Supporting Information

Convenient synthesis of tricyclic N(1)-C(2)-fused oxazino-indolones via [Au(I)] catalyzed hydrocarboxylation of allenes

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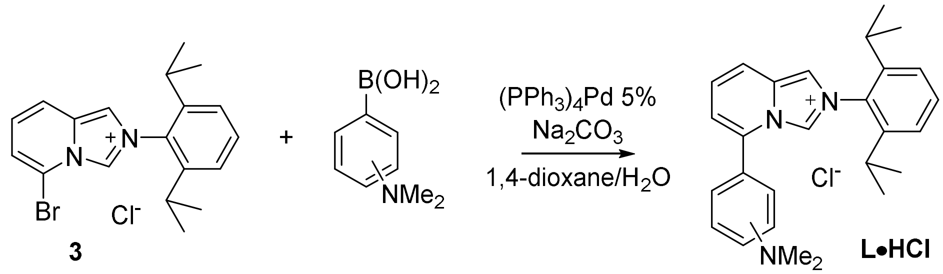
General methods

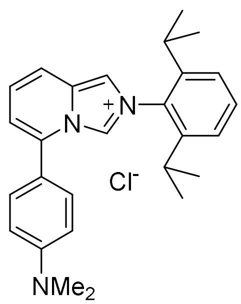
^{1}H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm). ^{19}F-NMR spectra were recorded on a Varian 400 (377 MHz). Chemical shifts are reported in ppm from $CFCl_3$. Two peaks of negative intensity in the ^{13}C NMR spectra at 21.3 and 135.2 ppm are sometimes present. They arise from a "spike" generated by two external radiofrequency interfering with the ^{13}C NMR frequency at 100 MHz. The presence of these peaks does not however prevent a clear understanding of the spectral data and, in all cases, the peaks in the interested region have been correctly identified. GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: m/z (rel. intense). LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Elemental analyses were carried out by using a EACE 1110 CHNOS analyzer. Melting points were determined with Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are not corrected. Chromatographic purification was done with 240-400 mesh silica gel. Anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Ethyl acetate was dried on activated 5 Å molecular sieves. Commercially available chemicals were purchased from Sigma Aldrich, Fluorochem, TCI and Thermo Fisher and used without any further purification.

Known starting materials were prepared according to the literature: **3**,[1] **4**,[2] **Cat1, Cat5** and **Cat6,**[3] (*R*)-tBu-**7**,[4] (*S*)-Ad-**7**,[5] and **11l**,[6] allenyl alcohols.[7]

Synthesis of L2•HCl and L3•HCl

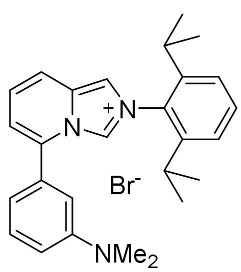


Adapted from reference[8] A two-necked-round bottom flask equipped with a condenser, under inert atmosphere, was charged with **3** (197 mg, 0.5 mmol), [Pd(PPh_3)$_4$] (29 mg, 0.025 mmol, 5 mol%), desired aryl boronic acid (0.6 mmol, 1.2eq) and 3.5 mL of degassed 1,4-dioxane. The reaction was stirred at room temperature for 30 min, then 1.2 mL of 0.5 M solution of Na_2CO_3 (1.2 eq) in degassed water was added and the reaction mixture heated at 80 °C. The reaction was monitored by TLC DCM/MeOH 10:1. After consumption of **3** the reaction mixture was extracted 3 times with CH_2Cl_2, dried on Na_2SO_4 and purified by flash chromatography with DCM/MeOH 20:1 as eluent.



L2•HCl, pale yellow powder, 72%. **MP**: decomposition.

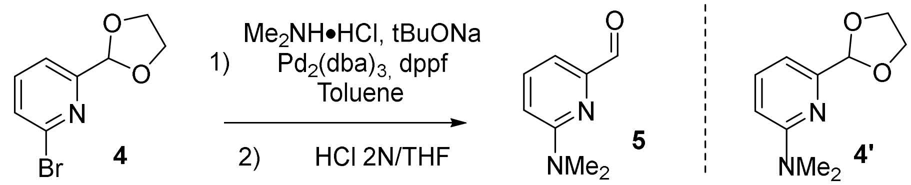
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (d, *J* = 1.9 Hz, 1H), 8.60 (dd, *J* = 2.0, 0.9 Hz, 1H), 8.42 (dt, *J* = 9.4, 1.0 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.37 – 7.16 (m, 5H), 6.98 (dd, *J* = 7.0, 1.1 Hz, 1H), 6.73 – 6.65 (m, 2H), 2.90 (s, 6H), 2.02 (hept, *J* = 6.8 Hz, 2H), 1.09 (d, *J* = 6.8 Hz, 6H), 1.00 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.85, 144.84, 135.73, 132.46, 132.08, 130.46, 128.86, 126.57, 124.56, 122.13, 118.51, 118.43, 118.37, 116.61, 112.44, 40.01, 28.59, 24.51, 24.17. **LC-MS (ESI)**: 398.6 [M -Cl$^-$]$^+$. **Anal. El.** Calc. for $C_{27}H_{32}ClN_3$: C 74.72; H 7.43; N, 9.68; found: C 74.94; H 7.36; N, 9.75.



L3•HBr, pale yellow powder, 67%. **MP**: decomposition.

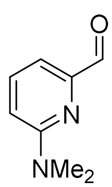
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.92 (d, *J* = 1.8 Hz, 1H), 8.59 (d, *J* = 9.4 Hz, 1H), 8.56 (d, *J* = 1.1 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.42 (dd, *J* = 9.3, 6.9 Hz, 1H), 7.32 (t, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.14 (dd, *J* = 6.9, 1.0 Hz, 1H), 6.82 – 6.71 (m, 3H), 2.91 (s, 6H), 2.07 (hept, J = 6.6 Hz, 2H), 1.15 (d, *J* = 6.8 Hz, 6H), 1.03 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.24, 144.89, 135.75, 132.27, 132.17, 131.39, 130.81, 130.43, 126.37, 124.62, 122.27, 119.80, 119.24, 118.87, 114.64, 114.61, 110.76, 40.18, 28.65, 24.50, 24.23. **LC-MS(ESI)**: 398.6 [M -Br$^-$]$^+$. **Anal. El.** Calc. for $C_{27}H_{32}BrN_3$: C 74.72; H 7.43; N, 9.68; found: C 74.82; H 7.51; N, 9.73.

Synthesis of L4•HCl



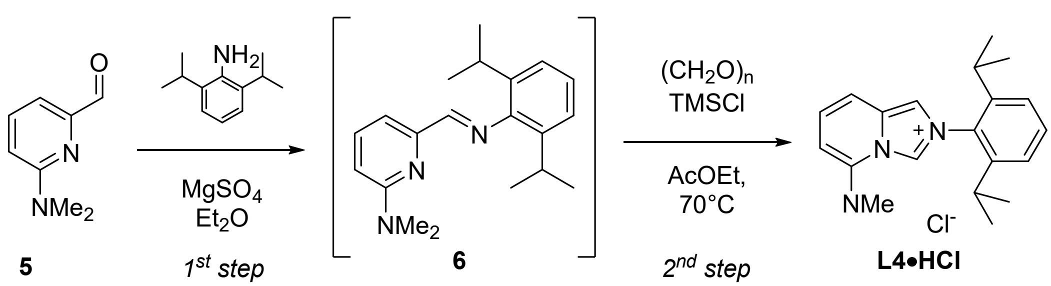
Step 1) To an oven dried Schlenk tube, under nitrogen atmosphere, Me_2NH•HCl (408 mg, 5 mmol), $Pd_2(dba)_3$ (31 mg, 30 µmol, 2.5mol%) and dppf (65 mg, 0.12 mmol, 10 mol%) were added. Then, 8 mL of dry toluene and **4** (460 mg, 2 mmol) were added and the mixture was degassed by nitrogen bubbling. Finally, *t*BuONa (1.15 g, 12 mmol) was added and the reaction mixture heated to reflux. The progress of the reaction was monitored *via* GC-MS. After complete consumption of **4** the reaction was cooled to room temperature, 10 mL of distilled water were added and the crude extracted with DCM (3 x 10 mL). The organic phase was filtered through Celite®, dried over Na_2SO_4 and solvents evaporated with rotavapor.

Step 2) Crude **4’** was dissolved in 6 mL of THF and transferred into a one neck flask. Equal volume of HCl 2 M (6 mL, 12 mmol) was added and reaction heated at 70 °C. Reaction monitoring was executed by picking up few drops of mixture and quenching it in a saturated solution of $NaHCO_3$. AcOEt was added to extract organic compound and TLC was done. After complete conversion the reaction was cooled to room temperature and transferred to an Erlenmeyer flask. Saturated solution of $NaHCO_3$ was slowly added until pH ≈ 8. The mixture was extracted with diethyl ether 3 x 15 mL and dried over Na_2SO_4. Solvents were evaporated and **5** was purified by flash chromatography using *n*Hex/AcOEt 20:1 as the eluent.



5, light yellow oil, 80% over 2 steps.

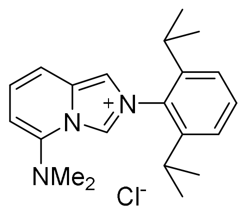
^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.87 (t, *J* = 2.5 Hz, 1H), 7.59 – 7.48 (m, 1H), 7.17 (dd, *J* = 7.3, 2.1 Hz, 1H), 6.68 (dd, *J* = 8.5, 2.1 Hz, 1H), 3.12 (d, *J* = 2.1 Hz, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 194.53, 159.31, 151.15, 137.63, 110.25, 109.89, 37.83. **GC-MS(EI)**: 135 (100%, -Me), 121 (90%), 150 (72%, $M^{•+}$). Anal. El. Calc. for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65; O, 10.65; found: C, 63.89; H, 6.81; N, 18.60; O, 10.69.



Step 1) A two necked-round-bottom flask charged with excess of $MgSO_4$ (500 mg/mmol of **5**) was dried under vacuum and putted under inert atmosphere of nitrogen. Then **5** (252 mg, 1.68 mmol), 3 mL of diethyl ether and 2,6-diisopropylaniline (378 µL, 2.02 mmol) were added. The reaction was stirred at room temperature overnight ad then the conversion of **5** was checked by GC-MS. After complete consumption, $MgSO_4$ was filtered off with Gooch funnel and rinsed with 2 x 10 mL of diethyl ether. The organic solution was evaporated and the excess of 2,6-diisopropylaniline was distilled

under vacuum at 140 °C for 3 hours. Purity of intermediate **6** was monitored by GC-MS to ensure absence of aniline.

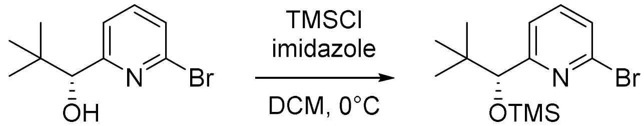
Step 2) **6** was transferred with 5 mL of dried AcOEt in a two-necked flask under inert atmosphere, paraformaldehyde (55 mg, 1.85 mmol) was added and then the reaction was heated at 70 °C. After 15 minutes, TMSCl (235 μL, 1.85 mmol) was added and the reaction maintained at the same temperature. Precipitate formation was observed, and the reaction was checked by TLC. The reaction mixture was cooled to room temperature, 5mL of diethyl ether were added to reduce the solubility of product **L4•HCl** that was filtered off and washed several times with diethyl ether. The brown powder was dried under vacuum and used for next step without further purification.



L4•HCl, brown powder, 80% over two steps. **MP**: decomposition.

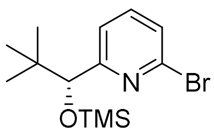
^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.70 (t, *J* = 8.6 Hz, 1H), 8.31 (s, 1H), 7.94 (dd, *J* = 9.3, 2.3 Hz, 1H), 7.55 (td, *J* = 7.8, 3.8 Hz, 1H), 7.37 (ddd, *J* = 9.7, 7.5, 2.8 Hz, 1H), 7.31 (dd, *J* = 7.9, 4.3 Hz, 2H), 6.68 (d, *J* = 7.2 Hz, 1H), 2.96 (d, *J* = 4.8 Hz, 6H), 2.12 (h, *J* = 6.7 Hz, 2H), 1.17 (ddd, *J* = 11.1, 7.0, 4.6 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.96, 144.15, 132.33, 132.04, 130.73, 127.44, 124.55, 123.84, 117.02, 113.40, 105.22, 41.95, 28.71, 24.55, 24.24. **LC-MS(ESI)**: 322.4 $[M-Cl]^+$. **Anal. El.** Calc. for $C_{21}H_{28}ClN_3$: C, 70.47; H, 7.89; N, 11.74; found: C, 70.58; H, 7.78; N, 11.84.

Synthesis of aldehydes 8a-d



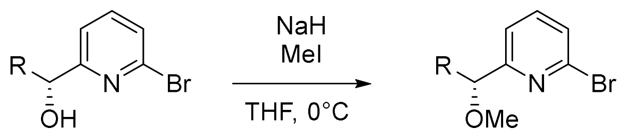
7a **8a**

In a two-necked-round bottom flask, under inert atmosphere of nitrogen, (*R*)-**7a** (244 mg, 1 mmol) was dissolved in 5 mL of DCM, then imidazole (87 mg, 1.3 mmol) was added, and the reaction cooled to 0 °C. After 5 minutes, TMSCl (140 µL, 1.1 mmol) was added dropwise. The reaction was slowly warmed-up to room temperature and let stirring until complete conversion of (*R*)-**7a**. The reaction was quenched with distilled water and extracted with DCM (3 x 10 mL) and the organic phases washed with brine (1 x 15 mL), dried over Na_2SO_4 and volatile compounds evaporated. (*R*)-**8a** was purified by flash chromatography using *n*Hex/AcOEt 20:1 as the eluent.



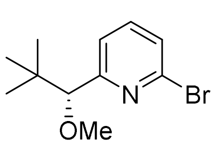
(*R*)-**8a**, white solid, 93%. **MP** = 81-83 °C. **[α]$^D_{20}$** = + 55.6° (*c* 1.18, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (t, *J* = 7.7 Hz, 1H), 7.37 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.29 (dd, *J* = 7.7, 1.0 Hz, 1H), 4.40 (s, 1H), 0.84 (s, 9H), -0.05 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 165.15, 139.89, 138.01, 126.17, 121.28, 82.69, 36.32, 26.06, 0.13. **GC-MS(EI):** 73 (100%), 261 (93%, -tBu (^{81}Br), 259 (93%, -tBu (^{79}Br), 302 (13%, -Me (^{81}Br)), 300 (13%, -Me (^{79}Br)). **Anal. El.** Calc. for $C_{13}H_{22}BrNOSi$: C, 49.36; H, 7.01; N, 4.43; O, 5.06; found: C, 49.66; H, 7.91; N, 11.65.



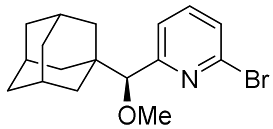
7 **8**

In a two necked-round-bottom flask, under inert atmosphere of nitrogen, **7** (0.82 mmol, 1 eq) was dissolved in THF and cooled to 0 °C, then NaH (43 mg, 60%wt in mineral oil, 1.06 mmol, 1.3 eq) was added one portion. After H_2 stops developing, MeI (102 µL, 1.64 mmol, 2eq) was added dropwise and the reaction was stirred at 0 °C for 30 minutes. After that time, the reaction was allowed to warm to room temperature. The reaction was checked by TLC and then quenched with saturated ammonium chloride solution. The crude was extracted with diethyl ether (3 x 15 mL) and the organic phases dried over Na_2SO_4. Product **8** was purified by flash chromatography using *n*Hex/AcOEt 15:1 as the eluent.



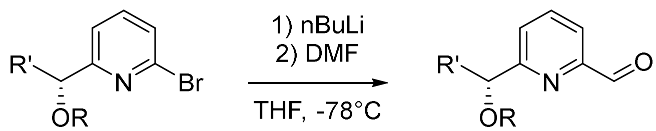
(*R*)-**8b**, crystalline white solid, 85%. **MP**: 70-73 °C. **[α]$^D_{20}$** = + 90.1° (*c* 1.24, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (t, *J* = 7.7 Hz, 1H), 7.33 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.30 (dd, *J* = 7.7, 1.0 Hz, 1H), 3.91 (s, 1H), 3.19 (s, 3H), 0.86 (s, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.42, 140.51, 138.08, 126.37, 120.65, 91.90, 57.87, 35.61, 26.00. **GC-MS(EI)**: 186 (100%, (^{79}Br)), 188 (95%, (^{81}Br)), 201 (48%, -tBu (^{79}Br)), 203 (47%, -tBu (^{81}Br)). **Anal. El.** Calc. for $C_{11}H_{16}BrNO$: C, 51.18; H, 6.25; Br, 30.95; N, 5.43; O, 6.20; found: C, 51.09; H, 6.40; N, 5.48; O, 6.08.



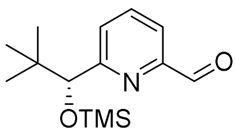
(*S*)-**8c**, crystalline white solid, 90%. **MP**: 80-82 °C. **[α]$^{D}_{20}$** = – 122.4° (*c* 0.99, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (t, *J* = 7.7 Hz, 1H), 7.33 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.25 (dd, *J* = 7.7, 1.0 Hz, 1H), 3.76 (s, 1H), 3.16 (s, 3H), 1.88 (p, *J* = 3.2 Hz, 3H), 1.62 (ddt, *J* = 13.6, 11.3, 2.5 Hz, 6H), 1.56 – 1.50 (m, 3H), 1.43 – 1.35 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.66, 140.55, 137.94, 126.35, 120.93, 92.61, 57.94, 38.11, 37.41, 36.98, 28.25. **GC-MS(EI)**: 135 (100%, $Ad^{\bullet+}$), 305 (7%, -OMe (^{79}Br)). **Anal. El.** Calc. for $C_{17}H_{22}BrNO$: C, 60.72; H, 6.59; N, 4.17; O, 4.76; found: C, 61.05; H, 6.43; N, 4.14; O, 4.84.



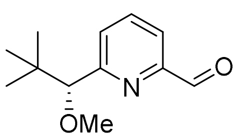
8 **9**

In a two necked-round-bottom flask, under inert atmosphere of nitrogen, **8** (0.90 mmol) was dissolved in 5 mL of THF and cooled to –78 °C with an acetone/liquid N_2 bath. *n*BuLi (430 μL, 1.08 mmol, 2.5 M in *n*Hex) was added dropwise and the solution turned light orange. After 15 minutes at the same temperature, DMF (140 μL, 1.8 mmol) was added one-shot. The reaction was let stirring at –78 °C for 30 minutes and then raised to room temperature. After complete consumption of bromopyridine **8**, monitored by TLC, the reaction was quenched with saturated aqueous ammonium chloride solution and extracted with diethyl ether (3 x 15 mL). The organic phases were dried over Na_2SO_4, evaporated and the product purified by flash chromatography using *n*Hex/AcOEt 15:1 as the eluent.



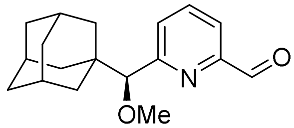
(*R*)-**9a'**, colourless oil, 66%. **[α]$^{D}_{20}$** = + 64.7° (*c* 1.12, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.02 (s, 1H), 7.83 – 7.77 (m, 2H), 7.66 (dd, *J* = 5.9, 3.2 Hz, 1H), 4.53 (s, 1H), 0.87 (s, 10H), -0.03 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 193.89, 164.10, 150.94, 136.31, 126.61, 119.92, 82.93, 36.04, 25.88, -0.12. **GC-MS(EI)**: 209 (100%, -tBu), 73 (91%), 178 (22%, $-SiMe_3$), 250 (10%, -Me). **Anal. El.** Calc. for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73; N, 5.28; O, 12.06; found: C, 63.51; H, 8.77; N, 5.23; O, 12.20.



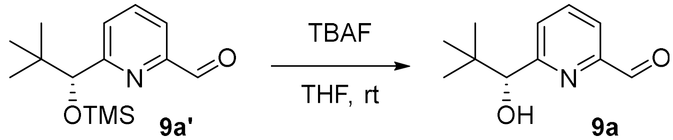
(*R*)-**9b**, colourless oil, 57%. **[α]$^{D}_{20}$** = + 90.3° (*c* 0.9, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.03 (s, 1H), 7.85 – 7.78 (m, 2H), 7.57 (dd, *J* = 5.5, 3.5 Hz, 1H), 4.03 (s, 1H), 3.22 (d, *J* = 0.6 Hz, 3H), 0.89 (d, *J* = 0.7 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 193.78, 161.57, 151.69, 136.64, 126.18, 120.23, 92.33, 57.92, 35.62, 26.06. **GC-MS(EI)**: 136 (100%), 151 (43%, -*t*Bu). **Anal. El.** Calc. for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76; O, 15.44; found: C, 69.61; H, 8.34; N, 6.68; O, 15.38.

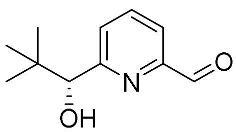


(*S*)-**9c**, white solid, 48%. **MP**: 75-77 °C. **[α]$^{D}_{20}$** = – 85.9° (*c* 0.86, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.98 (s, 1H), 7.83 – 7.74 (m, 2H), 7.48 (dd, *J* = 5.3, 3.7 Hz, 1H), 3.83 (s, 1H), 3.14 (s, 3H), 1.83 (p, *J* = 3.3 Hz, 3H), 1.58 (ddt, *J* = 23.5, 14.5, 2.6 Hz, 6H), 1.51 – 1.42 (m, 3H), 1.37 (dq, *J* = 12.2, 2.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 193.73, 160.72, 151.65, 136.44, 126.38, 120.21, 92.95, 57.90, 38.19, 37.34, 36.92, 28.19. **GC-MS(EI)**: 135 (100%, $Ad^{\bullet+}$), 285 (9%, $M^{\bullet+}$), 270 (5%, -Me). **Anal. El.** Calc. for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91; O, 11.21; found C, 75.86; H, 8.08; N, 4.84; O, 11.21.

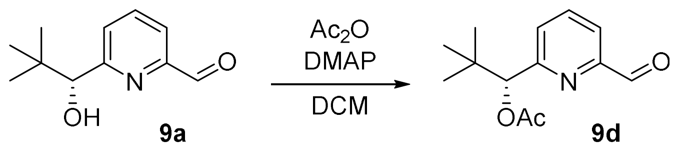


In a two necked-round-bottom flask, under inert atmosphere, (*R*)-**9a'** (157 mg, 0.59 mmol) was dissolved in 3 mL of THF, then tetrabutylammonium fluoride monohydrate (TBAF•H_2O, 182 mg, 0.65 mmol) was added one portion. The reaction was stirred at room temperature until full conversion of starting material monitored by TLC. The reaction was quenched with 5 mL of water and the mixture extracted 3 x 15 mL of diethyl ether. The organic phase was dried over Na_2SO_4, evaporated and the product purified by flash chromatography using *n*Hex/AcOEt 10:1 as the eluent.

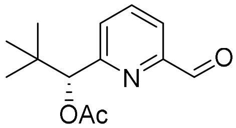


(*R*)-**9a**, colourless oil, 83%. **$[\alpha]^D_{20}$** = – 0.9° (*c* 1.18, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.01 (d, *J* = 0.8 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.42 (dd, *J* = 7.3, 1.6 Hz, 1H), 4.42 (d, *J* = 7.2 Hz, 1H), 4.06 (d, *J* = 7.3 Hz, 1H), 0.88 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 193.19, 161.09, 151.05, 136.61, 126.99, 120.24, 80.39, 36.30, 25.79. **GC-MS(EI)**: 137 (100%, -tBu), 178 (3%, -Me). **Anal. El.** Calc. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25; O, 16.56; found: C, 68.42; H, 7.72; N, 7.20; O, 16.63.



In a two necked-round-bottom flask, under inert atmosphere, (*R*)-**9a** (150 mg, 0.77 mmol) was dissolved in 3 mL of DCM, then some crystals of DMAP are added to the solution. Acetic anhydride (150 µL, 1.55 mmol) was added dropwise. The reaction was stirred at room temperature and the progress was monitored by TLC. Water (10 mL) was added to quench the reaction and the mixture extracted with DCM (3 x 10 mL). The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. (*R*)-**9d** was purified by flash chromatography using *n*-Hex/AcOEt 5:1 as the eluent.

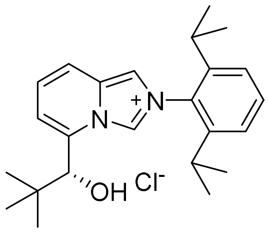


(*R*)-**9d**, colourless oil, 40%. **$[\alpha]^D_{20}$** = – 33.9° (*c* 1.28, DCM).

^{1}H NMR (401 MHz, $CDCl_3$) δ = 10.01 (d, *J* = 0.8 Hz, 1H), 7.85 – 7.74 (m, 2H), 7.45 (dd, *J* = 6.8, 2.1 Hz, 1H), 5.57 (s, 1H), 2.10 (s, 3H), 0.94 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 193.74, 170.26, 159.32, 151.64, 136.85, 125.96, 120.13, 83.14, 34.94, 26.02, 20.98. **GC-MS(EI)**: 137 (100%), 179 (16%, -tBu), 160 (15%). **Anal. El.** Calc. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95; O, 20.40; found: C, 66.51; H, 7.31; N, 5.86; O, 20.32.

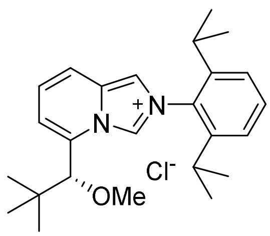
Synthesis of L11-14•HCl

The procedure adopted for the synthesis of **L11-14•HCl** is identical to the one utilized for **L4•HCl**.



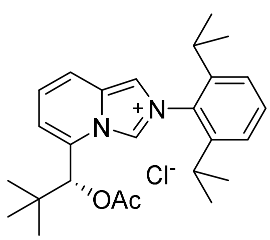
(*R*)-**L11•HCl**, pale yellow solid, 83%. **MP**: decomposition. **[α]^{D}$_{20}$** = – 23.8° (*c* 1.02, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.07 (d, *J* = 1.8 Hz, 1H), 7.75 (d, *J* = 9.3 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.36 – 7.25 (m, 3H), 6.98 (d, *J* = 6.9 Hz, 1H), 5.04 (s, 1H), 2.28 (hept, *J* = 6.7 Hz, 1H), 2.06 – 1.92 (m, 1H), 1.19 (d, *J* = 6.7 Hz, 3H), 1.16 – 1.08 (m, 9H), 1.00 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.72, 144.91, 132.08, 131.98, 130.48, 128.47, 125.89, 124.86, 124.34, 118.22, 116.41, 113.38, 79.00, 37.41, 28.62, 28.56, 26.78, 24.52, 24.50, 24.33, 24.22. **LC-MS(ESI+)**: 365.9 (-Cl^-). **Anal. El.** Calc. for $C_{24}H_{33}ClN_2O$: C, 71.89; H, 8.30; Cl, 8.84; N, 6.99; O, 3.99; found: C, 71.78; H, 8.35; N, 7.02; O, 4.02.



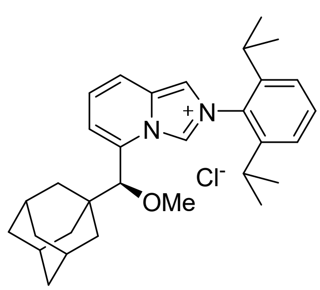
(*R*)-**12•HCl**, white solid, 82%. **MP**: decomposition. **[α]^{D}$_{20}$** = – 12.99° (*c* 0.84, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.91 (bs, 1H), 8.69 (bs, 1H), 8.54 (bs, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.31 – 7.28 (m, 2H), 7.15 (d, *J* = 6.9 Hz, 1H), 4.67 (s, 1H), 3.34 (s, 3H), 2.14 – 2.06 (m, 1H), 2.01 – 1.90 (m, 1H), 1.15 (dd, *J* = 6.7, 2.8 Hz, 6H), 1.11 (d, *J* = 6.5 Hz, 6H), 0.96 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, diagnostic signals) δ = 145.03, 144.87, 132.38, 132.07, 130.51, 124.94, 124.65, 124.48, 58.44, 37.87, 28.72, 26.51, 24.76, 24.37, 24.14, 23.76. **LC-MS(ESI+)**: 379.6 (-Cl^-). **Anal. El.** Calc. for C, 72.35; H, 8.50; N, 6.75; O, 3.86; found: C, 72.33; H, 8.58; N, 6.77; O, 3.78.



(*R*)-**13•HCl**, white solid, 97%. **MP**: 147–150 °C. **[α]^{D}$_{20}$** = – 54.8° (*c* 0.99, DCM).

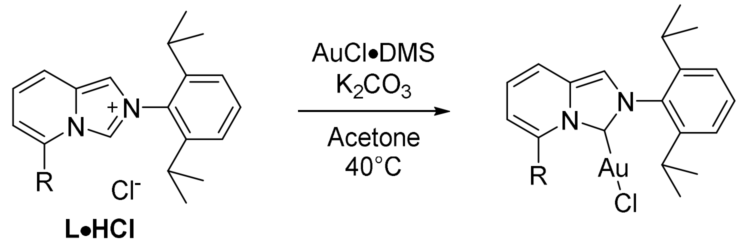
^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.65 (bs, 1H), 8.16 (bs, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.24 (ddd, *J* = 10.8, 8.7, 5.4 Hz, 3H), 6.99 (d, *J* = 7.0 Hz, 1H), 6.18 (s, 1H), 2.10 – 1.86 (m, 5H), 1.20 – 1.06 (m, 12H), 1.04 (s, 9H). Diagnostic **^{13}C NMR** (101 MHz, cdcl$_3$) δ 170.04, 145.10, 144.75, 131.80, 131.26, 130.73, 127.80, 124.92, 124.38, 124.17, 118.93, 116.22, 36.28, 28.76, 28.73, 25.22, 24.59, 23.65, 20.59. **LC-MS(ESI+)**: 407.2 (-Cl^-). **Anal. El.** Calc. for $C_{26}H_{35}ClN_2O_2$: C, 70.49; H, 7.96; N, 6.32; O, 7.22; found: C, 70.61; H, 7.86; N, 6.40; O, 7.19.



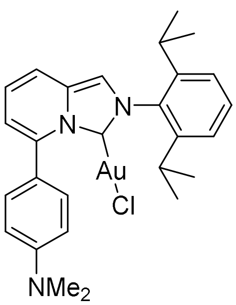
(*S*)-**L14•HCl**, pale yellow solid, 88%. **MP**: 132–135 °C. **[α]^{D}$_{20}$** = + 72.6° (*c* 1.07, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.04 (bs, 1H), 8.72 (bs, 1H), 8.44 (bs, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.15 (dd, *J* = 9.3, 7.0 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.01 – 6.93 (m, 1H), 3.11 (s, 3H), 1.95 – 1.64 (m, 5H), 1.35 (dt, *J* = 23.8, 12.6 Hz, 12H), 0.92 (dt, *J* = 32.1, 8.8 Hz, 12H). Diagnostic **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.84, 144.66, 131.92, 130.34, 124.80, 124.46, 124.32, 121.61, 120.41, 117.12, 58.27, 39.42, 39.04, 36.28, 28.56, 28.52, 27.90, 24.55, 24.08, 23.88, 23.53. **LC-MS(ESI+)**: 457.4 (-Cl^-). **Anal. El.** Calc. for $C_{31}H_{41}ClN_2O$: C, 75.51; H, 8.38; N, 5.68; O, 3.24; found: C, 75.58; H, 8.44; N, 5.62; O, 3.19.

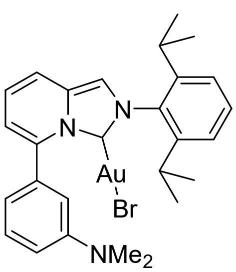
Synthesis of gold(I) complexes



Following known procedure[9] ligand precursor **L•HCl** (0.1 mmol), K_2CO_3 (41.4 mg, 0.3 mmol) and AuCl•DMS (29.4 mg, 0.1 mmol) are added into a vial. Then, 1 mL of acetone (reagent grade) was added, and the closed vial stirred at 40 °C for 2 h. After complete consumption of starting salts, acetone was evaporated under reduced pressure and the crude dissolved in DCM and filtered on Celite® pad. DCM was evaporated yielding [Au(I)] complexes that were triturated in *n*Hex before use.

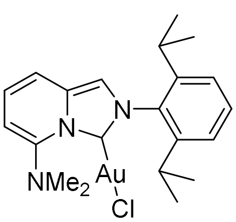


Cat2, orange powder, 97%. **MP**: decomposition.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.31 (m, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.01 (dd, *J* = 9.2, 6.7 Hz, 1H), 6.86 – 6.75 (m, 2H), 6.58 (dd, *J* = 6.7, 1.3 Hz, 1H), 2.99 (s, 6H), 2.19 (hept, *J* = 6.8 Hz, 2H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.09 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.99, 152.21, 145.12, 140.79, 135.73, 131.70, 130.44, 130.37, 123.99, 123.69, 121.56, 116.07, 115.99, 113.38, 112.57, 40.66, 28.35, 24.50, 24.28. **Exact mass**: calc. for $C_{27}H_{31}AuClN_3$: 629.1872, found: 629.1879.



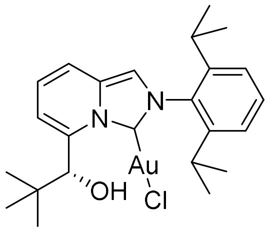
Cat3, orange powder, 99%. **MP**: decomposition.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 – 7.40 (m, 2H), 7.36 (dd, *J* = 8.4, 7.3 Hz, 1H), 7.29 (s, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.03 (dd, *J* = 9.2, 6.7 Hz, 1H), 6.90 (ddd, *J* = 8.5, 2.7, 0.9 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.64 (dd, *J* = 6.7, 1.3 Hz, 1H), 2.98 (s, 6H), 2.20 (hept, *J* = 6.9 Hz, 2H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.21 (dd, *J* = 6.8, 3.2 Hz, 3H), 1.15 – 1.04 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 150.74, 145.07, 140.89, 137.66, 135.60, 134.44, 131.54, 130.48, 129.86, 124.09, 123.93, 123.62, 117.06, 116.54, 115.68, 114.55, 113.75, 113.20, 40.52, 28.41, 28.36, 24.80, 24.50, 24.33, 24.28, 24.17. **Exact mass**: calc. for $C_{27}H_{31}AuClN_3$: 629.1872, found: 629.1868.



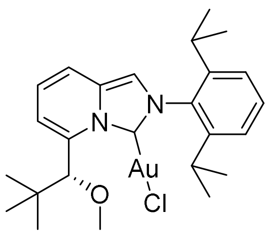
Cat4, light yellow powder, 96%. **MP**: decomposition.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (t, *J* = 7.8 Hz, 1H), 7.30 – 7.21 (m, 3H), 7.15 (d, *J* = 9.1 Hz, 1H), 6.96 (dd, *J* = 9.1, 7.0 Hz, 1H), 6.25 (d, *J* = 7.0 Hz, 1H), 2.92 (s, 6H), 2.20 (hept, *J* = 7.0 Hz, 2H), 1.29 (d, *J* = 6.8 Hz, 6H), 1.09 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 164.46, 148.58, 145.16, 135.74, 132.51, 130.53, 124.23, 124.08, 113.71, 112.47, 102.45, 44.23, 28.41, 24.46, 24.28. **Exact mass**: calc. for $C_{21}H_{27}AuClN_3$: 553.1559; found: 553.1563.



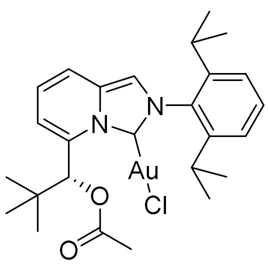
(*R*)-**Cat11**, pale yellow powder, 99%. **MP**: decomposition. **$[\alpha]^{D}_{20}$ =** + 92.2° (*c* 0.55, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (s, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.31 (s, 1H), 7.28 – 7.20 (m, 2H), 7.08 – 6.99 (m, 2H), 2.18 (hept, *J* = 6.7 Hz, 1H), 2.01 (hept, *J* = 6.5 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.24 (s, 3H), 1.09 (s, 9H), 1.08 (d, *J* = 2.4 Hz, 3H), 1.07 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.42, 145.29, 145.00, 142.31, 135.53, 131.93, 130.75, 124.23, 124.06, 123.01, 116.64, 114.72, 113.26, 73.34, 38.38, 28.44, 28.41, 25.83, 24.64, 24.34, 24.22, 24.05. **Exact mass**: calc. for $C_{24}H_{32}AuClN_2O$: 596.1869; found: 596.1863.



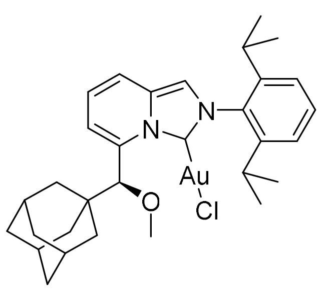
(*R*)-**Cat12**, white powder, 99%. **MP**: decomposition. **$[\alpha]^{D}_{20}$** = + 88.1° (*c* 0.54, DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (t, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 9.1, 1.3 Hz, 1H), 7.32 (s, 1H), 7.29 – 7.23 (m, 2H), 7.21 (s, 1H), 7.06 (dd, *J* = 9.1, 6.9 Hz, 1H), 6.91 (dd, *J* = 6.9, 1.4 Hz, 1H), 3.42 (s, 3H), 2.25 (hept, *J* = 6.8 Hz, 1H), 1.97 (hept, *J* = 7.1 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 6.9 Hz, 3H), 1.09 – 1.04 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.19, 145.41, 144.88, 140.52, 135.50, 132.04, 130.78, 124.25, 124.10, 123.00, 116.57, 114.18, 113.21, 83.43, 58.13, 38.30, 28.46, 28.42, 25.87, 24.67, 24.33, 24.31, 24.07. **Exact mass**: calc. for $C_{25}H_{34}AuClN_2O$: 610.2025; found: 610.2030.



(*R*)-**Cat13**, white powder, 99%. **MP**: decomposition. **$[\alpha]^{D}_{20}$** = – 30,3° (*c* 1.02, DCM).

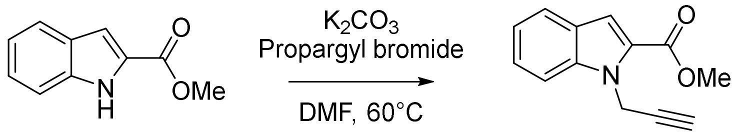
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (s, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.38 (dd, *J* = 9.2, 1.3 Hz, 1H), 7.32 (s, 1H), 7.25 (ddd, *J* = 10.9, 7.8, 1.4 Hz, 2H), 6.96 (dd, *J* = 9.2, 6.9 Hz, 1H), 6.71 (dd, *J* = 7.0, 1.3 Hz, 1H), 2.25 (p, *J* = 6.8 Hz, 1H), 2.08 (s, 3H), 2.02 (p, *J* = 6.9 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.18 (s, 9H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 169.96, 164.22, 145.27, 145.18, 139.93, 135.61, 131.68, 130.74, 124.29, 124.00, 122.47, 117.09, 113.47, 113.44, 75.39, 36.81, 28.48, 28.44, 26.03, 24.52, 24.31, 24.25, 24.12. **Exact mass**: calc. for $C_{26}H_{34}AuClN_2O_2$: 638.1974; found: 638.1978.



(*S*)-**Cat14**, white powder, 87%. **MP**: decomposition. $[\alpha]^{D}_{20}$ = – 153.6° (*c* 0.62, DCM).

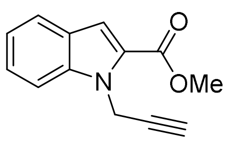
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (t, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 9.1, 1.3 Hz, 1H), 7.32 (s, 1H), 7.25 (ddd, *J* = 11.3, 7.8, 1.4 Hz, 2H), 7.12 (s, 1H), 7.05 (dd, *J* = 9.2, 6.9 Hz, 1H), 6.84 (dd, *J* = 6.9, 1.3 Hz, 1H), 3.41 (s, 3H), 2.35 – 2.22 (m, 1H), 2.12 – 2.02 (m, 3H), 2.00 – 1.86 (m, 4H), 1.62 – 1.55 (m, 6H), 1.49 (d, *J* = 11.9 Hz, 3H), 1.29 (d, *J* = 6.9 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.91, 145.48, 144.82, 139.33, 135.53, 132.04, 130.73, 124.25, 124.09, 122.95, 116.45, 114.18, 113.01, 83.85, 58.22, 40.26, 37.69, 36.89, 28.47, 28.42, 28.41, 24.67, 24.33, 24.18, 24.05. **Exact mass**: calc. for $C_{31}H_{41}AuClN_2O$: 689.2573; found: 689.2571.

General procedure for the synthesis of *N*-propargyl derivatives (11)



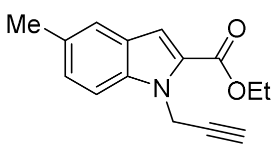
10a **11a**

In a two necked-round-bottom flask, under inert atmosphere of nitrogen, **10** (262 mg, 1.5 mmol) was dissolved in 10 mL of DMF and K_2CO_3 (621 mg, 4.5 mmol) was added. Then propargyl bromide (400 µL, 4.5 mmol) was added dropwise and the reaction heated to 60 °C. After 4 h the reaction was checked by TLC and quenched with saturated aqueous solution of sodium bicarbonate. The mixture was extracted with AcOEt (3 x 20 mL) and the organic phase washed with distilled water (2 x 25 mL) and brine (1 x 25 mL). The organic phase was dried over Na_2SO_4 and then evaporated. **11** was purified by flash chromatography using *c*Hex/AcOEt 20:1 as the eluent.



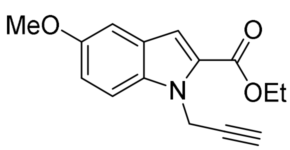
11a, white solid, 89%. **MP**: 92–94 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.41 (ddd, *J* = 8.4, 7.0, 1.2 Hz, 1H), 7.35 (d, *J* = 1.0 Hz, 1H), 7.22 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 5.42 (d, *J* = 2.5 Hz, 2H), 3.93 (s, 3H), 2.29 (t, *J* = 2.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.34, 138.95, 126.54, 126.24, 125.56, 122.84, 121.23, 111.56, 110.59, 78.80, 72.14, 51.79, 33.80. **GC-MS(EI)**: 198 (100, -Me), 213 (42%, $M^{\bullet+}$), 154 (40%, $-CO_2Me$). **Anal. El.** Calc. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57; O, 15.01; found: C, 73.28; H, 5.23; N, 6.55; O, 14.95.



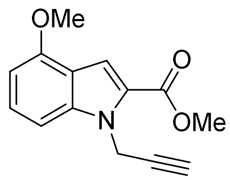
11b, white solid, 87%. **MP**: 95–98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (dt, *J* = 1.6, 0.9 Hz, 1H), 7.38 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.26 (d, *J* = 0.9 Hz, 1H), 7.24 – 7.20 (m, 1H), 5.41 (d, *J* = 2.5 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.46 (d, *J* = 0.9 Hz, 3H), 2.24 (t, *J* = 2.5 Hz, 1H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.01, 137.46, 130.46, 127.37, 126.87, 126.47, 122.04, 110.90, 110.21, 78.86, 71.87, 60.68, 33.83, 21.35, 14.34. **GC-MS(EI)**: 212 (100%, -Et), 241 (19%, $M^{\bullet+}$). **Anal. El.** Calc. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16; O, 14.08; found: C, 74.02; H, 5.75; N, 6.11; O, 14.12.



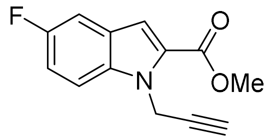
11c, white solid, 93%. **MP**: 95–98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (dd, *J* = 9.8, 0.9 Hz, 1H), 7.23 (d, *J* = 0.9 Hz, 1H), 7.05 (dq, *J* = 5.3, 2.5 Hz, 2H), 5.38 (d, *J* = 2.5 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 2.25 (t, *J* = 2.5 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 161.87, 154.99, 134.39, 127.13, 126.52, 116.86, 111.45, 110.79, 102.80, 78.82, 71.98, 60.68, 55.65, 33.89, 14.33. **GC-MS(EI)**: 228 (100%, -Et), 257 (26%, $M^{\bullet+}$). **Anal. El.** Calc. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76; O, 19.73; found: C, 69.06; H, 5.37; N, 5.87; O, 19.70.



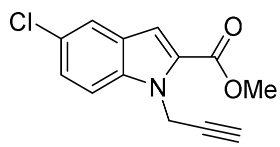
11d, white solid, 84%. **MP**: 119–121 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 0.9 Hz, 1H), 7.30 (dd, *J* = 8.4, 7.8 Hz, 1H), 7.07 (dt, *J* = 8.4, 0.8 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 5.40 (d, *J* = 2.5 Hz, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 2.24 (t, *J* = 2.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.29, 154.68, 140.37, 126.69, 125.17, 117.55, 109.23, 103.42, 100.28, 78.77, 71.99, 55.34, 51.70, 34.06. **GC-MS(EI)**: 228 (100%, -Me), 243 (72%, $M^{•+}$). **Anal. El.** Calc. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76; O, 19.73; found: C, 69.02; H, 5.42; N, 5.81; O, 19.75.



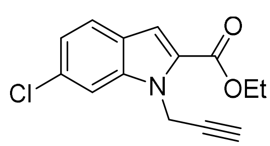
11e, white solid, 81%. **MP**: 125–127 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (ddt, *J* = 9.1, 4.2, 0.8 Hz, 1H), 7.30 (ddd, *J* = 9.1, 2.6, 0.7 Hz, 1H), 7.25 (d, *J* = 0.9 Hz, 1H), 7.14 (td, *J* = 9.1, 2.5 Hz, 1H), 5.41 (d, *J* = 2.6 Hz, 2H), 3.91 (s, 3H), 2.26 (t, *J* = 2.5 Hz, 1H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -122.52 (td, *J* = 9.1, 4.1 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.08, 158.40 (d, *J* = 237.5 Hz), 135.50, 127.84, 126.30 (d, *J* = 10.3 Hz), 114.54 (d, *J* = 27.0 Hz), 111.58 (d, *J* = 9.5 Hz), 111.11 (d, *J* = 5.3 Hz), 106.98 (d, *J* = 23.3 Hz), 78.35, 72.27, 51.89, 33.98. **GC-MS(EI)**: 216 (100%, -Me), 231 (39%, $M^{•+}$), 172 (28%, $-CO_2Me$). **Anal. El.** Calc. for $C_{13}H_{10}FNO_2$: C, 67.53; H, 4.36; N, 6.06; O, 13.84; found: C, 67.47; H, 4.34; N, 6.03; O, 13.89.



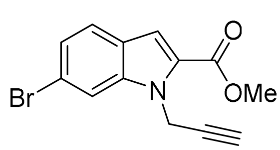
11f, white solid, 86%. **MP**: 129–132 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 2.0, 0.7 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.31 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.21 (d, *J* = 0.9 Hz, 1H), 5.39 (d, *J* = 2.5 Hz, 2H), 3.91 (s, 3H), 2.26 (t, *J* = 2.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.01, 137.15, 127.63, 127.01, 126.88, 125.93, 121.89, 111.73, 110.70, 78.22, 72.40, 51.95, 33.97. **GC-MS(EI)**: 232 (100%, -Me(^{35}Cl)), 247 (34%, (^{35}Cl)$M^{•+}$). **Anal. El.** Calc. for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66; O, 12.92; found: C, 63.12; H, 4.11; N, 5.59; O, 12.87.



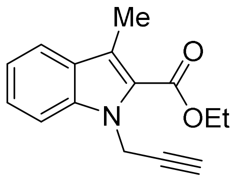
11g, white solid, 83%. **MP**: 88–90 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.47 (dt, *J* = 1.6, 0.7 Hz, 1H), 7.26 (d, *J* = 1.0 Hz, 1H), 7.12 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.35 (d, *J* = 2.5 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.28 (t, *J* = 2.5 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.58, 139.12, 131.48, 127.60, 124.65, 123.63, 122.14, 111.28, 110.50, 78.27, 72.50, 60.92, 33.94, 14.30. **GC-MS(EI)**: 232 (100%, -Et(^{35}Cl)), 261 (35%, (^{35}Cl)$M^{•+}$). **Anal. El.** Calc. for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66; O, 12.92; found: C, 63.08; H, 4.09; N, 5.57; O, 12.95.



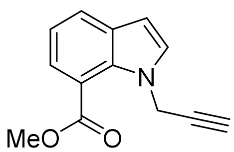
11h, white solid, 91%. **MP**: 119–120 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (s, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.25 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.23 (s, 1H), 5.34 (d, *J* = 2.5 Hz, 2H), 3.90 (s, 3H), 2.28 (t, *J* = 2.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.98, 139.45, 127.05, 124.92, 124.74, 123.95, 119.44, 113.57, 111.44, 78.19, 72.59, 51.94, 33.94. **GC-MS(EI)**: 276 (100%, -Me(^{79}Br)), 291 (37%, (^{79}Br)$M^{•+}$). **Anal. El.** Calc. for $C_{13}H_{10}BrNO_2$: C, 53.45; H, 3.45; N, 4.79; O, 10.95; found: C, 53.48; H, 3.49; N, 4.77; O, 10.90.



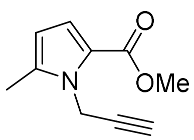
11k, colourless oil, 94%. Starting **10k** was prepared following a literature procedure.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.41 – 7.36 (m, 1H), 7.17 (ddt, *J* = 8.0, 6.7, 1.3 Hz, 1H), 5.35 (d, *J* = 2.4 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 2.20 (t, *J* = 2.5 Hz, 1H), 1.44 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.8, 138.1, 127.7, 125.7, 123.8, 122.3, 120.9, 120.3, 110.2, 79.2, 71.5, 60.6, 34.2, 14.3, 10.9. **GC-MS(EI)**: 212 (100%, -Et), 241 (25%, $M^{•+}$). **Anal. El.** Calc. for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81; O, 13.26; found: C, 74.68; H, 6.24; N, 5.90; O, 13.18.



11l, colourless oil, 87%.

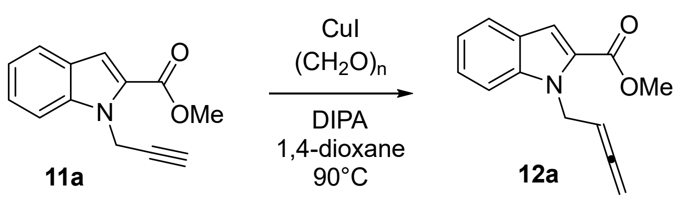
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.74 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.21 (d, *J* = 3.3 Hz, 1H), 7.15 (dd, *J* = 8.1, 7.2 Hz, 1H), 6.60 (d, *J* = 3.3 Hz, 1H), 5.18 (d, *J* = 2.5 Hz, 2H), 3.98 (s, 3H), 2.32 (t, *J* = 2.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.10, 132.63, 131.72, 130.75, 125.70, 125.29, 119.13, 116.55, 102.91, 78.41, 73.67, 52.31, 39.43. **GC-MS(EI)**: 193 (100%, -Me), 213 (99%, $M^{•+}$), 154 (68%, -CO_2Me). **Anal. El.** Calc. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57; O, 15.01; found: C, 73.22; H, 5.20; N, 6.58; O, 15.03



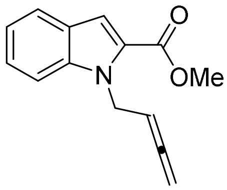
11n, colourless oil, 81%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.88 (d, *J* = 4.0 Hz, 1H), 5.91 (dq, *J* = 3.9, 0.8 Hz, 1H), 5.15 (d, *J* = 2.5 Hz, 2H), 3.78 (d, *J* = 0.5 Hz, 3H), 2.24 (ddd, *J* = 2.5, 2.0, 0.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.50, 136.94, 120.74, 118.08, 108.39, 78.74, 71.84, 50.94, 34.04, 12.28. Other data are in accordance with reported values.[11]

General procedure for the synthesis of *N*-allenyl derivatives (12)

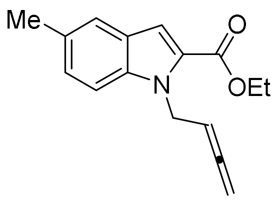


In a Schlenk tube, to a solution of pre-flamed CuI (143 mg, 0.75 mmol) in 1,4-dioxane (2.5 mL), **11a** (320 mg, 1.5 mmol) and paraformaldehyde (72 mg, 2.4 mmol) were added. Then diisopropyl amine (DIPA, 260 µL, 1.8 mmol) was added dropwise and the reaction heated at 90 °C for 16 h. The conversion was monitored by TLC and quenched with 5 mL of water ad diluted with 10 mL of AcOEt. Product was extracted with AcOEt (2 x 15 mL) and then, the organic phase, washed with diluted ammonia solution (2 x 20 mL) to remove copper traces from organic phase. Organic phase was dried over Na_2SO_4 and evaporated under reduced pressure, product **12a** was purified by flash chromatography using *c*Hex/AcOEt 10:1 as the eluent.



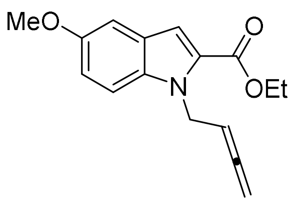
12a, white solid, 86%. **MP**: 51–55 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.0 Hz, 1H), 7.42 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.34 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1H), 7.29 (d, *J* = 0.9 Hz, 1H), 7.15 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 5.36 (p, *J* = 6.5 Hz, 1H), 5.20 (dt, *J* = 6.4, 2.7 Hz, 2H), 4.74 (dt, *J* = 6.6, 2.7 Hz, 2H), 3.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.77, 162.42, 139.10, 126.88, 126.11, 125.10, 122.66, 120.73, 110.81, 110.78, 87.86, 76.84, 51.66, 43.29. **GC-MS(EI)**: 168 (100%, -CO_2Me), 188 (33%, -CH=C=CH_2), 227 (29%, $M^{\bullet+}$). **Anal. El.** Calc. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16; O, 14.08; found: C, 73.96; H, 5.82; N, 6.14; O, 14.10.



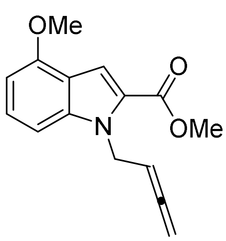
12b, colourless oil, 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (dt, *J* = 1.8, 0.9 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.21 (d, *J* = 0.9 Hz, 1H), 7.16 (dd, *J* = 8.6, 1.6 Hz, 1H), 5.34 (p, *J* = 6.5 Hz, 1H), 5.18 (dt, *J* = 6.5, 2.7 Hz, 2H), 4.74 (dt, *J* = 6.6, 2.7 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.75, 162.06, 137.60, 129.98, 127.21, 126.98, 126.35, 121.85, 110.43, 110.12, 87.95, 76.73, 60.50, 43.31, 21.33, 14.35. **GC-MS(EI)**: 182 (100%, -CO_2Et), 255 (27%, $M^{\bullet+}$). **Anal. El.** Calc. for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81; O, 13.26; found: C, 74.61; H, 6.31; N, 5.78; O, 13.27.



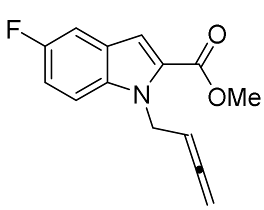
12c, colourless sticky oil, yield 39%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24 – 7.19 (m, 1H), 7.10 (d, *J* = 1.0 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.91 (ddd, *J* = 9.0, 2.5, 0.9 Hz, 1H), 5.24 (p, *J* = 6.5 Hz, 1H), 5.06 (dt, *J* = 6.2, 2.8 Hz, 2H), 4.64 (dq, *J* = 6.3, 2.2 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.61, 161.83, 154.58, 134.48, 127.34, 126.22, 116.45, 111.57, 109.90, 102.43, 87.85, 76.69, 60.39, 55.55, 43.28, 14.24. **GC-MS(EI)**: 198 (100%, -CO_2Et), 271 (44%, $M^{\bullet+}$), 242 (41%, -Et). **Anal. El.** Calc. for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44; O, 18.65; found: C, 70.09; H, 5.89; N, 5.44; O, 18.59.



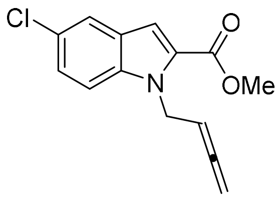
12d, white solid, 90%. **MP**: 62–65 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 1.0 Hz, 1H), 7.26 (dd, *J* = 8.5, 7.7 Hz, 1H), 7.02 (dt, *J* = 8.5, 0.8 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.38 (p, *J* = 6.5 Hz, 1H), 5.22 – 5.14 (m, 3H), 4.76 (dt, *J* = 6.6, 2.7 Hz, 2H), 3.94 (d, *J* = 1.0 Hz, 4H), 3.90 (d, *J* = 1.0 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.75, 162.34, 154.64, 140.59, 126.22, 125.57, 117.51, 108.55, 103.76, 99.78, 87.94, 76.84, 55.29, 51.56, 43.54. **GC-MS(EI)**: 198 (100%, -CO_2Me), 257 (71%, $M^{\bullet+}$), 226 (37%, -OMe). **Anal. El.** Calc. for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44; O, 18.65; found: C, 70.07; H, 5.90; N, 5.41; O, 18.61.



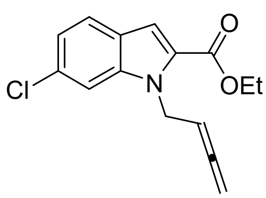
12e, white solid, 93%. **MP**: 72–75 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (dd, *J* = 9.1, 4.3 Hz, 1H), 7.29 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.21 (d, *J* = 1.0 Hz, 1H), 7.09 (td, *J* = 9.1, 2.5 Hz, 1H), 5.33 (p, *J* = 6.5 Hz, 1H), 5.17 (dt, *J* = 6.1, 2.8 Hz, 2H), 4.73 (dt, *J* = 6.5, 2.8 Hz, 2H), 3.90 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.71, 162.13, 158.18 (d, *J* = 236.9 Hz), 135.71, 128.18, 126.09 (d, *J* = 10.3 Hz), 114.15 (d, *J* = 26.9 Hz), 111.75 (d, *J* = 9.5 Hz), 110.34 (d, *J* = 5.4 Hz), 106.72 (d, *J* = 23.2 Hz), 87.74, 77.01, 51.75, 43.46. **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -123.13 (td, *J* = 9.1, 4.1 Hz). **GC-MS(EI)**: 186 (100%, $-CO_2Me$), 245 (33%, $M^{\bullet+}$), 230 (28%, -Me). **Anal. El.** Calc. for $C_{14}H_{12}FNO_2$: C, 68.56; H, 4.93; N, 5.71; O, 13.05; found: C, 68.61; H, 4.96; N, 5.67; O, 13.01.



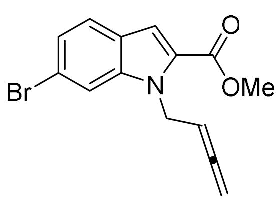
12f, white solid, 82%. **MP**: 77–78 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (dd, *J* = 2.0, 0.7 Hz, 1H), 7.32 (dt, *J* = 8.9, 0.8 Hz, 1H), 7.26 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.18 (d, *J* = 0.9 Hz, 1H), 5.32 (td, *J* = 6.7, 6.1 Hz, 1H), 5.15 (dt, *J* = 6.3, 2.8 Hz, 2H), 4.73 (dt, *J* = 6.6, 2.8 Hz, 2H), 3.90 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.69, 162.06, 137.35, 127.99, 126.87, 126.39, 125.52, 121.72, 111.93, 109.97, 87.68, 77.12, 51.80, 43.41. **GC-MS(EI)**: 202 (100%, $-CO_2Me(^{35}Cl)$), 261 (43%, $(^{35}Cl)M^{\bullet+}$). **Anal. El.** Calc. for $C_{14}H_{12}ClNO_2$: C, 64.25; H, 4.62; N, 5.35; O, 12.23; found: C, 64.28; H, 4.65; N, 5.32; O, 12.29.



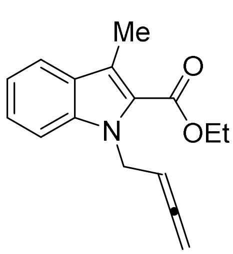
12g, white solid, 82%. **MP**: 88–90 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.5 Hz, 1H), 7.41 – 7.39 (m, 1H), 7.24 (d, *J* = 1.2 Hz, 1H), 7.10 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.33 (p, *J* = 6.5 Hz, 1H), 5.14 (dt, *J* = 6.0, 2.8 Hz, 2H), 4.76 (dt, *J* = 6.5, 2.8 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.70, 161.68, 139.34, 131.06, 128.05, 124.55, 123.49, 121.69, 110.72, 110.62, 87.60, 77.15, 60.74, 43.41, 14.31. **GC-MS(EI)**: 202 (100%, $-CO_2Et(^{35}Cl)$), 275 (29%, $(^{35}Cl)M^{\bullet+}$). **Anal. El.** Calc. for $C_{14}H_{12}ClNO_2$: C, 64.25; H, 4.62; N, 5.35; O, 12.23; found: C, 64.31; H, 4.58; N, 5.28; O, 12.32.



12h, white solid, 69%. **MP**: 72–73 °C.

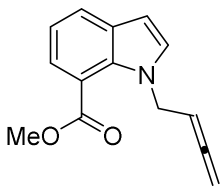
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 – 7.55 (m, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.22 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.21 (d, *J* = 1.0 Hz, 1H), 5.32 (p, *J* = 6.4 Hz, 1H), 5.11 (dt, *J* = 6.1, 2.8 Hz, 2H), 4.76 (dt, *J* = 6.6, 2.8 Hz, 2H), 3.89 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.71, 162.02, 139.67, 127.48, 124.81, 124.25, 123.81, 119.02, 113.80, 110.76, 87.58, 77.22, 51.79, 43.36. **GC-MS(EI)**: 167 (100%), 246 (79%, $-CO_2Me(^{79}Br)$), 305 (26%, $(^{79}Br)M^{\bullet+}$). **Anal. El.** Calc. for $C_{14}H_{12}BrNO_2$: C, 54.92; H, 3.95; N, 4.58; O, 10.45; found: C, 55.01; H, 3.99; N, 4.52; O, 10.39.



12k, colourless oil, 73%.

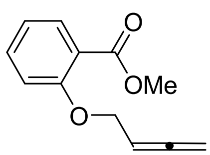
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.38 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.33 (ddd, *J* = 8.4, 6.6, 1.1 Hz, 1H), 7.13 (ddd, *J* = 7.9, 6.6, 1.2 Hz, 1H), 5.33 (p, *J* = 6.6 Hz, 1H), 5.12 (dt, *J* = 6.5, 2.6 Hz, 2H), 4.74 (dt, *J* = 6.6, 2.6 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.8, 162.9, 138.2, 127.5, 125.3, 124.2, 121.3, 120.8, 119.8, 110.5, 88.1, 76.5, 60.4, 43.7, 14.4, 10.8. **GC-MS(EI)**: 182 (100%,

-CO_2Et), 255 (35%, $M^{•+}$). **Anal. El.** Calc. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49; O, 12.53; found: C, 75.21; H, 6.80; N, 5.55; O, 12.44.



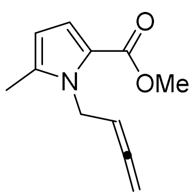
12l, colourless oil, 57%

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (dq, *J* = 7.8, 1.2 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.15 (d, *J* = 3.2 Hz, 1H), 7.14 – 7.09 (m, 1H), 6.58 (t, *J* = 2.4 Hz, 1H), 5.18 (pd, *J* = 6.6, 1.7 Hz, 1H), 4.98 (dt, *J* = 6.2, 2.8 Hz, 2H), 4.70 (ddt, *J* = 6.4, 4.8, 2.5 Hz, 2H), 3.96 (d, *J* = 1.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.52, 168.09, 132.76, 131.62, 131.00, 125.51, 125.10, 118.67, 116.59, 102.51, 87.91, 76.84, 52.27, 48.04. **GC-MS(EI)**: 226 (100%), 168 (74%, -CO_2Me), 227 (59%, $M^{•+}$). **Anal. El.** Calc. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16; O, 14.08; found: C, 73.92; H, 5.81; N, 6.19; O, 14.08.



12m, colourless oil, 71%.

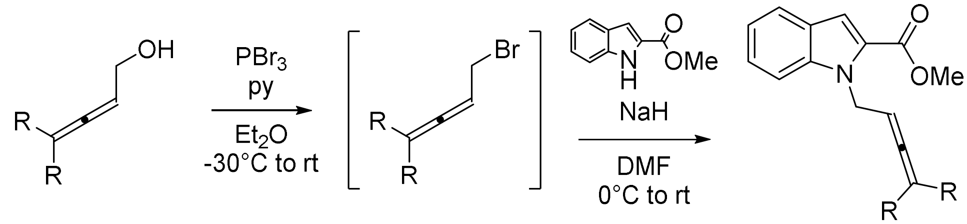
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.00 – 6.90 (m, 2H), 5.39 (p, *J* = 6.7 Hz, 1H), 4.83 (dt, *J* = 6.6, 2.6 Hz, 2H), 4.64 (dt, *J* = 6.7, 2.6 Hz, 2H), 3.86 (d, *J* = 0.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 209.36, 166.70, 157.83, 133.21, 131.63, 120.87, 120.55, 114.08, 86.97, 76.64, 66.88, 51.94. **GC-MS(EI)**: 120 (100%), 152 (38%), 173 (10%, -OMe). **Anal. El.** Calc. for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92; O, 23.50; found: C, 70.51; H, 5.95; O, 23.54.



12n, pale yellow oil, 81%.

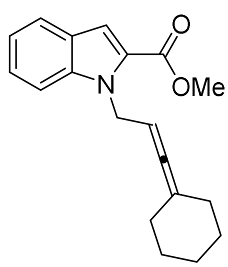
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.87 (d, *J* = 3.9 Hz, 1H), 5.89 (d, *J* = 3.9 Hz, 1H), 5.31 (p, *J* = 6.4 Hz, 1H), 4.91 (dt, *J* = 6.0, 2.9 Hz, 2H), 4.73 (dt, *J* = 6.7, 2.9 Hz, 2H), 3.77 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.46, 161.49, 136.90, 120.80, 117.62, 108.03, 88.33, 76.80, 50.81, 43.42, 12.48. **GC-MS(EI)**: 132 (100%, -CO_2Me), 117 (38%, -Me),191 (18%, $M^{•+}$), 158 (9%, -OMe). **Anal. El.** Calc. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32; O, 16.73; found: C, 69.16; H, 6.83; N, 7.26; O, 16.74.

General procedure for the synthesis of functionalized allenes



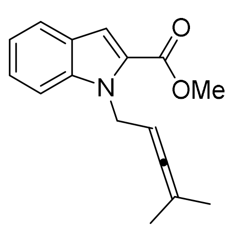
Step 1) In a three neck round bottomed flask equipped with condenser, under nitrogen atmosphere, allenyl alcohol (2.62 mmol) was dissolved in 2 mL of diethyl ether and then pyridine (30 0 µL, 3.73 mmol) was added. The reaction was cooled to -30 °C and PBr_3 (124 µL, 0.81 mmol) was added dropwise. After 15 minutes the reaction was warmed to room temperature and then heated to reflux. After complete consumption of the allenyl alcohol the reaction was cooled to 0 °C, quenched with 10mL of brine, extracted with diethyl ether (3 x 15 mL), organic phase dried over Na_2SO_4 and evaporated. The allenyl bromide was used in the next step without further purification and considered as pure (yield = 72%).

Step 2) In a three neck round bottomed flask equipped with dropping funnel, under inert atmosphere of nitrogen, **10a** (330 mg, 1.88 mmol) was dissolved in 3 mL of DMF and cooled to 0 °C, then NaH (83 mg, 2.07 mmol, 60 wt% in mineral oil) was added. After 20 minutes crude allenyl bromide (1.88 mmol), dissolved in 2 ml of DMF, was added dropwise. The reaction was warmed to RT and checked periodically to ensure the complete consumption of **10a**. The reaction was quenched with saturated aqueous solution of sodium bicarbonate and extracted with AcOEt (2 x 15 mL). Organic phase was washed with distilled water (2 x 20 ml) to remove DMF and dried over Na_2SO_4. Final product was purified by flash chromatography.



12i, colourless oil, 22% over two steps (not optimize).

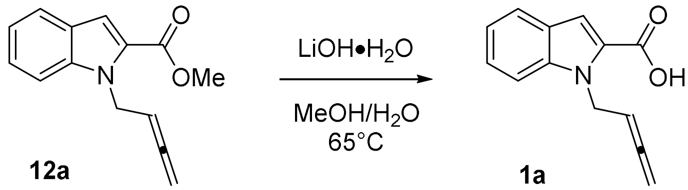
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.39 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.33 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.30 (d, *J* = 1.1 Hz, 1H), 7.14 (ddt, *J* = 7.9, 6.9, 1.0 Hz, 1H), 5.18 (s, 2H), 3.90 (d, *J* = 1.0 Hz, 3H), 1.89 – 1.79 (m, 4H), 1.42 (tq, *J* = 10.7, 4.5, 3.0 Hz, 3H), 1.28 (ddt, *J* = 12.4, 8.9, 4.5 Hz, 1H), 1.10 (ddd, *J* = 14.4, 9.1, 5.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 198.24, 162.37, 139.27, 127.03, 126.08, 124.81, 122.49, 120.54, 110.91, 110.58, 105.45, 86.17, 51.53, 43.85, 31.10, 26.67, 25.84. **GC-MS(EI)**: 236 (100%, -CO_2Me), 295 (43%, $M^{\cdot+}$). **Anal. El.** Calc. for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74; O, 10.83; found: C, 77.34; H, 7.21; N, 4.71; O, 10.74.



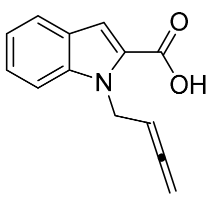
12j, colourless oil, 15% over two steps (not optimized).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.39 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.33 (ddd, *J* = 8.5, 6.8, 1.2 Hz, 1H), 7.29 (d, *J* = 0.9 Hz, 1H), 7.13 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 5.19 – 5.09 (m, 3H), 3.90 (s, 3H), 1.48 (d, *J* = 2.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 201.85, 162.40, 139.22, 127.07, 126.11, 124.84, 122.52, 120.54, 110.90, 110.56, 97.98, 86.23, 51.57, 44.04, 20.08. **GC-MS(EI)**: 196 (100%, -CO_2Me), 188 (92%), 255 (58%, $M^{\cdot+}$). **Anal. El.** Calc. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49; O, 12.53; found: C, 75.31; H, 6.77; N, 5.42; O, 12.49.

General procedure for the hydrolysis

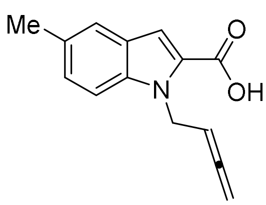


In a round bottomed flask containing 5 mL of MeOH, **12a** (227 mg, 1 mmol) was added, and the flask heated to 65 °C. Next, LiOH•H_2O (420 mg, 10 mmol) was dissolved in 5mL of water and the solution added to the methanolic one. The closed flask was maintained at the same temperature until **12a** was completely consumed. The mixture was concentred at rotavapor and then THF (10 mL) and brine (10 mL) were added. The biphasic mixture was cooled to 0 °C and HCl 2 M was added dropwise under vigorous stirring until pH ≈ 4. Water phase was extracted with THF (3 x15 mL), the organic phase dried over Na_2SO_4, evaporated and the product purified by flash chromatography using *c*Hex/THF 5:1 as the eluent.



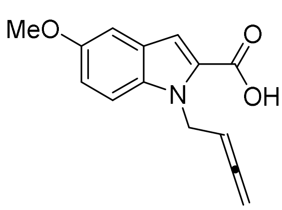
1a, white solid, 93%. **MP**: 164–170 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (dq, *J* = 8.1, 0.9 Hz, 1H), 7.46 (d, *J* = 0.8 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.37 (tt, *J* = 7.0, 0.9 Hz, 1H), 7.16 (ddt, *J* = 7.8, 6.9, 0.8 Hz, 1H), 5.37 (p, *J* = 6.5 Hz, 1H), 5.21 (dt, *J* = 6.1, 2.7 Hz, 2H), 4.79 – 4.72 (m, 2H). **^{13}C NMR** (100 MHz, Acetone-*d*$_6$) δ = 208.57, 162.37, 139.19, 127.21, 126.20, 124.89, 122.44, 120.59, 110.88, 110.62, 87.87, 76.11, 42.67. **LC-MS(ESI+)**: 214.4 $(M+H)^+$. **Anal. El.** Calc. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57; O, 15.01; found: C, 73.30; H, 5.23; N, 6.54; O, 14.95.



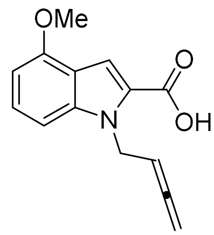
1b, white solid, 65%. **MP**: 187–190 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (dt, *J* = 1.7, 0.9 Hz, 1H), 7.36 (s, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 7.20 (dd, *J* = 8.6, 1.4 Hz, 1H), 5.34 (p, *J* = 6.5 Hz, 1H), 5.18 (dt, *J* = 6.1, 2.6 Hz, 2H), 4.74 (dt, *J* = 6.4, 2.7 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, Acetone-*d*$_6$) δ = 208.57, 162.36, 137.74, 129.66, 127.13, 126.78, 126.44, 121.68, 110.61, 110.07, 87.90, 76.02, 42.68, 20.44. **LC-MS(ESI+)**: 228.2 $(M+H)^+$. **Anal. El.** Calc. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16; O, 14.08; found: C, 74.06; H, 5.79; N, 6.13; O, 14.02.



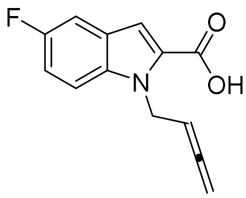
1c, white solid, 40%. **MP**: 128–131 °C.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ = 7.41 (dt, *J* = 9.1, 0.8 Hz, 1H), 7.21 (d, *J* = 0.9 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 6.98 (dd, *J* = 9.1, 2.5 Hz, 1H), 5.36 (p, *J* = 6.6 Hz, 1H), 5.22 (dt, *J* = 6.0, 2.8 Hz, 2H), 4.72 (dt, *J* = 6.6, 2.8 Hz, 2H), 3.80 (s, 3H). **^{13}C NMR** (100 MHz, Acetone-*d*$_6$) δ = 208.55, 162.28, 154.89, 134.62, 126.50, 125.14, 116.39, 111.78, 110.10, 102.37, 87.93, 76.06, 54.88, 42.74. **LC-MS(ESI+)**: 244.3 $(M+H)^+$. **Anal. El.** Calc. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76; O, 19.73; found: C, 69.16; H, 5.41; N, 5.74; O, 19.62.



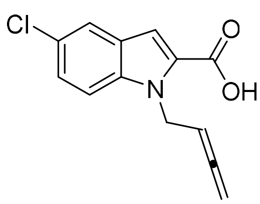
1d, white solid, 66%. **M.P**: 178–179 °C.

^{1}H NMR (400 MHz, Acetone-d_6) δ = 11.07 (bs, 1H), 7.33 (d, *J* = 0.9 Hz, 1H), 7.25 (dd, *J* = 8.5, 7.7 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 5.42 – 5.30 (m, 1H), 5.22 (dt, *J* = 6.1, 2.9 Hz, 2H), 4.71 (dt, *J* = 6.6, 2.8 Hz, 2H), 3.93 (s, 3H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ = 208.55, 162.18, 154.58, 140.64, 126.16, 125.80, 117.35, 108.01, 103.78, 99.81, 87.88, 76.07, 54.73, 42.92. **LC-MS(ESI+)**: 244.3 $(M+H)^+$. **Anal. El.** Calc. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76; O, 19.73; found: C, 69.10; H, 5.45; N, 5.79; O, 19.66.



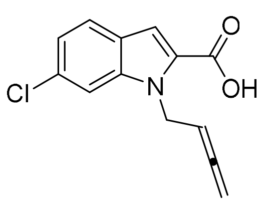
1e, white solid, 44%. **MP**: 137–142 °C.

^{1}H NMR (400 MHz, Acetone-d_6) δ = 7.54 (dd, *J* = 9.1, 4.3 Hz, 1H), 7.39 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.29 (d, *J* = 0.9 Hz, 1H), 7.15 (td, *J* = 9.2, 2.6 Hz, 1H), 6.94 (d, *J* = 0.8 Hz, 1H), 5.38 (td, *J* = 6.7, 5.8 Hz, 1H), 5.26 (dt, *J* = 6.1, 2.9 Hz, 2H), 4.71 (dt, *J* = 6.6, 2.8 Hz, 2H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ = 208.51, 162.07, 158.09 (d, *J* = 234.9 Hz), 135.84, 128.16, 126.25 (d, *J* = 10.3 Hz), 113.52 (d, *J* = 27.0 Hz), 112.28 (d, *J* = 9.8 Hz), 110.18 (d, *J* = 5.3 Hz), 106.35 (d, *J* = 23.4 Hz), 87.80, 76.25, 42.84. **^{19}F NMR** (377 MHz, Acetone-d_6) δ –124.77 (td, *J* = 9.5, 4.4 Hz). **LC-MS(ESI+)**: 232.3 $(M+H)^+$. **Anal. El.** Calc. for $C_{13}H_{10}FNO_2$: C, 67.53; H, 4.36; N, 6.06; O, 13.84; found: C, 67.49; H, 4.41; N, 6.02; O, 13.90.



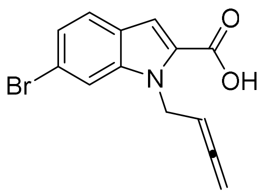
1f, with solid, 99%. **MP**: 195–197 °C.

^{1}H NMR (400 MHz, Acetone-d_6) δ = 7.71 (d, *J* = 2.1 Hz, 1H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.30 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.28 (d, *J* = 0.9 Hz, 1H), 6.94 (s, 1H), 5.39 (p, *J* = 6.5 Hz, 1H), 5.26 (dt, *J* = 6.0, 2.9 Hz, 2H), 4.71 (dt, *J* = 6.5, 2.8 Hz, 2H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ = 208.48, 162.01, 137.50, 128.72, 127.07, 125.76, 125.15, 124.97, 121.45, 112.52, 109.86, 87.75, 76.37. **LC-MS(ESI+)**: 248.1 $(^{35}Cl\ M+H)^+$, 250.1 $(^{37}Cl\ M+H)^+$. **Anal. El.** Calc. for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66; O, 12.92; found: C, 63.12; H, 4.11; N, 5.63; O, 12.95.



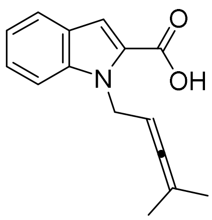
1g, white solid, 58%. **MP**: 187–189 °C.

^{1}H NMR (401 MHz, Acetone-d_6) δ = 7.68 (d, *J* = 8.5 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.31 (d, *J* = 0.9 Hz, 1H), 7.12 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.40 (p, *J* = 6.4 Hz, 1H), 5.25 (dt, *J* = 6.1, 2.9 Hz, 2H), 4.72 (dt, *J* = 6.7, 2.9 Hz, 2H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ = 208.47, 162.06, 139.43, 130.37, 128.40, 125.15, 123.76, 121.27, 110.77, 110.60, 87.75, 76.37, 42.71. **LC-MS(ESI+)**: 248.1 $(^{35}Cl\ M+H)^+$, 250.1 $(^{37}Cl\ M+H)^+$. **Anal. El.** Calc. for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66; O, 12.92; found: C, 63.06; H, 4.10; N, 5.68; O, 12.89.



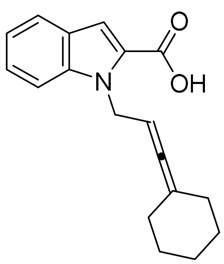
1h, white solid, 73%. **MP**: 185–188 °C.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ = 7.73 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 0.9 Hz, 1H), 7.25 (dd, *J* = 8.5, 1.7 Hz, 1H), 5.40 (p, *J* = 6.5 Hz, 1H), 5.26 (dt, *J* = 6.0, 2.9 Hz, 2H), 4.71 (dt, *J* = 6.6, 2.9 Hz, 2H). **^{13}C NMR** (100 MHz, Acetone-*d*$_6$) δ = 208.47, 162.02, 139.78, 125.14, 125.06, 124.02, 123.84, 118.20, 113.87, 110.60, 87.76, 76.37, 42.68. **LC-MS(ESI+)**: 292.2 (^{79}Br M+H)$^+$, 294.2 (^{81}Br M+H)$^+$. **Anal. El.** Calc. for $C_{13}H_{10}BrNO_2$: C, 53.45; H, 3.45; N, 4.79; O, 10.95; found: C, 53.38; H, 3.51; N, 4.76; O, 11.04.



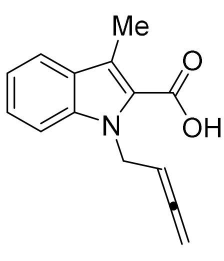
1i, white solid, 96%. **MP**: 142–143 °C.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ = 7.67 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.21 (d, *J* = 5.4 Hz, 2H), 5.13 (tp, *J* = 5.5, 2.7 Hz, 1H), 1.40 (d, *J* = 2.2 Hz, 6H). **^{13}C NMR** (100 MHz, Acetone-*d*$_6$) δ = 202.52, 163.37, 140.32, 127.18, 126.11, 125.58, 123.25, 121.36, 111.93, 111.34, 98.63, 87.46, 44.27, 20.25. **LC-MS(ESI+)**: 242.2 (M+H)$^+$. **Anal. El.** Calc. for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81; O, 13.26; found: C, 74.61; H, 6.31; N, 5.84; O, 13.25.



