Supporting information

Supported Gold Nanoparticles as an Efficient, Reusable and Green Heterogeneous Catalyst for Cycloisomerization Reactions

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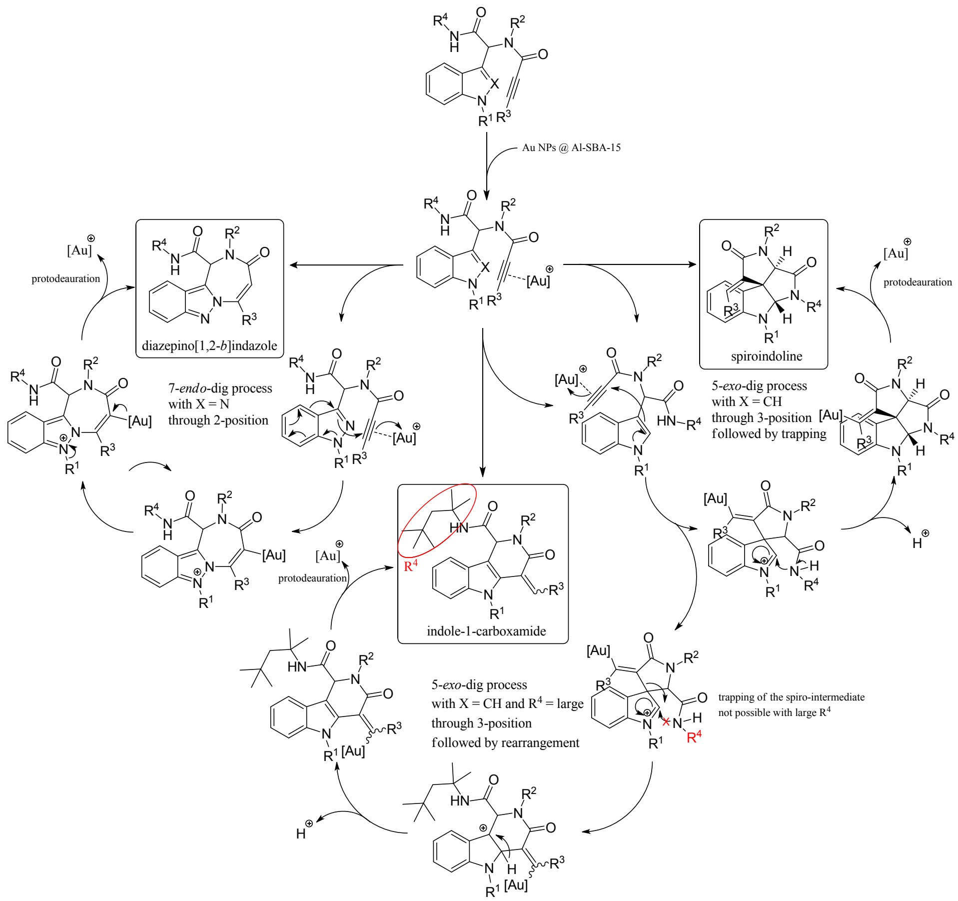
Contents

General Experimental Methods and Data

All NMR spectra were recorded on either a *Bruker Avance* 300 MHz NMR spectrometer with a bbo 5 mm probe or a *Bruker Avance* 2+ 600 MHz NMR spectrometer with a bbi 5 mm probe using CDCl3 and DMSO-d6 as solvents unless otherwise noted. The 1H and 13C chemical shifts are reported in ppm relative to the solvent residue peaks as internal standards. High resolution mass spectrometry was performed on a *Kratos* MS50TC mass spectrometer with a DIP-probe inlet, in EI mode (70 eV ionization energy), using a double focusing, magnetic sector analyzer and the *MASPEC II* data system. The resolution was 10000. The *Fluka Analytical* silica gel on TLC Al foil plates were purchased from *Sigma-Aldrich* using a fluorescent indicator at 254 nm and showing a medium pore diameter of 60 Å. Preparative silica gel chromatography was performed on *Acros Organics* 0.060 – 0.200 mm, 60 Å silica gel. All solvents and chemicals were used as purchased. All reactions were performed under air or N2 as protecting gas. The names of all products were generated using the *PerkinElmer* ChemBioDraw Ultra v.12 software package. NMR data was processed using the *MestReNova* 9.0.1 software package. The BET surface and porosity measurement was done by nitrogen adsorption measurement which was carried out at 77 K using an ASAP 2010 volumetric adsorption analyzer from *Micromeritics*. The samples were previously degassed for 24 h at 130°C under vacuum (p< 10-2 Pa) before performing the adsorption measurements. The surface areas were calculated according to the BET (Brunauer-Emmet-Teller) equation. Pore volumes (VBJH) and pore size distributions (DBJH) were obtained from the N2 desorption branch. X-Ray diffractogramms were taken with a *Siemens* D-5000 (40 kV, 25 mA) using Co Ka (l = 0.17903 nm) radiation in order to determine the structural regularity of the samples. The scans were performed over a 2θ range from 10 to 80 at step size of 0.02 ° with a counting time per step of 20 s. XPS measurements were performed in an ultra-high vacuum (UHV) multipurpose surface analysis system (Axis Ultra DLD) operating at pressures <10−10 mbar using a conventional X-ray source (XR-50, Monochromatic Al) in a "stop-and-go" mode to reduce potential damage due to sample irradiation. The survey and detailed high-resolution spectra (pass energy 160 and 40 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Hemispherical analyzer detector. The metal content (Cu, Zn, Al, Zr) in the materials were determined using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) in a *Philips* PU 70000 sequential spectrometer equipped with an Echelle monochromator (0.0075 nm resolution). The TEM micrographs were recorded on a *JEOL* 2010HR instrument operating at 300 kV fitted with a multiscan CCD camera for ease and speed of use and EDX system.

Mechanisms of the catalyzed post-Ugi cyclization



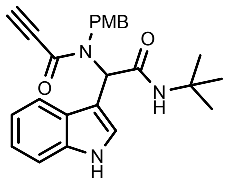
General procedure for the synthesis of the Ugi products 1a-w except 1n-q

A reaction flask was charged with indole-3-carbaldehyde **1a-j** or *N*-methylindole-3-carbaldehyde **1k-m** (1 eq), Na_2SO_4 (0.3g) and methanol (6 ml). Then the corresponding amine (1.2 eq) the alkynoic acid (1.2 eq) and the isonitrile (1.2 eq) were added successively. All reactions were dimensioned to give a theoretical amount of 1 g of product. The vial was equipped with a magnetic stirring bar and sealed with a screw cap. The reaction mixture was stirred at 50°C for 24-48 h. After observing no further conversion of the SMs by TLC the mixture was diluted with 20 ml EtOAc and washed with brine (3x10 ml). The combined aqueous phases were extracted with EtOAc (3x20 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure to give the crude product which was subjected to silica gel chromatography (**1:** EtOAc:Heptane = 1:1; **2:** DCM:Et_2O = 5:1) to afford the product as a sticky oil which was objected to co-distillation (sonic bath + rotavap) with pentane (3x2 ml) to give **1a-w** as solids.

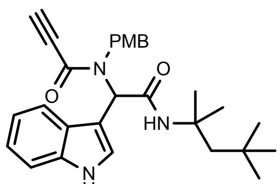
General procedure for the synthesis of the Ugi products 1n-q

A reaction flask was charged with indazole-3-carbaldehyde **1n-q** (1.1 eq), MS 4 Å (0.2g) and methanol (6 ml). Then the corresponding amine (1.0 eq) the alkynoic acid (1.0 eq) and the isonitrile (1.0 eq) were added successively. All reactions were dimensioned to give a theoretical amount of 200 mg of product.

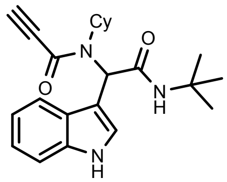
The vial was equipped with a magnetic stirring bar and sealed with a screw cap. The reaction mixture was stirred at 50°C for 24 h. After observing no further conversion of the SMs by TLC the mixture was filtered through celite and the celite carefully washed with DCM. The solvent was removed from the resulting filtrate under reduced pressure to give the crude product which was subjected to silica gel chromatography (EtOAc:Heptane = 1:1) to afford the product as a sticky oil which was objected to co-distillation (sonic bath + rotavap) with pentane (3x2 ml) to give **1n-q** as solids.



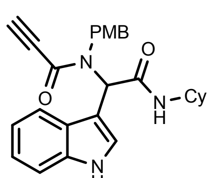
***N*-(2(*tert*-butylamino)-1-(1*H*-indole-3-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)-propiolamide 1a:** Yellow powder, yield 33% (mixture of rotamers 1:3.5). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.57 (bs, 0.22 H), 8.39 (bs, 0.78), 7.50 – 7.44 (m, 1 H), 7.42 – 7.34 (m, 1 H), 7.31 – 7.26 (m, 1 H), 7.24 – 7.13 (m, 1 H), 7.13 – 7.03 (m, 1 H), 6.89 – 6.83 (m, 2 H), 6.58 – 6.51 (m, 2 H), 6.35 (s, 0.21 H), 6.13 (s, 0.78 H), 5.89 (bs, 0.76 H), 5.56 (bs, 0.19 H), 4.85 – 4.69 (m, 1.6 H), 4.63 – 4.34 (m, 0.4 H), 3.67 (s, 0.7 H), 3.66 (s, 2.3 H), 3.32 (s, 0.19 H), 3.09 (s, 0.72 H), 1.27 (s, 7 H), 1.24 (s, 2 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.2, 158.6, 154.7, 135.7, 129.9, 129.1, 128.4 (2 C), 127.1, 126.2, 122.7, 120.3, 118.7, 113.4 (2 C), 111.3, 108.8, 79.7, 55.3, 54.7, 51.6, 50.6, 28.7 (3 C); **HRMS** calculated for $C_{25}H_{27}N_3O_3$ 417.2052, found 417.2049.



***N*-(1-(1*H*-indol-3-yl)-2-oxo-2-((2,4,4-trimethylpentan-2-yl)amino)ethyl)-*N*-(4-methoxybenzyl)propiolamide 1b:** Yellow powder, yield 12% (mixture of rotamers 1:3.5). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.41 (bs, 0.22 H), 8.26 (bs, 0.78 H), 7.53 (d, *J* = 2.52 Hz, 0.78 H), 7.49 (d, *J* = 8.20 Hz, 0.27 H), 7.40 – 7.03 (m, 4 H), 6.90 – 6.83 (m, 2 H), 6.56 – 6.49 (m, 2 H), 6.39 (s, 0.22 H), 6.09 (s, 0.78 H), 5.92 (bs, 0.76 H), 5.60 (bs, 0.20 H), 4.86 – 4.70 (m, 1.60 H), 4.57 – 4.44 (m, 0.46 H), 3.66 (s, 3 H), 3.31 (s, 0.20 H), 3.09 (s, 0.72 H), 1.70 – 1.56 (m, 2 H), 1.36 – 1.30 (m, 6 H), 0.92 (s, 2 H), 0.89 (s, 7 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 167.7, 158.6, 135.7, 129.8, 129.0, 128.4, 127.2, 126.3, 122.6, 120.3, 118.7, 113.4, 111.2, 108.8, 79.7, 77.4, 76.4, 55.6, 55.3, 54.8, 52.3, 50.7, 31.64, 31.58, 31.5 (3 C), 28.9, 28.7; **HRMS** calculated for $C_{29}H_{35}N_3O_3$ 473.2678, found 473.2688.

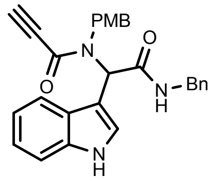


***N*-(2-(*tert*-butylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-*H*-cyclohexylpropiolamide 1c:** White powder, yield 23% (mixture of rotamers 1:7.3). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.54 (bs, 0.12 H), 8.45 (bs, 0.88 H), 7.83 (d, *J* = 2.35 Hz, 1 H), 7.48 – 7.08 (m, 4 H), 6.53 (bs, 0.89 H), 6.30 (bs, 0.10 H), 6.16 (s, 0.92 H), 5.70 (s, 0.08 H), 3.48 (dd, *J* = 14.57 Hz, 8.64 Hz, 1 H), 3.16 (s, 1 H), 1.67 – 1.39 (m, 5 H), 1.37 (s, 0.79 H), 1.34 (s, 8.18 H), 1.09 – 0.92 (m, 3 H), 0.87 – 0.68 (m, 2 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.5, 155.0, 135.5, 127.1, 126.3, 122.6, 120.3, 118.2, 111.4, 108.0, 80.0, 76.3, 54.9, 53.9, 51.3, 36.7, 30.8, 30.6, 28.6 (3 C), 26.3, 25.8, 25.7; **HRMS** calculated for $C_{23}H_{29}N_3O_2$ 379.2260, found 379.2264.

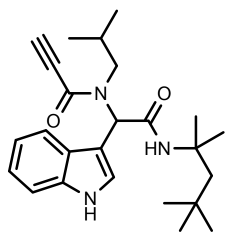


***N*-(2-(cyclohexylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)propiolamide 1d:** Yellow powder, yield 23% (mixture of rotamers 1:2.8). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.48 (bs, 0.26 H), 8.32 (bs, 0.74 H), 7.52 – 7.46 (m, 1 H), 7.42 – 7.35 (m, 1 H), 7.33 – 7.22 (m, 1 H), 7.21 – 7.14 (m, 1 H), 7.14 – 7.05 (m, 1 H), 6.95 – 6.85 (m, 2 H), 6.62 – 6.55 (m, 2 H), 6.43 (s, 0.22 H), 6.12 (s, 0.78 H), 5.92 (d, *J* =7.99 Hz, 0.8 H), 5.57 (d, *J* = 8.78 Hz, 0.2 H), 4.85 – 4.68 (m, 1.6 H), 4.68 – 4.26 (m, 0.4 H), 3.69 (s, 0.8 H), 3.68 (s, 2.2 H), 3.32 (s, 0.2 H), 3.09 (s, 0.7 H), 1.91 – 1.49 (m, 7 H), 1.14 – 0.96 (m, 3 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ

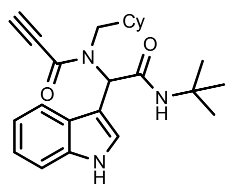
167.8, 158.6, 154.7, 135.6, 129.7, 128.8, 128.4 (2 C), 127.0, 126.2, 122.6, 120.3, 118.6, 113.4 (2 C), 111.2, 108.6, 79.6, 77.2, 55.2, 54.350.6, 48.5, 32.7, 32.6, 25.5, 24.7, 22.3; **HRMS** calculated for $C_{27}H_{29}N_3O_3$ 443.2209, found 443.2209.



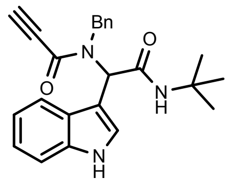
***N*-(2-(benzylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)propiolamide 1e:** yellow powder, yield 32% (mixture of rotamers 1:4). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.47(bs, 0.2 H), 8.37 (bs, 0.8 H), 7.49 – 7.44 (m, 1 H), 7.39 – 7.03 (m, 10 H), 6.96 – 6.75 (m, 2 H), 6.61 – 6.45 (m, 2 H), 6.34 (t, *J* = 5.60 Hz, 1 H), 6.07 (s, 1 H), 4.91 – 4.67 (m, 1.7 H), 4.61 – 4.42 (m, 0.3 H), 4.53 – 4.23 (m, 2 H), 3.68 (s, 2.5 H), 3.64 (s, 0.5 H), 3.28 (s, 0.17 H), 3.10 (s, 0.77 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.8, 158.6, 154.6, 137.8, 135.5, 129.3, 128.7 (2 C), 128.4 (2 C), 127.6 (2 C), 127.3, 126.9, 126.2, 122.6, 120.3, 118.4, 113.4 (2 C), 111.3, 108.3, 79.7, 76.7 (d), 55.2, 54.5, 51.1, 43.7; **HRMS** calculated for $C_{28}H_{25}N_3O_3$ 451.1896, found 451.1906.



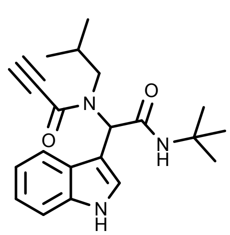
***N*-(1-(1*H*-indol-3-yl)-2-oxo-2-((2,4,4-trimethylpentan-2-yl)amino)ethyl)-*N*-isobutylpropiolamide 1f:** White powder, yield 10% (mixture of rotamers 1:9). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.95 (bs, 0.1 H), 8.77 (bs, 0.9 H), 7.76 (d, *J* = 2.37 Hz, 1 H), 7.51 – 7.39 (m, 2 H), 7.26 – 7.10 (m, 2 H), 6.33 (bs, 0.9 H), 6.30 (bs, 0.1 H), 5.99 (s, 0.9 H), 5.69 (s, 0.1 H), 3.52 – 3.42 (m, 1 H), 3.31 – 3.17 (m, 1 H), 3.15 (s, 1 H), 1.83 – 1.62 (m, 3 H), 1.40 (s, 6 H), 0.93 (s, 1 H), 0.89 (s, 8 H), 0.78 – 0.70 (m, 6 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 167.9, 154.8, 135.6, 127.0, 126.2, 122.6, 120.2, 118.2, 111.5, 108.2, 79.9, 76.4, 55.7, 55.5, 55.4, 52.5, 31.5, 31.4 (3 C), 28.8, 28.3, 27.7, 20.1, 19.9; **HRMS** calculated for $C_{25}H_{35}N_3O_2$ 409.2729, found 409.2726.



***N*-(2-(*tert*-butylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-*N*-(cyclohexylmethyl)propiolamide 1g:** White powder, yield 19% (mixture of rotamers 1:6.1). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.45 – 8.32 (m, 1 H), 7.70 – 7.15 (m, 5 H), 6.17 (s, 0.12 H), 5.93 (s, 0.82 H), 5.75 (s, 0.14 H), 5.32 (s, 0.86 H), 4.22 (bs, 1 H), 3.35 (s, 0.26 H), 3.15 (s, 0.77 H), 2.18 – 1.35 (m, 10 H), 1.24 (s, 9 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.2, 153.5, 135.6, 126.3, 125.1, 122.5, 120.2, 118.2, 111.5, 79.2, 77.2, 55.0, 51.3, 31.8, 31.7, 30.9 (3 C), 28.5 (2 C), 25.94, 25.89, 25.2; **HRMS** calculated for $C_{24}H_{31}N_3O_2$ 393.2416, found 393.2410.

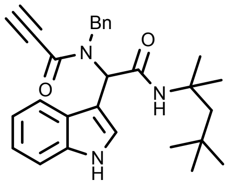


***N*-benzyl-*N*-(2-(*tert*-butylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)propiolamide 1h:** Yellow powder, yield 28% (mixture of rotamers 1:3.5). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.57 (bs, 0.22 H), 8.37 (bs, 0.78 H), 7.54 – 6.86 (m, 10 H), 6.38 (s, 0.19 H), 6.20 (s, 0.79 H), 5.89 (s, 0.74 H), 5.57 (s, 0.20 H), 4.96 – 4.75 (m, 1.5 H), 4.67 – 4.48 (m, 0.5 H), 3.33 (s, 0.22 H), 3.06 (s, 0.78 H), 1.28 (s,7 H), 1.24 (2 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.1, 154.0, 136.9, 135.6, 128.0, 127.8 (2 C), 126.8 (2 C), 126.7, 126.2, 122.2, 120.2, 118.5, 111.2, 108.5, 79.6, 76.2, 54.5, 51.5, 50.9, 28.5 (3 C); **HRMS** calculated for $C_{24}H_{25}N_3O_2$ 387.1947, found 387.1938.

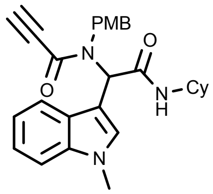


***N*-(2-(*tert*-butylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-*N*-isobutylpropiolamide 1i:** White powder, yield 23% (mixture of rotamers 1:3.5). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.63 (bs, 0.1 H), 8.52 (bs, 0.9 H), 7.78 (d, *J* = 2.36 Hz, 0.9 H), 7.60 (d, *J* = 8.33 Hz, 0.1 H), 7.49 – 7.38 (m, 2 H), 7.29 – 7.11 (m, 2 H), 6.41 (bs, 0.9 H), 6.29 (s, 0.1 H), 6.11 (s, 0.9 H), 5.67 (bs, 0.1 H), 3.50 – 3.41 (m, 1 H), 3.30 (s, 0.1 H), 3.20 – 3.11 (m, 1 H), 3.16 (s, 0.9 H), 1.89 – 1.76 (m, 1 H), 1.36 (s, 1 H), 1.33 (s, 8 H), 0.79 – 0.77 (m, 5.4

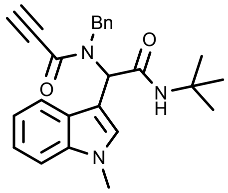
H), 0.65 – 0.40 (m, 0.6 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.5, 155.0, 135.6, 127.0, 126.2, 122.6, 120.3, 118.2, 111.4, 108.1, 80.0, 76.3, 55.12, 55.09, 28.6 (3 C), 27.6, 20.1, 19.9; **HRMS** calculated for $C_{21}H_{27}N_3O_2$ 353.2103, found 353.2106.



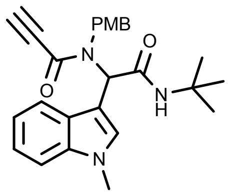
***N*-(1-(1*H*-indol-3-yl)-2-oxo-2-((2,4,4-trimethylpentan-2-yl)amino)ethyl)-*N*-benzylpropiolamide 1j:** White powder, yield 8% (mixture of rotamers 1:3). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.37 (bs, 0.25 H), 8.21 (bs, 0.75 H), 7.55 – 6.85 (m, 10 H), 6.41 (s, 0.25 H), 6.16 (s, 0.75 H), 5.91 (bs, 0.75 H), 6.00 (bs, 0.25 H), 4.96 – 4.70 (m, 1.5 H), 4.68 – 4.53 (m, 0.5 H), 3.33 (s, 0.25 H), 3.06 (s, 0.75 H), 1.70 – 1.56 (m, 2 H), 1.36 (s, 2.5 H), 1.34 – 1.32 (m, 2.5 H), 0.93 (s, 2 H), 0.90 (s, 7 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 167.7, 155.0, 137.0, 135.7, 127.9, 126.9, 126.8, 126.3, 122.7, 120.3, 118.7, 111.2, 108.7, 79.7, 77.4, 76.3, 55.7, 54.7, 52.3, 51.1, 31.7, 31.5, 28.9, 28.7; **HRMS** calculated for $C_{28}H_{33}N_3O_2$ 443.2573, found 443.2567.



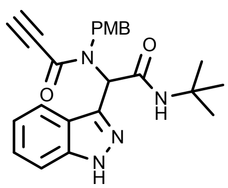
***N*-(2-(cyclohexylamino)-1-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)propiolamide 1k:** Yellow powder, yield 24% (mixture of rotamers 1:4). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.48 – 4.04 (m, 9 H), 6.93 – 6.83 (m, 2 H), 6.62 – 6.52 (m, 2 H), 6.41 (s, 0.2 H), 6.47 (s, 0.8 H), 5.95 (d, *J* = 7.99 Hz, 0.8 H), 5.60 (d, *J* = 7.51 Hz, 0.2 H), 4.88 – 4.63 (m, 1.6 H), 4.63 – 4.31 (m, 0.4 H), 3.76 (s, 1 H), 3.70 (s, 3 H), 3.69 (s, 3 H), 3.35 (s, 0.2 H), 3.09 (s, 0.8 H), 1.95 – 1.48 (m, 7 H), 1.14 – 0.93 (m, 3 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 167.8, 158.5, 154.5, 136.4, 130.7, 128.8, 128.3 (2 C), 127.5, 122.1, 119.8, 118.6, 113.2 (2 C), 109.3, 106.8, 79.5, 76.2, 55.2, 54.2, 32.8, 32.7, 32.6, 25.5, 24.74, 24.71, 22.3, 14.1; **HRMS** calculated for $C_{28}H_{31}N_3O_3$ 457.2365, found 457.2355.



***N*-benzyl-*N*-(2-(*tert*-butylamino)-1-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)propiolamide 1l:** Yellow powder, yield 24% (mixture of rotamers 1:4). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.52 – 6.85 (m, 10 H), 6.36 (s, 0.2 H), 6.19 (s, 0.8 H), 5.91 (bs, 0.8 H), 5.57 (bs, 0.2 H), 4.96 – 4.72 (m, 1.6 H), 4.57 (s, 0.4 H), 3.72 (s, 0.6 H), 3.66 (s, 2.4 H), 3.34 (s, 0.2 H), 3.06 (s, 0.8 H), 1.28 (s, 7.2 H), 1.24 (s, 1.8 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.1, 154.8, 136.9, 136.4, 130.8, 127.9, 127.6 (2 C), 127.5, 126.7 (2 C), 122.0, 119.8, 118.7, 109.2, 106.7, 79.5, 76.2, 54.3, 51.5, 50.8, 32.8, 28.5 (3 C); **HRMS** calculated for $C_{25}H_{27}N_3O_2$ 401.2103, found 401.2110.

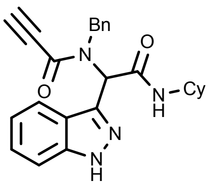


***N*-(2-(*tert*-butylamino)-1-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)propiolamide 1m:** Yellow powder, yield 24% (mixture of rotamers 1:4). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.49 – 7.03 (m, 5 H), 6.88 – 6.81 (m, 2 H), 6.58 – 6.50 (m, 2 H), 6.33 (s, 0.2 H), 6.12 (s, 0.8 H), 5.92 (bs, 0.8 H), 5.56 (bs, 0.2 H), 4.87 – 4.66 (m, 1.6 H), 4.59 – 4.37 (m, 0.4 H), 3.76 (s, 0.6 H), 3.70 (s, 2.4 H), 3.67 (s, 3 H), 3.45 (s, 0.2 H), 3.33 (s, 0.2 H), 3.09 (s, 0.8 H), 1.28 (s, 7.2 H), 1.24 (s, 1.8 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.1, 158.4, 154.6, 136.4, 130.7, 129.0, 128.2 (2 C), 127.5, 122.0, 119.8, 118.7, 113.1 (2 C), 109.2, 106.9, 79.5, 76.3, 55.2, 54.4, 51.4, 50.4, 32.8, 28.5 (3 C); **HRMS** calculated for $C_{26}H_{29}N_3O_3$ 431.2209, found 431.2208.

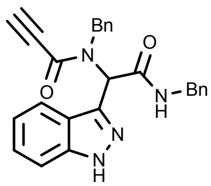


***N*-(2-(*tert*-butylamino)-1-(1*H*-indazol-3-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)propiolamide 1n:** White powder, yield 67% (mixture of rotamers 1:2). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.34 (bs, 1 H), 7.71 – 7.65 (m, 1 H), 7.62 – 7.08 (m, 4 H), 6.85 – 6.77 (m, 2 H), 6.59 (s, 0.33 H), 6.54 – 6.44 (m, 2 H), 6.47 (s, 0.67 H), 5.11 – 4.48 (m, 2 H), 3.64 (s, 1 H), 3.62 (s, 2 H), 3.34 (s, 0.33 H), 3.09 (s, 0.66 H), 1.29 (s, 6 H), 1.27 (s, 3

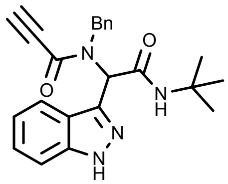
H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 166.2, 158.4, 154.7, 140.7, 139.8, 129.3, 128.1 (2 C), 127.1, 122.4, 121.4, 120.2, 113.2 (2 C), 109.9, 79.8, 76.0, 55.2, 51.8, 28.6 (3 C), 22.3; **HRMS** calculated for $C_{24}H_{26}N_4O_3$ 418.2005, found 418.2003.



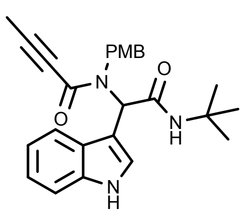
***N*-benzyl-*N*-(2-(cyclohexylamino)-1-(1*H*-indazol-3-yl)-2-oxoethyl)propiolamide 1o:** White powder, yield 51% (mixture of rotamers 1:1). **^{1}H-NMR (300 MHz, DMSO-d_6)** δ 13.09 (bs, 0.5 H), 12.93 (bs, 0.5 H), 8.20 (d, *J* = 7.74 Hz, 0.5 H), 8.08 (d, *J* = 7.71 Hz, 0.5 H), 7.57 (t, *J* = 8.27 Hz, 1 H), 7.45 – 7.21 (m, 2 H), 7.14 – 7.02 (m, 1 H), 6.94 – 6.84 (m, 3 H), 6.73 – 6.65 (m, 1 H), 6.62 – 6.56 (m, 1 H), 6.55 (s, 0.5 H), 6.46 (s, 0.5 H), 5.13 – 4.69 (m, 1 H), 4.92 – 4.32 (m, 1 H), 4.47 (s, 0.5 H), 4.45 (s, 0.5 H), 3.66 – 3.48 (m, 1 H), 1.71 – 1.46 (m, 5 H), 1.28 – 0.96 (m, 5 H); **^{13}C-NMR (75 MHz, MeOD)** δ 169.2, 156.0, 142.4, 139.5, 137.8, 128.5 (2 C), 127.6, 127.5, 127.2 (2 C), 123.6, 122.0, 122.6, 111.2, 60.8, 56.2, 52.5, 50.3, 33.5, 33.4, 26.6 (2 C), 26.0 (2 C); **HRMS** calculated for $C_{25}H_{26}N_4O_2$ 414.2056, found only fragments.



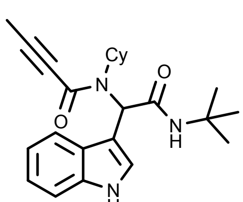
***N*-benzyl-*N*-(2-(benzylamino)-1-(1*H*-indazol-3-yl)-2-oxoethyl)propiolamide 1p:** Yellow powder, yield 69% (mixture of rotamers 1:2). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.36 (bs, 1H), 7.70 – 7.64 (m, 1 H), 7.42 – 7.06 (m, 7 H), 6.95 – 6.81 (m, 5 H), 6.77 (s, 0.33 H), 6.67 (s, 0.66 H), 5.20 – 4.31 (m, 4 H), 3.31 (s, 0.33 H), 3.05 (s, 0.66 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 167.1, 154.9, 140.7, 139.6, 137.7, 136.1, 128.6 (2 C), 127.8, 127.7 (4 C), 127.6, 127.3, 127.2, 122.3, 121.6, 120.1, 109.8, 80.0, 75.8, 54.6, 51.5, 43.9; **HRMS** calculated for $C_{26}H_{22}N_4O_2$ 422.1743, found 422.1714.



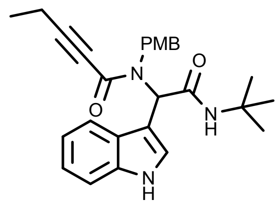
***N*-benzyl-*N*-(2-(*tert*-butylamino)-1-(1*H*-indazol-3-yl)-2-oxoethyl)propiolamide 1q:** White powder, yield 61% (mixture of rotamers 1:1). **^{1}H-NMR (300 MHz, DMSO-d_6)** δ 13.06 (s, 0.5 H), 12.90 (s, 0.5 H), 8.00 (s, 0.5 H), 7.86 (s, 0.5 H), 7.63 – 7.55 (m, 1 H), 7.44 – 7.21 (2 H), 7.12 – 7.02 (m, 1 H), 6.94 – 6.83 (m, 3 H), 6.73 – 6.67 (m, 1 H), 6.63 – 6.56 (m, 1 H), 6.53 (s, 0.5 H), 6.47 (s, 0.5 H), 5.12 – 4.32 (m, 2 H), 4.73 (s, 0.5 H), 4.44 (s, 0.5 H), 1.23 (s, 4 H), 1.18 (s, 5 H); **^{13}C-NMR (75 MHz, MeOD)** δ 169.3, 156.9, 142.4, 139.7, 137.9, 128.5 (2 C), 127.6, 127.5, 127.2 (2 C), 123.6, 121.0, 120.8, 111.2, 61.1, 56.6, 52.7, 52.5, 28.8 (3 C); **HRMS** calculated for $C_{23}H_{24}N_4O_2$ 388.1899, found only fragments.



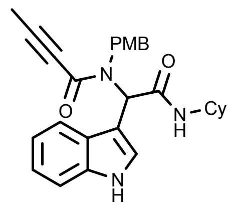
***N*-(2-(*tert*-butylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)but-2-ynamide 1q:** Yellow powder, yield 71% (mixture of rotamers 1:3.5). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.42 (bs, 0.24 H), 8.27 (bs, 0.76 H), 7.56 – 7.03 (m, 5 H), 6.98 – 6.82 (m, 2 H), 6.68 – 6.45 (m, 2 H), 6.34 (s, 0.24 H), 6.20 (s, 0.76 H), 5.99 (bs, 0.76 H), 5.55 (bs, 0.24 H), 4.79 – 4.08 (m, 2 H), 3.73 – 3.61 (m, 3 H), 2.07 (s, 0.85 H), 1.94 (s, 2.15 H), 1.26 (s, 6.4 H), 1.19 (s, 2.6 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.6, 158.5, 156.2, 135.8, 130.0, 128.5 (2 C), 127.2, 126.3, 122.5, 120.2, 118.8, 113.4 (2 C), 111.3, 109.0, 90.4, 74.1, 55.3, 54.5, 51.5, 50.4, 28.7 (3 C), 4.2; **HRMS** calculated for $C_{26}H_{29}N_3O_3$ 431.2209, found 431.2200.



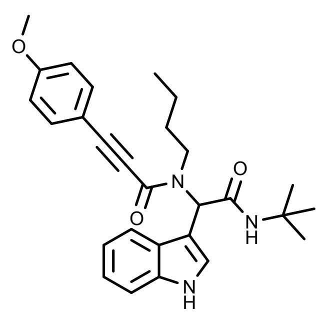
***N*-(2-(*tert*-butylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-*N*-cyclohexylbut-2-ynamide 1r:** Yellow powder, yield 45% (mixture of rotamers 1:4.8). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.39 – 8.24 (m, 1 H), 7.66 – 7.49 (m, 2 H), 2.45 – 2.35 (m, 1 H), 7.25 – 7.10 (m, 2 H), 6.18 (s, 0.17 H), 6.01 (s, 0.83 H), 5.82 (bs, 0.17 H), 5.36 (bs, 0.83 H), 4.26 – 4.06 (m, 1 H), 2.07 – 1.62 (m, 7 H), 1.42 – 1.35 (m, 3 H), 1.27 – 1.22 (m, 9 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.8, 155.0, 135.8, 126.5, 125.4, 122.4, 120.1, 118.4, 111.8, 111.1, 89.7, 59.4, 55.1, 51.3, 35.6, 31.9, 31.8, 28.6 (3 C), 26.1, 25.4, 22.8, 14.3, 4.3; **HRMS** calculated for $C_{24}H_{31}N_3O_2$ 393.2416, found 393.2416.



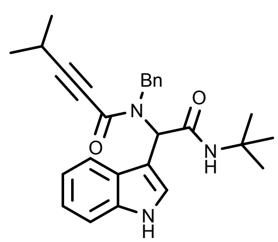
***N*-(2-(*tert*-butylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)-pent-2-ynamide 1s:** White powder, yield 85% (mixture of rotamers   1:2). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.30 (bs, 0.27 H), 8.18 (bs, 0.73 H), 7.57 – 7.27 (m, 3 H), 7.23 – 7.03 (m, 2 H), 7.00 – 7.83 (m, 2 H), 6.67 – 6.47 (m, 2 H), 6.37 (s, 0.27 H), 6.27 (s, 0.73 H), 5.98 (bs, 0.73 H), 5.54 (bs, 0.27 H), 4.77 – 4.06 (m, 2 H), 3.70 (s, 1.1 H), 3.67 (s, 1.9 H), 2.44 (q, *J* = 7.50 Hz, 0.5 H), 2.29 (q, *J* = 7.52 Hz, 1.5 H), 1.29 – 1.17 (m, 9.67 H), 1.10 (t, *J* = 7.49 Hz, 2.33 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.6, 158.5, 156.3, 135.8, 129.8, 128.5 (2 C), 127.2, 126.3, 122.5, 120.2, 118.8, 113.4 (2 C), 111.3, 109.0, 95.5, 74.2, 55.3, 54.5, 51.5, 50.4, 28.7 (3 C), 12.8, 12.8; **HRMS** calculated for $C_{27}H_{31}N_3O_3$ 445.2365, found 445.2361.



***N*-(2-(cyclohexylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)but-2-ynamide 1t:** White powder, yield 69% (mixture of rotamers   1:2.2). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.32 (bs, 0.28 H), 8.12 (bs, 0.72 H), 7.61 – 7.04 (m, 5 H), 6.99 – 6.85 (m, 2 H), 6.70 – 6.52 (m, 2 H), 6.46 (s, 0.28 H), 6.20 (s, 0.72), 6.01 (d, *J* =7.59 Hz, 0.72 H), 5.56 (d, *J* = 7.56 Hz, 0.28 H), 4.70 (s, 1.5 H), 4.10 – 4.05 (m, 0.25 H), 3.83 – 3.78 (m, 0.25 H), 3.75 – 3.74 (m, 4 H), 2.09 – 1.92 (m, 3 H), 1.91 – 1.47 (m, 6 H), 1.41 – 1.30 (m, 1 H), 1.19 – 0.90 (m, 3 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.4, 158.6, 156.1, 135.8, 129.5, 128.6 (2 C), 127.2, 126.4, 122.5, 120.2, 118.7, 113.5 (2 C), 111.4, 108.7, 90.4, 74.0, 55.3, 54.3, 50.6, 48.6, 32.7, 25.6, 24.8, 4.2; **HRMS** calculated for $C_{28}H_{31}N_3O_3$ 457.2365, found 457.2363.



***N*-butyl-*N*-(2-(*tert*-butylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-3-(4-methoxyphenyl)propiolamide 1u:** White powder, yield 53% (mixture of rotamers   1:4). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.36 – 8.24 (m, 1 H), 7.85 (d, *J* = 3.05 Hz, 0.2 H), 7.78 (d, *J* = 2.11 Hz, 0.8 H), 7.65 – 7.38 (m, 4 H), 7.56 – 7.11 (m, 6 H), 6.92 – 6.82 (m, 2 H), 6.37 (s, 0.2 H), 6.34 (s, 0.8 H), 6.23 (bs, 0.8 H), 5.78 (bs, 0.2 H), 3.86 – 3.78 (m, 3 H), 3.71 – 3.56 (m, 1 H), 3.50 – 3.36 (m, 1 H), 1.36 (s, 7.2 H), 1.26 (bs, 1.8 H), 1.23 – 1.05 (m, 3 H), 0.93 – 0.81 (m, 1 H), 0.72 (t, *J* = 7.03 Hz, 2.4 H), 0.63 (t, *J* = 7.04 Hz, 0.6 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 169.1, 161.2, 156.1, 135.8, 134.3 (2 C), 127.2, 126.1, 122.8, 120.4, 118.8, 114.4 (2 C), 112.5, 111.5, 109.0, 91.2, 81.5, 55.5, 54.1, 51.6, 47.1, 31.8, 28.7 (3 C), 20.3, 13.7; **HRMS** calculated for $C_{28}H_{33}N_3O_3$ 459.2522, found 459.2527.



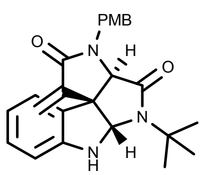
***N*-benzyl-*N*-(2-(*tert*-butylamino)-1-(1*H*-indol-3-yl)-2-oxoethyl)-4-methylpent-2-ynamide 1v:** Yellow powder, yield 48% (mixture of rotamers   1:4). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.33 (bs, 0.26 H), 8.20 (bs, 0.74 H), 7.56 – 6.90 (m, 10 H), 6.39 (s, 0.26 H), 6.30 (s, 0.74 H), 5.95 (bs, 0.76 H), 5.53 (bs, 0.26 H), 4.83 – 4.22 (m, 2 H), 2.80 (p, *J* = 6.87 Hz, 0.26 H), 2.58 (p, *J* = 6.90 Hz, 0.74 H), 1.28 (s, 6.64 H), 1.19 (s, 2.36 H), 1.06 (dd, *J* = 6.89 Hz, 2.11 Hz, 4.43 H), 0.99 – 0.79 (m, 1.57 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.6, 156.5, 137.9, 135.8, 128.6, 127.9, 127.0, 126.7, 126.3, 122.6, 120.3, 118.8, 111.3, 109.1, 99.1, 74.0, 54.3, 51.6, 50.8, 28.7, 21.8, 20.8. **HRMS** calculated for $C_{27}H_{31}N_3O_2$ 429.2416, found 429.2406.

General procedure for the gold catalyzed reaction under μ-wave irradiation 2a-q

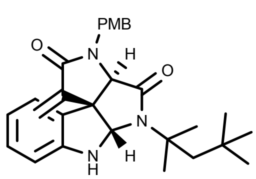
A 10 ml μ-wave vial was charged with 60 μmol of substrate, 3 mg (0.5 mol% Au as 2w% Au@Al-SBA15) of the catalyst, a magnetic stirring bar and 1 ml of EtOH as solvent. The reaction vial was sealed with a snap-cap and the reaction mixture was stirred for 20 min in the μ-wave oven at 110°C unless otherwise noted. After completion of the reaction the mixture was filtered through a micropore filter (Chromafil® 0-20/25 MS, PTFE) and the filter was washed with EtOH (3x1 ml) and DCM (3x1 ml). The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography (**1a-m** DCM:Et_2O = 10:1; **1n-q** DCM:Et_2O = 5:1) to give an oily product. To remove last solvent residues the oil was mixed with n-pentane and put in a sonic bath and again the solvent was removed under reduced pressure. To obtain a solvent free product this procedure had to be done min. three times.

General procedure for the gold catalyzed cyclization under conventional heating 2r-w

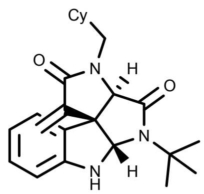
A 10 ml scre-cap vial was charged with 60 μmol of substrate, 3 mg (0.5 mol% Au as 2w% Au@Al-SBA15) of the catalyst, a magnetic stirring bar and 1 ml of EtOH as solvent. The reaction vial was sealed with a screw-cap and the reaction mixture was stirred for 48 h in an oil bath at 80°C unless otherwise noted. After completion of the reaction the mixture was filtered through a micropore filter (Chromafil® 0-20/25 MS, PTFE) and the filter was washed with EtOH (3x1 ml) and DCM (3x1 ml). The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography (**1r-u** DCM:Et_2O = 10:1)to give an oily product. To remove last solvent residues the oil was mixed with n-pentane and put in a sonic bath and again the solvent was removed under reduced pressure. To obtain a solvent free product this procedure had to be done min. three times.



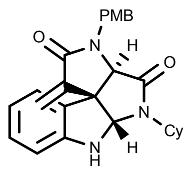
(±)-(3a*R*,5a*S*,10b*S*)-5-(*tert*-butyl)-3-(4-methoxybenzyl)-1-methylene-3,3a,5a,6-tetra-hydropyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2a: Yellow powder, yield 99%. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.37 – 7.31 (m, 2 H), 7.10 (ddd, *J* = 8.01 Hz, 6.77 Hz, 2.03 Hz, 1 H), 6.87 – 6.81 (m, 2 H), 6.78 – 6.70 (m, 2 H), 6.65 (d, *J* = 7.90 Hz, 1 H), 6.32 (s, 1 H), 5.48 (d, *J* = 4.33 Hz, 1 H), 5.30 (s, 1 H), 5.24 (d, *J* = 14.28 Hz, 1 H), 4.48 (d, *J* = 14.29 Hz, 1 H), 4.42 (d, *j* = 4.24 Hz, 1 H), 3.84 (s, 1 H), 3.77 (s, 3 H), 1.46 (s, 9 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 170.4, 165.9, 159.3, 148.8, 146.7, 130.9, 130.4 (2 C), 129.6, 128.0, 124.1, 121.0, 120.7, 114.2 (2 C), 110.6, 84.5, 65.4, 55.4, 55.3, 53.1, 44.8, 31.1, 28.2 (3 C); **HRMS** calculated for $C_{25}H_{27}N_3O_3$ 417.2052, found 417.2049.



