

Supporting Information

Catalytic Enantioselective Meerwein-Eschenmoser Claisen Rearrangement: Asymmetric Synthesis of Allyl Oxindoles

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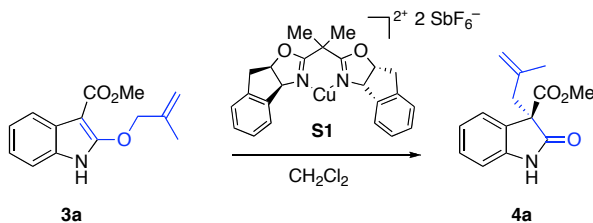
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General Considerations. Unless otherwise noted, all non-aqueous reactions were carried out under an atmosphere of dry N₂ in dried glassware. When necessary, solvents and reagents were dried prior to use. THF was distilled from sodium benzophenone ketyl. CH₃CN, CH₂Cl₂, TMEDA, and hexanes were distilled from CaH₂. Benzene was distilled from sodium.

Analytical thin layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica-gel 254-F plates. Visualization was accomplished with UV light. Chromatography was performed using a forced flow of the indicated solvent system on EM Reagents Silica Gel 60 (230-400 mesh).¹ Enantiomeric excesses were determined using analytical high performance liquid chromatography (HPLC), performed on a Waters 600 HPLC with UV detection at 254 nm. An analytical Chiralpak OD, AS and AD column (0.46 cm x 25 cm) from Daicel was used. ¹H NMR spectra were recorded on Bruker AM-500 (500 MHz), AM-360 (360 MHz), or AM-300 (300 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane (0 ppm) or from the solvent resonance (CDCl₃ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and number of protons. Decoupled ¹³C NMR spectra were recorded on a Bruker AM-500 (125 MHz) spectrometer. IR spectra were taken on a Perkin-Elmer FT-IR spectrometer using a thin film on NaCl plates or a CHCl₃ solution. Mass spectra were obtained on a low resonance Micromass Platform LC in electrospray mode and high resonance VG autospec with an ionization mode of either CI or ES. Melting points were obtained on Thomas Scientific Unimelt apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer Polarimeter 341 with a sodium lamp and are reported as follows [α]_D²³ (c g/100 mL, solvent).

Catalyst Screening:

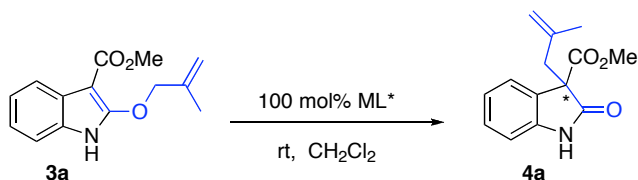
Catalyst Loadings with Copper/Indanol(bisoxazoline) Complex:



Cat. Loading	Temp.	conv.* (%)	Time	ee (%)
200 mol%	10 °C	100	10 min	82
100 mol%	10 °C	90	5 h	80
25 mol%	rt	78	2.5 h	76

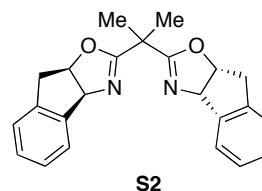
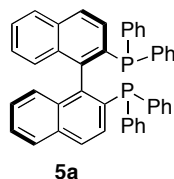
*By ¹H NMR spectroscopy.

Metal Screening with BINAP and Indanol(bisoxazoline) Ligands:

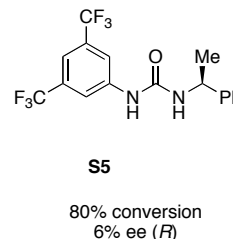
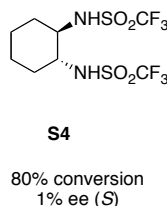
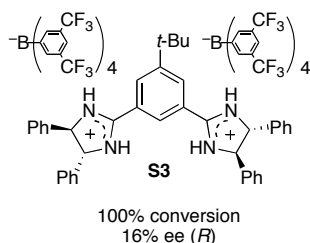
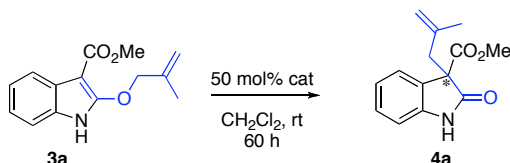


Metal	L*	T	Conv (%) ^a	ee (%)
AgSbF ₆	5a	1 h 20 min	100	10 (<i>S</i>)
Ni(SbF ₆) ₂	5a	15 min	100	12 (<i>R</i>)
Zn(SbF ₆) ₂	S2	2 h	30	24 (<i>S</i>)

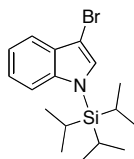
^aBy ¹H NMR spectroscopy.



Screening of Hydrogen-Bonding Catalysts:



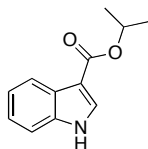
Preparation of Claisen Substrate Precursors 1a-1j:



3-Bromo-1-(triisopropylsilyl)-1H-indole (S6). A solution of indole (2.0 g, 17.1 mmol) in THF (100 mL) was cooled to 0 °C, at which time NaH (60% in oil, 3.4 g, 85.5 mmol) was added. The mixture was stirred together for 5 min, followed by addition of TIPSCl (10 mL, 46.7 mmol). After 1 h stirring at room temperature, the mixture was cooled to 0 °C, then H₂O was added. The organic layer was washed with 1 M HCl and brine, dried over Na₂SO₄, and concentrated under vacuum.

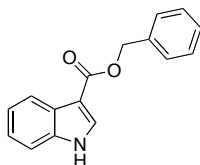
A solution of the TIPS-indole (4.67 g, 17.1 mmol) in THF was cooled to -78 °C, then recrystallized *N*-bromosuccinimide (3.0 g, 17.1 mmol) was added. After stirring for 3 h, another

aliquot of *N*-bromosuccinimide (1.5 g, 8.6 mmol) was added and stirring was continued for another 2 h. After warming to room temperature, pyridine (170 μ L) and hexanes (30.7 mL) were added and the mixture was concentrated. The precipitate was washed thoroughly with hexanes and the combined filtrate was concentrated. The residue was chromatographed (SiO₂, 100% hexanes) to afford **S6** (4.5 g) in 75% yield over the 2 steps as a white solid: mp 56-58 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.58-7.57 (m, 1H), 7.50-7.48 (m, 1H), 7.25 (s, 1H), 7.22-7.19 (m, 2H), 1.72-1.65 (m, 3H), 1.17 (d, *J* = 7.5 Hz, 18H); ¹³C NMR (500 MHz, CDCl₃) δ 140.1, 130.0, 129.7, 122.5, 121.6, 119.1, 114.1, 93.6, 18.0, 12.8; IR (film) 2949, 2868, 1463, 1285 cm⁻¹; HRMS (CI) *m/z* = 352.1109 calcd for C₁₇H₂₇BrNSi [MH]⁺, found 352.1018.

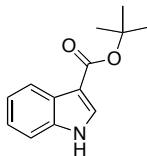


Isopropyl 1H-indole-3-carboxylate (1e). Indole **S6** (0.50 g, 1.42 mmol) was dissolved in Et₂O (14 mL) and cooled to -78 °C. A solution of *t*-BuLi (1.5 M in pentane, 2.1 mL, 3.12 mmol) was added dropwise, allowed to stir for 15 minutes, and then isopropyl chloroformate (1 M in PhCH₃, 1.71 mL, 1.71 mmol) was added. The reaction mixture stirred for 30 min at -78 °C, and then warmed to room temperature over 30 min. The reaction mixture was quenched with NaHCO₃, washed with H₂O and brine, dried over Na₂SO₄, and concentrated under vacuum.

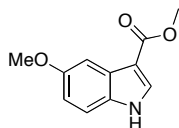
To a solution of the resultant carboxylate-indole (0.511 g, 1.42 mmol) in THF (14 mL) was added TBAF (1 M in THF, 1.4 mL, 1.42 mmol). After stirring 15 min, the mixture was quenched with NH₄Cl, washed with brine, dried over Na₂SO₄, and concentrated under vacuum. The oil was chromatographed (SiO₂, 25% EtOAc/hexanes) to give **1e** (0.26 g) in 90% yield over 2 steps. The ¹H NMR spectrum matches that of the reported compound.²



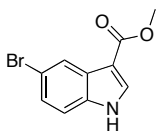
Benzyl 1H-indole-3-carboxylate (1d). Using the procedure from compound **1e** with benzyl chloroformate, **1d** (0.35 g, 1.41 mmol) was obtained in 62% yield as a white solid: mp 142-145 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.63 (bs, 1H), 8.23-8.18 (m, 1H), 7.96 (d, *J* = 3.0 Hz, 1H), 7.55-7.26 (m, 8H), 5.49 (s, 2H); ¹³C NMR (300 MHz, CDCl₃) δ 165.1, 136.7, 136.1, 131.4, 128.5, 128.0 (2), 127.0, 123.2, 122.1, 121.4, 111.6, 108.5, 65.6; IR (film) 3398, 3298, 3128, 3066, 2958, 2881, 1676, 1529, 1429, 1328, 1244 cm⁻¹; HRMS (ES) *m/z* = 252.0946 calcd for C₁₆H₁₄NO₂ [MH]⁺, found 252.1071.



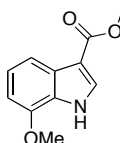
tert-Butyl 1H-indole-3-carboxylate (1f). Oxalyl chloride (320 μ L, 3.72 mmol) was added to a suspension of indole-3-carboxylic acid (0.20 g, 1.24 mmol) in anhydrous CH_2Cl_2 (10 mL), followed by a catalytic amount of anhydrous DMF (2 drops). The suspension was stirred at rt for 3 h. Removal of the solvent in vacuo gave the crude acid chloride as a yellow oil. To this material was added slightly warmed *t*-BuOH (1.7 mL), followed by KO*t*-Bu (0.226 g, 2.02 mmol). The resulting mixture was stirred for 90 min, diluted with Et_2O and washed with sat. aq. NH_4Cl and brine. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The oil was purified by chromatography (SiO_2 , 40% EtOAc/Hexanes) to yield **1f** (0.27 g, 1.24 mmol) in 100% yield as a white solid. The ^1H NMR spectrum matches that of the reported compound.³



Methyl 5-methoxy-1H-indole-3-carboxylate (1h). Pyridine (0.30 mL, 3.54 mmol) was added to a suspension of 5-methoxy-1H-indole (0.40 g, 2.72 mmol) in anhydrous THF (6 mL) at 0 $^\circ\text{C}$. A solution of trichloroacetyl chloride (0.40 mL, 3.54 mmol) in THF (6 mL) was added dropwise via an addition funnel over 1h. The reaction mixture was then allowed to warm to room temperature to stir for 16 h. The reaction mixture was quenched in 1 M HCl, dried over Na_2SO_4 , and concentrated under vacuum. The resulting solid was then dissolved in MeOH (54 mL), and aq. KOH (50 % by wt., 0.20 mL) was added. The reaction mixture was heated to reflux for 5 h, then stirred at ambient temperature for 1 h, followed by concentration under vacuum. The solid was purified by chromatography (SiO_2 , 25% EtOAc/Hexanes) to yield **1h** (0.50 g, 2.45 mmol) in 90% yield as a off-white solid: mp 141-142 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.87 (bs, 1H), 7.86 (d, J = 2.9 Hz, 1H), 7.68 (d, J = 2.3 Hz, 1H), 7.29 (d, J = 8.8 Hz, 1H), 6.91 (dd, J = 2.3 Hz, 8.8 Hz, 1H), 3.93 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (500) MHz, CDCl_3) δ 165.9, 155.8, 131.3, 131.0, 126.7, 113.7, 112.4, 108.2, 102.8, 55.7, 51.0; IR (film) 3236, 2950, 2835, 1661, 1529, 1444, 1367, 1282 cm^{-1} ; HRMS (ES) m/z = 206.0739 calcd for $\text{C}_{11}\text{H}_{12}\text{NO}_3$ $[\text{MH}]^+$, found 206.0850.

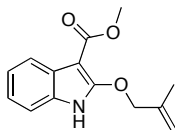


Methyl 5-bromo-1*H*-indole-3-carboxylate (1i). Using the procedure from **1h** with 5-bromo-1*H*-indole, **1i** (0.65 g, 2.57 mmol) was obtained in 50% yield as an off-white solid: mp 212-214 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.60 (bs, 1H), 8.34 (d, *J* = 1.3 Hz, 1H), 7.92 (d, *J* = 2.9 Hz, 1H), 7.38 (dd, *J* = 1.8 Hz, 8.6 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 3.94 (s, 3H); ¹³C NMR (500) MHz, CDCl₃) δ 165.0, 134.7, 131.7, 127.4, 126.3, 124.3, 115.7, 112.9, 108.8, 51.2; IR (film) 3290, 2943, 1684, 1529, 1452, 1359, 1189 cm⁻¹; HRMS (CI) *m/z* = 253.1323 calcd for C₁₀H₉BrNO₂ [MH]⁺, found 253.9817.



Methyl 7-methoxy-1*H*-indole-3-carboxylate (1j). Using the procedure from **1h** with 7-methoxy-1*H*-indole, **1j** (0.56 g, 2.72 mmol) was obtained in 100% yield as a white solid. ¹H NMR spectrum matches that of the reported compound.⁴

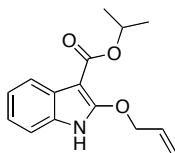
Representative Procedure (A) for Installation of an Allyl Alcohol to Indole Substrates:



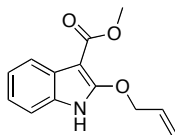
Methyl 2-(2-methylallyloxy)-1*H*-indole-3-carboxylate (3a). To a flame-dried round-bottom flask was added **1a** (3.0 g, 17.13 mmol). CH₂Cl₂ (15 mL) was added and upon cooling to 0 °C, distilled 1,4-dimethylpiperazine (1.29 mL, 9.60 mmol) and recrystallized *N*-chlorosuccinimide (2.52 g, 19.02 mmol) were added. The resulting solution was stirred at 0 °C for 2 h. In a separate flame-dried round bottom flask, the allyl alcohol **2a** (2.9 mL, 34.26 mmol) and trichloroacetic acid (0.67 g, 4.11 mmol) were dissolved in CH₂Cl₂ (15 mL). The solution was cooled to 0 °C, and transferred via cannula to the indole solution. This mixture was stirred for 2 h at 0 °C, at which time the reaction mixture was concentrated under vacuum. It was then loaded onto a base-washed SiO₂ column (1% Et₃N, 24% EtOAc, 75% Hexanes) and eluted with 25% EtOAc/Hexanes to afford **3a** (2.5 g) in 60% yield as a white solid: mp 92-94 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.63 (bs, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.23-7.14 (m, 3H), 5.18 (s, 1H), 5.05 (s, 1H), 4.81 (s, 2H), 3.93 (s, 3H), 1.86 (s, 3H); ¹³C NMR (360 MHz, THF-*d*₈) δ 164.5, 156.9, 141.4, 131.0, 127.2, 121.5, 121.4, 121.1, 113.1, 110.6, 89.9, 76.8, 49.9, 19.0; IR (film) 3231, 2949, 1660, 1552, 1475 cm⁻¹; HRMS (ES) *m/z* = 268.0950 calcd for C₁₄H₁₅NO₃Na [MNa]⁺, found 268.0950. This material rearranges at ambient temperature, but could be stored for up to one year

at $-20\text{ }^{\circ}\text{C}$. Since rearrangement would occur during the timeframe of the ^{13}C NMR experiment even in $\text{d}_8\text{-THF}$ which slows the rearrangement, purity was typically assessed by ^1H NMR spectroscopy.

Representative Procedure (B) for Installation of an Allyl Alcohol to Indole Substrates:

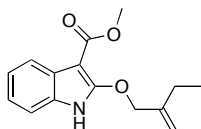


Isopropyl 2-(allyloxy)-1H-indole-3-carboxylate (3e). To a flame-dried round-bottom flask was added **1e** (0.15 g, 0.74 mmol). After dissolving in CH_2Cl_2 (3 mL) and cooling to $0\text{ }^{\circ}\text{C}$, 1,4-diazobicyclo[2.2.0]octane (DABCO) (0.046 g, 0.41 mmol) was added followed by recrystallized *N*-chlorosuccinimide (0.11 g, 0.82 mmol) were added. The resultant solution was stirred at $0\text{ }^{\circ}\text{C}$ for 30 min, followed by addition of allyl alcohol (0.10 mL, 1.48 mmol) and methanesulfonic acid (0.007 mL, 0.10 mmol). This mixture was stirred for 30 min at $0\text{ }^{\circ}\text{C}$, at which time the reaction mixture was concentrated under vacuum and chromatographed on a base-washed SiO_2 column (1% Et_3N , 24% EtOAc , 75% Hexanes) using 25% EtOAc /Hexanes as the eluent to afford **3e** (0.15 g, 0.59 mmol) in 80% yield as an off-white oil: ^1H NMR (300 MHz, CDCl_3) δ 8.22 (bs, 1H), 8.05 (d, $J = 7.0$ Hz, 1H), 7.25-7.19 (m, 3H), 6.18-6.05 (m, 1H), 5.49 (ddd, $J = 1.4, 2.9, 17.2$ Hz, 1H), 5.36 (ddd, 1.4, 2.9, 10.4 Hz, 1H), 5.35 (septet, $J = 6.3$ Hz, 1H), 4.96 (ddd, $J = 1.3, 2.7, 5.7$ Hz, 2H); 1.42 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (360 MHz, THF-d_8) δ 163.9, 156.9, 133.8, 131.5, 127.4, 121.5 (2), 121.3, 117.7, 110.7, 90.9, 74.4, 66.2, 22.3; IR (film) 3229, 2981, 2935, 1738, 1661, 1552, 1468, 1375, 1244, 1097 cm^{-1} ; HRMS (ES) $m/z = 260.12084$ calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_3$ $[\text{MH}]^+$, found 260.1281. This material rearranges at ambient temperature, but could be stored for up to one year at $-20\text{ }^{\circ}\text{C}$. Rearrangement would occur during the timeframe of the NMR experiment even in $\text{d}_8\text{-THF}$ which slows the rearrangement. As a consequence, purity was typically assessed by the more rapid ^1H NMR experiment.

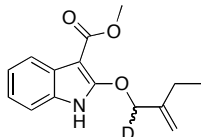


Methyl 2-(allyloxy)-1H-indole-3-carboxylate (3b). Following the general procedure (B) **3b** (0.224 g, 0.97 mmol) was obtained in 57% yield as a white solid: mp $80\text{--}82\text{ }^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 8.21 (bs, 1H), 8.05 (m, 1H), 7.22-7.18 (m, 3H), 6.13-6.05 (m, 1H), 5.49 (d, $J =$

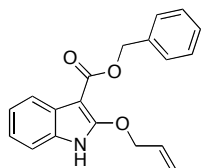
17.2 Hz, 1H), 5.36 (d, $J = 10.4$ Hz, 1H), 4.95 (d, $J = 5.7$ Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (360 MHz, THF- d_8) δ 164.7, 157.0, 133.7, 131.0, 127.3, 121.6, 121.5, 121.2, 117.8, 110.7, 90.3, 74.4, 50.0; IR (film) 3229, 2997, 2950, 1668, 1552, 1468, 1328, 1251, 1213 cm^{-1} ; HRMS (ES) $m/z = 254.0793$ calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{Na}$ $[\text{MNa}]^+$, found 254.0797. This material rearranges at ambient temperature, but could be stored for up to one year at -20°C . Rearrangement would occur during the timeframe of the NMR experiment even in d_8 -THF which slows the rearrangement. As a consequence, purity was typically assessed by the more rapid ^1H NMR experiment.



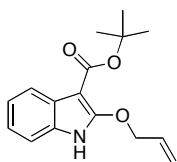
Methyl 2-(2-methylenebutoxy)-1H-indole-3-carboxylate (3c). Following the general procedure (A) **3c** (0.257 g, 0.99 mmol) was obtained in 43% yield as a yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 8.30 (bs, 1H), 8.04 (d, $J = 7.4$ Hz, 1H), 7.26-7.15 (m, 3H), 5.23 (s, 1H), 5.09 (s, 1H), 4.89 (s, 2H), 3.93 (s, 3H), 2.23 (q, $J = 7.0$ Hz, 2H), 1.13 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (360 MHz, THF- d_8) δ 165.1, 157.5, 147.4, 131.5, 127.7, 122.0, 121.9, 121.6, 111.8, 111.1, 90.4, 76.4, 50.4, 26.6, 12.5; IR (film) 3229, 2966, 2881, 1668, 1552, 1468, 1352, 1267 cm^{-1} ; HRMS (ES, negative ion) $m/z = 258.12084$ calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_3$ $[\text{M-H}]^-$, found 258.1123.



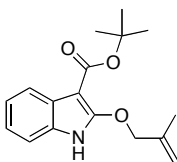
Methyl 2-(1-deutero-2-methylenebutoxy)-1H-indole-3-carboxylate (d-3c). Following the general procedure (A) **d-3c** (0.036 g, 0.14 mmol) was obtained in 17% yield as a yellow resin: ^1H NMR (300 MHz, CDCl_3) δ 8.22 (bs, 1H), 8.04 (d, $J = 7.2$ Hz, 1H), 7.26-7.16 (m, 3H), 5.23 (t, $J = 1.1$ Hz, 1H), 5.09 (s, 1H), 4.86 (s, 1H), 3.91 (s, 3H), 2.23 (q, $J = 7.4$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (360 MHz, THF- d_8) δ 164.5, 157.0, 147.0, 131.1, 127.3, 121.5, 121.4, 121.2, 111.5, 110.6, 90.0, 75.8 (t, $J = 22.3$ Hz), 49.9, 26.2, 12.3; IR (film) 3229, 3090, 2935, 2881, 1668, 1552, 1468, 1328, 1244 cm^{-1} ; HRMS (ES) $m/z = 283.1169$ calcd for $\text{C}_{15}\text{H}_{16}\text{DNO}_3\text{Na}$ $[\text{MNa}]^+$, found 283.1165.



Benzyl 2-(allyloxy)-1*H*-indole-3-carboxylate (3d). Following the general procedure (B) **3d** (0.121 g, 0.39 mmol) was obtained in 66% yield as a yellow oil: ^1H NMR (360 MHz, THF- d_8) δ 10.87 (bs, 1H), 8.07 (m, 1H), 7.53 (d, J = 7.3 Hz, 2H), 7.37-7.20 (m, 4H), 7.11-7.06 (m, 2H), 6.14-6.04 (m, 1H), 5.45 (dd, J = 1.6, 17.2 Hz, 1H), 5.39 (s, 2H), 5.24 (dd, J = 1.3, 10.5 Hz), 4.92 (m, 2H); ^{13}C NMR (360 MHz, THF- d_8) δ 164.1, 157.2, 138.4, 133.5, 131.2, 128.7, 128.2, 128.0, 127.3, 121.7, 121.6, 121.2, 118.0, 110.8, 90.1, 74.2, 64.9; IR (film) 3229, 3090, 3035, 2950, 2881, 1661, 1552, 1460, 1352, 1259, 1213 cm^{-1} ; HRMS (ES) m/z = 308.12084 calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_3$ $[\text{MH}]^+$, found 308.1285. This material rearranges at ambient temperature, but could be stored for up to one year at -20°C . Rearrangement would occur during the timeframe of the NMR experiment even in d_8 -THF which slows the rearrangement. As a consequence, purity was typically assessed by the more rapid ^1H NMR experiment.

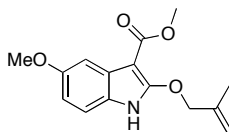


***tert*-Butyl 2-(allyloxy)-1*H*-indole-3-carboxylate (3f).** Following the general procedure (A) **3f** (0.53 g, 1.94 mmol) was obtained in 77% yield as a white solid: mp $124\text{--}126^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 8.36 (bs, 1H), 8.01 (d, J = 7.0 Hz, 1H), 7.25-7.13 (m, 3H), 6.15-6.02 (m, 1H), 5.46 (dd, J = 17.2, 1.4 Hz, 1H), 5.33 (dd, J = 10.4, 1.2 Hz, 1H), 4.92 (m, 2H), 1.66 (s, 9H); ^{13}C NMR (360 MHz, THF- d_8) δ 163.9, 156.7, 134.0, 130.9, 127.4, 121.4 (2), 121.3, 117.7, 110.6, 92.1, 81.6, 74.6, 28.6; IR (film) 3229, 2981, 2881, 1661, 1552, 1468, 1367, 1251, 1174, 1097; HRMS (ES) m/z = 274.1365 calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_3$ $[\text{MH}]^+$, found 274.1435. This material rearranges at ambient temperature, but could be stored for up to one year at -20°C . Rearrangement would occur during the timeframe of the NMR experiment even in d_8 -THF which slows the rearrangement. As a consequence, purity was typically assessed by the more rapid ^1H NMR experiment.

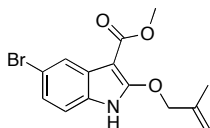


***tert*-Butyl 2-(2-methylallyloxy)-1*H*-indole-3-carboxylate (3g).** Following the general procedure (A) **3g** (0.12 g, 0.418 mmol) was obtained in 34% yield as a pale yellow solid: mp $105\text{--}107^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.20 (bs, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.15-7.08 (m, 3H), 5.13 (s, 1H), 5.01 (s, 1H), 4.77 (s, 2H), 1.82 (s, 3H), 1.60 (s, 9H); ^{13}C NMR (360 MHz, THF- d_8) δ 163.8, 156.6, 141.0, 129.9, 127.4, 121.2 (2), 121.1, 113.1, 110.4, 91.6, 78.6, 76.8, 28.6, 19.1; IR (film)

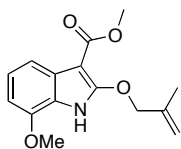
3237, 2976, 1656, 1552, 1459, 1366 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{Na}$ (MNa^+) 310.1419, found 310.1611.



