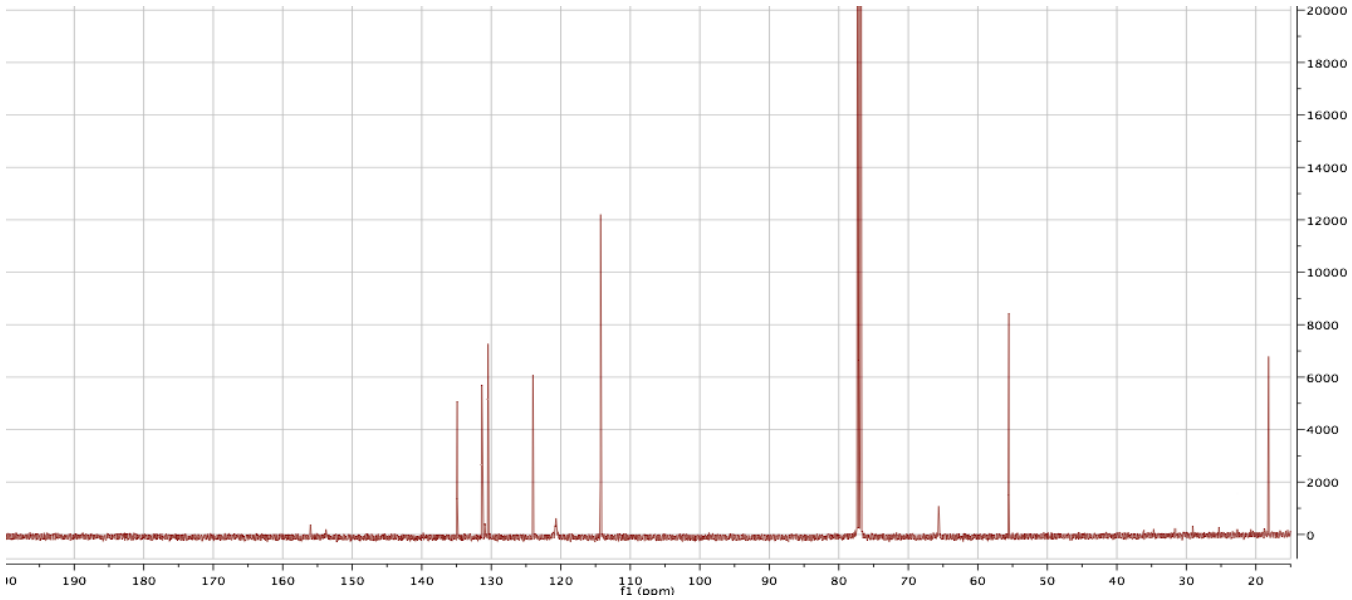
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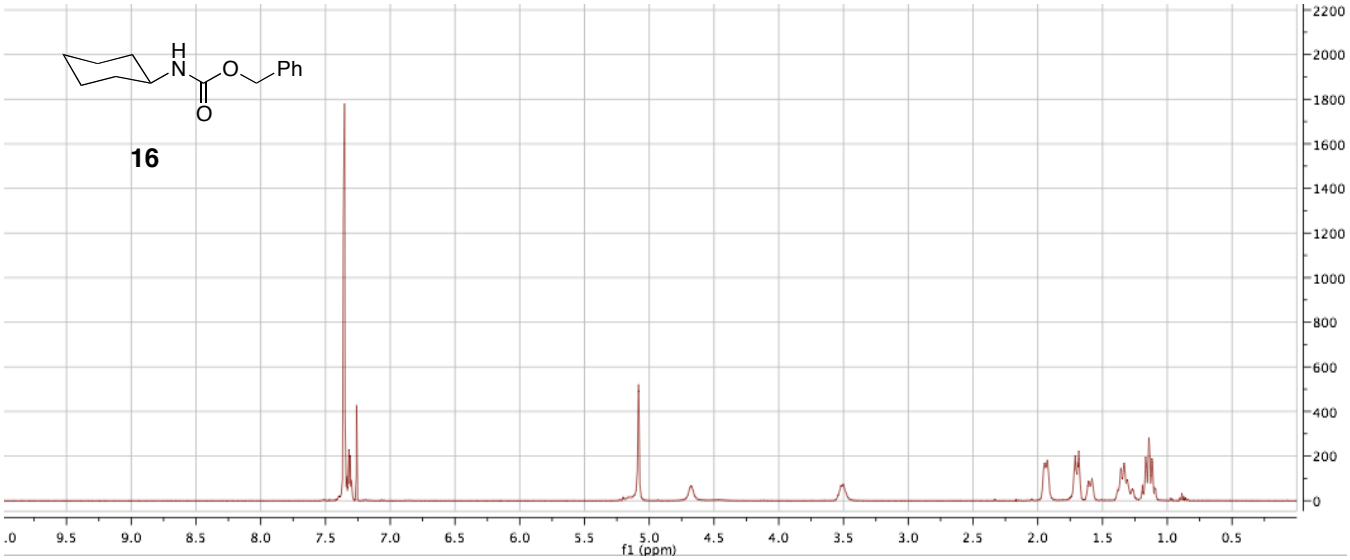
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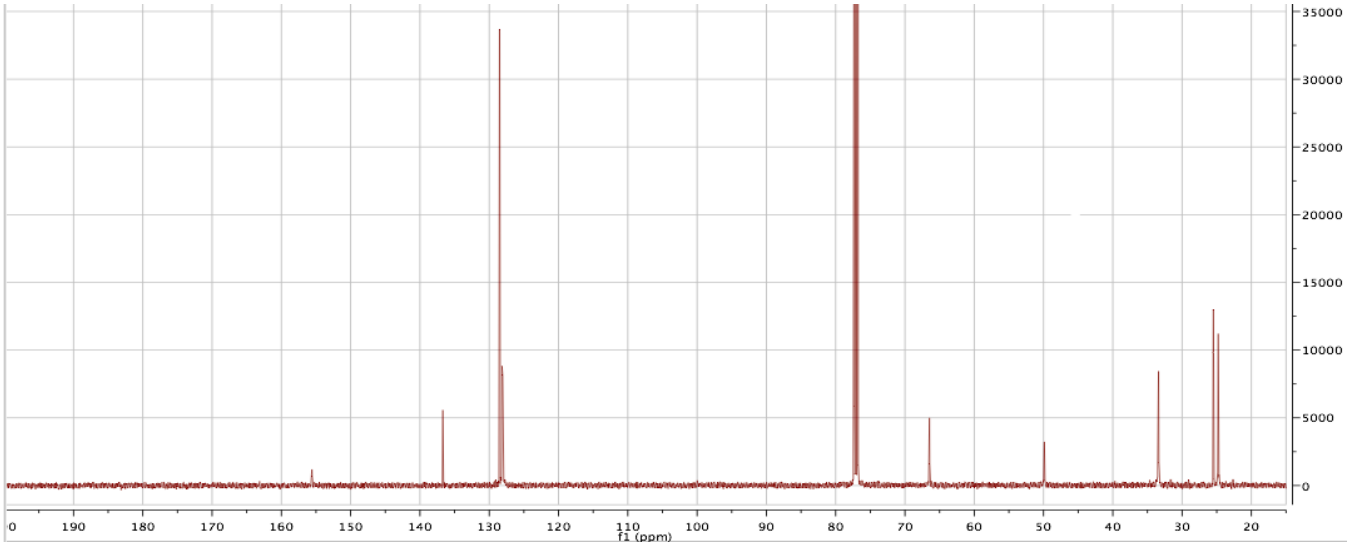
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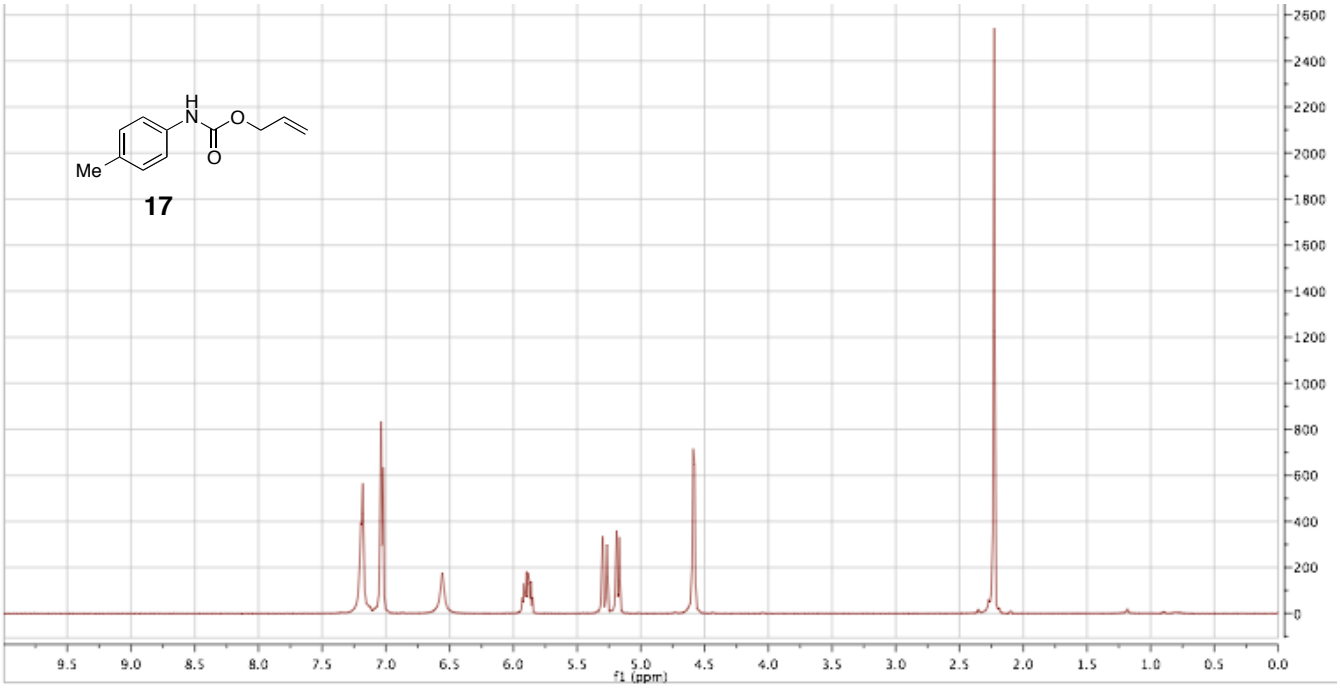
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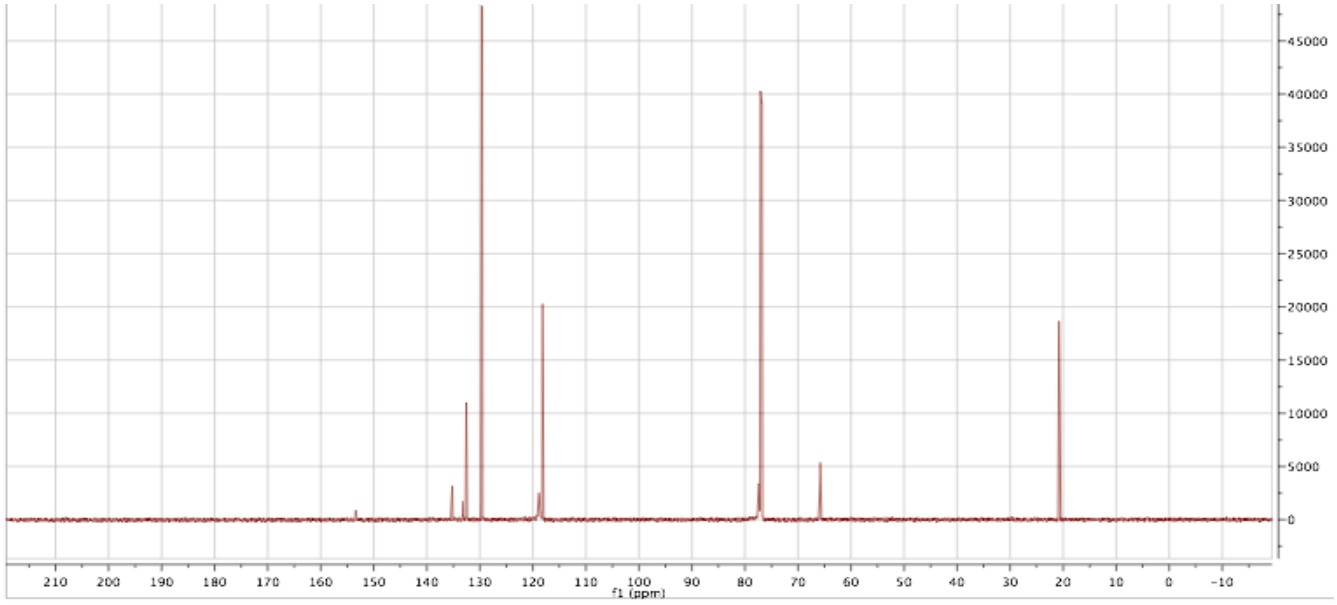