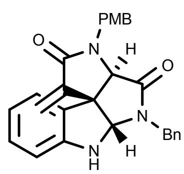
(±)-(3a*R*,5a*S*,10b*S*)-3-(4-methoxybenzyl)-1-methylene-5(2,4,4trimethylpentan-2-yl)-3,3a,5a,6-tetrahydropyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2b: Yellow powder, yield 54%. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 2.36 – 2.31 (m, 2 H), 7.0 (ddd, *J* = 7.89 Hz, 7.12 Hz, 1.69 Hz, 1 H), 6.87 – 6.81 (m, 2 H), 6.65 (d, *J* = 7.89 Hz, 3 H), 6.33 (s, 1 H), 5.55 (d, *J* = 4.61 Hz, 1 H), 5.34 (s, 1 H), 5.26 (d, *J* = 14.27 Hz, 1 H), 4.48 (d, *J* = 14.28 Hz, 1 H), 4.37 (d, *J* = 4.55 Hz, 1 H), 3.82 (s, 1 H), 3.77 (s, 3 H), 2.59 (d, *J* = 14.99 Hz, 1 H), 1.53 – 1.44 (m, 7 H), 0.93 (s, 9 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 170.2, 165.7, 159.1, 148.7, 146.6, 131.0, 130.2, 129.4, 127.8, 123.8, 120.9, 120.7, 114.1, 110.4, 85.2, 65.3, 59.4, 55.2, 52.7, 49.6, 44.5, 31.8, 31.4, 29.7, 27.7; **HRMS** calculated for $C_{29}H_{35}N_3O_3$ 473.2678, found 473.2666.



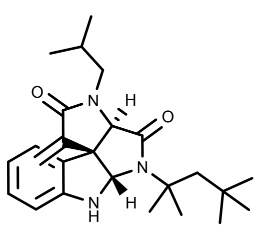
(±)-(3a*R*,5a*S*,10b*S*)-5-(*tert*-butyl)-3-(cyclohexylmethyl)-1-methylene-3,3a,5a,6-tetra-hydropyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2c: Yellow powder, yield 75%. **^{1}H-NMR (300 MHz, CDCl$_3$)** δ 7.17 (ddd, *J* = 7.86 Hz, 7.33 Hz, 1.49 Hz, 1 H), 6.71 (d, *J* = 7.88 Hz, 3 H), 6.26 (s, 1 H), 5.47 (d, *J* = 4.49 Hz, 1 H), 5.27 (s, 1 H), 4.43 (d, *J* = 4.39 Hz, 1 H), 4.02 (s, 1 H), 3.70 (dd, *J* = 13.57 Hz, 9.18 Hz, 1 H), 3.45 (dd, *J* = 13.51 Hz, 6.18 Hz, 1 H), 1.97 – 1.81 (m, 1 H), 1.88 (dddp, *J* = 12.16 Hz, 9.28 Hz, 6.28 Hz, 3.22 Hz, 3.13 Hz, 3.13 Hz, 6 H), 1.46 (s, 9 H), 1.23 – 1.17 (m, 2 H), 1.10 – 0.96 (m, 2 H); **^{13}C-NMR (75 MHz, CDCl$_3$)** δ 170.2, 166.3, 148.8, 146.3, 130.9, 129.6, 124.0, 121.0, 120.0, 110.6, 84.4, 67.1, 55.1, 53.2, 47.8, 35.0, 30.9, 30.4, 28.0, 26.4, 25.7, 25.6; **HRMS** calculated for $C_{24}H_{31}N_3O_2$ 393.2416, found 393.2426.



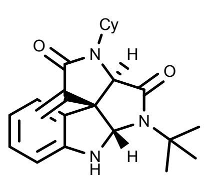
(±)-(3a*R*,5a*S*,10b*S*)-5-cyclohexyl-3-(4-methoxybenzyl)-1-methylene-3,3a,5a,6-tetra-hydropyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2d: Yellow powder, yield 76%. **^{1}H-NMR (300 MHz, CDCl$_3$)** δ 7.40 – 7.33 (m, 2 H), 7.12 (ddd, *J* = 7.94 hZ, 6.64 Hz, 2.12 Hz, 1 H), 6.89 – 6.82 (m, 2 H), 6.80 – 6.70 (m, 2 H), 6.67 (d, *J* = 7.91 Hz, 1 H), 6.28 (s, 1 H), 5.33 (d, *J* = 4.22 Hz, 1 H), 5.29 – 5.21 (m, 2 H), 4.50 -4.42 (m, 2 H), 3.93 (s, 1 H), 3.82 – 3.69 (m, 4 H), 1.94 – 1.06 (m, 10 H); **^{13}C-NMR (75 MHz, CDCl$_3$)** δ 168.9, 165.7, 159.2, 148.7, 145.9, 130.5, 130.3, 129.6, 127.8, 124.1, 120.9, 120.4, 114.0, 110.6, 82.7, 64.3, 55.2, 54.1, 52.8, 44.7, 31.8, 30.0, 25.8, 25.7, 25.5; **HRMS** calculated for $C_{27}H_{29}N_3O_3$ 443.2209, found 443.2209.



(±)-(3a*R*,5a*S*,10b*S*)-5-benzyl-3-(4-methoxybenzyl)-1-methylene-3,3a,5a,6-tetrahydro-pyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2e: Yellow powder, yield 68%. **^{1}H-NMR (300 MHz, CDCl$_3$)** δ 7.46 – 7.40 (m, 2 H), 7.36 – 7.28 (m, 3 H), 7.18 – 7.12 (m, 3 H), 6.91 – 6.86 (m, 2 H), 6.85 – 6.66 (m, 3 H), 6.20 (s, 1 H), 6.19 (d, *J* = 14.21 Hz, 1 H), 5.08 (s, 1 H), 4.97 (d, *J* = 4.30 Hz, 1 H), 4.91 (d, *J* = 14.92 Hz, 1 H), 4.57 (d, *J* = 14.22 Hz, 1 H), 4.33 (d, *J* = 4.27 Hz, 1 H), 4.18 (d, *J* = 14.93 Hz, 1 H), 4.06 (s, 1 H), 3.81 (s, 3 H); **^{13}C-NMR (75 MHz, CDCl$_3$)** δ 168.5, 165.9, 159.2, 148.7, 144.9, 135.0, 130.5, 130.3, 129.8, 129.0, 128.0, 128.0, 124.5, 121.5, 120.4, 114.1, 111.5, 82.0, 64.3, 55.3, 54.7, 45.0, 43.9; **HRMS** calculated for $C_{28}H_{25}N_3O_3$ 451.1896, found 451.1883.

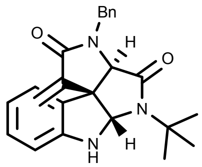


(±)-(3a*R*,5a*S*,10b*S*)-3-isobutyl-1-methylene-5-(2,4,4-trimethylpentan-2-yl)-3,3a,5a,6-tetrahydropyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2f: White powder, yield 22 %. **^{1}H-NMR (300 MHz, CDCl$_3$)** δ 7.16 (ddd, *J* = 7.86 Hz, 7.33 Hz, 1.50 Hz, 1 H), 6.92 – 6.79 (m, 2 H),6.71 (d, *J* = 7.88 Hz, 1 H), 6.29 (s, 1H), 5.55 (d *J* = 3.81 Hz, 1 H), 5.33 (s, 1 H), 4.40 (d, *J* = 3.25 Hz, 1 H), 4.03 (s, 1 H), 3.69 (dd, *J* =13.50 Hz, 9.63 Hz, 1 H), 3.47 (dd, *J* = 13.50 Hz, 5.75 Hz, 1 H), 2.53 (d, *J* = 14.98 Hz, 1 H), 2.19 (ddq, *J* = 13.09 Hz, 9.69 Hz, 6.61 Hz, 1 H), 1.54 – 1.45 (m, 7 H), 0.98 (d, *J* = 6.66 Hz, 3 H), 0.91 (s, 9 H), 0.89 (d, *J* = 6.69 Hz, 3 H); **^{13}C-NMR (151 MHz, CDCl$_3$)** δ 170.1, 166.1, 148.8, 146.4, 131.3, 129.5, 123.8, 121.0, 120.3, 110.5, 85.2, 66.8, 59.4, 52.8, 49.6, 48.7, 31.7, 31.4, 29.6, 27.7, 25.7, 20.3, 19.7; **HRMS** calculated for $C_{25}H_{23}N_3O_2$ 409.2729, found 409.2726.

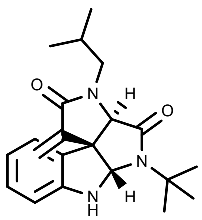


(±)-(3a*R*,5a*S*,10b*S*)-5-(*tert*-butyl)-3-cyclohexyl-1-methylene-3,3a,5a,6-tetrahydro-pyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2g: White powder, yield 75%. **^{1}H-NMR (300 MHz, CDCl$_3$)** δ 7.16 (ddd, *J* = 7.86 Hz, 7.35 Hz, 1.41 Hz, 1 H), 6.95 –

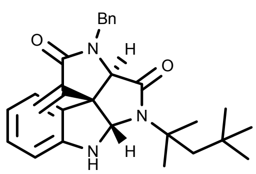
6.79 (m, 2 H), 6.70 (d, *J* = 7.89 Hz, 1 H), 6.22 (s, 1 H), 5.46 (d, *J* = 4.47 Hz, 1 H), 5.20 (s, 1 H), 4.41 (d *J* = 4.36 Hz, 1 H), 4.10 (s, 1 H), 3.98 (tt, *J* = 12.00 Hz, 12.00 Hz, 4.13 Hz, 4.13 Hz, 1 H), 2.23 (qd, *J* = 12.38 Hz, 12.38 Hz, 12.14 Hz, 3.43 Hz, 1 H), 1.98 – 1.63 (m, 6 H), 1.47 (s, 9 H), 1.41 – 1.28 (m, 3 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 170.5, 166.0, 148.8, 146.7, 130.8, 129.6, 124.0, 120.9, 119.2, 110.6, 83.8, 66.8, 55.0, 53.5, 30.3, 29.0, 27.9, 25.9, 25.8, 25.2; **HRMS** calculated for $C_{23}H_{29}N_3O_2$ 379.2260, found 379.2263.



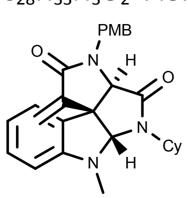
(±)-(3a*R*,5a*S*,10b*S*)-3-benzyl-5-(*tert*-butyl)-1-methylene-3,3a,5a,6-tetrahydropyrrolo-[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2h: White powder, yield 80%. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.42 – 7.37 (m, 2 H), 7.35 – 7.22 (m, 3 H), 7.11 (ddd, *J* = 7.95 Hz, 5.42 Hz, 3.38 Hz, 1 H), 6.78 – 6.71 (m, 2 H), 6.66 (d, *J* = 7.89 Hz, 1 H), 6.34 (s, 1 H), 5.49 (d, *J* = 4.53 Hz, 1 H), 5.34 – 5.26 (m, 2 H), 4.57 (d, *J* = 14.44 Hz, 1 H), 4.40 (d, *J* = 4.45 Hz, 1 H),3.85 (s, 1 H), 1.46 (s, 9 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 170.2, 165.9, 148.7, 146.3, 135.8, 130.7, 129.5, 128.7, 127.7, 123.9, 120.8, 120.7, 110.5, 84.4, 65.4, 55.1, 53.0, 45.2, 28.0; **HRMS** calculated for $C_{24}H_{25}N_3O_2$ 387.1947, found 387.1938.



(±)-(3a*R*,5a*S*,10b*S*)-5-(*tert*-butyl)-3-isobutyl-1-methylene-3,3a,5a,6-tetrahydropyrrolo-[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2i: White powder, yield 86%. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.16 (td, *J* = 7.81 Hz, 7.76 Hz, 1.28 Hz, 1 H), 6.94 – 6.79 (m, 2 H), 6.71 (d, *J* = 7.88 Hz, 1 H), 6.28 (s, 1 H), 5.48 (d, *J* = 4.48 Hz, 1 H), 5.29 (s, 1 H), 4.45 (d, *J* = 4.32 Hz, 1 H), 4.03 (s, 1 H), 3.67 (dd, *J* = 13.49 Hz, 9.54 Hz, 1 H), 3.45 (dd, *J* = 13.49 Hz, 5.87 Hz, 1 H), 2.18 (ddq, J = 13.14 Hz, 9.46 Hz, 6.64 Hz, 1 H), 1.46 (s, 9 H), 0.97 (d, *J* = 6.66 Hz, 3 H), 0.89 (d, *J* = 6.89 Hz, 3 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 170.2, 166.2, 148.8, 146.3, 130.9, 129.6, 123.9, 121.0, 120.2, 110.5, 84.4, 66.8, 55.1, 53.1, 48.9, 28.0, 25.8, 20.3, 19.7; **HRMS** calculated for $C_{21}H_{27}N_3O_2$ 353.2103, found 353.2105.

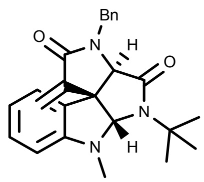


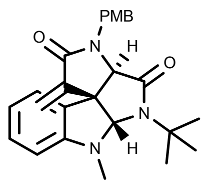
(±)-(3a*R*,5a*S*,10b*S*)-3-benzyl-1-methylene-5-(2,4,4-trimethylpentan-2-yl)-3,3a,5a,6-tetrahydropyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2j: White powder, yield 44%. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.42 – 7.22 (m, 5 H), 7.0 (ddd, *J* = 8.07 Hz, 6.44 Hz, 2.35 Hz, 1 H), 6.78 – 6.70 (m, 2 H), 6.65 (d, *J* = 7.90 Hz, 1 H), 6.35 (s, 1 H), 5.56 (s, 1 H), 5.36 (s, 1 H), 5.33 (d, *J* = 14.54 Hz, 1 H), 4.57 (d, *J* = 14.45 Hz, 1 H), 4.39 (bs, 1 H), 3.83 (s, 1 H), 2.59 (d, *J* = 14.99 Hz, 1 H), 1.53 – 1.45 (m, 7 H), 0.93 (s, 9 H); **^{13}C-NMR (151 MHz, $CDCl_3$)** δ 170.3, 166.0, 148.9, 146.6, 135.9, 131.1, 129.6, 128.9, 128.9, 127.9, 123.9, 121.1, 121.0, 110.6, 85.4, 65.5, 59.5, 52.9, 49.8, 45.2, 31.9, 31.6, 29.8, 27.9; **HRMS** calculated for $C_{28}H_{33}N_3O_2$ 443.2573, found 443.2562.



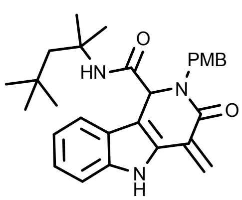
(±)-(3a*R*,5a*S*,10b*S*)-5-cyclohexyl-3-(4-methoxybenzyl)-6-methyl-1-methylene-3,3a,5a,6-tetrahydropyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2k: White powder, yield 87%. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.40 -7.32 (m, 2 H), 7.18 (ddd, *J* = 7.98 Hz, 7.27 Hz, 1.57 Hz, 1 H), 6.89 – 6.81 (m, 2 H), 6.79 – 6.65 (m, 2 H), 6.59 (d, *J* = 7.95 Hz, 1 H), 6.28 (s, 1 H), 5.23 (d, *J* = 14.21 Hz, 1 H), 5.16 (s, 1 H), 4.85 (s, 1 H), 4.45 (d, *J* = 14.23 Hz, 1 H), 3.88 (s, 1 H), 3.78 (s, 3 H), 3.53 (tt, *J* = 12.05 Hz, 12.05 Hz, 3.58 Hz, 3.58 Hz, 1 H), 3.07 (s, 3 H), 2.02 – 1.64 (m, 8 H), 1.39 – 1.14 (m, 2 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 169.2, 165.7, 159.2, 151.7, 146.1, 130.6, 130.3, 129.7, 127.8, 123.7, 120.5, 120.4, 114.0, 109.8, 91.8, 64.3, 55.2, 54.7, 53.6, 44.7, 38.6, 30.2, 29.4, 26.1, 26.0, 25.3; **HRMS** calculated for $C_{28}H_{31}N_3O_3$ 457.2365, found 457.2355.

(±)-(3a*R*,5a*S*,10b*S*)-3-benzyl-5-(*tert*-butyl)-6-methyl-1-methylene-3,3a,5a,6-tetra-hydro-pyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2l: White powder, yield 80%.**^{1}H-NMR (300 MHz, CDCl$_3$)** δ 7.41 – 7.23 (m, 5 H), 7.19 (ddd, *J* = 8.00 Hz, 6.71 Hz, 2.12 Hz, 1 H), 6.83 – 6.74 (m, 2 H), 6.66 (d, *J* = 7.99 Hz, 1 H), 6.34 (s, 1 H), 6.29 (s, 1 H), 5.23 (d, *J* = 14.48 Hz, 1 H), 5.01 (s, 1 H), 4.52 (d, *J* = 14.48 Hz, 1 H), 3.78 (s, 1 H), 2.99 (s, 3 H), 1.47 (s, 9 H); **^{13}C-NMR (75 MHz, CDCl$_3$)** δ 170.7, 166.1, 152.5, 145.3, 135.8, 130.7, 129.7, 128.8, 128.7, 127.7, 123.5, 121.2, 120.5, 111.3, 92.2, 65.3, 55.5, 53.6, 45.3, 39.7, 28.4; **HRMS** calculated for $C_{25}H_{27}N_3O_2$ 401.2103, found 401.2075.

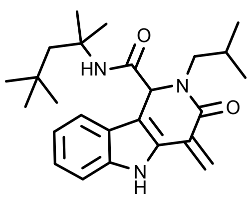




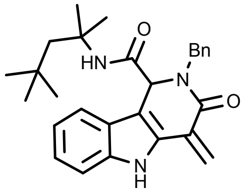
(±)-(3a*R*,5a*S*,10b*S*)-5-(*tert*-butyl)-3-(4-methoxybenzyl)-6-methyl-1-methylene-3,3a,5a,6-tetrahydropyrrolo[3',2':3,4]pyrrolo[2,3-*b*]indole-2,4(1*H*,5*H*)-dione 2m: White powder, yield 90%. **^{1}H-NMR (300 MHz, CDCl$_3$)** δ 7.37 – 7.30 (m, 2 H), 7.19 (ddd, *J* = 8.01 Hz, 7.25 Hz, 1.64 Hz, 1 H), 6.86 – 6.72 (m, 4 H), 6.66 (d, *J* = 7.98 Hz, 1 H), 6.32 (s, 1 H), 5.26 (s, 1 H), 5.18 (d, *J* = 14.29 Hz, 1 H), 4.99 (s, 1 H), 4.43 (d, *J* = 14.30 Hz, 1 H), 3.79 – 3.75 (m, 4 H), 2.99 (s, 3 H), 1.47 (s, 9 H); **^{13}C-NMR (75 MHz, CDCl$_3$)** δ 168.2, 154.9, 137.1, 136.6, 130.9, 128.0, 128.0, 127.7, 127.6, 126.9, 126.7, 122.2, 119.9, 118.8, 109.4, 106.9, 79.6, 76.3, 54.4, 51.6, 51.0, 32.9, 28.7; **HRMS** calculated for $C_{26}H_{29}N_3O_3$ 431.2209, found 431.2208.



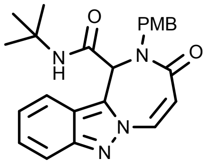
(±)-2-(4-methoxybenzyl)-4-methylene-3-oxo-*N*-(2,4,4-trimethylpentan-2-yl)-2,3,4,5-tetrahydro-1*H*-pyrido[4,3-*b*]indole-1-carboxamide 3b: White powder, yield 44% (minor impurities of unidentified side product). **^{1}H-NMR (300 MHz, CDCl$_3$)** δ 7.99 (s, 1 H), 7.63 (d, *J* = 7.67 Hz, 1 H), 7.37 (td, *J* = 7.67 Hz, 1.18 Hz, 1 H), 7.25 – 7.17 (m, 3 H), 7.02 (d, *J* = 7.76 Hz, 1 H), 6.89 – 6.84 (m, 2 H), 6.01 (s, 1 H), 5.35 (d, *J* = 14.58 Hz, 1 H), 4.94 (s, 1 H), 4.88 (bs, 1 H), 4.04 (d, *J* = 14.57 Hz, 1 H), 3.80 (s, 3 H), 3.73 (s, 1 H), 1.59 (d, *J* = 14.93 Hz, 1 H), 1.38 (s, 3 H), 1.34 (d, *J* = 14.96 Hz, 1 H), 1.24 (s, 3 H), 0.85 (s, 9 H); **^{13}C-NMR (151 MHz, CDCl$_3$)** δ 171.7, 166.9, 165.5, 159.6, 155.2, 140.9, 137.1, 130.3 (2 C), 129.5, 127.6, 127.4, 122.0, 121.5, 117.8, 114.5 (2 C), 64.1, 63.0, 56.5, 55.5, 53.3, 45.7, 31.5 (3 C), 28.3, 28.2; **HRMS** calculated for $C_{29}H_{35}N_3O_3$ 473.2678, found 473.2681.



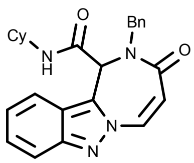
(±)-2-isobutyl-4-methylene-3-oxo-*N*-(2,4,4-trimethylpentan-2-yl)-2,3,4,5-tetra-hydro-1*H*-pyrido[4,3-*b*]indole-1-carboxamide 3f: White powder, yield 54% (minor impurities of unidentified side product). **^{1}H-NMR (300 MHz, CDCl$_3$)** δ 7.99 (s, 1 H), 7.67 (d, *J* = 7.70 Hz, 1 H), 7.43 (td, *J* = 7.66 Hz, 7.37 Hz, 1.77 Hz, 1 H), 7.33 – 7.23 (m, 2 H), 5.97 (s, 1 H), 5.16 (bs, 1 H), 4.92 (s, 1 H), 4.02 (s, 1 H), 3.81 (dd, *J* = 13.89 Hz, 9.55 Hz, 1 H), 2.90 (dd, *J* = 13.87 Hz, 5.46 Hz, 1 H), 1.39 (dtd, *J* = 12.22 Hz, 6.50 Hz, 6.39 Hz, 2.98 Hz, 1 H), 1.81 (d, *J* = 15.00 Hz, 1 H), 1.41 (d, *J* = 15.02 Hz, 1 H), 1.40 (s, 3 H), 1.28 (s, 3 H), 1.00 (s, 3 H), 0.98 (s, 3 H), 0.91 (s, 9 H); **^{13}C-NMR (151 MHz, CDCl$_3$)** δ 171.7, 167.4, 165.8, 154.9, 141.5, 136.7, 129.4, 127.6, 121.9, 121.3, 117.3, 65.3, 62.9, 56.5, 52.5, 49.7, 31.6, 31.4 (3 C), 28.6, 28.4, 26.7, 20.5, 20.2; **HRMS** calculated for $C_{25}H_{35}N_3O_2$ 409.2729, found 409.2715.



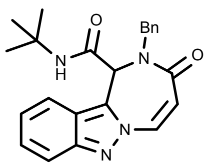
(±)-2-benzyl-4-methylene-3-oxo-*N*-(2,4,4-trimethylpentan-2-yl)-2,3,4,5-tetra-hydro-1*H*-pyrido[4,3-*b*]indole-1-carboxamide 3j: White powder, yield 39% (minor impurities of unidentified side product). **^{1}H-NMR (300 MHz, CDCl$_3$)** δ 8.00 (s, 1 H), 7.63 (d, *J* = 7.71 Hz, 1 H), 7.42 – 7.27 (m, 6 H), 7.21 (td, *J* = 7.53 Hz, 7.52 Hz, 0.83 Hz, 1 H), 7.03 (d, *J* = 7.42 Hz, 1 H), 6.03 (s, 1 H), 5.43 (d, *J* = 14.69 Hz, 1 H), 4.95 (s, 1 H), 4.88 (bs, 1 H), 4.08 (d, *J* = 14.68 Hz, 1 H), 3.74 (s, 1 H), 1.60 (d, *J* = 14.98 Hz, 1 H), 1.38 (s, 3 H), 1.33 (d, *J* = 14.97 Hz, 1 H), 1.24 (s, 3 H), 0.84 (s, 9 H); **^{13}C-NMR (151 MHz, $CDCl_3$)** δ 171.7, 167.0, 165.5, 155.2, 140.9, 136.9, 135.5, 129.5, 129.1, 129.0, 128.4, 127.7, 122.0, 121.5, 118.0, 64.1, 63.0, 56.5, 53.2, 46.3, 31.6, 31.5, 28.3, 28.2; **HRMS** calculated for $C_{28}H_{33}N_3O_2$ 443.2573, found 443.2555.



(±)-*N*-(*tert*-butyl)-2-(4-methoxybenzyl)-3-oxo-2,3-dihydro-1*H*-[1,4]diazepino[1,2-*b*]indazole-1-carboxamide 4n: White powder, yield 85%. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.89 Hz, 1 H), 7.59 (d, J = 10.13 Hz, 1 H), 7.37 – 7.26 (m, 3 H), 7.18 – 7.02 (m, 2 H), 6.92 – 6.81 (m, 2 H), 6.13 (d, *J* = 10.13 Hz, 1 H), 5.35 (s, 1 H), 5.03 – 4.89 (bs, 1 H), 4.85 (d, *J* = 14.44 Hz, 1 H), 4.74 (d, *J* = 14.44 Hz, 1 H), 3.80 (s, 3 H), 1.10 (s, 9 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 164.7, 164.5, 160.0, 150.1, 131.9, 131.2, 130.6 (2 C), 128.3, 127.8, 123.9, 121.0, 118.4, 118.3, 116.1, 114.9 (2 C), 55.6, 54.6, 52.4, 52.0, 28.5 (3 C); **HRMS** calculated for $C_{24}H_{26}N_4O_3$ 418.2005, found 418.1966.



(±)-2-benzyl-*N*-cyclohexyl-3-oxo-2,3-dihydro-1*H*-[1,4]diazepino[1,2-*b*]indazole-1-carboxamide 4o: White powder, yield 76%. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.91 Hz, 1 H), 7.57 (d, *J* = 10.14 Hz, 1 H), 7.38 – 7.27 (m, 6 H), 7.09 – 6.99 (m, 2 H), 6.14 (d, *J* = 10.14 Hz, 1 H), 5.37 (s, 1 H), 5.00 (d, *J* = 14.56 Hz, 1 H), 4.90 (d, *J* = 8.05 Hz, 1 H), 4.78 (d, *J* = 14.57 Hz, 1 H), 3.59 (tdq, *J* = 11.01 Hz, 11.01 Hz, 8.09 Hz 4.04 Hz, 4.04 Hz, 3.95 Hz, 1 H), 1.78 – 1.42 (m, 6 H), 1.19 – 0.63 (m, 4 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 164.9, 164.4, 150.1, 135.7, 131.7, 130.8, 129.5 (2 C), 129.2 (2 C), 128.6, 128.4, 124.0, 120.9, 118.3, 118.3, 116.3, 54.2, 52.6, 49.3, 32.8, 32.7, 25.3, 24.7, 24.7; **HRMS** calculated for $C_{25}H_{26}N_4O_2$ 414.2056, found 414.2047.



(±)-2-benzyl-*N*-(*tert*-butyl)-3-oxo-2,3-dihydro-1*H*-[1,4]diazepino[1,2-*b*]indazole-1-carboxamide 4q: White powder, yield 89%. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.90 Hz, 1 H), 7.60 (d *J* = 10.14 Hz, 1 H), 7.40 – 7.24 (m, 6 H), 7.14 – 7.01 (m, 2 H), 6.14 (d, *J* = 10.14 Hz, 1 H), 5.34 (s, 1 H), 4.91 (bs, 1 H), 4.873 (s, 1 H), 4.868 (s, 1 H), 1.10 (s, 9 H); **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 164.9, 164.4, 150.2, 135.9, 131.9, 131.1, 129.6 (2 C), 129.3 (2 C), 128.7, 128.4, 124.0, 121.0, 118.4, 116.1, 54.8, 52.6, 52.5, 28.5 (3 C); **HRMS** calculated for $C_{23}H_{24}N_4O_2$ 388.1899, found 388.1891.

The Spectra of the obtained products **2r – 2u** are in full accordance to the already published analytical data.

Procedure for the synthesis of the Al-SBA-15

The parent SBA-15 materials were prepared using tetraethylorthosilicate (TEOS) and aluminium isopropoxide as silica and aluminium sources, respectively. The triblock non-ionic copolymer EO20PO70EO20 (*Pluronic* P123 surfactant) was employed as template. All reagents were purchased from *Sigma-Aldrich*. The mesoporous material was prepared following a previously reported procedure [1]. The Pluronic (8 g) was dissolved in 300 mL HCl at pH 1.5 under stirring and the solution was kept at 40 ºC for 2 h. Upon complete dissolution, the quantity of precursor employed (to achieve theoretical Si/Al = 20 molar ratio) was stirred with the TEOS and the mixture was then stirred for 24 h at 35 °C, and subsequently subjected to a hydrothermal treatment at 100 ºC for 24 h. The white solid formed was filtered off and oven-dried at 60°C. The template was removed by calcination at 600°C for 8 h, under N2 (4 h) and air (4 h).

[1] A. Pineda, A.M. Balu, J.M. Campelo, R. Luque, A.A. Romero, J.C. Serrano-Ruiz, *Catal. Today*, **2012**, *187*, 65-69

Functionalization of Al-SBA-15 with Au nanoparticles

For the preparation of Au material, 1 g solid support and 0.083 g HAuCl4·3H2O reagent grade purchased from *Sigma-Aldrich* (equivalent to a theoretical 4 wt.% Au) were milled together in a Retsch PM-100 planetary ball mill using a 125 mL reaction chamber and eighteen 10 mm stainless steel balls. Optimised milling conditions [2] of 10 min and 350 rpm were used. Upon incorporation of the metal, the sample was calcined at 400 ºC (4 h, in air).

[2] A. Pineda , A.M. Balu, J.M. Campelo, A.A. Romero, D. Carmona, F. Balas, J. Santamaria, R. Luque, ChemSusChem , **2011**, *4*, 1561-1565

Determination of the Turn-Over-Number (TON)

The TON was determined for an Au nanoparticle rather than an Au atom. The reason for this is the fact that many Au atoms are inside the cluster of the nanoparticle and do not participate in the reaction at all. From the TEM images of the catalyst we determined an average nanoparticle size of 7 nm. Assuming a perfect sphere of the nanoparticle we calculated the number of Au atoms belonging to the average nanoparticle. Following we could calculate the average number of nanoparticles in the amount of catalyst used for the experiment (2 mg, 203.05 nmol, 0.0385 mol% Au as 2 wt% Au@Al-SBA15). The amount of substrate used was 527.9 μmol. The TON is defined as the number of molecules of substrate divided by the number of molecules of catalyst.

$$TON = \frac{N_{substrate}}{N_{catalyst}}$$

with $N_{substrate}$= number of substrate molecules and $N_{catalyst}$ = number of gold atoms

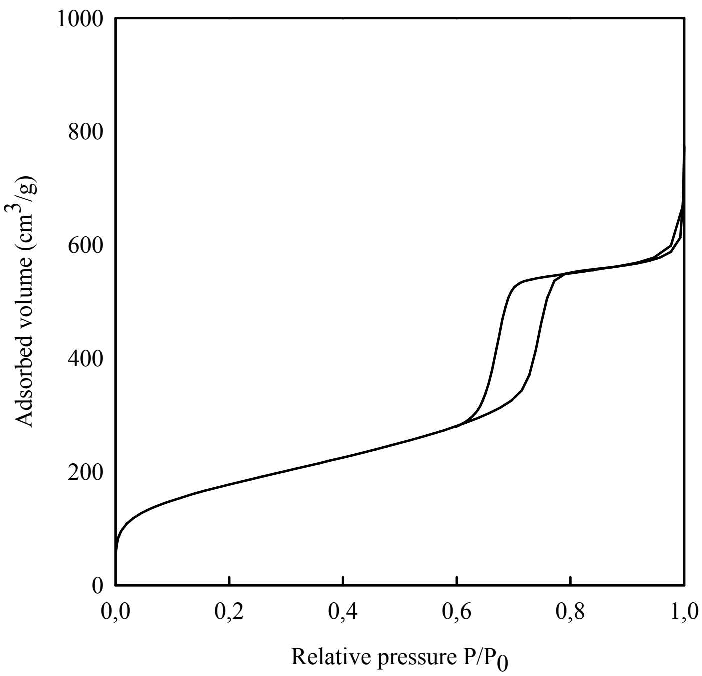
Discussion on the catalysts special characteristics

One might assume that under the harsh conditions of the ball milling process, giving hot spots with high pressure, the mesoporous character of the SBA15 would collapse. In fact it can clearly be seen in the TEM images on page 16 of the supporting information that the mesopores do not collapse during the milling process. Additional support is given by BET measurement of the catalyst which is shown on page 15 of the supporting information. The BET surface area is with 646.49 m^2/g in the range of SBA15 and the pore diameter of 7.79 nm as well as the volume with 0.7813 ml/g fit the characteristics of SBA 15 as well.

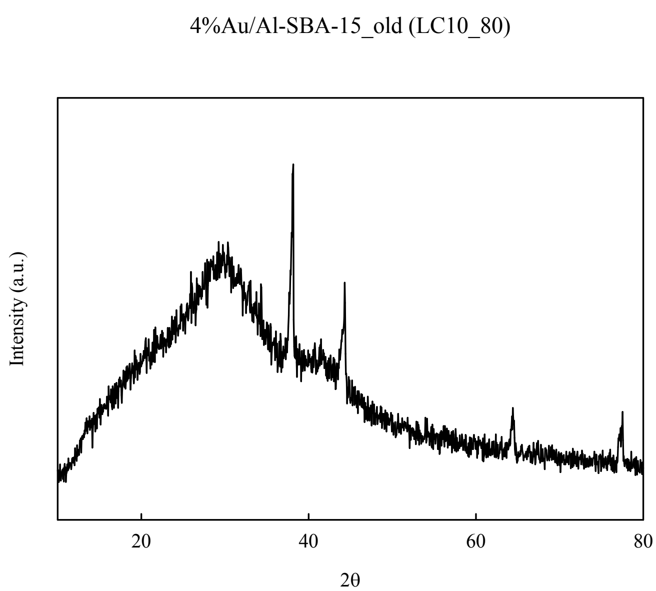
Characterization of the catalyst

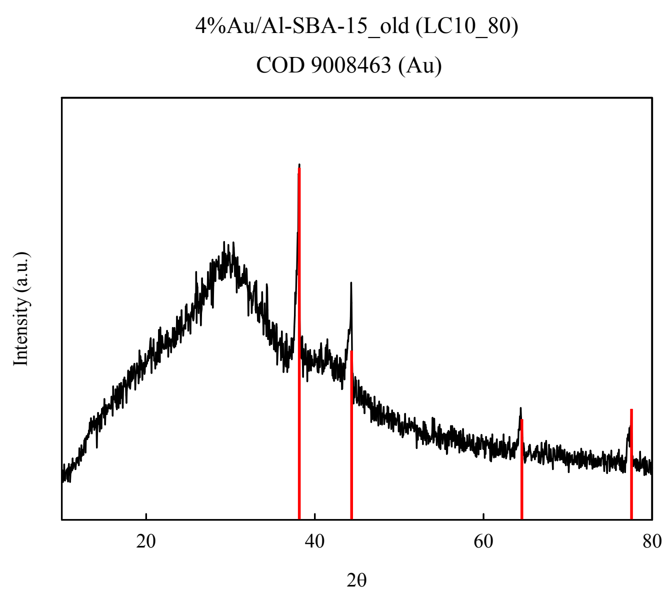
BET Surface Area and Porosity Measurment

Material	Surface Area ($m^2 g^{-1}$)	Pore Diameter (nm)	Pore Volume ($ml\ g^{-1}$)
4%Au/Al-SBA-15	646.09	7.79	0.7813



XRD Measurement

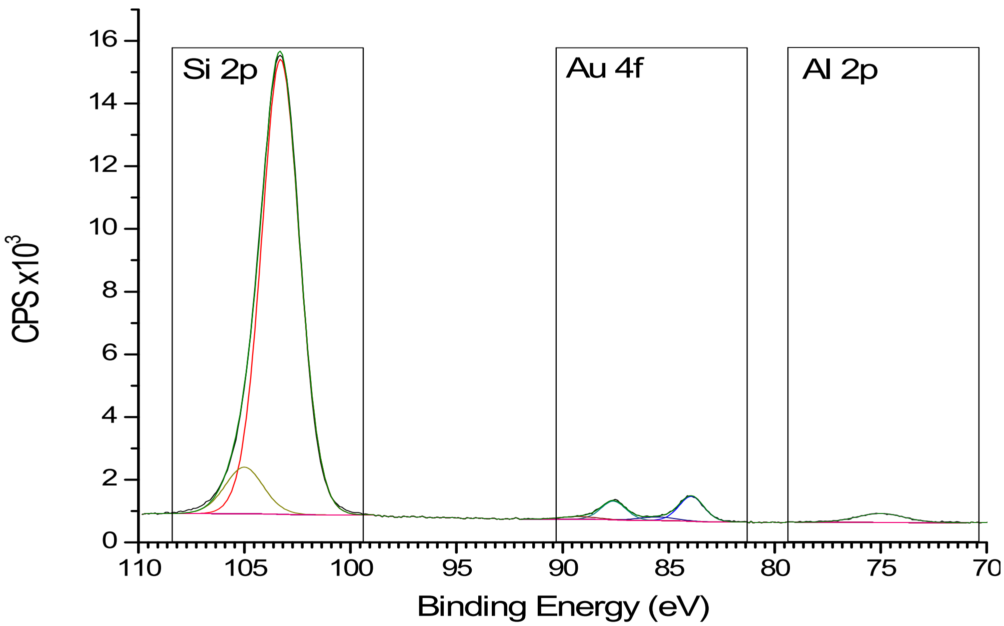


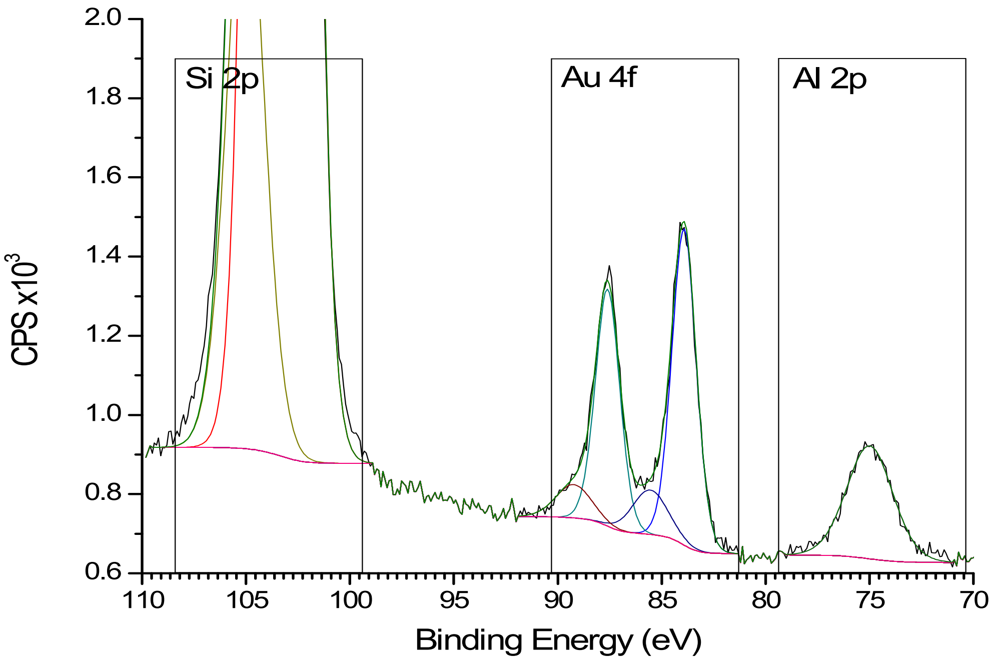


XPS Measurement

XPS experiments were performed on a Thermo Scientific K-Alpha apparatus, equipped with an Al Ka (1486.6 eV) X-ray anode. The catalysts were deposited on a carbon sticky tape in order to prevent charging. For analyzing the XPS spectra, the CasaXPS program is used.

