Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supporting Information

Tungsten and Molybdenum Catalyst–Mediated Cyclisation of *N*-Propargyl Amides

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General Methods:

All manipulations were carried out under nitrogen atmosphere. All commercial reagents were used without purification, and all solvents were dried with sodium hydride under nitrogen atmosphere. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using Merck silica gel 60 F_{254} percolated glass plates, which were visualized with UV light and then developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using Merck silica gel 60 (0.040-0.063 mm, 230-400 mesh). ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AVIII 400 instrument. All signals were expressed as ppm down field from Me_4Si for ^{1}H and ^{13}C NMR used as an internal standard (δ). Infrared spectra were recorded on a FTIR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High-resolution mass spectra were recorded on a LC/ HRMS mass spectrometer.

Experimental sections and analytic data

General methods to prepare propargylic amides:

To a CH_2Cl_2 solution of Et_3N (1 equiv), DMAP (0.05 equiv), and a propargylic amine (1 equiv) was added an acid chloride (1 equiv) at 0 ^{o}C. The mixture was then stirred overnight at room temperature. After completion of the reaction, the mixture was quenched with water and extracted with CH_2Cl_2. The organic layer was washed with brine and then dried with anhydrous magnesium sulfate. The crude product was concentrated in vacuo and purified by column chromatography on silica gel using ethyl acetate/*n*-hexane as the eluent to give a propagylic amide.

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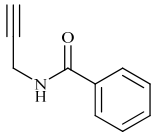
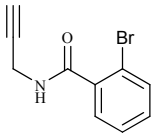
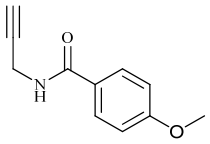


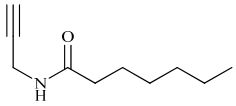
9a[1]: Yield: 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.57 - 7.49 (m, 1H), 7.45 (dd, *J* = 8.1, 6.7 Hz, 2H), 6.26 (s, 1H), 4.27 (dd, *J* = 5.2, 2.6 Hz, 2H), 2.29 (t, *J* = 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 133.8, 131.8, 128.7, 127.0, 79.48, 71.9, 29.8; IR (film) *v* 1645, 1487, 1215, 756, 677; HRMS (ESI) *m / z* calcd for $C_{10}H_9NO$ $(M + H)^+$ 160.0762, found 160.0762.



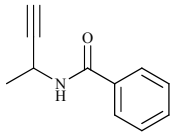
9b: Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (ddd, *J* = 13.1, 7.8, 1.4 Hz, 2H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29 (td, *J* = 7.7, 1.8 Hz, 1H), 6.21 (s, 1H), 4.27 (dd, *J* = 5.2, 2.6 Hz, 2H), 2.29 (t, *J* = 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 136.9, 133.4, 131.5, 129.7, 127.6, 119.4, 78.9, 72.1, 29.5; IR(film) *v* 1736, 1375, 1240, 1047, 847, 607; HRMS (ESI) *m / z* calcd for $C_{10}H_8BrNO$ $(M + H)^+$ 237.9868, found 237.9860.



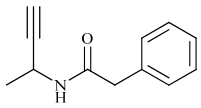
9c[2]: Yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.24 (m, 3H), 7.06 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 1H), 6.25 (s, 1H), 4.26 (dd, *J* = 5.2, 2.6 Hz, 2H), 3.85 (s, 3H), 2.29 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 159.8, 135.2, 129.6, 118.9, 118.0, 112.5, 79.6, 71.8, 55.4, 29.8; IR (film) *v* 1643, 1555, 1215, 754, 669; HRMS (ESI) *m / z* calcd for $C_{11}H_{11}NO_2$ $(M + H)^+$ 190.0868, found 190.0868.



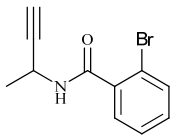
9d: Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (s, 1H), 4.06 (dd, *J* = 5.2, 2.6 Hz, 2H), 2.21 (dt, *J* = 15.3, 5.2 Hz, 3H), 1.63 (dd, *J* = 14.7, 7.1 Hz, 2H), 1.42 – 1.17 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 79.6, 71.3, 36.4, 31.5, 29.1, 28.9, 25.5 , 22.5, 13.9; IR (film) *v* 1666, 1510, 1421, 928, 740; HRMS (ESI) *m / z* calcd for $C_{10}H_{17}NO$ $(M + H)^+$ 168.1388, found 168.1389.



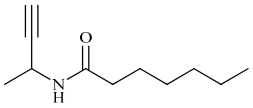
9f: Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.50 (dd, *J* = 6.3, 3.8 Hz, 1H), 7.44 (dt, *J* = 11.4, 5.8 Hz, 2H), 6.35 -6.28 (m, 1H), 5.06 -5.00 (m, 1H), 2.31 (t, *J* = 1.9 Hz, 1H), 1.53 (dd, *J* = 6.8, 3.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 133.9, 131.7, 128.6, 127.0, 84.2, 81.5, 70.7, 37.5, 22.4; IR (film) *v* 1647, 1510, 1215, 928,748; HRMS (ESI) *m / z* calcd for $C_{11}H_{11}NO$ $(M + H)^+$ 174.0919, found 174.0914.



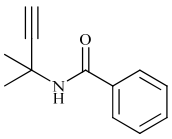
9g: Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.9, 6.4 Hz, 2H), 7.33 - 7.28 (m, 1H), 7.26 (t, *J* = 3.3 Hz, 2H), 5.54 (s, 1H), 4.81 (dqd, *J* = 13.8, 6.9, 2.3 Hz, 1H), 3.57 (s, 2H), 2.21 (d, *J* = 2.3 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 134.5, 129.4, 129.1, 127.4, 83.9, 70.4, 43.6, 37.0, 22.1; IR (film) *v* 1647, 1535, 1355, 1134,754, 511; HRMS (ESI) *m / z* calcd for $C_{12}H_{13}NO$ $(M + H)^+$ 188.1075, found 188.1076.



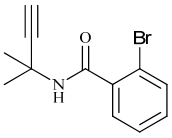
9h: Yield: 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (ddd, *J* = 16.1, 7.8, 1.4 Hz, 2H), 7.37 (td, *J* = 7.5, 1.1 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.18 (s, 1H), 5.03 (dqd, *J* = 13.8, 6.9, 2.3 Hz, 1H), 2.32 (d, *J* = 2.3 Hz, 1H), 1.55 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.41, 137.2, 133.3, 131.4, 129.6, 127.5, 119.3, 83.6, 70.9, 37.6, 22.1; ; IR (film) *v* 1666, 1504, 1265, 740, 704; HRMS (ESI) *m / z* calcd for $C_{11}H_{10}BrNO$ $(M + H)^+$ 252.0024, found 252.0017.



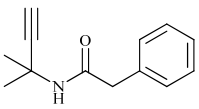
9i: Yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (s, 1H), 4.83 (ddd, *J* = 8.1, 6.9, 2.3 Hz, 1H), 2.25 (d, *J* = 2.3 Hz, 1H), 2.21 - 2.05 (m, 2H), 1.71 - 1.56 (m, 3H), 1.41 (d, *J* = 6.9 Hz, 3H), 1.33 - 1.27 (m, 5H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 84.3, 70.3, 36.8, 36.7, 31.5, 28.9, 25.5, 22.5, 22.4, 14.0; IR (film) *v* 1645, 1504, 1215, 1140, 748; HRMS (ESI) *m / z* calcd for $C_{11}H_{19}NO$ $(M + H)^+$ 182.1545, found 182.1558.



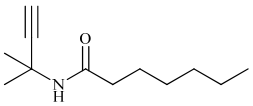
15a[3]: Yield: 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 6.21 (s, 1H), 2.39 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 134.8, 131.5, 128.5, 126.9, 87.2, 69.4, 47.9, 29.0; IR (film) *v* 1645, 1508, 1283, 1215, 756; HRMS (ESI) *m / z* calcd for $C_{12}H_{13}NO$ $(M + H)^+$ 188.1075, found 188.1073.



15b: Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (ddd, *J* = 7.3, 5.0, 1.3 Hz, 2H), 7.35 (td, *J* = 7.5, 1.1 Hz, 1H), 7.30 - 7.26 (m, 1H), 6.08 (s, 1H), 2.40 (s, 1H), 1.78 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 137.9, 133.3, 131.2, 129.6, 127.6, 119.2, 86.8, 69.7, 48.5, 28.8; IR (film) *v* 1666, 1504, 1298, 1215, 744; HRMS (ESI) *m / z* calcd for $C_{12}H_{12}BrNO$ $(M + H)^+$ 266.0181, found 266.0181.



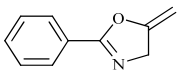
15c: Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.25 (s, 1H), 5.45 (s, 1H), 3.54 (s, 2H), 2.31 (s, 1H), 1.57 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 134.9, 129.3, 129.0, 127.3, 86.9, 69.2, 47.7, 44.4, 28.8; IR (film) *v* 1643, 1537, 1210, 748, 655; HRMS (ESI) *m / z* calcd for $C_{32}H_{15}NO$ $(M + H)^+$ 202.1232, found 202.1230.



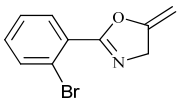
15d: Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (s, 1H), 2.33 (s, 1H), 2.18 - 2.05 (m, 2H), 1.64 (s, 6H), 1.63 - 1.57 (m, 2H), 1.30 (t, *J* = 4.8 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.27, 87.40, 68.93, 47.44, 37.22, 31.52, 28.89, 25.49, 22.46, 13.98; IR (film) *v* 1647, 1535, 1383, 1190, 756, 699; HRMS (ESI) *m / z* calcd for $C_{12}H_{21}NO$ $(M + H)^+$ 196.1701, found 196.1699.

General methods for $W(CO)_6$ catalyzed cyclisation of unsubstituted and monosubstituted propargyl amides

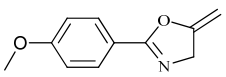
To a toluene solution of a propargyl amide (1 equiv) and DABCO (1 equiv) was added $W(CO)_6$ (0.2 equiv) under nitrogen. The mixture was then irradiated at 350 nm under Rayonet photoreactor for 20 hours at room temperature. After the completion of the reaction, the solvent was evaporated under reduced pressure. Then it was filtered through a short pad of Celite silica gel and washed with CH_2Cl_2 several times. After concentration in vacuo, the crude product was treated with trimethylamine N-Oxide dihydrate (2 equiv) in THF for 4 hours at room temperature. Then it was quenched with water, extracted with diethyl ether, washed with brine, and dried with anhydrous $MgSO_4$. The organic layer was evaporated under reduced pressure and the crude product was purified by silica gel column using ethyl acetate/*n*-hexane as the eluent to give the corresponding cyclised products.



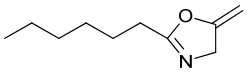
10a[4]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 - 7.90 (m, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 8.1, 6.8 Hz, 2H), 4.82 (d, *J* = 2.9 Hz, 1H), 4.65 (t, *J* = 2.8 Hz, 2H), 4.37 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 158.9, 131.8, 128.5, 128.0, 126.8, 83.8, 57.8; IR (film) *v* 1691, 1647, 1327, 1217, 1060, 692; HRMS (ESI) *m / z* calcd for $C_{10}H_9NO$ $(M + H)^+$ 160.0762, found 160.0764.



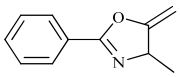
10b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.69 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.36 (dtd, *J* = 17.2, 7.5, 1.5 Hz, 2H), 4.86 - 4.74 (m, 1H), 4.72 (t, *J* = 2.9 Hz, 2H), 4.39 (q, *J* = 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 158.4, 134.3, 132.1, 131.5, 128.4, 127.2, 121.9, 84.1, 58.2; IR (film) *v* 1693, 1651, 1433, 1315, 1024, 729; HRMS (ESI) *m / z* calcd for $C_{10}H_8BrNO$ $(M + H)^+$ 237.9868, found 237.9874.



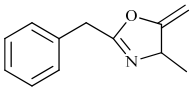
10c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.79 (d, *J* = 2.9 Hz, 1H), 4.62 (t, *J* = 2.8 Hz, 2H), 4.34 (d, *J* = 2.6 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 162.4, 159.0, 129.8, 127.6, 123.9, 119.3, 113.9, 113.9, 83.4, 57.7, 55.4; IR (film) *v* 1645, 1435, 1309, 1186, 910, 731; HRMS (ESI) *m / z* calcd for $C_{11}H_{11}NO_2$ $(M + H)^+$ 190.0868, found 190.0873.



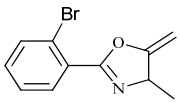
10d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (q, *J* = 3.0 Hz, 1H), 4.40 (dq, *J* = 4.3, 1.5 Hz, 2H), 4.24 (q, *J* = 2.6 Hz, 1H), 2.34 (dd, *J* = 10.9, 4.5 Hz, 2H), 1.76 – 1.64 (m, 2H), 1.35 - 1.26 (m, 6H), 0.92 - 0.83 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 159.6, 82.6, 57.20 (s), 31.40 (s), 28.81 (s), 28.17 (s), 25.46 (s), 22.49 (s), 14.01 (s); IR (film) *v* 1667, 1510, 1421, 927, 603; HRMS (ESI) *m / z* calcd for $C_{10}H_{17}NO$ $(M + H)^+$ 168.1388, found 168.1396.



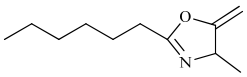
10f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 - 7.98 (m, 2H), 7.48 - 7.34 (m, 3H), 4.79 (dt, *J* = 6.8, 2.7 Hz, 2H), 4.31 (t, *J* = 2.6 Hz, 1H), 1.48 (d, *J* = 6.9 Hz, 3H).



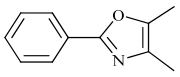
10g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.22 (m, 5H), 4.62 (t, *J* = 2.6 Hz,, 1H), 4.56 – 4.53 (m, 1H), 4.19 (t, *J* = 4.9 Hz, 1H), 3.68 (s, 2H), 1.36 (d, *J* = 7.0 Hz, 3H).



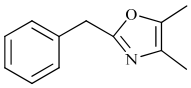
10h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.68 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.41 - 7.28 (m, 2H), 4.85 – 4.83 (m, 1 H), 4.82 (dd, *J* = 6.9, 2.6 Hz, 1H), 4.32 (t, *J* = 2.6 Hz, 1H), 1.51 (d, *J* = 6.9 Hz, 3H).



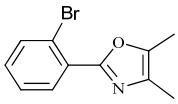
10i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (t, *J* = 2.7 Hz, 1H), 4.53 (d, *J* = 6.9 Hz, 1H), 4.18 (t, *J* = 2.5 Hz, 1H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.74 - 1.63 (m, 2H), 1.45 - 1.25 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H).



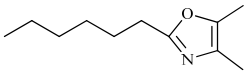
11f[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.41 (t, *J* = 4.9 Hz, 3H), 2.32 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 143.4, 131.9, 129.7, 128.7, 128.5, 128.1, 127.9, 125.8, 11.30, 10.11; IR (film) *v* 1645, 1448, 1085, 1026, 910, 775, 732; HRMS (ESI) *m / z* calcd for $C_{11}H_{11}NO$ $(M + H)^+$ 174.0919, found 174.0915.



11g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.22 (m, 5H), 4.01 (s, 2H), 2.17 (s, 3H), 2.05 (d, *J* = 0.8 Hz, 3H).



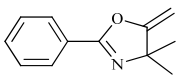
11h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.29 - 7.20 (m, 1H), 2.33 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 144.1, 134.3, 131.9, 131.0, 130.6, 128.9, 127.3, 120.8, 11.3, 10.1; IR (film) *v* 1645, 1610,1514, 1257, 1172, 1068, 731; HRMS (ESI) *m / z* calcd for $C_{11}H_{10}BrNO$ $(M + H)^+$ 252.0024, found 252.0024.



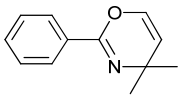
11i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (t, *J* = 7.7 Hz, 2H), 2.18 (s, 3H), 2.04 (s, 3H), 1.74 - 1.63 (m, 2H), 1.45 - 1.25 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H).

General methods for $W(CO)_6$ catalyzed cyclisation of disubstituted propargyl amides

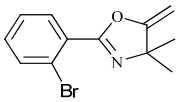
To a toluene solution of disubstituted propargyl amides (1 equiv) and DABCO (1 equiv) was added $W(CO)_6$ or $Mo(CO)_6$ (0.2 equiv) under a nitrogen atmosphere at room temperature. The mixture was irradiated at 350 nm under Rayonet photoreactor overnight at room temperature. After the completion of the reaction, the mixture was quenched with water, extracted with diethyl ether, washed with brine, and dried with anhydrous $MgSO_4$. The organic layer was evaporated under reduced pressure and the crude was purified by silica gel column using ethyl acetate/*n*-hexane as the eluent to give the oxazoline products.



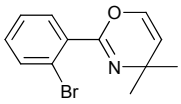
16a[6]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 - 7.91 (m, 2H), 7.56 - 7.46 (m, 1H), 7.46 - 7.34 (m, 2H), 4.74 (d, *J* = 2.8 Hz, 1H), 4.25 (d, *J* = 2.8 Hz, 1H), 1.46 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 159.9, 131.7, 128.5, 128.1, 127.0, 82.3, 69.1, 29.8; IR (film) *v* 1697, 1668, 1497, 1263, 976, 955, 733; HRMS (ESI) *m / z* calcd for $C_{12}H_{13}NO$ $(M + H)^+$ 188.1075, found 188.1090.



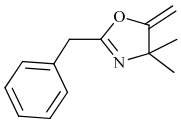
16b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.52 - 7.30 (m, 3H), 6.52 (d, *J* = 6.2 Hz, 1H), 5.01 (d, *J* = 6.2 Hz, 1H), 1.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 137.2 132.7 130.5 128.1, 127.2, 111.5, 49.5, 32.6; IR (film) *v* 1686, 1635, 1449, 1290, 1056, 694; HRMS (ESI) *m / z* calcd for $C_{12}H_{13}NO$ $(M + H)^+$ 188.1075, found 188.1078.



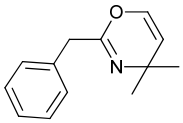
17a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.32 (dd, *J* = 7.8, 1.9 Hz, 1H), 4.73 (d, *J* = 2.9 Hz, 1H), 4.27 (d, *J* = 2.9 Hz, 1H), 1.49 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 159.2, 133.9, 131.9, 131.4, 129.1, 127.1, 121.9, 82.6, 69.6, 29.9; IR (film) *v* 1693, 1638, 1300, 1033, 759, 731; HRMS (ESI) *m / z* calcd for $C_{12}H_{12}BrNO$ $(M + H)^+$ 266.0181, found 266.0189.



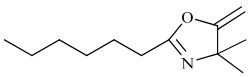
17b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.33 (td, *J* = 7.5, 1.2 Hz, 1H), 7.26 - 7.18 (m, 1H), 6.48 (d, *J* = 6.2 Hz, 1H), 5.03 (d, *J* = 6.2 Hz, 1H), 1.38 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 137.4, 135.2, 133.3, 130.9, 130.3, 127.3, 121.4, 111.6, 50.3, 32.5; IR (film) *v* 1693, 1657, 1643, 1450, 1327, 1060, 926, 777; HRMS (ESI) *m / z* calcd for $C_{12}H_{12}BrNO$ $(M + H)^+$ 266.1081, found 266.0173.



18a[6]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.28 (m, 5H), 4.58 (d, *J* = 2.8 Hz, 1H), 4.15 (d, *J* = 2.8 Hz, 1H), 3.71 (s, 2H), 1.37 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 161.9, 134.5, 128.9, 128.7, 127.1, 82.1, 68.6, 34.9, 29.5; IR (film) *v* 1697, 1672, 1496, 1265, 954, 732; HRMS (ESI) *m / z* calcd for $C_{13}H_{15}NO$ $(M + H)^+$ 202.1232, found 202.1238.



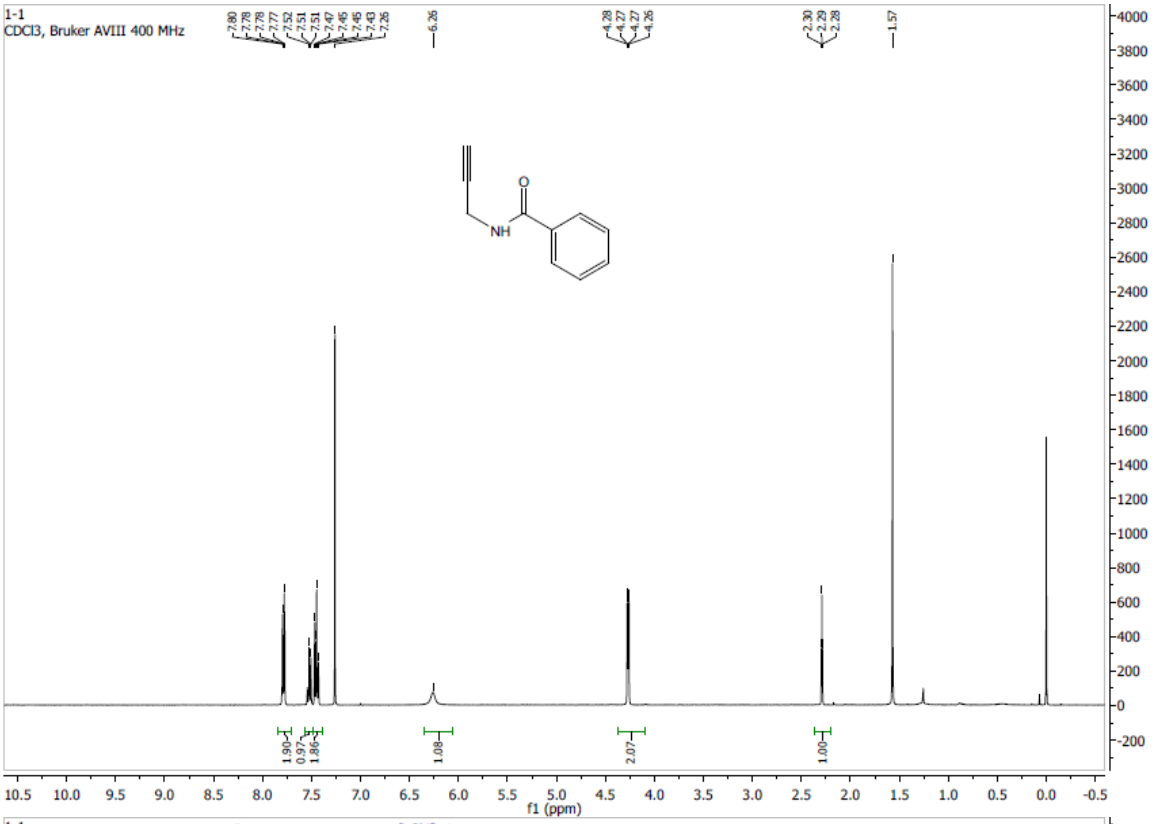
18b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.4 Hz, 4H), 7.29 - 7.25 (m, 1H), 6.30 (d, *J* = 6.2 Hz, 1H), 4.91 (d, *J* = 6.2 Hz, 1H), 3.54 (s, 2H), 1.29 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 137.2, 136.0, 128.8, 128.5, 126.8, 111.1, 49.3 , 41.6, 32.6; IR (film) *v* 1697, 1673, 1454, 1184, 955, 705; HRMS (ESI) *m / z* calcd for $C_{13}H_{15}NO$ $(M + H)^+$ 202.1232, found 202.1228.

