

Supplementary Information

Modular and Regioselective Synthesis of All-carbon Tetrasubstituted Olefins Enabled by An Alkenyl Catellani Reaction

Jianchun Wang¹, Zhe Dong¹, Cheng Yang¹ and Guangbin Dong*¹

¹ Department of Chemistry, University of Chicago, Chicago, Illinois 60637, United States

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I. General Information

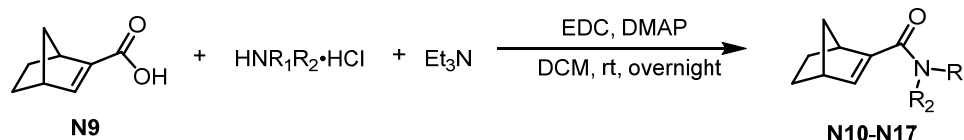
Unless noted otherwise, all solvents were dried by filtration through a Pure-Solv MD-5 Solvent Purification System (Innovative Technology). 1,4-dioxane and toluene were distilled freshly over sodium. Reaction temperatures were reported as the temperatures of the bath surrounding the flasks or vials. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glovebox with standard techniques. Cesium carbonate was purchased from Strem and stored in the glovebox. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical). Vials (15 x 45 mm 1 dram (4 mL) / 17 x 60 mm 3 dram (7.5 mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried prior to use. Mass spectra were recorded on an Agilent 6530 LC Q-TOF mass spectrometer using electrospray ionization with fragmentation voltage set at 115 V and processed with an Agilent MassHunter Operating System. X-ray diffraction data were collected at 100(2) K on a Bruker-Nonius Kappa CCD or Agilent SuperNova AtlasS2 CCD. Infrared spectra were recorded on a Nicolet 380 FTIR using neat thin film technique. Nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded with a Bruker Model DMX 500 or 400. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, $\delta=0.00\text{ppm}$) and are referenced to residual solvent (CDCl_3 , $\delta=7.26\text{ ppm}$ (^1H) and 77.00 ppm (^{13}C)). Coupling constants were reported in Hertz (Hz). Data for ^1H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). All other materials were obtained from Aldrich Chemical Company or Combi-blocks and were used as received.

II. Experimental Procedure and Characterization Data

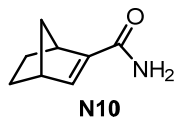
Preparation of modified norbornenes:

N2,¹ **N3**,² **N4**,³ **N5**,⁴ **N6**,⁴ **N7**,⁴ **N8**⁴ and **N9**⁴ were known compounds and were synthesized according to reported procedures.

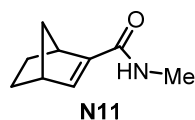
N10 – **N17** were synthesized according to the following procedures.



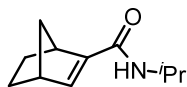
N9 (1 g, 7.2 mmol, 1.0 equiv), amine hydrochloride (14.4 mmol, 2.0 equiv), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (2.07 g, 10.8 mmol, 1.2 equiv), triethylamine (4 mL, 28.8 mmol, 4.0 equiv.), and 4-dimethylaminopyridine (12.2 mg, 0.72 mmol, 0.1 equiv.) were dissolved in dichloromethane (30 mL). The reaction mixture was stirred at room temperature overnight. Then it was diluted with diethyl ether, washed with water and brine, dried over MgSO_4 , and purified on silica gel chromatography (hexanes/ethyl acetate = 2:1) to afford norbornenes **N10** – **N17** as the product.



N10: White solid. Melting point = 158–159 °C. (2.0 mmol scale, 123 mg, 45% yield). R_f = 0.20 (hexane/ethyl acetate = 1:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.62 (d, J = 3.0 Hz, 1H), 5.79 – 5.23 (br, 2H), 3.11 (s, 1H), 2.95 (s, 1H), 1.79 – 1.64 (m, 2H), 1.51 – 1.39 (m, 1H), 1.15 (d, J = 8.4 Hz, 1H), 1.11 – 1.00 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 143.25, 142.18, 48.26, 43.45, 42.25, 24.92, 24.59 (the amide carbonyl signal cannot be located). **IR** (KBr, cm^{-1}): ν 3365, 3186, 2958, 2868, 1653, 1621, 1582, 1406. **HRMS** (ESI): Calcd for $\text{C}_8\text{H}_{12}\text{NO}^+$ ($\text{M}+\text{H}^+$): 138.0913, found: 138.0909.

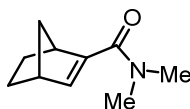


N11: White solid. Melting point = 111–112 °C. (7.2 mmol scale, 740 mg, 68% yield). R_f = 0.35 (hexane/ethyl acetate = 1:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.60 (s, 1H), 6.20 – 5.76 (br, 1H), 3.13 (s, 1H), 2.96 (s, 1H), 2.82 (dd, J = 12.3, 4.9 Hz, 3H), 1.78 – 1.62 (m, 2H), 1.50 – 1.38 (m, 1H), 1.16 (t, J = 9.2 Hz, 1H), 1.12 – 0.97 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 165.64, 143.91, 140.40, 48.30, 43.18, 42.12, 26.12, 25.01, 24.69. **IR** (KBr, cm^{-1}): ν 2951, 2871, 1625, 1587, 1497, 1394, 1272, 1153, 1052. **HRMS** (ESI): Calcd for $\text{C}_{10}\text{H}_{16}\text{NO}^+$ ($\text{M}+\text{H}^+$): 166.1226, found: 166.1235.



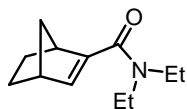
N12

N12: White solid. Melting point = 156–157 °C. (2.0 mmol scale, 260 mg, 73% yield). R_f = 0.45 (hexane/ethyl acetate = 1:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.62 (d, J = 3.1 Hz, 1H), 5.46 (s, 1H), 4.29 – 4.01 (m, 1H), 3.15 (s, 1H), 3.00 (s, 1H), 1.81 – 1.70 (m, 2H), 1.50 (dt, J = 8.4, 2.1 Hz, 1H), 1.20 (d, J = 3.3 Hz, 3H), 1.19 (d, J = 3.4 Hz, 3H), 1.15 – 1.08 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 164.05, 144.24, 140.10, 48.32, 43.19, 42.16, 41.10, 25.07, 24.72, 22.93, 22.91. **IR** (KBr, cm^{-1}): ν 3322, 2971, 2874, 179, 1637, 1526, 1458, 1280. **HRMS** (ESI): Calcd for $\text{C}_{11}\text{H}_{18}\text{NO}^+$ ($\text{M}+\text{H}^+$): 180.1383, found: 180.1393.



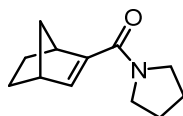
N13

N13: Colorless oil. (2.0 mmol scale, 280 mg, 85% yield). R_f = 0.40 (hexane/ethyl acetate = 1:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.20 (s, 1H), 3.23 – 2.90 (m, 8H), 1.80 – 1.68 (m, 2H), 1.44 (dq, J = 6.3, 1.9 Hz, 1H), 1.35 (t, J = 8.5 Hz, 1H), 1.16 (d, J = 8.4 Hz, 1H), 1.11 (t, J = 9.5 Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.44, 142.72, 138.38, 47.18, 44.95, 43.58, 38.64, 35.07, 25.27, 25.25. **IR** (KBr, cm^{-1}): ν 2951, 2871, 1625, 1587, 1497, 1394, 1272, 1153, 1052. **HRMS** (ESI): Calcd for $\text{C}_{10}\text{H}_{16}\text{NO}^+$ ($\text{M}+\text{H}^+$): 166.1226, found: 166.1235.



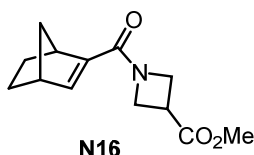
N14

N14: Colorless oil. (2.0 mmol scale, 242 mg, 63% yield, using diethylamine directly instead of corresponding hydrochloride salt). $R_f = 0.40$ (hexane/ethyl acetate = 1:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.14 (d, $J = 3.1$ Hz, 1H), 3.59 – 3.44 (m, 2H), 3.41 – 3.24 (m, 2H), 3.15 (s, 1H), 3.00 (s, 1H), 1.80 – 1.68 (m, 2H), 1.50 – 1.34 (m, 2H), 1.22 – 1.09 (m, 8H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.46, 143.15, 135.73, 47.28, 45.36, 43.44, 42.61, 39.23, 25.40, 25.27, 14.83, 12.85. **IR** (KBr, cm^{-1}): ν 2972, 2872, 1623, 1586, 1426, 1285, 1064. **HRMS** (ESI): Calcd for $\text{C}_{12}\text{H}_{20}\text{NO}^+$ ($\text{M}+\text{H}^+$): 194.1539, found: 194.1547.



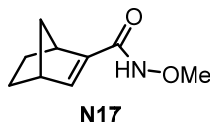
N15

N15: Colorless oil. (2.0 mmol scale, 230 mg, 60% yield, using pyrrolidine directly instead of corresponding hydrochloride salt). $R_f = 0.45$ (hexane/ethyl acetate = 1:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.33 (s, 1H), 3.70 – 3.35 (m, 4H), 3.28 (s, 1H), 3.01 (s, 1H), 2.06 – 1.78 (m, 4H), 1.79 – 1.68 (m, 2H), 1.48 – 1.36 (m, 1H), 1.34 – 1.19 (m, 1H), 1.19 – 1.00 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 165.82, 144.33, 139.33, 48.27, 47.08, 47.05, 46.17, 44.26, 44.24, 43.71, 43.69, 26.46, 25.21, 25.19, 25.08, 25.06, 24.08. **IR** (KBr, cm^{-1}): ν 2968, 2871, 1616, 1578, 1425, 1312. **HRMS** (ESI): Calcd for $\text{C}_{12}\text{H}_{18}\text{NO}^+$ ($\text{M}+\text{H}^+$): 192.1383, found: 192.1392.



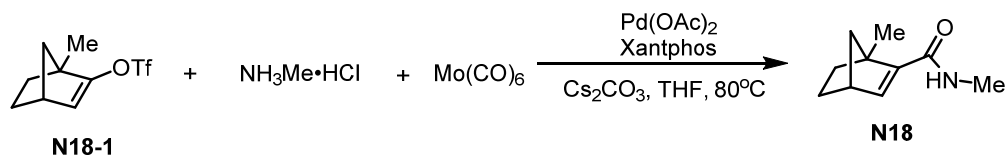
N16

N16: Colorless oil. (2.0 mmol scale, 315 mg, 67% yield). $R_f = 0.35$ (hexane/ethyl acetate = 1:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.34 (d, $J = 3.1$ Hz, 1H), 4.50 – 4.01 (m, 4H), 3.69 (s, 3H), 3.38 (p, $J = 7.6$ Hz, 1H), 3.20 (s, 1H), 2.94 (s, 1H), 1.72 – 1.62 (m, 2H), 1.35 (s, 1H), 1.14 – 1.04 (m, 2H), 1.04 – 0.88 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 141.85, 54.35, 52.39, 51.05, 47.54, 43.62, 42.72, 32.84, 24.78, 24.68. **IR** (KBr, cm^{-1}): ν 2955, 2873, 1736, 1626, 1578, 1432, 1361, 1206, 1178. **HRMS** (ESI): Calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_3^+$ ($\text{M}+\text{H}^+$): 236.1281, found: 236.1293.

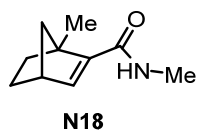


N17: White solid. Melting point = 87–88 °C. (2.0 mmol scale, 267 mg, 80% yield). R_f = 0.45 (hexane/ethyl acetate = 1:1). $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 8.30 (s, 1H), 6.74 (d, J = 3.2 Hz, 1H), 3.82 (s, 3H), 3.18 (s, 1H), 3.03 (s, 1H), 1.87 – 1.70 (m, 2H), 1.54 – 1.46 (m, 1H), 1.24 (d, J = 8.6 Hz, 1H), 1.19 – 1.06 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform- d) δ 142.61, 140.76, 64.63, 48.24, 43.21, 42.08, 24.82, 24.66. **IR** (KBr, cm^{-1}): ν 3191, 2969, 2871, 1648, 1597, 1499, 1300, 1045. **HRMS** (ESI): Calcd for $\text{C}_9\text{H}_{14}\text{NO}_2^+$ ($\text{M}+\text{H}^+$): 168.1019, found: 168.1013.

N18 was synthesized according to the following procedure:



An oven-dried 4.0 mL vial was charged with **N18-1**² (28.6 mg, 0.1 mmol, 1.0 equiv.), $\text{Mo}(\text{CO})_6$ (13.2 mg, 0.05 mmol, 0.5 equiv.), methylamine hydrochloride (13.5 mg, 0.2 mmol, 2.0 equiv.), $\text{Pd}(\text{OAc})_2$ (0.6 mg, 0.0025 mmol, 2.5 mol%), Xantphos (2.9 mg, 0.005 mg, 5.0 mol%) and Cs_2CO_3 (97.8 mg, 0.3 mmol, 3.0 equiv.). The vial was partially capped and transferred in a nitrogen-filled glovebox. In the glovebox, tetrahydrofuran (1 mL) was added and the vial was tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 80 °C for 5 h. Upon completion of the reaction, the mixture was filtered through a thin pad of silica gel. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The residue was purified by flash column chromatography on silica gel to yield the desired product.

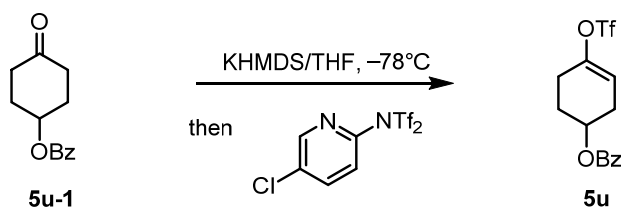


N18: White solid. Melting point = 77–78 °C. (0.1 mmol scale, 10 mg, 61% yield). $R_f = 0.30$ (hexane/ethyl acetate = 1:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 6.33 (d, $J = 3.1$ Hz, 1H), 5.55 (s, 1H), 2.79 – 2.73 (m, 4H), 1.87 – 1.76 (m, 1H), 1.48 – 1.37 (m, 4H), 1.30 – 1.20 (m, 2H), 1.14 – 1.06 (m, 1H), 1.04 (d, $J = 8.2$ Hz, 1H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 167.47, 146.46, 139.45, 54.34, 50.95, 42.20, 32.08, 28.18, 25.91, 17.49. **IR** (KBr, cm^{-1}): ν 3314, 2950, 2867, 1642, 1583, 1534, 1409, 1296. **HRMS** (ESI): Calcd for $\text{C}_{10}\text{H}_{16}\text{NO}^+$ ($\text{M}+\text{H}^+$): 166.1226, found: 166.1231.

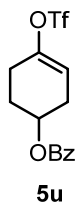
Preparation of vinyl halides or triflates:

5a,⁵ **5q**,⁶ **5r**,⁷ **5s**,⁸ **5t**,⁹ **5x**,¹⁰ **5y**,¹¹ **5z**,¹² **5aa**,¹³ **5ab**,¹⁴ **5ac**,¹⁵ **5ad**,¹⁶ **5ae**,¹⁷ and **5af**¹² are known compounds and were synthesized according to reported procedures. **5ag** was purchased from Sigma-Aldrich.

5u was synthesized by the following procedure:

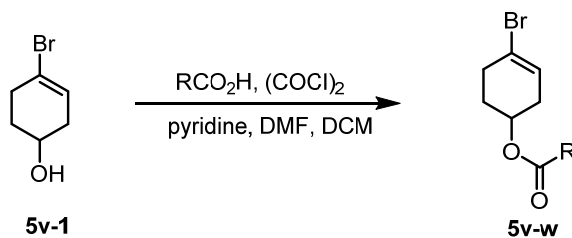


To the solution of KHMDS (1.60 g, 8.05 mmol, 1.15 equiv.) in anhydrous THF (10 mL) was slowly added a solution of **5u-1**¹⁸ (1.52 g, 7.0 mmol, 1.0 equiv.) in anhydrous THF (15 mL) at -78°C . After 1 h at -78°C under a nitrogen atmosphere, a solution of Comin's reagent (3.03 g, 7.7 mmol, 1.1 equiv.) in anhydrous THF (15 mL) was slowly added to the reaction mixture at -78°C . The solution mixture was allowed to warm to room temperature over 1 h and stirred for additional 3 h. The resulting solution was treated with saturated aqueous NaHCO_3 (20 mL) and extracted with Et_2O (3×20 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous MgSO_4 , filtered, and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography.

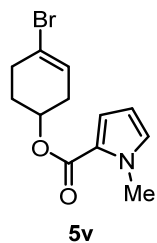


5u: Colorless oil. (7.0 mmol scale, 1.37 g, 56% yield). $R_f = 0.25$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.84 – 7.79 (m, 2H), 7.40 – 7.33 (m, 1H), 7.24 (ddd, $J = 8.0, 6.8, 1.1$ Hz, 2H), 5.54 (ddt, $J = 5.0, 2.9, 1.5$ Hz, 1H), 5.15 (dtd, $J = 7.1, 4.5, 2.6$ Hz, 1H), 2.50 – 2.35 (m, 2H), 2.34 – 2.19 (m, 2H), 2.05 – 1.92 (m, 1H), 1.91 – 1.76 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 165.84, 148.14, 133.18, 130.10, 129.60, 128.45, 118.54 (q, $J = 320.3$ Hz), 115.16, 66.86, 29.45, 26.88, 24.43. **IR** (KBr, cm^{-1}): ν 2941, 1720, 1417, 1278, 1211, 1142, 1115. **HRMS** (ESI): Calcd for $\text{C}_{14}\text{H}_{14}\text{F}_3\text{O}_5\text{S}^+$ ($\text{M}+\text{H}^+$): 351.0509, found: 351.0506.

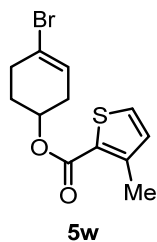
5v and **5w** were synthesized by the following procedure:



To a solution of corresponding carboxylic acid (2.2 mmol, 1.1 equiv.) and 1 drop of DMF in dichloromethane (1.0 mL) was added oxalyl chloride (203 μL , 2.4 mmol, 1.2 equiv.) dropwise at 0 $^\circ\text{C}$. The reaction mixture was stirred at room temperature for another 1 h until the bubbling stopped. A mixture of **5v-1** (354 mg, 2.0 mmol, 1.0 equiv.) and pyridine (161 μL , 2.0 mmol, 1.0 equiv.) were then added and the reaction was stirred for another 3 h. The organic layer was washed with diluted hydrochloric acid and then concentrated under vacuum. The resulting crude product was purified by column chromatography.

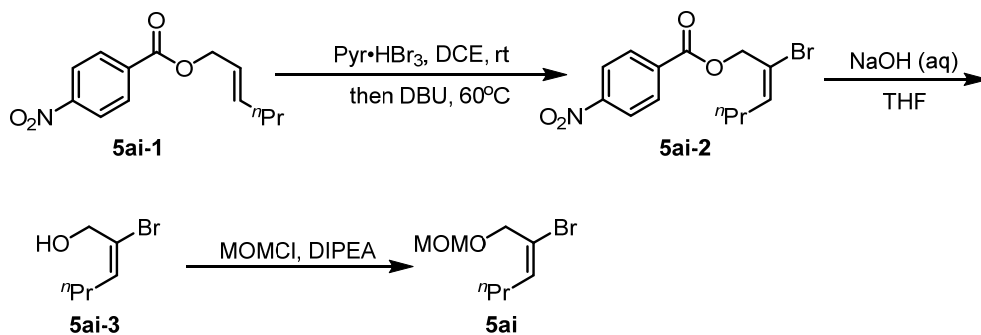


5v: Colorless oil. (2.0 mmol scale, 265 mg, 47% yield). $R_f = 0.25$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.97 (dd, $J = 3.9, 1.8$ Hz, 1H), 6.81 (t, $J = 2.2$ Hz, 1H), 6.13 (dd, $J = 4.0, 2.5$ Hz, 1H), 5.99 (tt, $J = 4.1, 1.7$ Hz, 1H), 5.24 (tt, $J = 5.7, 4.7$ Hz, 1H), 3.94 (s, 3H), 2.74 – 2.46 (m, 3H), 2.38 – 2.26 (m, 1H), 2.10 – 1.95 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 160.66, 129.62, 125.40, 122.61, 121.21, 118.06, 107.88, 66.54, 36.86, 32.82, 32.42, 28.86. **IR** (KBr, cm^{-1}): ν 2931, 2847, 1701, 1654, 1530, 1482, 1412, 1322, 1245, 1110. **HRMS** (ESI): Calcd for $\text{C}_{12}\text{H}_{15}\text{BrNO}_2^+$ ($\text{M}+\text{H}^+$): 284.0281, found: 284.0283.



5w: Colorless oil. (2.0 mmol scale, 270 mg, 37% yield). $R_f = 0.20$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.41 (d, $J = 5.0$ Hz, 1H), 6.93 (d, $J = 5.0$ Hz, 1H), 5.99 (dt, $J = 4.0, 2.2$ Hz, 1H), 5.29 (dtd, $J = 6.9, 5.1, 3.7$ Hz, 1H), 2.75 – 2.48 (m, 6H), 2.41 – 2.30 (m, 1H), 2.06 (tdd, $J = 6.5, 5.1, 3.9$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 162.33, 146.08, 131.80, 130.26, 127.16, 125.18, 121.22, 67.60, 32.71, 32.28, 28.71, 15.99. **IR** (KBr, cm^{-1}): ν 2928, 2847, 1701, 1654, 1541, 1414, 1257, 1225. **HRMS** (ESI): Calcd for $\text{C}_{12}\text{H}_{14}\text{BrO}_2\text{S}^+$ ($\text{M}+\text{H}^+$): 300.9892, found: 300.9888.

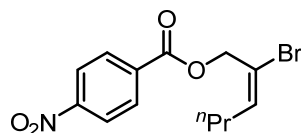
5ai, **5aj**, and **5ak** were synthesized by the following procedure:



Following a known procedure¹⁹: A mixture of **5ai-1** (12.1 g, 49 mmol, 1.0 equiv.) and pyridinium bromide perbromide (17.1 g, 53.5 mmol, 1.1 equiv.) in 1,2-dichloroethane (0.1 M) was stirred at room temperature for 12–14 h. 1,8-Diazabicyclo[5.4.0]undec-7-ene (22.6 mL, 150 mmol, 3.1 equiv.) was added to the reaction mixture at 0 °C and the reaction mixture was then heated to 60 °C. The reaction was quenched with 1 M aqueous HCl, and the reaction mixture was extracted with dichloromethane, concentrated in vacuo, and purified by silica gel column chromatography to afford **5ai-2** (14.3 g, 89%).

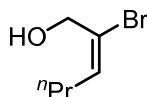
To a solution of **5ai-2** (10 g, 30.5 mmol, 1.0 equiv.) in tetrahydrofuran (60 mL) was added 2M aqueous NaOH solution (30.5 mL, 61 mmol, 2.0 equiv.) dropwise at room temperature. The reaction mixture was stirred at room temperature overnight. The reaction mixture was treated with 1 M HCl (aq) and extracted with Et₂O (3 × 60 mL). The combined organic extracts were washed with brine (40 mL), dried over anhydrous MgSO₄, filtered, and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography to afford **5ai-3** (4.83 g, 88%).

To a solution of **5ai-3** (1.79 g, 10.0 mmol, 1.0 equiv.) and *N,N*-diisopropylethylamine (2.17 mL, 12.5 mmol, 1.25 equiv.) in dichloromethane (30 mL) was added chloromethyl methyl ether (1.14 mL, 15.0 mmol, 1.5 equiv.) dropwise at 0 °C. The reaction mixture was stirred at room temperature overnight. The reaction mixture was treated with 1 M HCl (aq) and extracted with Et₂O (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous MgSO₄, filtered, and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography to afford **5ai** (2.00 g, 90%).



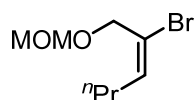
5ai-2

5ai-2: Colorless oil. (53.5 mmol scale, 14.3 g, 89% yield). $R_f = 0.50$ (hexane/ethyl acetate = 10:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 8.36 – 8.21 (m, 4H), 6.23 (t, $J = 7.9$ Hz, 1H), 5.10 (s, 2H), 2.22 (q, $J = 7.6$ Hz, 2H), 1.48 (h, $J = 7.4$ Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 164.19, 150.69, 139.26, 135.16, 130.95, 123.63, 116.83, 64.70, 31.90, 22.26, 13.57. **IR** (KBr, cm^{-1}): ν 2961, 2933, 2872, 1731, 1609, 1529, 1349, 1271, 1101. **HRMS** (ESI): Calcd for $\text{C}_{13}\text{H}_{15}\text{BrNO}_4^+$ ($\text{M}+\text{H}^+$): 328.0179, found: 328.0167.



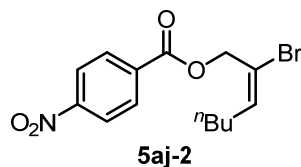
5ai-3

5ai-3: Colorless oil. (30.5 mmol scale, 4.83 g, 88% yield). $R_f = 0.25$ (hexane/ethyl acetate = 3:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 6.01 (t, $J = 7.9$ Hz, 1H), 4.30 (d, $J = 5.5$ Hz, 2H), 2.10 (q, $J = 7.6$ Hz, 2H), 2.02 (s, 1H), 1.42 (h, $J = 7.4$ Hz, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 135.21, 124.43, 62.58, 31.56, 22.39, 13.54. **IR** (KBr, cm^{-1}): ν 3354, 2960, 2931, 2872, 1457, 1047, 1013. **HRMS** (ESI): Calcd for $\text{C}_{12}\text{H}_{23}\text{Br}_2\text{O}_2^+$ ($2\text{M}+\text{H}^+$): 357.0059, found: 357.0062.

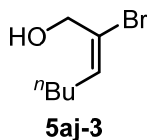


5ai

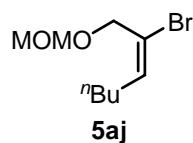
5ai: Colorless oil. (10.0 mmol scale, 2.00 g, 90% yield). $R_f = 0.50$ (hexane/ethyl acetate = 10:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 6.13 (t, $J = 7.9$ Hz, 1H), 4.65 (s, 2H), 4.29 (s, 2H), 3.40 (s, 3H), 2.11 (q, $J = 7.5$ Hz, 2H), 1.42 (h, $J = 7.4$ Hz, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 137.67, 120.23, 94.94, 66.10, 55.54, 31.66, 22.38, 13.55. **IR** (KBr, cm^{-1}): ν 2959, 2933, 2823, 1152, 1104, 1061, 1009. **HRMS** (ESI): Calcd for $\text{C}_8\text{H}_{16}\text{BrO}_2^+$ ($\text{M}+\text{H}^+$): 223.0328, found: 223.0338.



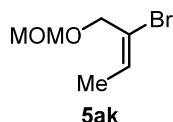
5aj-2: Colorless oil. (25 mmol scale, 7.20 g, 85% yield). $R_f = 0.50$ (hexane/ethyl acetate = 10:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 8.29 – 8.21 (m, 2H), 8.21 – 8.13 (m, 2H), 6.16 (t, $J = 7.9$ Hz, 1H), 5.02 (s, 2H), 2.17 (q, $J = 7.5$ Hz, 2H), 1.41 – 1.23 (m, 4H), 0.84 (t, $J = 7.2$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 139.48, 130.96, 123.63, 116.64, 64.70, 31.13, 29.69, 22.14, 13.83. **IR** (KBr, cm^{-1}): ν 2958, 2930, 2872, 1731, 1529m 1348, 1269, 1113, 1101. **HRMS** (ESI): Calcd for $\text{C}_{14}\text{H}_{16}\text{BrNO}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$): 364.0155, found: 364.0147.



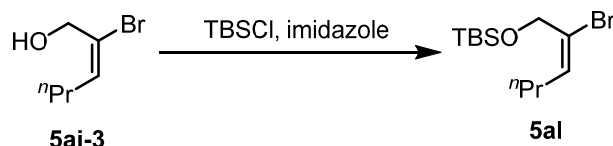
5aj-3: Colorless oil. (15 mmol scale, 2.70 g, 93% yield). $R_f = 0.25$ (hexane/ethyl acetate = 3:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 5.95 (t, $J = 7.9$ Hz, 1H), 4.24 (d, $J = 6.5$ Hz, 2H), 2.06 (q, $J = 7.4$ Hz, 2H), 1.87 (t, $J = 6.6$ Hz, 1H), 1.38 – 1.17 (m, 4H), 0.83 (t, $J = 7.2$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 135.42, 124.25, 62.59, 31.28, 29.33, 22.10, 13.81. **IR** (KBr, cm^{-1}): ν 3346, 2957, 2928, 2871, 2860, 1457, 1053, 1019. **HRMS** (ESI): Calcd for $\text{C}_{14}\text{H}_{27}\text{Br}_2\text{O}_2^+$ ($2\text{M}+\text{H}^+$): 385.0372, found: 385.0383.



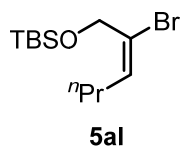
5aj: Colorless oil. (10.0 mmol scale, 2.15 g, 90% yield). $R_f = 0.50$ (hexane/ethyl acetate = 10:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 6.07 (t, $J = 7.9$ Hz, 1H), 4.59 (s, 2H), 4.22 (s, 2H), 3.34 (s, 3H), 2.07 (q, $J = 7.4$ Hz, 2H), 1.37 – 1.20 (m, 4H), 0.83 (t, $J = 7.1$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 137.88, 120.03, 94.96, 66.12, 55.54, 31.28, 29.43, 22.11, 13.83. **IR** (KBr, cm^{-1}): ν 2956, 2931, 2823, 1465, 1152, 1104, 1060, 1015. **HRMS** (ESI): Calcd for $\text{C}_9\text{H}_{17}\text{BrO}_2\text{Na}^+$ ($\text{M}+\text{Na}^+$): 259.0304, found: 259.0321.



5ak: Colorless oil. (3.0 mmol scale, 472 mg, 81% yield). $R_f = 0.50$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.20 (q, $J = 7.3$ Hz, 1H), 4.67 (s, 2H), 4.31 (s, 2H), 3.42 (s, 3H), 1.75 (d, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 132.24, 120.50, 94.95, 65.83, 55.55, 15.20. **IR** (KBr, cm^{-1}): ν 2939, 2887, 2824, 1152, 1126, 1103, 1056, 1017. **HRMS** (ESI): Calcd for $\text{C}_6\text{H}_{11}\text{BrO}_2^+$ ($\text{M}+\text{H}^+$): 195.0015, found: 195.0003.



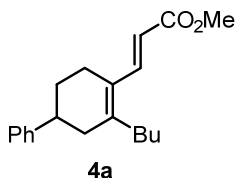
To a solution of **5ai-3** (0.54 g, 3.0 mmol, 1.0 equiv.) and imidazole (0.41 g, 6.0 mmol, 2.0 equiv.) in dichloromethane (10 mL), *tert*-butyldimethylsilyl chloride was slowly added. The reaction mixture was stirred at room temperature for another 6 h. The reaction mixture was treated with 1 M HCl (aq) and extracted with Et_2O (3×30 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous MgSO_4 , filtered, and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography to afford **5al** (0.58 g, 66%).



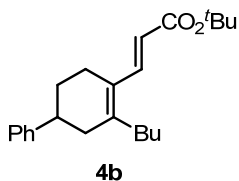
5al: Colorless oil. (3.0 mmol scale, 580 mg, 66% yield). $R_f = 0.80$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 5.86 (t, $J = 7.8$ Hz, 1H), 4.22 (s, 2H), 1.98 (q, $J = 7.6$ Hz, 2H), 1.30 (h, $J = 7.4$ Hz, 2H), 0.83 – 0.77 (m, 12H), 0.00 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 134.52, 124.38, 63.26, 31.65, 25.88, 22.44, 18.44, 13.61, -5.14. **IR** (KBr, cm^{-1}): ν 2958, 2930, 2858, 1472, 1463, 1252, 1142, 1102, 837. **HRMS** (ESI): Calcd for $\text{C}_{12}\text{H}_{25}\text{BrOSi}^+$ ($\text{M}+\text{H}^+$): 293.0931, found: 293.0919.

General procedure for Pd/NBE-catalyzed alkenyl Catellani reaction

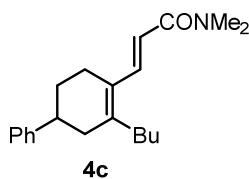
Unless otherwise noted, an oven-dried 8.0 mL vial was charged with Pd(cod)Cl₂ (8.6 mg, 0.03 mmol, 0.10 equiv) and Ph-DavePhos (11.4 mg, 0.03 mmol, 0.10 equiv). The vial was partially capped and transferred in a nitrogen-filled glovebox. In the glovebox, 1,4-dioxane (1 mL) was addition and the mixture was stirred for 1 min. Vinyl triflate **5** (0.30 mmol, 1.0 equiv), alkyl iodide **2** (0.9 mmol, 3.0 equiv), olefin **3** (0.45 mmol, 1.5 equiv), **N11** (22.7 mg, 0.15 mmol, 0.50 equiv), 5-(trifluoromethyl)-2-pyridinol (9.8 mg, 0.06 mmol, 0.20 equiv), Cs₂CO₃ (293 mg, 0.9 mmol, 3.0 equiv), and additional 1,4-dioxane (5 mL) were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 100 °C for 16 h. Upon completion of the reaction, the mixture was filtered through a thin pad of silica gel. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The residue was directly purified by flash column chromatography on silica gel to yield the desired product. (Note: an accurate palladium/ligand ratio and good solvent quality are important for the reproducibility.)



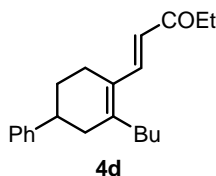
4a: Light yellow oil. (0.3 mmol scale, 66.2 mg, 74% yield from vinyl triflate **5a**; 63.5 mg, 71% yield from vinyl bromide **1a**). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, $J = 15.6$ Hz, 1H), 7.36 – 7.27 (m, 2H), 7.27 – 7.16 (m, 3H), 5.84 (d, $J = 15.6$ Hz, 1H), 3.76 (s, 3H), 2.88 – 2.72 (m, 1H), 2.55 – 2.21 (m, 6H), 2.12 – 1.94 (m, 1H), 1.85 – 1.69 (m, 1H), 1.56 – 1.40 (m, 2H), 1.40 – 1.29 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.50, 147.72, 146.27, 142.37, 128.50, 126.81, 126.79, 126.27, 114.82, 51.47, 40.03, 39.78, 33.38, 31.51, 29.42, 25.96, 22.82, 14.01. IR (KBr, cm⁻¹): ν 2958, 2929, 2872, 1705, 1619, 1367, 1304, 1149. HRMS (ESI): Calcd for C₂₀H₂₇O₂⁺ (M+H⁺): 299.2006, found: 299.2011.



4b: Light yellow oil. (0.3 mmol scale, 74.4 mg, 73% yield). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.83 (d, $J = 15.6$ Hz, 1H), 7.36 – 7.29 (m, 2H), 7.26 – 7.19 (m, 3H), 5.79 (d, $J = 15.6$ Hz, 1H), 2.86 – 2.71 (m, 1H), 2.51 – 2.21 (m, 6H), 2.11 – 1.97 (m, 1H), 1.84 – 1.66 (m, 1H), 1.53 (s, 9H), 1.48 – 1.39 (m, 2H), 1.39 – 1.30 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.48, 146.73, 146.36, 141.21, 128.48, 126.81, 126.24, 117.12, 79.90, 40.08, 39.73, 33.35, 31.49, 29.48, 28.29, 26.00, 22.86, 14.02. **IR** (KBr, cm^{-1}): ν 2954, 2929, 2871, 1720, 1620, 1303, 1171. **HRMS** (ESI): Calcd for $\text{C}_{23}\text{H}_{33}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 341.2475, found: 341.2478.

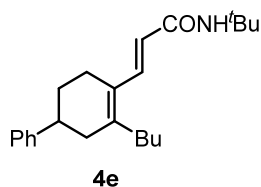


4c: Light yellow oil. (0.3 mmol scale, 70.9 mg, 76% yield). $R_f = 0.45$ (hexane/ethyl acetate = 1:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.87 (d, $J = 15.0$ Hz, 1H), 7.35 – 7.28 (m, 2H), 7.25 – 7.17 (m, 3H), 6.25 (d, $J = 15.0$ Hz, 1H), 3.10 (s, 3H), 3.04 (s, 3H), 2.88 – 2.72 (m, 1H), 2.48 – 2.22 (m, 6H), 2.09 – 1.98 (m, 1H), 1.88 – 1.69 (m, 1H), 1.49 – 1.37 (m, 2H), 1.38 – 1.27 (m, 2H), 0.90 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.77, 146.45, 145.71, 140.03, 128.47, 126.81, 126.21, 114.25, 40.14, 39.66, 37.35, 35.84, 33.39, 31.52, 29.54, 26.25, 22.90, 14.05. **IR** (KBr, cm^{-1}): ν 2954, 2927, 2870, 1646, 1596, 1390, 1133. **HRMS** (ESI): Calcd for $\text{C}_{21}\text{H}_{30}\text{NO}^+$ ($\text{M}+\text{H}^+$): 312.2322, found: 312.2332.

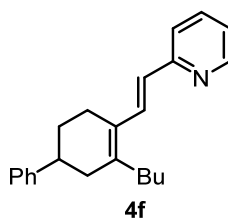


4d: Light yellow oil. (0.3 mmol scale, 40.0 mg, 45% yield). $R_f = 0.40$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.79 (d, $J = 15.8$ Hz, 1H), 7.35 – 7.29 (m, 2H),

7.25 – 7.19 (m, 3H), 6.17 (d, $J = 15.7$ Hz, 1H), 2.87 – 2.73 (m, 1H), 2.62 (q, $J = 7.3$ Hz, 2H), 2.52 – 2.22 (m, 6H), 2.11 – 2.01 (m, 1H), 1.82 – 1.70 (m, 1H), 1.51 – 1.40 (m, 2H), 1.40 – 1.30 (m, 2H), 1.15 (t, $J = 7.3$ Hz, 3H), 0.93 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.67, 148.52, 146.22, 139.68, 128.50, 127.10, 126.78, 126.28, 123.42, 40.03, 39.96, 34.17, 33.43, 31.56, 29.45, 26.01, 22.82, 14.00, 8.46. IR (KBr, cm^{-1}): ν 2956, 2928, 2871, 1685, 1663, 1617, 1588, 1456, 1191. HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{29}\text{O}^+$ ($\text{M}+\text{H}^+$): 297.2213, found: 297.2220.

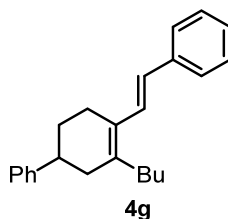


4e: Colorless needle-like crystal. Melting point = 162–163 °C. (0.3 mmol scale, 77.0 mg, 75% yield). $R_f = 0.55$ (hexane/ethyl acetate = 2:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, $J = 15.1$ Hz, 1H), 7.35 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 5.77 (d, $J = 15.1$ Hz, 1H), 5.56 (s, 1H), 2.87 – 2.69 (m, 1H), 2.49 – 2.16 (m, 6H), 2.06 – 1.95 (m, 1H), 1.81 – 1.69 (m, 1H), 1.52 – 1.40 (m, 2H), 1.38 (s, 9H), 1.37 – 1.26 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.74, 148.62, 146.92, 139.18, 130.28, 128.71, 128.33, 127.99, 121.22, 52.89, 42.05, 41.41, 35.14, 33.33, 31.57, 30.55, 28.11, 24.78, 15.75. IR (KBr, cm^{-1}): ν 3246, 2958, 2926, 2861, 1646, 1603, 1548, 1452, 1344. HRMS (ESI): Calcd for $\text{C}_{23}\text{H}_{34}\text{NO}^+$ ($\text{M}+\text{H}^+$): 340.2635, found: 340.2647.

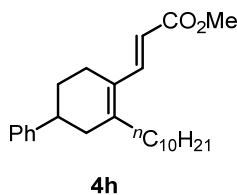


4f: Light yellow oil. (0.3 mmol scale, 66.6 mg, 70% yield). $R_f = 0.45$ (hexane/ethyl acetate = 5:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.51 (ddd, $J = 4.8, 1.9, 0.9$ Hz, 1H), 7.75 (d, $J = 15.9$ Hz, 1H), 7.55 (td, $J = 7.7, 1.9$ Hz, 1H), 7.28 (dd, $J = 7.9, 6.8$ Hz, 3H), 7.21 (dd, $J = 8.2, 1.4$ Hz, 2H), 7.20 – 7.14 (m, 1H), 7.02 (ddd, $J = 7.5, 4.9, 1.1$ Hz, 1H), 6.56 (d, $J = 15.8$ Hz, 1H), 2.86 – 2.70 (m, 1H), 2.58 – 2.46 (m, 1H), 2.46 – 2.24 (m, 5H), 2.09 – 1.98 (m, 1H), 1.83

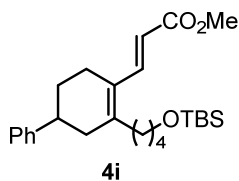
– 1.67 (m, 1H), 1.50 – 1.39 (m, 2H), 1.39 – 1.28 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 156.94, 149.58, 146.80, 141.62, 136.30, 130.82, 128.45, 127.54, 126.88, 126.14, 125.51, 121.33, 121.30, 40.34, 39.67, 33.29, 31.40, 29.77, 26.32, 22.92, 14.15. **IR** (KBr, cm^{-1}): ν 2954, 2926, 2869, 1624, 1582, 1467, 1428. **HRMS** (ESI): Calcd for $\text{C}_{23}\text{H}_{28}\text{N}^+$ ($\text{M}+\text{H}^+$): 318.2216, found: 318.2228.



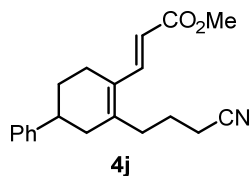
4g: Light yellow oil. (0.3 mmol scale, 45.4 mg, 48% yield). $R_f = 0.40$ (hexane/ethyl acetate = 20:1). ^1H NMR (400 MHz, Chloroform- d) δ 7.43 (d, $J = 7.3$ Hz, 2H), 7.35 – 7.25 (m, 7H), 7.24 – 7.17 (m, 2H), 6.52 (d, $J = 16.0$ Hz, 1H), 2.89 – 2.76 (m, 1H), 2.60 – 2.50 (m, 1H), 2.46 – 2.20 (m, 5H), 2.13 – 2.01 (m, 1H), 1.88 – 1.72 (m, 1H), 1.52 – 1.32 (m, 4H), 0.94 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 146.90, 139.01, 138.57, 128.60, 128.42, 127.55, 127.07, 126.87, 126.83, 126.17, 126.10, 125.56, 40.44, 39.63, 33.16, 31.36, 29.79, 26.30, 22.92, 14.11. **IR** (KBr, cm^{-1}): ν 3025, 2955, 2926, 2858, 1597, 1492, 1449. **HRMS** (ESI): Calcd for $\text{C}_{24}\text{H}_{29}^+$ ($\text{M}+\text{H}^+$): 317.2264, found: 317.2263.



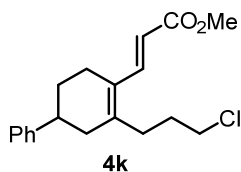
4h: Light yellow oil. (0.3 mmol scale, 87.1 mg, 76% yield). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). ^1H NMR (400 MHz, Chloroform- d) δ 7.90 (d, $J = 15.6$ Hz, 1H), 7.37 – 7.29 (m, 2H), 7.25 – 7.18 (m, 3H), 5.85 (d, $J = 15.6$ Hz, 1H), 3.77 (s, 3H), 2.86 – 2.72 (m, 1H), 2.54 – 2.22 (m, 6H), 2.10 – 2.00 (m, 1H), 1.86 – 1.71 (m, 1H), 1.56 – 1.38 (m, 2H), 1.39 – 1.18 (m, 15H), 0.93 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 168.47, 147.75, 146.27, 142.36, 128.50, 126.79, 126.27, 114.84, 51.45, 40.04, 39.77, 33.67, 31.94, 29.72, 29.64, 29.61, 29.52, 29.44, 29.37, 29.35, 25.97, 22.73, 14.16. **IR** (KBr, cm^{-1}): ν 2925, 2854, 1720, 1621, 1301, 1255, 1169, 1099. **HRMS** (ESI): Calcd for $\text{C}_{26}\text{H}_{39}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 383.2945, found: 383.2947.



4i: Light yellow oil. (0.3 mmol scale, 93.7 mg, 73% yield). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.88 (d, $J = 15.6$ Hz, 1H), 7.38 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 5.85 (d, $J = 15.6$ Hz, 1H), 3.77 (s, 3H), 3.67 – 3.58 (m, 2H), 2.87 – 2.70 (m, 1H), 2.54 – 2.25 (m, 6H), 2.10 – 2.00 (m, 1H), 1.83 – 1.72 (m, 1H), 1.61 – 1.46 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.38, 147.25, 146.20, 142.19, 128.49, 127.08, 126.78, 126.27, 115.07, 62.92, 51.45, 39.98, 39.61, 33.27, 32.73, 29.42, 25.99, 25.44, 18.36, -5.24. **IR** (KBr, cm^{-1}): ν 2950, 2929, 2857, 1720, 1621, 1301, 1255, 1169, 1099. **HRMS** (ESI): Calcd for $\text{C}_{26}\text{H}_{41}\text{O}_3\text{Si}^+$ ($\text{M}+\text{H}^+$): 429.2819, found: 429.2828.

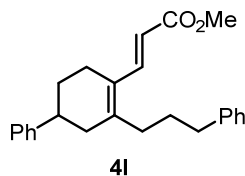


4j: Light yellow oil. (0.3 mmol scale, 63.7 mg, 68% yield). $R_f = 0.25$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.80 (d, $J = 15.5$ Hz, 1H), 7.36 – 7.29 (m, 2H), 7.26 – 7.19 (m, 3H), 5.90 (d, $J = 15.6$ Hz, 1H), 3.77 (s, 3H), 2.88 – 2.75 (m, 1H), 2.56 – 2.28 (m, 8H), 2.13 – 2.00 (m, 1H), 1.89 – 1.72 (m, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.10, 145.76, 143.93, 141.16, 128.75, 128.58, 126.73, 126.44, 119.29, 116.36, 51.61, 39.88, 39.54, 32.37, 29.21, 26.09, 24.82, 17.02. **IR** (KBr, cm^{-1}): ν 22928, 2882, 1715, 1621, 1434, 1303, 1274, 1192, 1169. **HRMS** (ESI): Calcd for $\text{C}_{20}\text{H}_{24}\text{NO}_2^+$ ($\text{M}+\text{H}^+$): 310.1802, found: 310.1808.

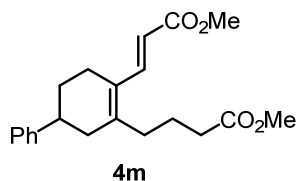


4k: Light yellow oil. (0.3 mmol scale, 53.6 mg, 56% yield). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.87 (d, $J = 15.6$ Hz, 1H), 7.36 – 7.29 (m, 2H),

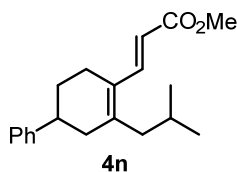
7.25 – 7.19 (m, 3H), 5.88 (d, $J = 15.7$ Hz, 1H), 3.77 (s, 3H), 3.55 (t, $J = 6.5$ Hz, 2H), 2.88 – 2.74 (m, 1H), 2.57 – 2.24 (m, 6H), 2.14 – 2.01 (m, 1H), 2.01 – 1.88 (m, 2H), 1.84 – 1.70 (m, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 168.24, 145.95, 145.11, 141.71, 128.55, 128.08, 126.75, 126.38, 115.78, 51.54, 44.46, 39.98, 39.68, 31.96, 30.78, 29.32, 26.04. IR (KBr, cm^{-1}): ν 2955, 2926, 1716, 1621, 1434, 1302, 1173. HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{24}\text{ClO}_2^+$ ($\text{M}+\text{H}^+$): 319.1459, found: 319.1470.



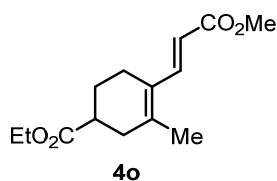
4l: Light yellow oil. (0.3 mmol scale, 82.2 mg, 76% yield). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). ^1H NMR (400 MHz, Chloroform- d) δ 7.86 (d, $J = 15.6$ Hz, 1H), 7.33 – 7.24 (m, 4H), 7.23 – 7.14 (m, 6H), 5.85 (d, $J = 15.6$ Hz, 1H), 3.76 (s, 3H), 2.82 – 2.70 (m, 1H), 2.64 (t, $J = 7.7$ Hz, 2H), 2.45 – 2.20 (m, 6H), 2.07 – 1.96 (m, 1H), 1.86 – 1.68 (m, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 168.40, 146.96, 146.20, 142.15, 141.94, 128.54, 128.40, 127.26, 126.81, 126.33, 125.88, 115.21, 51.51, 40.02, 39.68, 35.92, 33.34, 30.83, 29.41, 26.03. IR (KBr, cm^{-1}): ν 3026, 2929, 1717, 1618, 1434, 1302, 1271, 1165. HRMS (ESI): Calcd for $\text{C}_{25}\text{H}_{29}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 361.2162, found: 361.2168.



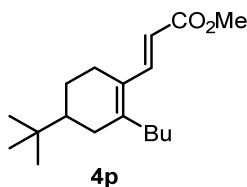
4m: Light yellow oil. (0.3 mmol scale, 70.9 mg, 69% yield). $R_f = 0.30$ (hexane/ethyl acetate = 5:1). ^1H NMR (400 MHz, Chloroform- d) δ 7.84 (d, $J = 15.6$ Hz, 1H), 7.37 – 7.28 (m, 2H), 7.25 – 7.16 (m, 3H), 5.86 (d, $J = 15.6$ Hz, 1H), 3.76 (s, 3H), 3.68 (s, 3H), 2.87 – 2.72 (m, 1H), 2.54 – 2.23 (m, 8H), 2.09 – 1.97 (m, 1H), 1.87 – 1.66 (m, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 173.62, 168.26, 146.04, 145.91, 141.84, 128.51, 127.78, 126.77, 126.31, 115.53, 51.62, 51.49, 39.96, 39.52, 33.60, 32.73, 29.34, 26.02, 24.19. IR (KBr, cm^{-1}): ν 2949, 2926, 1737, 1718, 1620, 1435, 1303, 1274, 1192, 1170. HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{27}\text{O}_4^+$ ($\text{M}+\text{H}^+$): 343.1904, found: 343.1912.



4n: Light yellow oil. (0.3 mmol scale, 35.9 mg, 40% yield). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.90 (d, $J = 15.6$ Hz, 1H), 7.35 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 5.85 (d, $J = 15.6$ Hz, 1H), 3.77 (s, 3H), 2.89 – 2.72 (m, 1H), 2.51 – 2.27 (m, 4H), 2.27 – 2.19 (m, 2H), 2.13 – 2.01 (m, 1H), 1.92 – 1.68 (m, 2H), 0.92 (d, $J = 5.1$ Hz, 3H), 0.90 (d, $J = 5.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.49, 146.67, 146.25, 142.70, 128.50, 127.81, 126.78, 126.28, 114.80, 51.47, 42.49, 40.31, 40.03, 29.44, 28.16, 26.15, 22.84, 22.41. **IR** (KBr, cm^{-1}): ν 2953, 2925, 2868, 1718, 1618, 1434, 1303, 1190, 1172. **HRMS** (ESI): Calcd for $\text{C}_{20}\text{H}_{27}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 229.2006, found: 229.2016.

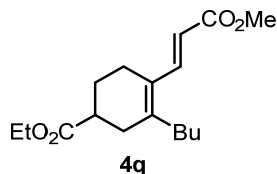


4o: Light yellow oil. (0.3 mmol scale, 37.9 mg, 50% yield, run with PhNMe_3I instead of MeI). $R_f = 0.40$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.83 (d, $J = 15.6$ Hz, 1H), 5.79 (d, $J = 15.6$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.75 (s, 3H), 2.62 – 2.52 (m, 1H), 2.52 – 2.40 (m, 1H), 2.40 – 2.26 (m, 2H), 2.24 – 2.05 (m, 2H), 1.94 (h, $J = 1.1$ Hz, 3H), 1.75 – 1.63 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 175.12, 168.25, 142.19, 141.39, 126.62, 114.98, 60.47, 51.45, 39.24, 35.25, 25.04, 24.56, 19.64, 14.23. **IR** (KBr, cm^{-1}): ν 2983, 2950, 1722, 1626, 1435, 1294, 1261, 1174. **HRMS** (ESI): Calcd for $\text{C}_{14}\text{H}_{21}\text{O}_4^+$ ($\text{M}+\text{H}^+$): 253.1434, found: 253.1443.

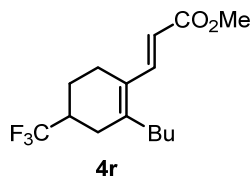


4p: Light yellow oil. (0.3 mmol scale, 54.4 mg, 65% yield). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.83 (d, $J = 15.6$ Hz, 1H), 5.77 (d, $J = 15.6$ Hz,

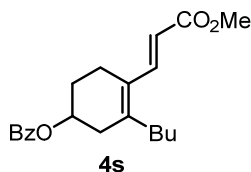
1H), 3.74 (s, 3H), 2.40 – 2.27 (m, 2H), 2.27 – 2.20 (m, 1H), 2.20 – 2.01 (m, 2H), 2.01 – 1.84 (m, 2H), 1.46 – 1.29 (m, 4H), 1.29 – 1.19 (m, 1H), 1.19 – 1.07 (m, 1H), 0.92 (t, $J = 7.1$ Hz, 3H), 0.88 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.57, 148.74, 142.59, 126.97, 114.23, 51.36, 44.02, 33.67, 33.29, 32.13, 31.75, 27.13, 26.72, 23.78, 22.84, 14.00. **IR** (KBr, cm^{-1}): ν 2956, 2871, 1721, 1622, 1434, 1297, 1262, 1191, 1169, 1155. **HRMS** (ESI): Calcd for $\text{C}_{18}\text{H}_{31}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 279.2319, found: 279.2326.



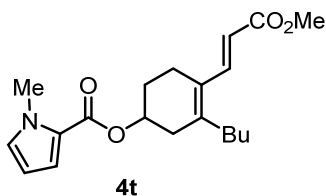
4q: Light yellow oil. (0.3 mmol scale, 56.4 mg, 64% yield). $R_f = 0.40$ (hexane/ethyl acetate = 5:1). **^1H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, $J = 15.6$ Hz, 1H), 5.77 (d, $J = 15.6$ Hz, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.72 (s, 3H), 2.58 – 2.21 (m, 6H), 2.21 – 2.09 (m, 1H), 2.09 – 2.00 (m, 1H), 1.75 – 1.58 (m, 1H), 1.46 – 1.35 (m, 2H), 1.35 – 1.27 (m, 2H), 1.24 (t, $J = 7.1$ Hz, 3H), 0.89 (t, $J = 7.2$ Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.19, 168.29, 146.04, 142.01, 126.46, 115.01, 60.47, 51.43, 39.29, 33.41, 33.24, 31.35, 25.00, 24.62, 22.72, 14.23, 13.94. **IR** (KBr, cm^{-1}): ν 2955, 2932, 2872, 1723, 1622, 1436, 1298, 1172. **HRMS** (ESI): Calcd for $\text{C}_{17}\text{H}_{27}\text{O}_4^+$ ($\text{M}+\text{H}^+$): 295.1904, found: 295.1914.



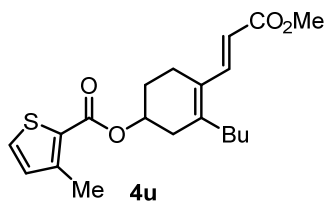
4r: Light yellow oil. (0.3 mmol scale, 67.1 mg, 77% yield). $R_f = 0.45$ (hexane/ethyl acetate = 10:1). **^1H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (d, $J = 15.7$ Hz, 1H), 5.75 (d, $J = 15.6$ Hz, 1H), 3.69 (s, 3H), 2.36 – 1.96 (m, 8H), 1.54 – 1.39 (m, 1H), 1.39 – 1.21 (m, 4H), 0.86 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.13, 144.40, 141.56, 127.61 (q, $J = 278.5$ Hz), 126.68, 115.66, 51.50, 38.58 (q, $J = 27.3$ Hz), 33.21, 31.35, 30.04, 30.01, 29.98, 29.96, 24.47, 22.70, 21.25, 21.23, 21.20, 21.17, 13.90. **IR** (KBr, cm^{-1}): ν 2957, 2936, 2874, 1721, 1624, 1434, 1299, 1277, 1259, 1173, 1156, 1124. **HRMS** (ESI): Calcd for $\text{C}_{15}\text{H}_{22}\text{F}_3\text{O}_2^+$ ($\text{M}+\text{H}^+$): 291.1566, found: 291.1572.



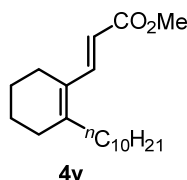
4s: Light yellow oil. (0.3 mmol scale, 59.2 mg, 58% yield). $R_f = 0.20$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.03 – 7.96 (m, 2H), 7.84 (d, $J = 15.7$ Hz, 1H), 7.59 – 7.50 (m, 1H), 7.46 – 7.38 (m, 2H), 5.85 (d, $J = 15.6$ Hz, 1H), 5.33 – 5.15 (m, 1H), 3.76 (s, 3H), 2.65 (dd, $J = 18.7, 5.0$ Hz, 1H), 2.52 – 2.38 (m, 2H), 2.38 – 2.20 (m, 3H), 2.09 – 1.86 (m, 2H), 1.46 – 1.27 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.27, 166.09, 144.27, 141.75, 132.92, 130.52, 129.52, 128.35, 126.58, 115.49, 69.64, 51.50, 36.49, 33.06, 31.21, 26.98, 22.98, 22.62, 13.94. **IR** (KBr, cm^{-1}): ν 2954, 2930, 2871, 1717, 1622, 1298, 1274, 1174, 1114. **HRMS** (ESI): Calcd for $\text{C}_{21}\text{H}_{27}\text{O}_4^+$ ($\text{M}+\text{H}^+$): 343.1904, found: 343.1910.



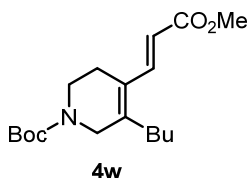
4t: Light yellow oil. (0.3 mmol scale, 58.2 mg, 56% yield, run with vinyl bromide instead of vinyl triflate). $R_f = 0.20$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.84 (d, $J = 15.6$ Hz, 1H), 6.90 (dd, $J = 4.0, 1.8$ Hz, 1H), 6.77 (t, $J = 2.2$ Hz, 1H), 6.10 (dd, $J = 4.0, 2.5$ Hz, 1H), 5.90 – 5.81 (m, 1H), 5.25 – 5.08 (m, 1H), 3.91 (s, 3H), 3.76 (s, 3H), 2.70 – 2.51 (m, 1H), 2.46 – 2.20 (m, 5H), 2.12 – 1.82 (m, 2H), 1.48 – 1.27 (m, 4H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.31, 160.83, 144.52, 141.83, 129.51, 126.55, 122.74, 117.92, 115.36, 107.83, 68.44, 51.49, 36.84, 36.67, 33.09, 31.22, 27.11, 23.05, 22.64, 13.95. **IR** (KBr, cm^{-1}): ν 2953, 2930, 2871, 1701, 1619, 1413, 1298, 1246, 1173, 1111. **HRMS** (ESI): Calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_4^+$ ($\text{M}+\text{H}^+$): 346.2013, found: 346.2012.



4u: Light yellow oil. (0.3 mmol scale, 56.0 mg, 52% yield, run with vinyl bromide instead of vinyl triflate). $R_f = 0.20$ (hexane/ethyl acetate = 10:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 7.77 (d, $J = 15.6$ Hz, 1H), 7.30 (d, $J = 5.0$ Hz, 1H), 6.82 (d, $J = 4.9$ Hz, 1H), 5.78 (dd, $J = 15.6, 0.9$ Hz, 1H), 5.22 – 5.06 (m, 1H), 3.69 (s, 3H), 2.61 – 2.51 (m, 1H), 2.44 (s, 3H), 2.42 – 2.13 (m, 5H), 2.00 – 1.80 (m, 2H), 1.41 – 1.22 (m, 4H), 0.83 (t, $J = 7.2$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 168.30, 162.47, 145.91, 144.23, 141.79, 131.76, 130.13, 127.30, 126.56, 115.41, 69.47, 51.50, 36.49, 33.05, 31.20, 26.90, 22.88, 22.64, 15.95, 13.94. **IR** (KBr, cm^{-1}): ν 2954, 2929, 2870, 1706, 1622, 1414, 1260, 1173, 1103. **HRMS** (ESI): Calcd for $\text{C}_{20}\text{H}_{27}\text{O}_4\text{S}^+$ ($\text{M}+\text{H}^+$): 363.1625, found: 363.1624.

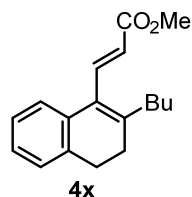


4v: Light yellow oil. (0.3 mmol scale, 66.6 mg, 73% yield). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 7.83 (d, $J = 15.6$ Hz, 1H), 5.77 (d, $J = 15.6$ Hz, 1H), 3.73 (s, 3H), 2.29 – 2.20 (m, 2H), 2.20 – 2.05 (m, 4H), 1.71 – 1.53 (m, 4H), 1.49 – 1.35 (m, 2H), 1.35 – 1.14 (m, 14H), 0.92 – 0.79 (m, 3H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 168.54, 148.49, 142.84, 127.02, 114.10, 51.33, 33.75, 31.91, 31.58, 29.69, 29.61, 29.59, 29.52, 29.41, 29.34, 25.24, 22.69, 22.54, 22.48, 14.11. **IR** (KBr, cm^{-1}): ν 2926, 2855, 1722, 1619, 1434, 1300, 1274, 1170. **HRMS** (ESI): Calcd for $\text{C}_{20}\text{H}_{35}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 307.2632, found: 307.2636.

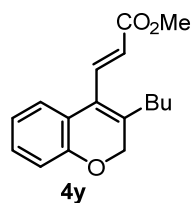


4w: Light yellow oil. (0.3 mmol scale, 60.0 mg, 62% yield). $R_f = 0.40$ (hexane/ethyl acetate =

5:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (d, J = 15.6 Hz, 1H), 5.76 (d, J = 15.7 Hz, 1H), 3.90 (s, 2H), 3.69 (s, 3H), 3.44 (t, J = 5.8 Hz, 2H), 2.23 – 2.14 (m, 4H), 1.42 – 1.24 (m, 14H), 0.85 (t, J = 7.1 Hz, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 168.04, 154.55, 141.15, 115.84, 79.86, 51.54, 31.88, 30.62, 28.45, 27.65, 24.96, 22.72, 13.88. **IR** (KBr, cm^{-1}): ν 22957, 2931, 2871, 1701, 1628, 1421, 1302, 1243, 1173, 1126. **HRMS** (ESI): Calcd for $\text{C}_{18}\text{H}_{30}\text{NO}_4^+$ ($\text{M}+\text{Na}^+$): 346.1989, found: 346.1983.

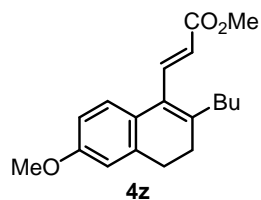


4x: Light yellow oil. (0.3 mmol scale, 71.2 mg, 88% yield). R_f = 0.30 (hexane/ethyl acetate = 10:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, J = 16.1 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.21 – 7.10 (m, 3H), 6.14 (d, J = 16.1 Hz, 1H), 3.81 (s, 3H), 2.76 – 2.65 (m, 2H), 2.48 – 2.38 (m, 2H), 2.38 – 2.24 (m, 2H), 1.57 – 1.33 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 167.98, 146.86, 141.45, 136.49, 134.01, 128.43, 127.34, 126.55, 126.22, 125.26, 120.67, 51.58, 34.35, 31.01, 29.54, 28.31, 22.76, 14.05. **IR** (KBr, cm^{-1}): ν 2954, 2931, 2860, 1719, 1624, 1434, 1298, 1271, 1169. **HRMS** (ESI): Calcd for $\text{C}_{18}\text{H}_{23}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 271.1693, found: 271.1703.

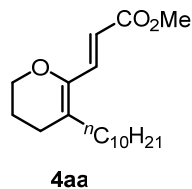


4y: Light yellow oil. (0.3 mmol scale, 58.9 mg, 72% yield). R_f = 0.45 (hexane/ethyl acetate = 10:1). **¹H NMR** (400 MHz, Acetone-*d*₆) δ 7.65 (d, J = 16.2 Hz, 1H), 7.27 (dd, J = 7.7, 1.6 Hz, 1H), 7.17 (ddd, J = 8.0, 7.4, 1.6 Hz, 1H), 6.96 (td, J = 7.6, 1.3 Hz, 1H), 6.87 (dd, J = 8.0, 1.2 Hz, 1H), 6.13 (d, J = 16.2 Hz, 1H), 4.64 (s, 2H), 3.76 (s, 3H), 2.45 – 2.33 (m, 2H), 1.56 – 1.31 (m, 4H), 0.93 (t, J = 7.3 Hz, 3H). **¹³C NMR** (101 MHz, Acetone-*d*₆) δ 205.24, 166.38, 154.23, 138.99, 138.45, 128.57, 125.12, 124.92, 122.84, 122.64, 121.37, 116.09, 67.87, 50.98, 30.32, 30.23, 22.41, 13.26. **IR** (KBr, cm^{-1}): ν 2956, 2930, 2860, 1720, 1634, 1488, 1457, 1273, 1241,

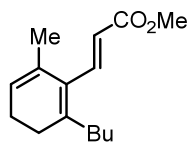
1171. **HRMS** (ESI): Calcd for $C_{17}H_{21}O_3^+$ ($M+H^+$): 273.1485, found: 273.1490.



