Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

An approach to functionalized carbazoles from *Z*-enoate propargylic alcohols. A unified total synthesis of *N*-Me-carazostatin, *N*-Me-carbazoquinocin C and *N*-Me-Lipocarbazole A4

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A. General information

All the solvents were distilled prior to use and anhydrous solvents were prepared according to the standard drying procedures. All non-aqueous reactions were carried out under an atmosphere of nitrogen in flame-dried glassware. Commercially available chemicals were purchased from Sigma-Aldrich, Alfa Aesar and Spectrochem Pvt. Ltd. and were used as received without further purification.

Infrared (IR) spectra were recorded on a JASCO 4100 FT-IR spectrometer.

^{1}H NMR spectra were measured on Bruker AVANCE 400 MHz or Bruker AVANCE 500 MHz spectrometers. Chemical shifts were reported in ppm relative to solvent signals. ^{13}C NMR spectra were recorded on Bruker AVANCE 100 MHz or Bruker AVANCE 125 MHz spectrometers with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard [$CDCl_3$ δ = 7.26 ppm for ^{1}H, δ = 77.16 for ^{13}C or calibrated to tetramethylsilane (δ = 0.00)]. The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; dq, doublet of quartet; td, triplet of doublet; tt, triplet of triplet; dq, doublet of quartet; br, broad; *J*, coupling constant in Hz. The coupling constant *J* (Hz) has been rounded to one decimal place for all compounds. Where a coupling pattern can be assigned as a combination of multiplicities, the above abbreviations have been combined to describe the observed patterns (i.e., dt, doublet of triplets).

Mass spectra were recorded by electrospray ionization (ESI) method on a Q-TOF Micro with lock spray source.

The crystal datas were collected and integrated using a BrukerAxs kappa apex2 CCD diffractometer, with graphite monochromated Mo-Kα radiation.

For thin layer chromatography (TLC) analysis throughout this work, E-merck precoated TLC plates (silica gel 60 F254 grade, 0.25 mm) were used and visualized using a UV lamp (366 or 254 nm) or by use of one of the following visualization reagents: PMA: 1 g phosphomolybdic acid/ 10 mL ethanol; $KMnO_4$: 0.15 g potassium permanganate, 1 g K_2CO_3, / 20 mL water. Acme (India) silica gel (100-200 mesh) was used for column chromatography.

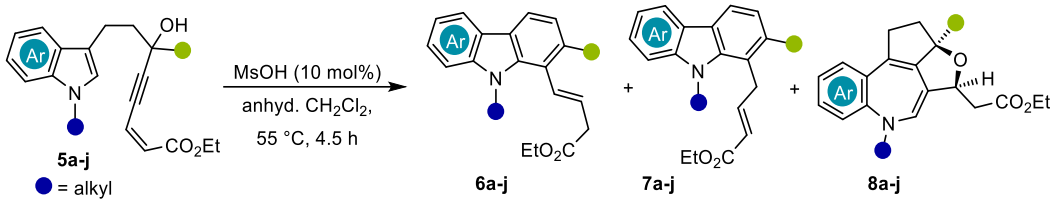
B. Abbreviations

equiv. – Equivalents; anhyd. – anhydrous; µL – Microliter; TLC – Thin Layer Chromatography; R_f – Retardation or retention factor; NMR – Nuclear magnetic resonance spectroscopy; IR – Infrared spectroscopy; ATR – Attenuated total reflection; HRMS (ESI) – High resolution electrospray ionization mass spectrometry; Calcd. For – Calculated for; M.P. – Melting point; ppm – Parts per million; ^{n}Bu – *n*-butyl group; Ts – *p*-toluenesulfonyl group; Bs – *p*-bromophenylsulfonyl group; Pd/C – Palladium on carbon; wt% – weight %; atm – atmosphere; NBS – N-Bromosuccinimide; DIBAL-H – Diisobutylaluminium hydride; *n*-BuLi – *n*-Butyllithium; $Pd(PPh_3)_2Cl_2$ – Bis(triphenylphosphine)palladium(II) dichloride; DMF – dimethylformamide; $BF_3.OEt_2$ – Boron trifluoride etherate; NaH – Sodium hydride.

B. Experimental procedures and characterization data for the tandem reactions.

(i) General Procedure 1: Synthesis of functionalized carbazoles and benzazepine derivatives

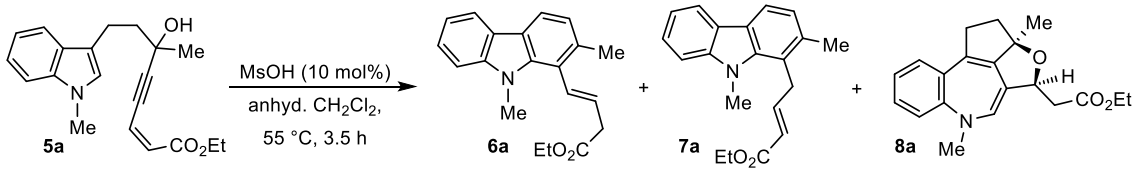
General Scheme of the reaction:



Procedure: To a well stirred solution of propargylic alcohols **5a-j** (1.0 equiv.) in anhydrous dichloromethane (CH_2Cl_2) (0.04 *M*), methanesulfonic acid (MsOH) (10 mol%) was added dropwise at room temperature under nitrogen atmosphere. The resulting mixture was transferred to a pre-heated oil bath and refluxed at 55 °C for 4.5 h.* After completion, the reaction mixture was cooled down to room temperature and saturated $NaHCO_3$ solution was added. After stirring vigorously for 15 min (during this period the color of the initial dark brown reaction mixture becomes light orangish yellow), the layers were separated, and the residual compound from aqueous layer was extracted with CH_2Cl_2 (3 times). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. Subsequent purification of the crude product via silica gel column chromatography (Hexane:EtOAc) provided the desired functionalized carbazoles **6a-j** and **7a-j** along with the benzazepine derivatives **8a-j**.

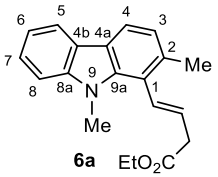
[***** Although the reaction of **5a** with MsOH was completed after 3.5 h, the duration of reactions for the other substrates (**5b-j**) was found to be between 4 h to 4.5 h. Therefore, all the reactions were continued for 4.5 h to ensure the complete consumption of the starting materials (i.e., **5b-j**) during exploration of the substrate scope.

Reaction of ethyl (*Z*)-6-hydroxy-6-methyl-8-(1-methyl-1*H*-indol-3-yl)oct-2-en-4-ynoate (5a)



According to the **General Procedure 1**, propargylic alcohol **5a** (130 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 µL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6a** as light-yellow liquid (86 mg, 0.28 mmol, 70%) by using Hexane/EtOAc (13:1) as eluent, carbazole **7a** as yellow liquid (20.9 mg, 0.068 mmol, 17%) by using Hexane/EtOAc (9:1) as eluent and benzazepine **8a** as yellow liquid (15.6 mg, 0.048 mmol, 12%) by using Hexane/EtOAc (7:1) as eluent.

Ethyl (*E*)-4-(2,9-dimethyl-9*H*-carbazol-1-yl)but-3-enoate (6a)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 16.1 Hz, 1H), 5.90 – 5.78 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.35 (d, *J* = 7.1 Hz, 2H), 2.43 (s, 3H) and 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

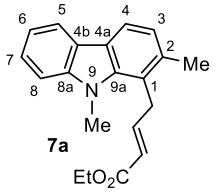
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 142.2, 139.3, 134.5, 130.5, 128.1, 125.4, 122.9, 122.2, 121.6, 121.0, 119.7, 119.0, 118.9, 108.8, 60.9, 38.9, 33.5, 21.0 and 14.4 ppm.

IR (ATR): 3054, 2983, 1731, 1589, 1467, 1443, 1405, 1291, 1266, 1160, 1026 and 739 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{20}H_{21}NO_2$ 307.1572; found 307.1552.

TLC: R_f = 0.75 (4:1 Hexanes/EtOAc).

Ethyl (*E*)-4-(2,9-dimethyl-9*H*-carbazol-1-yl)but-2-enoate (7a)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.37 (dt, *J* = 15.2, 6.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 5.57 – 5.47 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.08 – 4.03 (m, 2H), 3.96 (s, 3H), 2.42 (s, 3H) and 1.21 (t, *J* = 7.1 Hz, 3H) ppm.

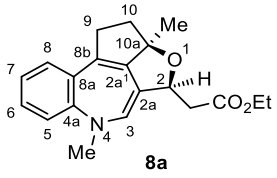
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 147.5, 142.1, 140.3, 135.5, 125.6, 123.2, 122.9, 122.9, 122.4, 119.7, 119.2, 118.9, 117.9, 108.7, 60.5, 32.5, 31.2, 20.2 and 14.3 ppm.

IR (ATR): 3442, 2978, 2930, 1716, 1651, 1595, 1466, 1271, 1226, 1166, 960 and 741 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{20}H_{21}NO_2$ 307.1572; found 307.1554.

TLC: R_f = 0.7 (4:1 Hexanes/EtOAc).

Ethyl 2-(4,10a-dimethyl-4,9,10,10a-tetrahydro-2*H*-1-oxa-4-azabenzo[*f*]cyclopenta[*cd*]azulen-2-yl)acetate (8a)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.21 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 5.84 (s, 1H), 5.40 (t, *J* = 6.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.01 (dd, *J* = 16.8, 6.1 Hz, 1H), 2.85 – 2.73 (m, 2H), 2.60 (dd, *J* = 15.5, 7.2 Hz, 1H), 2.22 (dd, *J* = 12.0, 5.3 Hz, 1H), 1.97 (td, *J* = 12.2, 6.4 Hz, 1H), 1.35 (s, 3H) and 1.27 (t, *J* = 7.1 Hz, 3H) ppm.

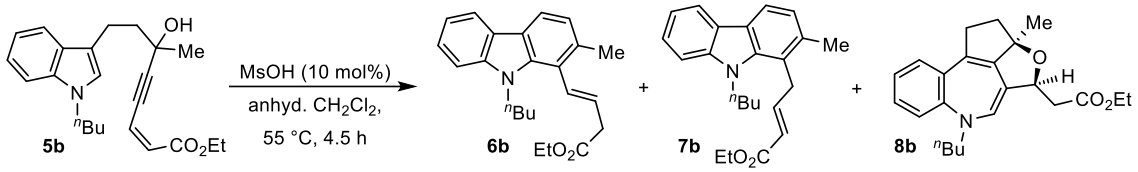
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 139.1, 137.4, 129.8, 126.2, 122.9, 119.4, 119.3, 116.9, 113.5, 109.2, 88.9, 80.5, 60.6, 41.4, 37.0, 30.9, 22.8, 20.1 and 14.3 ppm.

IR (ATR): 3443, 2925, 2852, 1734, 1468, 1373, 1160, 1121, 1095, 1057, 1030 and 740 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{20}H_{23}NO_3$ 325.1678; found 325.1667.

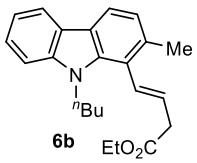
TLC: R_f = 0.62 (4:1 Hexanes/EtOAc).

Reaction of ethyl (*Z*)-8-(1-butyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate (5b)



According to the **General Procedure 1**, propargylic alcohol **5b** (147 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 μL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6b** as light-yellow liquid (90.9 mg, 0.26 mmol, 65%) by using Hexane/EtOAc (19:1) as eluent, carbazole **7b** as brownish-yellow liquid (22.4 mg, 0.064 mmol, 16%) by using Hexane/EtOAc (14:1) as eluent and benzazepine **8b** as yellow liquid (14.7 mg, 0.04 mmol, 10%) by using Hexane/EtOAc (9:1) as eluent.

Ethyl (*E*)-4-(9-butyl-2-methyl-9*H*-carbazol-1-yl)but-3-enoate (6b)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.90 (t, *J* = 8.5 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 16.1 Hz, 1H), 5.90 (dt, *J* = 16.0, 7.1 Hz, 1H), 4.49 – 4.41 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.36 (dd, *J* = 7.0, 1.1 Hz, 2H), 2.44 (d, *J* = 10.4 Hz, 3H), 1.67 (dt, *J* = 15.5, 7.7 Hz, 2H), 1.32 (dt, *J* = 14.3, 7.3 Hz, 5H) and 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

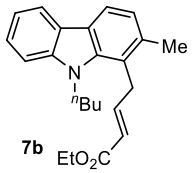
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 141.4, 138.4, 134.5, 130.0, 128.5, 125.3, 123.0, 122.2, 121.7, 120.9, 119.8, 119.0, 118.9, 109.1, 61.0, 44.3, 38.9, 31.9, 21.2, 20.3, 14.4 and 14.1 ppm.

IR (ATR): 2954, 2928, 2867, 1735, 1466, 1408, 1307, 1236, 1202, 1166, 781 and 733 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{23}H_{27}NO_2$ 349.2042; found 349.2034.

TLC: R_f = 0.75 (9:1 Hexanes/EtOAc).

Ethyl (*E*)-4-(9-butyl-2-methyl-9*H*-carbazol-1-yl)but-2-enoate (7b)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 1H), 7.91 (t, *J* = 8.6 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 5.55 – 5.42 (m, 1H), 4.32 – 4.22 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.98 (d, *J* = 2.7 Hz, 2H), 2.44 (s, 3H), 1.80 (dt, *J* = 15.7, 7.8 Hz, 2H), 1.50 – 1.39 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H) and 0.98 (t, *J* = 7.4 Hz, 3H) ppm.

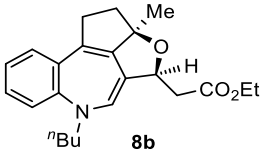
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 146.8, 141.5, 139.3, 135.5, 125.5, 123.1, 123.1, 122.9, 122.3, 119.8, 119.2, 118.9, 117.6, 109.0, 60.5, 44.9, 33.1, 31.2, 20.4, 14.3 and 14.0 ppm.

IR (ATR): 3025, 2925, 2859, 1718, 1455, 1299, 1172, 875, 790 and 726 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{23}H_{27}NO_2$ 349.2042; found 349.2040.

TLC: R_f = 0.7 (9:1 Hexanes/EtOAc).

Ethyl 2-(4-butyl-10a-methyl-4,9,10,10a-tetrahydro-2*H*-1-oxa-4-azabenzo[*f*]cyclopenta-[*cd*]azulen-2-yl)acetate (8b)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.77 (s, 1H), 5.40 (t, *J* = 6.5 Hz, 1H), 4.25 – 4.14 (m, 4H), 3.02 (dd, *J* = 16.9, 5.7 Hz, 1H), 2.80 (ddd, *J* = 21.5, 14.0, 6.1 Hz, 2H), 2.61 (dd, *J* = 15.4, 7.0 Hz, 1H), 2.22 (dd, *J* = 12.0, 5.4 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.86 – 1.76 (m, 1H), 1.76 – 1.66 (m, 1H), 1.38 (dd, *J* = 15.0, 7.7 Hz, 2H), 1.34 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H) and 0.95 (t, *J* = 7.4 Hz, 3H) ppm.

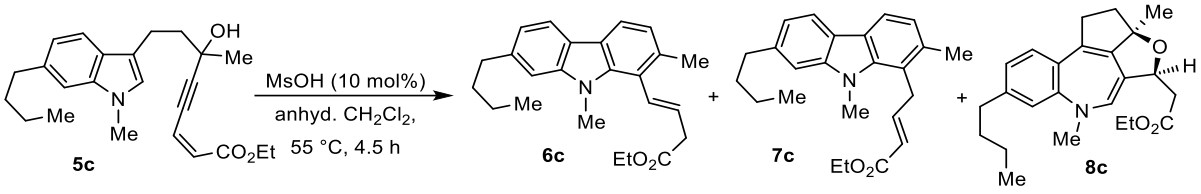
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 138.7, 137.3, 129.2, 126.4, 122.9, 119.4, 116.5, 113.8, 109.5, 89.1, 80.6, 60.7, 44.0, 41.6, 36.9, 32.4, 22.8, 20.4, 20.1, 14.4 and 14.0 ppm.

IR (ATR): 3033, 2966, 1735, 1625, 1458, 1404, 1297, 882 and 791 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{23}H_{29}NO_3$ 367.2147; found 367.2097.

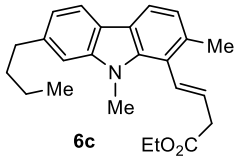
TLC: R_f = 0.56 (9:1 Hexanes/EtOAc).

Reaction of ethyl (*Z*)-8-(1-butyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate (5c)



According to the **General Procedure 1**, propargylic alcohol **5c** (152.6 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 μL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6c** as yellow liquid (98.9 mg, 0.27 mmol, 68%) by using Hexane/EtOAc (24:1) as eluent, carbazole **7c** as yellow liquid (20.4 mg, 0.056 mmol, 14%) by using Hexane/EtOAc (19:1) as eluent and benzazepine **8c** as brownish-yellow liquid (18.3 mg, 0.048 mmol, 12%) by using Hexane/EtOAc (9:1) as eluent.

Ethyl (*E*)-4-(7-butyl-2,9-dimethyl-9*H*-carbazol-1-yl)but-3-enoate (6c)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.13 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 16.1 Hz, 1H), 5.84 (dt, *J* = 16.1, 7.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.37 (dd, *J* = 7.1, 1.4 Hz, 2H), 2.81 – 2.77 (m, 2H), 2.43 (s, 3H), 1.73 – 1.66 (m, 2H), 1.44 – 1.37 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H) and 0.95 (t, *J* = 7.4 Hz, 3H) ppm.

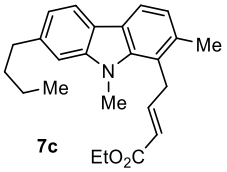
^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 142.7, 140.8, 139.4, 133.9, 130.6, 128.0, 122.3, 121.5, 120.9, 120.8, 120.0, 119.4, 118.6, 108.4, 61.0, 38.9, 36.7, 34.5, 33.5, 22.6, 20.9, 14.4 and 14.2 ppm.

IR (ATR): 2926, 2859, 1734, 1593, 1449, 1402, 1296, 1237, 1151, 1031, 799 and 735 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{24}H_{29}NO_2$ 363.2198; found 363.2179.

TLC: R_f = 0.78 (4:1 Hexanes/EtOAc).

Ethyl (*E*)-4-(7-butyl-2,9-dimethyl-9*H*-carbazol-1-yl)but-2-enoate (7c)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.37 (dt, *J* = 15.8, 4.7 Hz, 1H), 7.13 (s, 1H), 7.09 – 7.01 (m, 2H), 5.57 – 5.45 (m, 1H), 4.12 (q, *J* = 7.1 Hz,

2H), 4.05 (d, *J* = 2.8 Hz, 2H), 3.95 (s, 3H), 2.80 (t, *J* = 7.7 Hz, 2H), 2.41 (s, 3H), 1.74 – 1.65 (m, 2H), 1.45 – 1.36 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H) and 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

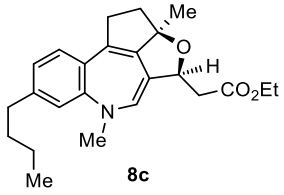
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 147.6, 142.5, 141.0, 140.4, 134.9, 123.2, 123.0, 122.3, 120.9, 120.1, 119.4, 118.6, 117.8, 108.4, 60.4, 36.7, 34.5, 32.5, 31.2, 29.8, 22.6, 20.1, 14.3 and 14.2 ppm

IR (ATR): 3027, 2926, 2861, 1719, 1452, 1298, 1170, 874, 792 and 727 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{24}H_{29}NO_2$ 363.2198; found 363.2185.

TLC: R_f = 0.69 (4:1 Hexanes/EtOAc).

Ethyl 2-(6-butyl-4,10a-dimethyl-4,9,10,10a-tetrahydro-2*H*-1-oxa-4-azabenzo[*f*]cyclopenta[*cd*]azulen-2-yl)acetate (8c)



8c

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.08 (s, 1H), 6.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.80 (s, 1H), 5.42 – 5.36 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.02 – 2.96 (m, 1H), 2.82 – 2.72 (m, 4H), 2.59 (dd, *J* = 15.5, 7.2 Hz, 1H), 2.20 (dd, *J* = 12.1, 5.3 Hz, 1H), 1.96 (td, *J* = 12.2, 6.3 Hz, 1H), 1.66 (ddd, *J* = 15.3, 11.0, 7.6 Hz, 2H), 1.40 – 1.36 (m, 2H), 1.34 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H) and 0.94 (t, *J* = 7.4 Hz, 3H) ppm.

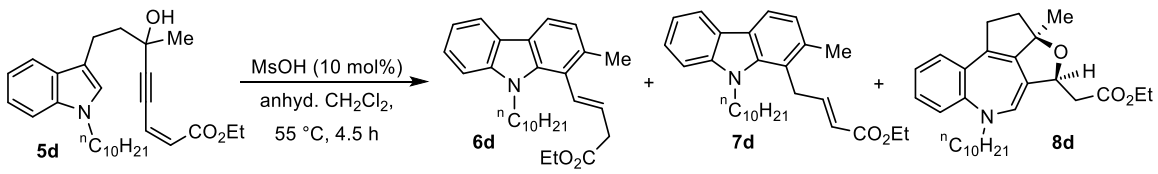
^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 139.5, 138.3, 137.5, 129.4, 124.3, 120.7, 119.0, 116.1, 113.5, 108.6, 89.0, 80.5, 60.7, 41.5, 37.1, 36.5, 34.5, 30.9, 29.8, 22.8, 22.6, 20.2, 14.4 and 14.2 ppm.

IR (ATR): 2925, 2856, 1734, 1652, 1616, 1462, 1374, 1170, 800 and 792 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{24}H_{31}NO_3$ 381.2304; found 381.2297.

TLC: R_f = 0.5 (4:1 Hexanes/EtOAc).

Reaction of ethyl (*Z*)-8-(1-decyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate (5d)

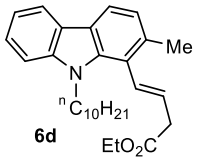


5d **6d** **7d** **8d**

According to the **General Procedure 1**, propargylic alcohol **5d** (180.7 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 μL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6d** as light-yellow liquid (116.2 mg, 0.268 mmol, 67%) by using Hexane/EtOAc (100:0 to 99:1) as eluent, carbazole **7d** as yellow liquid

(19.1 mg, 0.044 mmol, 11%) by using Hexane/EtOAc (99:1) as eluent and benzazepine **8d** as yellow liquid (23.5 mg, 0.052 mmol, 13%) by using Hexane/EtOAc (7:1) as eluent.

Ethyl (*E*)-4-(9-decyl-2-methyl-9*H*-carbazol-1-yl)but-3-enoate (6d)



6d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 16.1 Hz, 1H), 5.90 (dt, *J* = 15.9, 7.1 Hz, 1H), 4.50 – 4.38 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.37 (d, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.73 – 1.63 (m, 2H), 1.33 – 1.23 (m, 19H) and 0.88 (t, *J* = 6.8 Hz, 3H) ppm.

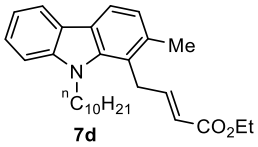
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 141.4, 138.4, 134.5, 130.0, 128.5, 125.3, 123.0, 122.2, 121.7, 121.0, 119.8, 119.0, 118.9, 109.1, 61.0, 44.6, 38.9, 32.0, 29.8, 29.7, 29.7, 29.6, 29.4, 27.1, 22.8, 21.2, 14.4 and 14.2 ppm.

IR (ATR): 2954, 2924, 2853, 1736, 1460, 1412, 1275, 1261, 1155, 1024, 767 and 740 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{29}H_{39}NO_2$ 433.2981; found 433.2945.

TLC: R_f = 0.8 (6:1 Hexanes/EtOAc).

Ethyl (*E*)-4-(9-decyl-2-methyl-9*H*-carbazol-1-yl)but-2-enoate (7d)



7d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.36 – 7.29 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.09 (dd, *J* = 7.8, 3.8 Hz, 1H), 5.54 – 5.42 (m, 1H), 4.25 (dd, *J* = 13.8, 5.5 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.97 (dd, *J* = 4.5, 1.9 Hz, 2H), 2.44 (s, 3H), 1.81 (dt, *J* = 15.7, 7.7 Hz, 2H), 1.28 – 1.25 (s, 17H), 1.21 (t, *J* = 7.1 Hz, 3H) and 0.88 (t, *J* = 6.7 Hz, 3H) ppm.

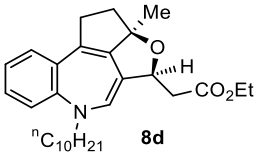
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 146.8, 141.5, 139.3, 135.5, 125.5, 123.12, 123.06, 122.9, 122.3, 119.8, 119.2, 118.9, 117.6, 109.0, 60.5, 45.1, 32.0, 31.2, 31.0, 29.8, 29.7, 29.6, 29.4, 27.1, 22.8, 20.4, 14.3 and 14.2 ppm

IR (ATR): 2953, 2923, 2852, 1720, 1461, 1269, 1173, 1162, 1039, 765 and 743 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{29}H_{39}NO_2$ 433.2981; found 433.2948.

TLC: R_f = 0.78 (6:1 Hexanes/EtOAc).

Ethyl 2-(4-decyl-10a-methyl-4,9,10,10a-tetrahydro-2*H*-1-oxa-4-azabenzo[*f*]cyclopenta-[*cd*]azulen-2-yl)acetate (8d)



8d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 5.76 (s, 1H), 5.40 (t, *J* = 6.5 Hz, 1H), 4.25 – 4.13 (m, 4H), 3.02 (dd, *J* = 16.8, 5.9 Hz, 1H), 2.86 – 2.73 (m, 2H), 2.61 (dd, *J* = 15.4, 7.0 Hz, 1H), 2.22 (dd, *J* = 12.1, 5.3 Hz, 1H), 1.99 (td, *J* = 12.3, 6.4 Hz, 1H), 1.76 (dtd, *J* = 21.3, 13.9, 7.1 Hz, 2H), 1.34 (s, 3H), 1.33 – 1.23 (m, 17H) and 0.87 (t, *J* = 6.8 Hz, 3H) ppm.

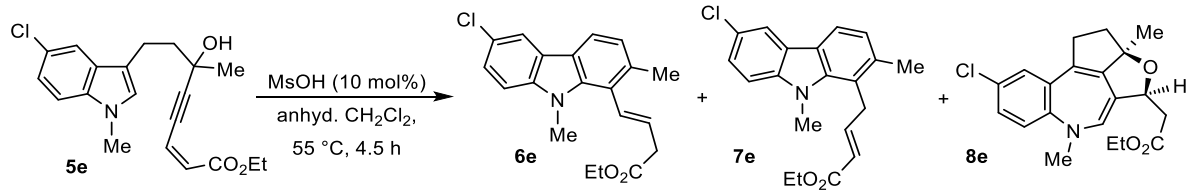
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 138.6, 137.3, 129.2, 126.4, 122.9, 119.4, 119.4, 116.4, 113.8, 109.5, 89.1, 80.6, 60.7, 44.3, 41.6, 36.9, 32.0, 30.3, 29.7, 29.5, 29.4, 27.2, 22.8, 22.8, 20.1, 14.4 and 14.2 ppm.

IR (ATR): 2924, 2852, 1733, 1697, 1653, 1611, 1462, 1371, 1123, 1057 and 738 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{29}H_{41}NO_3$ 451.3086; found 451.3052.

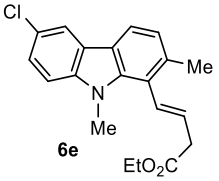
TLC: R_f = 0.6 (6:1 Hexanes/EtOAc).

Reaction of ethyl (*Z*)-8-(5-chloro-1-methyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate (5e)



According to the **General Procedure 1**, propargylic alcohol **5e** (144 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 μL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6e** as light-yellow liquid (94.3 mg, 0.276 mmol, 69%) by using Hexane/EtOAc (24:1) as eluent, carbazole **7e** as brown liquid (16.4 mg, 0.048 mmol, 12%) by using Hexane/EtOAc (14:1) as eluent and benzazepine **8e** as brownish-yellow liquid (15.8 mg, 0.044 mmol, 11%) by using Hexane/EtOAc (7:1) as eluent.

Ethyl (*E*)-4-(6-chloro-2,9-dimethyl-9*H*-carbazol-1-yl)but-3-enoate (6e)



6e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.5 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.34 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 16.0 Hz,

1H), 5.88 – 5.78 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.35 (d, *J* = 7.1 Hz, 2H), 2.42 (s, 3H) and 1.30 (t, *J* = 7.1 Hz, 3H) ppm.

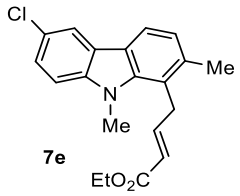
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 140.5, 139.7, 135.4, 130.2, 128.5, 125.3, 124.5, 123.9, 122.0, 121.2, 121.2, 119.4, 119.0, 109.8, 61.0, 38.8, 33.6, 21.0 and 14.4 ppm.

IR (ATR): 2980, 2927, 1733, 1465, 1400, 1275, 1159, 1141, 1079, 1030 and 806 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{20}H_{20}ClNO_2$ 341.1183; found 341.1181.

TLC: R_f = 0.8 (4:1 Hexanes/EtOAc).

Ethyl (*E*)-4-(6-chloro-2,9-dimethyl-9*H*-carbazol-1-yl)but-2-enoate (7e)



7e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.5 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.36 (ddd, *J* = 13.1, 9.1, 3.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 5.57 – 5.48 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.05 (d, *J* = 2.7 Hz, 2H), 3.95 (s, 3H), 2.42 (s, 3H) and 1.22 (t, *J* = 7.1 Hz, 3H) ppm.

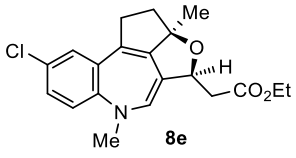
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 147.2, 140.8, 140.5, 136.4, 125.6, 124.7, 124.1, 123.3, 122.8, 121.9, 119.5, 119.1, 118.2, 109.8, 60.5, 32.7, 31.1, 20.2 and 14.3 ppm

IR (ATR): 2924, 1713, 1650, 1463, 1271, 1224, 1201, 1175, 1163, 1038, 802 and 740 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{20}H_{20}ClNO_2$ 341.1183; found 341.1162.

TLC: R_f = 0.75 (4:1 Hexanes/EtOAc).

Ethyl 2-(7-chloro-4,10a-dimethyl-4,9,10,10a-tetrahydro-2*H*-1-oxa-4-azabenzo[*f*]cyclopenta[*cd*]azulen-2-yl)acetate (8e)



8e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.21 – 7.15 (m, 2H), 5.88 (s, 1H), 5.40 (t, *J* = 6.6 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.95 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.83 – 2.70 (m, 2H), 2.60 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.22 (dd, *J* = 11.9, 5.2 Hz, 1H), 1.95 (td, *J* = 12.2, 6.4 Hz, 1H), 1.34 (s, 3H) and 1.27 (t, *J* = 7.2 Hz, 3H) ppm.

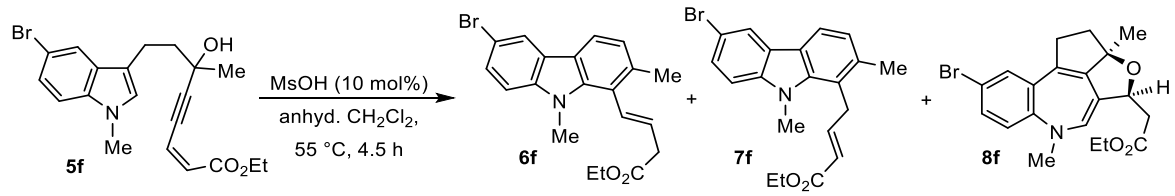
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 137.5, 137.1, 131.0, 127.2, 125.2, 123.1, 118.8, 117.9, 113.0, 110.2, 88.9, 80.6, 60.7, 41.3, 36.9, 31.1, 22.8, 20.0 and 14.4 ppm.

IR (ATR): 2924, 2851, 1730, 1611, 1469, 1371, 1271, 1054, 989, 793 and 737 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{20}H_{22}ClNO_3$ 359.1288; found 359.1280.

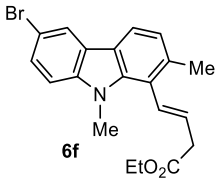
TLC: R_f = 0.6 (4:1 Hexanes/EtOAc).

Reaction of ethyl (*Z*)-8-(5-bromo-1-methyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-y-noate (5f)



According to the **General Procedure 1**, propargylic alcohol **5f** (161.2 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 μL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6f** as brownish-white solid (109.7 mg, 0.284 mmol, 71%) by using Hexane/EtOAc (24:1) as eluent, carbazole **7f** as yellow liquid (15.4 mg, 0.04 mmol, 10%) by using Hexane/EtOAc (14:1) as eluent and benzazepine **8f** as yellow liquid (19.3 mg, 0.048 mmol, 12%) by using Hexane/EtOAc (9:1) as eluent.

Ethyl (*E*)-4-(6-bromo-2,9-dimethyl-9*H*-carbazol-1-yl)but-3-enoate (6f)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 16.1 Hz, 1H), 5.82 (dt, *J* = 14.4, 7.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.35 (d, *J* = 7.1 Hz, 2H), 2.42 (s, 3H) and 1.30 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 140.7, 139.5, 135.4, 130.1, 128.5, 127.9, 124.5, 122.4, 122.1, 121.2, 121.0, 119.0, 111.8, 110.3, 61.0, 38.8, 33.5, 21.0 and 14.4 ppm.

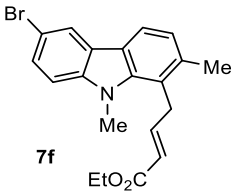
IR (ATR): 2978, 2923, 1732, 1463, 1399, 1274, 1158, 1141, 1065, 1030, 804 and 737 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{21}BrNO_2$ 386.0750; found 386.0742.

TLC: R_f = 0.78 (4:1 Hexanes/EtOAc).

M.P.: 75 – 78 °C.

Ethyl (*E*)-4-(6-bromo-2,9-dimethyl-9*H*-carbazol-1-yl)but-2-enoate (7f)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.5 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.36 (dt, *J* = 15.7, 4.6 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 1H), 7.09 (d, *J* = 7.9

Hz, 1H), 5.57 – 5.46 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.04 (dd, *J* = 4.4, 1.8 Hz, 2H), 3.94 (s, 3H), 2.42 (s, 3H) and 1.22 (t, *J* = 7.1 Hz, 3H) ppm.

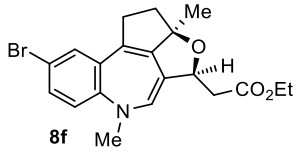
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 147.2, 140.8, 140.6, 136.4, 128.2, 124.7, 123.3, 122.9, 122.5, 121.8, 119.1, 118.2, 112.0, 110.3, 60.5, 32.7, 31.1, 20.2 and 14.3 ppm

IR (ATR): 2925, 1714, 1649, 1462, 1273, 1221, 1208, 1179, 1162, 1039, 806 and 737 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{21}BrNO_2$ 386.0750; found 386.0747.

TLC: R_f = 0.72 (4:1 Hexanes/EtOAc).

Ethyl 2-(7-bromo-4,10a-dimethyl-4,9,10,10a-tetrahydro-2*H*-1-oxa-4-azabenzo[*f*]cyclopenta[*cd*]azulen-2-yl)acetate (8f)



8f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 1.2 Hz, 1H), 7.30 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 5.88 (s, 1H), 5.40 (t, *J* = 6.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.94 (dd, *J* = 16.7, 5.8 Hz, 1H), 2.82 – 2.70 (m, 2H), 2.60 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.21 (dd, *J* = 11.8, 4.8 Hz, 1H), 1.94 (td, *J* = 12.2, 6.4 Hz, 1H), 1.33 (s, 3H) and 1.28 (d, *J* = 7.1 Hz, 2H) ppm.

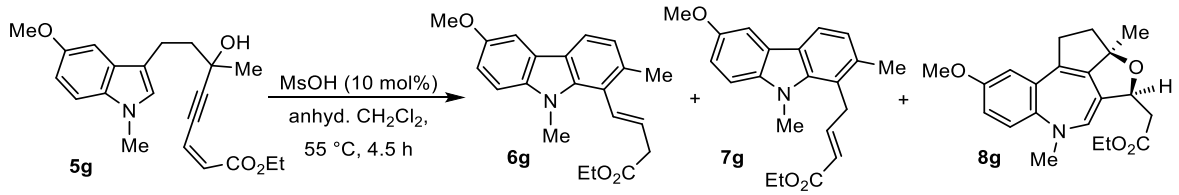
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 137.7, 137.0, 130.9, 127.9, 125.6, 121.9, 117.9, 112.9, 112.6, 110.7, 88.9, 80.6, 60.7, 41.3, 36.8, 31.1, 22.8, 19.4 and 14.4 ppm.

IR (ATR): 2924, 2850, 1730, 1468, 1370, 1190, 1167, 1095, 1051, 1027, 815 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{23}BrNO_3$ 404.0856; found 404.0862.

TLC: R_f = 0.55 (4:1 Hexanes/EtOAc).

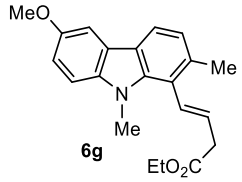
Reaction of ethyl (*Z*)-6-hydroxy-8-(5-methoxy-1-methyl-1*H*-indol-3-yl)-6-methyloct-2-en-4-ynoate (5g)



5g **6g** **7g** **8g**

According to the **General Procedure 1**, propargylic alcohol **5g** (142 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 μL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6g** as light-yellow liquid (101.2 mg, 0.3 mmol, 75%) by using Hexane/EtOAc (19:1) as eluent, carbazole **7g** as yellow liquid (14.8 mg, 0.044 mmol, 11%) by using Hexane/EtOAc (14:1) as eluent and benzazepine **8g** as brownish-yellow gummy liquid (11.4 mg, 0.032 mmol, 8%) by using Hexane/EtOAc (9:1) as eluent.

Ethyl (*E*)-4-(6-methoxy-2,9-dimethyl-9*H*-carbazol-1-yl)but-3-enoate (6g)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.19 (d, *J* = 8.9 Hz, 1H), 7.07 – 6.99 (m, 2H), 6.84 (d, *J* = 16.1 Hz, 1H), 5.82 (dt, *J* = 15.9, 7.1 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.83 (s, 3H), 3.33 (d, *J* = 7.1 Hz, 2H), 2.41 (s, 3H) and 1.28 (t, *J* = 7.1 Hz, 3H) ppm.

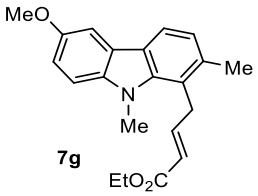
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 153.7, 139.8, 137.3, 134.4, 130.4, 128.0, 123.1, 121.9, 121.2, 121.0, 118.8, 114.3, 109.5, 102.8, 60.9, 56.1, 38.8, 33.5, 20.9 and 14.3 ppm.

IR (ATR): 2938, 2834, 17291479, 1446, 1208, 1160, 1028, 976, 803 and 732 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{23}NO_3$ 337.1678; found 337.1669.

TLC: R_f = 0.75 (4:1 Hexanes/EtOAc).

Ethyl (*E*)-4-(6-methoxy-2,9-dimethyl-9*H*-carbazol-1-yl)but-2-enoate (7g)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 7.36 (dt, *J* = 15.7, 4.7 Hz, 1H), 7.23 (d, *J* = 8.9 Hz, 1H), 7.10 – 7.02 (m, 2H), 5.58 – 5.47 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.05 – 3.99 (m, 2H), 3.92 (s, 6H), 2.41 (s, 3H) and 1.21 (t, *J* = 7.1 Hz, 3H) ppm.

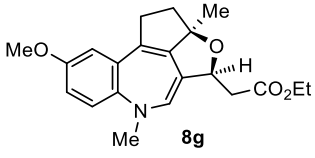
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 153.8, 147.5, 140.8, 137.2, 135.4, 123.2, 123.2, 122.7, 122.0, 118.8, 118.0, 114.6, 109.5, 102.8, 60.5, 56.2, 32.7, 31.1, 20.1 and 14.3 ppm

IR (ATR): 2929, 1715, 1648, 1484, 1277, 1207, 1170, 1042, 807 and 730 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{23}NO_3$ 337.1678; found 337.1674.

TLC: R_f = 0.68 (4:1 Hexanes/EtOAc).

Ethyl 2-(7-methoxy-4,10a-dimethyl-4,9,10,10a-tetrahydro-2*H*-1-oxa-4-azabenzo[*f*]cyclopenta[*cd*]azulen-2-yl)acetate (8g)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.8 Hz, 1H), 6.96 – 6.88 (m, 2H), 5.82 (s, 1H), 5.40 (t, *J* = 6.6 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 2.97 (dd, *J* = 16.6, 5.7 Hz, 1H), 2.82 – 2.73 (m, 2H), 2.59 (dd, *J* = 15.5, 7.2 Hz, 1H), 2.22 (dd, *J* = 12.0, 5.3 Hz, 1H), 1.96 (td, *J* = 12.1, 6.3 Hz, 1H), 1.35 (s, 3H) and 1.28 (d, *J* = 7.1 Hz, 3H) ppm.

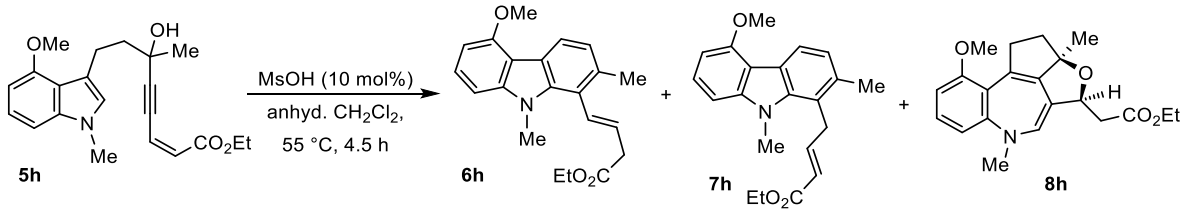
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 154.1, 137.5, 134.6, 130.3, 126.4, 116.7, 113.3, 113.0, 110.0, 100.9, 88.9, 80.5, 60.7, 56.1, 41.5, 37.1, 31.1, 22.8, 20.1 and 14.4 ppm.

IR (ATR): 2929, 2854, 1733, 1615, 1485. 1462, 1234, 1213, 1170, 1047, 798 and 729 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{25}NO_4$ 355.1784; found 355.1747.

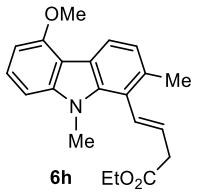
TLC: R_f = 0.57 (4:1 Hexanes/EtOAc).

Reaction of ethyl (*Z*)-6-hydroxy-8-(4-methoxy-1-methyl-1*H*-indol-3-yl)-6-methyloct-2-en-4-ynoate (5h)



According to the **General Procedure 1**, propargylic alcohol **5h** (142 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 μL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6h** light-yellow liquid (108 mg, 0.32 mmol, 80%) by using Hexane/EtOAc (19:1) as eluent, carbazole **7h** as brownish-white solid (13.5 mg, 0.04 mmol, 10%) by using Hexane/EtOAc (14:1) as eluent and benzazepine **8h** as light-brown gummy liquid (7.1 mg, 0.02 mmol, 5%) by using Hexane/EtOAc (9:1) as eluent.

Ethyl (*E*)-4-(5-methoxy-2,9-dimethyl-9*H*-carbazol-1-yl)but-3-enoate (6h)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (t, *J* = 8.3 Hz, 1H), 7.34 (t, *J* = 8.1 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 16.1 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 5.84 (dt, *J* = 16.0, 7.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 3H), 3.90 (s, 3H), 3.36 (dd, *J* = 7.1, 1.2 Hz, 2H), 2.43 (s, 3H) and 1.30 (t, *J* = 7.1 Hz, 3H) ppm.

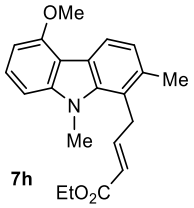
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 156.0, 143.7, 138.5, 133.4, 130.7, 127.9, 126.0, 121.8, 121.5, 120.4, 111.8, 101.9, 100.2, 60.9, 55.5, 38.9, 33.8, 20.9 and 14.4 ppm.

IR (ATR): 2944, 1734, 1587, 1496, 1461, 1402, 1299, 1258, 1164, 1101 and 728 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{23}NO_3$ 337.1678; found 337.1671.

TLC: R_f = 0.68 (4:1 Hexanes/EtOAc).

Ethyl (*E*)-4-(5-methoxy-2,9-dimethyl-9*H*-carbazol-1-yl)but-2-enoate (7h)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.52 – 5.44 (m, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 4.06 (s, 3H), 4.04 – 4.01 (m, 2H), 3.93 (s, 3H), 2.40 (s, 3H) and 1.20 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 156.0, 147.6, 143.6, 139.4, 134.4, 126.1, 123.1, 122.6, 122.3, 122.2, 121.8, 117.2, 101.7, 100.3, 60.4, 55.5, 32.8, 31.1, 20.1 and 14.3 ppm

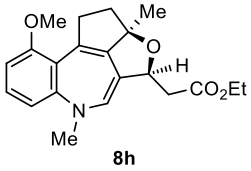
IR (ATR): 2940, 1717, 1587, 1457, 1264, 1171, 1043 and 730 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{23}NO_3$ 337.1678; found 337.1670.

TLC: R_f = 0.61 (4:1 Hexanes/EtOAc).

M.P.: 94 – 96 °C.

Ethyl 2-(8-methoxy-4,10a-dimethyl-4,9,10,10a-tetrahydro-2*H*-1-oxa-4-azabenzo[*f*]cyclopenta[*cd*]azulen-2-yl)acetate (8h)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 5.78 (s, 1H), 5.38 (t, *J* = 6.6 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 3.78 (s, 3H), 3.35 (dd, *J* = 17.7, 5.4 Hz, 1H), 2.95 (ddd, *J* = 17.6, 12.3, 5.6 Hz, 1H), 2.76 (dd, *J* = 15.4, 6.0 Hz, 1H), 2.59 (dd, *J* = 15.5, 7.2 Hz, 1H), 2.20 – 2.13 (m, 1H), 1.93 (td, *J* = 12.3, 6.2 Hz, 1H), 1.33 (s, 3H) and 1.27 (t, *J* = 7.1 Hz, 3H) ppm.

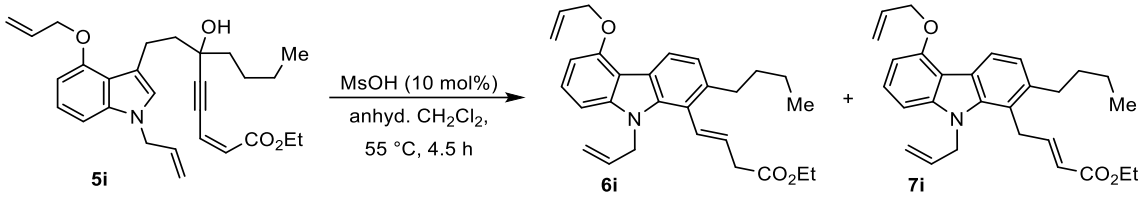
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 155.4, 140.6, 137.5, 128.3, 123.8, 116.6, 116.0, 113.9, 102.5, 99.4, 88.7, 80.4, 60.7, 55.3, 41.5, 37.4, 31.2, 22.7, 22.2 and 14.4 ppm.

IR (ATR): 2933, 2853, 1733, 1578, 1461, 1366, 1262, 1169, 1095, 1033, 757 and 737 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{25}NO_4$ 355.1784; found 355.1773.

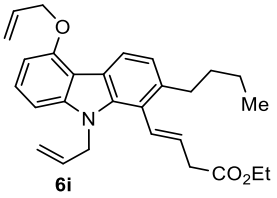
TLC: R_f = 0.54 (4:1 Hexanes/EtOAc).

Reaction of ethyl (*Z*)-6-(2-(1-allyl-4-(allyloxy)-1*H*-indol-3-yl)ethyl)-6-hydroxydec-2-en-4-ynoate (5i)



According to the **General Procedure 1**, propargylic alcohol **5i** (179.8 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 μL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6i** as light-yellow liquid (119.4 mg, 0.276 mmol, 69%) by using Hexane/EtOAc (99:1 to 49:1) as eluent, carbazole **7i** as brown liquid (6.9 mg, 0.016 mmol, 4%) by using Hexane/EtOAc (49:1) as eluent.

Ethyl (*E*)-4-(9-allyl-5-(allyloxy)-2-butyl-9*H*-carbazol-1-yl)but-3-enoate (6i)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 12.1, 9.1 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.22 (ddd, *J* = 22.1, 10.3, 5.0 Hz, 1H), 5.97 – 5.83 (m, 2H), 5.55 (d, *J* = 17.3 Hz, 1H), 5.34 (d, *J* = 10.6 Hz, 1H), 5.09 (d, *J* = 4.5 Hz, 3H), 4.84 – 4.77 (m, 3H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.31 (d, *J* = 7.0 Hz, 2H), 2.80 – 2.74 (m, 2H), 1.57 (dt, *J* = 15.4, 7.5 Hz, 3H), 1.42 – 1.33 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H) and 0.92 (t, *J* = 7.3 Hz, 3H) ppm.

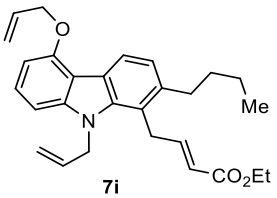
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 155.0, 143.2, 138.6, 137.8, 133.9, 133.8, 129.7, 127.8, 126.0, 122.1, 121.3, 121.3, 120.1, 117.3, 116.0, 112.3, 102.4, 101.6, 69.0, 60.9, 47.2, 38.9, 34.2, 33.4, 22.8, 14.4 and 14.2 ppm.

IR (ATR): 2928, 2857, 1737, 1587, 1450, 1407, 1260, 1143, 1104, 762, 750 and 727 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{28}H_{33}NO_3$ 431.2460; found 431.2454.

TLC: R_f = 0.75 (32:1 Hexanes/EtOAc after 6th run).

Ethyl (*E*)-4-(9-allyl-5-(allyloxy)-2-butyl-9*H*-carbazol-1-yl)but-2-enoate (7i)



[**N.B.**: Carbazole **7i** could not be isolated completely from **6i** and a (1:0.63) mixture of **7i** and **6i** could only be obtained at best after multiple column chromatography.]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.37 (dt, *J* = 15.7, 4.4 Hz, 1H), 7.34 – 7.26 (m, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.29 – 6.18 (m, 1H), 6.09 (ddd, *J* = 14.3, 8.7, 5.2 Hz, 1H), 5.59 – 5.3 (m, 1H), 5.50 – 5.44 (m, 1H), 5.38 – 5.33 (m, 1H), 5.17 (d, *J* = 10.5 Hz, 1H), 4.88 – 4.86 (m, 2H), 4.84 (d, *J* = 5.0 Hz, 1H), 4.82 – 4.78 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.97 – 3.87 (m, 2H), 2.70 – 2.65 (m, 2H), 1.66 – 1.58 (m, 2H), 1.44 – 1.36 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H) and 0.94 (t, *J* = 6.5 Hz, 3H) ppm.

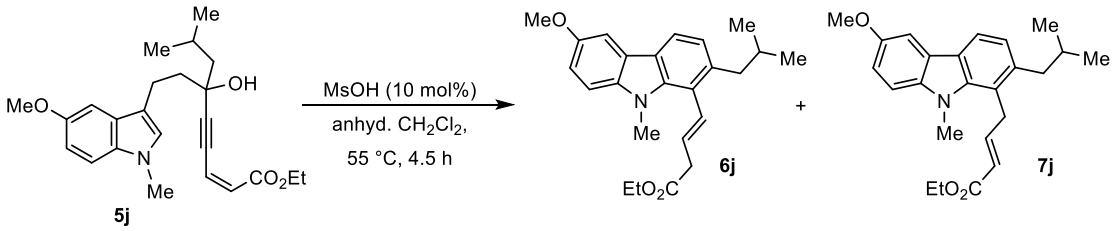
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 148.5, 143.4, 139.4, 139.1, 134.3, 133.8, 126.2, 123.1, 122.13, 122.07, 122.0, 117.5, 116.6, 116.3, 112.3, 102.1, 101.8, 69.1, 60.4, 47.4, 34.3, 33.2, 32.1, 30.3, 29.8, 23.0, 14.3 and 14.2 ppm.

IR (ATR): 2929, 2854, 1714, 1585, 1446, 1400, 1253, 1138, 1114, 783, 761 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{28}H_{33}NO_3$ 431.2460; found 431.2443.

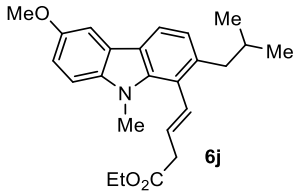
TLC: R_f = 0.74 (32:1 Hexanes/EtOAc after 6th run).

Reaction of ethyl (*Z*)-6-hydroxy-6-(2-(5-methoxy-1-methyl-1*H*-indol-3-yl)ethyl)-8-methyln-on-2-en-4-ynoate (5j)



According to the **General Procedure 1**, propargylic alcohol **5j** (159 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 μL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6j** as light-yellow liquid (113.8 mg, 0.3 mmol, 75%) by using Hexane/EtOAc (14:1) as eluent, carbazole **7j** as off-white solid (13.7 mg, 0.036 mmol, 9%) by using Hexane/EtOAc (6:1) as eluent.

Ethyl (*E*)-4-(2-isobutyl-6-methoxy-9-methyl-9*H*-carbazol-1-yl)but-3-enoate (6j)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.05 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 16.1 Hz, 1H), 5.82 (dt, *J* = 15.9, 7.1 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 3.34 (d, *J* = 7.1 Hz, 2H), 2.64 (d, *J* = 7.2 Hz, 2H), 1.90 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) and 0.91 (d, *J* = 6.6 Hz, 6H) ppm.

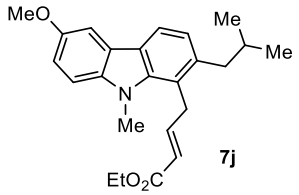
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 153.7, 139.9, 138.4, 137.4, 130.5, 128.1, 123.1, 121.9, 121.3, 121.1, 118.6, 114.4, 109.5, 102.8, 60.9, 56.2, 42.7, 38.9, 33.7, 30.1, 22.7 and 14.4 ppm.

IR (ATR): 2952, 2867, 1734, 1486, 1466, 1438, 1287, 1222, 1205, 1167, 1027 and 805 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{24}H_{29}NO_3$ 379.2147; found 379.2145.

TLC: R_f = 0.7 (6:1 Hexanes/EtOAc).

Ethyl (*E*)-4-(2-isobutyl-6-methoxy-9-methyl-9*H*-carbazol-1-yl)but-2-enoate (7j)



7j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.38 (dt, *J* = 15.7, 4.6 Hz, 1H), 7.25 (d, *J* = 10.3 Hz, 1H), 7.08 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.51 – 5.42 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.07 (dd, *J* = 4.4, 1.9 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 2.57 (d, *J* = 7.3 Hz, 2H), 1.95 – 1.84 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H) and 0.95 (d, *J* = 6.6 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 153.9, 148.1, 140.8, 139.0, 137.3, 123.4, 123.2, 122.5, 122.3, 118.6, 117.9, 114.6, 109.5, 102.7, 60.5, 56.3, 42.7, 32.7, 30.6, 30.5, 22.8 and 14.3 ppm.

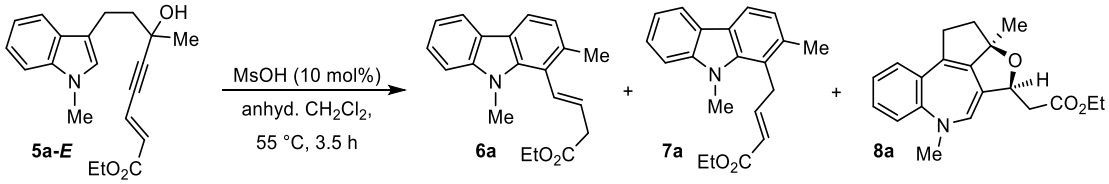
IR (ATR): 2924, 1712, 1650, 1486, 1268, 1165, 1033, 804 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{24}H_{29}NO_3$ 379.2147; found 379.2133.

TLC: R_f = 0.62 (4:1 Hexanes/EtOAc).

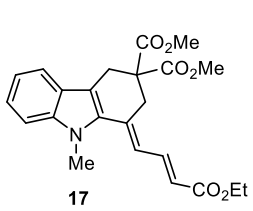
M.P.: 104 – 106 °C.

Reaction of ethyl (*E*)-6-hydroxy-6-methyl-8-(1-methyl-1*H*-indol-3-yl)oct-2-en-4-ynoate (5a-*E*)

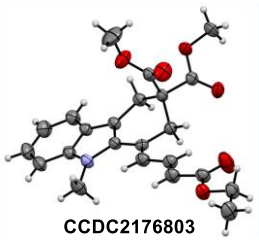


According to the **General Procedure 1**, propargylic alcohol **5a-*E*** (130 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (26 μL, 0.04 mmol, 10 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired carbazole **6a** as light-yellow liquid (90 mg, 0.29 mmol, 73%) by using Hexane/EtOAc (13:1) as eluent, carbazole **7a** as yellow liquid (13.5 mg, 0.044 mmol, 11%) by using Hexane/EtOAc (9:1) as eluent and benzazepine **8a** as yellow liquid (19.5 mg, 0.06 mmol, 15%) by using Hexane/EtOAc (7:1) as eluent.

Dimethyl (*E*)-1-((*E*)-4-ethoxy-4-oxobut-2-en-1-ylidene)-9-methyl-1,2,4,9-tetrahydro-3*H*-carbazole-3,3-dicarboxylate (17)



17



According to the **General Procedure 1**, *Z*-enoate **16** (164.6 mg, 0.4 mmol, 1.0 equiv.), was reacted with methanesulfonic acid (MsOH) (26 µL, 0.04 mmol, 10 mol%) in 10 mL anhydrous CH_2Cl_2 for 3 h, affording the tetrahydrocarbazole **17** as bright yellow crystalline solid (128.4 mg, 0.312 mmol, 78%) by using Hexane/EtOAc (13:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 15.0, 11.7 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.10 (dd, *J* = 10.7, 4.7 Hz, 1H), 6.63 (d, *J* = 11.7 Hz, 1H), 6.01 (d, *J* = 15.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.70 (s, 6H), 3.49 (s, 2H), 3.36 (s, 2H) and`1.33 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 173.5, 149.4, 138.5, 135.5, 134.8, 133.7, 130.6, 129.0, 128.5, 127.0, 125.3, 125.1, 124.9, 118.9, 117.5, 60.6, 38.1, 34.7, 31.5, 31.2, 28.8, 23.0, 19.8, 14.3 and 14.2 ppm.

IR (ATR): 2956, 2925, 2855, 2382, 2350, 1734, 1697, 1448, 1368, 1176 and 751 cm^{-1}.

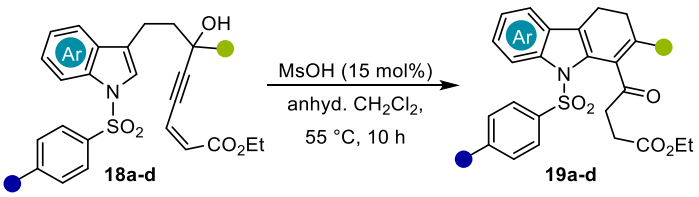
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{31}NO_5S$ 494.1996; found 494.1984.

TLC: R_f = 0.3 (6:1 Hexanes/EtOAc).

M.P.: 152 – 155 °C.

(ii) General Procedure 2: Synthesis of functionalized dihydrocarbazoles

General Scheme of the reaction:

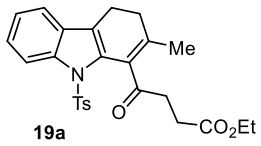


18a-d 19a-d

Procedure: To a well stirred solution of propargylic alcohols **18a-d** (1.0 equiv.) in anhydrous dichloromethane (0.04 *M*), methanesulfonic acid (MsOH) (15 mol%) was added dropwise at room temperature under nitrogen. The resulting mixture was transferred to a pre-heated oil bath and refluxed at 55 °C until the TLC showed complete consumption of the starting material. After completion, the reaction mixture was cooled down to room temperature and saturated $NaHCO_3$ solution was added. After stirring vigorously for 15 min (during this period the color of the initial dark brown reaction mixture becomes light orangish yellow), the layers were separated, and the residual compound from aqueous layer was extracted with

CH_2Cl_2 (3 times). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. Subsequent purification of the crude product via silica gel column chromatography (Hexane:EtOAc) provided the desired functionalized dihydrocarbazoles **19a-d**.

Ethyl 4-(2-methyl-9-tosyl-4,9-dihydro-3*H*-carbazol-1-yl)-4-oxobutanoate (19a)



19a

According to the **General Procedure 2**, propargylic alcohol **18a** (186.2 mg, 0.4 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (39 μL, 0.06 mmol, 15 mol%) were used in 10 mL anhydrous CH_2Cl_2, affording the desired dihydrocarbazole **19a** as brown waxy solid (158.3 mg, 0.34 mmol, 85%) by using Hexane/EtOAc (6:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.22 (m, 3H), 7.00 (d, *J* = 8.1 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.04 (t, *J* = 6.7 Hz, 2H), 2.77 (t, *J* = 6.8 Hz, 2H), 2.58 (t, *J* = 8.2 Hz, 2H), 2.32 – 2.25 (m, 5H), 2.24 (s, 3H) and 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

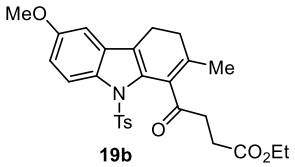
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 173.5, 144.7, 144.5, 138.4, 134.7, 132.5, 130.6, 129.2, 129.1, 127.1, 125.2, 125.0, 124.6, 118.9, 117.3, 60.6, 37.9, 32.9, 28.9, 21.7, 21.7, 19.6 and 14.3 ppm.

IR (ATR): 2928, 1731, 1697, 1605, 1469, 1456, 1355, 1282, 1225, 1185 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{28}NO_5S$ 466.1683; found 466.1649.

TLC: R_f = 0.3 (4:1 Hexanes/EtOAc).

Ethyl 4-(6-methoxy-2-methyl-9-tosyl-4,9-dihydro-3*H*-carbazol-1-yl)-4-oxobutanoate (19b)



19b

According to the **General Procedure 2**, propargylic alcohol **18b** (99 mg, 0.2 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (20 μL, 0.03 mmol, 15 mol%) were used in 5 mL anhydrous CH_2Cl_2, affording the desired dihydrocarbazole **19b** as brownish-yellow gummy liquid (92.2 mg, 0.186 mmol, 93%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 9.0 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.72 (s, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 3.05 (t, *J* = 6.6 Hz, 2H), 2.75 (t, *J* = 6.6 Hz, 2H), 2.54 (t, *J* = 8.1 Hz, 2H), 2.30 – 2.21 (m, 8H) and 1.25 (t, *J* = 6.7 Hz, 3H) ppm.

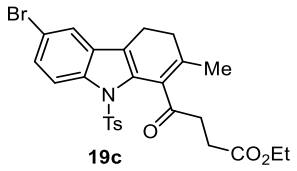
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 173.4, 157.6, 144.6, 144.5, 135.5, 132.6, 132.2, 131.7, 129.1, 129.0, 127.0, 124.7, 118.2, 113.4, 101.6, 60.4, 55.6, 37.8, 32.8, 28.8, 21.6, 21.6, 19.5 and 14.2 ppm.

IR (ATR): 2925, 1732, 1698, 1599, 1479, 1459, 1364, 1293, 1239, 1170 and 816 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{30}NO_6S$ 496.1788; found 496.1787.

TLC: R_f = 0.3 (2:1 Hexanes/EtOAc).

Ethyl 4-(6-bromo-2-methyl-9-tosyl-4,9-dihydro-3*H*-carbazol-1-yl)-4-oxobutanoate (19c)



19c

According to the **General Procedure 2**, propargylic alcohol **18c** (108.6 mg, 0.2 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (20 μL, 0.03 mmol, 15 mol%) were used in 5 mL anhydrous CH_2Cl_2, affording the desired dihydrocarbazole **19c** as brown gummy liquid (96.7 mg, 0.178 mmol, 89%) by using Hexane/EtOAc (6:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.02 (t, *J* = 6.6 Hz, 2H), 2.76 (t, *J* = 6.7 Hz, 2H), 2.54 (t, *J* = 8.2 Hz, 2H), 2.31 – 2.25 (m, 5H), 2.24 (s, 3H) and 1.25 (t, *J* = 7.1 Hz, 3H) ppm.

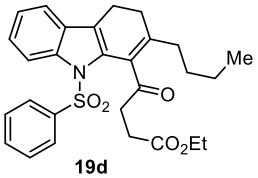
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 173.4, 145.6, 145.1, 137.0, 135.9, 132.3, 132.2, 129.3, 128.9, 127.8, 127.0, 123.5, 121.7, 118.6, 60.5, 37.8, 32.8, 28.8, 21.7, 21.6, 19.4 and 14.3 ppm.

IR (ATR): 2927, 2379, 2350, 2314, 1731, 1696, 1595, 1439, 1365, 1172 and 812 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{27}BrNO_5S$ 544.0788; found 544.0776.

TLC: R_f = 0.3 (4:1 Hexanes/EtOAc).

Ethyl 4-(2-butyl-9-(phenylsulfonyl)-4,9-dihydro-3*H*-carbazol-1-yl)-4-oxobutanoate (19d)



19d

According to the **General Procedure 2**, propargylic alcohol **18d** (100 mg, 0.2 mmol, 1.0 equiv.), methanesulfonic acid (MsOH) (20 μL, 0.03 mmol, 15 mol%) were used in 5 mL anhydrous CH_2Cl_2, affording the desired dihydrocarbazole **19d** as off-white solid (90.8 mg, 0.184 mmol, 92%) by using Hexane/EtOAc (6:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.43 – 7.38 (m, 1H), 7.34 – 7.27 (m, 2H), 7.24 – 7.19 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.03 (t, *J* = 6.8 Hz,

2H), 2.77 (t, *J* = 6.9 Hz, 2H), 2.54 (dd, *J* = 15.6, 7.8 Hz, 2H), 2.24 – 2.15 (m, 2H), 1.57 – 1.51 (m, 2H), 1.47 – 1.37 (m, 2H), 1.29 – 1.23 (m, 5H) and 0.97 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 173.5, 149.4, 138.5, 135.5, 134.8, 133.7, 130.6, 129.0, 128.5, 127.0, 125.3, 125.1, 124.9, 118.9, 117.5, 60.6, 38.1, 34.7, 31.5, 31.2, 28.8, 23.0, 19.8, 14.3 and 14.2 ppm.

IR (ATR): 2956, 2925, 2855, 2382, 2350, 1734, 1697, 1448, 1368, 1176 and 751 cm^{-1}.

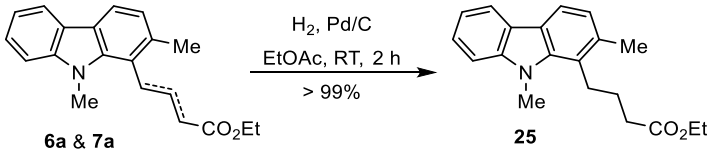
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{31}NO_5S$ 494.1996; found 494.1984.

TLC: R_f = 0.45 (4:1 Hexanes/EtOAc).

M.P.: 110 – 112 °C.

C. Experimental procedures and characterization data for total synthesis of *N*-Me-carazostatin (29) and *N*-Me-carbazoquinocin C (31).

Ethyl 4-(2,9-dimethyl-9*H*-carbazol-1-yl)butanoate (25)



To a well stirred solution of mixture of ethyl (*E*)-4-(2,9-dimethyl-9*H*-carbazol-1-yl)but-3-enoate **6a** and ethyl (*E*)-4-(2,9-dimethyl-9*H*-carbazol-1-yl)but-2-enoate **7a** (200 mg, 0.65 mmol, 1.0 equiv.) in EtOAc (10 mL) was added Pd/C (20 mg, 10 wt%). The resulting reaction mixture was stirred under Hydrogen (1 atm) atmosphere for 2 h at room temperature. After completion the reaction mixture was filtered through a Celite® pad by washing with EtOAc. The filtrate was concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (9:1 Hexanes/EtOAc) provided the desired reduced ester **25** (200.7 mg, 0.65 mmol, 99.7%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.15 – 3.02 (m, 2H), 2.51 – 2.41 (m, 5H), 2.00 – 1.88 (m, 2H) and 1.25 (t, *J* = 7.1 Hz, 3H) ppm.

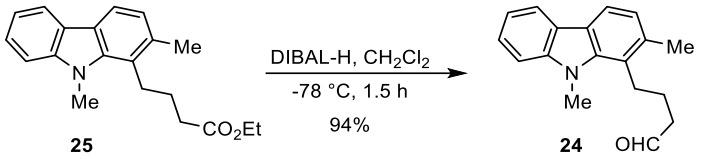
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 142.2, 139.8, 134.6, 125.3, 123.0, 122.9, 122.7, 122.4, 119.5, 118.9, 117.9, 108.7, 60.5, 34.2, 32.5, 27.7, 26.5, 20.1 and 14.3 ppm.

IR (ATR): 2926, 1728, 1590, 1456, 1217, 1190, 1157, 1121, 1025, 925, 807 and 739 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{20}H_{23}NO_2$ 309.1729; found 309.1712.

TLC: R_f = 0.28 (9:1 Hexanes/EtOAc).

4-(2,9-dimethyl-9*H*-carbazol-1-yl)butanal (24)



DIBAL-H (1.9 mL, 1.22 equiv., 1 *M* in CH_2Cl_2) was added dropwise to a solution of Ethyl 4-(2,9-dimethyl-9*H*-carbazol-1-yl)butanoate **25** (480 mg, 1.55 mmol, 1.0 equiv.) in CH_2Cl_2 (15 ml) at -78 °C. The reaction mixture was stirred at the same temperature for 1.5 h. The reaction was stopped by addition of MeOH (3 mL) followed by addition of Rochelle's salt (10 ml, 1 *M*) and CH_2Cl_2 (10 ml). The resultant mixture was stirred vigorously for 1.5 h until a clear biphasic mixture is obtained. The organic layer was separated, and aqueous phase was extracted with EtOAc (3 x 7 mL). The combined organic layers were washed with H_2O, brine and dried (Na_2SO_4) and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (4:1 Hexanes/EtOAc) provided the desired aldehyde **24** (386.6 mg, 1.46 mmol, 94% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.19 (dd, *J* = 12.5, 5.0 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 4.03 (s, 3H), 3.15 – 3.07 (m, 2H), 2.58 (t, *J* = 6.9 Hz, 2H), 2.48 (s, 3H) and 1.99 – 1.90 (m, 2H) ppm.

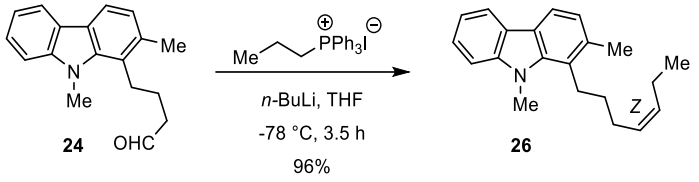
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 142.3, 139.9, 134.7, 125.4, 123.1, 122.8, 122.5, 119.6, 119.0, 118.0, 108.8, 43.8, 32.6, 27.6, 23.7 and 20.3 ppm.

IR (ATR): 2970, 2931, 1725, 1683, 1626, 1466, 1454, 1423, 1246, 996, 849, 821 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{18}H_{19}NO$ 265.1467; found 265.1447.

TLC: R_f = 0.48 (4:1 Hexanes/EtOAc).

(*Z*)-1-(hept-4-en-1-yl)-2,9-dimethyl-9*H*-carbazole (26)



To a flame dried round bottom flask were added triphenyl(propyl)phosphonium iodide (1.3 g, 3.02 mmol, 4 equiv.) and anhydrous THF (12 mL). After the mixture was cooled to -78 °C, *n*-BuLi (1.4 mL, 2.26 mmol, 3.0 equiv., 1.6 *M* in hexane) was added dropwise over 5 min. The resulting mixture was then stirred for 1 h at the same temperature followed by addition of 4-(2,9-dimethyl-9*H*-carbazol-1-yl)butanal **24** (200 mg, 0.75 mmol, 1.0 equiv.) in anhydrous THF (5 mL). The final reaction mixture was stirred for 2.5 h at –78 °C until the TLC showed complete consumption of the aldehyde. The color of the mixture changed from dark orange to white. After completion, a saturated NH_4Cl solution (10 mL) was added to quench the

reaction at 0 °C. Diethyl ether (5 mL) and water (5 mL) were added. After separation of the layers the residual compound from aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (Hexanes/EA) provided the desired alkene **26** (210.4 mg, 0.72 mmol, 96%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.81 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.40 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 5.59 – 5.39 (m, 2H), 4.00 (s, 3H), 3.12 – 3.03 (m, 2H), 2.48 (s, 3H), 2.31 – 2.18 (m, 2H), 2.15 – 2.03 (m, 2H), 1.76 – 1.66 (m, 2H) and 1.00 (td, *J* = 7.5, 2.2 Hz, 3H) ppm.

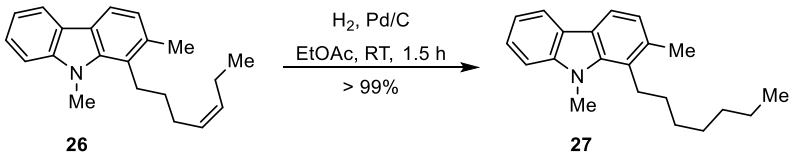
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.9, 134.6, 132.7, 128.3, 125.3, 124.0, 123.2, 122.7, 122.4, 119.6, 118.9, 117.7, 108.7, 32.7, 31.5, 28.1, 27.5, 20.8, 20.2 and 14.5 ppm.

IR (ATR): 2917, 1486, 1485, 1330, 1229 and 742 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{25}N$ 291.1987; found 291.1978.

TLC: R_f = 0.75 (9:1 Hexanes/EtOAc).

1-heptyl-2,9-dimethyl-9*H*-carbazole (27)



To a well stirred solution of (*Z*)-1-(hept-4-en-1-yl)-2,9-dimethyl-9*H*-carbazole **26** (200 mg, 0.69 mmol, 1.0 equiv.) in EtOAc (10 mL) was added Pd/C (20 mg, 10 wt%). The resulting reaction mixture was stirred under Hydrogen (1 atm) atmosphere for 2 h at room temperature. After completion the reaction mixture was filtered through a Celite® pad by washing with EtOAc. The filtrate was concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (19:1 Hexanes/EtOAc) provided the desired reduced product **27** (200.6 mg, 0.68 mmol, 99.6%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 4.06 (s, 3H), 3.14 – 3.06 (m, 2H), 2.50 (s, 3H), 1.72 – 1.63 (m, 2H), 1.55 – 1.47 (m, 2H), 1.43 – 1.29 (m, 6H) and 0.90 (t, *J* = 6.7 Hz, 3H) ppm.

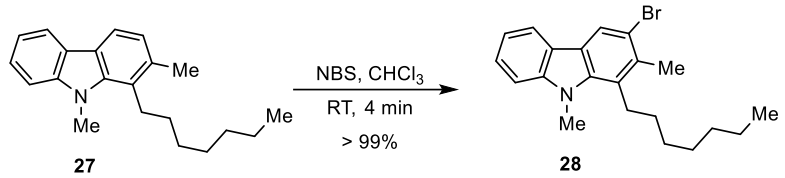
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.9, 134.5, 125.3, 124.3, 123.2, 122.7, 122.4, 119.6, 118.9, 117.6, 108.7, 32.6, 32.0, 31.7, 30.1, 29.3, 28.5, 22.8, 20.3 and 14.3 ppm.

IR (ATR): 3441, 2925, 2855, 1645, 1599, 1472, 1429, 1413, 1372, 1324, 1253, 1045, 866 and 737 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{27}N$ 293.2143; found 293.2129.

TLC: R_f = 0.3 (Hexanes).

3-bromo-1-heptyl-2,9-dimethyl-9*H*-carbazole (28)



To a solution of 1-heptyl-2,9-dimethyl-9*H*-carbazole **27** (150 mg, 0.51 mmol, 1.0 equiv.) in chloroform ($CHCl_3$) (10 ml) at room temperature was added *N*-bromosuccinimide (91 mg, 0.51 mmol, 1.0 equiv.) under nitrogen atmosphere. The reaction mixture was stirred at same temperature for 4 min until the TLC showed complete consumption of the starting material. After completion, water (10 mL) was added. The residual compound from aqueous layer was extracted with $CHCl_3$ (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (19:1 Hexanes/EA) provided the desired 3-bromo carbazole **28** (188.6 mg, 0.51 mmol, 99.3%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 3.86 (s, 3H), 3.03 – 2.96 (m, 2H), 2.50 (s, 3H), 1.57 (dt, *J* = 11.6, 7.4 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.38 – 1.28 (m, 6H) and 0.90 (t, *J* = 6.7 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 138.9, 132.8, 125.9, 123.6, 122.1, 121.5, 119.7, 119.2, 116.7, 108.8, 32.6, 32.0, 31.7, 30.0, 29.5, 29.2, 22.8, 19.8 and 14.3 ppm.

IR (ATR): 2924, 2858, 2385, 1469, 1404, 1274, 1138, 1014, 819, 770 and 739 cm^{-1}.

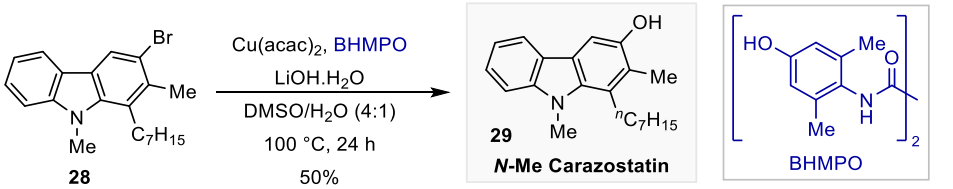
HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{26}BrN$ 371.1249; found 371.1265.

TLC: R_f = 0.42 (Hexanes).

M.P.: 126 – 130 °C.

1-heptyl-2,9-dimethyl-9*H*-carbazol-3-ol [*N*-methyl Carazostatin] (29)

Method A: Direct hydroxylation of **28** by combination of $Cu(acac)_2$ and BHMPO.[1]



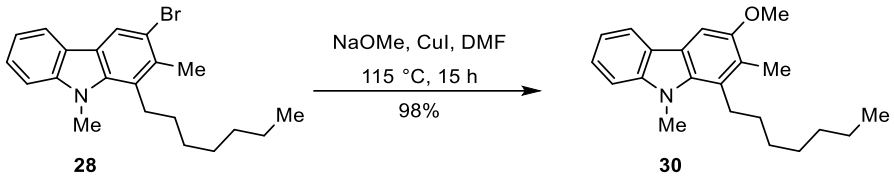
BHMPO - *N*,*N*′-bis(4-hydroxyl-2,6-dimethylphenyl)oxalamide

Following the reported procedure,[2] a reaction vial was charged with **28** (25 mg, 0.063 mmol, 1.0 equiv.), a solution of $Cu(acac)_2$ (1.65 mg, 6.3 μmol, 0.1.0 equiv.) and BHMPO (3.2 mg, 9.45 μmol, 0.15 equiv.) in DMSO (300 μL) and a solution of $LiOH{\cdot}H_2O$ (8 mg, 0.189 mmol, 3.0 equiv.) in degassed H_2O (100 μL) at room temperature. After stirring at 100 ˚C for 30 h, the cooled reaction mixture was quenched with 1 *M* HCl (5 mL). The residual compound from aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were

dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (4:1 Hexanes/EA) provided the desired *N*-methyl Carazostatin **29** (9.7 mg, 0.031 mmol, 49.7%) as a white waxy solid.

Method B: Synthesis of **29** from **28** employing sequential etherification-deprotection strategy

Step 1: Synthesis of **1-heptyl-3-methoxy-2,9-dimethyl-9*H*-carbazole (30)**



A 15 mL Schlenk tube equipped with a magnetic stirrer was evacuated and then backfilled with nitrogen. This process was repeated three times. Next, 2 mL of anhydrous MeOH was added, and the reaction vessel was cooled down to 0 °C. To this stirring MeOH solvent, sodium metal (124 mg, 5.4 mmol, 54 equiv.) was carefully added in portions under a positive nitrogen pressure to form a ~2.7 *M* solution of sodium methoxide (NaOMe) in MeOH. After complete dissolution of Na in MeOH, the solution became thick and light yellowish. Next, 3-bromo carbazole **28** (37 mg, 0.1 mmol, 1.0 equiv.) dissolved in DMF (1.4 mL) was added to this freshly prepared NaOMe solution followed by successive addition of CuI (76.2 mg, 0.4 mmol, 4.0 equiv.) under nitrogen atmosphere. The resulting reaction mixture was then transferred to a preheated oil bath and stirred at 115 °C for 15 h. After complete consumption of starting material **28** as indicated by TLC, the crude reaction mixture was filtered through a short plug of Celite® and washed with EtOAc. The filtrate was sequentially washed with saturated NH_4Cl solution (5 mL), water (10 mL) and brine (5 mL), dried over anhydrous Na_2SO_4 concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (9:1 Hexanes/EtOAc) provided the desired 3-methoxy carbazole **30** (31.7 mg, 0.098 mmol, 98%) as yellowish-white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 4.04 (s, 3H), 3.94 (s, 3H), 3.16 – 3.08 (m, 2H), 2.37 (s, 3H), 1.72 – 1.63 (m, 2H), 1.54 – 1.47 (m, 2H), 1.43 – 1.28 (m, 6H) and 0.90 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 142.4, 134.8, 125.8, 125.1, 124.7, 123.2, 121.8, 119.5, 118.4, 108.8, 99.1, 56.3, 32.8, 32.0, 31.7, 30.1, 29.3, 28.8, 22.8, 14.3 and 12.1 ppm.

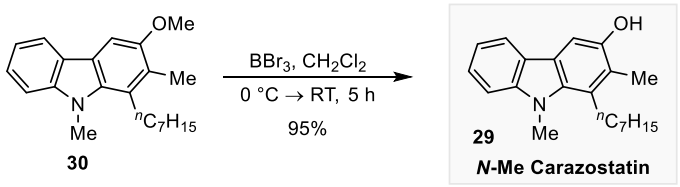
IR (ATR): 2925, 2859, 2382, 1461, 1414, 1283, 1210, 1146, 1109, 836 and 735 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{30}NO$ 324.2322; found 324.2314.

TLC: R_f = 0.23 (Hexanes).

M.P.: 135 – 140 °C.

Step 2: Synthesis of ***N*-methyl Carazostatin (29)**



To a stirred solution of **30** (27.5 mg, 0.085 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (4 mL) at 0 °C, was added a 1 *M* solution of boron tribromide (BBr_3) in CH_2Cl_2 (0.26 mL, 0.26 mmol, 3 equiv.) dropwise. The reaction mixture was then allowed to warm up to room temperature and stirred for further 4.5 h. The reaction was quenched with H_2O (5 mL). The organic layer was separated, and the residual compound from aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with H_2O, brine and dried (Na_2SO_4) and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (4:1 Hexanes/EtOAc) provided the desired *N*-methyl Carazostatin **29** (25 mg, 0.081 mmol, 95% yield) as a white semi-solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 4.70 (s, 1H), 4.00 (s, 3H), 3.13 – 3.05 (m, 2H), 2.37 (s, 3H), 1.71 – 1.59 (m, 2H), 1.53 – 1.45 (m, 2H), 1.42 – 1.29 (m, 6H) and 0.90 (t, *J* = 6.7 Hz, 3H) ppm.

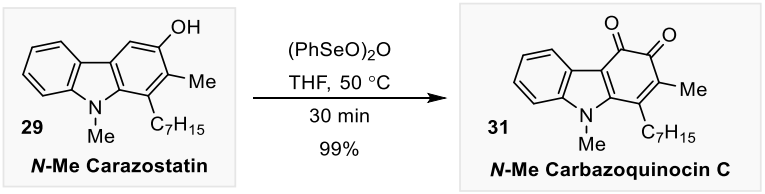
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 142.6, 135.1, 125.7, 125.4, 122.8, 122.5, 122.2, 119.7, 118.4, 108.7, 103.1, 32.7, 32.0, 31.7, 30.1, 29.3, 28.7, 22.8, 14.2 and 12.1 ppm.

IR (ATR): 2956, 2924, 2853, 2360, 2341, 1495, 1459, 1267, 1230, 909, 772 and 731 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{27}NO$ 309.2093; found 309.2051.

TLC: R_f = 0.28 (9:1, Hex/EtOAc).

1-heptyl-2,9-dimethyl-3*H*-carbazole-3,4(9*H*)-dione [*N*-methyl Carbazoquinocin C] (31)



To a solution of *N*-methyl Carazostatin **29** (24 mg, 0.077 mmol) in THF (4 mL) at RT under nitrogen atmosphere was added $(PhSeO)_2O$ (56. mg, 0.154 mmol, 2 equiv.). The reaction mixture was then stirred at 50 °C for 30 min. After bringing to room temperature the mixture was quenched with water, and the residual compound from aqueous layer was extracted with EtOAc (3 × 4 mL). The combined organic layers were washed with H_2O, brine and dried (Na_2SO_4) and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (3:1 Hexanes/EtOAc) provided the desired *N*-methyl Carbazoquinocin C **31** (24.8 mg, 0.077 mmol, 99% yield) as a dark brown glittering solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 6.0 Hz, 1H), 7.29 – 7.22 (m, 3H), 3.88 (s, 3H), 2.73 – 2.64 (m, 2H), 1.90 (s, 3H), 1.62 – 1.54 (m, 2H), 1.52 – 1.44 (m, 2H), 1.41 – 1.29 (m, 6H) and 0.90 (t, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 183.1, 173.5, 144.9, 142.6, 139.5, 134.4, 125.7, 124.8, 124.8, 121.7, 113.6, 110.9, 33.0, 31.8, 29.9, 29.8, 29.1, 28.3, 22.7, 14.2 and 11.8 ppm.

IR (ATR): 2955, 2924, 2853, 1668, 1642, 1630, 1484, 1461, 1424, 1378, 1254 and 772 cm^{-1}.

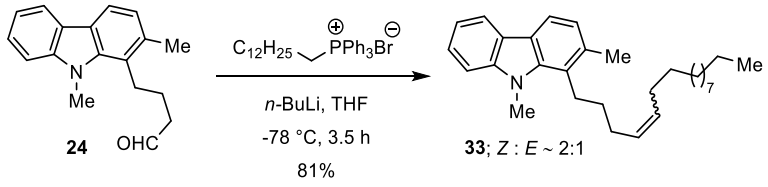
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{26}NO_2$ 324.1958; found 324.1959.

TLC: R_f = 0.29 (4:1, Hex/EtOAc).

M.P.: 150 – 152 °C.

D. Experimental procedures and characterization data for total synthesis of *N*-Me-Lipocarbazole A4 (32).

1-(heptadec-4-en-1-yl)-2,9-dimethyl-9*H*-carbazole (33)



To a flame dried round bottom flask were added triphenyl(tridecyl)phosphonium bromide (100 mg, 0.19 mmol, 2.5 equiv.) and anhydrous THF (7 mL). After the mixture was cooled to -78 °C, *n*-BuLi (0.1 mL, 0.16 mmol, 2.12 equiv., 1.6 *M* in hexane) was added dropwise over 5 min. The resulting mixture was then stirred for 1 h at the same temperature followed by addition of 4-(2,9-dimethyl-9*H*-carbazol-1-yl)butanal **24** (20 mg, 0.075 mmol, 1.0 equiv.) in anhydrous THF (3 mL). The final reaction mixture was stirred for 2.5 h at -78 °C until the TLC showed complete consumption of the aldehyde. The color of the mixture changed from dark orange to white. After completion a saturated NH_4Cl solution (5 mL) was added to quench the reaction at 0 °C. Diethyl ether (3 mL) and water (5 mL) were added. After separation of the layers the residual compound from aqueous layer was extracted with EtOAc (3 x 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (Hexanes/EA) provided the desired alkene **33** (*Z*:*E* ~ 2:1) (26.3 mg, 0.061 mmol, 81%) as colorless oil.[3]

Major isomer (*Z*):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 5.56 – 5.43 (m, 2H), 4.06 (s, 3H), 3.11 (dt, *J* = 11.3, 6.1 Hz, 2H), 2.50 (s, 3H), 2.29 – 2.23 (m, 2H), 2.12 – 2.05 (m, 2H), 1.78 – 1.69 (m, 2H), 1.38 – 1.25 (m, 20H) and 0.88 (t, *J* = 6.9 Hz, 3H) ppm.

Minor isomer (*E*):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 5.56 – 5.43 (m, 2H), 4.05 (s, 3H), 3.11 (dt, *J* = 11.3, 6.1 Hz, 2H), 2.49 (s, 3H), 2.23 – 2.16 (m, 2H), 2.03 – 1.98 (m, 2H), 1.78 – 1.69 (m, 2H), 1.38 – 1.25 (m, 20H) and 0.88 (t, *J* = 6.9 Hz, 3H) ppm.

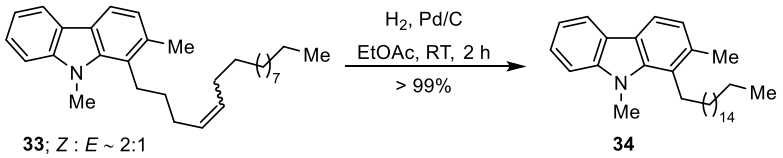
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.9, 134.6, 131.8, 131.2, 129.4, 128.9, 125.3, 124.0, 123.2, 122.7, 122.5, 119.6, 118.9, 117.7, 108.7, 33.0, 32.8, 32.7, 32.1, 31.8, 31.6, 31.4, 29.9, 29.8, 29.8, 29.7, 29.5, 29.4, 28.1, 27.9, 27.6, 27.5, 22.8, 20.2 and 14.3 ppm.

IR (ATR): 2921, 2858, 1605, 1485, 1325, 1250, 1182, 1013 and 754 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{31}H_{45}N$ 431.3552; found 431.3545.

TLC: R_f = 0.3 (Hexanes).

1-heptadecyl-2,9-dimethyl-9*H*-carbazole (34)



To a well stirred solution of *Z*, *E* isomeric mixture of 1-(heptadec-4-en-1-yl)-2,9-dimethyl-9*H*-carbazole **33** (15 mg, 0.035 mmol, 1.0 equiv.) in EtOAc (10 mL) was added Pd/C (1.5 mg, 10 wt%). The resulting reaction mixture was stirred under Hydrogen (1 atm) atmosphere for 2 h at room temperature. After completion the reaction mixture was filtered through a small Celite® pad by washing with EtOAc. The filtrate was concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (19:1 Hexanes/EtOAc) provided the desired reduced product **34** (15 mg, 0.035 mmol, 99.8%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 4.06 (s, 3H), 3.14 – 3.06 (m, 2H), 2.50 (s, 3H), 1.71 – 1.63 (m, 2H), 1.54 – 1.47 (m, 2H), 1.32 – 1.25 (m, 26H) and 0.88 (t, *J* = 6.6 Hz, 3H) ppm.

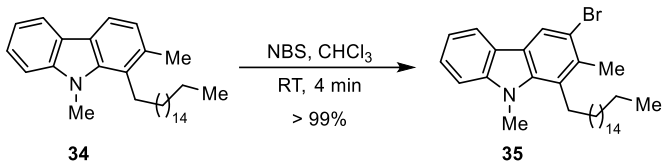
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.9, 134.5, 125.3, 124.3, 123.2, 122.7, 122.4, 119.6, 118.9, 117.6, 108.7, 32.6, 32.1, 31.7, 30.2, 29.8, 29.7, 29.5, 28.5, 22.8, 20.3 and 14.3 ppm.

IR (ATR): 3442, 2926, 2849, 1643, 1602, 1469, 1417, 1368, 1315, 1048, 859 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{31}H_{47}N$ 433.3709; found 433.3699.

TLC: R_f = 0.3 (Hexanes).

3-bromo-1-heptadecyl-2,9-dimethyl-9*H*-carbazole (35)



To a solution of 1-heptadecyl-2,9-dimethyl-9*H*-carbazole **34** (15 mg, 0.035 mmol, 1.0 equiv.) in $CHCl_3$ (3 ml) at room temperature was added *N*-bromosuccinimide (6.2 mg, 0.035 mmol, 1.0 equiv.) under nitrogen atmosphere. The reaction mixture was stirred at same temperature for 4 min until the TLC showed complete consumption of the starting material. After completion, water (4 mL) was added. The residual compound from aqueous layer was extracted with $CHCl_3$ (3 x 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (19:1 Hexanes/EA) provided the desired 3-bromo carbazole **35** (17.8 mg, 0.51 mmol, 99.4%) as a white semi-solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 4.04 (s, 3H), 3.19 – 3.11 (m, 2H), 2.58 (s, 3H), 1.70 – 1.62 (m, 2H), 1.54 – 1.47 (m, 2H), 1.32 – 1.26 (m, 26H) and 0.88 (t, *J* = 6.7 Hz, 3H) ppm.

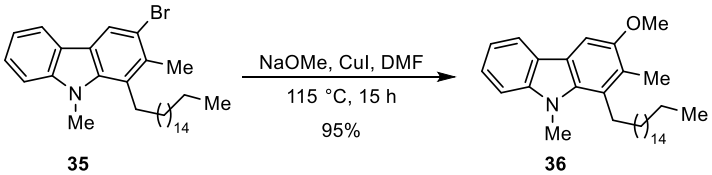
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 139.4, 133.0, 126.1, 123.7, 122.2, 121.7, 119.9, 119.3, 116.8, 114.2, 108.9, 34.0, 32.8, 32.1, 31.7, 31.6, 30.0, 29.8, 29.6, 29.5, 29.3, 29.1, 22.8, 19.9 and 14.3 ppm.

IR (ATR): 2928, 2849, 2378, 1462, 1400, 1268, 1132, 1011, 815, 765 and 734 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{31}H_{46}BrN$ 511.2814; found 511.2805.

TLC: R_f = 0.42 (Hexanes).

1-heptadecyl-3-methoxy-2,9-dimethyl-9*H*-carbazole (36)



A 10 mL Schlenk tube equipped with a magnetic stirrer was evacuated and then backfilled with nitrogen. This process was repeated three times. Next, 0.7 mL of anhydrous MeOH was added, and the reaction vessel was cooled down to 0 °C. To this stirring MeOH solvent, sodium metal (42 mg, 1.84 mmol, 54 equiv.) was carefully added in portions under a positive nitrogen pressure to form a ~2.7 *M* solution of NaOMe in MeOH. After complete dissolution of Na in MeOH, the solution became thick and light yellowish. Next, 3-bromo carbazole **35** (17.5 mg, 0.034 mmol, 1.0 equiv.) dissolved in DMF (0.7 mL) was added to this freshly prepared NaOMe solution followed by successive addition of CuI (25.8 mg, 0.14 mmol, 4.0 equiv.) under nitrogen atmosphere. The resulting reaction mixture was then transferred to a

preheated oil bath and stirred at 115 °C for 15 h. After complete consumption of starting material **35** as indicated by TLC, the crude reaction mixture was filtered through a short plug of Celite® and washed with EtOAc. The filtrate was sequentially washed with saturated NH_4Cl solution (3 mL), water (5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4 concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (9:1 Hexanes/EtOAc) provided the desired 3-methoxy carbazole **36** (15 mg, 0.032 mmol, 95%) as yellowish white waxy solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.16 (dd, *J* = 11.2, 4.3 Hz, 1H), 4.04 (s, 3H), 3.94 (s, 3H), 3.15 – 3.09 (m, 2H), 2.37 (s, 3H), 1.71 – 1.63 (m, 2H), 1.53 – 1.47 (m, 2H), 1.29 – 1.25 (m, 26H) and 0.88 (t, *J* = 6.8 Hz, 3H) ppm.

