Formation of Ketenimines *via* the Palladium Catalyzed Decarboxylative π-Allylic Rearrangement of *N*-Alloc Ynamides

Supporting Information

Juliana R. Alexander and Matthew J. Cook*

School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT9 5AG, Northern Ireland and Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717.

matthewcook@montana.edu

Contents

General Procedure A for the synthesis of carbamates

To an oven dried round bottom flask equipped with magnetic stirrer bar and purged with argon was added a solution of amine (1 equiv.) in anhydrous THF (0.5 M). $NaHCO_3$ (1.1 equiv.) was added in one portion. At 0 °C, allyl chloroformate (1.1 equiv.) was added dropwise and the mixture stirred for a further 15 minutes at 0 °C then at room temperature for 45 minutes. The reaction quenched with water and the aqueous layers washed with EtOAc (3 x 10 mL). The combined organic layers were washed with $NaHCO_3$ and brine. The solvent was dried over anhydrous Na_2SO_4 and removed *in vacuo* to give crude product which was purified by flash column chromatography.

General procedure B for the synthesis of carbamates

To an oven dried round bottom flask equipped with magnetic stirrer bar and purged with argon was added a solution of allyl alcohol (1 equiv.) and Et_3N (1.1 equiv.) in anhydrous CH_2Cl_2 (0.9 M). Phenyl isocyanate (1.1 equiv.) was injected slowly and the mixture stirred at room temperature for 2 hours. Solvent removed *in vacuo*. The crude reaction mixture was purified by flash column chromatography.

General Procedure C for the synthesis of ynecarbamates[1]

To an oven dried round bottom flask equipped with reflux condenser and magnetic stirrer bar and purged with argon was added alkynyl bromide (1.1 equiv.) in anhydrous toluene (0.18M). Carbamate (1 equiv.), $CuSO_4.5H_2O$ (0.1 equiv.), 1,10-phenanthroline (0.2 equiv.) and K_3PO_4 (2 equiv.) were added in one portion and the mixture stirred at 80 °C for 3 days. The mixture filtered through celite with CH_2Cl_2 and concentrated *in vacuo*. The crude product was purified by flash column chromatography.

General Procedure D for the synthesis of amides

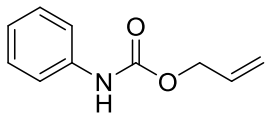
To an oven dried round bottom flask equipped with reflux condenser and magnetic stirrer bar and purged with argon was added $Pd(OAc)_2$ (5 mol%) and *rac*-BINAP (6 mol%) in anhydrous toluene (0.08 M). The mixture was stirred for 10 minutes before the addition of ynecarbamate (1 equiv.) in toluene followed by BEt_3 (1 equiv). The reaction was stirred at 50 °C until consumption of starting material by TLC analysis (ketenimine). At room temperature, a solution of 2M HCl (1 mL) in acetone (1 mL) was added and the mixture stirred overnight. The aqueous layer was extracted by EtOAc (3 x 10 mL). The combined organic layers were washed

with $NaHCO_3$ and brine. The solvent was dried over anhydrous Na_2SO_4 and removed *in vacuo* to give crude product which was purified by flash column chromatography.

General Procedure E for the synthesis of imines sulfides[2]

To an oven dried round bottom flask equipped with magnetic stirrer bar and purged with argon was added trimethylsulfonium iodide (2 equiv.) in THF (2 mL). At – 15°C, 1.6 M nBuLi (2.4 equiv.) was added dropwise and the mixture stirred at -15°C for 1 hour. A solution of ketenimine (1 equiv.) in THF (1 mL) was added to the sulfur ylide solution and stirred at -20 °C for 20 hours. The reaction quenched with brine and extracted with EtOAc (3 x 10 mL). The combined organic layers dried over Na_2SO_4 and solvent removed in vacuo to give the crude product which was purified by flash column chromatography.

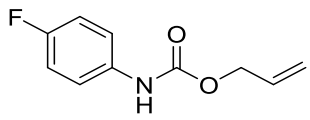
Phenyl carbamic acid allyl ester (S1)[3]



The title compound was prepared from general procedure A from aniline (0.46 mL, 5.05 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 9:1) to afford (S**1)** (840 mg, 95%) as a colorless solid

R_f: (Hexanes/EtOAc 5:1) = 0.64. ^{1}H-NMR (500MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.34-7.29 (m, 2H), 7.13 (s, 1H), 7.09 (1H, t, *J* = 7.3 Hz), 5.98 (1H, ddt, *J* = 17.2, 10.6, 5.5 Hz), 5.38 (1H, ddt, *J* = 17.2, 1.5 1.5 Hz), 5.27 (1H, ddt, *J* = 10.6, 1.5, 1.5 Hz), 4.70 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 153.4, 137.7, 132.3, 128.8, 123.2, 118.7, 117.9, 65.6. IR ν_{max} (thin film) 3312, 3131, 3060, 1721, 1599, 1537, 1444, ,1237, 994, 938, 747, 692 cm^{-1}. HRMS (ES^+) calc. for $C_{10}H_{12}NO_2$ $[M+H]^+$ 178.0868. Found 178.0860.

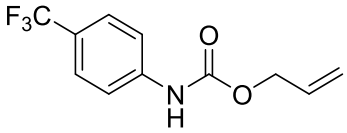
(4-Fluoro-phenyl)-carbamic acid allyl ester (S2)[4]



The title compound was prepared from general procedure A from 4-fluoroaniline (0.48 mL, 5.05 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 9:1) to afford **(S2)** (937 mg, 96%) as a yellow solid.

R_f: (Hexanes/EtOAc 5:1) = 0.62. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.39-7.30 (2H, m), 7.24 (1H, br. s), 6.98-6.93 (2H, m), 5.94 (1H, ddt, *J* = 17.1, 10.3, 5.4 Hz), 5.34 (1H, ddt, *J* = 17.1, 1.3, 1.3 Hz), 5.23 (1H, ddt, *J* = 10.3, 1.3, 1.3 Hz), 4.66 (2H, ddd, *J* = 5.7, 1.3, 1.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ= 158.8 (J_{C-F} = 242.2 Hz), 153.6, 133.7 (broad signal, J_{C-F} unobtainable), 132.3, 120.8 (broad signal, J_{C-F} unobtainable), 118.0, 115.3 (J_{C-F} = 22.7 Hz), 65.7. IR ν_{max} (thin film) 3425, 3053, 2986, 2304, 1733, 1511, 1409, 1275, 1261, 1211, 1056, 895, 834, 764, 749 cm^{-1}. HRMS (ES$^+$) calc. for $C_{10}H_{10}NFO_2Na$ $[M+Na]^+$ 218.0593 found 218.0594.

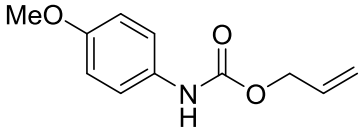
Allyl (4-(trifluoromethyl)phenyl)carbamate (S3)[5]



The title compound was prepared from general procedure A from 4-(trifluoromethyl)aniline (0.80 mL, 6.37 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 15:1) to afford **(S3)** (1.50 g, 96%) as a colorless solid.

R_f: (Hexanes/EtOAc 5:1) = 0.58. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.57-7.55 (2H, m), 7.52-7.50 (2H, m), 6.92 (1H, br. s), 5.97 (1H, ddt, *J* = 17.1, 10.5, 5.8 Hz), 5.38 (1H, ddt, *J* = 17.1, 1.4 1.4 Hz), 5.29 (1H, ddt, *J* = 10.5, 1.2, 1.2 Hz), 4.69 (2H, ddd, *J* = 5.8, 1.2 1.2 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 152.8, 140.9 (q, J_{C-F} = 1.8 Hz), 132.0, 126.3 (q, J_{C-F} = 3.6 Hz), 125.4 (q, J_{C-F} = 32.8 Hz), 125.3 (q, J_{C-F} = 270.6 Hz), 118.6, 118.1, 66.1. IR ν_{max} (thin film) 3331, 3056, 1710, 1617, 1598, 1538, 1513, 1412, 1323, 1265, 1219, 1163, 1116, 1067, 1014, 990, 941, 838, 767, 737, 701 cm^{-1}. HRMS (ES$^+$) calc. for $C_{11}H_{10}F_3NO_2$ $[M+H]^+$ 246.0736 found 246.0729.

(4-methoxy-phenyl)-carbamic acid allyl ester (S4)[4]

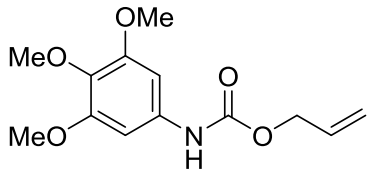


The title compound was prepared from general procedure A from *p*-anisidine (493 mg, 4.00 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 4:1) to afford **(S4)** (805 mg, 97%) as a colorless solid.

R_f: (Hexanes/EtOAc 5:1) = 0.38. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29 (2H, d, *J* = 8.0 Hz), 6.87-6.83 (2H, m), 6.55 (1H, s), 5.97 (1H, ddt, *J* = 17.1, 10.5, 5.6 Hz), 5.36 (1H, ddt, *J* = 17.1, 1.5, 1.5 Hz), 5.25 (1H, ddt, *J* = 10.5, 1.3, 1.3 Hz), 4.66 (2H, ddd, *J* = 5.6, 1.3 1.3 Hz), 3.79 (3H, s).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.0, 153.6, 132.5, 130.8, 120.7, 118.0, 114.2, 65.7, 55.4. IR ν_{max} (thin film) 3054, 2987, 2306, 1730, 1523, 1274, 1264, 764, 749 cm^{-1}. HRMS (ES$^+$) calc. for $C_{11}H_{14}NO_3$ $[M+H]^+$ 208.0974 found 208.0967**.**

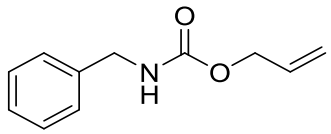
(3,4,5-trimethoxy-phenyl)-carbamic acid allyl ester (S5)



The title compound was prepared from general procedure A from 3,4,5-trimethoxyaniline (925 mg, 5.05 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 3:1) to afford **(S5)** (1.21 g, 91%) as a yellow solid.

R_f: (Hexanes/EtOAc 1:1) = 0.41. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.76 (1H, s), 6.68 (s, 2H), 5.96 (1H, ddt, *J* = 17.2, 10.5, 5.8 Hz), 5.35 (1H, ddt, *J* = 17.2, 1.5, 1.5 Hz), 5.25 (1H, ddt, *J* = 10.5, 1.5, 1.5 Hz), 4.65 (2H, ddd, *J* = 5.8, 1.5, 1.5 Hz), 3.81 (6H, s), 3.80 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.3, 153.2, 134.0, 133.9, 132.3, 118.0, 96.3, 65.7, 60.9, 55.9. IR ν_{max} (thin film) 3329, 2938, 1730, 1608, 1510, 1454, 1414, 1274, 1222, 1129, 980, 764, 749 cm^{-1}. HRMS (ES$^+$) calc. for $C_{13}H_{18}NO_5$ $[M+H]^+$ 268.1185 found 268.1182

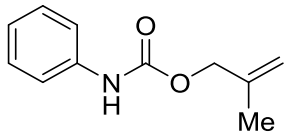
Benzyl carbamic acid allyl ester (S6)[4]



The title compound was prepared from general procedure A from benzylamine (0.55 mL, 5.05 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 9:1) to afford **(S6)** (910 mg, 95%) as a colorless solid.

R_f: (Hexanes/EtOAc 5:1) = 0.58. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.34-7.31 (2H, m), 7.29-7.25 (3H, m), 5.92 (1H, ddt, *J* = 17.1, 10.4, 5.4 Hz), 5.44 (1H, br. s), 5.32-5.29 (1H, m), 5.21 (1H, ddt, *J* = 10.4, 1.5, 1.5 Hz), 4.58-4.57 (2H, m), 4.35-4.34 (2H, m). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 156.2, 138.4, 132.7, 128.3, 127.2, 127.1, 117.3, 65.4, 44.8. IR ν_{max} (thin film) 3440, 3340, 3055, 2985, 2936, 2305, 1709, 1517, 1454, 1265, 1138, 1045, 986, 933, 738, 700 cm^{-1}. HRMS (ES$^+$) calc. for $C_{11}H_{13}NO_2Na$ $[M+Na]^+$ 214.0844 found 214.0847.

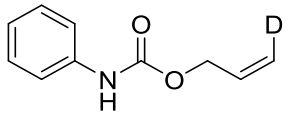
Phenyl-carbamic acid 2-methyl-allyl ester (S7)[5]



The title compound was prepared from general procedure B from 2-methyl-2-propen-1-ol (0.80 mL, 9.51 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 8:1) to afford **(S7)** (1.72 g, 95%) as a colorless solid.

R_f: (Hexanes/EtOAc 5:1) = 0.60. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.40 (2H, d, *J* = 7.7 Hz), 7.34-7.30 (2H, m), 7.10-7.06 (1H, m), 6.80 (1H, s), 5.05-5.02 (1H, d, *J* = 1.0 Hz), 4.97-4.96 (1H, d, *J* = 1.0 Hz), 4.60 (2H, s), 1.80 (3H, s).^{13}C-NMR (125 MHz, $CDCl_3$) δ 153.2, 140.1, 137.9, 128.9, 123.4, 118.6, 112.8, 68.3, 19.3. IR ν_{max} (thin film) 3423, 3052, 2985, 2304, 1734, 1262, 1212, 764 cm^{-1}. HRMS (ES$^+$) calc. for $C_{11}H_{14}NO_2$ $[M+H]^+$ 192.1025 found 192.1026.

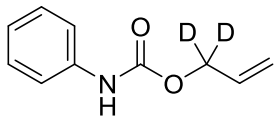
(*E*)-allyl-3-*d*-phenylcarbamate (S8)



The title compound was prepared from general procedure B from (*E*)-prop-2-en-3-*d*-1-ol[6] (1.10 g, 18.5 mmol) and phenyl isocyanate (2.20 mL, 20.4 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 15:1) to afford **(S8)** (2.42 g, 73%, approx. 75% D) as a yellow solid

R_f: (Hexanes/EtOAc 5:1) = 0.39. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.41-7.40 (2H, m), 7.33-7.29 (2H, m), 7.09-7.06 (1H, m), 6.84 (1H, s), 6.02-5.94 (1H, m), 5.29-5.24 (1H, m), 4.69 (2H, dd, J = 5.6, 1.5 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 153.2, 137.7, 132.3 (t, J_{C-D} = 14.6 Hz), 128.9, 123.4, 118.7, 117.8 (t, J_{C-D} = 23.4 Hz) 65.7.IR ν_{max} (thin film) 3308, 3047, 2941, 1713, 1600, 1539, 1500, 1444, 1312, 1225, 1085, 1061, 1027, 754, 693 cm^{-1}. HRMS (ES$^+$) calc. for $C_{10}H_{10}NO_2D$ $[M+H]^+$ 179.0925 found 179.0926.

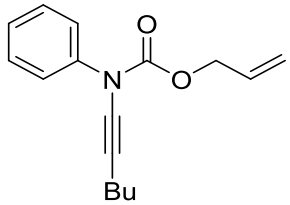
Allyl-1,1-d_2 phenylcarbamate (S9)



The title compound was prepared from general procedure B from prop-2-en-1,1-d_2-ol[7] (150 mg, 2.50 mmol) and phenyl isocyanate (0.30 mL, 2.75 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 15:1) to afford **(S9)** (291 mg, 65%) as a colorless solid.

R_f: (Hexanes/EtOAc 5:1) = 0.62. ^{1}H- NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, d, *J* = 7.9 Hz), 7.34-7.29 (2H, m), 7.10-7.05 (1H, m), 6.63 (1H, s), 5.98 (1H, dd, *J* = 17.2, 10.5 Hz), 5.38 (1H, dd, *J* = 17.2, 1.5 Hz), 5.28 (1H, dd, *J* = 10.5, 1.5 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.5, 137.7, 132.3, 129.0, 123.5, 118.6, 118.4, 70.5. HRMS (ES^+) calc. for $C_{10}H_{10}D_2NO_2$ $[M+H]^+$ 180.0978 found 180.0982.

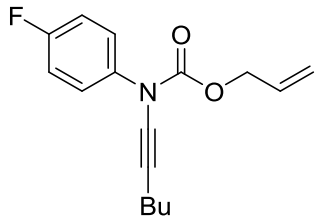
Hex-1-ynyl-phenyl-carbamic acid allyl ester (1a)



The title compound was prepared by general procedure C from phenyl carbamic acid allyl ester **(S1)** (998 mg, 5.64 mmol) and 1-bromohexyne[8] (1.00 g, 6.20 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1a)** (1.28 g, 88%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.73. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (2H, m), 7.40-7.36 (2H, m), 7.27-7.23 (1H, m), 5.98 (1H, ddt, *J* = 17.1, 10.5, 5.5 Hz), 5.38 (1H, ddt, *J* = 17.1, 1.5, 1.5 Hz), 5.27 (1H, ddt, *J* = 10.5, 1.5, 1.5 Hz), 4.73 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz), 2.34 (2H, t, *J* = 7.3 Hz), 1.57-1.39 (4H, m), 0.92 (3H, t, *J* = 7.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.5, 140.0, 131.7, 128.7, 126.6, 124.4, 118.3, 73.6, 69.8, 67.6, 30.9, 21.9, 18.2, 13.6. IR ν_{max} (thin film) 3053, 1734, 1275, 1265, 764 cm^{-1}. HRMS (ES^+) calc. for $C_{16}H_{20}NO_2$ $[M+H]^+$ 258.1494 found 258.1486.

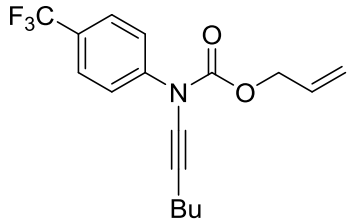
(4-Fluoro-phenyl)-hex-1-ynyl-carbamic acid allyl ester (1b)



The title compound was prepared by general procedure C from (4-fluoro-phenyl)-carbamic acid allyl ester **(S2)** (900 mg, 4.61 mmol) and 1-bromohexyne[8] (833 mg, 5.08 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1b)** (1.11 g, 88%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.70. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (2H, m), 7.09-7.03 (2H, m), 5.97 (1H, ddt, *J* = 17.1, 10.4, 5.5 Hz), 5.38 (1H, ddt, *J* = 17.1, 1.5, 1.5 Hz), 5.28 (1H, ddt, *J* = 10.4, 1.5, 1.5 Hz), 4.73 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz), 2.33 (2H, t, *J* = 7.0 Hz), 1.38-1.57 (4H, m), 0.92 (t, 3H, *J* = 7.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.8 (J_{C-F} = 246.9 Hz), 154.5, 135.9 (J_{C-F} = 2.6 Hz), 131.6, 126.3 (J_{C-F} = 8.6 Hz), 118.4, 115.6 (J_{C-F} = 22.8 Hz), 67.6, 30.9, 21.9, 18.1, 13.5. IR ν_{max} (thin film) 3054, 2935, 1732, 1507, 1266, 747 cm^{-1}. HRMS (ES$^+$) calc. for $C_{16}H_{18}FNO_2Na$ $[M+Na]^+$ 298.1219 found 298.1212.

Allyl hex-1-yn-1-yl(4-trifluoromethyl)phenyl)carbamate (1c)

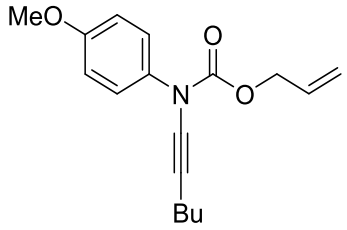


The title compound was prepared by general procedure C from allyl (4-(trifluoromethyl)phenyl)carbamate **(S3)** (750 mg, 3.06 mmol) and 1-bromohexyne[8] (542 mg, 3.36 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1c)** (357 mg, 36%) as a pale yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.91. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.71-7.69 (2H, m), 7.64-7.62 (2H, m), 5.99 (1H, ddt, *J* = 17.1, 10.5, 5.3 Hz), 5.42 (1H, ddt, *J* = 17.1, 1.5, 1.5 Hz), 5.31(1H, ddt, *J* = 10.5, 1.5, 1.5 Hz), 4.76 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz), 2.37 (2H, t, *J* = 7.0 Hz), 1.59-1.42 (4H, m), 0.93 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 153.9, 142.9, 131.3, 128.1 (q, J_{C-F} = 32.5 Hz), 125.8 (q, J_{C-F} = 4.5 Hz), 124.9 (q, J_{C-F} = 272.2 Hz), 123.6, 118.6, 72.4, 71.3, 67.8, 30.8, 21.9, 18.0, 13.5. IR ν_{max} (thin film) 2959, 2934, 2869, 2259, 1751, 1616,

1514, 1458, 1428, 1368, 1329, 1294, 1269, 1204, 1164, 1128, 1067, 1042, 1015, 991, 934, 843, 758 cm^{-1}. HRMS (ES^+) calc. for $C_{17}H_{18}F_3NO_2$ $[M+H]^+$ 326.1362 found 326.1352.

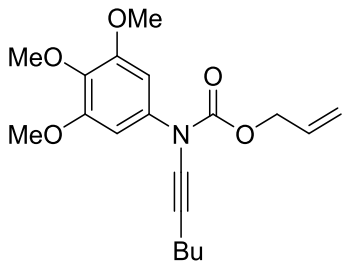
Hex-1-ynyl-(4-methoxy-phenyl)-carbamic acid allyl ester (1d)



The title compound was prepared by general procedure C from (4-methoxy-phenyl)-carbamic acid allyl ester **(S4)** (400 mg, 1.93 mmol) and 1-bromohexyne[8] (342 mg, 2.12 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1d)** (242 mg, 44%) as an orange oil.

R_f: (Hexanes/EtOAc 5:1) = 0.43. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (2H, m), 6.91-6.87 (2H, m), 5.96 (1H, ddt, *J* = 17.3, 10.5, 5.5 Hz), 5.36 (1H, ddt, *J* = 17.3, 1.6, 1.6 Hz), 5.26 (1H, ddt, *J* = 10.5, 1.4, 1.4 Hz), 4.71 (2H, ddd, *J* = 5.5, 1.4, 1.4 Hz), 3.81 (3H, s), 2.32 (2H, t, *J* = 8.0 Hz), 1.57-1.38 (4H, m), 0.91 (3H, t, *J* = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.2, 154.8, 132.9, 131.7, 126.1, 118.1, 114.0, 74.1. 69.2, 67.5, 55.4, 30.9, 21.8, 18.1, 13.5. IR ν_{max} (thin film) 3054, 2958, 2933, 2838, 2265, 1729, 1648, 1608, 1510, 1442, 1370, 1247, 1106, 1032, 832, 740, 598, 532 cm^{-1}. HRMS (ES^+) calc. for $C_{17}H_{22}NO_3$ $[M+H]^+$ 288.1600 found 288.1606.

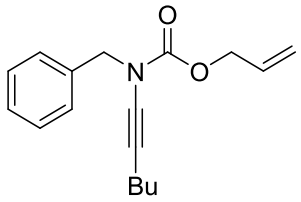
Hex-1-ynyl-(3,4,5-trimethoxy-phenyl)-carbamic acid allyl ester (1e)



The title compound was prepared by general procedure C from (3,4,5-trimethoxy-phenyl)-carbamic acid allyl ester **(S5)** (452 mg, 1.69 mmol) and 1-bromohexyne[8] (300 mg, 1.86 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 10:1) to afford **(1e)** (354 mg, 60%) as a yellow oil.

R_f: (Hexanes/EtOAc 1:1) = 0.66. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.74 (2H, s), 5.98 (1H, ddt, *J* = 17.3, 10.5, 5.5 Hz), 5.40 (1H, ddt, *J* = 17.3, 1.5, 1.5 Hz), 5.28 (1H, ddt, *J* = 10.5, 1.5, 1.5 Hz), 4.74 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz), 3.85 (6H, s), 3.84 (3H, s), 2.35 (2H, t, *J* = 7.0 Hz), 1.59-1.40 (4H, m), 0.92 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.5, 153.0, 136.6, 135.5, 131.6, 118.3, 102.3, 73.6, 70.0, 67.6, 60.8, 56.1, 30.9, 21.9, 18.1, 13.5. IR ν_{max} (thin film) 2936, 2263, 1734, 1598, 1506, 1464, 1273, 1129, 750 cm^{-1}. HRMS (ES$^+$) calc. for $C_{19}H_{25}NO_5Na$) $[M+Na]^+$ 370.1630 found 370.1642

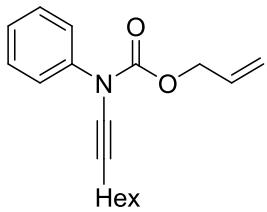
Benzyl-hex-1-ynyl-carbamic acid allyl ester (1f)



The title compound was prepared by general procedure C from benzyl carbamic acid allyl ester **(S6)** (1.20 g, 6.30 mmol) and 1-bromohexyne[8] (1.14 g, 6.93 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1f)** (1.12 g, 66%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.50. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (5H, m), 5.95 (1H, ddt, *J* = 16.8, 10.4, 5.4 Hz), 5.38 (1H, m), 5.25 (1H, ddt, *J* = 10.4, 1.5, 1.5 Hz), 4.69 (2H, ddd, *J* = 5.4, 1.5, 1.5 Hz), 4.61 (2H, s), 2.26 (2H, t, *J* = 7.0 Hz), 1.49-1.30 (4H, m), 0.88 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.4, 136.2, 131.9, 128.3, 128.2, 127.7, 117.8, 73.5, 70.4, 67.2, 53.7, 30.9, 21.6, 18.0, 13.5. IR ν_{max} (thin film) 3425, 3088, 3065, 3032, 2957, 2933, 2872, 2264, 2206, 1723, 1455, 1397, 1278, 1217, 931, 759, 700 cm^{-1}. HRMS (ES$^+$) calc. for $C_{17}H_{22}NO_2$ $[M+H]^+$ 272.1651 found 272.1652.

Allyl oct-1-yn-1-yl(phenyl)carbamate (1g)

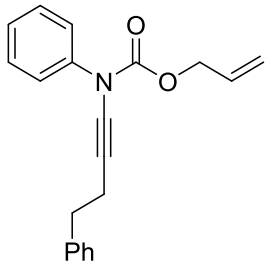


The title compound was prepared by general procedure C from phenyl carbamic acid allyl ester **(S1)** (1.00 g, 5.64 mmol) and 1-bromooctyne[9] (1.18 g, 6.20 mmol). The crude product was

purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1g)** (1.22 g, 76%) as a pale yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.86. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.52-7.49 (2H, m), 7.40-7.36 (2H, m), 7.26-7.23 (1H, m), 5.98 (1H, ddt, *J* = 17.2, 10.6, 5.2 Hz), 5.39 (1H, ddt, *J* = 17.2, 1.5, 1.5 Hz), 5.27 (1H, ddt, *J* = 10.6, 1.5, 1.5 Hz), 4.74 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz), 2.34 (2H, t, *J* = 7.0 Hz), 1.58-1.53 (2H, m), 1.45-1.39 (2H, m), 1.35-1.27 (4H, m), 0.90 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 154.4, 139.9, 131.6, 128.6, 126.4, 124.3, 118.1, 73.6, 69.8, 67.4, 31.2, 28.7, 28.4, 22.4, 18.4, 13.9. IR ν_{max} (thin film) 2923, 2855, 2259, 1719, 1646, 1595, 1492, 1460, 1372, 1296, 1269, 1198, 1098, 1049, 1023, 994, 926, 758, 687 cm^{-1}. HRMS (ES$^+$) calc. for $C_{18}H_{23}NO_2$ $[M+H]^+$ 286.1802 found 286.1793

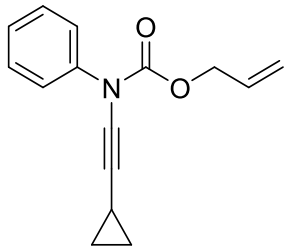
Phenyl-(4-phenyl-but-1-ynyl)-carbamic acid allyl ester (1h)



The title compound was prepared by general procedure C from phenyl carbamic acid allyl ester **(S1)** (231 mg, 1.30 mmol) and (4-bromobut-3-yn-1-yl)benzene[10] (297 mg, 1.43 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1h)** (230 mg, 58%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.71. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.20 (10H, m), 5.97 (1H, ddt, *J* = 17.5, 10.5, 5.5 Hz), 5.37 (1H, ddt, *J* = 17.5, 1.5, 1.5 Hz), 5.27 (1H, ddt, *J* = 10.5, 1.5, 1.5 Hz), 4.73 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz), 2.87 (2H, t, *J* = 7.0 Hz), 2.65 (2H, t, *J* = 7.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.4, 140.6, 139.7, 131.6, 128.7, 128.4, 128.3, 126.6, 126.1, 124.4, 118.3, 74.3, 69.0, 67.6, 35.1, 20.6. IR ν_{max} (thin film) 3350, 3027, 2267, 1734, 596, 1492, 1371, 1299, 1273, 757, 694 cm^{-1}; HRMS (ES$^+$) calc. for $C_{20}H_{20}NO_2$ $[M+H]^+$ 306.1494 found 306.1493.

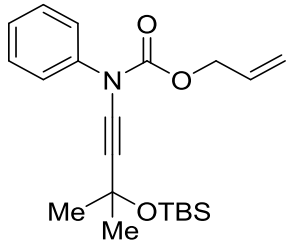
Allyl (cyclopropylethynyl)(phenyl)carbamate (1i)



The title compound was prepared by general procedure C from phenyl carbamic acid allyl ester **(S1)** (673 mg, 3.80 mmol) and (bromoethynyl)cyclopropane[11] (606 mg, 4.20 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1i)** (772 mg, 84%) as a yellow solid.

R_f: (Hexanes/EtOAc 5:1) = 0.70. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.48-7.46 (2H, m), 7.40-7.36 (2H, m), 7.27-7.23 (1H, m), 5.98 (1H, ddt, *J* = 17.1, 10.5, 5.5 Hz), 5.39 (1H, ddt, *J* = 17.1, 1.5, 1.5 Hz), 5.28 (1H, ddt, *J* = 10.5, 1.5, 1.5 Hz), 4.74 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz), 1.39 (1H, tt, *J* = 8.2, 4.9 Hz), 0.80 (2H, m), 0.72 (2H, m). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 154.6, 139.9, 131.6, 128.7, 126.6, 124.4, 118.1, 73.5, 69.1, 67.5, 8.4, -0.7. IR ν_{max} (thin film) cm^{-1}. 3088, 3013, 2937, 2882, 2264, 1727, 1647, 1595, 1491, 1454, 1385, 1367, 1291, 1216, 1177, 1103, 1041, 1021, 998, 930, 820, 758, 738, 690. HRMS (ES$^+$) calc. for $C_{15}H_{15}NO_2$ $[M+H]^+$ 242.1176 found 242.1170.

[3-(*tert*-Butyl-dimethyl-silanyloxy)-3-methyl-but-1-ynyl]-phenyl-carbamic acid allyl ester (1j)

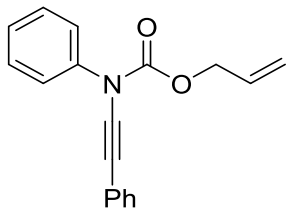


The title compound was prepared by general procedure C from phenyl carbamic acid allyl ester **(S1)** (291 mg, 1.64 mmol) and ((4-bromo-2-methylbut-3-yn-2-yl)oxy)trimethylsilane[12] (497 mg, 1.80 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1j)** (210 mg, 34%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.65. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (2H, m), 7.41-7.36 (2H, m), 7.29-7.24 (1H, m), 5.98 (1H, ddt, *J* = 17.4, 10.5, 5.0 Hz), 5.40 (1H, ddt, *J* = 17.4, 1.5,

1.5 Hz), 5.28 (1H, ddt, *J* = 10.5, 1.5, 1.5 Hz), 4.74 (2H, ddd, *J* = 5.6, 1.5, 1.5 Hz), 1.50 (6H, s), 0.86 (9H, s), 0.13 (6H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.2, 139.5, 131.5, 128.8, 126.8, 124.4, 118.4, 75.1, 67.6, 66.5, 33.0, 25.7, 17.8, 0.0, -3.1. IR ν_{max} (thin film) 2981, 2957, 2933, 2890, 2851, 2256, 1742, 1277, 1156, 1041, 836 cm^{-1}. HRMS (ES^+) calc. for $C_{21}H_{32}NO_3Si$ $[M+H]^+$ 374.2151 found 374.2149.

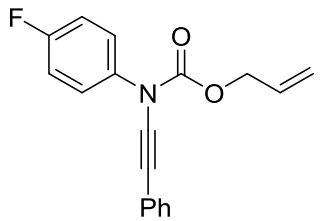
Phenyl-phenylethynyl-carbamic acid allyl ester (1k)



The title compound was prepared by general procedure C from phenyl carbamic acid allyl ester **(S1)** (1.33 g, 7.50 mmol) and 1-bromophenylacteylene[13] (1.48 g, 8.25 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1k)** (1.69 g, 80%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.69. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (2H, m), 7.45-7.40 (4H, m), 7.31-7.29 (4H, m), 6.01 (1H, ddt, *J* = 17.3, 10.5, 5.5 Hz), 5.44 (ddt, 1H, *J* = 17.2, 1.5, 1.5 Hz), 5.29 (ddt, 1H, *J* = 10.5, 1.3, 1.3 Hz), 4.79 (2H, ddd, *J* = 5.5, 1.3, 1.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.0, 139.5, 131.5, 131.3, 128.9, 128.3, 127.7, 126.9, 124.6, 122.9, 118.5, 82.7, 70.3, 67.8. IR ν_{max} (thin film) 3054, 2987,2305, 2252,1733, 1264, 749 cm^{-1}. HRMS (ES^+) calc. for $C_{18}H_{16}NO_2$ $[M+H]^+$ 278.1181 found 278.1187.

(4-Fluoro-phenyl)-phenylethynyl-carbamic acid allyl ester (1l)

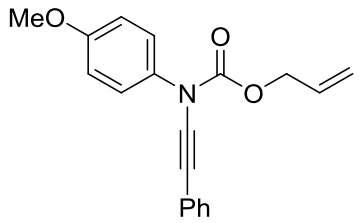


The title compound was prepared by general procedure C from (4-fluoro-phenyl)-carbamic acid allyl ester **(S2)** (900 mg, 4.61 mmol) and 1-bromophenylacteylene[13] (913 mg, 5.08 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1l)** (778 mg, 57%) as an orange oil.

R_f: (Hexanes/EtOAc 5:1) = 0.56. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.55-7.52 (2H, m), 7.44-7.42 (2H, m), 7.34-7.31 (3H, m), 7.13-7.09 (2H, m), 6.01 (1H, ddt, *J* = 17.1, 10.4, 5.5 Hz), 5.44

(ddt, 1H, *J* = 17.1, 1.5, 1.5 Hz), 5.31 (ddt, 1H, *J* = 10.4, 1.5, 1.5 Hz), 4.79 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ= 162.1, 153.9, 131.3, 131.2 (br.), 128.2, 127.8, 126.6 (J_{C-F} = 8.4 Hz), 122.7, 118.5, 115.8 (J_{C-F} = 22.8 Hz), 82.5, 70.3, 67.9, 24.8. IR ν_{max} (thin film) 2362, 2337, 2251, 1740, 1507, 1371, 1295, 1279, 1229 cm^{-1}. HRMS ($ES^{+)}$ calc. for $C_{18}H_{14}FNO_2$ $[M+Na]^+$ 318.0906 found 318.0897.

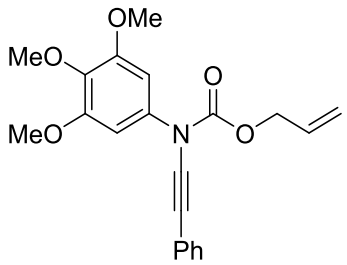
(4-Methoxy-phenyl)-phenylethynyl-carbamic acid allyl ester (1m)



The title compound was prepared by general procedure C from (4-methoxy-phenyl)-carbamic acid allyl ester **(S4)** (808 mg, 3.90 mmol) and 1-bromophenylacteylene[13] (686 mg, 4.29 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1m)** (700 mg, 59%) as an orange oil.

R_f: (Hexanes/EtOAc 5:1) = 0.48. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.46-7.40 (4H, m), 7.32-7.26 (3H, m), 6.96-6.92 (2H, m), 5.99 (1H, ddt, *J* = 17.5, 10.4, 5.5 Hz), 5.42 (1H, ddt, *J* = 17.5, 1.5, 1.5 Hz), 5.29 (1H, ddt, *J* = 10.5, 1.5, 1.5 Hz), 4.76 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz), 3.83 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 158.5, 154.3, 132.4, 131.5, 131.2, 128.2, 127.6, 126.3, 123.0, 118.3, 114.2, 83.2, 69.8, 67.7, 55.5. IR ν_{max} (thin film) 2360, 2340, 2250, 1736, 1651, 1556, 1539, 1508 cm^{-1}. HRMS (ES^+) calc. for $C_{19}H_{17}NO_3Na$ $[M+Na]^+$ 330.1106 found 330.1107.

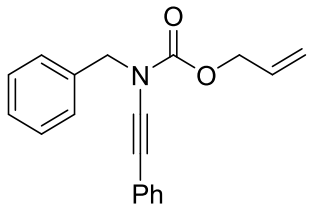
Phenylethynyl-(3,4,5-trimethoxy-phenyl)-carbamic acid allyl ester (1n)



The title compound was prepared by general procedure C from (3,4,5-trimethoxy-phenyl)-carbamic acid allyl ester **(S5)** (440 mg, 1.65 mmol) and1-bromophenylacteylene[13] (328 mg, 1.81 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1n)** (185 mg, 31%) as a yellow oil.

R_f: (Hexanes/EtOAc 1:1) = 0.79. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (2H, m), 7.34-7.29 (3H, m), 6.80 (2H, s), 6.02 (1H, ddt, *J* = 17.3, 10.5, 5.3 Hz), 5.45 (1H, ddt, *J* = 17.3, 1.5, 1.5 Hz), 5.31 (1H, ddt, *J* = 10.5, 1.5, 1.5 Hz), 4.79 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz), 3.88 (6H, s), 3.86 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.0, 153.2, 137.0, 135.0, 131.4, 131.1, 128.3, 127.7, 122.8, 118.5, 102.6, 82.7, 70.5, 67.8, 60.8, 56.2. IR ν_{max} (thin film) 3055, 2987, 2251, 2306, 1737, 1600, 1505, 1422, 1265, 1131

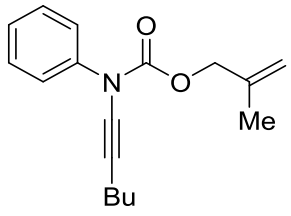
Benzyl-phenyl-ethynyl-carbamic acid allyl ester (1o)



The title compound was prepared by general procedure C from benzyl carbamic acid allyl ester **(S6)** (707 mg, 3.70 mmol) and 1-bromophenylacteylene[13] (732 mg, 4.07 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1o)** (459 mg, 43%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.59. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.47-7.38 (5H, m) 7.36-7.29 (3H, m), 6.04 (1H, ddt, *J* = 17.0, 10.6, 5.0 Hz), 5.49 (1H, m), 5.34 (1H, ddt, *J* = 10.6, 1.5, 1.5 Hz), 4.82 (2H, s), 4.80 (2H, ddd, *J* = 5.0, 1.5, 1.5 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 154.6, 135.7, 131.5, 130.8, 128.3, 128.0, 127.9, 127.2, 123.0, 117.8, 82.8, 71.3, 67.3, 53.7, 29.5. IR ν_{max} (thin film) 2364, 2338, 2247, 1951, 1725 cm^{-1}. HRMS (ES$^+$) calc. for $C_{19}H_{18}NO_2$ $[M+H]^+$ 292.1332 found 292.1336.

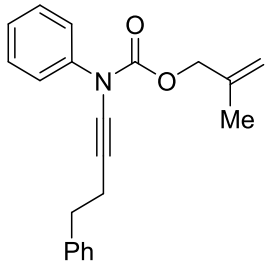
Hex-1-ynyl-phenyl carbamic acid 2-methyl-allyl ester (1p)



The title compound was prepared by general procedure C from phenyl-carbamic acid 2-methyl-allyl ester **(S7)** (382 mg, 2.00 mmol) and 1-bromohexyne[8] (352 mg, 2.20 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1p)** (290 mg, 53%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.71. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (2H, m), 7.41-7.36 (2H, m), 7.27-7.23 (1H, m), 5.06-5.03 (1H, m), 4.97-4.95 (1H, m), 4.66-4.64 (2H, s), 2.34 (2H, t, *J* = 7.0 Hz), 1.80-1.78 (3H, m), 1.59-1.39 (4H, m) 0.92 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.5, 139.9, 139.4, 128.7, 126.5, 124.3, 112.9, 73.5, 70.1, 69.7, 30.9, 21.9, 19.2, 18.1, 13.5. IR ν_{max} (thin film) 3343, 3064, 2959, 2933, 2873, 2265, 2212, 1736, 1598, 1535, 1492, 1301, 1274, 1073, 757, 692 cm^{-1}. HRMS (ES$^+$) calc. for $C_{17}H_{21}NO_2Na$ $[M+Na]^+$ 294.1470 found 294.1469.

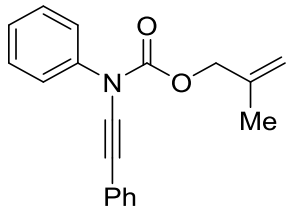
Phenyl-(4-phenyl-but-1-ynyl)-carbamic acid 2-methyl-allyl ester (1q)



The title compound was prepared by general procedure C from phenyl-carbamic acid 2-methyl-allyl ester **(S7)** (249 mg, 1.30 mmol) and (4-bromobut-3-yn-1-yl)benzene[10] (300 mg, 1.43 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1q)** (226 mg, 54%) as a pale yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.65. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.45-7.44 (2H, m), 7.40-7.37 (2H, m), 7.33-7.24 (6H, m), 5.06 (1H, s), 4.98 (1H, s) 4.68 (2H, s), 2.90 (2H, t, *J* = 7.3 Hz), 2.68 (2H, t, *J* = 7.3 Hz), 1.81 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 154.3, 140.6, 139.3, 128.7, 128.4, 128.2, 126.5, 126.1, 124.4, 112.8, 74.3, 70.0, 69.0, 35.1, 34.6, 20.5, 19.2. IR ν_{max} (thin film) 3028, 2925, 2267, 1735, 1596, 1492, 1454, 1372, 1274, 1301, 1203, 1075, 904, 756, 692 cm^{-1}. HRMS (ES$^+$) calc. for $C_{42}H_{46}N_3O_4$ $[2M+NH_4]^+$ 656.3488 found 656.3511.

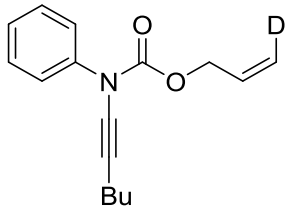
Phenyl-phenylethynyl-carbamic acid 2-methyl-allyl ester (1r)



The title compound was prepared by general procedure C from phenyl-carbamic acid 2-methyl-allyl ester **(S7)** (392 mg, 2.05 mmol) and 1-bromophenylacteylene[13] (408 mg, 2.25 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(1r)** (452 mg, 76%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.67. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.59-7.57 (2H, m), 7.45-7.41 (4H, m), 7.33-7.29 (4H, m), 5.10 (1H, s), 4.99 (1H, s), 4.71 (2H, s), 1.83 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 153.9, 139.4, 139.2, 131.1, 128.9, 128.2, 127.6, 126.9, 124.5, 122.9, 113.1, 82.7, 70.4, 70.3, 19.3. IR ν_{max} (thin film) 3053, 2981, 2251, 1736, 1594, 1491, 1368, 1275, 909, 751, 691 cm^{-1}. HRMS (ES$^+$) calc. for $C_{19}H_{18}NO_2$ $[M+H]^+$ 292.1338 found 292.1346.

(*E*)-allyl-3-*d*-hex-1-yn-1-yl(phenyl)carbamate (*d*-1a)

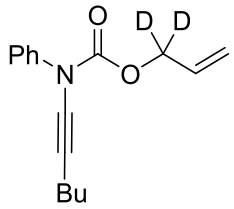


The title compound was prepared by general procedure C from (*E*)-allyl-3-*d*-phenylcarbamate **(S8)** (1.00 g, 5.61 mmol) and 1-bromohexyne[8] (994 mg, 6.17 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(*d*-1a)** (1.10 g, 76%, approx. 75% D) as a pale yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.75. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.50-7.48 (2H, m), 7.40-7.36 (2H, m), 7.26-7.23 (1H, m), 6.02-5.94 (1H, m), 5.29-5.24 (1H, m), 4.74 (2H, dd, J = 5.5, 1.0 Hz), 2.34 (2H, t, J = 7.0 Hz), 1.57-1.51 (2H, m), 1.48-1.40 (2H, m), 0.92 (3H, t, J = 7.0 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 154.5, 139.9, 131.6 (t, J_{C-D} = 14.5 Hz), 128.7, 126.5, 124.4, 117.9 (t, J_{C-D} = 23.7 Hz), 73.6, 69.8, 67.5 (t, J_{C-D} = 4.3 Hz), 30.9, 21.9, 18.1, 13.5. IR ν_{max} (thin film) 3060, 2957, 2931, 2868, 2264, 1734, 1593, 1492, 1456, 1382, 1344, 1288, 1270, 1202,

1048, 1023, 758, 690 cm^{-1}. HRMS (ES^+) calc. for $C_{16}H_{18}DNO_2$ [M+H]+ 259.1551 found 259.1551.

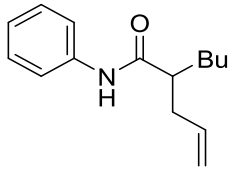
Allyl-1,1-*d*$_2$ hex-1-yn-1yl(phenyl)carbamate (*d*$_2$-1a)



The title compound was prepared by general procedure C from allyl-1,1-*d*$_2$ phenylcarbamate **(S9)** (240 mg, 1.39 mmol) and 1-bromohexyne[8] (247 mg, 1.53 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(*d*$_2$-1a)** (125 mg, 39%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.71. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (2H, m), 7.40-7.35 (2H, m), 7.27-7.22 (1H, m), 5.97 (1H, dd, *J* = 17.2, 10.5 Hz), 5.39 (1H, dd, *J* = 17.2, 1.5 Hz), 5.28 (1H, dd *J* = 10.5, 1.5 Hz), 2.33 (2H, t, *J* = 7.1 Hz), 1.58-1.40 (4H, m), 0.92 (3H, t, *J* = 7.1 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.5, 139.9, 131.5, 128.7, 126.5, 124.3, 118.4, 73.6, 69.7, 66.9 (t, J_{C-D} = 22.6 Hz), 30.9, 21.8, 18.1, 13.5. HRMS (ES^+) calc. for $C_{32}H_{34}D_4N_2O_4$ $[2M+Na]^+$ 541.2980 found 541.2996.

2-Allyl-hexanoic acid phenylamide (2a)

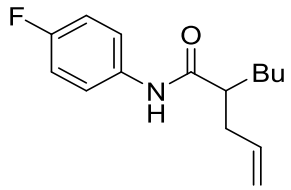


The title compound was prepared by general procedure D from hex-1-ynyl-phenyl-carbamic acid allyl ester **(1a)** (60.0 mg, 0.23 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2a)** (39.0 mg, 77 %) as a colorless oil.

R_f: (Hexanes/EtOAc 5:1) = 0.32. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.54-7.52 (2H, d, *J* = 6.8 Hz), 7.33-7.30 (2H, m), 7.20 (1H, s), 7.12-7.09 (1H, m), 5.82 (1H, ddt, *J* = 17.5, 10.3, 6.8 Hz), 5.11 (1H, ddt, *J* = 17.5, 1.5, 1.5 Hz), 5.05 (1H, ddt, *J* = 10.3, 1.5, 1.5 Hz), 2.49-2.43 (1H, m), 2.30-2.21 (2H, m), 1.76-1.71 (1H, m), 1.56-1.53 (1H, m), 1.37-1.26 (4H, m), 0.89 (3H, t, *J* = 6.8 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.5, 135.6, 128.9, 124.2, 119.9, 117.0, 48.8, 37.2, 32.2, 29.7, 27.4, 22.7, 13.9. IR ν_{max} (thin film) 3305, 3054, 2958, 2930, 2859, 2305, 1661, 1600,

1541, 1441, 1309, 1264, 1176, 896, 742, 703 cm^{-1}. HRMS (ES^+) calc. for $C_{15}H_{22}NO$ $[M+H]^+$ 232.1707 found 232.1700.

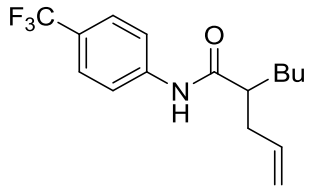
2-Allyl-hexanoic acid (4-fluoro-phenyl)-amide (2b)



The title compound was prepared by general procedure D from (4-fluoro-phenyl)-hex-1-ynyl-carbamic acid allyl ester **(1b)** (100 mg, 0.36 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2b)** (80.0 mg, 89%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.50. ^{1}H-NMR (400 MHz, $CDCl_3$) δ; 7.50-7.44 (2H, m), 7.25 (1H, s), 7.03-6.97 (2H, m), 5.80 (1H, ddt, *J* = 17.2, 10.3, 7.0 Hz), 5.11 (1H, ddt, *J* = 17.2, 1.5, 1.5 Hz), 5.05 (1H, ddt, *J* = 10.3, 1.5, 1.5 Hz), 2.48-2.40 (1H, m), 2.31-2.20 (2H, m), 1.77-1.66 (1H, m), 1.58-1.47 (1H, m), 1.38-1.25 (4H, m), 0.89 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.6, 159.4 (d, J_{C-F} = 242.4 Hz), 135.6, 133.7 (d, J_{C-F} = 2.6 Hz), 121.8 (d, J_{C-F} = 8.0 Hz), 117.1, 115.5 (d, J_{C-F} = 22.4 Hz), 48.6, 37.2, 32.3, 29.7, 22.7, 13.9. IR ν_{max} (thin film) 3426, 3312, 3054, 2959, 2932, 2860, 2301, 1666, 1509, 1406, 1226, 1265, 1212, 896, 919, 834, 741, 704, 516 cm^{-1}. HRMS (ES^+) calc. for $C_{15}H_{21}NOF$ $[M+H]^+$ 250.1607 found 250.1601.

2-allyl-*N*-(4-(trifluoromethyl)phenyl)hexanamide (2c)

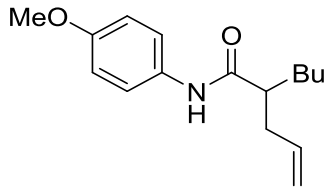


The title compound was prepared by general procedure D from allyl hex-1-yn-1-yl(4-trifluoromethyl)phenyl)carbamate **(1c)** (100 mg, 0.31 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2c)** (59.0 mg, 64%) as a yellow solid.

R_f: (Hexanes/EtOAc 5:1) = 0.66. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.67-7.65 (2H, m), 7.58-7.55 (2H, m), 7.53 (1H, s), 5.80 (1H, ddt, *J* = 17.1, 10.0, 6.9 Hz), 5.11 (1H, ddt, *J* = 17.1, 1.4, 1.4 Hz), 5.05 (1H, ddt, *J* = 10.0, 1.4, 1.4 Hz), 2.48-2.41 (1H, m), 2.33-2.26 (2H, m), 1.77-1.71 (1H, m), 1.58-1.50 (1H, m), 1.37-1.28 (4H, m), 0.89 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (125 MHz,

$CDCl_3$) δ 174.1, 140.8, 135.3, 128.4 (q, J_{C-F} = 270.1 Hz), 126.1 (J_{C-F} = 4.3 Hz), 126.0 (J_{C-F} = 33.3 Hz), 119.5, 117.2, 48.7, 37.1, 32.2, 29.6, 22.6, 13.8. IR ν_{max} (thin film) 3304, 3208, 3134, 3073, 2958, 2931, 2859, 1668, 1603, 1537, 1410, 1328, 1256, 1165, 1117, 1065, 917, 843 cm^{-1}. HRMS (ES^+) calc. for $C_{16}H_{20}NOF_3$ $[M+H]^+$ 300.1570 found 300.1560.

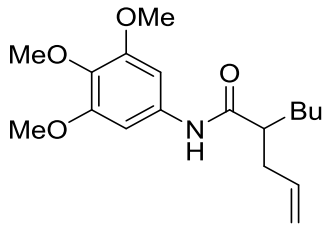
2-Allyl-hexanoic acid (4-methoxy-phenyl)-amide (2d)



The title compound was prepared by general procedure D from hex-1-ynyl-(4-methoxy-phenyl)-carbamic acid allyl ester **(1d)** (55.0 mg, 0.19 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 15:1) to afford **(2d)** (35.0 mg, 70%) as a colorless oil.

R_f: (Hexanes/EtOAc 5:1) = 0.41. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.43-7.40 (2H, m), 7.29 (1H, s), 6.85-6.82 (2H, m), 5.81 (1H, ddt, *J* = 17.0, 10.3, 6.7 Hz), 5.10 (1H, ddtt, *J* = 17.0, 1.5, 1.5 Hz), 5.03 (1H, ddt, *J* = 10.3, 1.5, 1.5 Hz), 3.79 (3H, s), 2.44 (1H, m), 2.28-2.20 (2H, m), 1.75-1.69 (1H, m), 1.54-1.48 (1H, m), 1.37-1.26 (4H, m), 0.88 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 173.4, 156.3, 135.7, 130.9, 121.8, 116.8, 114.0, 55.4, 48.4, 37.2, 32.2, 29.7, 22.7, 13.9. IR ν_{max} (thin film) 3054, 2987, 2305, 1513, 1265, 1421, 896, 743 cm^{-1}. HRMS (ES^+) calc. for $C_{16}H_{24}NO_2$ $[M+H]^+$ 262.1807 found 262.1807.

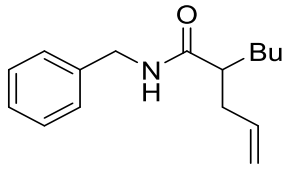
2-Allyl hexanoic acid (3,4,5-trimethoxy-phenyl)-amide (2e)



The title compound was prepared by general procedure D from hex-1-ynyl-(3,4,5-trimethoxy-phenyl)-carbamic acid allyl ester **(1e)** (180 mg, 0.52 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2e)** (165 mg, 74%) as a colorless oil.

