Electronic Supplementary Information for

Gold-catalyzed synthesis of tetrahydrocarbazole derivatives through an intermolecular cycloaddition of vinyl indoles and *N*-allenyl amides

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General remarks.

All reactions were carried out under N_2 atmosphere using standard Schlenck techniques. Dichloromethane and 1,2-dichloroethane (DCE) were distilled from CaH_2 under N_2 atmosphere. Toluene and THF were distilled from Na using benzophenone as indicator under N_2 atmosphere. Solvents for column chromatography were obtained from commercial supplier and used without further purification. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator. Flash column chromatography was carried out on silica gel (230-240 mesh). ^{1}H-NMR (300, 400 MHz) and ^{13}C-NMR (75.5 and 100 MHz) spectra were recorded at room temperature in the indicated solvent on a Bruker DPX-300, or Bruker AVANCE-300 MHz and 400 MHz instruments. Chemical shifts (δ) are given in ppm relative to TMS (^{1}H, 0.0 ppm) or $CDCl_3$ (^{13}C, 77.0 ppm). Carbon multiplicities were assigned by DEPT experiments. 2D-NMR experiments were recorded on a Bruker AVANCE-400 MHz. High-resolution mass spectra were recorded in an Agilent 6520Q-TOF and a Finnigan Mat95 spectrometers. This study was carried out using vinyl indoles **1** and **7**, allenamides **2**,[1] and vinyl benzofuran **10**, which were prepared according to literature procedures as indicated below. $AuCl_3$, $[Au(PPh_3)Cl]$, $PtCl_2$ and $PtBr_2$(cod) were purchased from commercial suppliers and used as received, the rest of the gold catalysts were prepared according to literature procedures.[2]

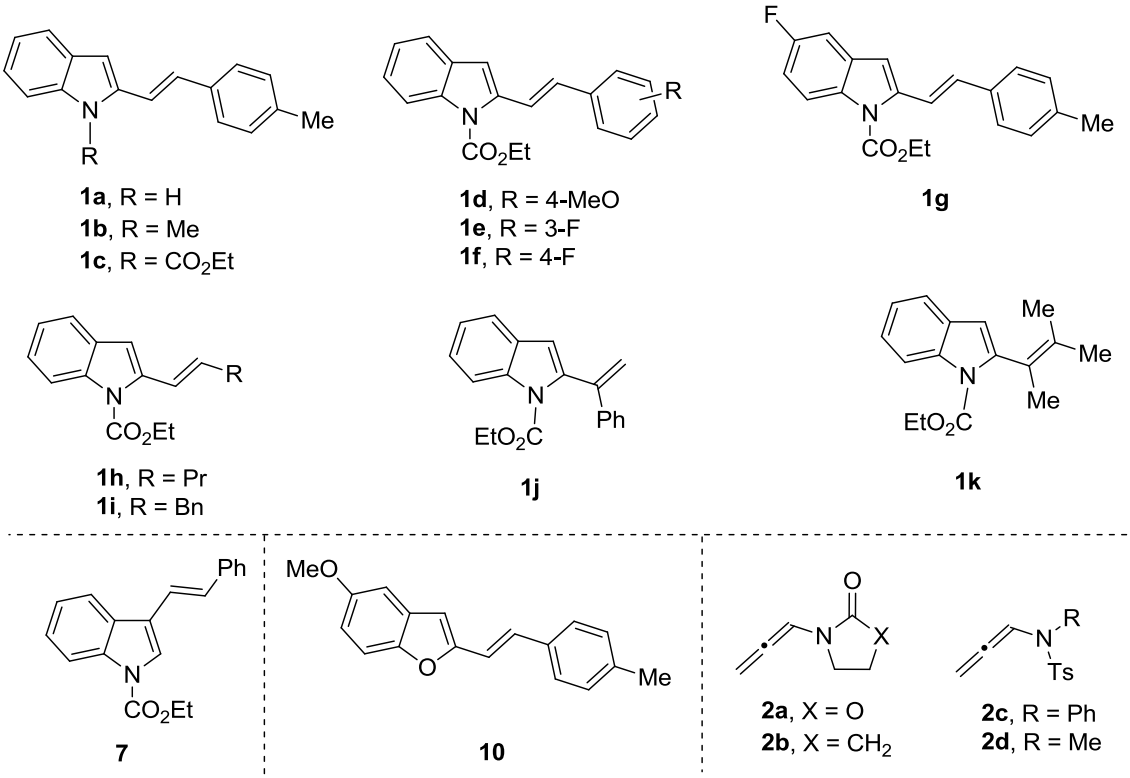
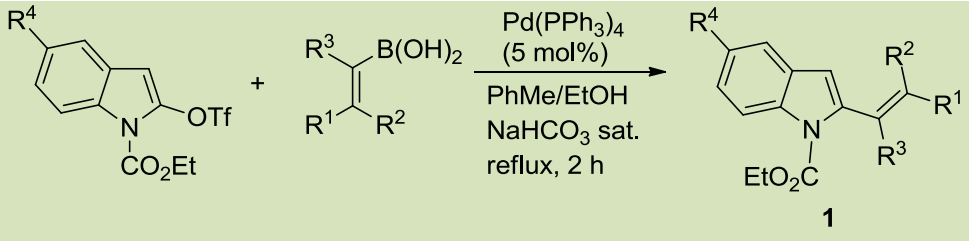


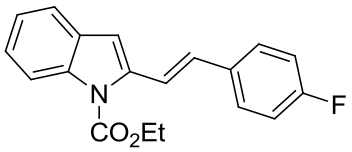
Figure S1. Starting materials used in this work.

Synthesis of starting materials.

Most of the 2-vinyl indoles used in this work were prepared according to the following previously reported procedure.[3] Only the characterization data for unreported compounds are given.



Representative procedure for the synthesis of 2-vinyl indoles 1: (*E*)-Ethyl 2-(4-fluorostyryl)-1*H*-indole-1-carboxylate (1f):



1f

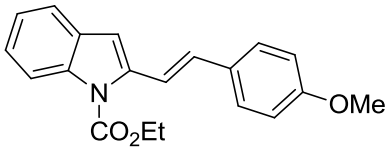
To a solution of ethyl 2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (0.5 g, 1.48 mmol) in anhydrous toluene (25 mL), $Pd(PPh_3)_4$ (86 mg, 0.074 mmol) was added. The reaction was stirred for 30 minutes at room temperature, then a solution of (*E*)-(4-fluorostyryl)boronic acid (0.37 g, 2.22 mmol) in EtOH-$NaHCO_3$ (sat.) (3:2, 25 mL) was added dropwise at room temperature. The mixture was then heated at reflux for 2 h, cooled at room temperature and washed with brine. The organic layer was dried over Na_2SO_4, filtered, and the solvent evaporated under vacuum. The crude was purified by flash chromatography (hexane/ethyl acetate 50:1) to yield **1f** (0.448 g, 98%) as a white solid (m.p. = 77.2-78.0 °C).

^{1}H-NMR (300 MHz, $CDCl_3$): 8.09 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 16.3 Hz, 1H), 7.58-7.41 (m, 3H), 7.36-7.16 (m, 2H), 7.13-6.96 (m, 3H), 6.87 (s, 1H), 4.54 (q, *J* = 7.3 Hz, 2H), 1.53 (m, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 162.7 (d, *J* = 247 Hz, C), 152.4 (C), 139.6 (C), 136.9 (C), 133.6 (d, *J* = 3.4 Hz, C), 129.9 (CH), 129.8 (C), 128.4 (d, *J* = 8 Hz, 2 x CH), 124.6 (CH), 123.5 (CH), 120.6 (CH), 120.4 (d, *J* = 2.2 Hz, CH), 116.1 (CH), 115.9 (d, *J* = 21 Hz, 2 x CH), 107.2 (CH), 63.6 (CH_2), 14.6 (CH_3).

^{19}F-NMR (282 MHz, $CDCl_3$): -114.1 (s).

HR-MS (EI): calc. for $[C_{19}H_{16}FNO_2]^+$ 309.1165, found 309.1170.



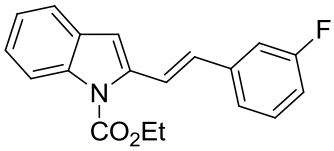
1d

(*E*)-Ethyl 2-(4-methoxystyryl)-1*H*-indole-1-carboxylate (1d): The representative procedure was followed using 2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (0.50 g, 1.48 mmol) and (*E*)-(4-methoxystyryl)boronic acid (0.40 g, 2.22 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 40:1) yielded **1d** (0.48 g 99%) as a white solid (m.p. = 110.5-111.2 °C).

^{1}H-NMR (300 MHz, $CDCl_3$): 8.13 (d, *J* = 8.15 Hz, 1H), 7.65 (d, *J* = 16.2 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.29-7.21 (m, 2H), 7.03 (d, *J* = 16.2 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.86 (s, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.55 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 159.5 (C), 152.2 (C), 139.9 (C), 136.7 (C), 130.6 (CH), 130.0 (C), 129.7 (C), 128.0 (2 x CH), 124.1 (CH), 123.2 (CH), 120.3 (CH), 118.2 (CH), 115.8 (CH), 114.2 (2 x CH), 106.4 (CH), 63.5 (CH_2), 55.3 (CH_3), 14.4 (CH_3).

HR-MS (EI): calc. for $[C_{20}H_{19}NO_3]^+$ 321.1365, found 321.1367.



1e

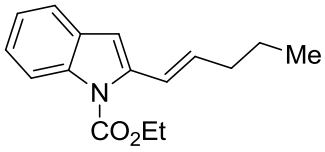
(*E*)-Ethyl 2-(3-fluorostyryl)-1*H*-indole-1-carboxylate (1e): The representative procedure was followed using 2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (0.50 g, 1.48 mmol) and (*E*)-(3-fluorostyryl)boronic acid (0.37 g, 2.22 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 50:1) yielded **1e** (0.434 g 95%) as a yellow solid (m.p. = 64.1-64.5 °C).

^{1}H-NMR (300 MHz, $CDCl_3$): 8.14 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 16.2 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.38-7.22 (m, 5H), 7.07-6.95 (m, 2H), 6.91 (s, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.54 (t, *J* = 7.07 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 163.2 (d, *J* = 245 Hz, C), 152.1 (C), 139.5 (d, *J* = 7.7 Hz, C), 139.0 (C), 136.8 (C), 130.1 (d, *J* = 8.4 Hz, CH), 129.6 (C), 129.5 (CH), 124.6 (CH), 123.4 (CH), 122.6 (CH), 121.7 (CH), 120.5 (CH), 115.9 (CH), 114.7 (d, *J* = 21 Hz, CH), 112.9 (d, *J* = 22 Hz, CH), 107.5 (CH), 63.4 (CH_2), 14.4 (CH_3).

^{19}F-NMR (282 MHz, $CDCl_3$): δ = -113.4 (s).

HR-MS (EI) calc. for $[C_{19}H_{16}FNO_2]^+$ 309.1165, found 309.1168.



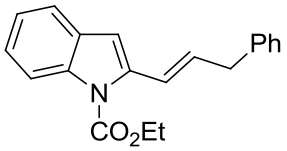
1h

(*E*)-Ethyl 2-(pent-1-en-1-yl)-1*H*-indole-1-carboxylate (1h): The representative procedure was followed using 2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (0.50 g, 1.48 mmol) and (*E*)-1-penten-1-ylboronic acid (0.25 g, 2.22 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 50:1) yielded **1h** (0.397 g, 99%) as a clear oil.

^{1}H-NMR (300 MHz, $CDCl_3$): 8.11 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.30-7.18 (m, 2H), 6.97 (d, *J* = 15.7 Hz, 1H), 6.67 (s, 1H), 6.22 (dt, *J* = 15.6, 7.1 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 2.25 (q, *J* = 7.1 Hz, 2H), 1.54 (m, 5H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 152.1 (C), 139.9 (C), 136.4 (C), 134.0 (CH), 129.6 (C), 123.8 (CH), 123.1 (CH), 122.1 (CH), 120.1 (CH), 115.7 (CH), 106.4 (CH), 63.1 (CH_2), 35.1 (CH_2), 22.3 (CH_2), 14.4 (CH_3), 13.75 (CH_3).

HR-MS (EI) calc. for $[C_{16}H_{19}NO_2]^+$ 257.1416, found 257.1420.

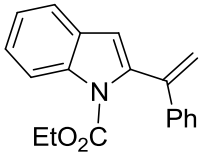


1i

(*E*)-Ethyl 2-(3-phenylprop-1-en-1-yl)-1*H*-indole-1-carboxylate (1i): The representative procedure was followed using 2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (0.50 g, 1.48 mmol) and (*E*)-3-phenyl-1-propen-1-ylboronic acid (0.36 g, 2.22 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 40:1) yielded **1i** (0.248 g, 55%) as a clear oil.

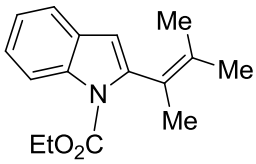
^{1}H-NMR (300 MHz, $CDCl_3$): 8.12 (m, 1H), 7.49 (m, 1H), 7.40-7.19 (m, 7H), 7.04 (dd, *J* = 15.6, 1.6 Hz, 1H), 6.70 (s, 1H), 6.36 (dt, *J* = 15.6, 6.9 Hz, 1H), 4.52 (q, *J* = 7.1 Hz, 2H), 3.62 (dd, *J* = 6.9, 1.6 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 152.1 (C), 139.8 (C), 139.3 (C), 136.5 (C), 132.0 (CH), 129.5 (C), 128.8 (2 x CH), 128.6 (2 x CH), 126.3 (CH), 124.0 (CH), 123.2 (CH), 123.1 (CH), 120.2 (CH), 115.7 (CH), 106.9 (CH), 63.12 (CH_2), 39.5 (CH_2), 14.2 (CH_3).
HR-MS (EI) calc. for $[C_{20}H_{19}NO_2]^+$ 305.1416, found 305.1417.



1j

Ethyl 2-(1-phenylvinyl)-1*H*-indole-1-carboxylate (1j): The representative procedure was followed using 2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (0.50 g, 1.48 mmol) and 1-phenylvinylboronic acid (0.33 g, 2.22 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 50:1) yielded **1j** (0.434 g, 99%) as a clear oil.
^{1}H-NMR (300 MHz, $CDCl_3$): 8.21 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.36 (m, 1H), 7.32-7.24 (m, 6H), 6.74 (s, 1H), 5.72 (d, *J* = 1.2 Hz, 1H), 5.53 (d, *J* = 1.2 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 1.08 (t, *J* = 7.1 Hz, 3H).
^{13}C-NMR (75 MHz, $CDCl_3$): 151.0 (C), 142.9 (C), 140.1 (C), 139.7 (C), 137.1 (C), 129.1 (C), 128.4 (2 x CH), 127.7 (CH), 125.9 (2 x CH), 124.6 (CH), 123.1 (CH), 120.6 (CH), 115.6 (CH), 115.3 (CH_2), 111.8 (CH), 62.9 (CH_2), 13.7 (CH_3).
HR-MS (EI) calc. for $[C_{19}H_{17}NO_2]^+$ 291.1259, found 291.1561.



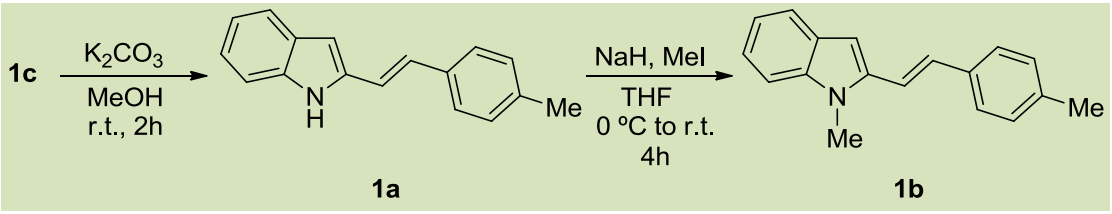
1k

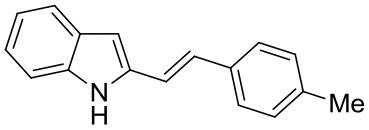
Ethyl 2-(3-methylbut-2-en-2-yl)-1*H*-indole-1-carboxylate (1k): The representative procedure was followed using 2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (0.50 g, 1.48 mmol) and 3-methyl-2-buten-2-ylboronic acid (0.25 g, 2.22 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 50:1) yielded **1k** (0.321 g, 84%) as a clear oil.
^{1}H-NMR (300 MHz, $CDCl_3$): 8.19 (d, *J* = 8.7 Hz, 1H), 7.51 (m, 1H), 7.34-7.18 (m, 2H), 6.29 (s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.93 (s, 3H), 1.84 (s, 3H), 1.66 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 151.9 (C), 142.8 (C), 136.6 (C), 131.3 (C), 130.1 (C), 124.0 (CH), 123.2 (CH), 120.5 (CH), 115.9 (CH), 108.5 (CH), 63.1 (CH_2), 22.7 (CH_3), 20.4 (2 x CH_3), 14.6 (CH_3) (a signal corresponding to a C carbon is missing).

HR-MS (EI) calc. for $[C_{16}H_{19}NO_2]^+$ 257.1416, found 257.1418.

Synthesis of vinyl indoles 1a-b.





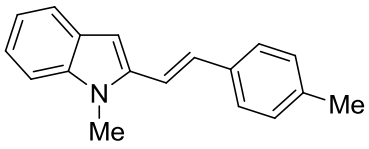
1a

(*E*)-2-(4-Methylstyryl)-1*H*-indole (1a): To a solution of (*E*)-ethyl 2-(4-methylstyryl)-1*H*-indole-1-carboxylate (**1c**) (0.50 g, 1.64 mmol) in dry methanol (16 mL), K_2CO_3 (0.23 g, 1.64 mmol) was added and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the crude taken up with water/ethyl acetate (15 mL each). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to yield **1a** (0.386 g, 99%) as a yellow solid (m.p. = 216.8-218.2 °C).

^{1}H-NMR (300 MHz, $CDCl_3$): 8.22 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.45-7.03 (m, 8H), 6.88 (d, *J* = 16.5 Hz, 1H), 6.59 (s, 1H), 2.37 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 138.0 (C), 137.1 (C), 136.8 (C), 134.3 (C), 129.7 (2 x CH), 129.6 (C), 127.4 (CH), 126.5 (2 x CH), 123.0 (CH), 120.8 (CH), 120.4 (CH), 118.3 (CH), 110.8 (CH), 103.7 (CH), 21.5 (CH_3).

HR-MS (EI) calc. for $[C_{17}H_{15}N]^+$ 233.1204, found 233.1206.



1b

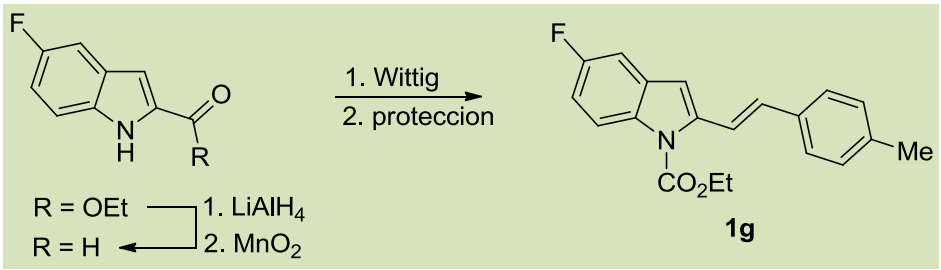
(*E*)-1-Methyl-2-(4-methylstyryl)-1*H*-indole (1b): To a suspension of NaH (27.1 mg, 1.13 mmol, 60% in mineral oil) in DMF (5 mL), (*E*)-2-(4-methylstyryl)-1*H*-indole (**1a**) (0.240 g, 1.03 mmol) was added at 0 °C and stirred for 30 minutes, then CH_3I (0.071 mL, 1.13 mmol) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 4 h. After that time water (5 mL) was added slowly and the aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with water (20 mL) and with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under vaccum. After column chromatography (SiO_2, hexane/EtOAc 40:1), **1b** (0.238 g, 93%) was obtained as a yellow solid (m.p. = 147.2-148.9 °C).

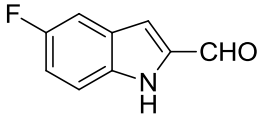
^{1}H-NMR (300 MHz, $CDCl_3$): 7.59 (m, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.34-7.02 (m, 7 H), 6.79 (s, 1H), 3.80 (s, 3H), 2.38 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 138.9 (C), 138.3 (C), 138.1 (C), 134.6 (C), 131.2 (CH), 129.7 (2 x CH), 128.3 (C), 126.6 (2 x CH), 121.8 (CH), 120.6 (CH), 120.1 (CH), 116.3 (CH), 109.3 (CH), 98.9 (CH), 30.1 (CH_3), 21.5 (CH_3).

HR-MS (EI) calc. for $[C_{18}H_{17}N]^+$ 247.1361, found: 247.1366.

Synthesis of 5-fluoro-2-vinyl indole 1g.





5-Fluoro-1*H*-indole-2-carbaldehyde: To a solution of ethyl 5-fluoro-1*H*-indole-2-carboxylate (0.925 g, 4.46 mmol) in THF (10 mL), $LiAlH_4$ (0.254 g, 6.70 mmol) was added slowly at 0 °C. After 1 h at room temperature the reaction was quenched by the

addition of H_2O (2 mL) and NH_3 (15% aq. sol., 1 mL). The resulting mixture was filtered through celite and the water layer was extracted with Et_2O (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum to yield (5-fluoro-1*H*-indol-2-yl)methanol (727 mg, 99%), which was used directly for the next step without further purification as judged enough clean by ^{1}H-NMR analysis.

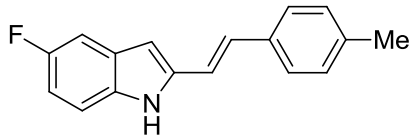
To a solution of (5-fluoro-1*H*-indol-2-yl)methanol (0.727 g, 4.4 mmol) in CH_2Cl_2 was added MnO_2 (1.9 g, 22 mol) and the resulting suspension was stirred vigorously at room temperature for 24 h. The mixture was filtered through celite and the solvent removed under vacuum. Purification by column chromatography (SiO_2, Hexane:EtOAc 5:1) yielded the corresponding aldehyde (0.46 g, 64%) as a yellow solid (m.p = 169.4-170.0 °C).

^{1}H-NMR (300 MHz, $CDCl_3$): 9.88 (s, 1H), 9.35 (s, 1H), 7.48-7.37 (m, 2H), 7.27 (m, 1H), 7.19 (td, *J* = 9.0, 2.5 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$ + DMSO): 187.0 (CH), 162.6 (d, *J* = 240 Hz, C), 142.2 (C), 140.0 (C), 131.83 (d, *J* = 11.6 Hz, C), 120.7 (d, *J* = 27.2 Hz, CH), 118.8 (CH), 118.7 (d, *J* = 3.1 Hz, CH), 111.7 (d, *J* = 21.5 Hz, CH).

^{19}F-NMR (282 MHz, $CDCl_3$): -122.0 (s).

HR-MS (EI) calc. for $[C_9H_6FNO]^+$ 163.0433, found 163.0436.



5-Fluoro-2-(4-methylstyryl)-1*H*-indole: NaH (145 mg, 95% in mineral oil, 5.75 mmol) was added to a suspension of *p*-tolyltriphenylphosphonium bromide (2.47 g, 5.52 mmol) in toluene (20 mL) at 0 °C. The solution was stirred for 30 min at room temperature, followed by the addition of 5-fluoro-1*H*-indole-2-carbaldehyde (0.75 g, 4.6 mmol). The mixture was heated at 80 °C for 2 h and quenched by saturated solution of NH_4Cl. The water phase was extracted with AcOEt (3 x 10 mL), the combined organic layers were dried over Na_2SO_4, filtered and concentrated under vaccum. The crude product was purified by column chromatography (SiO_2, Hexane:AcOEt 20:1 to 5:1) to yield *E*-isomer (0.51 g, 44%) as a yellow solid, (m.p. = 240.3-241.0 °C, dec.) and *Z*-isomer (0.57 g, 49%) as a thick yellow oil.

***E* isomer:**

^{1}H-NMR (300 MHz, acetone-D_6): 10.59 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.36 (dd, *J*= 8.8, 4.5 Hz, 1H), 7.26-7.17 (m, 5H), 6.91 (td, *J* = 9.2, 2.5 Hz, 1H), 6.61 (s, 1H), 2.34 (s, 3H).

^{13}C-NMR (75 MHz, acetone-D_6): 157.8 (d, *J* = 233 Hz, C), 138.9 (d, *J* = 10.2 Hz, C), 137.5 (C), 134.4 (C), 134.1 (d, *J* = 10.2 Hz, C), 129.4 (2 x CH), 128.0 (CH), 126.3 (2 x CH), 118.1 (CH), 111.5 (d, *J* = 10.5 Hz, CH), 110.0 (d, *J* = 26.2 Hz, CH), 104.5 (d, *J* = 24.1 Hz, CH), 102.7 (d, *J* = 4.4 Hz, CH), 20.4 (CH_3) (one C signal is missing).

^{19}F-NMR (282 MHz, acetone-D_6): -126.4 (s).

HR-MS (EI) calc. for $[C_{17}H_{14}FN]^+$ 251.1110, found: 251.1115.

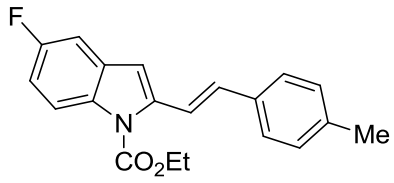
***Z*-isomer:**

^{1}H-NMR (300 MHz, $CDCl_3$): 7.94 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 2H), 7.21 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.04 (dd, *J* = 8.8, 4.4 Hz, 1H), 6.90 (td, *J* = 9.1, 2.5 Hz, 1H), 6.66 (d, *J* = 12.2 Hz, 1H), 6.54 (d, *J* = 12.2 Hz, 1H), 6.49 (d, *J* = 1.9 Hz, 1H), 2.45 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 158.0 (d, *J* = 240 Hz, C), 137.9 (C), 136.9 (C), 134.6 (C), 132.8 (C), 129.7 (2 x CH), 128.9 (CH), 128.4 (2 x CH), 128.2 (C), 120.1 (CH), 111.3 (d, *J* = 9.5 Hz, CH), 110.9 (d, *J* = 25.1 Hz, CH), 105.4 (d, *J* = 4.1 Hz, CH), 105.1 (d, *J* = 24.1 Hz, CH), 21.36 (CH_3).

^{19}F-NMR (282 MHz, $CDCl_3$): -124.512 (s).

HR-MS (EI) calc. for $[C_{17}H_{14}FN]^+$ 251.1110, found: 251.1156.



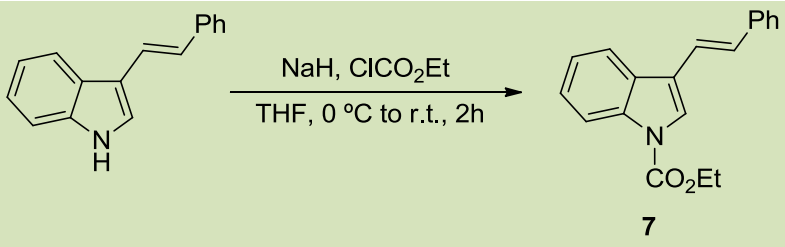
1g

(*E*)-Ethyl 5-fluoro-2-(4-methylstyryl)-1*H*-indole-1-carboxylate (1g): To a solution of (*E*)-5-fluoro-2-(4-methylstyryl)-1*H*-indole (350 mg, 1.39 mmol) in THF (6 mL), NaH (70.2 mg, 95% in mineral oil, 2.78 mmol) was added at 0 °C and the mixture was stirred for 30 min at room temperature. Ethylchloroformiate (226 mg, 2.09 mmol) was then added. After 2 h at room temperature, the reaction mixture was diluted with H_2O (6 mL) and extracted with Et_2O (3 x 6 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vaccum. After column chromatography (SiO_2, hexane/EtOAc 20:1), **1g** (434 mg, 97%) was obtained as a yellow solid (m.p. = 240.3-241.0 ºC, dec.).

^{1}H-NMR (300 MHz, $CDCl_3$): 8.07 (dd, *J* = 9.1, 4.6 Hz, 1H), 7.72 (d, *J* = 16.2 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.24-7.15 (m, 3H), 7.07 (d, *J* = 16.2 Hz, 1H), 7.00 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.82 (s, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.53 (t, *J* = 7.1 Hz, 3H).

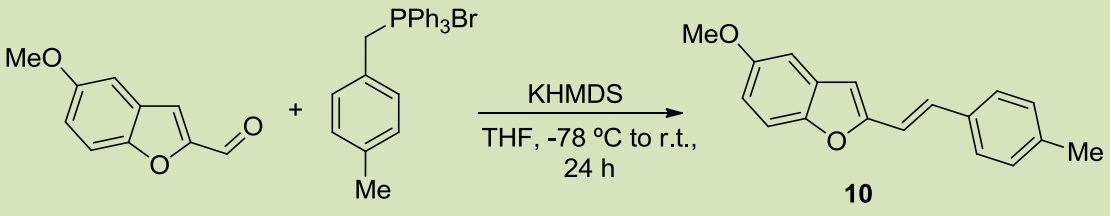
^{13}C-NMR (75 MHz, $CDCl_3$): 159.5 (d, *J* = 239 Hz, C), 151.9 (C), 141.3 (C), 138.1 (C), 134.2 (C), 133.1 (C), 131.6 (CH), 130.5 (d, *J* = 10.1 Hz, C), 129.5 (2 x CH), 126.7 (2 x CH), 119.0 (CH), 116.8 (d, *J* = 8.6 Hz, CH), 111.8 (d, *J* = 24.6 Hz, CH), 106.3 (d, *J* = 3.8 Hz, CH), 105.6 (d, *J* = 23.7 Hz, CH), 63.4 (CH_2), 21.3 (CH_2), 14.4 (CH_3).
^{19}F-NMR (282 MHz, ($CDCl_3$): -120.4 (s).
HR-MS (EI) calc. for $[C_{20}H_{18}FNO_2]^+$ 323.1322, found 323.1326.

Synthesis of 3-vinyl indole 7.



(*E*)-Ethyl 3-styryl-1*H*-indole-1-carboxylate (7): To a solution of (*E*)-3-styryl-1*H*-indole[4] (100 mg, 0. 46 mmol) in THF (2 mL), NaH (23.2 mg, 0.92 mmol, 95% mineral oil) was added at 0 °C and the mixture was stirred for 30 min at room temperature. Ethylchloroformiate (75 mg, 0.69 mmol) was then added. After 2 h at room temperature, the reaction mixture was diluted with H_2O (2 mL) and extracted with Et_2O (3 x 2 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vaccum. After column chromatography (SiO_2, hexane/EtOAc 40:1), **7** (120 mg, 90%) was obtained as a yellow solid (m.p. = 88.2-88.7 ºC).
^{1}H-NMR (300 MHz, $CDCl_3$): 8.28 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.86 (s, 1H), 7.60 (m, 2H), 7.46-7.35 (m, 4H), 7.34-7.26 (m, 3H), 5.36 (m, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H).
^{13}C-NMR (75 MHz, $CDCl_3$): 150.8 (C), 137.7 (2 x C), 136.1 (C), 128.9 (CH), 128.7 (2 x CH), 127.4 (CH), 126.1 (2 x CH), 124.9 (CH), 123.7 (CH), 123.2 (CH), 120.0 (CH), 119.7 (CH), 119.4 (C), 115.3 (CH), 63.2 (CH_2), 14.2 (CH_3).
HR-MS (EI) calc. for $[C_{19}H_{17}NO_2]^+$ 291.3438, found 291.3441.

Synthesis of 2-vinyl benzofuran 10.



5-methoxy-2-(4-methylstyryl)benzofuran (10): To suspension of *p*-tolyltriphenylphosphonium bromide (5.1 g, 11.4 mmol) in THF (40 mL), KHMDS (11.4 mL) was added and stirred at room temperature for 0.5 h. The reaction mixture was then cooled to -78 °C and 5-methoxy-benzofuran-2-carbaldehyde[5] (2.0 g, 11.4 mmol) was injected after solubilization in the minimun amount of THF. The resulting mixture was allowed to warm slowly to room temperature and stirred for 24 h. Water (50 mL) and ether (50 mL) were added to the flask and the organic layer was separated from the aqueous layer. The aqueous layer was extracted once with ether (50 mL) and once with dichloromethane (50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum and the crude was purified by column chromatography (hexane/ethyl acetate 99:1) to yield a separable mixture of ***Z*-10a** (0.891 g, 30%, clear oil) and ***E*-10a** (0.438 g, 15%, white solid; m.p. = 145.7-147.0 °C).

Spectroscopic Data for ***Z*-10a:**

^{1}H NMR (300 MHz, $CDCl_3$): 7.42 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.95-6.80 (m, 2H), 6.78 (d, *J* = 11.8 Hz, 1H), 6.61 (bs, 1H), 6.40 (d, *J* = 11.8 Hz, 1H), 3.82 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 156.2 (C), 155.1 (C), 149.5 (C), 137.9 (C), 134.2 (C), 131.8 (CH), 129.5 (C), 129.1 (2 x CH), 129.0 (2 x CH), 117.8 (CH), 113.6 (CH), 111.7 (CH), 106.3 (CH), 103.3 (CH), 55.1 (CH_3), 21.6 (CH_3).

HR-MS (EI) calc. for $[C_{18}H_{16}O_2]^+$ 264.3184, found 2643185.

Spectroscopic Data for ***E*-10a:**

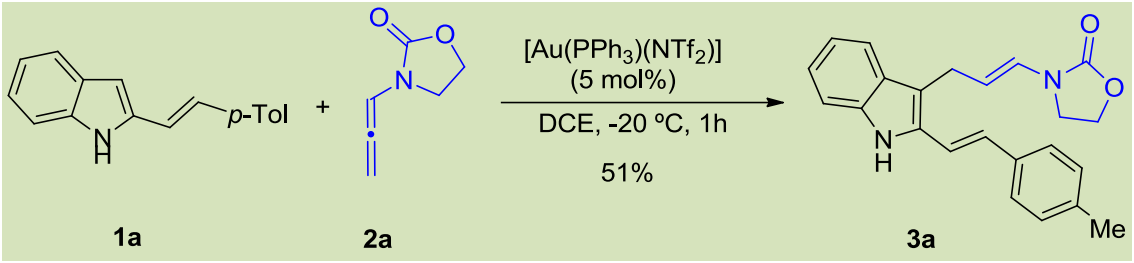
^{1}H NMR (300 MHz, $CDCl_3$): 7.47-7.29 (m, 3H), 7.27-7.13 (m, 3H), 7.06-6.94 (m, 2H), 6.92-6.90 (m, 1H), 6.60 (s, 1H), 3.85 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 156.4 (C), 156.3 (C), 150.1 (C), 138.4 (C), 134.1 (C), 130.4 (CH), 130.0 (C), 129.7 (2 x CH), 126.9 (2 x CH), 115.8 (CH), 113.3 (CH), 111.4 (CH), 105.1 (CH), 103.5 (CH), 56.1 (CH_3), 21.5 (CH_3).

HR-MS (EI) calc. for $[C_{18}H_{16}O_2]^+$ 264.1150, found 264.1155.

Preliminary experiments.

Experimental procedure for reactions showed in Scheme 1: To a solution of vinyl indole **1a-c** (0.2 mmol) and allenamide **2a** (0.3 mmol, 1.5 equiv.) in DCE (0.1 M) at -20 ºC, [Au(PPh$_3$)(NTf$_2$)] (5.0 mol%) was added. The resulting mixture was stirred at this temperature for 1 h (disappearance of the starting reagents was confirmed by TLC analysis). The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography (SiO$_2$).

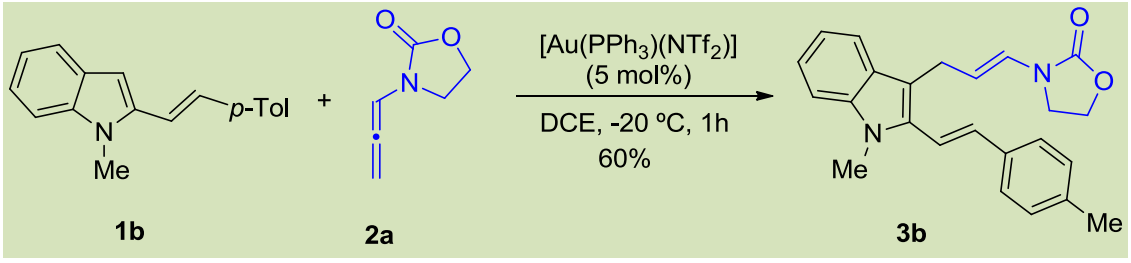


3-((*E*)-3-(2-((*E*)-4-Methylstyryl)-1*H*-indol-3-yl)prop-1-en-1-yl)oxazolidin-2-one (3a): The representative procedure was followed using **1a** (47 mg, 0.2 mmol) and **2a** (22 mg, 0.18 mmol). After column chromatography (SiO$_2$, hexane/EtOAc 4:1 + 1% Et$_3$N), **3a** (36 mg, 51%) was obtained as a yellow solid (m.p = 168.0-169.5 ºC, dec.).

^{1}H-NMR (300 MHz, CDCl$_3$): 8.16 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.27-7.03 (m, 5H), 6.87 (d, *J* = 4.2 Hz, 1H), 6.79 (d, *J* = 6.3 Hz, 1H), 4.98 (m, 1H), 4.37 (dd, *J* = 9.0, 7.1 Hz, 2H), 3.63 (m, 4H), 2.37 (s, 3H).

^{13}C-NMR (75 MHz, CDCl$_3$): 155.6 (C), 138.0 (C), 136.8 (C), 134.4 (C), 132.8 (C), 129.8 (2 x CH), 129.0 (C), 126.9 (CH), 126.4 (2 x CH), 124.5 (CH), 123.4 (CH), 120.0 (CH), 119.1 (CH), 116.0 (CH), 114.4 (C), 110.8 (CH), 110.4 (CH), 62.3 (CH_2), 42.8 (CH_2), 24.9 (CH_2), 21.5 (CH_3).

HR-MS (EI) calc. for [$C_{23}H_{22}N_2O_2$]$^+$ 358.1681, found 358.1680.



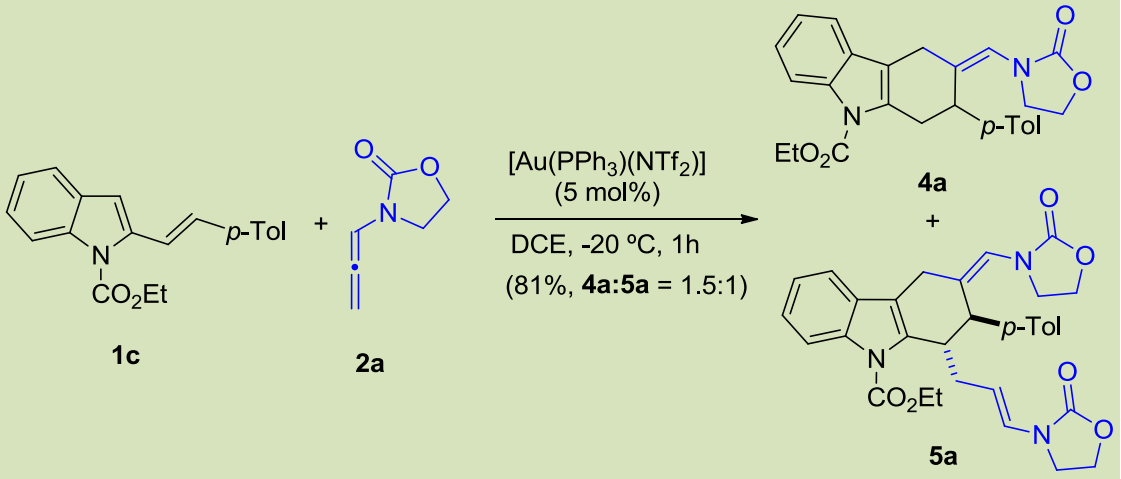
3-((*E*)-3-(1-Methyl-2-((*E*)-4-methylstyryl)-1*H*-indol-3-yl)prop-1-en-1-yl)oxazolidin-2-one (3b): The representative procedure was followed using **1b** (100 mg, 0.40 mmol)

and **2a** (45 mg, 0.36 mmol). After column chromatography (SiO_2, hexane/EtOAc 4:1 + 1% Et_3N), **3b** (89 mg, 60%) was obtained as a white solid (m.p. 130.9-132.5 °C).

^{1}H-NMR (300 MHz, $CDCl_3$): 7.59 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.25 (m, 4H), 7.13 (m, 2H), 6.92 (d, *J* = 16.4 Hz, 1H), 6.83 (d, *J* = 14.3 Hz, 1H), 5.07 (dt, *J* = 14.2, 6.4 Hz, 1H), 4.39 (dd, *J* = 8.2, 6.5 Hz, 2H), 3.83 (s, 3H), 3.72 (dd, *J* = 6.5, 1.5 Hz, 2H), 3.67 (dd, *J* = 8.3, 6.5 Hz, 2H), 2.41 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 155.7 (C), 138.4 (C), 138.0 (C), 135.3 (C), 134.8 (C), 133.4 (CH), 129.9 (2 x CH), 128.2 (C), 126.7 (2 x CH), 124.7 (CH), 122.6 (CH), 119.8 (CH), 119.2 (CH), 116.6 (CH), 112.2 (C), 110.9 (CH), 109.5 (CH), 62.4 (CH_2), 43.1 (CH_2), 31.2 (CH_3), 26.0 (CH_2), 21.7 (CH_3).

HR-MS (EI) calc. for $[C_{24}H_{24}N_2O_2]^+$ 372.1838, found 372.1844.



The representative procedure was followed using **1c** (61 mg, 0.2 mmol) and **2a** (38 mg, 0.3 mmol). After column chromatography (SiO_2, hexane/EtOAc 1:1 + 1% Et_3N), compounds **4a** (41 mg, white solid; m.p. = 163.7-164.3 ºC, dec.) and **5a** (37 mg, white solid; m.p. = 118.9-119.5 ºC) were obtained in a combined yield of 81% (assuming **1c** as limiting reagent also for compound **5a**).

(*Z*)-Ethyl 3-((2-oxooxazolidin-3-yl)methylene)-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4a):

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.19 (d, *J* = 8.2 Hz, 1H), 7.39-7.20 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.25 (d, *J* = 1.7 Hz, 1H), 4.59-4.40 (m, 5H), 3.98-3.84 (m, 3H), 3.49 (m, 1H), 3.32 (d, *J* = 17.5 Hz, 1H), 3.16 (d, *J* = 17.5 Hz, 1H), 2.28 (s, 3H), 1.53 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 157.9 (C), 152.3 (C), 138.8 (C), 136.7 (C), 136.5 (C), 134.2 (C), 133.2 (C), 129.4 (2 x CH), 129.2 (C), 127.3 (2 x CH), 124.2 (CH), 123.1

(CH), 119.4 (CH), 117.9 (CH), 116.3 (C), 115.9 (CH), 63.5 (CH_2), 62.7 (CH_2), 47.6 (CH_2), 38.9 (CH), 30.5 (CH_2), 25.9 (CH_2), 21.0 (CH_3), 14.6 (CH_3).

HR-MS (EI) calc. for $[C_{26}H_{26}N_2O_4]^+$ 430.1893, found 430.1894.

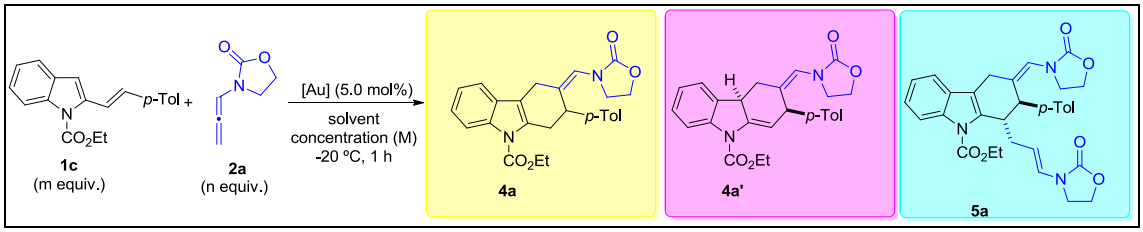
(*1S*,2R*,Z*)-Ethyl 1-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-3-((2-oxooxazolidin-3-yl)methylene)-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (5a):

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.13 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.33-7.21 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 14.4 Hz, 1H), 6.64 (s, 1H), 5.02 (ddd, *J* = 14.4, 9.0, 5.6 Hz, 1H), 4.56 (q, *J* = 7.2 Hz, 2H), 4.52-4.40 (m, 4H), 4.33 (s, 1H), 4.26 (d, *J* = 9.0 Hz, 1H), 4.15-4.04 (m, 1H), 3.84 (q, *J* = 8.9 Hz, 1H), 3.73 (dt, *J* = 8.0, 4.3 Hz, 2H), 3.41 (d, *J* = 18.7 Hz, 1H), 3.37 (d, *J* = 18.7, 1H), 2.69 (dddd, *J* = 14.1, 7.2, 5.2, 2.6 Hz, 1H), 2.34-2.23 (m, 1H, overlapped signal), 2.27 (s, 3H, overlapped signal), 1.56 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 158.3 (C), 155.6 (C), 152.2 (C), 138.7 (C), 137.1 (C), 136.6 (C), 136.5 (C), 129.4 (2 x CH), 129.1 (C), 127.6 (2 x CH), 126.2 (C), 126.0 (CH), 124.4 (CH), 123.4 (CH), 123.2 (CH), 118.2 (CH), 116.2 (CH), 116.1 (C), 109.3 (CH), 63.6 (CH_2), 62.8 (CH_2), 62.7 (CH_2), 47.4 (CH_2), 43.0 (CH_2), 42.6 (CH), 40.4 (CH), 36.2 (CH_2), 26.8 (CH_2), 20.9 (CH_3), 14.6 (CH_3).

HR-MS (EI) calc. for $[C_{32}H_{33}N_3O_6]^+$ 555.2369, found 555.2370.

Screening.