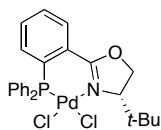
Methyl 2-(2-methylallyloxy)-5-methoxy-1H-indole-3-carboxylate (3h). Following the general procedure (B) **3h** (0.03 g, 0.11 mmol) was obtained in 22% yield as an off-white oil: ^1H NMR (300 MHz, CDCl_3) δ 8.44 (bs, 1H), 7.59 (m, 1H), 7.10 (d, J = 8.6 Hz, 1H), 6.78 (d, J = 8.6 Hz, 1H), 5.19 (s, 1H), 5.06 (s, 1H), 4.79 (s, 2H), 3.90 (s, 3H), 3.83 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (360 MHz, THF-d_8) δ 164.6, 157.1, 156.3, 141.5, 128.2, 125.6, 113.1, 111.2, 110.1, 104.2, 90.2, 76.8, 55.4, 49.9, 19.1; IR (film) 3244, 2950, 1668, 1591, 1552, 1468, 1352, 1274, 1205 cm^{-1} ; HRMS (ES) m/z = 298.1056 calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{Na}$ [MNa] $^+$, found 298.1066.



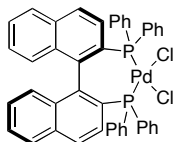
Methyl 2-(2-methylallyloxy)-5-bromo-1H-indole-3-carboxylate (3i). Following the general procedure (B) **3i** (0.07 g, 0.22 mmol) was obtained in 55% yield as an off-white oil: ^1H NMR (300 MHz, CDCl_3) δ 8.23 (bs, 1H), 8.17 (d, J = 2.0 Hz, 1H), 7.26 (m, 1H), 7.09 (d, J = 8.5 Hz, 1H), 5.20 (s, 1H), 5.10 (s, 1H), 4.85 (s, 2H), 3.93 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (360 MHz, THF-d_8) δ 164.2, 157.6, 141.1, 134.6, 129.1, 124.3, 123.5, 115.1, 113.4, 112.4, 89.7, 76.8, 50.7, 19.1; IR (film) 3221, 2950, 1668, 1552, 1483, 1352, 1251, 1213 cm^{-1} ; HRMS (ES) m/z = 346.0055 calcd for $\text{C}_{14}\text{H}_{14}\text{BrNO}_3\text{Na}$ [MNa] $^+$, found 346.0045.



Methyl 2-(2-methylallyloxy)-7-methoxy-1H-indole-3-carboxylate (3j). Following general procedure (B), **3j** (0.086 g, 0.31 mmol) was obtained in 43% yield as a white resin: ^1H NMR (500 MHz, CDCl_3) δ 8.45 (bs, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.66 (d, J = 7.9 Hz, 1H), 5.21 (s, 1H), 5.08 (s, 1H), 4.83 (s, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (360 MHz, THF-d_8) δ 164.0, 156.0, 145.4, 141.1, 127.5, 121.9, 121.3, 113.5, 112.6, 101.9, 90.5, 77.0, 54.6, 49.3, 18.6; IR (film) 3221, 1950, 2842, 1668, 1552, 1475, 1367, 1282, 1220 cm^{-1} ; HRMS (ES) m/z = 298.1056 calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{Na}$ [MNa] $^+$, found 298.1057.

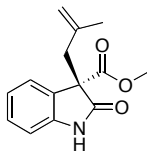


Pd(7d)Cl₂. To a round-bottom flask was added PdCl₂(MeCN)₂ (0.20 g, 0.52 mmol) and **7d** (0.133 g, 0.51 mmol), followed by addition of CH₂Cl₂ (12 mL). The resulting solution was allowed to stir at room temperature for 24 h, then concentrated under vacuum to give **Pd(7d)Cl₂** (0.29 g, 0.51 mmol) in 100% yield as a yellow solid.



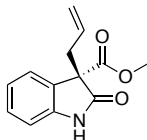
Pd(5a)Cl₂. To a round-bottom flask was added PdCl₂(MeCN)₂ (0.124 g, 0.48 mmol) and *R*-BINAP (**5a**, 0.300 g, 0.48 mmol), followed by addition of CH₂Cl₂ (15 mL). The resulting solution was allowed to stir at room temperature for 24 h, then concentrated under vacuum to give **Pd(5a)Cl₂** (0.384 g, 0.48 mmol) in 100% yield as a yellow solid.

General Procedure for the Asymmetric Meerwein-Eschenmoser Claisen Rearrangement:

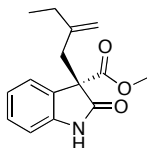


(S)-Methyl 3-(2-methylallyl)-2-oxoindoline-3-carboxylate (4a). To a solution of the **Pd(7d)Cl₂** complex (0.004 g, 0.008 mmol, 20 mol%) in CH₂Cl₂ (0.5 mL) was added via cannula a solution of AgSbF₆ (0.005 g, 0.014 mmol, 40 mol%) in CH₂Cl₂ (0.50 mL). The resulting solution was stirred in the absence of light for 3 h, and filtered through a PTFE filter to remove the precipitated AgCl. The resulting clear yellow solution was cooled to 0 °C, followed by addition of **3a** (0.009 g, 0.038 mmol) in CH₂Cl₂ (1.0 mL) via cannula. The reaction mixture was stirred at 0 °C until the starting material was completely consumed, as determined by TLC. Filtration through a plug of SiO₂ (5 mm x 2 cm) with 25% EtOAc/Hexanes and concentration of the solution under vacuum **4a** (0.008 g, 0.033 mmol) in 89% yield as a white resin: $[\alpha]_D^{23} +79.25$ (*c* 0.40, 89% ee, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.84 (bs, 1H), 7.27-7.26 (m, 2H), 7.05 (t, *J* = 7.9, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 4.65 (s, 1H), 4.63 (s, 1H), 3.69 (s, 3H), 3.06 (s, 2H), 1.41 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 176.1, 169.6, 141.3, 139.4, 129.1, 128.3, 124.4, 122.6, 115.7, 110.1,

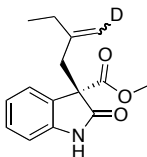
59.9, 53.1, 41.2, 23.6; IR (film) 3250, 2953, 1741, 1702, 1621, 1475 cm^{-1} ; HRMS (CI) m/z = 245.1052 calcd for $\text{C}_{14}\text{H}_{16}\text{NO}_3$ $[\text{MH}]^+$, found 246.1136; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_{\text{R}}(\text{R})$ = 16.5 min, $t_{\text{R}}(\text{S})$ = 20.3 min. The reaction was also conducted with 5 mol% catalyst (5mol% **Pd(7d)Cl₂** and 10 mol% AgSbF_6) following the same procedure to yield **4a** in 100% yield and 88% ee.



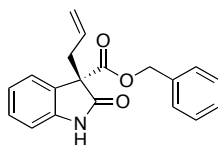
(S)-Methyl 3-allyl-2-oxoindoline-3-carboxylate (4b). Following the general procedure, **4b** (0.10 g, 0.043 mmol) was obtained in 100% yield as a white resin: $[\alpha]_{\text{D}}^{23}$ +51.30 (*c* 0.50, 83% ee, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.20 (bs, 1H), 7.28-7.25 (m, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.9 Hz, 1H), 5.49-5.41 (m, 1H), 5.08 (dd, J = 1.2, 17.0 Hz, 1H), 4.97 (d, J = 10.1 Hz, 1H), 3.71 (s, 3H), 3.04 (dd, J = 6.7, 13.8 Hz, 1H), 2.97 (dd, J = 7.9, 13.8 Hz, 1H); ^{13}C NMR (500 MHz, CDCl_3) δ 175.6, 169.3, 141.1, 130.8, 129.1, 128.0, 124.0, 122.8, 120.0, 110.0, 59.6, 53.1, 38.4; IR (film) 3252, 3090, 2958, 2858, 1715, 1622, 1475, 1437, 1336, 1236 cm^{-1} ; HRMS (ES) m/z = 254.0793 calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{Na}$ $[\text{MNa}]^+$, found 254.0791; CSP HPLC (Chiralpak AD, 1.0 mL/min, 95.5 hexanes:*i*-PrOH): $t_{\text{R}}(\text{S})$ = 18.4 min, $t_{\text{R}}(\text{R})$ = 20.6 min.



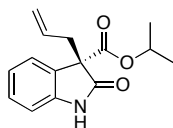
(S)-Methyl 3-(2-methylenebutyl)-2-oxoindoline-3-carboxylate (4c). Following the general procedure, **4c** (0.009 g, 0.03 mmol) was obtained in 82% yield as a white resin: $[\alpha]_{\text{D}}^{23}$ +59.00 (*c* 0.45, 92% ee, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.12 (bs, 1H), 7.28-7.23 (m, 2H), 7.05 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.7 Hz, 1H), 4.66 (t, J = 1.4 Hz, 1H), 4.64 (s, 1H), 3.69 (s, 3H), 3.08 (d, J = 16.7 Hz, 1H), 3.05 (d, J = 16.8 Hz, 1H), 1.68 (q, J = 7.4 Hz, 2H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (500 MHz, CDCl_3) δ 176.0, 169.7, 145.0, 141.3, 129.1, 128.3, 124.4, 122.6, 113.2, 110.0, 60.0, 53.1, 39.5, 29.7, 12.3; IR (film) 3275, 2927, 2858, 1715, 1622, 1444, 1236 cm^{-1} ; HRMS (CI) m/z = 260.1287 calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_3$ $[\text{MH}]^+$, found 259.1208; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_{\text{R}}(\text{R})$ = 13.6 min, $t_{\text{R}}(\text{S})$ = 15.8 min.



(S)-Methyl 3-(2-(deuteromethylene)butyl)-2-oxoindoline-3-carboxylate (d-4c). Following the general procedure, **d-4c** (0.008 g, 0.03 mmol) was obtained in 80% yield as a white resin: $[\alpha]_{\text{D}}^{23} +43.13$ (*c* 0.40, 92% ee, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.04 (bs, 1H), 7.32-7.24 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 4.63 (s, 0.5 H, *Z*-deutero), 4.62 (s, 0.5 H, *E*-deutero), 3.70 (s, 3H), 3.07 (d, *J* = 16.3 Hz, 1H), 3.04 (d, *J* = 16.2 Hz, 1H), 1.68 (q, *J* = 7.3 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 175.8, 169.9, 145.1, 141.4, 129.3, 128.6, 124.7, 122.8, 113.1 (t, *J*_{CD} = 23.6 Hz), 110.1, 60.2, 53.4, 39.7, 29.9, 12.5; IR (film) 3252, 3090, 2981, 2935, 1715, 1622, 1475, 1375, 1251, 1159 cm⁻¹; HRMS (ES) *m/z* = 283.1169 calcd for C₁₅H₁₆DNO₃Na [MNa]⁺, found 283.1173; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): *t*_R(*R*) = 13.6 min, *t*_R(*S*) = 15.8 min.

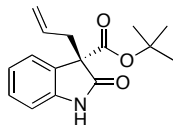


(S)-Benzyl 3-allyl-2-oxoindoline-3-carboxylate (4d). Following the general procedure except that **Pd(5a)Cl₂** was employed, **4d** (0.008 g, 0.03 mmol) was obtained in 74% yield as a white resin: $[\alpha]_{\text{D}}^{23} +51.38$ (*c* 0.40, 72% ee, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.28 (bs, 1H), 7.28-7.22 (m, 5H), 7.17-7.16 (m, 2H), 7.05 (td, *J* = 7.5, 0.9 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.50-5.41 (m, 1H), 5.16 (d, *J* = 15.5 Hz, 1H), 5.14 (d, *J* = 15.6 Hz, 1H), 5.08 (dd, *J* = 1.4, 16.9 Hz, 1H), 4.96 (dd, *J* = 1.7, 10.1 Hz, 1H), 3.05 (dd, *J* = 6.7, 13.9 Hz, 1H), 2.99 (dd, *J* = 7.9, 13.9 Hz, 1H); ¹³C NMR (500 MHz, CDCl₃) δ 175.3, 168.6, 141.2, 135.3, 130.8, 129.1, 128.4, 128.1, 128.0, 127.4, 124.0, 122.7, 120.0, 110.0, 67.3, 59.7, 38.2; IR (film) 3259, 3066, 2927, 1715, 1622, 1468, 1336 cm⁻¹; HRMS (ES) *m/z* = 308.12084 calcd for C₁₉H₁₈NO₃ [MH]⁺, found 308.1273; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): *t*_R(*R*) = 20.7 min, *t*_R(*S*) = 29.7 min.

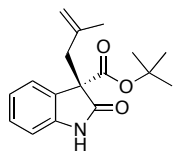


(S)-Isopropyl 3-allyl-2-oxoindoline-3-carboxylate (4e). Following the general procedure except that **Pd(5a)Cl₂** was employed, **4e** (0.01 g, 0.04 mmol) was obtained in 91% yield as a white resin: $[\alpha]_{\text{D}}^{23} +44.20$ (*c* 0.50, 74% ee, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.04 (bs, 1H), 7.25-7.23 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.50-5.41 (m, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 5.02 (m, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 3.01 (dd, *J* = 6.7, 13.8 Hz, 1H), 2.95 (dd, *J* = 7.8, 13.8, 1H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H); ¹³C NMR (500) MHz,

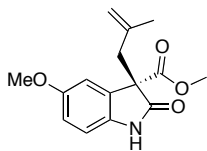
CDCl₃) δ 175.5, 168.3, 141.1, 131.0, 128.9, 128.4, 123.9, 122.7, 119.8, 109.8, 69.7, 59.8, 38.3, 21.5, 21.3; IR (film) 3252, 3090, 2981, 2927, 2858, 1722, 1622, 1468, 1236 cm⁻¹; HRMS (ES) m/z = 282.1208 calcd for C₁₅H₁₇NO₃Na [MNa]⁺, found 282.1092; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 11.8 min, $t_R(S)$ = 14.9 min.



(S)-tert-Butyl 3-allyl-2-oxoindoline-3-carboxylate (4f). Following the general procedure except that **Pd(5a)Cl₂** was employed, **4f** (0.006 g, 0.02 mmol) was obtained in 60% yield as a white resin: $[\alpha]_D^{23}$ +106.5 (*c* 0.30, 92% ee, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.95 (bs, 1H), 7.26-7.23 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.50 (m, 1H), 5.06 (d, *J* = 17.0 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 2.98-2.90 (m, 2H), 1.31 (s, 9H); ¹³C NMR (500 MHz, CDCl₃) δ 175.9, 167.7, 141.2, 131.2, 128.8, 128.7, 123.7, 122.6, 119.5, 109.7, 82.5, 60.5, 38.2, 27.7; IR (film) 3252, 3090, 2981, 2927, 1722, 1622, 1475, 1251, 1159 cm⁻¹; HRMS (CI) m/z = 274.1459 calcd for C₁₆H₂₀NO₃ [MH]⁺, found 274.1362; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 7.2 min, $t_R(S)$ = 8.8 min.

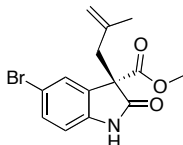


(S)-tert-Butyl 3-(2-methylallyl)-2-oxoindoline-3-carboxylate (4g). Following the general procedure except that **Pd(5a)Cl₂** was employed, **4g** (0.018 g, 0.063 mmol) was obtained in 82% yield as a white resin: $[\alpha]_D^{23}$ +66.89 (*c* 0.90, 82% ee, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 9.09 (bs, 1H), 7.23 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 4.61 (s, 2H), 3.04 (d, *J* = 13.9 Hz, 1H), 2.97 (d, *J* = 13.9 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 9H); ¹³C NMR (500 MHz, CDCl₃) δ 175.6, 167.9, 141.1, 139.9, 129.0, 128.8, 124.1, 122.4, 115.3, 109.6, 82.5, 60.7, 40.8, 27.7, 23.7; IR (film) 3262, 2980, 2930, 1733, 1621, 1475 cm⁻¹; HRMS (ES) m/z = 310.1419 calcd for C₁₇H₂₁NO₃Na [MNa]⁺, found 310.1416; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 6.1 min, $t_R(S)$ = 9.2 min.

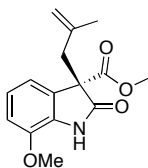


(S)-Methyl 5-methoxy-3-(2-methylallyl)-2-oxoindoline-3-carboxylate (4h). Following the general procedure, **4h** (0.006 g, 0.02 mmol) was obtained in 60% yield as a white resin: $[\alpha]_D^{23}$

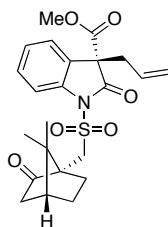
+40.83 (*c* 0.30, 91% ee, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 7.55 (bs, 1H), 6.88 (s, 1H), 6.80 (m, 2H), 4.70 (s, 1H), 4.65 (s, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.05 (d, *J* = 19.5 Hz, 1H), 3.02 (d, *J* = 19.4 Hz, 1H), 1.42 (s, 3H); ¹³C NMR (500) MHz, CDCl₃) δ 175.6, 169.6, 155.9, 139.4, 134.5, 129.5, 115.7, 113.9, 111.3, 110.3, 60.2, 55.8, 53.2, 41.2, 23.7; IR (film) 3259, 2927, 2858, 1715, 1607, 1491, 1444, 1236 cm⁻¹; HRMS (ES) *m/z* = 276.1158 calcd for C₁₅H₁₈NO₄ [MH]⁺, found 276.1248; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): *t_R*(*R*) = 20.7 min, *t_R*(*S*) = 23.8 min.



(S)-Methyl 5-bromo-3-(2-methylallyl)-2-oxoindoline-3-carboxylate (4i). Following the general procedure, **4i** (0.009 g, 0.03 mmol) was obtained in 82% yield as a white resin: [α]_D²³ +38.67 (*c* 0.45, 87% ee, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.34 (bs, 1H), 7.40 (m, 2H), 6.80 (d, *J* = 8.7 Hz, 1H), 4.70 (s, 1H), 4.63 (s, 1H), 3.72 (s, 3H), 3.05 (d, *J* = 19.8 Hz, 1H), 3.02 (d, *J* = 19.8 Hz, 1H), 1.46 (s, 3H); ¹³C NMR (500) MHz, CDCl₃) δ 175.3, 168.9, 140.2, 139.0, 132.0, 130.2, 127.7, 116.1, 115.2, 111.4, 59.9, 53.4, 41.2, 23.7; IR (film) 3252, 2958, 2858, 1738, 1614, 1475, 1228 cm⁻¹; HRMS (ES) *m/z* = 324.0157 calcd for C₁₄H₁₅BrNO₃ [MH]⁺, found 324.0240; CSP HPLC (Chiralpak AS, 1.0 mL/min, 92.5:7.5 hexanes:*i*-PrOH): *t_R*(*R*) = 15.1 min, *t_R*(*S*) = 25.5 min.



(S)-Methyl 7-methoxy-3-(2-methylallyl)-2-oxoindoline-3-carboxylate (4j). Following the general procedure, **4j** (0.009 g, 0.03 mmol) was obtained in 95% yield as a white resin: [α]_D²³ +82.78 (*c* 0.450, 85% ee, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.65 (bs, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 4.67 (s, 1H), 4.64 (s, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 3.04 (m, 2H), 1.43 (s, 3H); ¹³C NMR (500) MHz, CDCl₃) δ 174.7, 169.6, 143.8, 139.5, 130.1, 128.9, 123.1, 116.6, 115.6, 111.3, 60.5, 55.6, 53.1, 41.0, 23.7; IR (film) 3229, 3090, 2958, 2850, 1715, 1622, 1498, 1228 cm⁻¹; HRMS (ES) *m/z* = 298.1056 calcd for C₁₅H₁₇NO₄Na [MNa]⁺, found 298.1057; CSP HPLC (Chiralpak AS, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): *t_R*(*R*) = 21.3 min, *t_R*(*S*) = 27.0 min.



N-Camphorsulfonyl derivative of 4b (S7). To a solution of 60% NaH in oil (0.003 g, 0.13 mmol) in THF (2 mL) at 0 °C was added **4f** (0.018 g, 0.07 mmol). After stirring 5 min, camphorsulfonyl chloride (0.0180 g, 0.07 mmol) was added and the mixture was warmed to rt. After 2 h, H₂O was added, and the aqueous layer was extracted with CH₂Cl₂, dried over Na₂SO₄, and concentrated under vacuum to give the camphorsulfonyl derivative in 47% yield as a white solid (0.015 g, 0.03 mmol) which was used without further purification.

The camphorsulfonyl derivative (0.015 g, 0.03 mmol) was treated with a solution of 2,4-dinitrophenylhydrazine (0.26 mL, 0.12 M) in 1:1 H₂SO₄/MeOH. The resulting solution was allowed to stir for 10 min, then cooled to 0 °C, where upon formation of crystals were observed after 24 h. Instead of obtaining the expected hydrazone, the transesterified methyl ester product was observed. The configuration obtained from the crystal structure was used to establish the absolute stereochemistry of **4b**. The remaining compounds, **4a** and **4c-4j** were assigned by analogy.

¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.3 Hz, 1H), 7.39-7.32 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 5.46-5.36 (m, 1H), 5.12 (d, *J* = 17.0 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 3.86 (d, *J* = 15.0 Hz, 1H), 3.72 (s, 3H), 3.54 (d, *J* = 14.9 Hz, 1H), 3.06 (m, 2H), 2.50-2.38 (m, 2H), 2.16-2.14 (m, 1H), 2.11-2.04 (m, 1H), 1.98-1.94 (m, 1H), 1.82-1.76 (m, 1H), 1.50-1.44 (m, 1H), 1.16 (s, 3H), 0.91 (s, 3H).

X-ray Structure Determination of Compound S7.

Compound **S7**, C₂₃H₂₇NSO₆, crystallizes in the monoclinic space group P2₁ (systematic absences 0k0: k=odd) with *a*=8.7058(10)Å, *b*=13.931(2)Å, *c*=9.1612(10)Å, β=94.954(3)°, *V*=1106.9(2)Å³, *Z*=2 and *d*_{calc}=1.337 g/cm³. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K_α radiation (λ=0.71073 Å) at a temperature of 143K. Preliminary indexing was performed from a series of twelve 0.5° rotation images with exposures of 30 seconds. A total of 518 rotation images were collected with a crystal to detector distance of 35 mm, a 2θ swing angle of -10°, rotation widths of 0.5° and

exposures of 45 seconds: scan no. 1 was a ϕ -scan from 210° to 420° at $\omega = 10^\circ$ and $\chi = 20^\circ$; scan no. 2 was an ω -scan from -20° to 5° at $\chi = -90^\circ$ and $\phi = 45^\circ$; scan no. 3 was an ω -scan from -14° to 10° at $\chi = -90^\circ$ and $\phi = 0^\circ$. Rotation images were processed using CrystalClear⁵, producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the CrystalStructure⁶ program package for further processing and structure solution on a Dell Pentium III computer. A total of 7710 reflections were measured over the ranges $5.34 \leq 2\theta \leq 50.04^\circ$, $-9 \leq h \leq 10$, $-14 \leq k \leq 16$, $-10 \leq l \leq 10$ yielding 3619 unique reflections ($R_{\text{int}} = 0.0216$). The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB⁷ (minimum and maximum transmission 0.821, 1.000).

The structure was solved by direct methods (SIR97⁸). Refinement was by full-matrix least squares based on F^2 using SHELXL-97⁹. All reflections were used during refinement (F^2 's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w=1/[\sigma^2(F_o^2)+0.0624P^2+0.2669P]$ where $P=(F_o^2+2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to $R_1=0.0442$ and $wR_2=0.1074$ for 3275 reflections for which $F > 4\sigma(F)$ and $R_1=0.0495$, $wR_2=0.1130$ and $\text{GOF} = 1.050$ for all 3619 unique, non-zero reflections and 285 variables¹⁰. The maximum Δ/σ in the final cycle of least squares was 0.181 and the two most prominent peaks in the final difference Fourier were $+0.460$ and $-0.357 \text{ e}/\text{\AA}^3$.

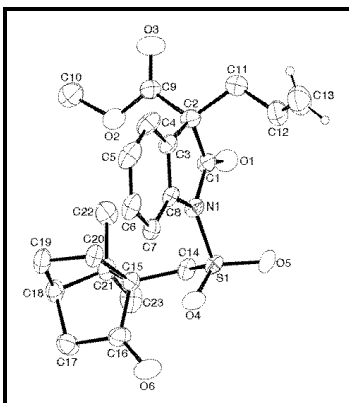


Figure S1. ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

Table S1 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Table S2. Anisotropic thermal parameters are in Table S3. Tables S4 and S5 list bond distances and bond angles. Figure S1 is an ORTEP¹¹ representation of the molecule with 30% probability thermal ellipsoids.