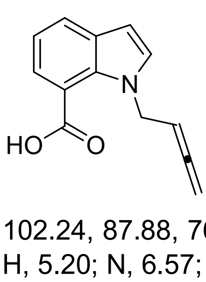
1j, white solid, 49%. **MP**: 135–139 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.0 Hz, 1H), 7.49 (s, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.35 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.15 (ddd, *J* = 8.0, 6.7, 1.2 Hz, 1H), 5.19 (s, 2H), 1.85 (t, *J* = 5.2 Hz, 4H), 1.42 (d, *J* = 11.7 Hz, 2H), 1.32 – 1.23 (m, 2H), 1.10 (qt, *J* = 8.7, 5.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 198.25, 167.31, 139.86, 126.23, 126.01, 125.49, 122.79, 120.74, 112.83, 111.02, 105.62, 86.07, 44.01, 31.08, 26.68, 25.82. **LC-MS(ESI+)**: 282.4 (M+H)$^+$. **Anal. El.** Calc. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98; O, 11.37; found: C, 76.91; H, 6.84; N, 4.96; O, 11.29.



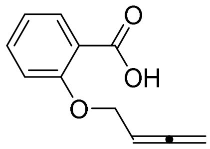
1k, white solid, 97%. **MP**: 183–186 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.44 – 7.35 (m, 2H), 7.16 (ddd, *J* = 8.0, 6.2, 1.6 Hz, 1H), 5.37 (p, *J* = 6.5 Hz, 1H), 5.18 (dt, *J* = 6.2, 2.7 Hz, 2H), 4.76 (dt, *J* = 6.6, 2.6 Hz, 2H), 2.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.8, 167.8, 138.9, 127.4, 126.1, 124.4, 122.9, 121.1, 120.1, 110.7, 88.1, 76.6, 43.8, 11.1. **LC-MS(ESI+)**: 228.2 (M+H)$^+$. **Anal. El.** Calc. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16; O, 14.08; found: C, 74.03; H, 5.71; N, 6.13; O, 14.13.



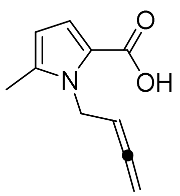
1l, white solid, 99%. **MP**: 83–86 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.21 – 7.12 (m, 2H), 6.61 (d, *J* = 3.2 Hz, 1H), 5.17 (p, *J* = 6.4 Hz, 1H), 5.08 (dt, *J* = 6.4, 2.8 Hz, 2H), 4.73 (dt, *J* = 6.0, 2.7 Hz, 2H). **^{13}C NMR** (100 MHz, Acetone-*d*$_6$) δ = 208.49, 168.27, 132.86, 131.91, 131.43, 125.21, 124.81, 118.45, 117.27, 102.24, 87.88, 76.06, 47.71. **LC-MS(ESI+)**: 214.4 (M+H)$^+$. **Anal. El.** Calc. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57; O, 15.01; found: C, 73.37; H, 5.21; N, 6.58; O, 14.95.



1m, white solid, 90%. **MP**: 60–62 °C.

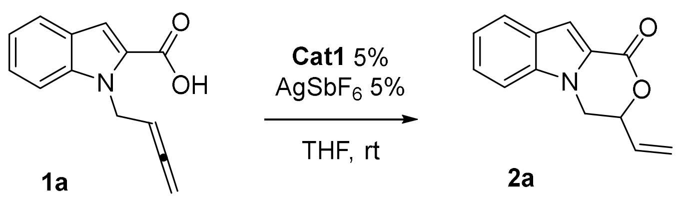
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.52 (bs, 1H), 8.08 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.48 (ddd, *J* = 8.4, 7.3, 1.9 Hz, 1H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 6.99 (dd, *J* = 8.4, 1.0 Hz, 1H), 5.38 (p, *J* = 6.4 Hz, 1H), 4.91 (dt, *J* = 6.6, 2.8 Hz, 2H), 4.72 (dt, *J* = 5.9, 2.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDcl_3$) δ = 209.40, 165.88, 157.06, 134.95, 133.58, 122.18, 117.91, 113.14, 85.80, 78.08, 67.13. **LC-MS(ESI+)**: 191.2 $(M+H)^+$. **Anal. El.** Calc. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30; O, 25.24; found: C, 69.41; H, 5.32; O, 25.27.



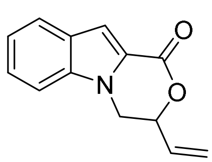
1n, yellow solid, 95%. **MP**:110–114°C.

^{1}H NMR (400 MHz, Acetone-d_6) δ = 6.85 (d, *J* = 3.8 Hz, 1H), 5.90 (d, *J* = 3.8 Hz, 1H), 5.32 (p, *J* = 6.4 Hz, 1H), 4.95 (dt, *J* = 6.1, 2.9 Hz, 2H), 4.75 (dt, *J* = 6.2, 2.8 Hz, 2H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, acetone) δ = 208.37, 161.84, 136.99, 117.87, 107.77, 106.87, 88.26, 76.09, 42.89, 11.60. **LC-MS(ESI+)**: 177.2 $(M+H)^+$. **Anal. El.** Calc. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90; O, 18.06; found: C, 67.86; H, 6.22; N, 7.93; O, 17.97.

General procedure for gold(I) catalysed intramolecular hydrocarboxylation

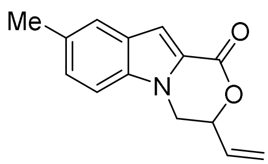


In a two neck round bottomed flask, dried and under nitrogen atmosphere, **Cat1** (3.6 mg, 5 µmol, 5 mol%) was dissolved in 1 mL of anhydrous THF. The flask was covered in foil to provide darkness and then $AgSbF_6$ (1.7 mg, 5 µmol) was added, and the reaction stirred for 10 minutes. Next, **1a** (21.3 mg, 0.1 mmol) was added. The reaction was stirred for 24 h and conversion of **1a** was monitored by TLC. To the reaction mixture was added dry silica and solvent evaporated. Final product was purified by flash chromatography using *n*Hex/AcOEt 5:1 as the eluent.



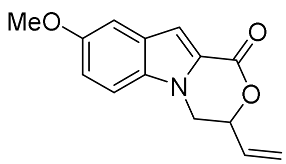
2a, white solid, 90%. **MP**: 108–109 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.42 (d, *J* = 0.9 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.34 – 7.31 (m, 1H), 7.19 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 6.01 (ddd, *J* = 17.3, 10.7, 5.8 Hz, 1H), 5.59 (ddd, *J* = 17.3, 1.5, 0.7 Hz, 1H), 5.44 (dt, *J* = 10.6, 1.1 Hz, 1H), 5.25 (dddt, *J* = 8.5, 6.1, 3.5, 1.4 Hz, 1H), 4.41 (dd, *J* = 12.8, 3.5 Hz, 1H), 4.08 (dd, *J* = 12.8, 9.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.35, 136.60, 131.98, 126.98, 126.07, 123.29, 123.25, 121.48, 120.22, 110.17, 109.88, 77.79, 44.12. **GC-MS(EI)**: 129 (100%), 213 (45%, $M^{+\cdot}$), 168 (19%). **Anal. El.** Calc. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57; O, 15.01; found: C, 73.31; H, 5.22; N, 6.16; O, 14.95.



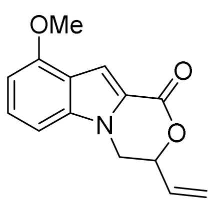
2b, white solid, 64%. **MP**: 106–109 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 1.8 Hz, 1H), 7.34 (s, 1H), 7.22 (d, *J* = 1.3 Hz, 2H), 6.01 (ddd, *J* = 16.7, 10.7, 5.8 Hz, 1H), 5.58 (d, *J* = 17.3 Hz, 1H), 5.43 (d, *J* = 10.7 Hz, 1H), 5.23 (tdd, *J* = 7.0, 3.7, 1.7 Hz, 1H), 4.37 (dd, *J* = 12.8, 3.5 Hz, 1H), 4.06 (dd, *J* = 12.8, 9.3 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.44, 137.59, 135.16, 132.04, 130.93, 128.12, 127.25, 122.43, 120.13, 109.63, 109.51, 77.76, 44.17, 21.39. **GC-MS(EI)**: 143 (100%), 227 (55%, $M^{•+}$), 171 (21%). **Anal. El.** Calc. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16; O, 14.08; found: C, 73.89; H, 5.81; N, 6.18; O, 14.12.



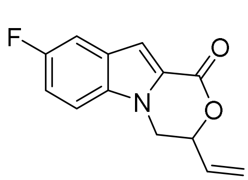
2c, white solid, 80%. **MP**: 125–128°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (s, 1H), 7.25 – 7.19 (m, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 7.05 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.01 (ddd, *J* = 17.1, 10.6, 5.8 Hz, 1H), 5.58 (ddd, *J* = 17.3, 1.4, 0.7 Hz, 1H), 5.47 – 5.39 (m, 1H), 5.28 – 5.19 (m, 1H), 4.35 (dd, *J* = 12.8, 3.5 Hz, 1H), 4.05 (dd, *J* = 12.8, 9.4 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.30, 155.17, 137.20, 132.00, 127.34, 123.48, 120.18, 118.16, 110.78, 109.50, 102.67, 77.76, 55.65, 44.22. **GC-MS(EI)**: 243 (100%, $M_{\cdot+}$), 159 (94%), 116 (97%). **Anal. El.** Calc. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76; O, 19.73; found: C, 69.17; H, 5.43; N, 5.68; O, 19.72.



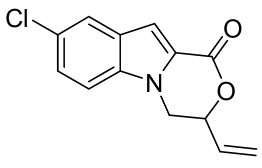
2d, white solid, 72%. **MP**: 138–140 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (s, 1H), 7.30 (t, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 6.00 (ddd, *J* = 16.9, 10.7, 5.8 Hz, 1H), 5.58 (d, *J* = 17.4 Hz, 1H), 5.42 (d, *J* = 10.7 Hz, 1H), 5.22 (dtd, *J* = 9.3, 3.7, 1.7 Hz, 1H), 4.35 (dd, *J* = 12.8, 3.5 Hz, 1H), 4.05 (dd, *J* = 12.8, 9.3 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.25, 154.98, 137.97, 132.01, 127.34, 121.97, 120.14, 118.67, 108.13, 102.56, 100.34, 77.68, 55.41, 44.37. **GC-MS(EI)**: 243 (100%, $M^{\cdot+}$), 159 (51%), 186 (17%). **Anal. El.** Calc. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76; O, 19.73; found: C, 69.05; H, 5.45; N, 5.74; O, 19.76.



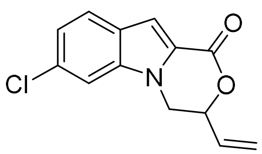
2e, white solid, 75%. **MP**: 125–128°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.33 (m, 2H), 7.27 (dd, *J* = 9.2, 4.4 Hz, 1H), 7.15 (td, *J* = 9.0, 2.4 Hz, 1H), 6.01 (ddd, *J* = 16.9, 10.7, 5.8 Hz, 1H), 5.59 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.45 (dd, *J* = 10.7, 1.3 Hz, 1H), 5.30 – 5.18 (m, 1H), 4.39 (dd, *J* = 12.8, 3.6 Hz, 1H), 4.09 (dd, *J* = 12.8, 9.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.60, 158.09 (d, *J* = 173.2 Hz), 133.29, 131.77, 127.08 (d, *J* = 10.3 Hz), 124.67, 120.41, 115.42 (d, *J* = 27.5 Hz), 110.84 (d, *J* = 9.6 Hz), 109.83 (d, *J* = 5.7 Hz), 107.44 (d, *J* = 23.4 Hz), 77.76, 44.30. **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -121.48 (td, *J* = 9.0, 4.2 Hz). **GC-MS(EI)**: 147 (100%), 231 (33%, $M^{•+}$), 175 (18%). **Anal. El.** Calc. for $C_{13}H_{10}FNO_2$: C, 67.53; H, 4.36; N, 6.06; O, 13.84; found: C, 67.58; H, 4.34; N, 5.99; O, 13.88.



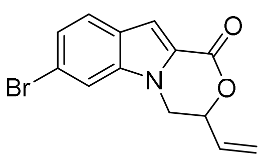
2f, white solid, 98%. **MP**: 153–155 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 2.0 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.25 (d, *J* = 8.5 Hz, 1H), 6.00 (ddd, *J* = 16.8, 10.7, 5.8 Hz, 1H), 5.59 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.45 (d, *J* = 10.6 Hz, 1H), 5.26 (tdd, *J* = 7.8, 3.1, 1.3 Hz, 1H), 4.38 (dd, *J* = 12.8, 3.6 Hz, 1H), 4.09 (dd, *J* = 12.8, 9.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.92, 134.86, 131.69, 127.71, 127.20, 126.61, 124.42, 122.36, 120.48, 111.02, 109.37, 77.75, 44.24. **GC-MS(EI)**: 163 (100%), 165 (39%), 247 (50%, (^{35}Cl)$M^{\bullet+}$) 249 (18%, (^{37}Cl)$M^{\bullet+}$)). **Anal. El.** Calc. for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66; O, 12.92; found: C, 62.99; H, 4.16; N, 5.54; O, 13.00.



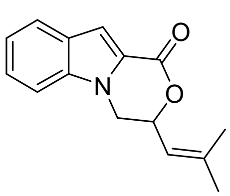
2g, white solid, 85%. **MP**: 134–135 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.6 Hz, 1H), 7.38 (d, *J* = 1.0 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.14 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.00 (ddd, *J* = 17.2, 10.7, 5.8 Hz, 1H), 5.63 – 5.54 (m, 1H), 5.48 – 5.41 (m, 1H), 5.25 (dddd, *J* = 10.6, 6.0, 3.1, 1.3 Hz, 1H), 4.36 (dd, *J* = 12.8, 3.5 Hz, 1H), 4.07 (dd, *J* = 12.8, 9.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.96, 136.81, 132.19, 131.72, 125.42, 124.21, 124.00, 122.57, 120.44, 110.23, 109.85, 77.68, 44.22. **GC-MS(EI)**: 163 (100%),247 (65%, (^{35}Cl)$M^{\bullet+}$), 249 (21%, (^{37}Cl)$M^{\bullet+}$). **Anal. El.** Calc. for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66; O, 12.92; found: C, 62.94; H, 4.14; N, 5.62; O, 12.99.



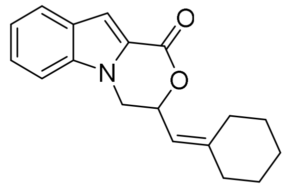
2h, white solid, 89%. **MP**: 124–126 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.6 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.37 (d, *J* = 1.0 Hz, 1H), 7.27 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.00 (ddd, *J* = 17.3, 10.7, 5.8 Hz, 1H), 5.58 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.47 – 5.41 (m, 1H), 5.25 (dddd, *J* = 10.8, 5.7, 3.5, 1.5 Hz, 1H), 4.36 (dd, *J* = 12.8, 3.6 Hz, 1H), 4.06 (dd, *J* = 12.8, 9.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.94, 137.14, 131.71, 125.69, 125.07, 124.44, 123.86, 120.45, 119.96, 112.96, 110.23, 77.69, 44.21. **GC-MS(EI)**: 207 (100%), 293 (60%, (^{81}Br)$M^{\bullet+}$), 291 (56%, (^{79}Br)$M^{\bullet+}$). **Anal. El.** Calc. for $C_{13}H_{10}BrNO_2$: C, 53.45; H, 3.45; N, 4.79; O, 10.95; found: C, 53.51; H, 3.48; N, 4.76; O, 10.89.



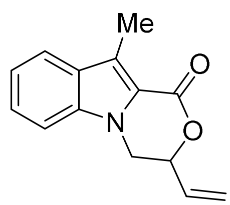
2i, white solid, 68%. **MP**: 118–120 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.40 (d, *J* = 4.6 Hz, 1H), 7.36 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.31 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.18 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 5.46 (td, *J* = 9.1, 3.4 Hz, 1H), 5.38 (dt, *J* = 8.7, 1.4 Hz, 1H), 4.30 (dd, *J* = 12.9, 3.4 Hz, 1H), 4.03 (dd, *J* = 12.9, 9.3 Hz, 1H), 1.81 (d, *J* = 1.4 Hz, 3H), 1.79 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 160.00, 142.29, 136.60, 126.98, 125.88, 123.48, 123.20, 121.37, 118.78, 109.92, 109.79, 75.02, 44.31, 25.80, 18.70. **LC-MS(ESI)**: 242.2 $[(M+1)]^+$. **Anal. El.** Calc. for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81; O, 13.26; found: C, 74.74; H, 6.21; N, 5.76; O, 13.30.



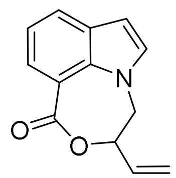
2j, white solid, 29%. **MP**: 124–126 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 8.1 Hz, 1H), 7.42 (s, 1H), 7.41 – 7.35 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.22 – 7.15 (m, 1H), 5.53 (td, *J* = 9.2, 3.5 Hz, 1H), 5.34 (d, *J* = 8.7 Hz, 1H), 4.29 (dd, *J* = 12.8, 3.5 Hz, 1H), 4.06 (dd, *J* = 12.9, 9.6 Hz, 1H), 2.34 – 2.26 (m, 1H), 2.25 – 2.11 (m, 3H), 1.67 – 1.57 (m, 6H). **^{13}C NMR** (100 MHz, $cdcl_3$) δ 160.07, 149.85, 136.59, 127.01, 125.85, 123.51, 123.24, 121.35, 115.40, 109.88, 109.82, 74.27, 44.63, 36.95, 29.74, 28.19, 27.74, 26.35. **LC-MS(ESI)**: 282.2 $[(M+H)]^+$. **Anal. El.** Calc. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98; O, 11.37; found: C, 76.82; H, 6.88; N, 4.97; O, 11.33.



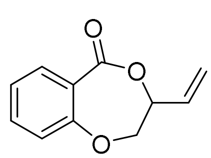
2k, white solid, 85%. **MP**: 108–110 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.39 (ddd, *J* = 8.3, 6.9, 1.1 Hz, 1H), 7.28 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.17 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 6.01 (ddd, *J* = 17.2, 10.7, 5.9 Hz, 1H), 5.57 (ddd, *J* = 17.3, 1.5, 0.8 Hz, 1H), 5.42 (ddd, *J* = 10.7, 1.3, 0.8 Hz, 1H), 5.22 – 5.15 (m, 1H), 4.36 (dd, *J* = 12.7, 3.5 Hz, 1H), 4.03 (dd, *J* = 12.7, 9.2 Hz, 1H), 2.67 (s, 3H). **^{13}C NMR** (100 MHz, $cdcl_3$) δ 160.07, 149.85, 136.59, 127.01, 125.85, 123.51, 123.24, 121.35, 115.40, 109.88, 109.82, 74.27, 44.63, 36.95, 29.74, 28.19, 27.74, 26.35. **LC-MS(ESI)**: 228.3 $[(M+H)]^+$. **Anal. El.** Calc. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16; O, 14.08; found: C, 73.94; H, 5.81; N, 6.18; O, 14.07.



2l, colourless sticky oil, 12%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 3.2 Hz, 1H), 6.61 (d, *J* = 3.2 Hz, 1H), 6.00 (ddd, *J* = 16.8, 10.6, 5.7 Hz, 1H), 5.57 (d, *J* = 17.2 Hz, 1H), 5.37 (d, *J* = 10.7 Hz, 1H), 5.32 (ddd, *J* = 7.4, 5.9, 1.5 Hz, 1H), 4.53 (dd, *J* = 14.3, 7.4 Hz, 1H), 4.49 – 4.42 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.35, 132.18, 132.18, 130.03, 129.04, 128.77, 127.39, 119.95, 119.10, 112.69, 102.90, 77.26, 54.20. GC-MS(EI): 129 (100%), 157 (30%), 213 (29%, $M^{\cdot+}$). **Anal. El.** Calc. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57; O, 15.01; found: C, 73.31; H, 5.22; N, 6.16; O, 14.95.



2m, colourless sticky oil, 11%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.54 – 7.44 (m, 1H), 7.19 – 7.09 (m, 1H), 7.02 (dd, *J* = 8.2, 1.3 Hz, 1H), 5.87 (ddd, *J* = 16.6, 10.7, 5.7 Hz, 1H), 5.54 – 5.44 (m, 1H), 5.40 – 5.32 (m, 1H), 5.07 – 4.98 (m, 1H), 4.39 (dd, *J* = 12.3, 8.6 Hz, 1H), 4.32 (dd, *J* = 12.5, 2.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.91, 154.92, 134.84, 133.20, 130.13, 123.19, 120.97, 119.70, 110.00, 76.51, 74.34. **GC-MS(EI)**: 105 (100%), 131 (28%), 190 (7%, $M^{\cdot+}$). **Anal. El.** Calc. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30; O, 25.24; found: C, 69.51; H, 5.29; O, 25.20.

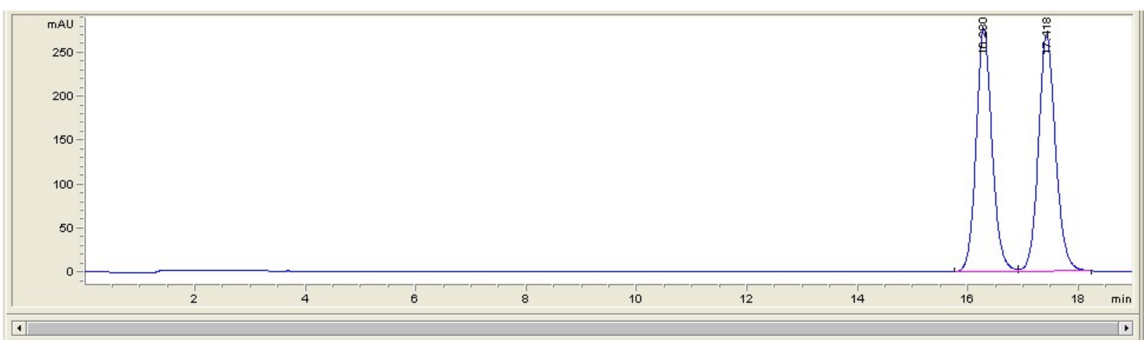
Enantioselective gold(I) catalysed intramolecular hydrocarboxylation

In a two neck round bottomed flask, dried and under nitrogen atmosphere, **Cat** (5 μmol, 5 mol%) was dissolved in 1 mL of anhydrous THF. The flask was covered with an aluminum foil to provide darkness and then additive (5 μmol) was added, and the reaction stirred for 10 minutes. Next, **1a** (21.3 mg, 0.1 mmol) was added. The reaction was stirred for 24 h and conversion of **1a** was monitored by TLC. To the reaction mixture was added dry silica and solvent evaporated. Final product was purified by flash chromatography using *n*Hex/AcOEt 5:1 as the eluent.

Entry	Cat	Additive	Temperature	Yield [%]	e.r.
1	(*R*)-Cat11	$AgSbF_6$	rt	89	66 : 33
2	(*R*)-Cat12	$AgSbF_6$	rt	80	75:25
3	(*R*)-Cat13	$AgSbF_6$	rt	89	72.5:27.5
4	(*S*)-Cat14	$AgSbF_6$	rt	86	19:81
5	(*S*)-Cat14	$AgSbF_6$	10 °C	81	25:75
6	(*S*)-Cat14	$AgSbF_6$	40 °C	66	26.5:73.5
7	(*S*)-Cat14	AgOTs	rt	31	53.5:46.5
8	(*S*)-Cat14	$Ag(NTf_2)$	rt	75	26:74
9 [a]	(*S*)-Cat14	AgTFA	rt	< 20	55:45
10 [a]	(*S*)-Cat14	$AgBF_4$	rt	< 20	0
11 [a]	(*S*)-Cat14	AgOTf	rt	< 20	32.5:67.5
12 [a]	(*S*)-Cat14	$AgPF_6$	rt	< 20	43:57
13	(*S*)-Cat14	NaBArF	rt	no reaction	-

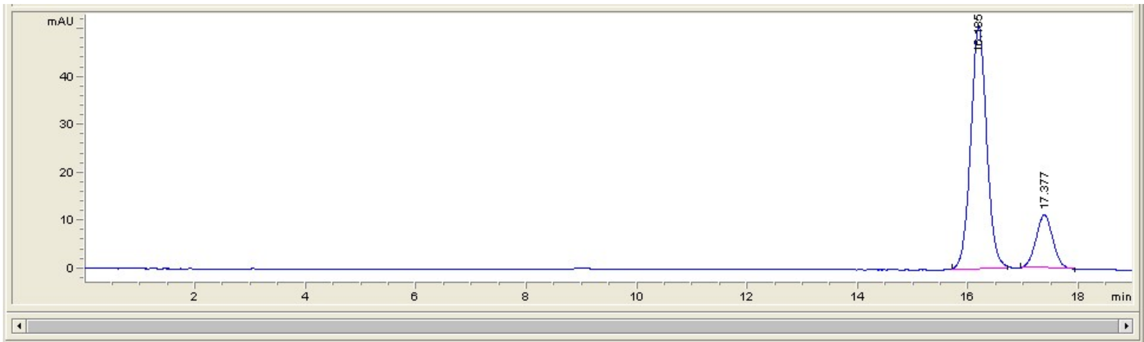
[a] e.r. determined on crude due to low conversion.

Chiral HPLC condition for separation of **2a** enantiomers: Chiralpack® IA (0.46 cm x 25 cm), eluent: 90/10 *n*-hexane/IPA, flow: 1 mL/min, T = 30 °C.



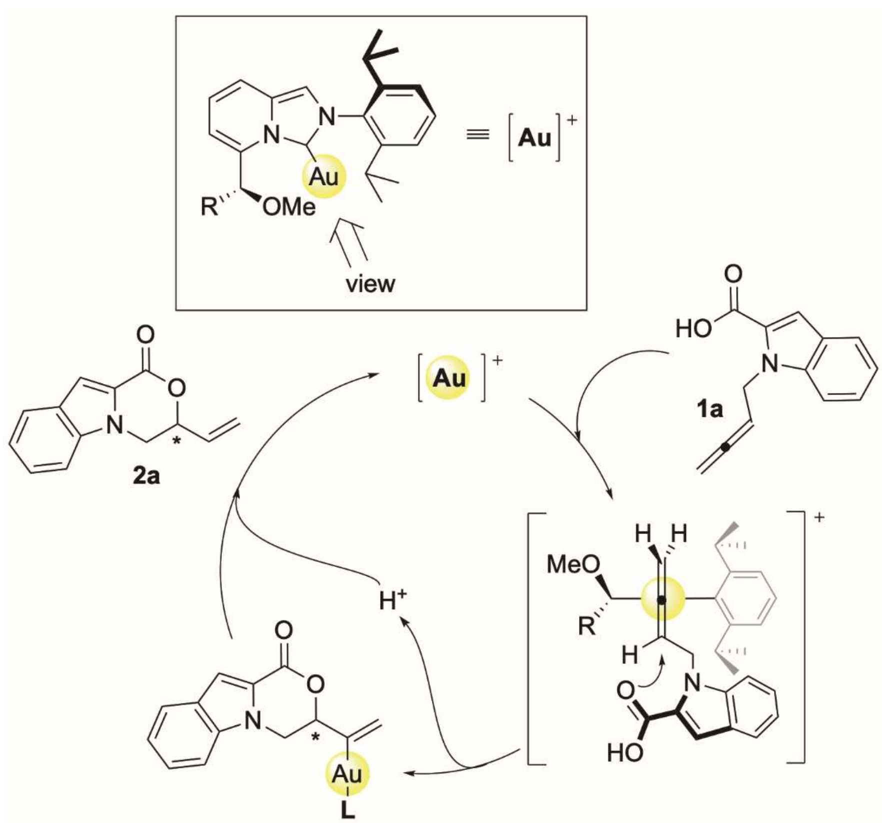
#	Time	Area	Height	Width	Area%	Symmetry
1	16.28	5568.9	276.5	0.307	48.846	0.861
2	17.418	5832.2	270.1	0.3279	51.154	0.849

Enantioenriched (+)-**2a**, $[\alpha]^D$= +35.14 (c=0.99): t(major)=16.2min; t(minor)=17.4min.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.185	1016.8	50.7	0.3061	80.932	0.949
2	17.377	239.6	11.2	0.3292	19.068	0.967

Plausible reaction mechanism for asymmetric transformation



Crystallographic analysis

The X-ray intensity data were measured on a Bruker Apex III CCD diffractometer. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in four sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.5° ω steps. The software SMART[3] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program,[12] and an empirical absorption correction was applied using SADABS.[13] The structures were solved by direct methods (SIR 2014)[14] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL)[15] using anisotropic thermal parameters for all non-hydrogen atoms. The aromatic, methyl, methylene and methine hydrogen atoms were placed in calculated positions, refined with isotropic thermal parameters $U(H)$ = 1.2 Ueq(C) or $U(H)$ = 1.5 $Ueq(C_{methyl})$ and allowed to ride on their carrier carbons. In **Cat11** one THF molecule was found in the asymmetric unit. Compound **Cat12** crystallizes as racemic twin in the chiral space group $P2_12_12_1$.

Crystal data and details of the data collection for compounds **Cat2-4**, **Cat11-14** and **2a** are reported in **Table S1, S3, S5** and **S7**. Molecular drawings were generated using Mercury.[16] The syntheses of **Cat11AuCl** and **Cat12AuCl** were carried put with the racemic mixtures of the ligands.

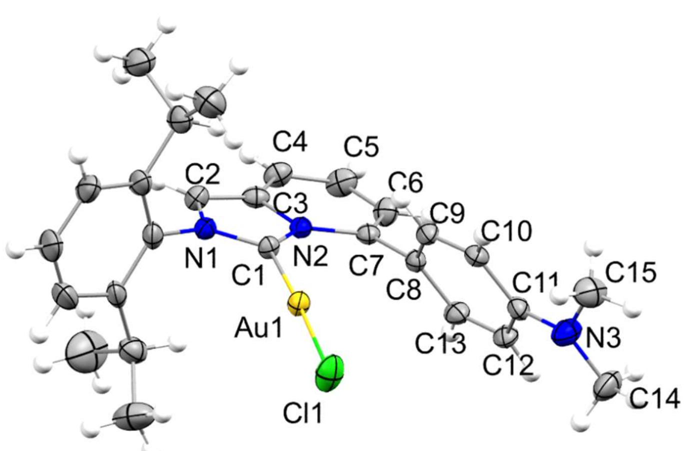
Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC 2167546-2167553. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/getstructures.

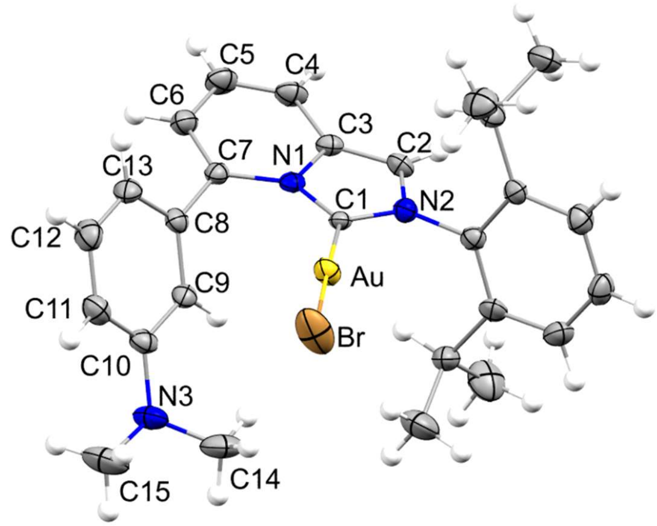
Table S1. Crystal data and structure refinement for compounds **Cat2-4.**

Compound	**Cat2**	**Cat3**	**Cat4**
Formula	$C_{27}H_{31}AuClN_3$	$C_{27}H_{31}AuBrN_3$	$C_{21}H_{27}AuClN_3$
Fw	629.96	674.42	553.87
T, K	296 (2)	296(2)	296 (2)
λ, Å	0.71073	0.71073	0.71073
Crystal symmetry	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a, Å	10.6885(8)	10.8669(7)	8.150(1)
b, Å	16.120(1)	11.9595(8)	15.359(2)
c, Å	15.127(1)	19.914(1)	17.032(2)
α	90	90	90
β	92.152 (2)	100.258(2)	90
γ	90	90	90
Cell volume, $Å^3$	2604.5(4)	2546.8(3)	2132.0(5)
Z	4	4	4
D_C, Mg m^{-3}	1.607	1.759	1.726
μ(Mo-K_α), mm^{-1}	5.770	7.364	7.035
F(000)	1240	1312	1080
Crystal size/ mm	0.15 x 0.13 x 0.08	0.32 x 0.16 x 0.14	0.24 x 0.22 x 0.11
θ limits, °	1.847 to 25.496	1.904 to 26.000	1.785 to 25.496
Reflections collected	31627	32398	20519
Unique obs. Reflections [F_o	4835 [R(int) = 0.0784]	5009 [R(int) = 0.0611]	3966 [R(int) = 0.0843]
Goodness-of-fit-on F^2	0.971	1.012	1.117
R_1 (F)[a], wR_2 (F^2)[b] [I > 2σ(I)]	R1 = 0.0487, wR2 = 0.1150	R1 = 0.0450, wR2 = 0.1080	R1 = 0.0412, wR2 = 0.0901
Largest diff. peak and hole, e. $Å^{-3}$	2.299 and -1.801	1.876 and -1.714	2.100 and -0.846

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

Figure S1. ORTEP molecular drawing with atom labelling of **Cat2-4**, thermal ellipsoids are draw at 30% of the probability level.





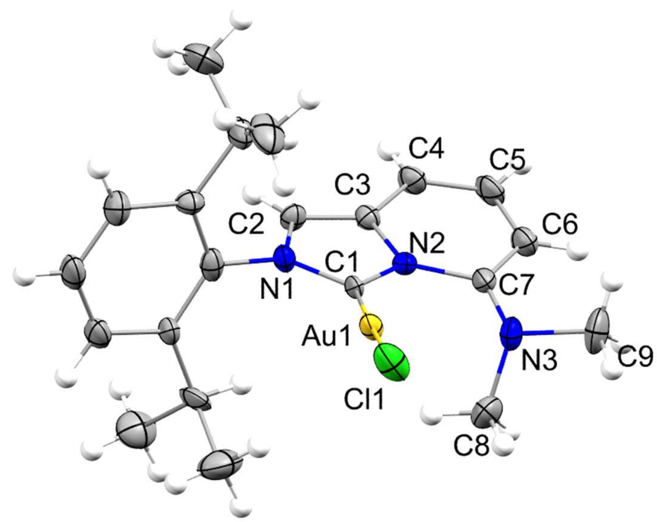


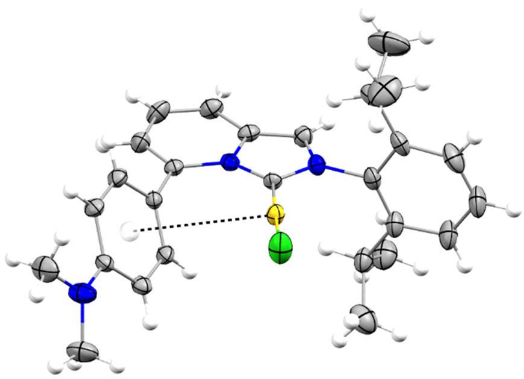
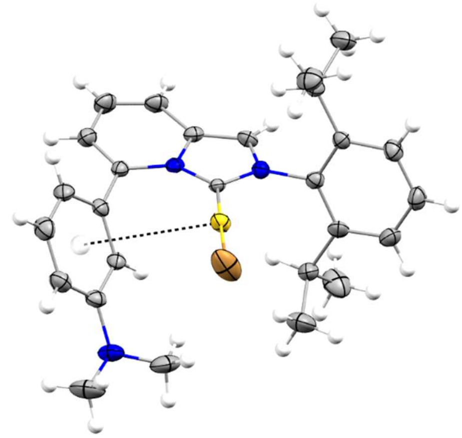
Table S2. Angles of -NMe_2 groups.

Cat2		
C11-N3-C14	C11-N3-C15	C14-N3-C15
120.5(8)°	119.7(8)°	117.1(8)°

Cat3		
C10-N3-C14	C10-N3-C15	C14-N3-C15
117.8(7)°	115.8(7)°	114.9(8)°

Cat4		
C7-N3-C8	C7-N3-C9	C8-N3-C9
114.4(1)°	113.6(1)°	110.0(1)°

Figure S1.1. Ar···Au π-interactions for **Cat2** and **Cat3**.

Complex	Ar···Au (Å)[a]
Cat2	3.623
Cat3	3.567

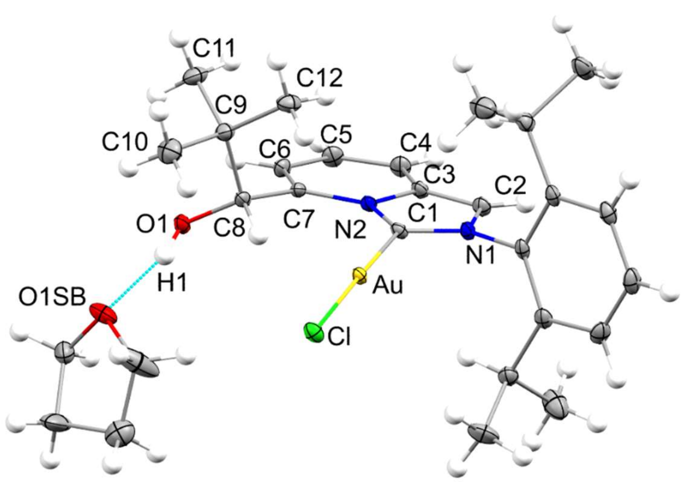
[a] distance between arene center of mass and gold(I), calculated by Mercury

Table S3. Crystal data and structure refinement for compounds **Cat11-12.**

Compound	**Cat11•THF**	**Cat12**
Formula	$C_{24}H_{32}AuClN_2O{\bullet}C_4H_8O$	$C_{25}H_{34}AuClN_2O$
Fw	669.03	610.96
T, K	100 (2)	100 (2)
λ, Å	0.71073	0.71073
Crystal symmetry	Triclinic	Orthorhombic
Space group	*P-1*	$P2_12_12_1$
a, Å	8.9407 (5)	10.118 (1)
b, Å	9.6395 (6)	12.940 (2)
c, Å	17.239 (1)	19.485 (3)
α	98.233 (2)	90
β	94.272 (2)	90
γ	106.185 (2)	90
Cell volume, $Å^3$	1401.9 (1)	2551.1 (6)
Z	2	4
D_C, Mg m^{-3}	1.585	1.591
μ(Mo-K_α), mm^{-1}	5.368	5.889
F(000)	668	1208
Crystal size/ mm	0.14 x 0.13 x 0.04	0.36 x 0.21 x 0.14
θ limits, °	2.348 to 25.500	1.889 to 25.993
Reflections collected	16780	33295
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	5216 [R(int) = 0.0290]	4997 [R(int) = 0.0371]
Goodness-of-fit-on F^2	1.180	1.028
R_1 (F)[a], wR_2 (F^2)[b] [I > 2σ(I)]	R1 = 0.0217, wR2 = 0.0492	R1 = 0.0200, wR2 = 0535
Largest diff. peak and hole, e. $Å^{-3}$	1.146 and -1.421	2.423 and -1.083

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

Figure S2. ORTEP molecular drawing with atom labelling of **Cat11-12**, thermal ellipsoids are draw at 30% of the probability level. In **Cat11** also the THF molecule is represented. The dotted light-blue line shows the presence of a classical O-H…O bond. In **Cat12** only the *R* enantiomer is shown.



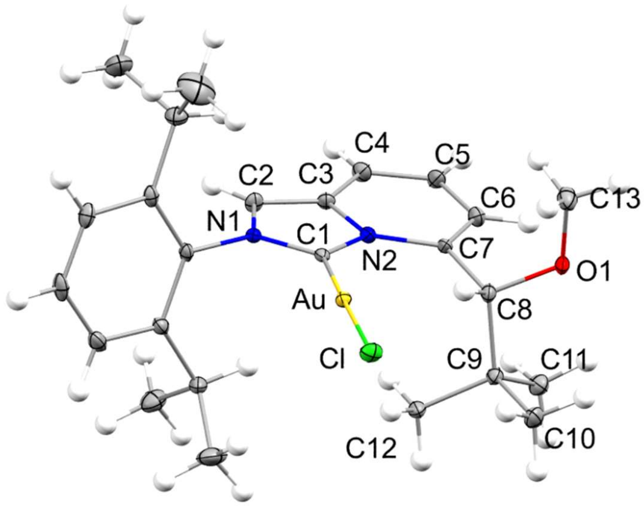


Table S4. Torsion angle between **ImPy** plane and alkyl functionalization.

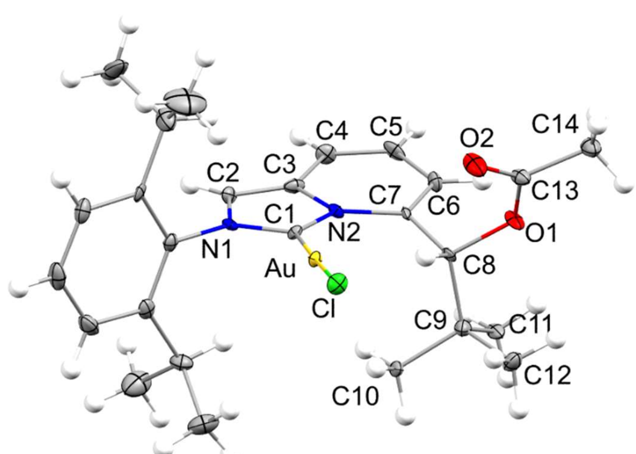
	N2-C7-C8-C9 torsion angle
Cat11•THF	94.1(3)°
Cat12	92.2(7)°

Table S5. Crystal data and structure refinement for compounds **Cat13-14.**

Compound	**Cat13**	**Cat14**
Formula	$C_{26}H_{34}AuClN_2O_2$	$C_{31}H_{40}AuClN_2O$
Fw	638.97	689.06
T, K	100 (2)	100(2)
λ, Å	0.71073	0.71079
Crystal symmetry	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	9.8777(7)	12.7402(8)
b, Å	13.289(1)	13.7979(8)
c, Å	19.872(1)	16.0681(9)
α	90	90
β	90	90
γ	90	90
Cell volume, Å^3	2608.4(3)	2824.6(3)
Z	4	4
D_C, Mg m^{-3}	1.627	1.620
μ(Mo-K$_\alpha$), mm^{-1}	5.766	5.329
F(000)	1264	1376
Crystal size/ mm	0.41 x 0.08 x 0.07	0.24 x 0.13 x 0.10
θ limits, °	1.844 to 25.248	1.945 to 30.572
Reflections collected	30416	63032
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	4669 [R(int) = 0.0626]	8646 [R(int) = 0.0600]
Goodness-of-fit-on F^2	0.766	1.024
R_1 (F)^a, wR_2 (F^2)^b [I > 2σ(I)]	R1 = 0.0388, wR2 = 0.0997	R1 = 0.0169, wR2 = 0.0384
Largest diff. peak and hole, e. Å^{-3}	2.630 and -2.891	1.638 and -0.748

a) $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. b $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

Figure S3. ORTEP molecular drawing with atom labelling of **Cat13-14**, thermal ellipsoids are draw at 30% of the probability level.



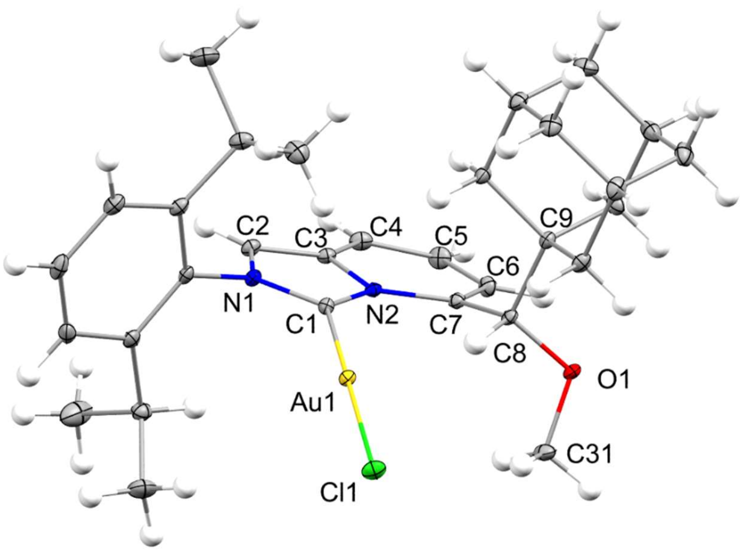


Table S6. Torsion angle between ImPy plane and alkyl functionalization

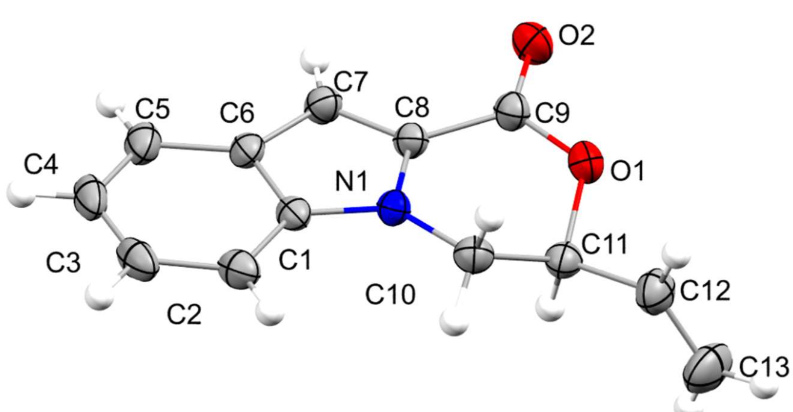
	N2-C7-C8-C9 torsion angle
Cat13	92(1)°
Cat14	93.4(3)°

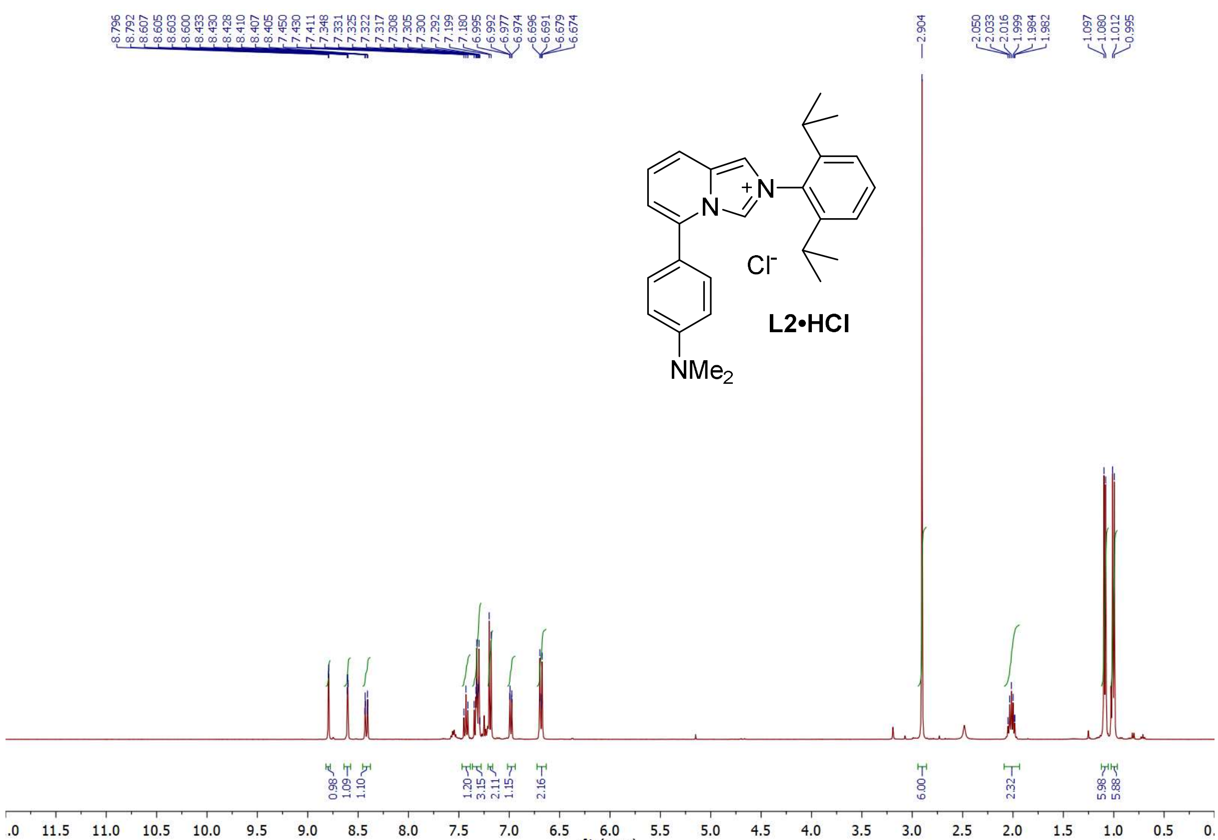
Table S7. Crystal data and structure refinement for compounds **2a.**

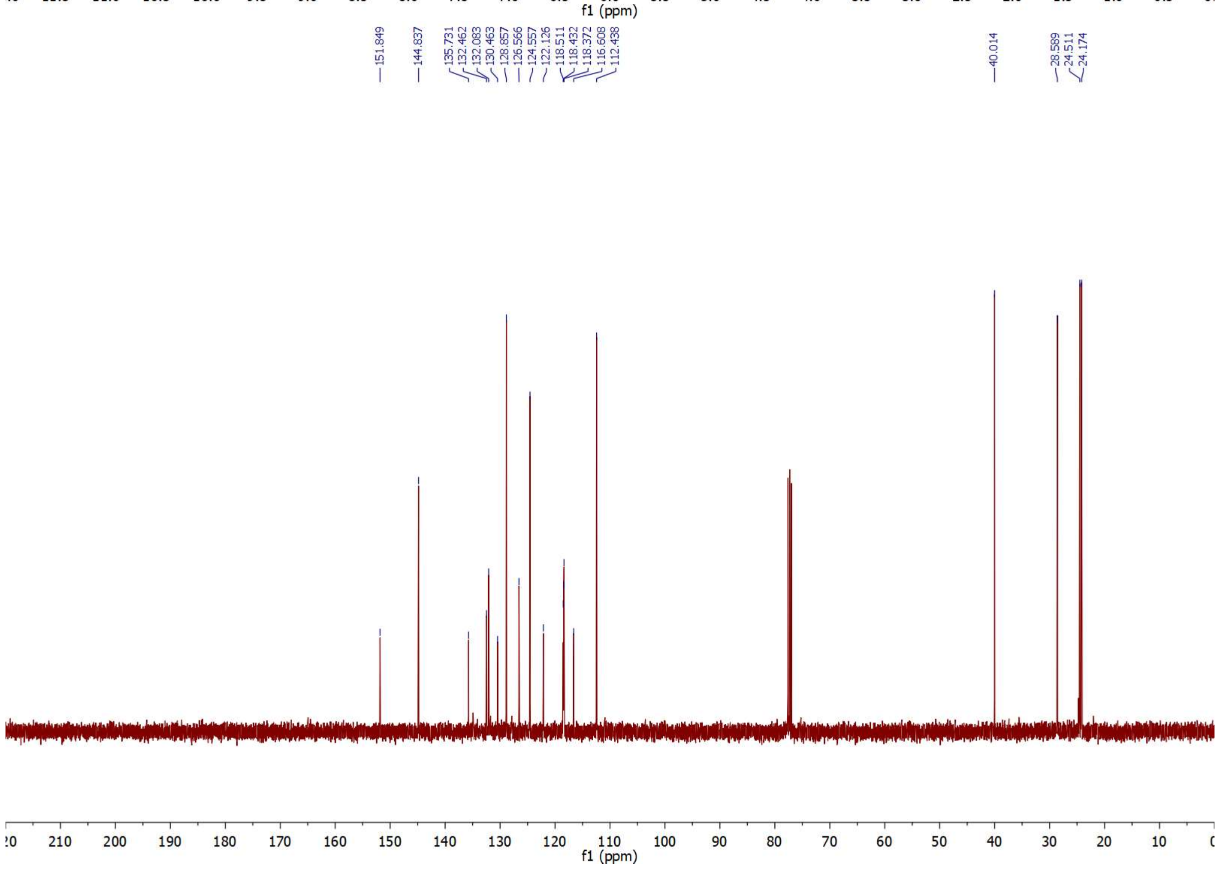
Compound	**2a**
Formula	$C_{13}H_{11}NO_2$
Fw	213.23
T, K	296 (2)
λ, Å	0.71073
Crystal symmetry	Monoclinic
Space group	*C2/c*
a, Å	18.836(1)
b, Å	7.3826(5)
c, Å	17.191(1)
α	90
β	115.542 (1)
γ	90
Cell volume, $Å^3$	2156.9(2)
Z	8
D_C, Mg m^{-3}	1.313
μ(Mo-K_α), mm^{-1}	0.089
F(000)	896
Crystal size/ mm	0.31 x 0.07 x 0.05
θ limits, °	2.397 to 25.497
Reflections collected	12671
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	1957 [R(int) = 0.0370]
Goodness-of-fit-on F^2	1.116
R_1 (F)[a], wR_2 (F^2)[b] [I > 2σ(I)]	R1 = 0.0641, wR2 = 0.1569
Largest diff. peak and hole, e. $Å^{-3}$	0.200 and -0.192

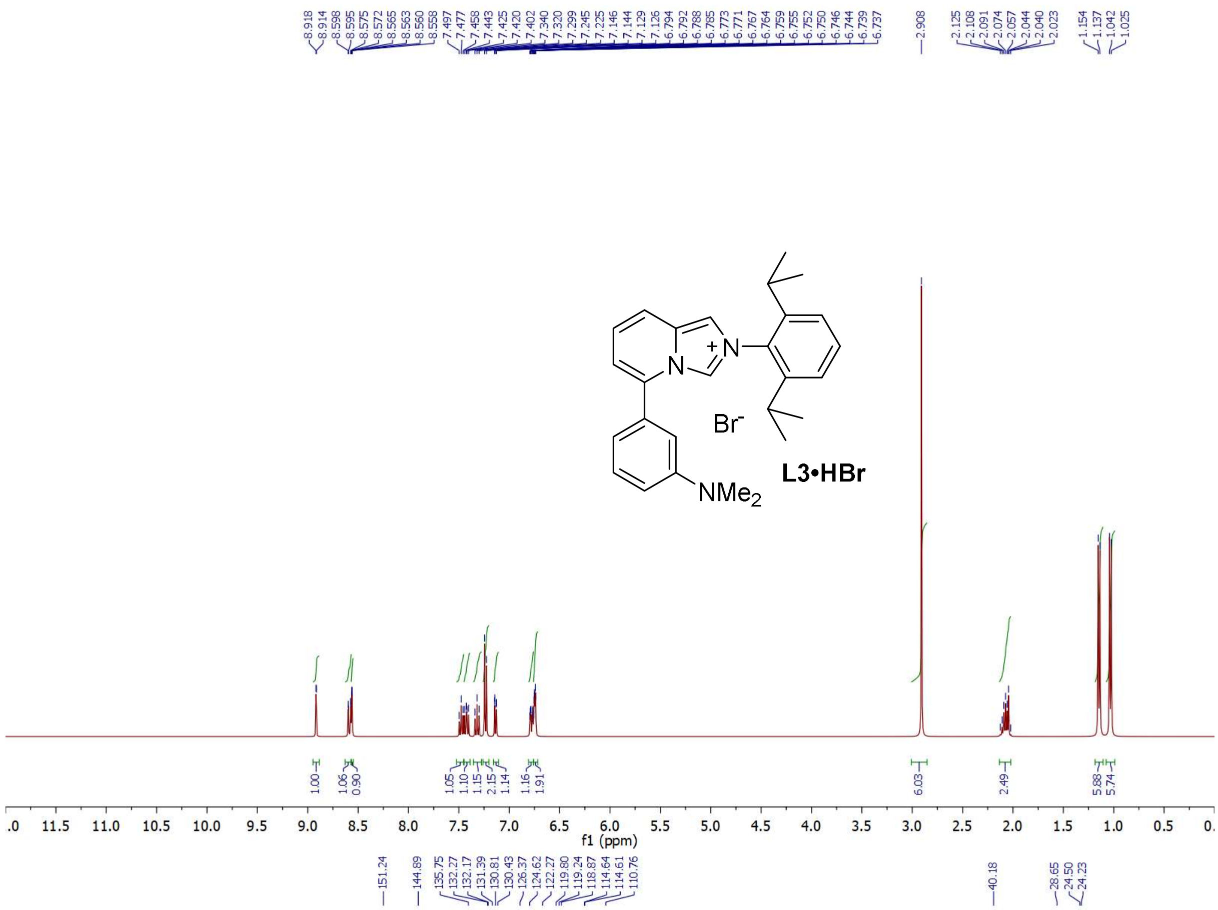
[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

Figure S4. ORTEP molecular drawing with atom labelling of **2a**, thermal ellipsoids are draw at 30% of the probability level.

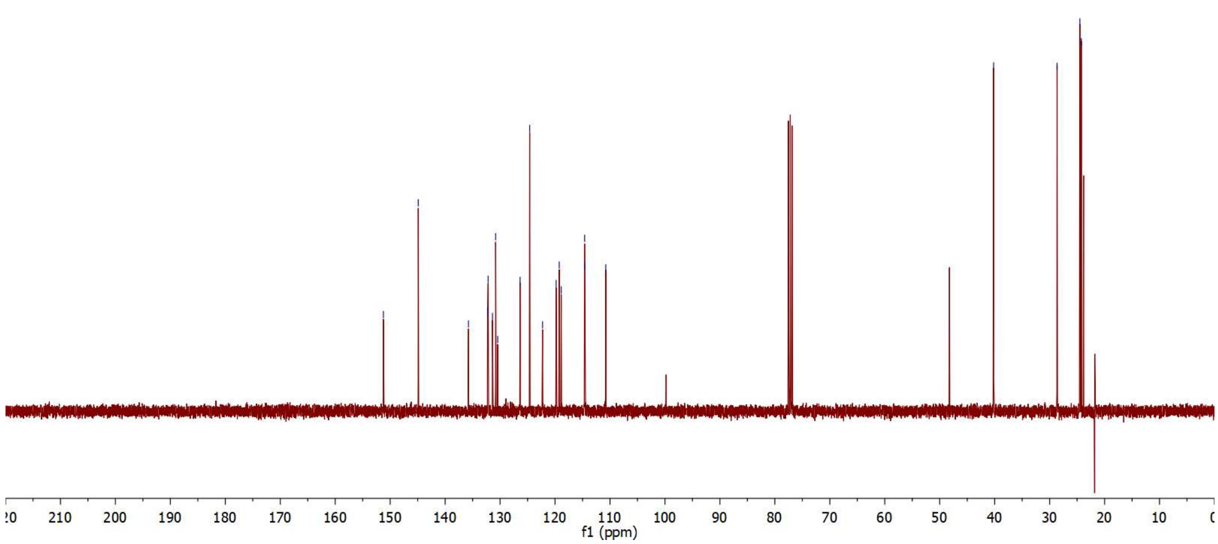


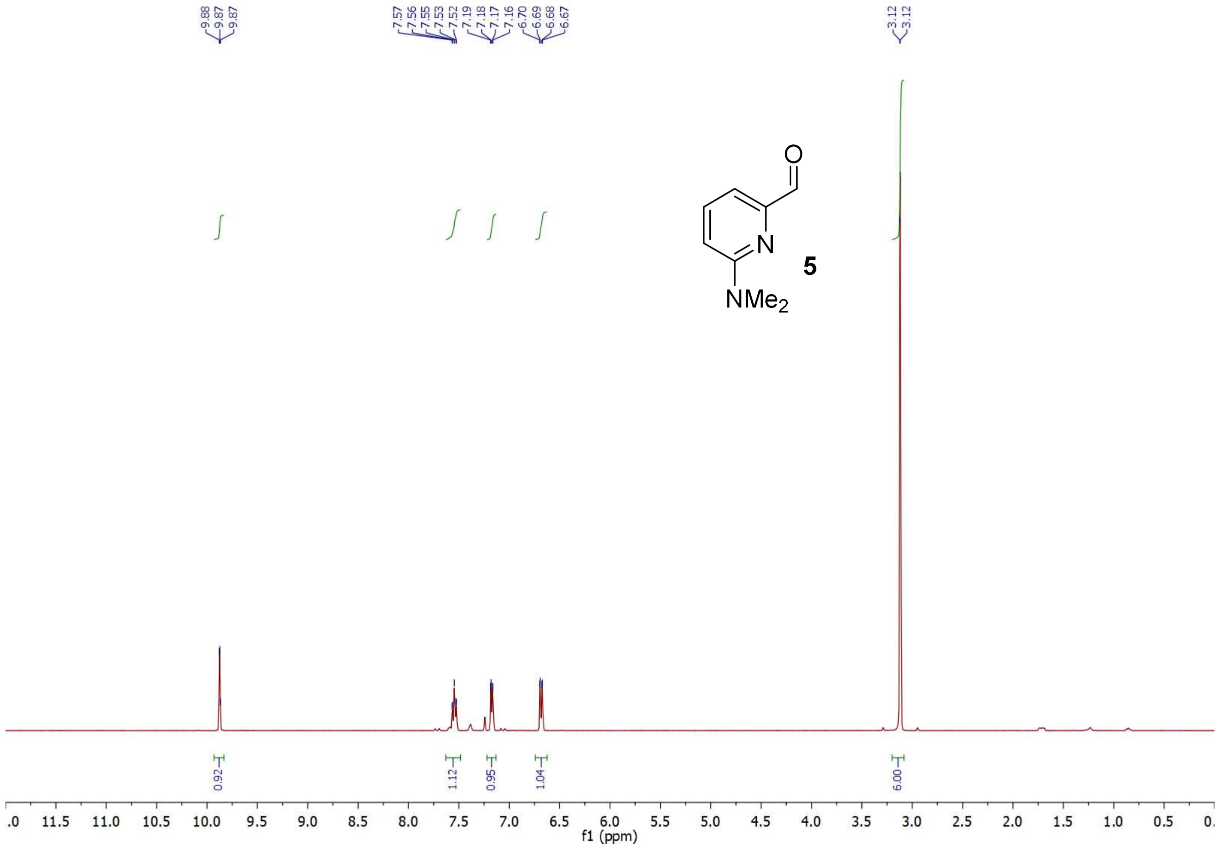

Cl⁻
L2•HCl
NMe2
f1 (ppm)

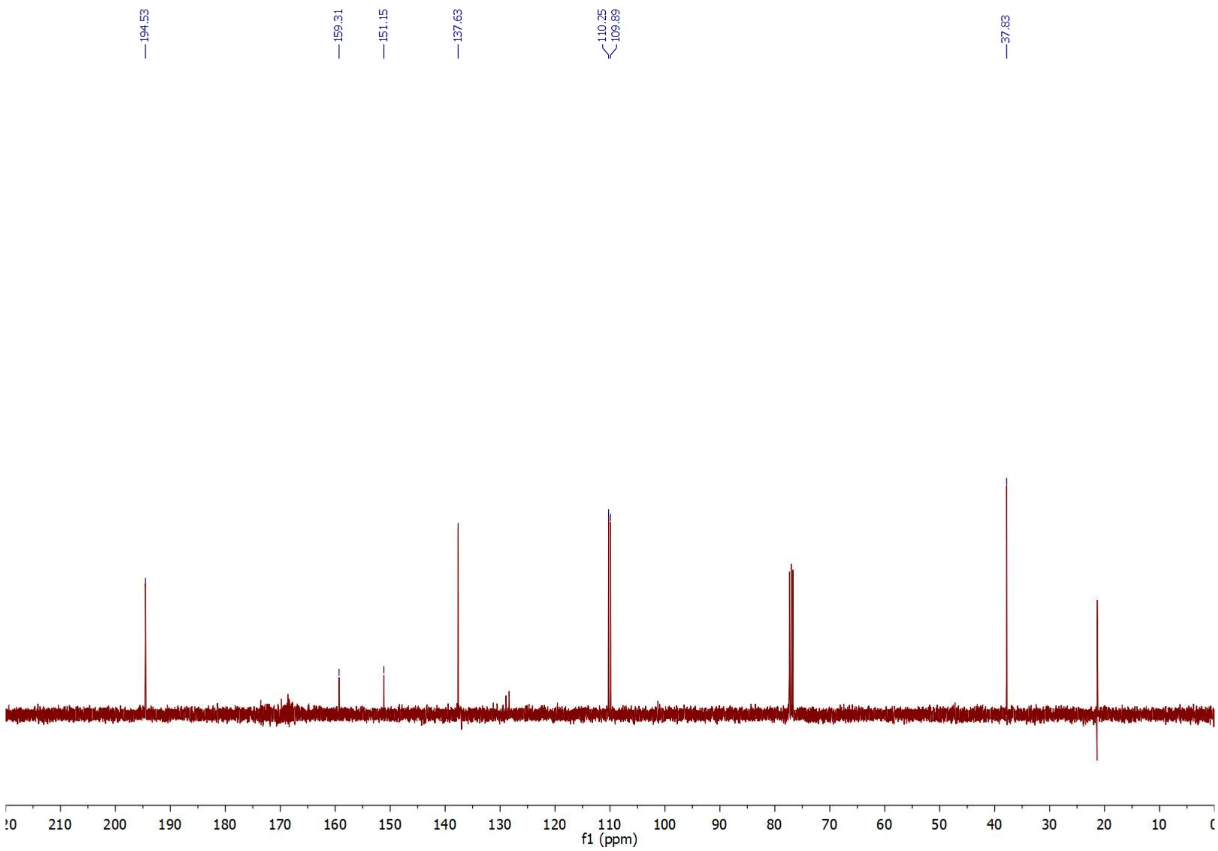

f1 (ppm)

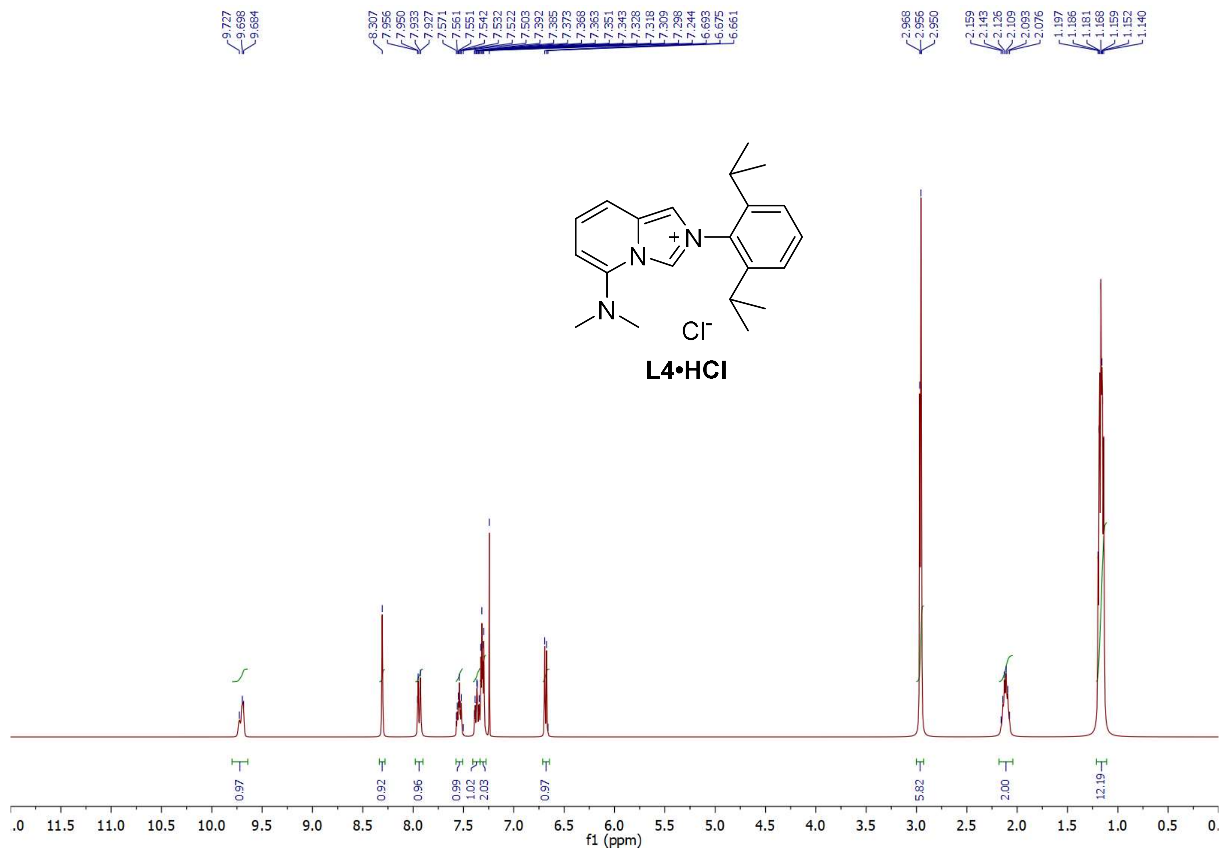


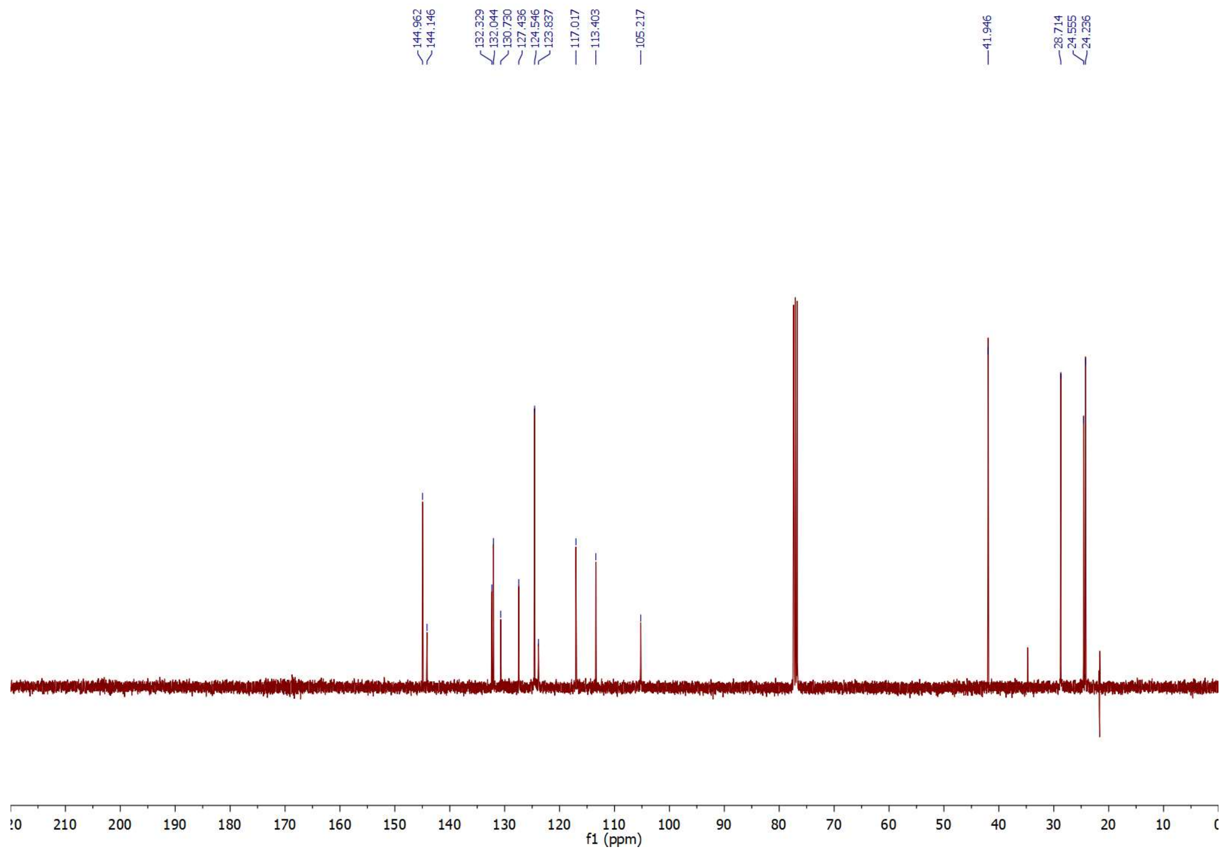
Br-
NMe2
L3•HBr

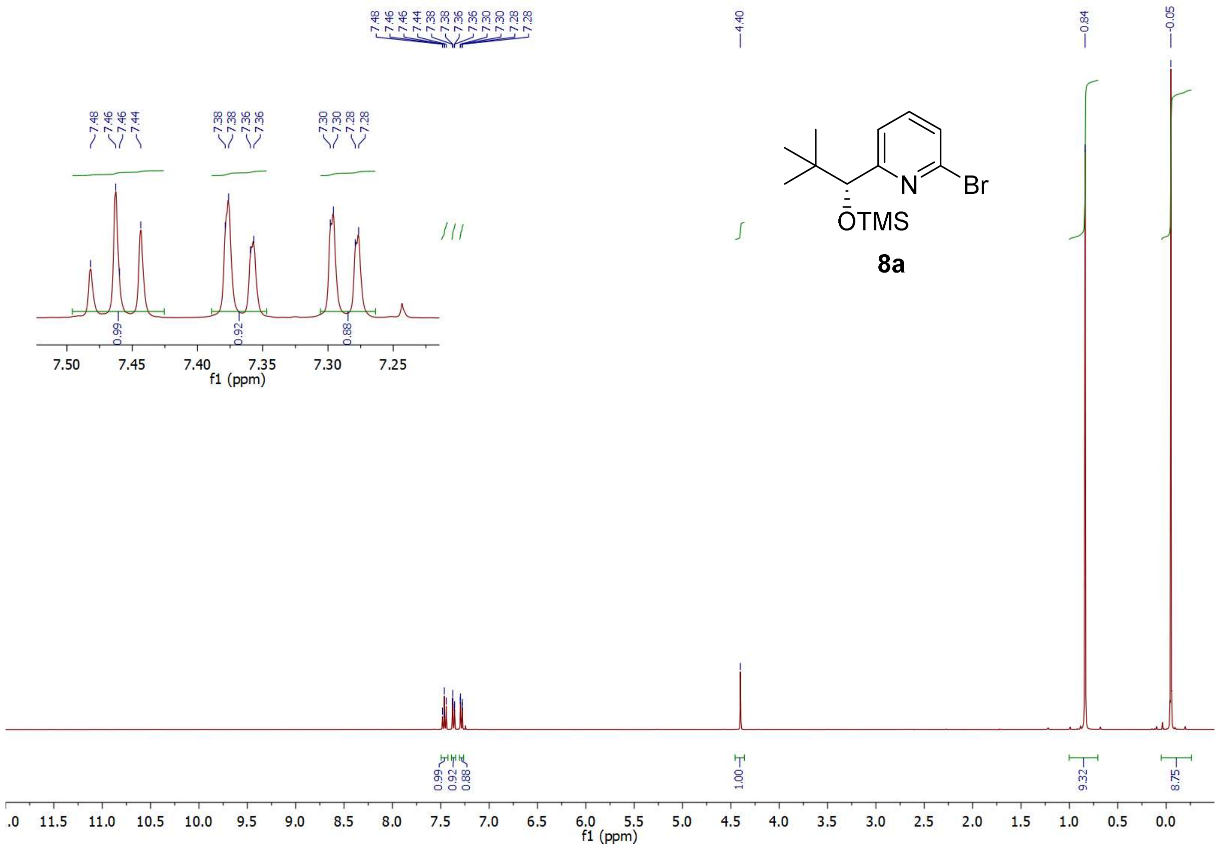


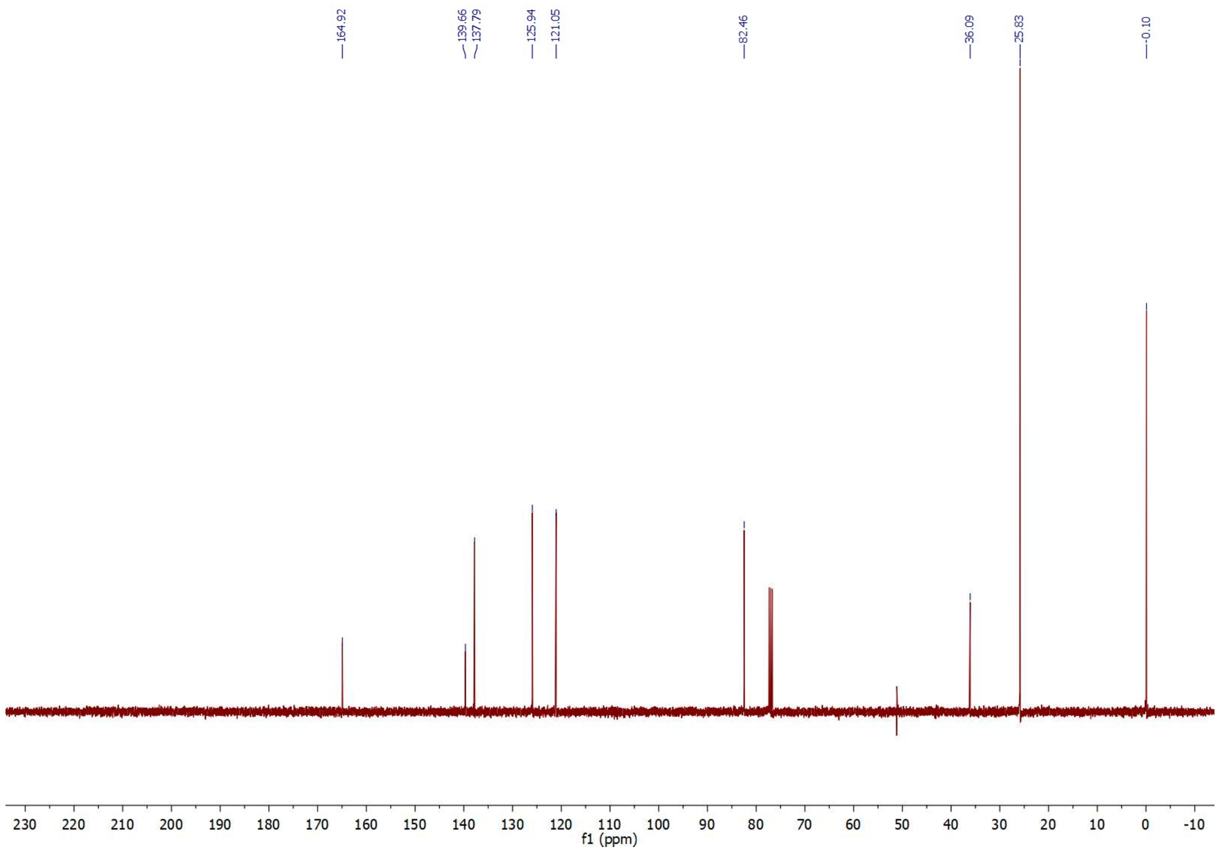

9.88
9.87
9.87
7.57
7.56
7.55
7.53
7.52
7.19
7.18
7.17
7.16
6.70
6.69
6.68
6.67
3.12
3.12
O
N
NMe2
5
0.92
1.12
0.95
1.04
6.00
f1 (ppm)

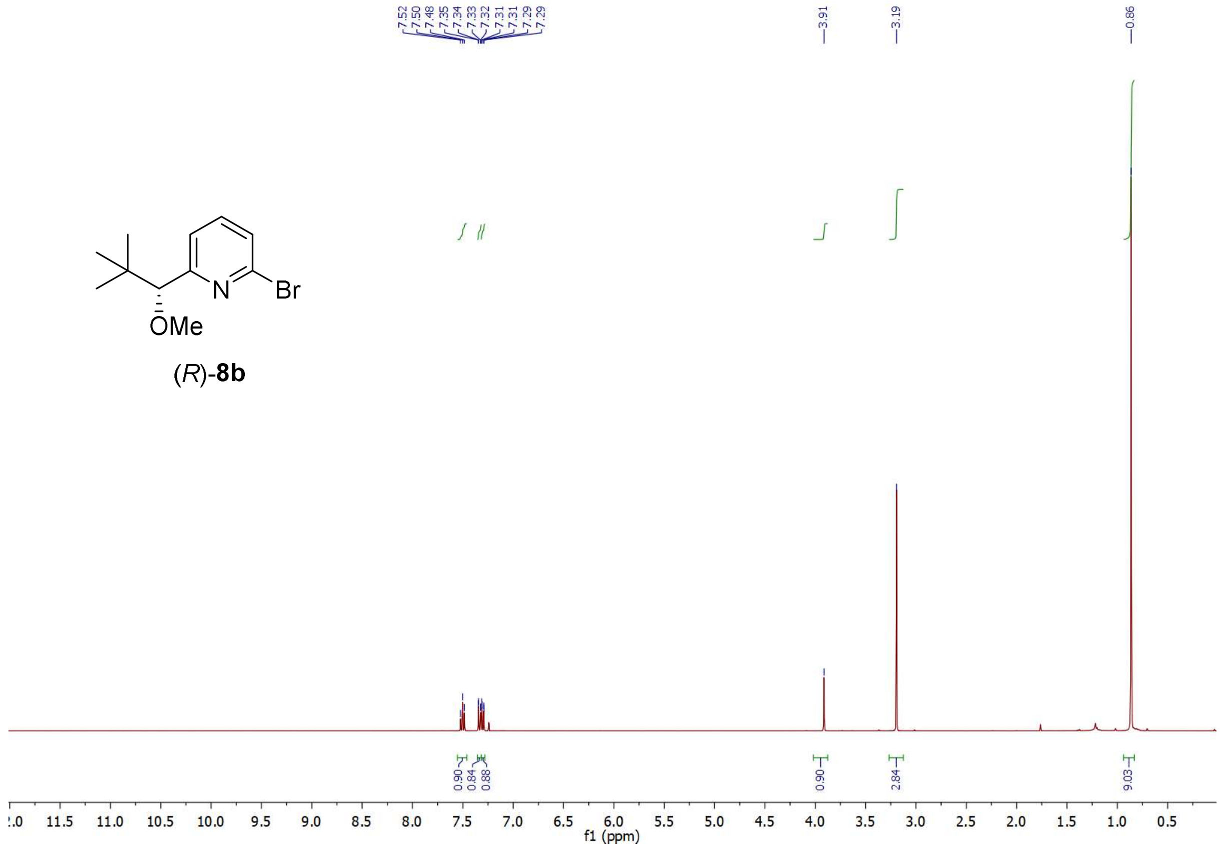

194.53
159.31
151.15
137.63
110.25
109.89
37.83
f1 (ppm)