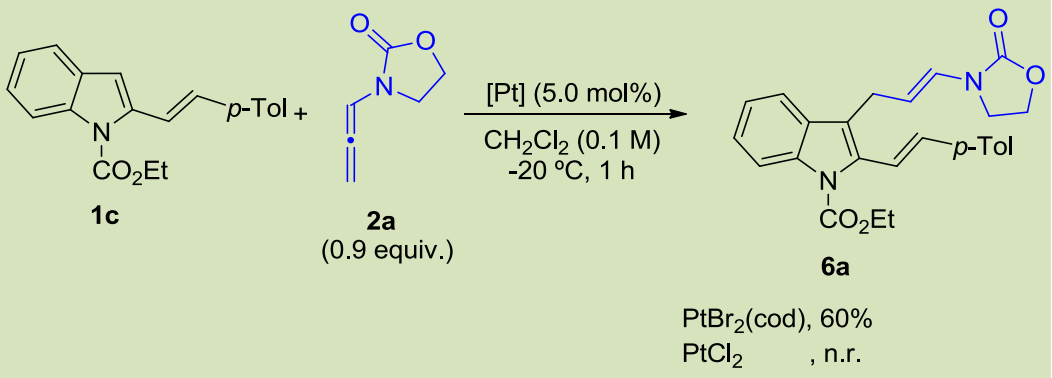
Entry	m	n	[Au]	Solvent	C (M)	Yield (%)[a]		
						4a	4a'	5a
1	1	1.5	$[Au(PPh_3)(NTf_2)]$	DCE	0.1	48	-	33
2	1	1.5	$[Au(IPr)(NTf_2)]$	DCE	0.1	15	44	35
3	1	1.5	$[Au(JohnPhos)(NTf_2)]$	DCE	0.1	16	51	33
4	1	1.5	$[Au((ArO)_3P)(NTf_2)]$	DCE	0.1	44	19	32
5	1	0.9	$[Au(PPh_3)(NTf_2)]$	DCE	0.1	52	-	7
6	1	2.5	$[Au(PPh_3)(NTf_2)]$	DCE	0.1	17	-	70
7	1	0.9	$[Au(PPh_3)(NTf_2)]$	DCE	0.1	54	-	9
8	1	0.9	$[Au(PPh_3)(NTf_2)]$	DCE	0.05	46	-	26
9	1	0.9	$[Au(PPh_3)(NTf_2)]$	PhMe	0.1	12	24	27
10	1	0.9	$[Au(PPh_3)(NTf_2)]$	THF	0.1	42	13	25
11	1	0.9	$[Au(PPh_3)(NTf_2)]$	CH_2Cl_2	0.1	55	-	13
12[b]	1	0.9	$[Au(PPh_3)(NTf_2)]$	CH_2Cl_2	0.1	68	-	13
13	1	0.9	$[Au(IPr)(NTf_2)]$	DCE	0.1	5	75	-
14	1	0.9	$[Au((ArO)_3P)(NTf_2)]$	DCE	0.1	65	18	-
15	1	0.9	$[Au(JohnPhos)(NTf_2)]$	DCE	0.1	-	81	8
16	1	0.9	$[Au(JohnPhos)(NTf_2)]$	DCE	0.05	-	79	-
17	1	0.9	$[Au(JohnPhos)(NTf_2)]$	CH_2Cl_2	0.05	-	80	-
18[c]	1	0.9	$[Au(PPh_3)Cl]$	CH_2Cl_2	0.1	-	15	-
19	1	0.9	$AuCl_3$	CH_2Cl_2	0.1	74	-	-
20[c]	1	0.9	$AuCl_3$	CH_2Cl_2	0.1	83		
21	1	2.5	$[Au(JohnPhos)(NTf_2)]$	CH_2Cl_2	0.1	-	-	95

Entries 1-6, procedure: To a solution of **1c** and **2a** in the indicated solvent (2 mL) at -20 ºC, gold catalyst was added and the mixture was stirred for 1h at the same temperature.

Entries 7-21, procedure: To a solution of **1c** and the gold catalyst in the indicated solvent (1 mL) at -20 ºC, a solution of **2a** (1 mL) was added dropwise via syringe and the mixture was stirred for 1h at the same temperature.

[a] Isolated yield. Yields for **5a** calculated considering **1c** as limiting reagent. [b] At -70 ºC. [c] At -50 ºC. (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; $(ArO)_3P$ = tris(2,4-di-*tert*-butylphenyl) phosphite).

Reaction with platinum catalysts.



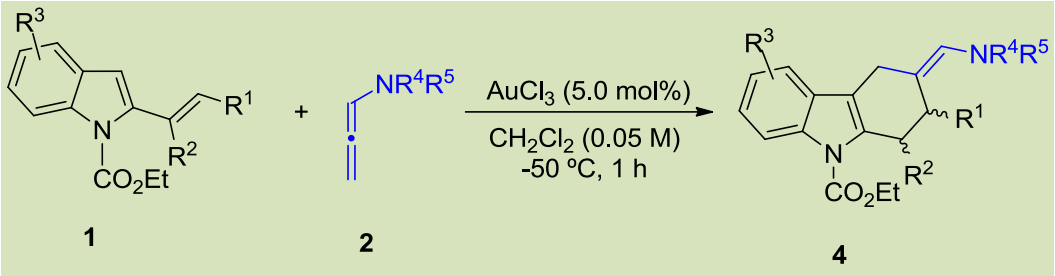
Ethyl 2-((*E*)-4-methylstyryl)-3-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-1*H*-indole-1-carboxylate (6a): The representative procedure described for entry 17 was followed using **1c** (92 mg, 0.3 mmol) and **2a** (34 mg, 0.27 mmol). After column chromatography (SiO_2, CH_2Cl_2/EtOAc 99:1 + 1% Et_3N), **6a** (69 mg, 60%) was obtained as white solid (m.p. = 144.8-145.5 °C).

^{1}H-NMR (300 MHz, $CDCl_3$): 8.16 (d, *J* = 8.2 Hz, 1H), 7.55 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.47-7.24 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 14.5 Hz, 1H), 6.75 (d, *J* = 14.4 Hz, 1H), 5.05 (td, *J* = 14.4, 6.3 Hz, 1H), 4.52 (q, *J* = 7.1 Hz, 2H), 4.44 (dd, *J* = 8.1, 6.4 Hz, 2H), 3.72-3.64 (m, 4H), 2.40 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H).

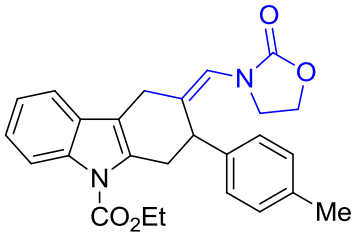
^{13}C-NMR (75 MHz, $CDCl_3$): 155.7 (C), 152.5 (C), 138.4 (C), 136.2 (C), 135.7 (C), 134.6 (C), 132.9 (CH), 130.6 (C), 129.9 (2 x CH), 126.9 (2 x CH), 125.4 (CH), 125.1 (CH), 123.4 (CH), 119.44 (CH), 119.37 (CH), 118.5 (C), 116.2 (CH), 109.7 (CH), 63.6 (CH_2), 62.6 (CH_2), 43.0 (CH_2), 26.1 (CH_2), 21.7 (CH_3), 14.9 (CH_3).

HR-MS (EI) calc. for $[C_{26}H_{26}N_2O_4]^+$ 430.1893, found 430.1891.

Gold-catalyzed cycloadditions of vinyl indoles 3 with allenamides 4: Synthesis of tetrahydrocarbazole derivatives 4.

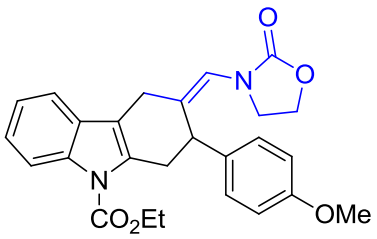


Representative procedure: (*Z*)-Ethyl 3-((2-oxooxazolidin-3-yl)methylene)-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4a):



4a

To a solution of the vinyl indole **1c** (61 mg, 0.2 mmol) and $AuCl_3$ (3.0 mg, 5.0 mol%) in CH_2Cl_2 at -50 ºC (0.1 M) was added dropwise via syringe a solution of **2a** (22 mg, 0.18 mmol) in CH_2Cl_2 (0.1 M, final concentration ca. 0.05 M). The mixture was stirred at the same temperature until disappearance of the starting reagents (checked by TLC; 1 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO_2, hexane:EtOAc = 1:1 + 1% Et_3N) to yield **4a** (64 mg, 83%) as white solid. Appropriate crystals for X-Ray analysis were obtained by slow diffusion of Et_2O in a solution of **4a** in CH_2Cl_2 at -20 ºC. The crystallographic data with the number **CCDC 923923** are available free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.uk/data_request/cif. (Spectroscopic data were in agreement with those reported above).



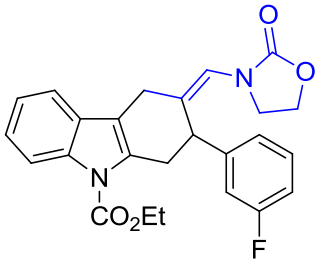
4b

(*Z*)-Ethyl 2-(4-methoxyphenyl)-3-((2-oxooxazolidin-3-yl)methylene)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4b): The representative procedure was followed using vinyl indole **1d** (64 mg, 0.2 mmol) and allenamide **2a** (22 mg, 0.18 mmol). Purification by flash chromatography (SiO_2, CH_2Cl_2:Hexane = 7:3 + 1% Et_3N) yielded **4b** (69 mg, 83%) as a yellow solid (m.p. = 125 °C, dec.).

^{1}H-NMR (300 MHz, $CDCl_3$): 8.15 (dd, *J* = 1.1, 7.0 Hz, 1H), 7.33-7.19 (m, 3H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.77 (m, 2H), 6.20 (d, *J* = 1.1 Hz, 1H), 4.56-4.42 (m, 5H), 3.99-3.82 (m, 2H), 3.79 (s, 1H), 3.73 (s, 3H), 3.47 (m, 1H), 3.26 (d, *J* = 17.1 Hz, 1H), 3.12 (d, *J* = 17.1 Hz, 1H), 1.50 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 158.5 (C), 157.8 (C), 152.2 (C), 136.5 (C), 133.9 (C), 133.8 (C), 133.5 (C), 129.1 (C), 128.2 (2 x CH), 124.2 (CH), 123.1 (CH), 118.8 (CH), 117.8 (CH), 116.3 (C), 115.8 (CH), 114.1 (2 x CH), 63.2 (CH_2), 62.4 (CH_2), 55.4 (CH), 47.5 (CH_2), 38.5 (CH_3), 30.6 (CH_2), 25.9 (CH_2), 14.6 (CH_3).

HR-MS (EI) calc. for $[C_{26}H_{26}N_2O_5]^+$ 446.1842, found 446.1847.



4c

(*Z*)-Ethyl 2-(3-fluorophenyl)-3-((2-oxooxazolidin-3-yl)methylene)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4c): The representative procedure was followed using vinyl indole **1e** (62 mg, 0.2 mmol) and allenamide **2a** (22 mg, 0.18 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 2:1 + 1% Et_3N) yielded **4c** (59 mg, 75%) as white solid (m.p. = 153.2-153.8 °C, dec.).

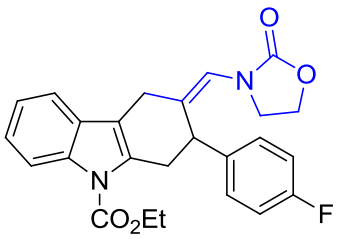
^{1}H-NMR (300 MHz, CD_2Cl_2): 8.19 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.31 (dd, *J* = 7.2, 1.4 Hz 1H), 7.28-7.22 (m, 2H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 10.6 Hz, 1H), 6.92 (td, *J* = 8.5, 2.5 Hz, 1H), 6.25 (d, *J* = 1.8 Hz, 1H), 4.59-4.50 (m, 3H), 4.48 (t, *J*

= 7.8 Hz, 2H), 3.92 (m, 3H), 3.53 (m, 1H), 3.34 (d, *J* = 17.4 Hz, 1H), 3.16 (d, *J* = 17.6 Hz, 1H), 1.53 (q, *J* = 7.2 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 162.9 (d, *J* = 242 Hz, C), 157.4 (C), 151.9 (C), 144.4 (d, *J* = 8.3 Hz, C), 136.3 (C), 133.4 (C), 132.3 (C), 129.8 (d, *J* = 8.4 Hz, CH), 128.7 (C), 123.9 (CH), 122.9 (CH), 122.7 (CH), 119.5 (CH), 117.6 (CH), 115.9 (C), 115.5 (CH), 114.1 (d, *J* = 21.8 Hz, CH), 113.3 (d, *J* = 21.1 Hz, CH), 63.1 (CH_2), 62.4 (CH_2), 47.1 (CH_2), 38.8 (CH), 29.9 (CH_2), 25.5 (CH_2), 14.2 (CH_3).

^{19}F-NMR (282 MHz, CD_2Cl_2): -113.85 (s).

HR-MS (EI) calc. for $[C_{25}H_{23}FN_2O_4]^+$ 434.1642, found 434.1644.



4d

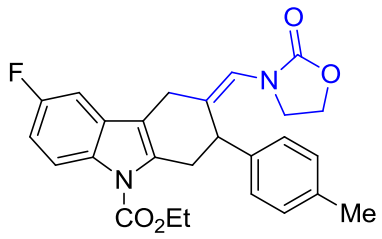
(*Z*)-Ethyl 2-(4-fluorophenyl)-3-((2-oxooxazolidin-3-yl)methylene)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4d): The representative procedure was followed using vinyl indole **1f** (62 mg, 0.2 mmol) and allenamide **2a** (22 mg, 0.18 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 2:1 + 1% Et_3N) yielded **4d** (55 mg, 72%) as a white solid (m.p. = 158.5-160.2 °C)

^{1}H-NMR (300 MHz, $CDCl_3$): 8.16 (d, *J* = 7.6 Hz, 1H), 7.34-7.16 (m, 5H), 6.91 (t, *J* = 8.4 Hz, 2H), 6.18 (d, *J* = 1.5 Hz, 1H), 4.59-4.39 (m, 5H), 3.94-3.80 (m, 3H), 3.52 (m, 1H), 3.26 (d, *J* = 17.6 Hz, 1H), 3.18 (d, *J* = 17.6 Hz, 1H), 1.50 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 161.8 (d, *J* = 245.1 Hz, C), 157.8 (C), 152.2 (C), 137.1 (d, *J* = 3.1 Hz, C), 136.4 (C), 133.9 (C), 133.5 (C), 129.0 (C), 128.8 (d, *J* = 7.9 Hz, 2 x CH), 124.3 (CH), 123.1 (CH), 119.1 (CH), 117.9 (CH), 116.3 (C), 115.9 (CH), 115.5 (d, *J* = 21.2 Hz, 2 x CH), 63.3 (CH_2), 62.4 (CH_2), 47.5 (CH_2), 38.6 (CH), 30.5 (CH_2), 25.8 (CH_2), 14.6 (CH_3).

^{19}F-NMR (282 MHz, $CDCl_3$): -116.6 (s).

HR-MS (EI) calc. for $[C_{25}H_{23}FN_2O_4]^+$ 434.1642, found 434.1642.



4e

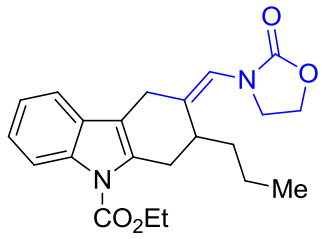
(*Z*)-Ethyl 2-(4-fluorophenyl)-3-((2-oxooxazolidin-3-yl)methylene)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4e): The representative procedure was followed using vinyl indole **1g** (65 mg, 0.2 mmol) and allenamide **2a** (22 mg, 0.18 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 2:1 + 1% Et_3N) yielded **4e** (74 mg, 92%) as a white solid (m.p. = 193.5-194.1 ºC).

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.15 (dd, *J* = 9.7, 4.7 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.02 (m, 2H), 6.24 (d, *J* = 1.5 Hz, 1H), 4.59-4.41 (m, 5H), 3.93 (m, 2H), 3.87 (s, 1H), 3.49 (m, 1H), 3.26 (d, *J* = 17.5 Hz, 1H), 3.12 (d, *J* = 17.5 Hz, 1H), 2.30 (s, 3H), 1.52 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 159.7 (d, *J* = 240 Hz, C), 157.8 (C), 152.1 (C), 138.7 (C), 136.6 (C), 136.2 (C), 133.0 (C), 132.7 (C), 130.1 (d, *J* = 9.4 Hz, C), 129.5 (2 x CH), 127.2 (2 x CH), 119.6 (CH), 116.9 (d, *J* = 8.9 Hz, CH), 116.1 (d, *J* = 3.4 Hz, C), 111.4 (d, *J* = 24.7 Hz, CH), 103.6 (d, *J* = 23.8 Hz CH), 63.6 (CH_2), 62.8 (CH_2), 47.5 (CH_2), 38.8 (CH), 30.5 (CH_2), 25.8 (CH_2), 21.0 (CH_3), 14.6 (CH_3).

^{19}F-NMR (282 MHz, $CDCl_3$): -121.4 (s).

HR-MS (EI) calc. for $[C_{26}H_{25}FN_2O_4]^+$ 448.1798, found 448.1801.



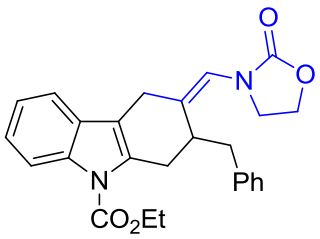
4f

(*Z*)-Ethyl 3-((2-oxooxazolidin-3-yl)methylene)-2-propyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4f): The representative procedure was followed using vinyl indole **1h** (52 mg, 0.2 mmol) and allenamide **2a** (22 mg, 0.18 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 1:1 + 1% Et_3N) yielded **4f** (30 mg, 44%) as clear oil.

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.16 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.32-7.24 (m, 2H), 6.20 (d, *J* = 1.7 Hz, 1H), 4.54-4.42 (m, 4H), 3.93-3.79 (m, 2H), 3.48 (d, *J* = 17.6 Hz, 1H), 3.32 (d, *J* = 17.6 Hz, 1H), 3.25-3.13 (m, 3H), 1.49 (t, *J* = 7.2 Hz, 3H), 1.45-1.35 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 157.3 (C), 151.9 (C), 136.2 (C), 134.0 (C), 132.5 (C), 129.0 (C), 123.6 (CH), 122.6 (CH), 118.7 (CH), 117.5 (CH), 115.4 (CH), 115.0 (C), 62.9 (CH_2), 62.2 (CH_2), 47.1 (CH_2), 34.6 (CH_2), 34.4 (CH), 31.9 (CH_2), 25.3 (CH_2), 21.0 (CH_2), 14.2 (CH_3), 13.9 (CH_3).

HR-MS (EI) calc. for $[C_{22}H_{26}N_2O_4]^+$ 382.1893, found 382.1899.



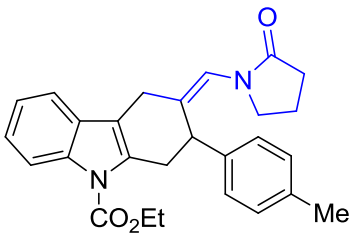
4g

(*Z*)-Ethyl 2-benzyl-3-((2-oxooxazolidin-3-yl)methylene)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4g): The representative procedure was followed using vinyl indole **1i** (61 mg, 0.2 mmol) and allenamide **2a** (22 mg, 0.18 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 1:1 + 1% Et_3N) yielded **4g** (25 mg, 32%) as a clear oil.

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.21 (d, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.28 (m, 7H), 6.03 (d, *J* = 2.2 Hz, 1H), 4.48 (m, 2H), 4.29 (t, *J* = 8.0 Hz, 2H), 3.68 (d, *J* = 18.0 Hz, 1H), 3.47-3.34 (m, 3H), 3.29 (m, 2H), 3.18 (m, 1H), 2.90 (dd, *J* = 13.3, 8.4 Hz, 1H), 2.78 (dd, *J* = 13.3, 7.1 Hz, 1H), 1.46 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 156.9 (C), 151.8 (C), 140.6 (C), 136.3 (C), 133.6 (C), 132.1 (C), 129.2 (2 x CH), 129.0 (C), 128.2 (2 x CH), 126.1 (CH), 123.7 (CH), 122.7 (CH), 119.0 (CH), 117.5 (CH), 115.5 (CH), 114.7 (C), 62.9 (CH_2), 62.2 (CH_2), 46.5 (CH_2), 38.6 (CH_2), 37.4 (CH), 31.0 (CH_2), 25.5 (CH_2), 14.1 (CH_3).

HR-MS (EI) calc. for $[C_{26}H_{26}N_2O_4]^+$ 430.1893, found 430.1898.



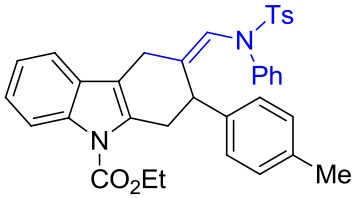
4h

(*Z*)-Ethyl 3-((2-oxopyrrolidin-1-yl)methylene)-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4h): The representative procedure was followed using vinyl indole **1c** (61 mg, 0.2 mmol) and allenamide **2b** (22 mg, 0.18 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 2:1 + 1% Et_3N) yielded **4h** (58 mg, 75%) as a white solid (m.p. = 160.8-163.9 ºC).

^{1}H-NMR (300 MHz, CD_2Cl_2): 7.82 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.33-7.20 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.34 (s, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 4.44 (d, *J* = 5.9 Hz, 1H), 3.87 (d, *J* = 18.5 Hz, 1H), 3.78 (m, 2H), 3.51 (m, 1H), 3.31 (d, *J* = 17.5 Hz, 1H), 3.15 (d, *J* = 17.5 Hz, 1H), 2.47 (t, *J* = 8.1 Hz, 2H), 2.29 (s, 3H), 2.23 (m, 2H), 1.53 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 175.3 (C), 152.4 (C), 146.6 (C), 139.2 (C), 136.7 (C), 136.4 (C), 134.4 (C), 132.0 (C), 129.3 (2 x CH), 127.3 (2 x CH), 124.1 (CH), 123.0 (CH), 119.9 (CH), 117.9 (CH), 116.6 (C), 115.9 (CH), 63.6 (CH_2), 50.2 (CH_2), 39.3 (CH), 31.0 (CH_2), 30.4 (CH_2), 26.1 (CH_2), 21.0 (CH_3), 19.2 (CH_2), 14.6 (CH_3).

HR-MS (EI) calc. for $[C_{27}H_{28}N_2O_3]^+$ 428.2100, found 428.2105.



4i

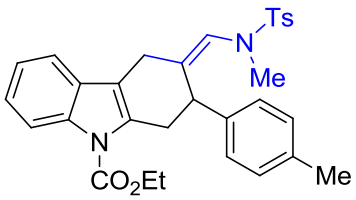
(*Z*)-Ethyl 3-((4-methyl-*N*-phenylphenylsulfonamido)methylene)-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4i): The representative procedure was followed using vinyl indole **1c** (61 mg, 0.2 mmol) and allenamide **2c** (51 mg, 0.18 mmol) at -70 ºC and C = 0.01M. Purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1 + 1% Et_3N) yielded **4i** (99 mg, 93%, *Z*/*E* = 6:1) as a white solid (m.p. = 163.8-164.2 ºC, dec.).

^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 8.12 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.32-7.16 (m, 7H), 7.17-7.04 (m, 7H), 6.12 (s, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 3.90 (t, *J* =

5.7 Hz, 1H), 3.63 (dd, *J* = 17.9, 5.6 Hz, 1H), 3.46 (dd, *J* = 17.9, 5.6 Hz, 1H), 3.37 (d, *J* = 19.9 Hz, 1H), 3.03 (d, *J* = 19.9 Hz, 1H), 2.33 (s, 6H), 1.47 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 151.9 (C), 143.7 (C), 141.3 (C), 139.8 (C), 138.3 (C), 136.2 (C), 136.1 (C), 134.6 (C), 133.6 (C), 129.3 (2 x CH), 129.1 (2 x CH), 129.0 (2 x CH), 128.8 (C), 127.8 (2 x CH), 127.4 (2 x CH), 126.9 (CH), 126.7 (2 x CH), 123.9 (CH), 123.0 (CH), 122.8 (CH), 117.7 (CH), 115.5 (CH), 115.0 (C), 62.9 (CH_2), 44.7 (CH), 31.1 (CH_2), 22.6 (CH_2), 21.5 (CH_3), 21.0 (CH_3), 14.4 (CH_3).

HR-MS (EI) calc. for $[C_{36}H_{34}N_2O_4S]^+$ 590.2239, found 590.2243.



4j

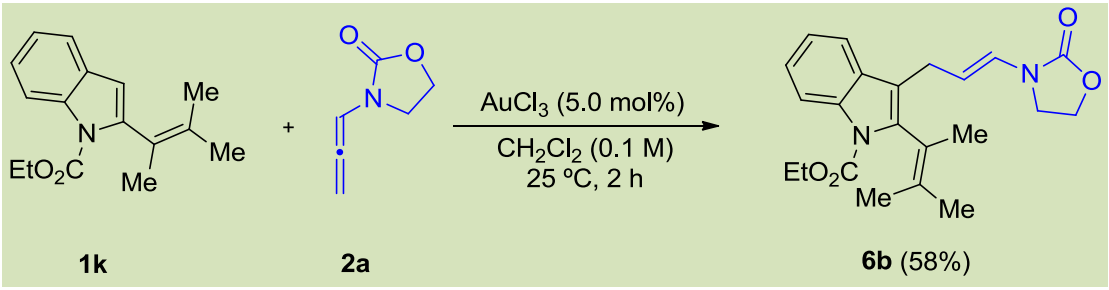
(*Z*)-Ethyl 3-((*N*,4-dimethylphenylsulfonamido)methylene)-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (4k): The representative procedure was followed using vinyl indole **1c** (61 mg, 0.2 mmol) and allenamide **2d** (40 mg, 0.18 mmol) at -70 ºC and C = 0.01M. Purification by flash chromatography (SiO_2, hexane:EtOAc = 5:1 + 1% Et_3N) yielded **4k** (87 mg, 91%) as a white solid (m.p. = 126.1-126.7 ºC, dec.).

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.26 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.43-7.22 (m, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 5.45 (d, *J* = 1.6 Hz, 1H), 4.97 (d, *J* = 6.2 Hz, 1H), 4.56 (dd, *J* = 7.2, 1.7 Hz, 2H), 3.84 (d, *J* = 18.4 Hz, 1H), 3.57 (m, 1H), 3.24 (d, *J* = 17.5 Hz, 1H), 3.11 (d, *J* = 17.5 Hz, 1H), 2.95 (s, 3H), 2.47 (s, 3H), 2.31 (s, 3H), 1.54 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 152.3 (C), 144.4 (C), 143.9 (C), 139.4 (C), 136.9 (C), 136.5 (C), 134.9 (C), 133.6 (C), 130.1 (2 x CH), 129.4 (2 x CH), 129.2 (C), 128.3 (2 x CH), 127.4 (2 x CH), 124.2 (CH), 123.1 (CH), 122.4 (CH), 117.8 (CH), 116.0 (CH), 115.6 (C), 63.5 (CH_2), 39.1 (CH), 30.5 (CH_2), 25.4 (CH_2), 22.0 (CH_3), 21.7 (CH_3), 21.0 (CH_3), 14.6 (CH_3).

HR-MS (EI) calc. for $[C_{31}H_{32}N_2O_4S]^+$ 528.2083, found 528.2089.

Reaction with vinyl indole 1k:



1k **2a** **6b** (58%)

To a solution of the vinyl indole **1k** (52 mg, 0.2 mmol) and $AuCl_3$ (3.0 mg, 5.0 mol%) in CH_2Cl_2 at 25 ºC (0.1 M) was added dropwise via syringe a solution of **2a** (22 mg, 0.18 mmol) in CH_2Cl_2 (0.1 M, final concentration ca. 0.05 M). The mixture was stirred at the same temperature for 2 h (the disappearance of the starting reagents was checked by TLC). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO_2, hexane:EtOAc = 1:1 + 1% Et_3N) to yield **6b** (40 mg, 58%) as a colorless oil.

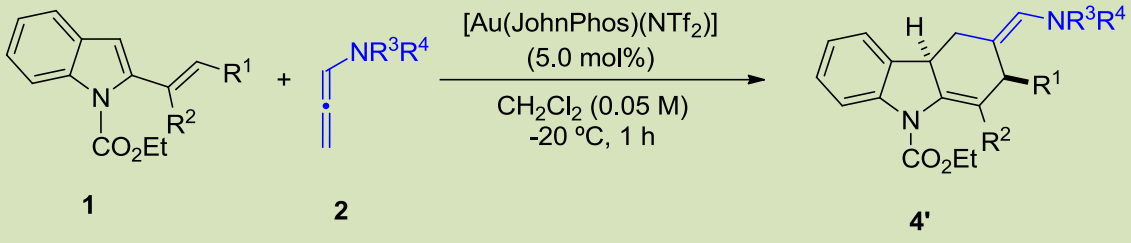
(*E*)-Ethyl 2-(3-methylbut-2-en-2-yl)-3-(3-(2-oxooxazolidin-3-yl)allyl)-1*H*-indole-1-carboxylate (6b):

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.22 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.33-7.23 (m, 2H), 6.75 (d, *J* = 14.2 Hz, 1H), 4.95 (td, *J* = 14.2, 6.8 Hz, 1H), 4.45-4.37 (m, 4H), 3.64 (dd, *J* = 8.3, 7.8 Hz, 2H), 3.37 (dd, *J* = 6.9, 1.4 Hz, 2H), 1.92 (s, 3H), 1.88 (s, 3H), 1.57 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H).

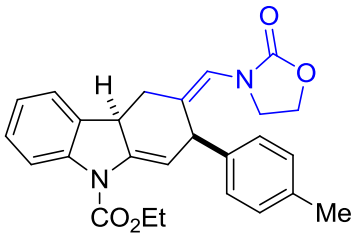
^{13}C-NMR (75 MHz, CD_2Cl_2): 155.2 (C), 151.4 (C), 138.5 (C), 136.1 (C), 131.9 (C), 129.8 (C), 124.6 (CH), 123.7 (CH), 122.4 (CH), 121.5 (C), 118.7 (CH), 116.1 (C), 115.5 (CH), 108.7 (CH), 62.6 (CH_2), 62.2 (CH_2), 42.5 (CH_2), 24.9 (CH_2), 22.1 (CH_3), 19.5 (CH_3), 19.5 (CH_3), 13.9 (CH_3).

HR-MS (EI) calc. for $[C_{22}H_{26}N_2O_4]^+$ 382.1893, found 382.1894.

Gold-catalyzed cycloadditions of vinyl indoles 1 with allenamides 2: Synthesis of tetrahydrocarbazole derivatives 4'.



Representative procedure: (*2R*,4aR*,Z*)-Ethyl 3-((2-oxooxazolidin-3-yl)methylene)-2-(*p*-tolyl)-4,4a-dihydro-2*H*-carbazole-9(3*H*)-carboxylate (4a'):



4a'

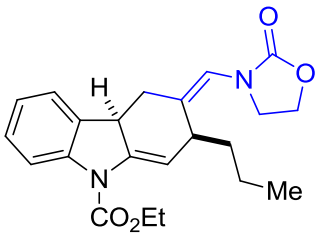
To a solution of the vinyl indole **1c** (61 mg, 0.2 mmol) and [Au(JohnPhos)(NTf_2)] (7.5 mg, 5.0 mol%) in CH_2Cl_2 at -20 ºC (0.1 M) was added dropwise via syringe a solution of **2a** (22 mg, 0.18 mmol) in CH_2Cl_2 (0.1 M, final concentration ca. 0.05 M). The mixture was stirred at the same temperature until disappearance of the starting reagents (checked by TLC; 1 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (hexane:EtOAc = 1:1 + 1% Et_3N) to yield **4a'** (62 mg, 80%) as a white solid (m.p = 165-165.6 °C). Appropriate crystals for X-Ray analysis were obtained by slow diffusion of Et_2O in a solution of **4a'** in CH_2Cl_2 at -20 ºC. The crystallographic data with the number **CCDC 923924** are available free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.uk/data_request/cif.

^{1}H-NMR (400 MHz, CD_2Cl_2): 7.82 (d, *J* = 8.1 Hz, 1H), 7.32-7.25 (m, 2H), 7.21-7.07 (m, 5H), 6.34 (s, 1H), 6.07 (bs, 1H), 4.75 (bs, 1H), 4.42-4.34 (m, 2H), 4.28 (dt, *J* = 8.3, 1.4 Hz, 2H), 4.03-3.97 (m, 1H), 3.67 (q, *J* = 8.6 Hz, 1H), 3.57 (ddd, *J* = 8.6, 8.6, 6.9 Hz, 1H), 3.06 (dd, *J* = 12.7, 4.7 Hz, 1H), 2.51 (ddd, *J* = 12.0, 12.0, 1.6 Hz, 1H), 2.34 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (100 MHz, CD_2Cl_2): 156.2 (C), 151.7 (C), 142.0 (C), 141.1 (C), 140.1 (C), 135.6 (C), 130.8 (C), 128.7 (2 x CH), 128.5 (C), 127.3 (CH), 126.4 (2 x CH), 122.7

(CH), 122.4 (CH), 120.2 (CH), 114.8 (CH), 109.9 (CH), 61.7 (CH_2), 61.5 (CH_2), 45.2 (CH_2), 42.1 (CH), 40.4 (CH), 33.0 (CH_2), 20.0 (CH_3), 13.7 (CH_3).

HR-MS (EI) calc. for $[C_{26}H_{26}N_2O_4]^+$ 430.1893, found 43.1892.



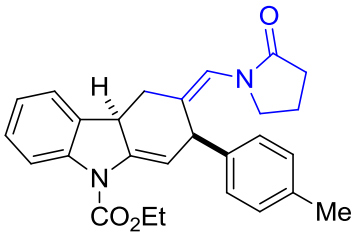
4f'

(*2R*,4aR*,Z*)-Ethyl 3-((2-oxooxazolidin-3-yl)methylene)-2-propyl-4,4a-dihydro-2*H*-carbazole-9(3*H*)-carboxylate (4f'): The representative procedure was followed using vinyl indole **1h** (52 mg, 0.2 mmol) and allenamide **2a** (22 mg, 0.18 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 2:1 + 1% Et_3N) yielded **4f'** (26 mg, 37%) as a yellow oil.

^{1}H-NMR (300 MHz, CD_2Cl_2): 7.79 (d, *J* = 8.4 Hz, 1H), 7.28-7.22 (m, 2H), 7.08 (ddd, *J* = 8.4, 7.4, 1.0 Hz, 1H), 6.29 (s, 1H), 6.02 (dd, *J* = 3.3 ,3.2 Hz, 1H), 4.46-4.36 (m, 4H), 4.03 (ddd, *J* = 8.5, 8.0, 7.3 Hz, 1H), 3.93-3.80 (m, 2H), 3.48 (bs, 1H), 2.85 (dd, *J* = 12.2, 4.8 Hz, 1H), 2.33 (dd, *J* = 12.2, 11.4 Hz, 1H), 1.60-1.40 (m, 4H, overlapping signal), 1.44 (t, *J* = 7.1 Hz, 3H, overlapping signal), 0.94 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 157.1 (C), 152.4 (C), 142.6 (C), 140.9 (C), 131.6 (C), 129.6 (C), 127.7 (CH), 123.3 (CH), 122.9 (CH), 119.3 (CH), 115.4 (CH), 110.3 (CH), 62.3 (CH_2), 62.0 (CH_2), 46.1 (CH_2), 43.6 (CH), 39.4 (CH_2), 35.5 (CH), 32.7 (CH_2), 19.9 (CH_2), 14.3 (CH_3), 14.1 (CH_3).

HR-MS (EI) calc. for $[C_{22}H_{26}N_2O_4]^+$ 382.1893, found 382.1890.



4h'

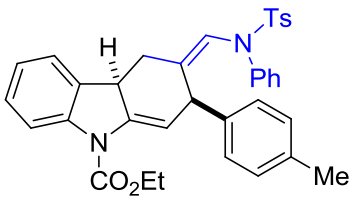
(*2R*,4aR*,Z*)-Ethyl 3-((2-oxopyrrolidin-1-yl)methylene)-2-(*p*-tolyl)-4,4a-dihydro-2*H*-carbazole-9(3*H*)-carboxylate (4h'): The representative procedure was followed using

vinyl indole **1c** (61 mg, 0.2 mmol) and allenamide **2b** (22 mg, 0.18 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 1:1 + 1% Et_3N) yielded **4h'** (63 mg, 75%) as a white solid (mp. = 148.8-149.4 °C).

^{1}H-NMR (300 MHz, CD_2Cl_2): 7.82 (d, *J* = 8.1 Hz, 1H), 7.30-7.24 (m, 2H), 7.17-7.05 (m, 5H), 6.34 (s, 1H), 6.03 (dd, *J* = 3.2 ,3.2 Hz, 1H), 4.76 (bs, 1H), 4.37 (dq, *J* = 7.1, 2.0 Hz, 2H), 4.03-3.94 (m, 1H), 3.51 (ddd, *J* = 9.6, 6.8, 6.8 Hz, 1H), 3.36 (ddd, *J* = 9.6, 7.2, 7.2 Hz, 1H), 3.03 (dd, *J* = 12.7, 4.8 Hz, 1H), 2.49 (dd, *J* = 11.9, 11.9 Hz, 1H), 2.39-2.30 (m, 2H, overlapping signal), 2.23 (s, 3H, overlapping signal), 2.02-1.90 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 174.5 (C), 152.8 (C), 143.0 (C), 142.3 (C), 141.1 (C), 136.4 (C), 131.9 (C), 129.9 (C), 129.5 (2 x CH), 128.2 (CH), 127.5 (2 x CH), 123.7 (CH), 123.4 (CH), 121.4 (CH), 115.8 (CH), 111.1 (CH), 62.5 (CH_2), 49.0 (CH_2), 43.3 (CH), 41.8 (CH), 34.1 (CH_2), 30.9 (CH_2), 21.0 (CH_3), 19.0 (CH_2), 14.6 (CH_3).

HR-MS (EI) calc. for $[C_{27}H_{28}N_2O_3]^+$ 428.2100, found 428.2106.



4i'

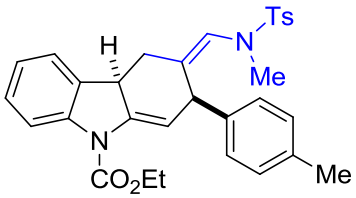
(*2R*,4aR*,Z*)-Ethyl 3-((4-methyl-*N*-phenylphenylsulfonamido)methylene)-2-(*p*-tolyl)-4,4a-dihydro-2*H*-carbazole-9(3*H*)-carboxylate (4i'): The representative procedure was followed using vinyl indole **1c** (31 mg, 0.1 mmol) and allenamide **2c** (26 mg, 0.18 mmol) at -70 ºC and C = 0.01M. Purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1 + 1% Et_3N) yielded **4i'** (43 mg, 81%) as a white solid (m.p. = 132.5-132.9 ºC, dec.)

^{1}H-NMR (300 MHz, $CDCl_3$): 7.82 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.25-7.17 (m, 7H), 7.11-7.06 (m, 3H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.31 (s, 1H), 5.87 (dd, *J* = 3.4 ,3.4 Hz, 1H), 4.59 (dd, *J* = 3.4 ,3.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.92-3.86 (m, 1H), 2.90 (dd, *J* = 12.4, 4.8 Hz, 1H), 2.48 (ddd, *J* = 12.4, 11.3 Hz, 1H, overlapping signal), 2.42 (s, 3H, overlapping signal), 2.27 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): 152.4 (C), 143.8 (C), 142.6 (C), 140.9 (C), 140.0 (C), 139.9 (C), 138.9 (C), 135.8 (C), 134.2 (C), 131.1 (C), 129.4 (2 x CH), 128.9 (2 x CH), 128.8 (2 x CH), 128.1 (CH), 127.9 (2 x CH), 127.6 (2 x CH), 126.9 (CH), 126.8 (2 x CH), 123.4

(CH), 122.80 (CH), 122.75 (CH), 115.6 (CH), 110.7 (CH), 62.1 (CH_2), 42.9 (CH), 40.9 (CH), 32.4 (CH_2), 21.6 (CH_3), 21.0 (CH_3), 14.5 (CH_3).

HR-MS (EI) calc. for $[C_{36}H_{34}N_2O_4S]^+$ 590.2239, found 590.2241.



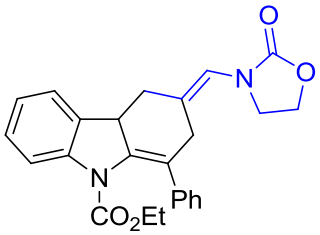
4j'

(*2R*,4aR*,Z*)-Ethyl 3-((*N*,4-dimethylphenylsulfonamido)methylene)-2-(*p*-tolyl)-4,4a-dihydro-2*H*-carbazole-9(3*H*)-carboxylate (4j'): The representative procedure was followed using vinyl indole **1c** (61 mg, 0.2 mmol) and allenamide **2d** (40 mg, 0.18 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 5:1 + 1% Et_3N) yielded **4j'** (95 mg, 98%) as a white solid (m.p. = 126.1-126.7 ºC, dec.).

^{1}H-NMR (300 MHz, CD_2Cl_2): 7.90 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.34-7.22 (m, 4H), 7.15-7.07 (m, 3H), 6.02 (bs, 1H), 5.32 (s, 1H), 5.13 (bs, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.07-3.94 (m, 1H), 2.84 (dd, *J* = 12.4, 4.8 Hz, 1H), 2.61 (s, 3H), 2.50-2.42 (m, 1H, overlapped signal), 2.48 (s, 3H, overlapping signal), 2.33 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 152.8 (C), 144.6 (C), 144.4 (C), 143.3 (C), 141.5 (C), 141.0 (C), 136.6 (C), 133.6 (C), 131.6 (C), 130.0 (2 x CH), 129.4 (2 x CH), 128.3 (4 x CH), 123.69 (CH), 123.68 (CH), 123.2 (CH), 115.9 (CH), 110.6 (CH), 62.5 (CH_2), 43.4 (CH), 41.7 (CH), 37.8 (CH_3), 31.9 (CH_2), 21.7 (CH_3), 21.0 (CH_3), 14.7 (CH_3) (a signal corresponding to a C(sp^2)-H is overlapped).

HR-MS (EI) calc. for $[C_{31}H_{32}N_2O_4S]^+$ 528.2083, found 528.2083.



4k'

(*Z*)-Ethyl 3-((2-oxooxazolidin-3-yl)methylene)-1-phenyl-4,4a-dihydro-2*H*-carbazole-9(3*H*)-carboxylate (4k'): The representative procedure was followed using

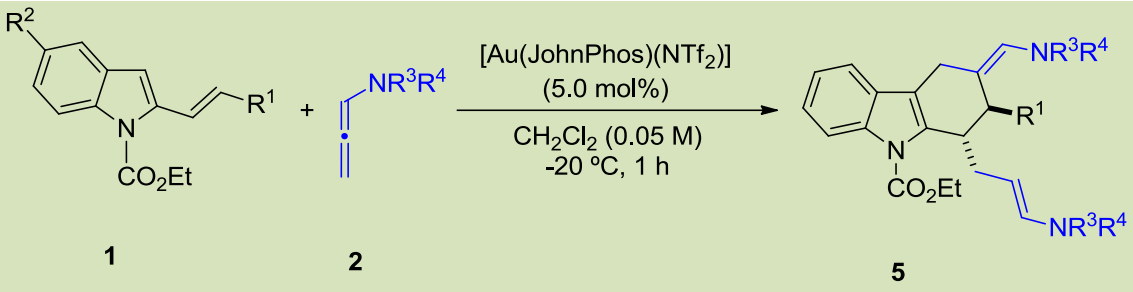
vinyl indole **1j** (29 mg, 0.1 mmol) and allenamide **2a** (11 mg, 0.09 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 1:1 + 1% Et_3N) yielded **4k'** (36 mg, 96%) as a white solid (m.p = 132.5-132.9 °C, dec).

^{1}H-NMR (300 MHz, CD_2Cl_2): 7.82 (d, *J* = 7.7 Hz, 1H), 7.40-7.22 (m, 7H), 7.13 (dt, *J* = 7.6, 1.1 Hz, 1H), 6.68 (bs, 1H), 4.85 (bs, 1H), 4.45-4.32 (m, 2H), 4.15-4.04 (m, 2H), 3.91-3.79 (m, 1H), 3.54-3.40 (m, 1H), 2.77 (dddd, *J* = 11.6, 11.6, 4.0, 4.0 Hz, 1H), 2.53-2.44 (m, 2H), 2.33-2.23 (m, 1H), 0.82 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 157.4 (C), 152.0 (C), 142.9 (C), 142.7 (C), 135.9 (C), 133.4 (C), 128.7 (2 x CH), 128.0 (CH), 126.9 (CH), 126.6 (2 x CH), 124.8 (C), 124.3 (CH), 123.1 (C), 122.7 (CH), 122.0 (CH), 116.2 (CH), 62.9 (CH_2), 62.1 (CH_2), 45.3 (CH_2), 42.1 (CH), 31.5 (CH_2), 30.4 (CH_2), 14.0 (CH_3).

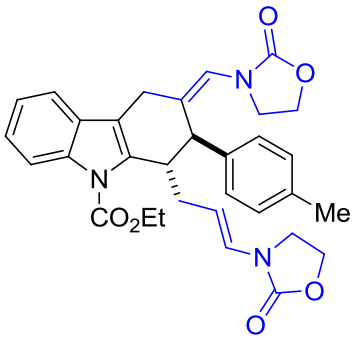
HR-MS (EI) calc. for $[C_{25}H_{24}N_2O_4]^+$ 416.1736, found 416.1738.

Gold-catalyzed multicomponent cycloadditions of vinyl indoles 1 with allenamides 2: Synthesis of tetrahydrocarbazole derivatives 5.



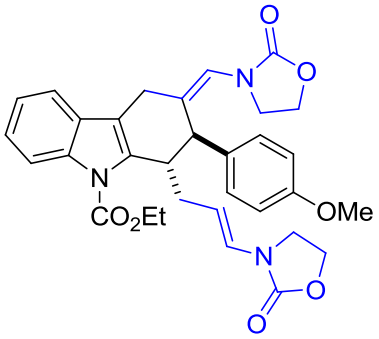
1 **2** **5**

Representative procedure: (*1S*,2R*,Z*)-Ethyl 1-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-3-((2-oxooxazolidin-3-yl)methylene)-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (5a):



5a

To a solution of the vinyl indole **1c** (61 mg, 0.2 mmol) and [Au(JohnPhos)(NTf_2)] (7.5 mg, 5.0 mol%) in CH_2Cl_2 at -20 ºC (0.1 M) was added dropwise via syringe a solution of **2a** (63 mg, 0.5 mmol) in CH_2Cl_2 (0.1 M, final concentration of **1c** ca. 0.05 M). The mixture was stirred at the same temperature until disappearance of the starting reagents (checked by TLC; 1 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO_2, CH_2Cl_2:EtOAc = 99:1 + 1% Et_3N) to yield **5a** (105 mg, 95%) as a yellow solid. Appropriate crystals for X-Ray analysis were obtained by slow diffusion of Et_2O in a solution of **5a** in CH_2Cl_2 at -20 ºC. The crystallographic data with the number **CCDC 924119** are available free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.uk/data_request/cif. (Spectroscopic data were in agreement with those reported above).