Table S1. Summary of Structure Determination of Compound S7

Formula:	C ₂₃ H ₂₇ NSO ₆
Formula weight:	445.52
Crystal class:	monoclinic
Space group:	P2 ₁ (#4)
Z	2
Cell constants:	
a	8.7058(10)Å
b	13.931(2)Å
c	9.1612(10)Å
β	94.954(3)°
V	1106.9(2)Å ³
μ	1.86 cm ⁻¹
crystal size, mm	0.48 x 0.12 x 0.05
D _{calc}	1.337 g/cm ³
F(000)	472
Radiation:	Mo-K _α (λ=0.71073 Å)
2θ range	5.34 – 50.04 °
hkl collected:	-9 ≤ h ≤ 10; -14 ≤ k ≤ 16; -10 ≤ l
≤ 10	
No. reflections measured:	7710
No. unique reflections:	3619 (R _{int} =0.0216)
No. observed reflections	3275 (F>4σ)
No. reflections used in refinement	3619
No. parameters	285
R indices (F>4σ)	R ₁ =0.0442 wR ₂ =0.1074
R indices (all data)	R ₁ =0.0495 wR ₂ =0.1130
GOF:	1.050
Final Difference Peaks, e/Å ³	+0.460, -0.357

Table S2. Refined Positional Parameters for Compound S7

Atom	x	y	z	U _{eq} , Å ²
C1	0.2847(4)	0.4315(2)	0.4329(3)	0.0441(7)
C2	0.2538(4)	0.5300(2)	0.4986(3)	0.0478(8)
C3	0.1541(4)	0.5783(2)	0.3757(3)	0.0435(7)
C4	0.0863(4)	0.6678(3)	0.3718(5)	0.0603(10)
H4	0.0977	0.7081	0.4529	0.080
C5	0.0006(4)	0.6967(3)	0.2443(5)	0.0631(10)
H5	-0.0449	0.7571	0.2393	0.084
C6	-0.0168(4)	0.6368(3)	0.1267(4)	0.0551(9)
H6	-0.0744	0.6580	0.0426	0.073
C7	0.0474(3)	0.5458(2)	0.1265(3)	0.0434(7)
H7	0.0349	0.5059	0.0449	0.058
C8	0.1319(3)	0.5172(2)	0.2559(3)	0.0364(6)
C9	0.4073(4)	0.5810(3)	0.5277(4)	0.0533(8)
C10	0.6404(5)	0.6321(4)	0.4226(5)	0.0771(12)
H10a	0.6281	0.6948	0.4635	0.116
H10b	0.6758	0.6381	0.3266	0.116
H10c	0.7146	0.5964	0.4844	0.116
C11	0.1749(5)	0.5158(3)	0.6411(4)	0.0646(10)
H11a	0.2450	0.4821	0.7116	0.086
H11b	0.1538	0.5782	0.6819	0.086
C12	0.0293(6)	0.4612(4)	0.6189(4)	0.0732(11)
H12	0.0330	0.4023	0.5716	0.097
C13	-0.1013(6)	0.4877(5)	0.6590(5)	0.096(2)
H13a	-0.1103	0.5461	0.7067	0.128
H13b	-0.1873	0.4485	0.6404	0.128
C14	0.3905(3)	0.2936(2)	0.1779(4)	0.0435(7)
H14a	0.4459	0.3009	0.2738	0.058
H14b	0.3932	0.2260	0.1532	0.058
C15	0.4796(3)	0.3474(2)	0.0688(3)	0.0406(7)
C16	0.4556(4)	0.3094(3)	-0.0854(4)	0.0581(10)
C17	0.5880(4)	0.3450(3)	-0.1680(4)	0.0636(11)
H17a	0.5525	0.3884	-0.2466	0.085
H17b	0.6439	0.2922	-0.2078	0.085
C18	0.6869(4)	0.3975(3)	-0.0456(4)	0.0532(9)
H18	0.7955	0.4048	-0.0639	0.071
C19	0.6044(4)	0.4919(3)	-0.0192(4)	0.0607(10)
H19a	0.5761	0.5251	-0.1106	0.081
H19b	0.6681	0.5337	0.0453	0.081
C20	0.4579(4)	0.4580(2)	0.0548(4)	0.0491(8)
H20a	0.4536	0.4875	0.1503	0.065

H20b	0.3644	0.4736	-0.0058	0.065
C21	0.6598(3)	0.3378(3)	0.0926(3)	0.0479(8)
C22	0.7274(4)	0.3816(3)	0.2370(4)	0.0607(10)
H22a	0.6968	0.3439	0.3173	0.091
H22b	0.6901	0.4461	0.2452	0.091
H22c	0.8379	0.3824	0.2393	0.091
C23	0.7139(4)	0.2340(3)	0.0842(5)	0.0695(11)
H23a	0.8239	0.2326	0.0818	0.104
H23b	0.6661	0.2046	-0.0031	0.104
H23c	0.6856	0.1994	0.1685	0.104
N1	0.2095(3)	0.4283(2)	0.2905(3)	0.0393(6)
O1	0.3594(3)	0.3681(2)	0.4914(3)	0.0591(6)
O2	0.4882(3)	0.5804(2)	0.4120(3)	0.0634(7)
O3	0.4526(4)	0.6166(3)	0.6400(3)	0.113(2)
O4	0.1190(2)	0.3487(2)	0.0561(2)	0.0501(6)
O5	0.1331(3)	0.2542(2)	0.2837(3)	0.0515(6)
O6	0.3535(3)	0.2556(3)	-0.1322(3)	0.0849(10)
S1	0.19753(8)	0.32482(5)	0.19402(8)	0.0398(2)

$$U_{eq} = 1/3 [U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$$

Table S3. Refined Thermal Parameters (U's) for Compound S7

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C1	0.048(2)	0.038(2)	0.045(2)	0.0040(14)	-0.0051(13)	-0.0003(14)
C2	0.052(2)	0.043(2)	0.047(2)	-0.0056(14)	0.0016(14)	0.000(2)
C3	0.043(2)	0.034(2)	0.053(2)	-0.0016(14)	0.0035(13)	0.0009(14)
C4	0.055(2)	0.035(2)	0.090(3)	-0.011(2)	0.001(2)	0.005(2)
C5	0.046(2)	0.032(2)	0.110(3)	0.003(2)	-0.002(2)	0.012(2)
C6	0.040(2)	0.040(2)	0.083(2)	0.020(2)	-0.010(2)	0.000(2)
C7	0.035(2)	0.042(2)	0.052(2)	0.0088(14)	-0.0026(13)	-0.0029(13)
C8	0.030(2)	0.027(2)	0.051(2)	0.0041(12)	0.0017(11)	-0.0018(11)
C9	0.058(2)	0.053(2)	0.048(2)	-0.003(2)	-0.001(2)	-0.006(2)
C10	0.082(3)	0.066(3)	0.082(3)	-0.001(2)	-0.004(2)	-0.004(2)
C11	0.073(3)	0.069(3)	0.053(2)	-0.006(2)	0.006(2)	-0.009(2)
C12	0.079(3)	0.073(3)	0.070(2)	0.004(2)	0.024(2)	-0.010(2)
C13	0.086(4)	0.118(5)	0.088(3)	0.013(3)	0.018(3)	-0.018(3)
C14	0.034(2)	0.033(2)	0.064(2)	0.0042(13)	0.0071(13)	0.0031(12)
C15	0.033(2)	0.040(2)	0.049(2)	0.0006(13)	0.0013(12)	-0.0007(12)
C16	0.039(2)	0.076(3)	0.059(2)	-0.016(2)	0.0031(14)	-0.011(2)
C17	0.049(2)	0.091(3)	0.051(2)	-0.006(2)	0.007(2)	-0.010(2)
C18	0.037(2)	0.065(2)	0.057(2)	0.008(2)	0.0057(14)	-0.010(2)
C19	0.052(2)	0.061(3)	0.069(2)	0.017(2)	0.003(2)	-0.017(2)
C20	0.044(2)	0.042(2)	0.061(2)	0.009(2)	0.003(2)	-0.004(2)
C21	0.0294(14)	0.059(2)	0.056(2)	0.004(2)	0.0043(12)	-0.003(2)
C22	0.033(2)	0.089(3)	0.059(2)	0.005(2)	-0.004(2)	-0.006(2)
C23	0.045(2)	0.068(3)	0.098(3)	0.015(2)	0.021(2)	0.016(2)
N1	0.0392(14)	0.0313(14)	0.0458(13)	-0.0002(11)	-0.0055(10)	0.0041(11)
O1	0.072(2)	0.0438(14)	0.0585(14)	0.0104(10)	-0.0132(12)	0.0081(12)
O2	0.054(2)	0.070(2)	0.0656(14)	-0.0122(13)	0.0045(12)	-0.0122(13)
O3	0.106(3)	0.160(4)	0.075(2)	-0.053(2)	0.020(2)	-0.067(2)
O4	0.0390(11)	0.052(2)	0.0569(12)	-0.0115(11)	-0.0097(9)	0.0018(10)
O5	0.0448(13)	0.0340(13)	0.078(2)	0.0004(11)	0.0152(11)	-0.0103(10)
O6	0.058(2)	0.112(3)	0.086(2)	-0.045(2)	0.0128(14)	-0.031(2)
S1	0.0304(3)	0.0318(4)	0.0570(4)	-0.0045(3)	0.0019(3)	-0.0016(3)

The form of the anisotropic displacement parameter is:

$$\exp[-2p^2(a^*{}^2U_{11}h^2+b^*{}^2U_{22}k^2+c^*{}^2U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)].$$

Table S4. Bond Distances in Compound S7 (Å).

C1-O1	1.195(4)	C1-N1	1.408(4)	C1-C2	1.532(5)
C2-C9	1.517(5)	C2-C3	1.518(4)	C2-C11	1.540(5)
C3-C4	1.379(5)	C3-C8	1.388(4)	C4-C5	1.390(6)
C5-C6	1.360(6)	C6-C7	1.386(5)	C7-C8	1.398(4)
C8-N1	1.434(4)	C9-O3	1.178(4)	C9-O2	1.322(4)
C10-O2	1.504(5)	C11-C12	1.477(6)	C12-C13	1.279(7)
C14-C15	1.515(4)	C14-S1	1.754(3)	C15-C16	1.506(4)
C15-C20	1.556(4)	C15-C21	1.571(4)	C16-O6	1.212(4)
C16-C17	1.517(5)	C17-C18	1.538(5)	C18-C19	1.527(6)
C18-C21	1.551(4)	C19-C20	1.567(4)	C21-C23	1.525(6)
C21-C22	1.528(5)	N1-S1	1.690(3)	O4-S1	1.423(2)
O5-S1	1.428(2)				

Table S5. Bond Angles in Compound S7 (degrees).

O1-C1-N1	125.7(3)	O1-C1-C2	126.3(3)	N1-C1-C2	108.0(3)
C9-C2-C3	111.2(3)	C9-C2-C1	107.9(3)	C3-C2-C1	102.4(2)
C9-C2-C11	111.2(3)	C3-C2-C11	114.7(3)	C1-C2-C11	108.9(3)
C4-C3-C8	120.2(3)	C4-C3-C2	129.5(3)	C8-C3-C2	110.3(3)
C3-C4-C5	118.7(3)	C6-C5-C4	120.2(3)	C5-C6-C7	123.0(3)
C6-C7-C8	116.2(3)	C3-C8-C7	121.6(3)	C3-C8-N1	108.9(2)
C7-C8-N1	129.5(3)	O3-C9-O2	122.7(3)	O3-C9-C2	125.0(3)
O2-C9-C2	112.2(3)	C12-C11-C2	112.9(3)	C13-C12-C11	125.8(5)
C15-C14-S1	118.8(2)	C16-C15-C14	114.0(3)	C16-C15-C20	105.4(3)
C14-C15-C20	118.6(3)	C16-C15-C21	99.0(2)	C14-C15-C21	115.3(2)
C20-C15-C21	102.0(3)	O6-C16-C15	126.0(3)	O6-C16-C17	126.3(3)
C15-C16-C17	107.6(3)	C16-C17-C18	101.2(3)	C19-C18-C17	106.5(3)
C19-C18-C21	103.0(3)	C17-C18-C21	103.0(3)	C18-C19-C20	102.8(3)
C15-C20-C19	103.7(3)	C23-C21-C22	109.0(3)	C23-C21-C18	113.5(3)
C22-C21-C18	114.7(3)	C23-C21-C15	112.5(3)	C22-C21-C15	113.1(3)
C18-C21-C15	93.5(2)	C1-N1-C8	110.5(2)	C1-N1-S1	120.9(2)
C8-N1-S1	127.9(2)	C9-O2-C10	118.2(3)	O4-S1-O5	119.29(14)
O4-S1-N1	105.59(12)	O5-S1-N1	107.25(13)	O4-S1-C14	111.93(14)
O5-S1-C14	107.73(14)	N1-S1-C14	103.83(14)		

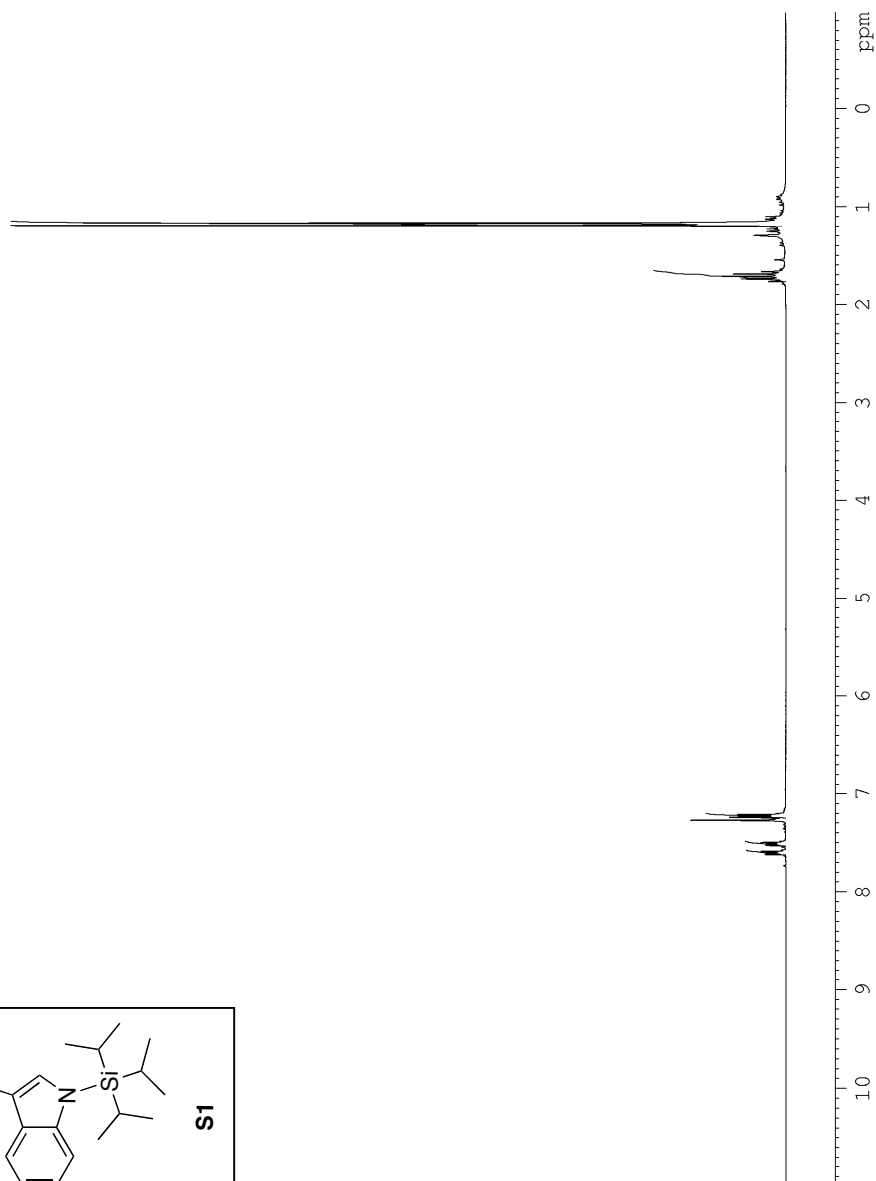
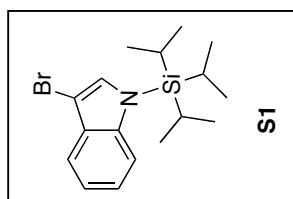
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- (6) CrystalStructure: Crystal Structure Analysis Package, Rigaku Corp. Rigaku/MSD (2002).
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- (9) SHELXL-97: Program for the Refinement of Crystal Structures, Sheldrick, G.M. (1997), University of Göttingen, Germany.
- (10)
$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

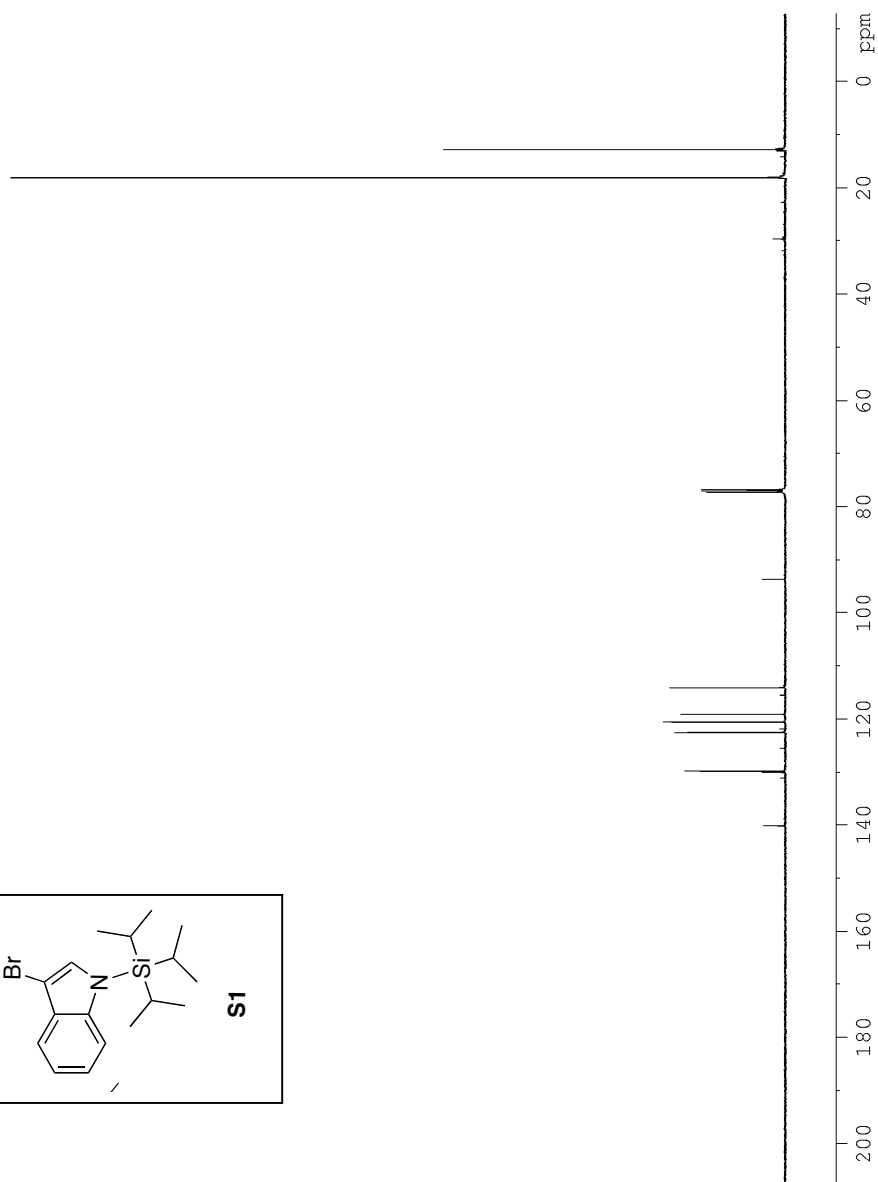
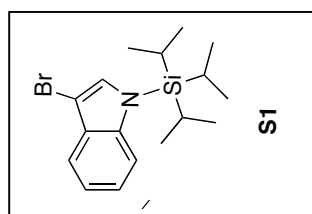
$$wR_2 = \{ \sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$$

$$GOF = \{ \sum w (F_o^2 - F_c^2)^2 / (n - p) \}^{1/2}$$

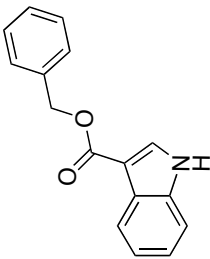
where n = the number of reflections and p = the number of parameters refined.
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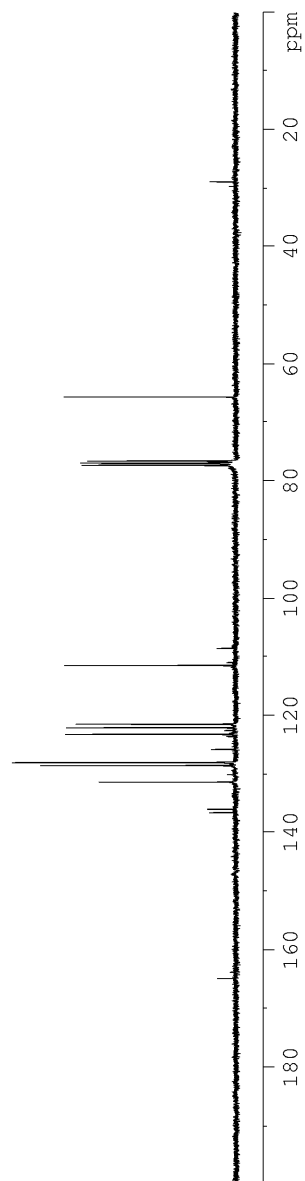
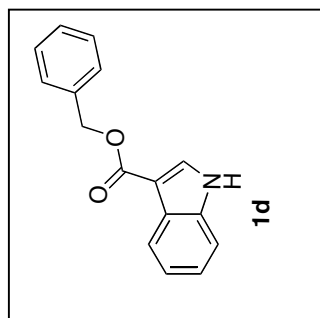
500 MHz ^1H NMR Spectrum of Compound **S1** in CDCl_3



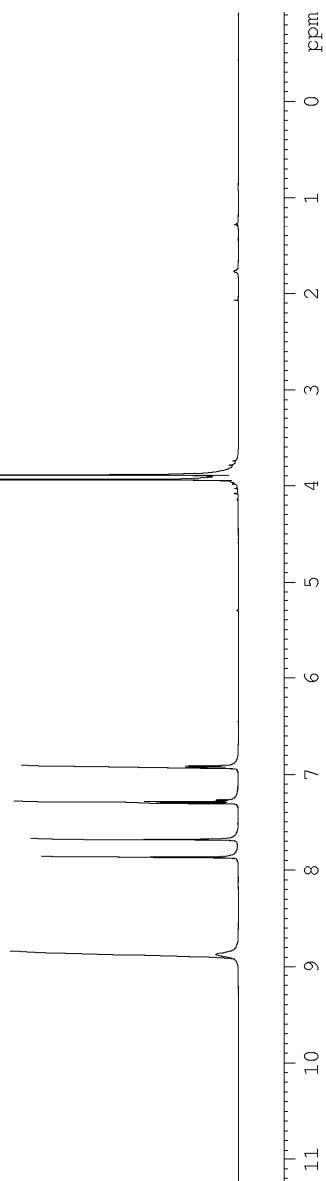
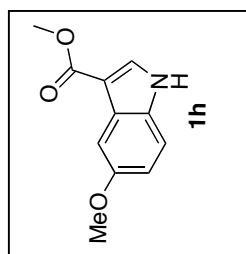
125 MHz ^{13}C NMR Spectrum of Compound **S1** in CDCl_3



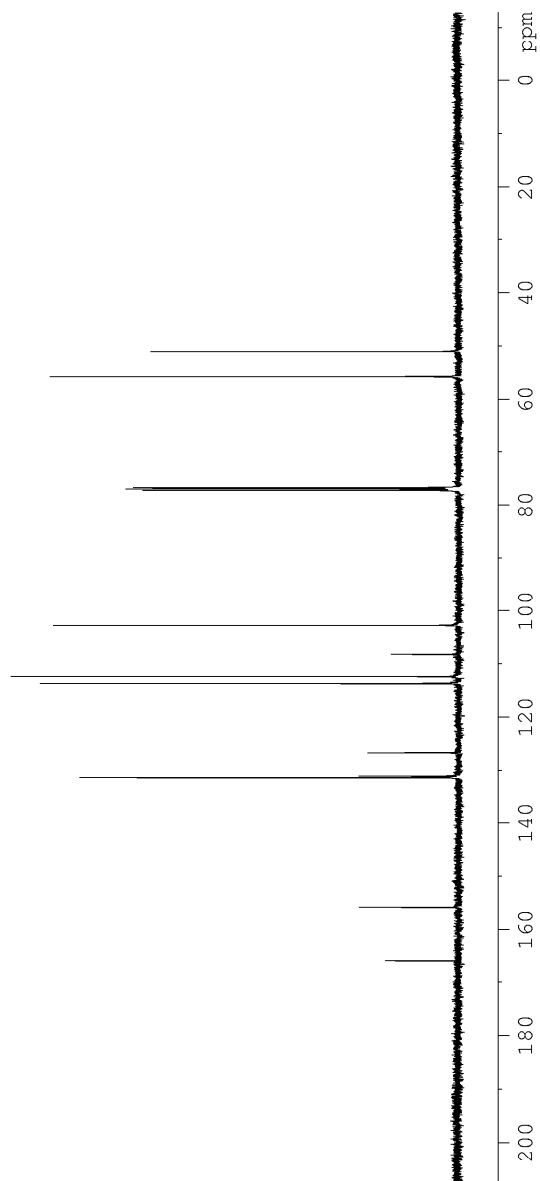
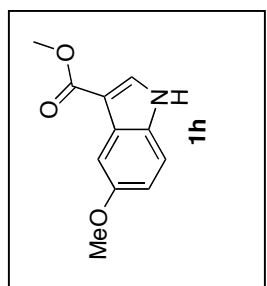
500 MHz ^1H NMR Spectrum of Compound **1d** in CDCl_3

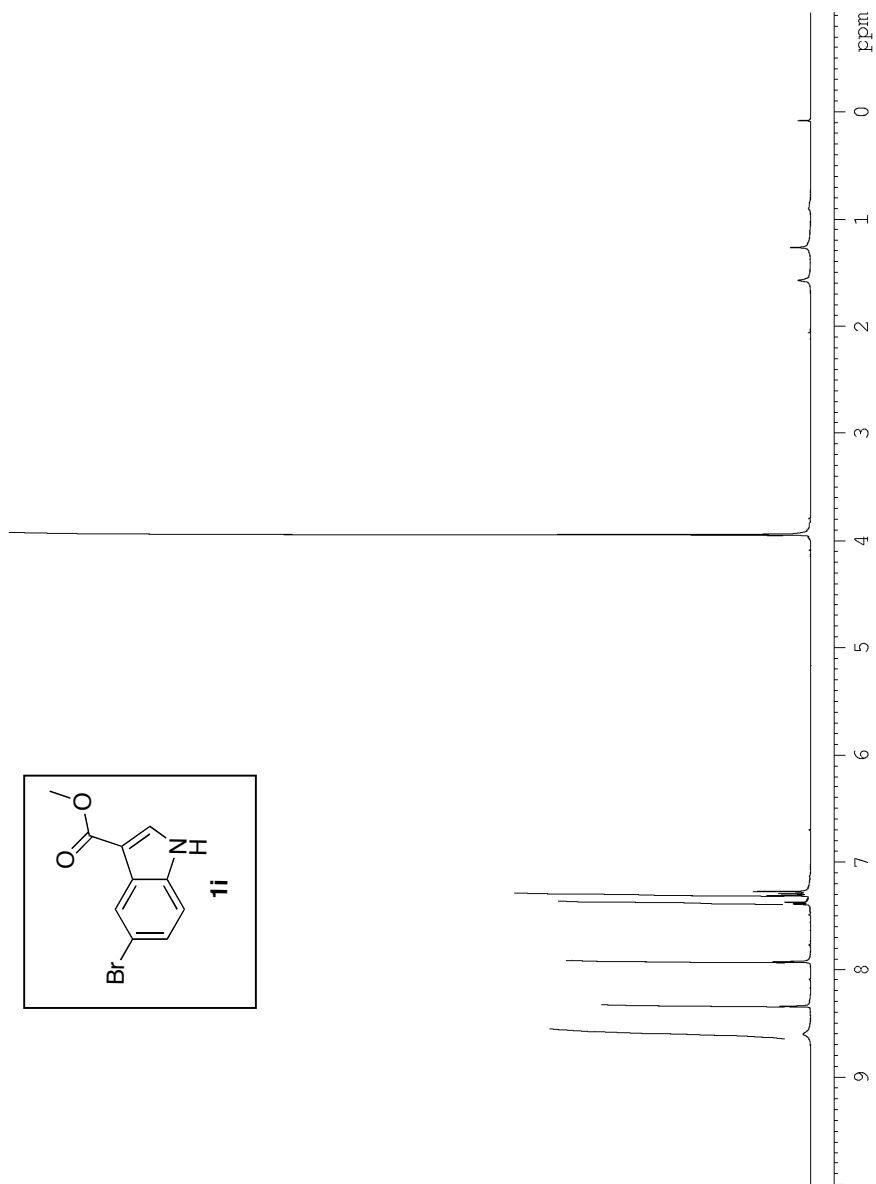
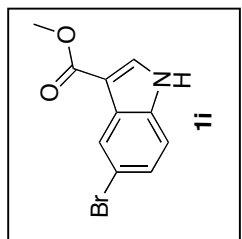