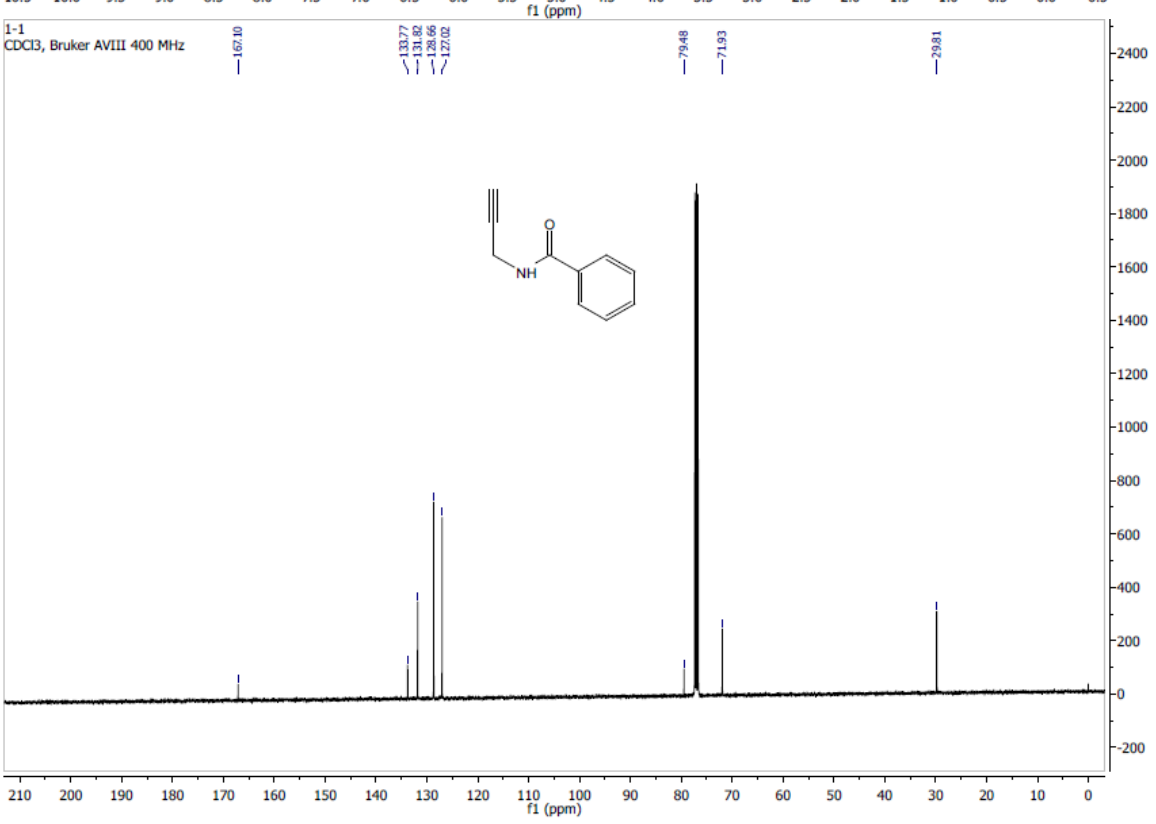


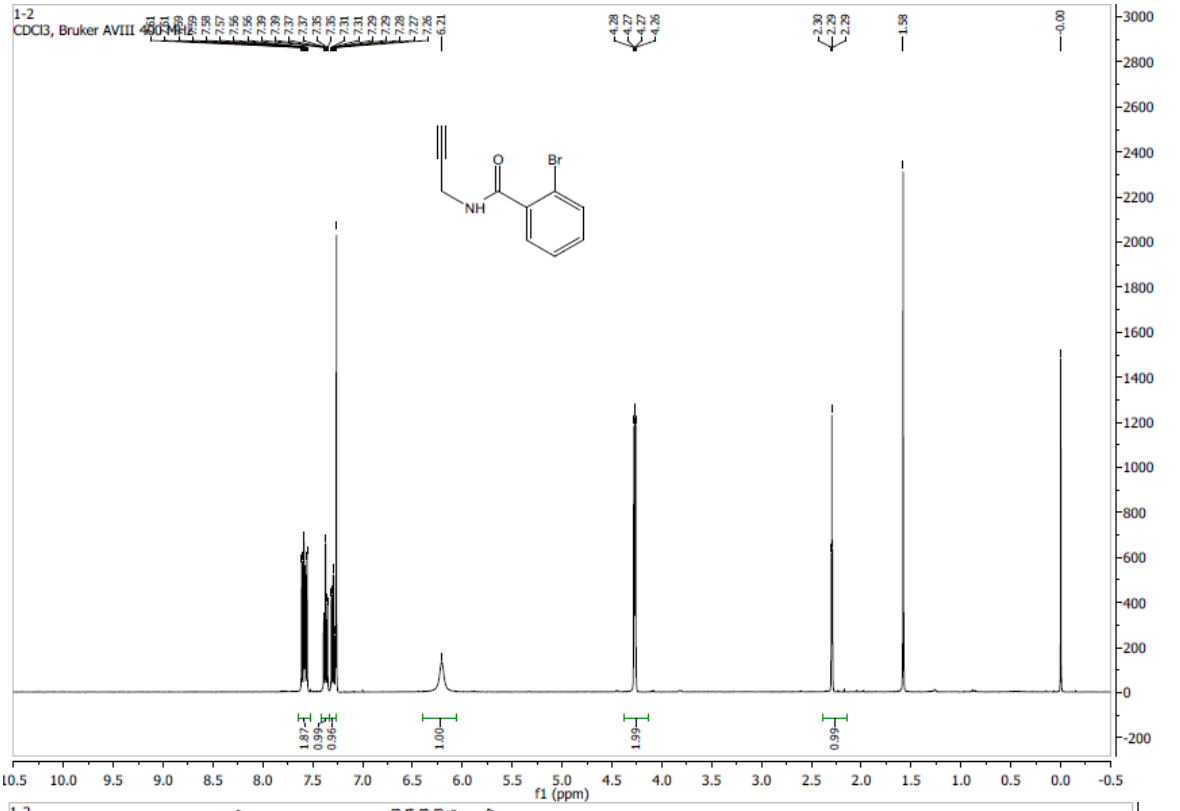
19a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 (d, J = 2.7 Hz, 1H), 4.13 (d, J = 2.7 Hz, 1H), 2.49 - 2.22 (m, 2H), 1.66 (dt, J = 15.2, 7.5 Hz, 2H), 1.33 (s, 6H), 1.43 - 1.18 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 168.3, 163.8, 81.4, 68.3, 31.4, 29.6, 28.7, 28.1, 25.6, 22.5, 13.9; ; IR (film) *v* 1672, 1573, 1199, 910, 733; HRMS (ESI) *m / z* calcd for $C_{12}H_{21}NO$ $(M + H)^+$ 196.1701, found 196.1722.

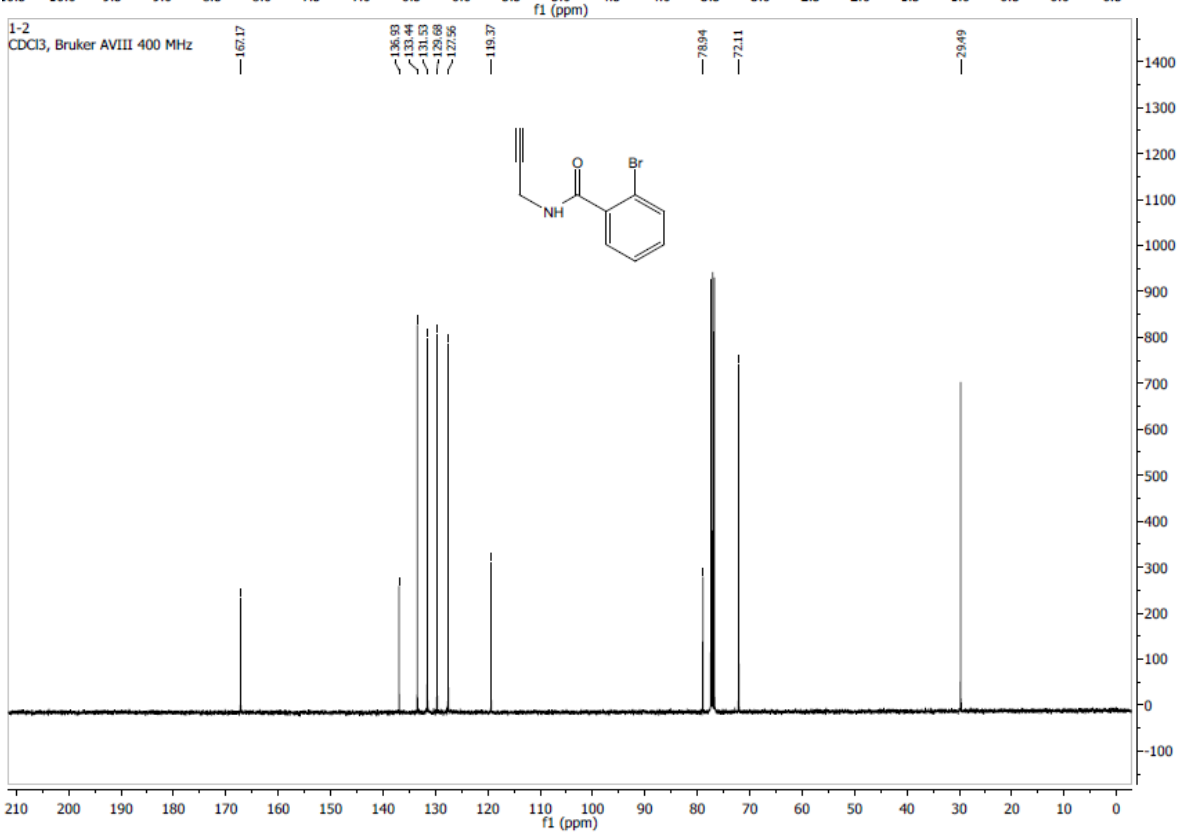
Reference:

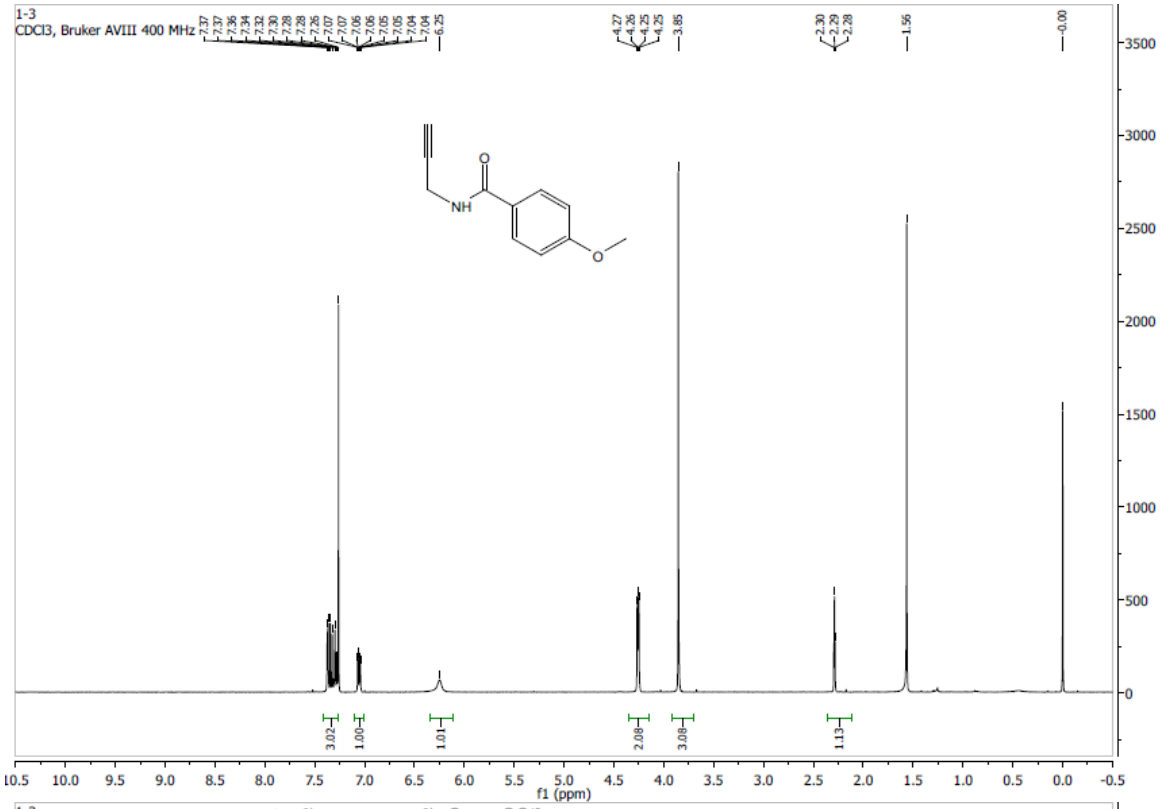
1. A. S. K. Hashmi, J. P. Weyrauch, W. Frey and J. W. Bats, *Org. Lett*., 2004, **6**, 4391.
2. E. M. Beccall, E. Borsini, G. Broggin, G. Palmisan and S. Sottocornola, *J. Org. Chem.* 2008, **73**, 4746.
3. T. Andrea, T. Raffaella, T. Lorenzo, T. Marcello, *Synth. Commun.,* 2010, **40**, 295.
4. Weyrauch, Jan P.; Hashmi, A. Stephen K, A. Schuster, T. Hengst, S. Schetter, A. Littmann, M. Rudolph, M. Hamzic, J. Visus, F. Rominger, W. Frey and J. W. Bats, *Chem. Eur. J*. 2010, **16**, 956.
5. X. H. Cai, H. J. Yang and G. L. Zhang, *Synthesis*, 2005, **10**, 1569
6. M. Harmata and C. F. Huang, *Synlett*, 2008, 1399.

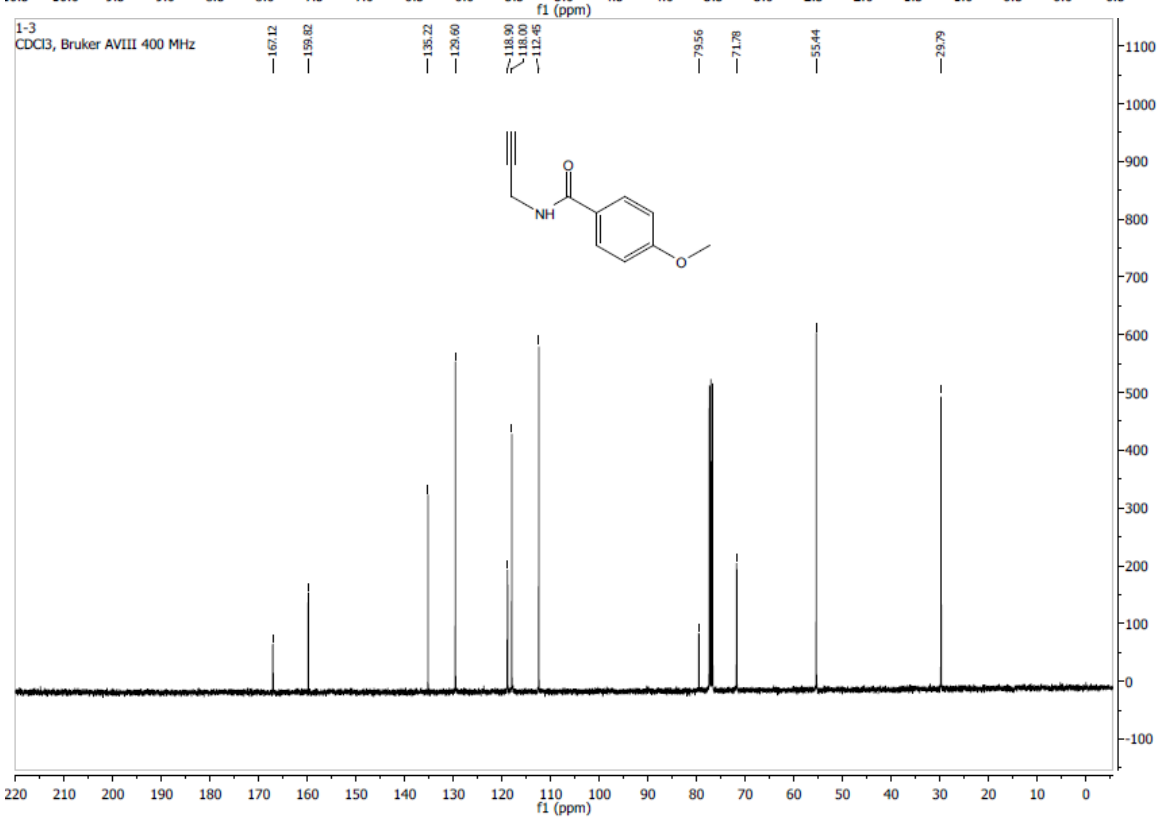

1-1
CDCl3, Bruker AVIII 400 MHz
7.80
7.78
7.78
7.77
7.52
7.51
7.51
7.47
7.45
7.45
7.43
7.26
6.26
4.28
4.27
4.27
4.26
2.30
2.29
2.28
1.57
NH
O
1.90
0.97
1.86
1.08
2.07
1.00
f1 (ppm)

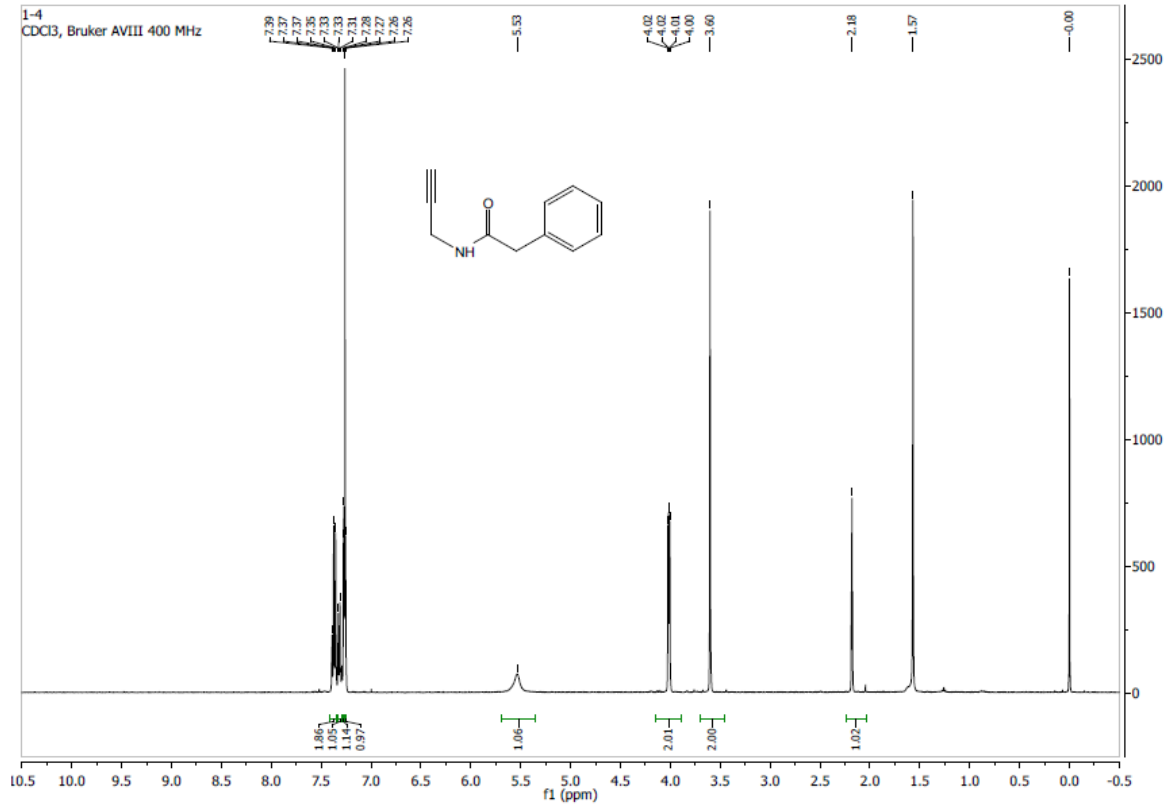

1-1
CDCl3, Bruker AVIII 400 MHz
167.10
133.77
131.82
128.66
127.02
79.48
71.93
29.81
NH
O
f1 (ppm)

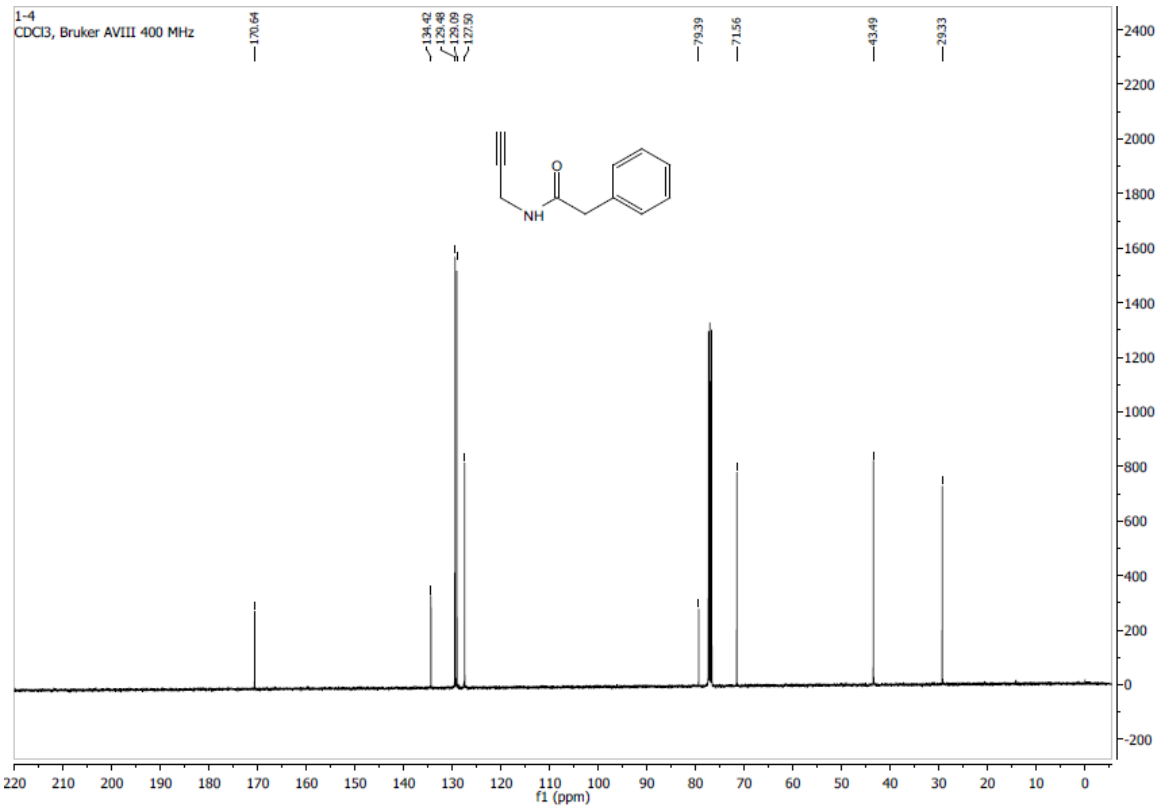

1-2
CDCl3, Bruker AVIII 400 MHz
7.61
7.59
7.58
7.57
7.56
7.39
7.37
7.35
7.31
7.29
7.28
7.27
7.26
6.21
4.28
4.27
4.27
4.26
2.30
2.29
2.29
1.58
0.00
O
Br
NH
1.87
0.99
0.96
1.00
1.99
0.99
f1 (ppm)

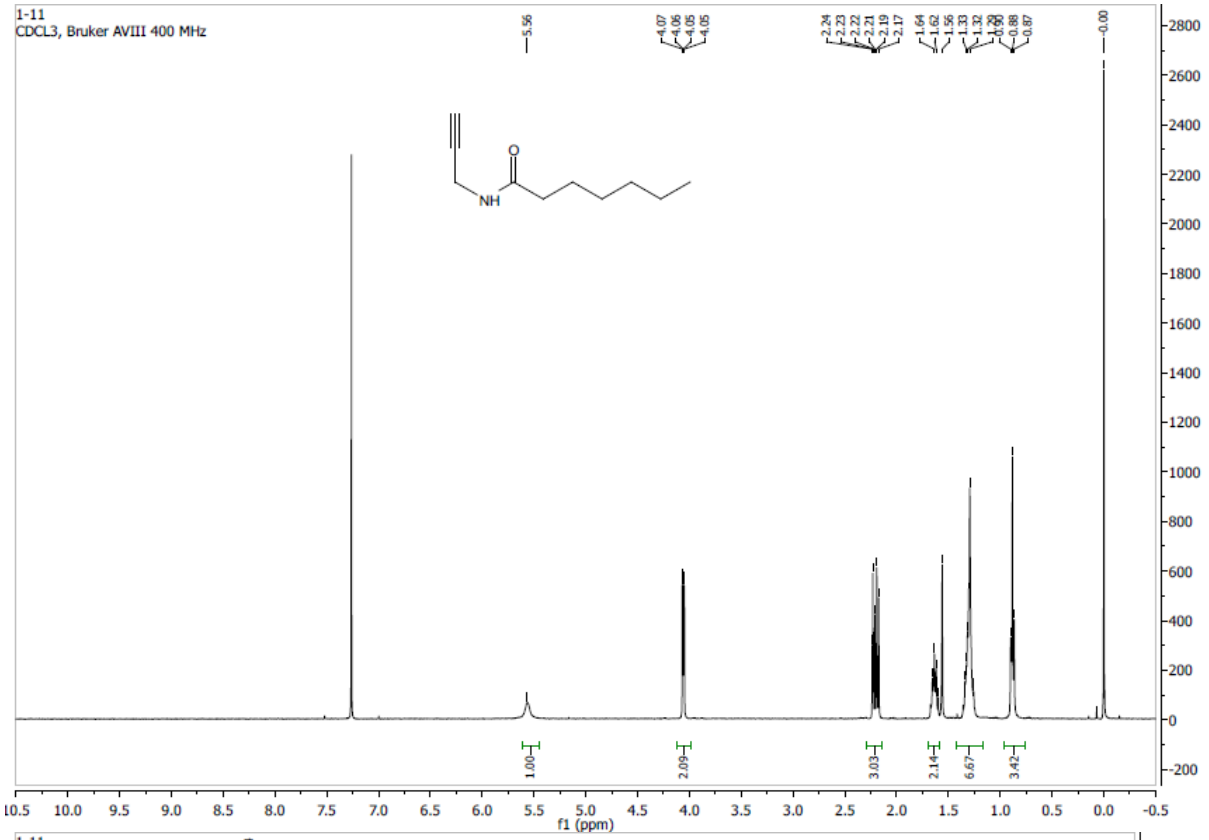

1-2
CDCl3, Bruker AVIII 400 MHz
167.17
136.93
133.44
131.53
129.68
127.56
119.37
78.94
72.11
29.49
O
Br
NH
f1 (ppm)

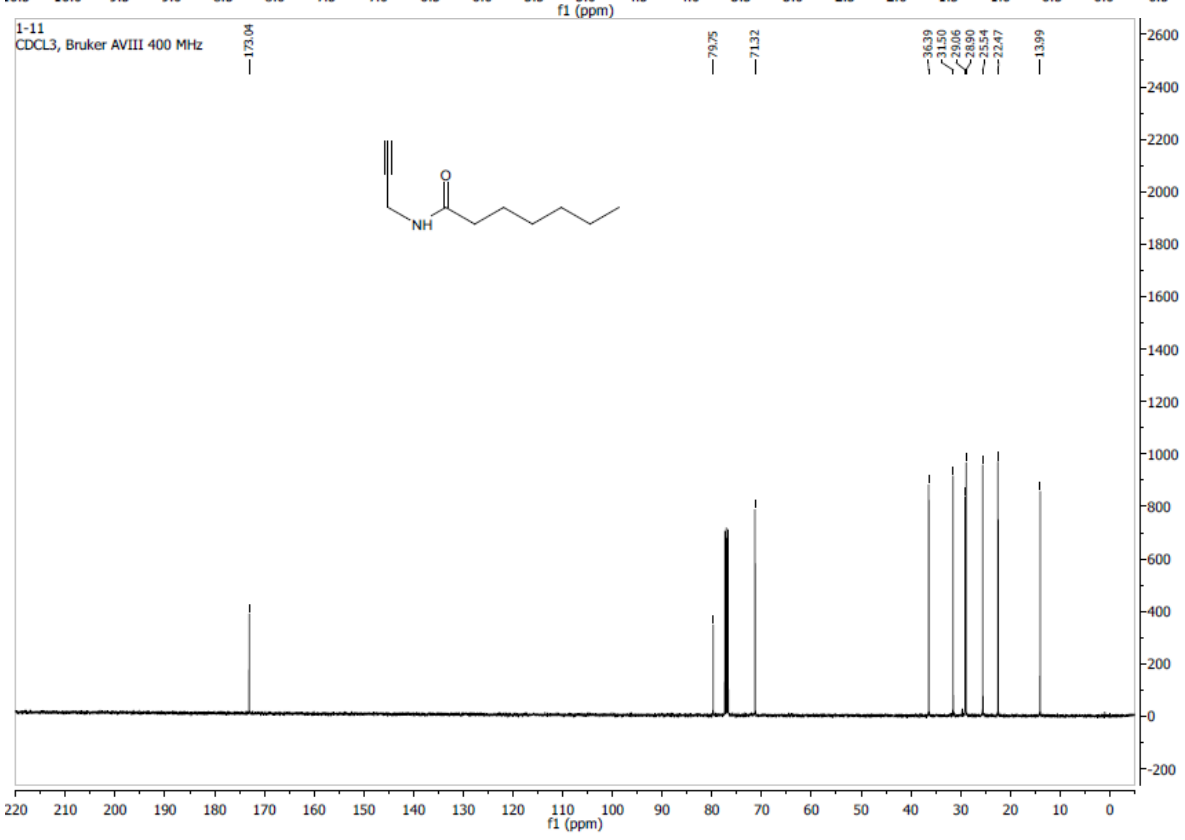

1-3
CDCl3, Bruker AVIII 400 MHz
7.37
7.37
7.36
7.34
7.32
7.30
7.28
7.28
7.26
7.07
7.07
7.06
7.06
7.05
7.05
7.04
7.04
6.25
4.27
4.26
4.25
4.25
3.85
2.30
2.29
2.28
1.56
0.00
NH
O
O
3.02
1.00
1.01
2.08
3.08
1.13
f1 (ppm)