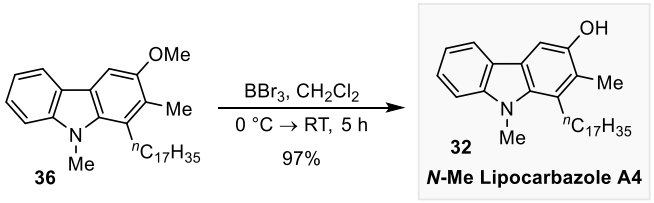
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 142.4, 134.8, 125.8, 125.1, 124.7, 123.2, 121.8, 119.5, 118.4, 108.8, 99.1, 56.3, 32.8, 32.1, 31.8, 31.7, 30.1, 29.8, 29.7, 29.5, 28.8, 22.8, 14.3 and 12.1 ppm.

IR (ATR): 2929, 2853, 1646, 1451, 1426, 1269, 1221, 1108, 1015, 836, 813 and 735 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{32}H_{50}NO$ 464.3887; found 464.3881.

TLC: R_f = 0.17 (Hexanes).

1-heptadecyl-2,9-dimethyl-9*H*-carbazol-3-ol [*N*-methyl Lipocarbazole A4] (32)



To a stirred solution of **36** (7 mg, 0.015 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (2.5 mL) at 0 °C, was added a 1 *M* solution of BBr_3 in CH_2Cl_2 (0.06 mL, 0.06 mmol, 4 equiv.) dropwise. The mixture was then allowed to warm up to room temperature and stirred for further 4.5 h. The reaction was quenched with H_2O (5 mL). The organic layer was separated, and the residual compound from aqueous layer was extracted with EtOAc (3 × 3 mL). The combined organic layers were washed with H_2O, brine and dried (Na_2SO_4) and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (7:1 Hexanes/EtOAc) provided the desired *N*-methyl Lipocarbazole A4 **32** (6.6 mg, 0.015 mmol, 97% yield) as a white semi-solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.62 (br-s, 1H), 4.03 (s, 3H), 3.15 – 3.06 (m, 2H), 2.39 (s, 3H), 1.71 – 1.63 (m, 2H), 1.55 – 1.47 (m, 2H), 1.43 – 1.25 (m, 26H) and 0.88 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 142.7, 135.1, 125.7, 125.4, 122.8, 122.4, 119.7, 118.5, 108.8, 103.1, 32.8, 32.1, 31.7, 30.1, 29.8, 29.7, 29.5, 28.7, 22.8, 14.3 and 12.1 ppm.

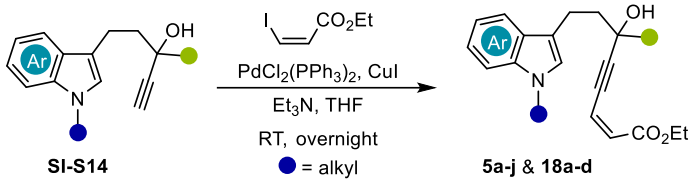
IR (ATR): 3321, 2921, 2852, 2386, 1459, 12936, 1235, 1067 and 733 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{31}H_{47}NO$ 449.3658; found 449.3638.

TLC: R_f = 0.4 (9:1 Hexanes/EtOAc).

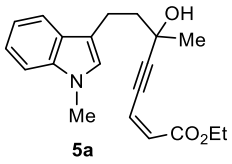
E. Experimental procedures and characterization data for the synthesis of substrates.

(i) General procedure 3: Procedure for Sonogashira reaction



To a solution of the corresponding (*Z*)-3-iodo-acrylate[4] (1.0 equiv.) and the terminal alkyne **S1-14** (1.0 equiv.) in tetrahydrofuran (THF) were added $PdCl_2(PPh_3)_2$ (1.3 mol%) and copper iodide (CuI) (10 mol%) followed by addition of triethylamine (Et_3N) (0.5 mL/ mmol). The resulting mixture was stirred at room temperature until the TLC showed complete consumption of the (*Z*)-3-iodo-acrylate. After completion, the reaction was quenched by addition of saturated NH_4Cl solution. The residual compound from aqueous layer was extracted with EtOAc (3 times). The combined organic layers were dried over anhydrous sodium sulphate (Na_2SO_4), filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (Hexanes/EtOAc) provided the desired propargyl alcohols **5a-j** and **18a-d**.

Ethyl (*Z*)-6-hydroxy-6-methyl-8-(1-methyl-1*H*-indol-3-yl)oct-2-en-4-ynoate (5a)



According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 3-methyl-5-(1-methyl-1*H*-indol-3-yl)pent-1-yn-3-ol **S1**[5] (227 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5a** as brown oil (305.9 mg, 0.94 mmol, 94%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.88 (s, 1H), 6.19 (d, *J* = 11.5 Hz, 1H), 6.10 (d, *J* = 11.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 3.15 – 2.89 (m, 3H), 2.22 – 2.07 (m, 2H), 1.63 (s, 3H) and 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

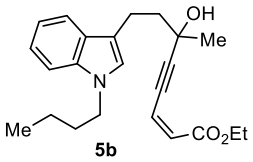
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 137.2, 128.8, 127.9, 126.2, 122.9, 121.6, 119.2, 118.7, 114.7, 109.2, 105.5, 80.6, 68.9, 60.6, 44.0, 32.7, 29.7, 20.5 and 14.39 ppm.

IR (ATR): 3434, 2979, 2930, 1710, 1610, 1474, 1375, 1183, 1124, 1021, 818 and 741 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{20}H_{23}NO_3$ 325.1678; found 325.1625.

TLC: R_f = 0.18 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-8-(1-butyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate (5b)



5b

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 5-(1-butyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol **S2** (269 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5b** as brown oil (334.4 mg, 0.91 mmol, 91%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.92 (s, 1H), 6.18 (d, *J* = 11.5 Hz, 1H), 6.09 (d, *J* = 11.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.03 (t, *J* = 7.1 Hz, 2H), 3.19 (br-s, 1H), 3.13 – 2.96 (m, 2H), 2.22 – 2.09 (m, 2H), 1.81 – 1.73 (m, 2H), 1.63 (s, 3H), 1.37 – 1.26 (m, 5H) and 0.92 (t, *J* = 7.4 Hz, 3H) ppm.

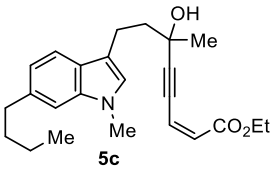
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 136.5, 128.7, 128.0, 125.1, 122.9, 121.4, 119.3, 118.5, 114.5, 109.4, 105.6, 80.6, 68.9, 60.6, 45.9, 43.9, 32.5, 29.7, 20.6, 20.3, 14.4 and 13.8 ppm.

IR (ATR): 3438, 2931, 2867, 1713, 1610, 1462, 1405, 1372, 1188, 1091, 818 and 742 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{23}H_{29}NO_3$ 367.2147; found 367.2112.

TLC: R_f = 0.2 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-8-(6-butyl-1-methyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate (5c)



5c

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 5-(6-butyl-1-methyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol **S3** (283.4 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5c** as brown oil (328 mg, 0.86 mmol, 86%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 1H), 7.06 (s, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.82 (s, 1H), 6.18 (d, *J* = 11.5 Hz, 1H), 6.10 (d, *J* = 11.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 3.11 – 2.93 (m, 2H), 2.85 (br-s, 1H), 2.76 – 2.70 (m, 2H), 2.20 – 2.07 (m, 2H), 1.70 – 1.60 (m, 5H), 1.39 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H) and 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

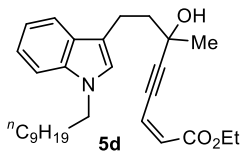
^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 137.5, 136.8, 128.7, 126.0, 125.7, 122.9, 119.9, 118.9, 114.5, 108.6, 105.5, 80.6, 69.0, 60.6, 44.0, 36.3, 34.6, 32.6, 29.7, 22.6, 20.6, 14.4 and 14.2 ppm.

IR (ATR): 3438, 2929, 2863, 1714, 1613, 1469, 1412, 1378, 1329, 1187, 1026 and 813 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{24}H_{31}NO_3$ 381.2304; found 381.2260.

TLC: R_f = 0.2 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-8-(1-decyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate (5d)



5d

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 5-(1-decyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol **S4** (353.5 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5d** as brown oil (383.9 mg, 0.85 mmol, 85%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.91 (s, 1H), 6.17 (d, *J* = 11.5 Hz, 1H), 6.08 (d, *J* = 11.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.01 (t, *J* = 7.2 Hz, 2H), 3.33 (br-s, 1H), 3.13 – 2.96 (m, 2H), 2.23 – 2.09 (m, 2H), 1.82 – 1.73 (m, 2H), 1.63 (s, 3H), 1.31 – 1.22 (m, 17H) and 0.87 (t, *J* = 6.6 Hz, 3H) ppm.

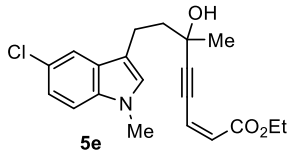
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 136.5, 128.6, 128.0, 125.1, 123.0, 121.4, 119.3, 118.5, 114.6, 109.3, 105.7, 80.5, 68.8, 60.6, 46.2, 43.9, 31.9, 30.4, 29.6, 29.62, 29.59, 29.4, 27.1, 22.8, 20.5, 14.3 and 14.2 ppm.

IR (ATR): 3436, 2928, 2870, 1711, 1608, 1466, 1403, 1376, 1193, 1090, 816 and 740 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{42}NO_3$ 452.3159; found 452.3151.

TLC: R_f = 0.3 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-8-(5-chloro-1-methyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate (5e)



5e

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 5-(1-decyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol **S5** (262 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5e** as brown oil (341.8 mg, 0.95 mmol, 95%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.67 – 7.60 (m, 2H), 6.88 (s, 1H), 6.18 (d, *J* = 11.4 Hz, 1H), 6.11 (d, *J* = 11.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 3.26 (br-s, 1H), 3.09 – 2.93 (m, 2H), 2.17 – 2.06 (m, 2H), 1.63 (s, 3H) and 1.29 (t, *J* = 7.2 Hz, 3H) ppm.

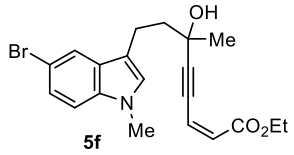
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 135.6, 129.0, 128.8, 127.5, 124.5, 122.9, 121.8, 118.7, 114.5, 110.2, 105.2, 68.8, 60.7, 44.0, 32.8, 29.7, 20.3 and 14.4 ppm.

IR (ATR): 2980, 2931, 2379, 2350, 1709, 1610, 1478, 1422, 1218, 1186, 821 and 793 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{23}ClNO_3$ 360.1361; found 360.1348.

TLC: R_f = 0.2 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-8-(5-bromo-1-methyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate (5f)



5f

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 5-(5-bromo-1-methyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol **S6**[5] (306 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5f** as brown oil (384 mg, 0.95 mmol, 95%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 1.5 Hz, 1H), 7.25 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.84 (s, 1H), 6.18 (d, *J* = 11.5 Hz, 1H), 6.10 (d, *J* = 11.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 3H), 3.53 (br-s, 1H), 3.09 – 2.91 (m, 2H), 2.17 – 2.04 (m, 2H), 1.63 (s, 3H) and 1.28 (t, *J* = 7.1 Hz, 3H) ppm.

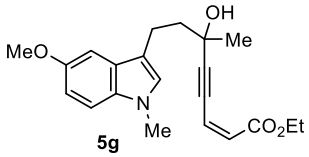
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 135.7, 129.6, 128.7, 127.3, 124.3, 123.0, 121.8, 114.5, 112.1, 110.7, 105.4, 80.6, 68.7, 60.7, 43.9, 32.7, 29.7, 20.3 and 14.3 ppm.

IR (ATR): 2927, 2861, 1712, 1611, 1476, 1377, 1293, 1187, 1093, 1032, 932 and 786 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{23}BrNO_3$ 404.0856; found 404.0845.

TLC: R_f = 0.4 (2:1 Hexanes/EtOAc).

Ethyl (*Z*)-6-hydroxy-8-(5-methoxy-1-methyl-1*H*-indol-3-yl)-6-methyloct-2-en-4-ynoate (5g)



5g

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 5-(5-methoxy-1-methyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol **S7**[5] (257 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and

0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5g** as brown oil (291.5 mg, 0.82 mmol, 82%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 1.9 Hz, 1H), 6.87 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.84 (s, 1H), 6.18 (d, *J* = 11.5 Hz, 1H), 6.09 (d, *J* = 11.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.67 (s, 3H), 3.39 (br-s, 1H), 3.09 – 2.92 (m, 2H), 2.20 – 2.07 (m, 2H), 1.63 (s, 3H) and 1.28 (t, *J* = 7.1 Hz, 3H) ppm.

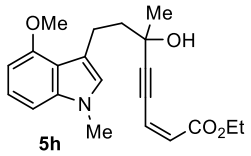
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 153.7, 132.6, 128.6, 128.1, 126.8, 123.0, 114.1, 111.7, 109.9, 105.7, 101.2, 80.5, 68.8, 60.6, 56.1, 43.7, 32.8, 29.7, 20.5 and 14.3 ppm.

IR (ATR): 2927, 1713, 1614, 1491, 1456, 1297, 1223, 1184, 1030, 765 and 730 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{25}NO_4$ 355.1784; found 355.1748.

TLC: R_f = 0.2 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-6-hydroxy-8-(4-methoxy-1-methyl-1*H*-indol-3-yl)-6-methyloct-2-en-4-ynoate (5h)



5h

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 5-(4-methoxy-1-methyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol **S8** (257 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5h** as brown oil (312.8 mg, 0.88 mmol, 88%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.76 (s, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 6.15 (d, *J* = 11.5 Hz, 1H), 6.06 (d, *J* = 11.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.66 (s, 3H), 3.14 – 3.07 (m, 2H), 3.01 (br-s, 1H), 2.17 – 2.11 (m, 2H), 1.61 (s, 3H) and 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

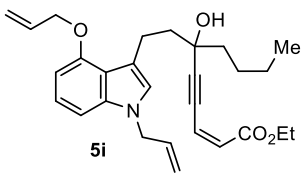
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 154.8, 139.0, 128.4, 125.3, 123.0, 122.4, 117.7, 115.1, 106.0, 102.7, 99.0, 80.3, 68.9, 60.6, 55.2, 45.5, 32.8, 29.4, 22.2 and 14.4 ppm.

IR (ATR): 3443, 2979, 2936, 1711, 1610, 1496, 1462, 1256, 1184, 1091, 1026 and 732 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{25}NO_4$ 355.1784; found 355.1732.

TLC: R_f = 0.17 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-6-(2-(1-allyl-4-(allyloxy)-1*H*-indol-3-yl)ethyl)-6-hydroxydec-2-en-4-ynoate (5i)



5i

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 3-(2-(1-allyl-4-(allyloxy)-1H-indol-3-yl)ethyl)hept-1-yn-3-ol **S9** (351.5 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5i** as brown oil (337 mg, 0.75 mmol, 75%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (dd, *J* = 18.2, 10.2 Hz, 1H), 6.89 – 6.79 (m, 2H), 6.45 (d, *J* = 7.8 Hz, 1H), 6.20 – 6.09 (m, 2H), 6.05 (dd, *J* = 11.5, 2.7 Hz, 1H), 5.93 (ddt, *J* = 15.7, 10.4, 5.4 Hz, 1H), 5.45 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.26 (dd, *J* = 10.5, 1.2 Hz, 1H), 5.14 (dd, *J* = 10.2, 1.0 Hz, 1H), 5.04 (dd, *J* = 16.9, 1.0 Hz, 1H), 4.64 (d, *J* = 5.2 Hz, 2H), 4.59 (d, *J* = 5.3 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.16 (dd, *J* = 8.7, 7.4 Hz, 2H), 2.76 (br-s, 1H), 2.20 – 2.08 (m, 2H), 1.81 – 1.70 (m, 2H), 1.63 – 1.48 (m, 2H), 1.37 (dd, *J* = 14.7, 7.3 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H) and 0.92 (t, *J* = 7.3 Hz, 3H) ppm.

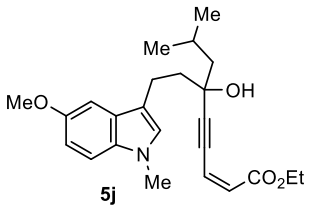
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 153.8, 138.5, 133.9, 133.7, 128.3, 124.3, 122.9, 122.3, 118.0, 117.4, 117.1, 115.8, 105.4, 103.1, 100.3, 81.3, 72.1, 68.9, 60.5, 48.8, 43.6, 41.8, 26.4, 23.0, 21.9, 14.4 and 14.1 ppm.

IR (ATR): 2955, 2920, 1710, 1609, 1496, 1257, 1233, 1181, 1028, 992, 921 and 731 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{28}H_{35}NO_4$ 449.2566; found 449.2464.

TLC: R_f = 0.25 (6:1 Hexanes/EtOAc).

Ethyl (*Z*)-6-hydroxy-6-(2-(5-methoxy-1-methyl-1*H*-indol-3-yl)ethyl)-8-methylnon-2-en-4-ynoate (5j)



5j

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 3-(2-(5-methoxy-1-methyl-1*H*-indol-3-yl)ethyl)-5-methylhex-1-yn-3-ol **S10** (299 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5j** as brown oil (318 mg, 0.80 mmol, 80%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 2.1 Hz, 1H), 6.86 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.84 (s, 1H), 6.18 (d, *J* = 11.5 Hz, 1H), 6.09 (d, *J* = 11.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.67 (s, 3H), 3.10 – 2.84 (m, 3H), 2.14 – 2.00 (m, 3H), 1.77 – 1.67 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H) and 1.06 – 1.02 (m, 6H) ppm.

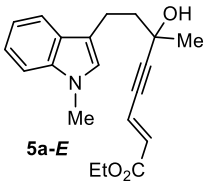
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 153.7, 132.6, 128.6, 128.1, 126.8, 122.8, 114.2, 111.8, 109.9, 105.3, 101.2, 82.0, 71.9, 60.5, 56.1, 50.3, 43.2, 32.8, 24.9, 24.4, 24.3, 20.1 and 14.3 ppm.

IR (ATR): 2951, 2921, 1709, 1611, 1491, 1454, 1224, 1178, 1035, 792 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{24}H_{31}NO_4$ 397.2253; found 397.2208.

TLC: R_f = 0.25 (4:1 Hexanes/EtOAc).

Ethyl (*E*)-6-hydroxy-6-methyl-8-(1-methyl-1*H*-indol-3-yl)oct-2-en-4-ynoate (5a-*E*)



According to the **General Procedure 3**, ethyl (*E*)-3-iodoacrylate **S37** (226 mg, 1 mmol, 1.0 equiv.), 3-methyl-5-(1-methyl-1*H*-indol-3-yl)pent-1-yn-3-ol **S1**[5] (227 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **5a-*E*** as brown oil (305.9 mg, 0.94 mmol, 94%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.88 – 6.76 (m, 2H), 6.23 (d, *J* = 15.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 3.06 – 2.89 (m, 2H), 2.57 (br-s, 1H), 2.18 – 2.04 (m, 2H), 1.58 (s, 3H) and 1.28 (t, *J* = 7.1 Hz, 3H). ppm.

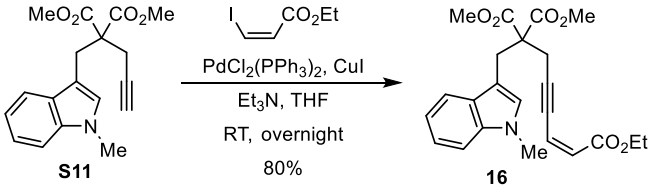
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 137.2, 130.6, 127.8, 126.1, 124.9, 121.72, 121.68, 119.0, 118.8, 114.2, 109.3, 102.2, 80.6, 68.8, 60.9, 43.9, 32.6, 29.7, 20.5 and 14.3 ppm.

IR (ATR): 3434, 2978, 2929, 1708, 1612, 1469, 1375, 1185, 1117, 1024, 821 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{20}H_{23}NO_3$ 325.1678; found 325.1639.

TLC: R_f = 0.2 (4:1 Hexanes/EtOAc).

1-ethyl 6,6-dimethyl (*Z*)-7-(1-methyl-1*H*-indol-3-yl)hept-1-en-3-yne-1,6,6-tricarboxylate (16)



According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), dimethyl 2-((1-methyl-1*H*-indol-3-yl)methyl)-2-(prop-2-yn-1-yl)malonate **S11** (313 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **16** as brown oil (329 mg, 0.8 mmol, 80%) by using Hexane/EtOAc (9:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.17 (d, *J* = 11.5 Hz, 1H), 6.11 (d, *J* = 11.5 Hz, 1H), 4.23

(q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.71 (s, 6H), 3.61 (s, 2H), 3.06 (s, 2H) and 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

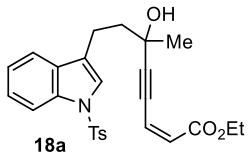
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 164.6, 136.8, 128.8, 128.5, 123.0, 121.5, 119.0, 119.0, 109.25, 107.7, 98.2, 80.6, 60.4, 58.3, 52.9, 32.8, 27.7, 24.4 and 14.3 ppm.

IR (ATR): 2952, 1736, 1722, 1612, 1473, 1436, 1288, 1178, 1065, 1041, 819 and 741 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{23}H_{25}NNaO_6$ 434.1574; found 434.1570.

TLC: R_f = 0.4 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-6-hydroxy-6-methyl-8-(1-tosyl-1*H*-indol-3-yl)oct-2-en-4-ynoate (18a)



18a

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 3-methyl-5-(1-tosyl-1*H*-indol-3-yl)pent-1-yn-3-ol **S12** (367.4 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **18a** as brown oil (372.5 mg, 0.80 mmol, 80%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.38 (s, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.19 (dd, *J* = 12.0, 7.9 Hz, 1H), 6.16 (d, *J* = 11.4 Hz, 1H), 6.10 (d, *J* = 11.5 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 1H), 3.43 (br-s, 1H), 3.05 – 2.90 (m, 1H), 2.30 (s, 1H), 2.16 – 2.04 (m, 1H), 1.63 (s, 1H) and 1.27 (t, *J* = 7.1 Hz, 1H) ppm.

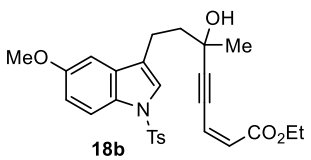
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 144.8, 135.4, 131.2, 129.8, 128.9, 126.8, 124.7, 123.1, 123.0, 122.9, 122.7, 119.7, 113.8, 105.0, 80.7, 68.5, 60.7, 42.6, 29.8, 21.6, 20.4 and 14.3 ppm.

IR (ATR): 2927, 1711, 1610, 1489, 1253, 1224, 1176, 1041, 995, 911 and 734 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{26}H_{31}N_2O_5S$ 483.1948; found 483.1936.

TLC: R_f = 0.2 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-6-hydroxy-8-(5-methoxy-1-tosyl-1*H*-indol-3-yl)-6-methyloct-2-en-4-ynoate (18b)



18b

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), 5-(5-methoxy-1-tosyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol **S13** (397.5 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and

0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **18b** as brown oil (406.4 mg, 0.82 mmol, 82%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.33 (s, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.90 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.16 (d, *J* = 11.5 Hz, 1H), 6.11 (d, *J* = 11.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.21 (br-s, 1H), 3.00 – 2.85 (m, 2H), 2.31 (s, 3H), 2.16 – 1.98 (m, 3H), 1.62 (s, 3H) and 1.27 (t, *J* = 7.1 Hz, 3H) ppm.

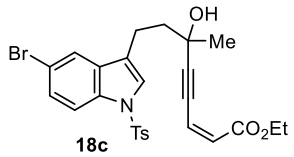
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 156.4, 144.7, 135.4, 132.2, 130.2, 129.8, 129.0, 126.8, 123.5, 123.2, 122.8, 114.7, 113.4, 104.9, 102.5, 80.8, 68.5, 60.7, 55.8, 42.4, 29.8, 21.6, 20.4 and 14.3 ppm.

IR (ATR): 2924, 2360, 2340, 1708, 1611, 1474, 1367, 1216, 1170, 1119, 812 and 735 cm^{-1}.

HRMS (ESI) m/z: $[M+NH_4]^+$ Calcd. for $C_{27}H_{33}N_2O_6S$ 513.2054; found 513.2034.

TLC: R_f = 0.15 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-8-(5-bromo-1-tosyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate (18c)



18c

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (226 mg, 1 mmol, 1.0 equiv.), ethyl (*Z*)-8-(5-bromo-1-tosyl-1*H*-indol-3-yl)-6-hydroxy-6-methyloct-2-en-4-ynoate **S14** (445 mg, 1 mmol, 1.0 equiv.), CuI (19 mg, 0.1 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (9 mg, 0.013 mmol, 1.3 mol %) and 0.5 mL of triethylamine were used in 15 mL THF, affording the desired propargylic alcohol **18c** as brown oil (477.9 mg, 0.88 mmol, 88%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 3H), 7.38 (d, *J* = 5.9 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.16 (d, *J* = 11.4 Hz, 1H), 6.12 (d, *J* = 11.4 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.42 (br-s, 1H), 3.03 – 2.88 (m, 2H), 2.32 (s, 3H), 2.21 – 2.00 (m, 2H), 1.63 (s, 3H) and 1.28 (t, *J* = 7.2 Hz, 3H) ppm.

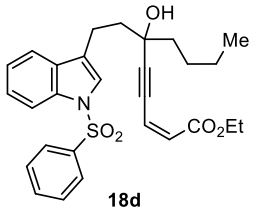
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 145.1, 135.2, 134.1, 133.0, 130.0, 129.1, 127.6, 126.8, 123.9, 122.8, 122.6, 116.7, 115.2, 104.7, 80.8, 68.4, 60.8, 42.5, 29.8, 21.6, 20.2 and 14.3 ppm.

IR (ATR): 2929, 2360, 2335, 1716, 1611, 1443, 1371, 1293, 1188, 1173 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M+NH_4]^+$ Calcd. for $C_{26}H_{30}BrN_2O_5S$ 561.1053; found 561.1049.

TLC: R_f = 0.22 (4:1 Hexanes/EtOAc).

Ethyl (*Z*)-6-hydroxy-6-(2-(1-(phenylsulfonyl)-1*H*-indol-3-yl)ethyl)dec-2-en-4-ynoate (18d)



18d

According to the **General Procedure 3**, (*Z*)-3-iodo-acrylate[4] (56.5 mg, 0.25 mmol, 1.0 equiv.), 3-(2-(1-(phenylsulfonyl)-1*H*-indol-3-yl)ethyl)hept-1-yn-3-ol **S15** (99 mg, 0.25 mmol, 1.0 equiv.), CuI (4.8 mg, 0.025 mmol, 10 mol%), $Pd(PPh_3)_2Cl_2$ (2.3 mg, 0.003 mmol, 1.3 mol %) and 0.13 mL of triethylamine were used in 7 mL THF, affording the desired propargylic alcohol **18d** as brown oil (111 mg, 0.22 mmol, 90%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 13.6, 6.0 Hz, 3H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.17 (d, *J* = 11.5 Hz, 1H), 6.12 (d, *J* = 11.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.05 – 2.92 (m, 2H), 2.68 (br-s, 1H), 2.11 – 2.03 (m, 2H), 1.81 – 1.75 (m, 2H), 1.59 – 1.50 (m, 2H), 1.37 (dq, *J* = 14.8, 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H) and 0.93 (t, *J* = 7.3 Hz, 3H) ppm.

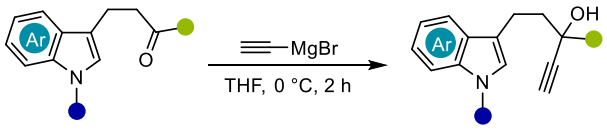
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 138.5, 135.5, 133.7, 131.2, 129.3, 129.1, 126.8, 124.8, 123.5, 123.2, 122.7, 122.6, 119.9, 113.8, 104.2, 81.9, 71.8, 60.6, 42.1, 41.0, 26.5, 23.0, 20.1, 14.4 and 14.2 ppm.

IR (ATR): 2955, 2926, 1709, 1447, 1369, 1175, 1120, 781 and 724 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{28}H_{31}NO_5S$ 493.1923; found 493.1884.

TLC: R_f = 0.2 (4:1 Hexanes/EtOAc).

(ii) General procedure 4: Preparation of the terminal propargylic alcohols

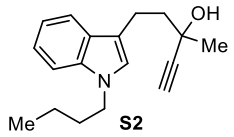


S17-20, **S23-25** and **S27-30**

S2-5, **S8-10** and **S12-15**

To the stirred solution of appropriate ketone **S17-20**, **S23-25** and **S27-30** (1.0 equiv.) in anhydrous THF was added ethynyl magnesium bromide (2.0 equiv., 0.5 *M* in THF) dropwise at 0 °C under nitrogen. The mixture was stirred at same temperature for 2 h. The reaction mixture was then quenched with saturated NH_4Cl solution. The residual compound from aqueous layer was extracted with EtOAc (3 times). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via silica gel column chromatography (Hexanes/EA) provided the desired propargyl alcohol **S2-5**, **S8-10**, and **S12-15**.

5-(1-butyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol (S2)



S2

According to the **General Procedure 4**, 4-(1-butyl-1*H*-indol-3-yl)butan-2-one **S17** (243 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S2** as colorless oil (237 mg, 0.88 mmol, 88%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.90 (s, 1H), 4.03 (t, *J* = 7.1 Hz, 2H), 3.07 – 2.93 (m, 2H), 2.51 (s, 1H), 2.25 (br-s, 1H), 2.15 – 2.01 (m, 2H), 1.81 – 1.73 (m, 2H), 1.56 (s, 3H), 1.32 (dt, *J* = 15.1, 7.5 Hz, 2H) and 0.92 (t, *J* = 7.4 Hz, 3H) ppm.

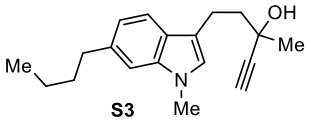
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 127.9, 125.1, 121.5, 119.1, 118.7, 114.3, 109.5, 87.7, 71.8, 68.3, 46.0, 43.9, 32.5, 30.0, 20.5, 20.3 and 13.8 ppm.

IR (ATR): 2929, 2861, 1618, 1468, 1372, 1330, 1245, 1182, 1094, 908 and 739 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{18}H_{23}NO$ 269.1780; found 269.1765.

TLC: R_f = 0.5 (4:1 Hexanes/EtOAc).

5-(6-butyl-1-methyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol (S3)



S3

According to the **General Procedure 4**, 4-(6-butyl-1-methyl-1*H*-indol-3-yl)butan-2-one **S18** (257 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S3** as colorless oil (252 mg, 0.89 mmol, 89%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.06 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 3.66 (s, 3H), 3.04 – 2.90 (m, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.50 (s, 1H), 2.34 – 2.24 (m, 1H), 2.13 – 1.99 (m, 2H), 1.75 – 1.61 (m, 2H), 1.55 (s, 3H), 1.37 (dt, *J* = 14.9, 7.3 Hz, 2H) and 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

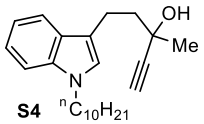
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.8, 125.9, 125.6, 120.0, 118.7, 114.2, 108.7, 87.7, 71.8, 68.3, 44.0, 36.3, 34.5, 32.5, 30.0, 22.6, 20.5 and 14.1 ppm.

IR (ATR): 2927, 2862, 1619, 1469, 1375, 1328, 1241, 1180, 1093, 905 and 800 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{19}H_{25}NO$ 283.1936; found 283.1919.

TLC: R_f = 0.23 (4:1 Hexanes/EtOAc).

5-(1-decyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol (S4)



According to the **General Procedure 4**, 4-(1-decyl-1*H*-indol-3-yl)butan-2-one **S19** (327.5 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S4** as colorless oil (289.9 mg, 0.82 mmol, 82%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.90 (s, 1H), 4.03 (t, *J* = 7.2 Hz, 2H), 3.07 – 2.94 (m, 2H), 2.52 (s, 1H), 2.17 (s, 1H), 2.13 – 2.02 (m, 2H), 1.83 – 1.75 (m, 2H), 1.57 (s, 3H), 1.30 – 1.23 (m, 14H) and 0.88 (t, *J* = 6.5 Hz, 3H) ppm.

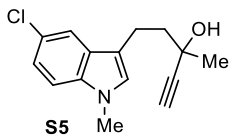
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 127.9, 125.1, 121.5, 119.2, 118.7, 114.3, 109.5, 87.7, 71.8, 68.4, 46.3, 43.9, 32.0, 30.4, 30.0, 29.6, 29.6, 29.4, 27.2, 22.8, 20.5 and 14.2 ppm.

IR (ATR): 2923, 2852, 2359, 2340, 1468, 1370, 1333 and 737 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{24}H_{35}NO$ 353.2719; found 353.2682.

TLC: R_f = 0.6 (4:1 Hexanes/EtOAc).

5-(5-chloro-1-methyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol (S5)



According to the **General Procedure 4**, 4-(5-chloro-1-methyl-1*H*-indol-3-yl)butan-2-one **S20**[6] (235 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S5** as colorless oil (220 mg, 0.84 mmol, 84%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.15 – 7.11 (m, 2H), 6.84 (s, 1H), 3.66 (s, 3H), 3.00 – 2.86 (m, 2H), 2.53 (s, 1H), 2.42 (s, 1H), 2.09 – 1.96 (m, 2H) and 1.56 (s, 3H) ppm.

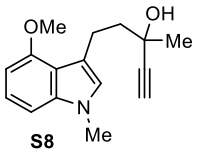
^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 128.8, 127.4, 124.6, 121.9, 118.5, 114.2, 110.3, 87.5, 72.0, 68.2, 43.8, 32.8, 30.0 and 20.3 ppm.

IR (ATR): 2923, 2852, 2359, 2340, 1468, 1370, 1333 and 737 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{15}H_{16}BrNO$ 305.0415; found 305.0385.

TLC: R_f = 0.3 (4:1 Hexanes/EtOAc).

5-(4-methoxy-1-methyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol (S8)



S8

According to the **General Procedure 4**, 4-(4-methoxy-1-methyl-1*H*-indol-3-yl)butan-2-one **S23** (231 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S8** as colorless oil (203 mg, 0.79 mmol, 79%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.74 (s, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 3.92 (s, 3H), 3.69 (s, 3H), 3.07 (dd, *J* = 9.5, 6.6 Hz, 2H), 2.49 (s, 1H), 2.32 (s, 1H), 2.10 – 2.05 (m, 2H) and 1.56 (s, 3H) ppm.

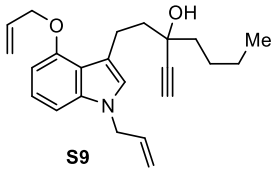
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 139.1, 125.1, 122.5, 117.6, 115.1, 102. 8, 99.1, 88.0, 71.3, 68.4, 55.2, 45.6, 32.9, 29.9 and 22.2 ppm.

IR (ATR): 2934, 1577, 1499, 1461, 1325, 1258, 1090, 909 and 733 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{16}H_{19}NO_2$ 257.1416; found 257.1408.

TLC: R_f = 0.28 (4:1 Hexanes/EtOAc).

3-(2-(1-allyl-4-(allyloxy)-1*H*-indol-3-yl)ethyl)hept-1-yn-3-ol (S9)



S9

According to the **General Procedure 4**, 1-(1-allyl-4-(allyloxy)-1*H*-indol-3-yl)heptan-3-one **S24** (325.4 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S9** as colorless oil (291.7 mg, 0.83 mmol, 83%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.78 (s, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 6.16 (dtd, *J* = 15.9, 10.6, 5.4 Hz, 1H), 5.93 (dtd, *J* = 15.6, 10.5, 5.4 Hz, 1H), 5.46 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 5.15 (dd, *J* = 10.2, 1.3 Hz, 1H), 5.05 (dd, *J* = 17.0, 1.3 Hz, 1H), 4.65 (dd, *J* = 4.0, 1.3 Hz, 2H), 4.59 (d, *J* = 5.4 Hz, 2H), 3.20 – 3.07 (m, 2H), 2.47 (s, 1H), 2.21 (s, 1H), 2.14 – 2.01 (m, 2H), 1.73 – 1.67 (m, 2H), 1.56 – 1.48 (m, 2H), 1.40 – 1.30 (m, 2H) and 0.93 (d, *J* = 7.3 Hz, 3H) ppm.

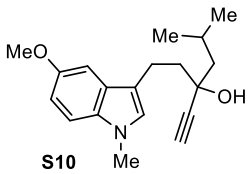
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 138.5, 134.0, 133.7, 124.2, 122.4, 117.9, 117.5, 117.1, 115.7, 103.2, 100.3, 87.2, 72.4, 71.4, 68.9, 48.8, 43.8, 42.0, 26.4, 23.0, 21.9 and 14.2 ppm.

IR (ATR): 2924, 2861, 1610, 1578, 1496, 1454, 1328, 1234, 1058, 991, 920 and 727 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{23}H_{29}NO_2$ 351.2198; found 351.2185.

TLC: R_f = 0.3 (9:1 Hexanes/EtOAc).

3-(2-(5-methoxy-1-methyl-1*H*-indol-3-yl)ethyl)-5-methylhex-1-yn-3-ol (S10)



S10

According to the **General Procedure 4**, 1-(5-methoxy-1-methyl-1*H*-indol-3-yl)-5-methylhexan-3-one **S25** (273 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S10** as colorless oil (182.6 mg, 0.61 mmol, 61%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.8 Hz, 1H), 7.07 (d, *J* = 2.1 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.83 (s, 1H), 3.86 (s, 3H), 3.68 (s, 3H), 3.03 – 2.91 (m, 2H), 2.56 (s, 1H), 2.14 (s, 1H), 2.09 – 1.99 (m, 3H), 1.71 – 1.59 (m, 2H), 1.04 (d, *J* = 3.6 Hz, 3H) and 1.02 (d, *J* = 3.6 Hz, 3H) ppm.

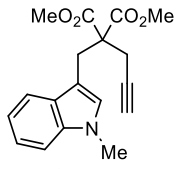
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 132.7, 128.1, 126.8, 114.0, 111.9, 110.1, 101.1, 87.1, 73.2, 71.5, 56.1, 50.5, 43.2, 32.8, 25.0, 24.5, 24.3 and 20.1 ppm.

IR (ATR): 2951, 2920, 1491, 1454, 1423, 1222, 1174, 1062, 1037, 1037, 899 and 793 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{19}H_{25}NO_2$ 299.1885; found 299.1850.

TLC: R_f = 0.2 (9:1 Hexanes/EtOAc).

Procedure for synthesis of dimethyl 2-((1-methyl-1*H*-indol-3-yl)methyl)-2-(prop-2-yn-1-yl)malonate (S11)



S11

To the stirred solution of dimethyl 2-((1-methyl-1*H*-indol-3-yl)methyl)malonate **S26**[7] (370 mg, 1.35 mmol, 1.0 equiv.) in anhydrous DMF (7 mL) was added K_2CO_3 (1.01 g, 7.8 mmol, 6.0 equiv.) at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 10 mins followed by sequential addition of propargyl bromide (0.23 mL, 2.43 mmol, 1.8 equiv., 80% w/w in toluene) and NaI (40.5 mg, 0.27 mmol, 0.2 equiv.). The reaction mixture was stirred at same temperature until the TLC showed complete consumption of the starting material. After completion, the reaction was quenched by addition of water. The residual compound from aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (3 times), dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography by using Hexane/EtOAc (9:1) as eluent provided the desired terminal alkyne **S11** (397.6 mg, 1.27 mmol, 94%) as a brownish-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 1H), 3.72 – 3.67 (m, 9H), 3.58 (s, 2H), 2.83 – 2.76 (m, 2H) and 2.20 – 2.13 (m, 1H) ppm.

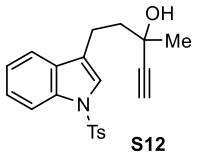
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 136.7, 128.5, 128.2, 121.6, 119.1, 118.9, 109.2, 107.8, 79.8, 72.0, 58.3, 52.8, 32.7, 27.4 and 22.8 ppm.

IR (ATR): 3287, 2952, 1733, 1473, 1436, 1325, 1290, 1200, 1181, 1058, 855 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{18}H_{19}NO_4$ 313.1314; found 313.1306.

TLC: R_f = 0.65 (4:1 Hexanes/EtOAc).

3-methyl-5-(1-tosyl-1*H*-indol-3-yl)pent-1-yn-3-ol (S12)



S12

According to the **General Procedure 4**, 4-(1-tosyl-1*H*-indol-3-yl)butan-2-one **S27**[8] (341.5 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S12** as colorless oil (301.3 mg, 0.82 mmol, 82%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.33 (s, 1H), 7.33 – 7.28 (m, 1H), 7.25 – 7.16 (m, 3H), 2.98 – 2.84 (m, 2H), 2.52 (s, 1H), 2.32 (s, 3H), 2.22 (br-s, 1H), 2.11 – 1.97 (m, 2H) and 1.58 (s, 3H) ppm.

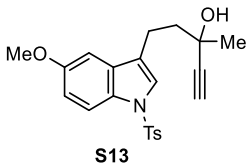
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 135.4, 131.0, 129.9, 126.8, 124.8, 123.1, 122.8, 122.6, 119.58, 113.9, 87.2, 72.2, 67.9, 42.5, 30.2, 21.6 and 20.3 ppm.

IR (ATR): 2935, 1614, 1599, 1468, 1218, 1792, 1120, 1016, 978, 805 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{21}NO_3S$ 367.1242; found 367.1218.

TLC: R_f = 0.16 (4:1 Hexanes/EtOAc).

5-(5-methoxy-1-tosyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol (S13)



S13

According to the **General Procedure 4**, 4-(5-methoxy-1-tosyl-1*H*-indol-3-yl)butan-2-one **S28** (371.5 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S13** as colorless oil (290.0 mg, 0.73 mmol, 73%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.29 (s, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.96 – 6.88 (m, 2H), 3.81 (s, 3H), 2.93 – 2.80 (m, 2H), 2.52 (s, 1H), 2.32 (s, 3H), 2.15 (br-s, 1H), 2.09 – 1.96 (m, 2H) and 1.58 (s, 3H) ppm.

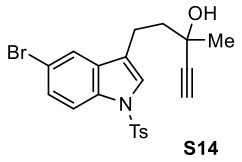
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 144.7, 135.2, 132.1, 130.1, 129.8, 126.7, 123.3, 123.0, 114.7, 113.5, 102.2, 87.3, 72.0, 67.8, 55.7, 42.2, 30.1, 21.5 and 20.2 ppm.

IR (ATR): 2929, 1611, 1597, 1473, 1364, 1215, 1168, 1117, 1032, 976, 811 and 737 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{22}H_{23}NO_4S$ 397.1348; found 397.1346.

TLC: R_f = 0.15 (4:1 Hexanes/EtOAc).

5-(5-bromo-1-tosyl-1*H*-indol-3-yl)-3-methylpent-1-yn-3-ol (S14)



S14

According to the **General Procedure 4**, 4-(5-bromo-1-tosyl-1*H*-indol-3-yl)butan-2-one **S29** (419 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S14** as colorless oil (387.2 mg, 0.87 mmol, 87%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.64 (s, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.33 (s, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 2.93 – 2.81 (m, 2H), 2.53 (s, 1H), 2.35 (s, 3H), 2.08 – 1.93 (m, 3H) and 1.58 (s, 3H) ppm.

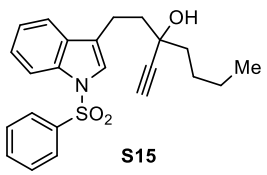
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 135.1, 134.1, 132.8, 130.0, 127.7, 126.8, 123.8, 122.4, 122.3, 116.7, 115.3, 87.1, 72.3, 67.8, 42.3, 30.2, 21.6 and 20.2 ppm.

IR (ATR): 2925, 1596, 1442, 1368, 1169, 1120, 1092, 969, 809, 796 and 735 cm^{-1}.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{20}BrNNaO_3S$ 468.0239; found 468.0233.

TLC: R_f = 0.15 (4:1 Hexanes/EtOAc).

3-(2-(1-(phenylsulfonyl)-1*H*-indol-3-yl)ethyl)hept-1-yn-3-ol (S15)



S15

According to the **General Procedure 4**, 1-(1-(phenylsulfonyl)-1*H*-indol-3-yl)heptan-3-one **S30** (369.5 mg, 1 mmol, 1.0 equiv.) was reacted with ethynyl magnesium bromide (4 mL, 2.0 mmol, 0.5 *M* in THF) in 15 mL anhydrous THF to afford the desired propargylic alcohol **S15** as colorless oil (284.7 mg, 0.72 mmol, 72%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (dd, *J* = 14.0, 6.2 Hz, 2H), 7.26 – 7.22 (m, 1H),

2.93 (dd, *J* = 10.0, 6.7 Hz, 2H), 2.52 (s, 1H), 2.13 – 1.96 (m, 3H), 1.75 – 1.70 (m, 2H), 1.57 – 1.48 (m, 2H), 1.42 – 1.33 (m, 2H) and 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

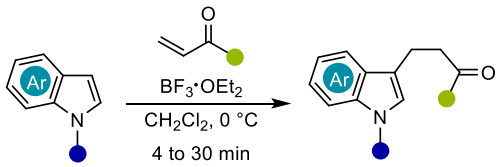
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 135.5, 133.8, 131.1, 129.3, 126.8, 124.9, 123.2, 122.5, 119.7, 113.9, 86.4, 73.2, 71.1, 42.2, 41.0, 26.4, 22.9, 20.0 and 14.2 ppm.

IR (ATR): 2925, 2361, 2340, 1286, 1269, 1250, 775, 758 and 737 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{23}H_{25}NO_3S$ 395.1555; found 395.1509.

TLC: R_f = 0.18 (4:1 Hexanes/EtOAc).

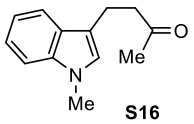
(iii) General procedure 5: Nucleophilic addition of *N*-alkylindole to alkylvinyl ketones



S16-19 and **S23-25**

To the stirred solution of appropriate *N*-alkylindole (1.0 equiv.) and vinylketone (1.5 equiv.) in anhydrous CH_2Cl_2 at 0 °C was added $BF_3.OEt_2$ (10 mol%, ~45-50% BF_3) dropwise under nitrogen. The mixture was stirred at same temperature until the TLC showed complete consumption of the *N*-alkylindole. After completion, the reaction was quenched by addition of saturated $NaHCO_3$ solution. The residual compound from aqueous layer was extracted with CH_2Cl_2 (3 times). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (Hexanes/EA) provided the desired ketone **S16-19** and **S23-25**.

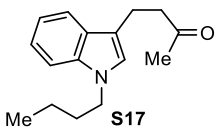
4-(1-butyl-1*H*-indol-3-yl)butan-2-one (S16)



S16

According to the **General Procedure 5**, a mixture of commercially available 1-methyl-1*H*-indole (262 mg, 2 mmol, 1.0 equiv.) and methyl vinyl ketone (0.25 mL, 3.0 mmol, 1.5 equiv.) was reacted with $BF_3.OEt_2$ (~45-50% BF_3) (25 µL, 0.2 mmol, 10 mol%) in 15 mL anhydrous CH_2Cl_2 at 0 °C for 4 mins to afford the desired methyl ketone **S16** as brown oil (386 mg, 1.9 mmol, 96%) by using Hexane/EtOAc (4:1) as eluent. The spectroscopic data matched with the literature report.[9]

4-(1-butyl-1*H*-indol-3-yl)butan-2-one (S17)



S17

According to the **General Procedure 5**, a mixture of 1-butyl-1*H*-indole[10] (346 mg, 2 mmol, 1.0 equiv.) and methyl vinyl ketone (0.25 mL, 3.0 mmol, 1.5 equiv.) was reacted with $BF_3.OEt_2$ (~45-50% BF_3) (25 µL, 0.2 mmol, 10 mol%) in 15 mL anhydrous CH_2Cl_2 at 0 °C

for 6 mins to afford the desired methyl ketone **S17** as brown oil (462.4 mg, 1.9 mmol, 95%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 1H), 4.04 (t, *J* = 7.1 Hz, 2H), 3.03 (t, *J* = 7.4 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.12 (s, 3H), 1.82 – 1.73 (m, 2H), 1.37 – 1.27 (m, 2H) and 0.92 (t, *J* = 7.3 Hz, 3H) ppm.

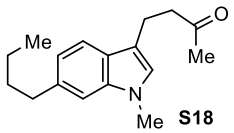
^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 136.4, 127.7, 125.4, 121.5, 118.9, 118.7, 113.6, 109.5, 46.0, 44.4, 32.5, 30.2, 20.3, 19.4 and 13.8 ppm.

IR (ATR): 3410, 2953, 2929, 1712, 1640, 1625, 1462, 1362, 1190, 1158 and 740 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{16}H_{21}NO$ 243.1623; found 243.1605.

TLC: R_f = 0.53 (7:1 Hexanes/EtOAc).

4-(6-butyl-1-methyl-1*H*-indol-3-yl)butan-2-one (S18)



S18

According to the **General Procedure 5**, a mixture of 6-butyl-1-methyl-1*H*-indole **S31** (374.6 mg, 2 mmol, 1.0 equiv.) and methyl vinyl ketone (0.25 mL, 3.0 mmol, 1.5 equiv.) was reacted with $BF_3.OEt_2$ (~45-50% BF_3) (25 μL, 0.2 mmol, 10 mol%) in 15 mL anhydrous CH_2Cl_2 at 0 °C for 4 mins to afford the desired methyl ketone **S18** as brown oil (437.2 mg, 1.7 mmol, 85%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1 Hz, 1H), 7.07 (s, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.76 (s, 1H), 3.69 (s, 3H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.13 (s, 3H), 1.66 (dt, *J* = 15.3, 7.5 Hz, 2H), 1.44 – 1.34 (m, 2H) and 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

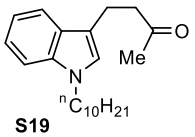
^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 137.5, 136.9, 125.9, 125.8, 120.0, 118.5, 113.6, 108.7, 44.5, 36.3, 34.6, 32.6, 30.1, 22.6, 19.5 and 14.1 ppm.

IR (ATR): 2926, 2862, 1713, 1620, 1556, 1469, 1430, 1368, 1328, 1163 and 801 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{17}H_{23}NO$ 257.178; found 257.1769.

TLC: R_f = 0.3 (4:1 Hexanes/EtOAc).

4-(1-decyl-1*H*-indol-3-yl)butan-2-one (S19)



S19

According to the **General Procedure 5**, a mixture of 1-decyl-1*H*-indole[11] (514.8 mg, 2 mmol, 1.0 equiv.) and methyl vinyl ketone (0.25 mL, 3.0 mmol, 1.5 equiv.) was reacted with $BF_3.OEt_2$ (~45-50% BF_3) (25 μL, 0.2 mmol, 10 mol%) in 15 mL anhydrous CH_2Cl_2 at 0 °C

for 15 mins to afford the desired methyl ketone **S19** as brown oil (628.3 mg, 1.92 mmol, 96%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 1H), 4.02 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.4 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.12 (s, 3H), 1.82 – 1.74 (m, 2H), 1.31 – 1.23 (m, 14H) and 0.87 (t, *J* = 6.7 Hz, 3H) ppm.

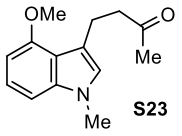
^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 136.4, 127.7, 125.4, 121.5, 118.9, 118.7, 113.6, 109.5, 46.3, 44.4, 32.0, 30.4, 30.2, 29.6, 29.4, 27.1, 22.8, 19.4 and 14.2 ppm.

IR (ATR): 2925, 2857, 1714, 1639, 1623, 1462, 1361, 1238, 1158, 789 and 735 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{22}H_{33}NO$ 327.2562; found 327.2575.

TLC: R_f = 0.2 (19:1 Hexanes/EtOAc).

4-(4-methoxy-1-methyl-1*H*-indol-3-yl)butan-2-one (S23)



S23

According to the **General Procedure 5**, a mixture of 4-methoxy-1-methyl-1*H*-indole[12] (322 mg, 2 mmol, 1.0 equiv.) and methyl vinyl ketone (0.25 mL, 3.0 mmol, 1.5 equiv.) was reacted with $BF_3.OEt_2$ (~45-50% BF_3) (25 μL, 0.2 mmol, 10 mol%) in 15 mL anhydrous CH_2Cl_2 at 0 °C for 30 mins to afford the desired methyl ketone **S23** as brown oil (407 mg, 1.76 mmol, 88%) by using Hexane/EtOAc (13:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.68 (s, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 3.90 (s, 3H), 3.65 (s, 3H), 3.11 (t, *J* = 7.5 Hz, 2H), 2.81 (t, *J* = 7.5 Hz, 2H) and 2.12 (s, 3H) ppm.

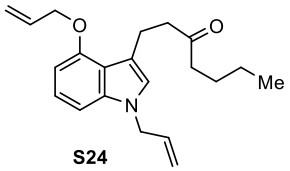
^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 154.8, 138.9, 125.3, 122.4, 117.4, 114.3, 102.7, 99.0, 55.2, 46.0, 32.8, 30.1 and 21.4 ppm.

IR (ATR): 2939, 1711, 1578, 1501, 1463, 1430, 1361, 1322, 1258, 1170, 1093 and 734 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{14}H_{17}NO_2$ 231.1259, found 231.1260.

TLC: R_f = 0.3 (4:1 Hexanes/EtOAc).

1-(1-allyl-4-(allyloxy)-1*H*-indol-3-yl)heptan-3-one (S24)



S24

According to the **General Procedure 5**, a mixture of 1-allyl-4-(allyloxy)-1*H*-indole **S32** (426 mg, 2 mmol, 1.0 equiv.) and hept-1-en-3-one[13] (336.5 mg, 3.0 mmol, 1.5 equiv.) was reacted with $BF_3.OEt_2$ (~45-50% BF_3) (25 μL, 0.2 mmol, 10 mol%) in 15 mL anhydrous CH_2Cl_2 at 0

°C for 15 mins to afford the desired methyl ketone **S24** as brown oil (449 mg, 1.38 mmol, 69%) by using Hexane/EtOAc (13:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.74 (s, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 6.11 (ddt, *J* = 17.1, 10.4, 5.1 Hz, 1H), 5.93 (dtd, *J* = 15.6, 10.5, 5.4 Hz, 1H), 5.47 – 5.41 (m, 1H), 5.29 – 5.25 (m, 1H), 5.18 – 5.13 (m, 1H), 5.08 – 5.01 (m, 1H), 4.65 – 4.62 (m, 2H), 4.61 – 4.58 (m, 2H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.56 – 1.48 (m, 2H), 1.31 – 1.22 (m, 2H) and 0.87 (t, *J* = 7.3 Hz, 3H) ppm.

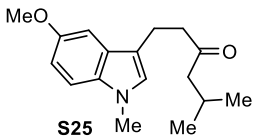
^{13}C NMR (100 MHz, $CDCl_3$) δ 211.8, 153.7, 138.5, 133.8, 133.7, 124.5, 122.4, 117.8, 117.2, 117.1, 114.9, 103.2, 100.2, 68.7, 48.8, 45.1, 42.8, 26.0, 22.5, 21.5 and 14.0 ppm.

IR (ATR): 2928, 2870, 1709, 1578, 1496, 1455, 1255, 990, 920, 776 and 727 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{27}NO_2$ 325.2042; found 325.2033.

TLC: R_f = 0.26 (6:1 Hexanes/EtOAc).

1-(5-methoxy-1-methyl-1*H*-indol-3-yl)-5-methylhexan-3-one (S25)



S25

According to the **General Procedure 5**, a mixture of 5-methoxy-1-methyl-1*H*-indole[14] (322 mg, 2 mmol, 1.0 equiv.) and 5-methylhex-1-en-3-one[14] (336.5 mg, 3.0 mmol, 1.5 equiv.) was reacted with $BF_3.OEt_2$ (~45-50% BF_3) (25 μL, 0.2 mmol, 10 mol%) in 15 mL anhydrous CH_2Cl_2 at 0 °C for 30 mins to afford the desired methyl ketone **S25** as brown oil (459.3 mg, 1.68 mmol, 84%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.79 (s, 1H), 3.86 (s, 3H), 3.67 (s, 3H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.27 (d, *J* = 7.0 Hz, 2H), 2.19 – 2.08 (m, 1H), 0.90 (s, 3H) and 0.88 (s, 3H) ppm.

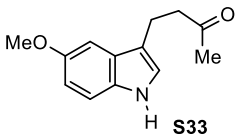
^{13}C NMR (100 MHz, $CDCl_3$) δ 210.8, 153.8, 132.5, 127.9, 127.0, 113.3, 111.8, 110.0, 100.8, 56.1, 52.1, 43.9, 32.8, 24.7, 22.7 and 19.2 ppm.

IR (ATR): 2954, 2871, 1710, 1492, 1455, 1424, 1367, 1225, 1173, 1058, 1037 and 793 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{17}H_{23}NO_2$ 273.1729; found 273.1711.

TLC: R_f = 0.4 (4:1 Hexanes/EtOAc).

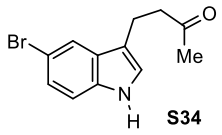
4-(5-methoxy-1*H*-indol-3-yl)butan-2-one (S33)



S33

According to the **General Procedure 5**, a mixture of 5-methoxy-1*H*-indole (294.5 mg, 2 mmol, 1.0 equiv.) and methyl vinyl ketone (0.25 mL, 3.0 mmol, 1.5 equiv.) was reacted with $BF_3.OEt_2$ (~45-50% BF_3) (25 µL, 0.2 mmol, 10 mol%) in 15 mL anhydrous CH_2Cl_2 at 0 °C for 30 mins to afford 4-(5-methoxy-1*H*-indol-3-yl)butan-2-one **S33** as brown oil (404 mg, 1.86 mmol, 93%) by using Hexane/EtOAc (4:1) as eluent. The spectroscopic data of the product matched with the literature report.[16]

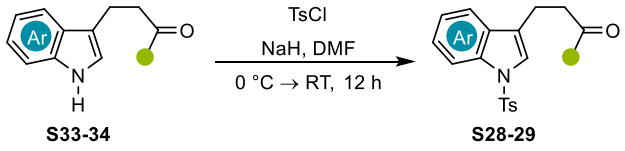
4-(5-bromo-1*H*-indol-3-yl)butan-2-one (S34)



S34

According to the **General Procedure 5**, a mixture of 5-bromo-1*H*-indole (390 mg, 2 mmol, 1.0 equiv.) and methyl vinyl ketone (0.25 mL, 3.0 mmol, 1.5 equiv.) was reacted with $BF_3.OEt_2$ (~45-50% BF_3) (25 µL, 0.2 mmol, 10 mol%) in 15 mL anhydrous CH_2Cl_2 at 0 °C for 30 mins to afford 4-(5-methoxy-1*H*-indol-3-yl)butan-2-one **S34** as brown oil (482 mg, 1.82 mmol, 91%) by using Hexane/EtOAc (4:1) as eluent. The spectroscopic data of the product matched with the literature report.[15]

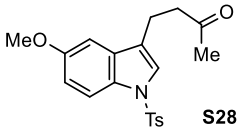
(iv) General procedure 6: *N*-Tosylation of the derivatives of 4-(1*H*-indol-3-yl)butan-2-one



S33-34 **S28-29**

To the stirred solution of indole **S33-34** (1.0 equiv.) in anhydrous DMF at 0 °C was added NaH (1.2 equiv., 55-60% dispersion in mineral oil) under nitrogen. The mixture was stirred at same temperature for 20 mins followed by addition of *p*-toluenesulfonyl chloride (1.5 equiv.). The reaction mixture was allowed to slowly warm up to room temperature and stirred for 12 h. After completion, the reaction was quenched by slow addition of ice-cold water. The residual compound from aqueous layer was extracted with EtOAc (3 times). The combined organic layers were washed with brine (4 times) dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (Hexanes/EA) provided the desired *N*-tosylated indole **S28-29**.

4-(5-methoxy-1-tosyl-1*H*-indol-3-yl)butan-2-one (S28)



S28

According to the **General Procedure 6**, 4-(5-methoxy-1*H*-indol-3-yl)butan-2-one **S33** (434 mg, 2 mmol, 1.0 equiv.) was reacted with NaH (55-60% dispersion in mineral oil) (101 mg, 2.4 mmol, 1.2 equiv.) and *p*-toluenesulfonyl chloride (572 mg, 3.0 mmol, 1.5 equiv.) in 10

mL anhydrous DMF to afford the desired *N*-tosylated indole **S28** as brown waxy solid (682.6 mg, 1.84 mmol, 92%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.26 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.94 – 6.86 (m, 2H), 3.81 (s, 3H), 2.91 – 2.85 (m, 2H), 2.83 – 2.76 (m, 2H), 2.32 (s, 3H) and 2.15 (s, 3H) ppm.

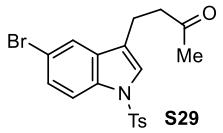
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 156.4, 144.7, 135.1, 131.8, 130.0, 129.8, 126.7, 123.6, 122.2, 114.7, 113.6, 101.9, 55.7, 42.4, 30.1, 21.5 and 18.8 ppm.

IR (ATR): 2921, 1714, 1611, 1597, 1474, 1438, 1364, 1219, 1170, 1119, 982 and 795 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}NO_4S$ 372.1264; found 372.1256.

TLC: R_f = 0.25 (4:1 Hexanes/EtOAc).

4-(5-bromo-1-tosyl-1*H*-indol-3-yl)butan-2-one (S29)



S29

According to the **General Procedure 6**, 4-(5-bromo-1*H*-indol-3-yl)butan-2-one **S34** (530 mg, 2 mmol, 1.0 equiv.) was reacted with NaH (55-60% dispersion in mineral oil) (101 mg, 2.4 mmol, 1.2 equiv.) and *p*-toluenesulfonyl chloride (572 mg, 3.0 mmol, 1.5 equiv.) in 10 mL anhydrous DMF to afford the desired *N*-tosylated indole **S29** as brown waxy solid (695.5 mg, 1.66 mmol, 83%) by using Hexane/EtOAc (4:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.58 (s, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.32 (s, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.90 – 2.84 (m, 2H), 2.83 – 2.75 (m, 2H), 2.31 (s, 3H) and 2.14 (s, 3H) ppm.

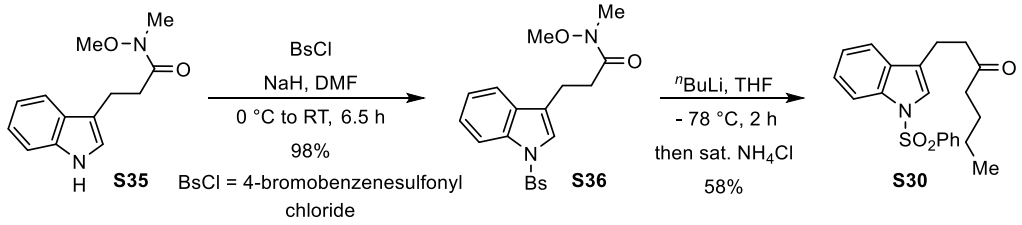
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 145.2, 134.9, 134.0, 132.5, 130.0, 127.6, 126.8, 124.2, 122.2, 121.4, 116.7, 115.3, 42.5, 30.1, 21.6 and 18.6 ppm.

IR (ATR): 2922, 1714, 1442, 1369, 1170, 1123, 1100, 800 and 737 cm^{-1}.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{18}BrNNaO_3S$ 442.0083; found 442.0079.

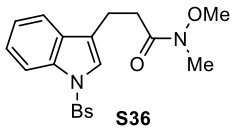
TLC: R_f = 0.24 (4:1 Hexanes/EtOAc).

(v) Synthesis of 1-(1-(phenylsulfonyl)-1*H*-indol-3-yl)heptan-3-one (S30)



S35 **S36** **S30**

3-(1-((4-bromophenyl)sulfonyl)-1*H*-indol-3-yl)-*N*-methoxy-*N*-methylpropanamide (S36)



S36

To the stirred solution of Weinreb amide **S35**[17] (464 mg, 2.0 mmol, 1.0 equiv.) in anhydrous DMF at 0 °C was added NaH (55-60% dispersion in mineral oil) (101 mg, 2.4 mmol, 1.2 equiv.) under nitrogen. The mixture was stirred at same temperature for 20 mins followed by addition of *p*-bromobenzenesulfonyl chloride (766.5 mg, 3.0 mmol, 1.5 equiv.). The reaction mixture was allowed to slowly warm up to room temperature and stirred for 6 h. After completion, the reaction was quenched by slow addition of ice-cold water. The residual compound from aqueous layer was extracted with EtOAc (3 times). The combined organic layers were washed with brine (4 times) dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (2:1 Hexanes/EA) provided the desired *N*-brosylated indole **S36** as off-white solid (882 mg, 1.96 mmol, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.51 (t, *J* = 6.4 Hz, 3H), 7.35 (s, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 3.59 (s, 3H), 3.18 (s, 3H), 3.01 (t, *J* = 7.6 Hz, 2H) and 2.80 (t, *J* = 7.4 Hz, 2H) ppm.

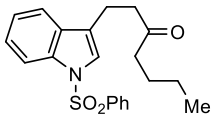
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 135.2, 132.5, 131.0, 128.9, 128.2, 125.0, 123.5, 123.1, 122.8, 119.6, 113.7, 61.3, 31.2 and 19.9 ppm.

IR (ATR): 2925, 1657, 1574, 1447, 1389, 1371, 1266, 1174, 1119, 1093, 978 and 733 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{20}BrN_2O_4S$ 451.0322; found 451.0319.

M.P.: 114 – 116 °C.

1-(1-(phenylsulfonyl)-1*H*-indol-3-yl)heptan-3-one (S30)



S30

To the stirred solution of Weinreb amide **S36** (450 mg, 1 mmol, 1.0 equiv.) in anhydrous THF (15 mL) at –78 °C was added *n*-butyllithium (1.25 mL, 2 mmol, 2.0 equiv., 1.6 *M* in hexanes) dropwise under nitrogen. The mixture was stirred at same temperature for 2.5 h. The reaction mixture was then quenched with saturated NH_4Cl solution. The residual compound from aqueous layer was extracted with EtOAc (3 x 7 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via silica gel column chromatography (6:1 Hexanes/EA) provided the ketone **S30** (214.3 mg, 0.58 mmol, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.49 (dd, *J* = 15.8, 7.7 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.24 (dd, *J* = 12.0, 4.8 Hz,

1H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.38 (t, *J* = 7.5 Hz, 2H), 1.58 – 1.49 (m, 2H), 1.33 – 1.22 (m, 3H) and 0.88 (t, *J* = 7.3 Hz, 3H) ppm.

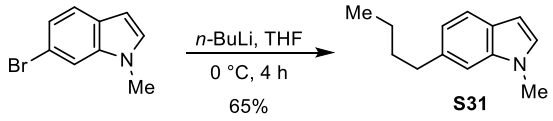
^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 138.3, 135.4, 133.8, 130.8, 129.3, 126.8, 124.9, 123.3, 122.9, 122.4, 119.5, 113.9, 42.8, 41.8, 26.0, 22.4, 18.9 and 13.9 ppm.

IR (ATR): 2958, 2922, 1712, 1447, 1367, 1174, 1120, 1098, 1089, 975 and 736 cm^{-1}.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{21}H_{23}NO_3S$ 369.1399; found 369.1401.

(vi) Procedure for the synthesis of *N*-alkylated indoles.

6-butyl-1-methyl-1*H*-indole (S31)



To the stirred solution of 6-bromo-1-methyl-1*H*-indole[18] (530 mg, 2.54 mmol, 1.0 equiv.) in anhydrous THF was added *n*-BuLi (2.38 mL, 1.5 equiv., ~1.6 *M* in hexane) dropwise at 0 °C under nitrogen. The mixture was stirred at same temperature for 4 h. The reaction mixture was then quenched with saturated NH_4Cl solution. The organic layer was separated and the residual compound from aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via silica gel column chromatography (19:1 Hexanes/EA) provided the desired indole **S31** (308.7 mg, 1.65 mmol mmol, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 6.99 – 6.93 (m, 2H), 6.42 (d, *J* = 2.9 Hz, 1H), 3.75 (s, 3H), 2.74 (t, *J* = 7.7 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.44 – 1.34 (m, 2H) and 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

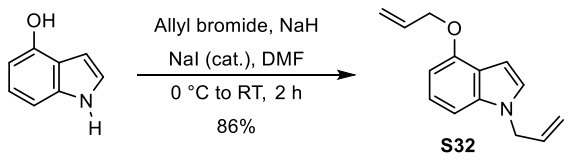
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 136.7, 128.4, 126.6, 120.6, 120.6, 108.6, 100.8, 36.34, 34.6, 32.9, 22.6 and 14.2 ppm.

IR (ATR): 2925, 2856, 2312, 1849, 1725, 1575, 1480, 1347, 1237, 1009, 876 and 738 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{18}N$ 188.1434; found 188.1425.

TLC: R_f = 0.78 (9:1 Hexanes/EtOAc).

1-allyl-4-(allyloxy)-1*H*-indole (S32)



To the stirred solution of 4-hydroxyindole (400.5 mg, 3 mmol, 1.0 equiv.) in anhydrous DMF (10 mL) at 0 °C was added NaH (303 mg, 7.2 mmol, 2.4 equiv.) under nitrogen. The mixture was stirred at 0 °C for 20 mins and then allyl bromide (0.8 mL, 9.0 mmol, 3.0 equiv.) and NaI (90 mg, 0.6 mmol, 0.2 equiv.) were added sequentially. The reaction mixture was allowed to stir for 2 h. After completion, the reaction was quenched by slow addition of ice-cold water.

The residual compound from aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (4 times) dried over anhydrous Na_2SO_4, filtered, and concentrated *in-vacuo*. Purification of crude product via a silica gel column chromatography (2:1 Hexanes/EA) provided **S32** as brownish-yellow oil (550 mg, 2.58 mmol, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 3.1 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.66 – 6.63 (m, 1H), 6.51 (d, *J* = 7.7 Hz, 1H), 6.14 (ddd, *J* = 22.4, 10.5, 5.2 Hz, 1H), 5.96 (ddd, *J* = 22.4, 10.5, 5.3 Hz, 1H), 5.47 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.28 (dd, *J* = 10.5, 1.4 Hz, 1H), 5.16 (dd, *J* = 10.3, 1.1 Hz, 1H), 5.04 (dd, *J* = 17.1, 1.1 Hz, 1H) and 4.70 – 4.65 (m, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 137.8, 133.9, 133.6, 126.4, 122.4, 119.6, 117.2, 103.3, 100.8, 98.9, 68.9 and 49.1 ppm.

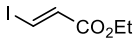
IR (ATR): 2918, 1578, 1493, 1357, 1299, 1252, 1223, 1154, 1052, 1025, 989 and 730 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{16}NO$ 214.1226; found 214.1219.

TLC: R_f = 0.8 (9:1 Hexanes/EtOAc).

(vii) Procedure for isomerization of ethyl (*Z*)-3-iodoacrylate.

Ethyl (*E*)-3-iodoacrylate (S37)



S37

To a well stirred solution of ethyl (*Z*)-3-iodo-acrylate[4] (600 mg, 2.65 mmol) in toluene (3 mL) was added a 57% aqueous solution of hydroiodic acid (0.1 mL) under nitrogen. The resulting mixture was heated to 80 ºC for 20 h, whereupon the dark brown solution was cooled to room temperature and diluted with diethyl ether (10 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL), 10% aqueous solution of $Na_2S_2O_3$ (0.9 mL) and brine (10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and the solvent was evaporated under reduced pressure to afford **S37** (551.4 mg, 2.44 mmol, 92%) as a pale-yellow oil. [The spectroscopic data was consistent with the data reported in the literature.[19]]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 14.8 Hz, 1H), 6.87 (d, *J* = 14.8 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H) and 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 136.7, 99.3, 61.1 and 14.3 ppm.

F. References:

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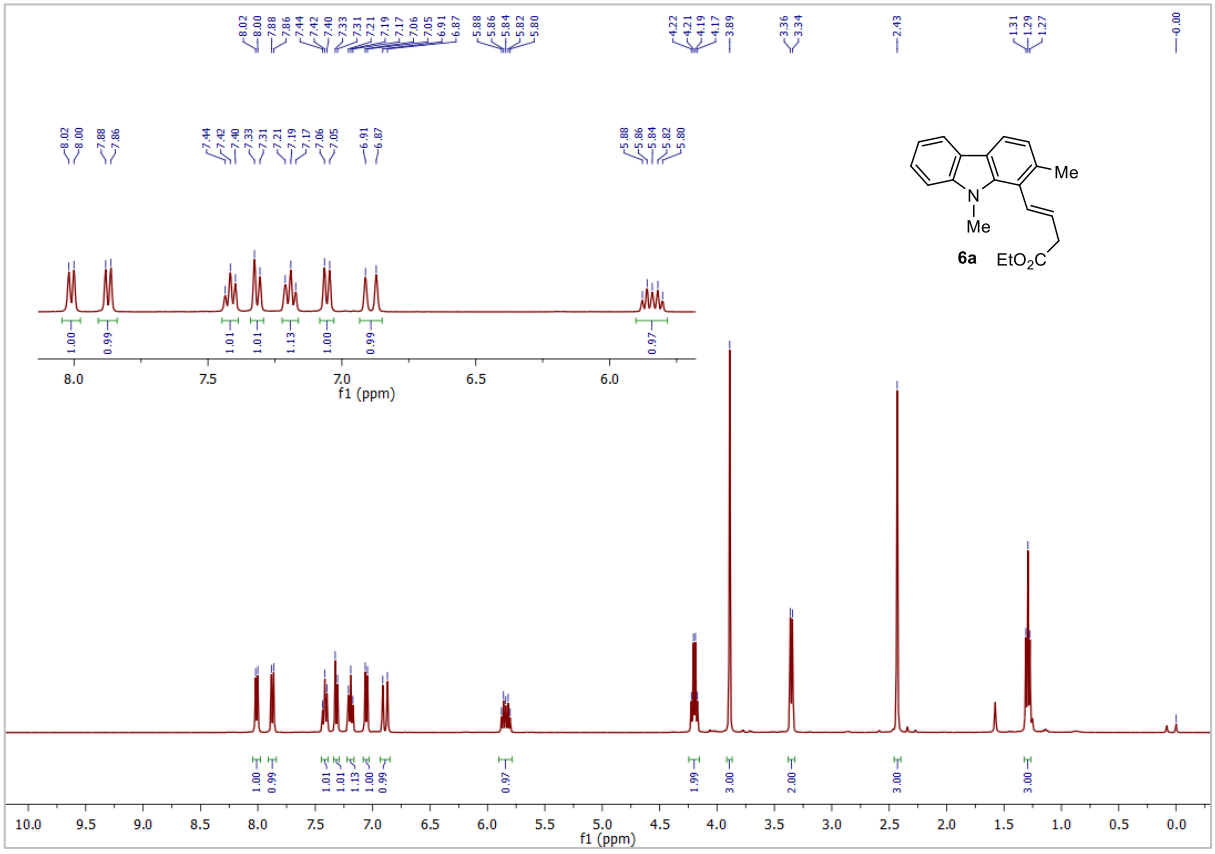
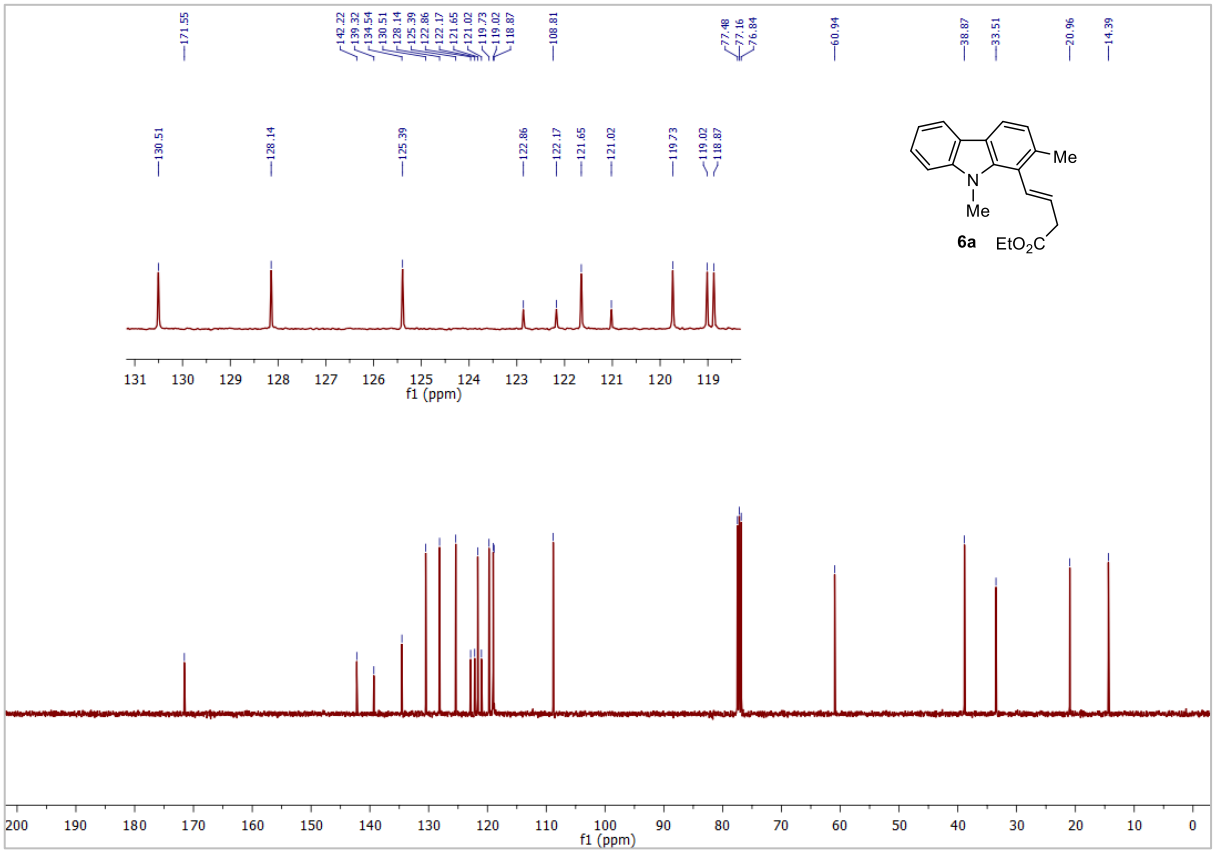
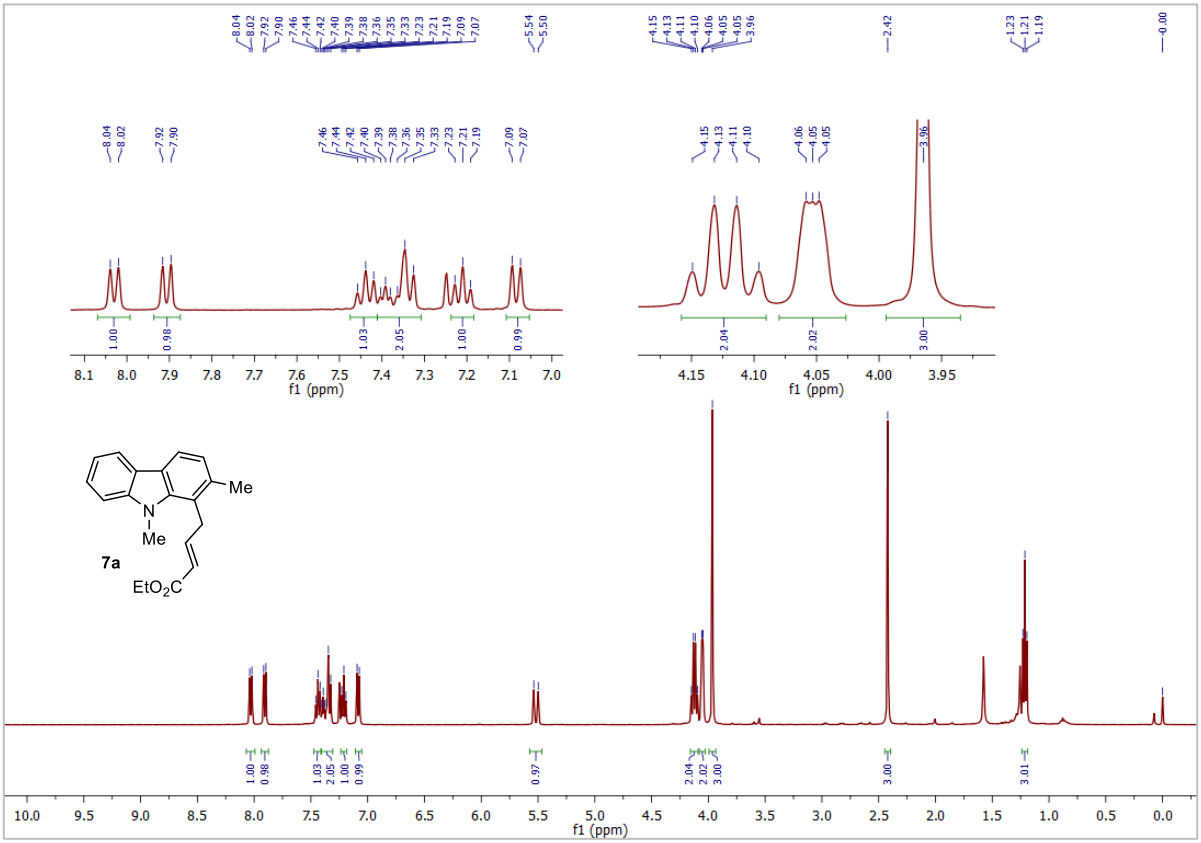
G. Copy of ^{1}H and ^{13}C NMR spectra of all new compounds

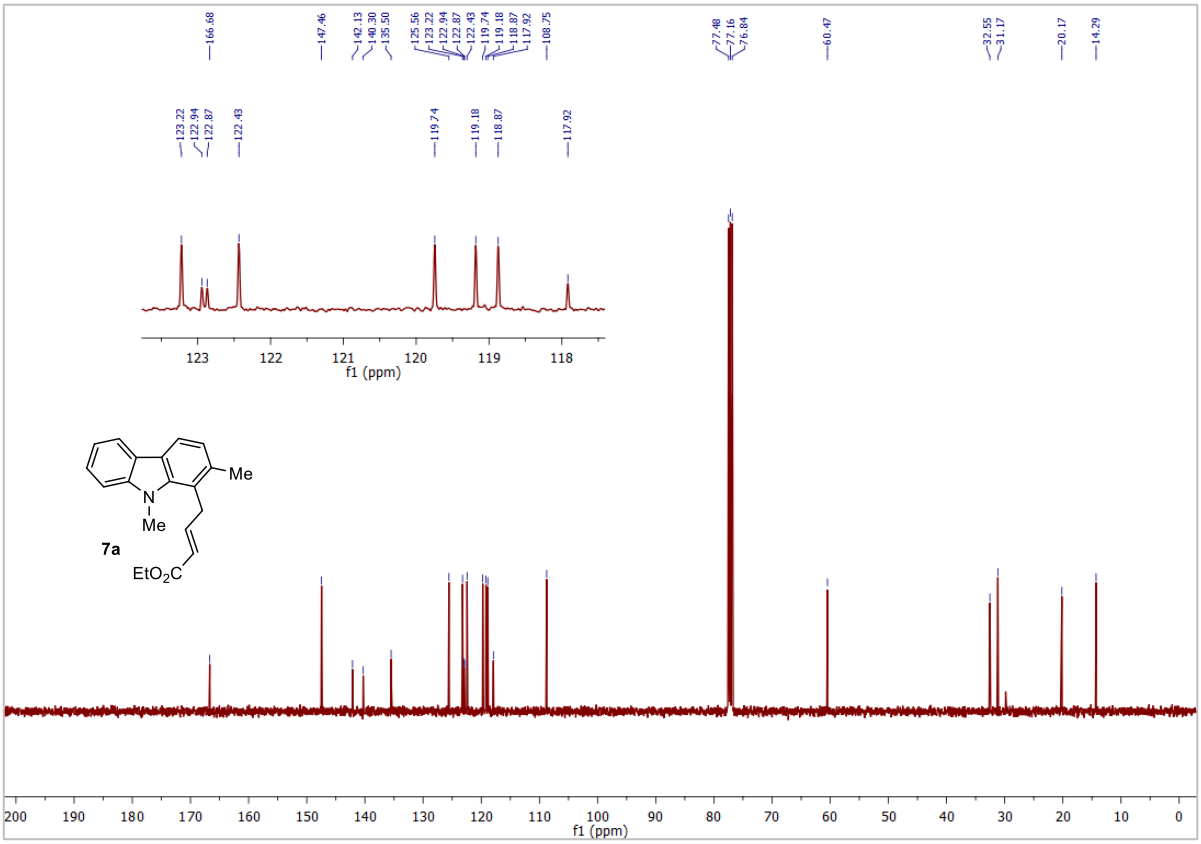
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **6a**.



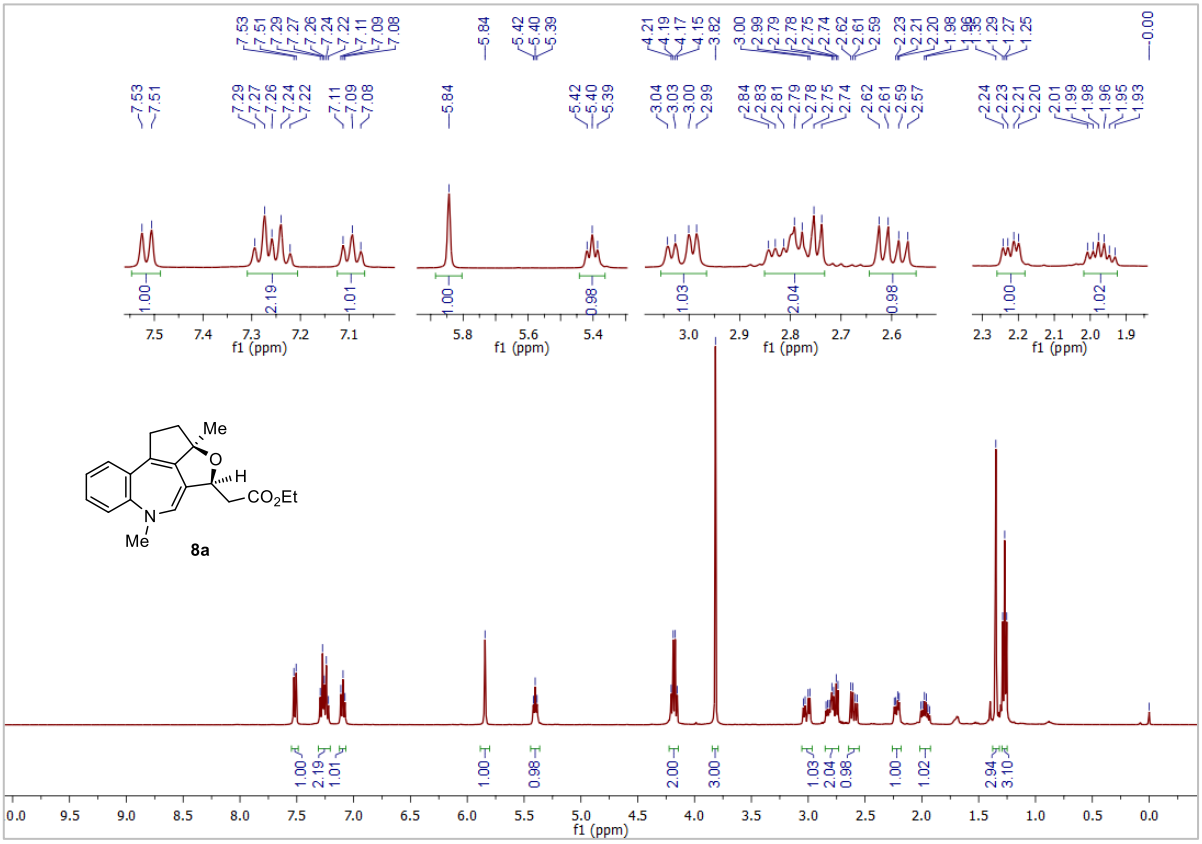


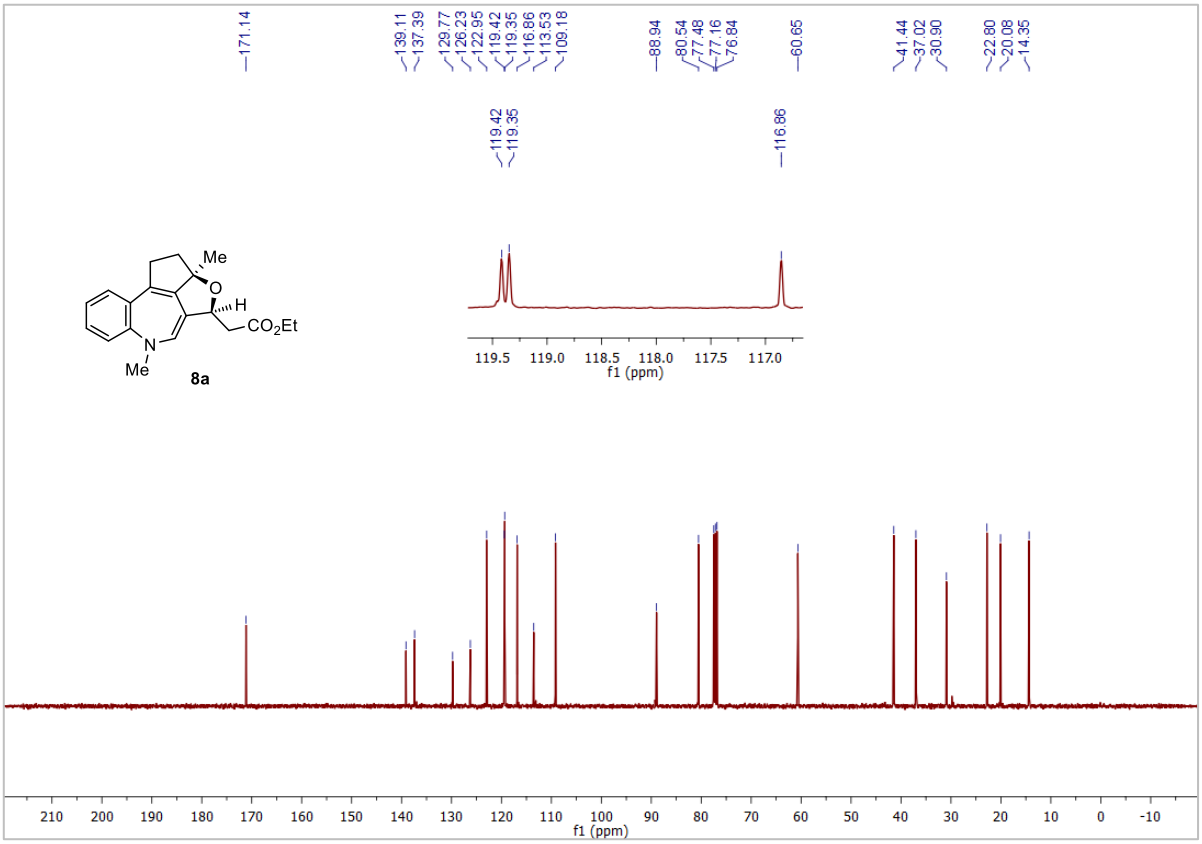
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **7a**.