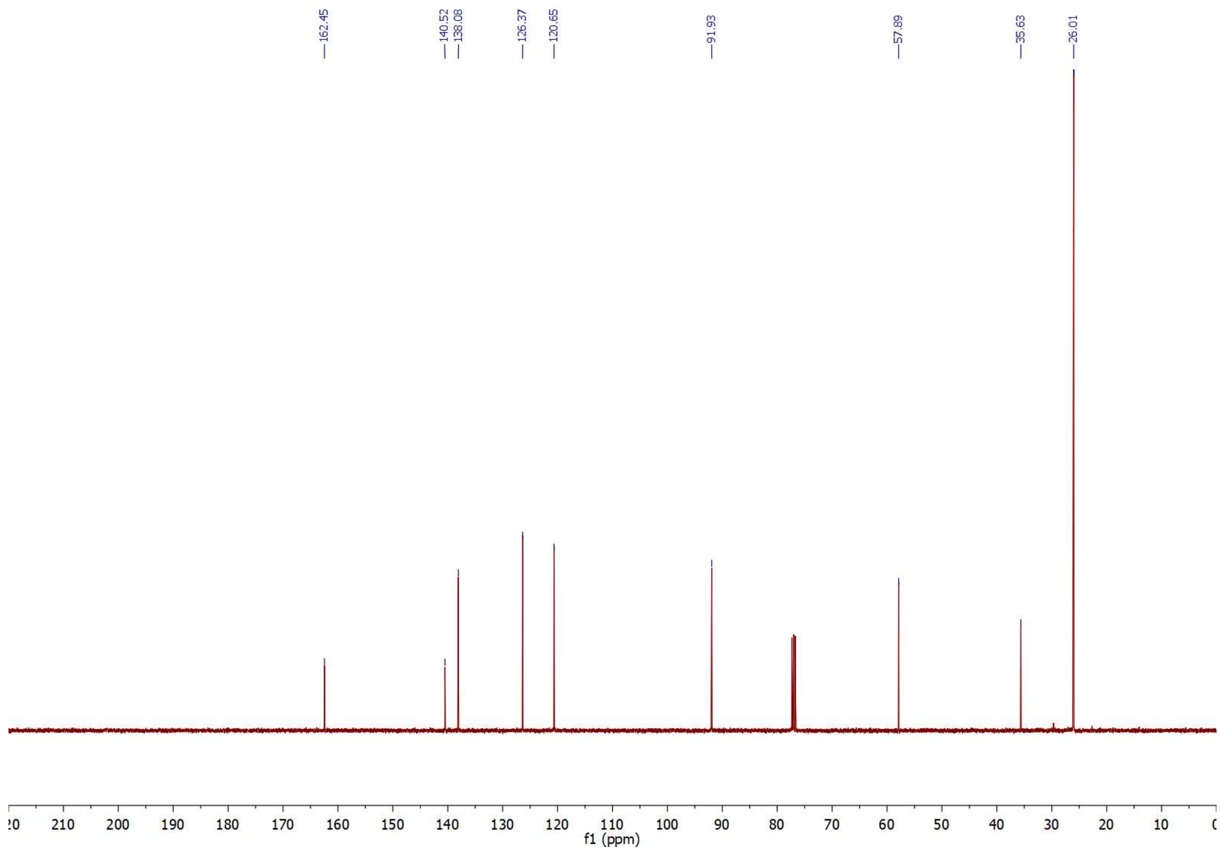

9.727
9.698
9.684
8.307
7.956
7.950
7.933
7.927
7.571
7.561
7.551
7.542
7.532
7.522
7.503
7.392
7.385
7.373
7.368
7.363
7.351
7.343
7.328
7.318
7.309
7.298
7.244
6.693
6.675
6.661
2.968
2.956
2.950
2.159
2.143
2.126
2.109
2.093
2.076
1.197
1.186
1.181
1.168
1.159
1.152
1.140
Cl⁻
L4•HCl
0.97
0.92
0.96
0.99
1.02
2.03
0.97
5.82
2.00
12.19
f1 (ppm)

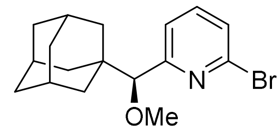

144.962
144.146
132.329
132.044
130.730
127.436
124.546
123.837
117.017
113.403
105.217
41.946
28.714
24.555
24.236
f1 (ppm)


7.48 7.46 7.46 7.44 7.38 7.38 7.36 7.36 7.30 7.30 7.28 7.28
4.40
0.84
-0.05
OTMS
N
Br
8a
0.99
0.92
0.88
1.00
9.32
8.75
f1 (ppm)

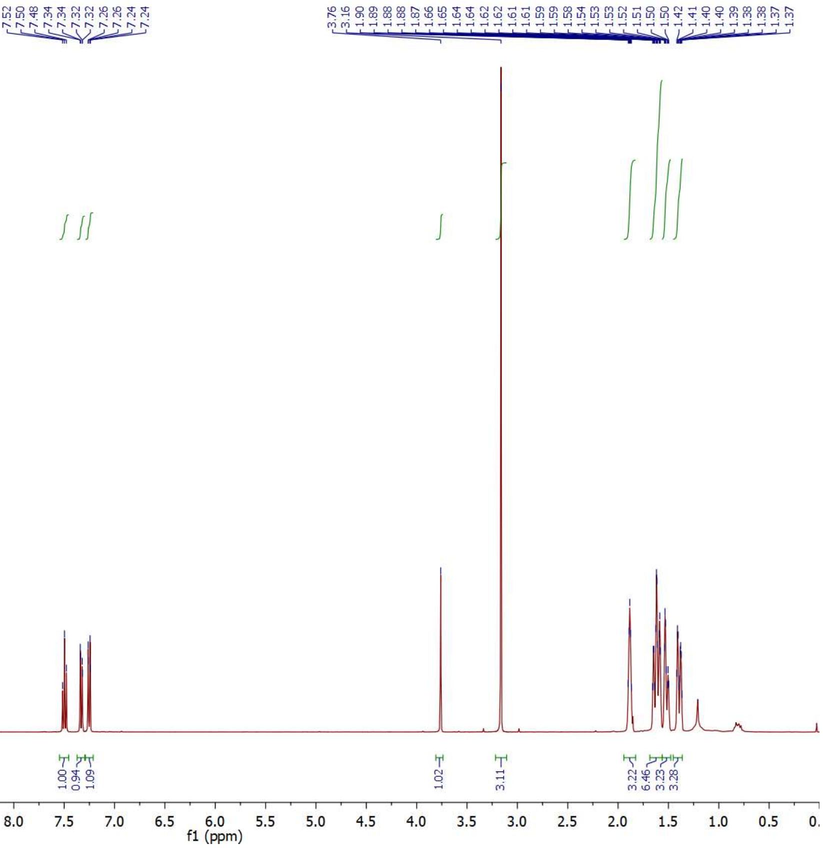

164.92
139.66
137.79
125.94
121.05
82.46
36.09
25.83
-0.10
f1 (ppm)

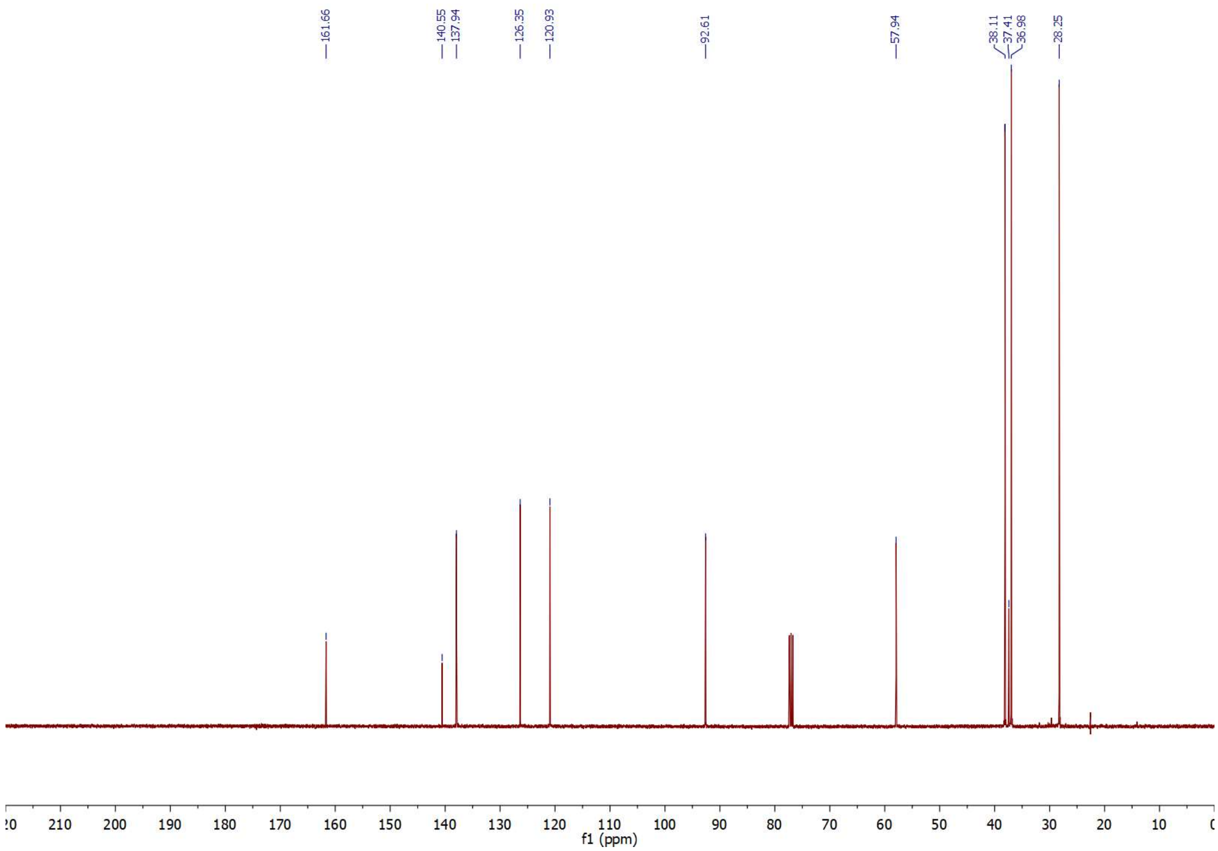

N
Br
OMe
(*R*)-**8b**
7.52
7.50
7.48
7.35
7.34
7.33
7.32
7.31
7.31
7.29
7.29
3.91
3.19
0.86
0.90
0.84
0.88
0.90
2.84
9.03
f1 (ppm)

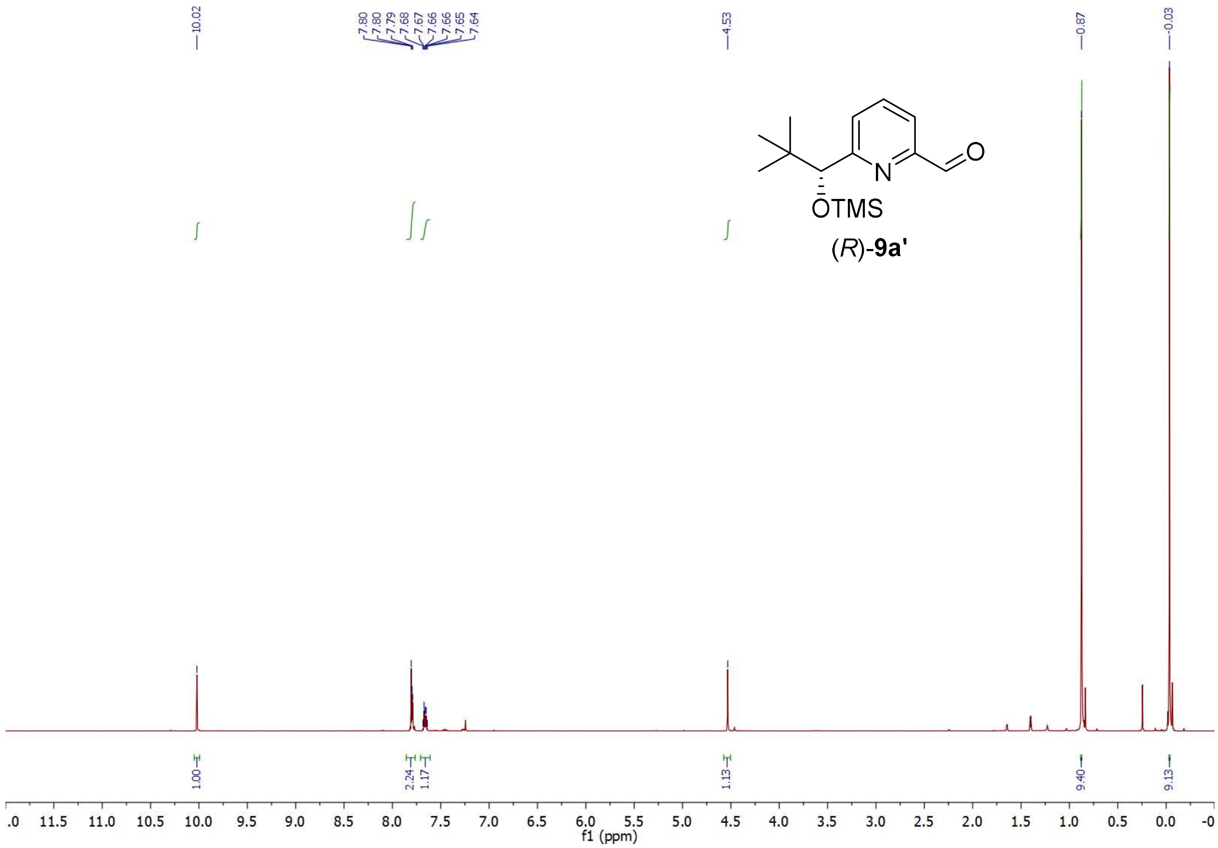

162.45
140.52
138.08
126.37
120.65
91.93
57.89
35.63
26.01
f1 (ppm)

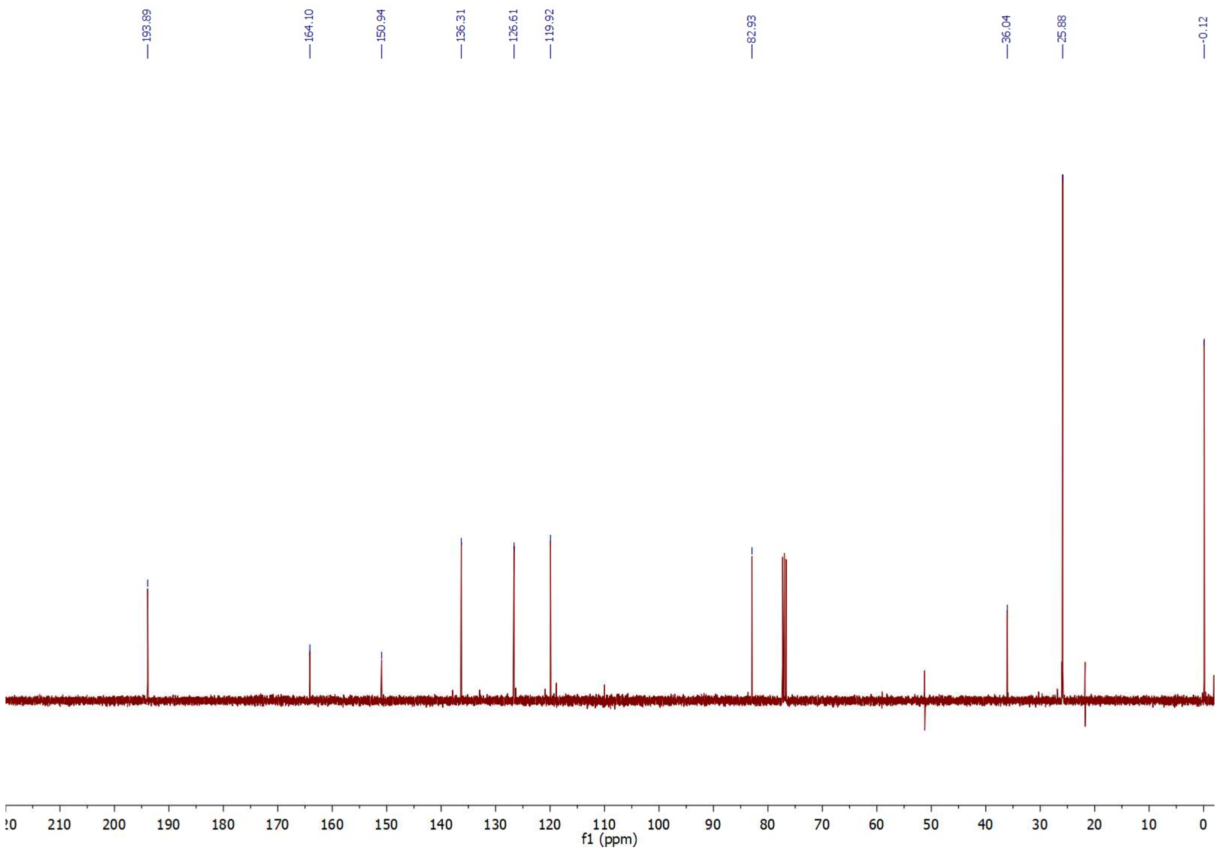


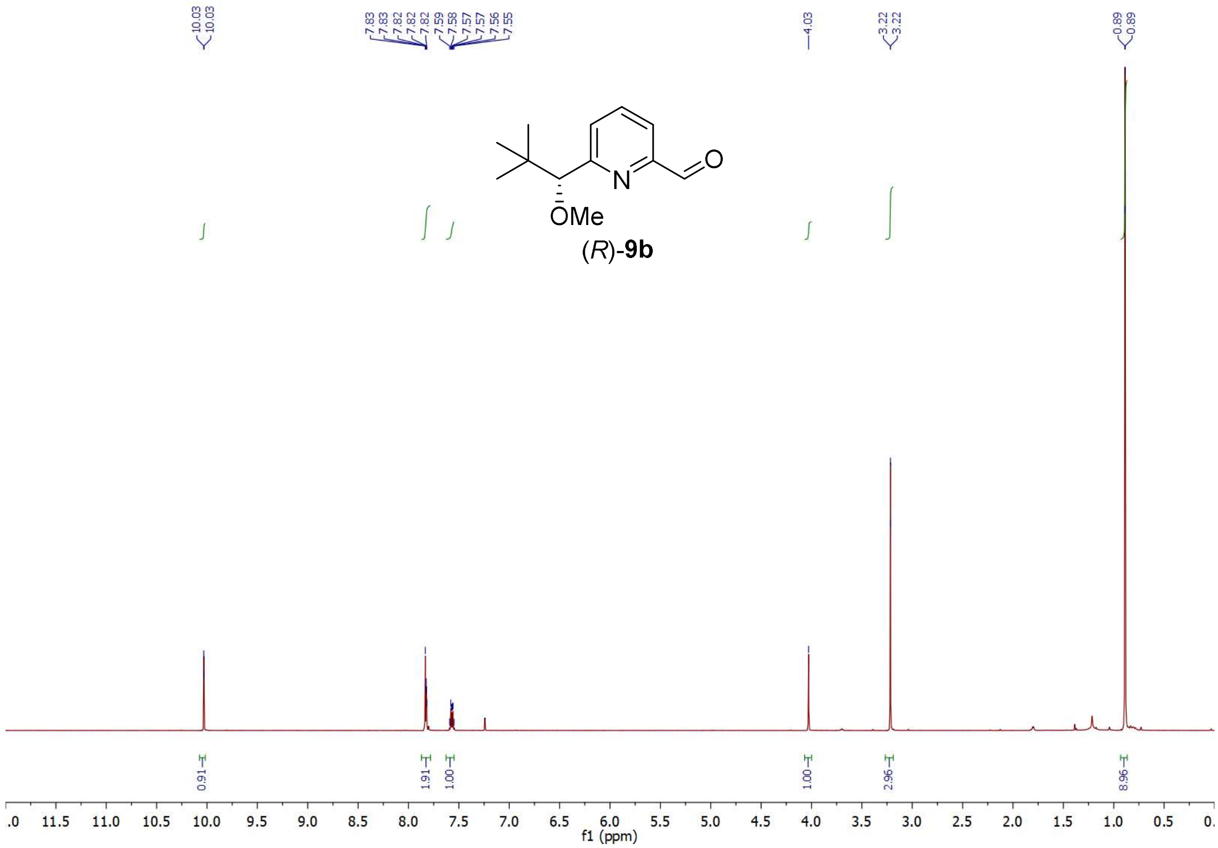
(*S*)-**8c**

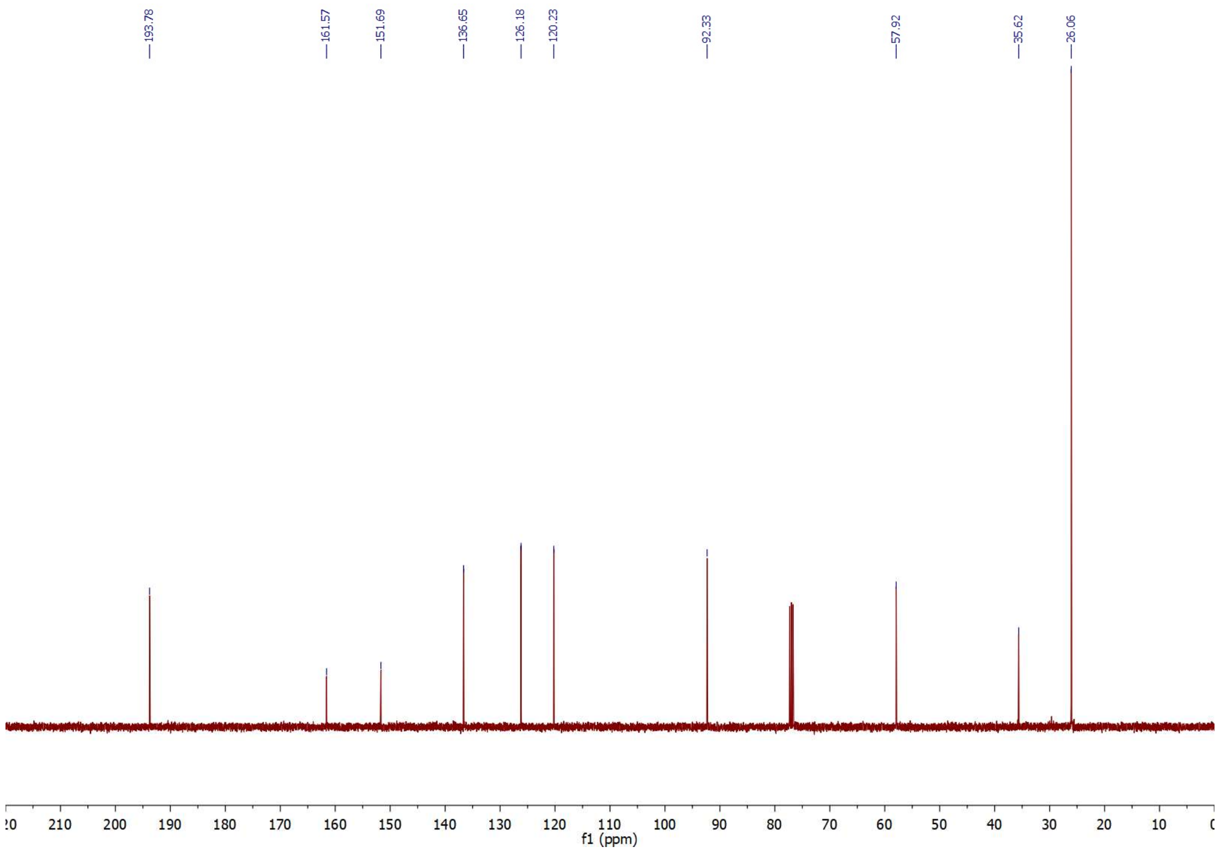


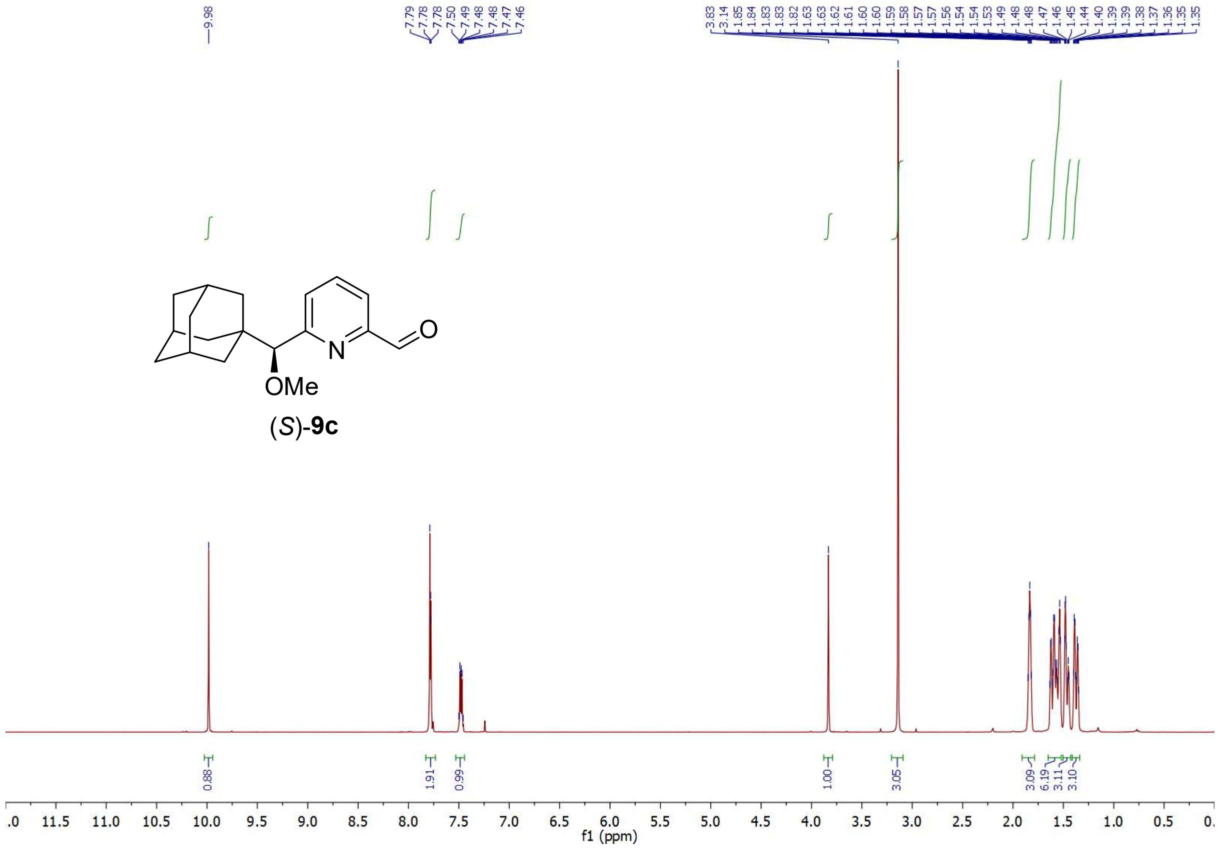


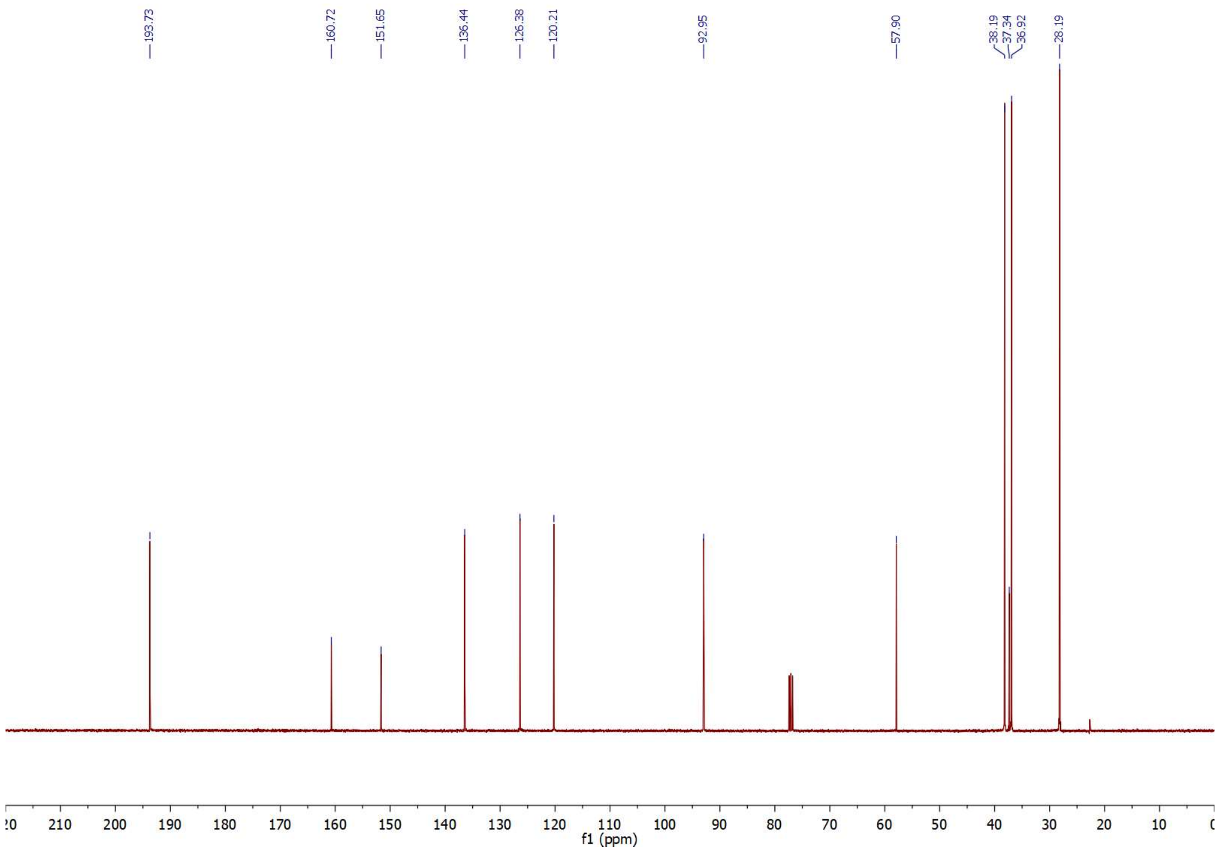

10.02
7.80
7.80
7.79
7.68
7.67
7.66
7.66
7.65
7.64
4.53
0.87
-0.03
OTMS
N
O
(R)-9a'
1.00
2.24
1.17
1.13
9.40
9.13
f1 (ppm)

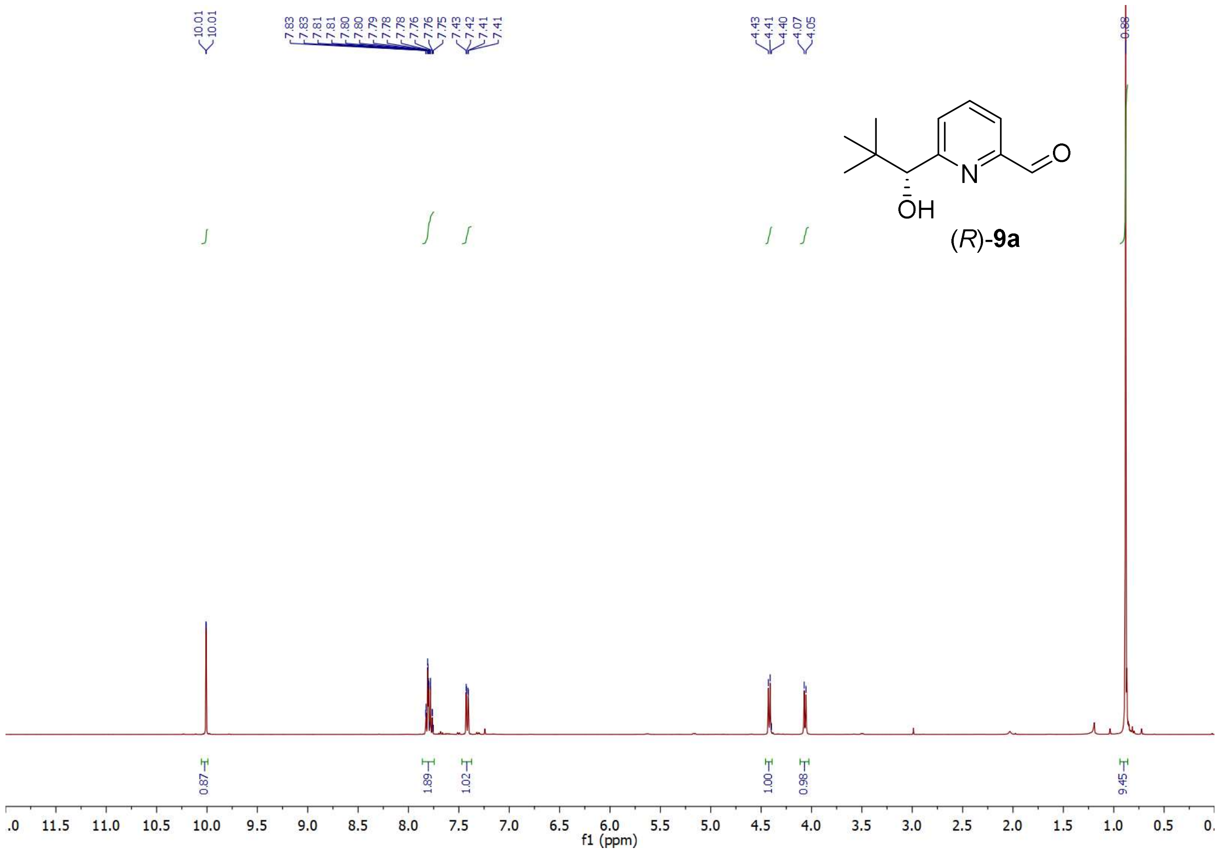

193.89
164.10
150.94
136.31
126.61
119.92
82.93
36.04
25.88
-0.12
f1 (ppm)

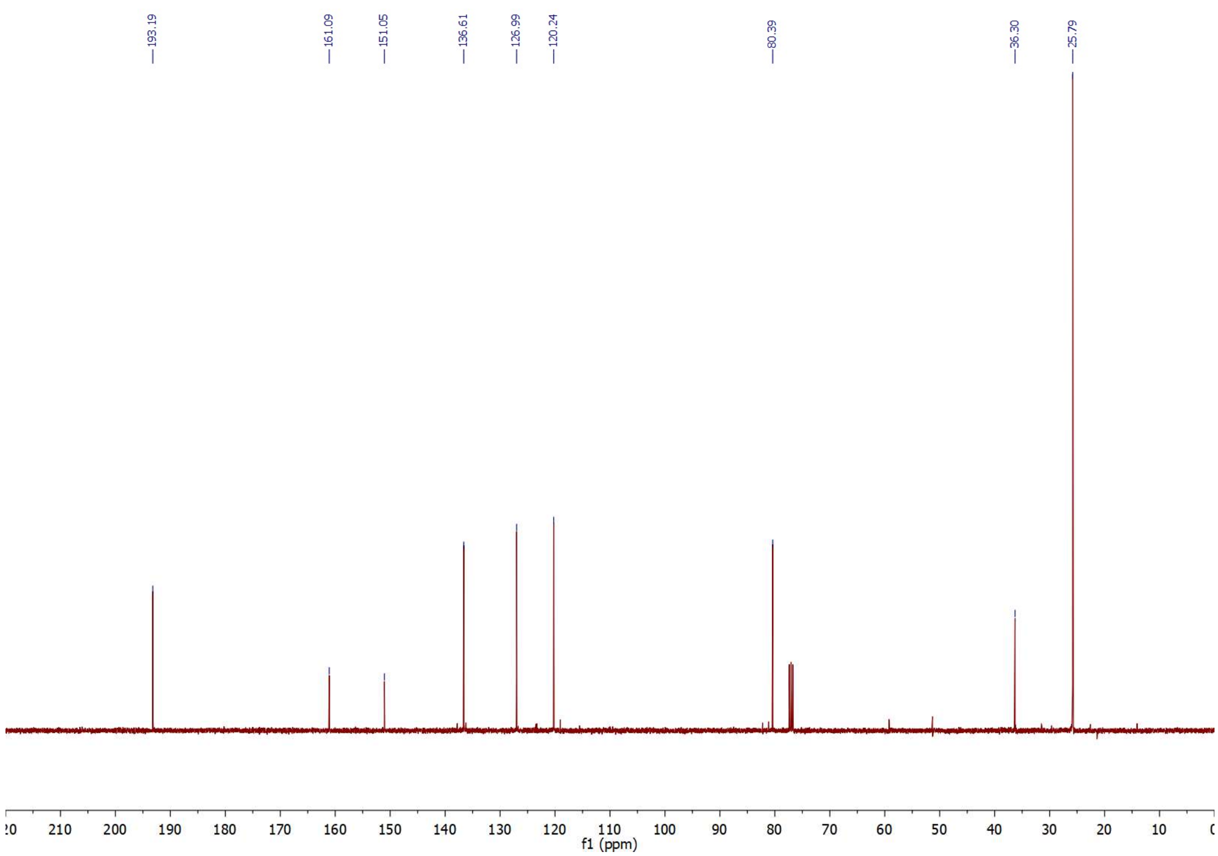

10.03
10.03
7.83
7.83
7.82
7.82
7.82
7.59
7.58
7.57
7.57
7.56
7.55
4.03
3.22
3.22
0.89
0.89
OMe
N
O
(R)-9b
0.91
1.91
1.00
1.00
2.96
8.96
f1 (ppm)

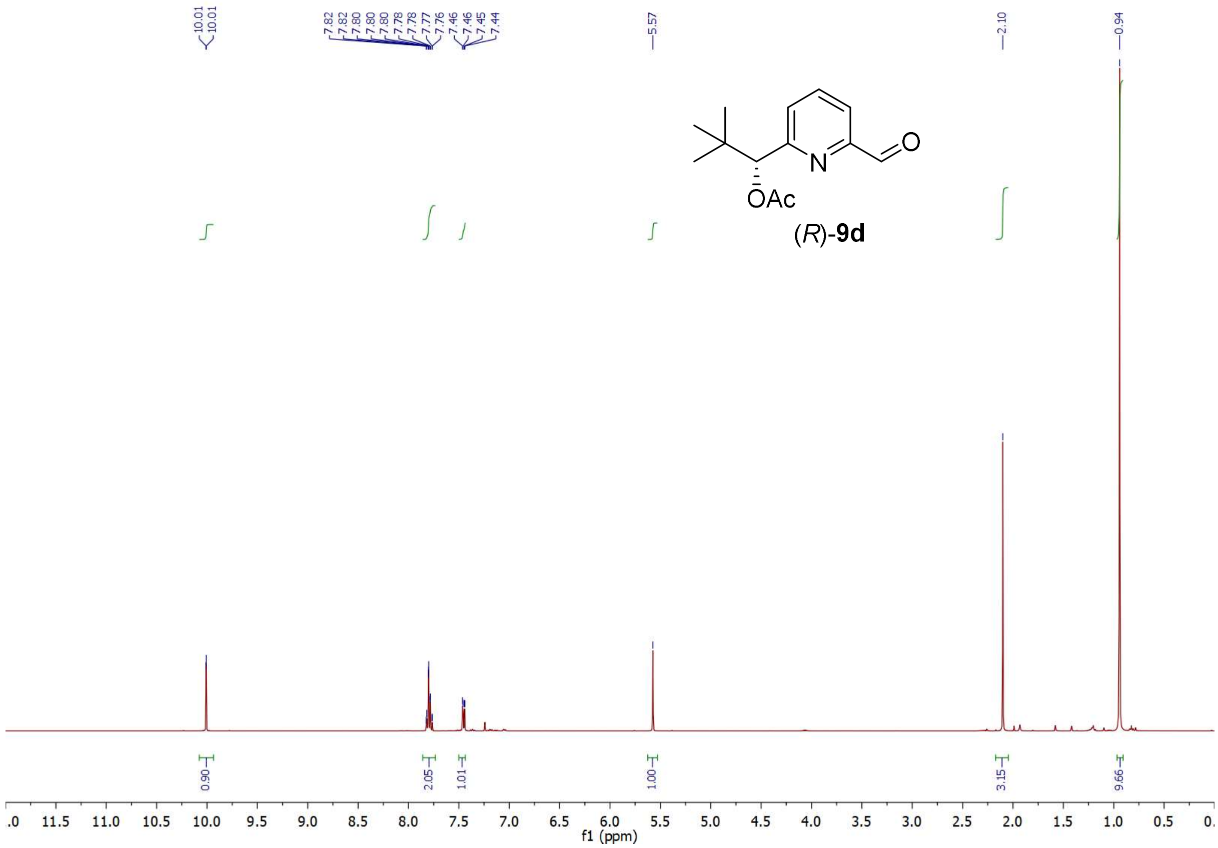

193.78
161.57
151.69
136.65
126.18
120.23
92.33
57.92
35.62
26.06
f1 (ppm)

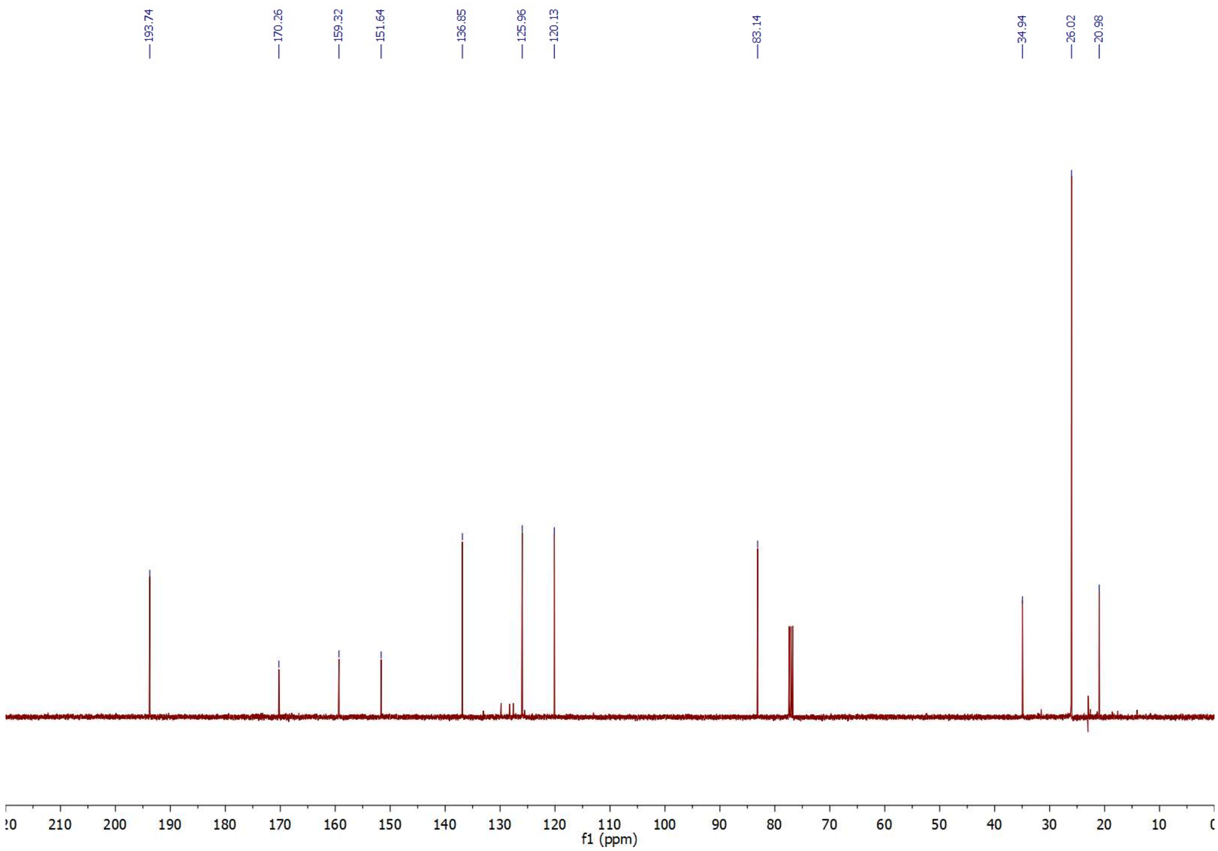

9.98
7.79 7.78 7.78 7.50 7.49 7.48 7.48 7.47 7.46
3.83 3.14 1.85 1.84 1.83 1.83 1.82 1.63 1.63 1.62 1.61 1.60 1.60 1.59 1.58 1.57 1.57 1.56 1.56 1.54 1.54 1.53 1.49 1.48 1.48 1.47 1.46 1.45 1.44 1.40 1.39 1.39 1.38 1.37 1.36 1.35 1.35
N
O
OMe
(S)-9c
0.88
1.91
0.99
1.00
3.05
3.09
6.19
3.11
3.10
f1 (ppm)

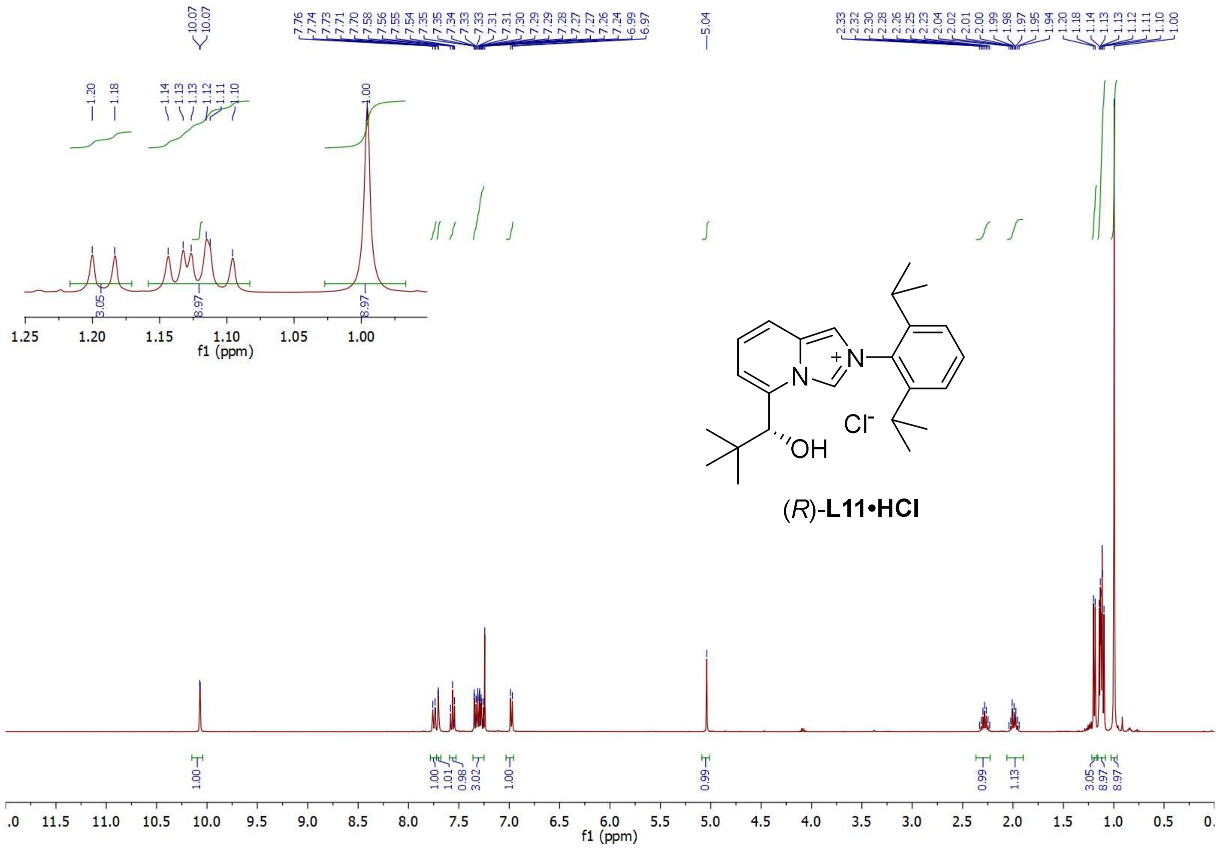

193.73
160.72
151.65
136.44
126.38
120.21
92.95
57.90
38.19
37.34
36.92
28.19
f1 (ppm)

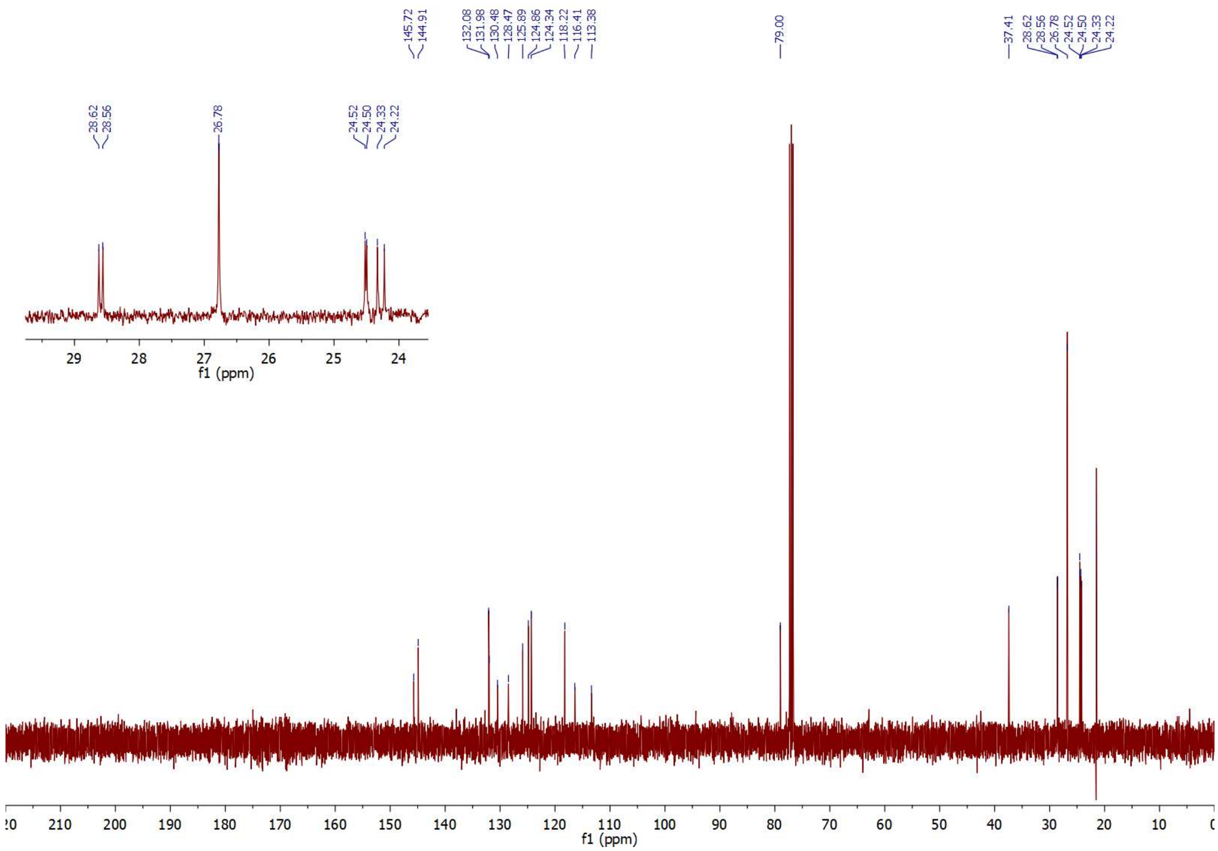

10.01
10.01
7.83
7.83
7.81
7.80
7.80
7.79
7.78
7.76
7.76
7.75
7.43
7.42
7.41
7.41
4.43
4.41
4.40
4.07
4.05
0.88
N
OH
O
(R)-9a
0.87
1.89
1.02
1.00
0.98
9.45
f1 (ppm)

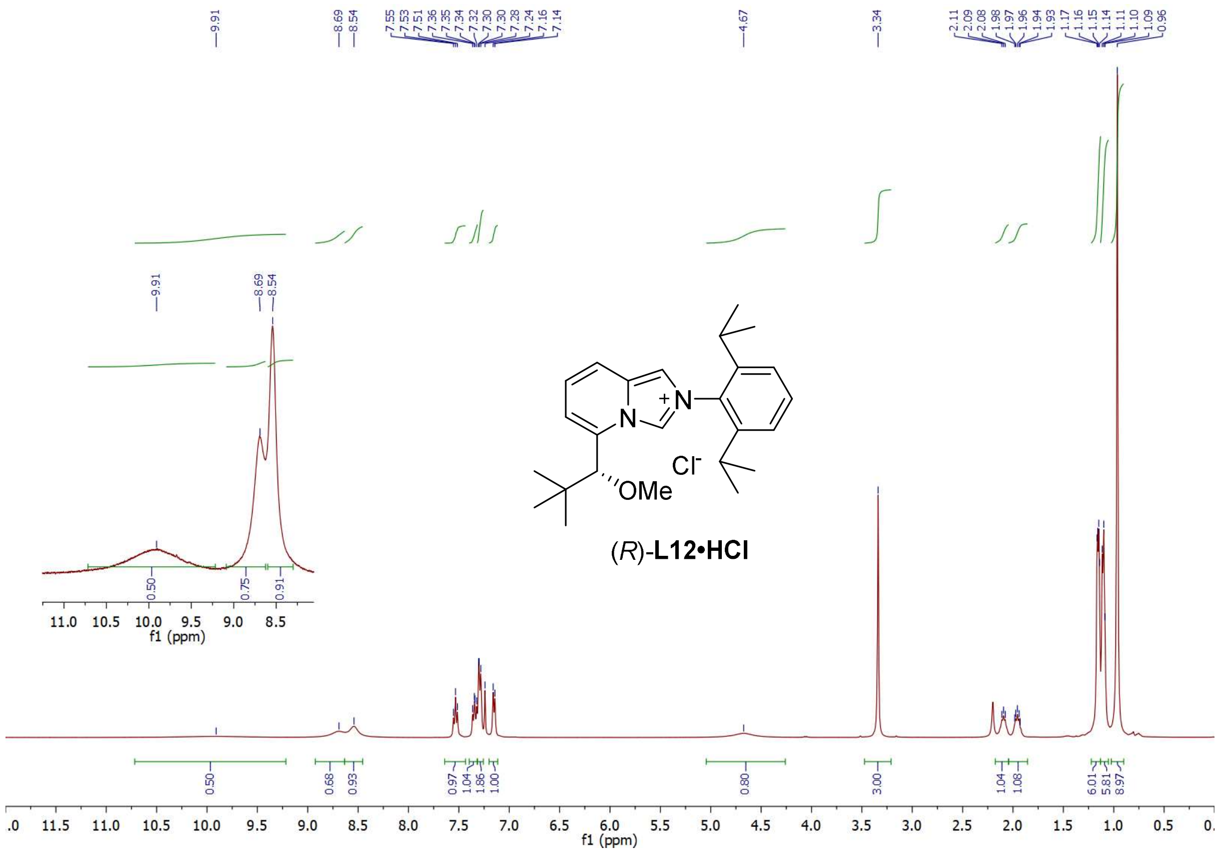

193.19
161.09
151.05
136.61
126.99
120.24
80.39
36.30
25.79
f1 (ppm)

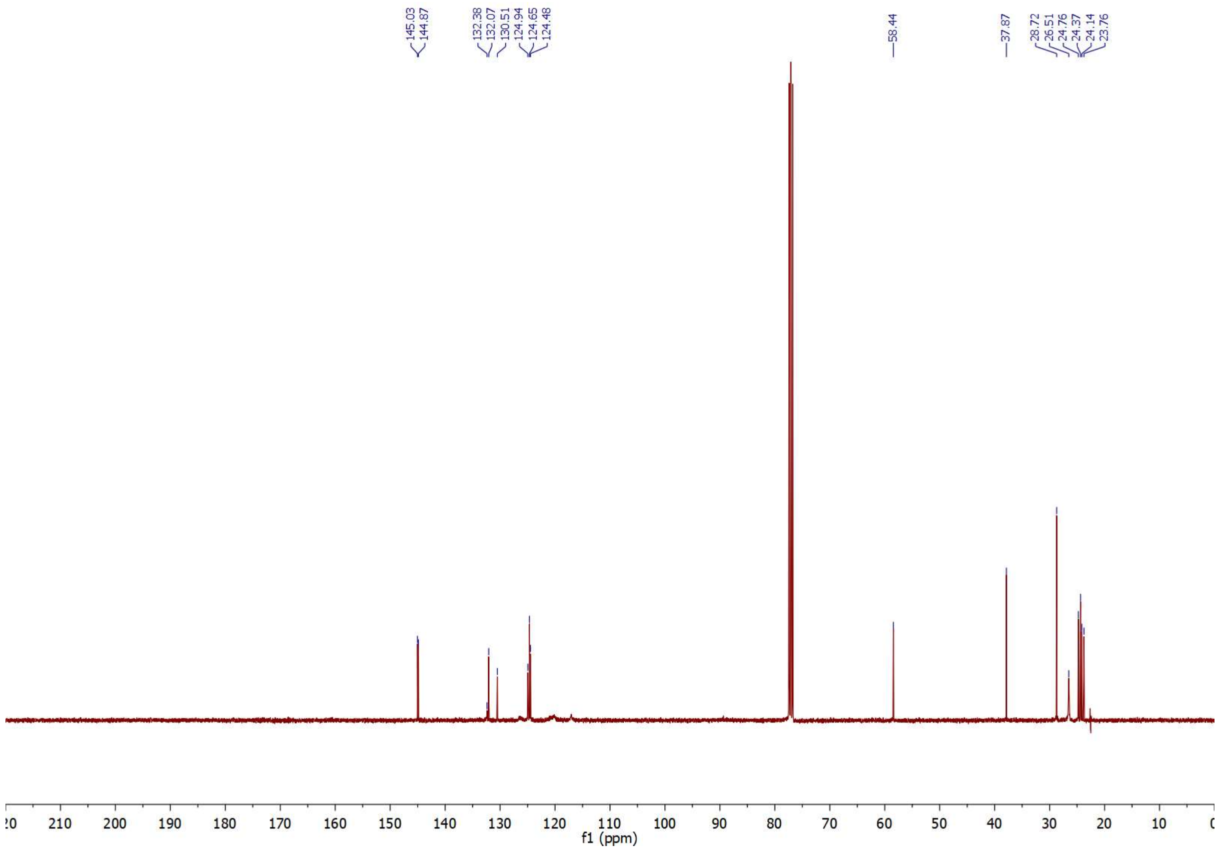

10.01
10.01
7.82
7.82
7.80
7.80
7.80
7.78
7.78
7.77
7.76
7.46
7.46
7.45
7.44
5.57
2.10
0.94
N
O
OAc
(R)-9d
0.90
2.05
1.01
1.00
3.15
9.66
f1 (ppm)

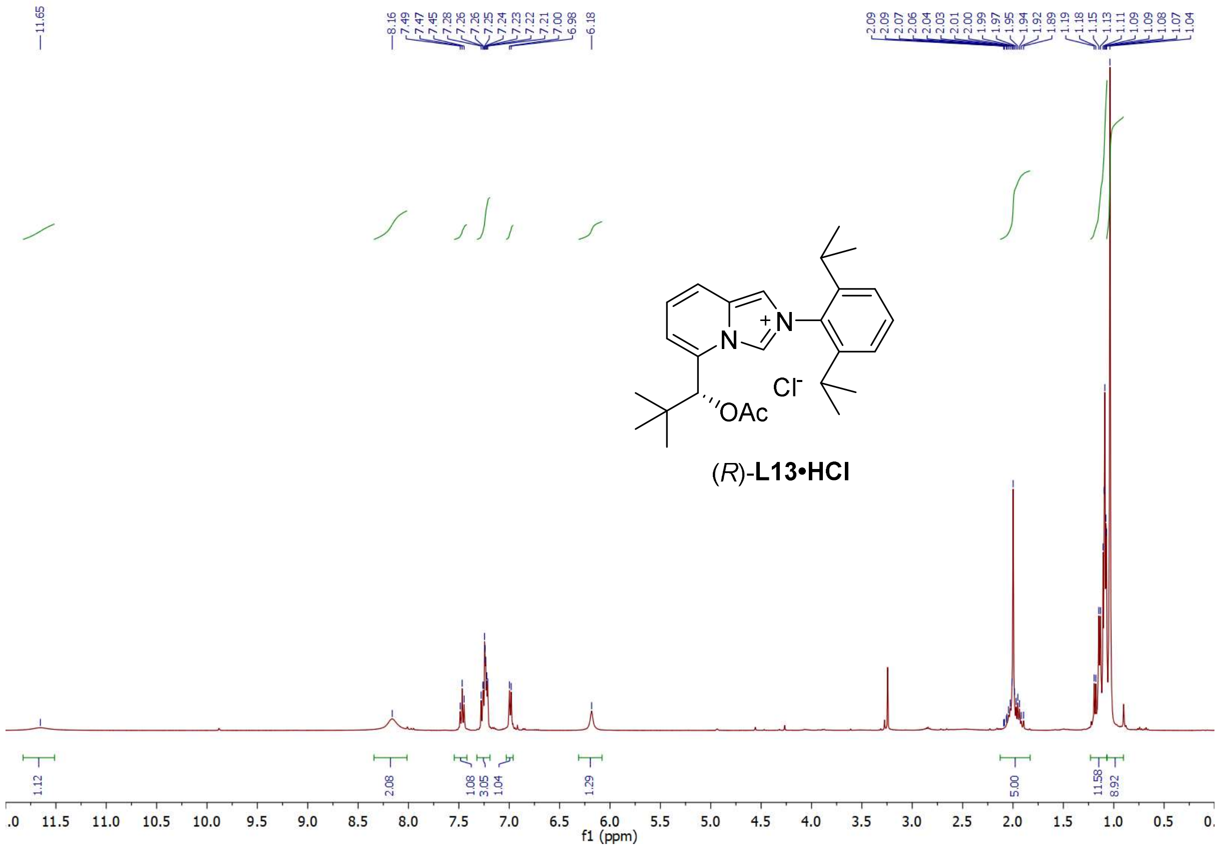

193.74
170.26
159.32
151.64
136.85
125.96
120.13
83.14
34.94
26.02
20.98
f1 (ppm)


(R)-L11•HCl
Cl⁻
f1 (ppm)

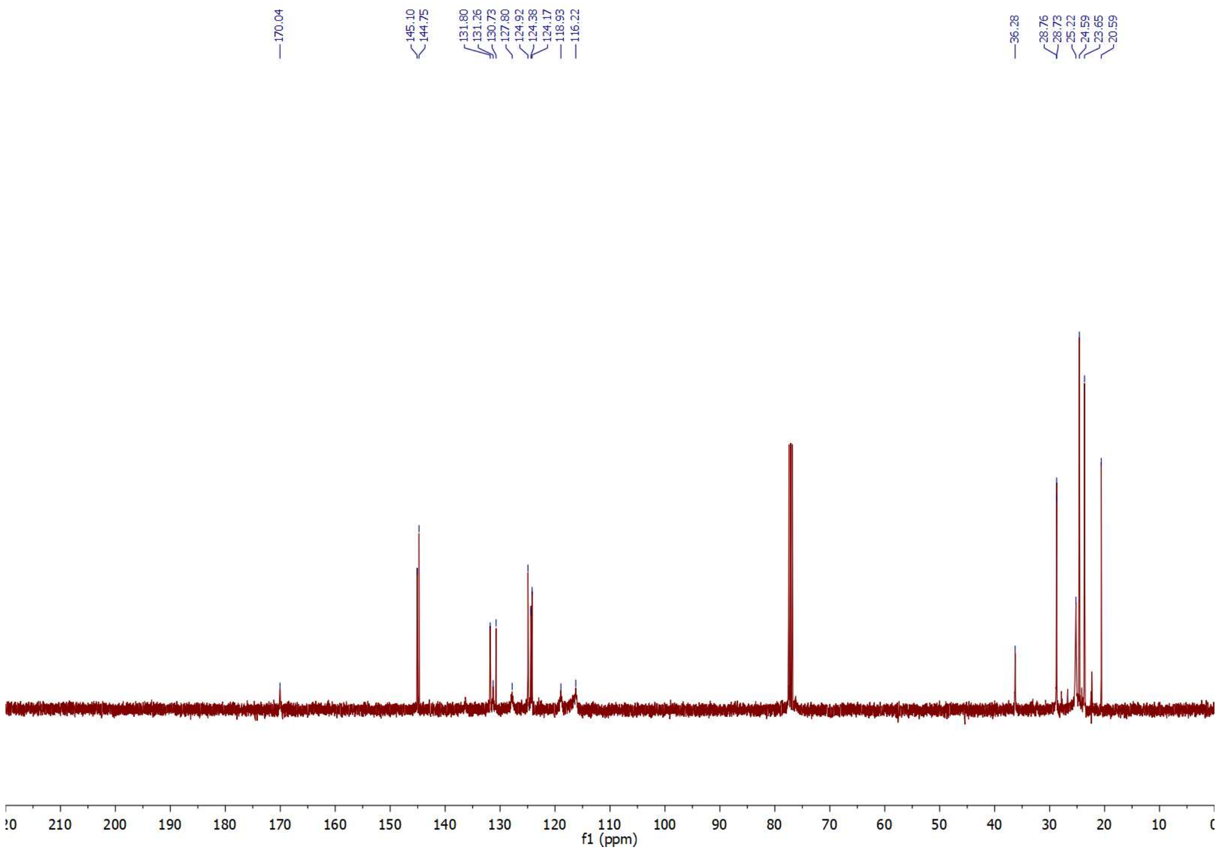

f1 (ppm)


9.91
8.69
8.54
7.55
7.53
7.51
7.36
7.35
7.34
7.32
7.30
7.30
7.28
7.24
7.16
7.14
4.67
3.34
2.11
2.09
2.08
1.98
1.97
1.96
1.94
1.93
1.17
1.16
1.15
1.14
1.11
1.10
1.09
0.96
N
N
+
Cl-
OMe
(R)-L12•HCl
0.50
0.75
0.91
f1 (ppm)
0.50
0.68
0.93
0.97
1.04
1.86
1.00
0.80
3.00
1.04
1.08
6.01
5.81
8.97
f1 (ppm)

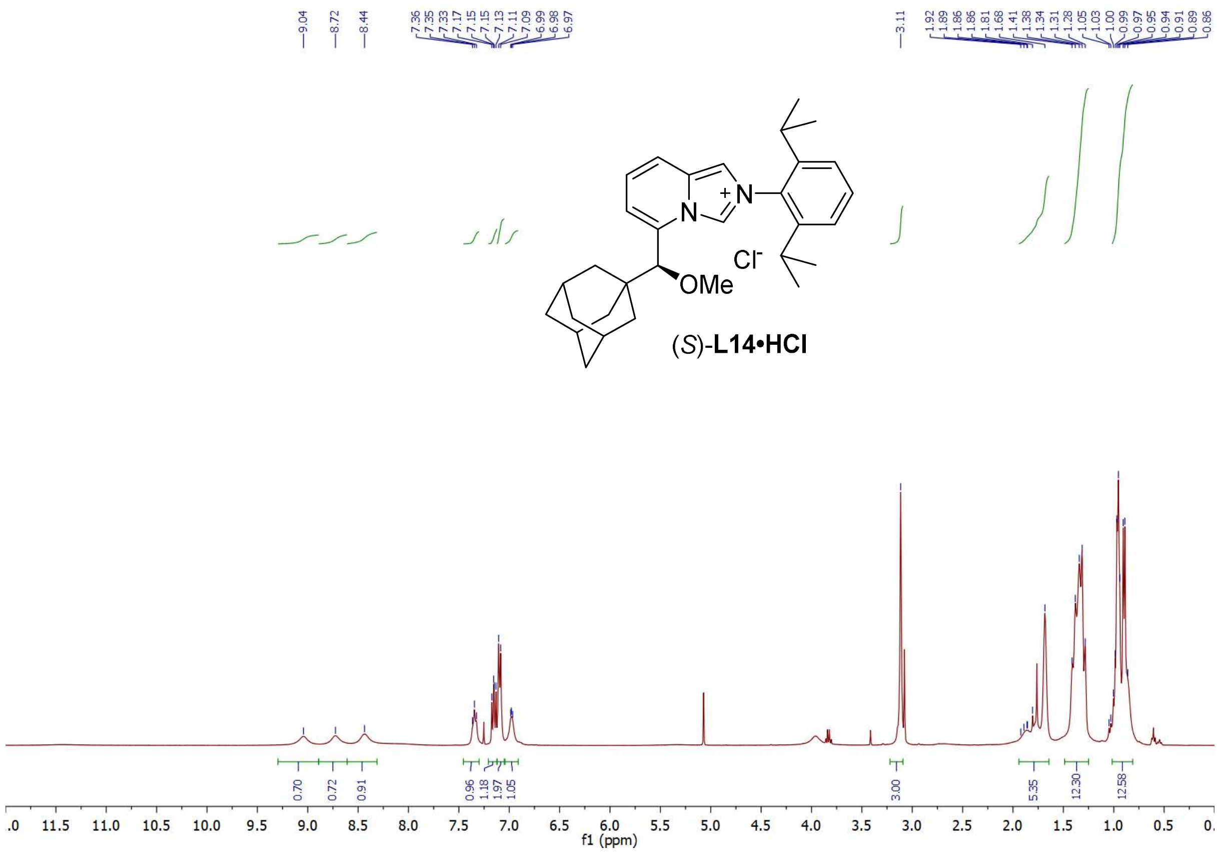

145.03
144.87
132.38
132.07
130.51
124.94
124.65
124.48
58.44
37.87
28.72
26.51
24.76
24.37
24.14
23.76
f1 (ppm)

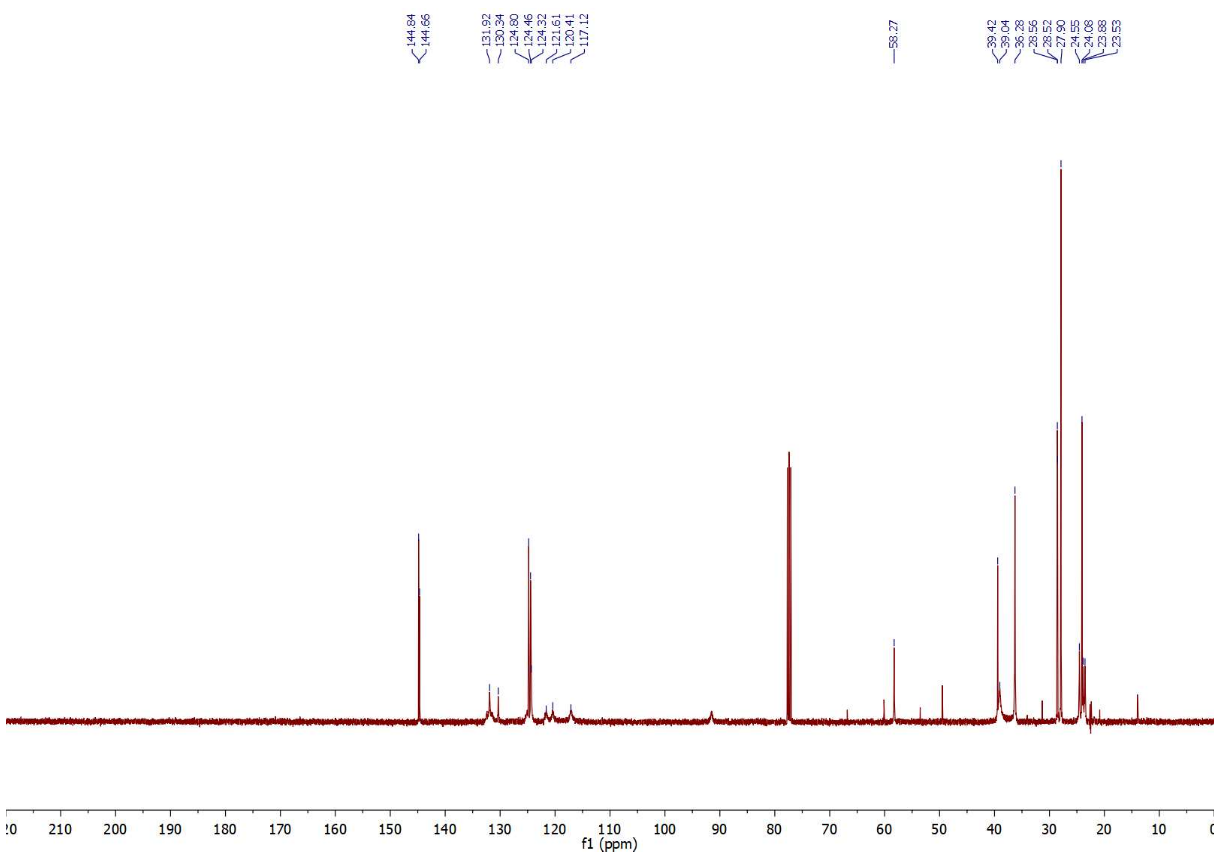


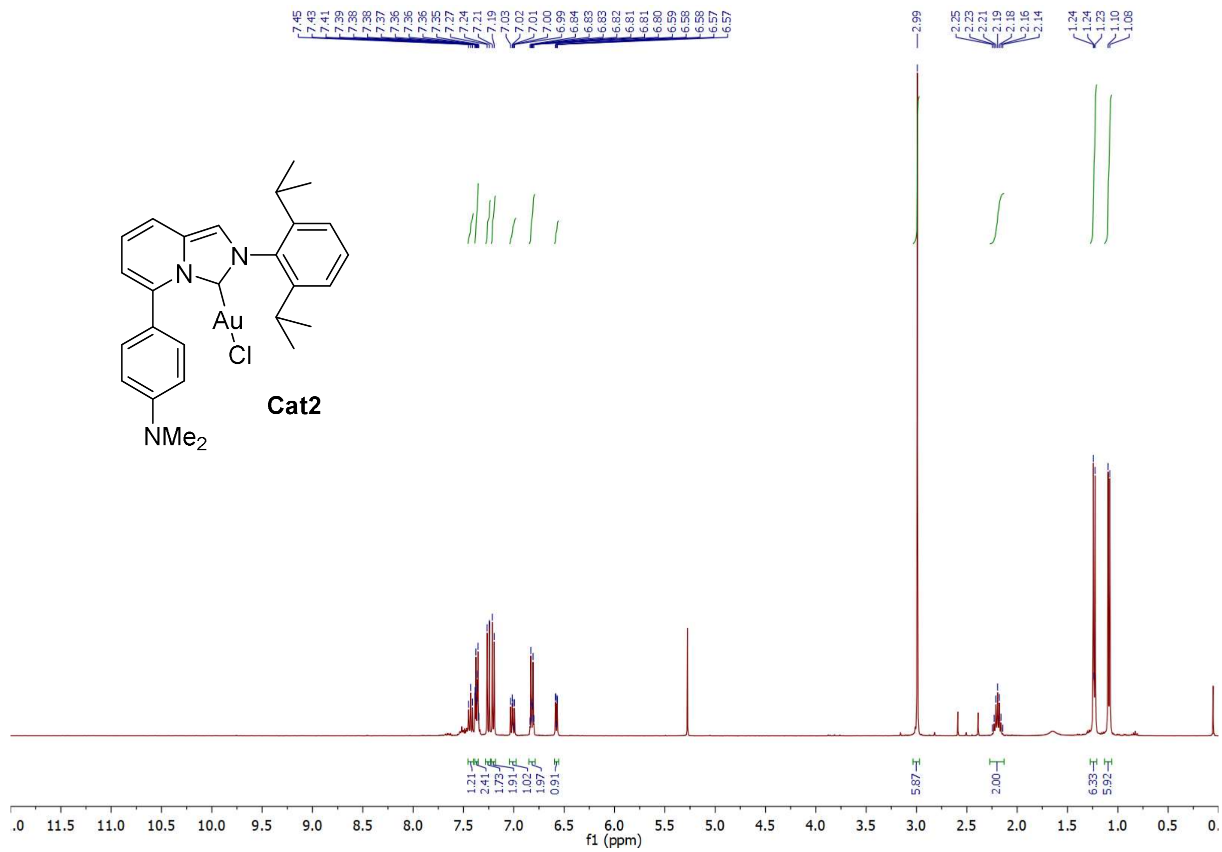
Cl⁻
OAc
(*R*)-**L13•HCl**
f1 (ppm)

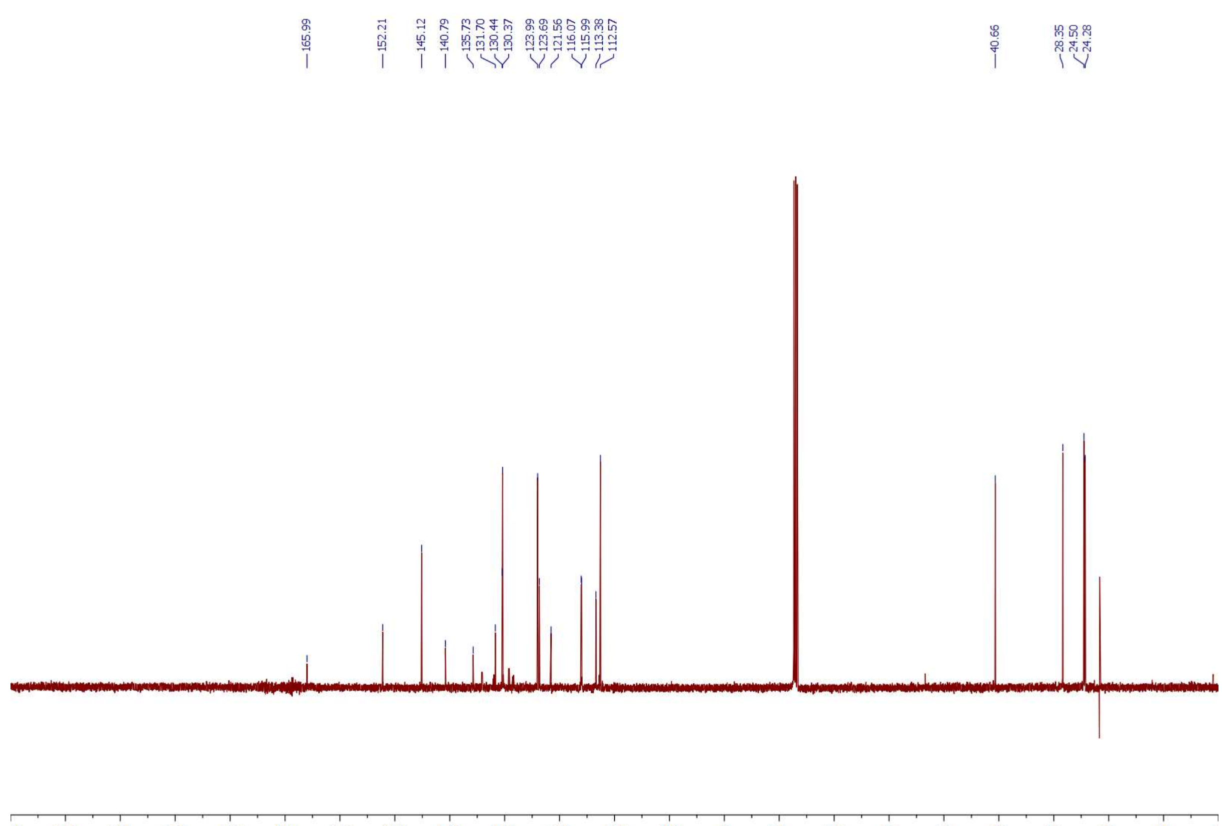


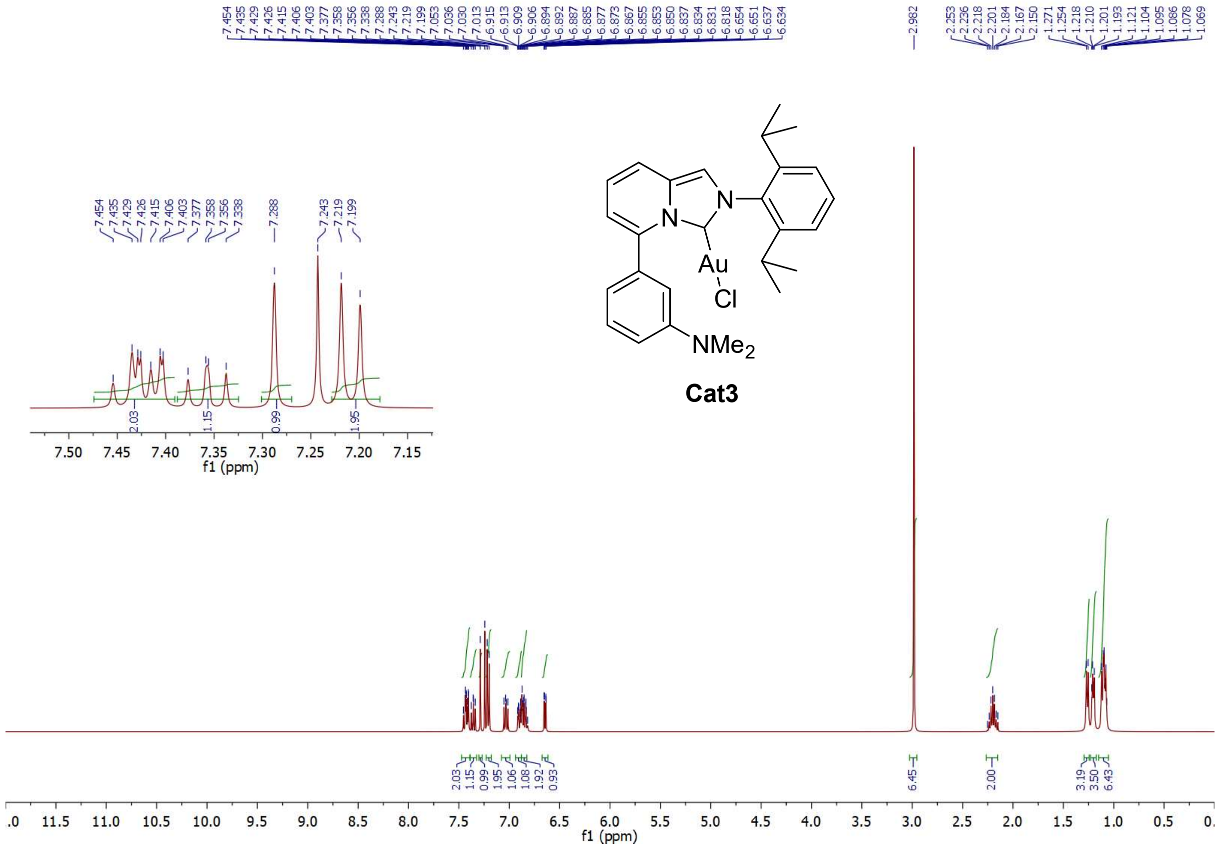
f1 (ppm)