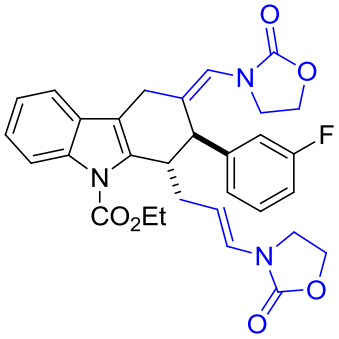
5b

(*1S*,2R*,Z*)-Ethyl 2-(4-methoxyphenyl)-1-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-3-((2-oxooxazolidin-3-yl)methylene)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (5b): The representative procedure was followed using vinyl indole **1d** (64 mg, 0.2 mmol) and allenamide **2a** (63 mg, 0.5 mmol). Purification by flash chromatography (SiO_2, CH_2Cl_2:EtOAc = 99:1 + 1% Et_3N) yielded **5b** (114 mg, 99%) as a white solid (m.p = 103.6-104.4 ºC).

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.13 (d, *J* = 8.1 Hz, 1H), 7.38 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.33-7.21 (m, 4H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 14.1 Hz, 1H), 6.61 (s, 1H), 5.02 (ddd, *J* = 14.1, 9.2, 5.7 Hz, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 4.46-4.40 (m, 4H), 4.32 (s, 1H), 4.24 (d, *J* = 9.2 Hz, 1H), 4.14-4.05 (m, 1H), 3.83 (q, *J* = 8.3 Hz, 1H), 3.76-3.69 (m, 2H, overlapped signal), 3.73 (s, 3H, overlapped signal), 3.42 (d, *J* = 18.6 Hz, 1H), 3.34 (dd, *J* = 18.6, 1.9 Hz, 1H), 2.69 (ddd, *J* = 14.1, 5.0, 2.2 Hz, 1H), 2.27 (td, *J* = 14.1, 9.3 Hz, 1H), 1.56 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 158.6 (C), 158.2 (C), 155.6 (C), 152.2 (C), 137.0 (C), 136.6 (C), 133.6 (C), 129.1 (C), 128.7 (2 x CH), 126.7 (CH), 125.9 (C), 124.4 (2 x CH), 123.2 (CH), 118.2 (CH), 116.2 (2 x CH), 116.1 (C), 114.0 (CH), 109.3 (CH), 63.6 (CH_2), 62.8 (CH_2), 62.7 (CH_2), 55.5 (CH_3), 47.5 (CH_2), 43.0 (CH_2), 42.2(CH), 40.5 (CH), 36.2 (CH_2), 26.8 (CH_2), 14.6 (CH_3).

HR-MS (EI) calc. for $[C_{32}H_{33}N_3O_7]^+$ 571.2319, found 571.2325.



5c

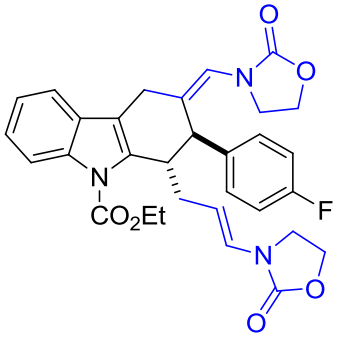
(*1S*,2R*,Z*)-Ethyl 2-(3-fluorophenyl)-1-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-3-((2-oxooxazolidin-3-yl)methylene)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (5c): The representative procedure was followed using vinyl indole **1e** (62 mg, 0.2 mmol) and allenamide **2a** (63 mg, 0.5 mmol). Purification by flash chromatography (SiO_2, CH_2Cl_2:EtOAc = 99:1 + 1% Et_3N) yielded **5c** (97 mg, 87%) as a white solid (m.p = 162.8-163.5 ºC).

^{1}H-NMR (400 MHz, CD_2Cl_2): 8.13 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.27-7.17 (m, 3H), 7.13 (d, *J* = 10.7 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 14.3 Hz, 1H), 6.62 (s, 1H), 5.01 (ddd, *J* = 14.3, 9.3, 5.5 Hz, 1H), 4.57 (q, *J* = 7.2 Hz, 2H), 4.52-4.41 (m, 4H), 4.37 (s, 1H), 4.25 (d, *J* = 9.2 Hz, 1H), 4.04 (q, *J* = 8.8 Hz, 1H), 3.82 (q, *J* = 8.8 Hz, 1H), 3.77-3.67 (m, 2H), 3.43 (d, *J* = 18.7 Hz, 1H), 3.37 (dd, *J* = 18.7, 2.3 Hz, 1H), 2.71 (ddd, *J* = 14.2, 5.3, 2.5 Hz, 1H), 2.26 (td, *J* = 14.2, 9.5 Hz, 1H), 1.56 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, CD_2Cl_2): 162.9 (d, *J* = 243.7 Hz, C), 157.69 (C), 155.25 (C), 151.81 (C), 144.32 (d, *J* = 6.6 Hz, C), 136.29 (C), 136.17 (C), 129.76 (d, *J* = 8.1 Hz, CH), 128.57 (C), 125.71 (CH), 125.47 (C), 124.18 (CH), 123.49 (CH), 123.16 (CH), 122.86 (CH), 117.90 (CH), 115.87 (CH), 115.70 (C), 114.53 (d, *J* = 22.2 Hz, CH), 113.22 (d, *J* = 21.2 Hz, CH), 108.69 (CH), 63.25 (CH_2), 62.37 (2 x CH_2), 47.02 (CH_2), 42.62 (CH_2), 42.38 (CH), 39.98 (CH), 35.76 (CH_2), 26.40 (CH_2), 14.24 (CH_3).

^{19}F-NMR (282 MHz, CD_2Cl_2): -113.74 (s).

HR-MS (EI) calc. for $[C_{31}H_{30}FN_3O_6]^+$ 559.2119, found 559.2125.



5d

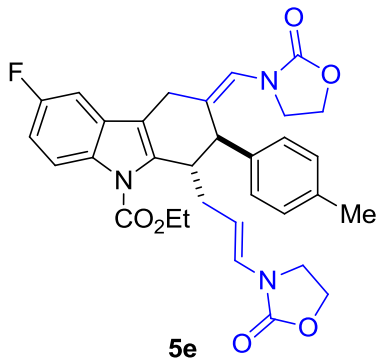
(*1S*,2R*,Z*)-Ethyl 2-(4-fluorophenyl)-1-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-3-((2-oxooxazolidin-3-yl)methylene)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (5d): The representative procedure was followed using vinyl indole **1f** (31 mg, 0.1 mmol) and allenamide **2a** (31 mg, 0.25 mmol). Purification by flash chromatography (SiO_2, CH_2Cl_2:EtOAc = 99:1 + 1% Et_3N) yielded **5d** (52 mg, 93%) as a white solid (m.p = 141.8-142.5 ºC).

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.12 (d, *J* = 8.0 Hz, 1H), 7.40-7.34 (m, 3H), 7.30 (ddd, *J* = 8.0, 7.3, 1.5 Hz, 1H), 7.24 (ddd, *J* = 7.5, 7.3, 1.2 Hz, 1H), 6.94 (dd, *J* = 8.8, 8.7 Hz, 2H), 6.71 (d, *J* = 14.3 Hz, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 5.00 (ddd, *J* = 14.3, 9.2, 5.5 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 4.54-4.41 (m, 4H), 4.34 (s, 1H), 4.22 (d, *J* = 9.4 Hz, 1H), 4.04 (ddd, *J* = 8.8, 8.8, 6.7 Hz, 1H), 3.82 (ddd, *J* = 8.8, 8.8, 7.8 Hz, 1H), 3.75-3.60 (m, 2H), 3.41 (d, *J* = 18.5 Hz, 1H), 3.31 (dd, *J* = 18.5, 2.3 Hz, 1H), 2.70 (dddd, *J* = 14.1, 5.4, 4.4, 1.7 Hz, 1H), 2.24 (ddd, *J* = 14.2, 9.3, 9.3 Hz, 1H), 1.55 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 161.5 (d, *J* = 242.3 Hz, C), 157.7 (C), 155.3 (C), 151.8 (C), 137.2 (d, *J* = 2.3 Hz, C), 136.4 (C), 136.2 (C), 129.1 (d, *J* = 8.3 Hz, 2 x CH), 128.6 (C), 126.4 (C), 125.6 (CH), 124.2 (CH), 123.0 (CH), 122.9 (CH), 117.90 (CH), 115.9 (CH), 115.7 (C) 115.0 (d, *J* = 21.2 Hz, 2 x CH), 108.8 (CH), 63.2 (CH_2), 62.4 (2 x CH_2), 47.1 (CH_2), 42.6 (CH_2), 41.9 (CH), 40.1 (CH), 35.8 (CH_2), 26.4 (CH_2), 14.2 (CH_3).

^{19}F-NMR (282 MHz, CD_2Cl_2): -117.41 (s).

HR-MS (EI) calc. for $[C_{31}H_{30}FN_3O_6]^+$ 559.2119, found 559.2122.



5e

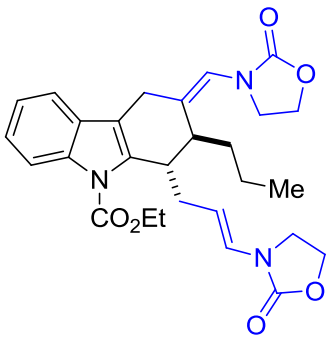
(1*S,2*R**,*Z*)-Ethyl 6-fluoro-1-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-3-((2-oxooxazolidin-3-yl)methylene)-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (5e)**: The representative procedure was followed using vinyl indole **1g** (65 mg, 0.2 mmol) and allenamide **2a** (63 mg, 0.5 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc:CH_2Cl_2 = 1:2:1 + 1% Et_3N) yielded **5e** (105 mg, 92%) as a white solid (m.p. = 132.8-133.9 ºC).

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.08 (ddd, *J* = 8.6, 4.6, 0.9 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.10-6.97 (m, 4H), 6.71 (d, *J* = 14.5 Hz, 1H), 6.65 (bs, 1H), 5.01 (ddd, *J* = 14.5, 9.2, 5.6 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 4.52-4.40 (m, 4H), 4.33 (s, 1H), 4.24 (ddd, *J* = 9.3, 2.3, 2.3 Hz, 1H), 4.07 (ddd, *J* = 8.9, 8.9, 6.1 Hz, 1H), 3.82 (ddd, *J* = 8.9, 8.9, 7.6 Hz, 1H), 3.77-3.68 (m, 2H), 3.34 (bs, 2H), 2.70 (dddd, *J* = 14.1, 4.4, 2.2, 1.7 Hz, 1H), 2.32-2.20 (m, 1H, overlapped signal), 2.27 (s, 3H, overlapped signal), 1.55 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 159.3 (d, *J* = 239.6 Hz, C), 157.8 (C), 155.2 (C), 151.5 (C), 138.6 (C), 138.1 (C), 136.2 (C), 132.5 (C), 129.7 (d, *J* = 9.2 Hz, C), 129.1 (2 x CH), 127.1 (2 x CH), 125.7 (CH), 125.2 (C), 123.3 (CH), 116.9 (d, *J* = 9.0 Hz, CH), 115.4 (d, *J* = 3.7 Hz, C), 111.3 (d, *J* = 24.8 Hz, CH), 108.7 (CH), 103.6 (d, *J* = 23.5 Hz, CH), 63.4 (CH_2), 62.41 (CH_2), 62.35 (CH_2), 47.0 (CH_2), 42.6 (CH_2), 42.0 (CH), 40.0 (CH), 35.7 (CH_2), 26.3 (CH_2), 20.5 (CH_3), 14.2 (CH_3).

^{19}F-NMR (282 MHz, CD_2Cl_2): -121.16 (s).

HR-MS (EI) calc. for $[C_{32}H_{32}FN_3O_6]^+$ 573.2275, found 573.2280.



3*Z*-5f

(*1S*,2S*,Z*)-Ethyl 1-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-3-((2-oxooxazolidin-3-yl)methylene)-2-propyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (5f): The representative procedure was followed using vinyl indole **1h** (52 mg, 0.2 mmol) and allenamide **2a** (63 mg, 0.5 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc:CH_2Cl_2 = 1:2:1 + 1% Et_3N) yielded a separable mixture of **(3*Z*)-5f** (69 mg, clear oil) and **(3*E*)-5f** (24 mg, clear oil) in a combined yield of 92% (*Z*/*E* = 2.8:1).

Spectroscopic Data for **(3*Z*)-5f**:

^{1}H-NMR (400 MHz, CD_2Cl_2): 8.13 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.34-7.24 (m, 2H), 6.62 (d, *J* = 14.6 Hz, 1H), 6.41 (d, *J* = 2.2 Hz, 1H), 4.93 (ddd, *J* = 14.6, 9.2, 5.6 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 4.50-4.40 (m, 4H), 4.01 (dd, *J* = 8.8, 6.2 Hz 1H), 3.81-3.67 (m, 3H), 3.58 (d, *J* = 9.8 Hz, 1H), 3.49 (dd, *J* = 18.4, 2.2 Hz, 1H), 3.35 (d, *J* = 18.4 Hz, 1H), 3.00 (dt, *J* = 7.3, 1.7 Hz, 1H), 2.54 (dddd, *J* = 14.2, 5.2, 4.6, 2.3 Hz, 1H), 2.09 (dd, *J* = 14.2, 9.4 Hz, 1H), 1.52 (t, *J* = 7.1 Hz, 3H, overlapped signal), 1.55-1.30 (m, 4H, overlapped signal), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (100 MHz, CD_2Cl_2): 157.6 (C), 155.2 (C), 151.7 (C), 136.9 (C), 136.2 (C), 128.9 (C), 127.9 (C), 125.1 (CH), 123.9 (CH), 122.6 (CH), 121.1 (CH), 117.8 (CH), 115.8 (CH), 115.2 (C), 109.3 (CH), 63.0 (CH_2), 62.3 (CH_2), 62.2 (CH_2), 47.2 (CH_2), 42.7 (CH_2), 40.5 (CH), 38.2 (CH), 35.6 (CH_2), 34.4 (CH_2), 26.0 (CH_2), 21.2 (CH_2), 14.2 (CH_3), 14.1 (CH_3).

HR-MS (EI) calc. for $[C_{28}H_{33}N_3O_6]^+$ 507.2369, found 507.2366.

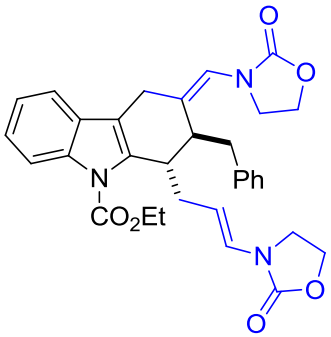
Spectroscopic Data for **(3*E*)-5f**:

^{1}H-NMR (400 MHz, CD_2Cl_2): 8.19 (d, *J* = 7.4 Hz, 1H), 7.59 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.34-7.27 (m, 2H), 6.71 (d, *J* = 14.3 Hz, 1H), 6.33 (s, 1H), 4.90 (ddd, *J* = 14.3, 8.7, 6.2 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 4.44 (dd, *J* = 8.3, 7.8 Hz, 2H), 4.20 (ddd, *J* = 8.7, 8.7, 4.1 Hz, 1H), 4.14-4.07 (m, 1H), 3.70 (dd, *J* = 9.3, 7.1 Hz, 2H), 3.48-3.41 (m, 2H), 3.27 (q, *J* = 9.1 Hz, 1H), 2.66 (dd, *J* = 12.8, 2.8 Hz, 1H), 2.56 (ddd, *J* = 13.7, 8.7, 2.1 Hz,

1H), 2.24-2.09 (m, 3H), 1.53 (t, *J* = 7.2 Hz, 3H, overlapped signal), 1.55-1.30 (m, 4H, overlapped signal), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, CD_2Cl_2): 157.8 (C), 155.2 (C), 151.6 (C), 141.3 (C), 136.4 (C), 127.3 (C), 125.6 (CH), 124.1 (CH), 123.3 (CH), 120.9 (C), 119.7 (CH), 118.8 (CH), 116.0 (CH), 115.2 (C), 108.8 (CH), 63.5 (CH_2), 62.6 (CH_2), 62.3 (CH_2), 46.4 (CH_2), 42.6 (CH_2), 41.0 (CH), 35.8 (CH), 35.6 (CH_2), 35.3 (CH_2), 31.8 (CH_2), 20.2 (CH_2), 14.2 (CH_3), 14.1 (CH_3).

HR-MS (EI) calc. for $[C_{28}H_{33}N_3O_6]^+$ 507.2369, found 507.2376.



(3*Z*)-5g

(*1S*,2R*,Z*)-Ethyl 2-benzyl-1-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-3-((2-oxooxazolidin-3-yl)methylene)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (5g): The representative procedure was followed using vinyl indole **1i** (61 mg, 0.2 mmol) and allenamide **2a** (63 mg, 0.5 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc: CH_2Cl_2 = 1:2:1 + 1% Et_3N) yielded a separable mixture of **(3*Z*)-5g** (44 mg, clear oil) and **(3*E*)-5g** (29 mg, clear oil) in a combined yield of 66% (*Z*/*E* = 1.5:1).

Spectroscopic Data for **(3*Z*)-5g**:

^{1}H-NMR (300 MHz, CD_2Cl_2): 8.20 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.52 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.36-7.27 (m, 4H), 7.25-7.21 (m, 1H), 7.17 (dd, *J* = 8.2, 1.4 Hz, 2H), 6.54 (d, *J* = 14.3 Hz, 1H), 6.30 (d, *J* = 2.0 Hz, 1H), 4.62 (ddd, *J* = 14.3, 9.6, 5.4 Hz, 1H), 4.50-4.30 (m, 6H), 3.74-3.68 (m, 2H), 3.61-3.44 (m, 4H), 3.33 (ddd, *J* = 8.8, 8.8, 6.6 Hz, 1H), 3.19 (dd, *J* = 8.0, 7.0 Hz, 1H), 3.04 (dd, *J* = 13.3, 6.3 Hz, 1H), 2.67 (dd, *J* = 13.3, 8.9 Hz, 1H), 2.48 (dddd, *J* = 14.0, 7.6, 5.1, 2.7 Hz, 1H), 2.00 (ddd, *J* = 14.0, 9.6, 9.6 Hz, 1H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 157.3 (C), 155.2 (C), 151.6 (C), 140.6 (C), 136.5 (C), 136.4 (C), 129.4 (2 x CH), 128.9 (C), 128.2 (2 x CH), 128.0 (C), 126.1 (CH), 125.0 (CH), 124.0 (CH), 122.8 (CH), 121.4 (CH), 117.9 (CH), 115.9 (CH), 115.0 (C), 109.1

(CH), 63.0 (CH_2), 62.3 (CH_2), 62.2 (CH_2), 46.8 (CH_2), 42.5 (CH_2), 41.0 (CH), 39.3 (CH), 38.1 (CH_2), 35.6 (CH_2), 26.2 (CH_2), 14.1 (CH_3).

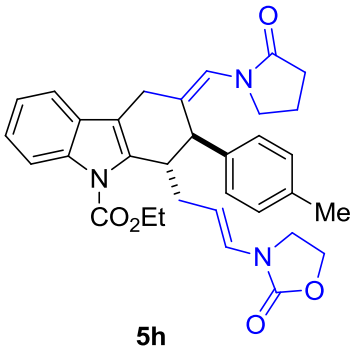
HR-MS (EI) calc. for $[C_{32}H_{33}N_3O_6]^+$ 555.2369, found 555.2375.

Spectroscopic Data for **(3*E*)-5g**:

^{1}H-NMR (400 MHz, CD_2Cl_2): 8.23 (d, *J* = 7.3 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.40-7.30 (m, 4H), 7.27-7.23 (m, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.64 (d, *J* = 14.3 Hz, 1H), 6.34 (s, 1H), 4.59 (ddd, *J* = 14.3, 8.8, 6.0 Hz, 1H, overlapped signal), 4.53-4.38 (m, 4H, overlapped signal), 4.27 (ddd, *J* = 8.7, 8.7, 4.2 Hz, 1H), 4.16 (q, *J* = 8.7 Hz, 1H), 3.60-3.45 (m, 4H), 3.42 (q, *J* = 9.0 Hz, 1H), 2.80-2.61 (m, 3H), 2.52-2.44 (m, 2H), 2.26 (dd, *J* = 13.0, 3.8 Hz, 1H), 2.13 (ddd, *J* = 14.6, 9.3, 9.3 Hz, 1H), 1.46 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, CD_2Cl_2): 157.7 (C), 155.1 (C), 151.5 (C), 140.7 (C), 140.6 (C), 136.6 (C), 129.3 (2 x CH), 128.2 (2 x CH), 127.3 (C), 126.0 (CH), 125.5 (CH), 124.3 (CH), 123.3 (CH), 120.7 (C), 119.6 (CH), 119.2 (CH), 116.0 (CH), 115.3 (C), 108.6 (CH), 63.5 (CH_2), 62.6 (CH_2), 62.2 (CH_2), 46.5 (CH_2), 42.5 (CH_2), 39.3 (CH), 39.2 (CH_2), 38.2 (CH), 35.6 (CH_2), 32.3 (CH_2), 14.1 (CH_3).

HR-MS (EI) calc. for $[C_{32}H_{33}N_3O_6]^+$ 555.2369, found 555.2377.



5h

(*1S*,2R*,Z*)-Ethyl 1-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-3-((2-oxopyrrolidin-1-yl)methylene)-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (5h): To a solution of the vinyl indole **1c** (61 mg, 0.2 mmol) and [Au(JohnPhos)(NTf_2)] (7.8 mg, 5.0 mol%) in CH_2Cl_2 at -20 ºC (0.1 M) was added dropwise via syringe a solution of **2b** (24 mg, 0.2 mmol) in CH_2Cl_2 (0.1 M). The mixture was stirred at the same temperature for 4.5 h. Then, a solution of **2a** (28 mg, 0.22 mmol) in CH_2Cl_2 (0.1M) was added and the resulting mixture was stirred 48 h at -20 ºC. The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO_2,

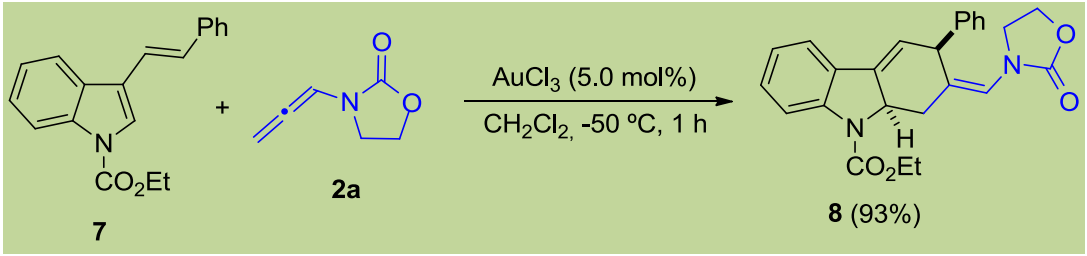
hexane:EtOAc: CH_2Cl_2 = 1:2:1 + 1% Et_3N) to yield **5h** (86 mg, 78%, inseparable *Z/E* mixture, *Z*:*E* = 4:1) as a white solid (m.p = 113.6-114.2 ºC of the mixture).

^{1}H-NMR (400 MHz, CD_2Cl_2, Major isomer): 8.12 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.32-7.20 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H), 6.66 (d, *J* = 14.6 Hz, 1H), 4.97 (ddd, *J* = 14.6, 9.3, 5.6 Hz, 1H), 4.56 (q, *J* = 7.2 Hz, 2H), 4.49-4.34 (m, 2H), 4.32 (s, 1H), 4.25 (d, *J* = 9.2 Hz, 1H), 3.92 (ddd, *J* = 14.7, 7.8, 7.8 Hz, 1H), 3.77-3.63 (m, 3H), 3.42 (d, *J* = 18.6 Hz, 1H), 3.36 (dd, *J* = 18.6, 1.5 Hz, 1H), 2.69-2.59 (m, 2H), 2.47-2.25 (m, 2H, overlapped signal), 2.27 (m, 3H, overlapped signal), 2.16-2.08 (m, 2H), 1.56 (t, *J* = 7.2 Hz, 3H). Minor isomer (only assignable signals are listed): 6.88 (d, *J* = 14.5 Hz, 1H), 5.07 (ddd, *J* = 14.5, 9.3, 5.4 Hz, 1H), 4.33 (s, 1H), 3.55 (ddd, *J* = 7.8, 7.8, 1.4 Hz, 1H).

^{13}C-NMR (75 MHz, CD_2Cl_2, Major isomer): 175.7 (C), 155.1 (C), 151.8 (C), 138.6 (C), 136.8 (C), 136.2 (C), 136.0 (C), 129.0 (2 x CH), 128.7 (C), 127.2 (2 x CH), 125.5 (CH), 124.2 (CH), 124.0 (CH), 123.6 (CH), 117.8 (CH), 115.9 (C), 115.8 (CH), 108.9 (CH), 63.1 (CH_2), 62.3 (CH_2), 49.7 (CH_2), 42.6 (CH_2), 42.5 (CH), 39.9 (CH), 35.7 (CH_2), 30.2 (CH_2), 26.7 (CH_2), 20.6 (CH_3), 19.1 (CH_2), 14.3 (CH_3). Minor isomer (only assignable signals are listed): 175.6 (C), 172.5 (C), 125.4 (CH), 123.8 (CH), 123.4 (CH), 122.8 (CH), 109.6 (CH), 45.2 (CH_2), 35.9 (CH_2), 31.1 (CH_2), 20.8 (CH_3), 17.5 (CH_2), 14.0 (CH_3).

HR-MS (EI) calc. for $[C_{33}H_{35}N_3O_5]^+$ 553.2577, found 553.2584 (of the mixture).

Gold-catalyzed reactions with 3-vinyl indole 7: Synthesis of tetrahydrocarbazole derivatives 8-9.

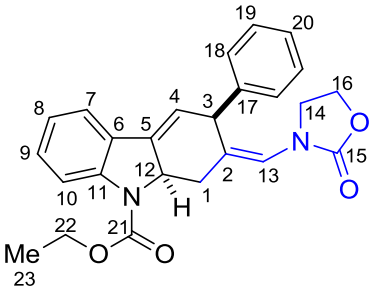


(*3S*,9aR*,Z*)-Ethyl 2-((2-oxooxazolidin-3-yl)methylene)-3-phenyl-2,3-dihydro-1*H*-carbazole-9(9a*H*)-carboxylate (8): To a solution of the 3-vinyl indole **7** (58 mg, 0.2 mmol) and $AuCl_3$ (3.0 mg, 5.0 mol%) in CH_2Cl_2 at -50 ºC (0.1 M) was added dropwise via syringe a solution of **2a** (23 mg, 0.18 mmol) in CH_2Cl_2 (0.1 M, final concentration ca. 0.05 M). The mixture was stirred at the same temperature until disappearance of the starting reagents (checked by TLC; 1 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO_2, hexane:EtOAc = 1:1 + 1% Et_3N) to yield **8** (70 mg, 93%) as a white solid (m.p. = 161.8-162.5 ºC).

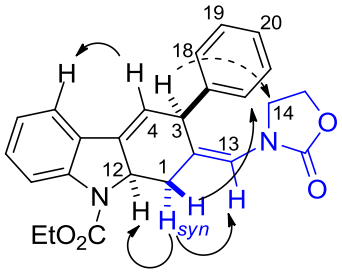
^{1}H-NMR (300 MHz, CD_2Cl_2): 7.88 (bs, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.37-7.20 (m, 6H), 7.0 (ddd, *J* = 7.5, 7.5, 0.8 Hz, 1H), 6.33 (bs, 1H), 5.94 (dd, *J* = 2.8, 2.8 Hz, 1H), 4.76-4.70 (m, 1H), 4.70 (d, *J* = 2.8 Hz, 1H), 4.44-4.32 (m, 2H), 4.24-4.14 (m, 2H), 3.58 (ddd, *J* = 8.8, .8.8, 6.3 Hz, 1H), 3.59-3.48 (m, 1H), 3.40 (ddd, *J* = 8.8, 8.8, 6.3 Hz, 1H), 2.50 (dd, *J* = 11.5, 11.4 Hz, 1H), 1.43 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, CD_2Cl_2): 156.8 (C), 154.0 (C), 145.0 (C), 144.6 (C), 137.2 (C), 129.7 (CH), 129.2 (2 x CH), 128.7 (C), 128.1 (C), 127.6 (2 x CH), 127.0 (CH), 123.2 (CH), 123.1 (CH), 120.3 (CH), 119.8 (CH), 115.7 (CH), 62.7 (CH_2), 62.3 (CH), 62.2 (CH_2), 46.1 (CH_2), 42.9 (CH), 36.6 (CH_2), 14.8 (CH_3).

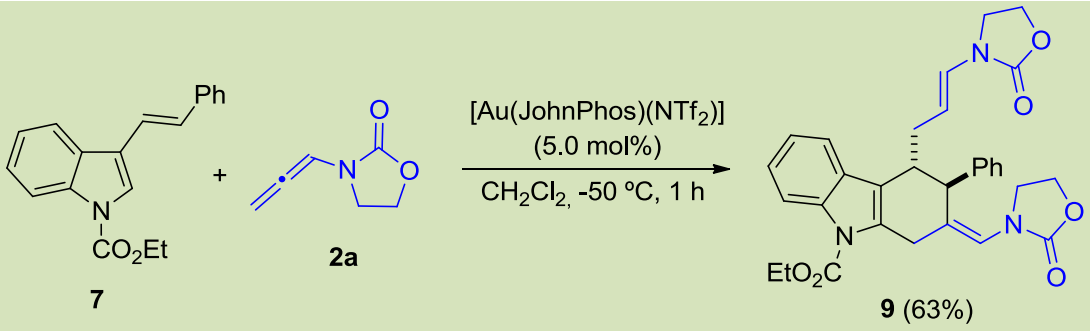
HR-MS (EI) calc. for $[C_{25}H_{24}N_2O_4]^+$ 416.1736, found 416.1740.



8



Site	^{13}C-NMR	^{1}H-NMR	COSY	HMBC	NOESY (selected)
1	36.6 (CH_2)	**H1 *syn***; 2.50 (dd, *J* = 11.5, 11.4 Hz) **H1 *anti***; 3.59-3.48 (m)	H1 *anti*, H12, H13 H1 *syn*, H12	C12, C2, C13 C12, C13	H18 H12, H13
2	128.7 (C)				
3	42.9 (CH)	**H3**; 4.70 (d, *J* = 2.8 Hz)	H4, H13($^4J_{allyl}$)	C4, C18, C17, C5	H4, H14
4	119.8 (CH)	**H4**; 5.94 (dd, *J* = 2.8, 2.8 Hz)	H3, H12	C3, C12, C17, C2	H3, H7
5	137.2 (C)				
6	128.1 (C)				
7	120.3 (CH)	**H7**; 7.38 (d, *J* = 7.5 Hz)	H8	C9, C5, C11	H4
8	123.1 (CH)	**H8**; 7.0 (ddd, *J* = 7.5, 7.5, 0.8 Hz)	H7	C10, C6,	
9	127.0 (CH)	7.37-7.20 (m, 6H)			
10	115.7 (CH)	**H10**; 7.88 (bs)			
11	145.0 (C)				
12	62.3 (CH)	**H12**; 4.76-4.70 (m)	H1 syn/anti, H4	C1, C4, C5	
13	123.2 (CH)	**H13**; 6.33 (bs, 1H)	H1 *syn*, H3($^4J_{allyl}$)	C1, C3, C14, C15, C2	
14	46.1 (CH_2)	**H14**; 3.58 (ddd, *J* = 8.8, .8.8, 6.3 Hz) **H14'**; 3.40 (ddd, *J* = 8.8, 8.8, 6.3 Hz)	H14', H16 H14,H16	C15, C16 C15, C16	
15	156.8 (C)				
16	62.7 (CH_2)	**H16**; 4.24-4.14 (m, 2H)	H14, H14'	C14, C15	
17	144.6 (C)				
18	127.6 (CH)	7.37-7.20 (m, 6H)			
19	129.2 (CH)	7.37-7.20 (m, 6H)			
20	129.7 (CH)	7.37-7.20 (m, 6H)			
21	154.0 (C)				
22	62.2 (CH_2)	**H22**; 4.44-4.32 (m, 2H)	H23	C23	
23	14.8 (CH_3)	**H23**; 1.43 (t, *J* = 7.1 Hz)	H22	C22	



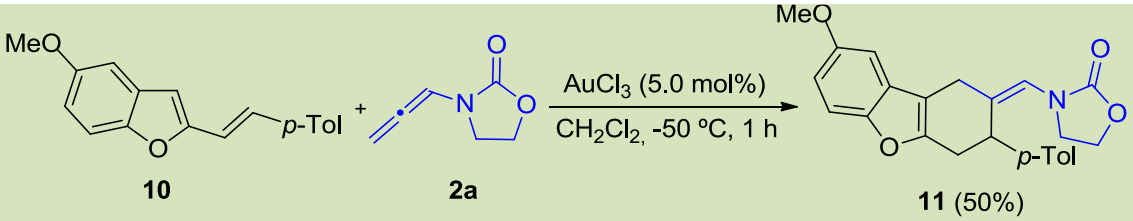
(*3S*,4R*,Z*)-Ethyl 4-((*E*)-3-(2-oxooxazolidin-3-yl)allyl)-2-((2-oxooxazolidin-3-yl)methylene)-3-phenyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (9): To a solution of the vinyl indole **7** (58 mg, 0.2 mmol) and [Au(JohnPhos)(NTf_2)] (7.5 mg, 5.0 mol%) in CH_2Cl_2 at -20 ºC (0.1 M) was added dropwise via syringe a solution of **2a** (64 mg, 0.5 mmol) in CH_2Cl_2 (0.1 M, final concentration ca. 0.05 M). The mixture was stirred at the same temperature until disappearance of the starting reagents (checked by TLC; 1 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO_2, hexane:EtOAc = 1:1 + 1% Et_3N) to yield **9** (68 mg, 63%) as a yellow oil.

^{1}H-NMR (400 MHz, CD_2Cl_2): 8.19-8.15 (m, 1H), 7.57-7.53 (m, 1H), 7.34-7.14 (m, 7H), 6.71 (d, *J* = 14.1 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H), 4.95 (ddd, *J* = 14.1, 8.8, 6.3 Hz, 1H), 4.53-4.35 (m, 6H), 4.30 (bs, 1H), 4.14-4.06 (m, 1H), 3.90-3.83 (m, 2H), 3.69-3.58 (m, 4H), 2.63 (dddd, *J* = 15.1, 4.9, 4.9, 1.7 Hz, 1H), 2.42 (ddd, *J* = 15.1, 8.6, 8.6 Hz, 1H), 1.47 (t, *J* = 7.1 Hz, 3H) (trans configuration was established based on the nOe observed between the benzyl H and the exocyclic CH_2).

^{13}C-NMR (100 MHz, CD_2Cl_2): 157.7 (C), 155.2 (C), 151.7 (C), 141.4 (C), 136.3 (C), 133.6 (C), 128.8 (C), 128.4 (2 x CH), 127.2 (2 x CH), 126.9 (CH), 126.4 (CH), 126.0 (C), 125.3 (CH), 123.8 (CH), 123.6 (C), 122.6 (CH), 118.0 (CH), 115.7 (CH), 108.9 (CH), 63.1 (CH_2), 62.4 (CH_2), 62.3 (CH_2), 47.0 (CH_2), 42.5 (CH_2 + CH), 37.5 (CH), 36.4 (CH_2), 31.2 (CH_2), 14.1 (CH_3).

HR-MS (EI) calc. for $[C_{31}H_{31}N_3O_6]^+$ 541.2213, found 541.2219.

Gold-catalyzed reactions with 2-vinyl benzofuran 10: Synthesis of benzofuran derivative 11.

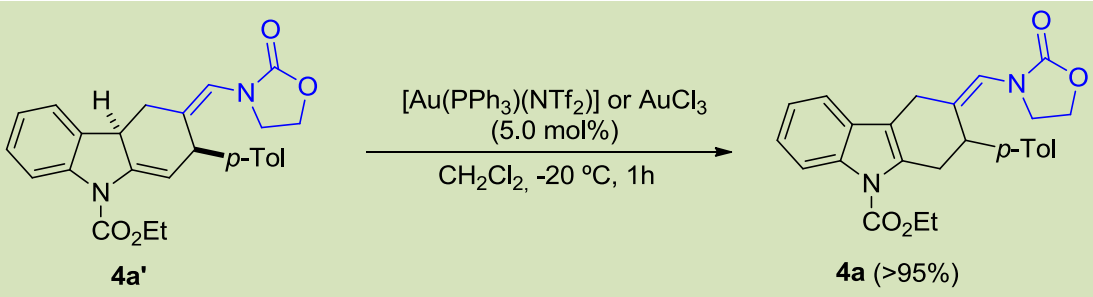


(*Z*)-3-((8-Methoxy-3-(*p*-tolyl)-3,4-dihydrodibenzo[*b,d*]furan-2(1*H*)-ylidene)methyl) oxazolidin-2-one (11): To a solution of the benzofuran **10** (53 mg, 0.20 mmol) and $AuCl_3$ (3.0 mg, 5.0 mol%) in CH_2Cl_2 at -20 ºC (0.1 M) was added dropwise via syringe a solution of **2a** (23 mg, 0.18 mmol) in CH_2Cl_2 (0.1 M, final concentration ca. 0.05 M). The mixture was stirred at the same temperature until disappearance of the starting reagents (checked by TLC; 1 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO_2, hexane:EtOAc = 1:1) to yield **11** (39 mg, 50%) as a white solid (m.p. = 169.8-170.2 ºC, dec.).

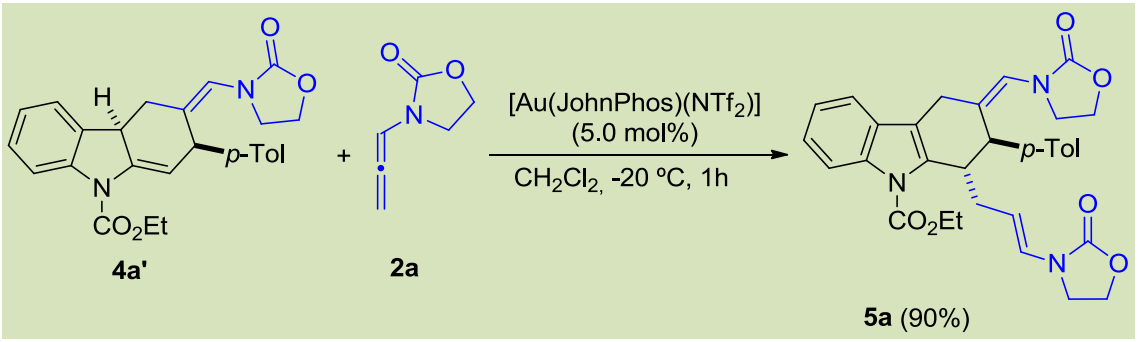
^{1}H-NMR (300 MHz, $CDCl_3$): 7.31 (d, *J* = 9.5 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.84-6.75 (m, 2H), 6.22 (s, 1H), 4.50-4.39 (m, 3H), 3.89 (dd, *J* = 9.0, 7.7 Hz, 2H), 3.81 (s, 3H), 3.36-3.30 (m, 2H), 3.20-3.13 (m, 2H), 2.27 (s, 3H).
^{13}C-NMR (75 MHz, $CDCl_3$): 157.8 (C), 156.0 (C), 153.1 (C), 150.1 (C), 138.0 (C), 136.5 (C), 133.4 (C), 129.5 (2 x CH), 128.6 (C), 127.0 (2 x CH), 119.9 (CH), 112.2 (C), 111.7 (CH), 111.6 (CH), 101.7 (CH), 62.4 (CH_2), 56.2 (CH_3), 47.5 (CH_2), 38.6 (CH), 28.4 (CH_2), 25.6 (CH_2), 21.1 (CH_3).
HR-MS (EI) calc. for $[C_{24}H_{23}NO_4]^+$ 389.1627, found 389.1631.

Additional experiments and mechanistic rationale.

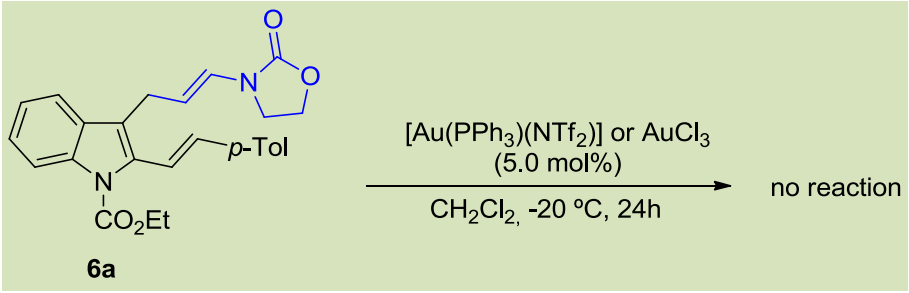
In order to gain insight on the formation of tetrahydrocarbazole derivatives **4**, **4'** and **5**, we conducted various control experiments as show below (See Scheme 2, main text).



A solution of tetrahydrocarbazole **4a'** (30 mg, 0.07 mmol) and [Au(PPh$_3$)(NTf$_2$)] (2.5 mg, 5.0 mol%) or AuCl$_3$ (1.0 mg, 5.0 mol%) in CH$_2$Cl$_2$ at -20 ºC was stirred until disappearance of **4a'** (TLC analysis). The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography to afford **4a** (29 or 30 mg, respectively) in quantitative yields. The spectroscopic data are in accordance with those reported above.



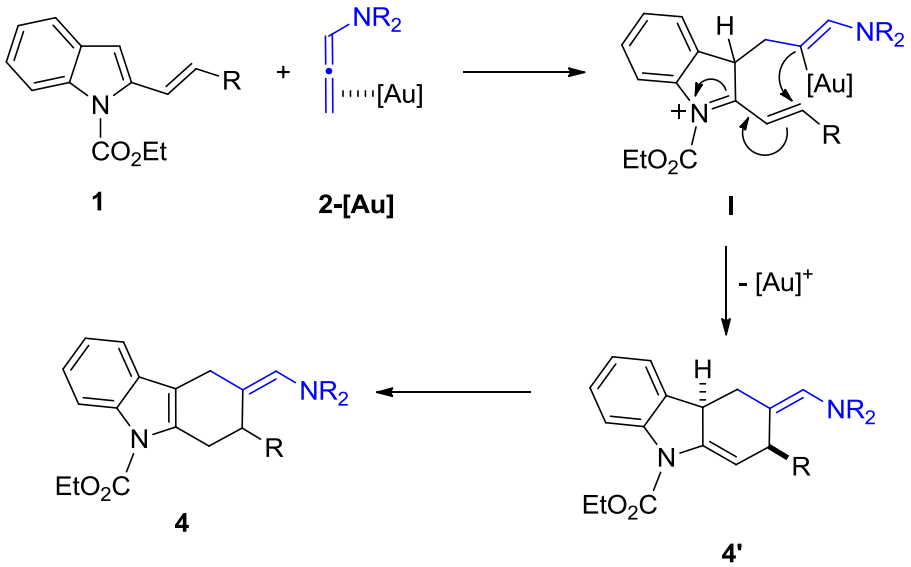
To a solution of tetrahydrocarbazole **4a'** (30 mg, 0.07 mmol) and [Au(JohnPhos)(NTf$_2$)] (2.7 mg, 5.0 mol%) in CH$_2$Cl$_2$ at -20 ºC, a solution of **2a** (10 mg, 0.08 mmol) in CH$_2$Cl$_2$ was added at -20 ºC. The resulting mixture was stirred until disappearance of **4a'** (TLC analysis). The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography to afford **5a** (35 mg, 90%). The spectroscopic data are in accordance with those reported above.



6a

A solution of vinyl indole **6a** (30 mg, 0.07 mmol) and $[Au(PPh_3)(NTf_2)]$ (2.5 mg, 5.0 mol%) or $AuCl_3$ (1.0 mg, 5.0 mol%) in CH_2Cl_2 at -20 ºC was stirred at this temperature for 24 h. The solvent was removed under reduced pressure and the resulting residue was analyzed by ^{1}H-NMR, which showed **6a** unaltered (CH_2Br_2 as internal standard).

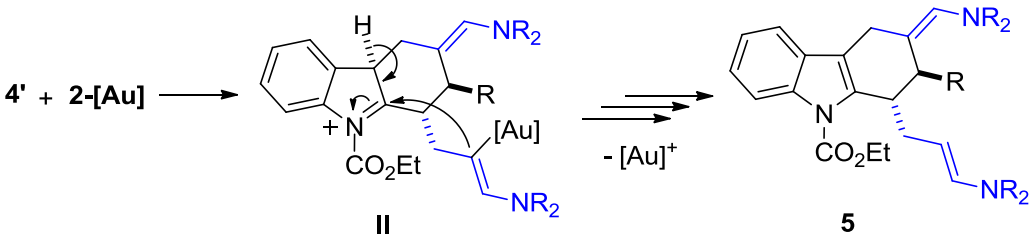
According to these experiments, and without further detailed studies, a plausible mechanistic rationale for these transformations is depicted below. Gold-promoted activation of the allene triggers the hydroarylation to afford intermediate **I**.[6] Since hydroarylation product **6** is not competent to accomplish the cyclization, and considering literature precedents, it is likely that the cyclization occurred from intermediate **I**, in a process which is faster than a protodemetallation. This cyclization leads to tetrahydrocarbazole **4'**, which depending on reaction conditions could be isolated, or to the aromatized indole **4**. This aromatization could be accomplished by some of the gold catalysts, although the presence of adventitious acid traces (especially in the case of $AuCl_3$) could also influence this process. This mechanism accounts for the formation of benzofuran derivative **12** as well.



1 **2-[Au]** **I** **4** **4'**

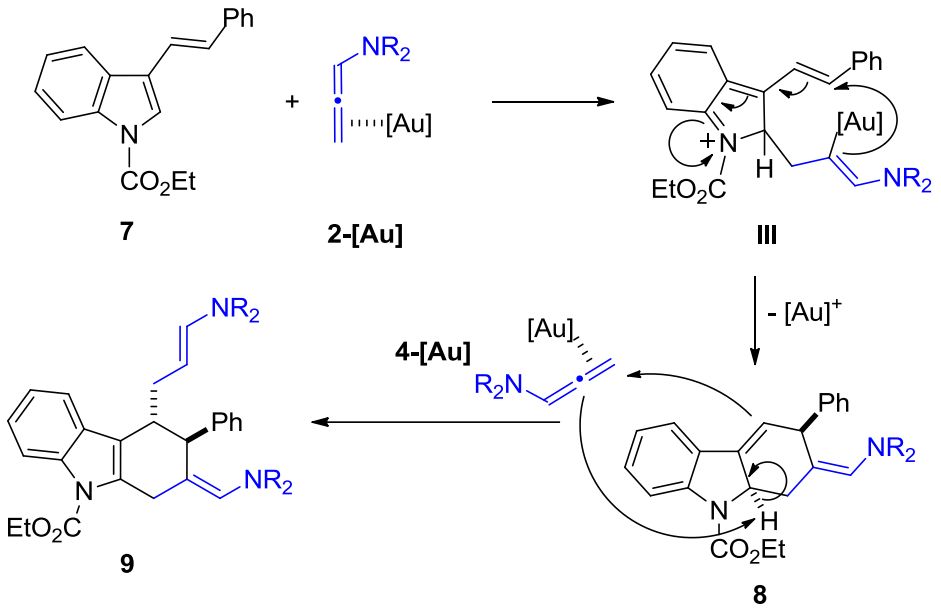
Scheme S1. Mechanistic proposal for the formation of compounds **4** and **4'**.