4z: Light yellow oil. (0.3 mmol scale, 70.2 mg, 78% yield). $R_f = 0.45$ (hexane/ethyl acetate = 5:1). **1H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (d, $J = 16.1$ Hz, 1H), 7.17 (d, $J = 8.3$ Hz, 1H), 6.72 – 6.57 (m, 2H), 6.02 (d, $J = 16.1$ Hz, 1H), 3.71 (d, $J = 3.3$ Hz, 6H), 2.58 (dd, $J = 8.7, 6.3$ Hz, 2H), 2.38 – 2.26 (m, 2H), 2.26 – 2.12 (m, 2H), 1.45 – 1.23 (m, 4H), 0.85 (t, $J = 7.2$ Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.07, 158.15, 144.81, 141.62, 138.36, 128.01, 126.97, 126.43, 120.28, 113.41, 110.82, 55.25, 51.56, 34.20, 31.08, 29.51, 28.75, 22.73, 14.05. **IR** (KBr, cm^{-1}): ν 2953, 2932, 2859, 1719, 1618, 1499, 1433, 1295, 1253, 1168. **HRMS** (ESI): Calcd for $C_{19}H_{25}O_3^+$ ($M+H^+$): 301.1798, found: 301.1801.

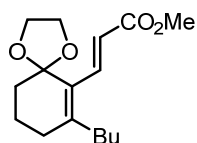


4aa: Light yellow oil. (0.3 mmol scale, 50.8 mg, 55% yield). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). **1H NMR** (400 MHz, Methylene Chloride-*d*₂) δ 7.47 (d, $J = 15.2$ Hz, 1H), 6.06 (d, $J = 15.2$ Hz, 1H), 4.04 – 3.92 (m, 2H), 3.72 (s, 3H), 2.28 – 2.13 (m, 4H), 1.94 – 1.80 (m, 2H), 1.43 (dd, $J = 9.6, 5.6$ Hz, 2H), 1.29 (d, $J = 7.8$ Hz, 14H), 0.89 (t, $J = 6.7$ Hz, 3H). **^{13}C NMR** (101 MHz, Methylene Chloride-*d*₂) δ 167.80, 144.45, 135.34, 122.96, 115.36, 65.38, 51.19, 32.01, 31.89, 29.58, 29.49, 29.33, 29.31, 29.21, 25.89, 22.66, 22.56, 13.85. **IR** (KBr, cm^{-1}): ν 2926, 2855, 1719, 1629, 1298, 1263, 1164. **HRMS** (ESI): Calcd for $C_{19}H_{33}O_3^+$ ($M+H^+$): 309.2425, found: 309.2429.



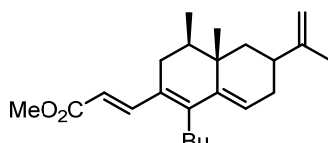
4ab

4ab: Light yellow oil. (0.3 mmol scale, 57.0 mg, 60% yield). $R_f = 0.40$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Methylene Chloride- d_2) δ 7.43 (d, $J = 16.2$ Hz, 1H), 5.70 (d, $J = 16.1$ Hz, 1H), 5.59 – 5.49 (m, 1H), 3.64 (s, 3H), 2.22 – 2.14 (m, 2H), 2.04 (dd, $J = 10.3, 7.1$ Hz, 2H), 1.95 – 1.85 (m, 2H), 1.71 (s, 3H), 1.42 – 1.31 (m, 2H), 1.27 – 1.13 (m, 15H), 0.83 – 0.75 (m, 3H). $^{13}\text{C NMR}$ (101 MHz, Methylene Chloride- d_2) δ 167.30, 144.74, 141.97, 132.02, 129.30, 121.97, 120.38, 51.24, 34.31, 31.92, 29.61, 29.59, 29.48, 29.34, 29.11, 28.95, 22.70, 22.21, 20.76, 13.89. **IR** (KBr, cm^{-1}): ν 22925, 2854, 1724, 1619, 1435, 1295, 1266, 1194, 1166. **HRMS** (ESI): Calcd for $\text{C}_{21}\text{H}_{35}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 319.2632, found: 319.2640.



4ac

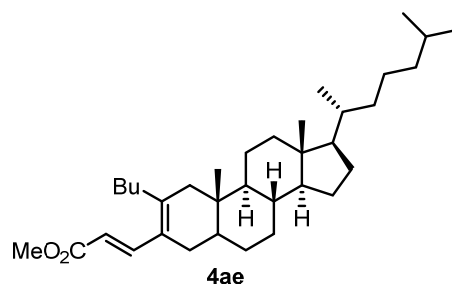
4ac: Light yellow oil. (0.3 mmol scale, 31.8 mg, 38% yield, run with the corresponding vinyl iodide instead of vinyl triflate). $R_f = 0.20$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz,) δ 7.45 (d, $J = 16.2$ Hz, 1H), 5.94 (d, $J = 16.2$ Hz, 1H), 4.09 – 3.92 (m, 4H), 3.71 (s, 3H), 2.20 (dt, $J = 15.5, 6.6$ Hz, 4H), 1.82 – 1.64 (m, 4H), 1.50 – 1.28 (m, 4H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz,) δ 167.65, 151.45, 151.44, 140.06, 128.34, 119.91, 107.79, 64.30, 51.19, 34.27, 33.33, 31.20, 30.79, 22.76, 19.84, 13.67. **IR** (KBr, cm^{-1}): ν 2951, 2872, 1718, 1624, 1437, 1293, 1272, 1192, 1169. **HRMS** (ESI): Calcd for $\text{C}_{16}\text{H}_{25}\text{O}_4^+$ ($\text{M}+\text{H}^+$): 281.1747, found: 281.1752.



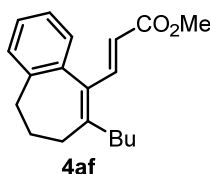
4ad

4ad: Light yellow oil. (0.3 mmol scale, 51.2 mg, 50% yield). $R_f = 0.50$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Methylene Chloride- d_2) δ 7.80 (d, $J = 15.6$ Hz, 1H), 5.97 (dd, J

= 5.6, 2.9 Hz, 1H), 5.81 (d, $J = 15.5$ Hz, 1H), 4.67 (s, 2H), 3.64 (s, 3H), 2.48 – 2.36 (m, 2H), 2.35 – 2.22 (m, 2H), 2.17 (dd, $J = 17.6, 5.4$ Hz, 1H), 2.04 – 1.81 (m, 2H), 1.73 – 1.62 (m, 4H), 1.53 – 1.42 (m, 1H), 1.37 – 1.20 (m, 4H), 1.12 (t, $J = 12.5$ Hz, 1H), 0.88 – 0.80 (m, 6H), 0.73 (s, 3H). ^{13}C NMR (101 MHz, Methylene Chloride- d_2) δ 167.97, 150.13, 143.44, 142.70, 142.40, 127.10, 124.98, 115.73, 108.37, 51.19, 41.12, 38.07, 36.58, 36.16, 32.92, 32.23, 32.13, 27.93, 22.88, 20.46, 16.94, 14.81, 13.75. IR (KBr, cm^{-1}): ν 2955, 2930, 2876, 1719, 1600, 1433, 1297, 1192, 1159.

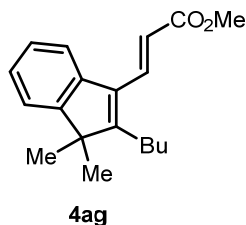


4ae: Viscous colorless liquid. (0.3 mmol scale, 117.4 mg, 77% yield). $R_f = 0.55$ (hexane/ethyl acetate = 10:1). ^1H NMR (400 MHz, Chloroform- d) δ 7.83 (d, $J = 15.5$ Hz, 1H), 5.80 (d, $J = 15.5$ Hz, 1H), 3.75 (s, 3H), 2.43 – 2.31 (m, 1H), 2.20 – 1.96 (m, 4H), 1.95 – 1.77 (m, 3H), 1.75 – 1.67 (m, 1H), 1.63 – 1.46 (m, 4H), 1.45 – 0.98 (m, 21H), 0.95 – 0.91 (m, 6H), 0.88 (dd, $J = 6.6, 1.9$ Hz, 6H), 0.68 (d, $J = 5.2$ Hz, 6H). ^{13}C NMR (101 MHz, Chloroform- d) δ 142.40, 114.28, 56.44, 56.29, 53.77, 51.35, 46.20, 42.48, 41.21, 39.96, 39.53, 36.19, 35.82, 35.52, 34.57, 33.41, 31.67, 31.50, 30.33, 28.49, 28.23, 28.03, 24.22, 23.88, 22.85, 22.77, 22.59, 21.13, 18.72, 14.03, 12.01, 11.83. IR (KBr, cm^{-1}): ν 2931, 2868, 1722, 1622, 1298, 1190, 1173, 1155. HRMS (ESI): Calcd for $\text{C}_{35}\text{H}_{59}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 511.4510, found: 511.4519.

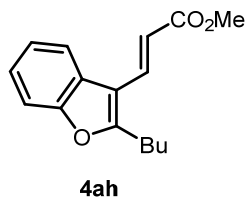


4af: Light yellow oil. (0.3 mmol scale, 49.4 mg, 58% yield). $R_f = 0.50$ (hexane/ethyl acetate = 10:1). ^1H NMR (400 MHz, Chloroform- d) δ 7.98 (d, $J = 15.5$ Hz, 1H), 7.25 – 7.14 (m, 4H), 5.69 (d, $J = 15.5$ Hz, 1H), 3.72 (s, 3H), 2.60 – 2.41 (m, 4H), 2.14 – 2.00 (m, 2H), 2.00 – 1.91 (m, 2H), 1.59 – 1.38 (m, 4H), 0.97 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ

168.46, 151.12, 141.74, 140.51, 137.91, 132.06, 128.98, 128.26, 127.20, 125.77, 118.47, 51.41, 34.07, 33.37, 31.95, 31.71, 31.45, 22.90, 14.06. **IR** (KBr, cm^{-1}): ν 2932, 2858, 1717, 1615, 1452, 1434, 1293, 1260, 1168. **HRMS** (ESI): Calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 285.1849, found: 285.1851.



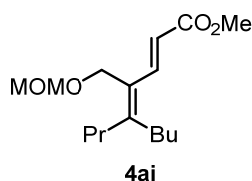
4ag: Light yellow oil. (0.3 mmol scale, 78.1 mg, 92% yield). $R_f = 0.40$ (hexane/ethyl acetate = 10:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 7.81 (d, $J = 16.3$ Hz, 1H), 7.62 – 7.55 (m, 1H), 7.33 (ddd, $J = 7.2, 1.5, 0.6$, 1H), 7.27 (td, $J = 7.3, 1.2$ Hz, 1H), 7.22 (td, $J = 7.3, 1.2$ Hz, 1H), 6.53 (d, $J = 16.3$ Hz, 1H), 3.83 (s, 3H), 2.54 – 2.45 (m, 2H), 1.66 – 1.38 (m, 4H), 1.29 (s, 6H), 0.97 (t, $J = 7.1$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 168.16, 164.99, 152.71, 140.35, 137.57, 130.28, 126.64, 125.19, 121.47, 120.40, 118.19, 51.67, 50.79, 32.80, 26.03, 24.43, 23.48, 13.87. **IR** (KBr, cm^{-1}): ν 2958, 2932, 2863, 1721, 1631, 1434, 1311, 1276. **HRMS** (ESI): Calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 285.1849, found: 285.1858.



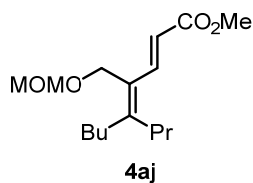
4ah: Light yellow oil. (0.3 mmol scale, 37.1 mg, 48% yield). $R_f = 0.30$ (hexane/ethyl acetate = 10:1). **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*) δ 7.84 – 7.75 (m, 2H), 7.49 – 7.42 (m, 1H), 7.33 – 7.27 (m, 2H), 6.53 (d, $J = 16.0$ Hz, 1H), 3.83 (s, 3H), 2.97 – 2.87 (m, 2H), 1.80 – 1.69 (m, 2H), 1.47 – 1.35 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, Chloroform-*d*) δ 167.99, 163.00, 154.37, 135.38, 126.05, 124.38, 123.50, 120.48, 116.25, 112.25, 111.24, 51.65, 30.39, 26.57, 22.37, 13.79. **IR** (KBr, cm^{-1}): ν 2956, 2930, 2872, 1720, 1637, 1435, 1300, 1273, 1171. **HRMS** (ESI): Calcd for $\text{C}_{16}\text{H}_{19}\text{O}_3^+$ ($\text{M}+\text{H}^+$): 259.1329, found: 259.1338.

General procedure for acyclic vinyl bromide substrates

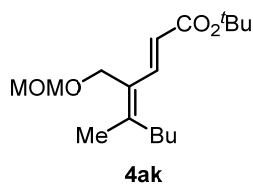
An oven-dried 8.0 mL vial was charged with Pd(cod)Cl₂ (8.6 mg, 0.03 mmol, 0.10 equiv) and Ph-DavePhos (11.4 mg, 0.03 mmol, 0.10 equiv). The vial was partially capped and transferred in a nitrogen-filled glovebox. In the glovebox, 1,4-dioxane (1 mL) was addition and the mixture was stirred for 1 min. Vinyl bromide **5** (0.30 mmol, 1.0 equiv), alkyl iodide **2** (0.9 mmol, 3.0 equiv), olefin **3** (0.45 mmol, 1.5 equiv), **N11** (22.7 mg, 0.15 mmol, 0.50 equiv), 5-(trifluoromethyl)2-pyridinol (9.8 mg, 0.06 mmol, 0.20 equiv), K₃PO₄ (191 mg, 0.9 mmol, 3.0 equiv), and additional 1,4-dioxane (2 mL) and toluene (3 mL) were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 100 °C for 16 h. Upon completion of the reaction, the mixture was filtered through a thin pad of silica gel. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The residue was directly purified by flash column chromatography on silica gel to yield the desired product. (Note: an accurate Pd/ligand ratio and good solvent quality are important for the reproducibility.)



4ai: Light yellow oil. (0.3 mmol scale, 44.5 mg, 52% yield). $R_f = 0.45$ (hexane/ethyl acetate = 5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, $J = 15.7$ Hz, 1H), 6.05 (d, $J = 15.7$ Hz, 1H), 4.64 (s, 2H), 4.27 (s, 2H), 3.75 (s, 3H), 3.41 (s, 3H), 2.39 – 2.30 (m, 2H), 2.29 – 2.21 (m, 2H), 1.54 – 1.30 (m, 6H), 0.94 (dt, $J = 8.3, 7.1$ Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.36, 156.22, 141.93, 126.99, 116.60, 95.70, 62.86, 55.57, 51.47, 36.10, 32.77, 31.93, 22.96, 22.62, 14.40, 13.94. IR (KBr, cm⁻¹): ν 2957, 2931, 2872, 1623, 1582, 1559, 1467, 1429. HRMS (ESI): Calcd for C₁₆H₂₈O₄Na⁺ (M+Na⁺): 307.1880, found: 307.1890.

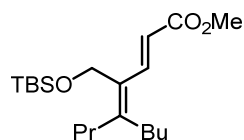
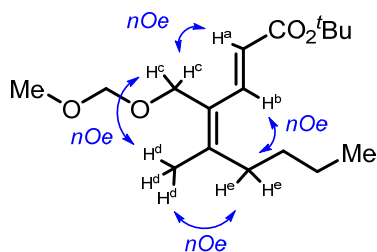


4aj: Light yellow oil. (0.3 mmol scale, 42.5 mg, 50% yield). $R_f = 0.45$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.69 (d, $J = 15.7$ Hz, 1H), 5.97 (d, $J = 15.7$ Hz, 1H), 4.57 (s, 2H), 4.20 (s, 2H), 3.68 (s, 3H), 3.34 (s, 3H), 2.32 – 2.15 (m, 4H), 1.49 – 1.37 (m, 2H), 1.37 – 1.21 (m, 4H), 0.89 (t, $J = 7.3$ Hz, 3H), 0.85 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.38, 156.26, 141.96, 127.02, 116.56, 95.70, 62.87, 55.57, 51.47, 35.04, 33.86, 31.55, 23.09, 22.97, 14.35, 13.94. **IR** (KBr, cm^{-1}): ν 2957, 2930, 2874, 1719, 1619, 1435, 1313, 1288, 1176, 1160, 1150. **HRMS** (ESI): Calcd for $\text{C}_{16}\text{H}_{28}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$): 307.1880, found: 307.1885.



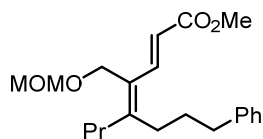
4ak: Light yellow oil. (0.3 mmol scale, 47.2 mg, 53% yield). $R_f = 0.45$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.71 (d, $J = 15.7$ Hz, 1H), 5.95 (d, $J = 15.7$ Hz, 1H), 4.63 (s, 2H), 4.29 (s, 2H), 3.41 (s, 3H), 2.41 – 2.28 (m, 2H), 1.98 (s, 3H), 1.49 (s, 9H), 1.47 – 1.30 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.32, 151.09, 140.35, 126.85, 118.56, 95.44, 79.91, 62.90, 55.46, 34.67, 30.97, 28.23, 22.77, 20.30, 13.96. **IR** (KBr, cm^{-1}): ν 2925, 2855, 1722, 1619, 1434, 1305, 1192, 1162. **HRMS** (ESI): Calcd for $\text{C}_{18}\text{H}_{33}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 281.2475, found: 281.2483. **IR** (KBr, cm^{-1}): ν 2958, 2932, 2875, 1706, 1621, 1367, 1311, 1283, 1149. **HRMS** (ESI): Calcd for $\text{C}_{17}\text{H}_{30}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$): 321.2036, found: 321.2039.

Note: the stereochemistry of **4ak** was confirmed by the NOESY experiment.



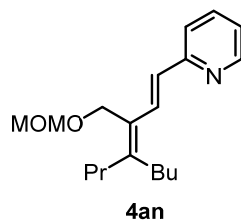
4al

4al: Light yellow oil. (0.3 mmol scale, 48.9 mg, 46% yield). $R_f = 0.15$ (hexane/ethyl acetate = 20:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, $J = 15.7$ Hz, 1H), 5.96 (d, $J = 15.7$ Hz, 1H), 4.25 (s, 2H), 3.67 (s, 3H), 2.26 – 2.18 (m, 2H), 2.17 – 2.09 (m, 2H), 1.47 – 1.20 (m, 7H), 0.88 – 0.82 (m, 6H), 0.81 (s, 9H), 0.00 (s, 6H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 168.60, 153.55, 142.15, 130.14, 116.49, 58.96, 51.40, 36.14, 32.70, 31.78, 25.90, 22.92, 22.65, 18.29, 14.42, 13.94, -5.21. **IR** (KBr, cm⁻¹): ν 2957, 2931, 2859, 1720, 1619, 1435, 1307, 1257, 1176, 1158. **HRMS** (ESI): Calcd for C₂₀H₃₉O₃Si⁺ (M+H⁺): 355.2663, found: 355.2659.

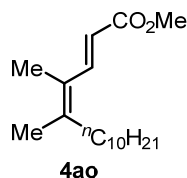


4am

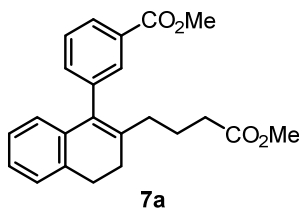
4am: Light yellow oil. (0.3 mmol scale, 52.0 mg, 50% yield). $R_f = 0.45$ (hexane/ethyl acetate = 5:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, $J = 15.7$ Hz, 1H), 7.33 – 7.27 (m, 2H), 7.19 (ddt, $J = 8.2, 3.4, 1.5$ Hz, 3H), 6.05 (d, $J = 15.7$ Hz, 1H), 4.63 (s, 2H), 4.26 (s, 2H), 3.76 (s, 3H), 3.40 (s, 3H), 2.67 (t, $J = 7.7$ Hz, 2H), 2.41 – 2.32 (m, 2H), 2.31 – 2.21 (m, 2H), 1.78 (td, $J = 9.5, 6.8, 5.6$ Hz, 2H), 1.52 – 1.36 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 168.25, 155.43, 141.74, 141.66, 128.38, 128.35, 127.37, 125.89, 116.98, 95.68, 62.81, 55.59, 51.50, 36.01, 35.99, 32.63, 31.23, 22.58, 14.36. **IR** (KBr, cm⁻¹): ν 2961, 2927, 2874, 2855, 1717, 1653, 1617. **HRMS** (ESI): Calcd for C₂₁H₃₀O₄Na⁺ (M+Na⁺): 369.2036, found: 369.2040.



4an: Light yellow oil. (0.3 mmol scale, 28.8 mg, 32% yield). $R_f = 0.20$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 8.55 (dt, $J = 3.9, 1.0$ Hz, 1H), 7.67 (d, $J = 15.9$ Hz, 1H), 7.60 (td, $J = 7.7, 1.8$ Hz, 1H), 7.30 (d, $J = 7.9$ Hz, 1H), 7.07 (ddd, $J = 7.5, 4.9, 1.1$ Hz, 1H), 6.79 (d, $J = 15.9$ Hz, 1H), 4.70 (s, 2H), 4.40 (s, 2H), 3.45 (s, 3H), 2.46 – 2.32 (m, 2H), 2.31 – 2.21 (m, 2H), 1.58 – 1.32 (m, 6H), 0.95 (td, $J = 7.2, 6.3$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, Chloroform- d) δ 156.77, 150.35, 149.54, 136.23, 130.26, 127.69, 127.15, 121.48, 121.35, 95.66, 63.22, 55.53, 35.89, 32.59, 31.80, 23.06, 22.76, 14.42, 14.07. **IR** (KBr, cm^{-1}): ν 2957, 2931, 2872, 1623, 1582, 1559, 1467, 1429. **HRMS** (ESI): Calcd for $\text{C}_{17}\text{H}_{26}\text{NO}_2^+$ ($\text{M}+\text{H}^+$): 276.1958, found: 276.1963.

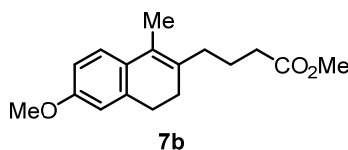


4ao: Light yellow oil. (0.3 mmol scale, 27.2 mg, 33% yield). $R_f = 0.40$ (hexane/ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, Methylene Chloride- d_2) δ 7.72 (d, $J = 15.4$ Hz, 1H), 5.67 (d, $J = 15.5$ Hz, 1H), 3.58 (s, 3H), 2.23 – 2.17 (m, 2H), 1.74 (s, 3H), 1.66 (s, 3H), 1.34 – 1.24 (m, 2H), 1.20 – 1.11 (m, 14H), 0.79 – 0.72 (m, 3H). $^{13}\text{C NMR}$ (101 MHz, Methylene Chloride- d_2) δ 168.14, 146.50, 143.15, 125.86, 114.99, 51.13, 34.56, 31.90, 29.61, 29.59, 29.52, 29.51, 29.33, 29.03, 22.68, 20.49, 13.95, 13.87. **IR** (KBr, cm^{-1}): ν 2925, 2855, 1722, 1619, 1434, 1305, 1192, 1162. **HRMS** (ESI): Calcd for $\text{C}_{18}\text{H}_{33}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 281.2475, found: 281.2483.

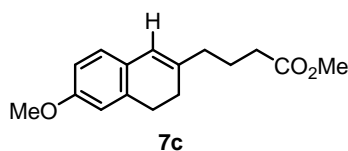


7a: Light yellow oil. (0.3 mmol scale, 76.4 mg, 70% yield, run with 0.45 mmol **6a** instead of

3). $R_f = 0.30$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.02 (dt, $J = 7.8, 1.5$ Hz, 1H), 7.84 (td, $J = 1.8, 0.5$ Hz, 1H), 7.49 (td, $J = 7.7, 0.6$ Hz, 1H), 7.36 (dt, $J = 7.6, 1.4$ Hz, 1H), 7.19 – 7.12 (m, 1H), 7.08 (td, $J = 7.3, 1.4$ Hz, 1H), 7.00 (td, $J = 7.6, 1.5$ Hz, 1H), 6.48 (dd, $J = 7.7, 1.2$ Hz, 1H), 3.91 (s, 3H), 3.58 (s, 3H), 2.88 (t, $J = 8.0$ Hz, 2H), 2.45 – 2.36 (m, 2H), 2.19 (t, $J = 7.5$ Hz, 2H), 2.05 (t, $J = 7.7$ Hz, 2H), 1.80 – 1.66 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 173.75, 167.11, 139.91, 137.74, 136.42, 135.03, 134.88, 133.83, 131.34, 130.43, 128.54, 128.07, 127.14, 126.32, 126.27, 125.46, 52.13, 51.47, 33.94, 33.67, 28.41, 27.53, 23.41. **IR** (KBr, cm^{-1}): ν 3021, 2950, 2884, 1724, 1437, 1260, 1197, 1111. **HRMS** (ESI): Calcd for $\text{C}_{23}\text{H}_{35}\text{O}_4^+$ ($\text{M}+\text{H}^+$): 365.1748, found: 365.1750.

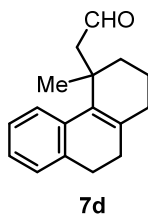


7b: Light yellow oil. (0.3 mmol scale, 43.3 mg, 53% yield, run with 0.45 mmol **6c** instead of **3**). $R_f = 0.55$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.16 (d, $J = 8.5$ Hz, 1H), 6.72 (dd, $J = 8.5, 2.8$ Hz, 1H), 6.68 (d, $J = 2.7$ Hz, 1H), 3.79 (s, 3H), 3.66 (s, 3H), 2.73 – 2.66 (m, 2H), 2.34 (t, $J = 7.5$ Hz, 2H), 2.32 – 2.25 (m, 2H), 2.19 (t, $J = 8.4$ Hz, 2H), 1.99 (s, 3H), 1.80 (p, $J = 7.6$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 174.12, 157.76, 137.38, 132.76, 130.24, 125.62, 123.88, 113.20, 110.82, 55.26, 51.53, 33.58, 33.34, 29.09, 28.43, 23.59, 14.12. **IR** (KBr, cm^{-1}): ν 2935, 2832, 1735, 1608, 1498, 1436, 1252. **HRMS** (ESI): Calcd for $\text{C}_{17}\text{H}_{23}\text{O}_3^+$ ($\text{M}+\text{H}^+$): 275.1642, found: 275.1641.

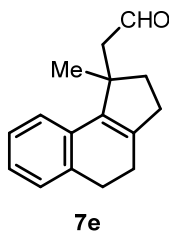


7c: Light yellow oil. (0.3 mmol scale, 28.6 mg, 37% yield, run with 0.45 mmol **6b** instead of **3**). $R_f = 0.55$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.87 – 6.80 (m, 1H), 6.64 – 6.55 (m, 2H), 6.09 (s, 1H), 3.71 (s, 3H), 3.59 (s, 3H), 2.70 (t, $J = 8.1$ Hz, 2H), 2.27 (t, $J = 7.5$ Hz, 2H), 2.13 (t, $J = 7.4$ Hz, 4H), 1.77 (p, $J = 7.5$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 174.11, 158.15, 137.98, 136.11, 127.92, 126.29, 122.31, 113.51, 111.07, 55.28, 51.53, 36.63, 33.51, 28.64, 26.90, 22.79. **IR** (KBr, cm^{-1}): ν 2948, 2832, 1737, 1607, 1499,

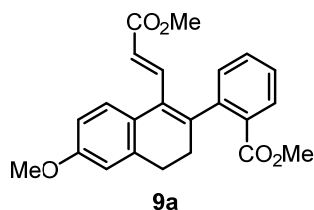
1434, 1297, 1251, 1160. **HRMS** (ESI): Calcd for C₁₆H₂₁O₃⁺ (M+H⁺): 261.1485, found: 261.1490.



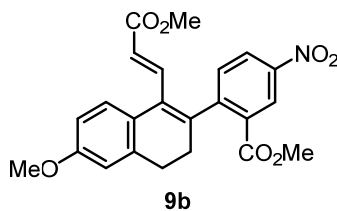
7d: Light yellow oil. (0.3 mmol scale, 60.6 mg, 84% yield, run with 0.9 mmol **6d** instead of **2** and **3**). $R_f = 0.25$ (hexane/ethyl acetate = 20:1). **¹H NMR** (400 MHz, Methylene Chloride-*d*₂) δ 9.33 (dd, $J = 4.0, 2.0$ Hz, 1H), 7.41 (dd, $J = 7.9, 1.1$ Hz, 1H), 7.11 – 7.02 (m, 2H), 6.98 (td, $J = 7.3, 1.2$ Hz, 1H), 2.92 (dd, $J = 15.7, 2.1$ Hz, 1H), 2.56 – 2.46 (m, 2H), 2.34 (dd, $J = 15.7, 4.0$ Hz, 1H), 2.30 – 2.16 (m, 1H), 2.16 – 1.98 (m, 2H), 1.98 – 1.87 (m, 1H), 1.76 – 1.52 (m, 4H), 1.45 (s, 3H). **¹³C NMR** (101 MHz, Methylene Chloride-*d*₂) δ 203.63, 138.66, 137.92, 134.48, 132.39, 127.58, 125.64, 125.46, 124.76, 53.12, 40.65, 35.26, 31.94, 30.05, 28.96, 27.73, 18.27. **IR** (KBr, cm⁻¹): ν 2931, 2885, 2827, 1719, 1481, 1451, 1426. **HRMS** (ESI): Calcd for C₁₇H₂₁O₃⁺ (M+H⁺): 241.1587, found: 241.1594.



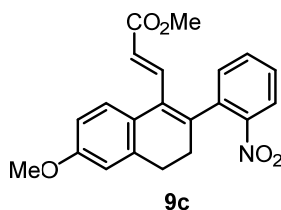
7e: Light yellow oil. (0.3 mmol scale, 39.5 mg, 58% yield, run with 0.9 mmol **6e** instead of **2** and **3**). $R_f = 0.25$ (hexane/ethyl acetate = 20:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 9.66 (d, $J = 2.2$ Hz, 1H), 7.35 – 7.30 (m, 1H), 7.20 – 7.14 (m, 2H), 7.13 – 7.07 (m, 1H), 2.90 – 2.77 (m, 3H), 2.69 (dd, $J = 14.9, 4.1$ Hz, 1H), 2.56 – 2.33 (m, 2H), 2.28 (ddt, $J = 9.4, 8.0, 1.5$ Hz, 2H), 2.11 (ddd, $J = 12.8, 8.5, 6.3$ Hz, 1H), 1.92 (ddd, $J = 12.8, 8.6, 5.4$ Hz, 1H), 1.46 (s, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 203.73, 142.21, 137.69, 136.66, 132.44, 128.12, 126.26, 126.08, 122.07, 52.64, 47.51, 39.06, 33.52, 29.13, 26.35, 24.97. **IR** (KBr, cm⁻¹): ν 2928, 2833, 1720, 1485, 1451, 1384, 1317. **HRMS** (ESI): Calcd for C₁₆H₁₉O₃⁺ (M+H⁺): 227.1430, found: 227.1436.



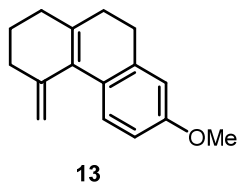
9a: Light yellow oil. (0.3 mmol scale, 70.1 mg, 62% yield, run with 0.6 mmol **8a** instead of **2**). $R_f = 0.25$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.02 (dd, $J = 7.9$, 1.0 Hz, 1H), 7.54 (td, $J = 7.5$, 1.4 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.35 (d, $J = 16.2$ Hz, 1H), 7.19 (dd, $J = 7.6$, 0.9 Hz, 1H), 6.82 (d, $J = 2.7$ Hz, 1H), 6.78 (dd, $J = 8.5$, 2.8 Hz, 1H), 6.05 (d, $J = 16.1$ Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.68 (s, 3H), 3.10 – 2.97 (m, 1H), 2.85 – 2.73 (m, 1H), 2.69 – 2.59 (m, 1H), 2.59 – 2.44 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.71, 167.13, 158.69, 144.59, 143.23, 142.03, 139.00, 132.29, 130.87, 129.66, 129.42, 129.02, 127.54, 126.87, 126.40, 120.38, 113.66, 110.88, 55.31, 52.18, 51.45, 31.78, 28.85. **IR** (KBr, cm^{-1}): ν 2949, 2837, 1723, 1610, 1500, 1433, 1293, 1257, 1170. **HRMS** (ESI): Calcd for $\text{C}_{23}\text{H}_{23}\text{O}_5^+$ ($\text{M}+\text{H}^+$): 379.1540, found: 379.1550.



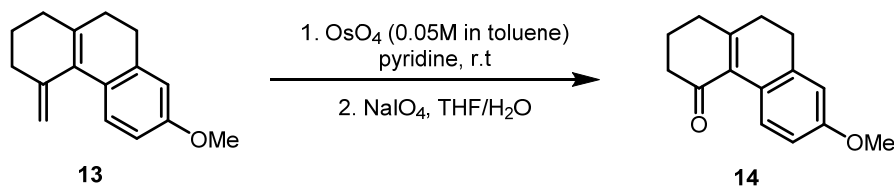
9b: Yellow oil. (0.3 mmol scale, 45.5 mg, 36% yield, run with 0.6 mmol **8b** instead of **2**). $R_f = 0.20$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Methylene Chloride-*d*₂) δ 8.71 (d, $J = 2.4$ Hz, 1H), 8.26 (dd, $J = 8.4$, 2.5 Hz, 1H), 7.33 (d, $J = 8.4$ Hz, 1H), 7.25 (d, $J = 8.5$ Hz, 1H), 7.13 (d, $J = 16.0$ Hz, 1H), 6.73 (d, $J = 2.7$ Hz, 1H), 6.68 (dd, $J = 8.6$, 2.7 Hz, 1H), 5.88 (d, $J = 16.1$ Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.55 (s, 3H), 2.91 (ddd, $J = 15.9$, 10.4, 5.9 Hz, 1H), 2.72 (dt, $J = 14.7$, 6.9 Hz, 1H), 2.53 (dt, $J = 13.9$, 6.7 Hz, 1H), 2.41 (ddd, $J = 16.2$, 10.4, 5.8 Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, Methylene Chloride-*d*₂) δ 166.82, 165.20, 159.25, 149.82, 146.82, 140.90, 140.46, 138.89, 131.38, 131.13, 130.28, 126.93, 126.50, 125.81, 125.79, 122.46, 113.65, 111.01, 55.26, 52.71, 51.41, 31.03, 28.52. **IR** (KBr, cm^{-1}): ν 2950, 2837, 1722, 1606, 1524, 1434, 1349, 1255, 1170, 1138, 1123. **HRMS** (ESI): Calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_7^+$ ($\text{M}+\text{H}^+$): 424.1391, found: 424.1390.



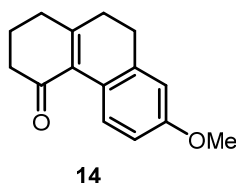
9c: Yellow oil. (0.3 mmol scale, 43.8 mg, 40% yield, run with 0.6 mmol **8c** instead of **2**). $R_f = 0.25$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Methylene Chloride- d_2) δ 7.99 (dd, $J = 8.2, 1.1$ Hz, 1H), 7.57 (td, $J = 7.5, 1.3$ Hz, 1H), 7.43 (ddd, $J = 8.2, 7.4, 1.5$ Hz, 1H), 7.29 – 7.20 (m, 2H), 7.16 (dt, $J = 16.1, 1.0$ Hz, 1H), 6.74 – 6.70 (m, 1H), 6.67 (dd, $J = 8.5, 2.8$ Hz, 1H), 5.89 (d, $J = 16.1$ Hz, 1H), 3.74 (s, 3H), 3.55 (s, 3H), 2.91 (ddd, $J = 15.8, 10.5, 5.8$ Hz, 1H), 2.71 (ddd, $J = 14.6, 7.9, 5.8$ Hz, 1H), 2.62 – 2.46 (m, 1H), 2.41 (ddd, $J = 15.8, 10.2, 5.5$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, Methylene Chloride- d_2) δ 166.95, 159.16, 147.95, 140.84, 139.25, 138.88, 137.20, 133.55, 131.14, 130.38, 128.60, 126.91, 125.81, 124.85, 122.03, 113.61, 110.99, 55.25, 51.38, 30.66, 28.59. **IR** (KBr, cm^{-1}): ν 2948, 2847, 2839, 1717, 1606, 1524, 1500, 1434, 1346, 1253, 1171. **HRMS** (ESI): Calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_5^+$ ($\text{M}+\text{H}^+$): 366.1336, found: 366.1337.



13: White solid. Melting point = 68–69 °C. (0.3 mmol scale, 54.4 mg, 80% yield, run with 0.9 mmol **12** instead of **2** and **3**). $R_f = 0.60$ (hexane/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, Methylene Chloride- d_2) δ 7.42 (d, $J = 8.5$ Hz, 1H), 6.69 (d, $J = 2.8$ Hz, 1H), 6.64 (dd, $J = 8.5, 2.8$ Hz, 1H), 5.04 (d, $J = 1.9$ Hz, 1H), 4.97 (s, 1H), 3.75 (s, 3H), 2.65 – 2.55 (m, 2H), 2.44 – 2.36 (m, 2H), 2.32 (t, $J = 6.4$ Hz, 2H), 2.10 (t, $J = 7.5$ Hz, 2H), 1.83 (tt, $J = 8.9, 5.1$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, Methylene Chloride- d_2) δ 157.52, 142.62, 139.01, 136.29, 129.32, 126.88, 126.55, 113.11, 110.12, 109.23, 55.03, 34.51, 31.68, 30.26, 28.62, 24.20. **IR** (KBr, cm^{-1}): ν 2932, 2860, 2830, 1608, 1497, 1429, 1302, 1279, 1251, 1158. **HRMS** (ESI): Calcd for $\text{C}_{16}\text{H}_{19}\text{O}^+$ ($\text{M}+\text{H}^+$): 227.1430, found: 227.1438.

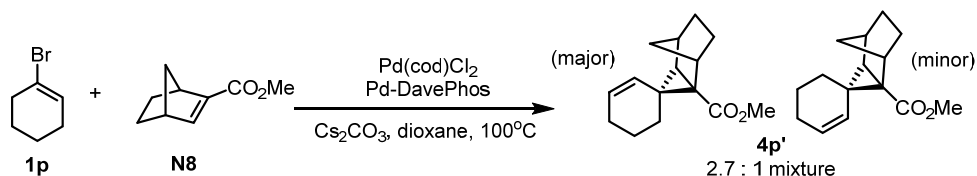


Following a reported procedure: To a solution of **13** (11.3 mg, 0.05 mmol) in 4 mL dry pyridine was added a solution of OsO₄ in toluene (0.05 M, 1.1 mL, 0.055 mmol). The dark reaction mixture was stirred overnight. Aqueous NaHSO₃ solution was added. After further reaction for 90 min, the mixture was diluted with water and extracted with CHCl₃ (3 × 10 mL) and then with ethyl acetate (3 × 10 mL). Drying over MgSO₄ and evaporation of the solvent from the organic phase gave residue that can be used directly in the next step. To a solution of the above crude diol in 3 mL THF/H₂O (1:1) was added NaIO₄ (11.8 mg, 0.055 mmol) at 0 °C. The solution was warmed to room temperature and stirred for additional 3 hours, and then diluted with ethyl acetate before it was quenched with aqueous Na₂S₂O solution. The organic layer was separated, washed with water and brine, dried over anhydrous MgSO₄, filtered and concentrated. The residue was purified by flash column chromatography to afford **14** in 52% yield over two steps.

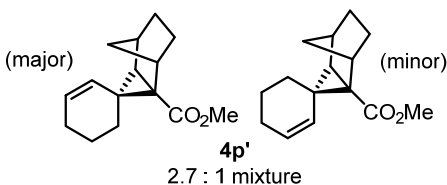


14: White solid. Melting point = 107–108 °C. (0.05 mmol scale, 5.9 mg, 52% yield). R_f = 0.25 (hexane/ethyl acetate = 5:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (d, J = 8.7 Hz, 1H), 6.76 (dd, J = 8.7, 2.8 Hz, 1H), 6.72 – 6.65 (m, 1H), 3.80 (s, 3H), 2.71 (t, J = 7.6 Hz, 2H), 2.60 – 2.50 (m, 4H), 2.46 – 2.32 (m, 2H), 2.03 (dq, J = 7.9, 6.2 Hz, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 197.48, 158.31, 157.94, 137.58, 130.21, 128.35, 123.89, 113.27, 110.84, 55.22, 39.37, 32.13, 30.74, 27.83, 21.97. **IR** (KBr, cm⁻¹): ν 2936, 2926, 1655, 1598, 1494, 1386, 1250. **HRMS** (ESI): Calcd for C₁₅H₁₇O₂⁺ (M+H⁺): 229.1223, found: 229.1232.

Characterization of a typical side-product



An oven-dried 8.0 mL vial was charged with $\text{Pd}(\text{cod})\text{Cl}_2$ (8.6 mg, 0.03 mmol, 0.10 equiv), Ph-DavePhos (11.4 mg, 0.03 mmol, 0.10 equiv). The vial was partially capped and transferred in a nitrogen-filled glovebox. In the glovebox, 1,4-dioxane (1 mL) was addition and the mixture was stirred for 1 min. **1p** (53.1 mg, 0.33 mmol, 1.1 equiv), **N8** (45.6 mg, 0.3 mmol, 1.0 equiv), Cs_2CO_3 (196 mg, 0.6 mmol, 2.0 equiv), and additional 1,4-dioxane (5 mL) were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 100°C for 16 h. Upon completion of the reaction, the mixture was filtered through a thin pad of silica gel. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The residue was directly purified by flash column chromatography on silica gel to yield the desired product.



4p': Colorless oil. (0.3 mmol scale, 50.6 mg, 73% yield) $R_f = 0.25$ (hexane/ethyl acetate = 20:1). Isolated as an inseparable 2.7 : 1 mixture.

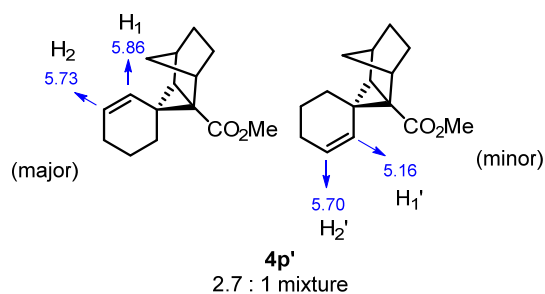
Major: $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 5.86 (d, $J = 10.2$, 1H), 5.73 (dt, $J = 10.2$, 3.5, 1H), 3.67 (s, 3H), 2.71 – 2.74 (m, 1H), 2.47 – 2.42 (m, 1H), 2.15 – 1.99 (m, 2H), 1.81 – 1.60 (m, 3H), 1.60 – 1.35 (m, 4H), 1.36 – 1.18 (m, 3H), 0.83 (d, $J = 11.1$, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 173.4, 130.3, 128.5, 51.7, 41.6, 40.2, 39.6, 39.2, 36.8, 32.9, 31.2, 29.3, 29.0, 25.7, 22.2.

Minor: $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 5.70 (dt, $J = 10.3$, 3.4, 1H), 5.16 (d, $J = 10.3$, 1H), 3.66 (s, 3H), 2.71 – 2.74 (m, 1H), 2.52 – 2.49 (m, 1H), 2.15 – 1.99 (m, 1H), 1.96 – 1.86 (m, 2H), 1.81 – 1.60 (m, 3H), 1.60 – 1.35 (m, 3H), 1.36 – 1.18 (m, 3H), 0.82 (d, $J = 11.1$, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 173.7, 132.4, 128.0, 51.7, 42.1, 40.2, 39.6, 39.2, 36.7, 33.1, 31.3, 29.3, 26.9, 24.5, 22.9.

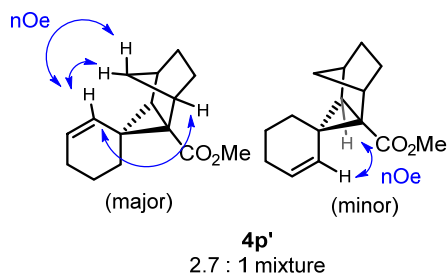
IR (KBr, cm^{-1}): ν 2950, 2877, 1726, 1434, 1308, 1247, 1226, 1189, 1149, 1111, 1083. **HRMS** (ESI): Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2^+$ ($\text{M}+\text{H}^+$): 233.1536, found: 233.1544.

The assignment of the major and minor structures was based on the following analysis:

1. The proton chemical shift for H_1 in the major product is 5.86 ppm while that of the minor product (H_1') is 5.16 ppm. (*vide infra*)

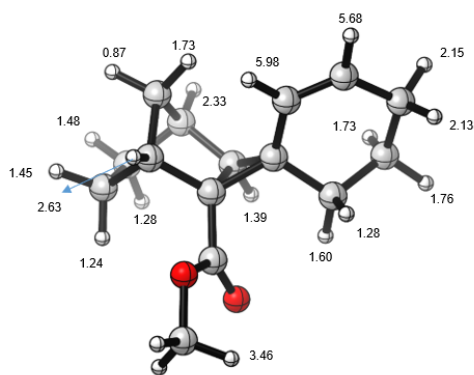


2. Based on NOESY, the H_1 in the major component has nOe signals with the three protons highlighted below. The assignment of these three peaks were confirmed by COSY. In contrast, the H_1' in the minor component only has one nOe signal.

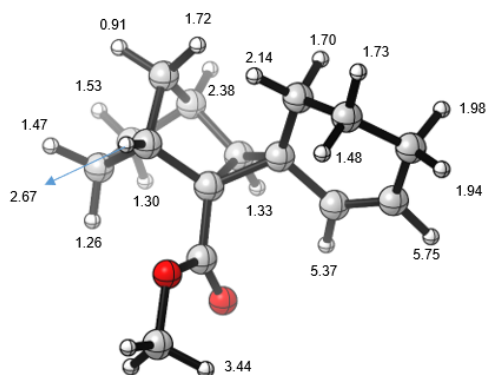


To further prove our structure, chemical shifts for the two structures were predicted at mPW1PW91/6-311+G(2d,p) (giao, smd)// B3LYP/6-31+G(d,p) (gas phase) level of theory, following a method described by Tantillo.²⁰ Calculated chemical shifts matched well with experimental data.

Calculated ^1H NMR data

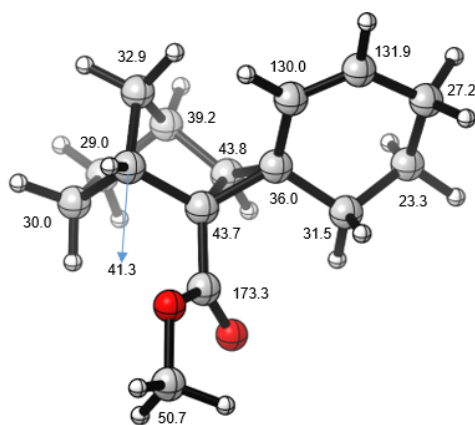


major

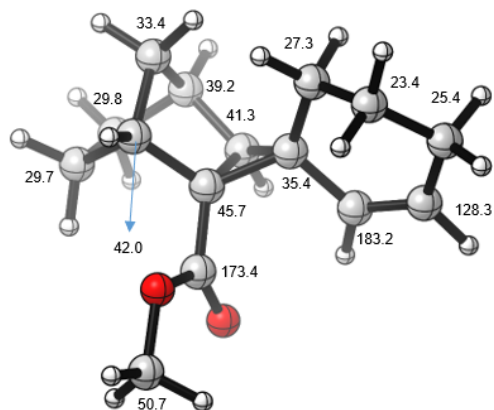


minor

Calculated ^{13}C NMR data



major

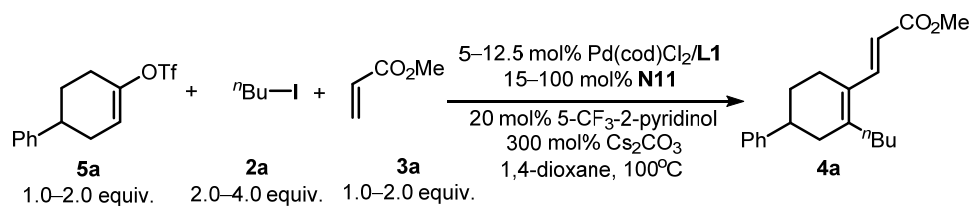


minor

III. Kinetic Studies

General method

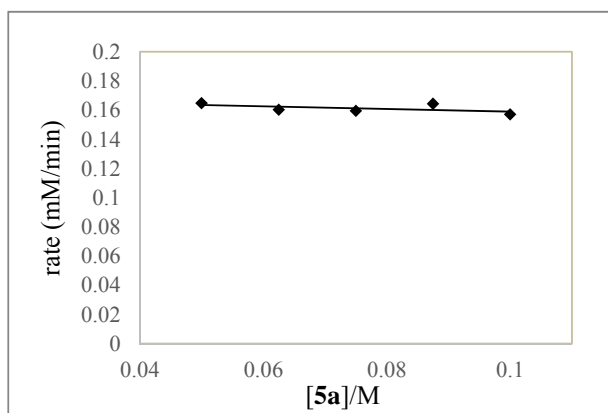
The reaction between vinyl triflate **5a**, butyl iodide **2a**, and methyl acrylate **3a** was selected as the model reaction for the kinetic studies (see the scheme below). The kinetics of the alkenyl Catellani reaction was monitored by ^1H NMR. The reaction procedure was similar to that described in the general procedure section. Stock solutions of **5a**, **2a**, **3a**, **N11**, and 5-trifluoromethyl-2-pyridinol in 1,4-dioxane were prepared prior to use. Six identical reactions were set up in six different vials. For each reaction, $\text{Pd}(\text{cod})\text{Cl}_2$, **L1**, and Cs_2CO_3 were weighted into a 4 mL vial, and indicated volume of the above stock solutions were added to the vial by syringe in the glovebox. The vials were transferred out of the glovebox and put into an aluminum block preheated to 100 °C. Timing was started and a vial was taken out of the pie-block every 20 min. The sampled reaction mixture was quickly filtered through a thin pad of silica gel. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The yields were determined by ^1H NMR using dichloroethane as the internal standard.



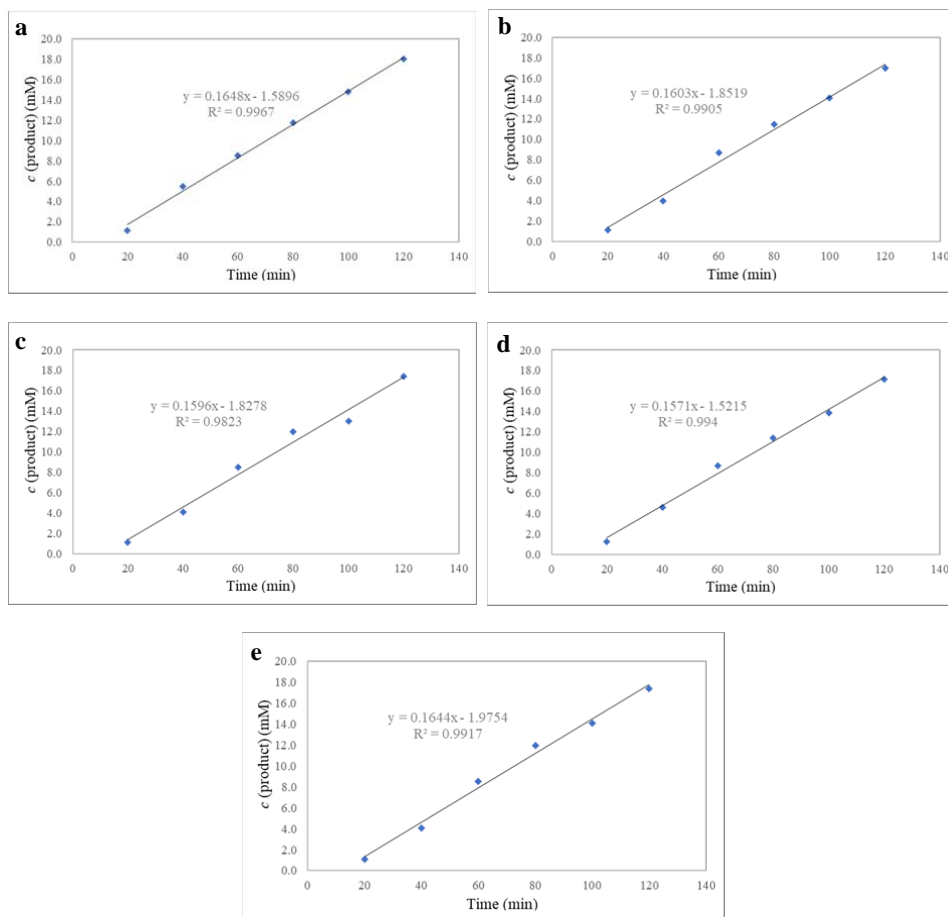
Dependence of initial rate on **5a**

Supplementary Table 1. Initial-Rate Dependence on [**5a**]

Equivalency of 5a	1.0	1.25	1.5	1.75	2.0
[5a]/M	0.05	0.0625	0.075	0.0875	0.10
[2a]/M	0.15	0.15	0.15	0.15	0.15
[3a]/M	0.075	0.075	0.075	0.075	0.075
[N11]/M	0.025	0.025	0.025	0.025	0.025
[$\text{Pd}(\text{cod})\text{Cl}_2$]/mM	5.0	5.0	5.0	5.0	5.0
[L1]/mM	5.0	5.0	5.0	5.0	5.0
[5- CF_3 -pyridinone]/M	0.01	0.01	0.01	0.01	0.01
$\text{Cs}_2\text{CO}_3/\text{mmol}\cdot\text{mL}^{-1}$	0.15	0.15	0.15	0.15	0.15
initial rate/ $\text{mM}\cdot\text{min}^{-1}$	0.1648	0.1603	0.1596	0.1644	0.1571



Supplementary Figure 1. Initial-rate dependence on [5a]. Conditions: [5a] = 0.05-0.10 M, [2a] = 0.15 M, [3a] = 0.075 M, [N11] = 0.025 M, [Pd(cod)Cl₂] = 5.0 mM, [L1] = 5.0 mM, [5-CF₃-pyridinone] = 0.01 M, Cs₂CO₃ 0.15 mmol·mL⁻¹.

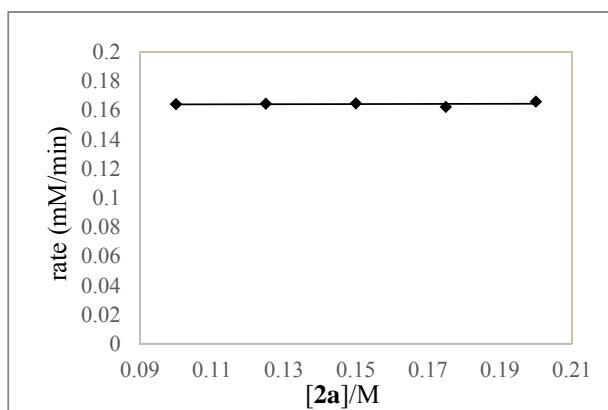


Supplementary Figure 2. Kinetic time courses for measuring initial-rate dependence on [5a].
 a: [5a] = 0.05 M, b: [5a] = 0.0625 M, c: [5a] = 0.075 M, d: [5a] = 0.0875 M, e: [5a] = 0.10 M.

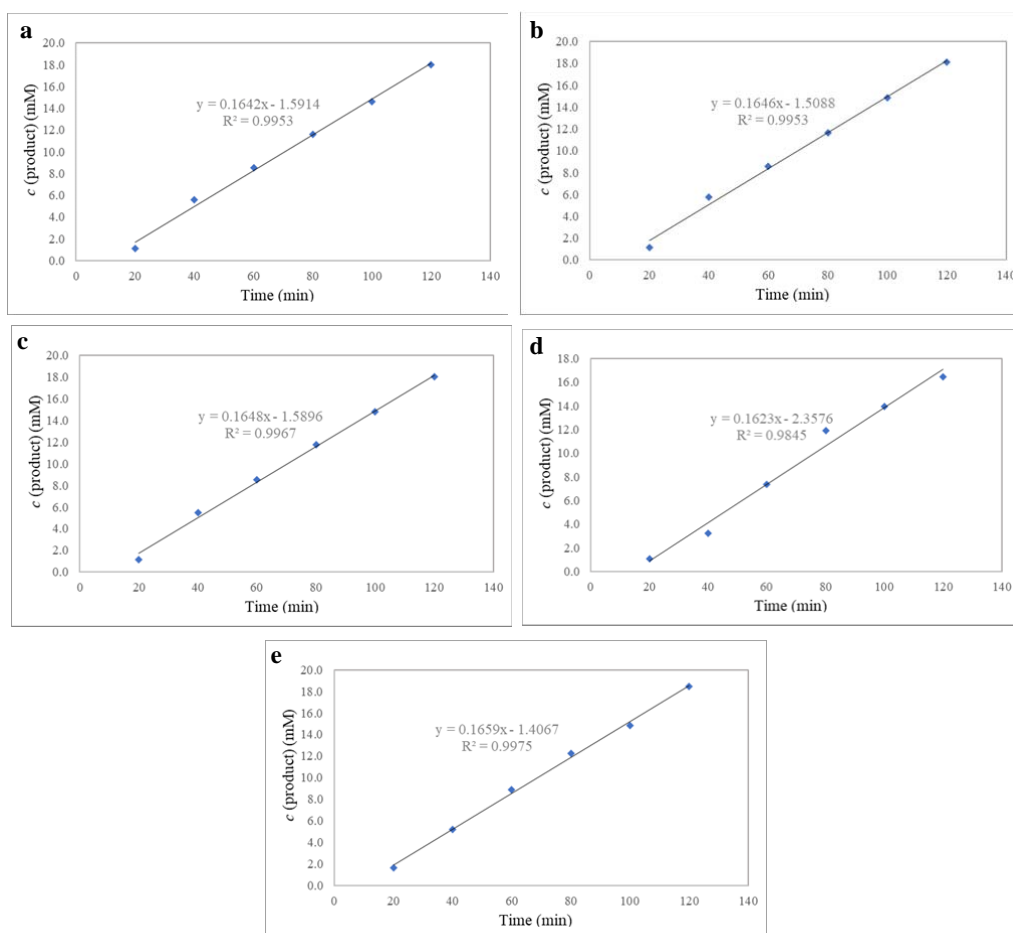
Dependence of initial rate on **2a**

Supplementary Table 2. Initial-Rate Dependence on [**2a**]

Equivalency of 2a	2.0	2.5	3.0	3.5	4.0
[2a]/M	0.10	0.125	0.15	0.175	0.20
[5a]/M	0.05	0.05	0.05	0.05	0.05
[3a]/M	0.075	0.075	0.075	0.075	0.075
[N11]/M	0.025	0.025	0.025	0.025	0.025
[Pd(cod)Cl ₂]/mM	5.0	5.0	5.0	5.0	5.0
[L1]/mM	5.0	5.0	5.0	5.0	5.0
[5-CF ₃ -pyridinone]/M	0.01	0.01	0.01	0.01	0.01
Cs ₂ CO ₃ /mmol·mL ⁻¹	0.15	0.15	0.15	0.15	0.15
initial rate/mM·min ⁻¹	0.1642	0.1646	0.1648	0.1623	0.1659



Supplementary Figure 3. Initial-rate dependence on [**2a**]. Conditions: [**2a**] = 0.10-0.20 M, [**5a**] = 0.05 M, [**3a**] = 0.075 M, [**N11**] = 0.025 M, [Pd(cod)Cl₂] = 5.0 mM, [**L1**] = 5.0 mM, [5-CF₃-pyridinone] = 0.01 M, Cs₂CO₃ 0.15 mmol·mL⁻¹.



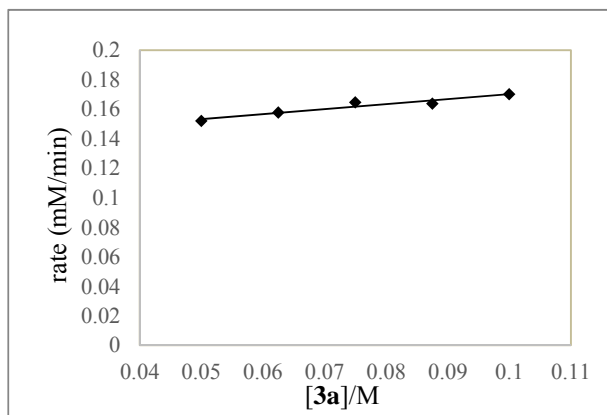
Supplementary Figure 4. Kinetic time courses for measuring initial-rate dependence on [5a].

a: [5a] = 0.10 M, b: [5a] = 0.125 M, c: [5a] = 0.15 M, d: [5a] = 0.175 M, e: [5a] = 0.20 M.

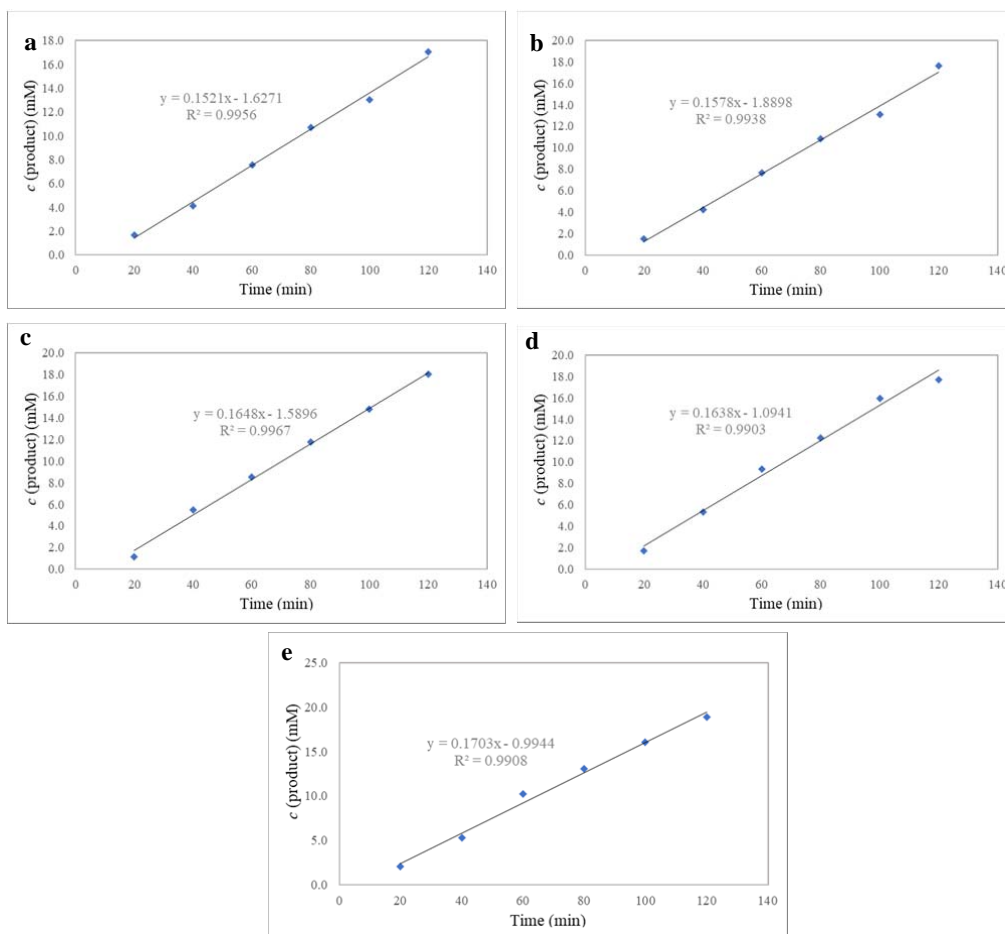
Dependence of initial rate on 3a

Supplementary Table 3. Initial-Rate Dependence on [3a]

Equivalency of 3a	1.0	1.25	1.5	1.75	2.0
[3a]/M	0.05	0.0625	0.075	0.0875	0.10
[2a]/M	0.15	0.15	0.15	0.15	0.15
[5a]/M	0.05	0.05	0.05	0.05	0.05
[N11]/M	0.025	0.025	0.025	0.025	0.025
[Pd(cod)Cl ₂]/mM	5.0	5.0	5.0	5.0	5.0
[L1]/mM	5.0	5.0	5.0	5.0	5.0
[5-CF ₃ -pyridinone]/M	0.01	0.01	0.01	0.01	0.01
Cs ₂ CO ₃ /mmol·mL ⁻¹	0.15	0.15	0.15	0.15	0.15
initial rate/mM·min ⁻¹	0.1521	0.1578	0.1648	0.1638	0.1703



Supplementary Figure 5. Initial-rate dependence on [3a]. Conditions: [3a] = 0.05-0.10 M, [2a] = 0.15 M, [5a] = 0.05 M, [N11] = 0.025 M, [Pd(cod)Cl₂] = 5.0 mM, [L1] = 5.0 mM, [5-CF₃-pyridinone] = 0.01 M, Cs₂CO₃ 0.15 mmol·mL⁻¹.