9.04 8.72 8.44 7.36 7.35 7.33 7.17 7.15 7.15 7.13 7.11 7.09 6.99 6.98 6.97
3.11 1.92 1.89 1.86 1.86 1.81 1.68 1.41 1.38 1.34 1.31 1.28 1.05 1.03 1.00 0.99 0.97 0.95 0.94 0.91 0.89 0.86
N
+N
Cl-
OMe
(S)-L14•HCl
0.70 0.72 0.91 0.96 1.18 1.97 1.05 3.00 5.35 12.30 12.58
f1 (ppm)


144.84 144.66 131.92 130.34 124.80 124.46 124.32 121.61 120.41 117.12 58.27 39.42 39.04 36.28 28.56 28.52 27.90 24.55 24.08 23.88 23.53
f1 (ppm)


Cat2




7.454
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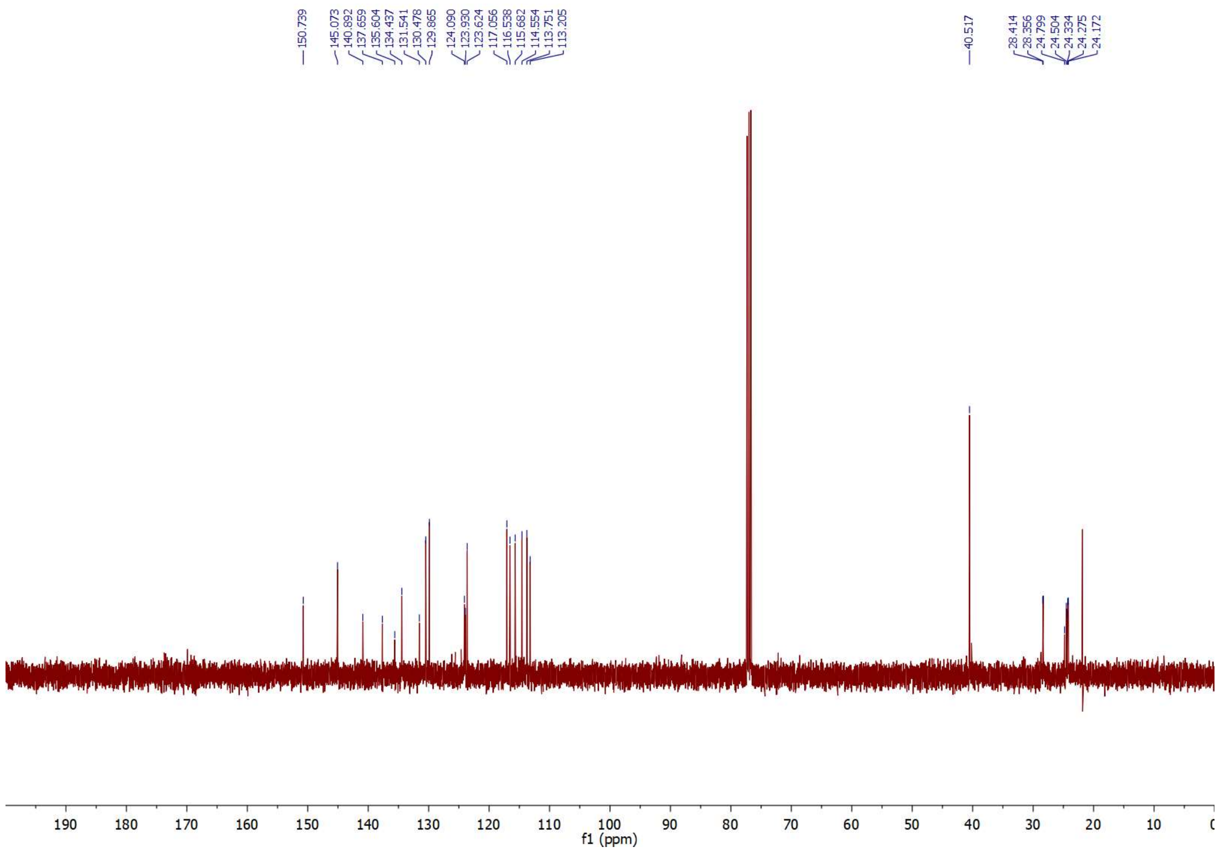
7.426
7.415
7.406
7.403
7.377
7.358
7.356
7.338
7.288
7.243
7.219
7.199
7.053
7.036
7.030
7.013
6.915
6.913
6.909
6.906
6.894
6.892
6.887
6.885
6.877
6.873
6.867
6.855
6.853
6.850
6.837
6.834
6.831
6.818
6.654
6.651
6.637
6.634
2.982
2.253
2.236
2.218
2.201
2.184
2.167
2.150
1.271
1.254
1.218
1.210
1.201
1.193
1.121
1.104
1.095
1.086
1.078
1.069
2.03
1.15
0.99
1.95
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
2.03
1.15
0.99
1.95
1.06
1.08
1.92
0.93
6.45
2.00
3.19
3.50
6.43
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
N
N
Au
Cl
NMe2

Cat3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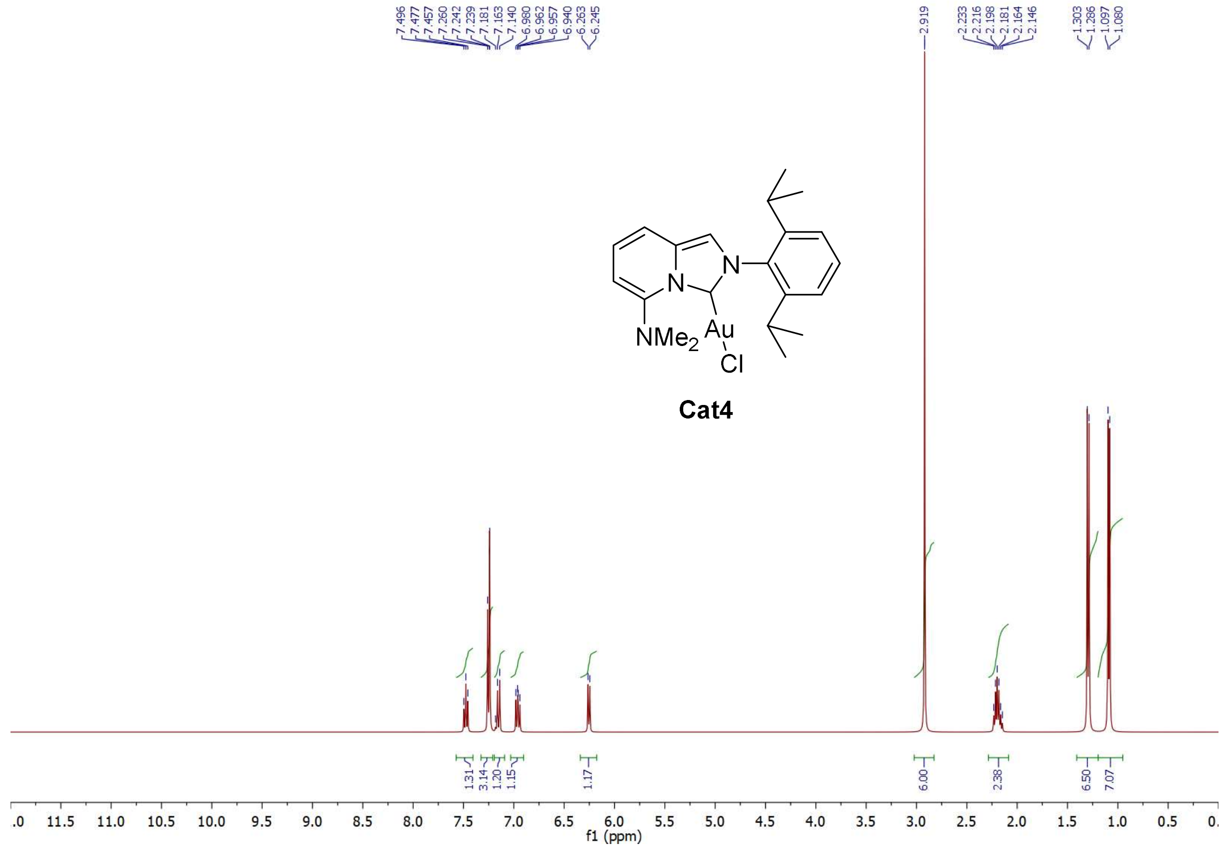
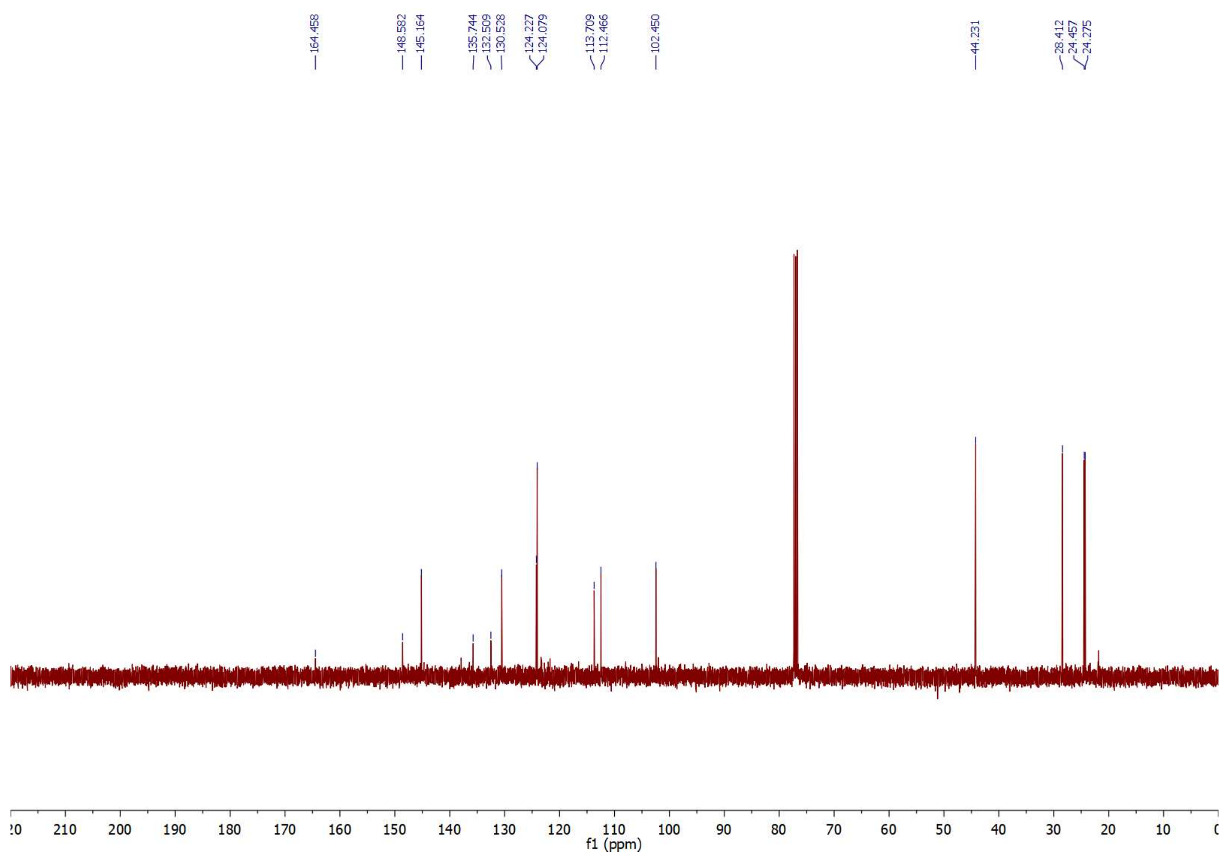
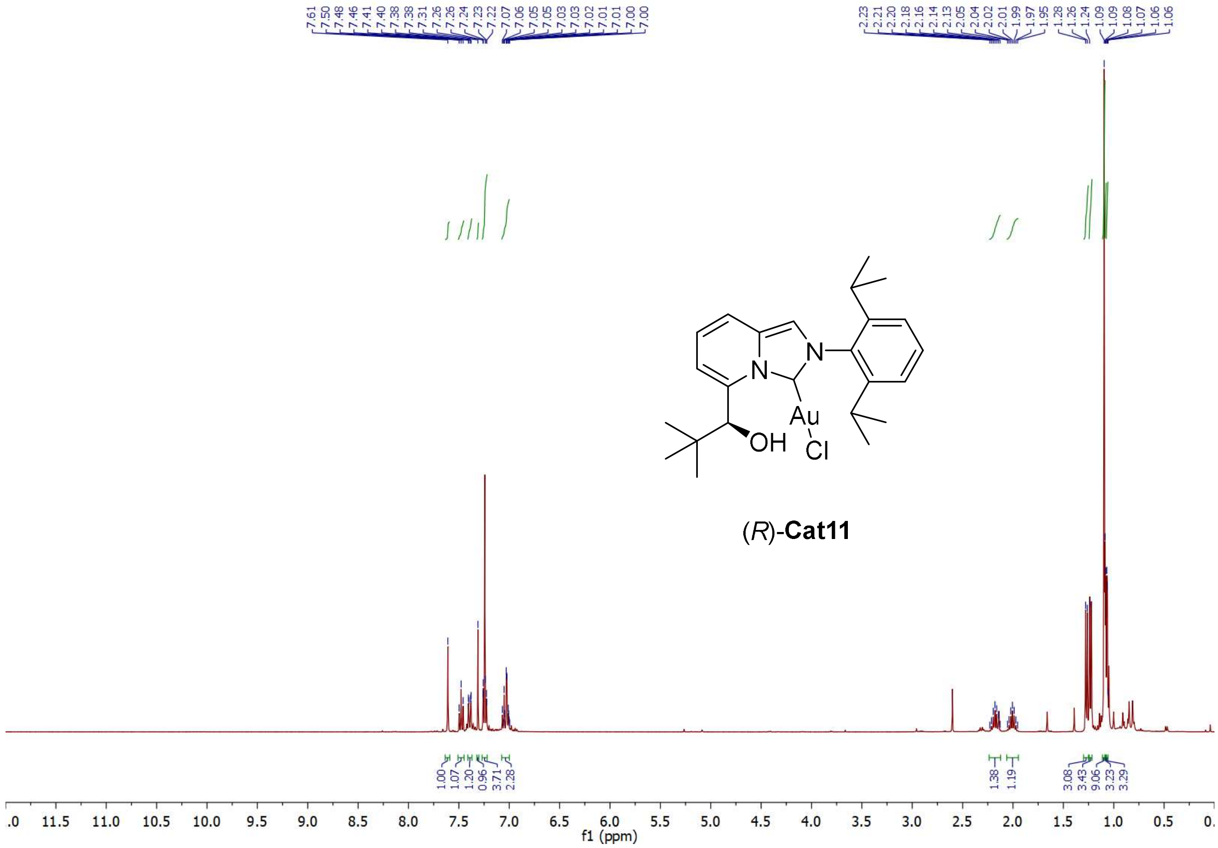
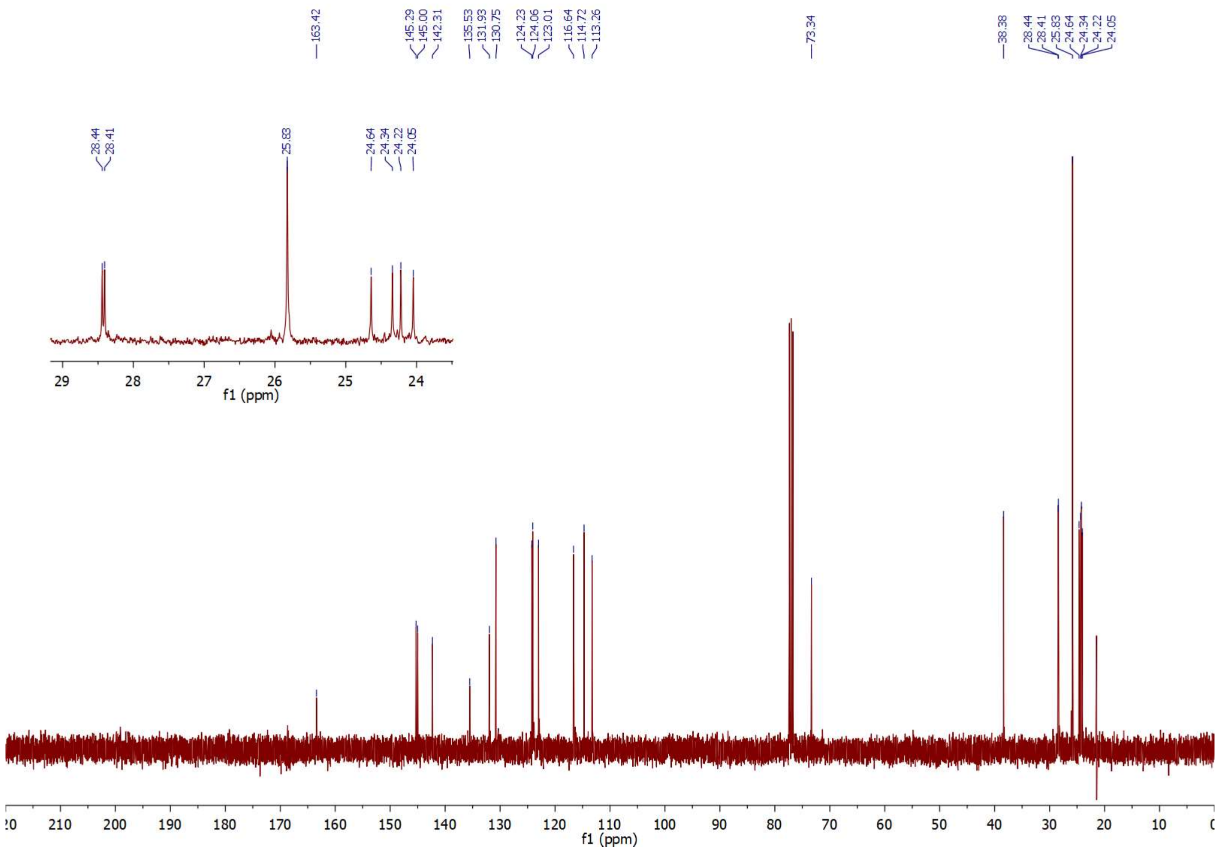
140.892
137.659
135.604
134.437
131.541
130.478
129.865
124.090
123.930
123.624
117.056
116.538
115.682
114.554
113.751
113.205
40.517
28.414
28.356
24.799
24.504
24.334
24.275
24.172
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

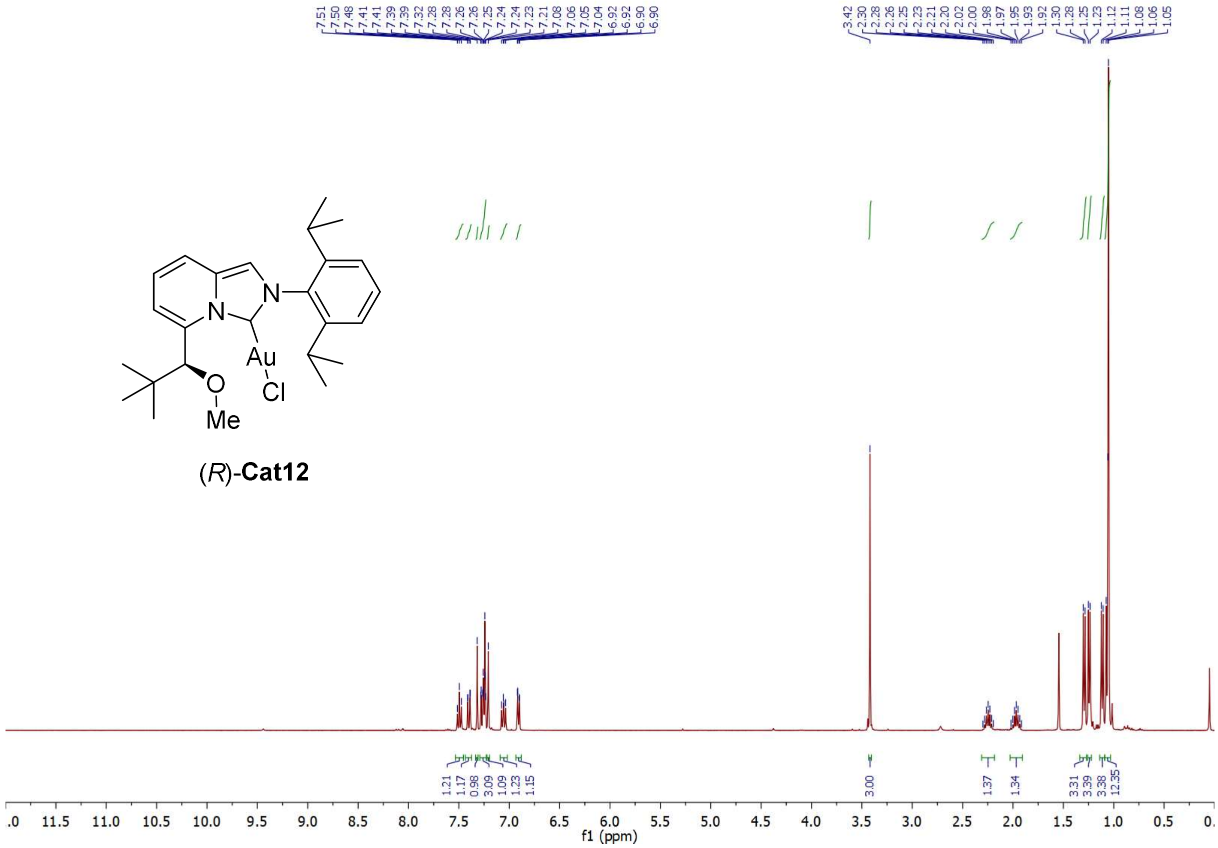

7.496 7.477 7.457 7.260 7.242 7.239 7.181 7.163 7.140 6.980 6.962 6.957 6.940 6.263 6.245
2.919
2.233 2.216 2.198 2.181 2.164 2.146
1.303 1.286 1.097 1.080
N
N
NMe2
Au
Cl
Cat4
1.31 3.14 1.20 1.15 1.17 6.00 2.38 6.50 7.07
f1 (ppm)


164.458
148.582 145.164
135.744 132.509 130.528
124.227 124.079
113.709 112.466
102.450
44.231
28.412 24.457 24.275
f1 (ppm)



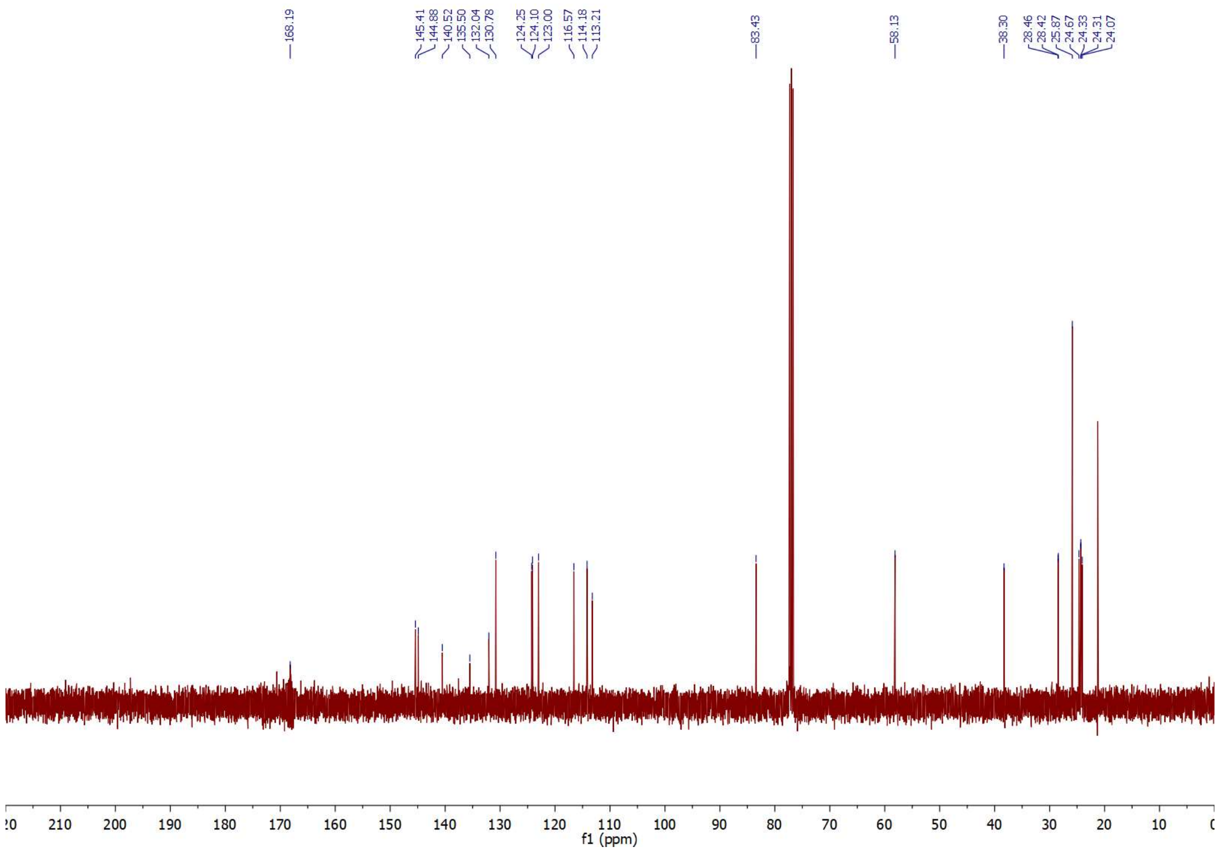
(*R*)-**Cat11**



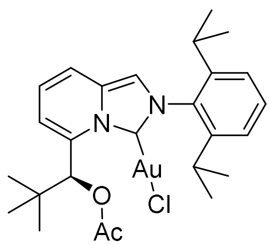


Au
Cl
N
N
O
Me
7.51 7.50 7.48 7.41 7.39 7.39 7.32 7.28 7.28 7.26 7.26 7.25 7.24 7.24 7.23 7.21 7.08 7.06 7.05 7.04 6.92 6.92 6.90 6.90
3.42 2.30 2.28 2.26 2.25 2.23 2.21 2.20 2.02 2.00 1.98 1.97 1.95 1.93 1.92 1.30 1.28 1.25 1.23 1.12 1.11 1.08 1.06 1.05
1.21 1.17 0.98 3.09 1.09 1.23 1.15
3.00
1.37 1.34
3.31 3.39 3.38 12.35
f1 (ppm)

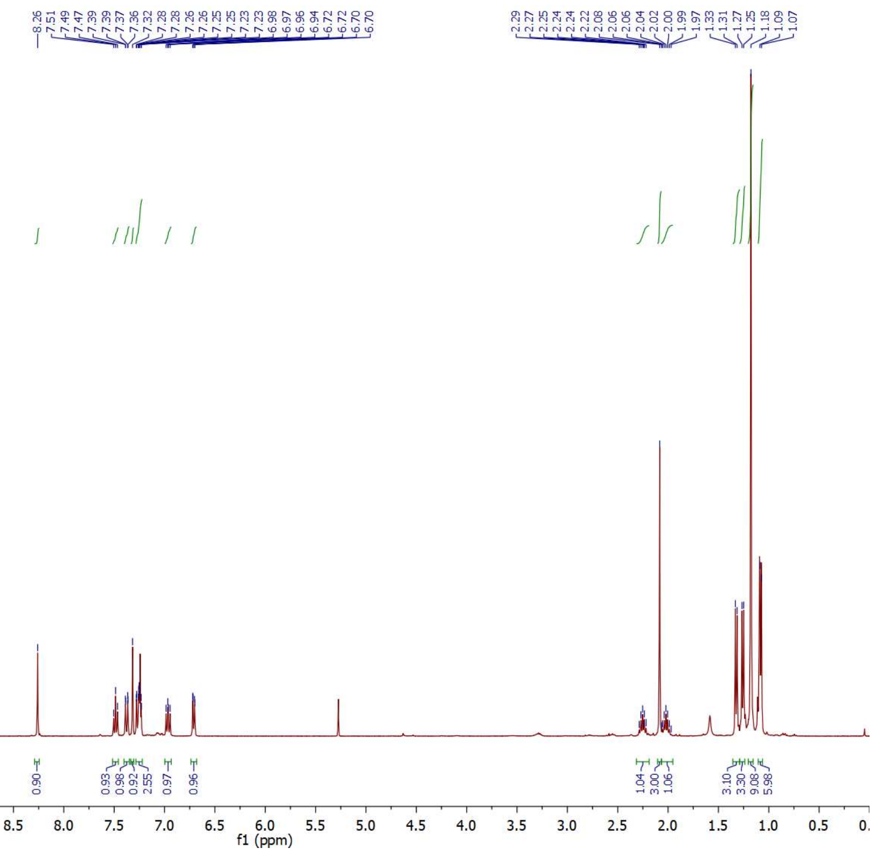
(*R*)-**Cat12**

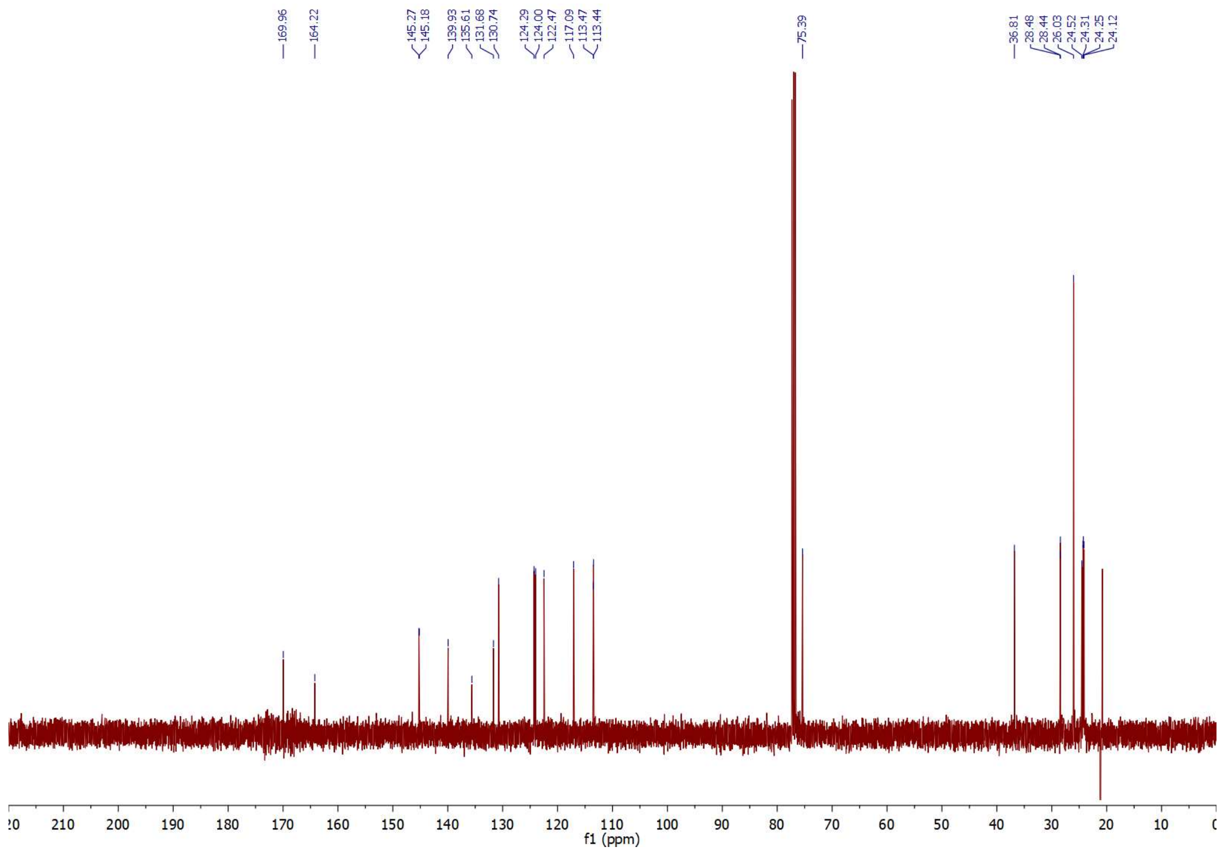


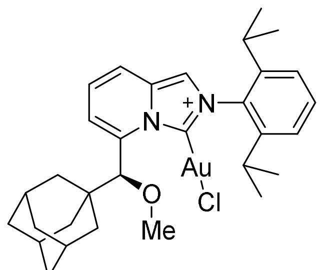
168.19
145.41 144.88 140.52 135.50 132.04 130.78
124.25 124.10 123.00 116.57 114.18 113.21
83.43
58.13
38.30
28.46 28.42 25.87 24.67 24.33 24.31 24.07
f1 (ppm)


N
N
Au
Cl
O
Ac

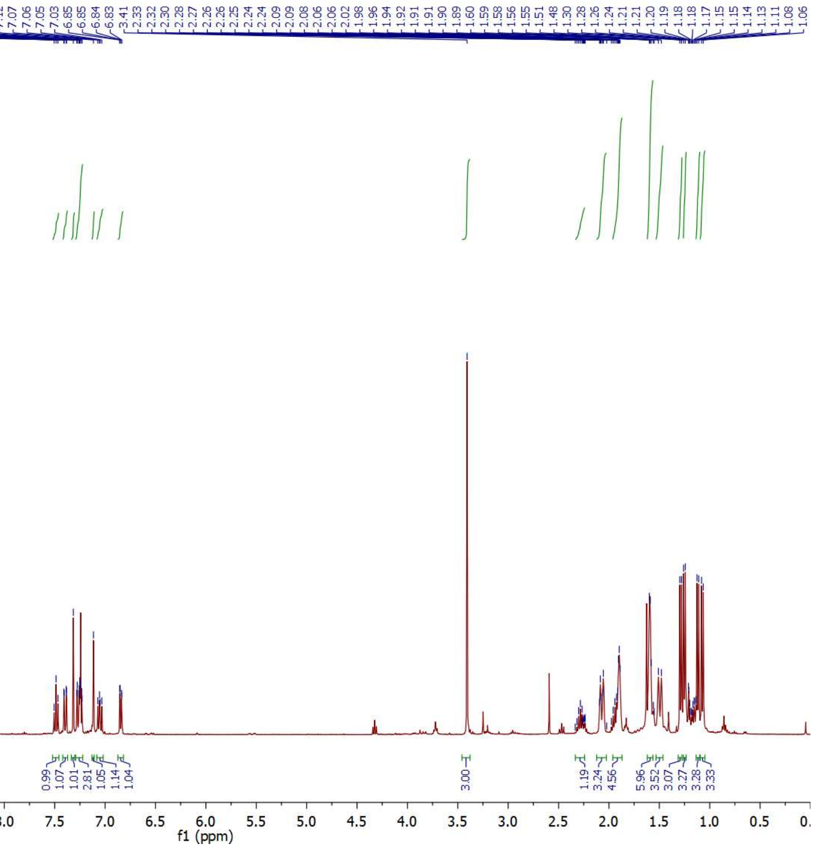
(*R*)-**Cat13**

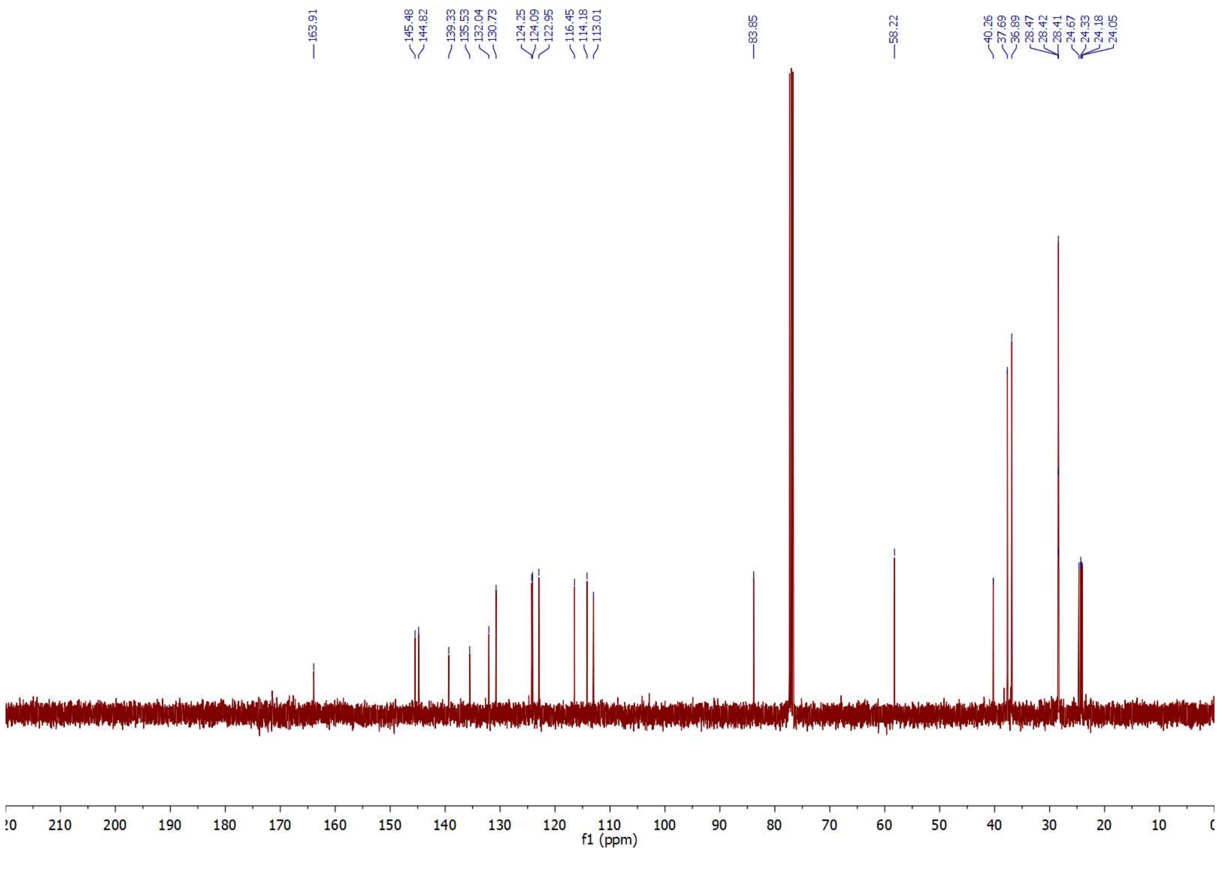

8.26
7.51
7.49
7.47
7.39
7.39
7.37
7.36
7.32
7.28
7.28
7.26
7.26
7.25
7.25
7.23
7.23
6.98
6.97
6.96
6.94
6.72
6.70
6.70
2.29
2.27
2.25
2.24
2.24
2.22
2.08
2.06
2.06
2.04
2.02
2.00
1.99
1.97
1.33
1.31
1.27
1.25
1.18
1.09
1.07
0.90
0.93
0.98
0.92
2.55
0.97
0.96
1.04
3.00
1.06
3.10
3.30
9.08
5.98
f1 (ppm)


169.96
164.22
145.27
145.18
139.93
135.61
131.68
130.74
124.29
124.00
122.47
117.09
113.47
113.44
75.39
36.81
28.48
28.44
26.03
24.52
24.31
24.25
24.12
f1 (ppm)

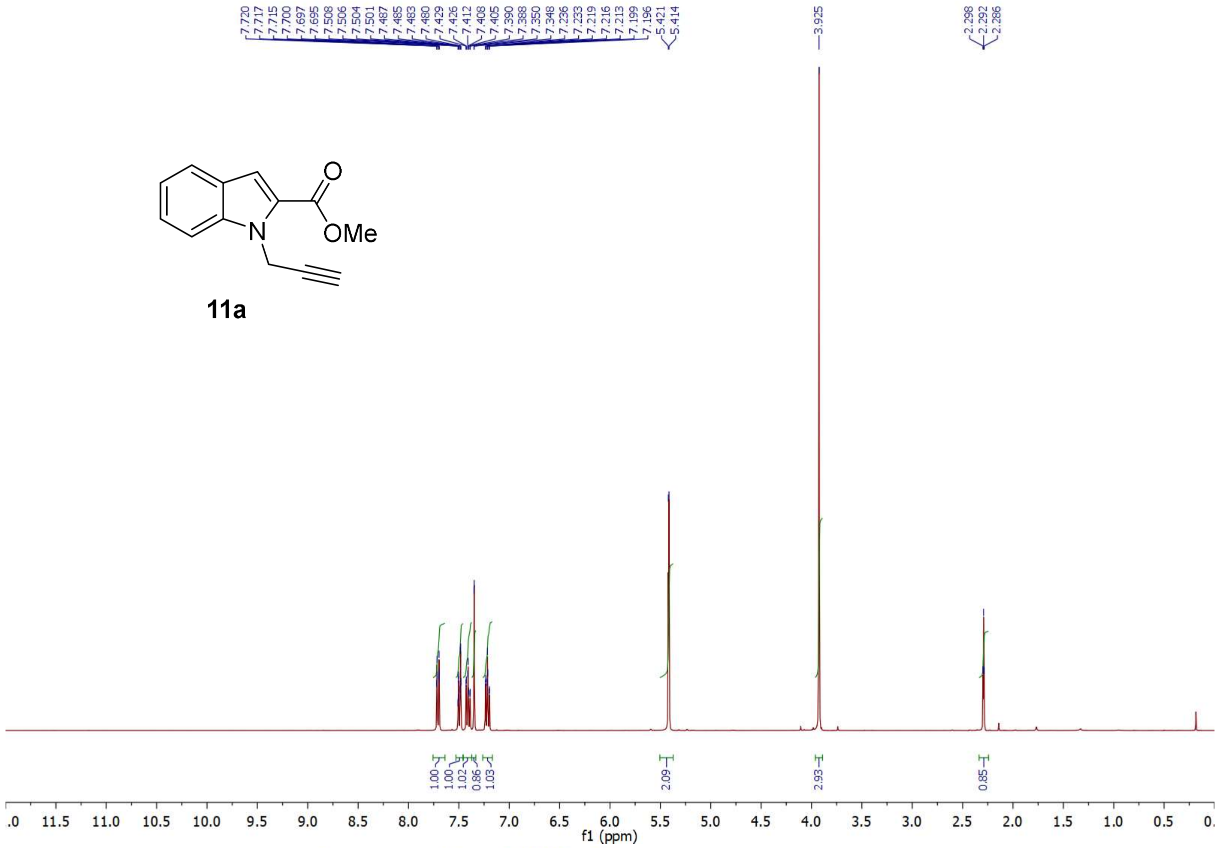

N
N
+
Au
Cl
O
Me

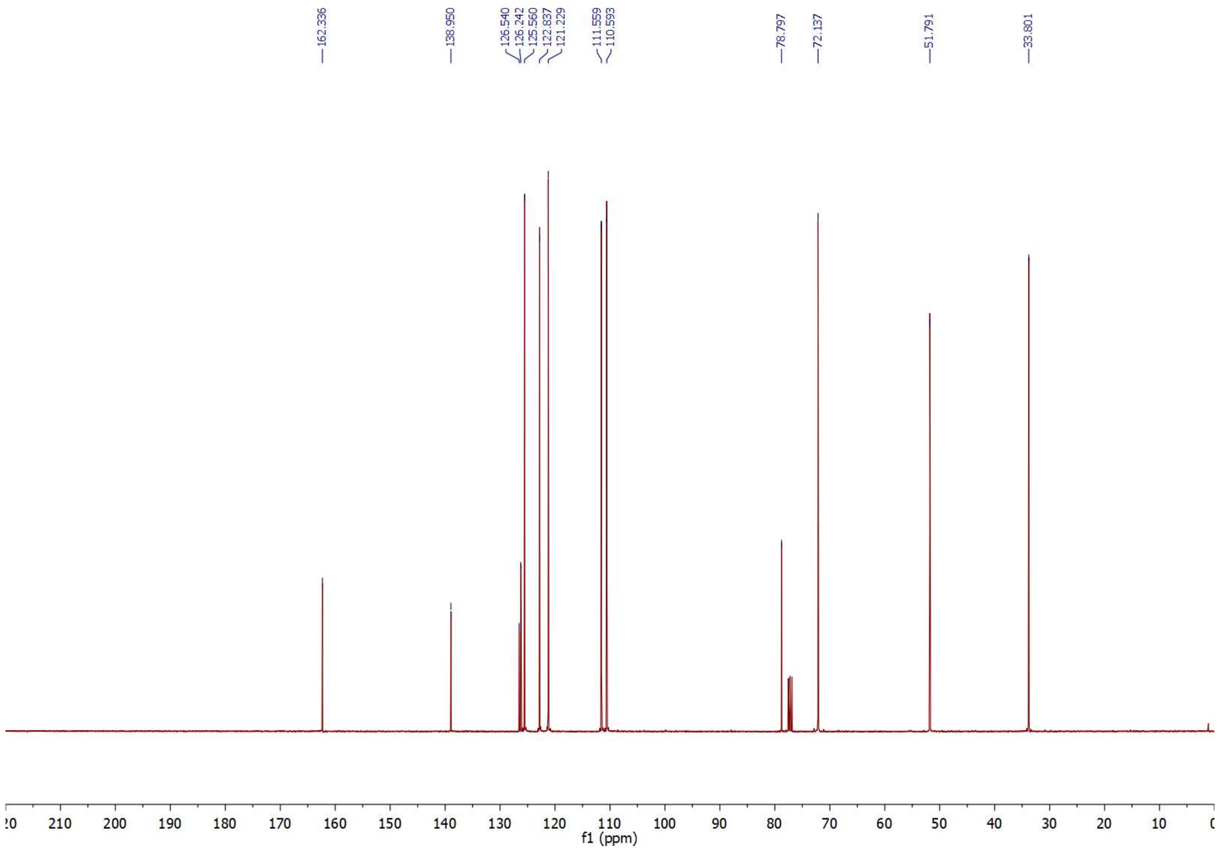
(*S*)-**Cat14**

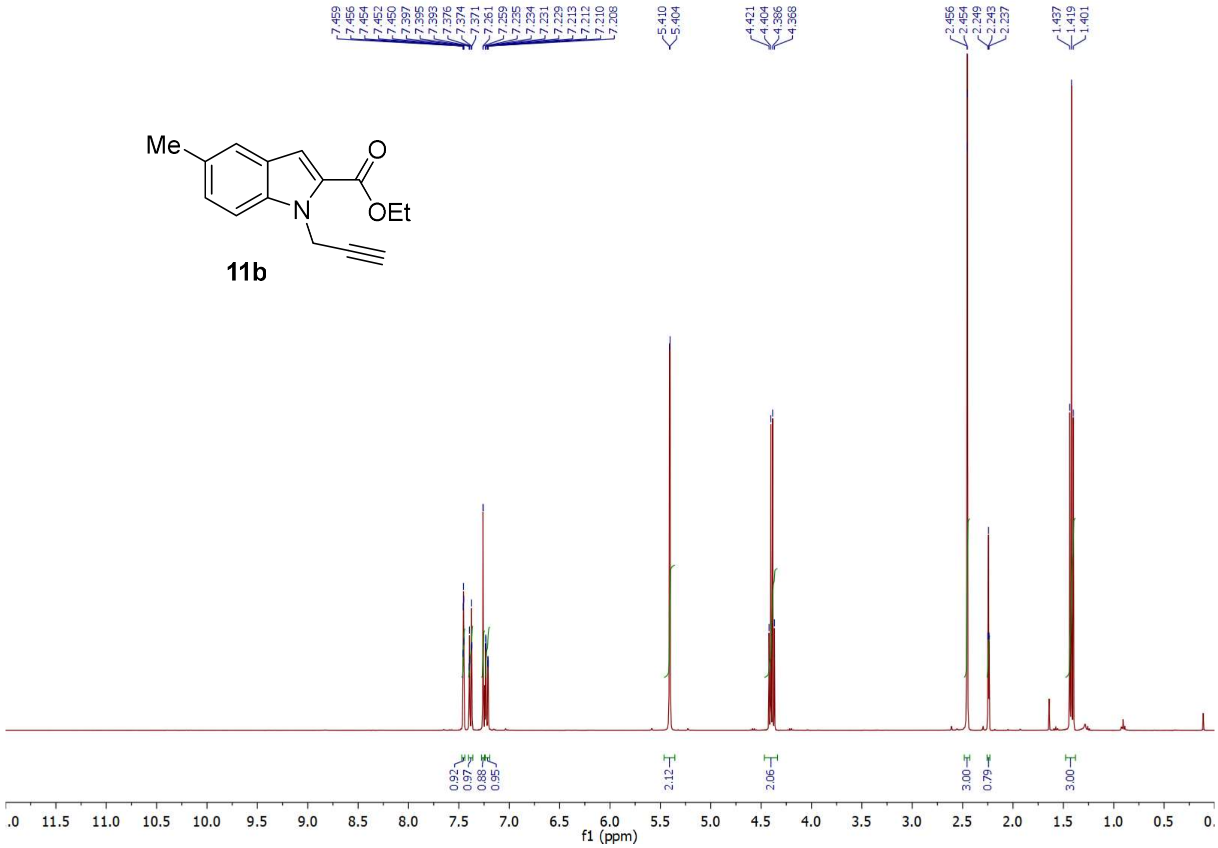

7.51 7.49 7.47 7.41 7.39 7.38 7.32 7.28 7.28 7.26 7.26 7.25 7.25 7.23 7.23 7.12 7.07 7.06 7.05 7.03 6.85 6.85 6.84 6.83 3.41 2.33 2.32 2.30 2.28 2.27 2.26 2.26 2.25 2.24 2.24 2.09 2.09 2.08 2.06 2.06 2.02 1.98 1.96 1.94 1.92 1.91 1.91 1.90 1.89 1.60 1.59 1.58 1.56 1.55 1.51 1.48 1.30 1.28 1.26 1.24 1.21 1.21 1.20 1.19 1.18 1.18 1.17 1.15 1.15 1.14 1.13 1.11 1.08 1.06
0.99 1.07 1.01 2.81 1.05 1.14 1.04
3.00
1.19 3.24 4.56
5.96 3.52 3.07 3.27 3.28 3.33
f1 (ppm)


163.91
145.48 144.82 139.33 135.53 132.04 130.73 124.25 124.09 122.95 116.45 114.18 113.01
83.85
58.22
40.26 37.69 36.89 28.47 28.42 28.41 24.67 24.33 24.18 24.05
f1 (ppm)

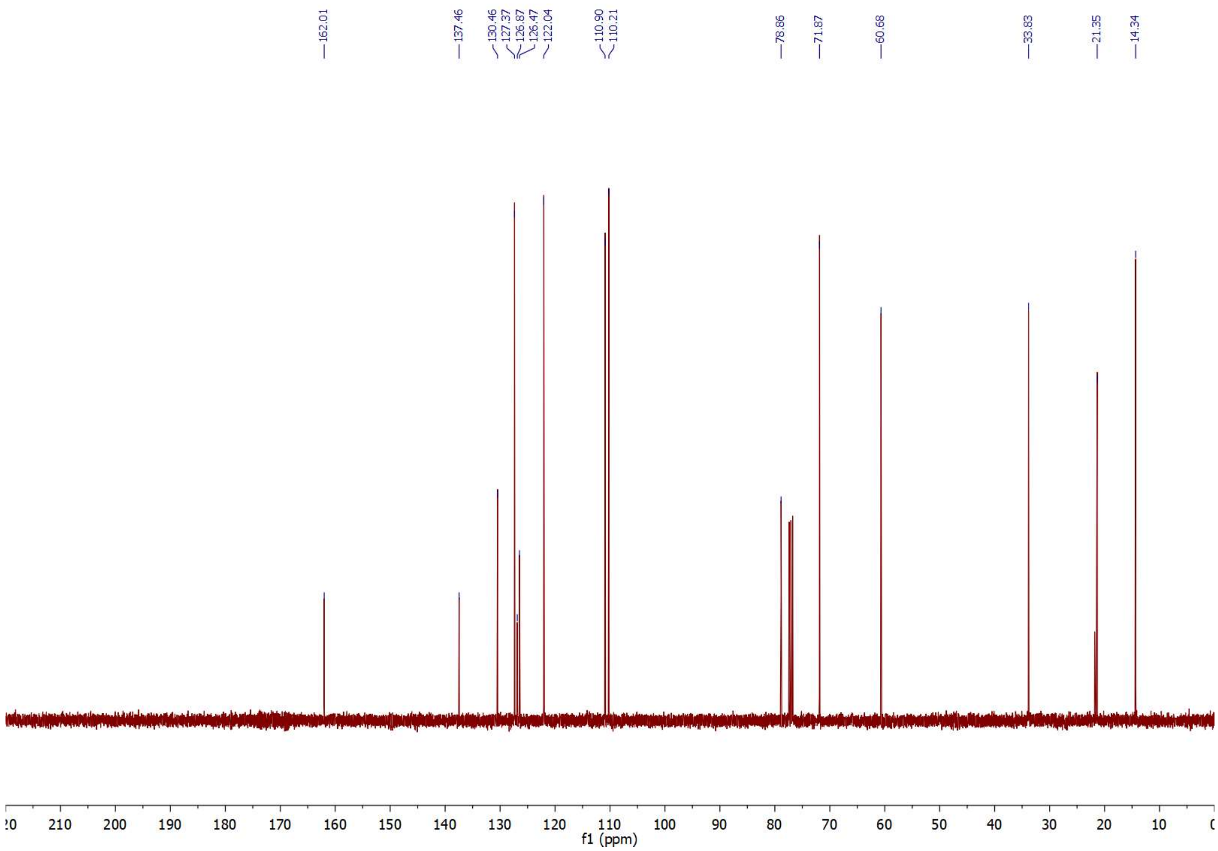
11a

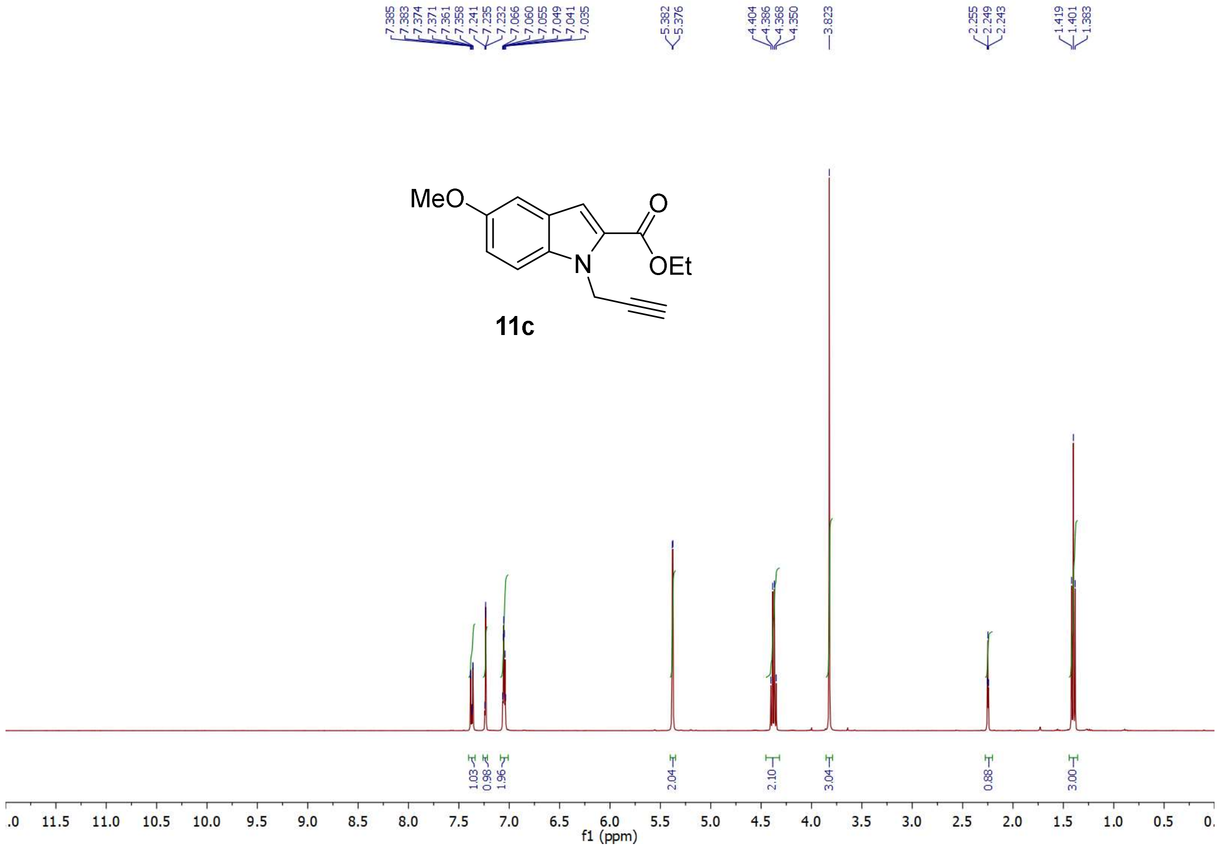

O
N
OMe
7.720
7.717
7.715
7.700
7.697
7.695
7.508
7.506
7.504
7.501
7.487
7.485
7.483
7.480
7.429
7.426
7.412
7.408
7.405
7.390
7.388
7.350
7.348
7.236
7.233
7.219
7.216
7.213
7.199
7.196
5.421
5.414
3.925
2.298
2.292
2.286
1.00
1.00
1.02
0.86
1.03
2.09
2.93
0.85
f1 (ppm)


162.336
138.950
126.540
126.242
125.560
122.837
121.229
111.559
110.593
78.797
72.137
51.791
33.801
f1 (ppm)



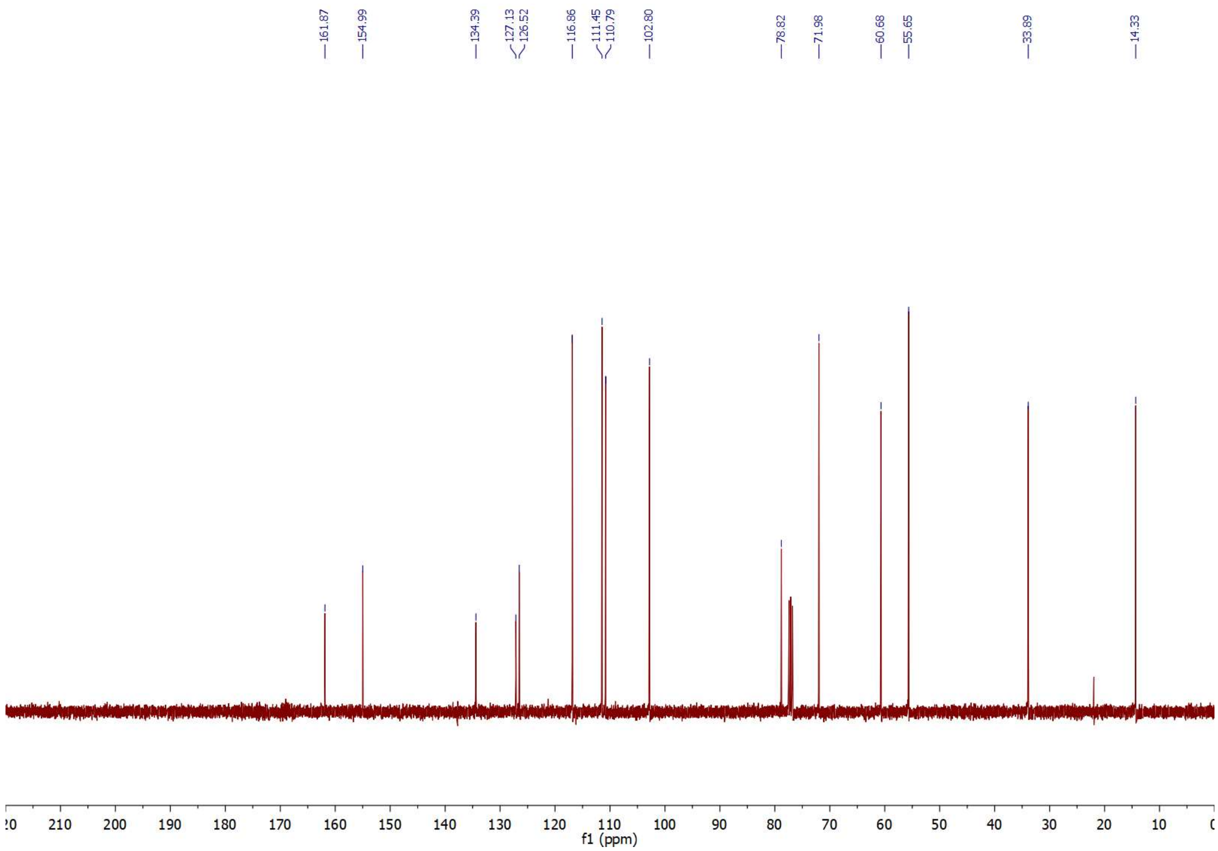
11b



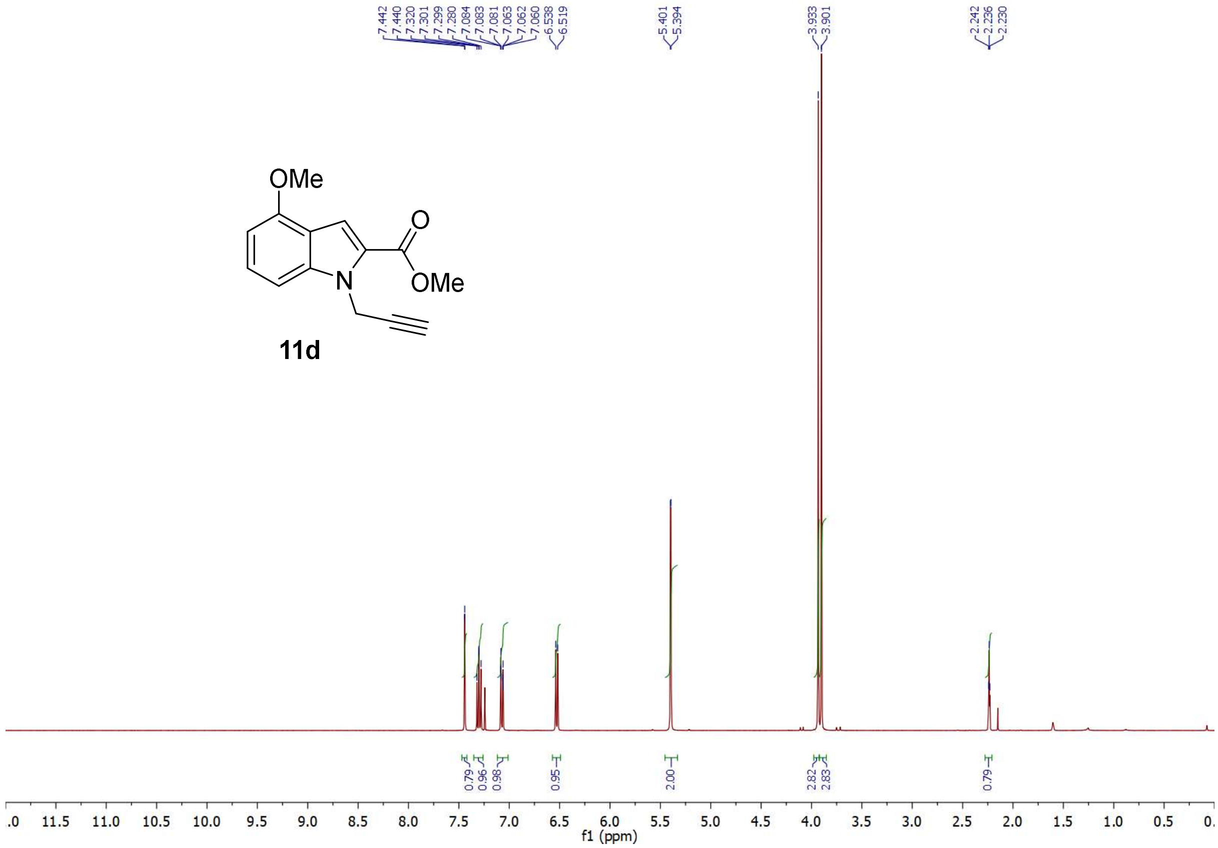


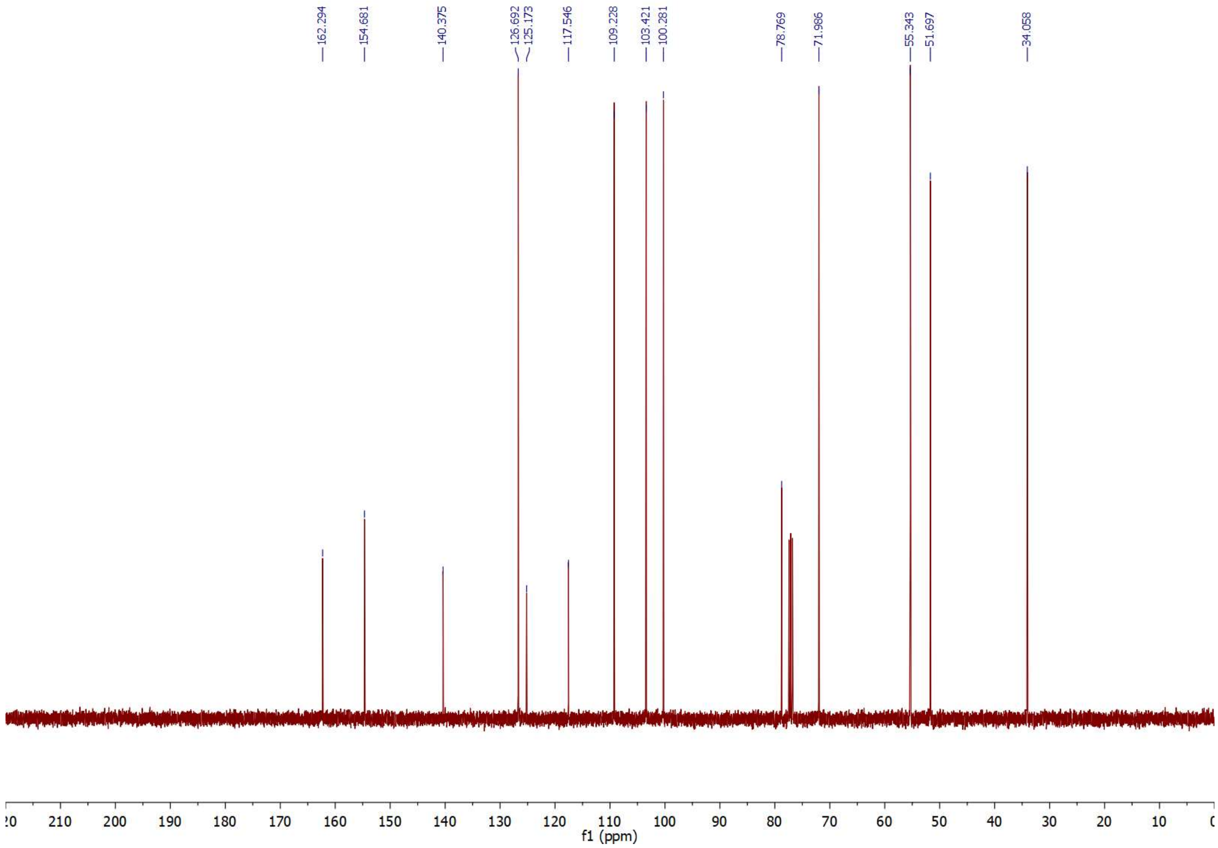
7.385
7.383
7.374
7.371
7.361
7.358
7.241
7.235
7.232
7.066
7.060
7.055
7.049
7.041
7.035
5.382
5.376
4.404
4.386
4.368
4.350
3.823
2.255
2.249
2.243
1.419
1.401
1.383
MeO
O
OEt
N
1.03
0.98
1.96
2.04
2.10
3.04
0.88
3.00
f1 (ppm)

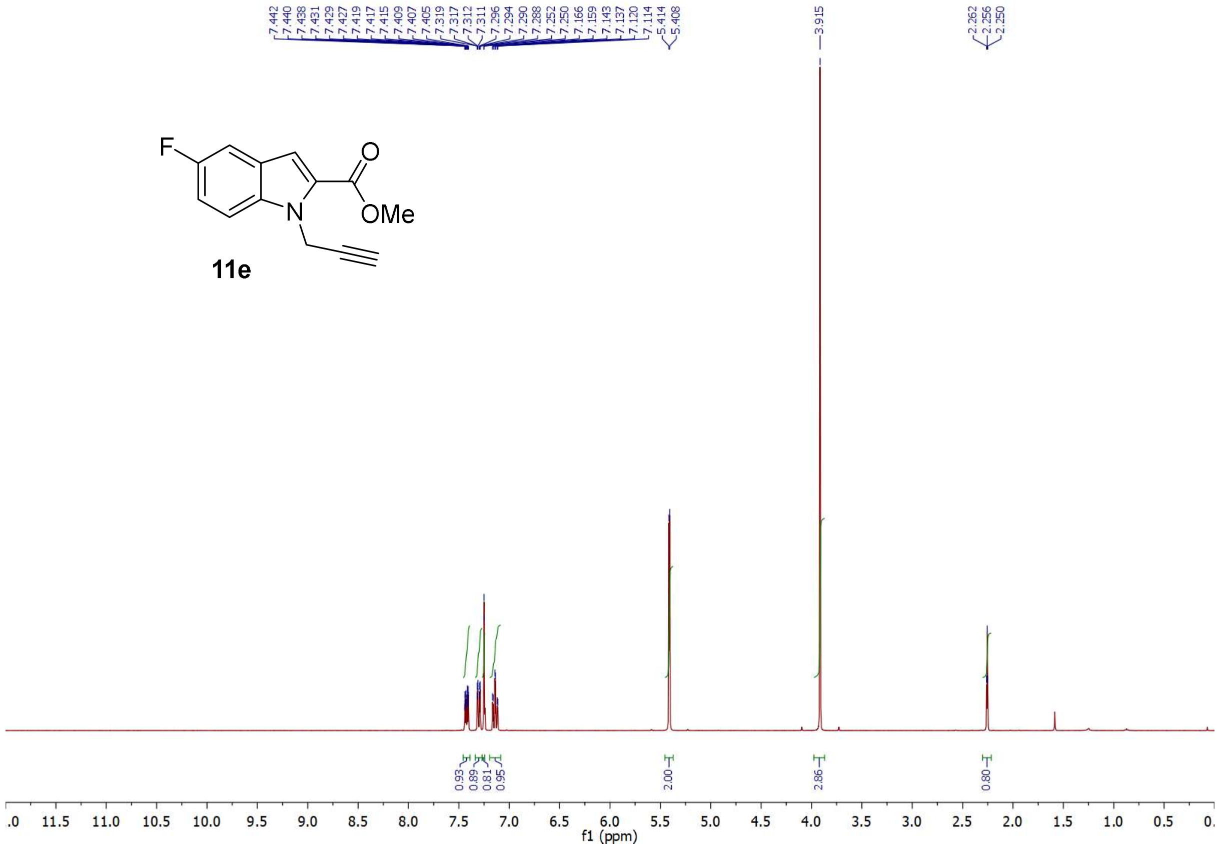
11c



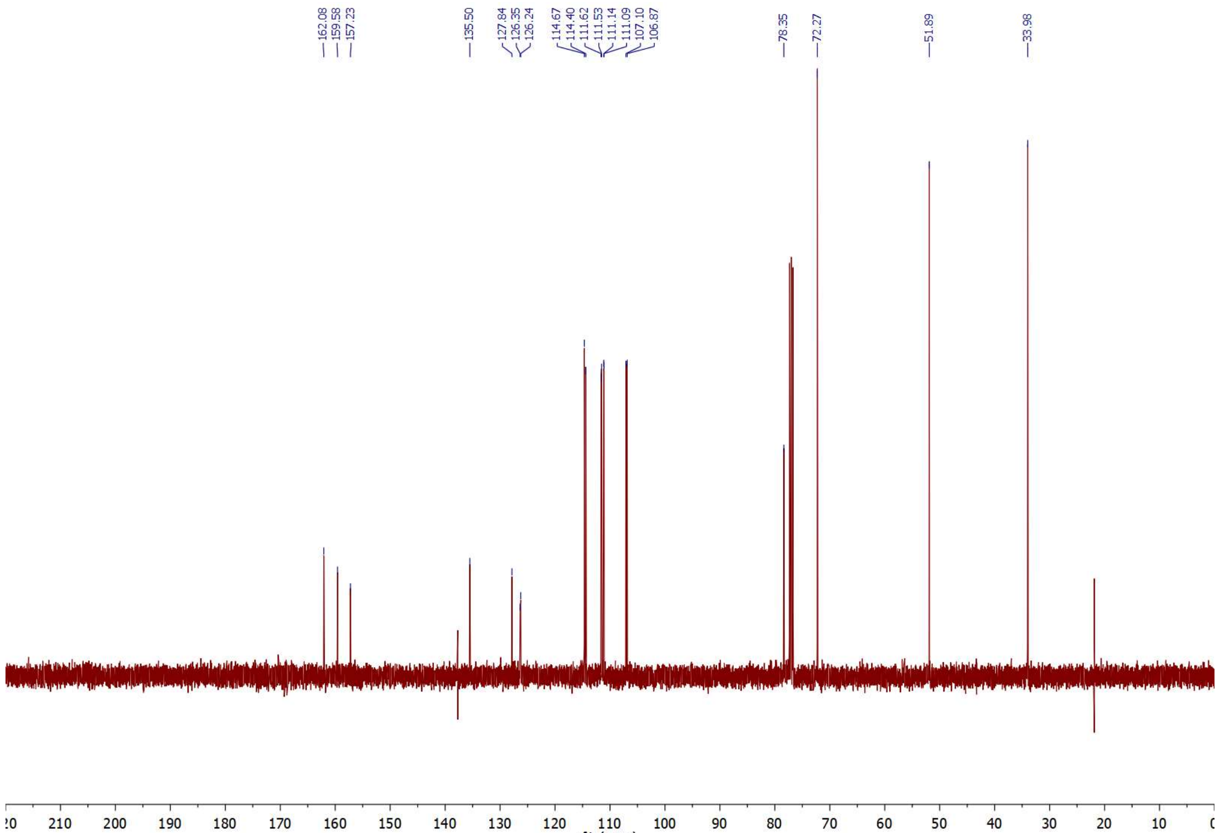
161.87
154.99
134.39
127.13
126.52
116.86
111.45
110.79
102.80
78.82
71.98
60.68
55.65
33.89
14.33
f1 (ppm)


OMe
O
N
OMe
11d
7.442
7.440
7.320
7.301
7.299
7.280
7.084
7.083
7.081
7.063
7.062
7.060
6.538
6.519
5.401
5.394
3.933
3.901
2.242
2.236
2.230
0.79
0.96
0.98
0.95
2.00
2.82
2.83
0.79
f1 (ppm)

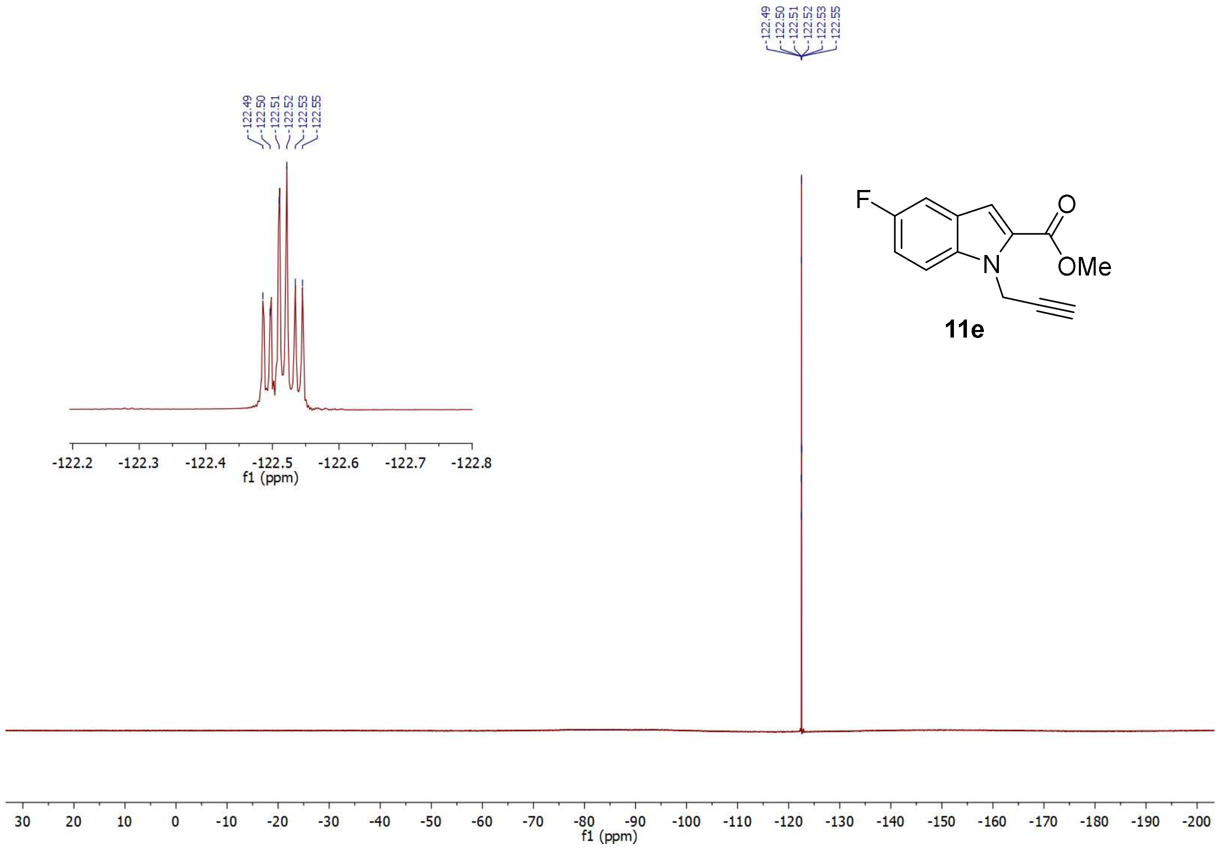

162.294
154.681
140.375
126.692
125.173
117.546
109.228
103.421
100.281
78.769
71.986
55.343
51.697
34.058
f1 (ppm)



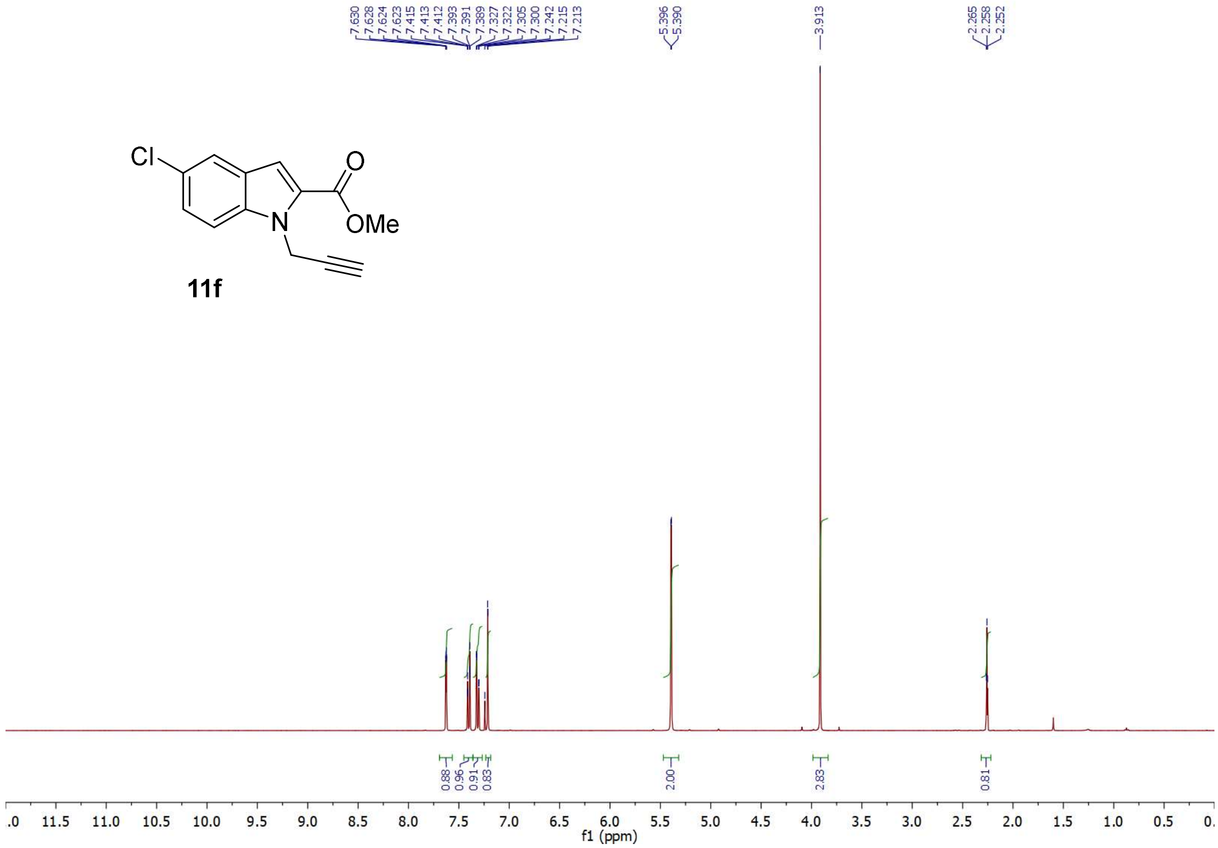
11e
7.442 7.440 7.438 7.431 7.429 7.427 7.419 7.417 7.415 7.409 7.407 7.405 7.319 7.317 7.312 7.311 7.296 7.294 7.290 7.288 7.252 7.250 7.166 7.159 7.143 7.137 7.120 7.114 5.414 5.408
3.915
2.262 2.256 2.250
0.93 0.89 0.81 0.95
2.00
2.86
0.80
f1 (ppm)