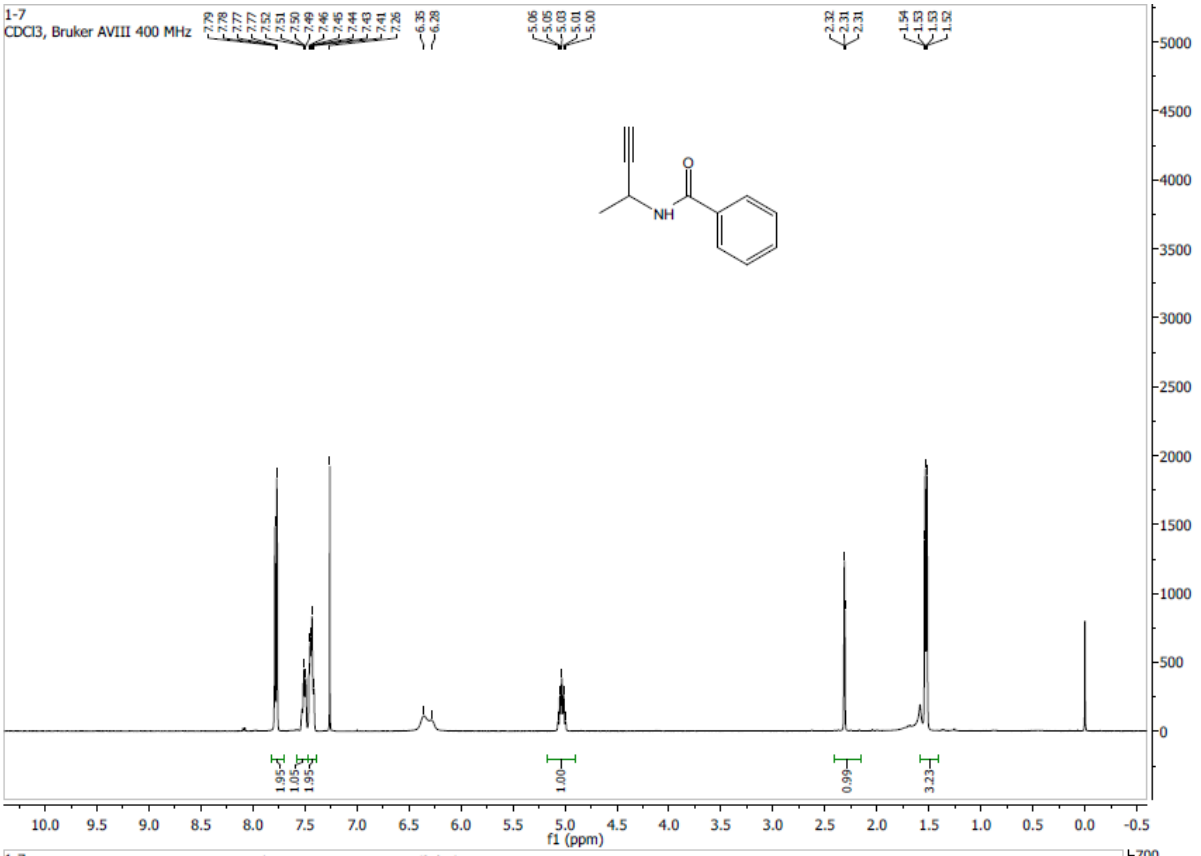

1-3
CDCl3, Bruker AVIII 400 MHz
167.12
159.82
135.22
129.60
118.90
118.00
112.46
79.56
71.78
55.44
29.79
NH
O
O
f1 (ppm)

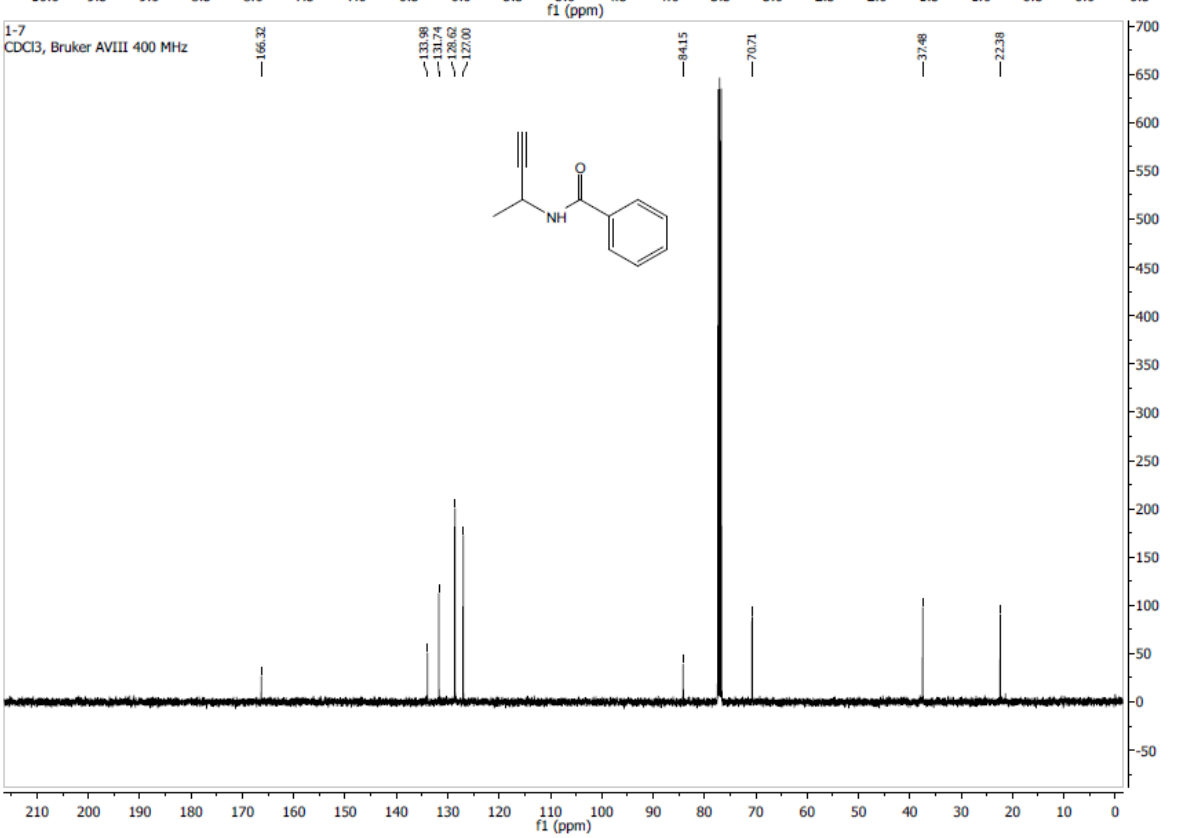

1-4
CDCl3, Bruker AVIII 400 MHz
7.39
7.37
7.37
7.35
7.33
7.33
7.31
7.28
7.27
7.26
7.26
5.53
4.02
4.02
4.01
4.00
3.60
2.18
1.57
0.00
1.86
1.05
1.14
0.97
1.06
2.01
2.00
1.02
O
NH
f1 (ppm)

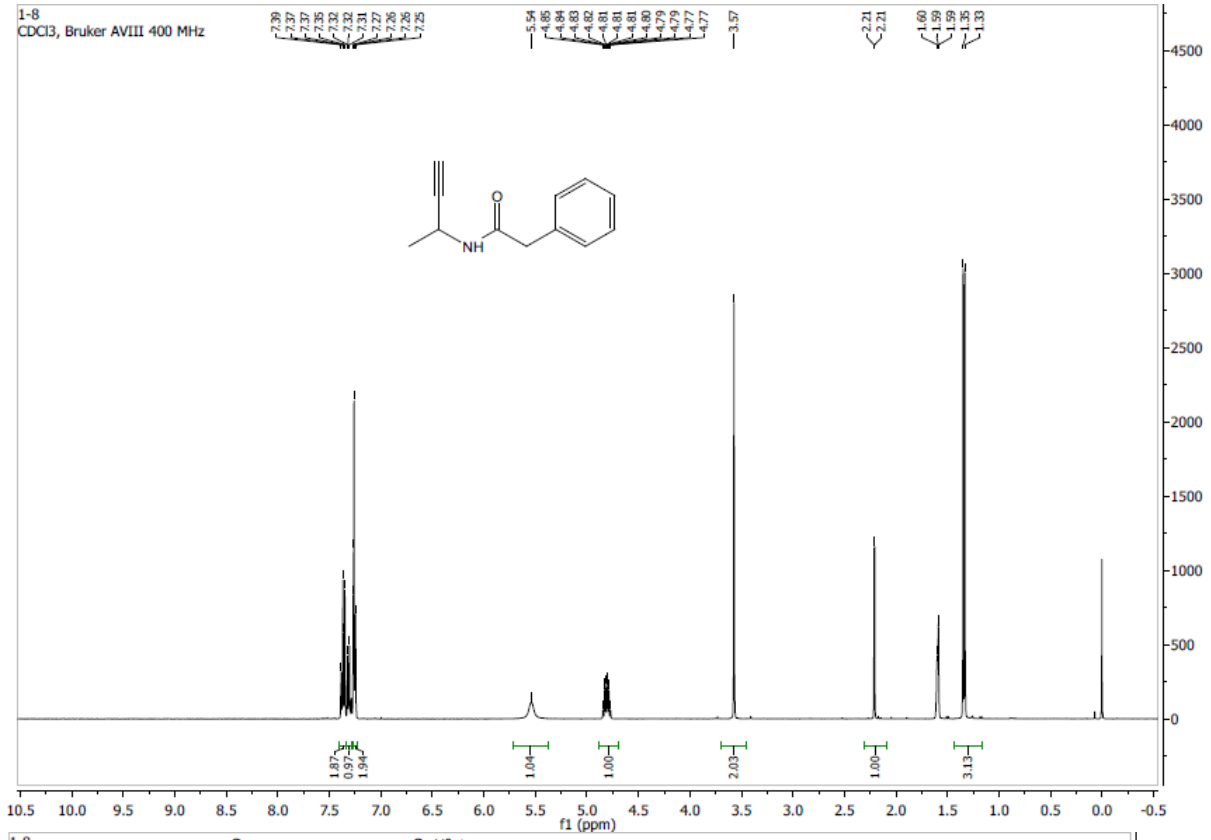

1-4
CDCl3, Bruker AVIII 400 MHz
170.64
134.42
129.48
129.09
127.50
79.39
71.56
43.49
29.33
O
NH
f1 (ppm)

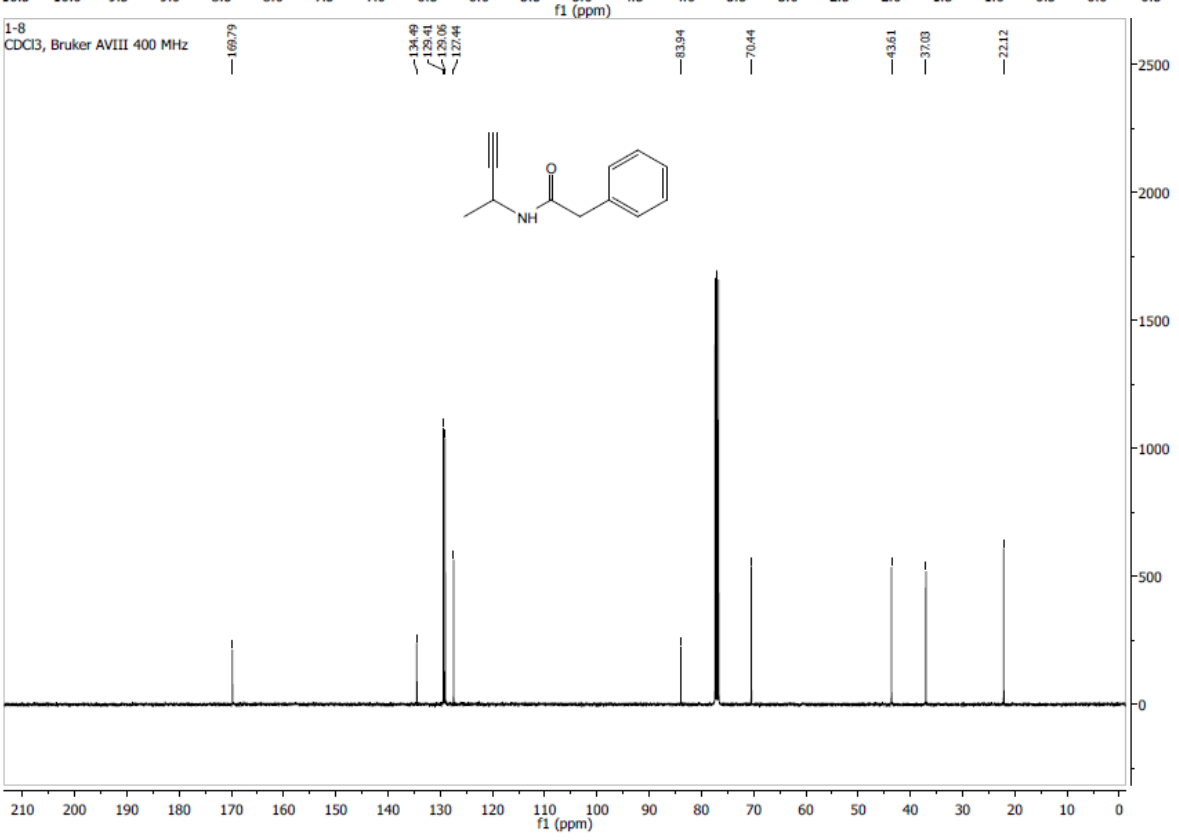


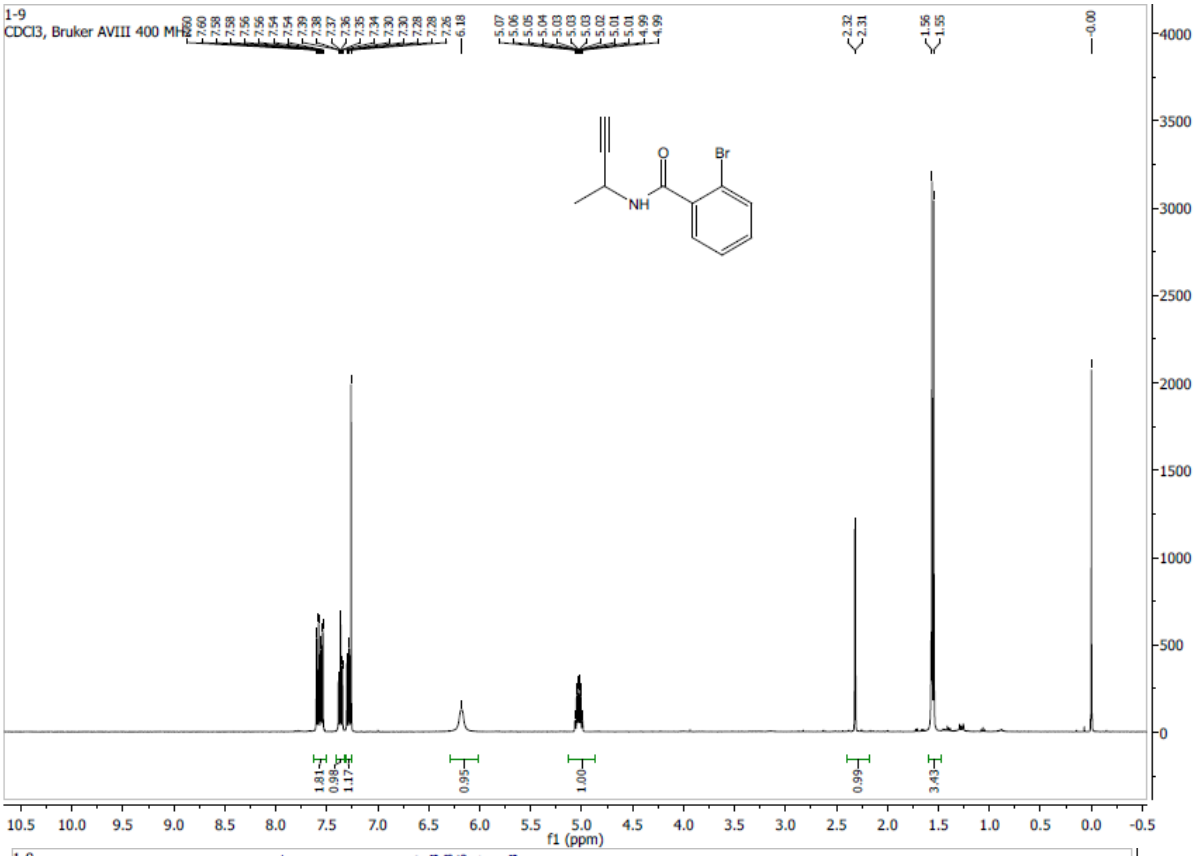


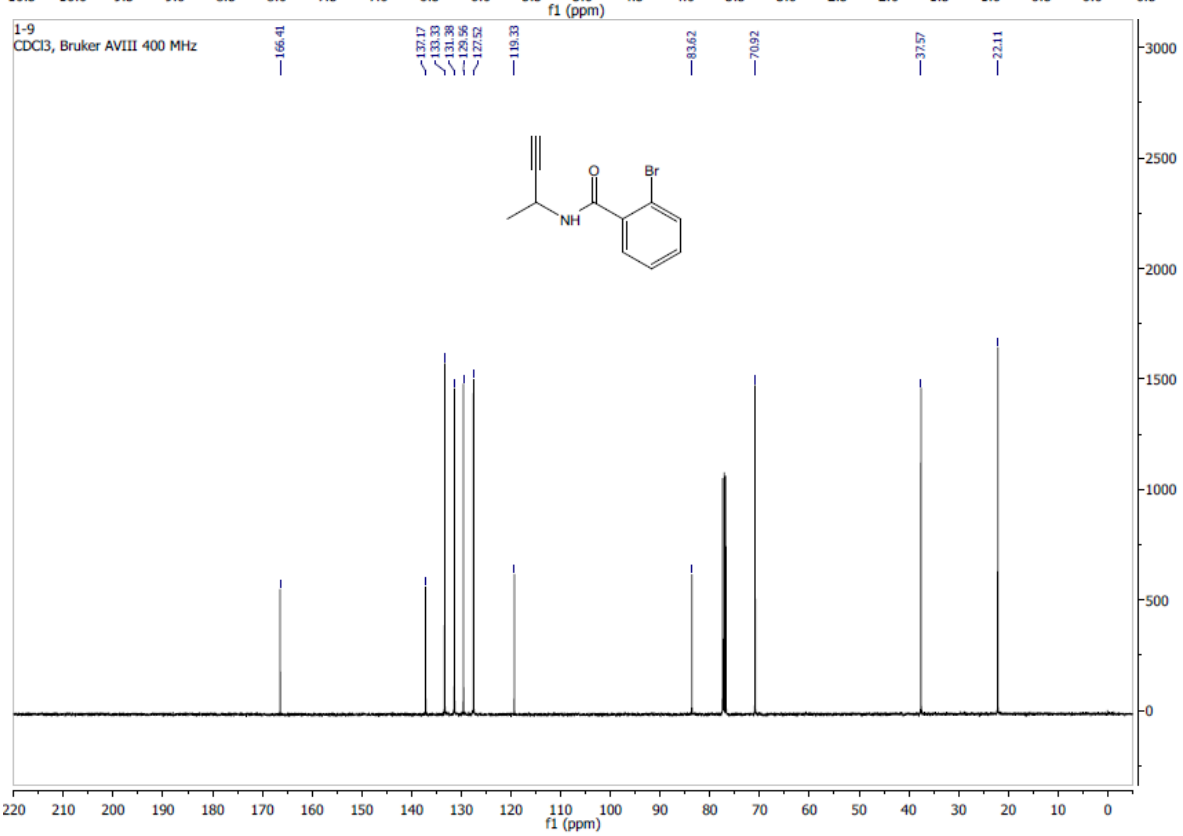

1-7
CDCl3, Bruker AVIII 400 MHz
7.79
7.78
7.77
7.77
7.52
7.51
7.50
7.49
7.46
7.45
7.44
7.43
7.41
7.26
6.35
6.28
5.06
5.05
5.03
5.01
5.00
2.32
2.31
2.31
1.54
1.53
1.53
1.52
NH
O
1.95
1.05
1.95
1.00
0.99
3.23
f1 (ppm)

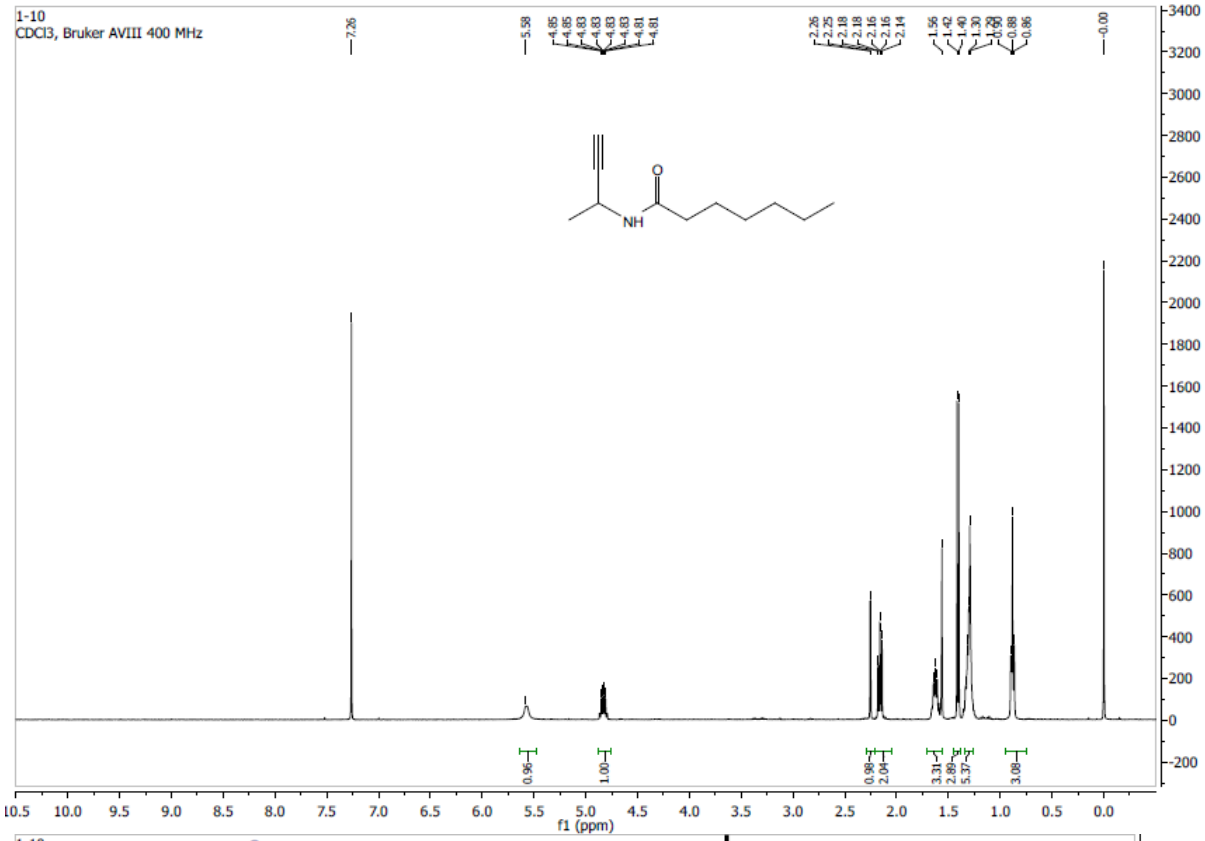

1-7
CDCl3, Bruker AVIII 400 MHz
166.32
133.98
131.74
128.62
127.00
84.15
70.71
37.48
22.38
NH
O
f1 (ppm)