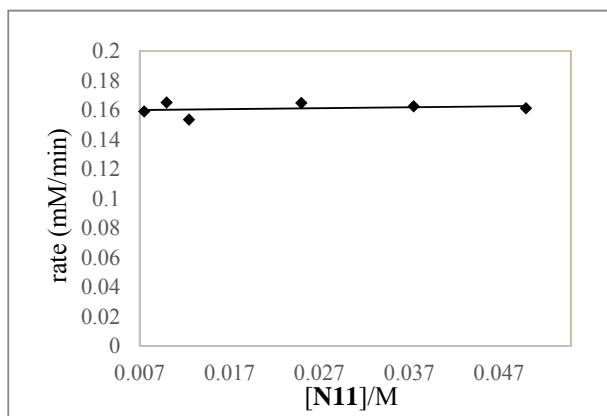


Supplementary Figure 6. Kinetic time courses for measuring initial-rate dependence on [3a].
a: [3a] = 0.05 M, **b:** [3a] = 0.0625 M, **c:** [3a] = 0.075 M, **d:** [3a] = 0.0875 M, **e:** [3a] = 0.10 M.

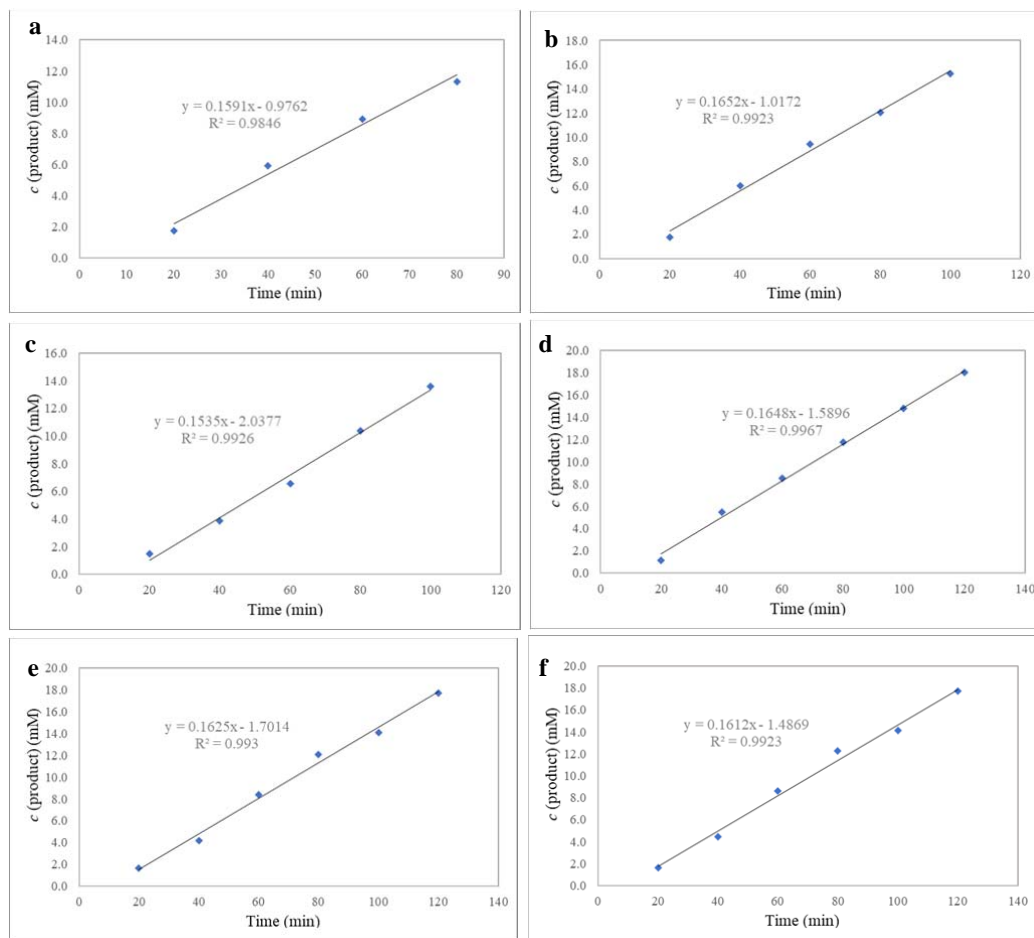
Dependence of initial rate on *NII*

Supplementary Table 4. Initial-Rate Dependence on [N11]

Equivalency of N11	0.15	0.20	0.25	0.5	0.75	1.00
[N11]/M	0.0075	0.01	0.0125	0.025	0.0375	0.05
[2a]/M	0.15	0.15	0.15	0.15	0.15	0.15
[3a]/M	0.075	0.075	0.075	0.075	0.075	0.075
[5a]/M	0.05	0.05	0.05	0.05	0.05	0.05
[Pd(cod)Cl ₂]/mM	5.0	5.0	5.0	5.0	5.0	5.0
[L1]/mM	5.0	5.0	5.0	5.0	5.0	5.0
[5-CF ₃ -pyridinone]/M	0.01	0.01	0.01	0.01	0.01	0.01
Cs ₂ CO ₃ /mmol·mL ⁻¹	0.15	0.15	0.15	0.15	0.15	0.15
initial rate/mM·min ⁻¹	0.1591	0.1652	0.1535	0.1648	0.1625	0.1612



Supplementary Figure 7. Initial-rate dependence on [N11]. Conditions: [N11] = 0.0075-0.05 M, [2a] = 0.15 M, [3a] = 0.075 M, [5a] = 0.05 M, [Pd(cod)Cl₂] = 5.0 mM, [L1] = 5.0 mM, [5-CF₃-pyridinone] = 0.01 M, Cs₂CO₃ 0.15 mmol·mL⁻¹.



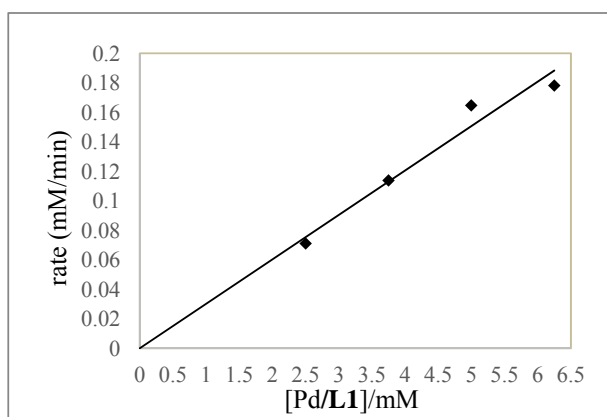
Supplementary Figure 8. Kinetic time courses for measuring initial-rate dependence on [N11].

a: [N11] = 0.0075 M, **b:** [N11] = 0.01 M, **c:** [N11] = 0.0125 M, **d:** [N11] = 0.025 M, **e:** [N11] = 0.0375 M, **f:** [N11] = 0.05 M

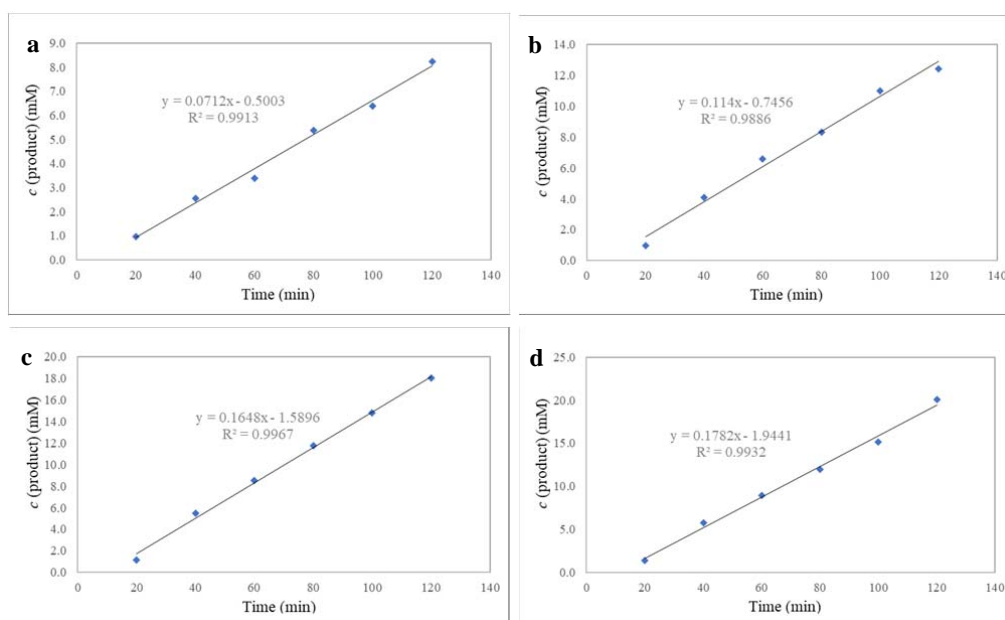
Dependence of initial rate on Pd/L1

Supplementary Table 5. Initial-Rate Dependence on [Pd/L1]

Equivalency of Pd/L1	0.05	0.075	0.10	0.125
[Pd(cod)Cl ₂]/mM	2.5	3.75	5.0	6.25
[L1]/mM	2.5	3.75	5.0	6.25
[2a]/M	0.15	0.15	0.15	0.15
[3a]/M	0.075	0.075	0.075	0.075
[5a]/M	0.05	0.05	0.05	0.05
[N11]/M	0.025	0.025	0.025	0.025
[5-CF ₃ -pyridinone]/M	0.01	0.01	0.01	0.01
Cs ₂ CO ₃ /mmol·mL ⁻¹	0.15	0.15	0.15	0.15
initial rate/mM·min ⁻¹	0.0712	0.1140	0.1648	0.1782



Supplementary Figure 9. Initial-rate dependence on [Pd/L1]. Conditions: [Pd/L1] = 2.5-6.25 mM, [2a] = 0.5 M, [3a] = 0.075 M, [5a] = 0.05 M, [5-CF₃-pyridinone] = 0.01 M, [2a] = 0.15 M, Cs₂CO₃ 0.15 mmol·mL⁻¹.

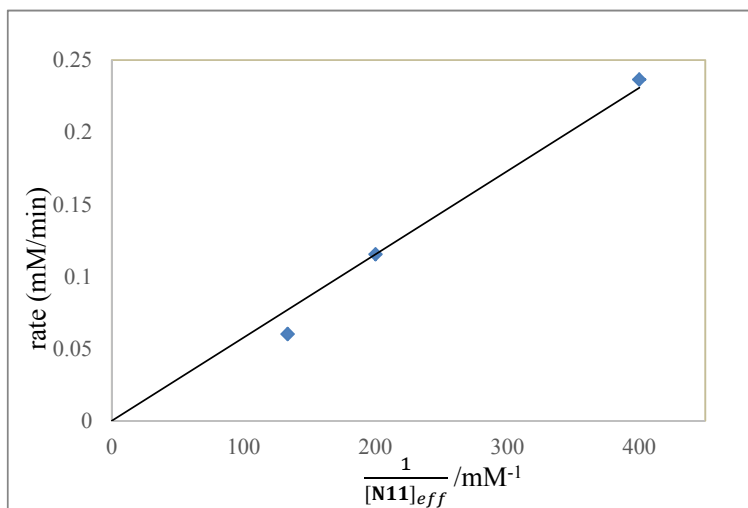


Supplementary Figure 10. Kinetic time courses for measuring initial-rate dependence on [Pd/L1]. **a:** [Pd/L1] = 2.5 mM, **b:** [Pd/L1] = 3.75 mM, **c:** [Pd/L1] = 5.0 mM, **d:** [Pd/L1] = 6.25 mM.

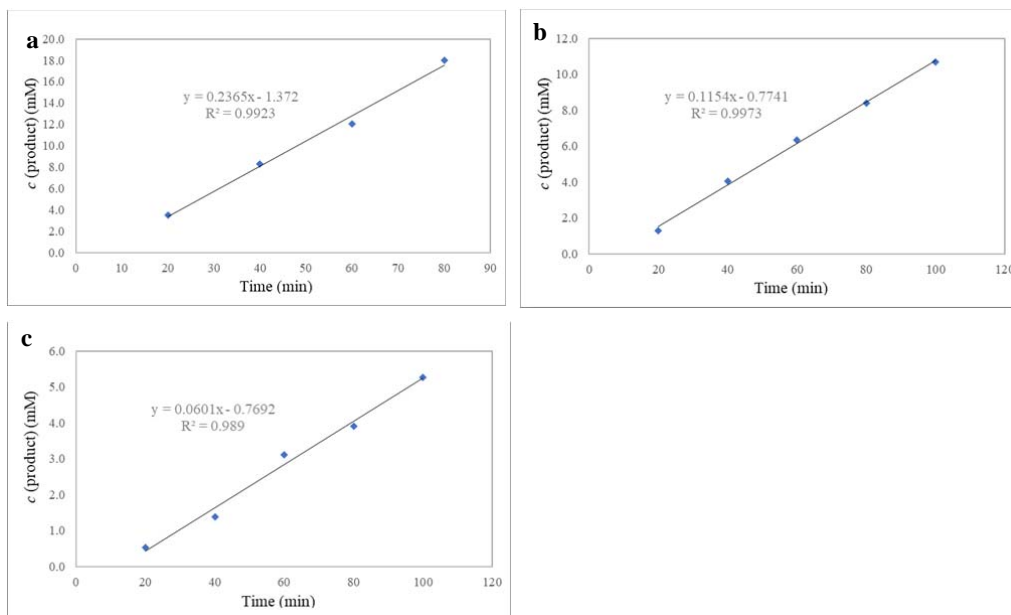
Dependence of initial rate for side-product **4a''** on **N11**

Supplementary Table 6. Initial-Rate Dependence for Side-product **4a''** on **[N11]**

Equivalency of N11	0.15	0.20	0.25
[N11] /M	0.0075	0.01	0.0125
Effective [N11] /M	0.0025	0.0050	0.0075
[2a] /M	0.15	0.15	0.15
[3a] /M	0.075	0.075	0.075
[5a] /M	0.05	0.05	0.05
[Pd(cod)Cl ₂]/mM	5.0	5.0	5.0
[L1] /mM	5.0	5.0	5.0
[5-CF ₃ -pyridinone]/M	0.01	0.01	0.01
Cs ₂ CO ₃ /mmol·mL ⁻¹	0.15	0.15	0.15
initial rate/mM·min ⁻¹	0.2365	0.1154	0.0601

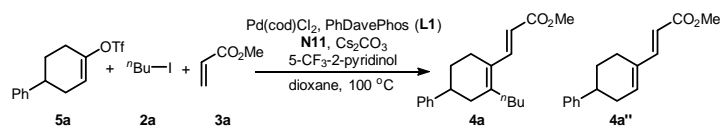


Supplementary Figure 11. Initial-rate dependence on **[N11]**. Conditions: **[N11]** = 0.0075-0.0125 M, **[2a]** = 0.15 M, **[3a]** = 0.075 M, **[5a]** = 0.05 M, [Pd(cod)Cl₂] = 5.0 mM, **[L1]** = 5.0 mM, [5-CF₃-pyridinone] = 0.01 M, Cs₂CO₃ 0.15 mmol·mL⁻¹.



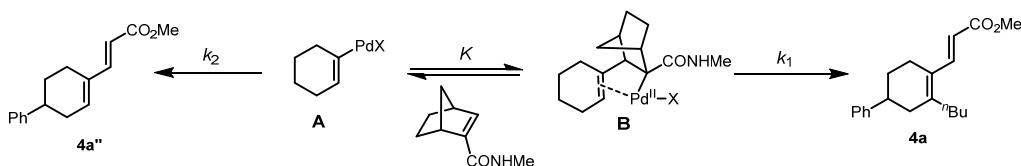
Supplementary Figure 12. Kinetic time courses for measuring initial-rate dependence on [N11]. **a:** [N11] = 0.0075 M, **b:** [N11] = 0.01 M, **c:** [N11] = 0.0125 M.

Supplementary Table 7. Yield Dependence for **4a** and **4a''** on [N11]



[N11]	Yield (4a)	Yield (4a'')
100 mol%	77	n.d.
50 mol%	76	4
25 mol%	53	14
20 mol%	40	20
15 mol%	28	36

Derivation of the rate law:



Supplementary Figure 13. Simplified scheme for the formation of **4a** and **4a''**

The rate for the formation of product **4a** has a zero-order dependence of $[\mathbf{N11}]$; while the rate for the formation of side-product **4a''** has a negative first-order dependence of $[\mathbf{N11}]_{\text{eff}}$. These kinetic data are most consistent with the scenario that norbornene insertion/de-insertion is a pre-equilibrium before the turnover-limiting steps (k_1 and k_2).

If we assume $[A] + [B] = [\text{Pd}]$, which should be proportional to the total amount of palladium pre-catalyst added in the reaction mixture, then:

$$\frac{d[\mathbf{4a}]}{dt} = k_1 \frac{K[\mathbf{N11}]}{1 + K[\mathbf{N11}]} [\text{Pd}]$$
$$\frac{d[\mathbf{4a''}]}{dt} = k_2 \frac{1}{1 + K[\mathbf{N11}]} [\text{Pd}]$$

If K is very large, then:

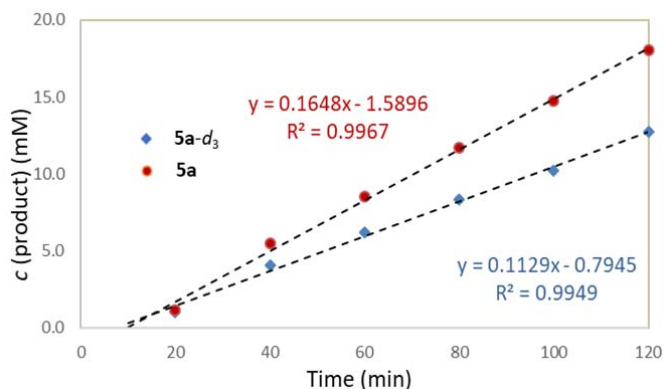
$$\frac{d[\mathbf{4a}]}{dt} = k_1 [\text{Pd}]$$
$$\frac{d[\mathbf{4a''}]}{dt} = k_2 \frac{1}{K[\mathbf{N11}]} [\text{Pd}]$$

Therefore, these kinetic data suggest that the equilibrium for norbornene **N11** insertion favors B over A. Although in theory only a catalytic amount (10 mol%) of **N11** was required, 50 mol% of **N11** is needed in this reaction in order to suppress Heck side product **4a''** by shifting the pre-equilibrium towards B.

Measurement of the kinetic isotopic effect (KIE):

Parallel kinetic isotope effect: following the general method, parallel kinetic isotope effect (KIE) in the C–H metallation process was measured by two sets of parallel experiments employing **5a** and **5a-d₃**, respectively. The KIE was obtained by the ratio of reaction rates (k_H/k_D):

$$KIE = \frac{k_H}{k_D} = \frac{0.1648}{0.1129} = 1.5$$



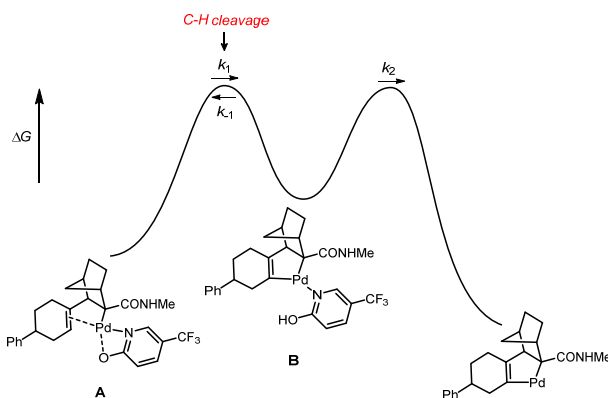
Supplementary Figure 14. Kinetic time courses for measuring the parallel KIE.

Competition kinetic isotope effect: following the general procedure, the reaction was run with a mixture of **5a** (50 mol%) and **5a-d₃** (50 mol%) as the reactants. The reaction was stopped at 1h and 2h, respectively. After isolation of the products by column chromatography, the competition KIE was obtained by the ratio of yields of products **4a** and **4a-d₂** (P_H/P_D):

Supplementary Table 8. Competition KIE values obtained from different reaction times

Reaction time	Ratio of 4a : 4a-d₂	KIE
1 h	61.5% : 38.5%	1.6
2 h	60.5% : 39.5%	1.5

Discussion:



Supplementary Figure 15. Hypothetical reaction profile.

According to the literature,²¹ a parallel KIE of 1.5 and competition KIE of 1.6 are most consistent with the reaction profile in Supplementary Figure 15.

Consider the rate law for the reaction profile above:

$$\frac{d[P]}{dt} = k_2[B] = \frac{k_1 k_2 [A]}{k_{-1} + k_2} \quad (\text{eq 1})$$

(1) If $k_{-1} \ll k_2$, then (eq 1) could be reduced to:

$$\frac{d[P]}{dt} = k_1[A]$$

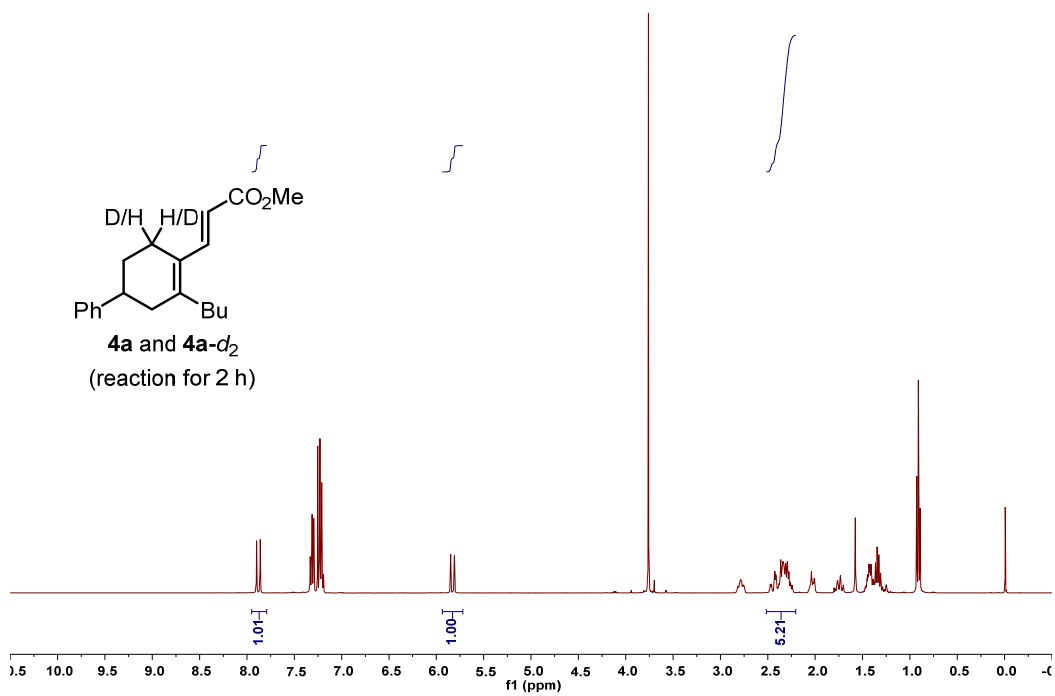
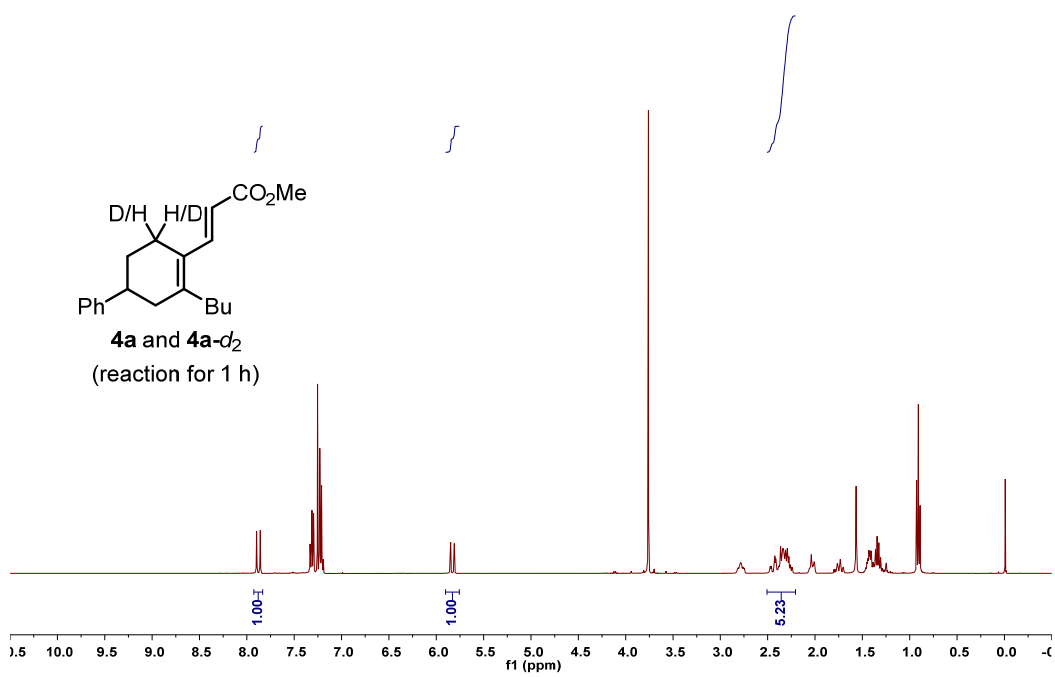
a **large primary** KIE (>3) would be expected.

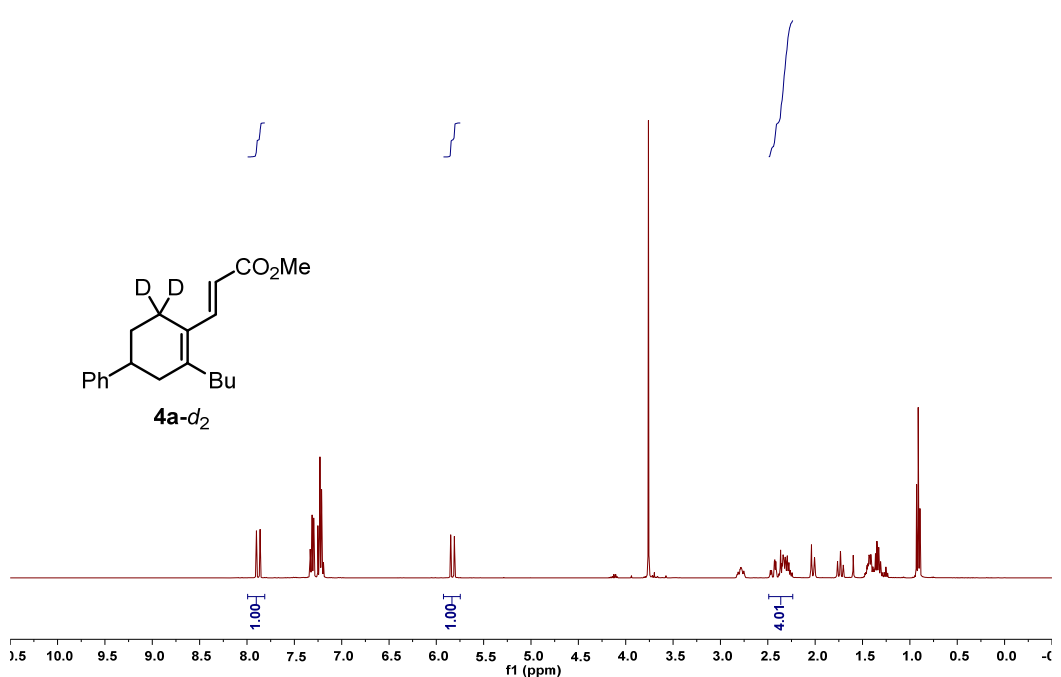
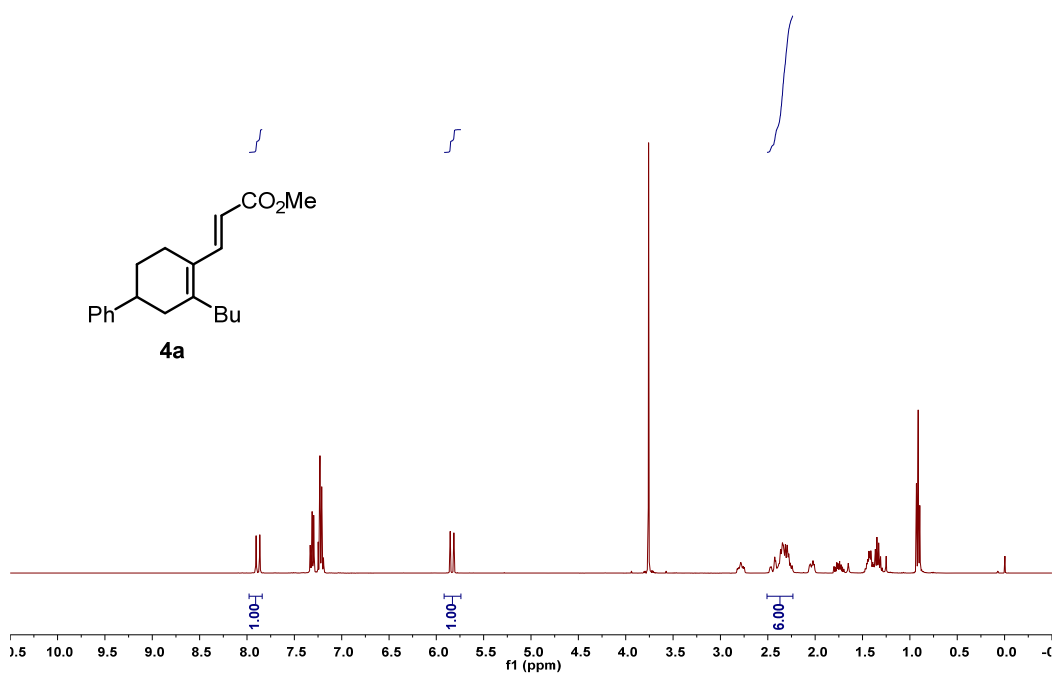
(2) If $k_{-1} \gg k_2$, then (eq 1) could be reduced to:

$$\frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1}} [A]$$

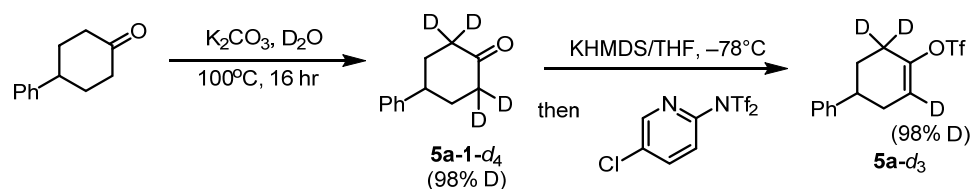
an equilibrium isotope effect (in this case, close to 1 or less than 1) would be expected.

(3) If $k_{-1} \approx k_2$, C–H cleavage is only partially turnover-limiting and that another elementary step either before or after C–H cleavage (*e.g.* ligand dissociation/exchange) also contributes to the catalytic turnover rate. We are expecting to get a **small primary** KIE in this case. This scenario is most consistent with our experimental results.



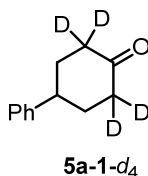


Preparation of **5a-d₃**:

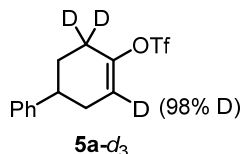


A suspension containing 4-phenylcyclohexan-1-one (3.48 g, 20 mmol, 1.0 equiv.) and potassium carbonate (5.52 g, 40 mmol, 2.0 equiv.) in 35 mL of deuterium oxide and 5 mL of acetone- d_6 was heated at reflux for 16 h. After cooling, the reaction mixture was extracted with ether, and the combined organic phase was concentrated under reduced pressure. H/D exchange was repeated to afford **5a-1-d₄**, which was directly used in the next step without further purification.

To the solution of KHMDS (955 mg, 4.8 mmol, 1.2 equiv.) in anhydrous THF (5 mL) was slowly added a solution of **5a-1-d₄** (712 mg, 4.0 mmol, 1.0 equiv.) in anhydrous THF (10 mL) at $-78^\circ C$. After 1 h at $-78^\circ C$ under a nitrogen atmosphere, a solution of Comin's reagent (1.89 g, 4.8 mmol, 1.2 equiv.) in anhydrous THF (10 mL) was slowly added to the reaction mixture at $-78^\circ C$. The solution mixture was allowed to warm to room temperature over 1 h and stirred for additional 3 h. The resulting solution was treated with saturated aqueous $NaHCO_3$ (20 mL) and extracted with Et_2O (3×20 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous $MgSO_4$, and filtered. The solvent was removed in vacuo. The resulting crude product was purified by column chromatography.

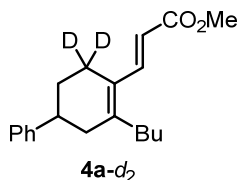


5a-1-d₄: White solid. Melting point = $75-76^\circ C$. (20 mmol scale, 3.14 g, 90% yield, 98% D). $R_f = 0.80$ (hexane/ethyl acetate = 20:1). **¹H NMR** (400 MHz, Chloroform- d) δ 7.36 – 7.30 (m, 2H), 7.27 – 7.20 (m, 3H), 3.03 (tt, $J = 12.1, 3.5$ Hz, 1H), 2.27 – 2.16 (m, 2H), 1.94 (t, $J = 12.8$ Hz, 2H). **¹³C NMR** (101 MHz, Chloroform- d) δ 144.80, 128.62, 126.69, 126.59, 42.74, 33.89. **IR** (KBr, cm^{-1}): ν 2937, 2867, 2360, 1694, 1451, 1239, 1145. **HRMS** (ESI): Calcd for $C_{12}H_{11}D_4O^+$ ($M+H^+$): 179.1368, found: 179.1364.



5a-d₃: Colorless oil. (4.0 mmol scale, 0.59 g, 48% yield, 98% D). $R_f = 0.65$ (hexane/ethyl acetate = 20:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.33 (tt, $J = 7.1, 1.0$ Hz, 2H), 7.26 – 7.20 (m, 3H), 2.85 (dddd, $J = 11.5, 10.0, 5.3, 3.1$ Hz, 1H), 2.47 (ddd, $J = 17.7, 5.3, 1.6$ Hz, 1H), 2.33 (dd, $J = 17.7, 10.1$ Hz, 1H), 2.07 (ddd, $J = 12.9, 3.0, 1.5$ Hz, 1H), 1.95 (t, $J = 12.4$ Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 144.57, 128.64, 126.75, 126.66, 38.69, 31.46, 29.49. **IR** (KBr, cm^{-1}): ν 3030, 2926, 1674, 1454, 1417, 1210, 1143, 1013. **HRMS** (ESI): Calcd for $\text{C}_{13}\text{H}_{11}\text{D}_3\text{F}_3\text{O}_3\text{S}^+$ ($\text{M}+\text{H}^+$): 310.0799, found: 310.0792.

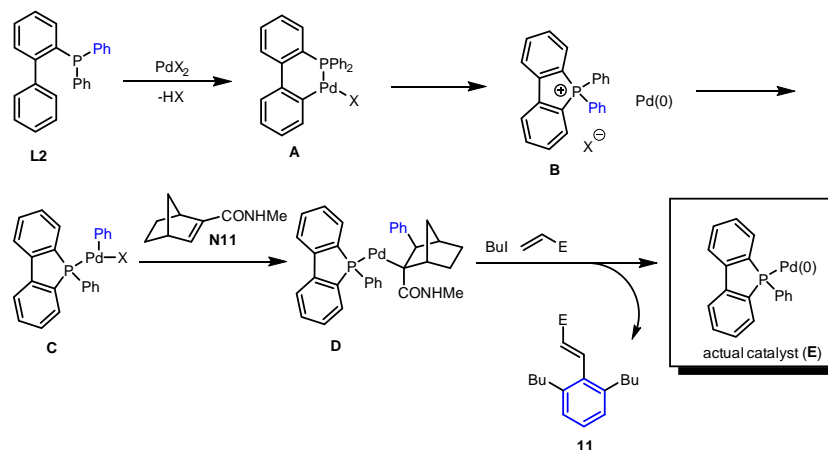
Characterization data of **4a-d₂**:



4a-d₂: Light yellow oil. $R_f = 0.35$ (hexane/ethyl acetate = 10:1). $R_f = 0.35$ (hexane/ethyl acetate = 10:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (d, $J = 15.6$ Hz, 1H), 7.37 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 5.84 (d, $J = 15.6$ Hz, 1H), 3.77 (s, 3H), 2.85 – 2.73 (m, 1H), 2.51 – 2.23 (m, 4H), 2.03 (d, $J = 12.8$ Hz, 1H), 1.74 (t, $J = 12.4$ Hz, 1H), 1.51 – 1.25 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 168.49, 147.76, 146.28, 142.38, 128.49, 126.79, 126.72, 126.26, 114.82, 51.46, 39.99, 39.77, 33.37, 31.50, 29.22, 22.81, 13.99. **IR** (KBr, cm^{-1}): ν 2954, 2929, 2871, 1718, 1618, 1434, 1299, 1172. **HRMS** (ESI): Calcd for $\text{C}_{20}\text{H}_{25}\text{D}_2\text{O}_2^+$ ($\text{M}+\text{H}^+$): 301.2131, found: 301.2140.

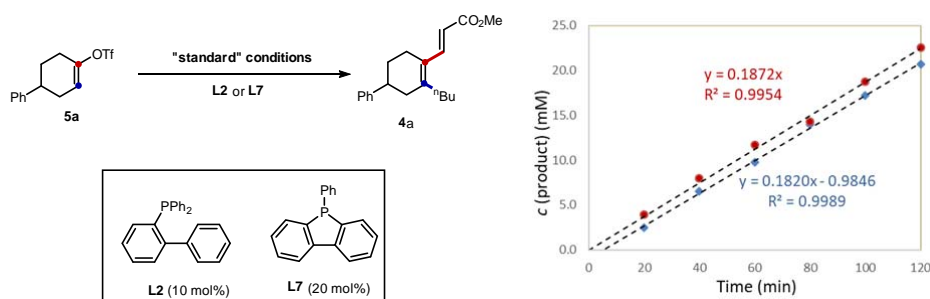
Identification of the actual ligand:

The isolation of cyclic phosphine oxide **10** and by-product **11** led us to propose a reaction mechanism of how the active catalyst was generated.²² The reaction is initiated by the C–H palladation of **L2** with PdX₂ to form the cyclopalladated complex **A**. Subsequent reductive elimination from **A** leads to the formation of phosphonium **B** along with Pd(0). The phosphonium **B** can then undergo oxidative addition with Pd(0), which provides complex **C** through cleavage of the C–P bond. The resulting phenyl Pd(II) species could undergo migratory insertion into **N11**, and further a normal Catellani reaction takes place to give the actual catalyst **E** along with **11** as the by-product.



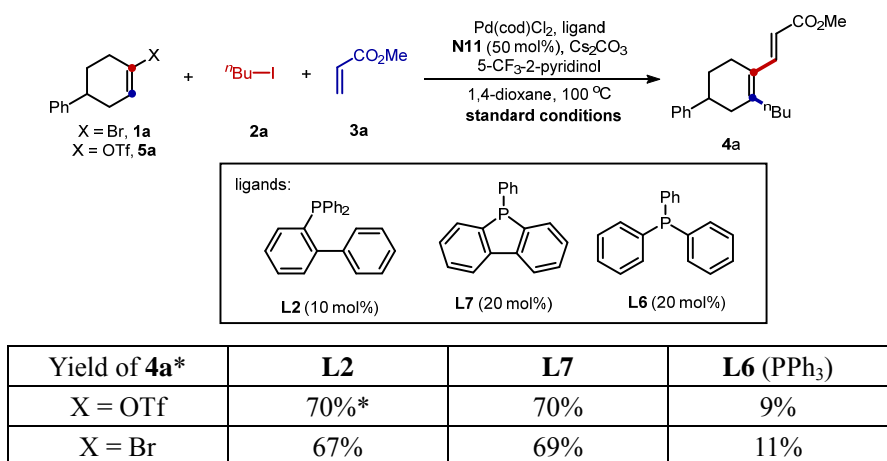
Supplementary Figure 16. Proposed mechanism for the formation of the active catalyst.

To confirm that **L7** was the actual active ligand, the parallel kinetic study of reactions using **L2** or **L7** as the ligand was conducted, following the general method. A sacrificial additional 10 mol% of **L7** was used to reduce Pd(II) into Pd(0), which was not required in the case of **L2**.



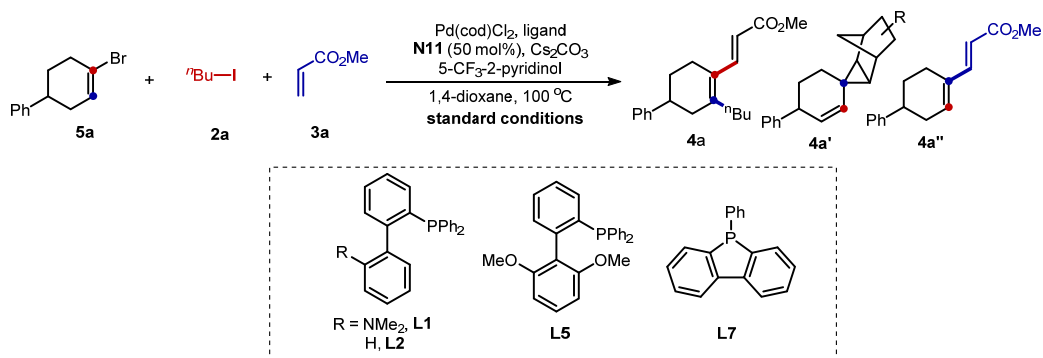
Supplementary Figure 17. Kinetic time courses for reactions using **L2** and **L7**.

Supplementary Table 9. Performance of **L2**, **L7** and **L6** (PPh₃) in the standard conditions



* Yields were determined by ¹H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

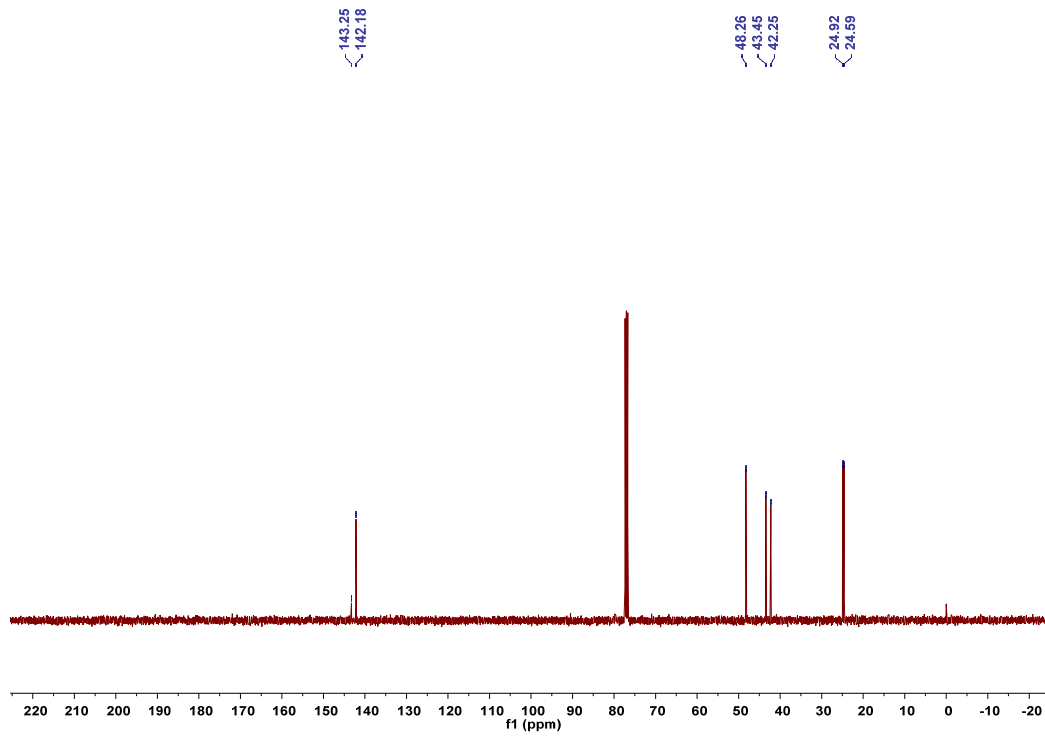
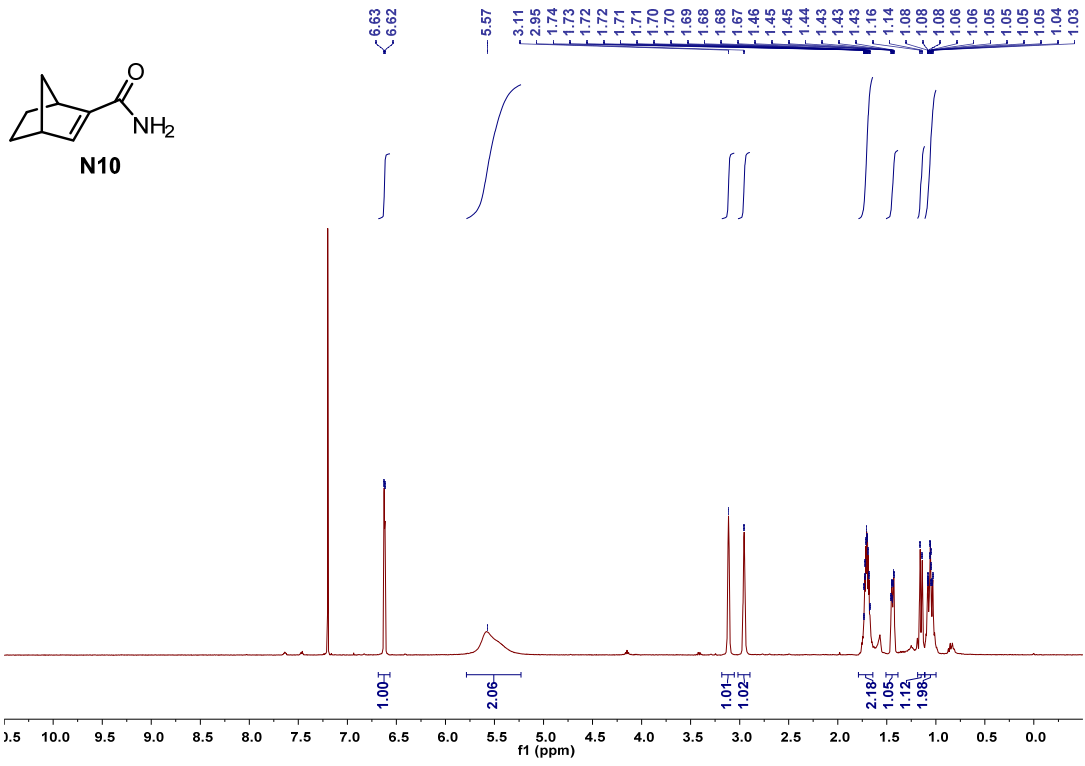
Supplementary Table 10. Ligand effect

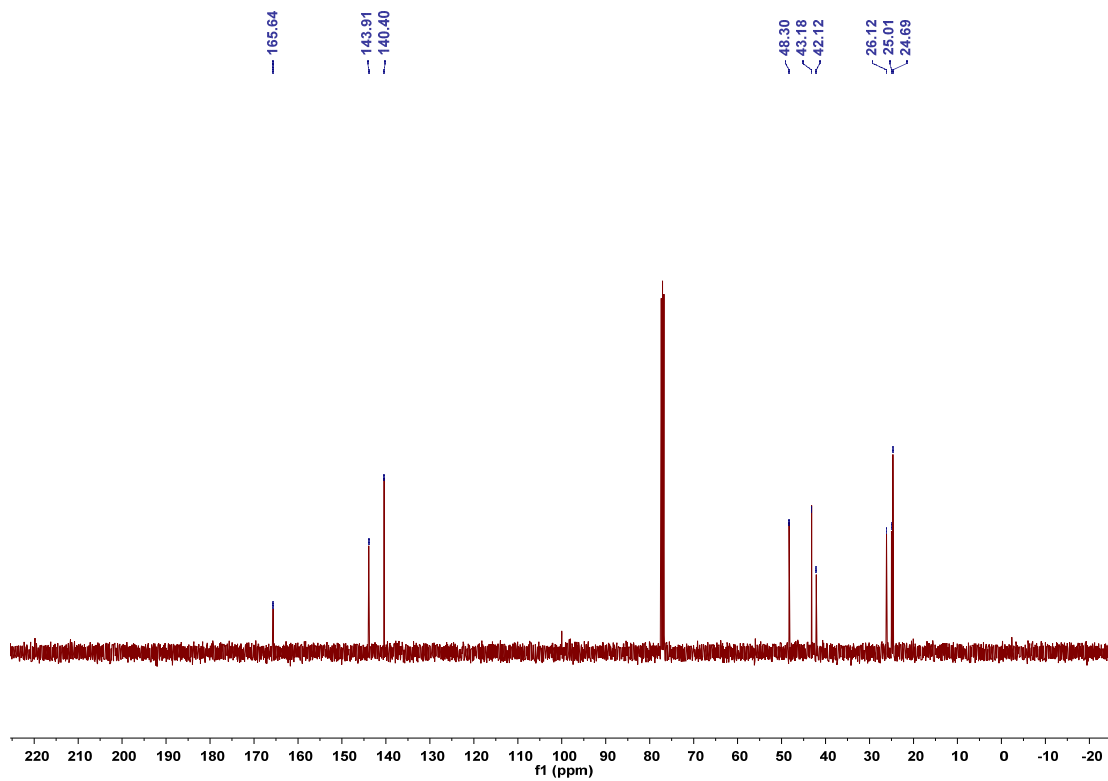
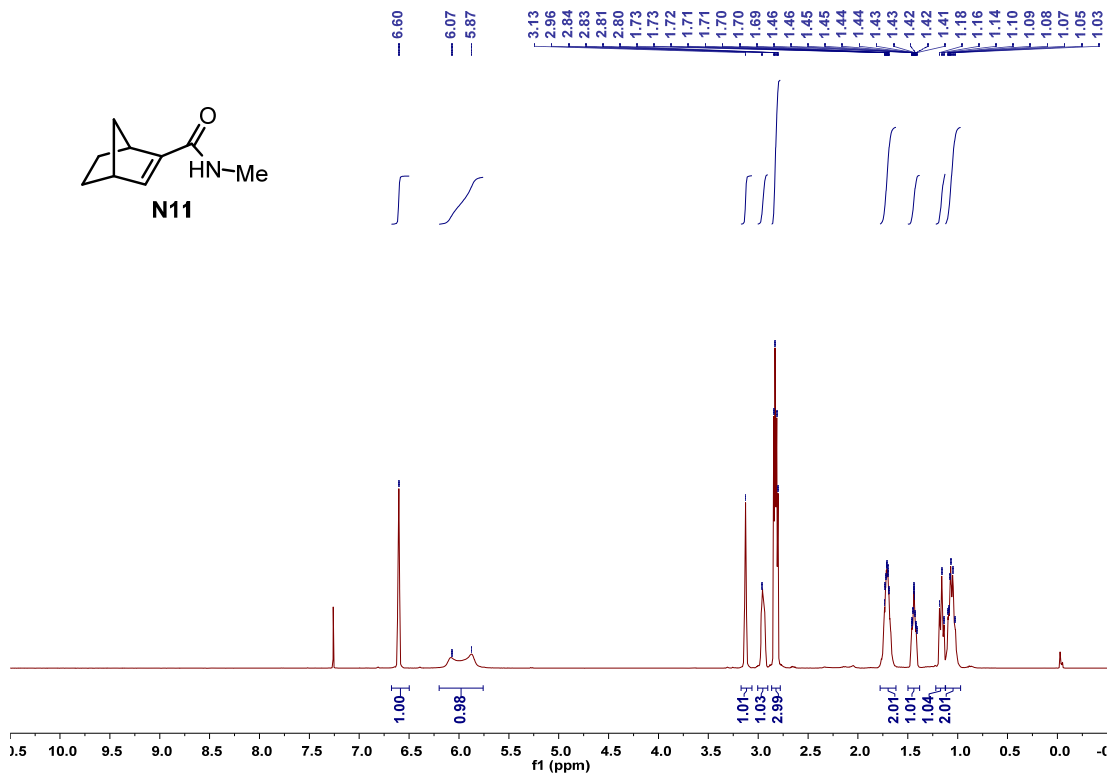
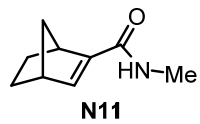


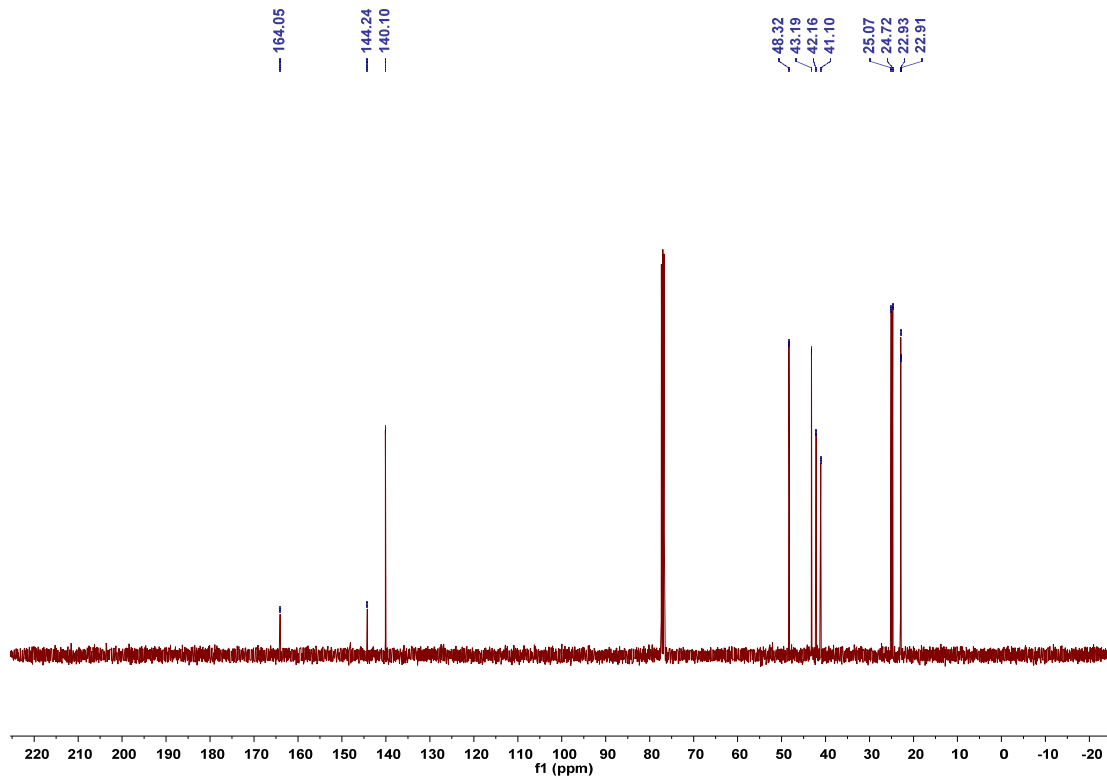
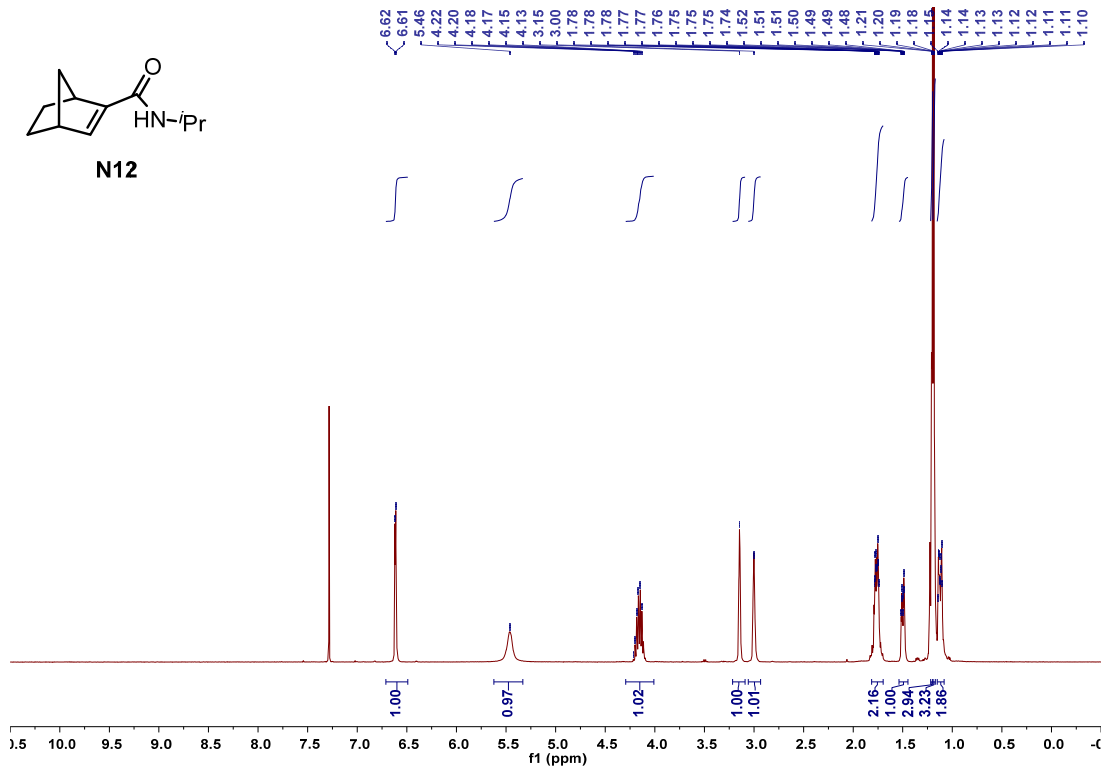
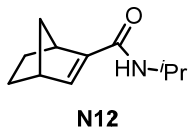
	Yield of 4a *	Yield of 4a' **	Yield of 4a'' **
L1 (10 mol%)	74%	<5%	6%
L2 (10 mol%)	67%	<5%	6%
L7 (20 mol%)	69%	<5%	6%
L5 (10 mol%)	12%	6%	10%
PPh ₃ (20 mol%) ^a	11%	<5%	5%
dppe (10 mol%)	14%	6%	6%
P(2-furyl) ₃ (20 mol%)	3%	9%	5%
CyJohnPhos (10 mol%)	3%	18%	20%
DPEPhos (10 mol%)	10%	9%	6%
PCy ₃ (20 mol%) ^b	<5%	9%	7%
PPh ₂ Me (20 mol%)	20%	21%	6%

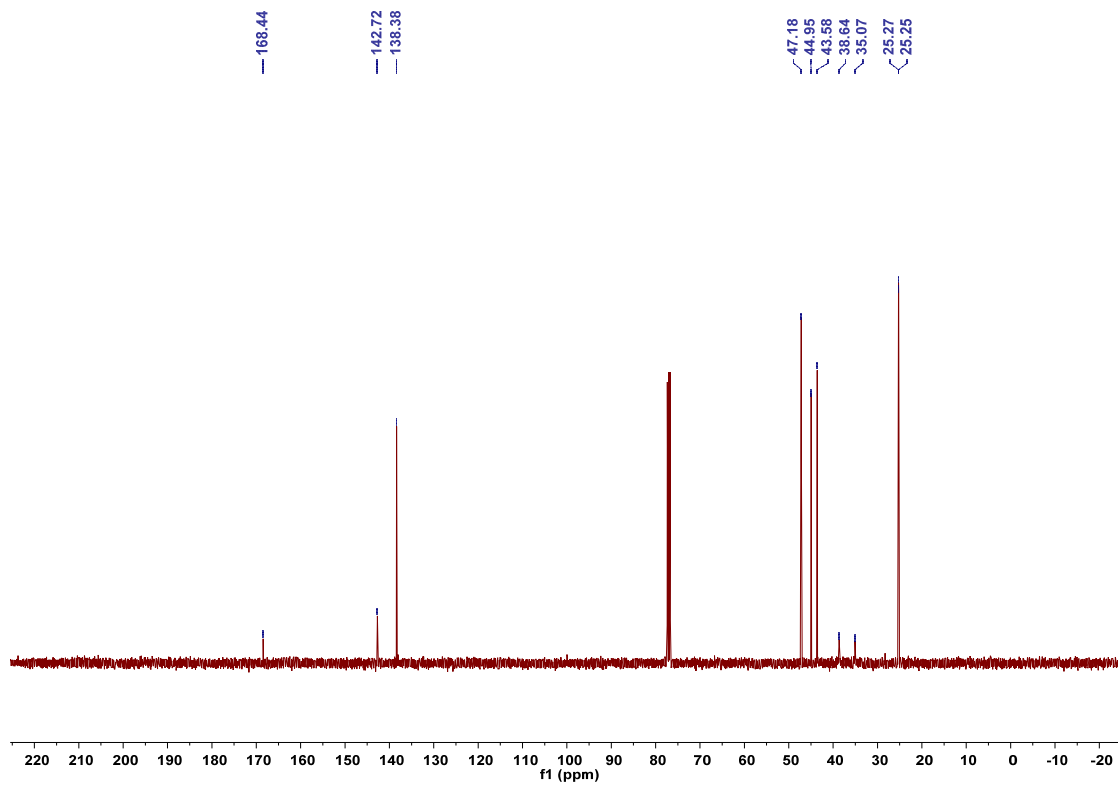
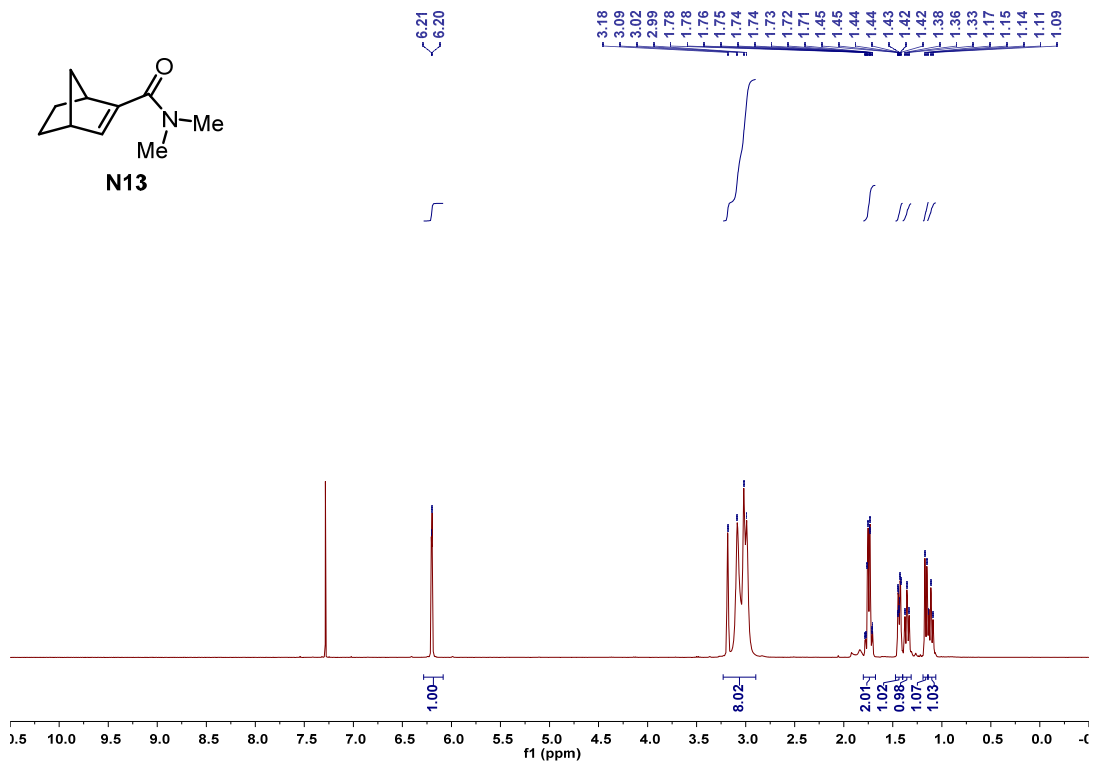
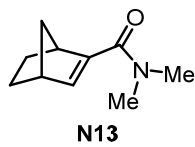
* Yields were determined by ¹H NMR using 1,1,2,2-tetrachloroethane as the internal standard. ^a 19% of **5a** was decomposed to corresponding diene. ^b Conversion is 60%.