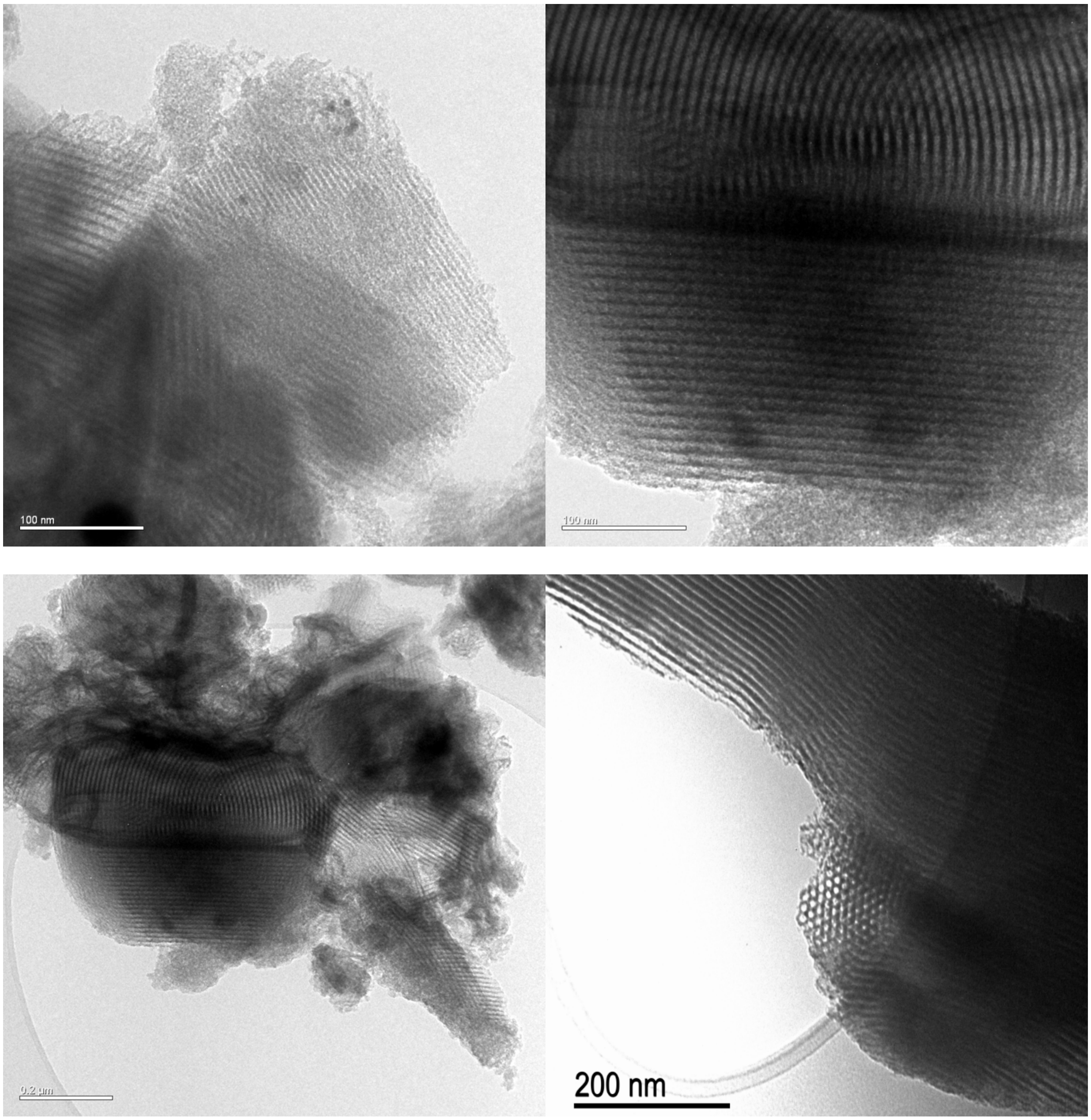
	Si 2p	*Au 4f*	*Au 4f*	*Al 2p*	*Si 2p*	*Au 4f*	*Au 4f*
Binding Energy eV	103,3	83,66	87,34	75,08	105,22	85,7	89,38

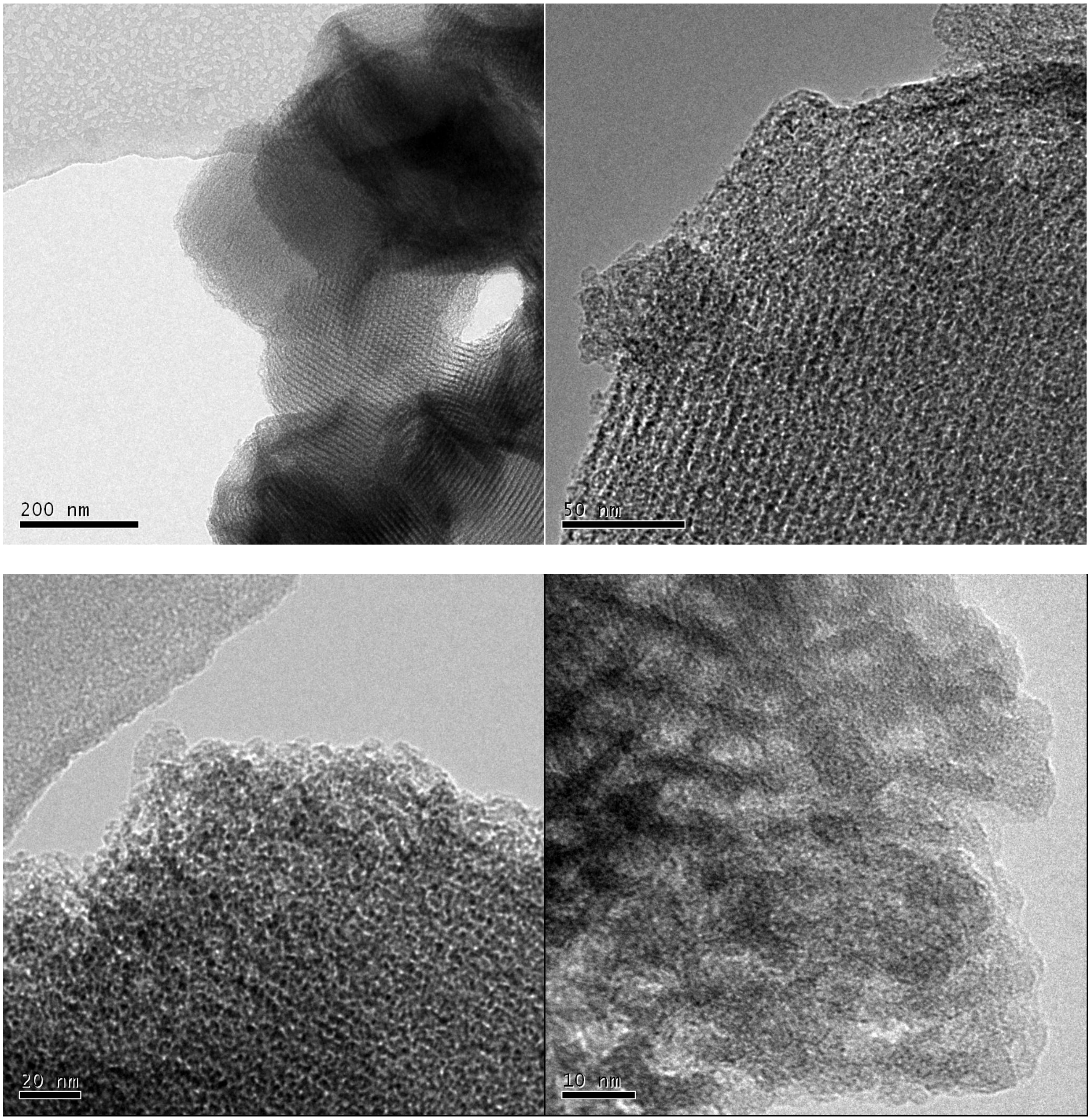




TEM Images

Bright-field TEM analysis has been performed on a Tecnai 20 apparatus equipped with a field emission gun at 200 keV.





Crystallography

Single crystals of **4n**, suitable for X-ray diffraction were obtained by slow evaporation from ethanol at room temperature. X-ray intensity data were collected at 100K on an Agilent Supernova diffractometer, equipped with an Atlas CCD detector, using Mo Kα radiation (λ = 0.71073 Å). The images were interpreted and integrated with the CrysAlisPro software from Agilent Technologies [1]. Using Olex2 [2], the structure was solved with the ShelxS [3] structure solution program using Direct Methods and refined with the ShelxL [3] refinement package using full-matrix least squares minimization on F2. As the structure was twinned, HKLF5 refinements were performed. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors were fixed at 1.2 times Ueq of the parent atoms (1.5 for methyl groups). CCDC 1033069 contains the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Crystallographic data

$C_{24}H_{26}N_4O_3$, M =418.49 g mol^{-1}, triclinic, P-1 (no. 2), a = 6.6676(7) Å, b = 7.3731(7) Å, c = 21.962(3) Å, α = 98.895(9)°, β = 91.912(9)°, γ = 99.057(8)°, V = 1051.55(19) Å^3, T = 100.01(10) K, Z = 2, ρ_{calcd} = 1.322 g cm^{-3}, μ(Mo Kα) = 0.089 mm-1, F(000) = 444, crystal size 0.2 x 0.2 x 0.2 mm^3, 4555 reflections measured, 4041 unique which were used in all calculations. The final wR_2 was 0.1519 (all data) and R_1 was 0.0563 (>2sigma(I)).

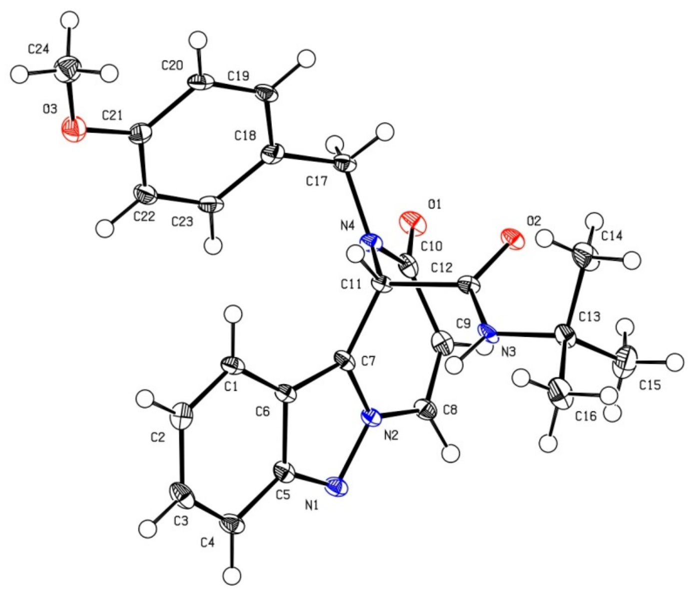


Figure 1: Asymmetric unit of **4n**. The thermal ellipsoids are drawn at 50% probability level.

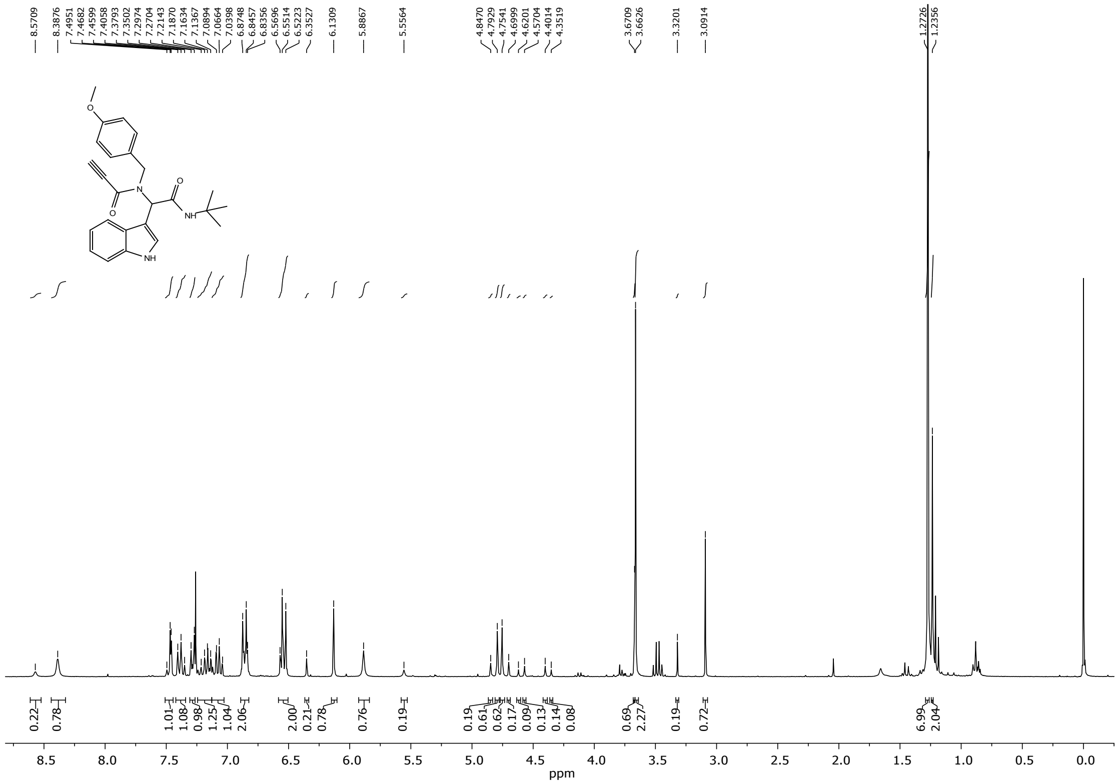
[1] CrysAlis PRO **2012**, Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England.

[2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. **2009**, *42*, 339-341.

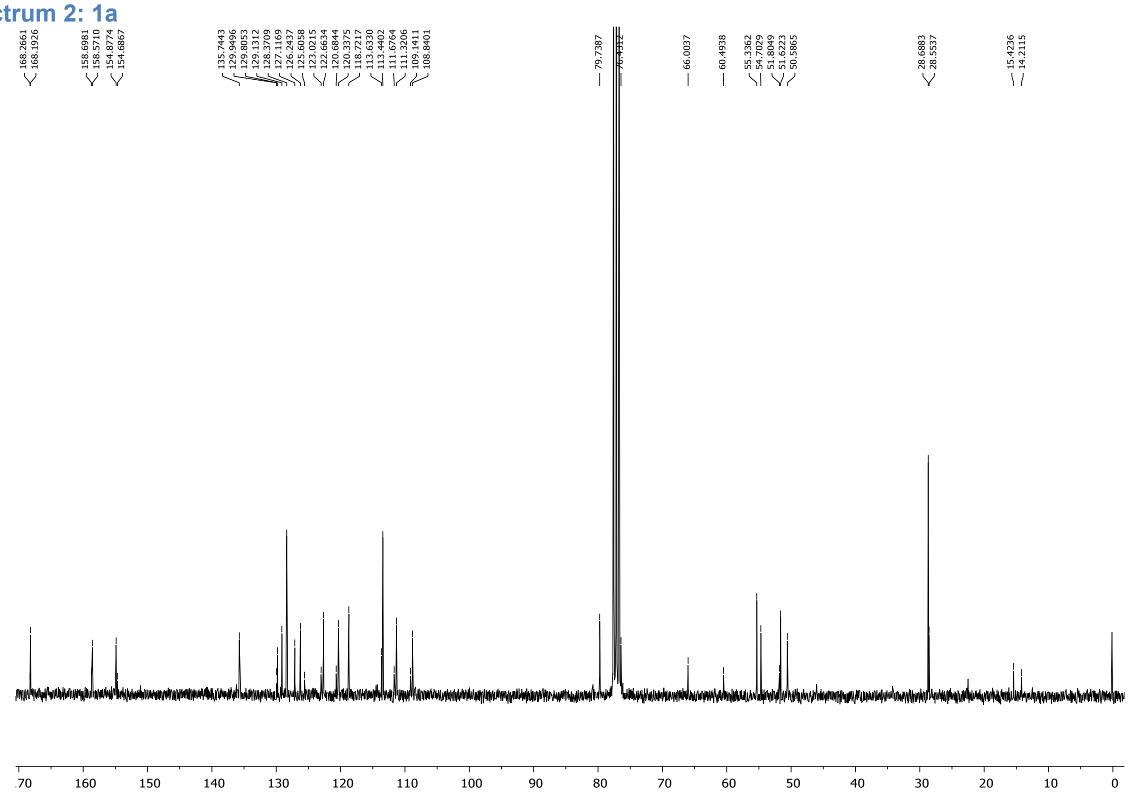
[3] G.M. Sheldrick, Acta Cryst. **2008**. A64, 112-122.