When an excess of the allene is employed, a second addition of the allene likely takes place from **4'** to afford tetrahydrocarbazole **5**. A sequence comprising a hydroarylation of the allene through intermediate **II**, followed by a protodemetallation/aromatization might account for the results. Enamides structurally related with **4'** have been proposed to react with *N*-allenamides through an analogous mechanism in a sequence comprising a nucleophilic attack of the enamide onto the activated allene, followed by ring closure to afford [2+2]-cycloadducts.[7] In the present reaction, protodemetallation is faster than ring closure.



Scheme S2. Mechanistic proposal for the formation of compounds **5**.

In the same manner, when using 3-vinyl indole **7**, the reaction might take place by means of a hydroarylation mechanism through position C-2 of the indole (Scheme S3). Hydroarylation of allenamides at position C-2 has been previously reported for substrates bearing substituents at position C3.[6] A subsequent cyclization on intermediate **III** would afford carbazole **8**. When the reaction takes places in the presence of an excess of the allene, a second addition takes place. This second addition cannot occur through a hydroarylation. However, an intermolecular ene-reaction might account for the formation of compound **9**. Aromatization of the indole ring could serve as a driving force for this reaction. In literature there are reports on gold-catalyzed ene-reaction.[8] This ene-type reaction could account for the formation of compounds **5** as well. Thus, without further evidences, we cannot exclude this mechanism being operative.



Scheme S3. Mechanistic proposal for the formation of compounds **9-10.**

References.

[1] L.-L. Wei, J. A. Mulder, H. Xiong, C. A. Zificsak, C. J. Douglas, R. P. Hsung, Tetrahedron, **2001**, *57*, 459.

[2] a) N. Mézailles, L. Ricard, F. Gagosz, *Org. Lett.* **2005**, *7*, 4133; b) L. Ricard, F. Gagosz, *Organometallics*, **2007**, *26*, 4704.

[3] E. Rossi, G. Abbiati, V. Canevari, G. Celentano, E. Magri, *Synthesis* **2006**, 299.

[4] N. P. Grimster, C. Gauntlett, C. R. A. Godfrey, M. J. Gaunt, *Angew. Chem. Int. Ed.* **2005**, *44*, 3125.

[5] J. Maillard, M. Langlois, V. V. Tri, C. Guillonneau, J. Legeai, M. Benharkate, M. Blozovski, Eur. J. Med. Chem. **1983**, *18*, 353.

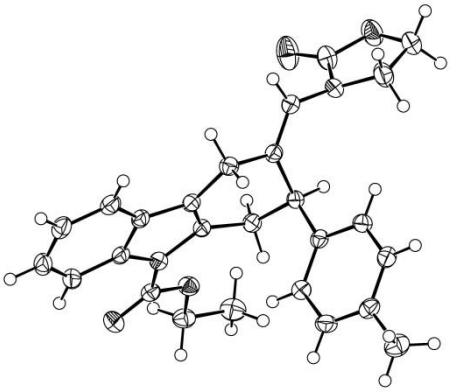
[6] M. C. Kimber, *Org. Lett.* **2010**, *12*, 1128.

[7] (a) X.-X. Li, L.-L. Zhu, W. Zhou, Z. Chen, *Org. Lett.* **2012**, *14*, 436; (b) S. Suárez-Pantiga, C. Hernández-Díaz, M. Piedrafita, E. Rubio, J. M. González, *Adv. Synth. Catal.* **2012**, *354*, 1651; (c) H. Faustino, P. Bernal, L. Castedo, F. López, J. L. Mascareñas, *Adv. Synth. Catal.* **2011**, *354*, 1658.

[8] For an example of *intramolecular* gold-catalyzed Alder-ene reaction, see: G. Lemière, V. Gandon, N. Agenet, J.-P. Goddard, A. de Kozak, C. Aubert, L. Fensterbank, M. Malacria, *Angew. Chem. Int. Ed.* **2006**, *45*, 7596.

ORTEP diagrams for the structure of compounds 4a, 4a' and 5a.

(See details for crystallization on the corresponding characterization section).



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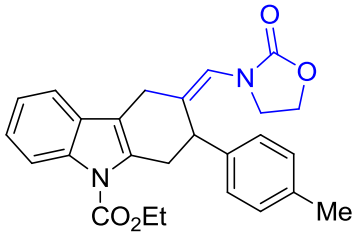
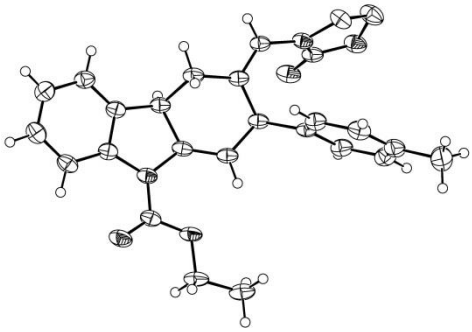


4a



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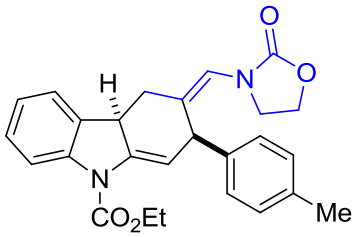
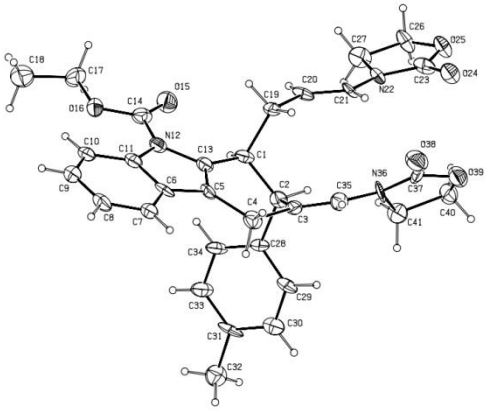


4a'



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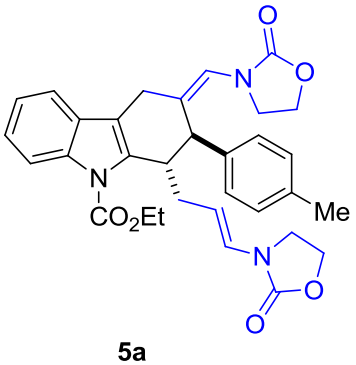
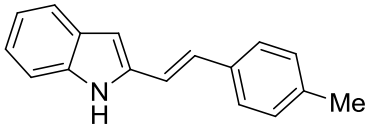
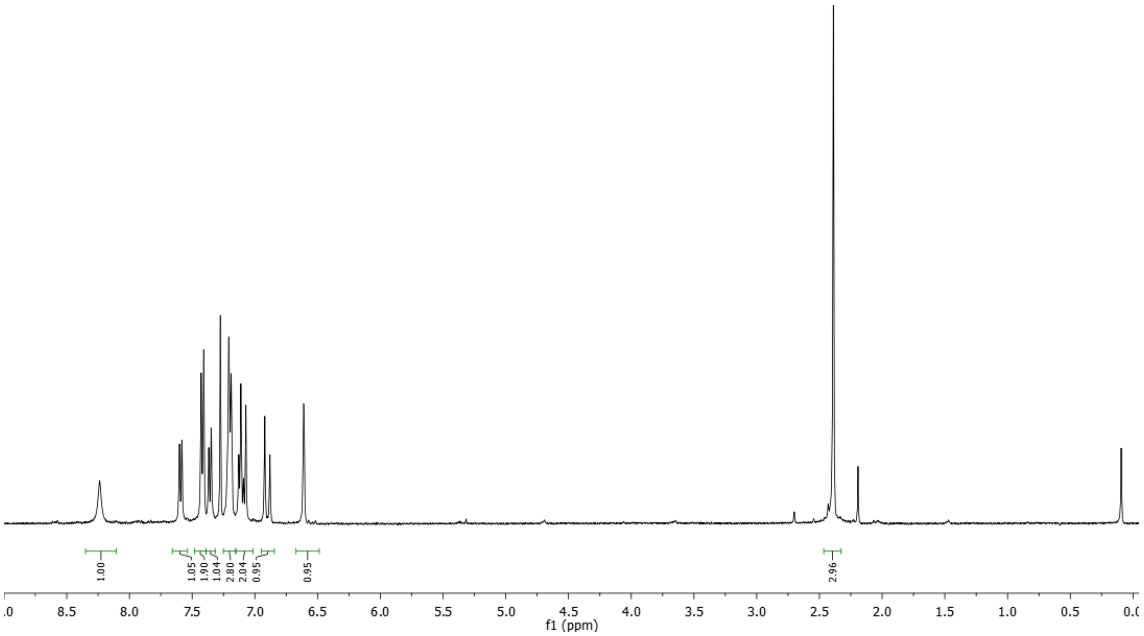


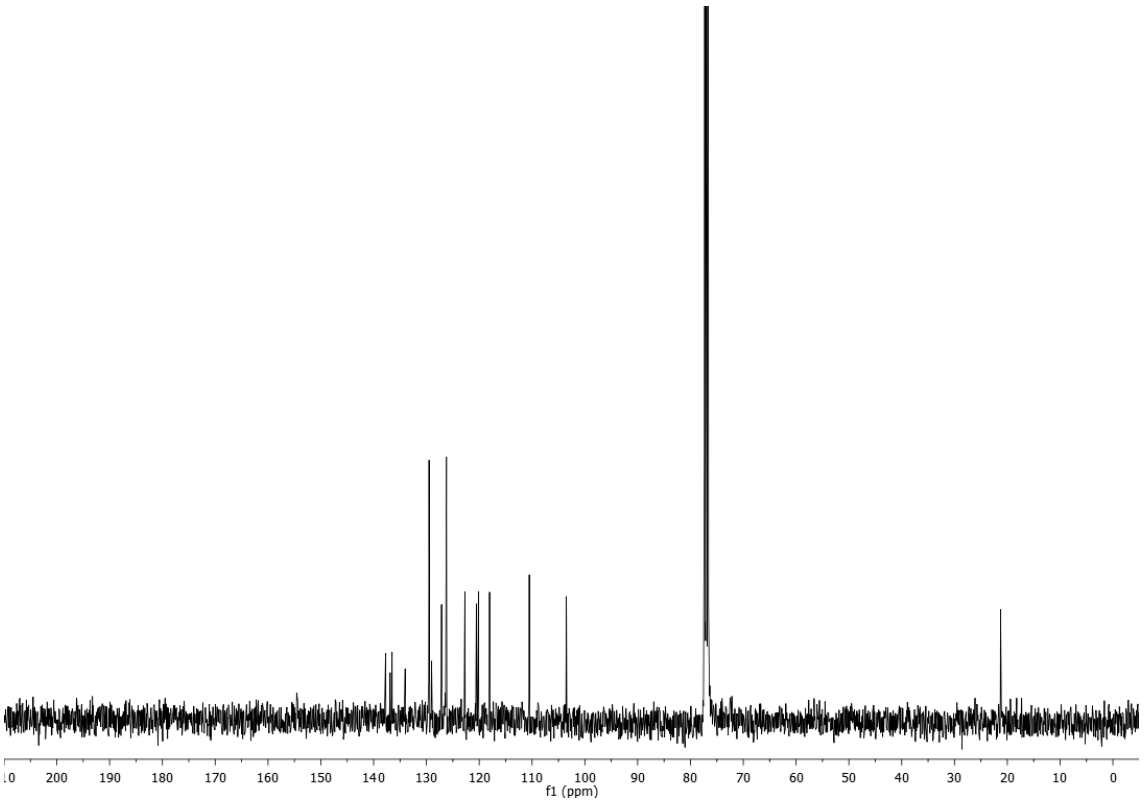
5a

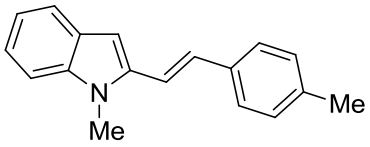
The measurements were perfomed up to 1.2 Å since at higher resolution no diffraction was observed, which caused various warnings on the checkCIF. Nevertheless, the analysis is sufficiently suitable to unequivocally establish the structure of ***5a****.*



1a







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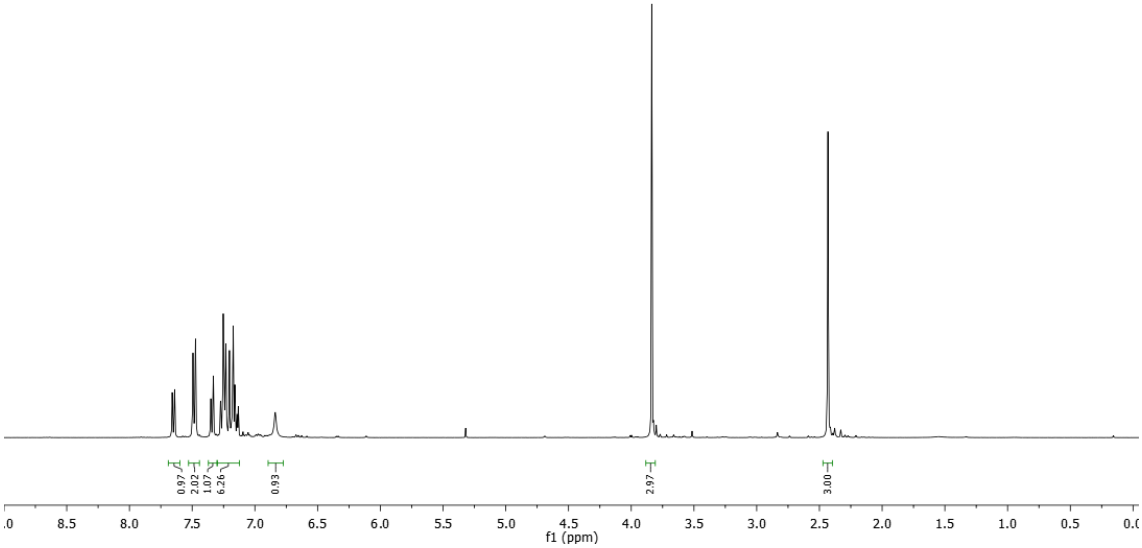

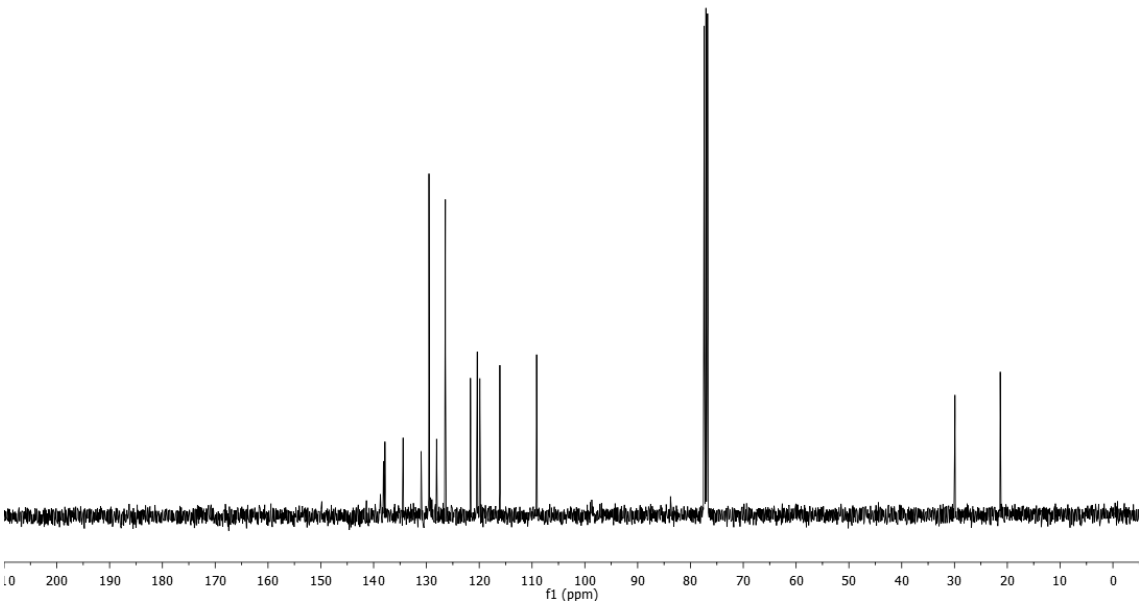

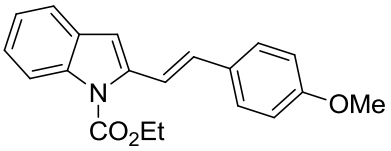
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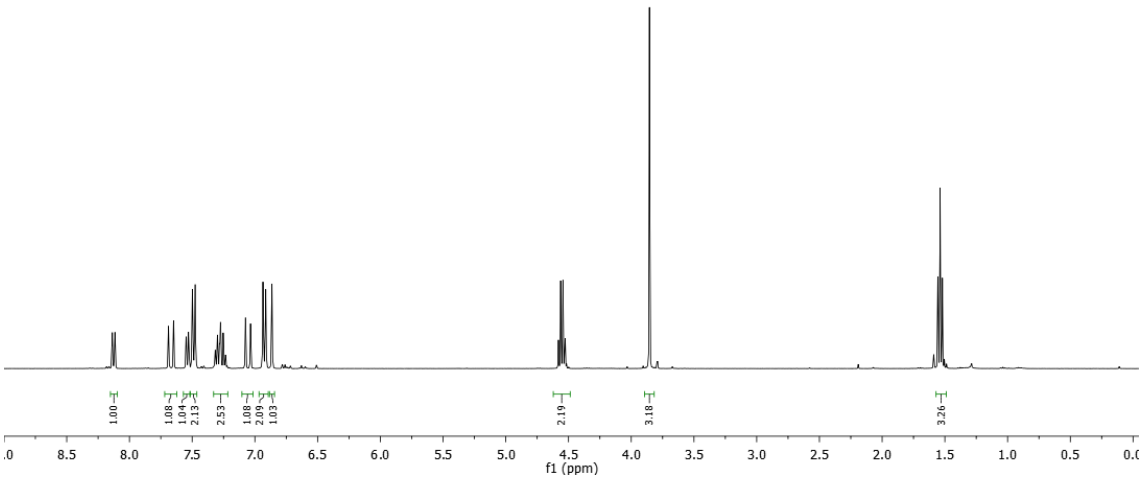
CO2Et
OMe

1c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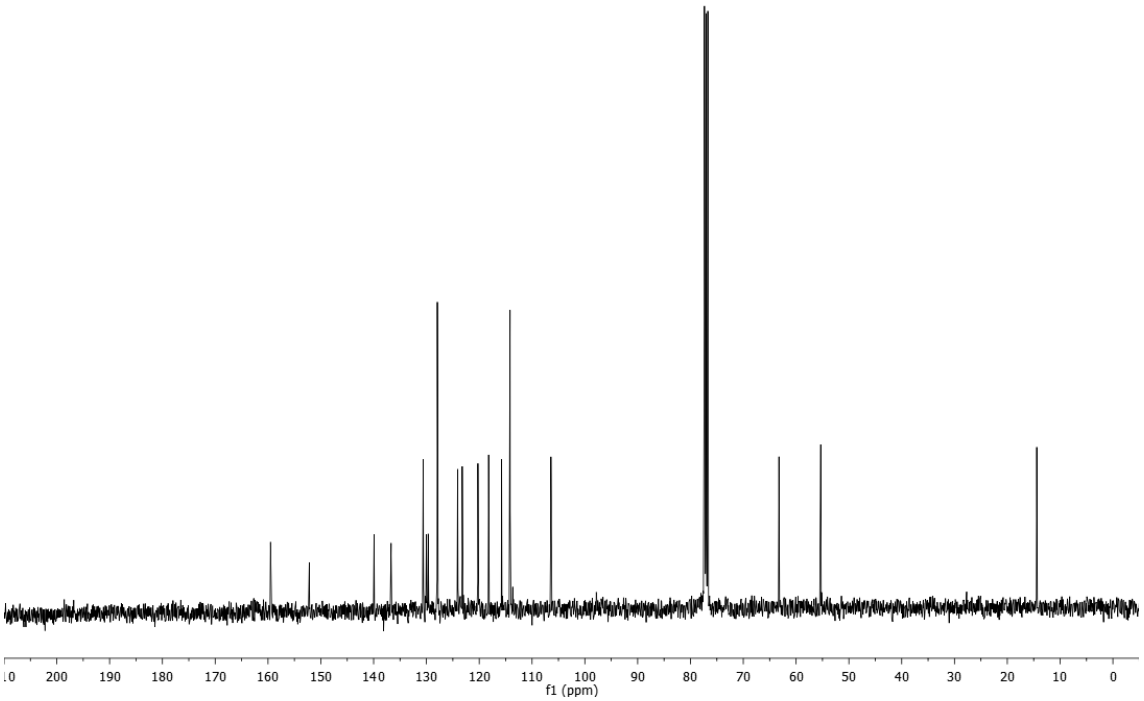
f1 (ppm)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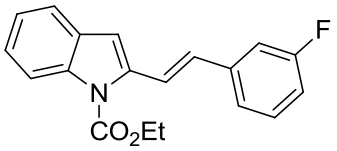
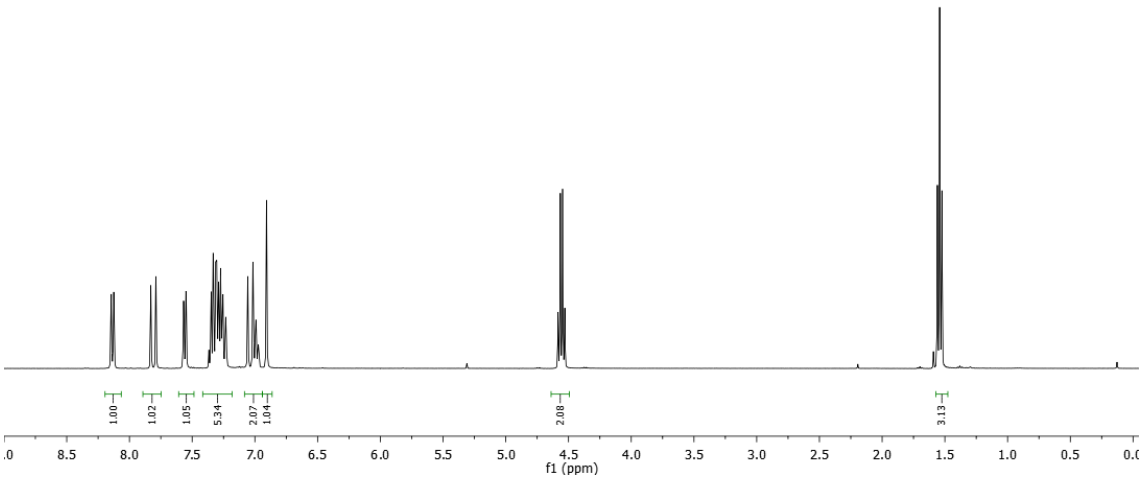
f1 (ppm)


F
N
CO2Et

1e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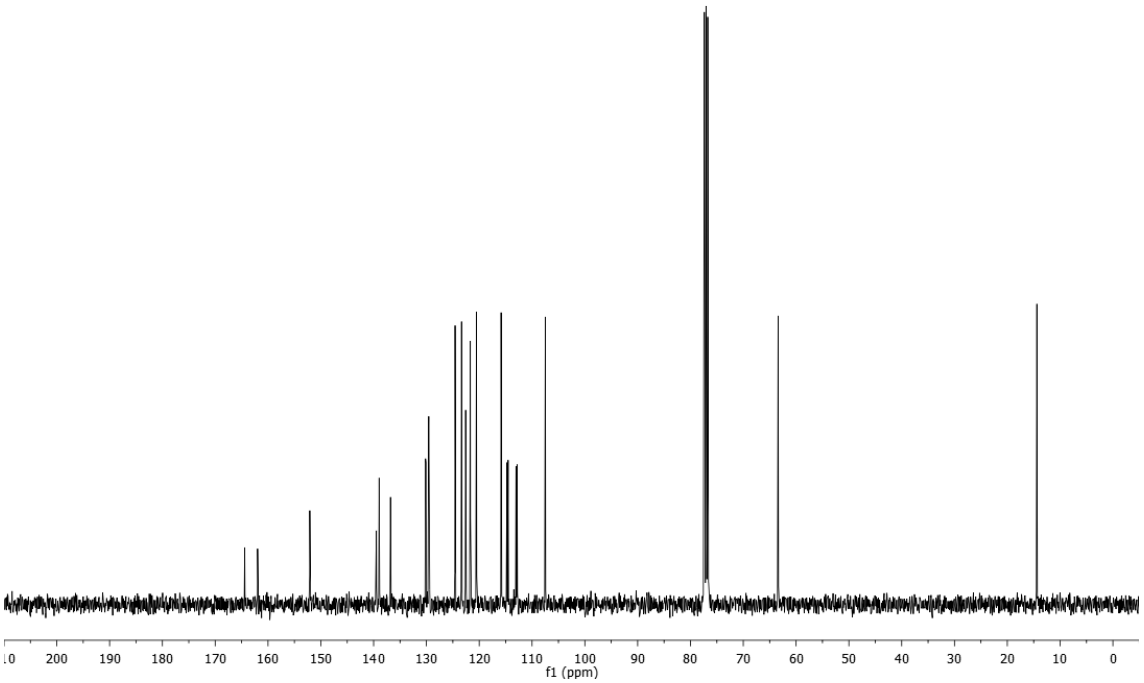
0.5
f1 (ppm)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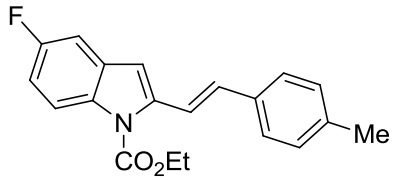
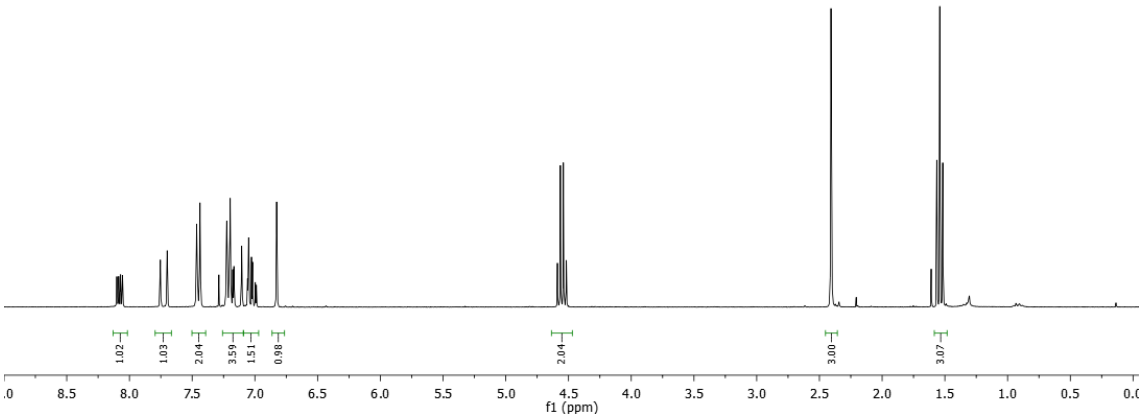
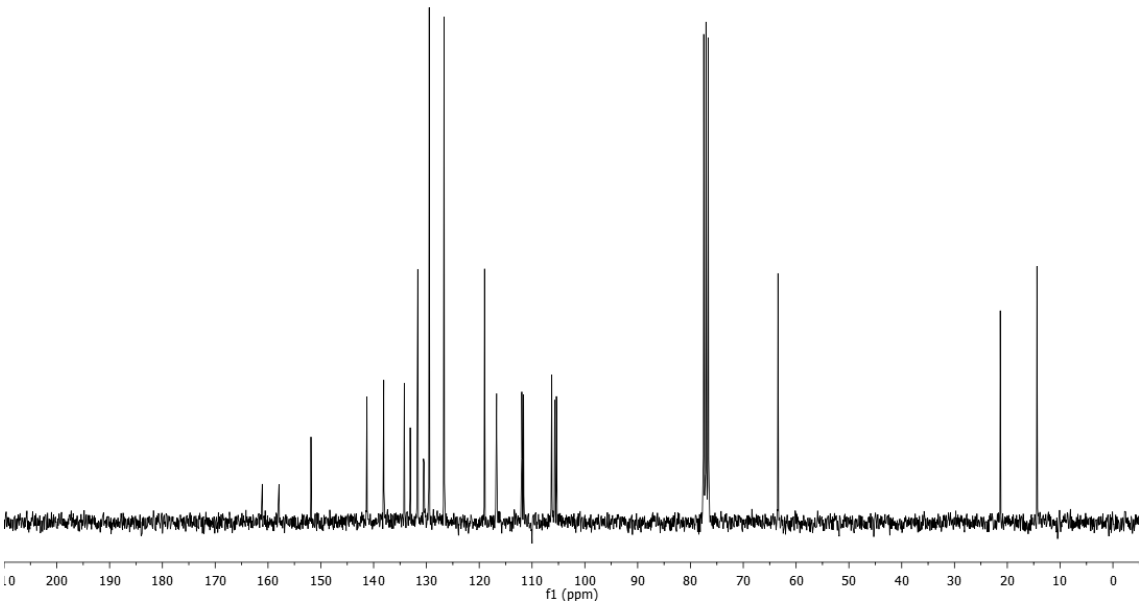
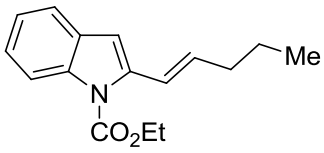
f1 (ppm)



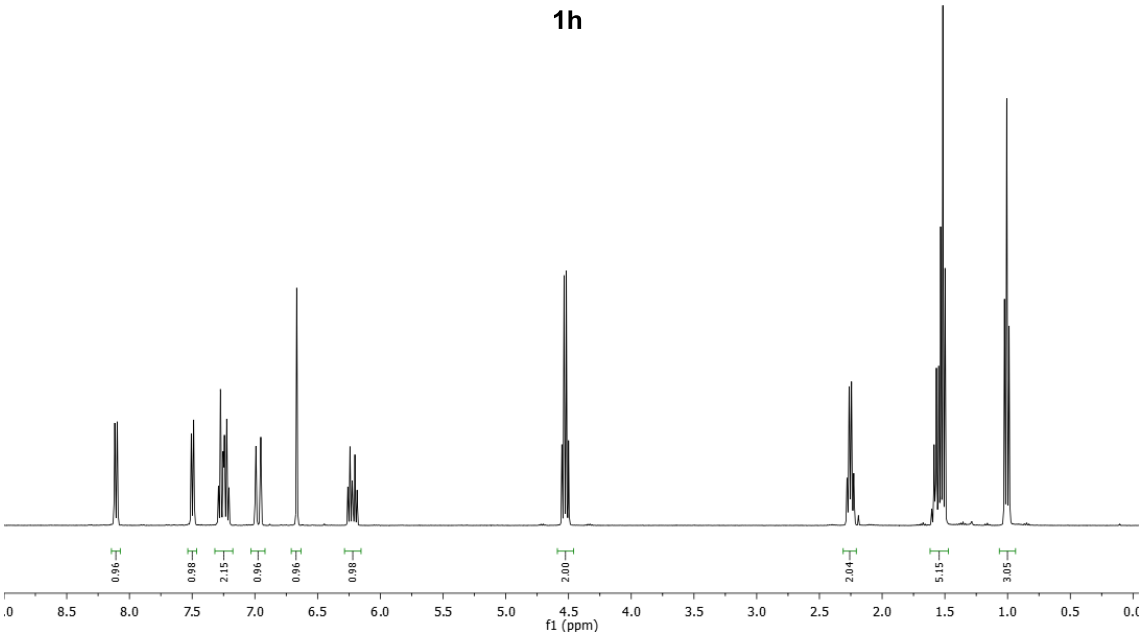
1g

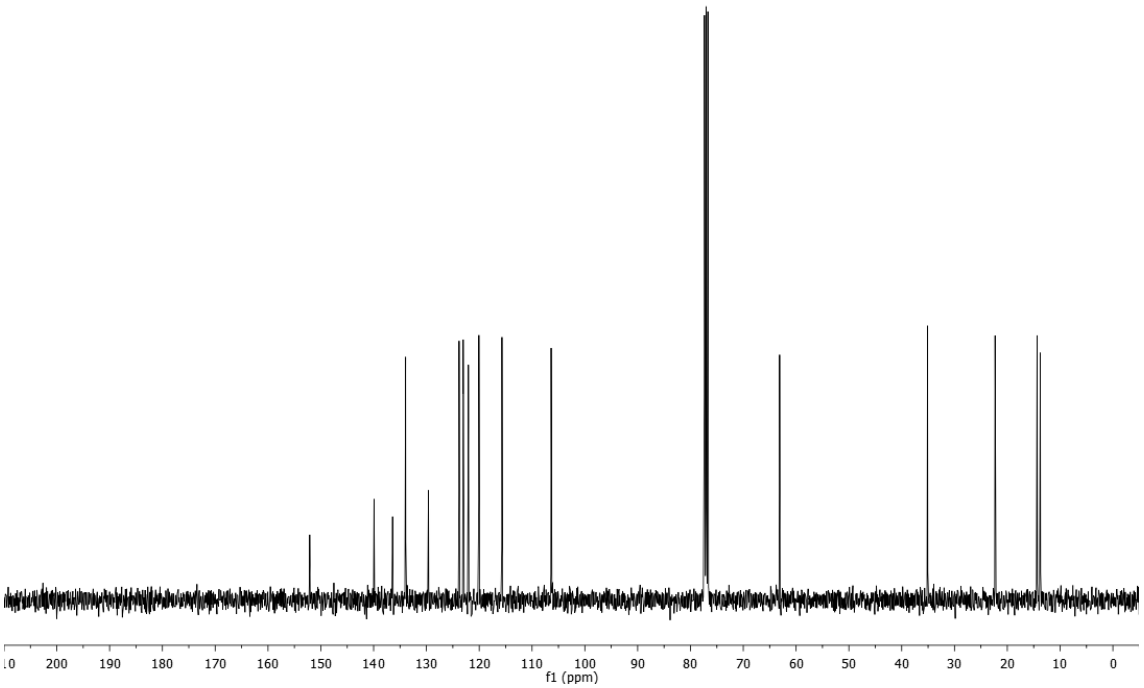


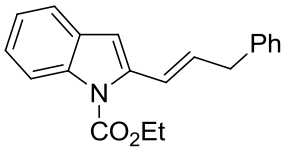




1h







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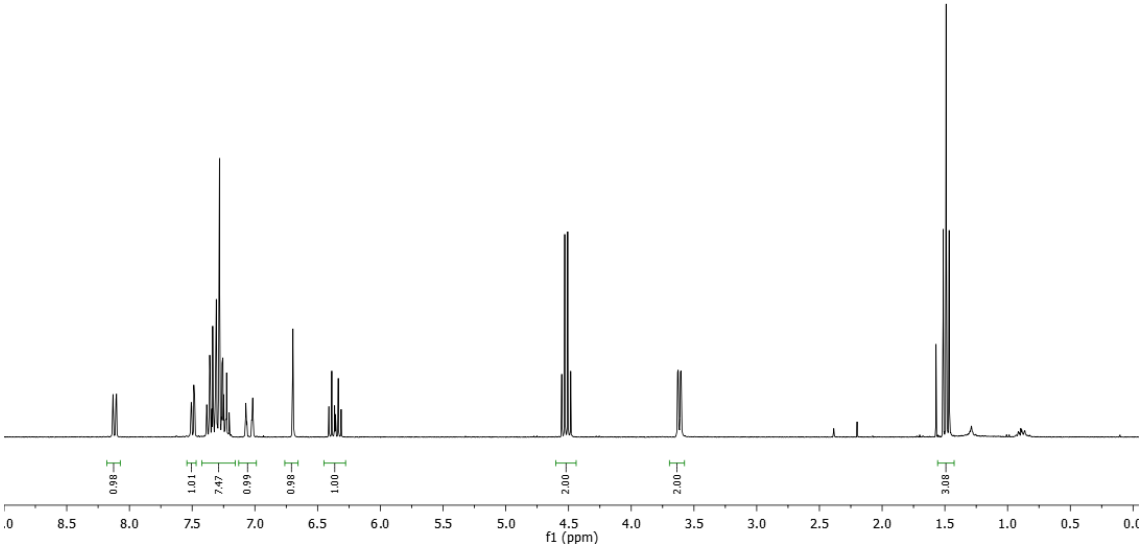

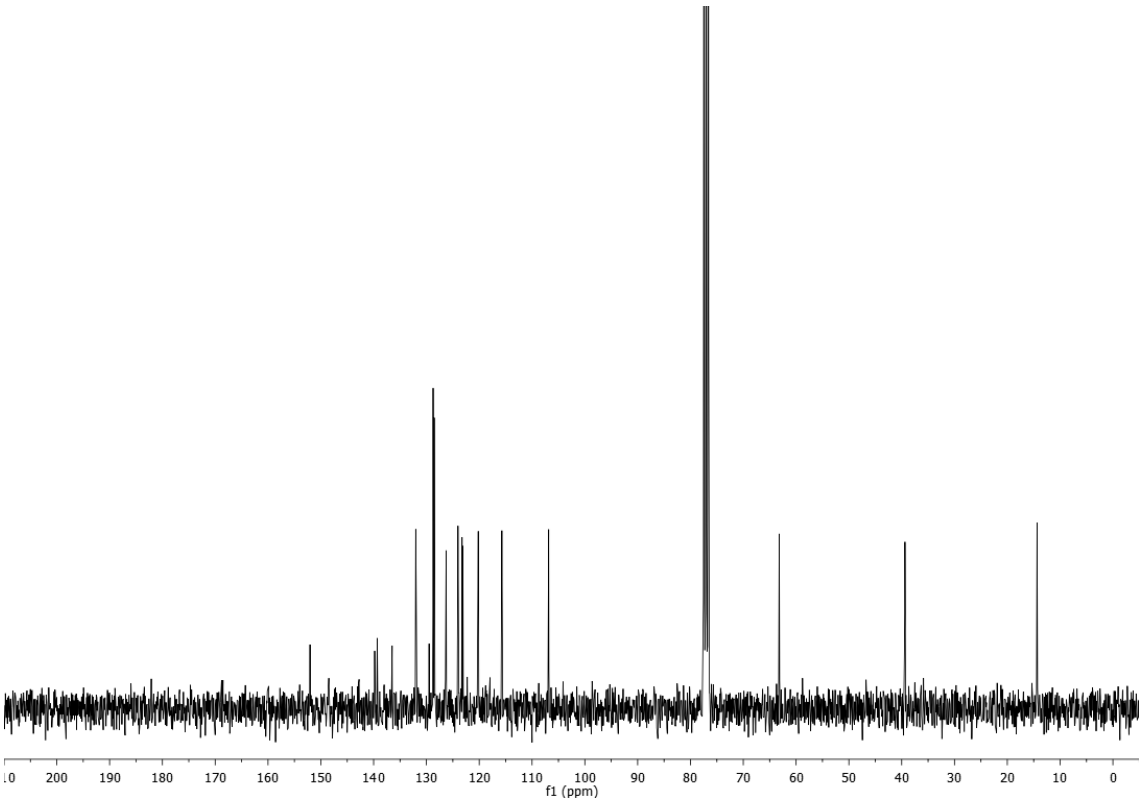

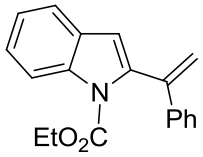

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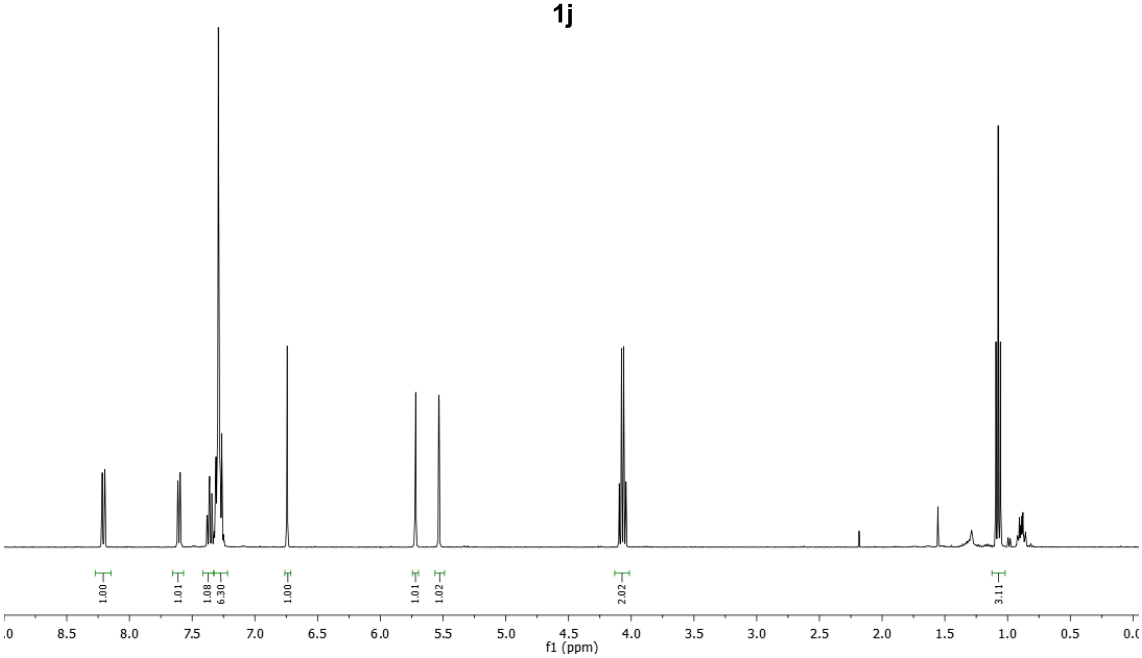
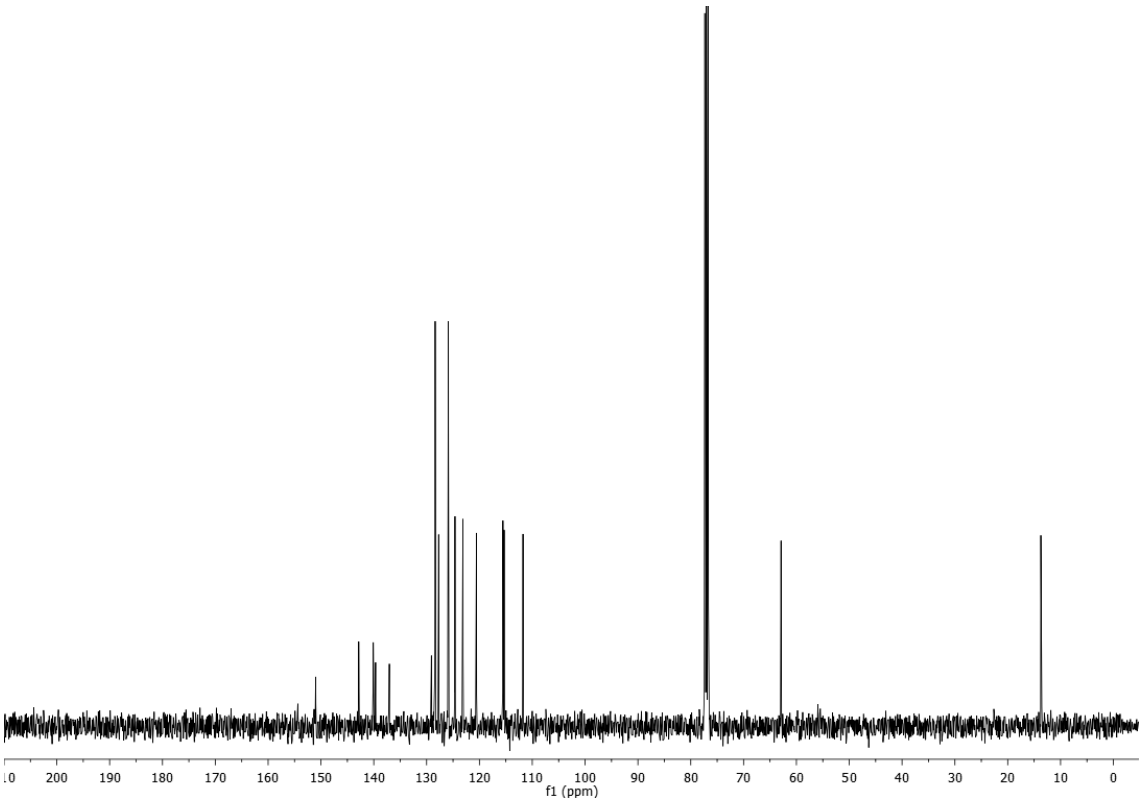
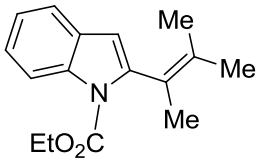
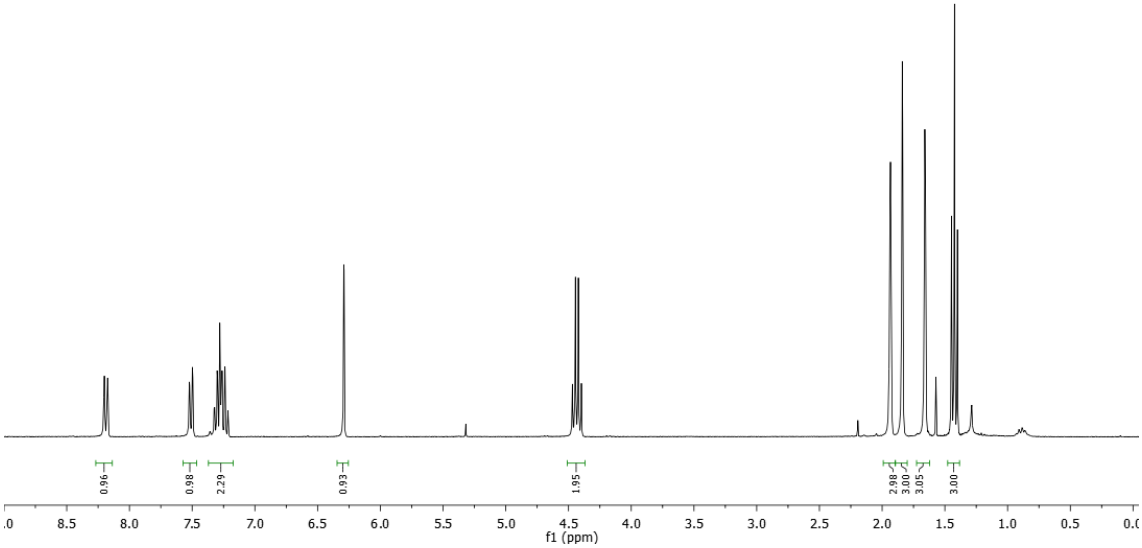
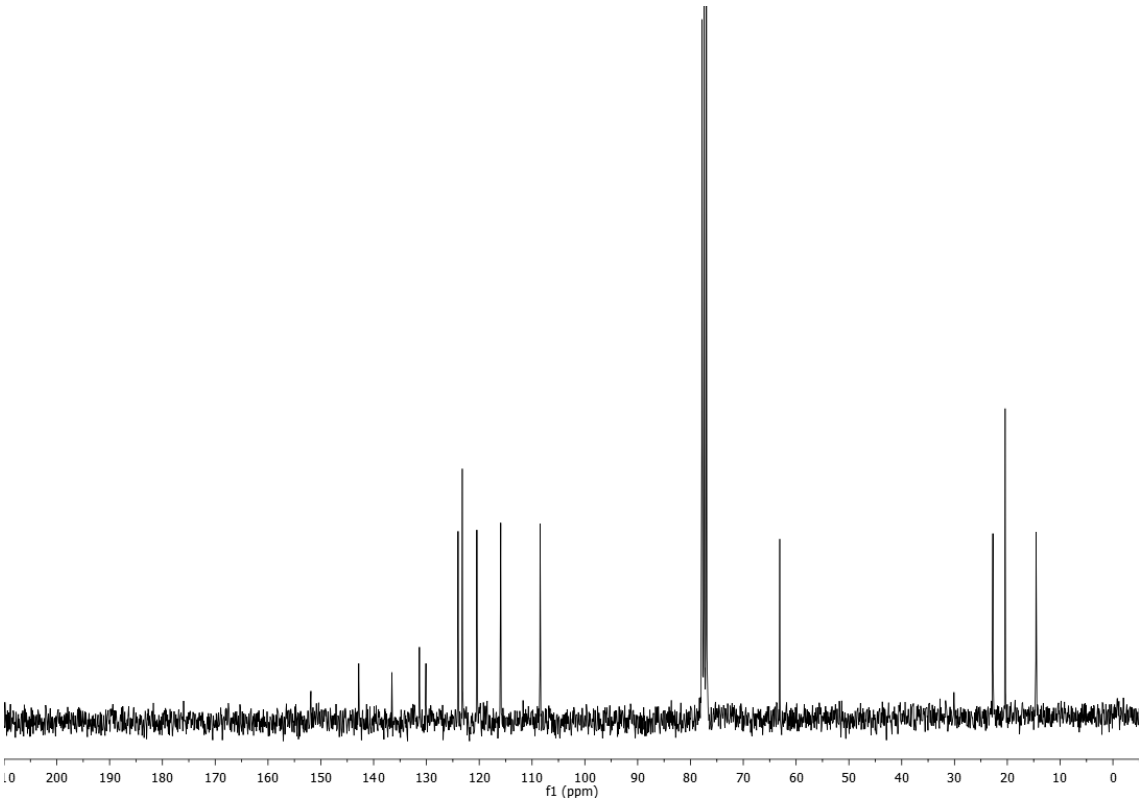