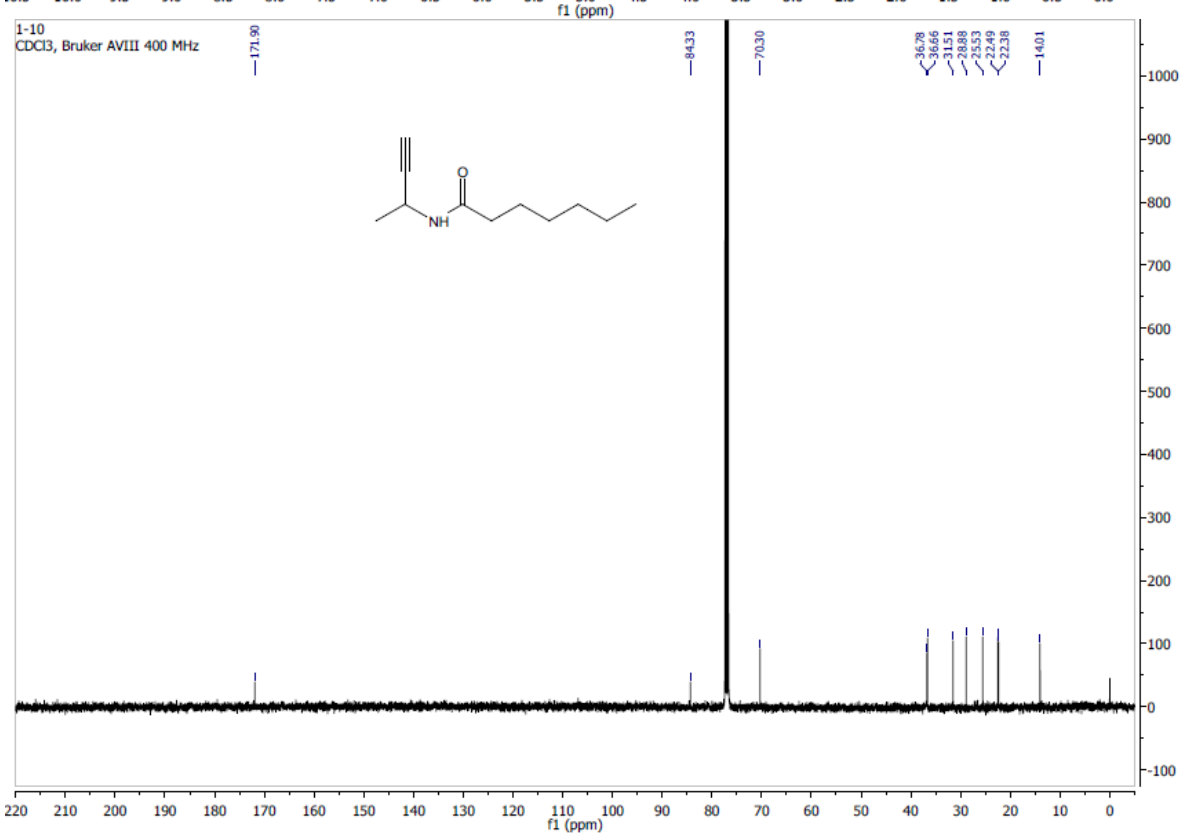

1-8
CDCl3, Bruker AVIII 400 MHz
7.39
7.37
7.37
7.35
7.32
7.32
7.31
7.27
7.26
7.26
7.25
5.54
4.85
4.84
4.83
4.82
4.81
4.81
4.81
4.80
4.79
4.79
4.77
4.77
3.57
2.21
2.21
1.60
1.59
1.59
1.35
1.33
O
NH
1.87
0.97
1.94
1.04
1.00
2.03
1.00
3.13
f1 (ppm)

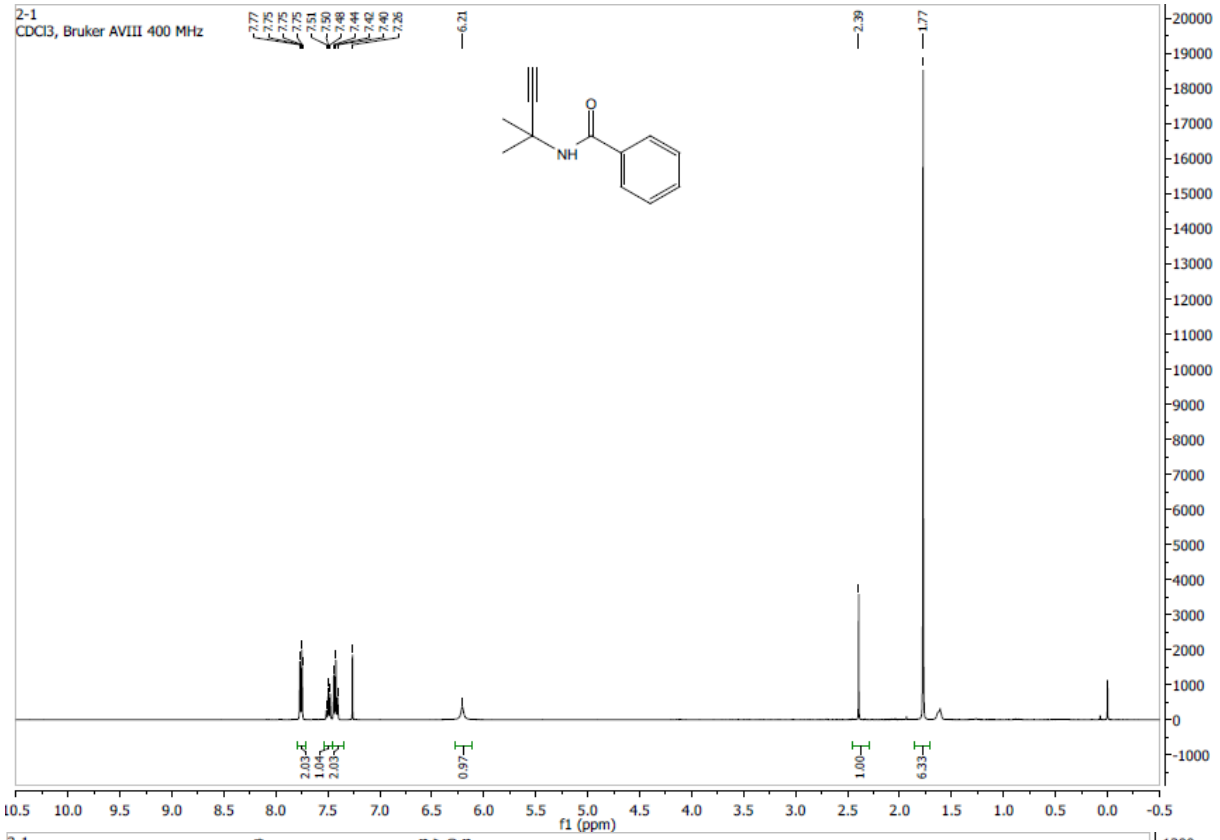

1-8
CDCl3, Bruker AVIII 400 MHz
169.79
134.49
129.41
129.06
127.44
83.94
70.44
43.61
37.03
22.12
O
NH
f1 (ppm)

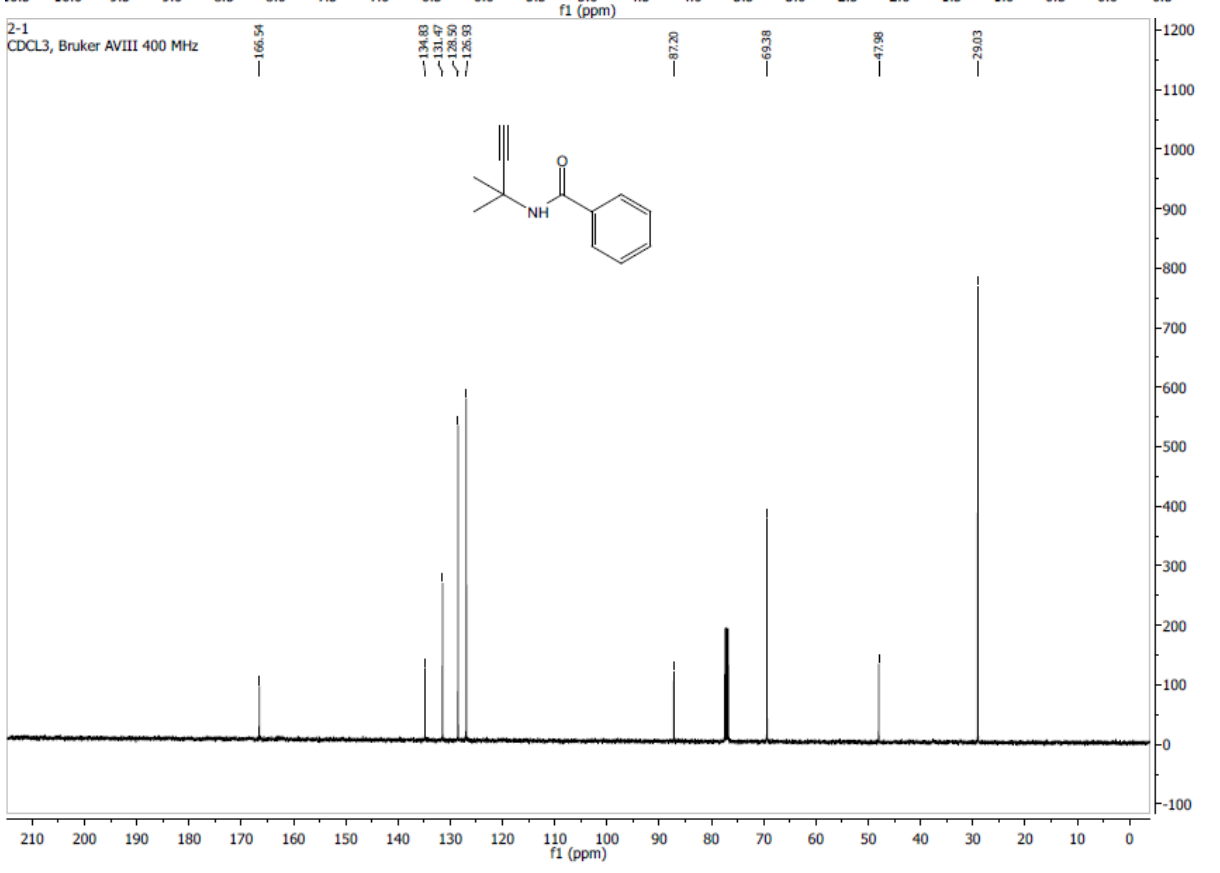

1-9
CDCl3, Bruker AVIII 400 MHz
f1 (ppm)

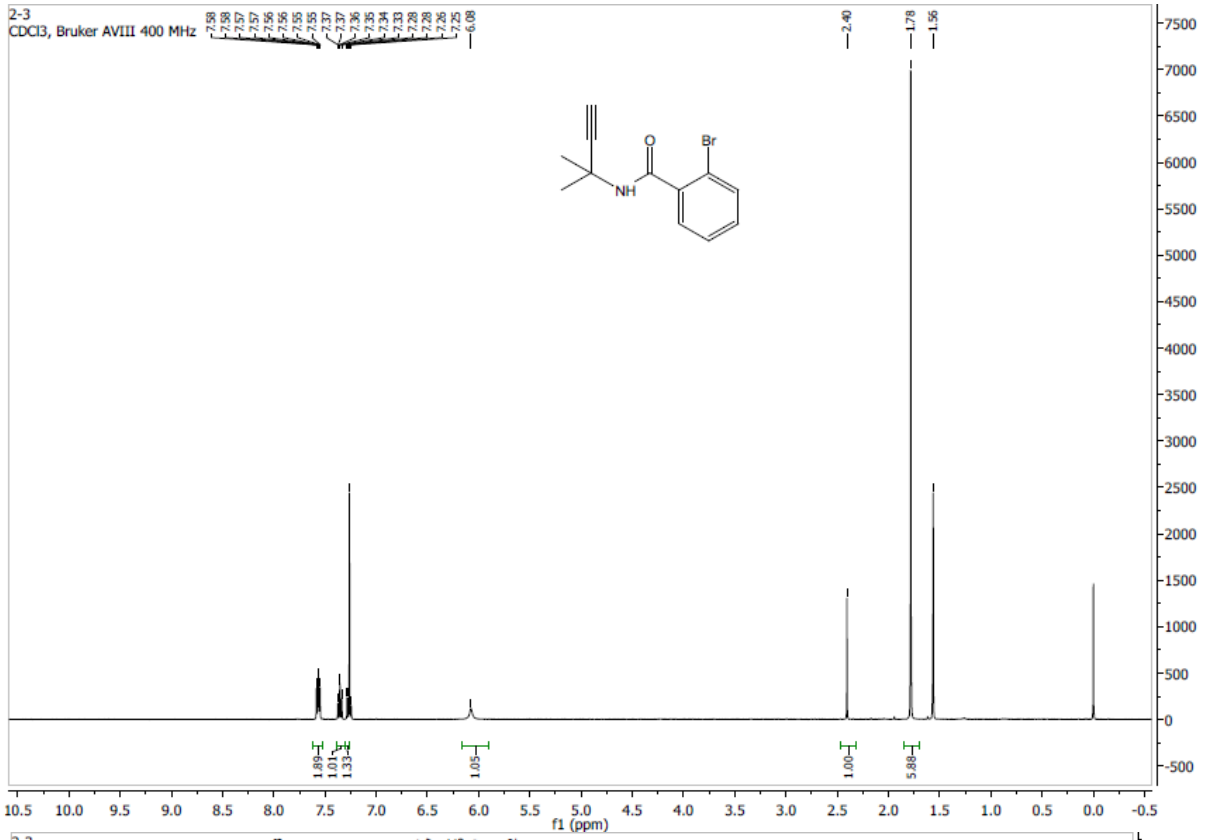

1-9
CDCl3, Bruker AVIII 400 MHz
f1 (ppm)

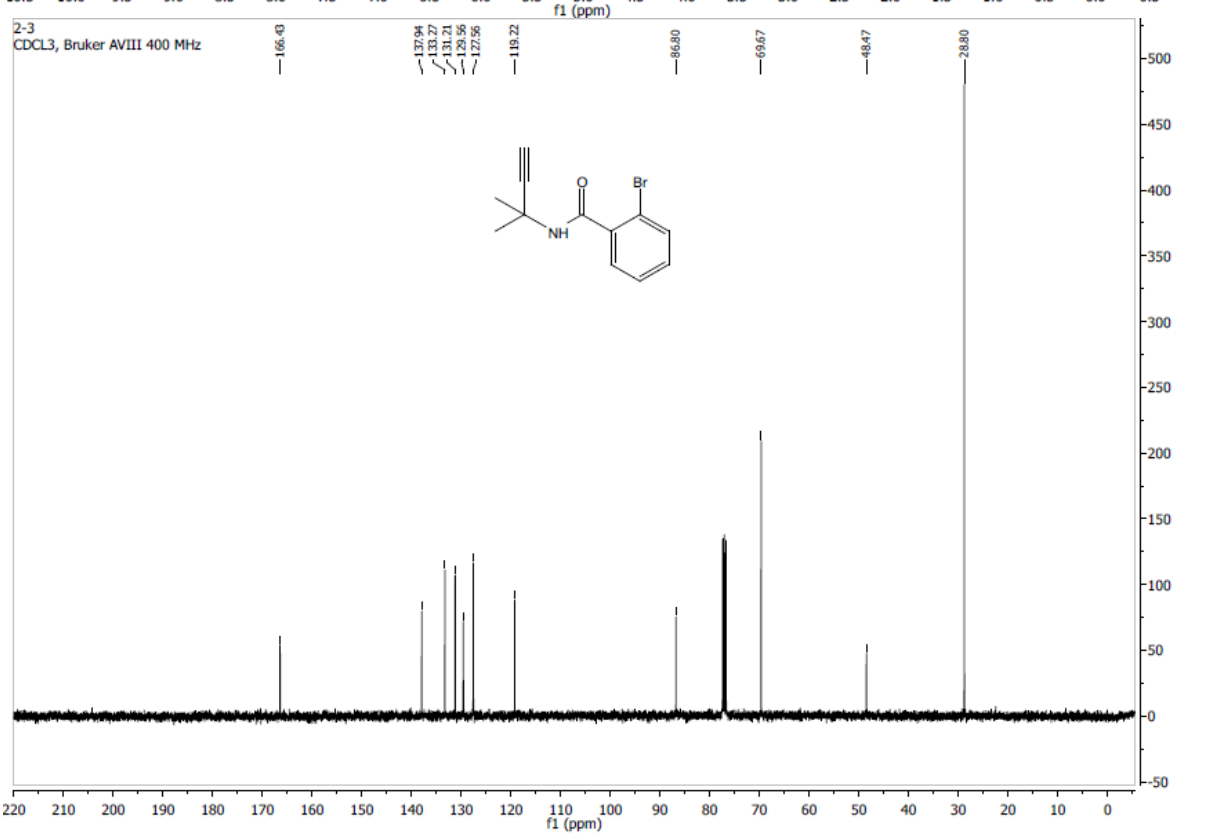

1-10
CDCl3, Bruker AVIII 400 MHz
7.26
5.58
4.85
4.85
4.83
4.83
4.83
4.83
4.81
4.81
2.26
2.25
2.18
2.18
2.16
2.16
2.14
1.56
1.42
1.40
1.30
0.90
0.88
0.86
0.00
NH
O
0.96
1.00
0.98
2.04
3.31
2.89
5.37
3.08
f1 (ppm)

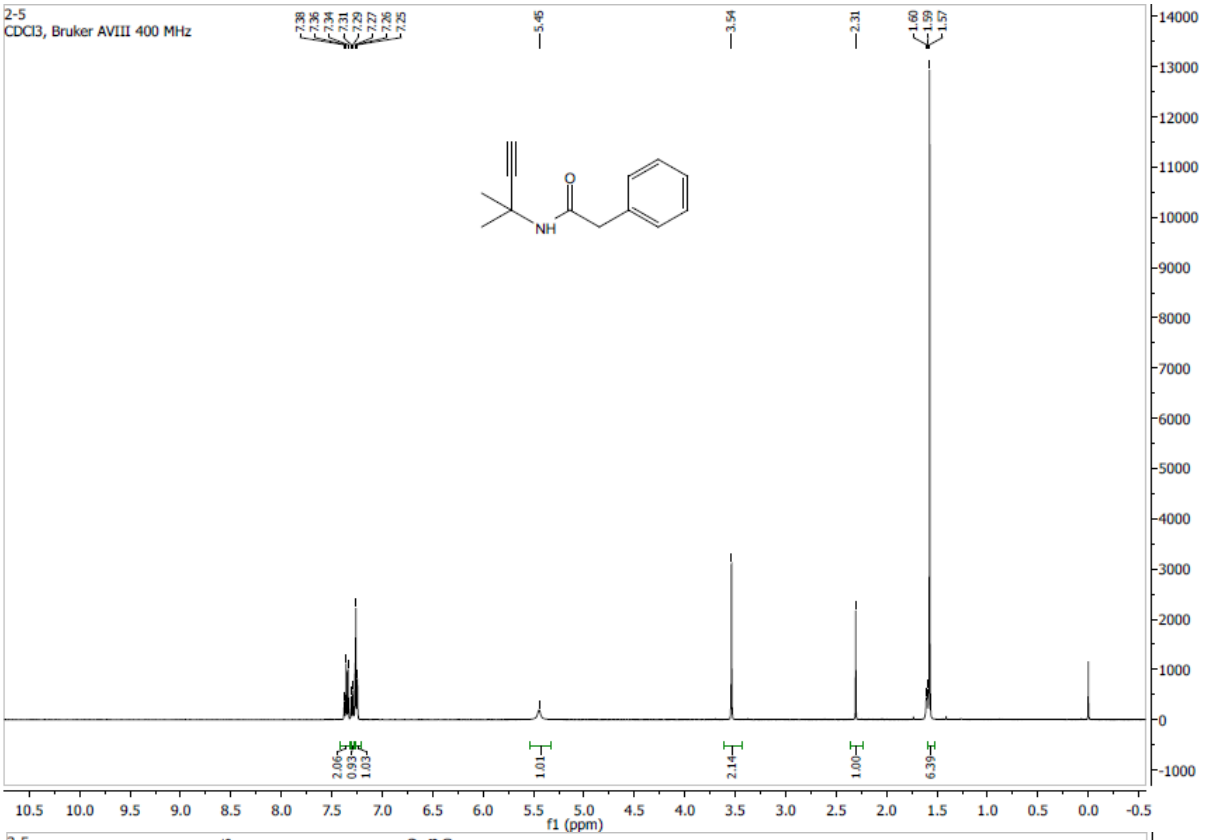

1-10
CDCl3, Bruker AVIII 400 MHz
171.90
84.33
70.30
36.78
36.66
31.51
28.88
25.53
22.49
22.38
14.01
NH
O
f1 (ppm)

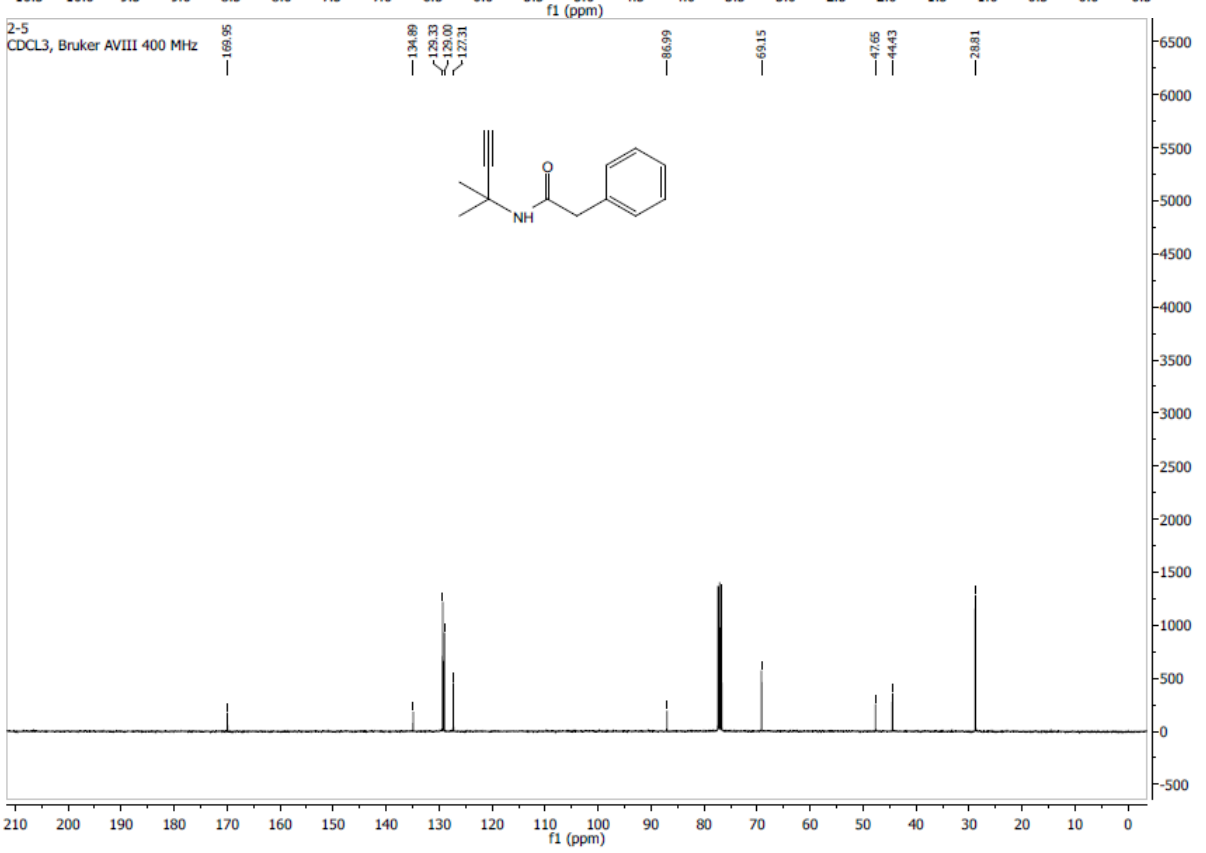

2-1
CDCl3, Bruker AVIII 400 MHz
7.77
7.75
7.75
7.75
7.51
7.50
7.48
7.44
7.42
7.40
7.26
6.21
2.39
1.77
NH
O
2.03
1.04
2.03
0.97
1.00
6.33
f1 (ppm)

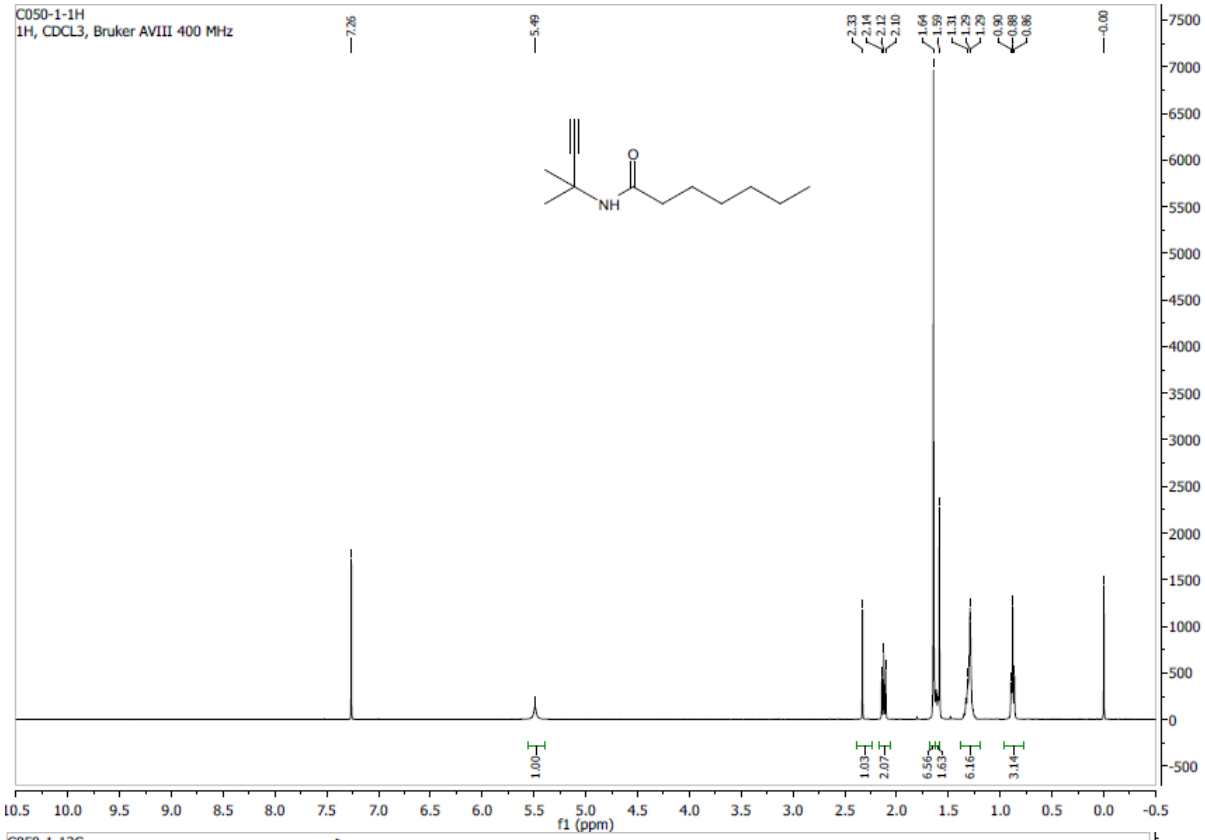

2-1
CDCL3, Bruker AVIII 400 MHz
166.54
134.83
131.47
128.50
126.93
87.20
69.38
47.98
29.03
NH
O
f1 (ppm)