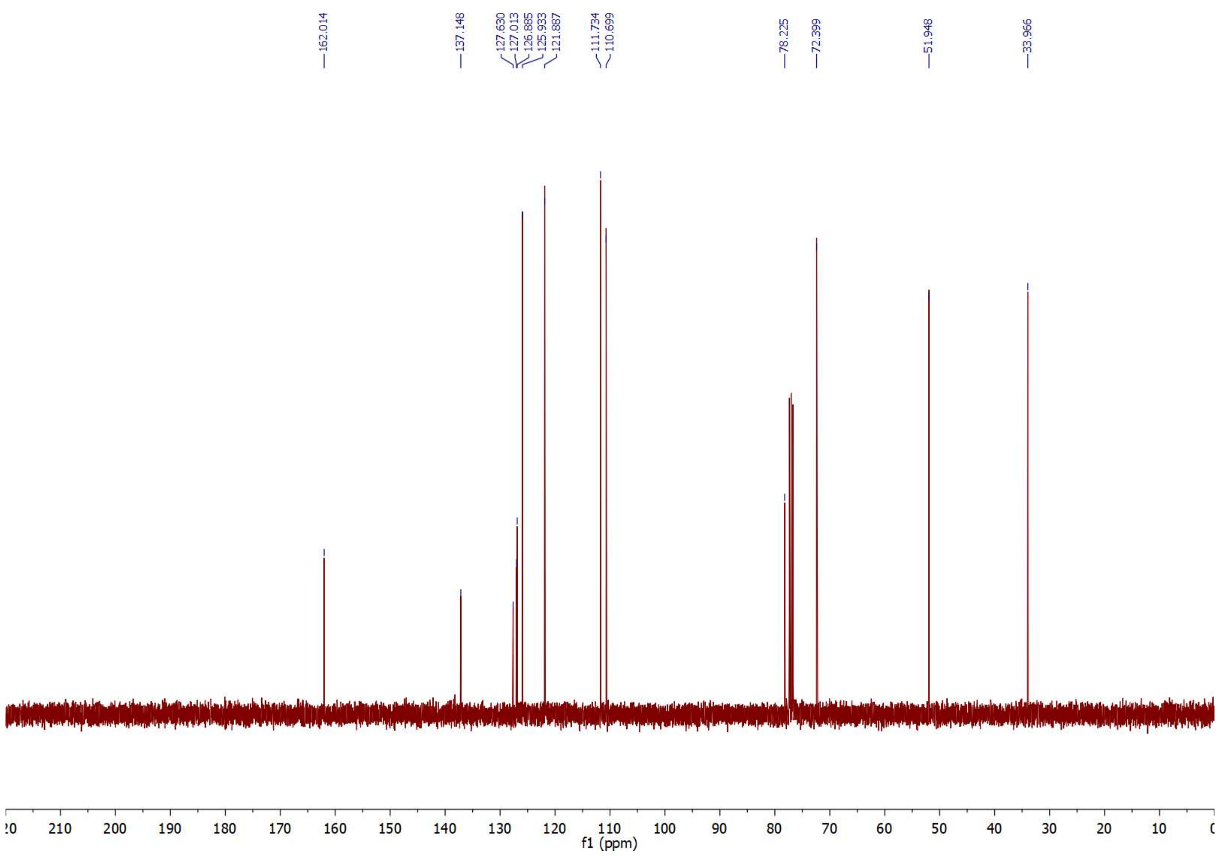


162.08 159.58 157.23
135.50
127.84 126.35 126.24
114.67 114.40 111.62 111.53 111.14 111.09 107.10 106.87
78.35
72.27
51.89
33.98
f1 (ppm)

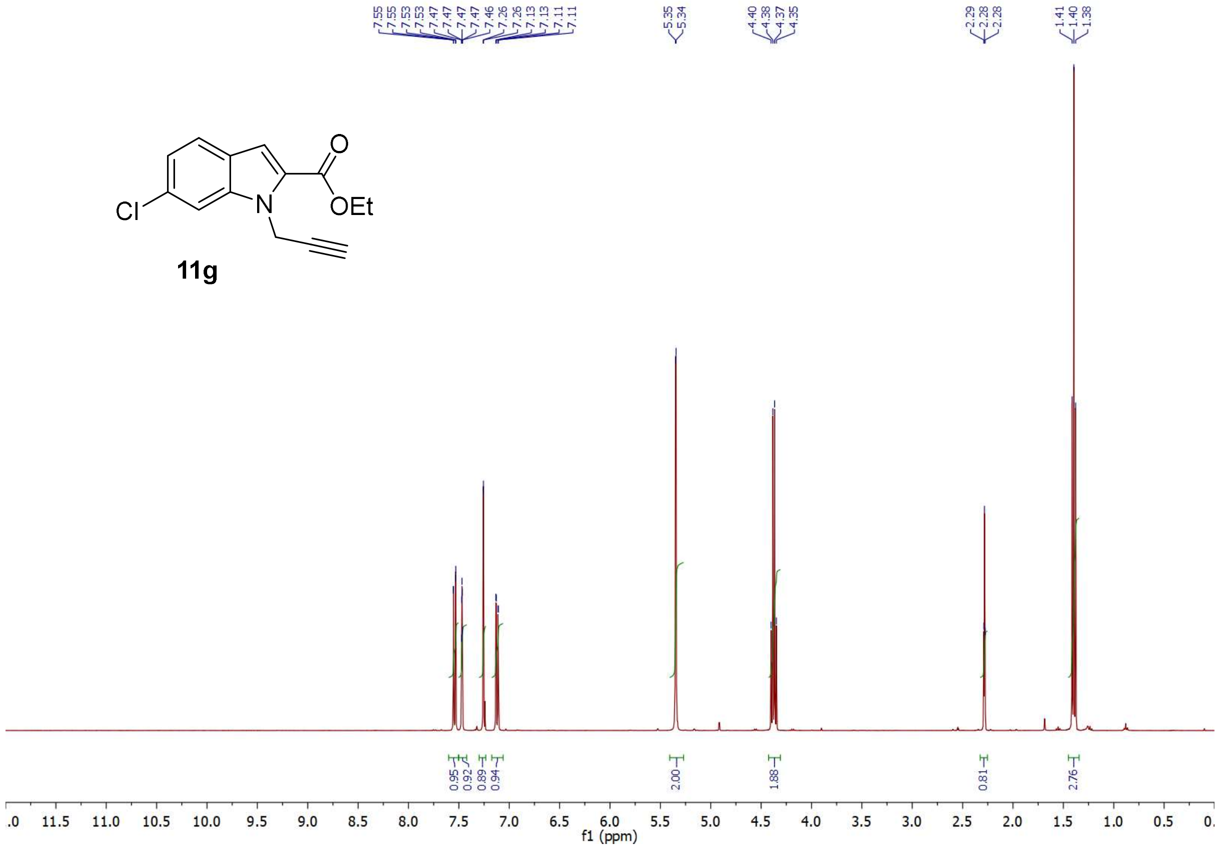

-122.49
-122.50
-122.51
-122.52
-122.53
-122.55
-122.2
-122.3
-122.4
-122.5
-122.6
-122.7
-122.8
f1 (ppm)
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)
F
O
OMe
N

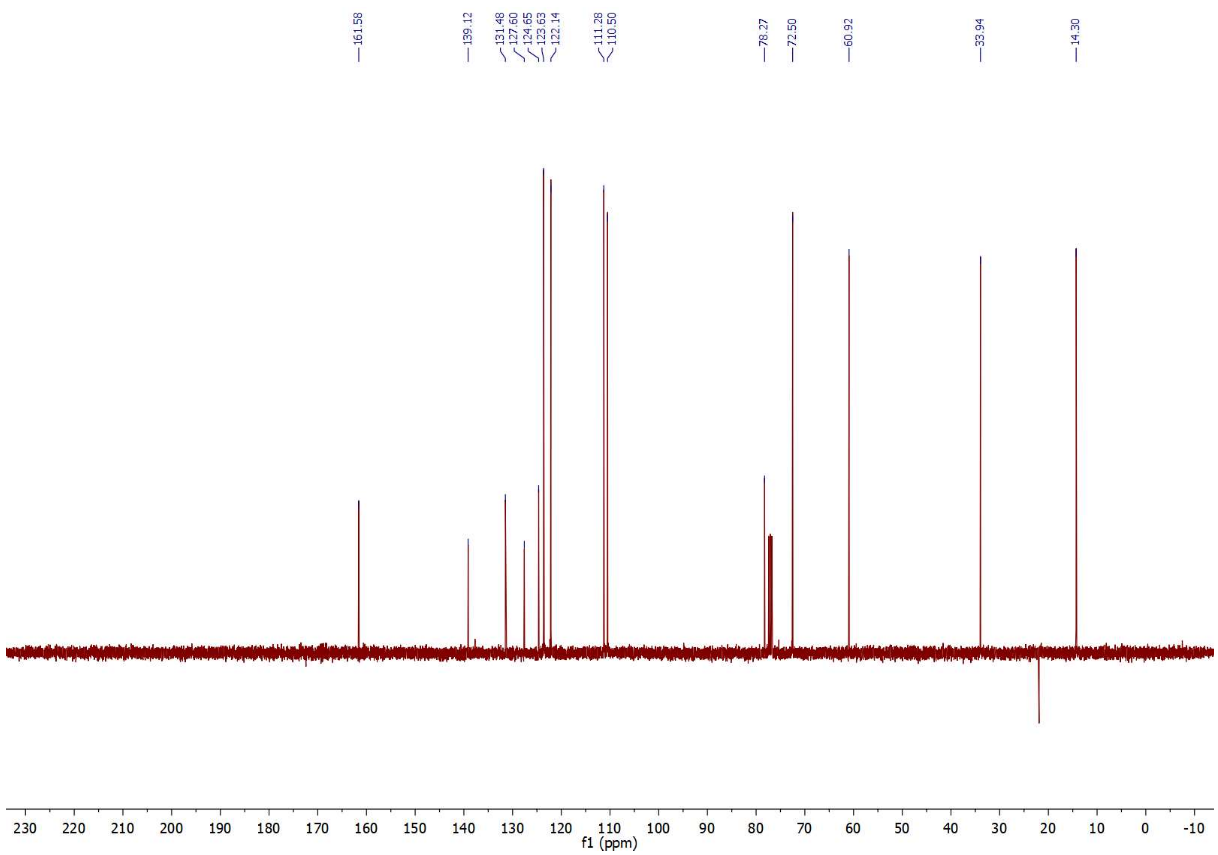
11e

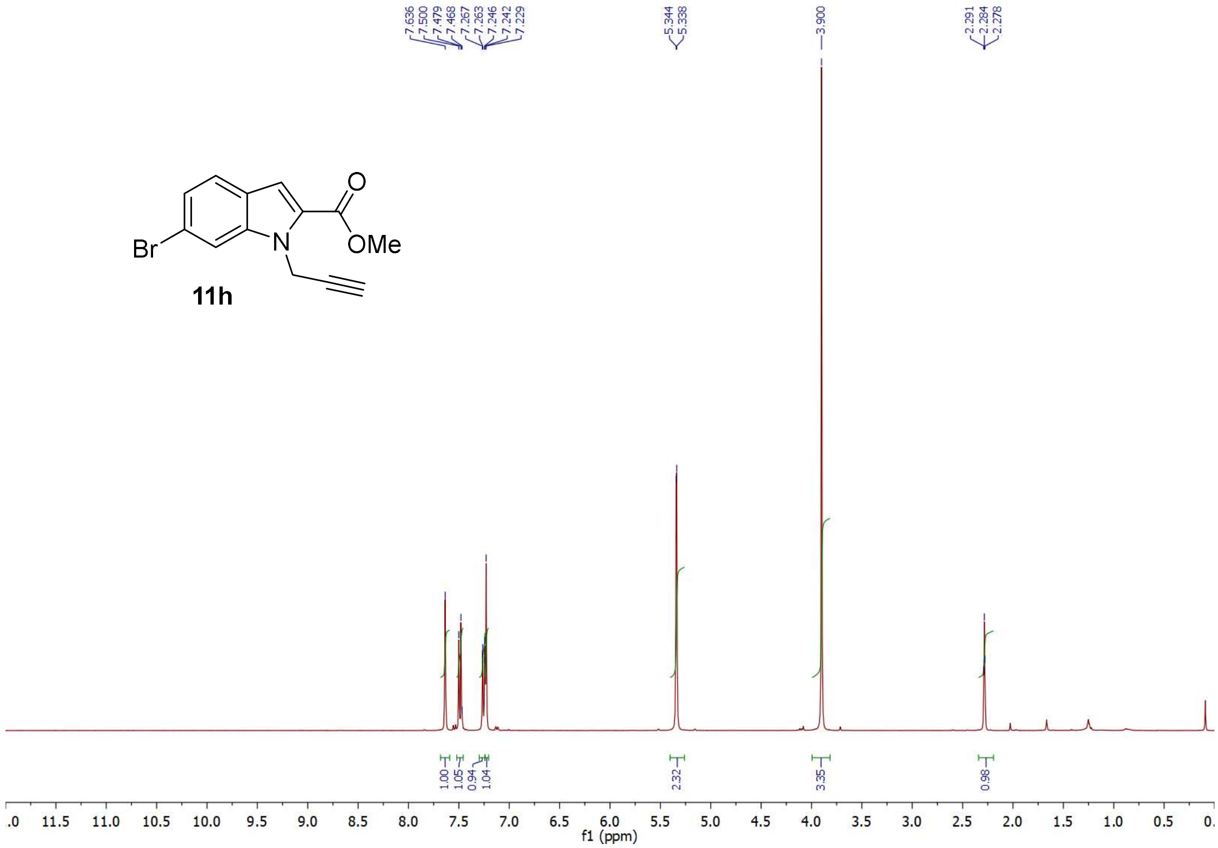

Cl
O
OMe
N
11f
7.630
7.628
7.624
7.623
7.415
7.413
7.412
7.393
7.391
7.389
7.327
7.322
7.305
7.300
7.242
7.215
7.213
5.396
5.390
3.913
2.265
2.258
2.252
0.88
0.96
0.91
0.83
2.00
2.83
0.81
f1 (ppm)


162.014
137.148
127.630
127.013
126.885
125.933
121.887
111.734
110.699
78.225
72.399
51.948
33.966
f1 (ppm)

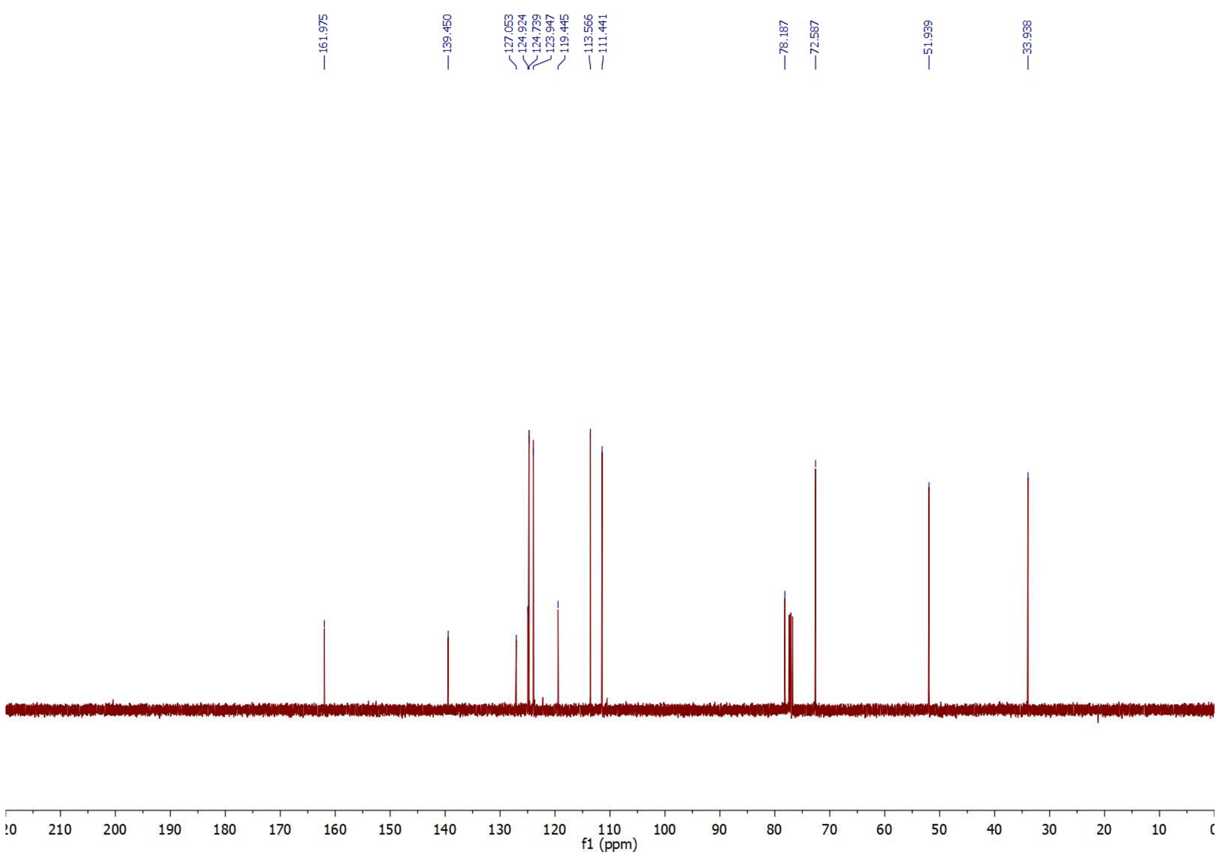
11g

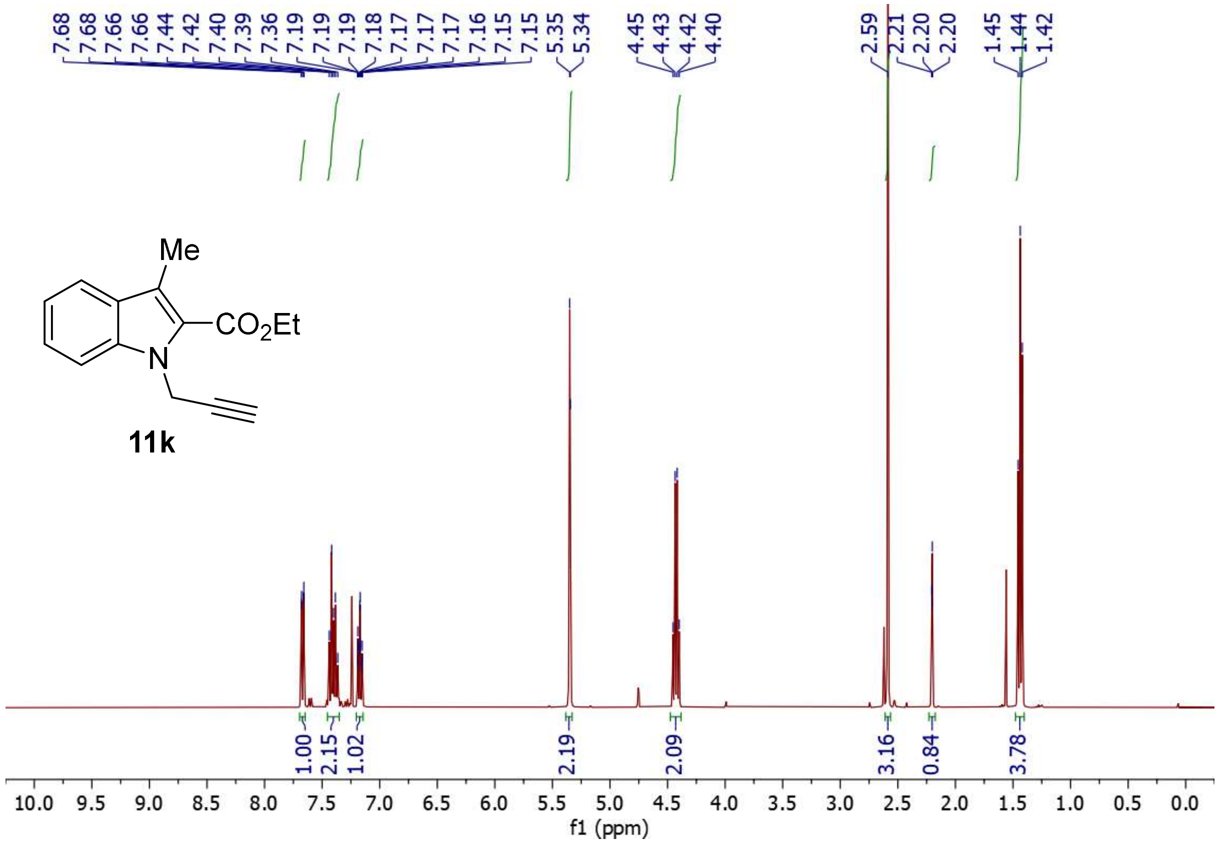

O
OEt
Cl
N
7.55
7.55
7.53
7.53
7.47
7.47
7.47
7.46
7.26
7.26
7.13
7.13
7.11
7.11
5.35
5.34
4.40
4.38
4.37
4.35
2.29
2.28
2.28
1.41
1.40
1.38
0.95
0.92
0.89
0.94
2.00
1.88
0.81
2.76
f1 (ppm)

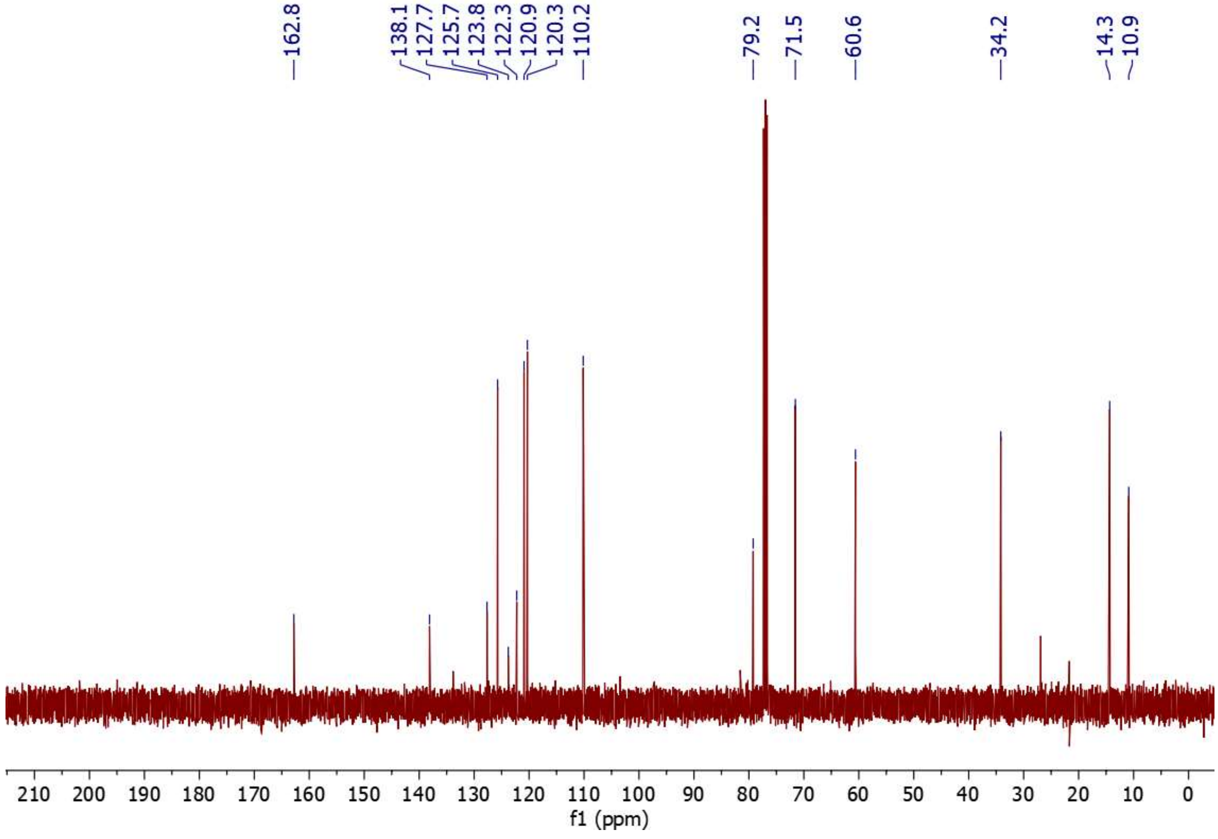

161.58
139.12
131.48
127.60
124.65
123.63
122.14
111.28
110.50
78.27
72.50
60.92
33.94
14.30
f1 (ppm)

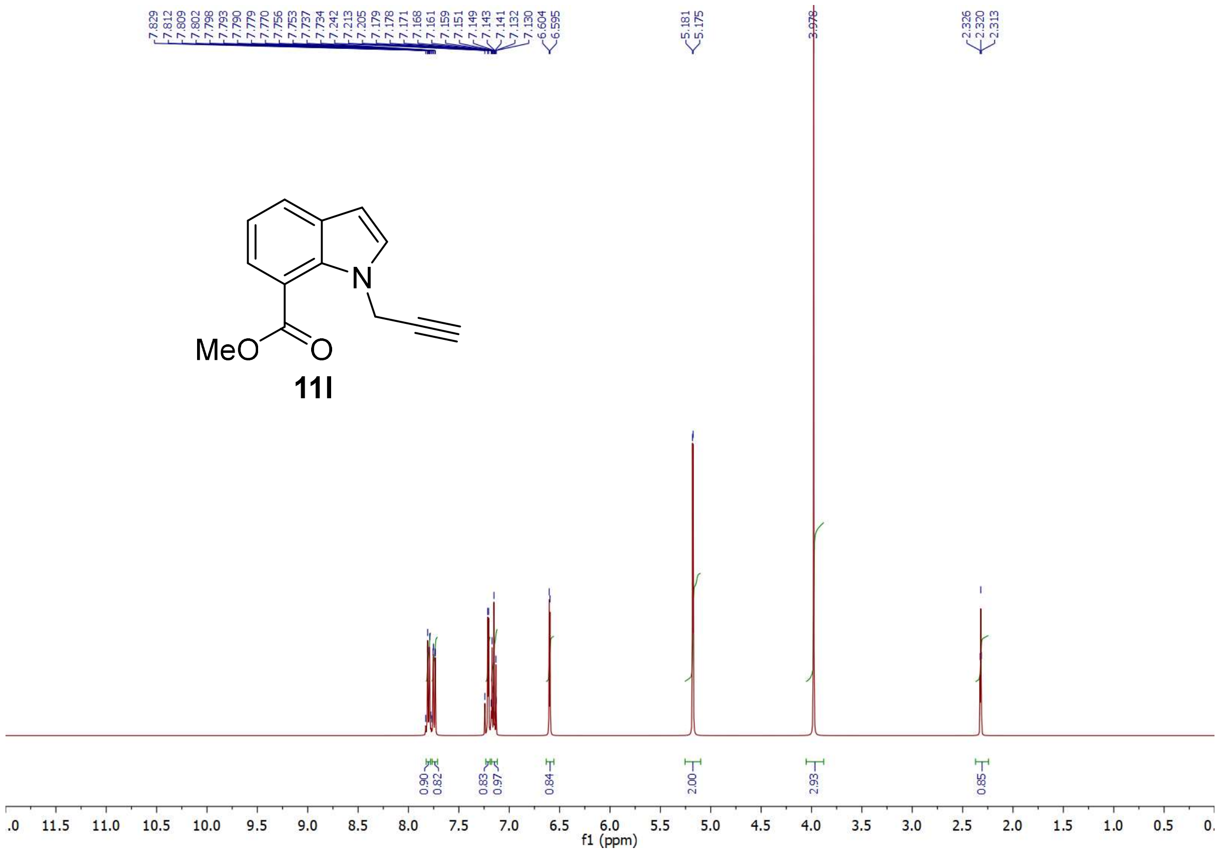


11h

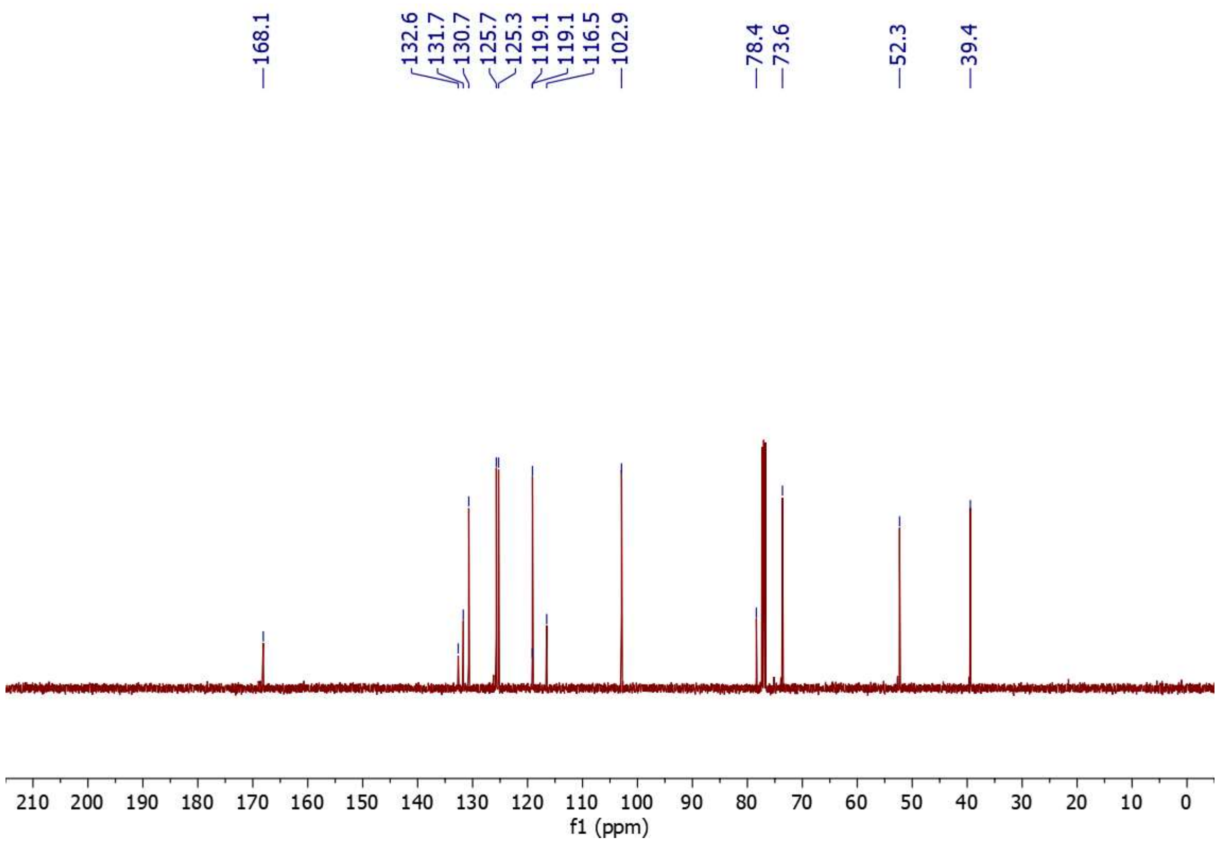



7.68
7.68
7.66
7.66
7.44
7.42
7.40
7.39
7.36
7.19
7.19
7.19
7.18
7.17
7.17
7.17
7.16
7.15
7.15
5.35
5.34
4.45
4.43
4.42
4.40
2.59
2.21
2.20
2.20
1.45
1.44
1.42
1.00
2.15
1.02
2.19
2.09
3.16
0.84
3.78
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Me
CO2Et
N
11k

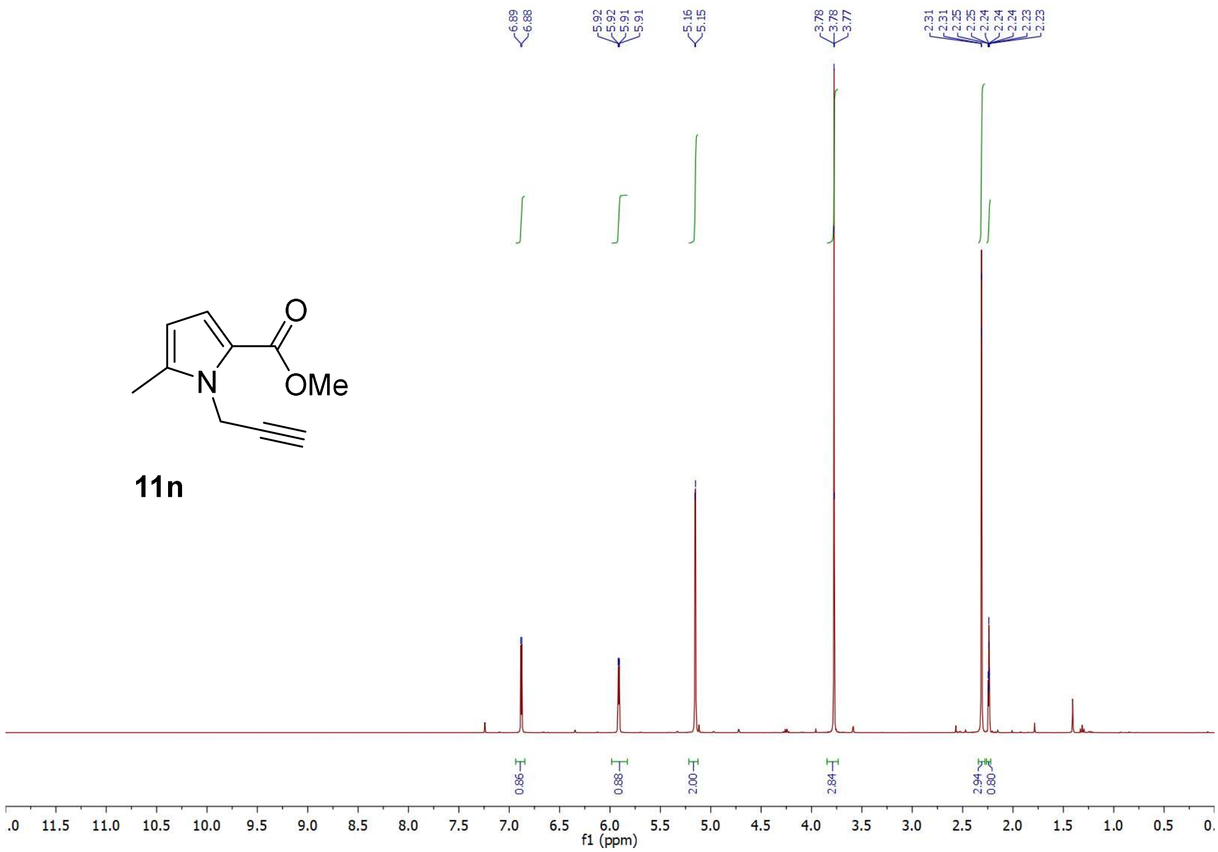

162.8
138.1
127.7
125.7
123.8
122.3
120.9
120.3
110.2
79.2
71.5
60.6
34.2
14.3
10.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

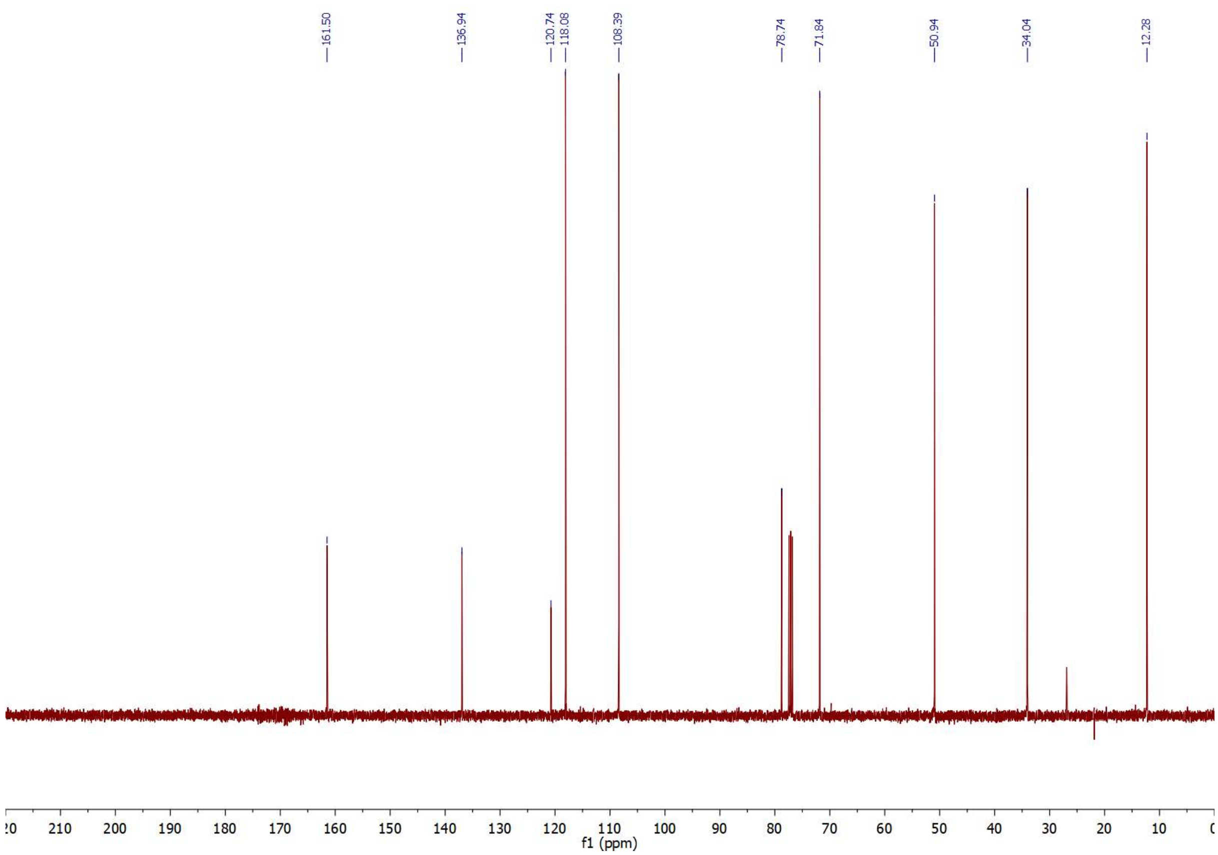


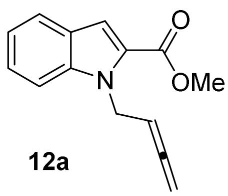
7.829 7.812 7.809 7.802 7.798 7.793 7.790 7.779 7.770 7.756 7.753 7.737 7.734 7.242 7.213 7.205 7.179 7.178 7.171 7.168 7.161 7.159 7.151 7.149 7.143 7.141 7.132 7.130 6.604 6.595
5.181 5.175
3.978
2.326 2.320 2.313
MeO
O
N
11l
0.90 0.82 0.83 0.97 0.84 2.00 2.93 0.85
f1 (ppm)



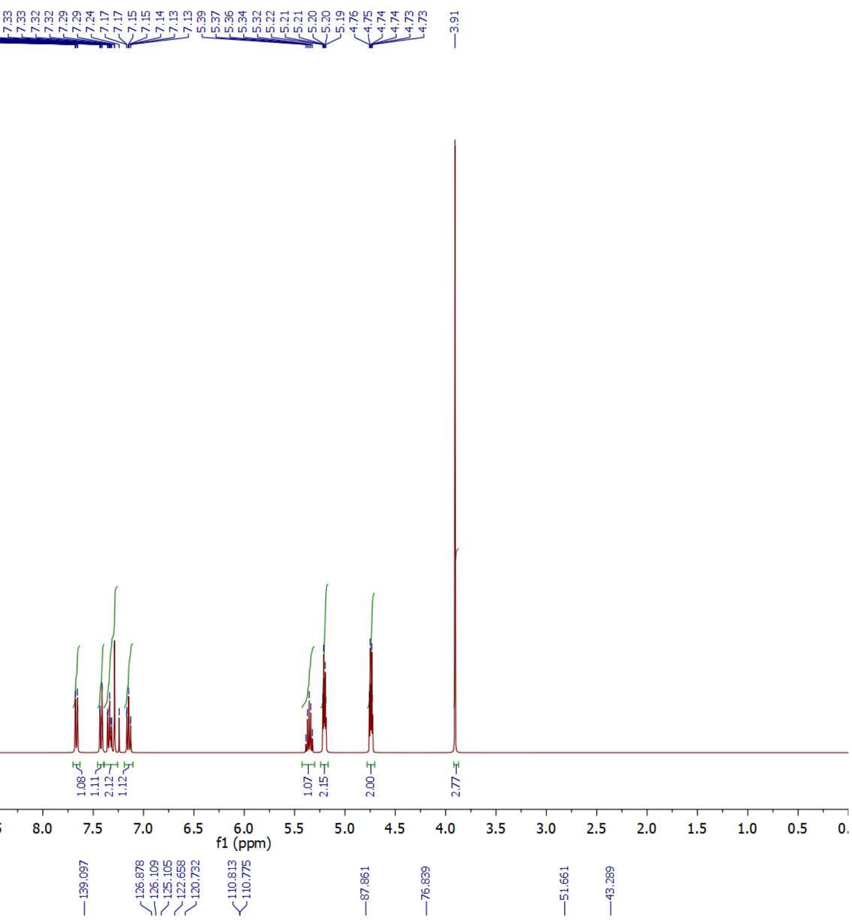
168.1
132.6 131.7 130.7 125.7 125.3 119.1 119.1 116.5 102.9
78.4 73.6
52.3
39.4
f1 (ppm)

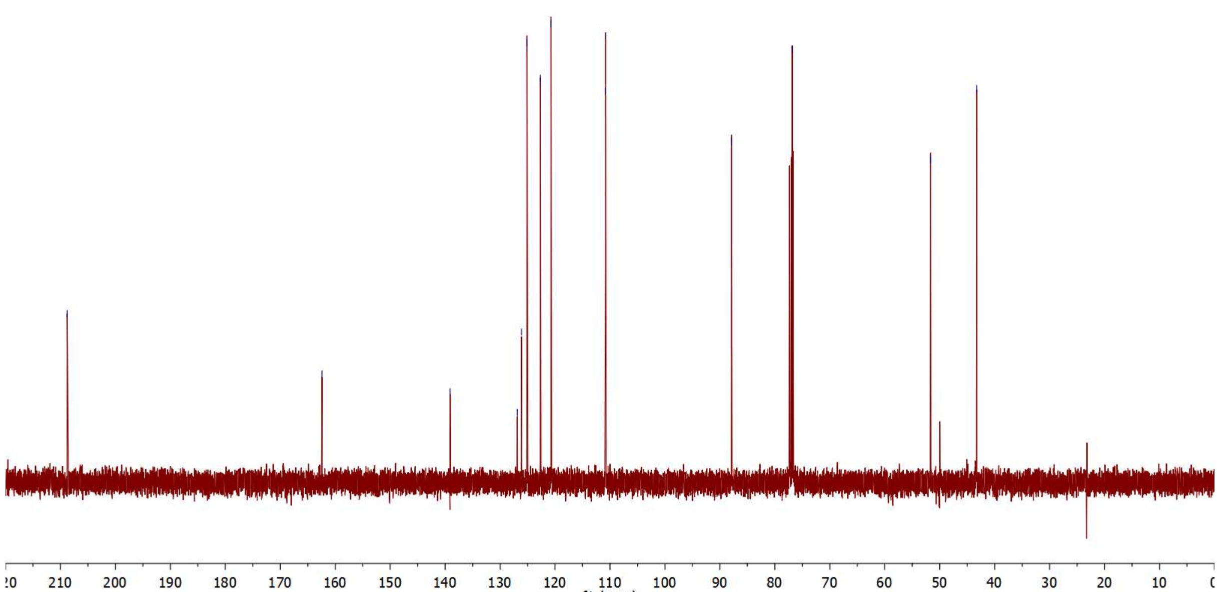

OMe
N
11n
6.89
6.88
5.92
5.92
5.91
5.91
5.16
5.15
3.78
3.78
3.77
2.31
2.31
2.25
2.25
2.24
2.24
2.24
2.23
2.23
0.86
0.88
2.00
2.84
2.94
0.80
f1 (ppm)

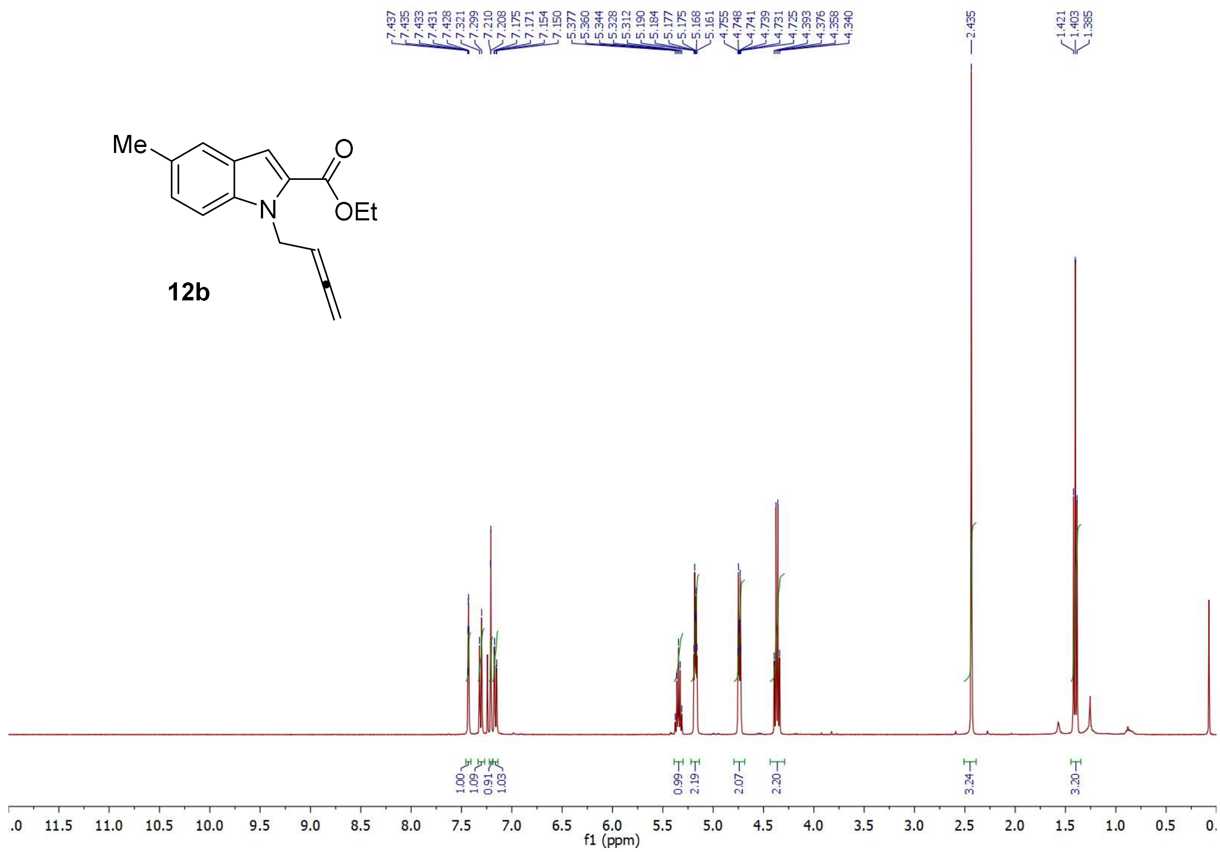

161.50
136.94
120.74
118.08
108.39
78.74
71.84
50.94
34.04
12.28
f1 (ppm)

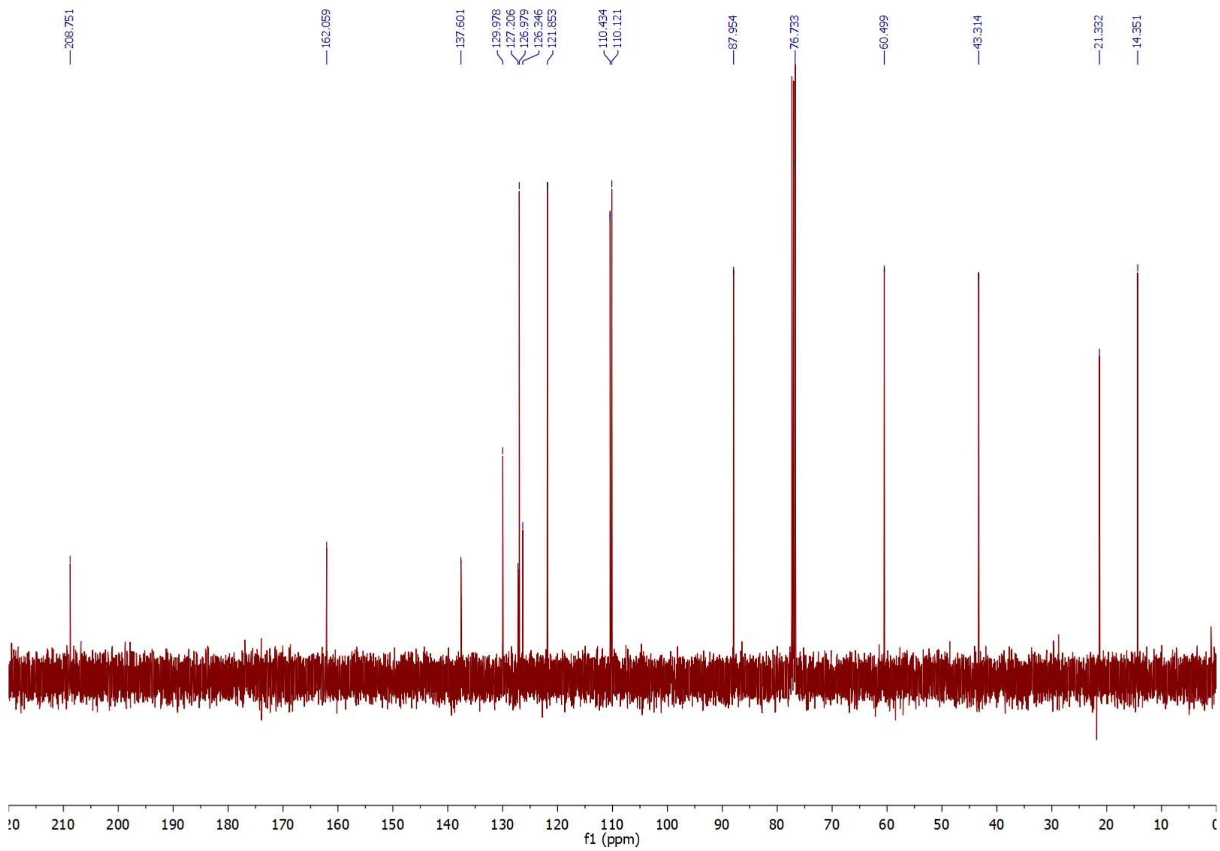


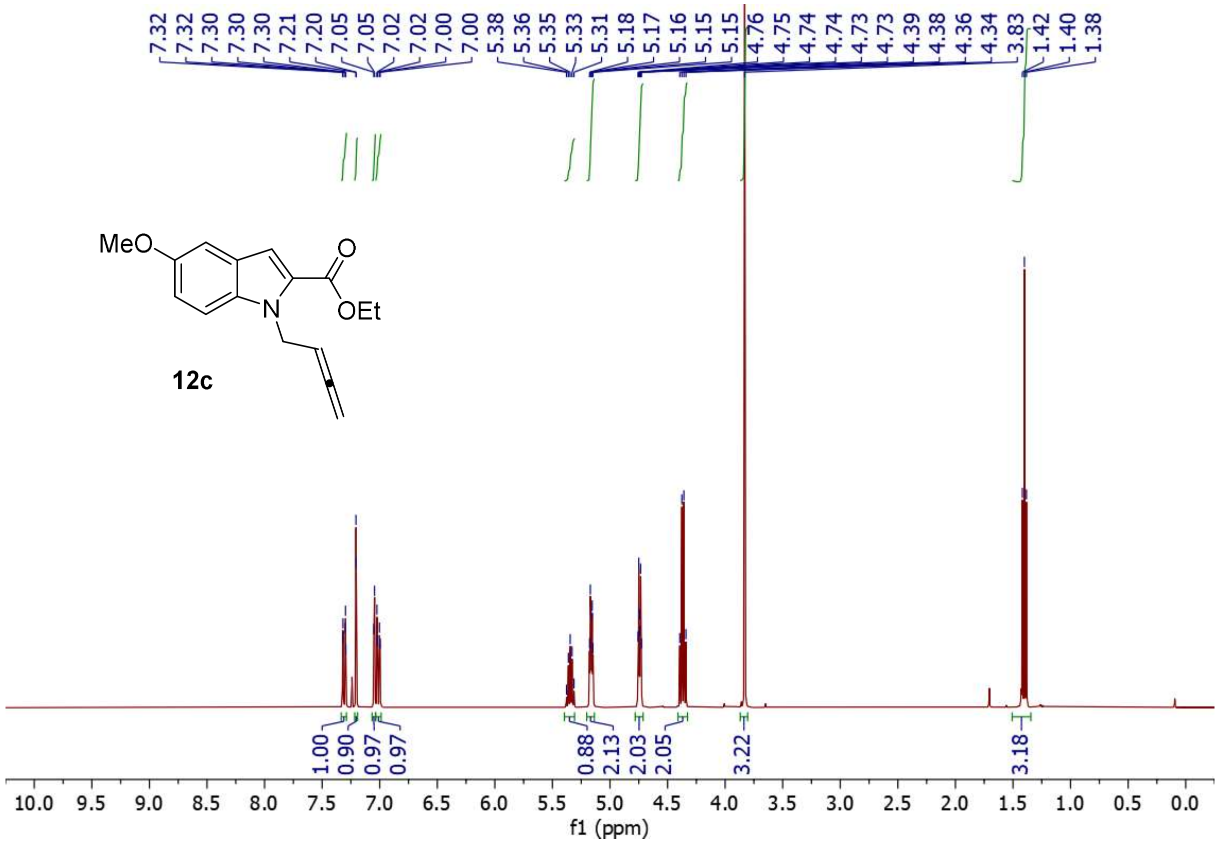
12a



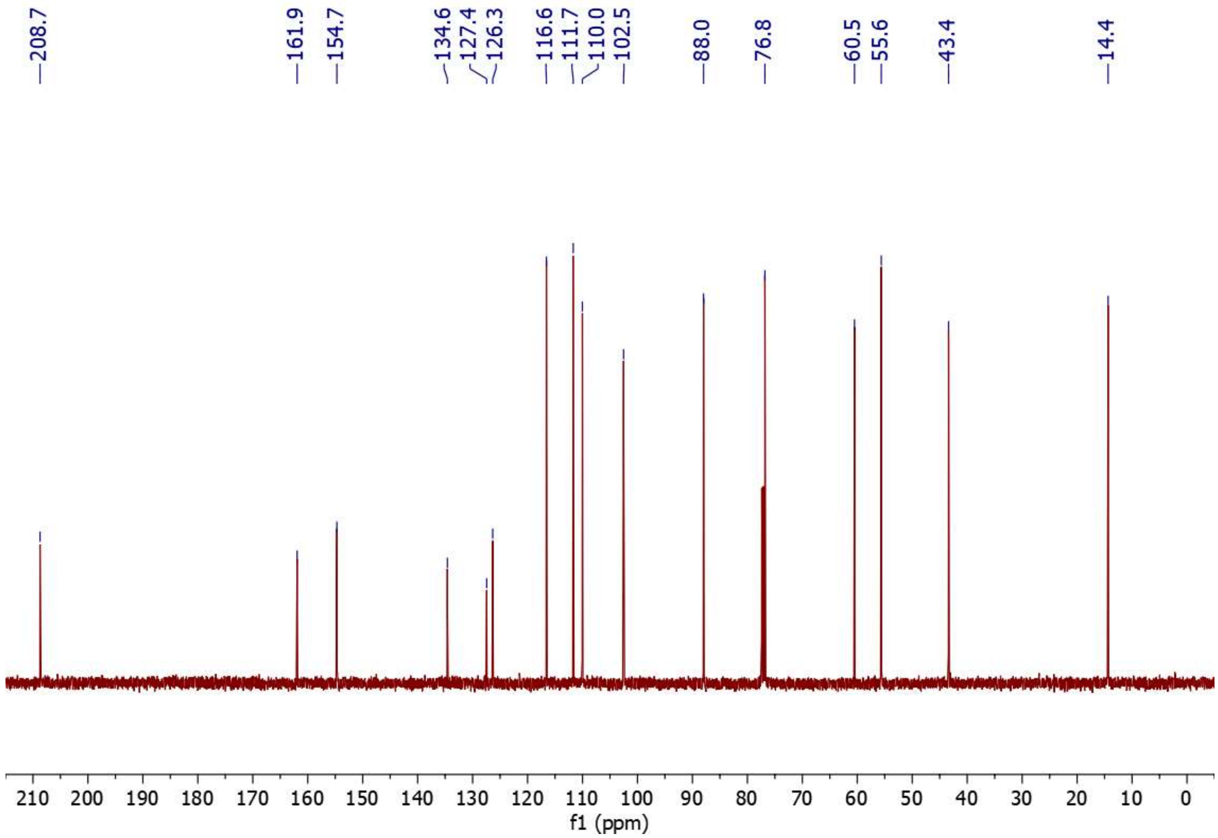



Me
O
OEt
N
12b
7.437
7.435
7.433
7.431
7.428
7.321
7.299
7.210
7.208
7.175
7.171
7.154
7.150
5.377
5.360
5.344
5.328
5.312
5.190
5.184
5.177
5.175
5.168
5.161
4.755
4.748
4.741
4.739
4.731
4.725
4.393
4.376
4.358
4.340
2.435
1.421
1.403
1.385
1.00
1.09
0.91
1.03
0.99
2.19
2.07
2.20
3.24
3.20
f1 (ppm)

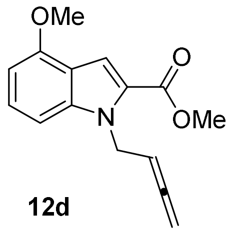

208.751
162.059
137.601
129.978
127.206
126.979
126.346
121.853
110.434
110.121
87.954
76.733
60.499
43.314
21.332
14.351
f1 (ppm)



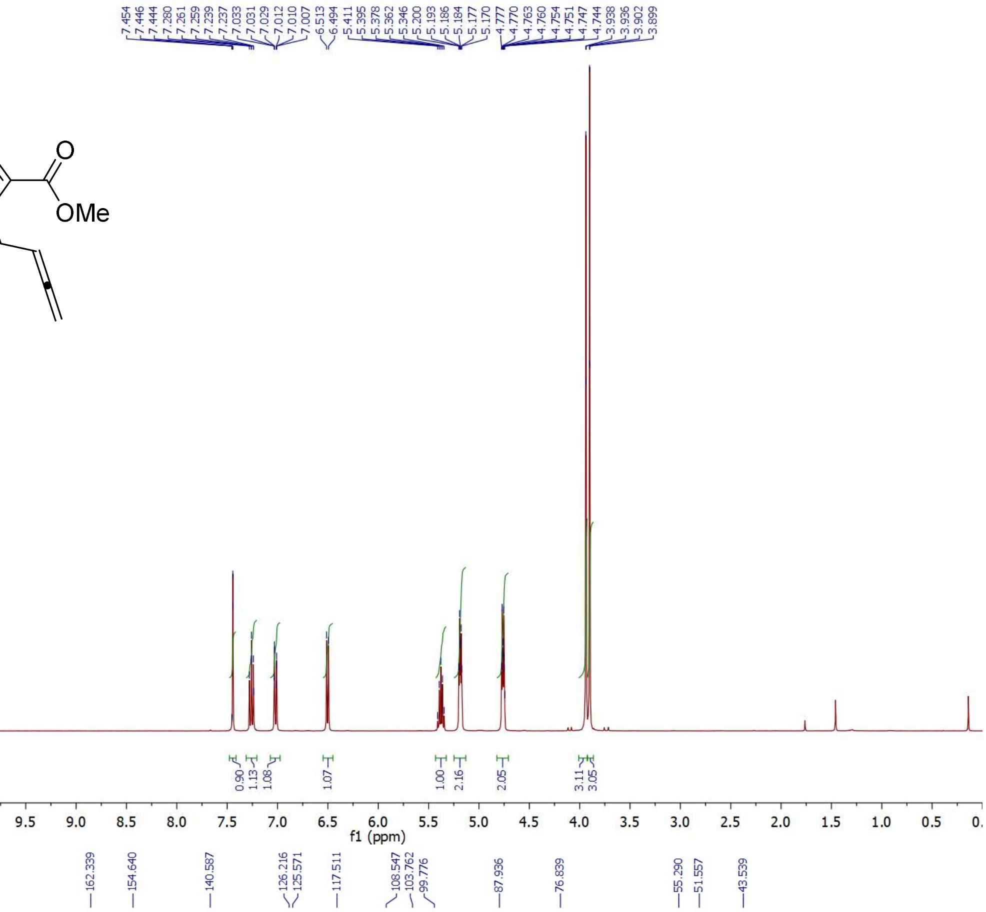
MeO
O
OEt
N
12c
7.32 7.32 7.30 7.30 7.30 7.21 7.20 7.05 7.05 7.02 7.02 7.00 5.38 5.36 5.35 5.33 5.31 5.18 5.17 5.16 5.15 5.15 4.76 4.75 4.74 4.74 4.73 4.73 4.39 4.38 4.36 4.34 3.83 1.42 1.40 1.38
1.00 0.90 0.97 0.97 0.88 2.13 2.03 2.05 3.22 3.18
f1 (ppm)



208.7 161.9 154.7 134.6 127.4 126.3 116.6 111.7 110.0 102.5 88.0 76.8 60.5 55.6 43.4 14.4
f1 (ppm)


OMe
O
N
OMe

12d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7.444
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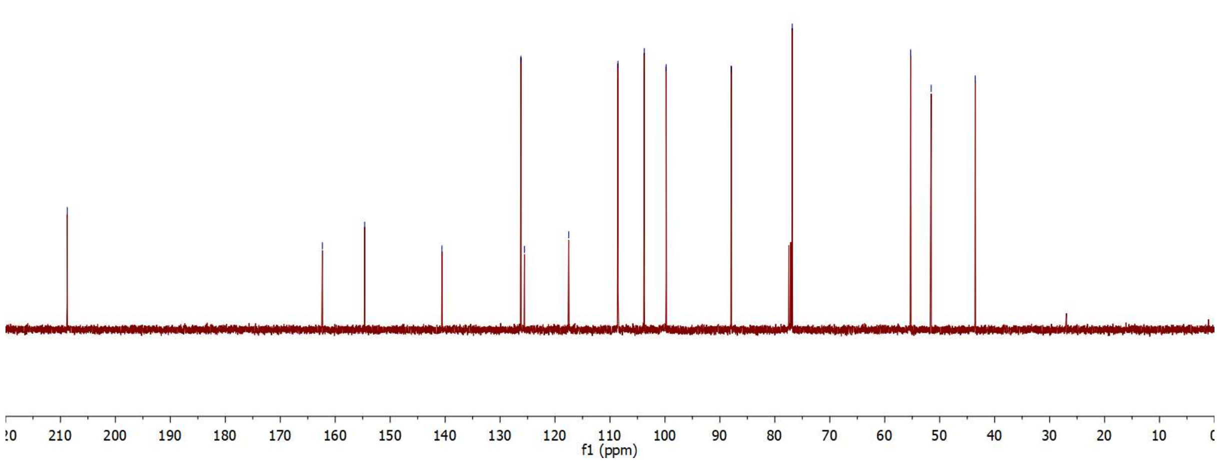
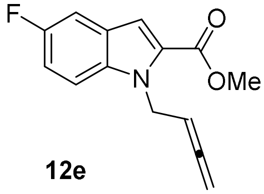
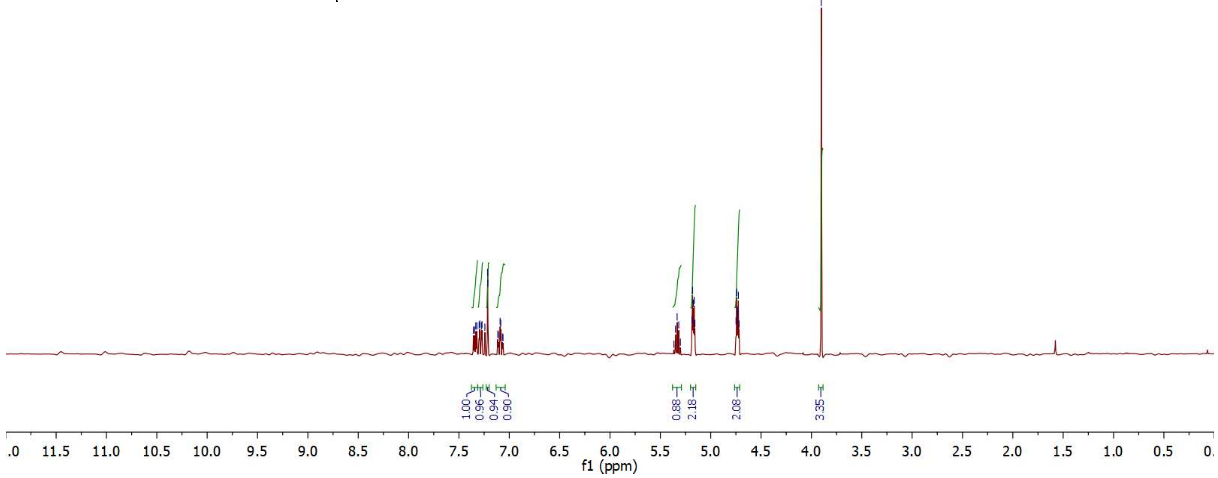
7.261
7.259
7.239
7.237
7.033
7.031
7.029
7.012
7.010
7.007
6.513
6.494
5.411
5.395
5.378
5.362
5.346
5.200
5.193
5.186
5.184
5.177
5.170
4.777
4.770
4.763
4.760
4.754
4.751
4.747
4.744
3.938
3.936
3.902
3.899
0.90
1.13
1.08
1.07
1.00
2.16
2.05
3.11
3.05
f1 (ppm)

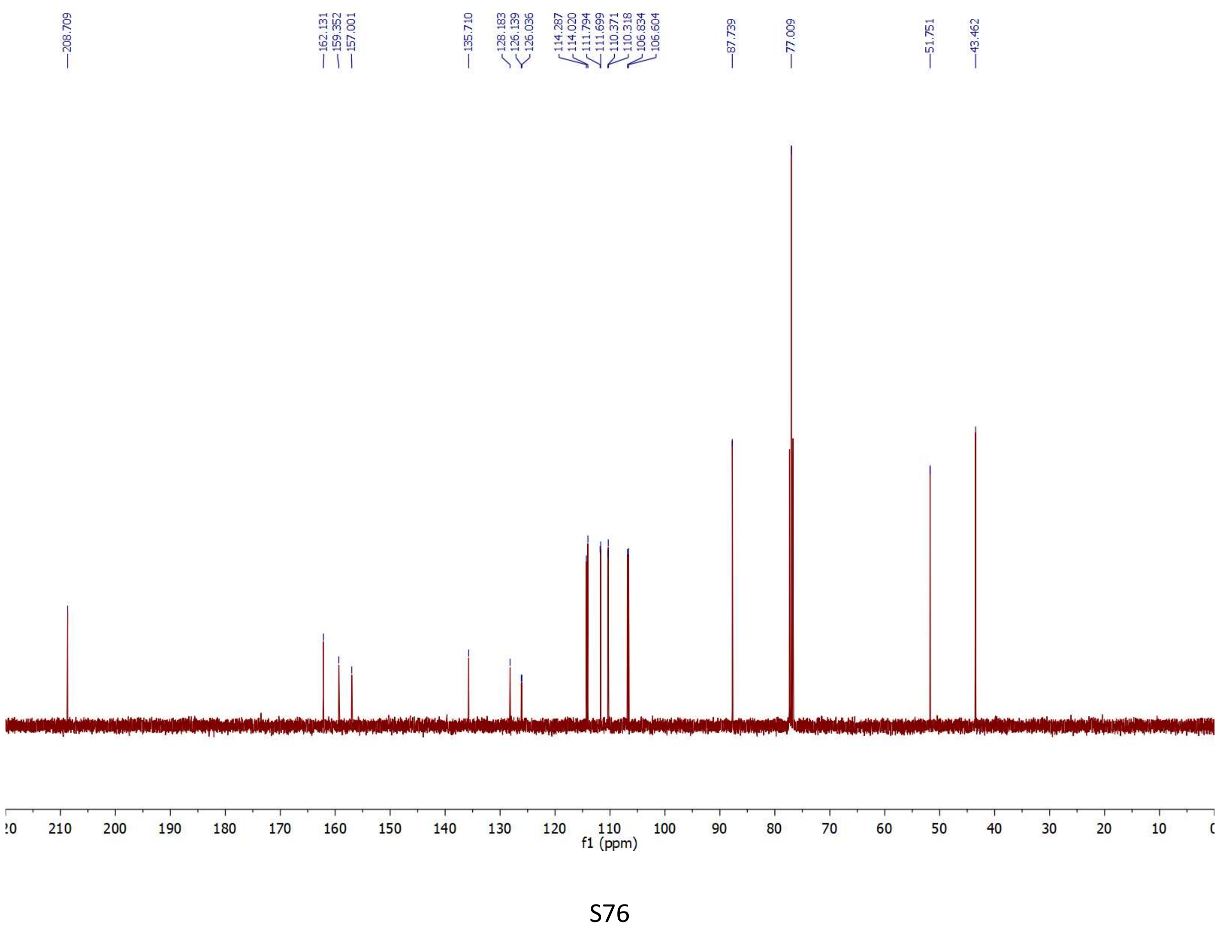

208.755
162.339
154.640
140.587
126.216
125.571
117.511
108.547
103.762
99.776
87.936
76.839
55.290
51.557
43.539
f1 (ppm)



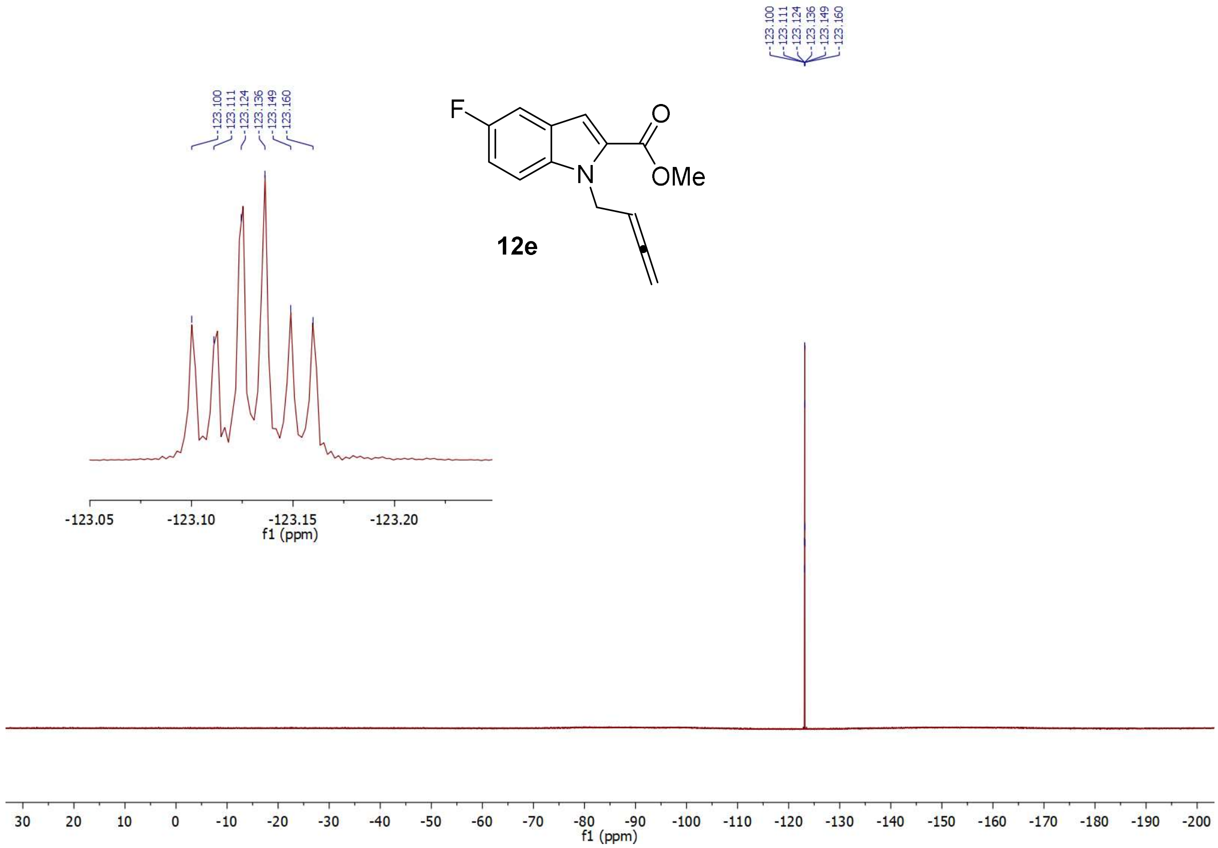
12e



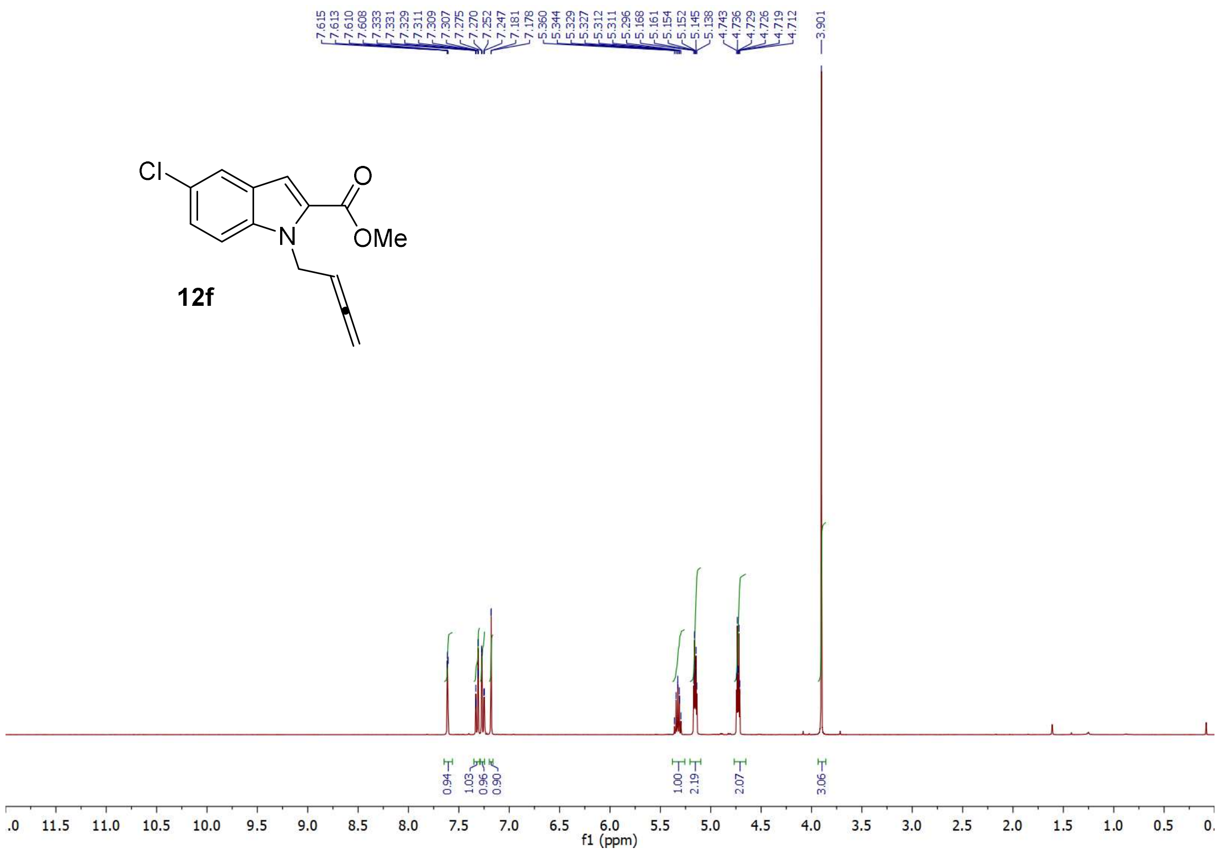
7.356
7.345
7.333
7.322
7.299
7.293
7.277
7.271
7.242
7.216
7.213
7.114
7.108
7.091
7.085
7.068
7.062
5.366
5.349
5.333
5.317
5.301
5.187
5.180
5.172
5.164
5.157
4.749
4.742
4.735
4.732
4.725
4.718
3.902
1.00
0.96
0.94
0.90
0.88
2.18
2.08
3.35
f1 (ppm)



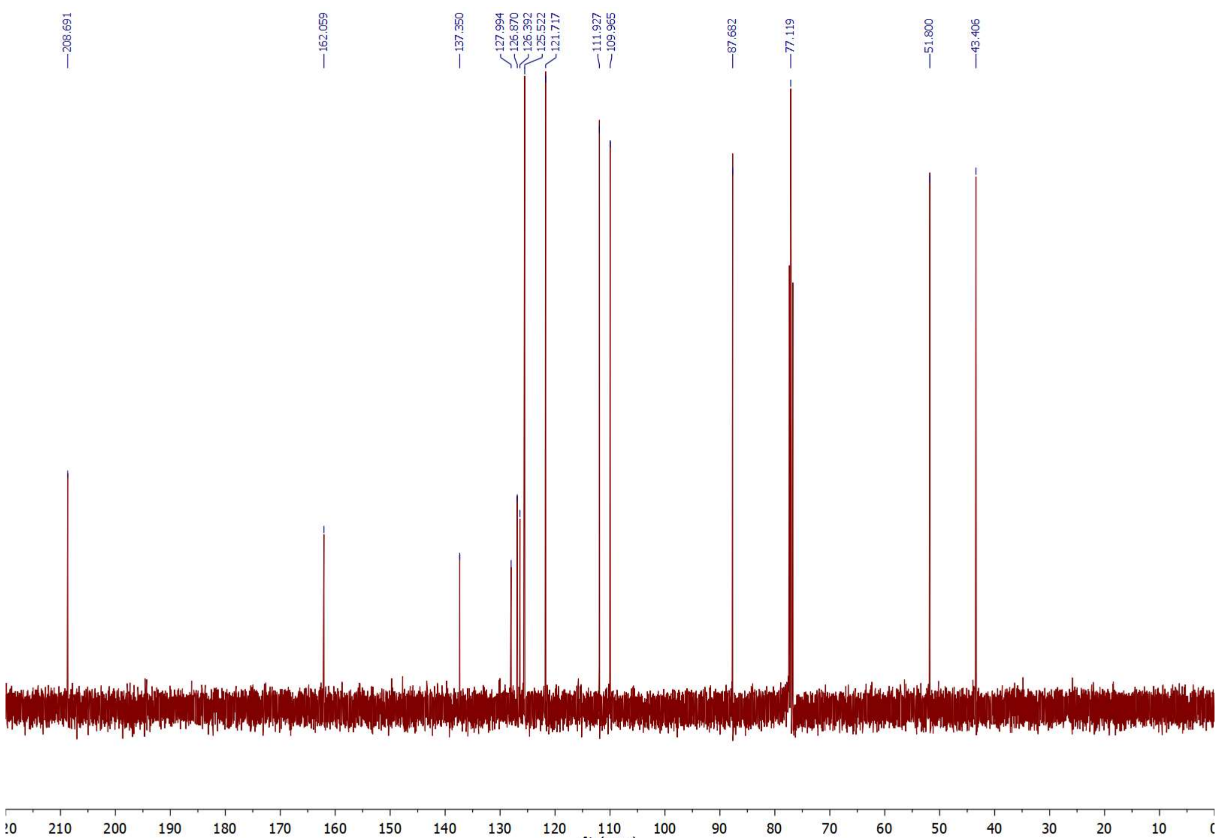
208.709
162.131
159.352
157.001
135.710
128.183
126.139
126.036
114.287
114.020
111.794
111.699
110.371
110.318
106.834
106.604
87.739
77.009
51.751
43.462
f1 (ppm)



-123.100
-123.111
-123.124
-123.136
-123.149
-123.160
12e
OMe
-123.05
-123.10
-123.15
-123.20
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


Cl
O
OMe
N
7.615
7.613
7.610
7.608
7.333
7.331
7.329
7.311
7.309
7.307
7.275
7.270
7.252
7.247
7.181
7.178
5.360
5.344
5.329
5.327
5.312
5.311
5.296
5.168
5.161
5.154
5.152
5.145
5.138
4.743
4.736
4.729
4.726
4.719
4.712
3.901
0.94
1.03
0.96
0.90
1.00
2.19
2.07
3.06
f1 (ppm)