^{1}H-NMR and ^{13}C-NMR Spectra

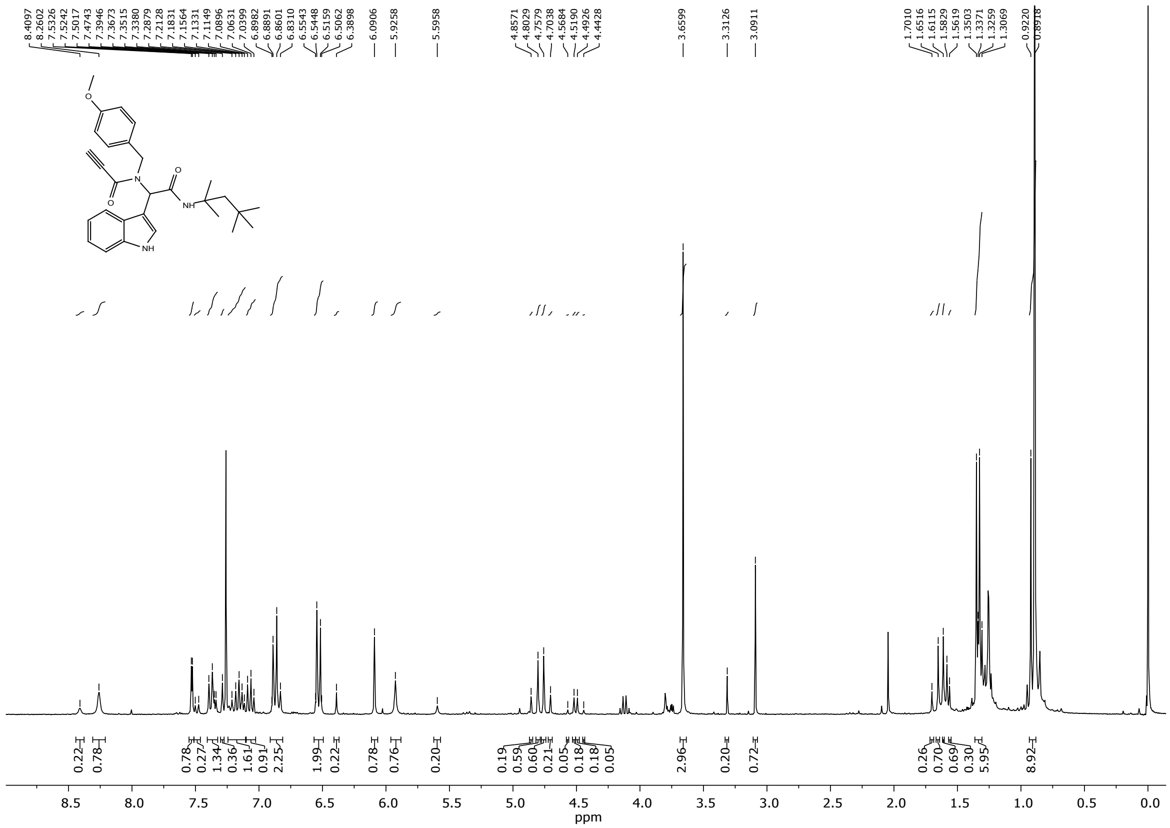
Spectrum 1: 1a



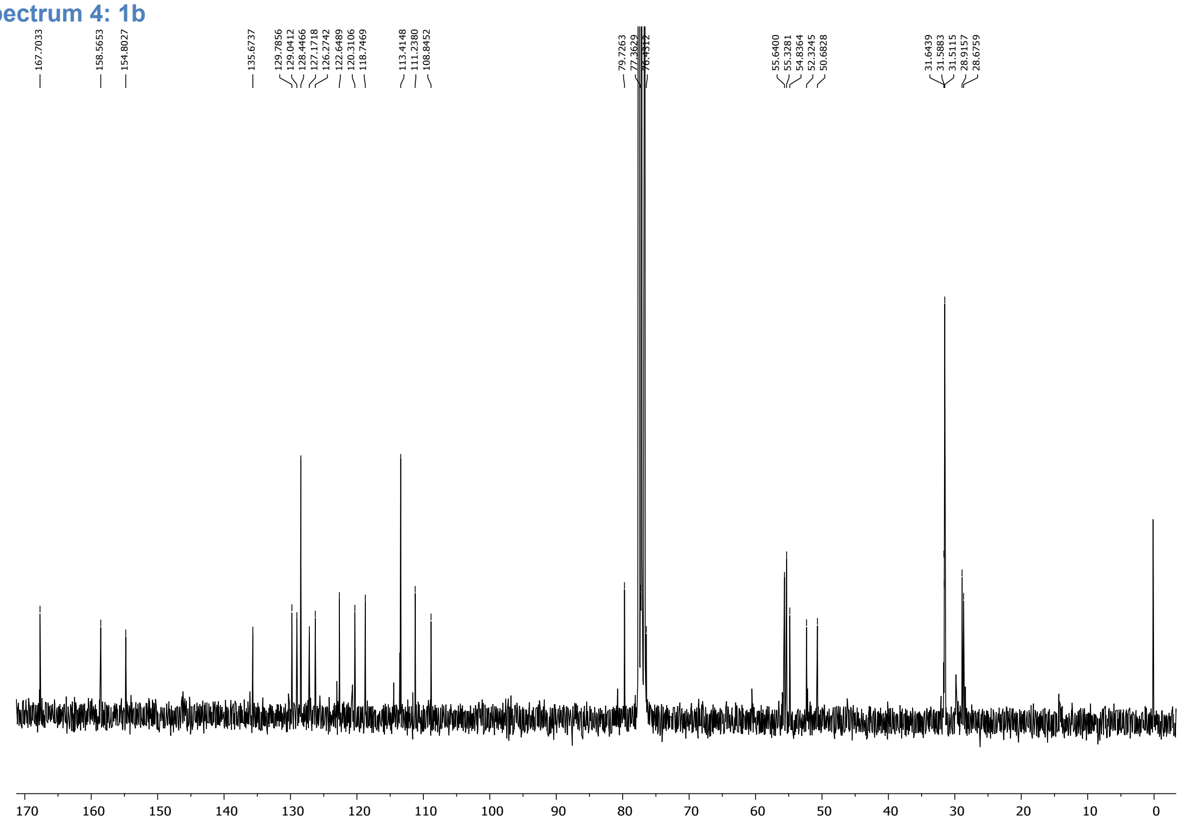
Spectrum 2: 1a



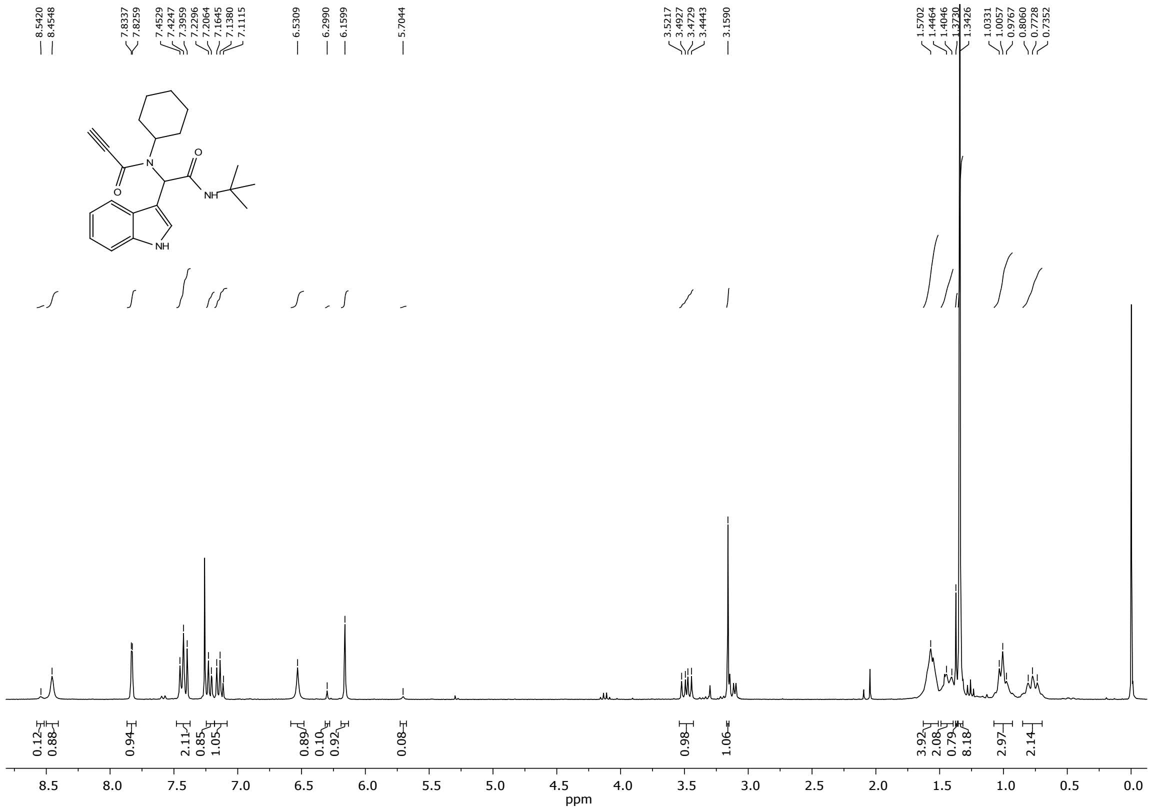
Spectrum 3: 1b



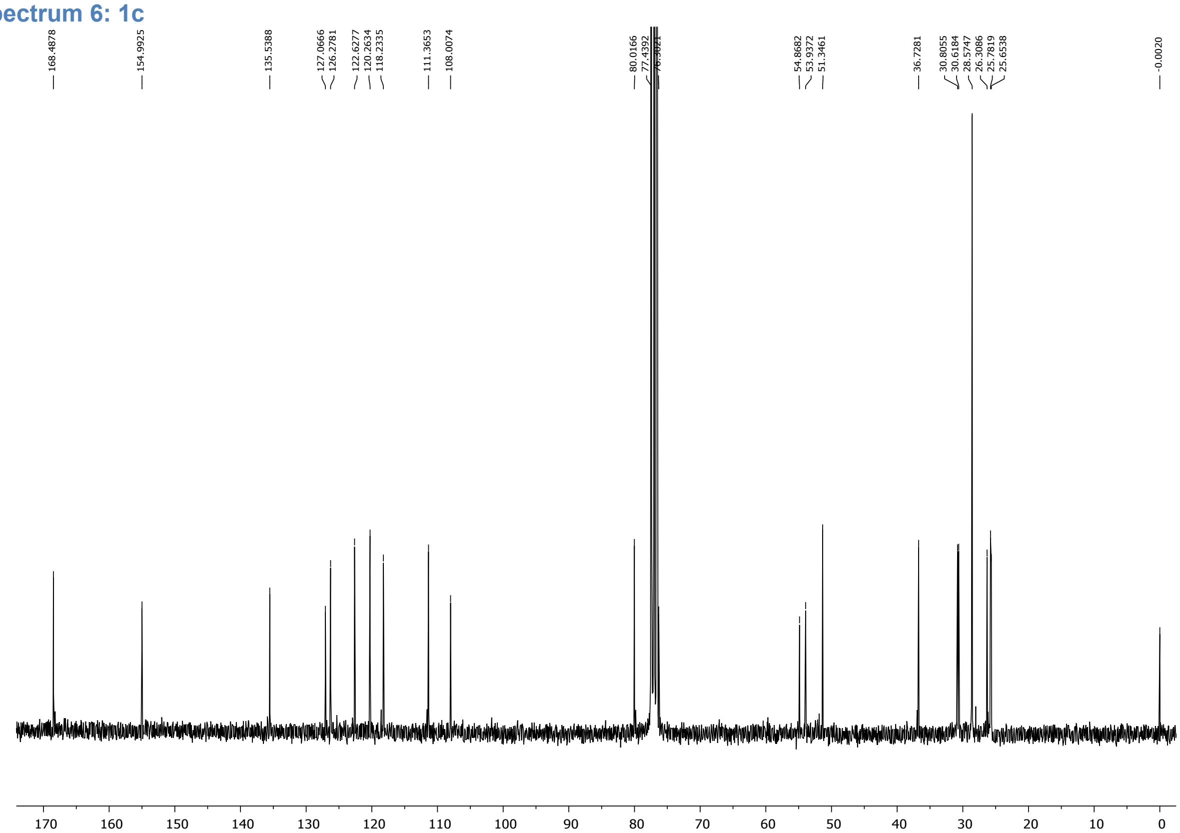
Spectrum 4: 1b



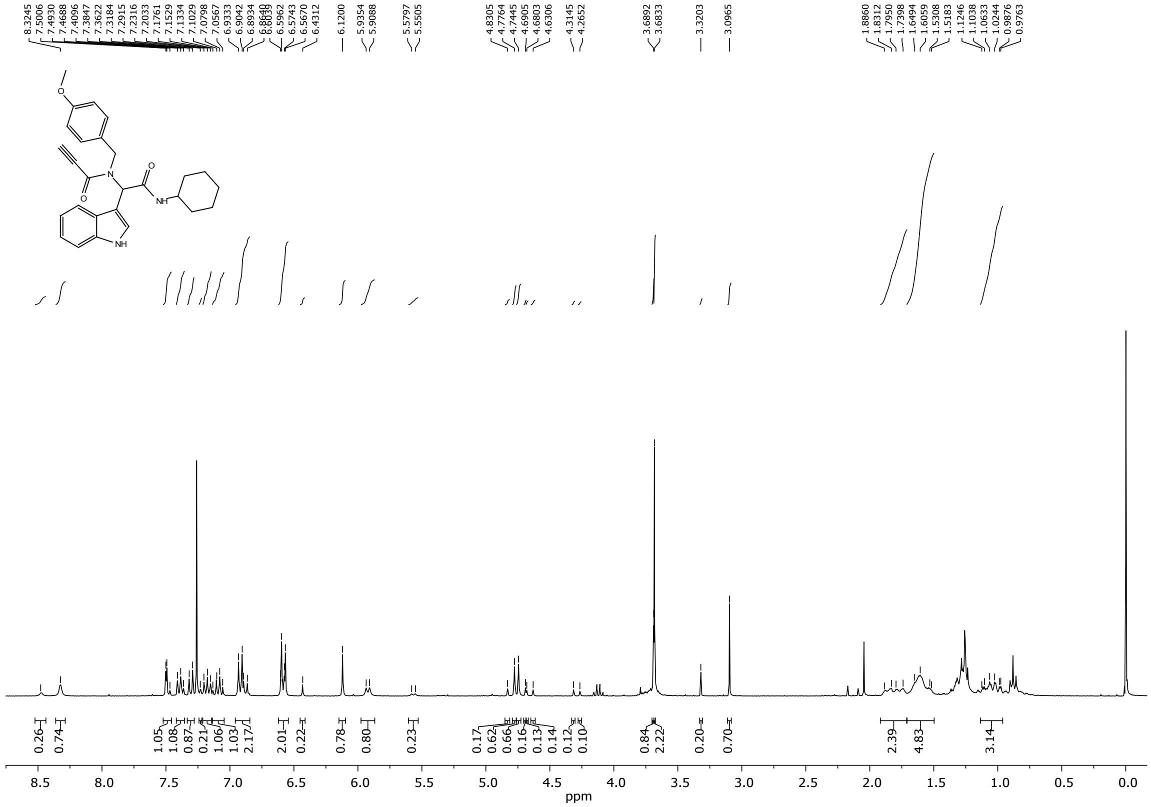
Spectrum 5: 1c



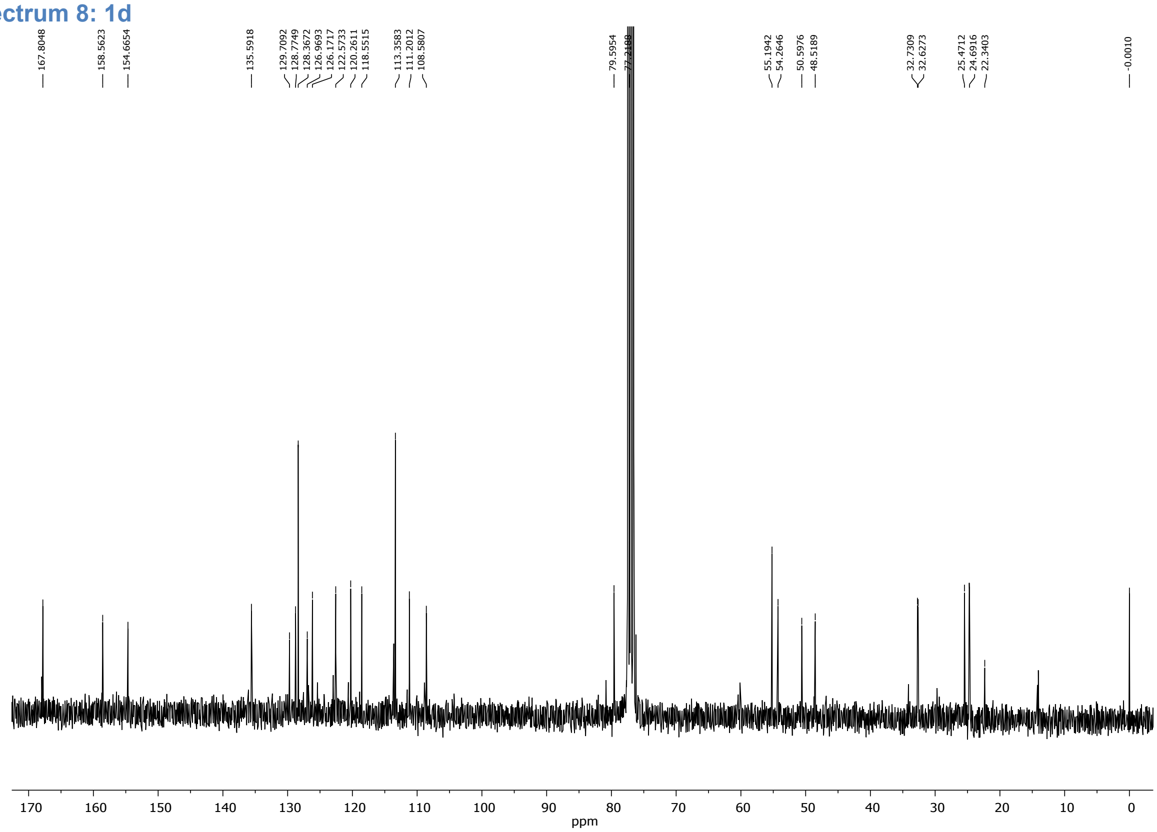
Spectrum 6: 1c



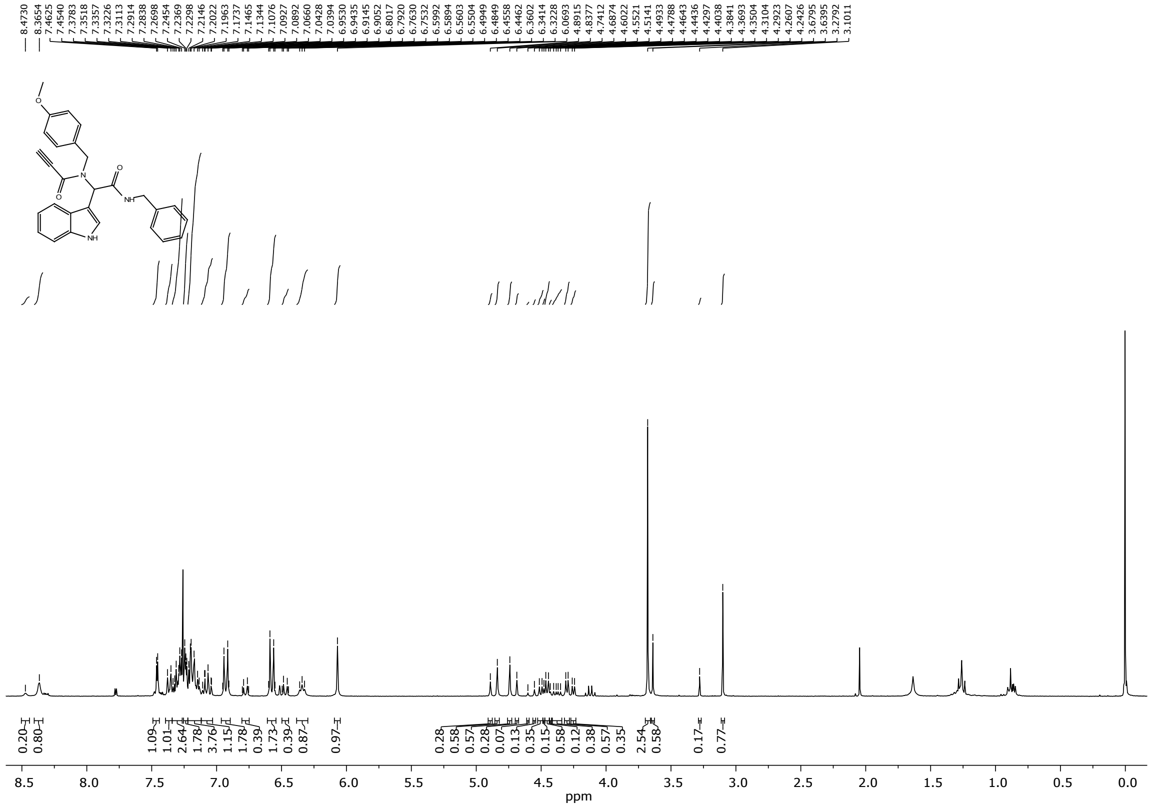
Spectrum 7: 1d



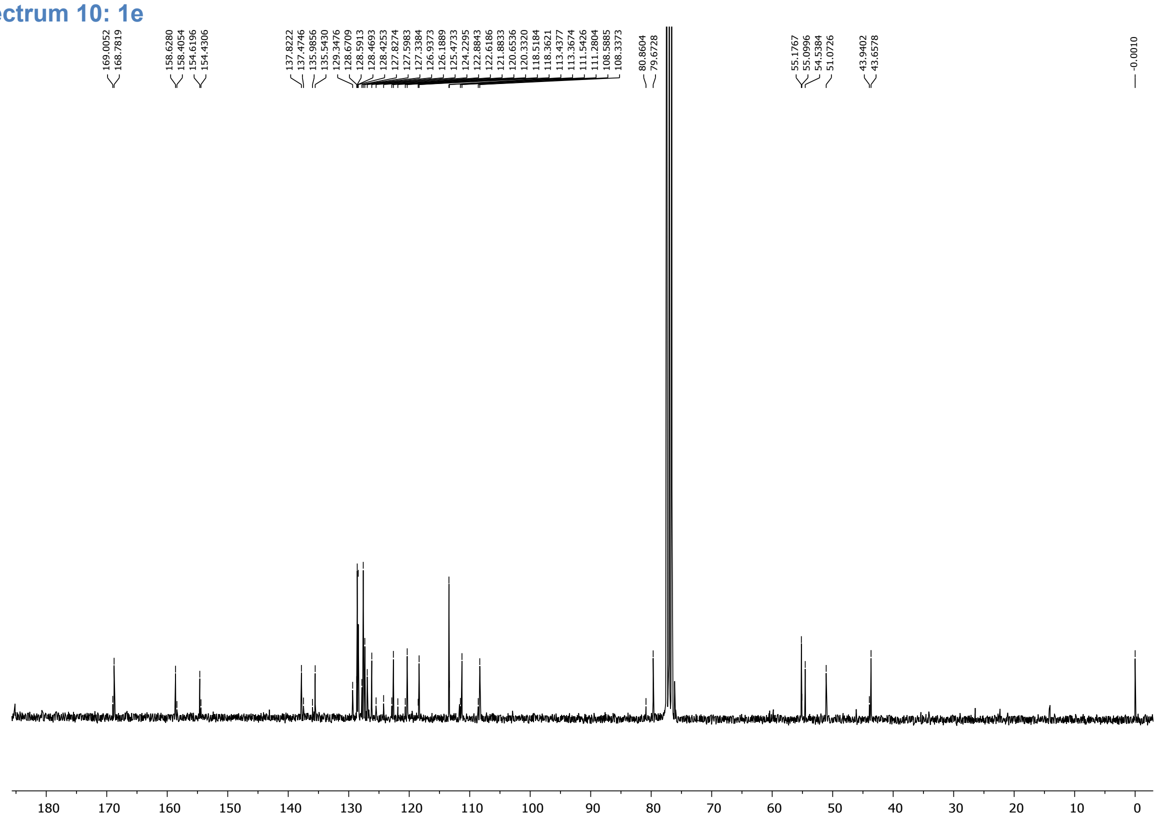
Spectrum 8: 1d



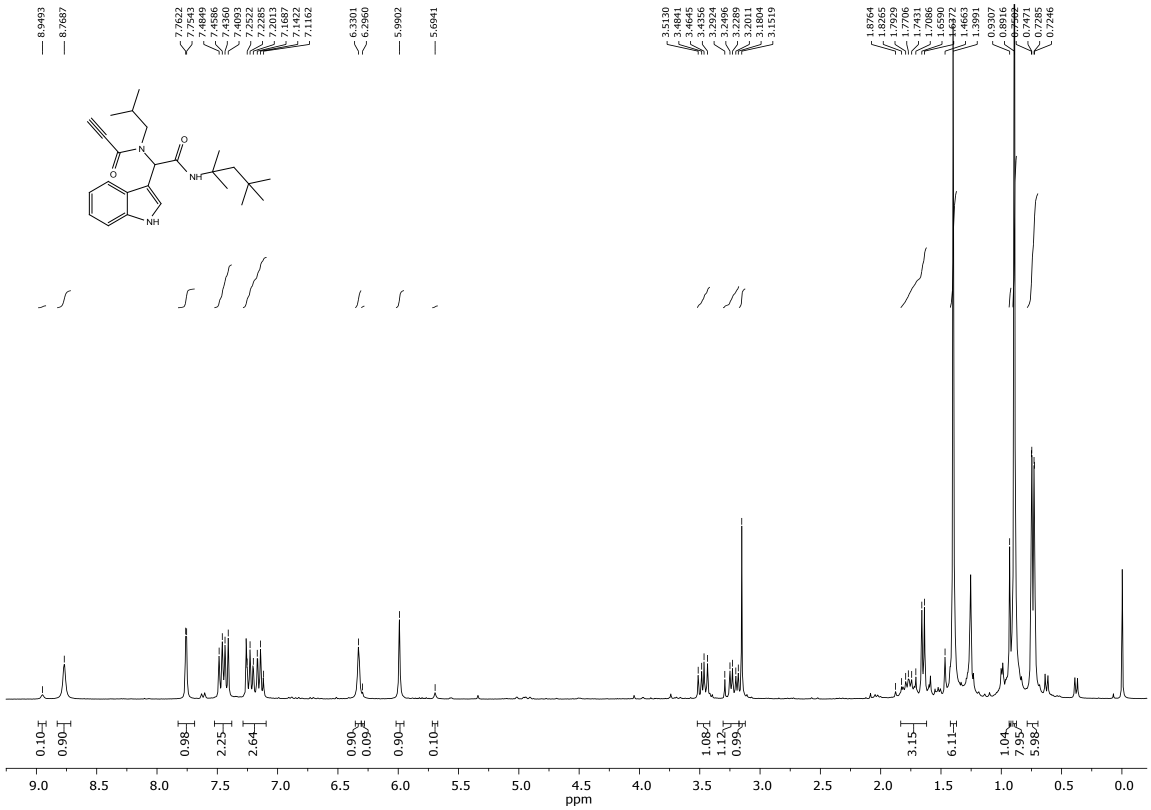
Spectrum 9: 1e



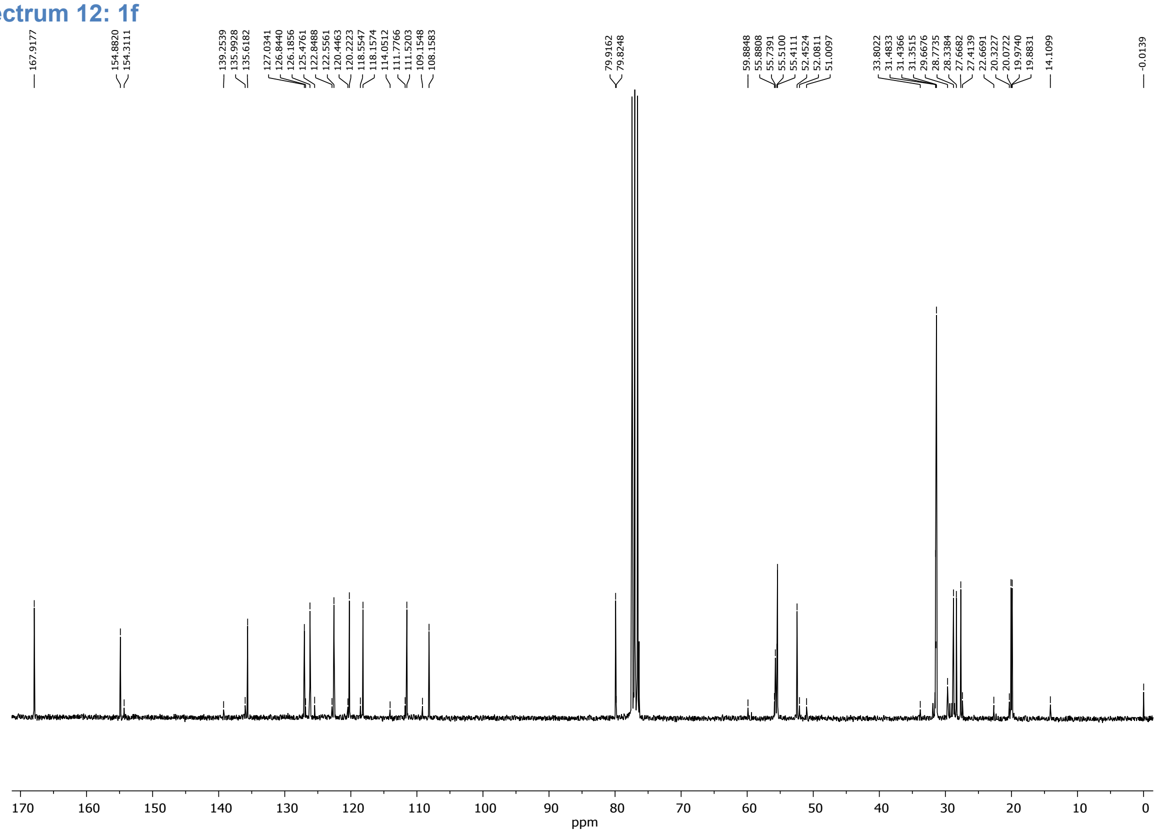
Spectrum 10: 1e



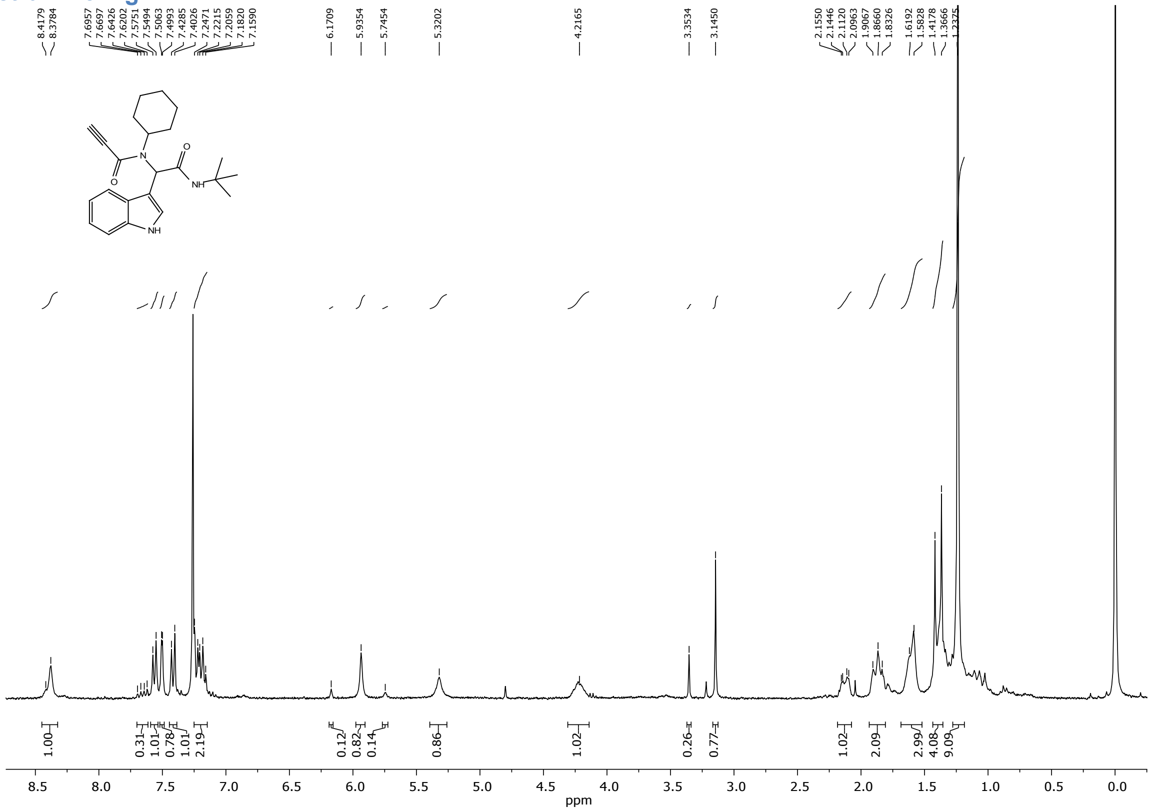
Spectrum 11: 1f



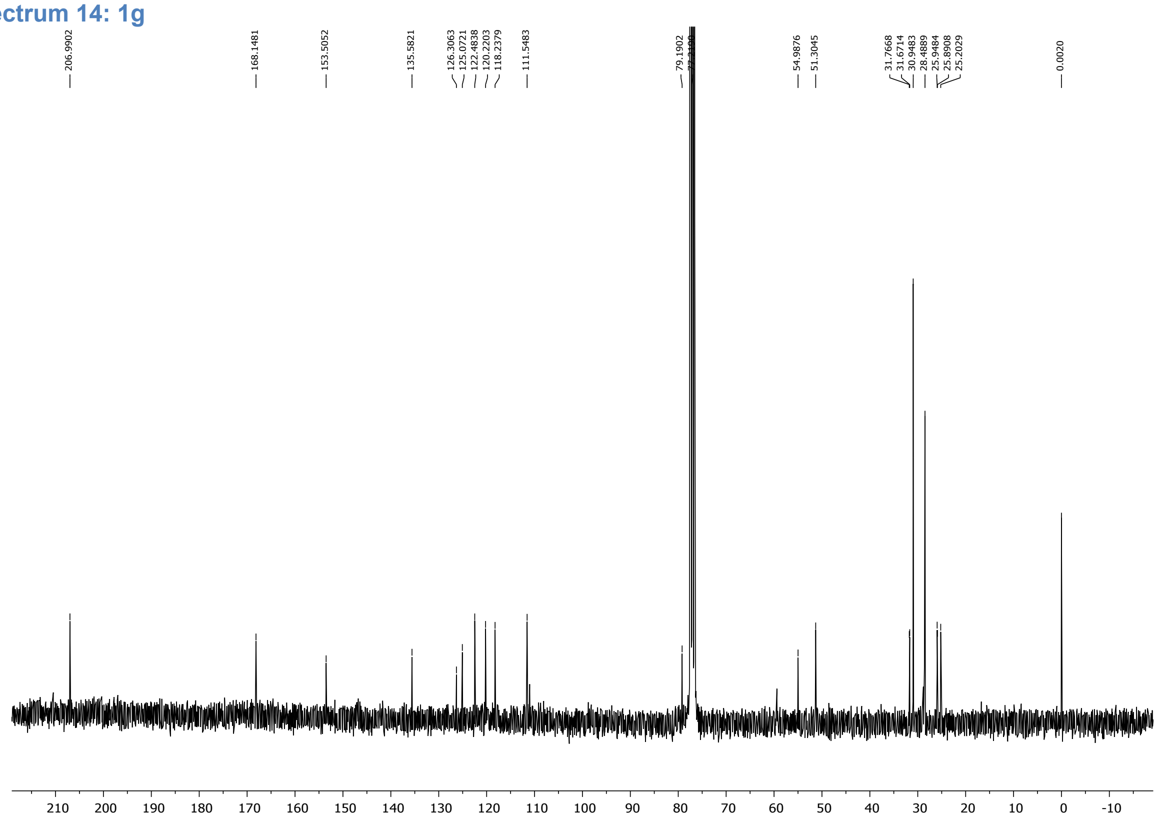
Spectrum 12: 1f



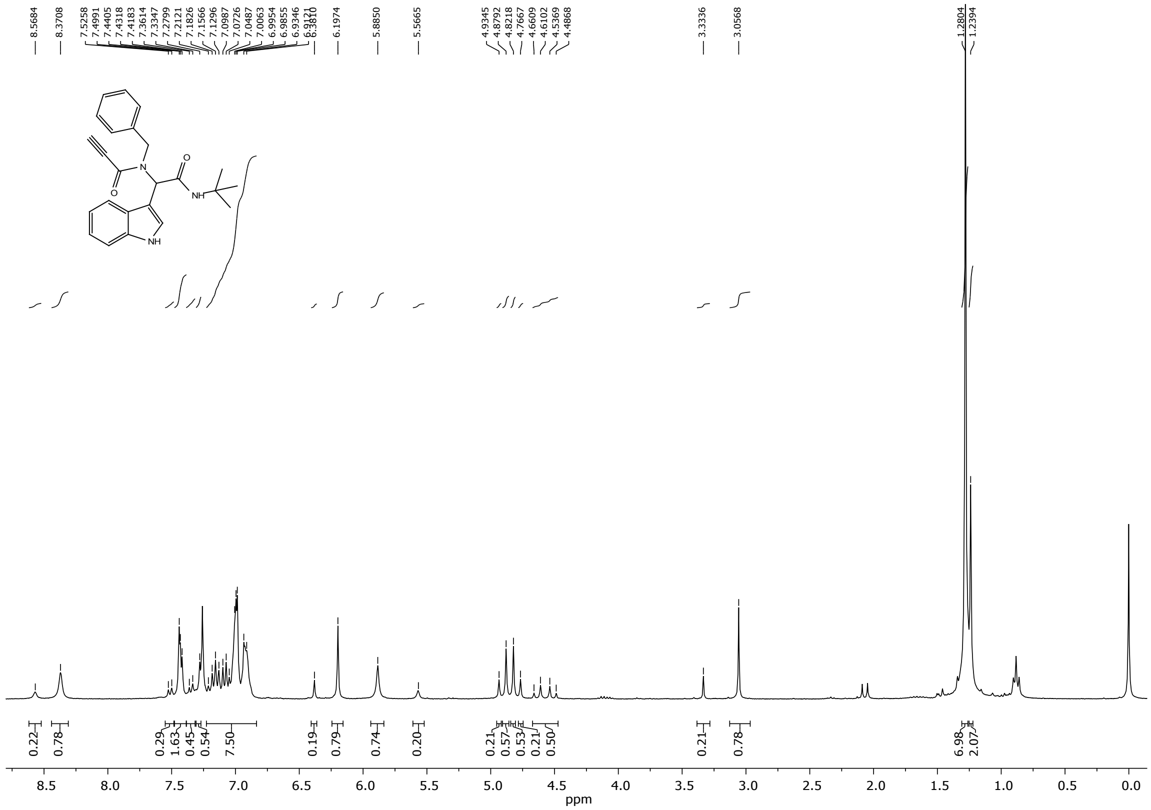
Spectrum 13: 1g



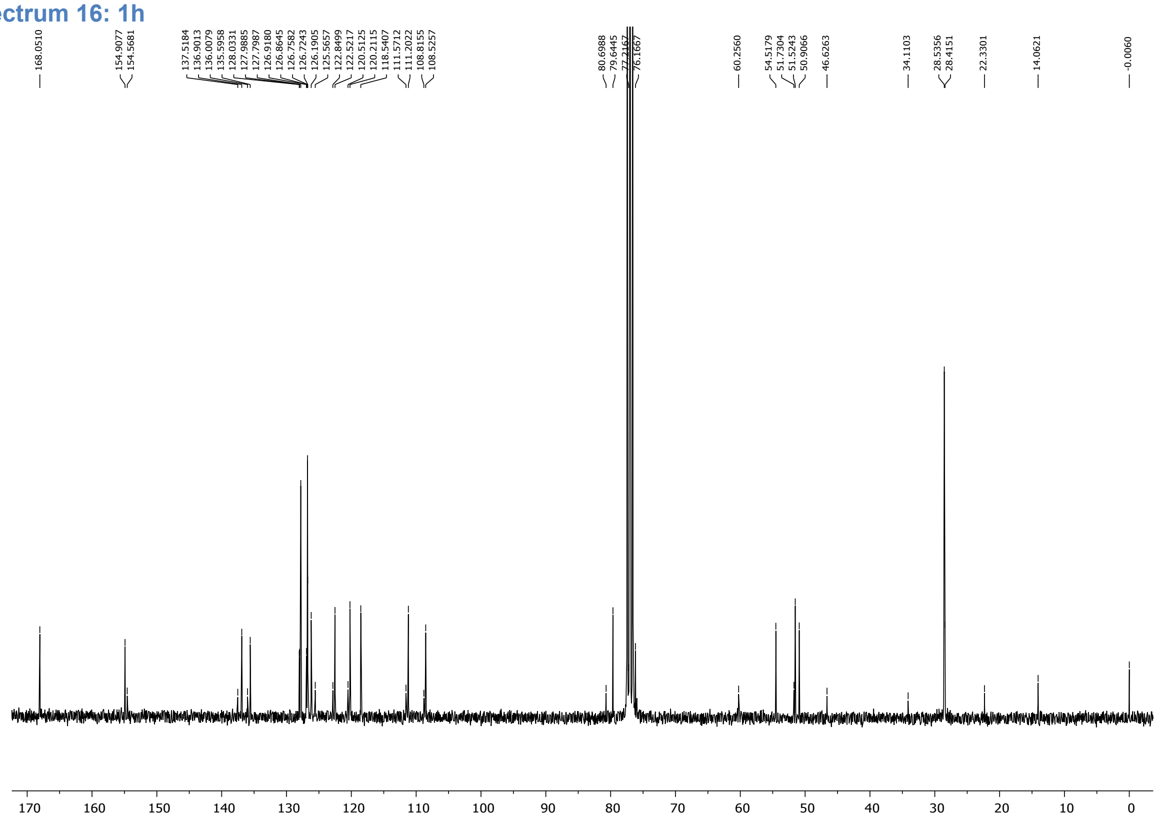
Spectrum 14: 1g



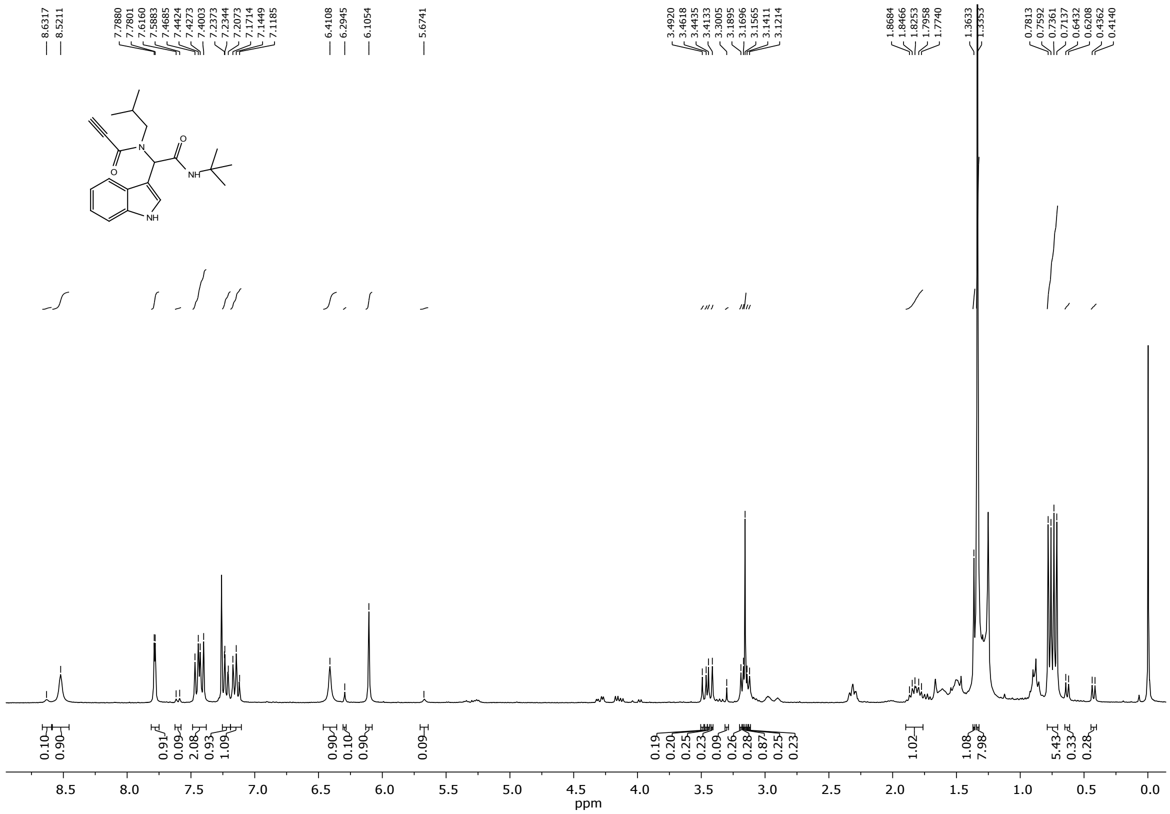
Spectrum 15: 1h



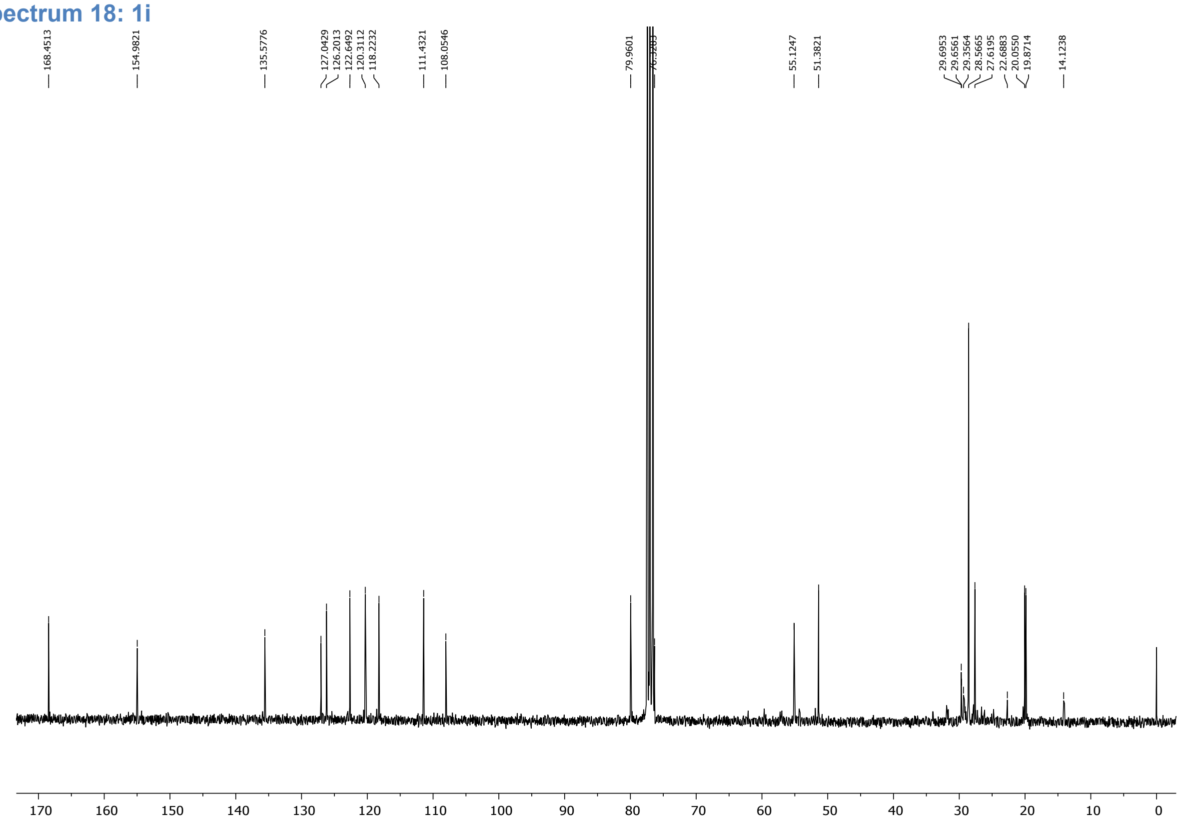
Spectrum 16: 1h