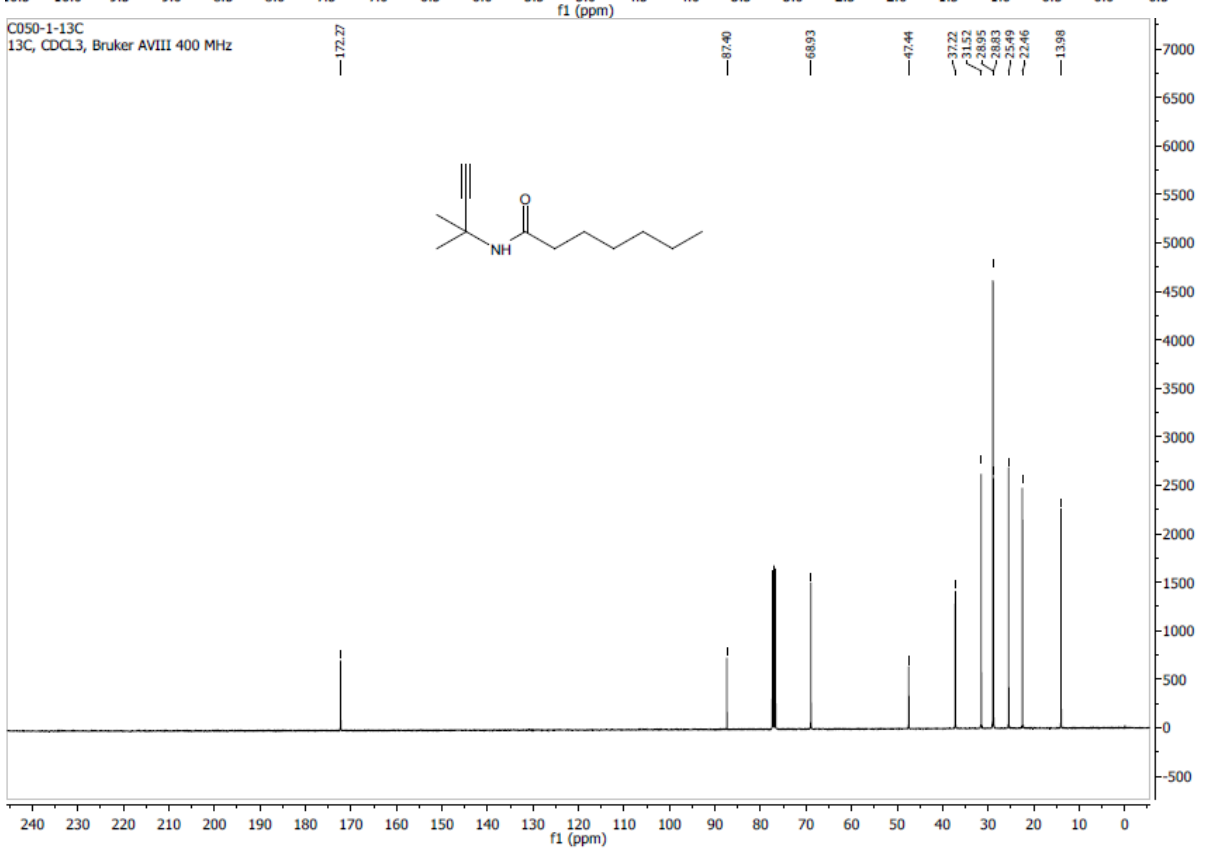


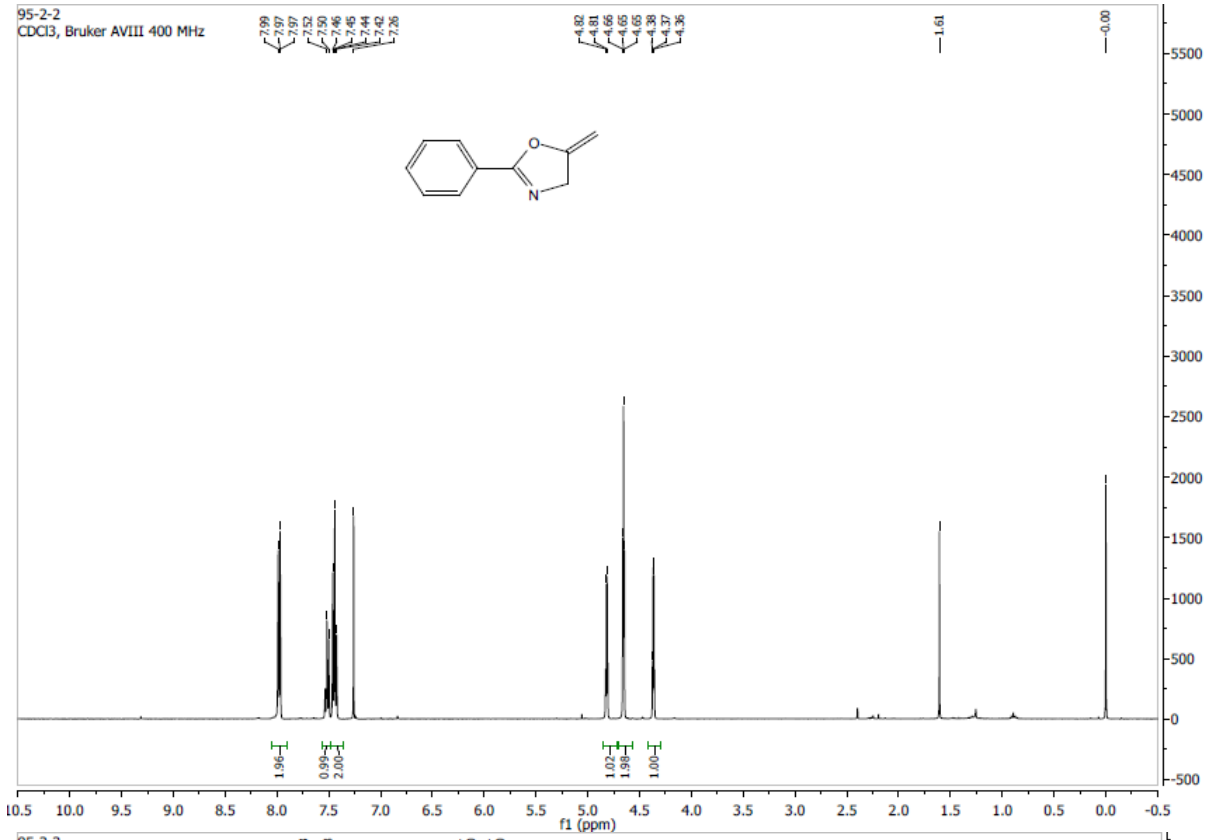


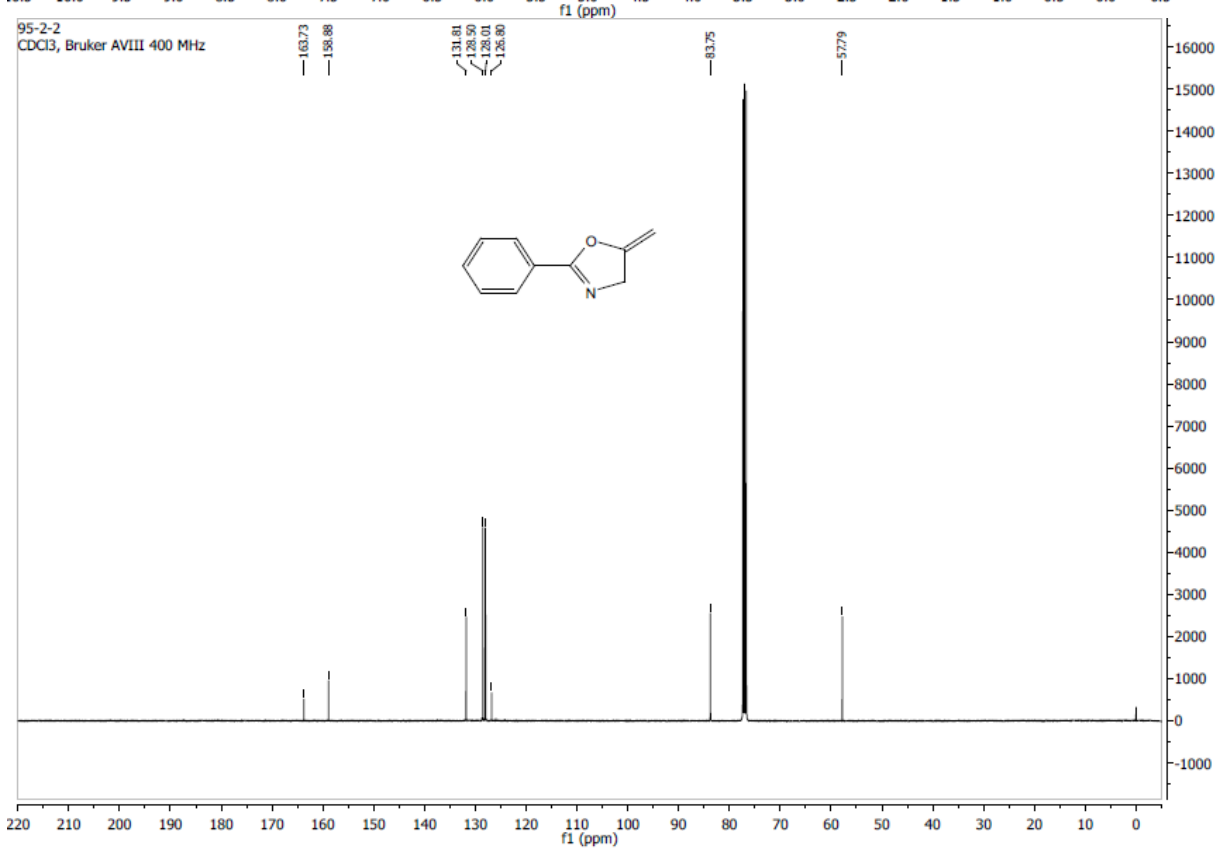


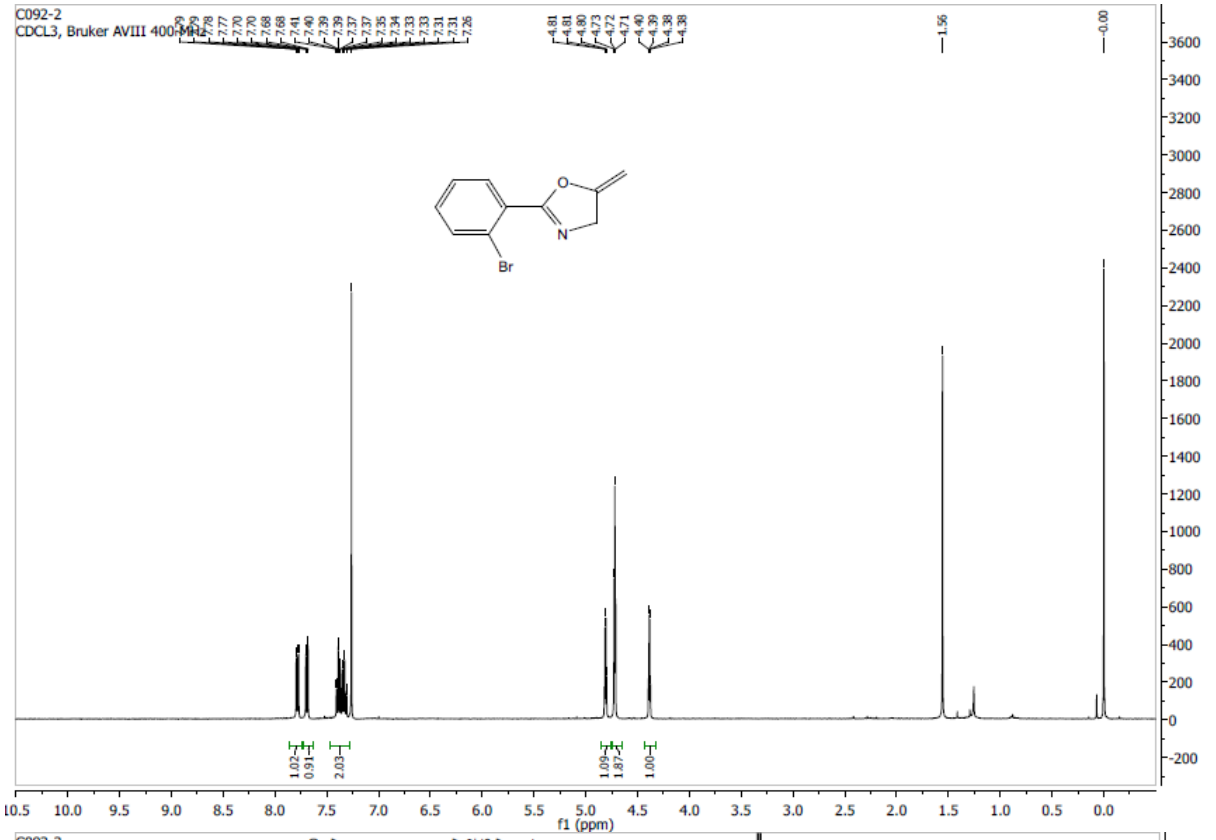


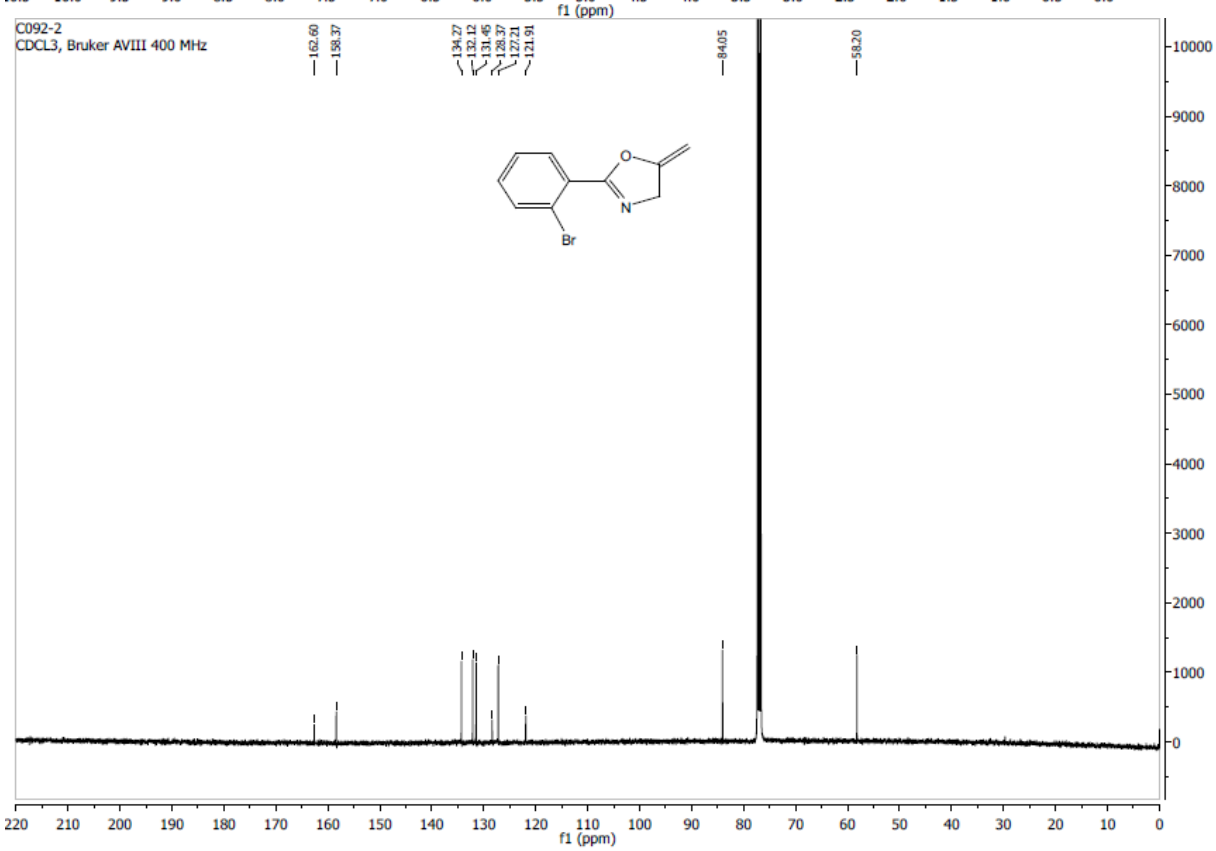

C050-1-1H
1H, CDCL3, Bruker AVIII 400 MHz
7.26
5.49
2.33
2.14
2.12
2.10
1.64
1.59
1.31
1.29
1.29
0.90
0.88
0.86
0.00
NH
O
1.00
1.03
2.07
6.56
1.63
6.16
3.14
f1 (ppm)

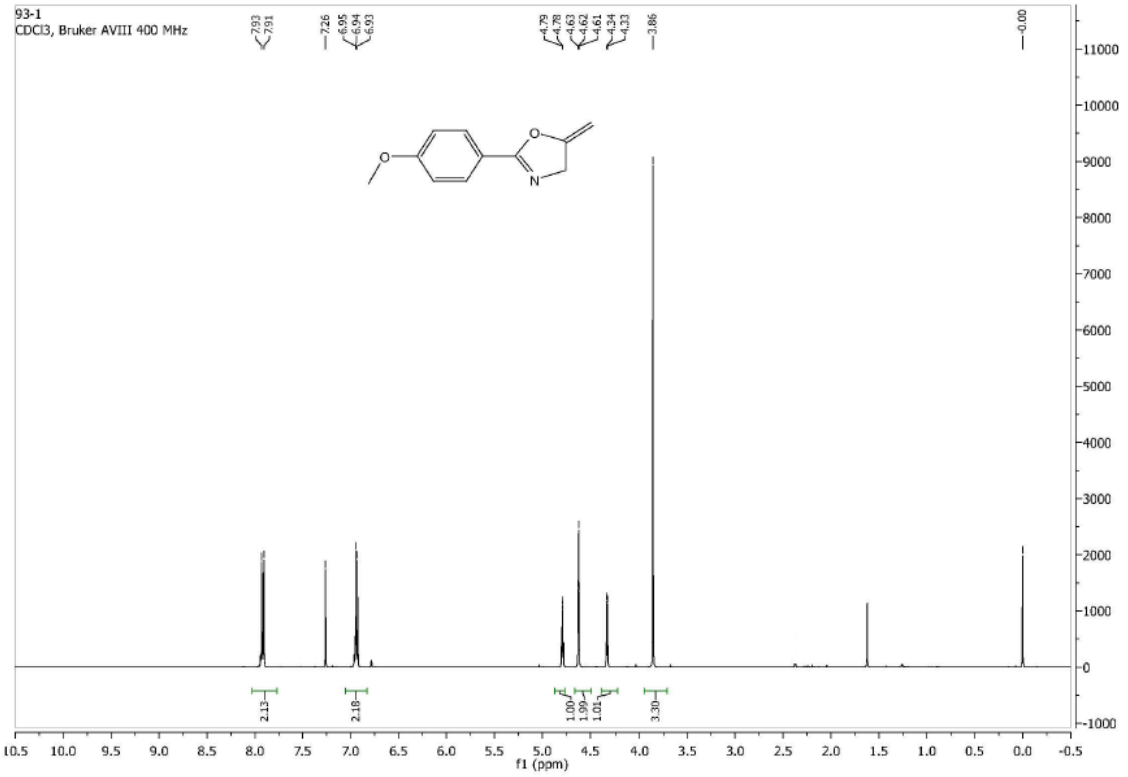

C050-1-13C
13C, CDCL3, Bruker AVIII 400 MHz
172.27
87.40
68.93
47.44
37.22
31.52
28.95
28.83
25.49
22.46
13.98
NH
O
f1 (ppm)

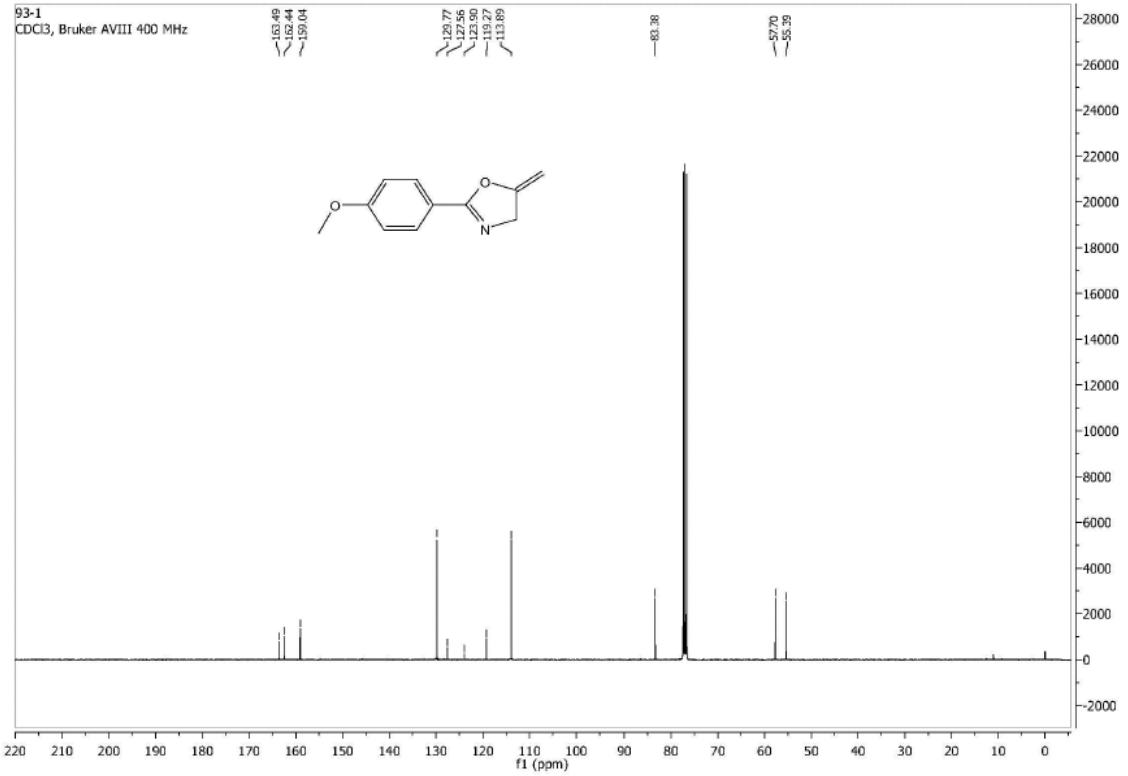

95-2-2
CDCl3, Bruker AVIII 400 MHz
7.99
7.97
7.97
7.52
7.50
7.46
7.45
7.44
7.42
7.26
4.82
4.81
4.66
4.65
4.65
4.38
4.37
4.36
1.61
0.00
1.96
0.99
2.00
1.02
1.98
1.00
f1 (ppm)

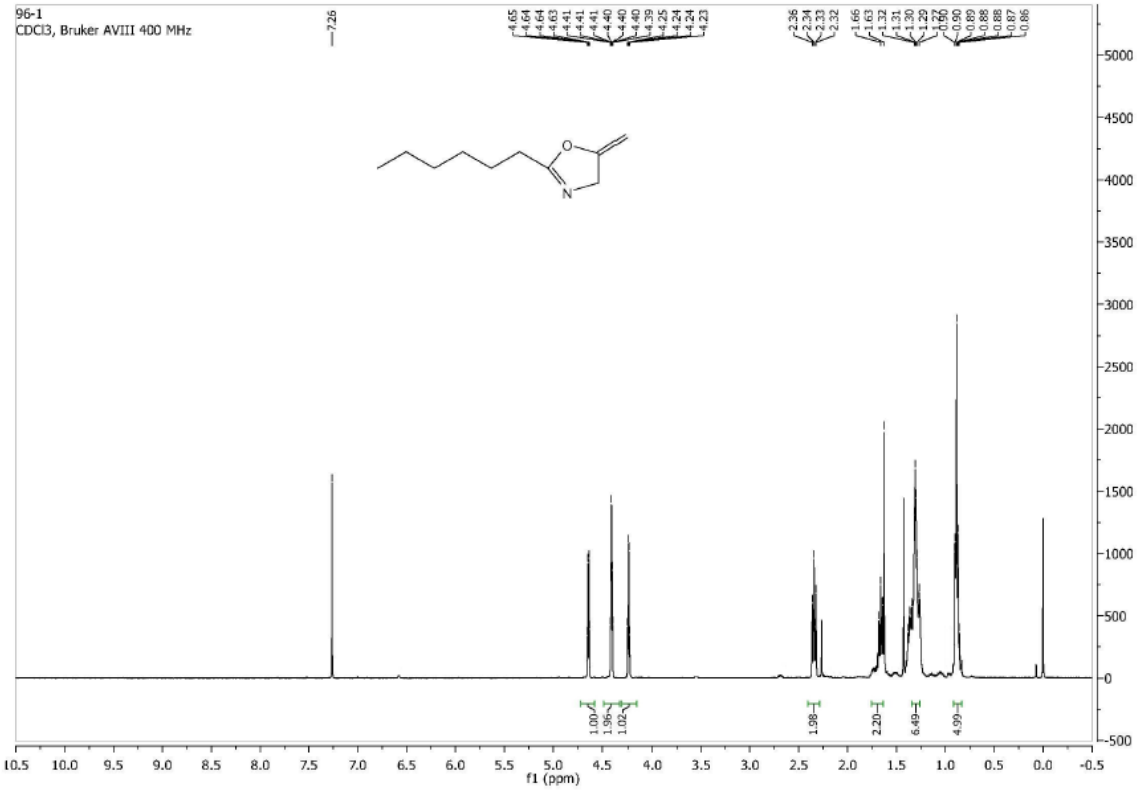

95-2-2
CDCl3, Bruker AVIII 400 MHz
163.73
158.88
131.81
128.50
128.01
126.80
83.75
57.29
f1 (ppm)