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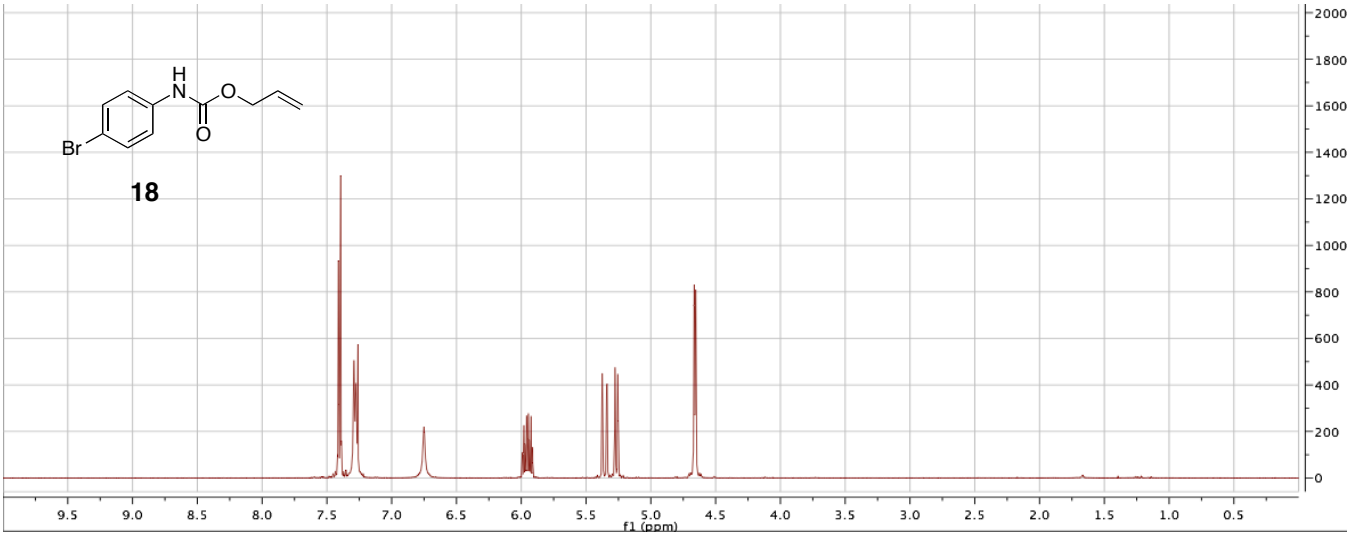
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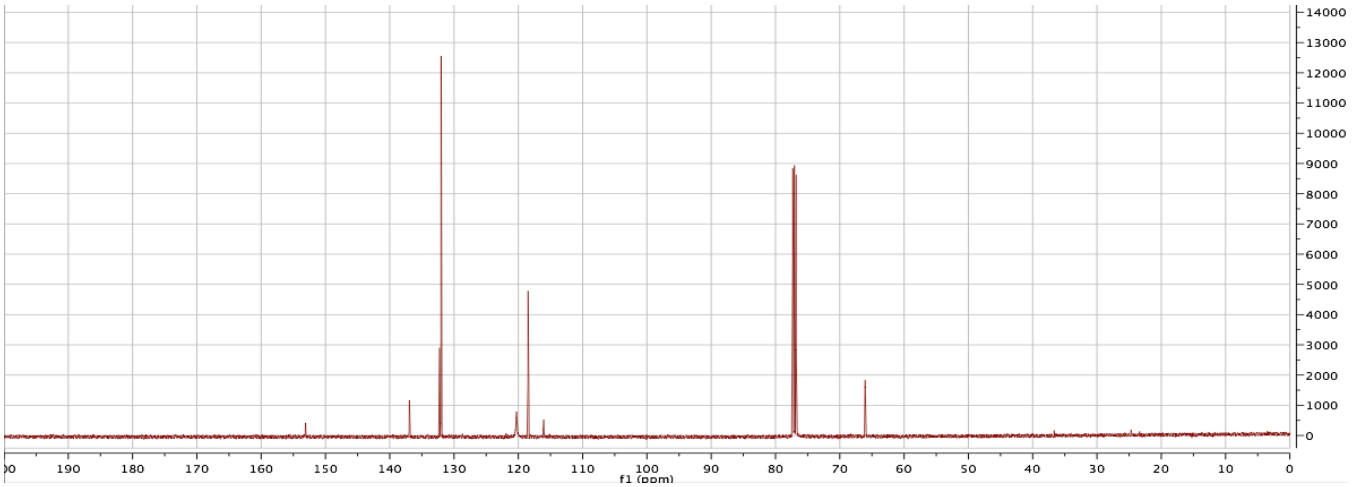
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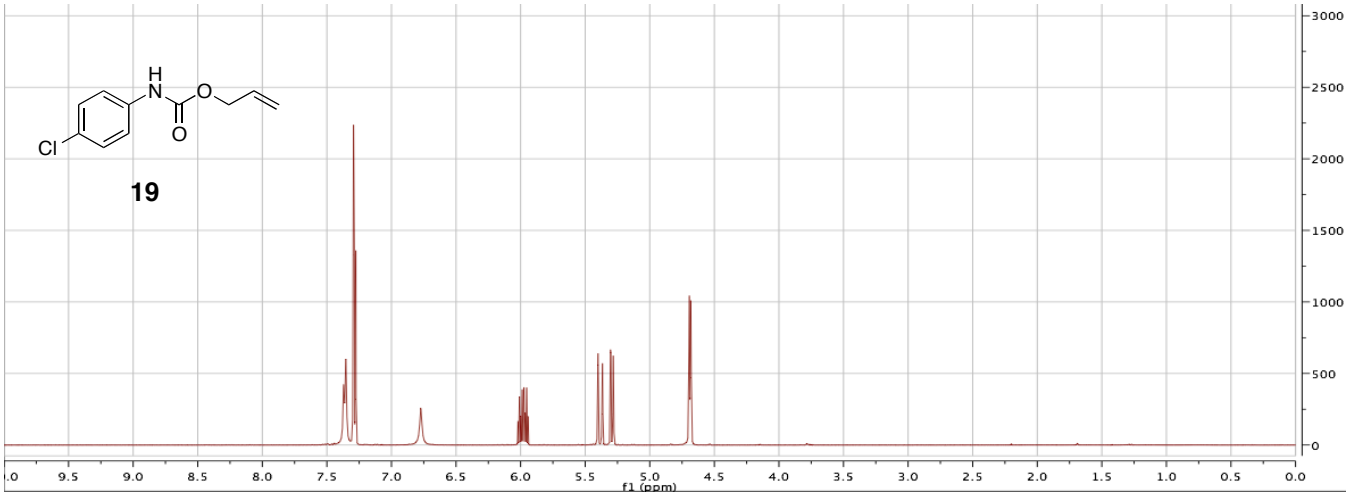
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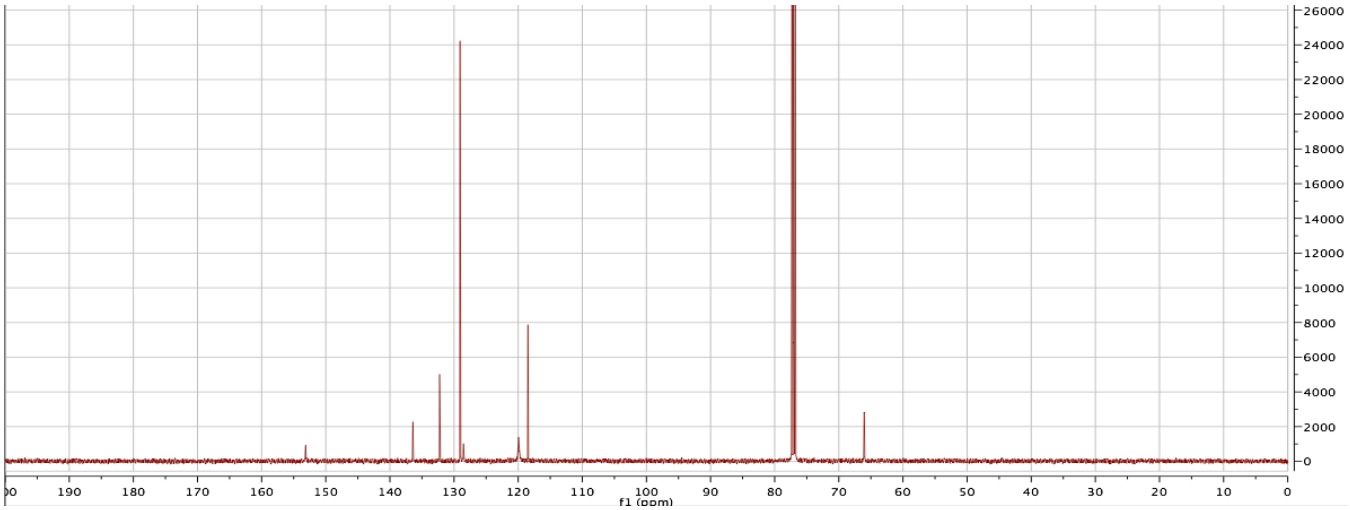