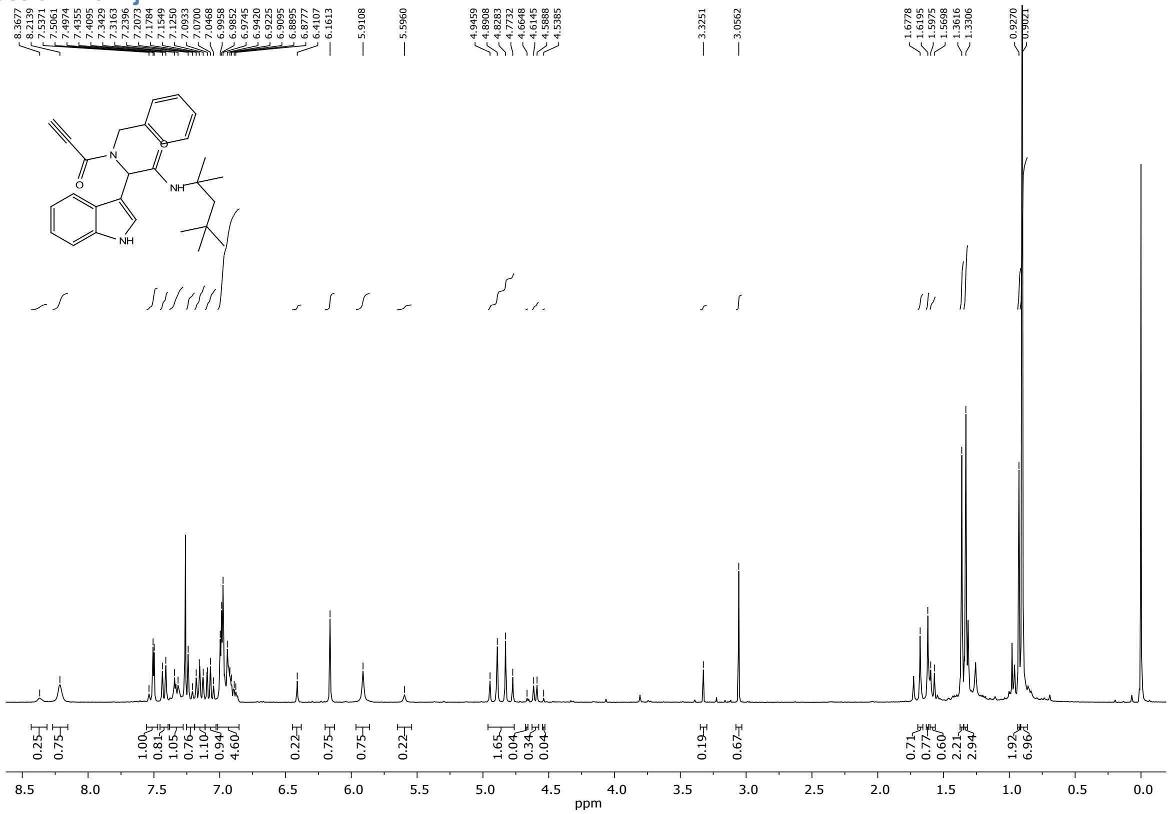
Spectrum 17: 1i



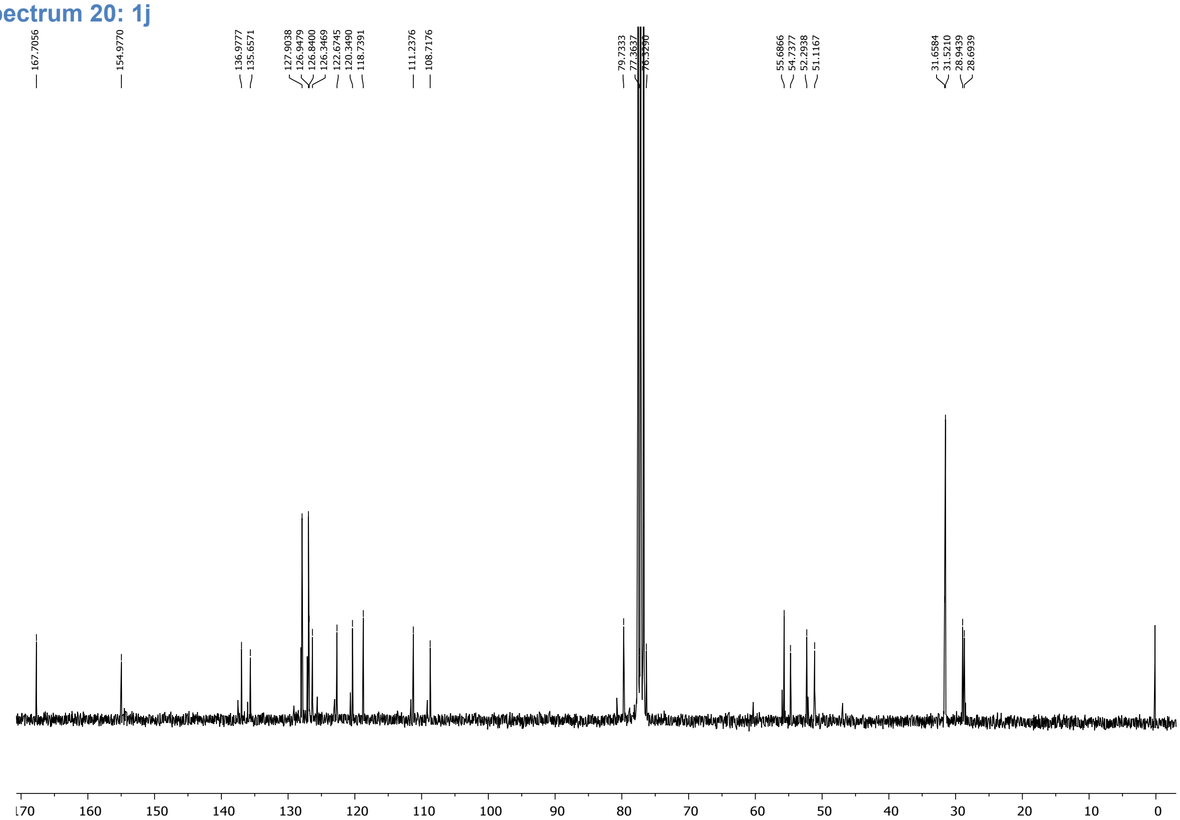
Spectrum 18: 1i



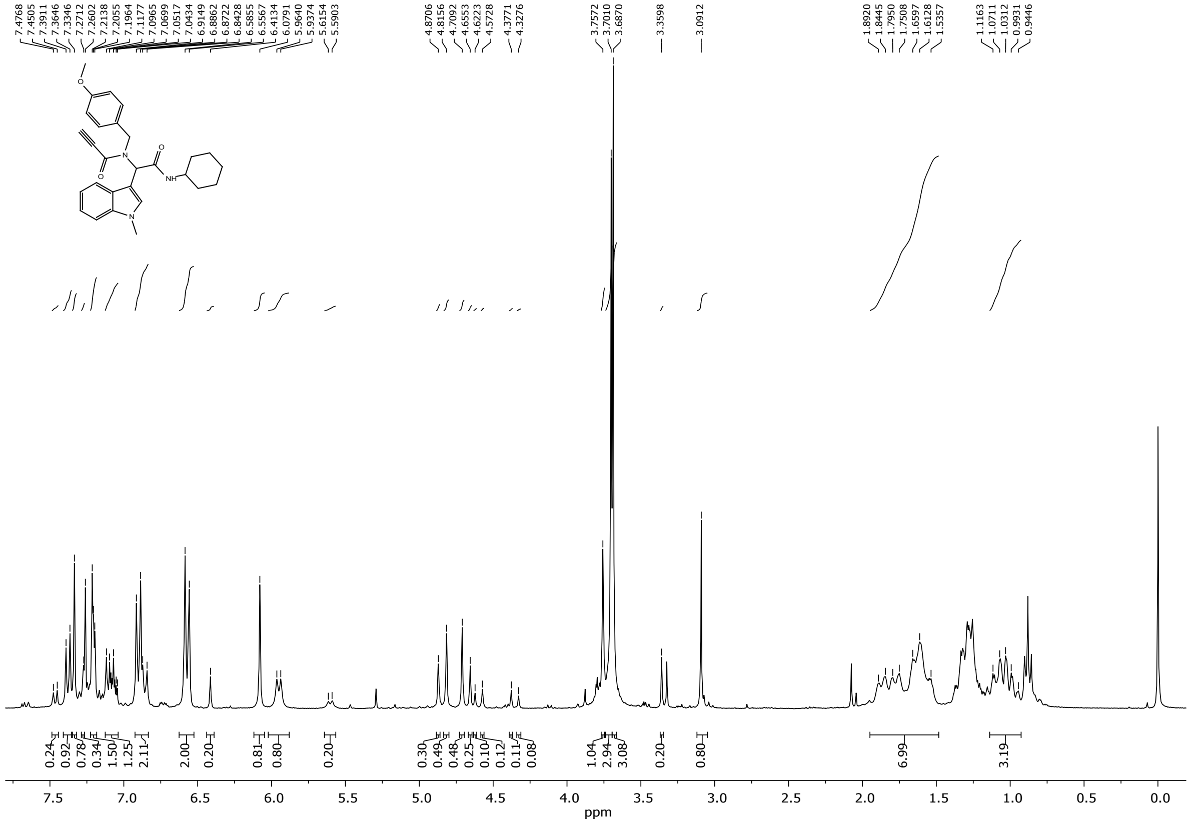
Spectrum 19: 1j



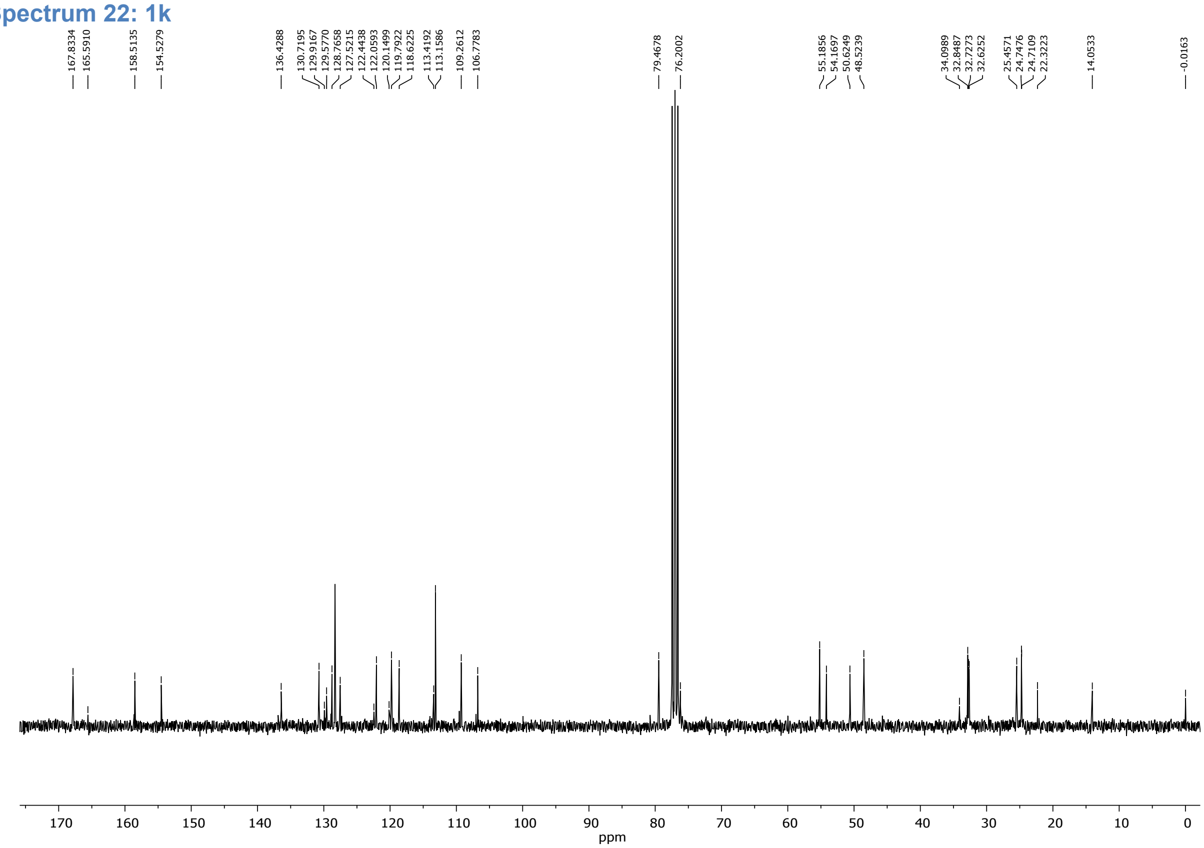
Spectrum 20: 1j



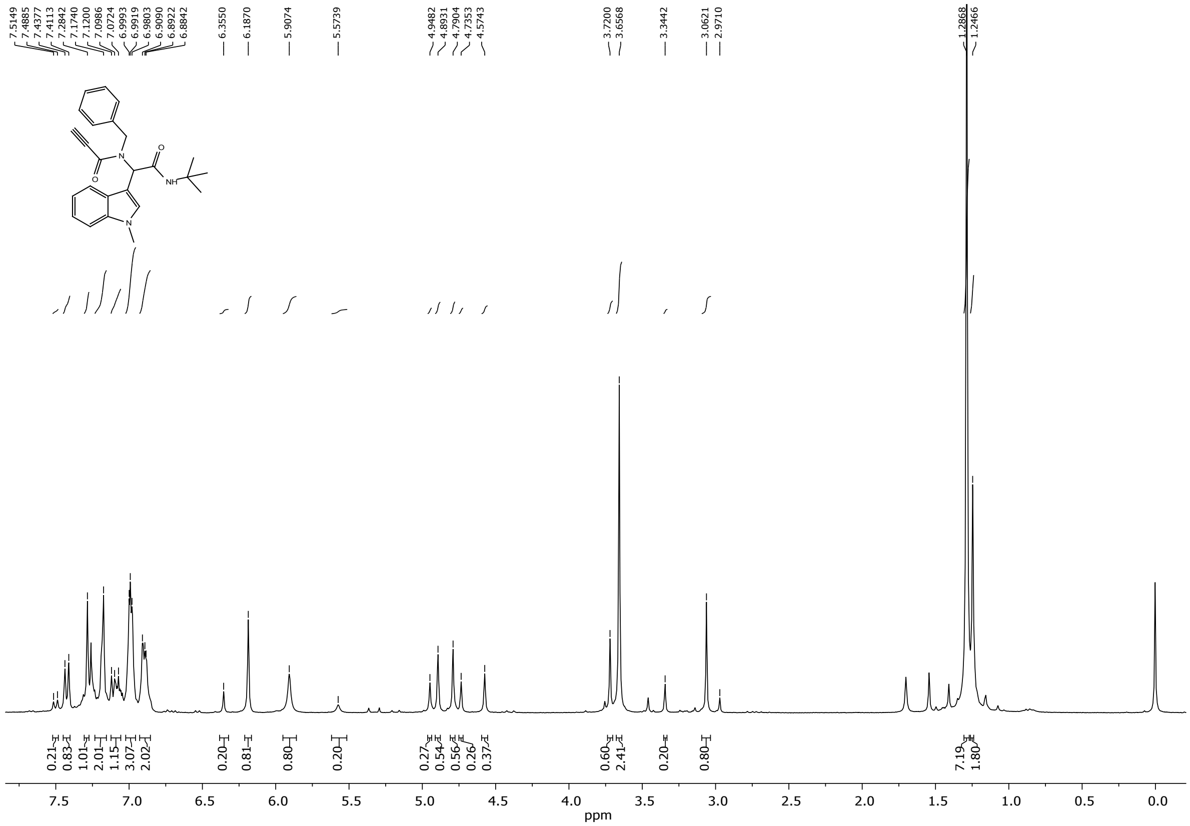
Spectrum 21: 1k



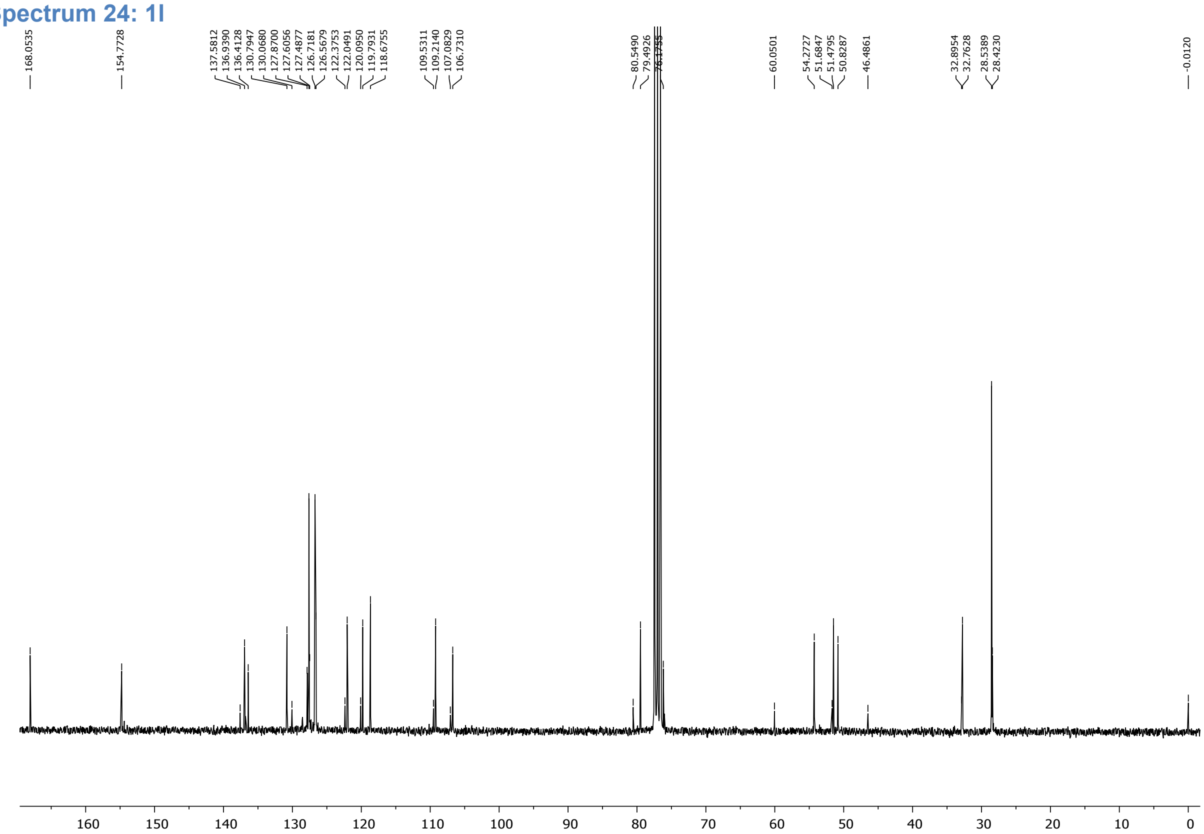
Spectrum 22: 1k



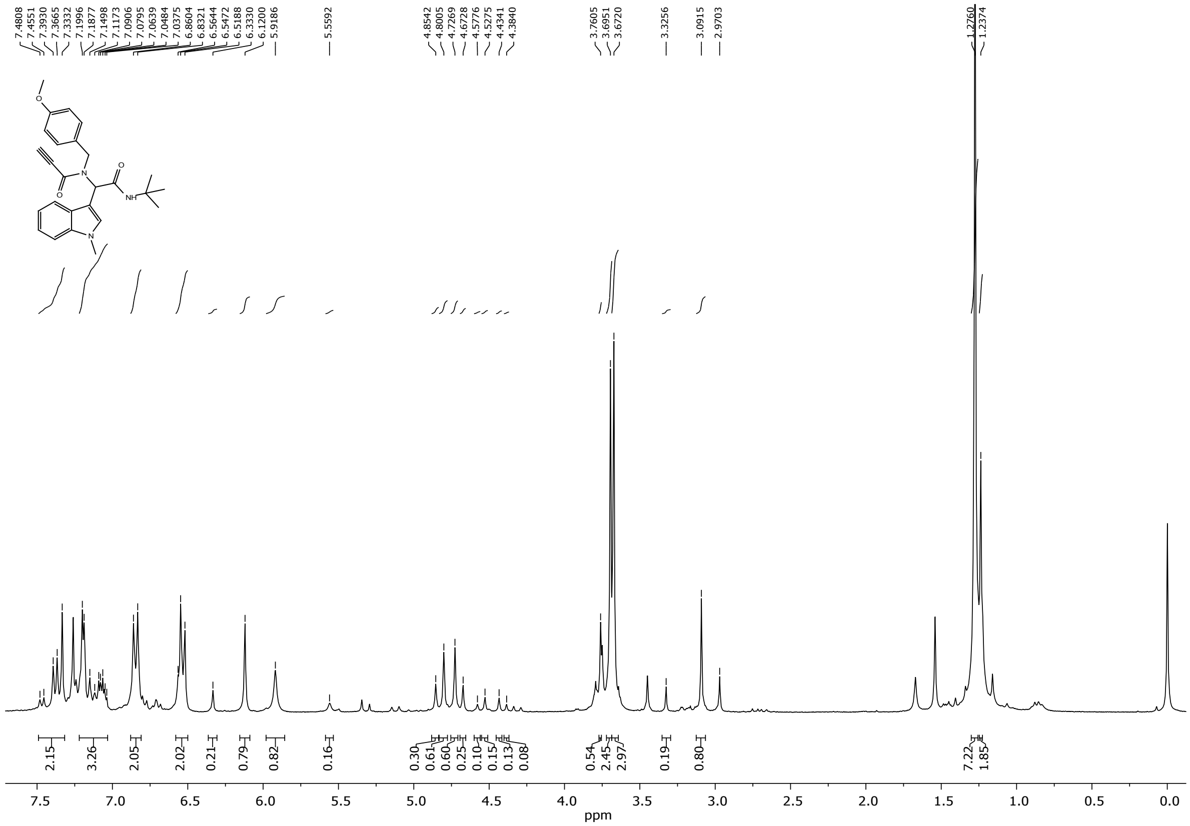
Spectrum 23: 1l



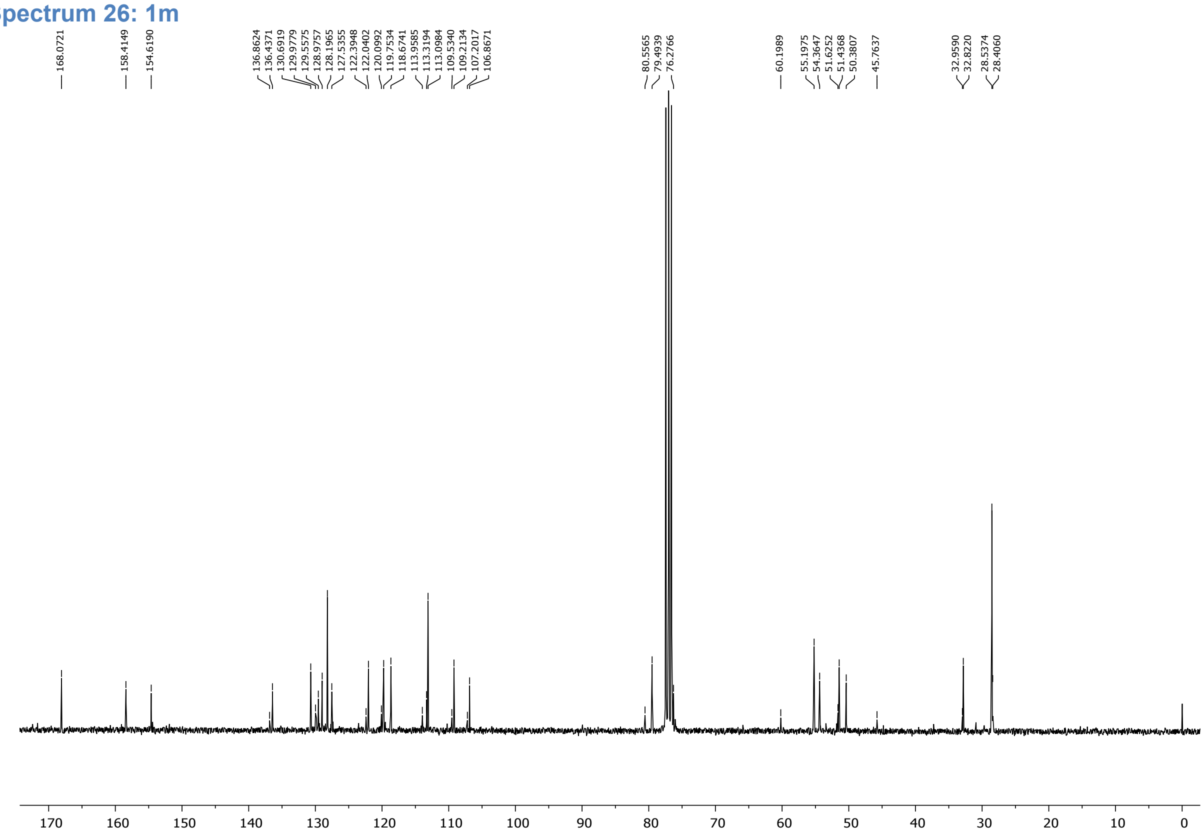
Spectrum 24: 1l



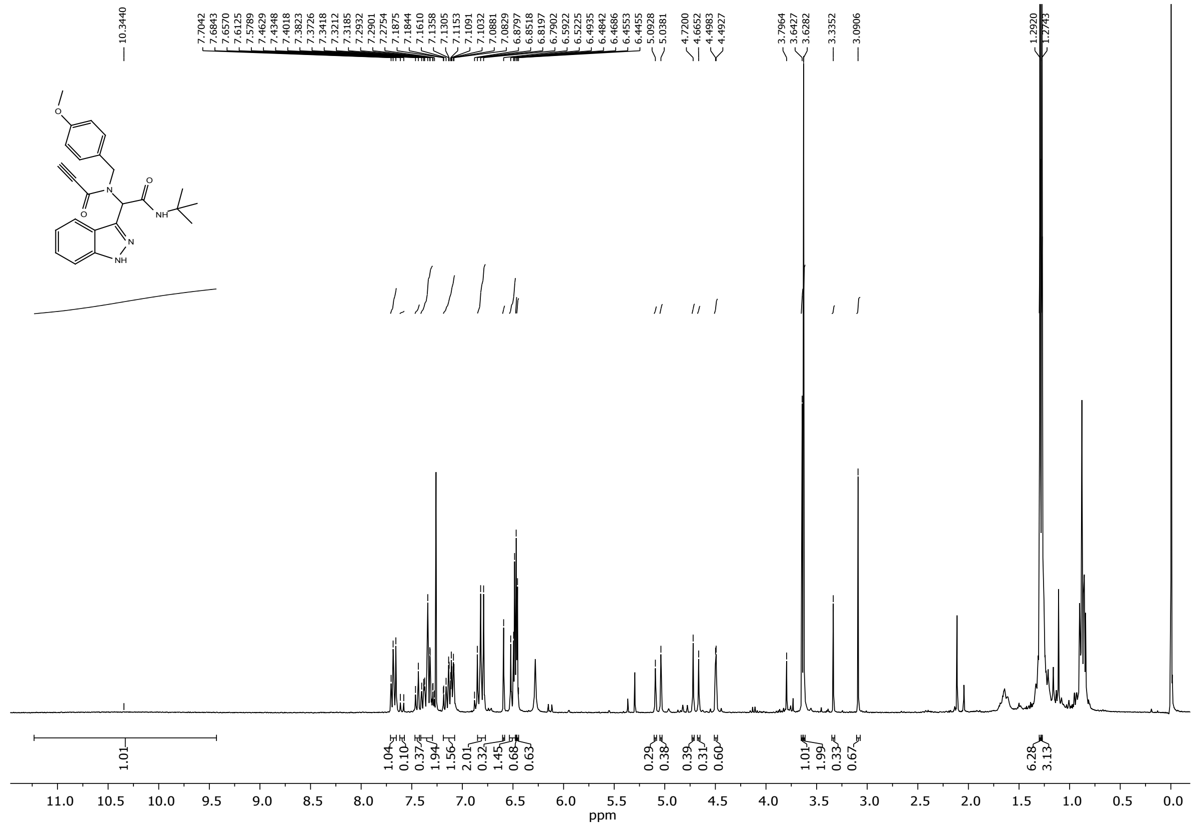
Spectrum 25: 1m



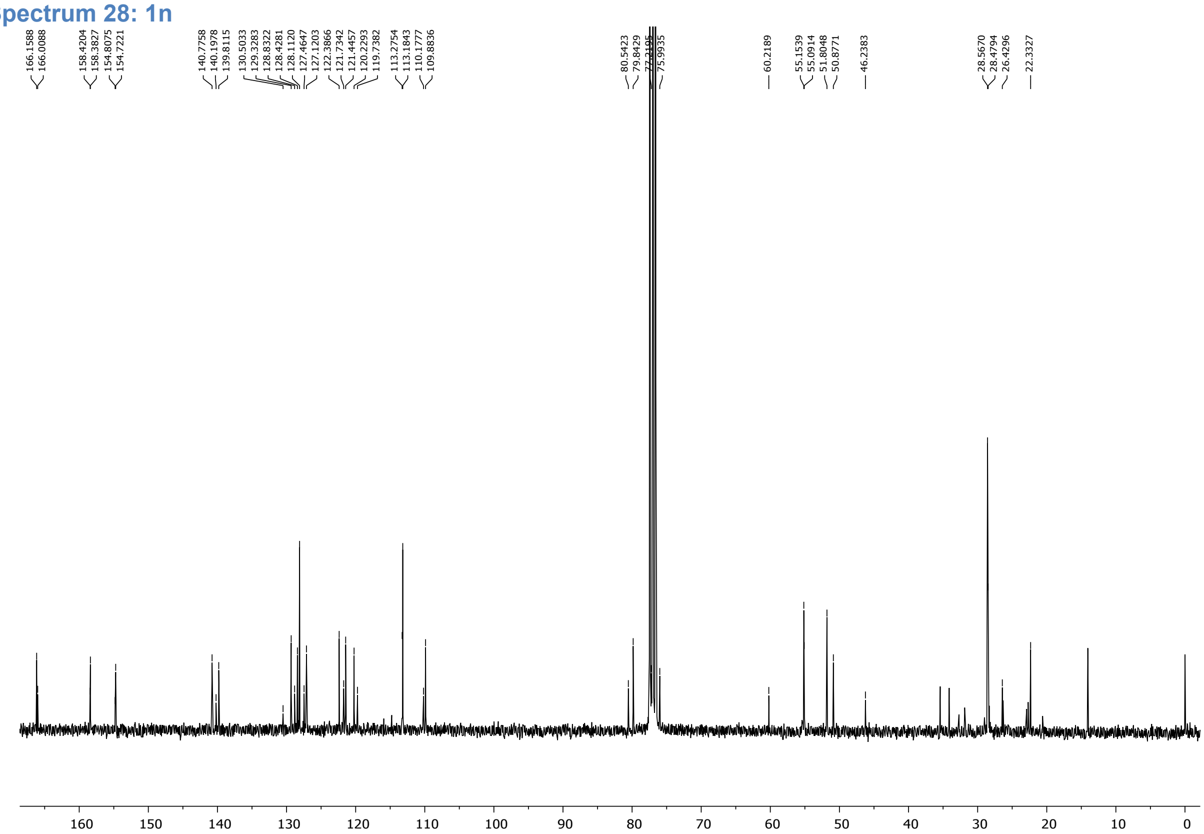
Spectrum 26: 1m



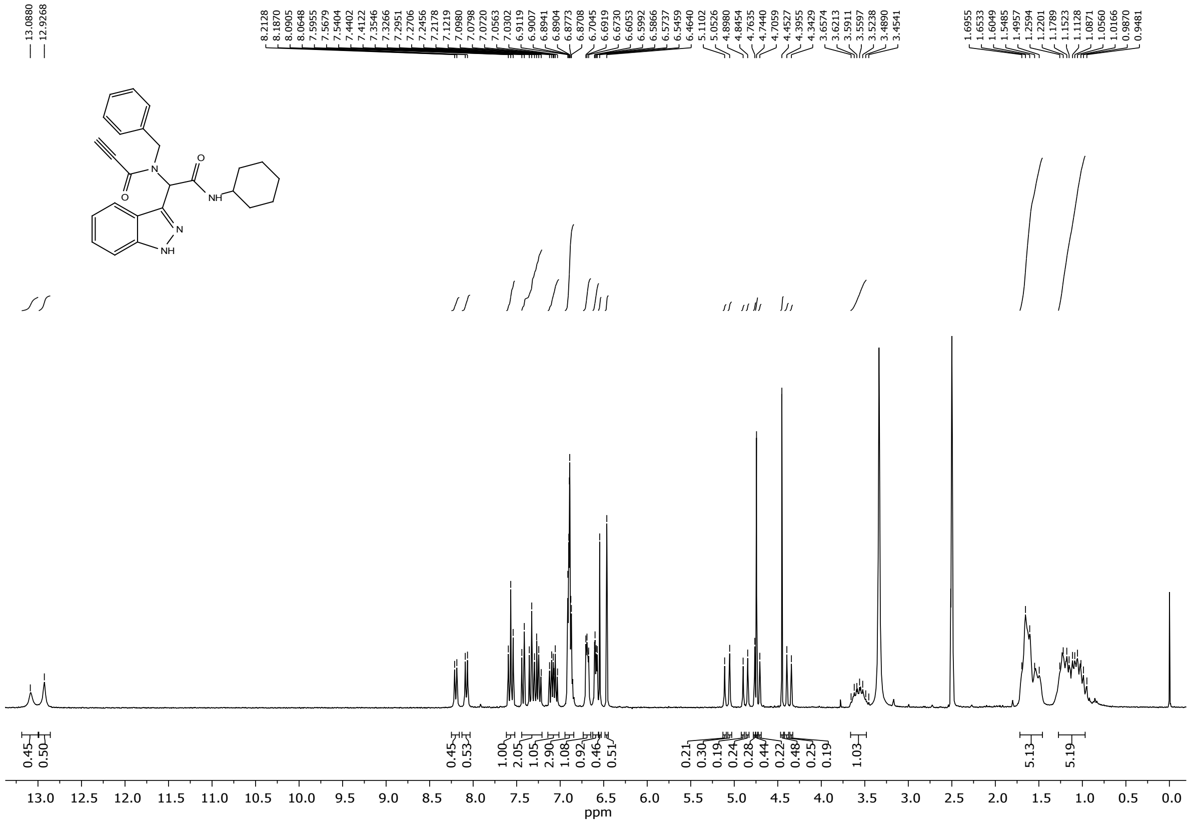
Spectrum 27: 1n



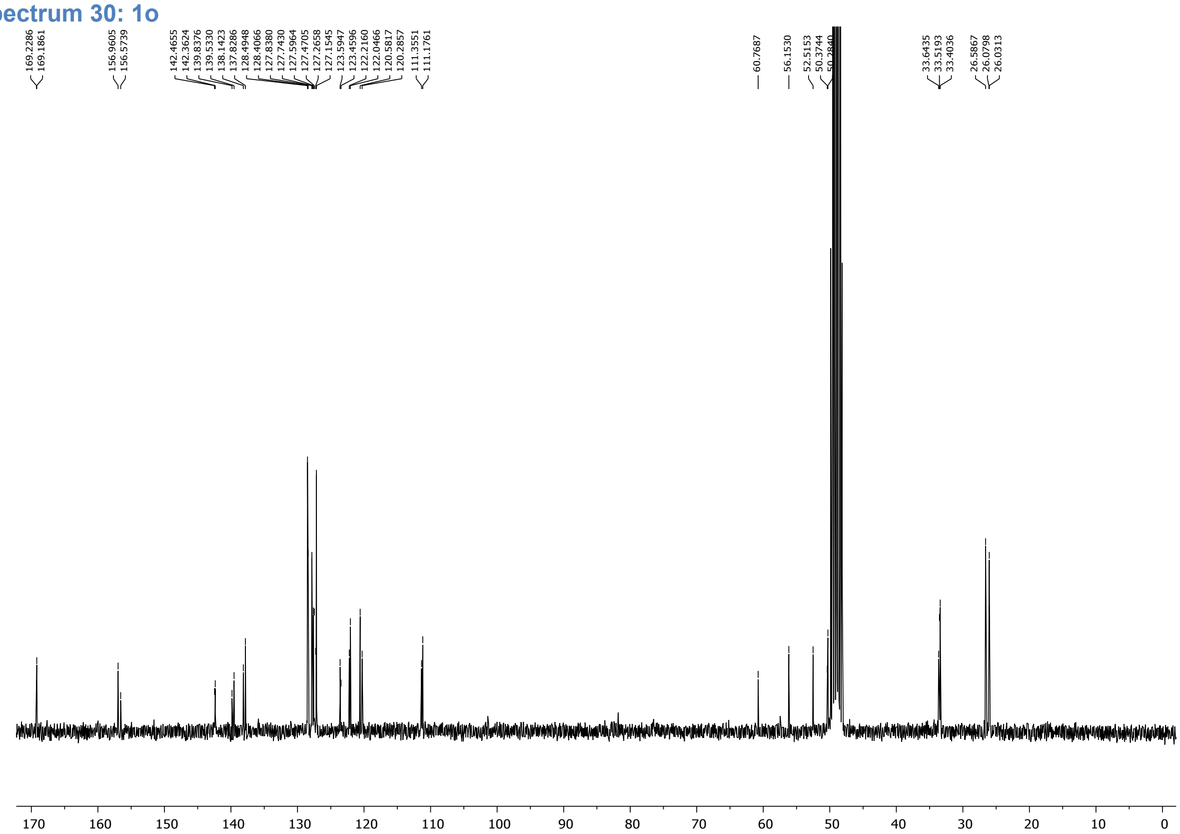
Spectrum 28: 1n



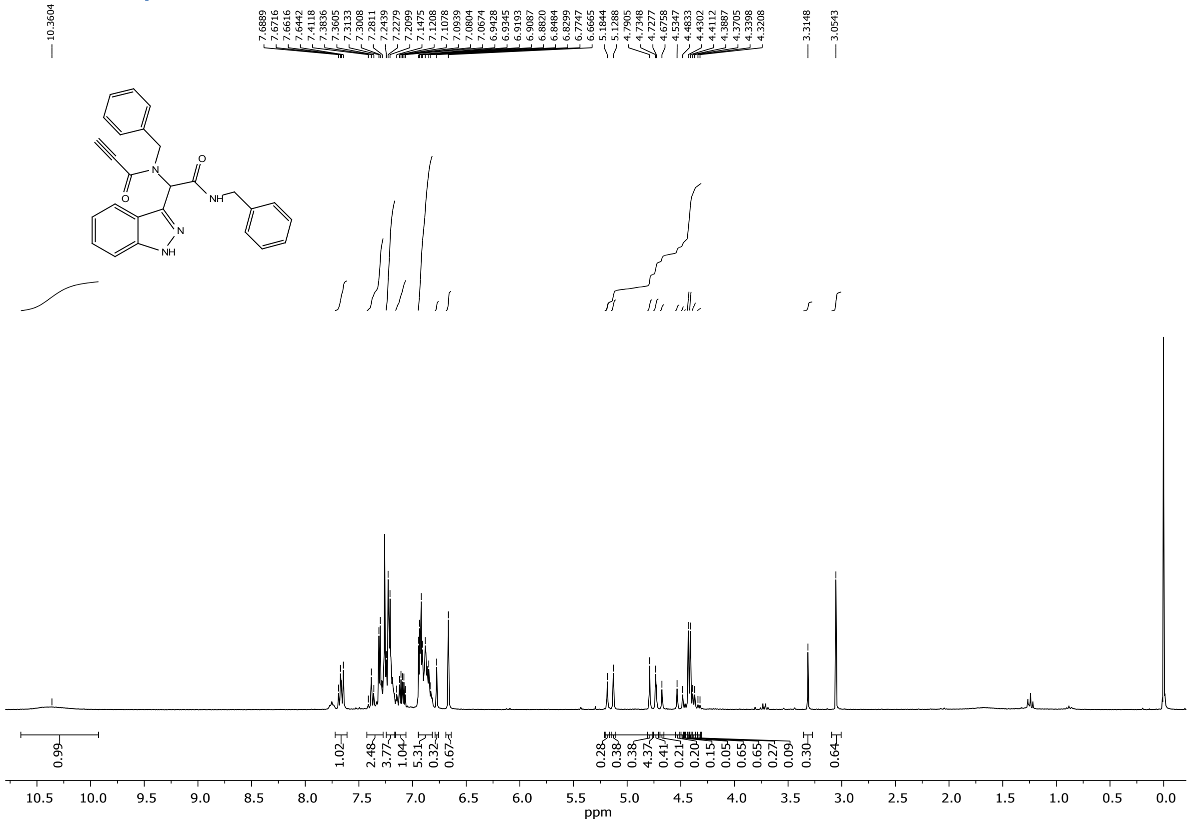
Spectrum 29: 1o



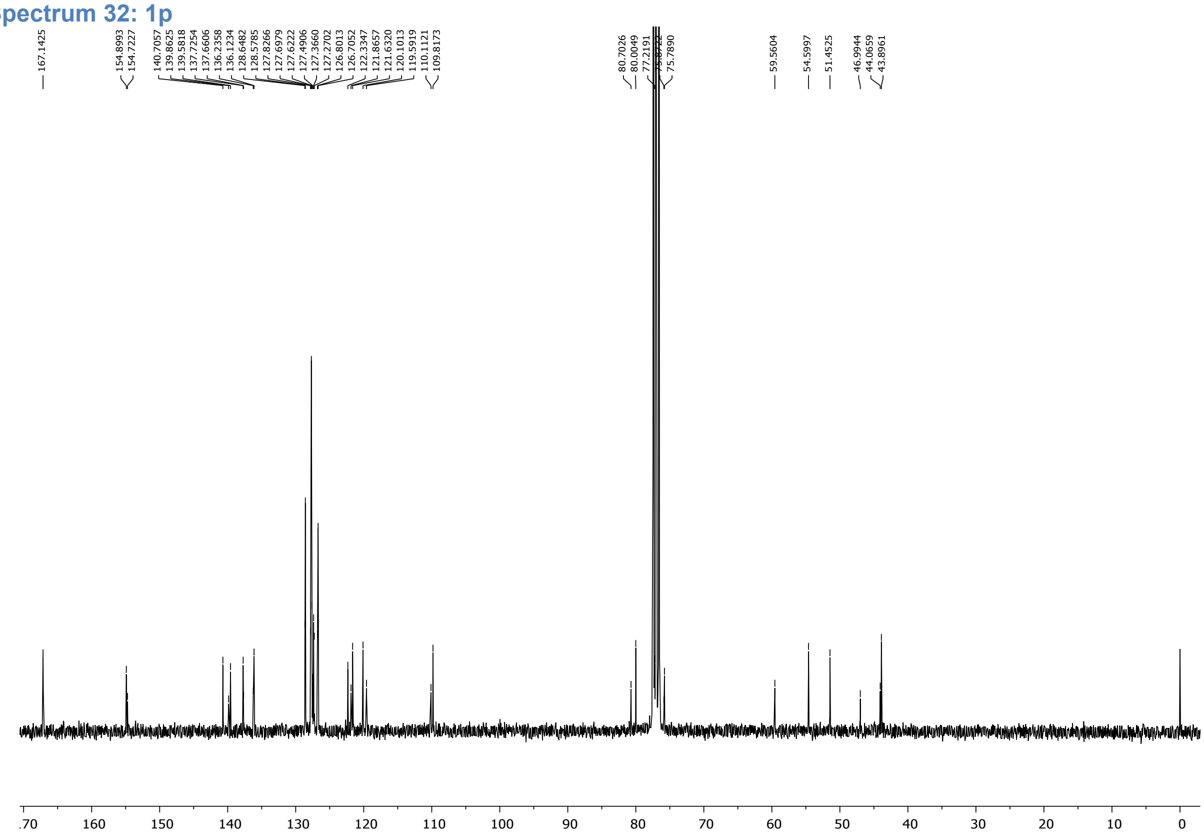
Spectrum 30: 1o



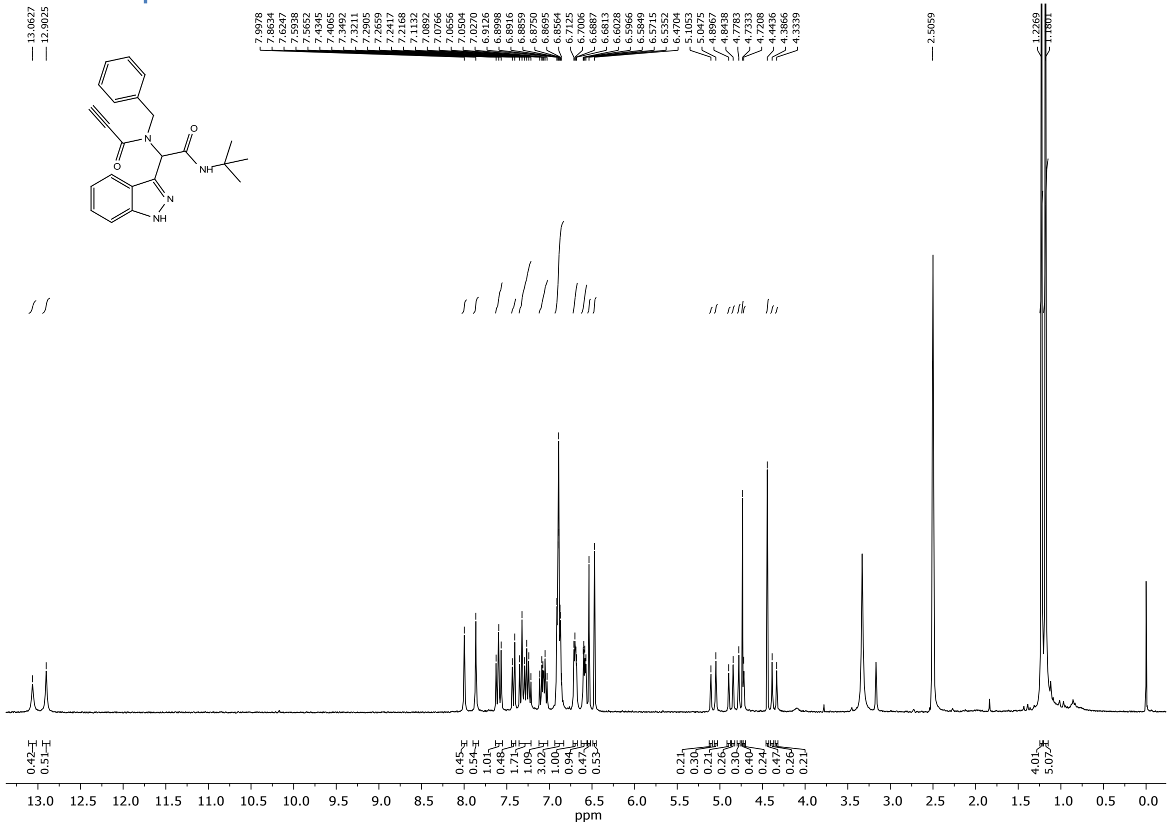
Spectrum 31: 1p



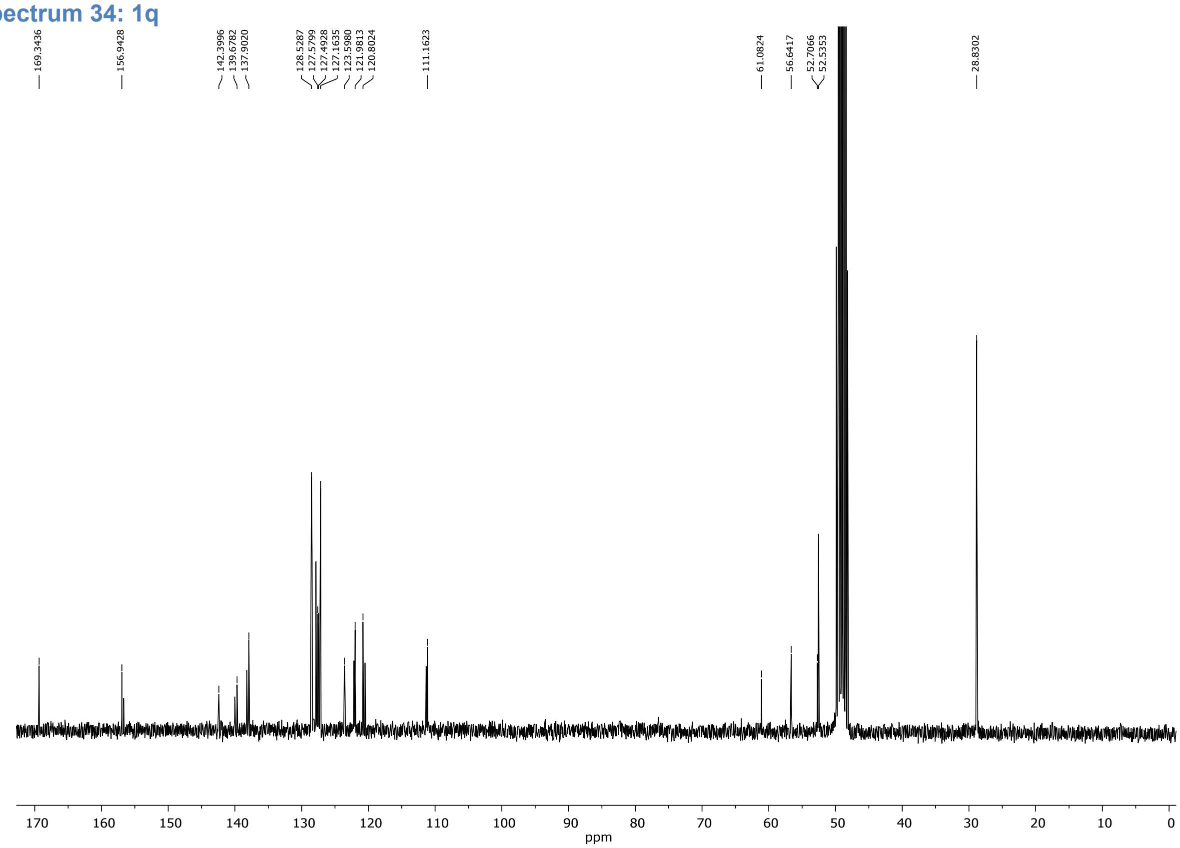
Spectrum 32: 1p



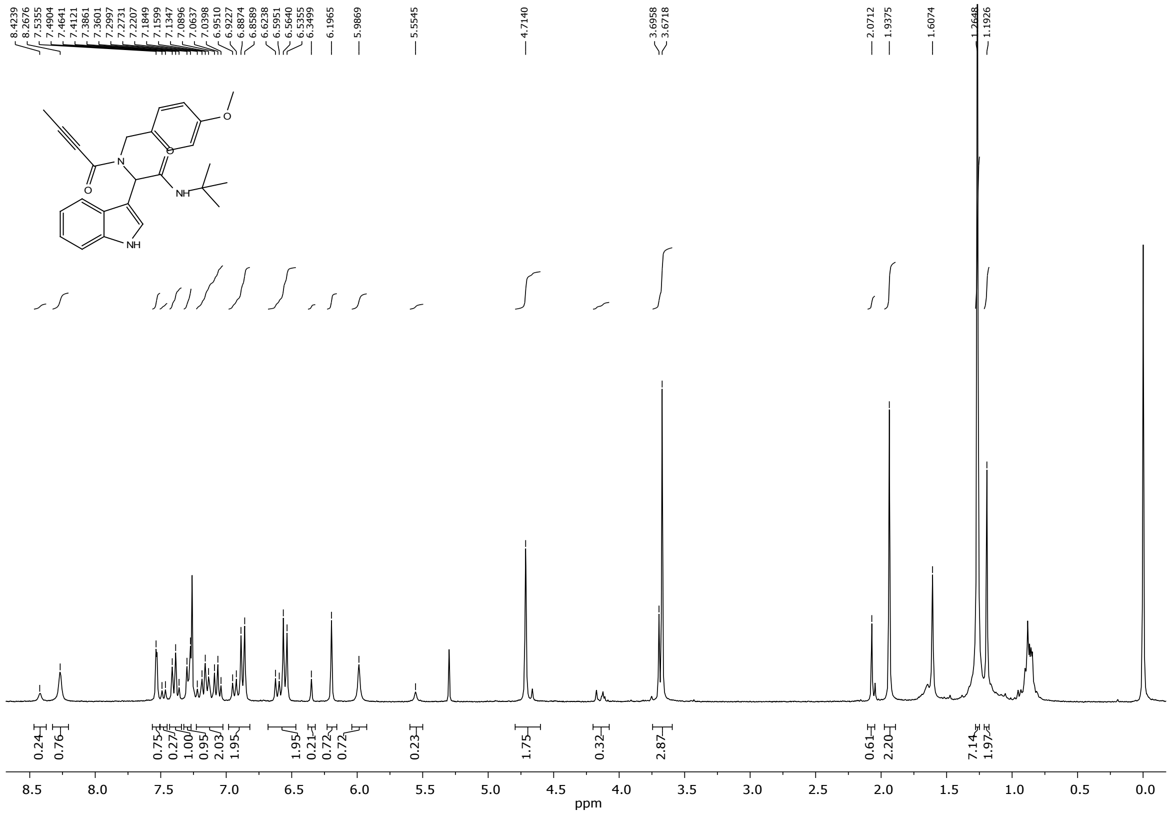