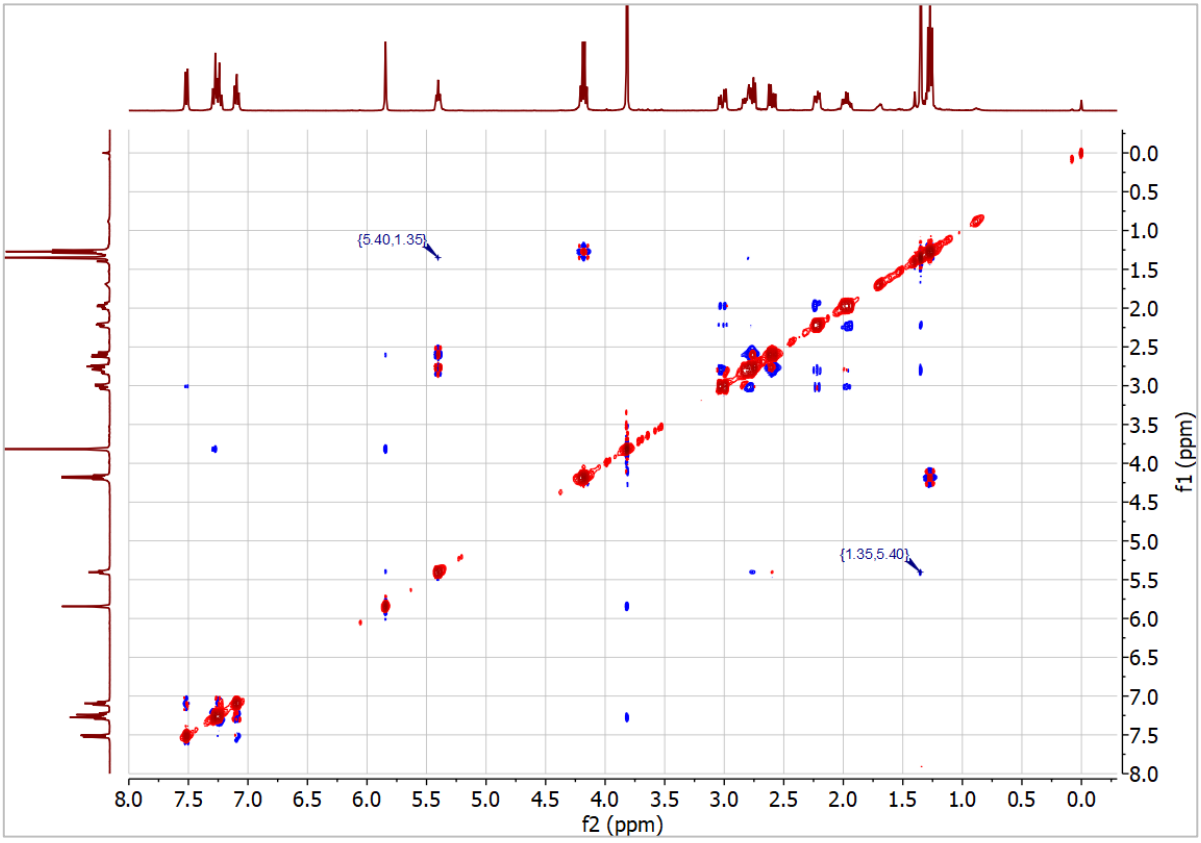


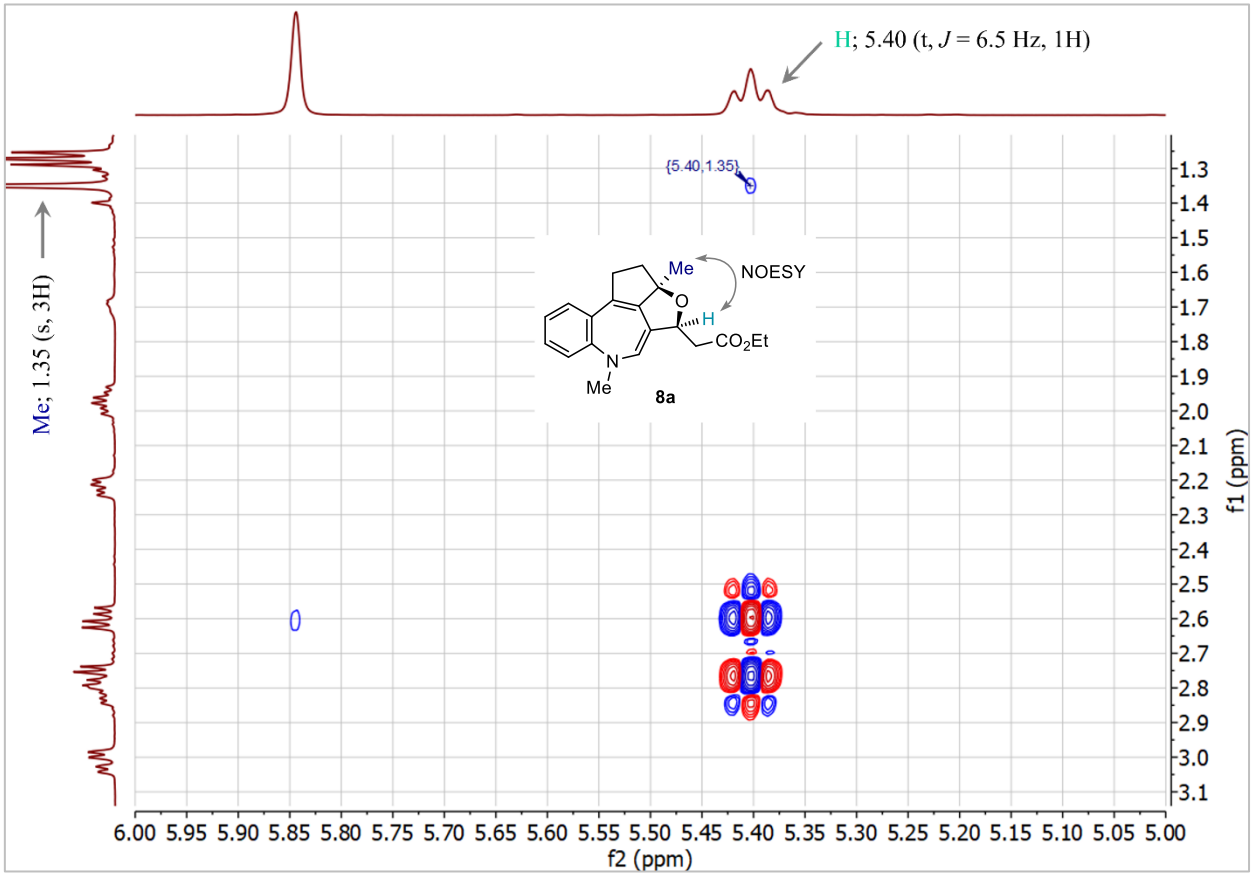
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **8a**



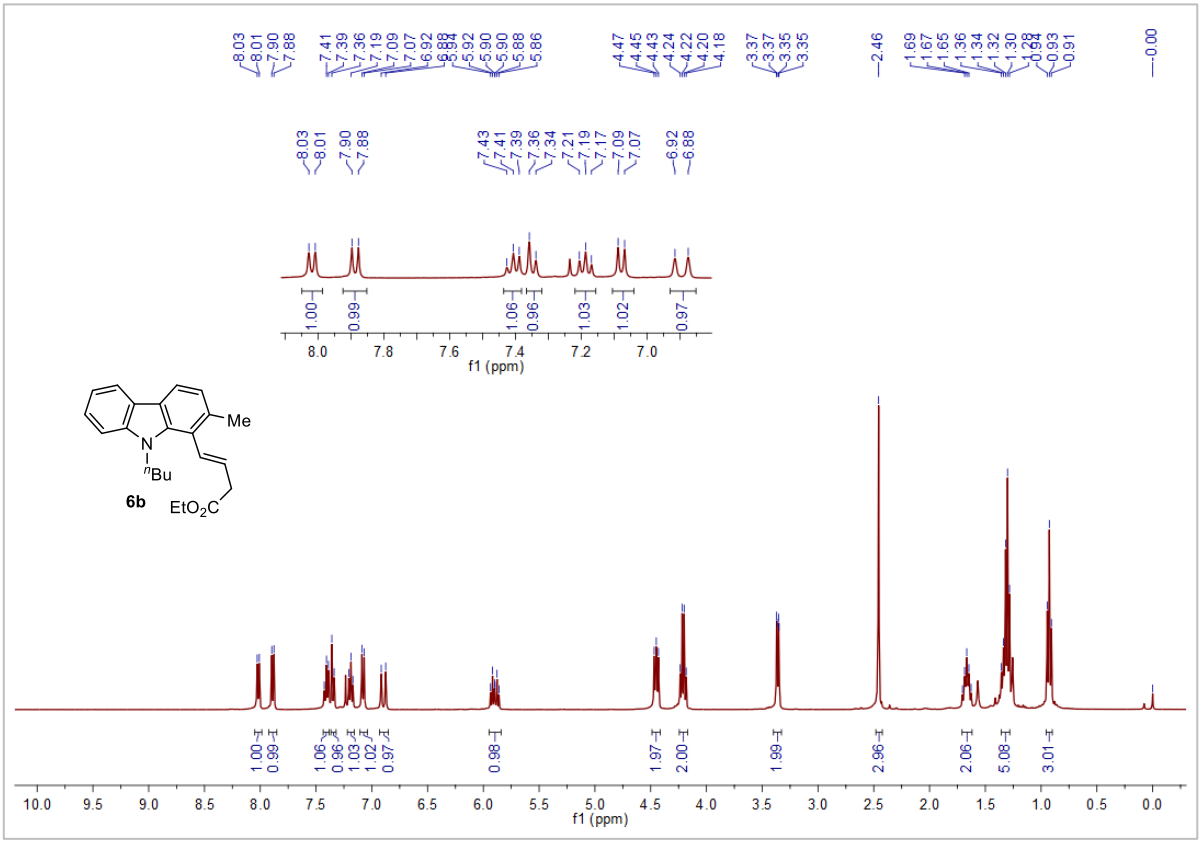


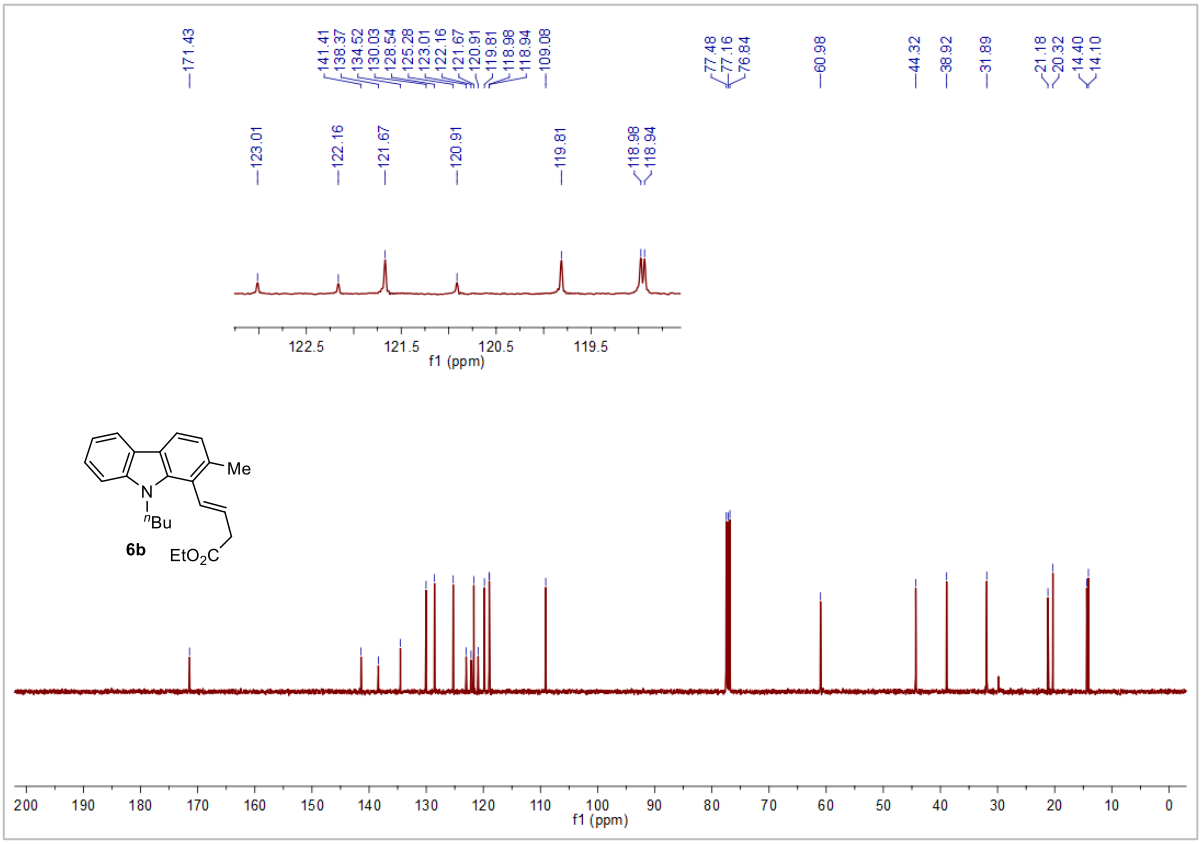
Full and zoomed view of NOESY NMR (400 MHz, $CDCl_3$) of **8a**.



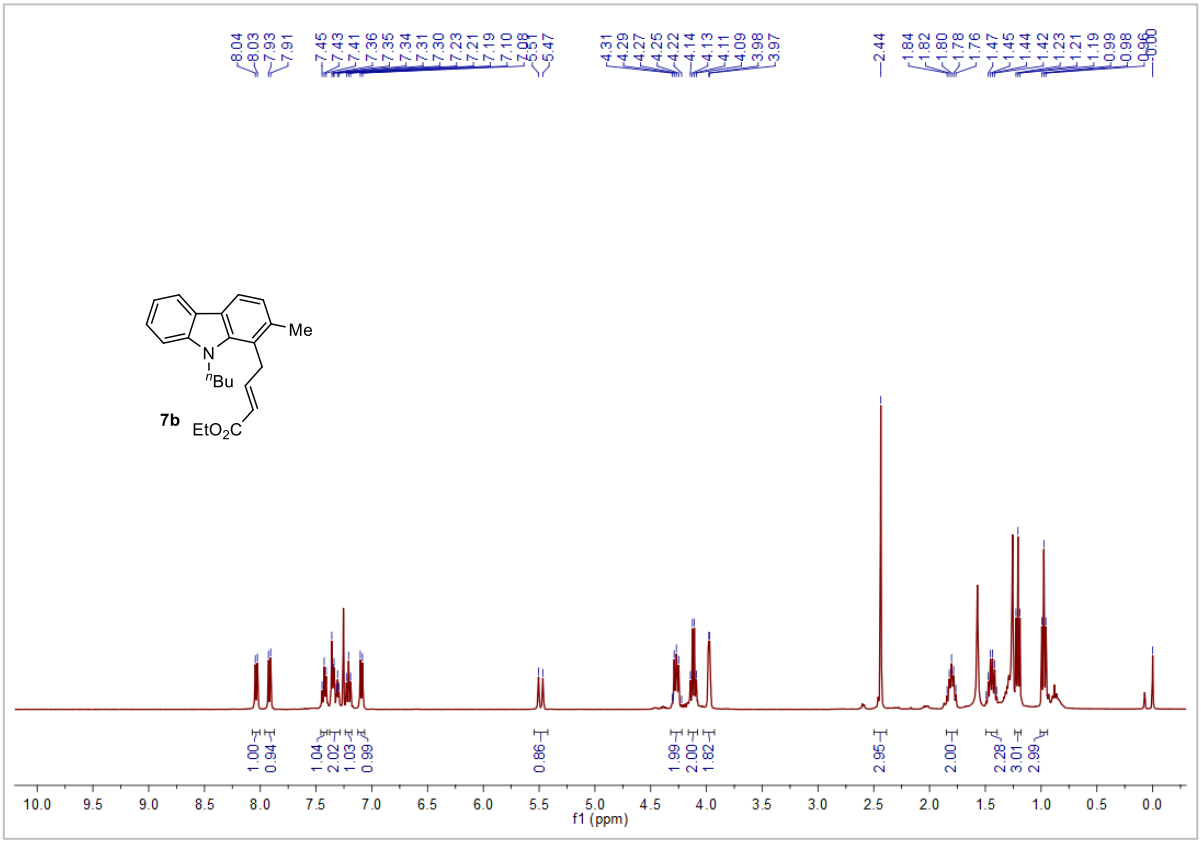


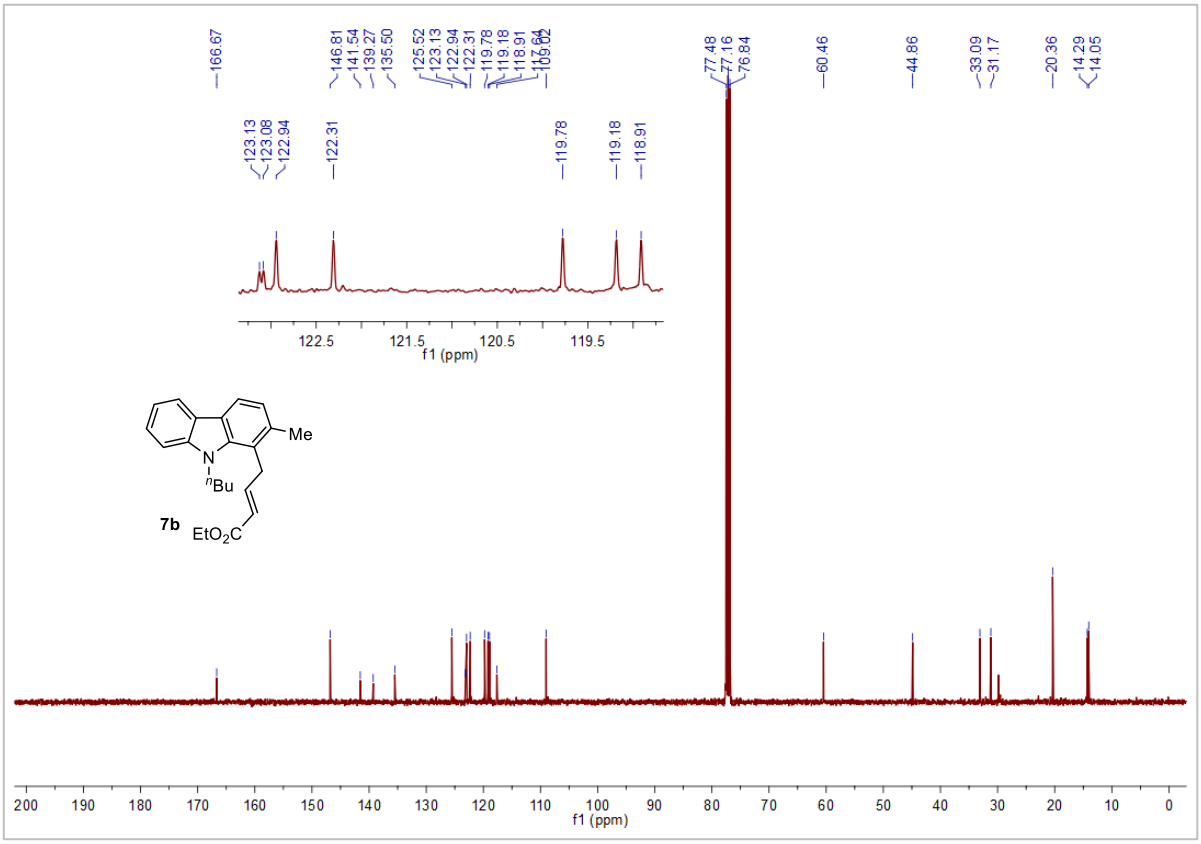
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **6b**.



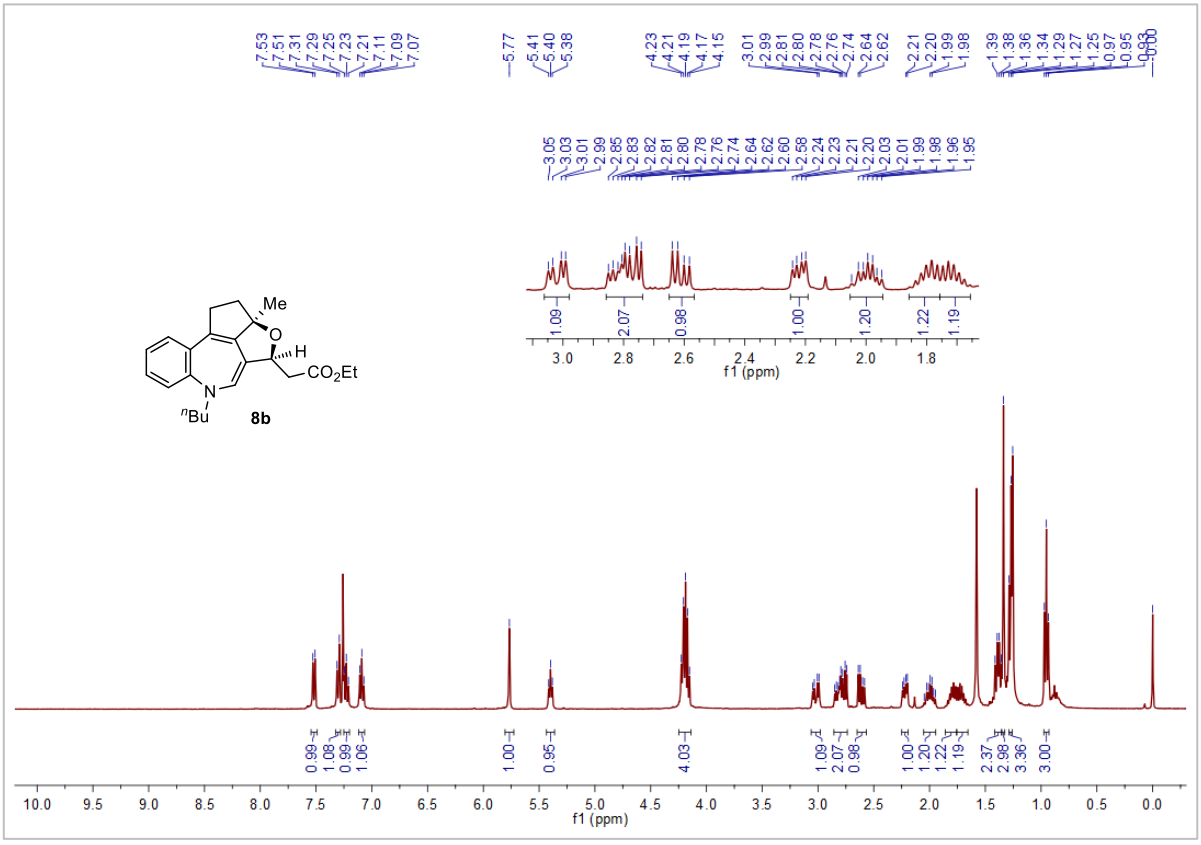


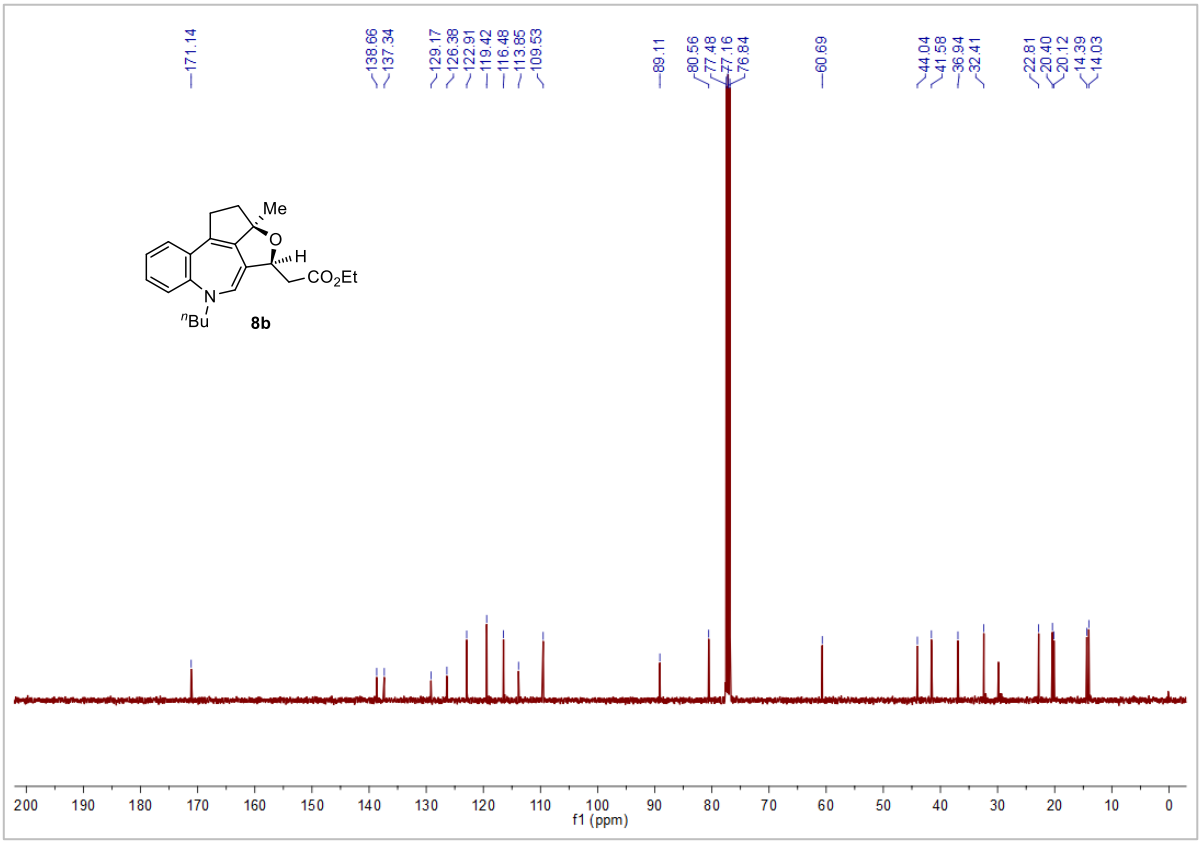
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **7b**.



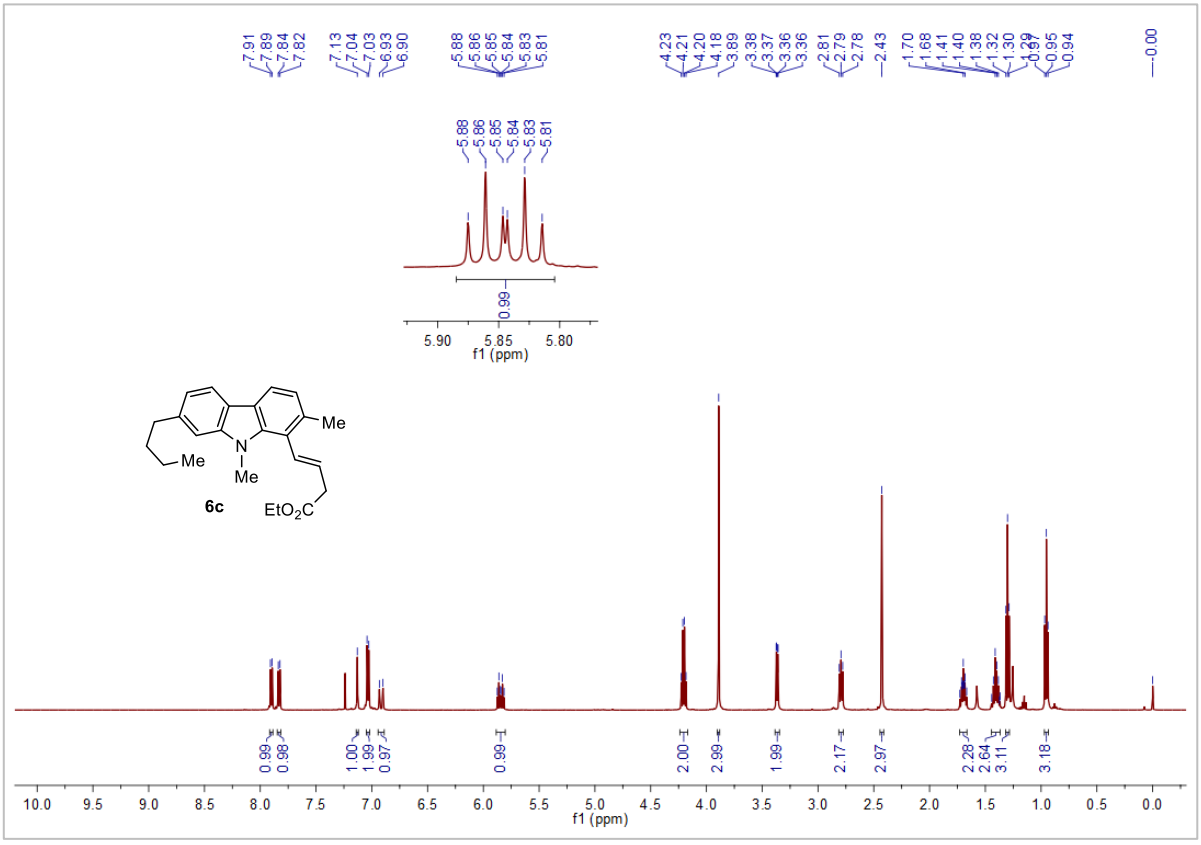


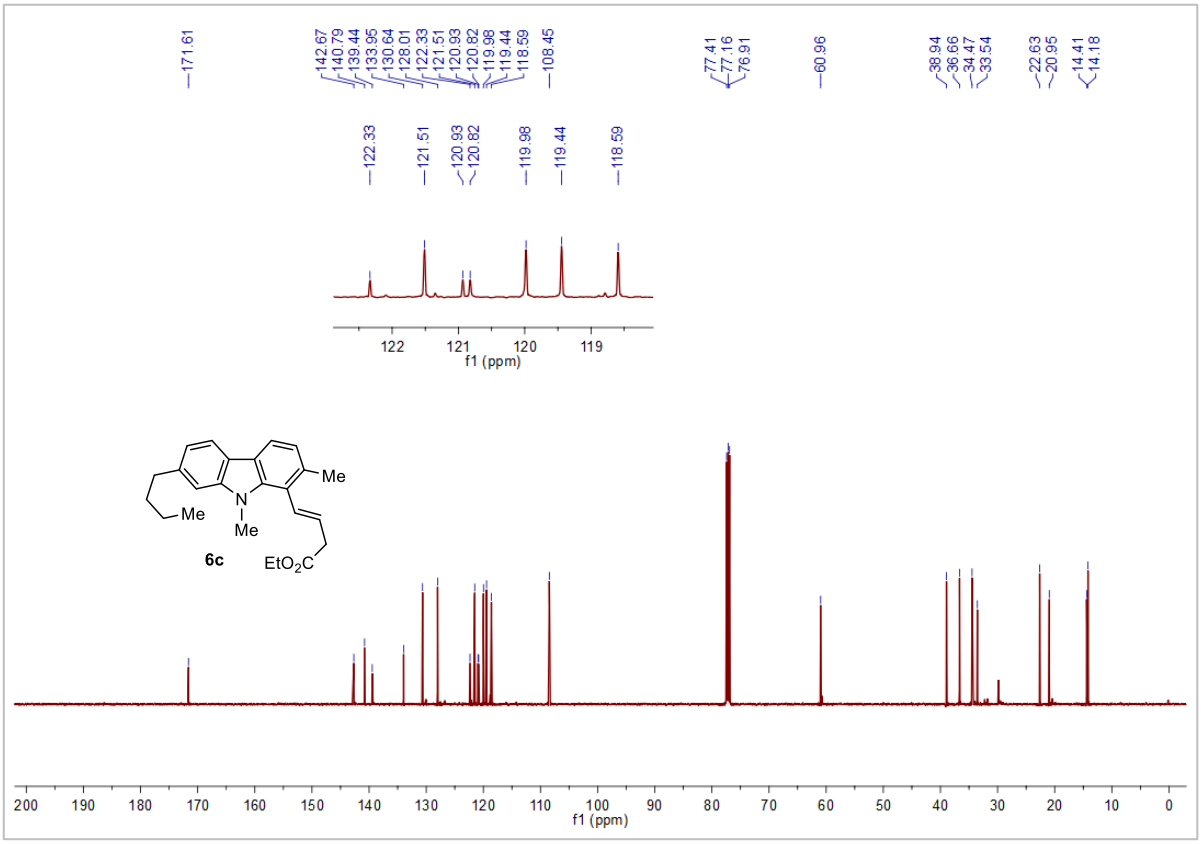
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **8b**.



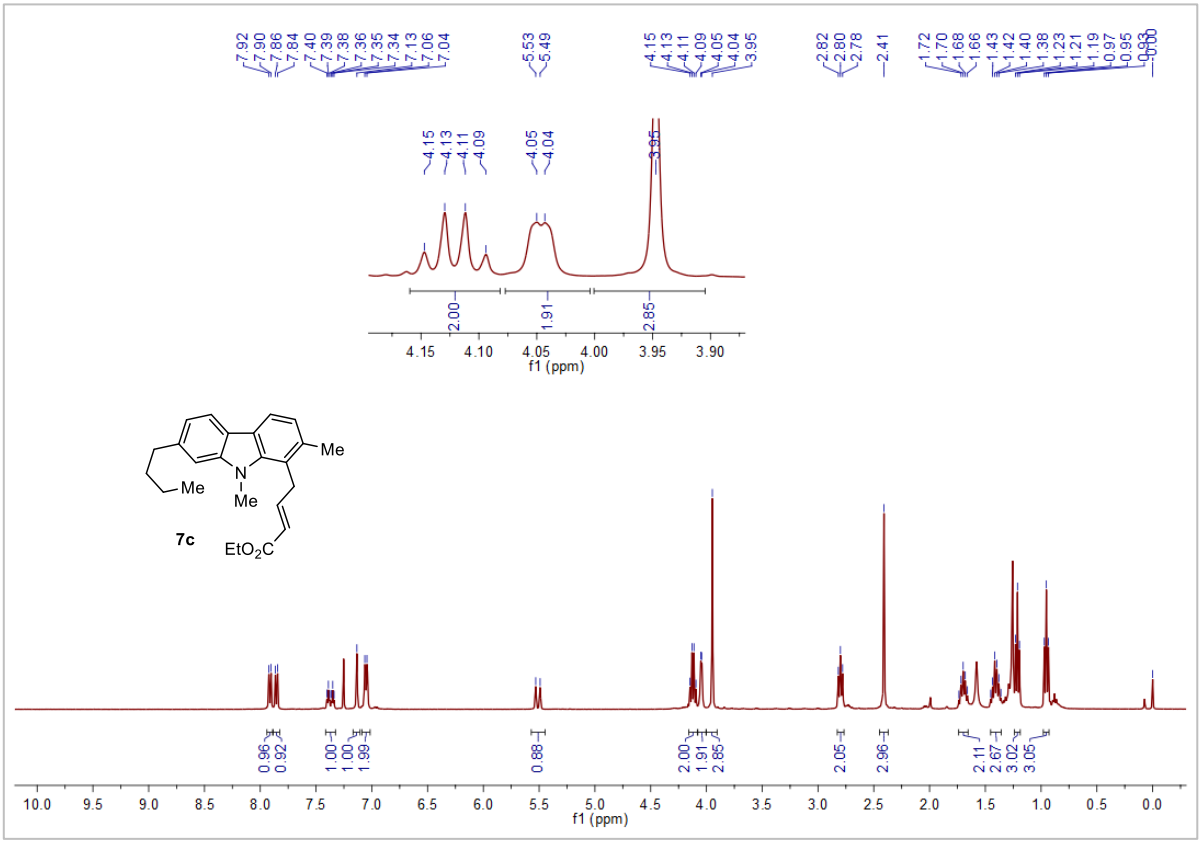


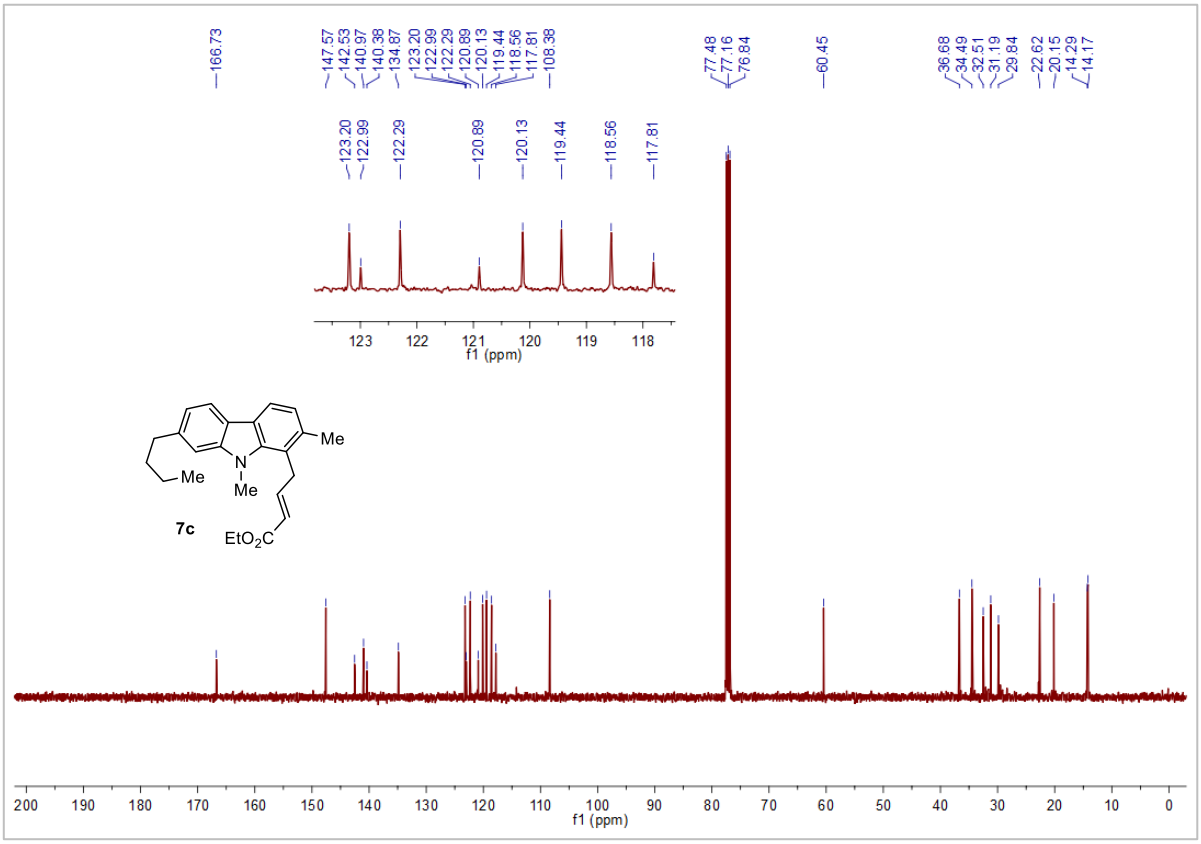
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **6c**.



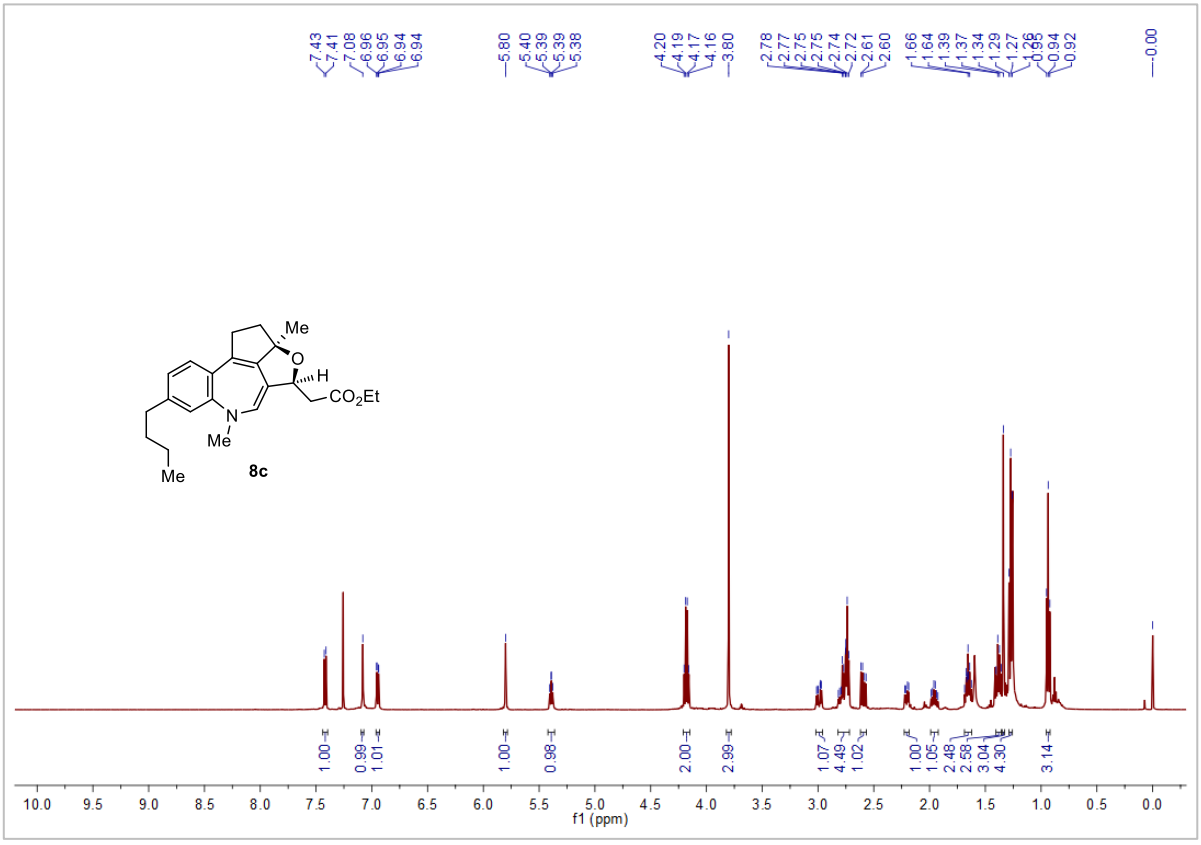


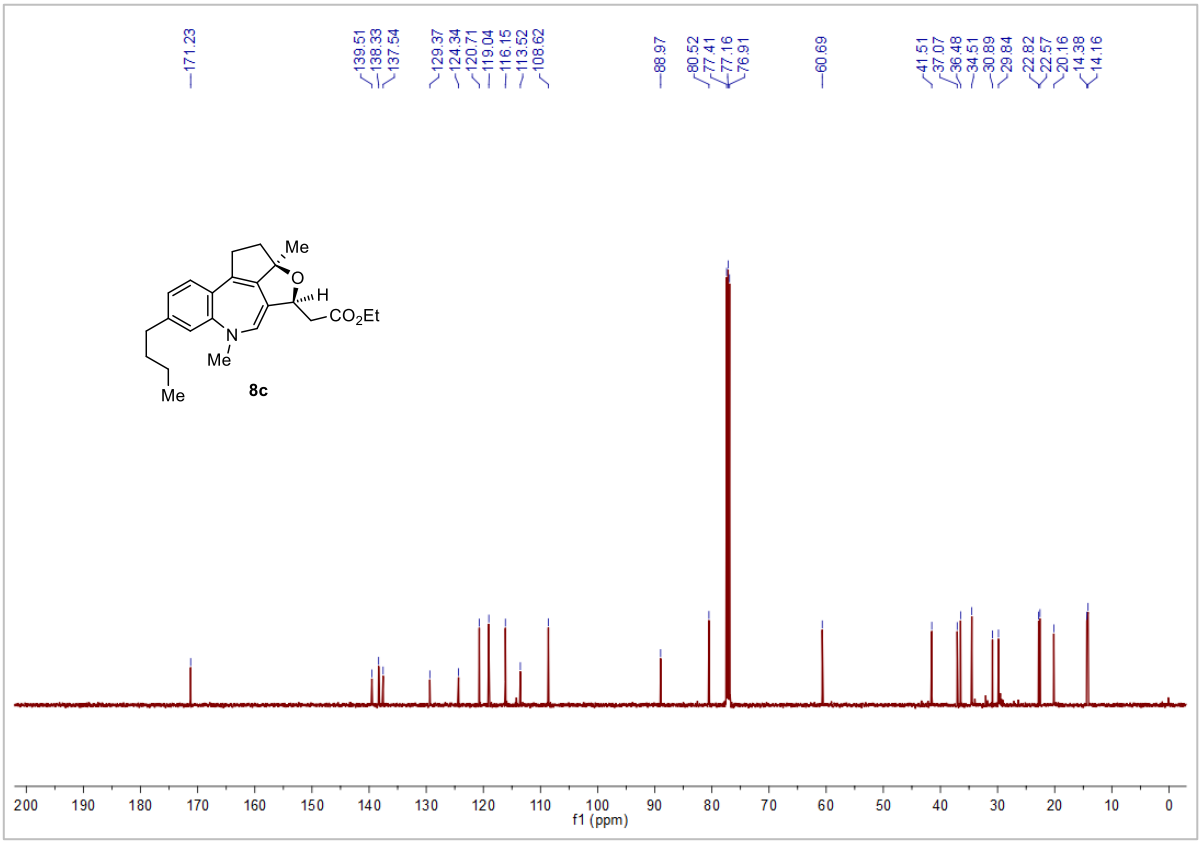
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **7c**.



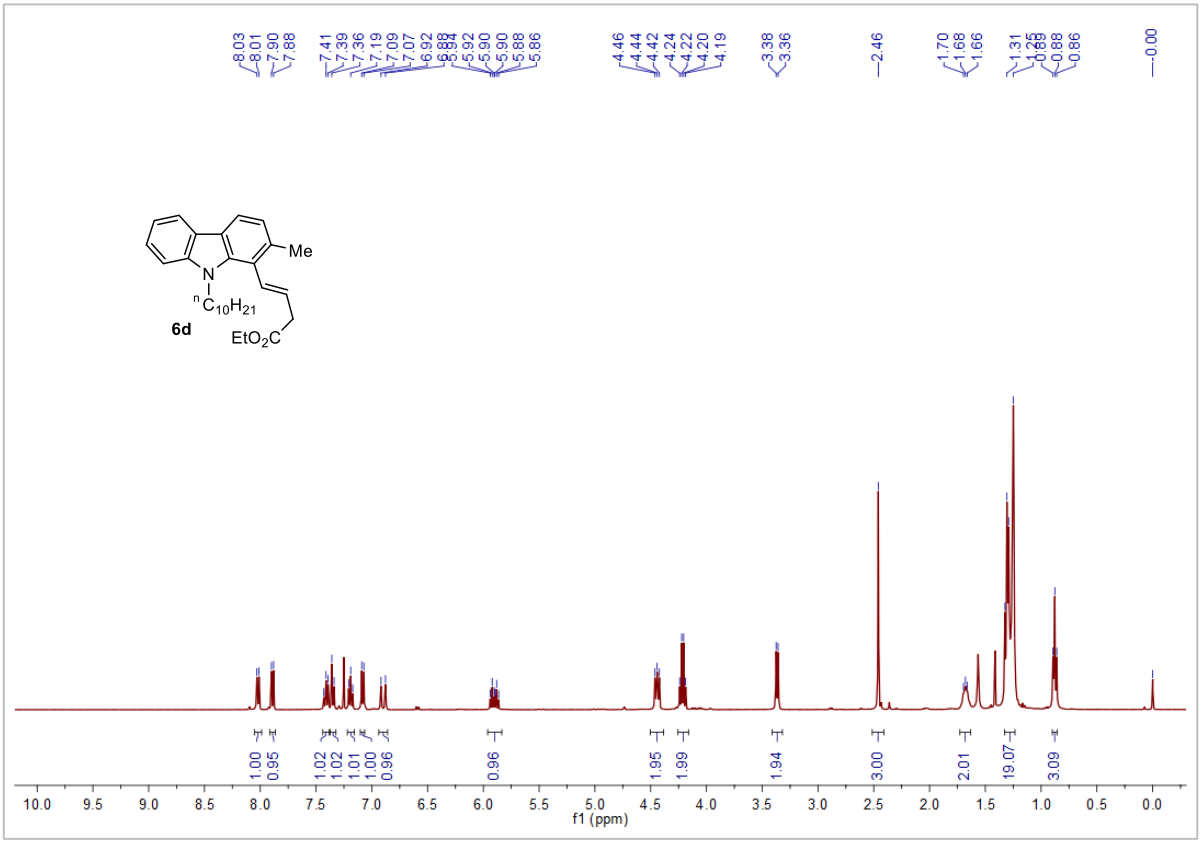


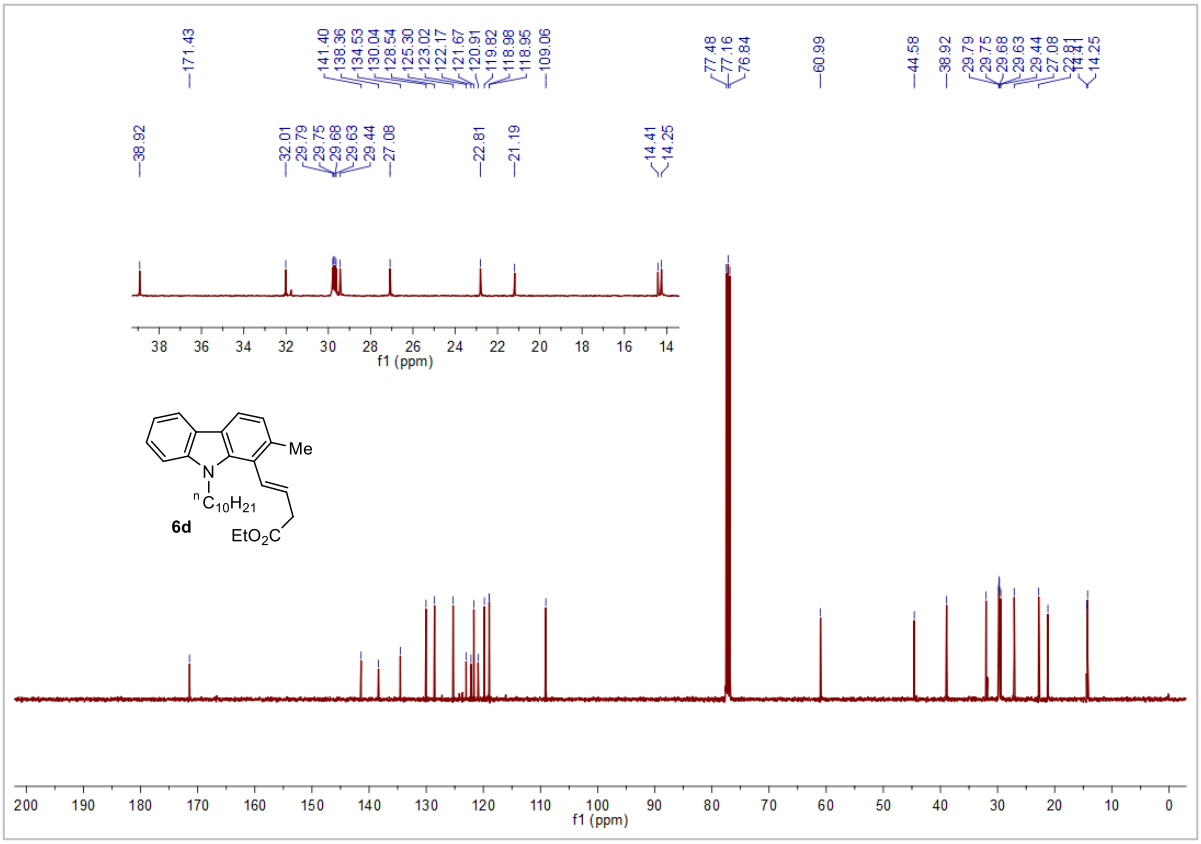
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **8c**.



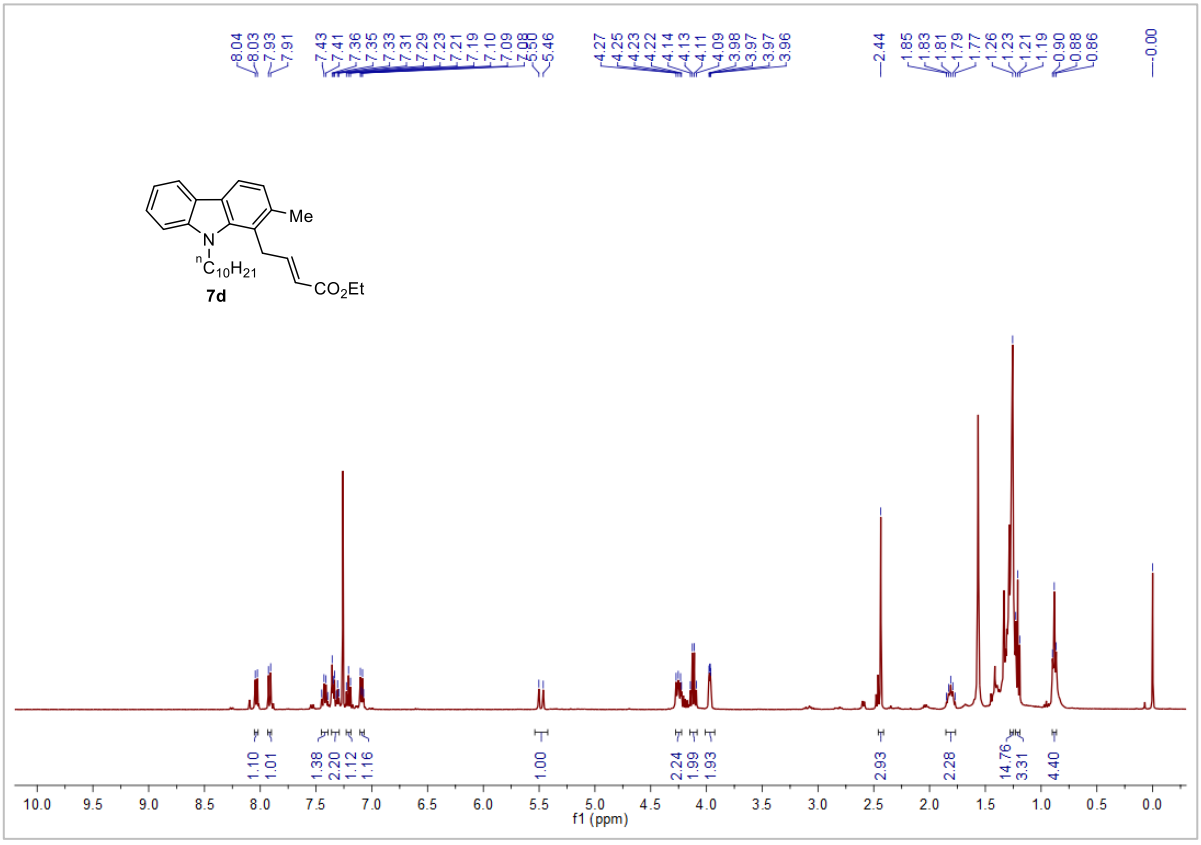


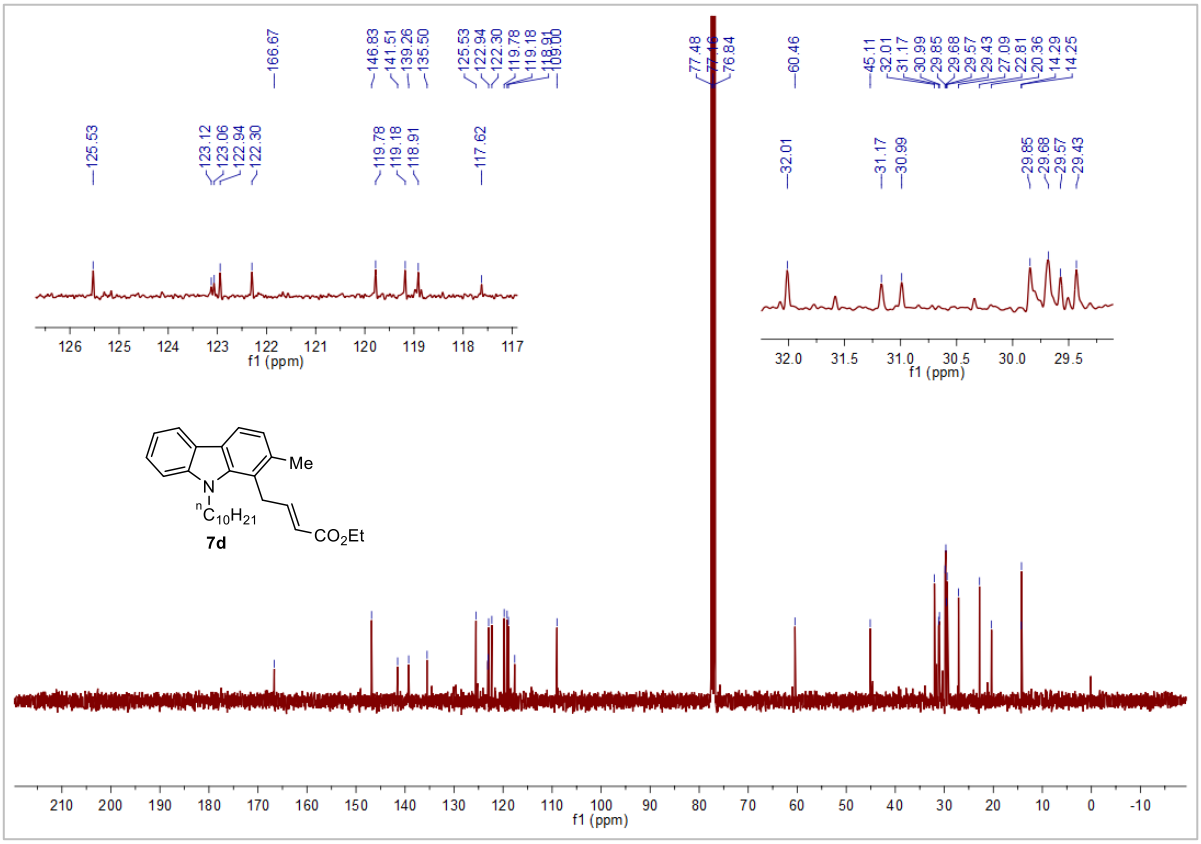
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **6d**.



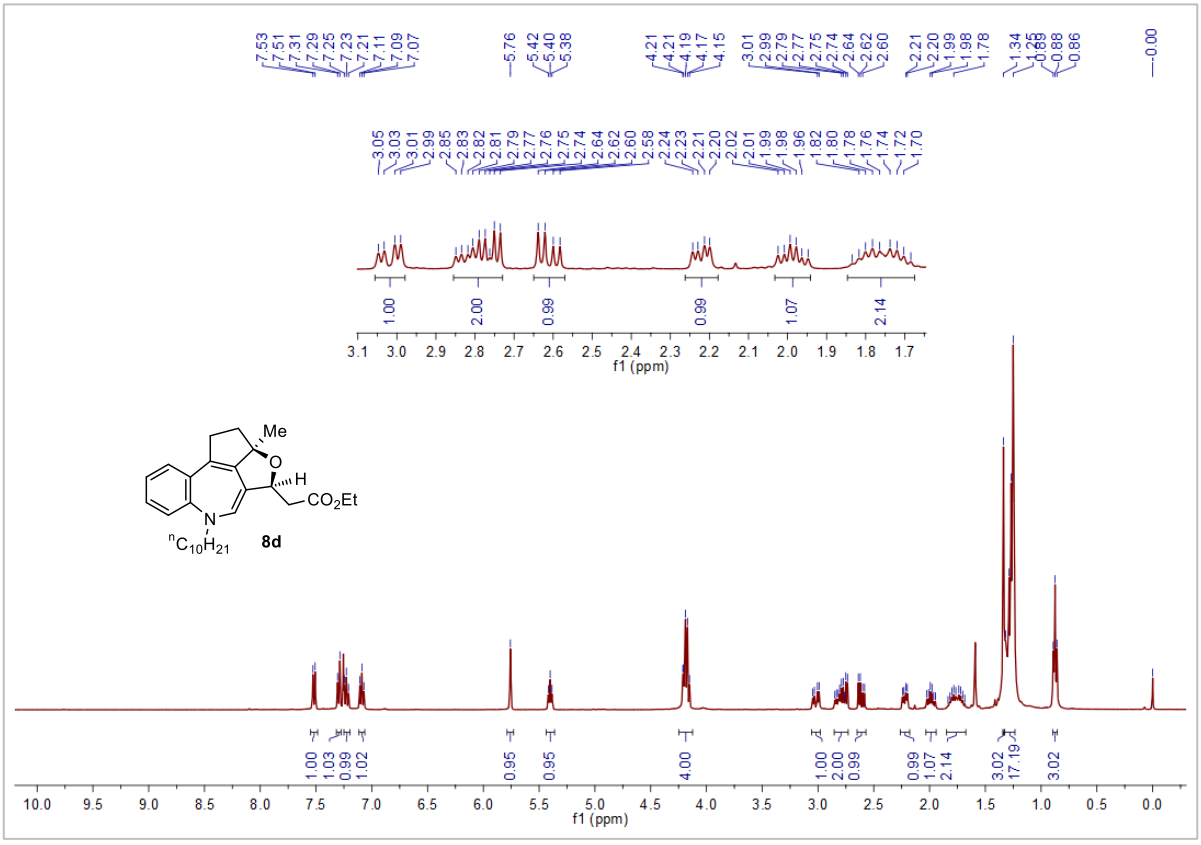


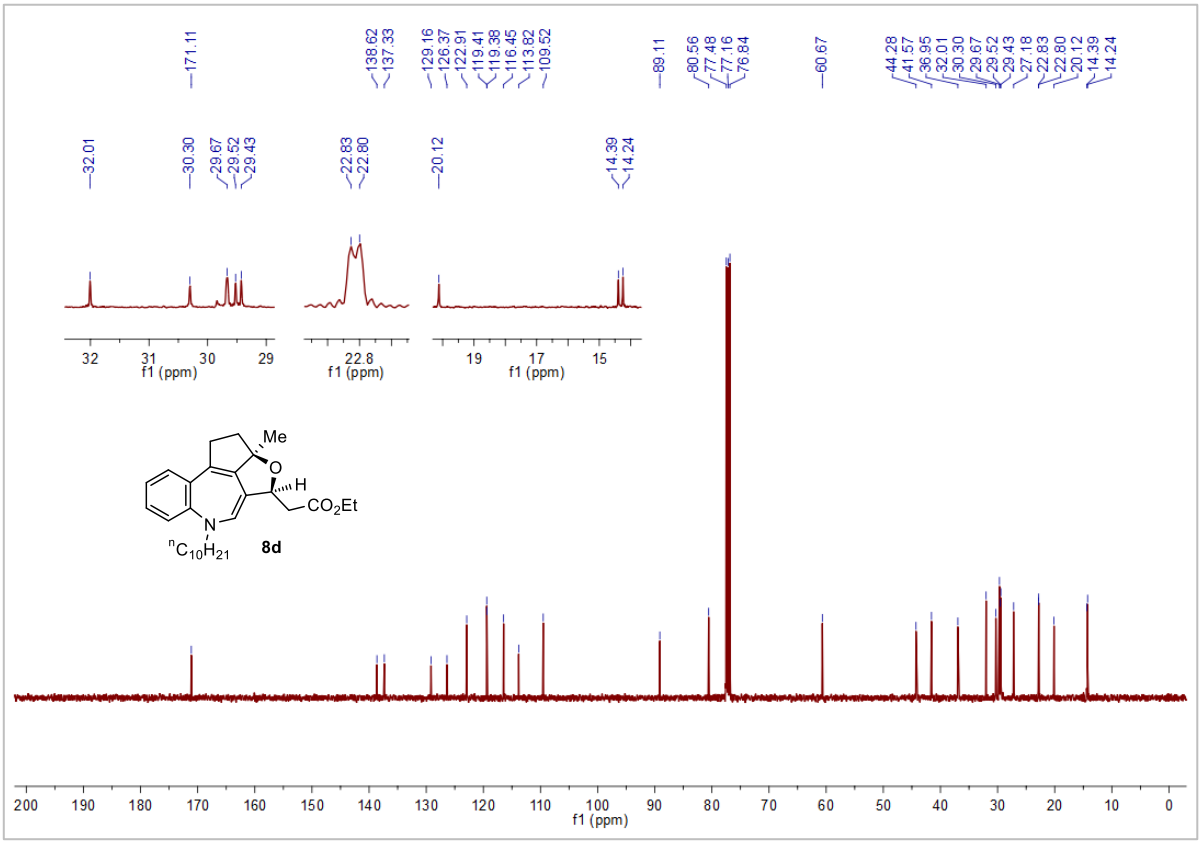
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **7d**.



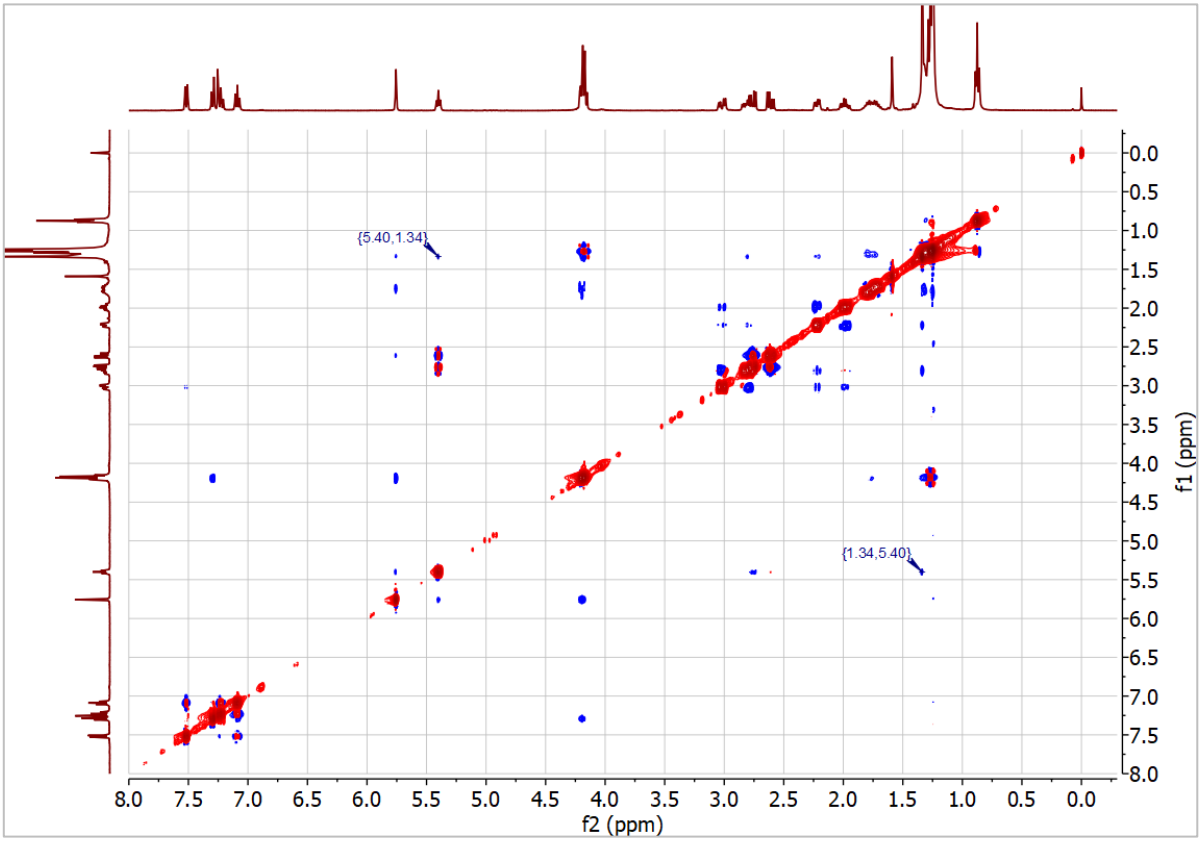


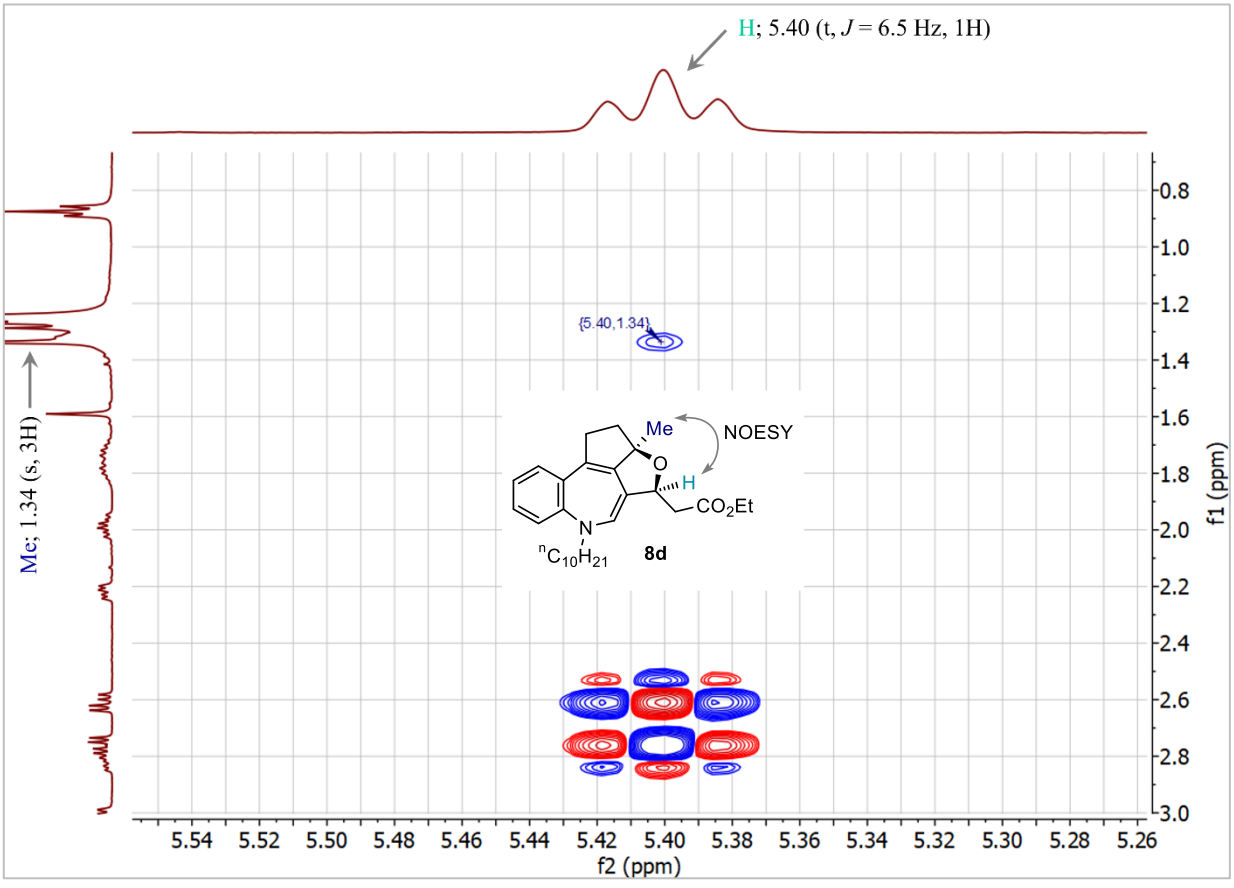
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **8d**.



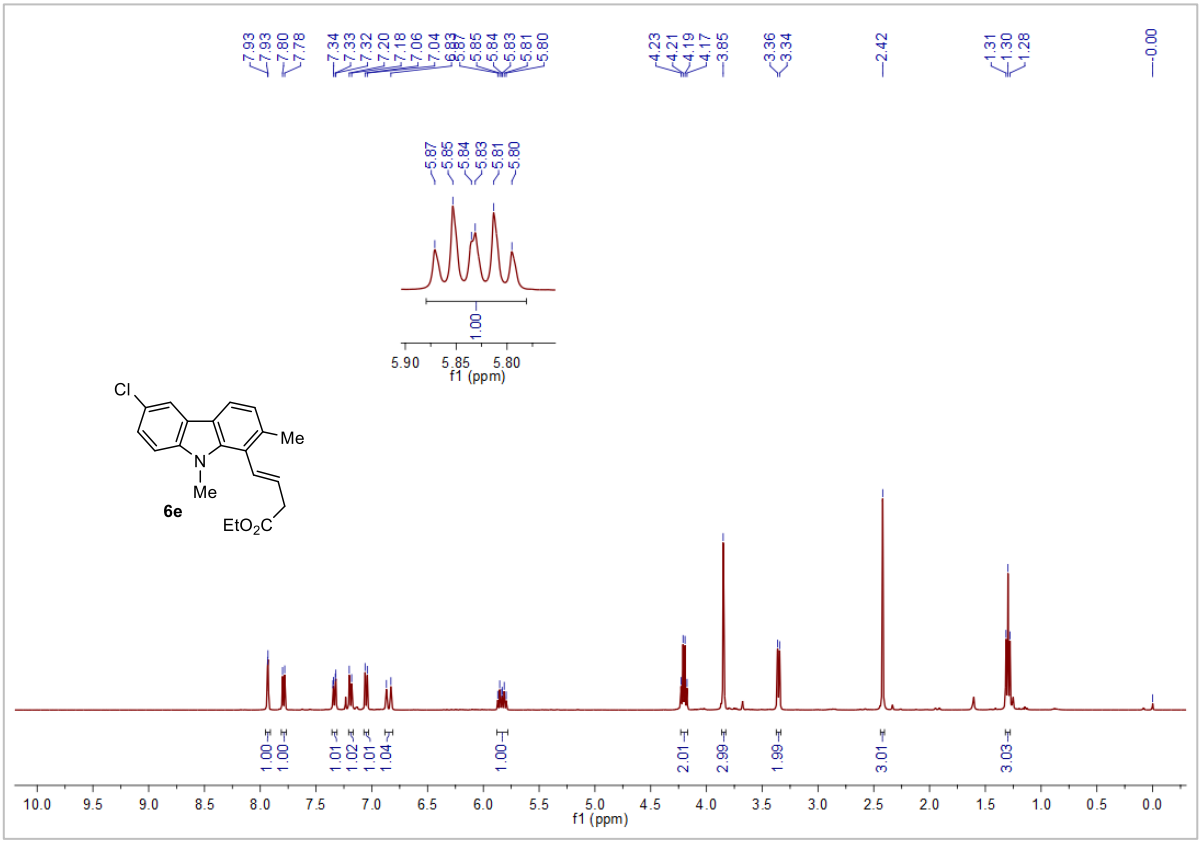


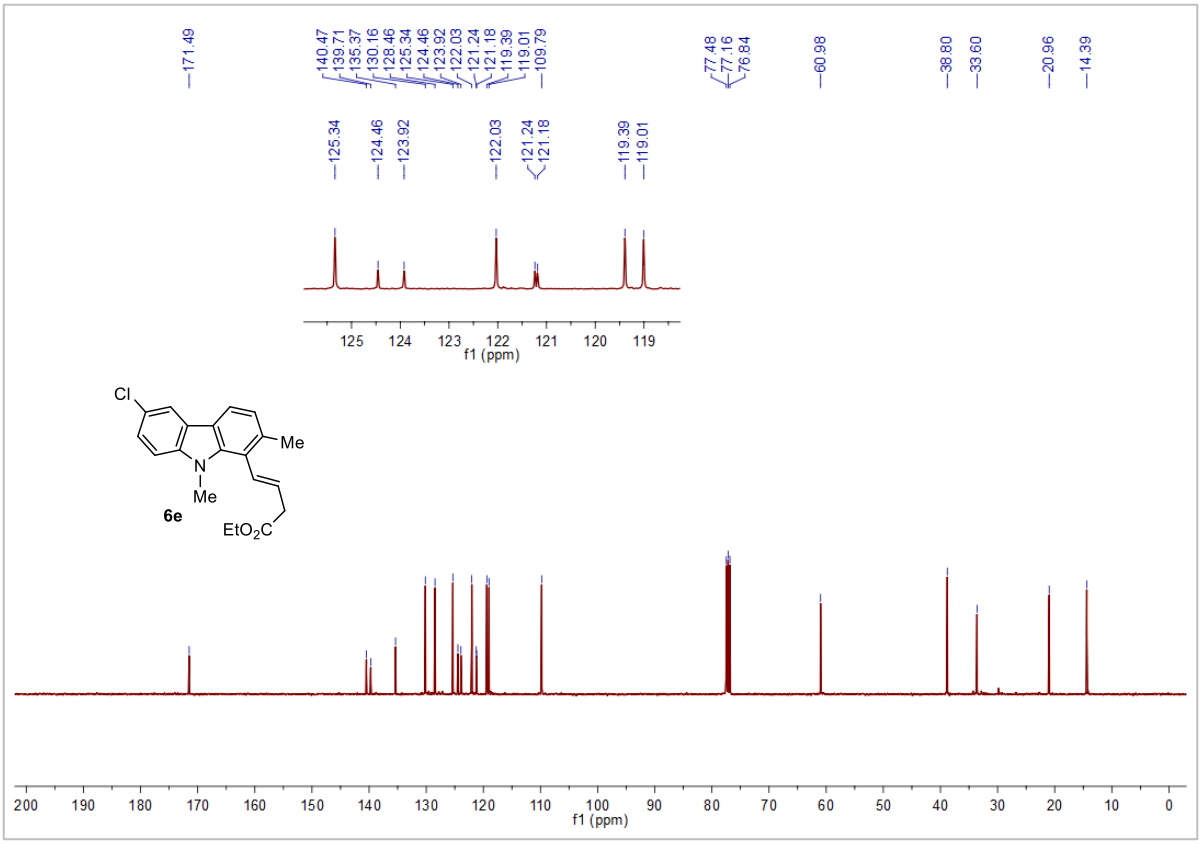
Full and zoomed view of NOESY NMR (400 MHz, $CDCl_3$) of **8d**.



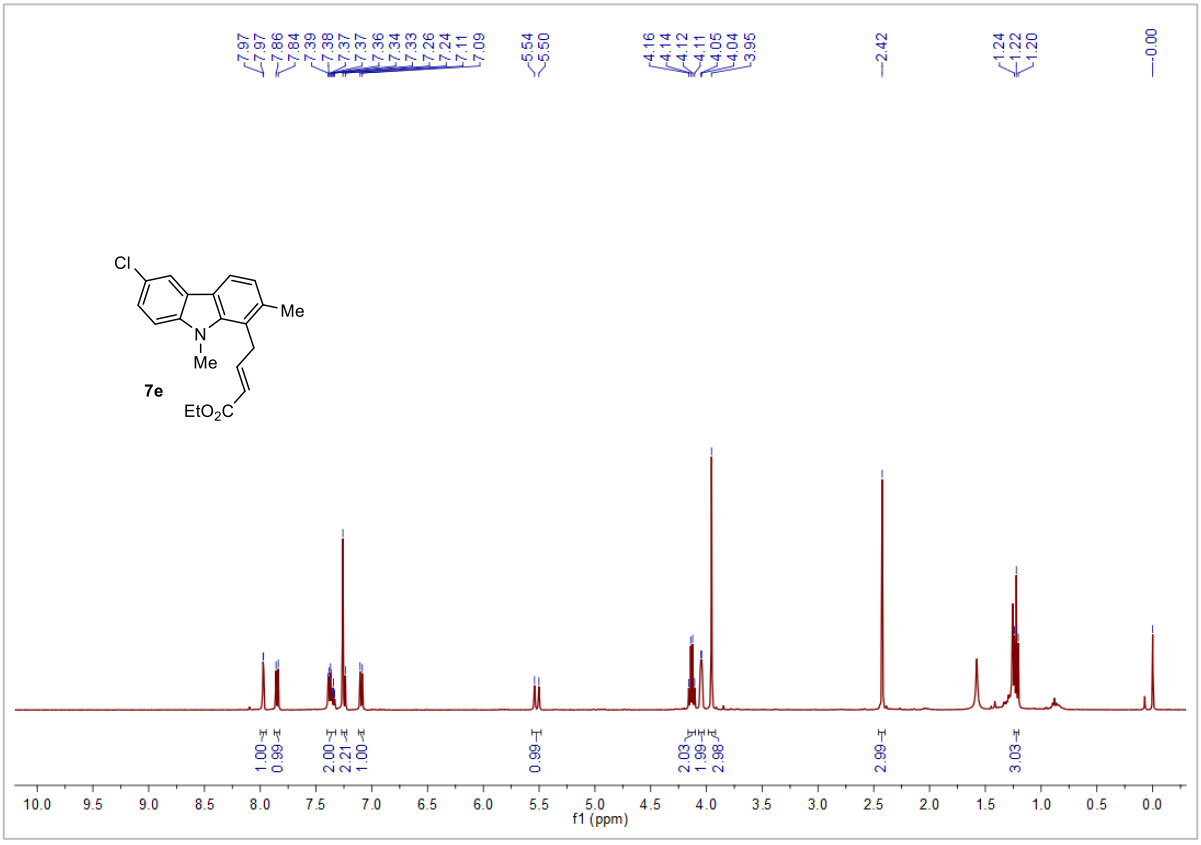


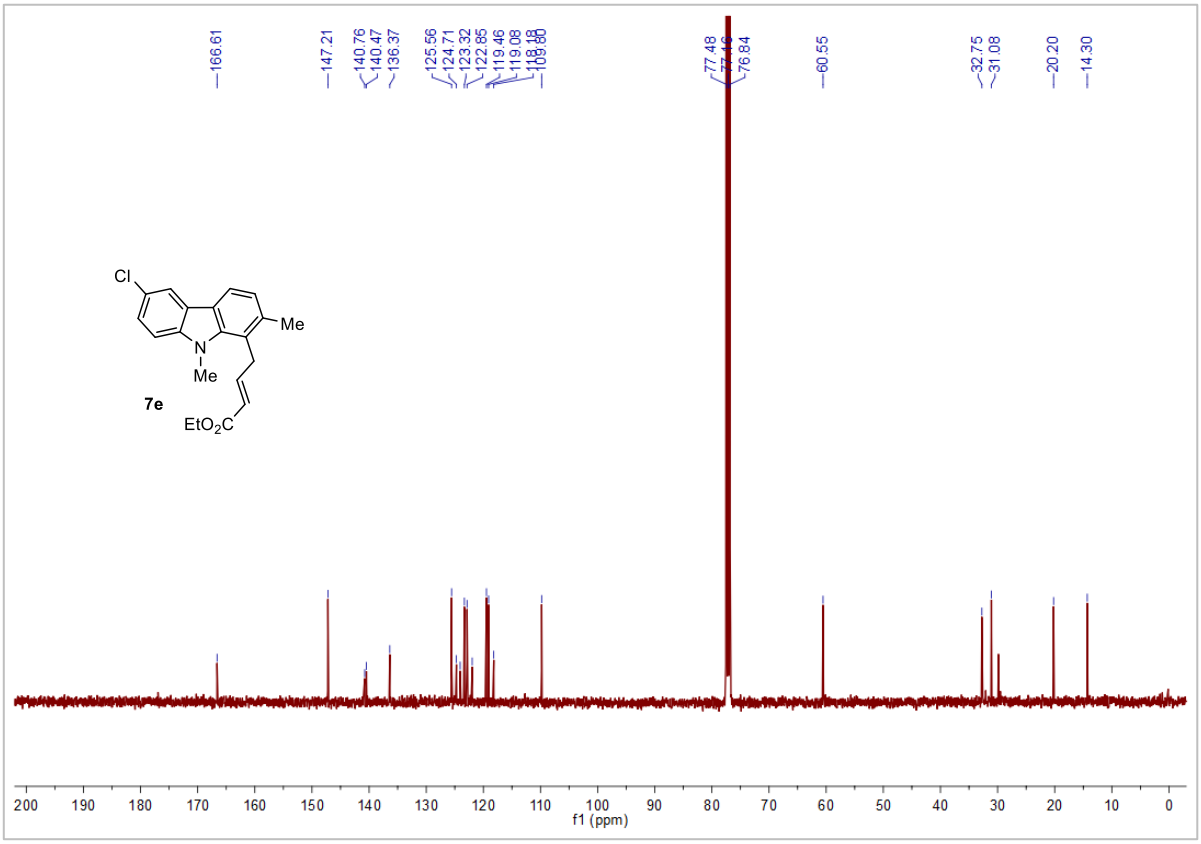
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **6e**.



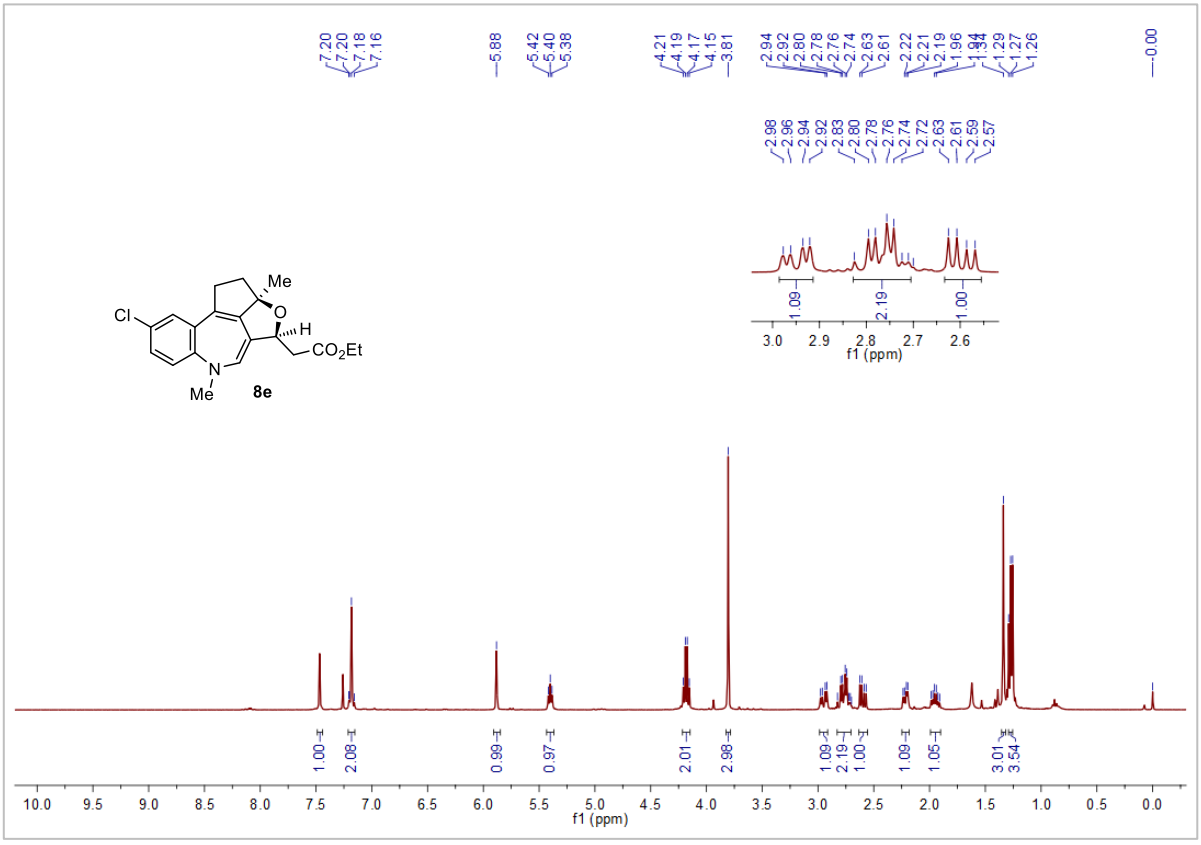


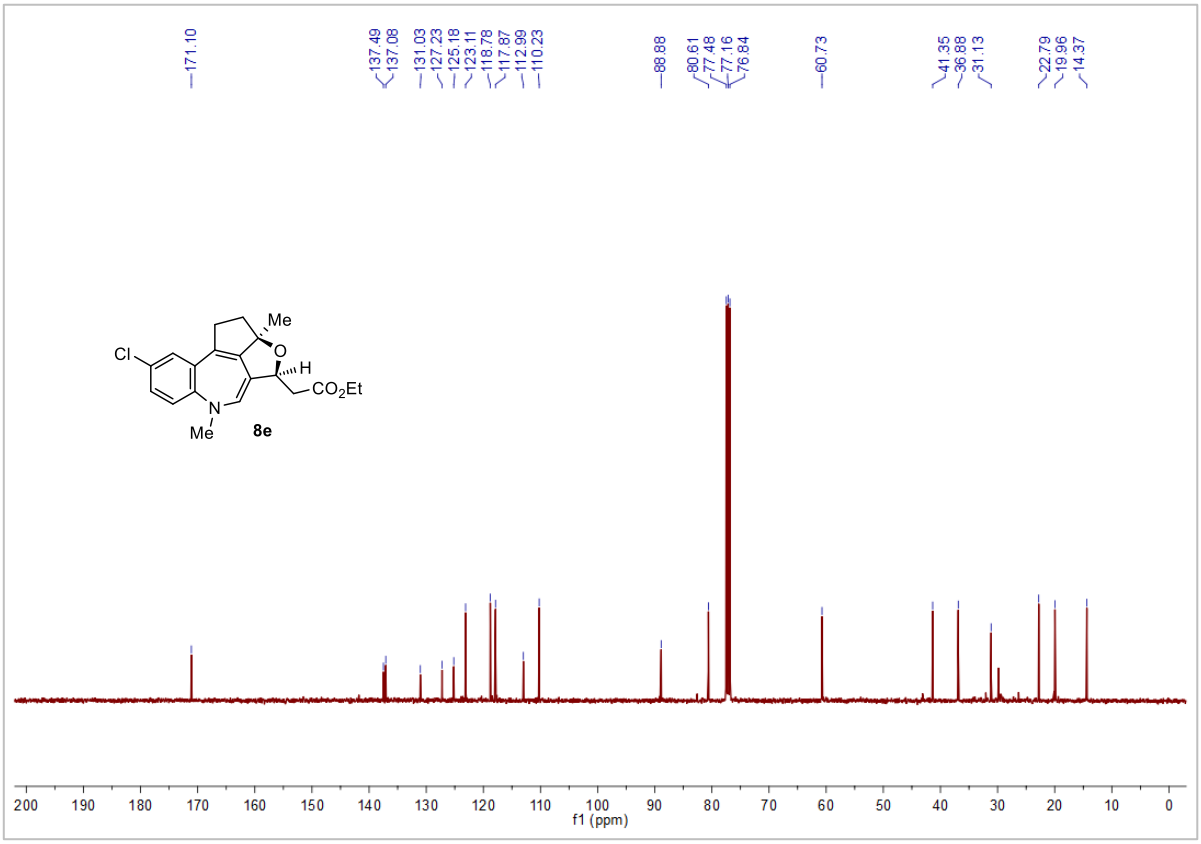
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **7e**.



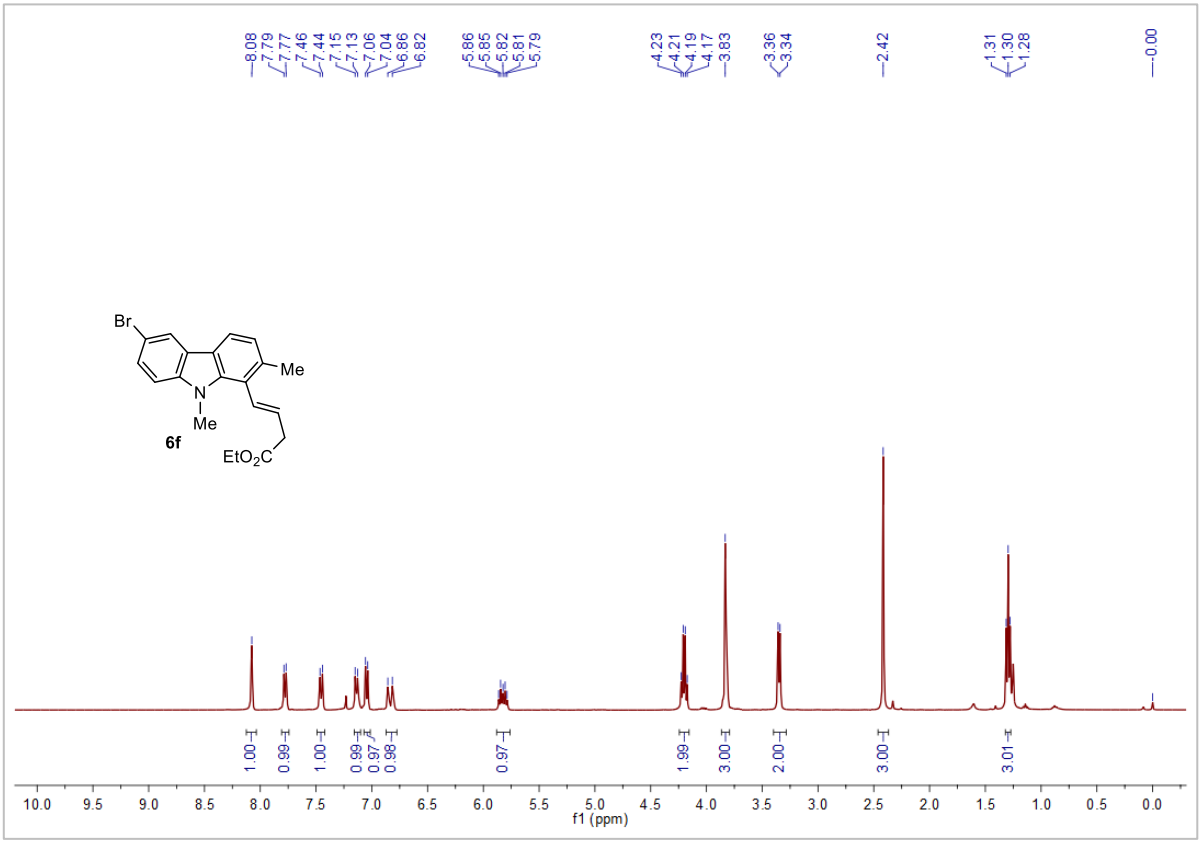


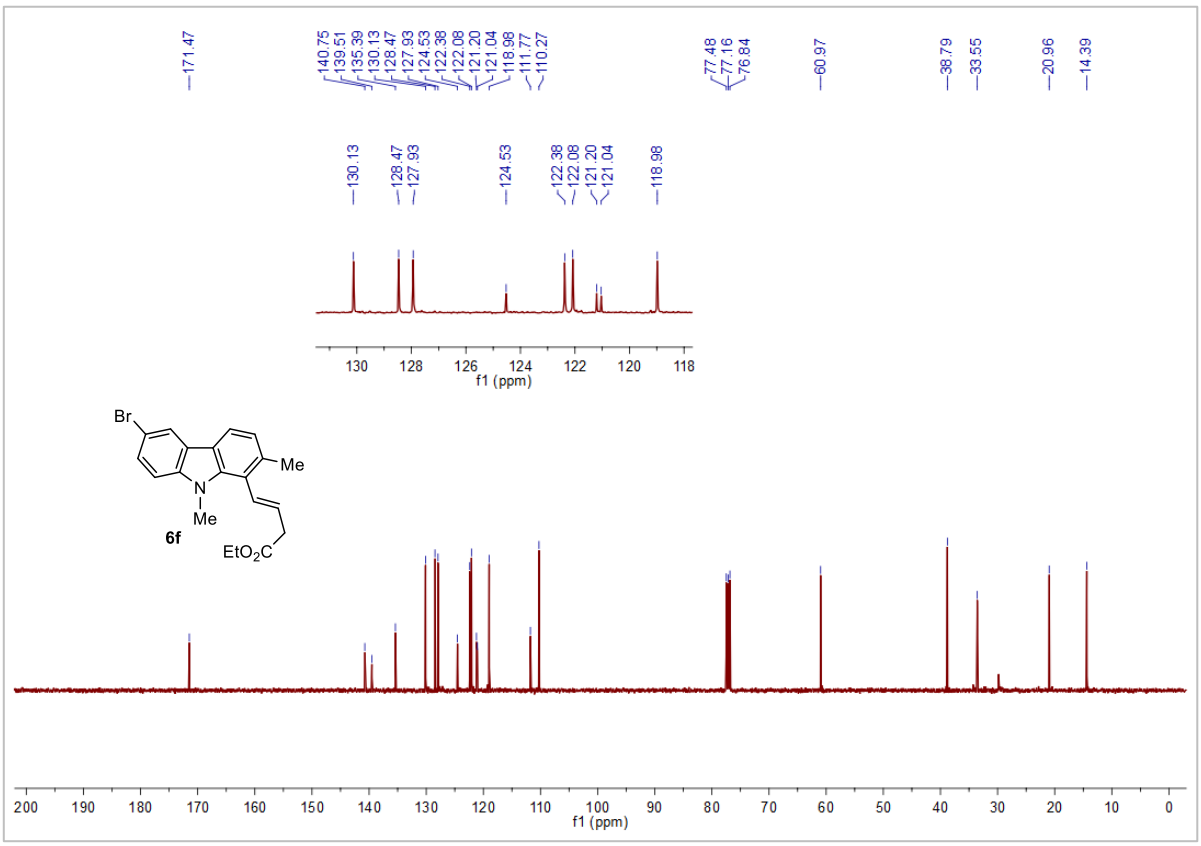
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **8e**.