R_f: (Hexanes/EtOAc 1:1) = 0.45. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.13 (1H, s), 6.87 (2H, s), 5.82 (1H, ddt, *J* = 17.5, 10.3, 6.8 Hz), 5.12, (1H, ddt, *J* = 17.5, 1.5, 1.5 Hz), 5.05 (1H, ddt, *J* = 10.3, 1.5, 1.5 Hz), 3.85 (6H, s), 3.81 (3H, s), 2.49-2.42 (1H, m), 2.30-2.17 (2H, m), 1.77-1.68 (1H, m), 1.57-1.49 (1H, m), 1.39-1.24 (4H, m), 0.89 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.6, 153.3, 135.6, 134.6, 133.9, 117.1, 97.3, 60.9, 56.1, 49.0, 37.2, 32.3, 29.7, 22.7, 13.9. IR ν_{max} (thin film) 3315, 3146, 3076, 2956, 2933, 1659, 1609, 1544, 1508, 1452, 1412, 1233, 1129, 1006 cm^{-1}. HRMS (ES$^+$) calc. for $C_{18}H_{28}NO_4$ $[M+H]^+$ 322.2018 found 322.2009.

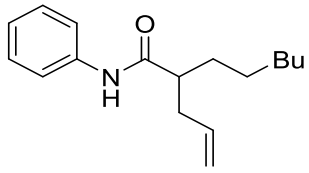
2-Allyl-hexanoic acid benzylamide (2f)



The title compound was prepared by general procedure D from benzyl-hex-1-ynyl-carbamic acid allyl ester **(1f)** (100 mg, 0.37 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2f)** (51.0 mg, 56%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.62. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (5H, m), 5.95 (1H, s), 5.74 (1H, ddt, *J* = 17.2, 10.3, 6.8 Hz), 5.05 (1H, ddt, *J* = 17.2, 1.6, 1.6 Hz), 4.99 (1H, ddt, *J* = 10.3, 1.6. 1.6 Hz), 4.44-4.42 (1H, d, *J* = 1.6 Hz) 4.42-4.41 (1H, d, *J* = 1.6 Hz), 2.37 (1H, ddd, *J* = 14.6, 7.6, 7.6 Hz), 2.19 (1H, ddd, *J* = 14.6, 7.6, 7.6 Hz), 2.12 (1H, tt, *J* = 7.6, 5.2 Hz), 1.69-1.60 (1H, m), 1.47-1.41 (1H, m), 1.32-1.19 (4H, m), 0.87 (3H, t, *J* = 7.0 Hz).). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.0, 138.4, 135.9, 128.5, 127.8, 127.3, 116.6, 47.7, 43.3, 37.1, 32.1, 29.7, 22.6, 13.9. IR ν_{max} (thin film) 3284, 3076, 2956, 2930, 2858, 1643, 1550, 1454, 1254, 1029, 994, 914, 736, 697 cm^{-1} HRMS (ES$^+$) calc. for $C_{16}H_{23}NONa$ $[M+Na]^+$ 268.1677 found 268.1665.

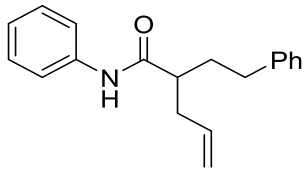
2-allyl-*N*-phenyloctamide (2g)



The title compound was prepared by general procedure D from allyl oct-1-yn-1-yl(phenyl)carbamate **(1g)** (125 mg, 0.44 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2g)** (89.0 mg, 78%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.61. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.52 (2H, m), 7.34 (1H, s), 7.32-7.29 (2H, m), 7.11-7.09 (1H, m), 5.82 (1H, ddt, *J* = 17.1, 10.1, 6.9 Hz), 5.11 (1H, ddt, *J* = 17.1, 1.4, 1.4 Hz), 5.05-5.03 (1H, m), 2.49-2.41 (1H, m), 2.30-2.23 (2H, m), 1.77-1.69 (1H, m), 1.55-1.48 (1H, m), 1.37-1.22 (6H, m), 0.87 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.6, 137.8, 125.6, 128.9, 124.2, 119.9, 116.9, 48.7, 37.1, 32.5, 31.6, 29.3, 27.5, 22.5, 14.0. IR ν_{max} (thin film) 3299, 3198, 3139, 3070, 2956, 2928, 2859, 1714, 1662, 1599, 1541, 1499, 1439, 1378, 1309, 1250, 1180, 992, 915, 755, 691cm^{-1}. HRMS (ES$^+$) calc. for $C_{17}H_{25}NO$ $[M+H]^+$ 260.2009 found 260.2002.

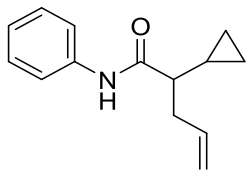
2-Phenethyl-pent-4-enoic acid phenylamide (2h)



The title compound was prepared by general procedure D from Phenyl-(4-phenyl-but-1-ynyl)-carbamic acid allyl ester **(1h)** (122 mg, 0.44 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2h)** (112 mg, 83%) as a colorless oil.

R_f: (Hexanes/EtOAc 5:1) = 0.46. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.56 (2H, d, *J* = 8.0 Hz), 7.47 (1H, s), 7.35-7.29 (4H, m), 7.24-7.19 (3H, m), 7.16-7.11 (1H, m), 5.80 (1H, ddt, *J* = 17.5, 10.3, 7.0 Hz), 5.12 (1H, ddt, *J* = 17.5, 1.5, 1.5 Hz), 5.06 (1H, ddt, *J* = 10.3, 1.5, 1.5 Hz), 2.81-2.74 (1H, m), 2.66-2.60 (1H, m), 2.56-2.47 (1H, m), 2.34-2.28 (2H, m), 2.11 (1H, ddt, *J* = 17.5, 7.0, 5.0 Hz), 1.91-1.84 (1H, m). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.2, 141.3, 137.7, 135.3, 128.9, 128.4, 128.3, 125.9, 124.2, 120.0, 117.1, 47.4, 37.2, 33.6, 33.9. IR ν_{max} (thin film) 3054, 2986, 2929, 2305, 1689, 1598, 1521, 1439, 1265, 896, 744, 704 cm^{-1}. HRMS (ES$^+$) calc. for $C_{19}H_{22}NO$ $[M+H]^+$ 280.1701 found 280.1697.

2-cyclopropyl-*N*-phenylpent-4-enamide (2i)

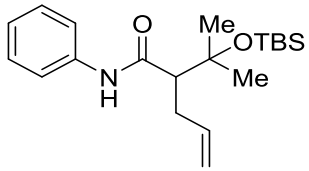


The title compound was prepared by general procedure D from allyl (cyclopropylethynyl)(phenyl)carbamate **(1i)** (265 mg, 1.10 mmol). The crude product was

purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2i)** (164 mg, 69%) as a colorless solid.

R_f: (Hexanes/EtOAc 5:1) = 0.45. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.67 (1H, s), 7.56-7.53 (2H, m), 7.33-7.29 (2H, m), 7.12-7.09 (1H, m), 5.88 (1H, ddt, *J* = 17.2, 10.0, 7.1 Hz), 5.13 (1H, ddt, *J* = 17.2, 1.5, 1.5 Hz), 5.04 (1H, ddt, *J* = 10.0, 1.5, 1.5 Hz), 2.63-2.57 (1H, m), 2.54-2.48 (1H, m), 1.65-1.60 (1H, m), 1.05-1.01 (1H, m), 0.69-0.60 (2H, m), 0.37-0.33 (1H, m), 0.27-0.22 (1H, m). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.8, 137.8, 135.6, 128.8, 124.1, 119.9, 116.8, 52.8, 36.7, 13.2, 4.7, 4.0. IR ν_{max} (thin film) cm^{-1}. 3299, 1708, 1663, 1596, 1540, 1501, 1440, 1375, 1298, 1246, 1176, 1026, 997, 916, 822, 752, 692. HRMS (ES$^+$) calc. for $C_{14}H_{17}NO$ $[M+H]^+$ 216.1383 found 216.1376.

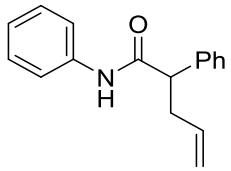
2-[1-(*tert*-Butyl-dimethyl-silanyloxy)-1-methyl-ethyl]-pent-4-enoic acid phenylamide (2j)



The title compound was prepared by general procedure D from [3-(*tert*-Butyl-dimethyl-silanyloxy)-3-methyl-but-1-ynyl]-phenyl-carbamic acid allyl ester **(1j)** (100 mg, 0.27 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2j)** (52.0 mg, 54%) as a colorless oil.

R_f: (Hexanes/EtOAc 5:1) = 0.53. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.92 (1H, s), 7.53-7.50 (2H, m), 7.34-7.29 (2H, m), 7.11-7.09 (1H, m), 5.85 (1H, ddt, *J* = 17.0, 10.0, 7.3 Hz), 5.11 (1H, ddt, *J* = 17.0, 1.4, 1.6 Hz), 5.03 (1H, ddt, *J* = 10.0, 1.4, 1.4 Hz) 2.52-2.47 (2H, m), 2.32 (1H, dd, *J* = 8.9, 6.8 Hz), 1.43 (3H, s), 1.39 (3H, s), 0.96 (9H, s), 0.18 (3H, s), 0.17 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.8, 135.8, 128.9, 123.9, 119.9, 116.7, 74.9, 61.1, 32.8, 28.9, 28.2, 25.9, 18.2, -2.0 IR ν_{max} (thin film) 3054, 2986, 2957, 2931, 2865, 2305, 1654, 1265, 1041, 896, 831, 747 cm^{-1}. HRMS (ES$^+$) calc. for $C_{20}H_{33}NO_2SiNa$ $[M+Na]^+$ 370.2178 found 370.2162.

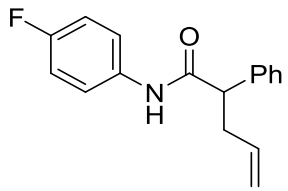
2-Phenyl-pent-4-enoic acid phenylamide (2k)



The title compound was prepared by general procedure D from phenyl-phenylethynyl-carbamic acid allyl ester **(1k)** (130 mg, 0.47 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2k)** (86.0 mg, 73%) as a colorless oil.

R_f: (Hexanes/EtOAc 5:1) = 0.50. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.43-7.42 (2H, m), 7.37-7.36 (4H, m), 7.31-7.25 (3H, m), 7.15 (1H, s), 7.06 (1H, t, *J* = 5.5 Hz), 5.76 (1H, ddt, *J* = 17.0, 10.3, 7.6 Hz), 5.09 (1H, ddt, *J* = 17.0, 1.4, 1.4 Hz), 5.01 (1H, ddt, *J* = 10.3, 1.4, 1.4 Hz), 3.57 (1H, dd, *J* = 8.2, 7.6 Hz), 3.00 (1H, ddd, *J* = 14.1, 6.9, 6.9 Hz), 2.59 (1H, ddd, *J* = 14.1, 6.9, 6.9 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.9, 138.9, 137.7, 135.6, 129.0, 128.8, 128.0, 127.6, 124.2, 119.7, 117.1, 54.1, 37.4. IR ν_{max} (thin film) 3302, 2924, 1660, 1599, 1543, 1495, 1441, 1262, 750, 697 cm^{-1}. HRMS (ES$^+$) calc. for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1388 found 252.1381.

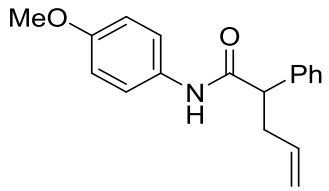
2-Phenyl-pent-4-enoic acid (4-fluoro-phenyl)-amide (2l)



The title compound was prepared by general procedure D from (4-fluoro-phenyl)-phenylethynyl-carbamic acid allyl ester **(1l)** (100 mg, 0.34 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2l)** (74.0 mg, 81%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.47. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.40-7.33 (7H, m), 7.05 (1H, s), 6.99-6.94 (2H, m), 5.76 (1H, ddt, *J* = 17.1, 10.4, 7.0 Hz), 5.10 (1H, ddt, *J* = 17.1, 1.5, 1.5 Hz), 5.01 (1H, ddt, *J* = 10.4, 1.5, 1.5 Hz), 3.56 (1H, dd, *J* = 8.9, 7.0 Hz), 3.03-2.98 (1H, m), 2.62-2.57 (1H, m). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.0, 159.2 (d, J_{C-F} = 242.4 Hz), 138.9 (d, J_{C-F} = 2.0 Hz), 135.5, 133.6, 129.0, 128.0, 127.6, 121.6 (d, J_{C-F} = 7.0 Hz), 117.0, 115.5 (d, J_{C-F} = 22.2 Hz), 53.9, 37.4. IR ν_{max} (thin film) 3292, 2929, 2359, 2340, 1651, 1557, 1537, 1507 cm^{-1}. HRMS (ES$^+$) calc. for $C_{17}H_{17}NOF$ $[M+H]^+$ 270.1289 found 270.1298.

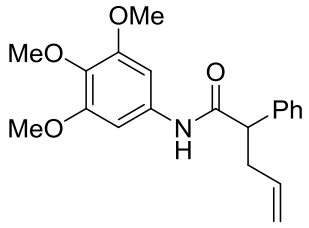
2-Phenyl-pent-4-enoic acid (4-methoxy-phenyl)-amide (2m)



The title compound was prepared by general procedure D from (4-methoxy-phenyl)-phenylethynyl-carbamic acid allyl ester **(1m)** (120 mg, 0.39 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 15:1) to afford **(2m)** (73.0 mg, 67%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.26. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38-7.29 (7H, m), 7.06 (1H, s), 6.83-6.79 (2H, m), 5.77 (1H, ddt, *J* = 17.5, 10.4, 6.5 Hz), 5.09 (1H, ddt, *J* = 17.5, 1.3, 1.3 Hz), 5.05 (1H, ddt, *J* = 10.4, 1.3, 1.3 Hz), 3.76 (3H, s), 3.55 (1H, dd, *J* = 10.0, 7.5 Hz), 3.00 (1H, m), 2.59 (1H, m). ^{13}C-NMR (125MHz, $CDCl_3$) δ 170.7, 156.4, 139.1, 135.7, 130.8, 128.9, 128.0, 127.5, 121.6, 116.9, 114.0, 55.4, 53.9, 37.4. IR ν_{max} (thin film) 3287, 2920, 2356, 2337, 1654, 1537, 1509, 1295, 1242, 1171 cm^{-1}. HRMS (ES$^+$) calc. for $C_{18}H_{20}NO_2$ $[M+H]^+$ 282.1494 found 282.1489.

2-Phenyl-pent-4-enoic acid (3,4,5-trimethoxy-phenyl)-amide (2n)

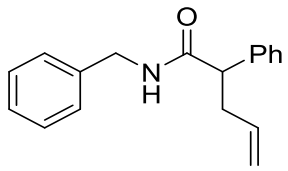


The title compound was prepared by general procedure D from phenylethynyl-(3,4,5-trimethoxy-phenyl)-carbamic acid allyl ester **(1n)** (90.0 mg, 0.24 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2n)** (62.0 mg, 76%) as a colorless oil.

R_f: (Hexanes/EtOAc 1:1) = 0.45. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.39-7.33 (4H, m), 7.32-7.29 (1H, m), 7.17 (1H, s), 6.77 (2H, s), 5.76 (1H, ddt, *J* = 17.0, 10.3, 7.0 Hz), 5.09 (1H, ddt, *J* = 17.0, 1.5, 1.5 Hz), 5.01 (1H, ddt, *J* = 10.3, 1.5, 1.5 Hz), 3.80 (6H, s), 3.78 (3H, s), 3.55 (1H, dd, *J* = 10.3, 7.0 Hz), 2.99 (1H, m), 2.59 (1H,m). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.9, 153.2, 135.5, 133.9, 129.0, 128.0, 127.6, 117.0, 97.2, 60.9, 56.0, 54.2, 44.3, 37.4, 24.9. IR ν_{max} (thin

film) 3420, 3331, 3054, 2986, 2939, 2840, 2684, 2304, 1686, 1605, 1507, 1130, 745, 703 cm^{-1}. HRMS (ES^+) calc. for $C_{20}H_{24}NO_4$ $[M+H]^+$ 342.1705 found 342.1712.

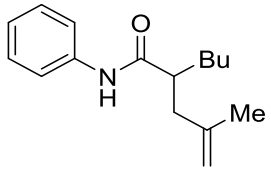
2-Phenyl-pent-4-enoic acid benzylamide (2o)



The title compound was prepared by general procedure D from benzyl-phenyl-ethynyl-carbamic acid allyl ester **(1o)** (80.0 mg, 0.27 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2o)** (50.0 mg, 70%) as a yellow oil.

R_f: (Hexanes/EtOAc 5:1) = 0.26. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35-7.21 (8H, m), 7.14-7.12 (2H, m), 5.76 (1H, m), 5.72 (1H, ddt, *J* = 17.5, 10.0, 7.0 Hz), 5.06 (1H, ddt, *J* = 17.5, 1.5, 1.5 Hz), 4.98 (1H, ddt, *J* = 10.0, 1.2, 1.2 Hz), 4.43 (1H, dd, *J* = 15.0, 5.5 Hz), 4.33 (1H, dd, *J* = 15.0, 5.5 Hz), 3.44 (1H, dd, *J* = 7.3, 7.3 Hz), 2.97 (1H, ddddd, *J* = 14.7, 7.3, 7.3, 1.2, 1.2 Hz), 2.56 (1H, ddddd, *J* = 14.7, 7.3, 7.3, 1.2, 1.2 Hz). ^{13}C-NMR (125 MHz, CDCl3) δ 172.6, 139.3, 138.1, 135.8, 128.8, 128.5, 128.0, 127.4, 127.3, 116.7, 53.2, 43.5, 37.3, 24.8. IR ν_{max} (thin film) 3301, 3068, 2916, 2358, 2336, 1648, 1558, 1539 cm^{-1}. HRMS (ES^+) calc. for $C_{18}H_{20}NO$ $[M+H]^+$ 266.1539 found 266.1542.

2-(2-Methyl-allyl)-hexanoic acid phenylamide (2p)

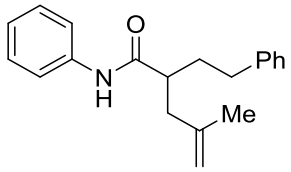


The title compound was prepared by general procedure D from hex-1-ynyl-phenyl carbamic acid 2-methyl-allyl ester **(1p)** (128 mg, 0.47 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2p)** (78.0 mg, 67%) as a colorless oil.

R_f: (Hexanes/EtOAc 5:1) = 0.60. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.51 (2H, d, *J* = 7.0 Hz), 7.33-7.29 (2H, m), 7.21 (1H, s), 7.12-7.08 (1H, m), 4.82-4.80 (1H, m), 4.79-4.77 (1H, m), 2.47-2.34 (2H, m), 2.22 (1H, dd, *J* = 14.0, 5.0 Hz), 1.76 (s, 3H) 1.74-1.71 (1H, m), 1.55-1.47 (1H, m), 1.40-1.28 (4H, m), 0.89 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.7, 143.1, 137.8, 128.9, 124.2, 119.9, 112.5, 47.2, 41.0, 32.5, 29.7, 22.7, 22.5, 13.9. IR ν_{max} (thin film) 3054,

2933, 2986, 2960, 2305, 1688, 1597, 1521, 1439, 1265, 896, 745 cm^{-1}. HRMS (ES^+) calc. for $C_{16}H_{24}NO$ $[M+H]^+$ 246.1858 found 246.1852.

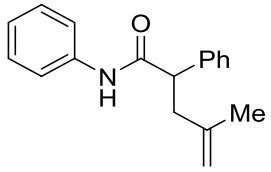
4-Methyl-2-phenethyl-pent-4-enoic acid phenylamide (2q)



The title compound was prepared by general procedure D from phenyl-(4-phenyl-but-1-ynyl)-carbamic acid 2-methyl-allyl ester **(1q)** (100 mg, 0.31 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2q)** (59.0 mg, 64%) as a colorless oil.

R_f: (Hexanes/EtOAc 5:1) = 0.42. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (2H, m), 7.37-7.28 (4H, m), 7.23-7.18 (3H, m), 7.14-7.10 (1H, m), 7.06 (1H, s), 4.82-4.81 (1H, m), 4.78-4.76 (1H, m), 2.82-2.75 (1H, m), 2.66-2.58 (1H, m), 2.49-2.44 (1H, m), 2.40-2.39 (1H, m), 2.28-2.23 (1H, m), 2.13-2.03 (1H, m), 1.91-1.83 (1H,m), 1.72 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.3, 142.8, 141.6, 137.7, 128.9, 128.4, 128.4, 126.0, 124.3, 119.9, 112.8, 46.0, 41.0, 33.7, 33.3, 22.5. IR ν_{max} (thin film) 3299, 3062, 3026, 2927, 2856, 1659, 1600, 1541, 1497, 1442, 1250, 894, 753, 697 cm^{-1}. HRMS (ES^+) calc. for $C_{20}H_{24}NO$ $[M+H]^+$ 294.1858 found 294.1860.

4-Methyl-2-phenyl-pent-4-enoic acid phenylamide (2r)

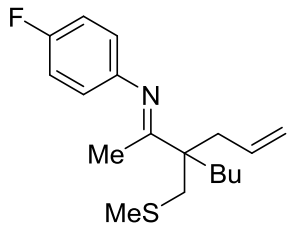


The title compound was prepared by general procedure D from phenyl-phenylethynyl-carbamic acid 2-methyl-allyl ester **(1r)** (130 mg, 0.44 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(2r)** (77.0 mg, 65%) as a colorless oil.

R_f: (Hexanes/EtOAc 5:1) = 0.60. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.44-7.25 (10H, m), 7.09-7.05 (1H, m), 4.76 (1H, s), 4.71 (1H, s), 3.75 (1H, t, *J* = 7.5 Hz), 3.03 (1H, dd, *J* = 14.0, 7.5 Hz), 2.56 (1H, dd, *J* = 14.0, 7.5 Hz), 1.73 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 142.8, 139.2, 137.8, 128.9, 128.8, 128.0, 127.5, 124.2, 119.8, 112.4, 52.6, 40.9, 22.6. IR ν_{max} (thin

film) 3055, 1662, 1598, 1524, 1497, 1440, 1265, 896, 749 cm^{-1}. HRMS (ES^+) calc. for $C_{18}H_{20}NO$ $[M+H]^+$ 266.1545 found 266.1540.

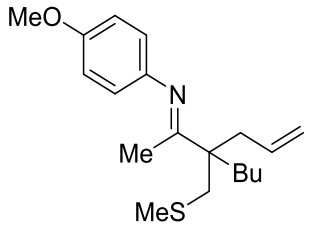
(2-Allyl-1-methyl-2-methylsulfanylmethyl-hexylidene)-(4-fluoro-phenyl)-imine (7a)



The title compound was prepared by general procedure E from (4-fluoro-phenyl)-hex-1-ynyl-carbamic acid allyl ester **(1b)** (100 mg, 0.36 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(7a)** (71.0 mg, 64%) as a yellow oil.

R_f: (Hexanes/EtOAc 9:1) = 0.82. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.01-6.95 (2H, m), 6.60-6.55 (2H, m), 5.75 (1H, ddt, *J* = 17.2, 10.0, 7.3 Hz), 5.17-5.09 (2H, m), 2.93 (1H, d, *J* = 12.5 Hz), 2.84 (1H, d, *J* = 12.5 Hz), 2.58 (1H, dd, *J* = 14.0, 7.3 Hz), 2.40 (1H, dd, *J* = 14.0, 7.3 Hz), 2.13 (3H, s), 1.75 (3H, s), 1.72-1.67 (1H, m), 1.62-1.55 (1H, m), 1.38-1.13 (4H, m), 0.93 (3H, t, *J* = 7.3 Hz).^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.1 159.0 (d, J_{C-F} = 240 Hz), 147.2 (d, J_{C-F} = 3.0 Hz), 133.8, 120.1 (d, J_{C-F} = 8.2 Hz), 117.8, 115.6 (d, J_{C-F} = 22.6 Hz), 50.2, 40.1, 39.0, 35.1, 26.0, 23.2, 17.1, 16.1, 14.0. IR ν_{max} (thin film) 2930, 1651, 1499, 1208, 843, 761 cm^{-1}. HRMS (ES^+) calc. for $C_{18}H_{27}NSF$ $[M+H]^+$ 308.1848 found 308.1837.

(2-Allyl-1-methyl-2-methylsulfanylmethyl-hexylidene)-(4-methoxy-phenyl)-imine (7b)

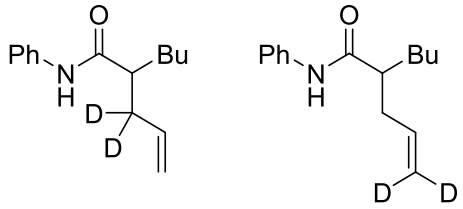


The title compound was prepared by general procedure E from hex-1-ynyl-(4-methoxy-phenyl)-carbamic acid allyl ester **(1d)** (70.0 mg, 0.24 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(7b)** (43.0 mg, 56%) as a yellow oil.

R_f: (Hexanes/EtOAc 9:1) = 0.49. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.87-6.83 (2H, m), 6.59-6.55 (2H, m), 5.76 (1H, ddt, *J* = 16.0, 10.0, 7.3 Hz), 5.17-5.09 (2H, m), 3.79 (3H, s), 2.90 (2H, m), 2.58 (1H, dd, *J* = 14.5, 7.3 Hz), 2.40 (1H, dd, *J* = 14.5, 7.3 Hz), 2.13 (3H, s), 1.75 (3H, s),

1.75-1.68 (1H, m), 1.62-1.54 (1H, m), 1.43-1.14 (4H, m), 0.93 (3H, t, J = 7.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.5, 155.5, 145.1, 134.0, 120.0, 117.7, 114.2, 55.4, 50.1, 40.0, 39.1, 35.1, 26.0, 23.1, 17.1, 15.9, 14.0. IR ν_{max} (thin film) 2957, 2931, 2859, 1647, 1606, 1502, 1466, 1440, 1363, 1265, 1240, 1180, 1102, 1037, 917, 843, 739, 704, 522 cm^{-1}. HRMS (ES$^+$) calc. for $C_{19}H_{29}NOSNa$ $[M+H]^+$ 342.1868 found 342.1866.

2-(allyl-1,1-*d*$_2$)-*N*-phenylhexanamide (8a) and 2-(allyl-3,3-*d*$_2$)-*N*-phenylhexanamide (8b)

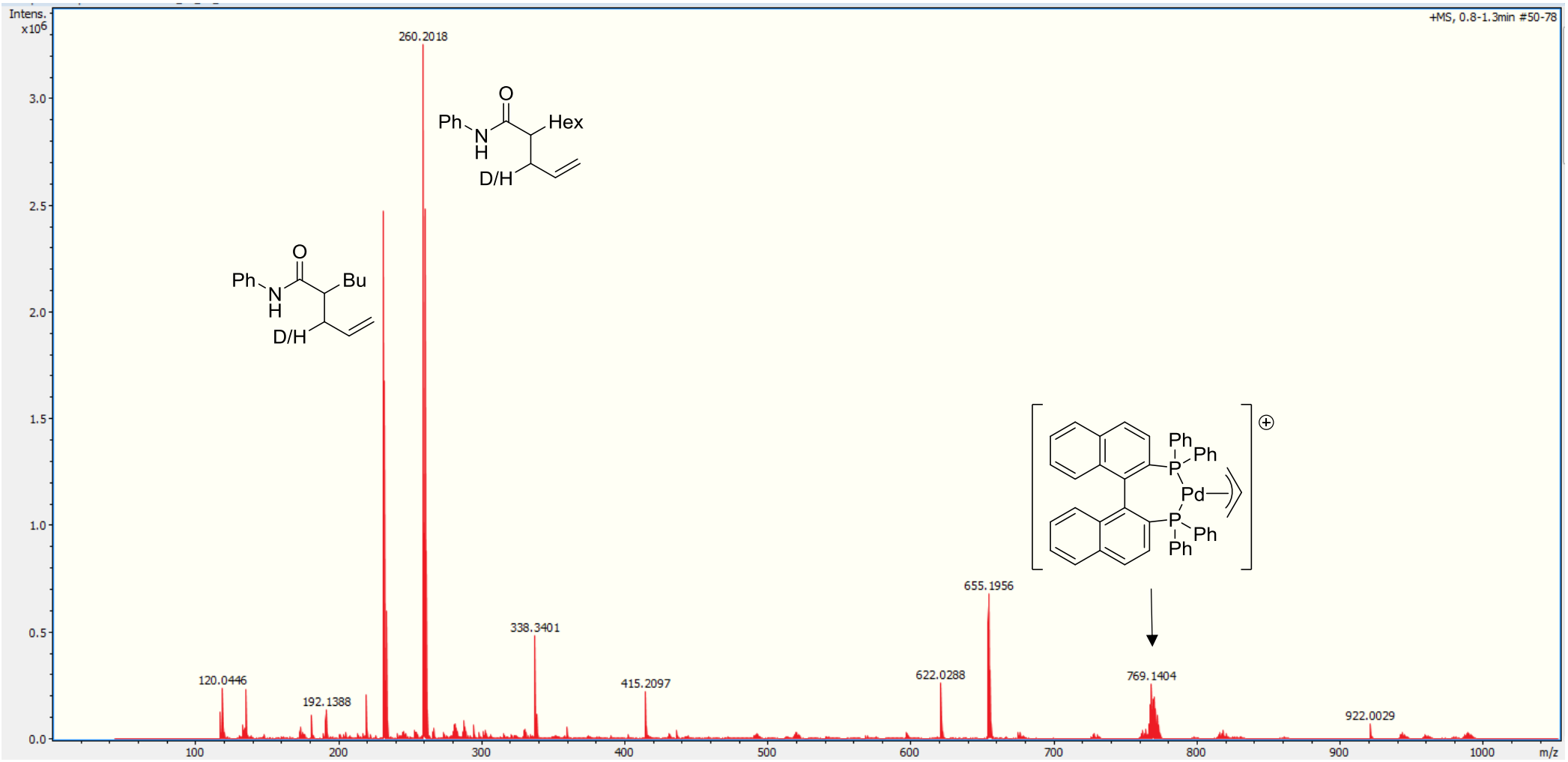


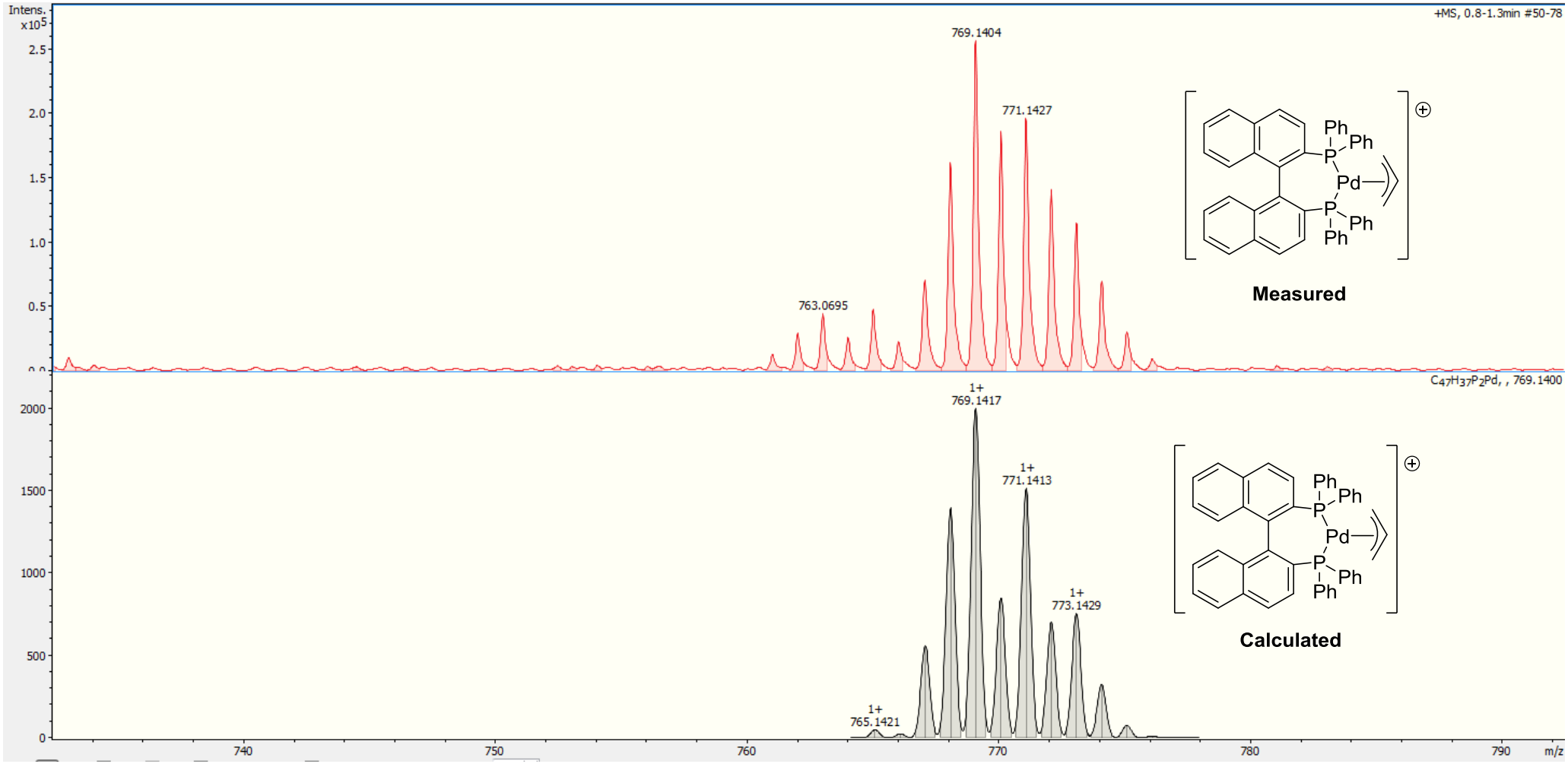
The title compound was prepared by general procedure D from allyl-1,1-*d*$_2$-hex-1-yn-1yl(phenyl)carbamate **(*d*$_2$-1a)** (60.0 mg, 0.23 mmol). The crude product was purified by silica chromatography (Hexanes/EtOAc 20:1) to afford **(8a/8b)** (46.0 mg, 48%, 55:45) as a colorless oil.

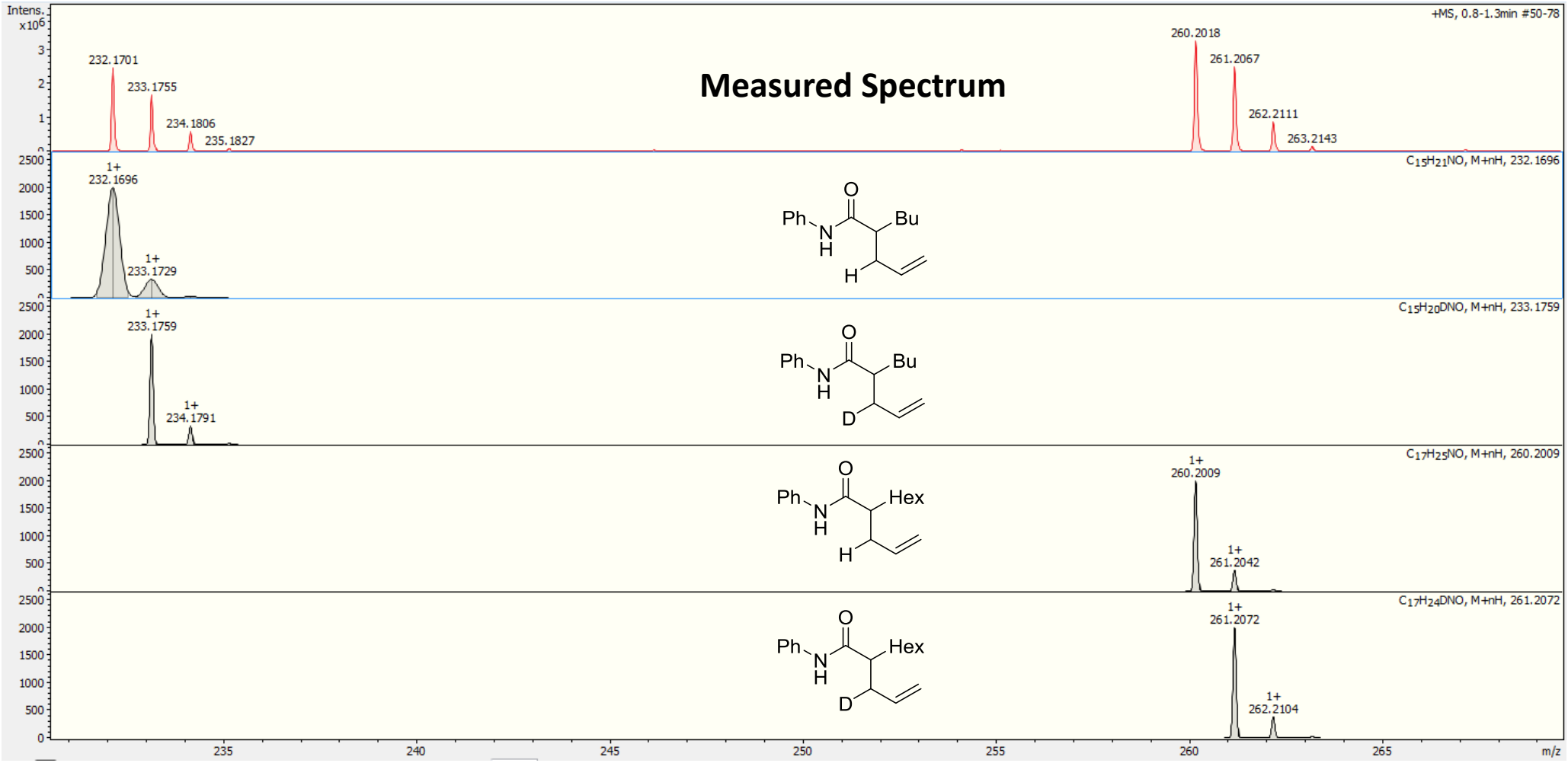
R_f: (Hexanes/EtOAc 5:1) = 0.53. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (2H, m), 7.34-7.30 (2H, m), 7.25 (1H, br. s), 7.12-7.09 (1H, m), 5.85-5.78 (1H, m), 5.15-5.09 (0.55H, m), 5.07-5.03 (0.55H, m), 2.49-2.42 (0.45H, m), 2.31-2.23 (1H, m), 1.80-1.69 (1H, m), 1.58-1.47 (1H, m), 1.39-1.30 (4H, m), 0.89 (3H, t, J = 7.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.6, 137.8, 135.5, 135.4, 128.9, 124.2, 119.9, 117.0, 48.7, 32.2, 29.7, 22.7, 13.9.

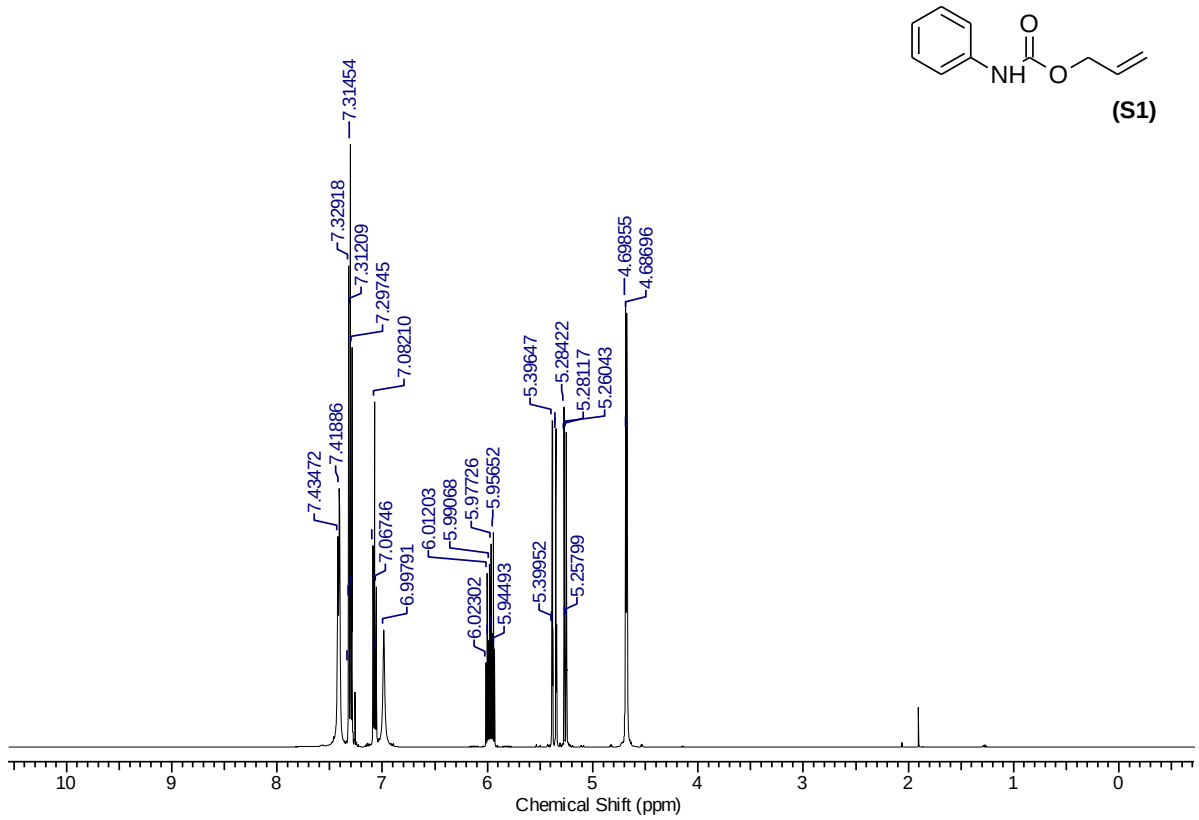
1. Zhang, Y.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C. M.; Vera, E. L., *Org. Lett.* **2004,** *6* (7), 1151-1154.
2. Hiroi, K.; Sato, S., *Chem. Pharm. Bull.* **1985,** *33* (6), 2331-2338.
3. Hemming, D. S.; Talbot, E. P.; Steel, P. G., *Tetrahedron Lett.* **2017,** *58* (1), 17-20.
4. Yoganathan, S.; Miller, S. J., *Org. Lett.* **2013,** *15* (3), 602-605.
5. Nicolaou, K. C.; Baran, P. S.; Zhong, Y. L.; Barluenga, S.; Hunt, K. W.; Kranich, R.; Vega, J. A., *J. Am. Chem. Soc.* **2002,** *124* (10), 2233-2244.
6. Jeon, K. O. Y., J. S.; Lee, C. K., *Bull. Korean. Chem. Soc* **2003,** *24* (12), 1845.
7. Biswas, B.; Collins, S. C.; Singleton, D. A., *J. Am. Chem. Soc.* **2014,** *136* (10), 3740-3743.
8. Niggemann, M.; Jelonek, A.; Biber, N.; Wuchrer, M.; Plietker, B., *J. Org. Chem.* **2008,** *73* (18), 7028-7036.
9. Fujihara, T.; Horimoto, Y.; Mizoe, T.; Sayyed, F. B.; Tani, Y.; Terao, J.; Sakaki, S.; Tsuji, Y., *Org. Lett.* **2014,** *16* (18), 4960-4963.

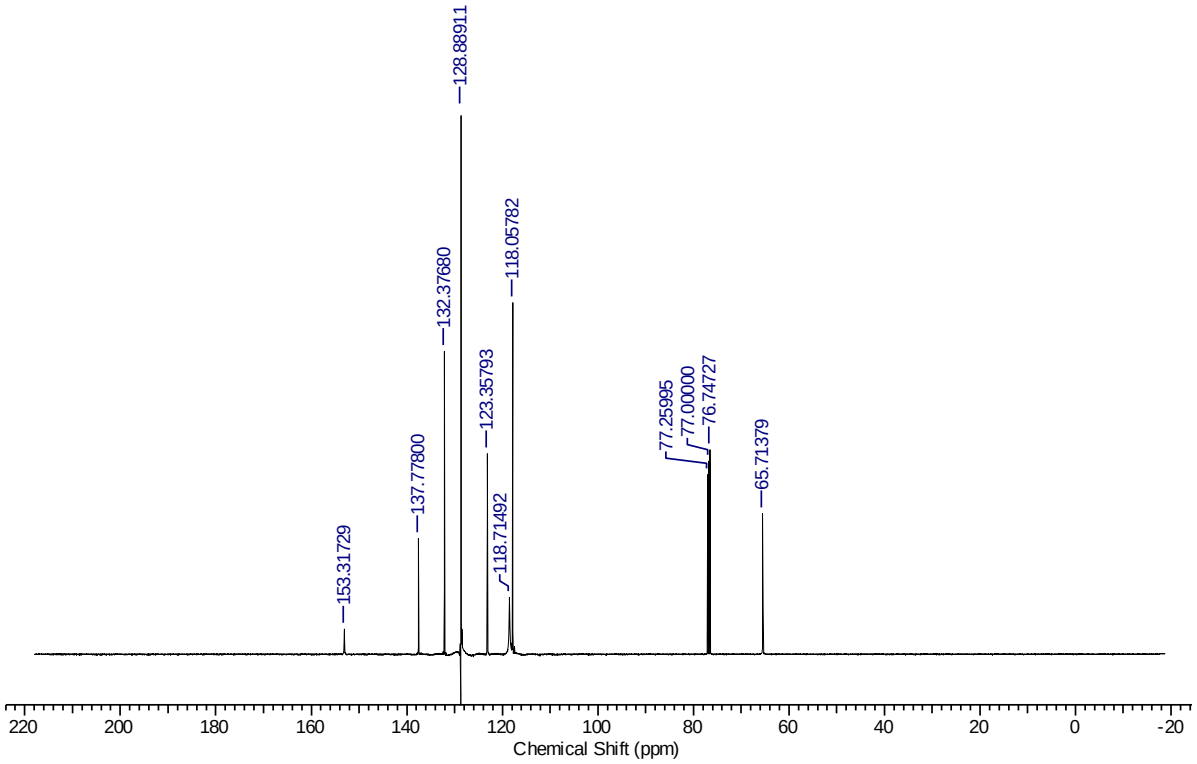
10. Nicolai, S.; Waser, J., *Org. Lett.* **2011,** *13* (23), 6324-6327.
11. Chen, X. Y.; Wang, L.; Frings, M.; Bolm, C., *Org. Lett.* **2014,** *16* (14), 3796-3799.
12. Marino, J. P.; Nguyen, H. N., *J. Org. Chem.* **2002,** *67* (19), 6841-6844.
13. Chen, K.; Shi, G.; Zhang, W.; Li, H.; Wang, C., *J. Am. Chem. Soc.* **2016,** *138* (43), 14198-14201.