125 MHz ^{13}C NMR Spectrum of Compound **1d** in CDCl_3

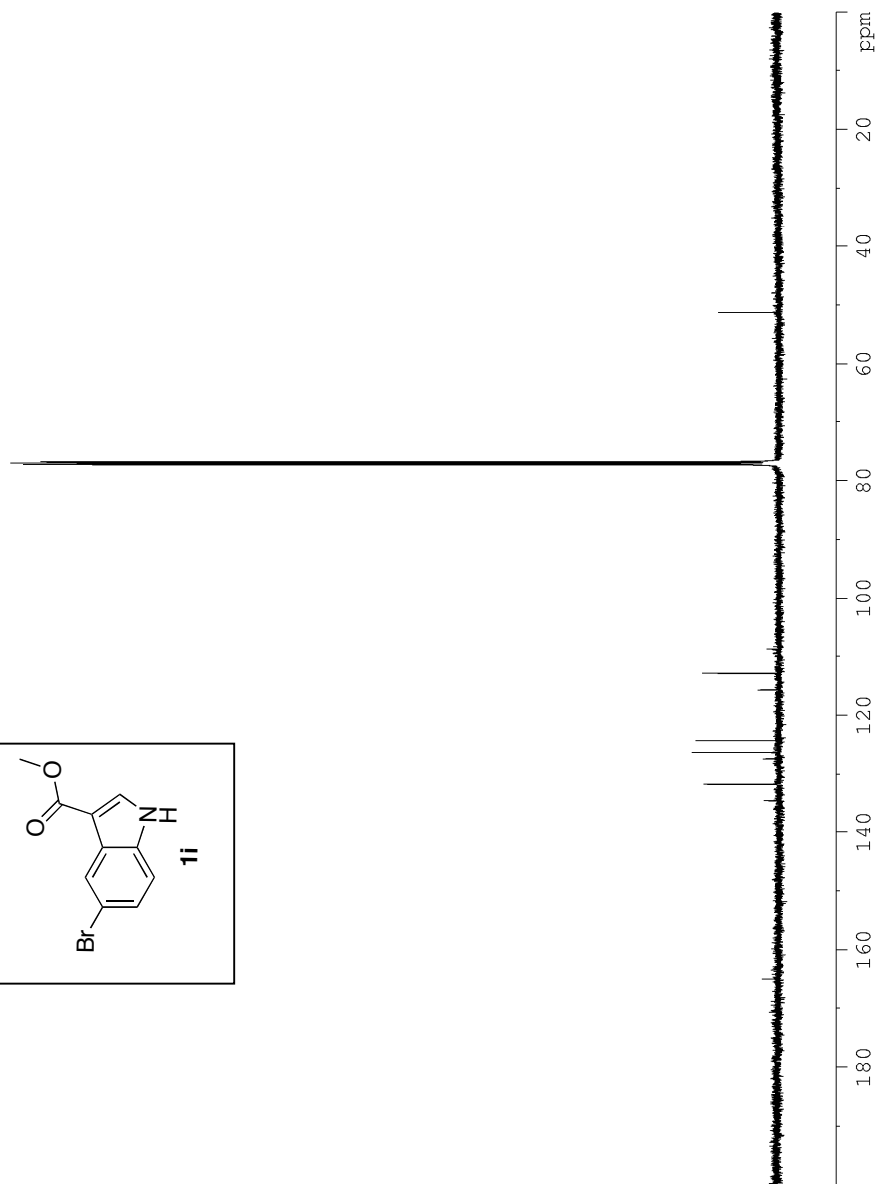
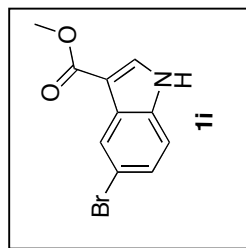


500 MHz ^1H NMR Spectrum of Compound **1h** in CDCl_3

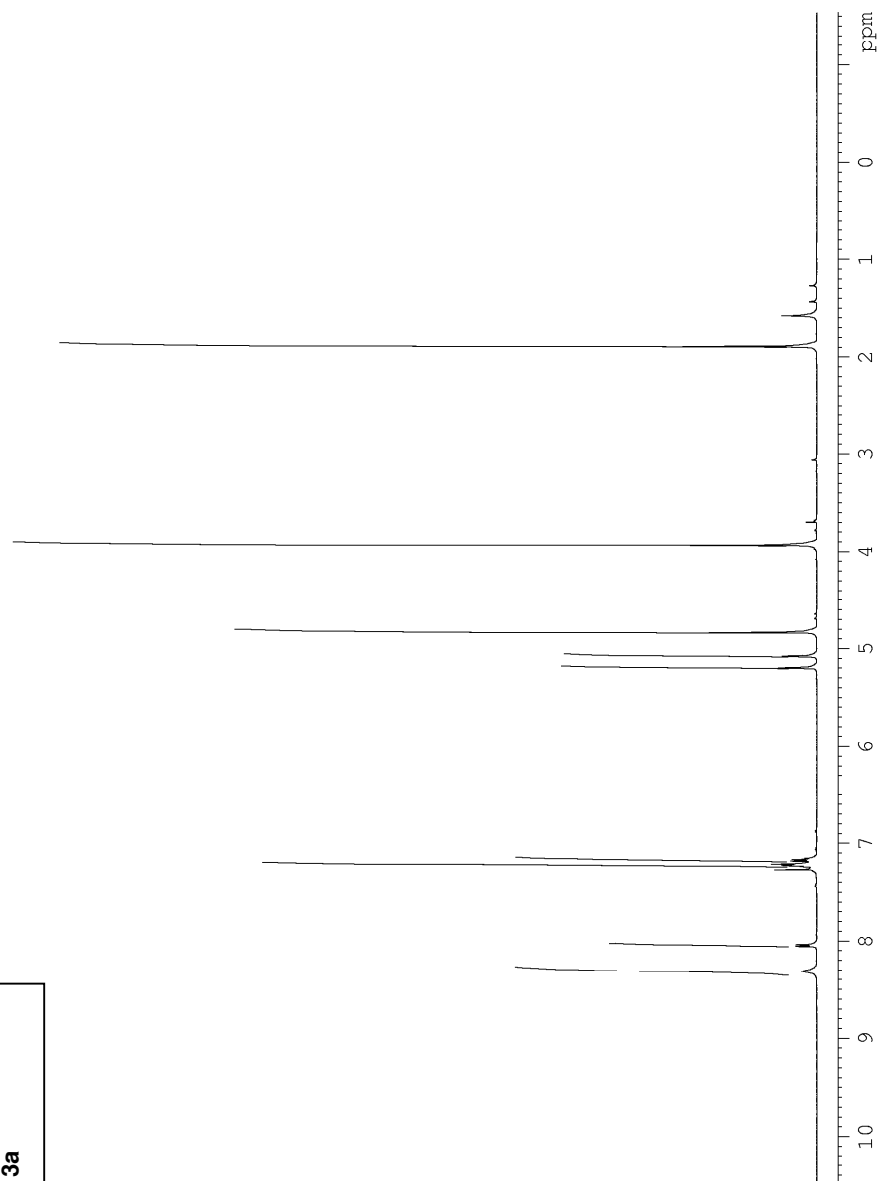
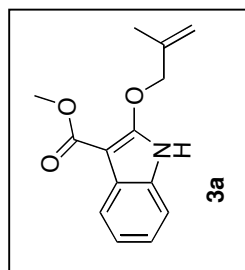




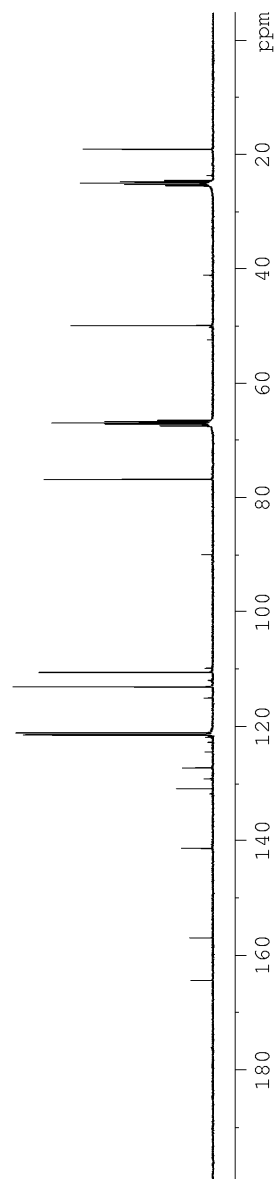
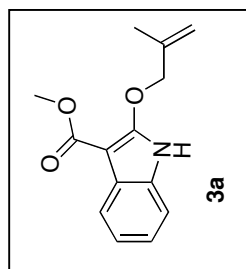
500 MHz ^1H NMR Spectrum of Compound **1i** in CDCl_3



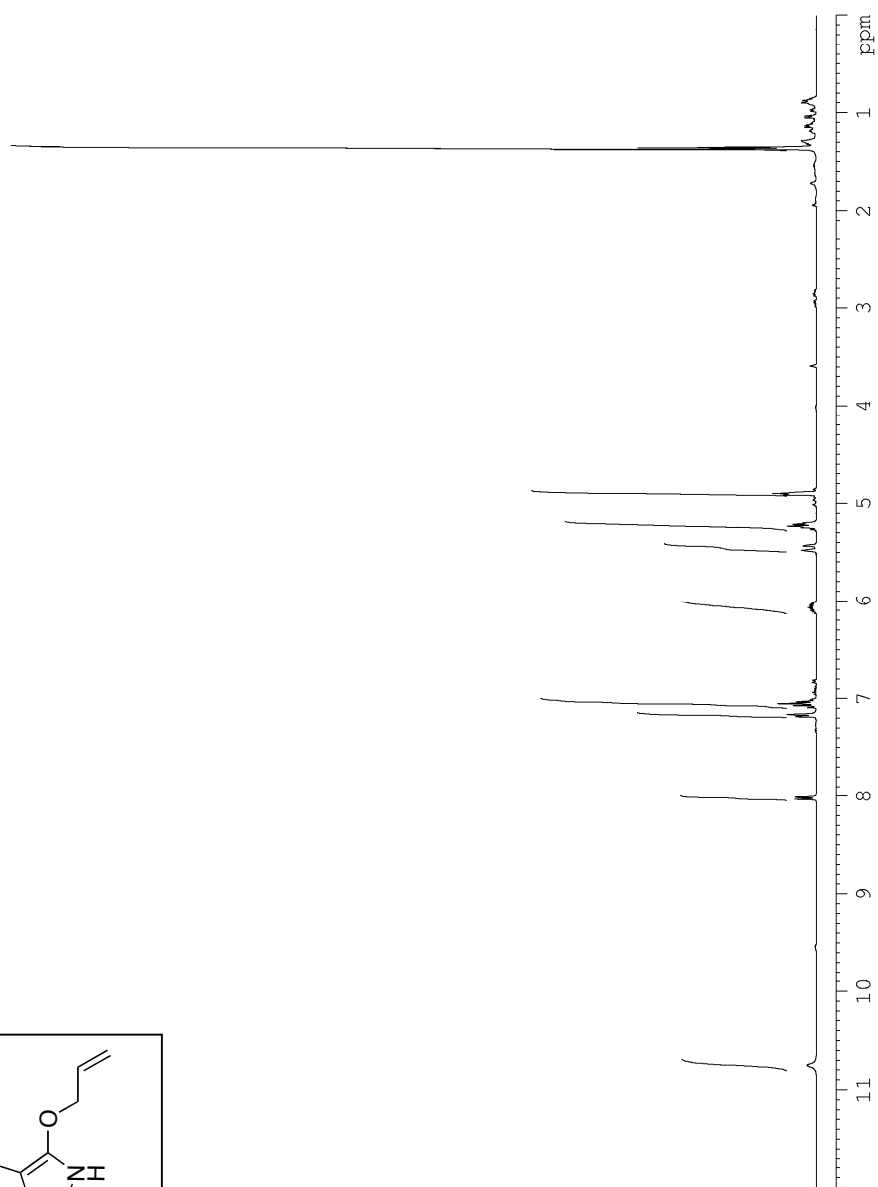
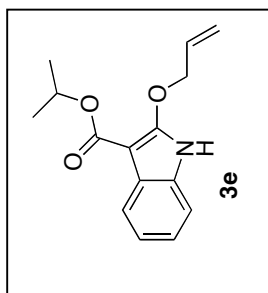
125 MHz ^{13}C NMR Spectrum of Compound **1i** in CDCl_3



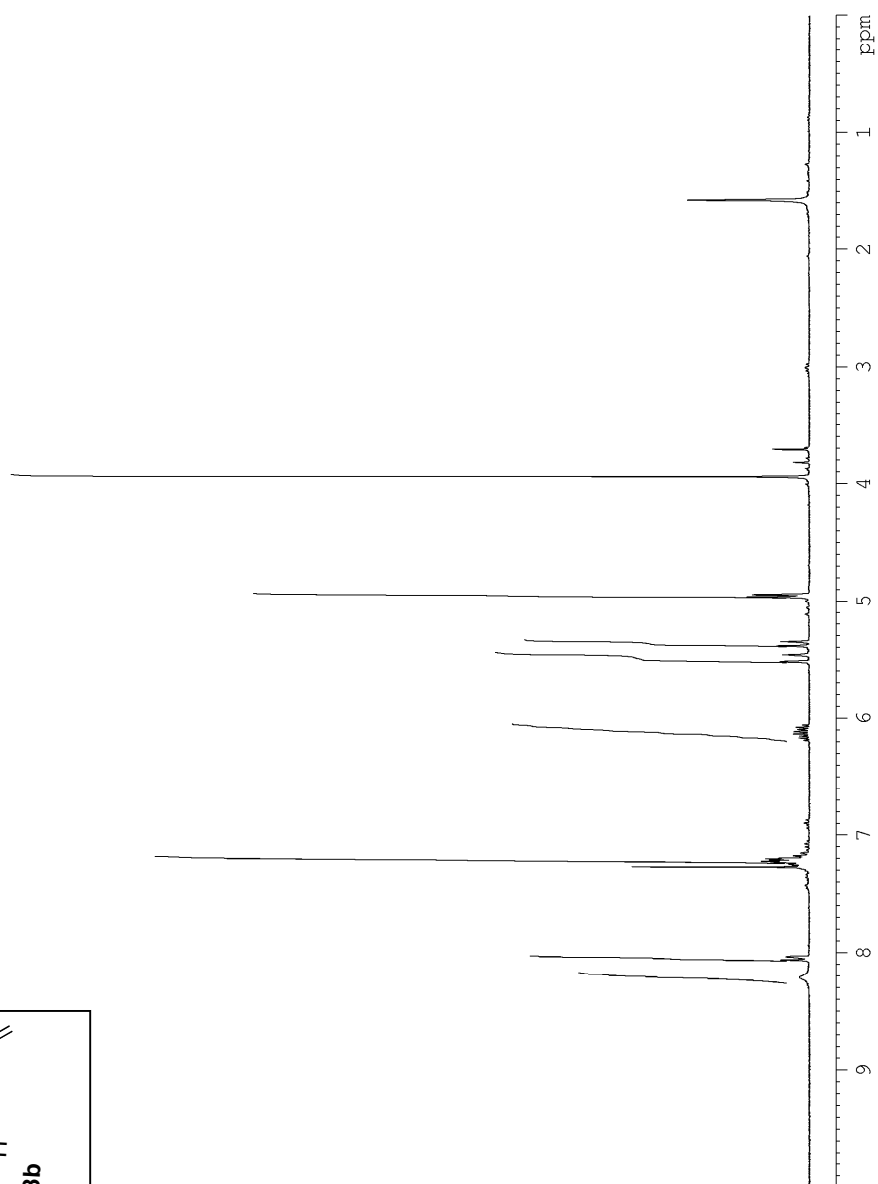
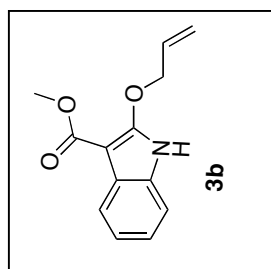
360 MHz ^1H NMR Spectrum of Compound **3a** in CDCl_3



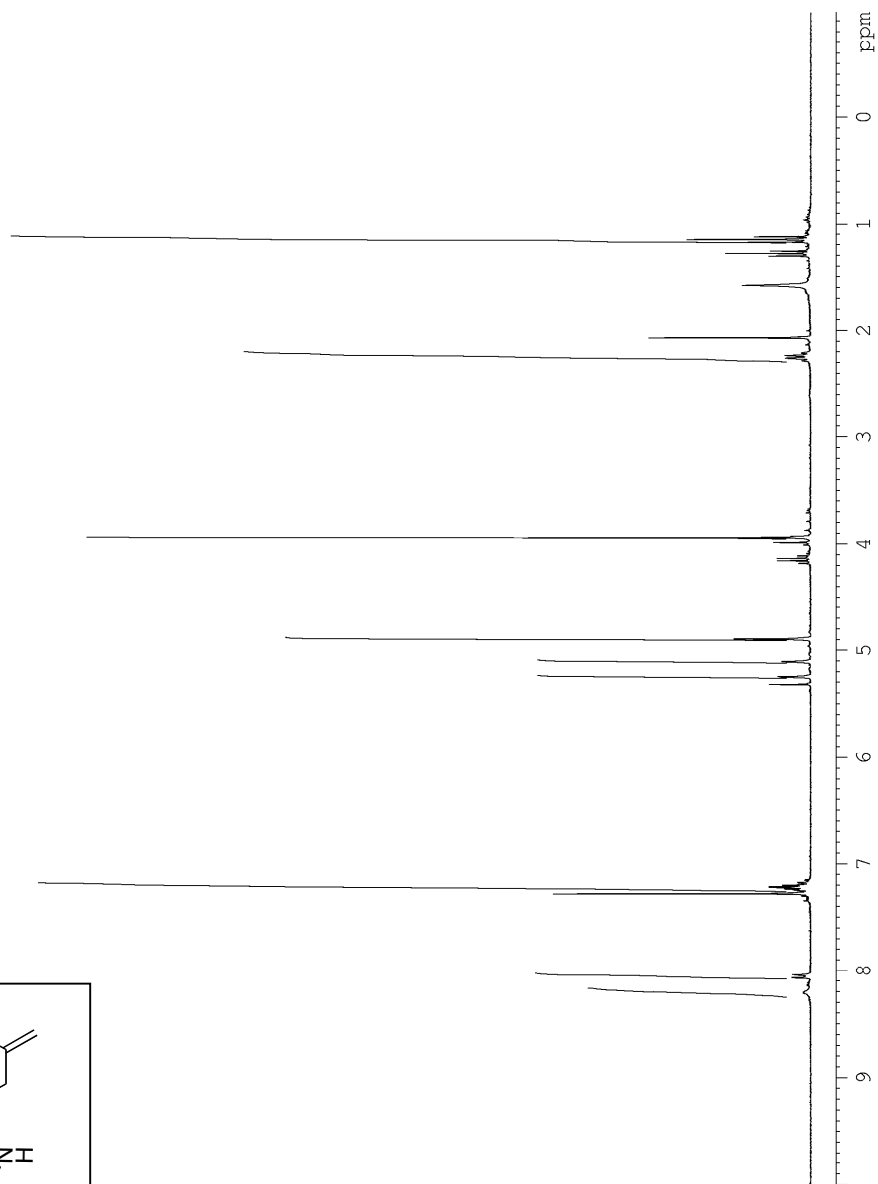
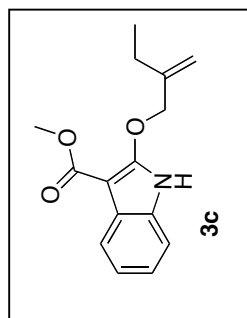
90 MHz ^{13}C NMR Spectrum of Compound **3a** in THF- d_8



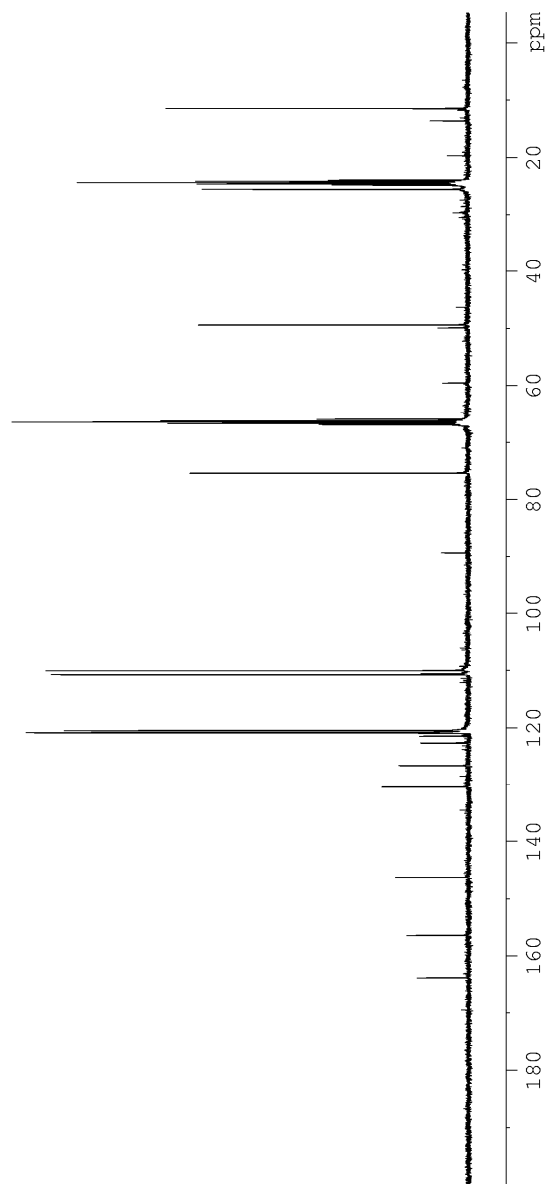
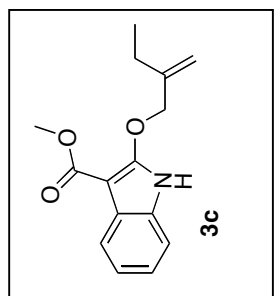
300 MHz ¹H NMR Spectrum of Compound **3e** in CDCl₃



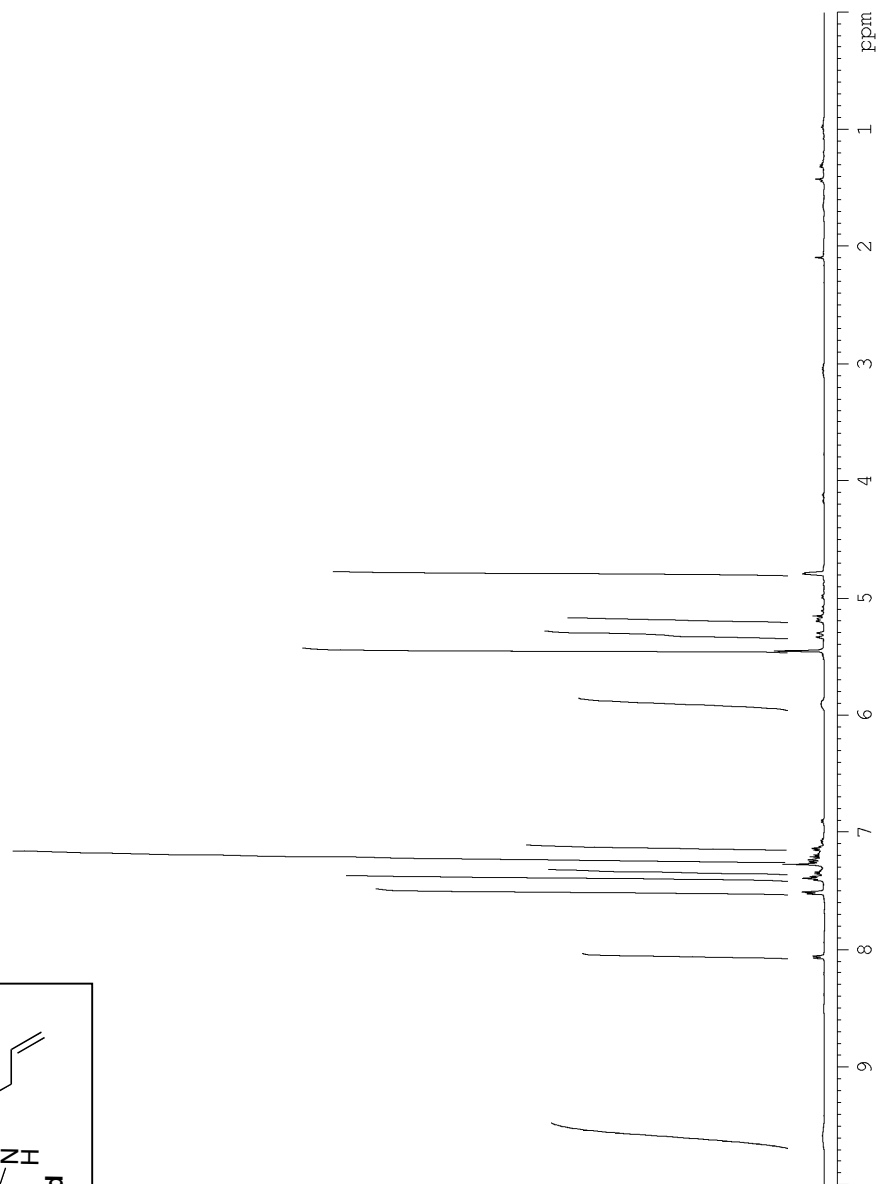
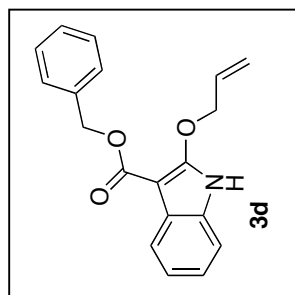
125 MHz ^1H NMR Spectrum of Compound **3b** in CDCl_3