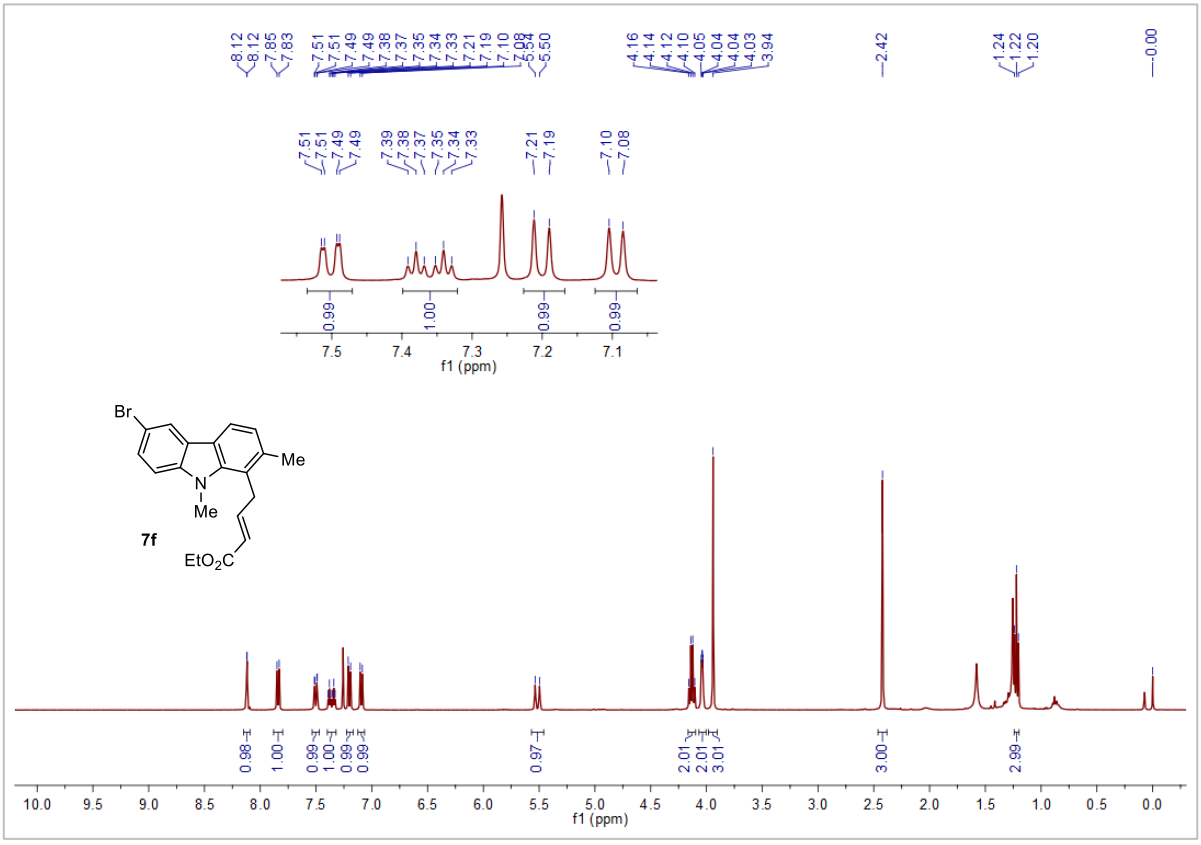


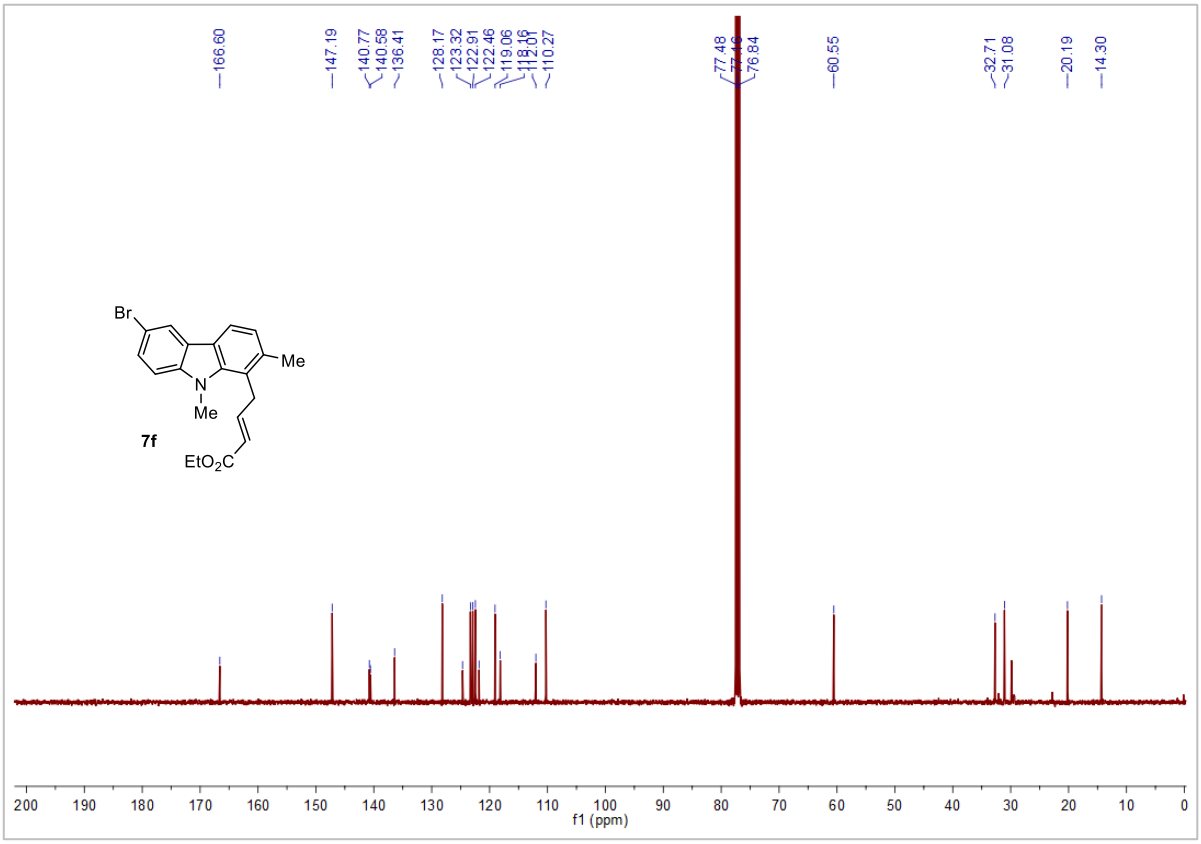
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **6f**.



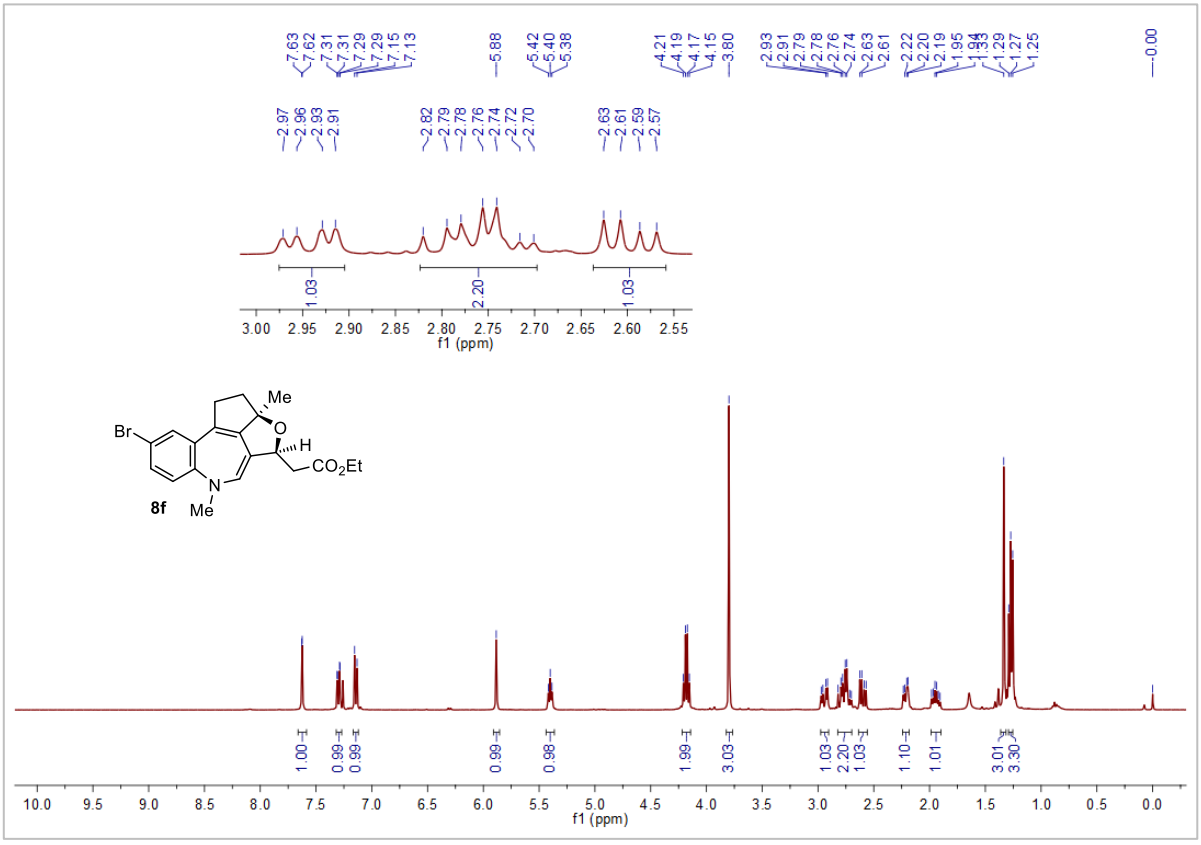


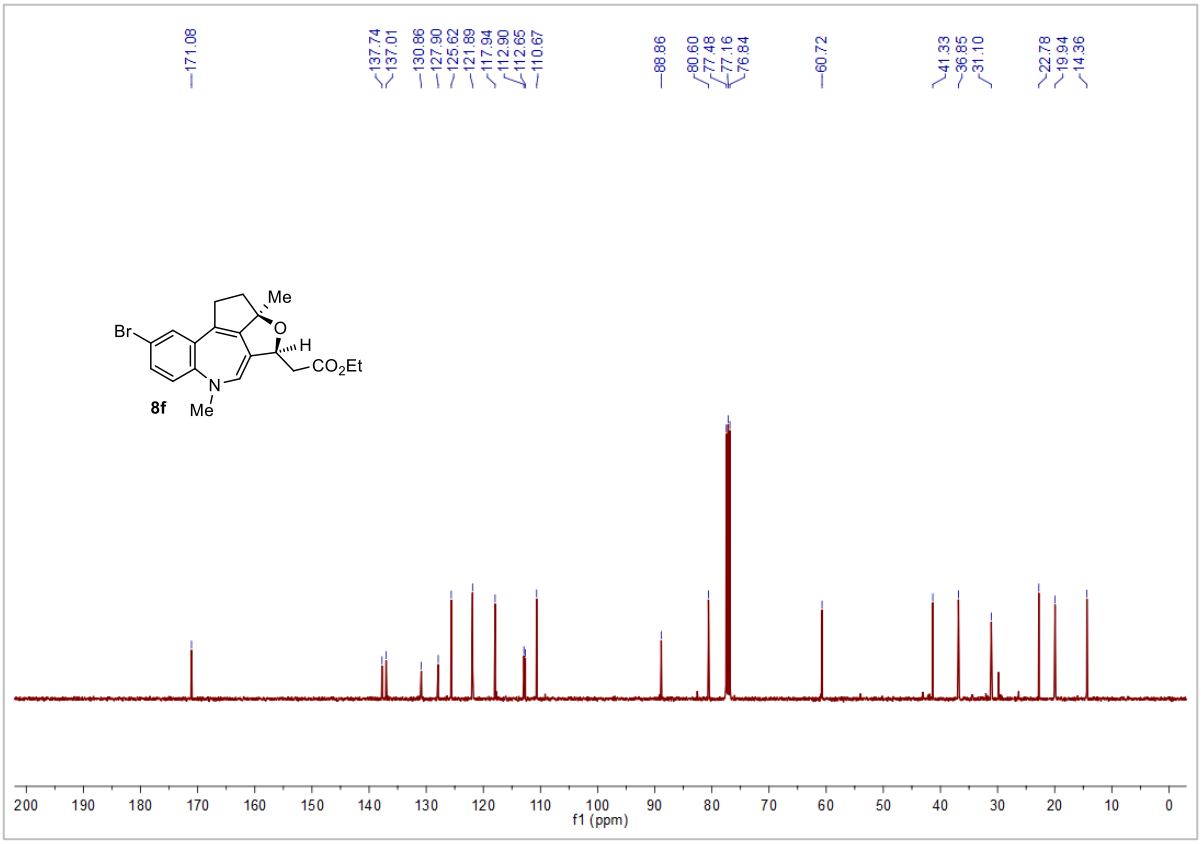
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **7f**.



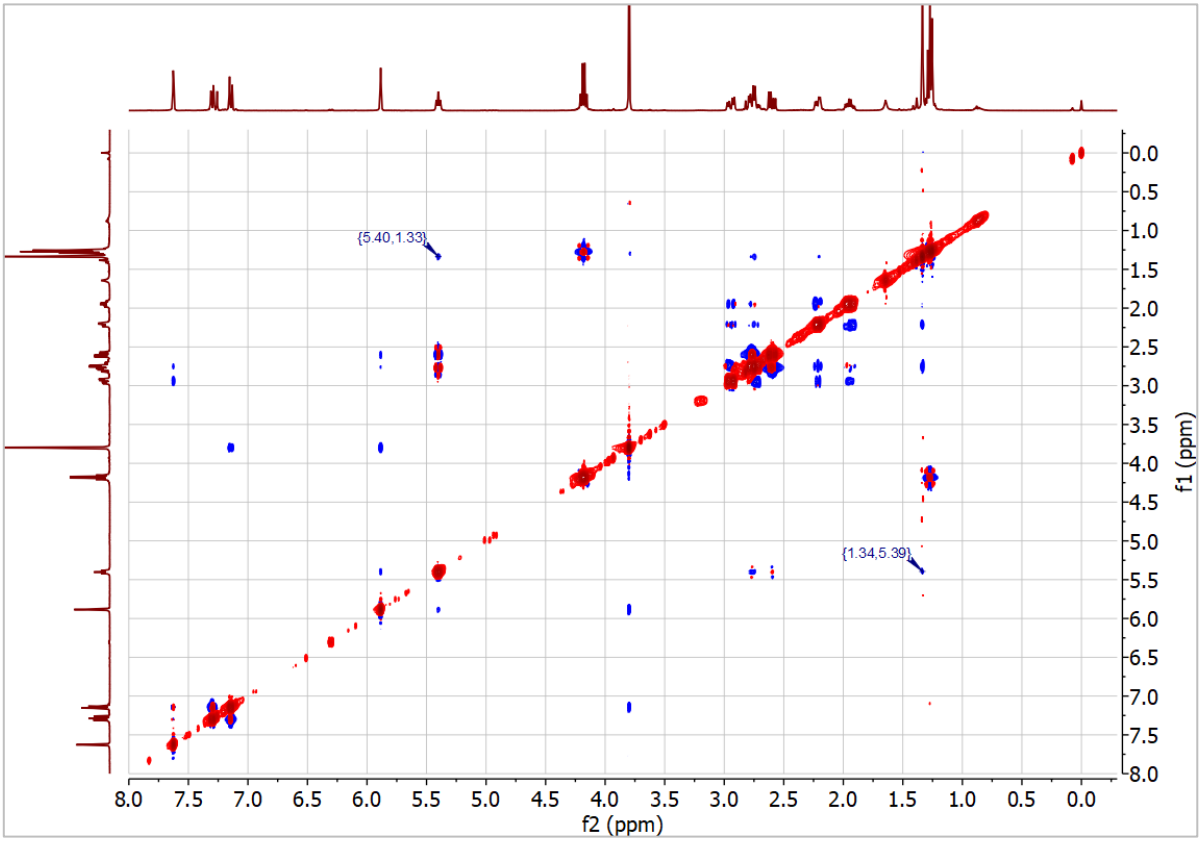


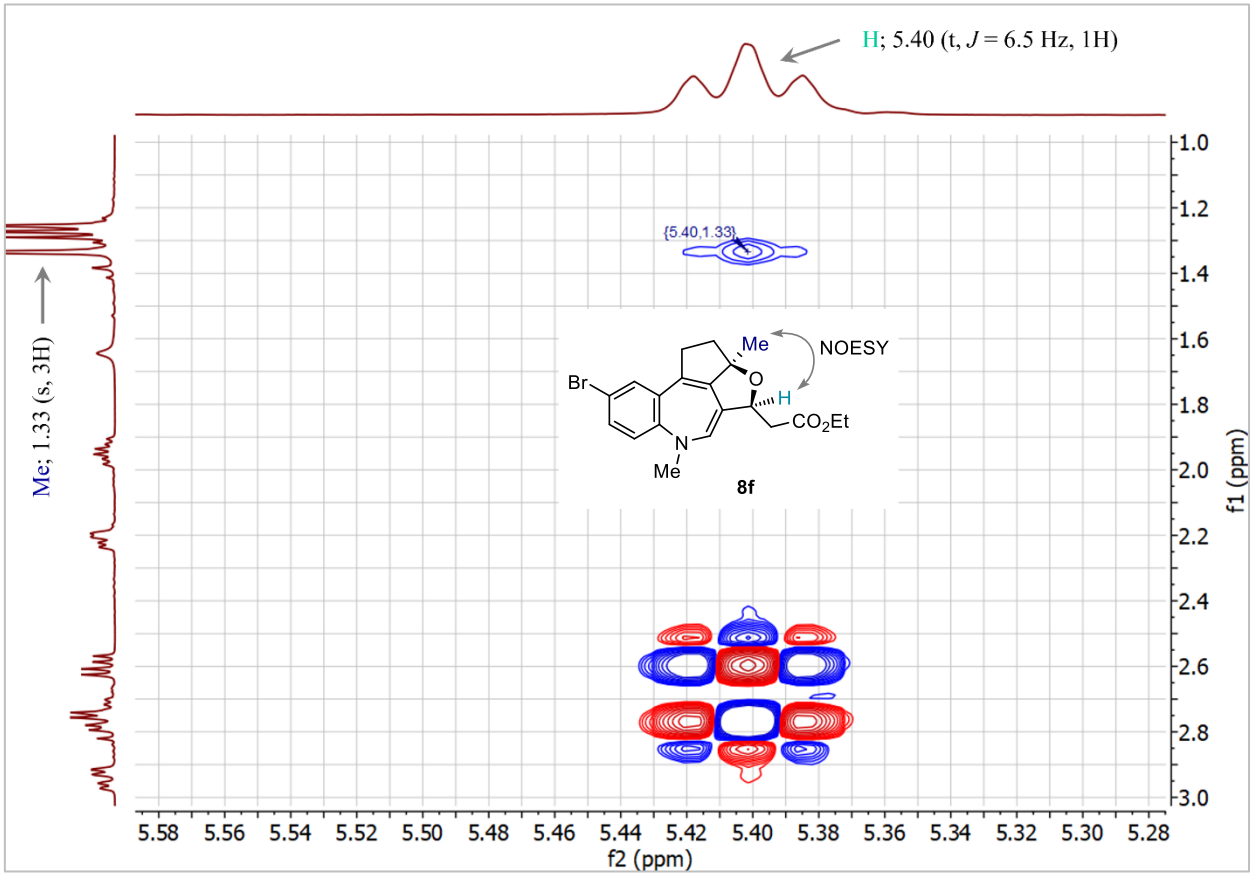
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **8f**.



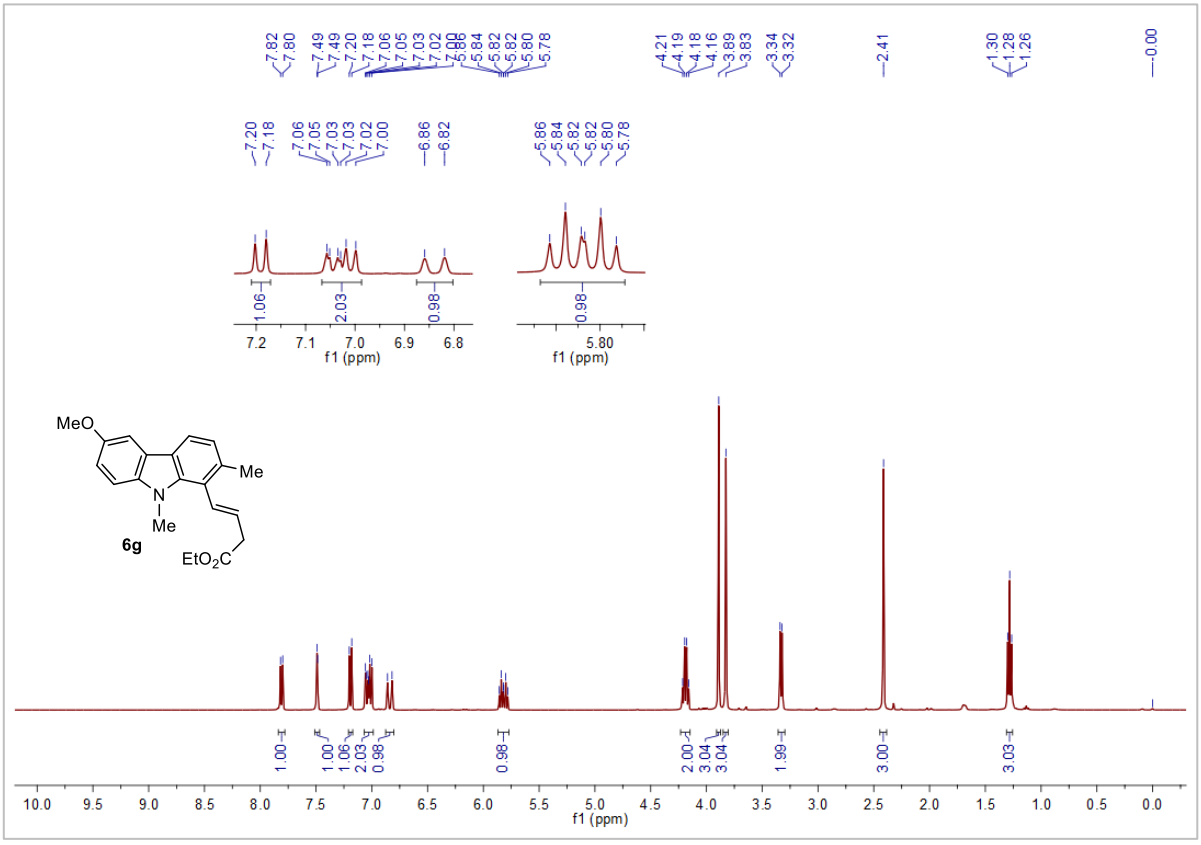


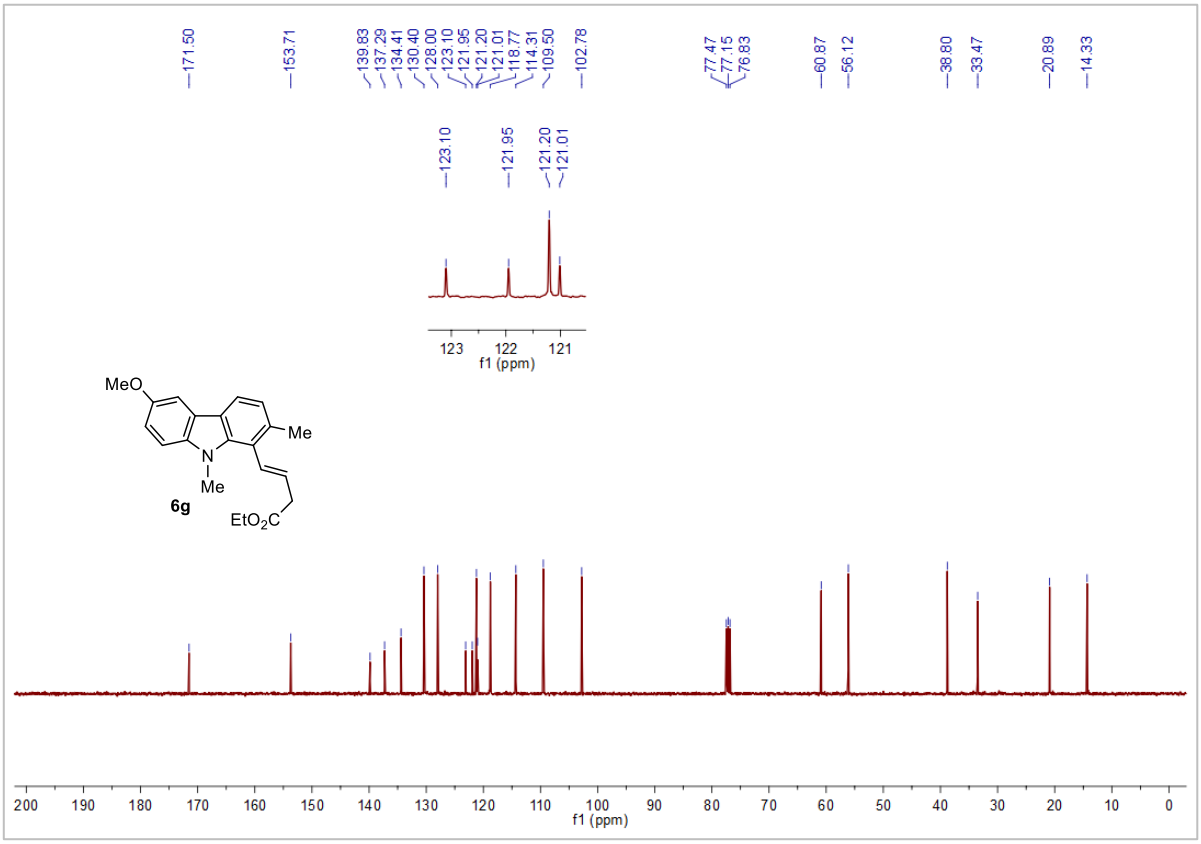
Full and zoomed view of NOESY NMR (400 MHz, $CDCl_3$) of **8f**.



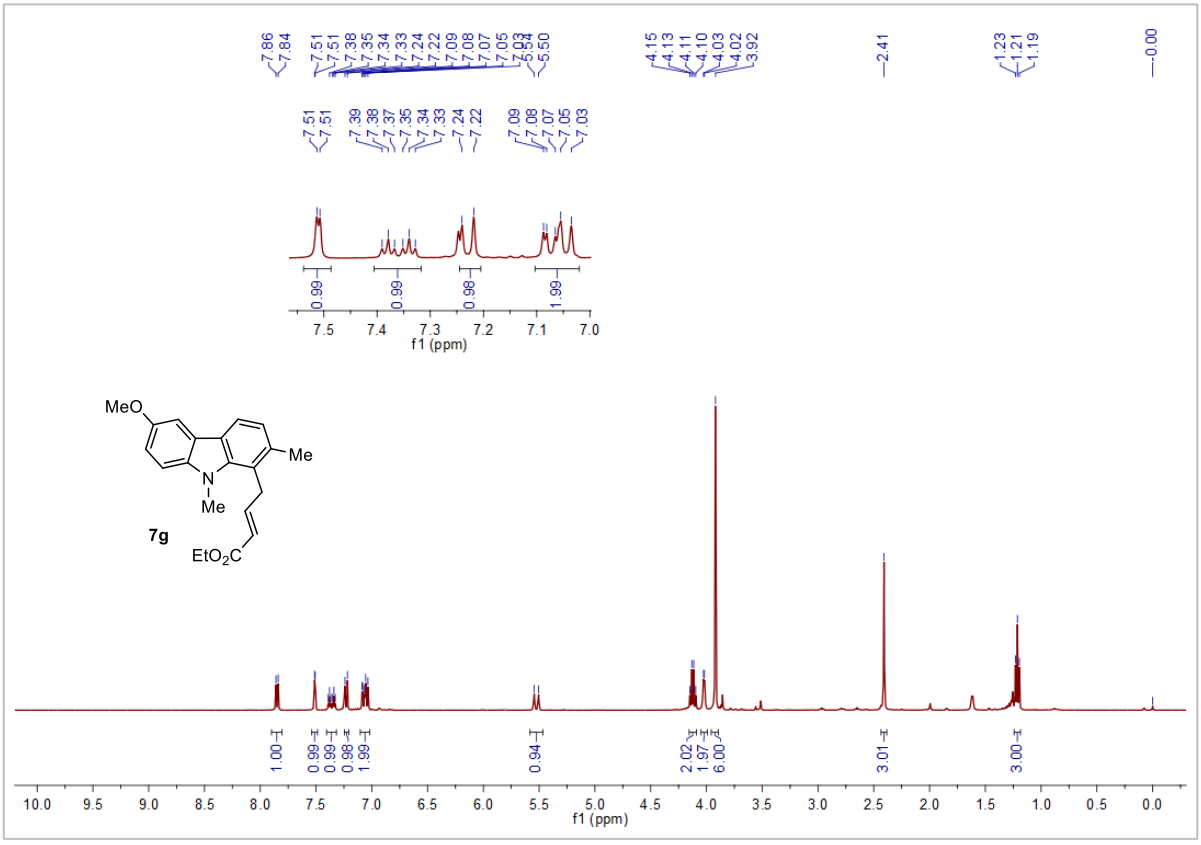


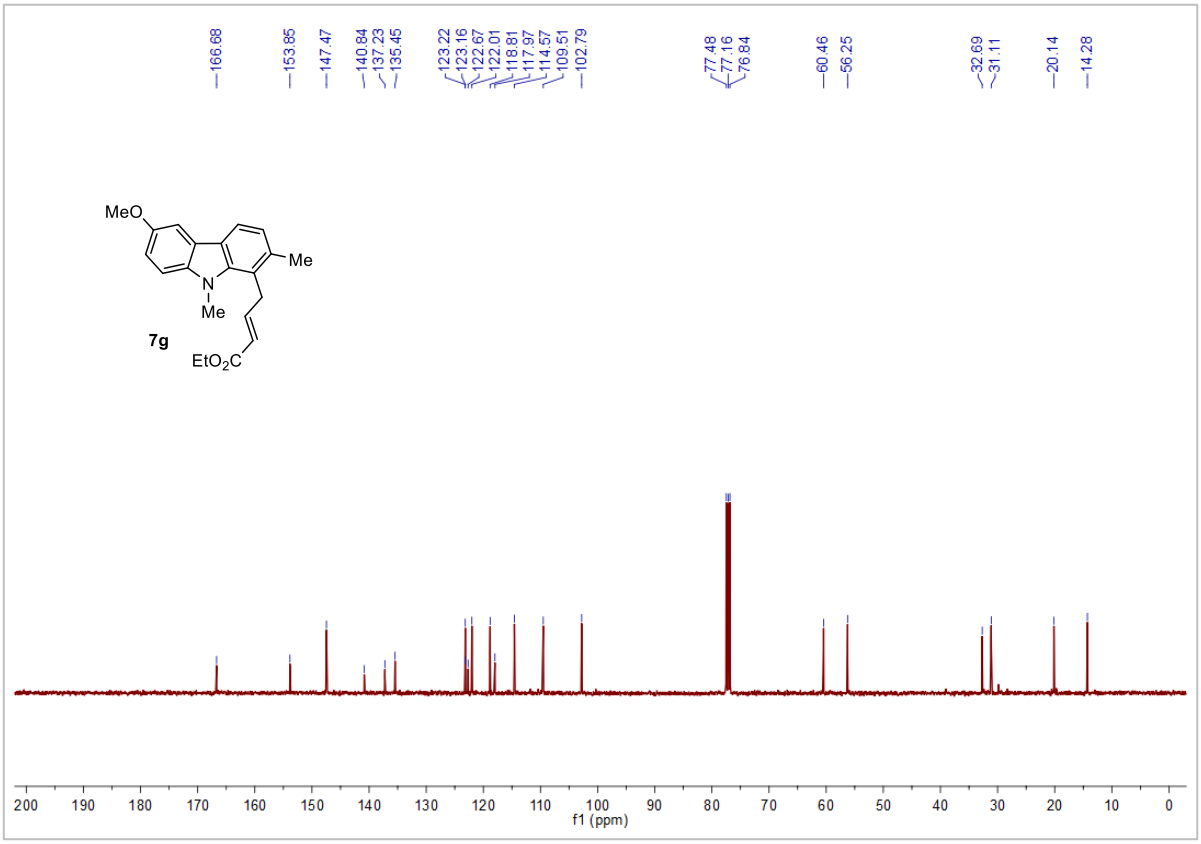
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **6g**.



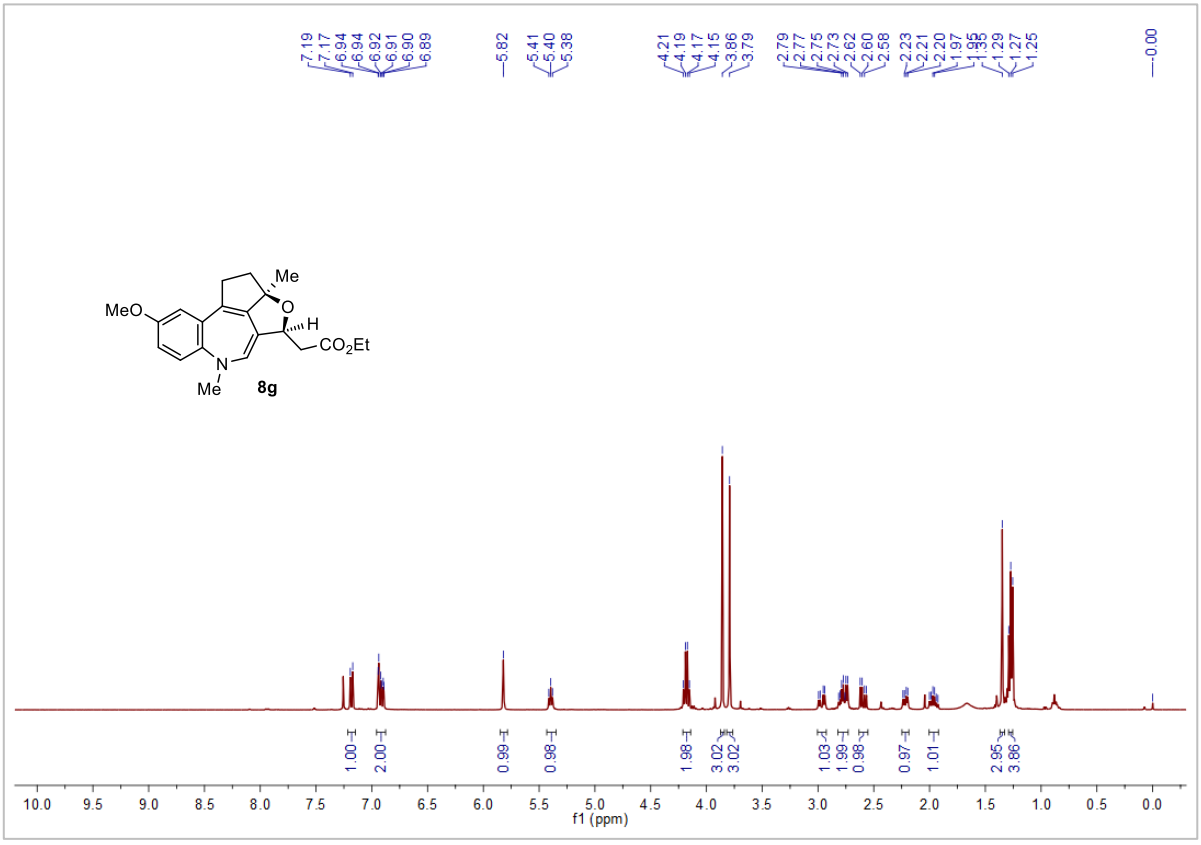


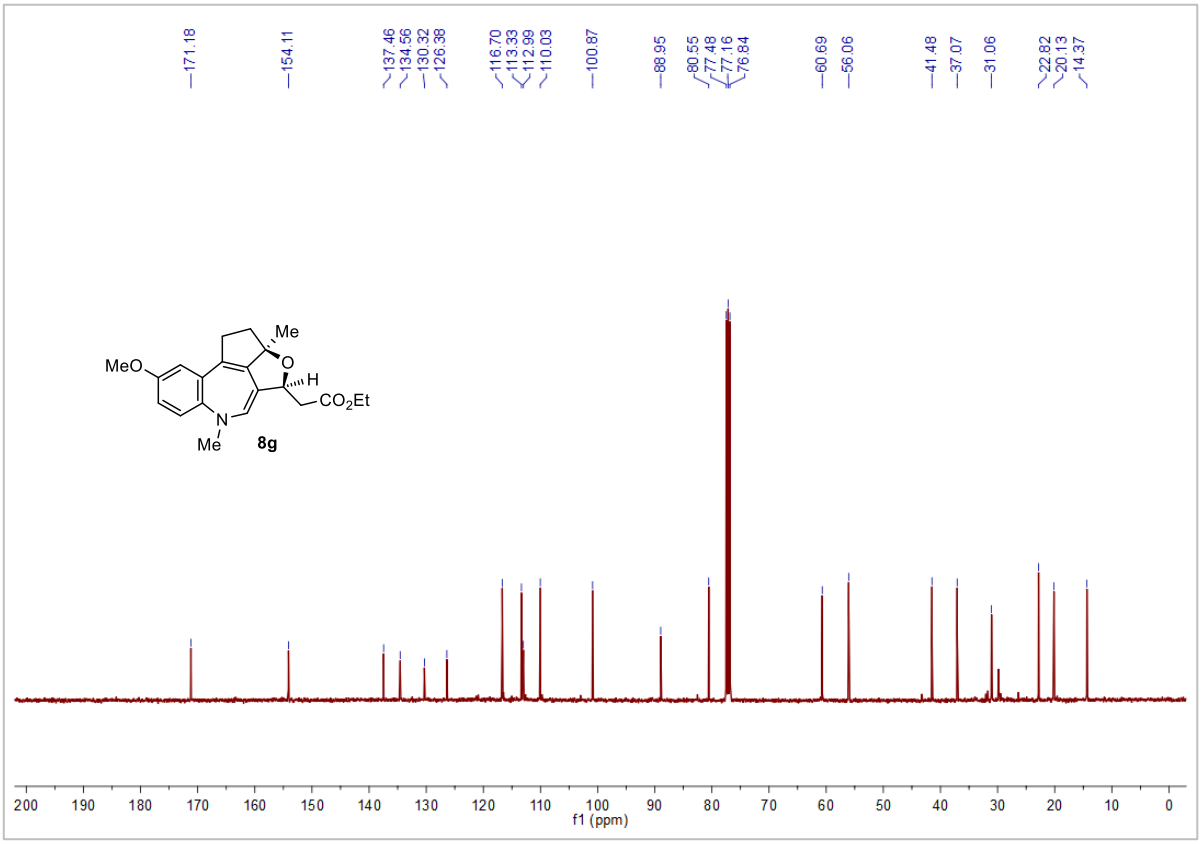
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **7g**.



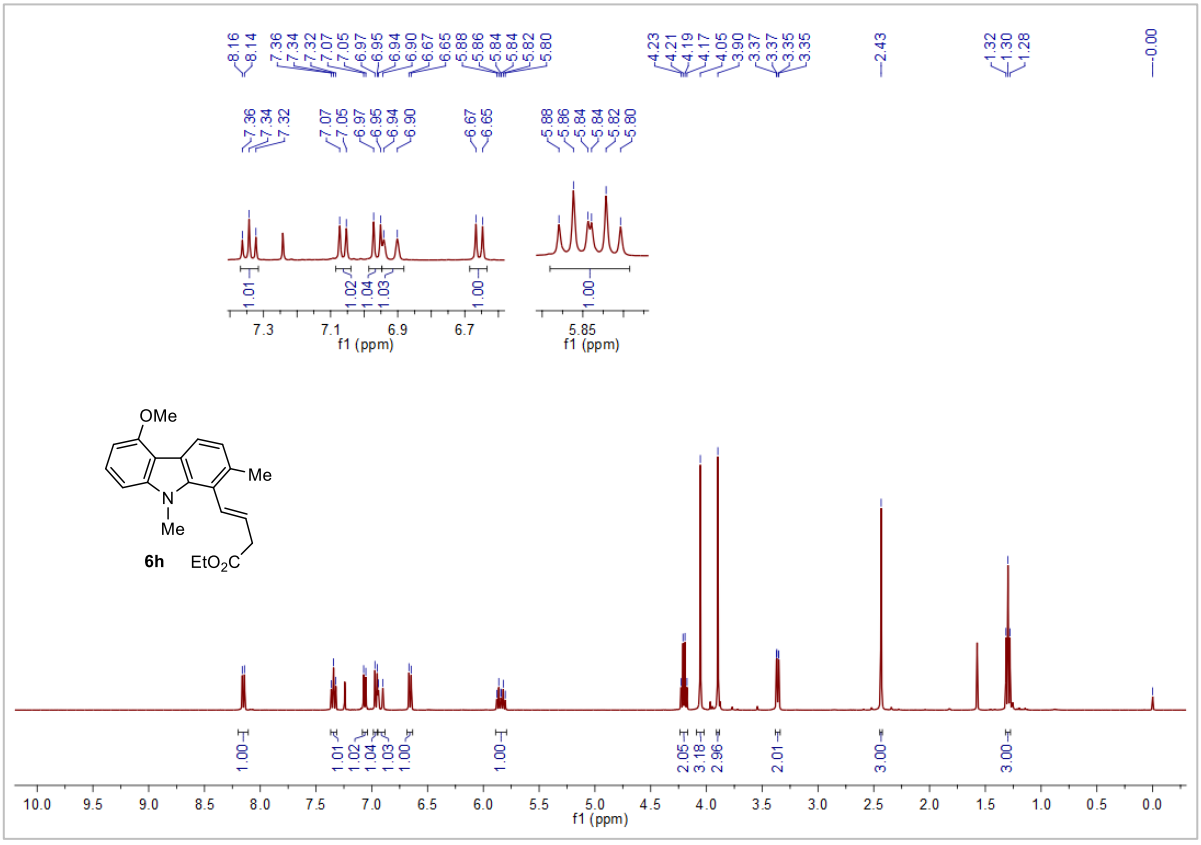


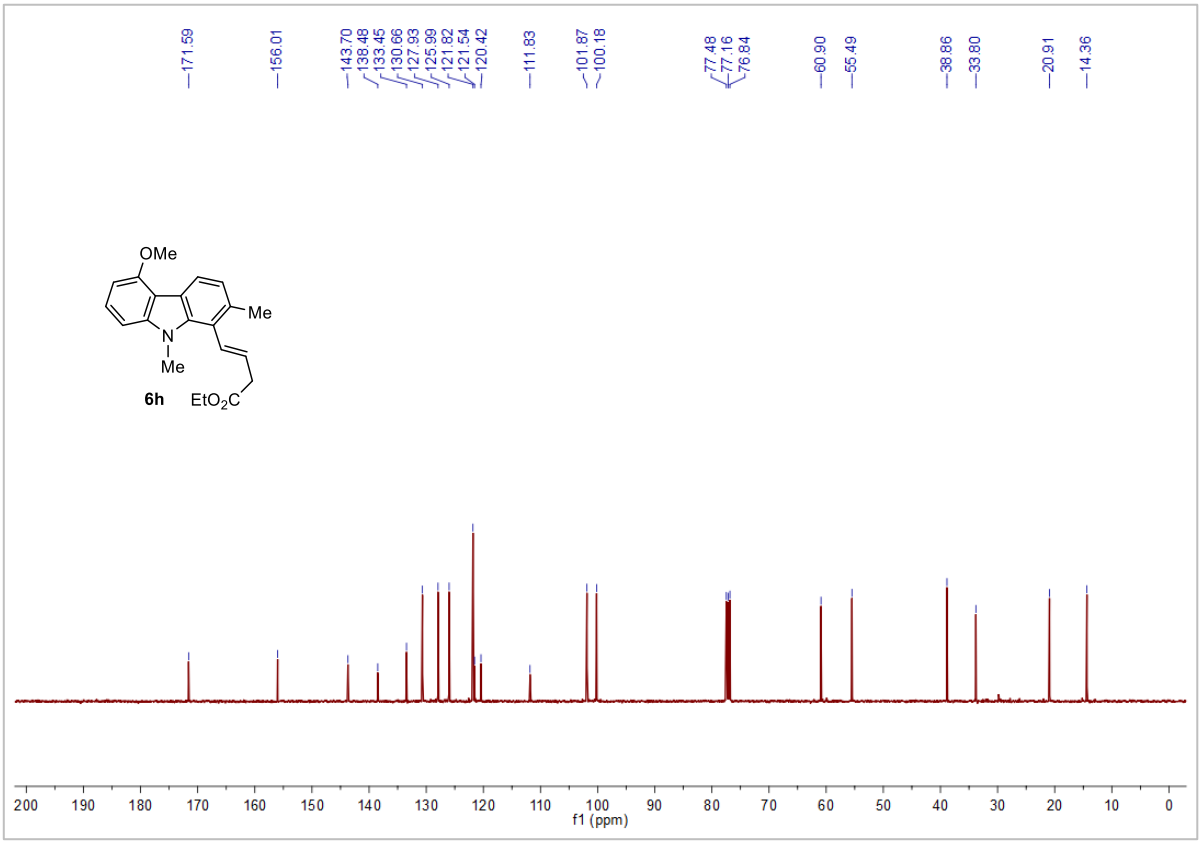
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **8g**.



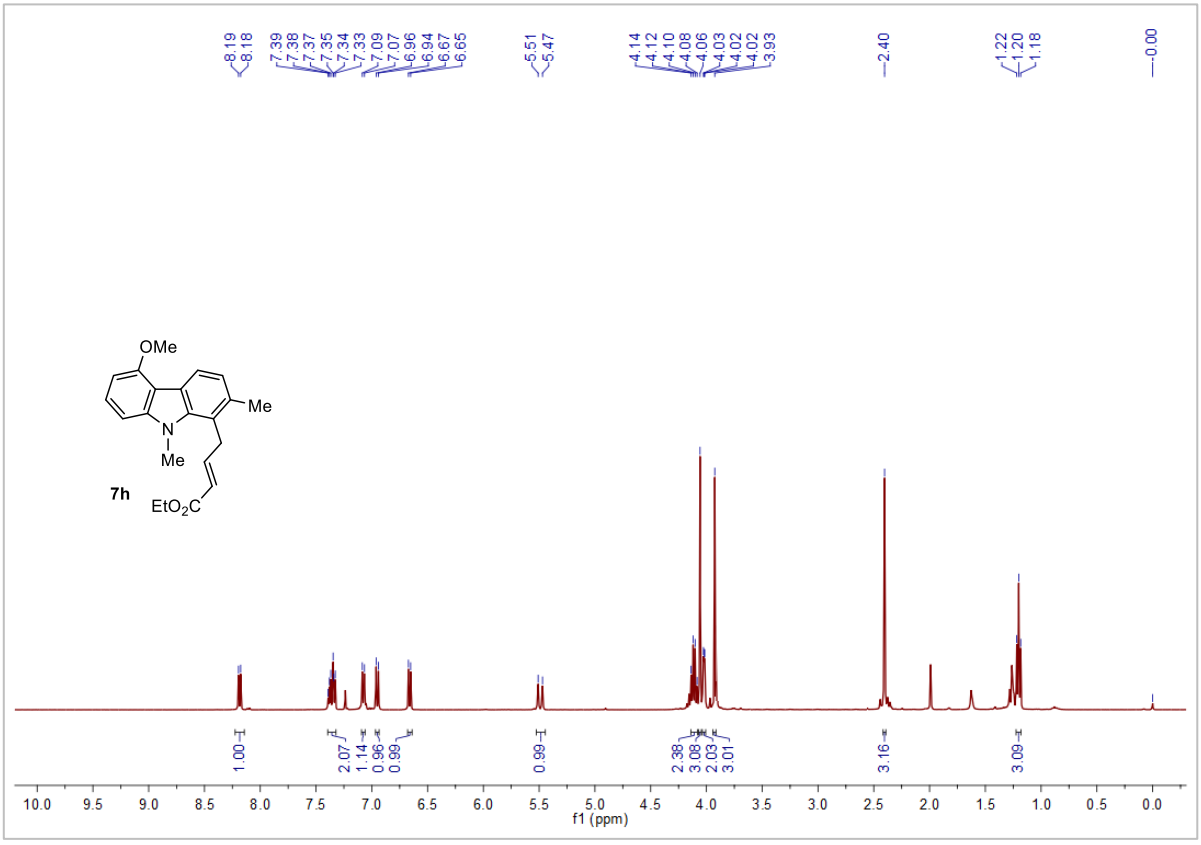


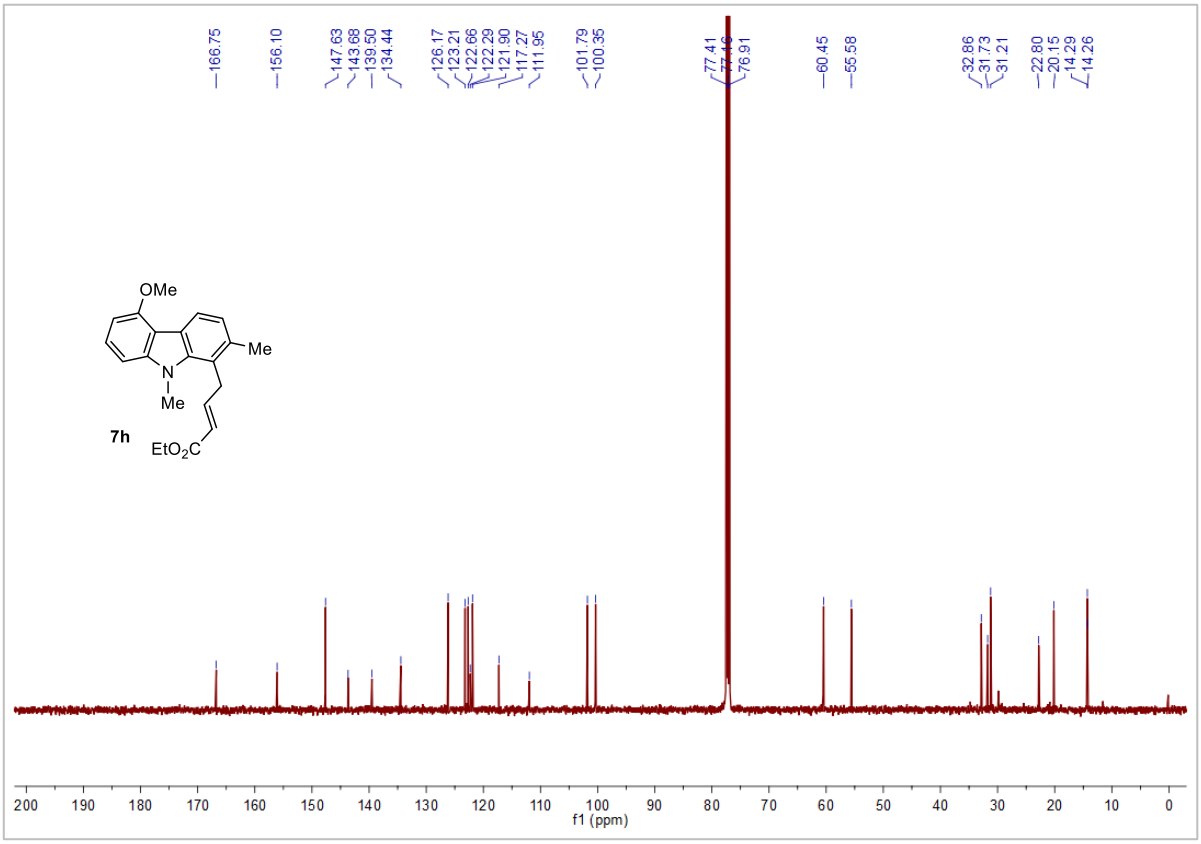
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **6h**.



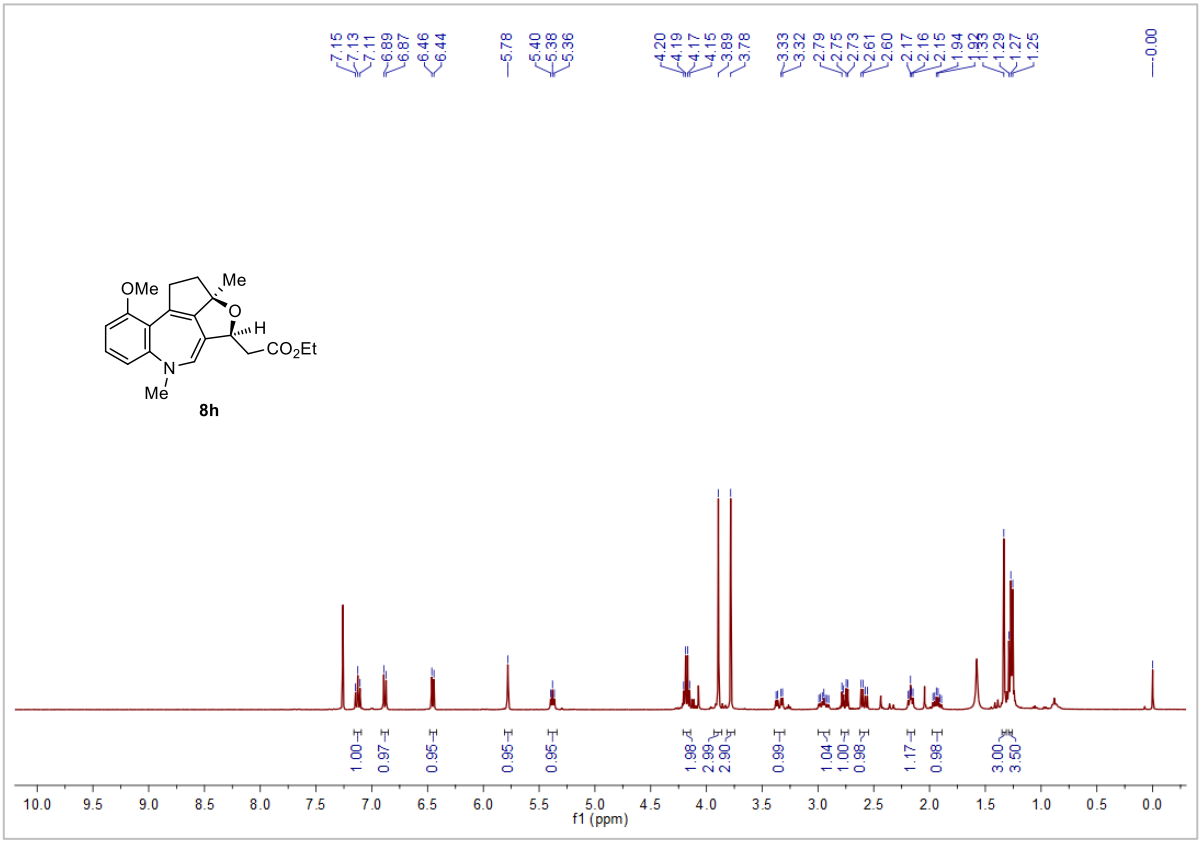


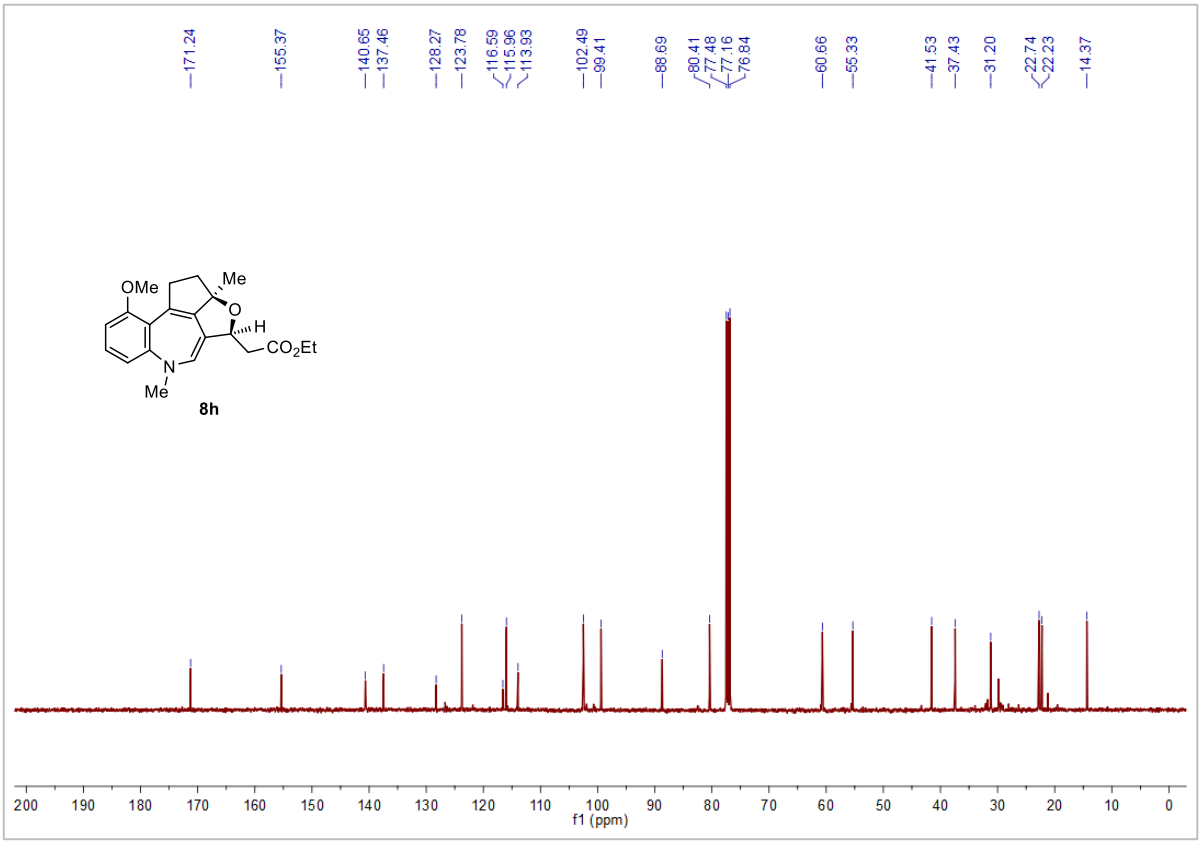
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **7h**.



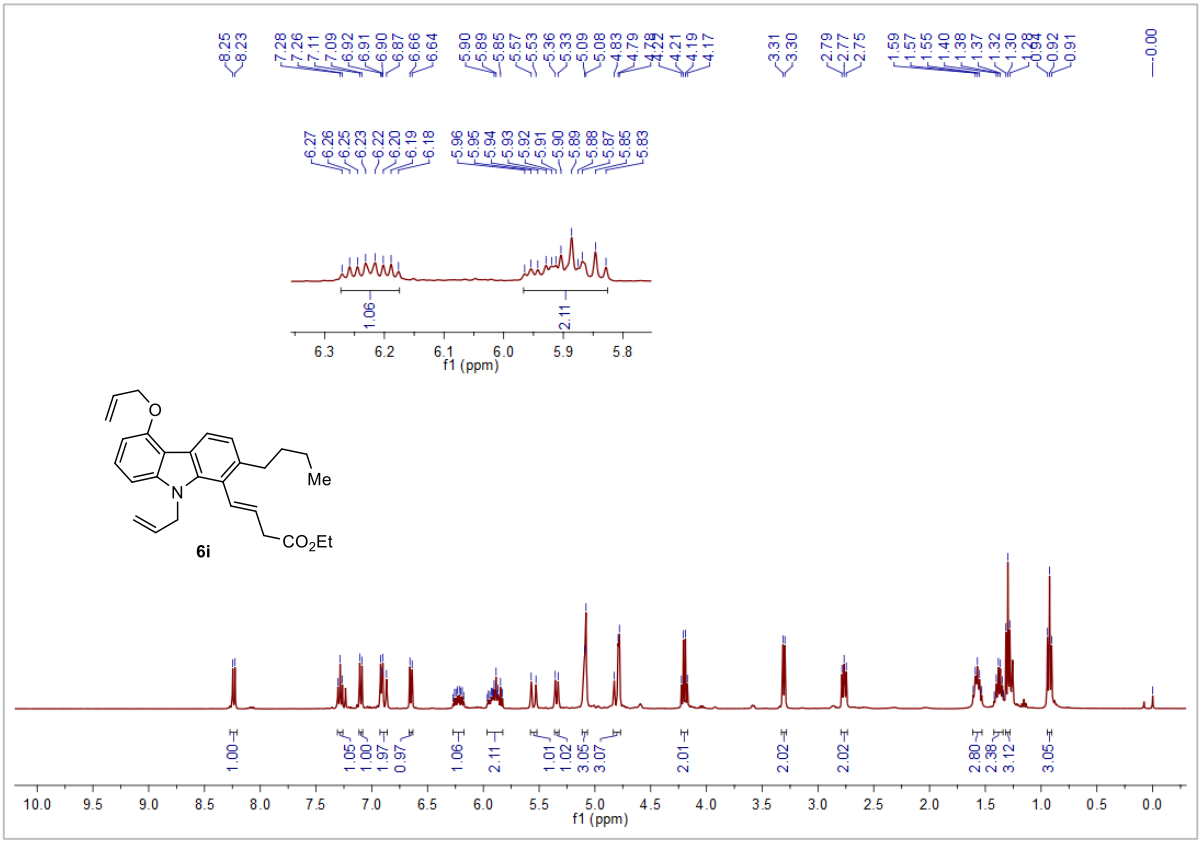


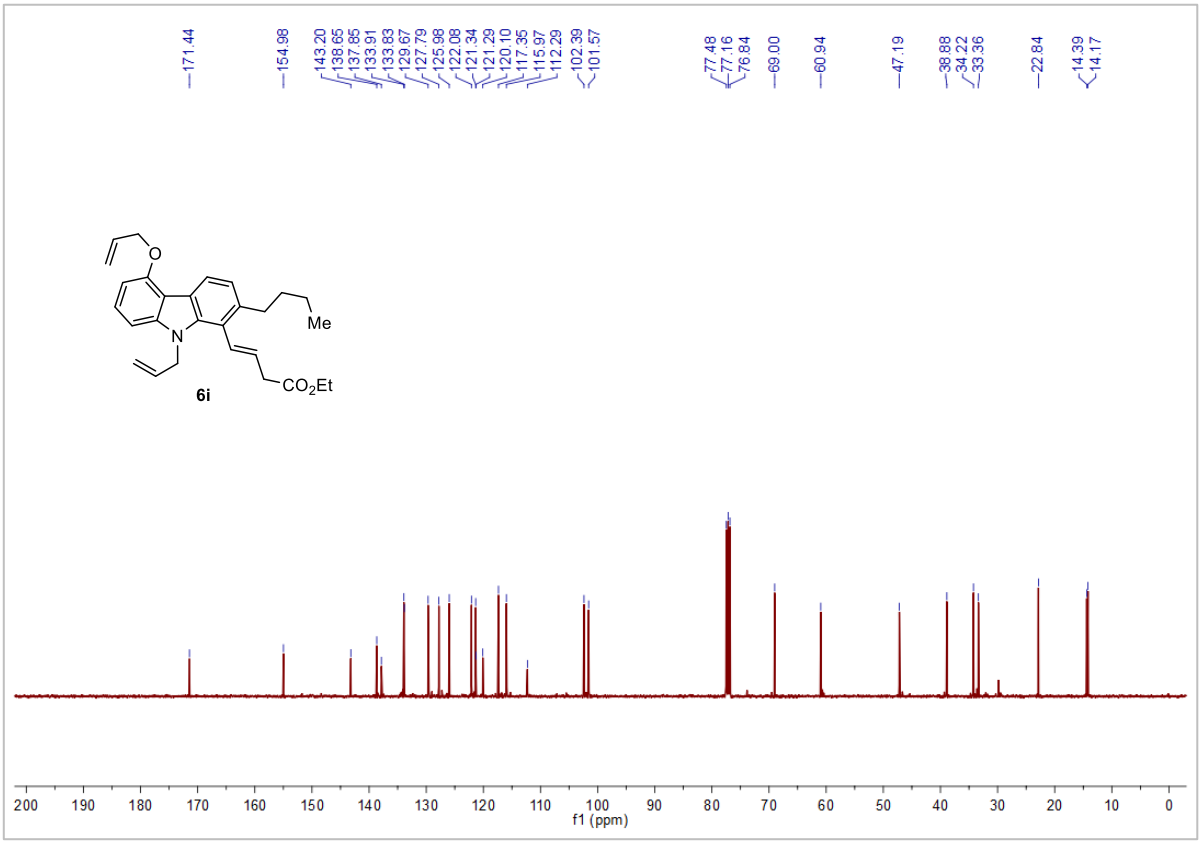
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **8h**.



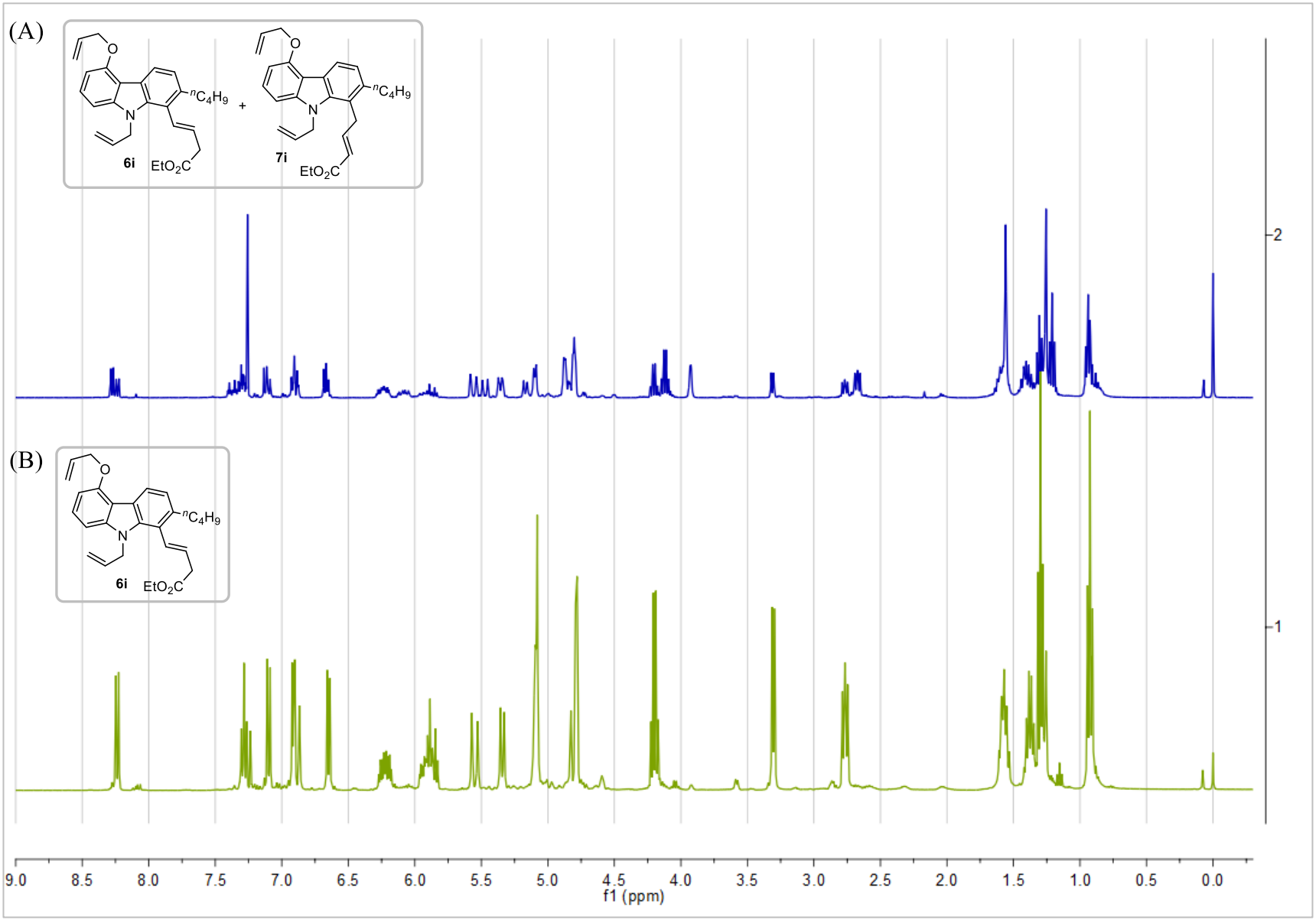


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **6i**.

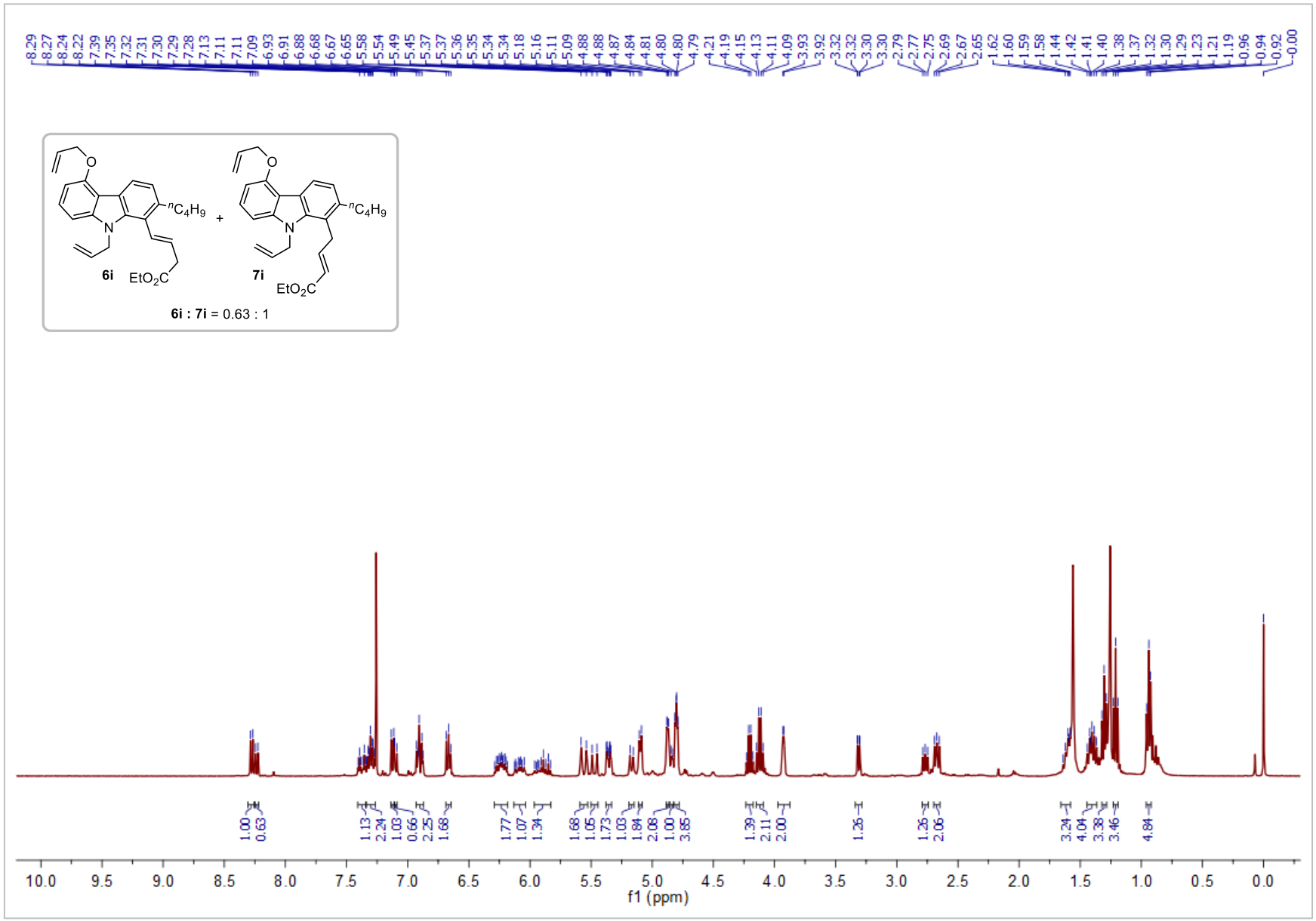




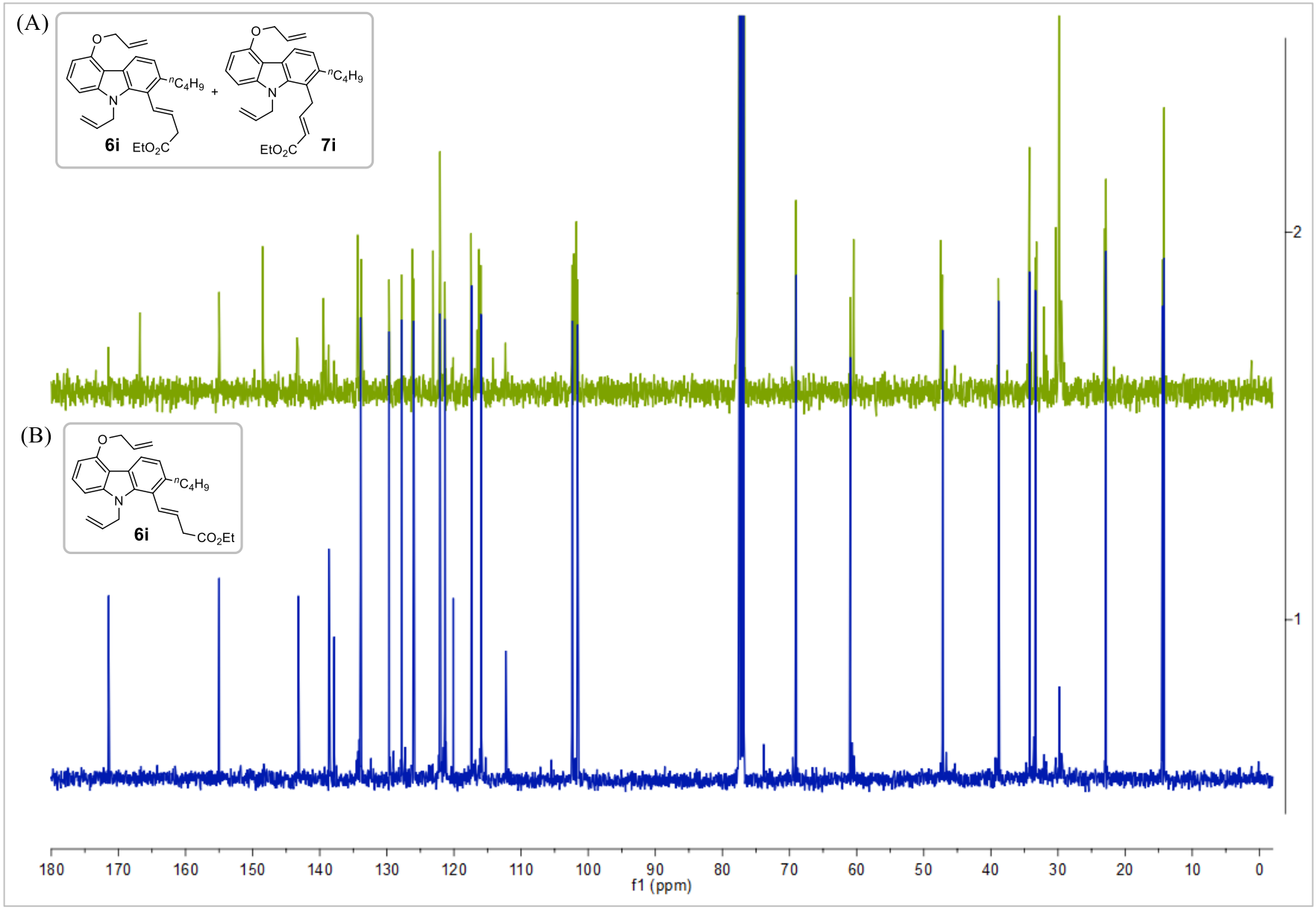
Stacked ^{1}H NMR (400 MHz, $CDCl_3$) spectra of (A) mixture of **6i** and **7i** and (B) pure **6i**.



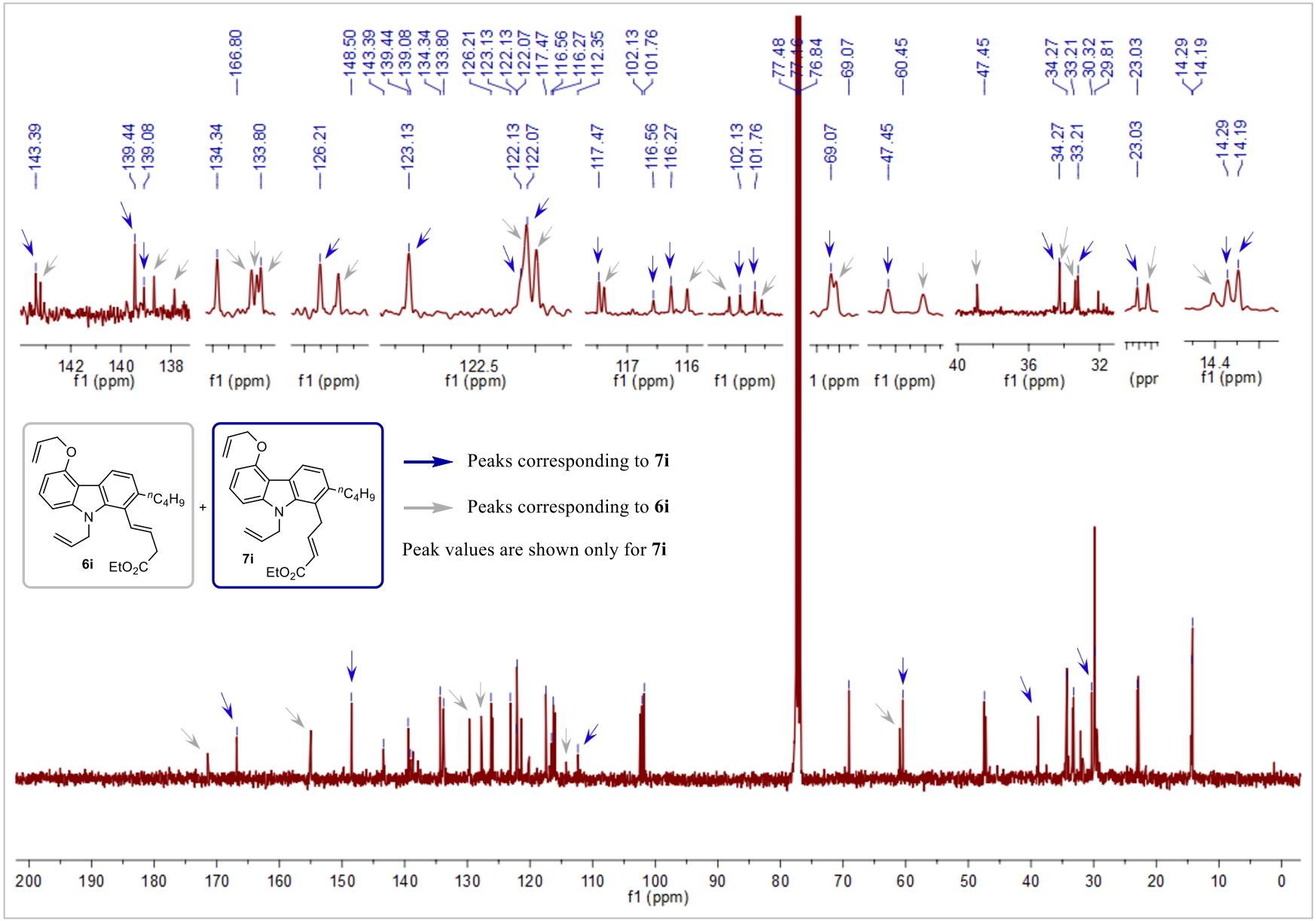
^{1}H NMR (400 MHz, $CDCl_3$) spectra of mixture of **6i** and **7i**.



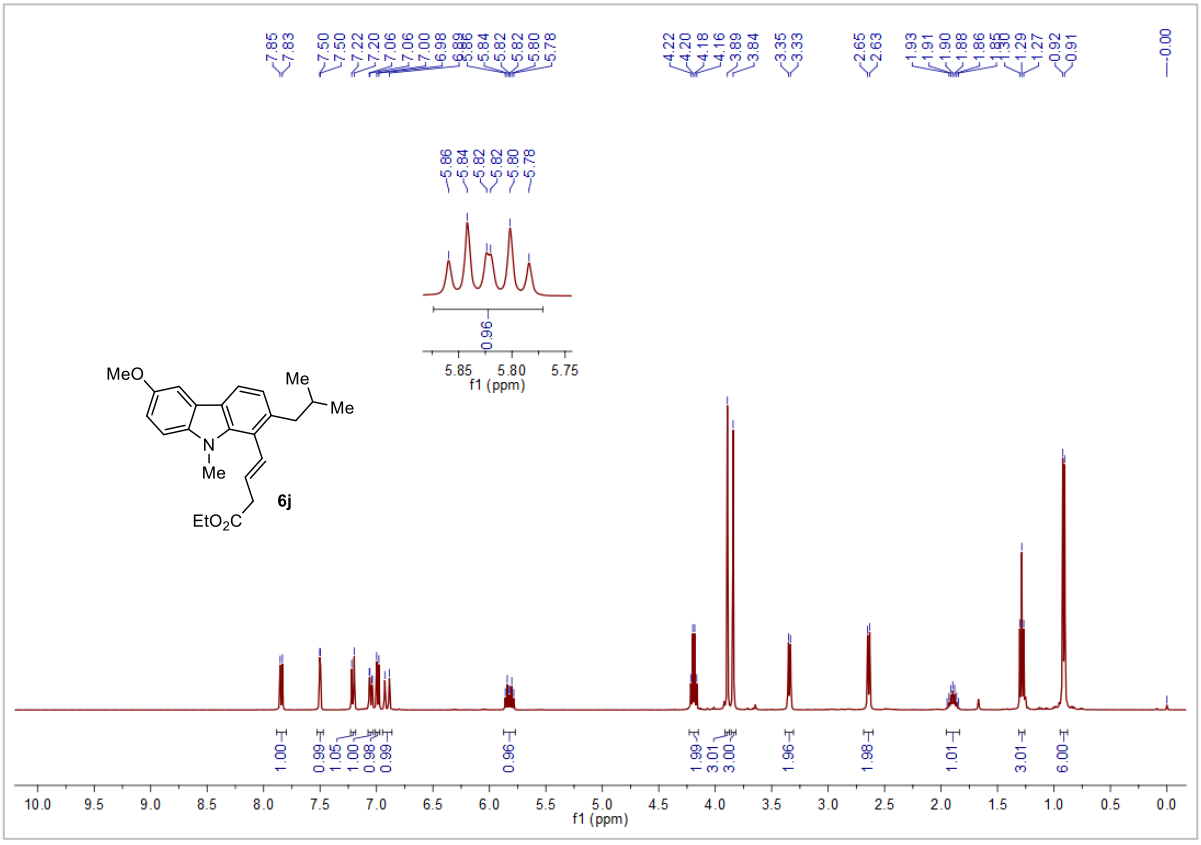
Stacked ^{13}C NMR (100 MHz, $CDCl_3$) spectra of (A) mixture of **6i** and **7i** and (B) pure **6i**.

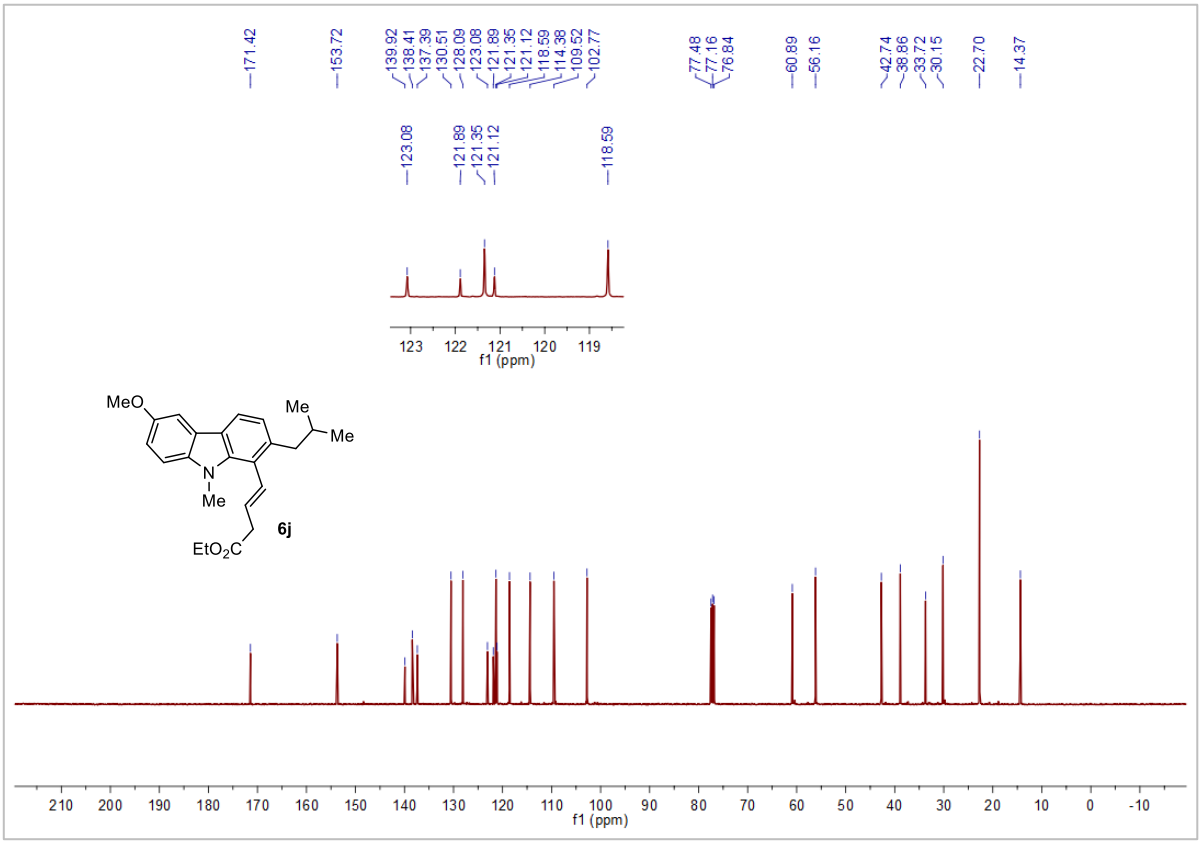


^{13}C NMR (100 MHz, $CDCl_3$) spectra of mixture of **6i** and **7i**.

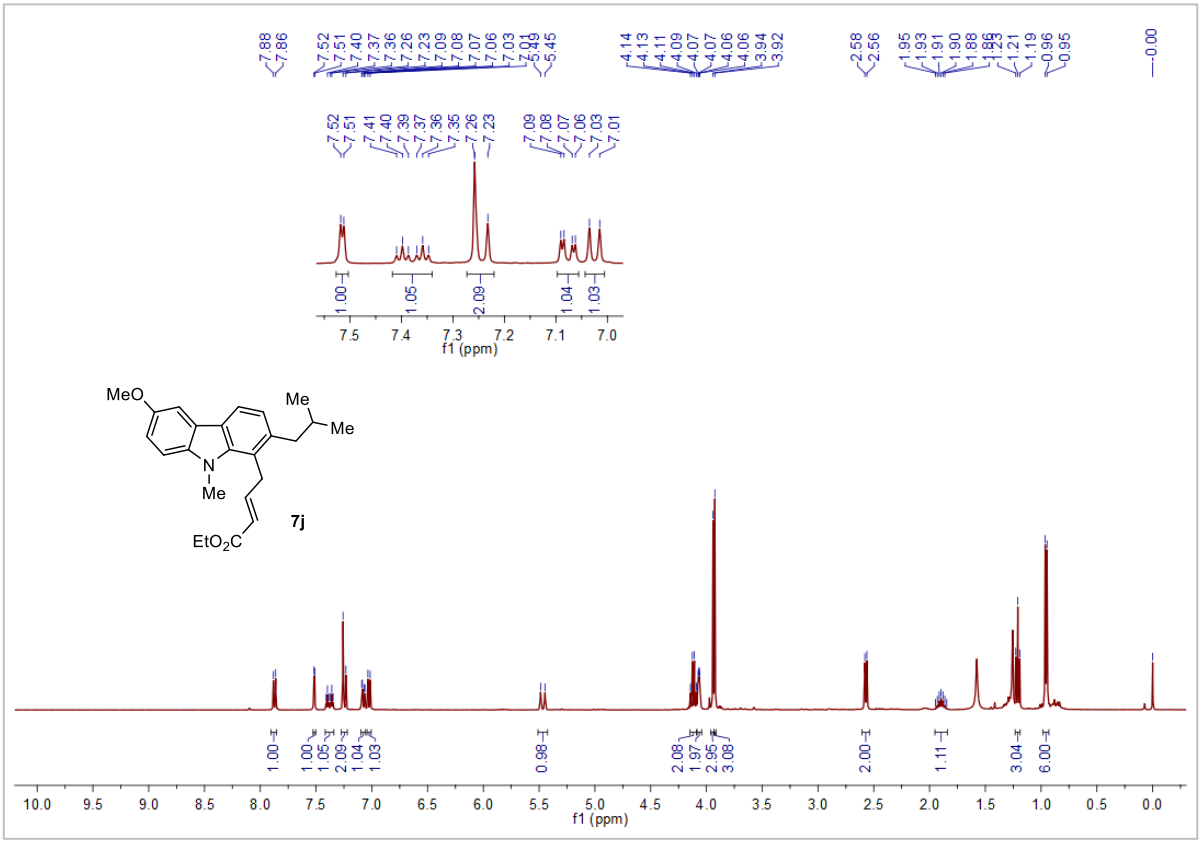


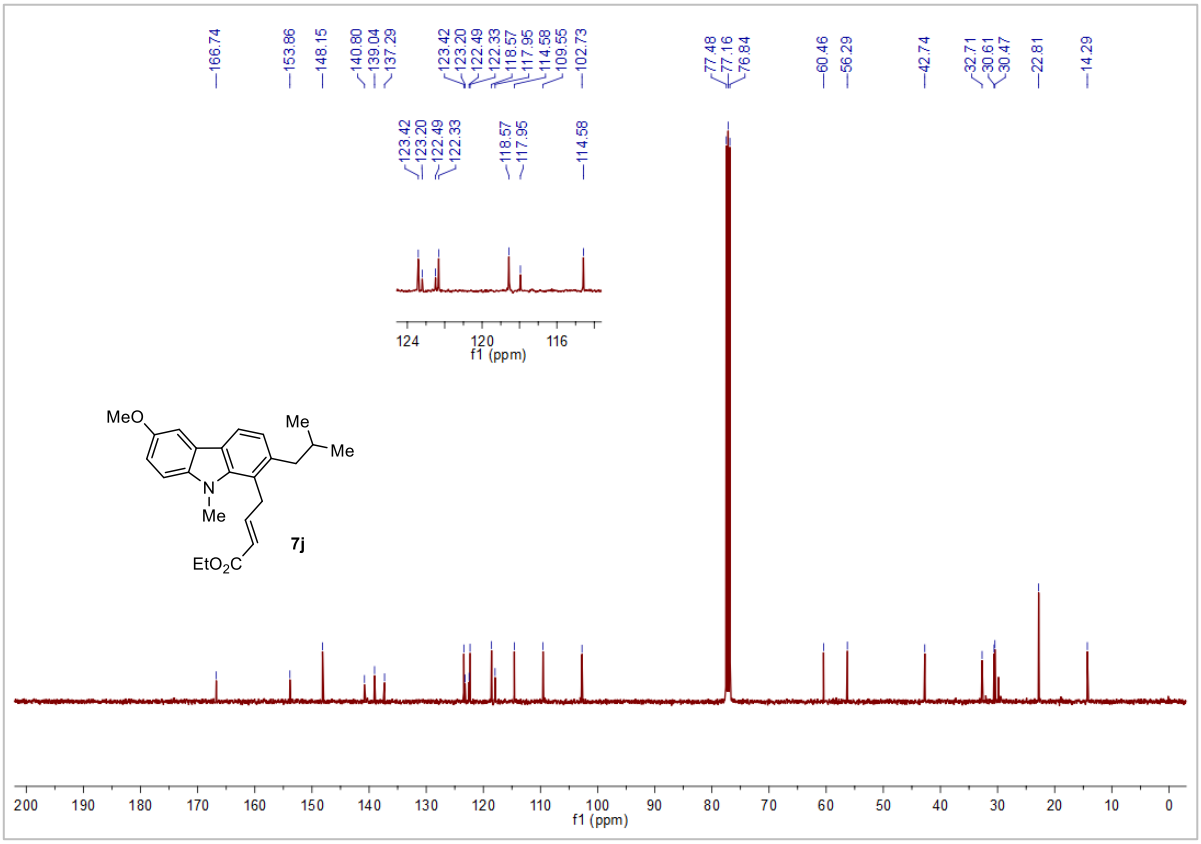
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **6j**.



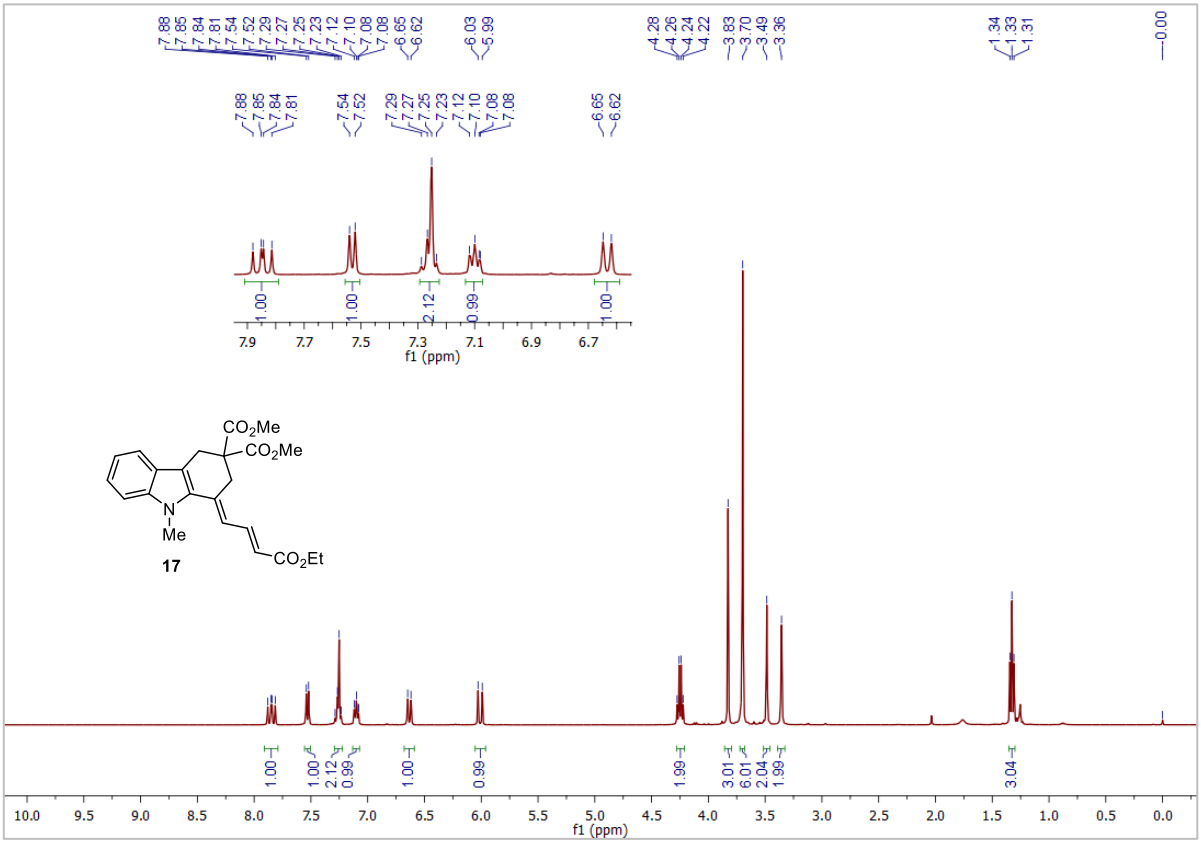


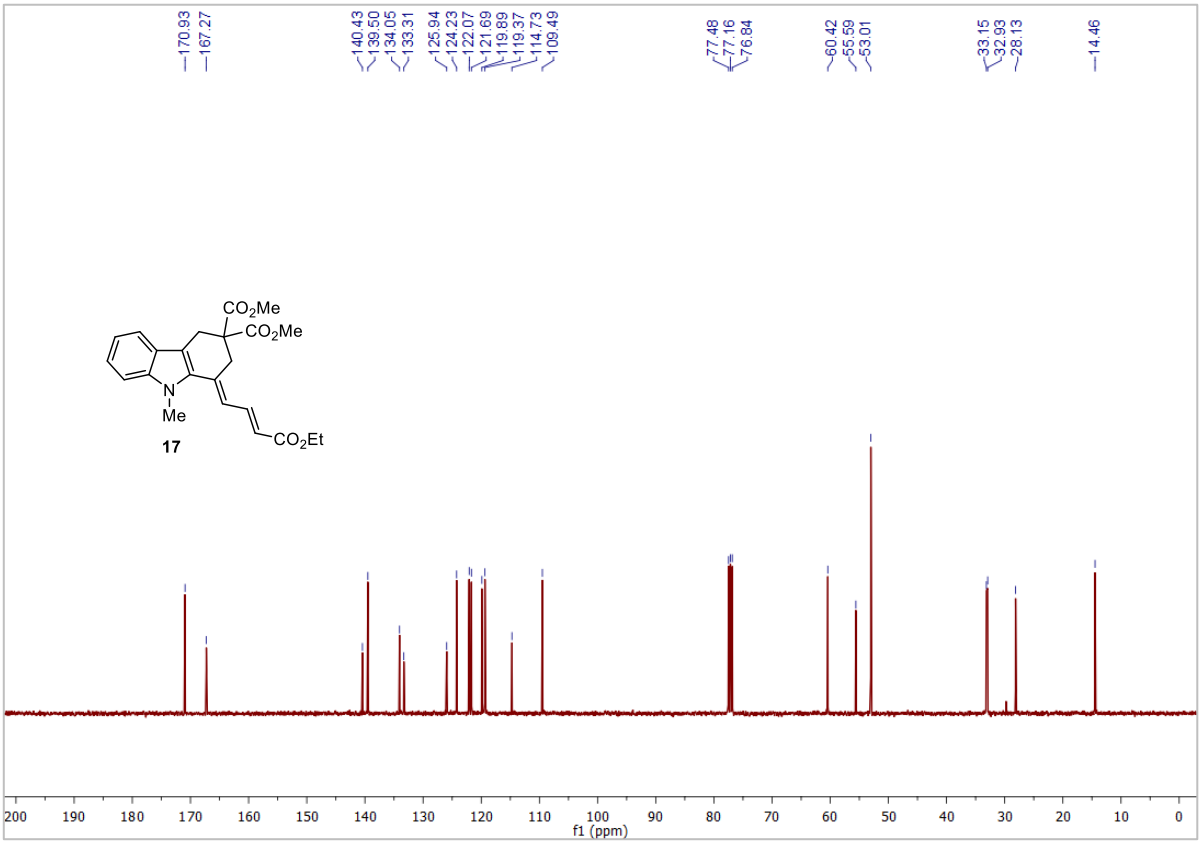
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **7j**.