12f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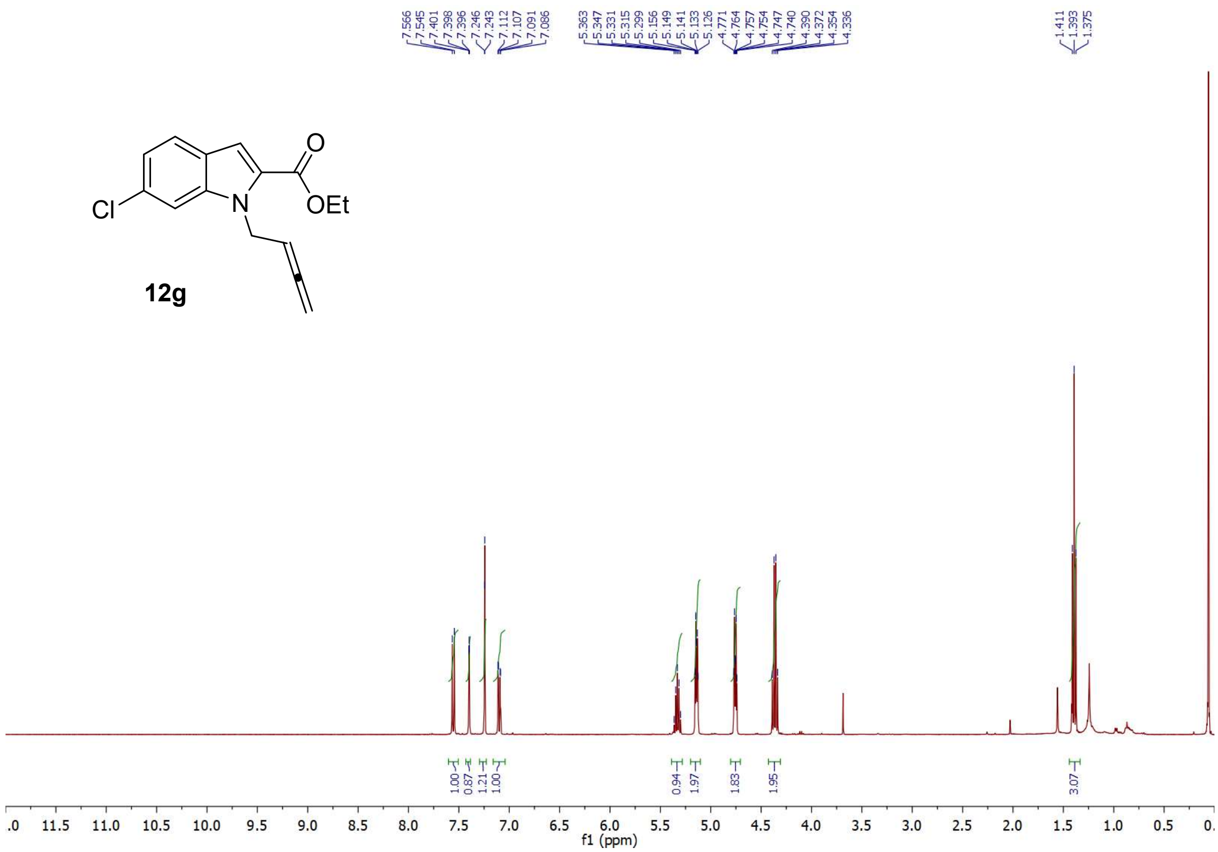
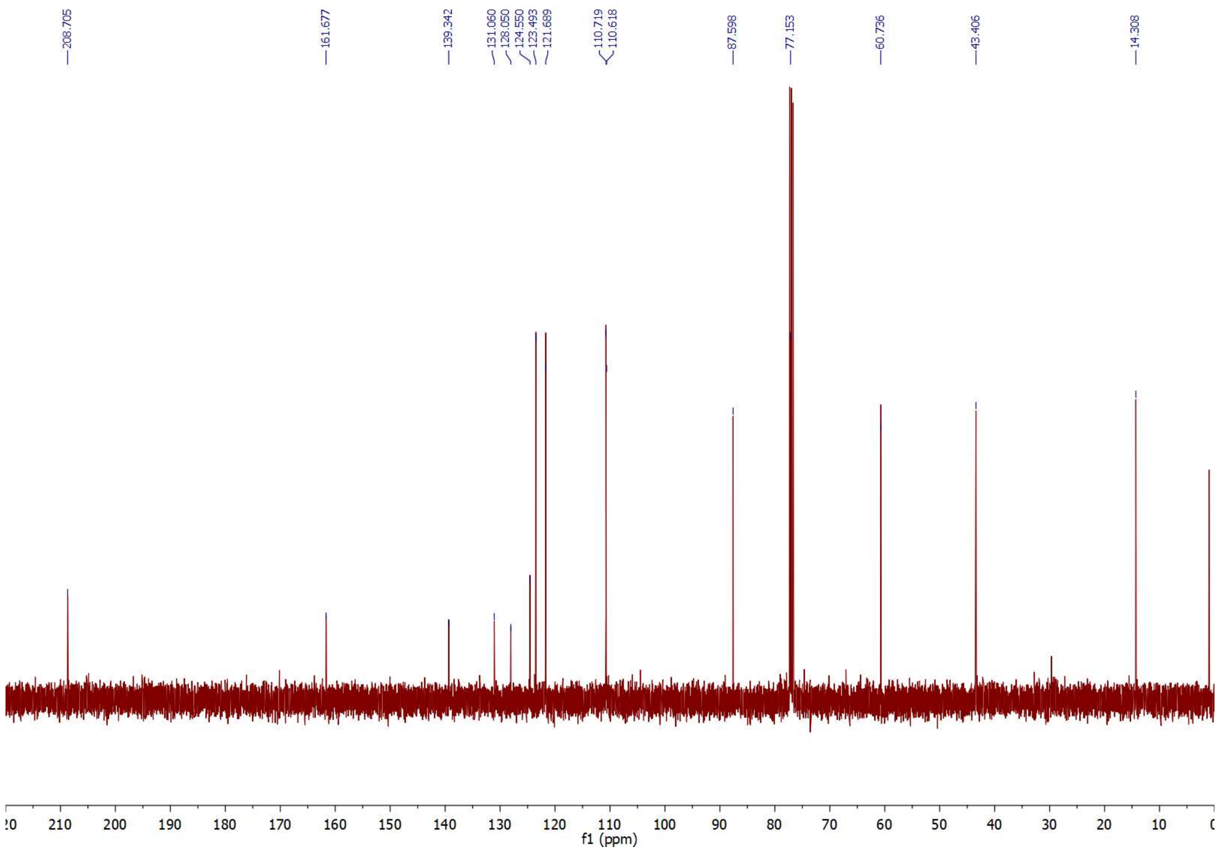
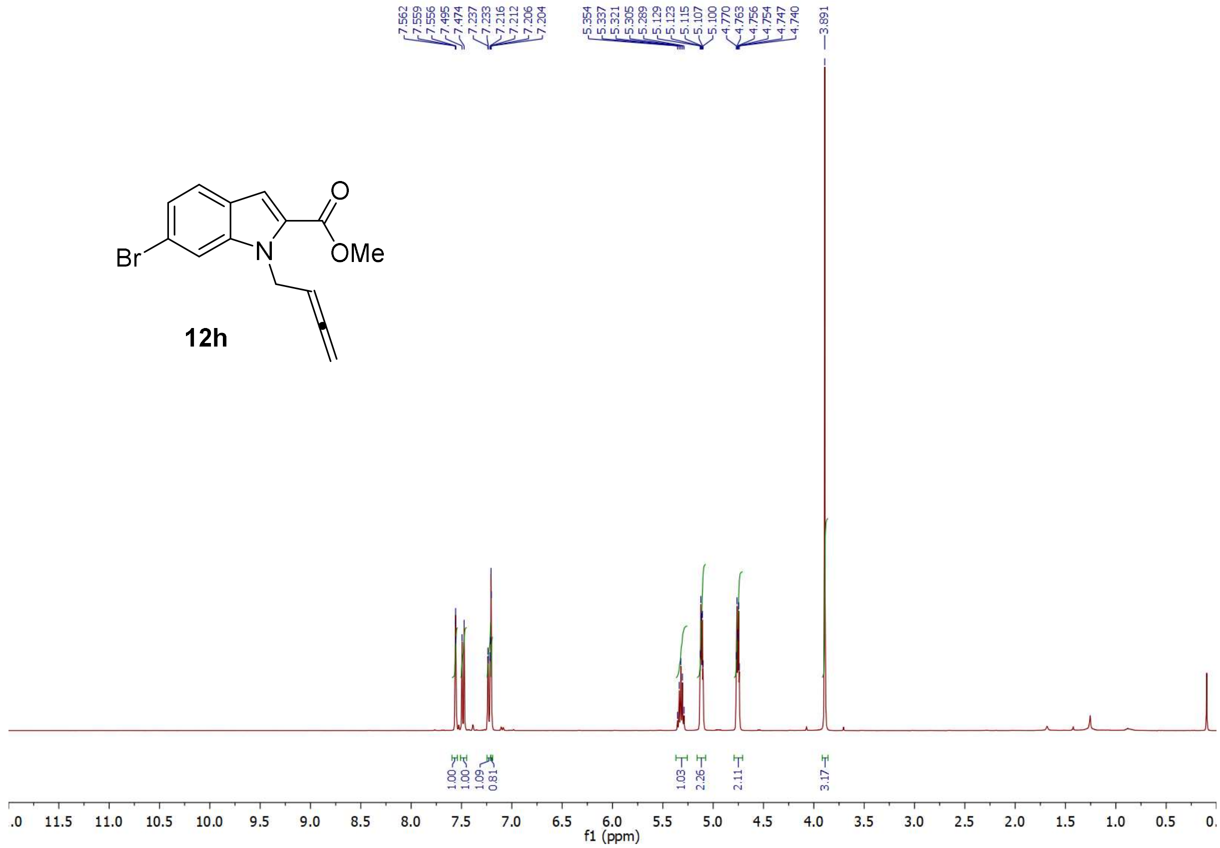
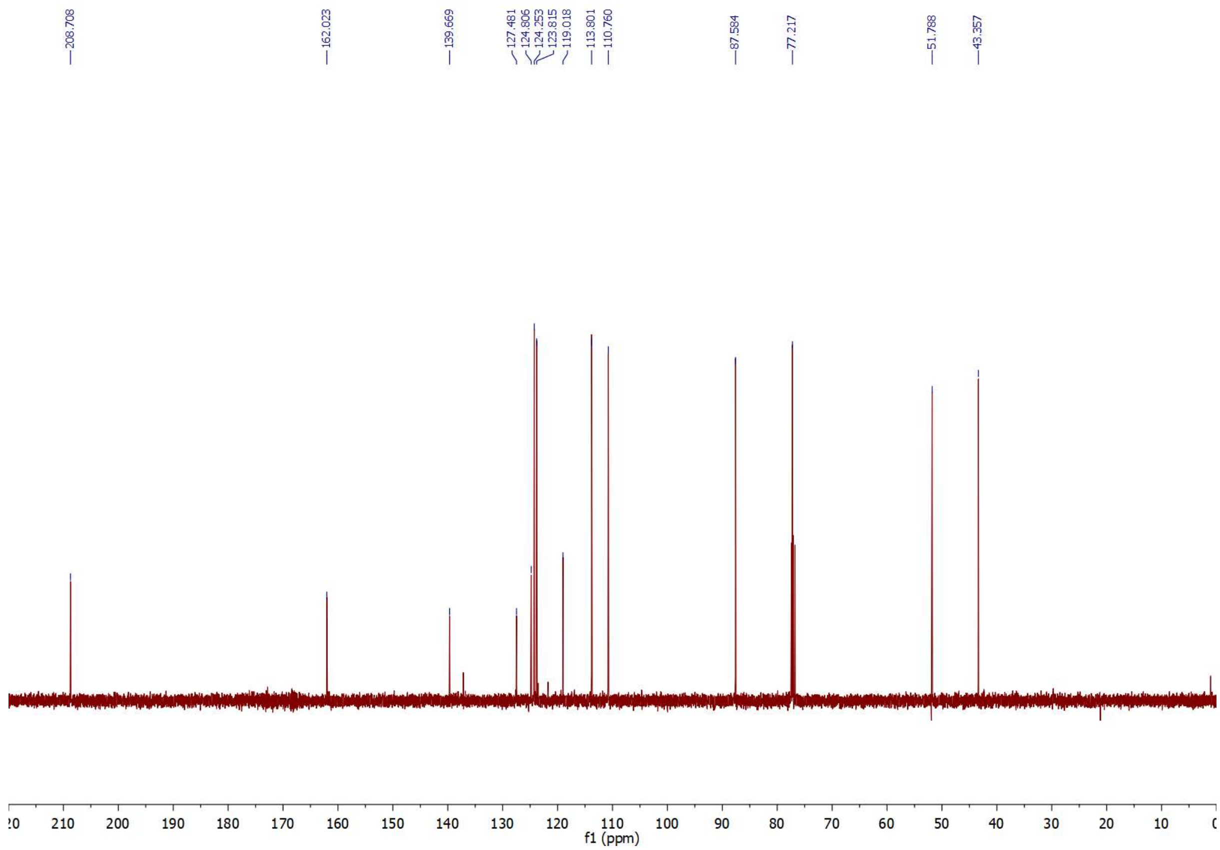
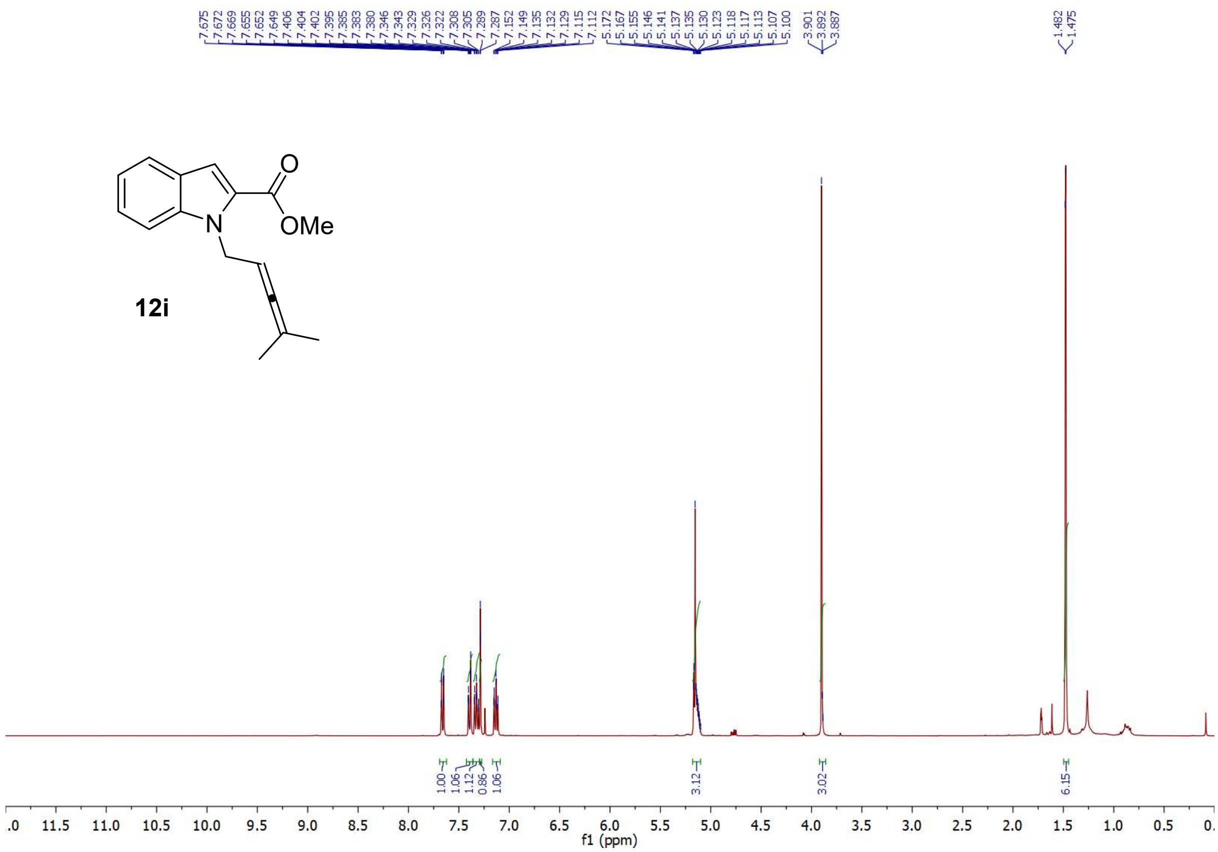
162.059
137.350
127.994
126.870
126.392
125.522
121.717
111.927
109.965
87.682
77.119
51.800
43.406
f1 (ppm)


OEt
Cl
N
O
12g
7.566
7.545
7.401
7.398
7.396
7.246
7.243
7.112
7.107
7.091
7.086
5.363
5.347
5.331
5.315
5.299
5.156
5.149
5.141
5.133
5.126
4.771
4.764
4.757
4.754
4.747
4.740
4.390
4.372
4.354
4.336
1.411
1.393
1.375
1.00
0.87
1.21
1.00
0.94
1.97
1.83
1.95
3.07
f1 (ppm)

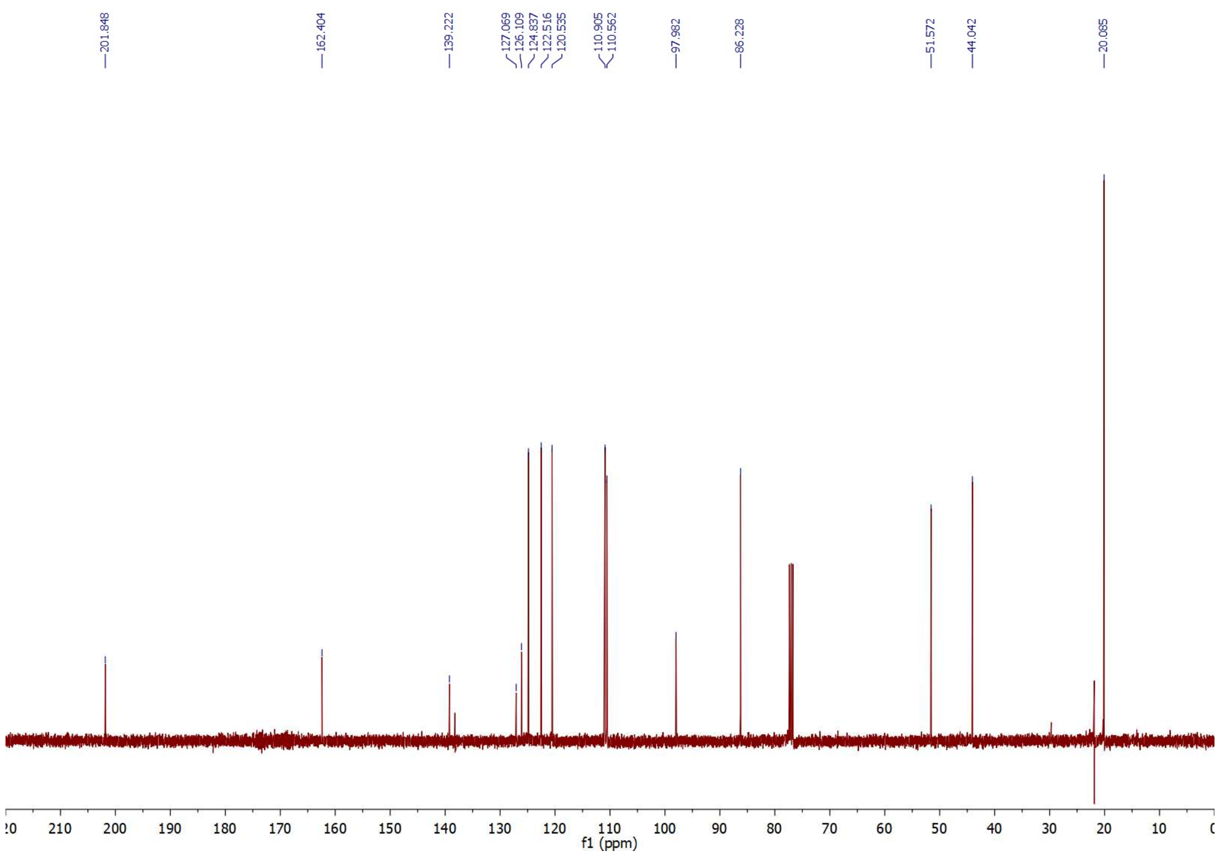

208.705
161.677
139.342
131.060
128.050
124.550
123.493
121.689
110.719
110.618
87.598
77.153
60.736
43.406
14.308
f1 (ppm)


Br
N
O
OMe
12h
7.562
7.559
7.556
7.495
7.474
7.237
7.233
7.216
7.212
7.206
7.204
5.354
5.337
5.321
5.305
5.289
5.129
5.123
5.115
5.107
5.100
4.770
4.763
4.756
4.754
4.747
4.740
3.891
1.00
1.00
1.09
0.81
1.03
2.26
2.11
3.17
f1 (ppm)

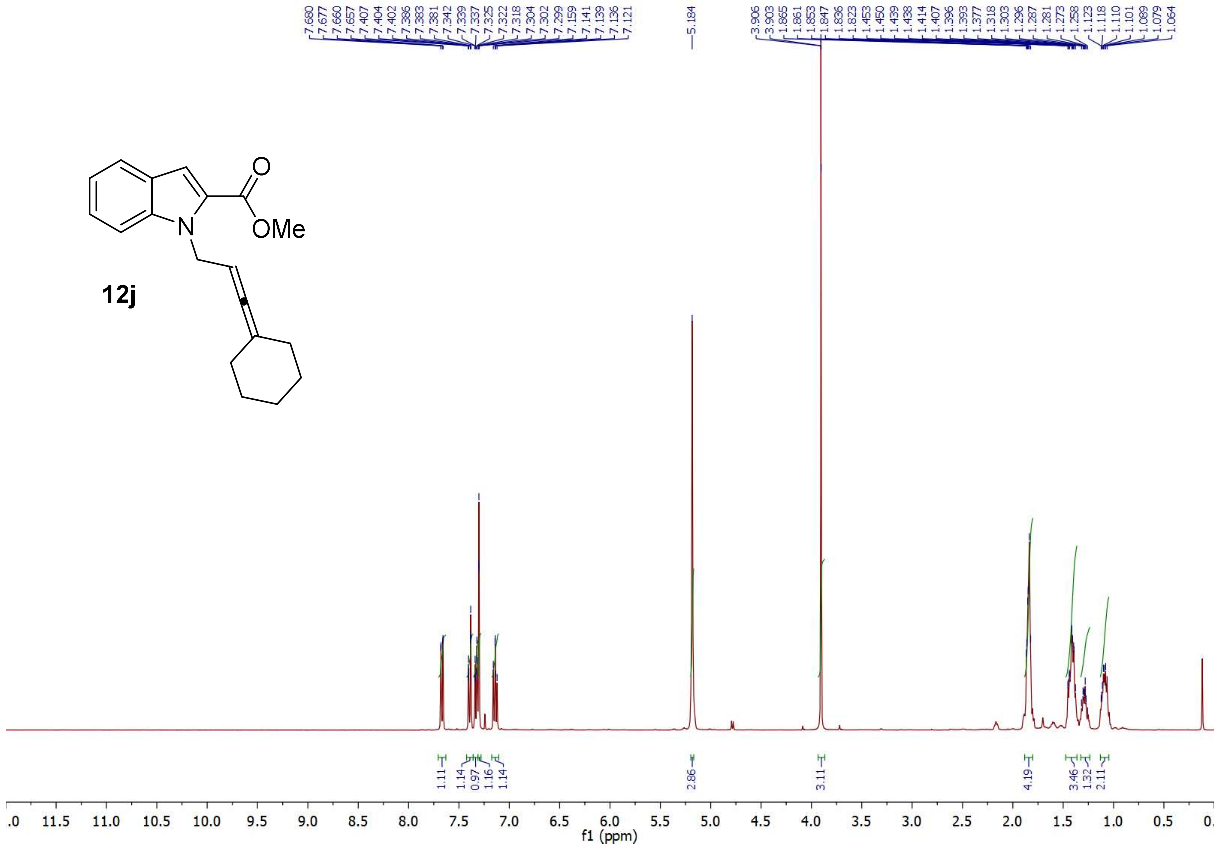

208.708
162.023
139.669
127.481
124.806
124.253
123.815
119.018
113.801
110.760
87.584
77.217
51.788
43.357
f1 (ppm)



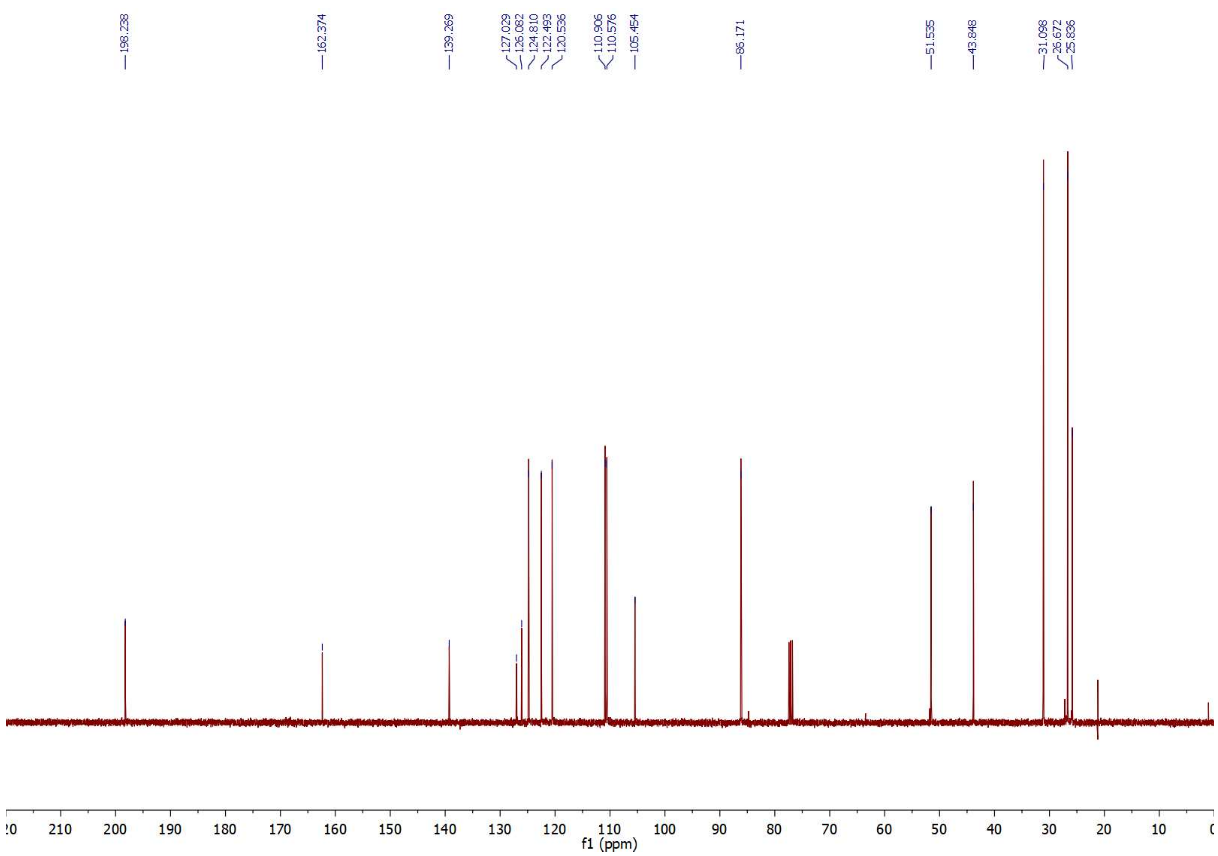
7.675 7.672 7.669 7.655 7.652 7.649 7.406 7.404 7.402 7.395 7.385 7.383 7.380 7.346 7.343 7.329 7.326 7.322 7.308 7.305 7.289 7.287 7.152 7.149 7.135 7.132 7.129 7.115 7.112 5.172 5.167 5.155 5.146 5.141 5.137 5.135 5.130 5.123 5.118 5.117 5.113 5.107 5.100
3.901 3.892 3.887
1.482 1.475
O
N
OMe
12i
1.00 1.06 1.12 0.86 1.06
3.12
3.02
6.15
f1 (ppm)

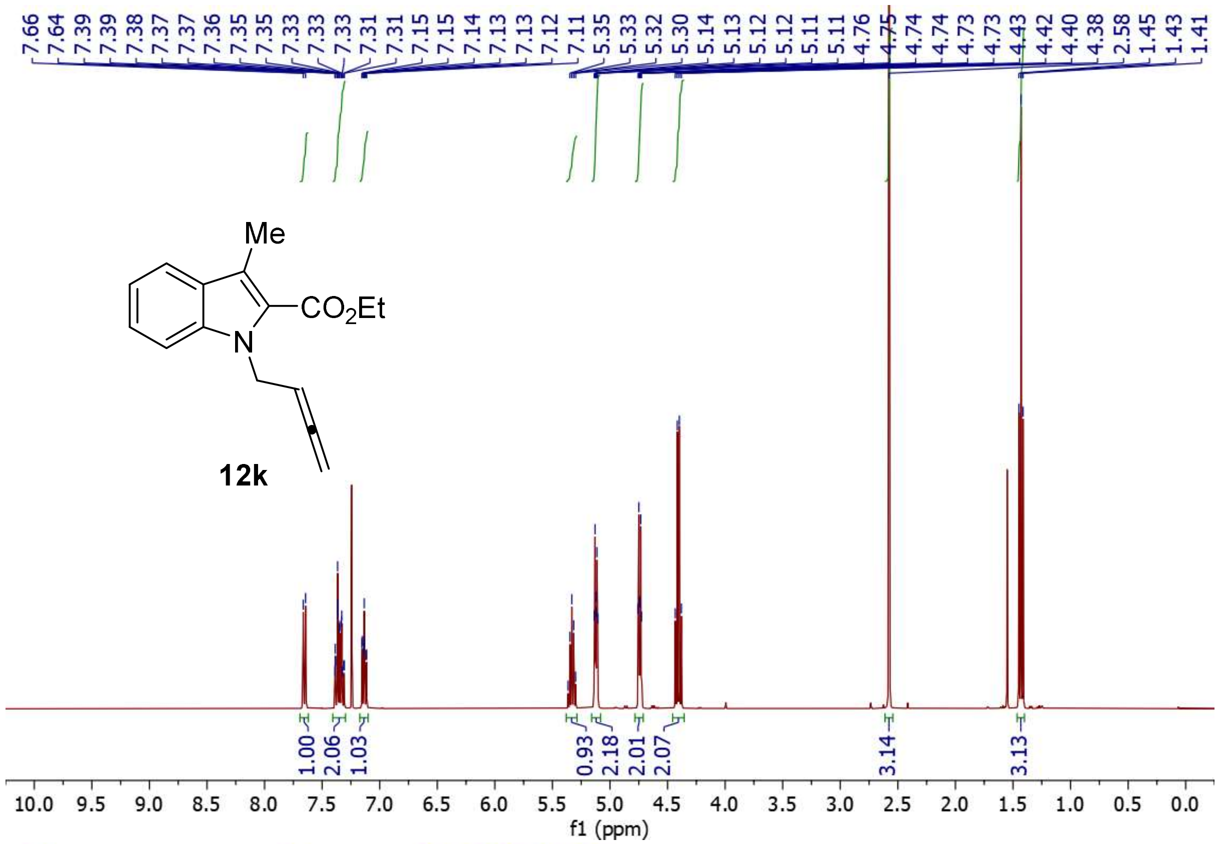


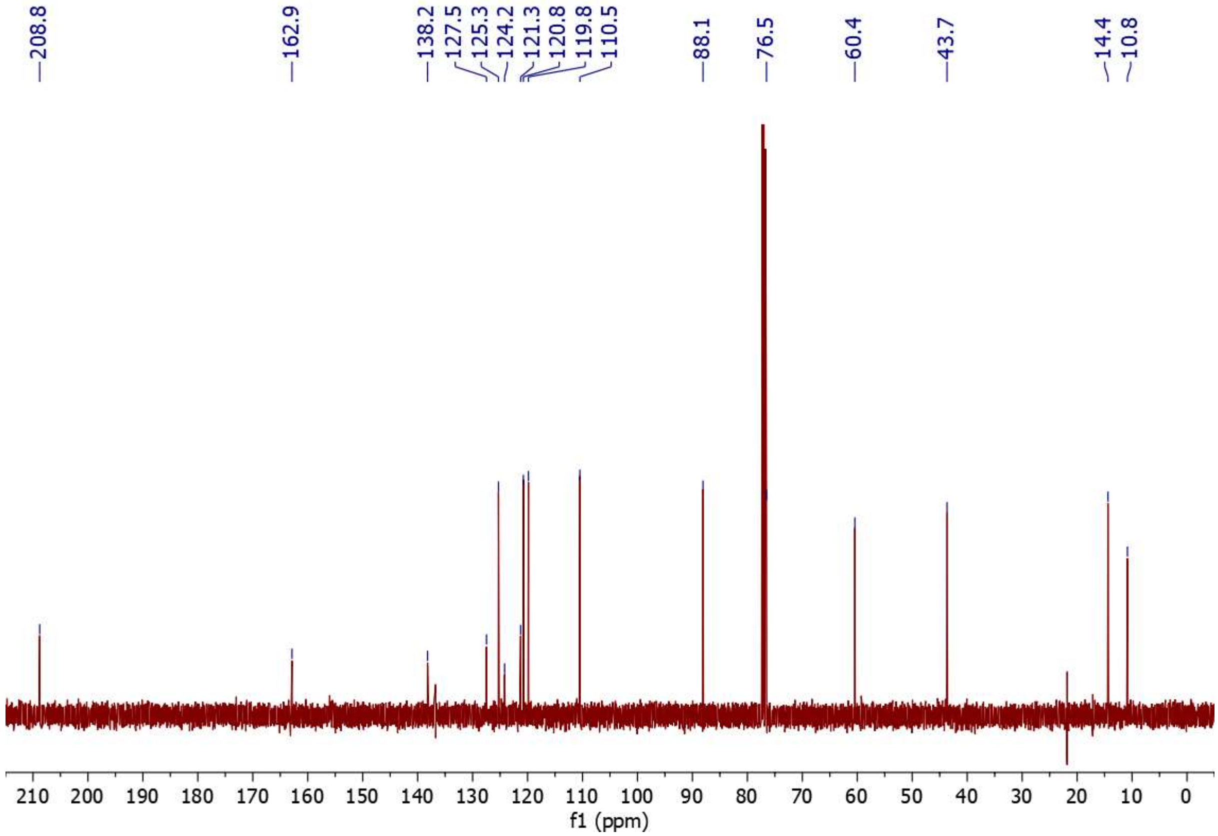
201.848
162.404
139.222
127.069 126.109 124.837 122.516 120.535
110.905 110.562
97.982
86.228
51.572
44.042
20.085
f1 (ppm)

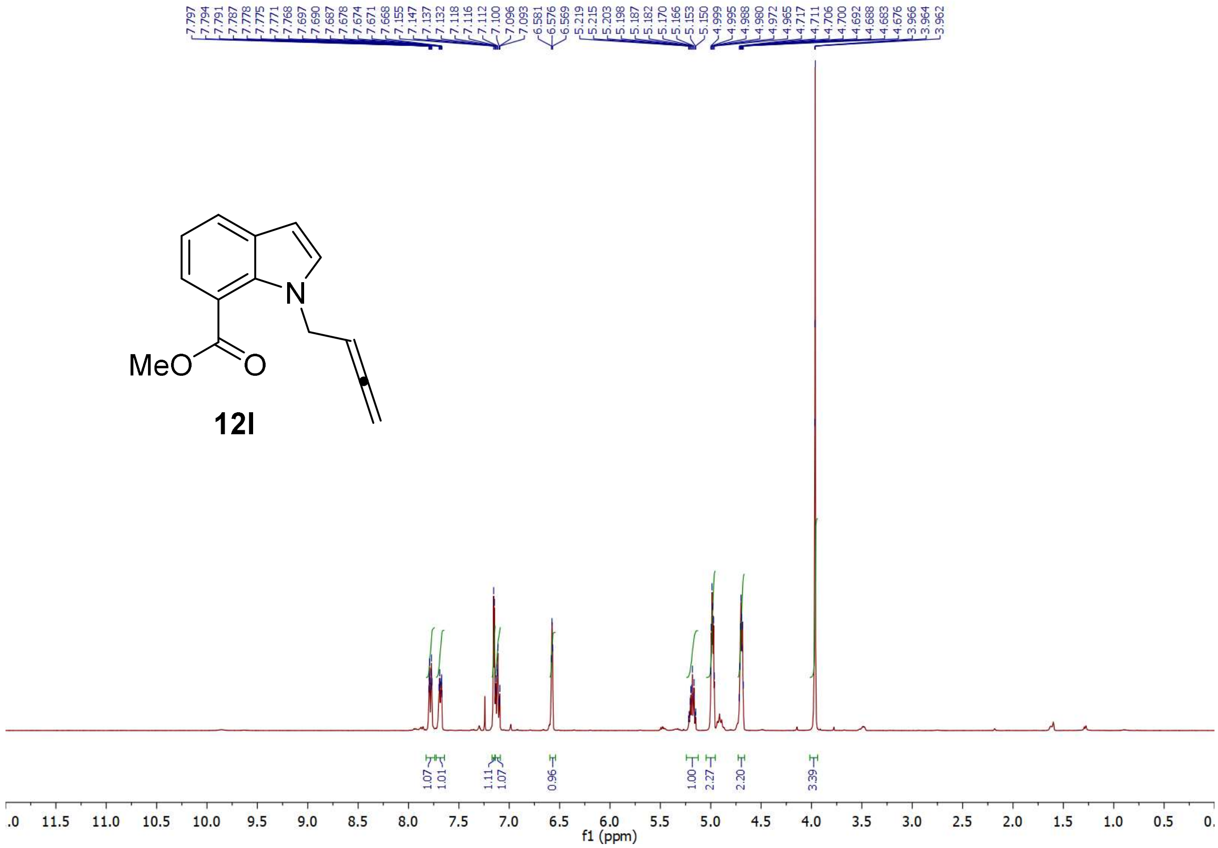


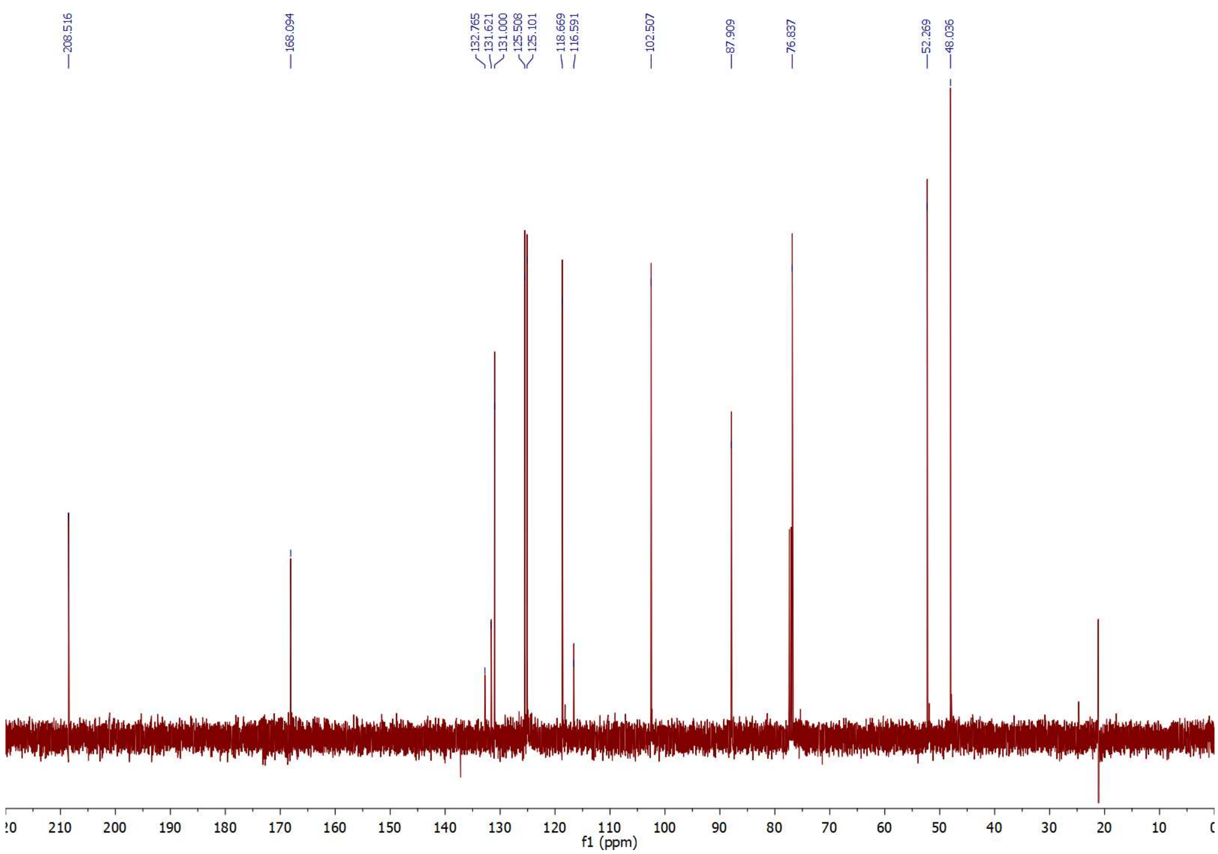
12j

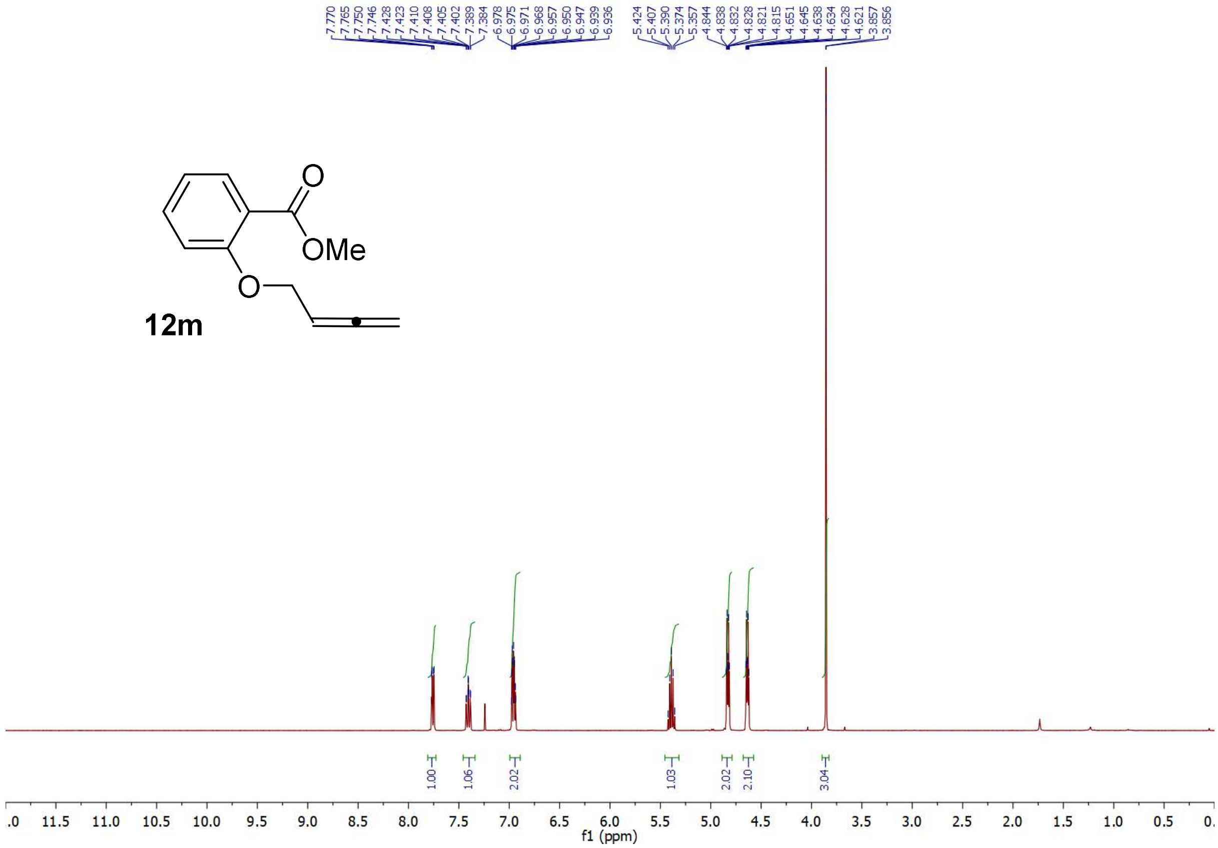


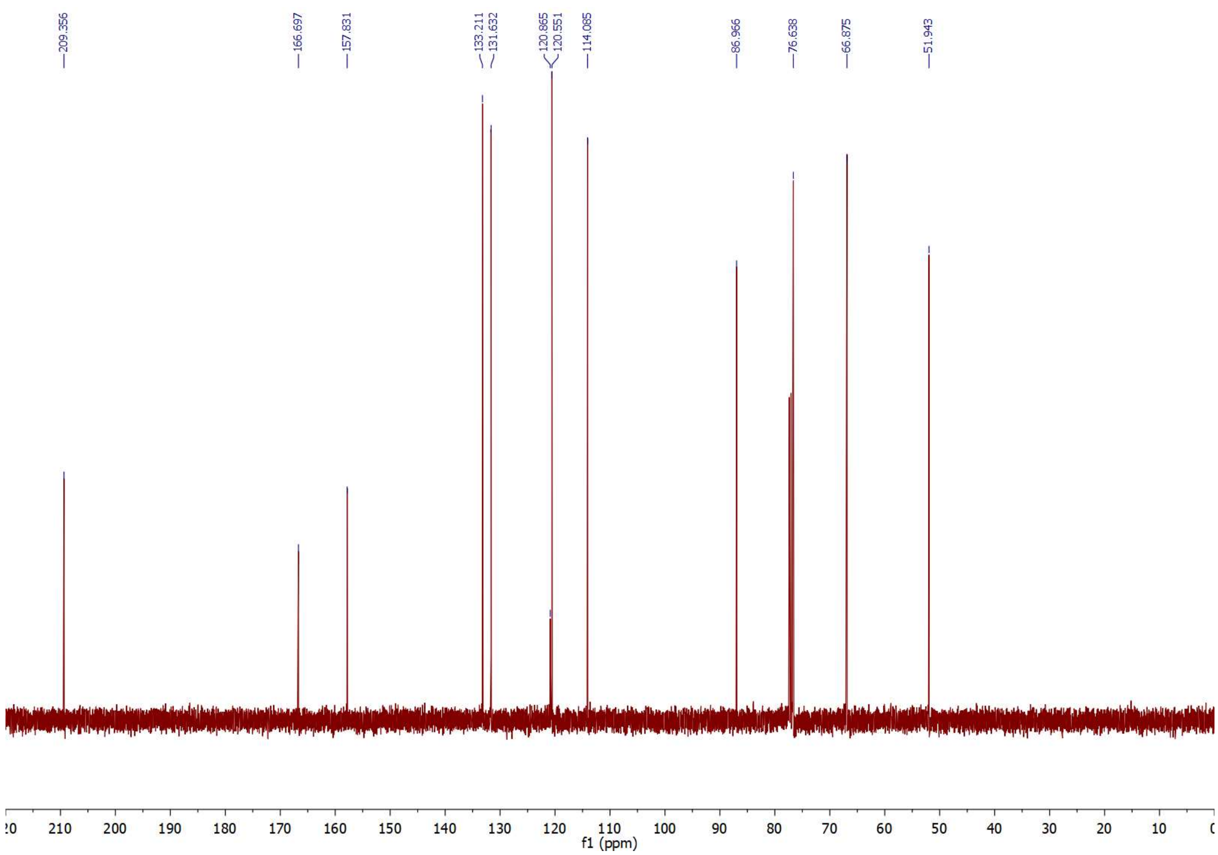

7.66 7.64 7.39 7.39 7.38 7.37 7.37 7.36 7.35 7.35 7.33 7.33 7.33 7.31 7.31 7.15 7.15 7.14 7.13 7.13 7.12 7.11 5.35 5.33 5.32 5.30 5.14 5.13 5.12 5.12 5.11 5.11 4.76 4.75 4.74 4.74 4.73 4.73 4.43 4.42 4.40 4.38 2.58 1.45 1.43 1.41
Me
CO_2Et
N
12k
1.00 2.06 1.03 0.93 2.18 2.01 2.07 3.14 3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

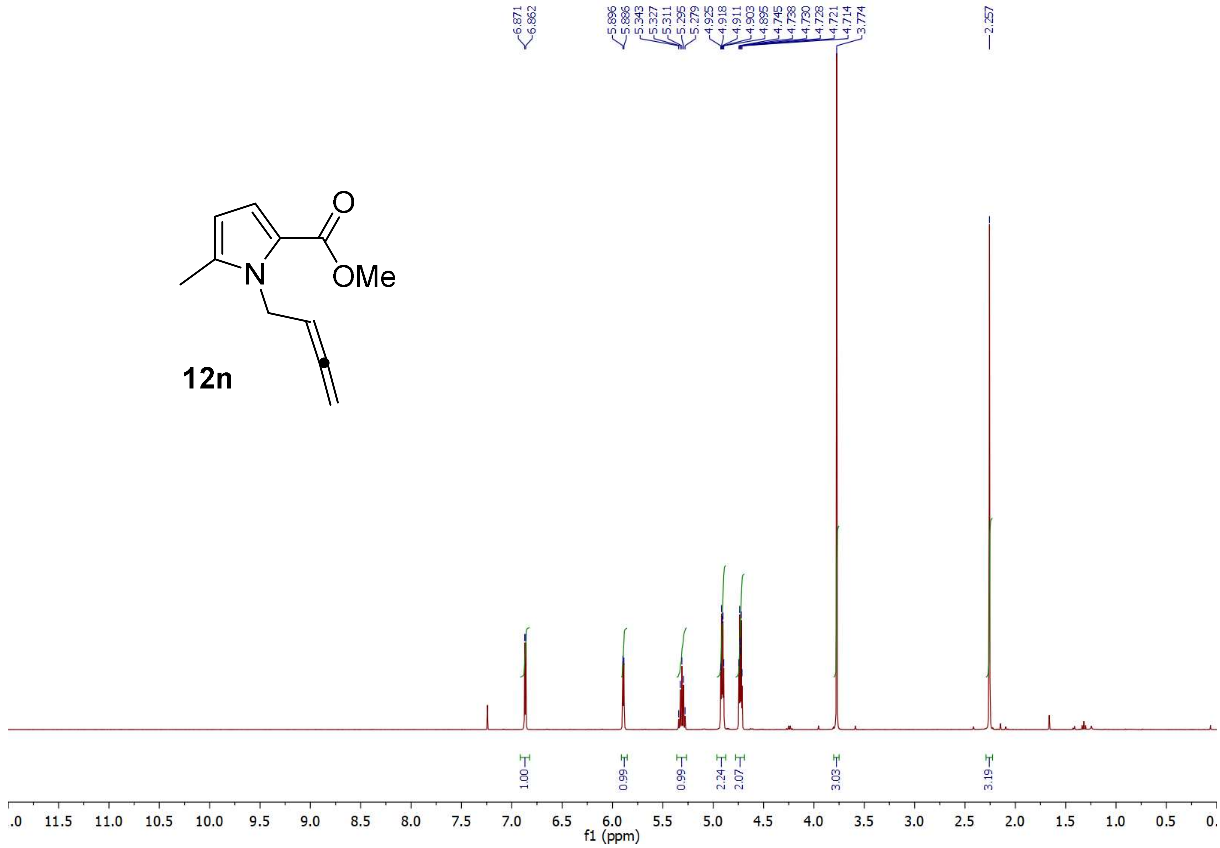

208.8 162.9 138.2 127.5 125.3 124.2 121.3 120.8 119.8 110.5 88.1 76.5 60.4 43.7 14.4 10.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.797 7.794 7.791 7.787 7.778 7.775 7.771 7.768 7.697 7.690 7.687 7.678 7.674 7.671 7.668 7.155 7.147 7.137 7.132 7.118 7.116 7.112 7.100 7.096 7.093 6.581 6.576 6.569 5.219 5.215 5.203 5.198 5.187 5.182 5.170 5.166 5.153 5.150 4.999 4.995 4.988 4.980 4.972 4.965 4.717 4.711 4.706 4.700 4.692 4.688 4.683 4.676 3.966 3.964 3.962
N
MeO
O
12l
1.07
1.01
1.11
1.07
0.96
1.00
2.27
2.20
3.39
f1 (ppm)


208.516
168.094
132.765
131.621
131.000
125.508
125.101
118.669
116.591
102.507
87.909
76.837
52.269
48.036
f1 (ppm)

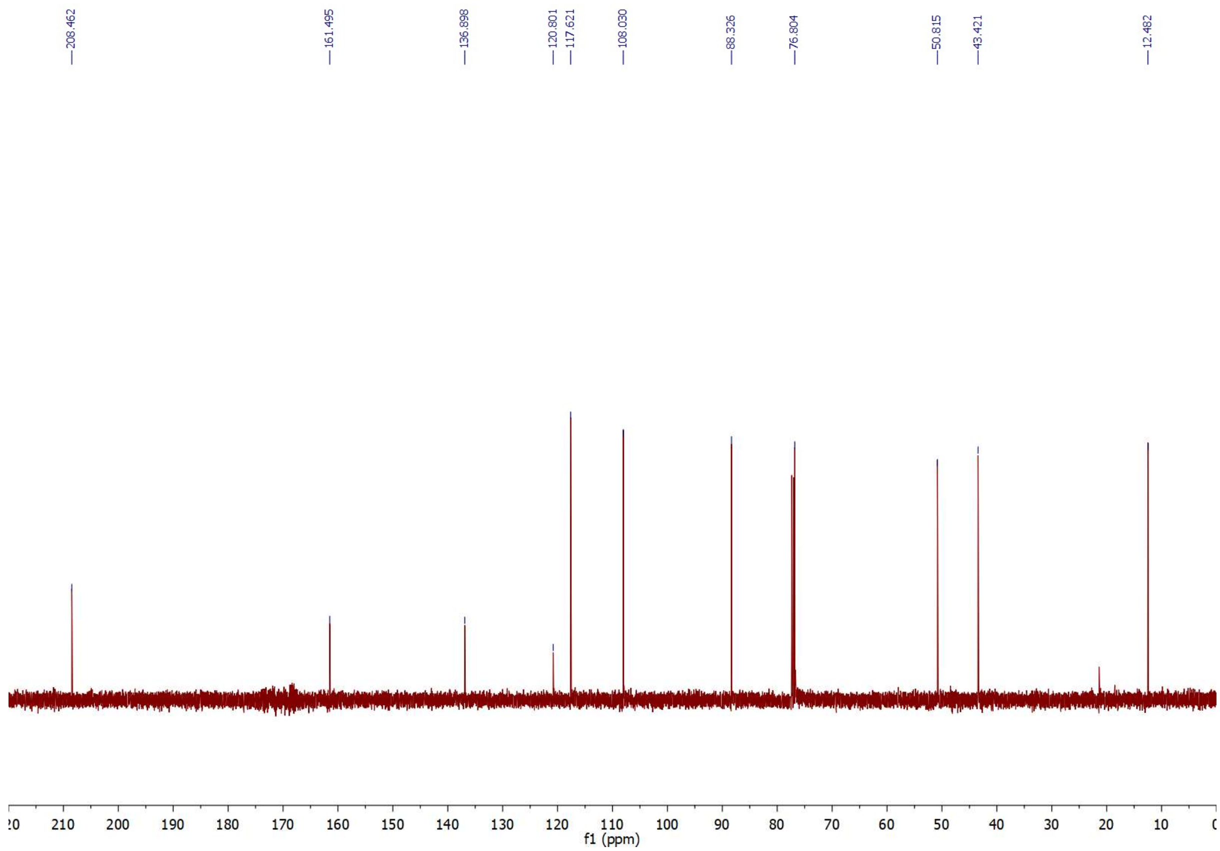

O
OMe
O
12m
f1 (ppm)


209.356
166.697
157.831
133.211
131.632
120.865
120.551
114.085
86.966
76.638
66.875
51.943
f1 (ppm)



12n

6.871
6.862
5.896
5.886
5.343
5.327
5.311
5.295
5.279
4.925
4.918
4.911
4.903
4.895
4.745
4.738
4.730
4.728
4.721
4.714
3.774
2.257
1.00
0.99
0.99
2.24
2.07
3.03
3.19
f1 (ppm)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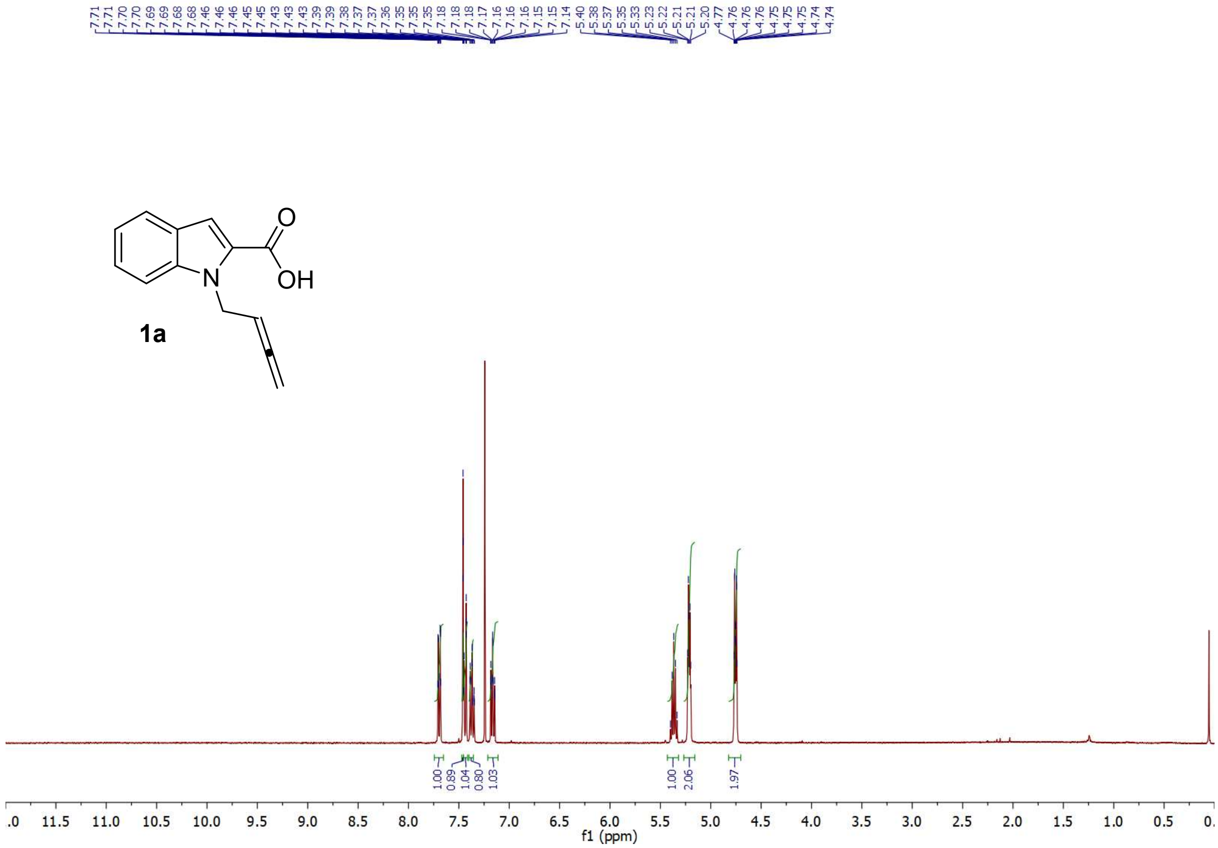
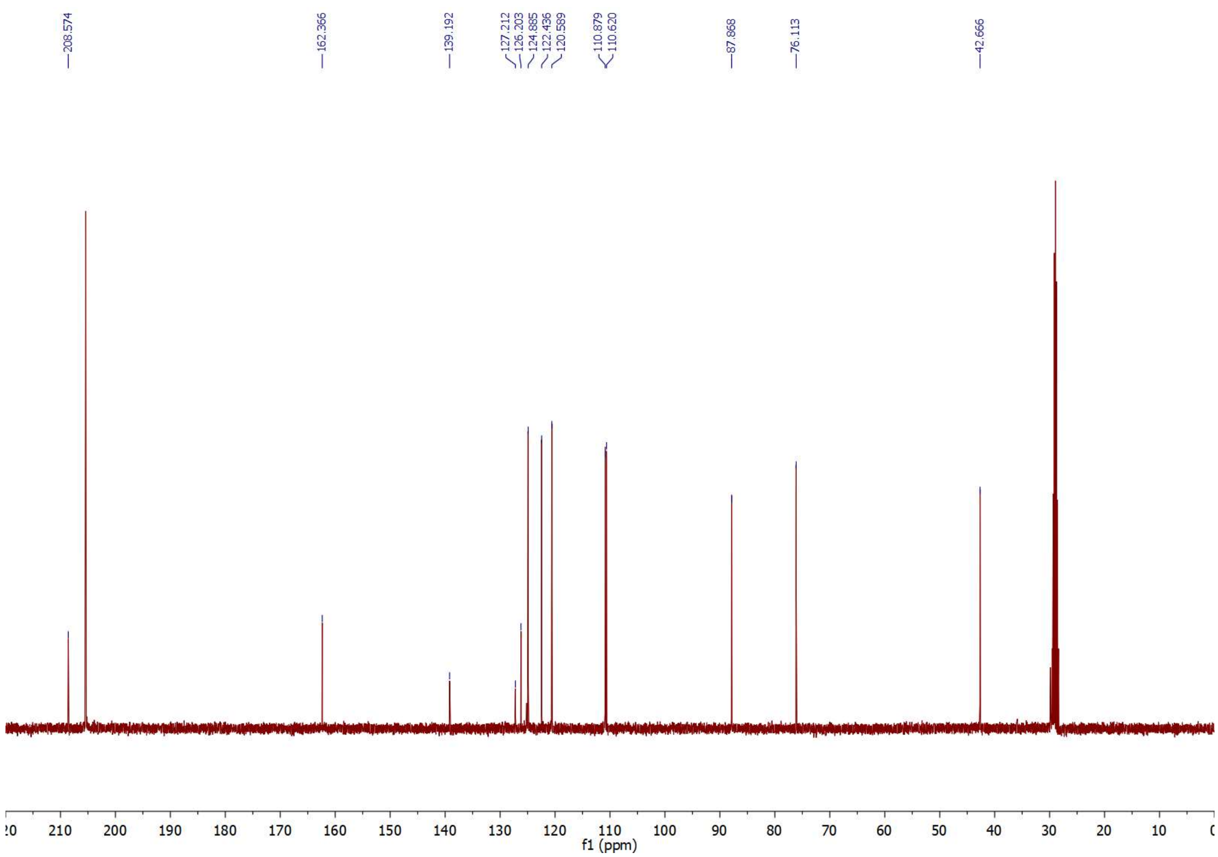
108.030
88.326
76.804
50.815
43.421
12.482
f1 (ppm)


7.71 7.71 7.70 7.69 7.69 7.68 7.46 7.46 7.45 7.43 7.43 7.43 7.39 7.39 7.38 7.37 7.37 7.36 7.35 7.35 7.35 7.18 7.18 7.17 7.16 7.16 7.15 7.15 7.14 5.40 5.38 5.37 5.35 5.33 5.23 5.22 5.21 5.21 5.20 4.77 4.76 4.76 4.75 4.75 4.75 4.74 4.74
O
N
OH
1a
1.00 0.89 1.04 0.80 1.03 1.00 2.06 1.97
f1 (ppm)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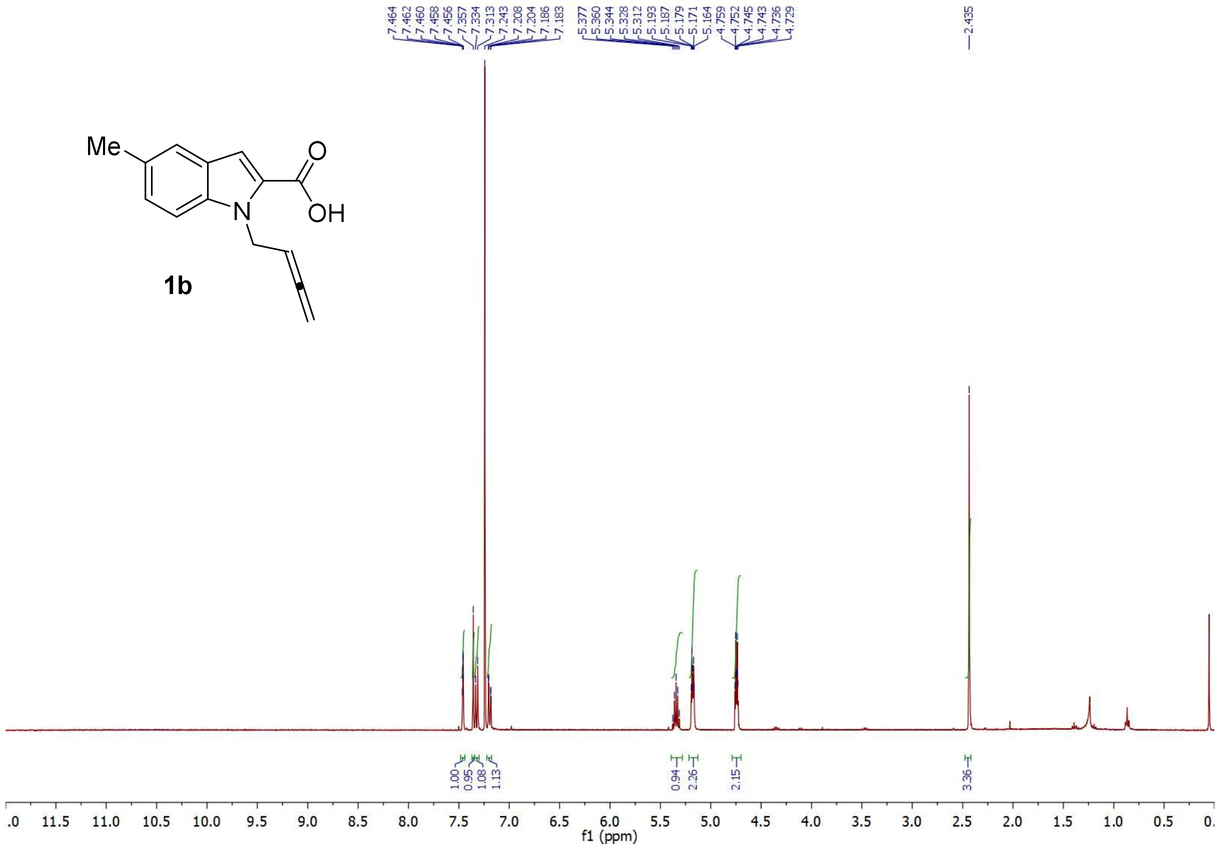
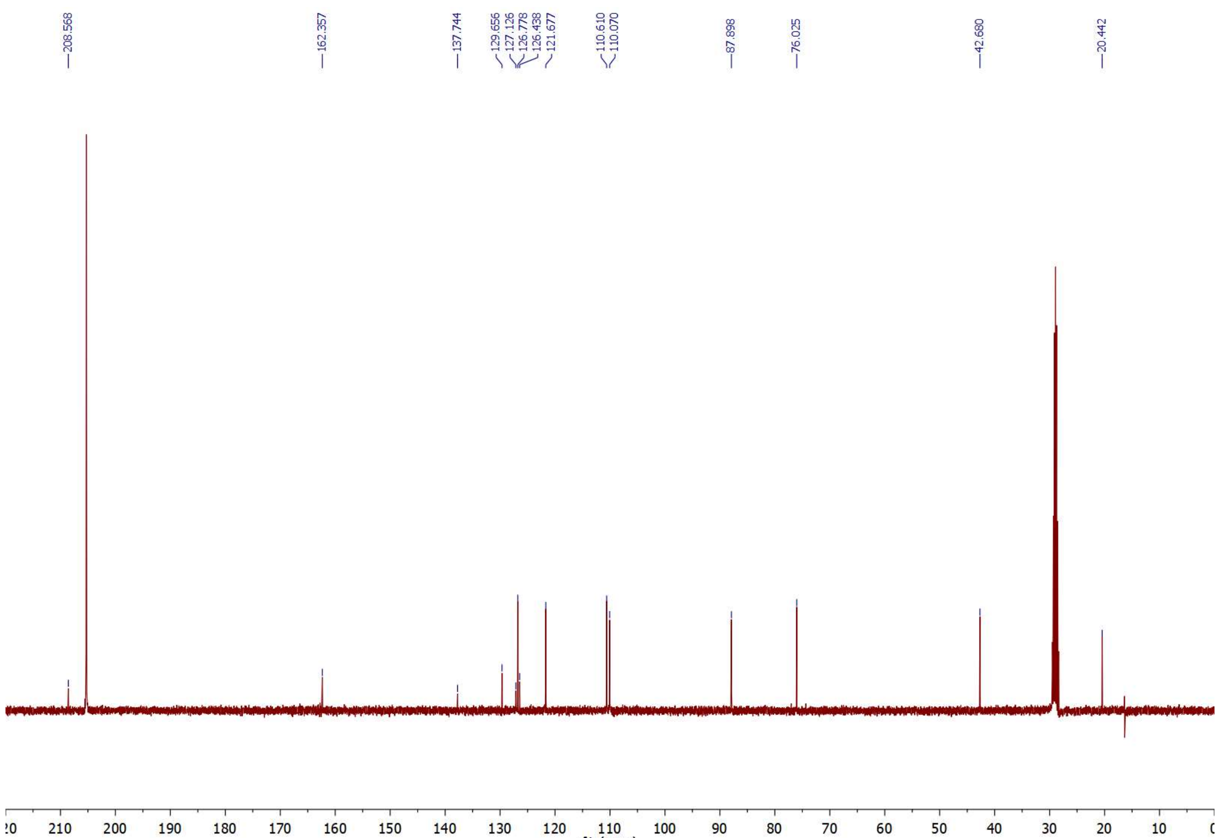
127.212 126.203 124.885 122.436 120.589
110.879 110.620
87.868
76.113
42.666
f1 (ppm)


Me
O
OH
N
1b
7.464
7.462
7.460
7.458
7.456
7.357
7.334
7.313
7.243
7.208
7.204
7.186
7.183
5.377
5.360
5.344
5.328
5.312
5.193
5.187
5.179
5.171
5.164
4.759
4.752
4.745
4.743
4.736
4.729
2.435
1.00
0.95
1.08
1.13
0.94
2.26
2.15
3.36
f1 (ppm)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110.070
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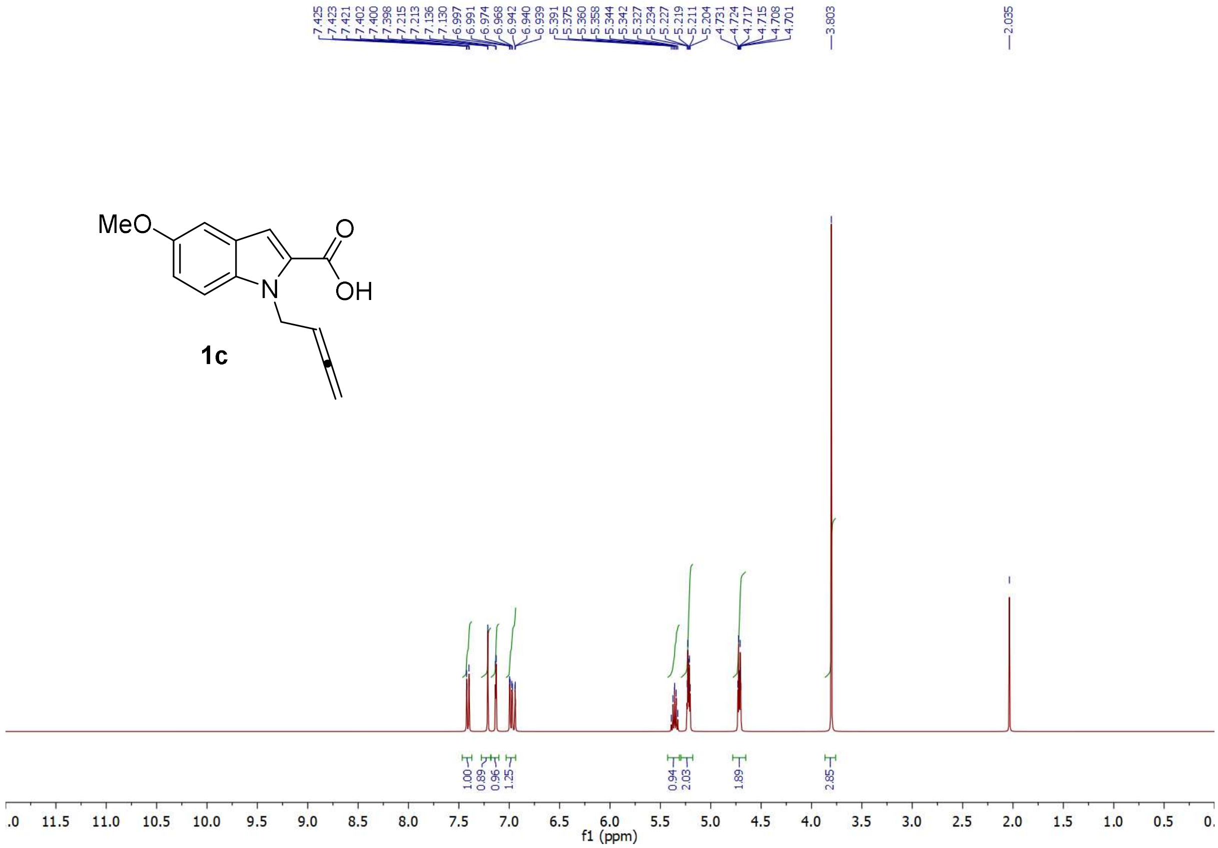
42.680
20.442
f1 (ppm)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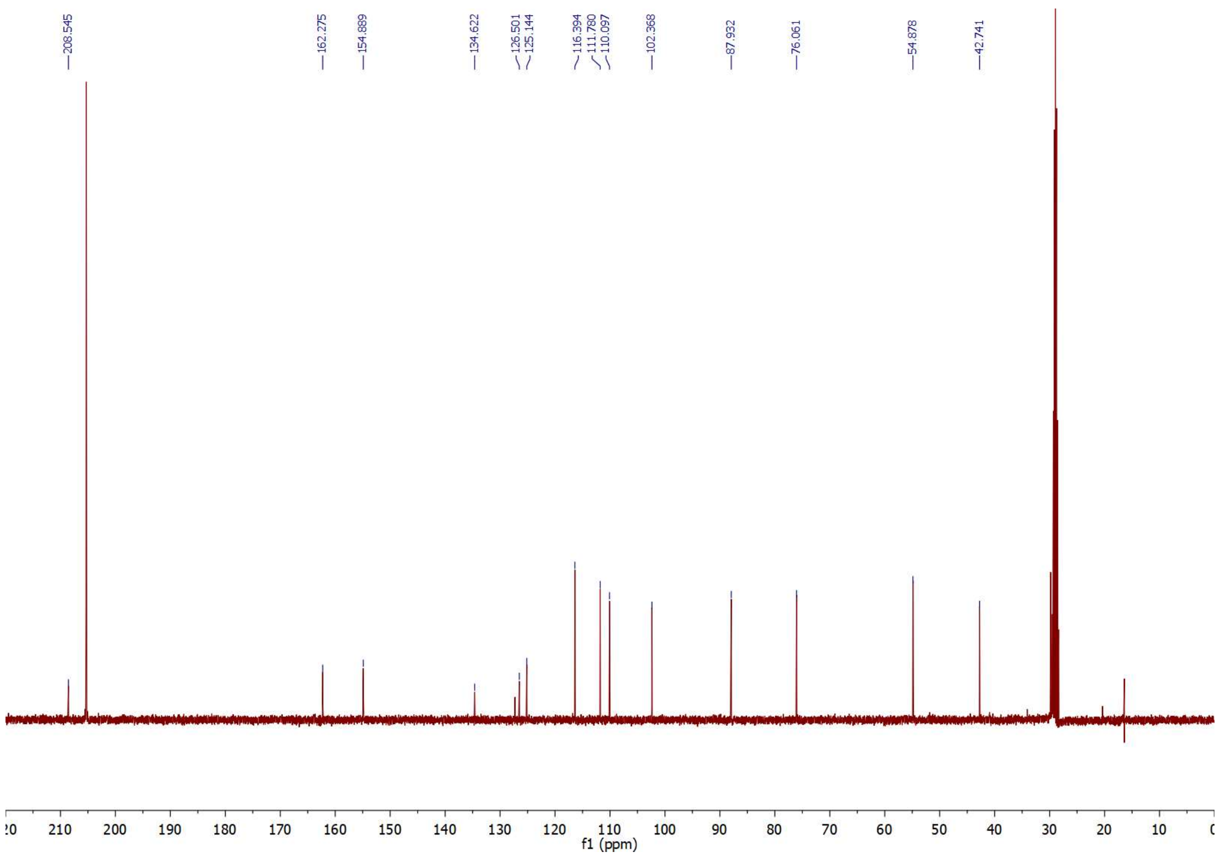
7.421
7.402
7.400
7.398
7.215
7.213
7.136
7.130
6.997
6.991
6.974
6.968
6.942
6.940
6.939
5.391
5.375
5.360
5.358
5.344
5.342
5.327
5.234
5.227
5.219
5.211
5.204
4.731
4.724
4.717
4.715
4.708
4.701
3.803
2.035
MeO
O
OH
N
1c
1.00
0.89
0.96
1.25
0.94
2.03
1.89
2.85
f1 (ppm)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102.368
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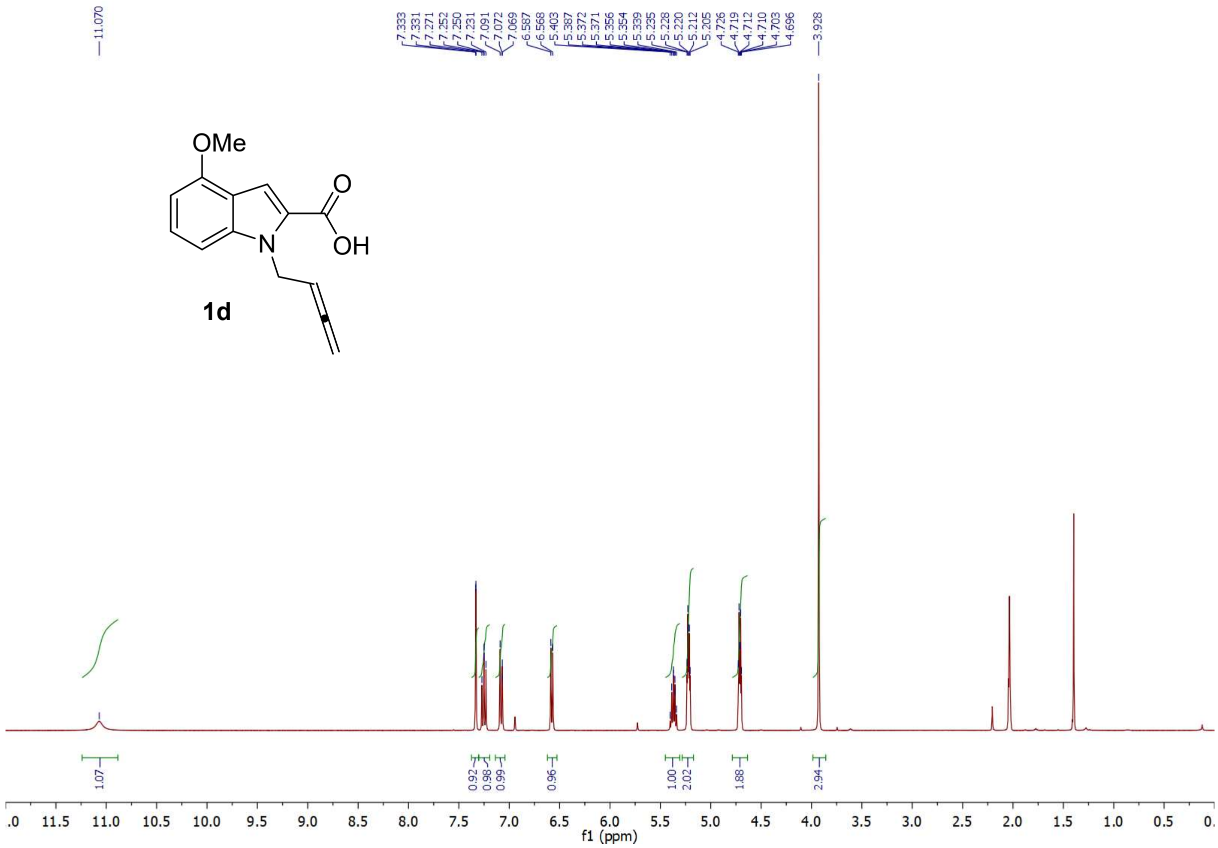
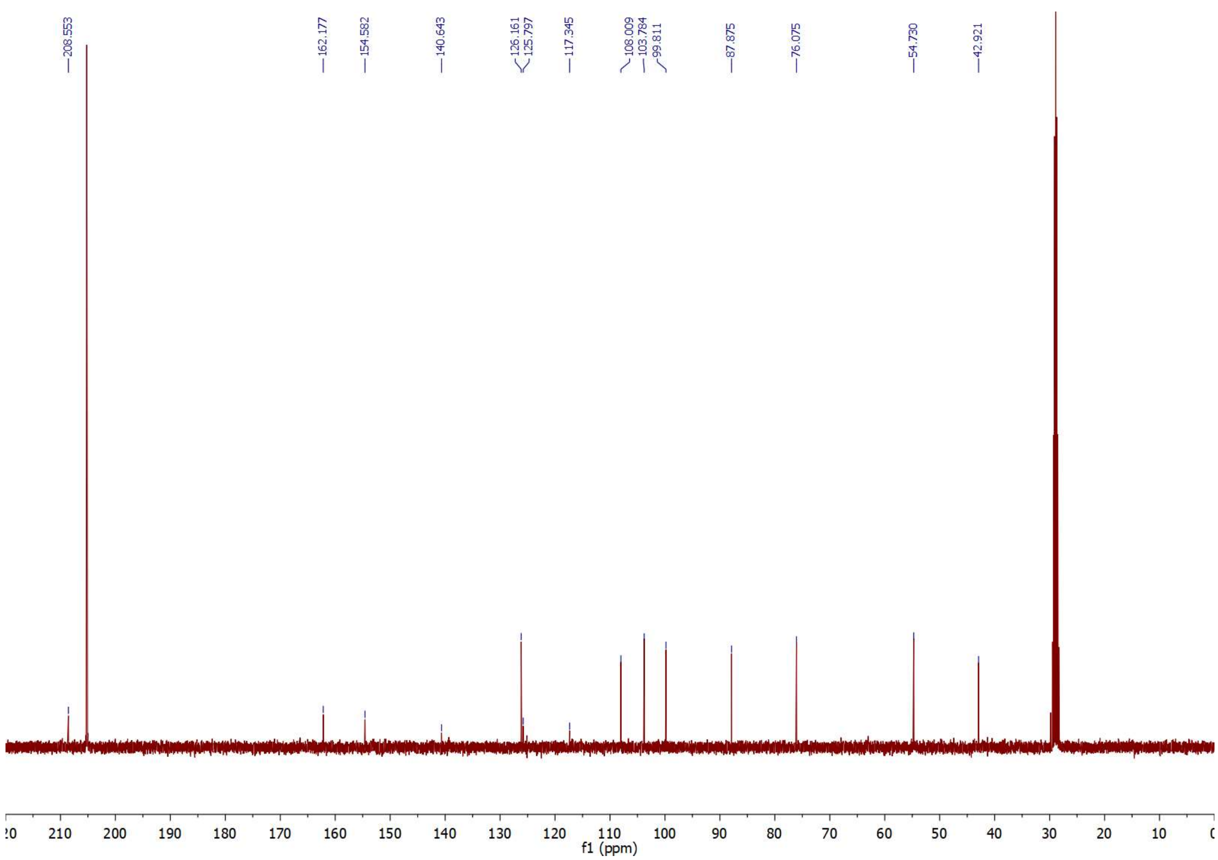
42.741
f1 (ppm)