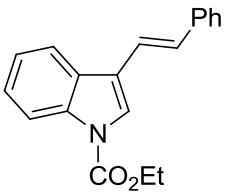




1k







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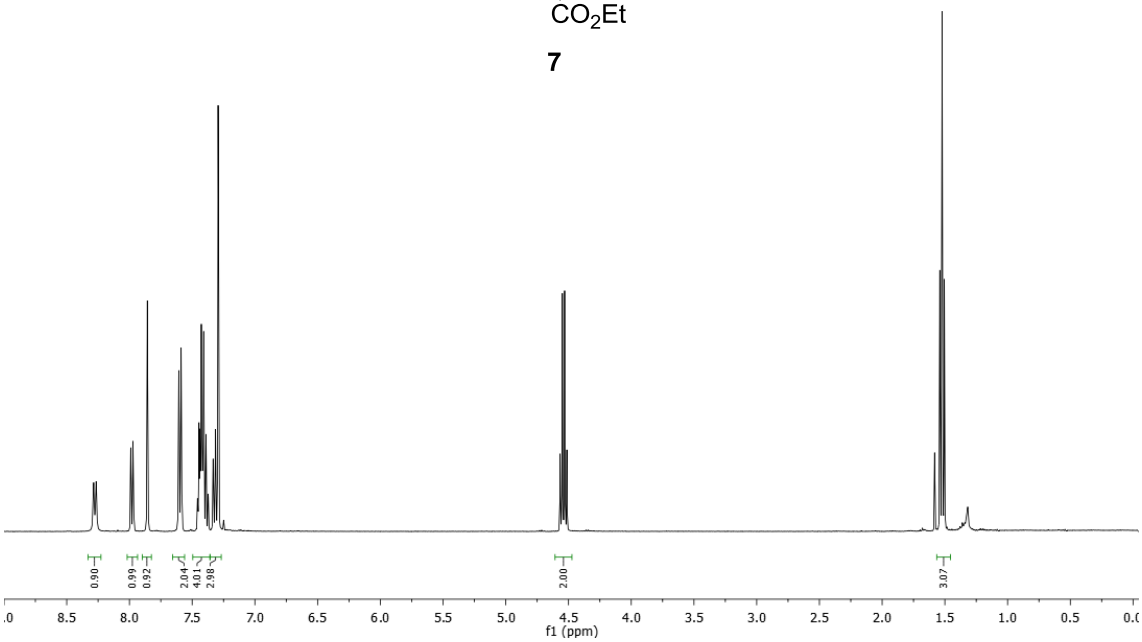
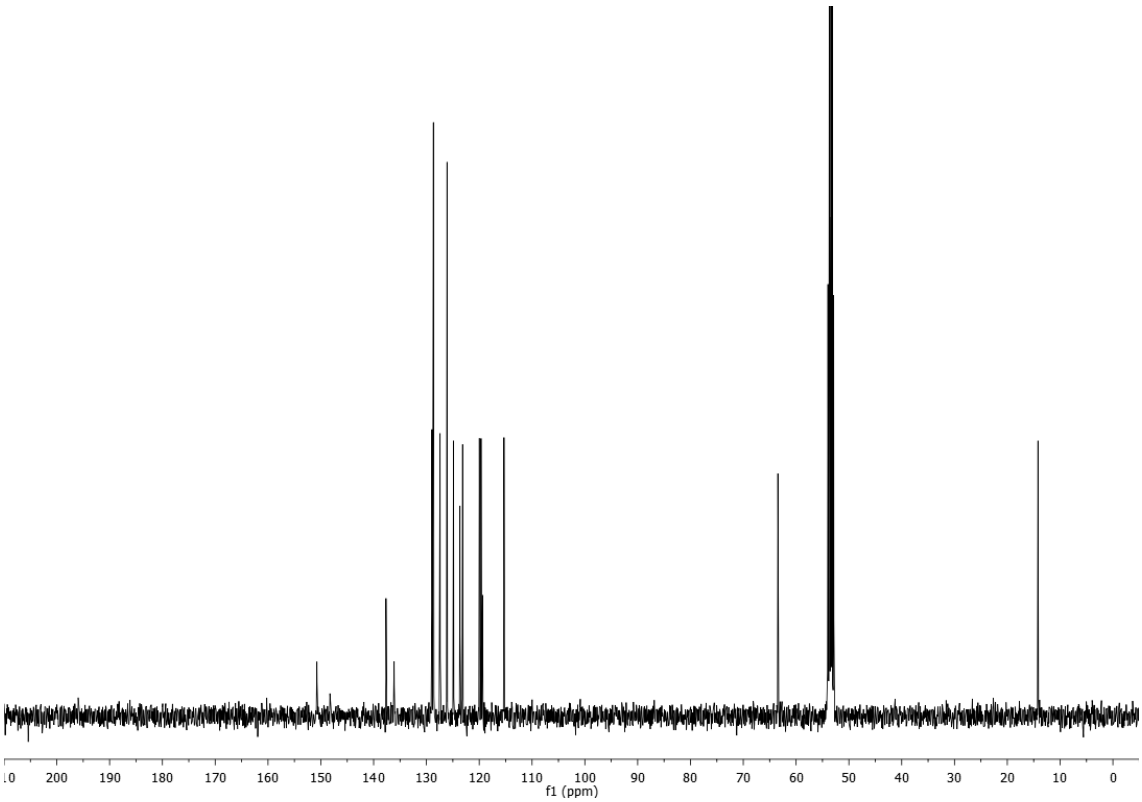
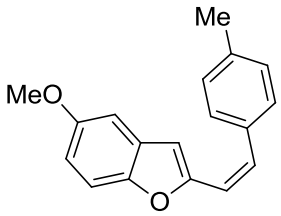
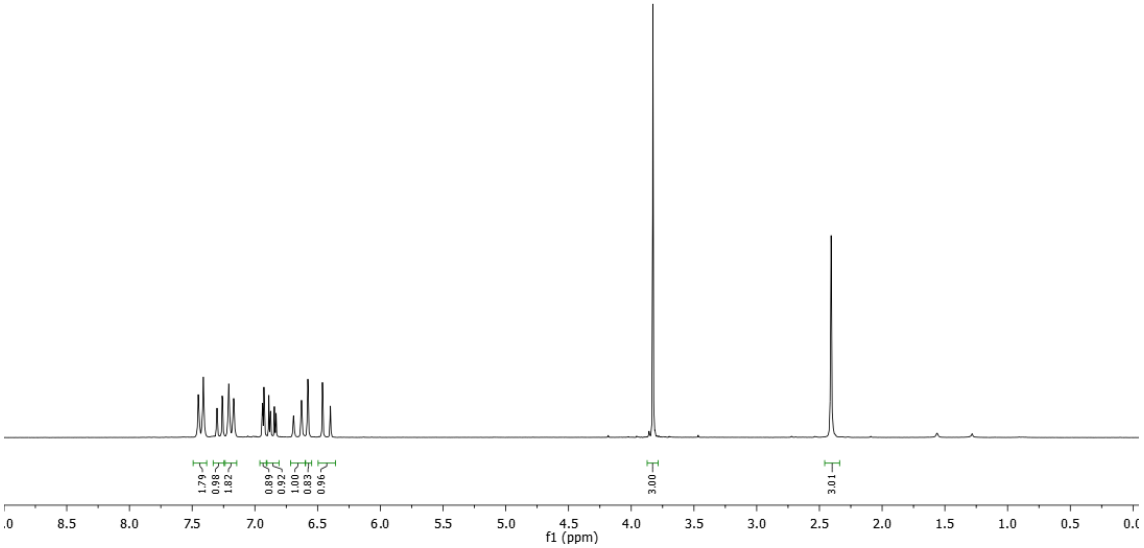
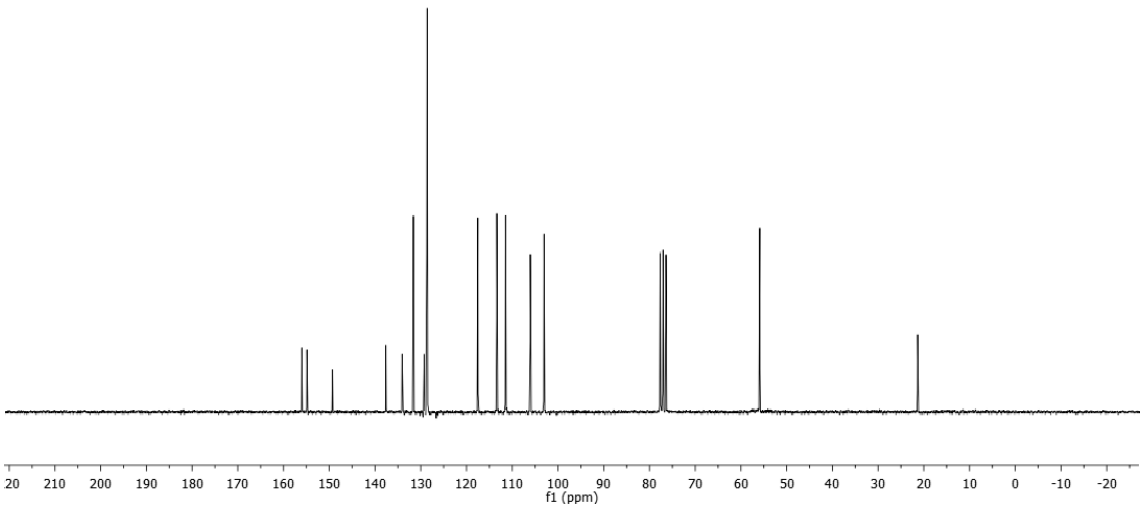


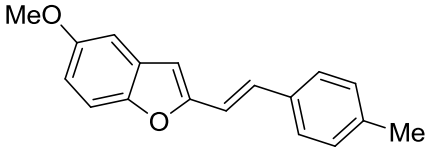




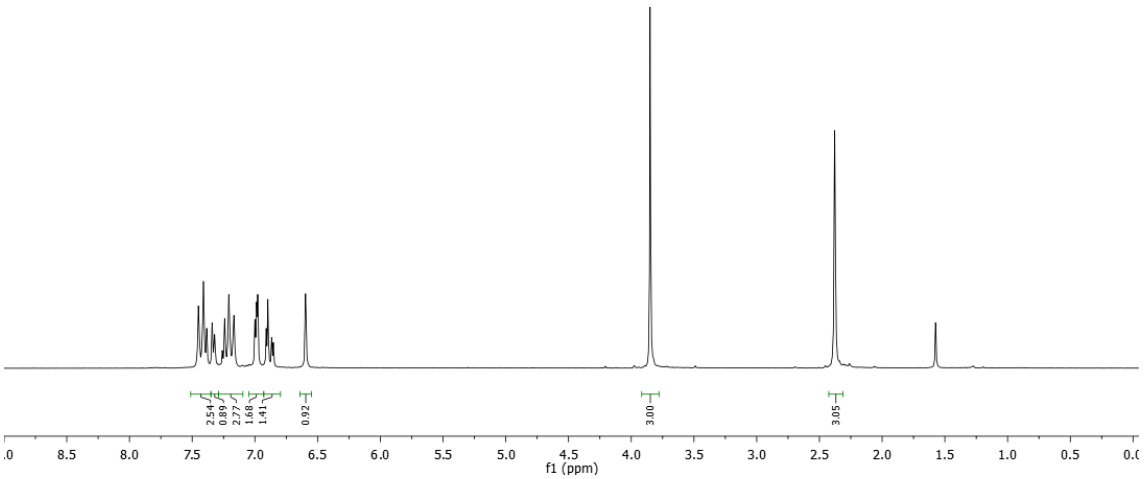
***Z*-10**

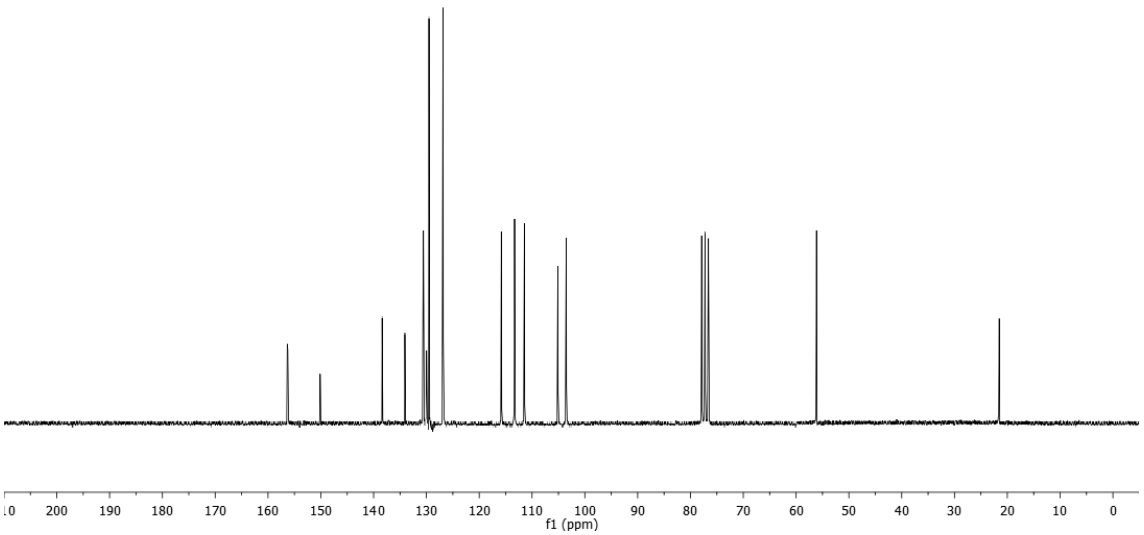


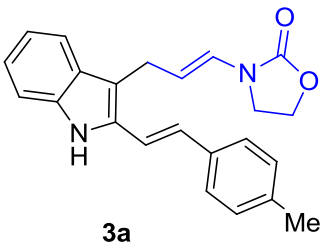




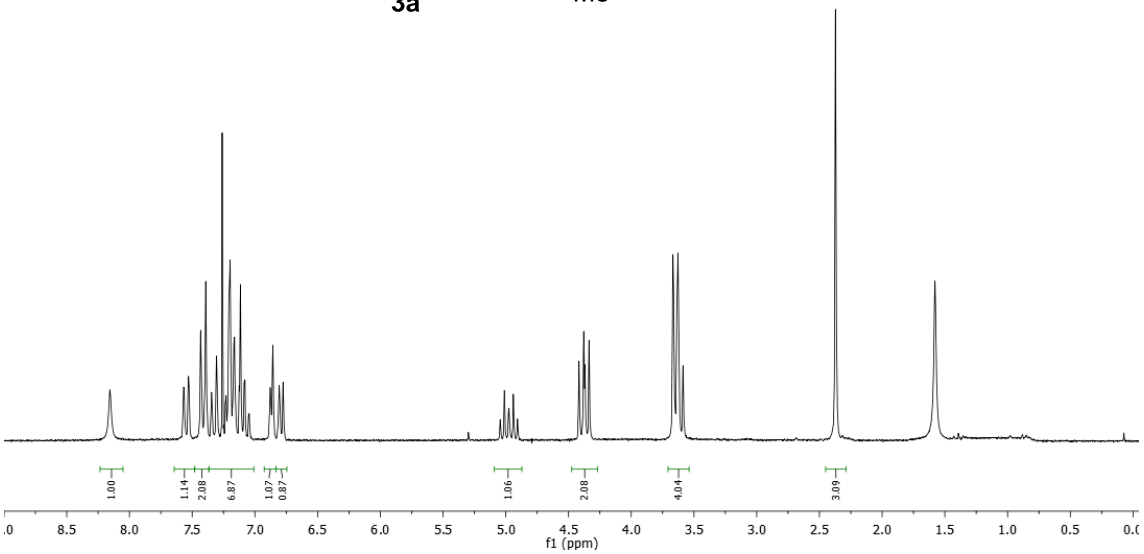
***E*-10**

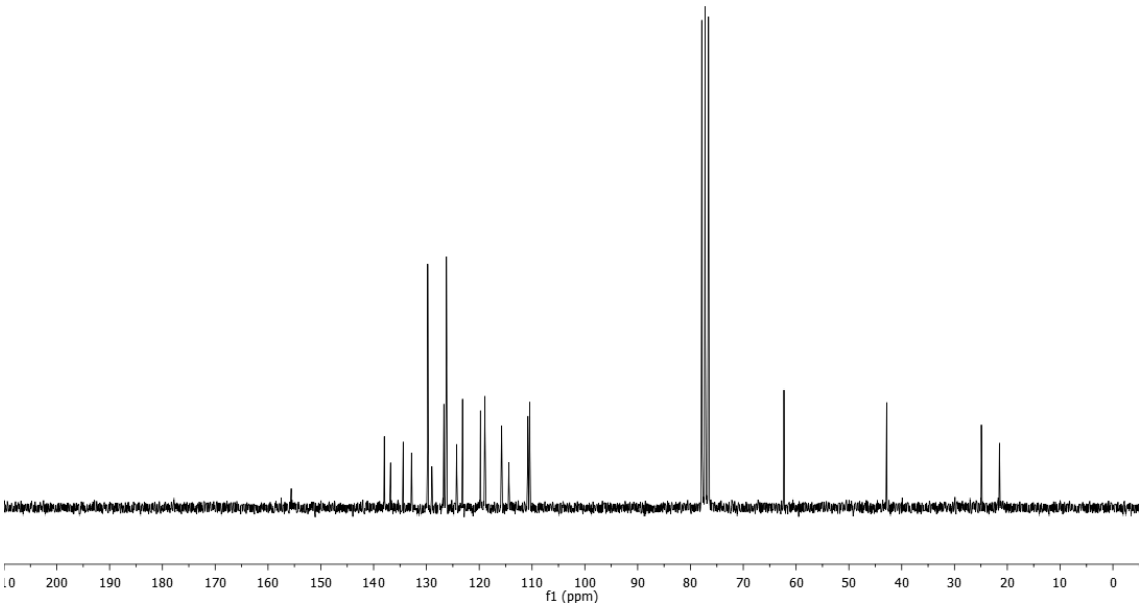


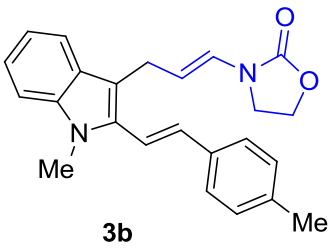




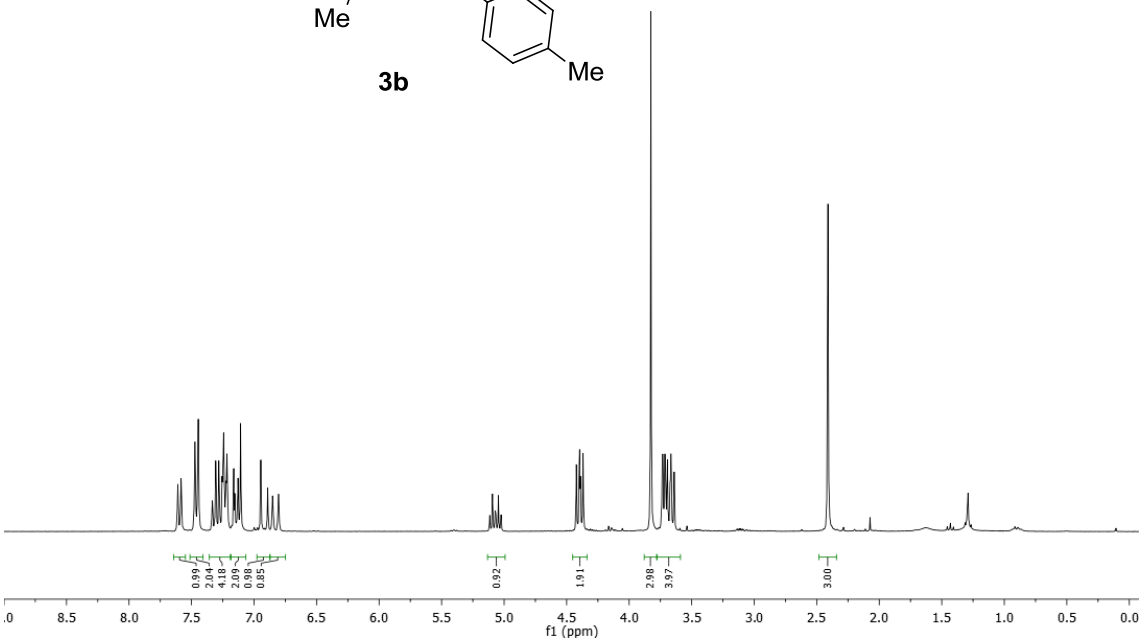
3a

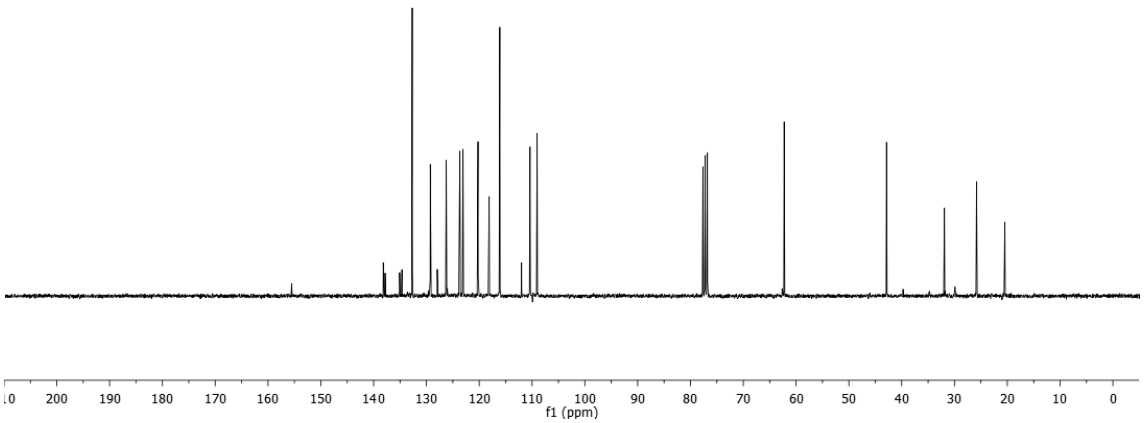


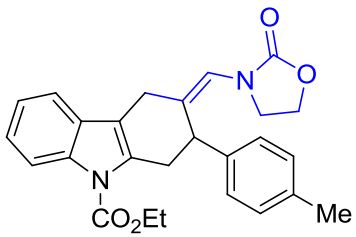




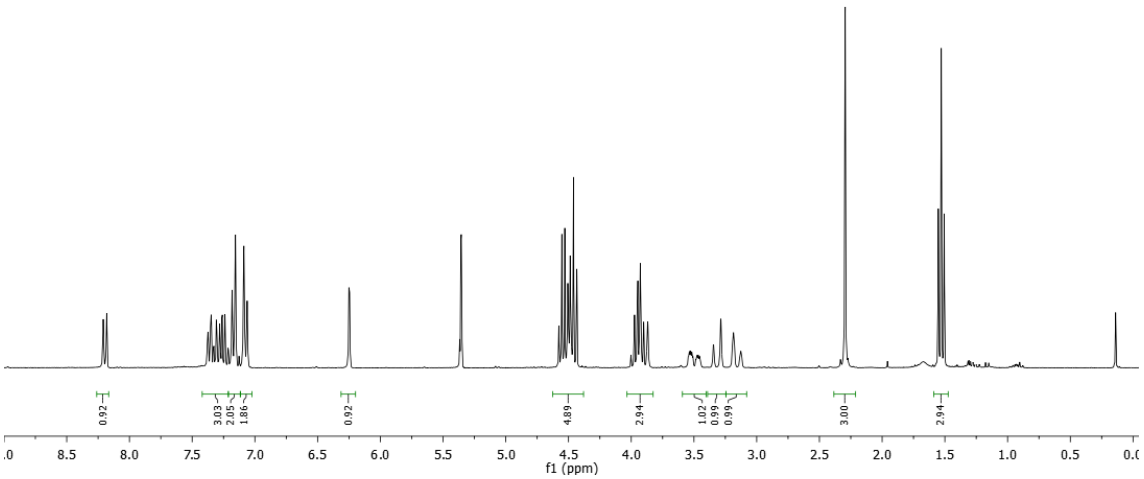
3b






O
N
O
N
CO2Et
Me

4a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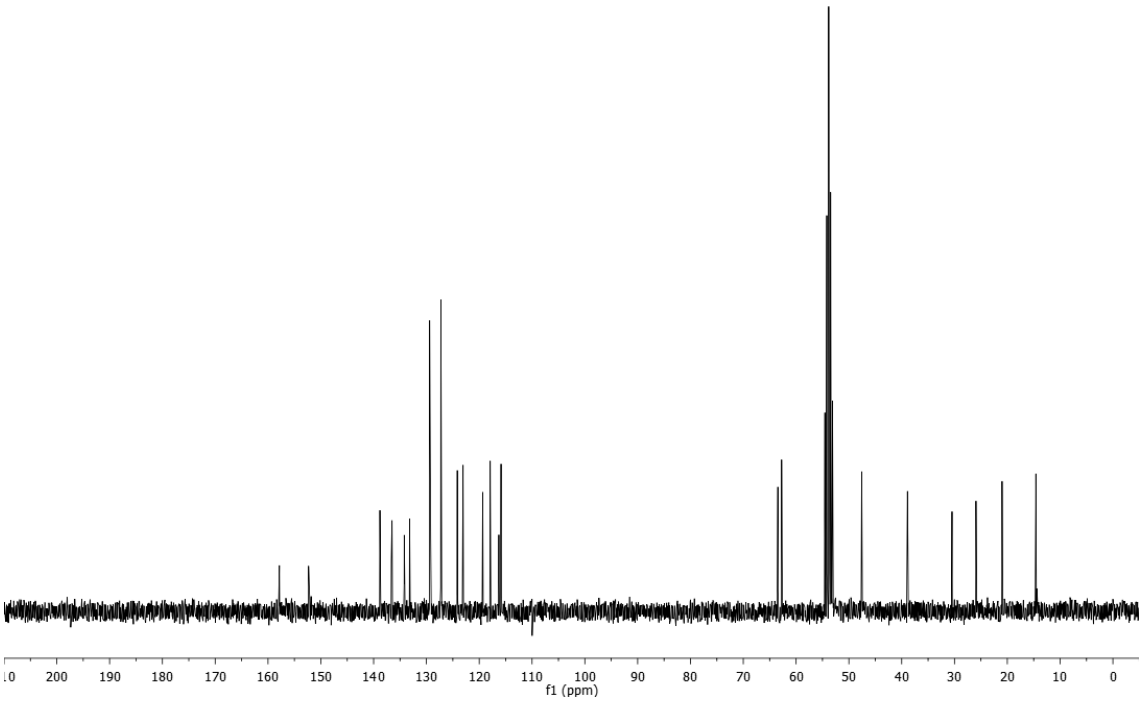
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50
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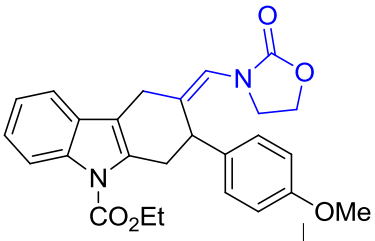
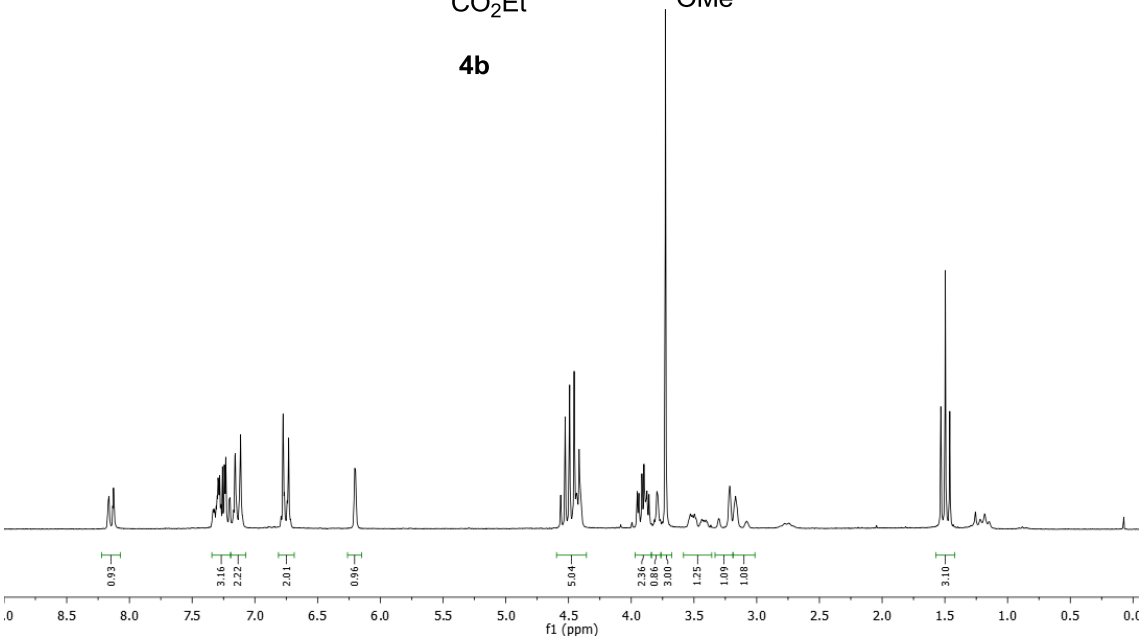
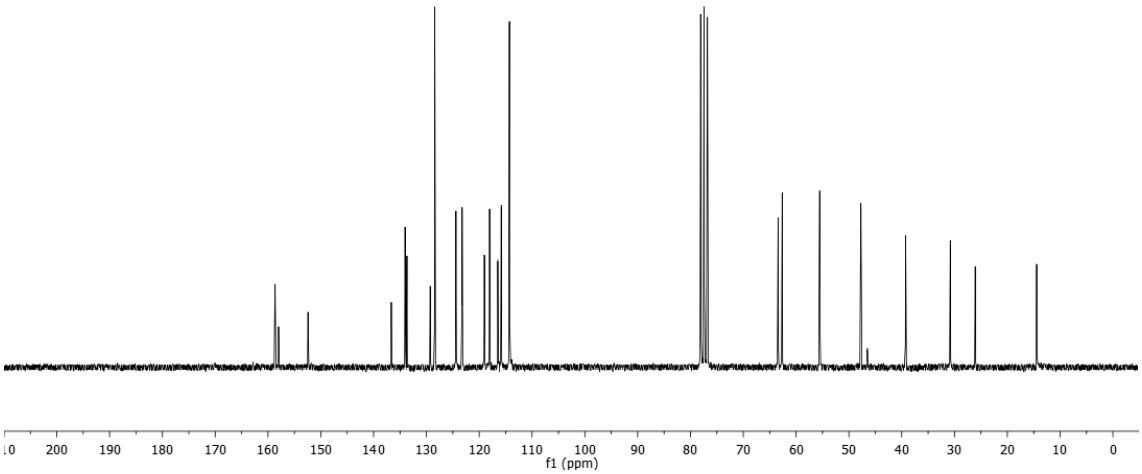
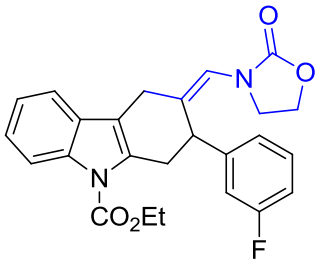
f1 (ppm)



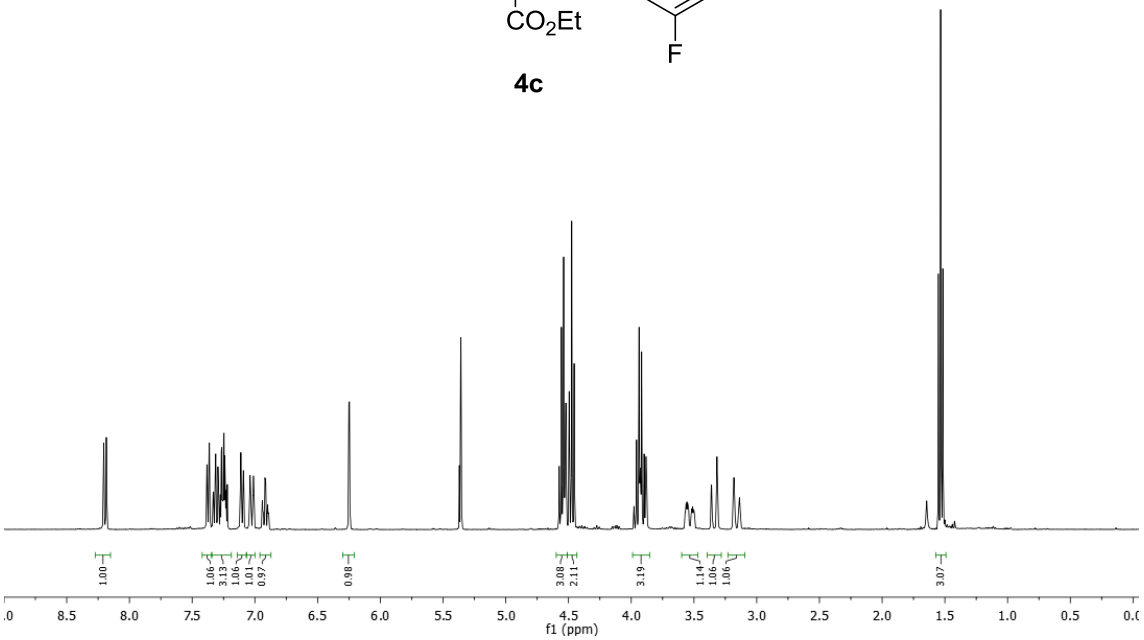
4b






O
N
O
N
CO2Et
F

4c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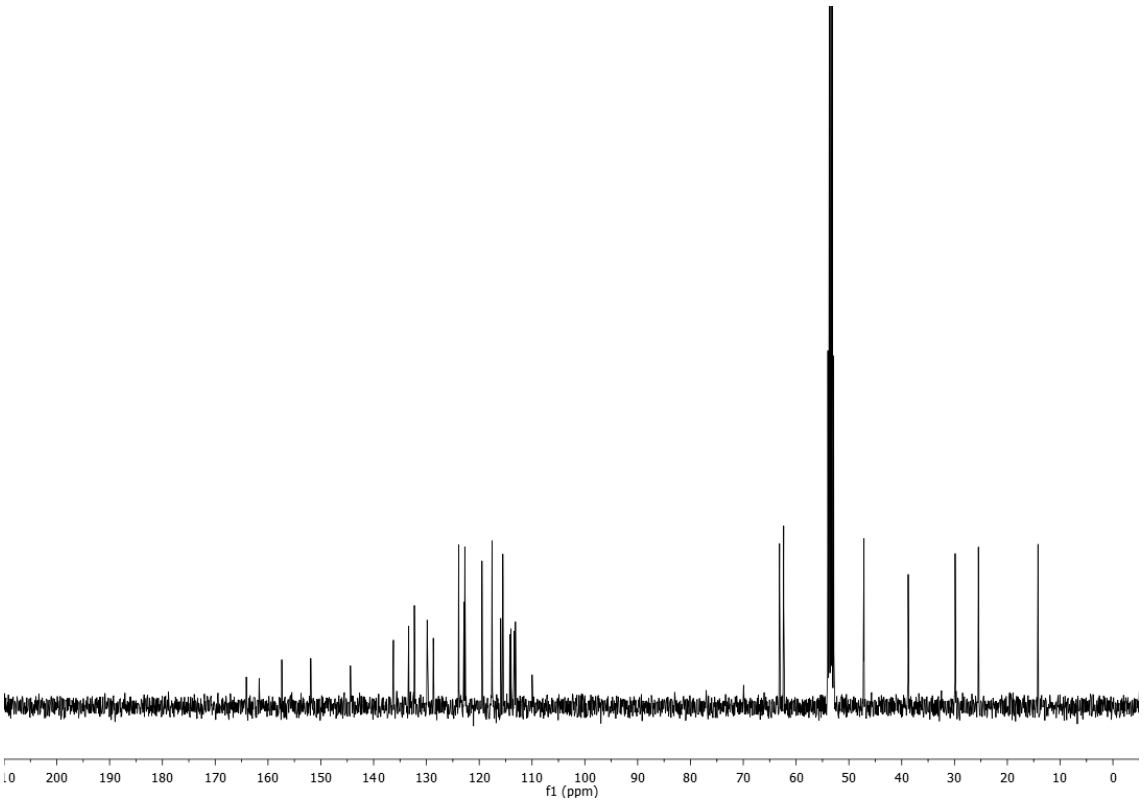
f1 (ppm)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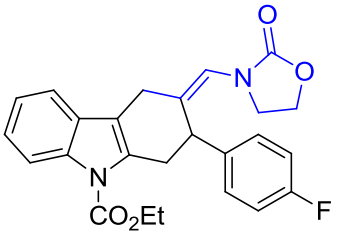
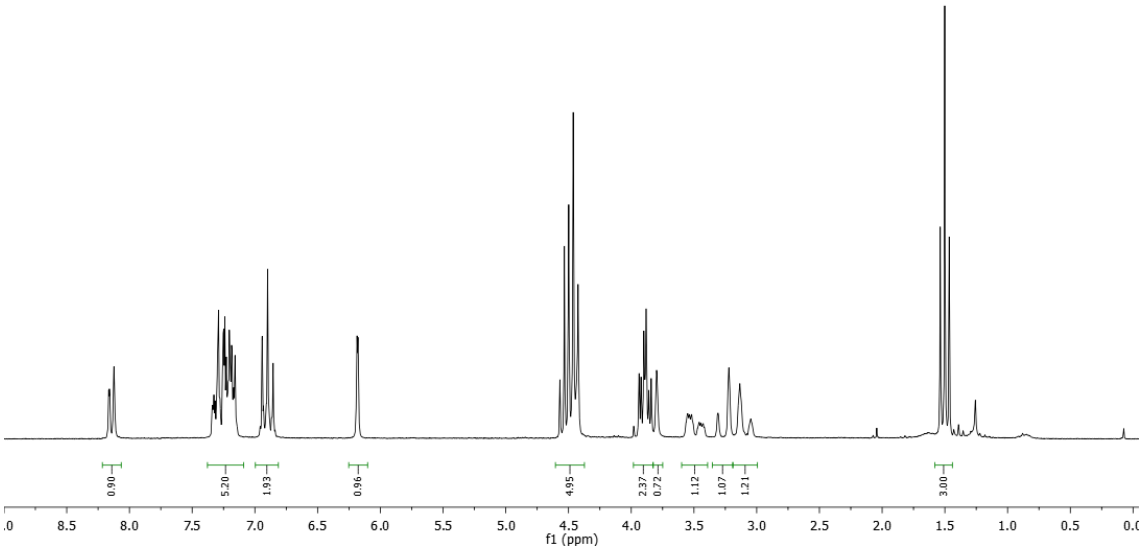
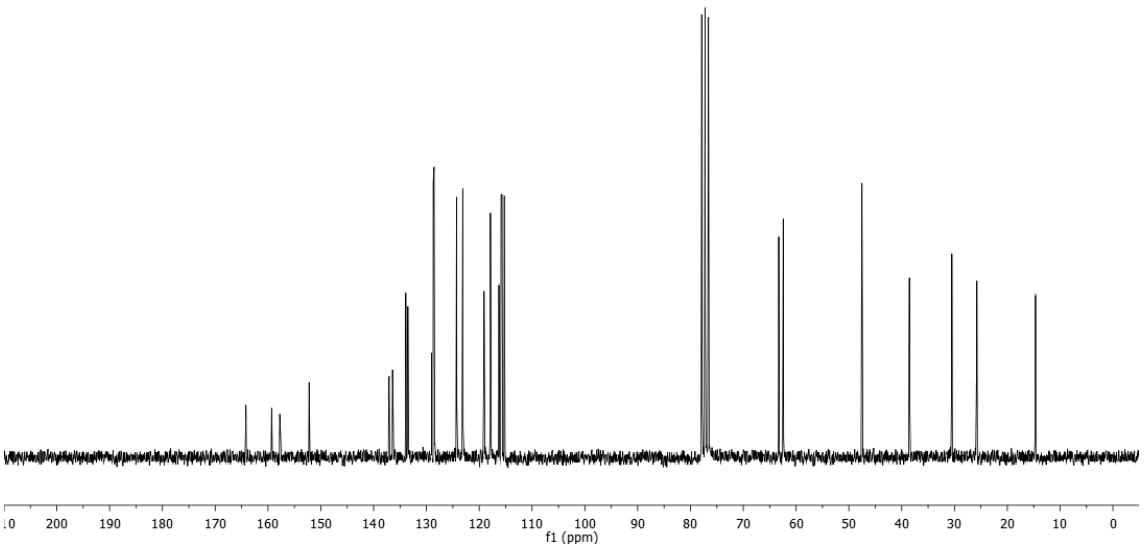
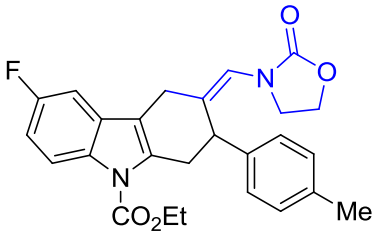
0
f1 (ppm)



4d







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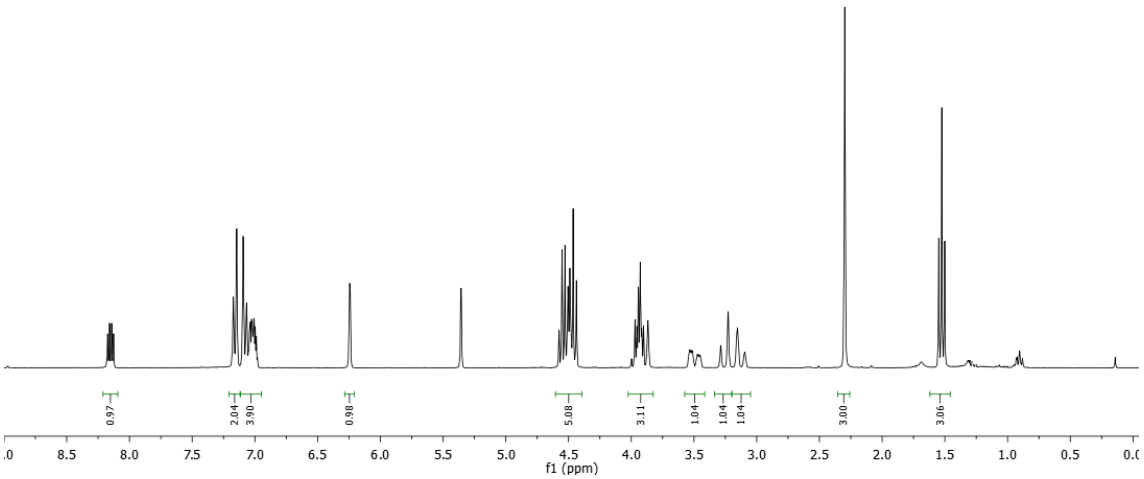