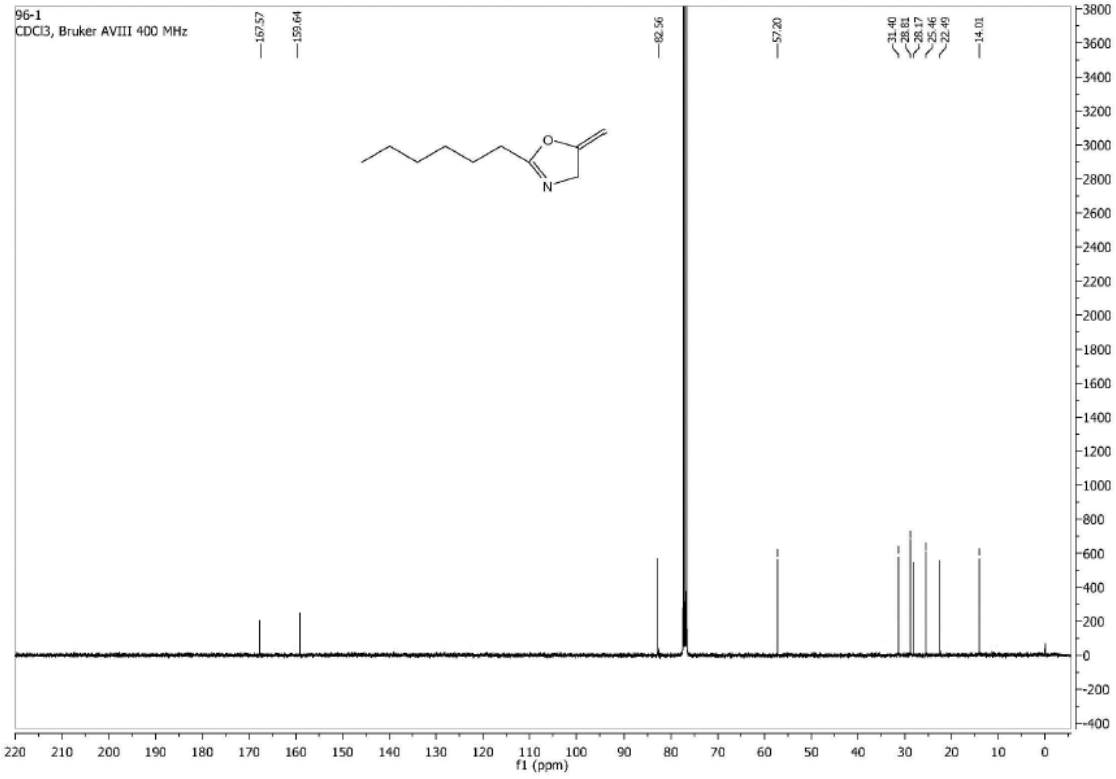

C092-2
CDCL3, Bruker AVIII 400 MHz
7.79
7.78
7.77
7.70
7.70
7.68
7.68
7.41
7.40
7.39
7.39
7.37
7.37
7.35
7.34
7.33
7.33
7.31
7.31
7.26
4.81
4.81
4.80
4.73
4.72
4.71
4.40
4.39
4.38
4.38
1.56
0.00
O
N
Br
1.02
0.91
2.03
1.09
1.87
1.00
f1 (ppm)

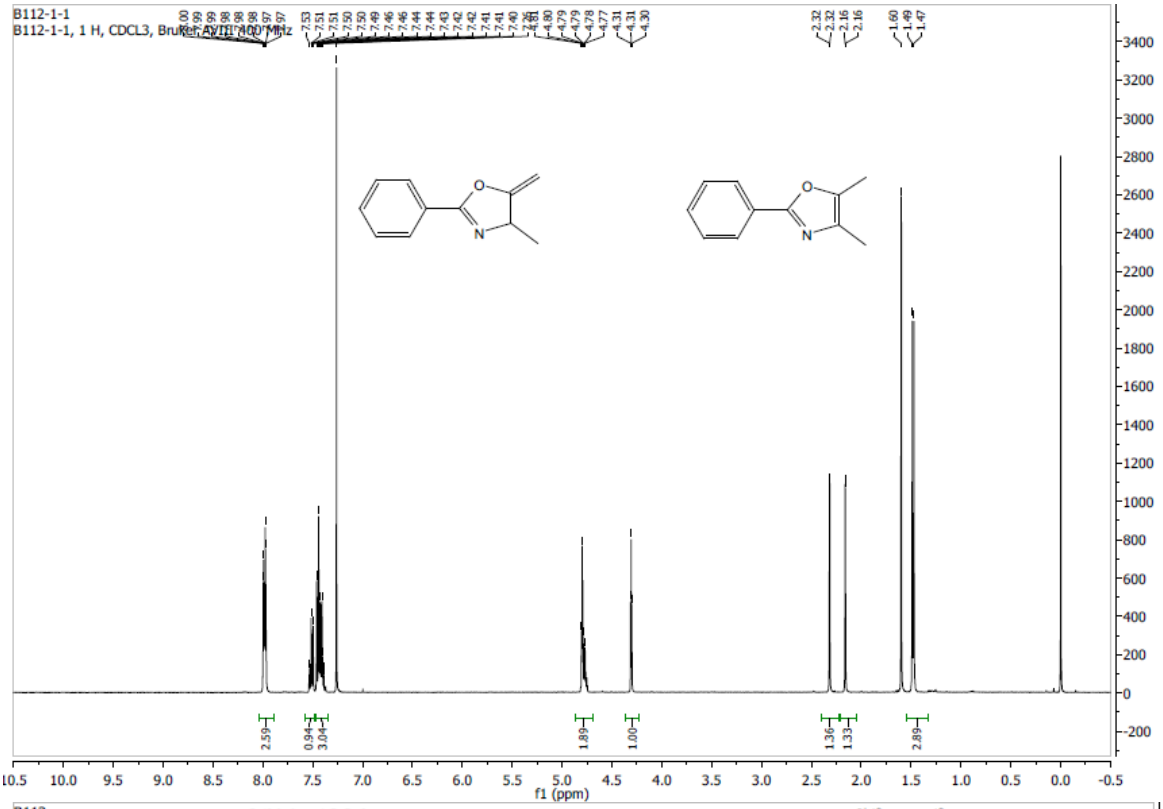

C092-2
CDCL3, Bruker AVIII 400 MHz
162.60
158.37
134.27
132.12
131.45
128.37
127.21
121.91
84.05
58.20
O
N
Br
f1 (ppm)

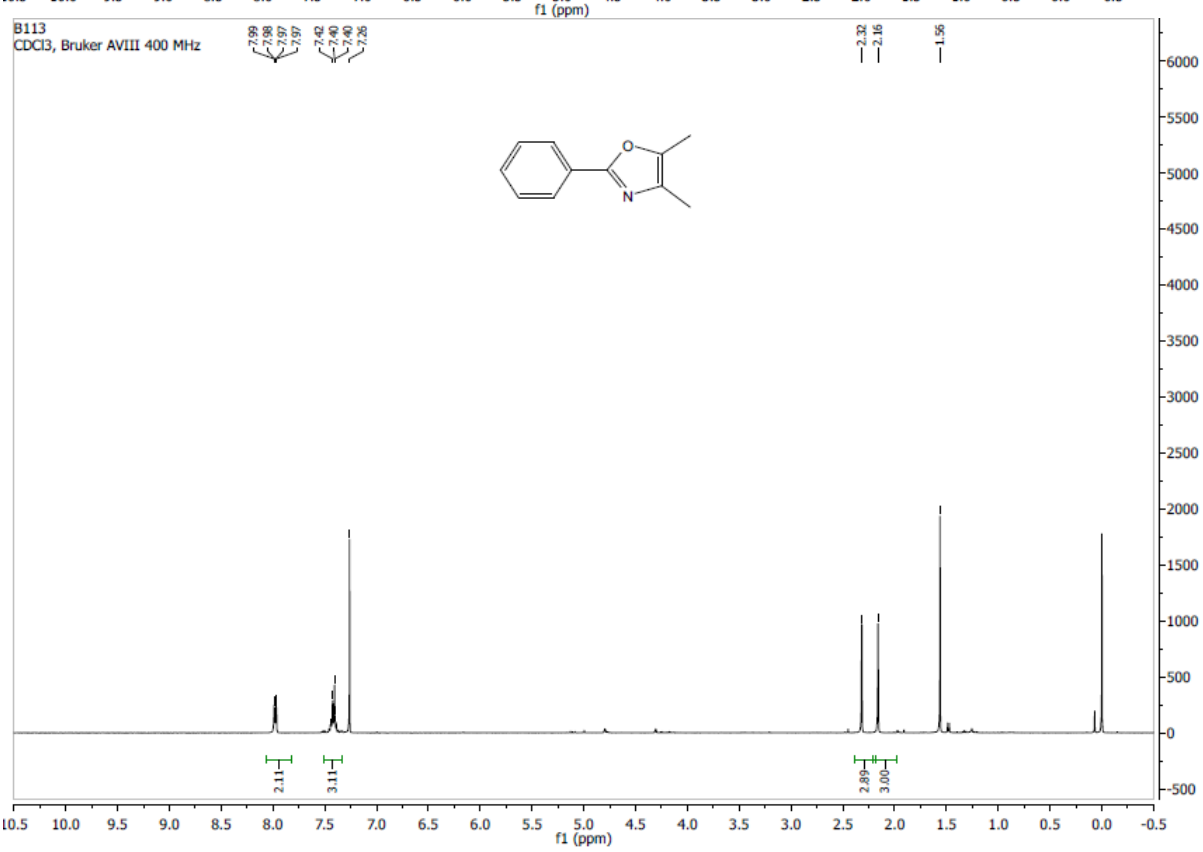

93-1
CDCl3, Bruker AVIII 400 MHz
7.93
7.91
7.26
6.95
6.94
6.93
4.79
4.78
4.63
4.62
4.61
4.34
4.33
3.86
0.00
2.13
2.18
1.00
1.99
1.01
3.30
f1 (ppm)

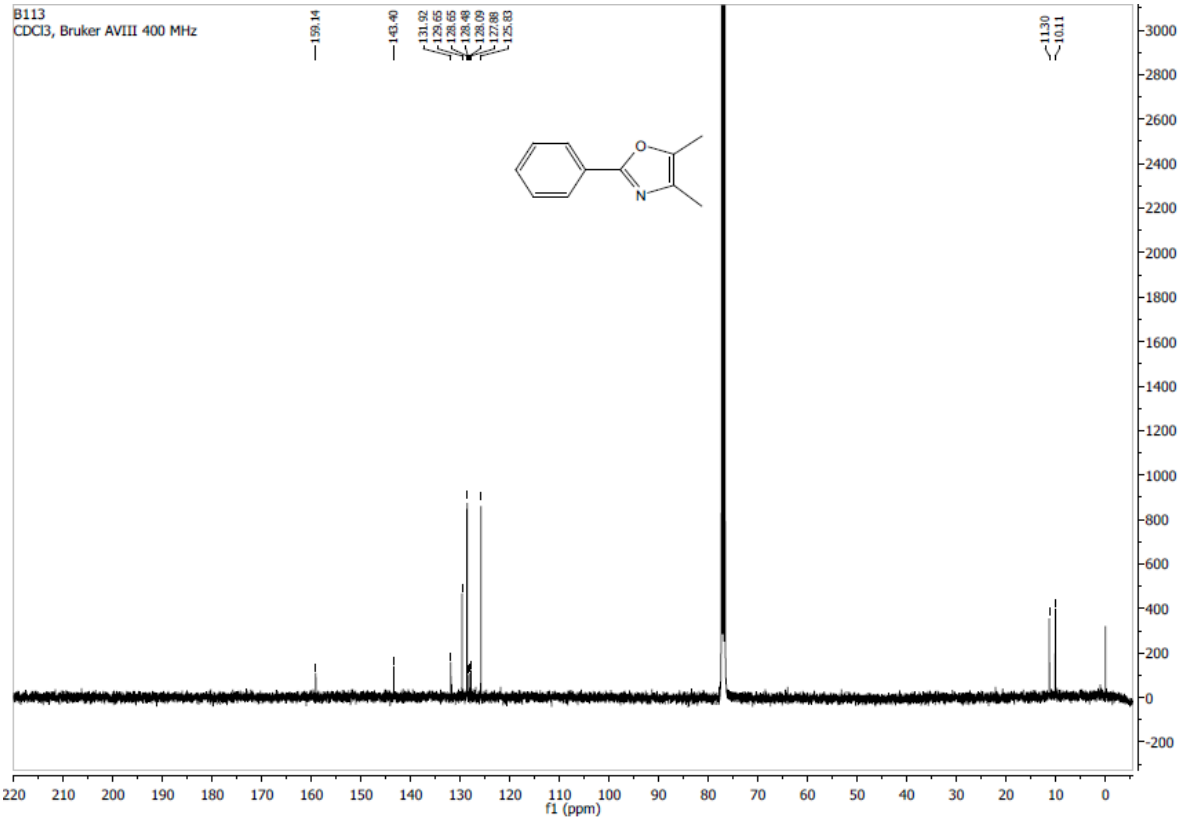

93-1
CDCl3, Bruker AVIII 400 MHz
163.49
162.44
159.04
129.77
127.56
123.90
119.27
113.89
83.38
57.70
55.39
f1 (ppm)

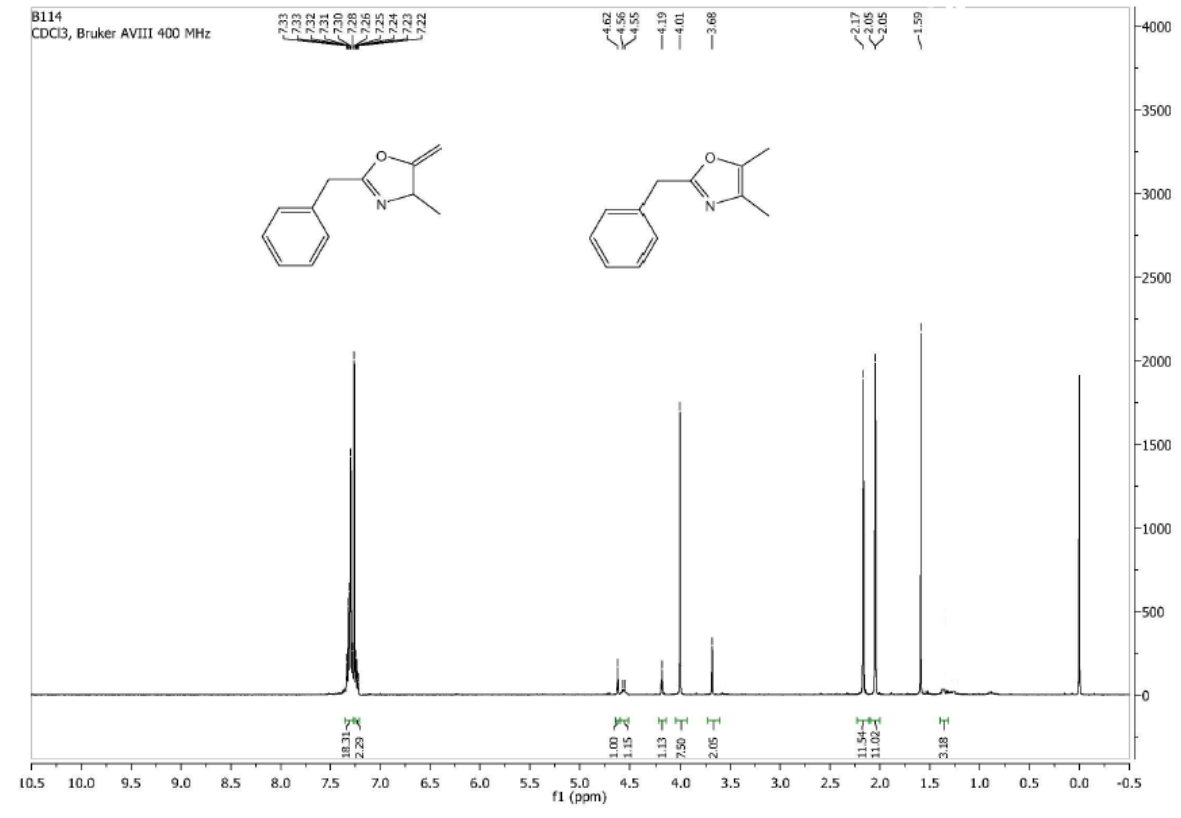

96-1
CDCl3, Bruker AVIII 400 MHz
f1 (ppm)

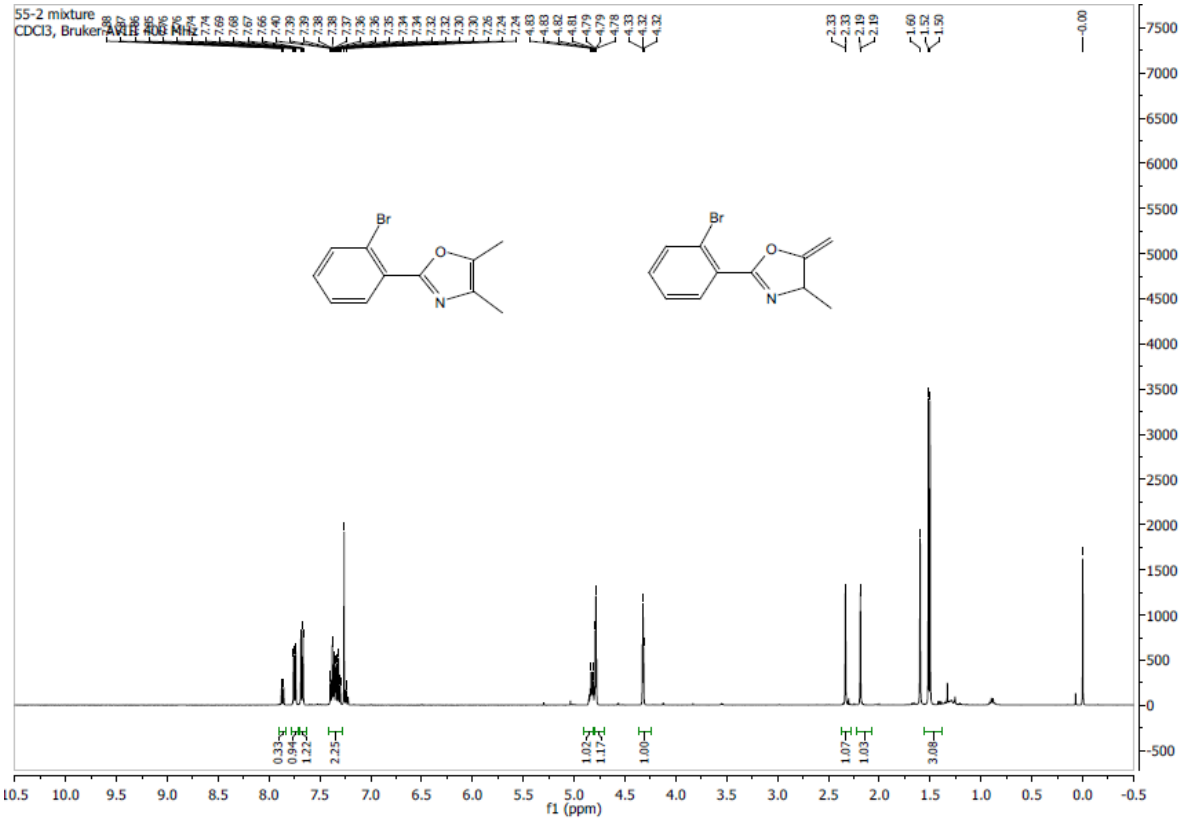

96-1
CDCl3, Bruker AVIII 400 MHz
f1 (ppm)

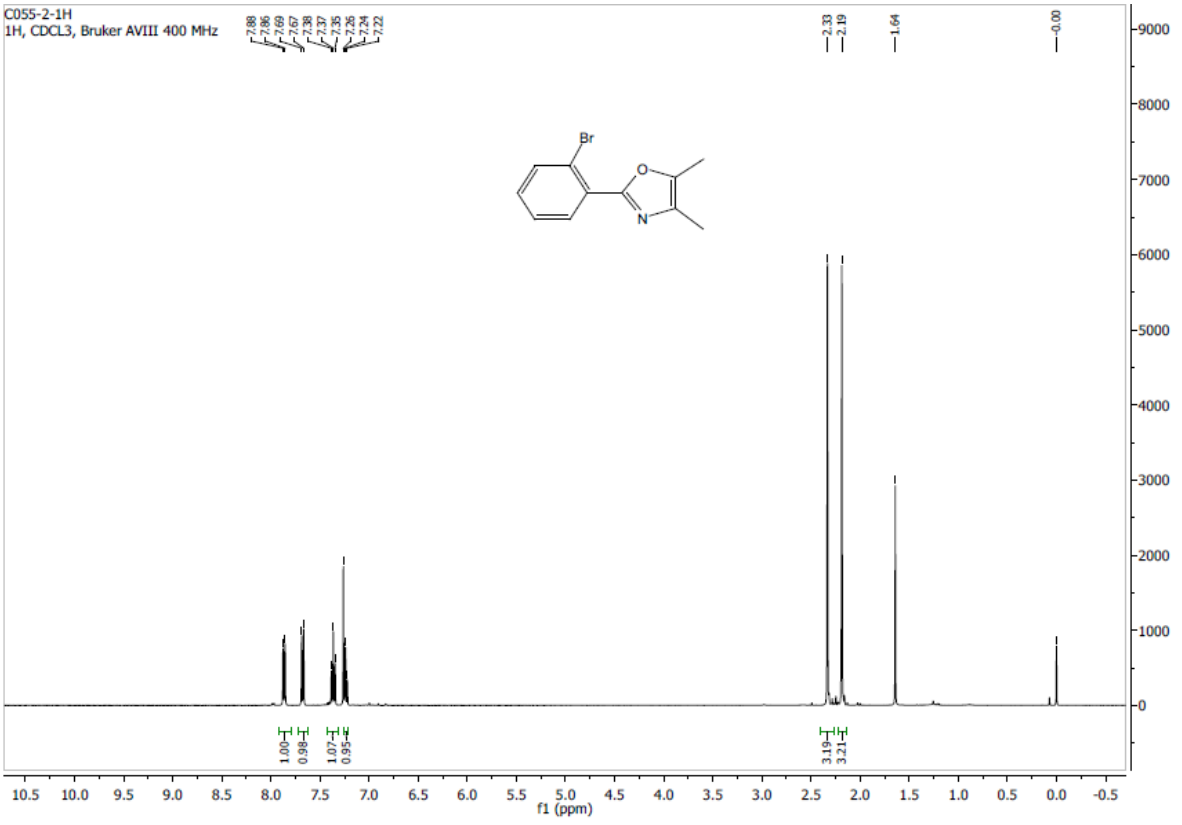

B112-1-1
B112-1-1, 1 H, CDCL3, Bruker AVIII 400 MHz
f1 (ppm)

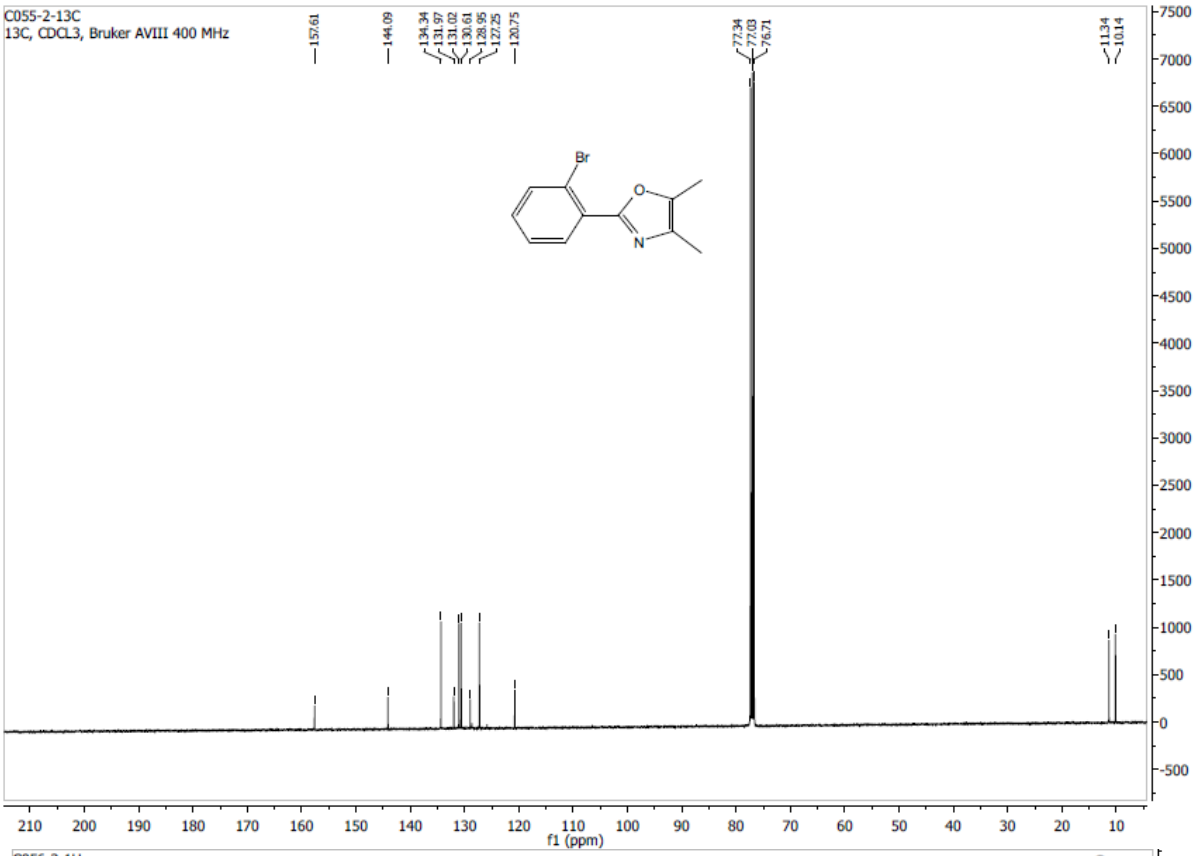

B113
CDCl3, Bruker AVIII 400 MHz
f1 (ppm)