Spectrum 33: 1q



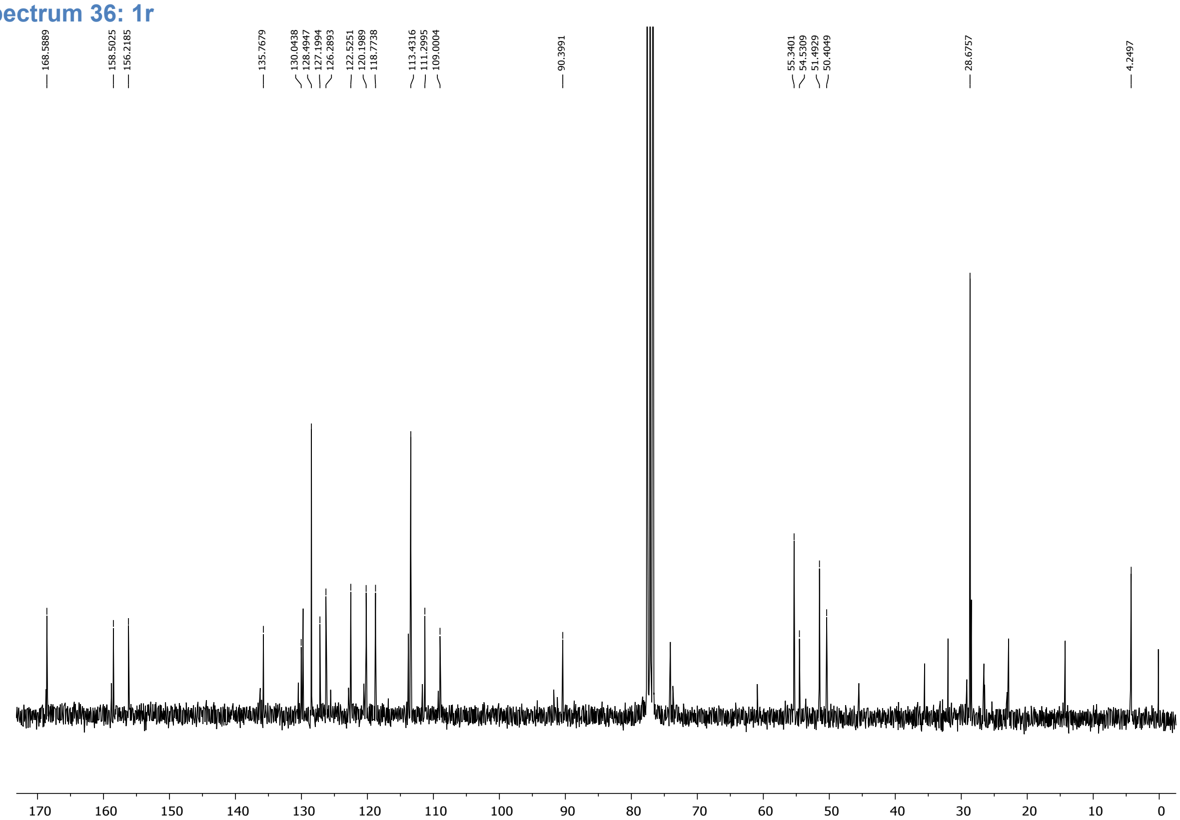
Spectrum 34: 1q



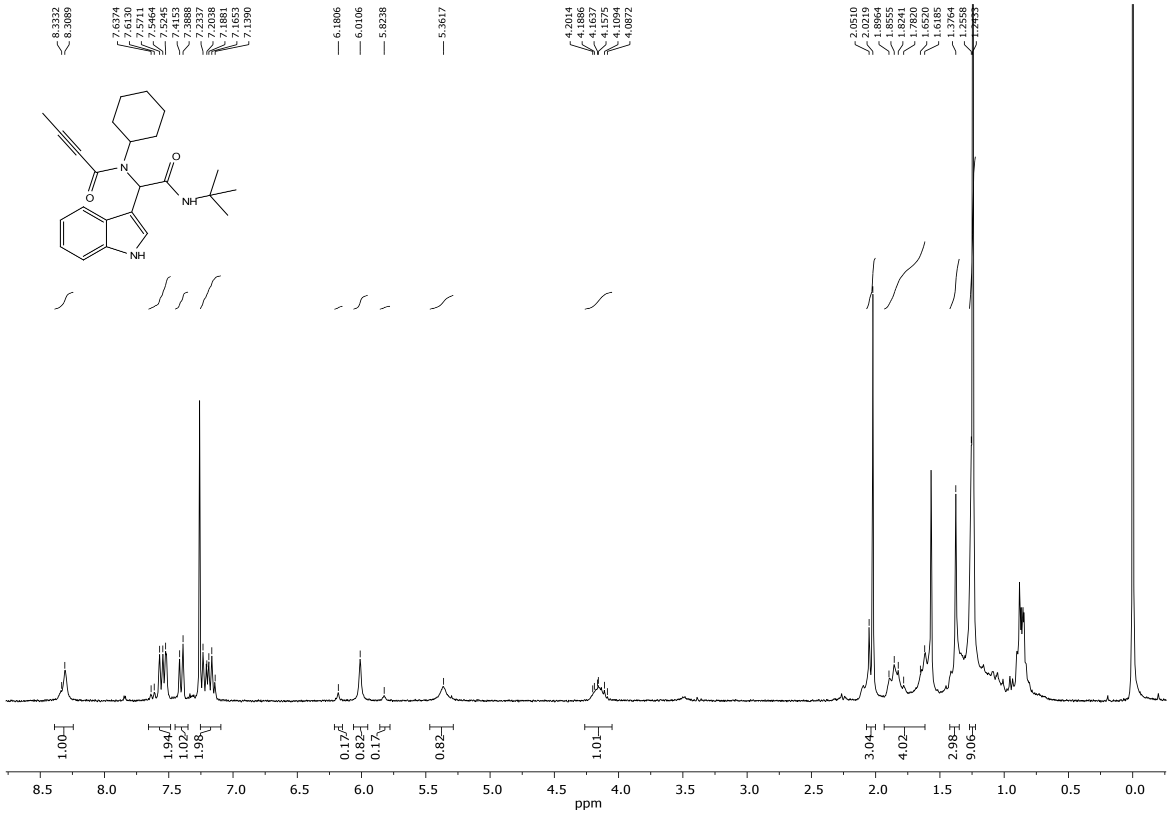
Spectrum 35: 1r



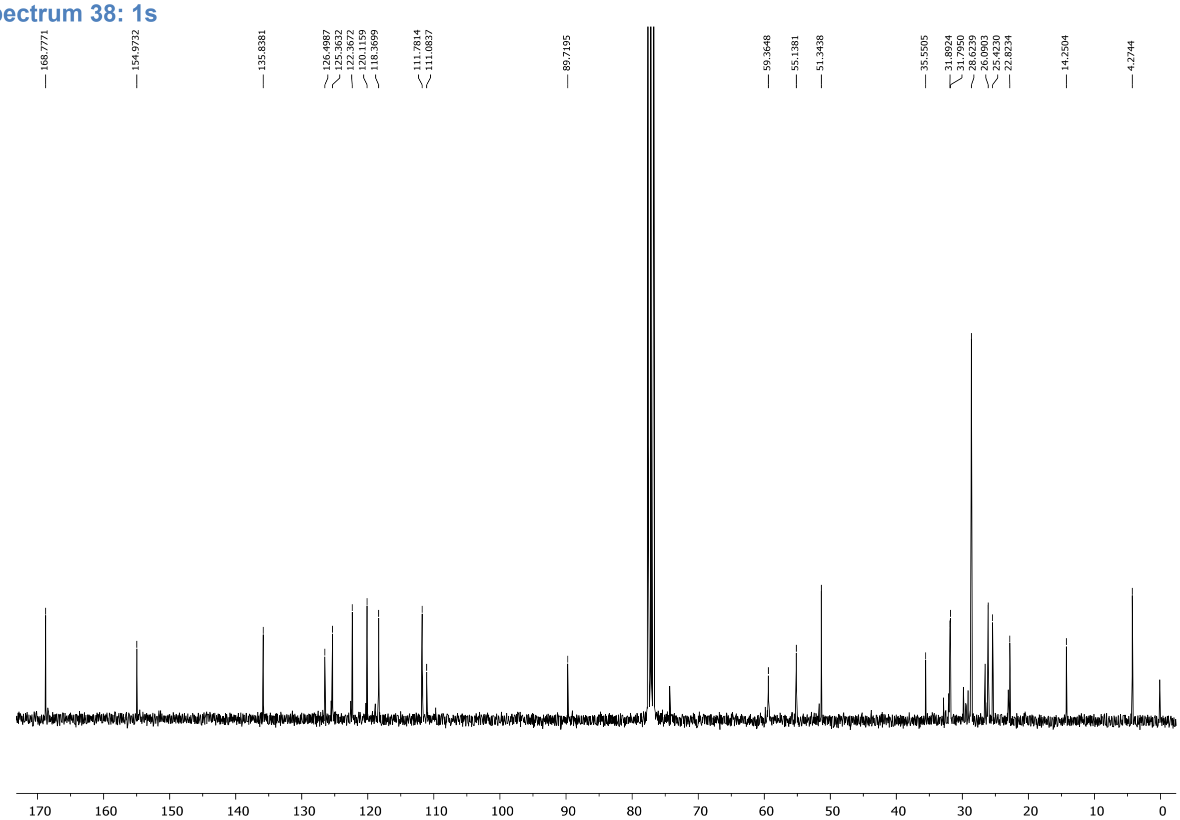
Spectrum 36: 1r



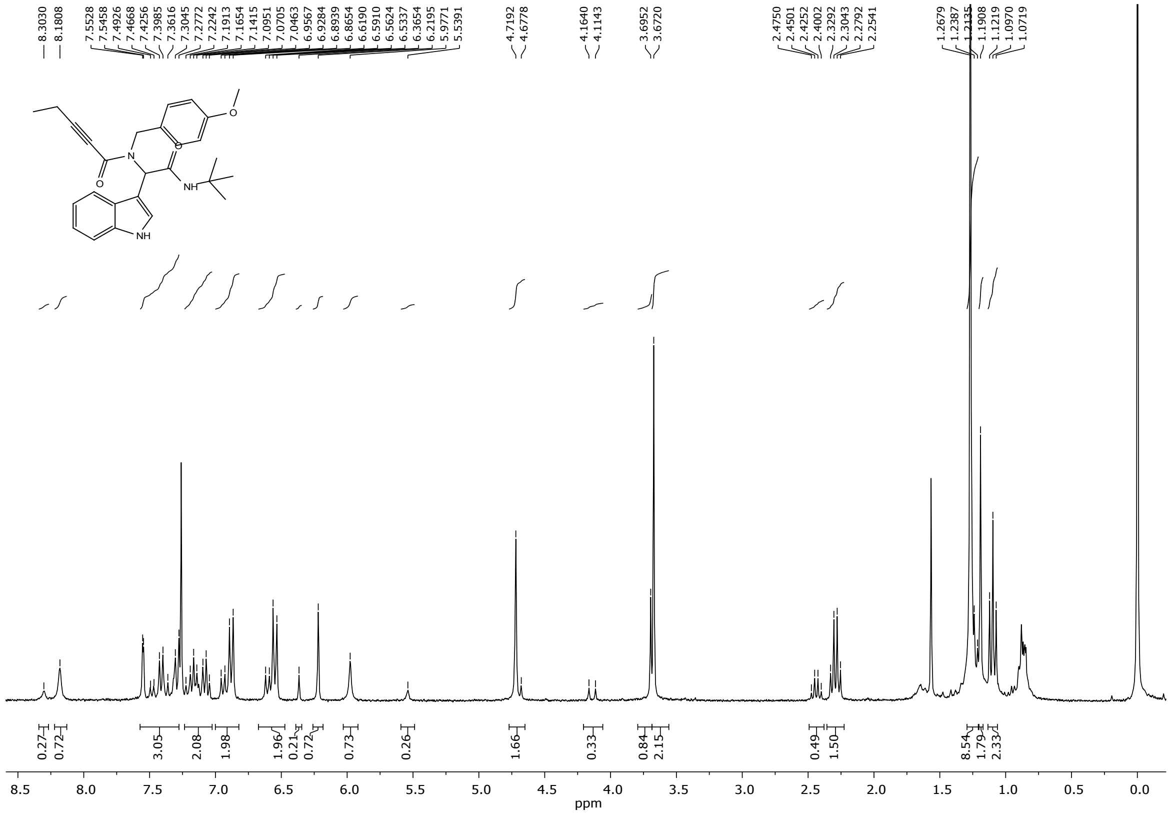
Spectrum 37: 1s



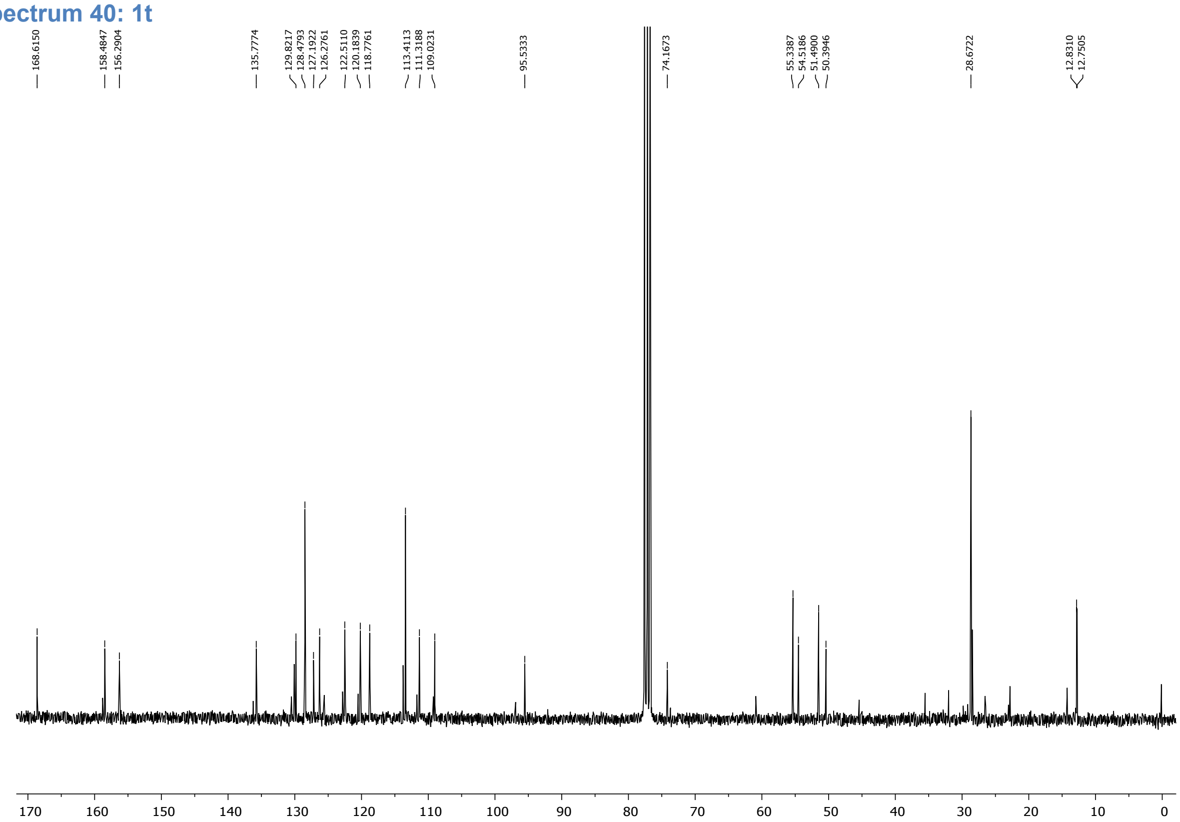
Spectrum 38: 1s



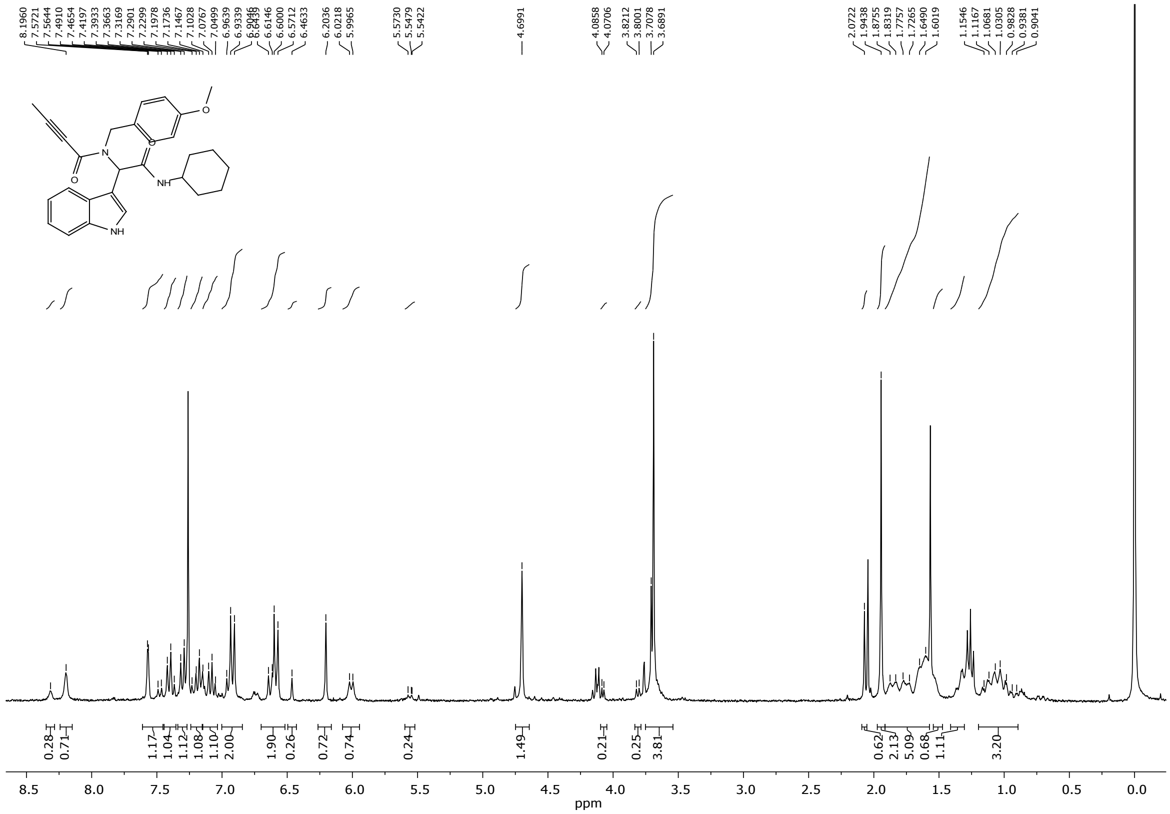
Spectrum 39: 1t



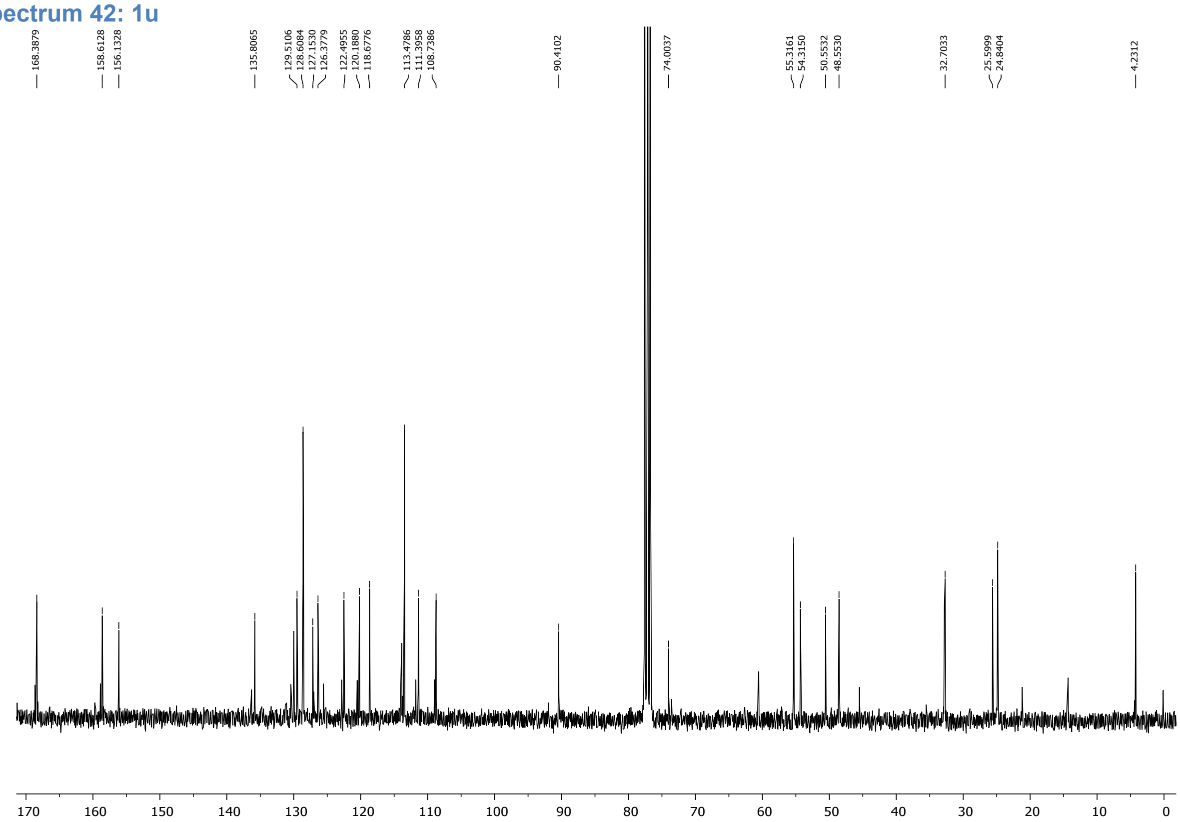
Spectrum 40: 1t



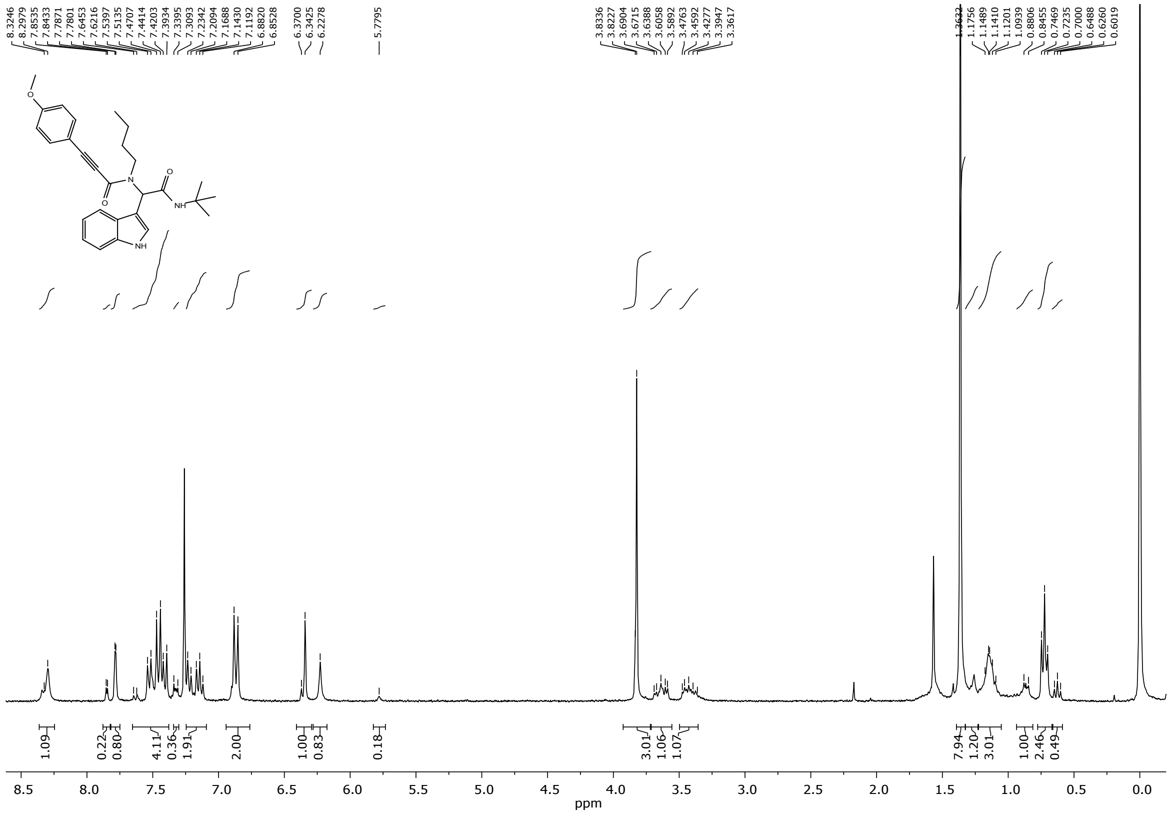
Spectrum 41: 1u



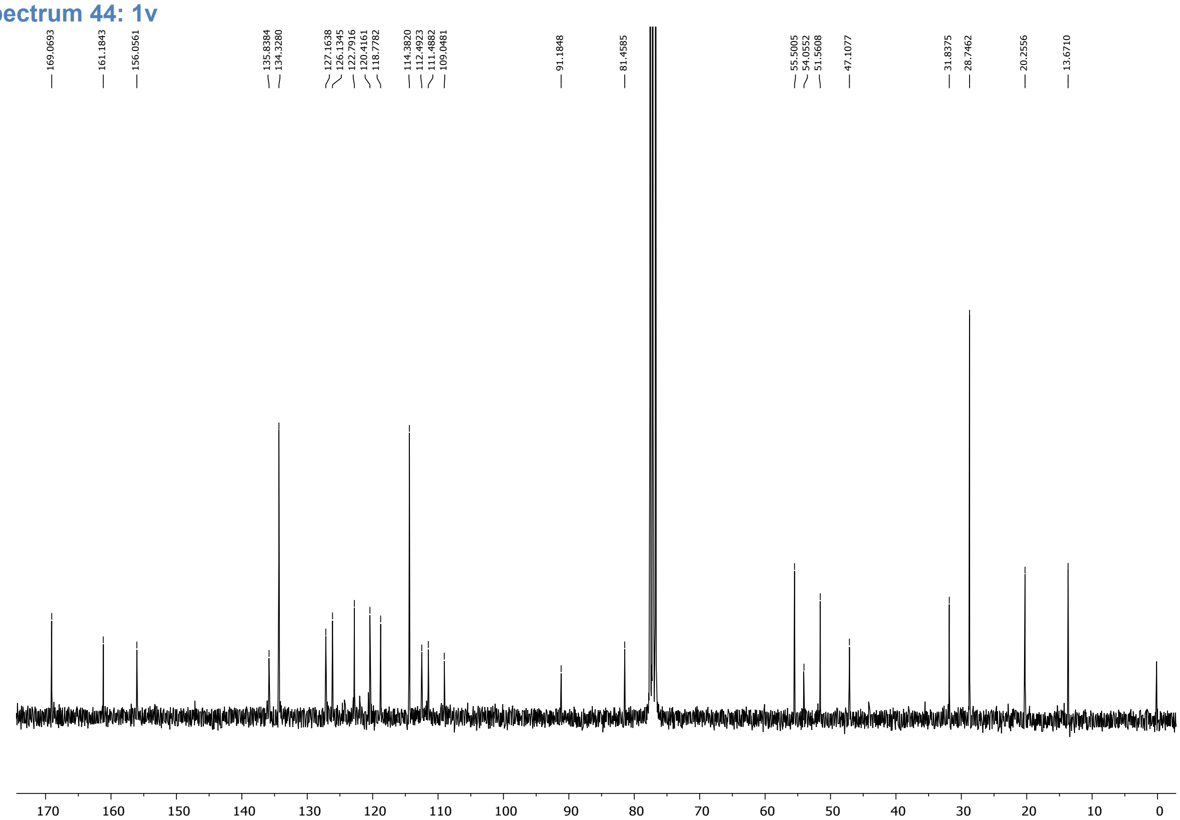
Spectrum 42: 1u



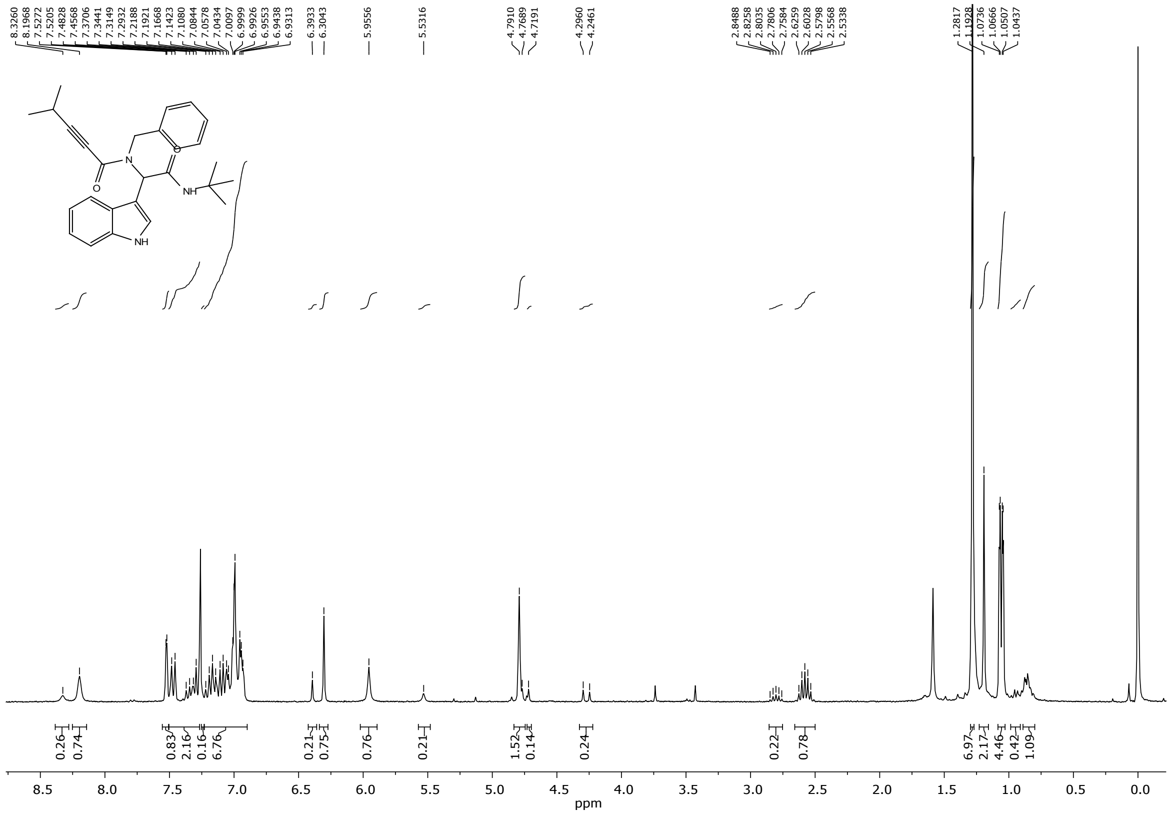
Spectrum 43: 1v



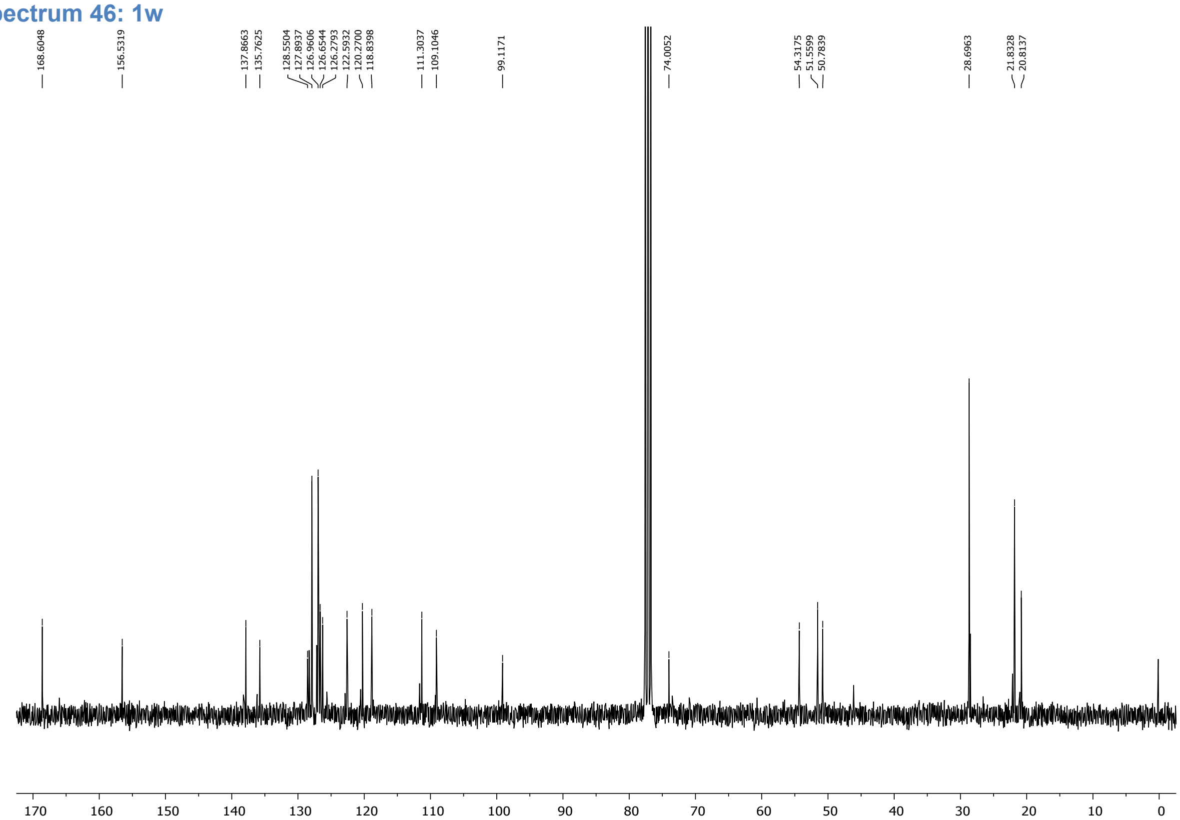
Spectrum 44: 1v



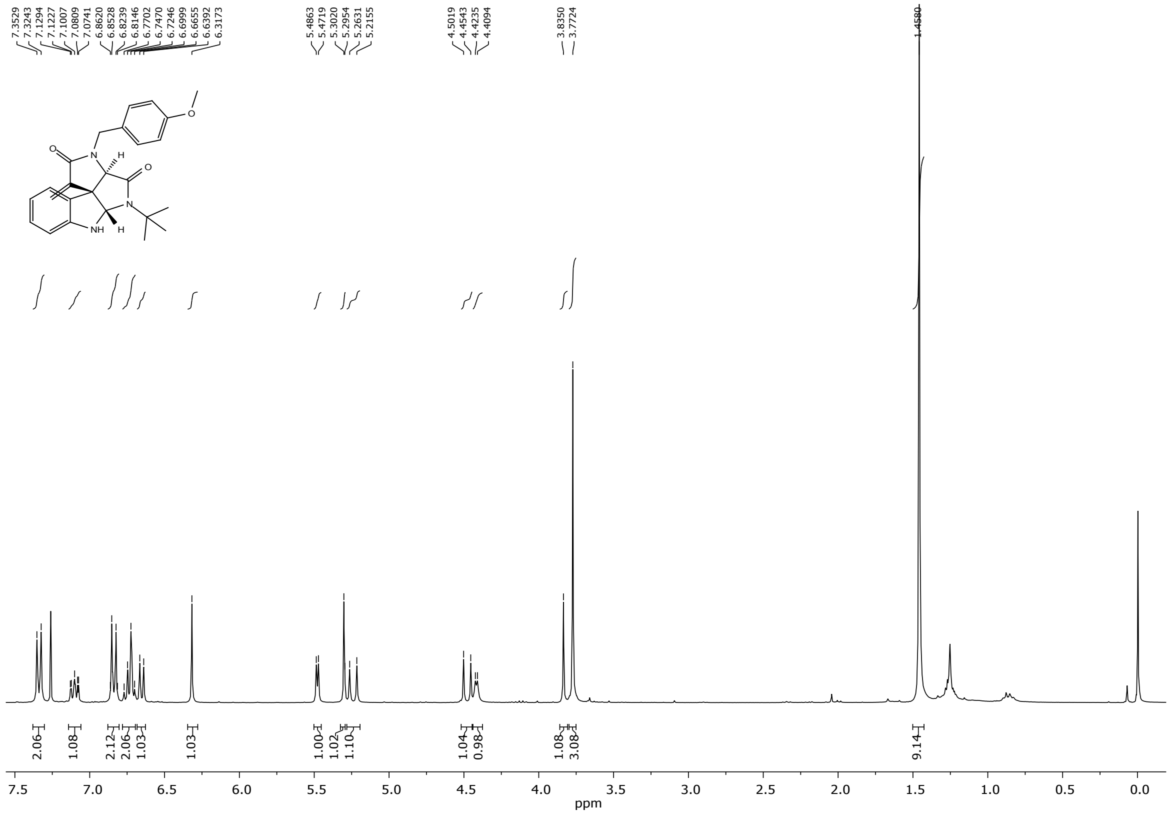
Spectrum 45: 1w



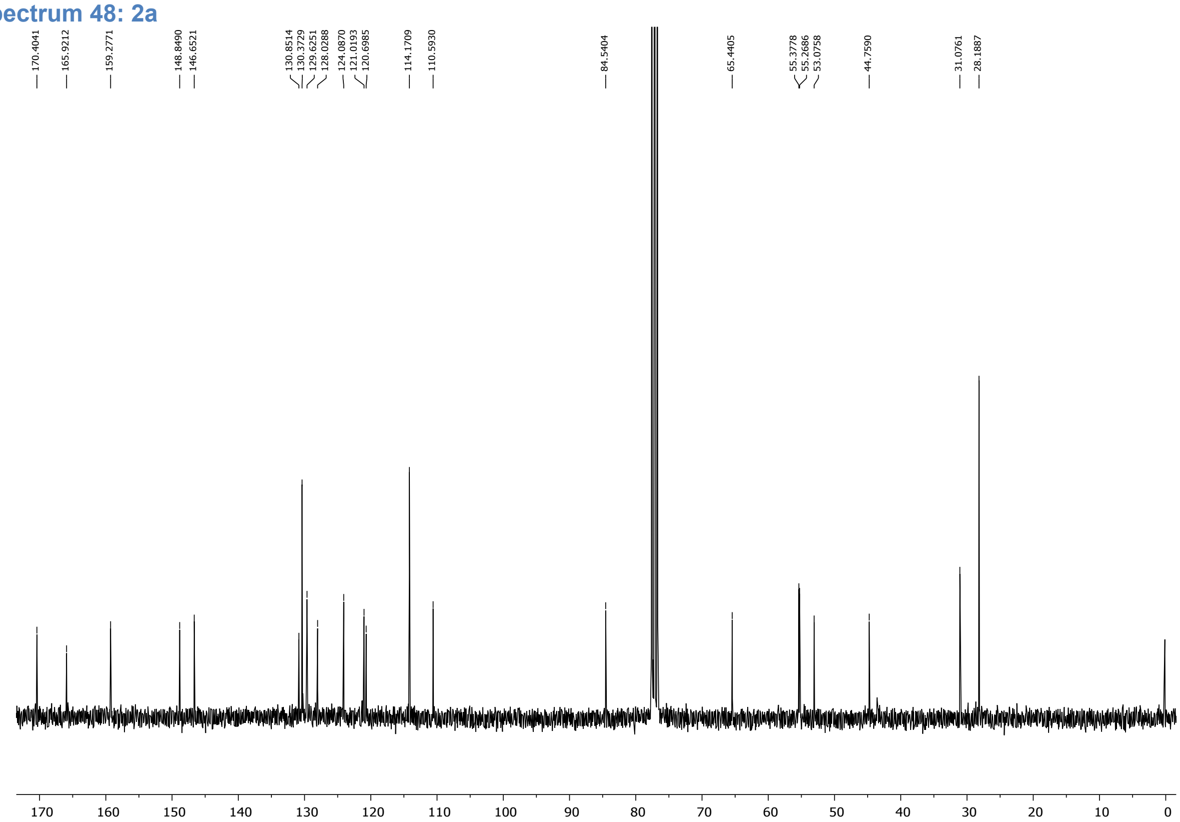
Spectrum 46: 1w



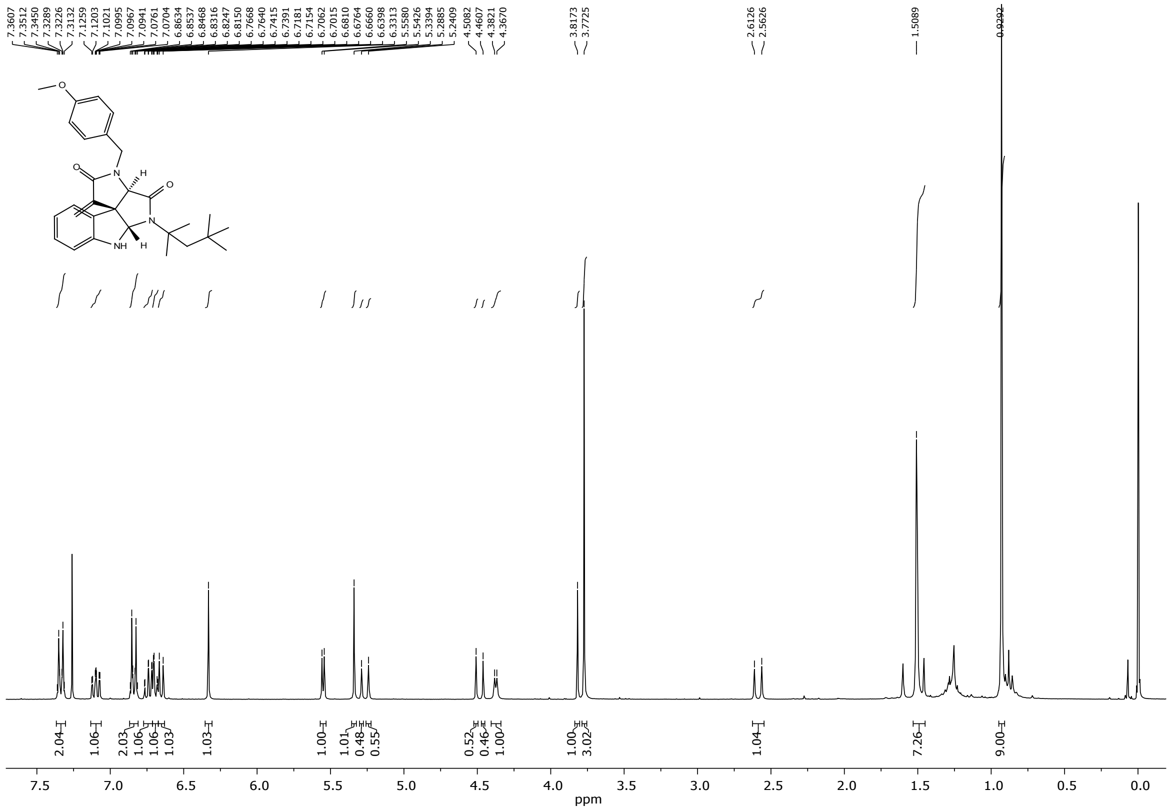
Spectrum 47: 2a



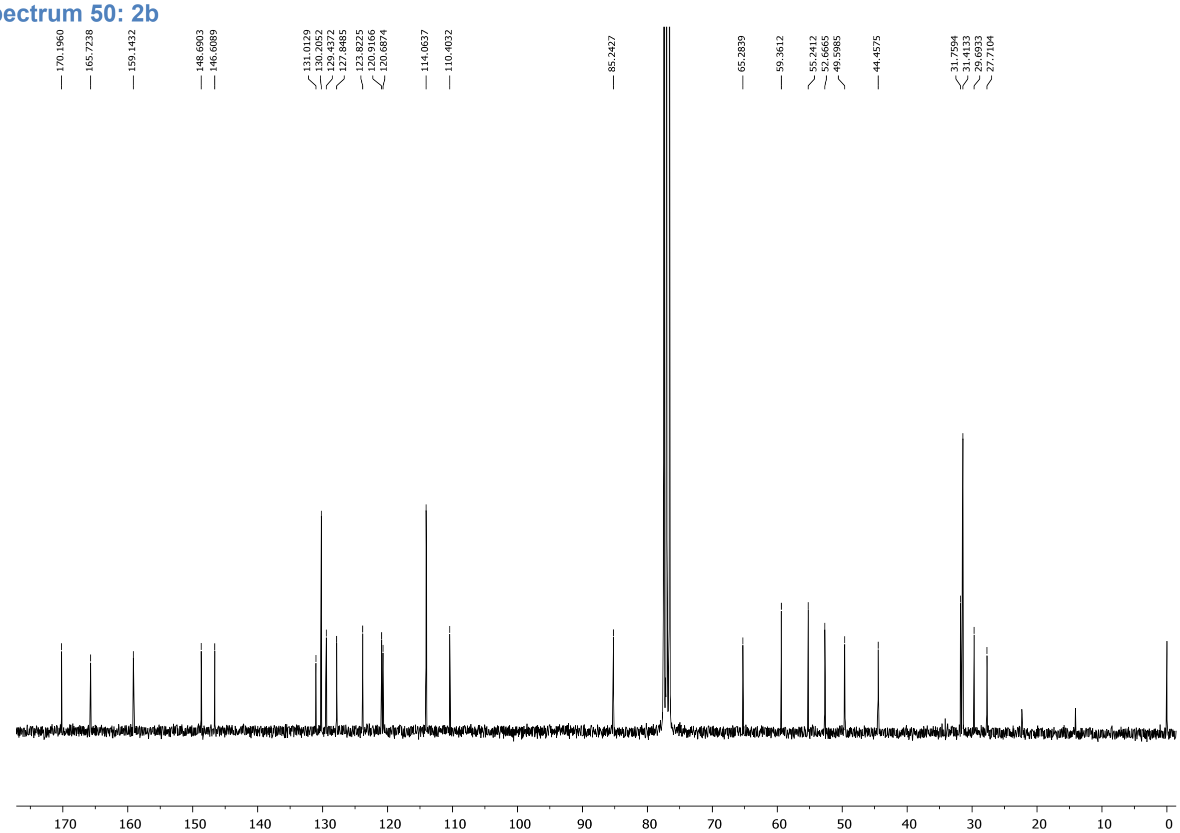
Spectrum 48: 2a



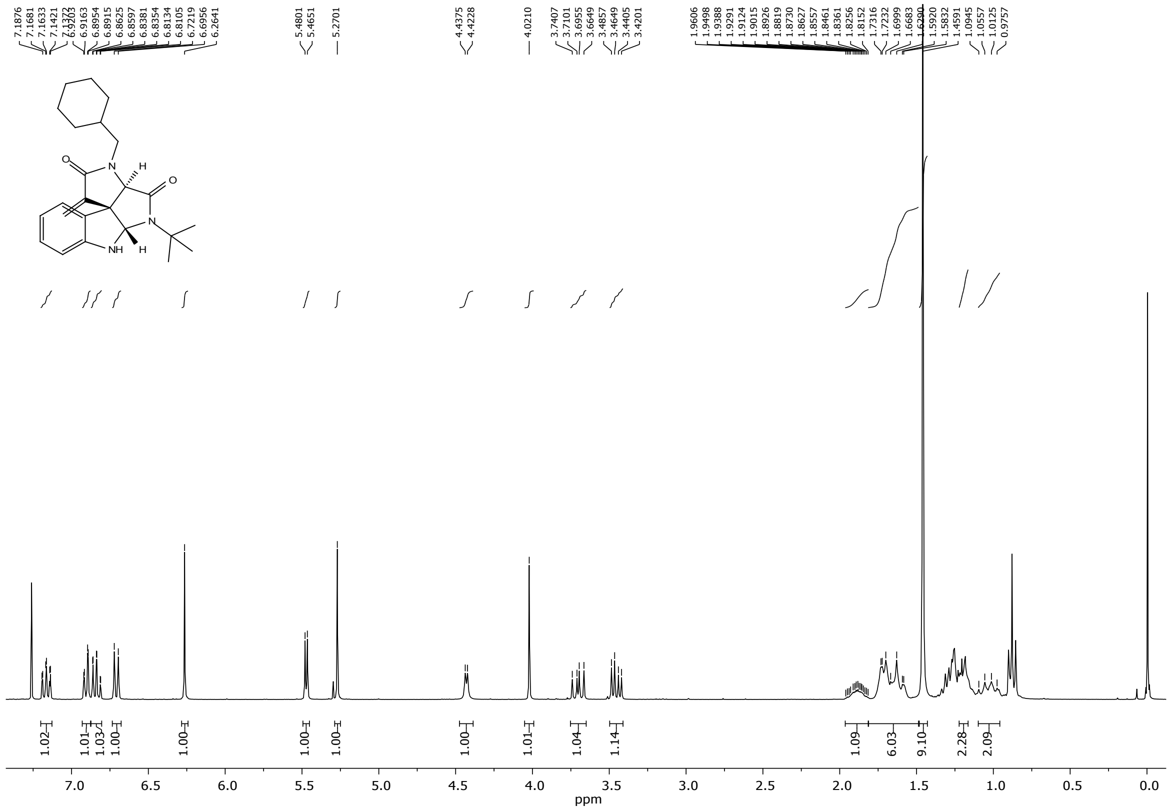
Spectrum 49: 2b