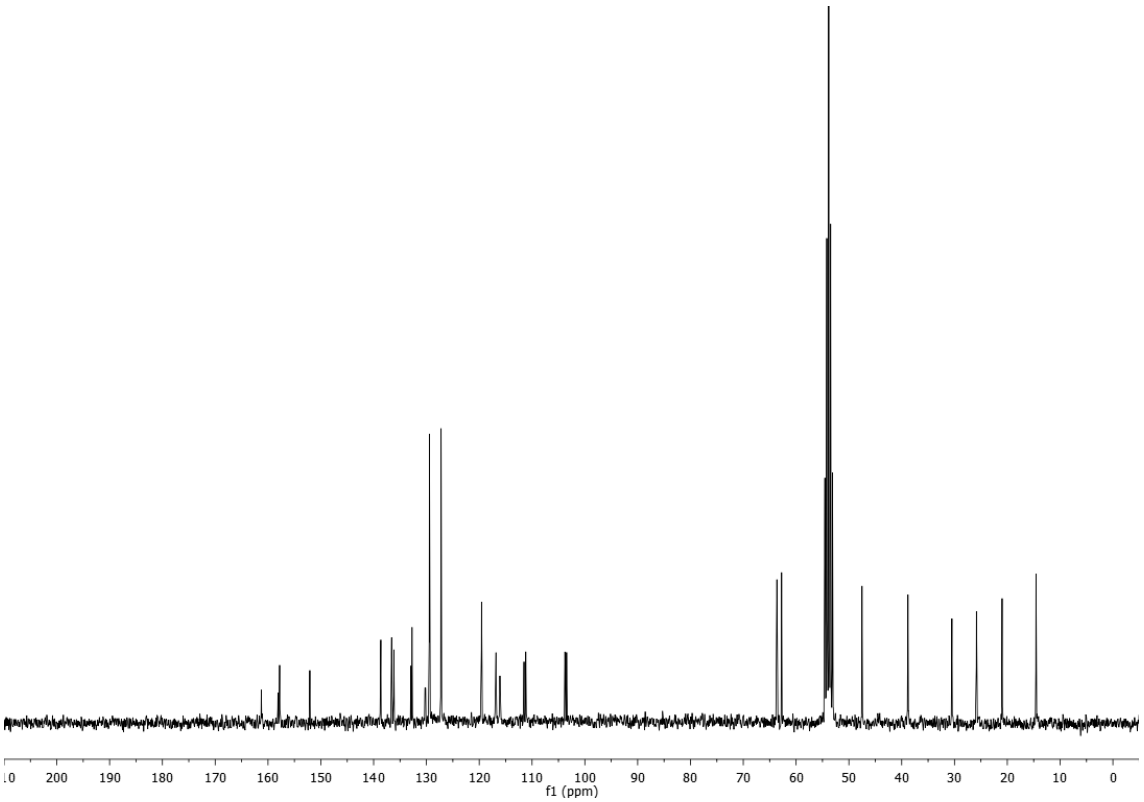

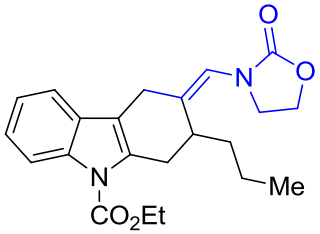

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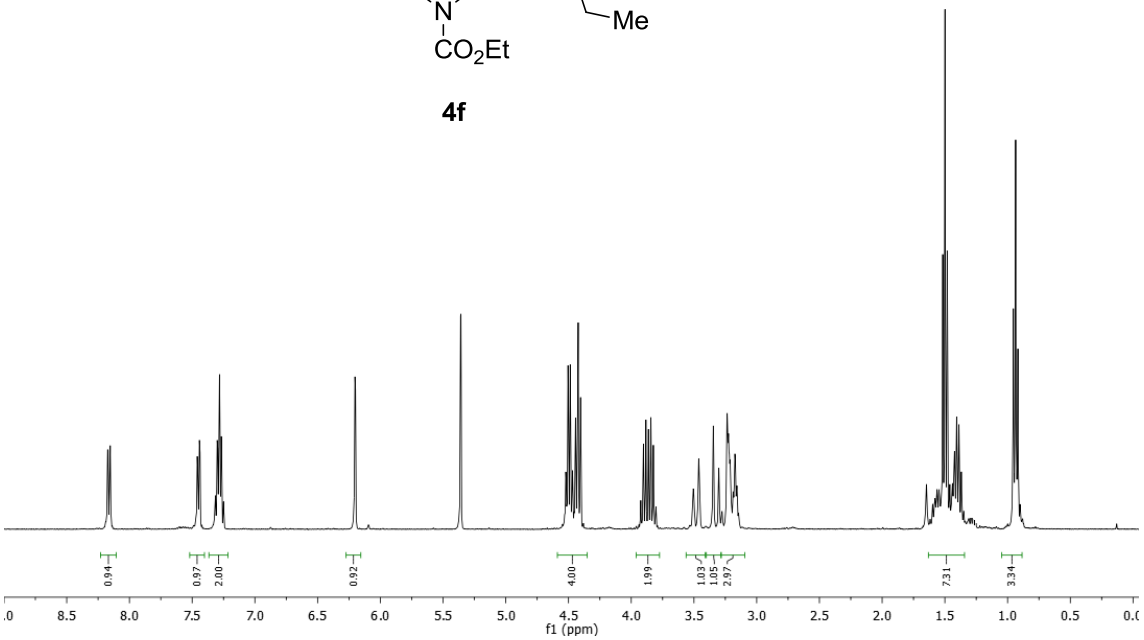
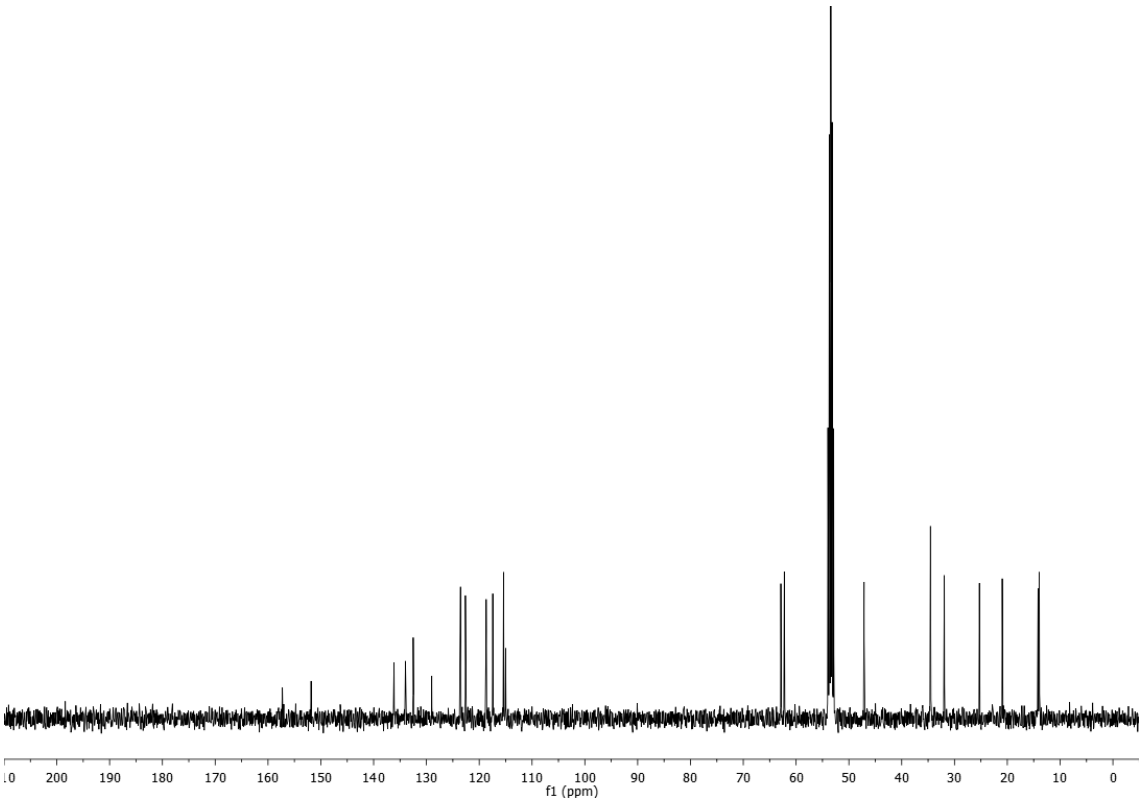
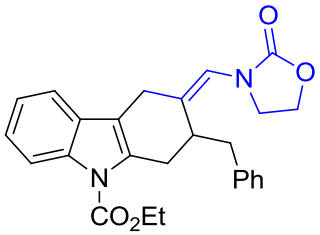
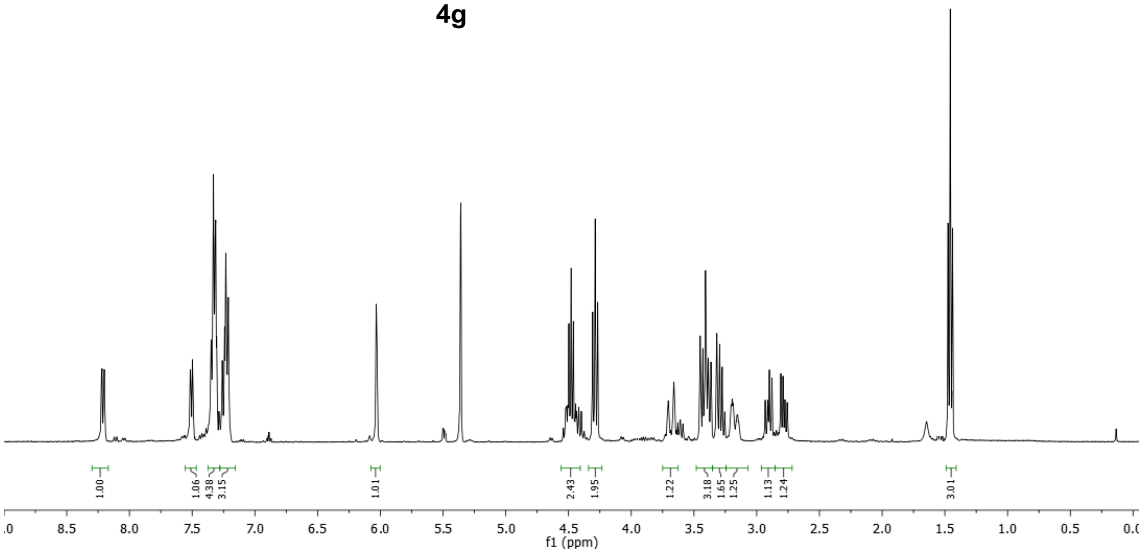





O
N
O
N
Ph
CO2Et

4g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1.06
4.38
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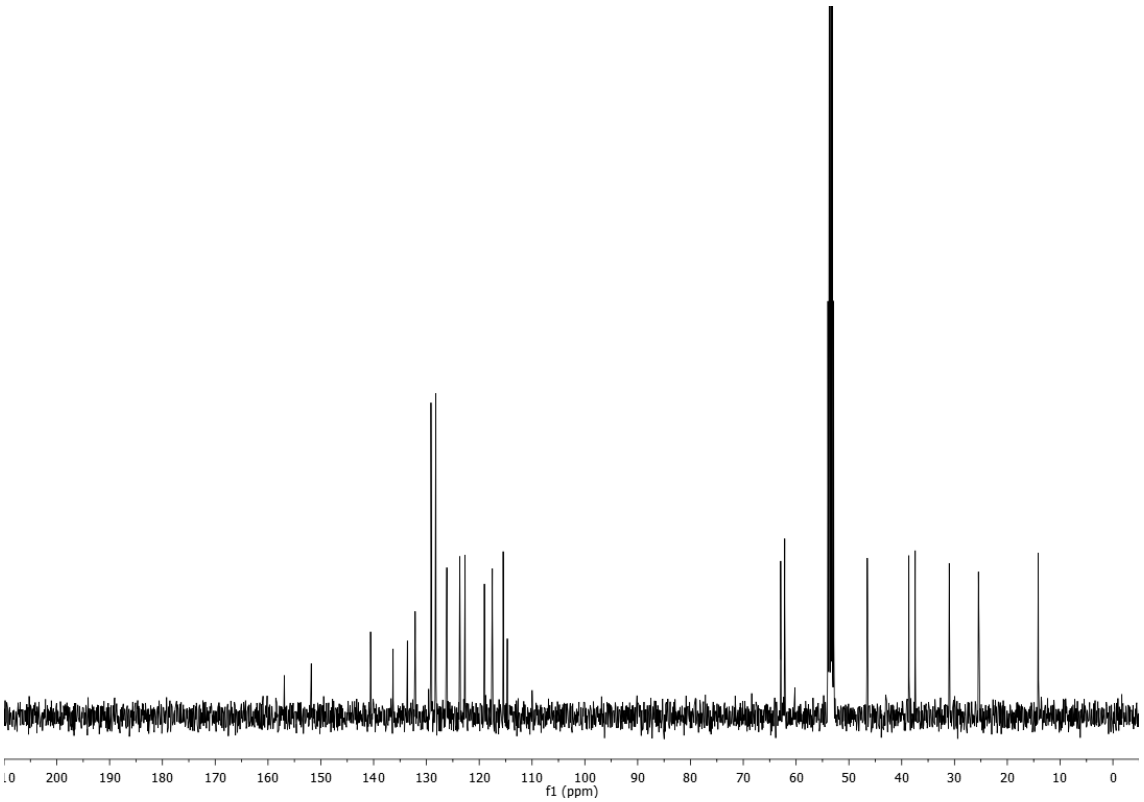
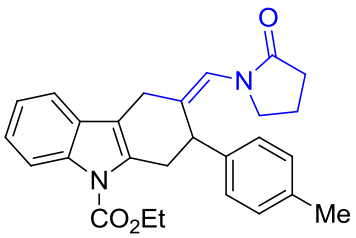
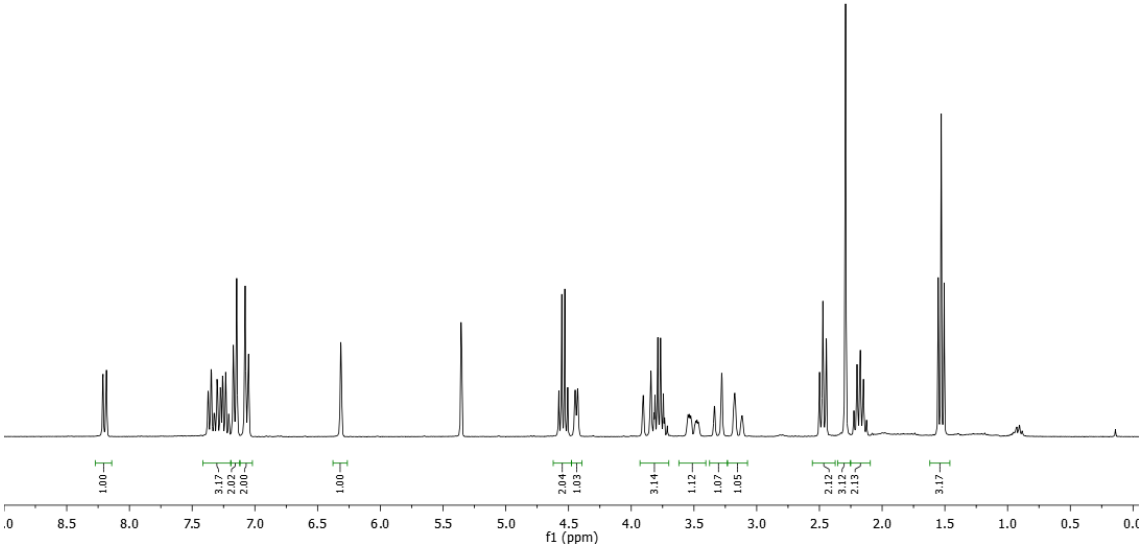
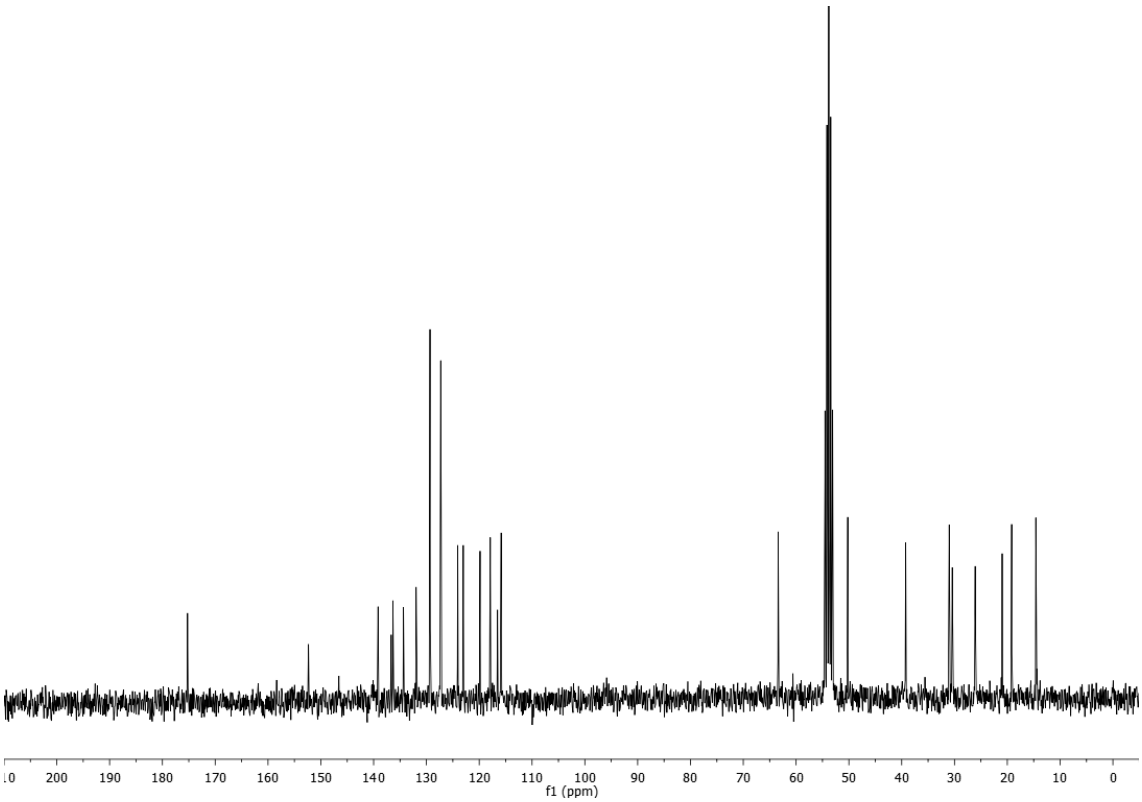
1.01
2.43
1.95
1.22
3.18
1.65
1.25
1.13
1.24
3.01
f1 (ppm)

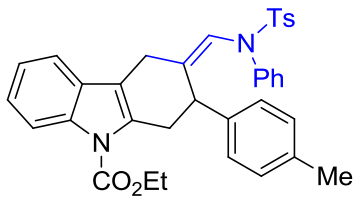

f1 (ppm)



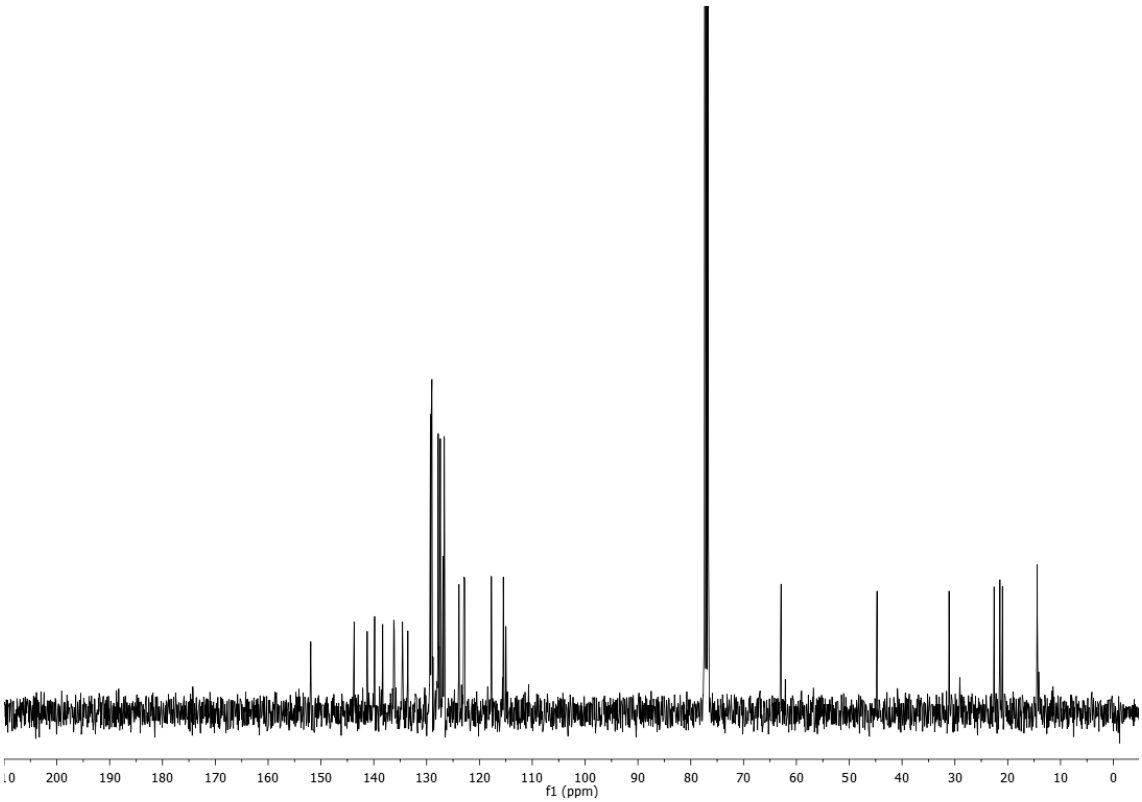
4h

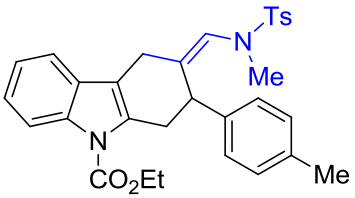




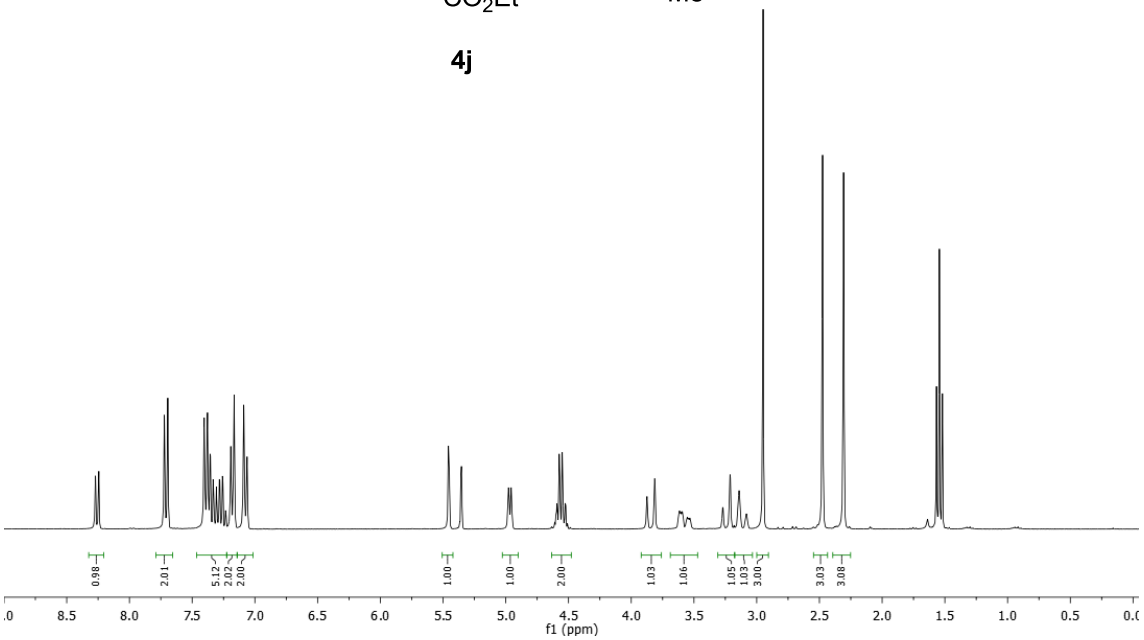


4i




Ts
N
Me
N
CO2Et
Me

4j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5.12
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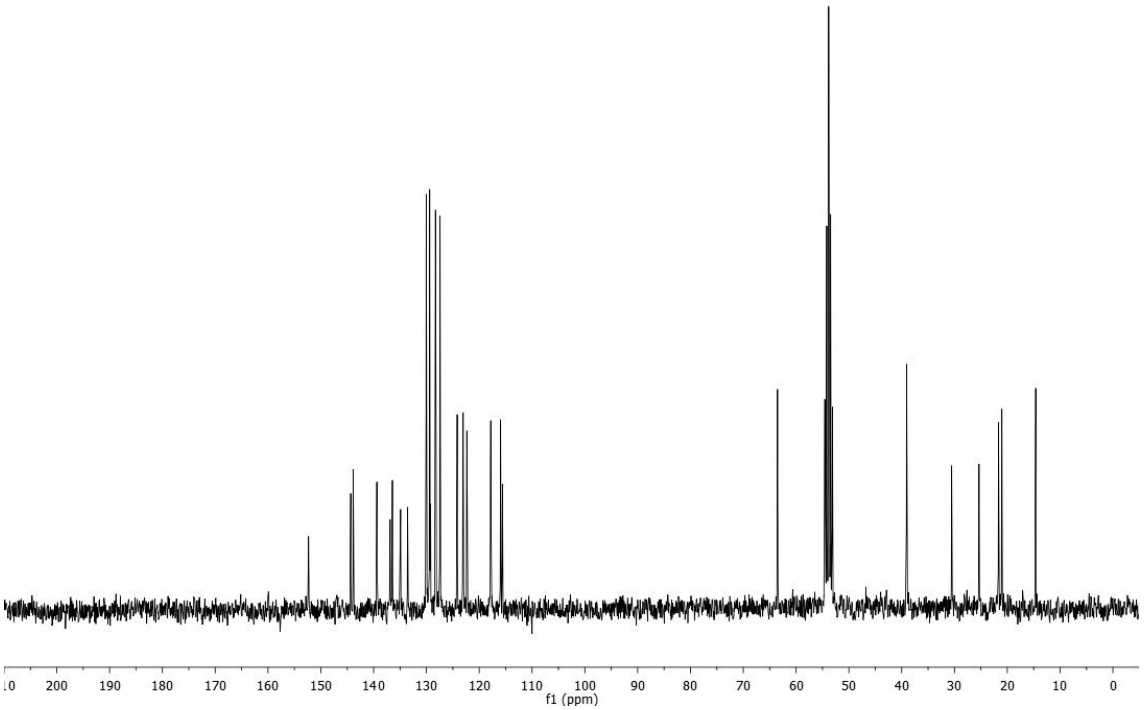
2.00
1.00
1.00
2.00
1.03
1.06
1.05
1.03
3.00
3.03
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


200
190
180
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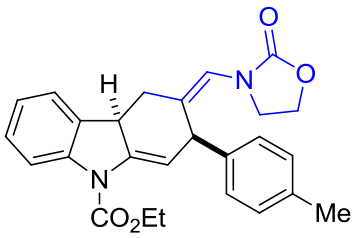
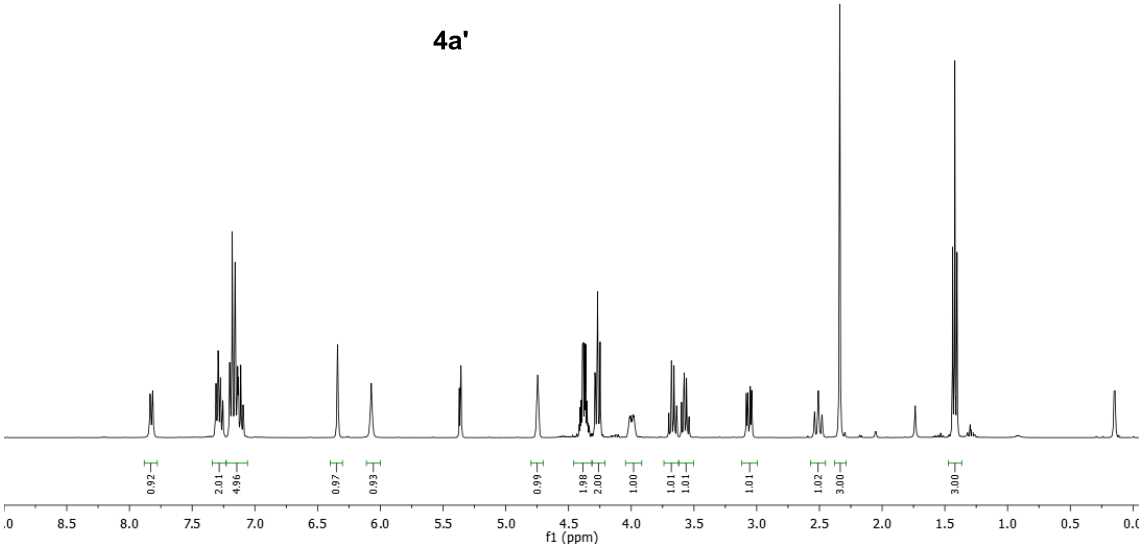
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
H
N
O
N
CO2Et
Me

4a'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0.99
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1.00
1.01
1.01
1.01
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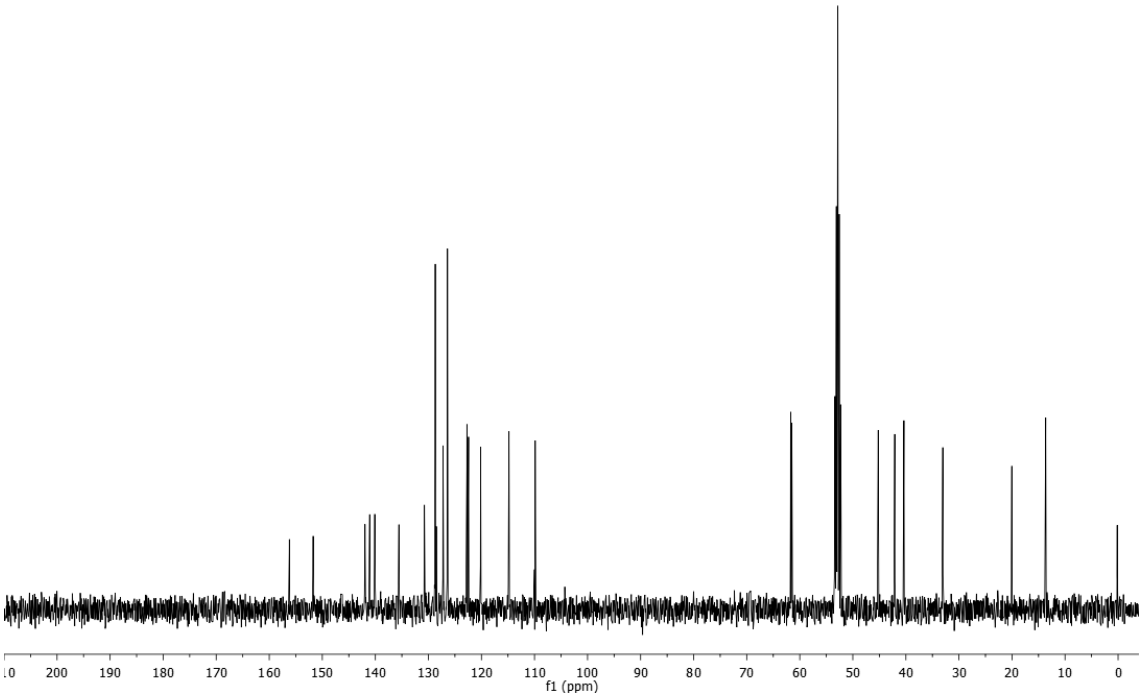
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


200
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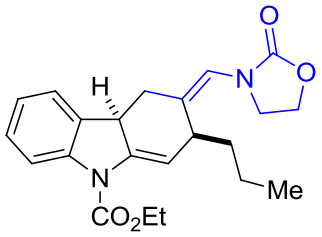
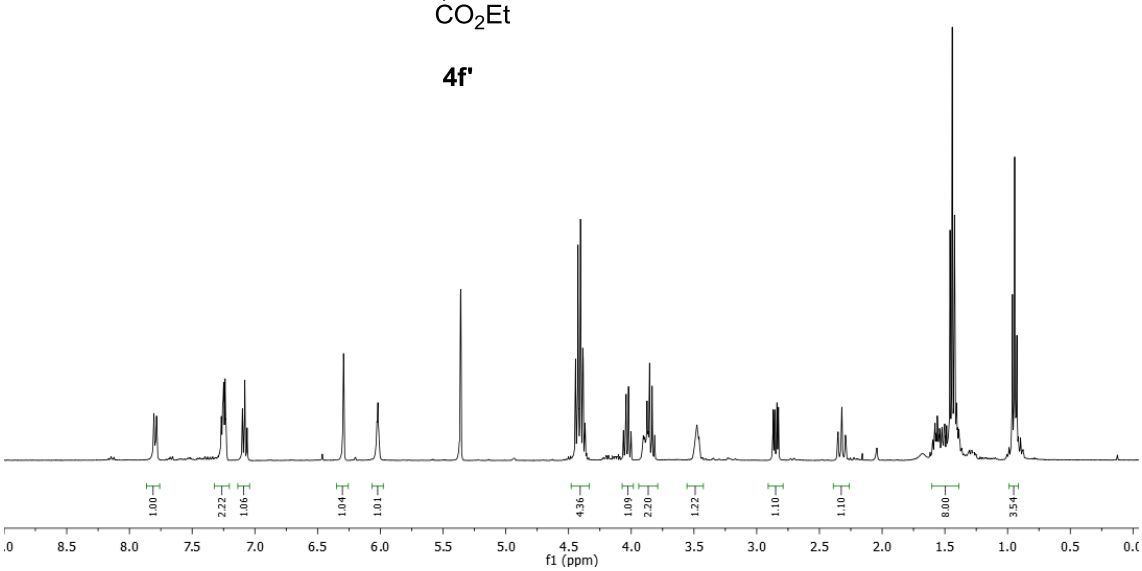
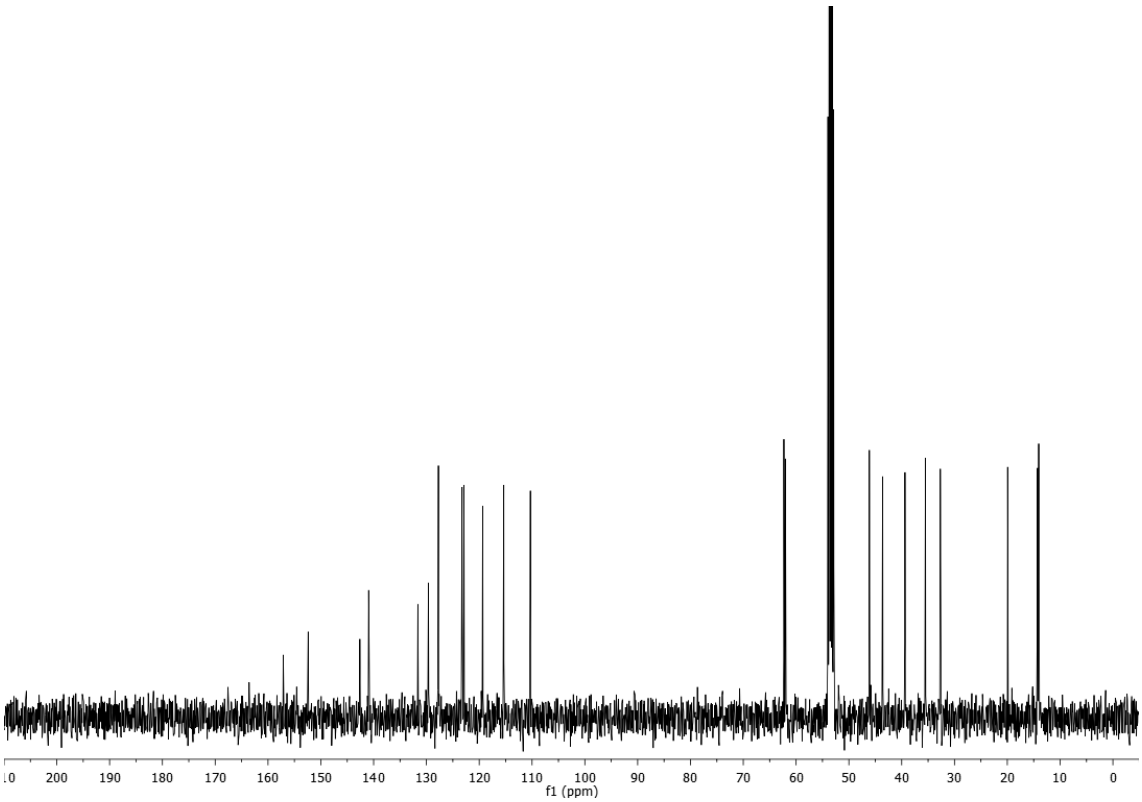
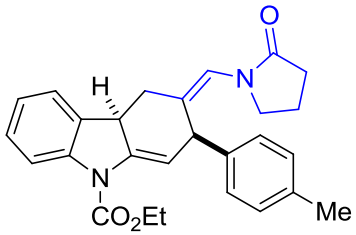
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



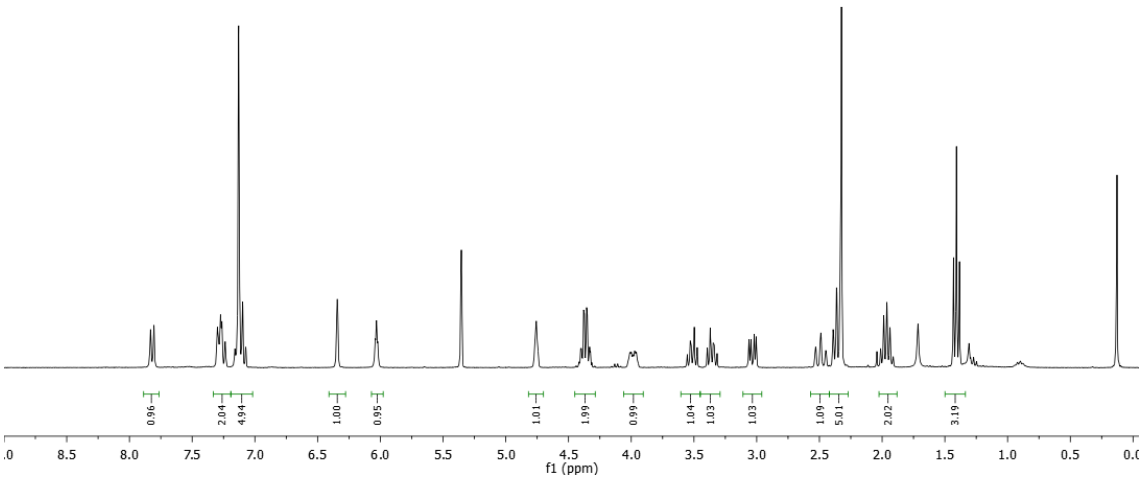
4f'






O
N
H
N
CO2Et
Me

4h'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1.03
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2.02
3.19
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
2.5
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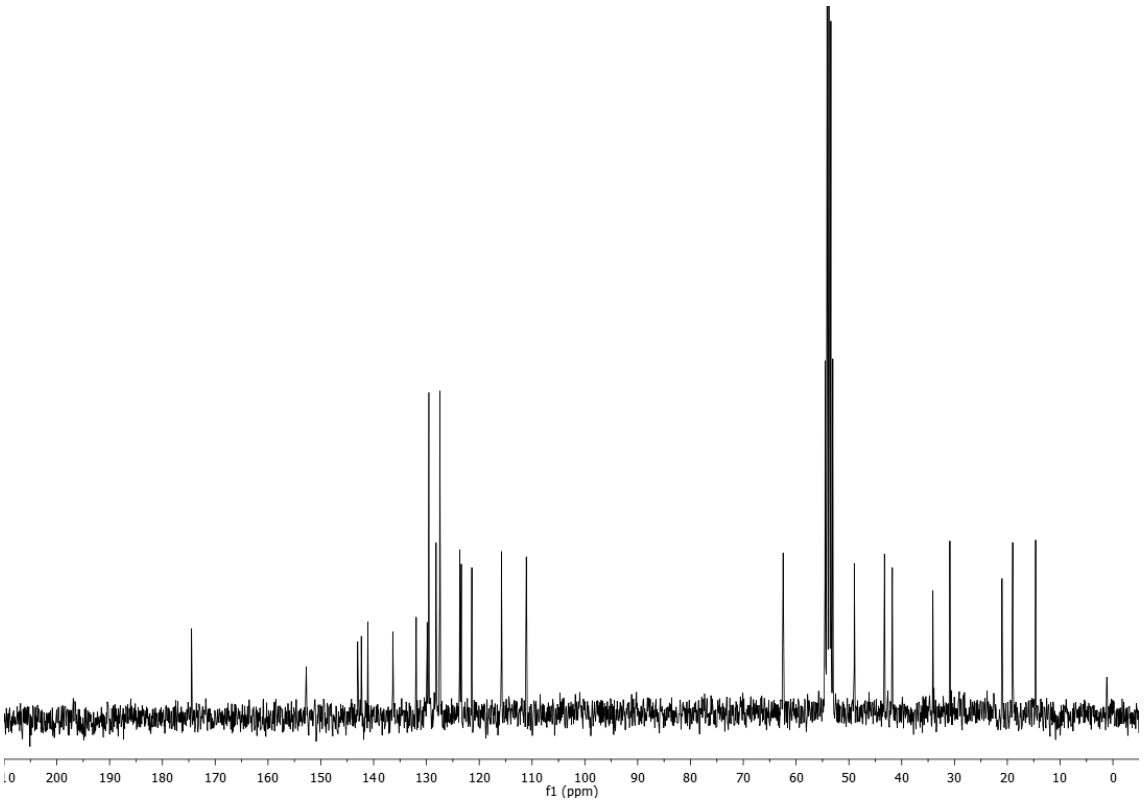
1.5
1.0
0.5
f1 (ppm)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120
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90
80
70
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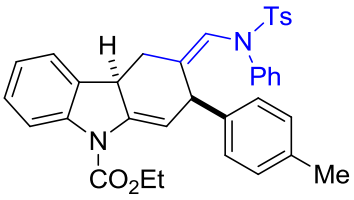
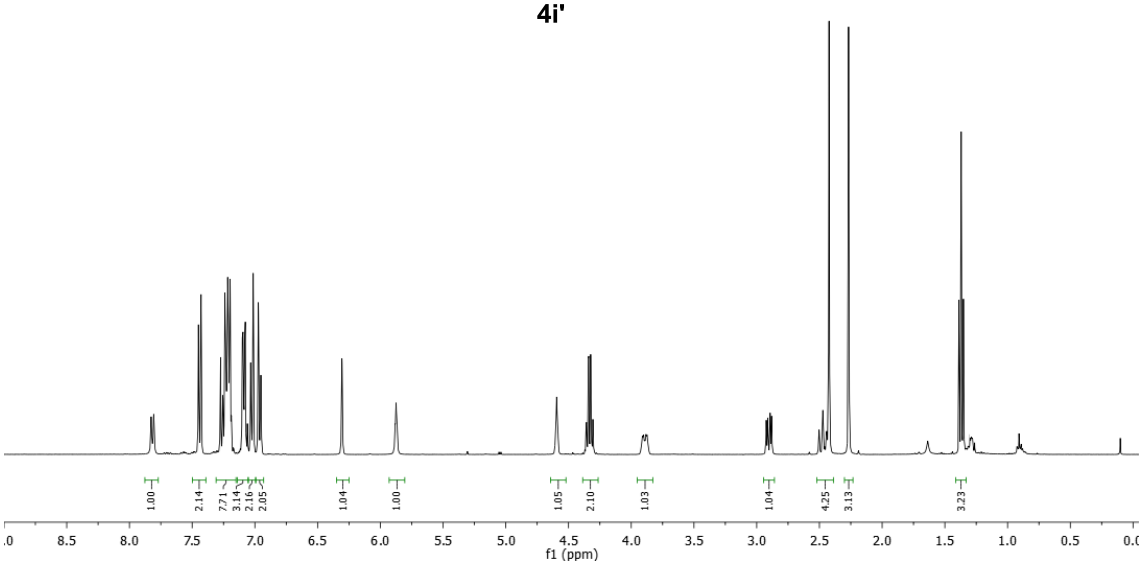
50
40
30
20
10
0
f1 (ppm)


Ts
N
H
Ph
N
CO2Et
Me

4i'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1.04
1.00
1.05
2.10
1.03
1.04
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3.13
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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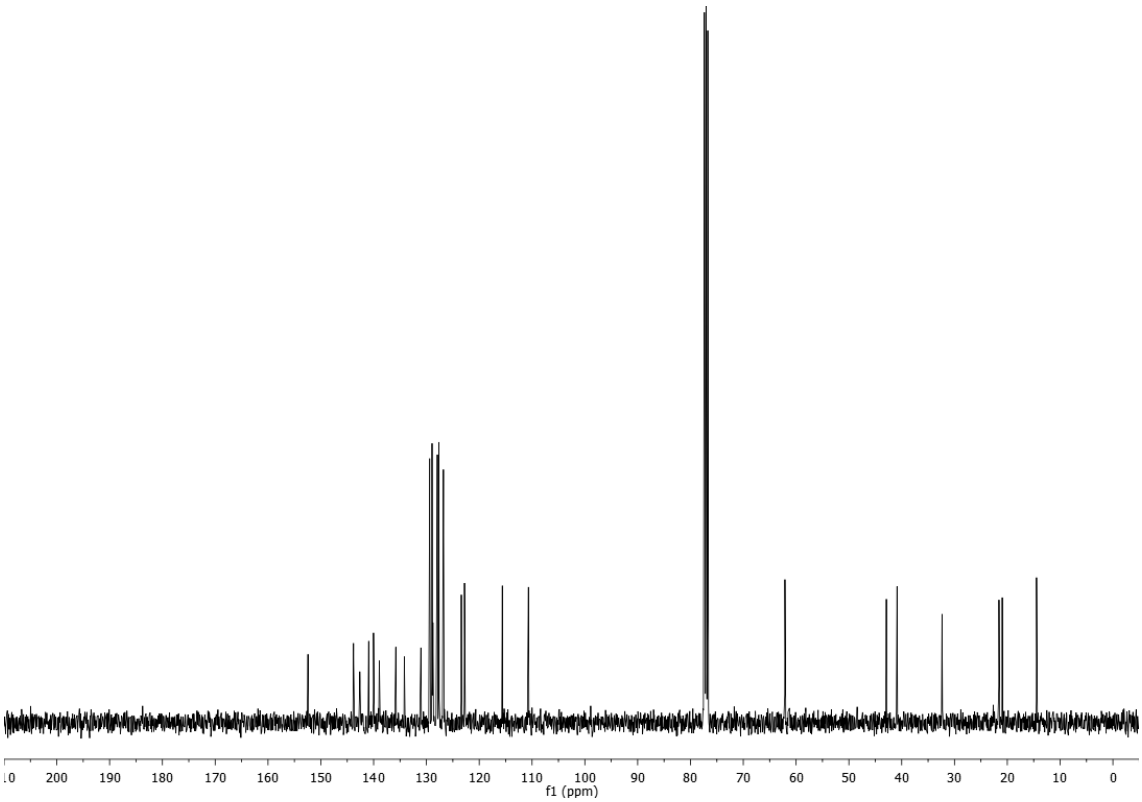
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