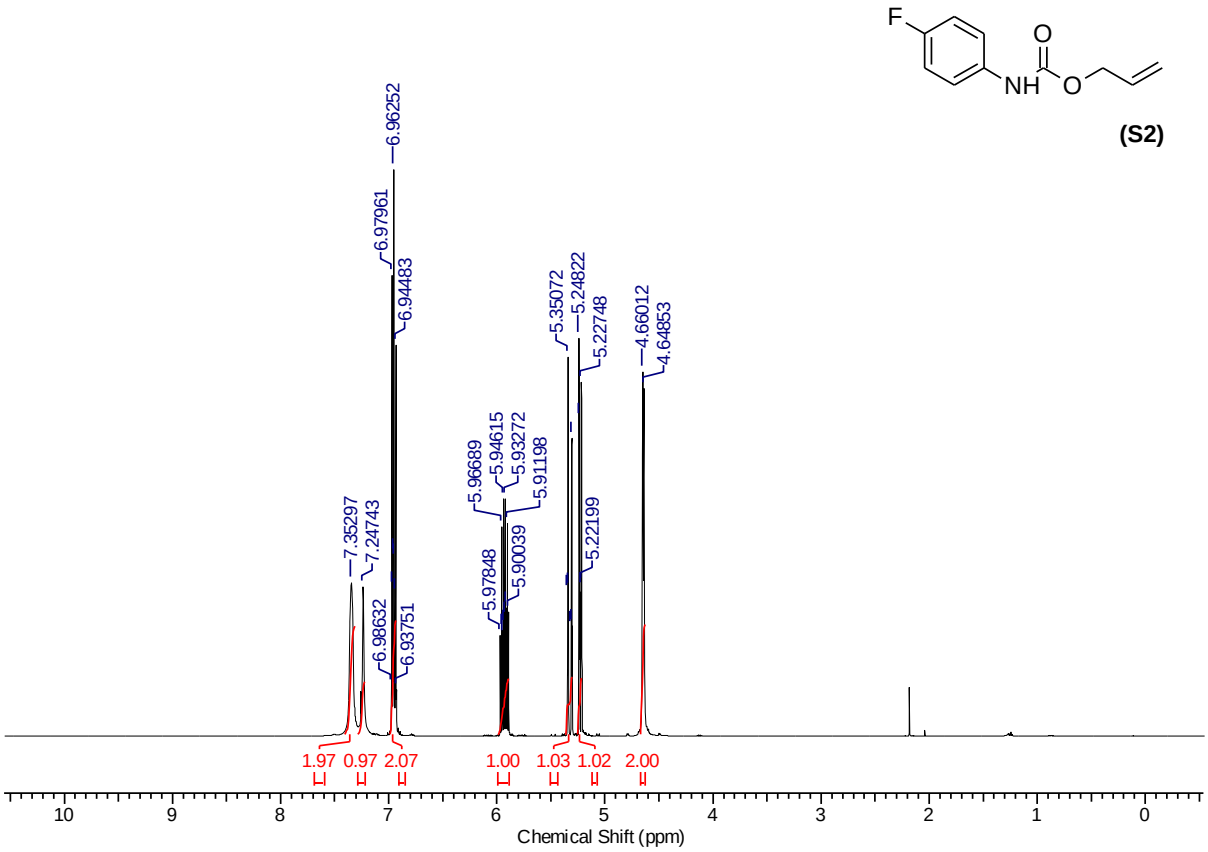

Intens.
x10^6
+MS, 0.8-1.3min #50-78
260.2018
338.3401
415.2097
622.0288
655.1956
769.1404
922.0029
120.0446
192.1388
Ph
N
H
O
Hex
D/H
Bu
Pd
P
Ph
m/z

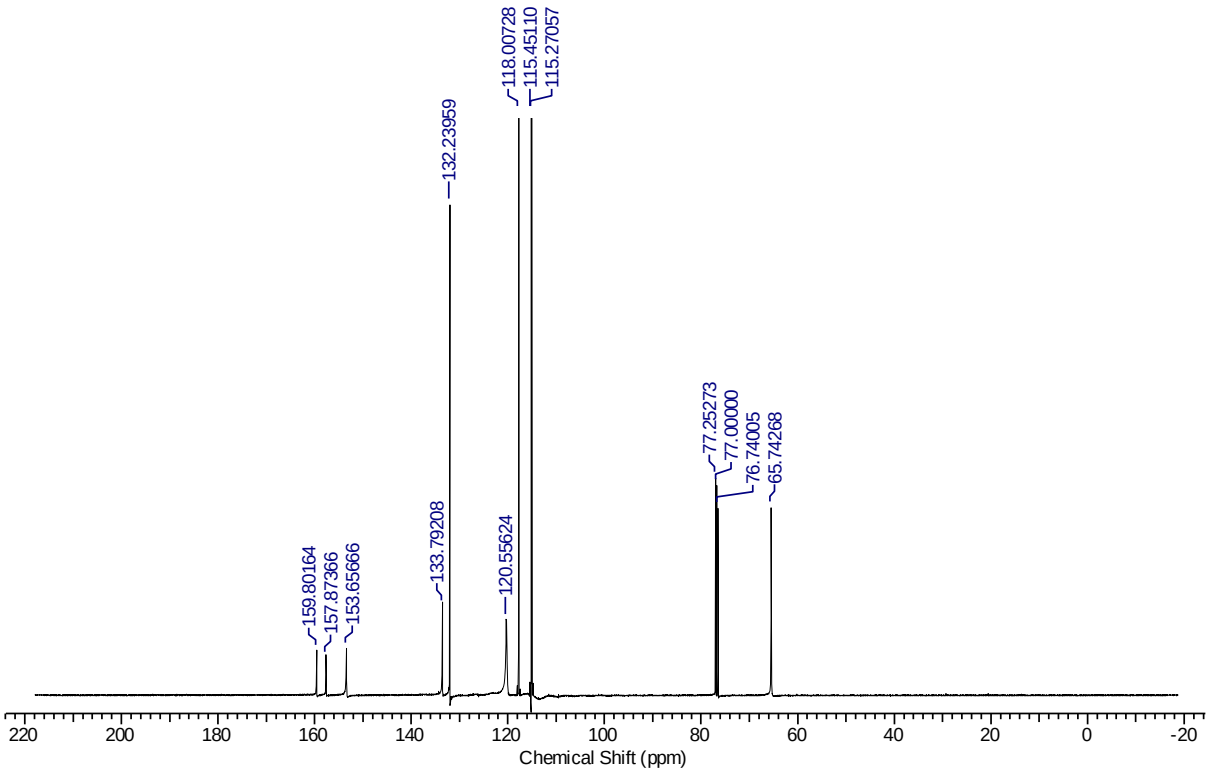

Intens.
x10^5
2.5
2.0
1.5
1.0
0.5
0.0
+MS, 0.8-1.3min #50-78
769.1404
771.1427
763.0695
Measured
C47H37P2Pd, , 769.1400
2000
1500
1000
500
0
1+
769.1417
1+
771.1413
1+
773.1429
1+
765.1421
Calculated
740
750
760
770
780
790
m/z

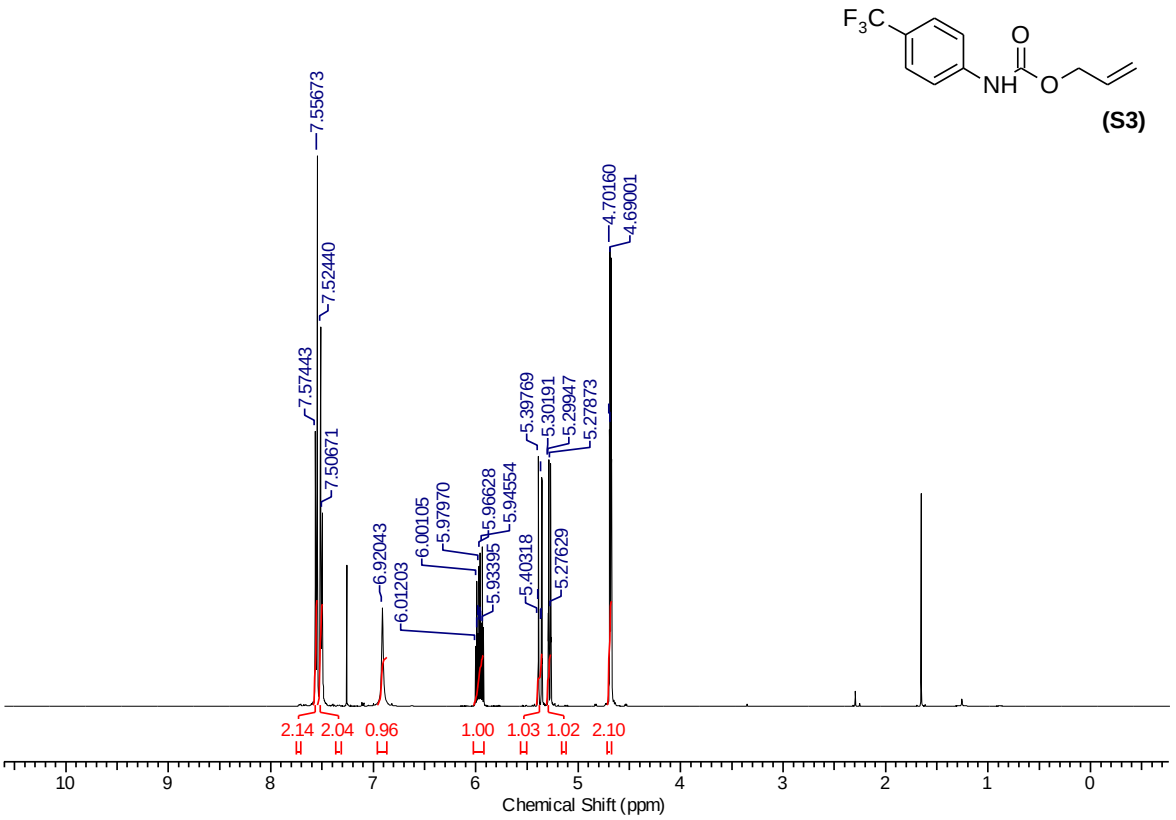

Measured Spectrum
Intens.
x10^6
+MS, 0.8-1.3min #50-78
232.1701
233.1755
234.1806
235.1827
260.2018
261.2067
262.2111
263.2143
C15H21NO, M+nH, 232.1696
1+
232.1696
1+
233.1729
C15H20DNO, M+nH, 233.1759
1+
233.1759
1+
234.1791
C17H25NO, M+nH, 260.2009
1+
260.2009
1+
261.2042
C17H24DNO, M+nH, 261.2072
1+
261.2072
1+
262.2104
m/z

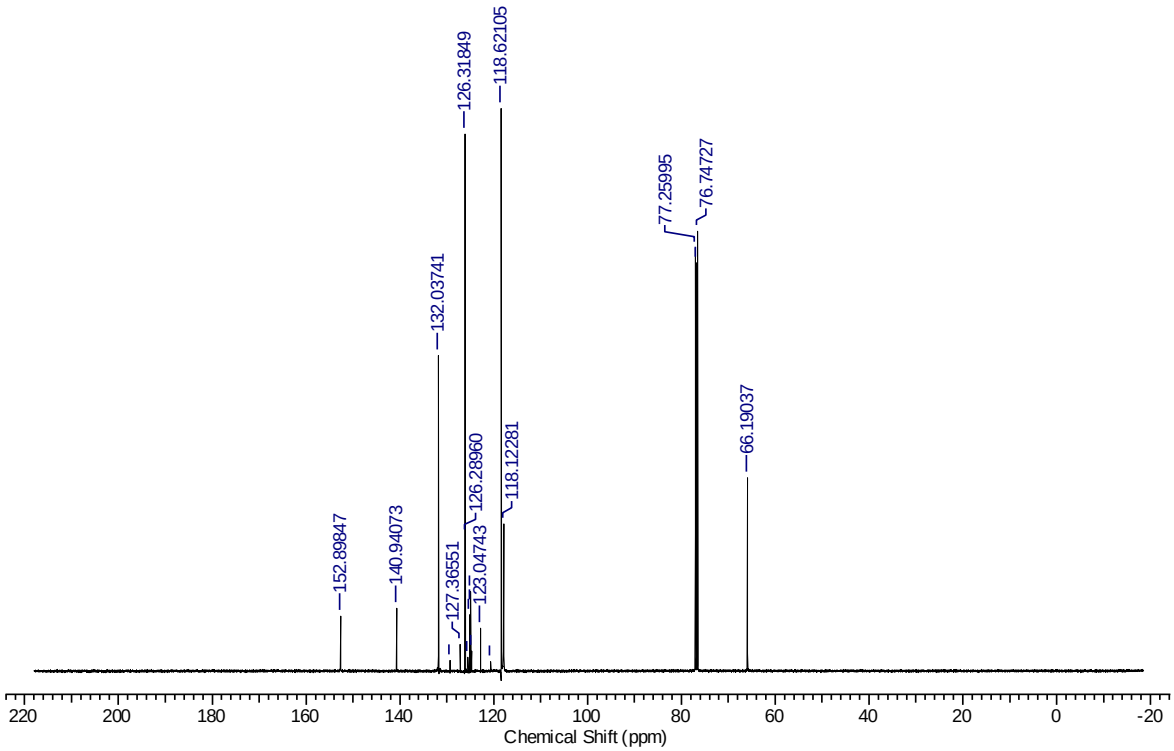

NH
O
O
(S1)
7.31454
7.32918
7.31209
7.29745
7.08210
7.41886
7.43472
7.06746
6.99791
6.01203
5.99068
5.97726
5.95652
6.02302
5.94493
5.39647
5.28422
5.28117
5.26043
5.39952
5.25799
4.69855
4.68696
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

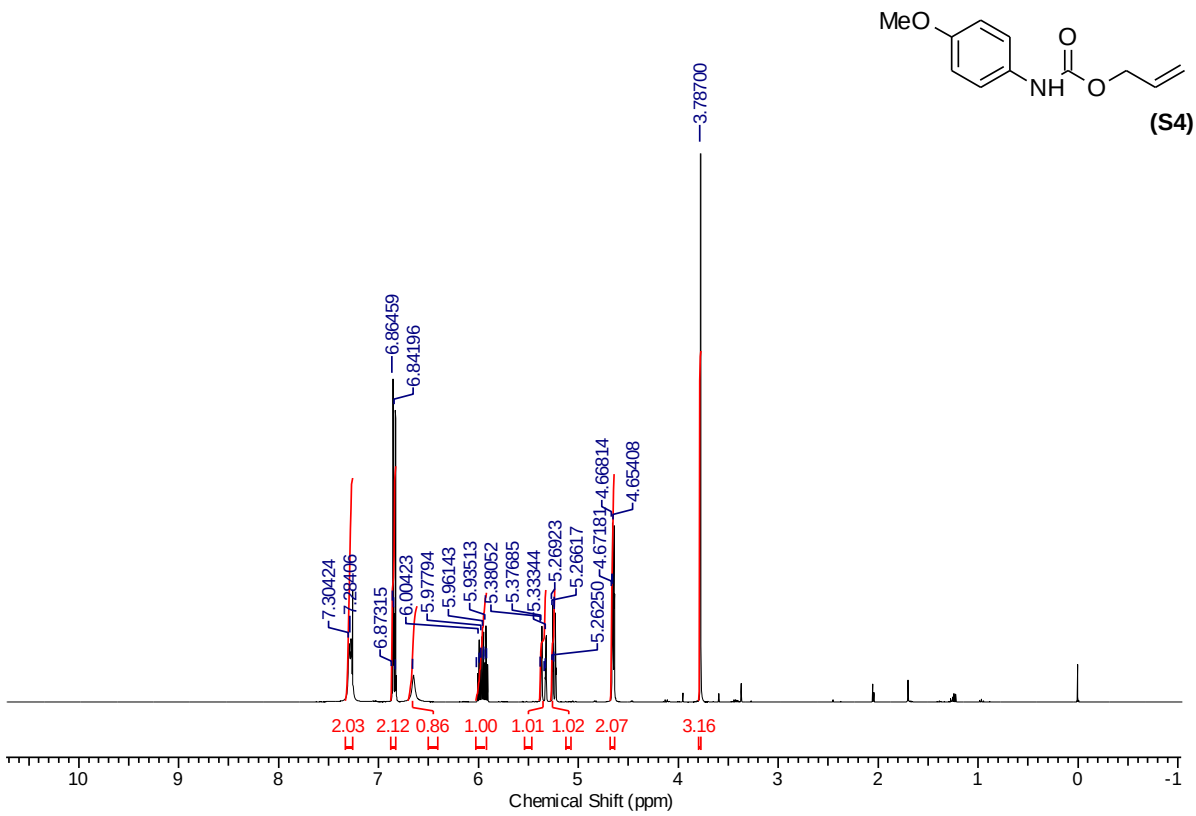

128.88911
132.37680
118.05782
123.35793
137.77800
153.31729
118.71492
77.25995
77.00000
76.74727
65.71379
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

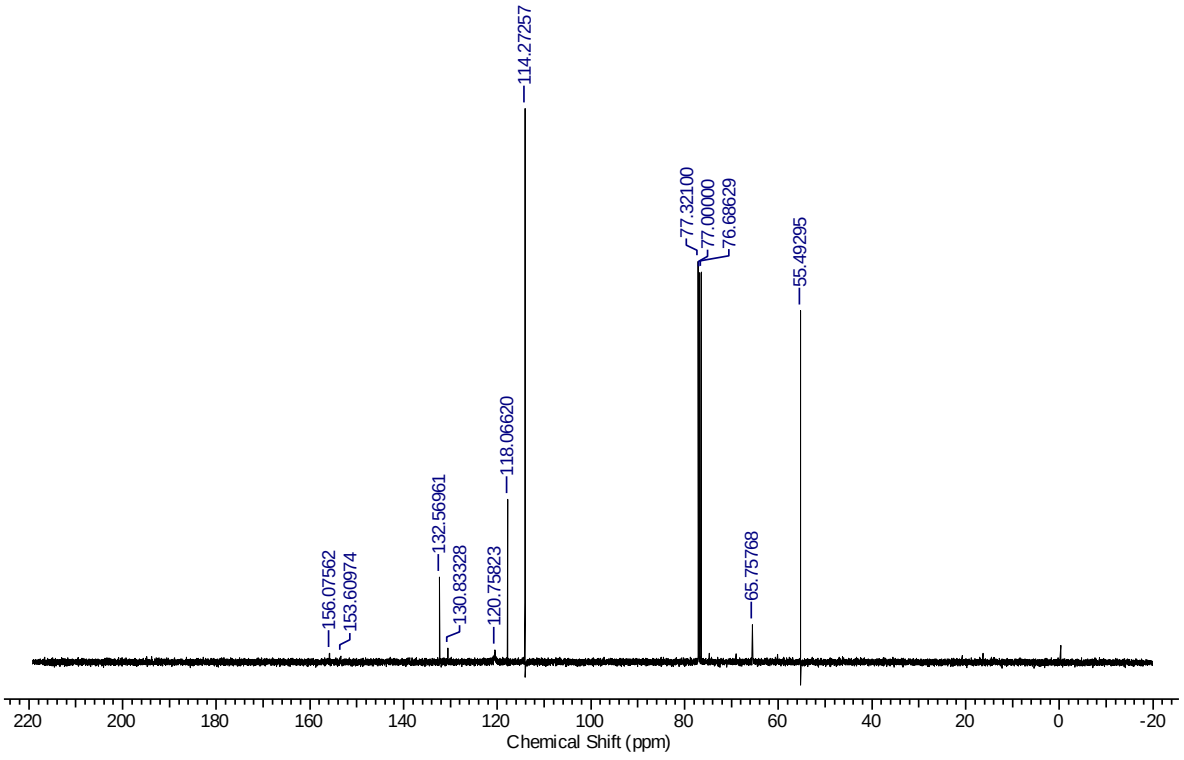

F
O
NH
O
(S2)
6.96252
6.97961
6.94483
7.35297
7.24743
6.98632
6.93751
5.96689
5.94615
5.93272
5.91198
5.97848
5.90039
5.35072
5.24822
5.22748
5.22199
4.66012
4.64853
1.97 0.97 2.07 1.00 1.03 1.02 2.00
Chemical Shift (ppm)

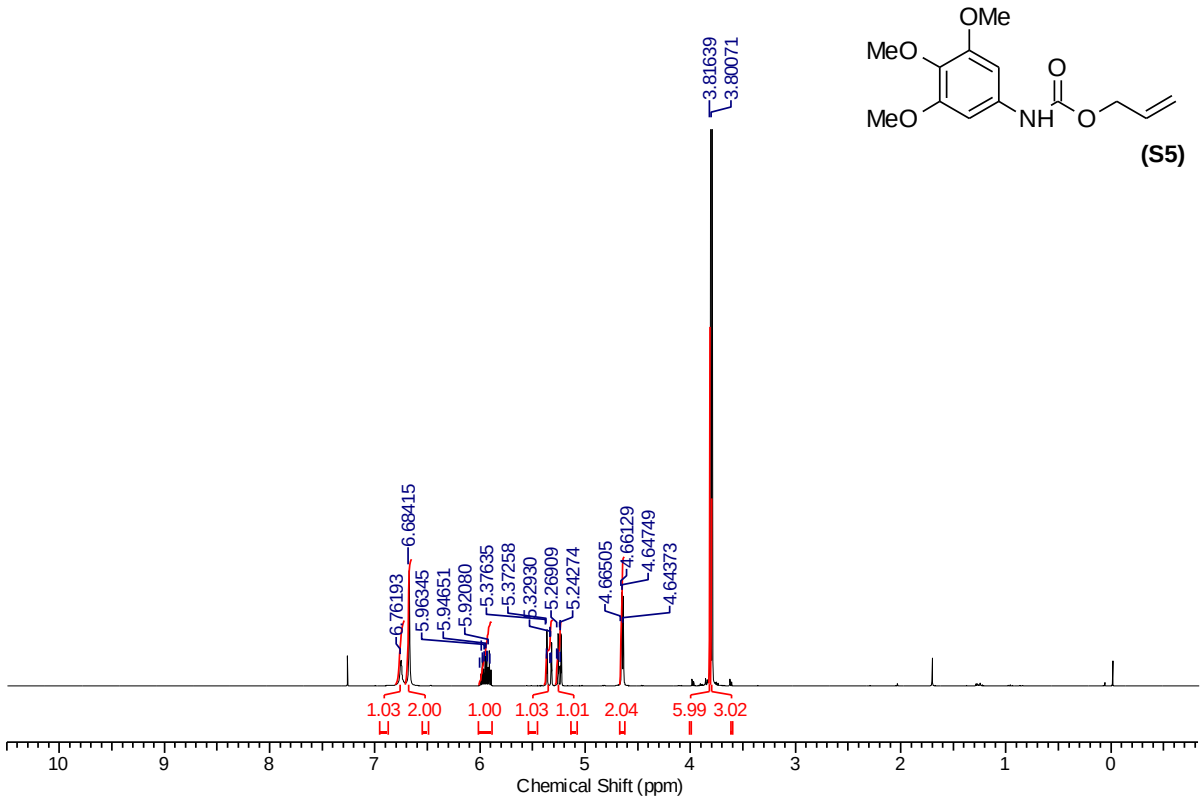

118.00728
115.45110
115.27057
132.23959
159.80164
157.87366
153.65666
133.79208
120.55624
77.25273
77.00000
76.74005
65.74268
Chemical Shift (ppm)

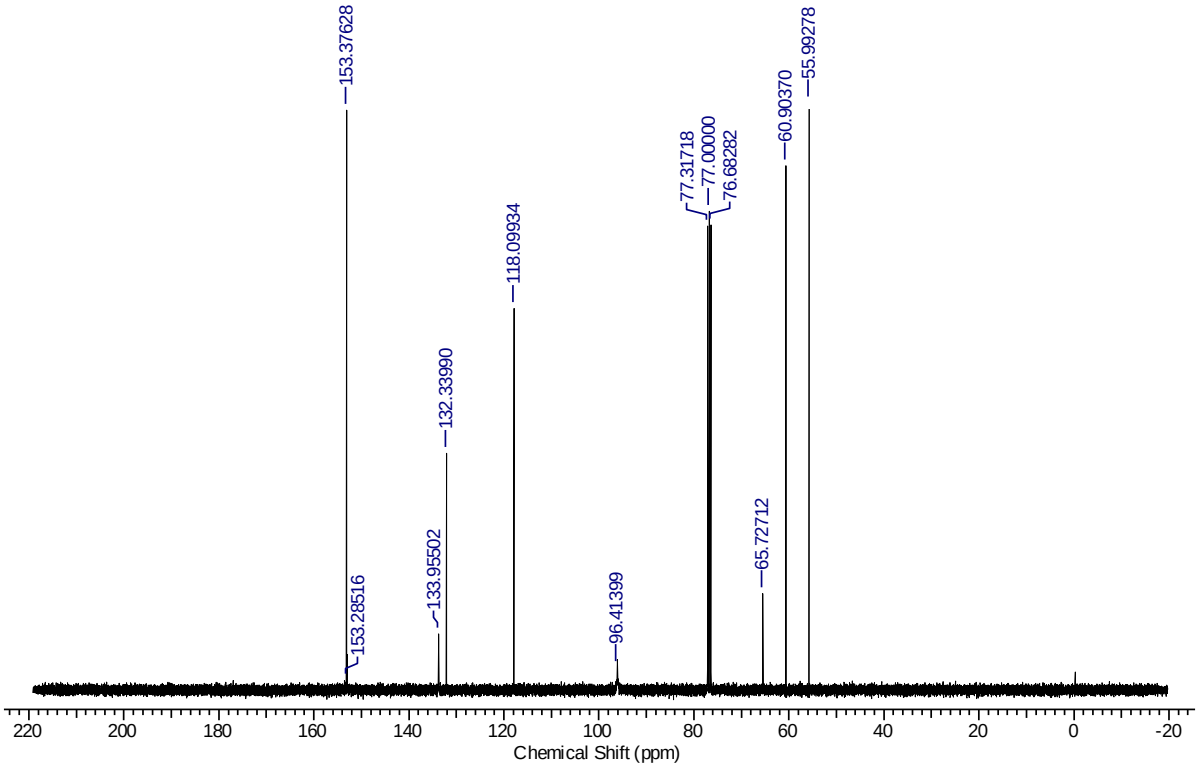

F3C
O
NH
O
(S3)
7.55673
7.52440
7.57443
7.50671
6.92043
6.01203
6.00105
5.97970
5.96628
5.94554
5.93395
5.40318
5.39769
5.30191
5.29947
5.27873
5.27629
4.70160
4.69001
2.14 2.04 0.96 1.00 1.03 1.02 2.10
Chemical Shift (ppm)

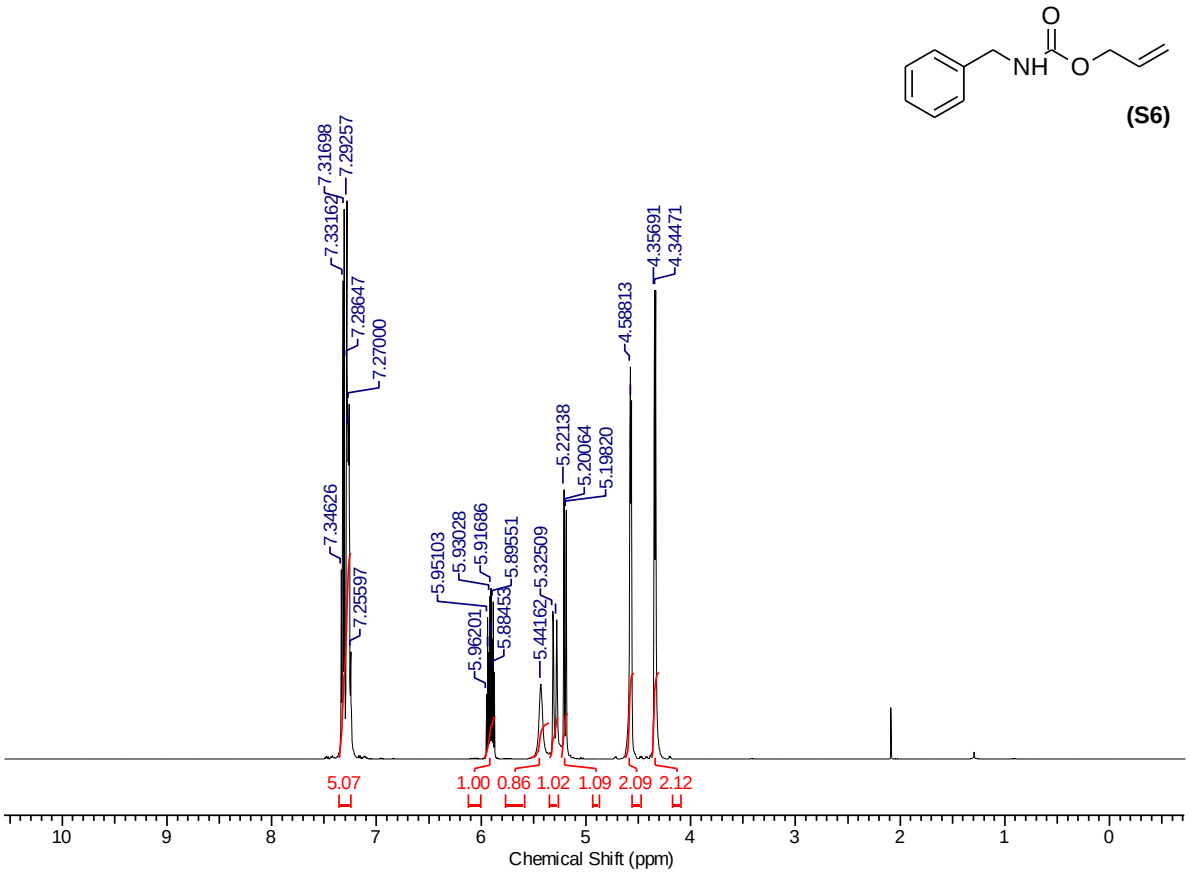

126.31849
118.62105
132.03741
77.25995
76.74727
66.19037
152.89847
140.94073
127.36551
126.28960
123.04743
118.12281
Chemical Shift (ppm)

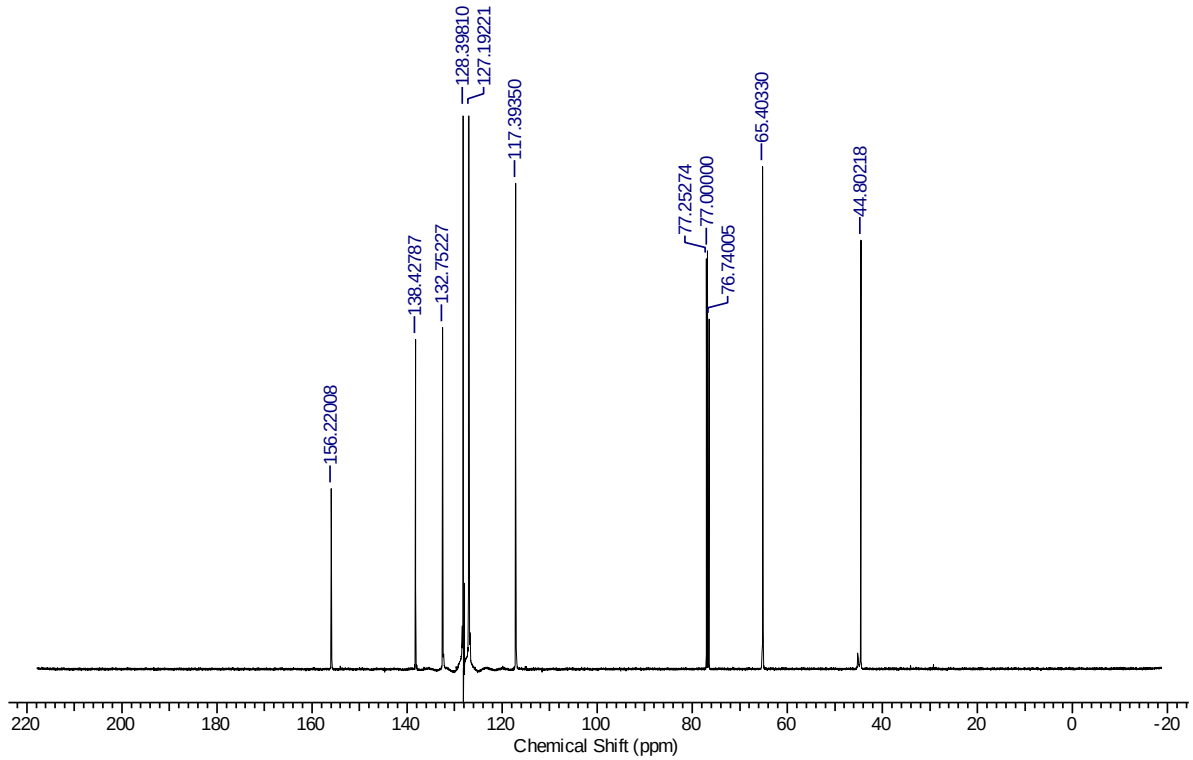

MeO
NH
O
O
(S4)
3.78700
6.86459
6.84196
4.66814
4.65408
7.30424
7.28466
6.87315
6.00423
5.97794
5.96143
5.93513
5.38052
5.37685
5.33344
5.26923
5.26617
4.67181
5.26250
2.03 2.12 0.86 1.00 1.01 1.02 2.07 3.16
10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift (ppm)

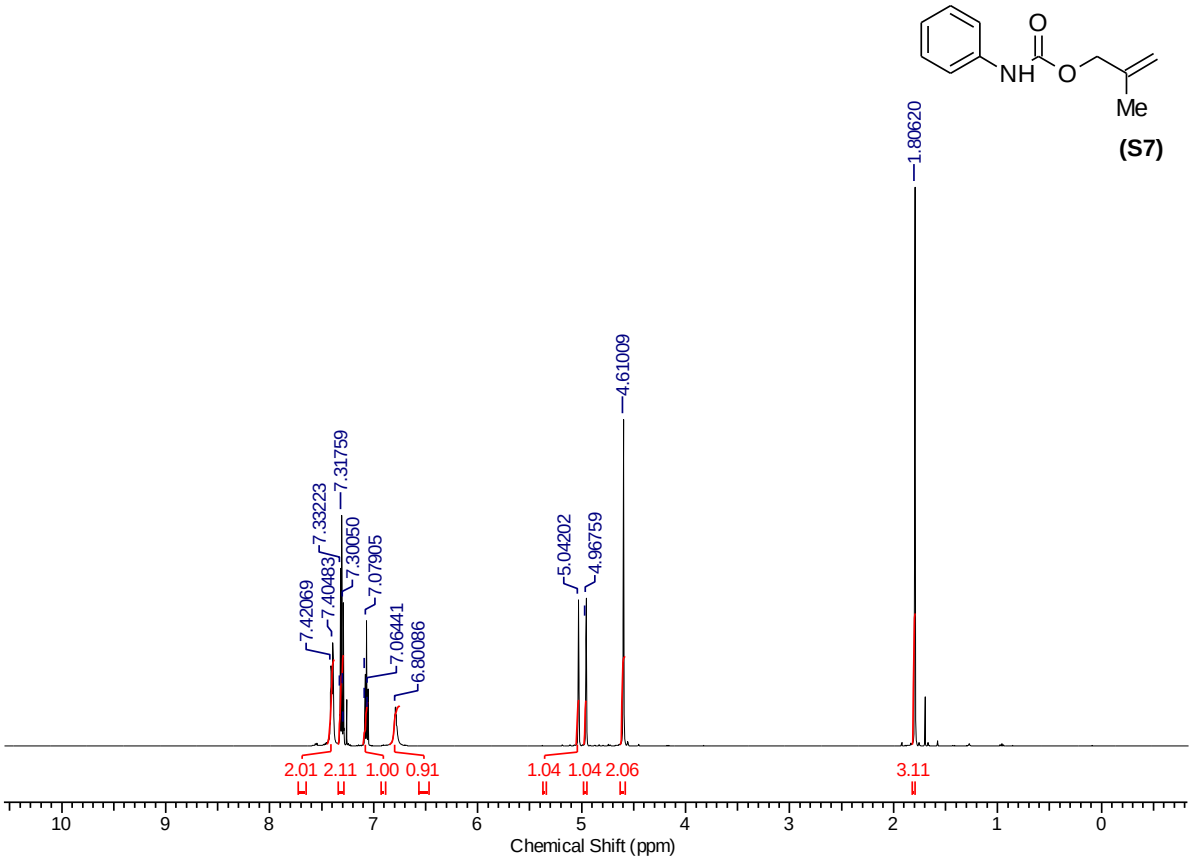

114.27257
77.32100
77.00000
76.68629
55.49295
118.06620
132.56961
156.07562
153.60974
130.83328
120.75823
65.75768
220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)

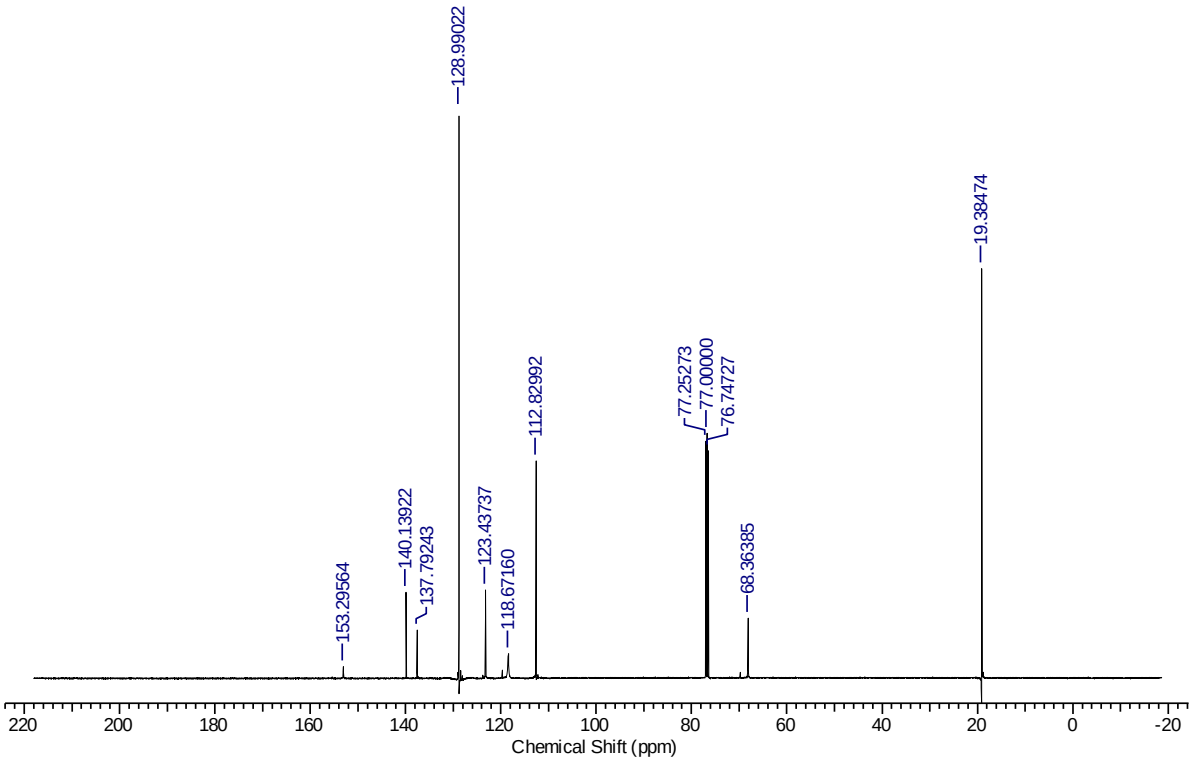

OMe
MeO
MeO
NH
O
O
(S5)
3.81639
3.80071
6.68415
6.76193
5.96345
5.94651
5.92080
5.37635
5.37258
5.32930
5.26909
5.24274
4.66505
4.66129
4.64749
4.64373
1.03 2.00 1.00 1.03 1.01 2.04 5.99 3.02
Chemical Shift (ppm)

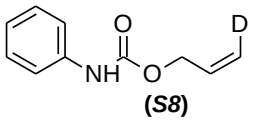

153.37628
153.28516
133.95502
132.33990
118.09934
96.41399
77.31718
77.00000
76.68282
65.72712
60.90370
55.99278
Chemical Shift (ppm)


O
NH
O
(S6)
7.31698
7.29257
7.33162
7.28647
7.27000
7.34626
7.25597
5.95103
5.93028
5.91686
5.89551
5.96201
5.88453
5.32509
5.44162
5.22138
5.20064
5.19820
4.58813
4.35691
4.34471
5.07
1.00
0.86
1.02
1.09
2.09
2.12
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

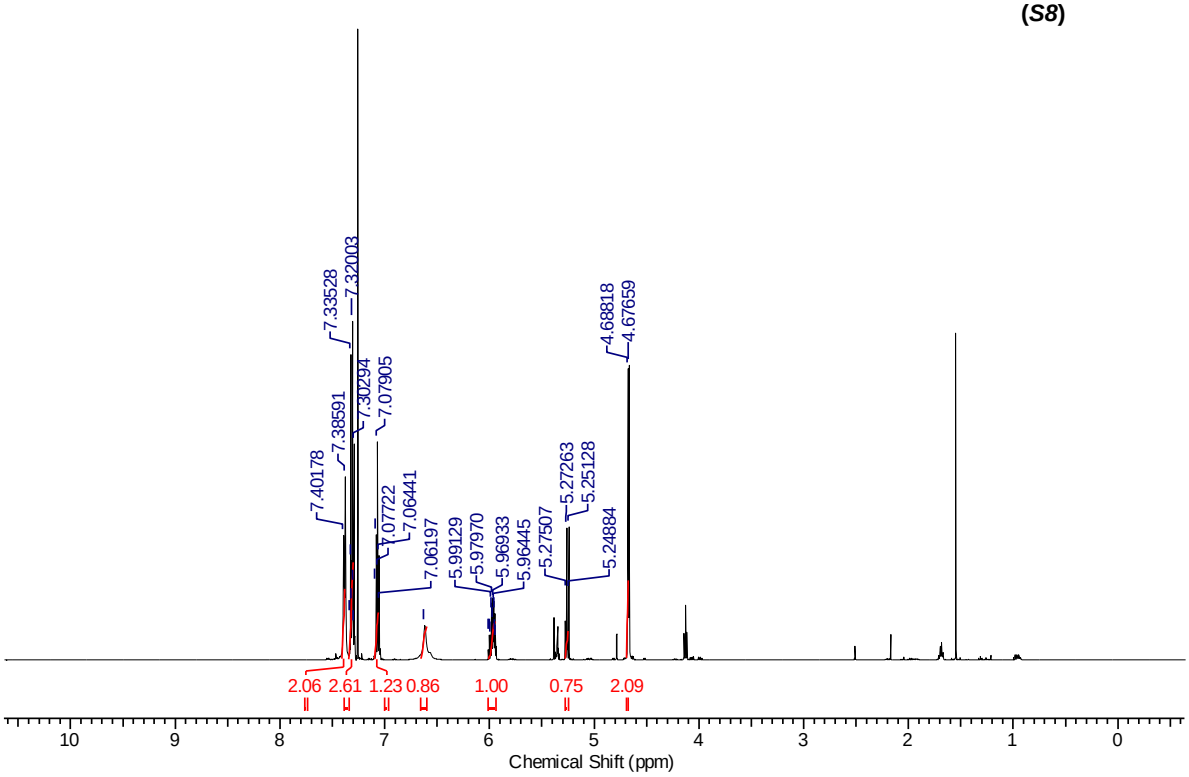

128.39810
127.19221
117.39350
138.42787
132.75227
156.22008
77.25274
77.00000
76.74005
65.40330
44.80218
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

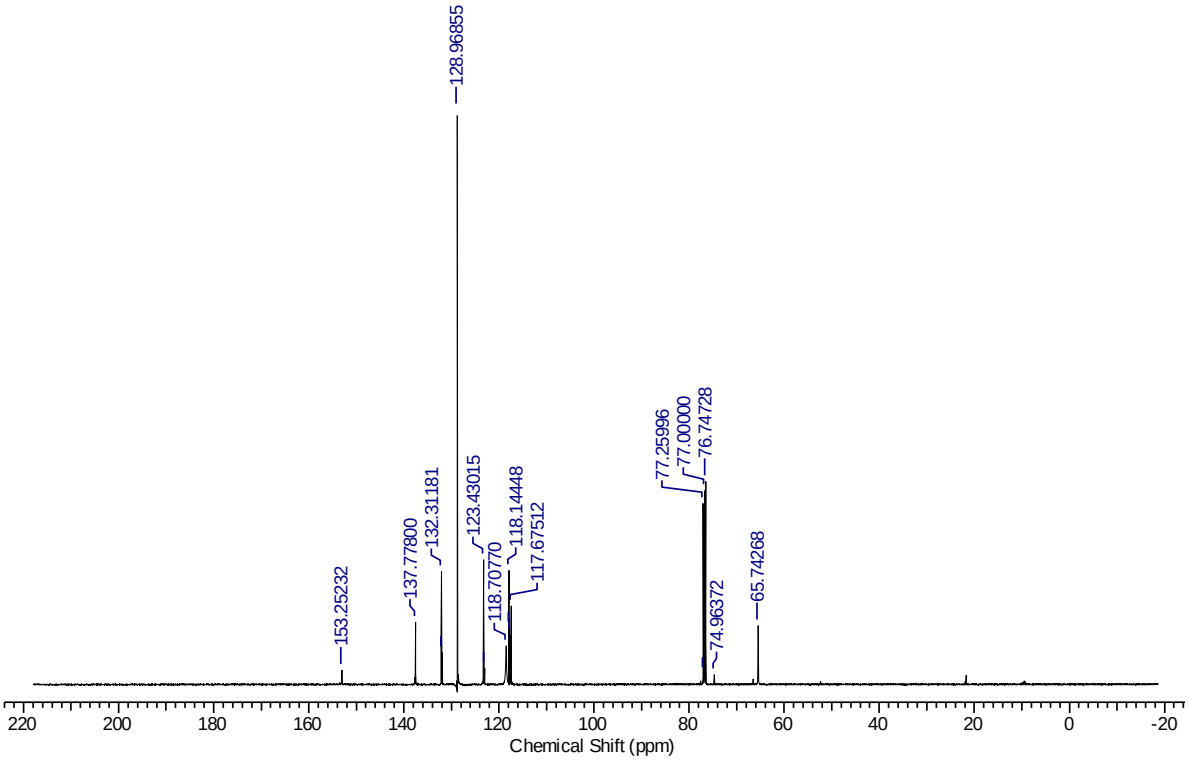

O
NH
O
Me
(S7)
1.80620
4.61009
5.04202
4.96759
7.42069
7.40483
7.33223
7.31759
7.30050
7.07905
7.06441
6.80086
2.01 2.11 1.00 0.91
1.04 1.04 2.06
3.11
Chemical Shift (ppm)

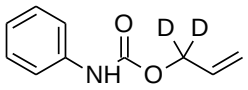

128.99022
19.38474
77.25273
77.00000
76.74727
112.82992
140.13922
137.79243
123.43737
118.67160
153.29564
68.36385
Chemical Shift (ppm)


O
D
NH
O

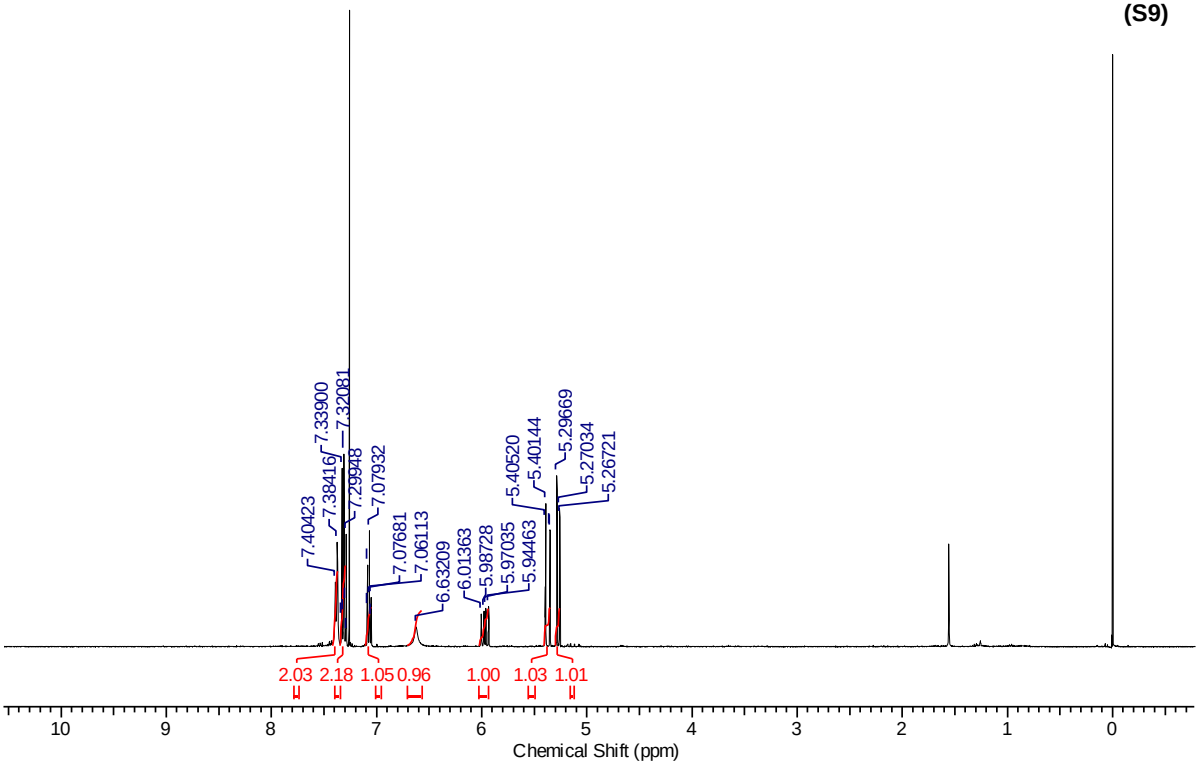
(*S8*)

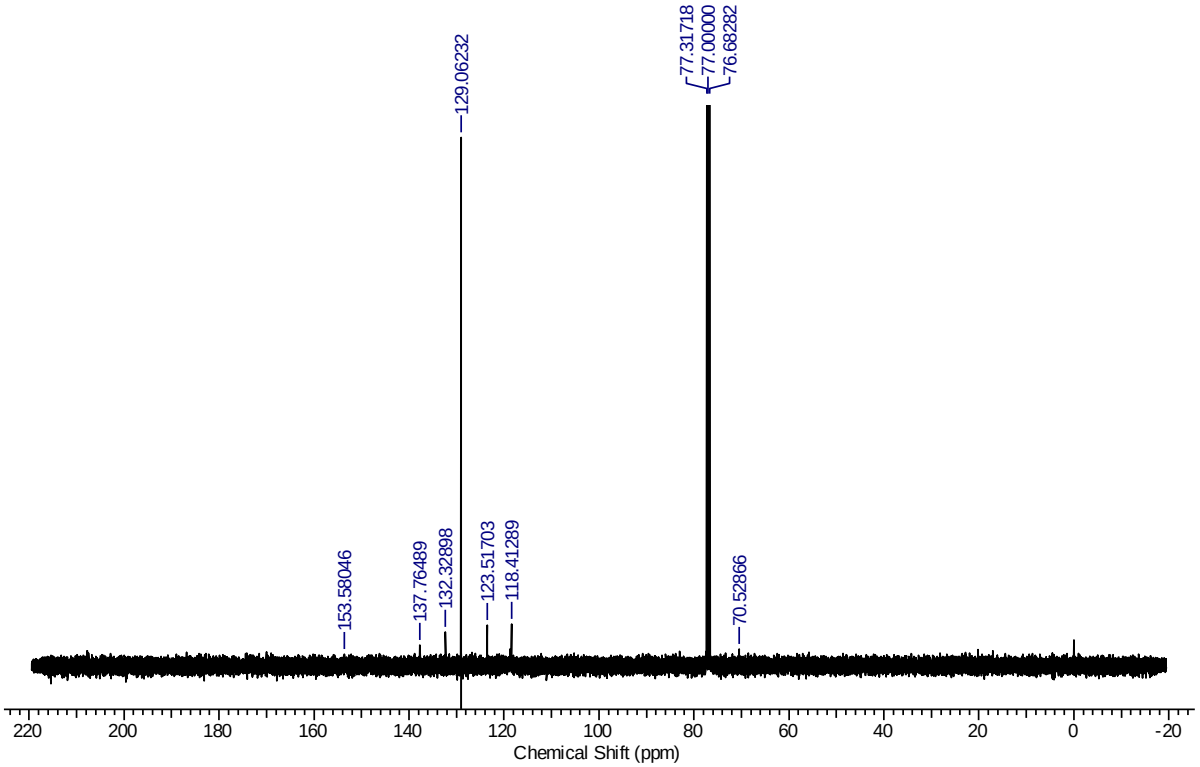

7.33528
7.32003
7.30294
7.07905
7.38591
7.40178
7.07722
7.06441
7.06197
5.99129
5.97970
5.96933
5.96445
5.27507
5.27263
5.25128
5.24884
4.68818
4.67659
2.06
2.61
1.23
0.86
1.00
0.75
2.09
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

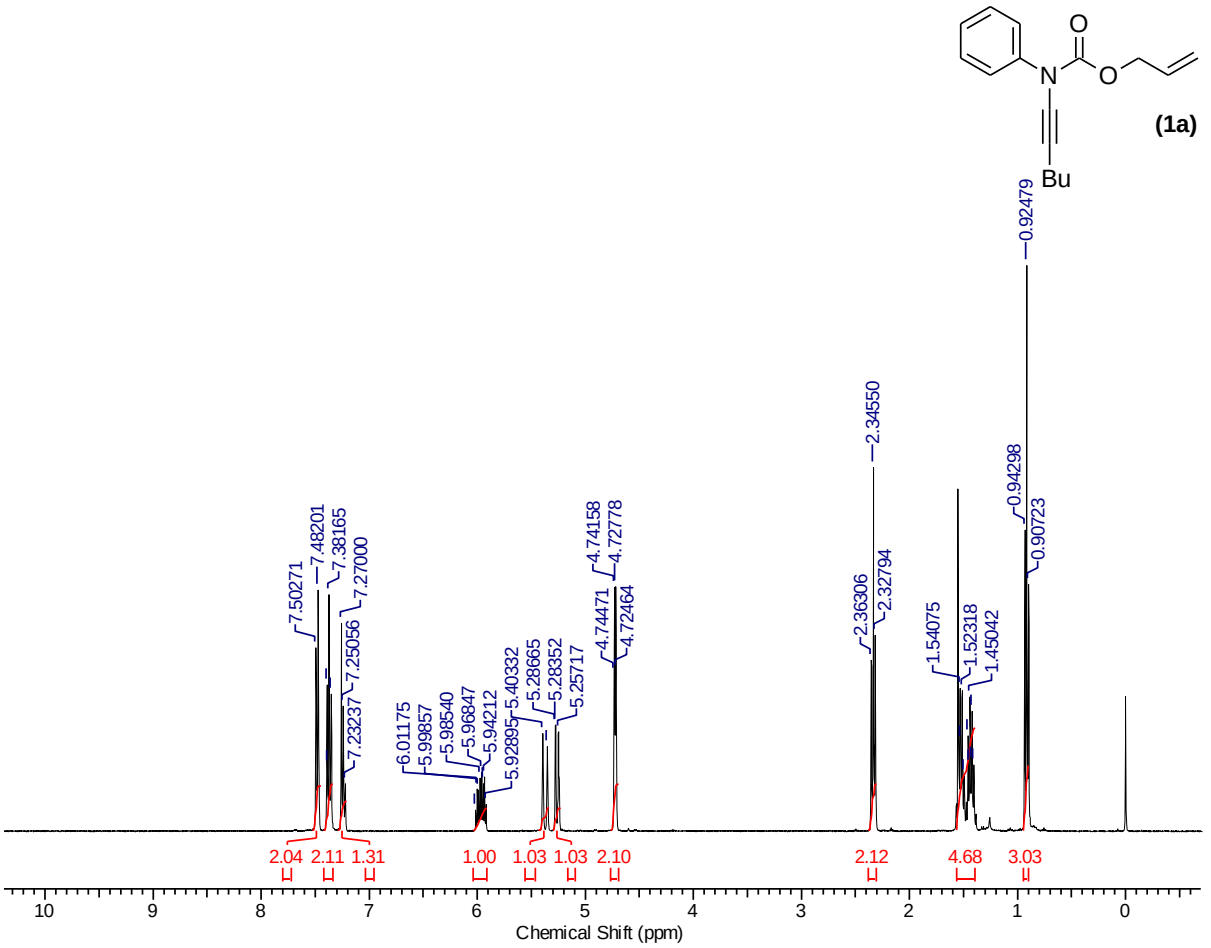

128.96855
153.25232
137.77800
132.31181
123.43015
118.70770
118.14448
117.67512
77.25996
77.00000
76.74728
74.96372
65.74268
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

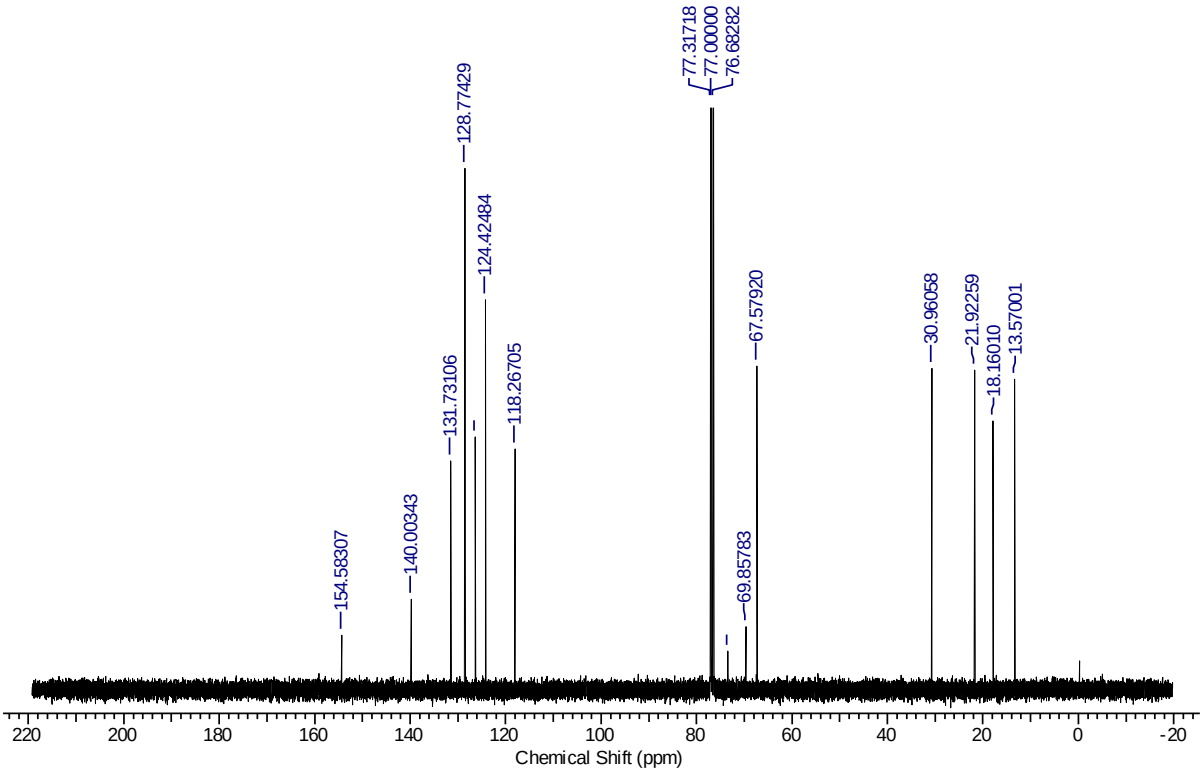

O
D
D
NH
O

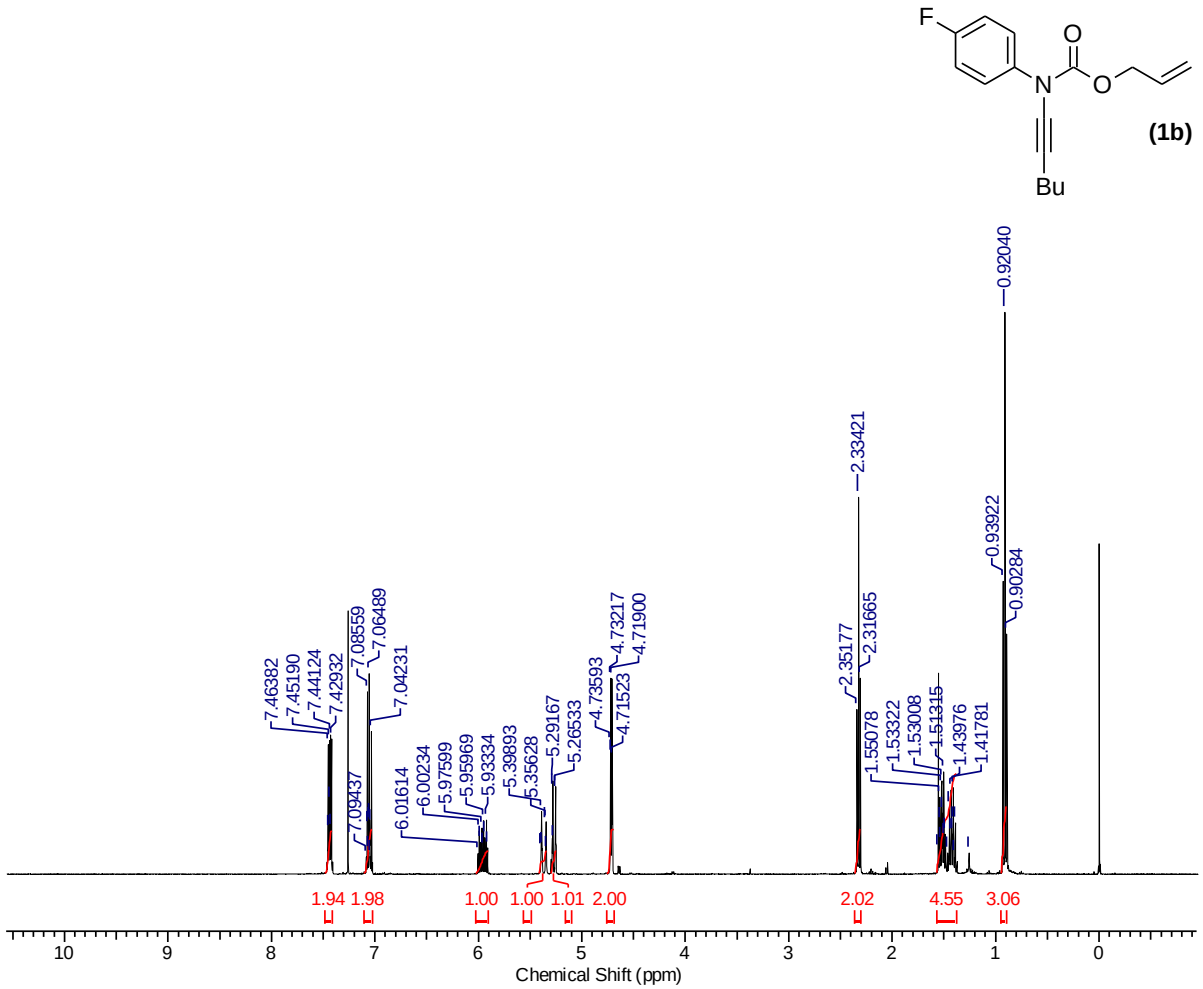
(S9)