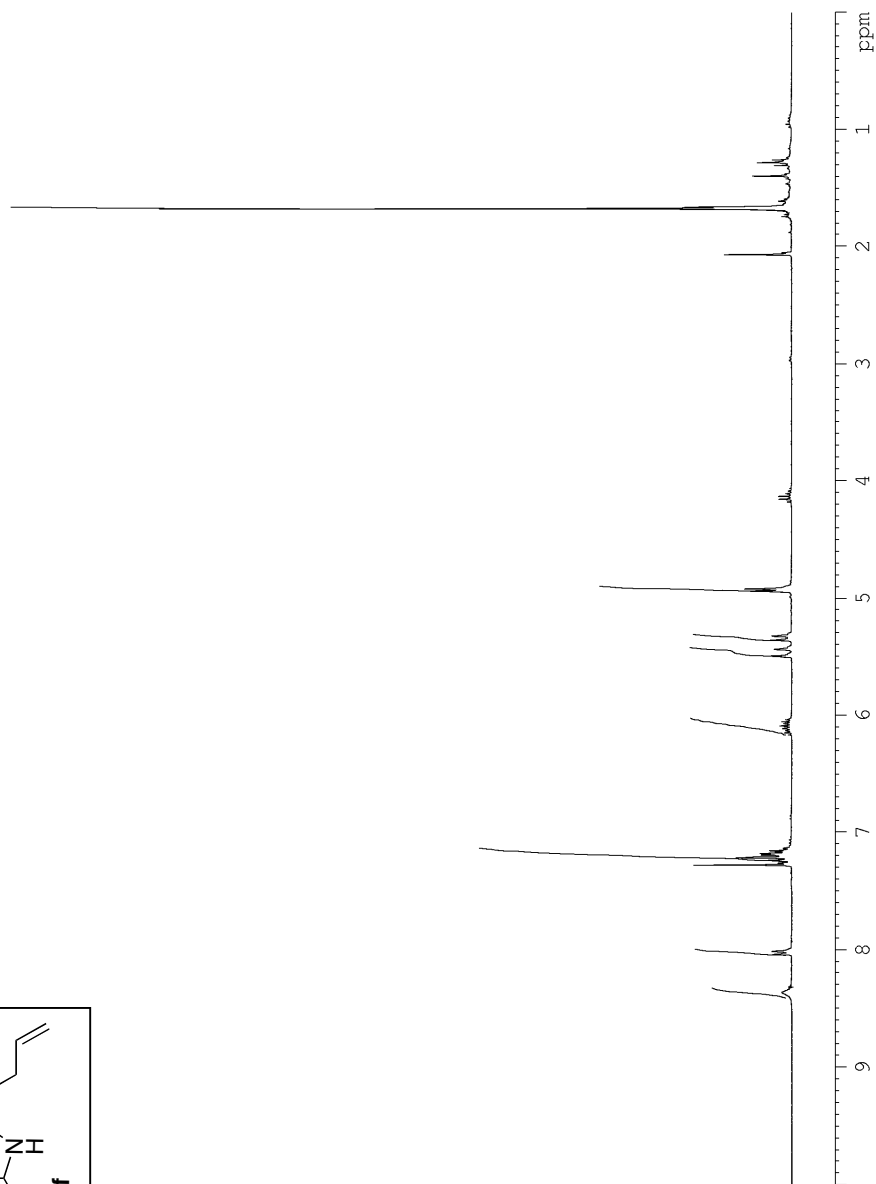
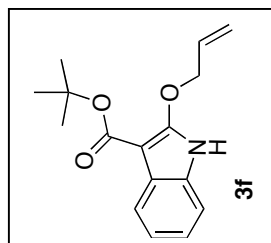
300 MHz ^1H NMR Spectrum of Compound **3c** in CDCl_3



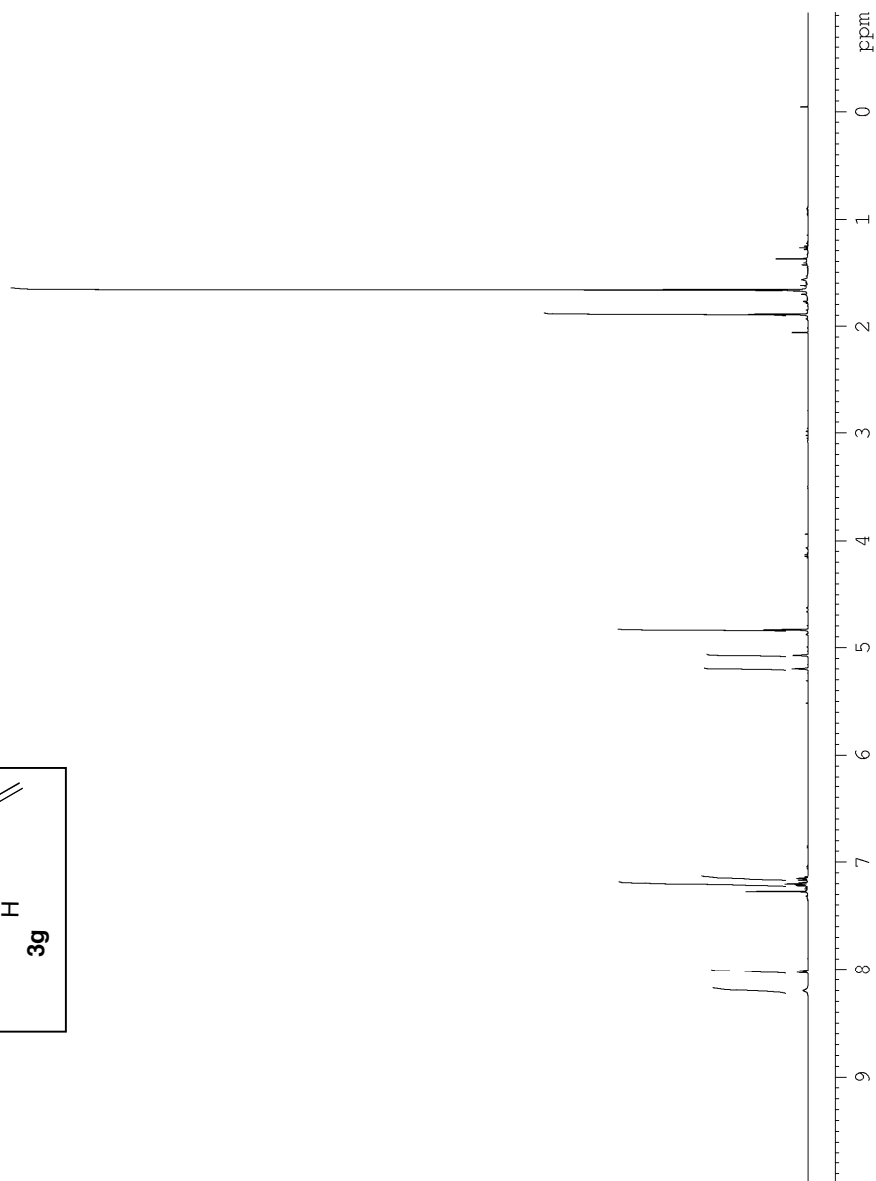
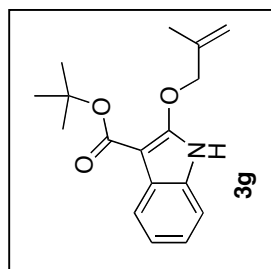
90 MHz ^{13}C NMR Spectrum of Compound **3c** in THF- d_8



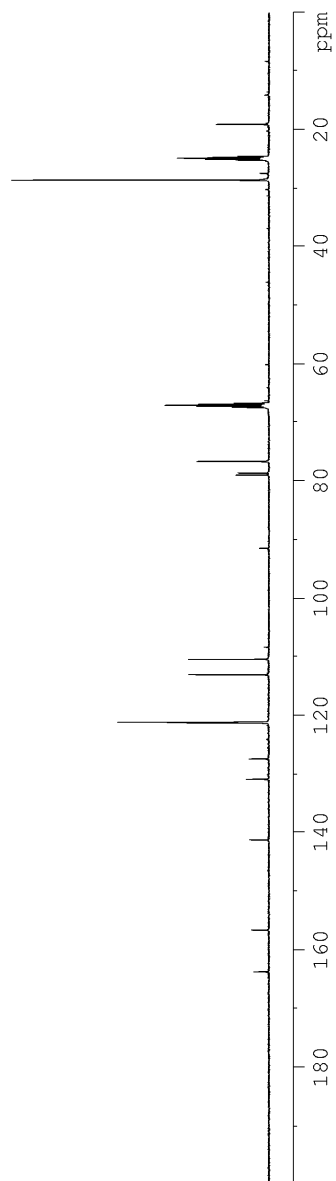
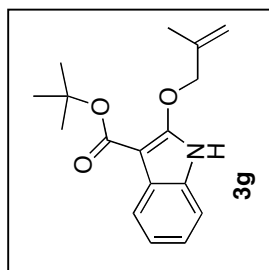
360 MHz ¹H NMR Spectrum of Compound **3d** in THF-d₈



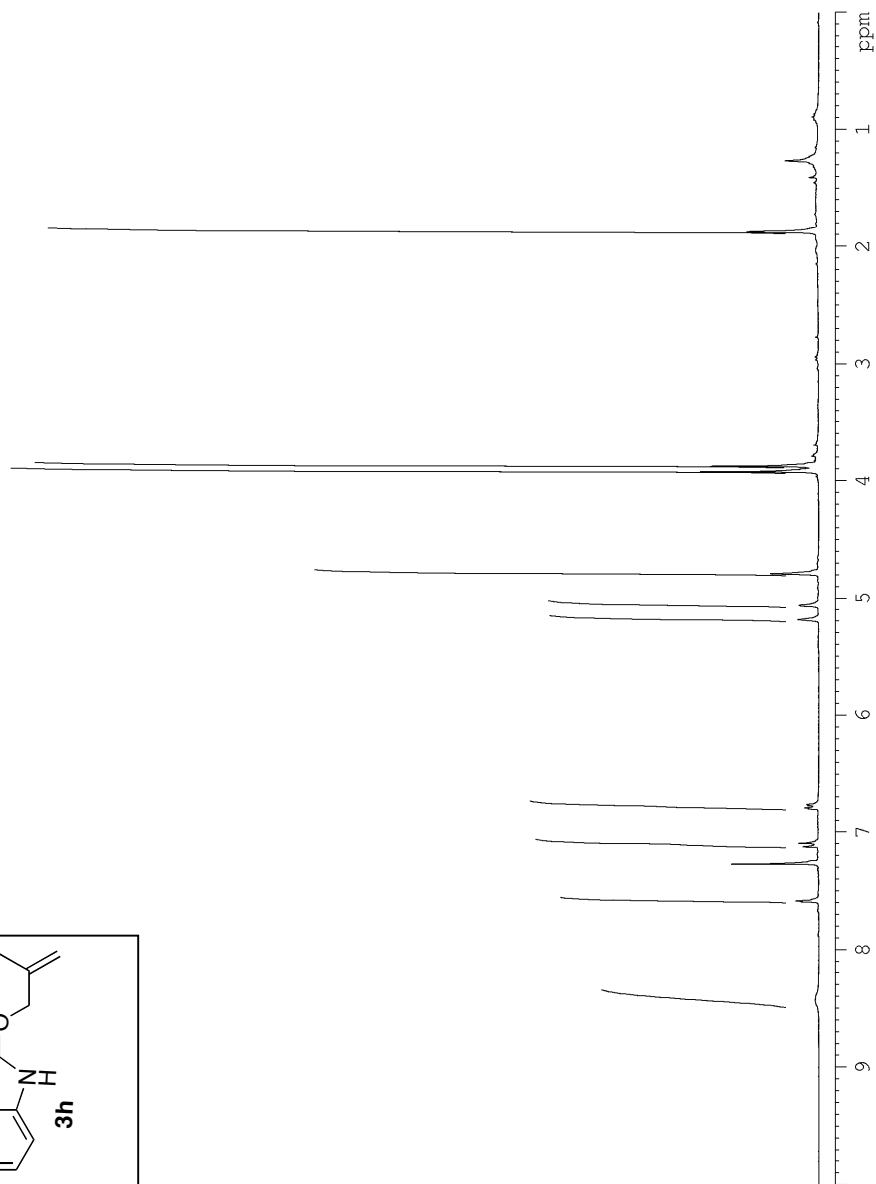
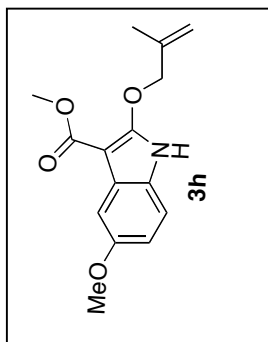
300 MHz ^1H NMR Spectrum of Compound **3f** in CDCl_3

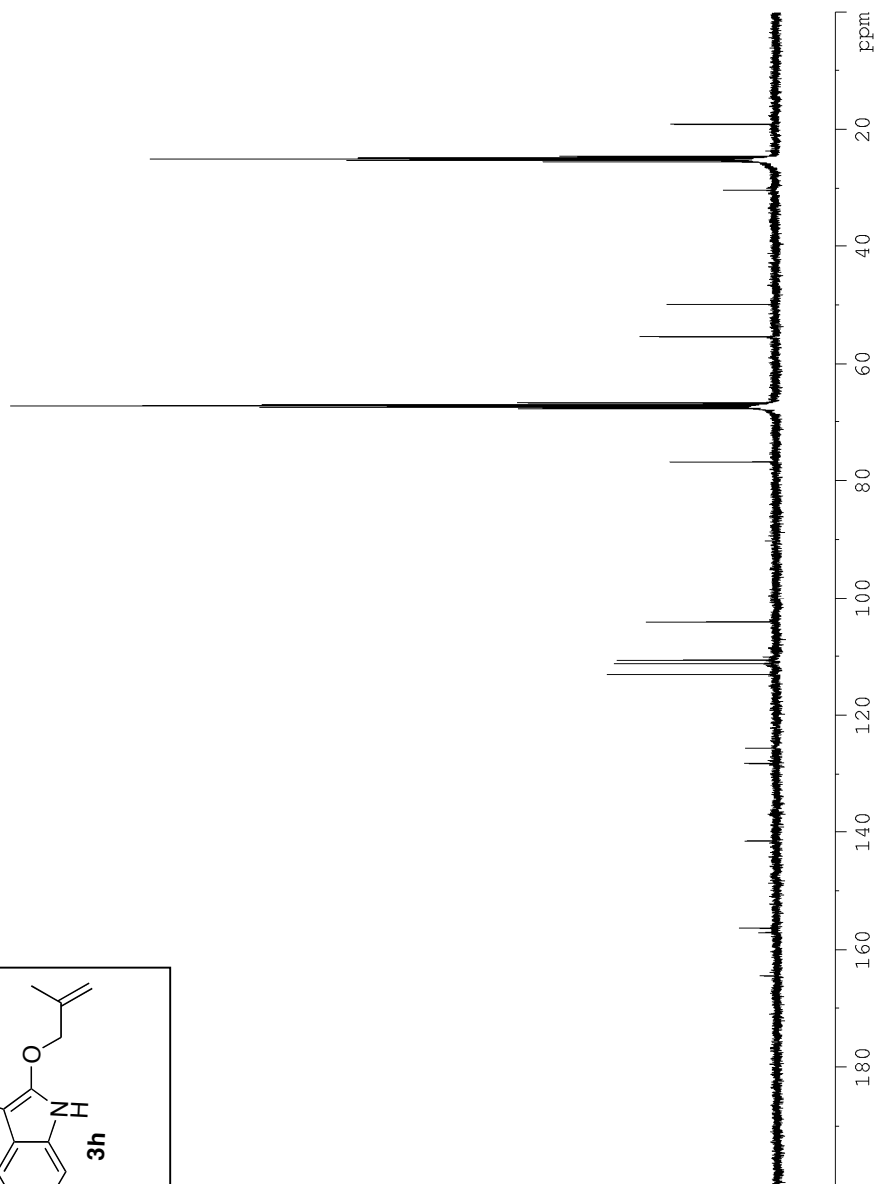
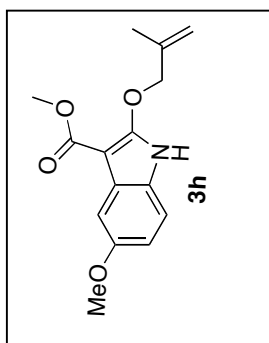


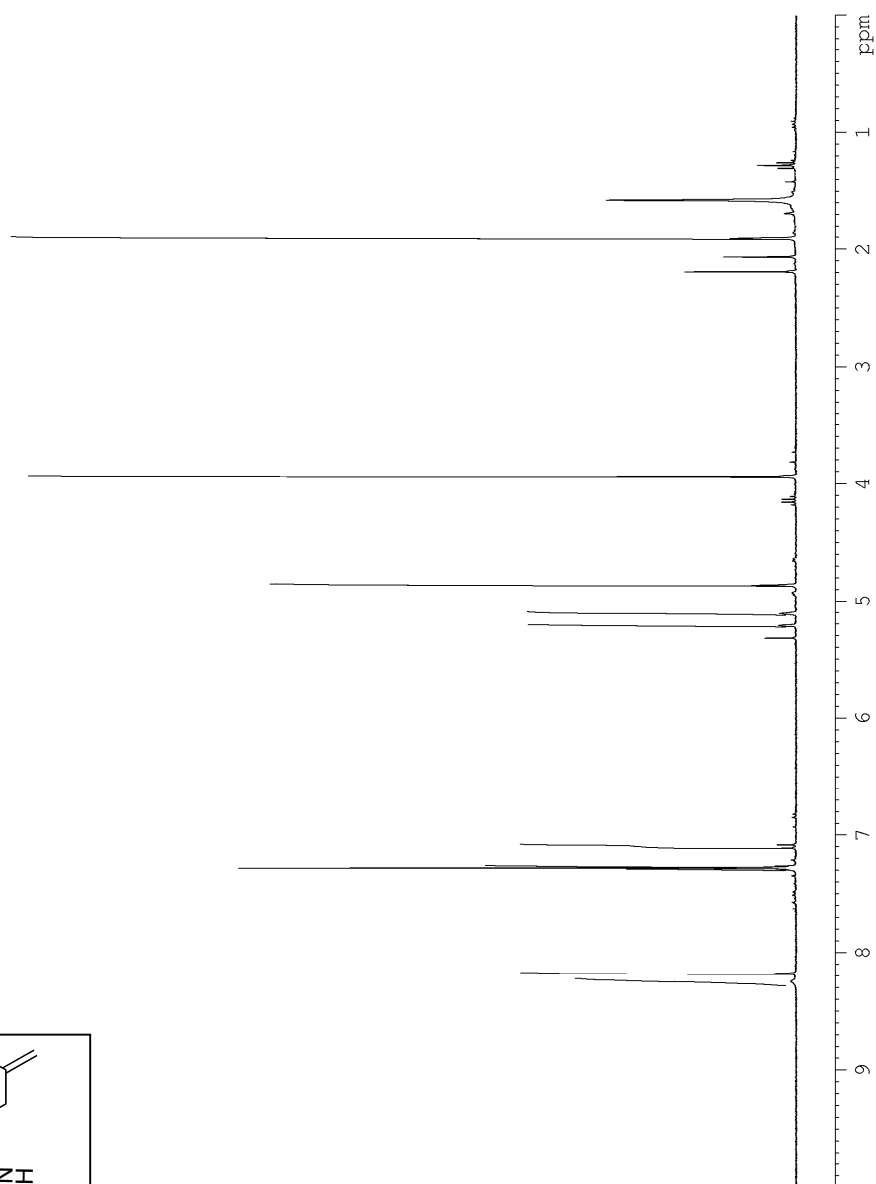
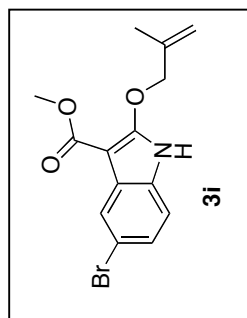
500 MHz ^1H NMR Spectrum of Compound **3g** in CDCl_3



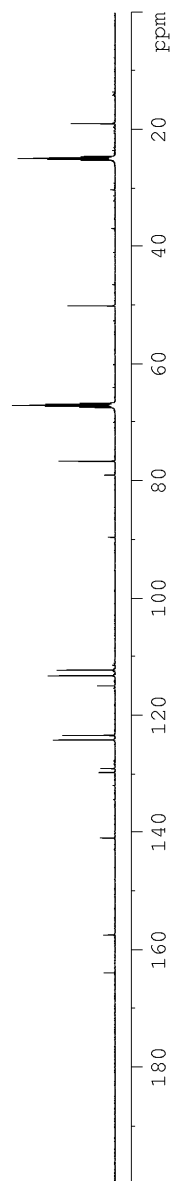
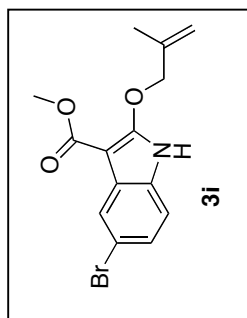
125 MHz ^{13}C NMR Spectrum of Compound **3g** in THF- d_8



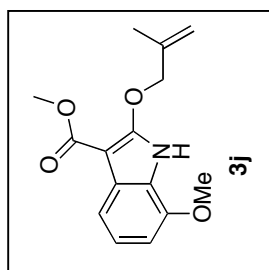




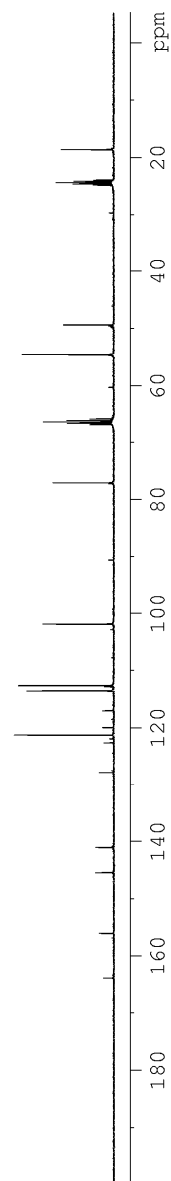
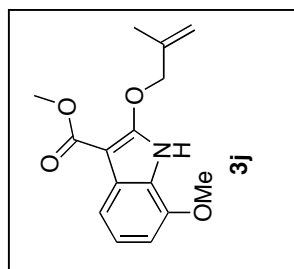
300 MHz ^1H NMR Spectrum of Compound **3i** in CDCl_3



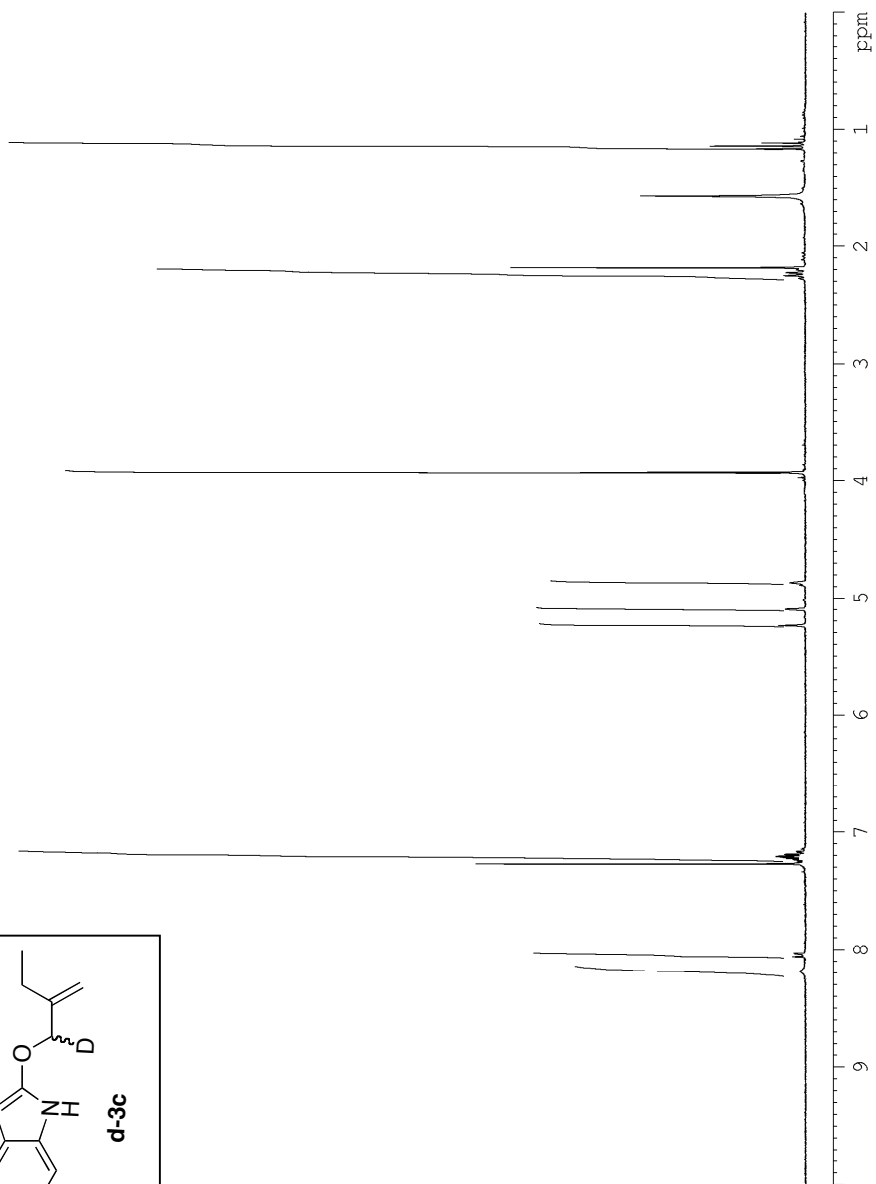
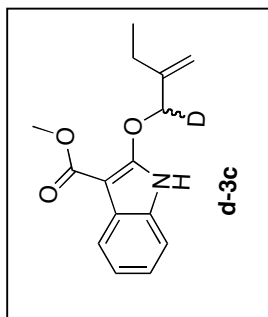
90 MHz ^{13}C NMR Spectrum of Compound **3i** in THF- d_8