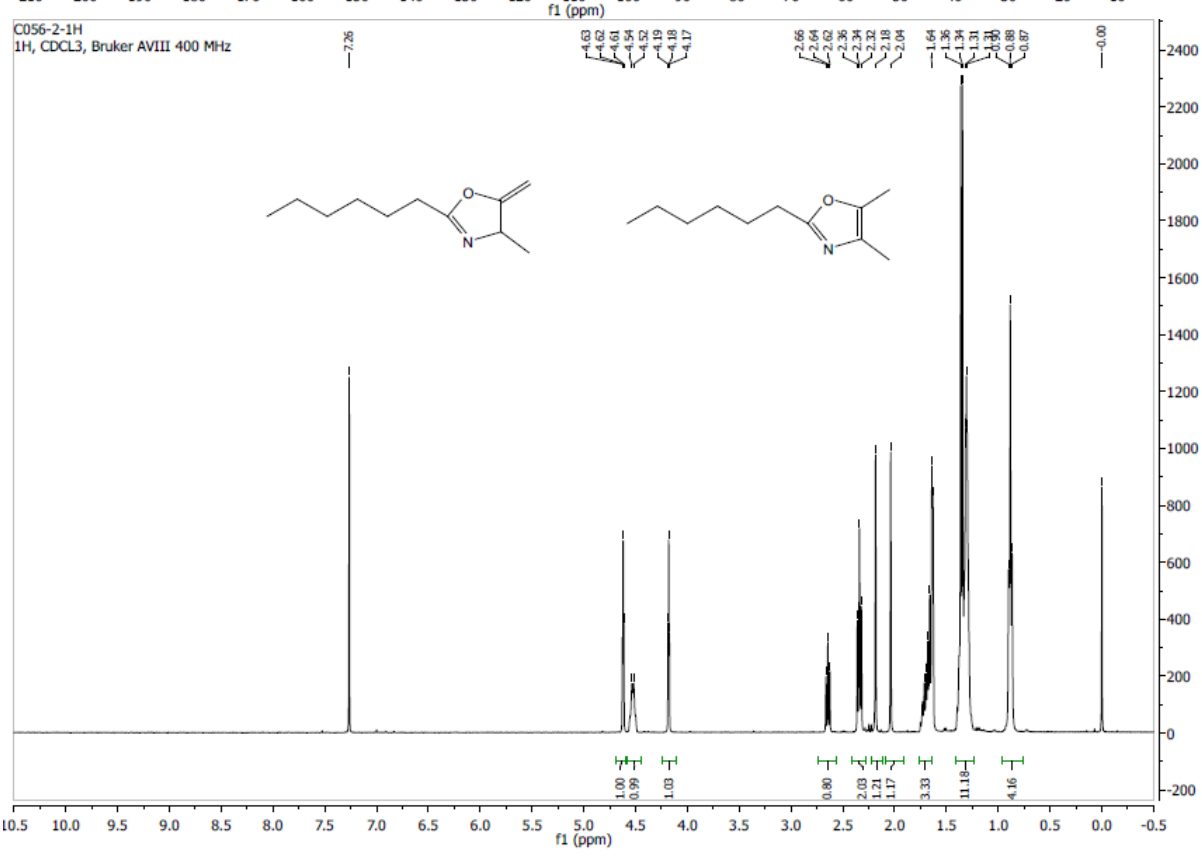


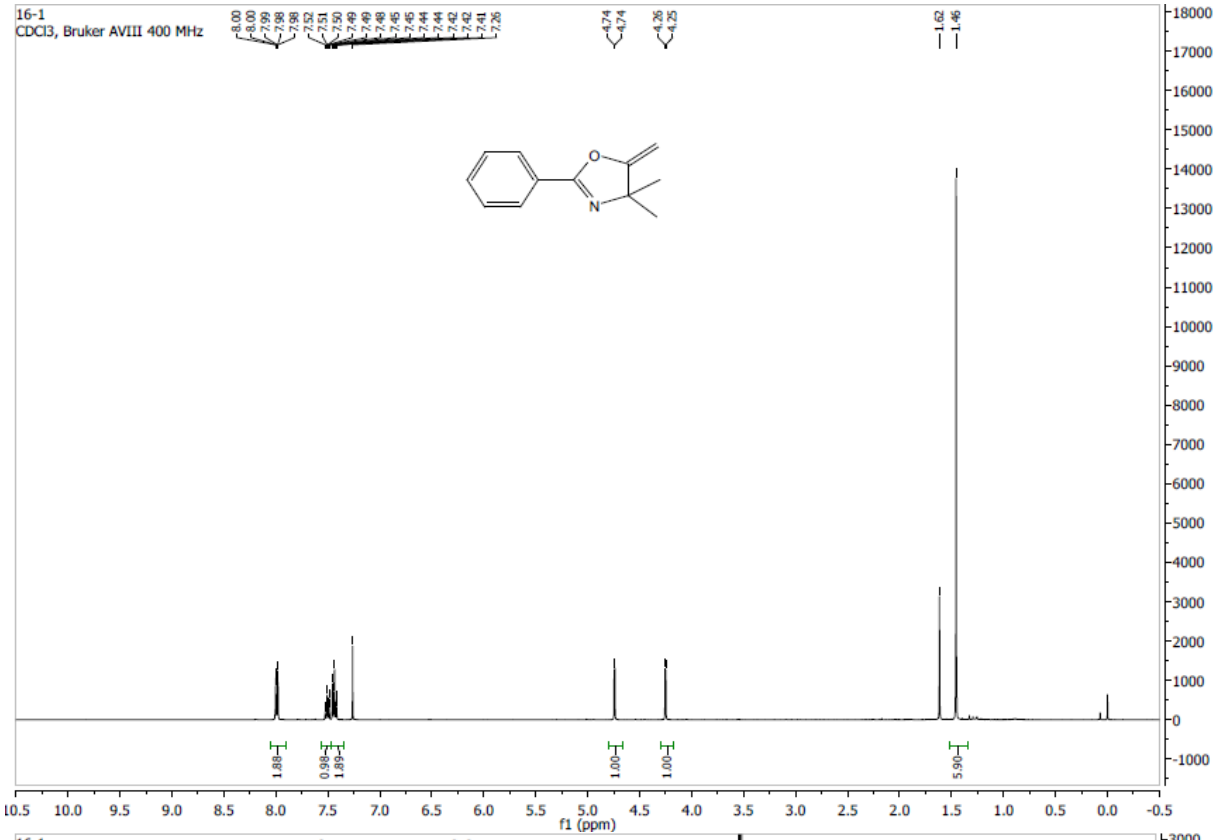


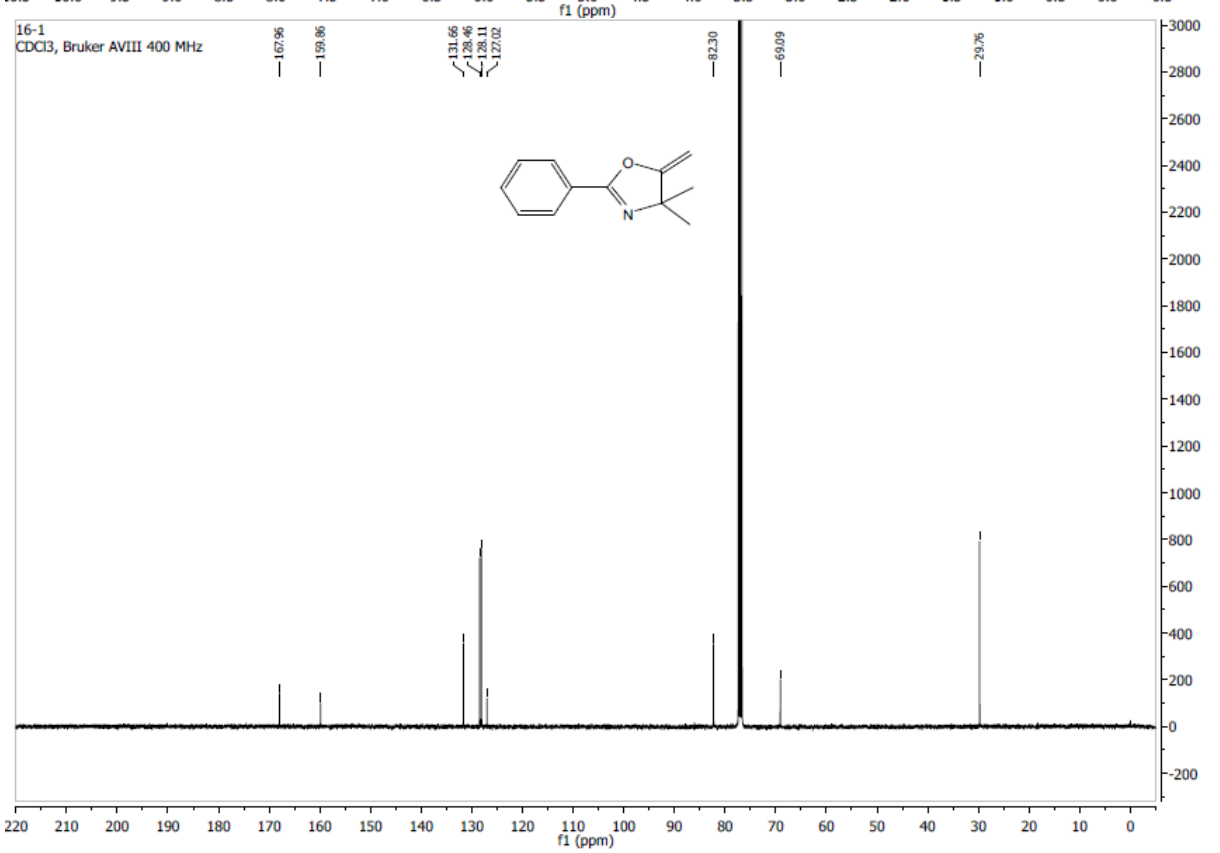

55-2 mixture
CDCl3, Bruker AVIII 400 MHz
Br
O
N
Br
O
N
f1 (ppm)

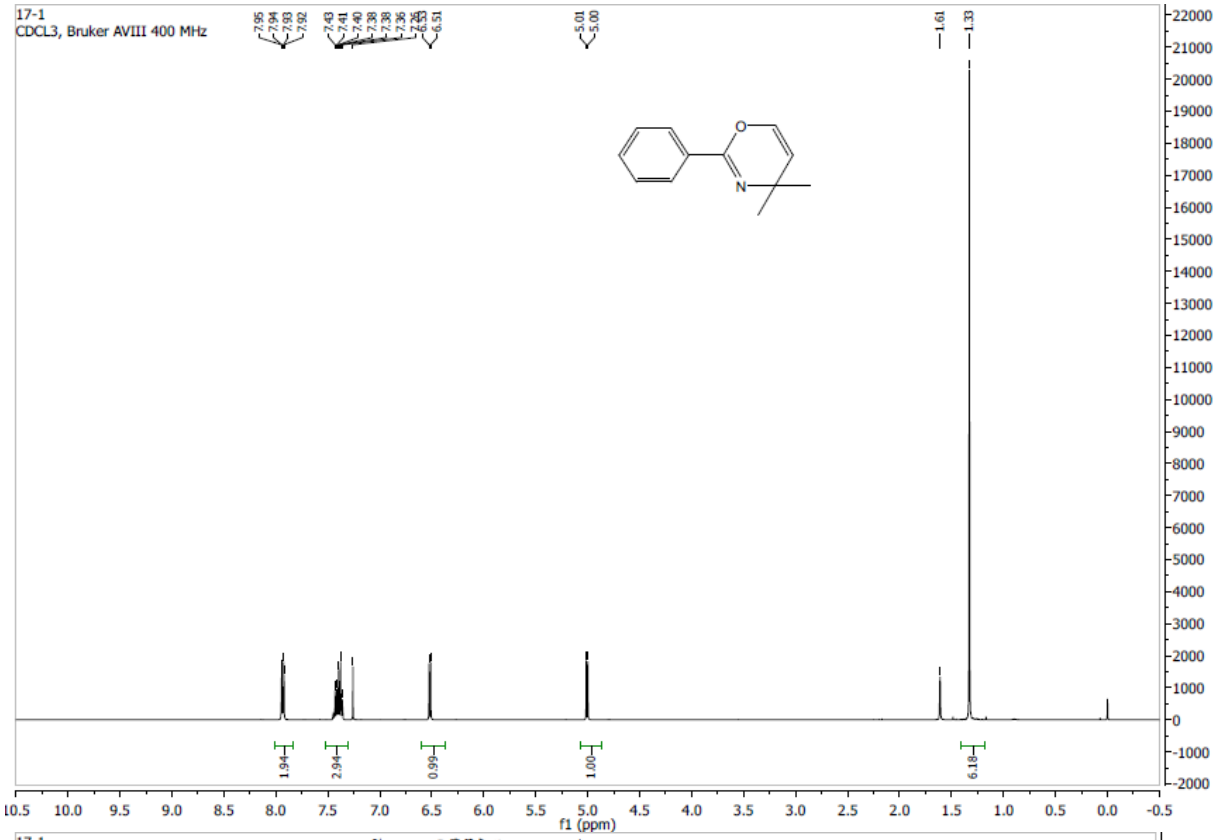

C055-2-1H
1H, CDCL3, Bruker AVIII 400 MHz
Br
O
N
f1 (ppm)

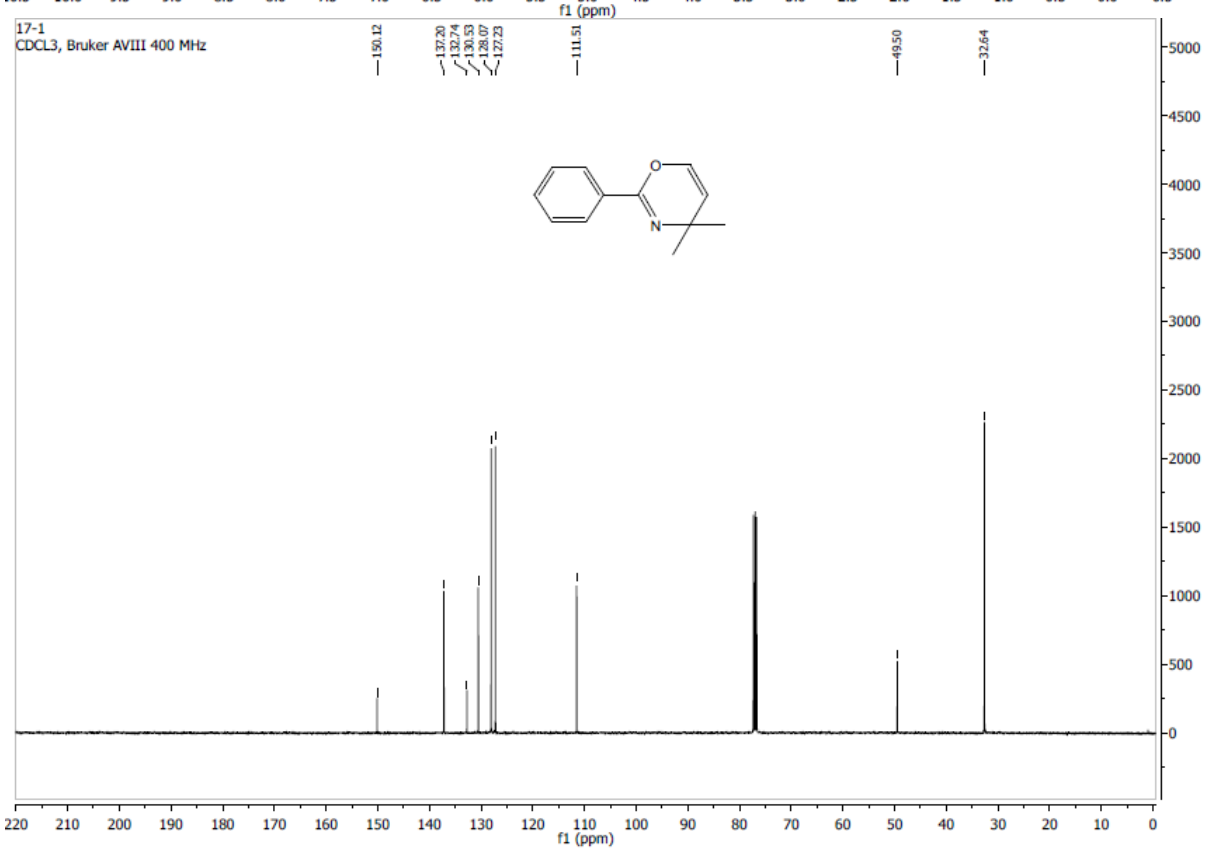

C055-2-13C
13C, CDCL3, Bruker AVIII 400 MHz
157.61
144.09
134.34
131.97
131.02
130.61
128.95
127.25
120.75
77.34
77.03
76.71
11.34
10.14
Br
O
N
f1 (ppm)

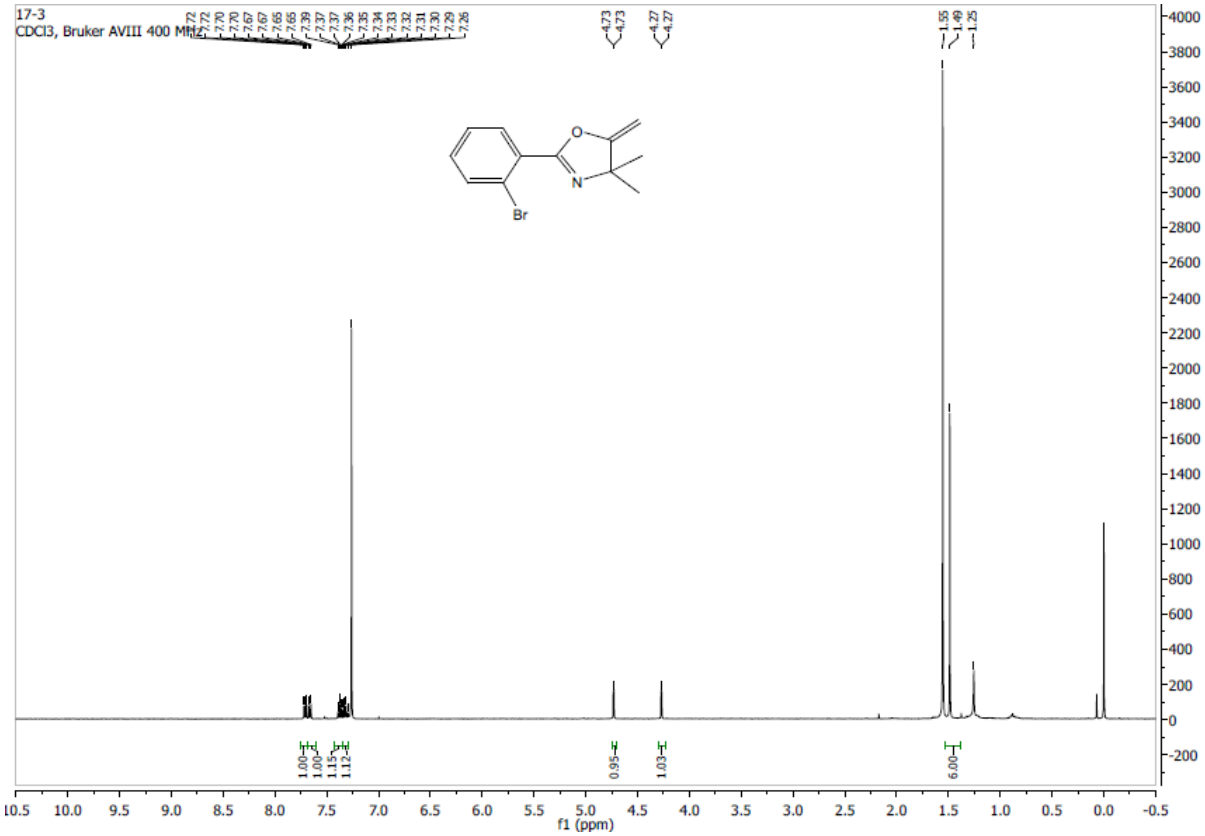

C056-2-1H
1H, CDCL3, Bruker AVIII 400 MHz
7.26
4.63
4.62
4.61
4.54
4.52
4.19
4.18
4.17
2.66
2.64
2.62
2.36
2.34
2.32
2.18
2.04
1.64
1.36
1.34
1.31
0.90
0.88
0.87
0.00
O
N
1.00
0.99
1.03
0.80
2.03
1.21
1.17
3.33
11.18
4.16
f1 (ppm)

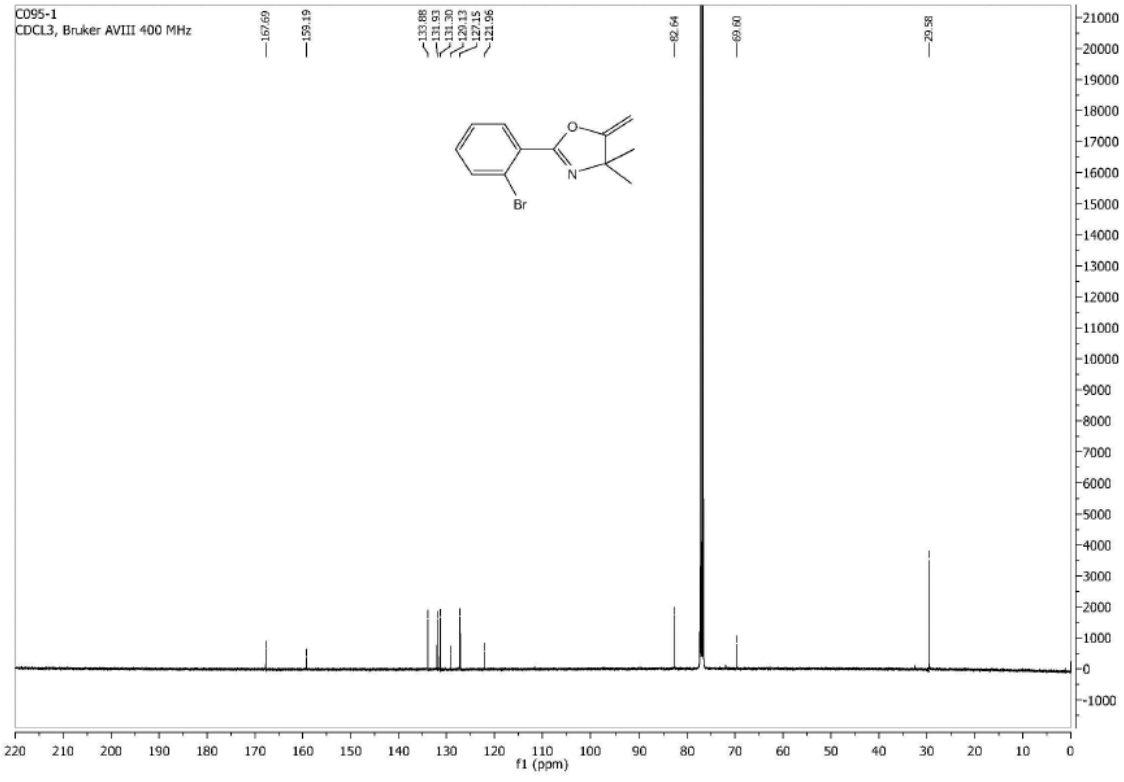

16-1
CDCl3, Bruker AVIII 400 MHz
8.00
8.00
7.99
7.98
7.98
7.52
7.51
7.50
7.49
7.49
7.48
7.45
7.45
7.44
7.44
7.42
7.42
7.41
7.26
4.74
4.74
4.26
4.25
1.62
1.46
O
N
1.88
0.98
1.89
1.00
1.00
5.90
f1 (ppm)

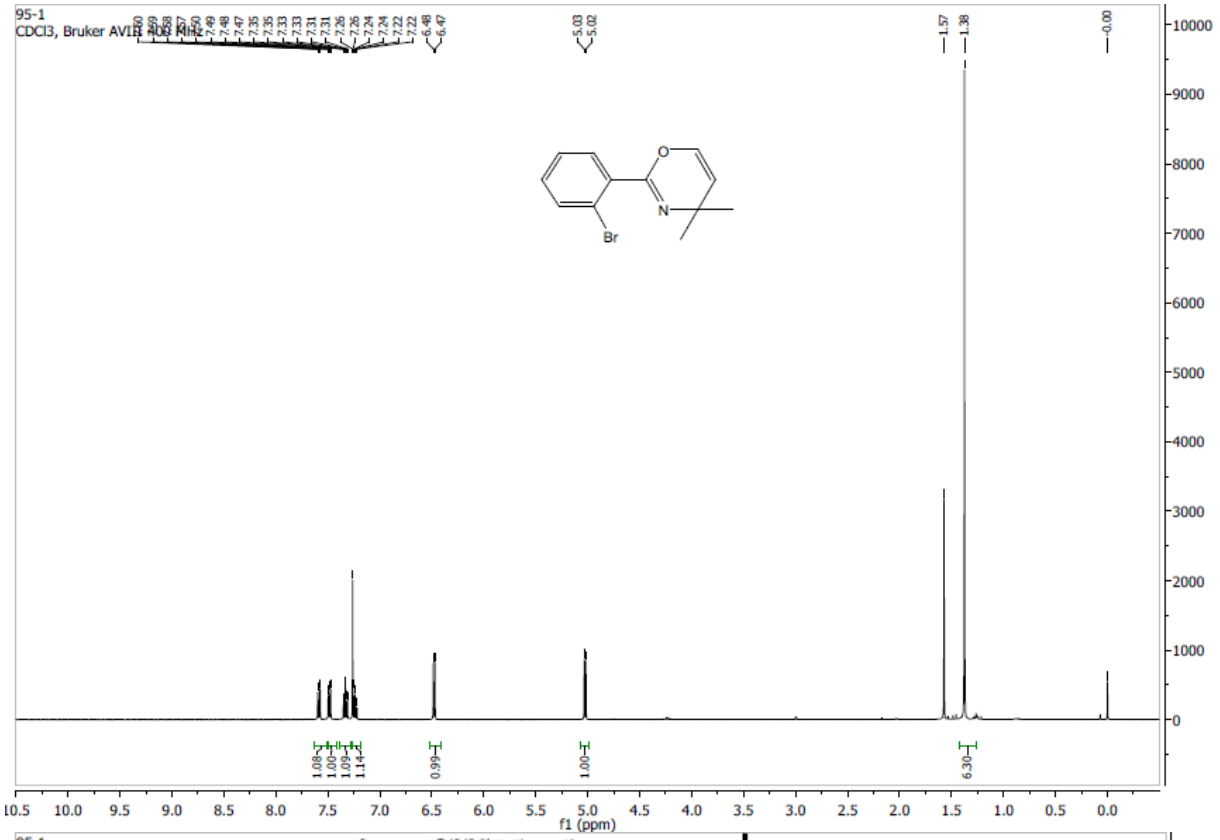

16-1
CDCl3, Bruker AVIII 400 MHz
167.96
159.86
131.66
128.46
128.11
127.02
82.30
69.09
29.76
O
N
f1 (ppm)