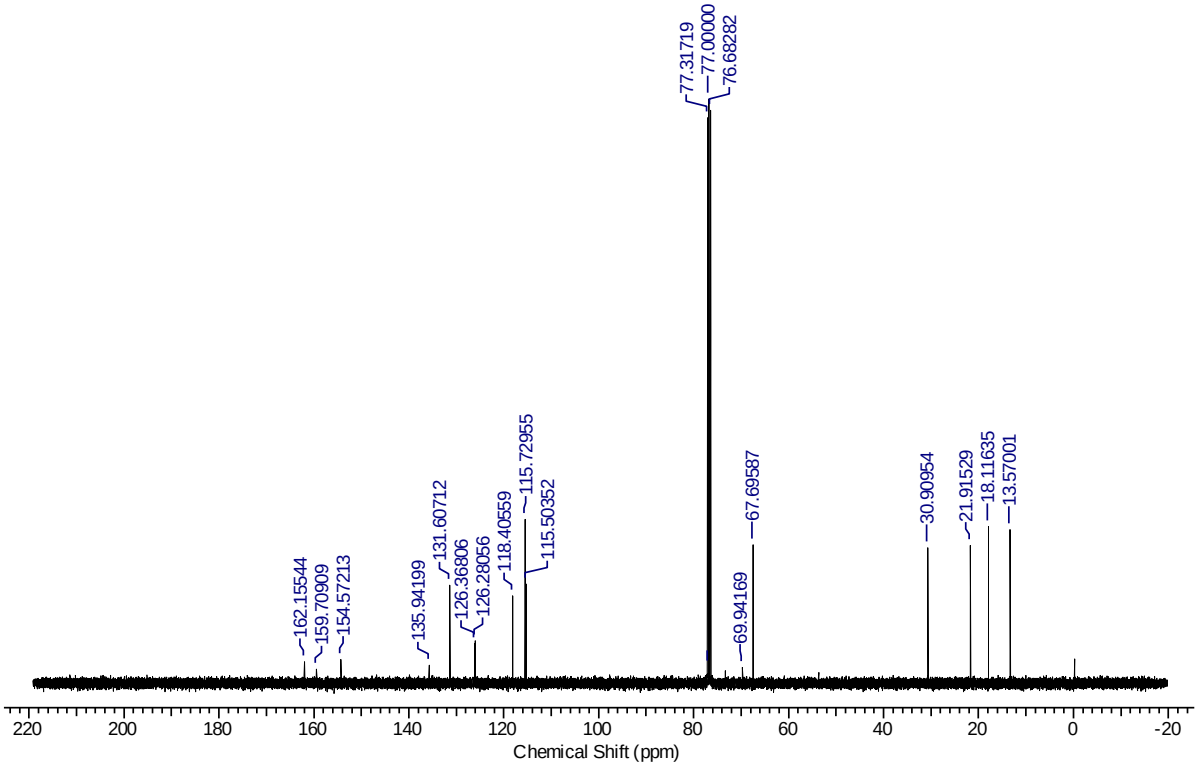

7.40423
7.38416
7.33900
7.32081
7.29948
7.07932
7.07681
7.06113
6.63209
6.01363
5.98728
5.97035
5.94463
5.40520
5.40144
5.29669
5.27034
5.26721
2.03
2.18
1.05
0.96
1.00
1.03
1.01
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

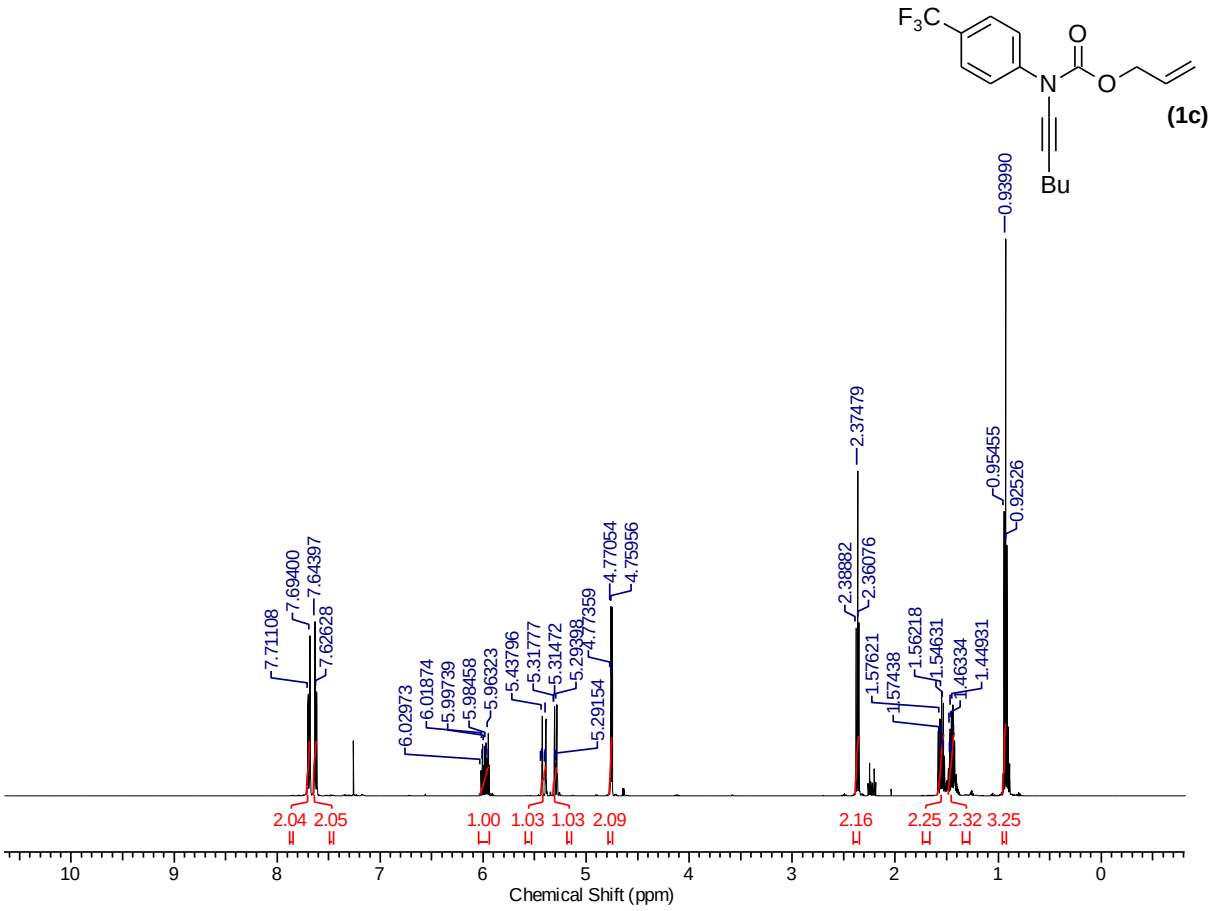

153.58046
137.76489
132.32898
129.06232
123.51703
118.41289
77.31718
77.00000
76.68282
70.52866
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

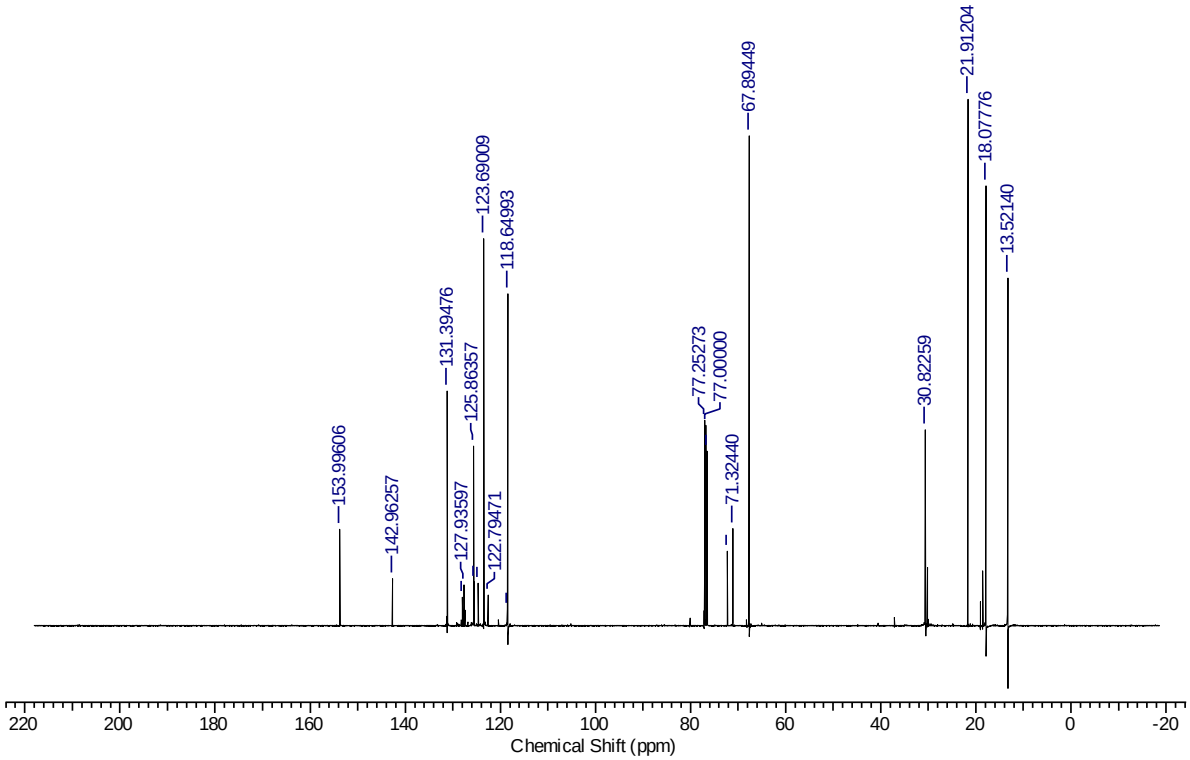

O
N
O
Bu
(1a)
7.50271
7.48201
7.38165
7.27000
7.25056
7.23237
6.01175
5.99857
5.98540
5.96847
5.94212
5.92895
5.40332
5.28665
5.28352
5.25717
4.74158
4.72778
4.74471
4.72464
2.36306
2.34550
2.32794
1.54075
1.52318
1.45042
0.94298
0.92479
0.90723
2.04 2.11 1.31 1.00 1.03 1.03 2.10 2.12 4.68 3.03
Chemical Shift (ppm)

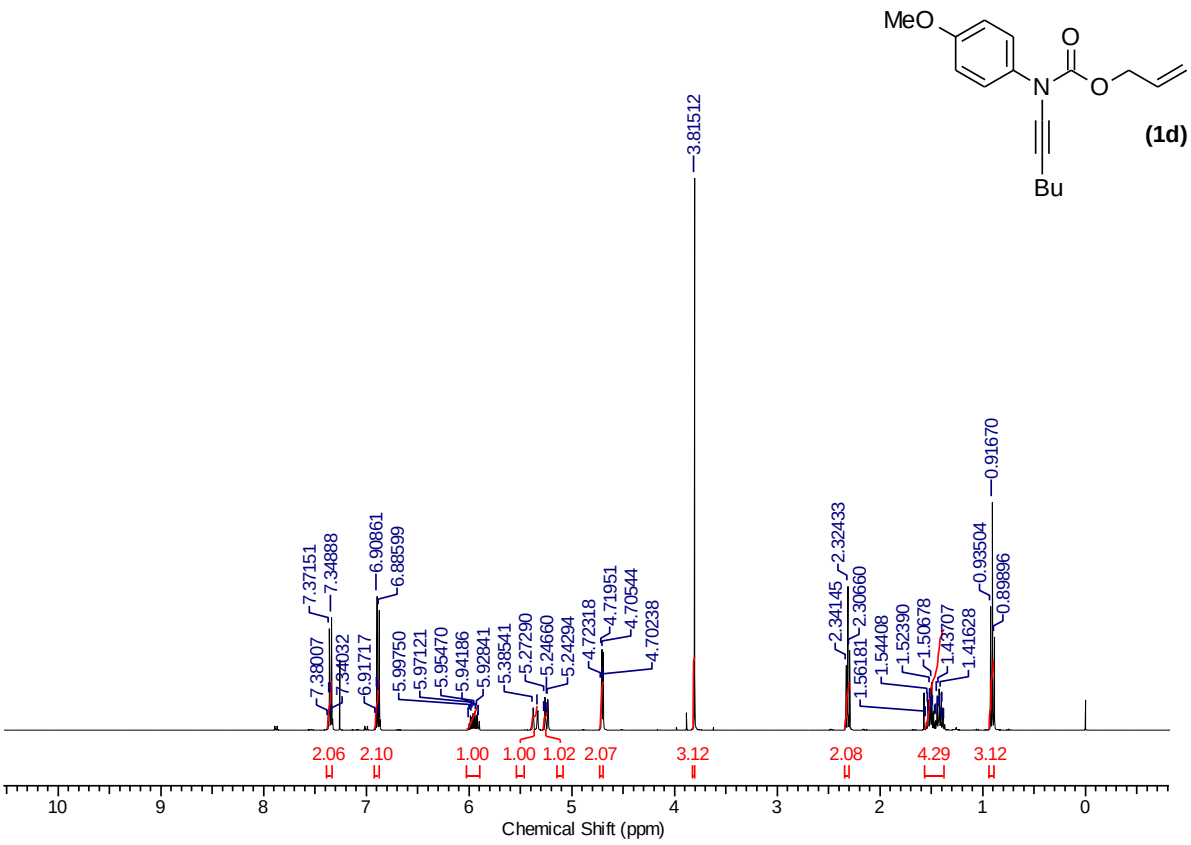

77.31718
77.00000
76.68282
128.77429
124.42484
131.73106
118.26705
154.58307
140.00343
67.57920
69.85783
30.96058
21.92259
18.16010
13.57001
Chemical Shift (ppm)

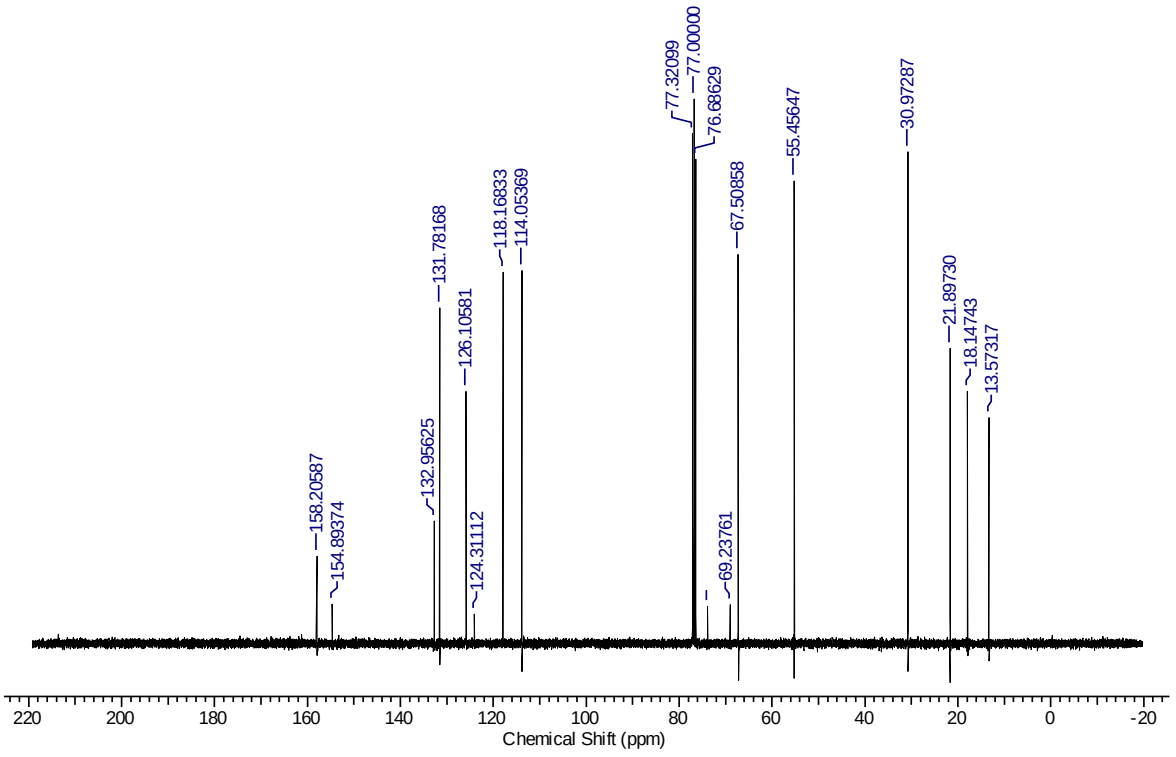

F
O
N
O
Bu
(1b)
7.46382
7.45190
7.44124
7.42932
7.09437
7.08559
7.06489
7.04231
6.01614
6.00234
5.97599
5.95969
5.93334
5.39893
5.35628
5.29167
5.26533
4.73593
4.73217
4.71900
4.71523
2.35177
2.33421
2.31665
1.55078
1.53322
1.53008
1.51315
1.43976
1.41781
0.93922
0.92040
0.90284
1.94 1.98 1.00 1.00 1.01 2.00 2.02 4.55 3.06
Chemical Shift (ppm)

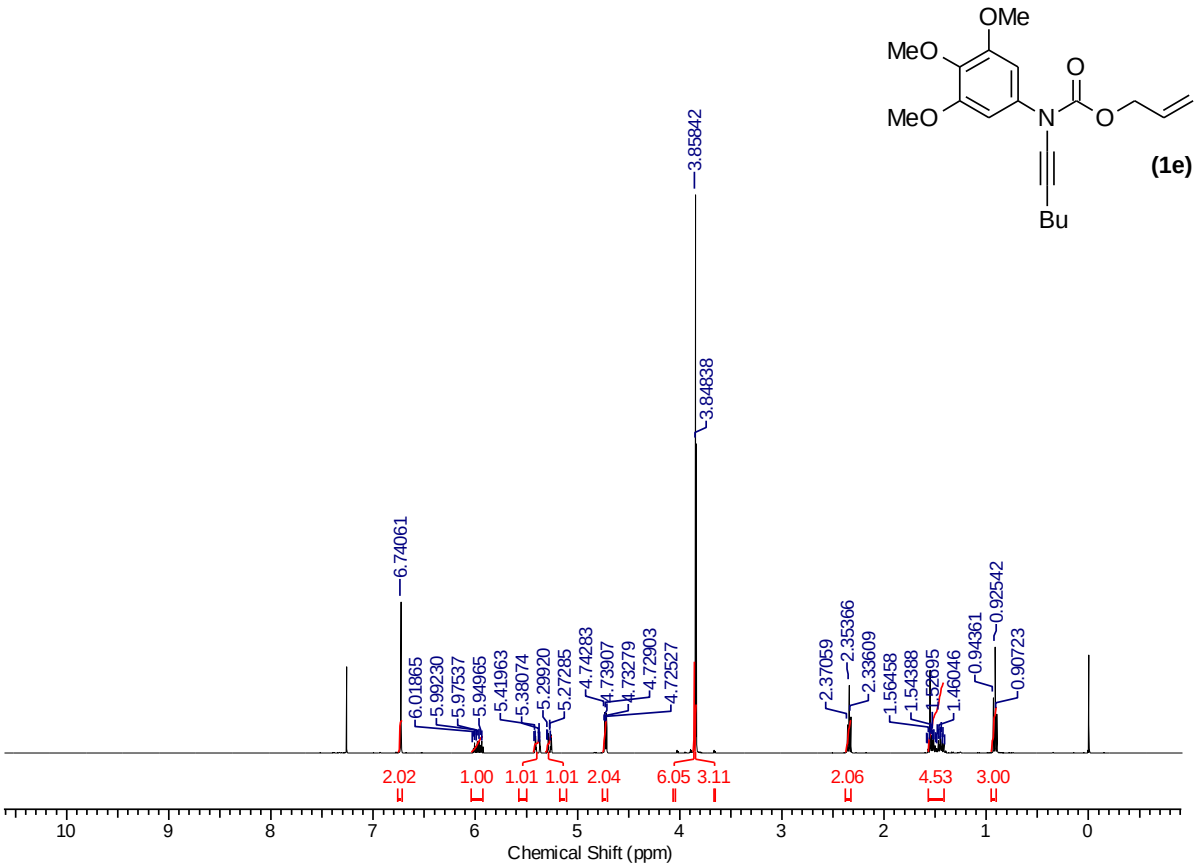

77.31719
77.00000
76.68282
162.15544
159.70909
154.57213
135.94199
131.60712
126.36806
126.28056
118.40559
115.72955
115.50352
69.94169
67.69587
30.90954
21.91529
18.11635
13.57001
Chemical Shift (ppm)

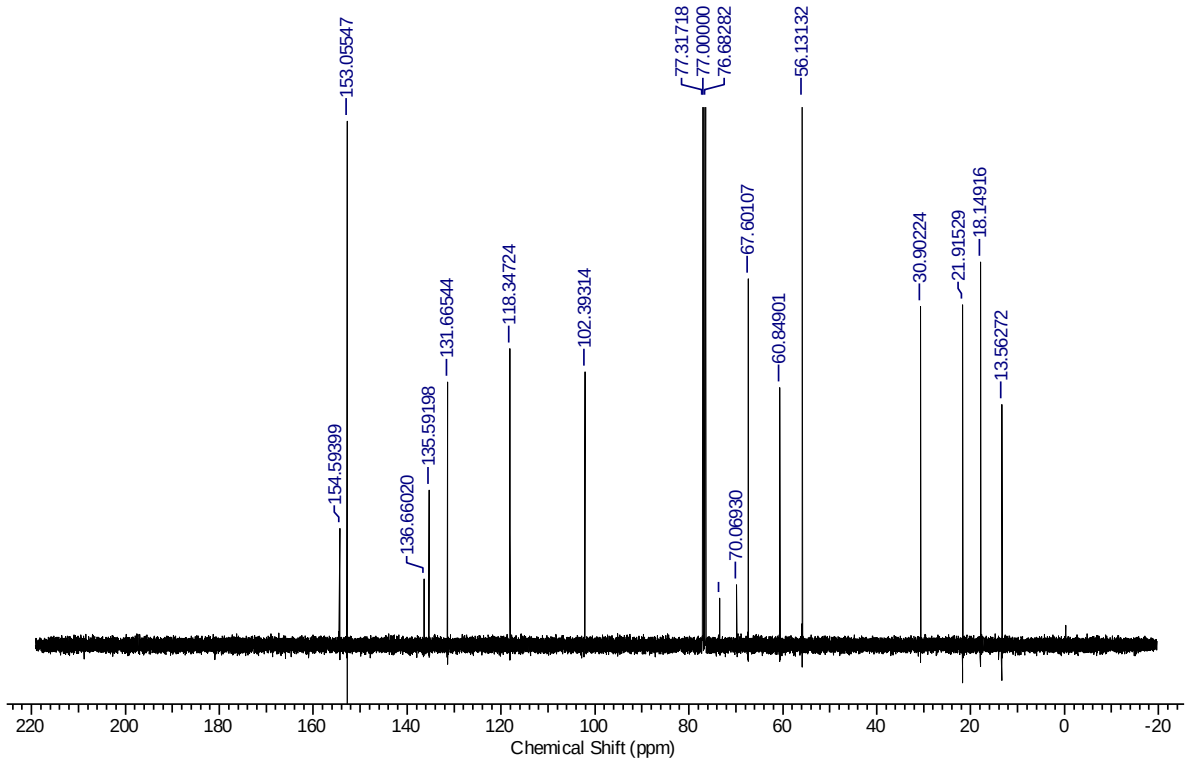

F3C
O
N
O
Bu
(1c)
7.71108
7.69400
7.64397
7.62628
6.02973
6.01874
5.99739
5.98458
5.96323
5.43796
5.31777
5.31472
5.29398
4.77359
5.29154
4.77054
4.75956
2.38882
2.36076
2.37479
1.57621
1.57438
1.56218
1.54631
1.46334
1.44931
0.95455
0.92526
0.93990
2.04 2.05 1.00 1.03 1.03 2.09 2.16 2.25 2.32 3.25
Chemical Shift (ppm)

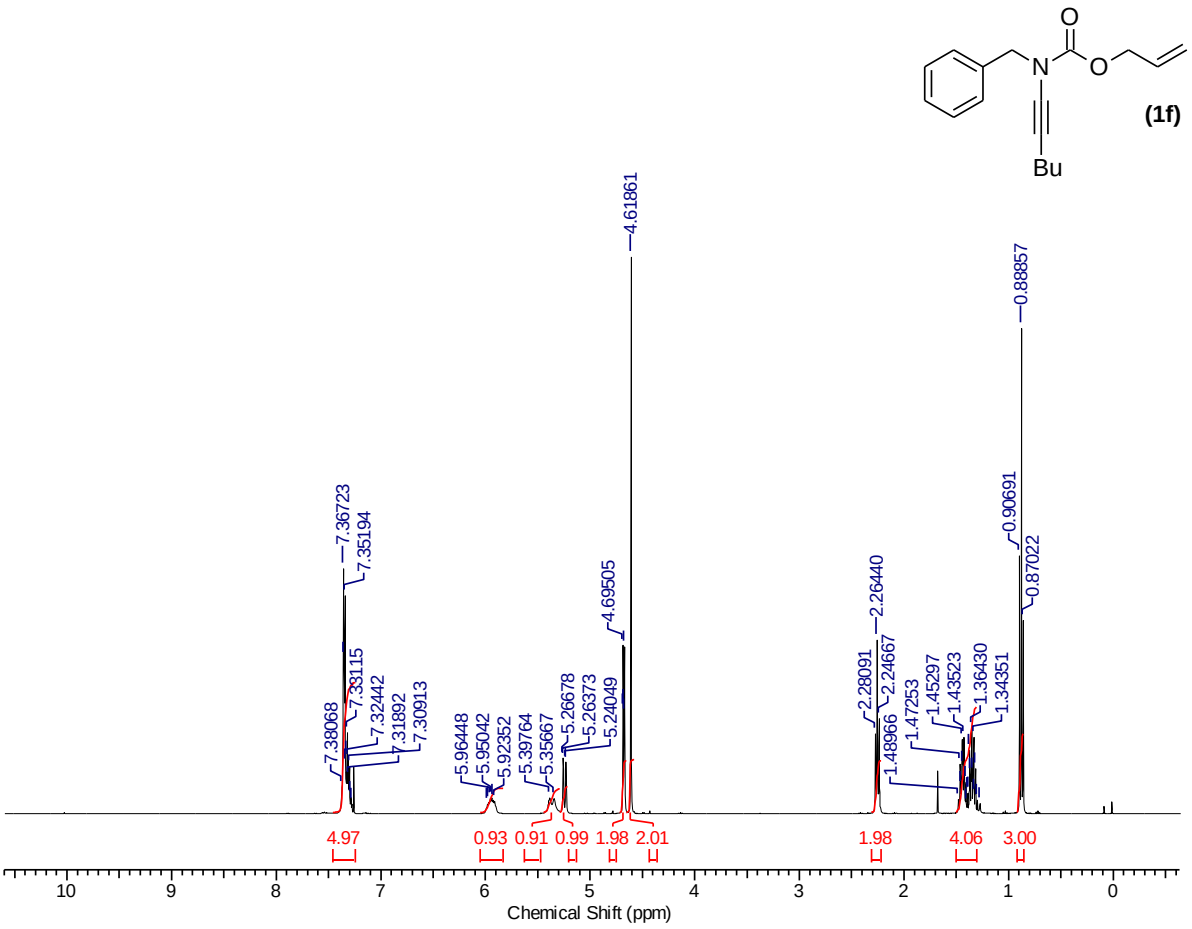

153.99606
142.96257
131.39476
125.86357
127.93597
122.79471
123.69009
118.64993
77.25273
77.00000
71.32440
67.89449
30.82259
21.91204
18.07776
13.52140
Chemical Shift (ppm)

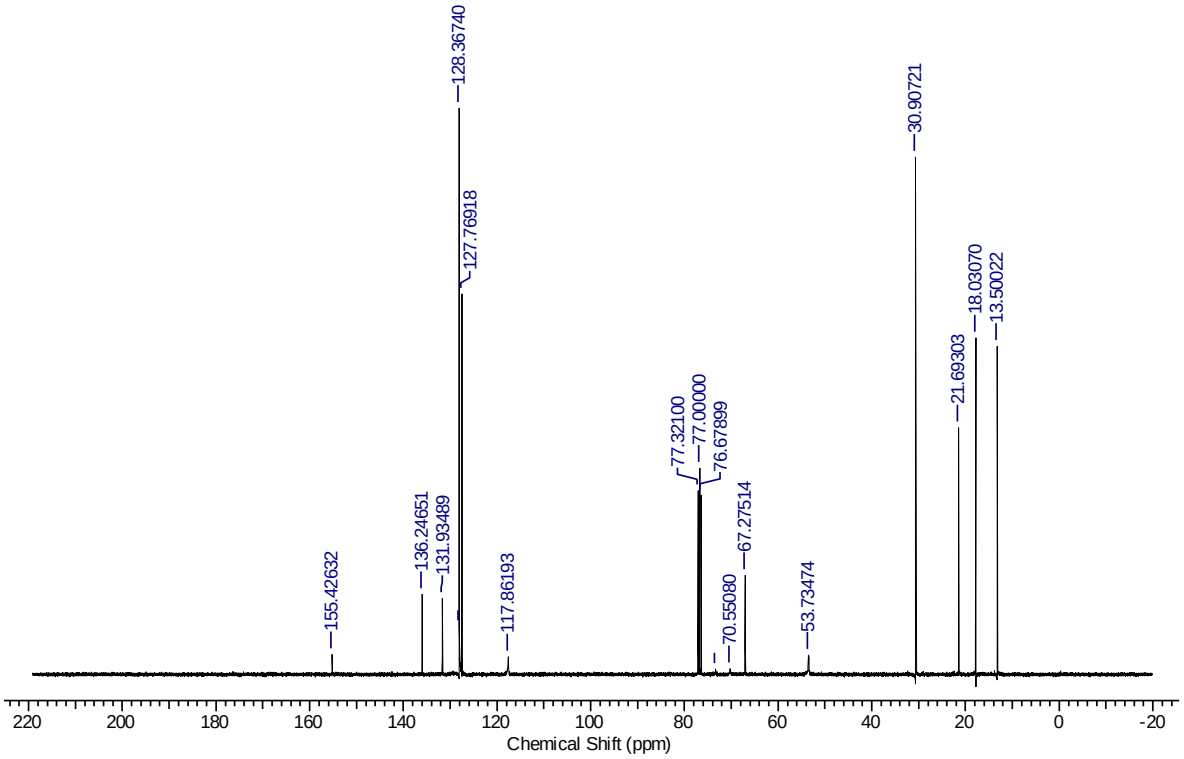

MeO
O
N
O
Bu
(1d)
3.81512
7.37151
7.34888
7.34032
7.38007
6.90861
6.88599
6.91717
5.99750
5.97121
5.95470
5.94186
5.92841
5.38541
5.27290
5.24660
5.24294
4.72318
4.71951
4.70544
4.70238
2.34145
2.32433
2.30660
1.56181
1.54408
1.52390
1.50678
1.43707
1.41628
0.93504
0.91670
0.89896
2.06
2.10
1.00
1.00
1.02
2.07
3.12
2.08
4.29
3.12
Chemical Shift (ppm)

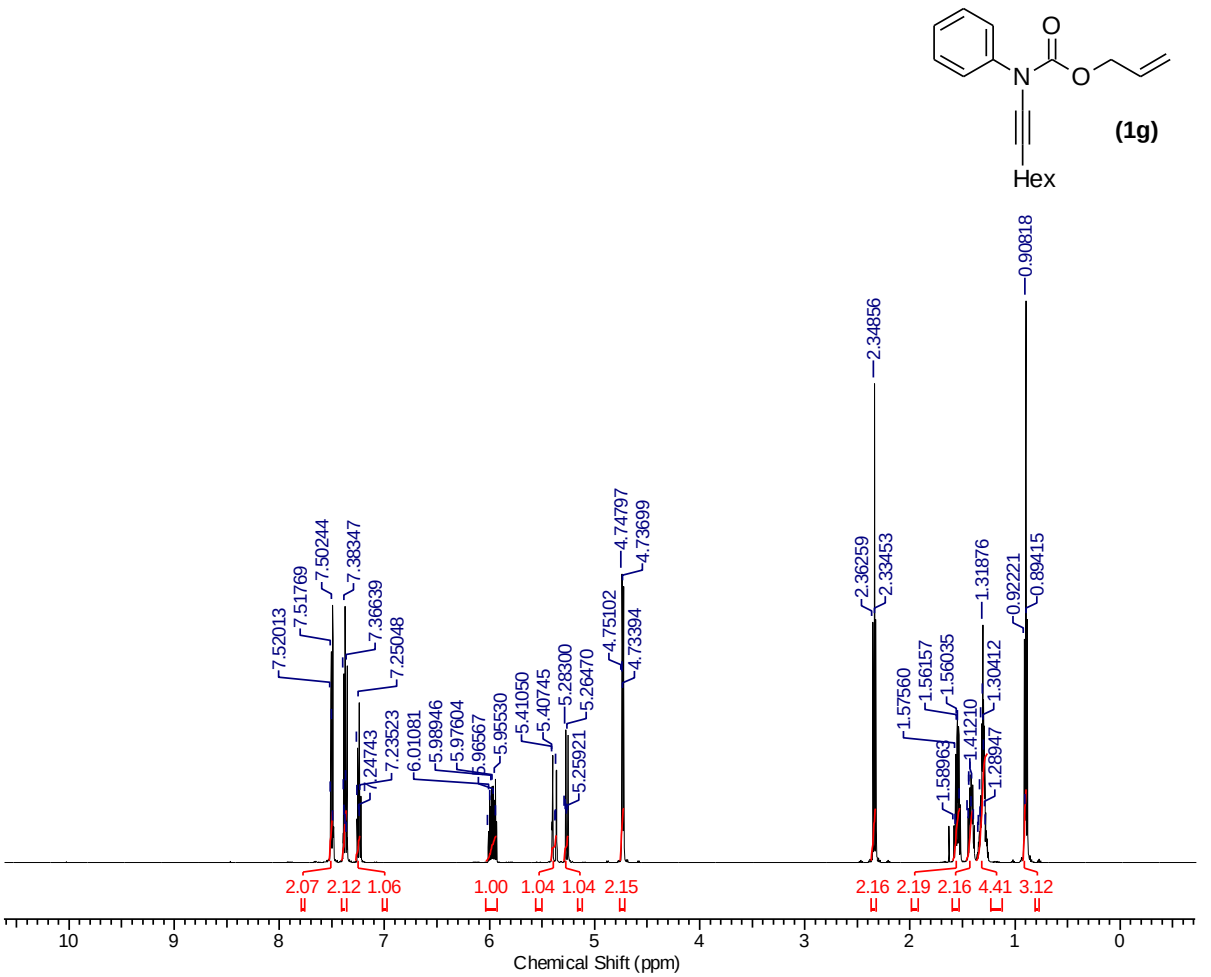

77.32099
77.00000
76.68629
67.50858
55.45647
30.97287
21.89730
18.14743
13.57317
158.20587
154.89374
132.95625
131.78168
126.10581
124.31112
118.16833
114.05369
69.23761
Chemical Shift (ppm)

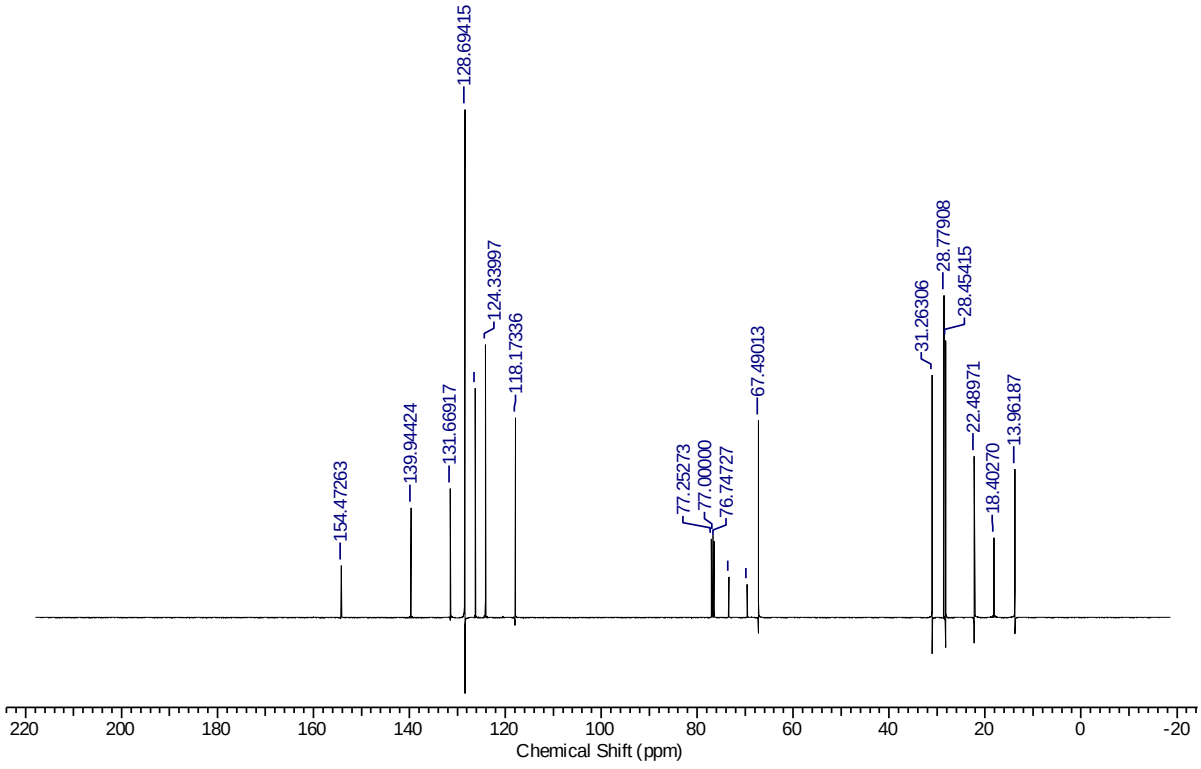

OMe
MeO
MeO
O
N
O
Bu
(1e)
3.85842
3.84838
6.74061
6.01865
5.99230
5.97537
5.94965
5.41963
5.38074
5.29920
5.27285
4.74283
4.73907
4.73279
4.72903
4.72527
2.37059
2.35366
2.33609
1.56458
1.54388
1.52695
1.46046
0.94361
0.92542
0.90723
2.02
1.00
1.01
1.01
2.04
6.05
3.11
2.06
4.53
3.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

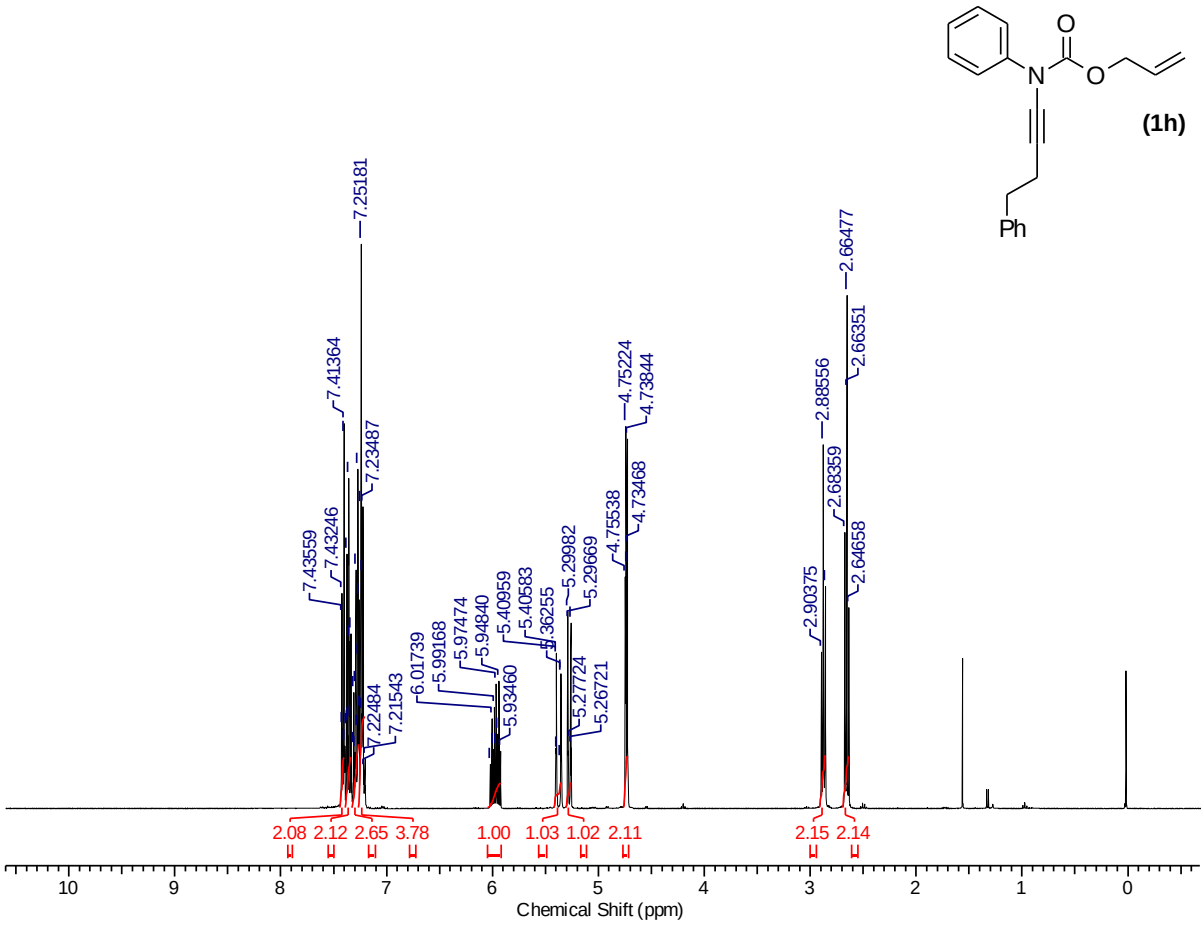

153.05547
154.59399
136.66020
135.59198
131.66544
118.34724
102.39314
77.31718
77.00000
76.68282
70.06930
67.60107
60.84901
56.13132
30.90224
21.91529
18.14916
13.56272
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

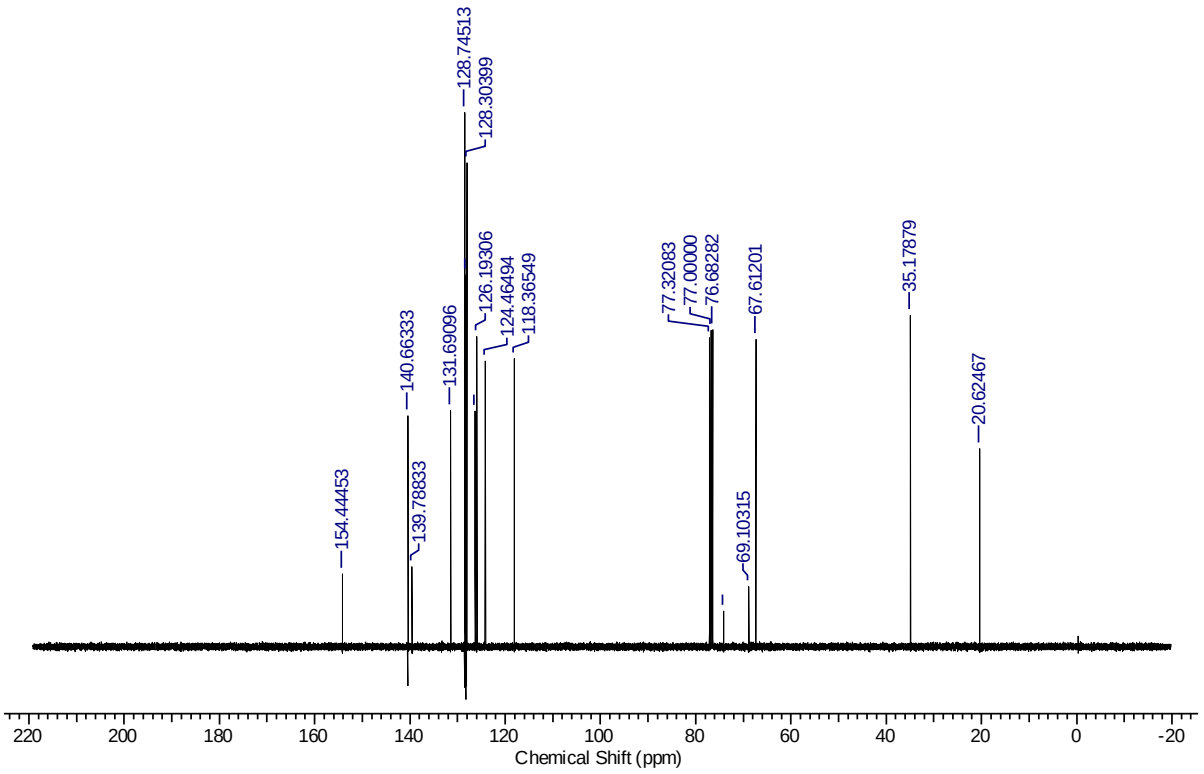

O
N
O
Bu
(1f)
4.61861
0.88857
7.36723
7.35194
0.90691
0.87022
4.69505
2.26440
7.38068
7.33115
7.32442
7.31892
7.30913
5.96448
5.95042
5.92352
5.39764
5.35667
5.26678
5.26373
5.24049
2.28091
2.24667
1.48966
1.47253
1.45297
1.43523
1.36430
1.34351
4.97
0.93
0.91
0.99
1.98
2.01
1.98
4.06
3.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

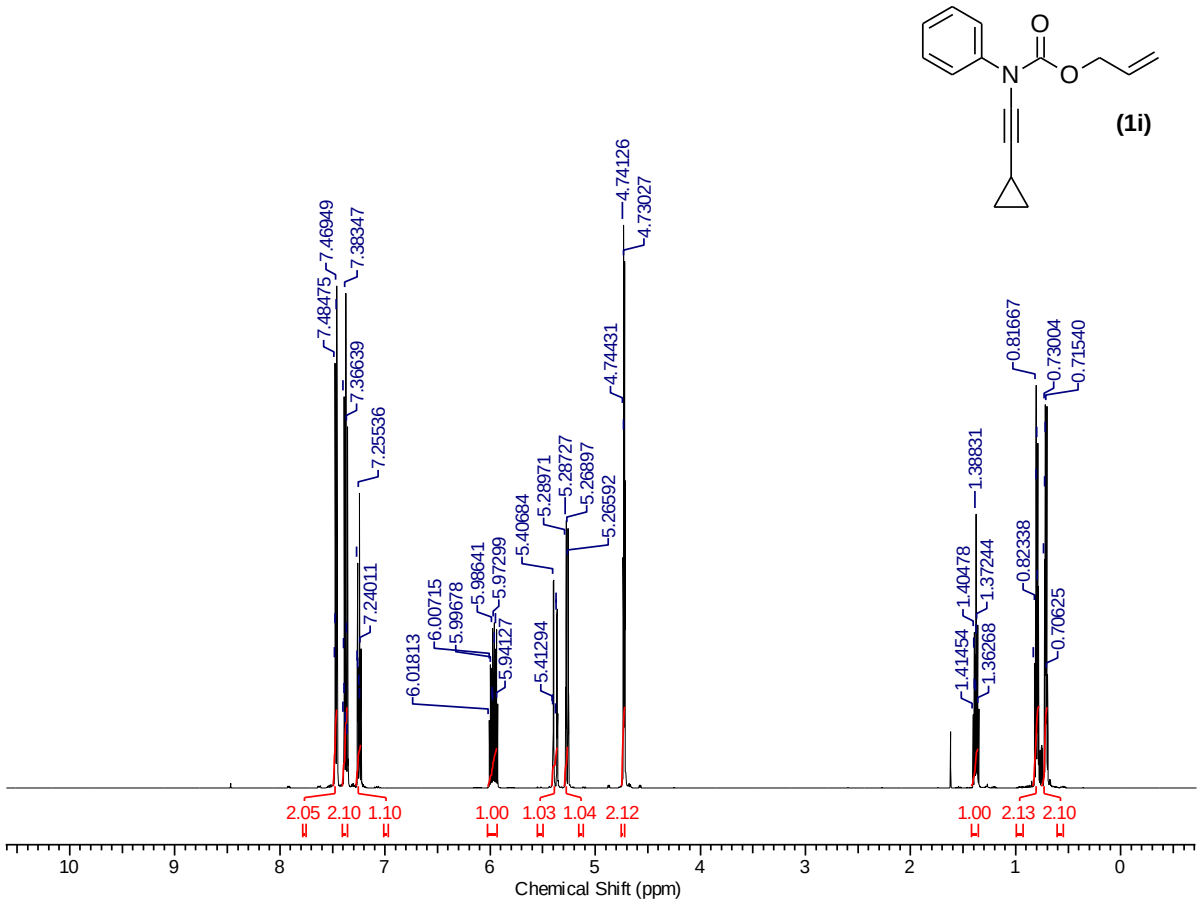

128.36740
30.90721
127.76918
18.03070
13.50022
21.69303
77.32100
77.00000
76.67899
136.24651
131.93489
67.27514
155.42632
117.86193
70.55080
53.73474
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

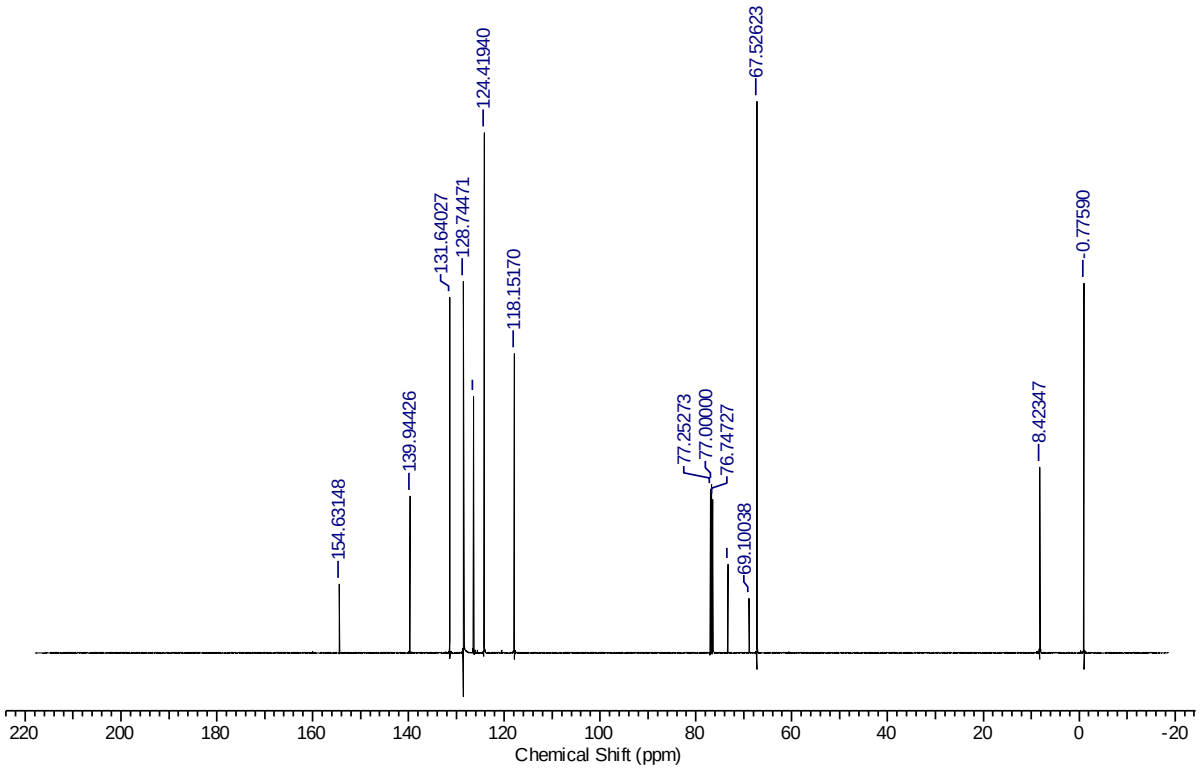

O
N
O
Hex
(1g)
7.52013
7.51769
7.50244
7.38347
7.36639
7.25048
7.24743
7.23523
6.01081
5.98946
5.97604
5.96567
5.95530
5.41050
5.40745
5.28300
5.26470
5.25921
4.75102
4.74797
4.73699
4.73394
2.36259
2.34856
2.33453
1.57560
1.56157
1.56035
1.58963
1.41210
1.31876
1.30412
1.28947
0.92221
0.90818
0.89415
2.07 2.12 1.06
1.00 1.04 1.04 2.15
2.16 2.19 2.16 4.41 3.12
Chemical Shift (ppm)