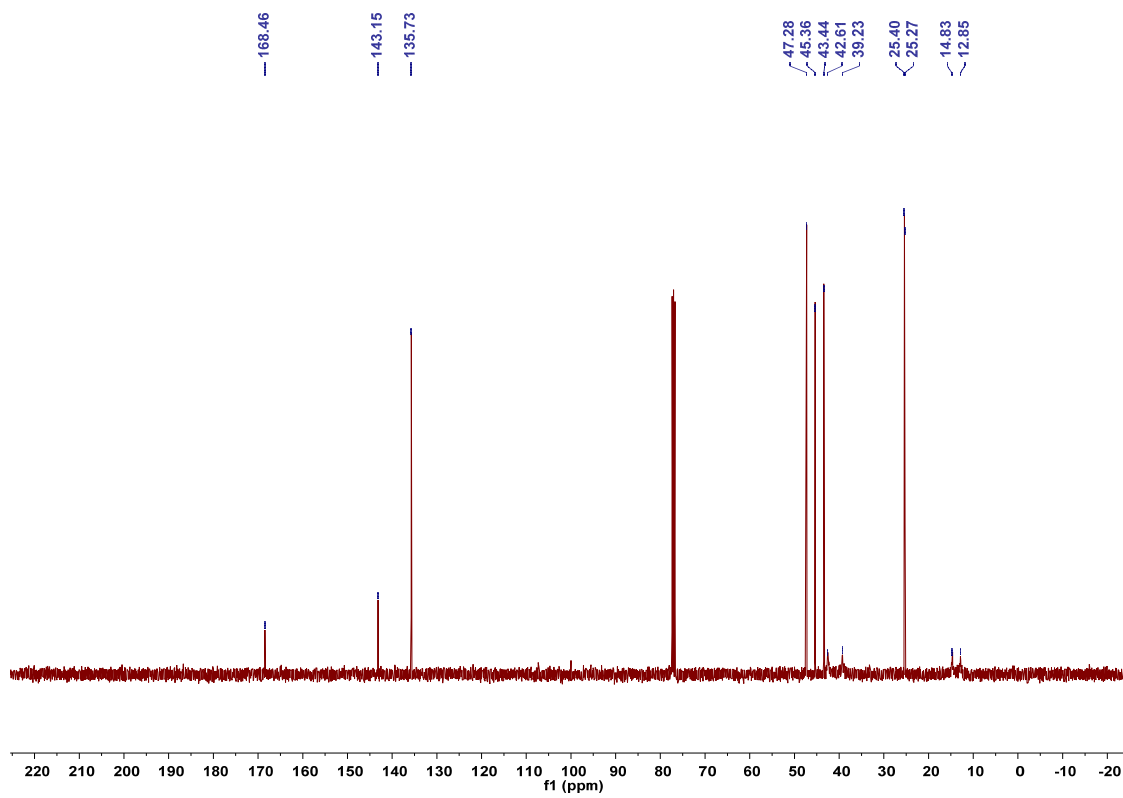
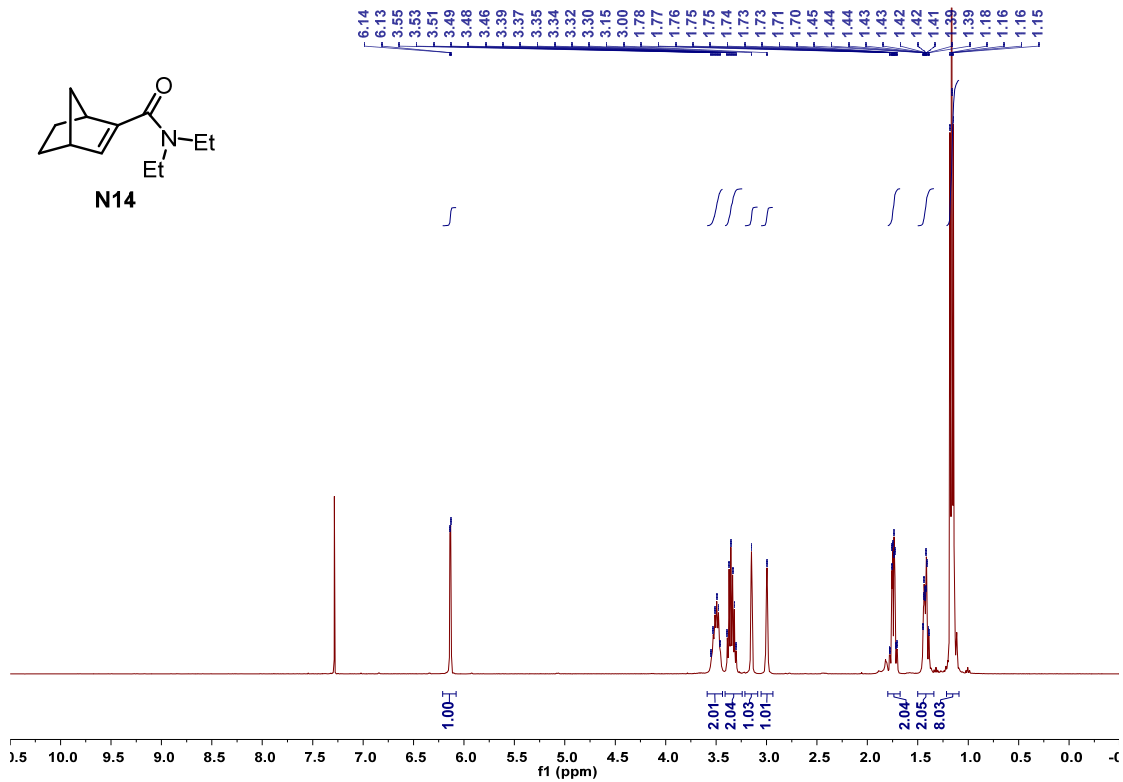
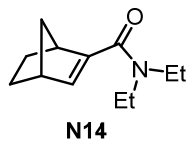
IV. Spectra

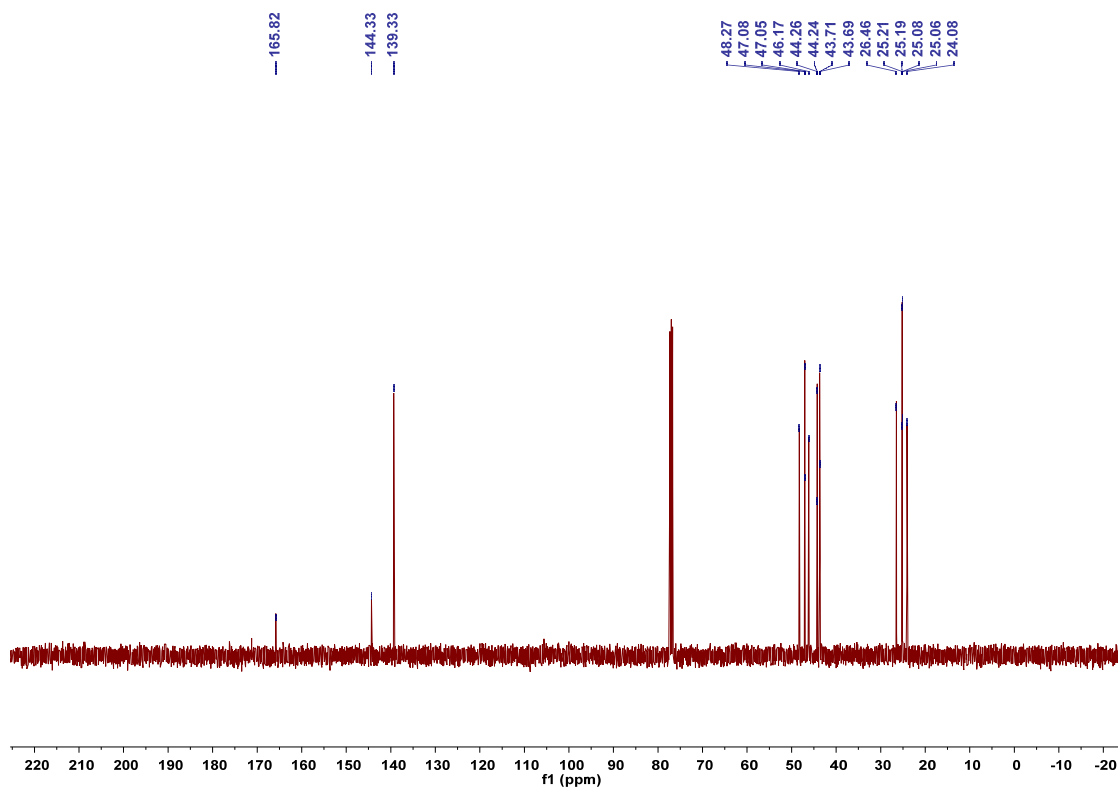
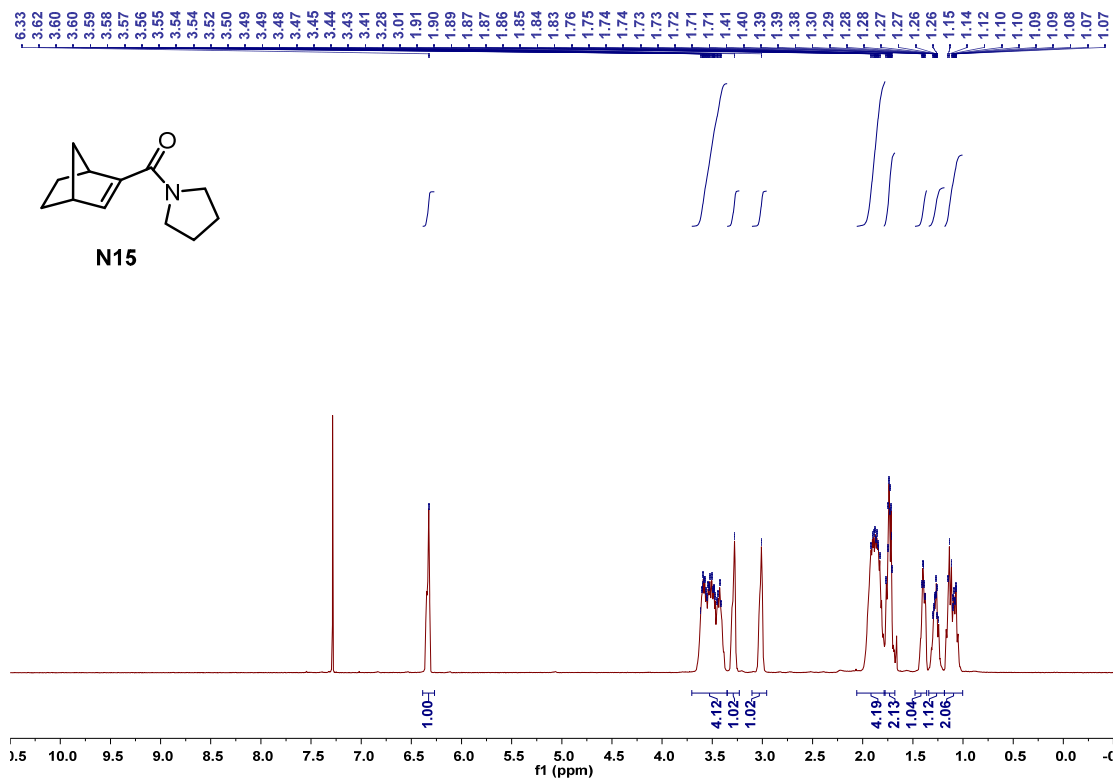


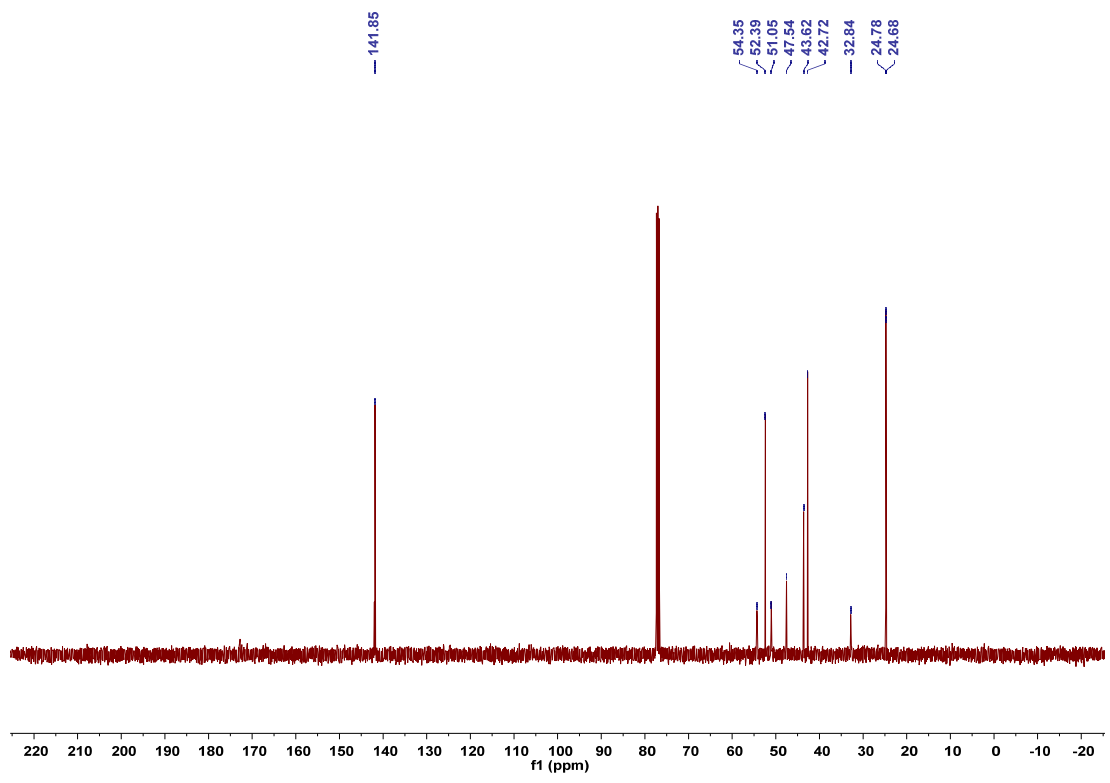
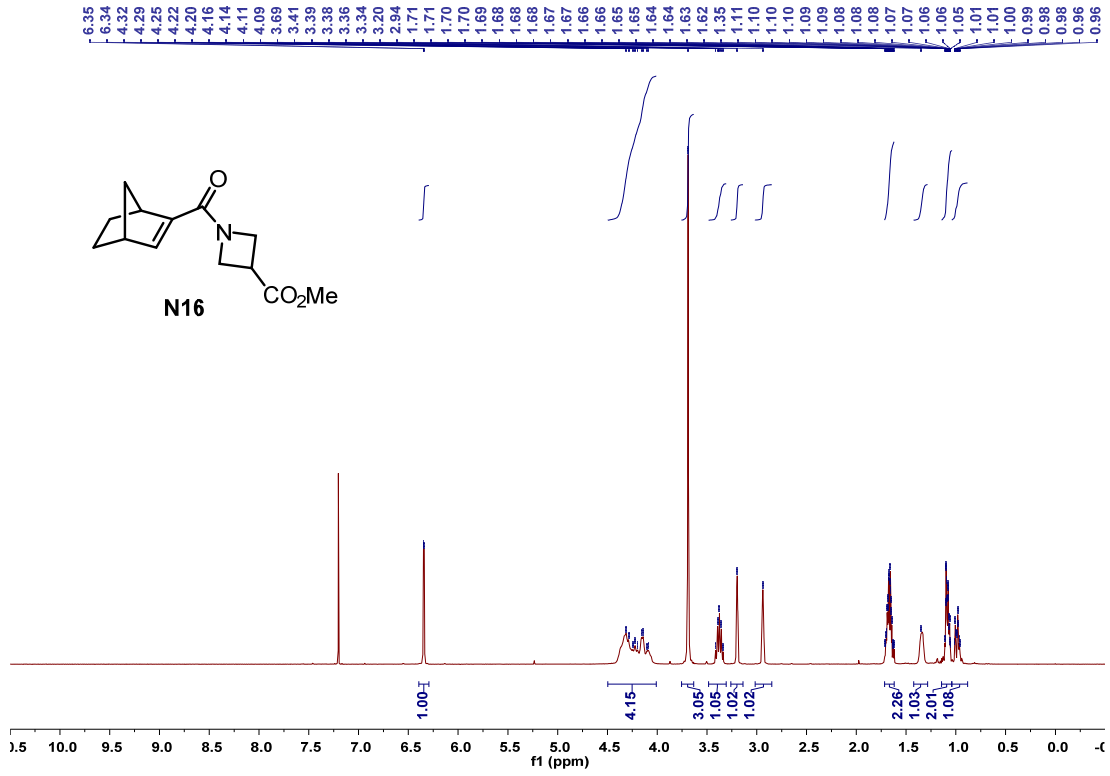


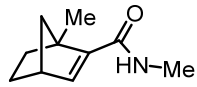




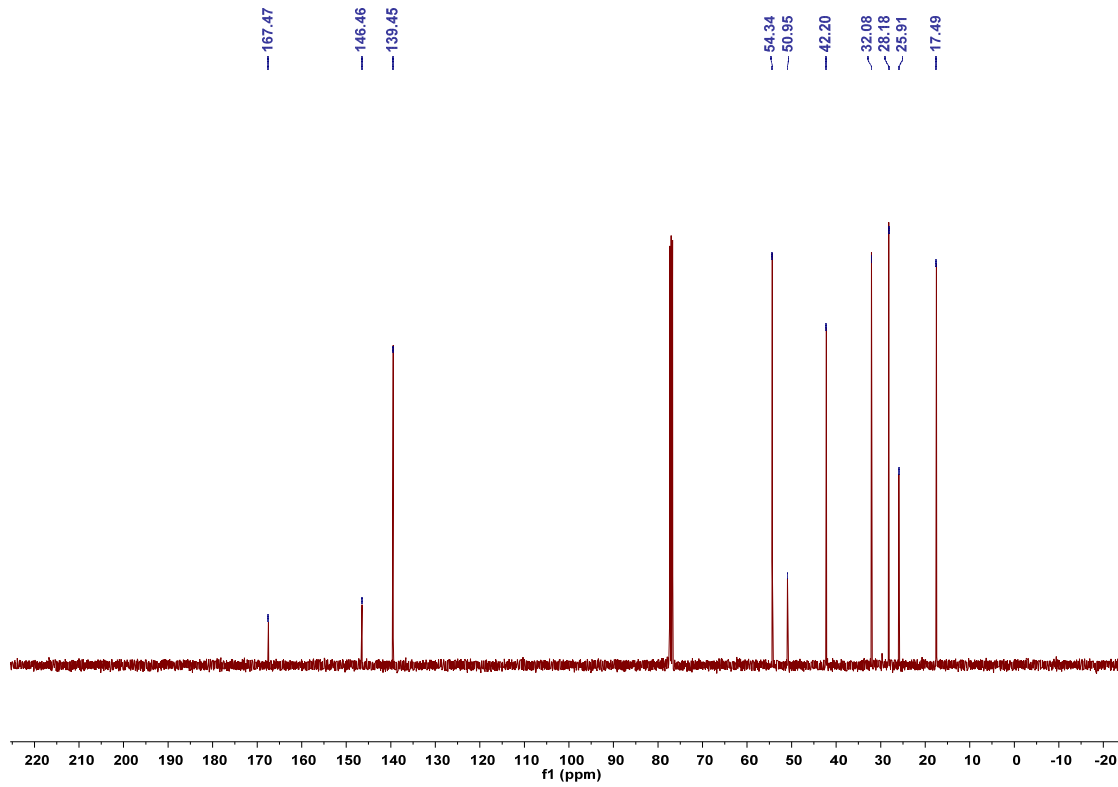
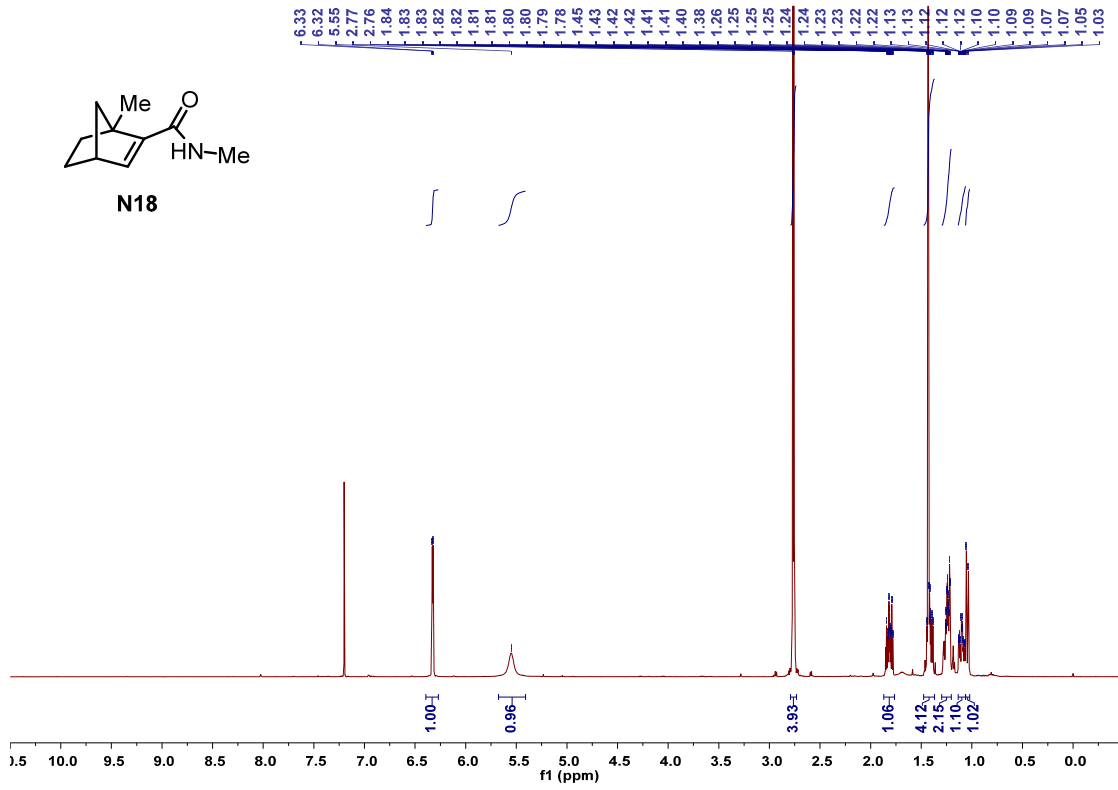


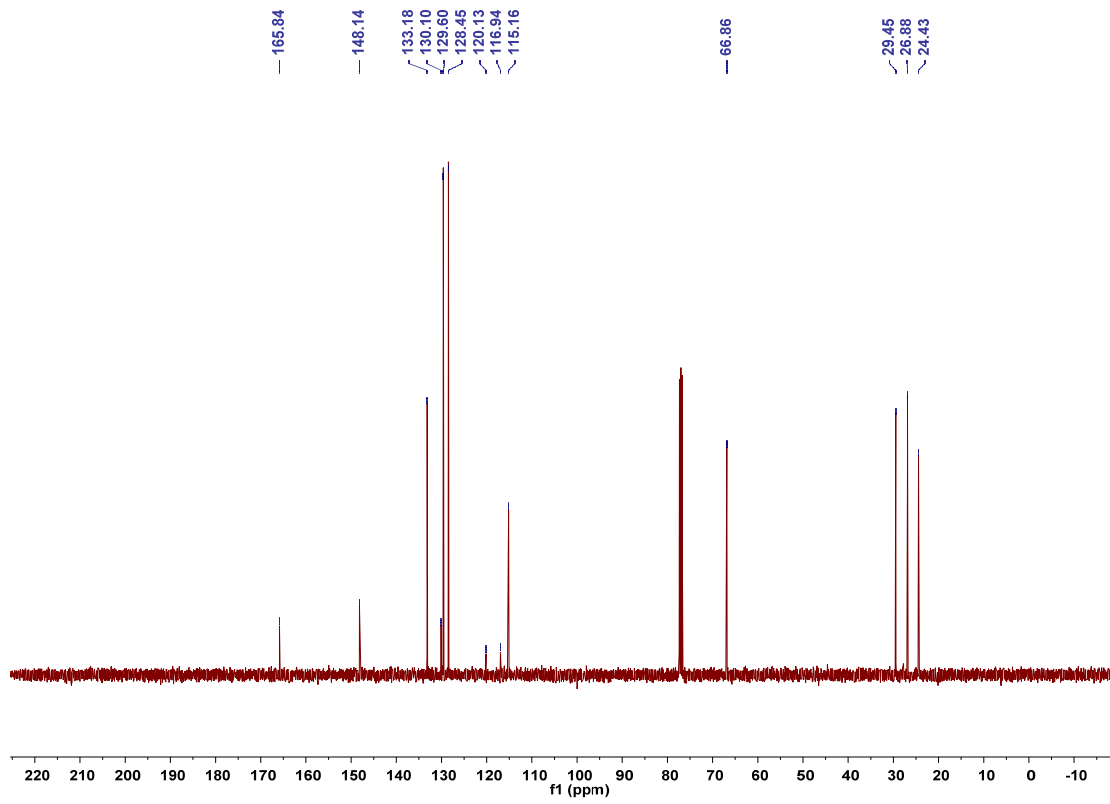
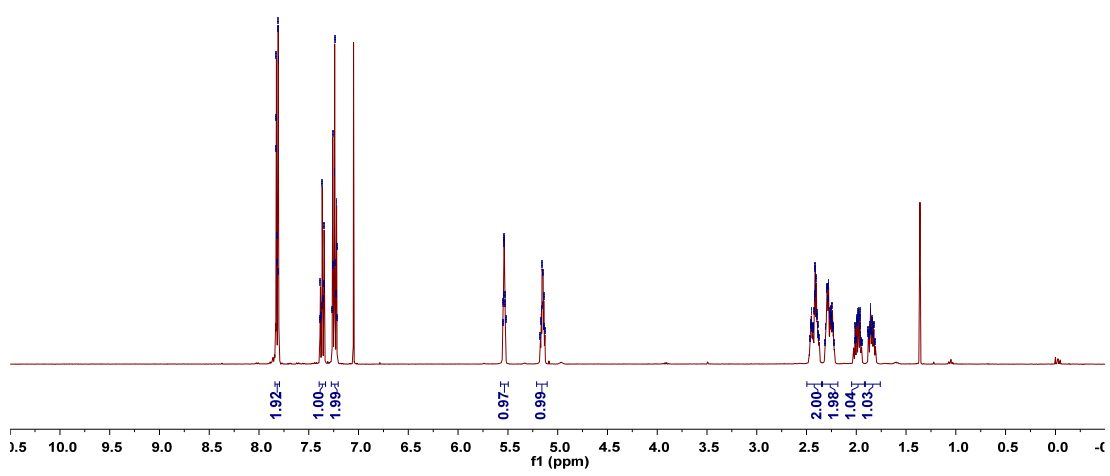
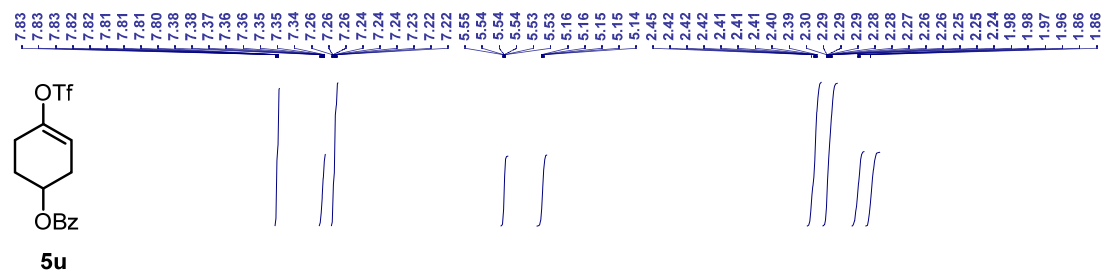


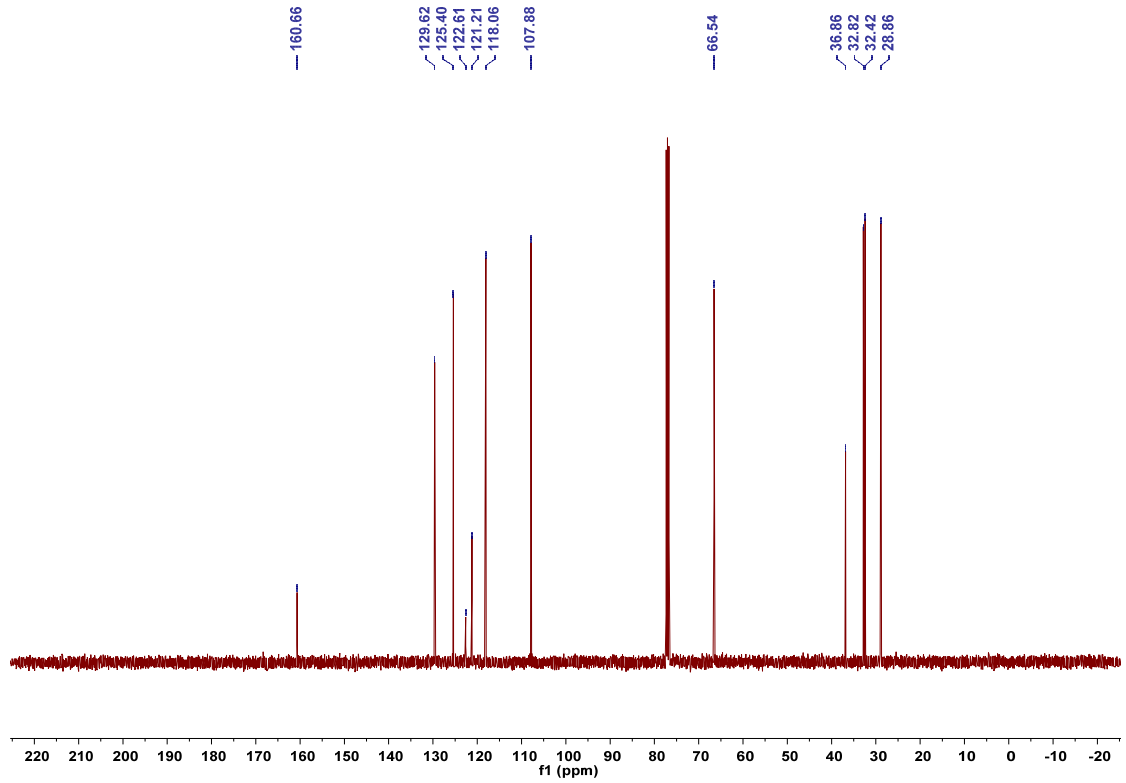
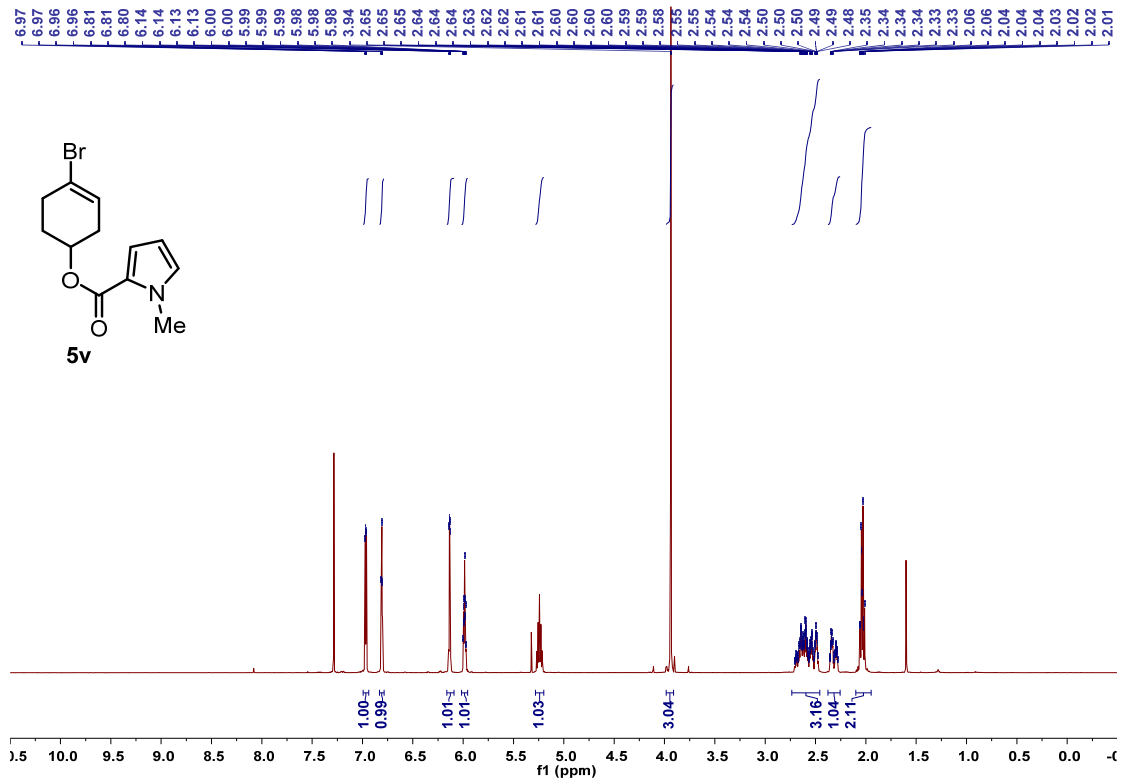


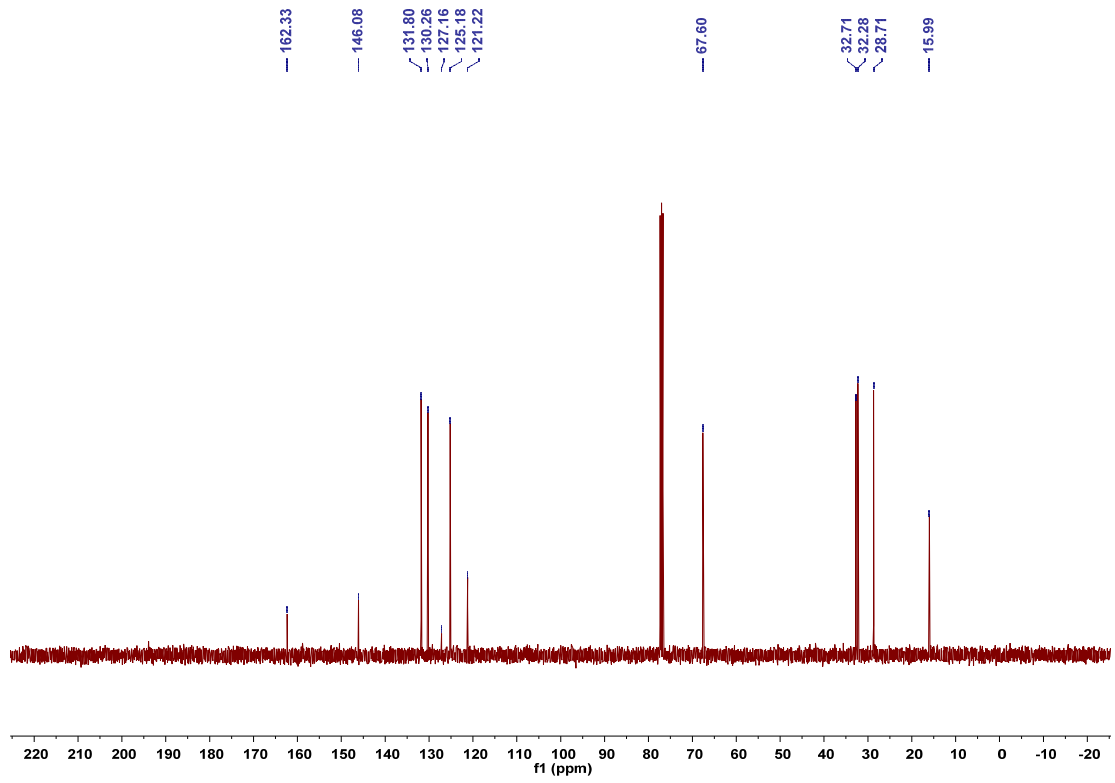
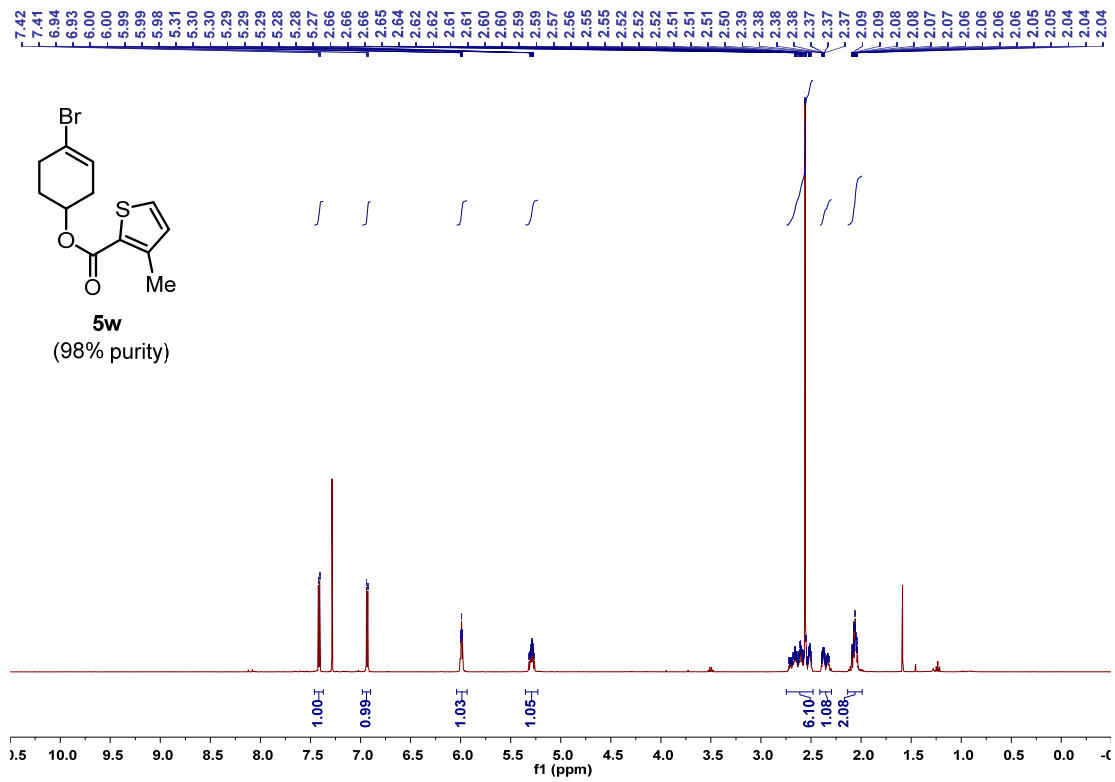


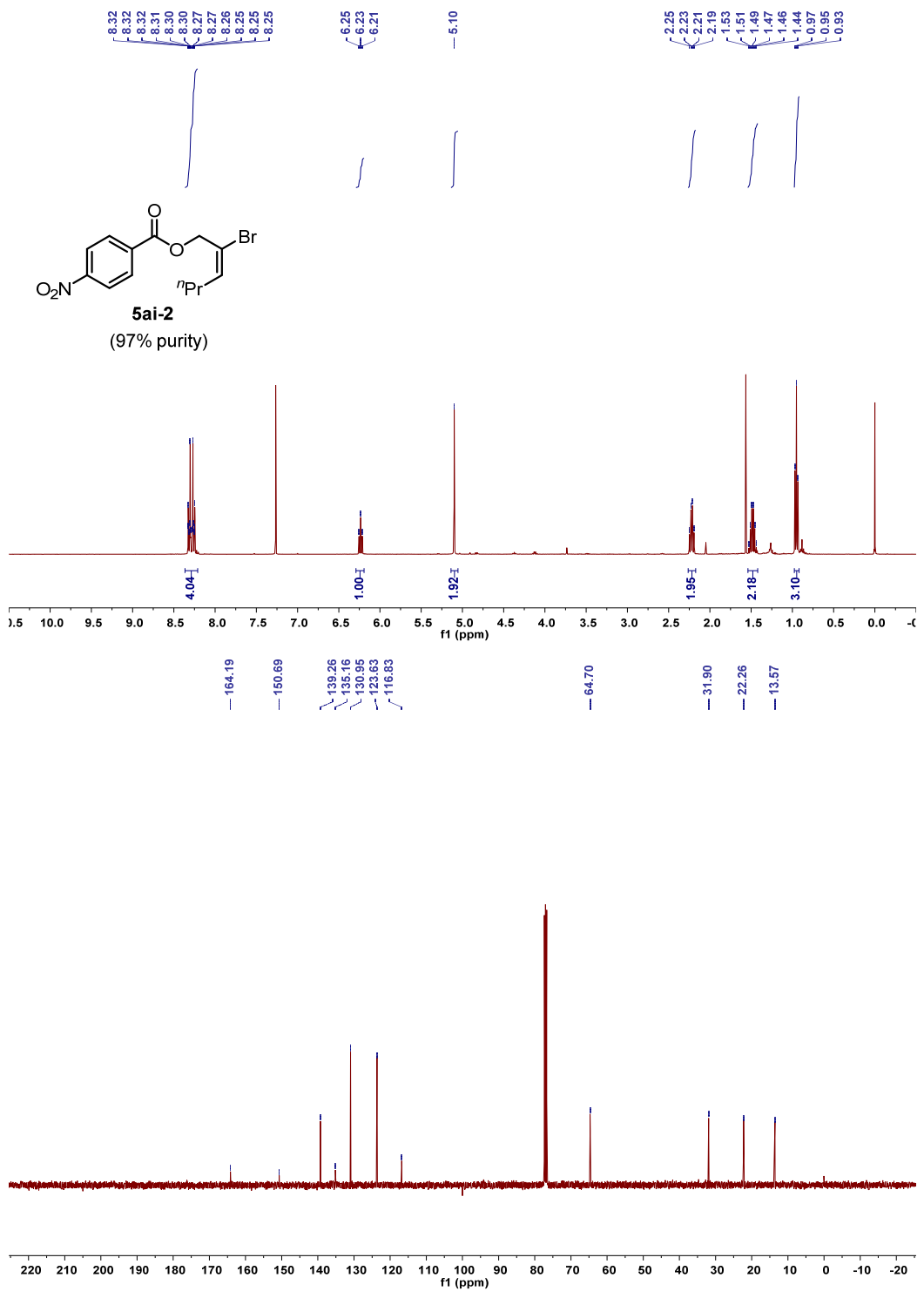
N18

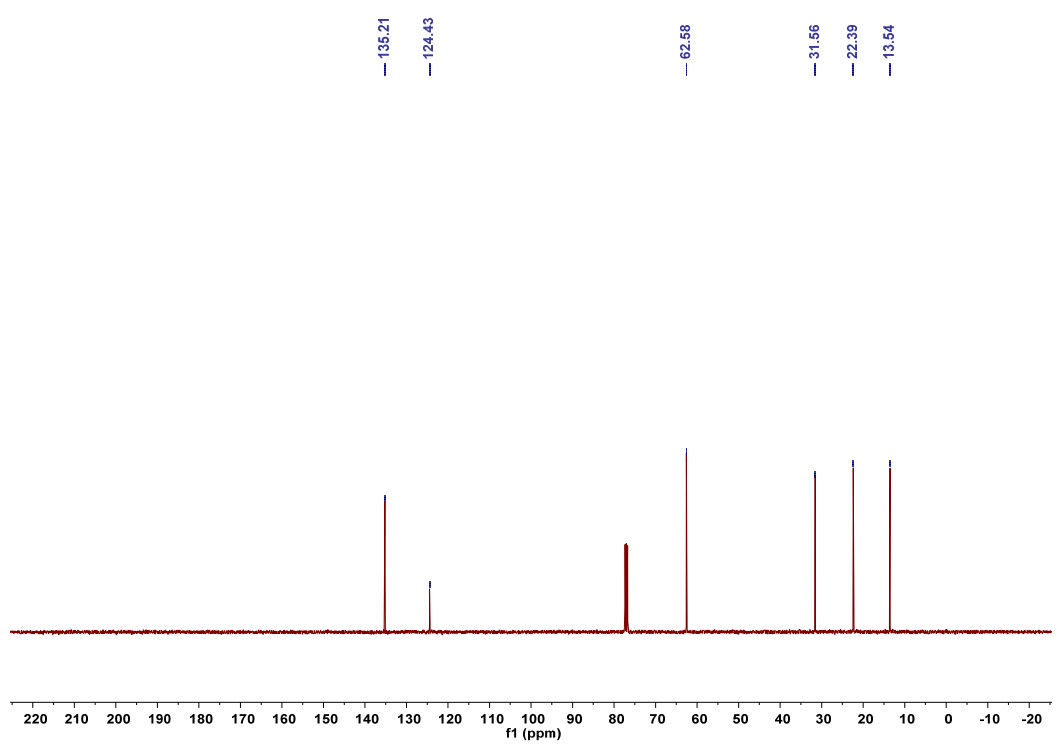
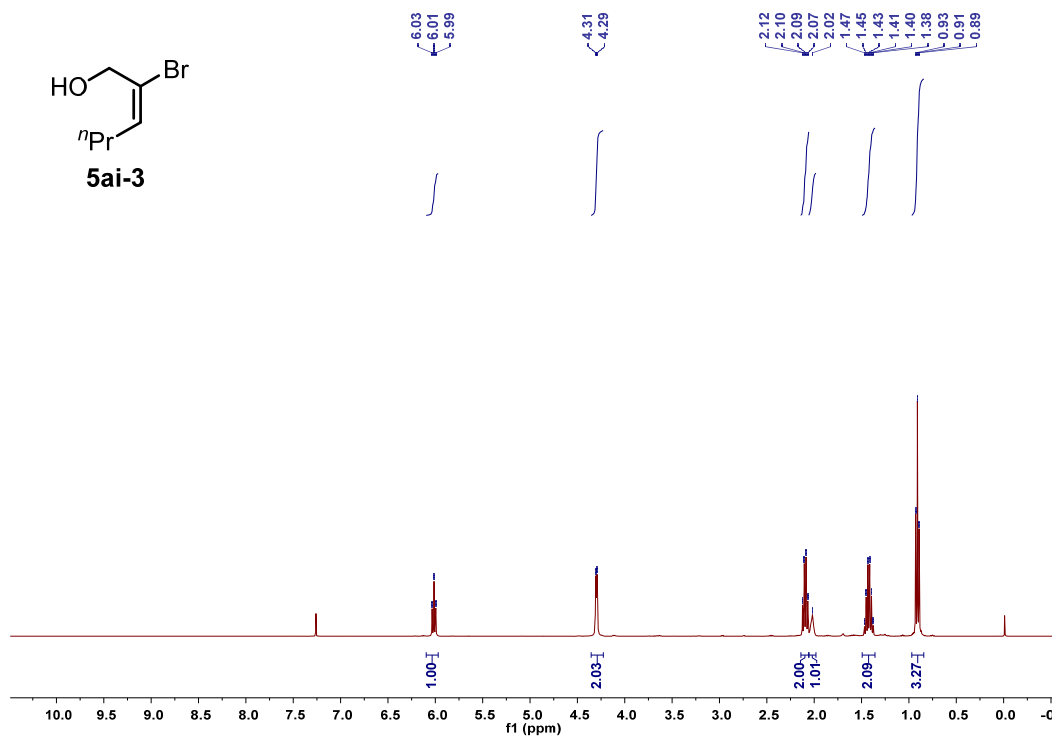
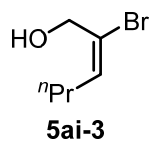


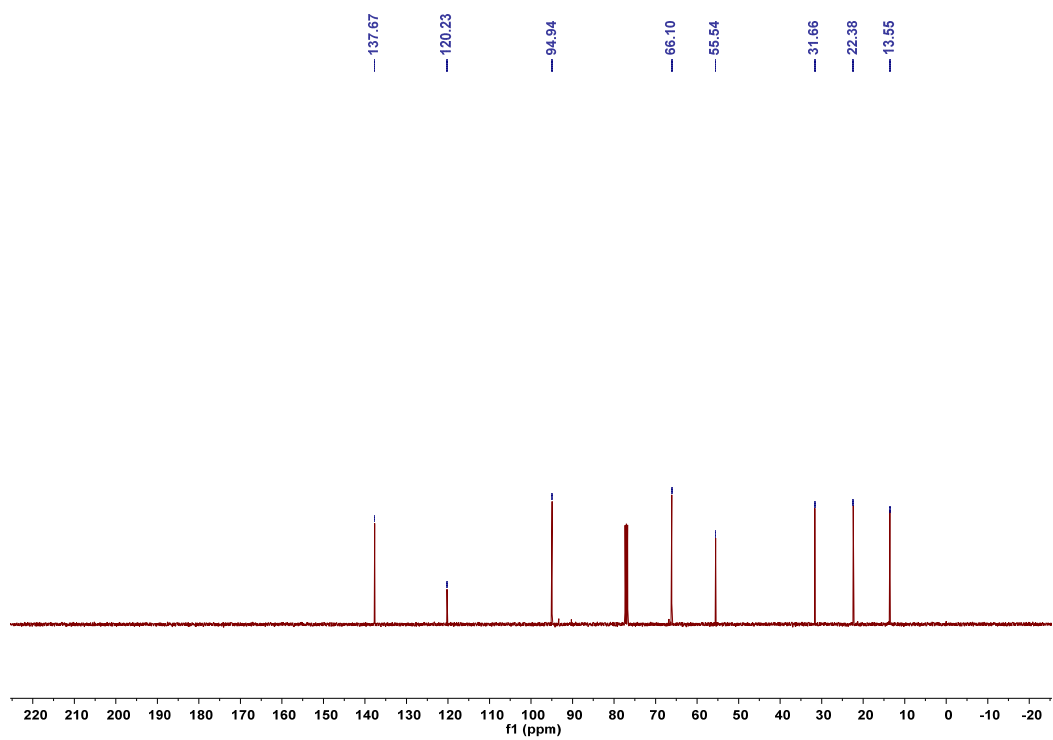
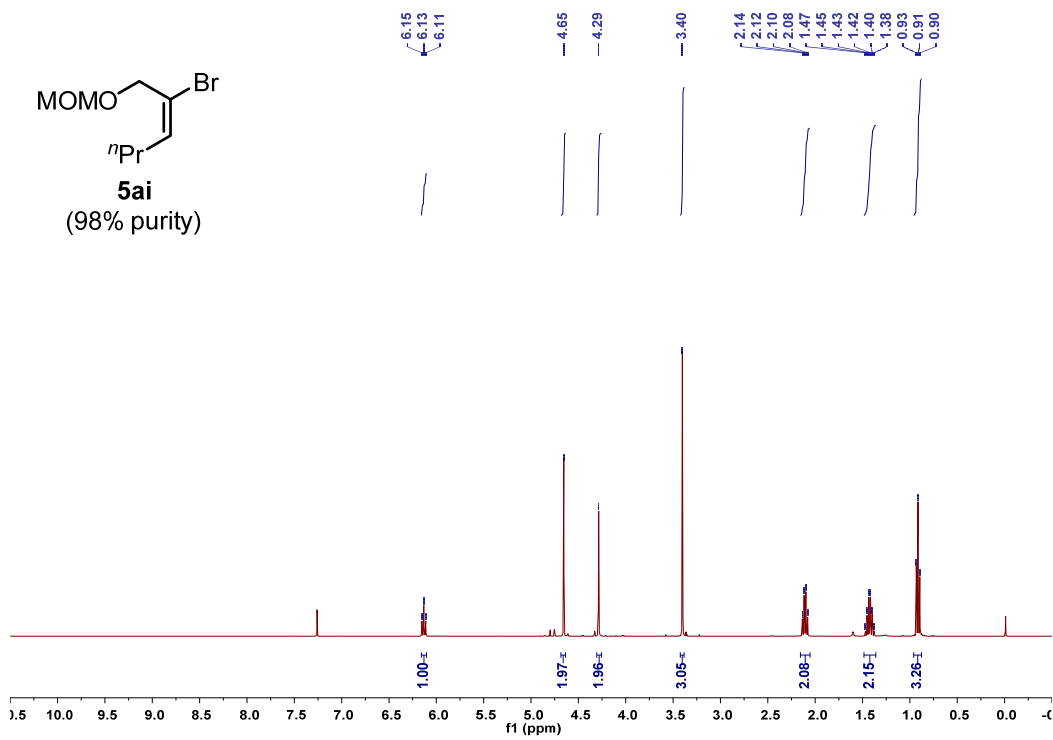
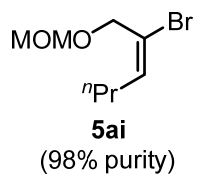


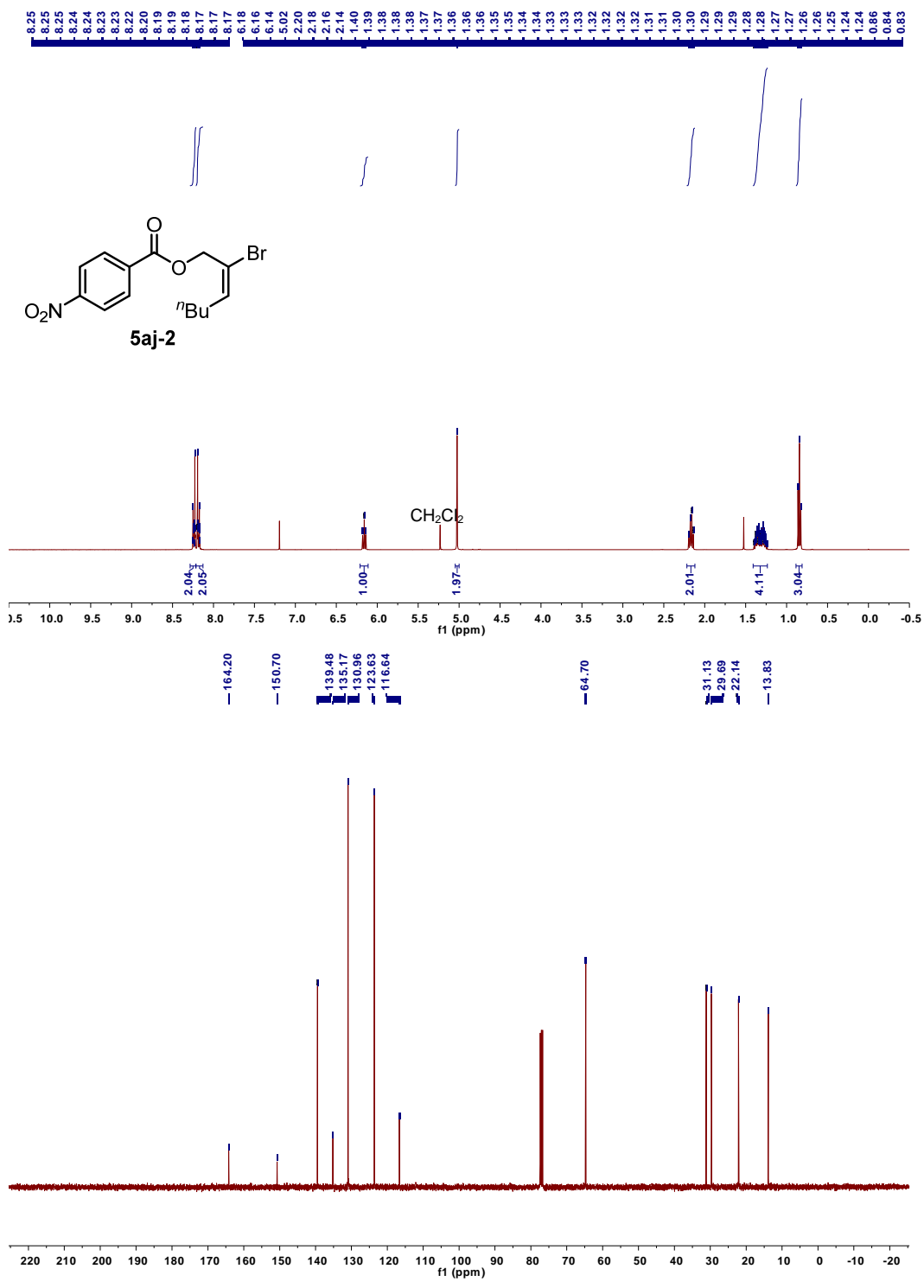


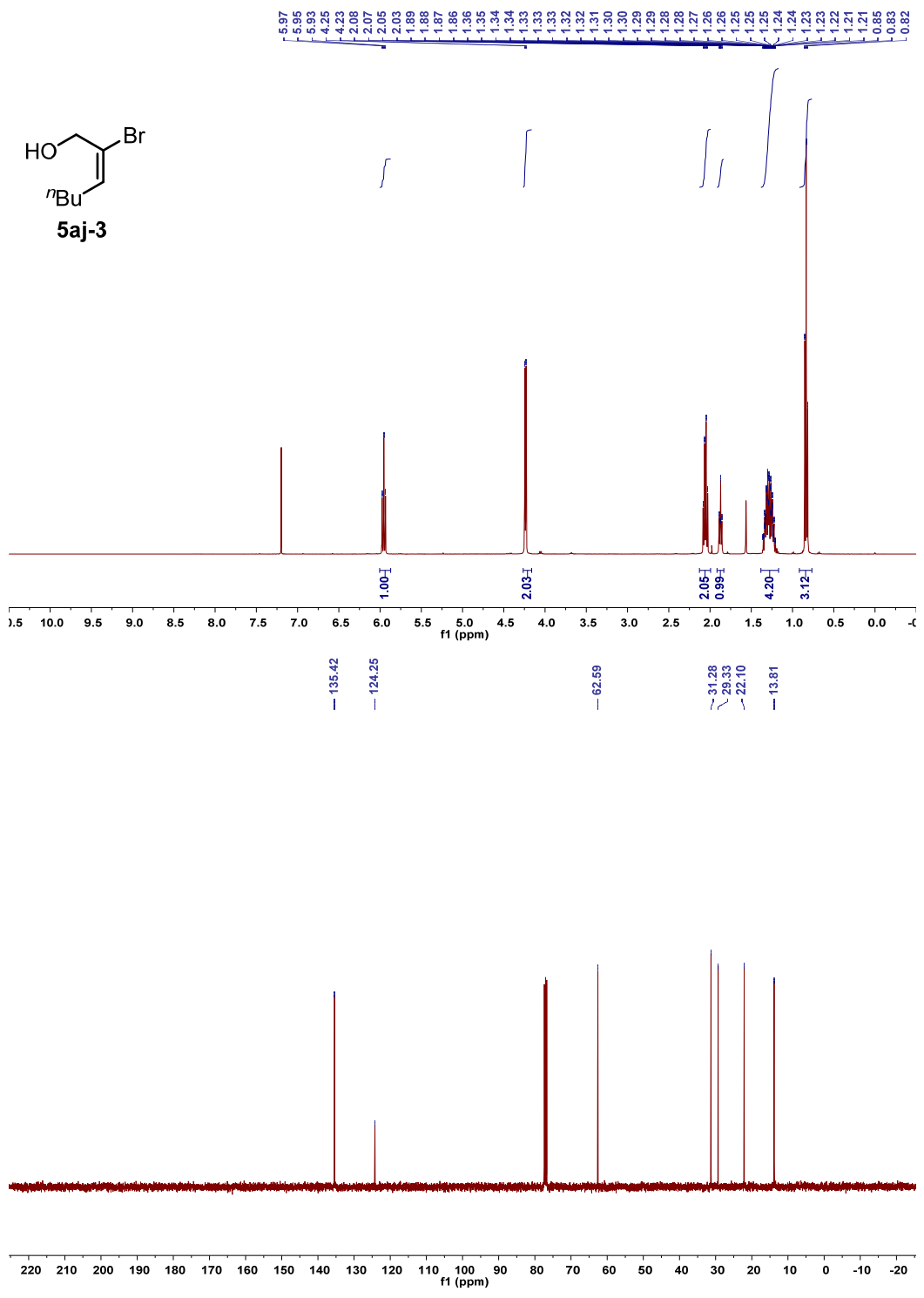


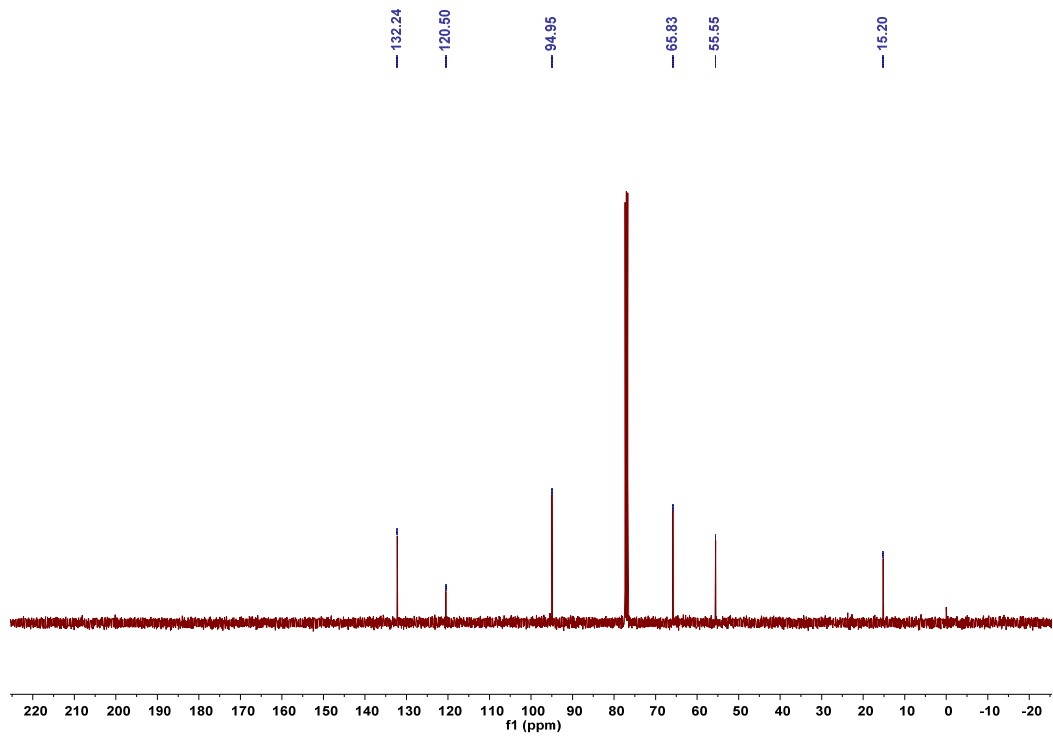
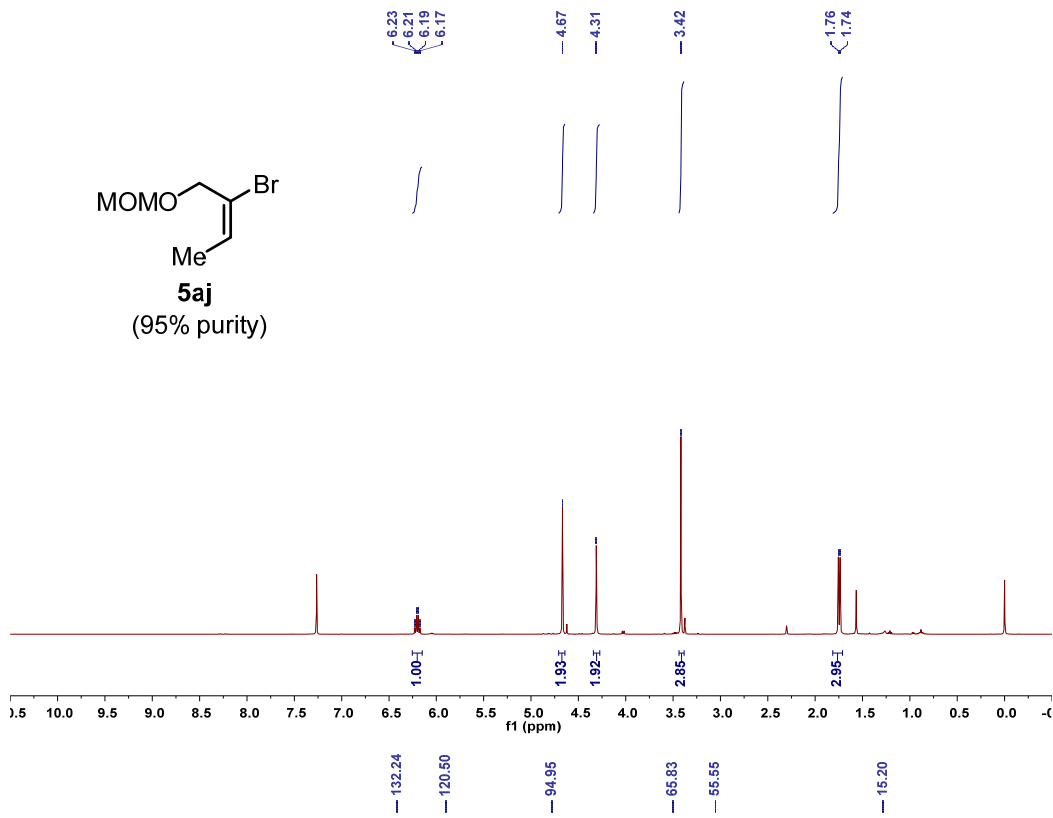
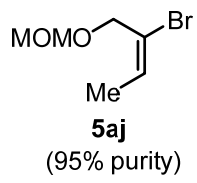