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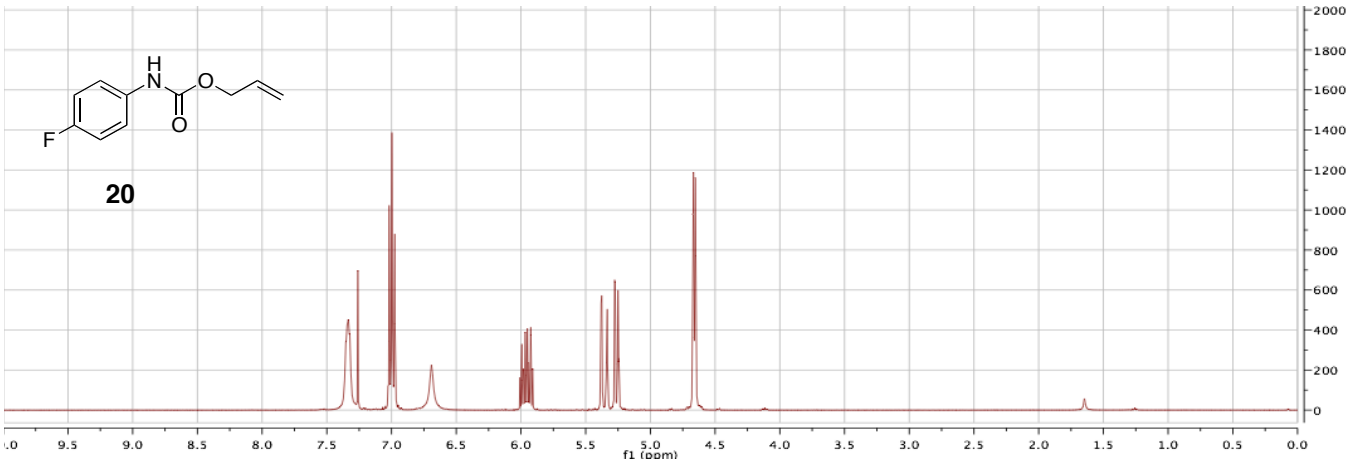
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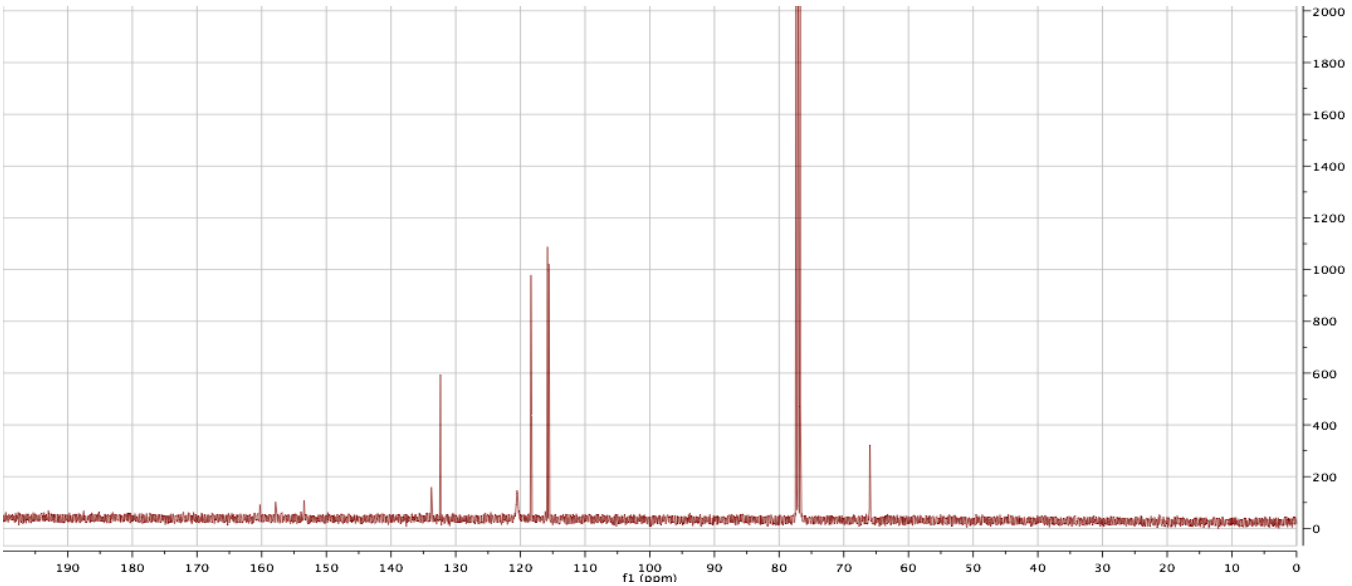
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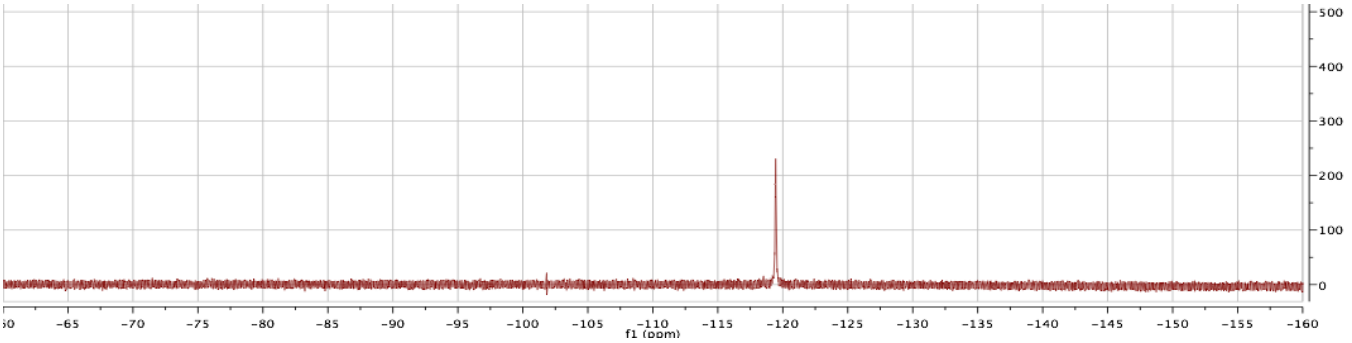
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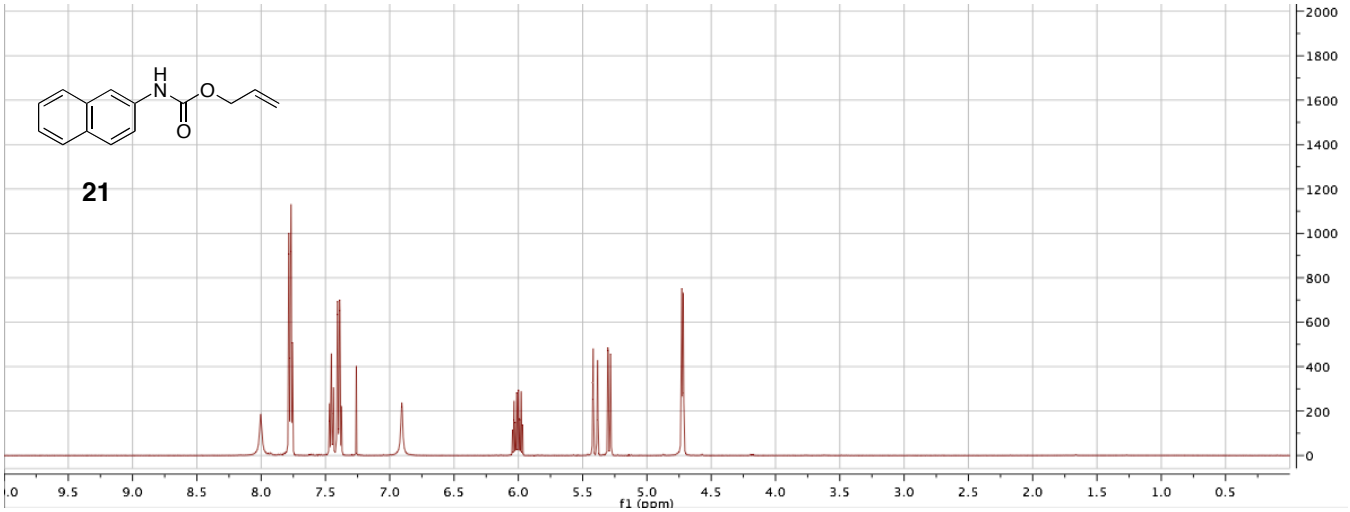