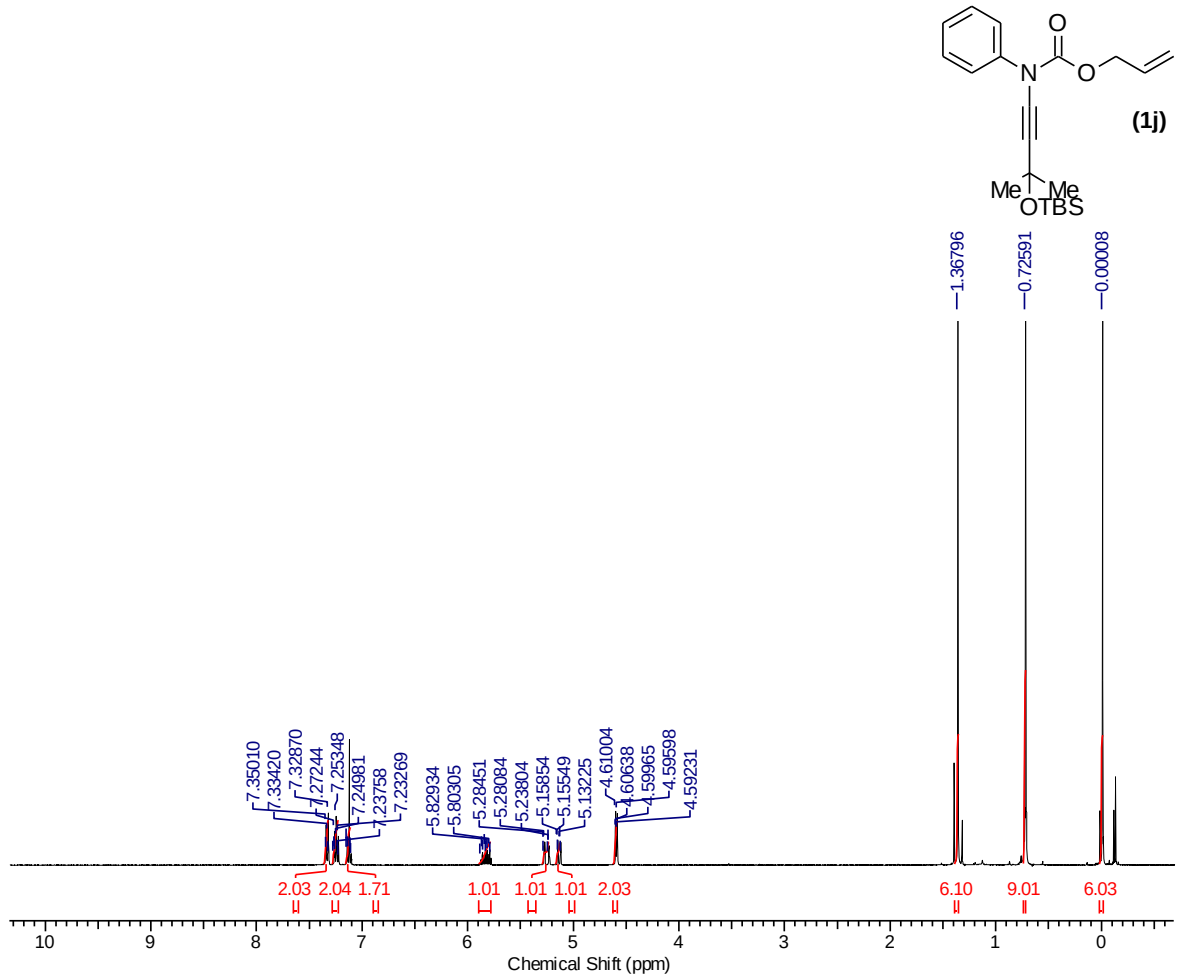

154.47263
139.94424
131.66917
128.69415
124.33997
118.17336
77.25273
77.00000
76.74727
67.49013
31.26306
28.77908
28.45415
22.48971
18.40270
13.96187
Chemical Shift (ppm)

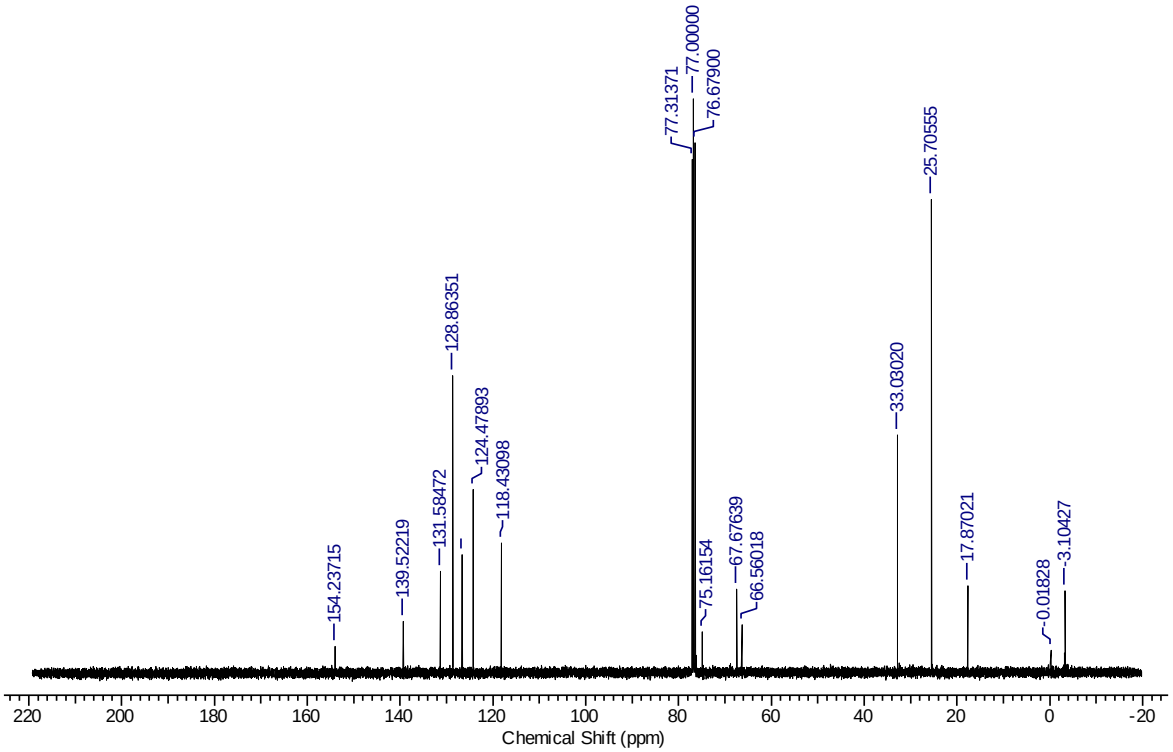

(1h)
Ph
7.25181
7.41364
7.43559
7.43246
7.23487
7.22484
7.21543
6.01739
5.99168
5.97474
5.94840
5.93460
5.40959
5.40583
5.36255
5.29982
5.29669
5.27724
5.26721
4.75538
4.75224
4.73844
4.73468
2.90375
2.88556
2.68359
2.66477
2.66351
2.64658
2.08 2.12 2.65 3.78
1.00 1.03 1.02 2.11
2.15 2.14
Chemical Shift (ppm)

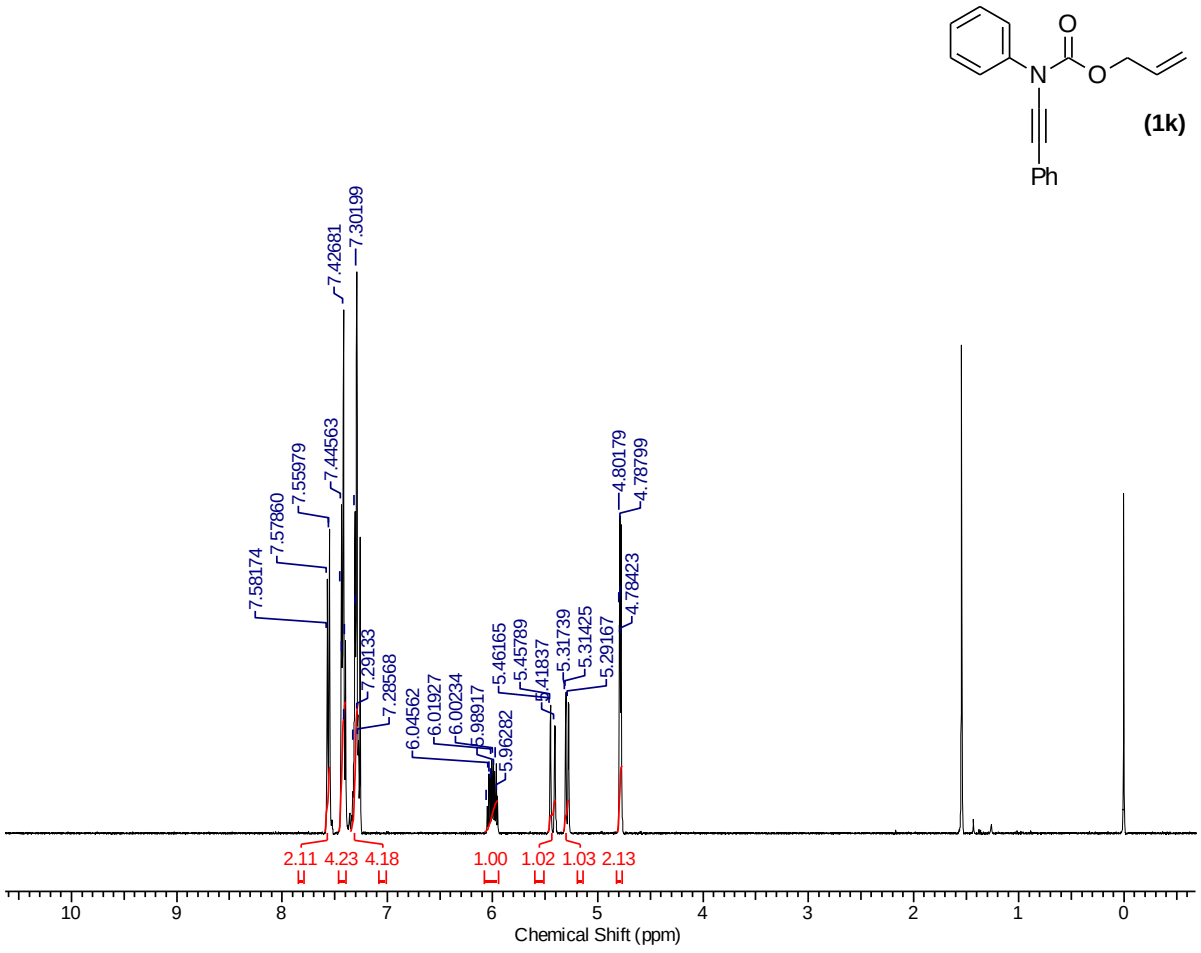

154.44453
140.66333
139.78833
131.69096
128.74513
128.30399
126.19306
124.46494
118.36549
77.32083
77.00000
76.68282
69.10315
67.61201
35.17879
20.62467
Chemical Shift (ppm)

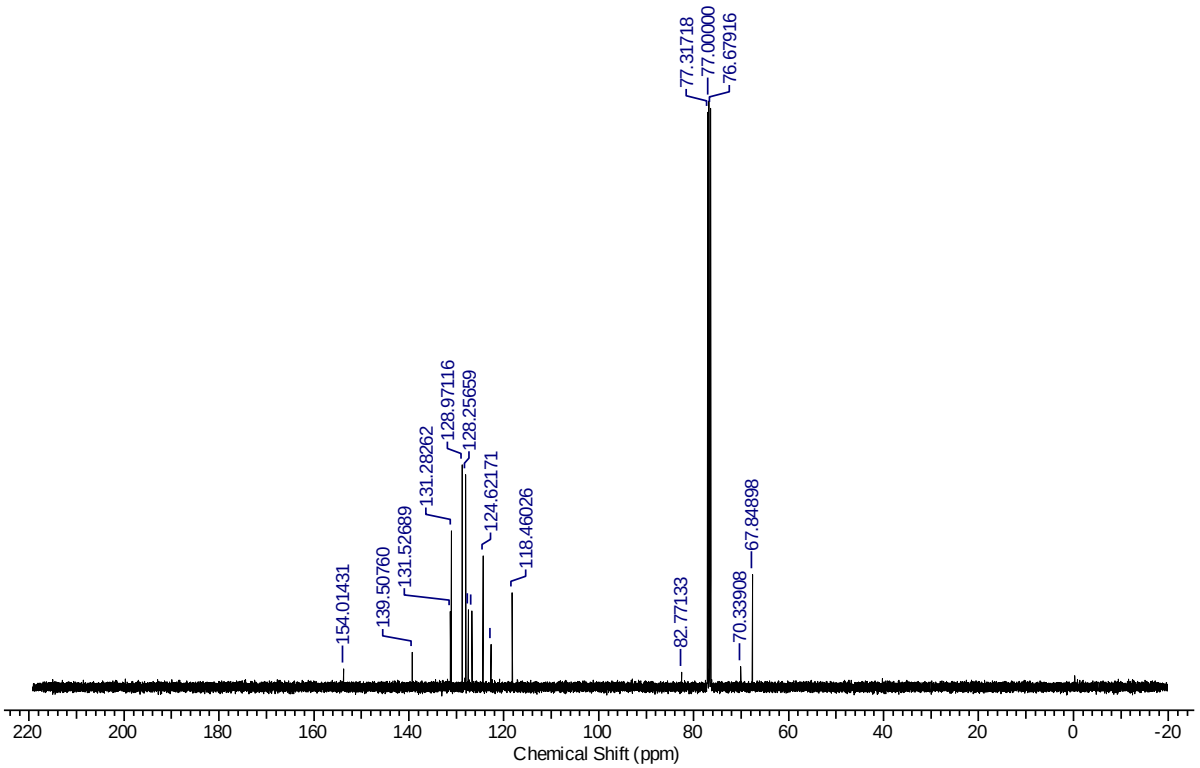

(1i)
7.48475
7.46949
7.38347
7.36639
7.25536
7.24011
6.01813
6.00715
5.99678
5.98641
5.97299
5.94127
5.41294
5.40684
5.28971
5.28727
5.26897
5.26592
4.74431
4.74126
4.73027
1.41454
1.40478
1.38831
1.37244
1.36268
0.82338
0.81667
0.73004
0.71540
0.70625
2.05 2.10 1.10
1.00 1.03 1.04 2.12
1.00 2.13 2.10
Chemical Shift (ppm)

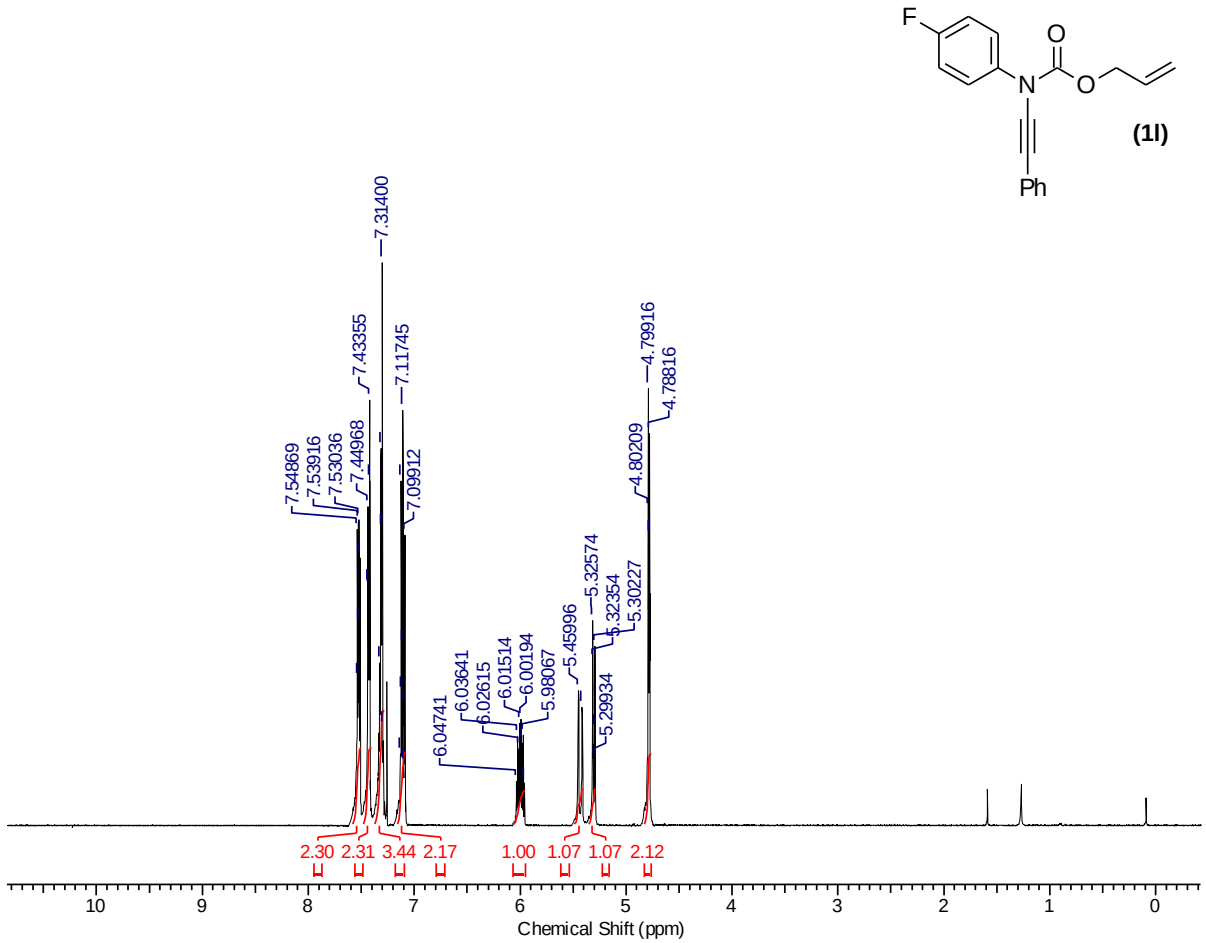

154.63148
139.94426
131.64027
128.74471
124.41940
118.15170
77.25273
77.00000
76.74727
69.10038
67.52623
8.42347
-0.77590
Chemical Shift (ppm)

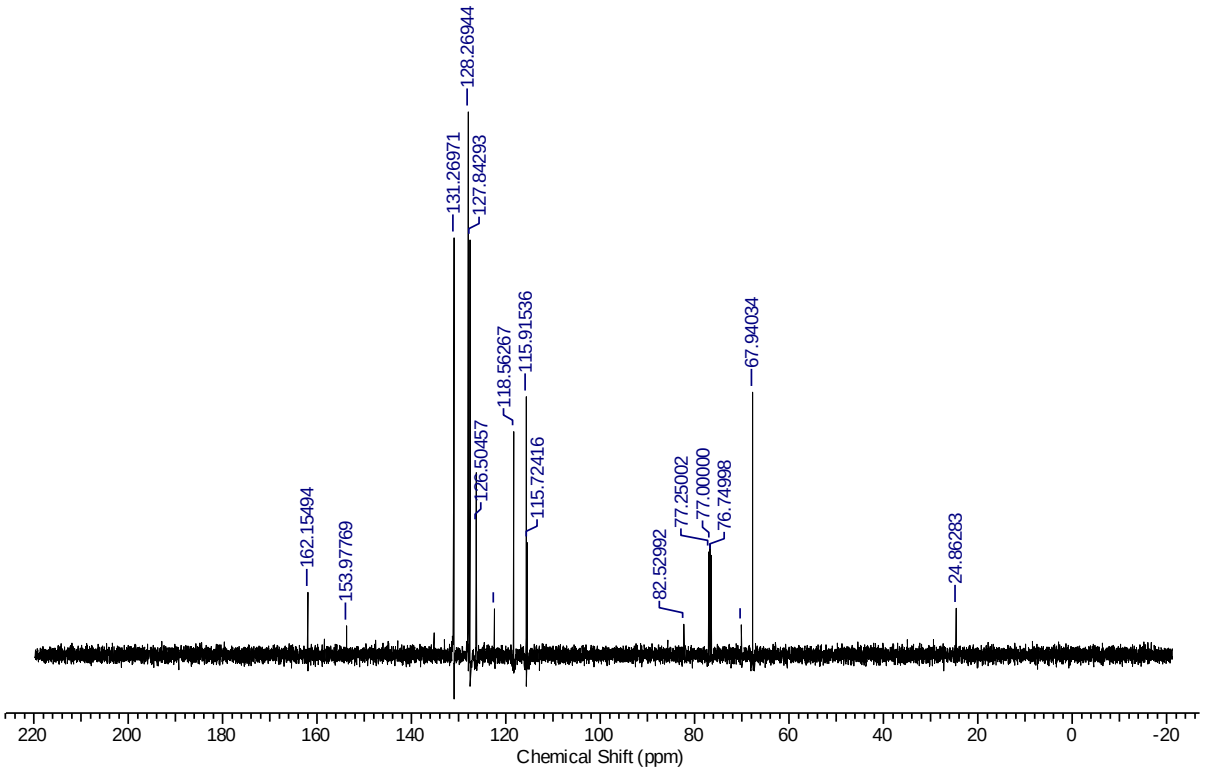

(1j)
Me
Me
OTBS
1.36796
0.72591
0.00008
7.35010
7.33420
7.32870
7.27244
7.25348
7.24981
7.23758
7.23269
5.82934
5.80305
5.28451
5.28084
5.23804
5.15854
5.15549
5.13225
4.61004
4.60638
4.59965
4.59598
4.59231
2.03
2.04
1.71
1.01
1.01
1.01
2.03
6.10
9.01
6.03
Chemical Shift (ppm)

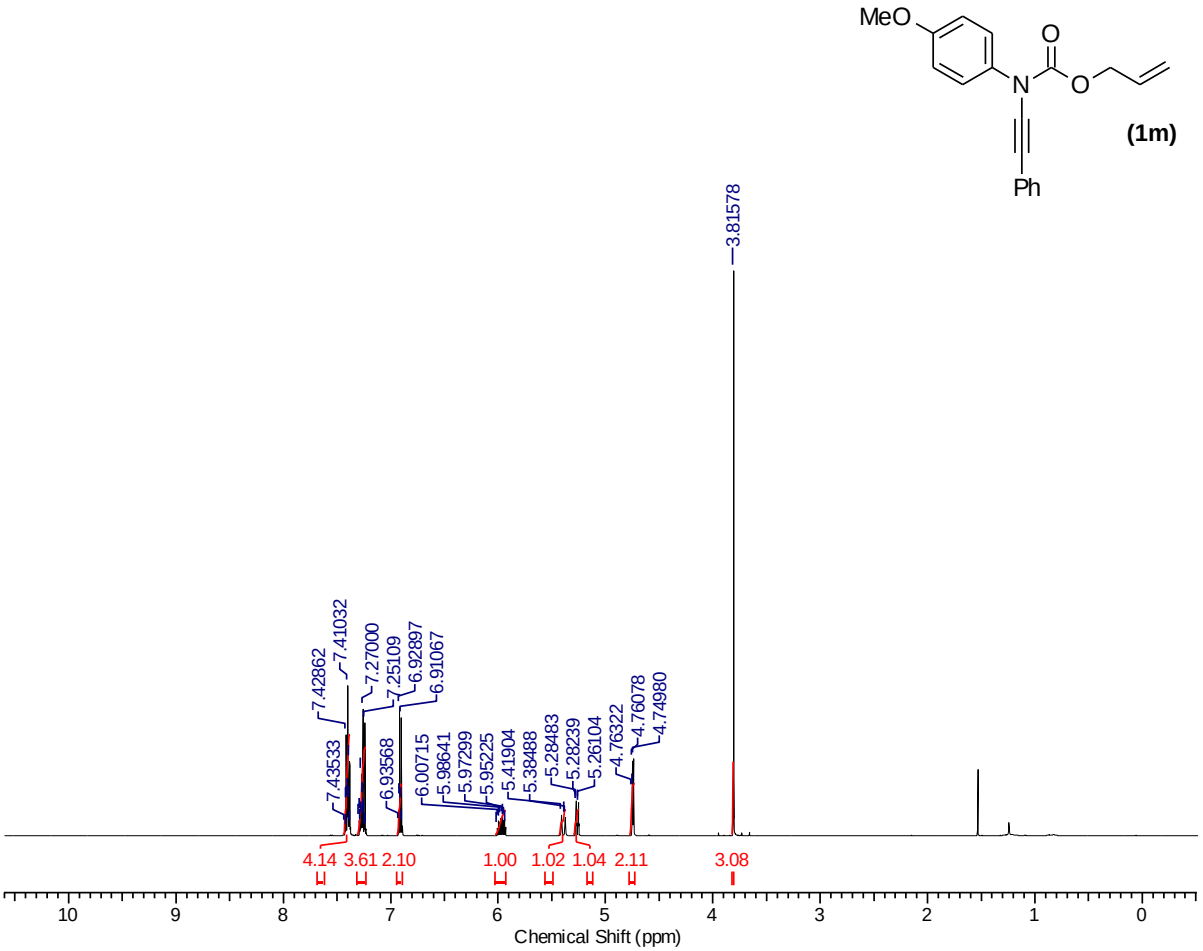

77.31371
77.00000
76.67900
154.23715
139.52219
131.58472
128.86351
124.47893
118.43098
75.16154
67.67639
66.56018
33.03020
25.70555
17.87021
0.01828
-3.10427
Chemical Shift (ppm)

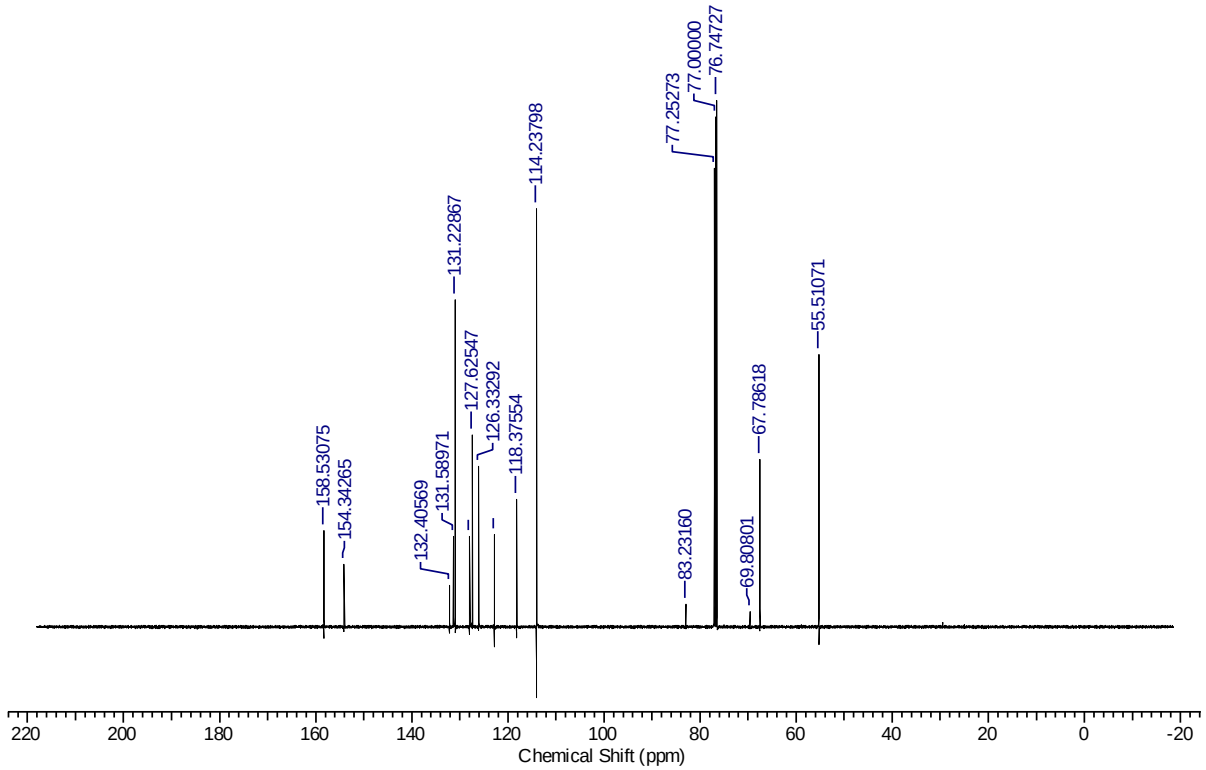

O
N
O
Ph
(1k)
7.58174
7.57860
7.55979
7.44563
7.42681
7.30199
7.29133
7.28568
6.04562
6.01927
6.00234
5.98917
5.96282
5.46165
5.45789
5.41837
5.31739
5.31425
5.29167
4.80179
4.78799
4.78423
2.11 4.23 4.18
1.00 1.02 1.03 2.13
Chemical Shift (ppm)

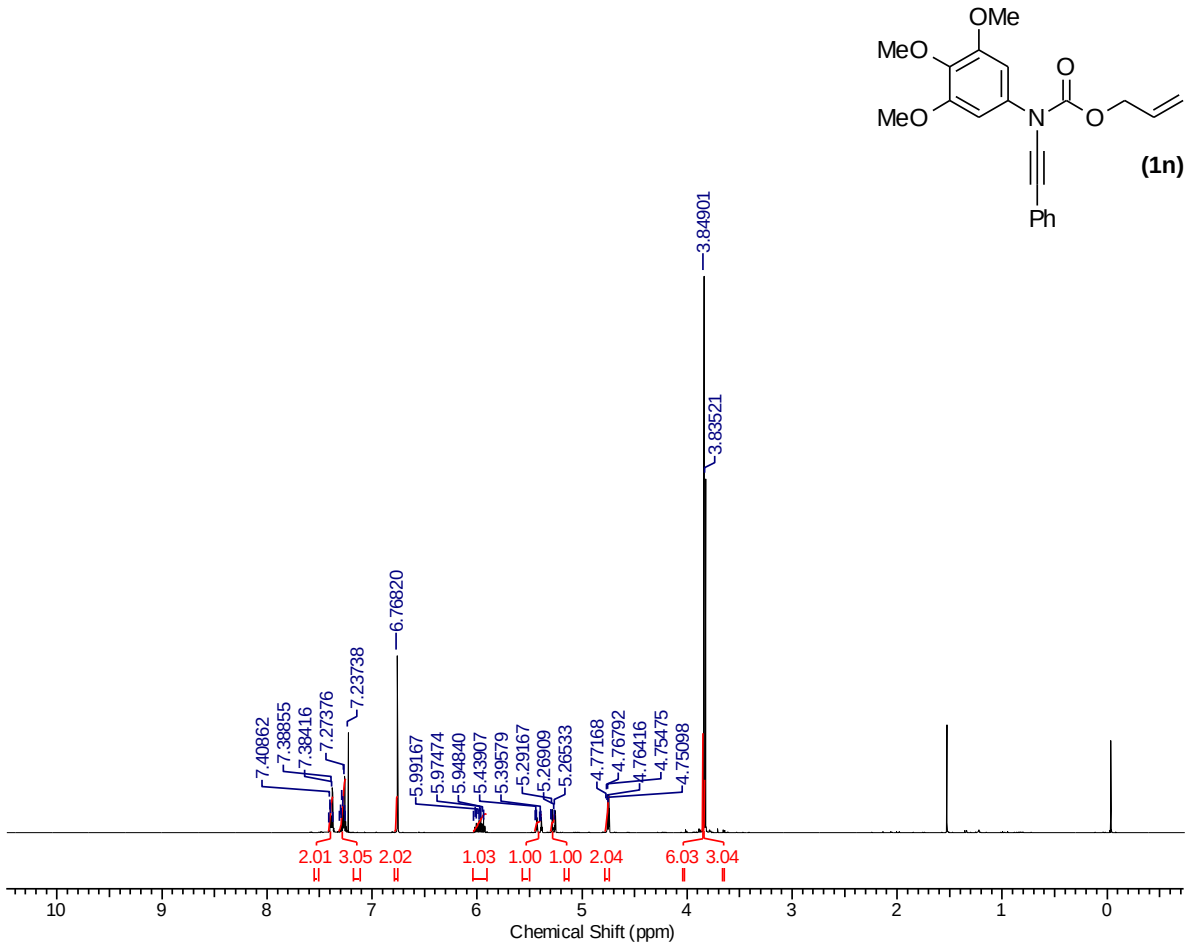

77.31718
77.00000
76.67916
154.01431
139.50760
131.52689
131.28262
128.97116
128.25659
124.62171
118.46026
82.77133
70.33908
67.84898
Chemical Shift (ppm)

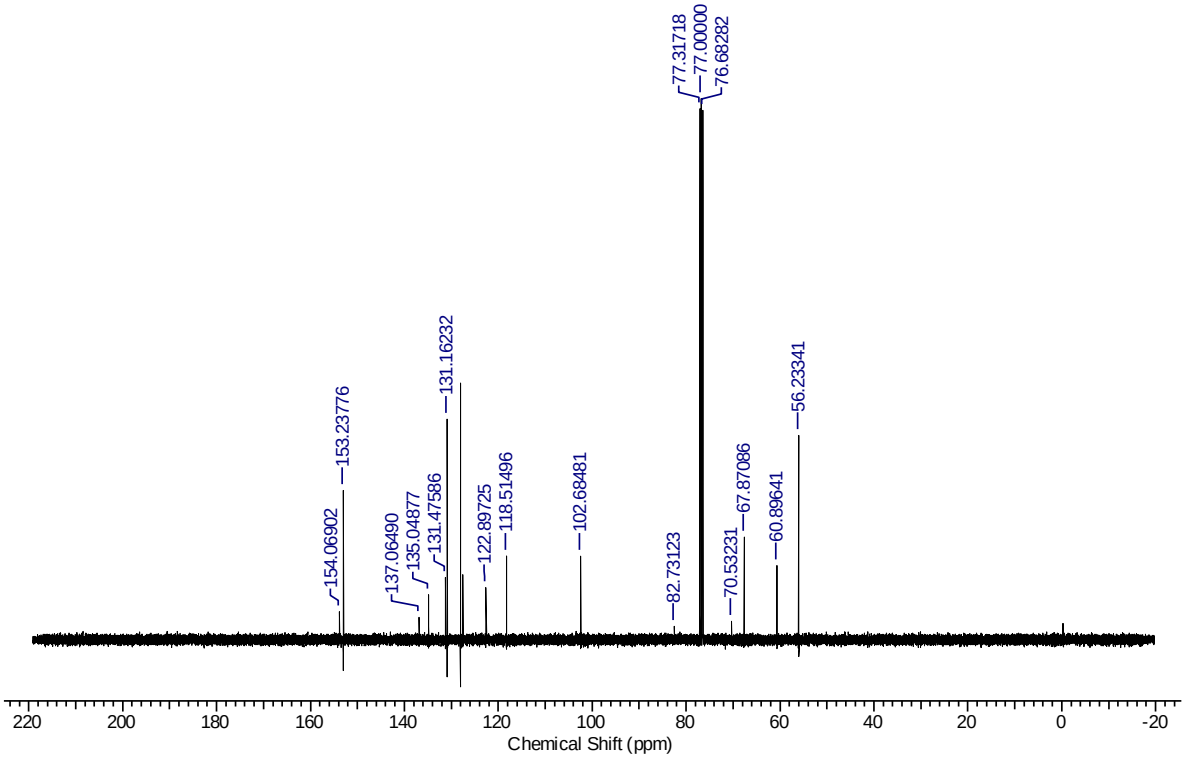

F
O
N
O
Ph
(1l)
7.54869
7.53916
7.53036
7.44968
7.43355
7.31400
7.11745
7.09912
6.04741
6.03641
6.02615
6.01514
6.00194
5.98067
5.45996
5.32574
5.32354
5.30227
5.29934
4.80209
4.79916
4.78816
2.30 2.31 3.44 2.17
1.00 1.07 1.07 2.12
Chemical Shift (ppm)

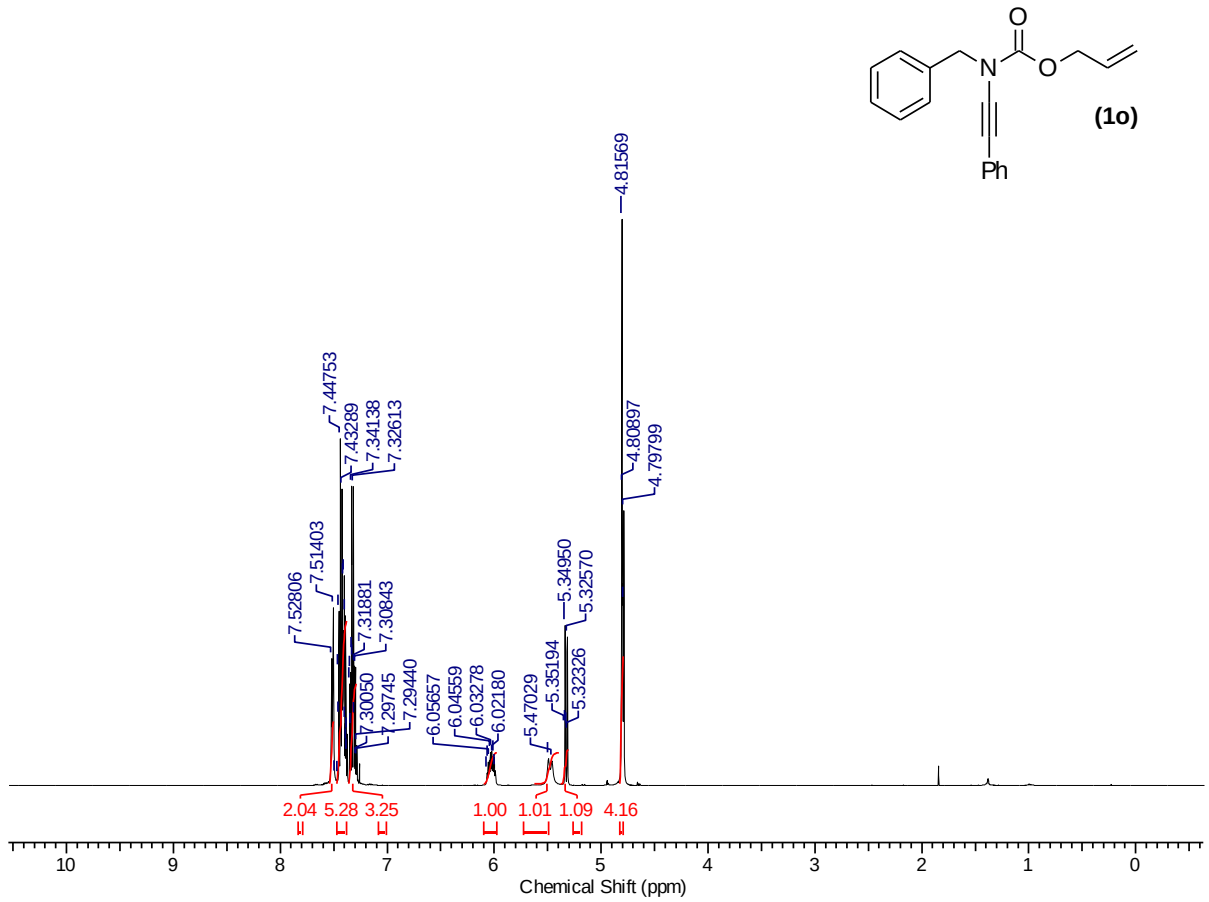

162.15494
153.97769
131.26971
128.26944
127.84293
126.50457
118.56267
115.91536
115.72416
82.52992
77.25002
77.00000
76.74998
67.94034
24.86283
Chemical Shift (ppm)

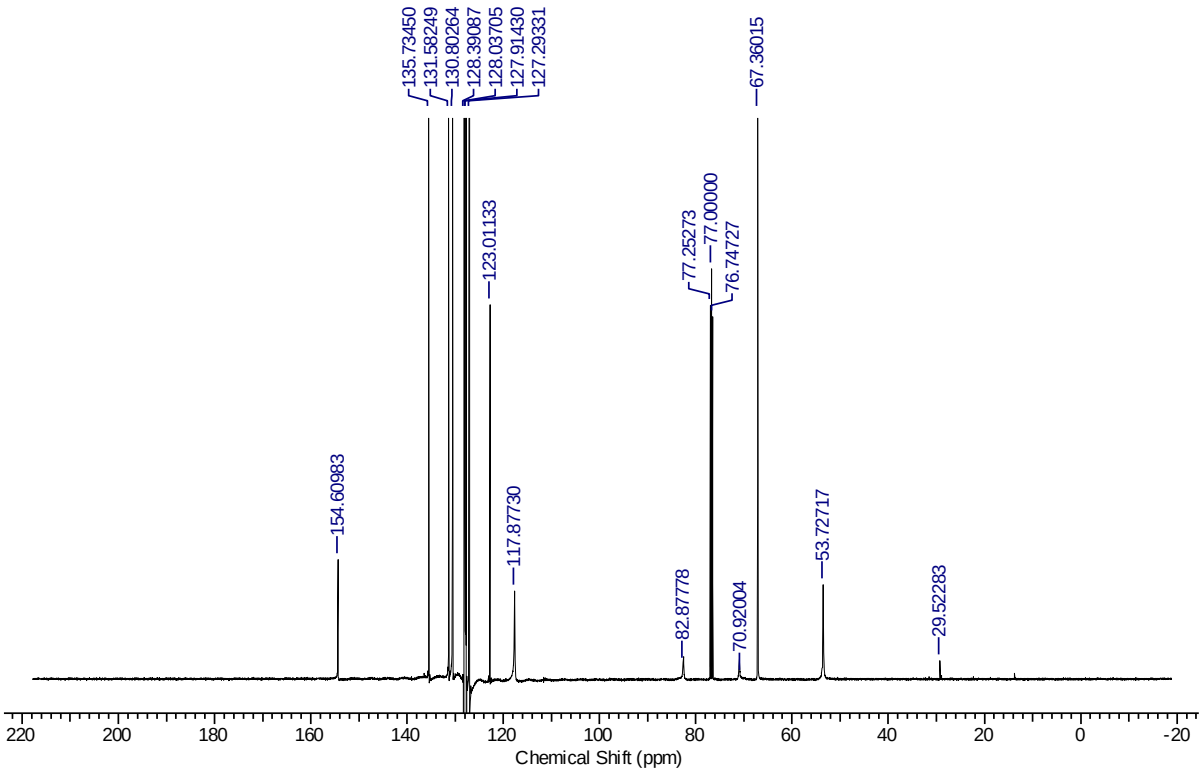

MeO
O
N
O
Ph
(1m)
3.81578
7.42862
7.41032
7.27000
7.25109
6.92897
6.91067
7.43533
6.93568
6.00715
5.98641
5.97299
5.95225
5.41904
5.38488
5.28483
5.28239
5.26104
4.76322
4.76078
4.74980
4.14
3.61
2.10
1.00
1.02
1.04
2.11
3.08
Chemical Shift (ppm)

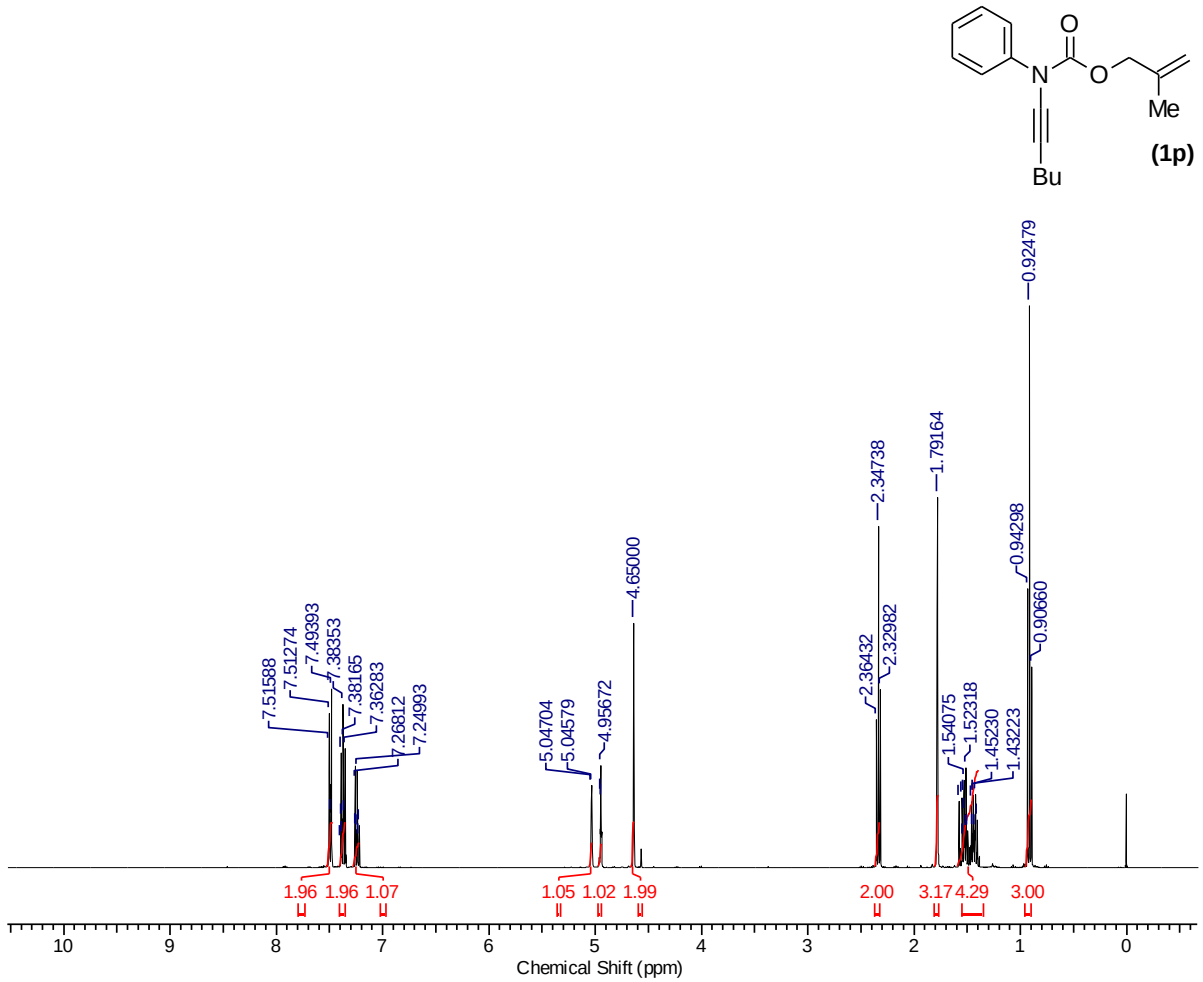

158.53075
154.34265
132.40569
131.58971
131.22867
127.62547
126.33292
118.37554
114.23798
77.25273
77.00000
76.74727
83.23160
69.80801
67.78618
55.51071
Chemical Shift (ppm)

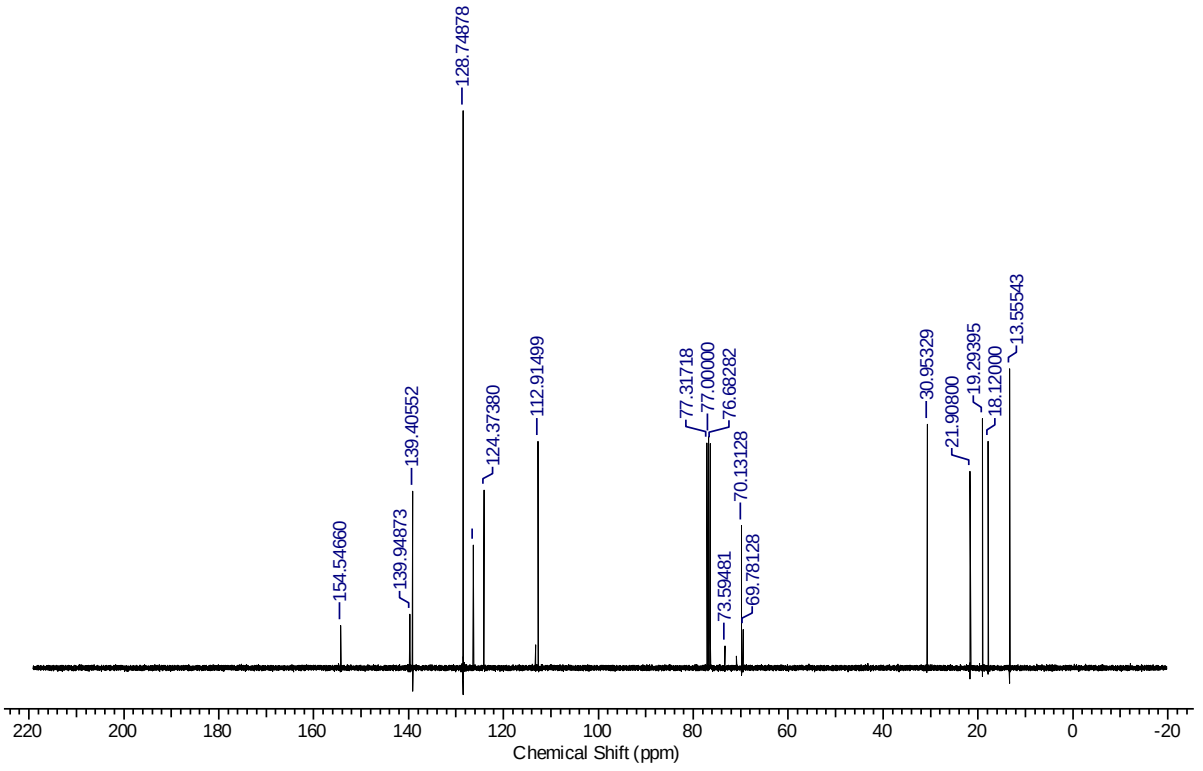

OMe
MeO
MeO
O
N
O
Ph
(1n)
3.84901
3.83521
6.76820
7.23738
7.40862
7.38855
7.38416
7.27376
5.99167
5.97474
5.94840
5.43907
5.39579
5.29167
5.26909
5.26533
4.77168
4.76792
4.76416
4.75475
4.75098
2.01 3.05 2.02 1.03 1.00 1.00 2.04 6.03 3.04
Chemical Shift (ppm)

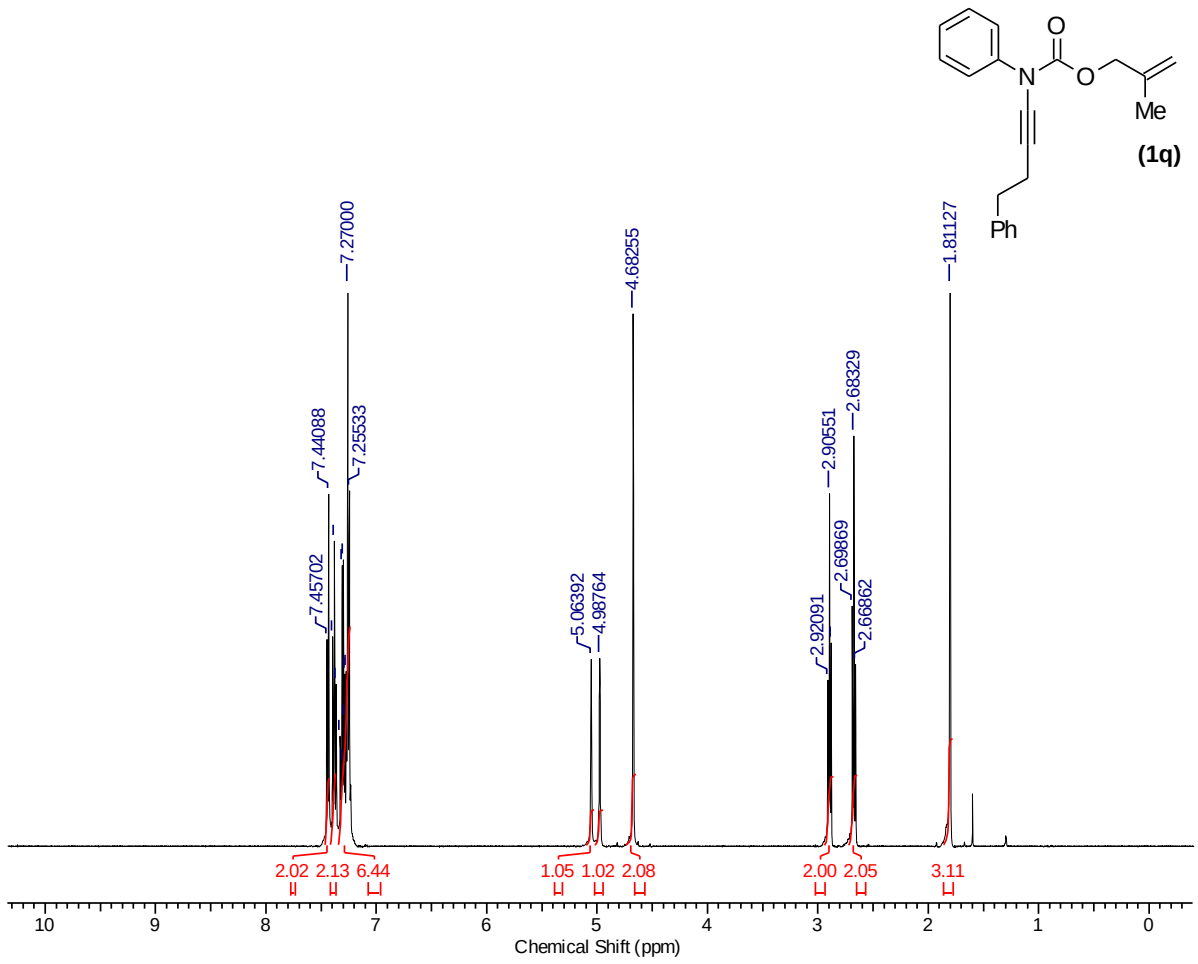

77.31718
77.00000
76.68282
153.23776
131.16232
56.23341
154.06902
137.06490
135.04877
131.47586
122.89725
118.51496
102.68481
82.73123
70.53231
67.87086
60.89641
Chemical Shift (ppm)