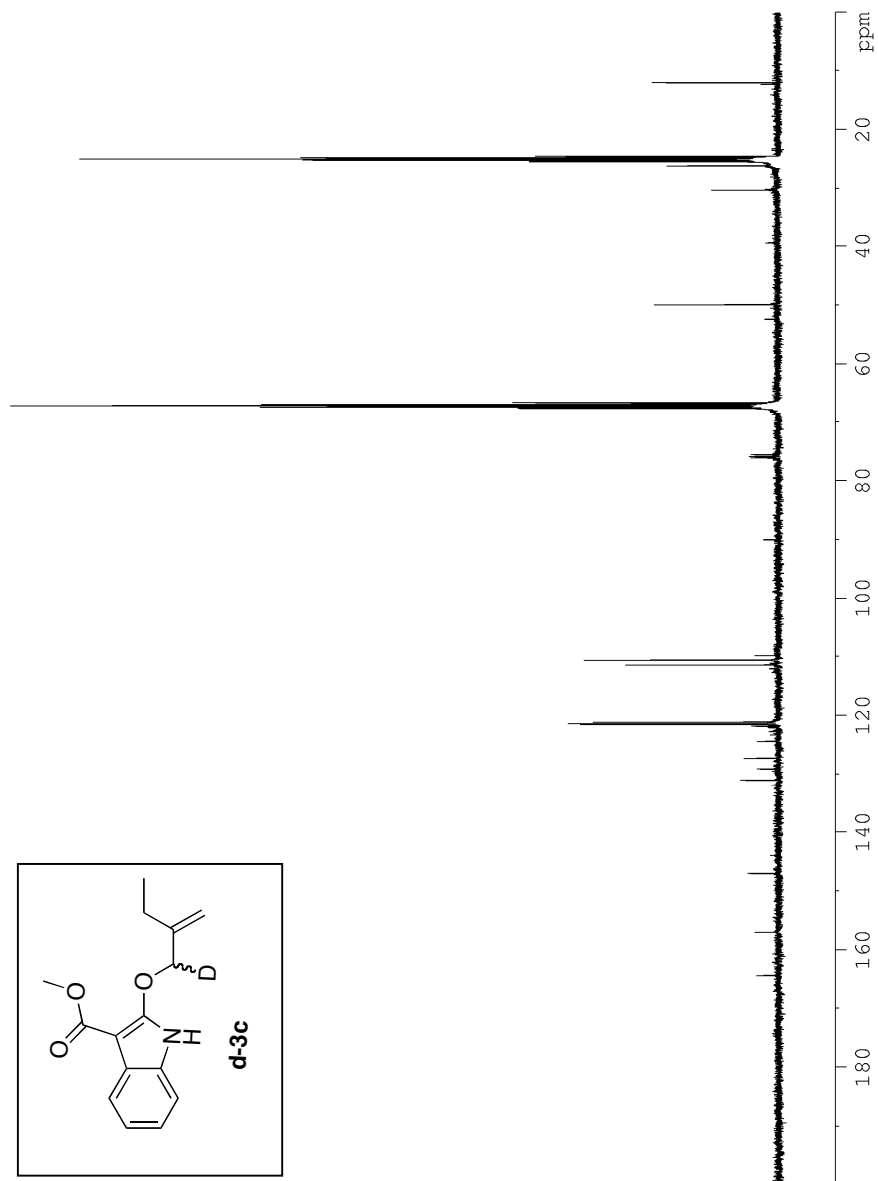
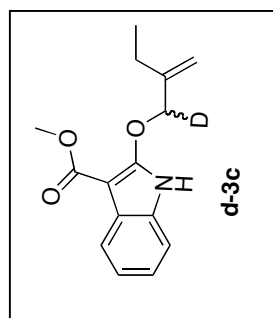
500 MHz ^1H NMR Spectrum of Compound **3j** in CDCl_3



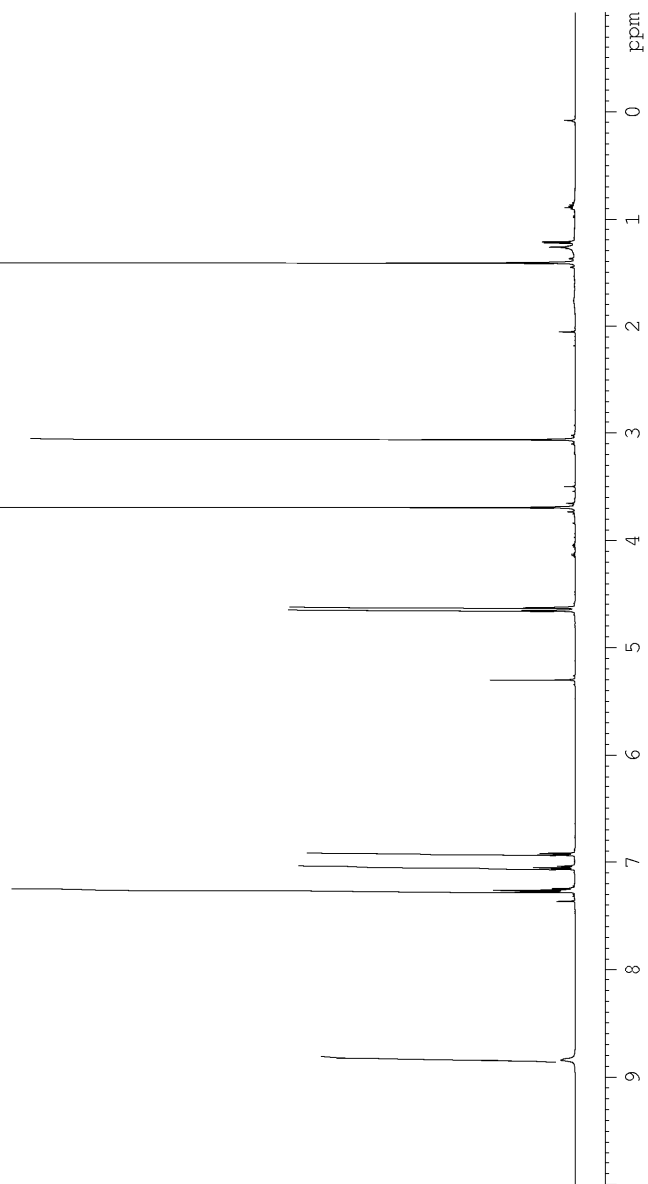
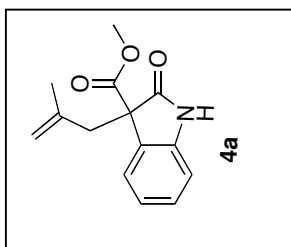
90 MHz ¹³C NMR Spectrum of Compound **3j** in THF-d₈

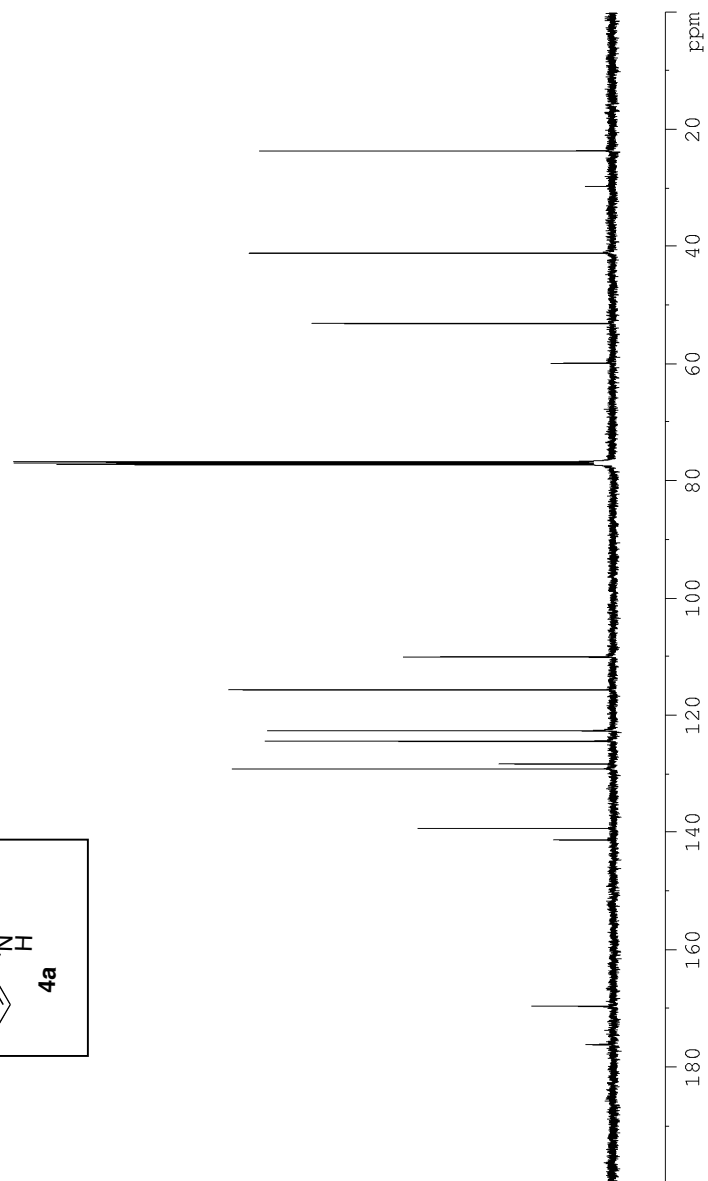
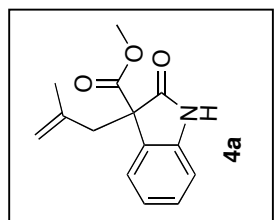


500 MHz ^1H NMR Spectrum of Compound **d-3c** in CDCl_3

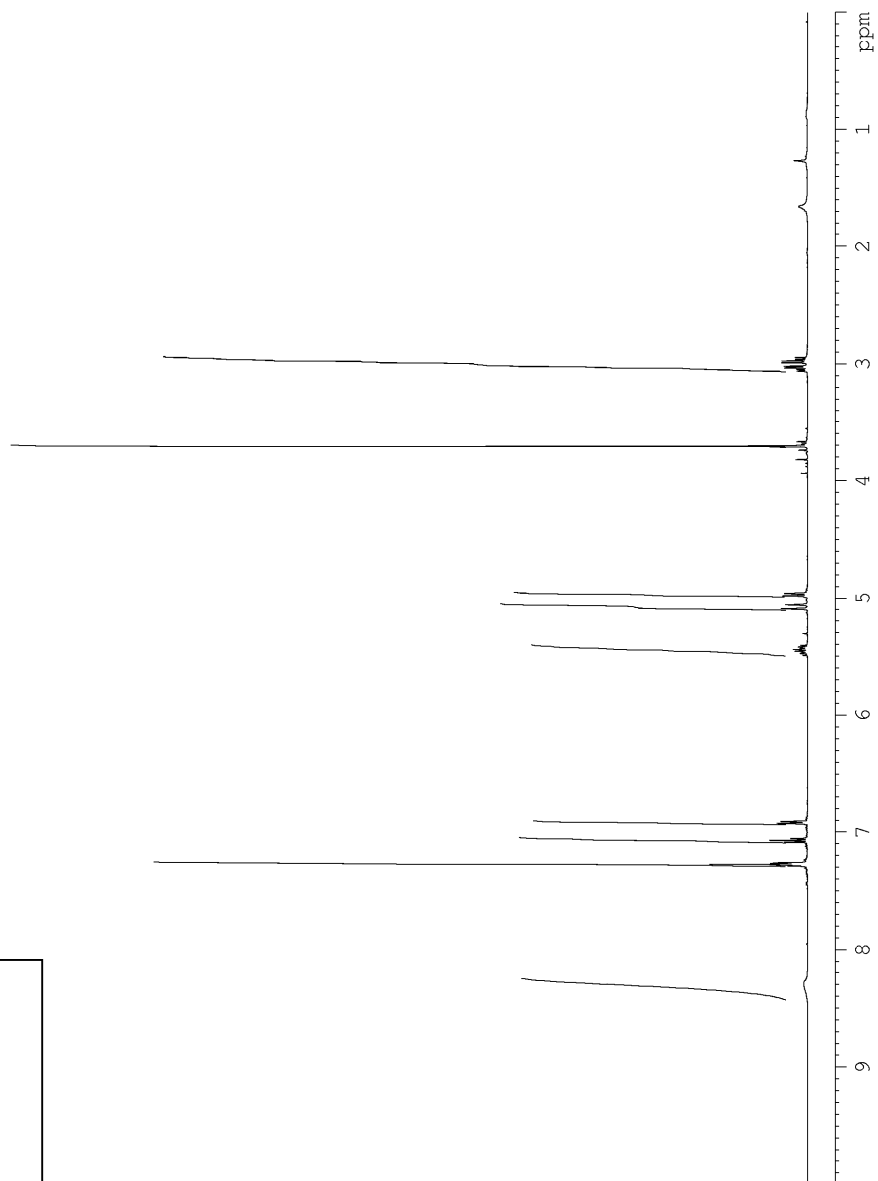
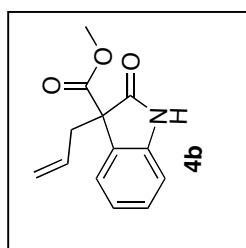


90 MHz ^{13}C NMR Spectrum of Compound **d-3c** in THF- d_8

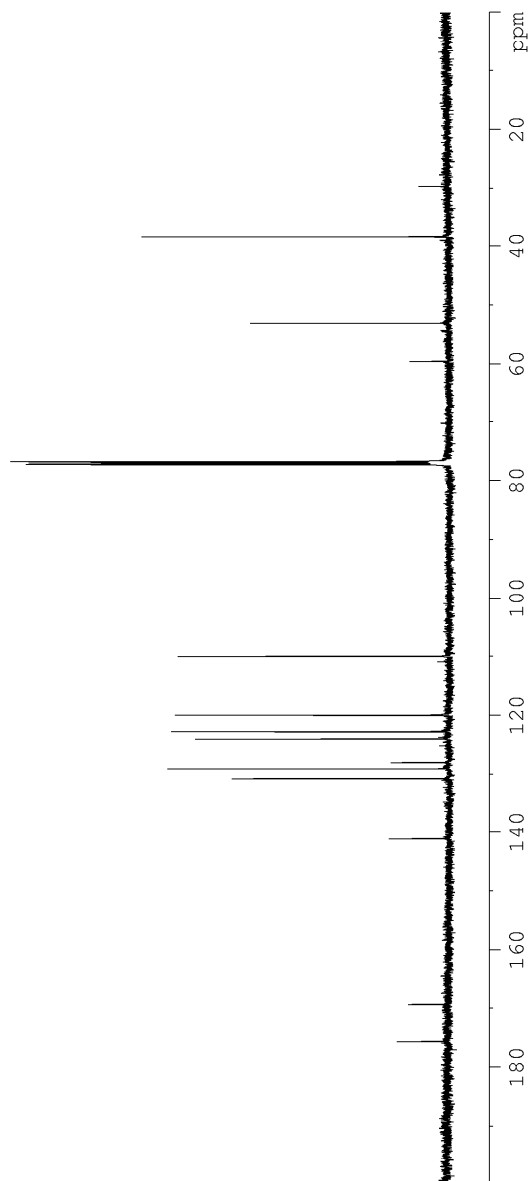
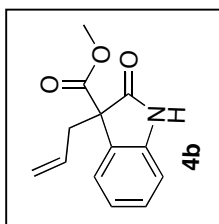




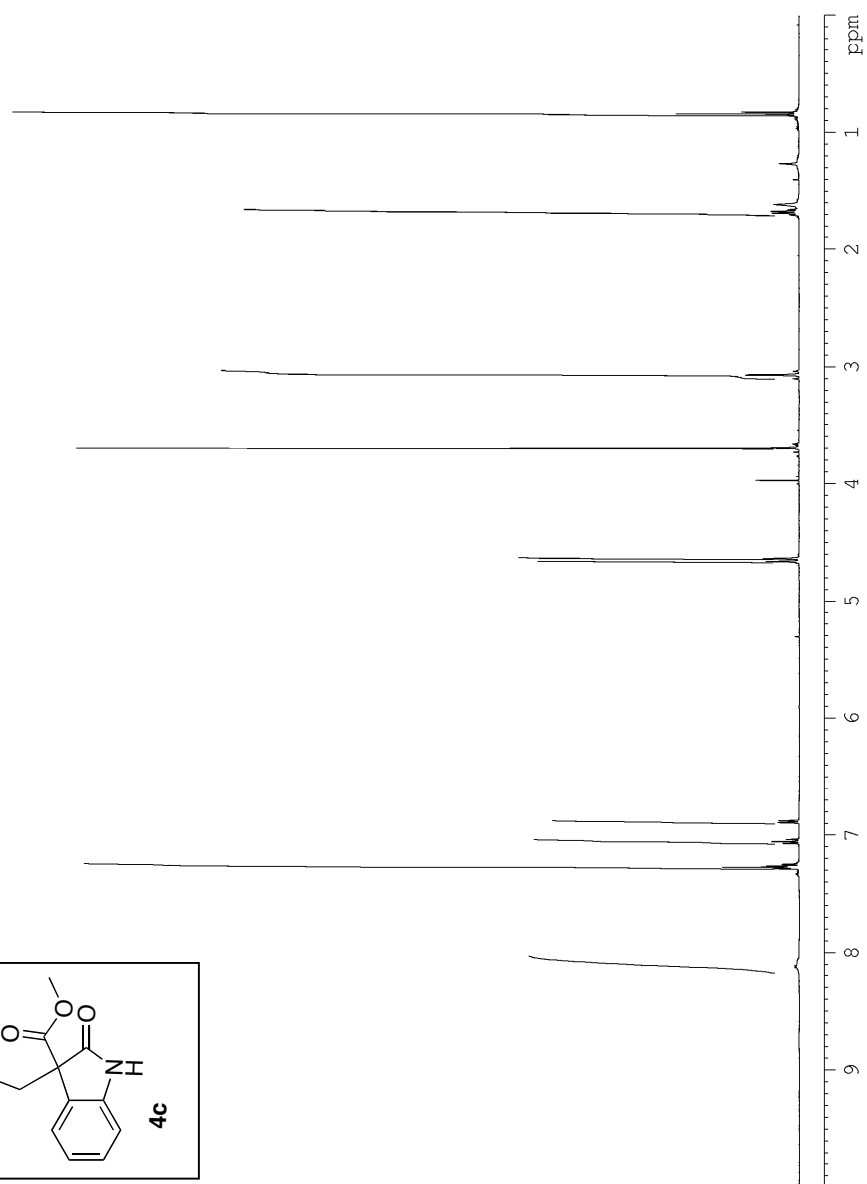
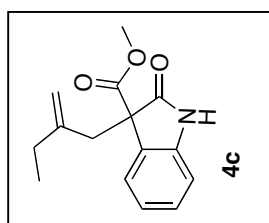
125 MHz ^1H NMR Spectrum of Compound **4a** in CDCl_3



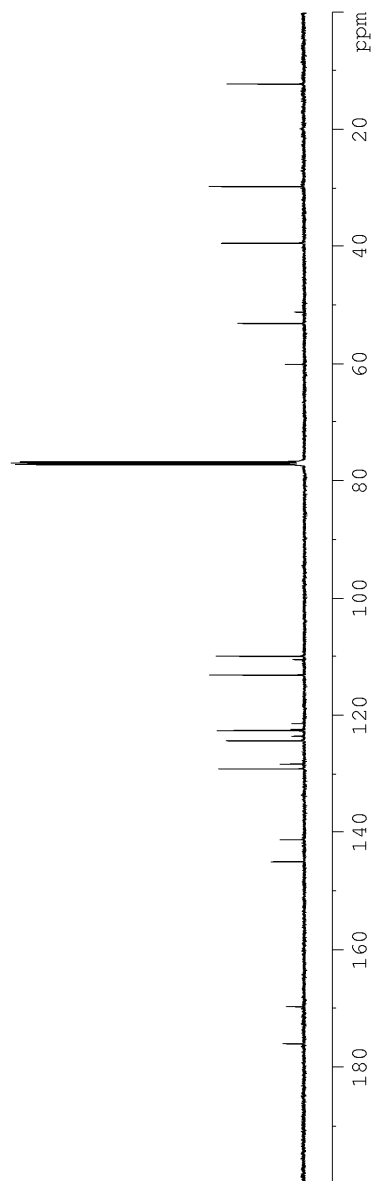
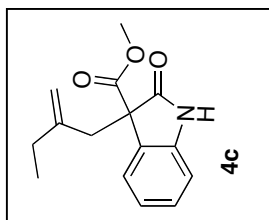
500 MHz ^1H NMR Spectrum of Compound **4b** in CDCl_3



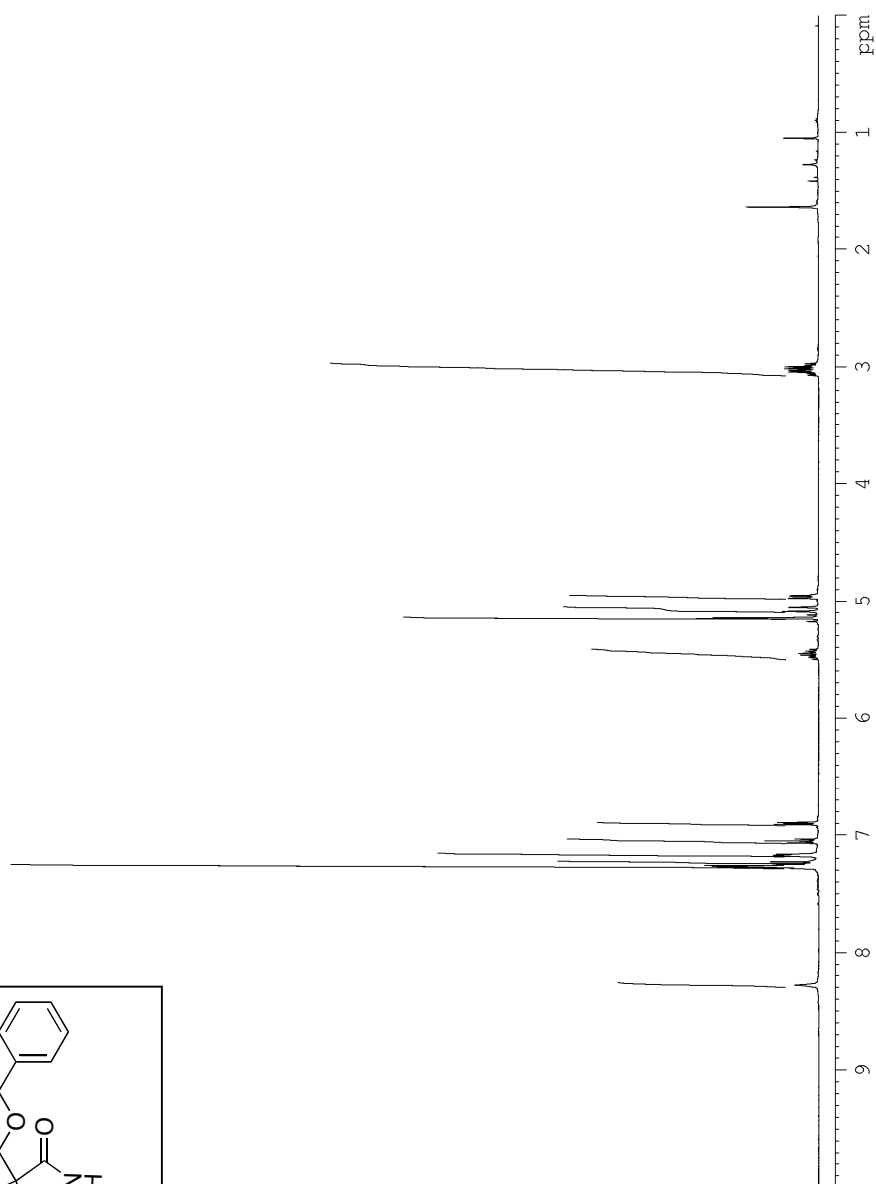
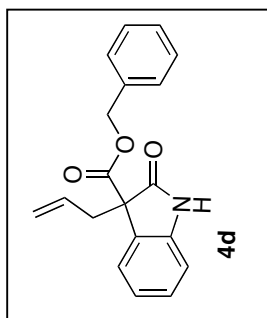
125 MHz ^{13}C NMR Spectrum of Compound **4b** in CDCl_3