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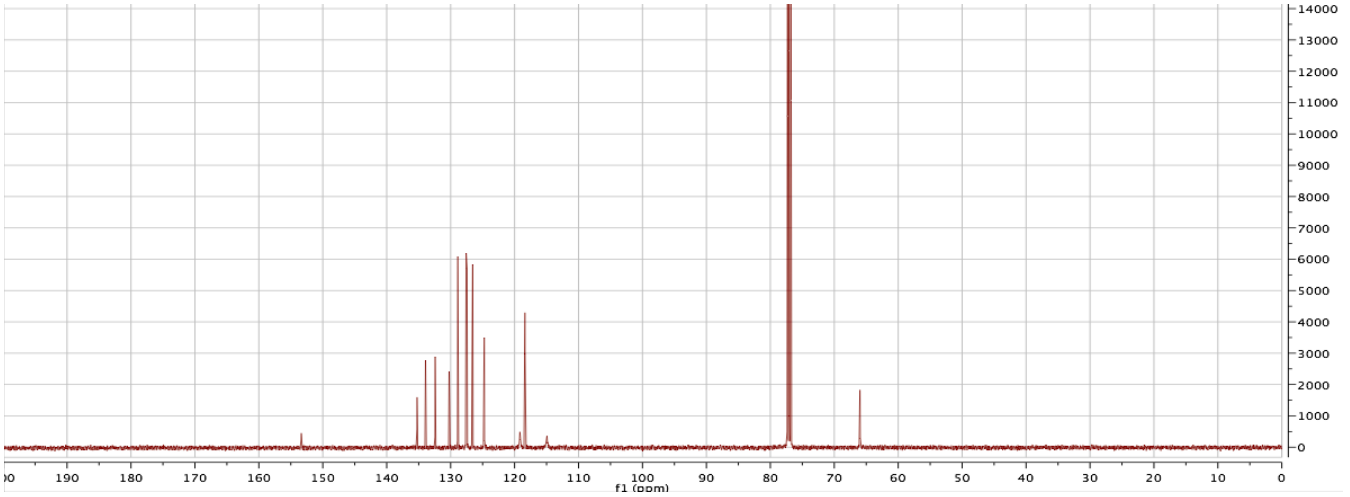
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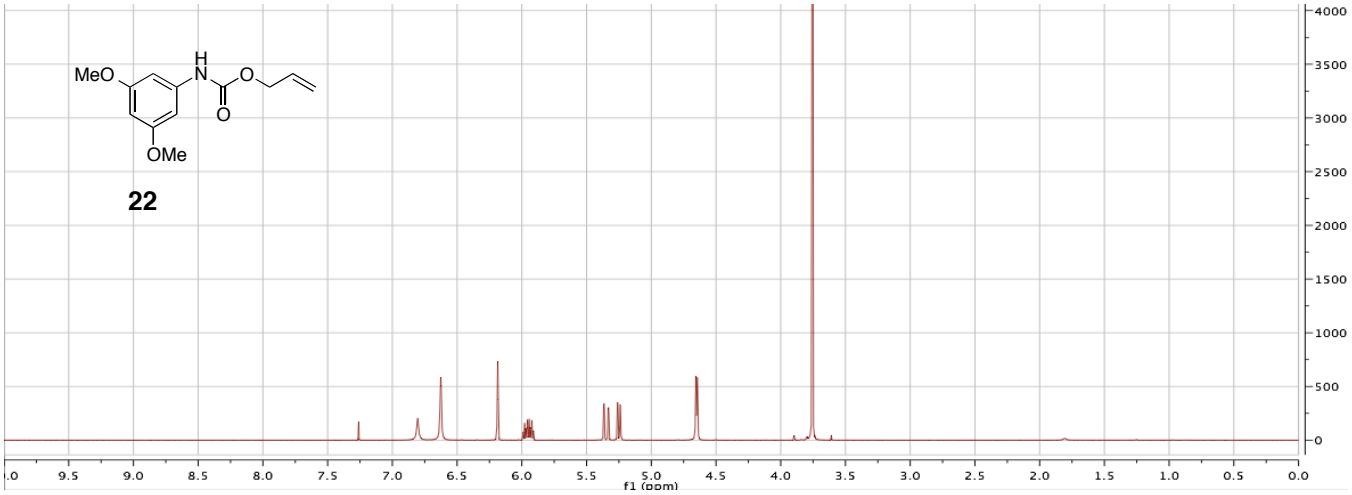
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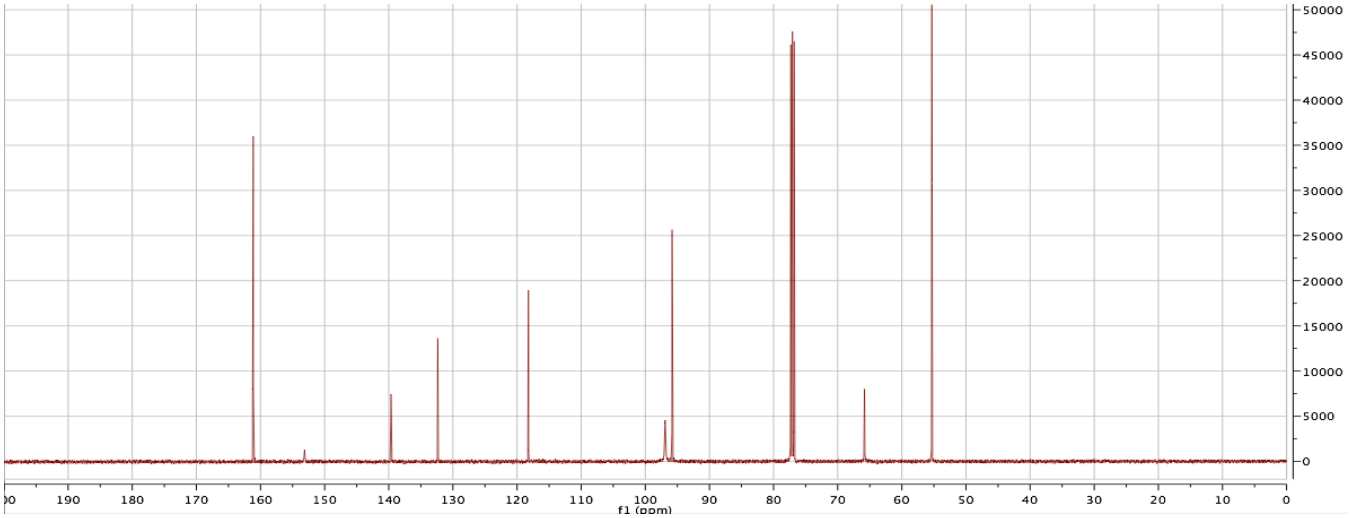
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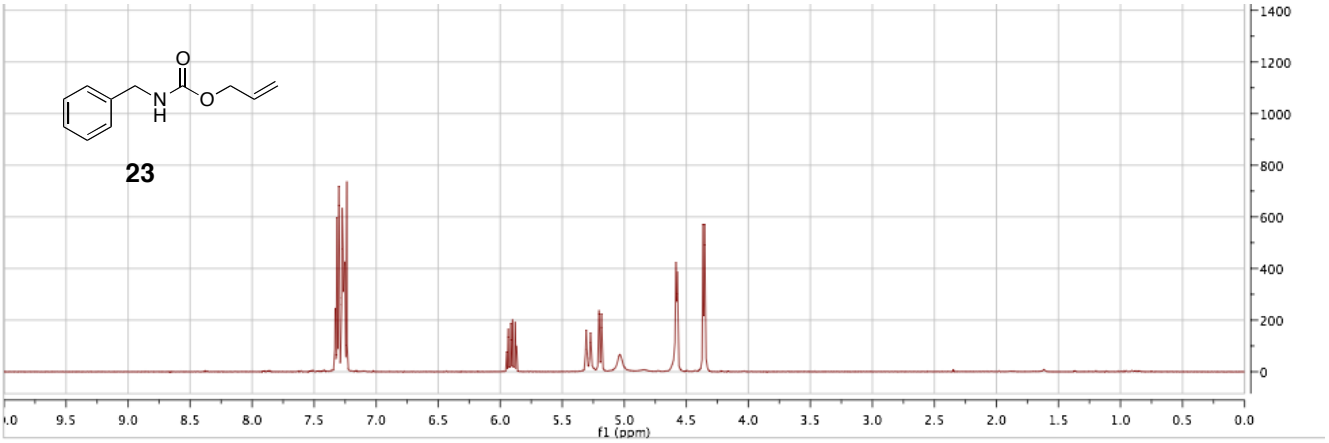