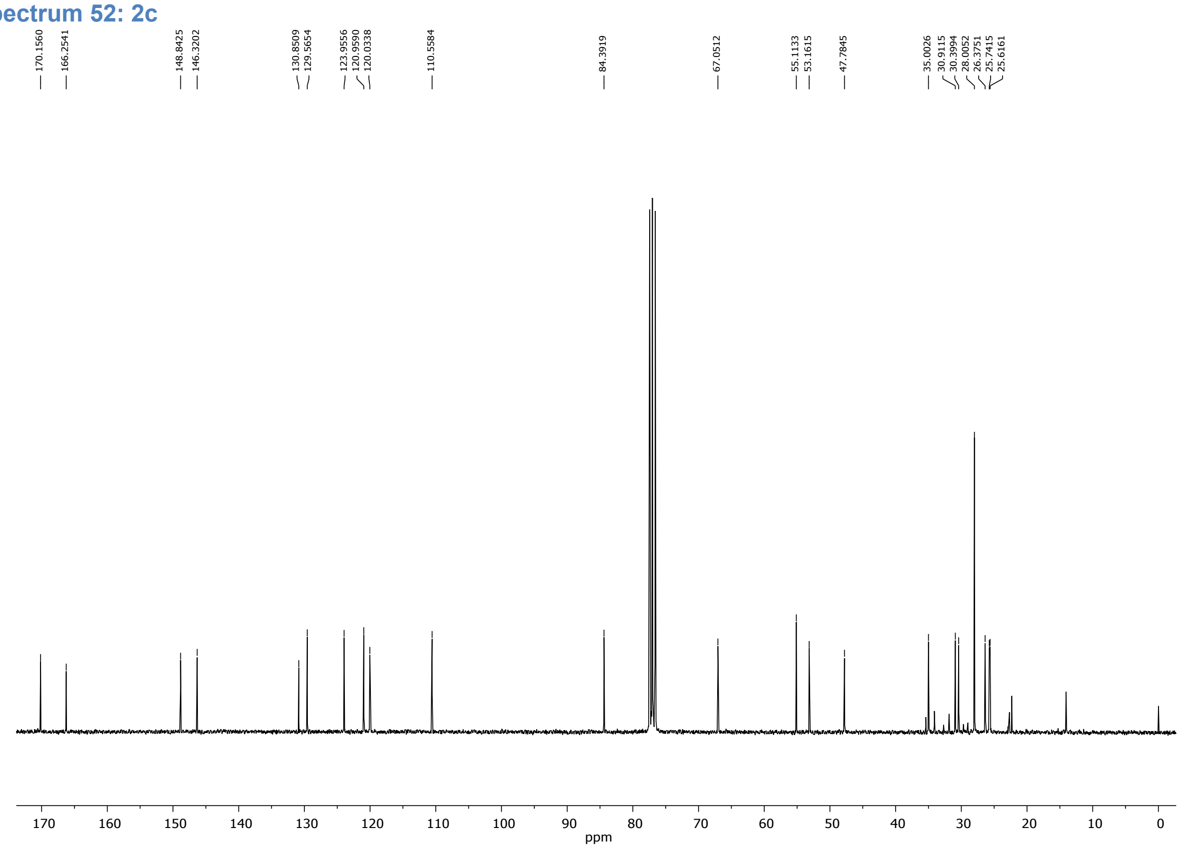
Spectrum 50: 2b



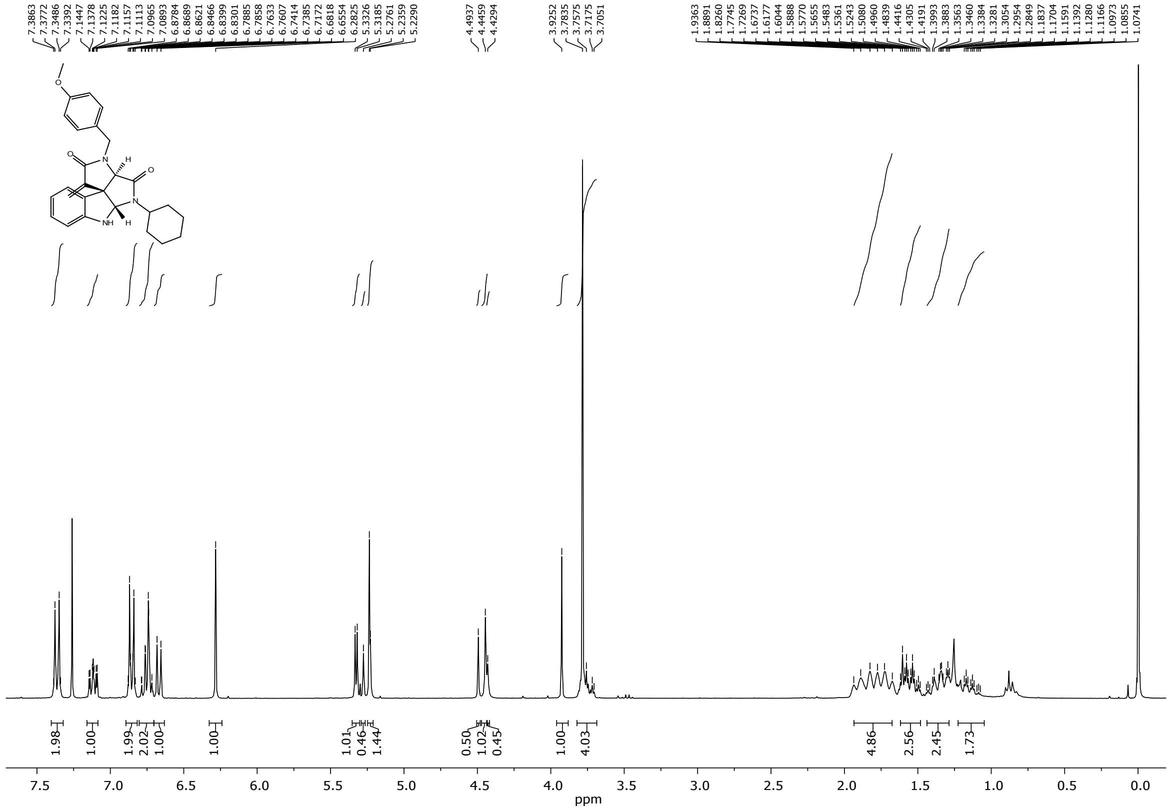
Spectrum 51: 2c



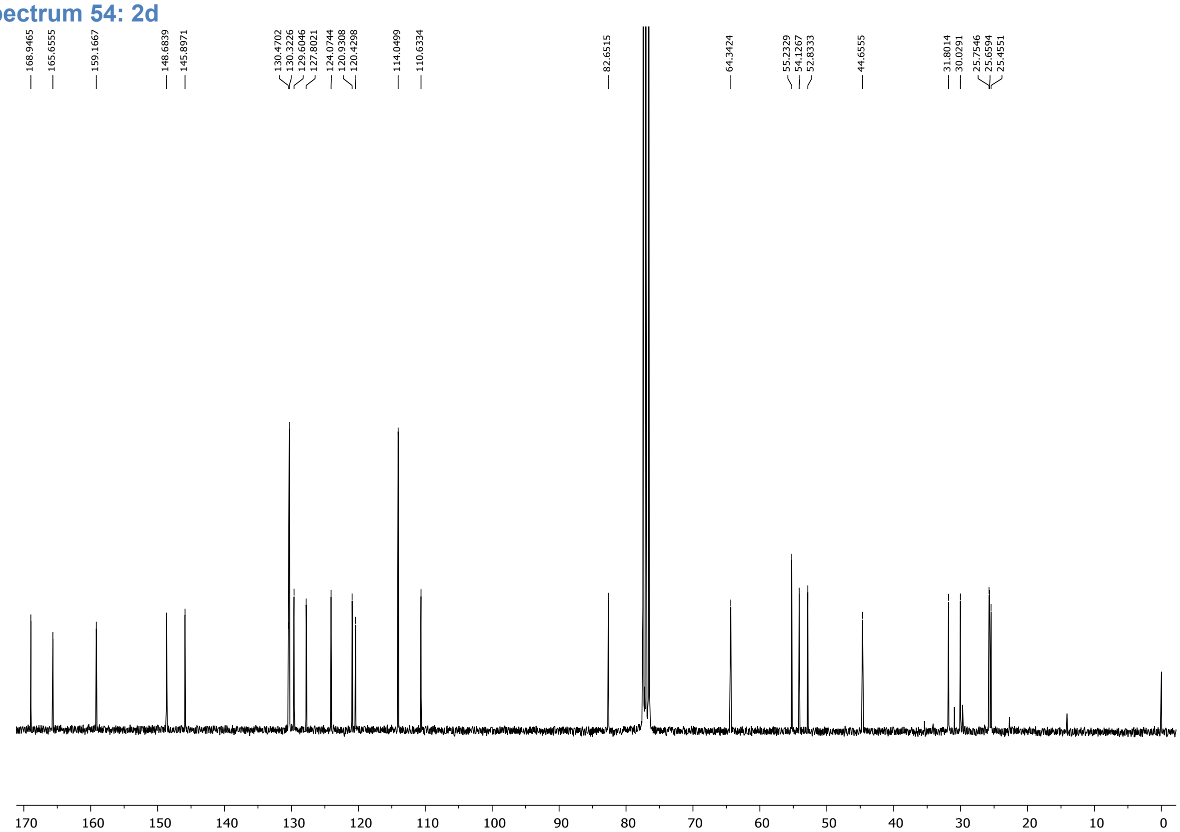
Spectrum 52: 2c



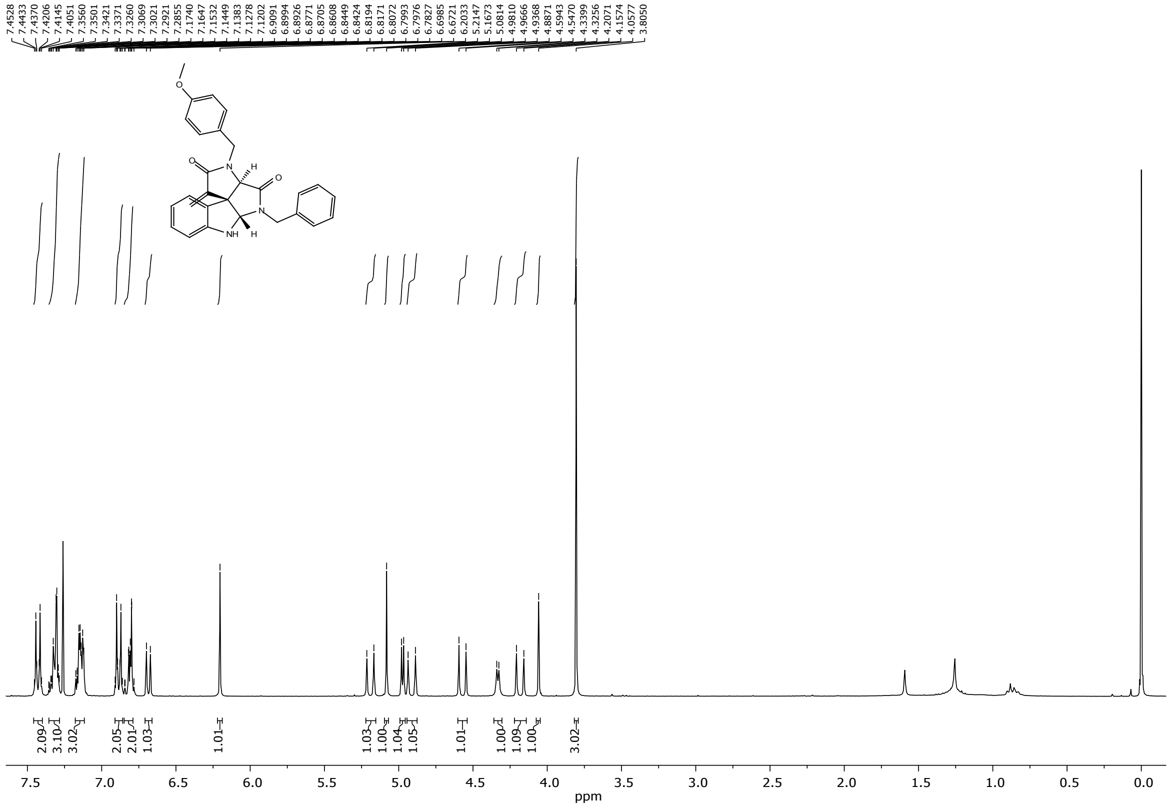
Spectrum 53: 2d



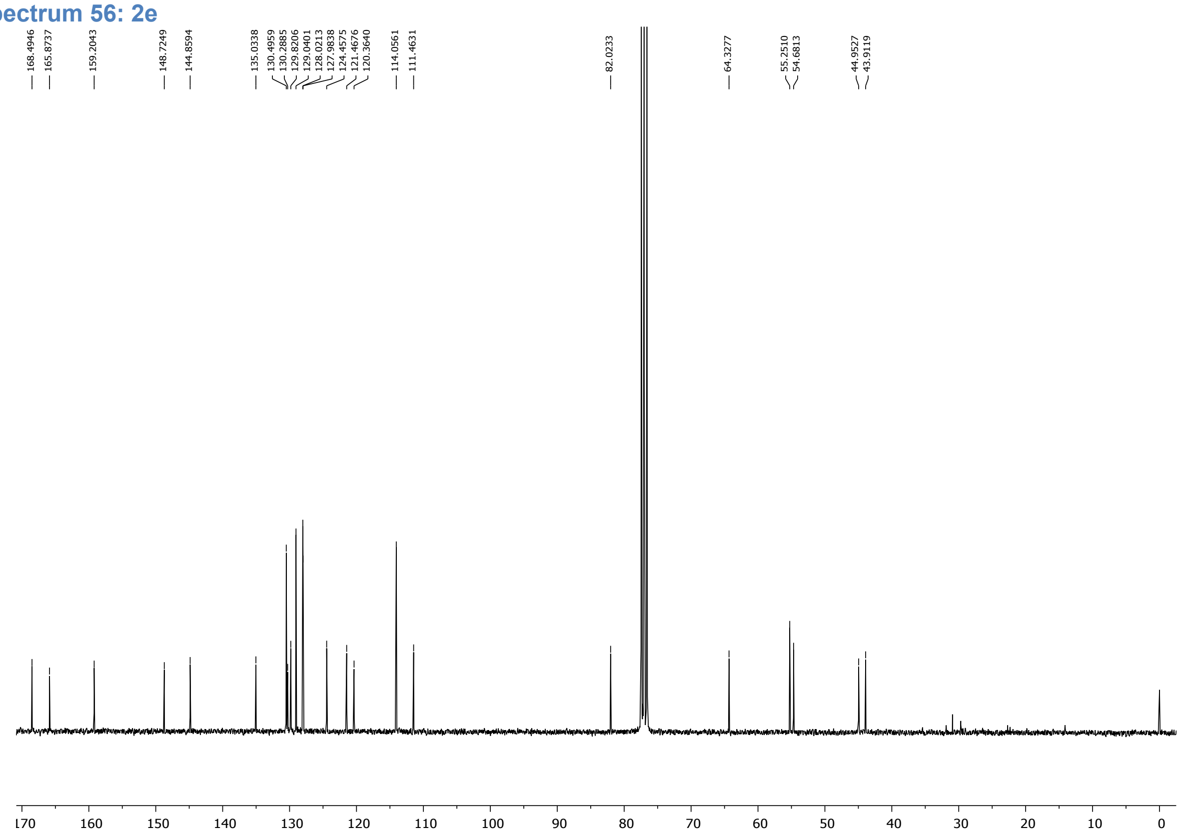
Spectrum 54: 2d



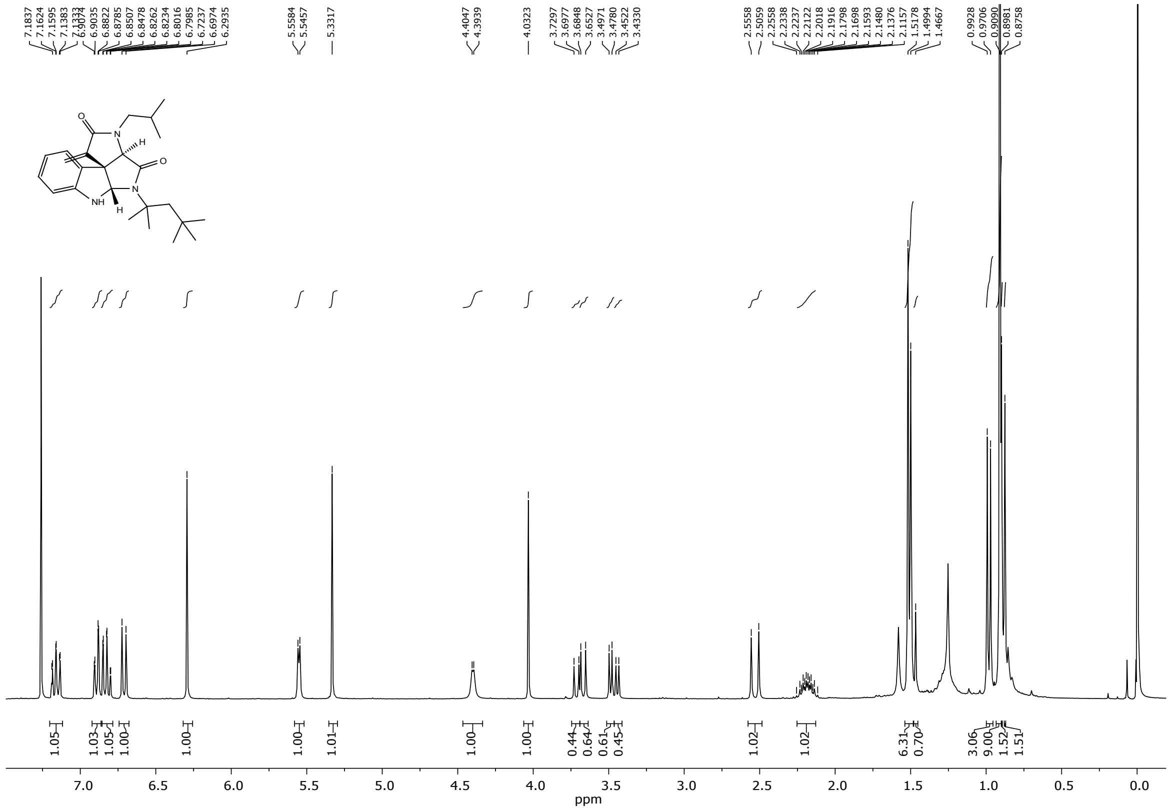
Spectrum 55: 2e



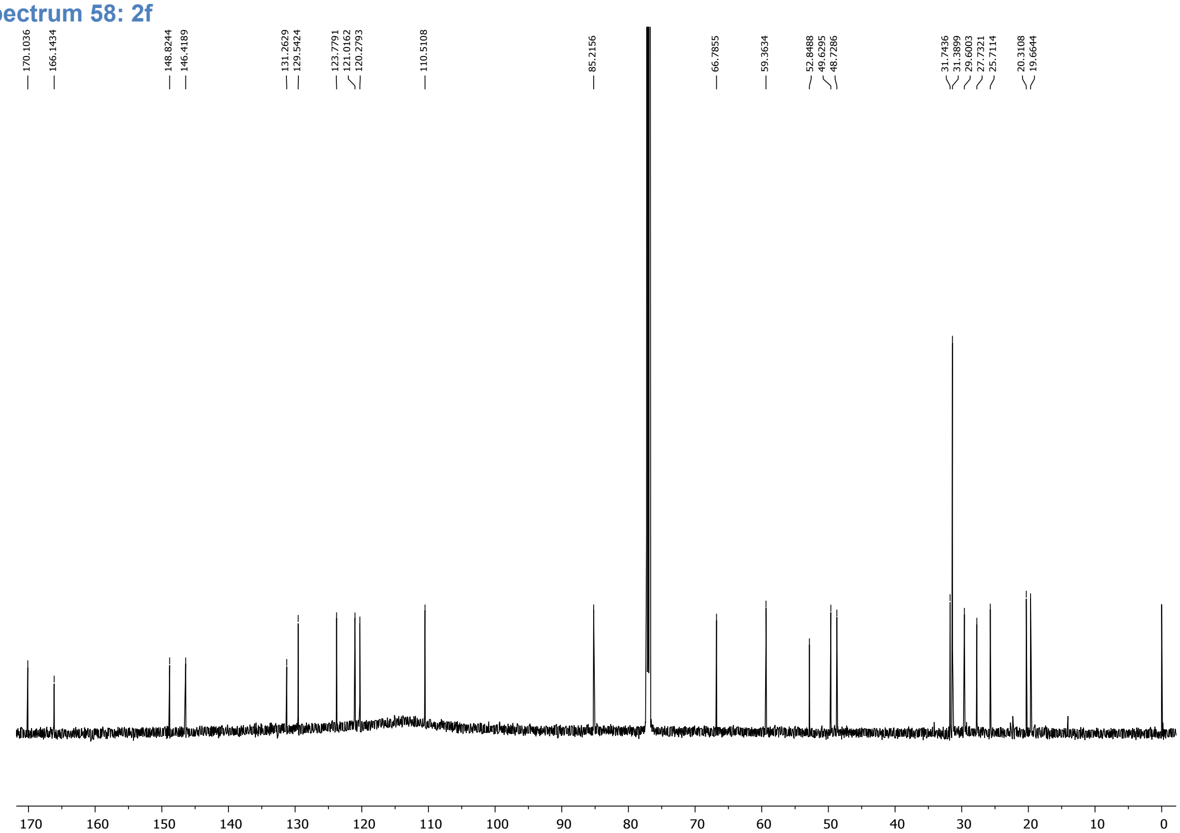
Spectrum 56: 2e



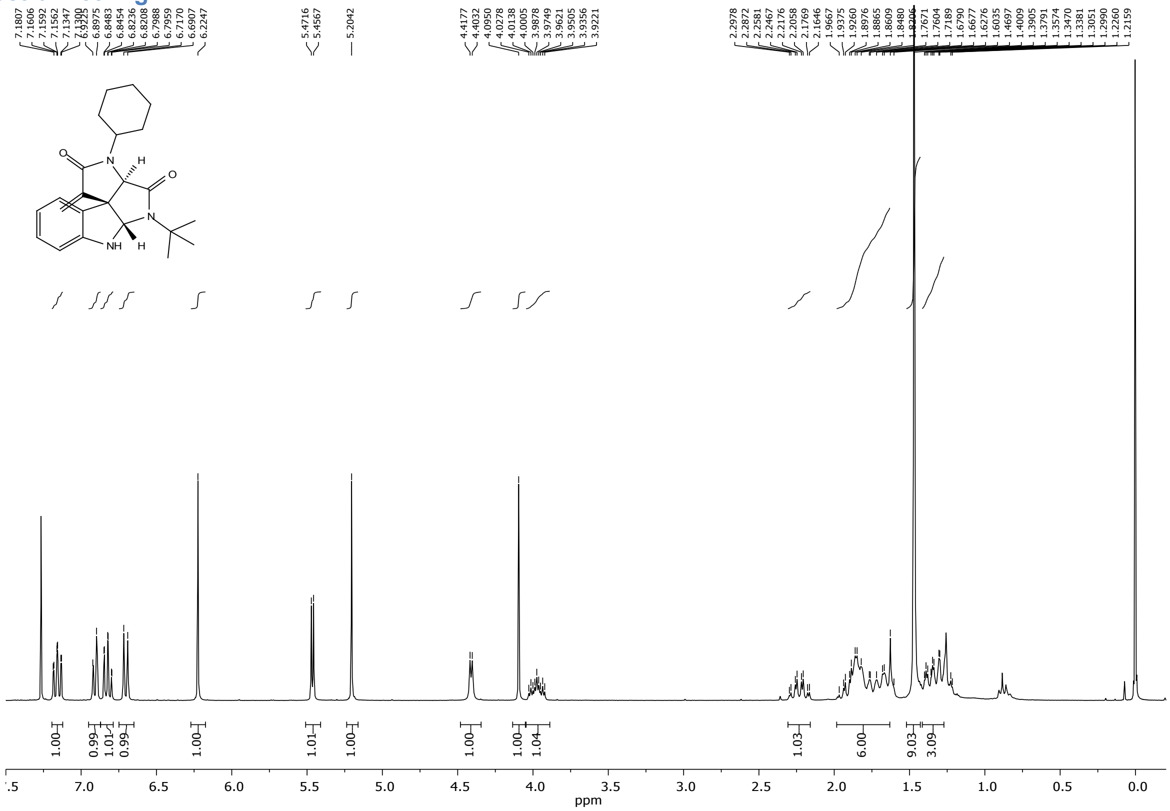
Spectrum 57: 2f



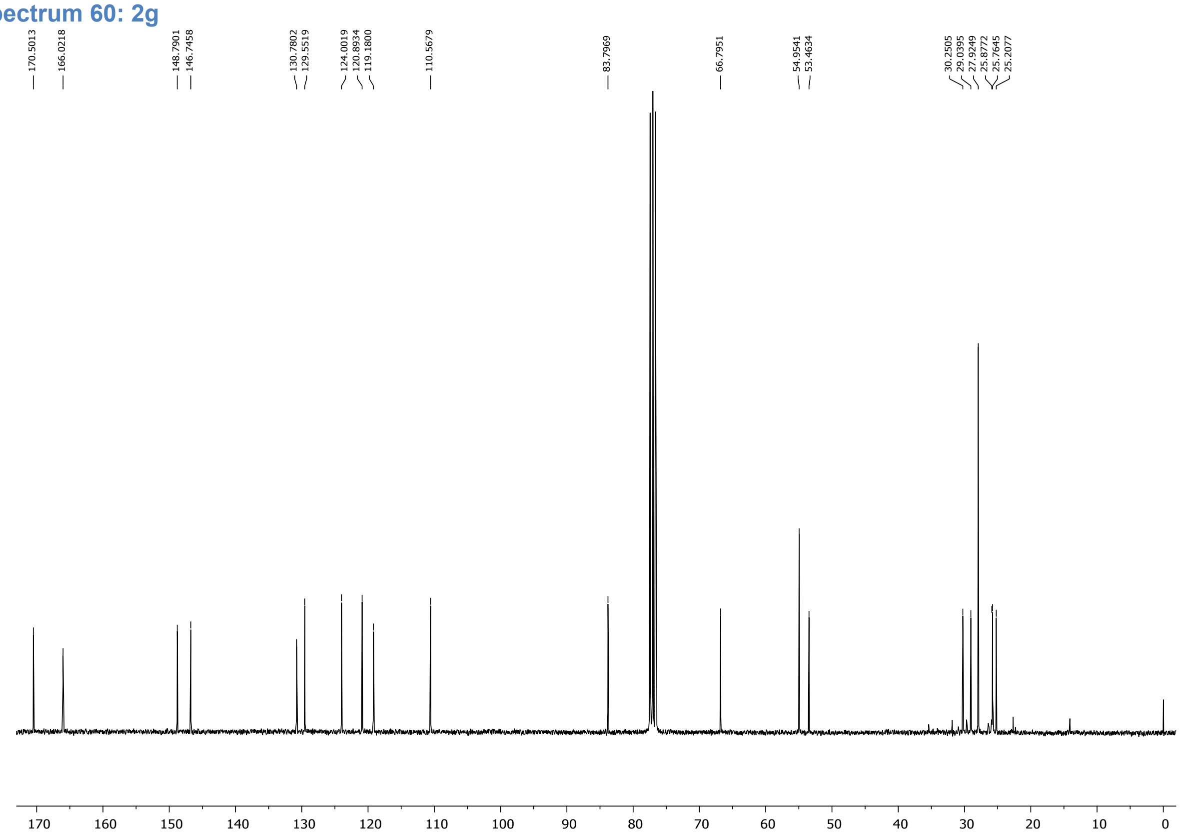
Spectrum 58: 2f



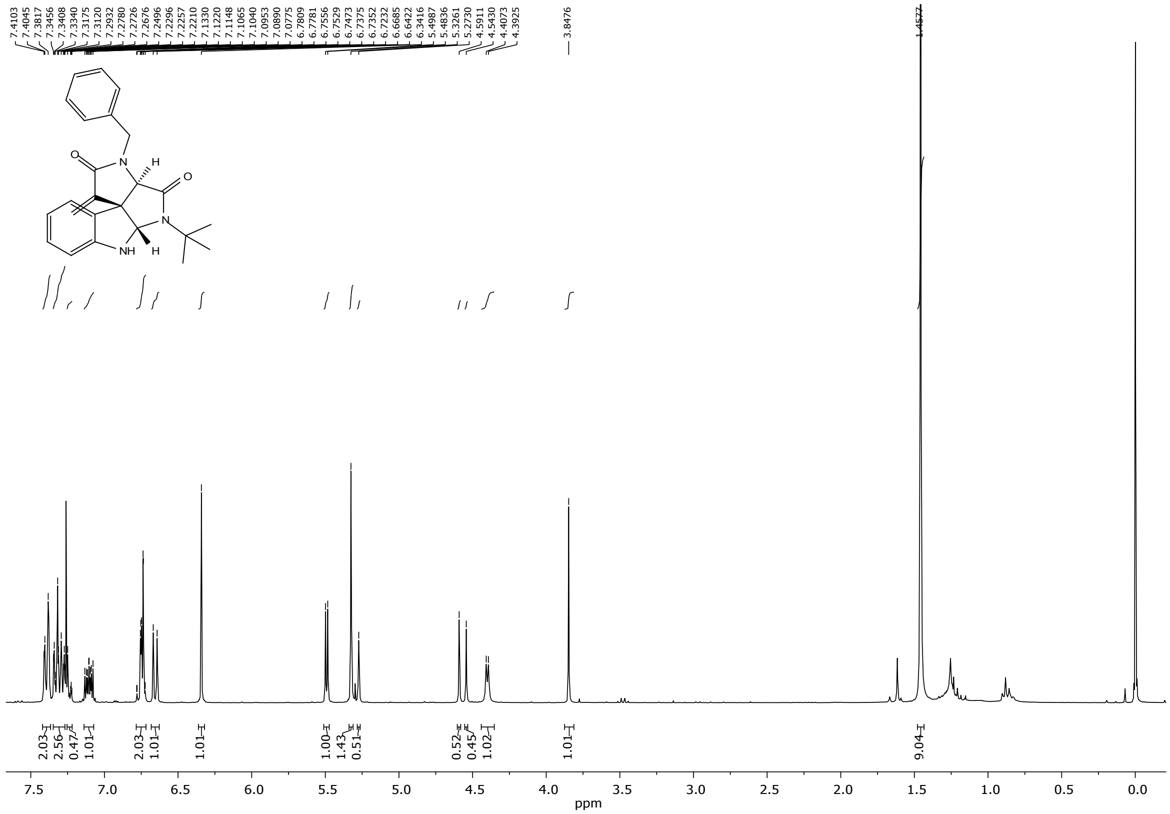
Spectrum 59: 2g



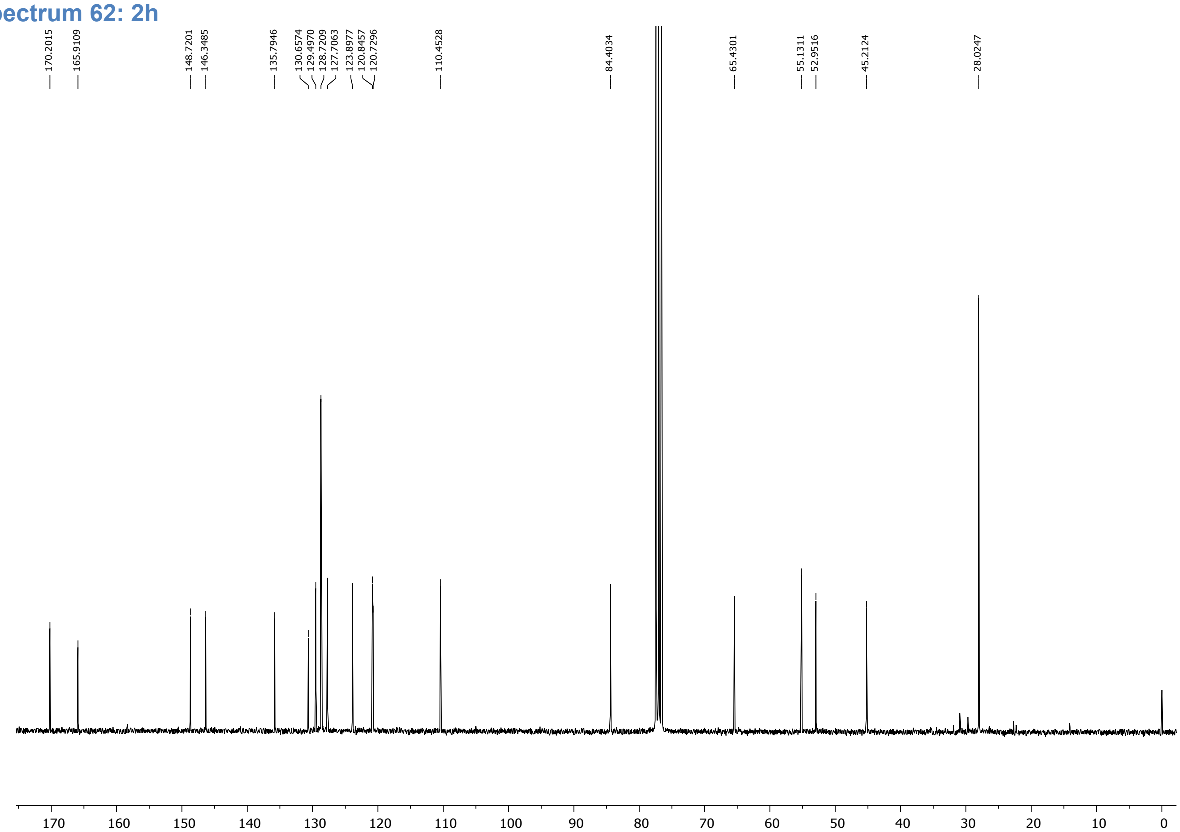
Spectrum 60: 2g



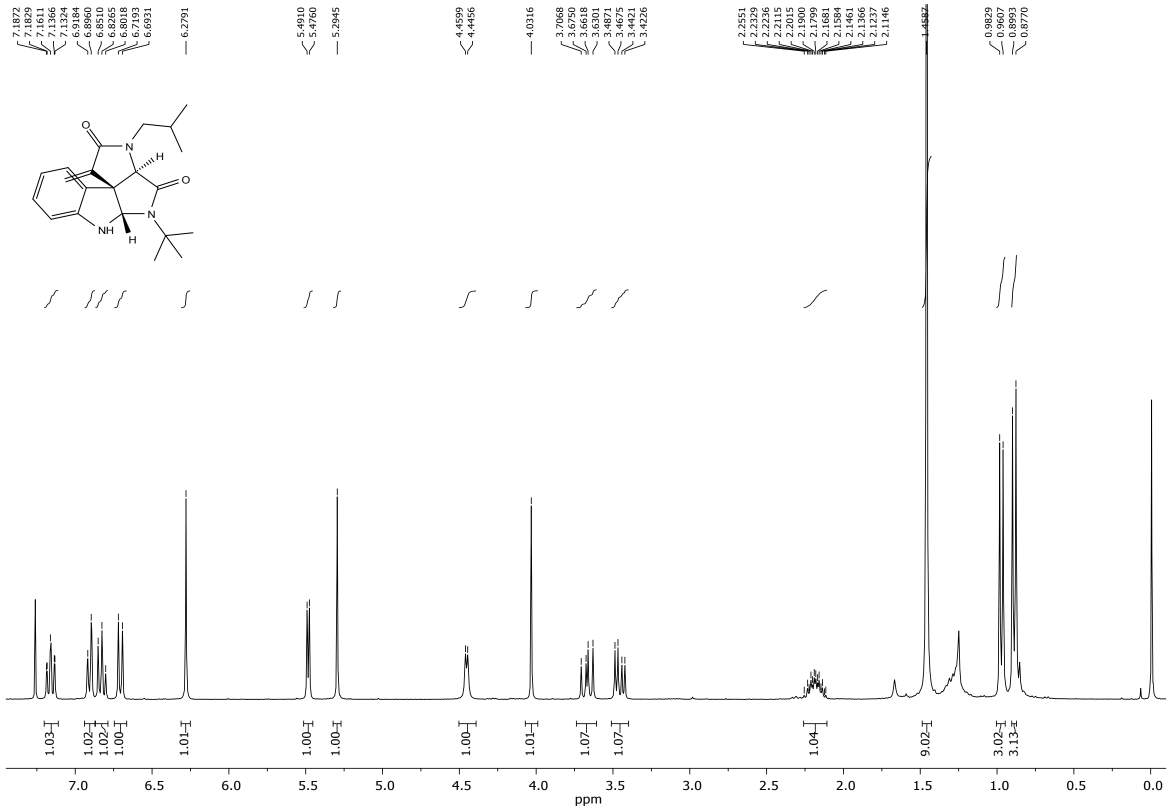
Spectrum 61: 2h



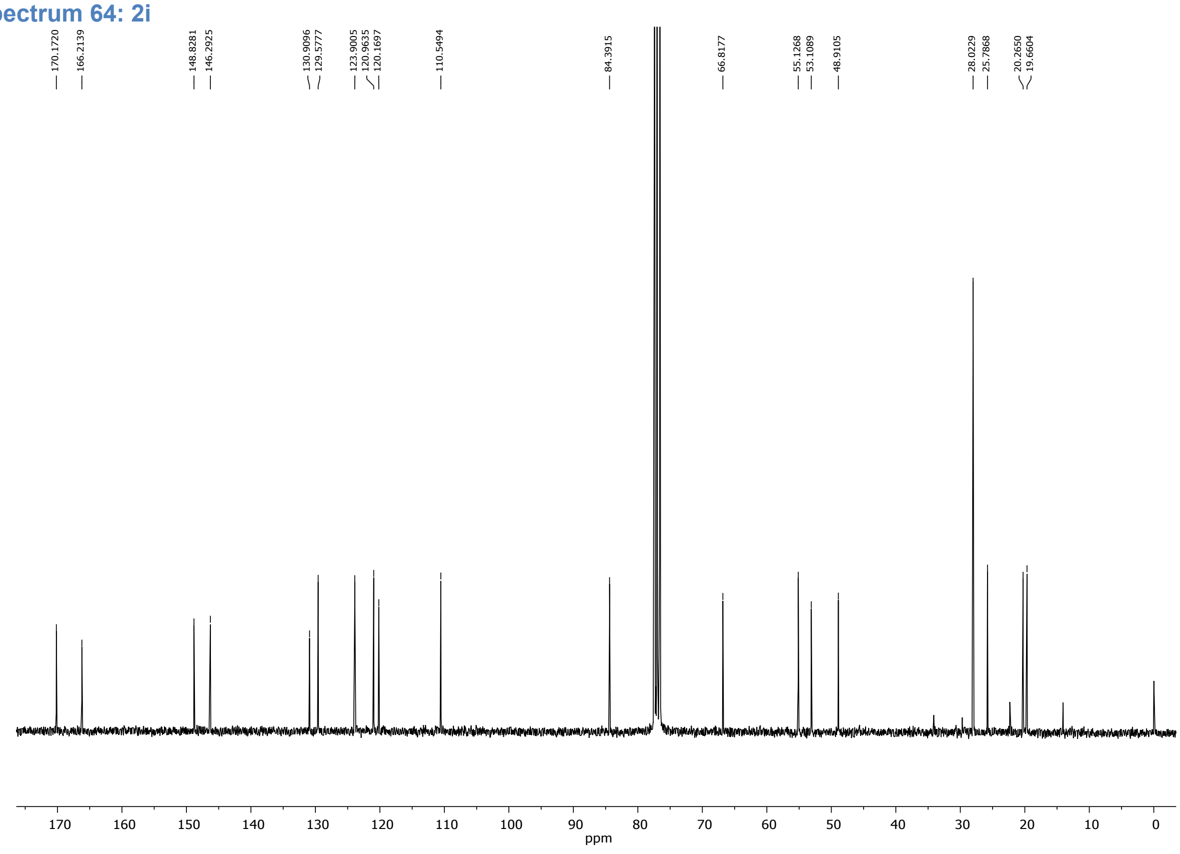
Spectrum 62: 2h



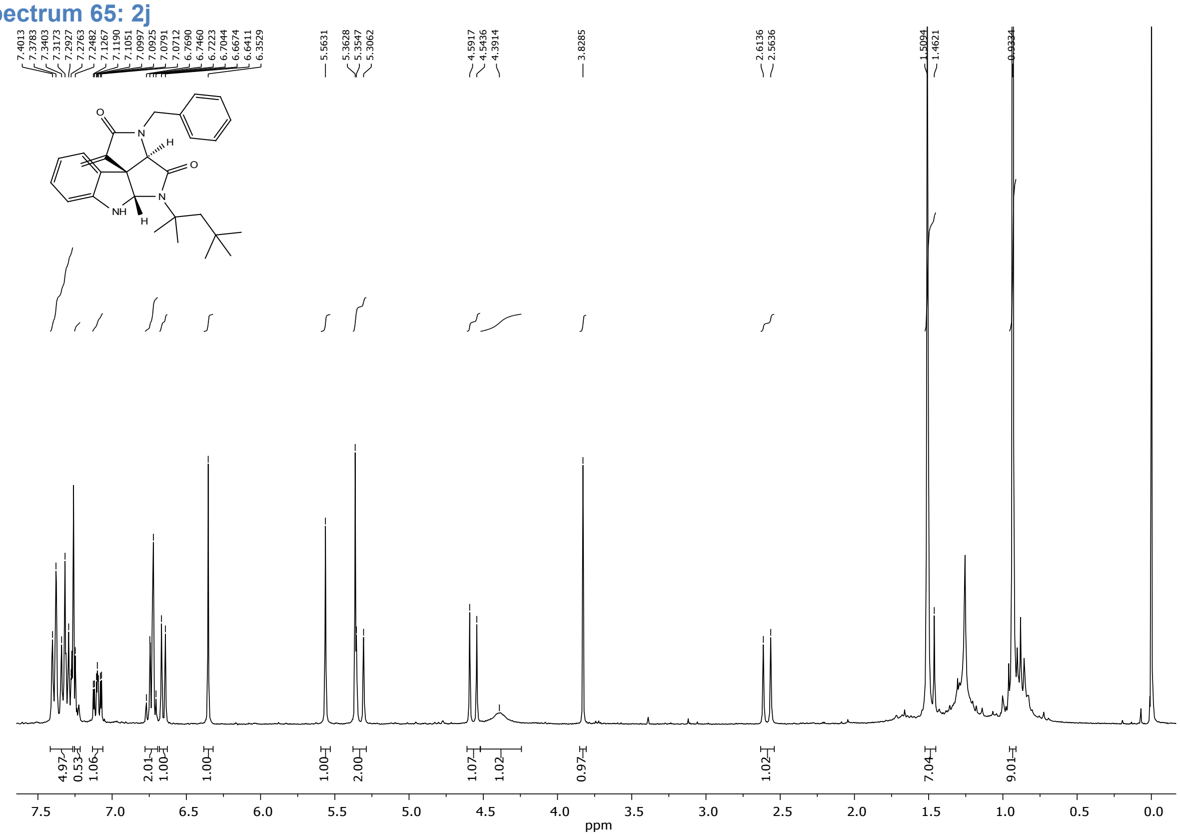
Spectrum 63: 2i



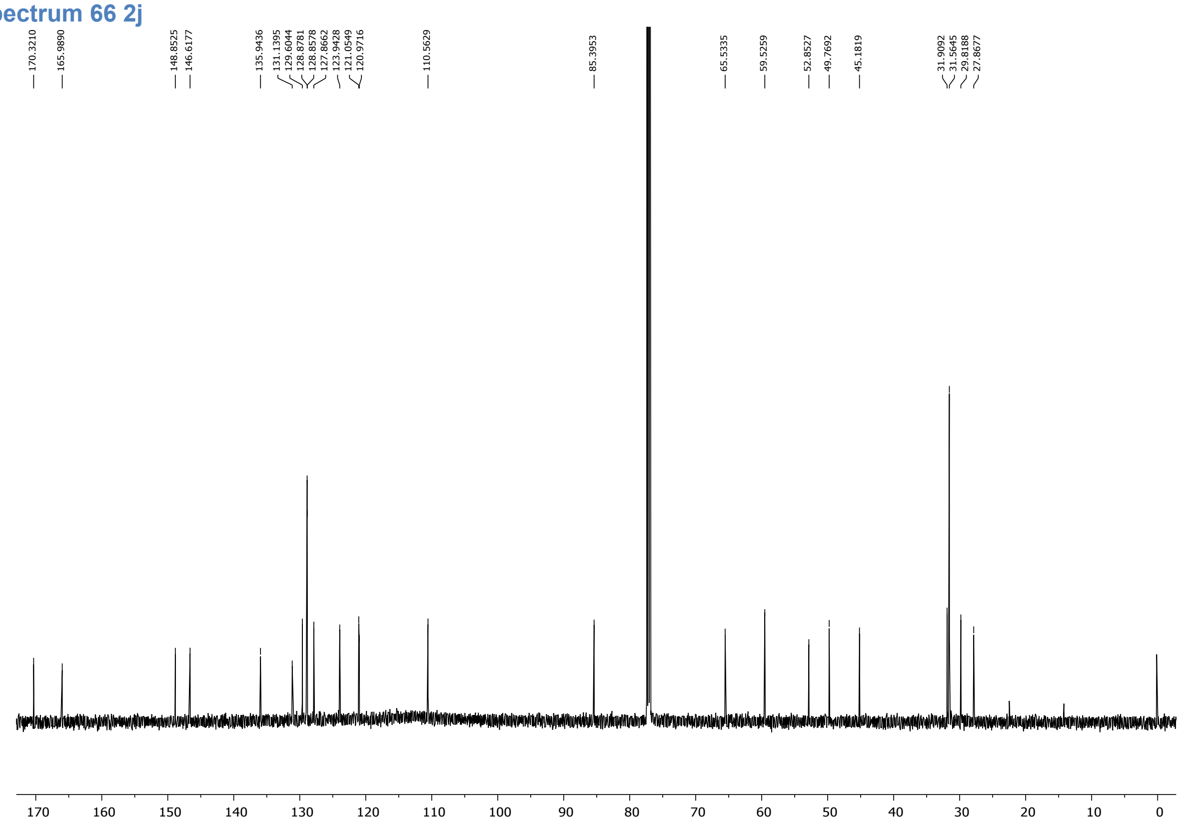
Spectrum 64: 2i



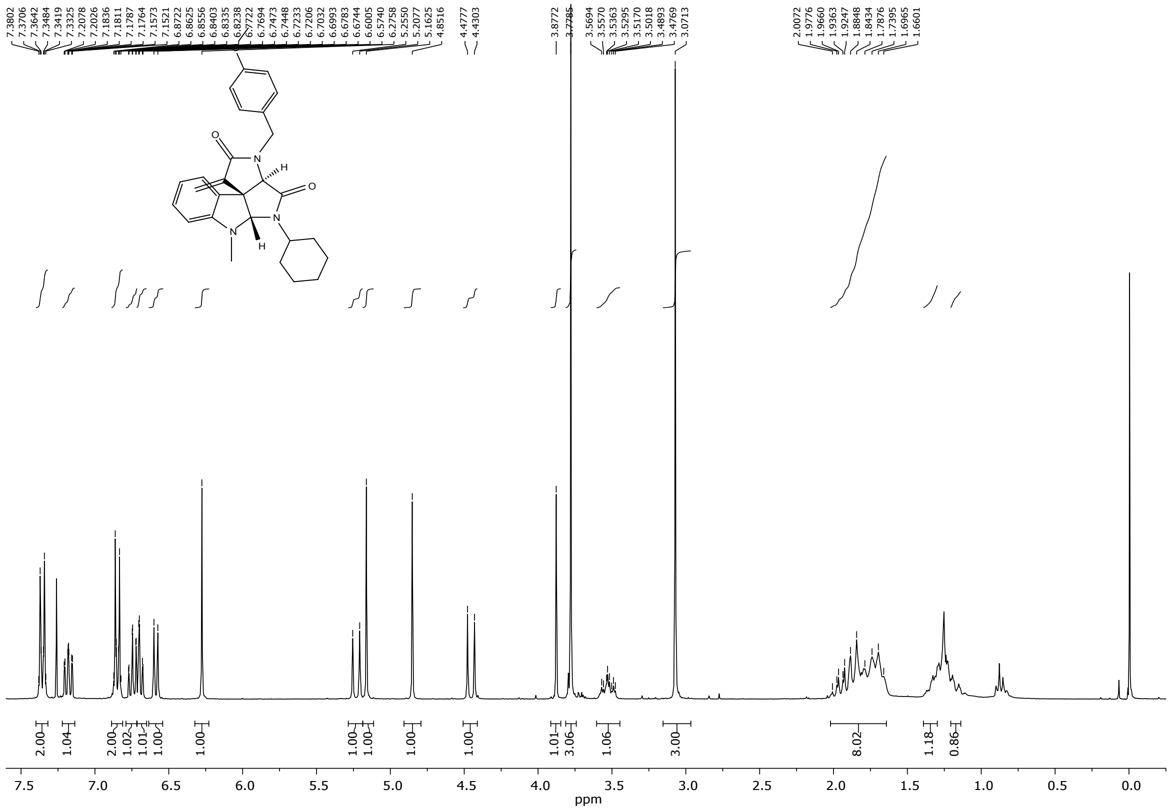
Spectrum 65: 2j



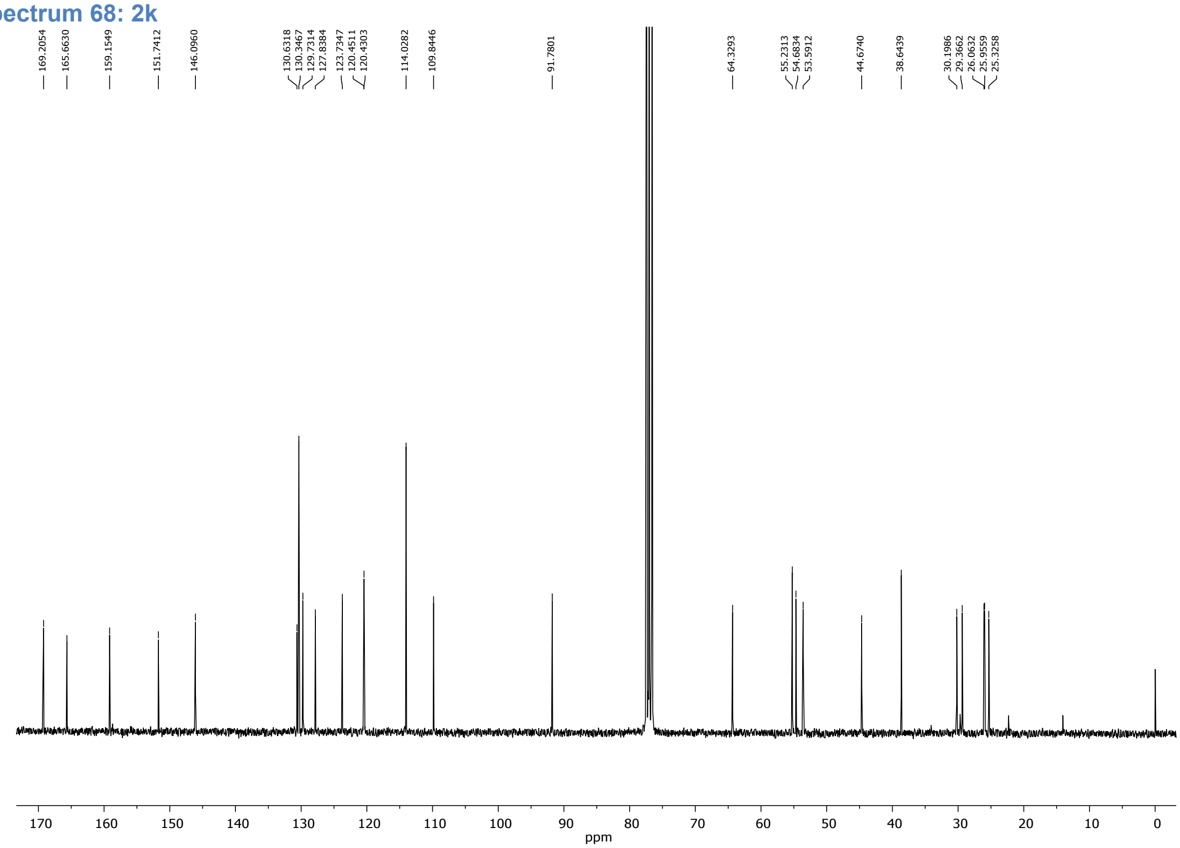