200
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140
130
120
110
100
90
80
70
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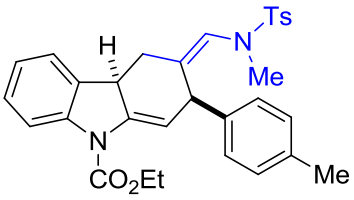
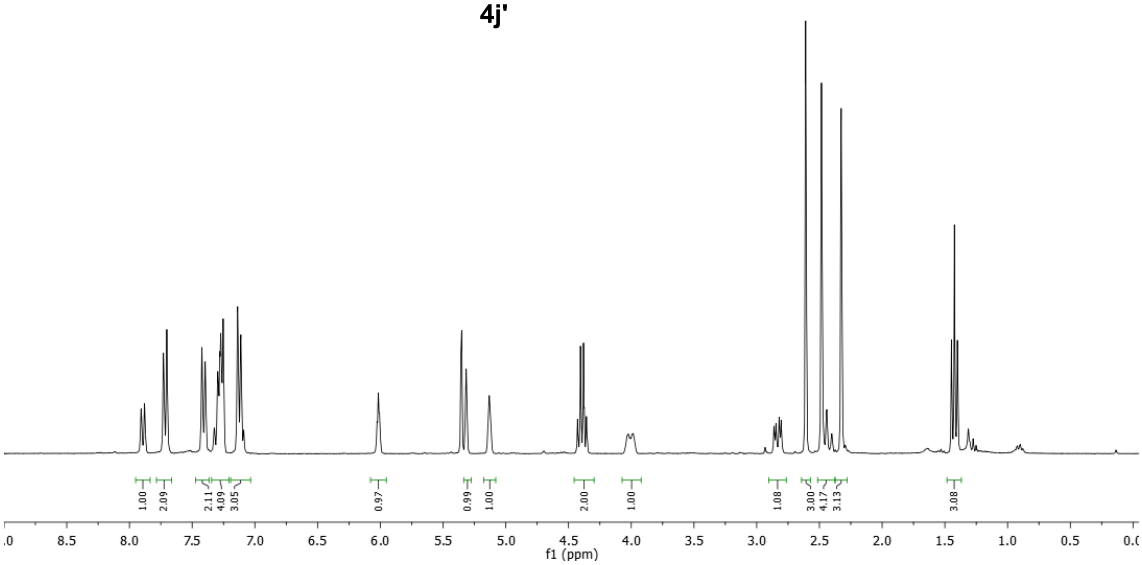
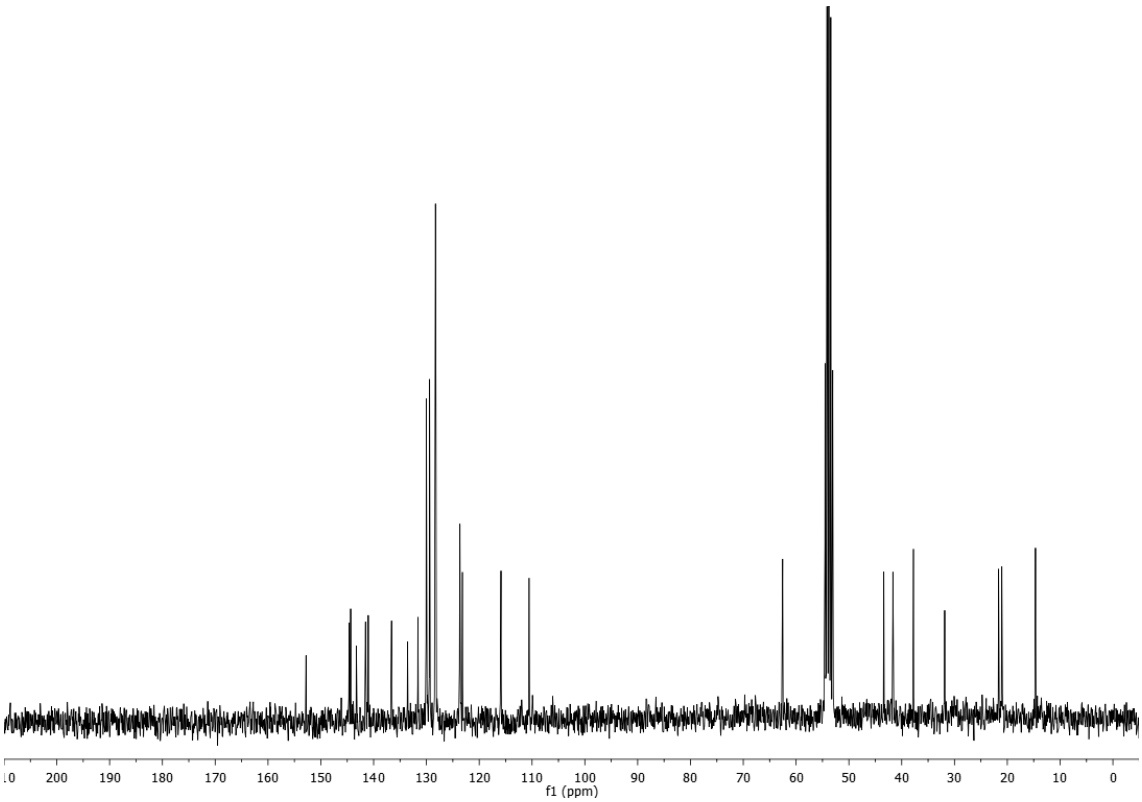
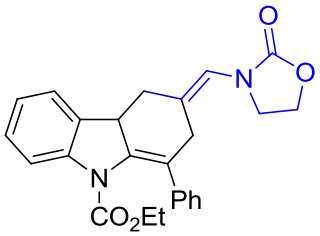
50
40
30
20
10
0
f1 (ppm)



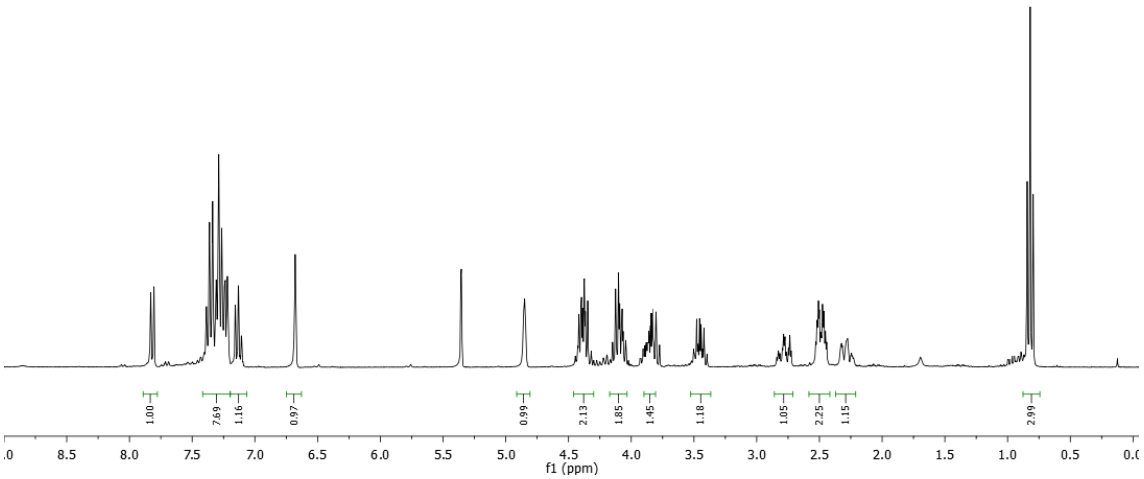
4j'






O
N
O
N
CO2Et
Ph

4k'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0.99
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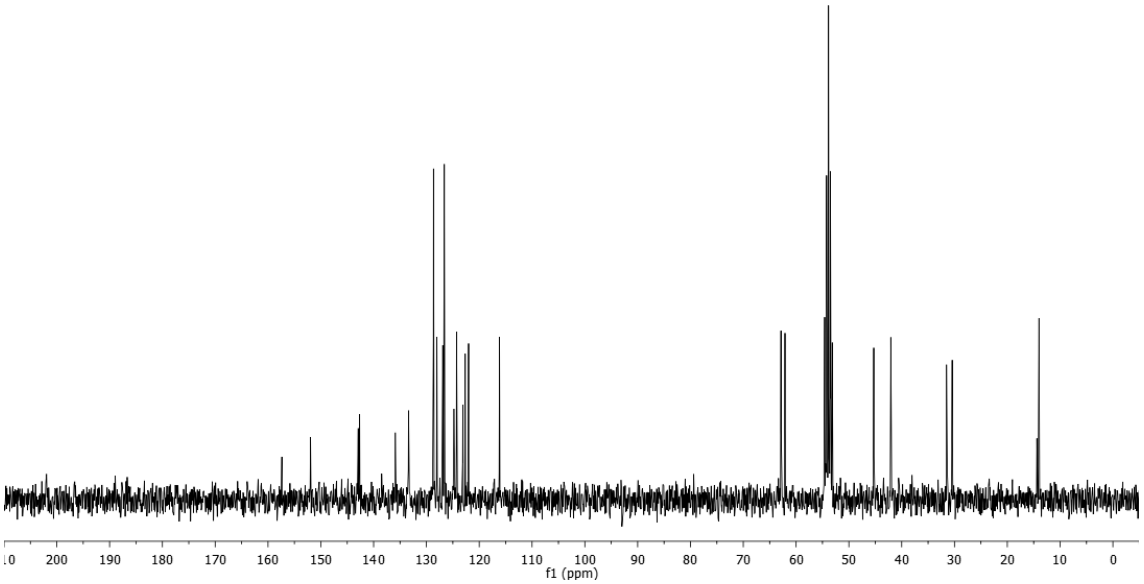
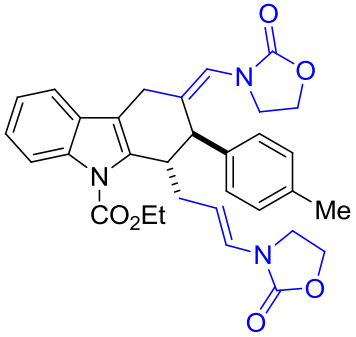
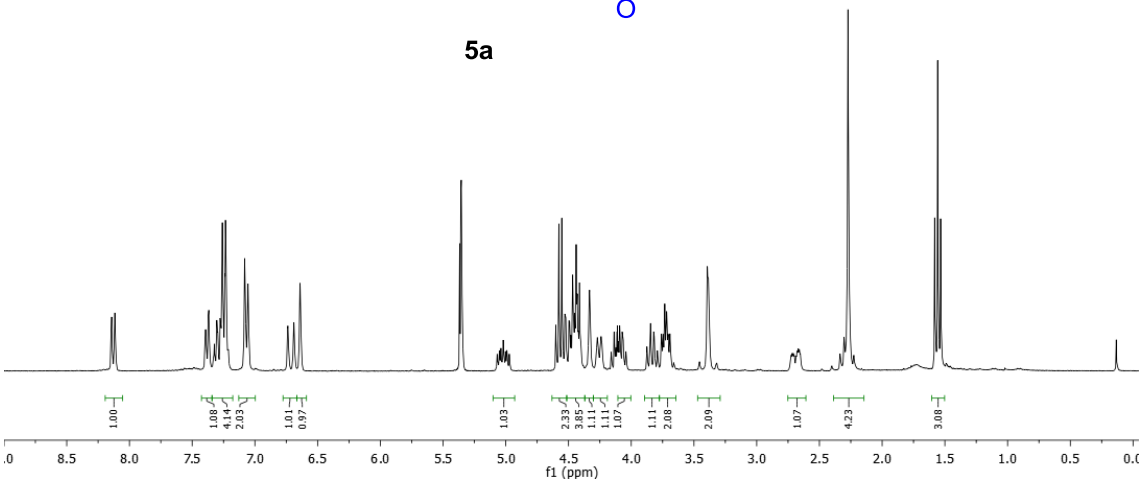
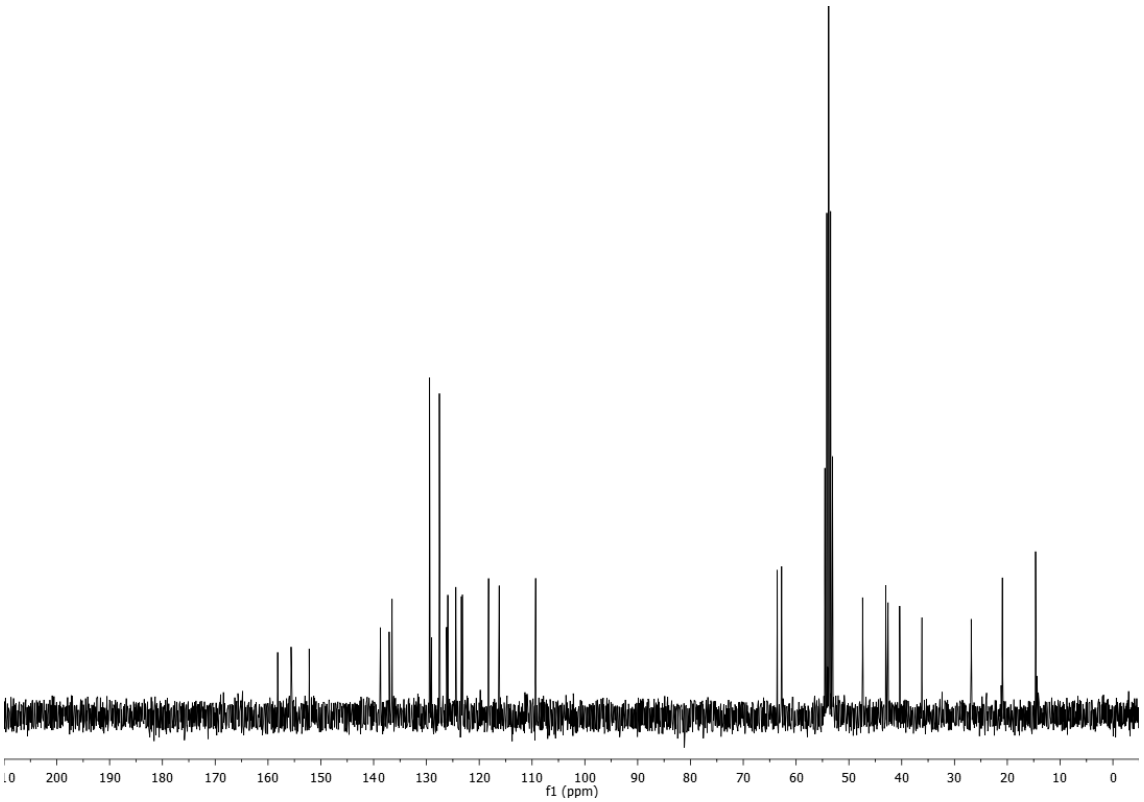
1.18
1.05
2.25
1.15
2.99
f1 (ppm)

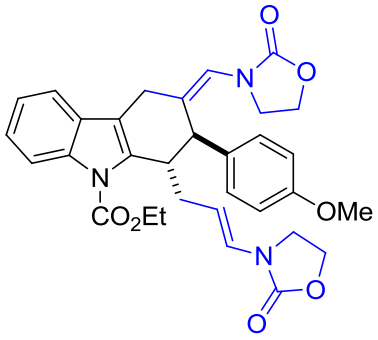

f1 (ppm)



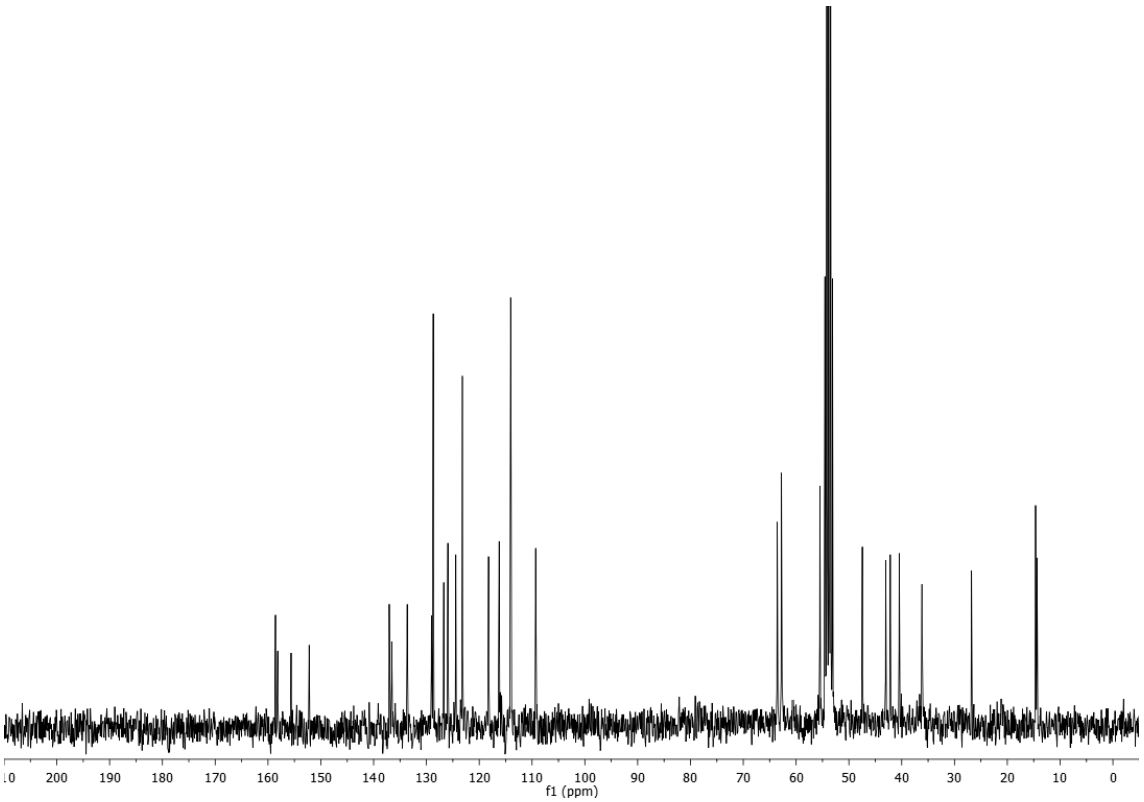
5a

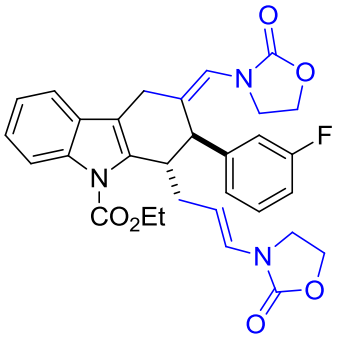




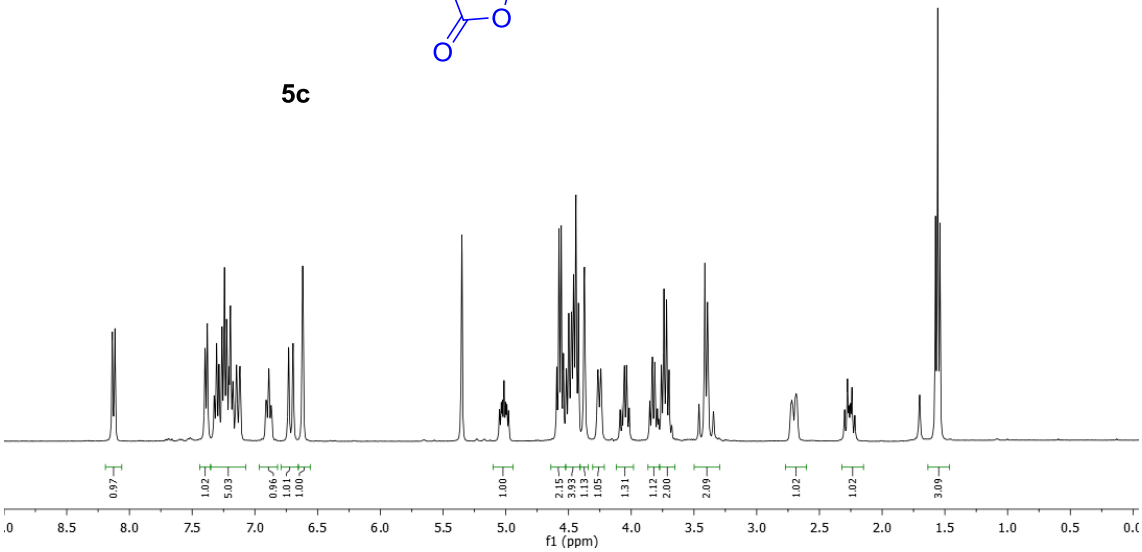


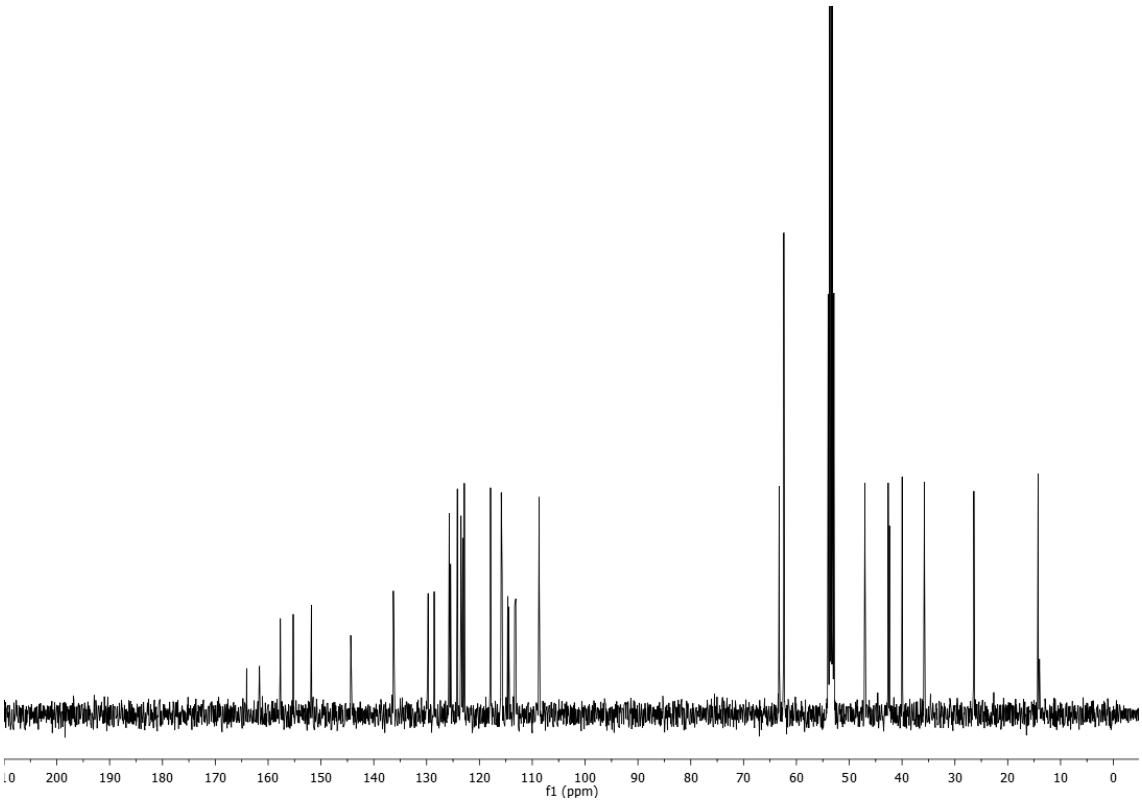
5b

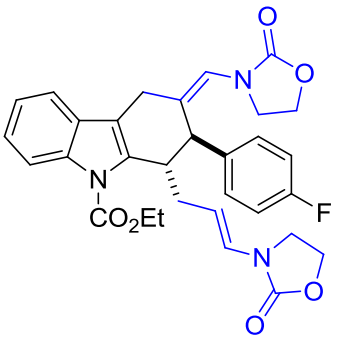




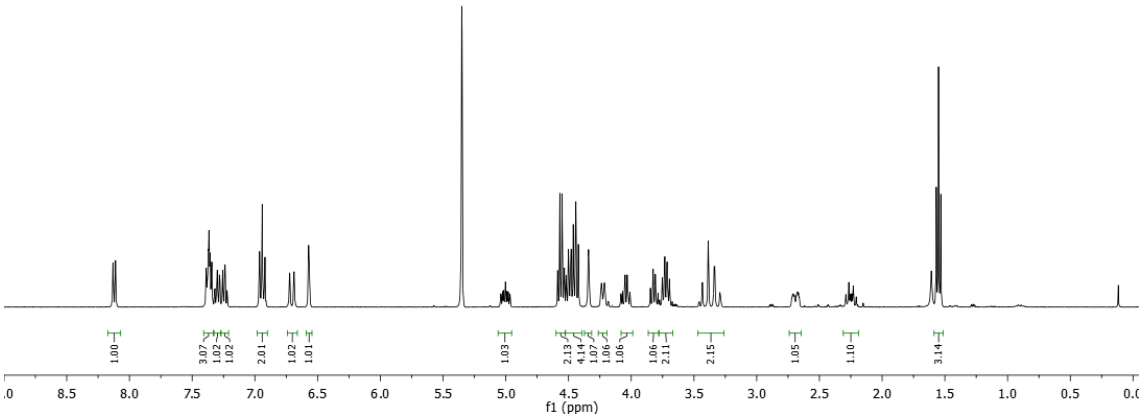
5c

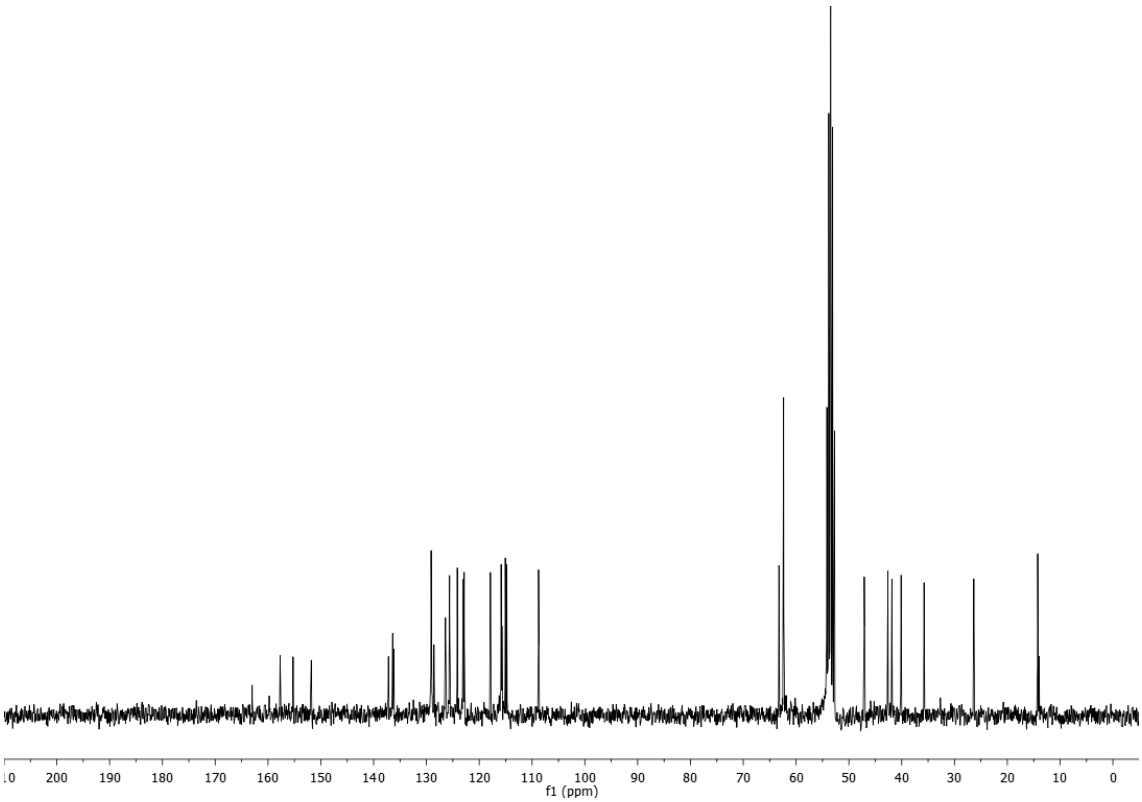


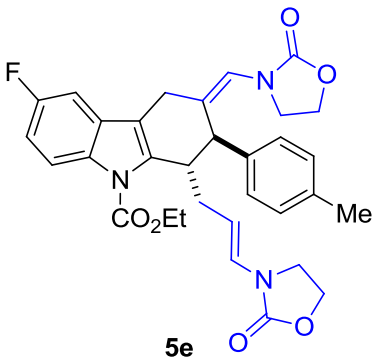




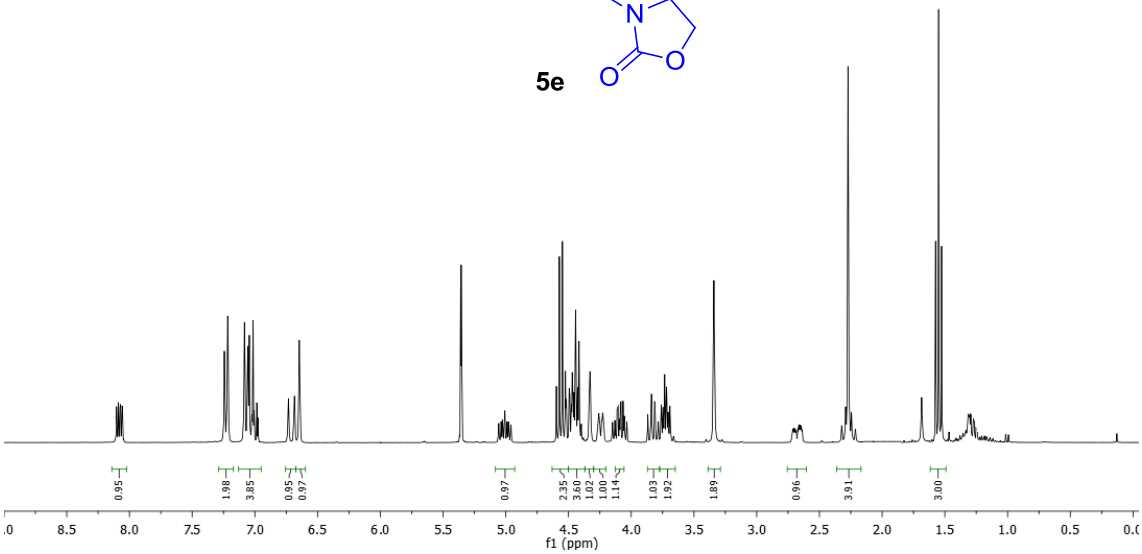
5d

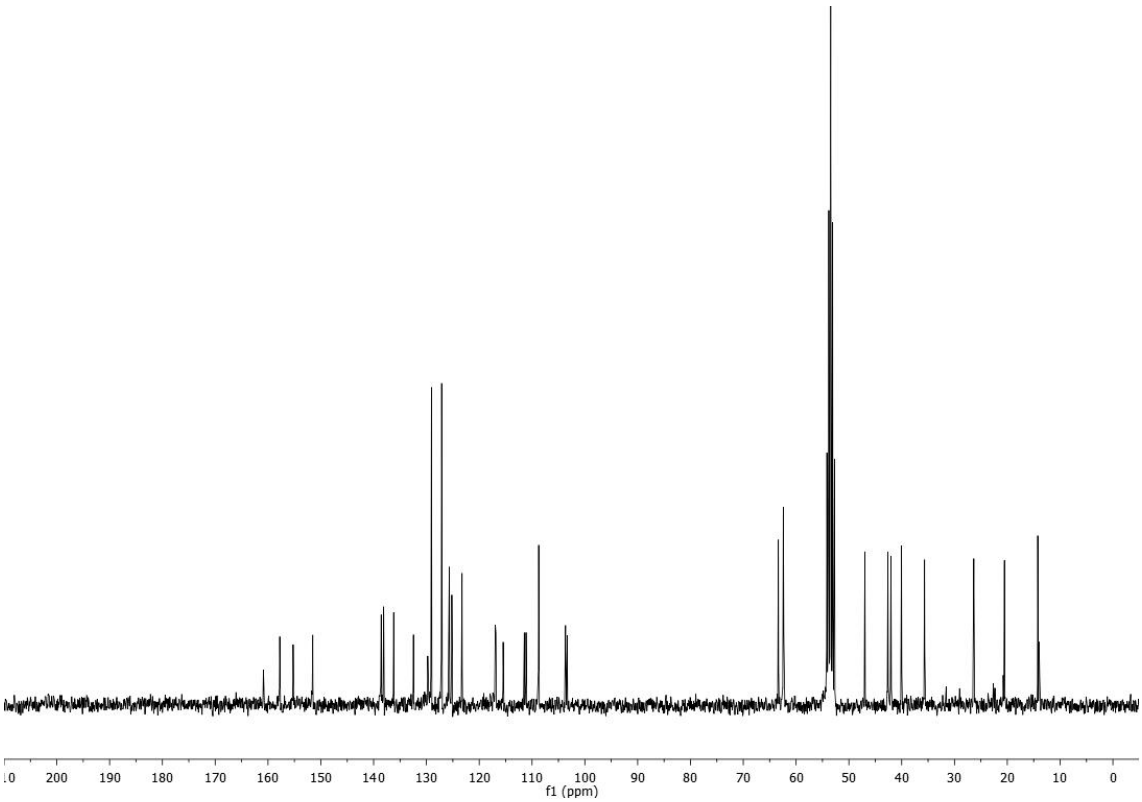


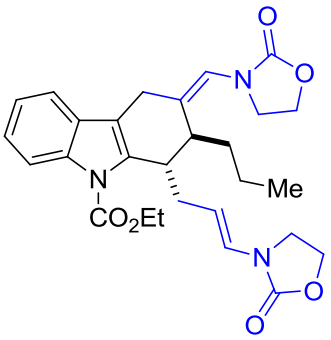




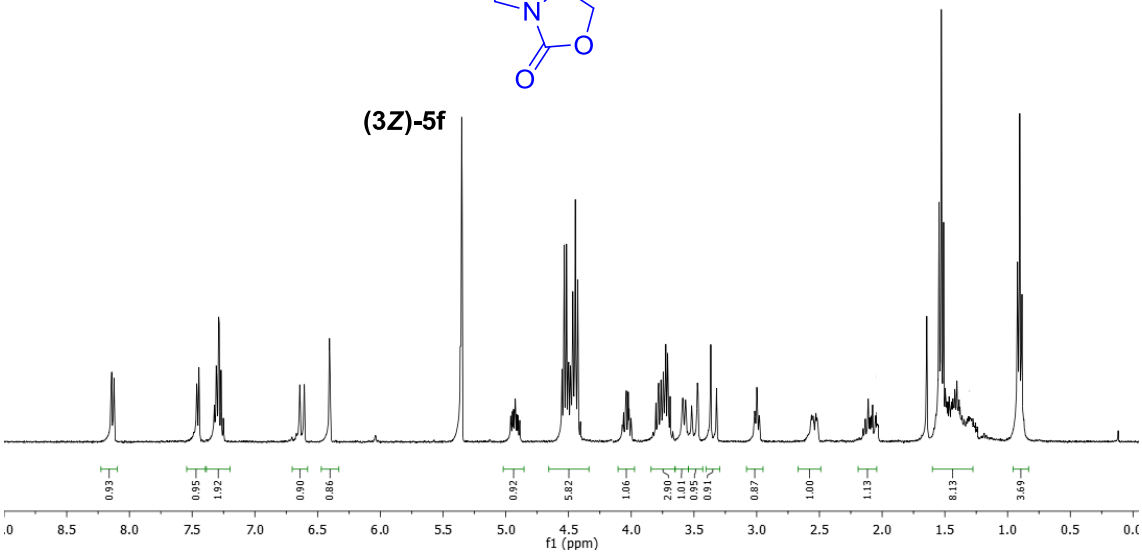
5e

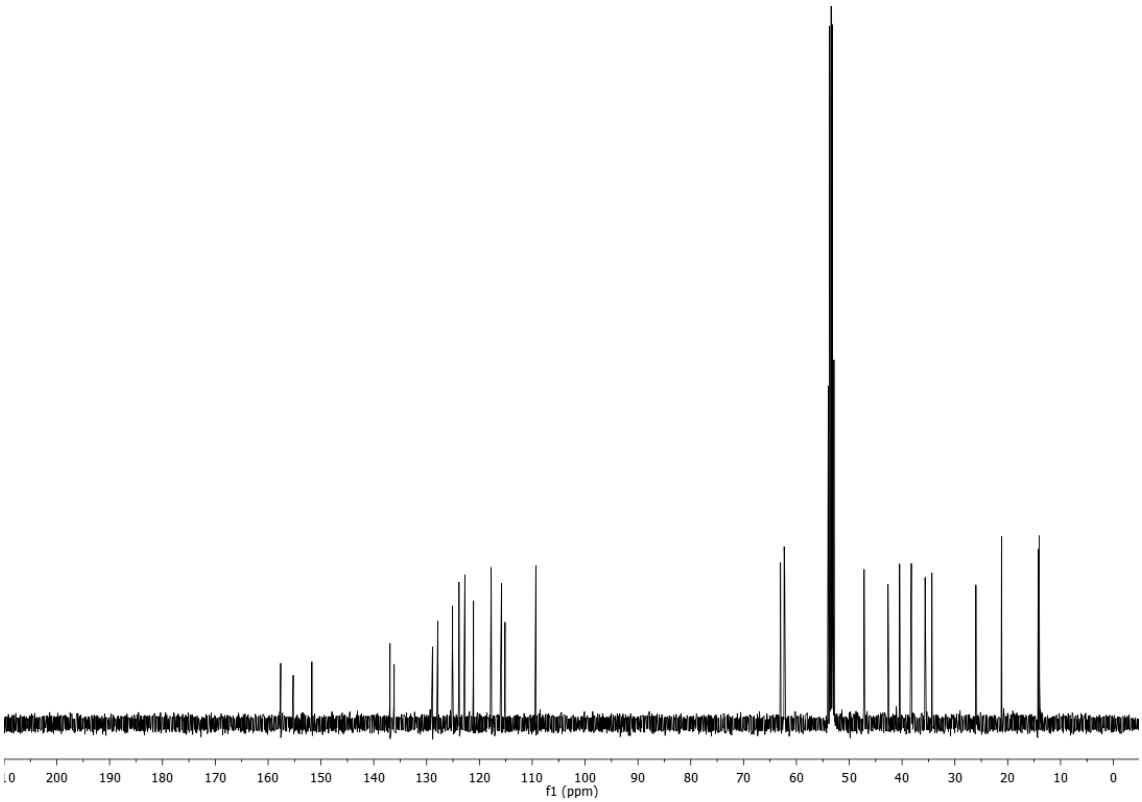


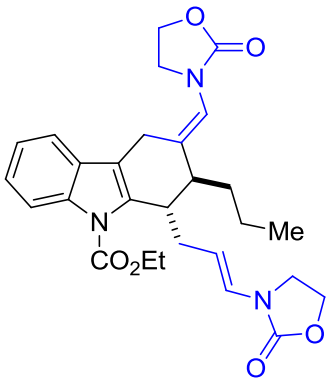




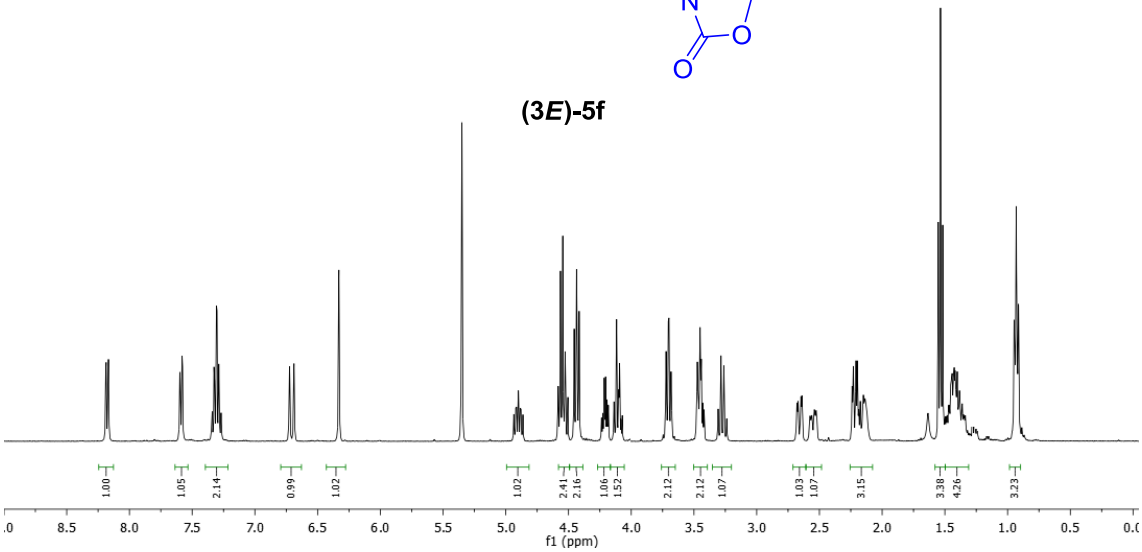
(3*Z*)-5f

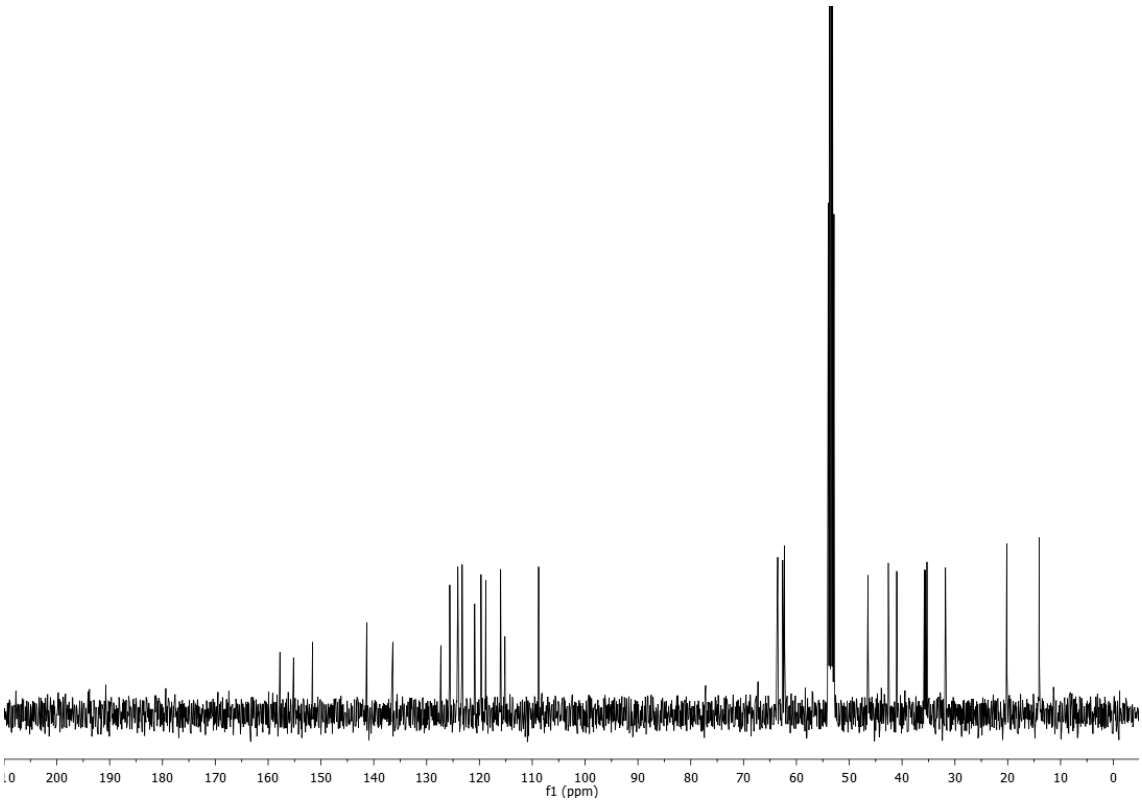


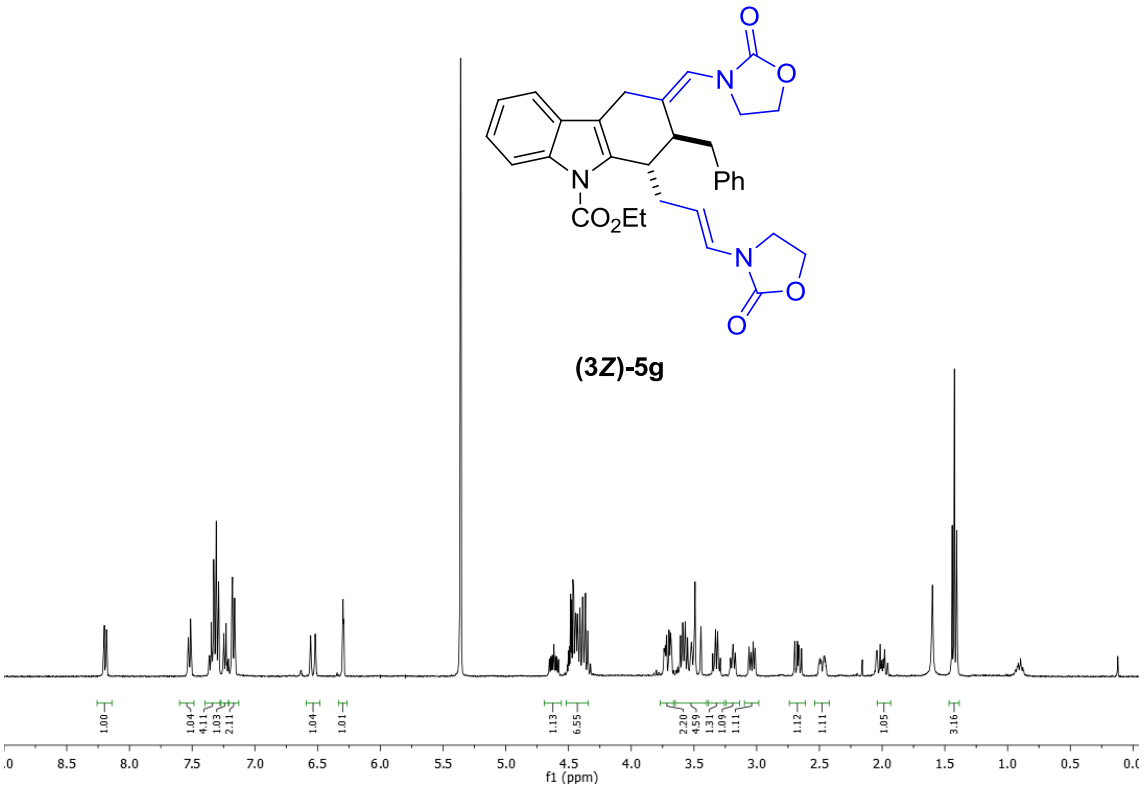




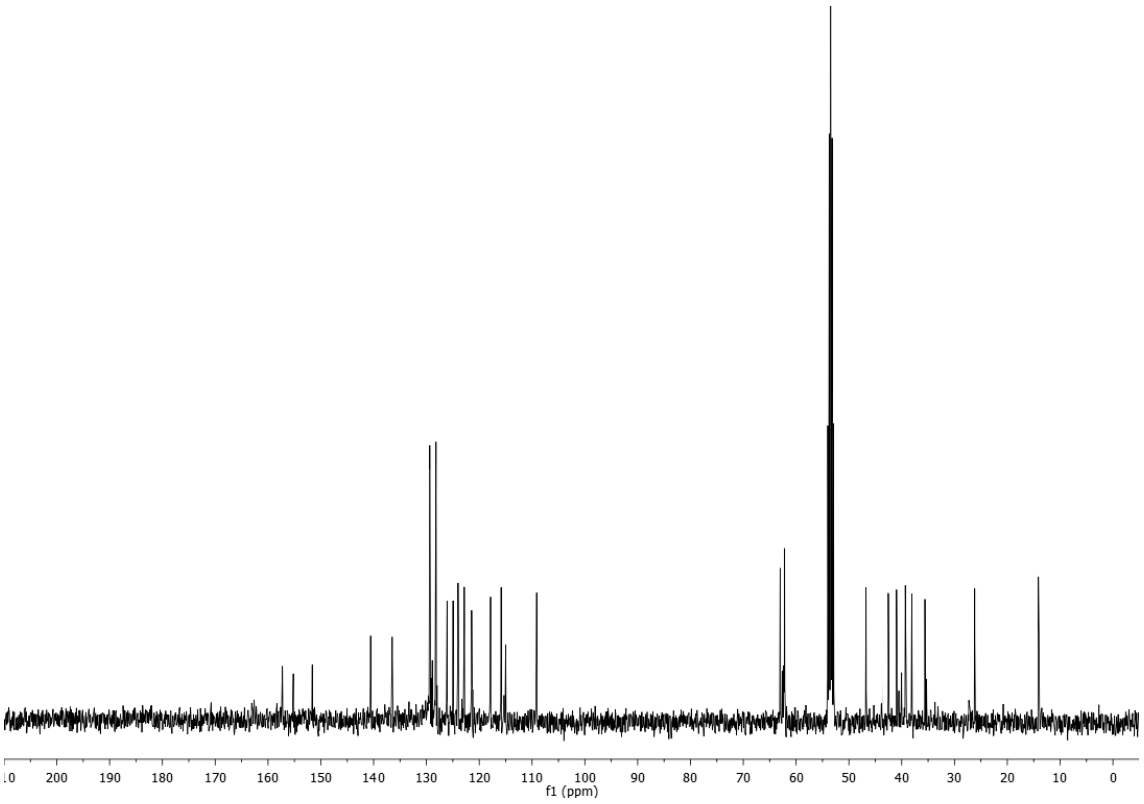
(3*E*)-5f

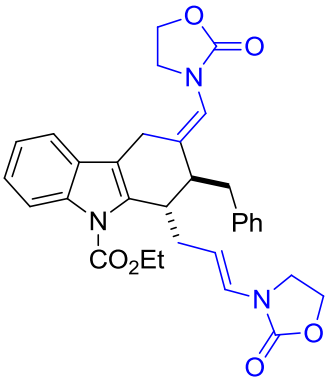




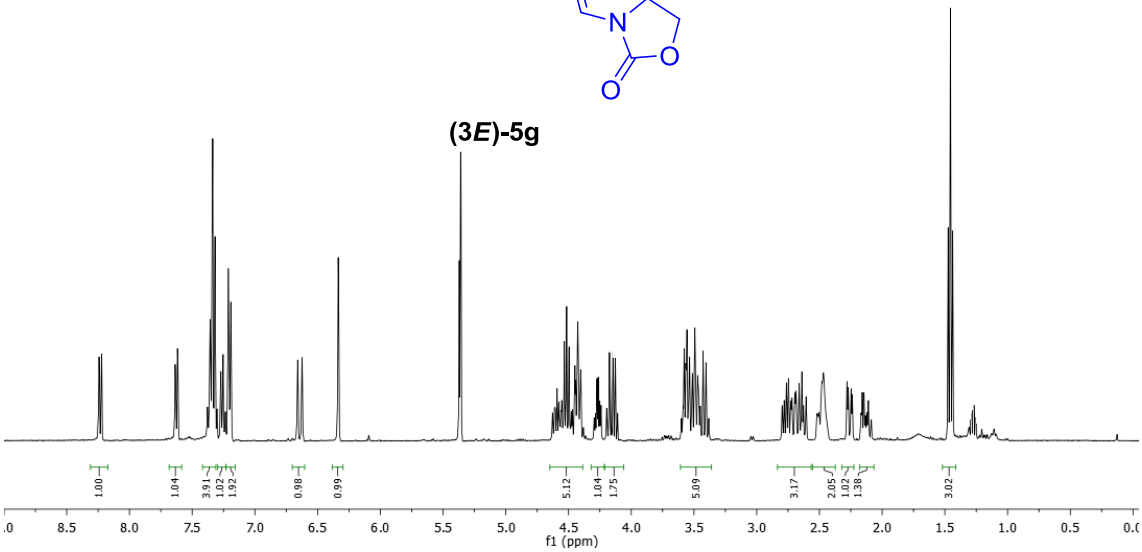

O
N
O
Ph
N
CO2Et
N
O
O
1.00
1.04
4.11
1.03
2.11
1.04
1.01
1.13
6.55
2.20
4.59
1.31
1.09
1.11
1.12
1.11
1.05
3.16
f1 (ppm)