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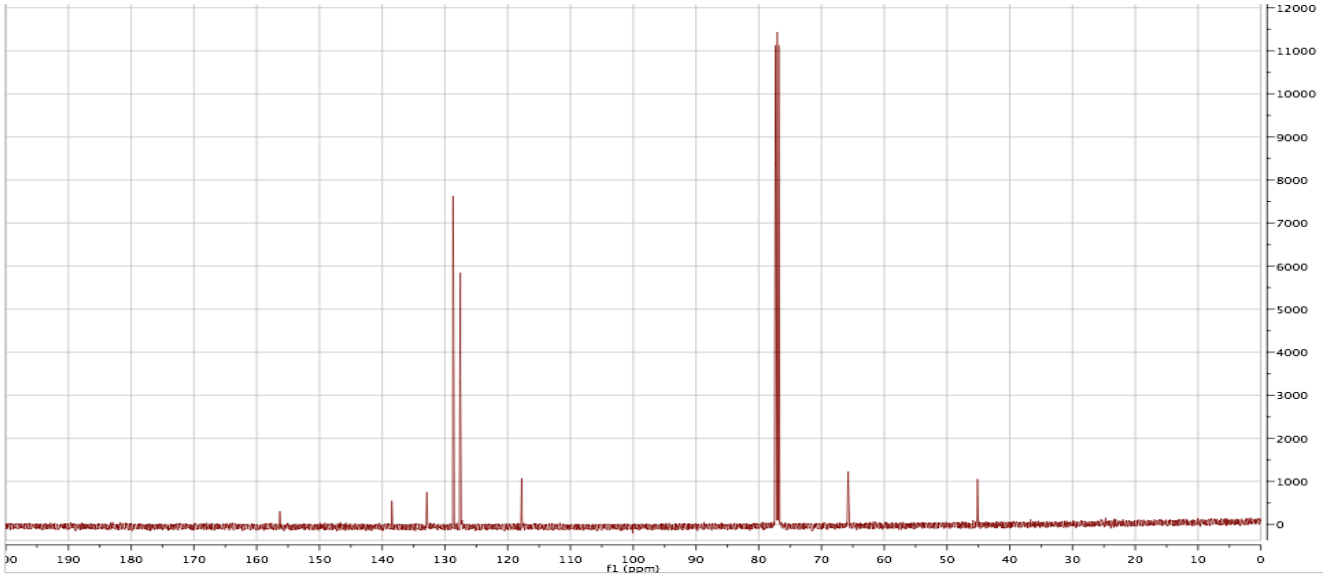
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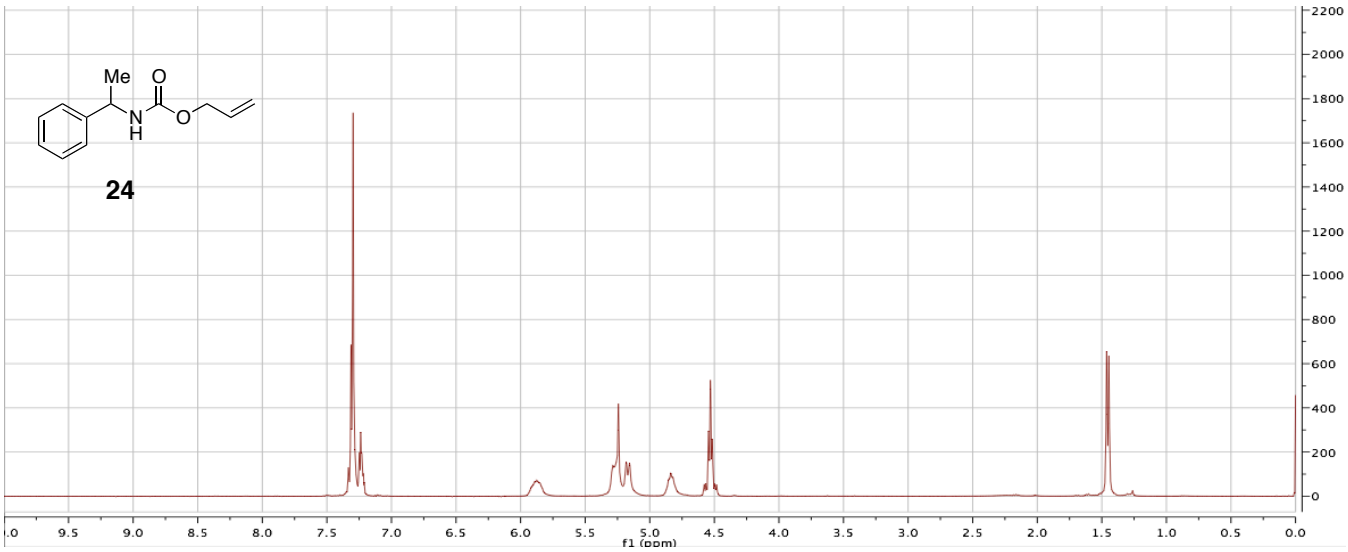
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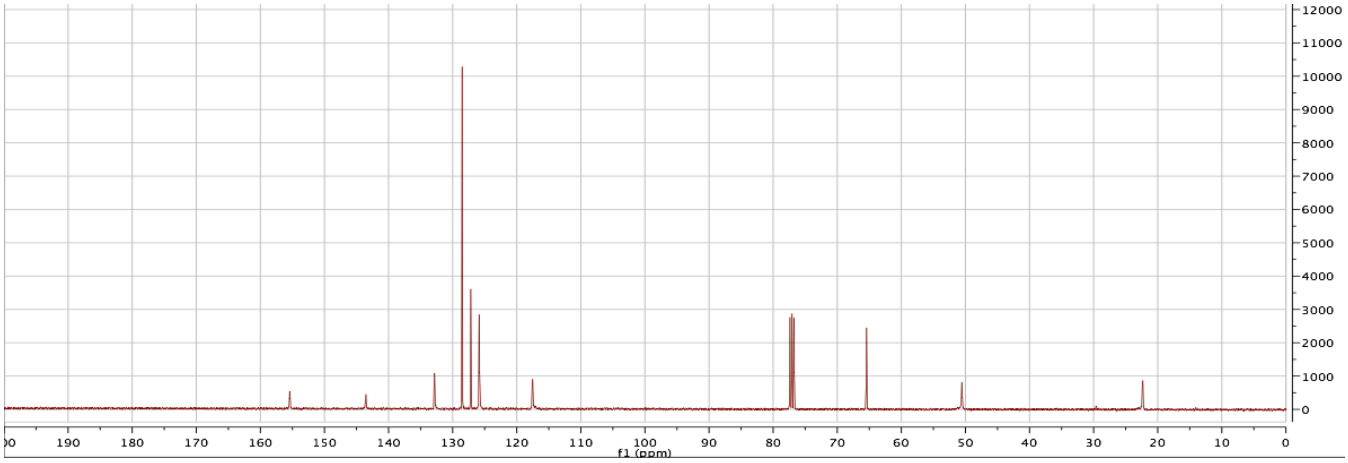
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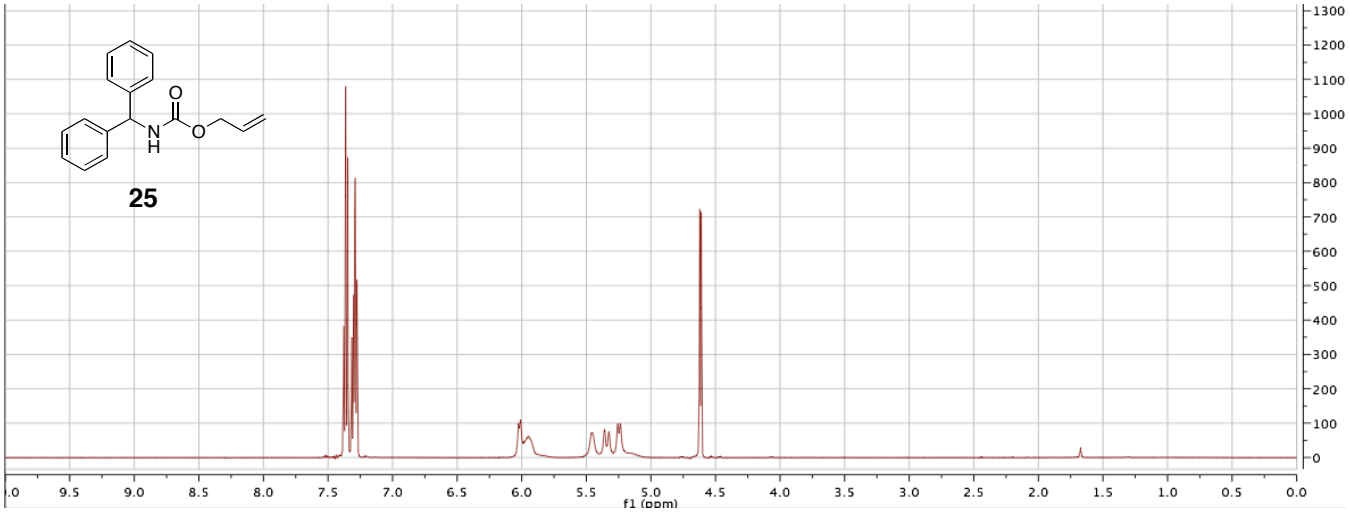