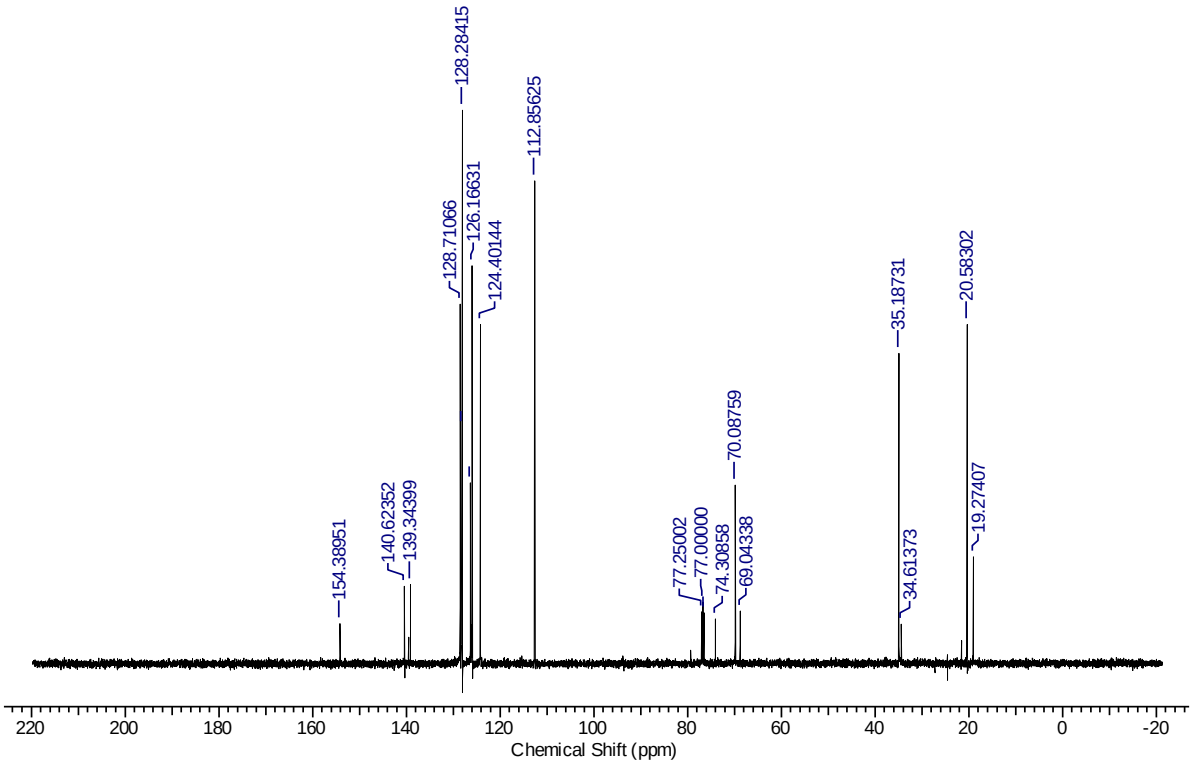

(1o)
Ph
7.52806
7.51403
7.44753
7.43289
7.34138
7.32613
7.31881
7.30843
7.30050
7.29745
7.29440
6.05657
6.04559
6.03278
6.02180
5.47029
5.35194
5.34950
5.32570
5.32326
4.81569
4.80897
4.79799
2.04 5.28 3.25 1.00 1.01 1.09 4.16
Chemical Shift (ppm)

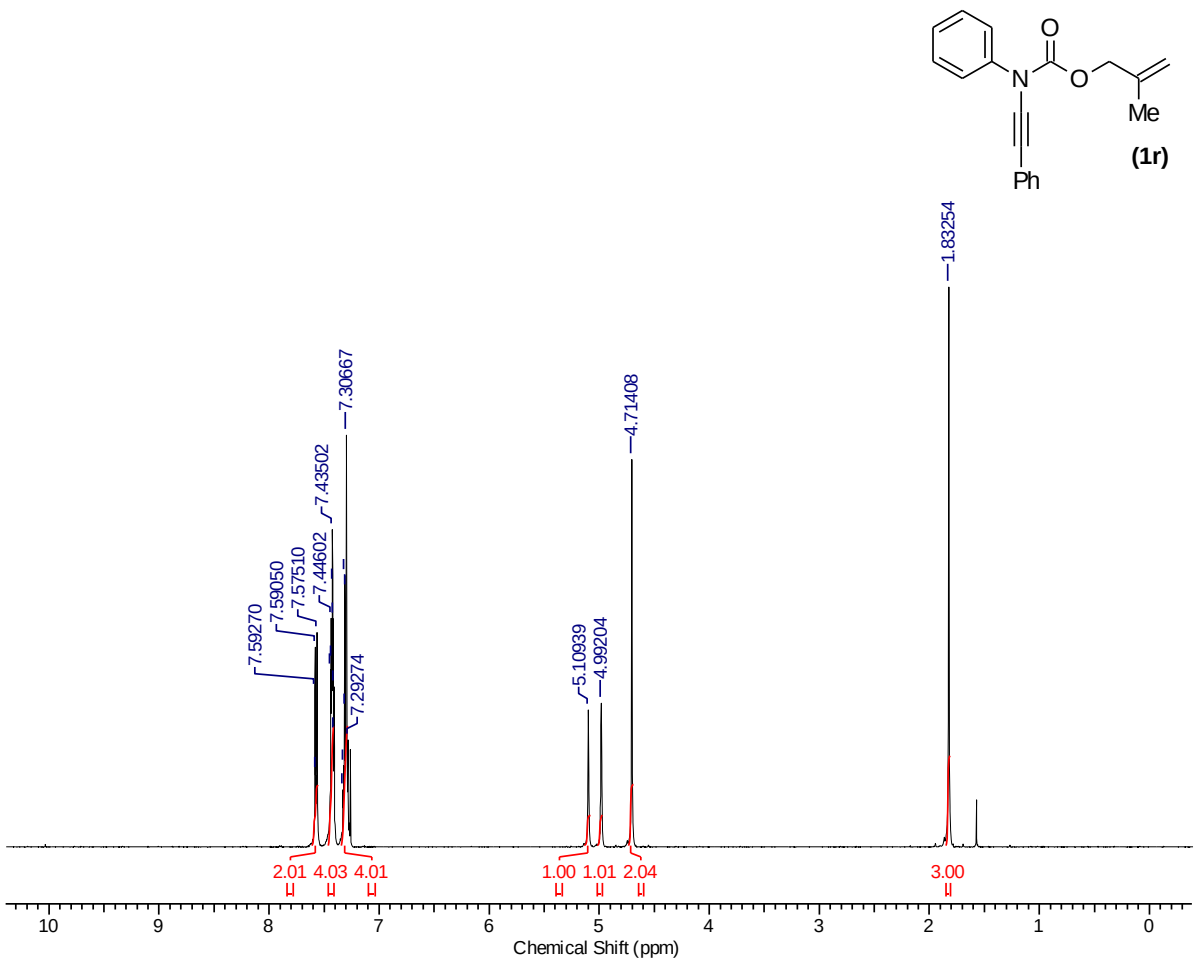

135.73450
131.58249
130.80264
128.39087
128.03705
127.91430
127.29331
123.01133
117.87730
154.60983
82.87778
77.25273
77.00000
76.74727
70.92004
67.36015
53.72717
29.52283
Chemical Shift (ppm)

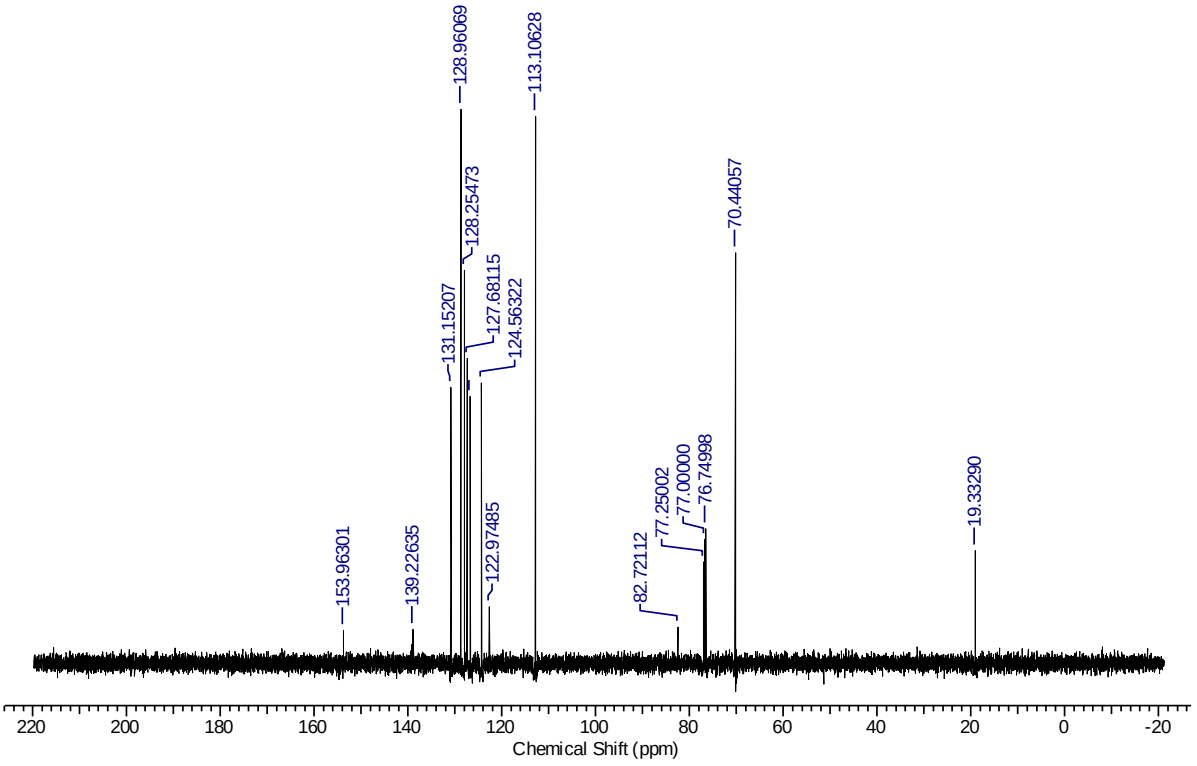

O
N
O
Me
Bu
(1p)
7.51588
7.51274
7.49393
7.38353
7.38165
7.36283
7.26812
7.24993
5.04704
5.04579
4.95672
4.65000
2.36432
2.32982
2.34738
1.79164
1.54075
1.52318
1.45230
1.43223
0.94298
0.92479
0.90660
1.96 1.96 1.07
1.05 1.02 1.99
2.00 3.17 4.29 3.00
Chemical Shift (ppm)

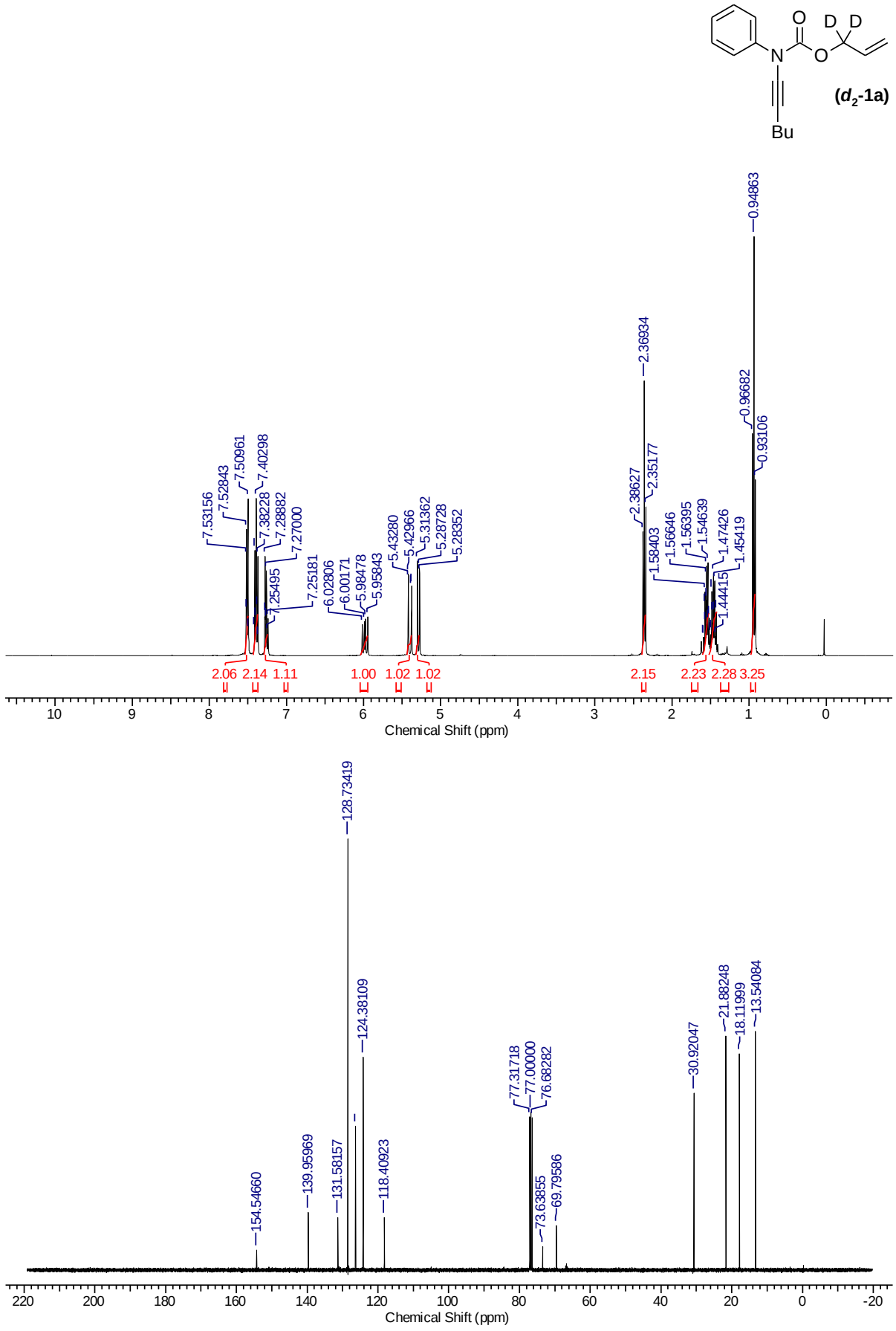

154.54660
139.94873
139.40552
128.74878
124.37380
112.91499
77.31718
77.00000
76.68282
73.59481
70.13128
69.78128
30.95329
21.90800
19.29395
18.12000
13.55543
Chemical Shift (ppm)

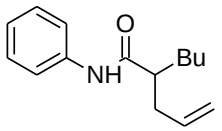

O
N
O
Me
Ph
(1q)
7.27000
7.44088
7.25533
7.45702
4.68255
5.06392
4.98764
1.81127
2.90551
2.68329
2.69869
2.66862
2.92091
2.02 2.13 6.44
1.05 1.02 2.08
2.00 2.05
3.11
Chemical Shift (ppm)


128.28415
112.85625
128.71066
126.16631
124.40144
154.38951
140.62352
139.34399
70.08759
77.25002
77.00000
74.30858
69.04338
35.18731
20.58302
34.61373
19.27407
Chemical Shift (ppm)

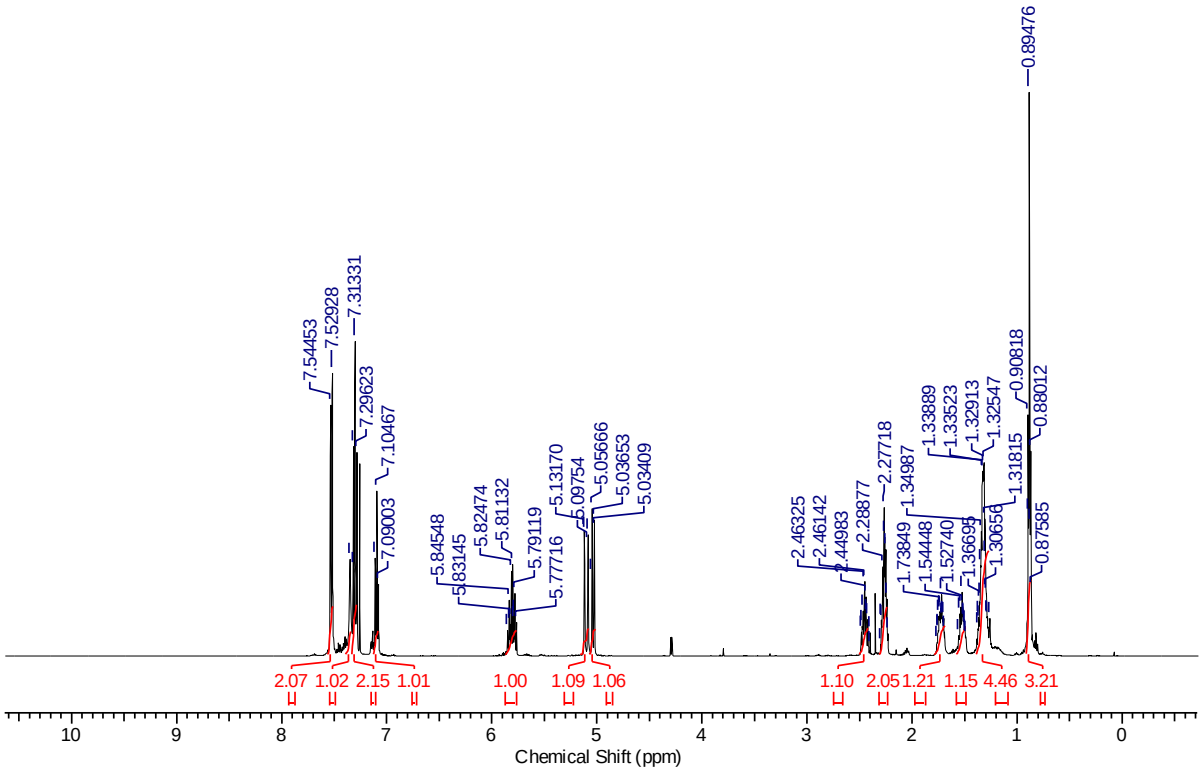

O
N
O
Me
Ph
(1r)
7.59270
7.59050
7.57510
7.44602
7.43502
7.30667
7.29274
5.10939
4.99204
4.71408
1.83254
2.01 4.03 4.01
1.00 1.01 2.04
3.00
Chemical Shift (ppm)

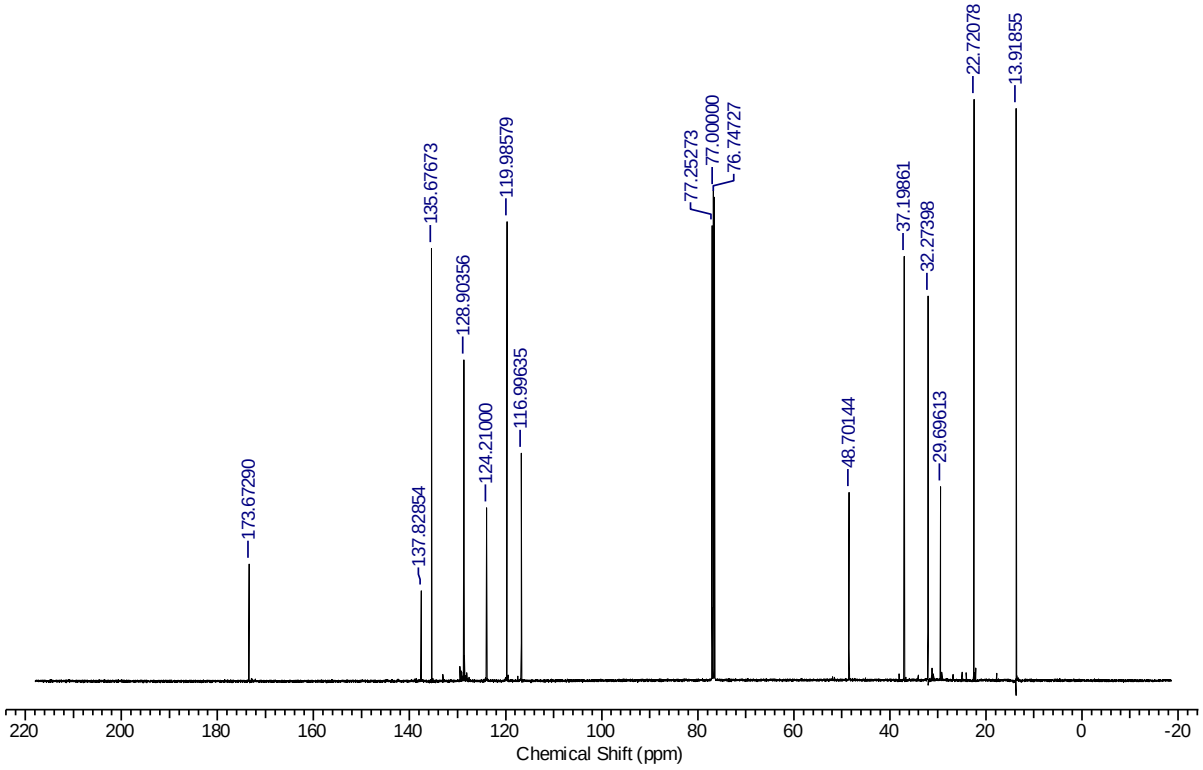

153.96301
139.22635
131.15207
128.96069
128.25473
127.68115
124.56322
122.97485
113.10628
82.72112
77.25002
77.00000
76.74998
70.44057
19.33290
Chemical Shift (ppm)

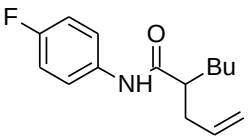

O
D D
N
O
Bu
(d2-1a)
7.53156
7.52843
7.50961
7.40298
7.38228
7.28882
7.27000
7.25181
7.25495
6.02806
6.00171
5.98478
5.95843
5.43280
5.42966
5.31362
5.28728
5.28352
2.36934
2.38627
2.35177
1.58403
1.56646
1.56395
1.54639
1.47426
1.45419
1.44415
0.96682
0.94863
0.93106
2.06 2.14 1.11 1.00 1.02 1.02 2.15 2.23 2.28 3.25
Chemical Shift (ppm)
128.73419
124.38109
154.54660
139.95969
131.58157
118.40923
77.31718
77.00000
76.68282
73.63855
69.79586
30.92047
21.88248
18.11999
13.54084
Chemical Shift (ppm)


O
NH
Bu

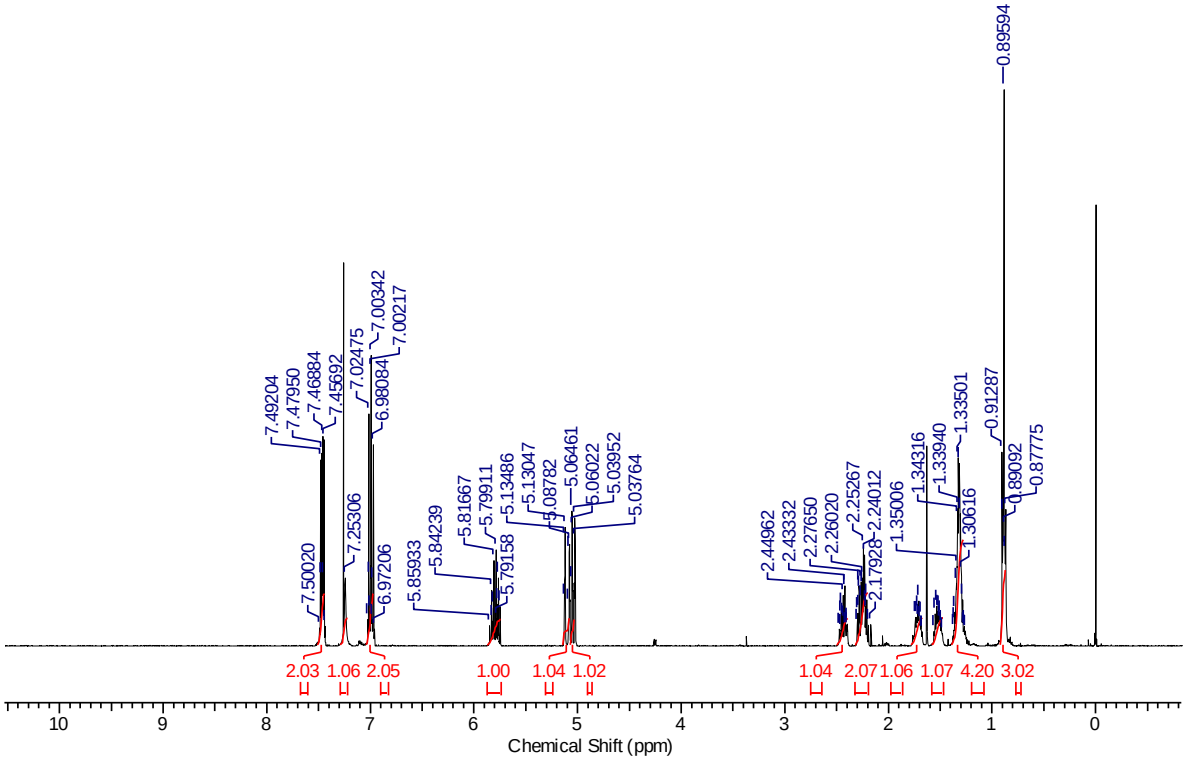
(2a)

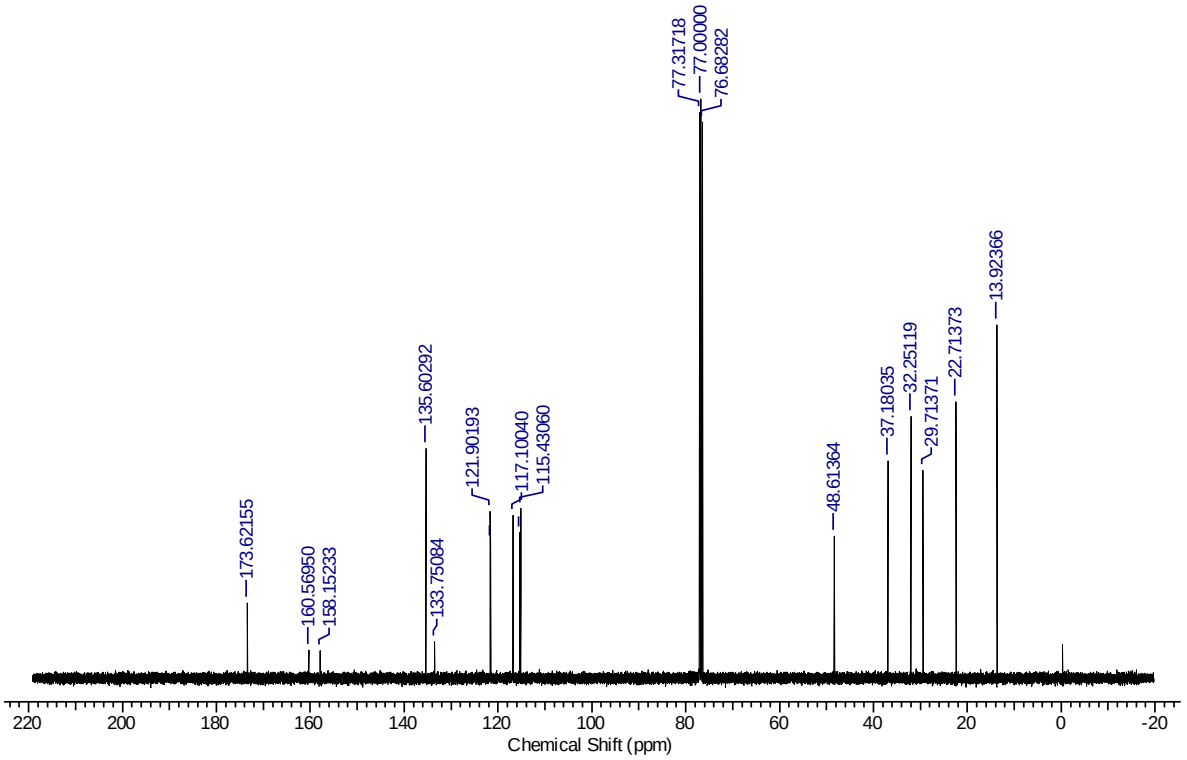

7.54453
7.52928
7.31331
7.29623
7.10467
7.09003
5.84548
5.83145
5.82474
5.81132
5.79119
5.77716
5.13170
5.09754
5.05666
5.03653
5.03409
2.46325
2.46142
2.44983
2.28877
2.27718
1.73849
1.54448
1.52740
1.36695
1.34987
1.33889
1.33523
1.32913
1.32547
1.31815
1.30656
0.90818
0.88012
0.87585
0.89476
2.07 1.02 2.15 1.01 1.00 1.09 1.06 1.10 2.05 1.21 1.15 4.46 3.21
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

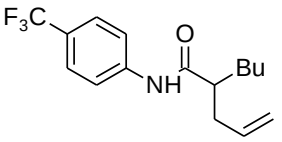

173.67290
137.82854
135.67673
128.90356
124.21000
119.98579
116.99635
77.25273
77.00000
76.74727
48.70144
37.19861
32.27398
29.69613
22.72078
13.91855
220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)


F
O
NH
Bu

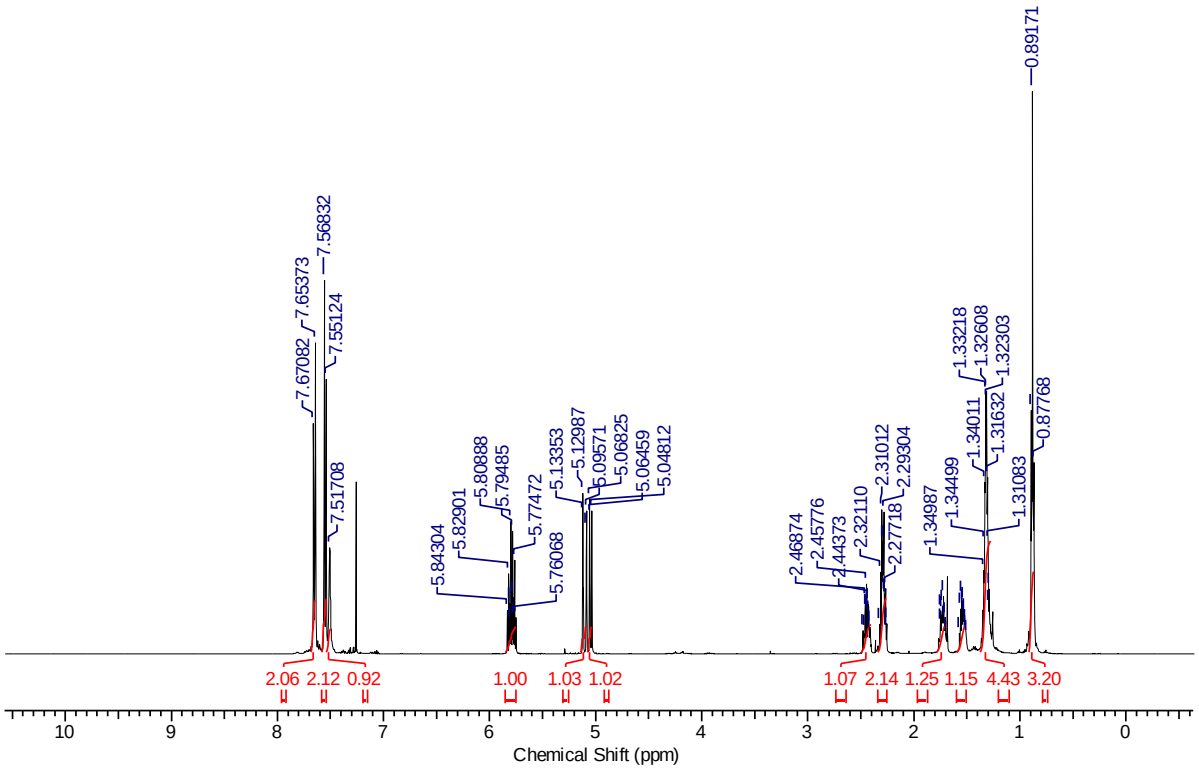
(2b)

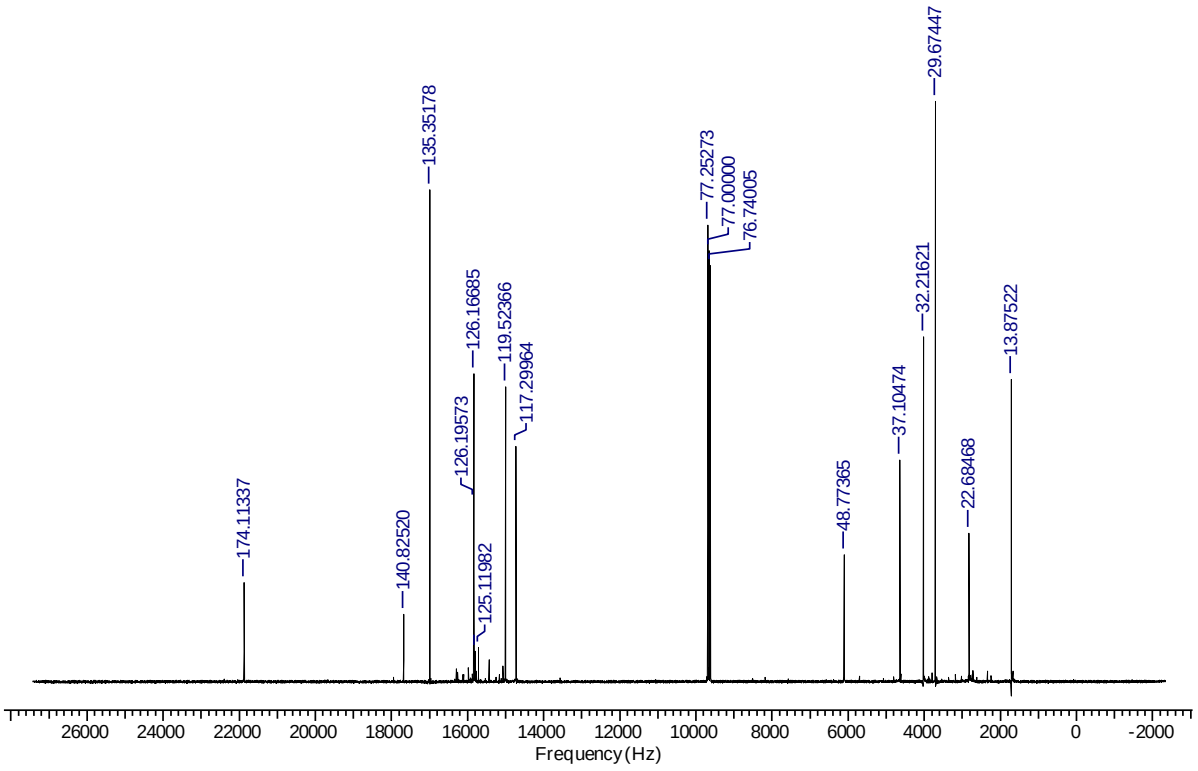

7.49204
7.47950
7.46884
7.45692
7.25306
7.02475
7.00342
7.00217
6.98084
6.97206
7.50020
5.85933
5.84239
5.81667
5.79911
5.79158
5.13486
5.13047
5.08782
5.06461
5.06022
5.03952
5.03764
2.44962
2.43332
2.27650
2.26020
2.25267
2.24012
2.17928
1.35006
1.34316
1.33940
1.33501
1.30616
0.91287
0.89594
0.89092
0.87775
2.03 1.06 2.05 1.00 1.04 1.02 1.04 2.07 1.06 1.07 4.20 3.02
Chemical Shift (ppm)

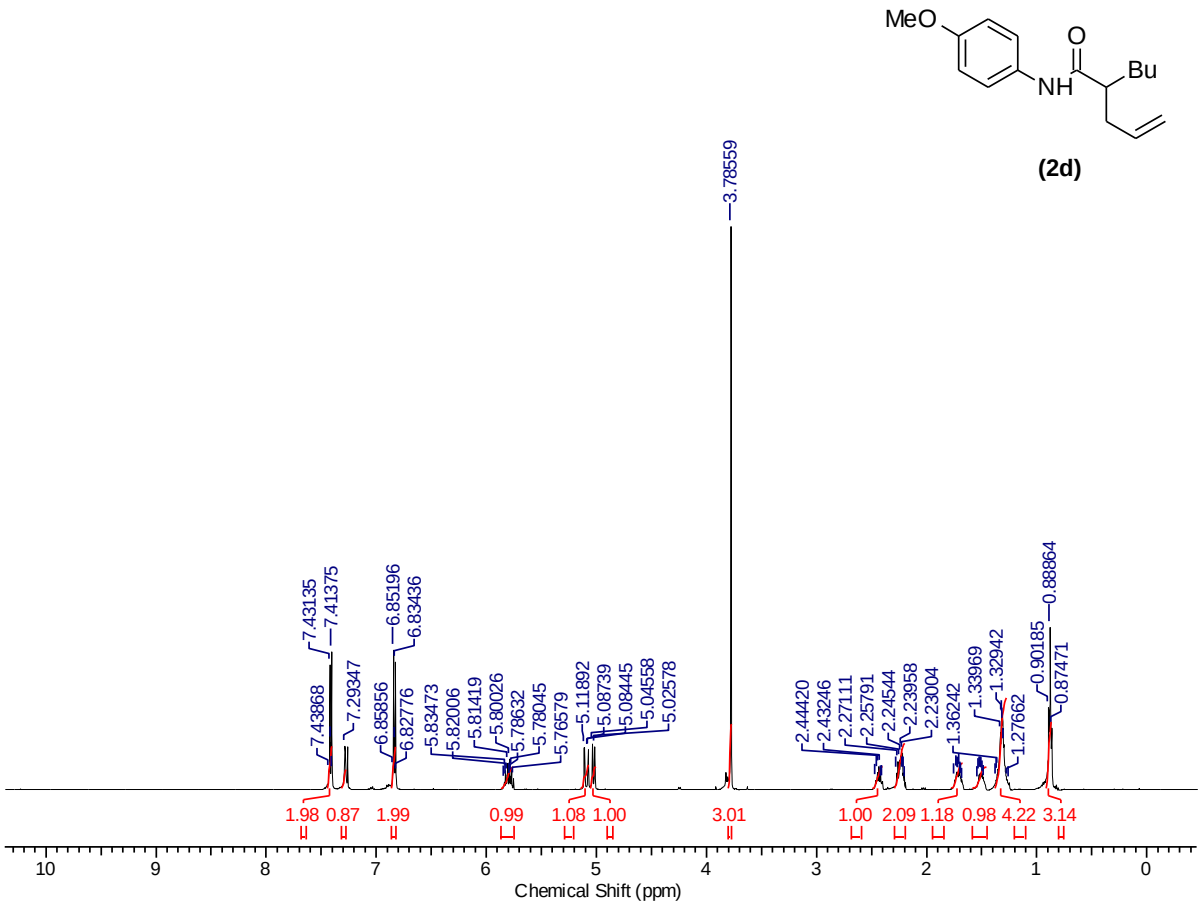

77.31718
77.00000
76.68282
173.62155
160.56950
158.15233
135.60292
133.75084
121.90193
117.10040
115.43060
48.61364
37.18035
32.25119
29.71371
22.71373
13.92366
Chemical Shift (ppm)

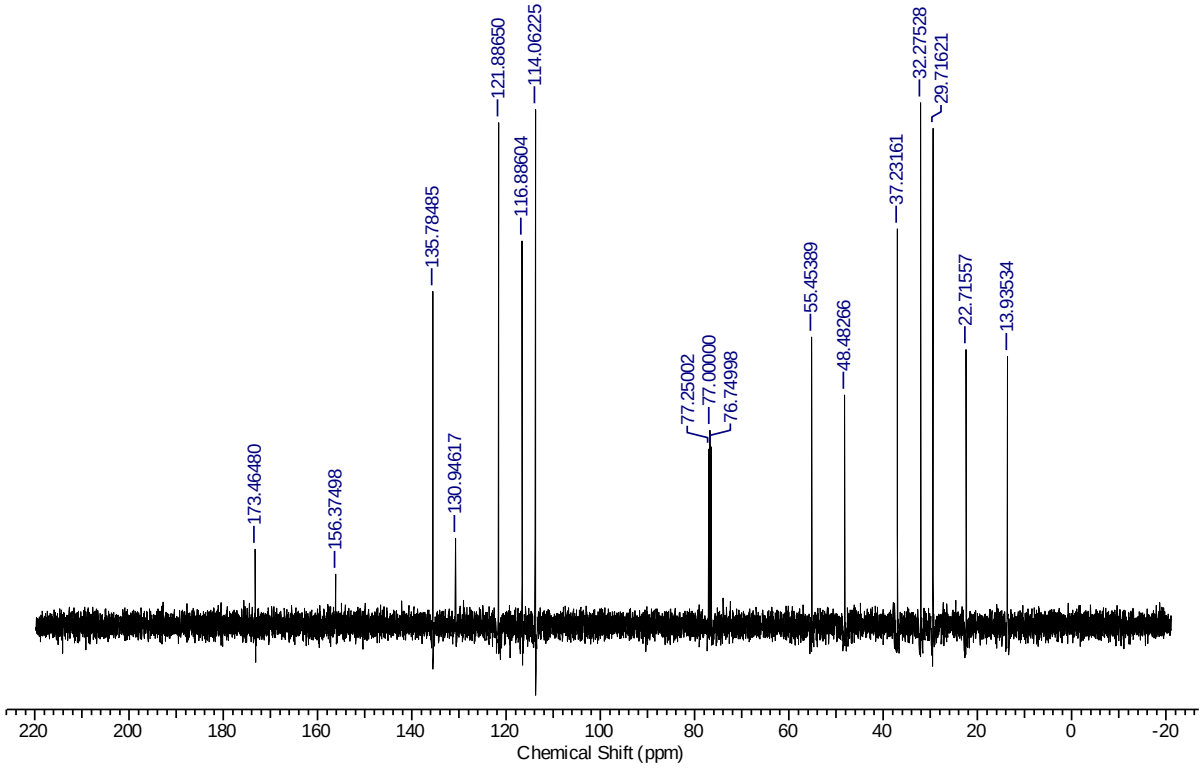

F3C
O
NH
Bu

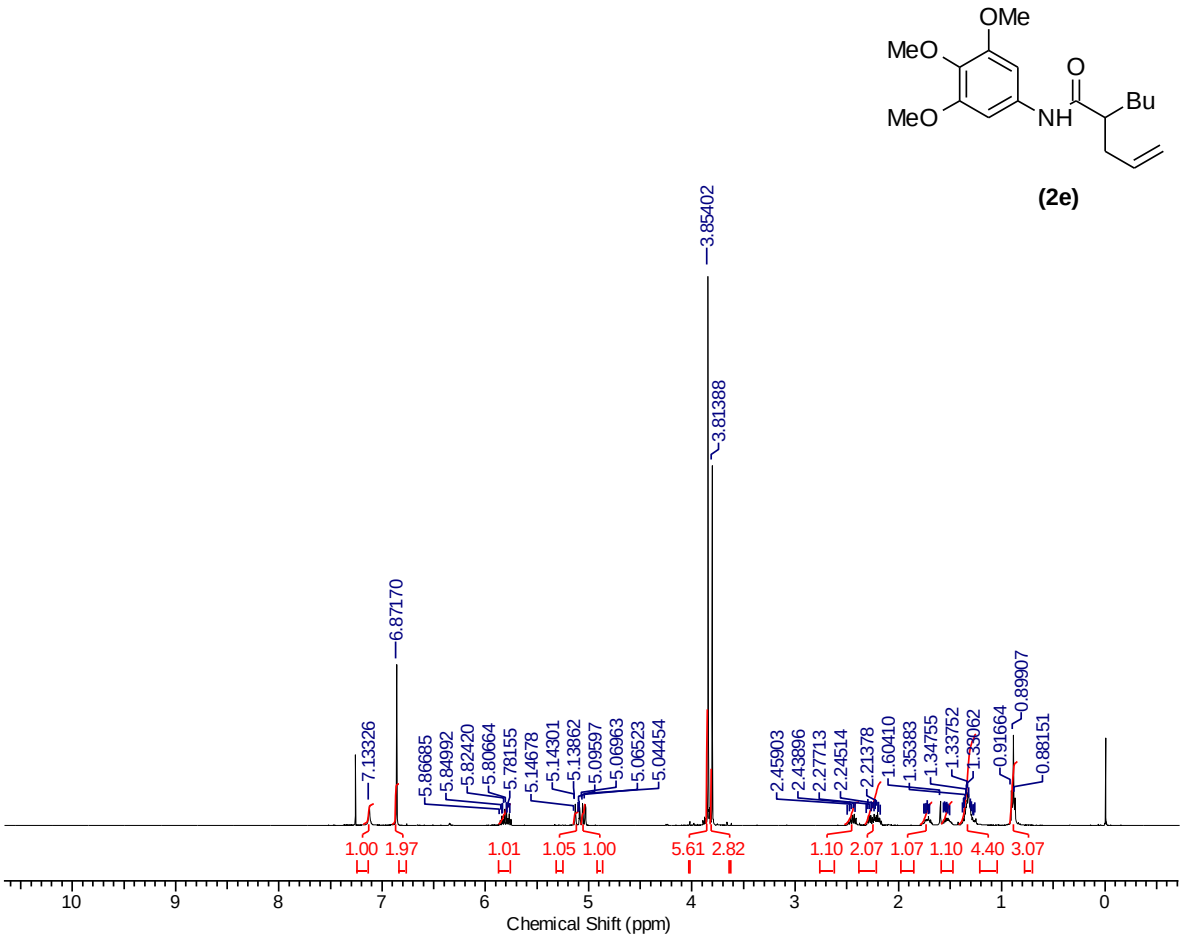
(2c)

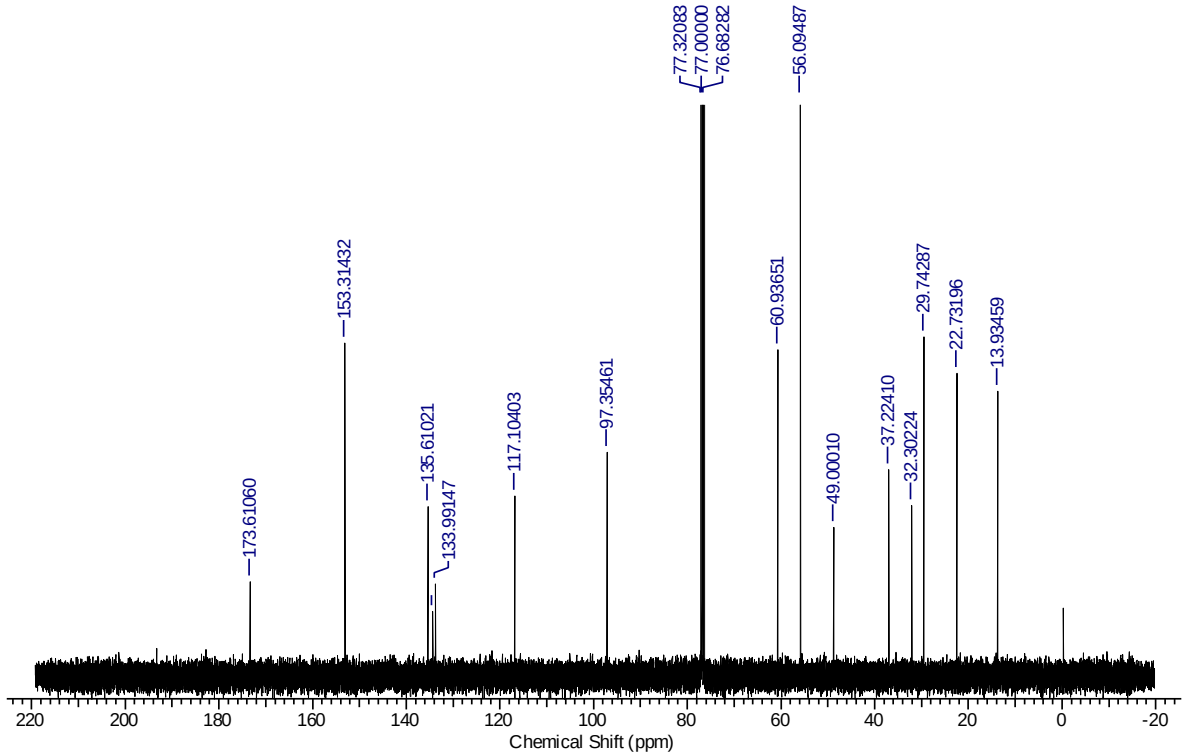

7.67082
7.65373
7.56832
7.55124
7.51708
5.84304
5.82901
5.80888
5.79485
5.77472
5.76068
5.13353
5.12987
5.09571
5.06825
5.06459
5.04812
2.46874
2.45776
2.44373
2.32110
2.31012
2.29304
2.27718
1.34987
1.34499
1.34011
1.33218
1.32608
1.32303
1.31632
1.31083
0.89171
0.87768
2.06 2.12 0.92
1.00
1.03 1.02
1.07 2.14 1.25 1.15 4.43 3.20
Chemical Shift (ppm)

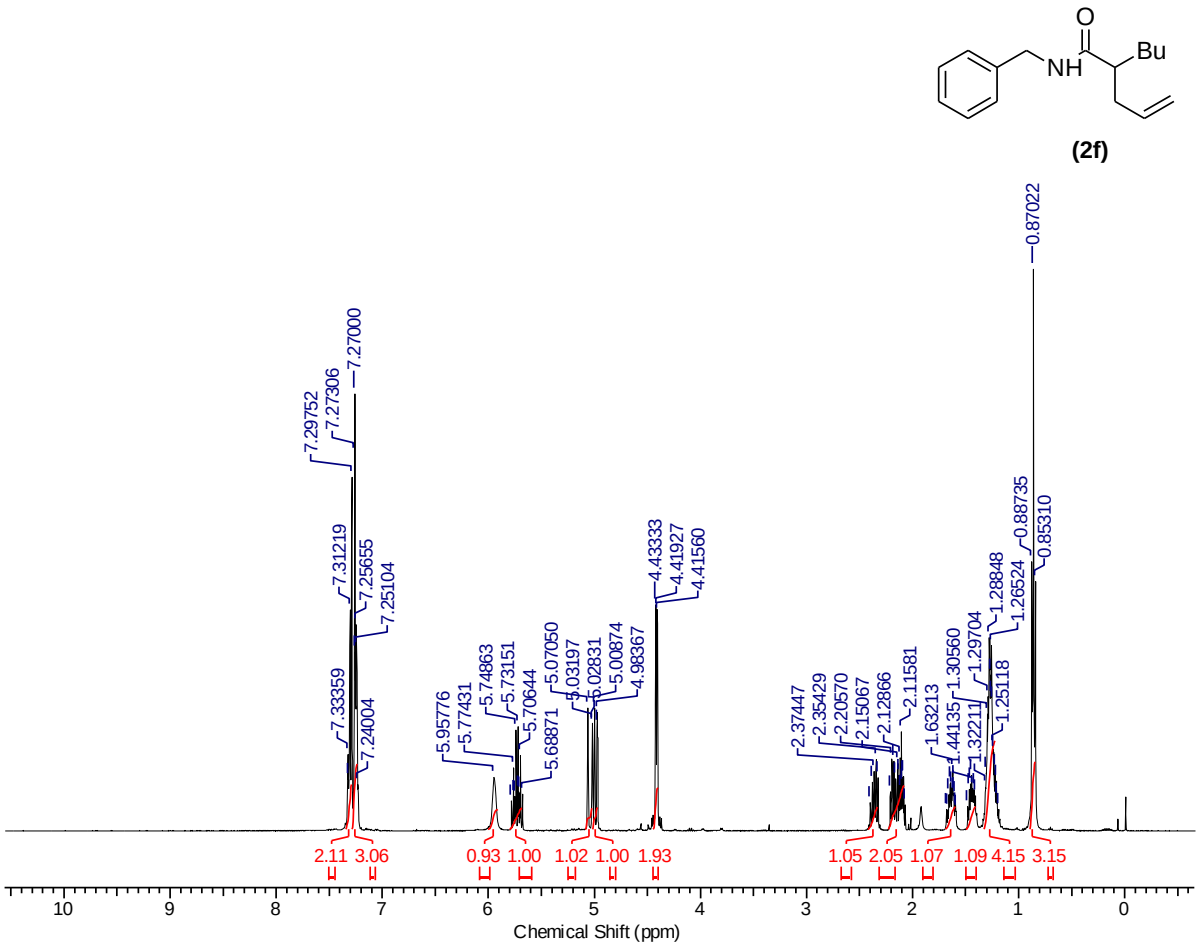

174.11337
140.82520
135.35178
126.19573
126.16685
125.11982
119.52366
117.29964
77.25273
77.00000
76.74005
48.77365
37.10474
32.21621
29.67447
22.68468
13.87522
Frequency (Hz)

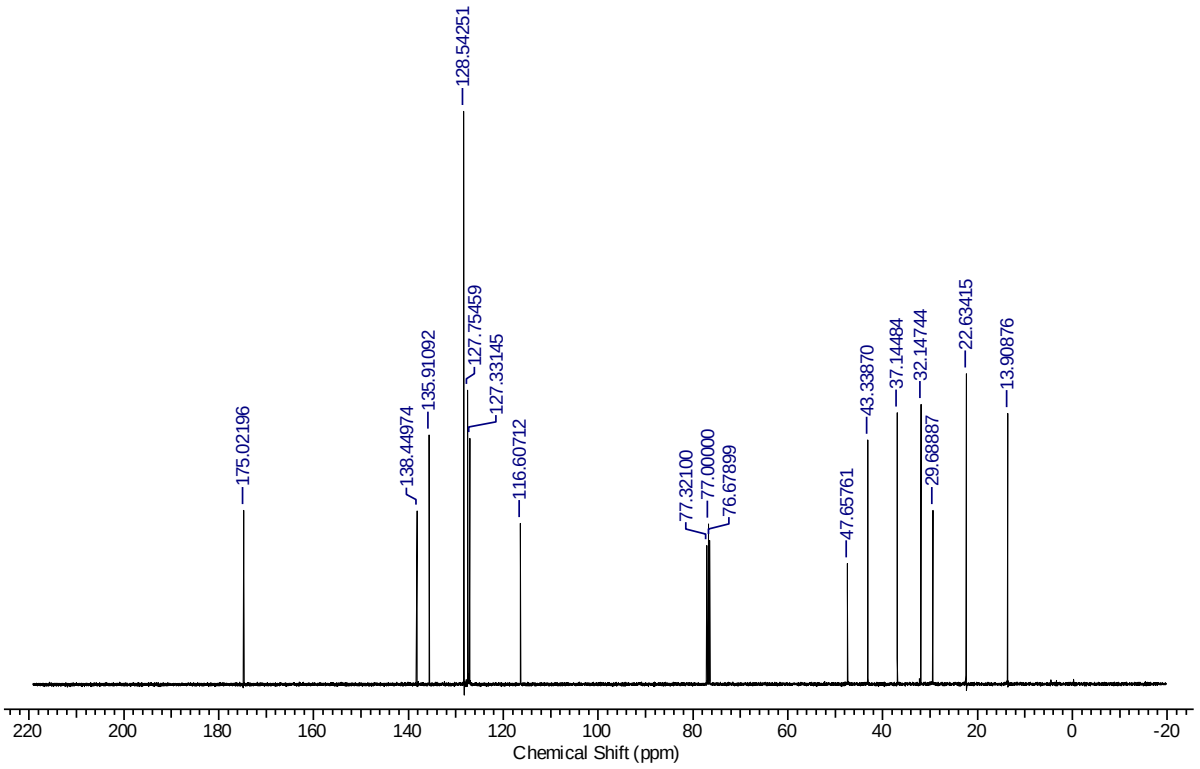

MeO
O
NH
Bu
(2d)
3.78559
7.43135
7.41375
7.43868
7.29347
6.85196
6.83436
6.85856
6.82776
5.83473
5.82006
5.81419
5.80026
5.78632
5.78045
5.76579
5.11892
5.08739
5.08445
5.04558
5.02578
2.44420
2.43246
2.27111
2.25791
2.24544
2.23958
2.23004
1.36242
1.33969
1.32942
1.27662
0.90185
0.88864
0.87471
1.98 0.87 1.99 0.99 1.08 1.00 3.01 1.00 2.09 1.18 0.98 4.22 3.14
Chemical Shift (ppm)