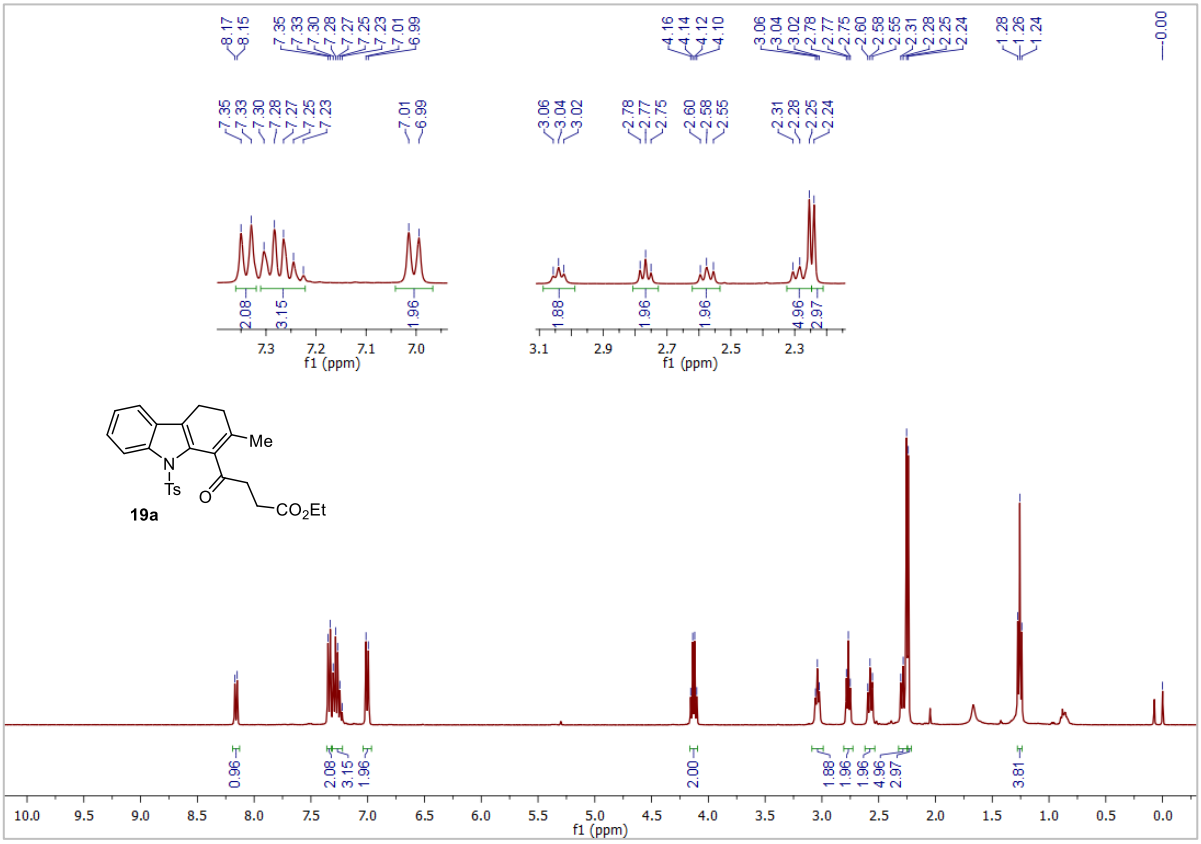


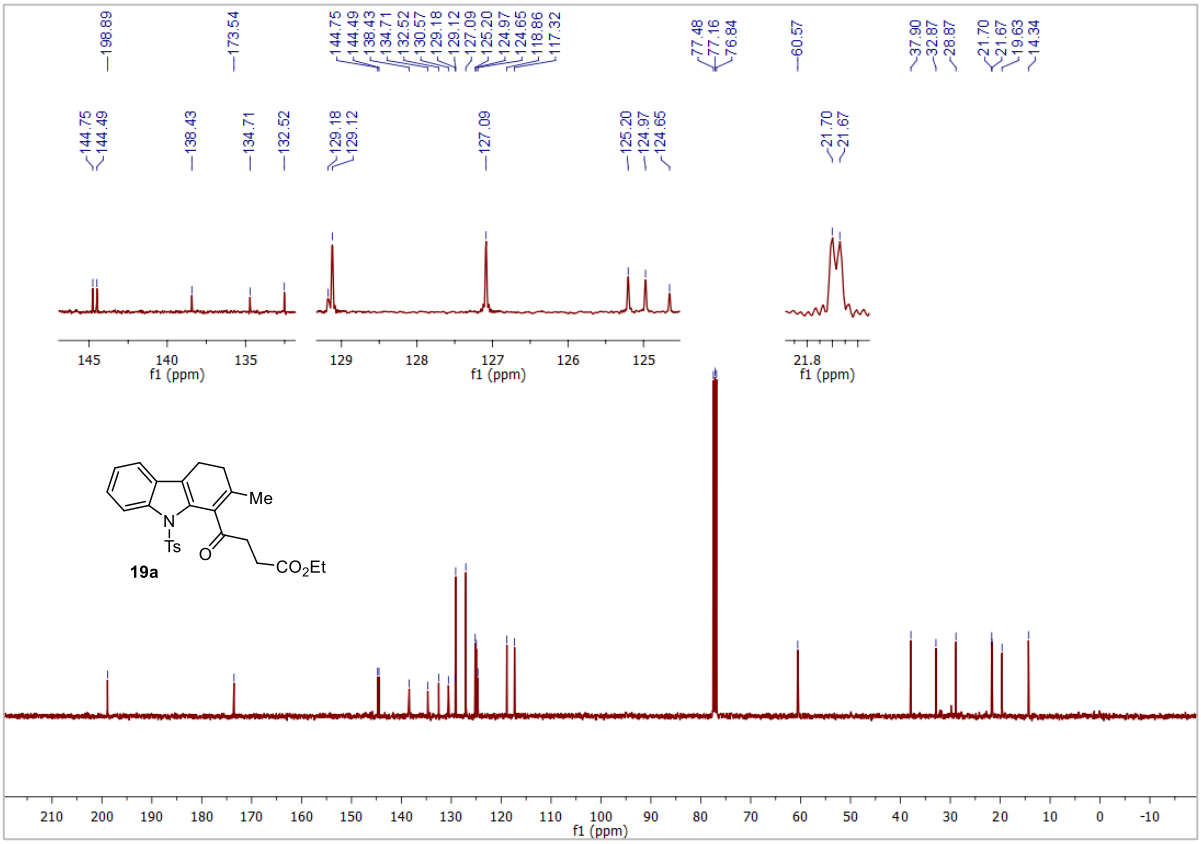
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **17**.



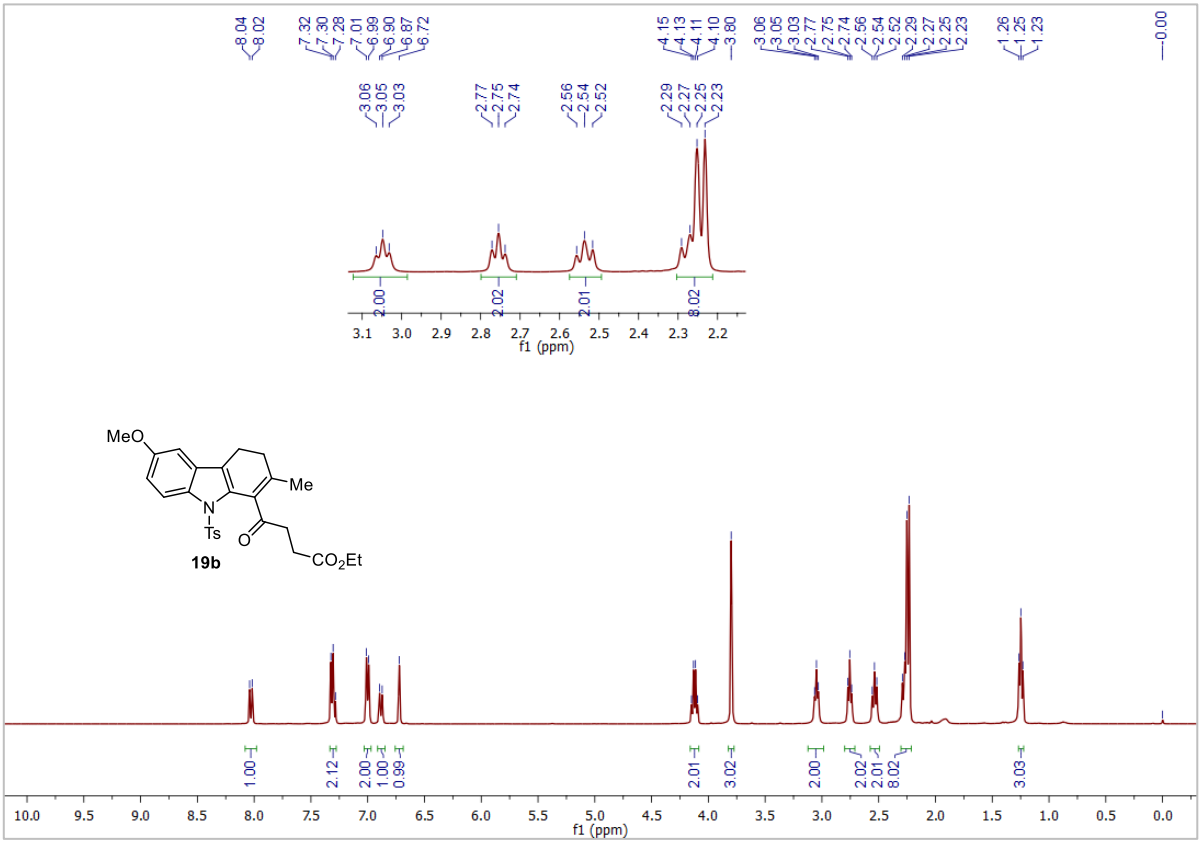


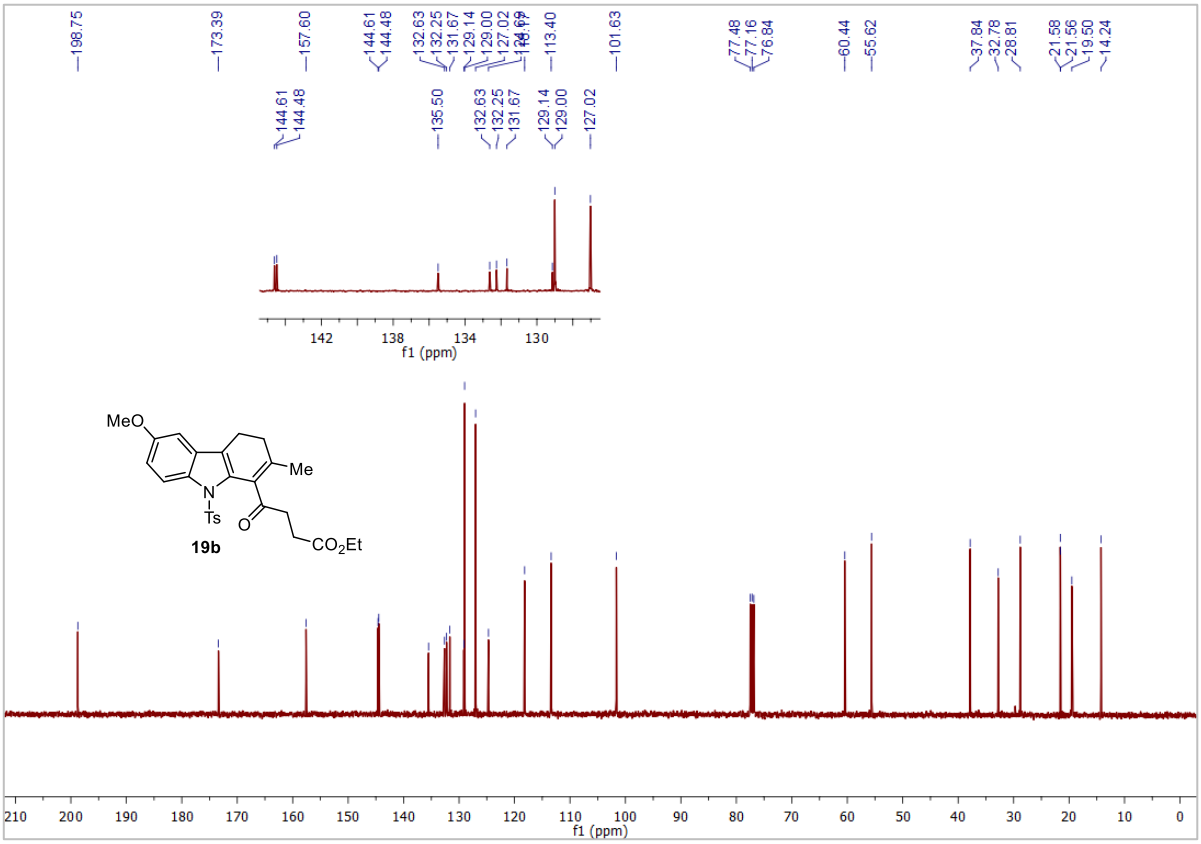
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **19a**.



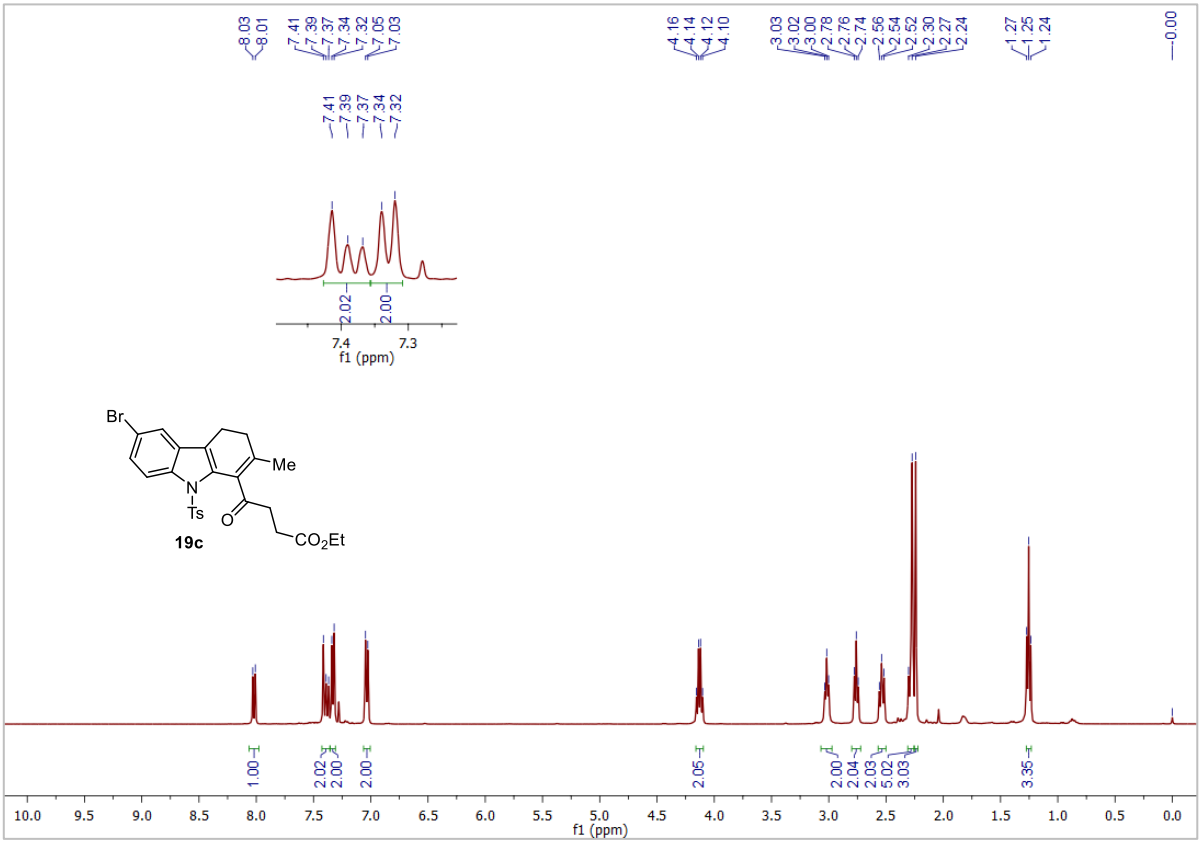


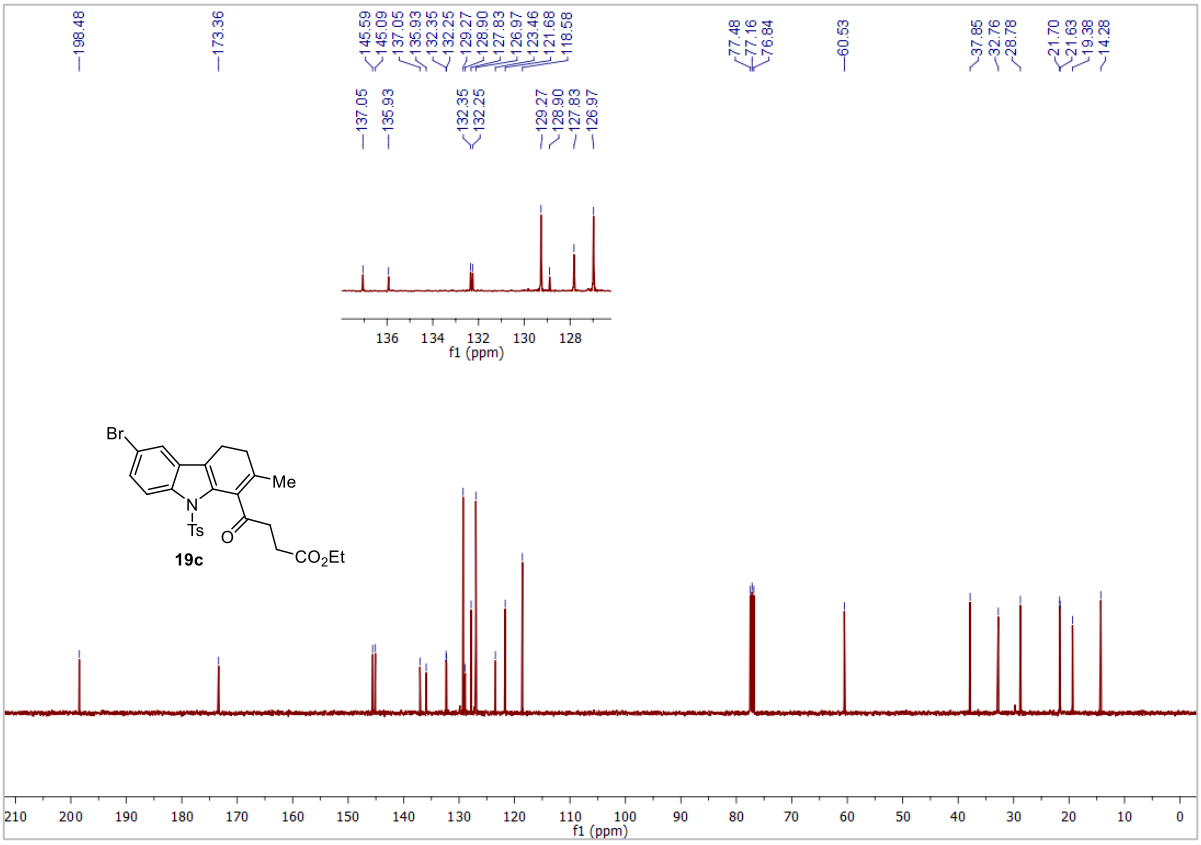
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **19b**.



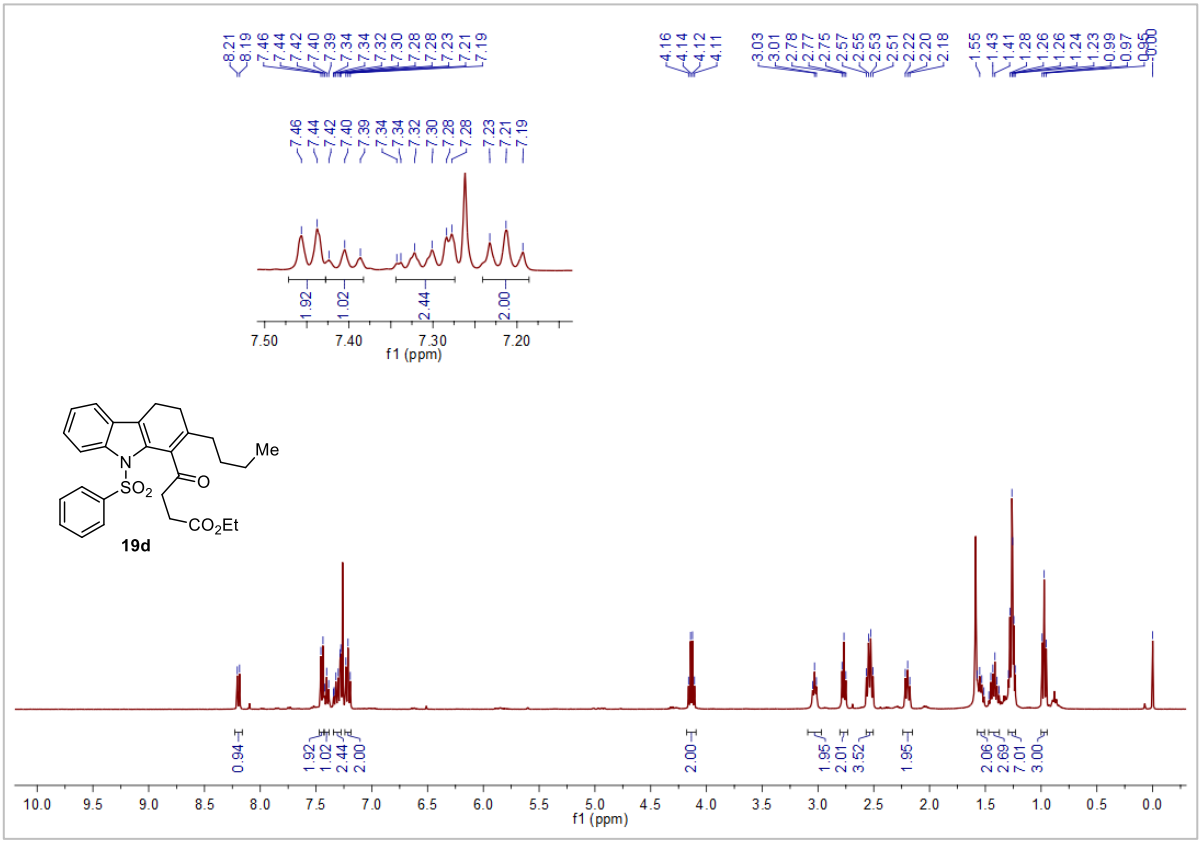


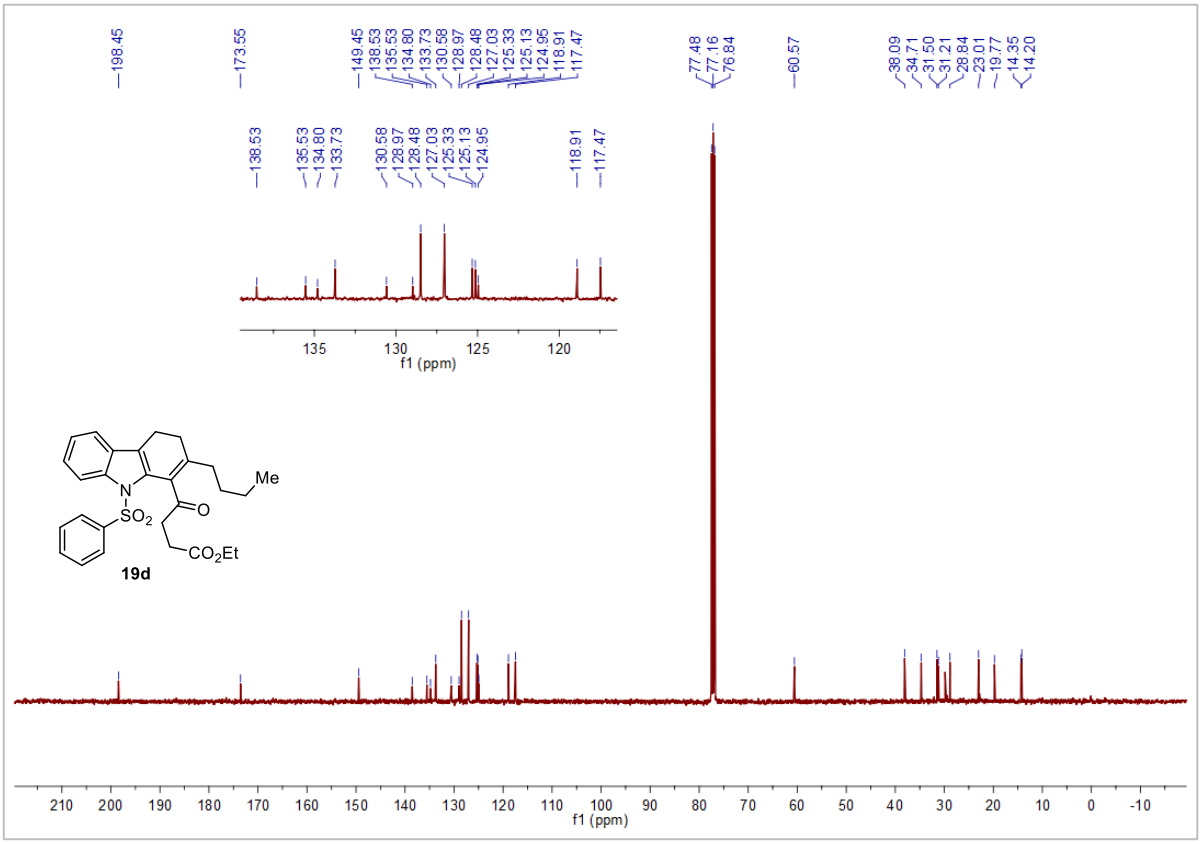
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **19c**.



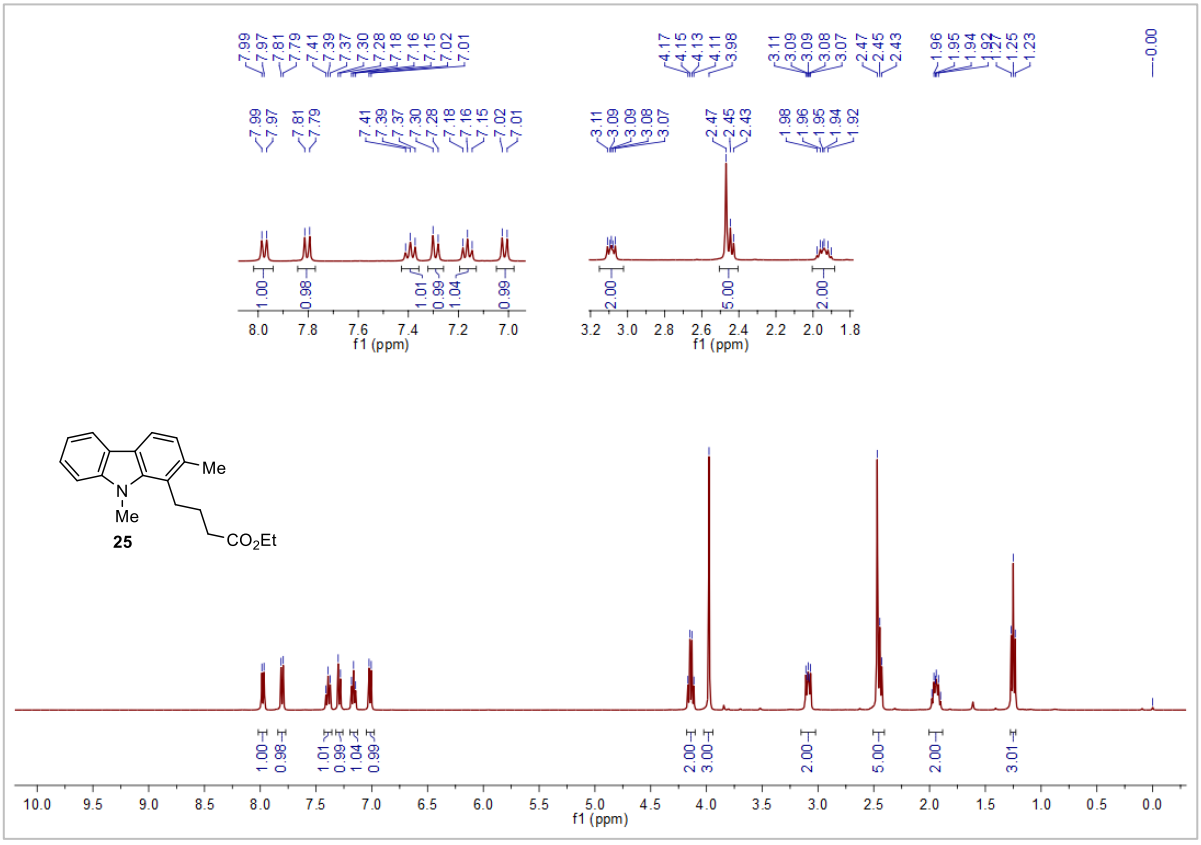


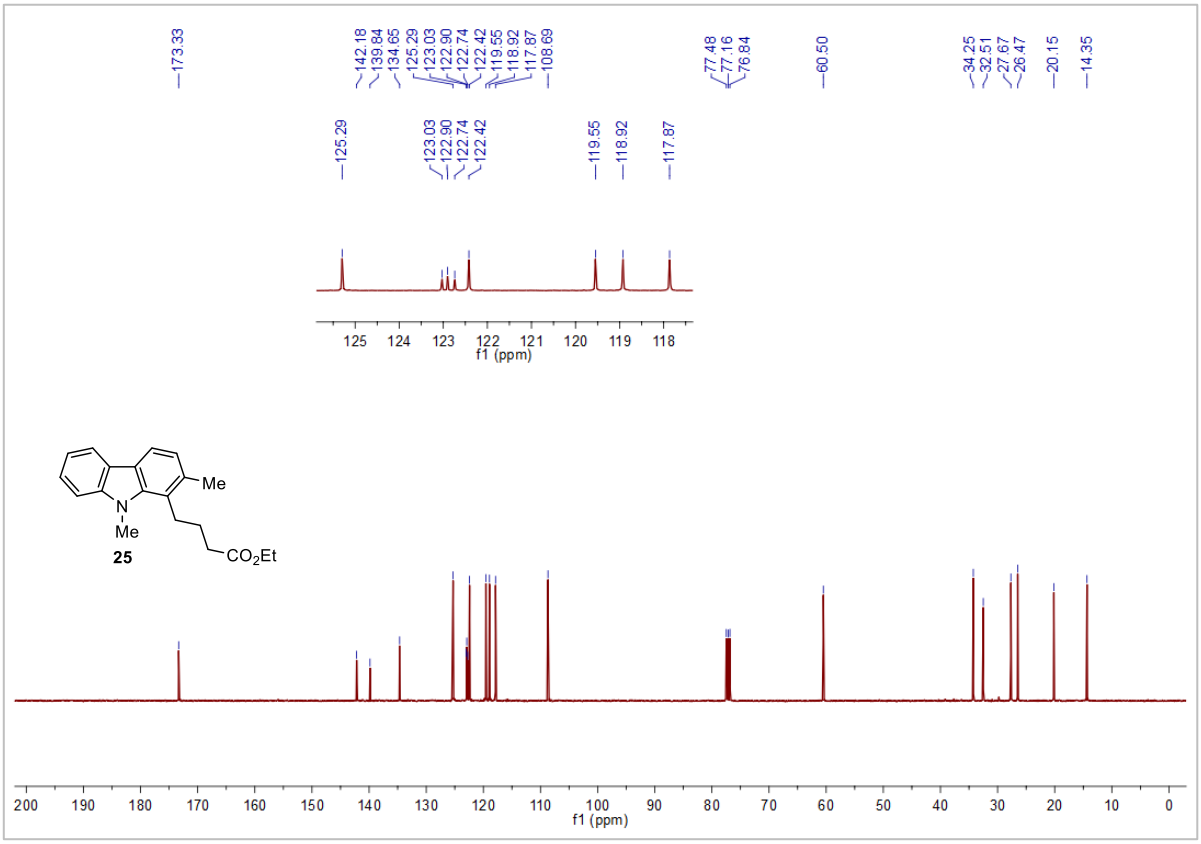
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **19d**.



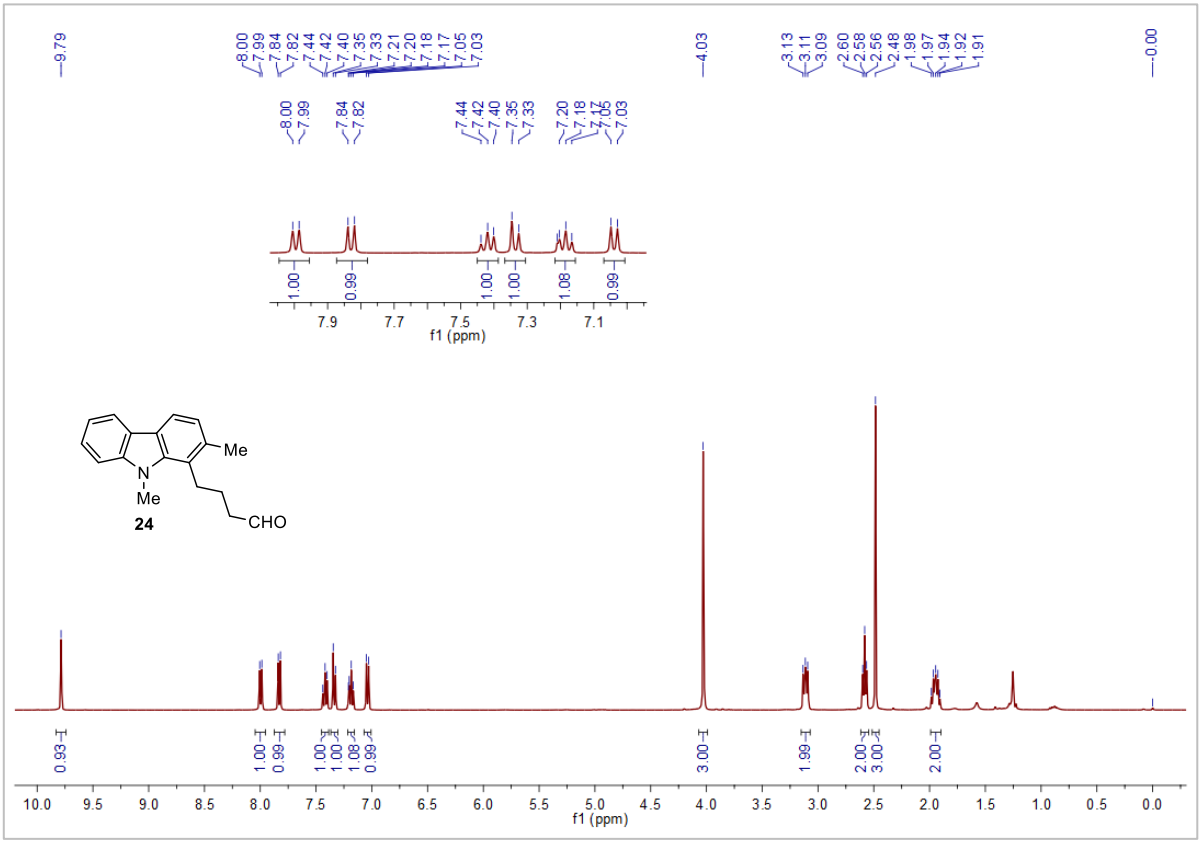


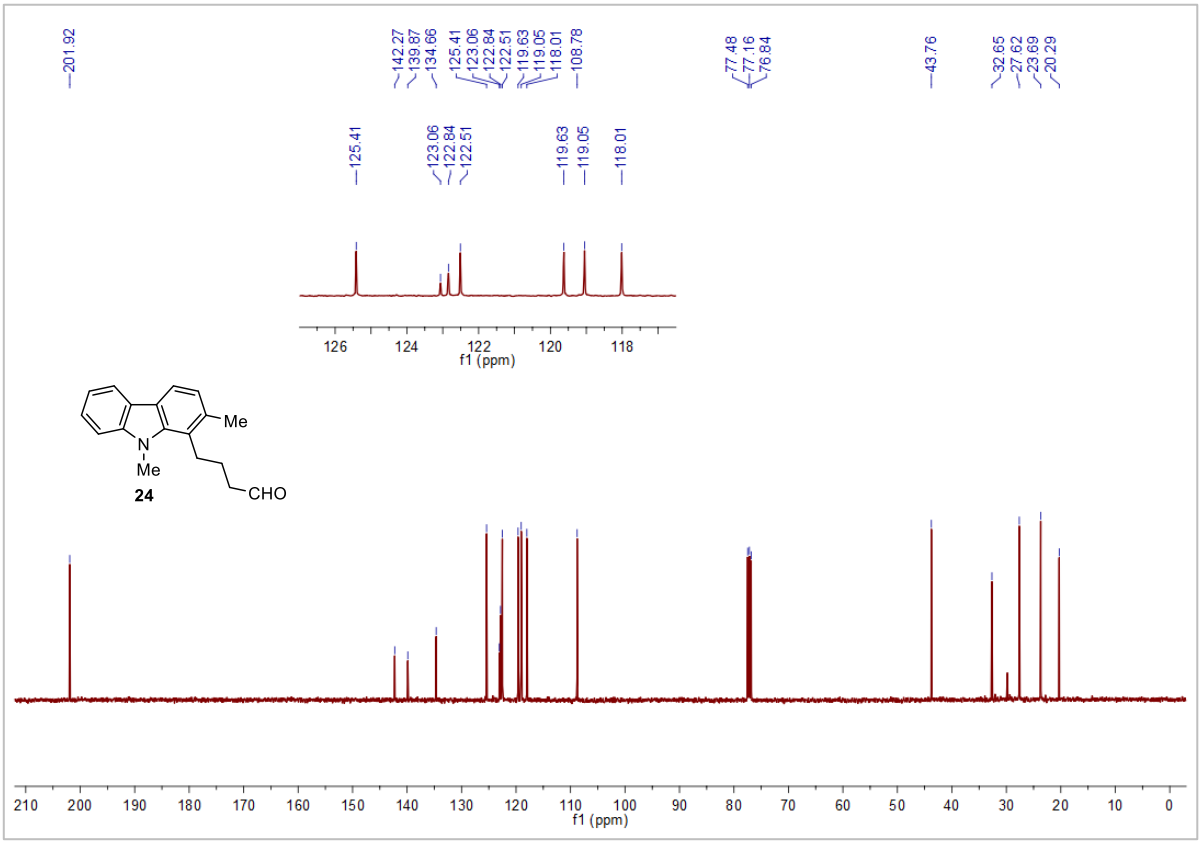
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **25**.



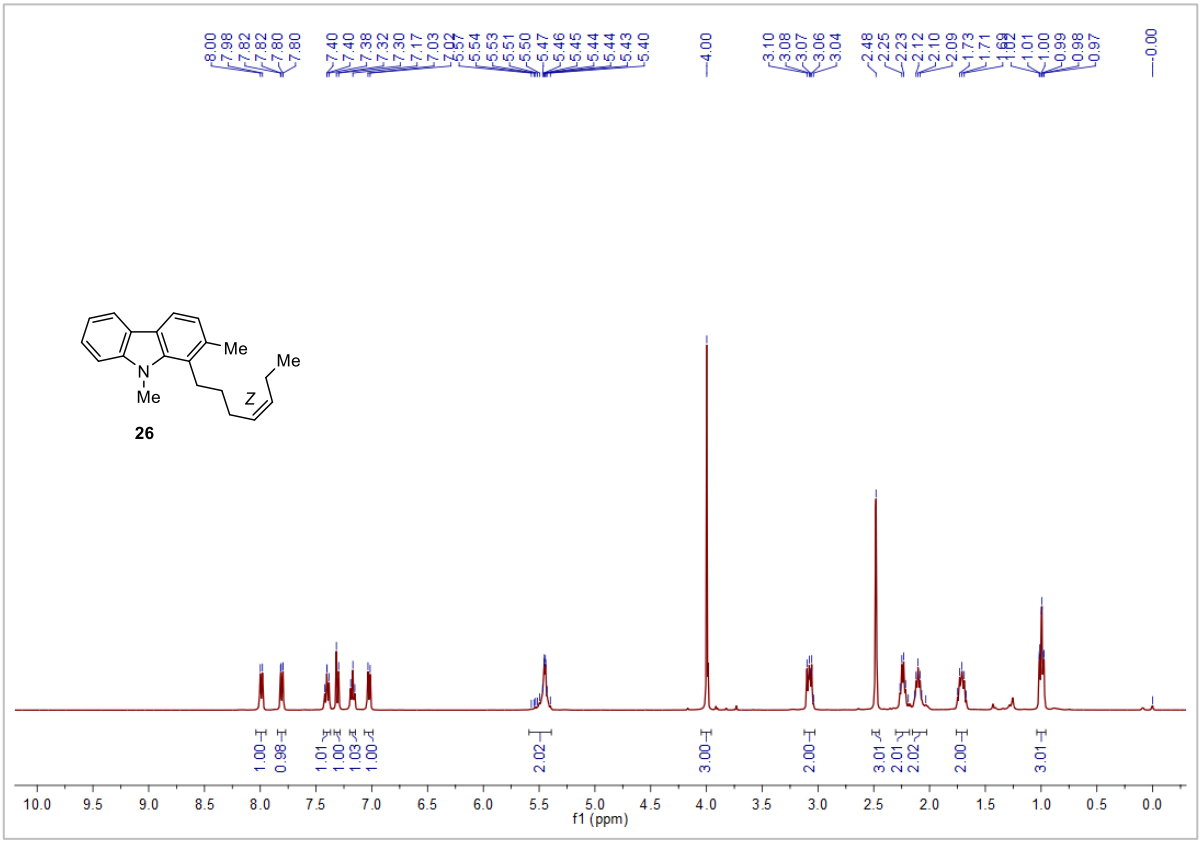


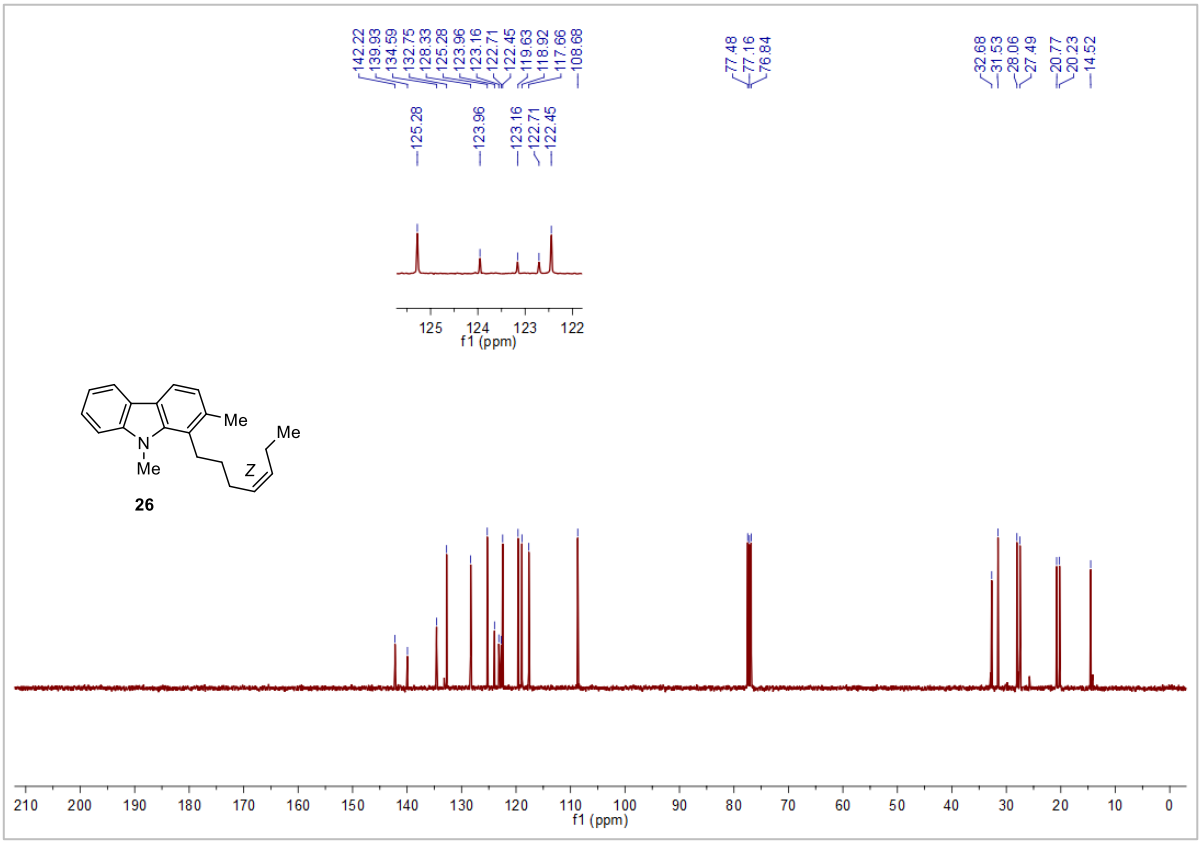
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **24**.



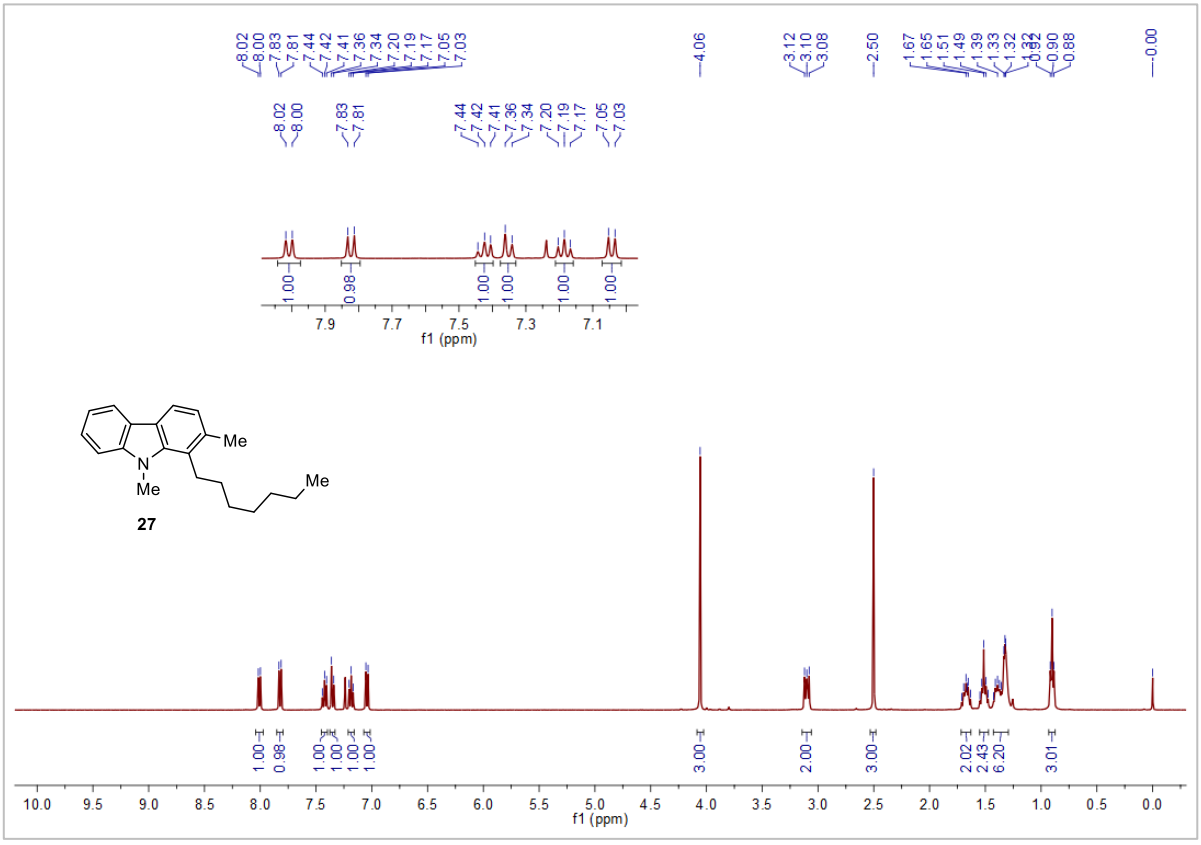


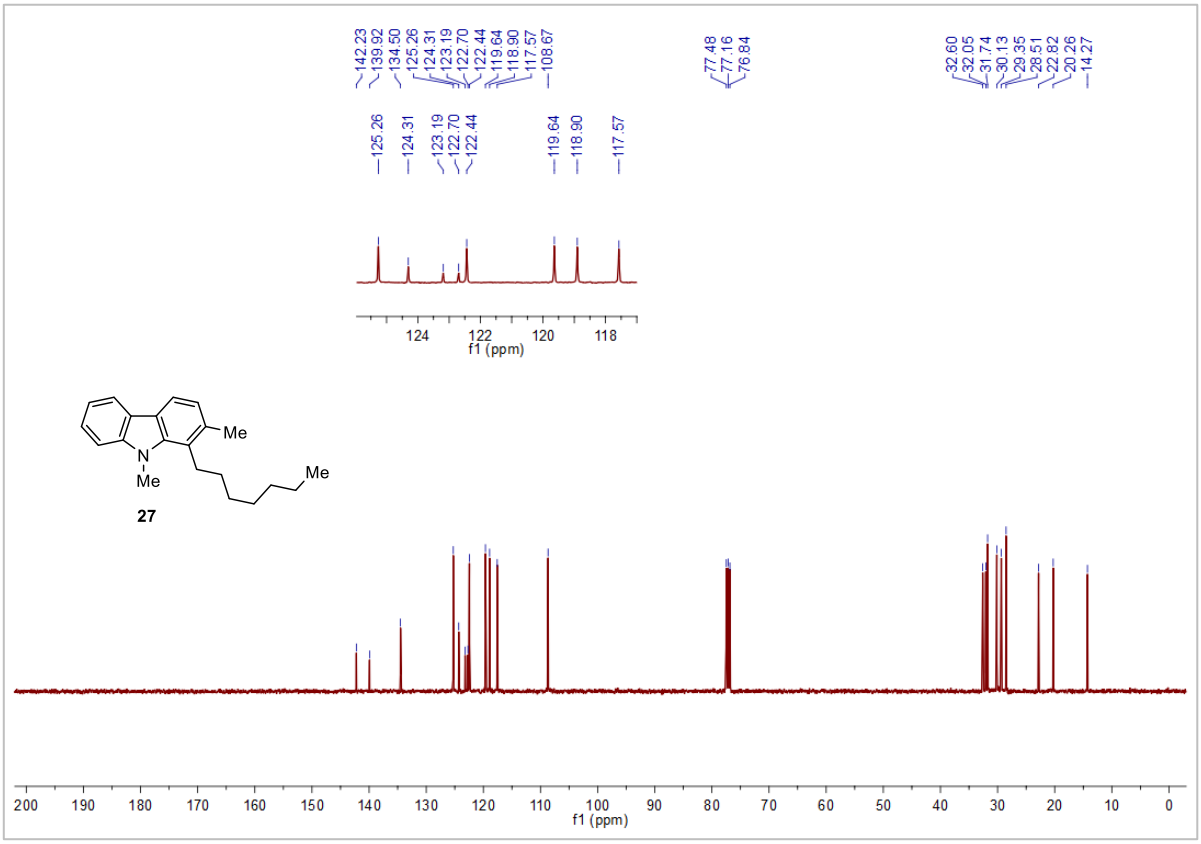
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **26**.



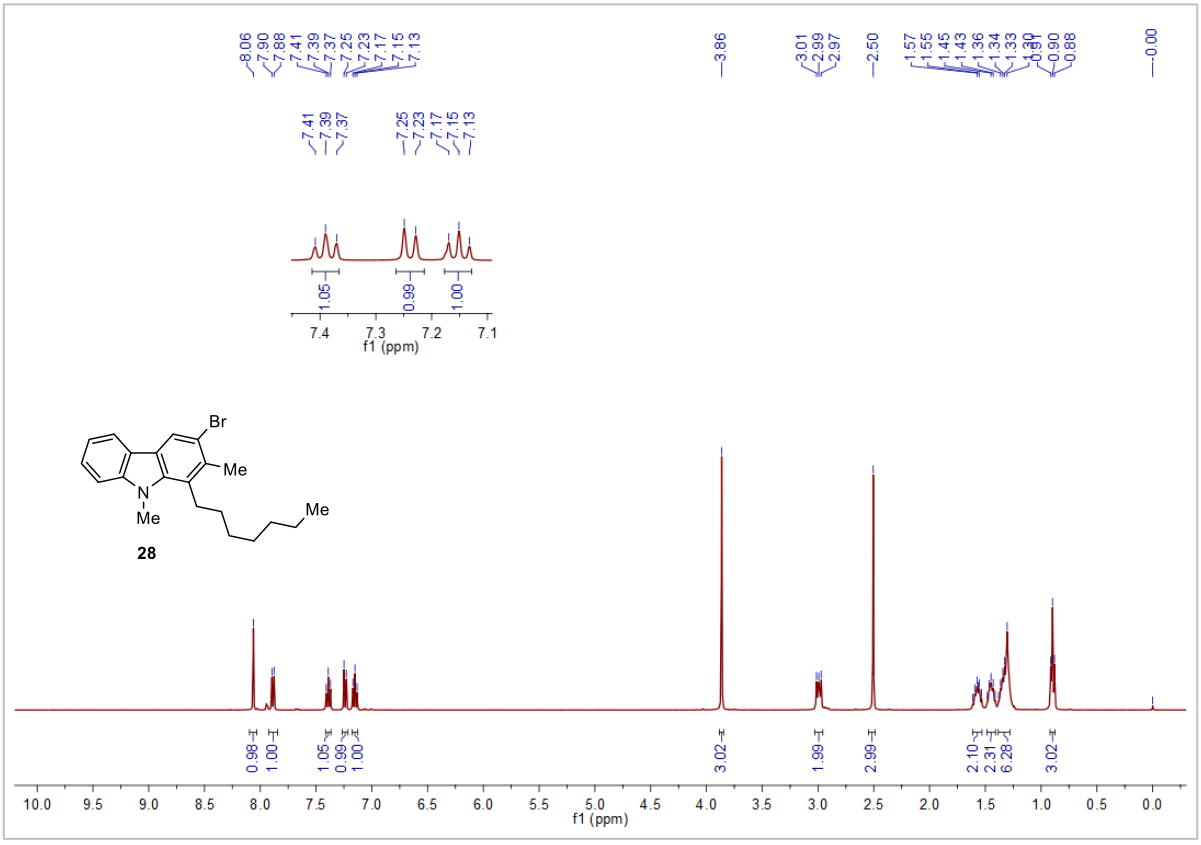


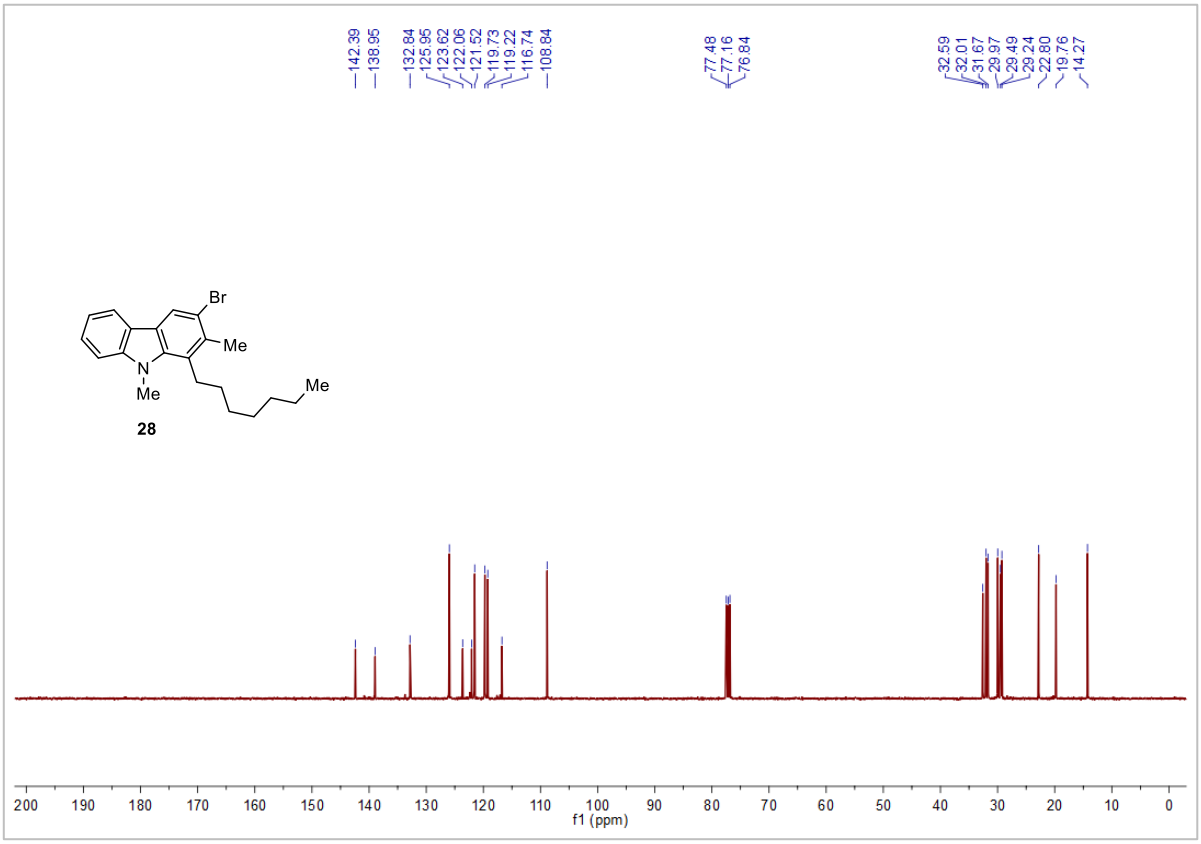
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **27**.



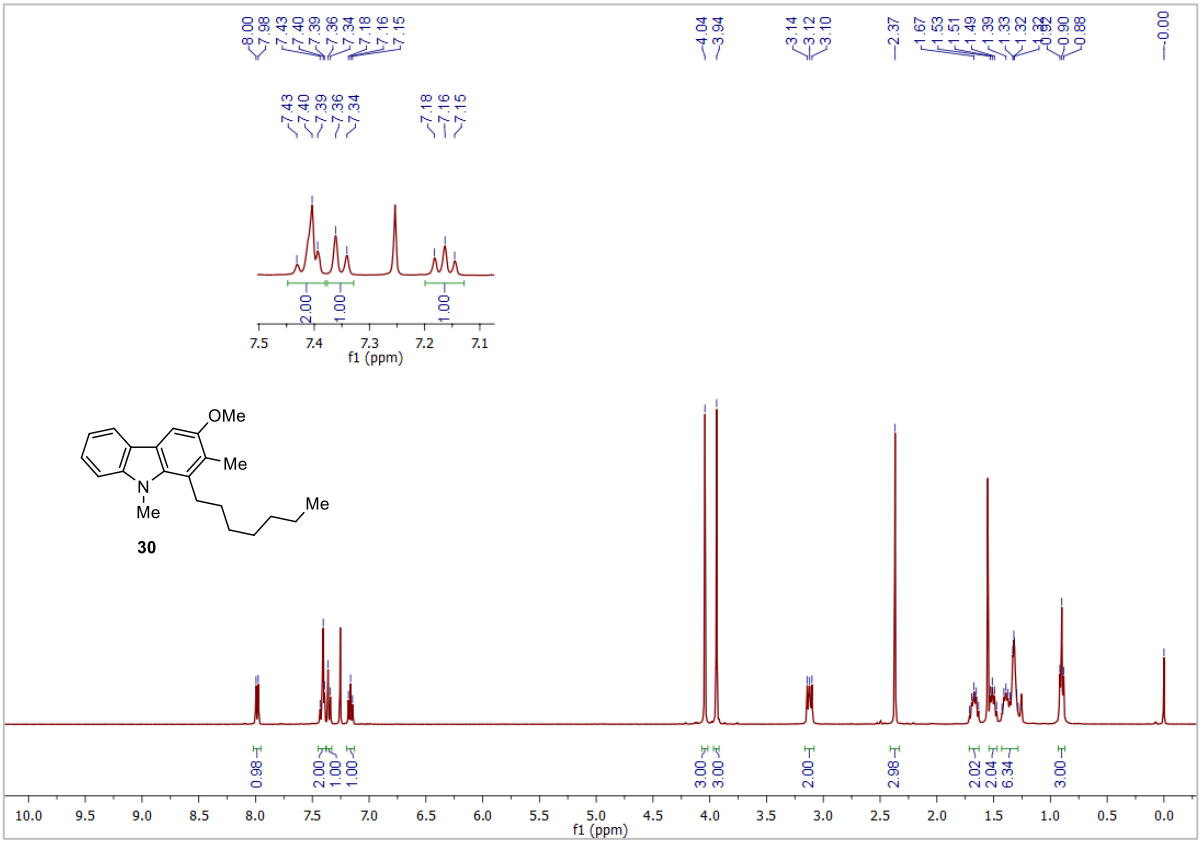


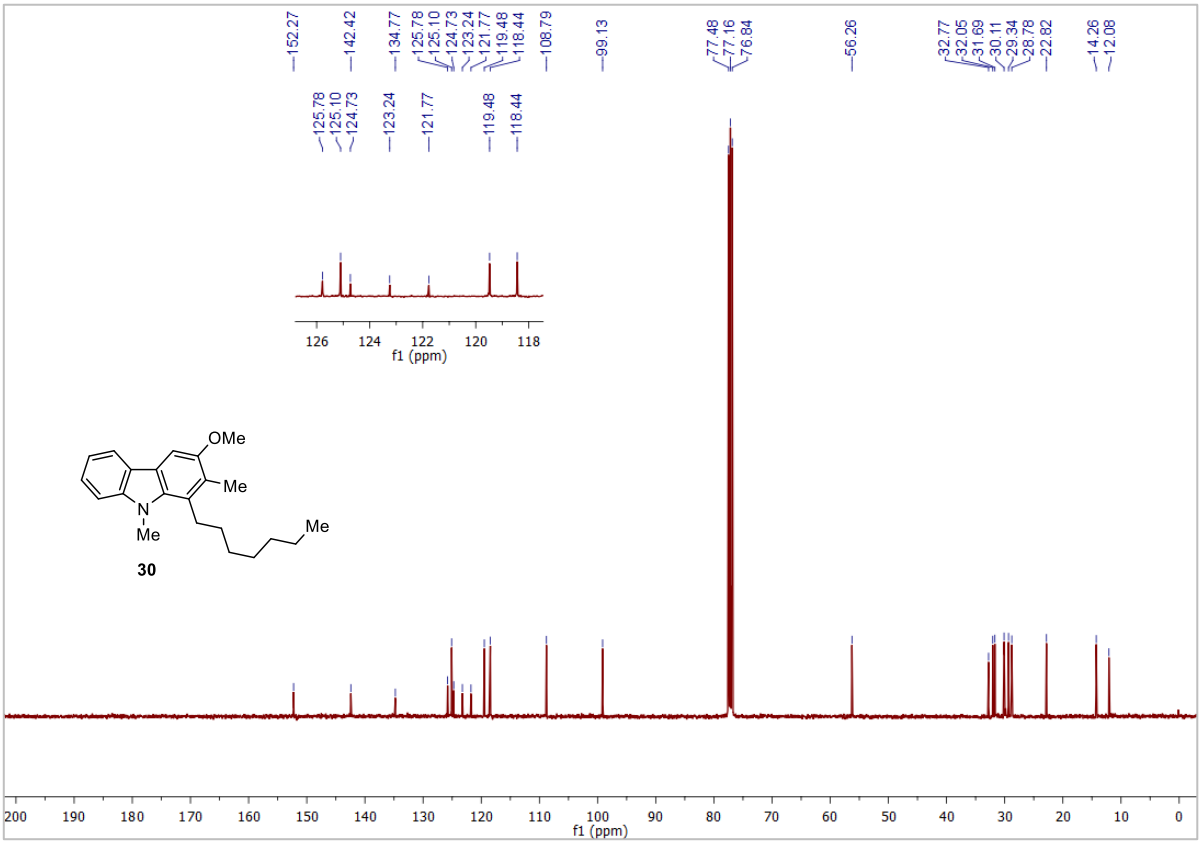
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **28**.



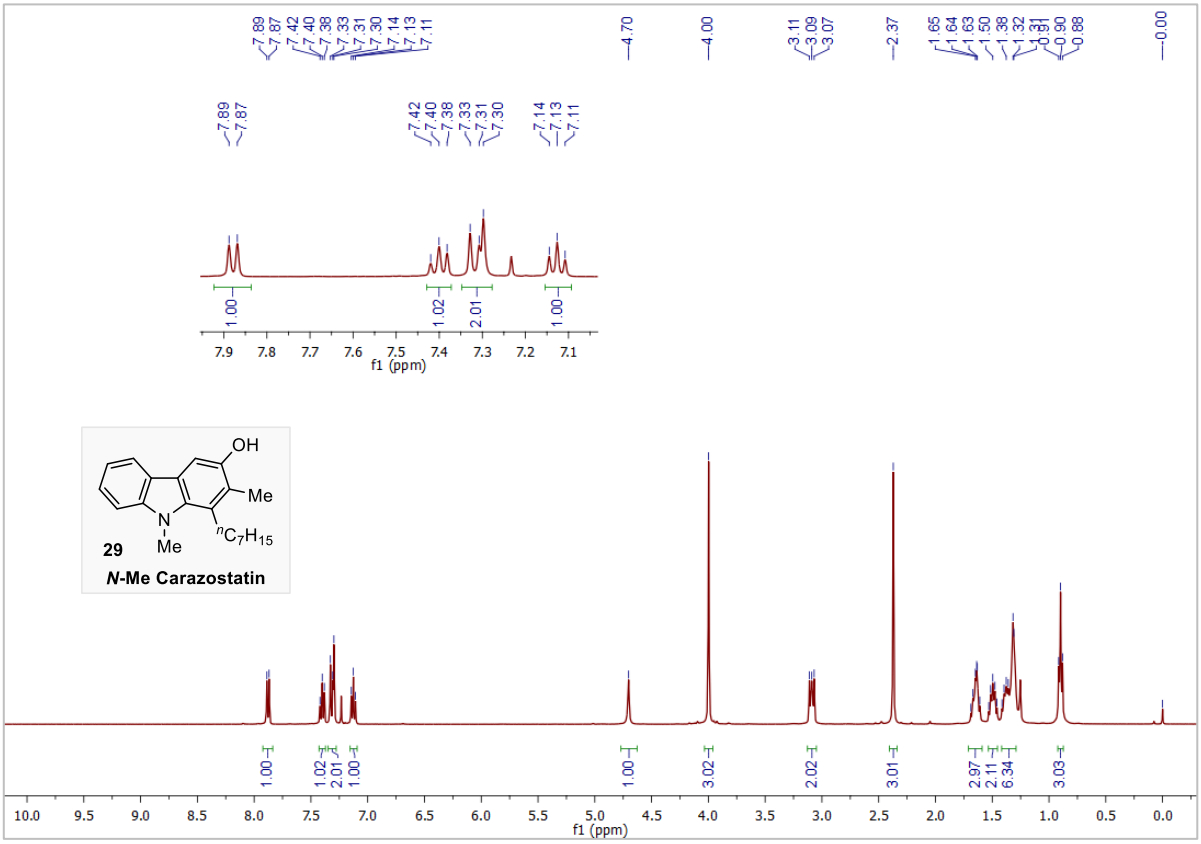


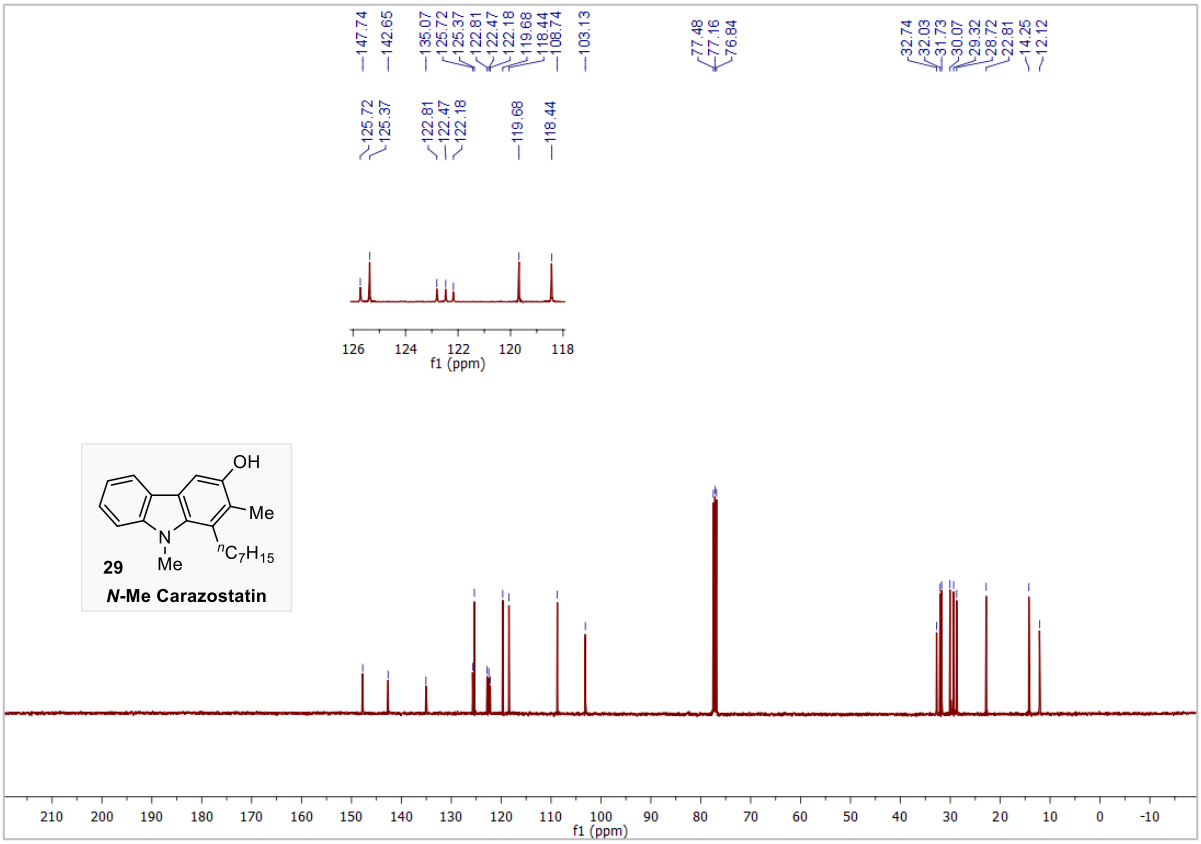
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **30**.



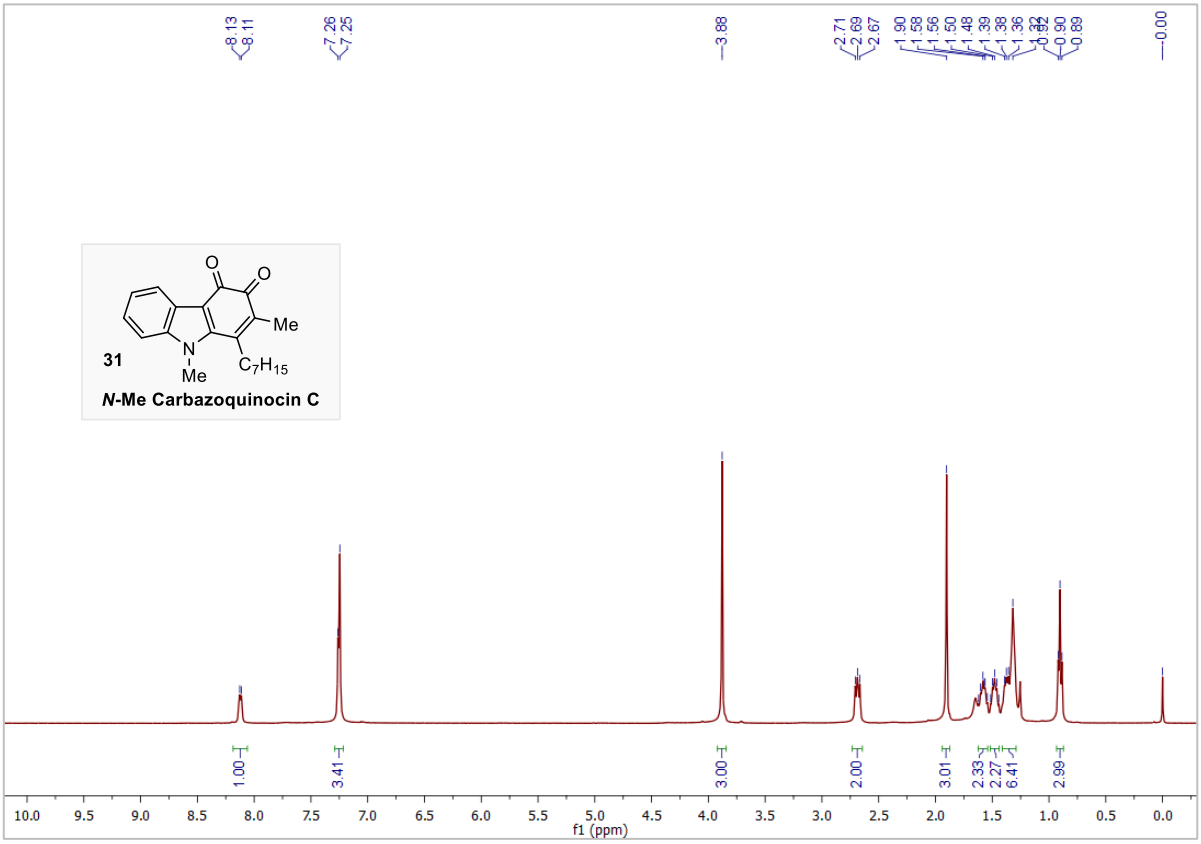


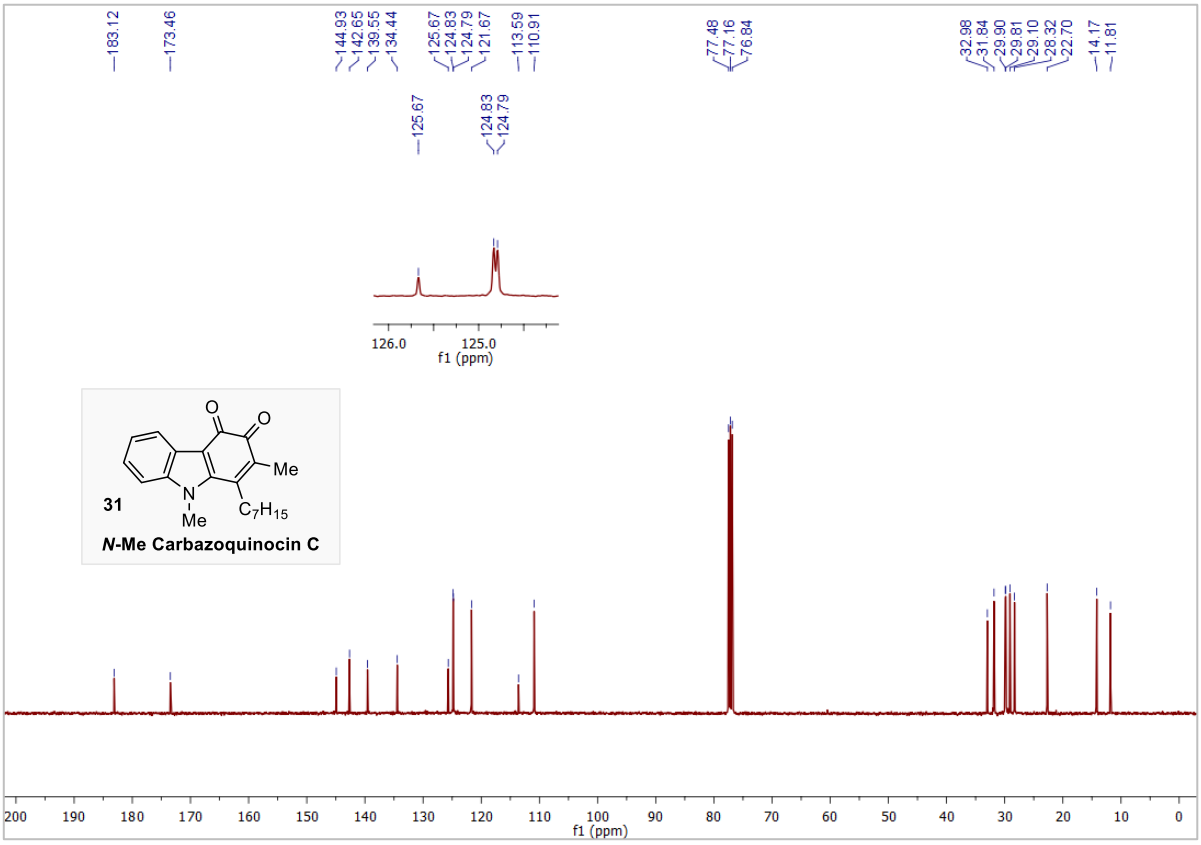
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of *N*-methyl Carazostatin **29**.



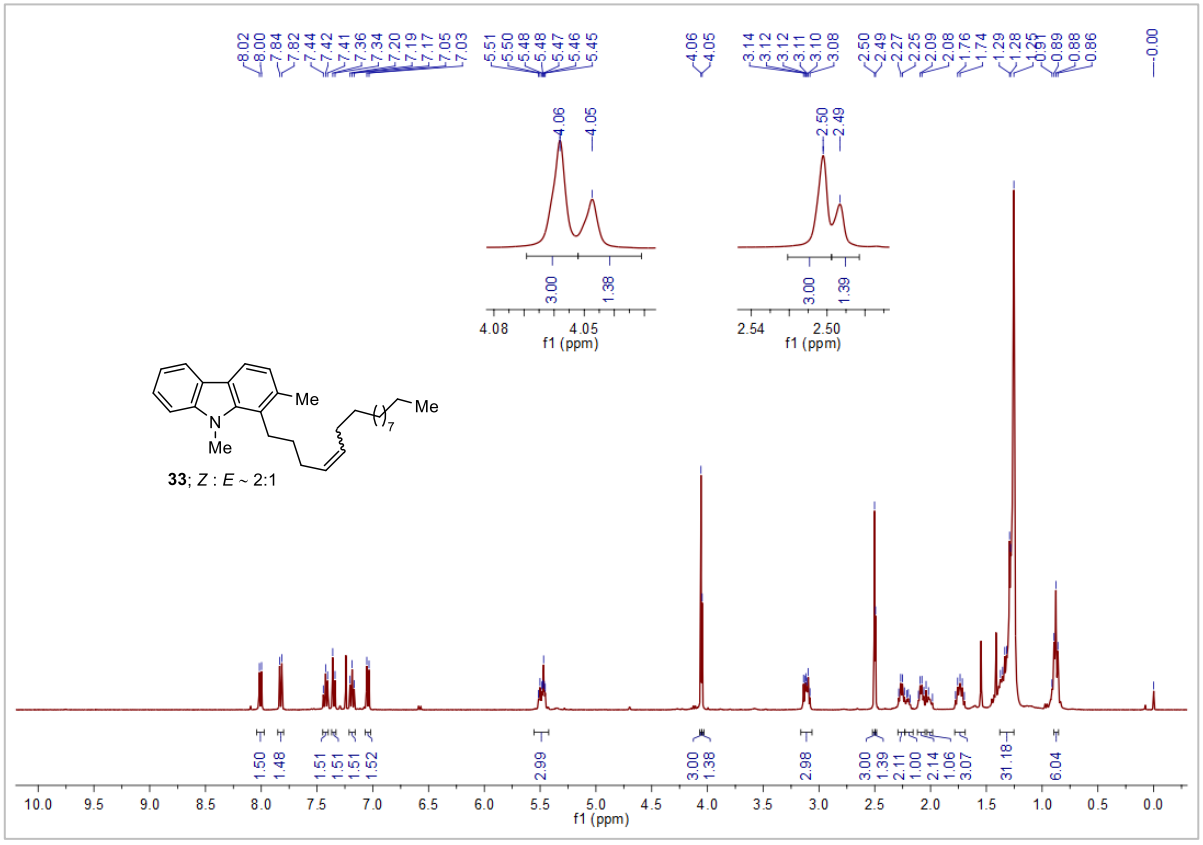


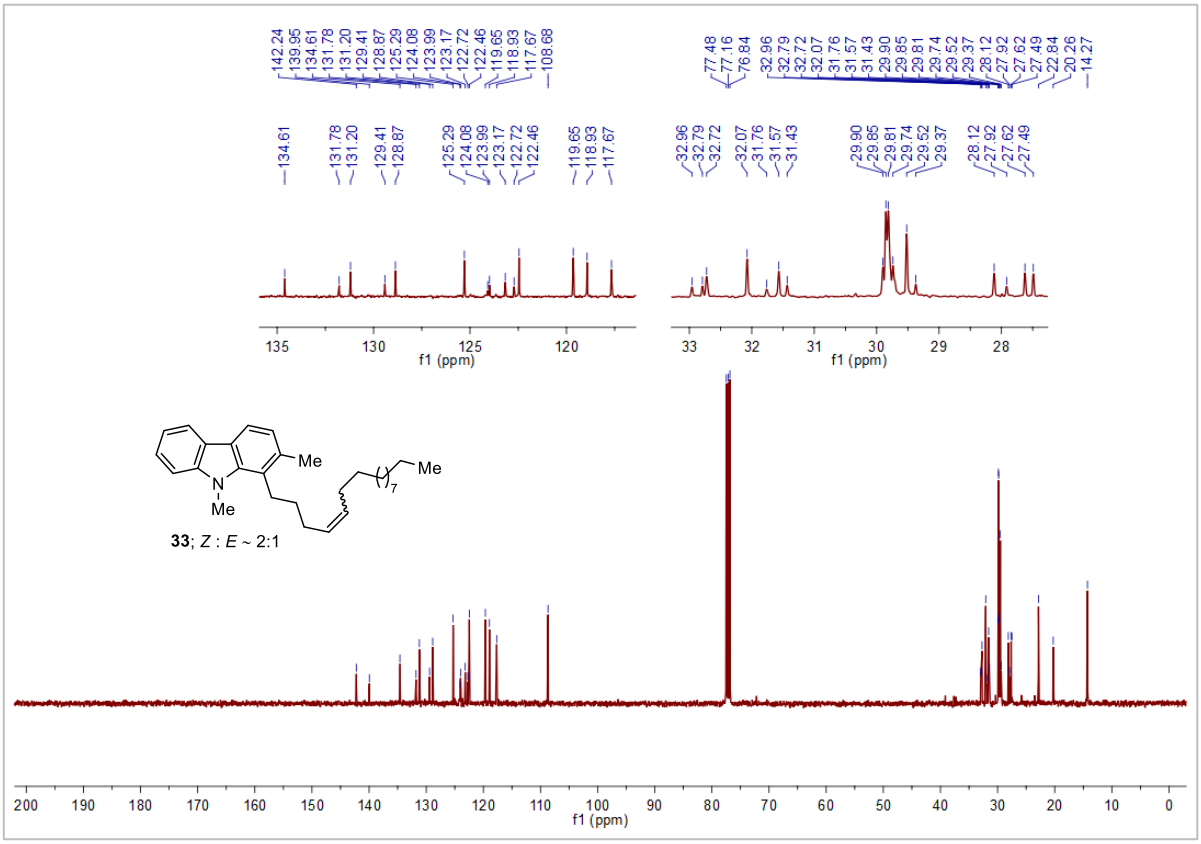
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of *N*-methyl Carbazoquinocin C **31**.



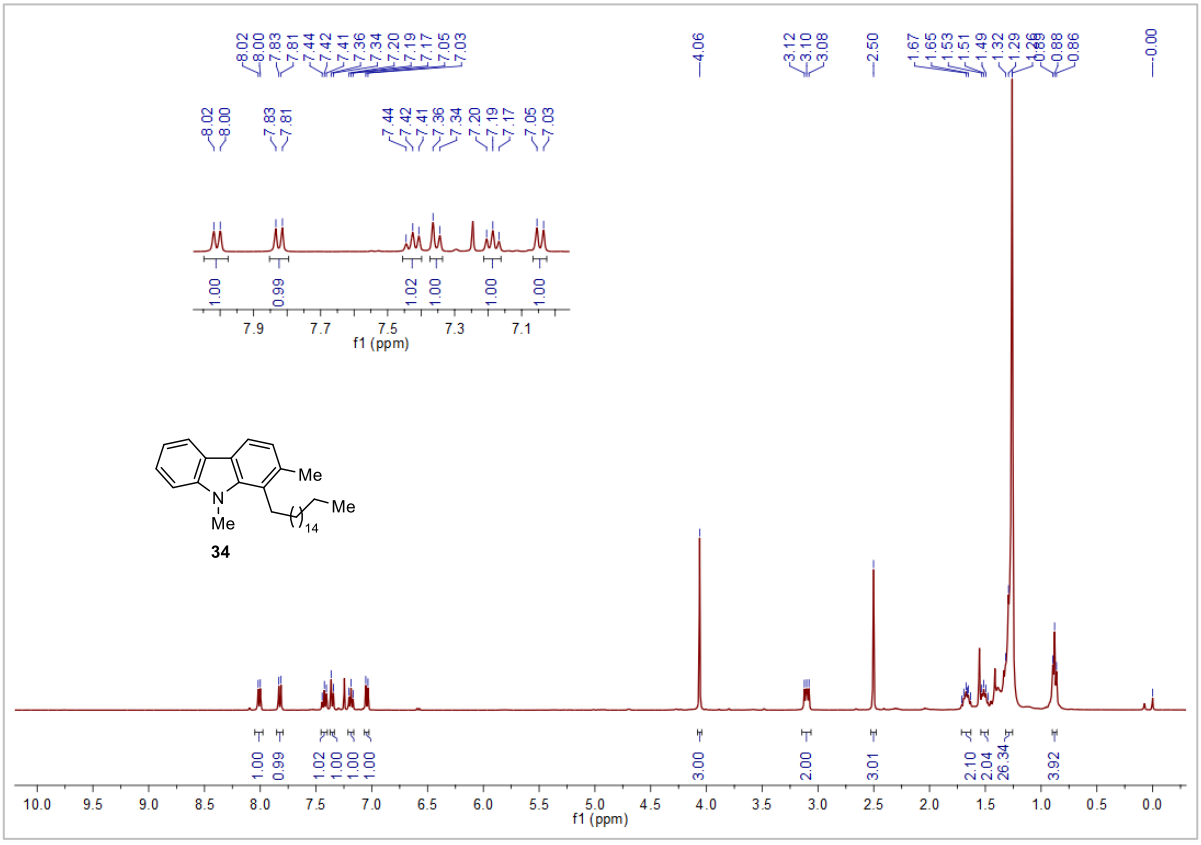


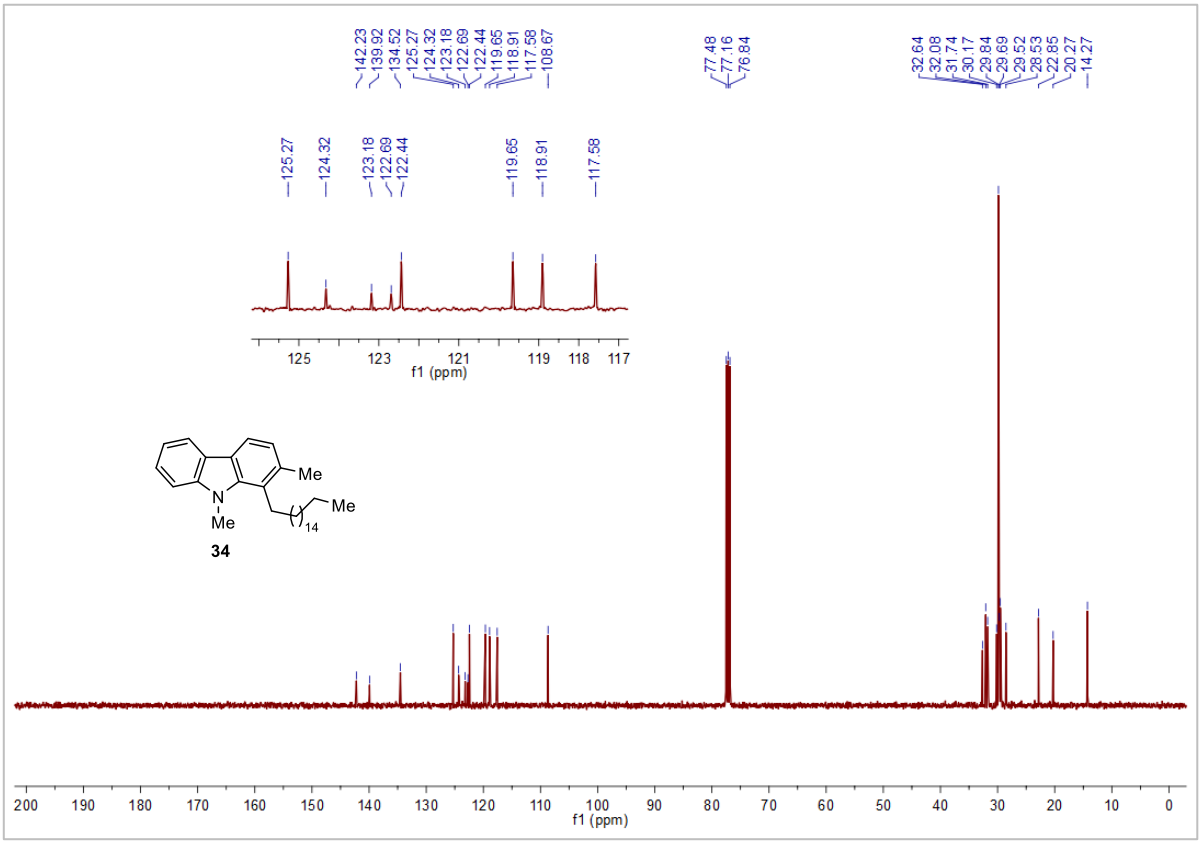
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **33**.



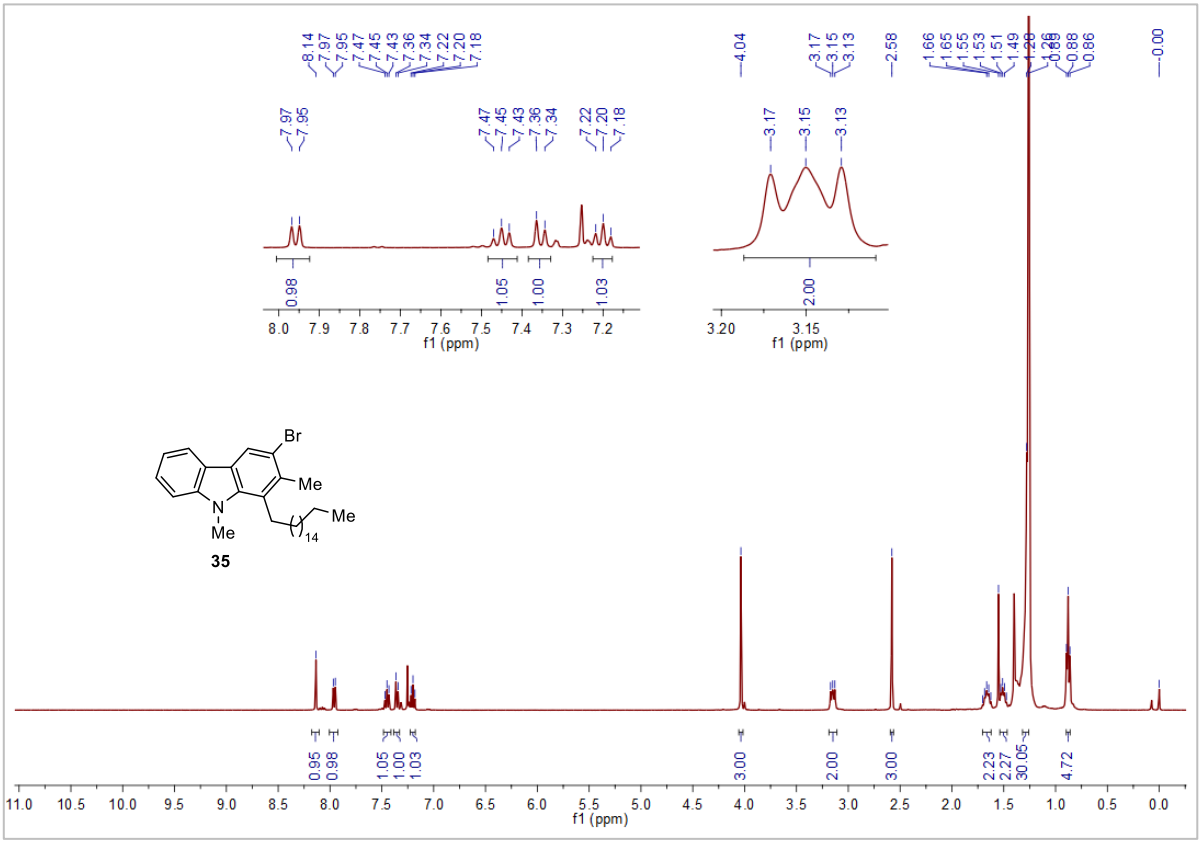


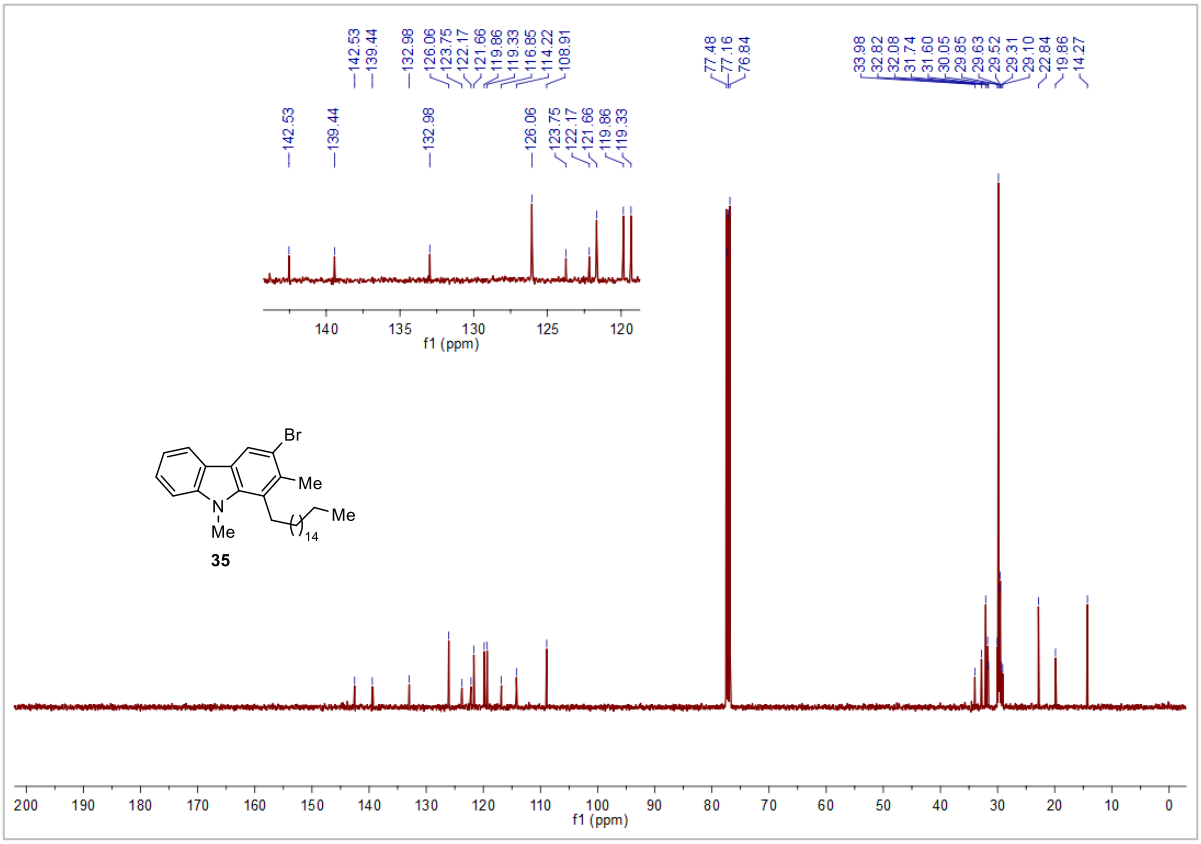
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **34**.