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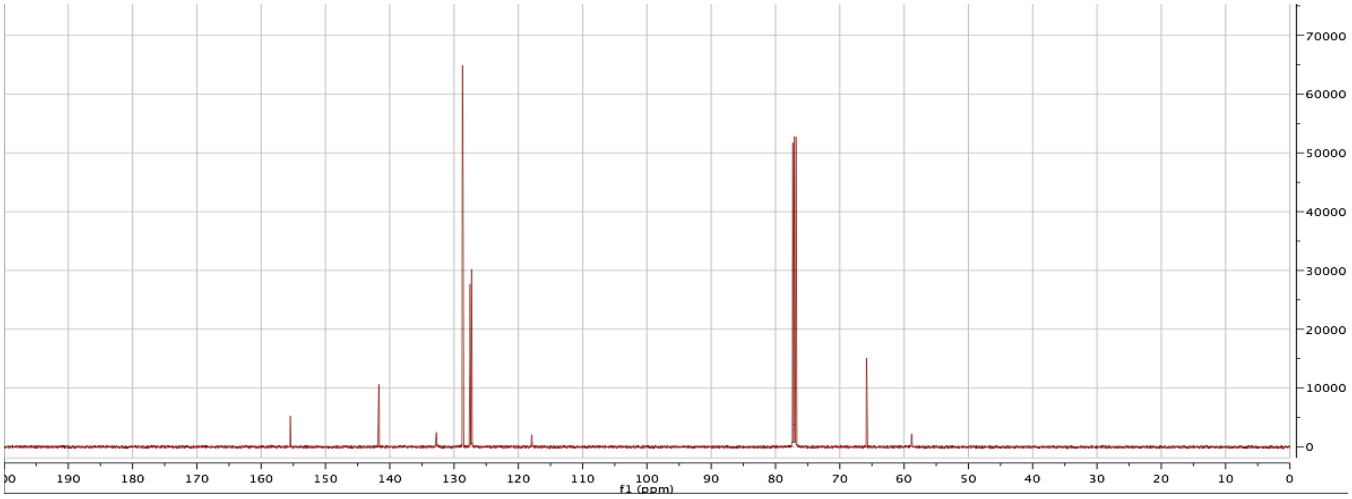
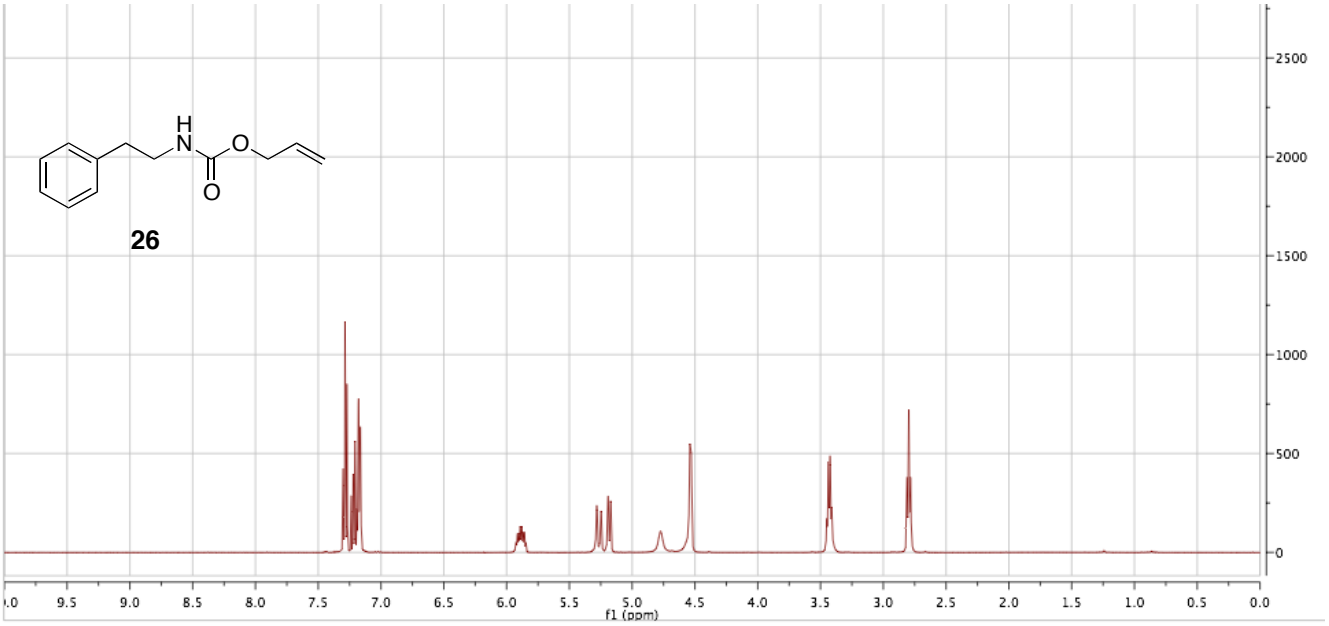
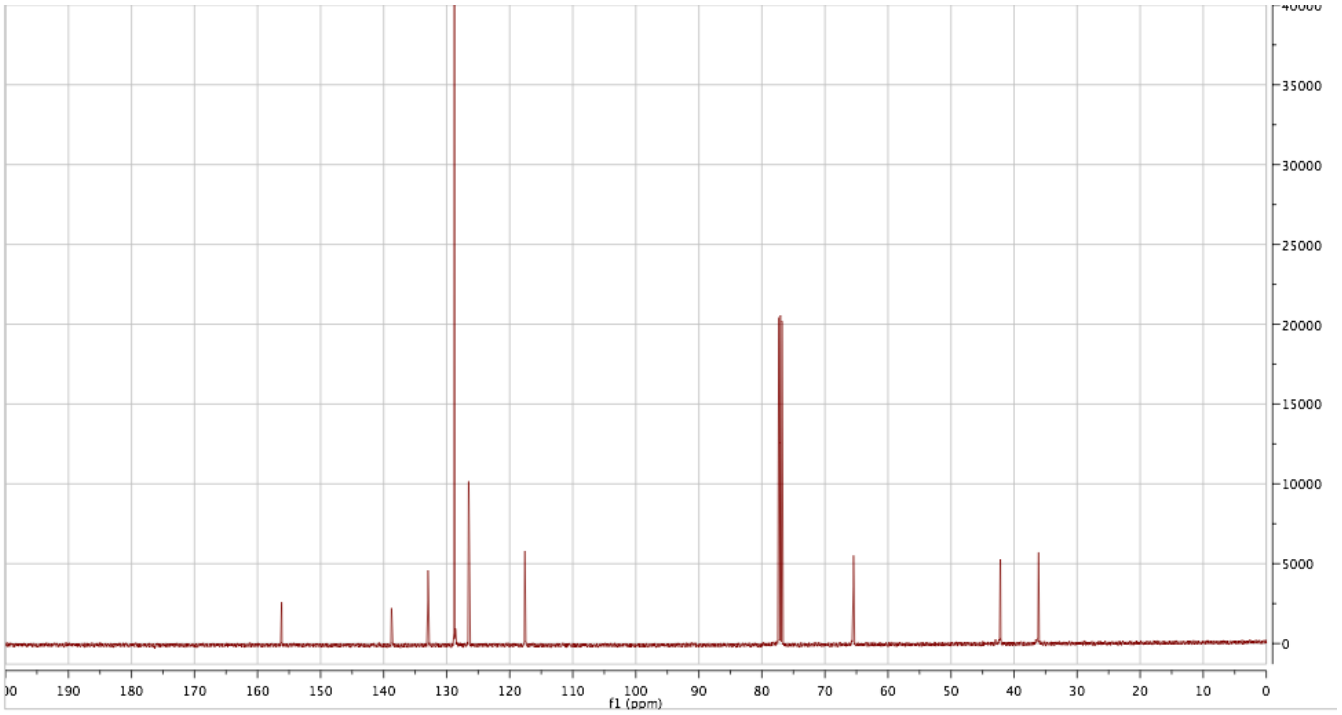
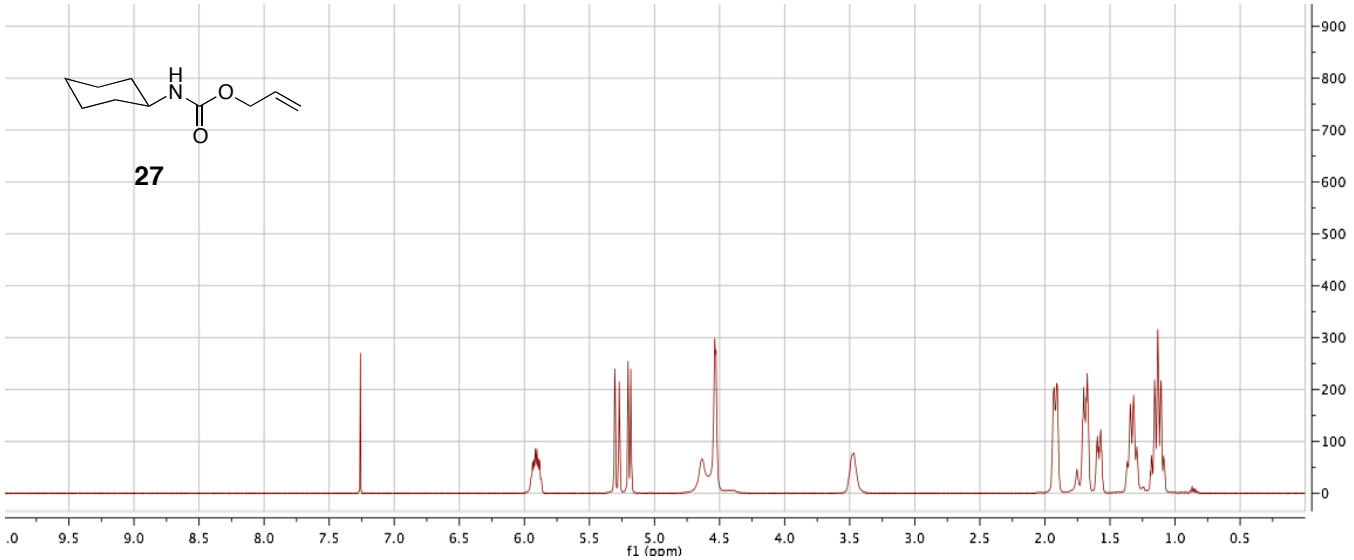
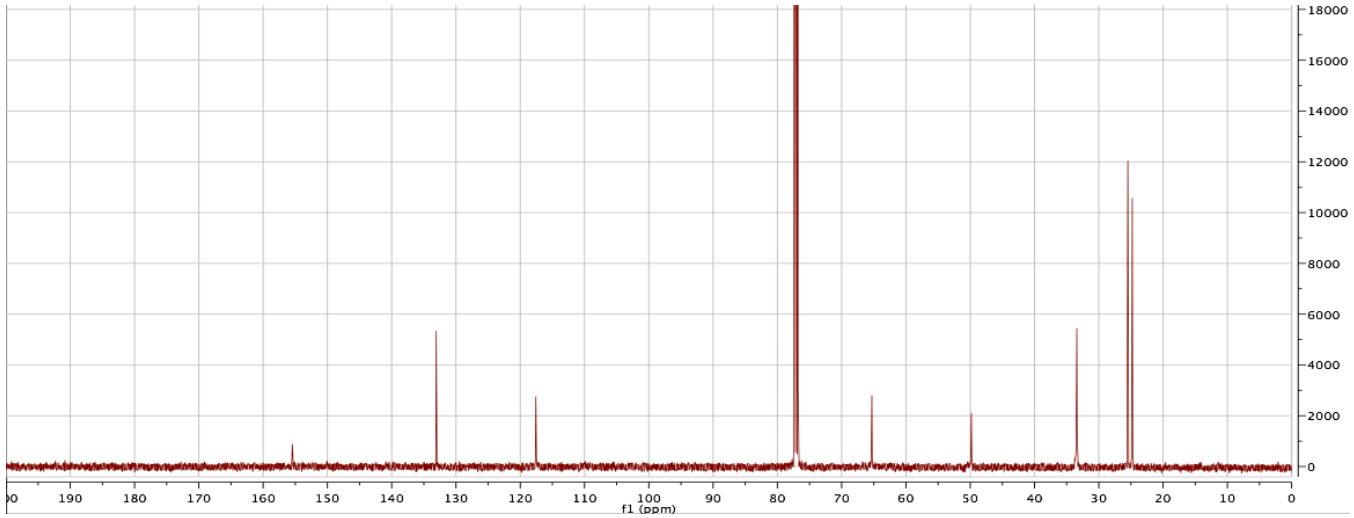
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

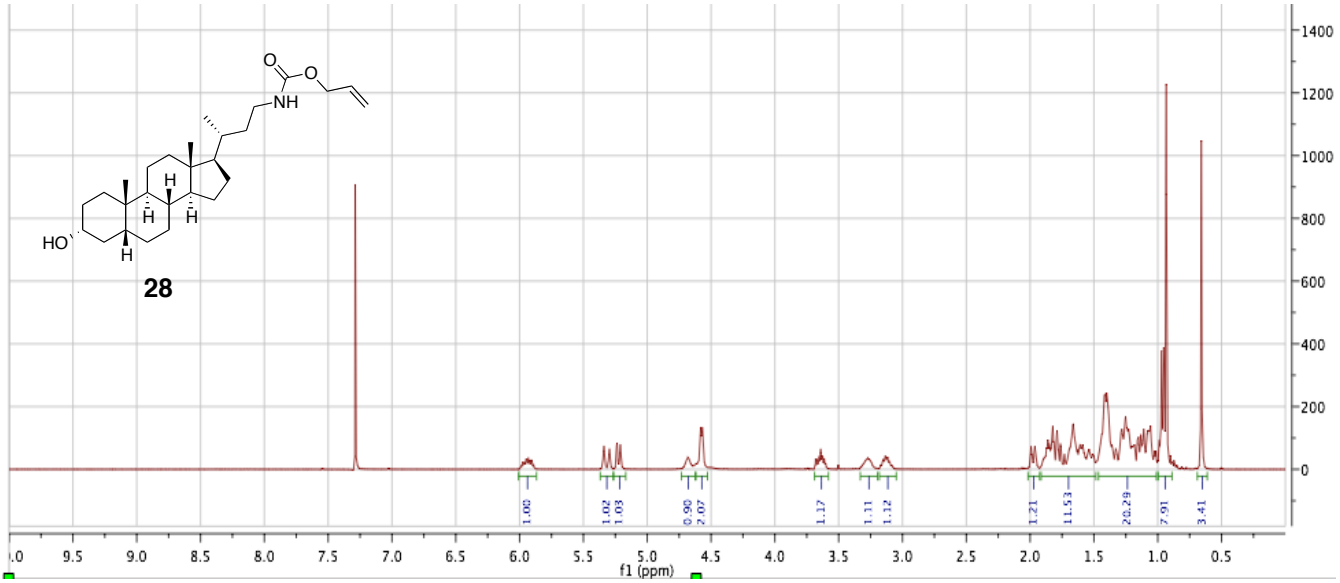