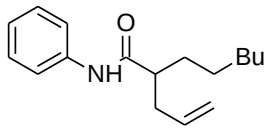

173.46480
156.37498
135.78485
130.94617
121.88650
116.88604
114.06225
77.25002
77.00000
76.74998
55.45389
48.48266
37.23161
32.27528
29.71621
22.71557
13.93534
Chemical Shift (ppm)


OMe
MeO
MeO
NH
O
Bu
(2e)
3.85402
3.81388
6.87170
7.13326
5.86685
5.84992
5.82420
5.80664
5.78155
5.14678
5.14301
5.13862
5.09597
5.06963
5.06523
5.04454
2.45903
2.43896
2.27713
2.24514
2.21378
1.60410
1.35383
1.34755
1.33752
1.33062
0.91664
0.89907
0.88151
1.00 1.97 1.01 1.05 1.00 5.61 2.82 1.10 2.07 1.07 1.10 4.40 3.07
Chemical Shift (ppm)

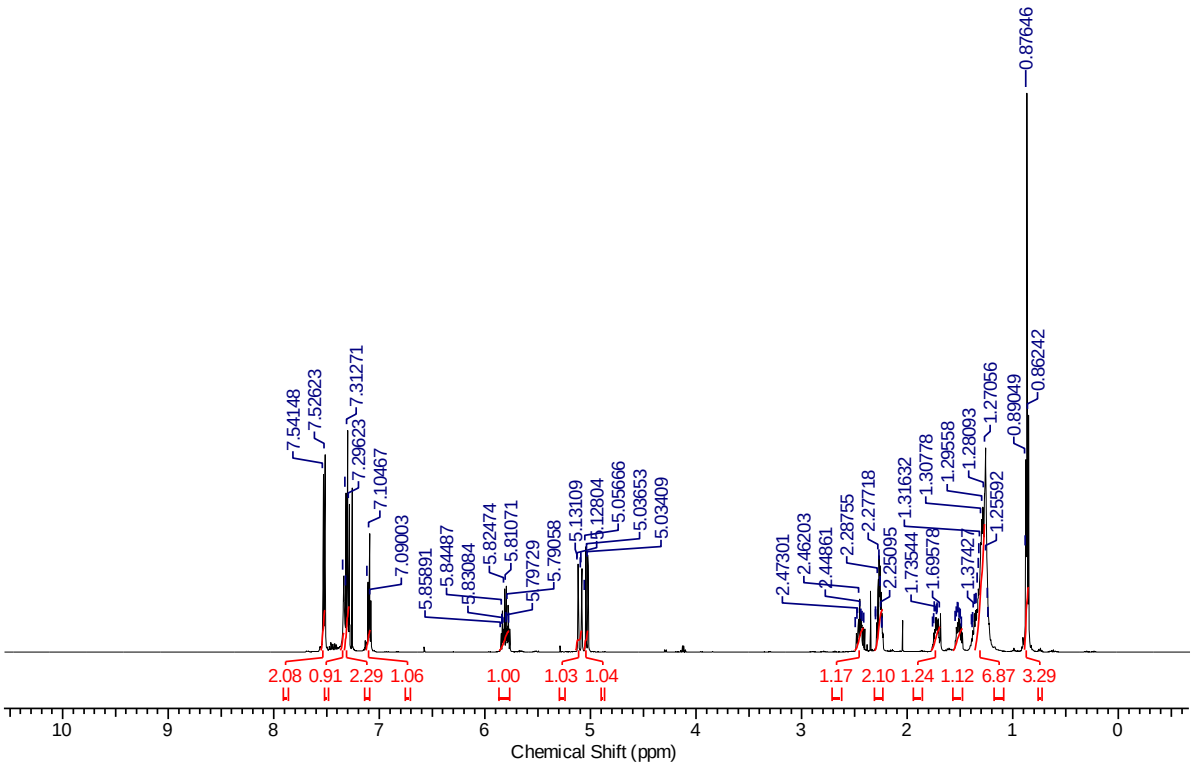

77.32083
77.00000
76.68282
56.09487
153.31432
60.93651
29.74287
22.73196
13.93459
135.61021
133.99147
117.10403
97.35461
49.00010
37.22410
32.30224
173.61060
Chemical Shift (ppm)

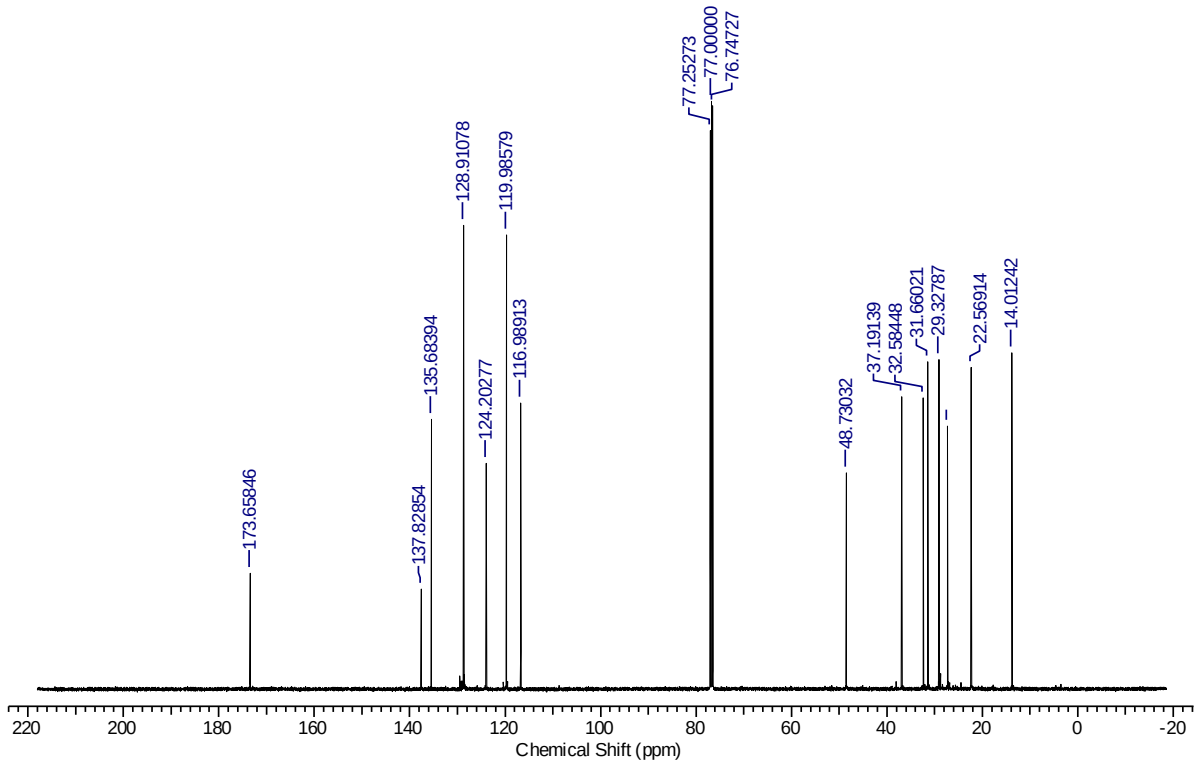

O
NH
Bu
(2f)
0.87022
7.29752
7.27306
7.27000
7.31219
7.25655
7.25104
0.88735
0.85310
4.43333
4.41927
4.41560
1.28848
1.26524
7.33359
7.24004
5.95776
5.77431
5.74863
5.73151
5.70644
5.68871
5.07050
5.03197
5.02831
5.00874
4.98367
1.30560
1.29704
1.25118
2.37447
2.35429
2.20570
2.15067
2.12866
2.11581
1.63213
1.44135
1.32211
2.11 3.06
0.93 1.00
1.02 1.00 1.93
1.05 2.05 1.07 1.09 4.15 3.15
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

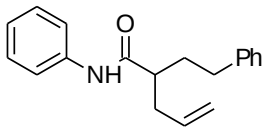

128.54251
127.75459
127.33145
135.91092
138.44974
175.02196
116.60712
77.32100
77.00000
76.67899
47.65761
43.33870
37.14484
32.14744
29.68887
22.63415
13.90876
220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)


O
NH
Bu

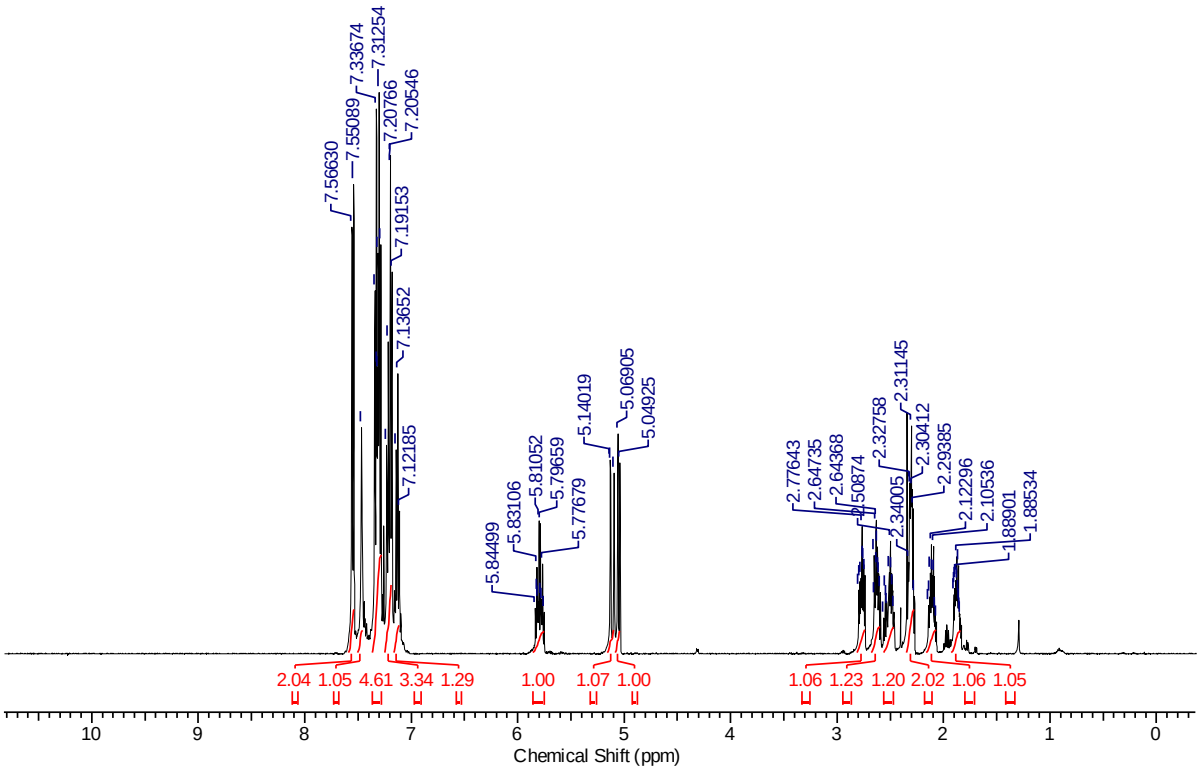
(2g)

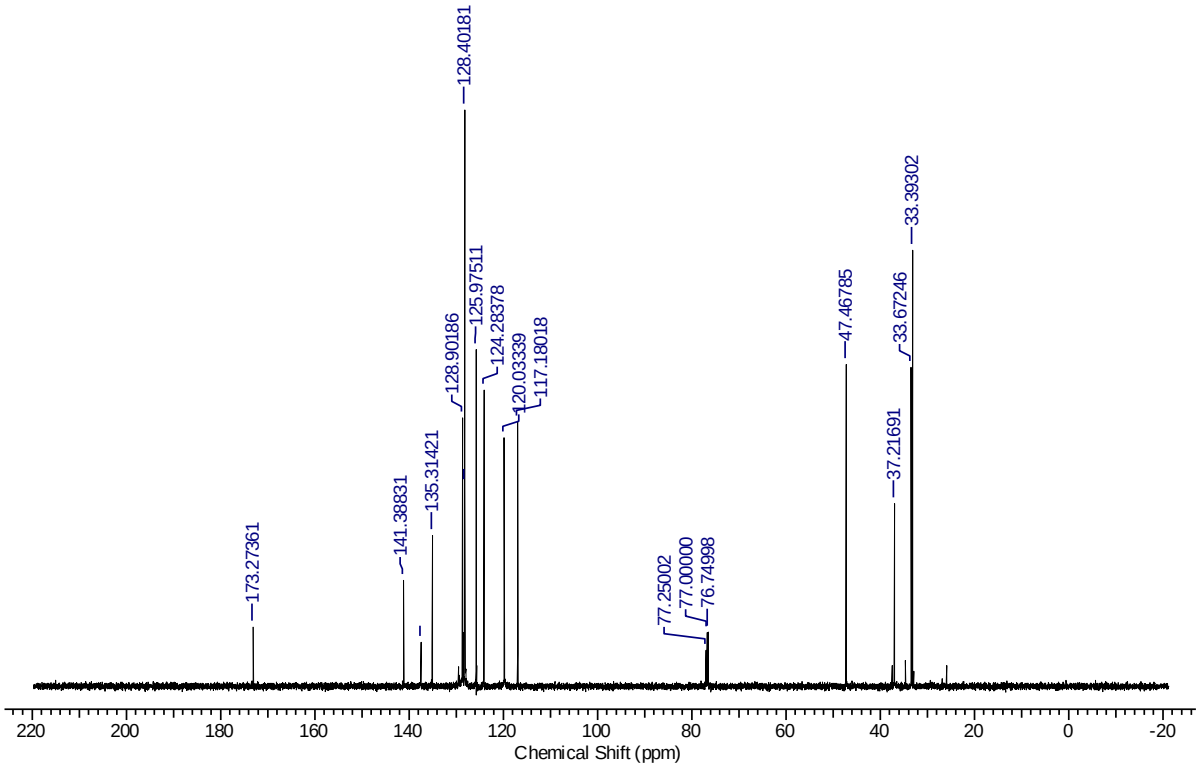

7.54148
7.52623
7.31271
7.29623
7.10467
7.09003
5.85891
5.84487
5.83084
5.82474
5.81071
5.79729
5.79058
5.13109
5.12804
5.05666
5.03653
5.03409
2.47301
2.46203
2.44861
2.28755
2.27718
2.25095
1.73544
1.69578
1.37427
1.31632
1.30778
1.29558
1.28093
1.27056
1.25592
0.89049
0.87646
0.86242
2.08 0.91 2.29 1.06 1.00 1.03 1.04 1.17 2.10 1.24 1.12 6.87 3.29
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

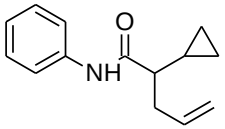

173.65846
137.82854
135.68394
128.91078
124.20277
119.98579
116.98913
77.25273
77.00000
76.74727
48.73032
37.19139
32.58448
31.66021
29.32787
22.56914
14.01242
220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)


O
NH
Ph

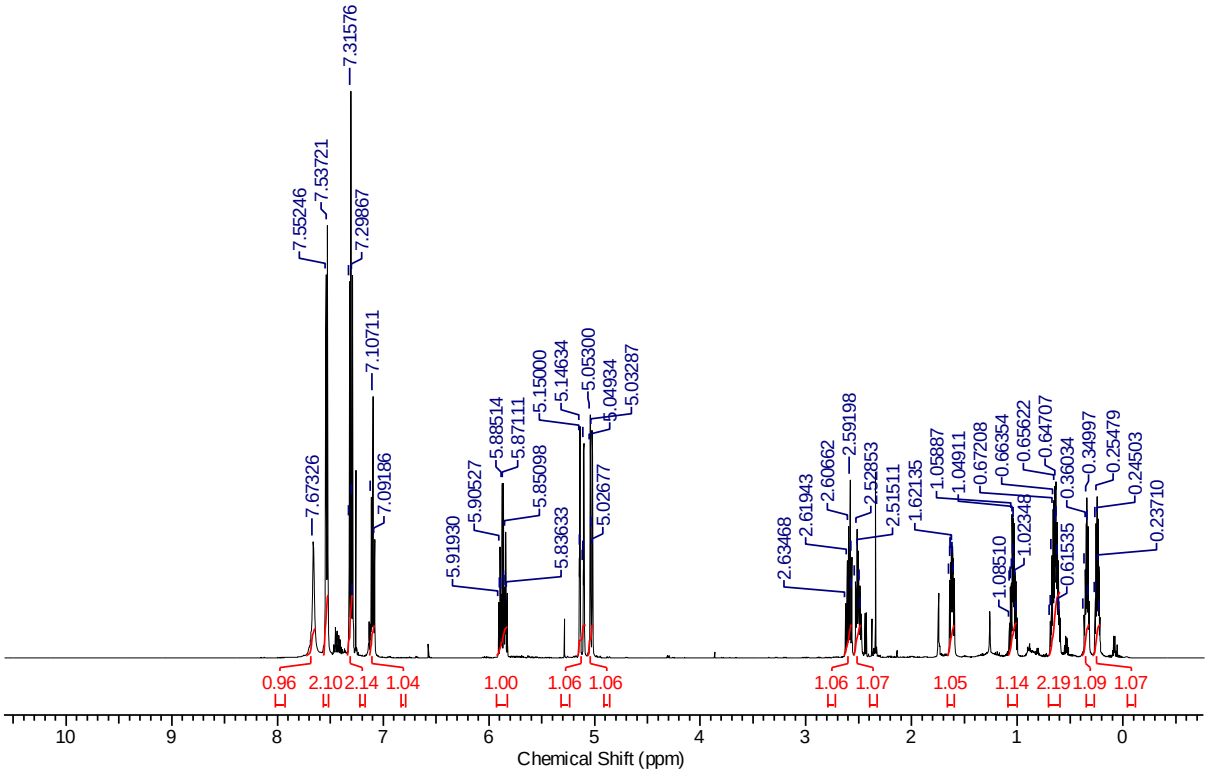
(2h)

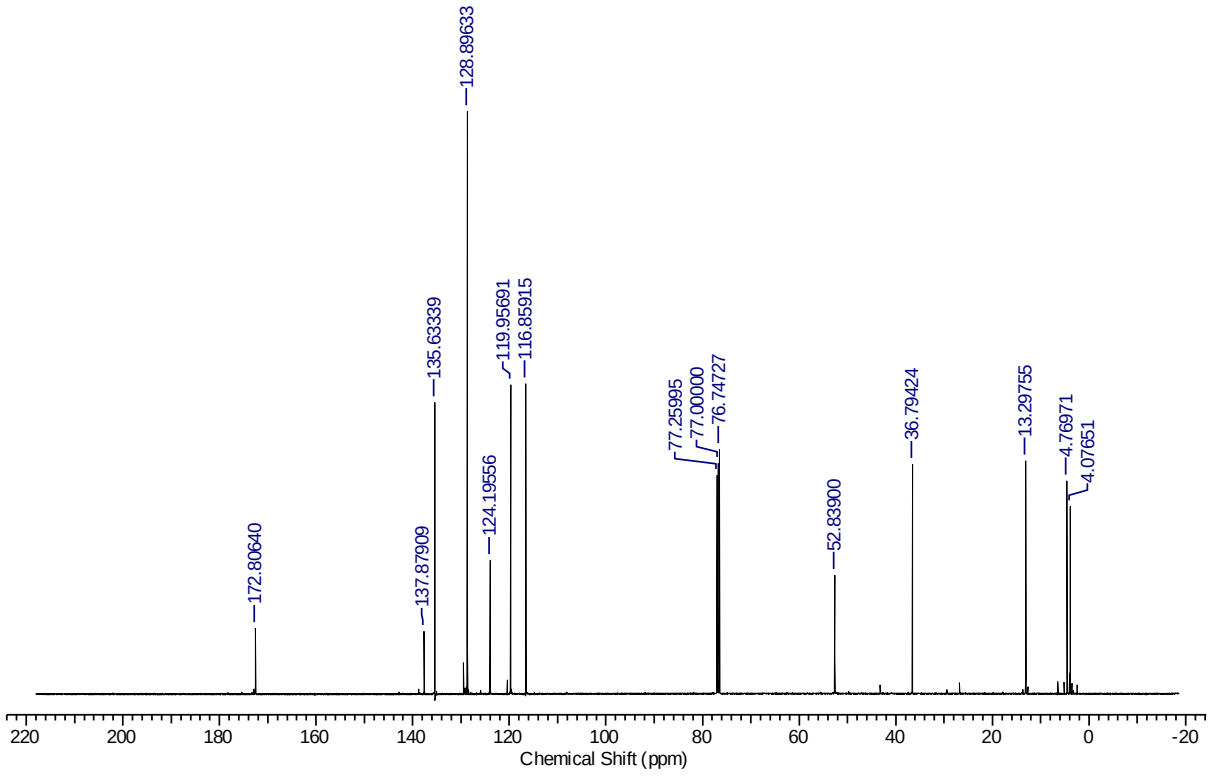

7.56630
7.55089
7.33674
7.31254
7.20766
7.20546
7.19153
7.13652
7.12185
5.84499
5.83106
5.81052
5.79659
5.77679
5.14019
5.06905
5.04925
2.77643
2.64735
2.64368
2.50874
2.34005
2.32758
2.31145
2.30412
2.29385
2.12296
2.10536
1.88901
1.88534
2.04 1.05 4.61 3.34 1.29
1.00 1.07 1.00
1.06 1.23 1.20 2.02 1.06 1.05
Chemical Shift (ppm)

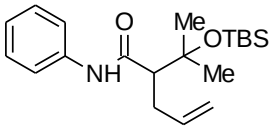

173.27361
141.38831
135.31421
128.90186
128.40181
125.97511
124.28378
120.03339
117.18018
77.25002
77.00000
76.74998
47.46785
37.21691
33.67246
33.39302
Chemical Shift (ppm)


O
NH

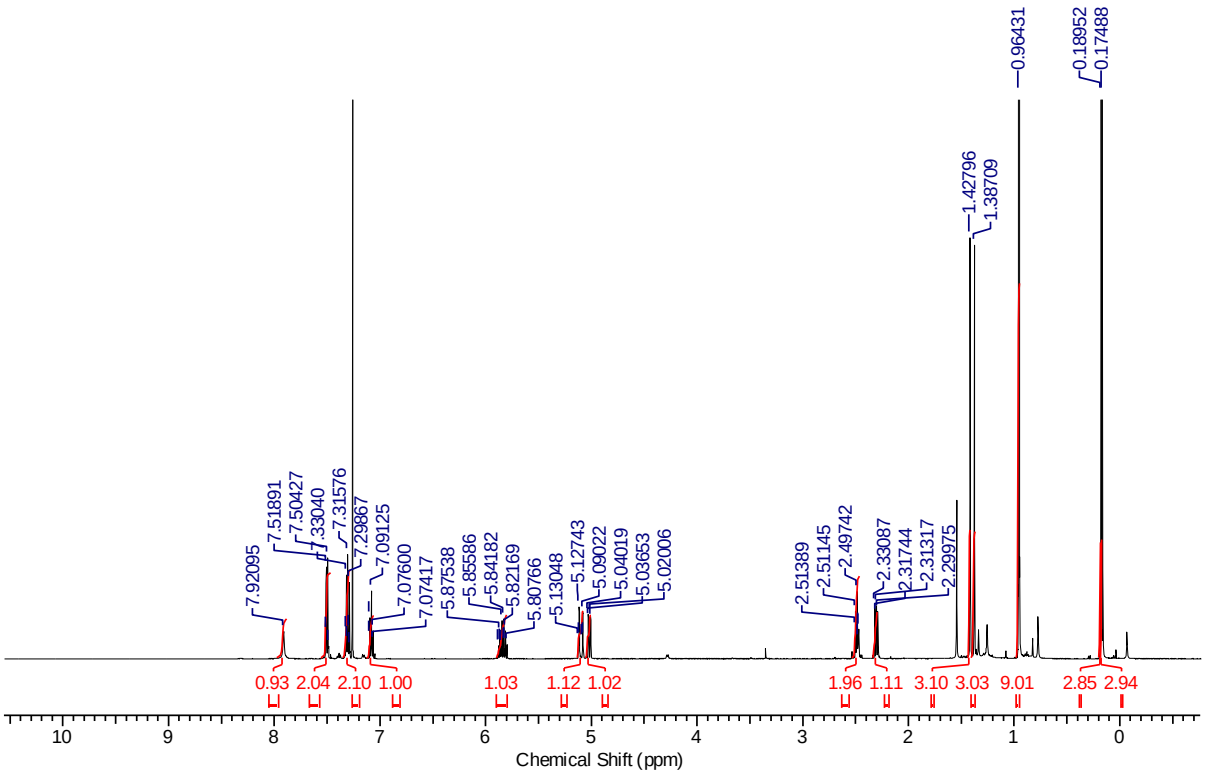
(2i)

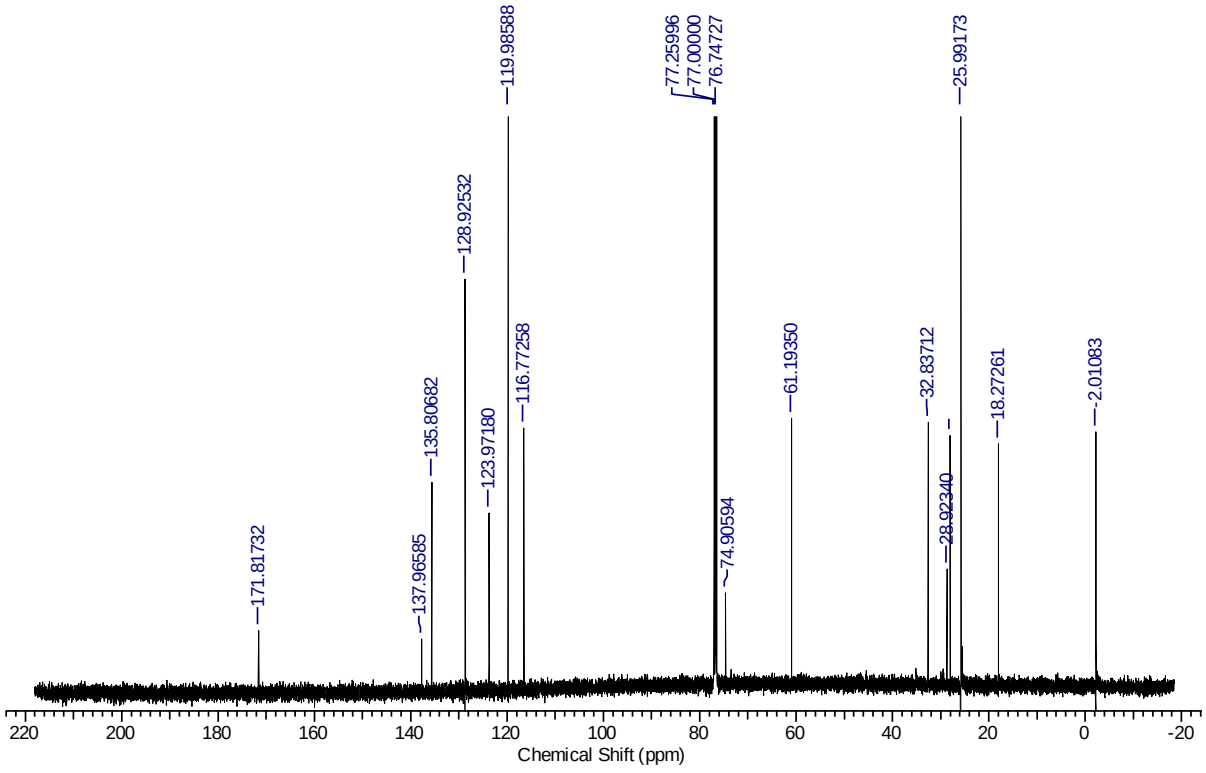

7.55246
7.53721
7.31576
7.29867
7.10711
7.67326
7.09186
5.91930
5.90527
5.88514
5.87111
5.85098
5.83633
5.15000
5.14634
5.05300
5.04934
5.03287
5.02677
2.63468
2.61943
2.60662
2.59198
2.52853
2.51511
1.62135
1.08510
1.05887
1.04911
1.02348
0.67208
0.66354
0.65622
0.64707
0.61535
0.36034
0.34997
0.25479
0.24503
0.23710
0.96 2.10 2.14 1.04 1.00 1.06 1.06 1.06 1.07 1.05 1.14 2.19 1.09 1.07
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

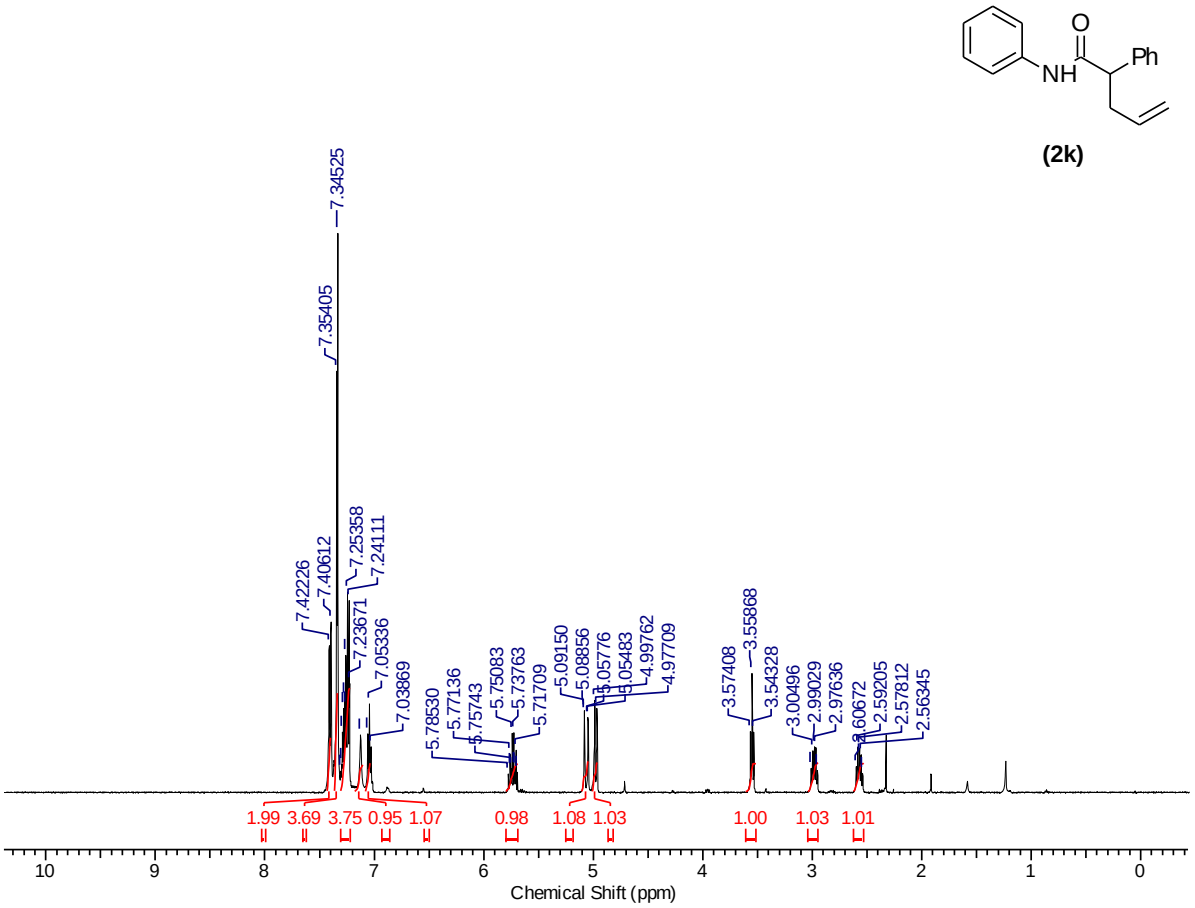

172.80640
137.87909
135.63339
128.89633
124.19556
119.95691
116.85915
77.25995
77.00000
76.74727
52.83900
36.79424
13.29755
4.76971
4.07651
220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)

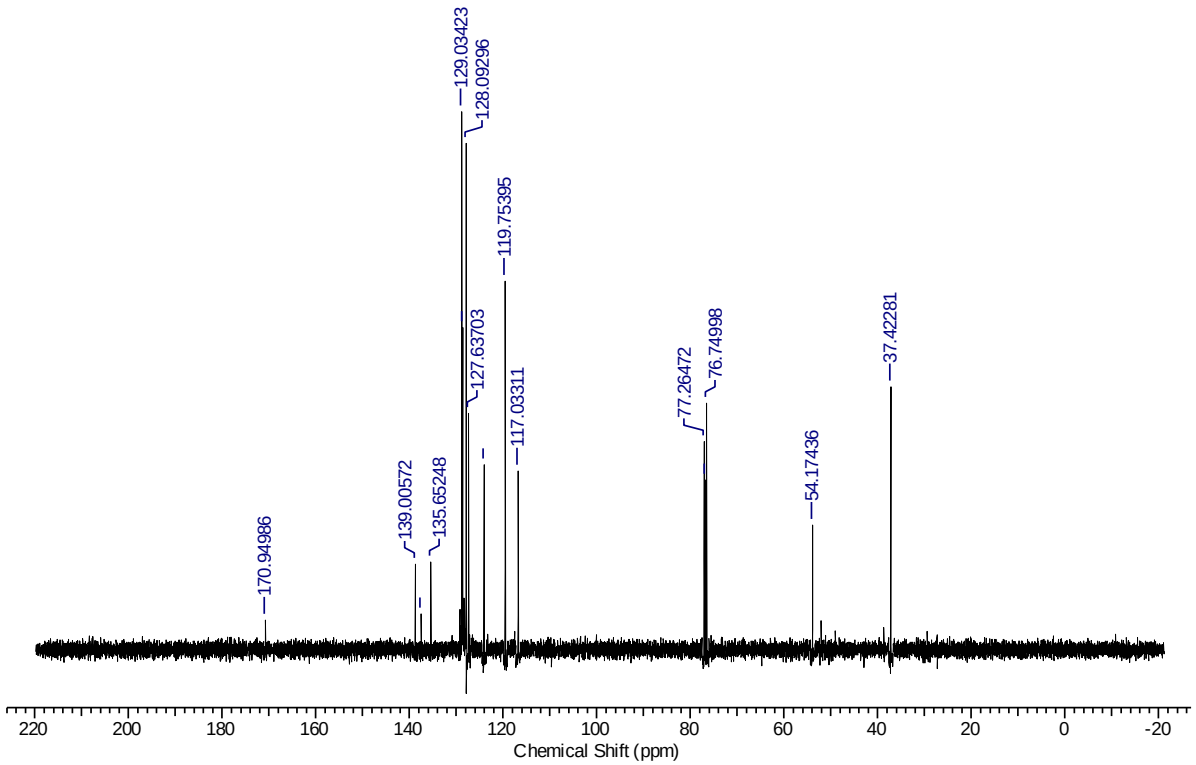

O
Me
OTBS
NH
Me

(2j)

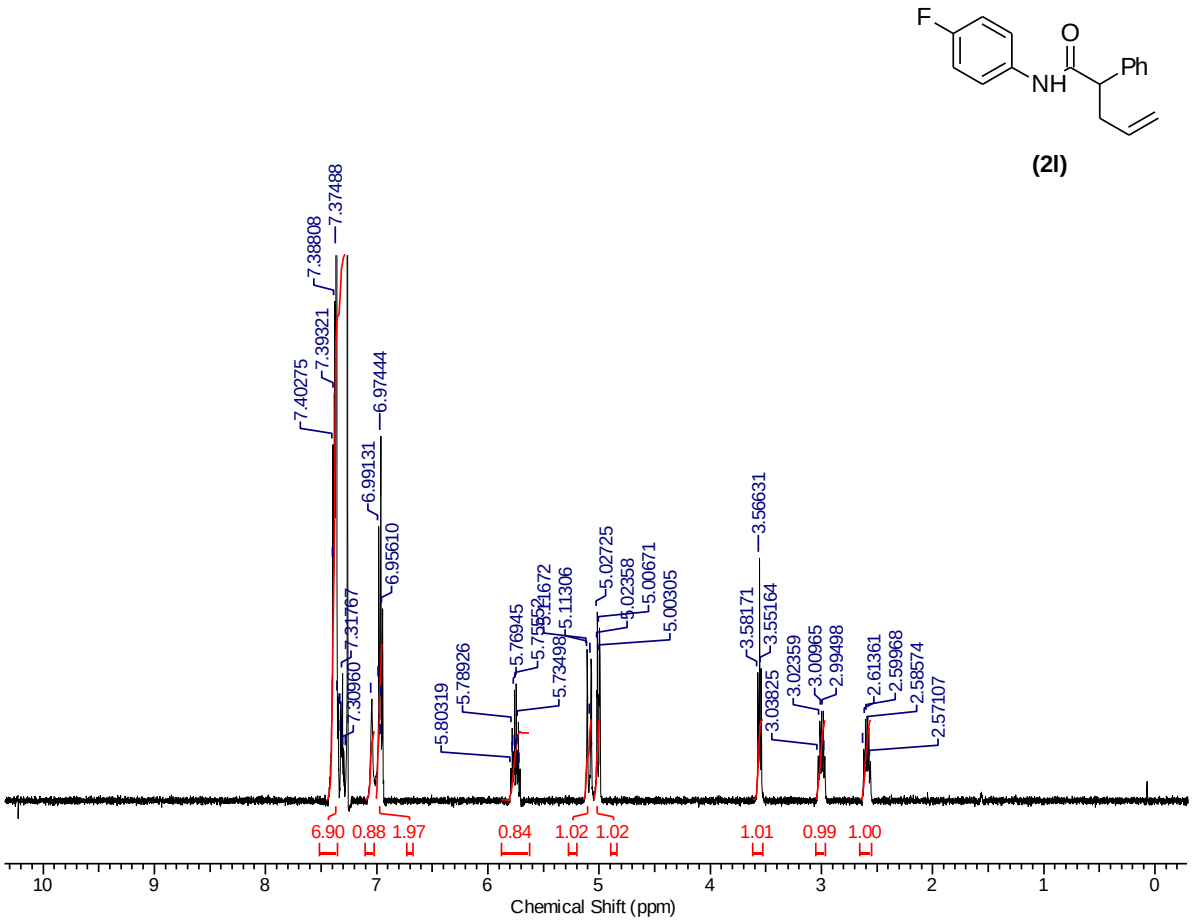

7.92095
7.51891
7.50427
7.33040
7.31576
7.29867
7.09125
7.07600
7.07417
5.87538
5.85586
5.84182
5.82169
5.80766
5.13048
5.12743
5.09022
5.04019
5.03653
5.02006
2.51389
2.51145
2.49742
2.33087
2.31744
2.31317
2.29975
1.42796
1.38709
0.96431
0.18952
0.17488
0.93 2.04 2.10 1.00 1.03 1.12 1.02 1.96 1.11 3.10 3.03 9.01 2.85 2.94
Chemical Shift (ppm)


171.81732
137.96585
135.80682
128.92532
123.97180
119.98588
116.77258
77.25996
77.00000
76.74727
74.90594
61.19350
32.83712
28.92340
25.99173
18.27261
2.01083
Chemical Shift (ppm)

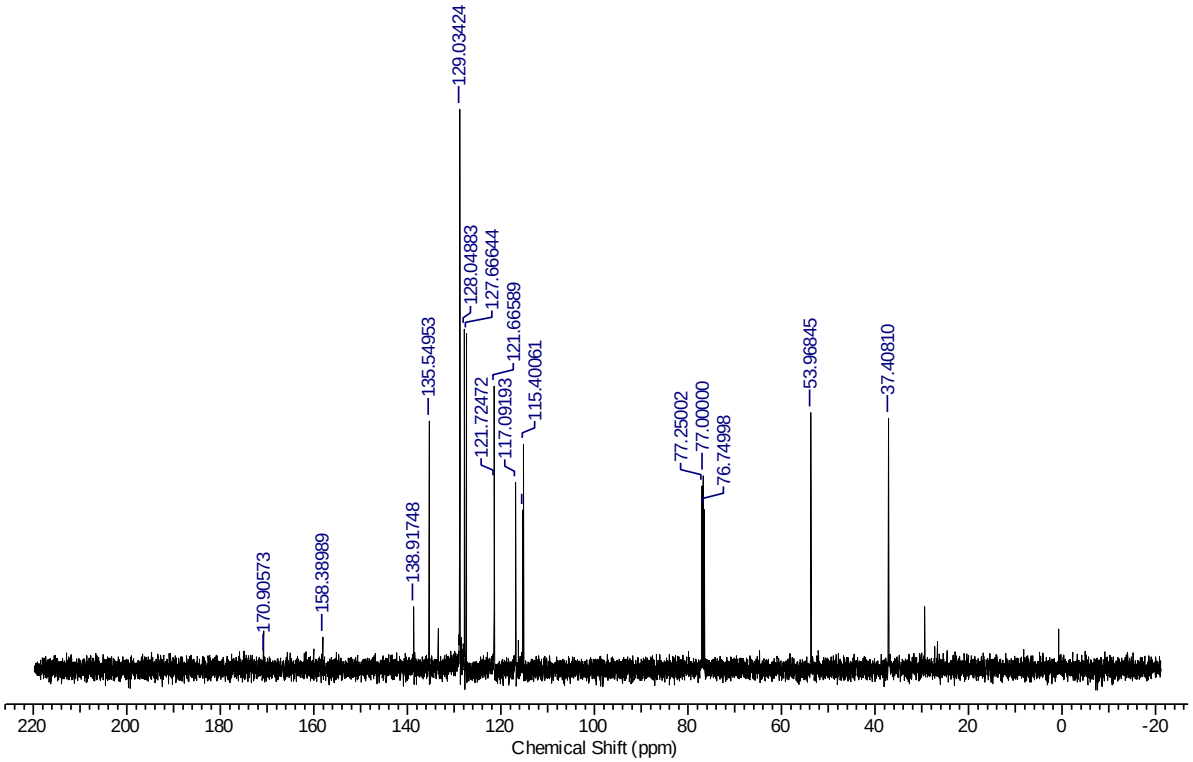

O
NH
Ph
7.34525
7.35405
7.42226
7.40612
7.25358
7.24111
7.23671
7.05336
7.03869
5.78530
5.77136
5.75743
5.75083
5.73763
5.71709
5.09150
5.08856
5.05776
5.05483
4.99762
4.97709
3.57408
3.55868
3.54328
3.00496
2.99029
2.97636
2.60672
2.59205
2.57812
2.56345
1.99 3.69 3.75 0.95 1.07
0.98
1.08 1.03
1.00
1.03 1.01
Chemical Shift (ppm)

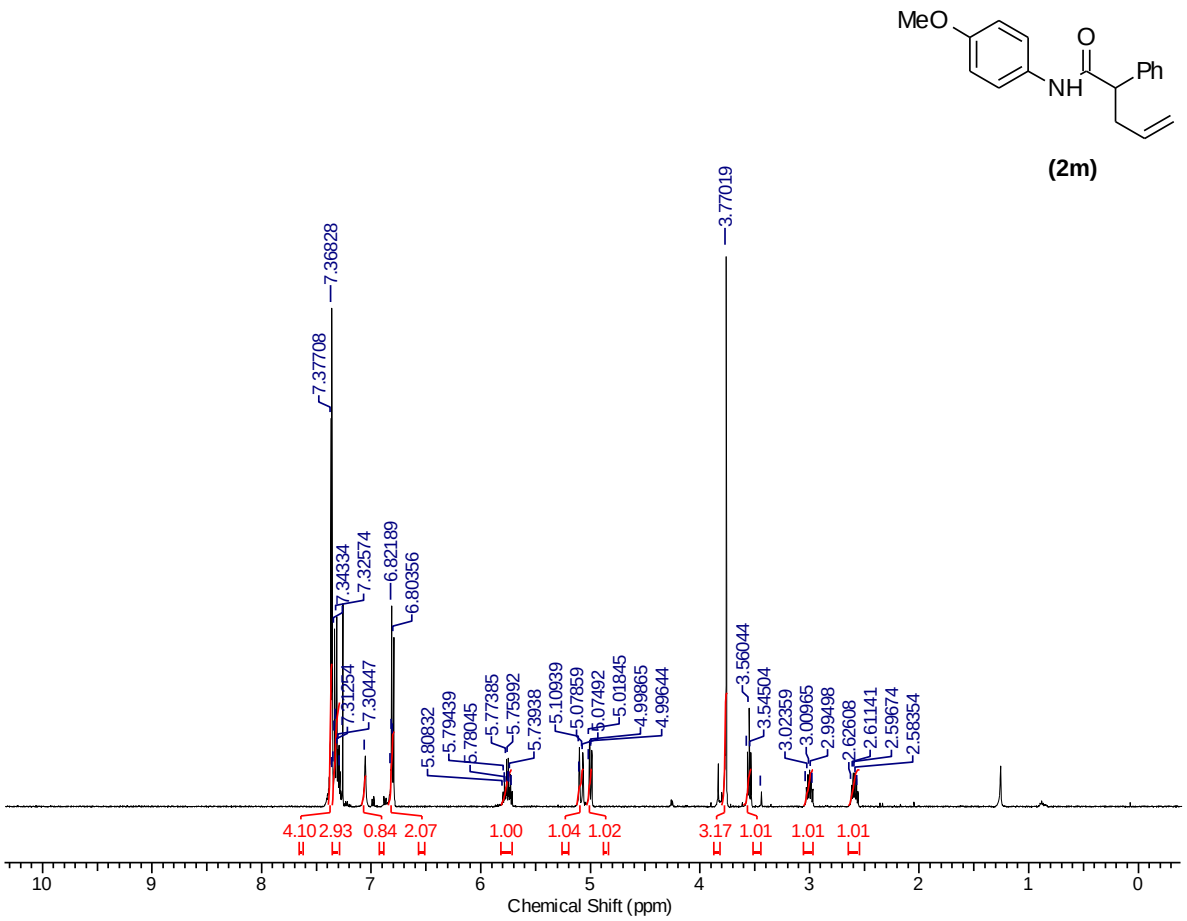

129.03423
128.09296
119.75395
127.63703
117.03311
139.00572
135.65248
170.94986
77.26472
76.74998
54.17436
37.42281
Chemical Shift (ppm)

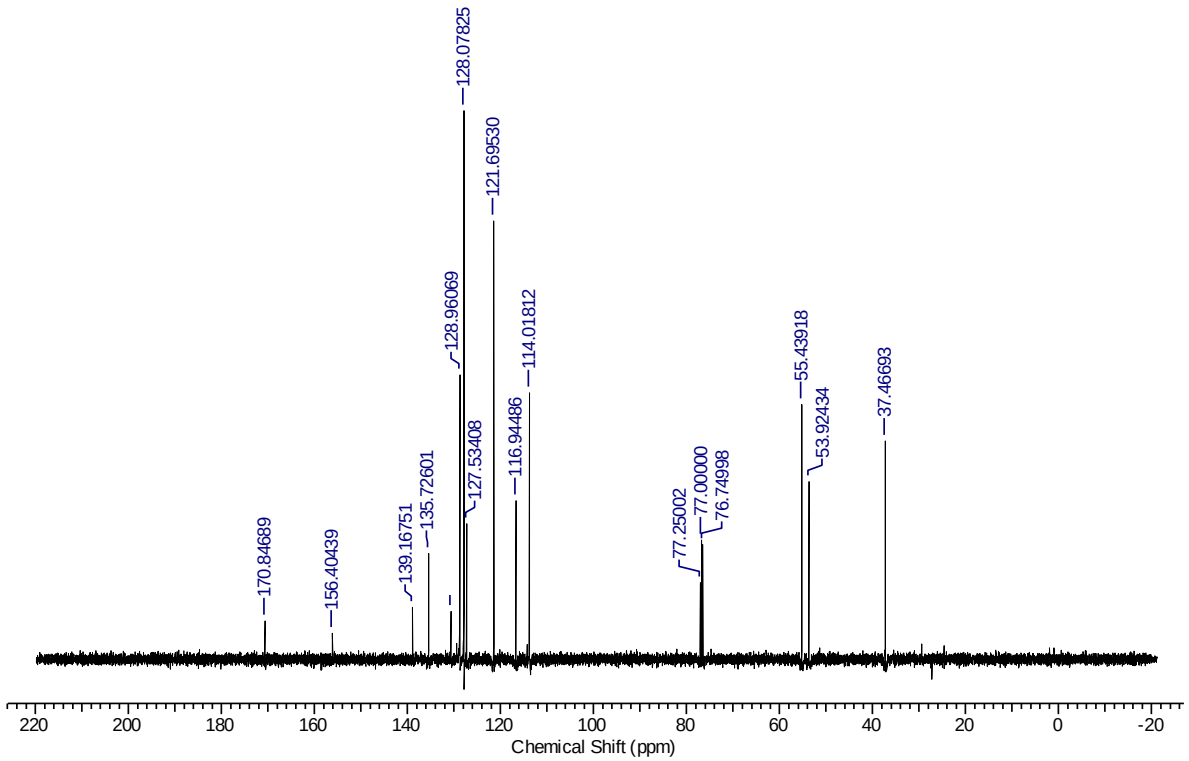
(2k)

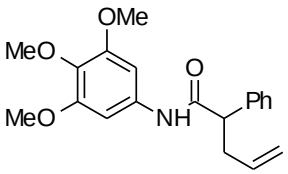

F
O
NH
Ph
7.40275
7.39321
7.38808
7.37488
7.31767
7.30960
6.99131
6.97444
6.95610
5.80319
5.78926
5.76945
5.75552
5.73498
5.11306
5.02725
5.02358
5.00671
5.00305
3.58171
3.56631
3.55164
3.03825
3.02359
3.00965
2.99498
2.61361
2.59968
2.58574
2.57107
6.90
0.88
1.97
0.84
1.02
1.02
1.01
0.99
1.00
Chemical Shift (ppm)

(2l)

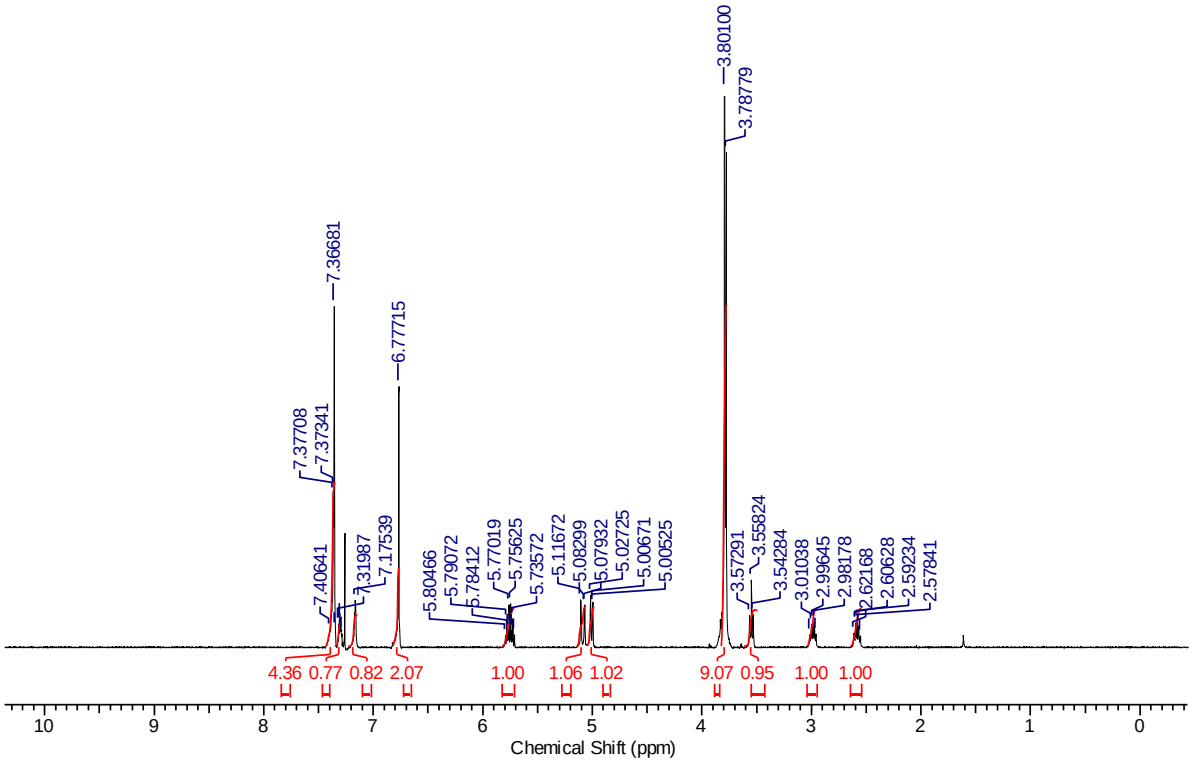

170.90573
158.38989
138.91748
135.54953
129.03424
128.04883
127.66644
121.66589
121.72472
117.09193
115.40061
77.25002
77.00000
76.74998
53.96845
37.40810
Chemical Shift (ppm)