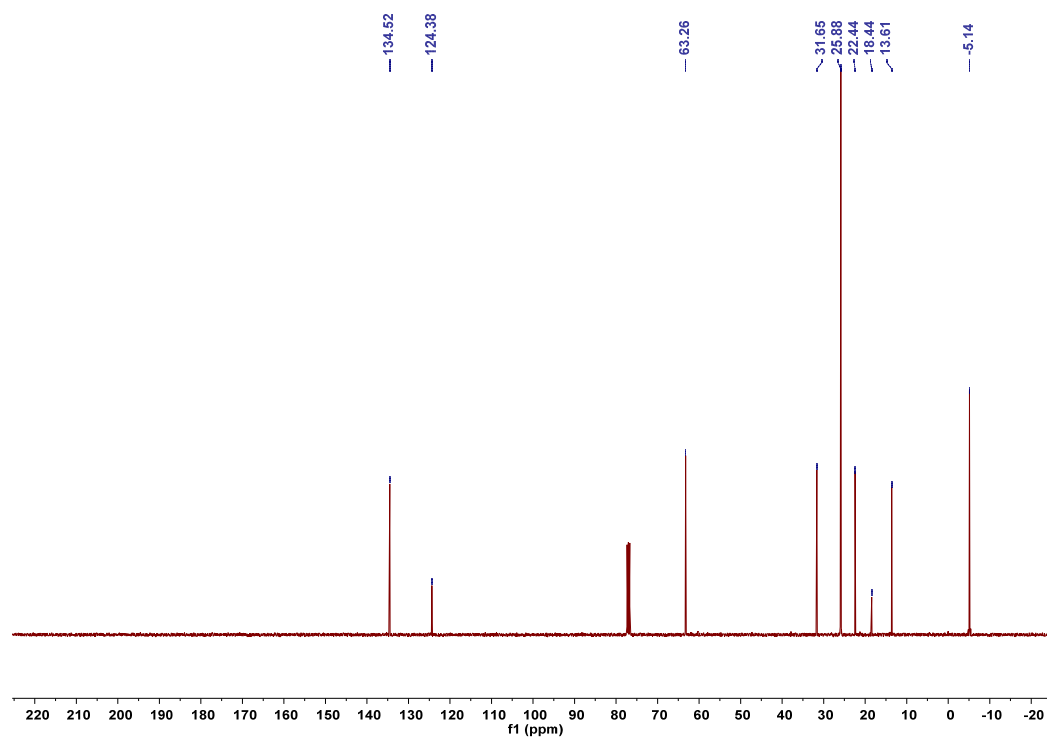
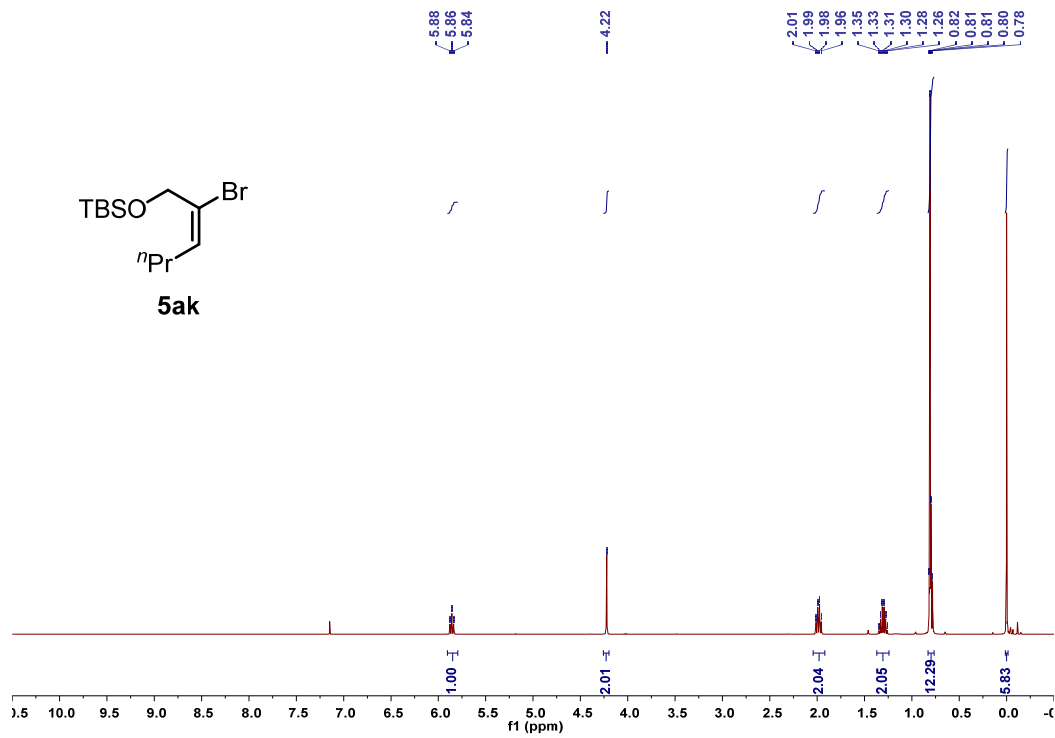
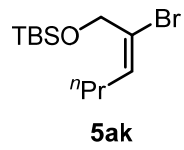


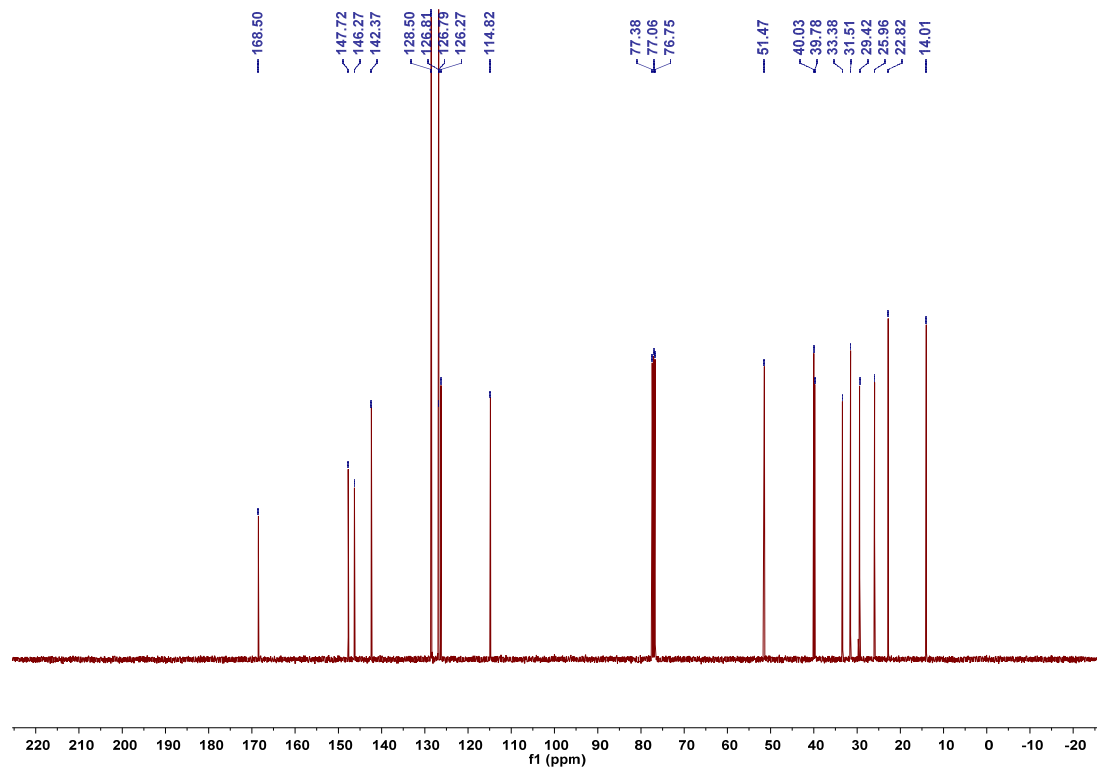
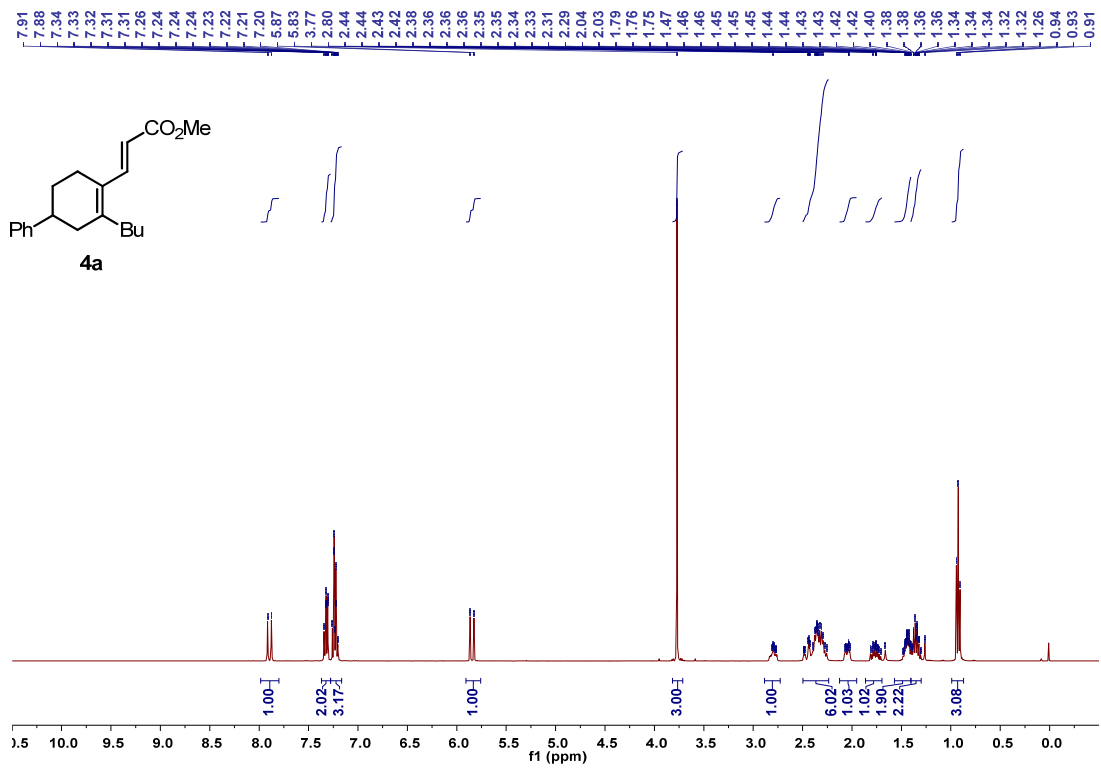


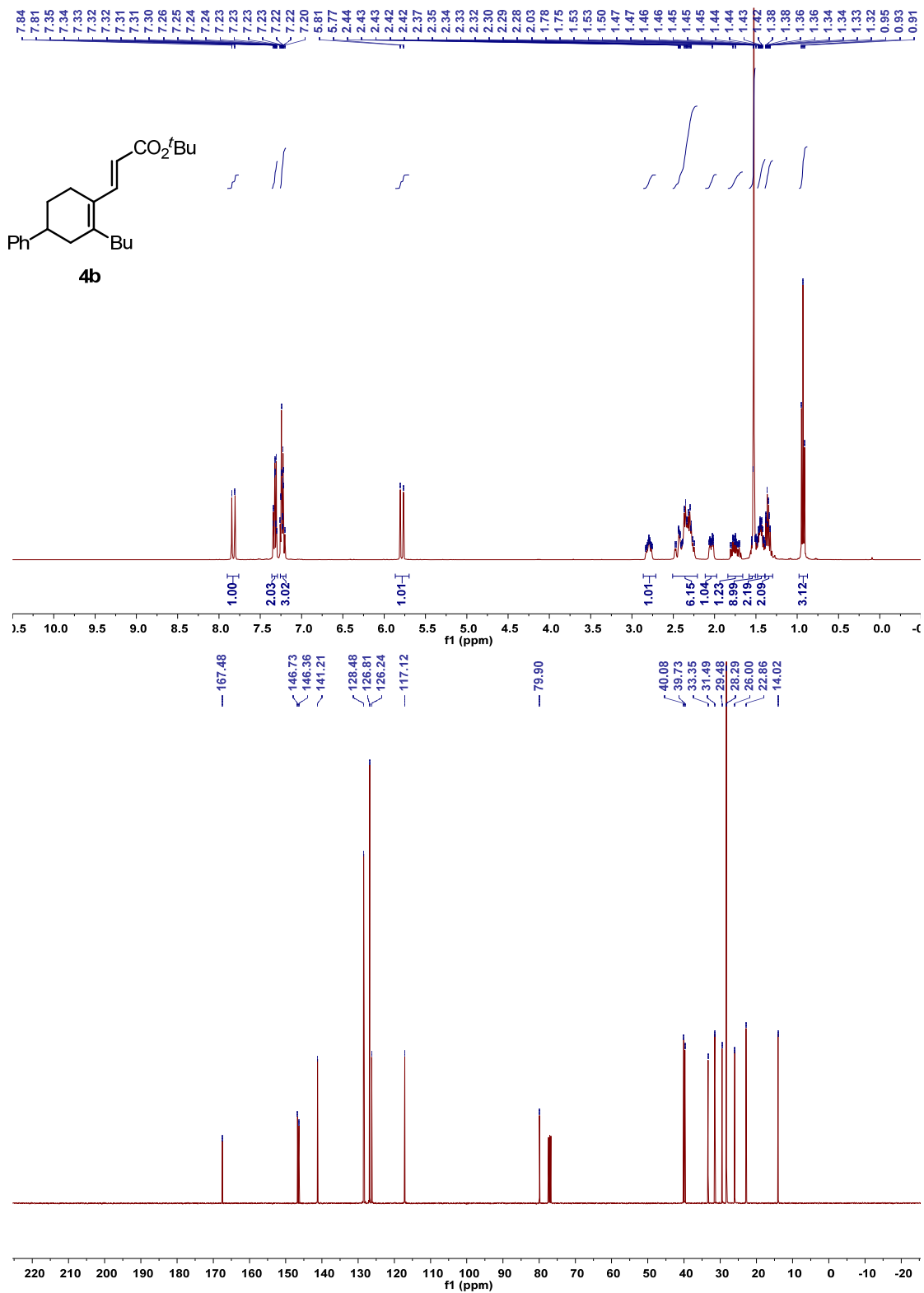


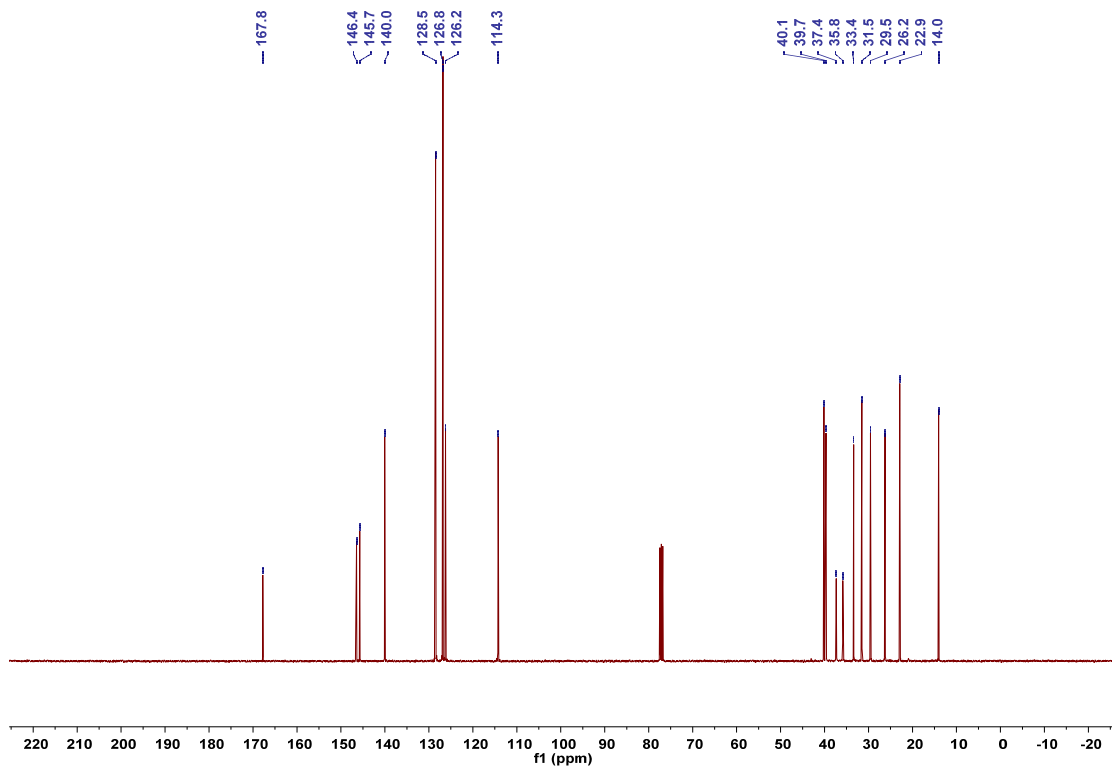
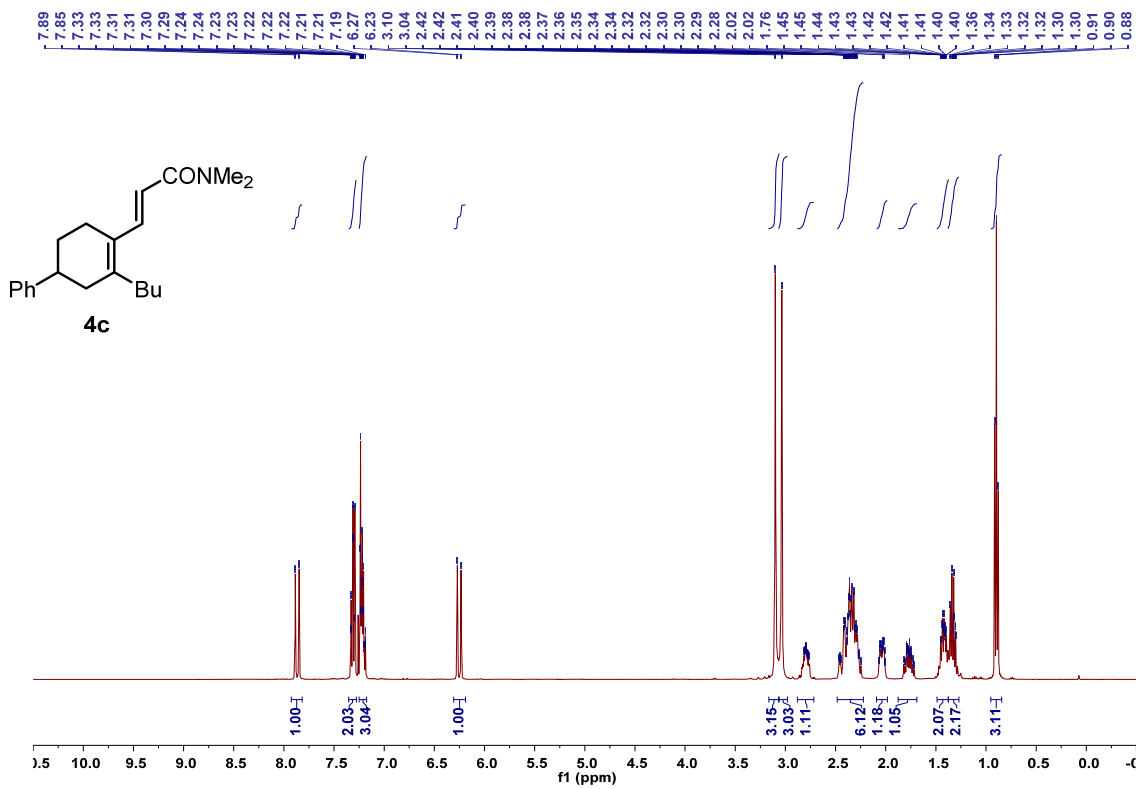


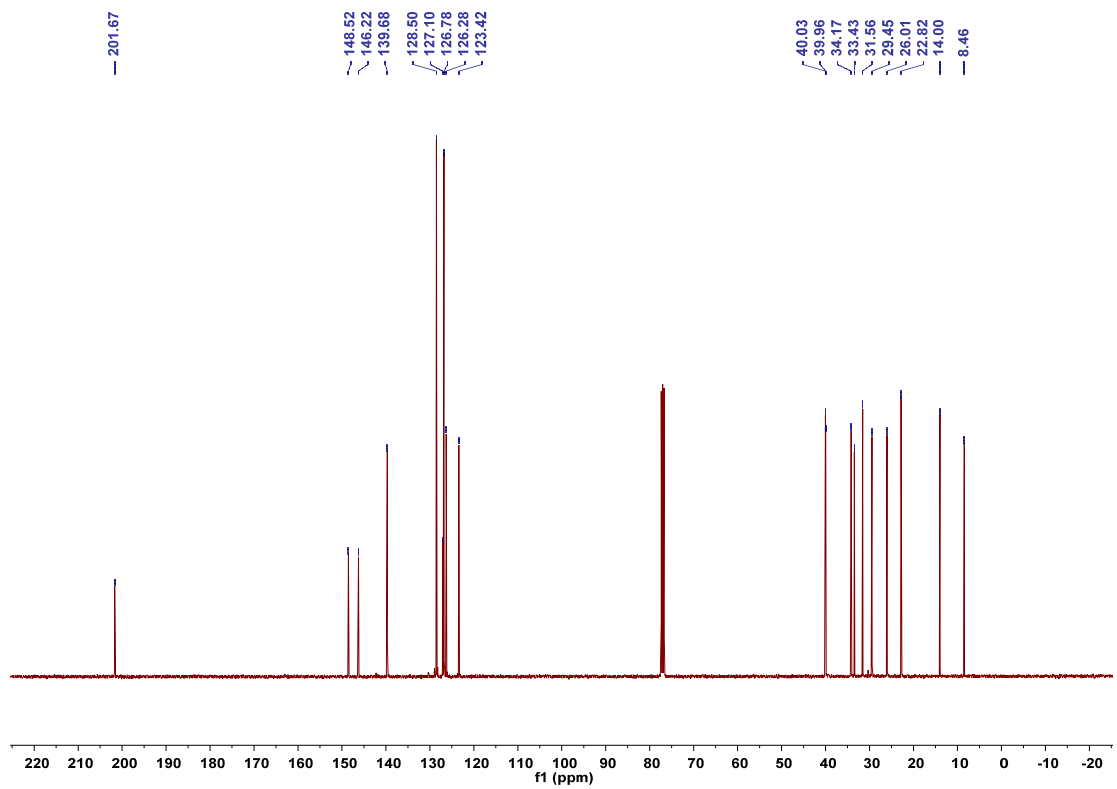
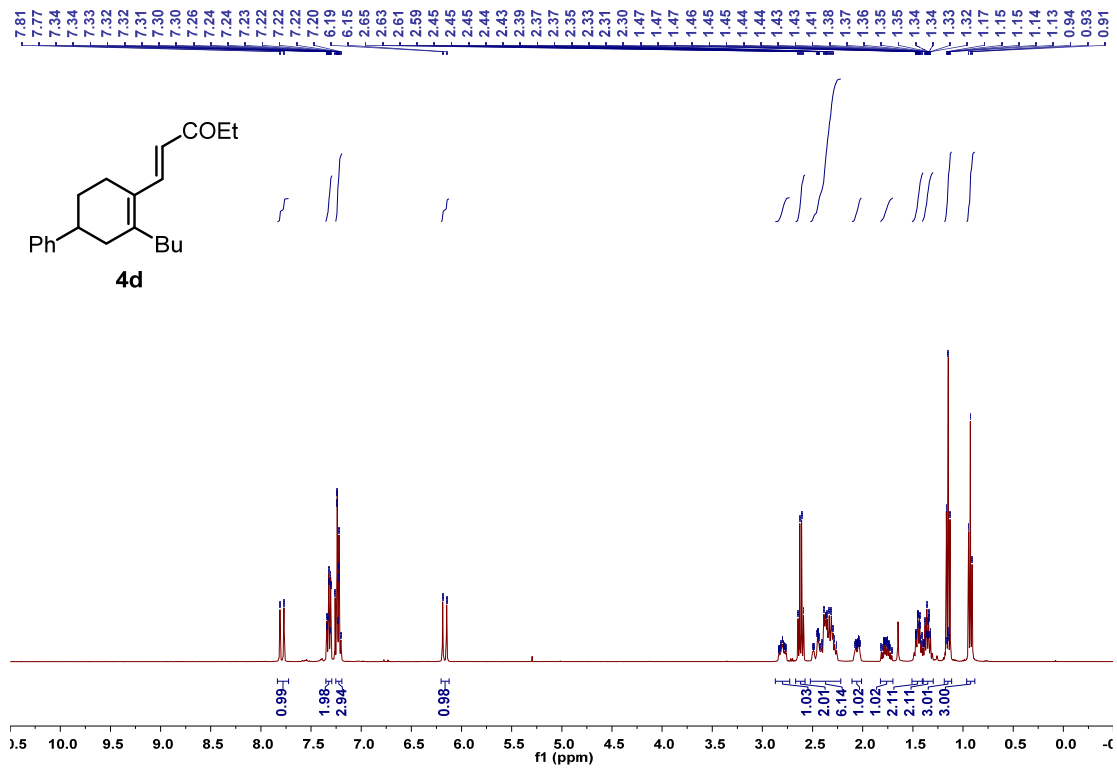


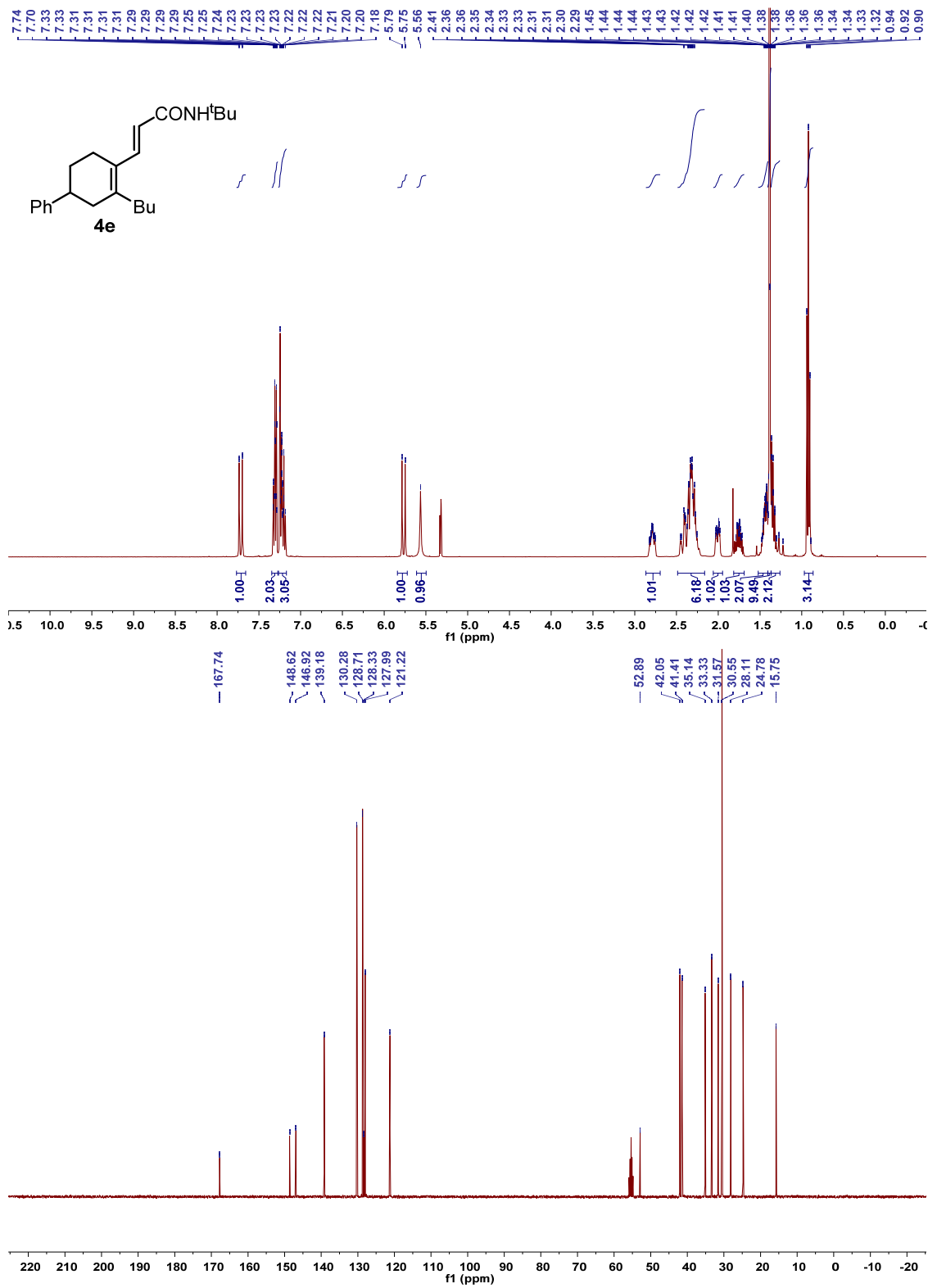


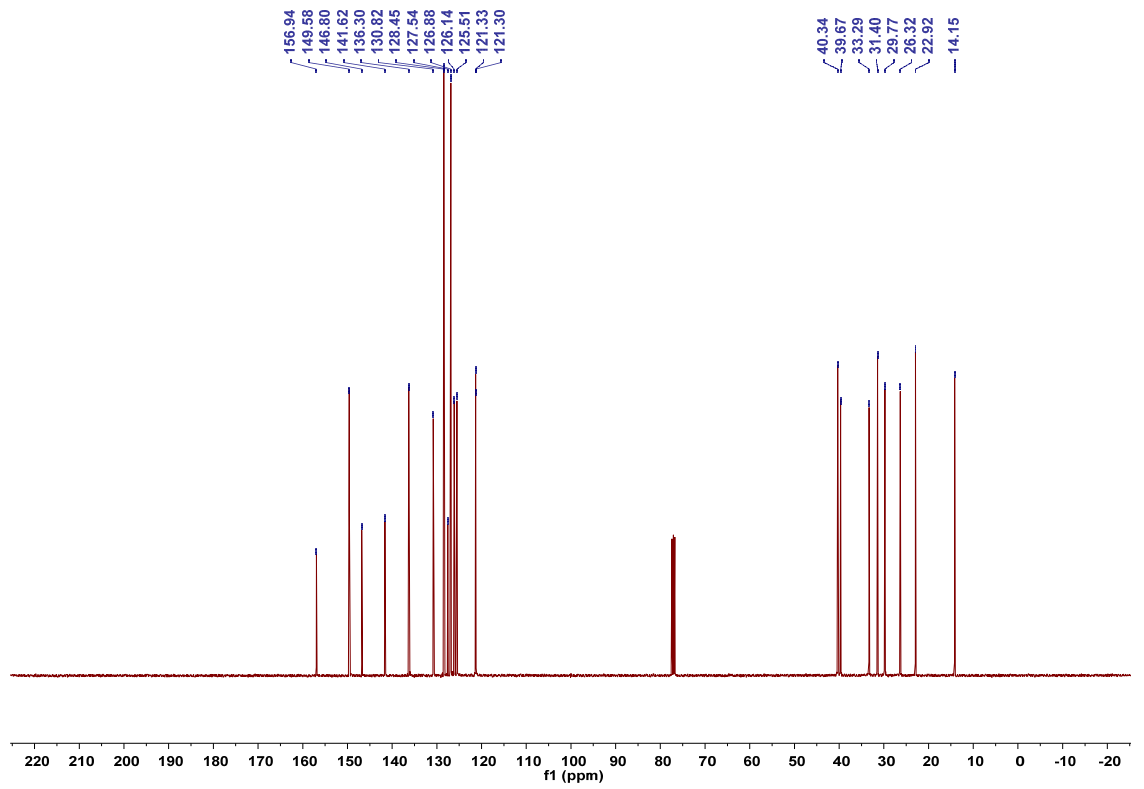
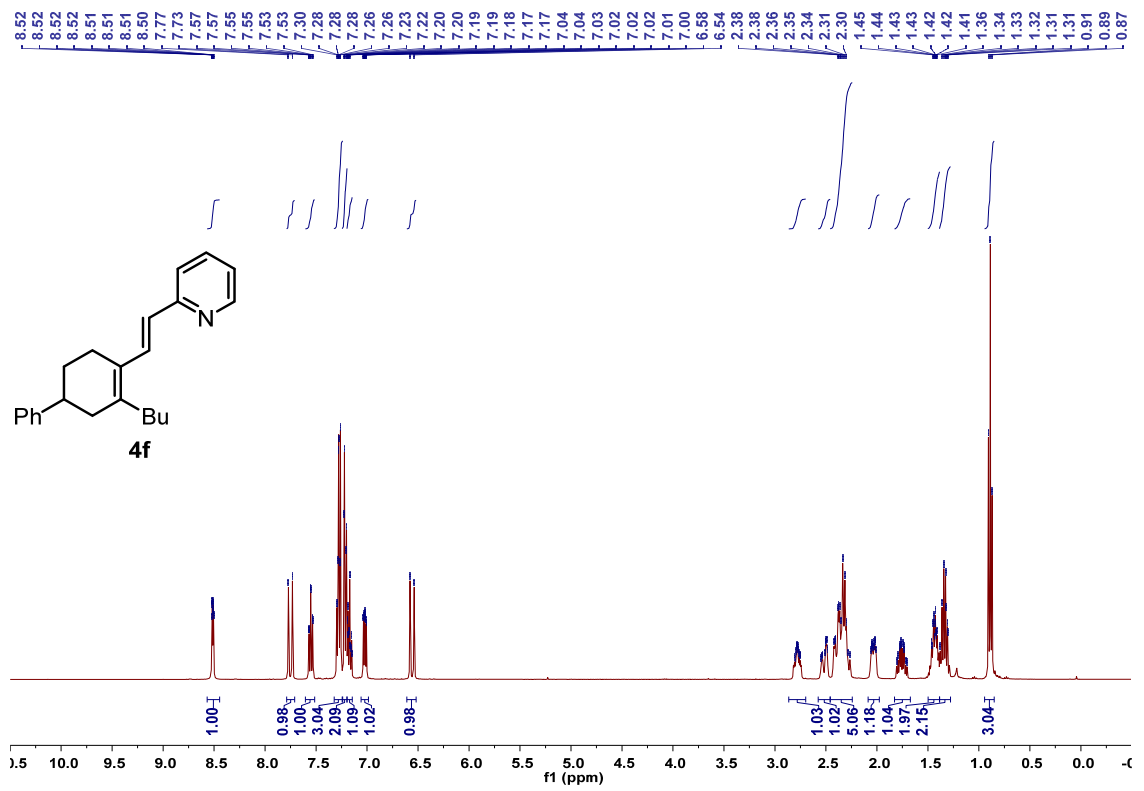


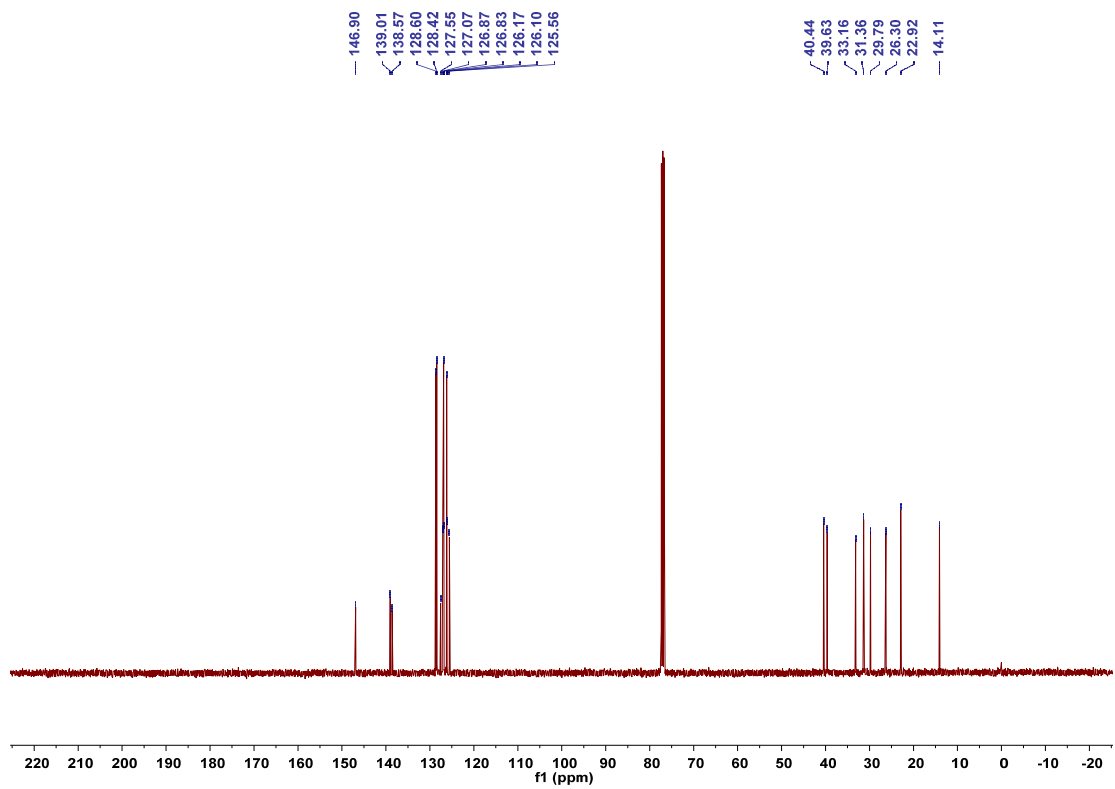
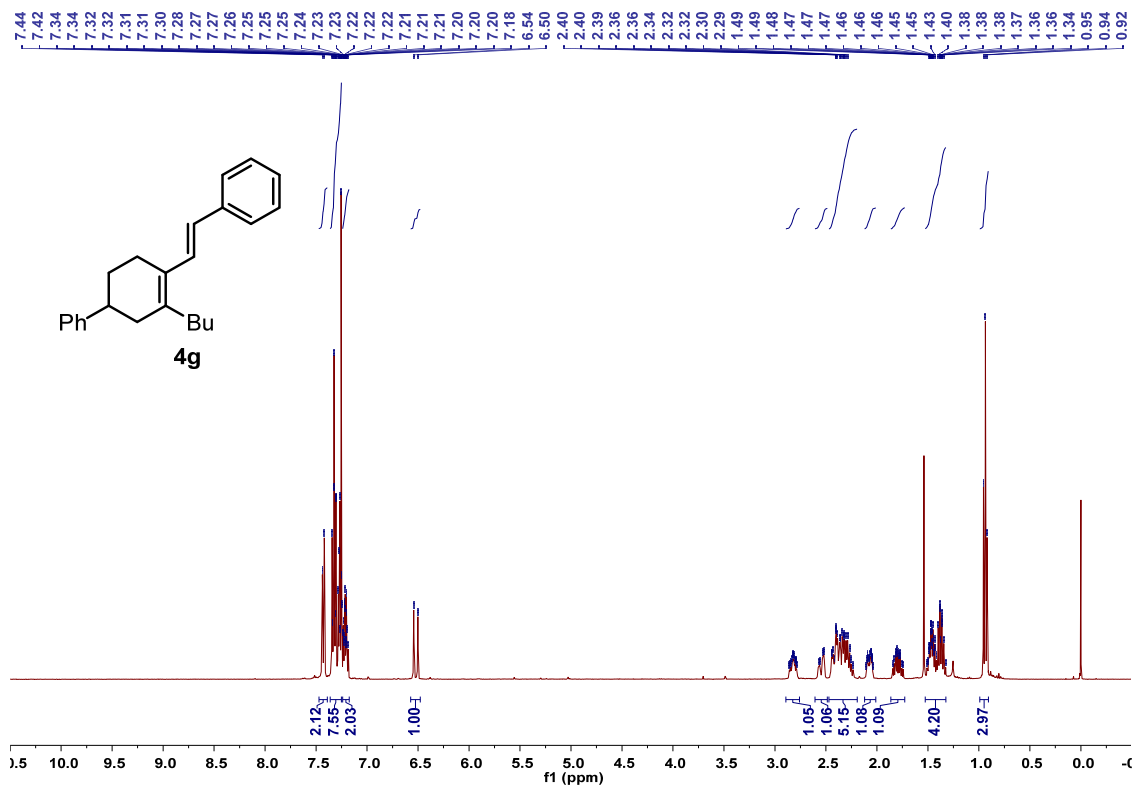


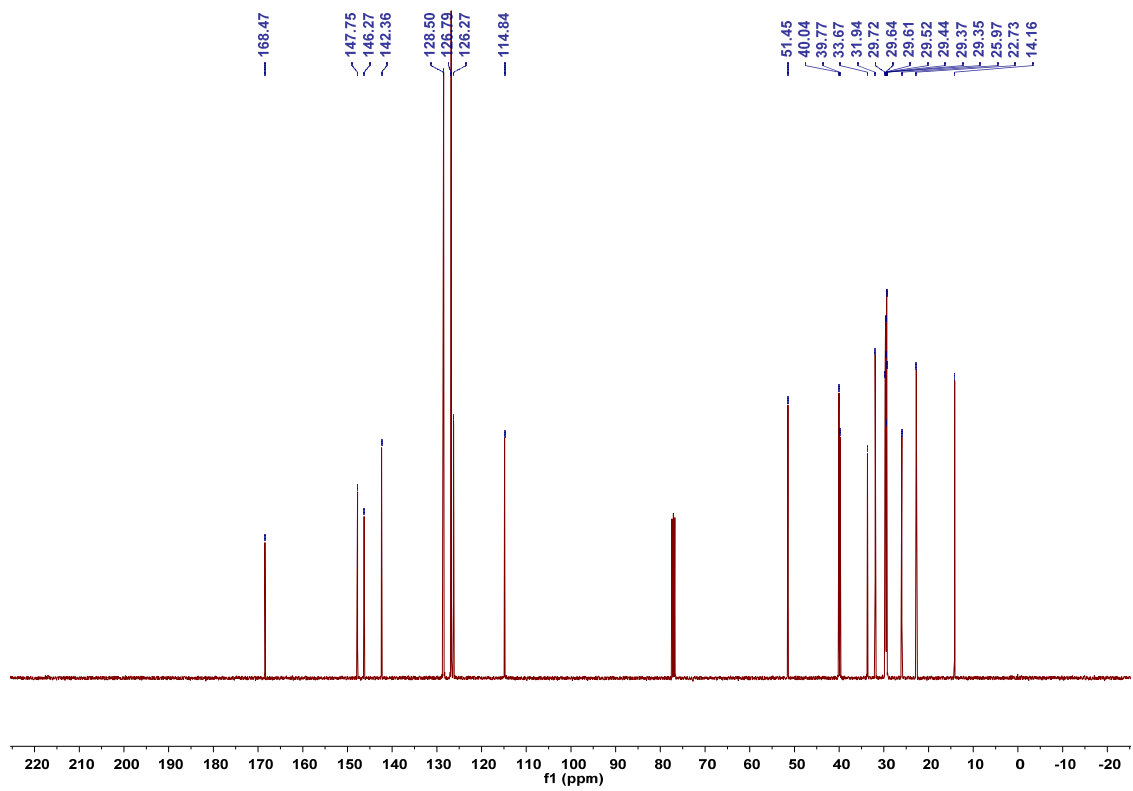
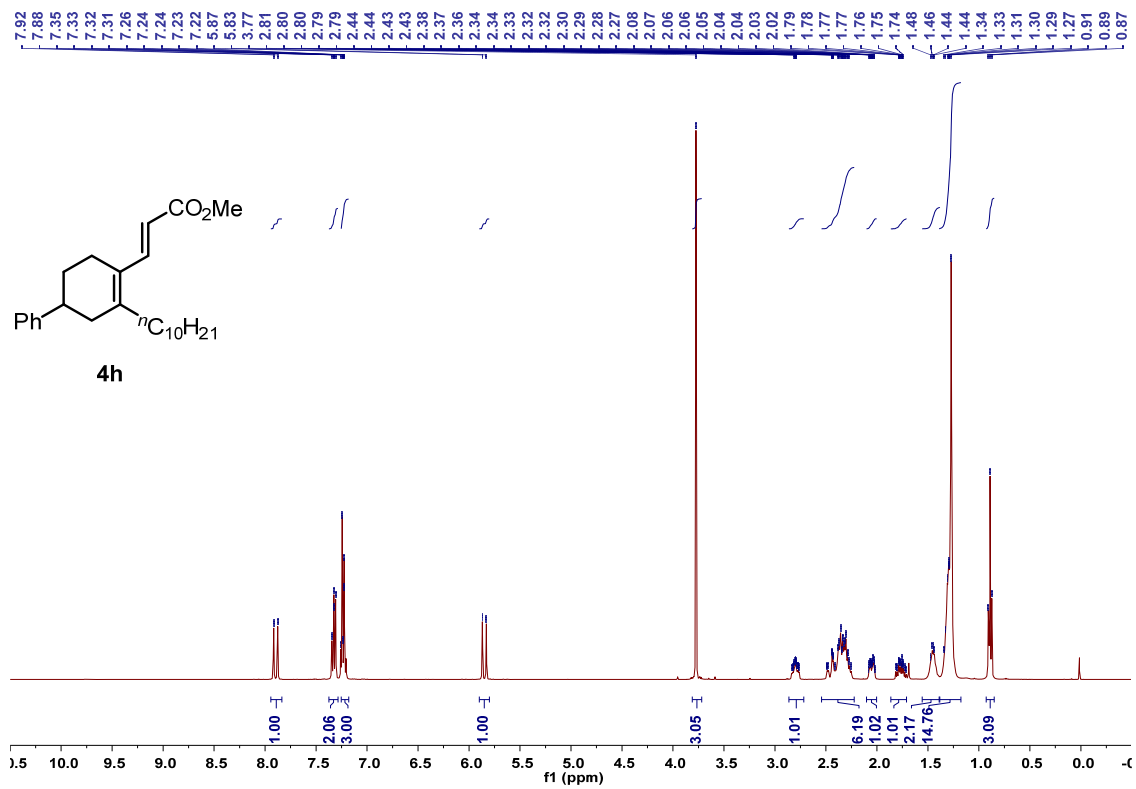


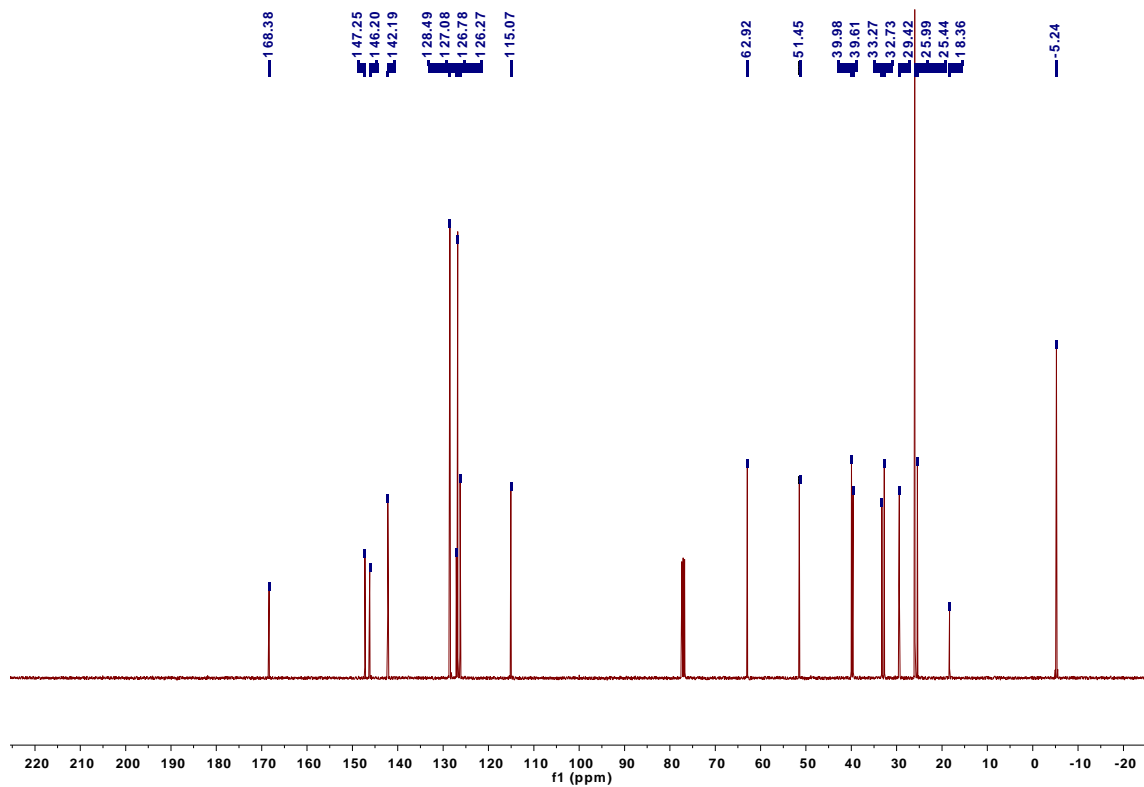
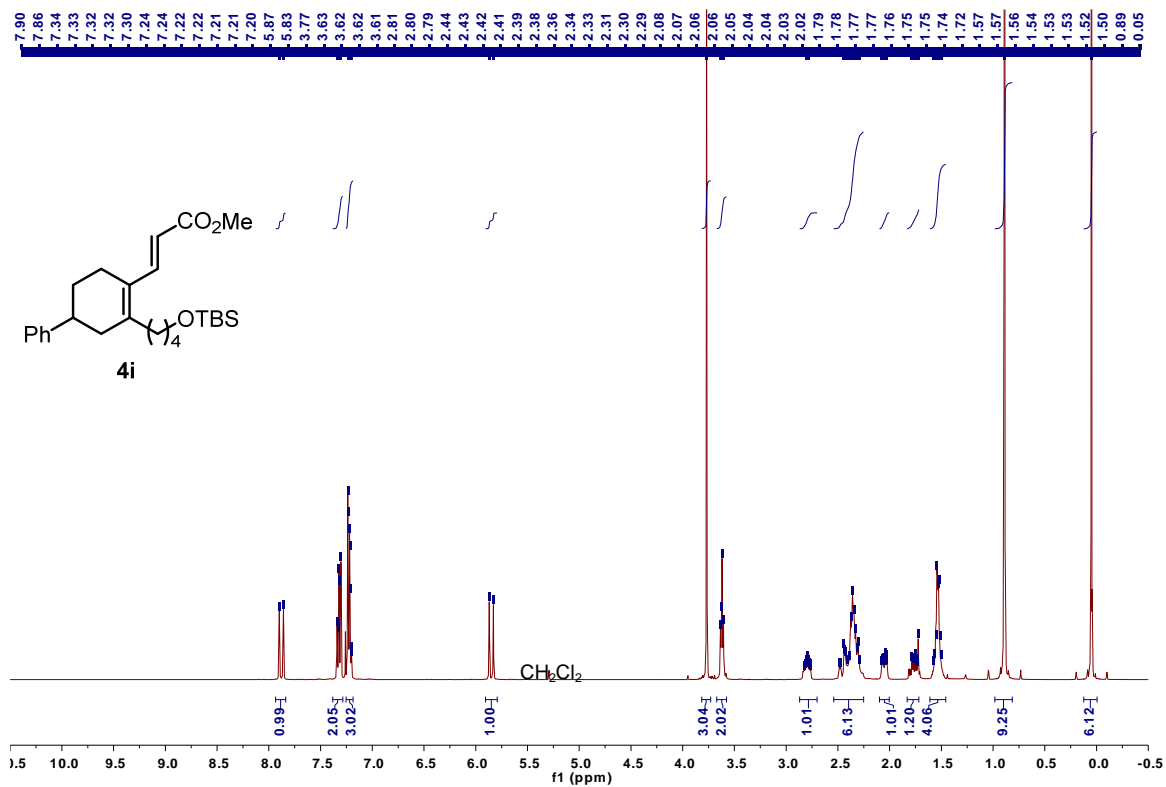


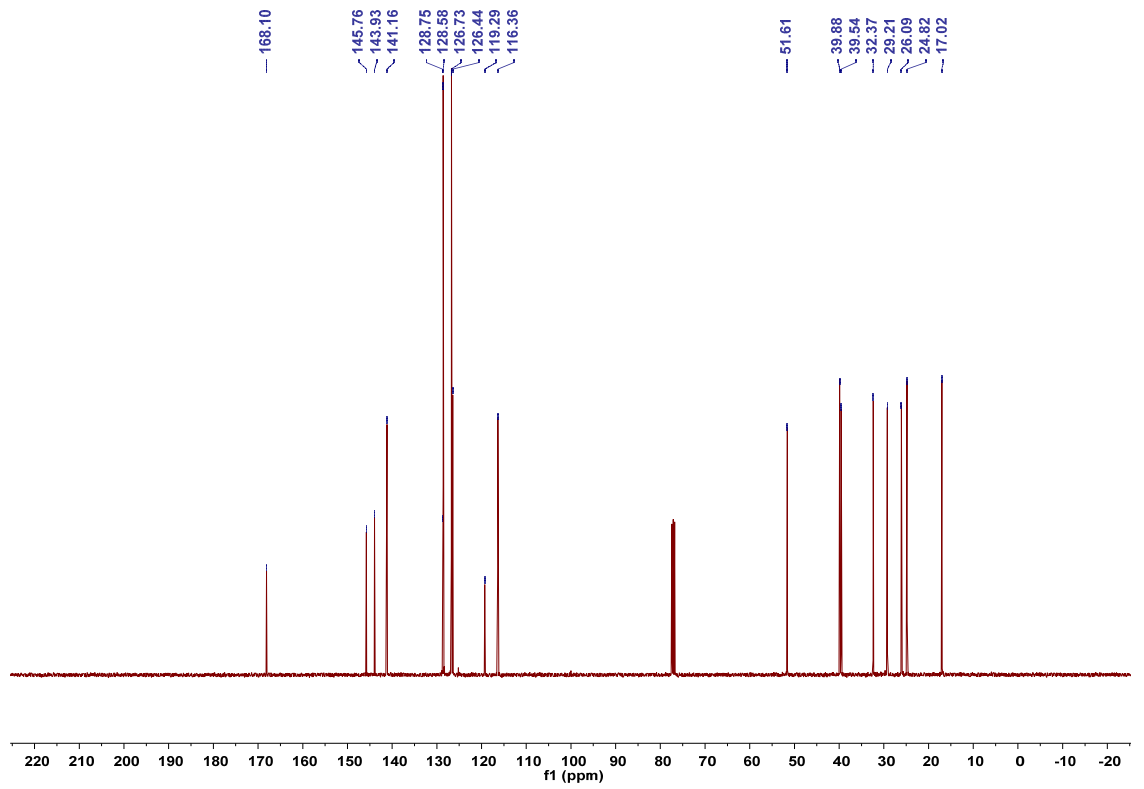
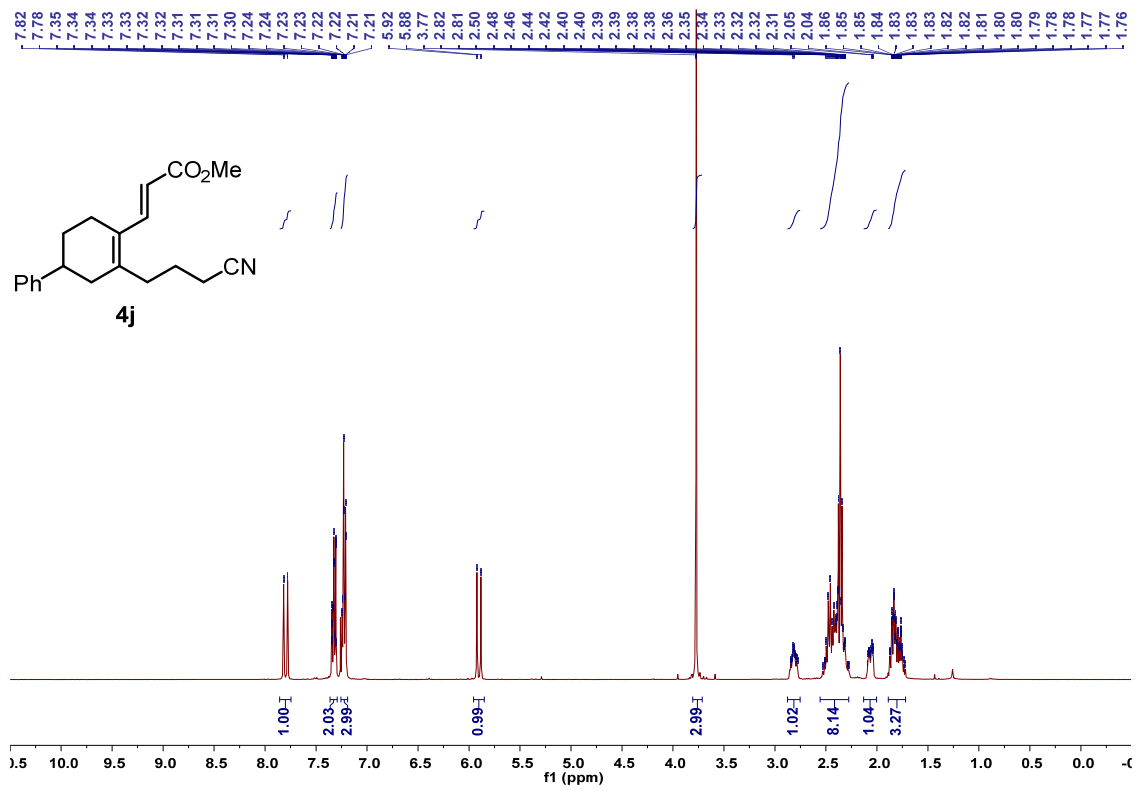


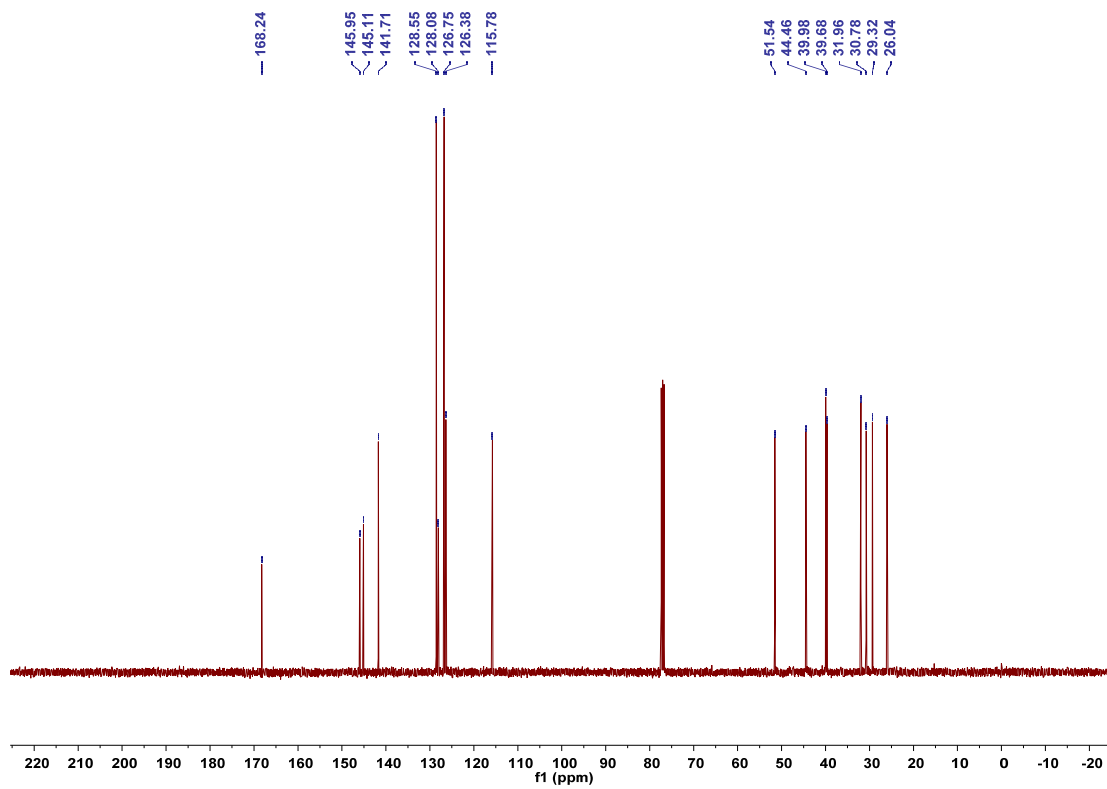
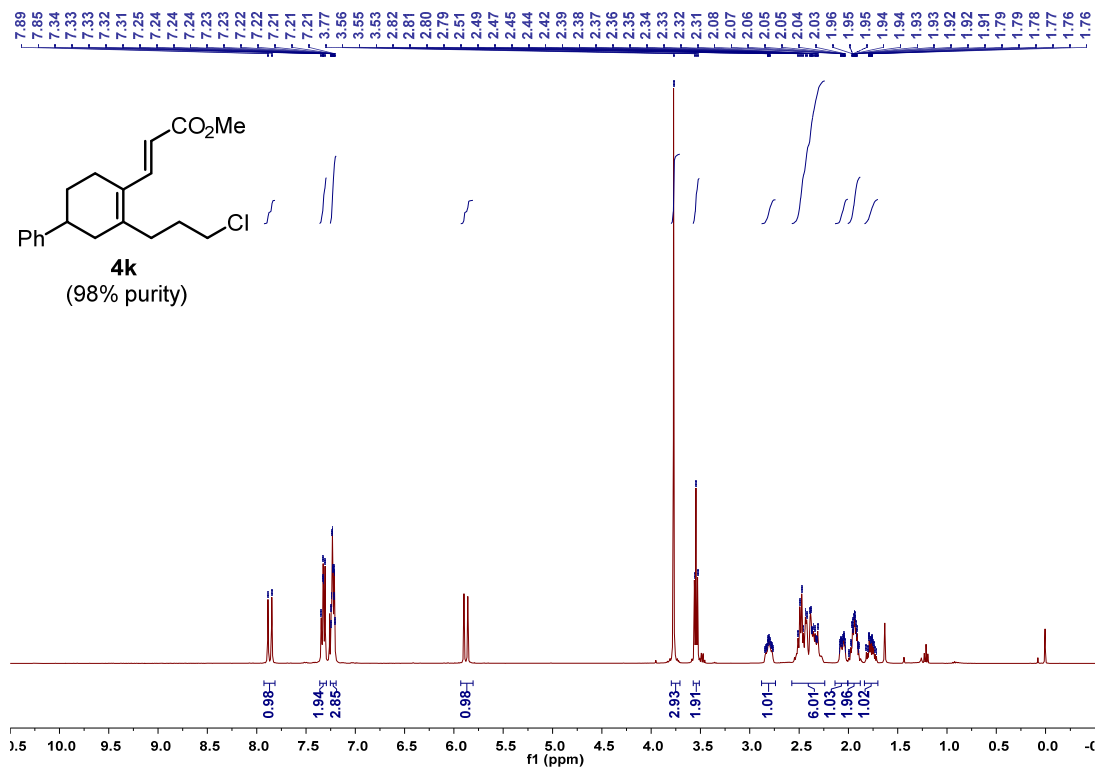


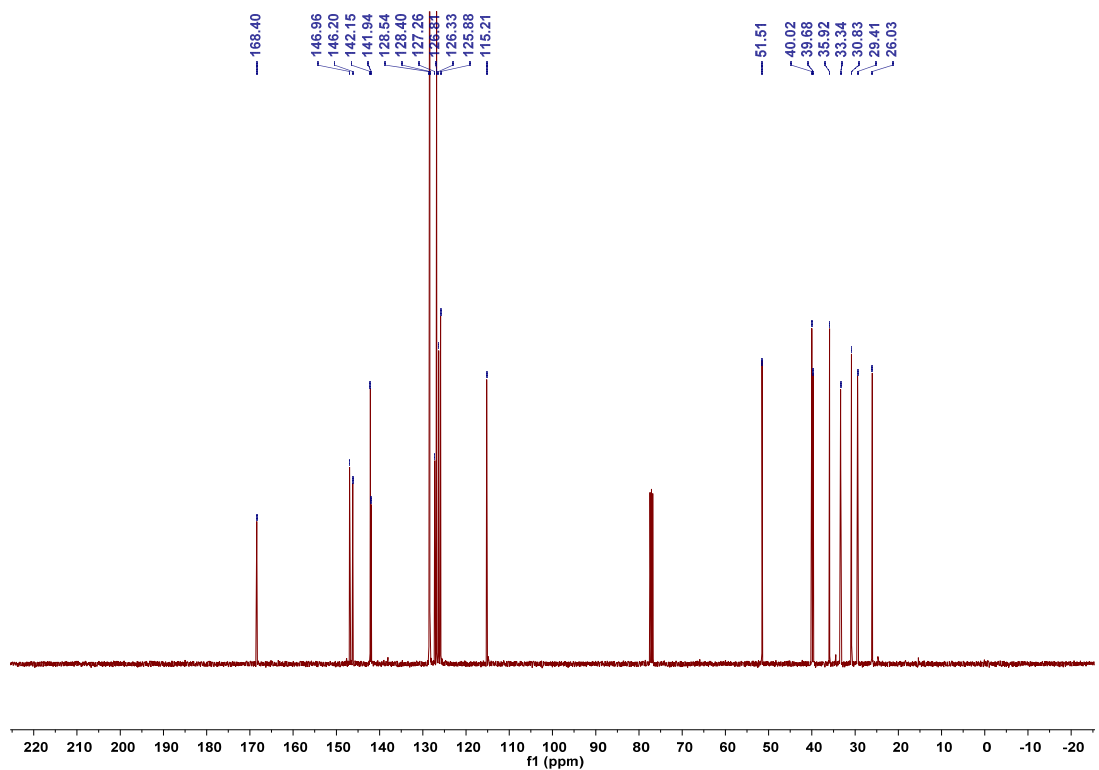
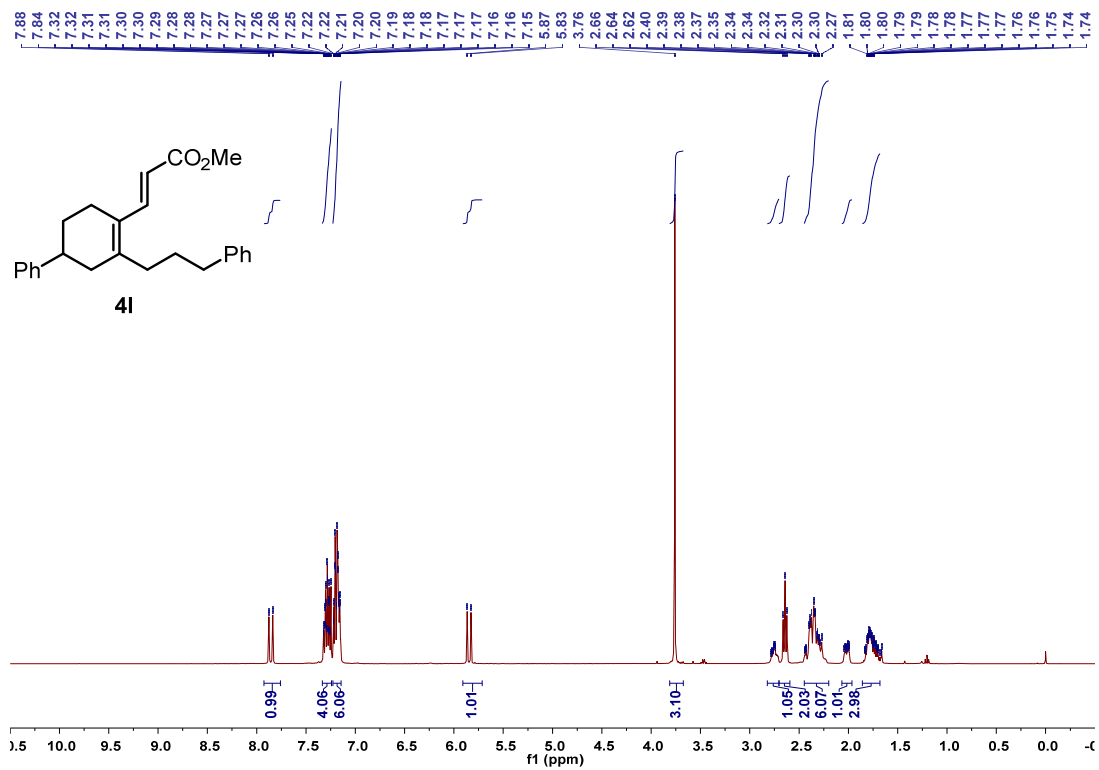