70000
60000
50000
40000
30000
20000
10000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

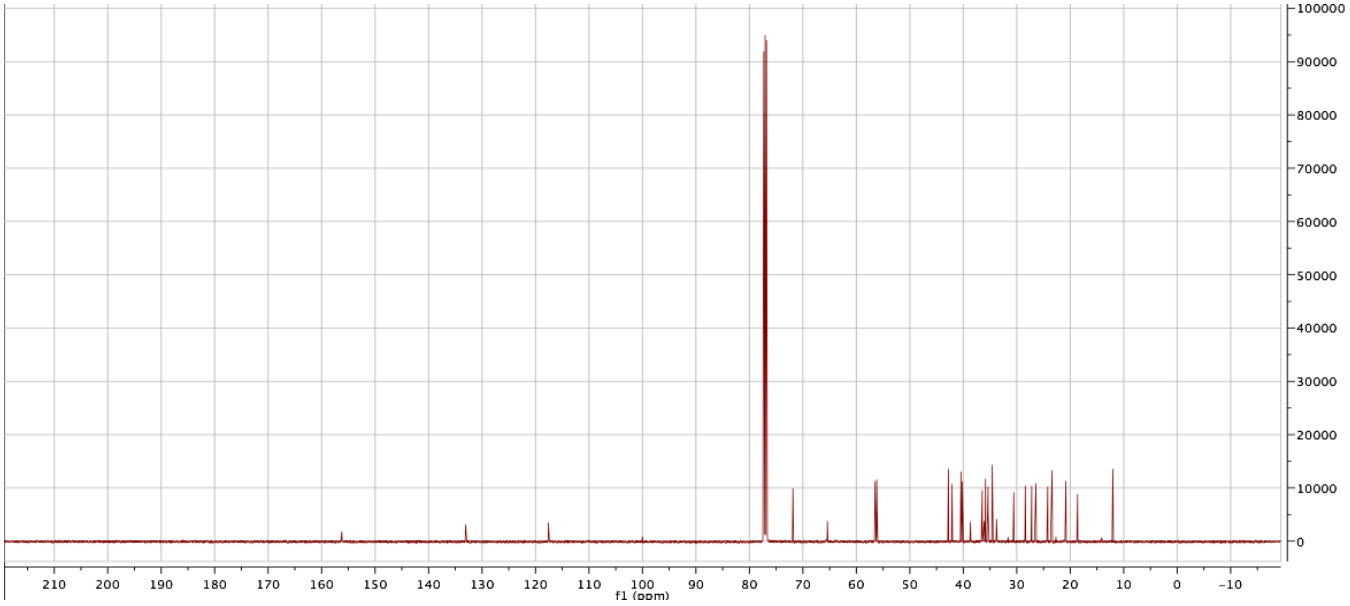

H
N
O
O
26
2500
2000
1500
1000
500
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


35000
30000
25000
20000
15000
10000
5000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
N
O
O
27
900
800
700
600
500
400
300
200
100
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


18000
16000
14000
12000
10000
8000
6000
4000
2000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
NH
H
H
H
HO
H
28
1400
1200
1000
800
600
400
200
0
1.00
1.02
1.03
0.90
2.07
1.17
1.11
1.12
1.21
11.53
26.29
7.91
3.41
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
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)