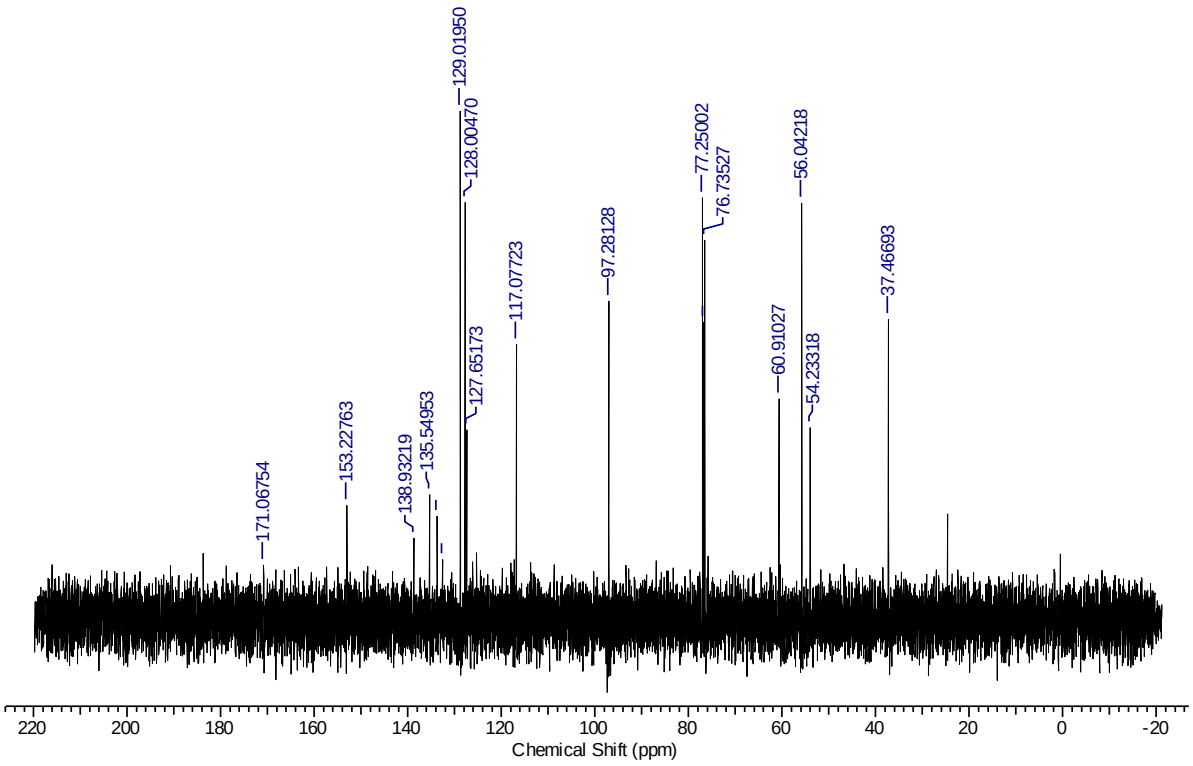

MeO
O
NH
Ph
(2m)
7.37708
7.36828
7.34334
7.32574
7.31254
7.30447
6.82189
6.80356
5.80832
5.79439
5.78045
5.77385
5.75992
5.73938
5.10939
5.07859
5.07492
5.01845
4.99865
4.99644
3.77019
3.56044
3.54504
3.02359
3.00965
2.99498
2.62608
2.61141
2.59674
2.58354
4.10 2.93 0.84 2.07 1.00 1.04 1.02 3.17 1.01 1.01 1.01
Chemical Shift (ppm)

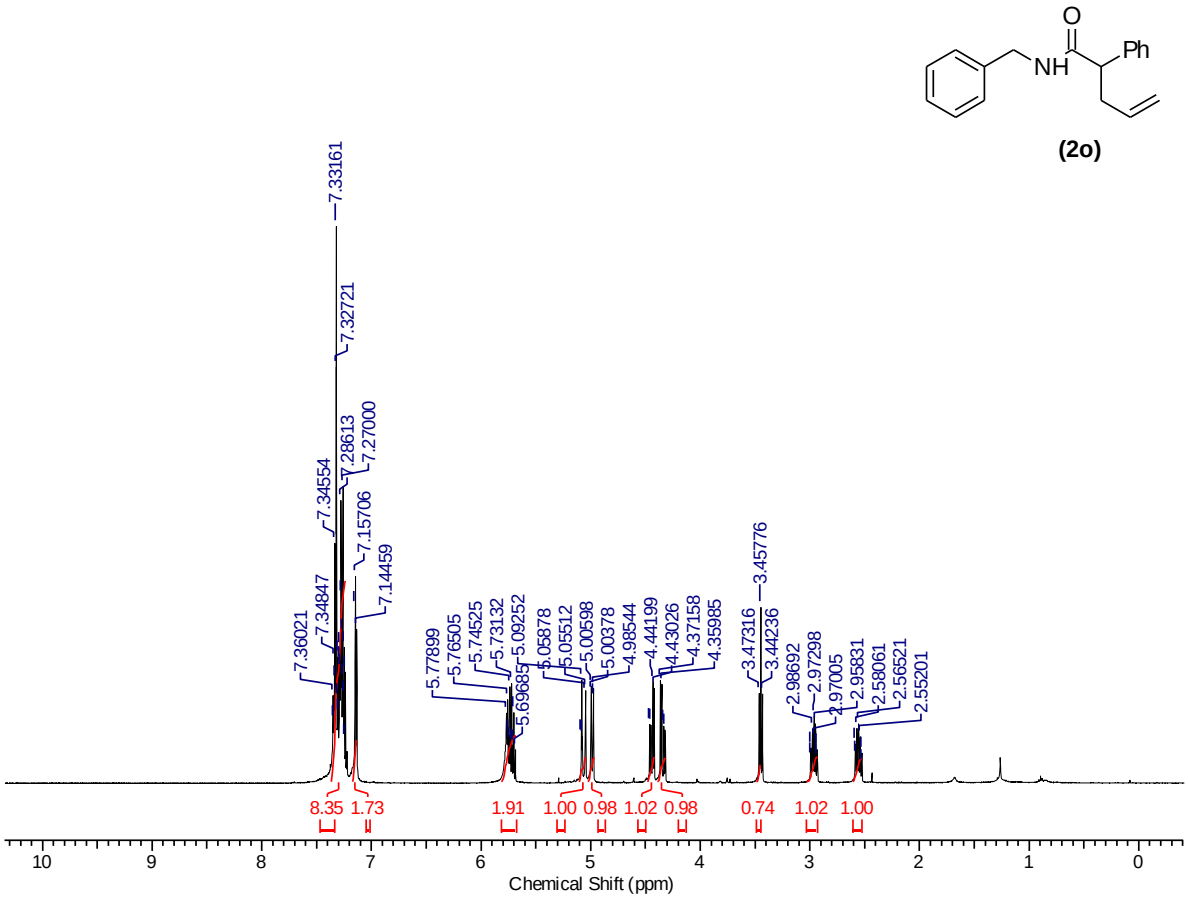

170.84689
156.40439
139.16751
135.72601
128.96069
128.07825
127.53408
121.69530
116.94486
114.01812
77.25002
77.00000
76.74998
55.43918
53.92434
37.46693
Chemical Shift (ppm)

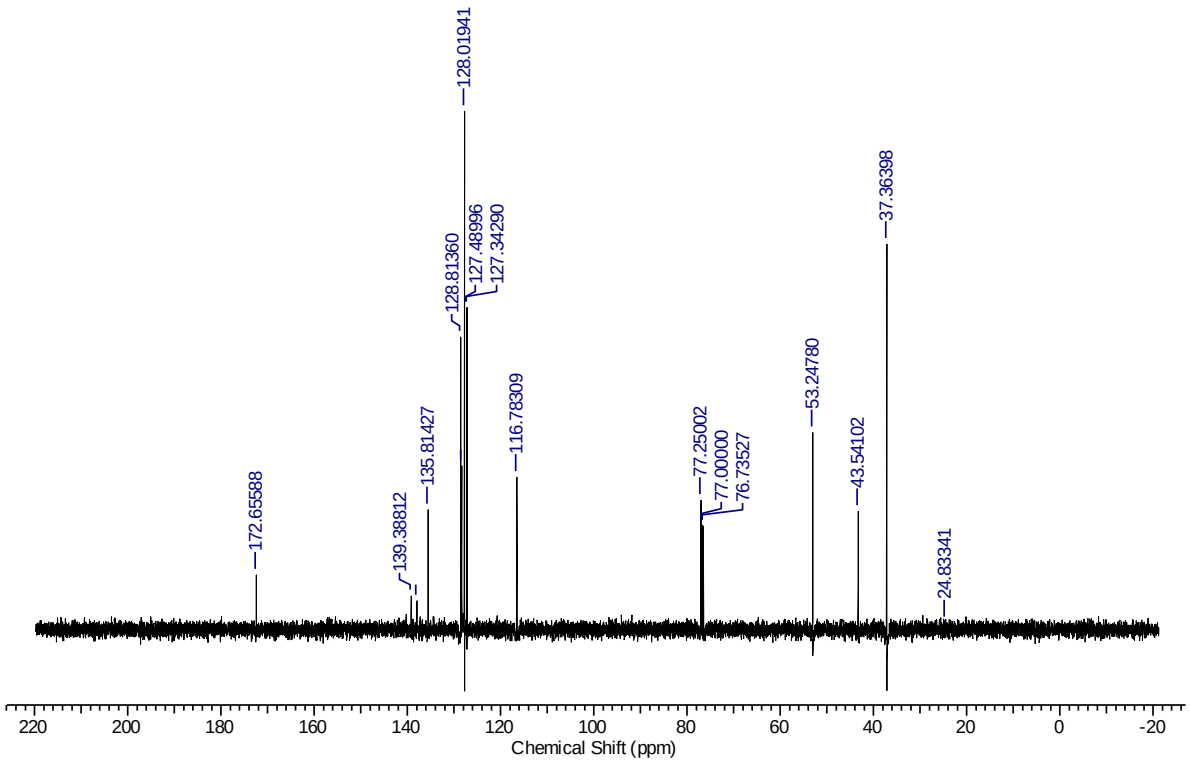

OMe
MeO
MeO
NH
O
Ph

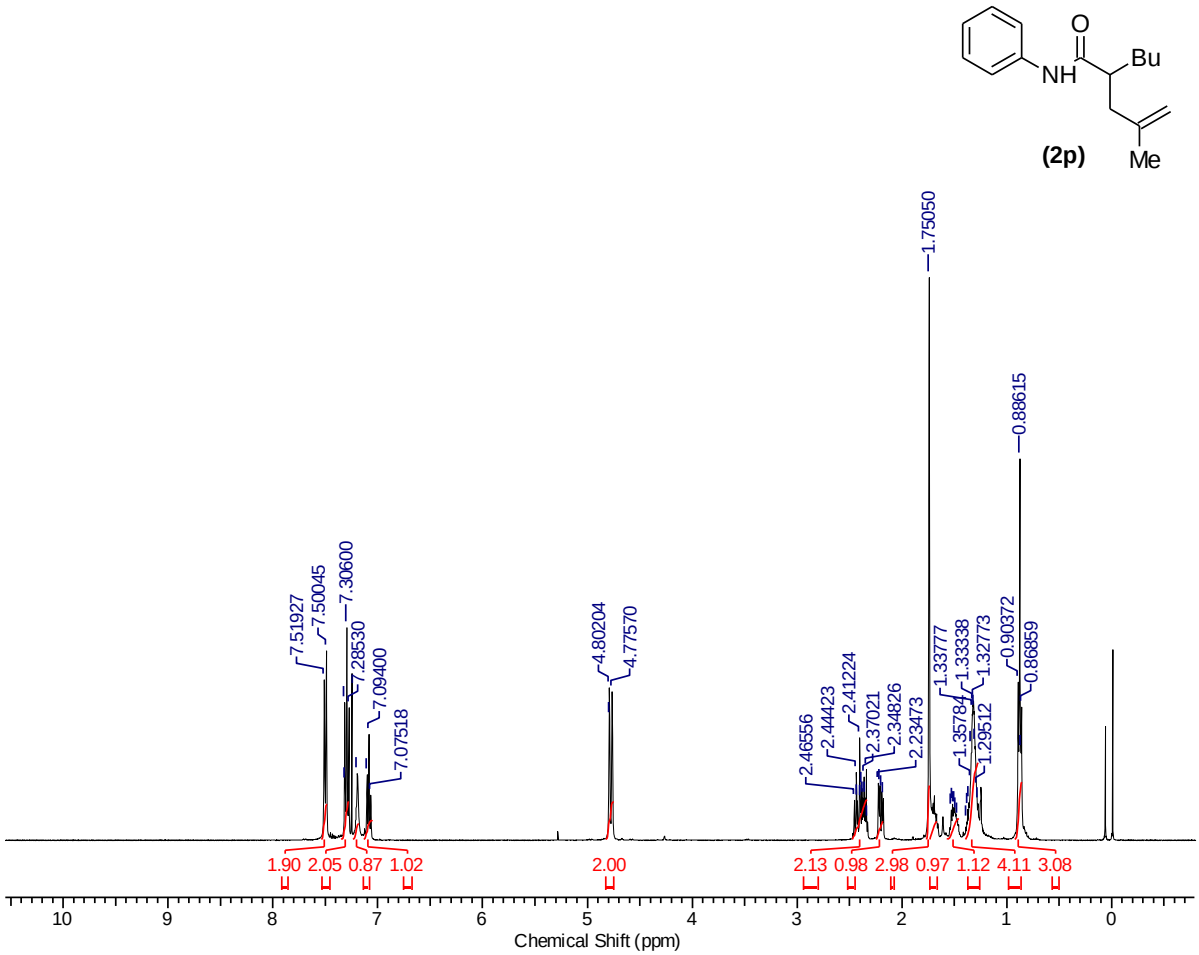
(2n)

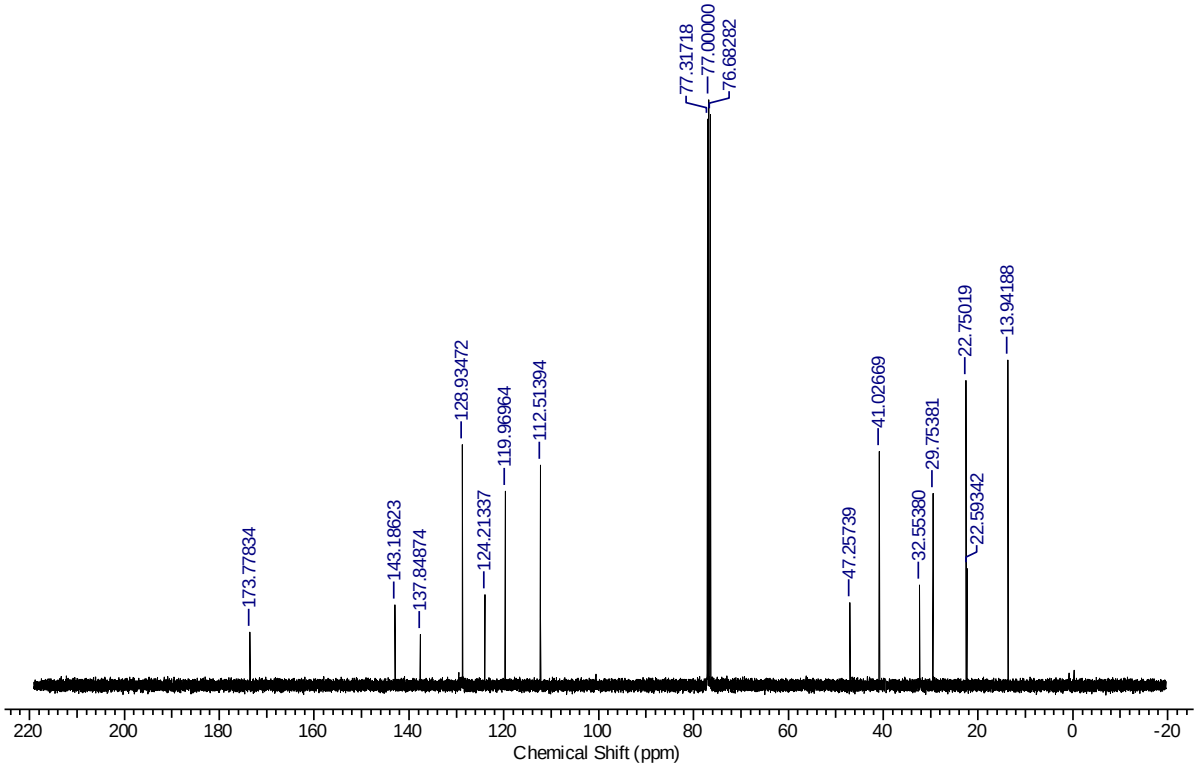

7.37708
7.37341
7.36681
7.40641
7.31987
7.17539
6.77715
5.80466
5.79072
5.78412
5.77019
5.75625
5.73572
5.11672
5.08299
5.07932
5.02725
5.00671
5.00525
3.80100
3.78779
3.57291
3.55824
3.54284
3.01038
2.99645
2.98178
2.62168
2.60628
2.59234
2.57841
4.36 0.77 0.82 2.07 1.00 1.06 1.02 9.07 0.95 1.00 1.00
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

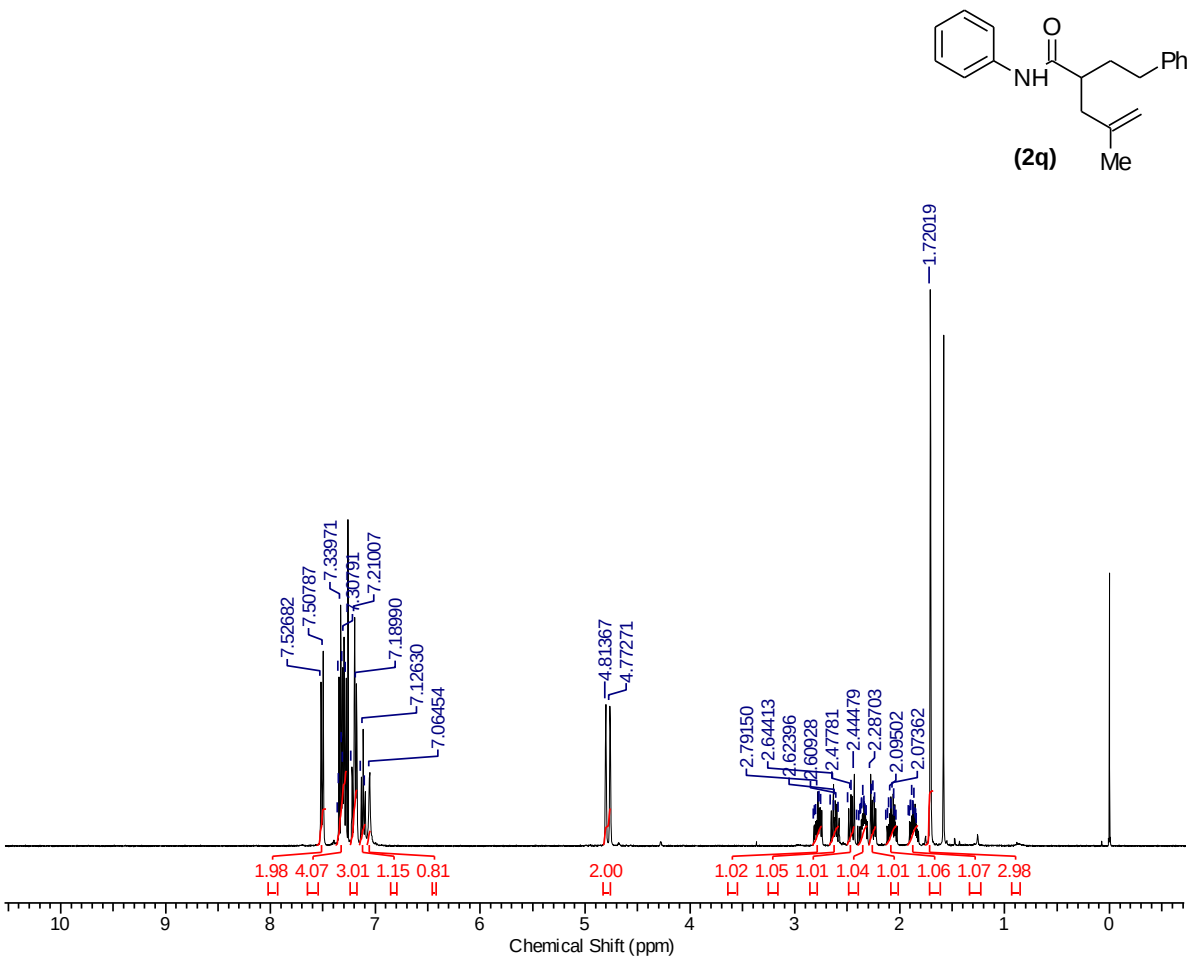

171.06754
153.22763
138.93219
135.54953
129.01950
128.00470
127.65173
117.07723
97.28128
77.25002
76.73527
60.91027
56.04218
54.23318
37.46693
220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)

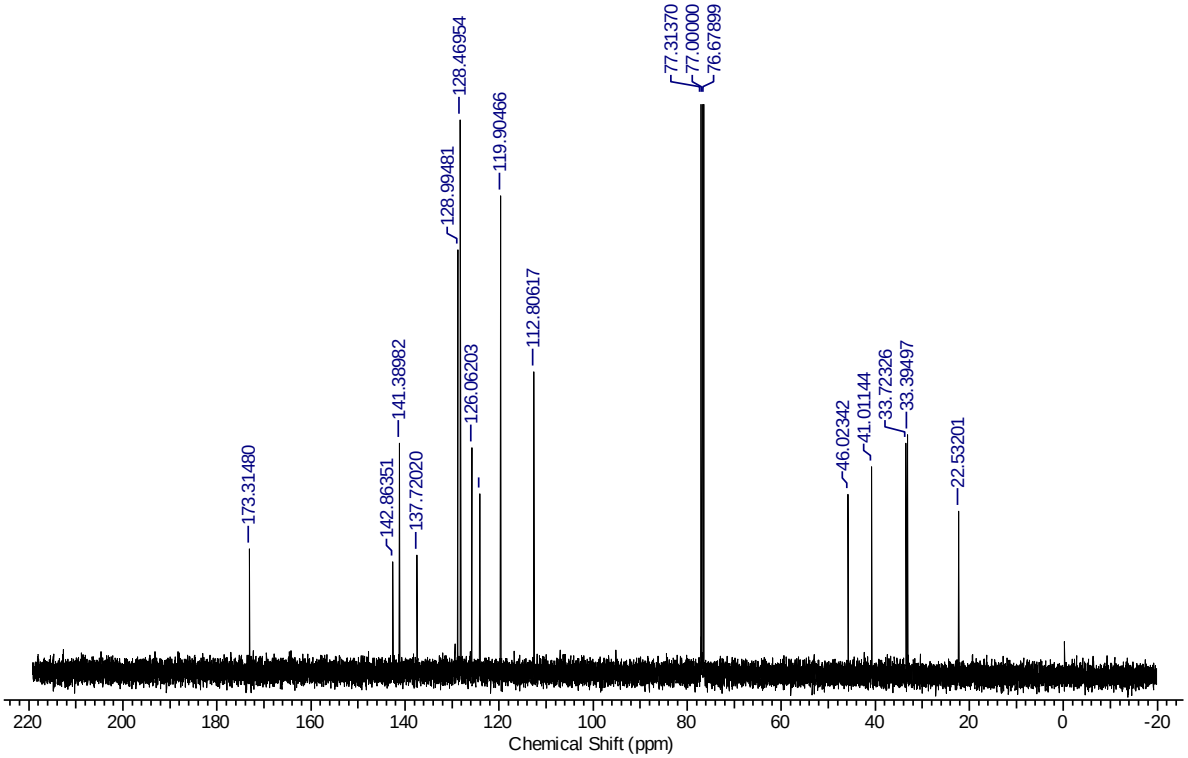

O
NH
Ph
(2o)
7.33161
7.32721
7.28613
7.27000
7.34554
7.15706
7.14459
7.36021
7.34847
5.77899
5.76505
5.74525
5.73132
5.09252
5.69685
5.05878
5.05512
5.00598
5.00378
4.98544
4.44199
4.43026
4.37158
4.35985
3.45776
3.47316
3.44236
2.98692
2.97298
2.97005
2.95831
2.58061
2.56521
2.55201
8.35 1.73 1.91 1.00 0.98 1.02 0.98 0.74 1.02 1.00
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

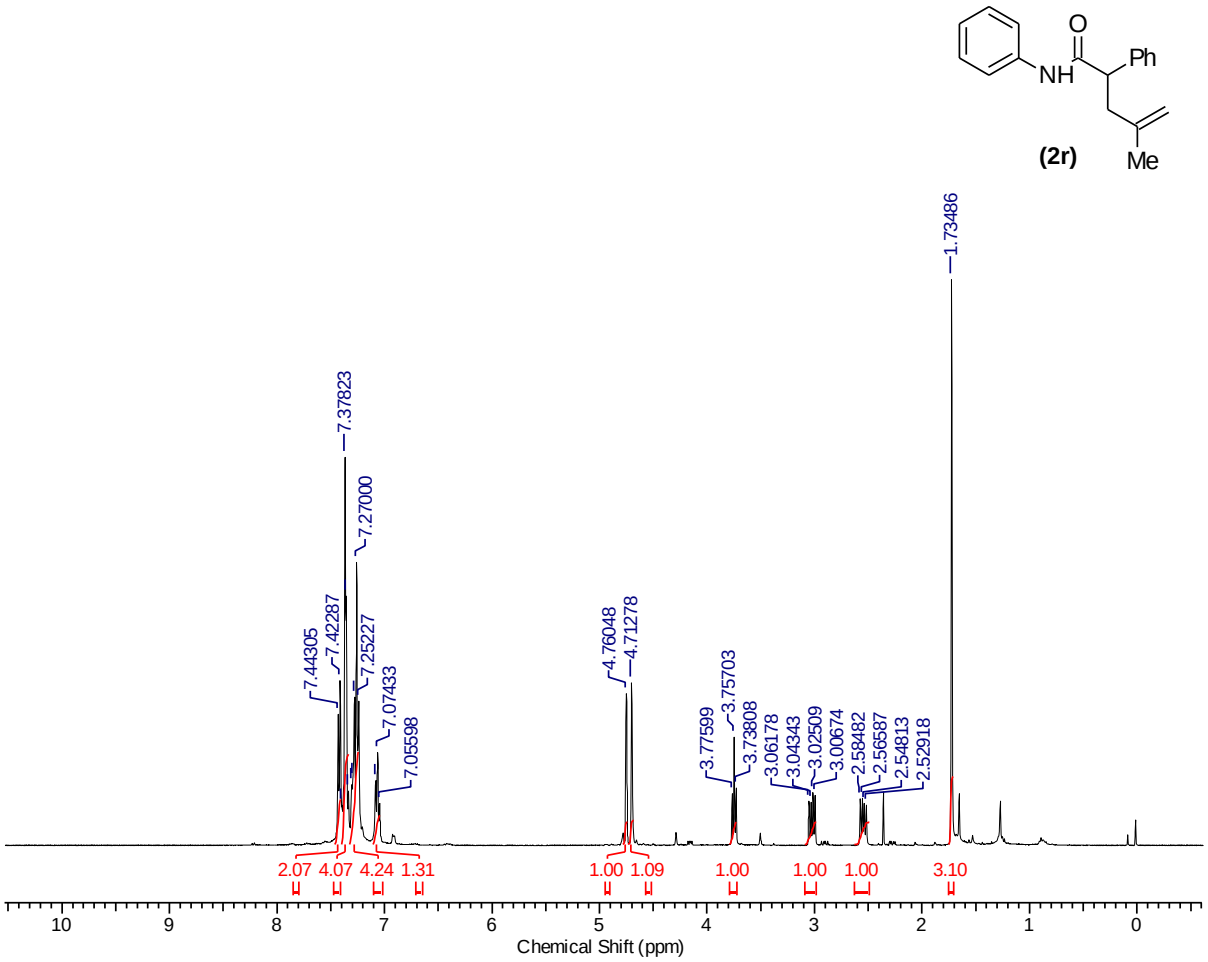

128.01941
128.81360
127.48996
127.34290
116.78309
135.81427
139.38812
172.65588
77.25002
77.00000
76.73527
53.24780
43.54102
37.36398
24.83341
220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)

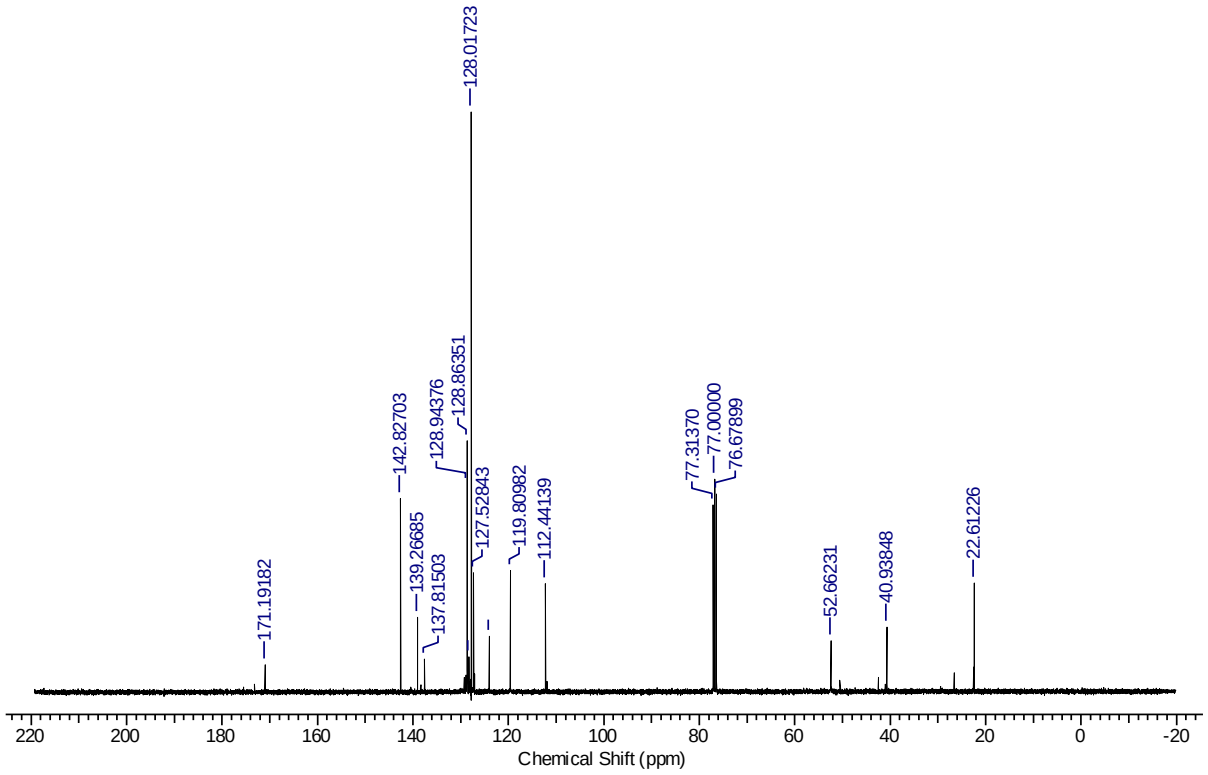

O
NH
Bu
Me
(2p)
7.51927
7.50045
7.30600
7.28530
7.09400
7.07518
4.80204
4.77570
2.46556
2.44423
2.41224
2.37021
2.34826
2.23473
1.75050
1.33777
1.33338
1.32773
1.35784
1.29512
0.90372
0.88615
0.86859
1.90 2.05 0.87 1.02
2.00
2.13 0.98 2.98 0.97 1.12 4.11 3.08
Chemical Shift (ppm)

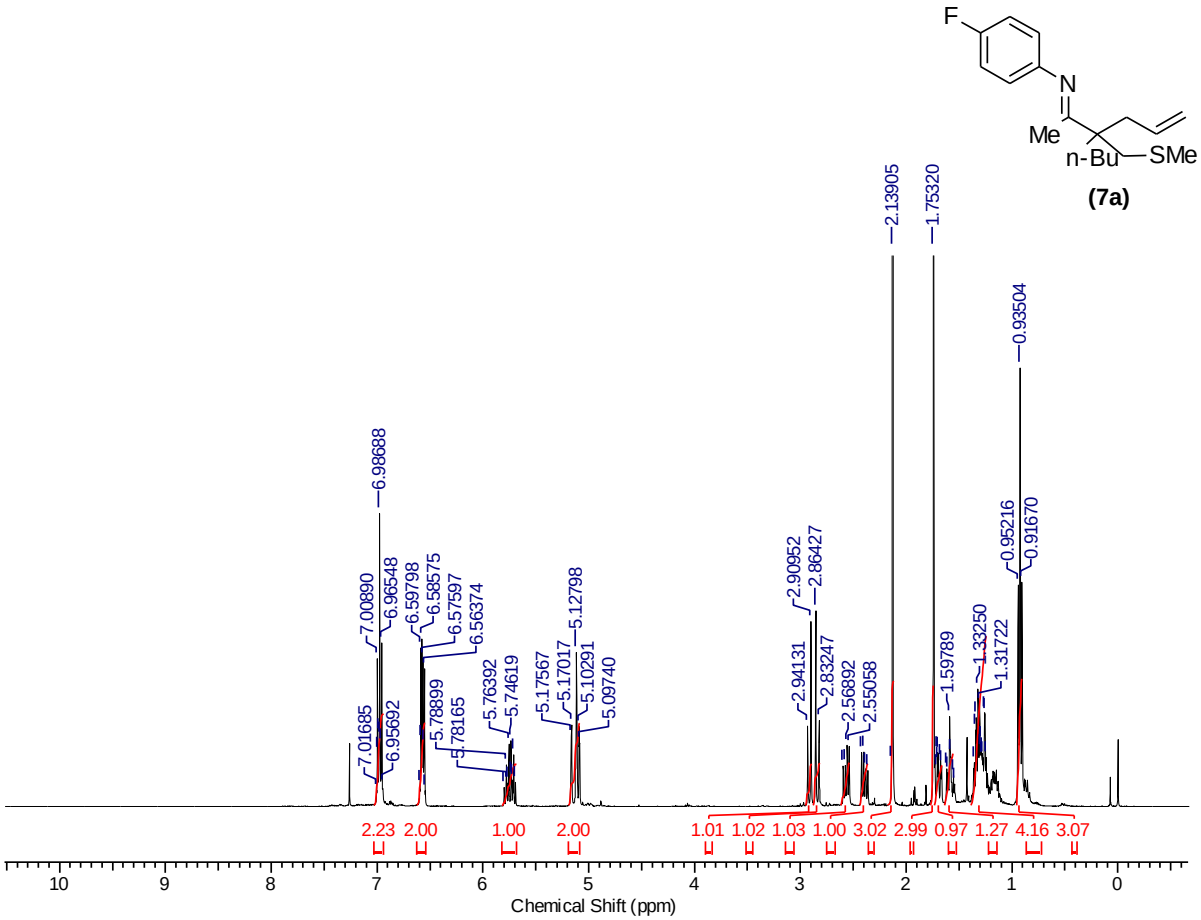

77.31718
77.00000
76.68282
173.77834
143.18623
137.84874
128.93472
124.21337
119.96964
112.51394
47.25739
41.02669
32.55380
29.75381
22.75019
22.59342
13.94188
Chemical Shift (ppm)

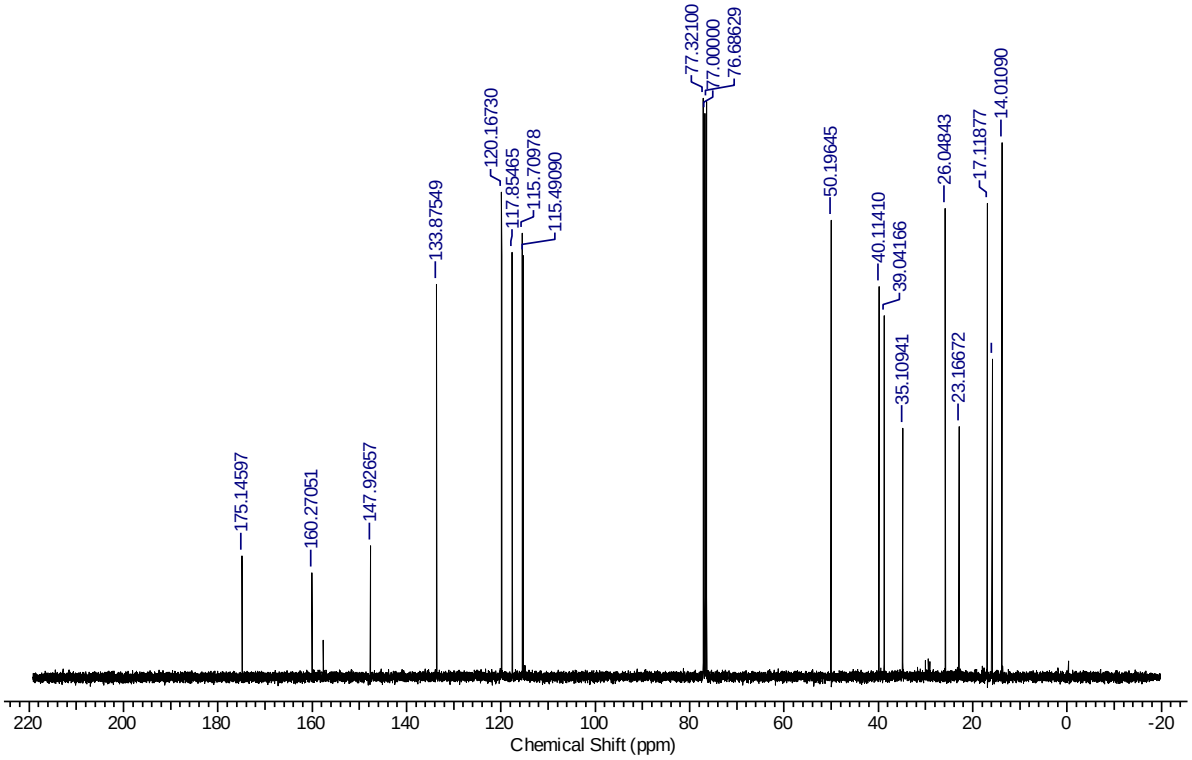

O
NH
Ph
Me
(2q)
7.52682
7.50787
7.33971
7.30791
7.21007
7.18990
7.12630
7.06454
4.81367
4.77271
2.79150
2.64413
2.62396
2.60928
2.47781
2.44479
2.28703
2.09502
2.07362
1.72019
1.98 4.07 3.01 1.15 0.81
2.00
1.02 1.05 1.01 1.04 1.01 1.06 1.07 2.98
Chemical Shift (ppm)

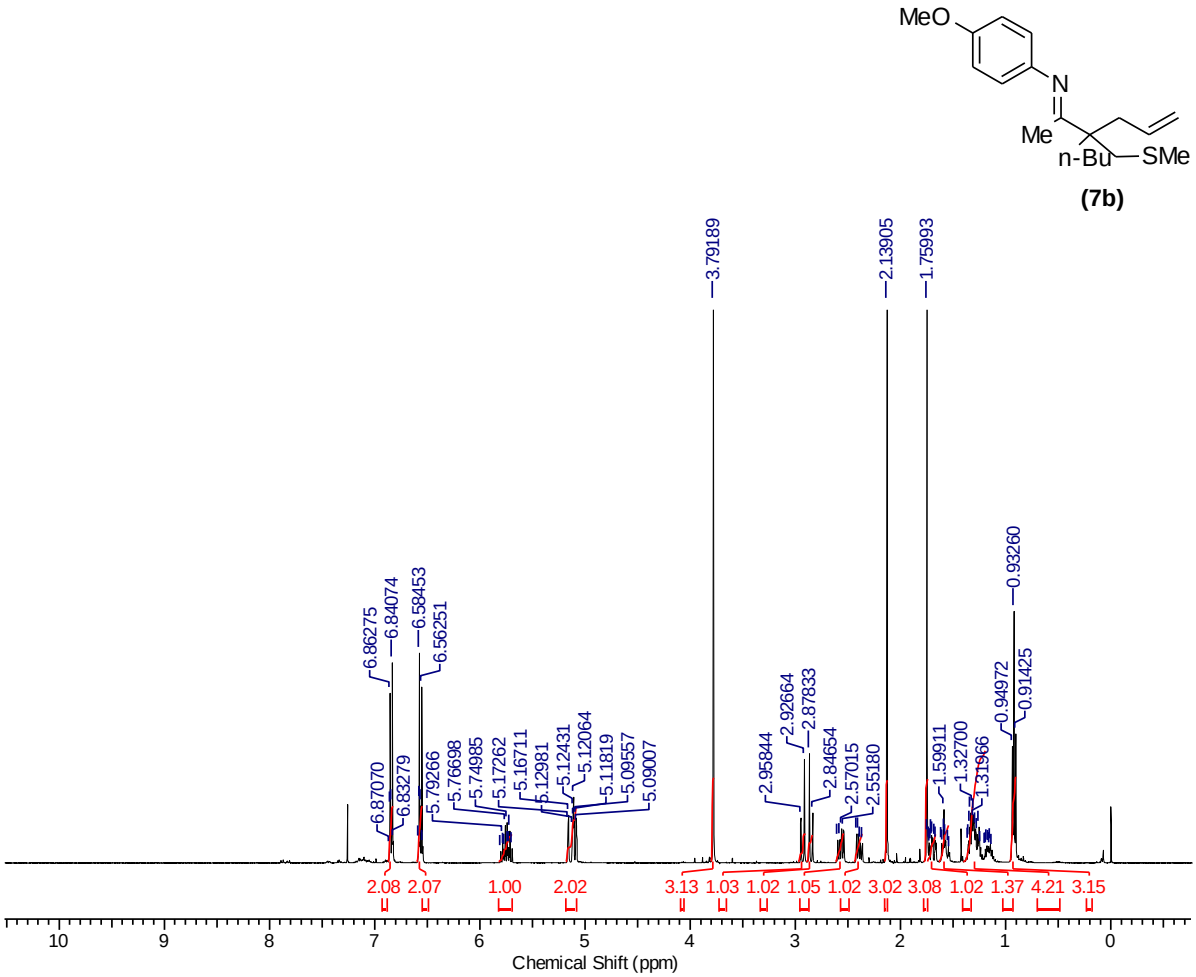

173.31480
142.86351
141.38982
137.72020
128.99481
128.46954
126.06203
119.90466
112.80617
77.31370
77.00000
76.67899
46.02342
41.01144
33.72326
33.39497
22.53201
Chemical Shift (ppm)

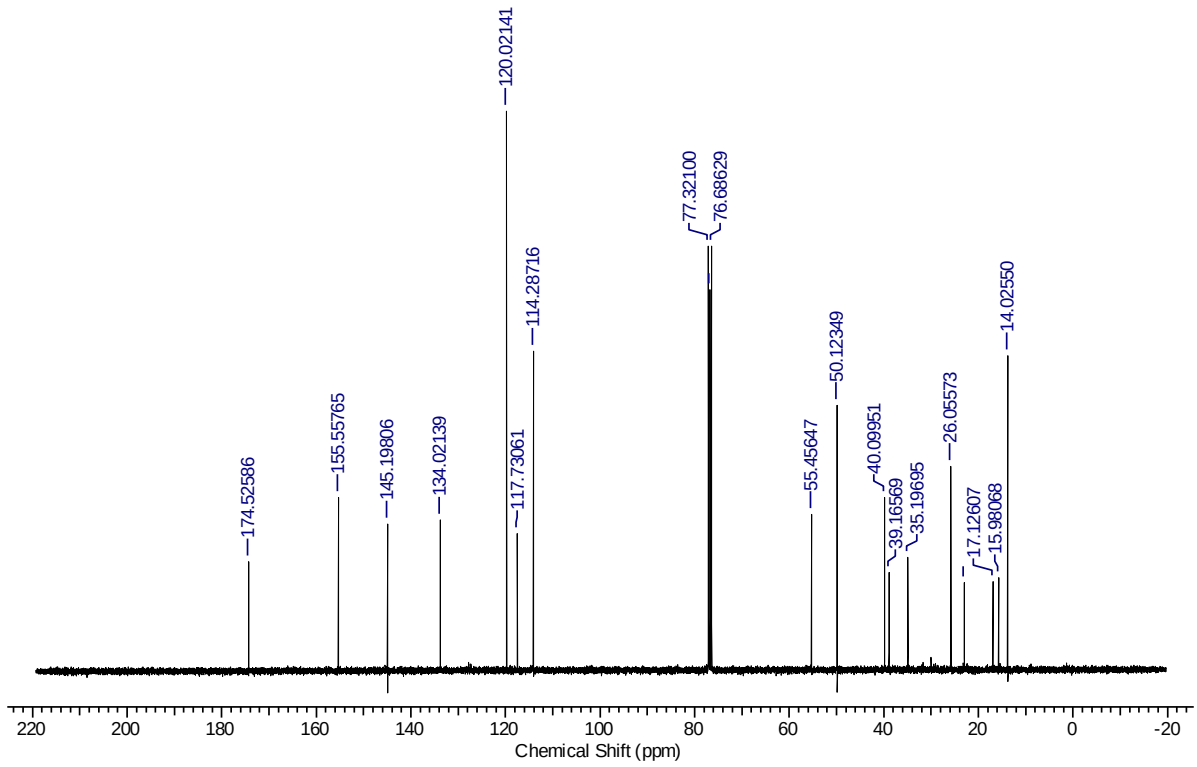

O
NH
Ph
Me
(2r)
1.73486
7.37823
7.27000
7.44305
7.42287
7.25227
7.07433
7.05598
4.76048
4.71278
3.77599
3.75703
3.73808
3.06178
3.04343
3.02509
3.00674
2.58482
2.56587
2.54813
2.52918
2.07 4.07 4.24 1.31
1.00 1.09 1.00 1.00 1.00 3.10
Chemical Shift (ppm)

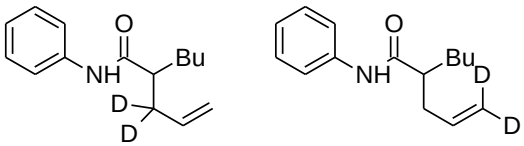

128.01723
142.82703
128.94376
128.86351
127.52843
119.80982
112.44139
139.26685
137.81503
171.19182
77.31370
77.00000
76.67899
52.66231
40.93848
22.61226
Chemical Shift (ppm)


F
N
Me
n-Bu
SMe
(7a)
7.01685
7.00890
6.98688
6.96548
6.95692
6.59798
6.58575
6.57597
6.56374
5.78899
5.78165
5.76392
5.74619
5.17567
5.17017
5.12798
5.10291
5.09740
2.94131
2.90952
2.86427
2.83247
2.56892
2.55058
2.13905
1.75320
1.59789
1.33250
1.31722
0.95216
0.93504
0.91670
2.23 2.00 1.00 2.00 1.01 1.02 1.03 1.00 3.02 2.99 0.97 1.27 4.16 3.07
Chemical Shift (ppm)


175.14597
160.27051
147.92657
133.87549
120.16730
117.85465
115.70978
115.49090
77.32100
77.00000
76.68629
50.19645
40.11410
39.04166
35.10941
26.04843
23.16672
17.11877
14.01090
Chemical Shift (ppm)

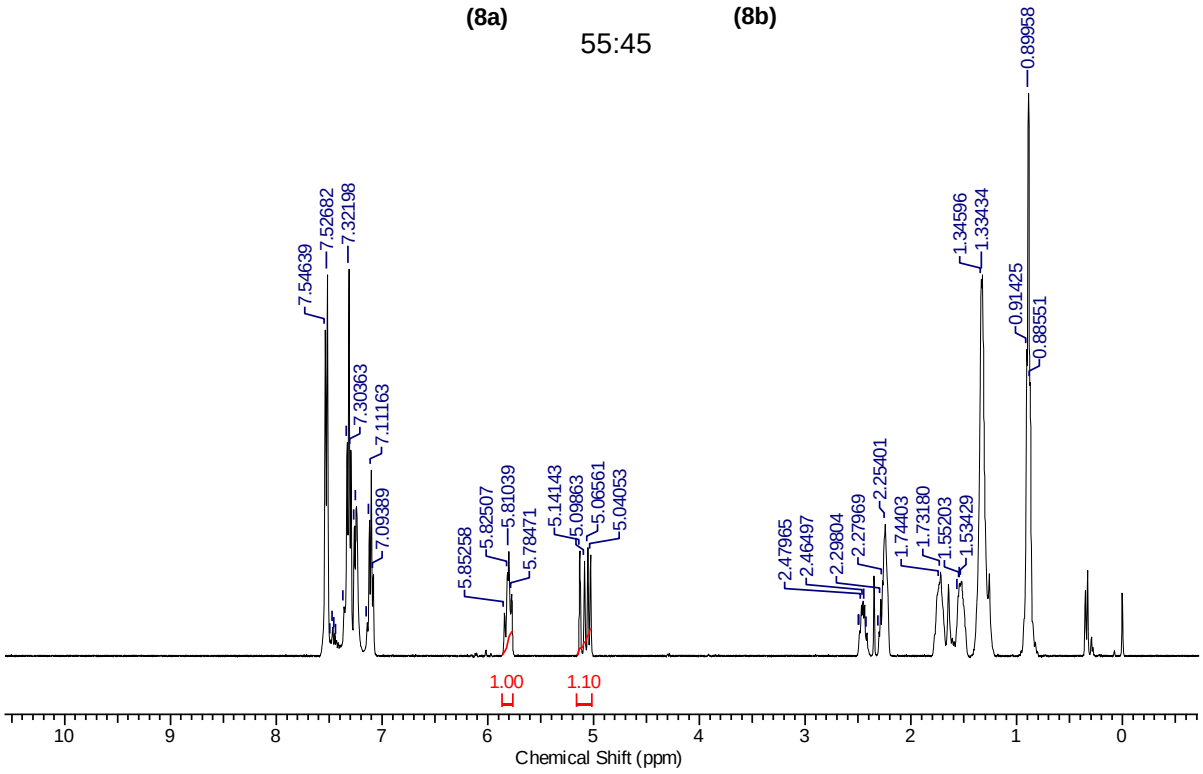

MeO
N
Me
n-Bu
SMe
(7b)
3.79189
2.13905
1.75993
6.86275
6.84074
6.58453
6.56251
0.93260
6.87070
6.83279
5.79266
5.76698
5.74985
5.17262
5.16711
5.12981
5.12431
5.12064
5.11819
5.09557
5.09007
2.95844
2.92664
2.87833
2.84654
2.57015
2.55180
1.59911
1.32700
1.31966
0.94972
0.91425
2.08 2.07 1.00 2.02 3.13 1.03 1.02 1.05 1.02 3.02 3.08 1.02 1.37 4.21 3.15
Chemical Shift (ppm)

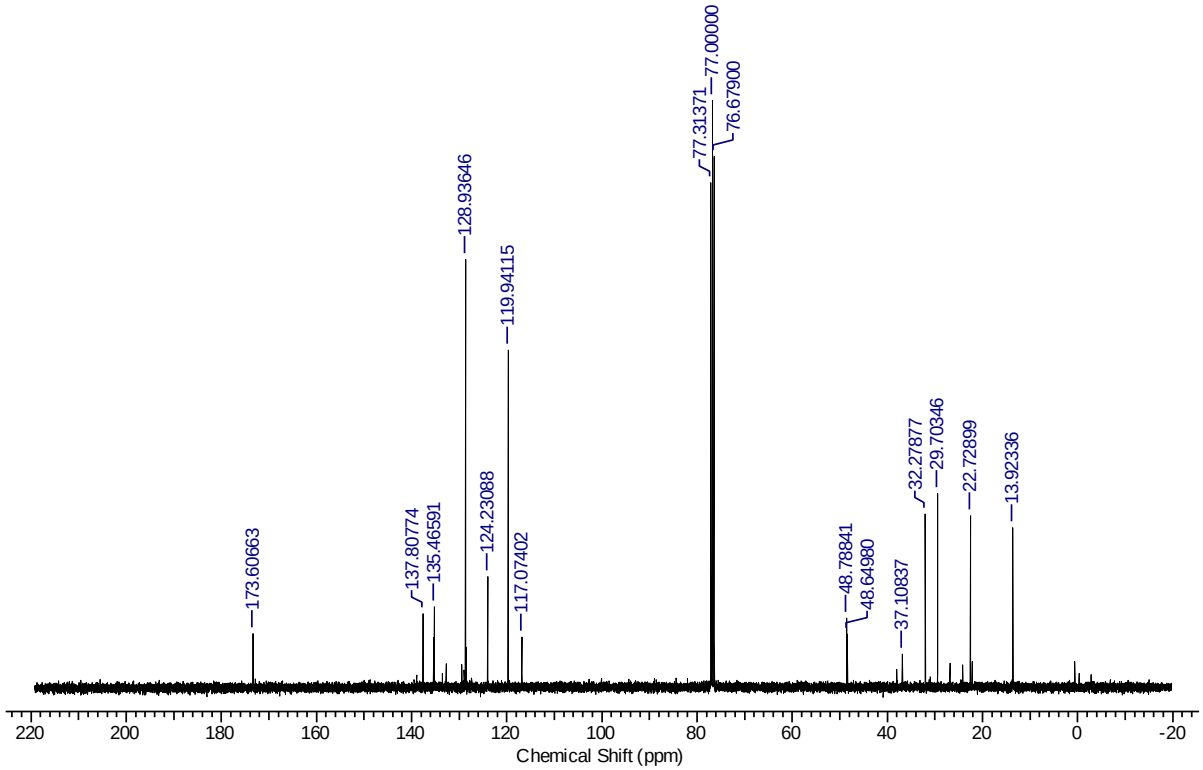

120.02141
77.32100
76.68629
114.28716
174.52586
155.55765
145.19806
134.02139
117.73061
55.45647
50.12349
40.09951
39.16569
35.19695
26.05573
17.12607
15.98068
14.02550
Chemical Shift (ppm)


O
NH
Bu
D
D
D
O
NH
Bu
D
D

(8a) **(8b)**

55:45


7.54639
7.52682
7.32198
7.30363
7.11163
7.09389
5.85258
5.82507
5.81039
5.78471
5.14143
5.09863
5.06561
5.04053
2.47965
2.46497
2.29804
2.27969
2.25401
1.74403
1.73180
1.55203
1.53429
1.34596
1.33434
0.91425
0.88551
0.89958
1.00
1.10
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


173.60663
137.80774
135.46591
128.93646
124.23088
119.94115
117.07402
77.31371
77.00000
76.67900
48.78841
48.64980
37.10837
32.27877
29.70346
22.72899
13.92336
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)