Spectrum 66 2j



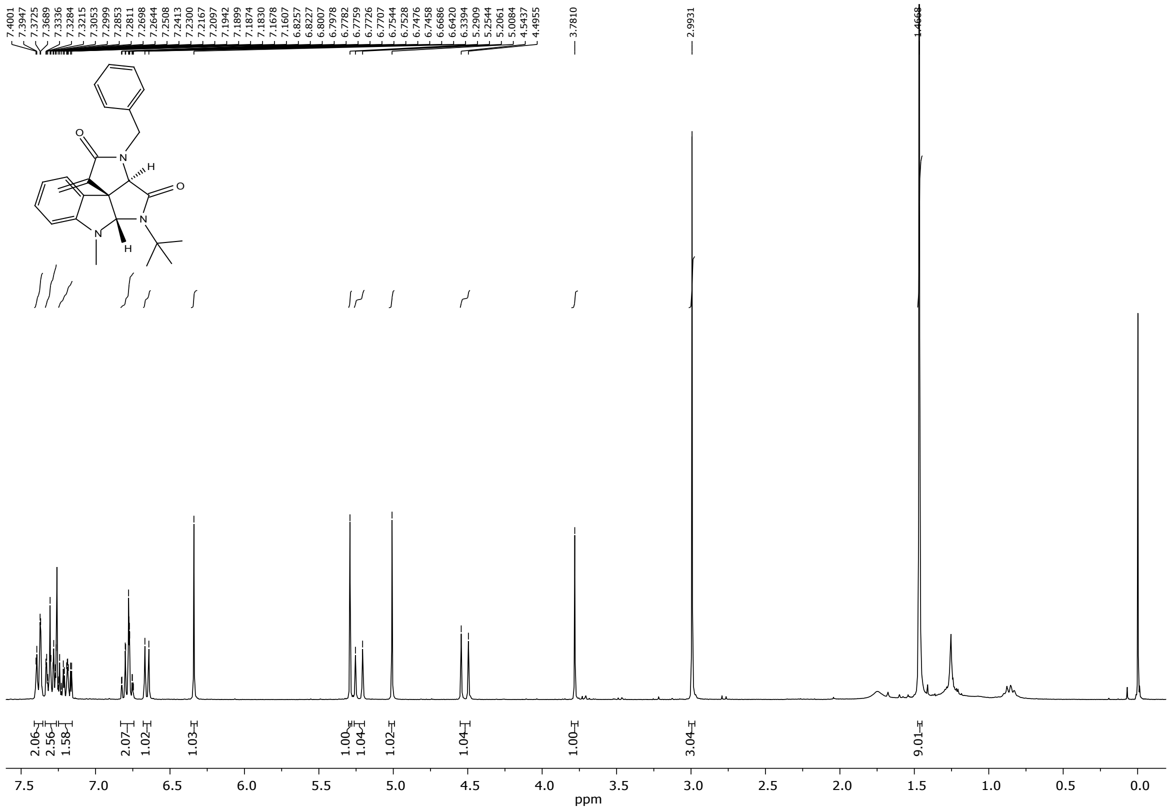
Spectrum 67: 2k



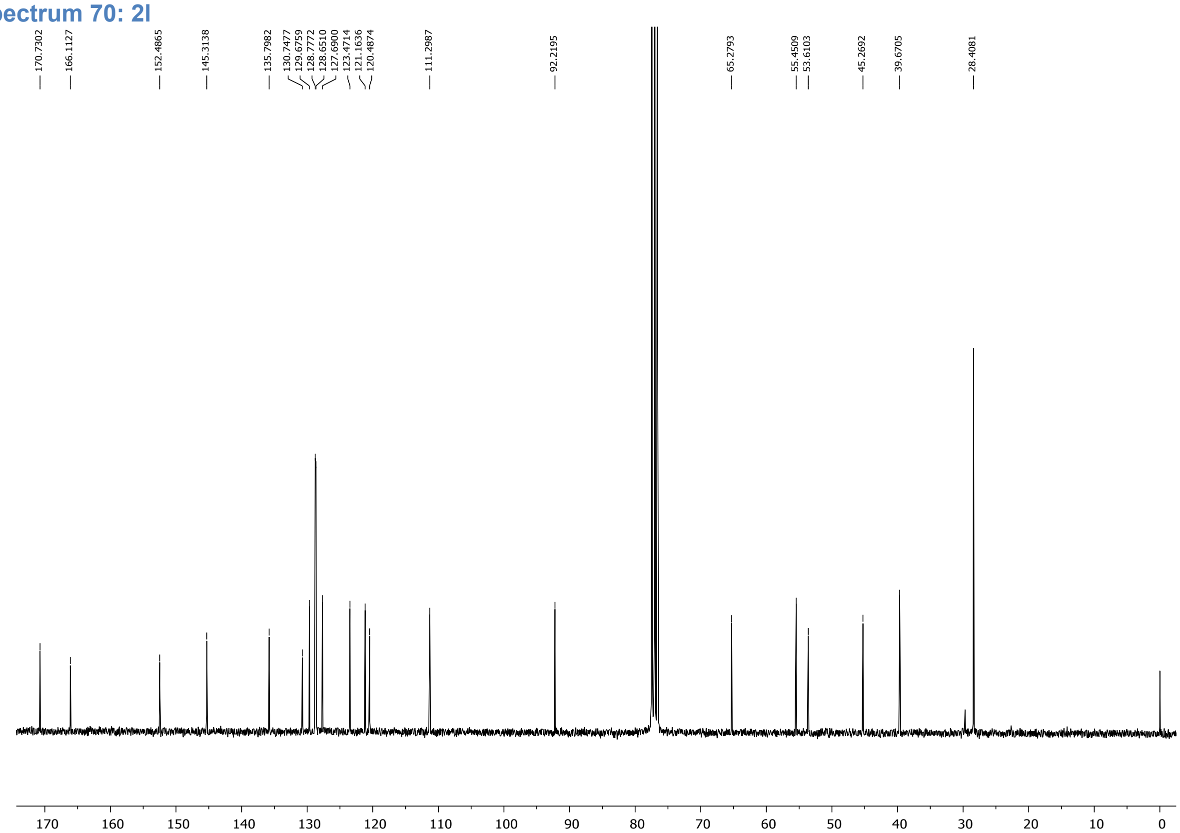
Spectrum 68: 2k



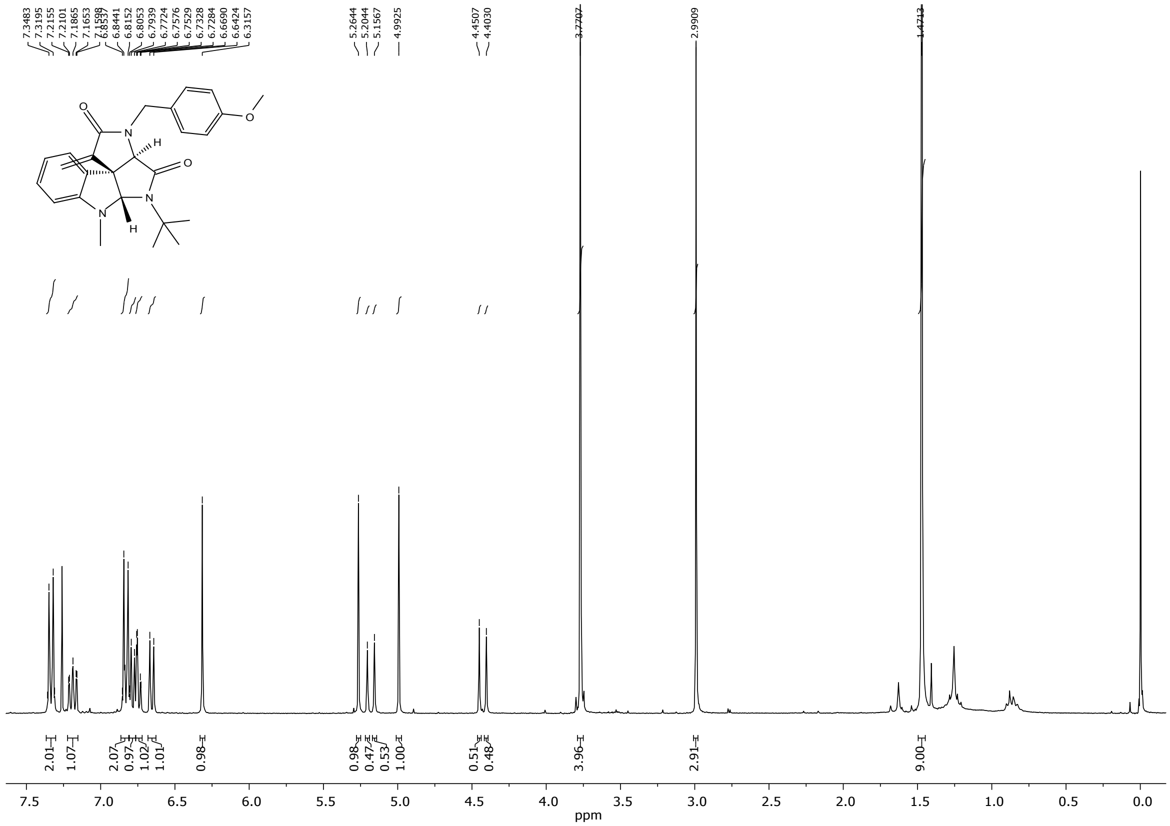
Spectrum 69: 2l



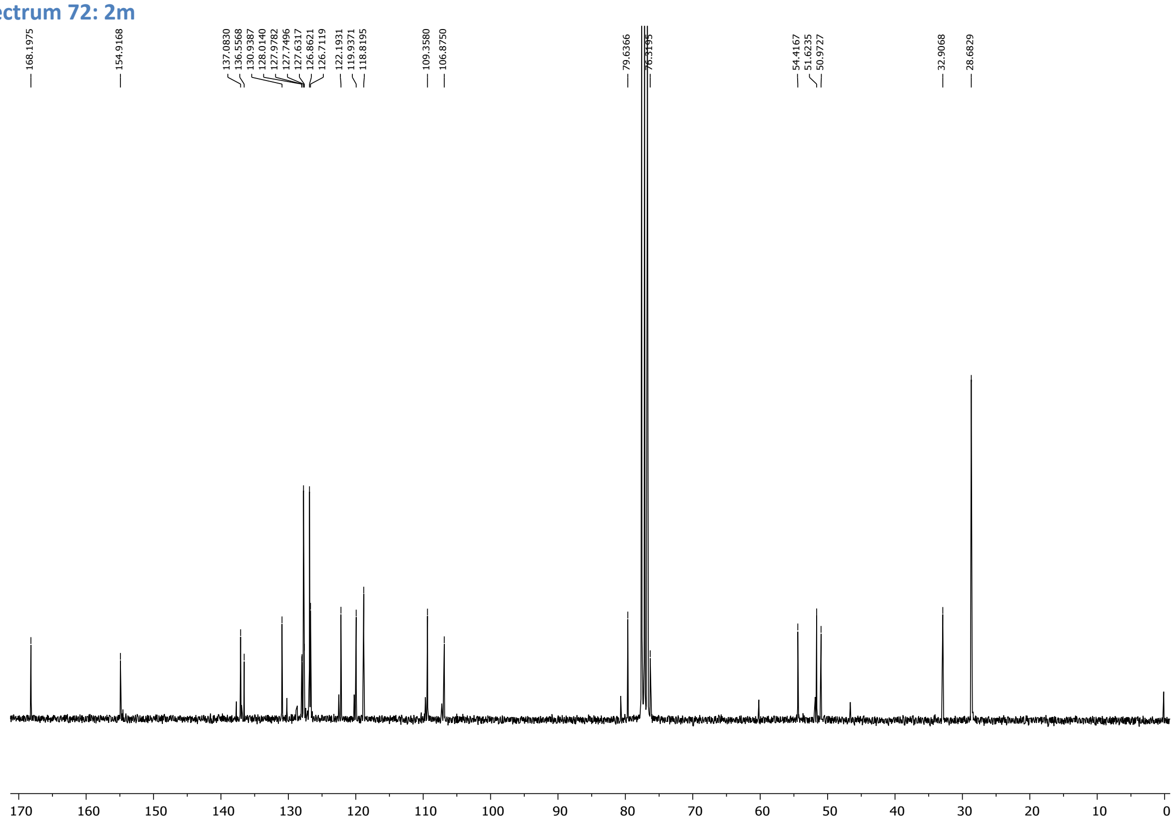
Spectrum 70: 2l



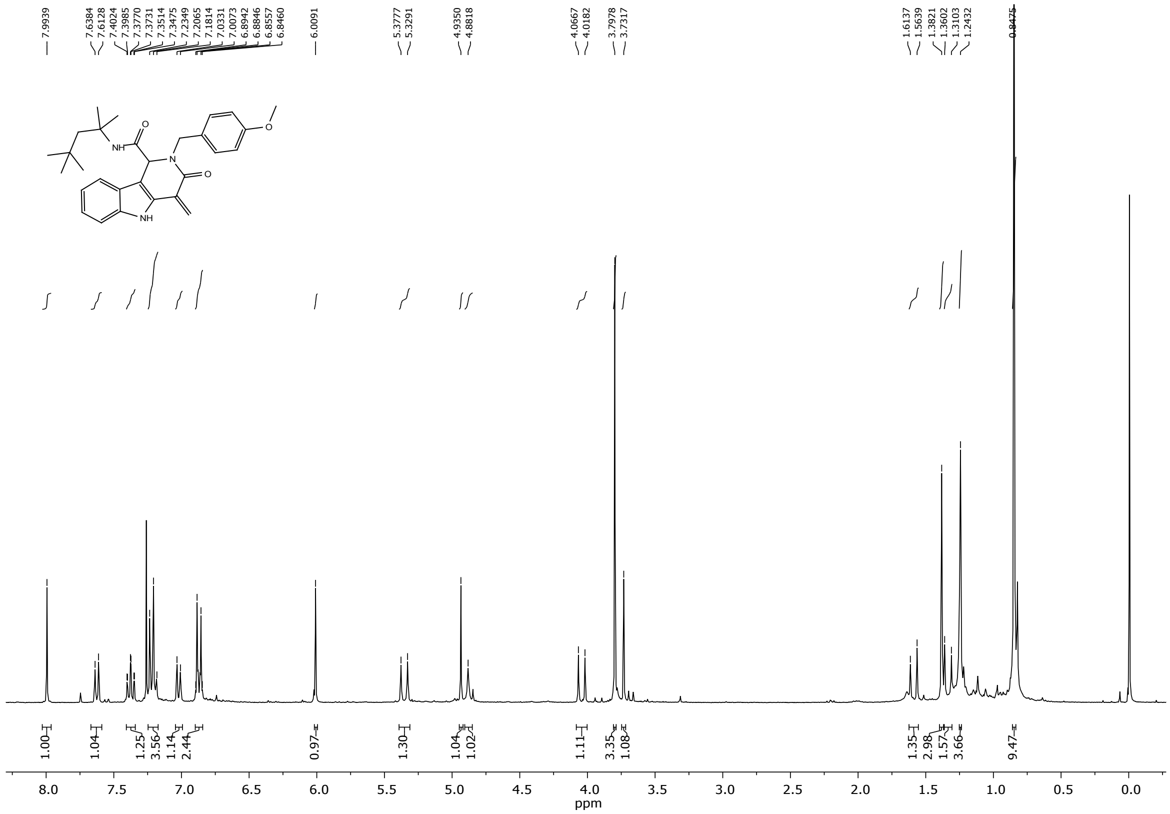
Spectrum 71: 2m



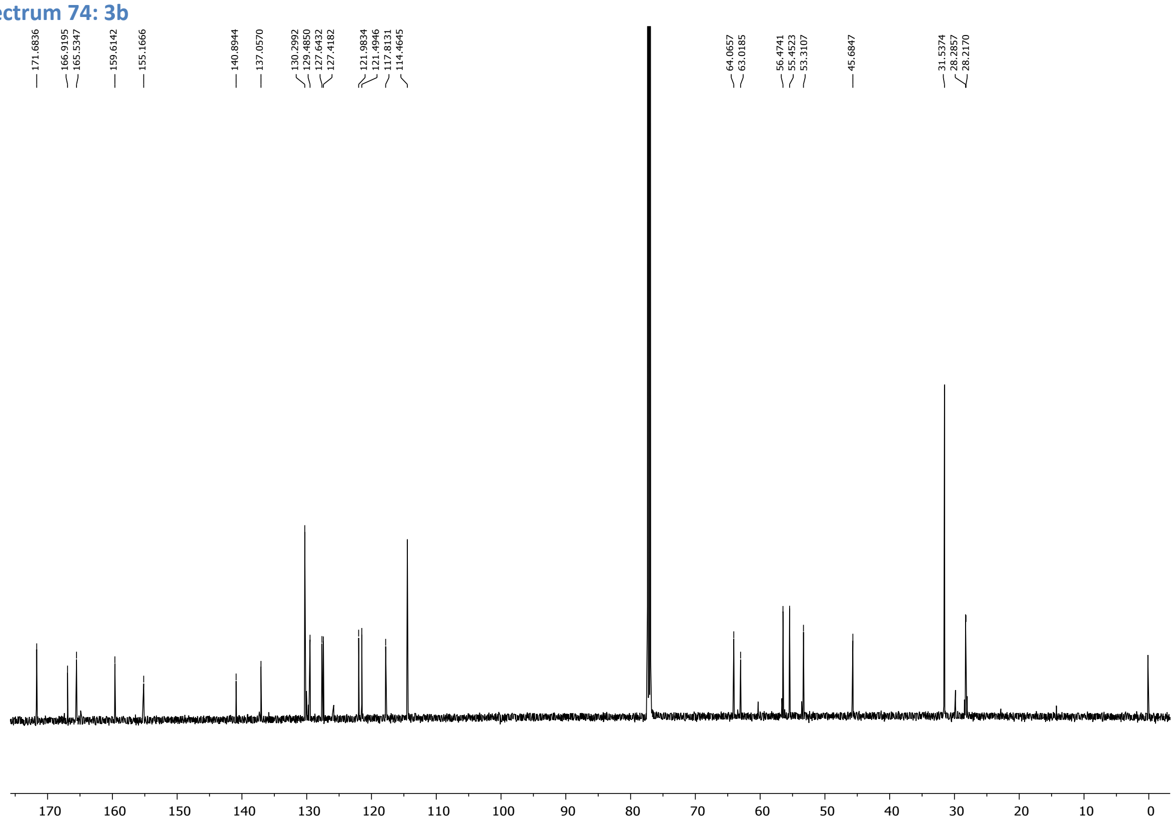
Spectrum 72: 2m



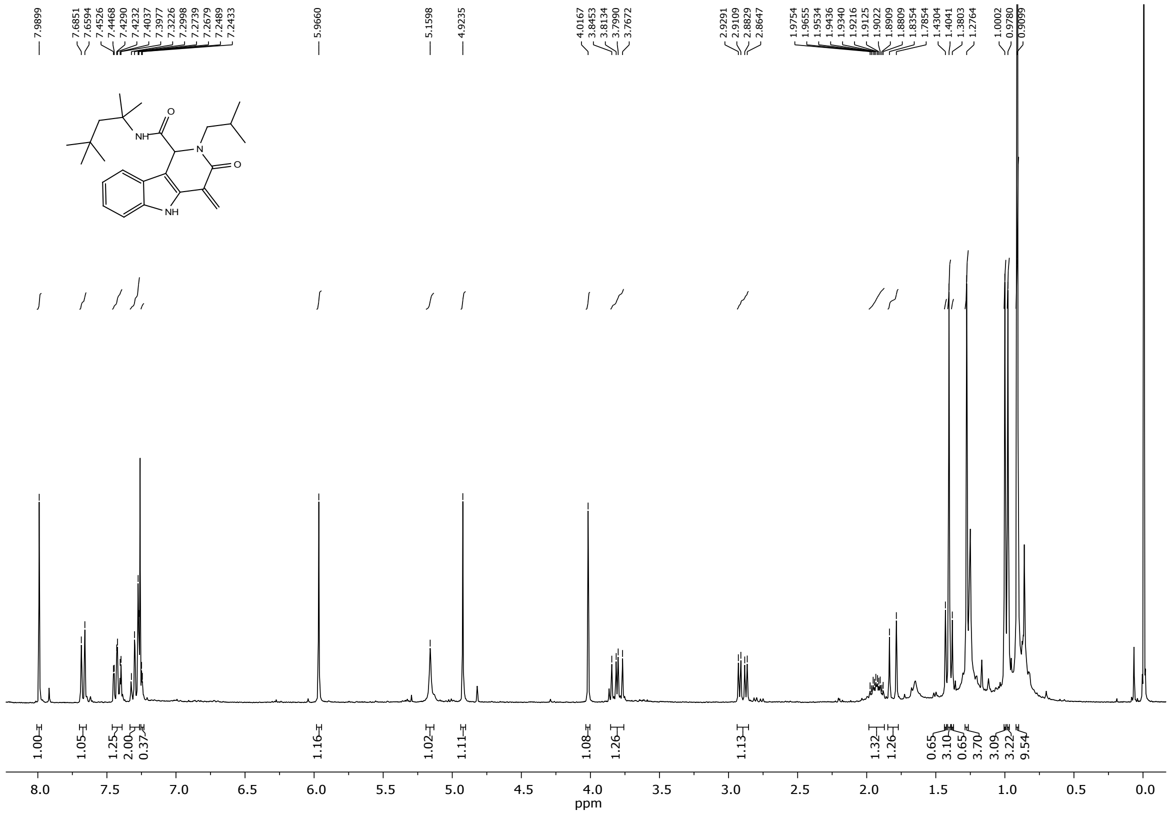
Spectrum 73: 3b



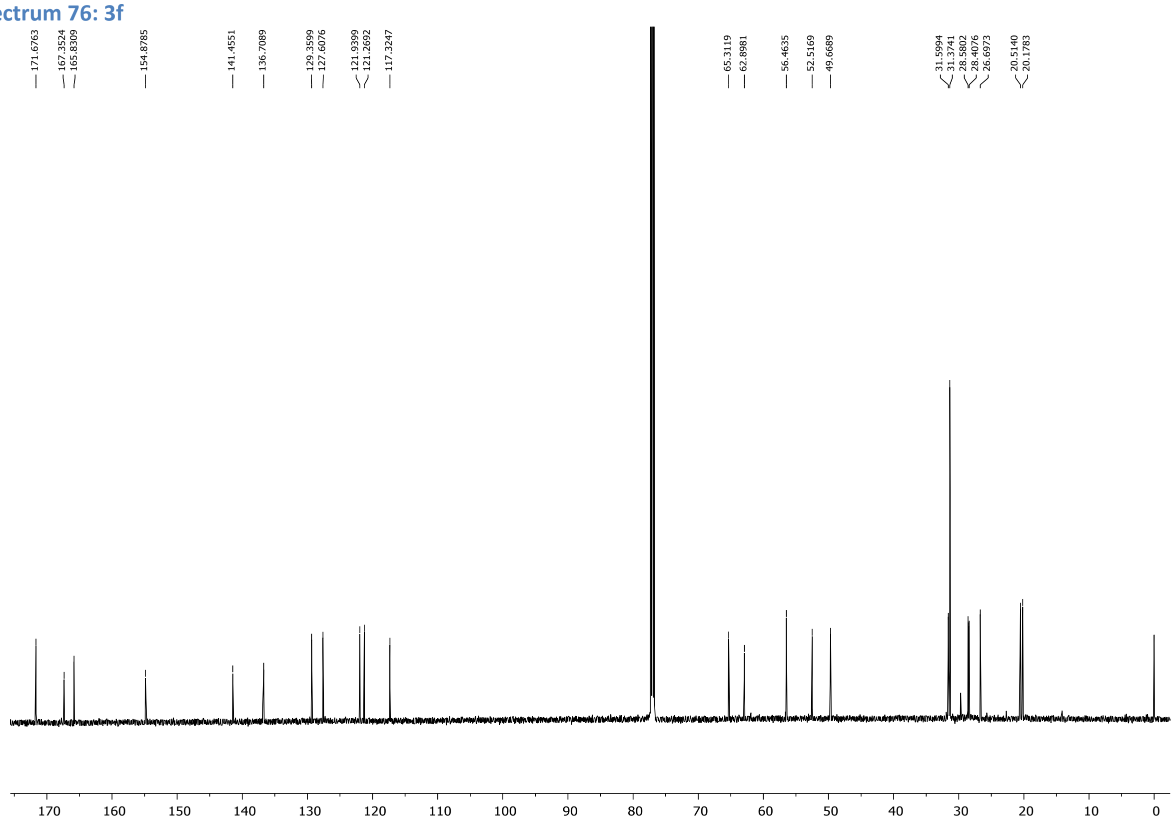
Spectrum 74: 3b



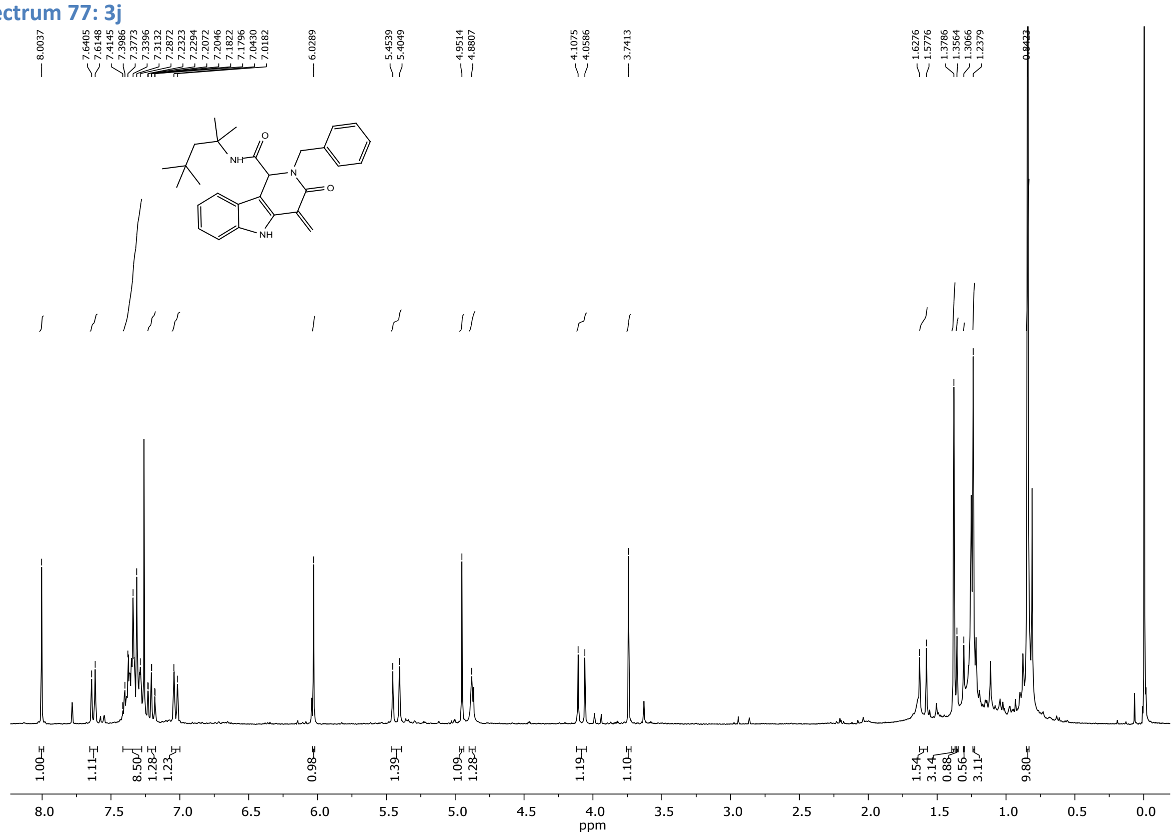
Spectrum 75: 3f



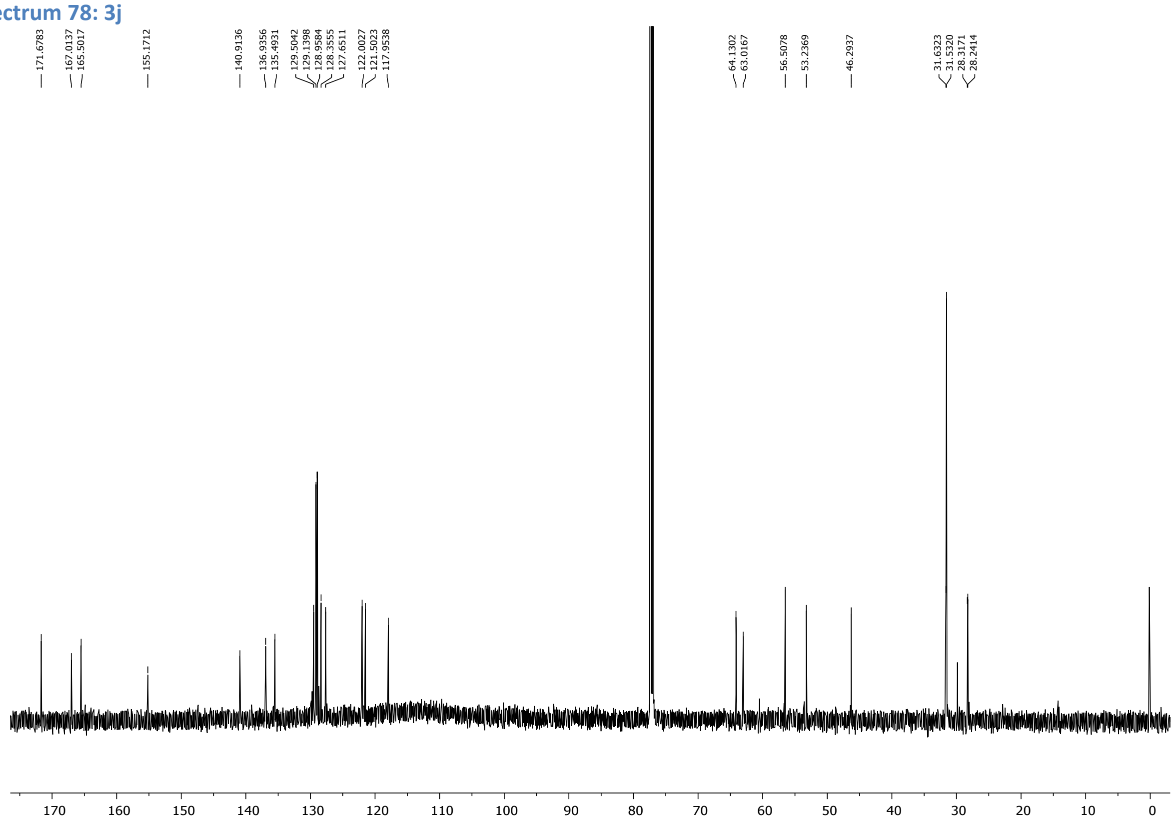
Spectrum 76: 3f



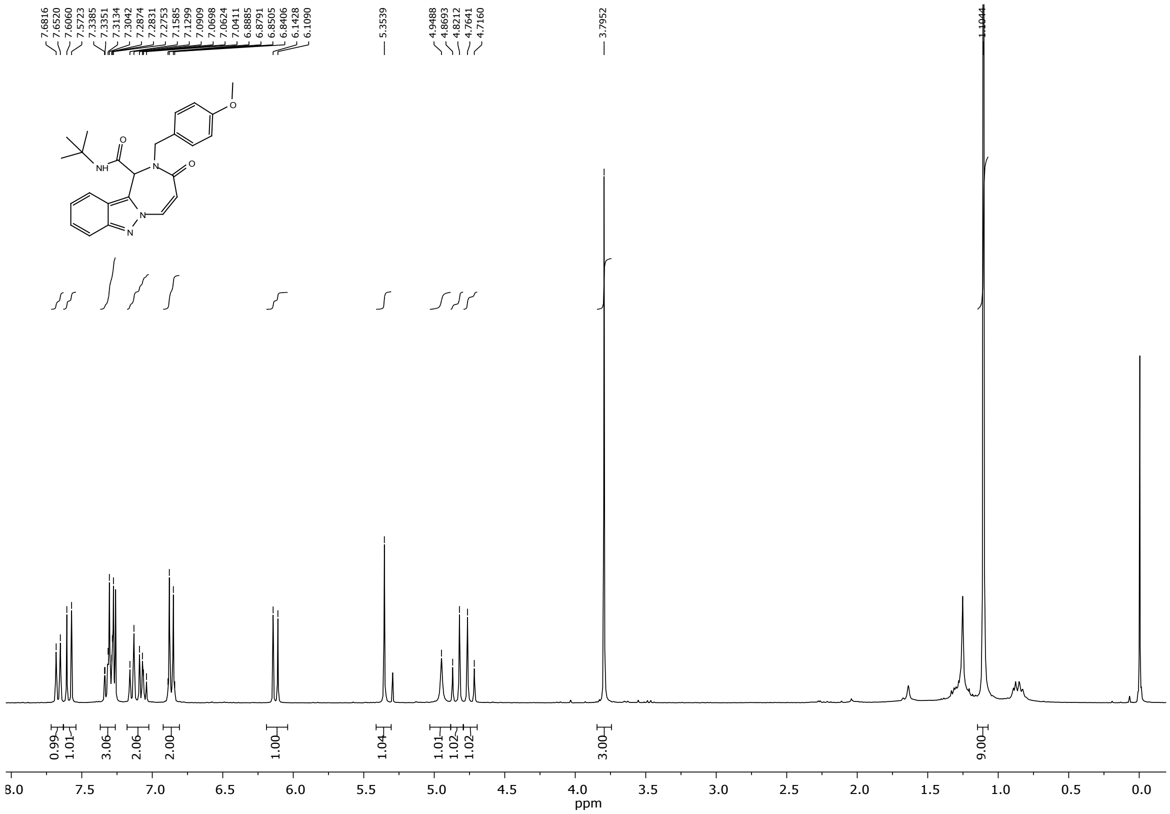
Spectrum 77: 3j



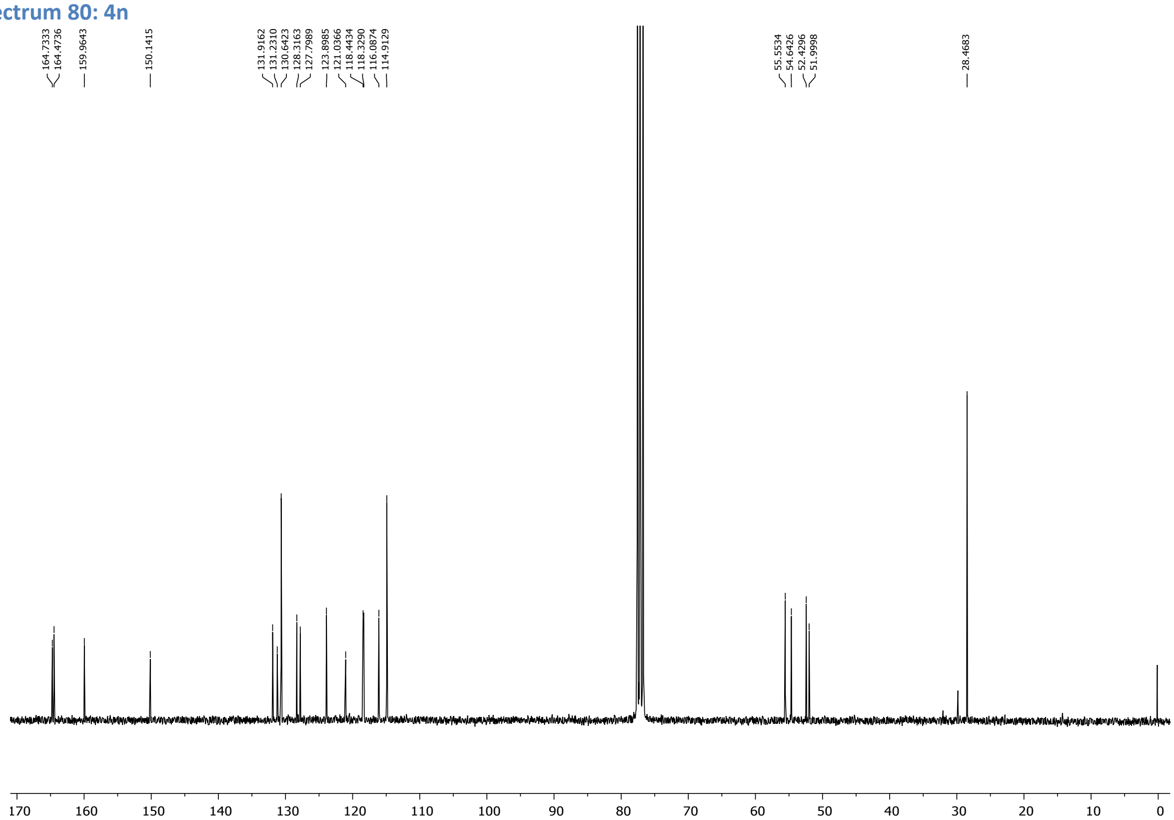
Spectrum 78: 3j



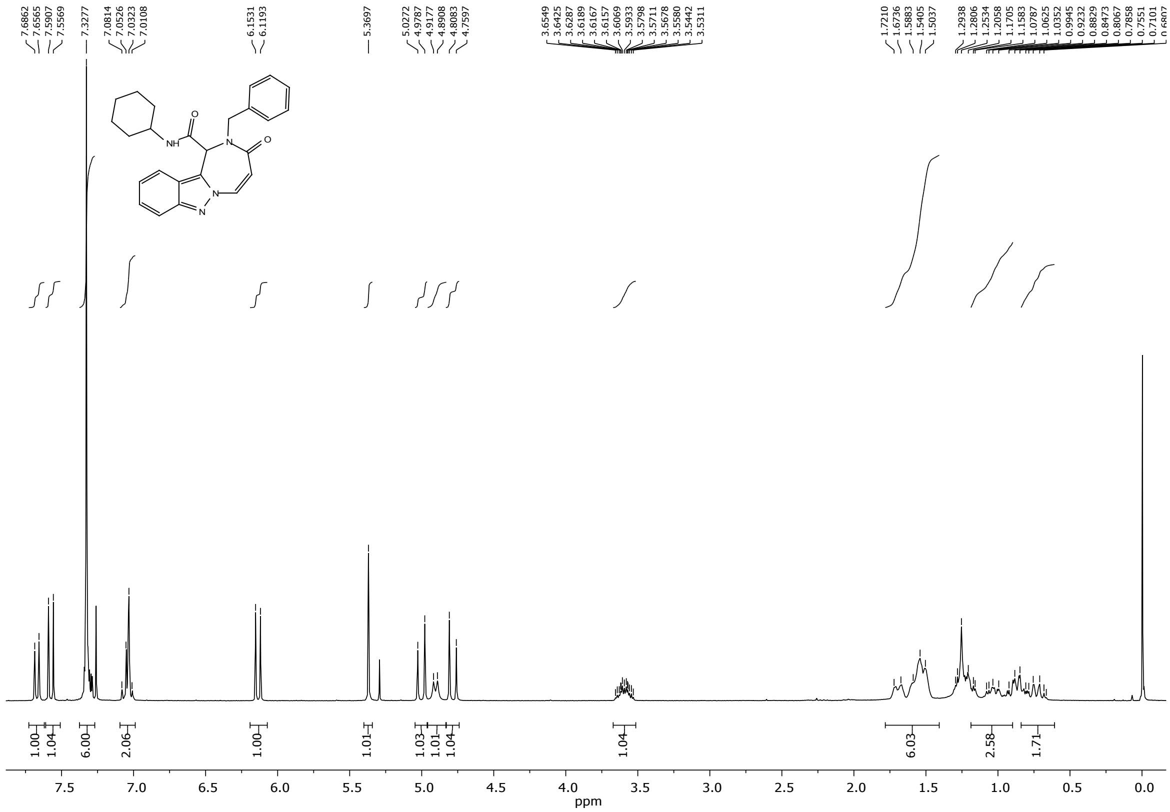
Spectrum 79: 4n



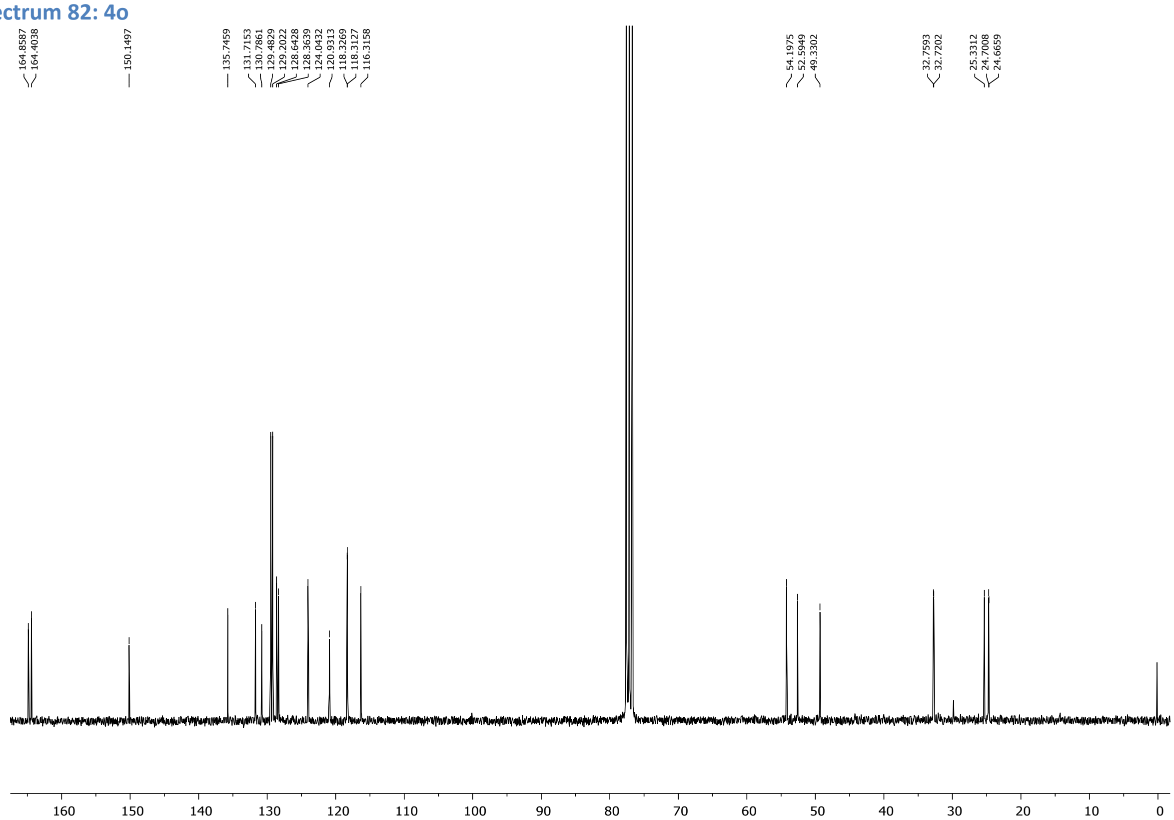
Spectrum 80: 4n



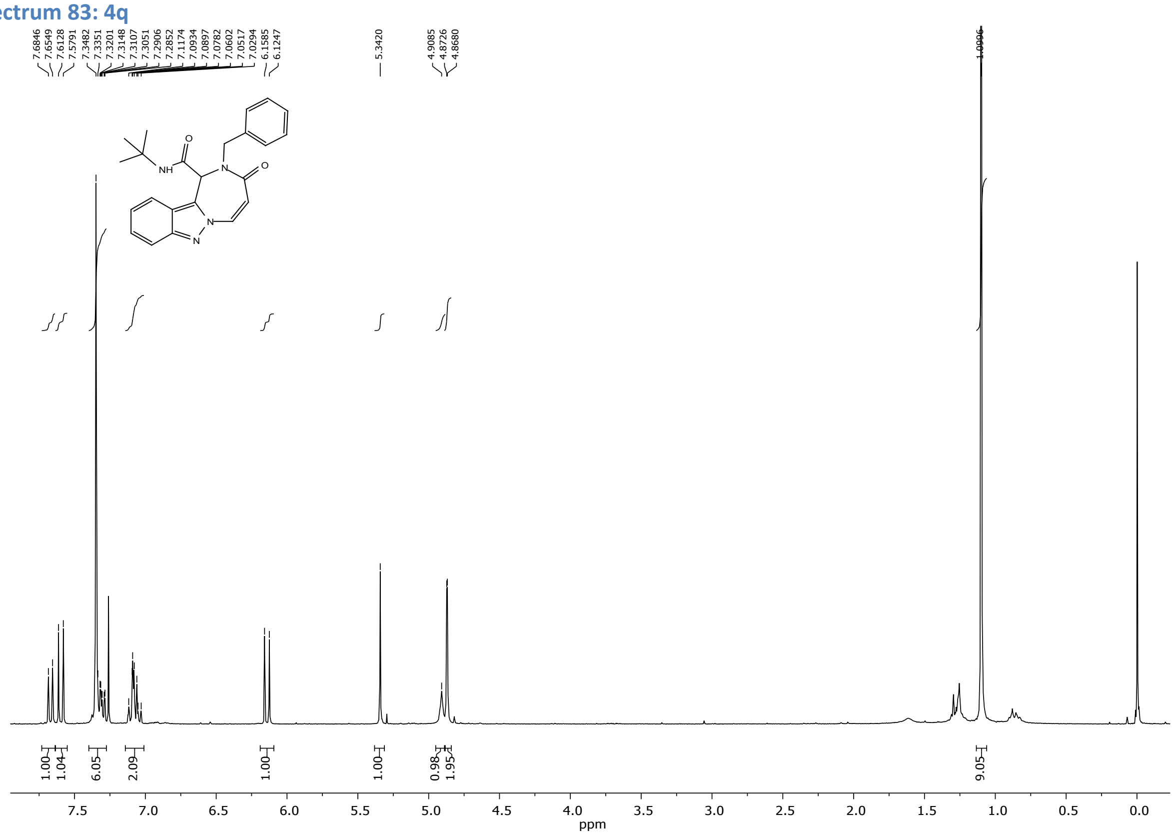
Spectrum 81: 4o



Spectrum 82: 4o



Spectrum 83: 4q



Spectrum 84: 4q