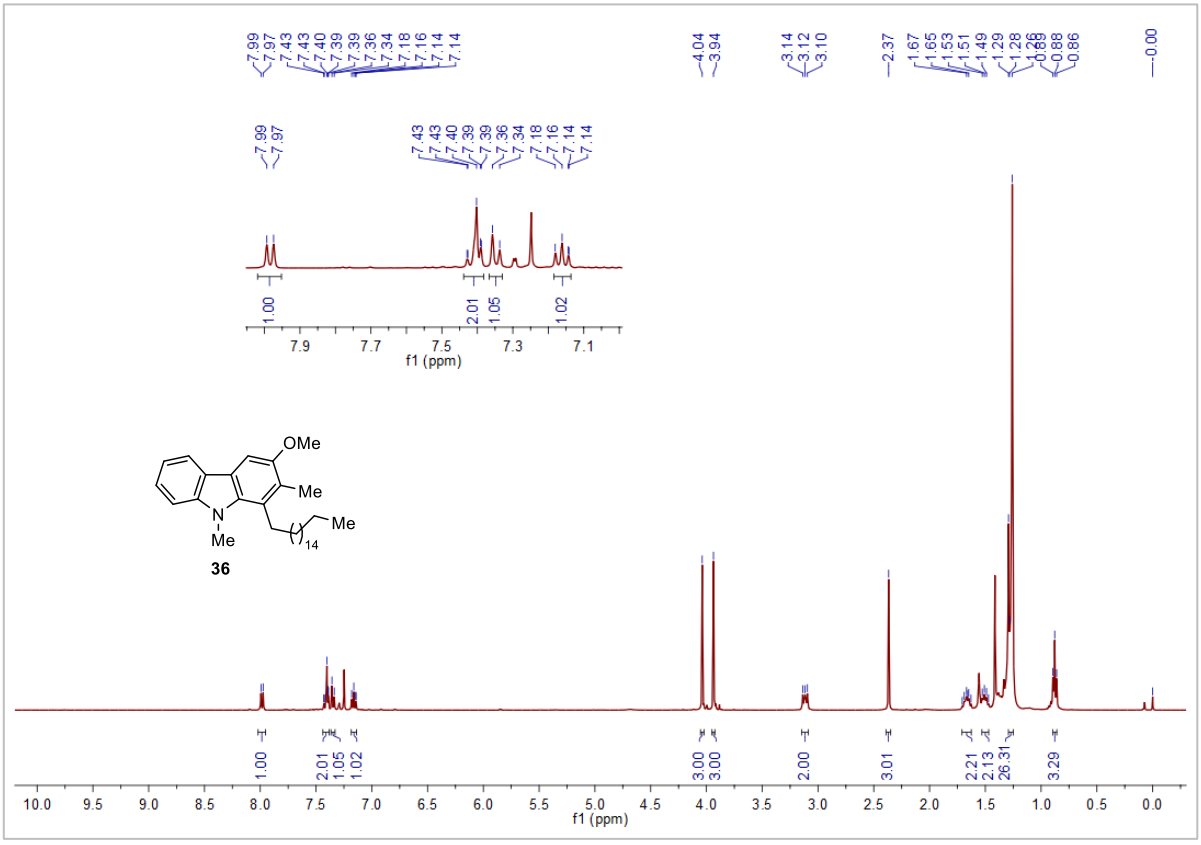


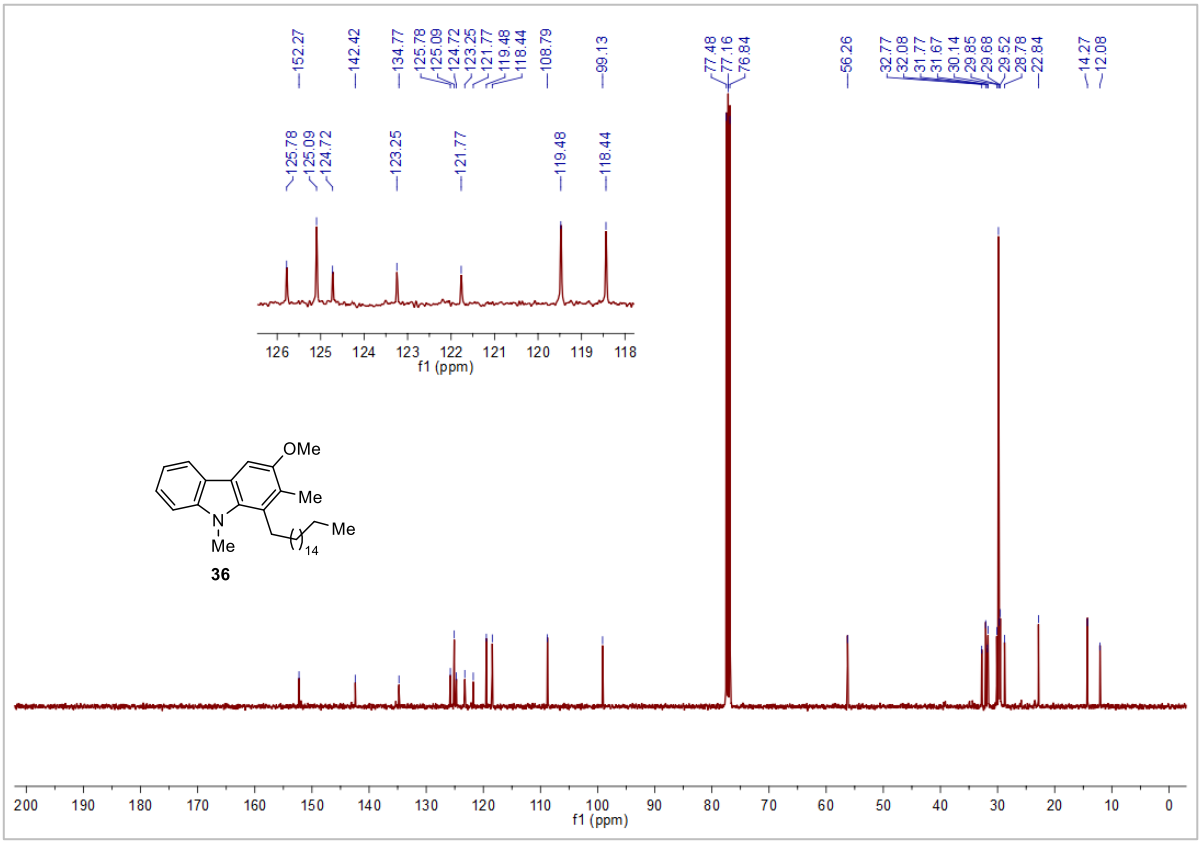
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **35**.



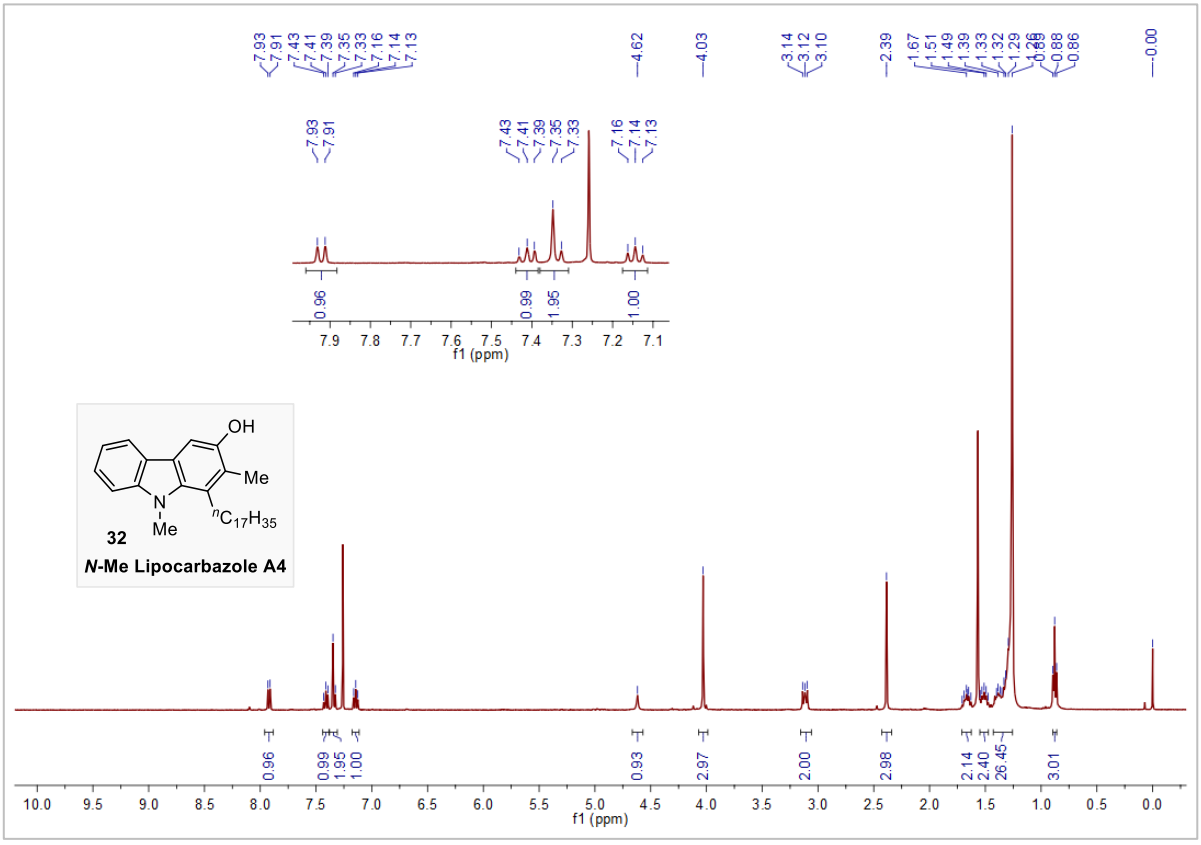


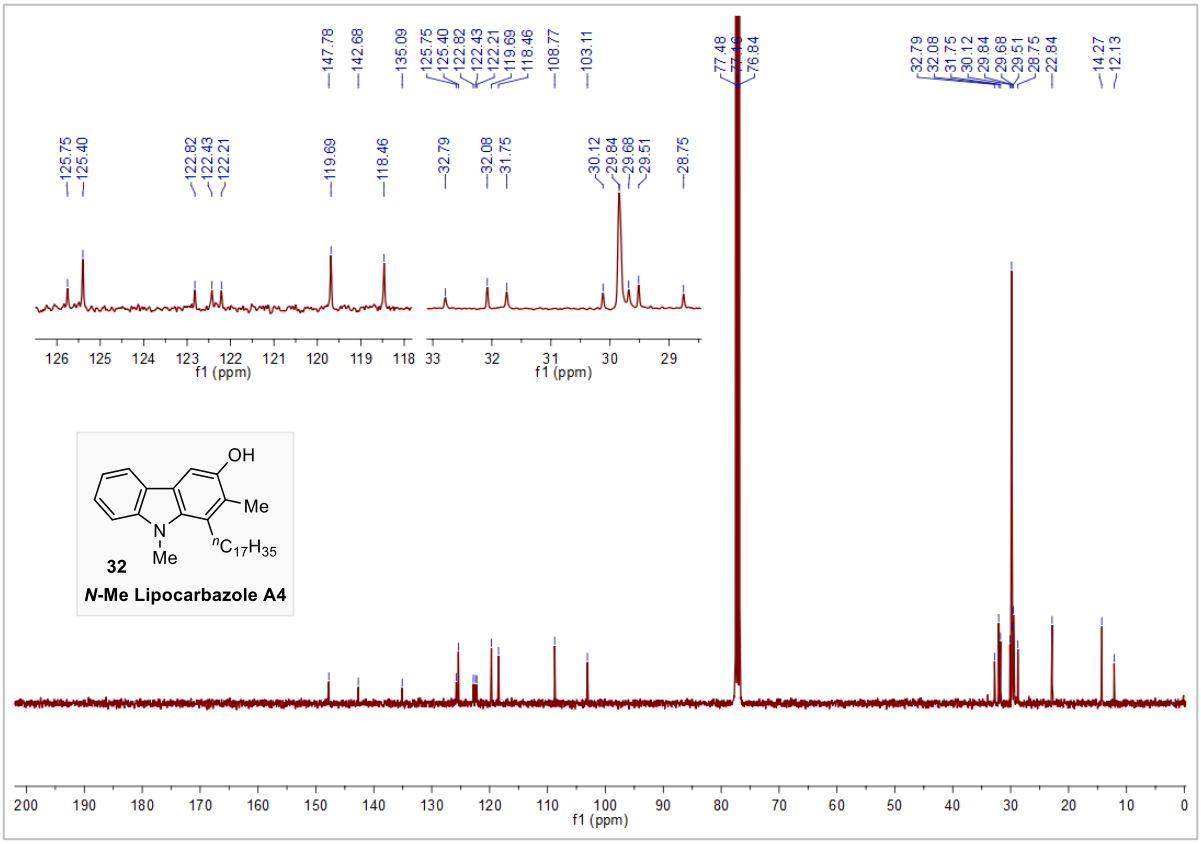
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **36**.



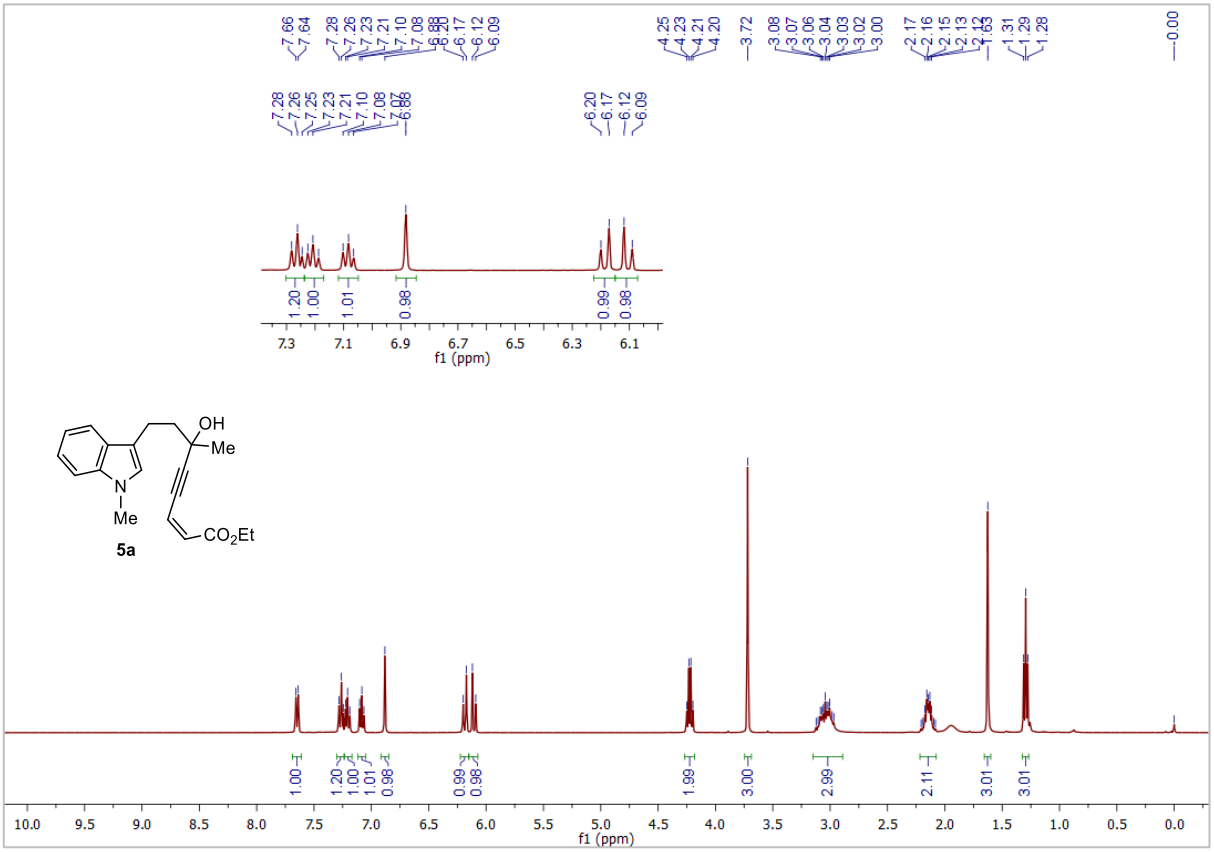


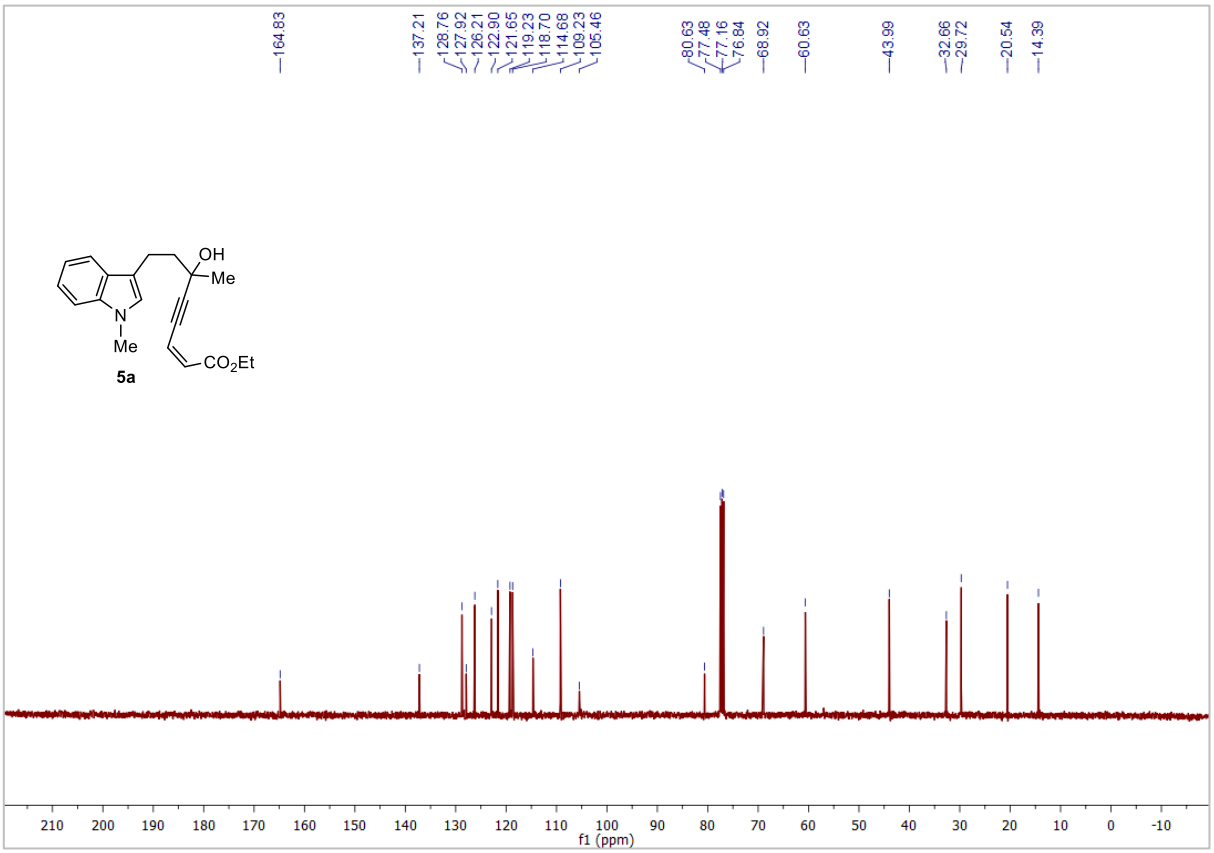
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of *N*-methyl Lipocarbazole A4 **32**.



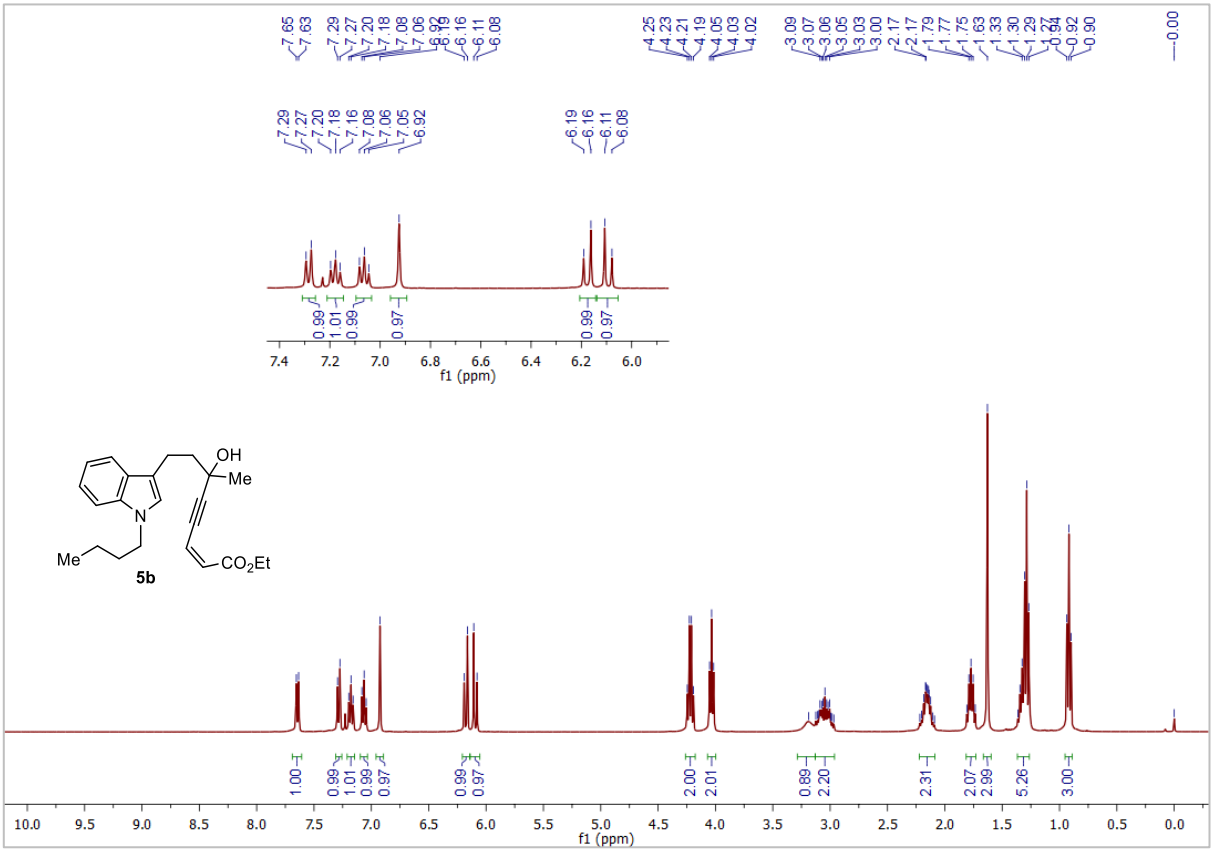


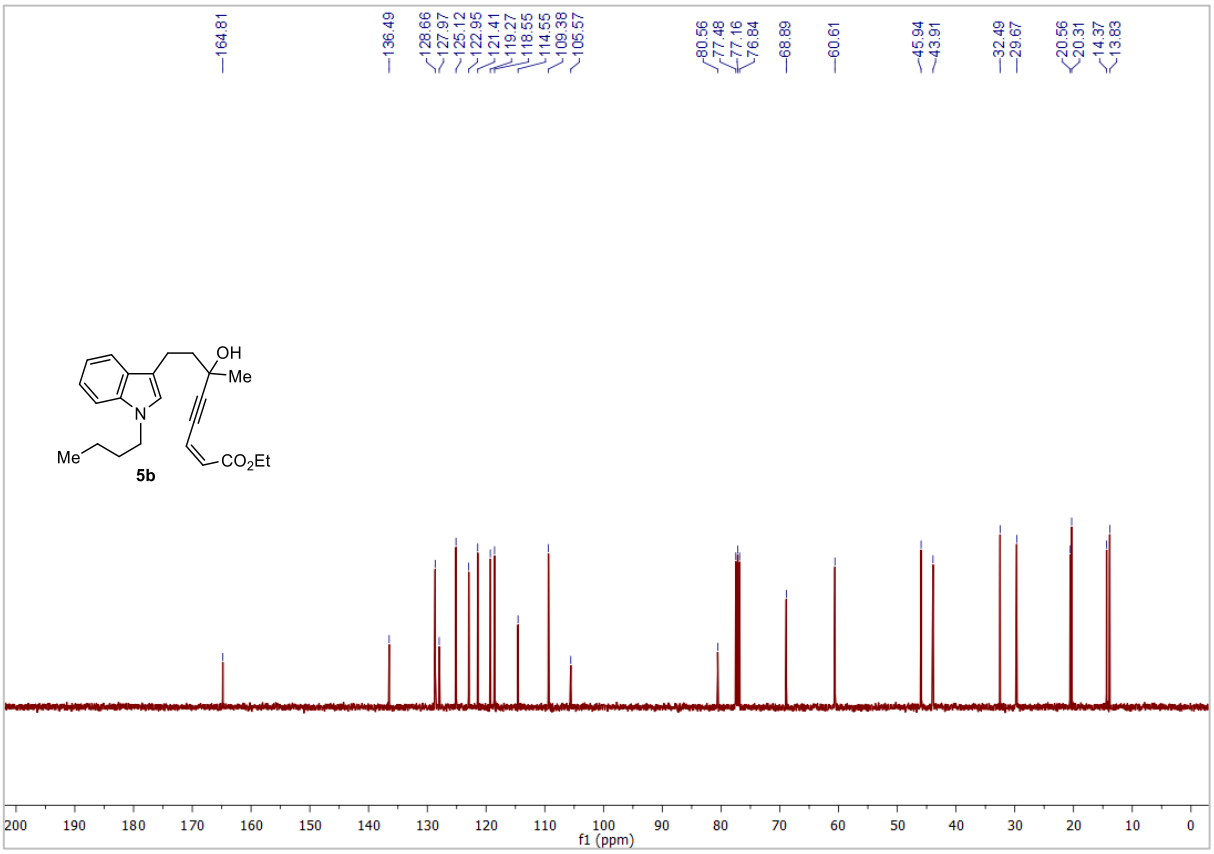
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5a**.



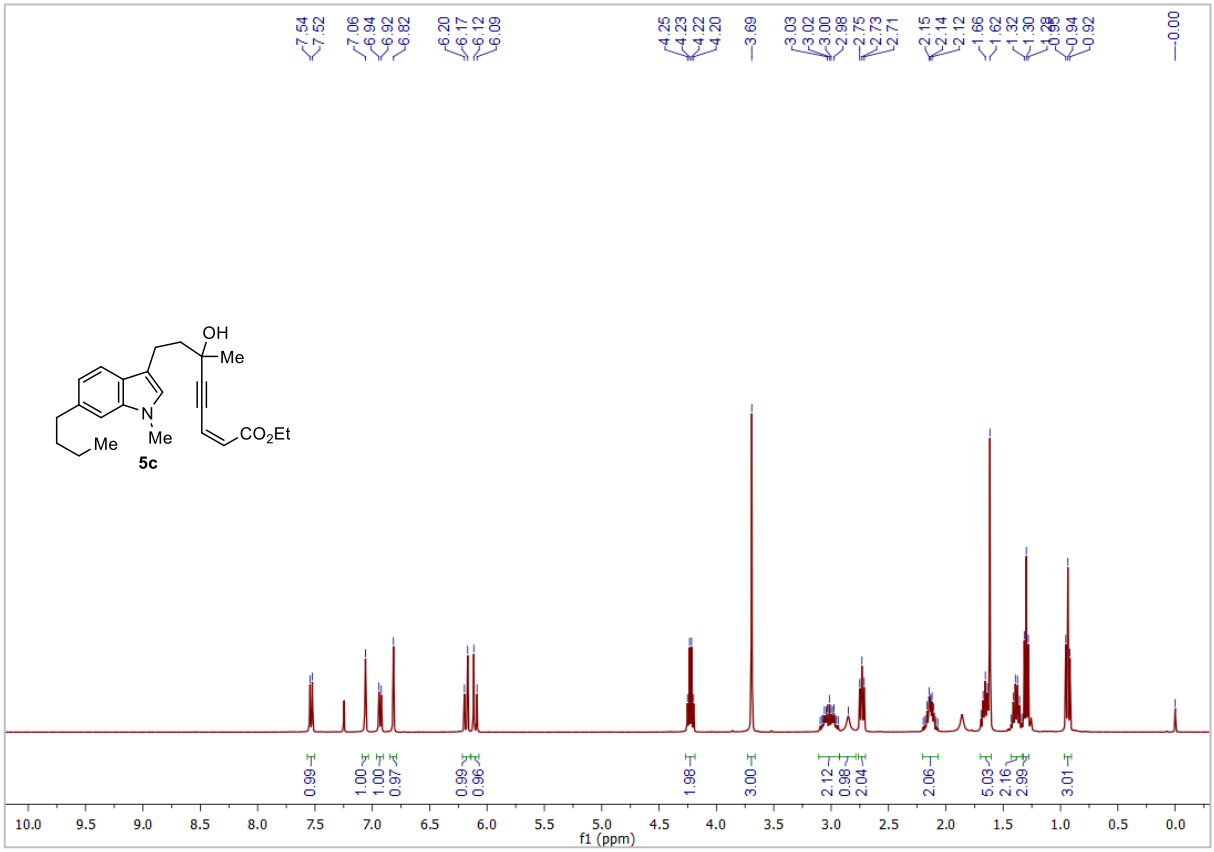


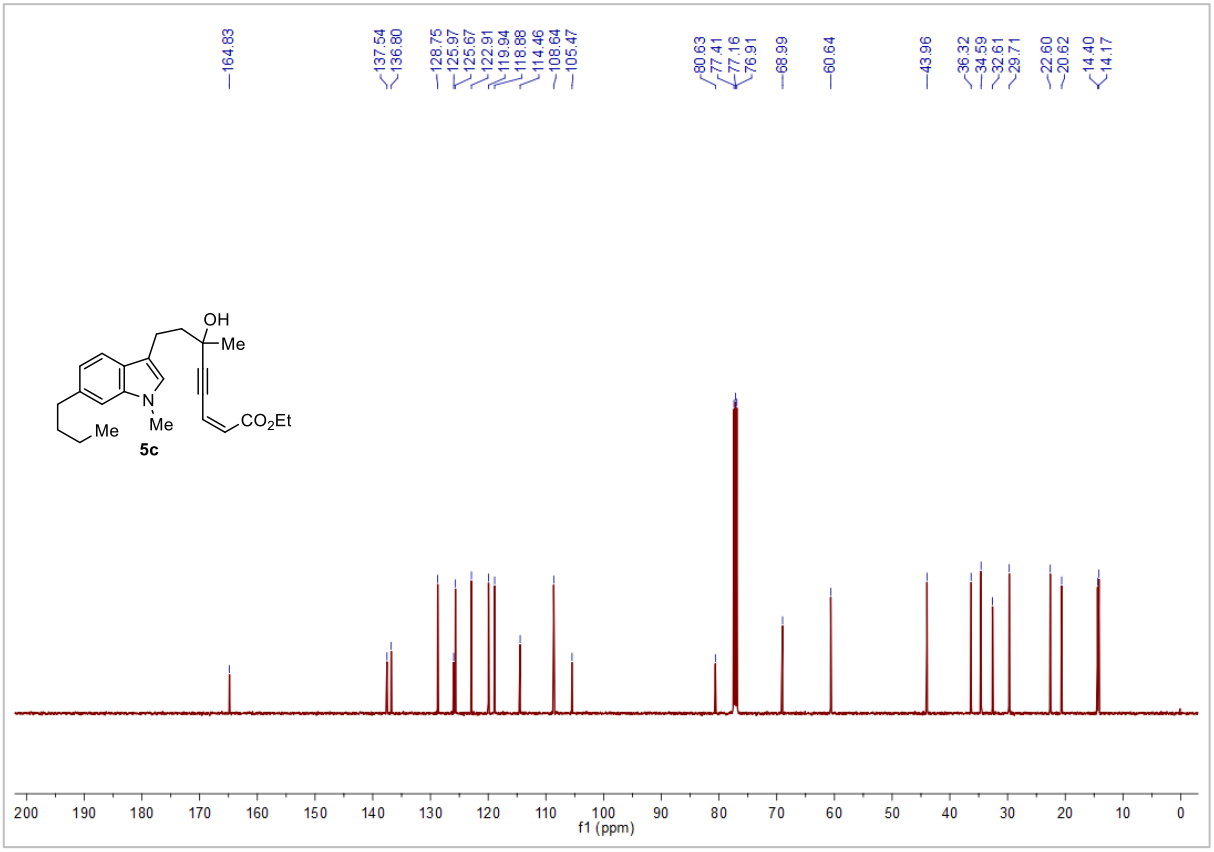
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5b**.



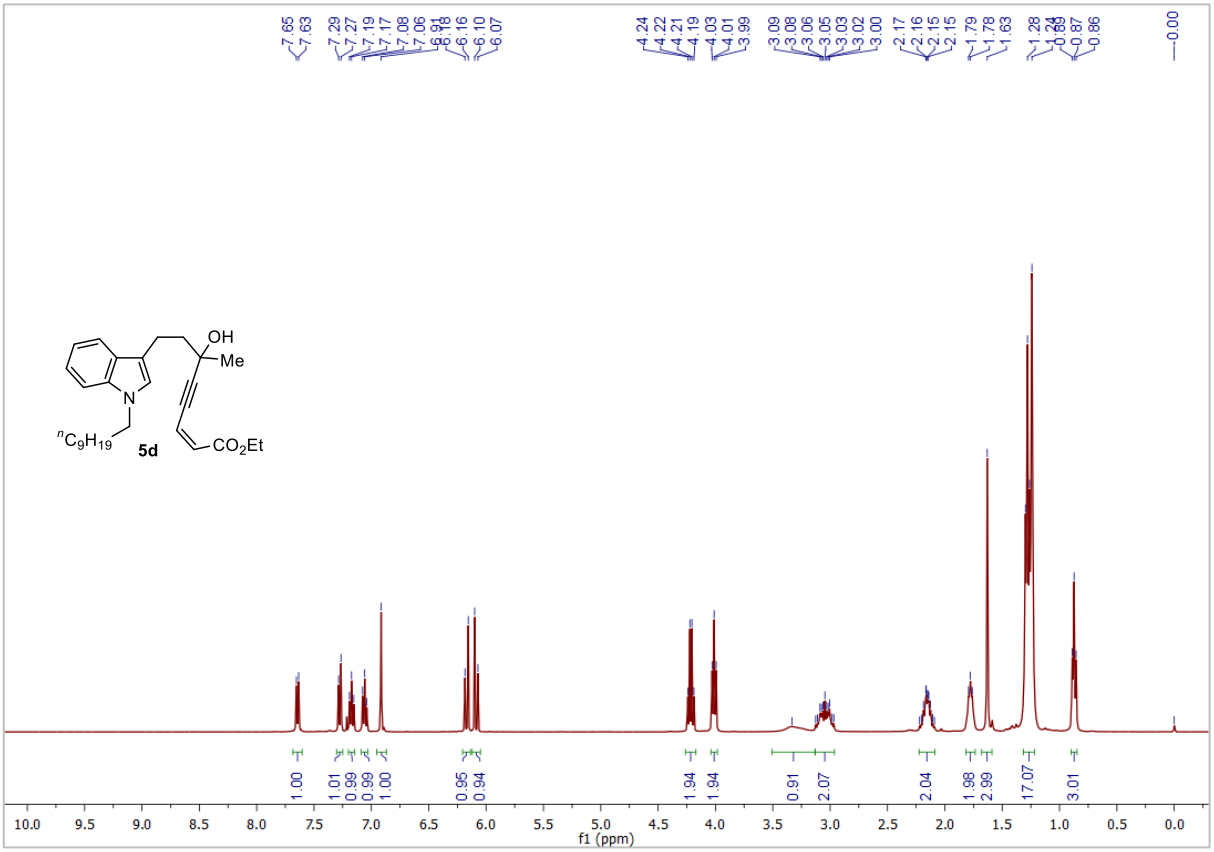


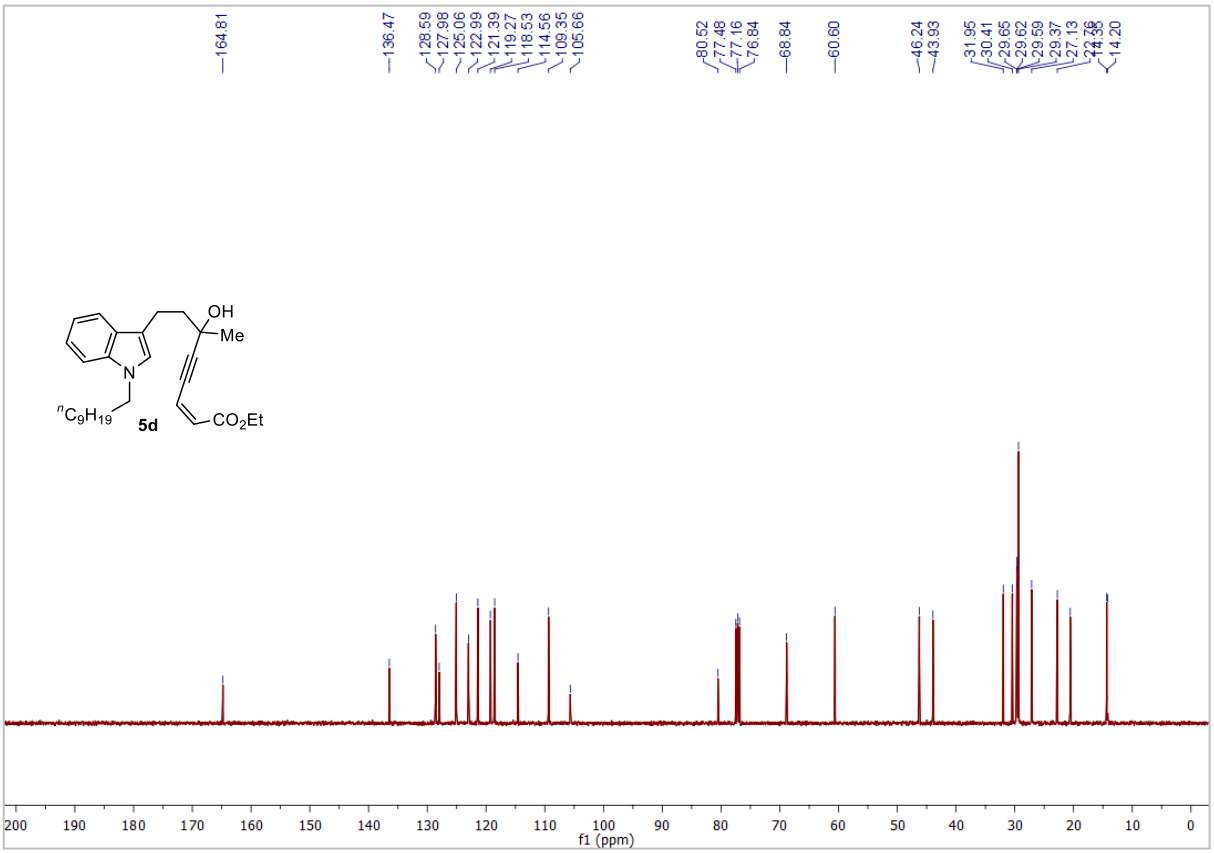
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5c**.



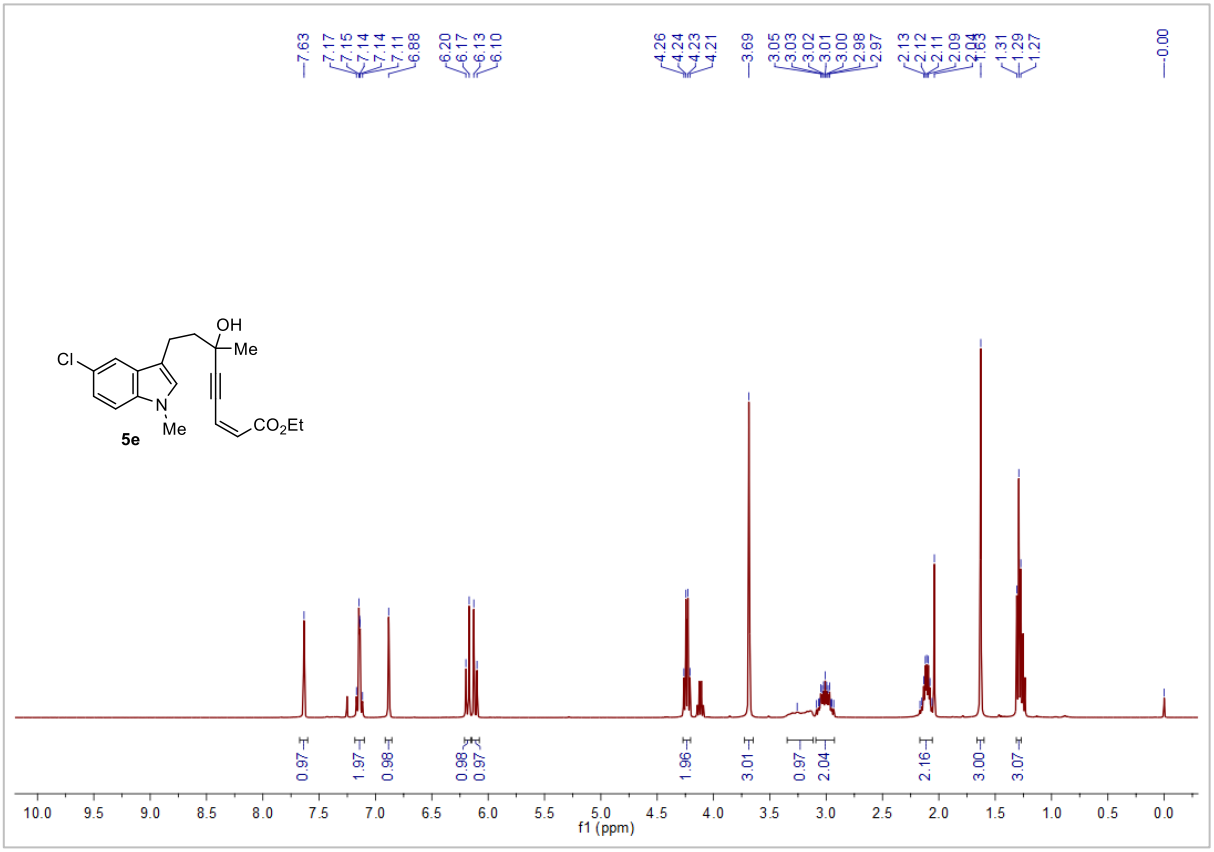


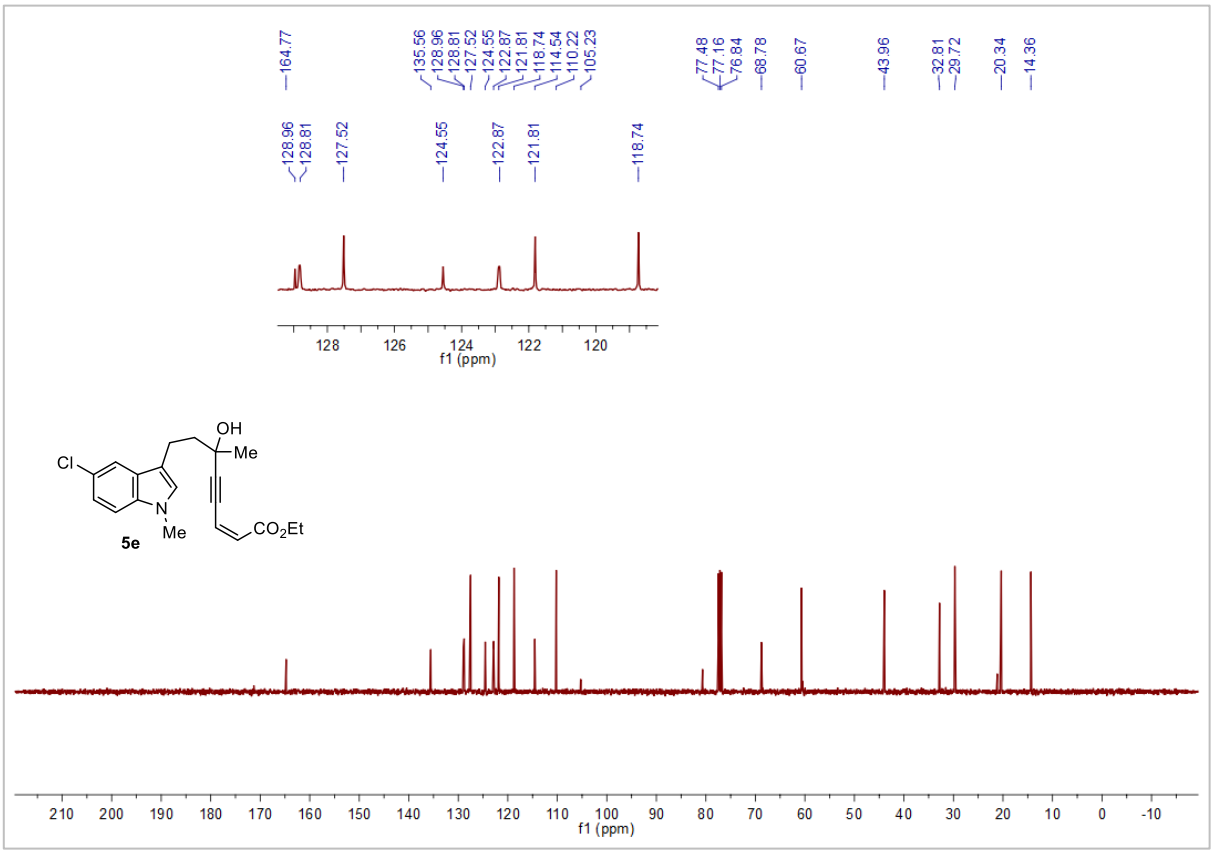
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5d**.



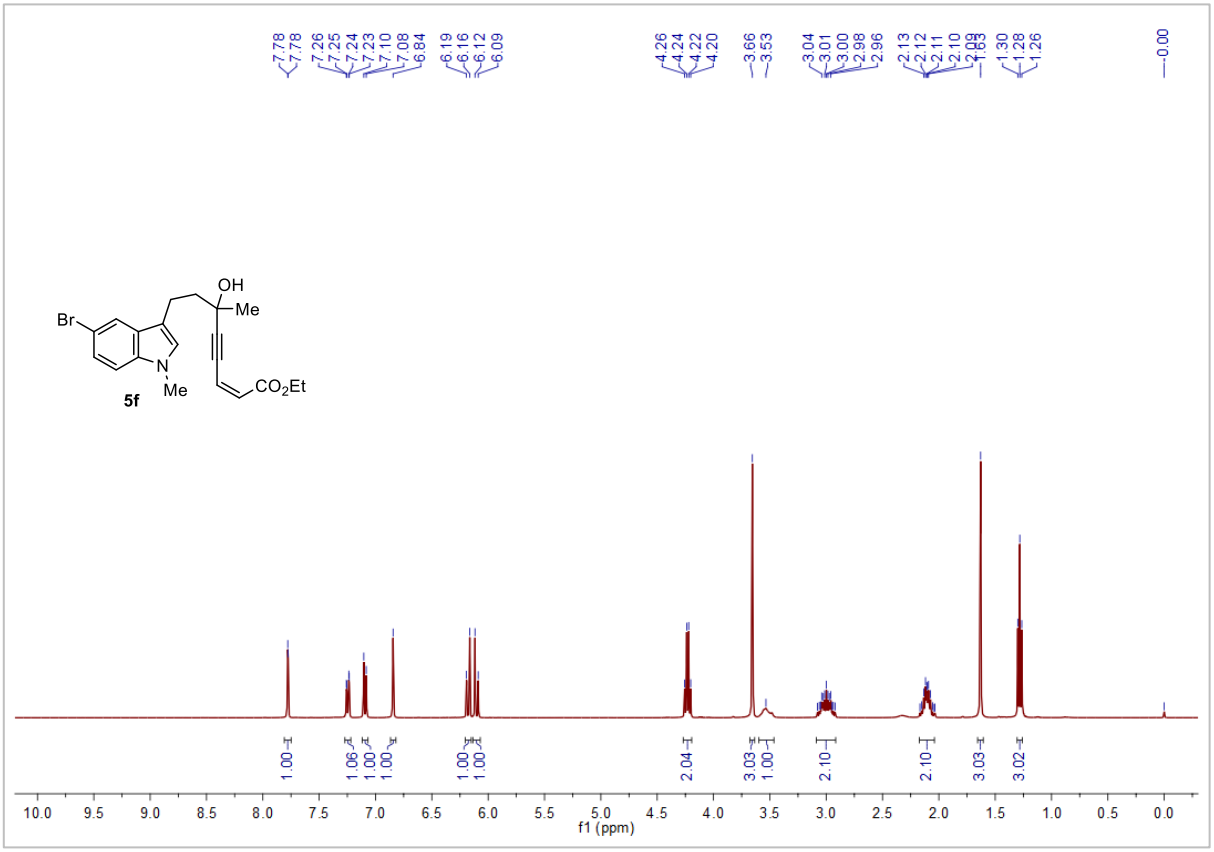


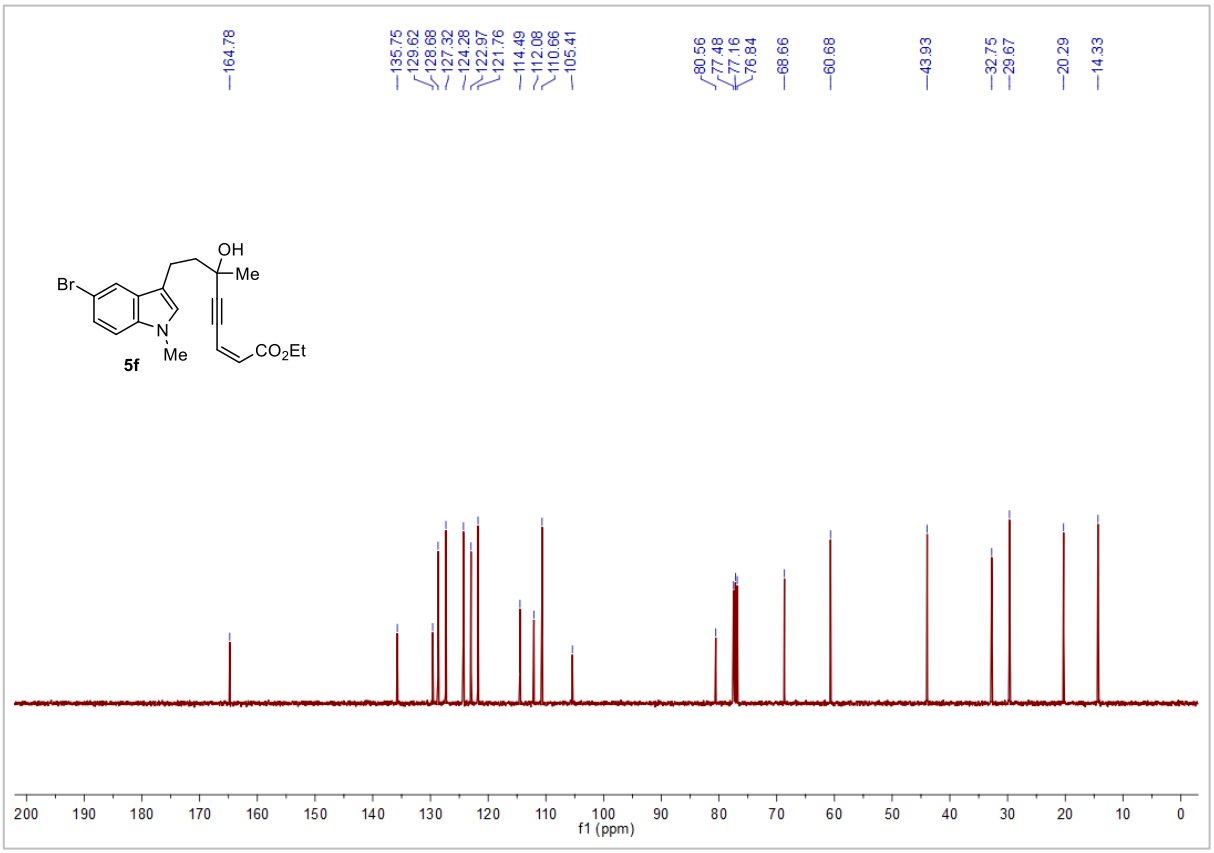
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5e**.



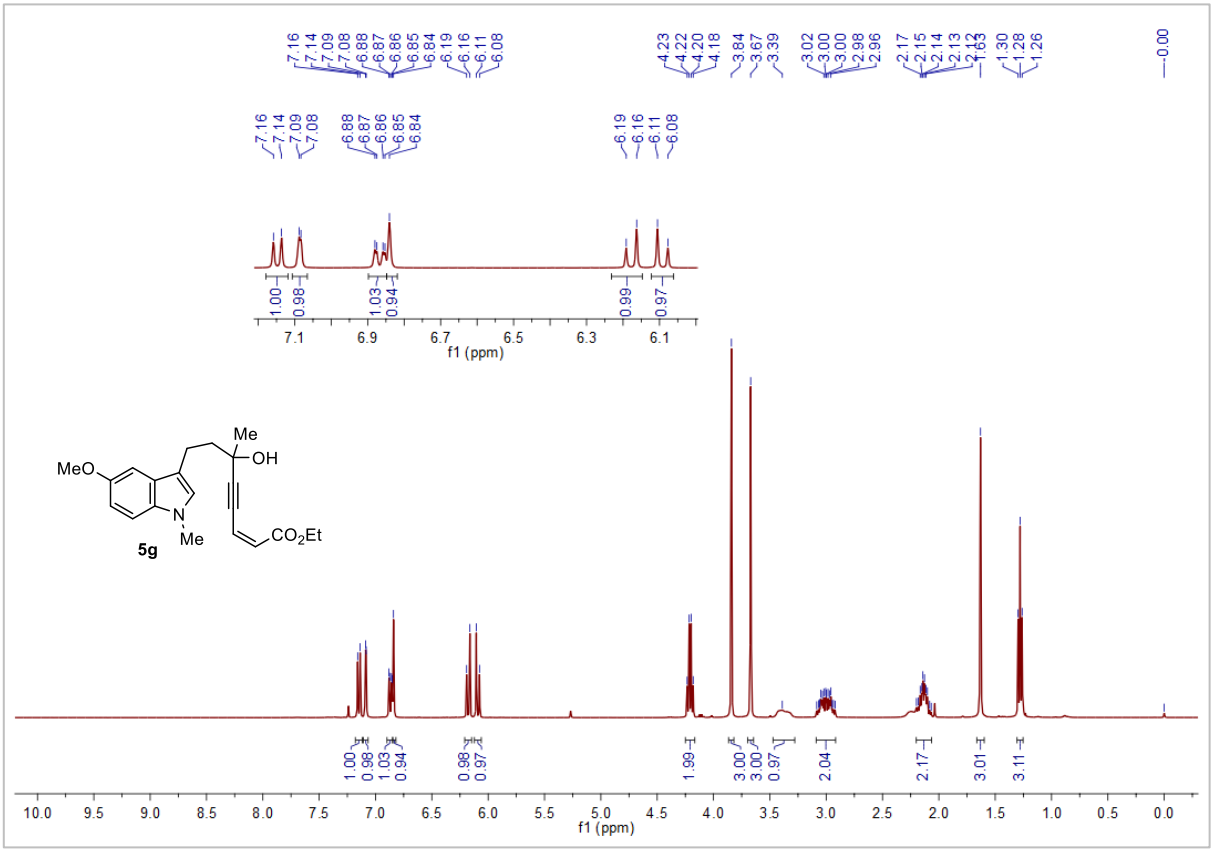


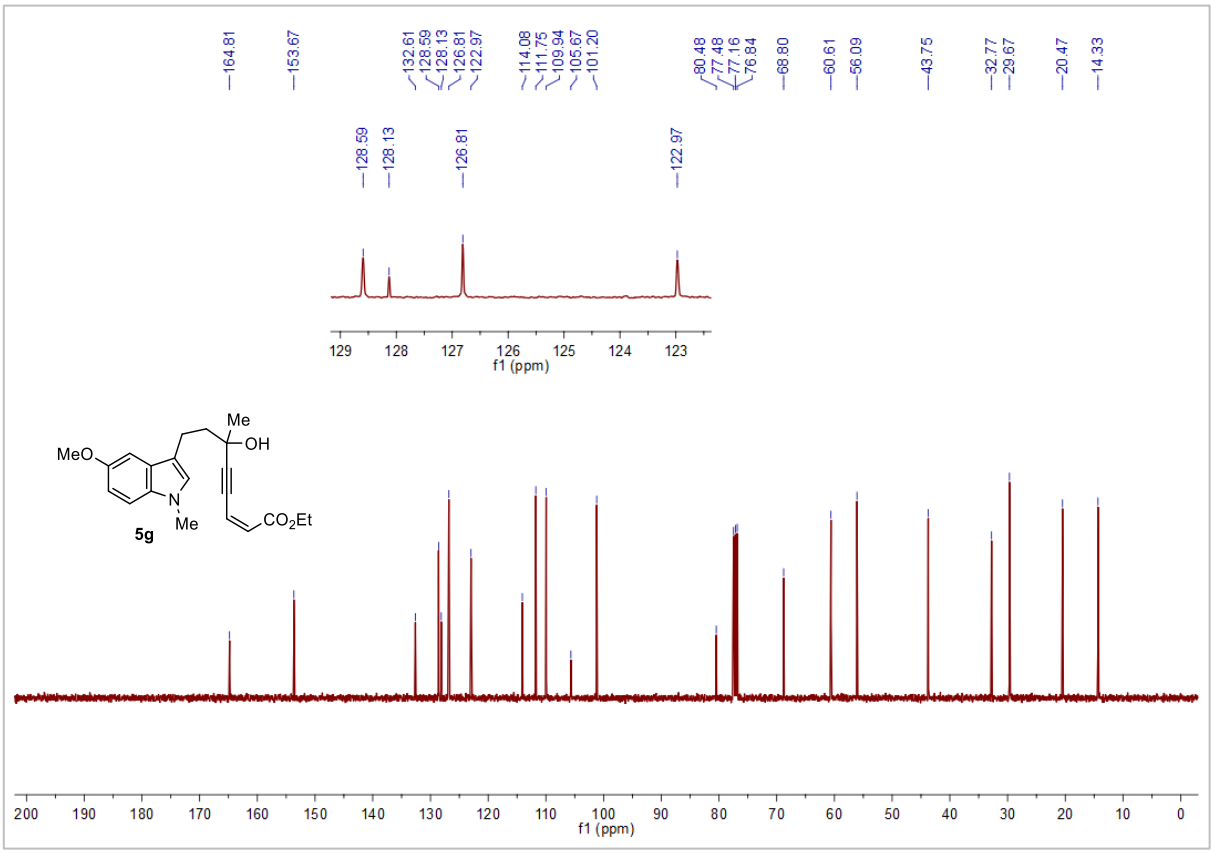
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5f**.



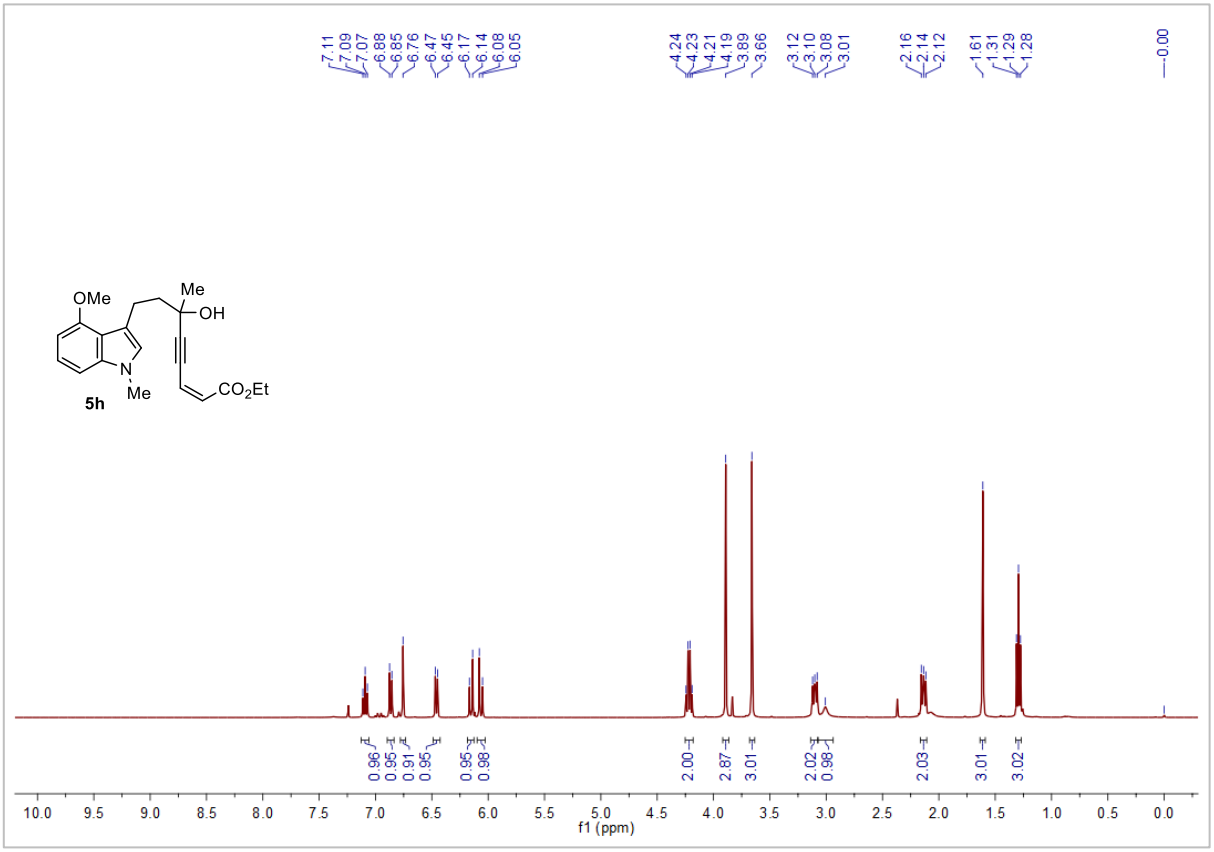


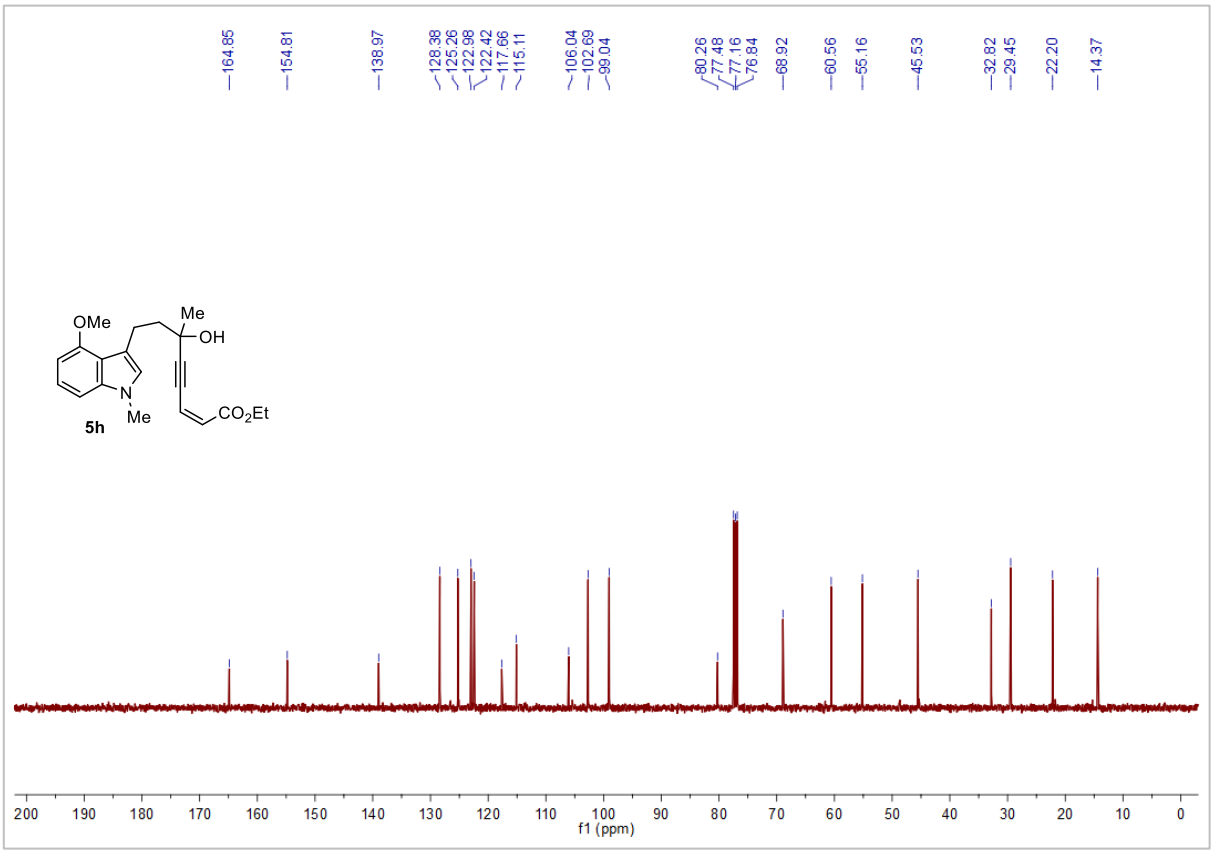
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5g**.



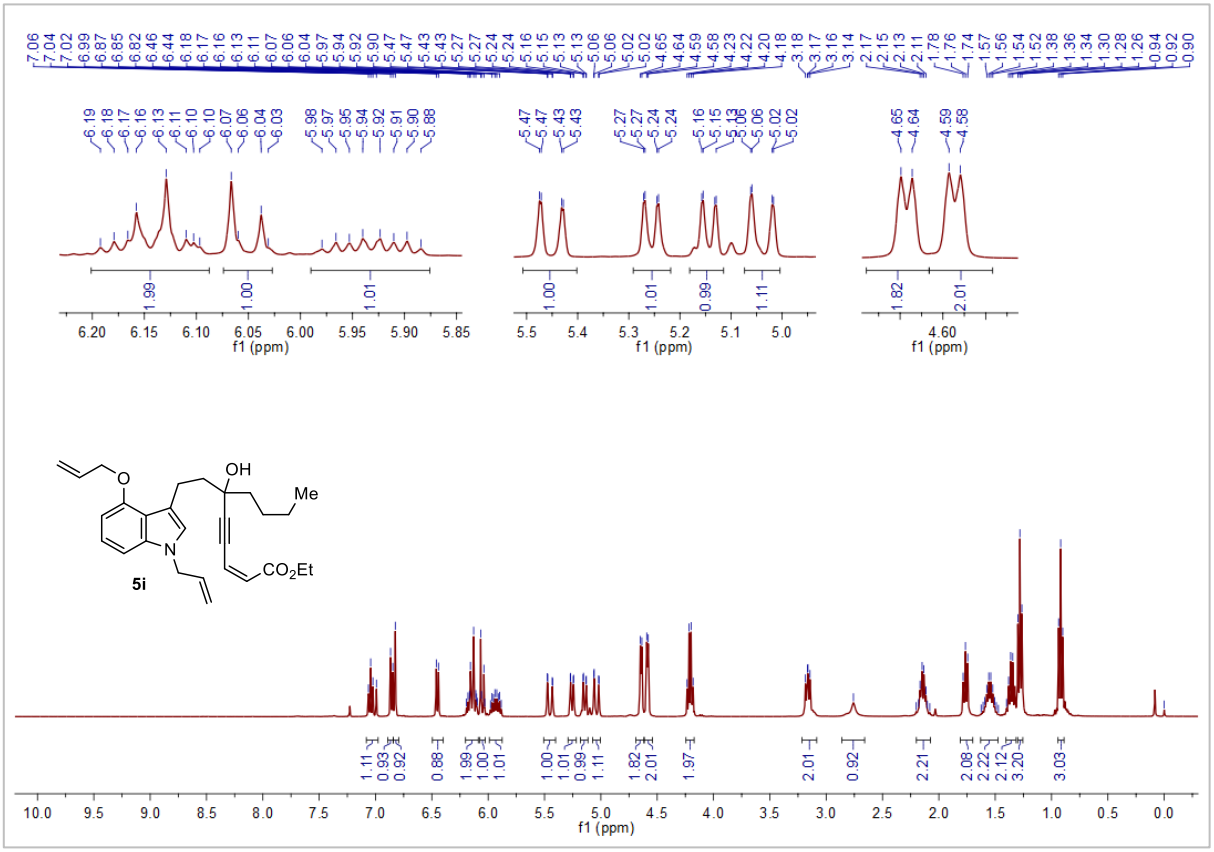


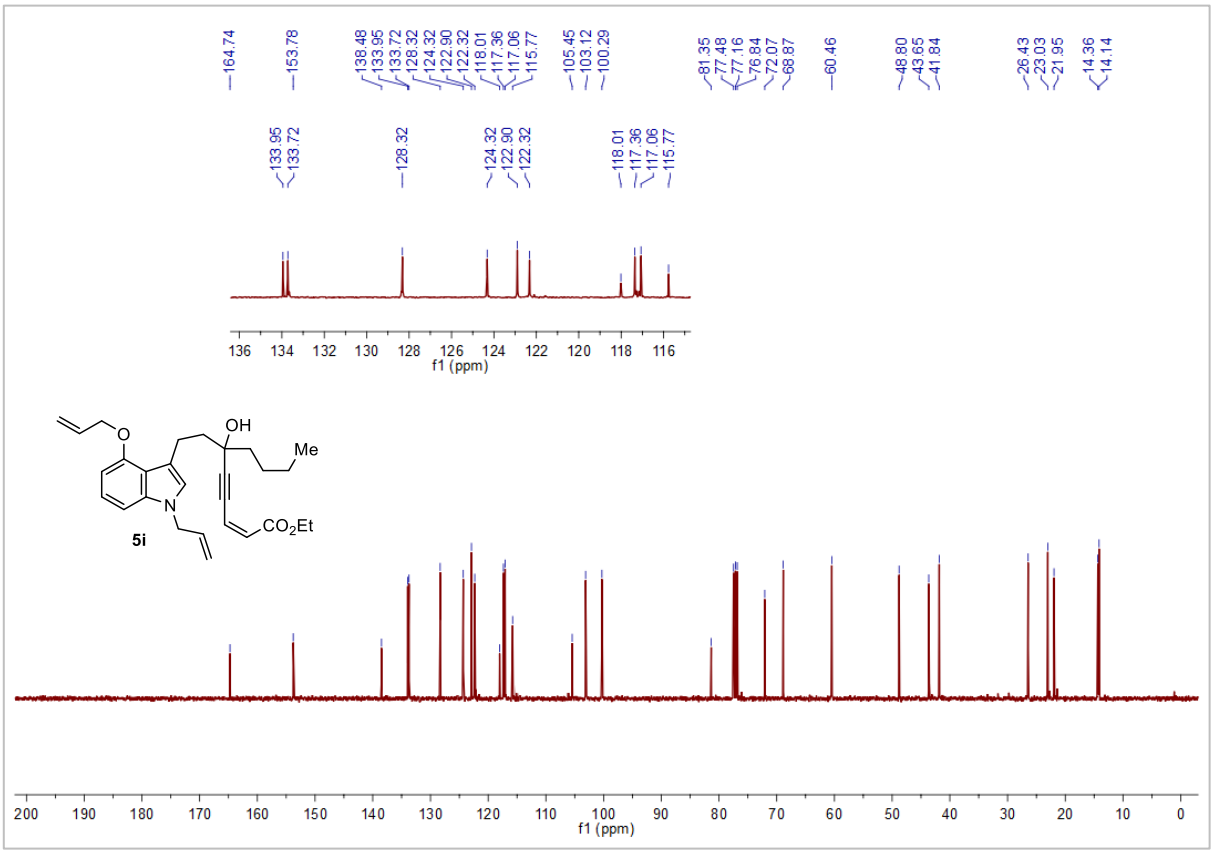
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5h**.



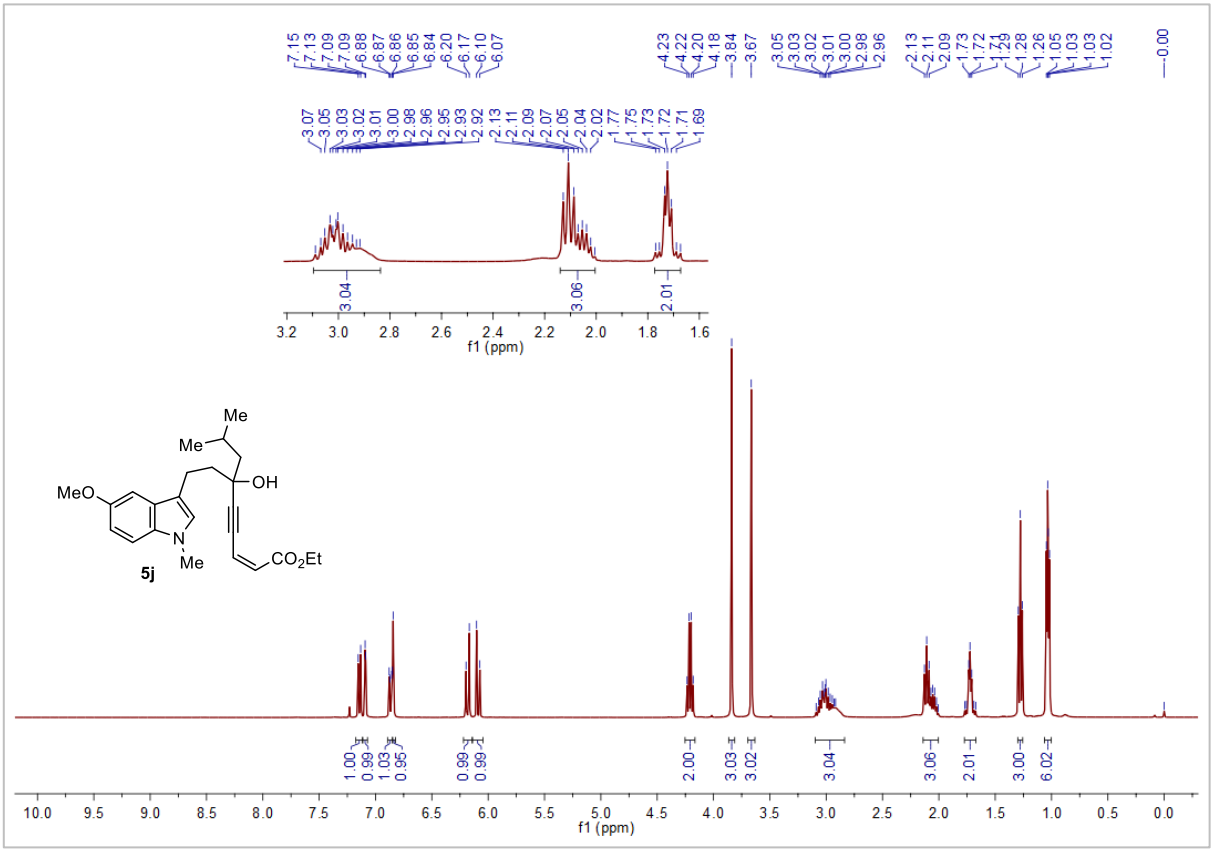


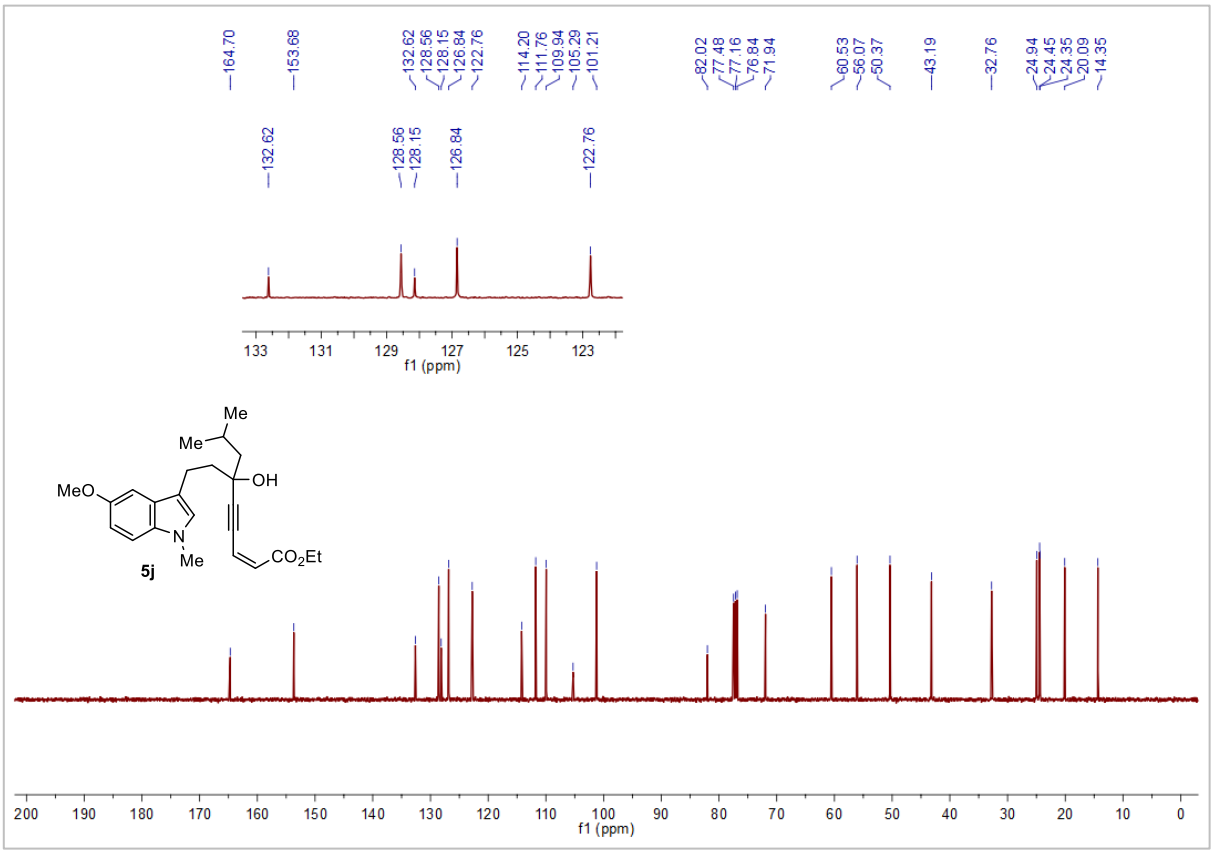
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5i**.



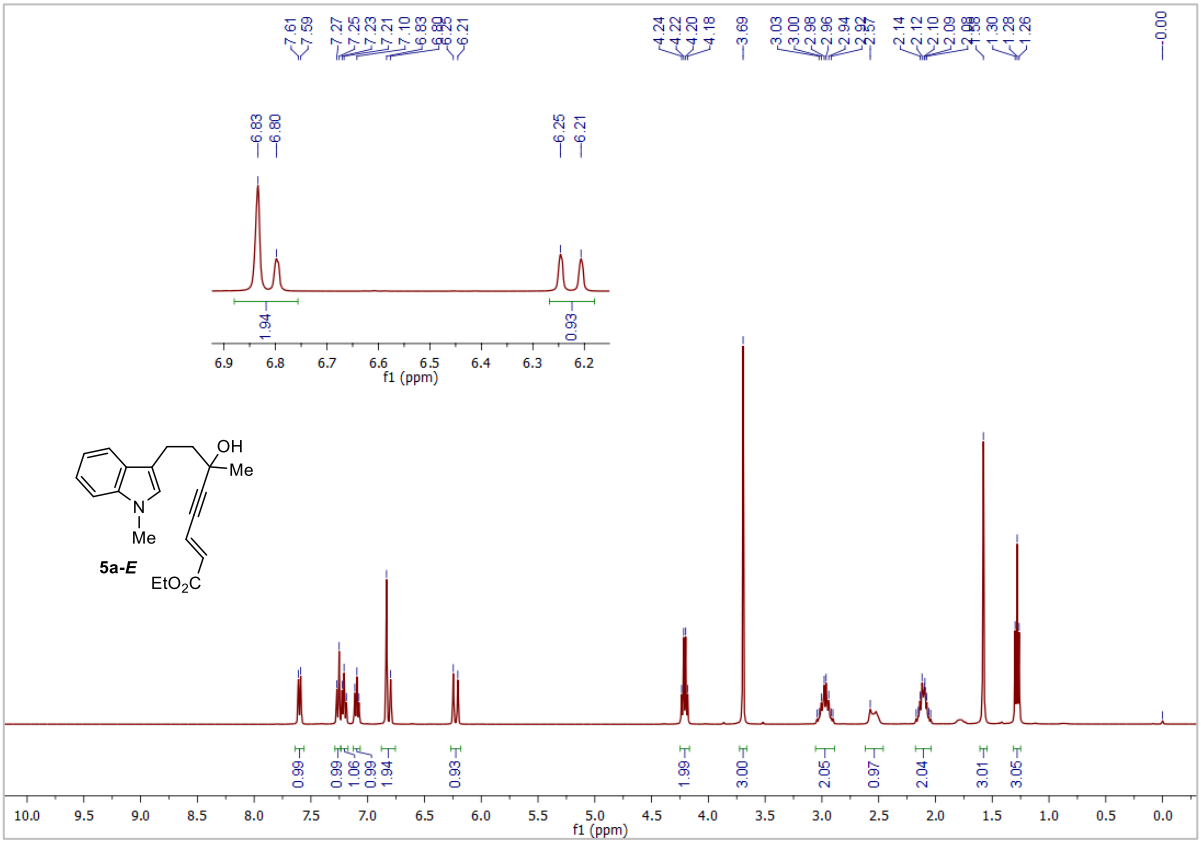


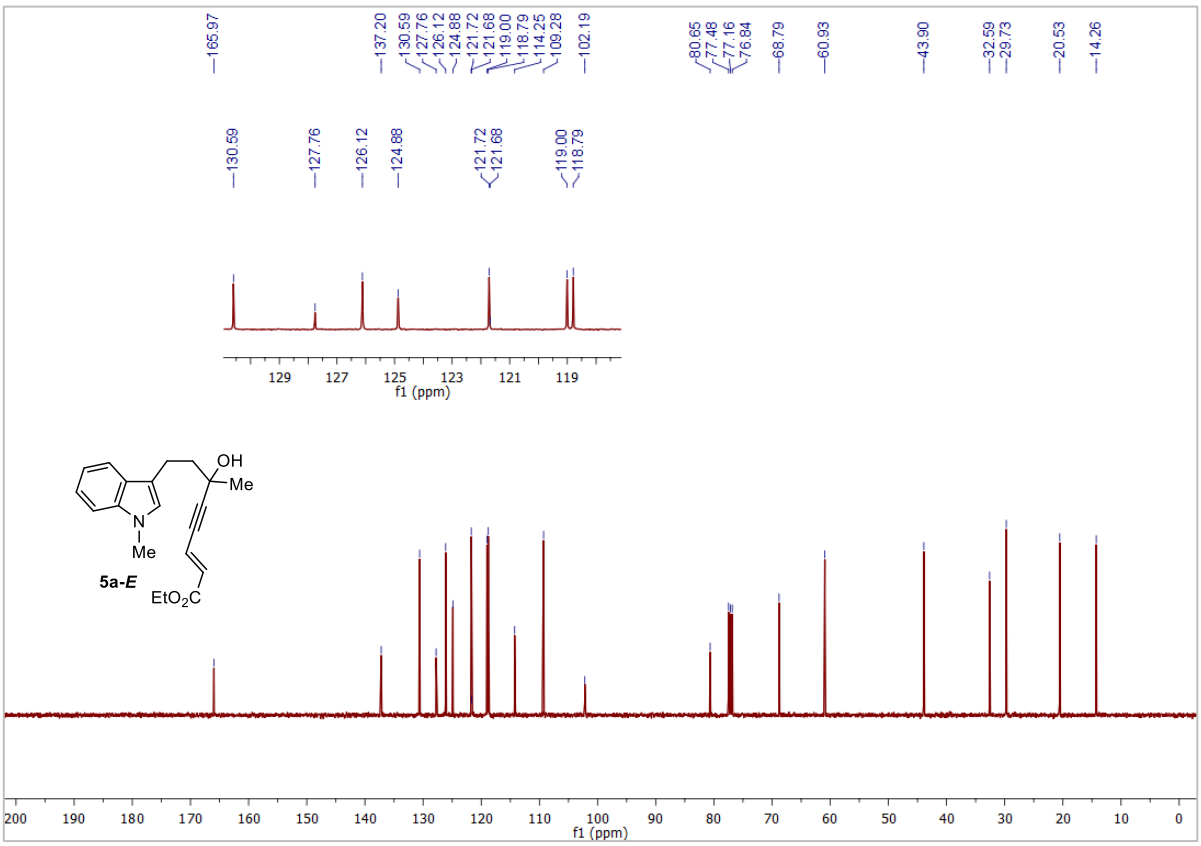
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5j**.



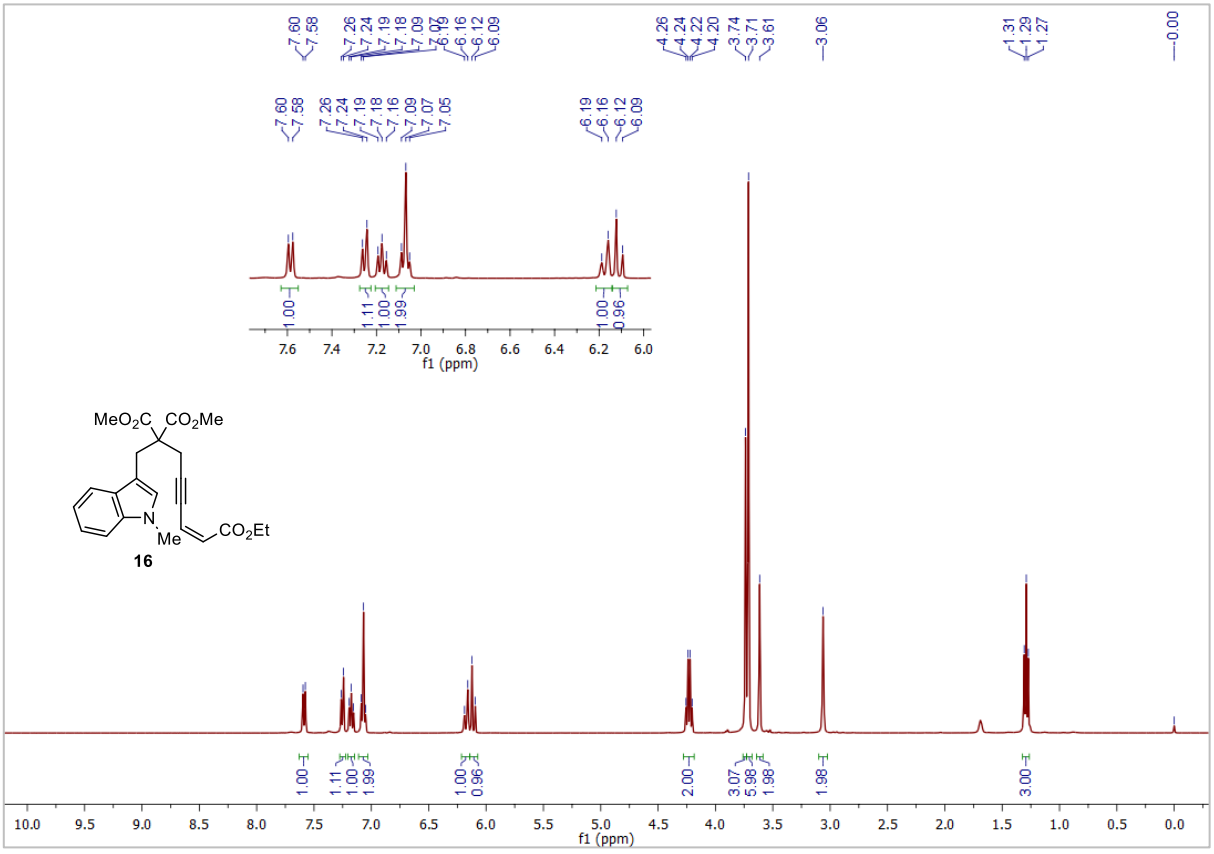


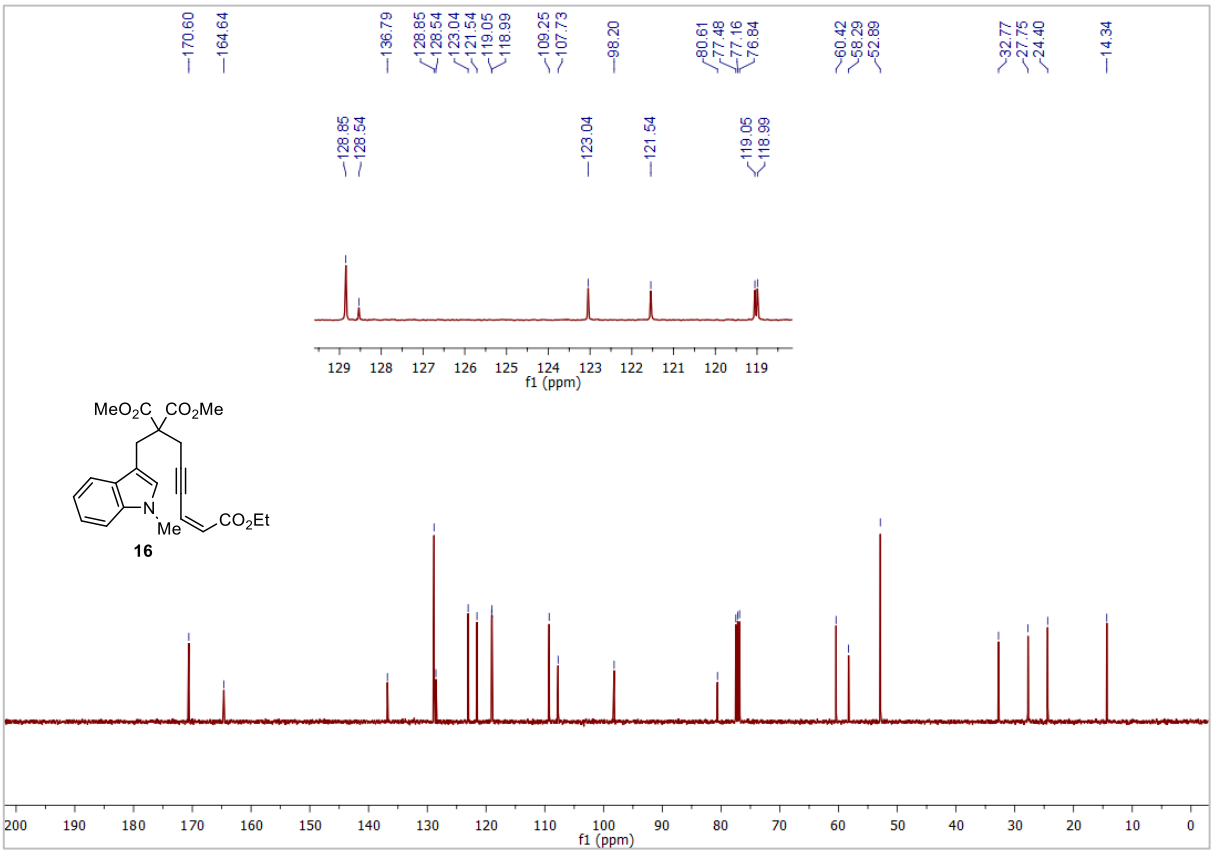
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5a-*E***.