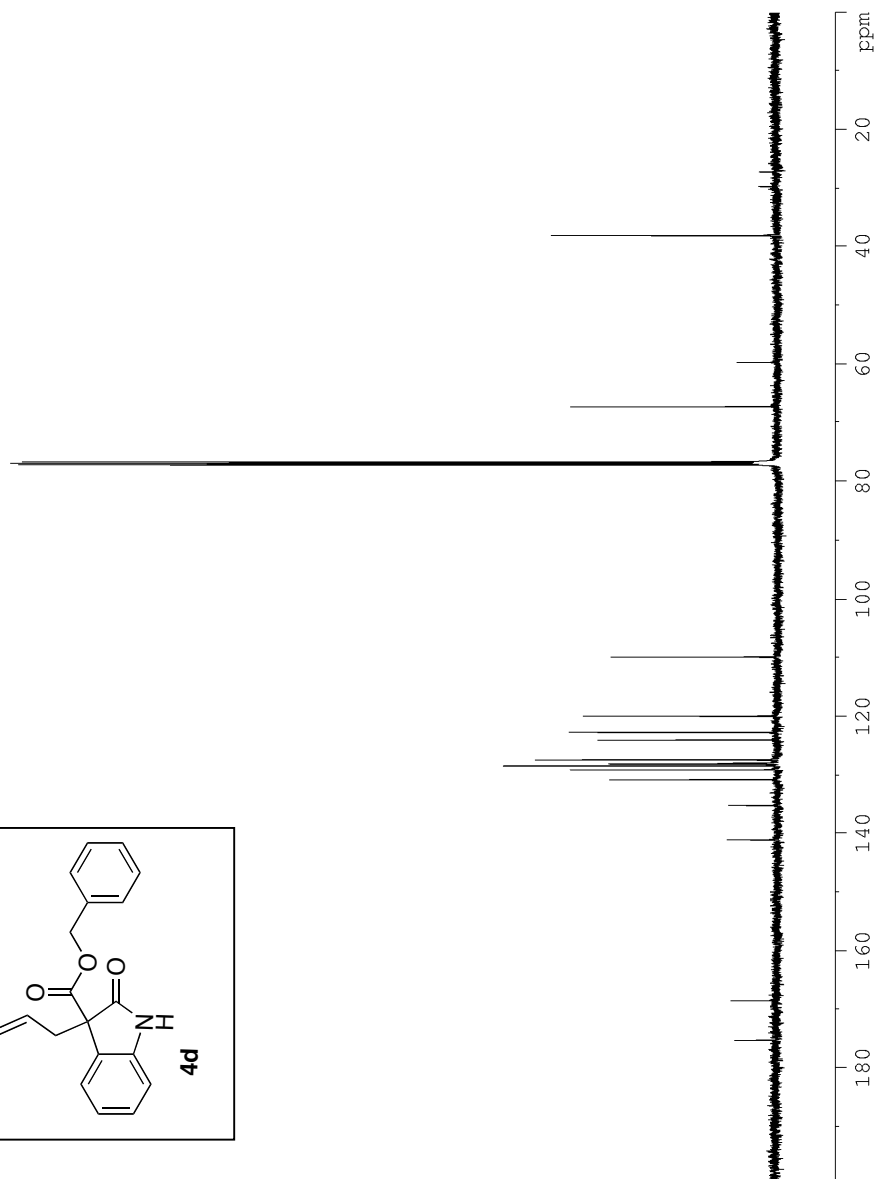
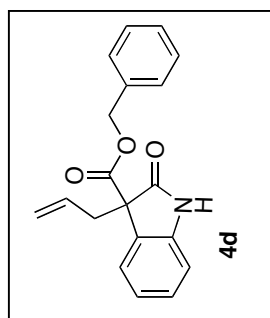
500 MHz ^1H NMR Spectrum of Compound **4c** in CDCl_3



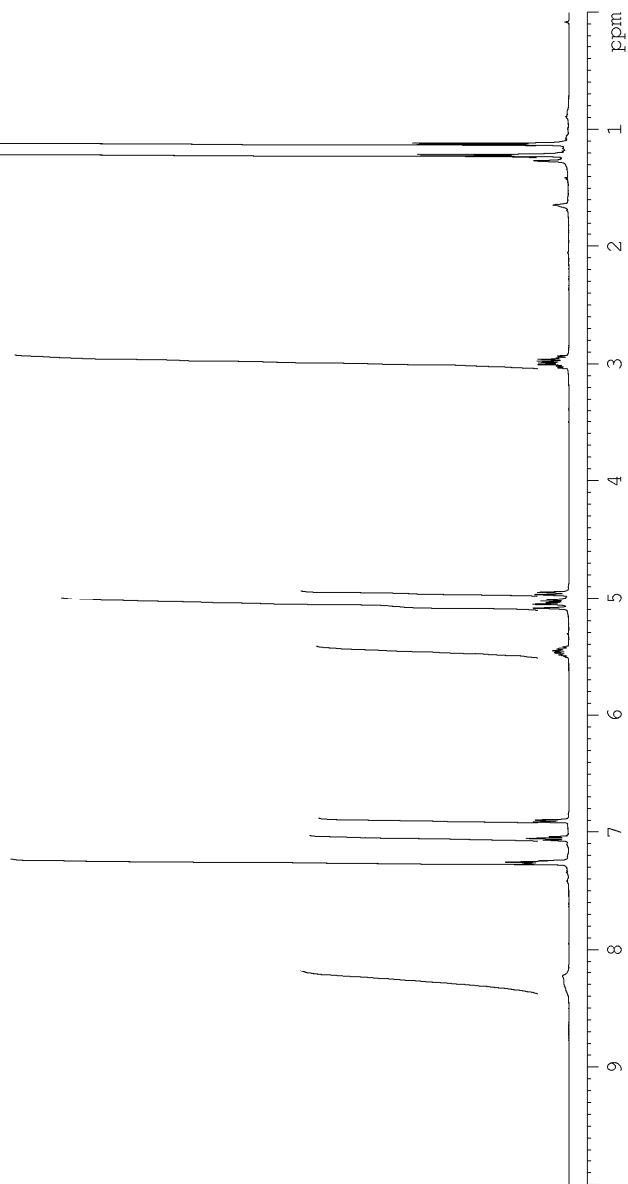
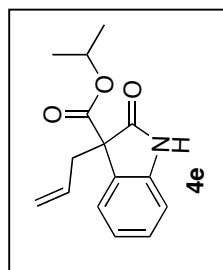
125 MHz ¹³C NMR Spectrum of Compound **4c** in CDCl₃



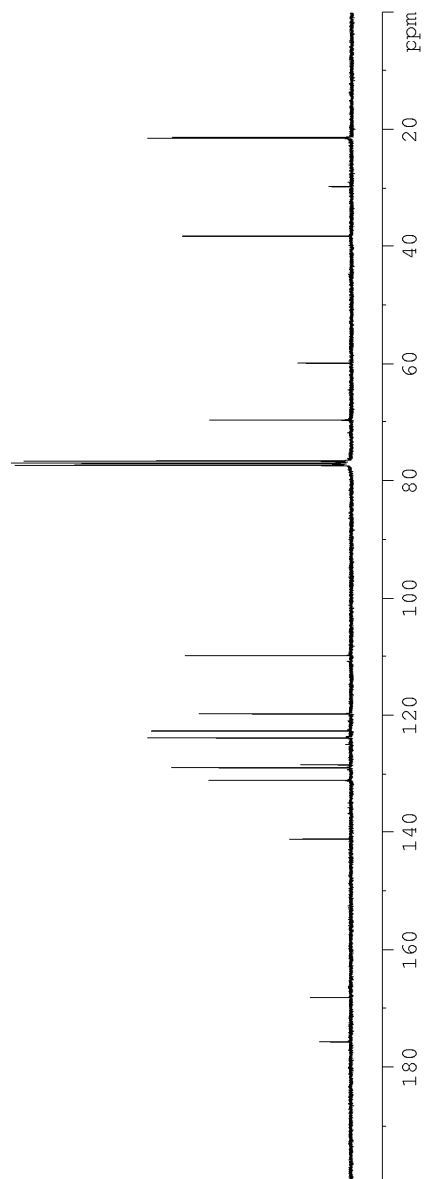
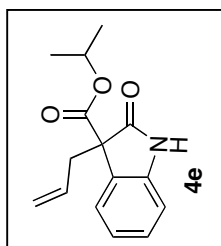
500 MHz ^1H NMR Spectrum of Compound **4d** in CDCl_3



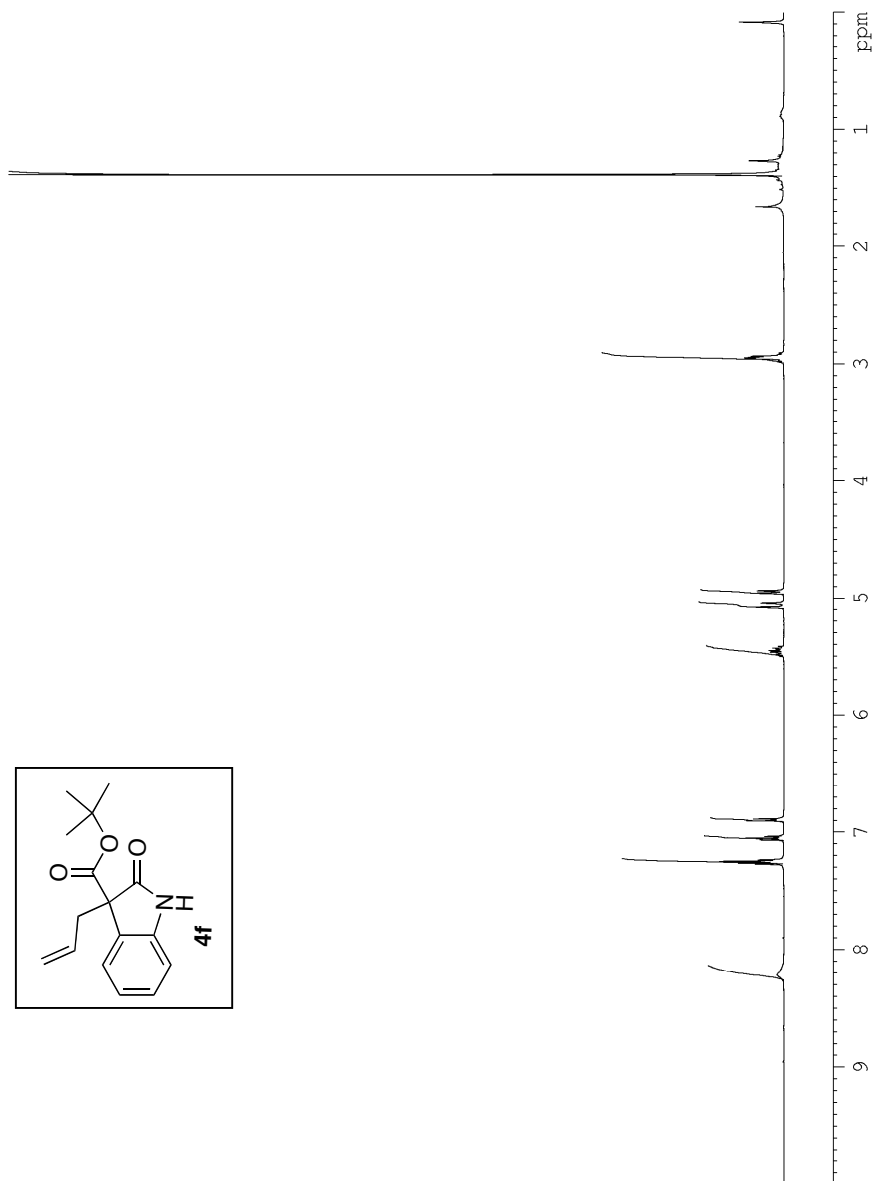
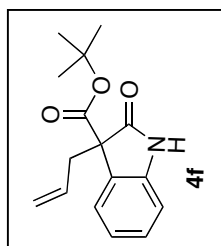
125 MHz ^{13}C NMR Spectrum of Compound **4d** in CDCl_3



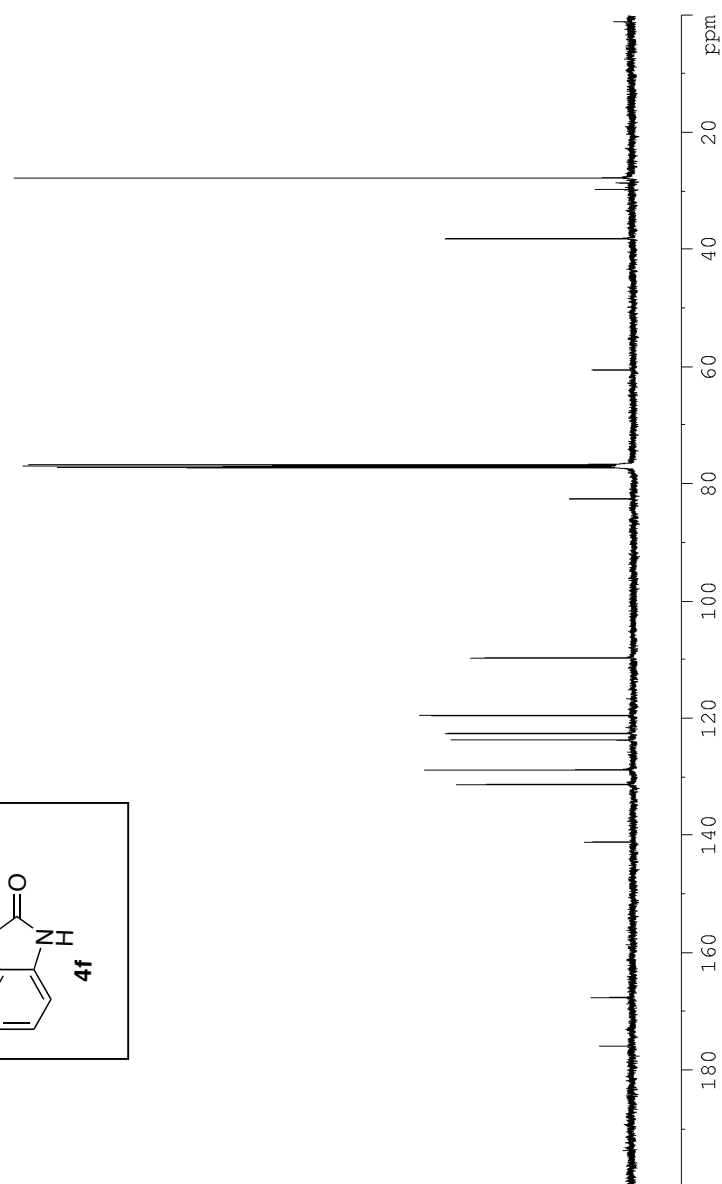
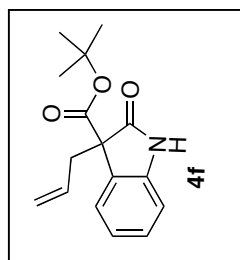
500 MHz ^1H NMR Spectrum of Compound **4e** in CDCl_3



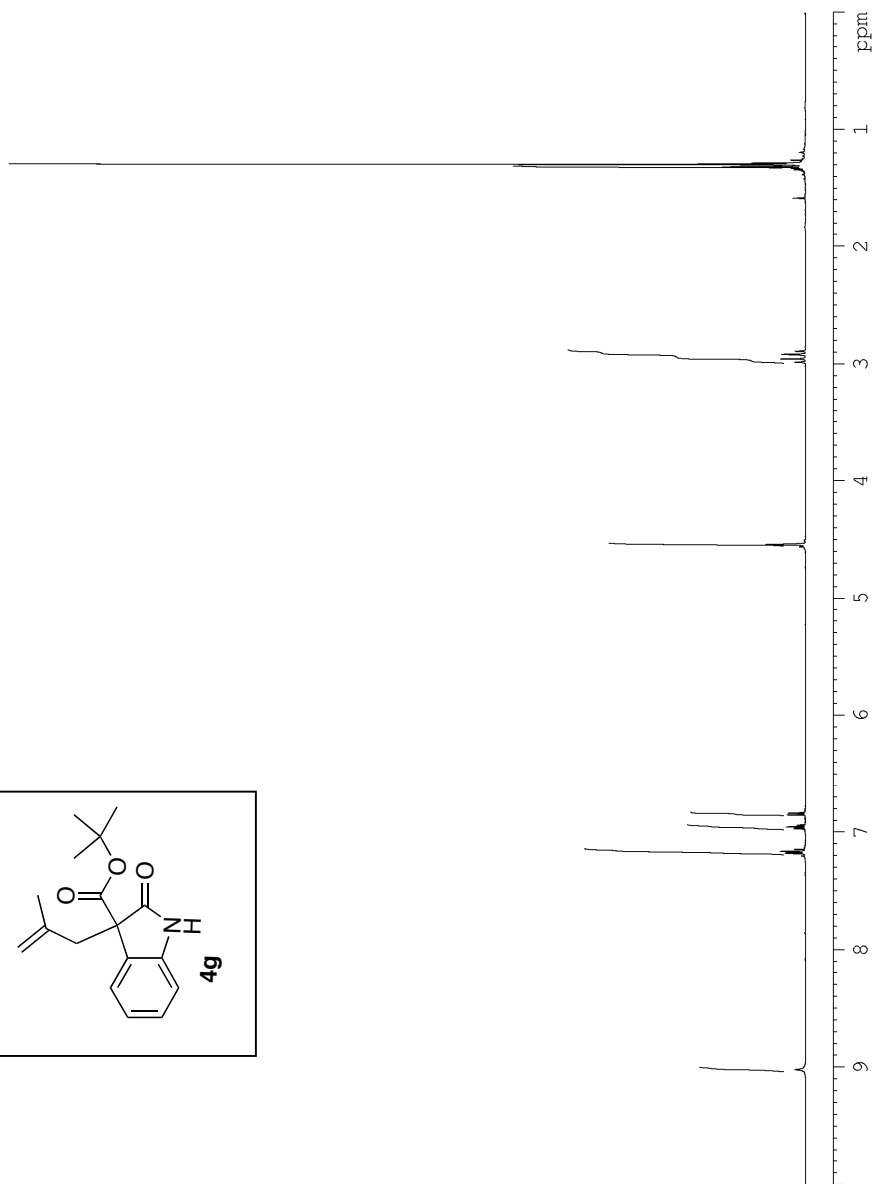
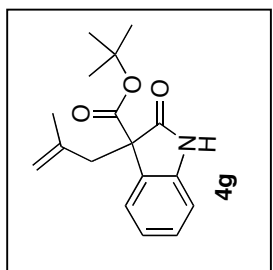
90 MHz ^{13}C NMR Spectrum of Compound **4e** in CDCl_3



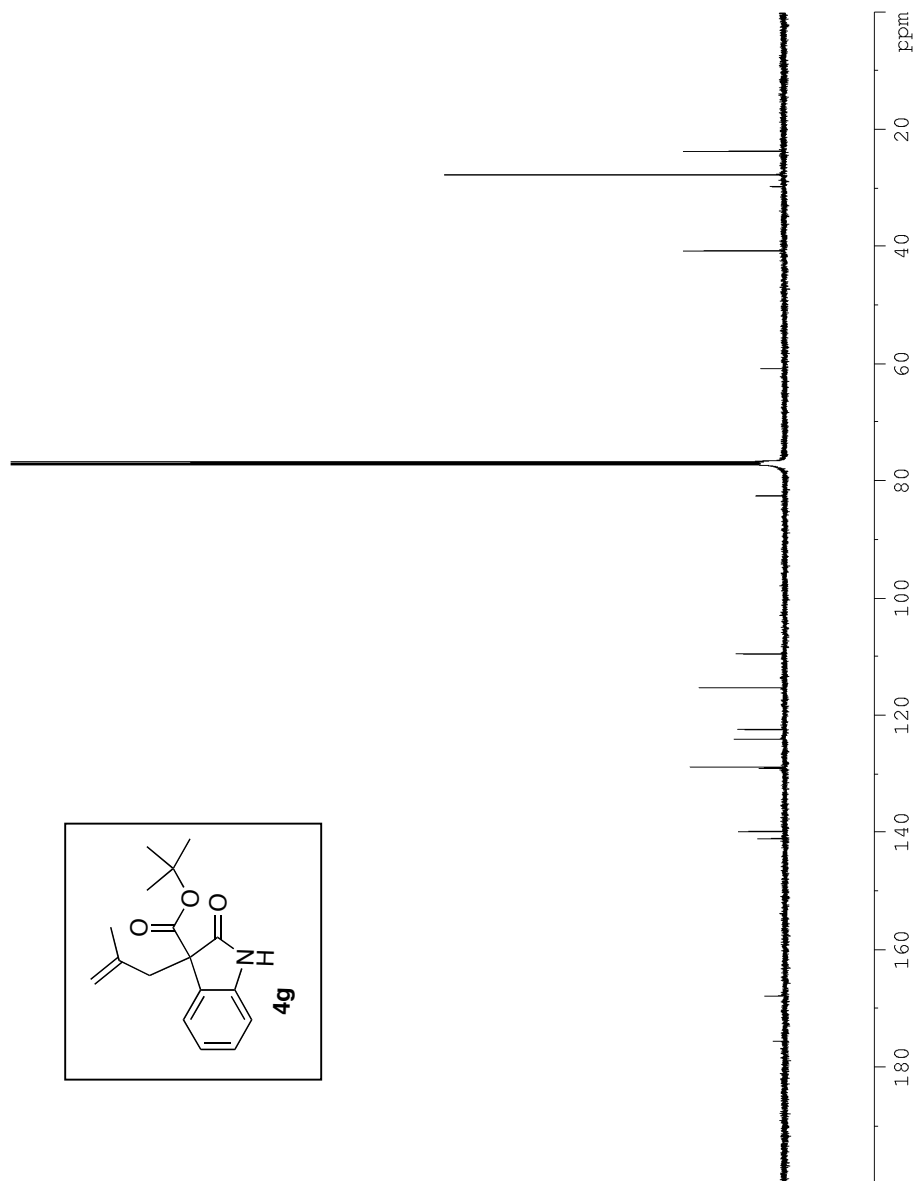
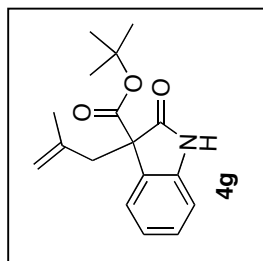
500 MHz ^1H NMR Spectrum of Compound **4f** in CDCl_3



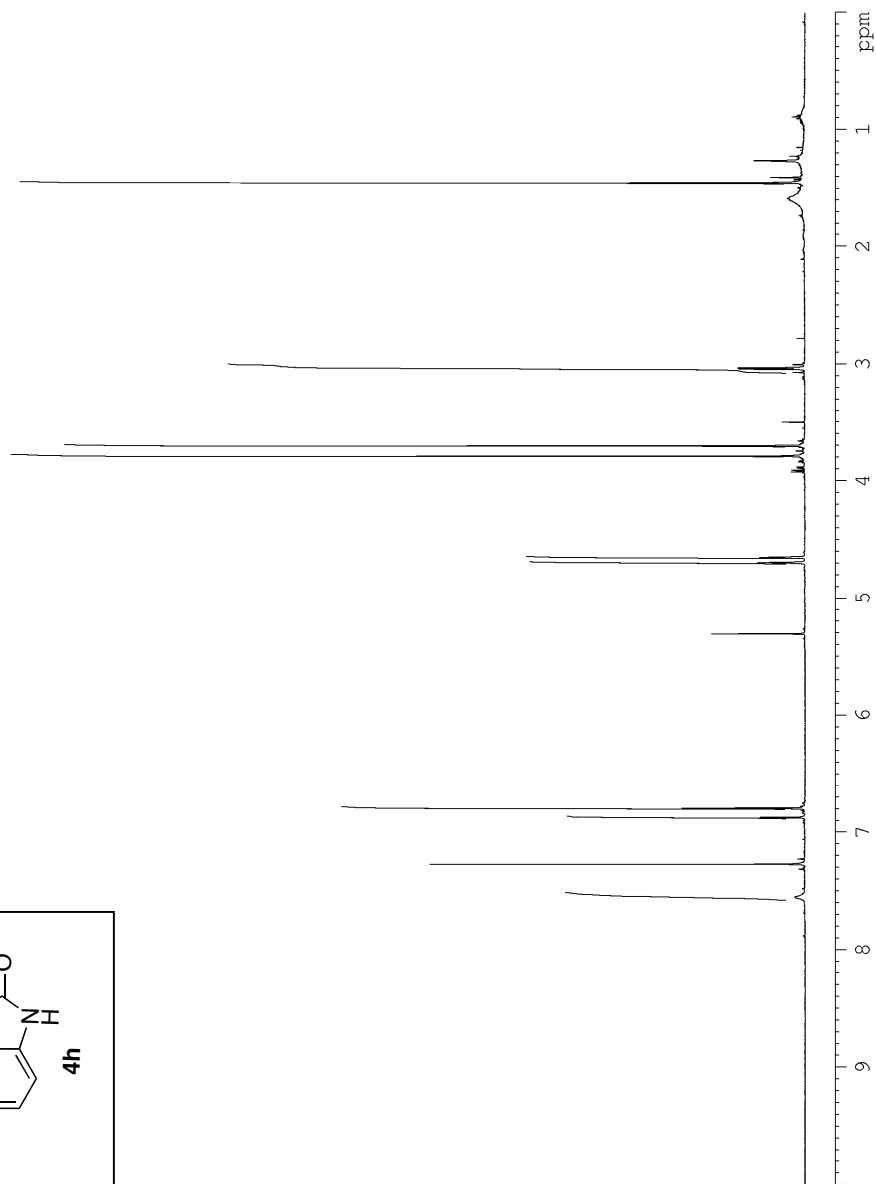
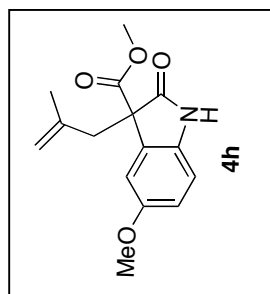
125 MHz ¹³C NMR Spectrum of Compound **4f** in CDCl₃