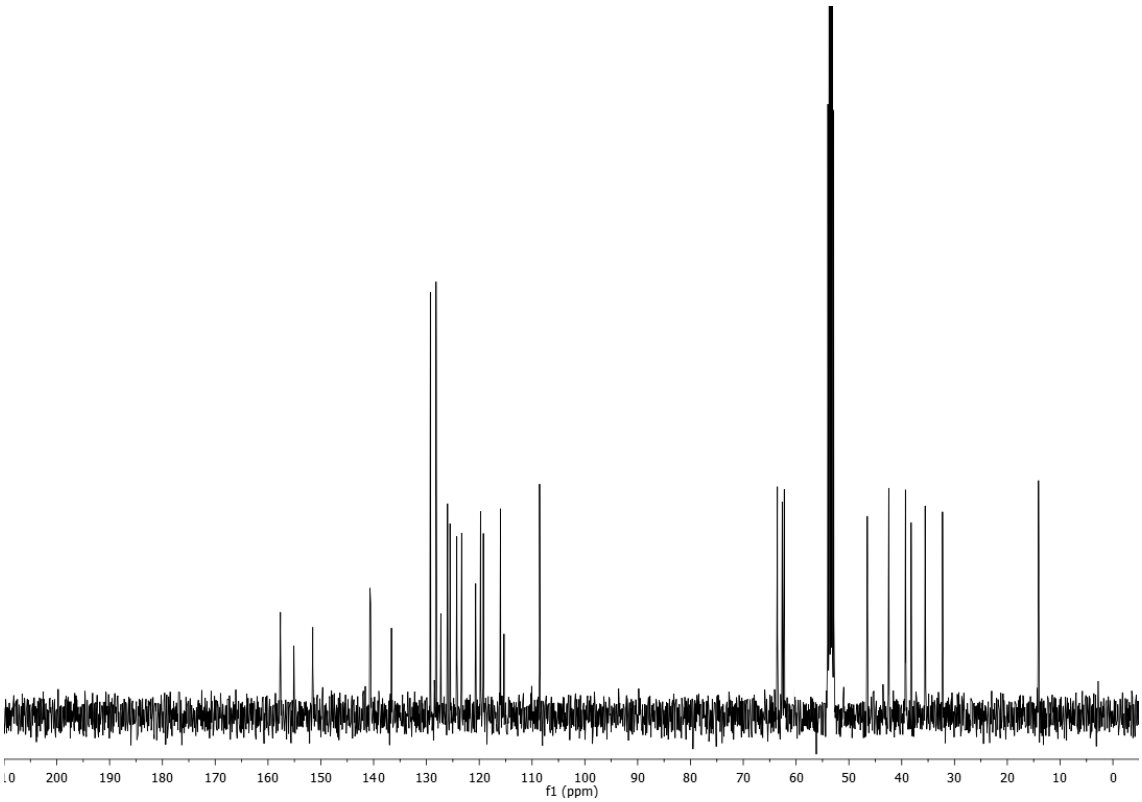
(3*Z*)-5g

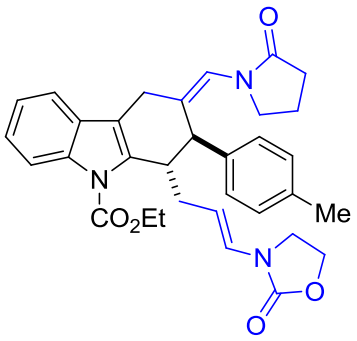

f1 (ppm)


O
O
N
Ph
N
CO2Et
N
O
O

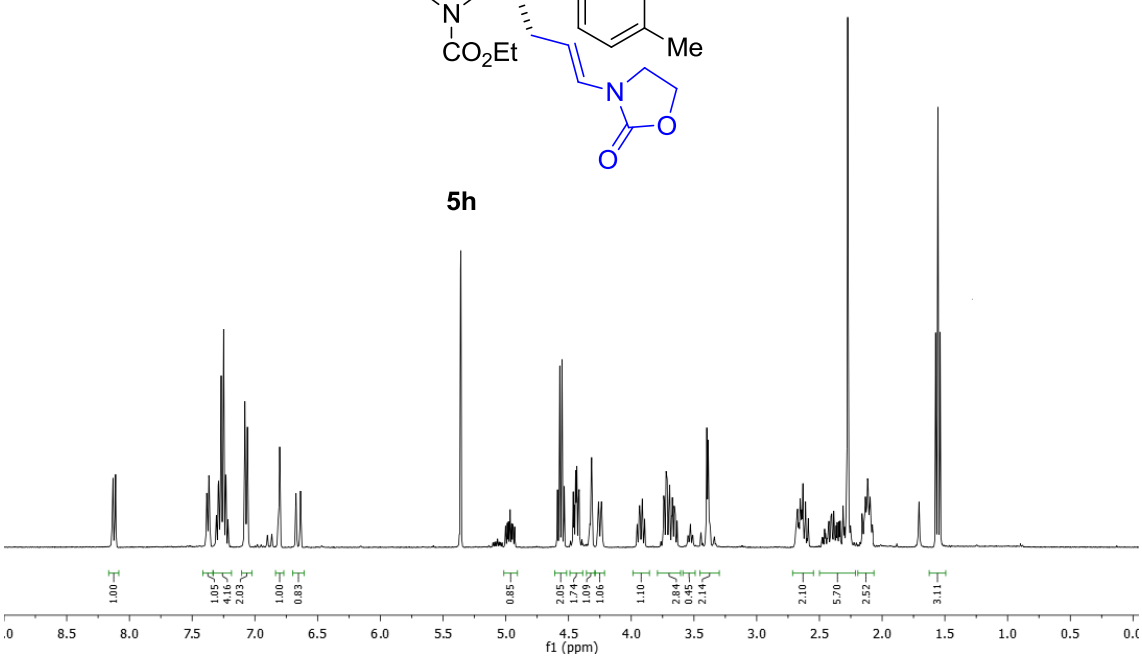
(3*E*)-5g

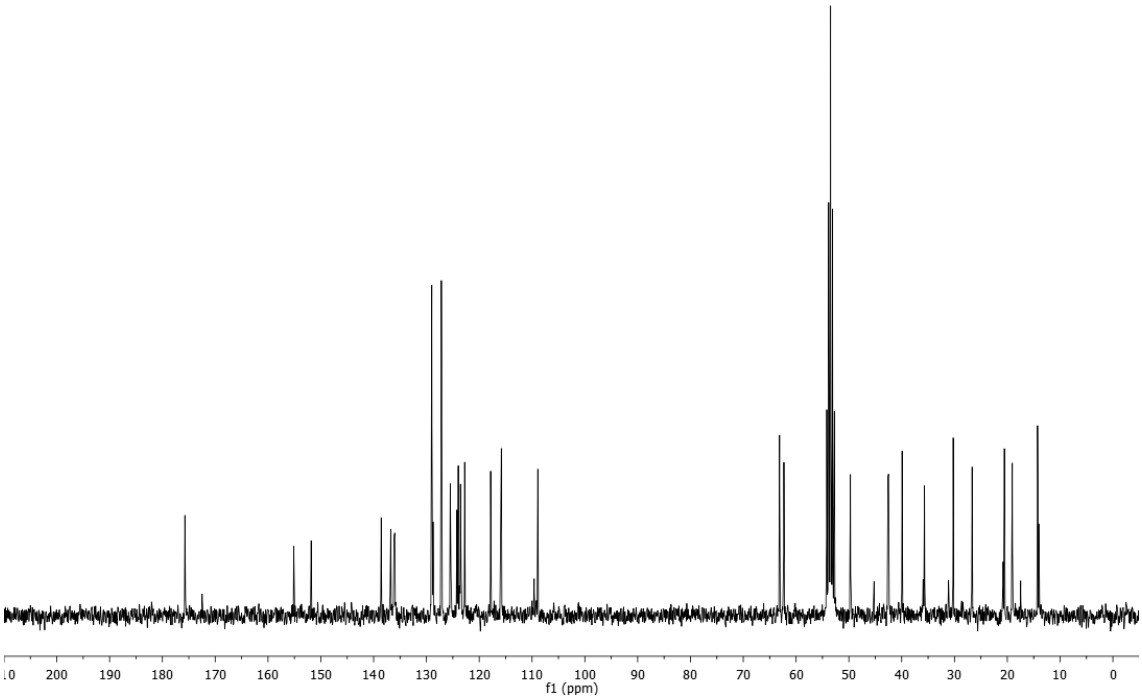

1.00
1.04
3.91
1.02
1.92
0.98
0.99
5.12
1.04
1.75
5.09
3.17
2.05
1.02
1.38
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

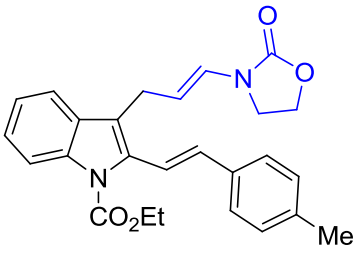

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



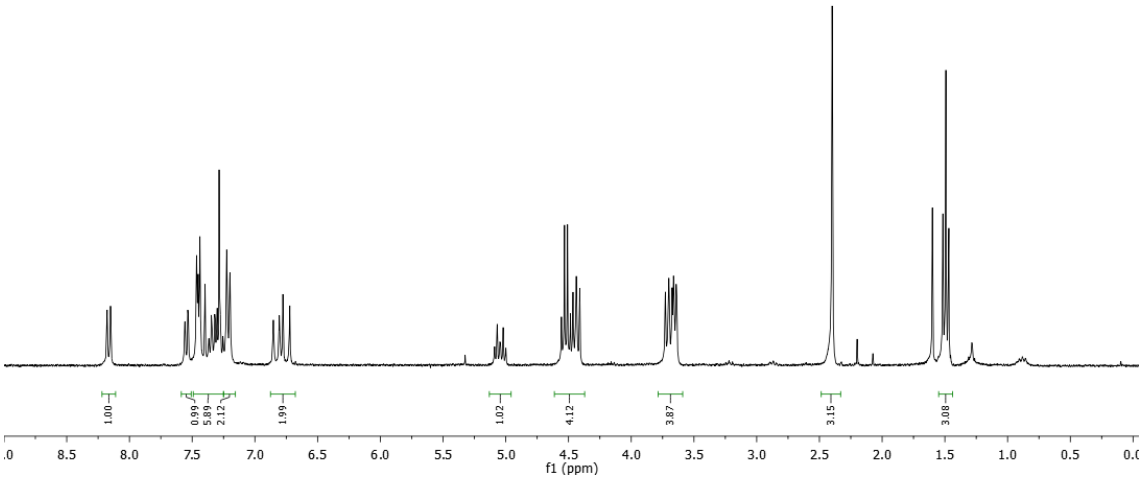
5h

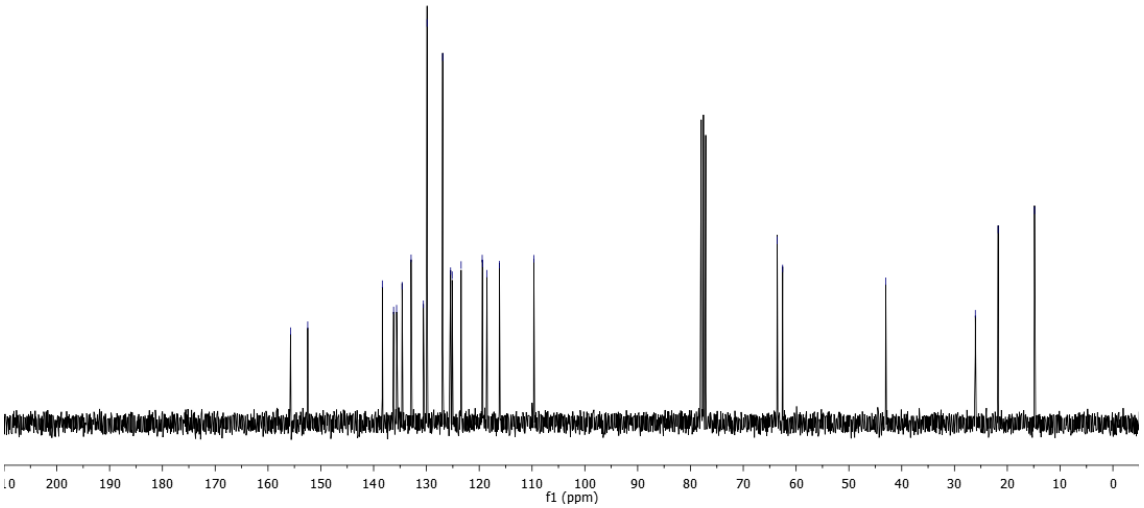


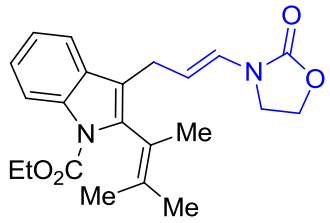




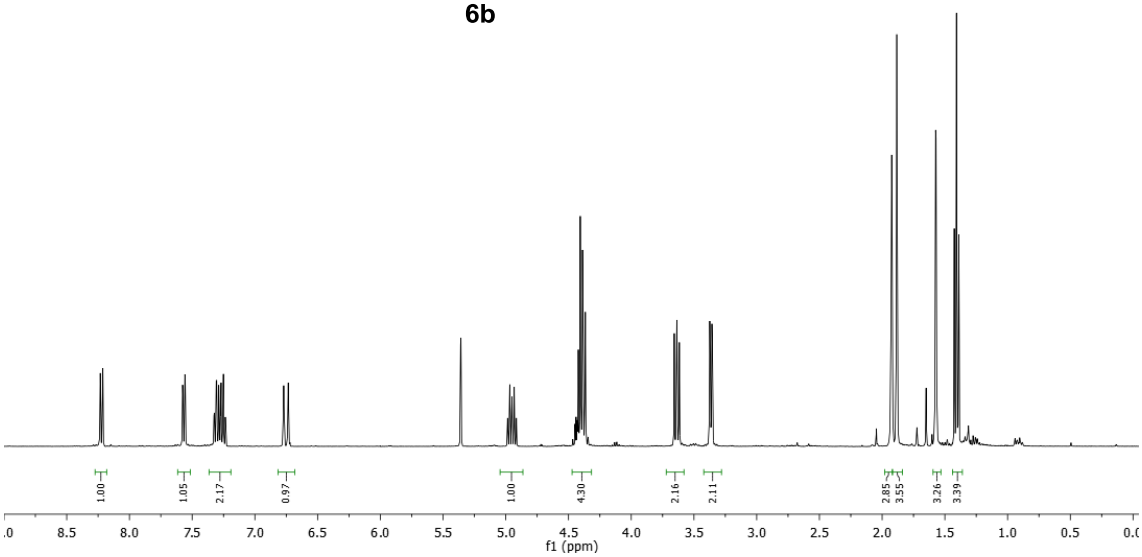
6a

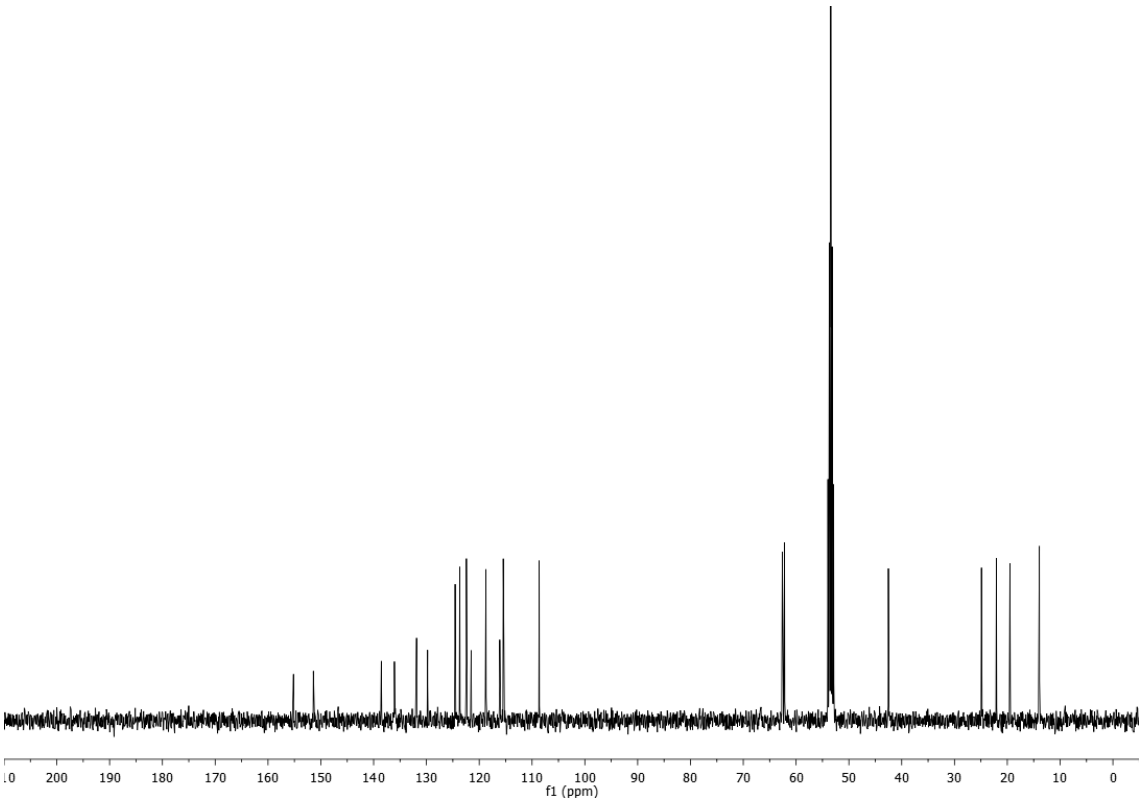


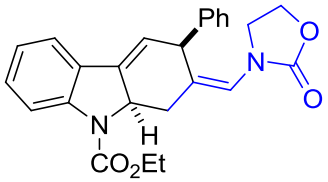




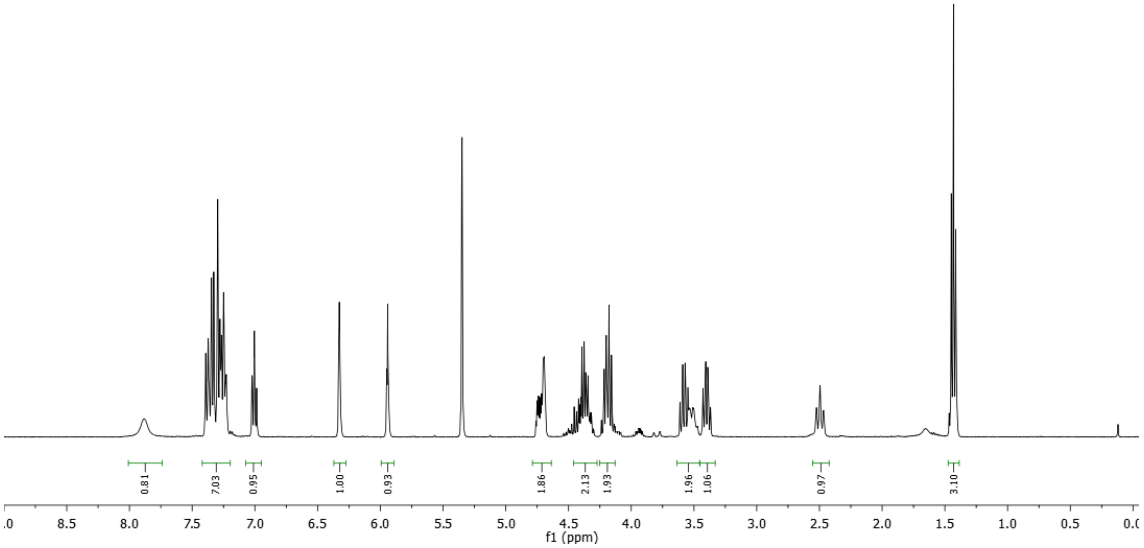
6b

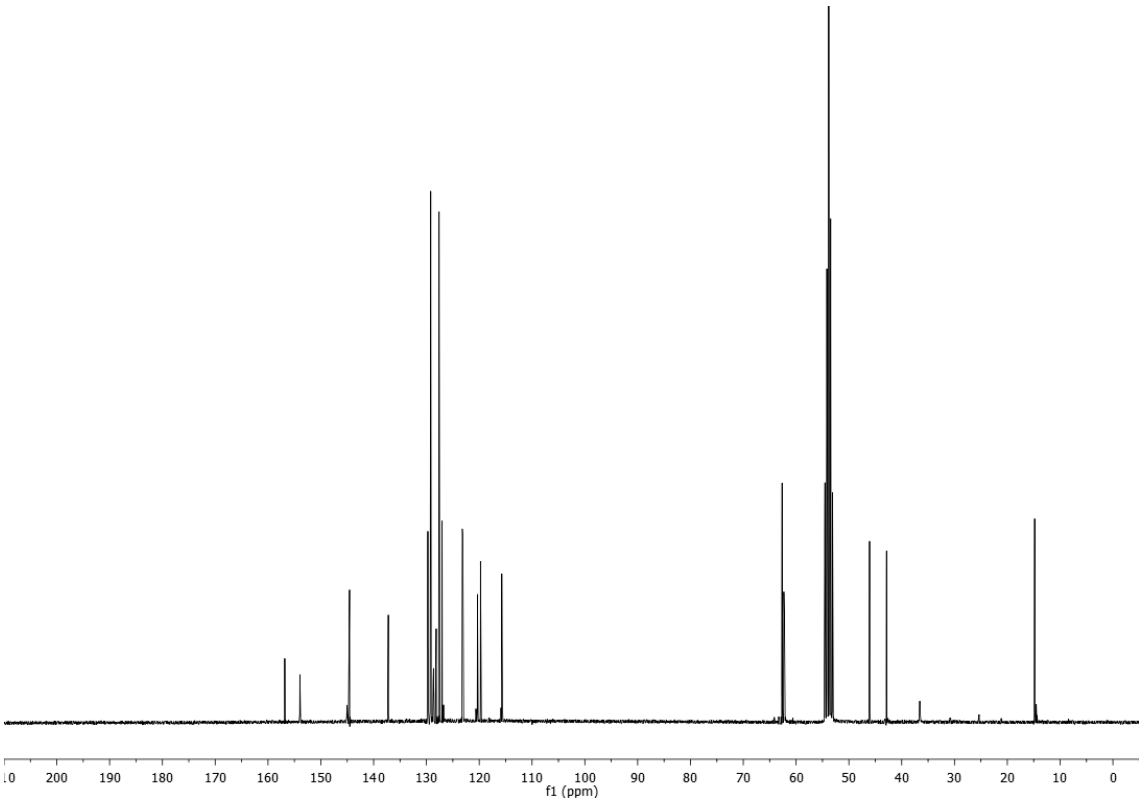




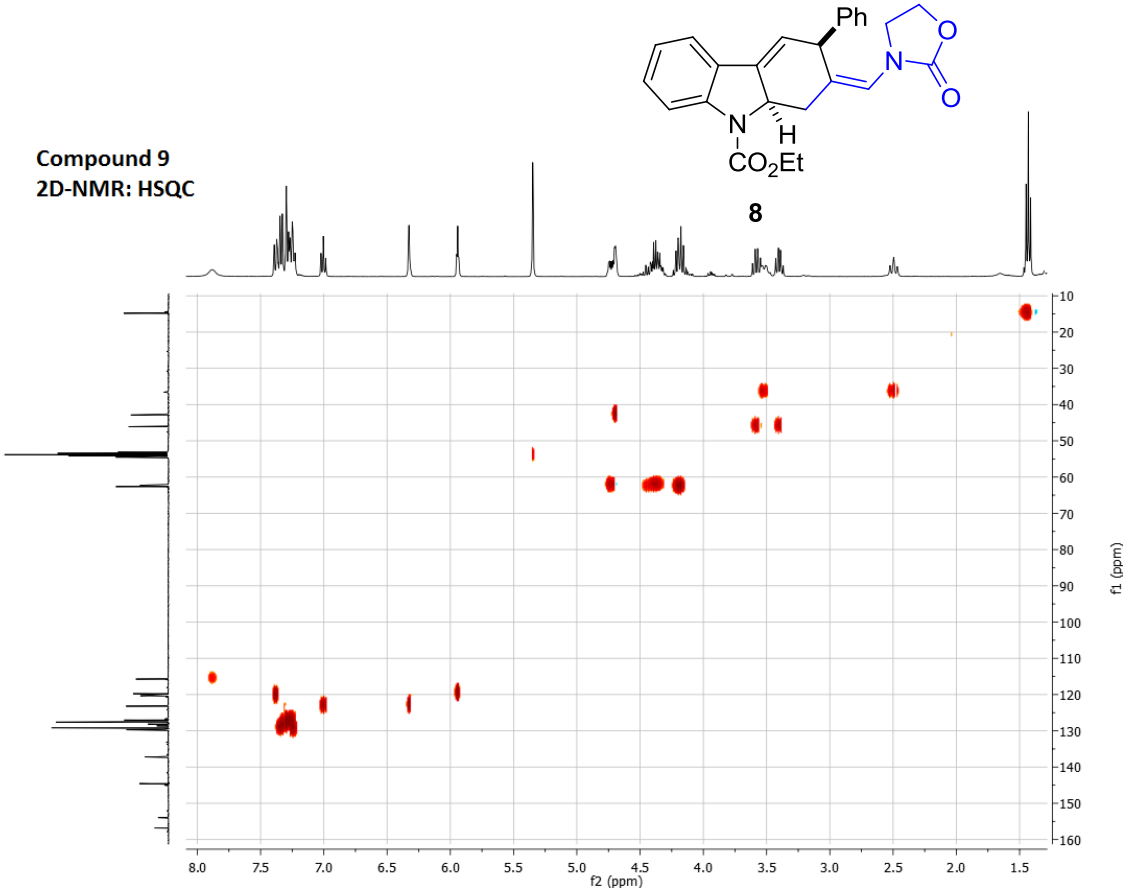

Ph
O
N
O
N
H
CO2Et

8


0.81
7.03
0.95
1.00
0.93
1.86
2.13
1.93
1.96
1.06
0.97
3.10
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)

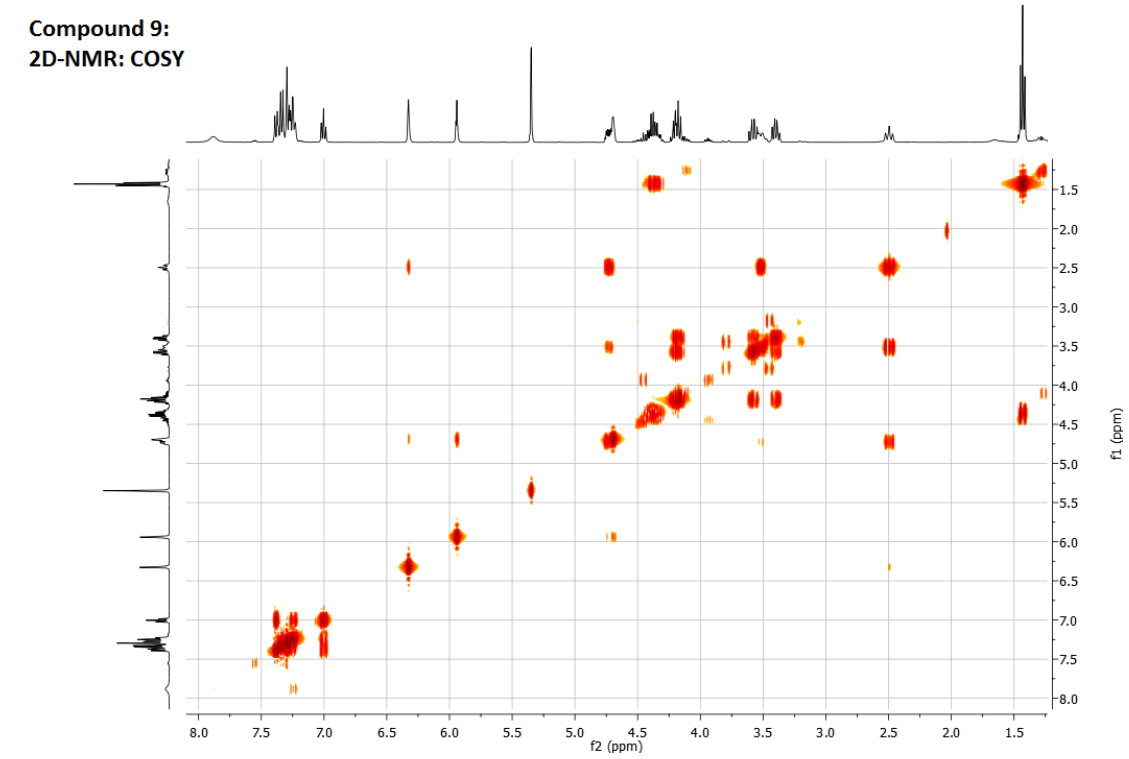

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

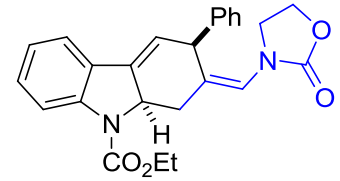
Compound 9
2D-NMR: HSQC



8

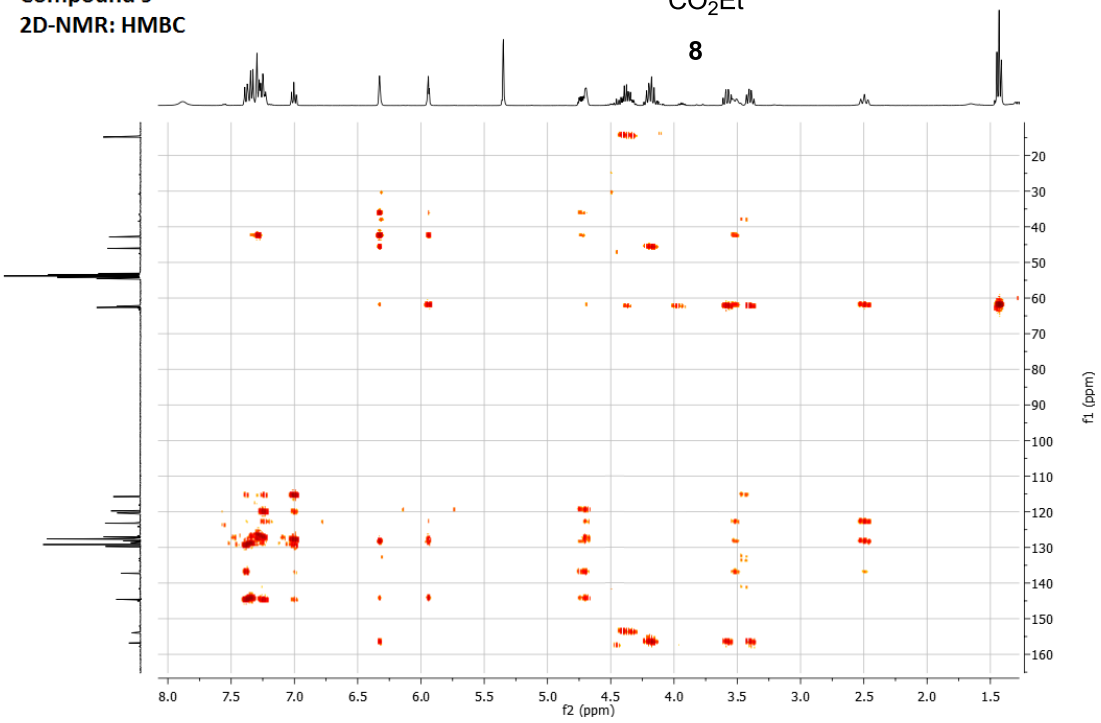
Compound 9:
2D-NMR: COSY



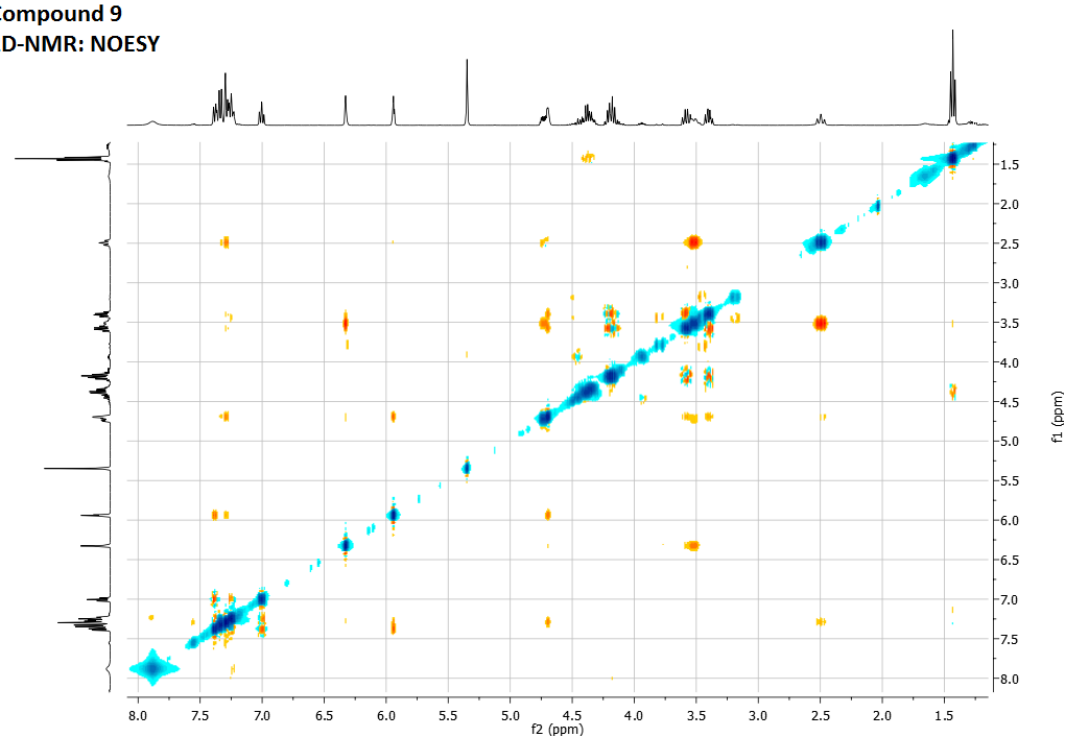


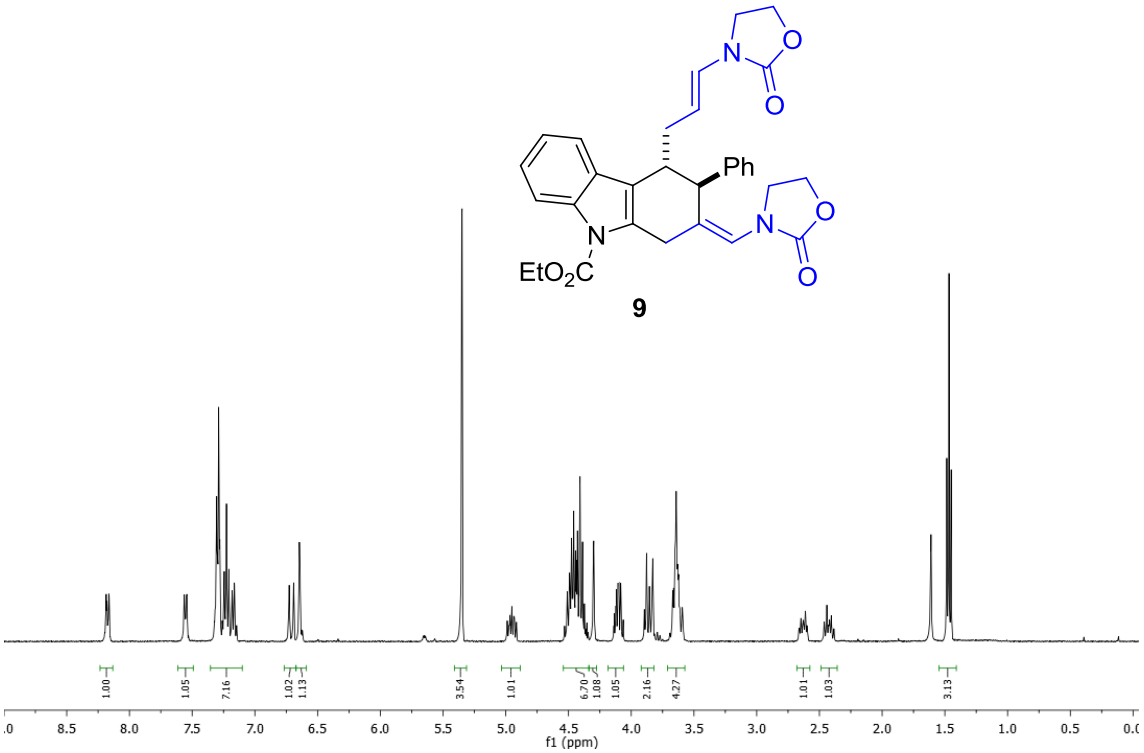
8

Compound 9
2D-NMR: HMBC

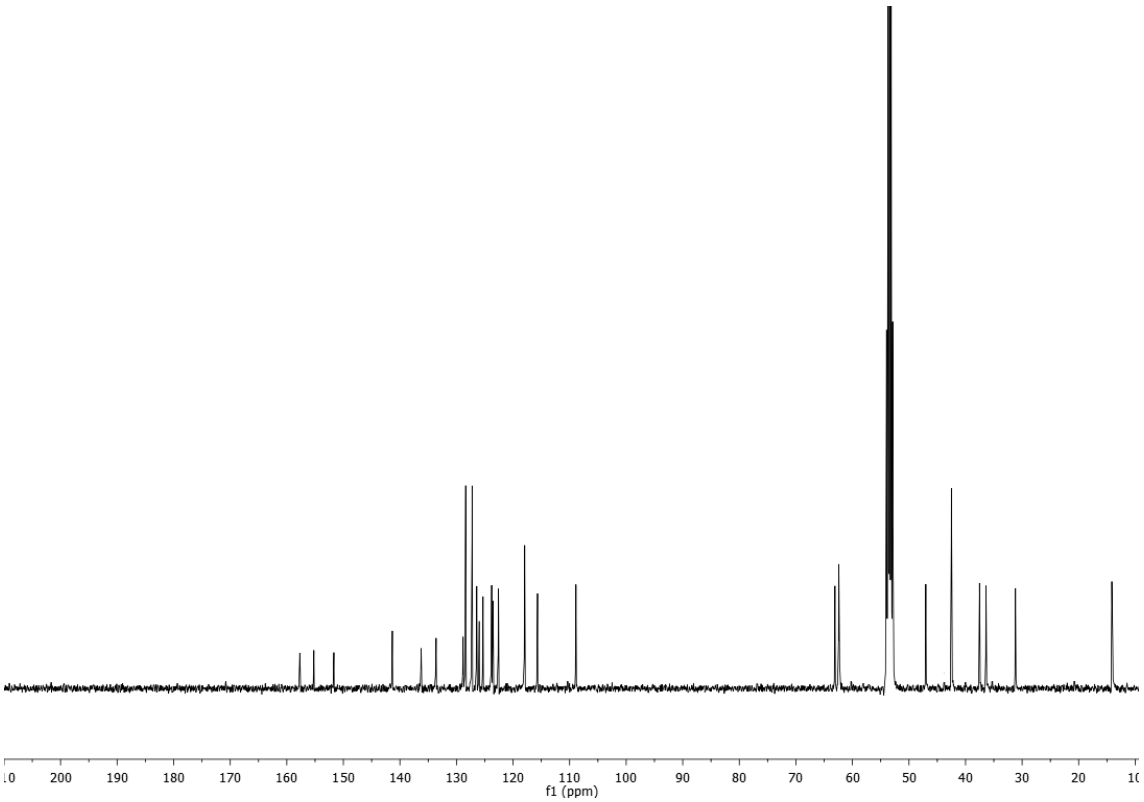


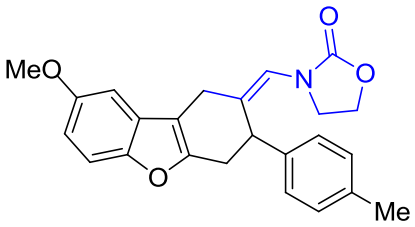
Compound 9
2D-NMR: NOESY





9





11