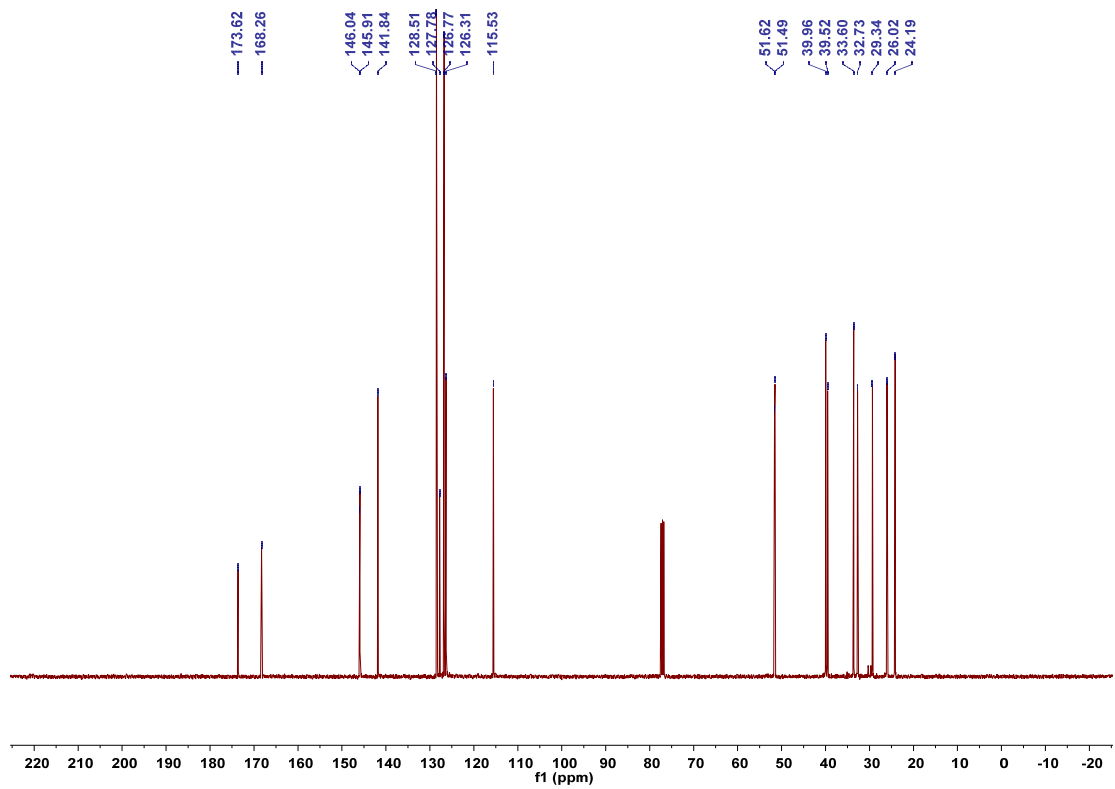
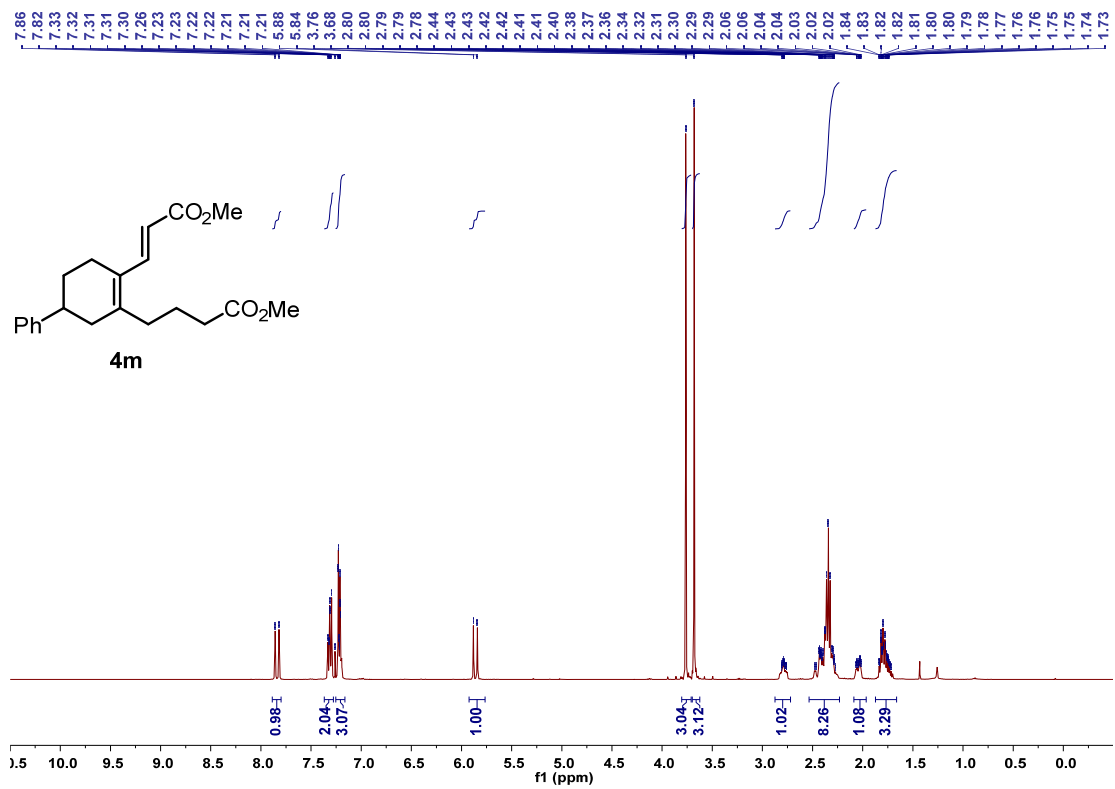


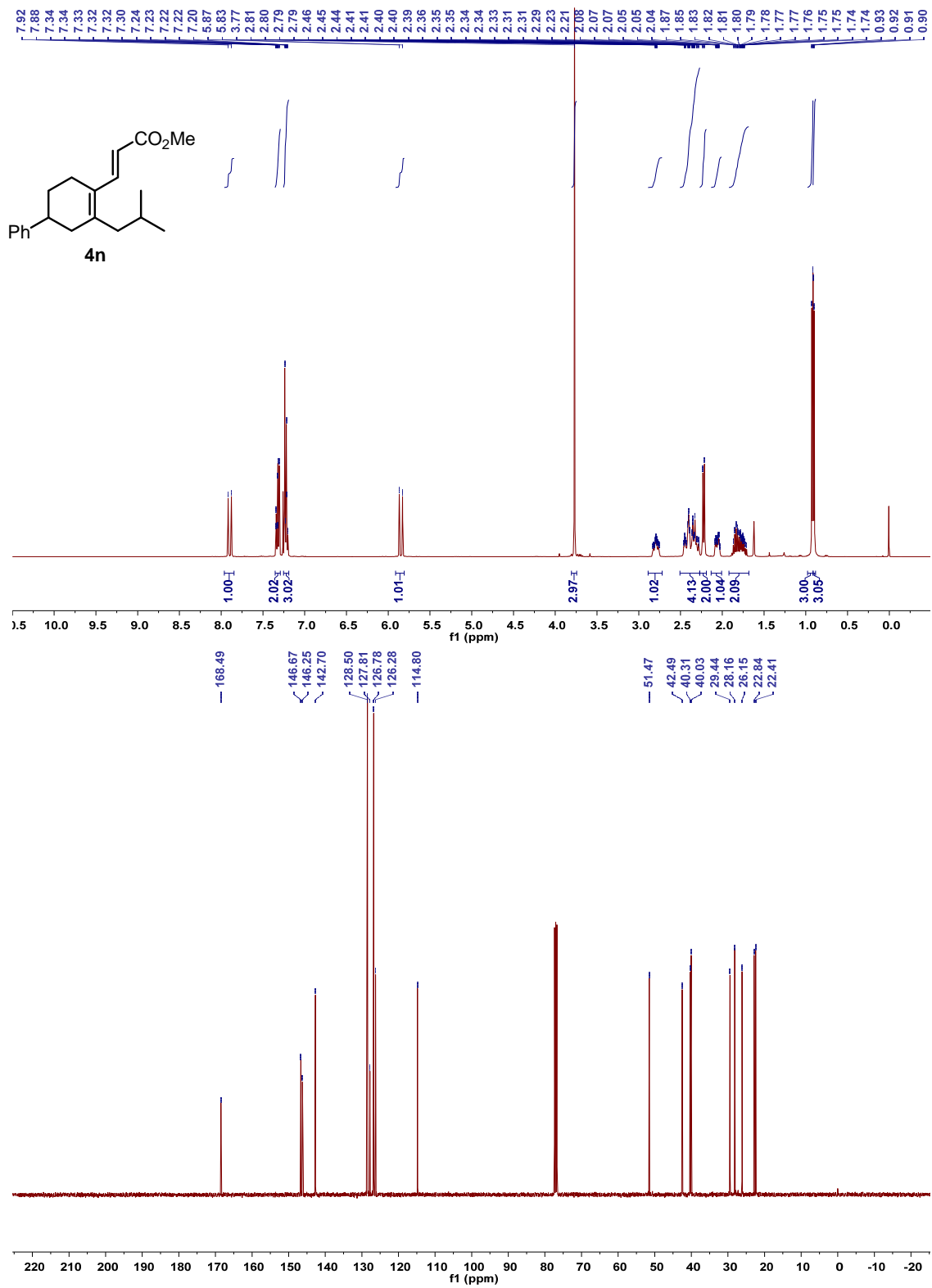


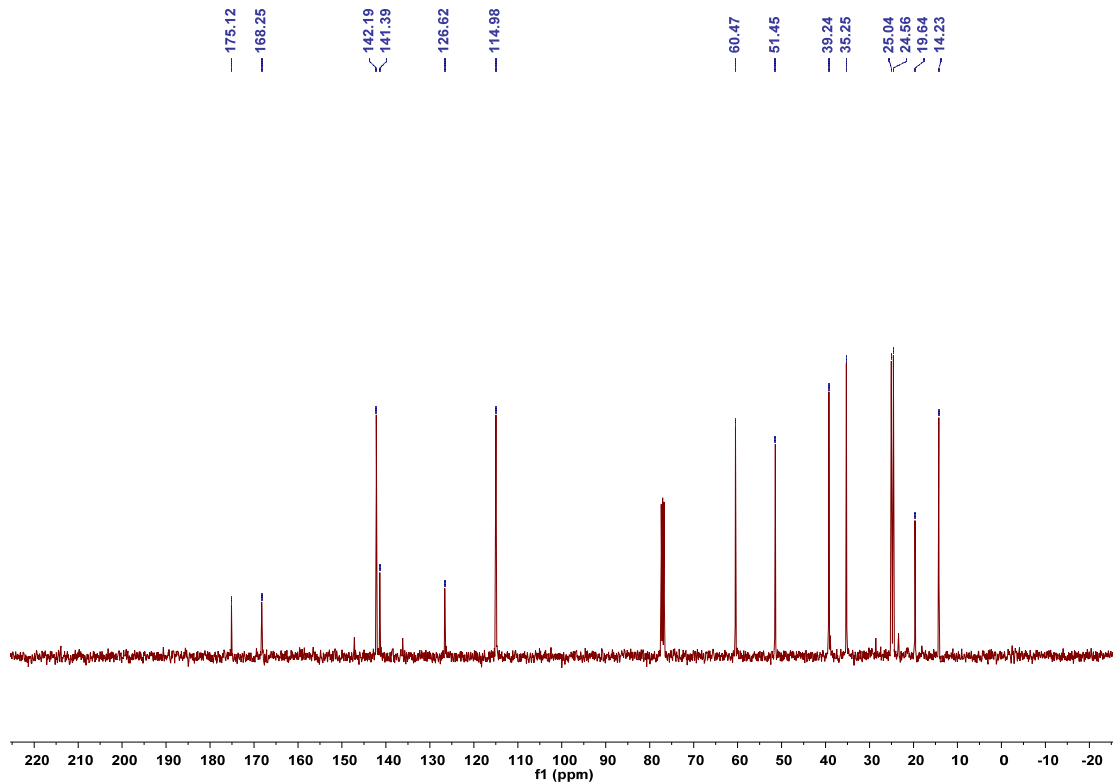
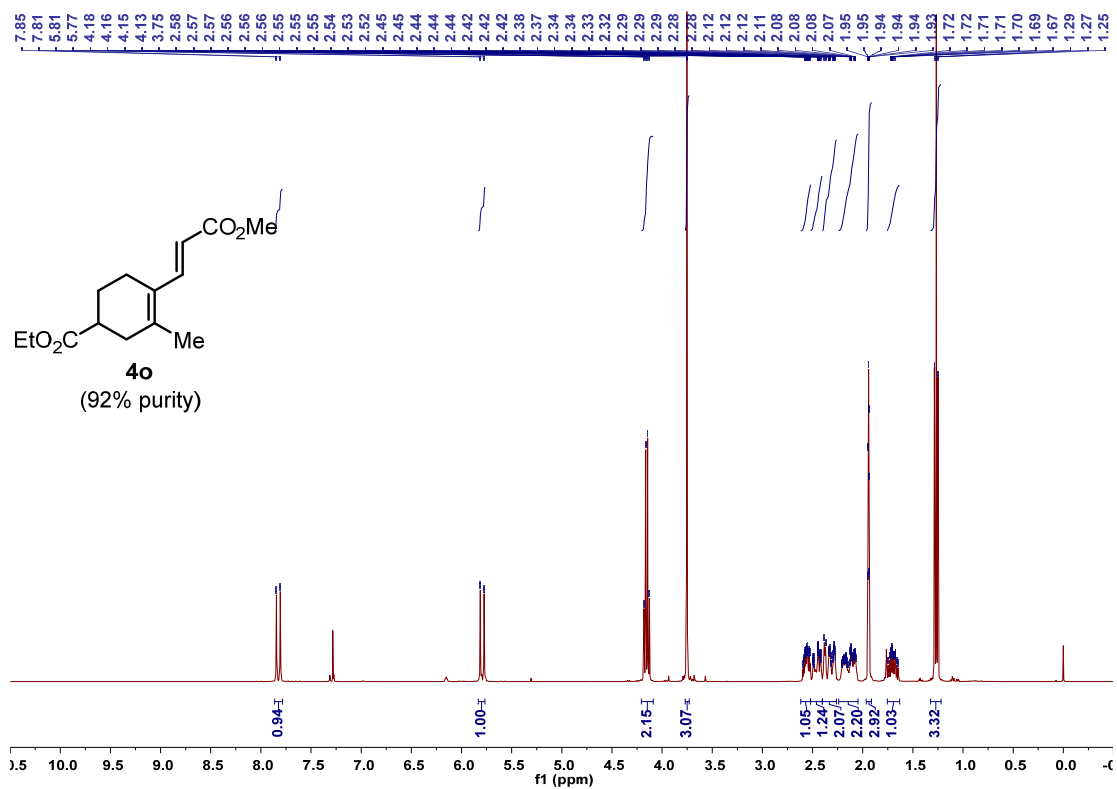


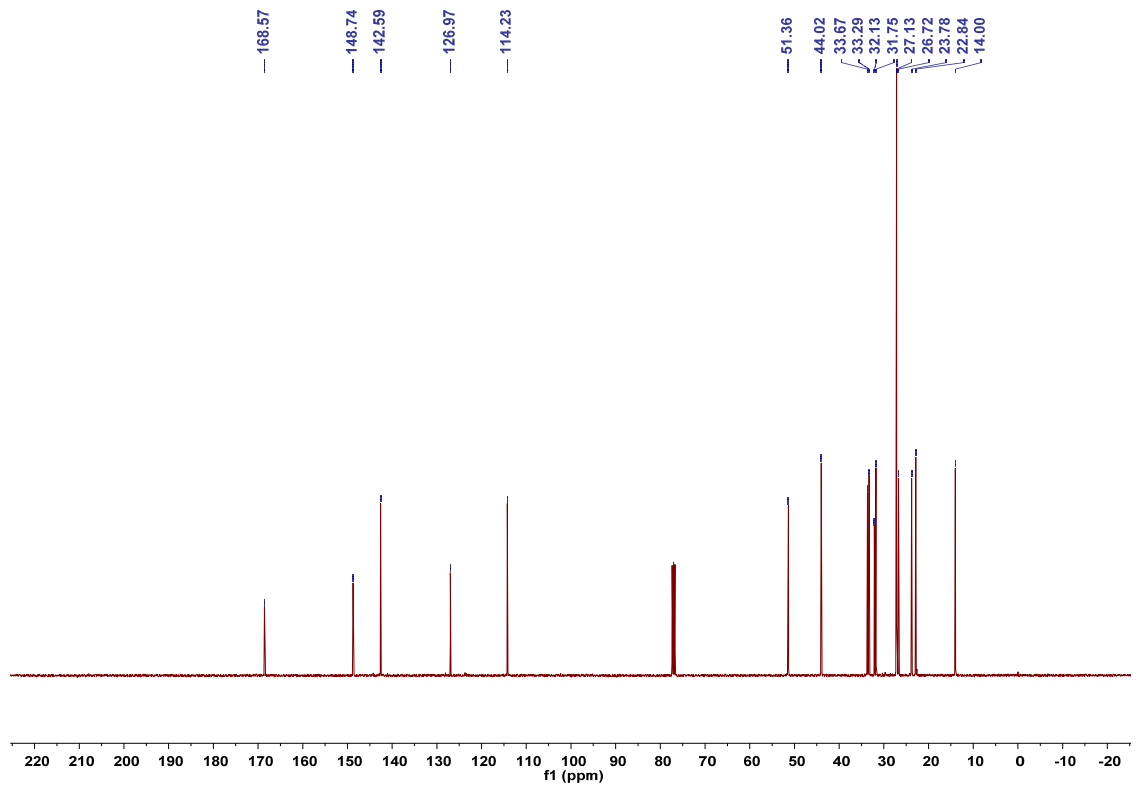
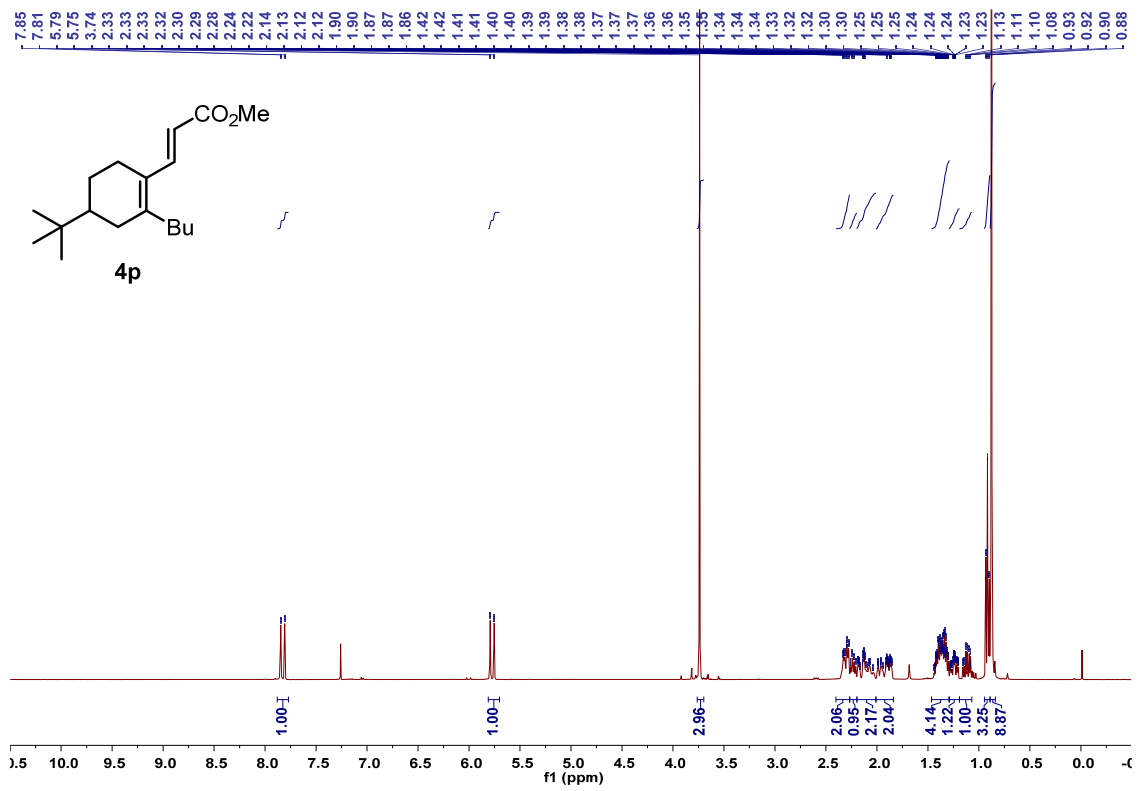


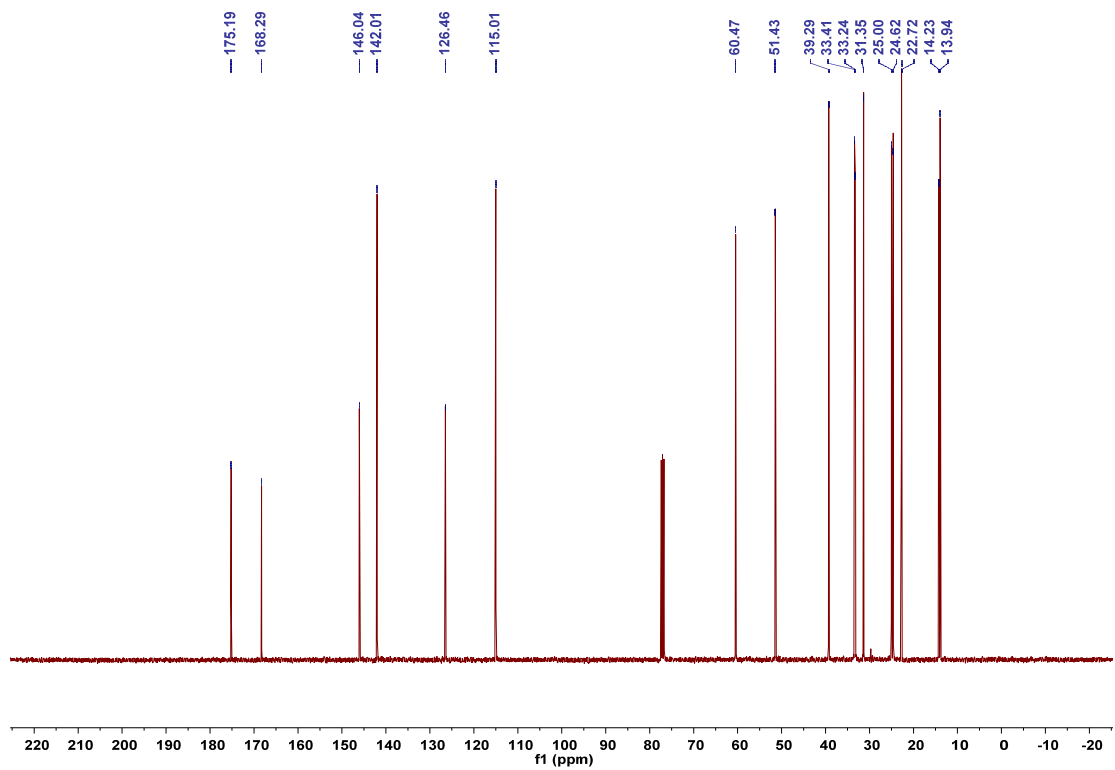
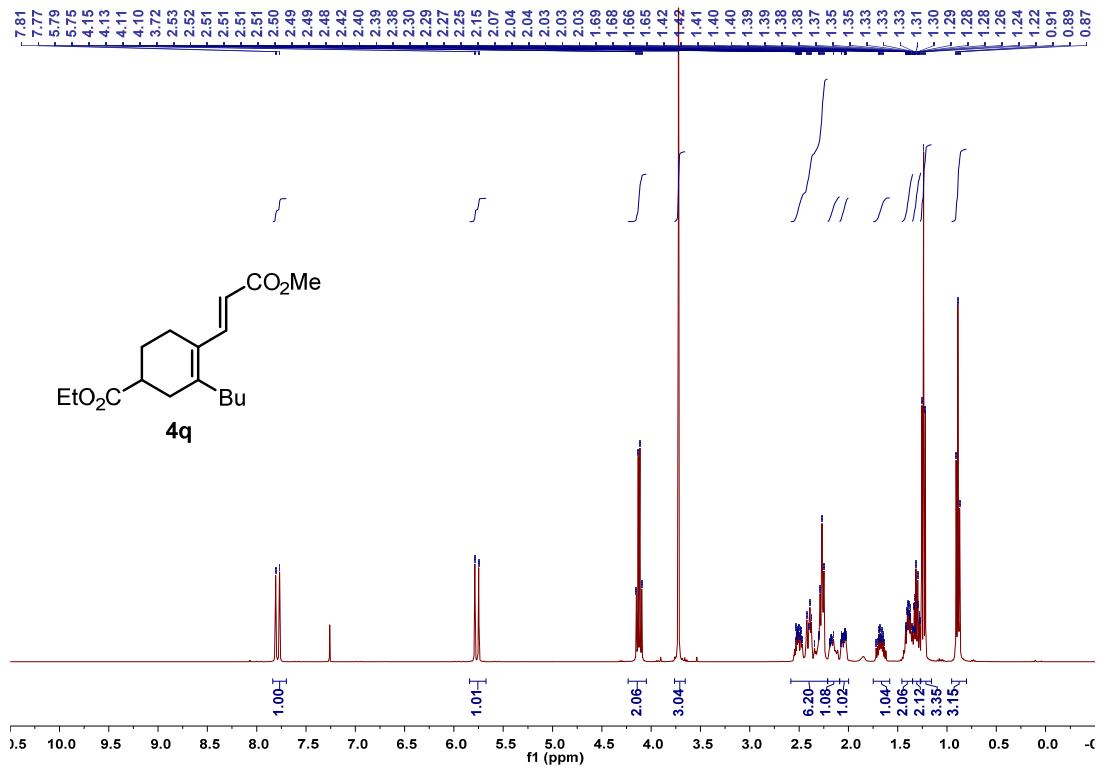


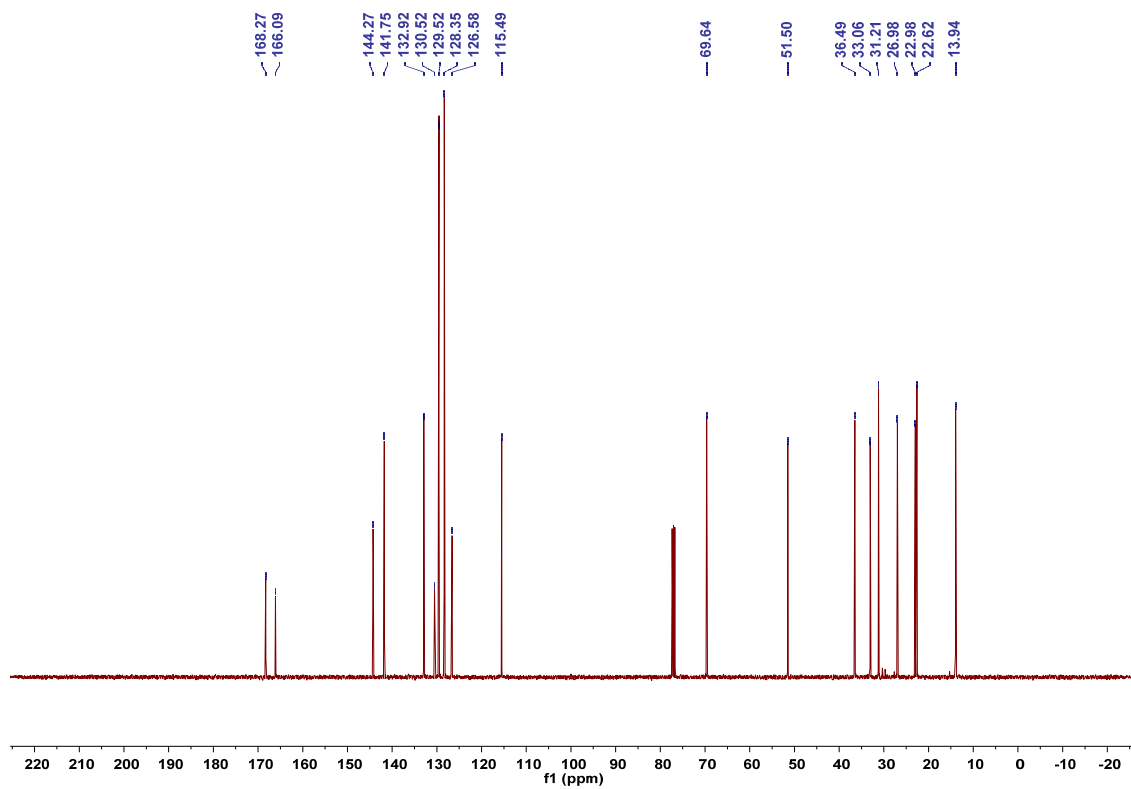
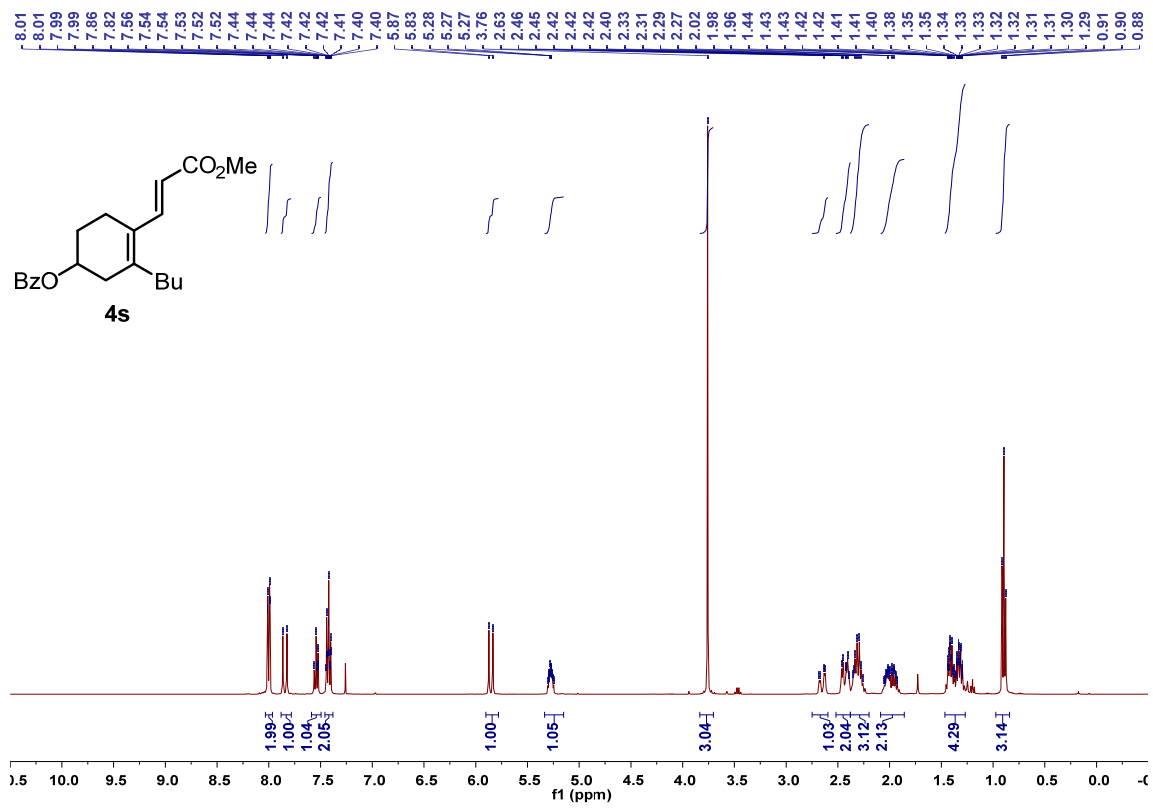


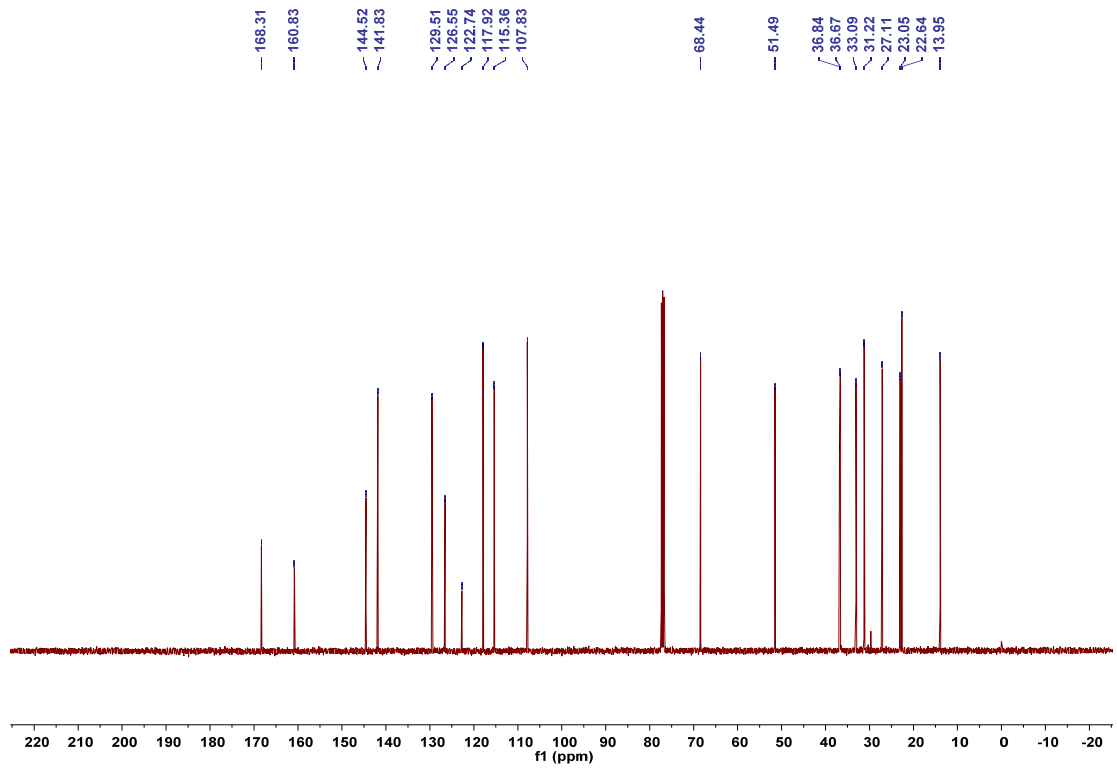
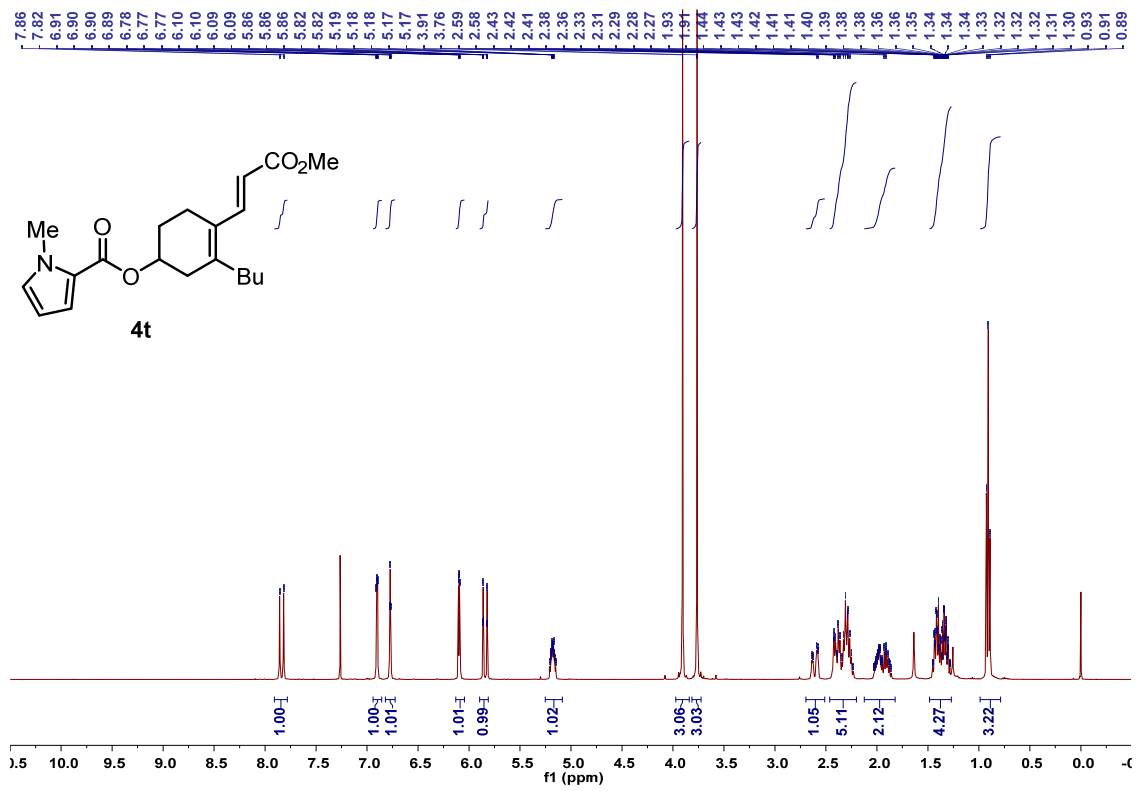


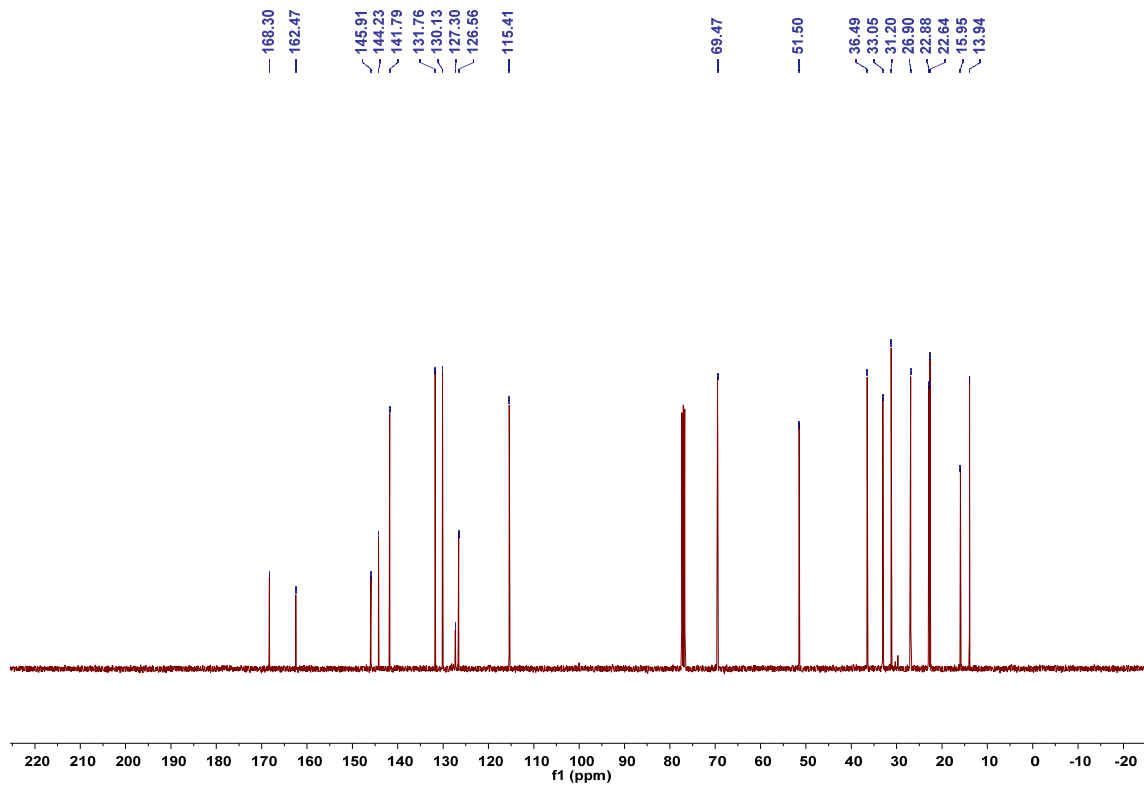
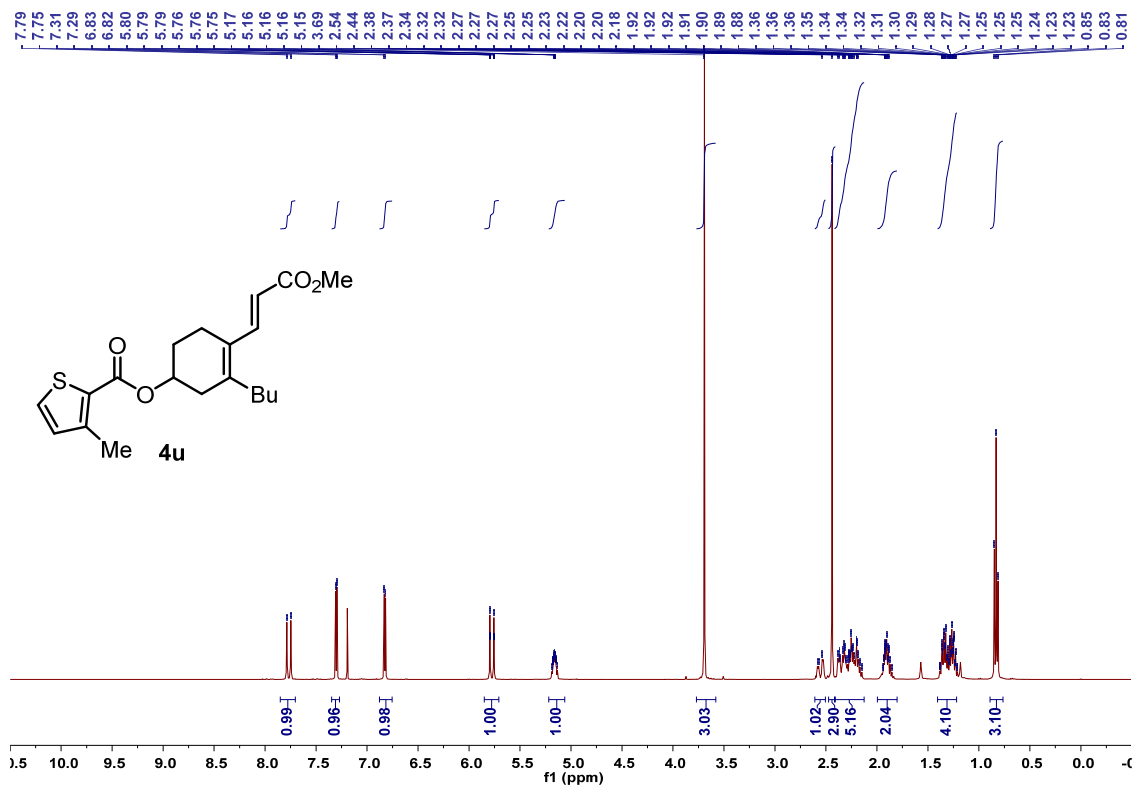


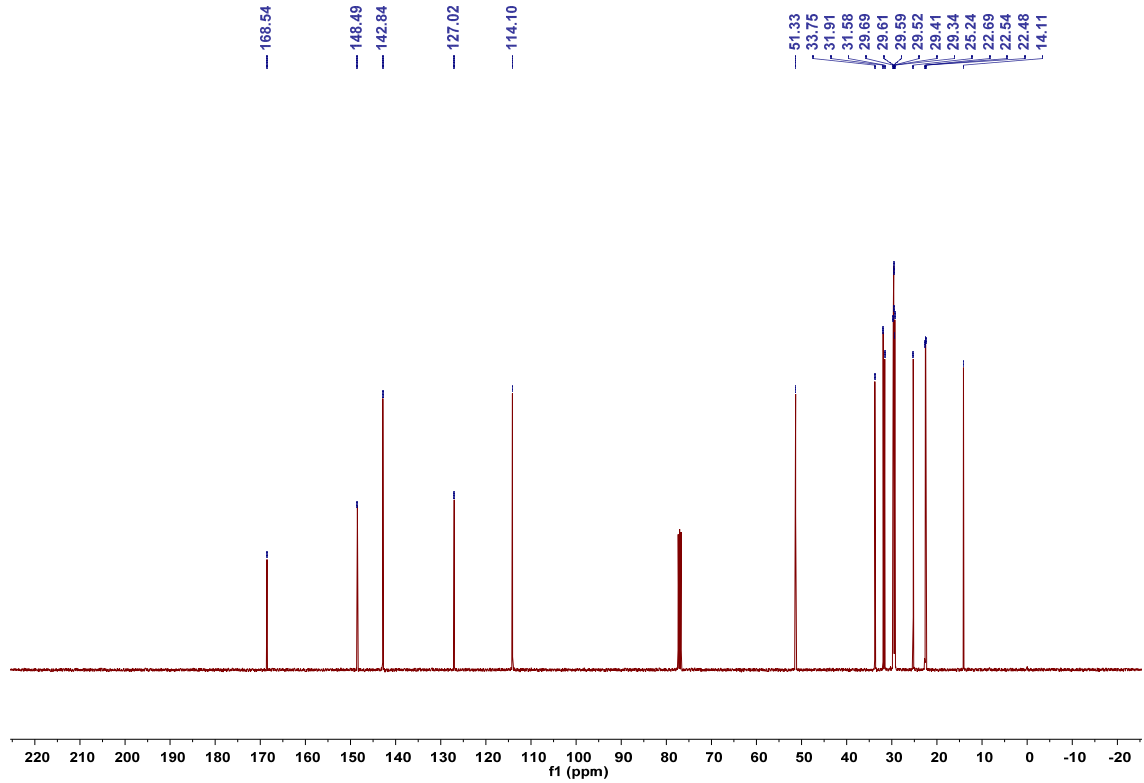
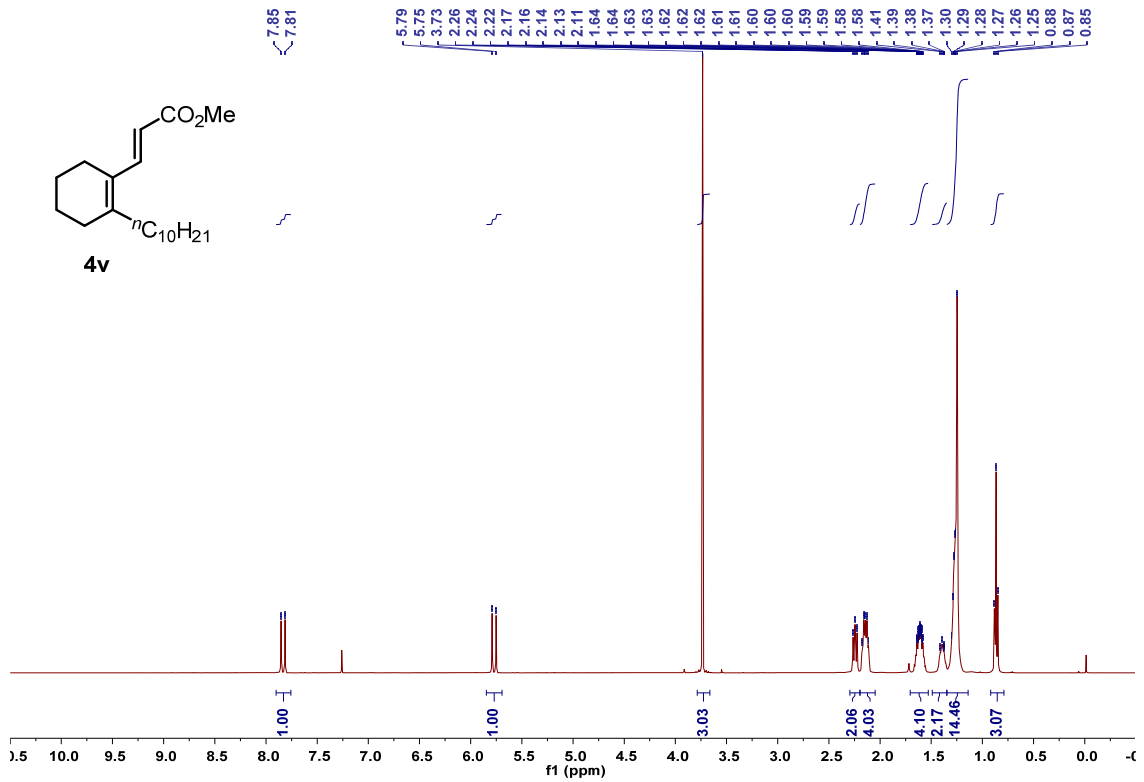


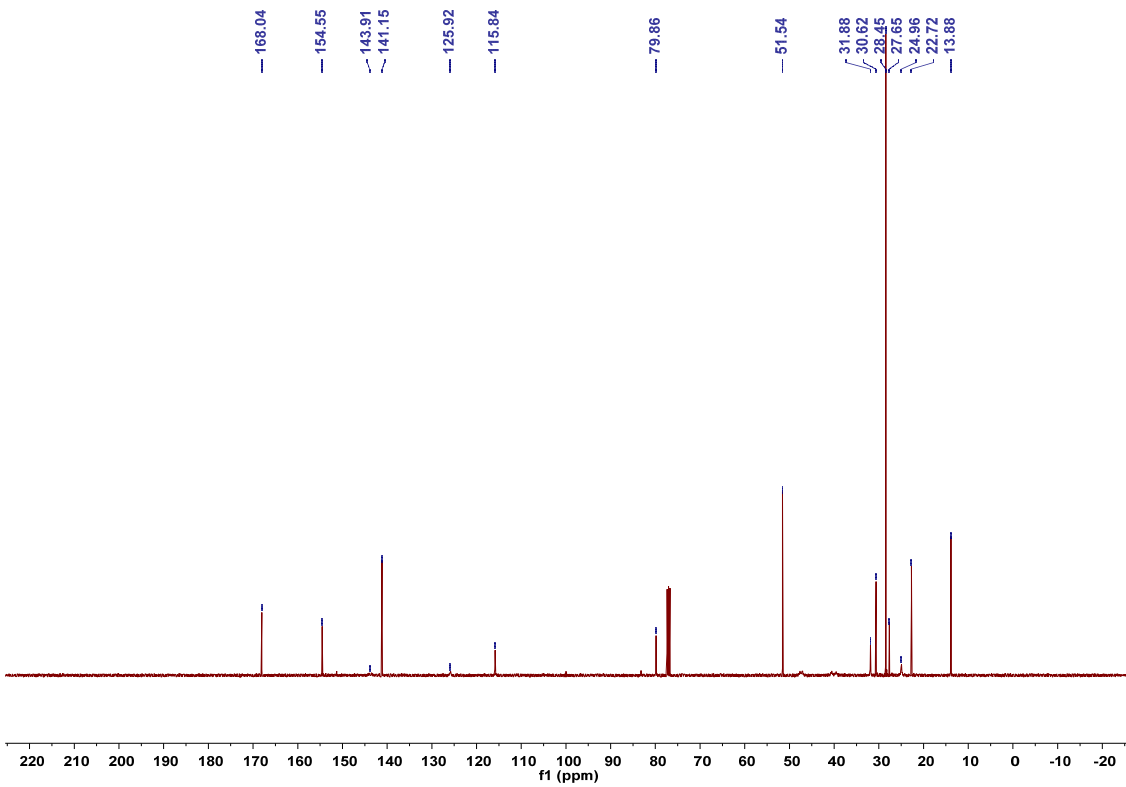
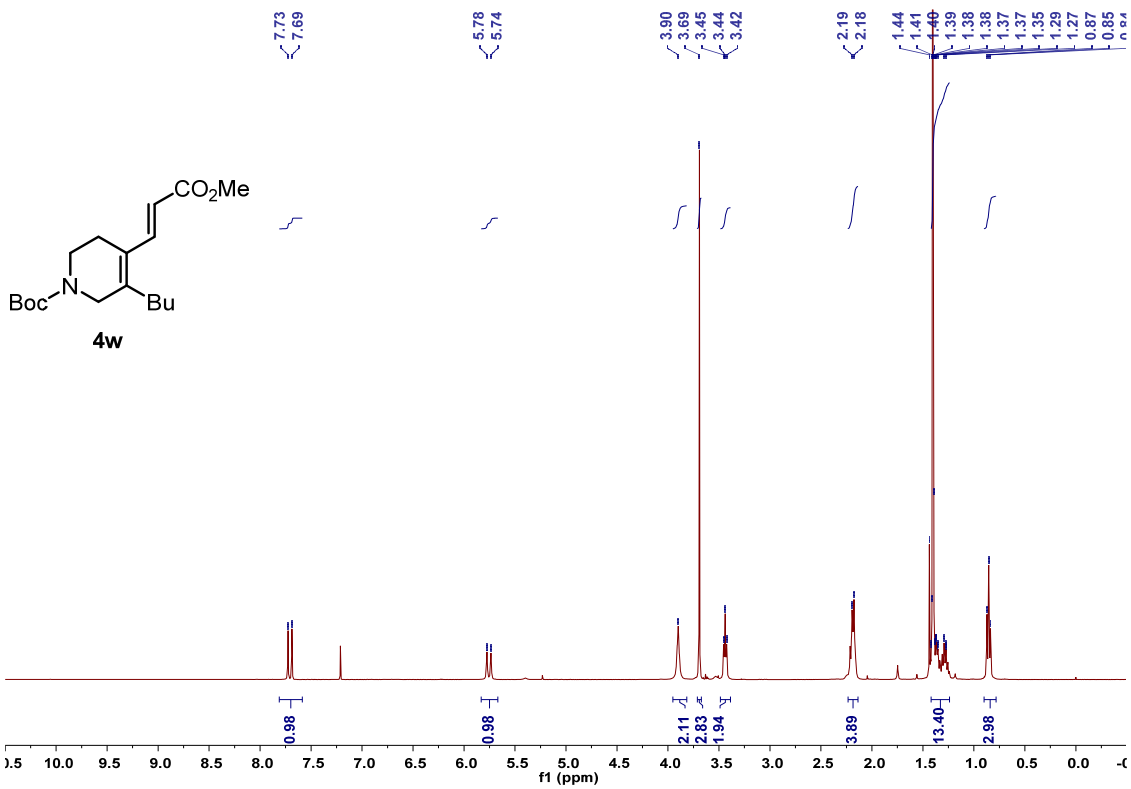


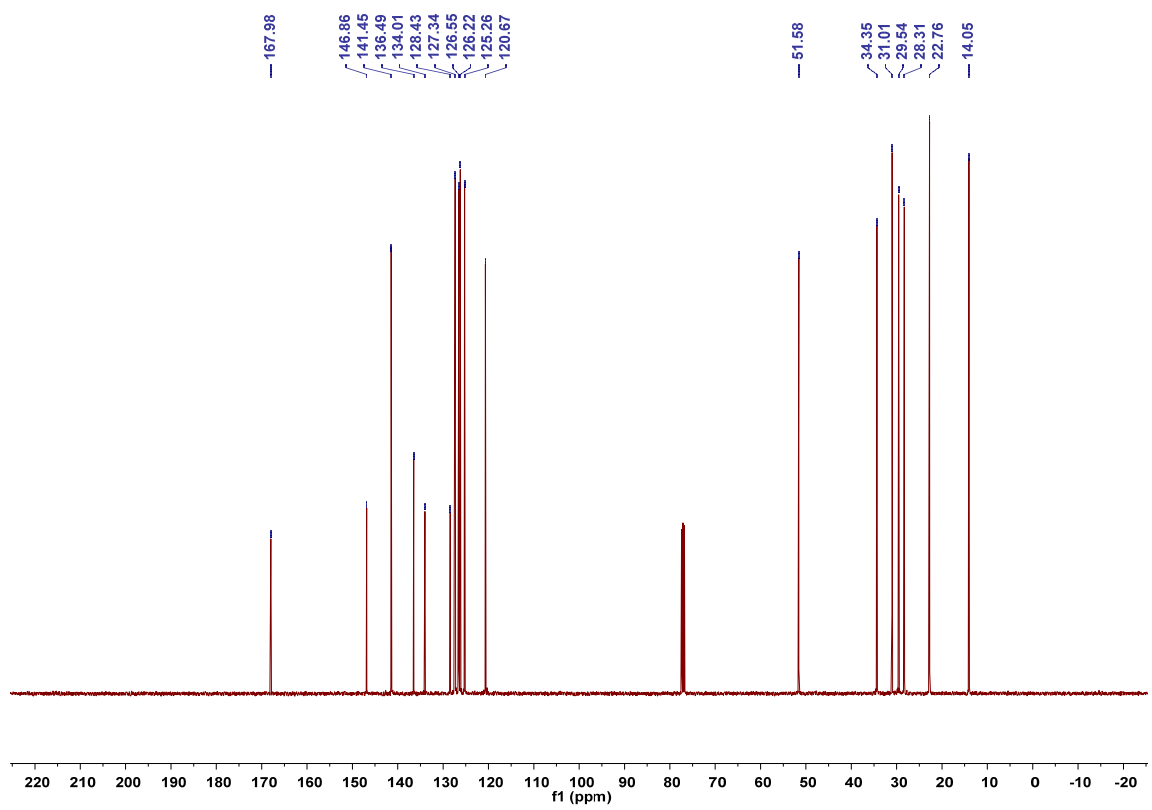
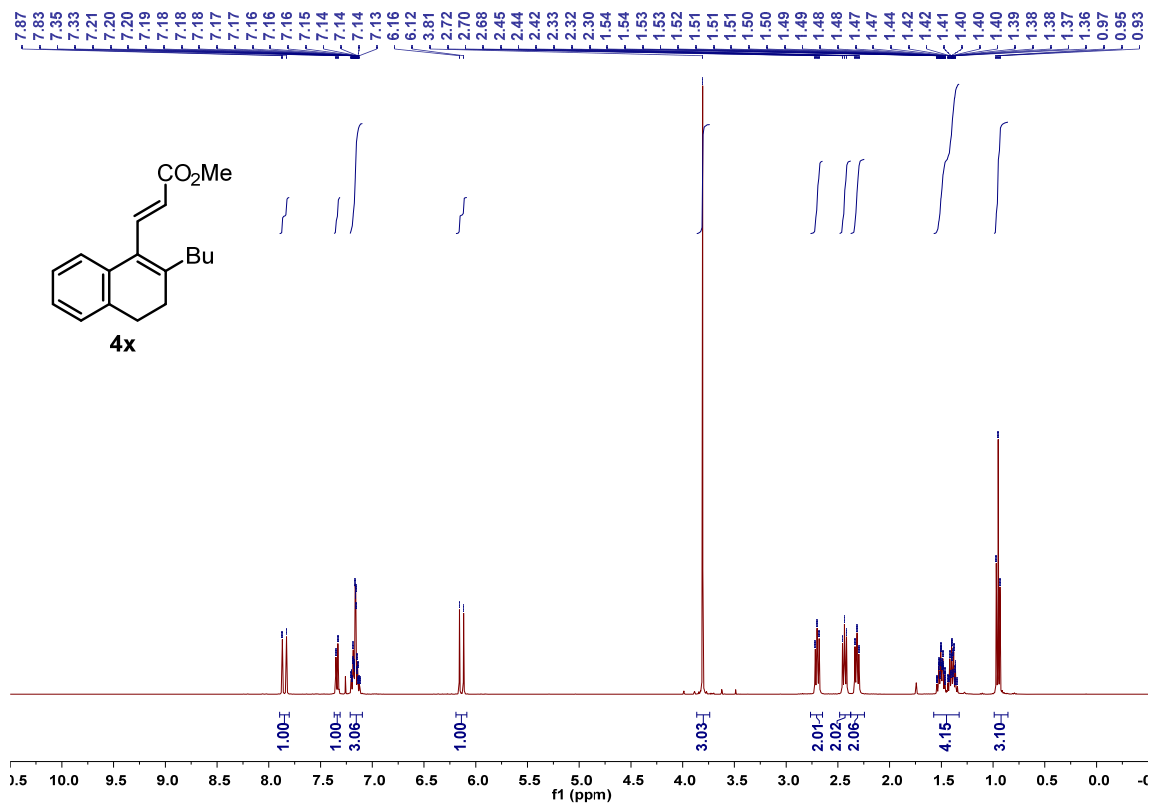


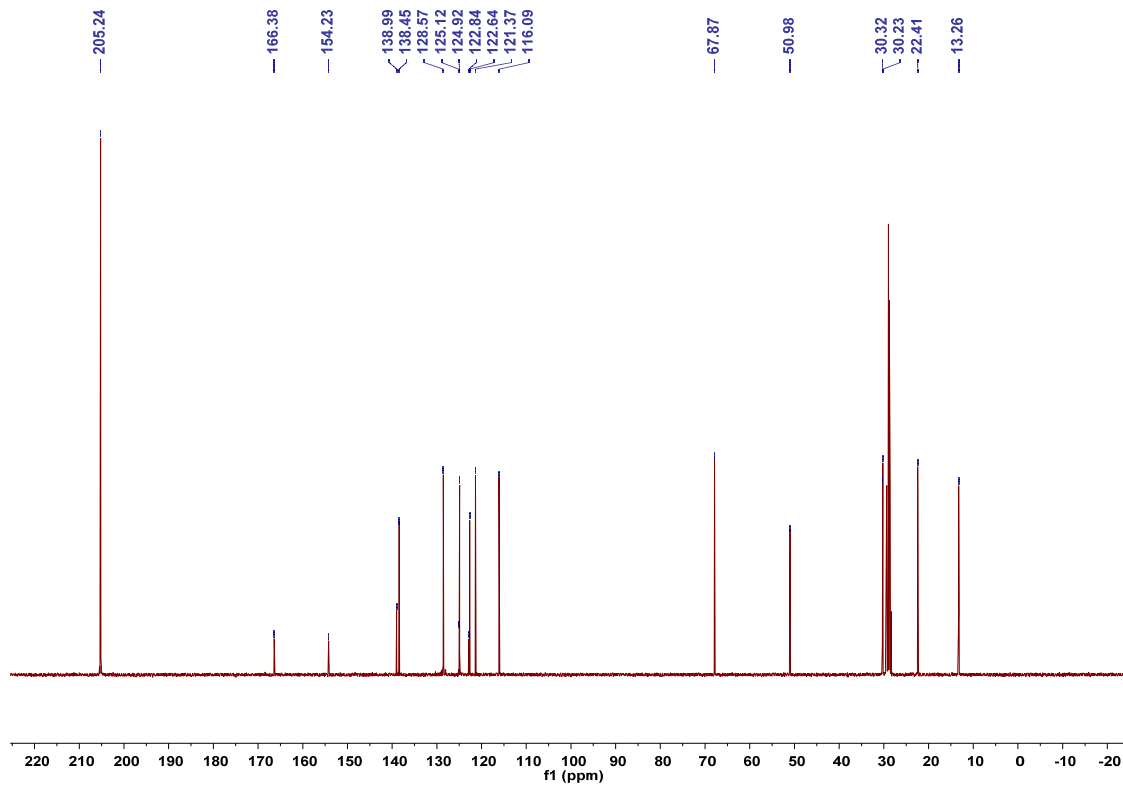
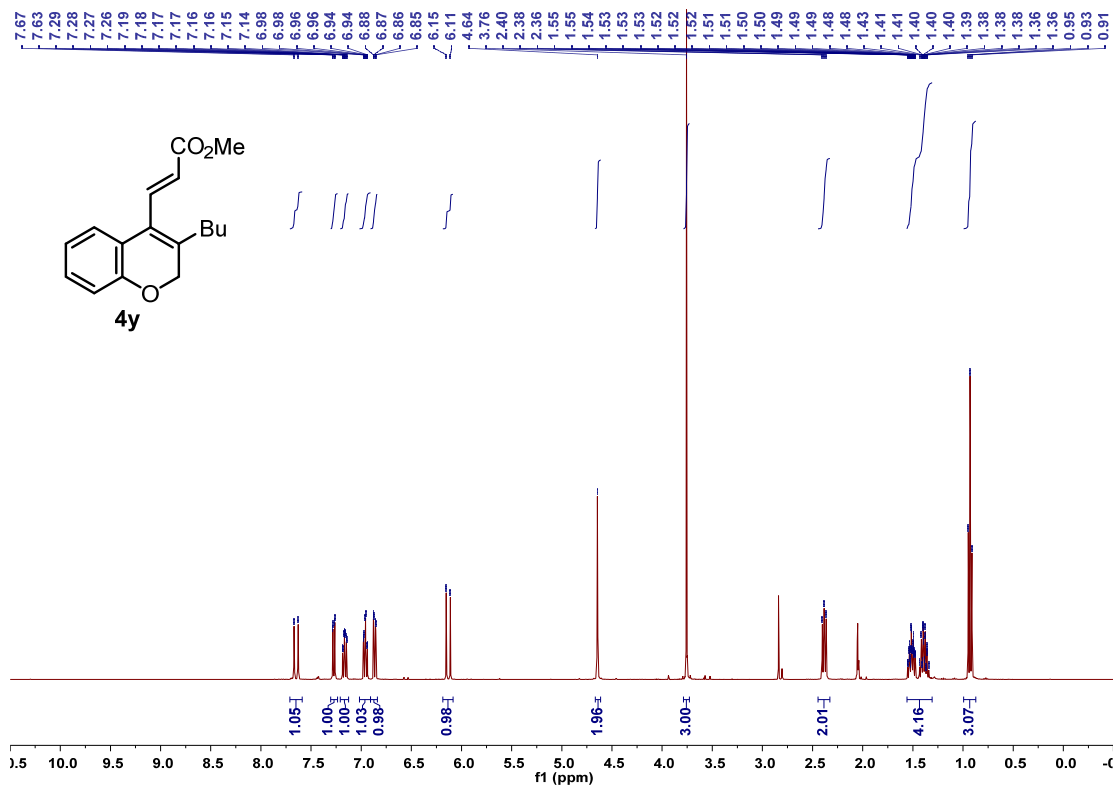