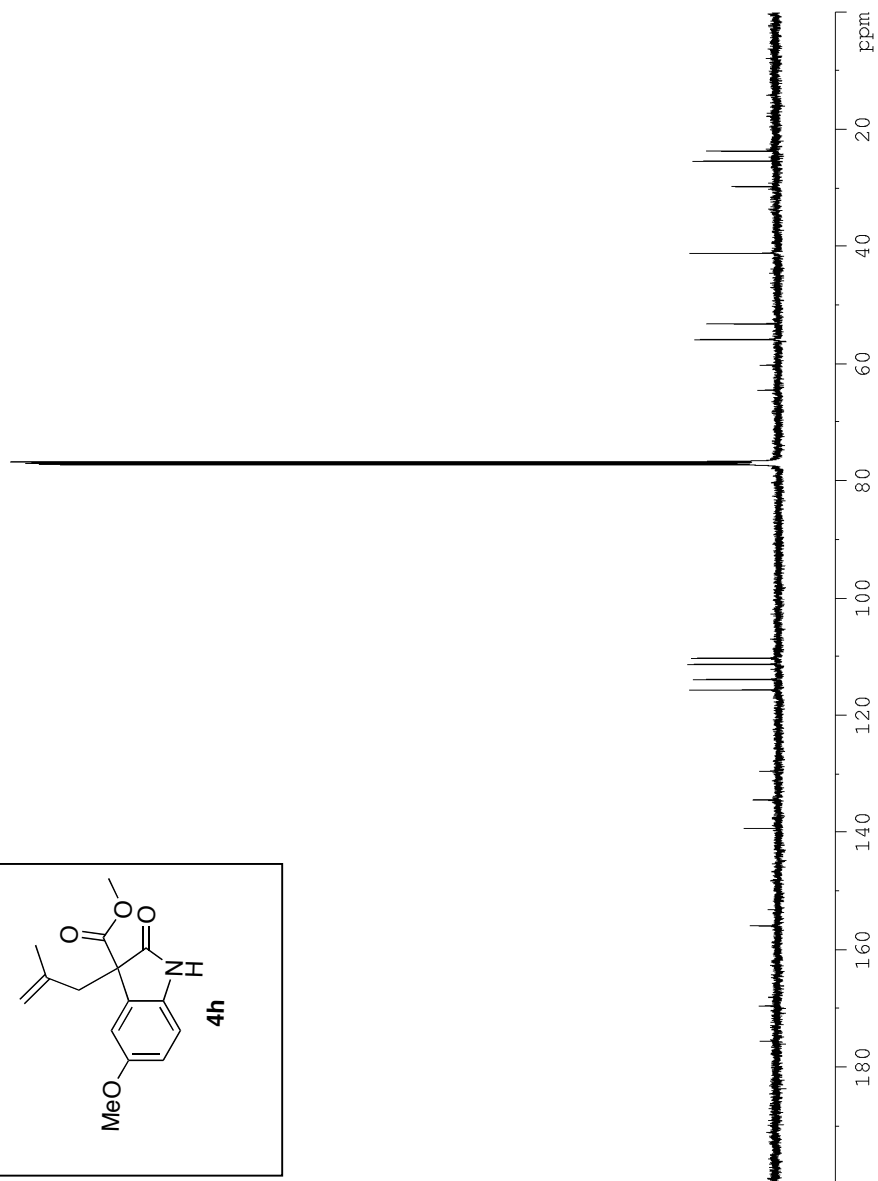
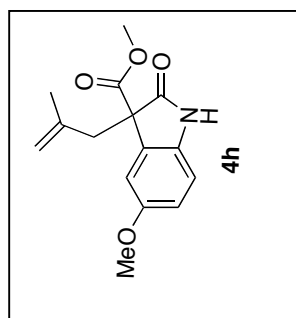
500 MHz ¹H NMR Spectrum of Compound **4g** in CDCl₃



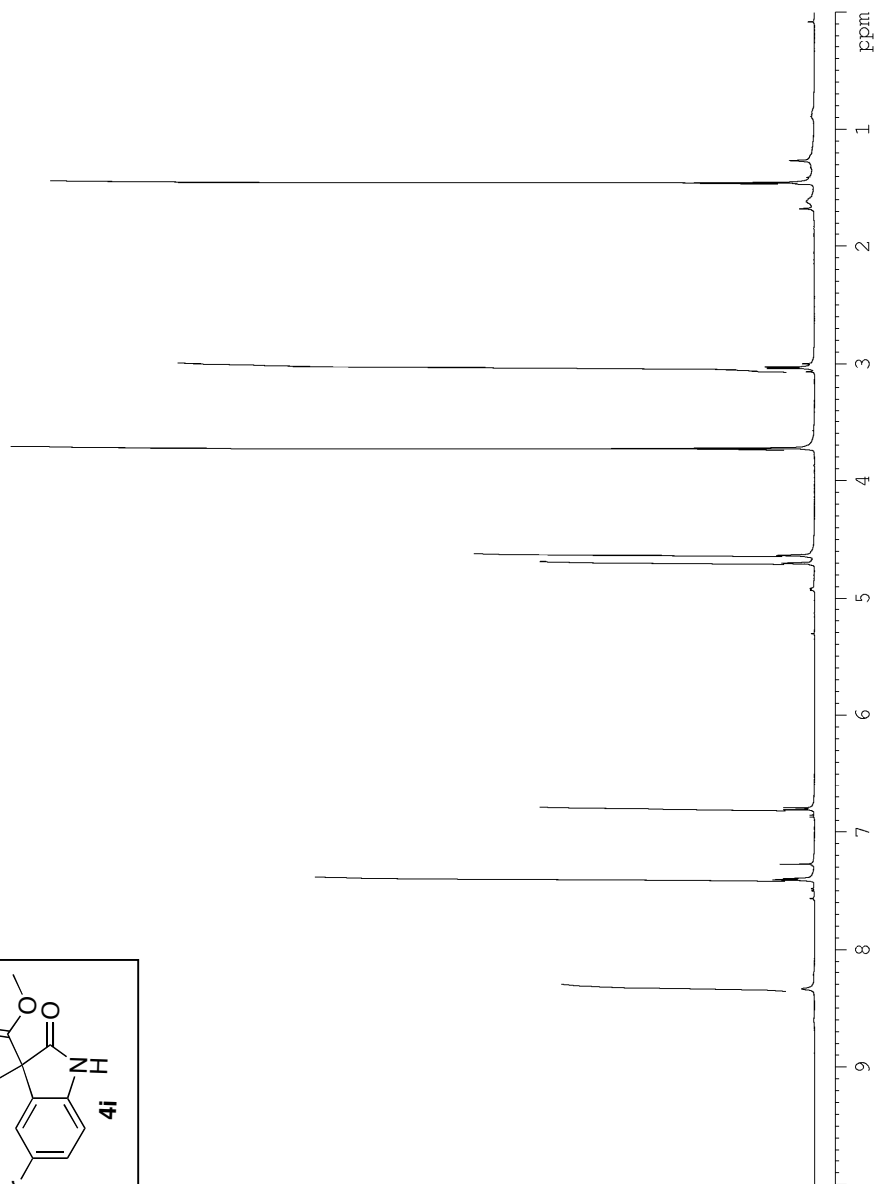
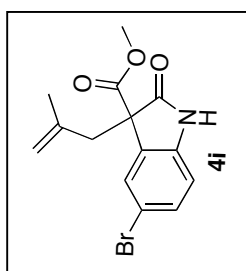
125 MHz ^{13}C NMR Spectrum of Compound **4g** in CDCl_3

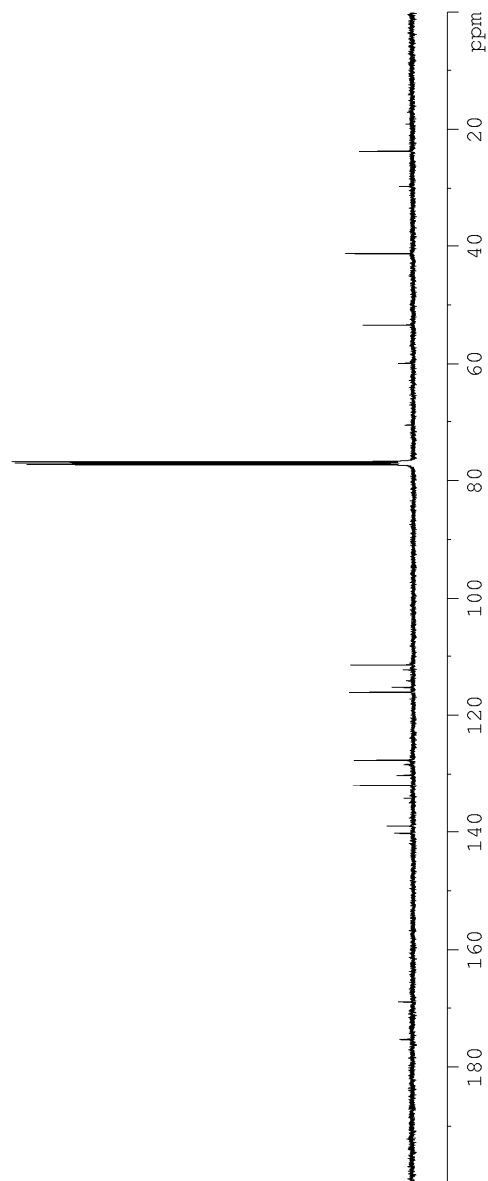
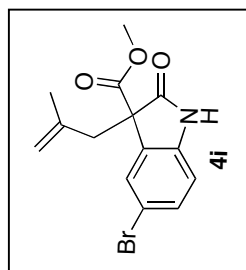


500 MHz ^1H NMR Spectrum of Compound **4h** in CDCl_3

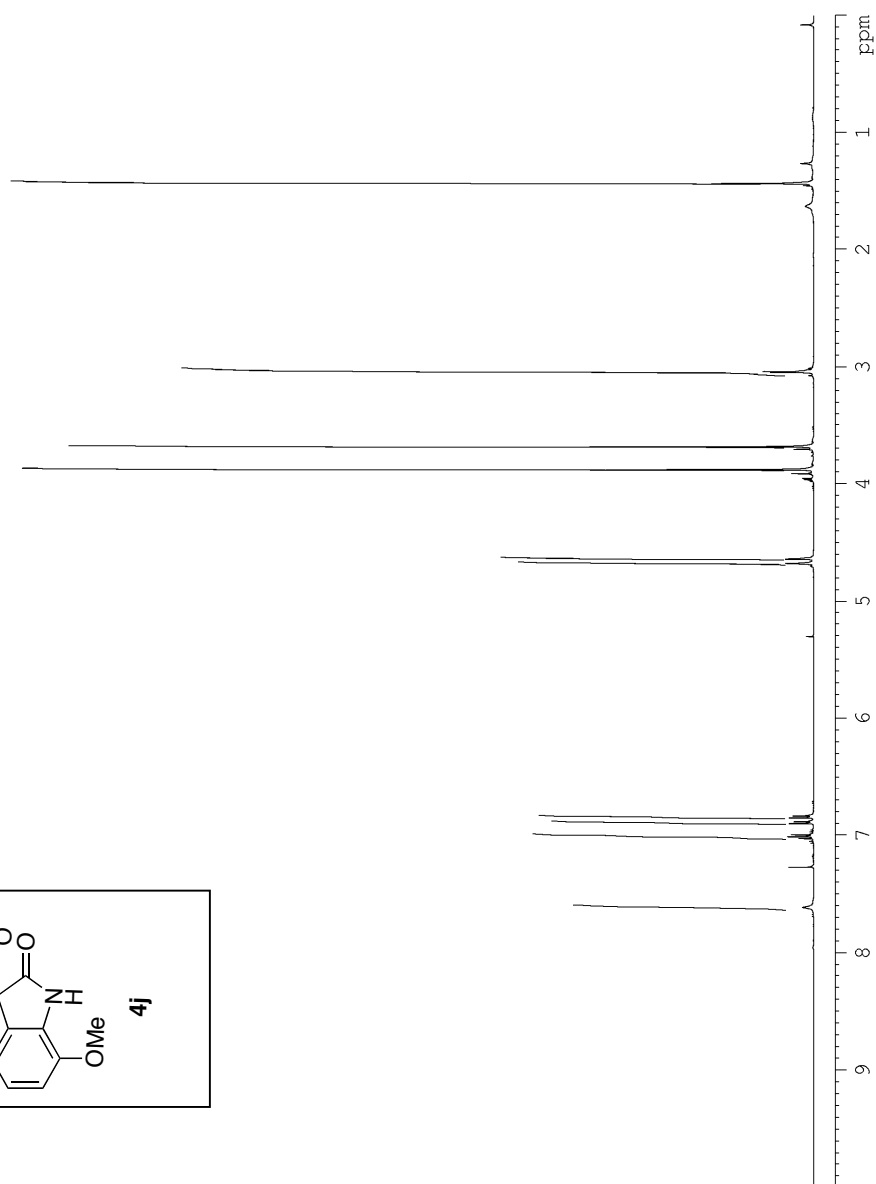
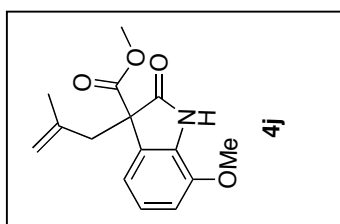


125 MHz ^{13}C NMR Spectrum of Compound **4h** in CDCl_3

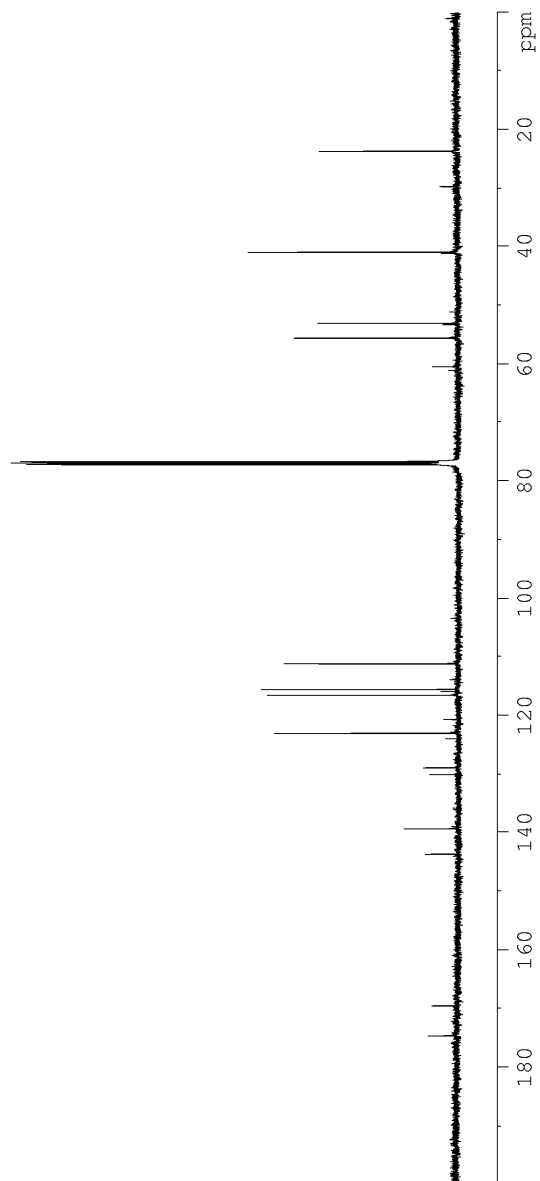
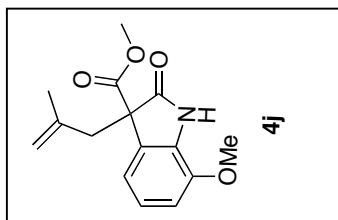




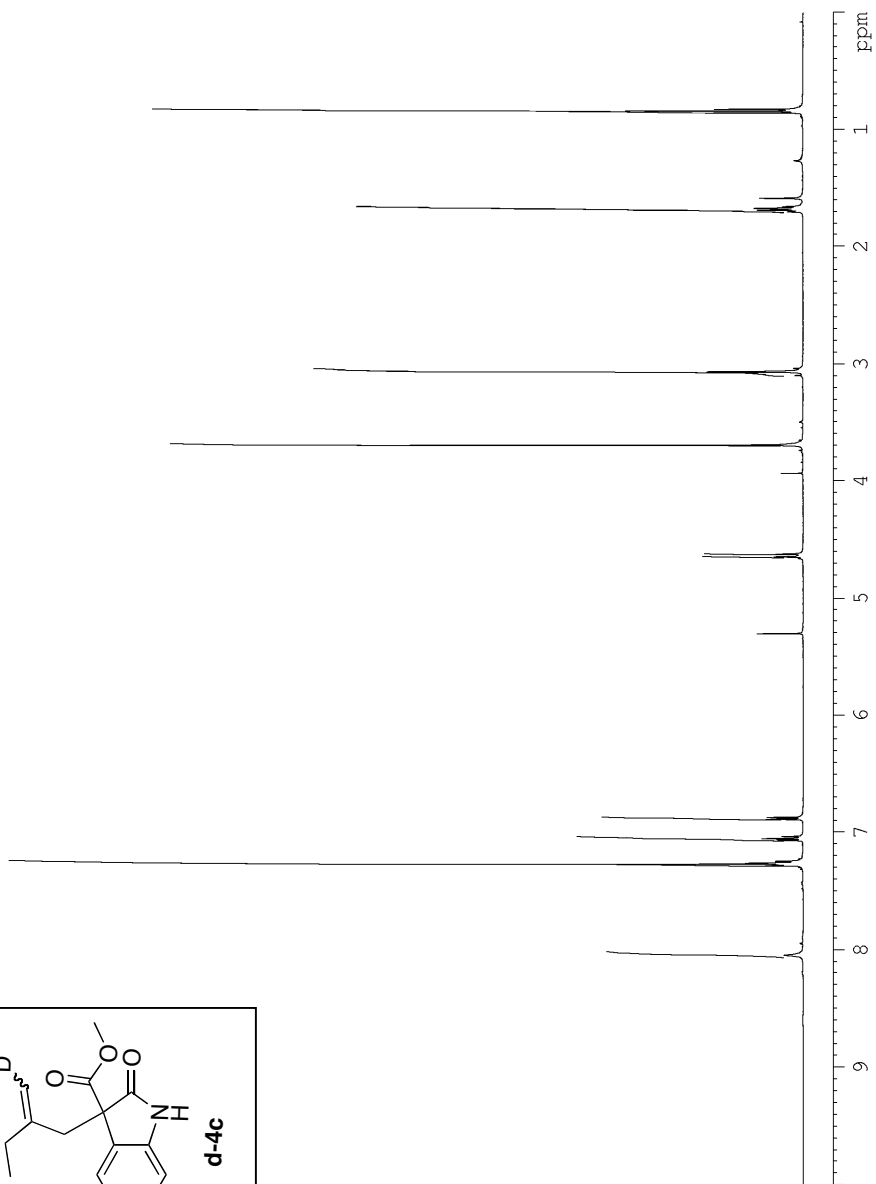
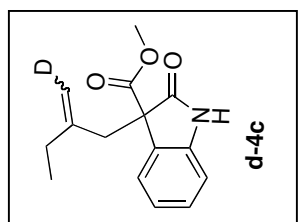
125 MHz ^{13}C NMR Spectrum of Compound **4i** in CDCl_3

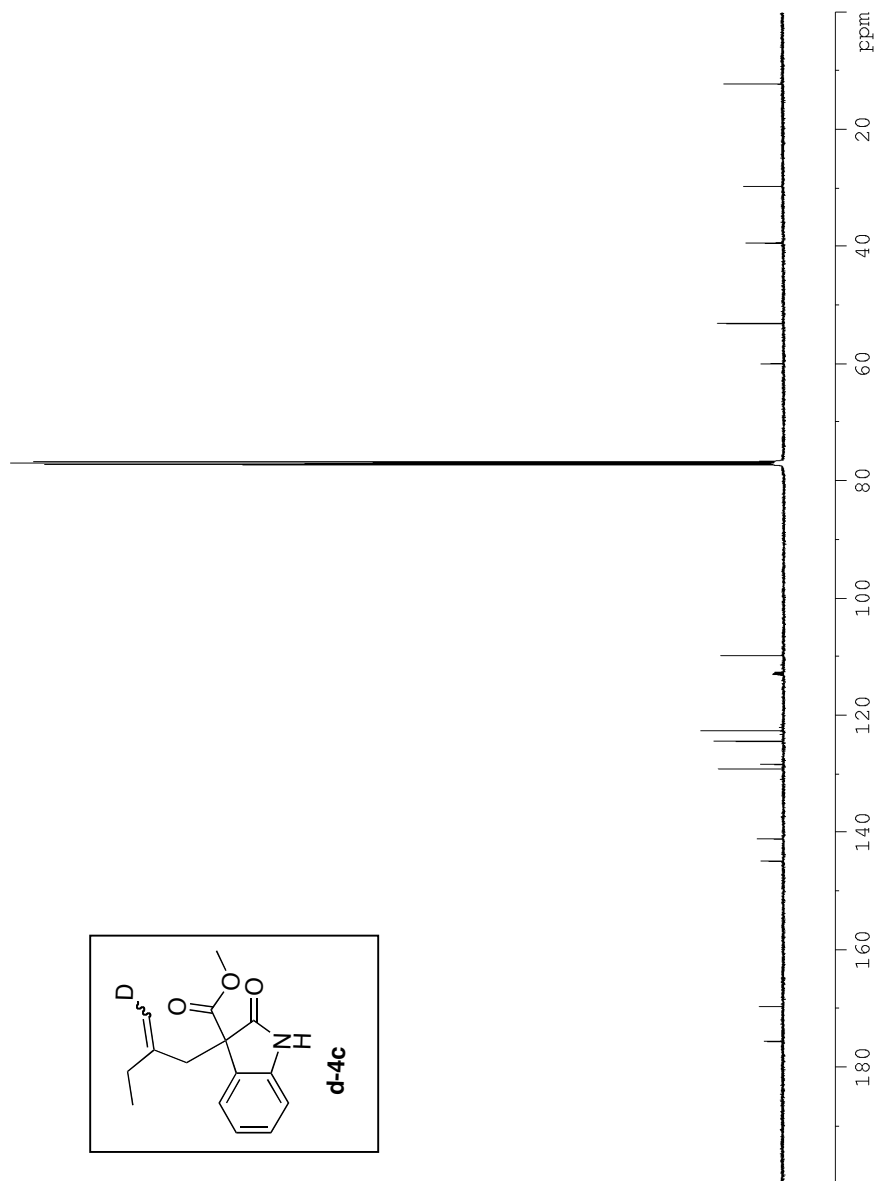
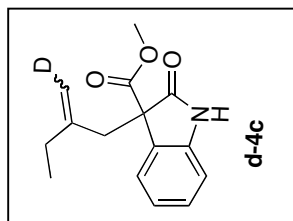


500 MHz ^1H NMR Spectrum of Compound **4j** in CDCl_3

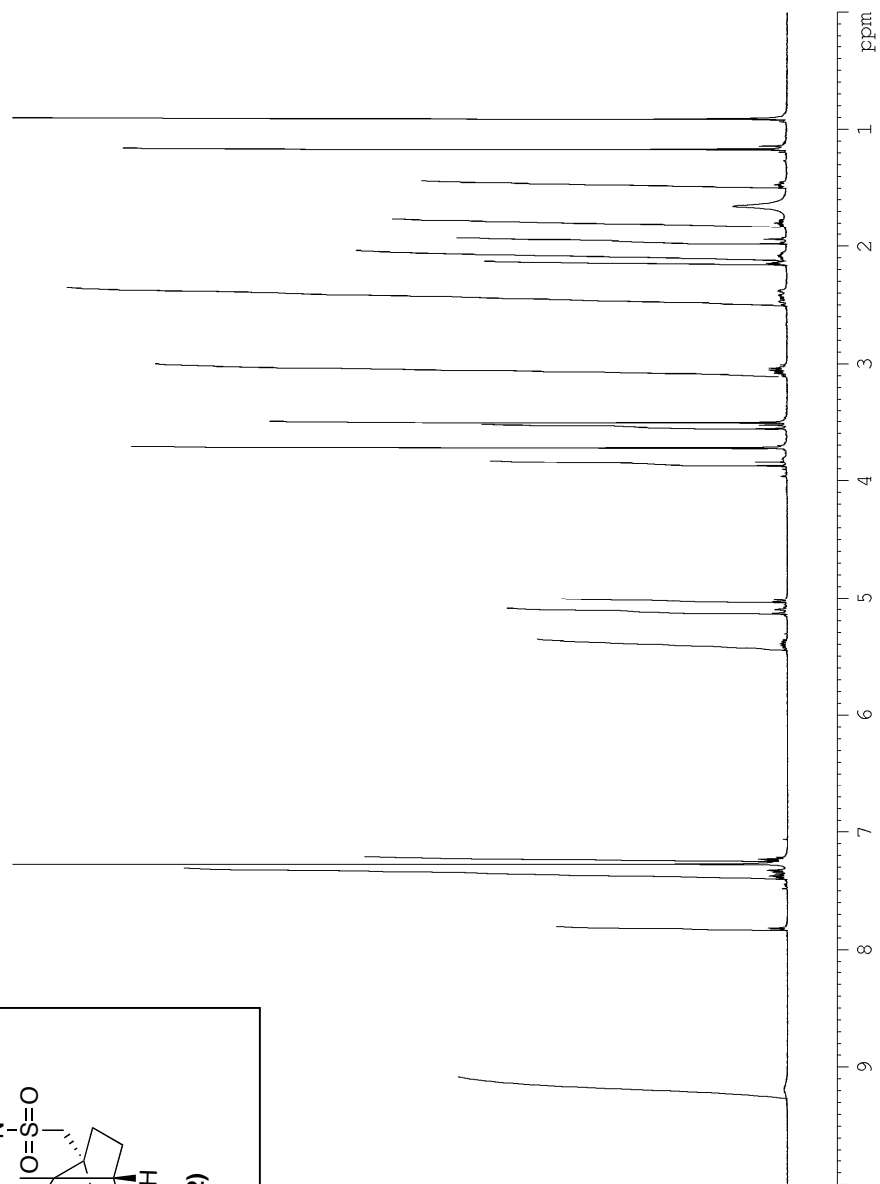
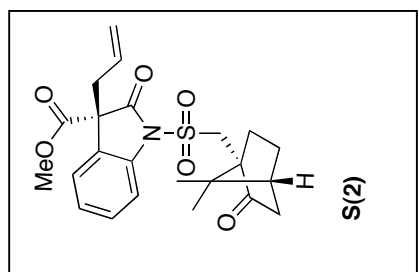


125 MHz ^{13}C NMR Spectrum of Compound **4j** in CDCl_3





125 MHz ^{13}C NMR Spectrum of Compound **d-4c** in CDCl_3



500 MHz ^1H NMR Spectrum of Compound **S2** in CDCl_3