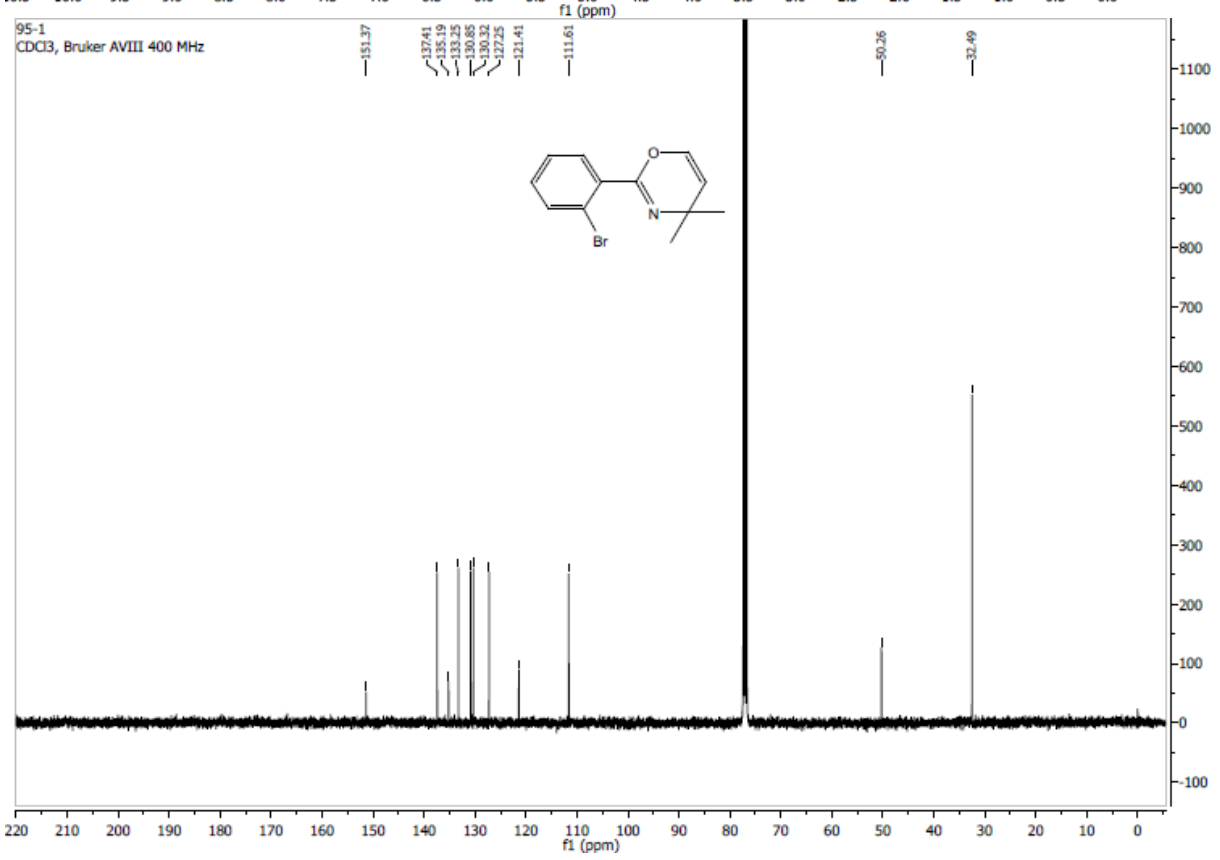


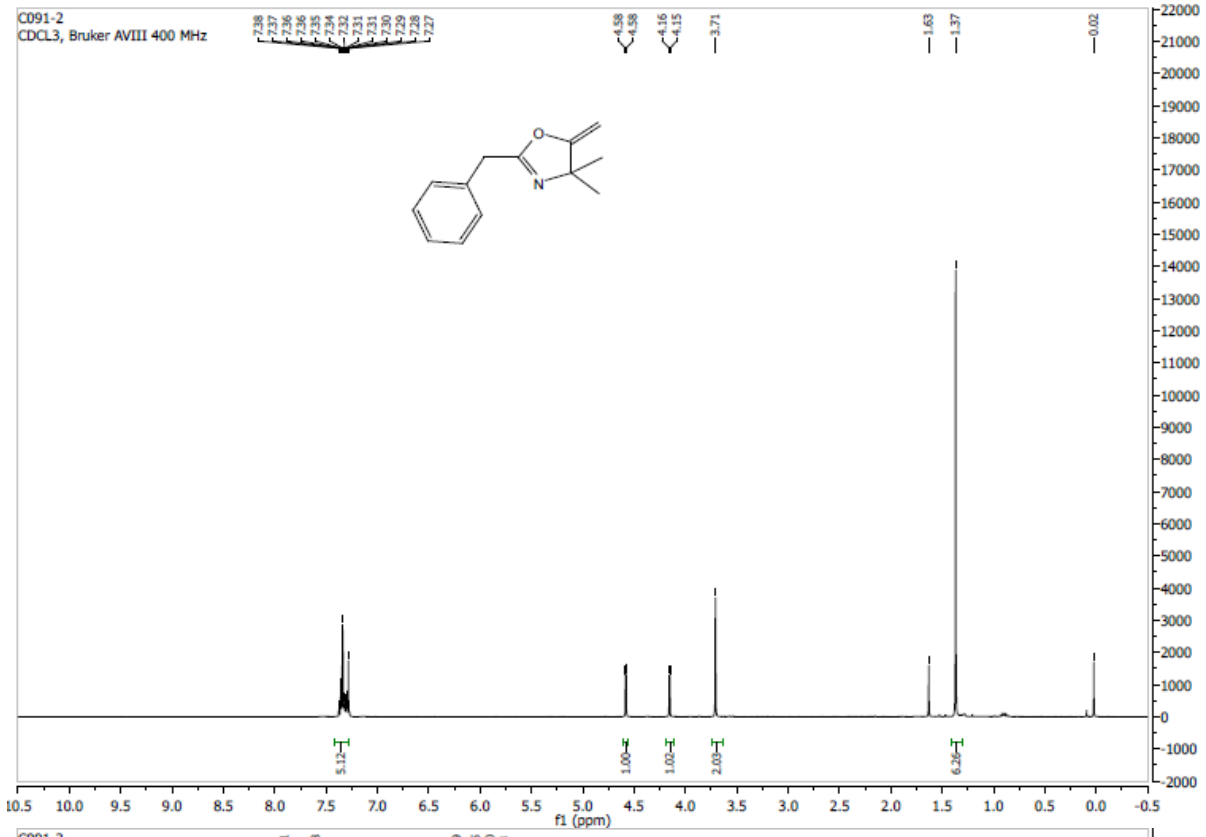


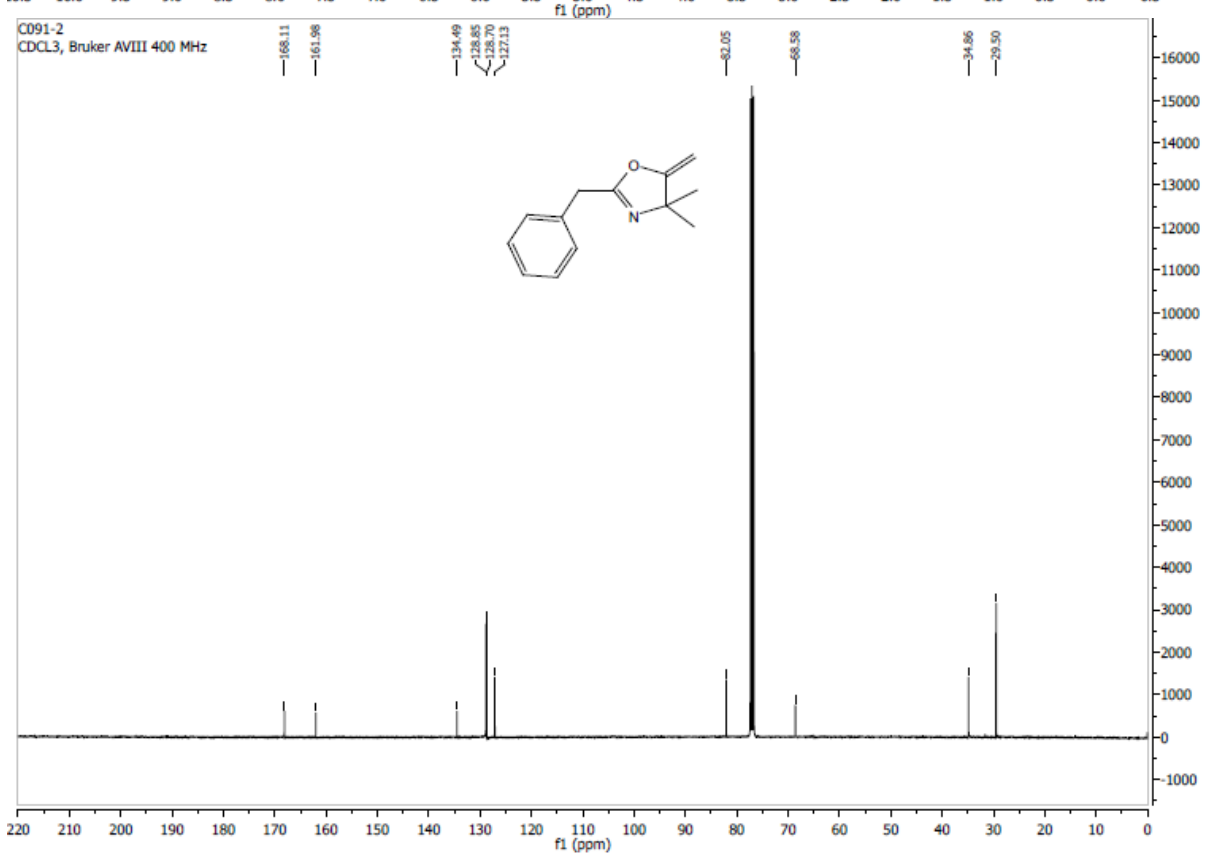

17-3
CDCl3, Bruker AVIII 400 MHz
f1 (ppm)

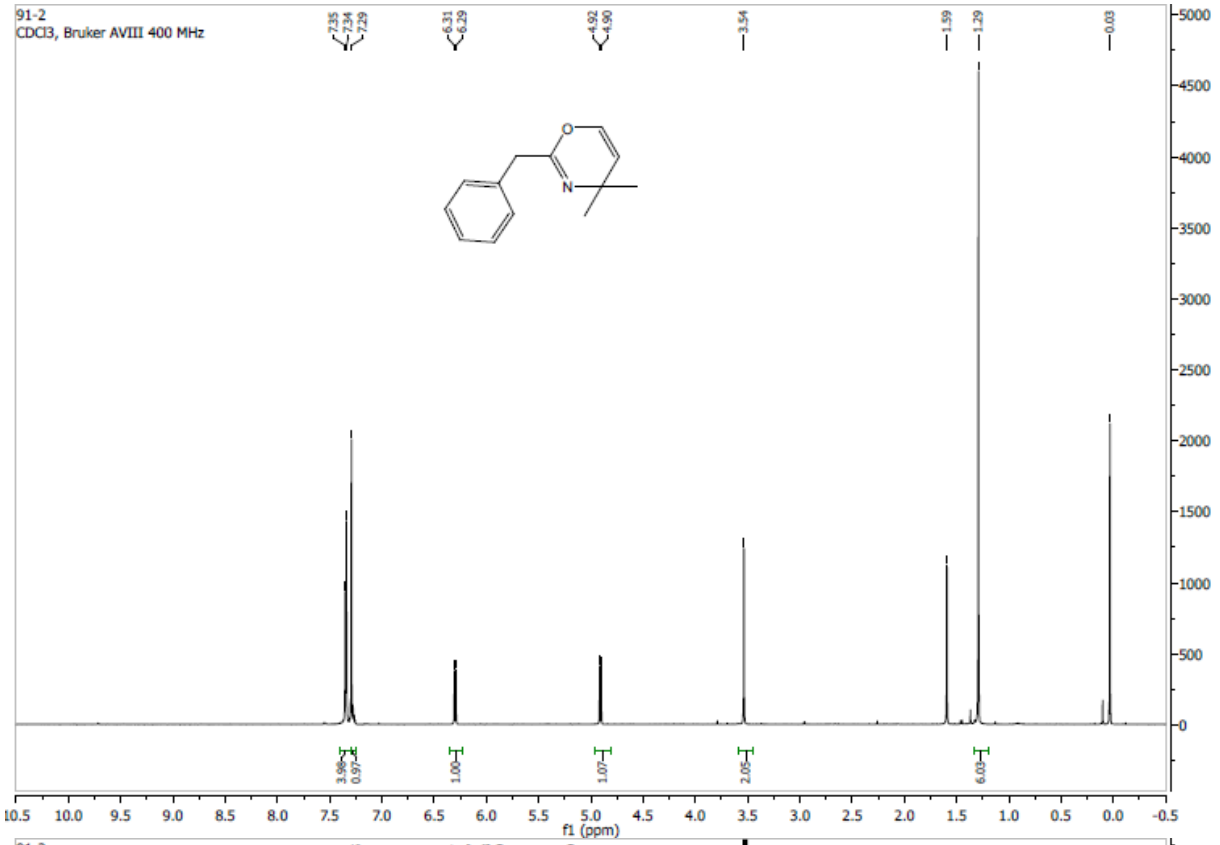

C095-1
CDCL3, Bruker AVIII 400 MHz
f1 (ppm)

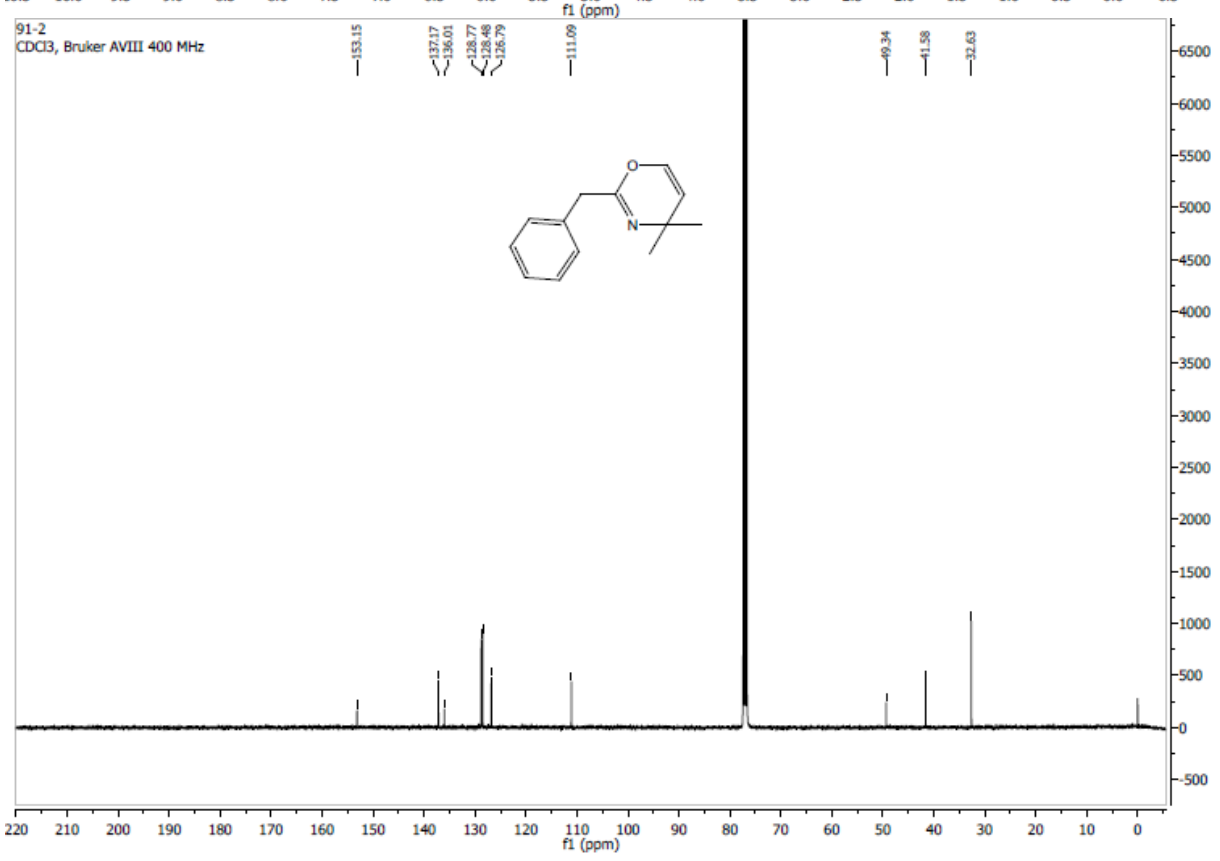

95-1
CDCl3, Bruker AVIII 400 MHz
7.60
7.59
7.58
7.57
7.50
7.49
7.48
7.47
7.35
7.33
7.31
7.31
7.26
7.24
7.24
7.22
7.22
6.48
6.47
5.03
5.02
1.57
1.38
0.00
O
N
Br
1.08
1.00
1.09
1.14
0.99
1.00
6.30
f1 (ppm)

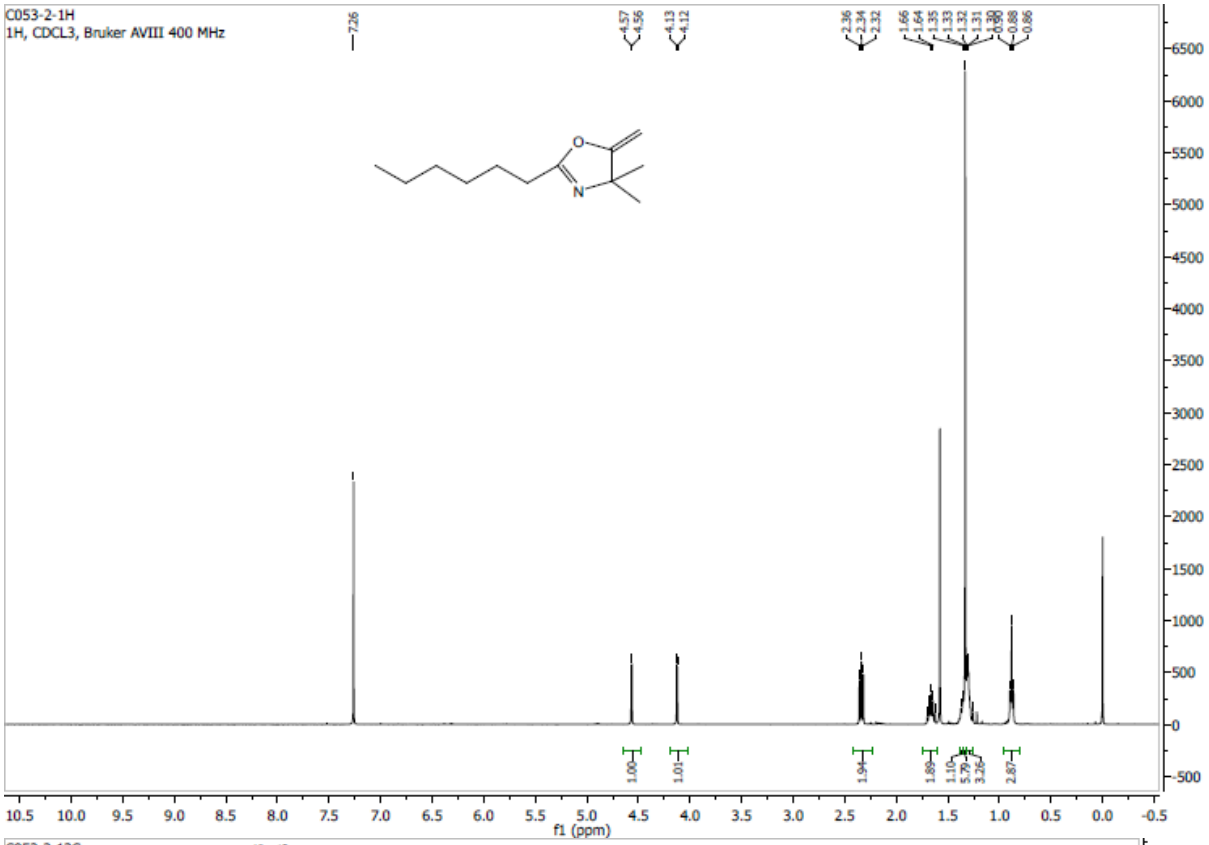

95-1
CDCl3, Bruker AVIII 400 MHz
151.37
137.41
135.19
133.25
130.85
130.32
127.25
121.41
111.61
50.26
32.49
O
N
Br
f1 (ppm)

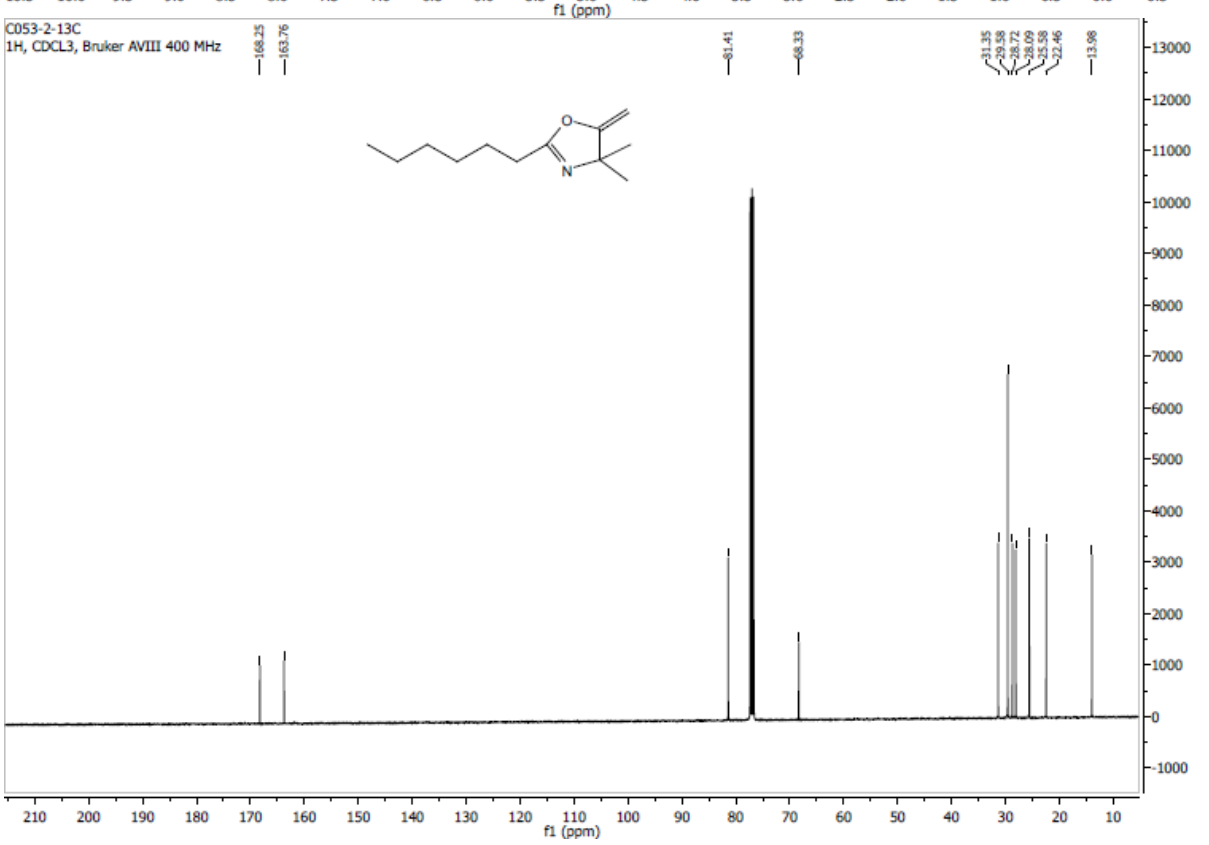

C091-2
CDCL3, Bruker AVIII 400 MHz
7.38
7.37
7.36
7.36
7.35
7.34
7.32
7.31
7.31
7.30
7.29
7.28
7.27
4.58
4.58
4.16
4.15
3.71
1.63
1.37
0.02
O
N
5.12
1.00
1.02
2.03
6.26
f1 (ppm)


C091-2
CDCL3, Bruker AVIII 400 MHz
168.11
161.98
134.49
128.85
128.70
127.13
82.05
68.58
34.86
29.50
O
N
f1 (ppm)


91-2
CDCl3, Bruker AVIII 400 MHz
7.35
7.34
7.29
6.31
6.29
4.92
4.90
3.54
1.59
1.29
0.03
3.98
0.97
1.00
1.07
2.05
6.03
f1 (ppm)


91-2
CDCl3, Bruker AVIII 400 MHz
153.15
137.17
136.01
128.77
128.48
126.79
111.09
49.34
41.58
32.63
f1 (ppm)


C053-2-1H
1H, CDCL3, Bruker AVIII 400 MHz
7.26
4.57
4.56
4.13
4.12
2.36
2.34
2.32
1.66
1.64
1.35
1.33
1.32
1.31
1.30
0.90
0.88
0.86
1.00
1.01
1.94
1.89
1.10
5.79
3.26
2.87
f1 (ppm)


C053-2-13C
1H, CDCL3, Bruker AVIII 400 MHz
168.25
163.76
81.41
68.33
31.35
29.58
28.72
28.09
25.58
22.46
13.98
f1 (ppm)