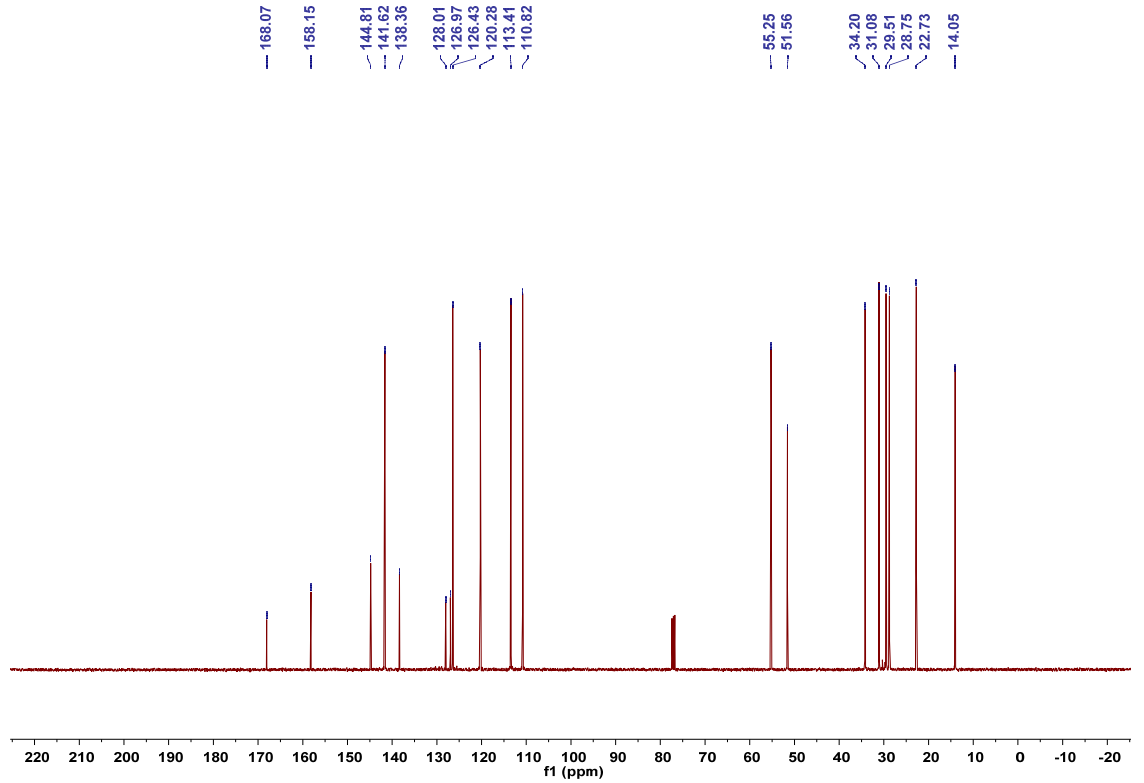
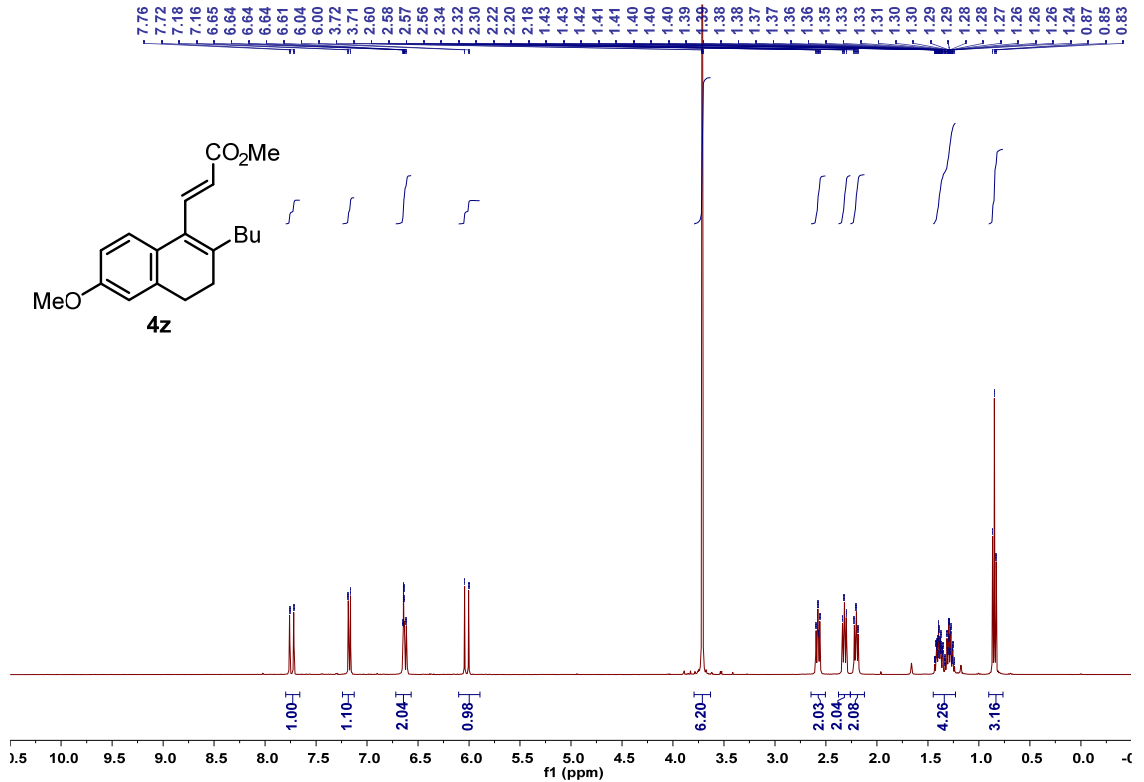


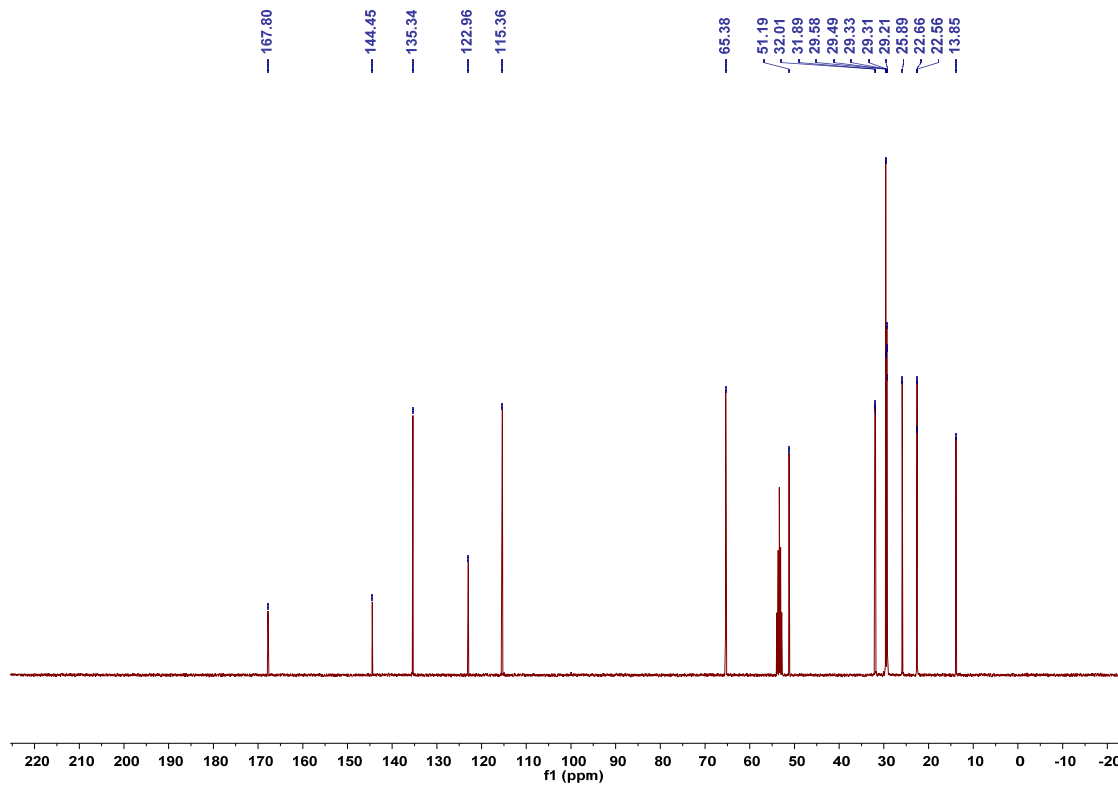
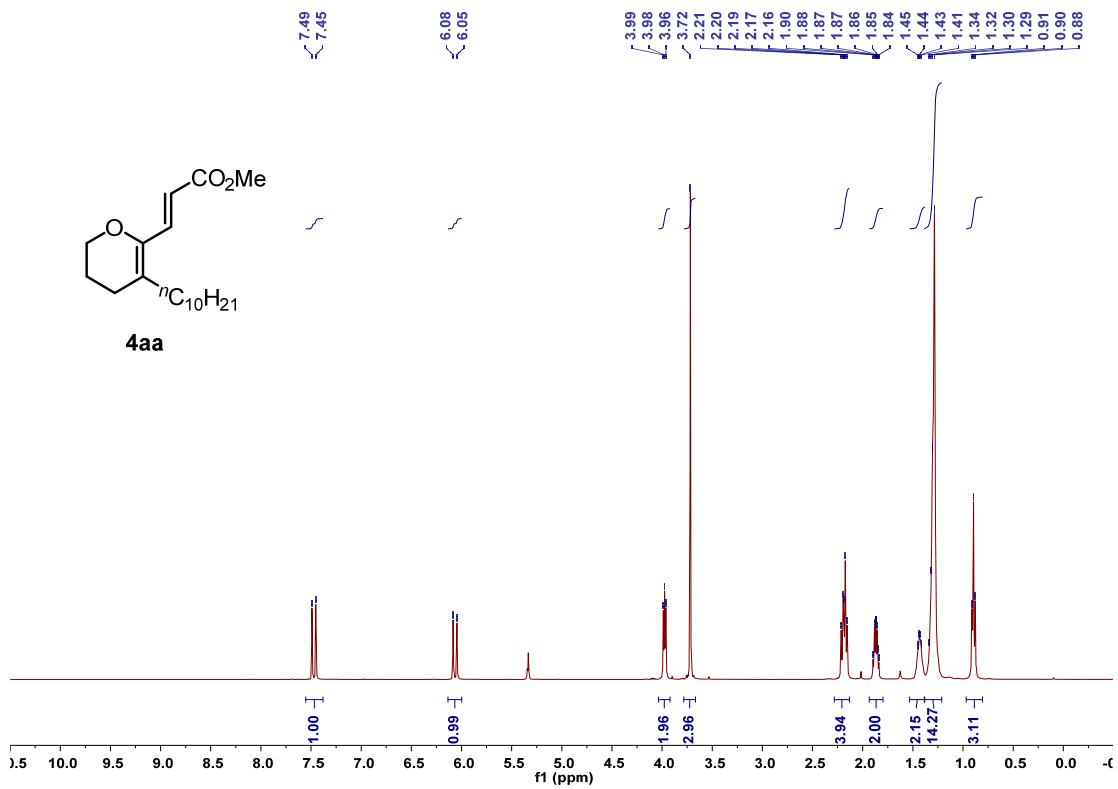


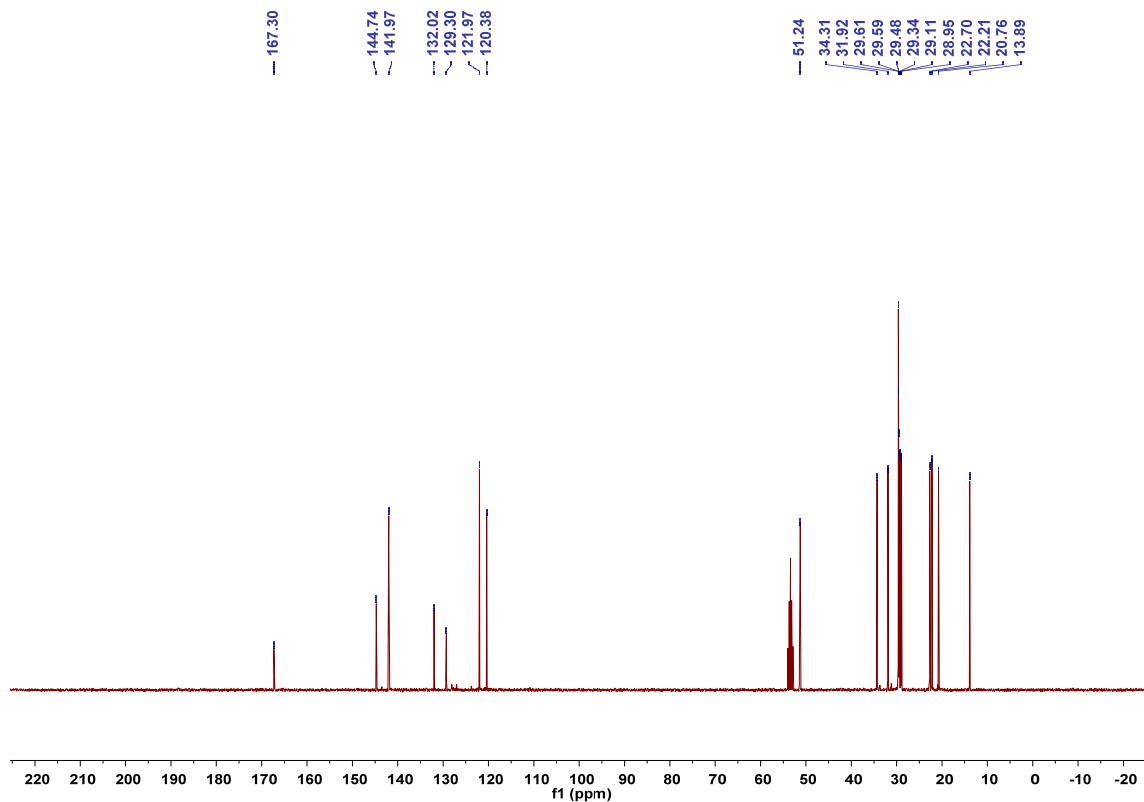
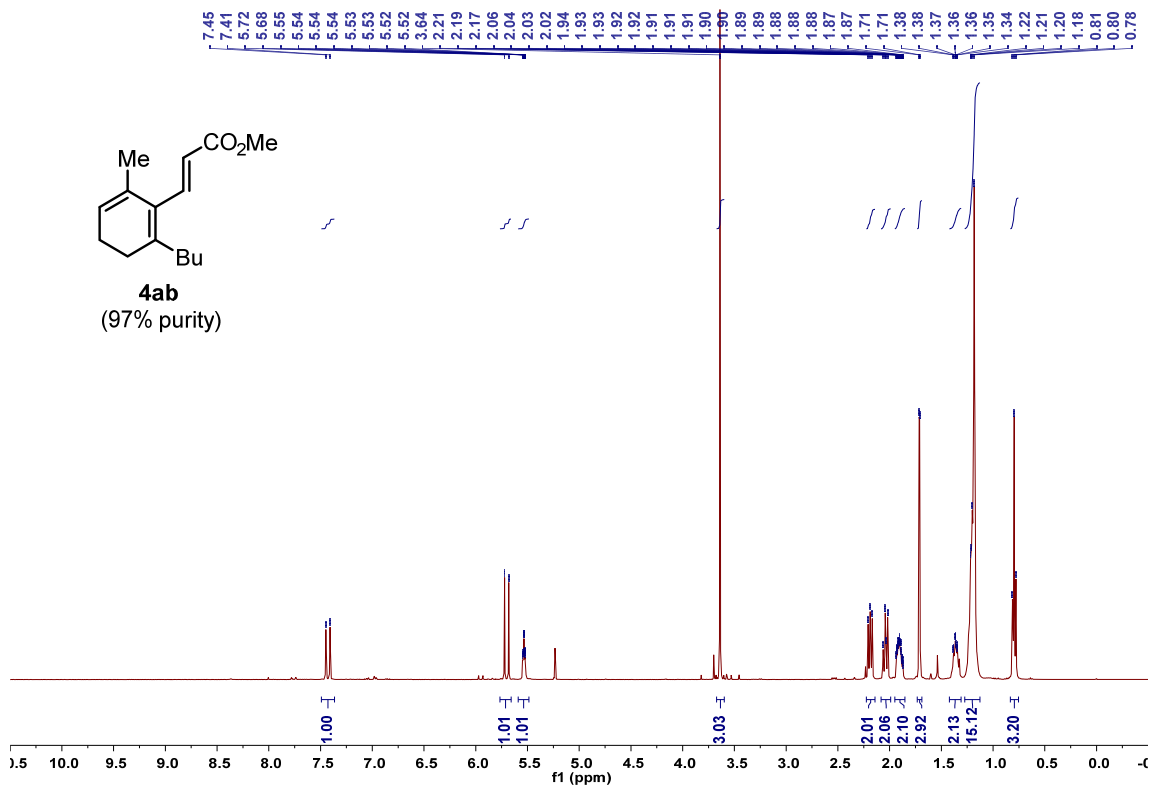


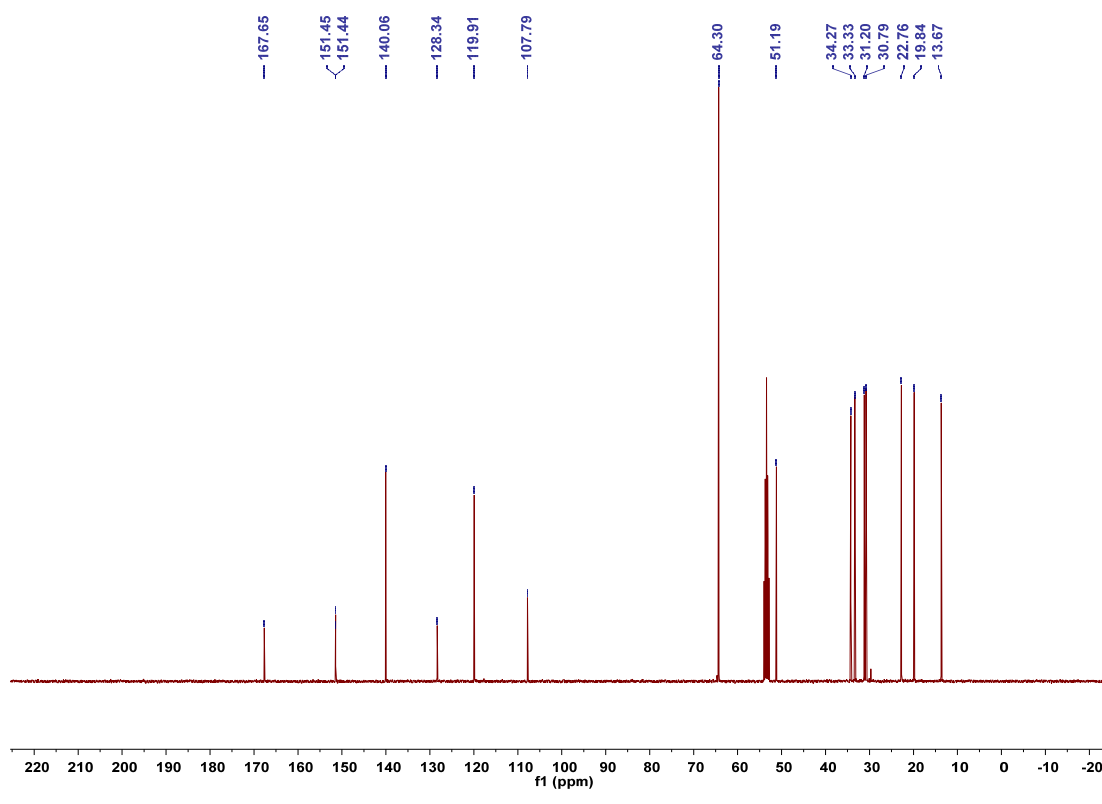
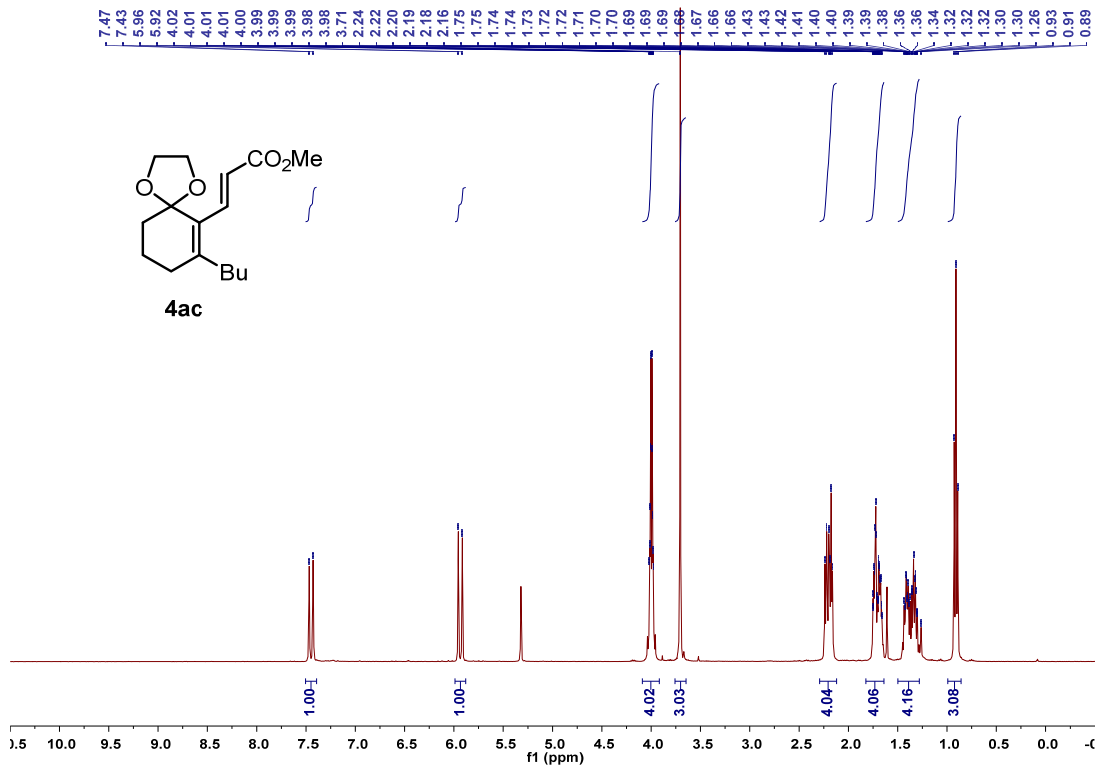


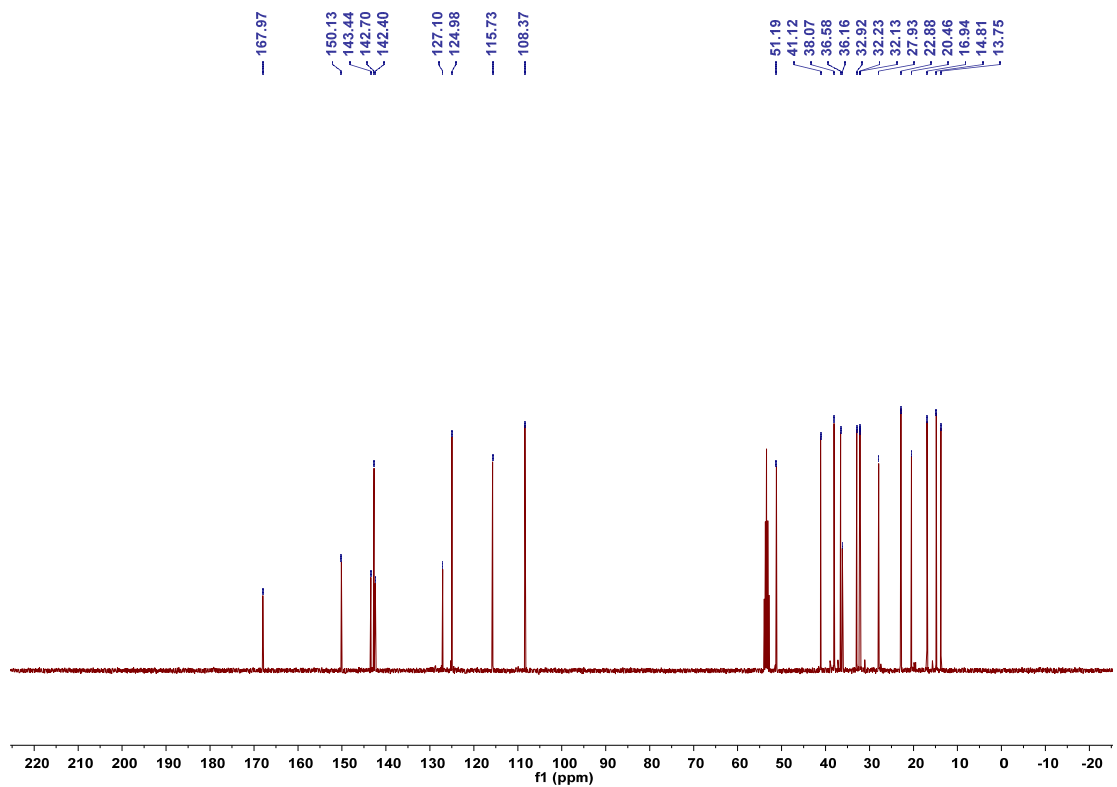
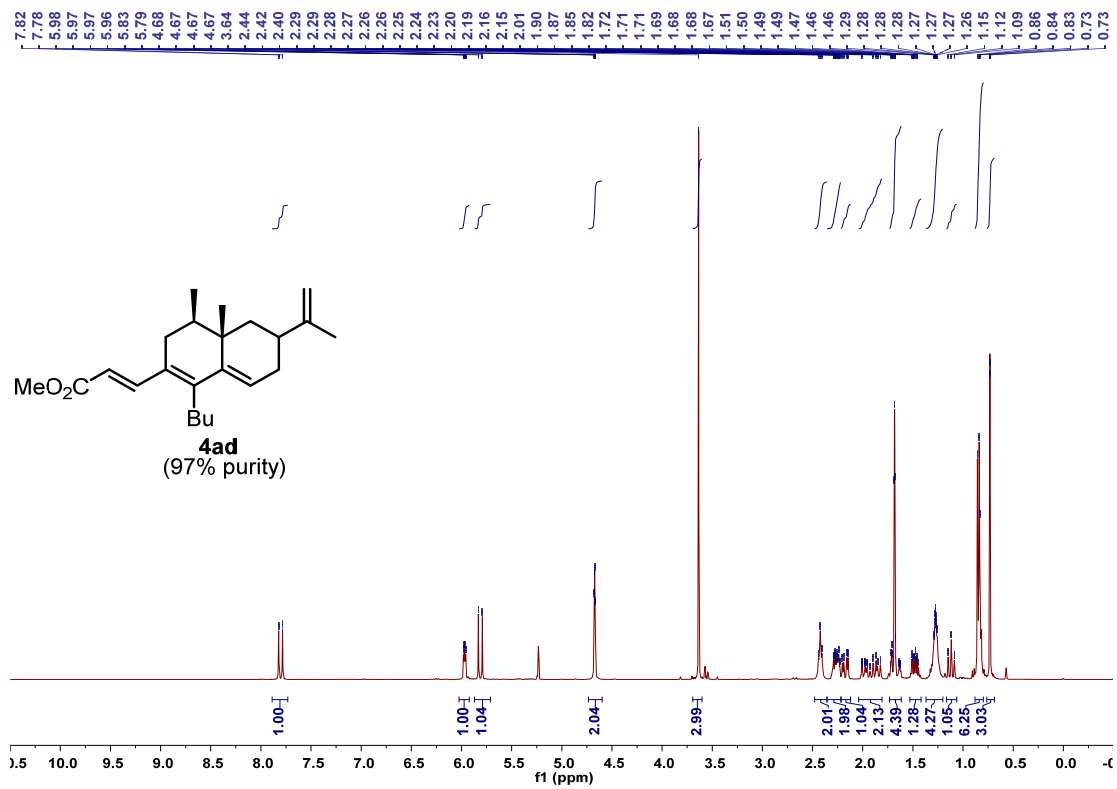


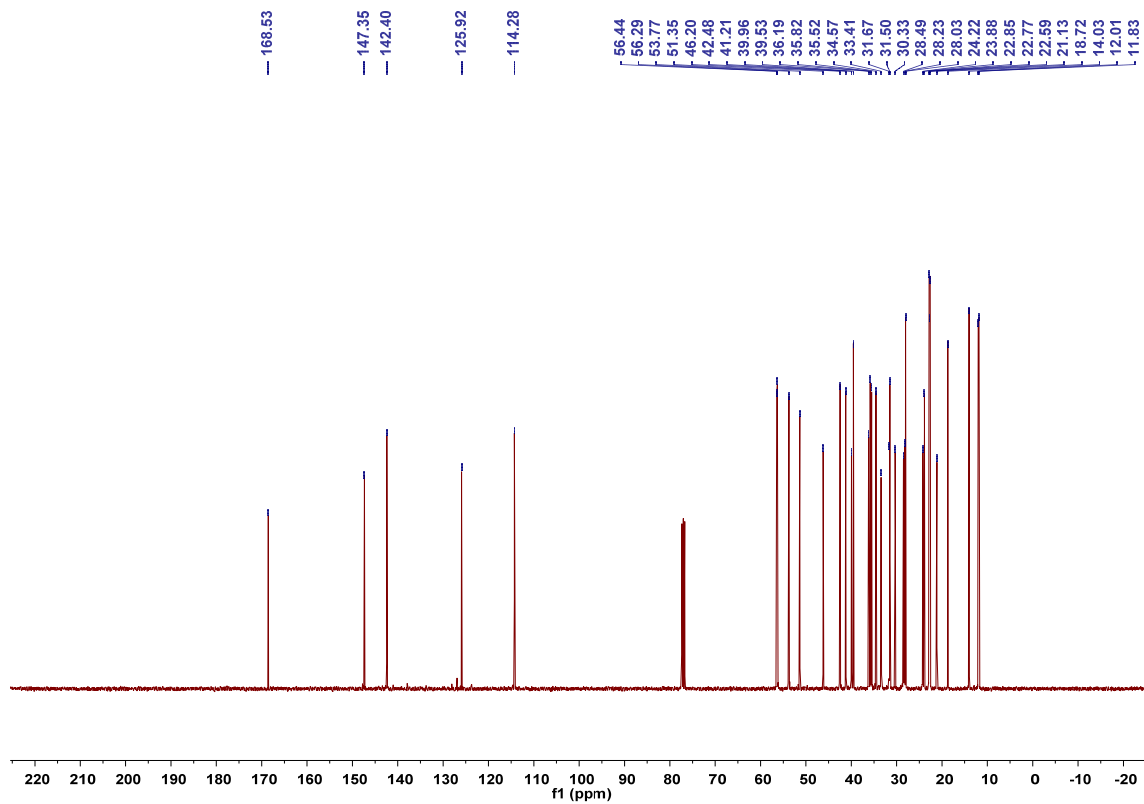
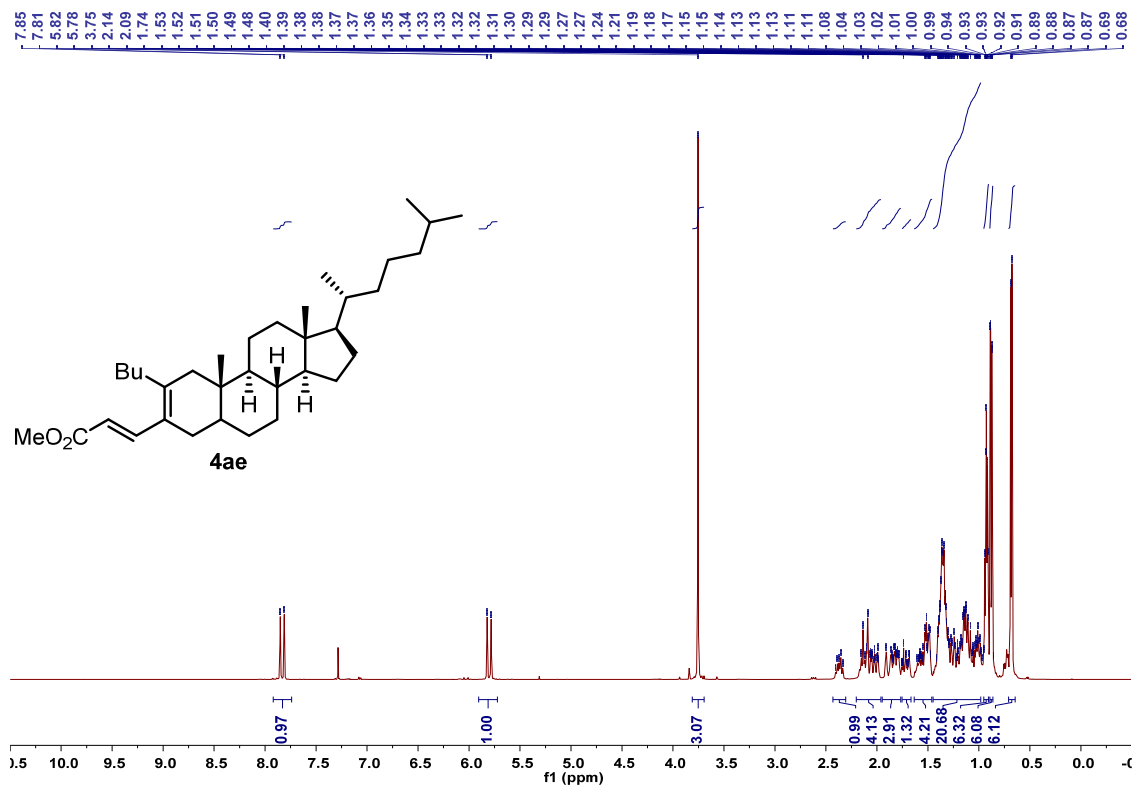


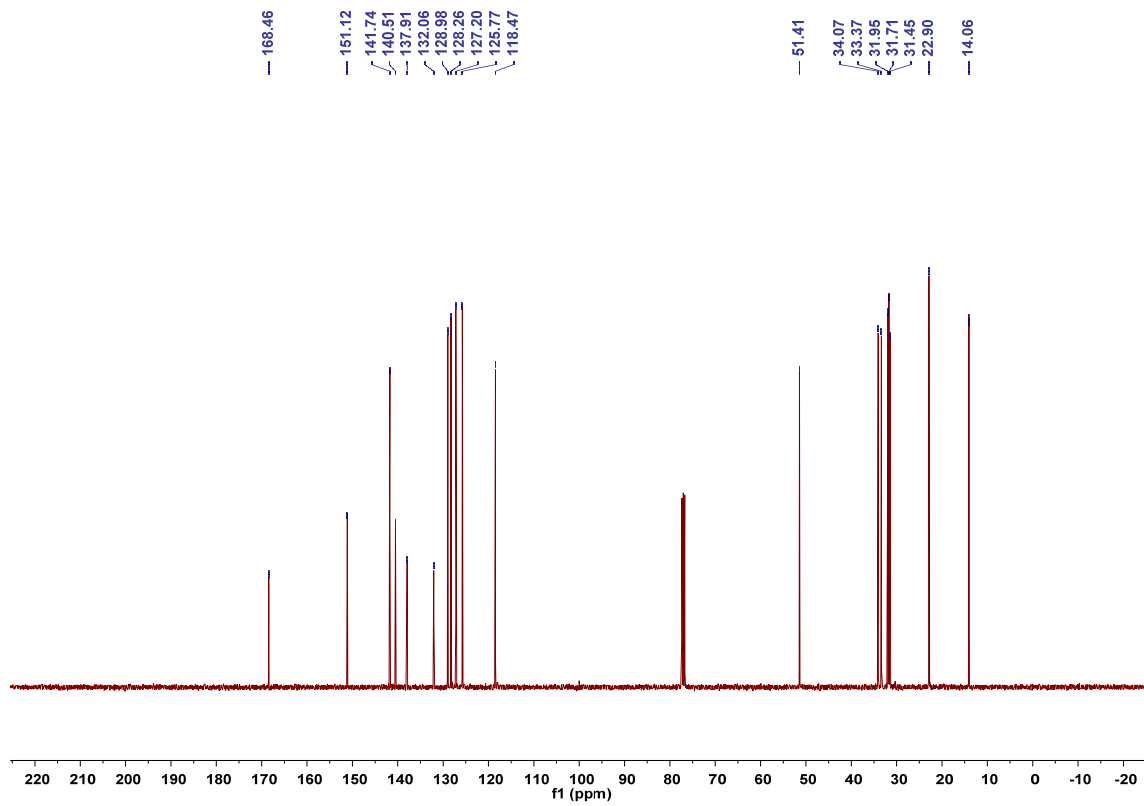
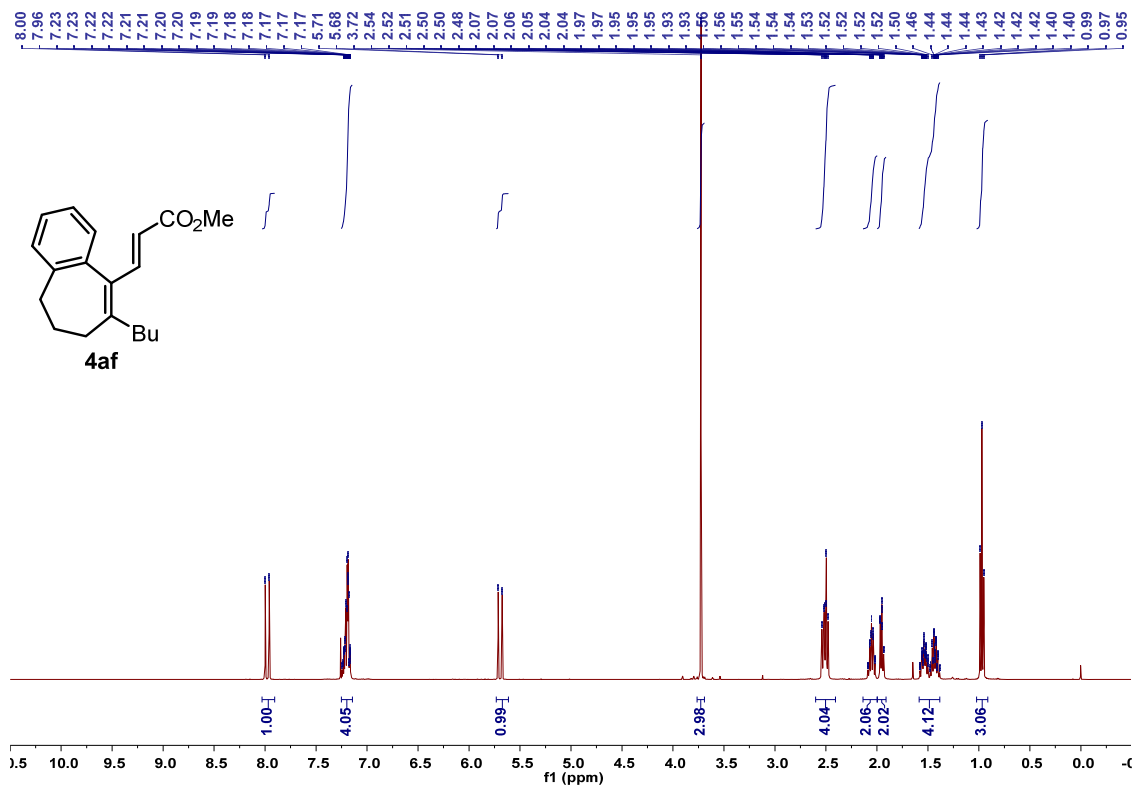


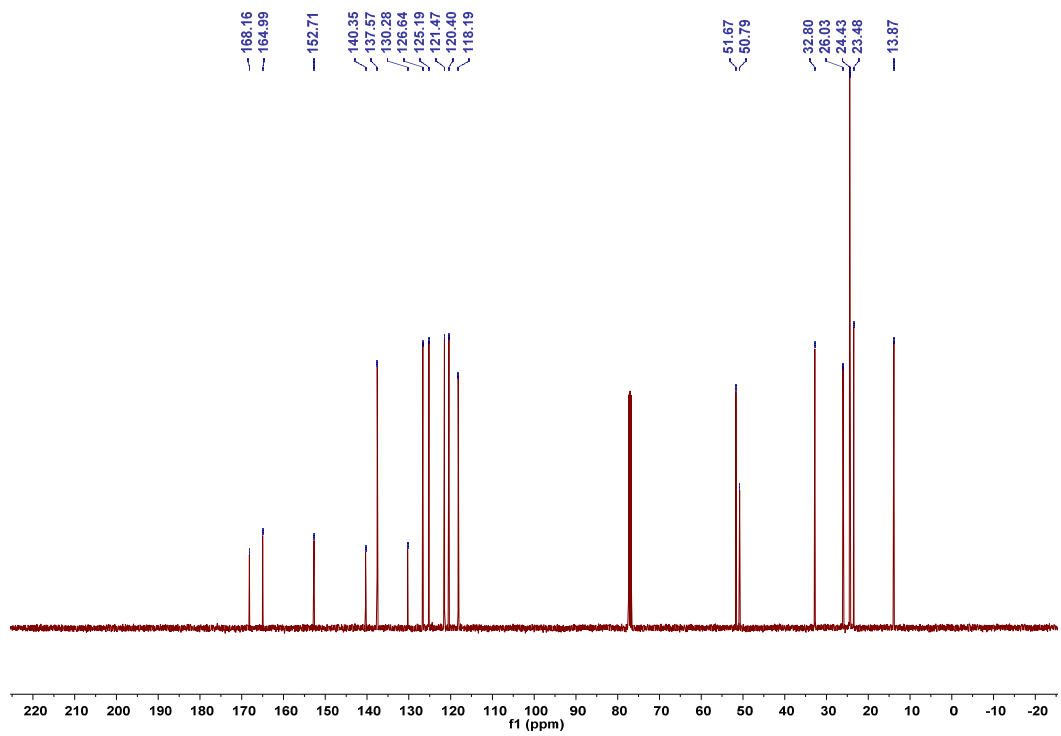
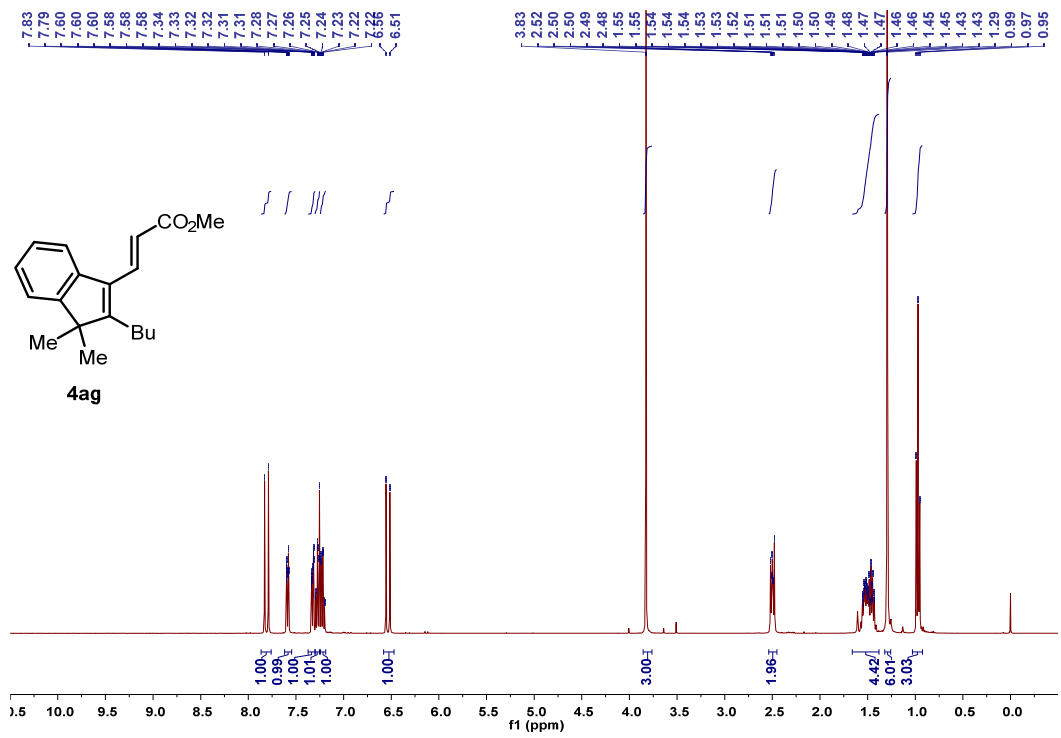


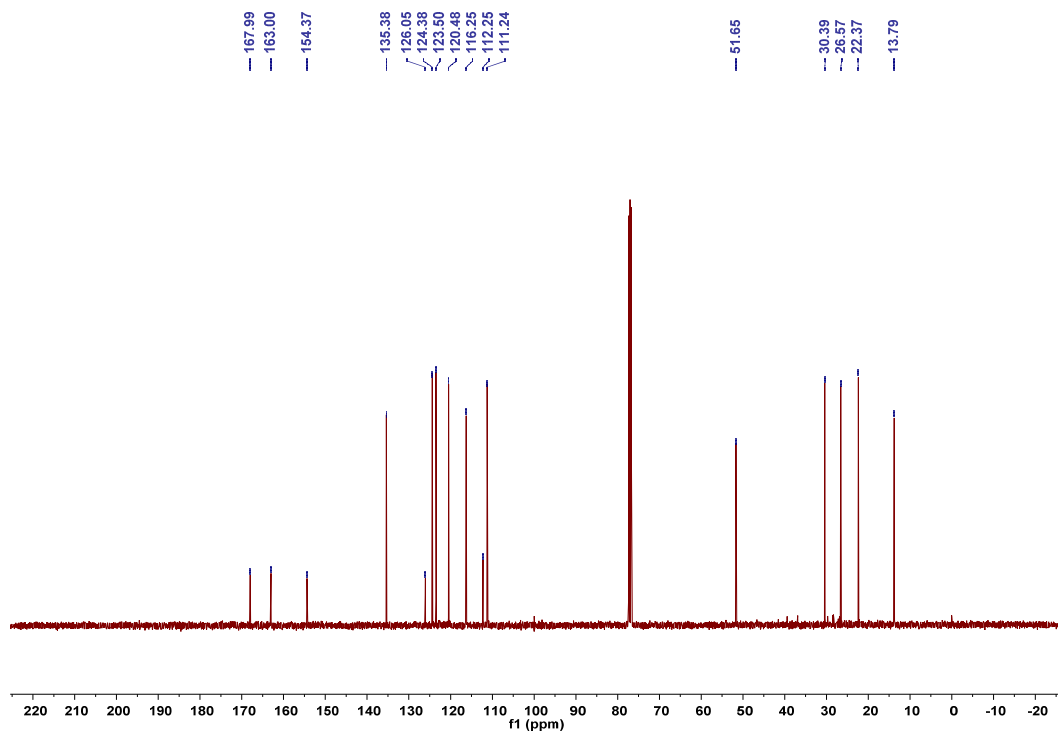
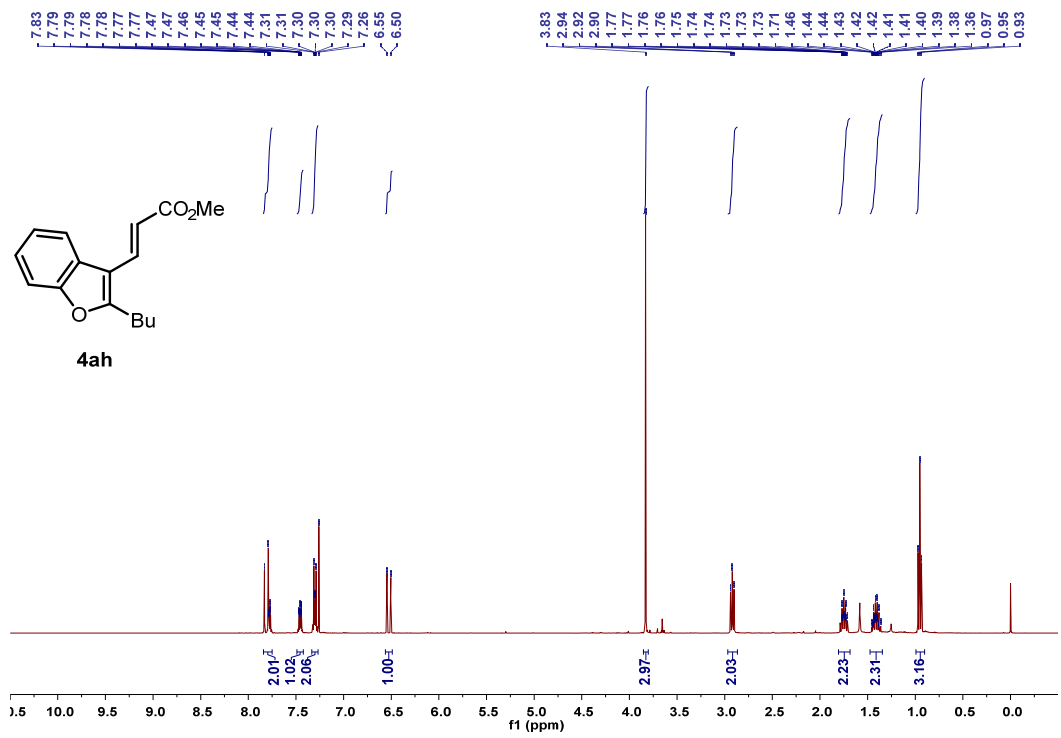


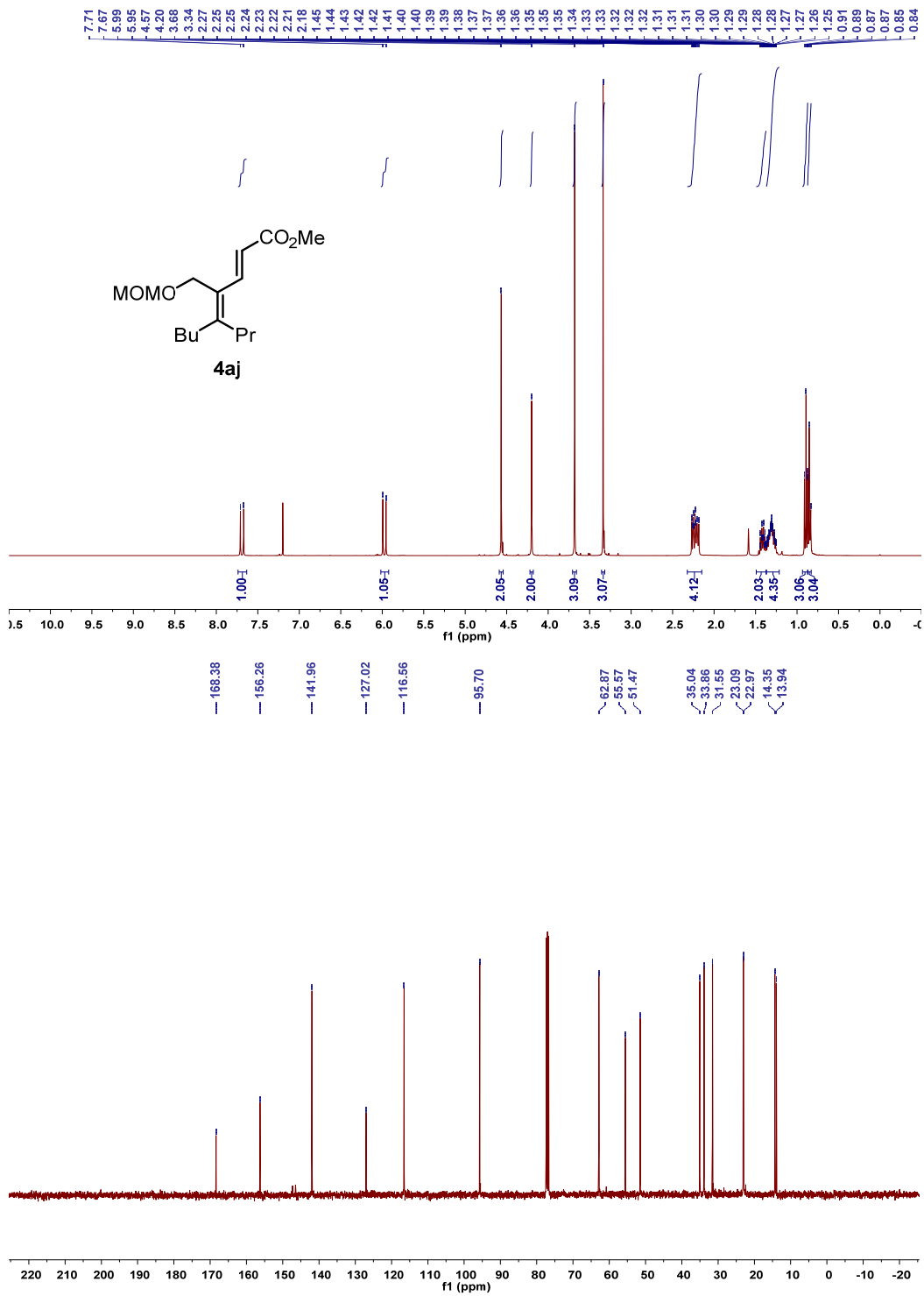


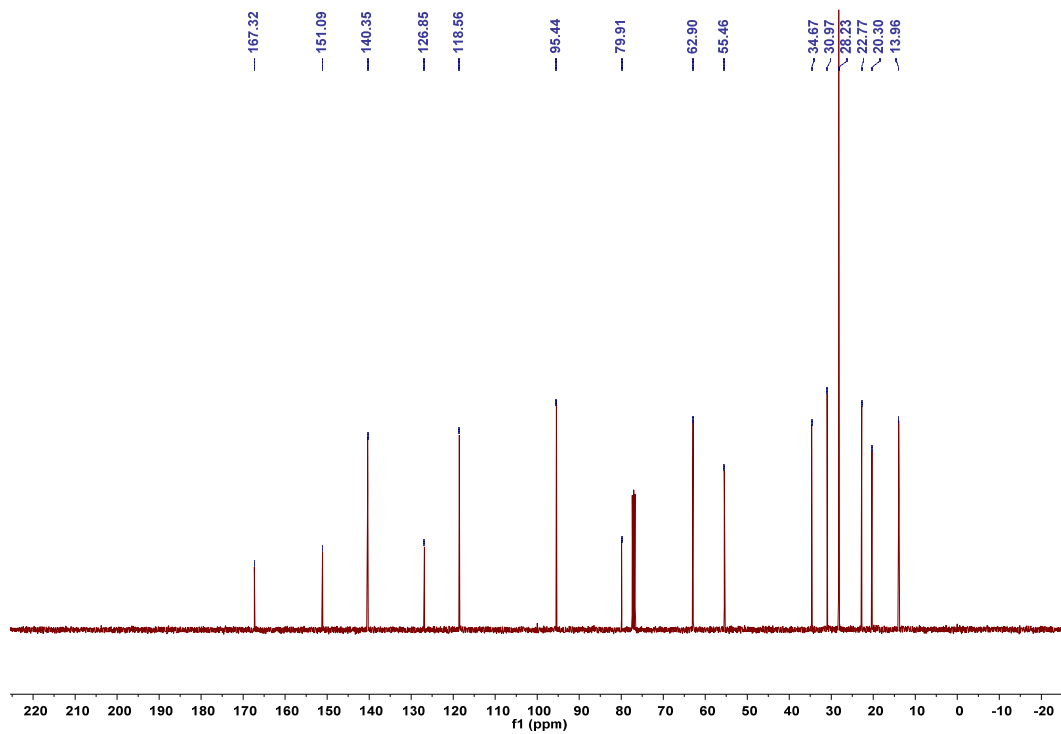
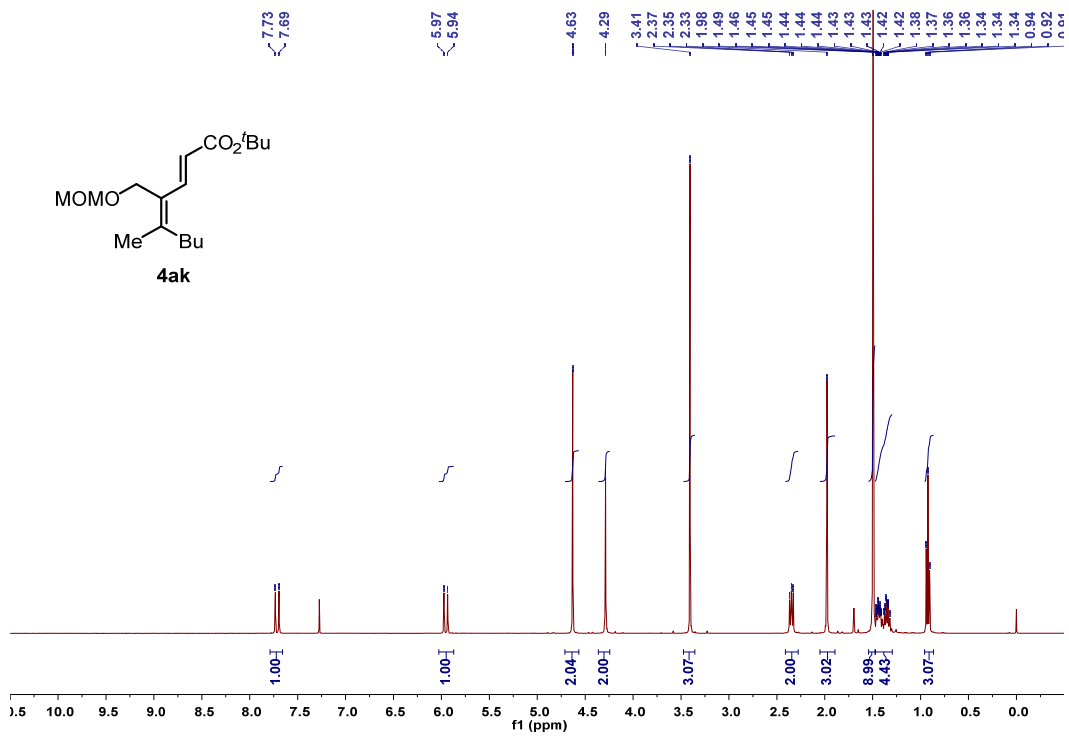


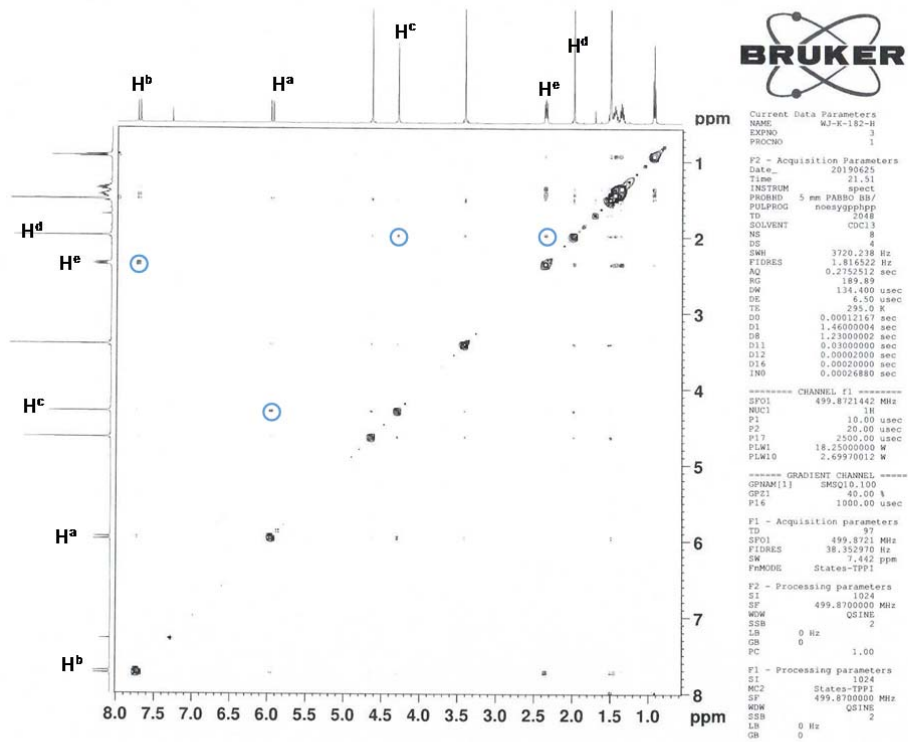
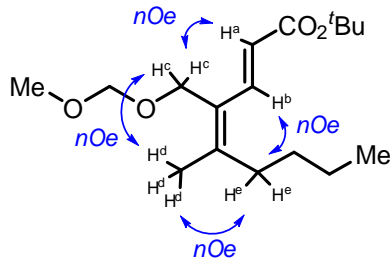


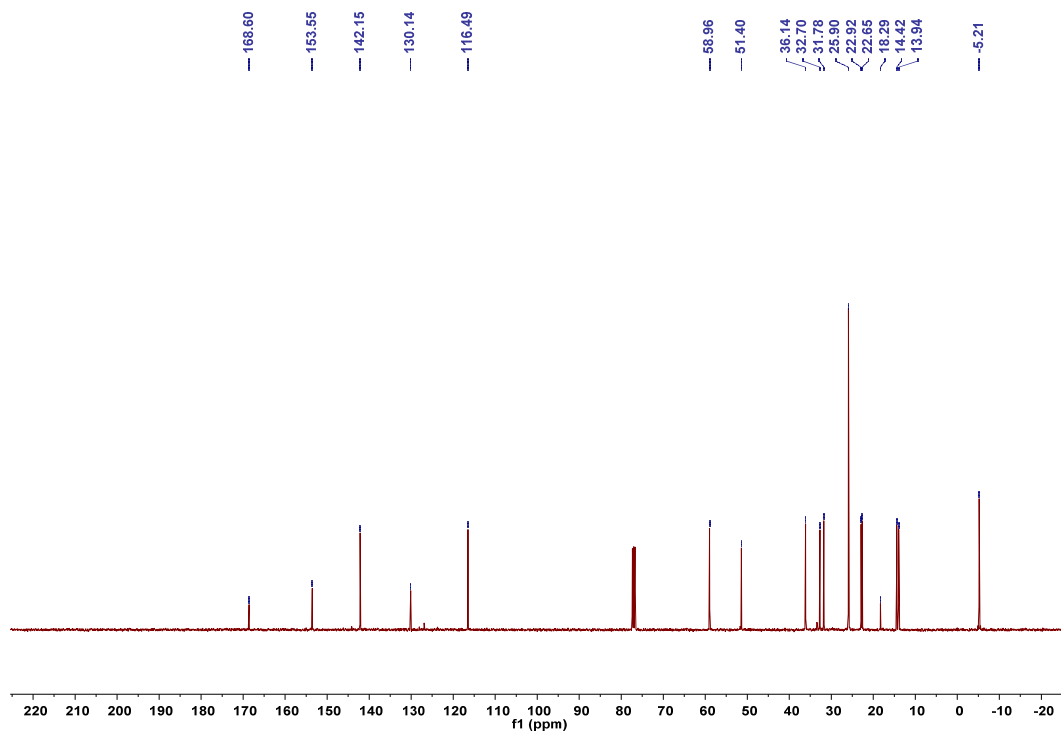
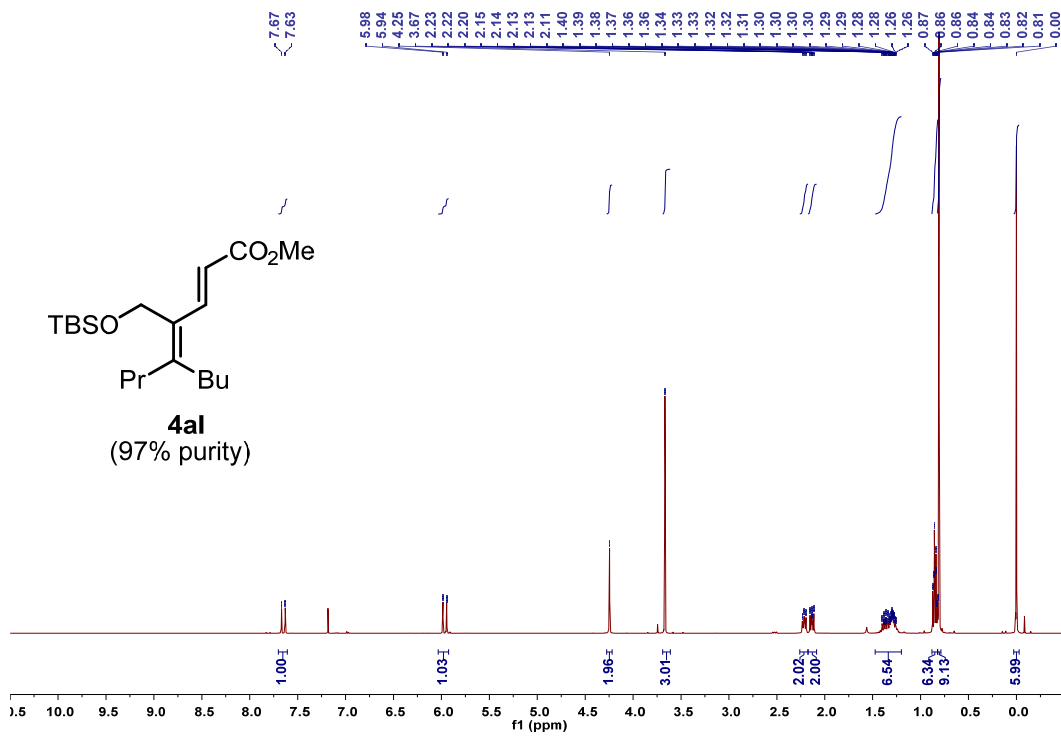