11.070
7.333
7.331
7.271
7.252
7.250
7.231
7.091
7.072
7.069
6.587
6.568
5.403
5.387
5.372
5.371
5.356
5.354
5.339
5.235
5.228
5.220
5.212
5.205
4.726
4.719
4.712
4.710
4.703
4.696
3.928
OMe
O
OH
N
1d
1.07
0.92
0.98
0.99
0.96
1.00
2.02
1.88
2.94
f1 (ppm)



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140.643
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125.797
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108.009
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76.075
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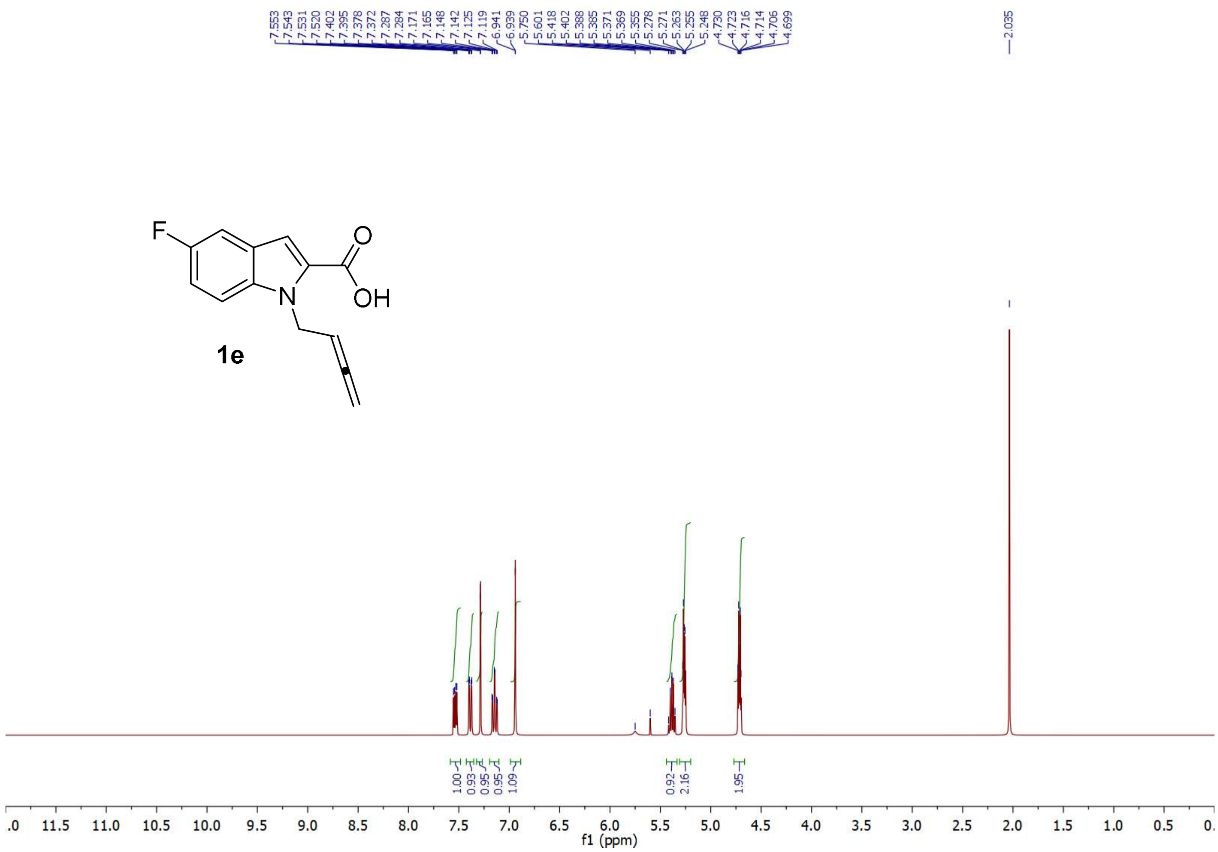
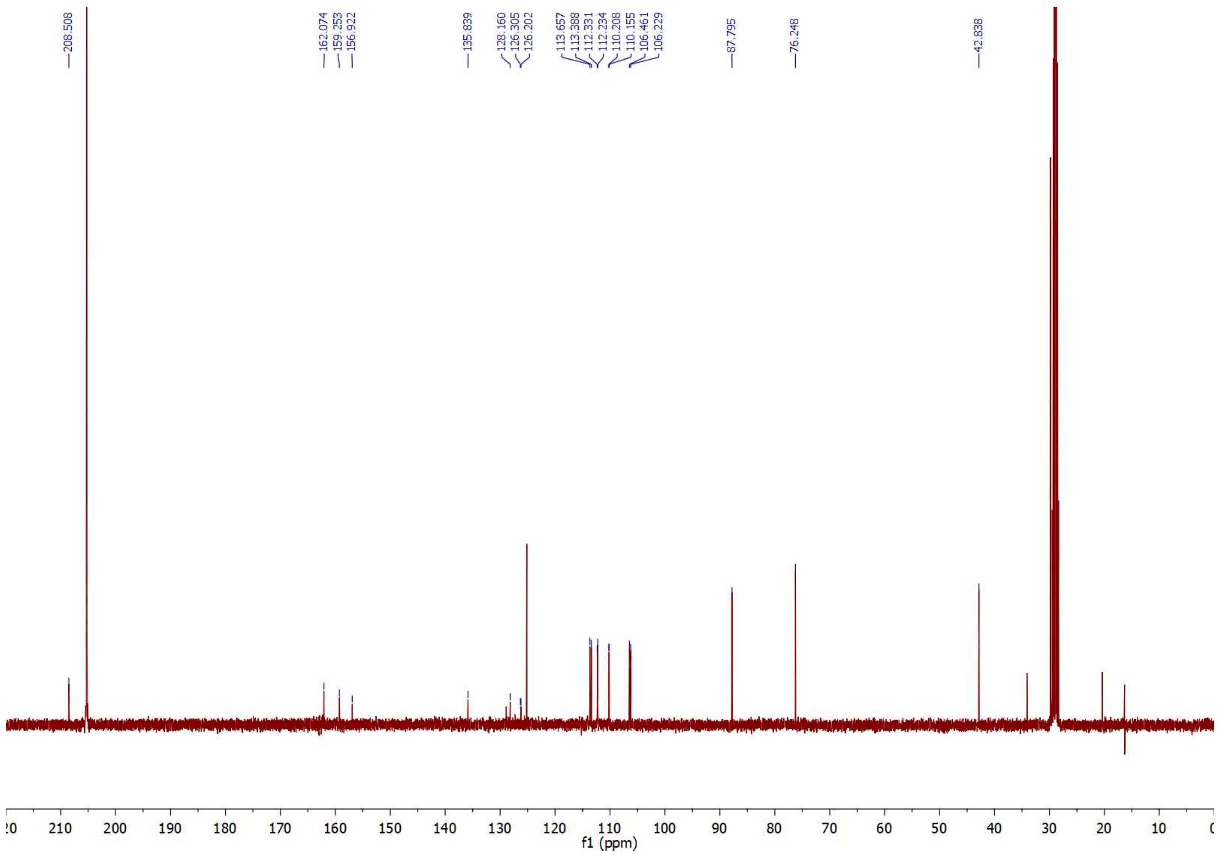
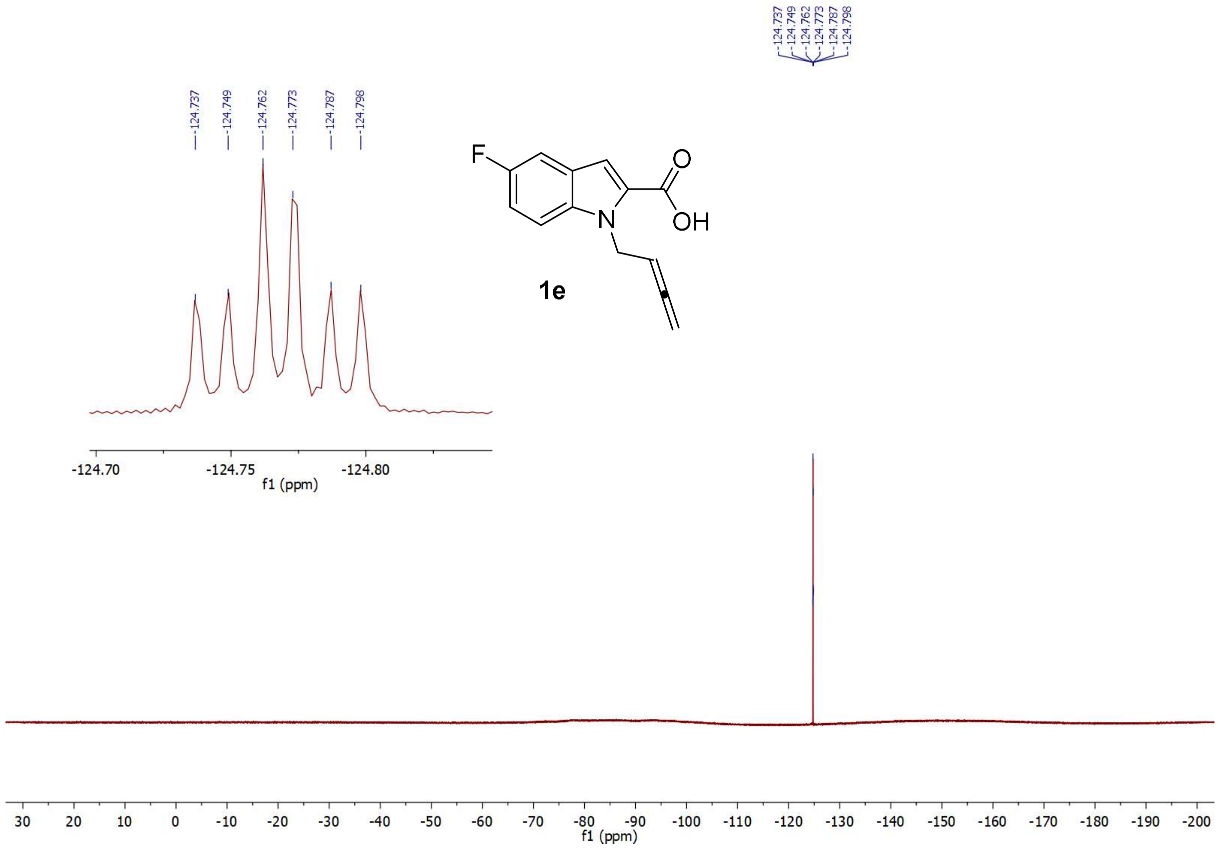
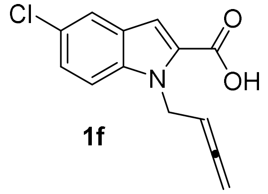
42.921
f1 (ppm)

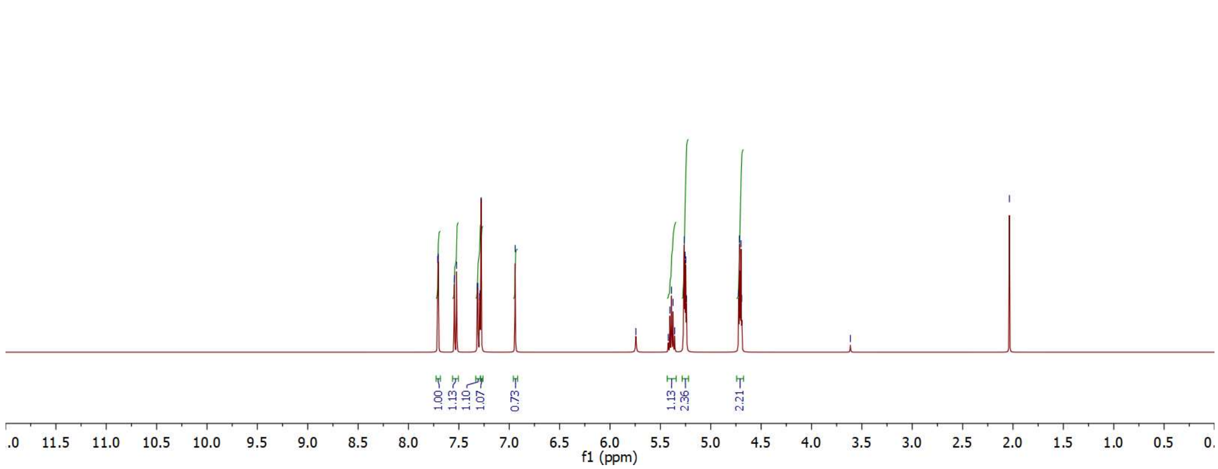

7.553
7.543
7.531
7.520
7.402
7.395
7.378
7.372
7.287
7.284
7.171
7.165
7.148
7.142
7.125
7.119
6.941
6.939
5.750
5.601
5.418
5.402
5.388
5.385
5.371
5.369
5.355
5.278
5.271
5.263
5.255
5.248
4.730
4.723
4.716
4.714
4.706
4.699
2.035
F
O
OH
N
1e
1.00
0.93
0.95
0.95
1.09
0.92
2.16
1.95
f1 (ppm)

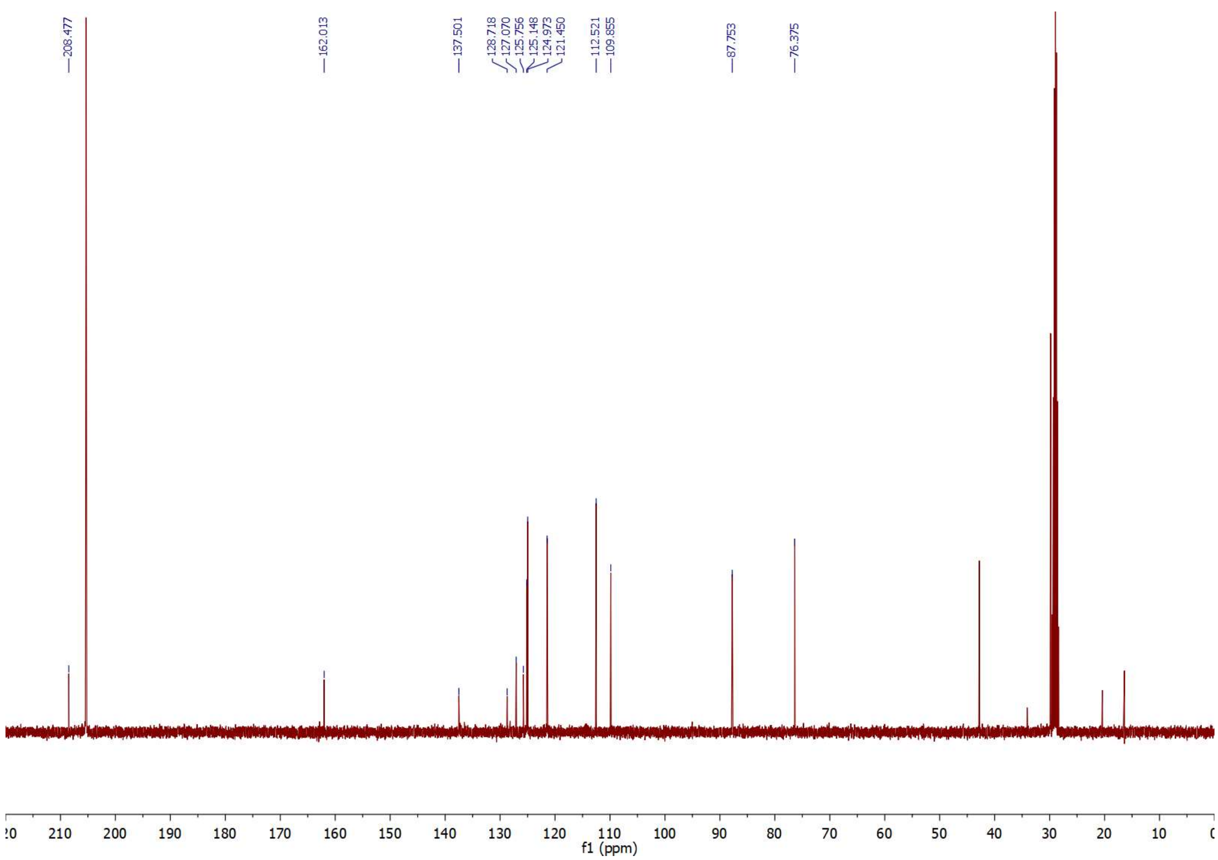

208.508
162.074
159.253
156.922
135.839
128.160
126.305
126.202
113.657
113.388
112.331
112.234
110.208
110.155
106.461
106.229
87.795
76.248
42.838
f1 (ppm)

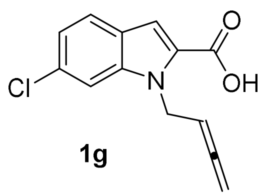

-124.737
-124.749
-124.762
-124.773
-124.787
-124.798
F
O
OH
N
1e
-124.70
-124.75
-124.80
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


Cl
O
OH
N

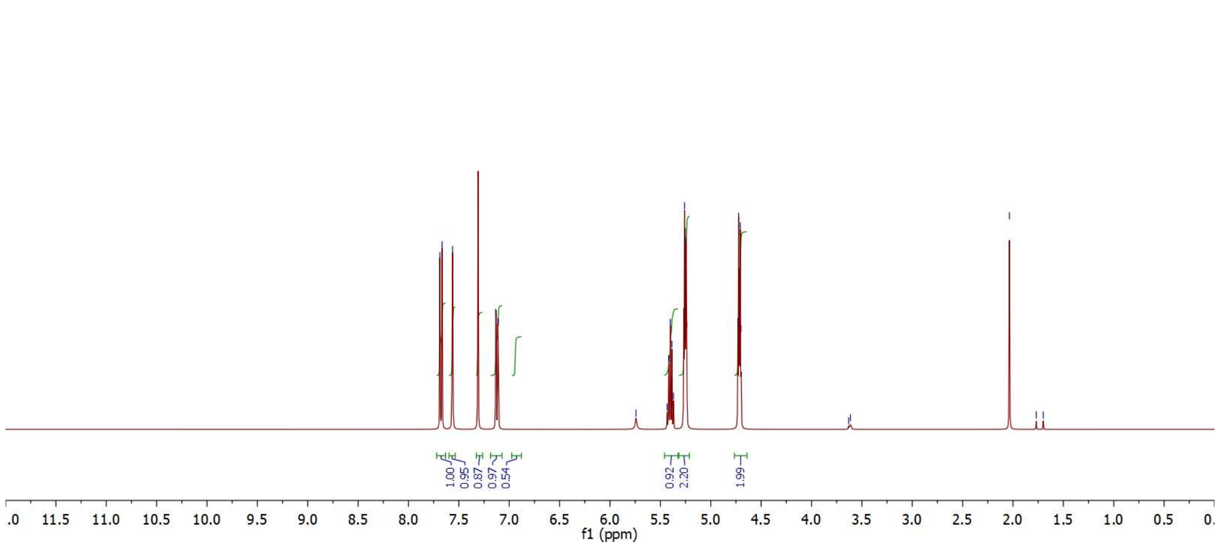
1f

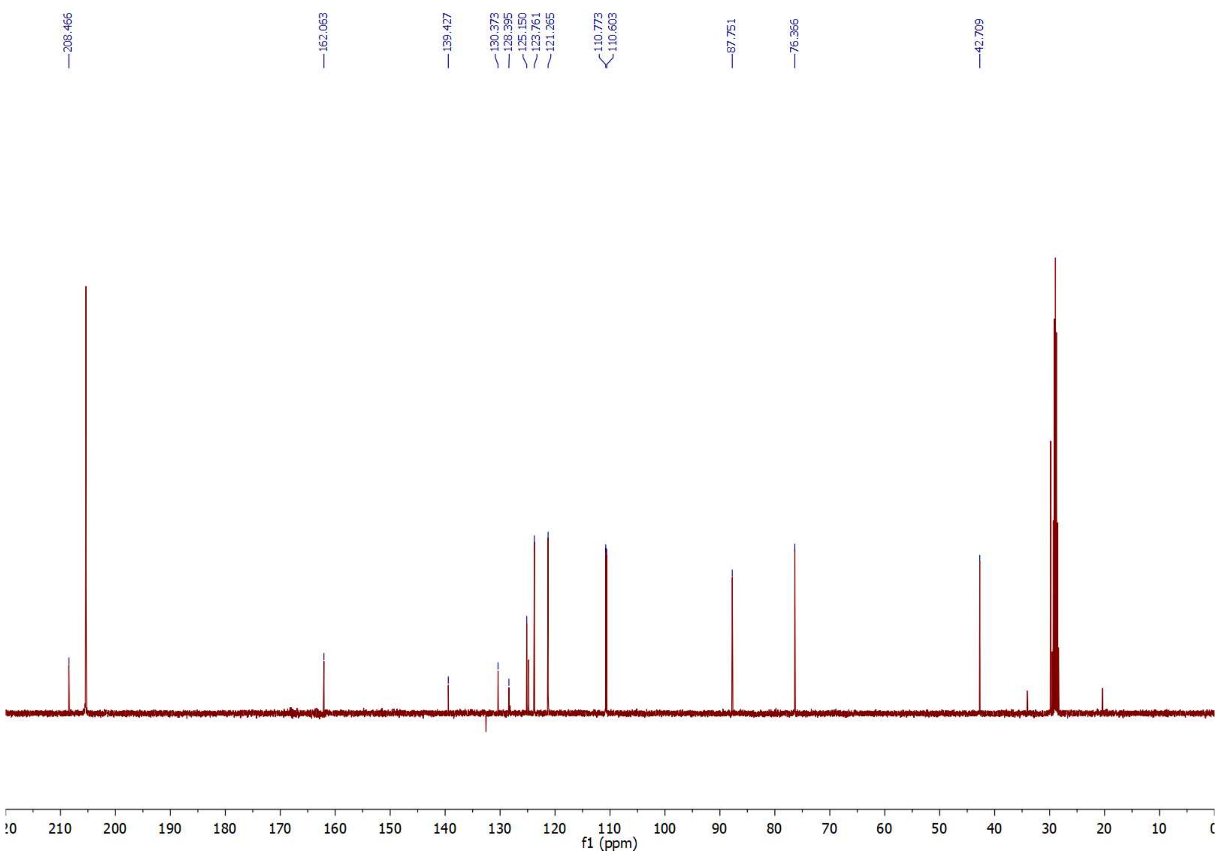

7.710
7.705
7.545
7.522
7.316
7.311
7.294
7.289
7.281
7.279
6.941
5.743
5.421
5.405
5.390
5.374
5.358
5.270
5.263
5.255
5.248
5.240
4.723
4.716
4.709
4.707
4.700
4.692
3.614
2.036
1.00
1.13
1.10
1.07
0.73
1.13
2.36
2.21
f1 (ppm)

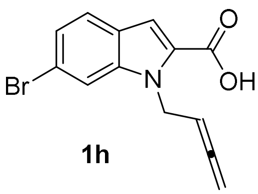

208.477
162.013
137.501
128.718
127.070
125.756
125.148
124.973
121.450
112.521
109.855
87.753
76.375
f1 (ppm)



1g

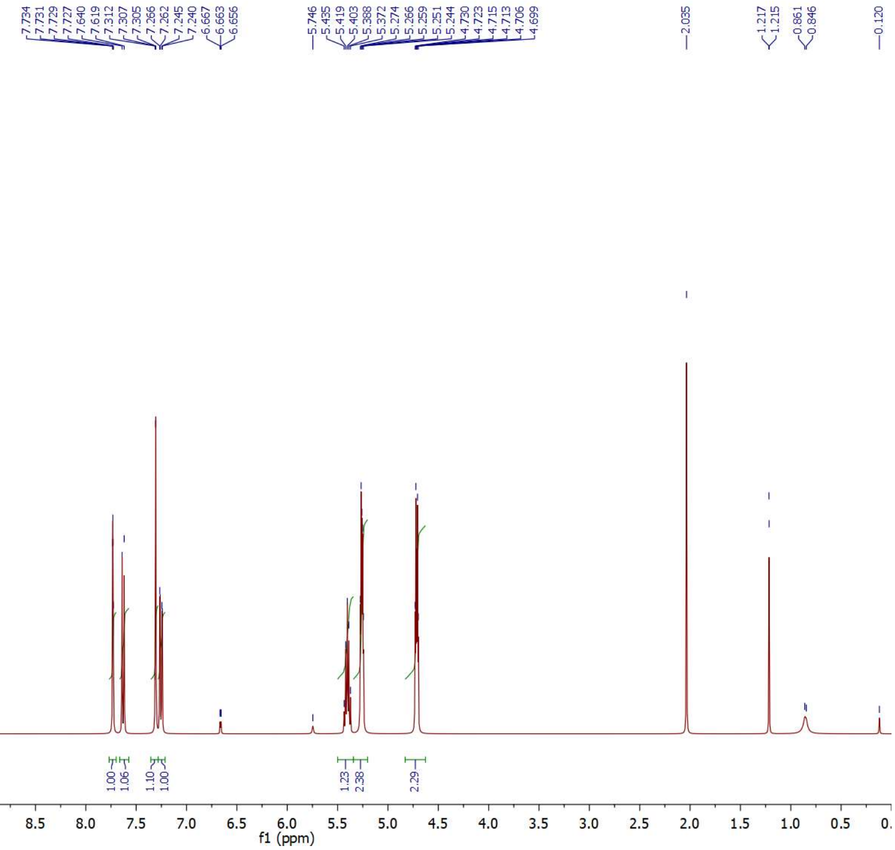




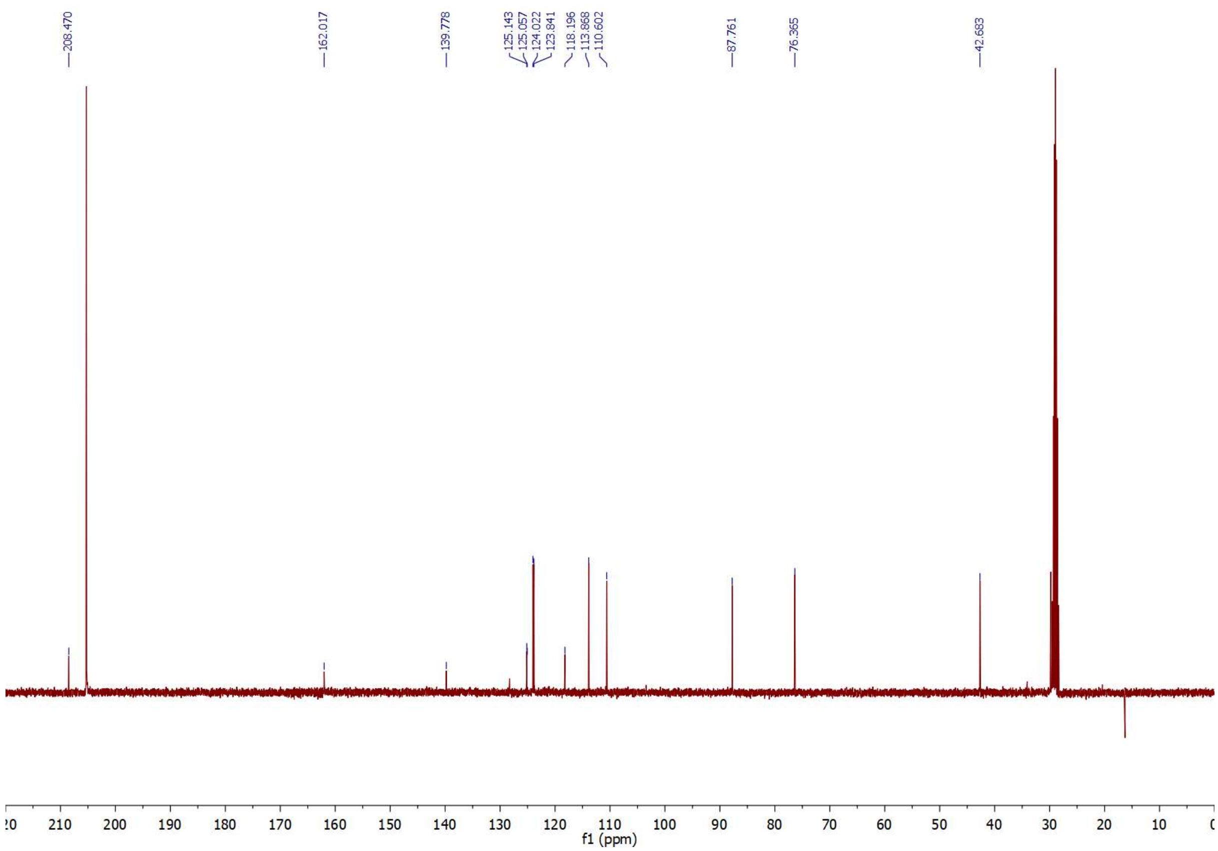


Br
N
O
OH

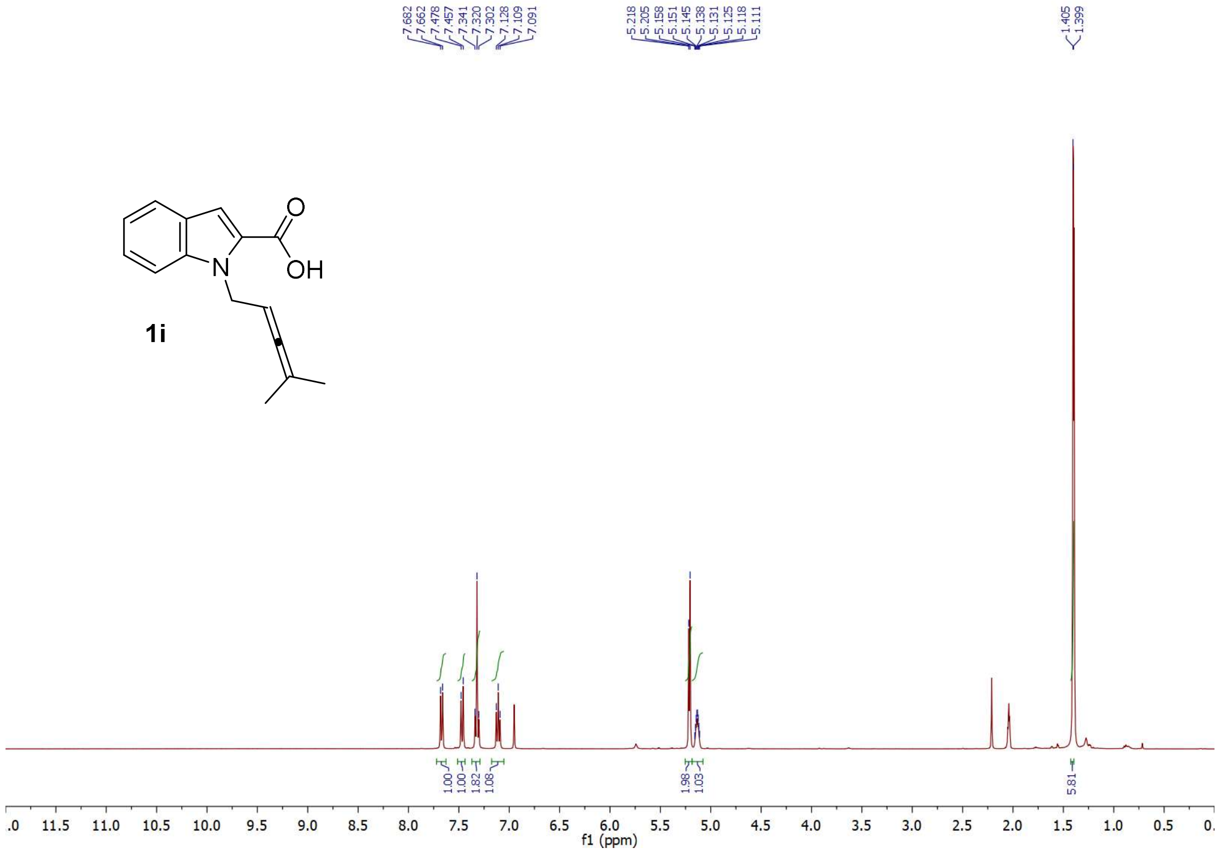
1h



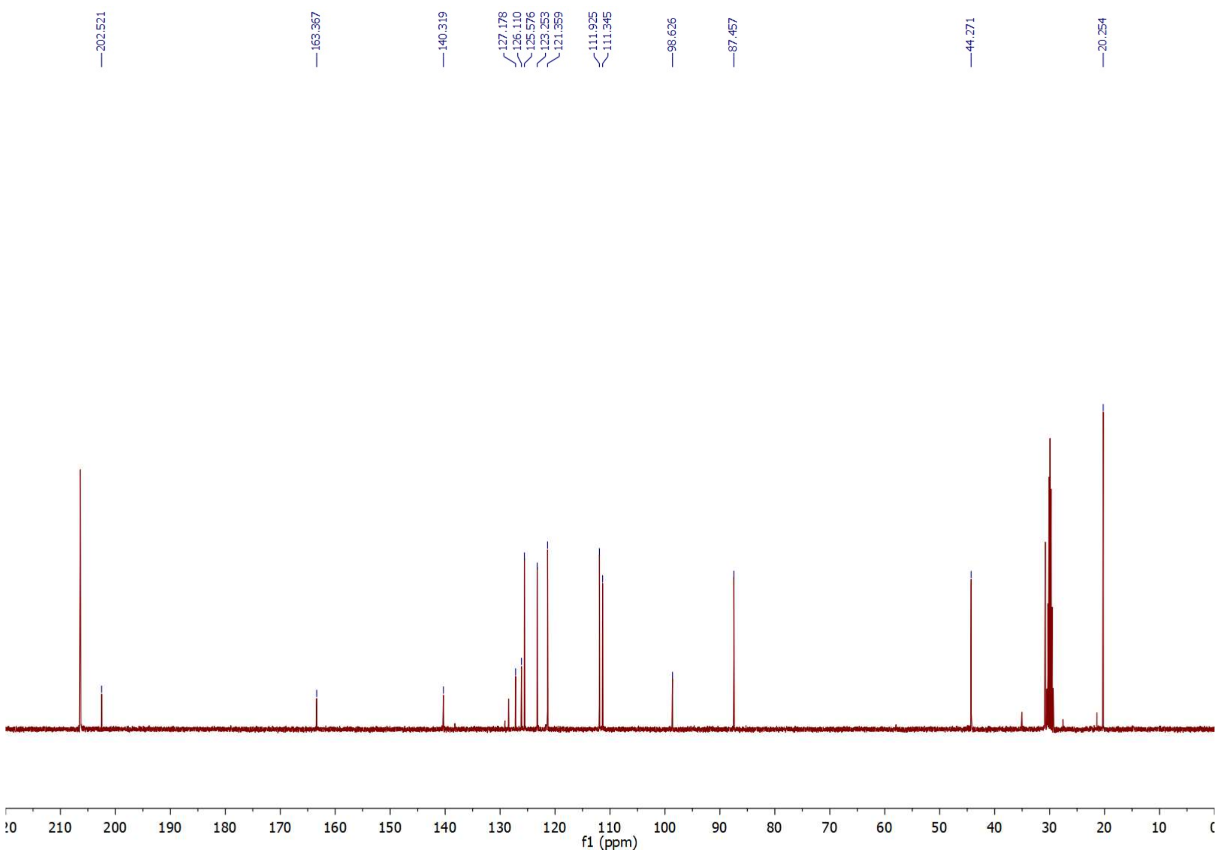
7.734
7.731
7.729
7.727
7.640
7.619
7.312
7.307
7.305
7.266
7.262
7.245
7.240
6.667
6.663
6.656
5.746
5.435
5.419
5.403
5.388
5.372
5.274
5.266
5.259
5.251
5.244
4.730
4.723
4.715
4.713
4.706
4.699
2.035
1.217
1.215
0.861
0.846
0.120
1.00
1.06
1.10
1.00
1.23
2.38
2.29
f1 (ppm)



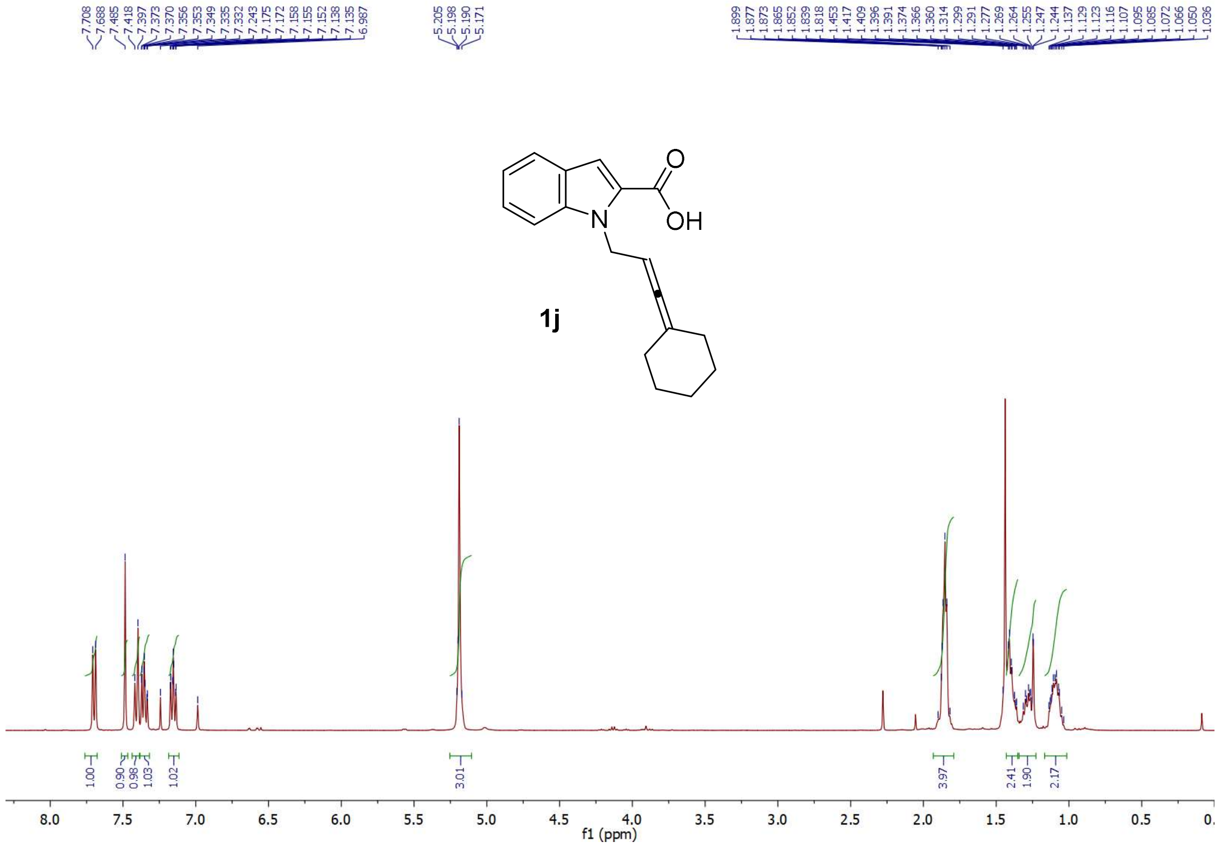
208.470
162.017
139.778
125.143
125.057
124.022
123.841
118.196
113.868
110.602
87.761
76.365
42.683
f1 (ppm)



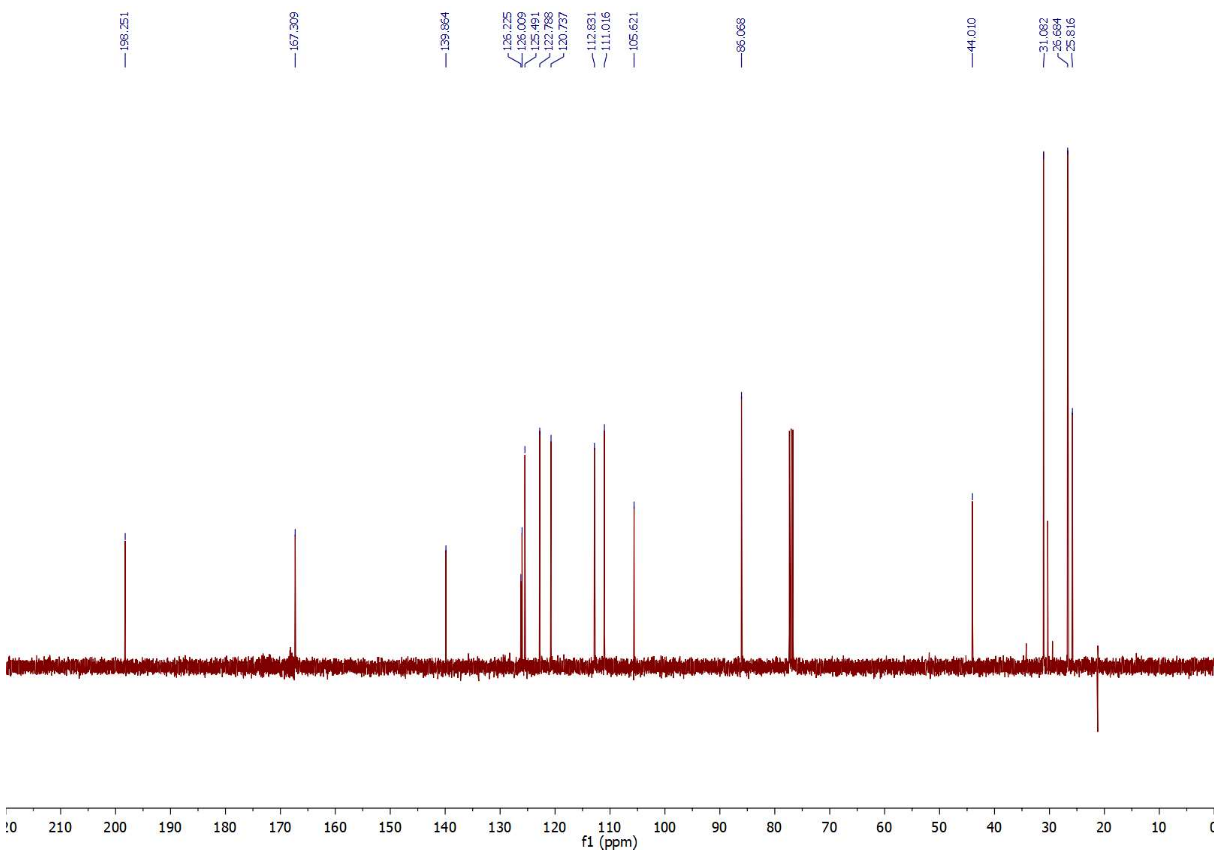
7.682
7.662
7.478
7.457
7.341
7.320
7.302
7.128
7.109
7.091
5.218
5.205
5.158
5.151
5.145
5.138
5.131
5.125
5.118
5.111
1.405
1.399
OH
N
O
1i
1.00
1.00
1.82
1.08
1.98
1.03
5.81
f1 (ppm)

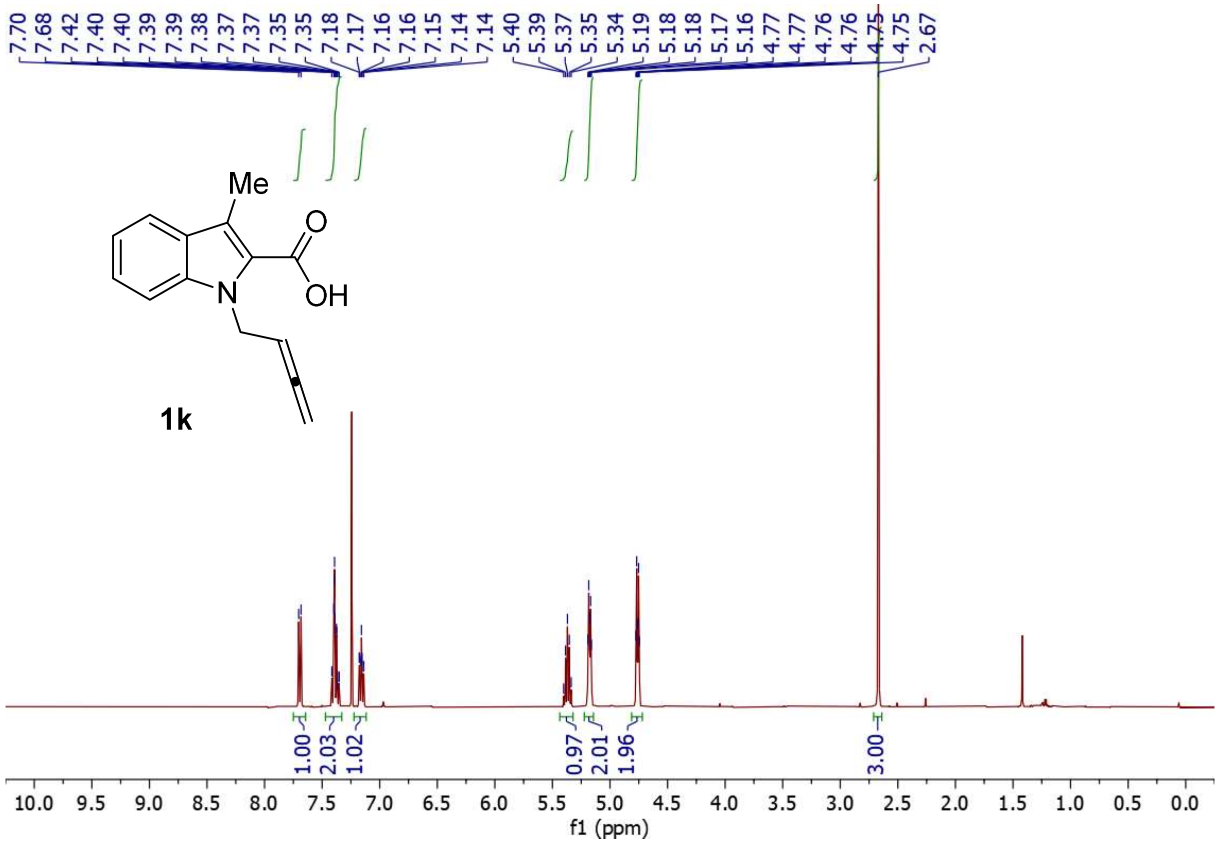


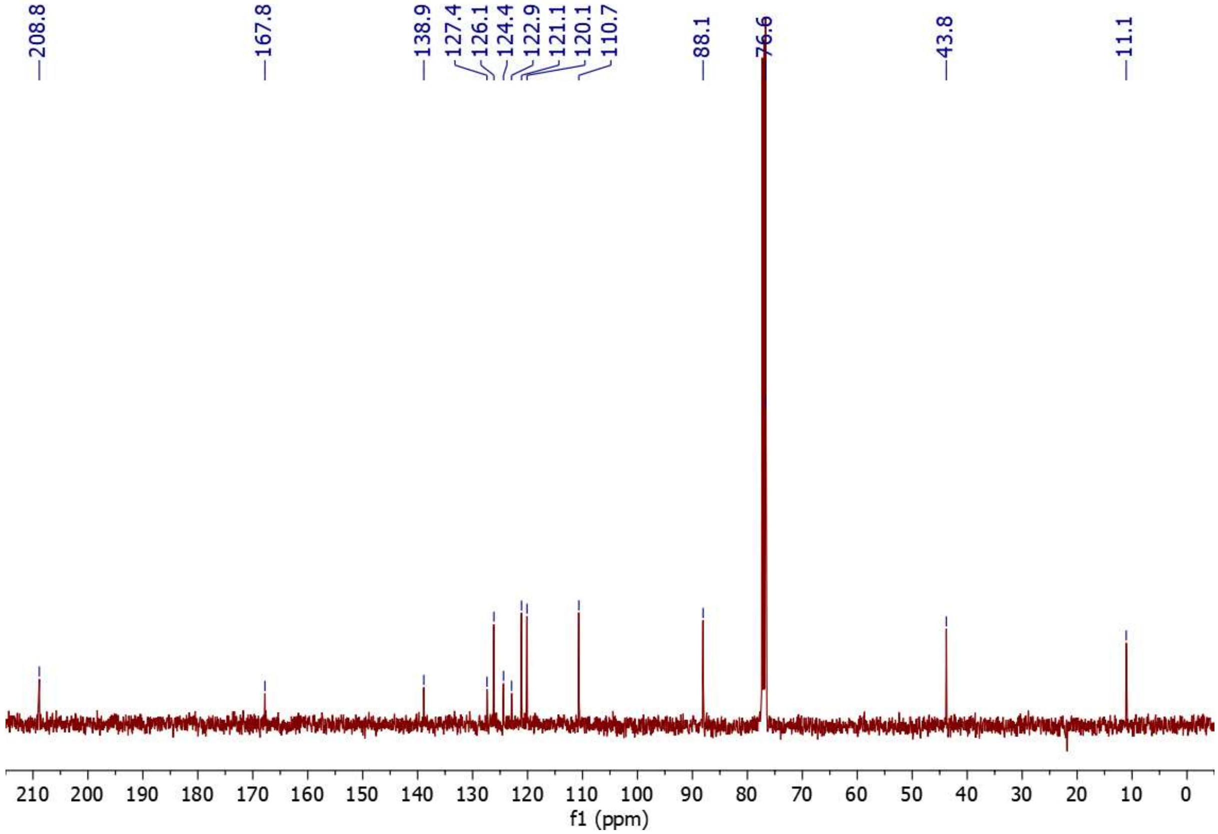
202.521
163.367
140.319
127.178
126.110
125.576
123.253
121.359
111.925
111.345
98.626
87.457
44.271
20.254
f1 (ppm)

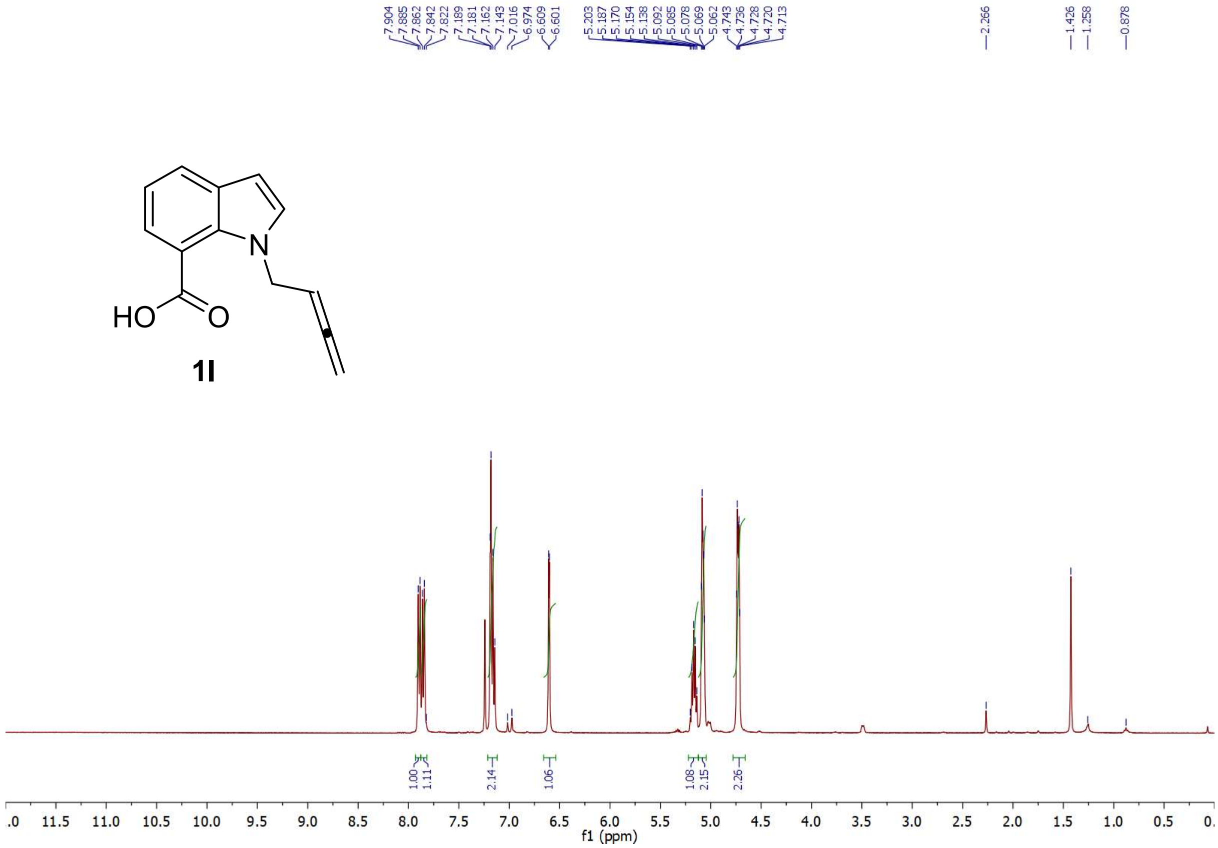

7.708
7.688
7.485
7.418
7.397
7.373
7.370
7.356
7.353
7.349
7.335
7.332
7.243
7.175
7.172
7.158
7.155
7.152
7.138
7.135
6.987
5.205
5.198
5.190
5.171
1.899
1.877
1.873
1.865
1.852
1.839
1.818
1.453
1.417
1.409
1.396
1.391
1.374
1.366
1.360
1.314
1.299
1.291
1.277
1.269
1.264
1.255
1.247
1.244
1.137
1.129
1.123
1.116
1.107
1.095
1.085
1.072
1.066
1.050
1.036
O
OH
N
1.00
0.90
0.98
1.03
1.02
3.01
3.97
2.41
1.90
2.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

1j

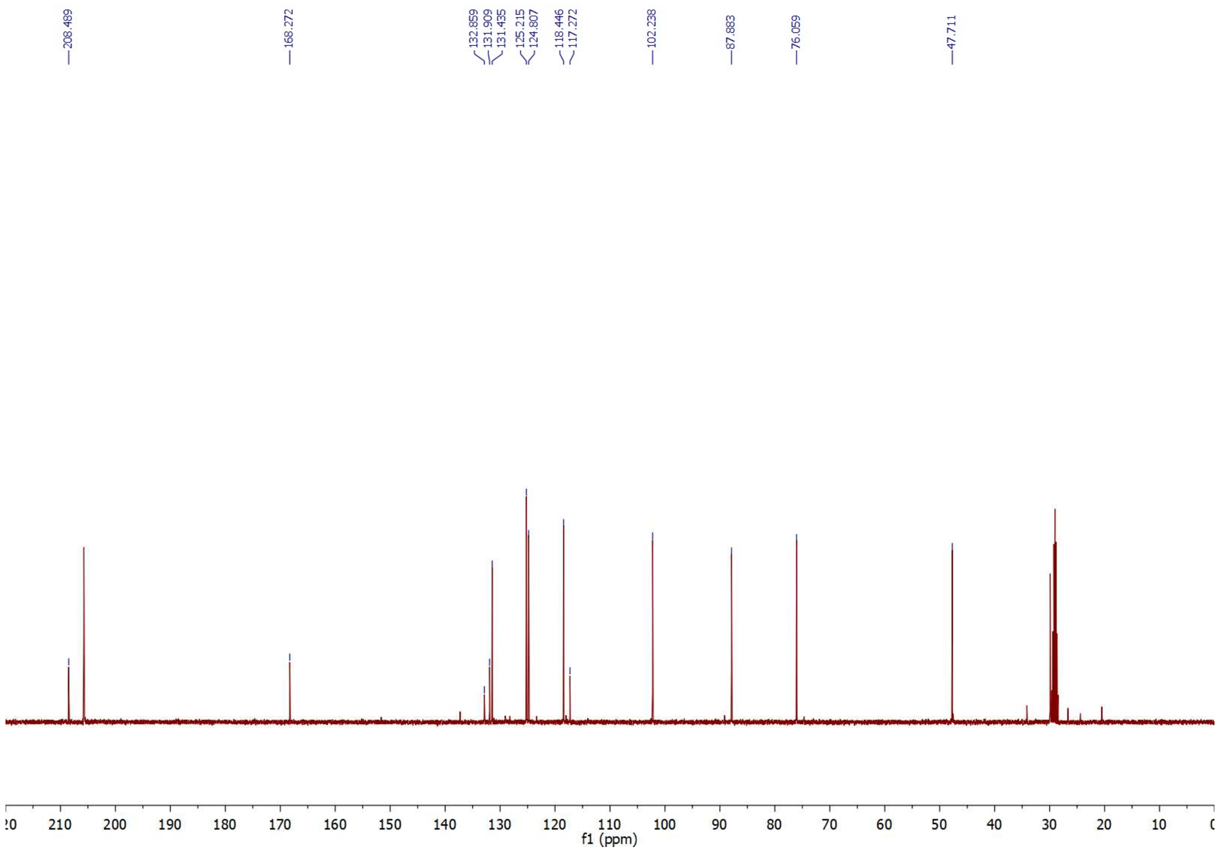

198.251
167.309
139.864
126.225
126.009
125.491
122.788
120.737
112.831
111.016
105.621
86.068
44.010
31.082
26.684
25.816
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

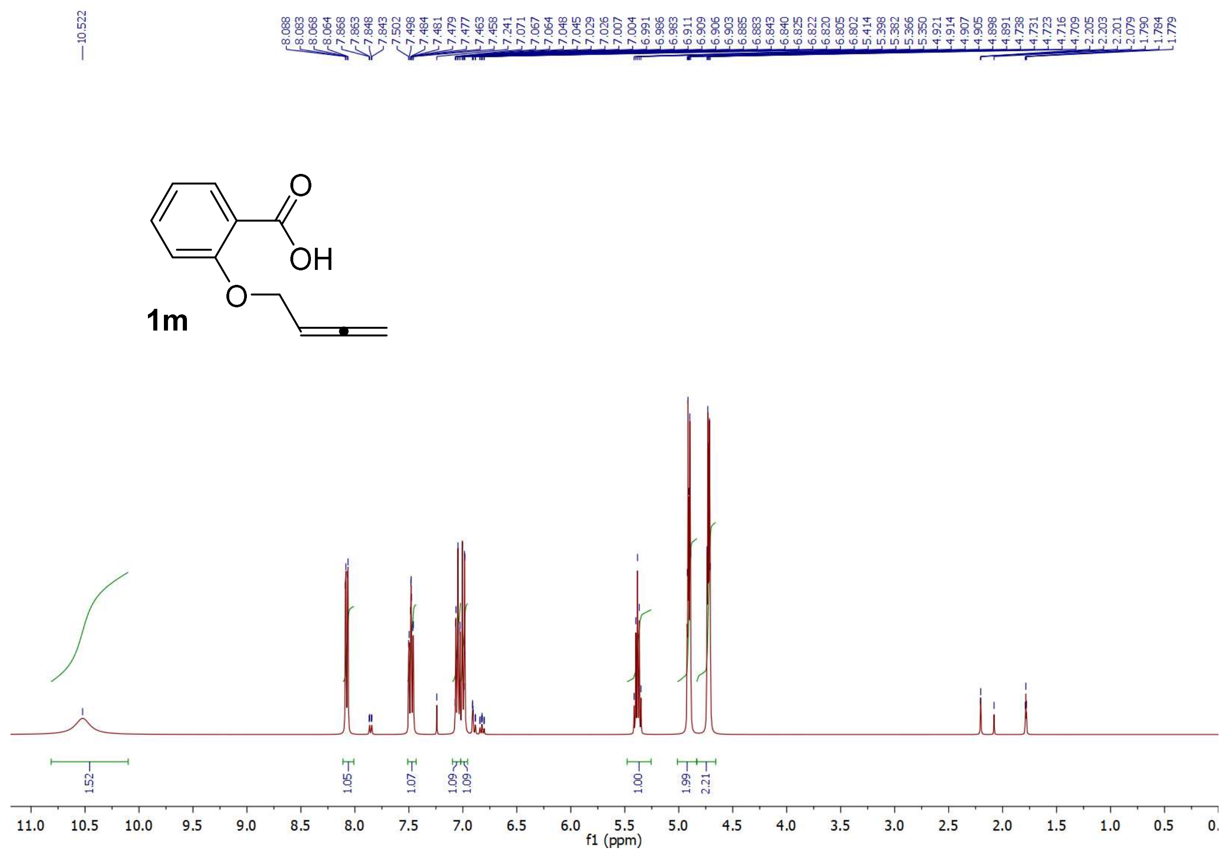

7.70
7.68
7.42
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.35
7.35
7.18
7.17
7.16
7.16
7.15
7.14
7.14
5.40
5.39
5.37
5.35
5.34
5.19
5.18
5.18
5.17
5.16
4.77
4.77
4.76
4.76
4.75
4.75
2.67
Me
O
N
OH
1k
1.00
2.03
1.02
0.97
2.01
1.96
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

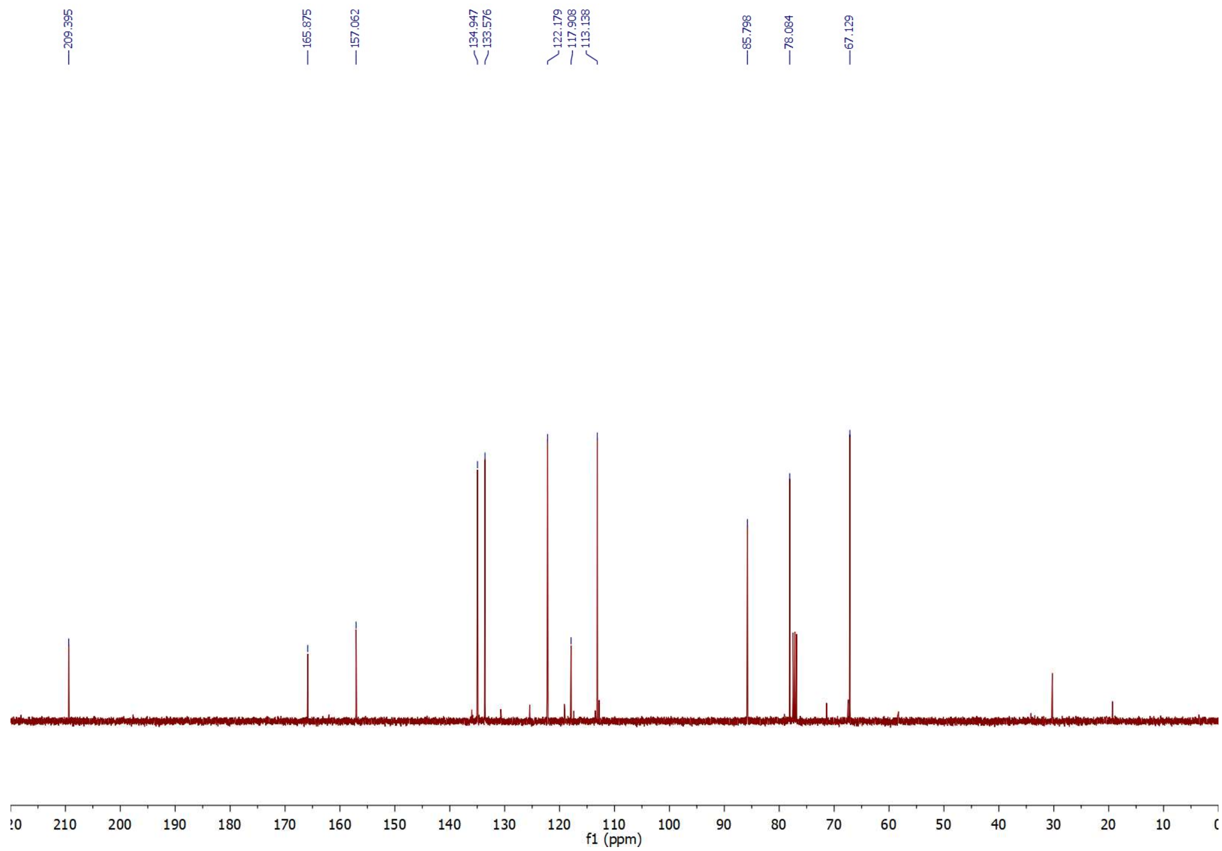

208.8
167.8
138.9
127.4
126.1
124.4
122.9
121.1
120.1
110.7
88.1
76.6
43.8
11.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

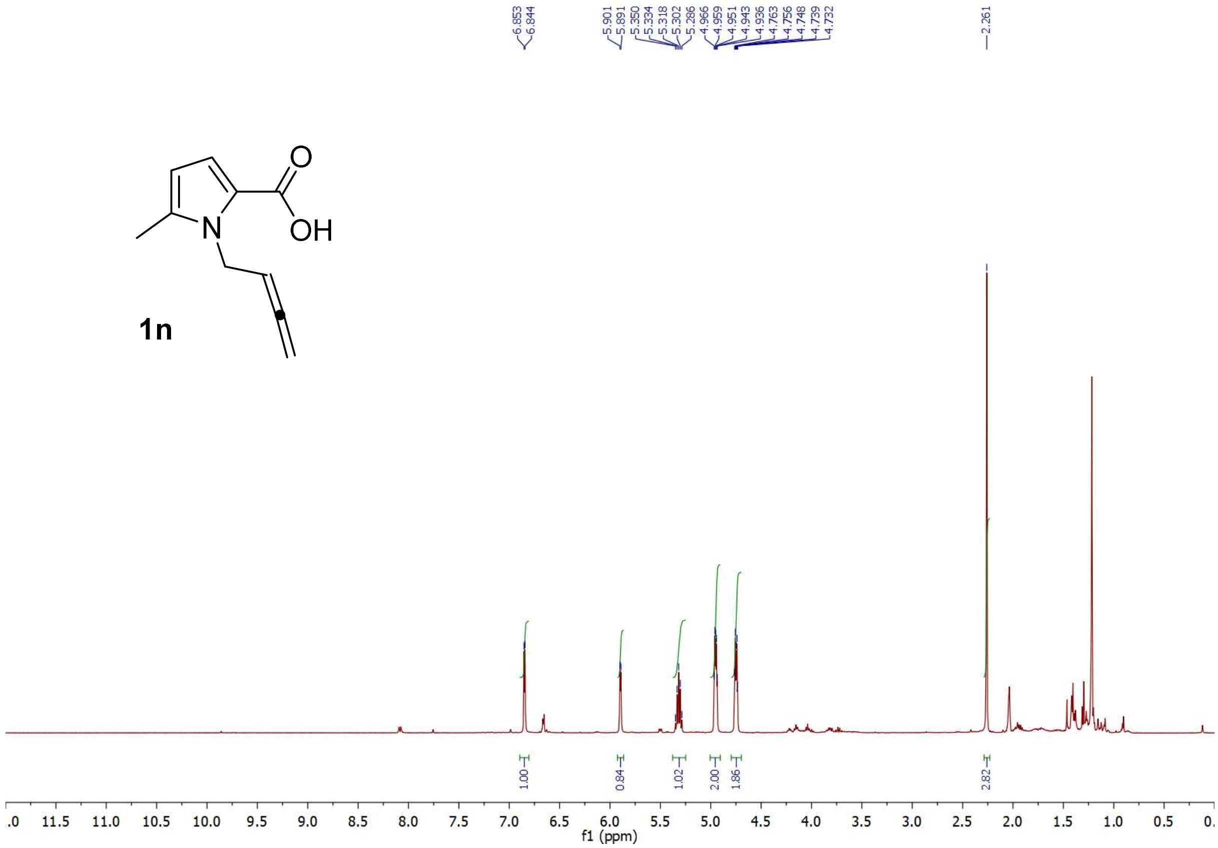


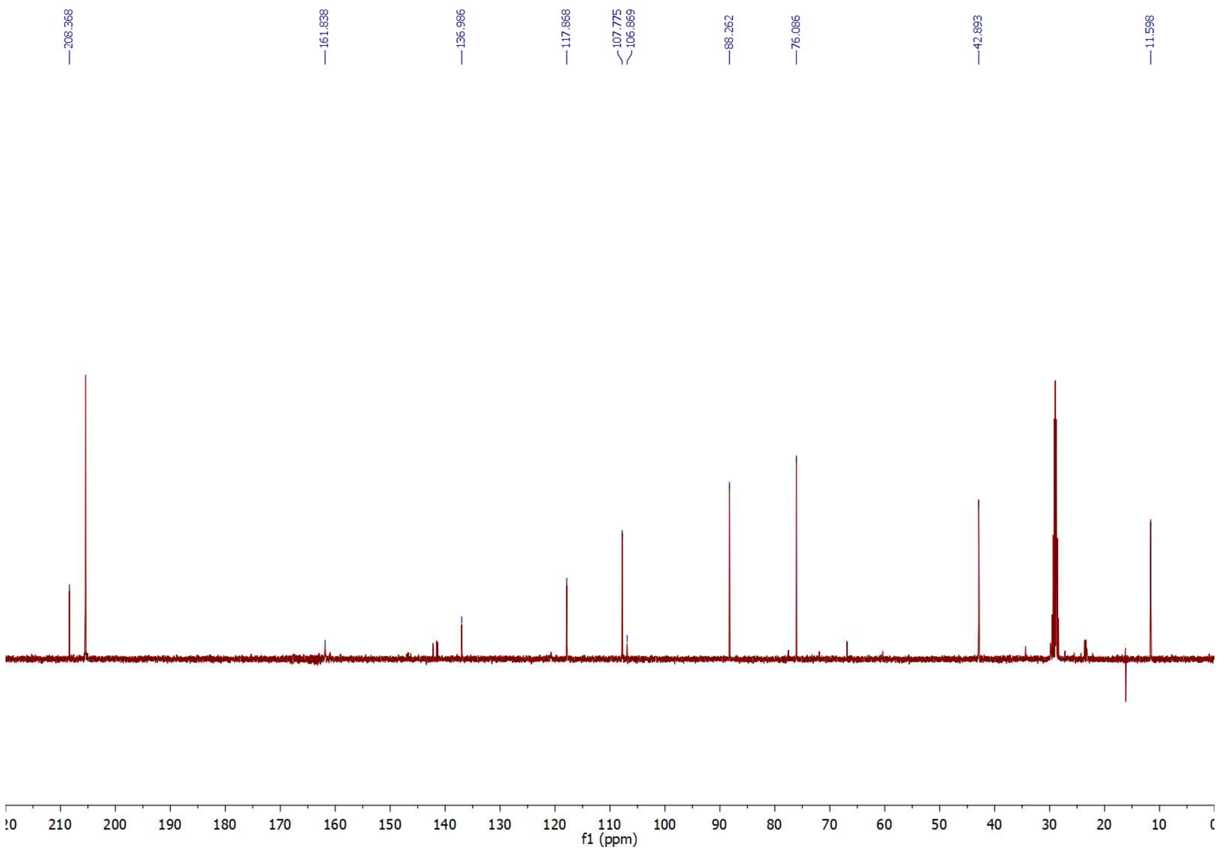
1l

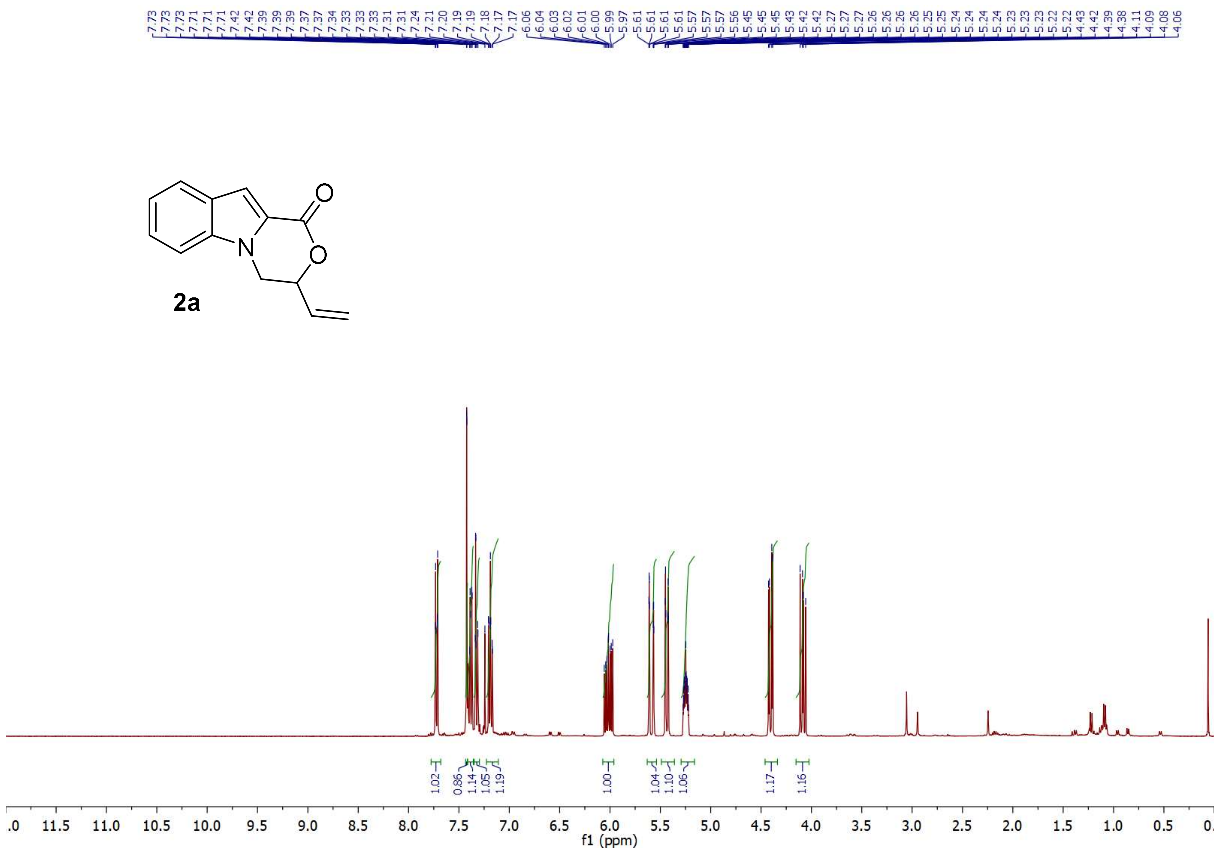



1m
f1 (ppm)


209.395
165.875
157.062
134.947
133.576
122.179
117.908
113.138
85.798
78.084
67.129
f1 (ppm)

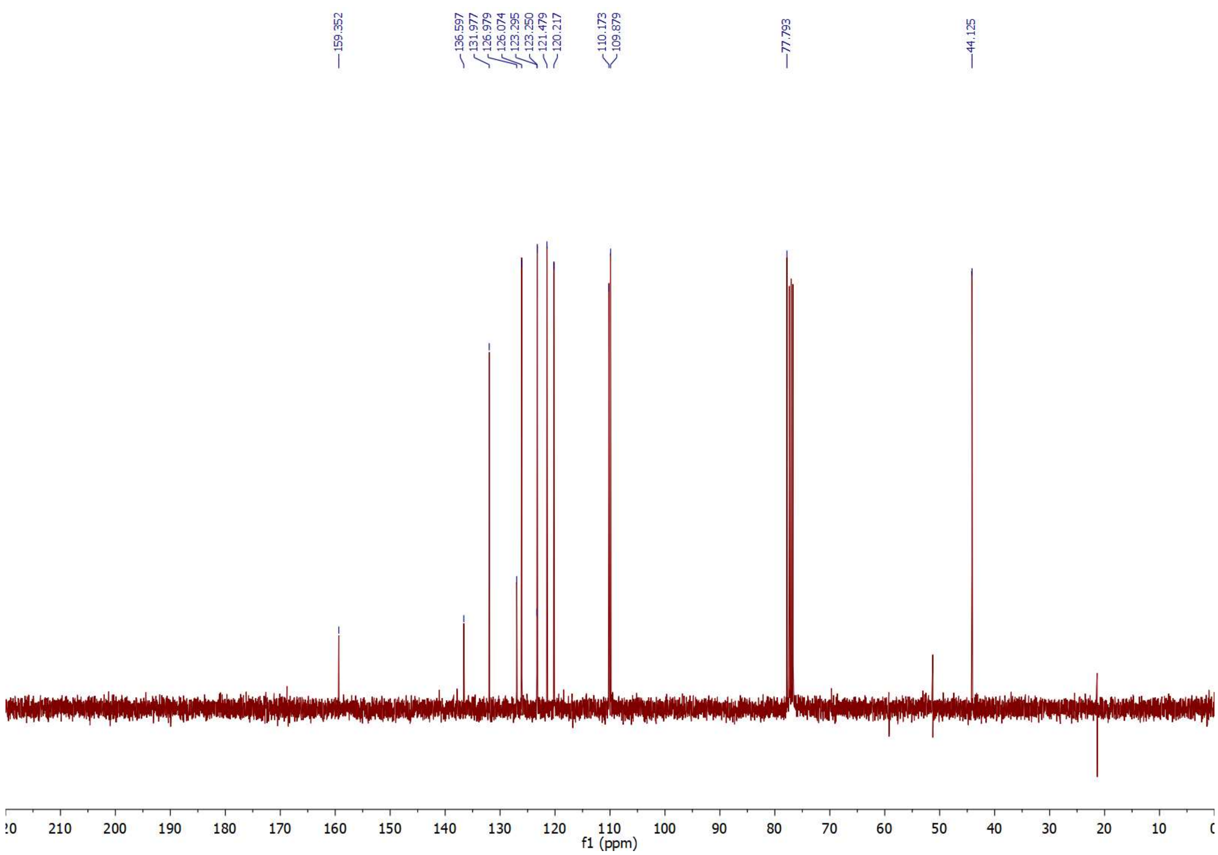

O
OH
N
1n
6.853
6.844
5.901
5.891
5.350
5.334
5.318
5.302
5.286
4.966
4.959
4.951
4.943
4.936
4.763
4.756
4.748
4.739
4.732
2.261
1.00
0.84
1.02
2.00
1.86
2.82
f1 (ppm)


208.368
161.838
136.986
117.868
107.775
106.869
88.262
76.086
42.893
11.598
f1 (ppm)

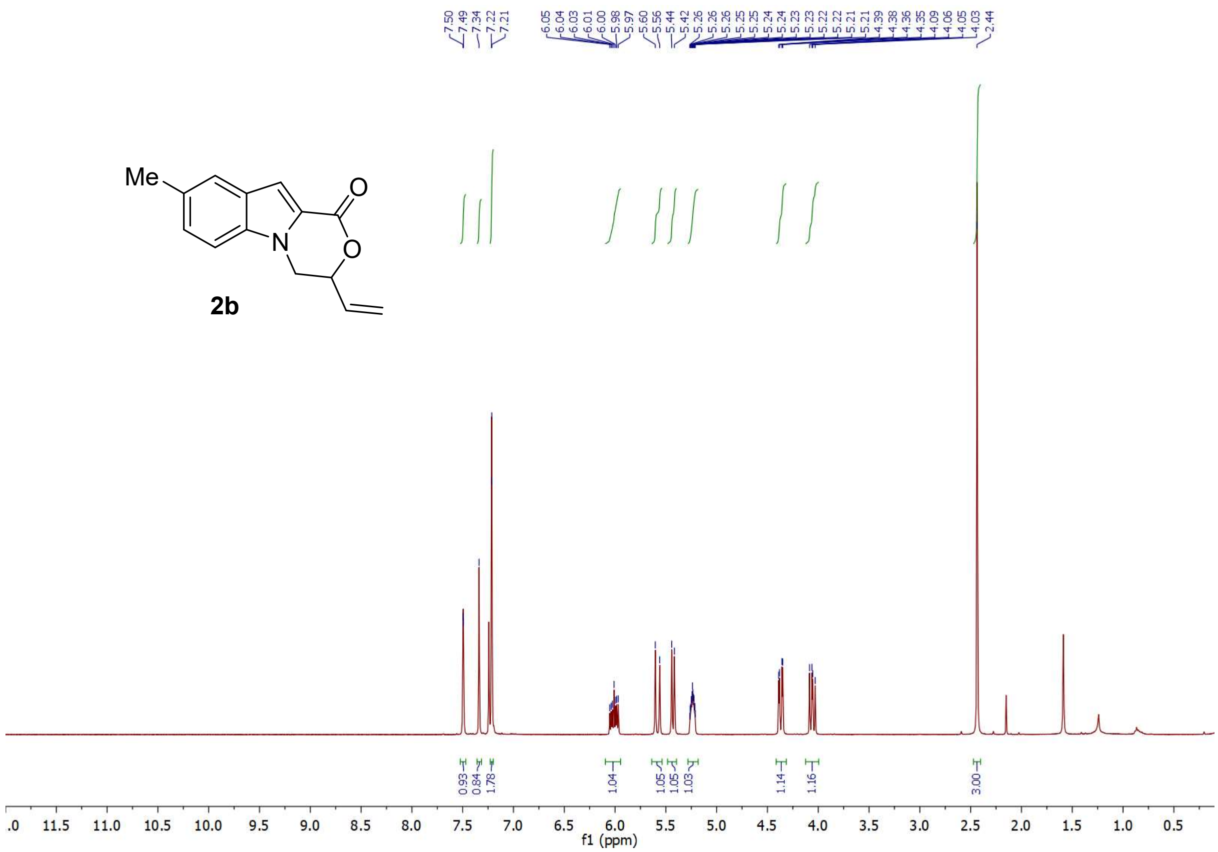


7.73 7.73 7.73 7.71 7.71 7.42 7.42 7.39 7.39 7.39 7.37 7.37 7.34 7.33 7.33 7.33 7.31 7.31 7.24 7.21 7.20 7.19 7.19 7.18 7.17 7.17 6.06 6.04 6.03 6.02 6.01 6.00 5.99 5.97 5.61 5.61 5.61 5.61 5.57 5.57 5.56 5.45 5.45 5.43 5.42 5.27 5.27 5.27 5.26 5.26 5.26 5.25 5.25 5.24 5.24 5.24 5.23 5.23 5.23 5.22 4.43 4.42 4.39 4.38 4.11 4.09 4.08 4.06
1.02 0.86 1.14 1.05 1.19 1.00 1.04 1.10 1.06 1.17 1.16
f1 (ppm)