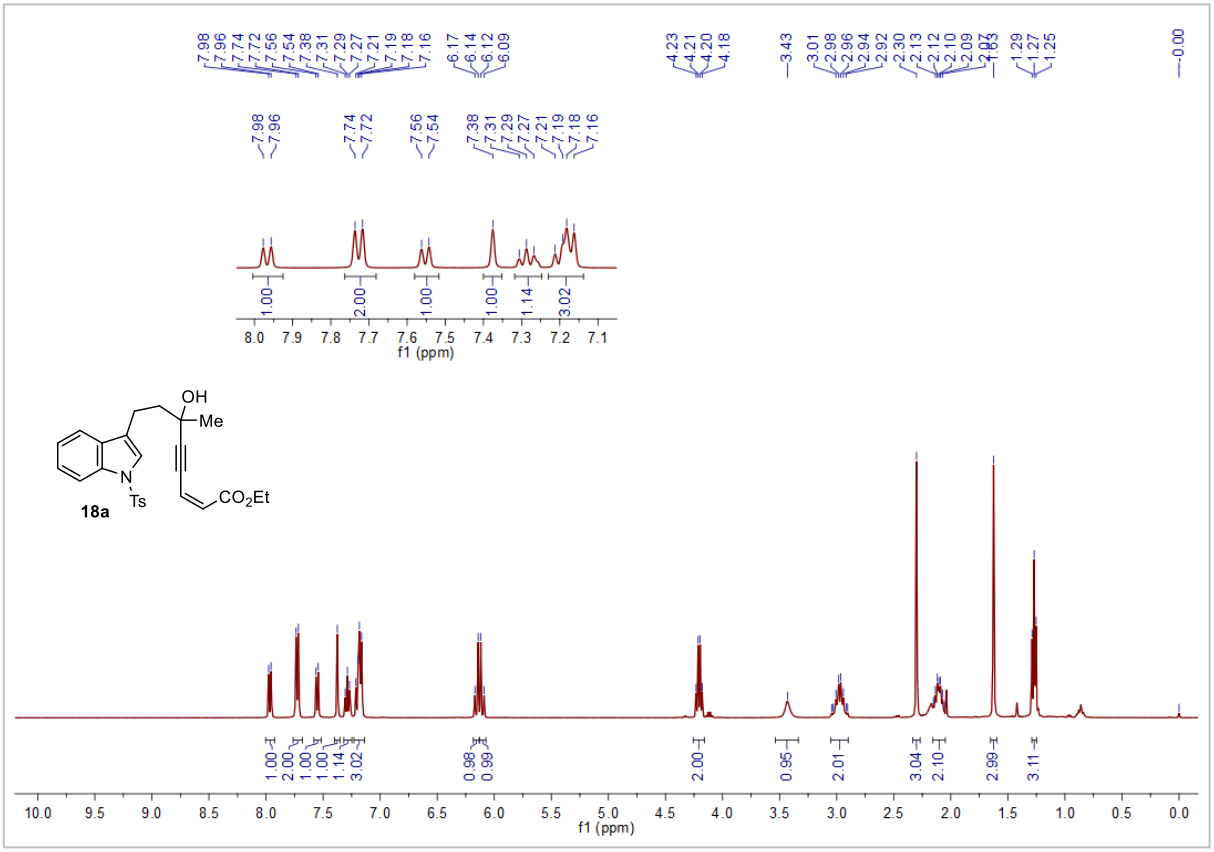


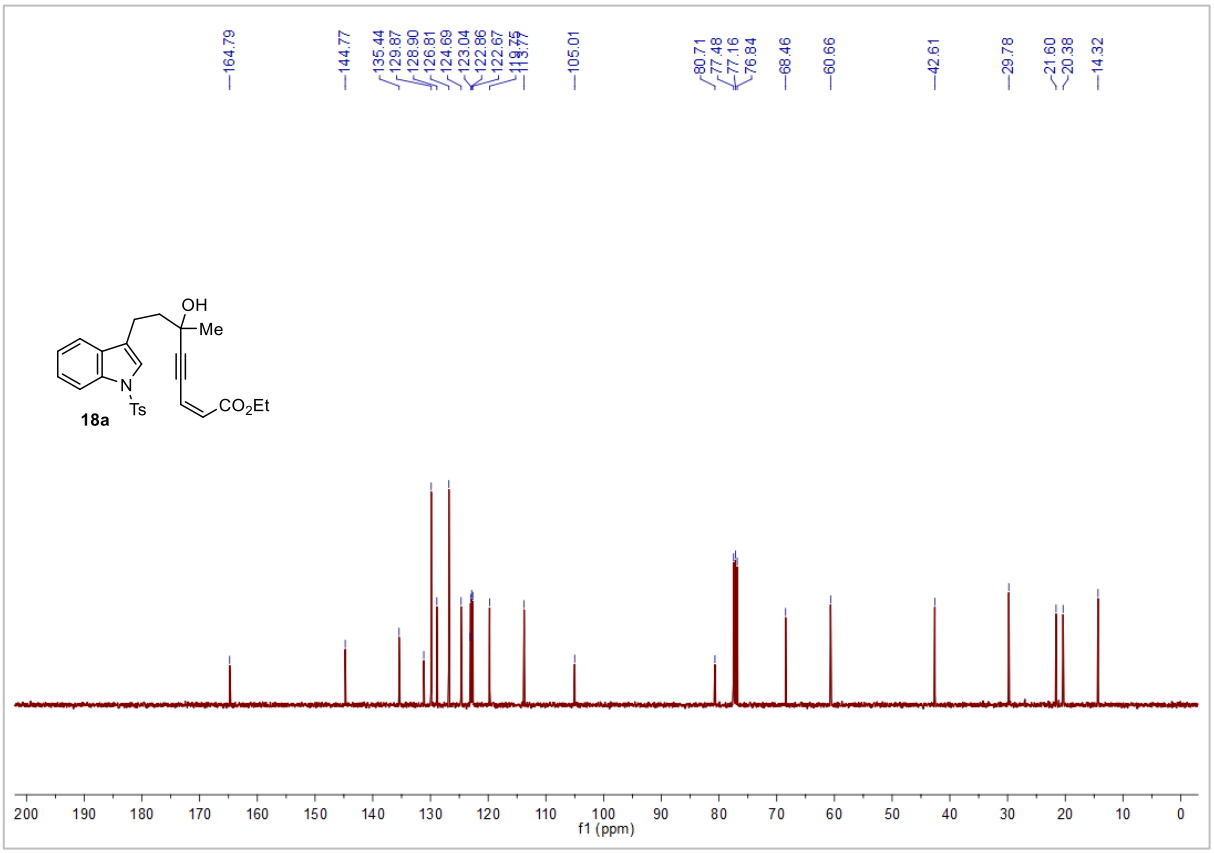
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **16**.



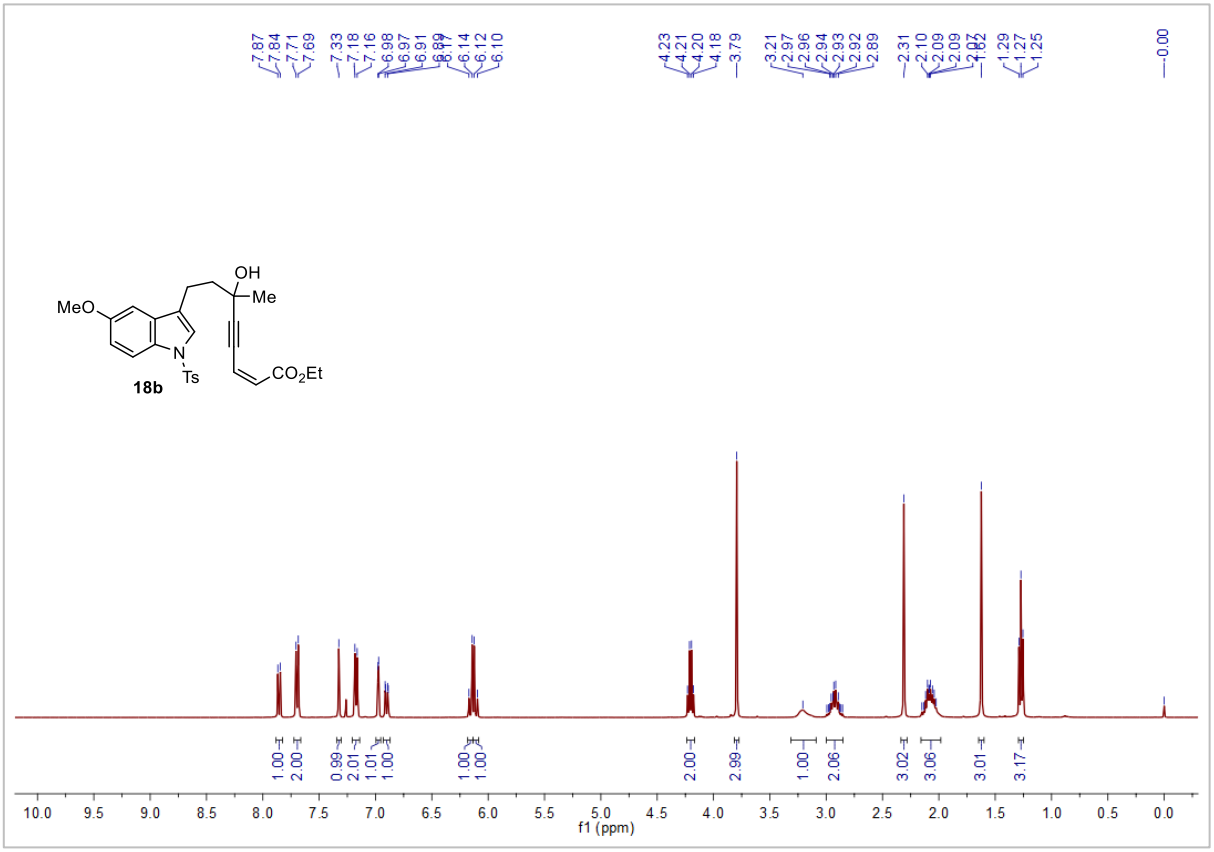


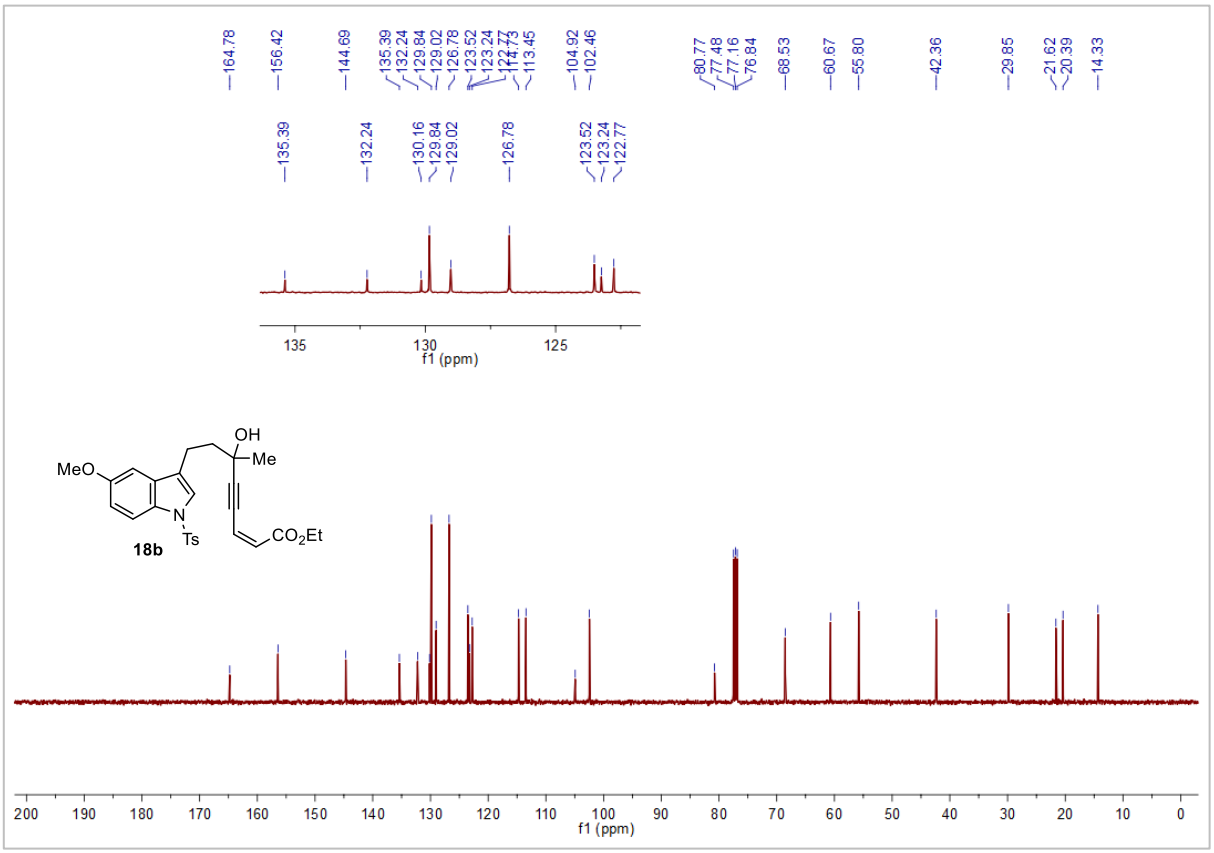
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **18a**.



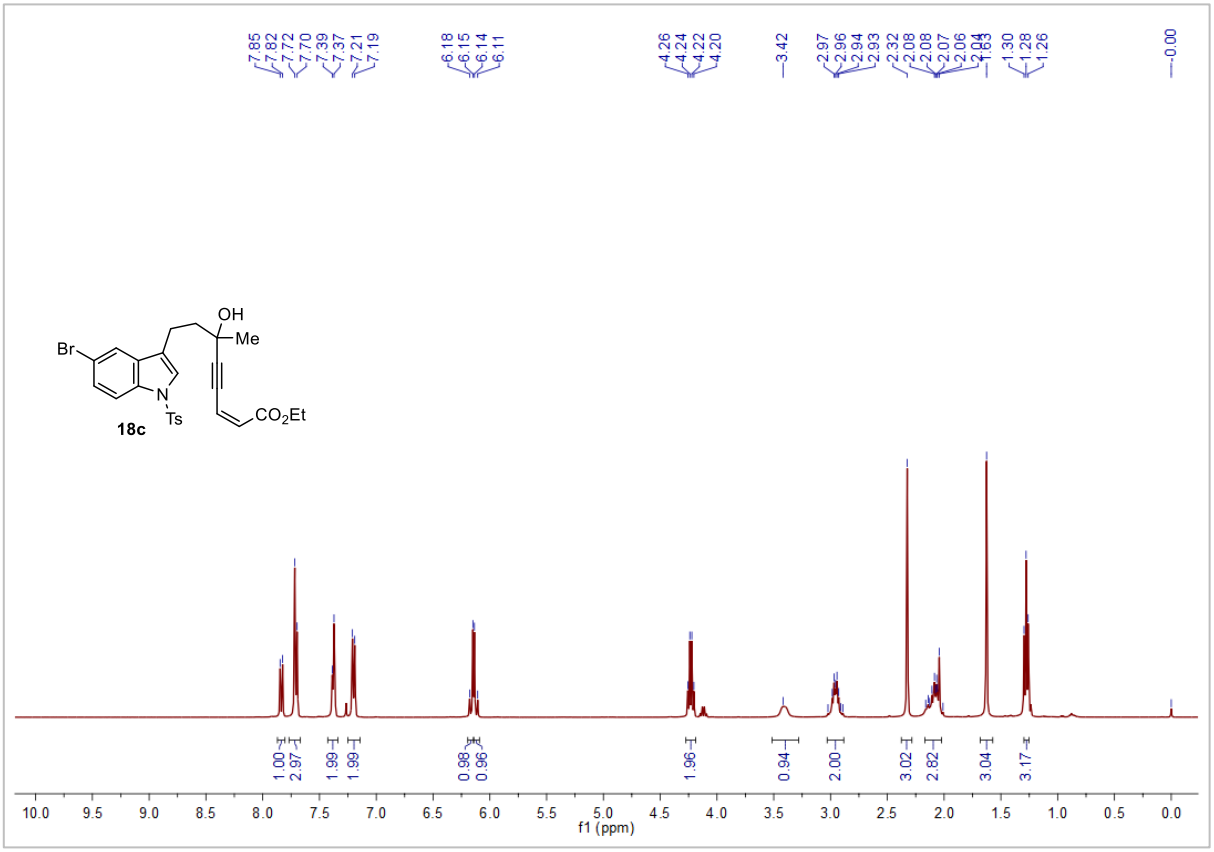


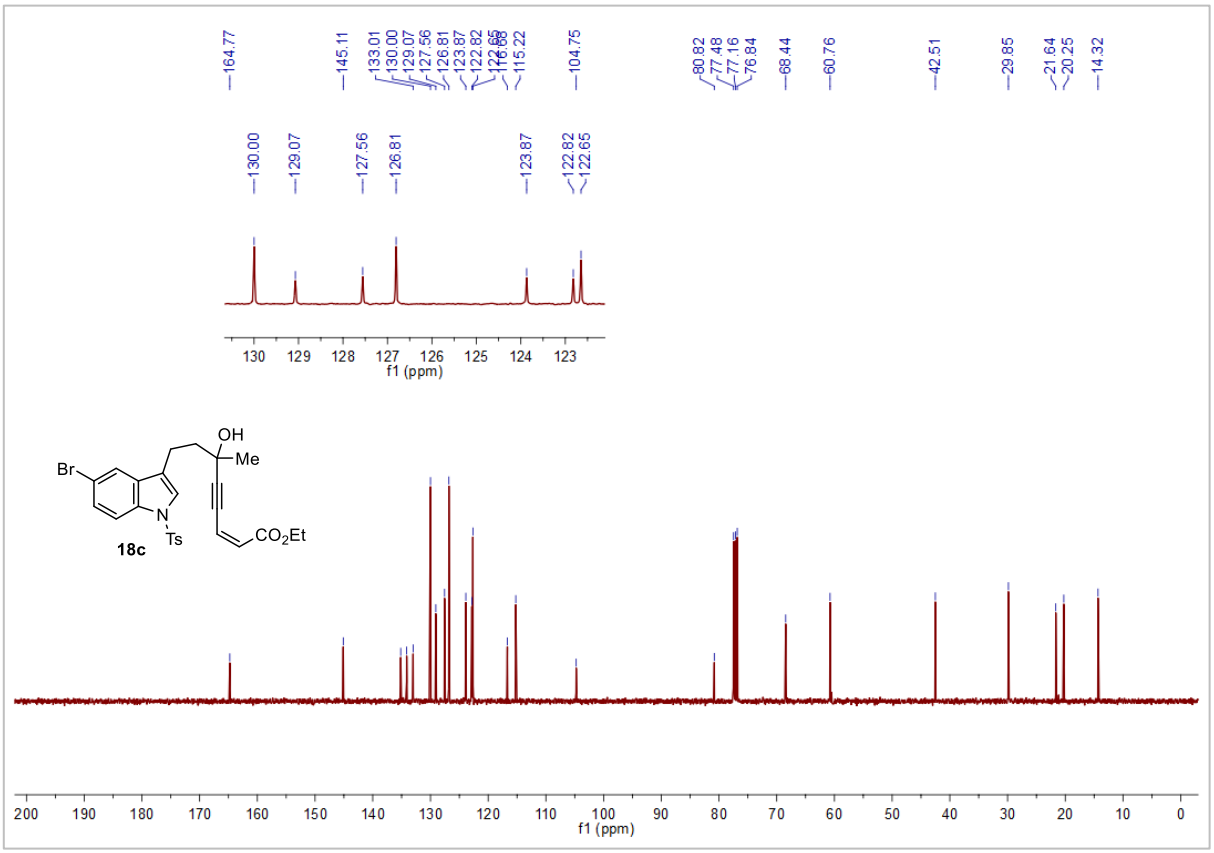
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **18b**.



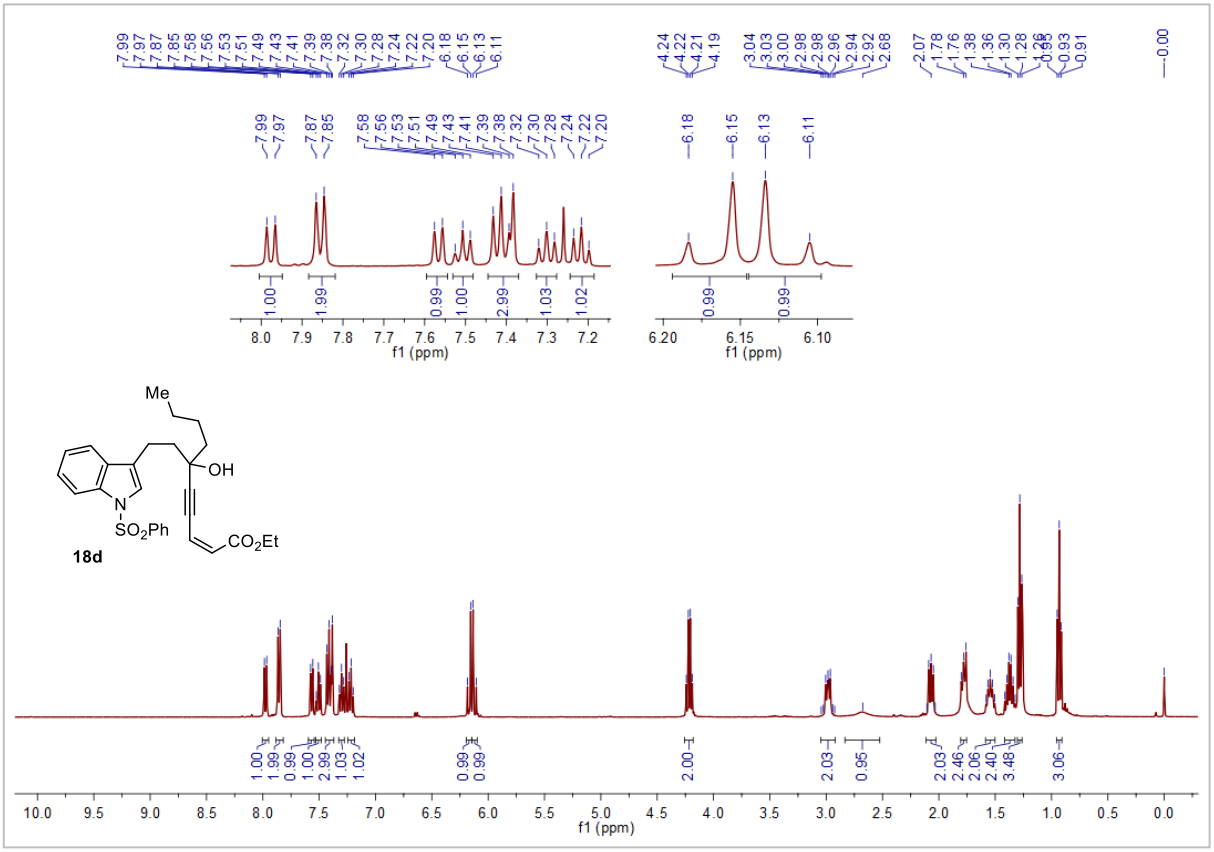


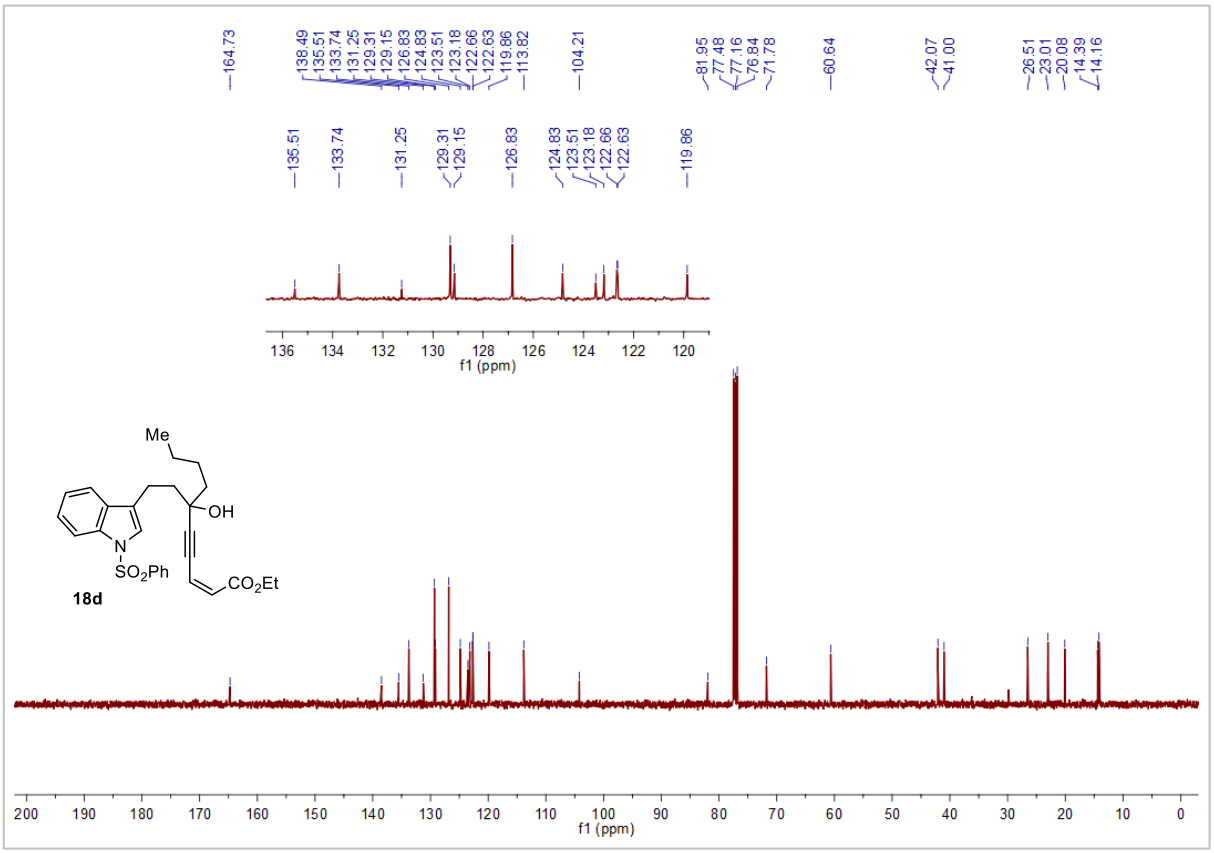
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **18c**.



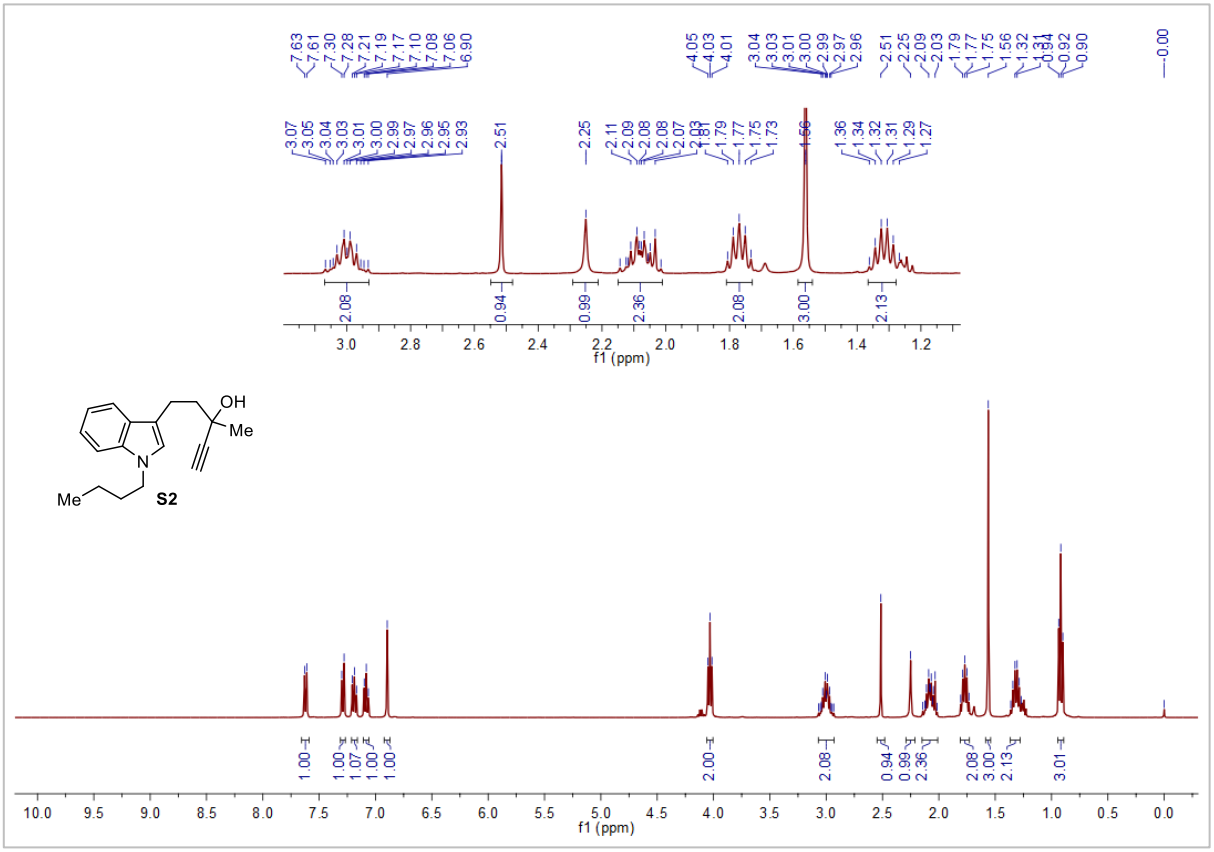


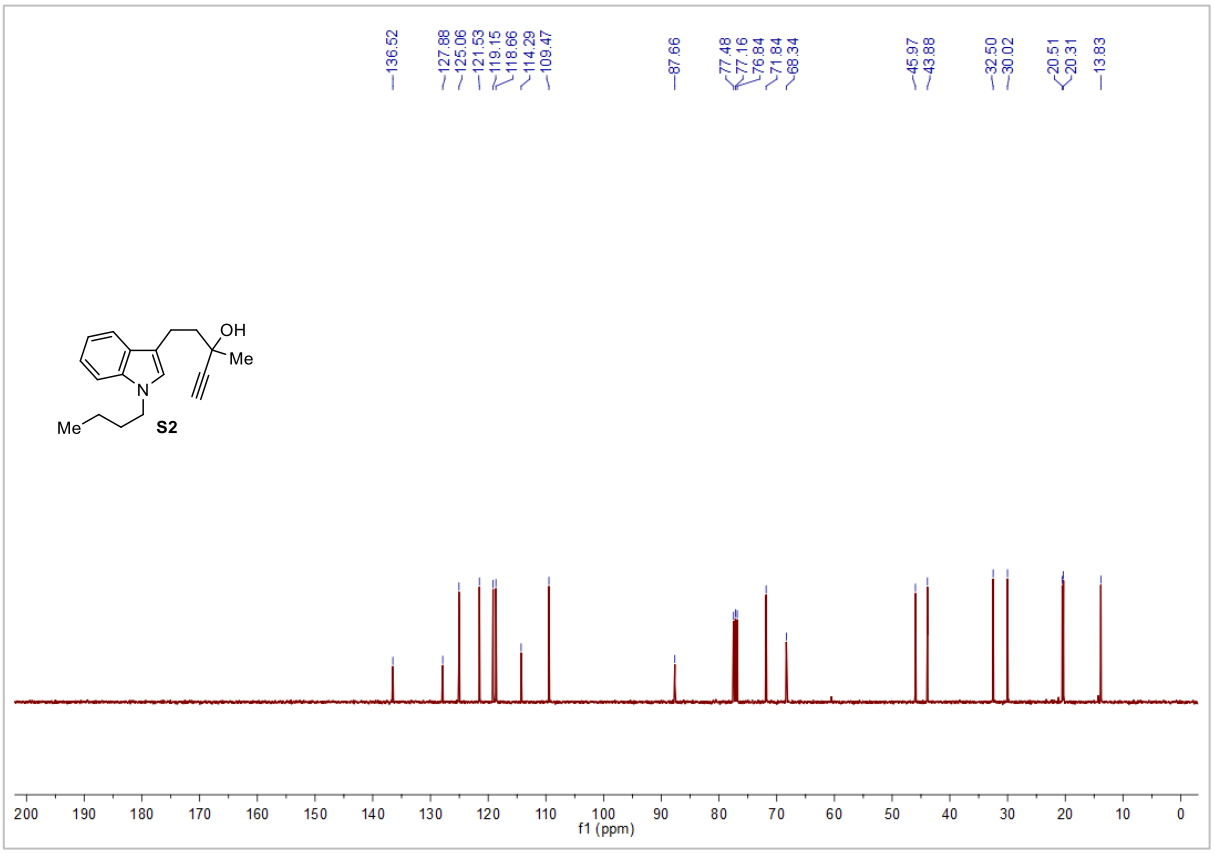
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **18d**.



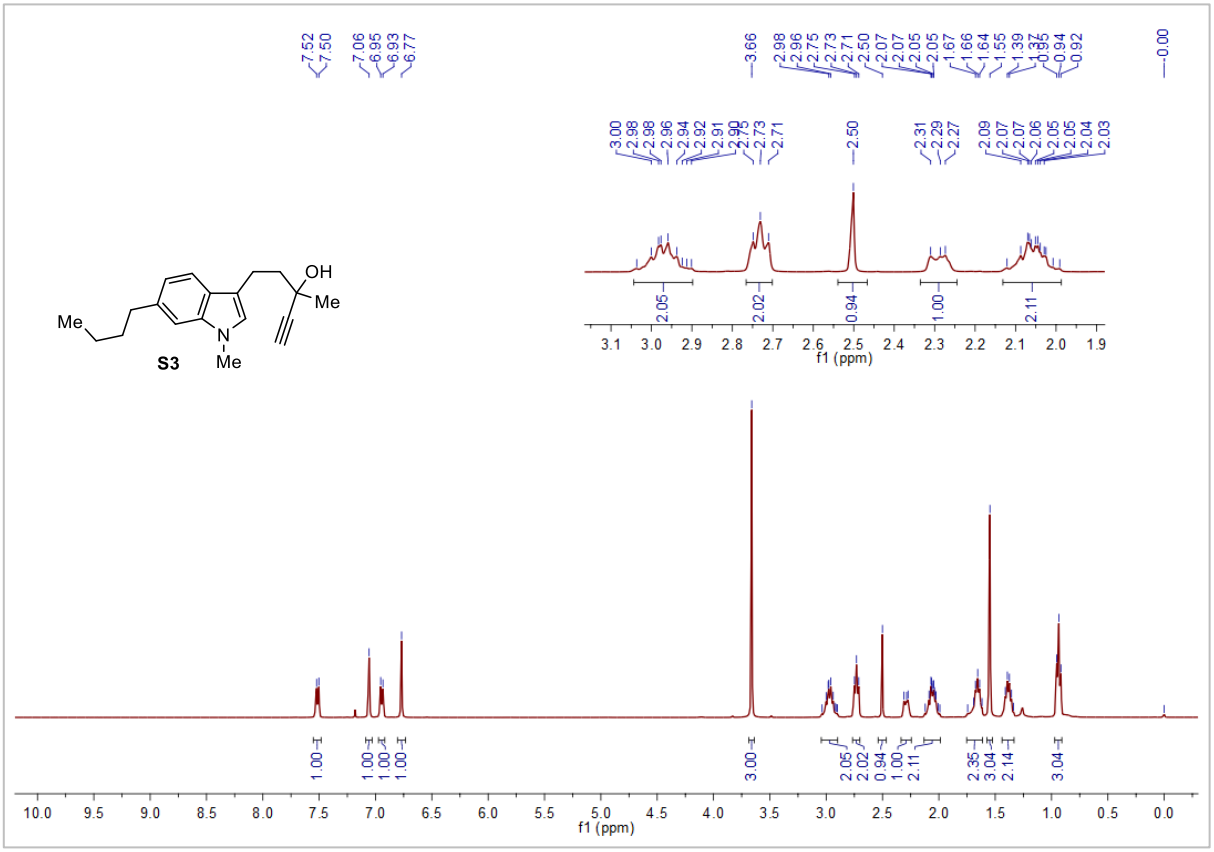


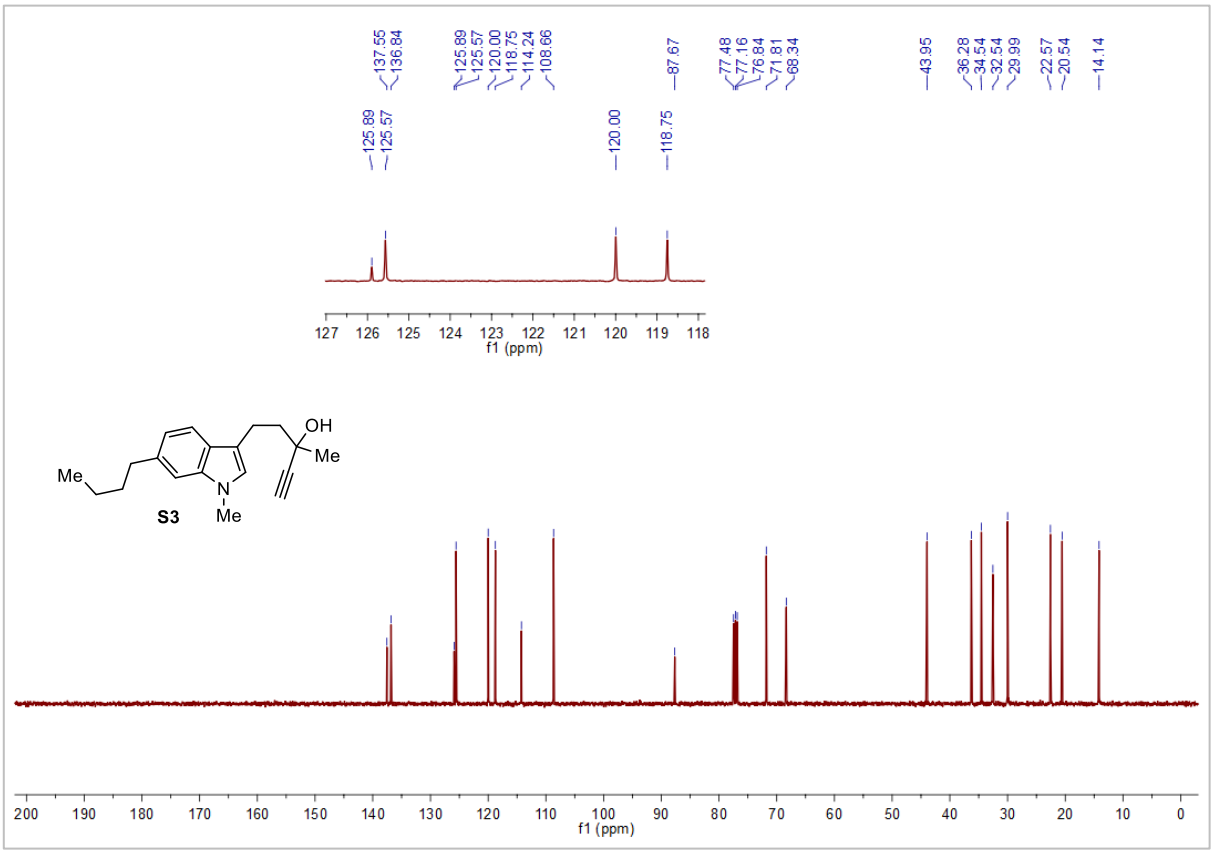
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S2**.



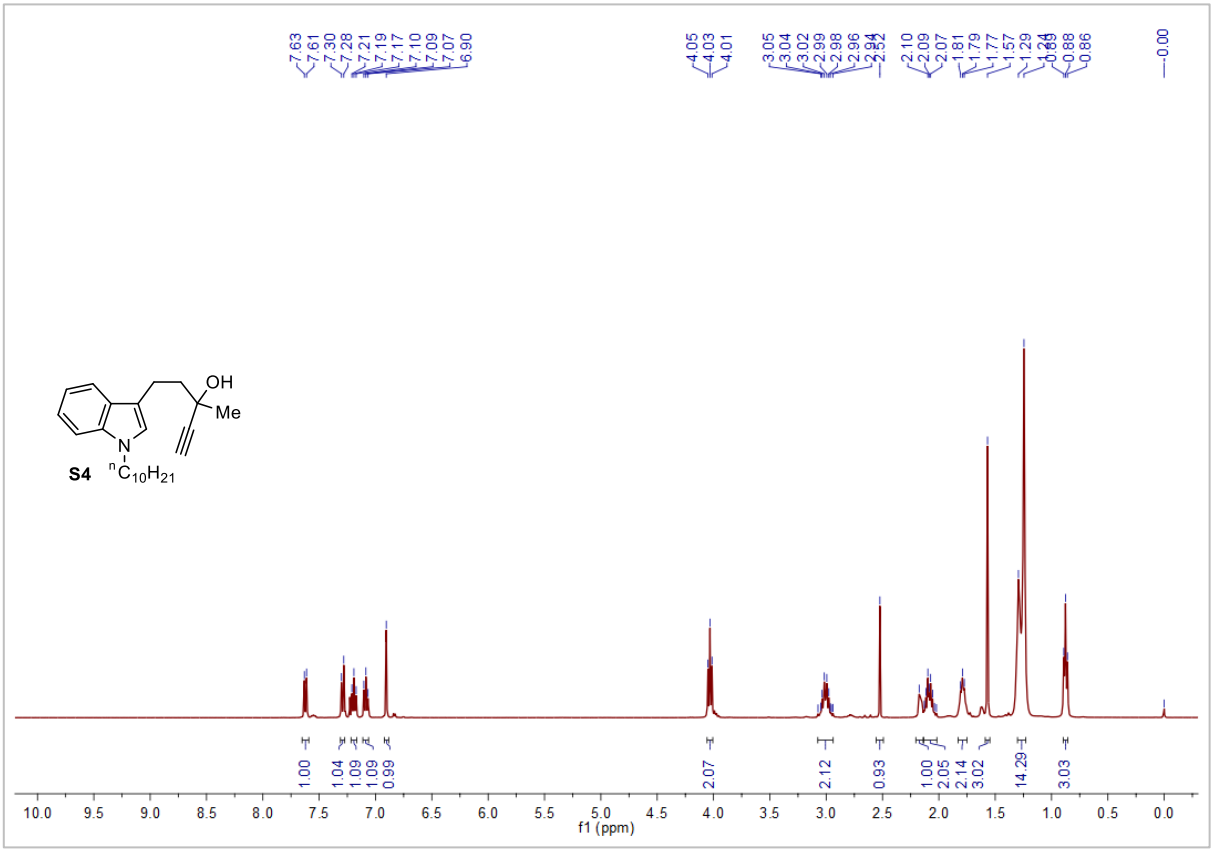


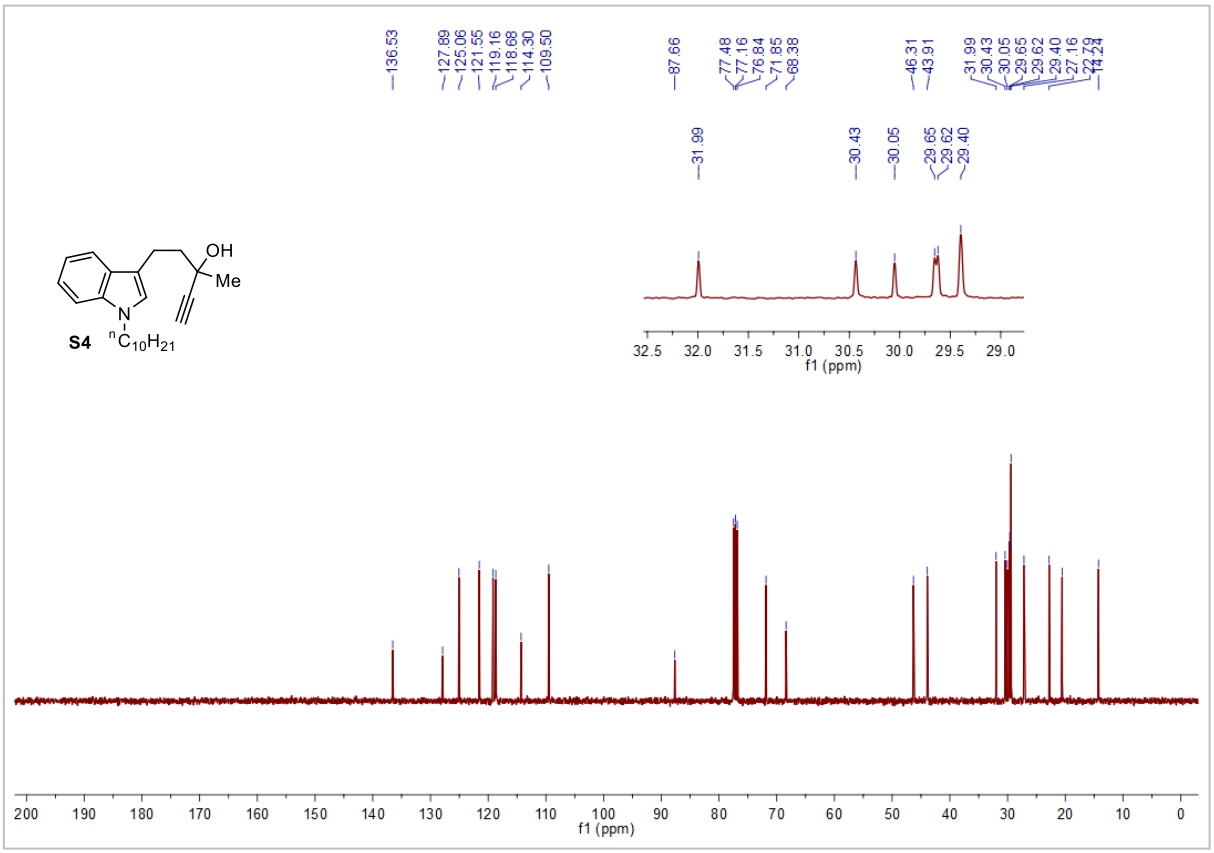
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S3**.



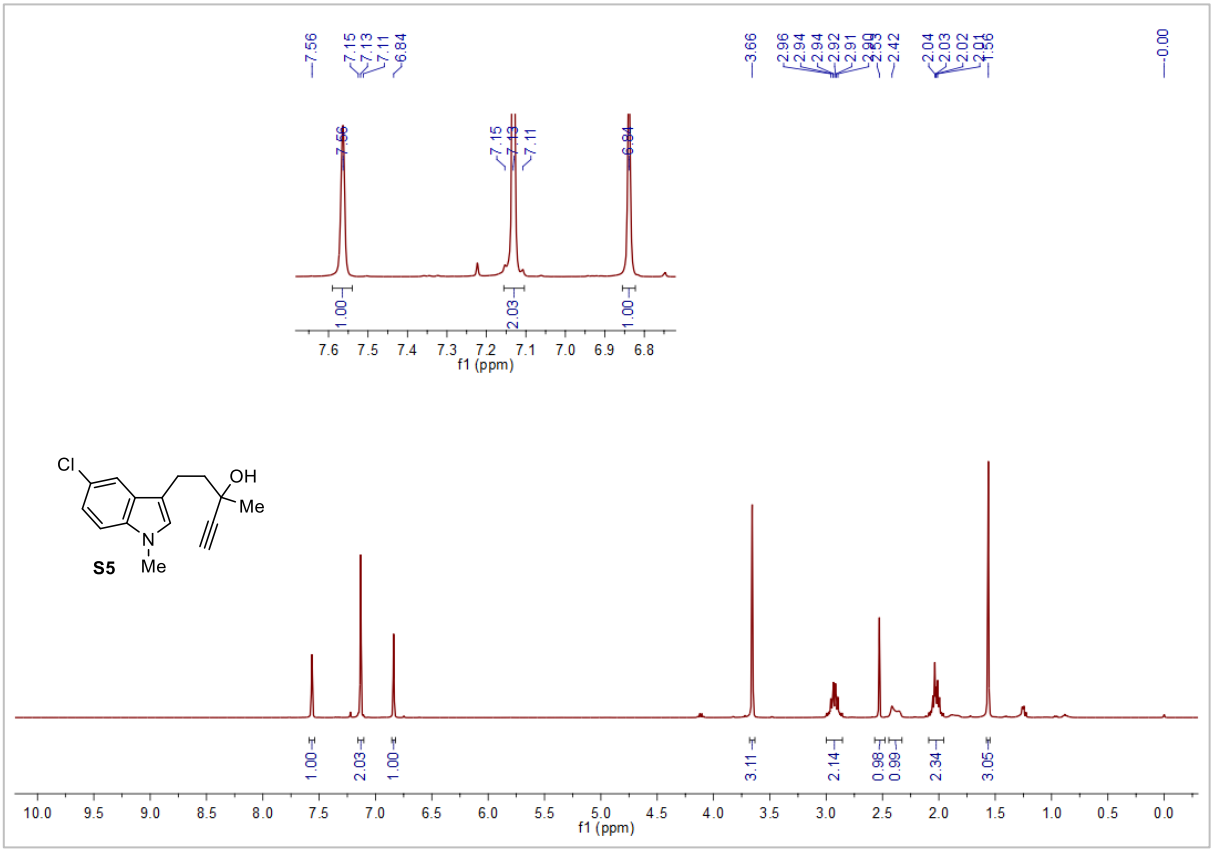


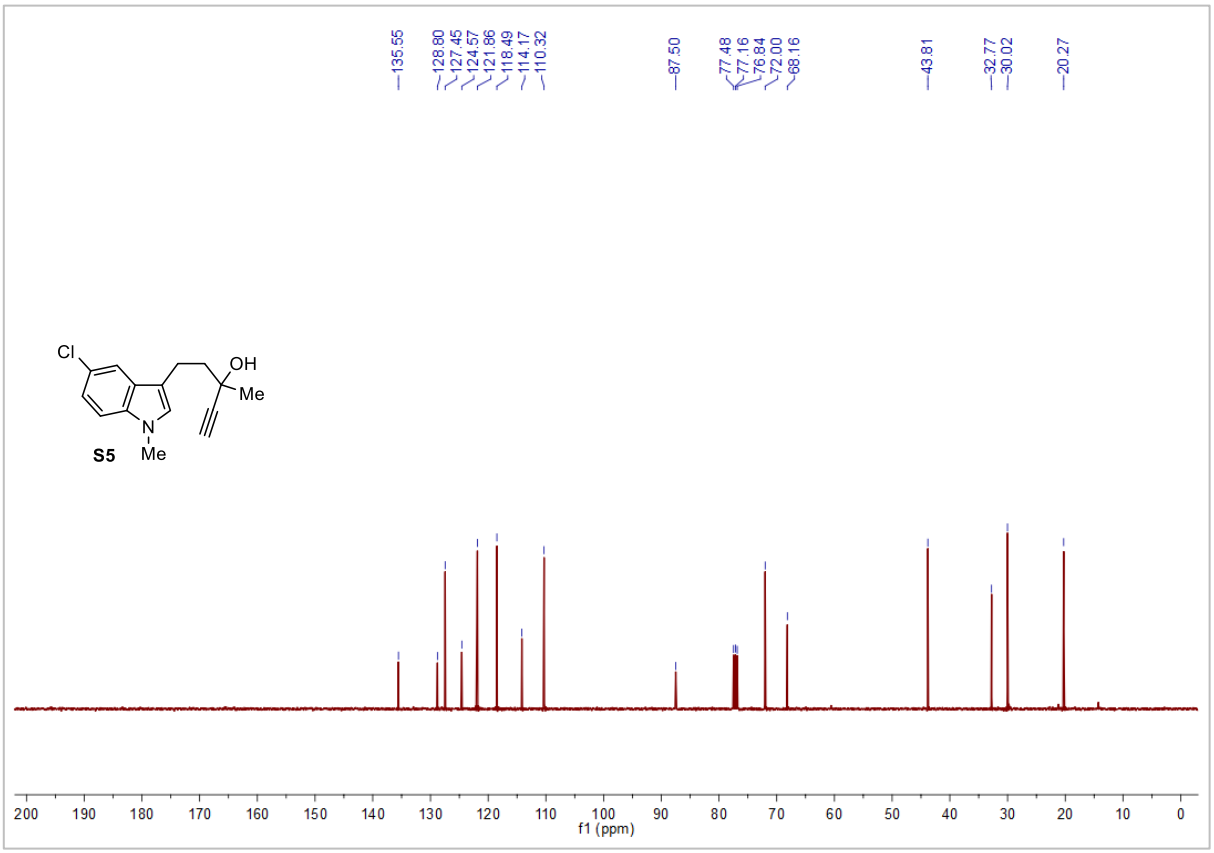
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S4**.



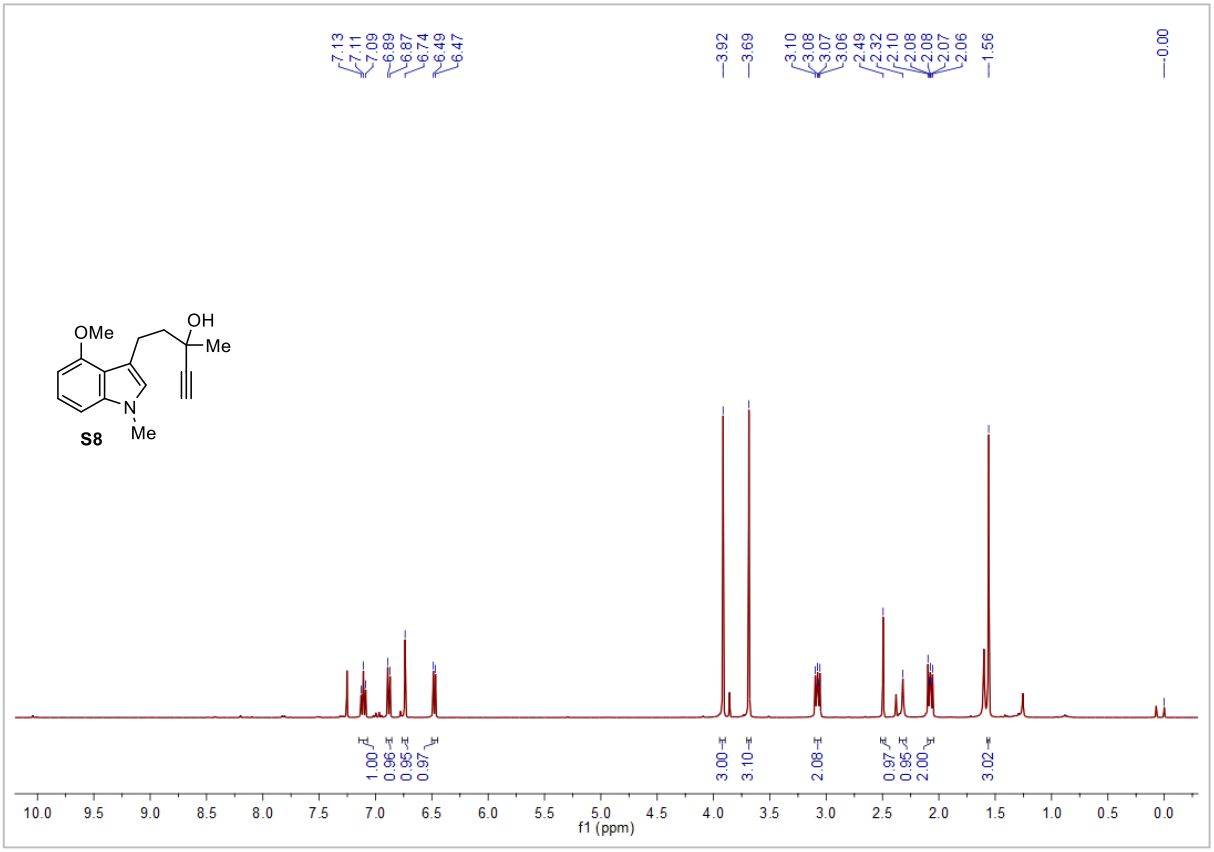


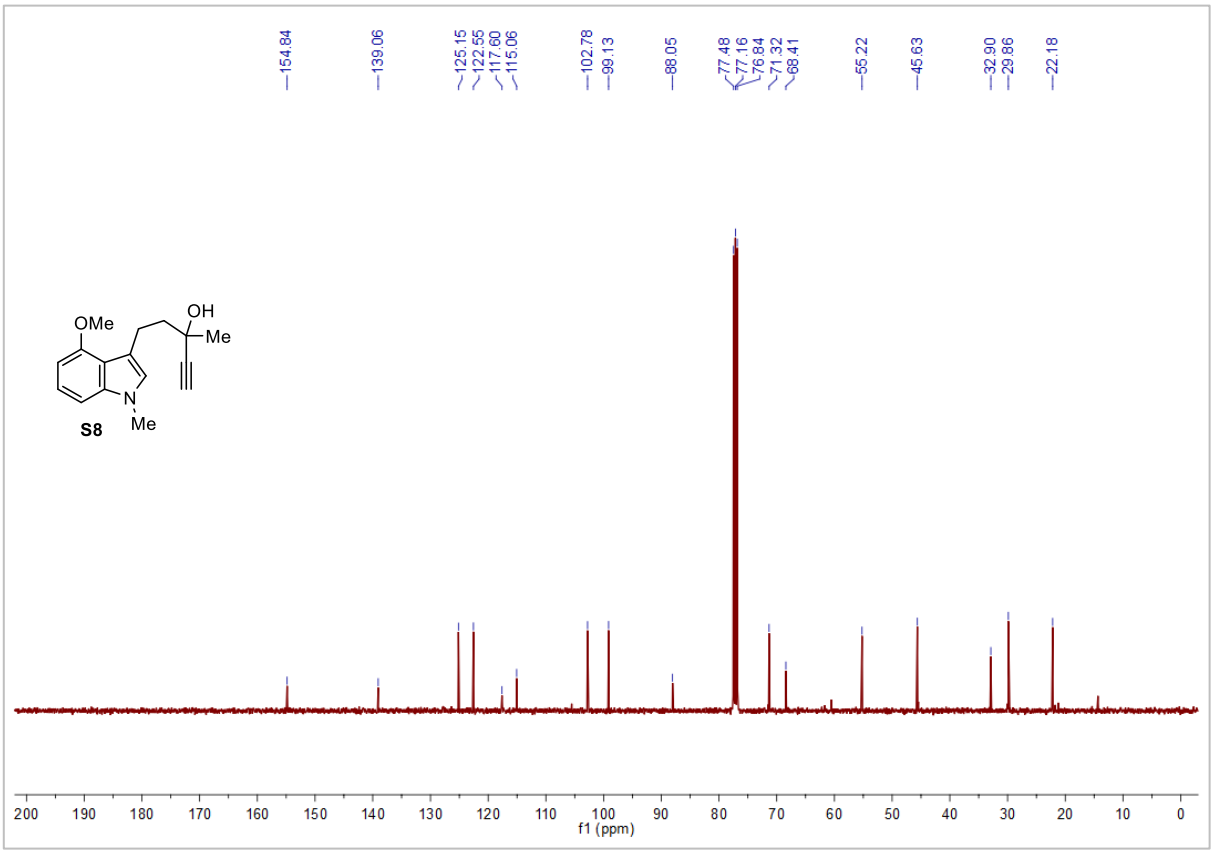
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S5**.



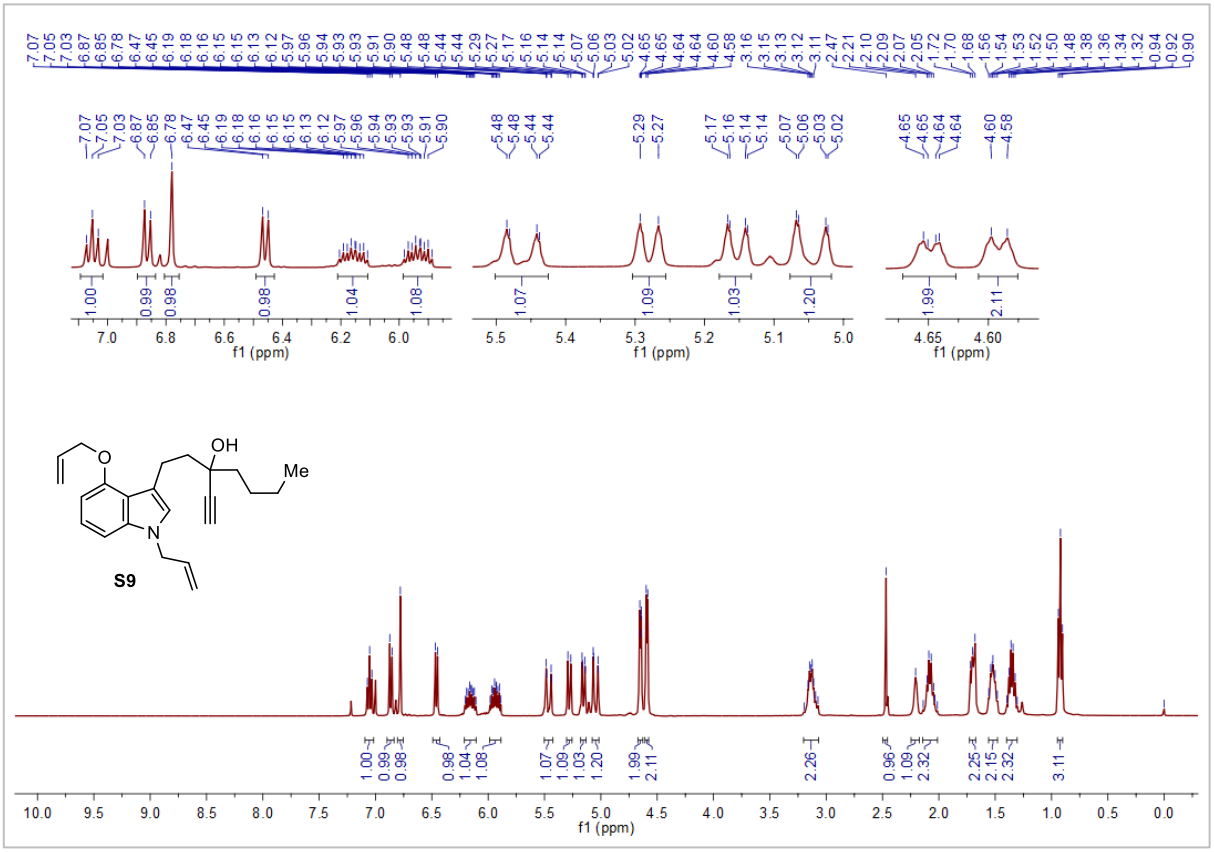


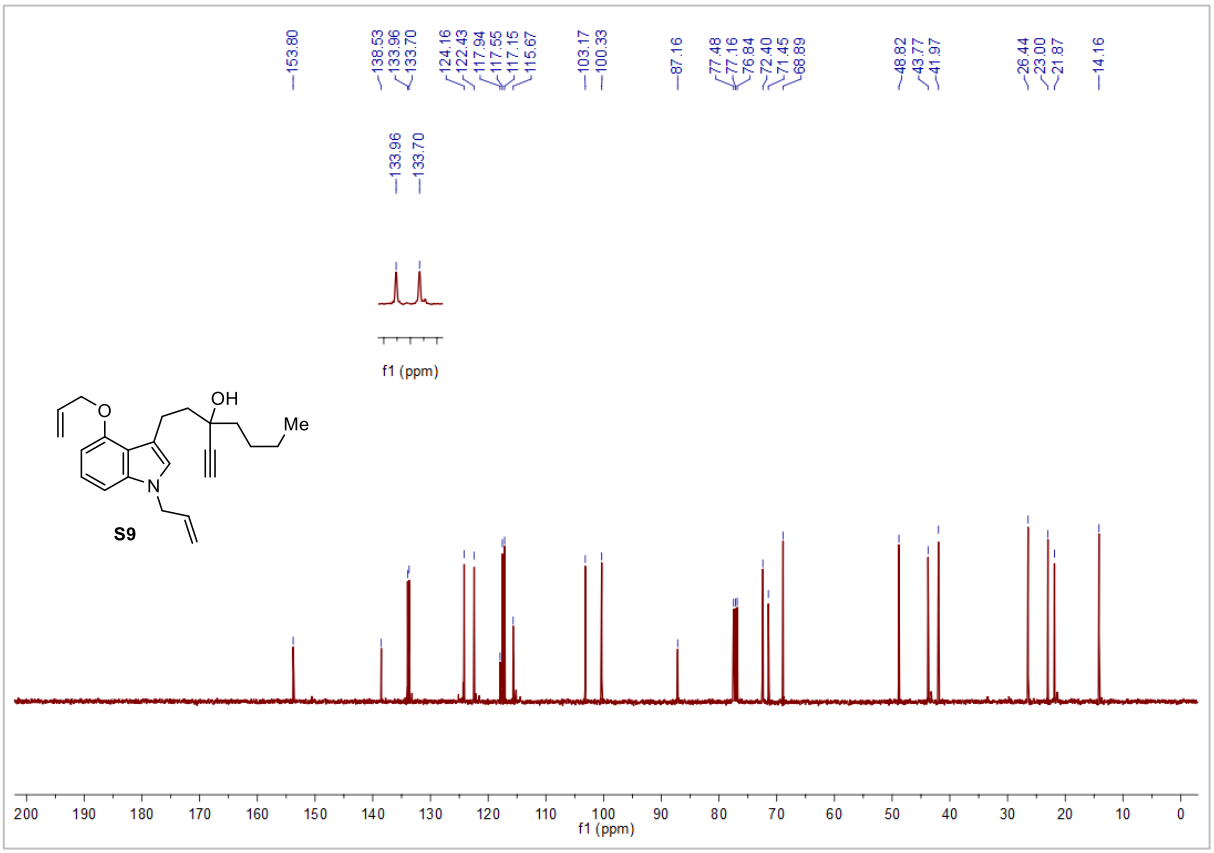
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S8**.



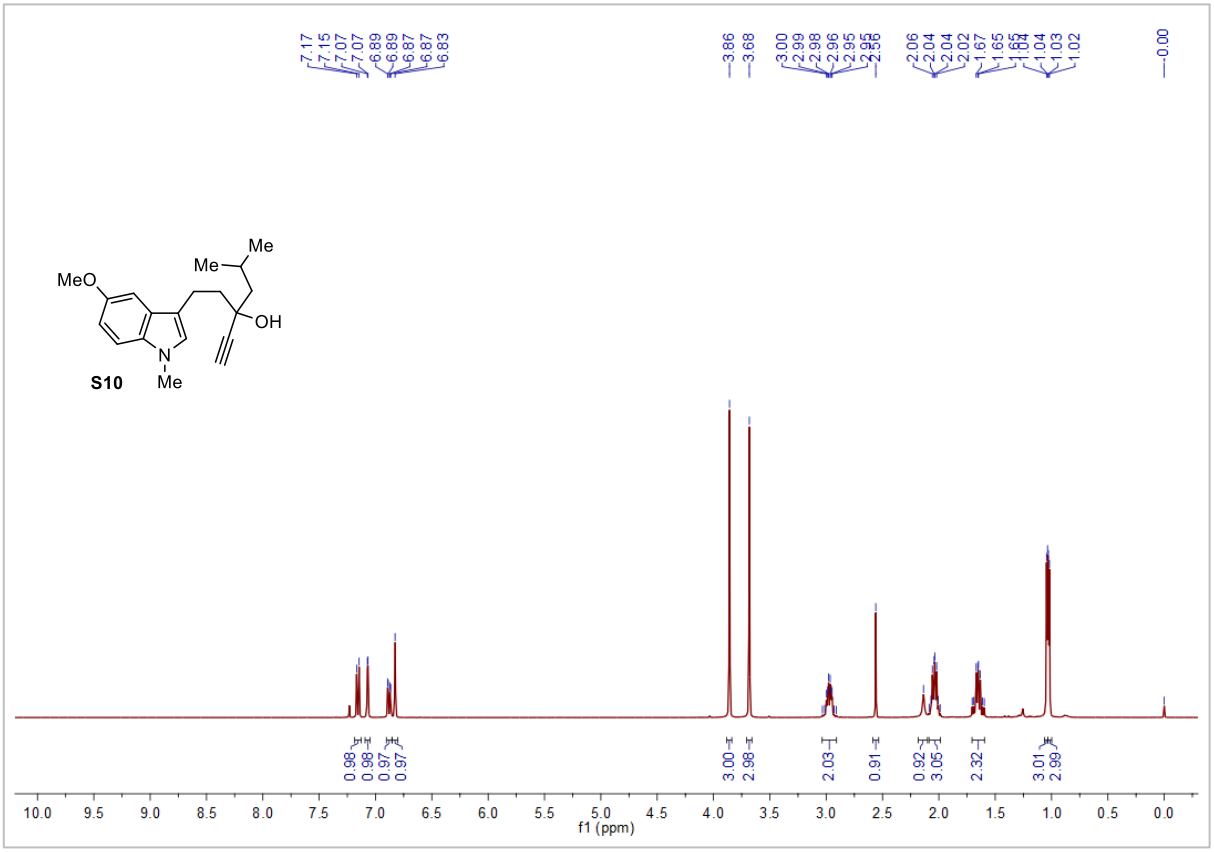


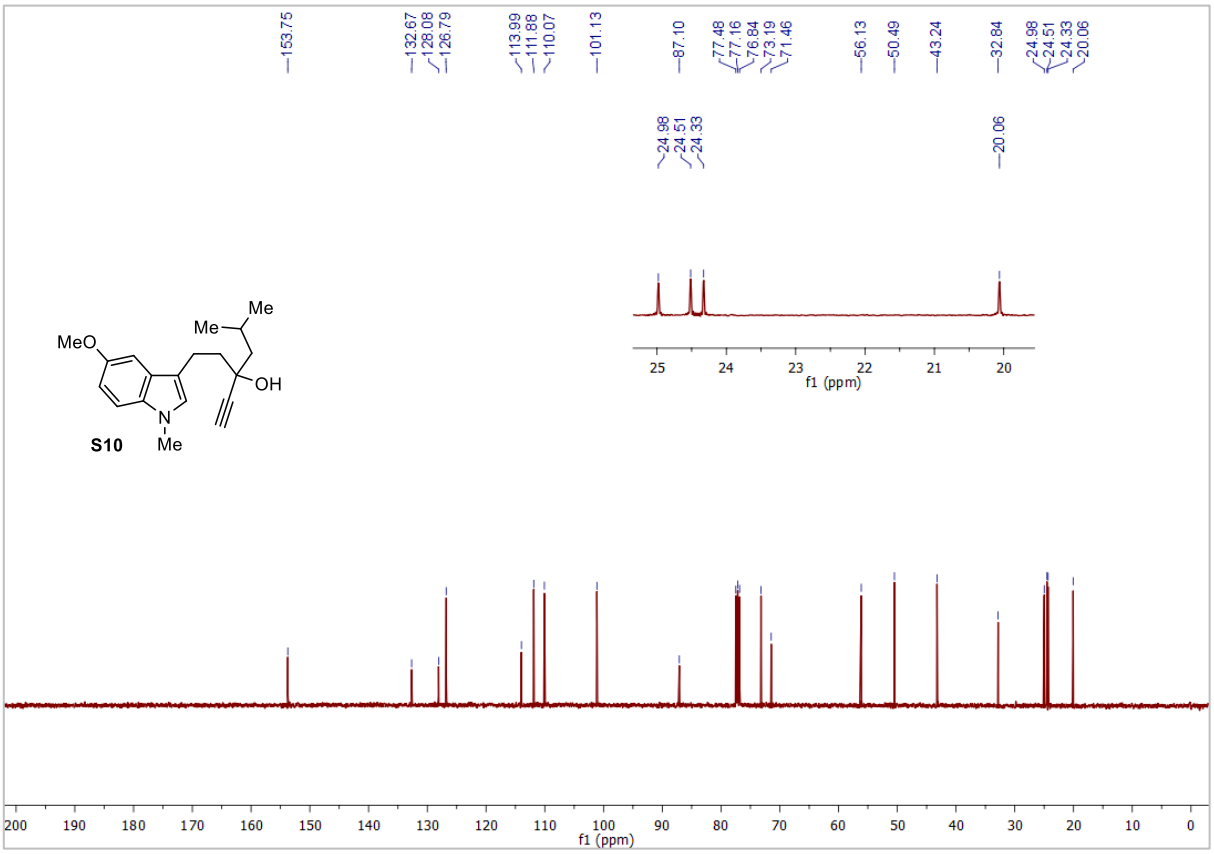
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S9**.



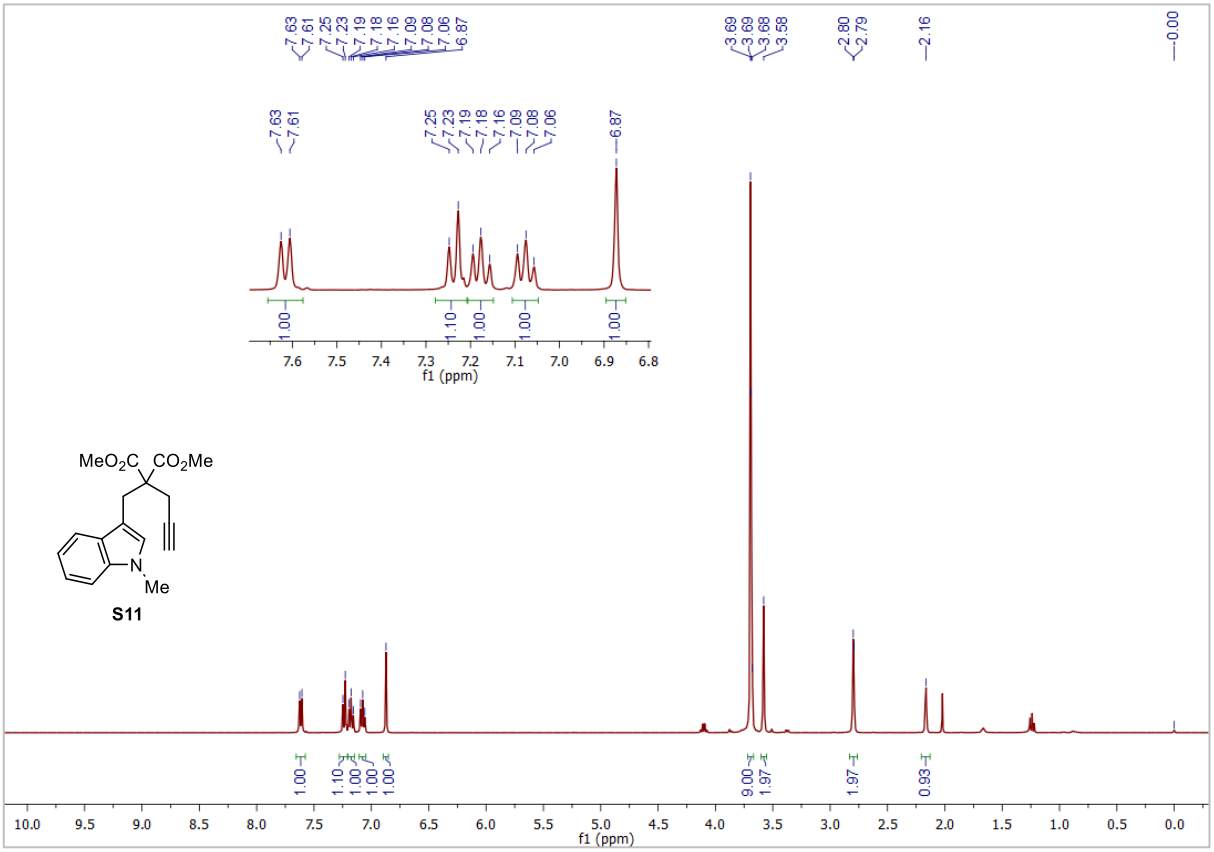


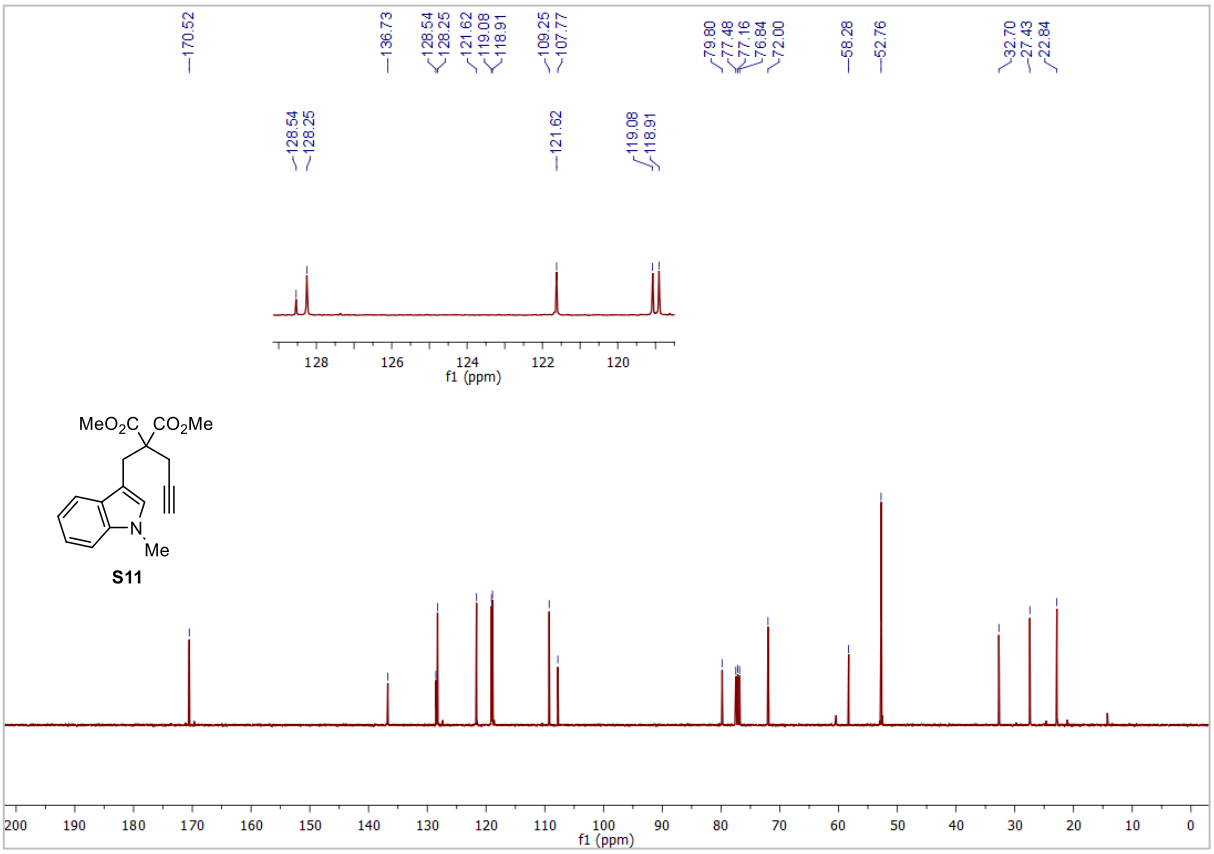
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S10**.



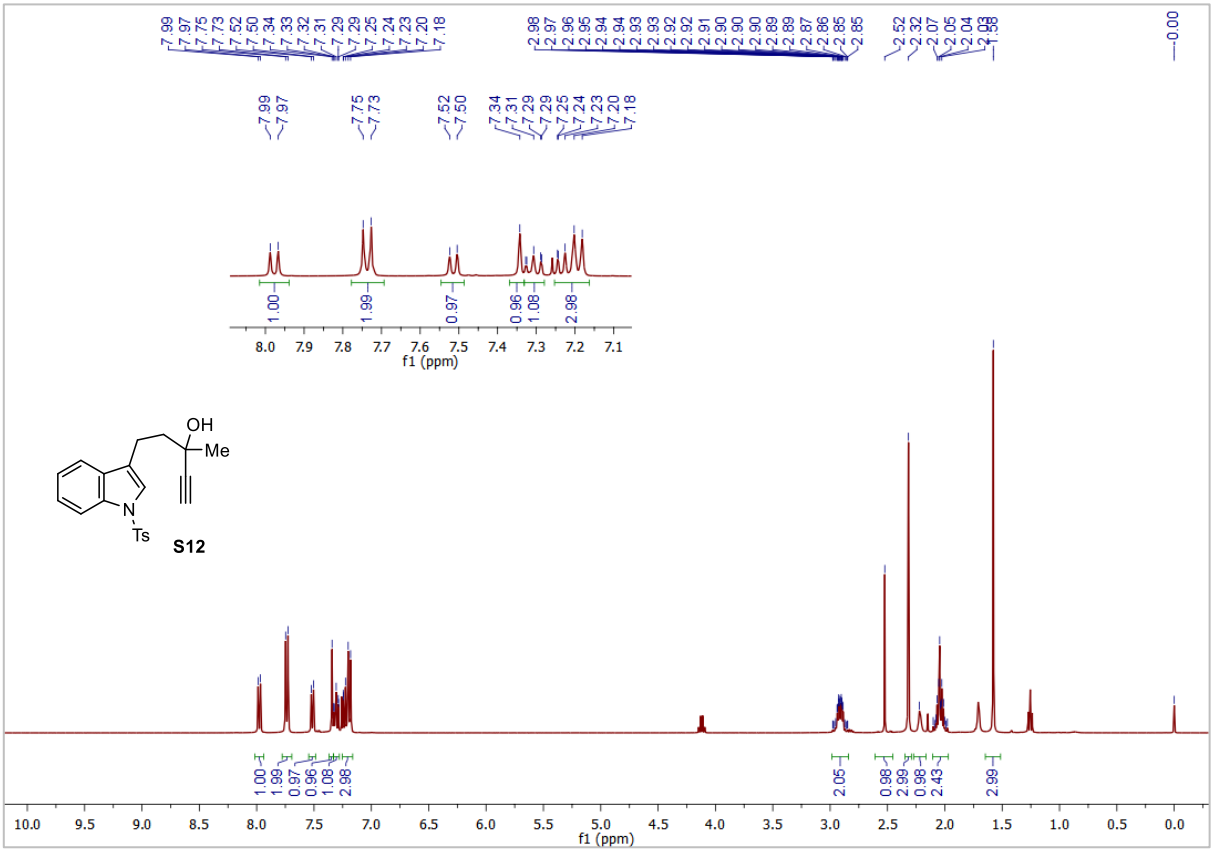


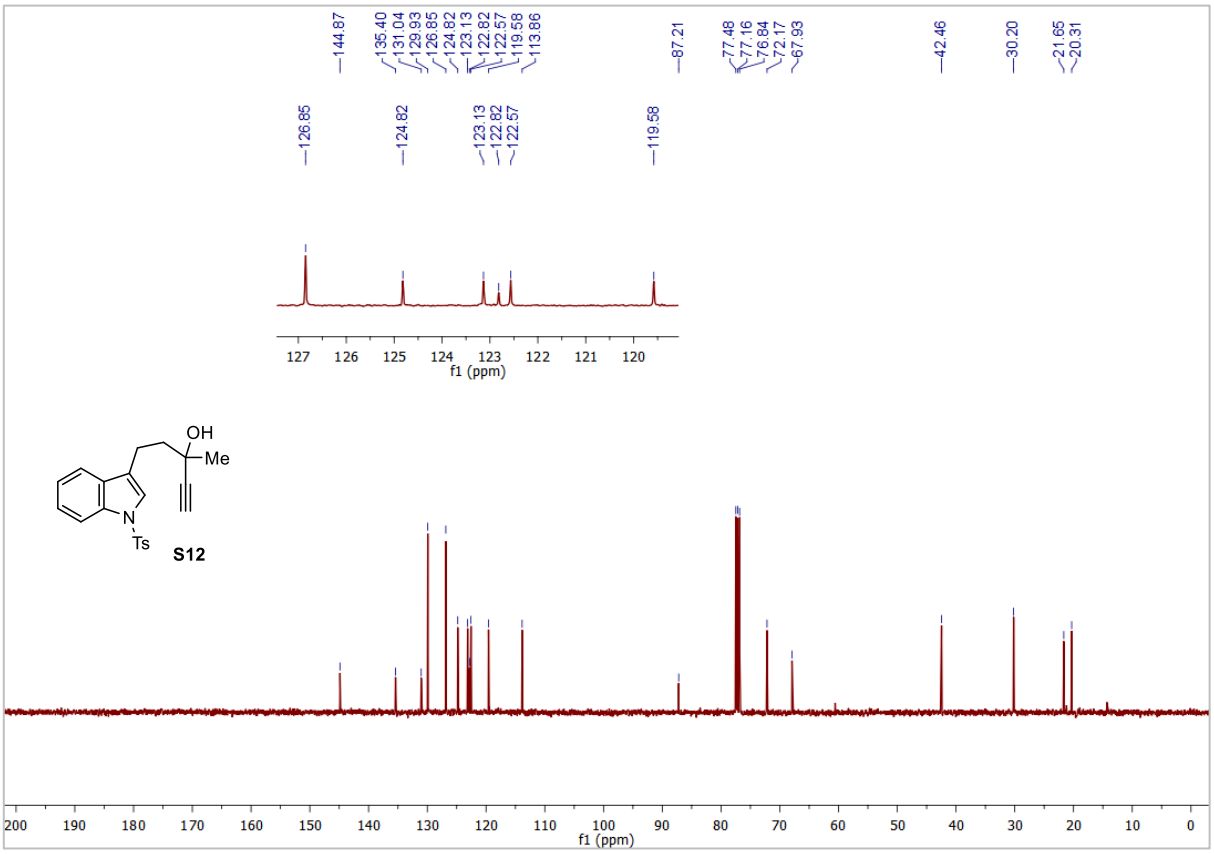
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S11**.



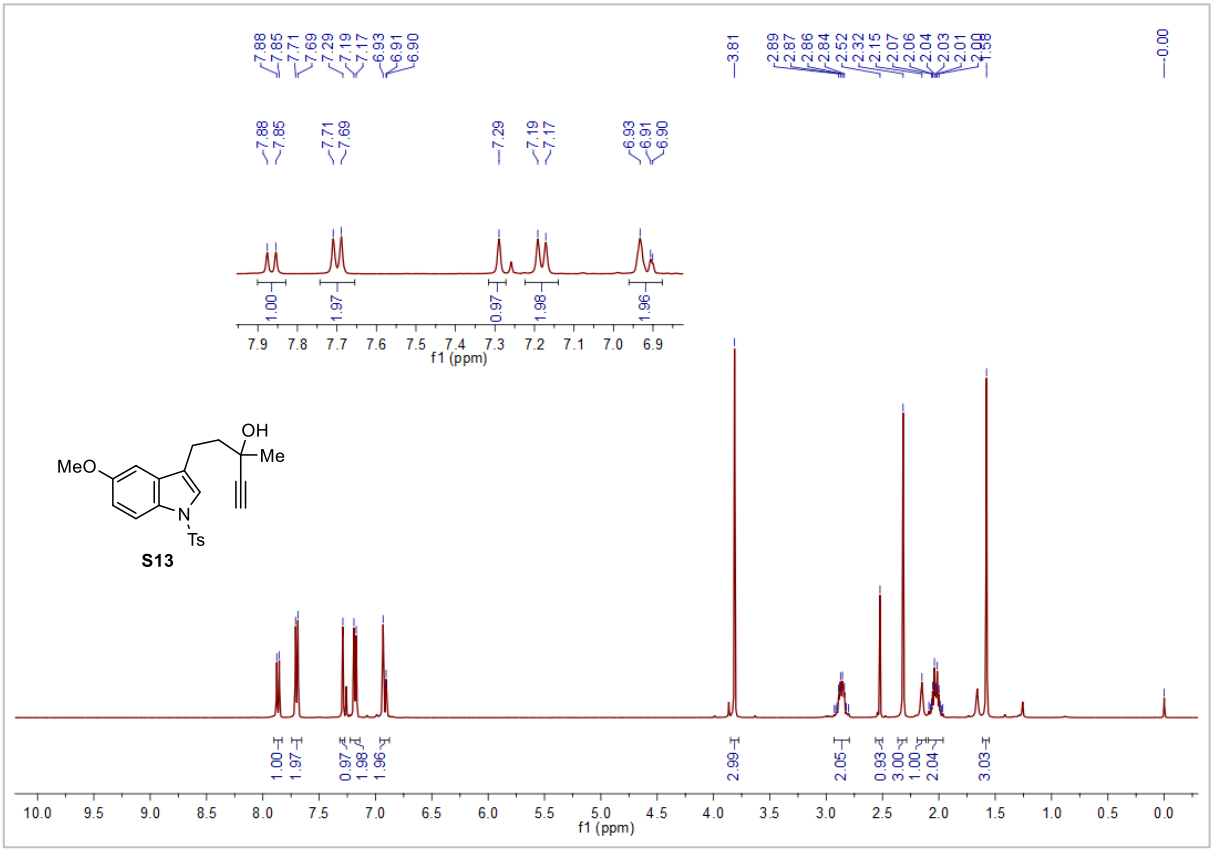


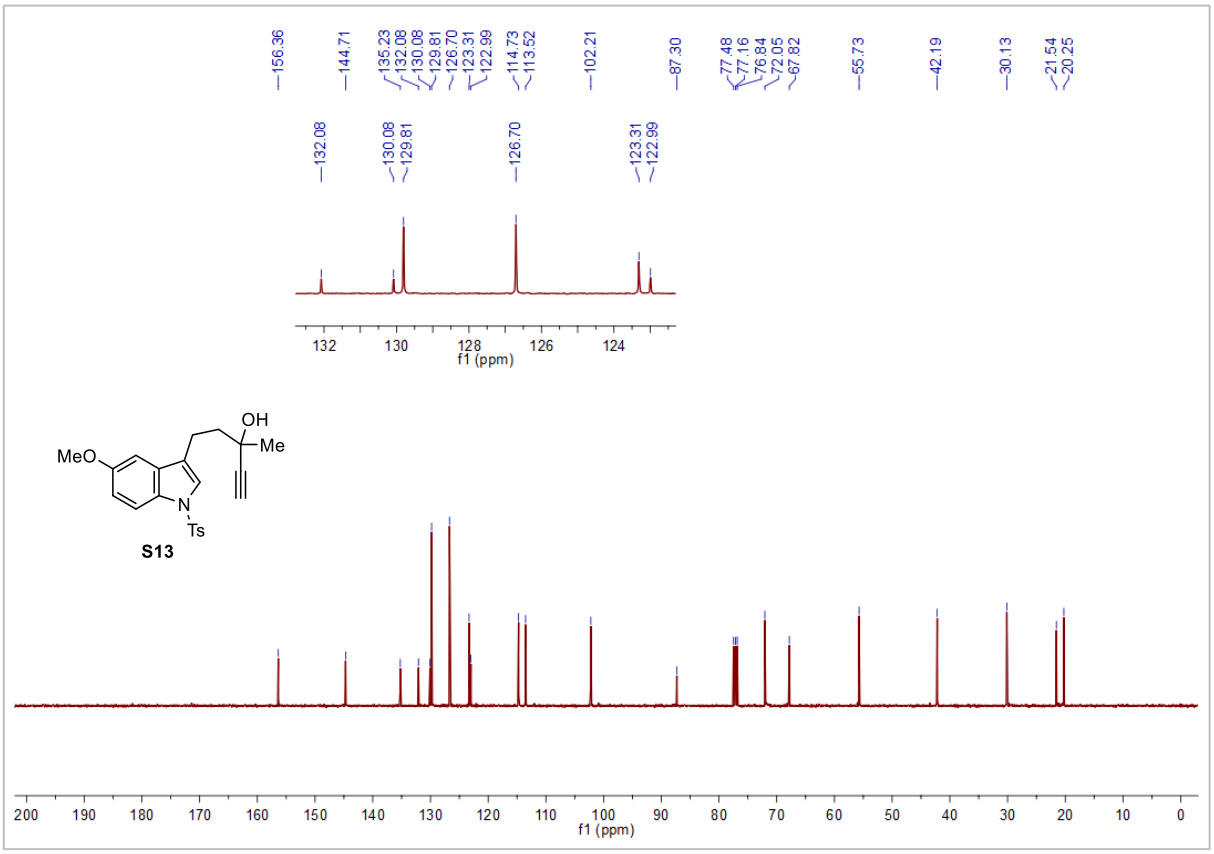
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S12**.



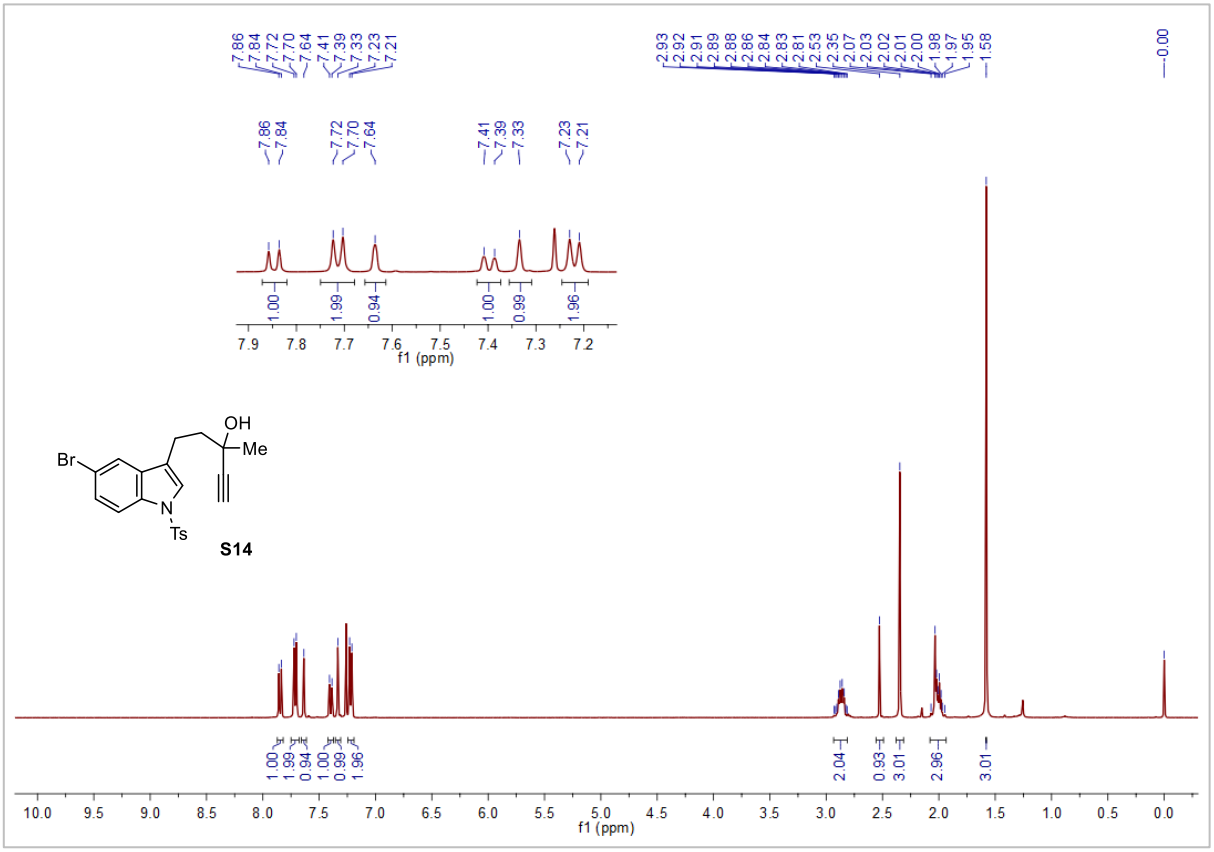


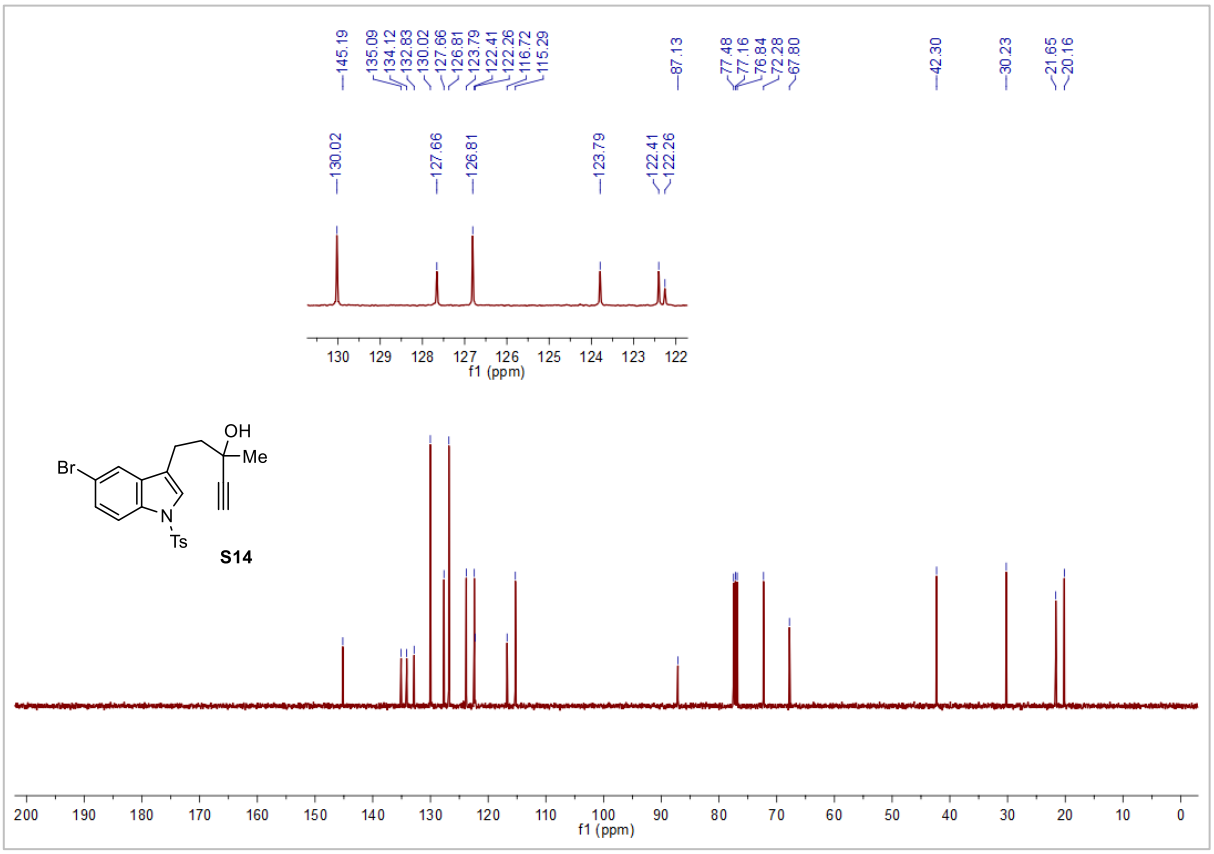
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S13**.