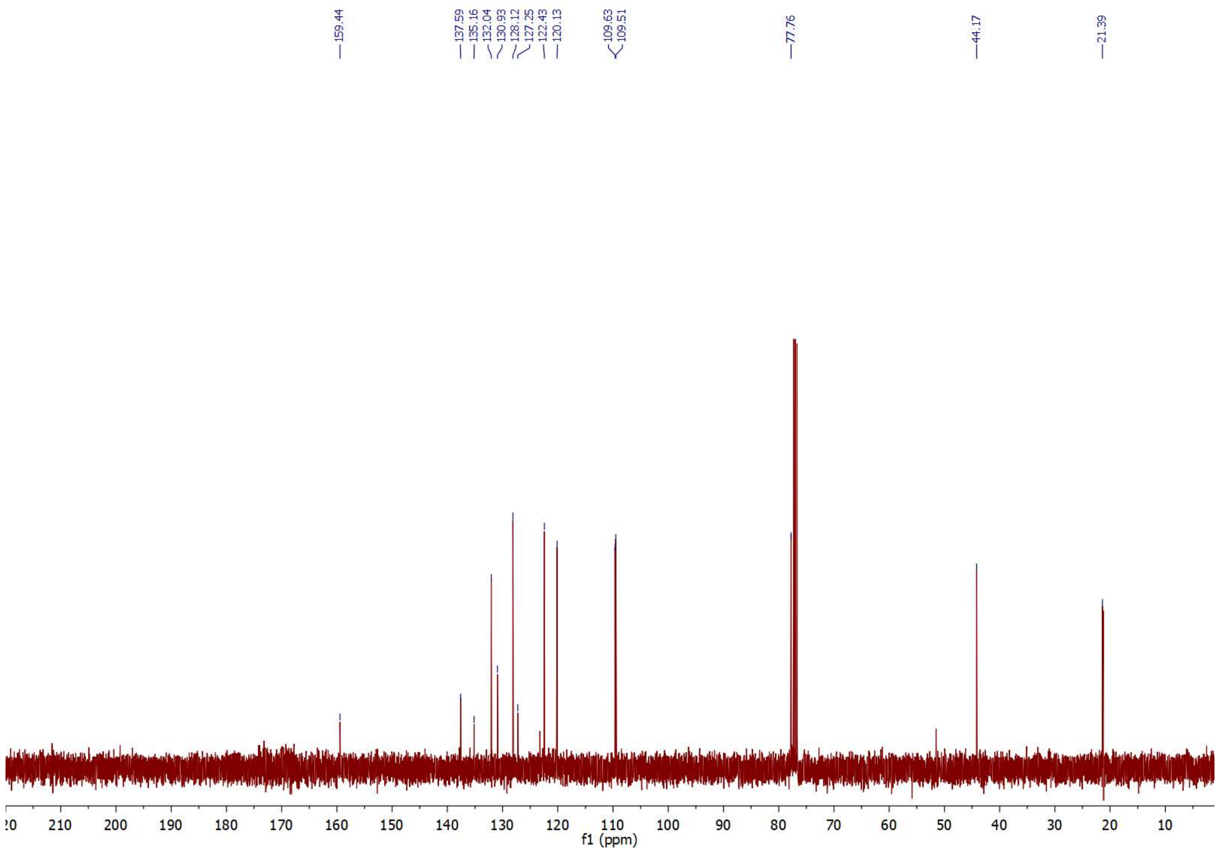
2a



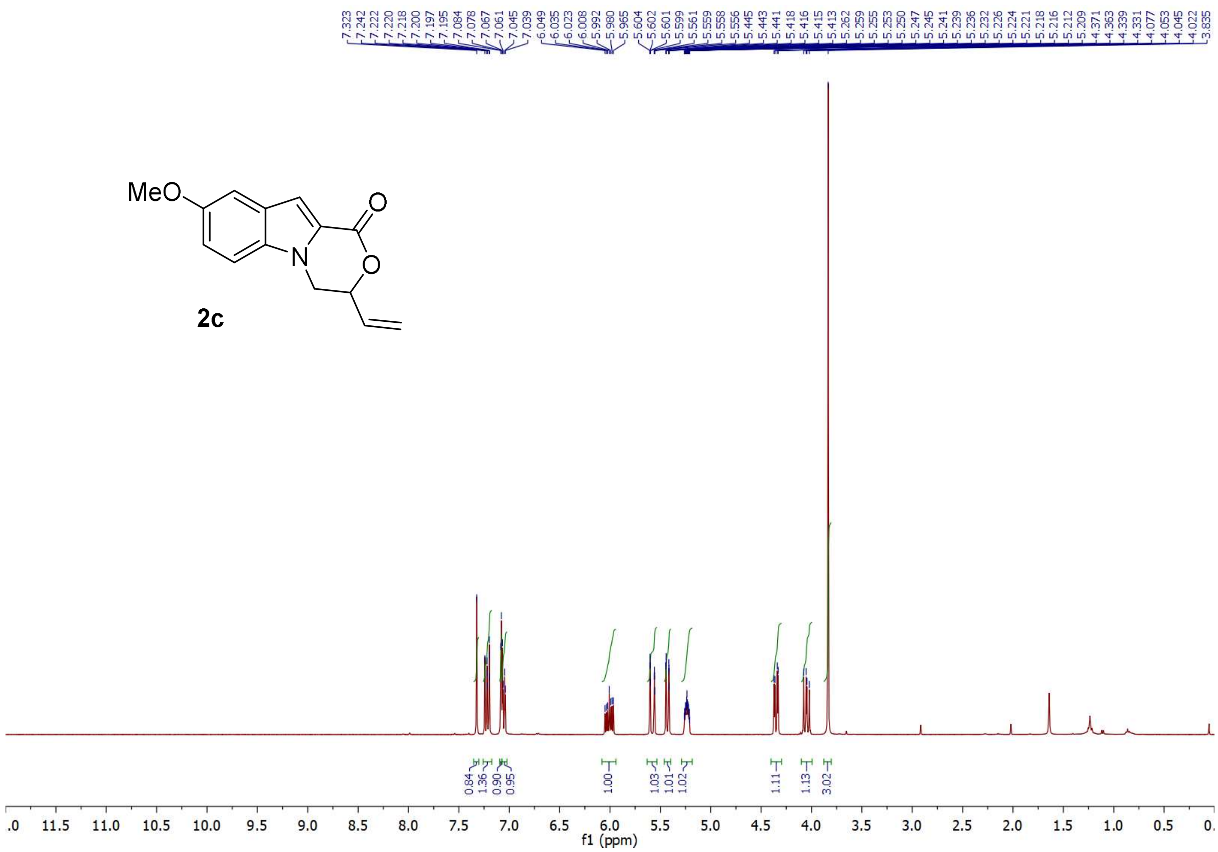
159.352
136.597 131.977 126.979 126.074 123.295 123.250 121.479 120.217
110.173 109.879
77.793
44.125
f1 (ppm)

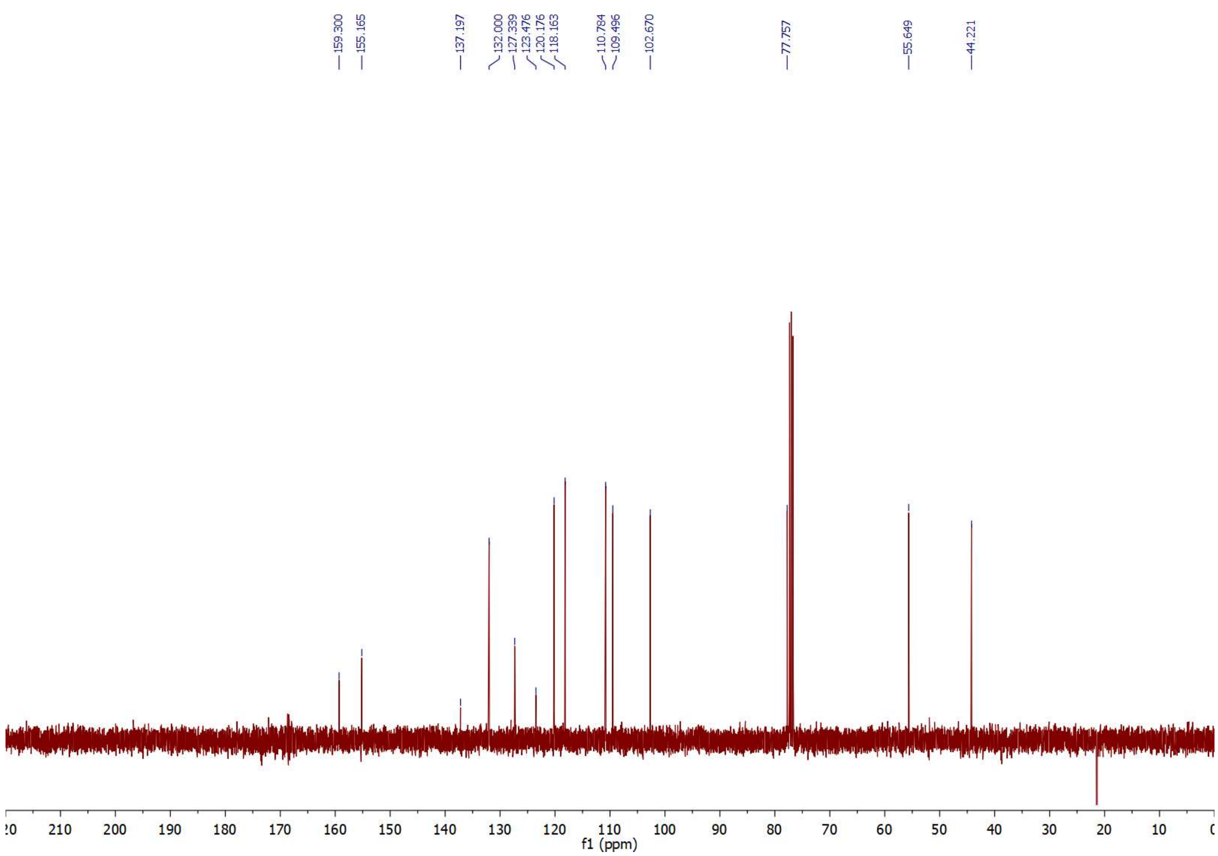


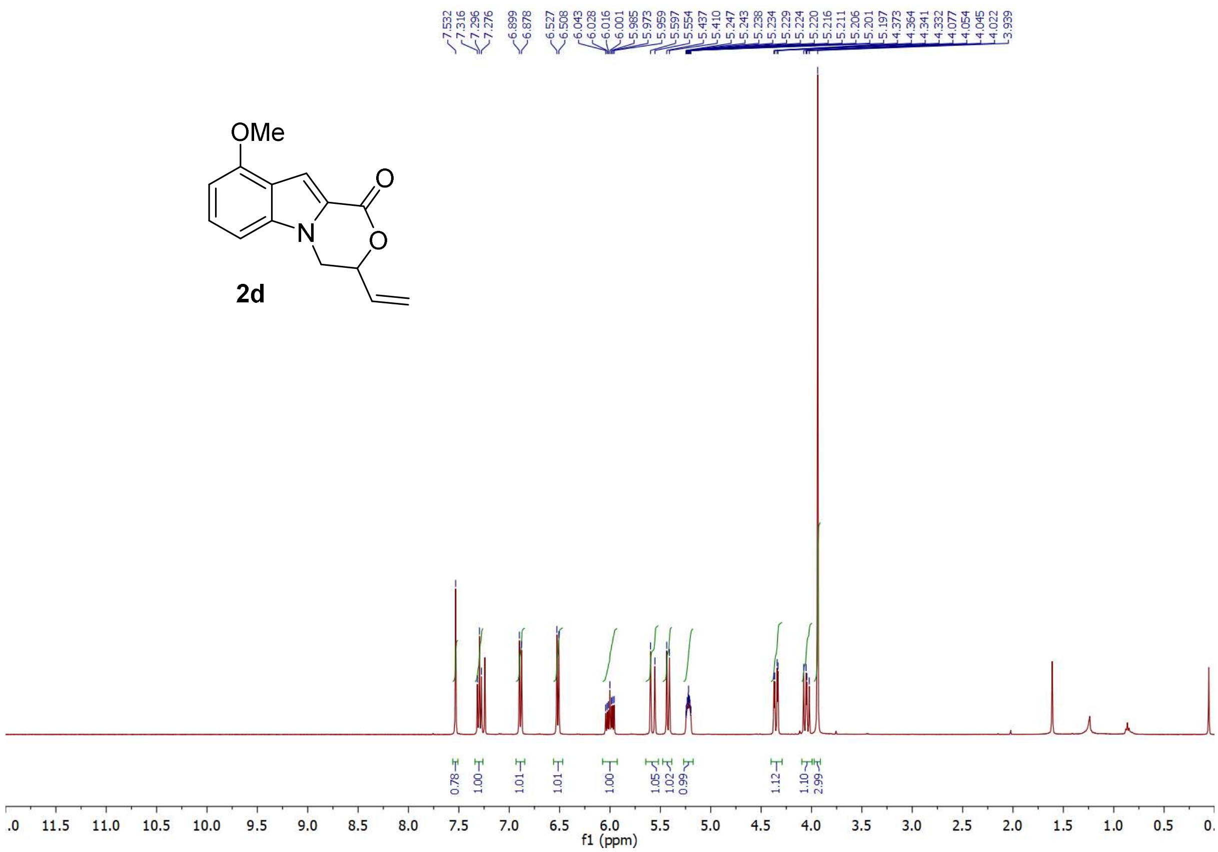
7.50
7.49
7.34
7.22
7.21
6.05
6.04
6.03
6.01
6.00
5.98
5.97
5.60
5.56
5.44
5.42
5.26
5.26
5.26
5.25
5.25
5.24
5.24
5.23
5.23
5.22
5.22
5.21
5.21
4.39
4.38
4.36
4.35
4.09
4.06
4.05
4.03
2.44
Me
O
N
O
2b
0.93
0.84
1.78
1.04
1.05
1.05
1.03
1.14
1.16
3.00
f1 (ppm)



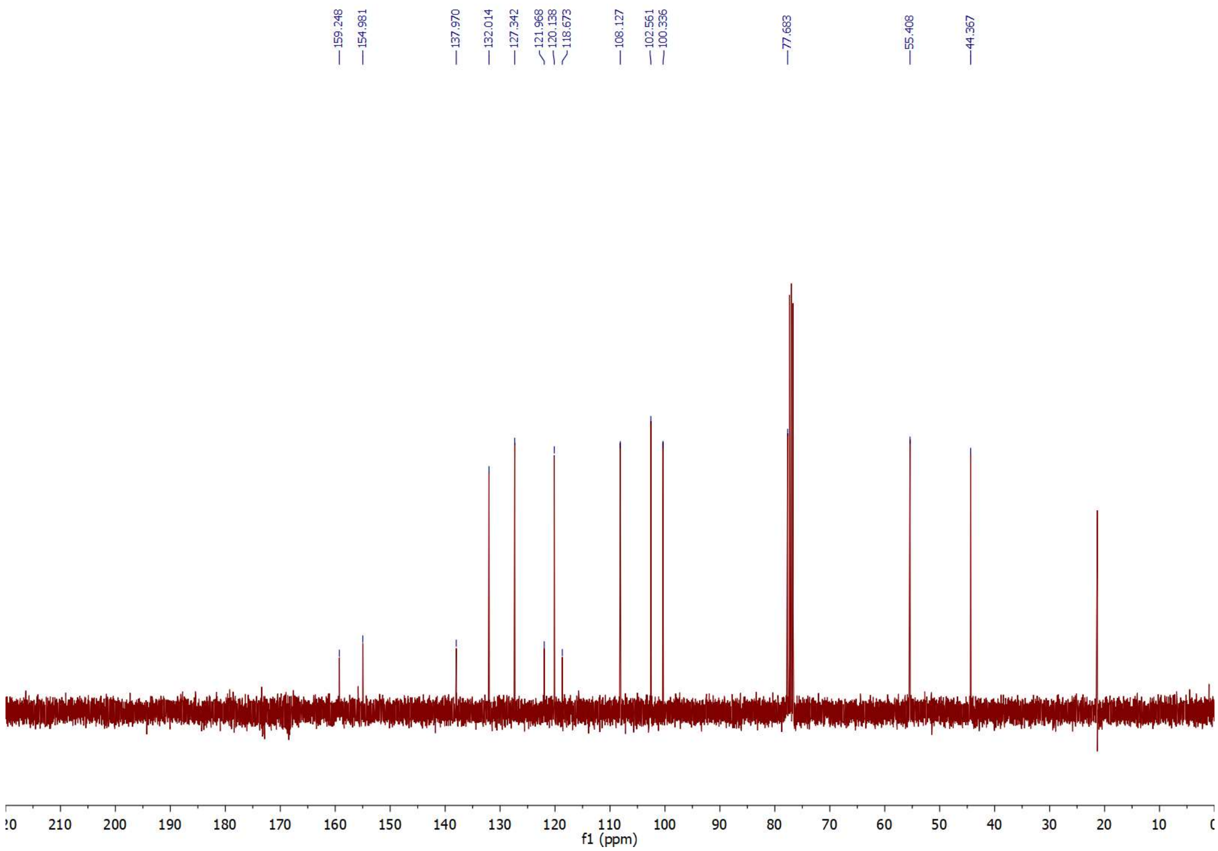
159.44
137.59
135.16
132.04
130.93
128.12
127.25
122.43
120.13
109.63
109.51
77.76
44.17
21.39
f1 (ppm)

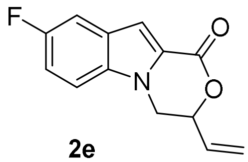

7.323 7.242 7.222 7.220 7.218 7.200 7.197 7.195 7.084 7.078 7.067 7.061 7.045 7.039 6.049 6.035 6.023 6.008 5.992 5.980 5.965 5.604 5.602 5.601 5.599 5.561 5.559 5.558 5.556 5.445 5.443 5.441 5.418 5.416 5.415 5.413 5.262 5.259 5.255 5.253 5.250 5.247 5.245 5.241 5.239 5.236 5.232 5.226 5.224 5.221 5.218 5.216 5.212 5.209 4.371 4.363 4.339 4.331 4.077 4.053 4.045 4.022 3.835
MeO
N
O
2c
0.84 1.36 0.90 0.95 1.00 1.03 1.01 1.02 1.11 1.13 3.02
f1 (ppm)


159.300 155.165 137.197 132.000 127.339 123.476 120.176 118.163 110.784 109.496 102.670 77.757 55.649 44.221
f1 (ppm)

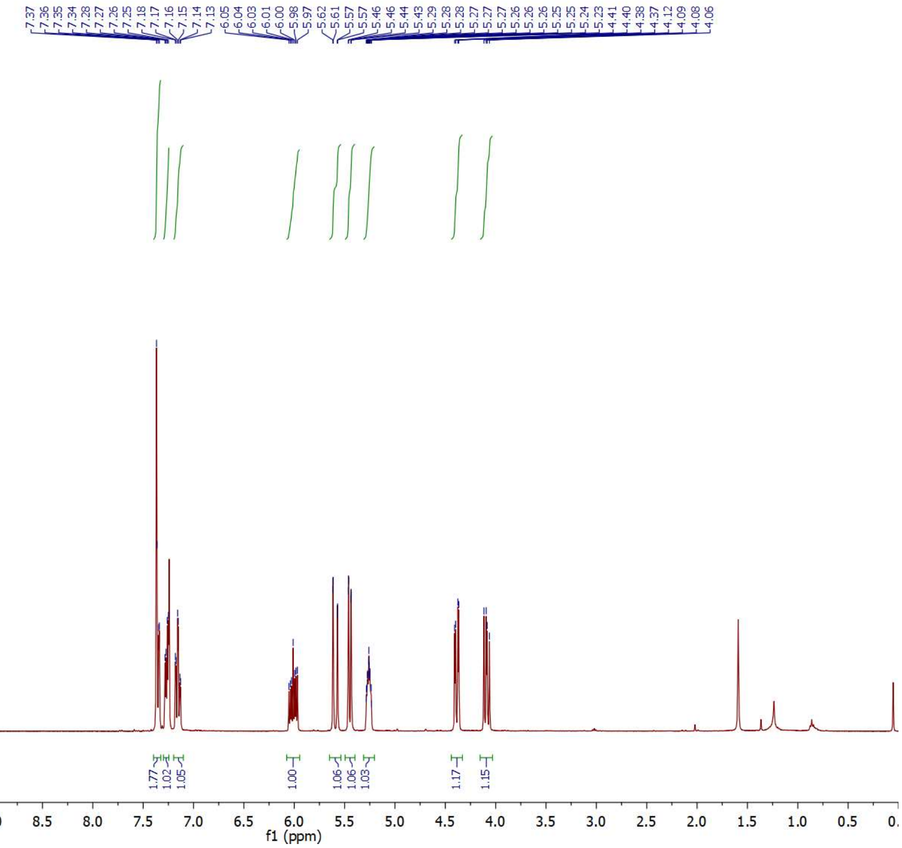

OMe
O
N
O
7.532
7.316
7.296
7.276
6.899
6.878
6.527
6.508
6.043
6.028
6.016
6.001
5.985
5.973
5.959
5.597
5.554
5.437
5.410
5.247
5.243
5.238
5.234
5.229
5.224
5.220
5.216
5.211
5.206
5.201
5.197
4.373
4.364
4.341
4.332
4.077
4.054
4.045
4.022
3.939
0.78
1.00
1.01
1.01
1.00
1.05
1.02
0.99
1.12
1.10
2.99
f1 (ppm)

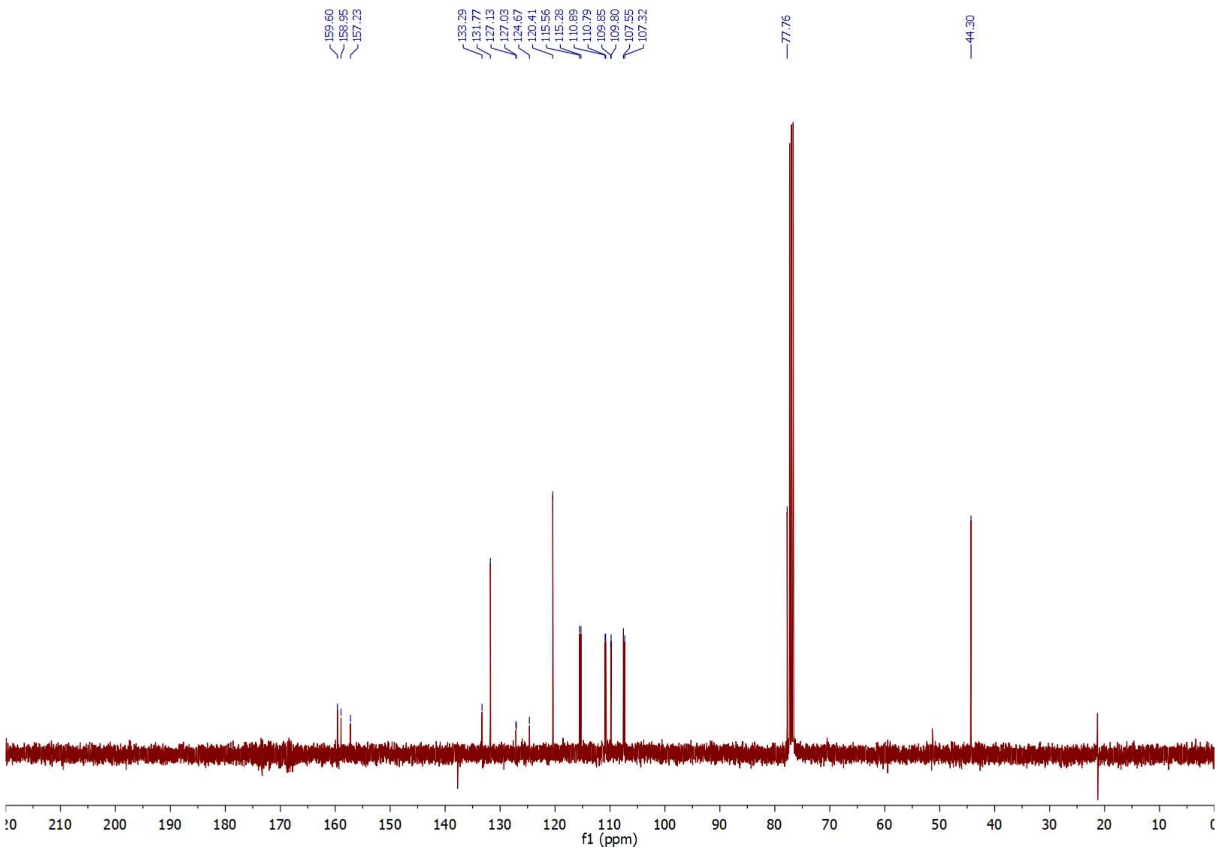
2d

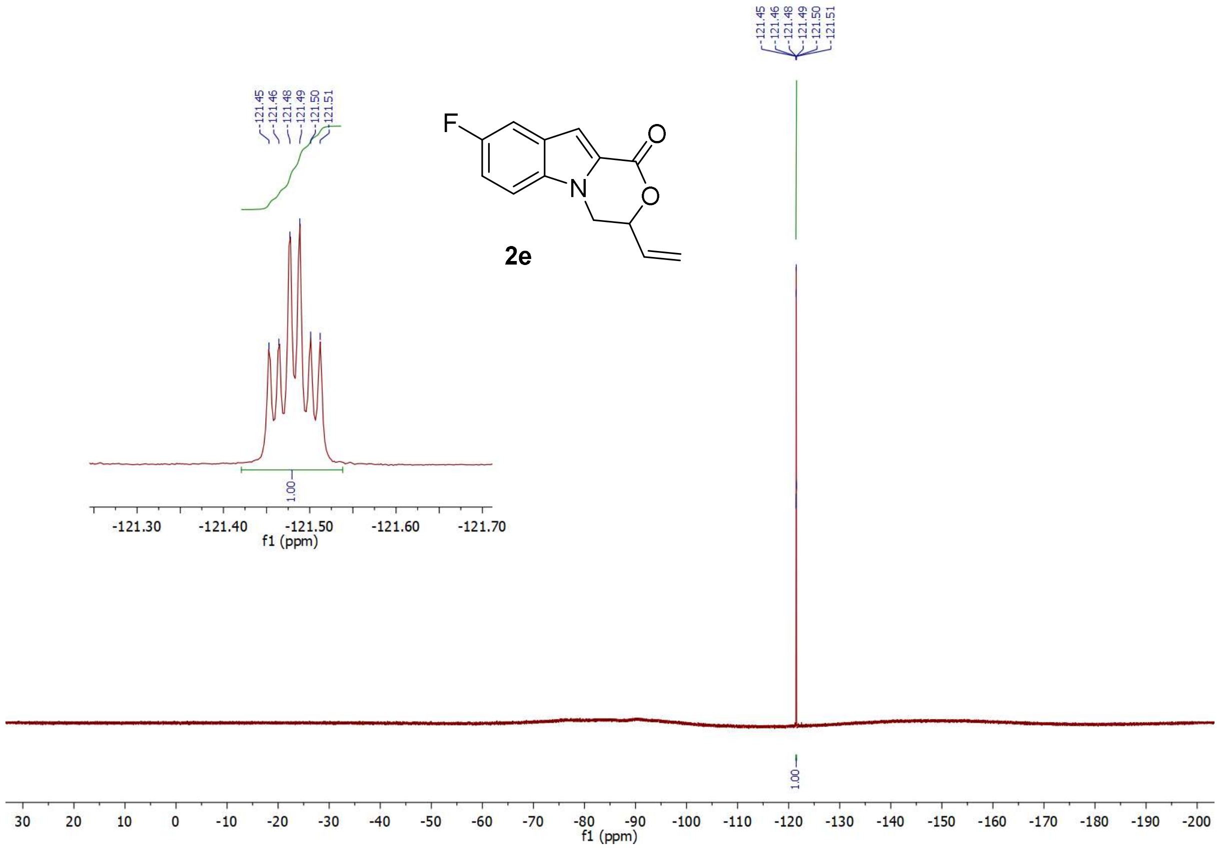

159.248
154.981
137.970
132.014
127.342
121.968
120.138
118.673
108.127
102.561
100.336
77.683
55.408
44.367
f1 (ppm)

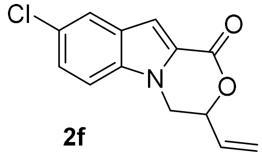


2e


7.37 7.36 7.35 7.34 7.28 7.27 7.26 7.25 7.18 7.17 7.16 7.15 7.14 7.13 6.05 6.04 6.03 6.01 6.00 5.98 5.97 5.62 5.61 5.57 5.57 5.46 5.44 5.43 5.29 5.28 5.28 5.27 5.27 5.26 5.26 5.25 5.24 5.23 4.41 4.40 4.38 4.37 4.12 4.09 4.08 4.06
1.77 1.02 1.05 1.00 1.06 1.06 1.03 1.17 1.15
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

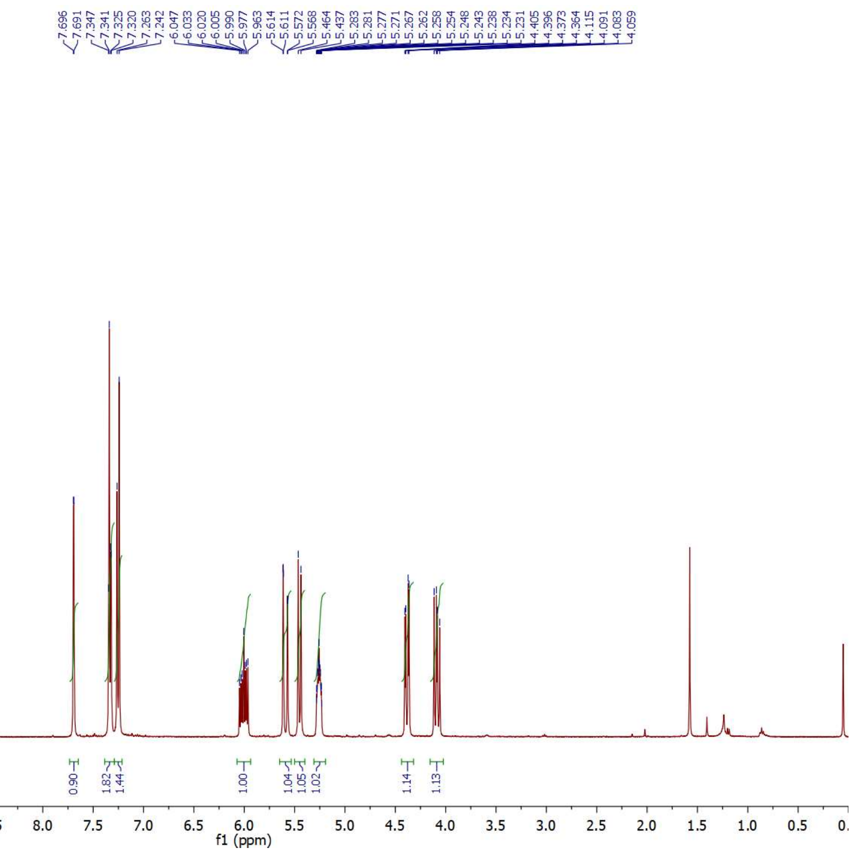

159.60 158.95 157.23 133.29 131.77 127.13 127.03 124.67 120.41 115.56 115.28 110.89 110.79 109.85 109.80 107.55 107.32
77.76
44.30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-121.45
-121.46
-121.48
-121.49
-121.50
-121.51
F
O
N
O
2e
1.00
-121.30
-121.40
-121.50
-121.60
-121.70
f1 (ppm)
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

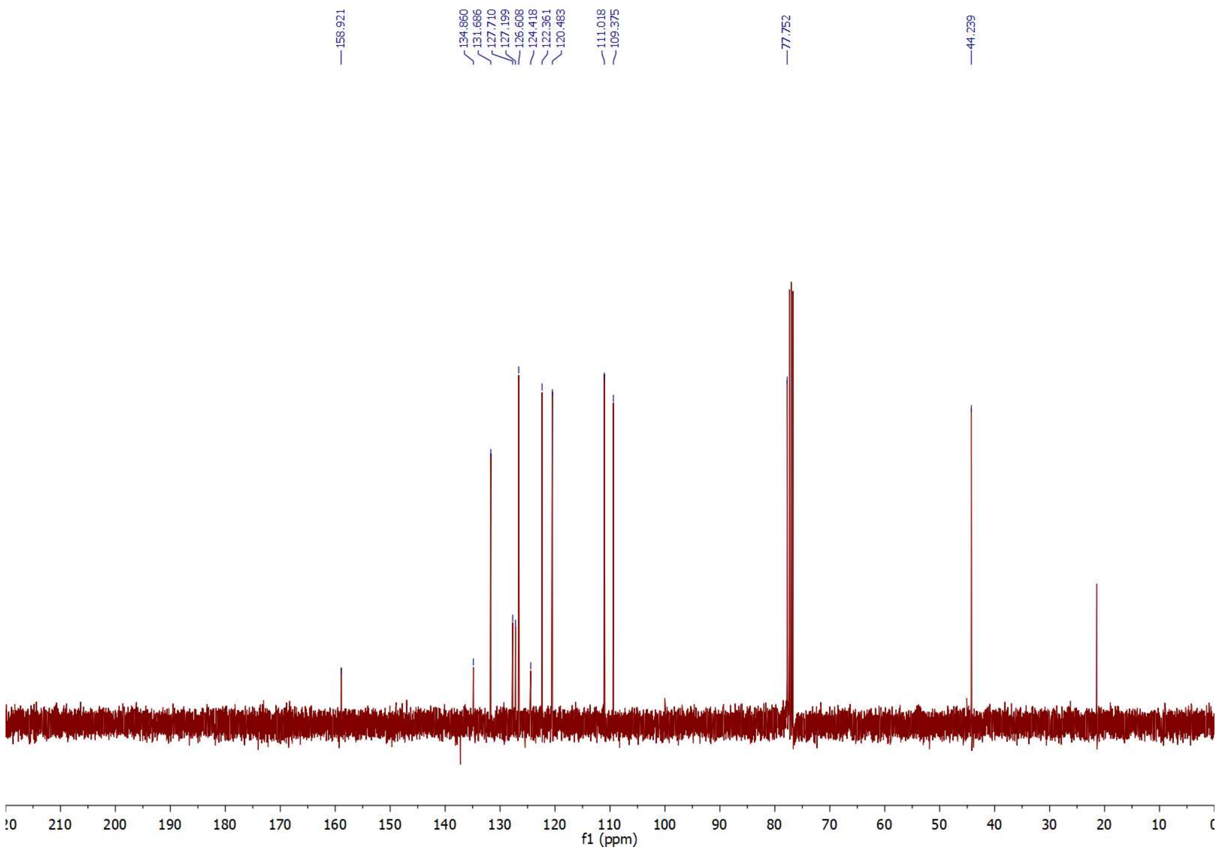


Cl
O
N
O

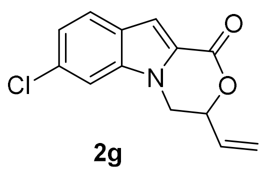
2f



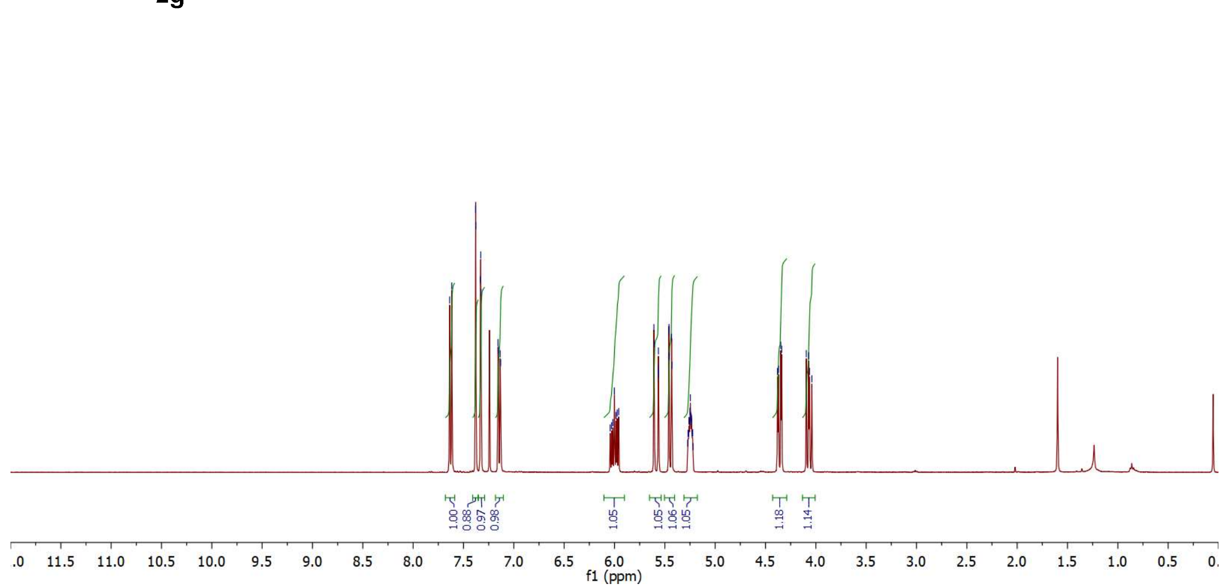
7.696
7.691
7.347
7.341
7.325
7.320
7.263
7.242
6.047
6.033
6.020
6.005
5.990
5.977
5.963
5.614
5.611
5.572
5.568
5.464
5.437
5.283
5.281
5.277
5.271
5.267
5.262
5.258
5.254
5.248
5.243
5.238
5.234
5.231
4.405
4.396
4.373
4.364
4.115
4.091
4.083
4.059
0.90
1.82
1.44
1.00
1.04
1.05
1.02
1.14
1.13
f1 (ppm)

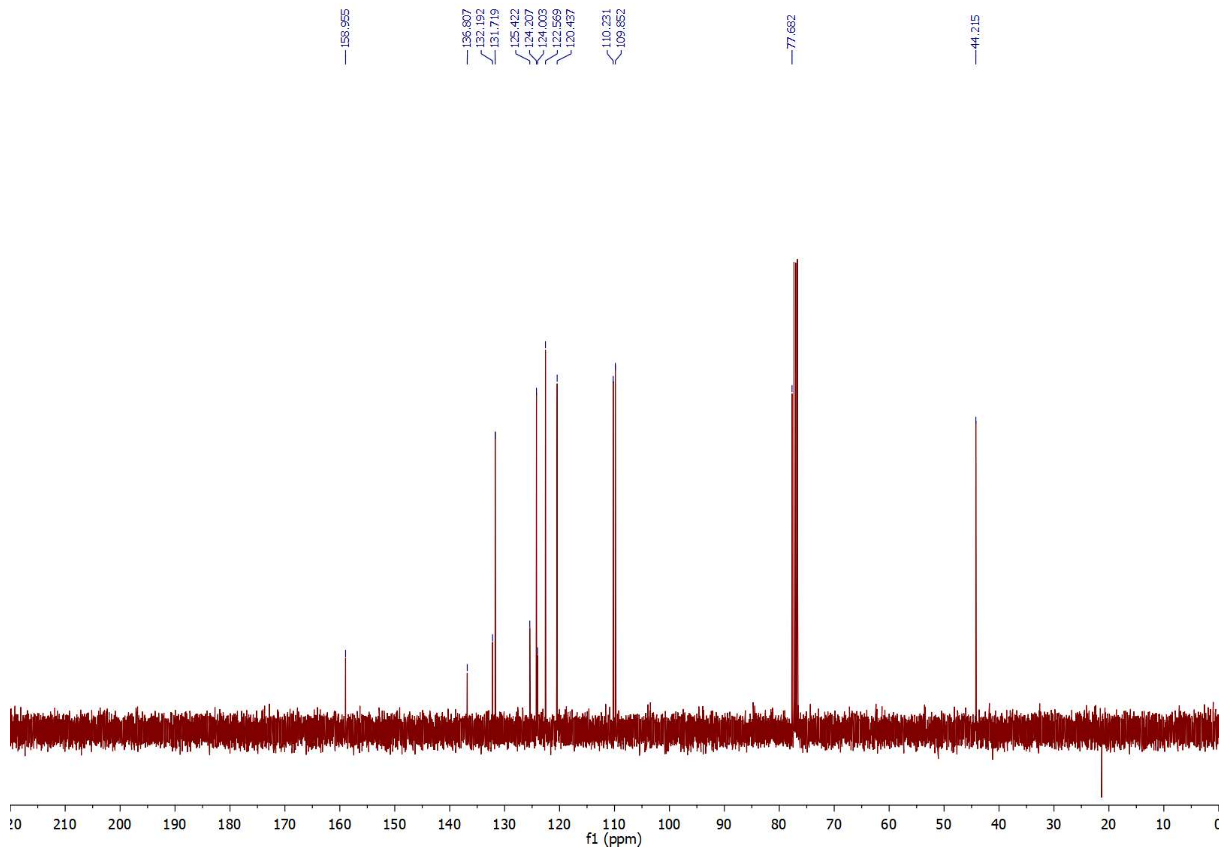


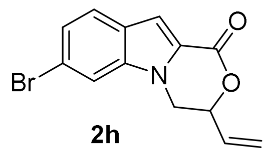
158.921
134.860
131.686
127.710
127.199
126.608
124.418
122.361
120.483
111.018
109.375
77.752
44.239
f1 (ppm)



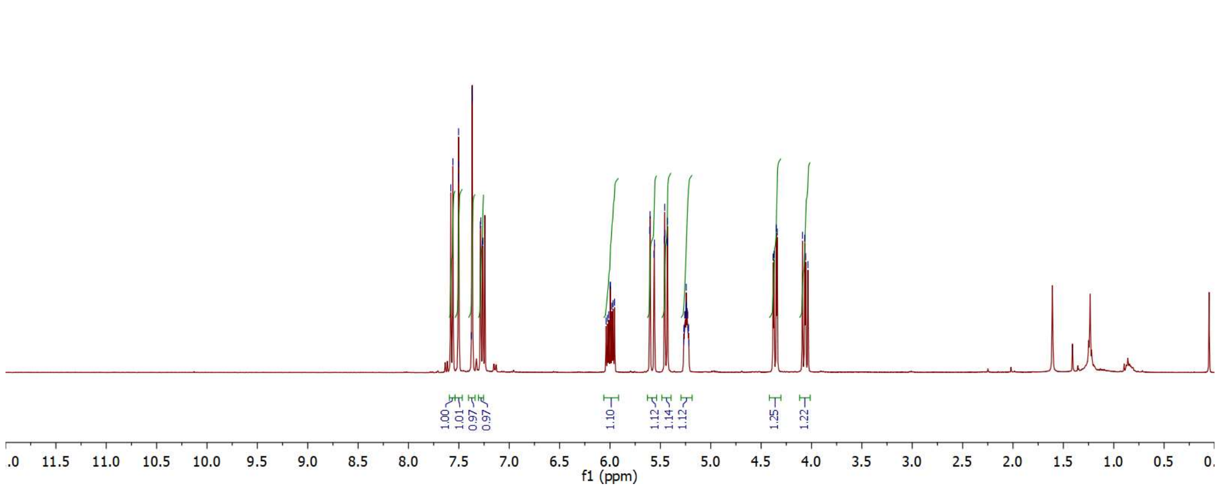
2g

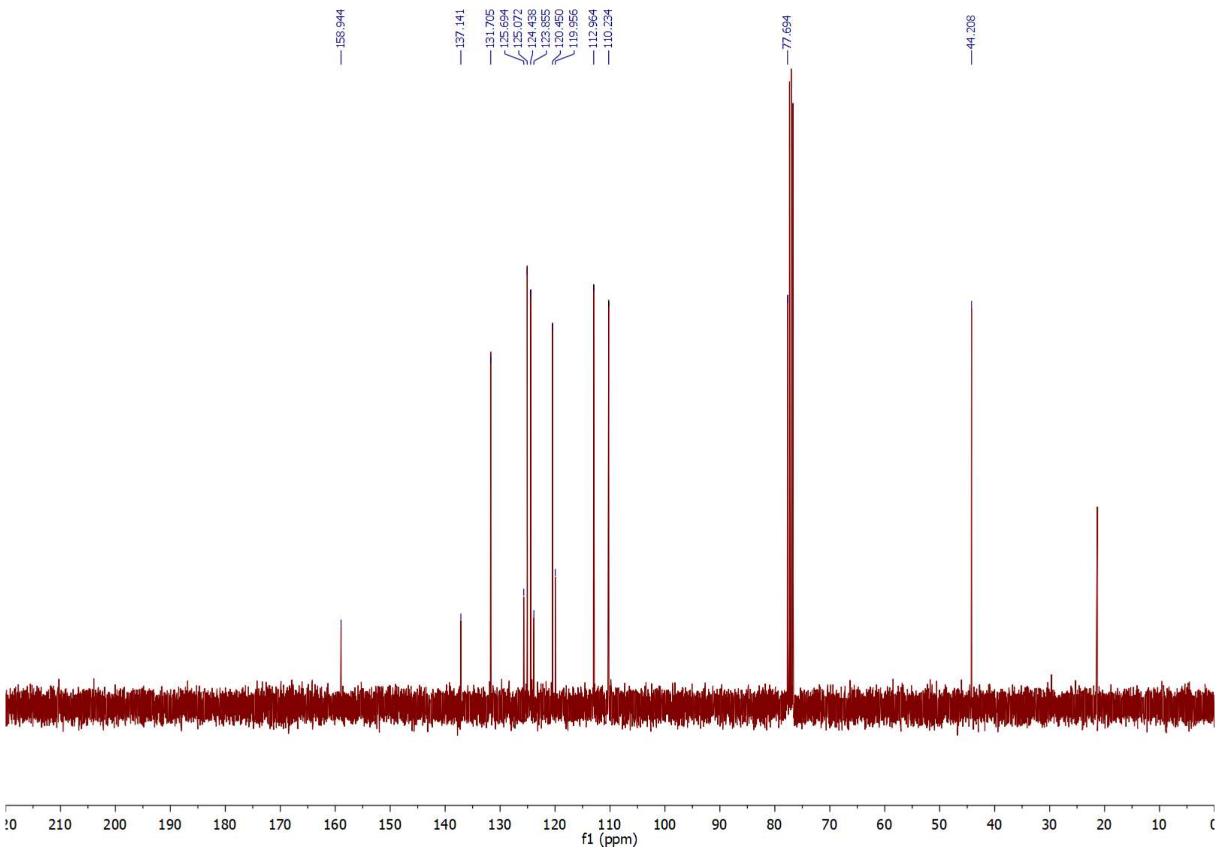


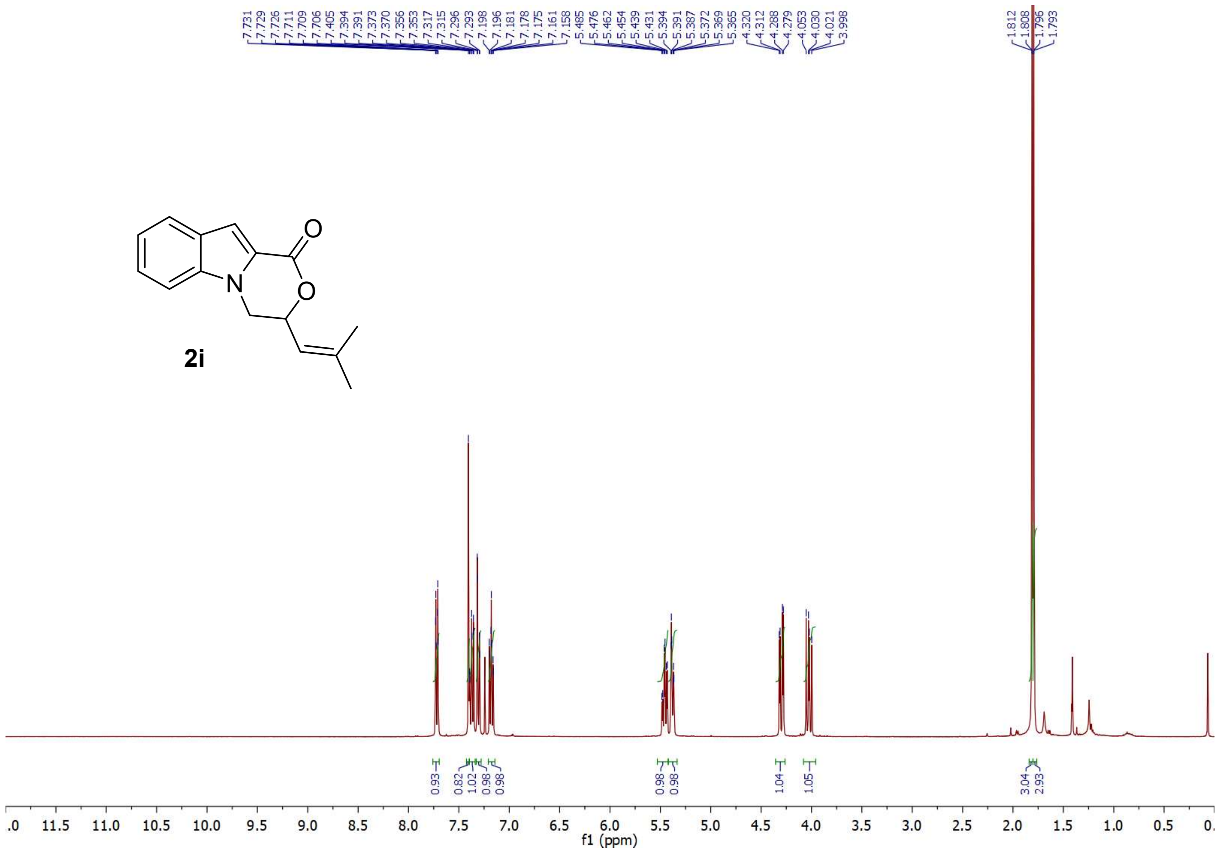


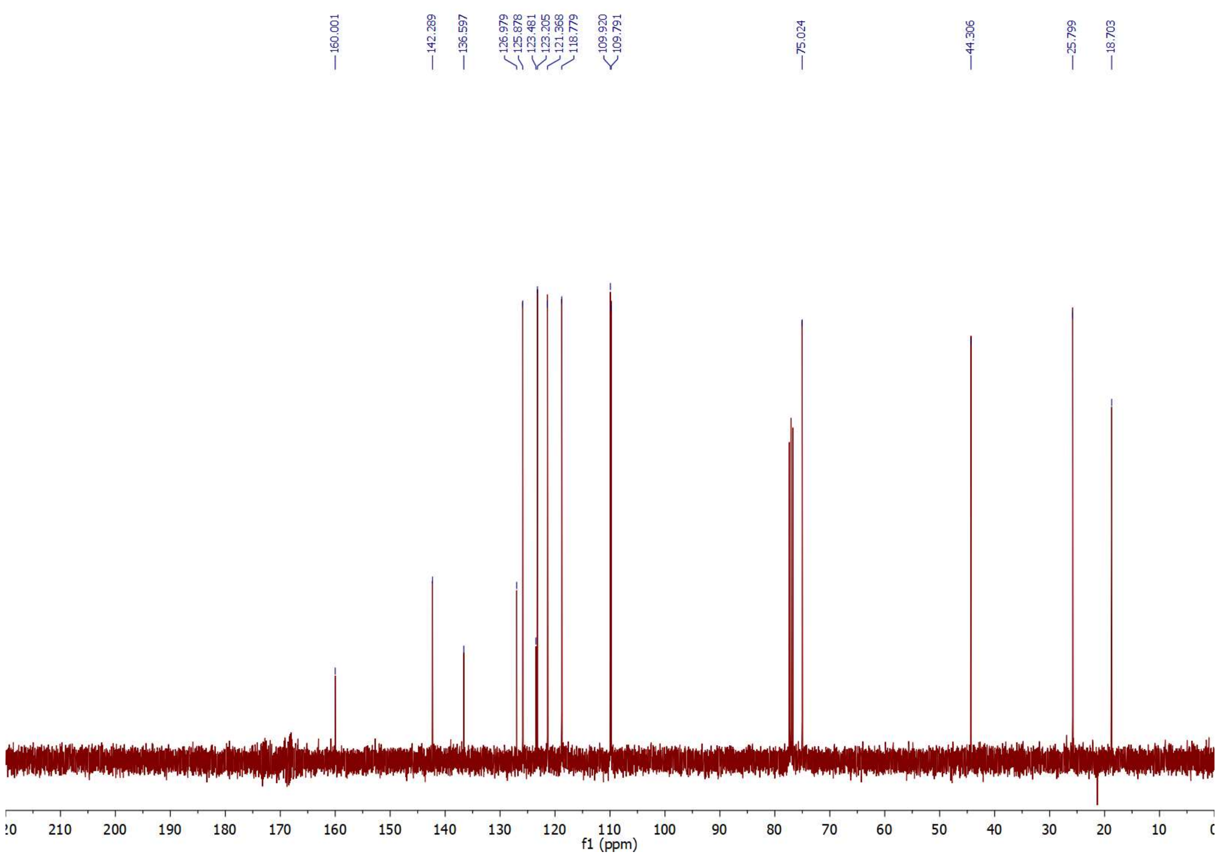

Br
N
O
O

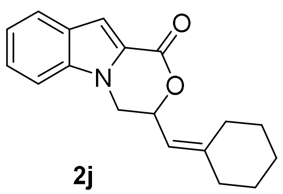
2h


7.581
7.559
7.506
7.503
7.501
7.376
7.368
7.366
7.287
7.282
7.265
7.261
6.039
6.024
6.012
5.998
5.996
5.981
5.969
5.955
5.606
5.602
5.563
5.559
5.459
5.457
5.455
5.432
5.430
5.428
5.269
5.266
5.263
5.260
5.257
5.254
5.252
5.247
5.243
5.240
5.234
5.231
5.229
5.224
5.220
5.217
4.381
4.372
4.349
4.340
4.090
4.067
4.058
4.035
1.00
1.01
0.97
0.97
1.10
1.12
1.14
1.12
1.25
1.22
f1 (ppm)

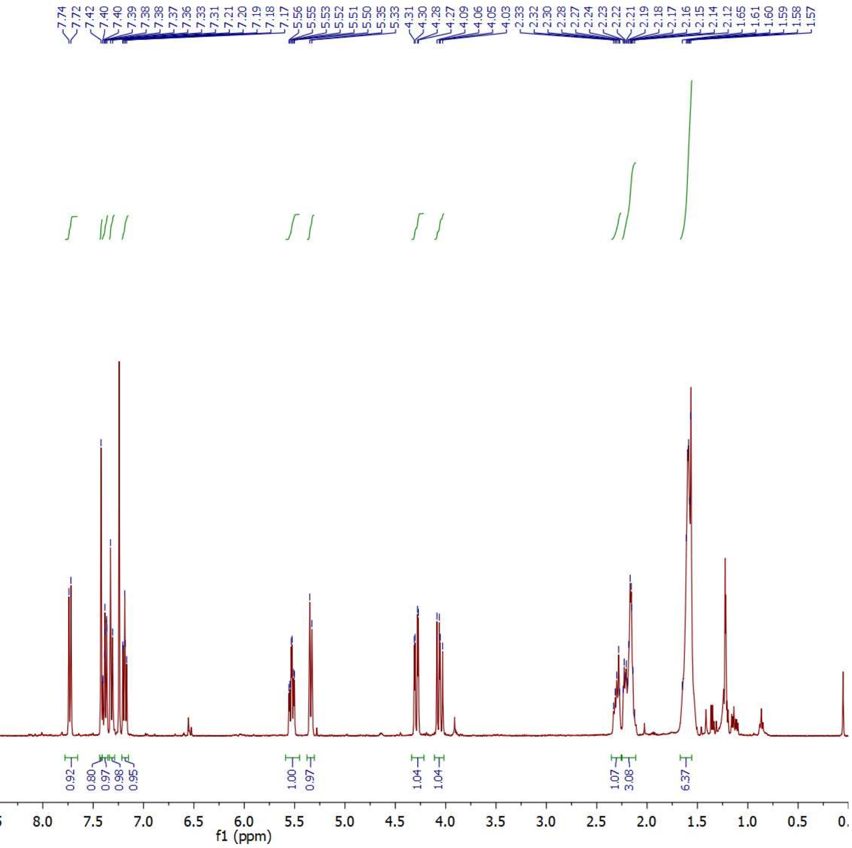

158.944
137.141
131.705
125.694
125.072
124.438
123.855
120.450
119.956
112.964
110.234
77.694
44.208
f1 (ppm)

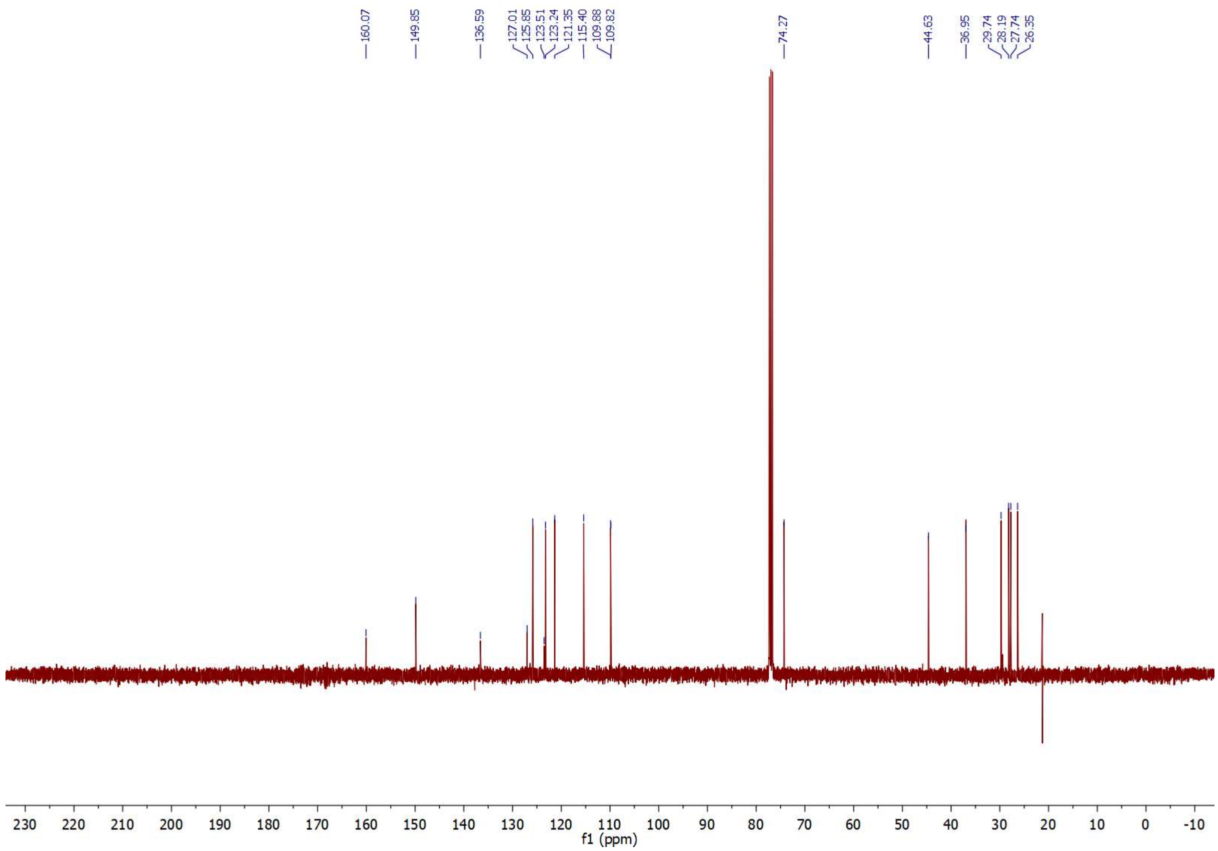

O
N
O
2i
7.731
7.729
7.726
7.711
7.709
7.706
7.405
7.394
7.391
7.373
7.370
7.356
7.353
7.317
7.315
7.296
7.293
7.198
7.196
7.181
7.178
7.175
7.161
7.158
5.485
5.476
5.462
5.454
5.439
5.431
5.394
5.391
5.387
5.372
5.369
5.365
4.320
4.312
4.288
4.279
4.053
4.030
4.021
3.998
1.812
1.808
1.796
1.793
0.93
0.82
1.02
0.98
0.98
0.98
0.98
1.04
1.05
3.04
2.93
f1 (ppm)

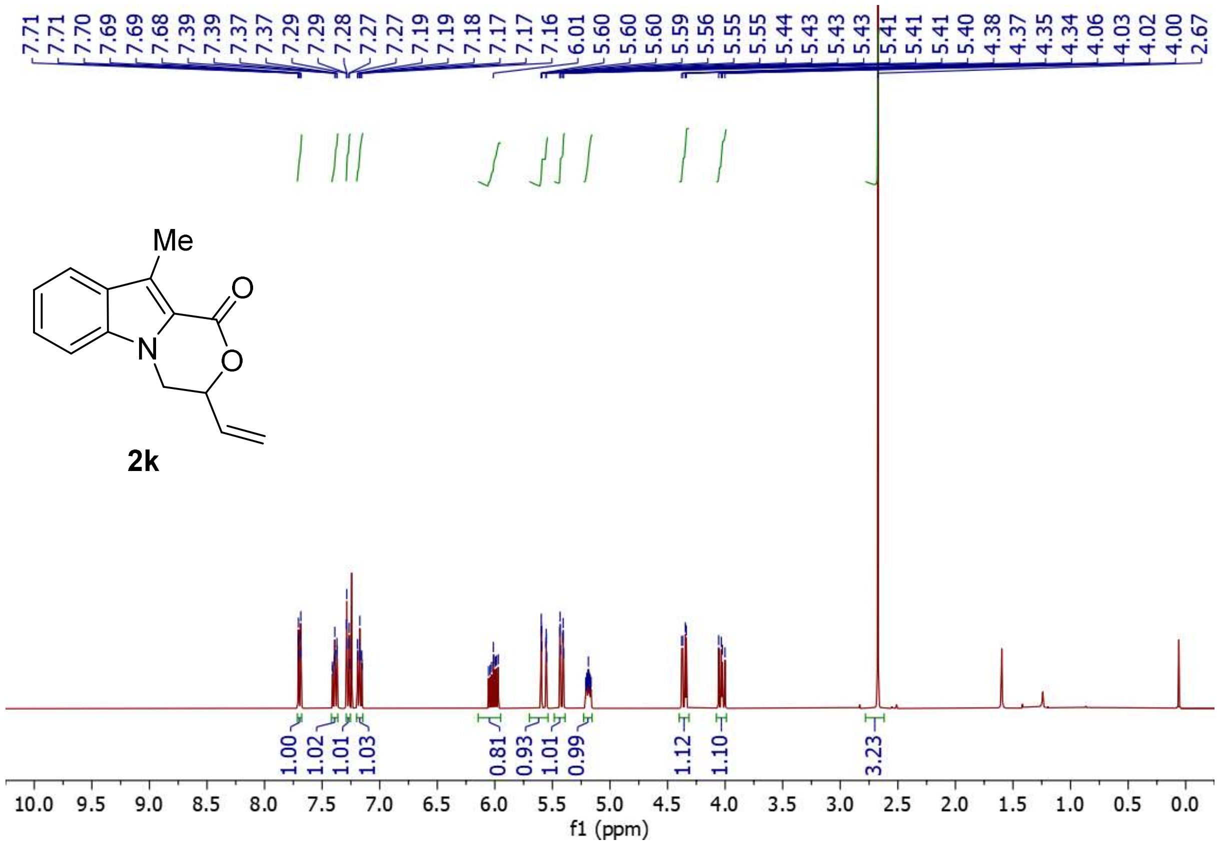

160.001
142.289
136.597
126.979
125.878
123.481
123.205
121.368
118.779
109.920
109.791
75.024
44.306
25.799
18.703
f1 (ppm)



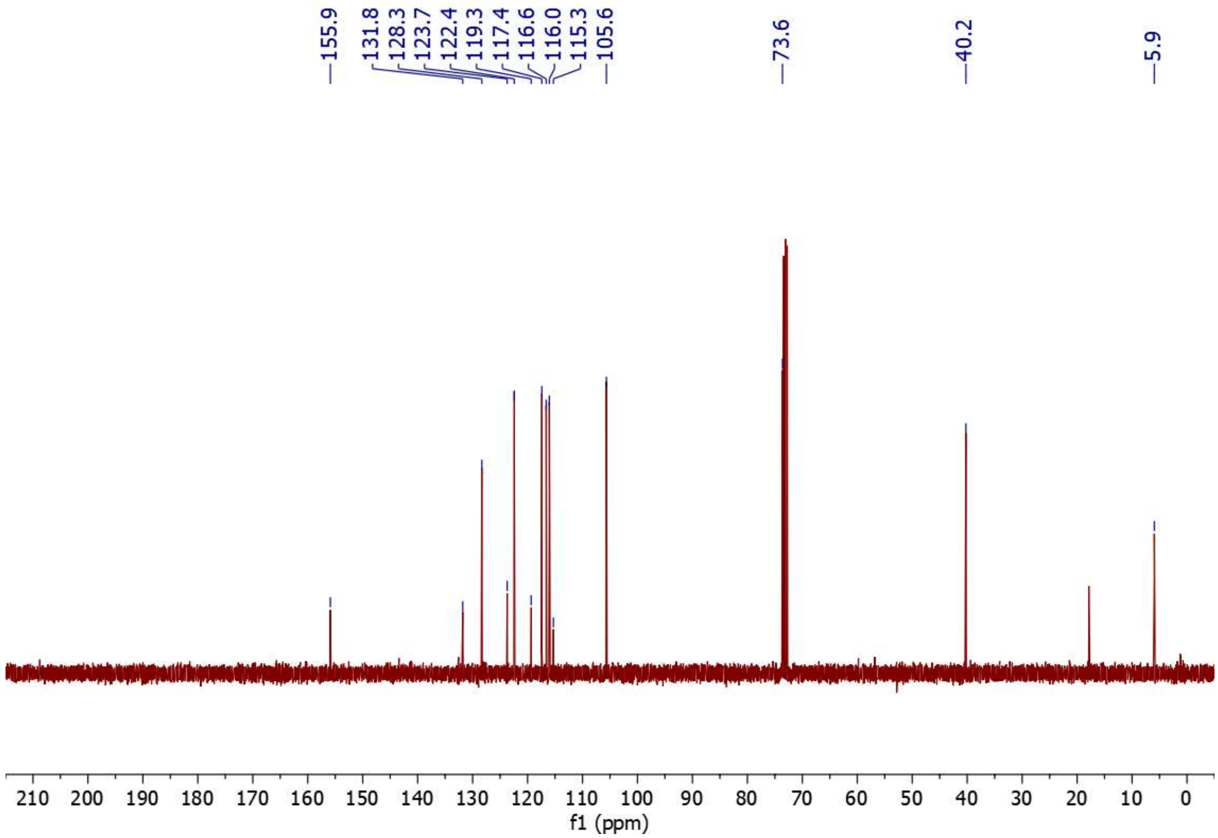
2j


7.74
7.72
7.42
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.33
7.31
7.21
7.20
7.19
7.18
7.17
5.56
5.55
5.53
5.52
5.51
5.50
5.35
5.33
4.31
4.30
4.28
4.27
4.09
4.06
4.05
4.03
2.33
2.32
2.30
2.28
2.27
2.24
2.23
2.22
2.21
2.19
2.18
2.17
2.16
2.15
2.14
2.12
1.65
1.61
1.60
1.59
1.58
1.57
0.92
0.80
0.97
0.98
0.95
1.00
0.97
1.04
1.04
1.07
3.08
6.37
f1 (ppm)

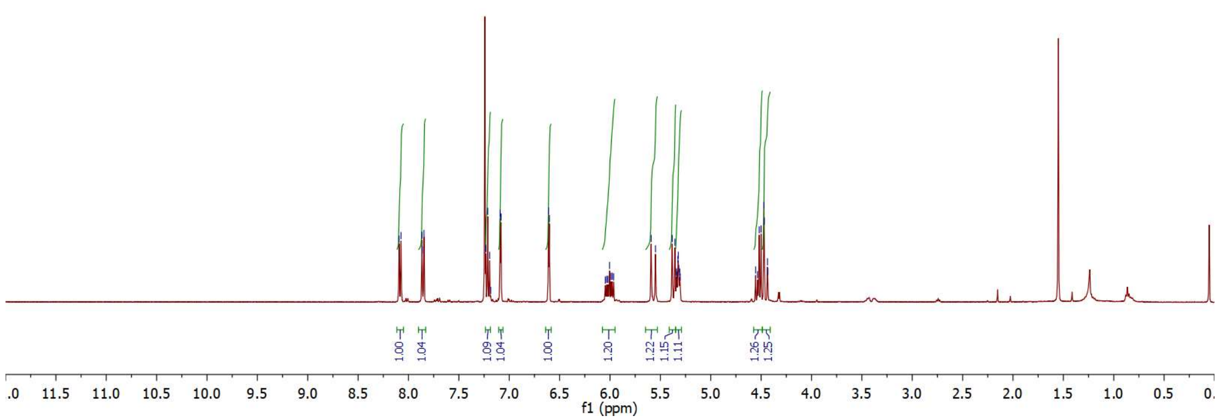

160.07
149.85
136.59
127.01
125.85
123.51
123.24
121.35
115.40
109.88
109.82
74.27
44.63
36.95
29.74
28.19
27.74
26.35
f1 (ppm)

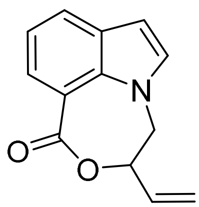


7.71 7.71 7.70 7.69 7.69 7.68 7.39 7.39 7.37 7.37 7.29 7.29 7.28 7.27 7.27 7.19 7.19 7.18 7.17 7.17 7.16 6.01 5.60 5.60 5.60 5.59 5.56 5.55 5.55 5.44 5.43 5.43 5.43 5.41 5.41 5.41 5.40 4.38 4.37 4.35 4.34 4.06 4.03 4.02 4.00 2.67
Me
O
N
O
2k
1.00 1.02 1.01 1.03 0.81 0.93 1.01 0.99 1.12 1.10 3.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

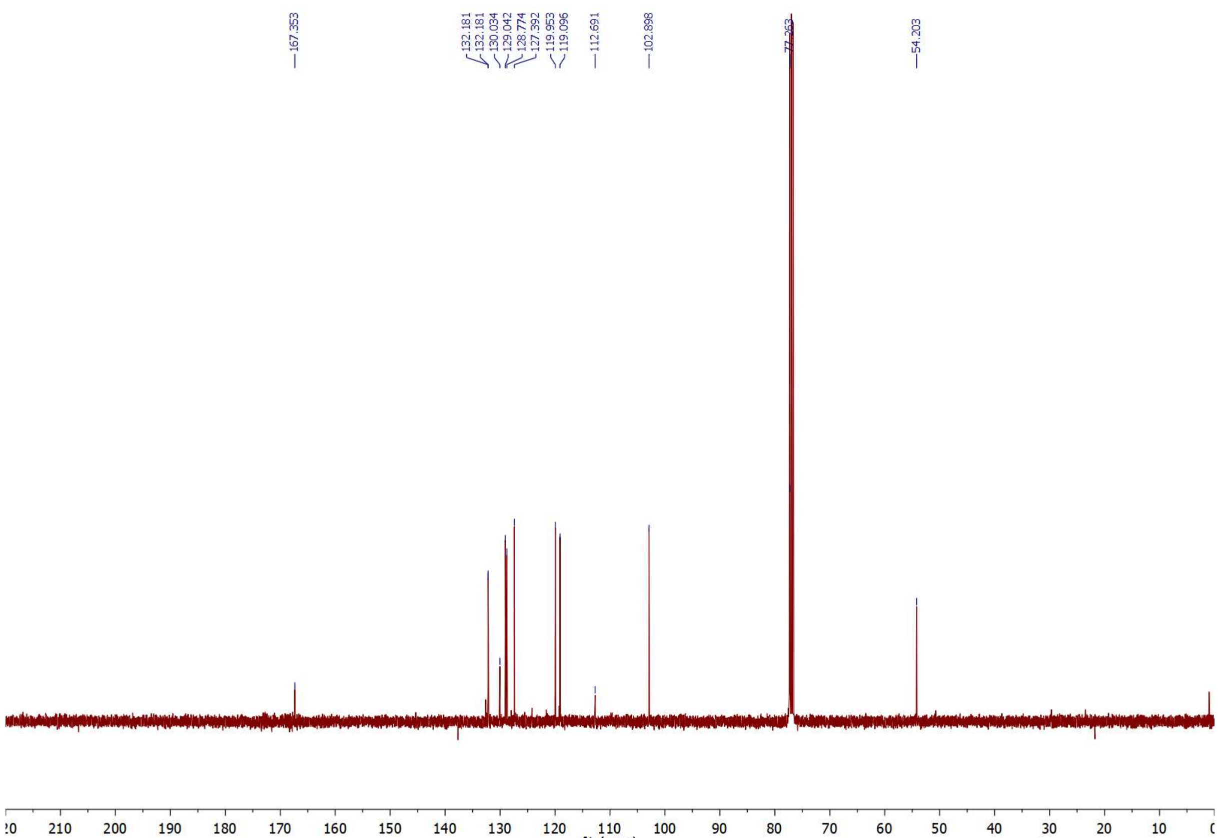


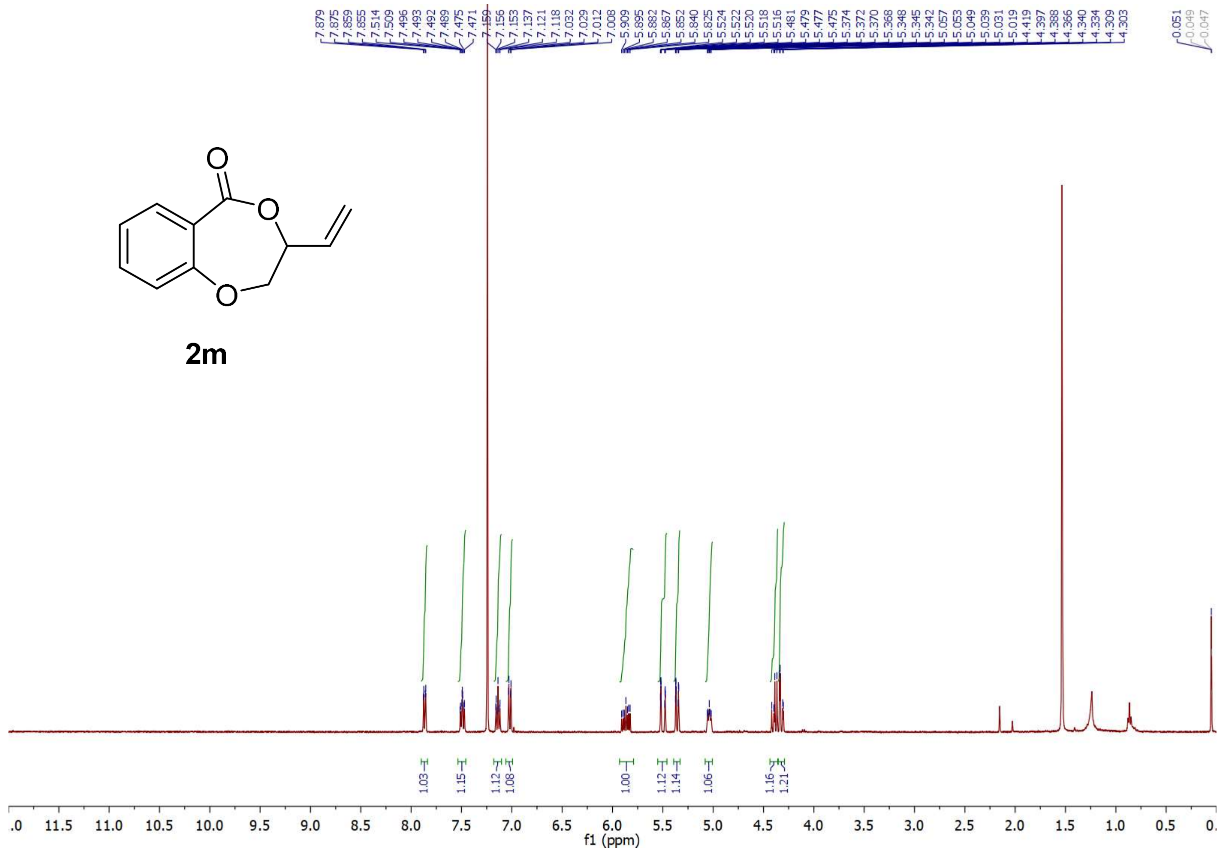
155.9 131.8 128.3 123.7 122.4 119.3 117.4 116.6 116.0 115.3 105.6 73.6 40.2 5.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

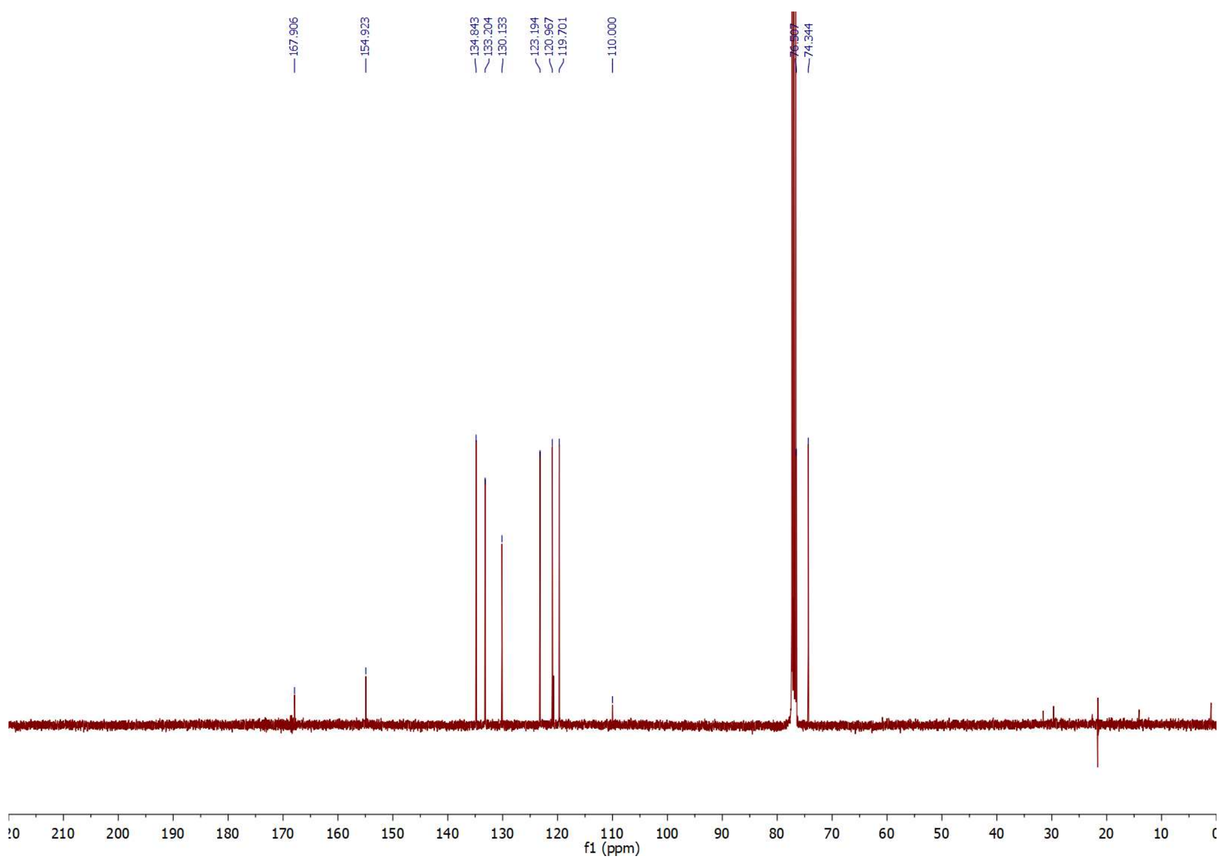

8.094
8.074
7.866
7.863
7.847
7.232
7.214
7.194
7.184
7.089
7.081
6.610
6.602
6.047
6.032
6.020
6.005
5.989
5.977
5.963
5.591
5.548
5.382
5.356
5.340
5.336
5.326
5.322
5.318
5.307
5.303
4.554
4.536
4.519
4.500
4.472
4.469
4.436
4.433
1.00
1.04
1.09
1.04
1.00
1.20
1.22
1.15
1.11
1.26
1.25
f1 (ppm)


N
O
O

2l


167.353
132.181
132.181
130.034
129.042
128.774
127.392
119.953
119.096
112.691
102.898
77.263
54.203
f1 (ppm)


2m
f1 (ppm)


f1 (ppm)

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