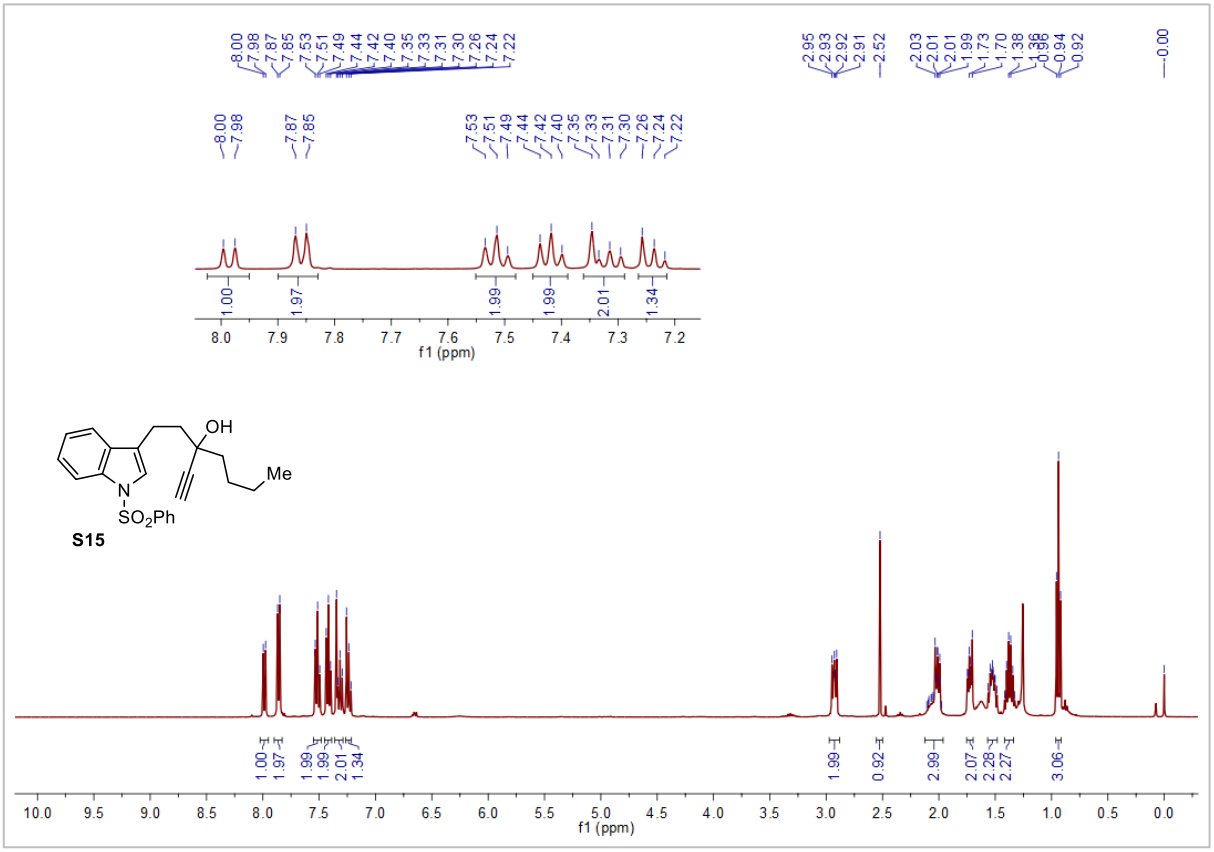


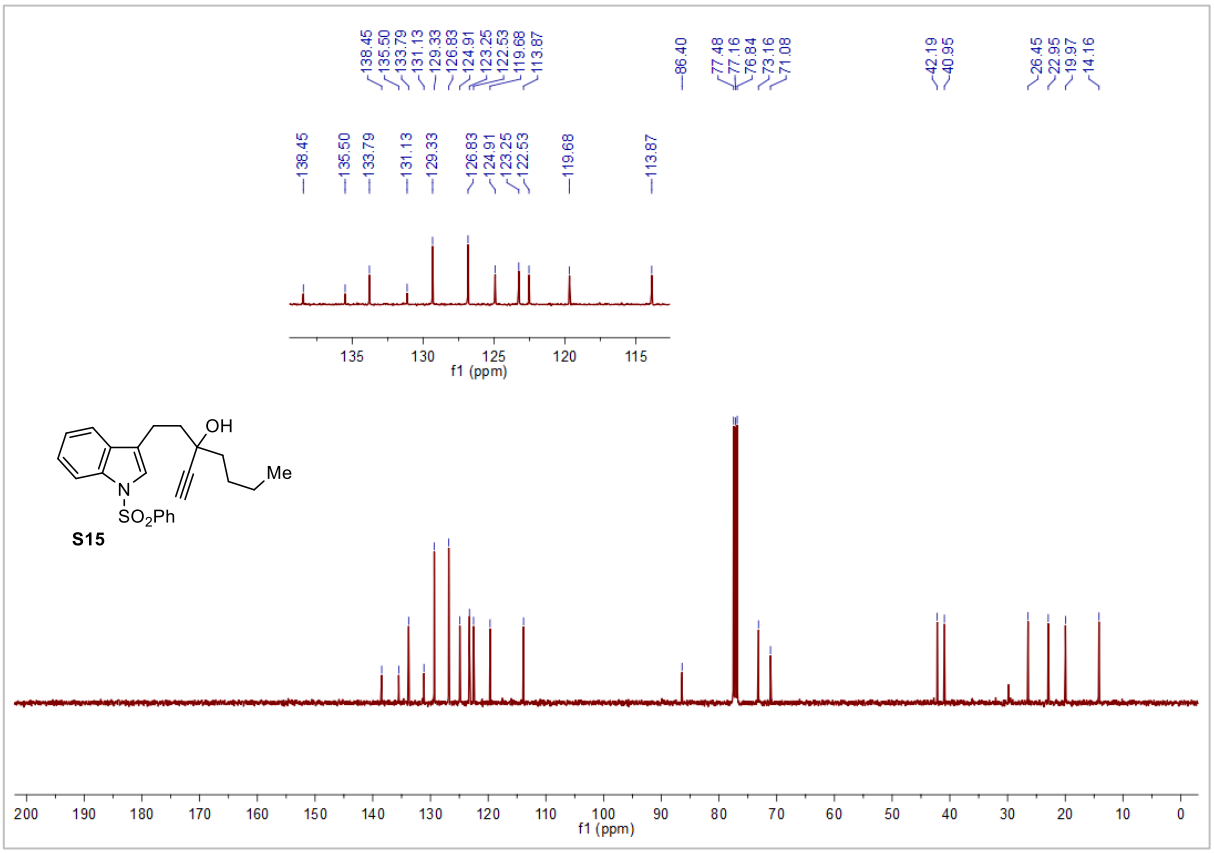
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S14**.



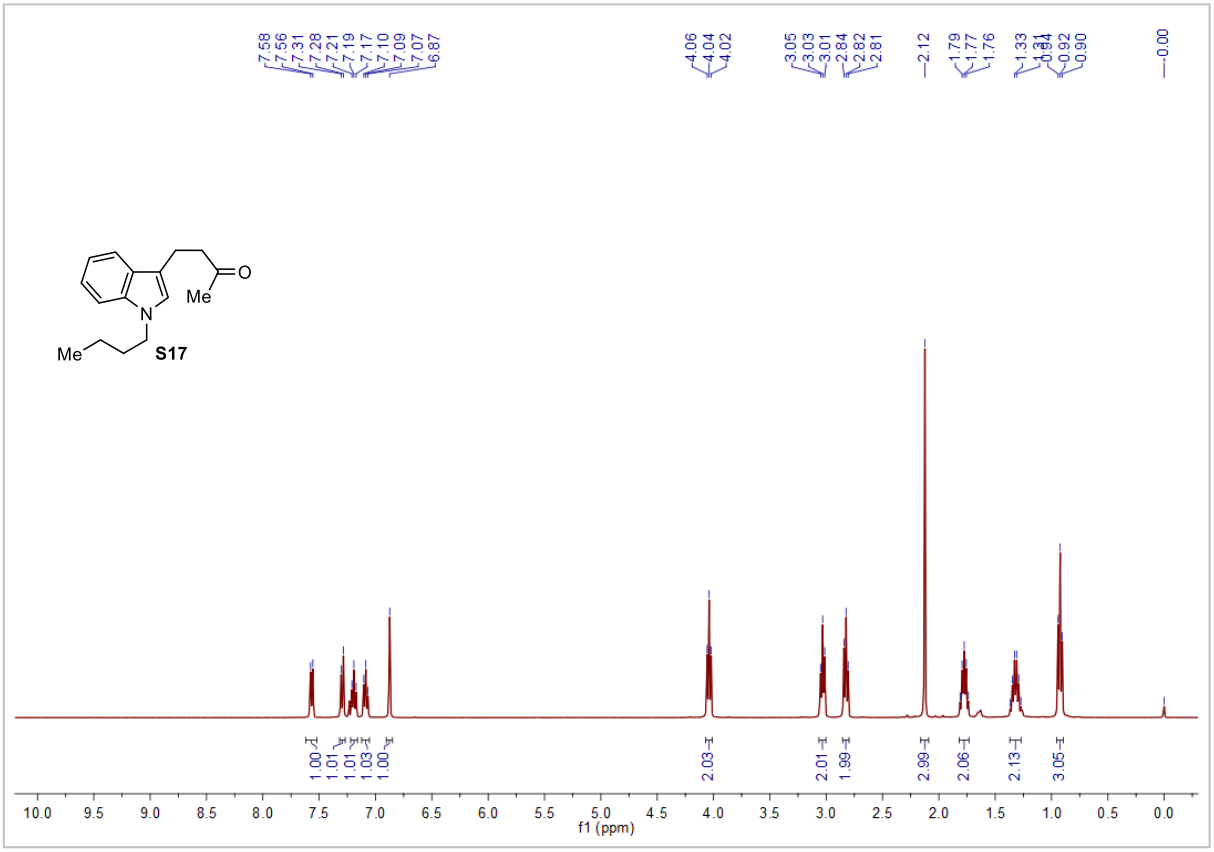


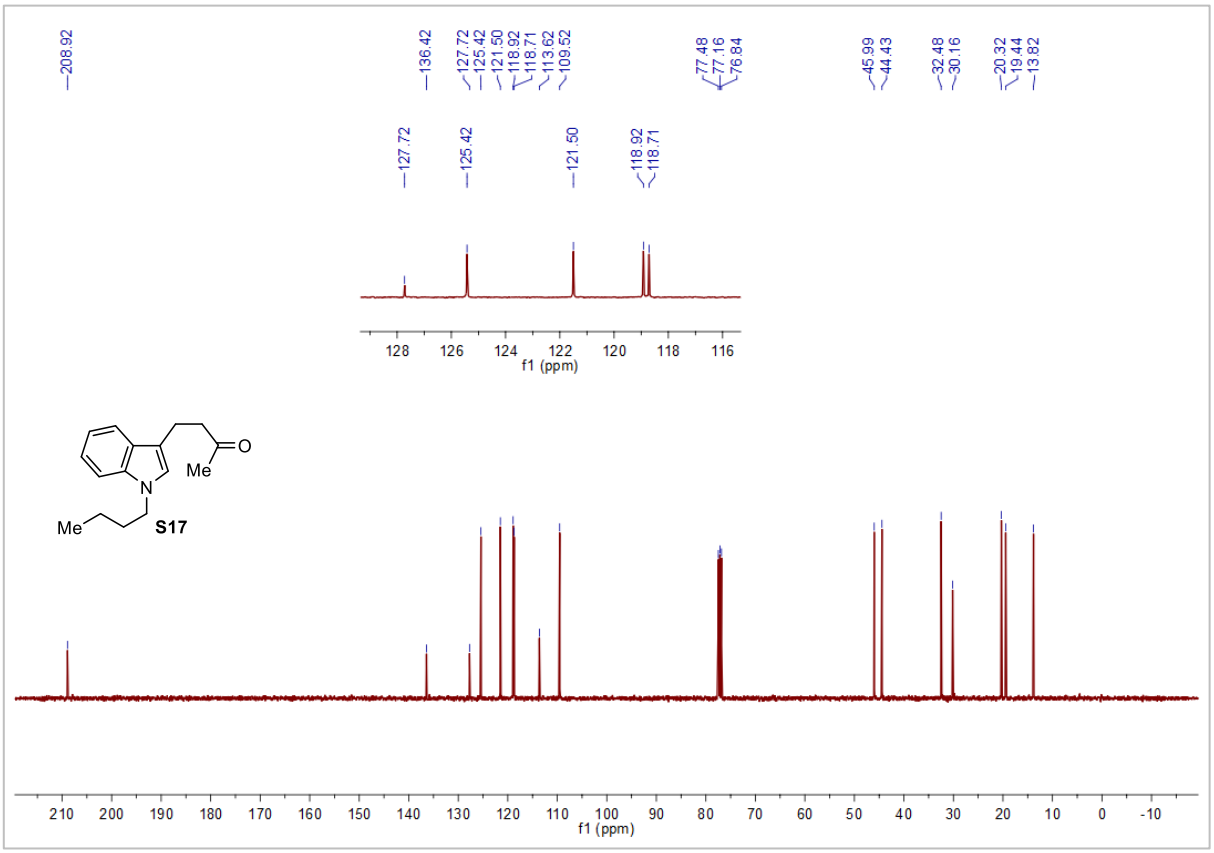
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S15**.



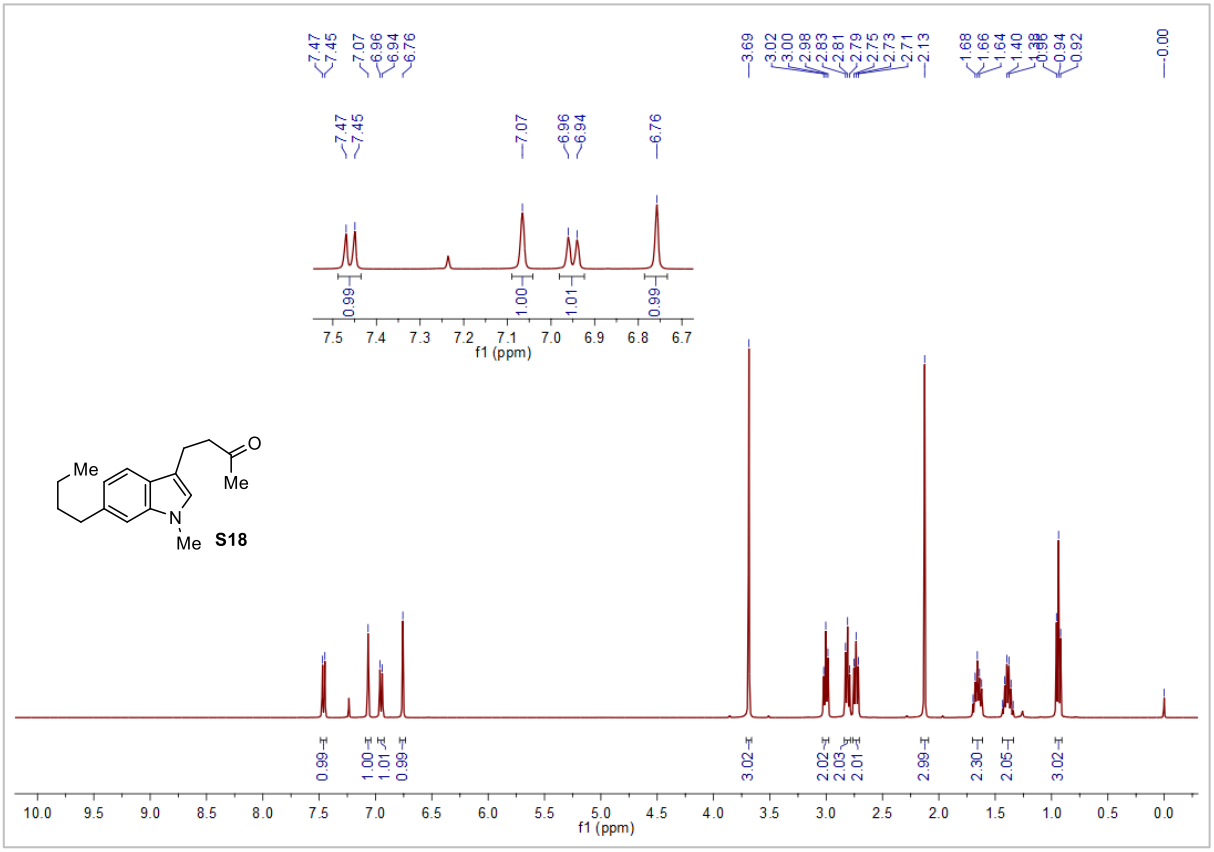


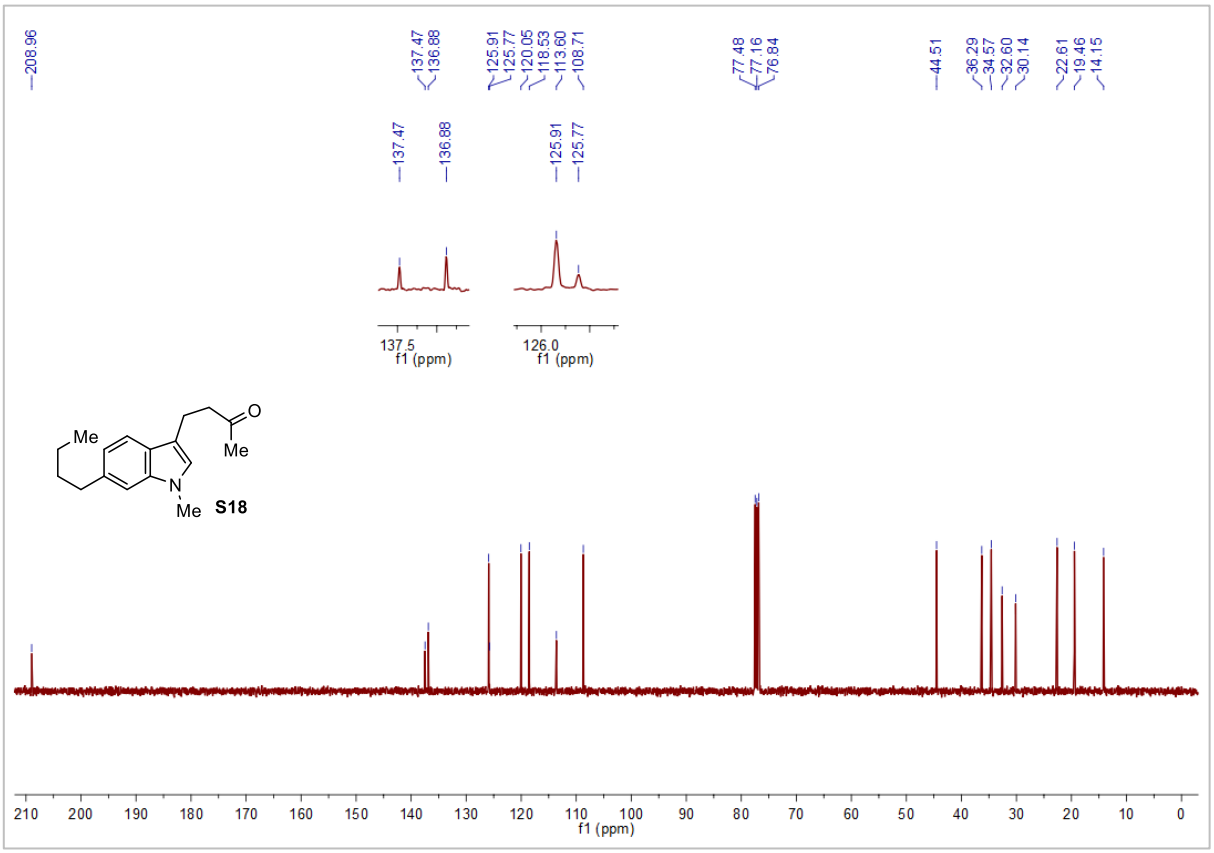
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S17**.



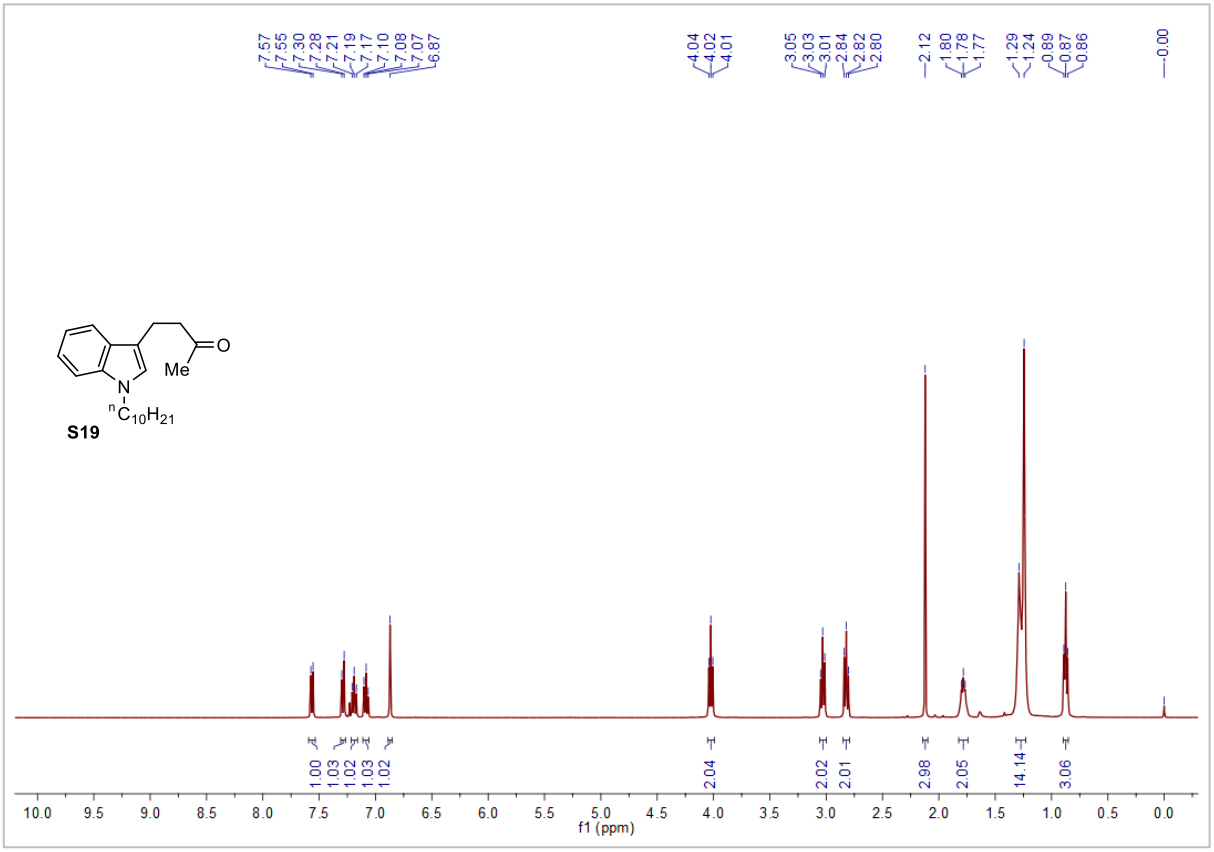


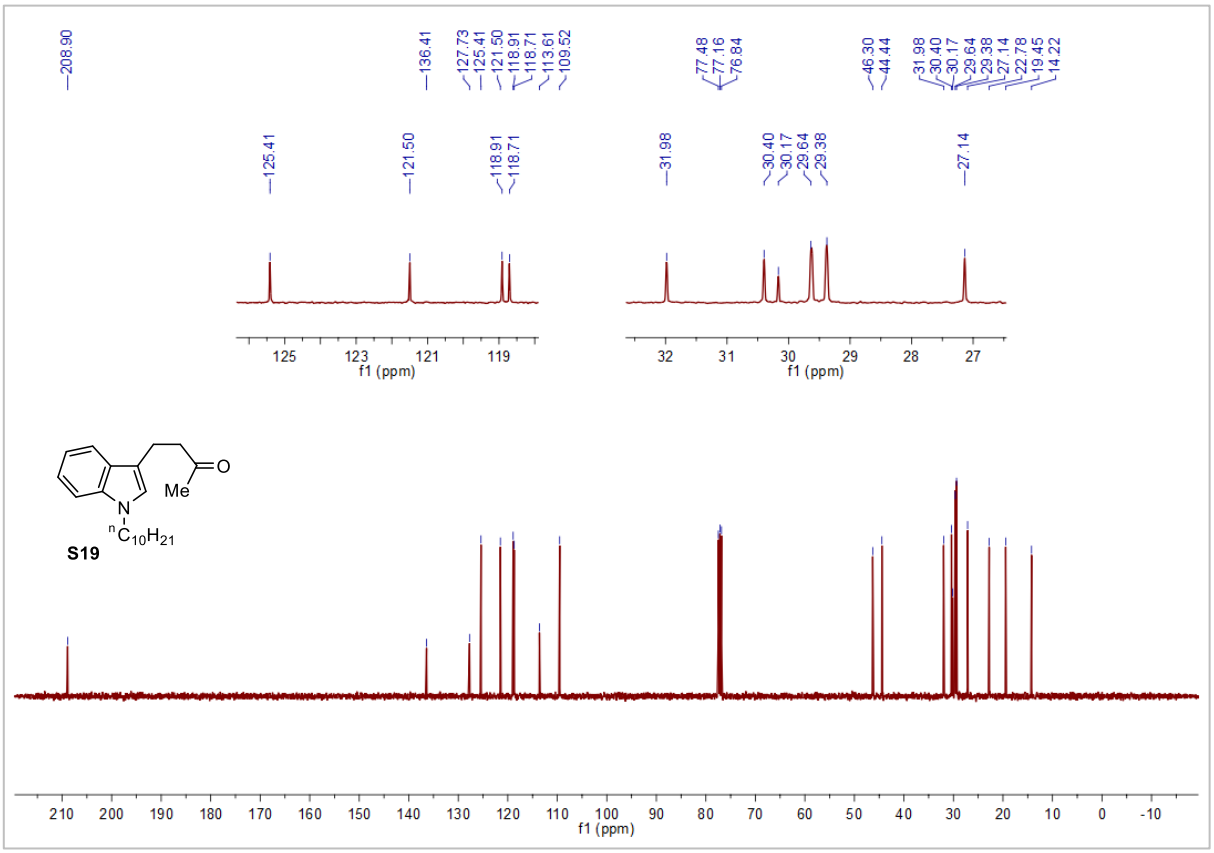
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S18**.



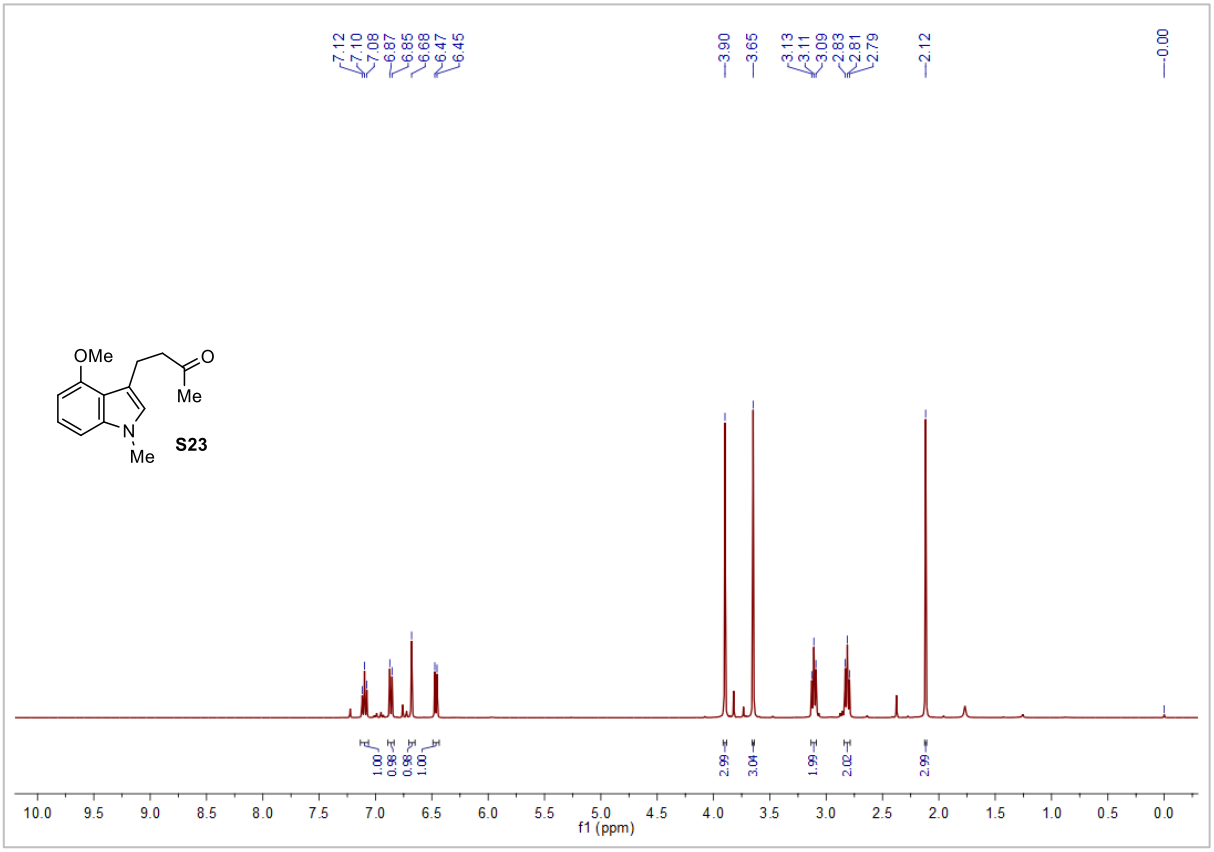


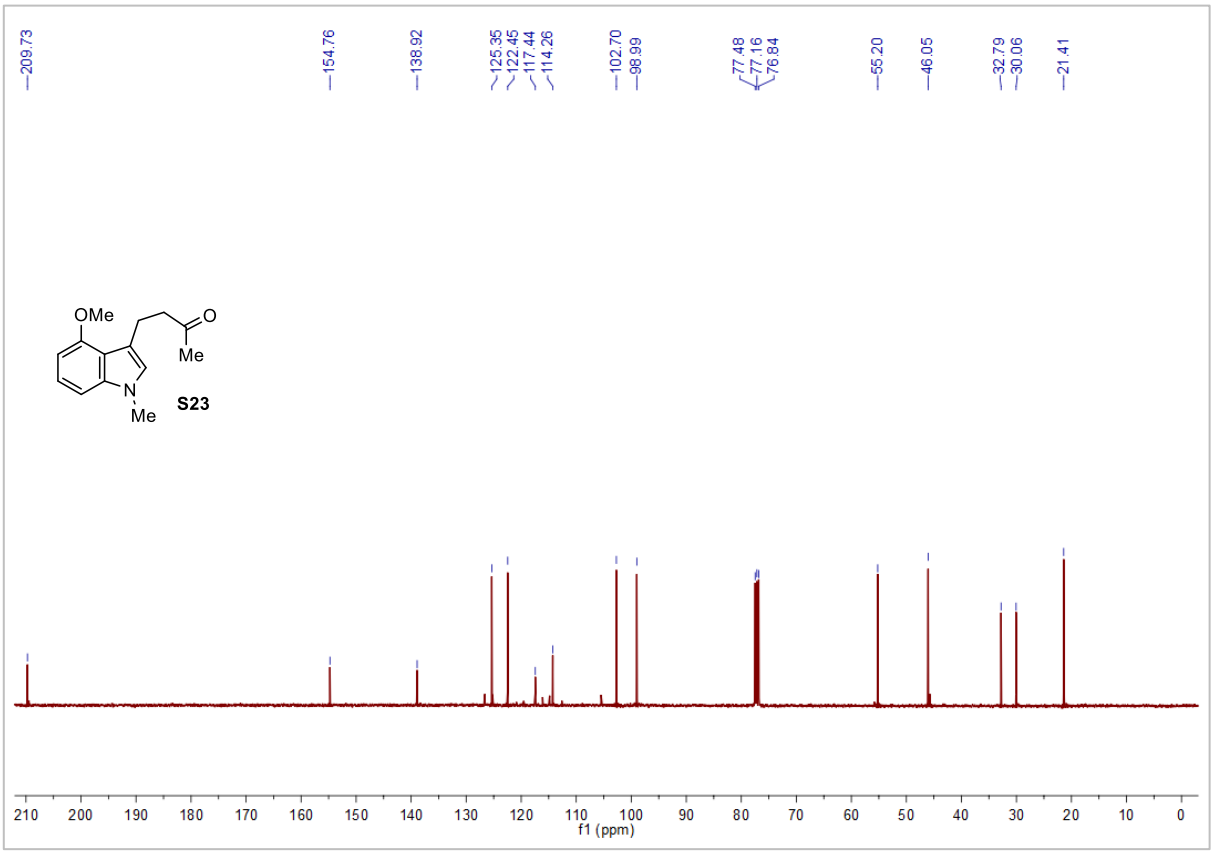
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S19**.



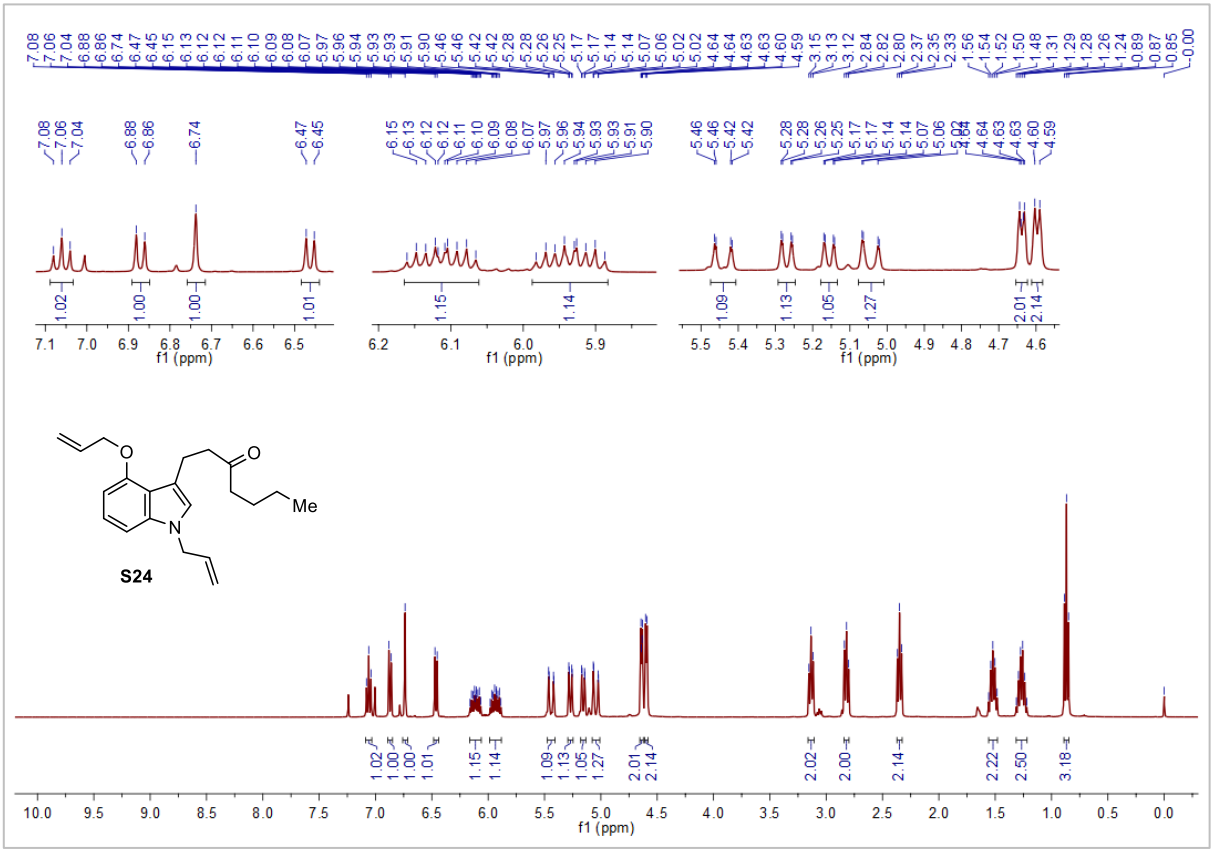


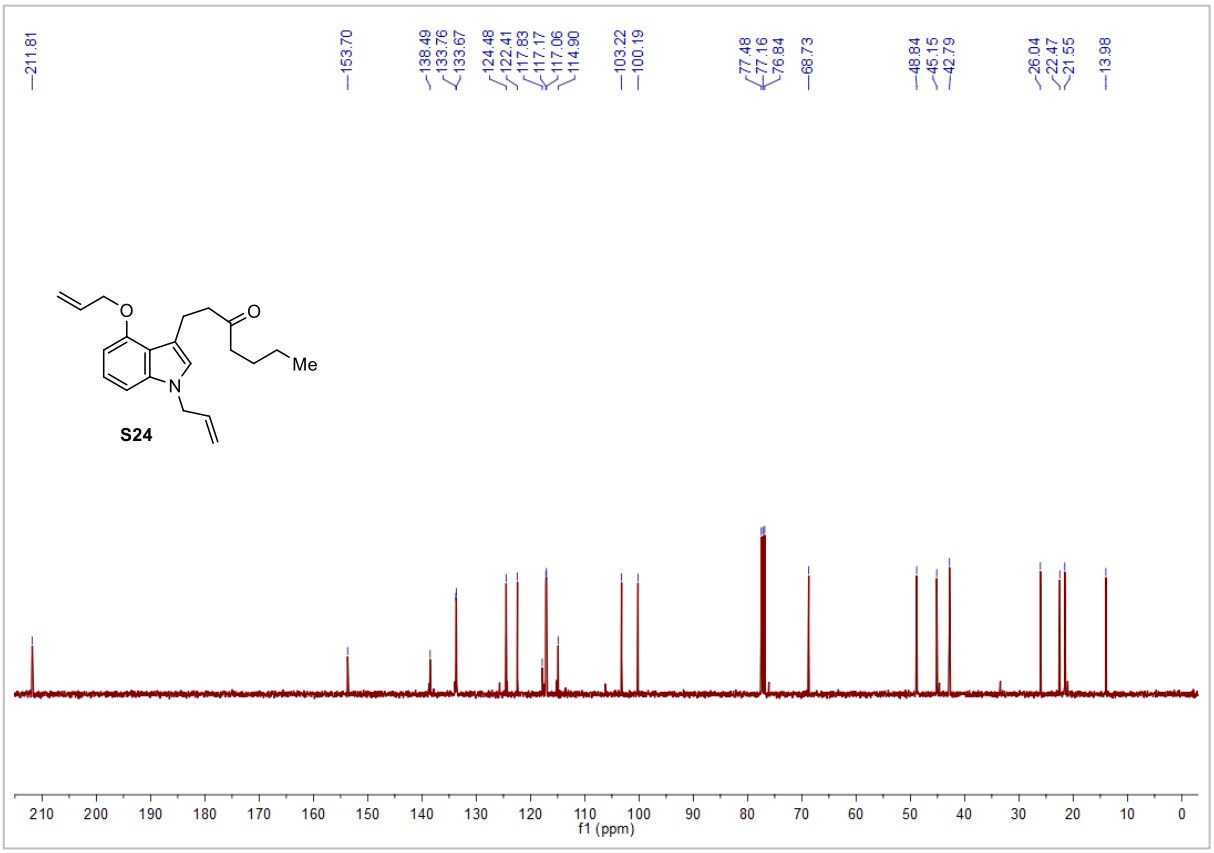
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S23**.



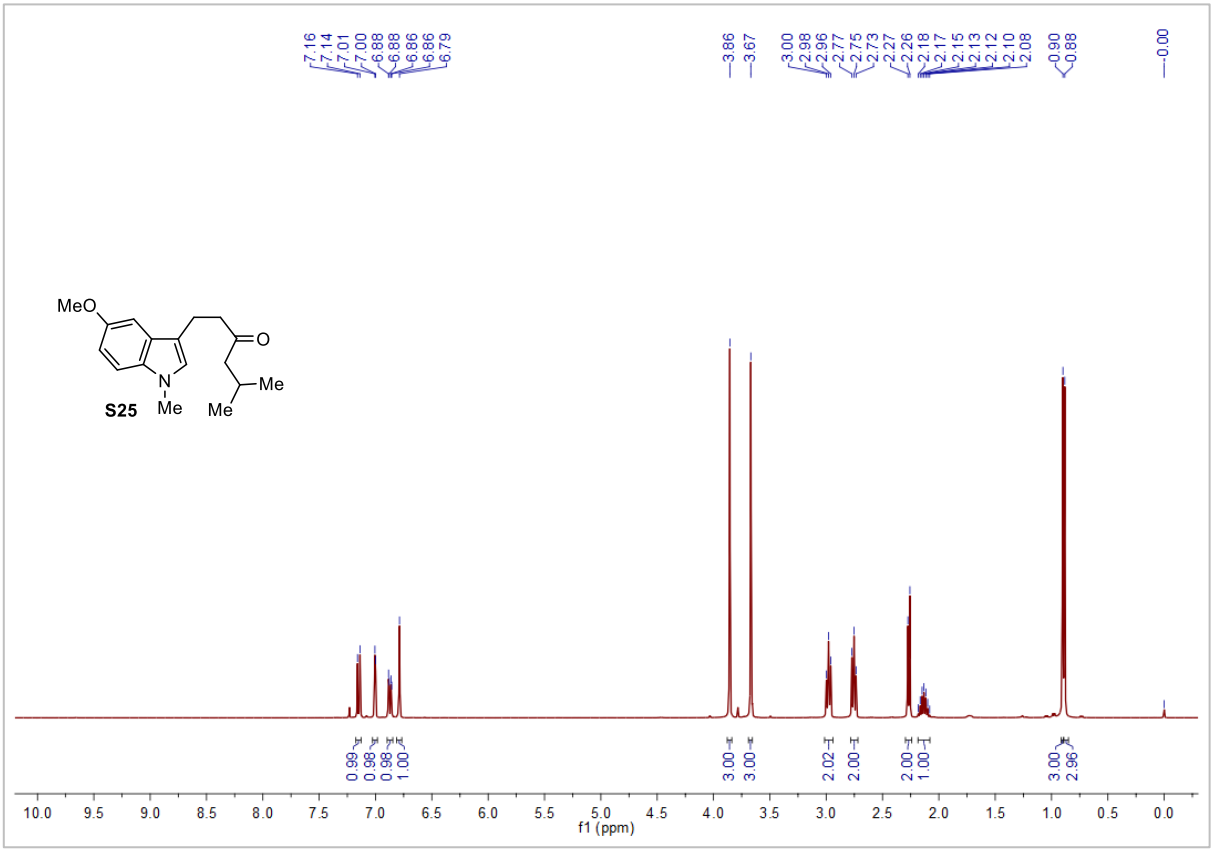


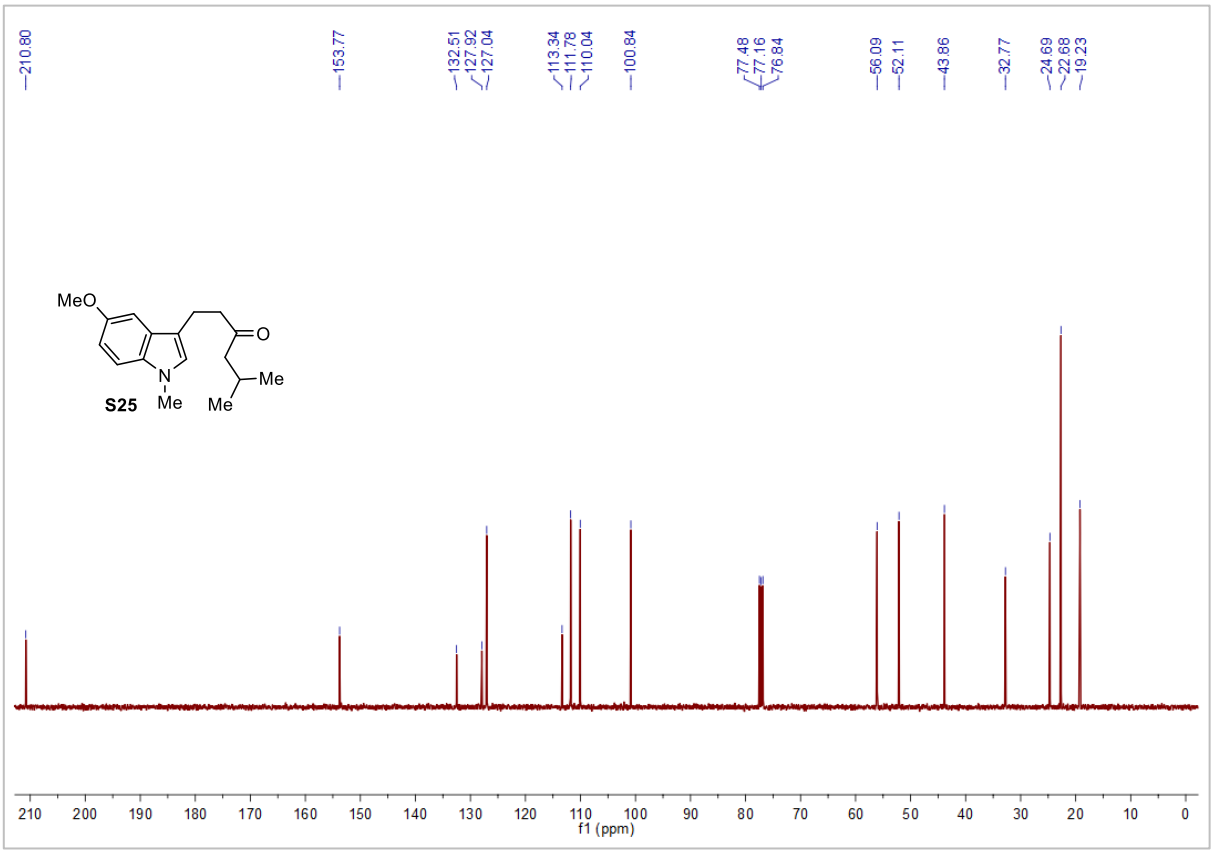
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S24**.



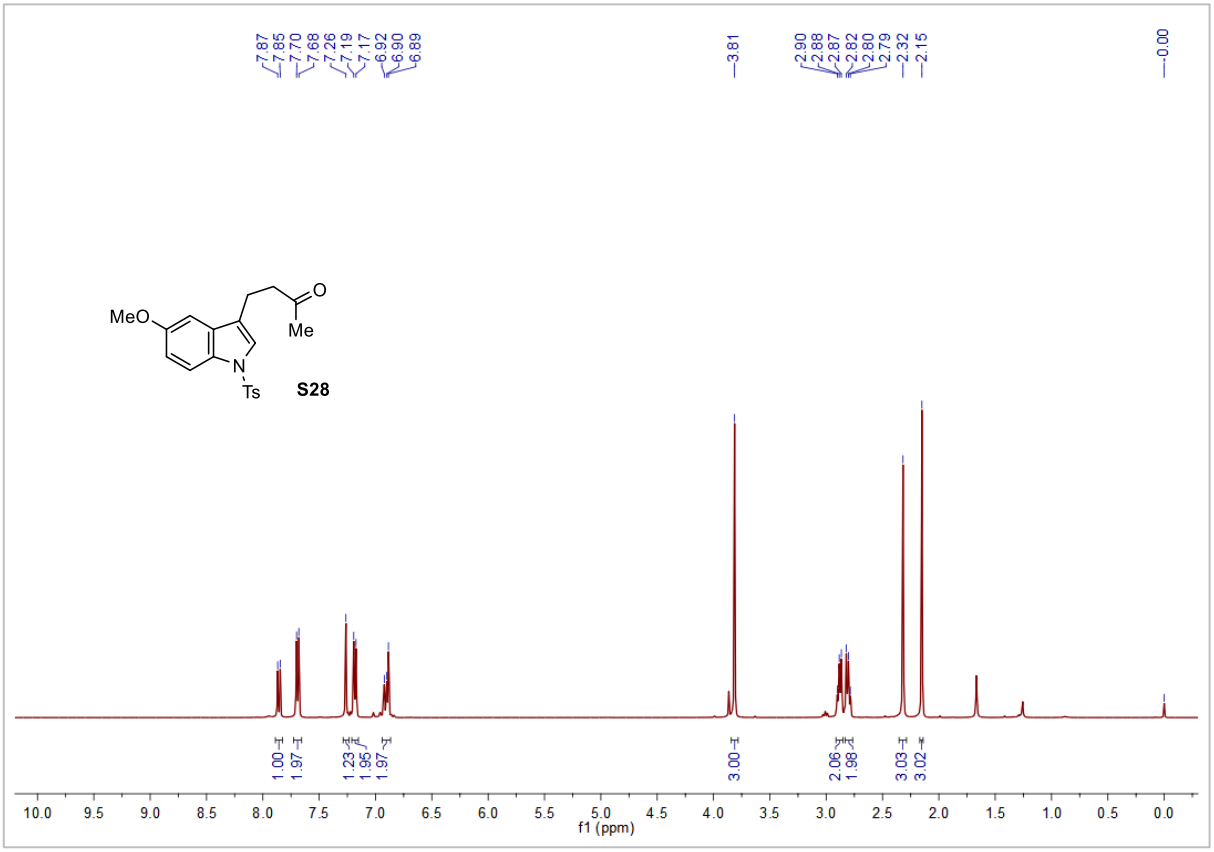


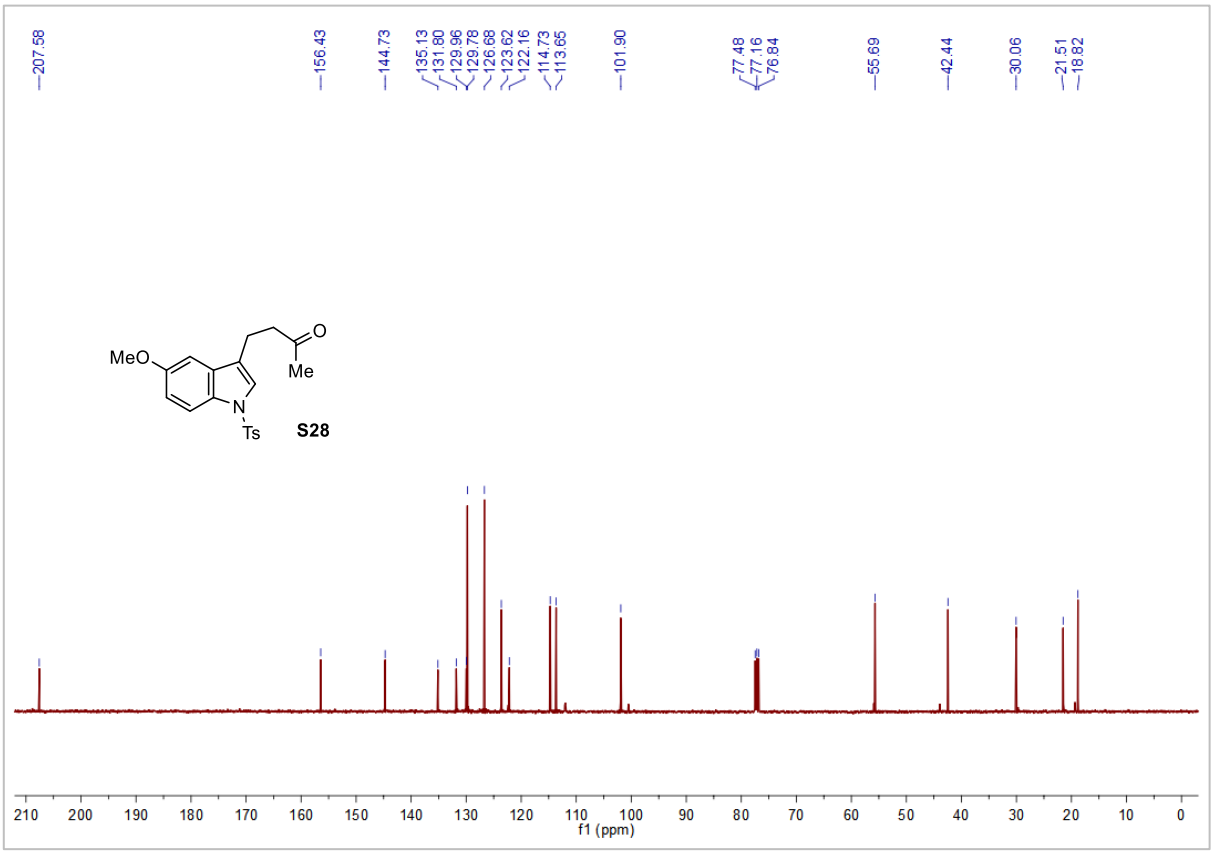
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S25**.



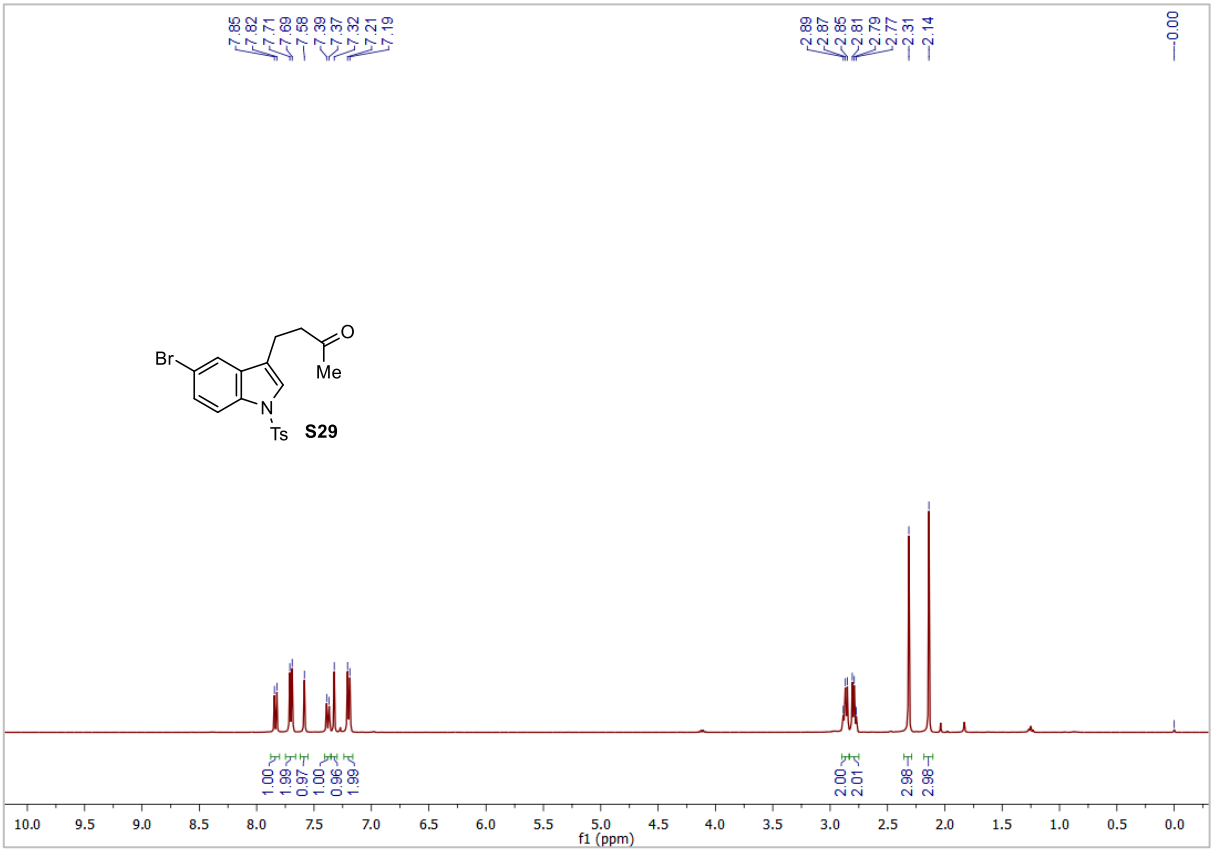


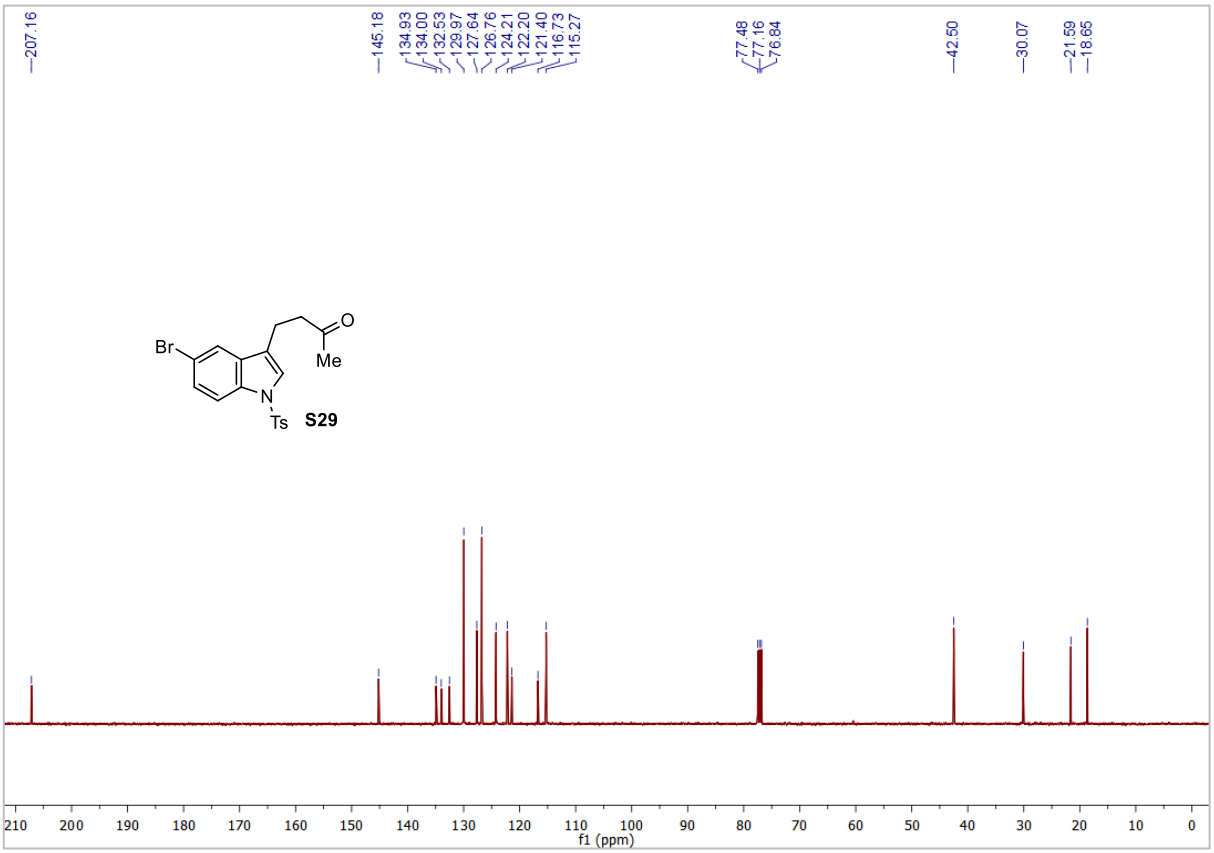
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S28**.



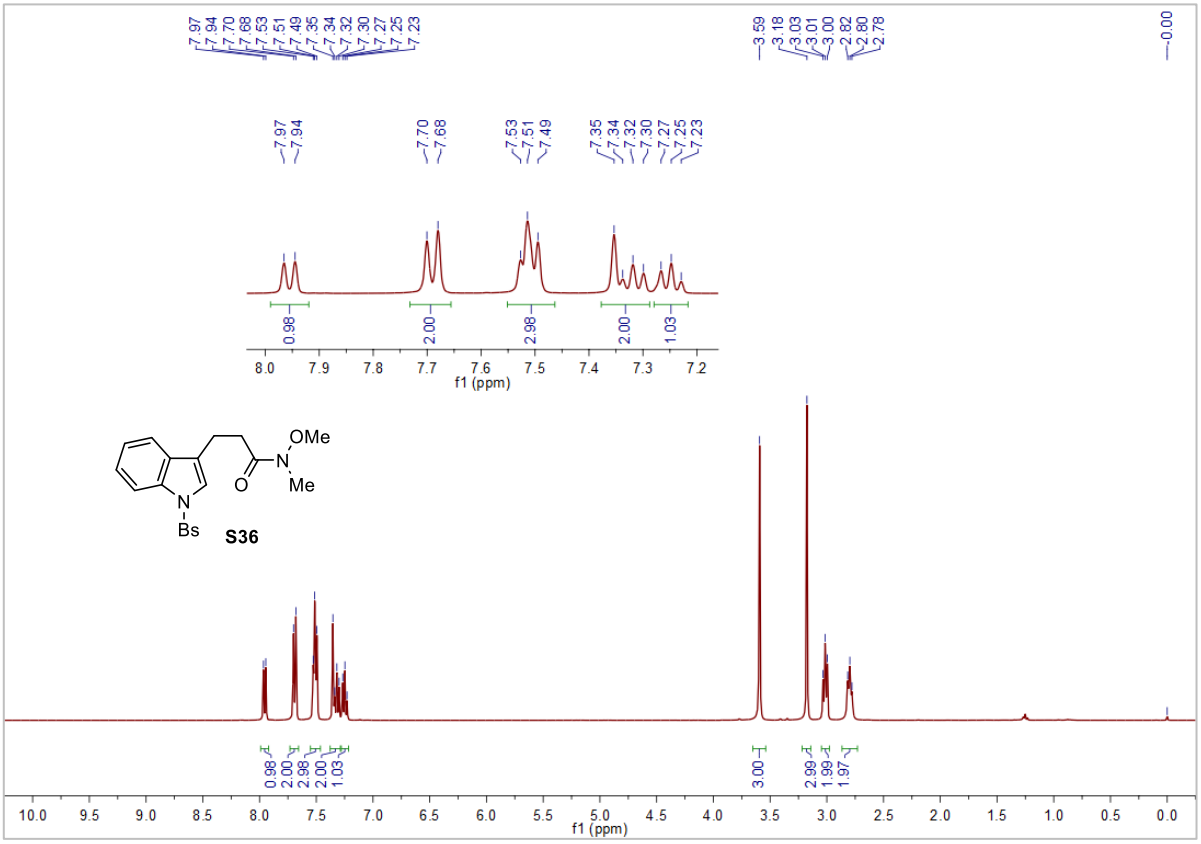


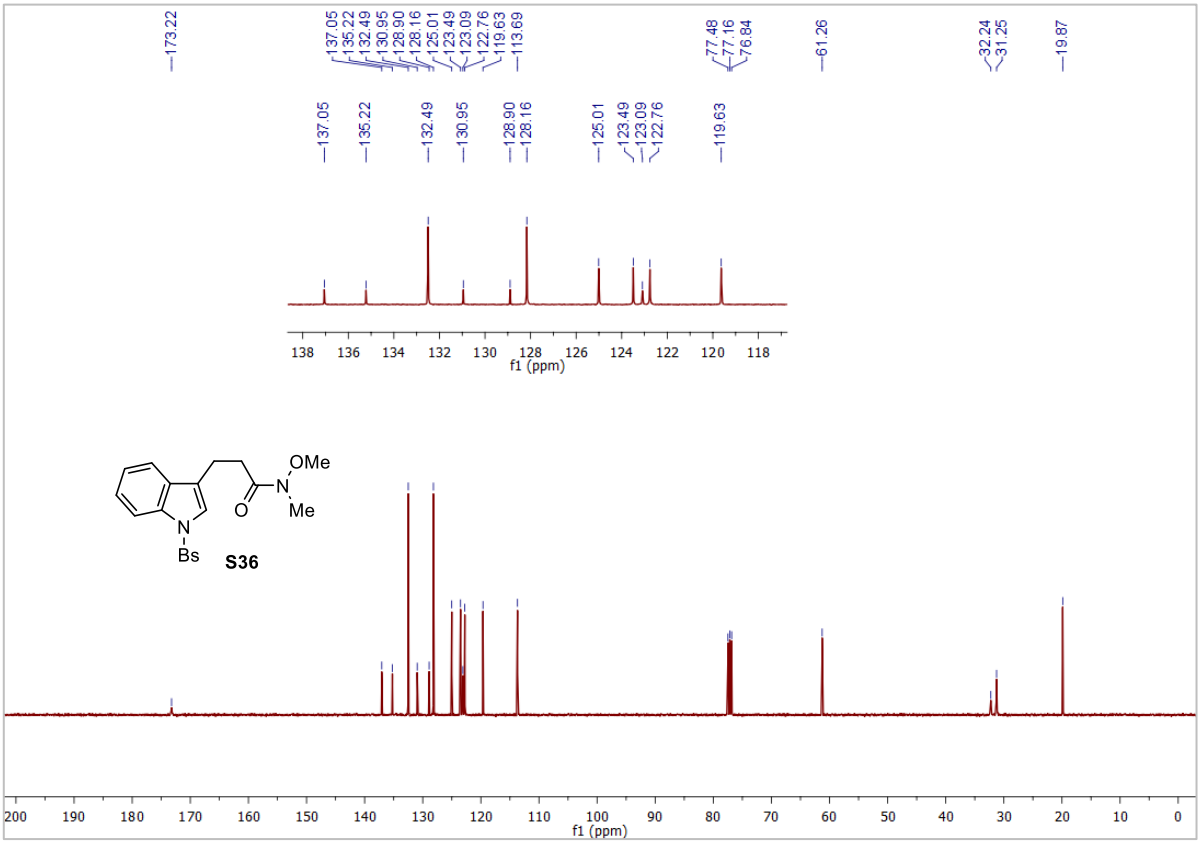
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S29**.



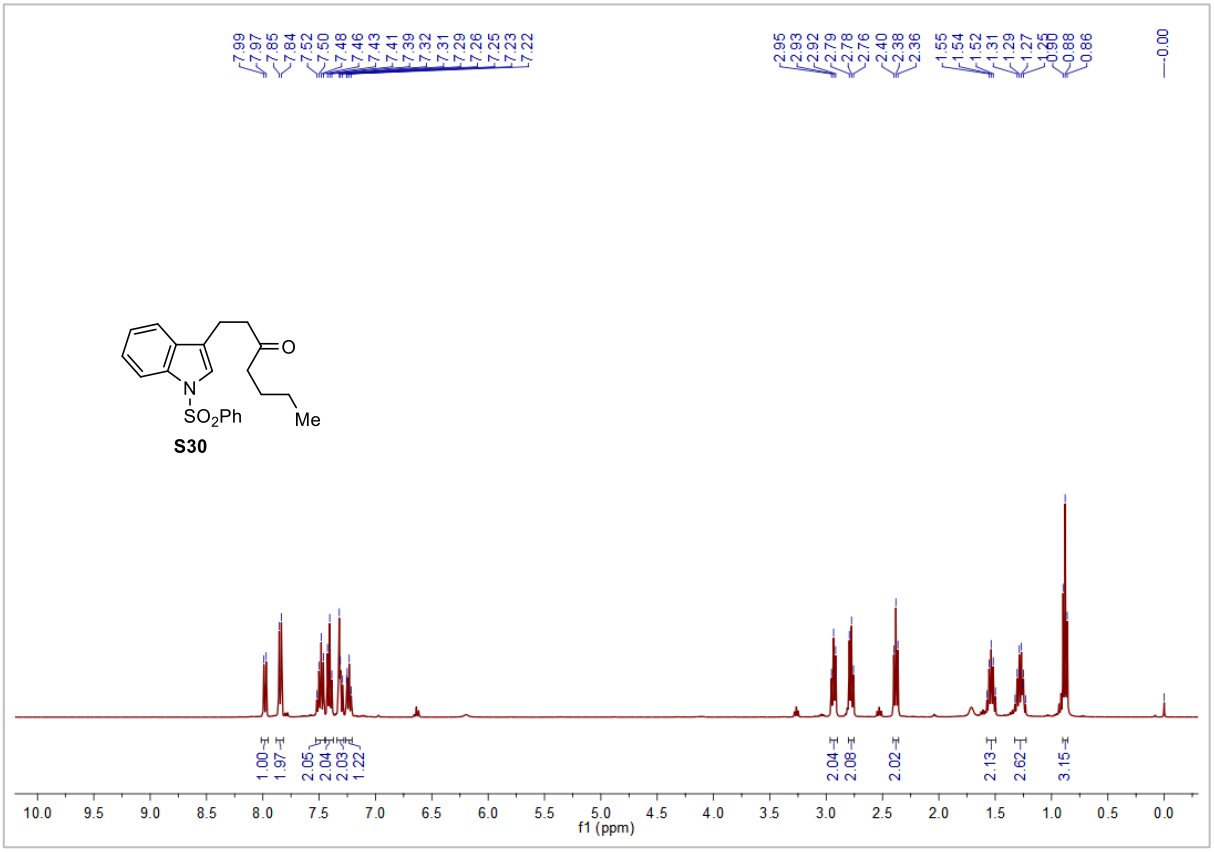


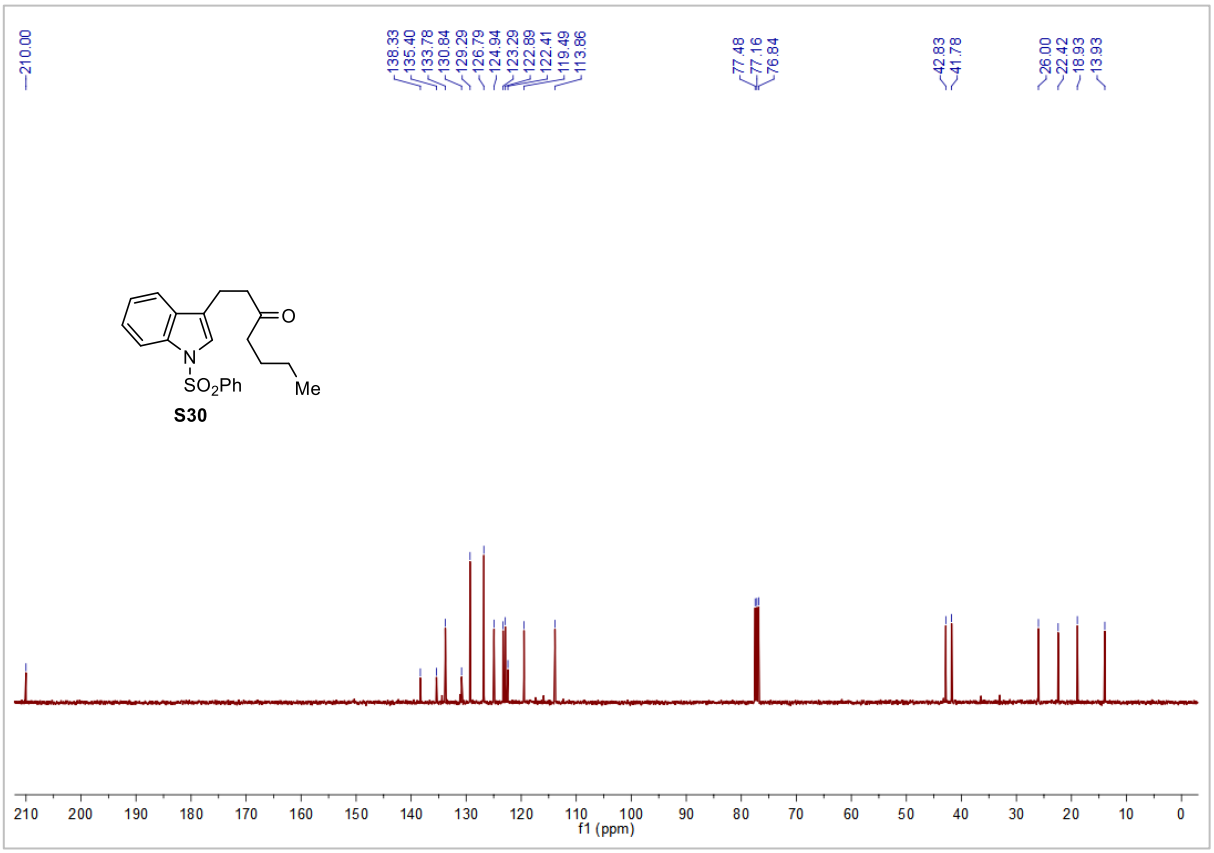
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S36**.



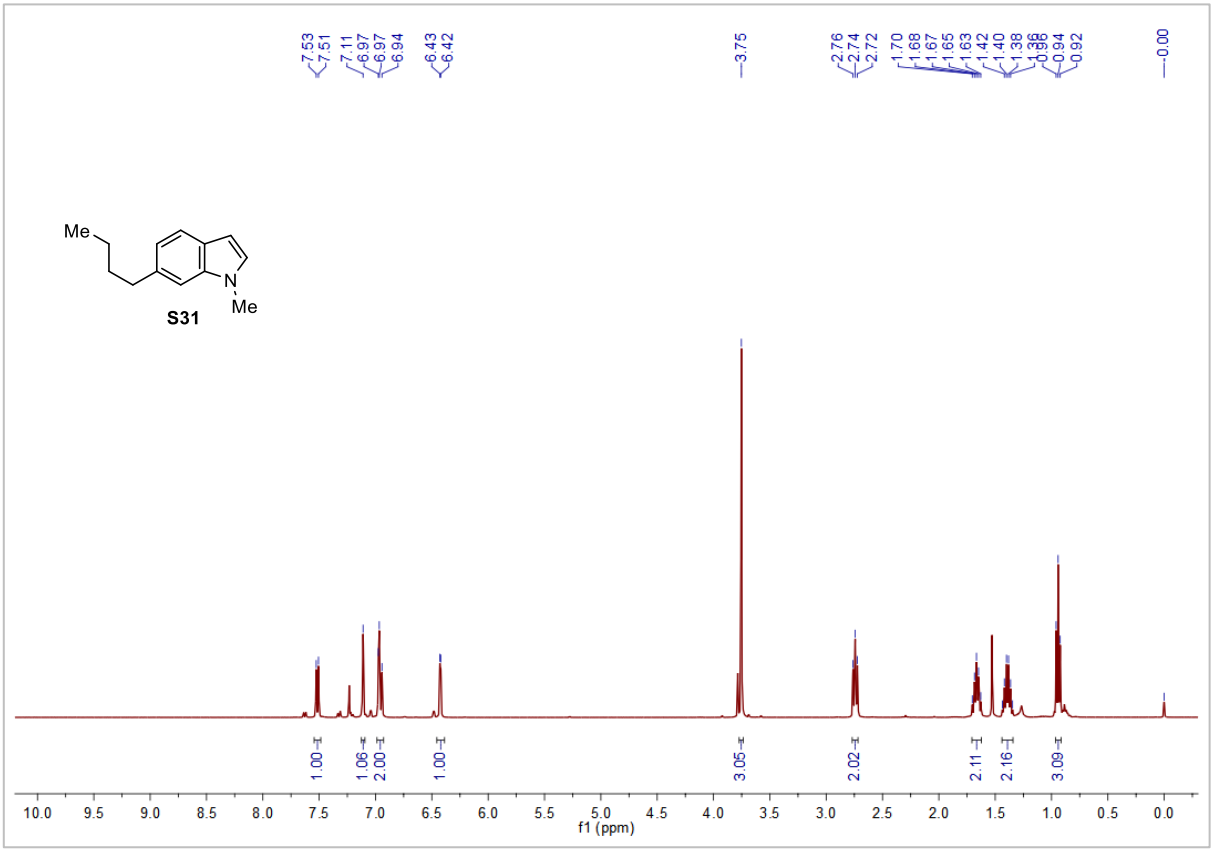


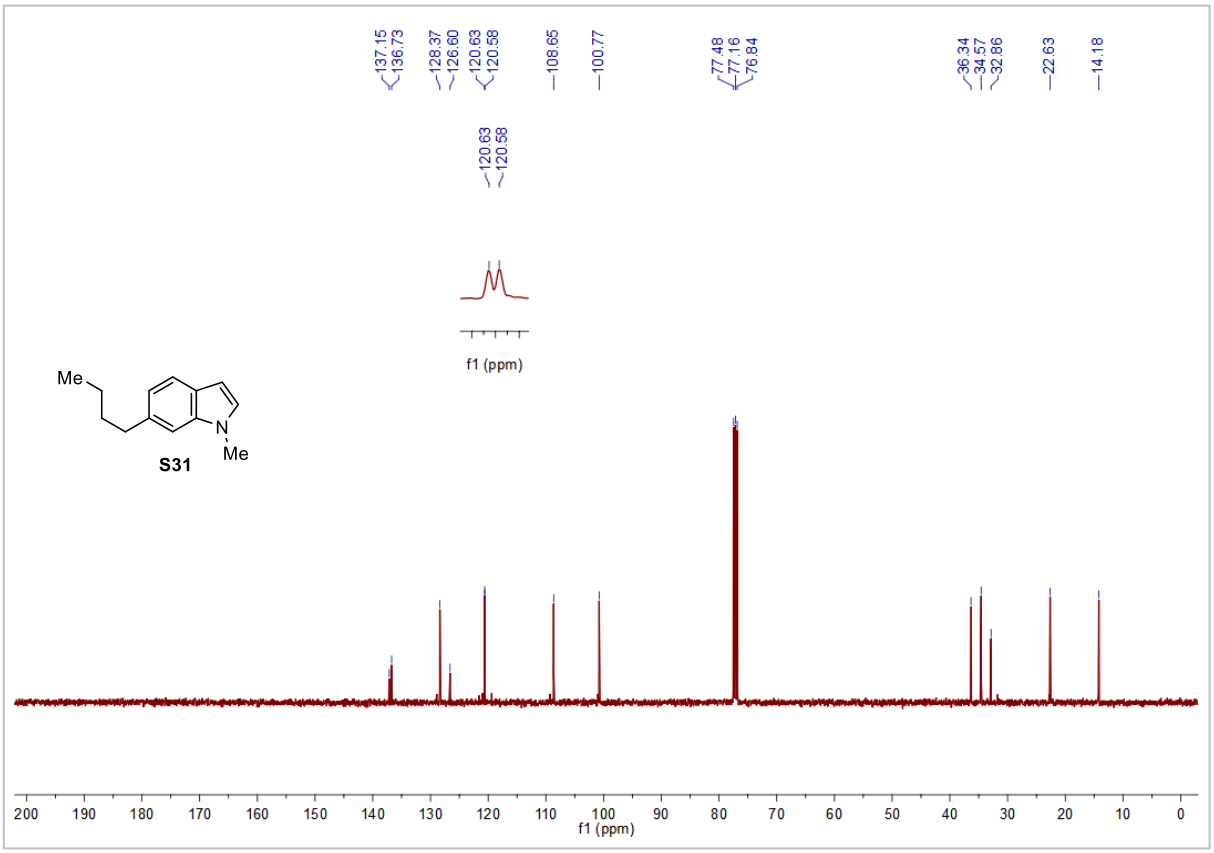
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S30**.



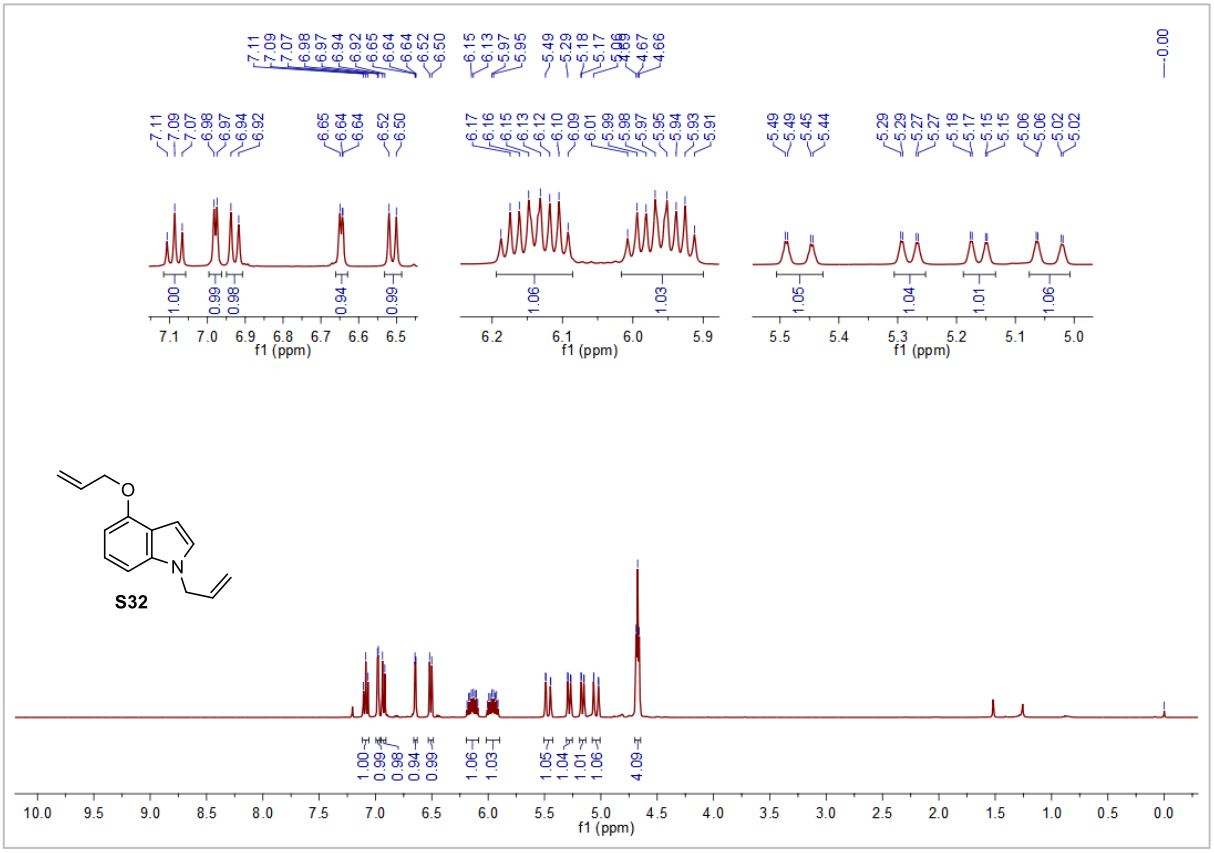


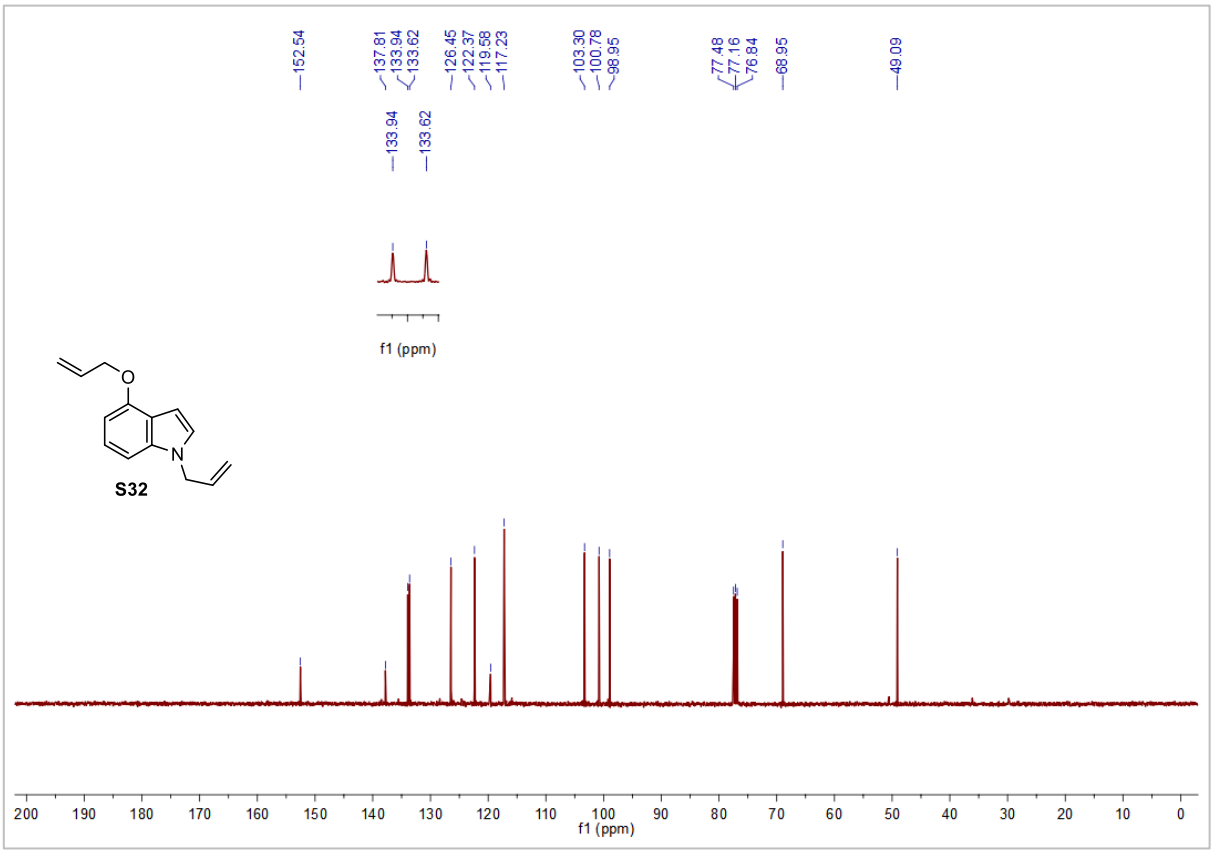
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S31**.



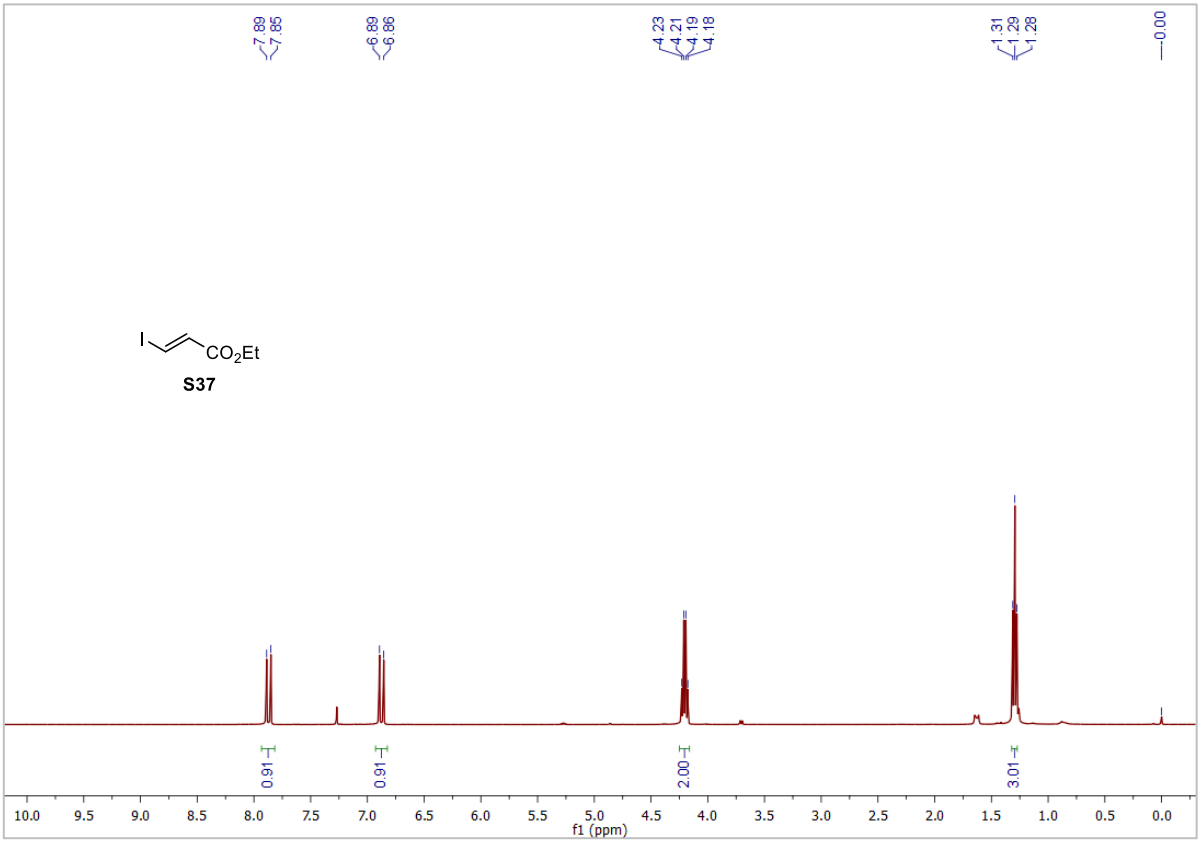


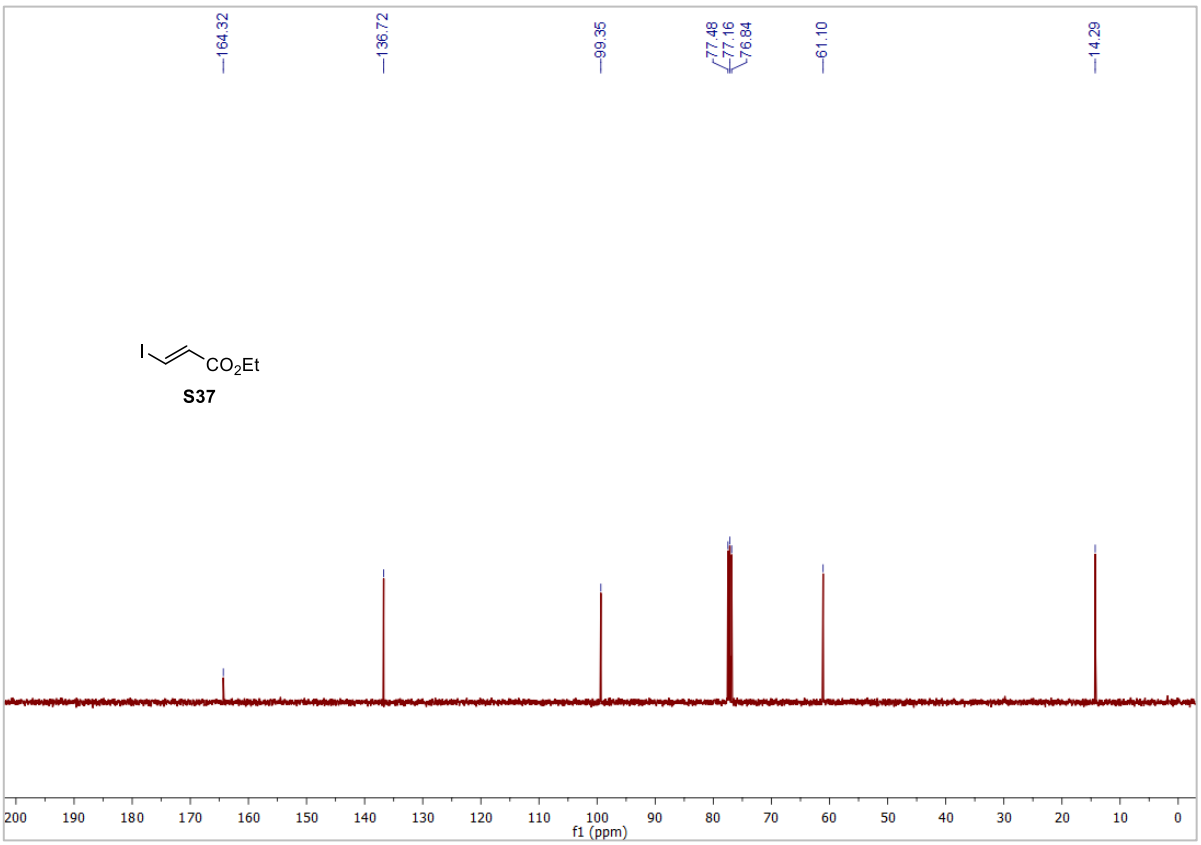
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S32**.

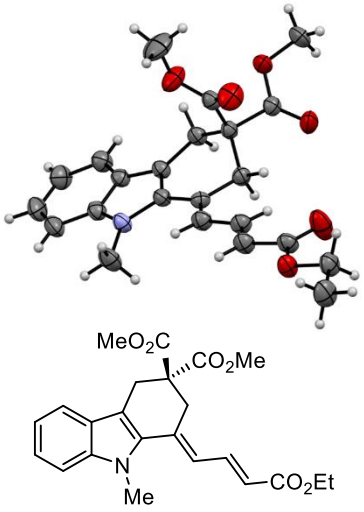




^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **S37**.





H. Crystallographic Data and Structure Refinements Summary of Compound 17	
Molecular Structure (ORTEP Diagram) For compound **17**	
CCDC number	CCDC2176803
Formula	$C_{23}H_{25}NO_6$
Formula weight	411.44
Colour of the crystal	Bright yellow
Temperature	296 (2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
a	8.3160 (3) Å
b	10.2395 (5) Å
c	12.7297 (6) Å
α	83.941 (2)°
β	84.824 (2)°
γ	74.004 (2)°
Volume	1034.04 (8) $Å^3$
Z	2

Calculated density	1.321 mg/m^3
Absorption coefficient, μ	0.096 mm^{-1}
F (000)	436
Crystal size	0.180 x 0.120 x 0.100 mm
θ range for data collection	2.076 to 24.998 °
Limiting indices	-7<=h<=9, -12=k<=12, -15<=l<=15
Reflections collected / unique	14629 / 3630 [R(int) = 0.0347]
Completeness to θ = 24.998	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3630 / 0 / 276
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.0977
R indices (all data)	R1 = 0.0611, wR2 = 0.1103
Extinction coefficient	0.014 (2)
Largest diff. peak and hole	0.204 and -0.189 $e.Å^{-3}$