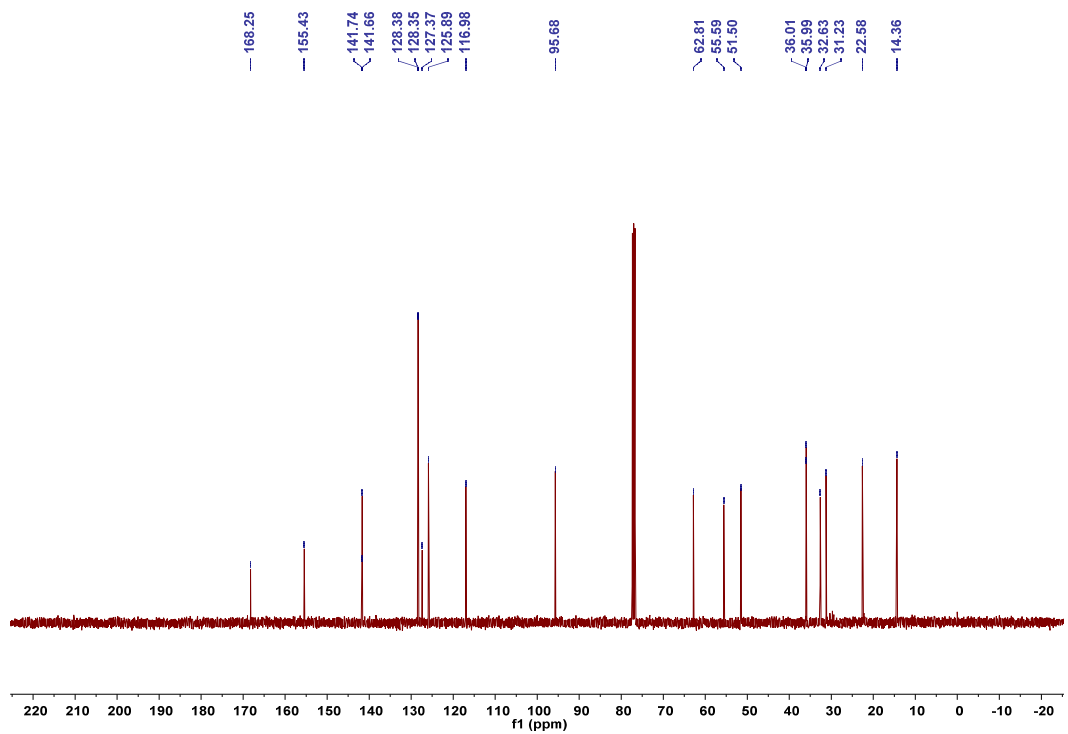
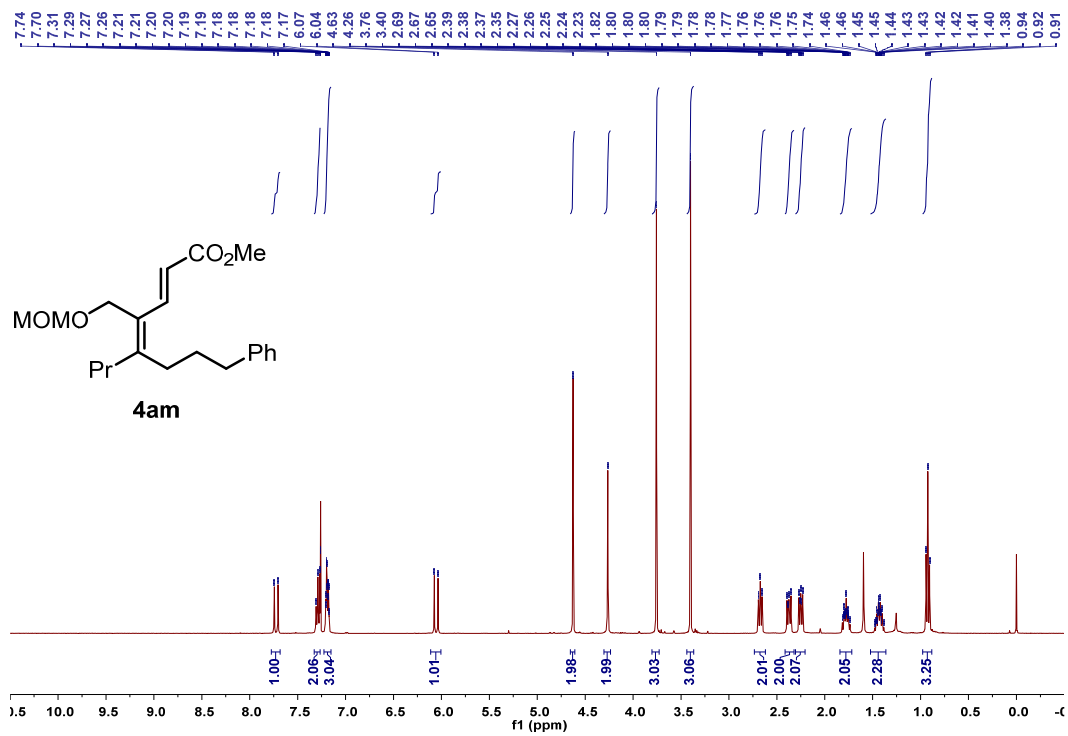


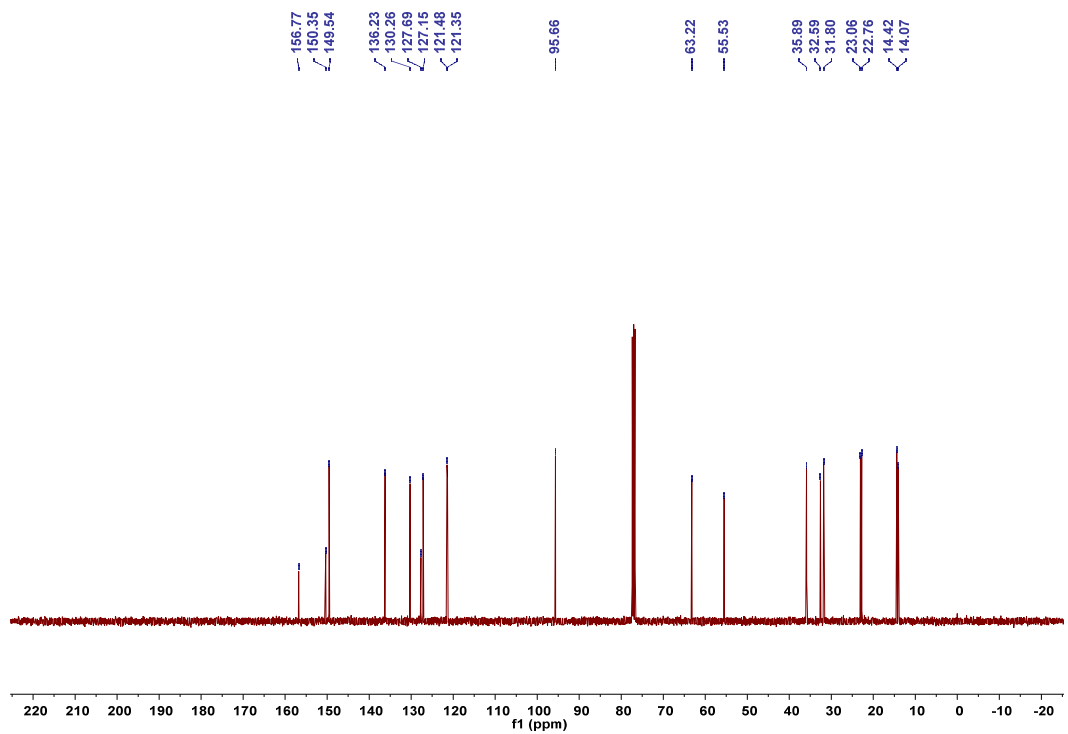
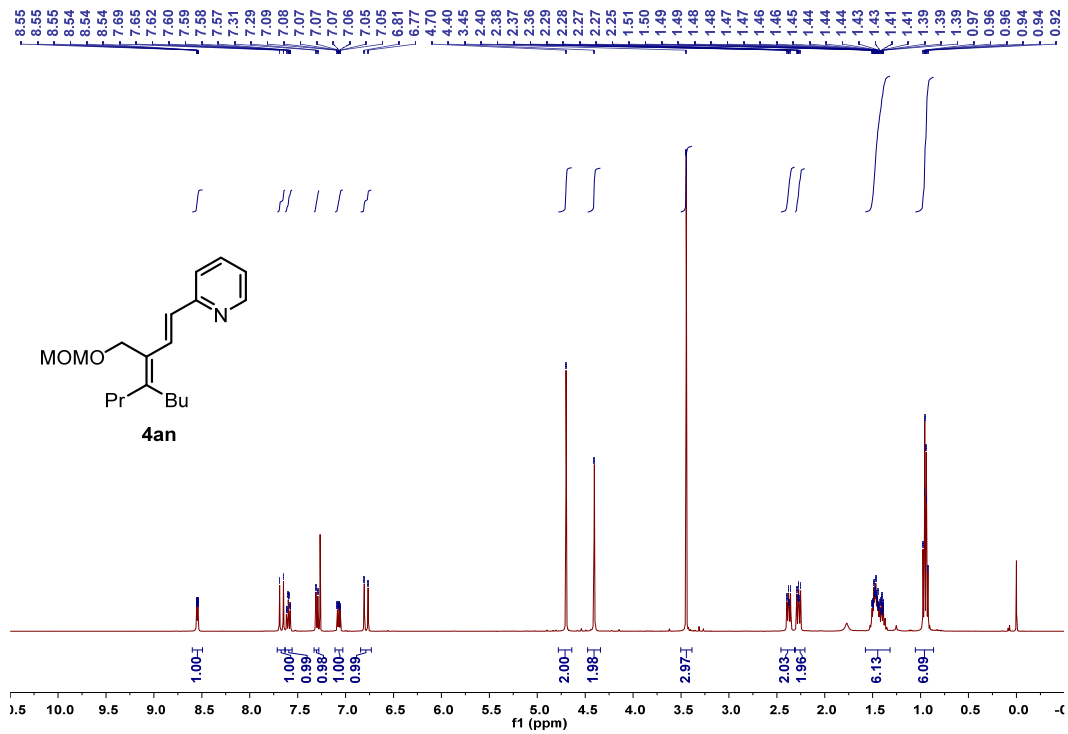


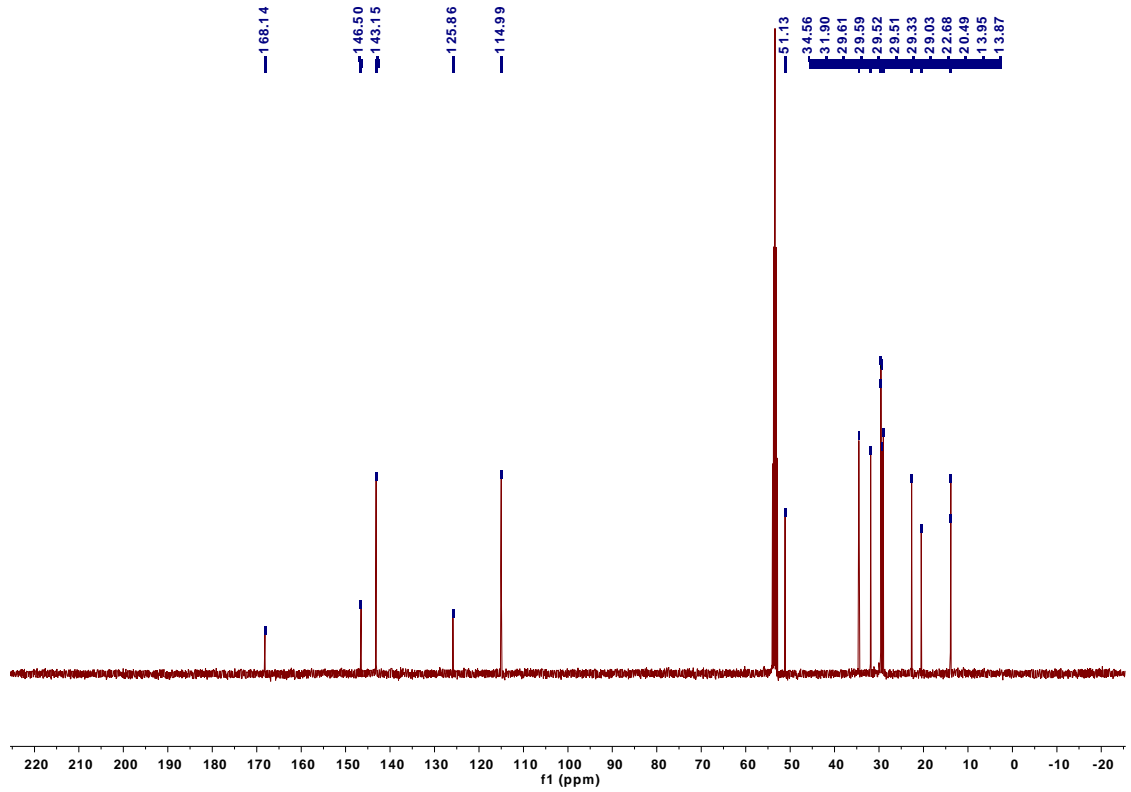
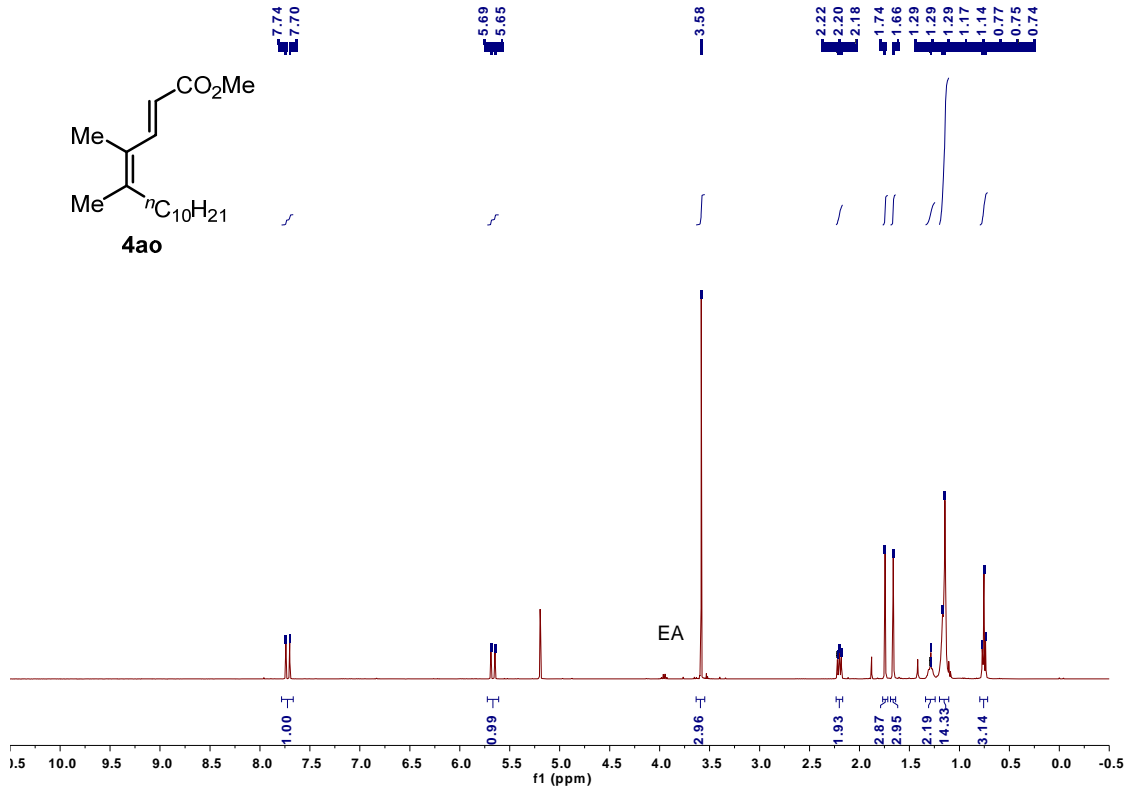


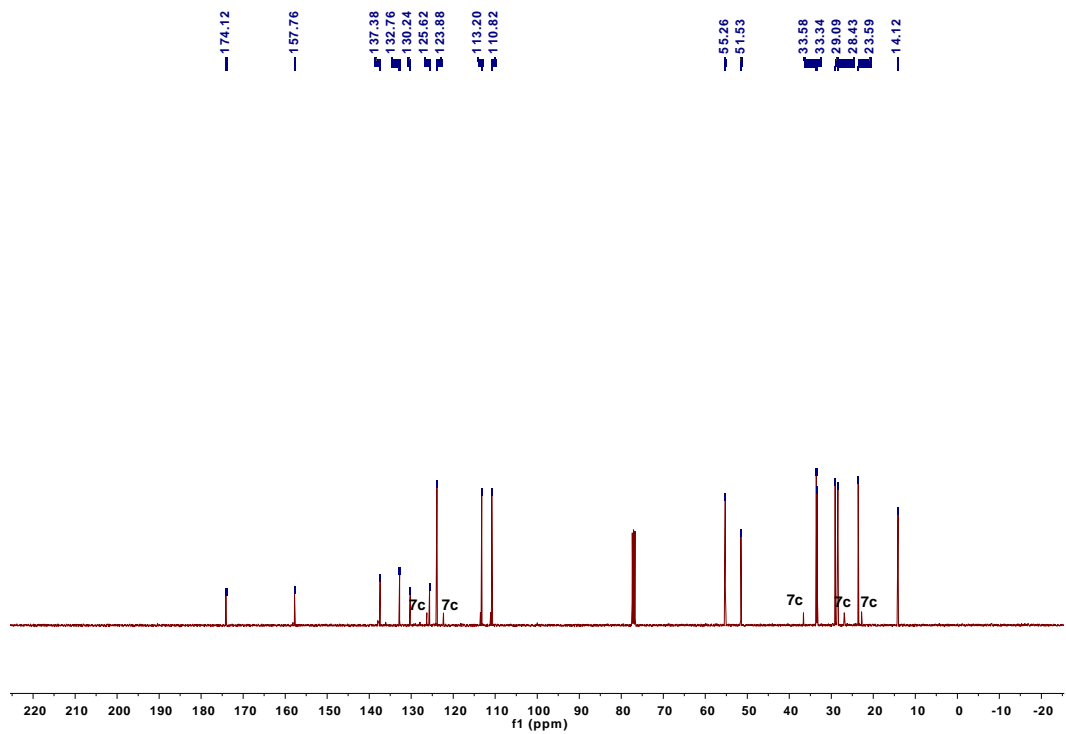
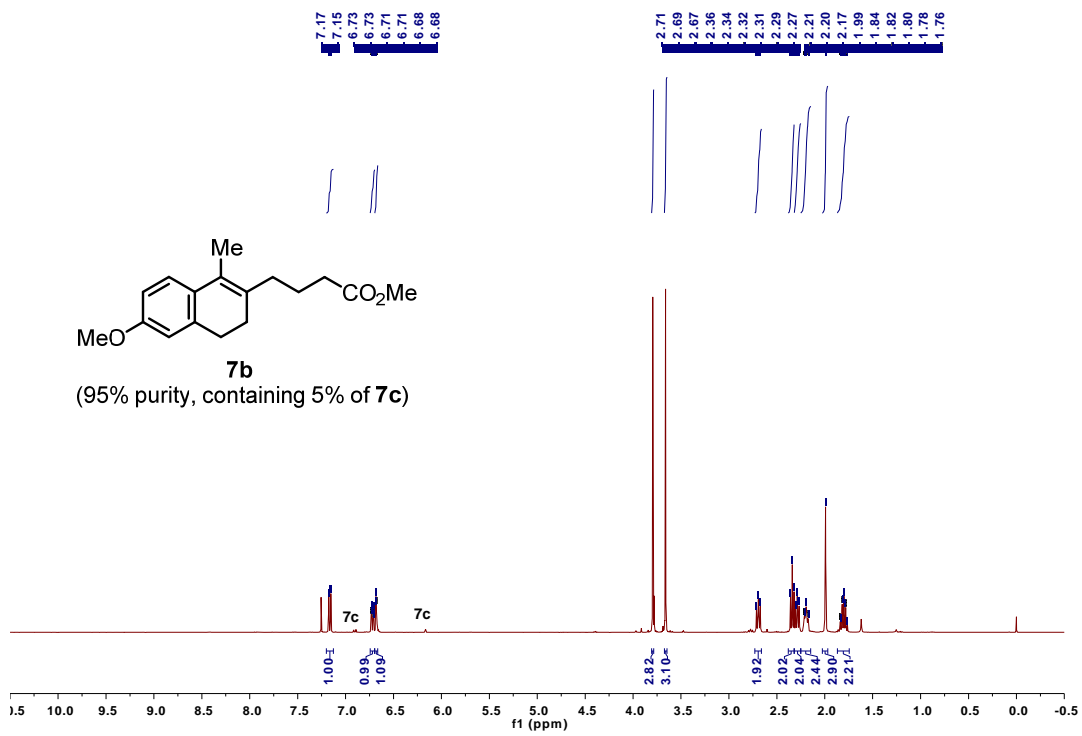


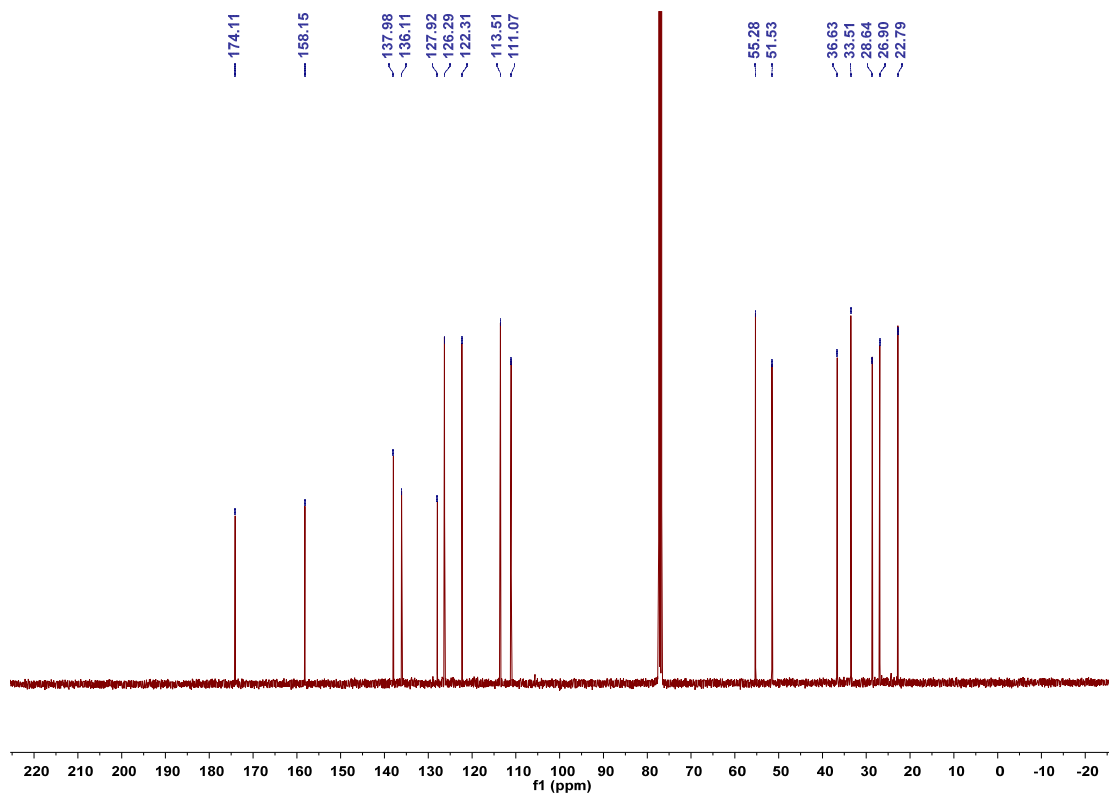
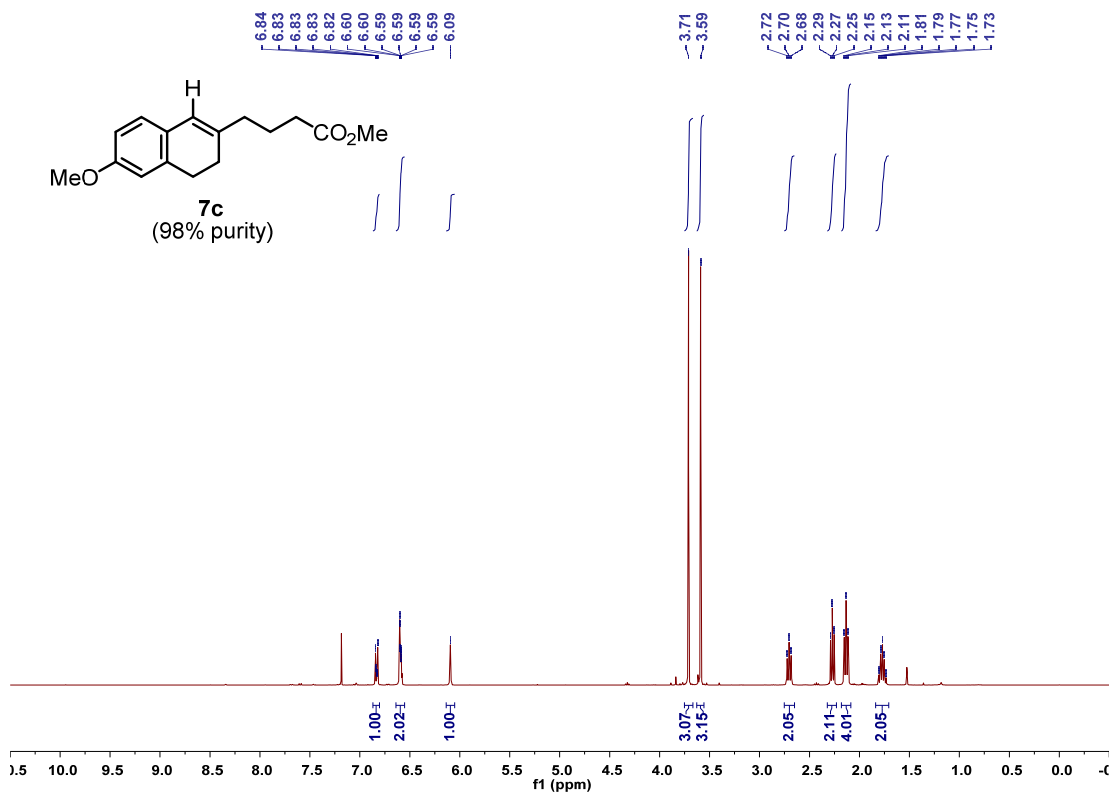


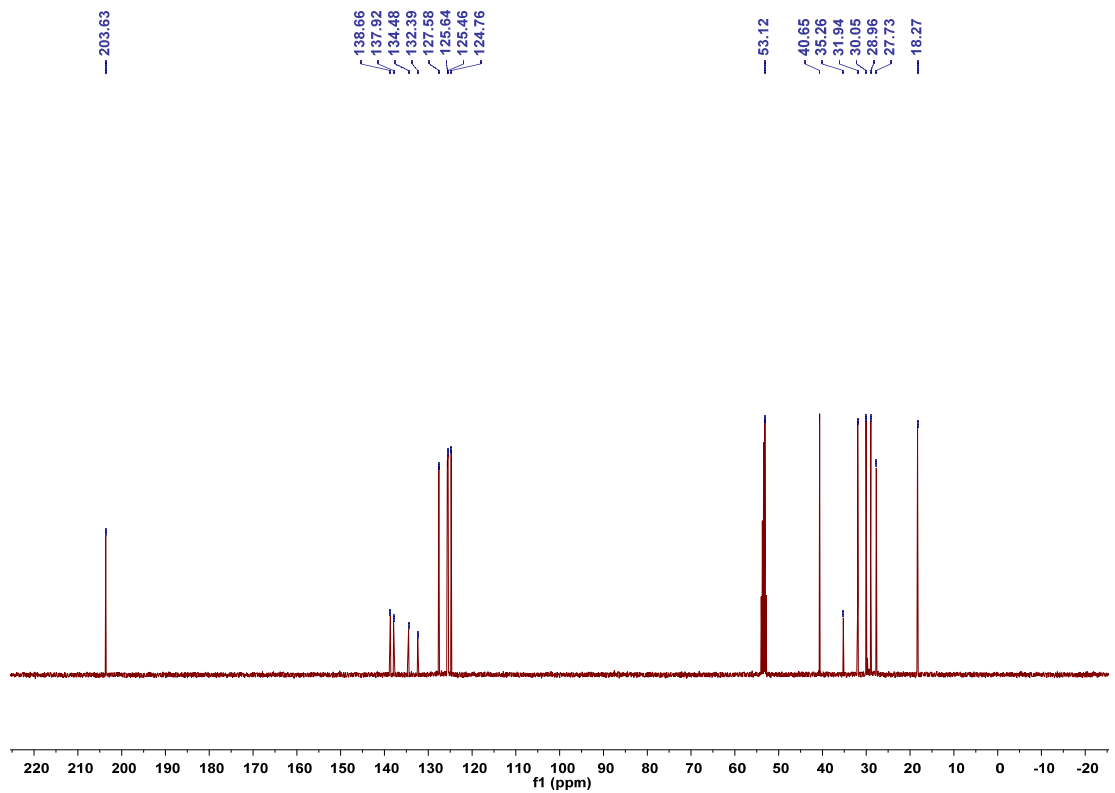
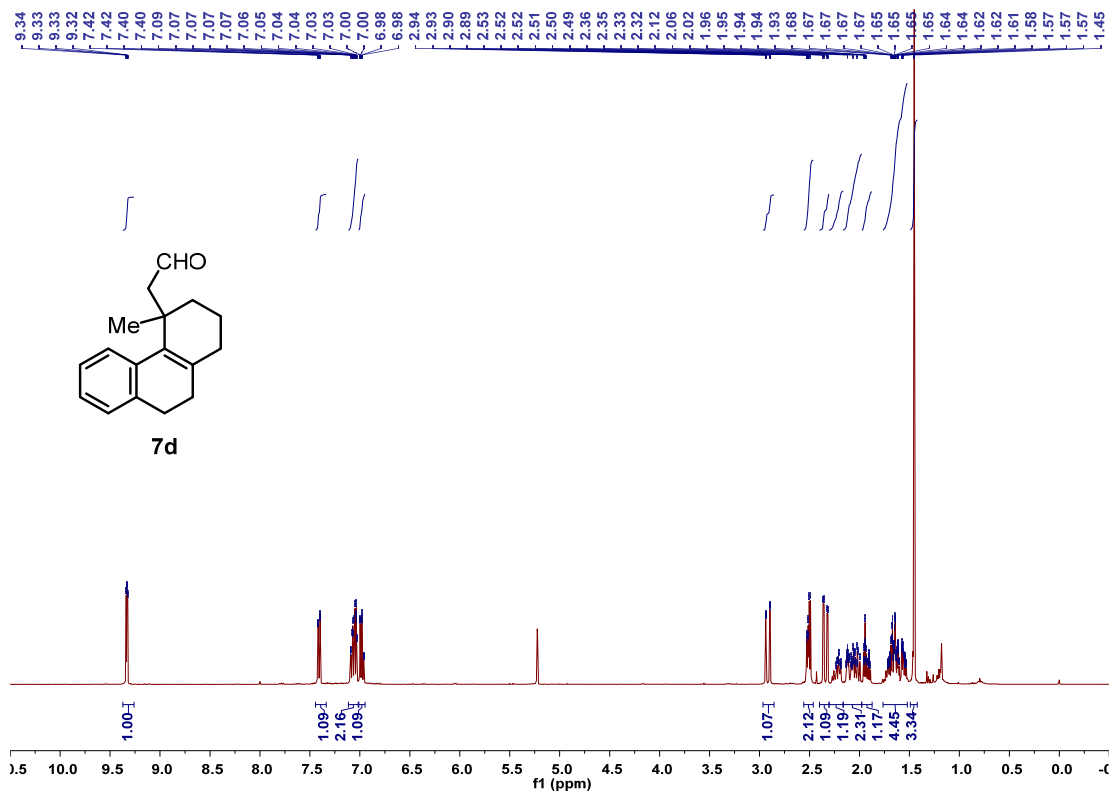


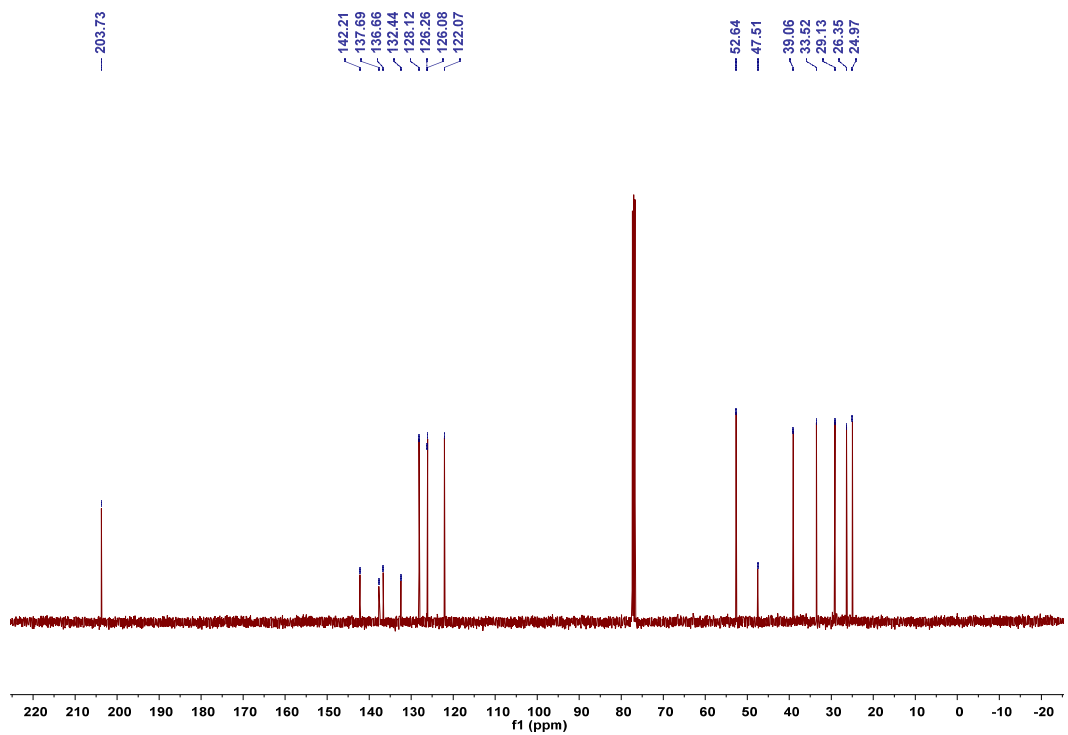
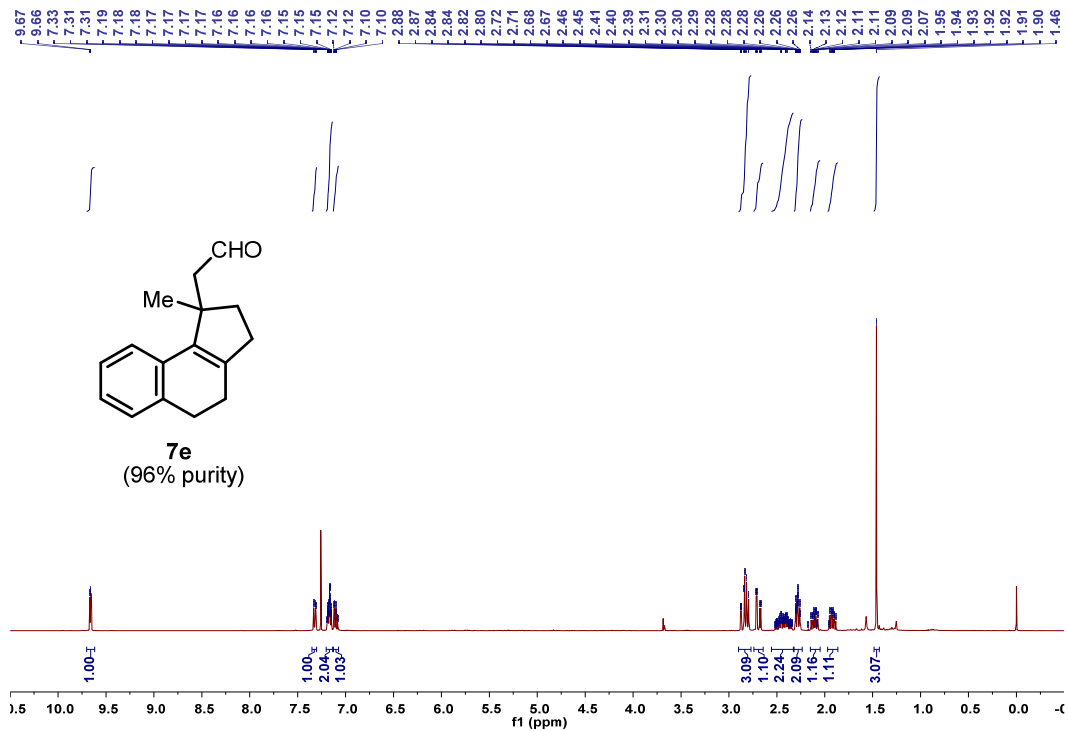


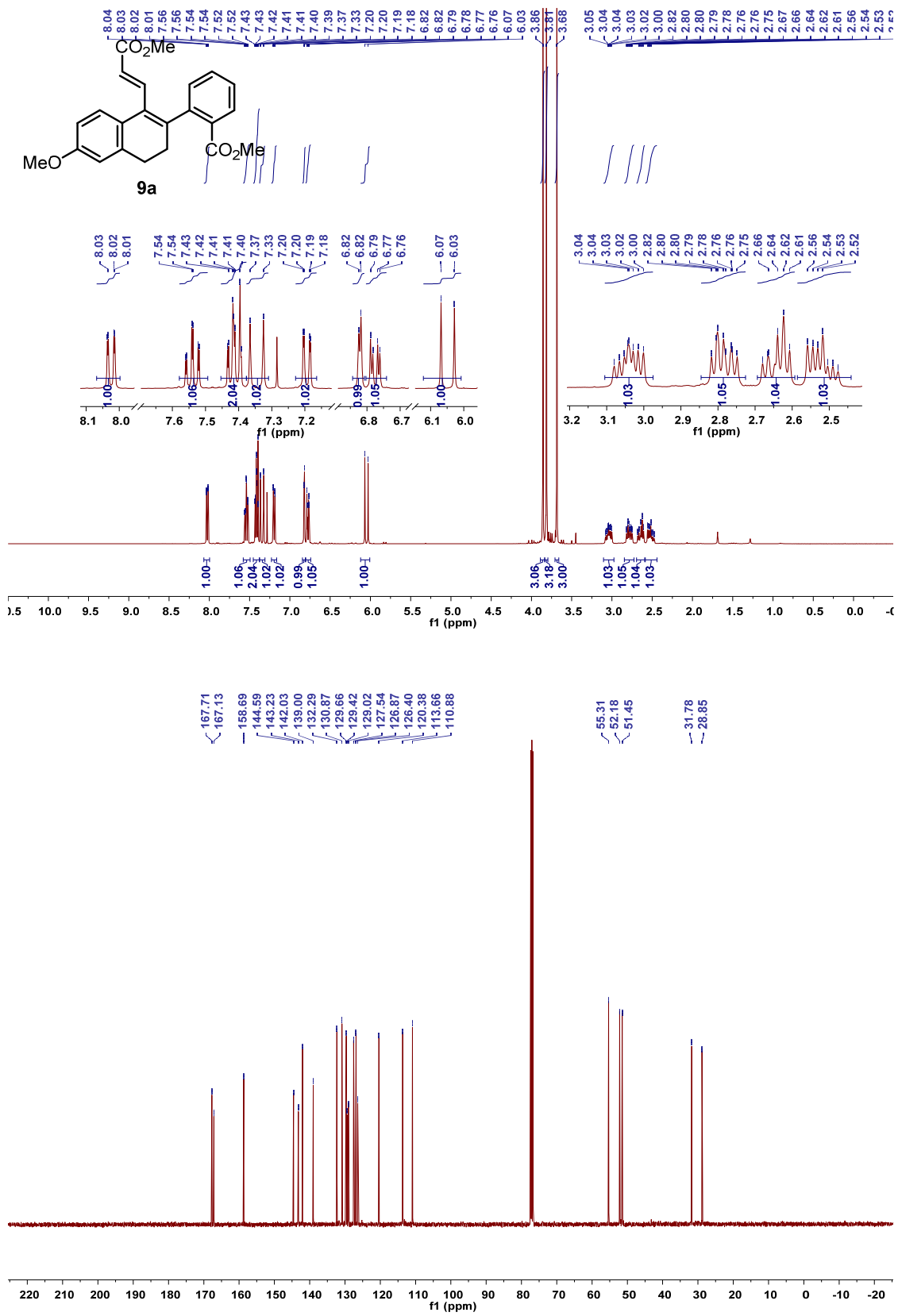


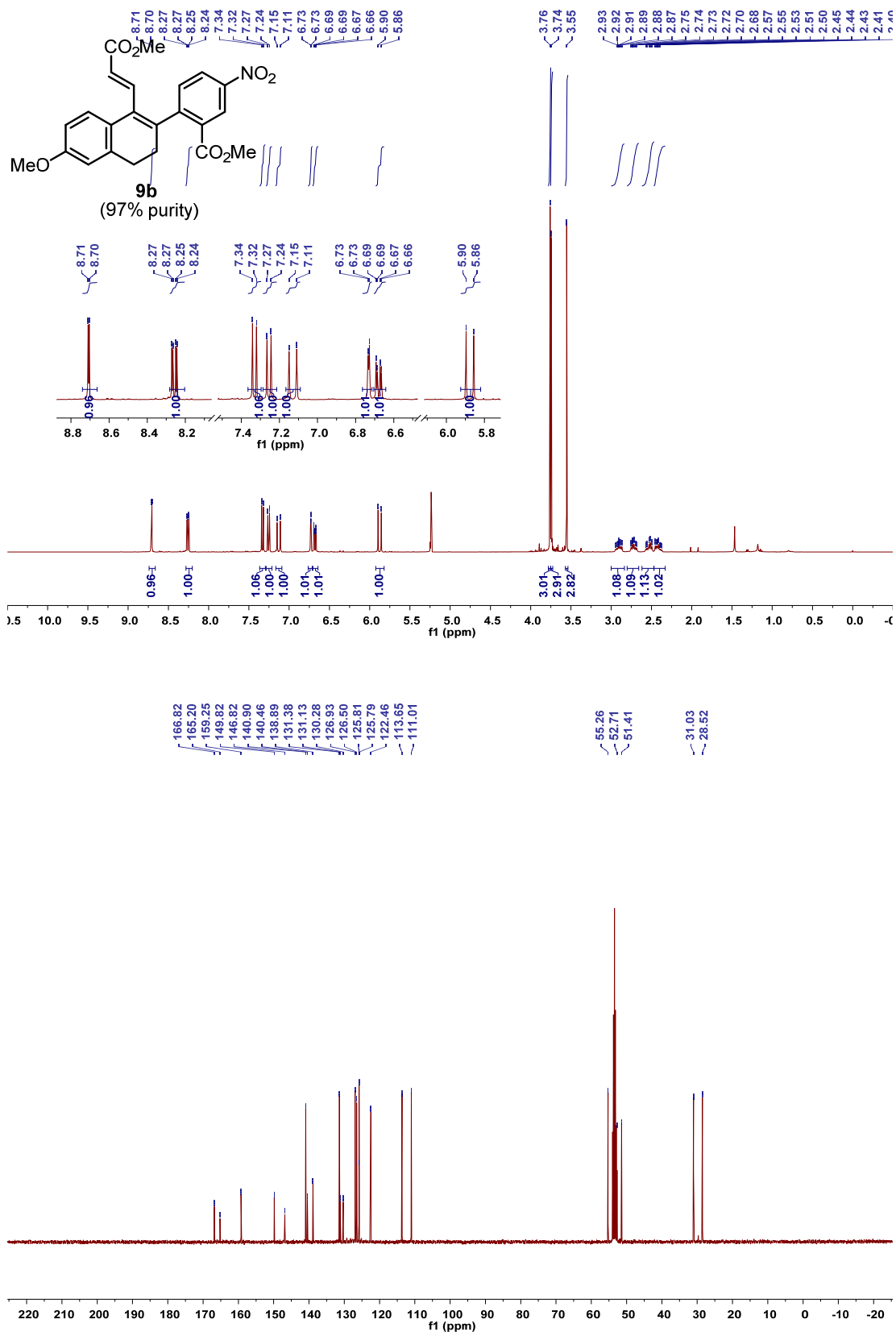


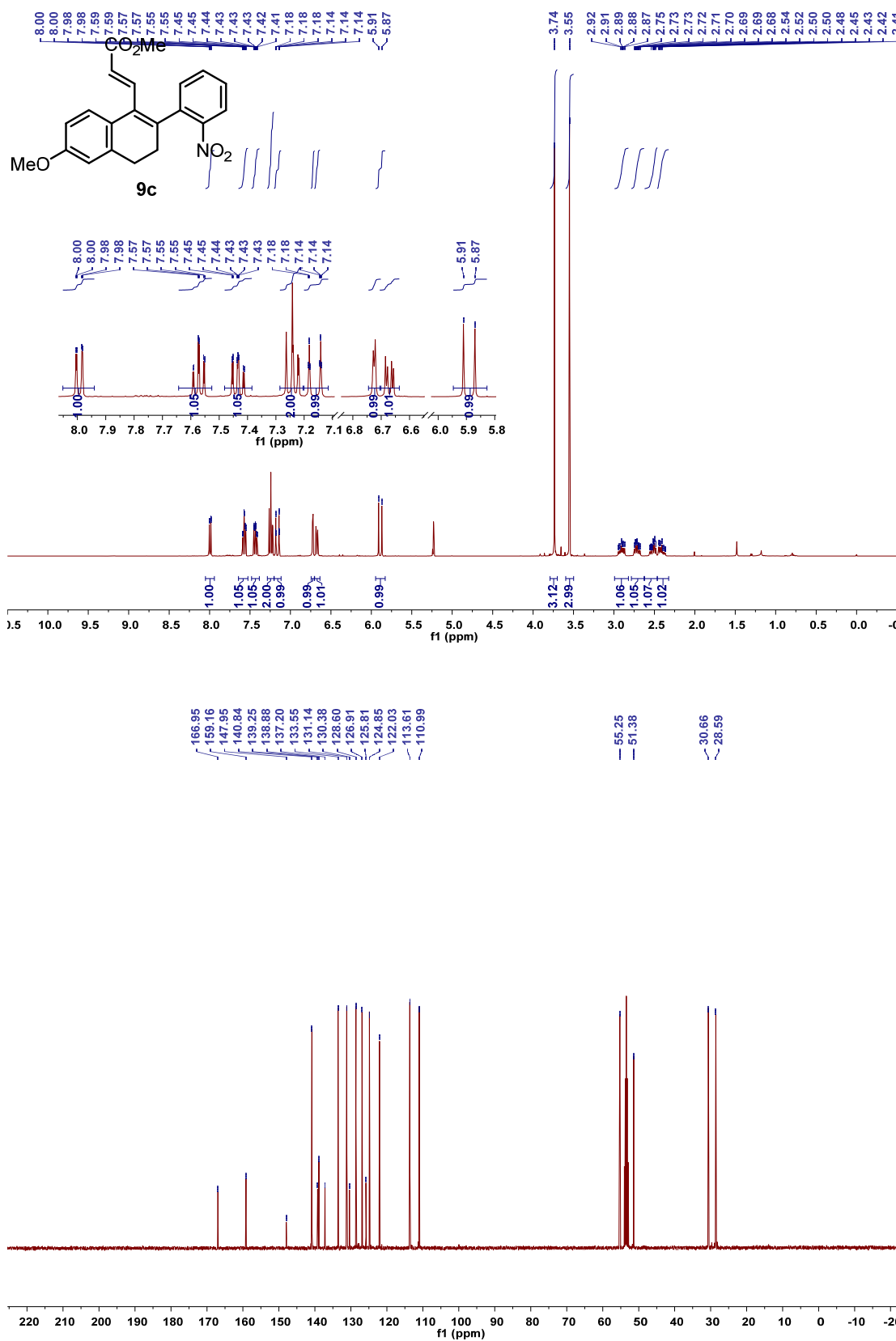


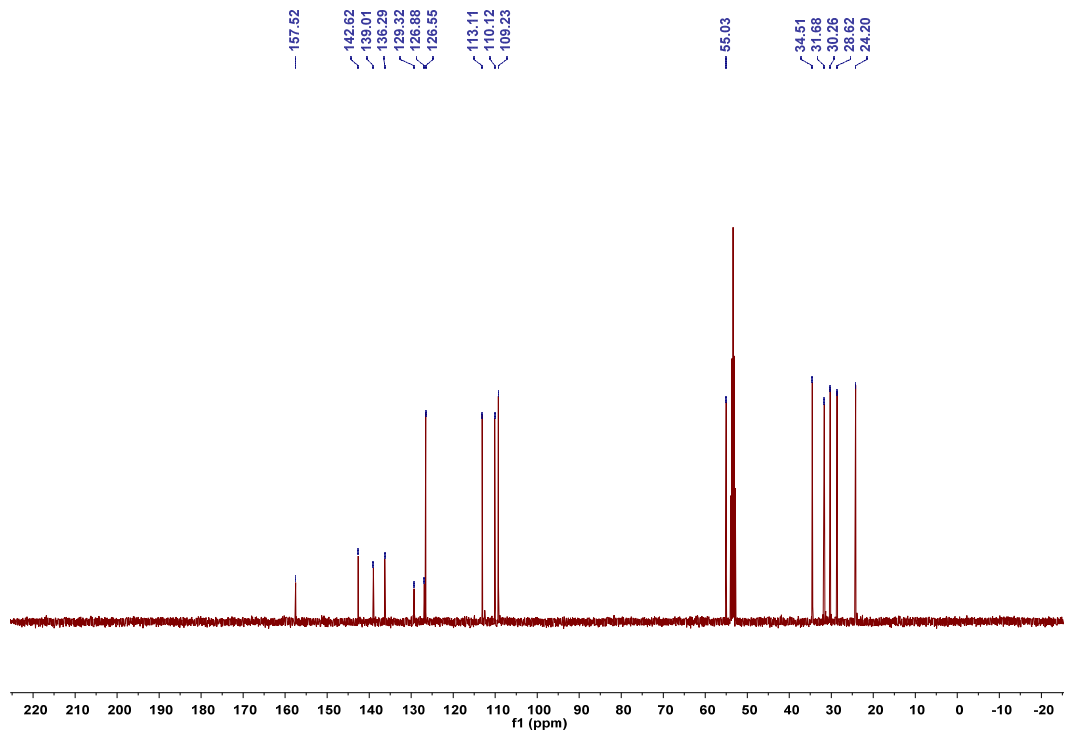
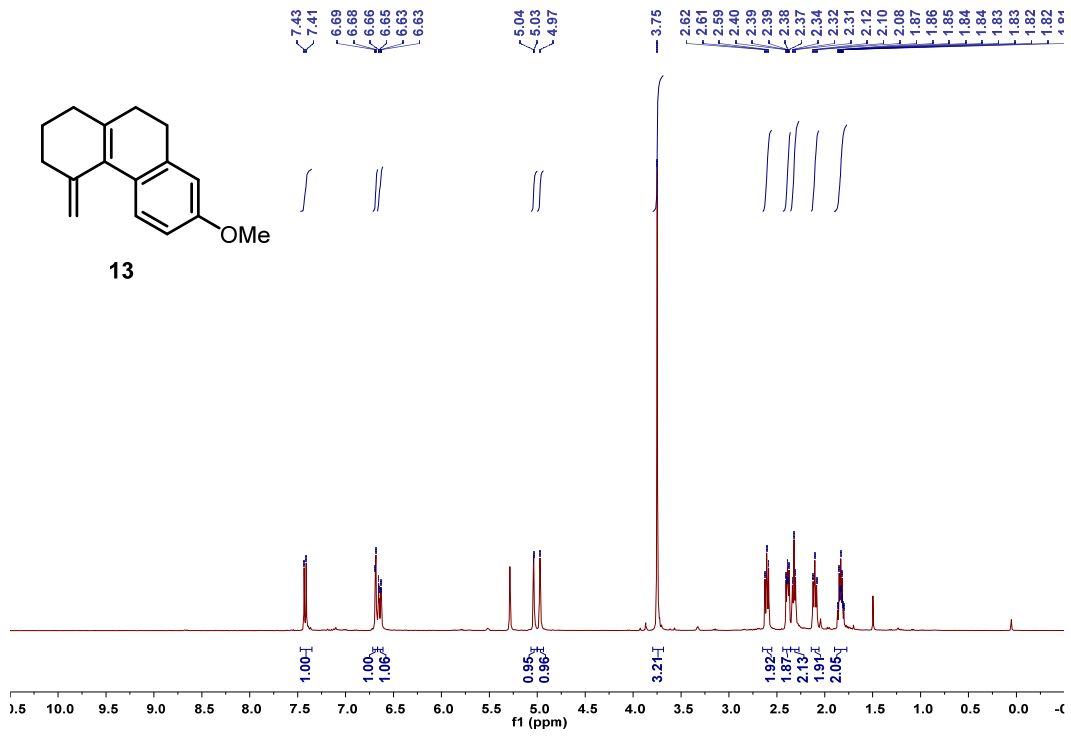


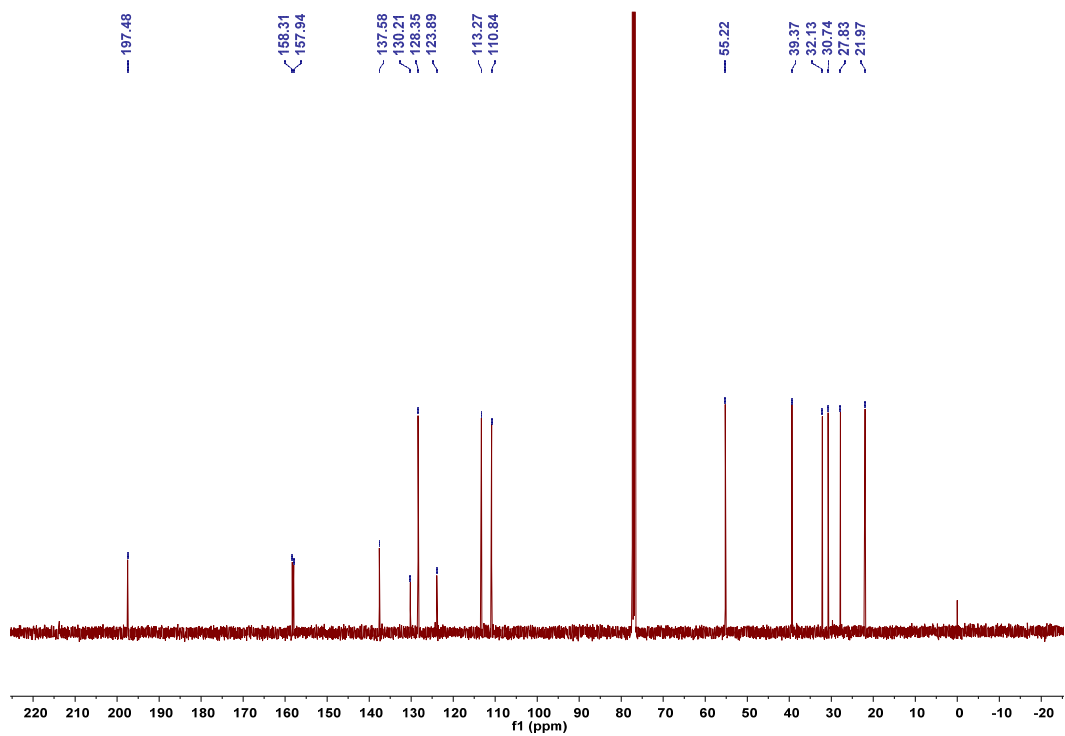
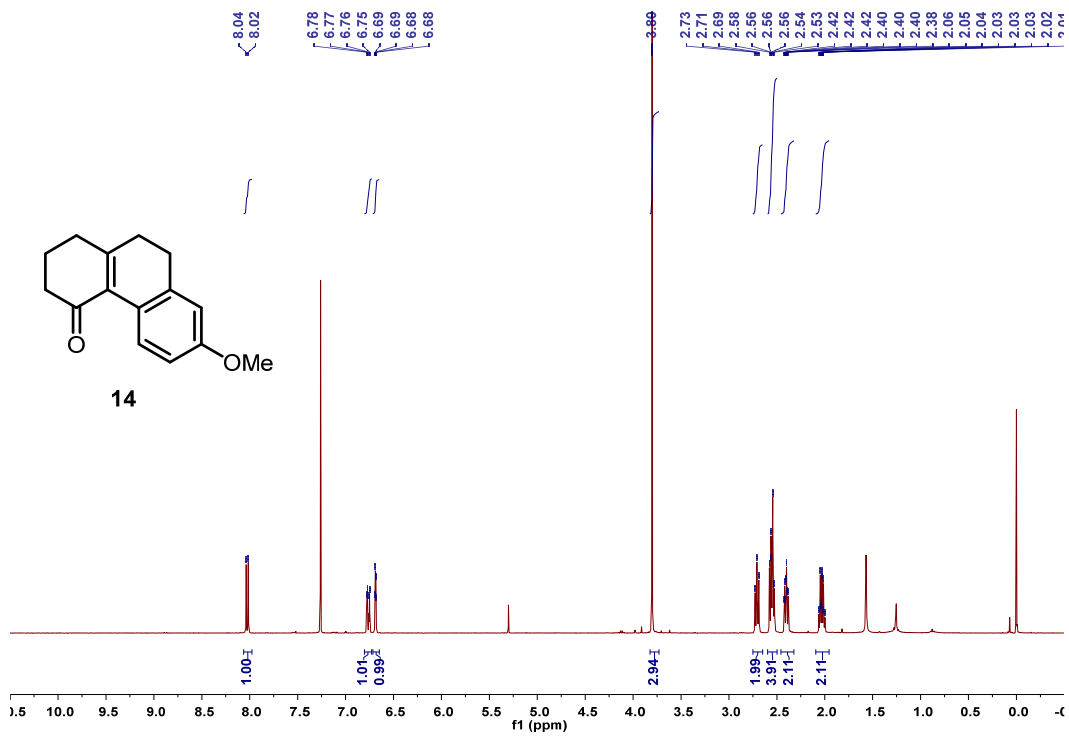


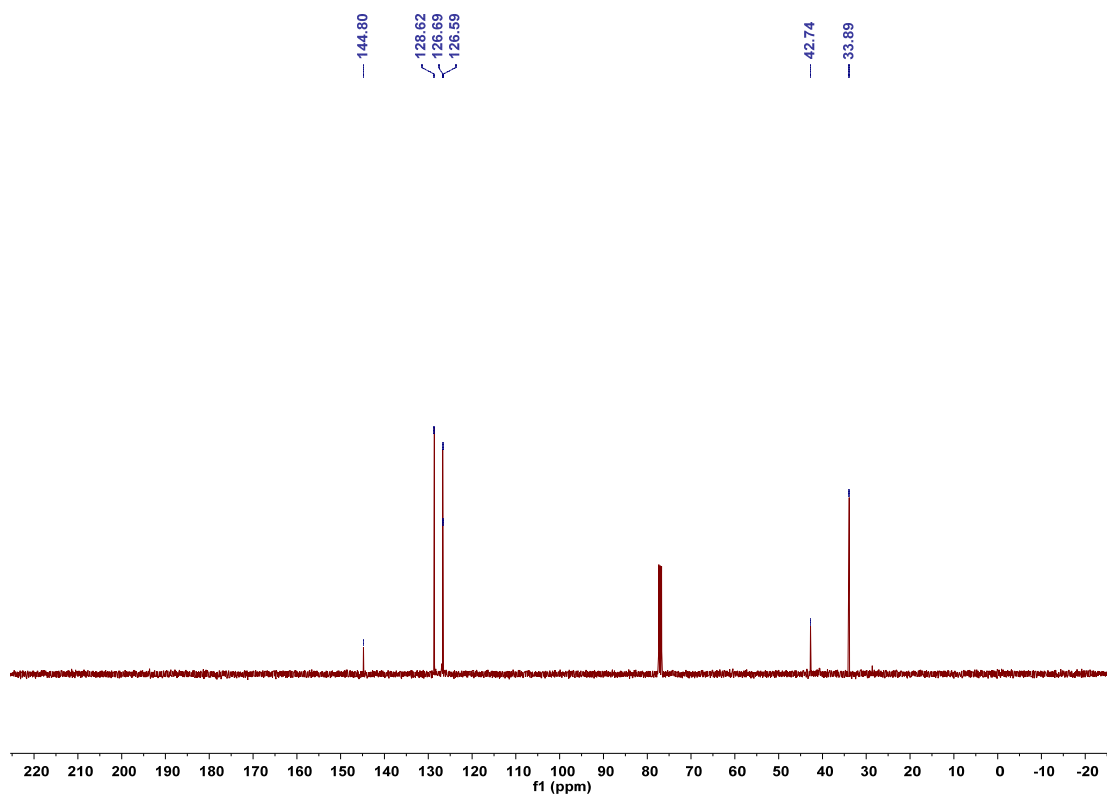
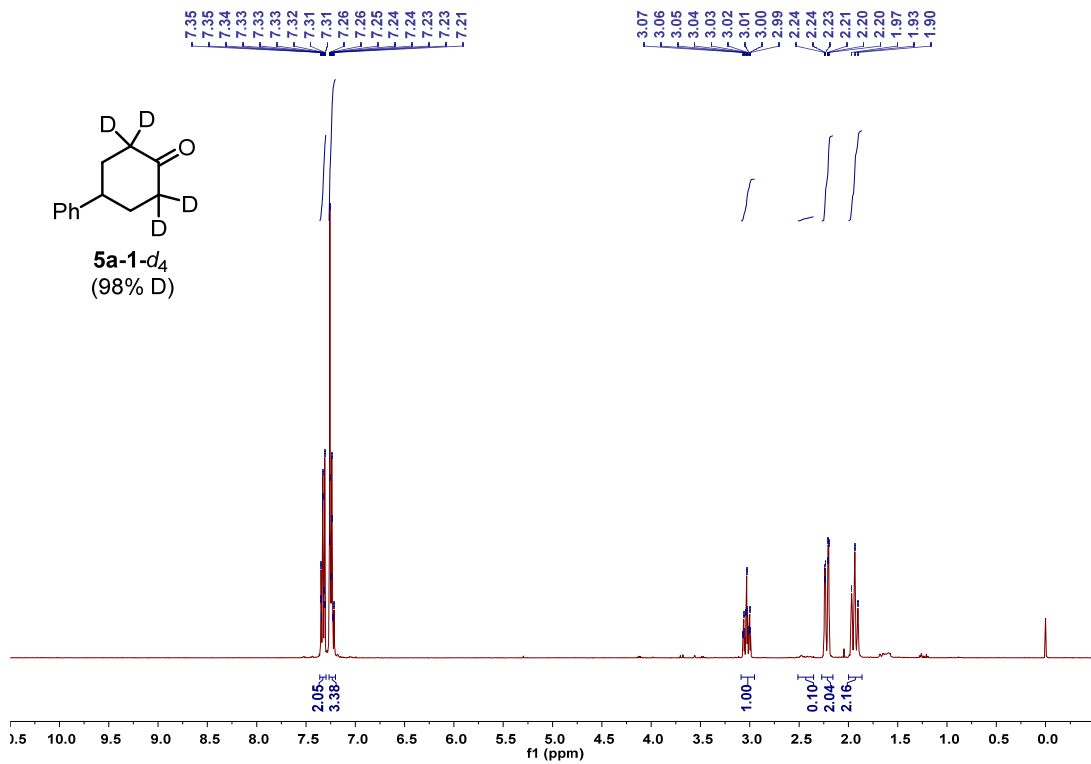


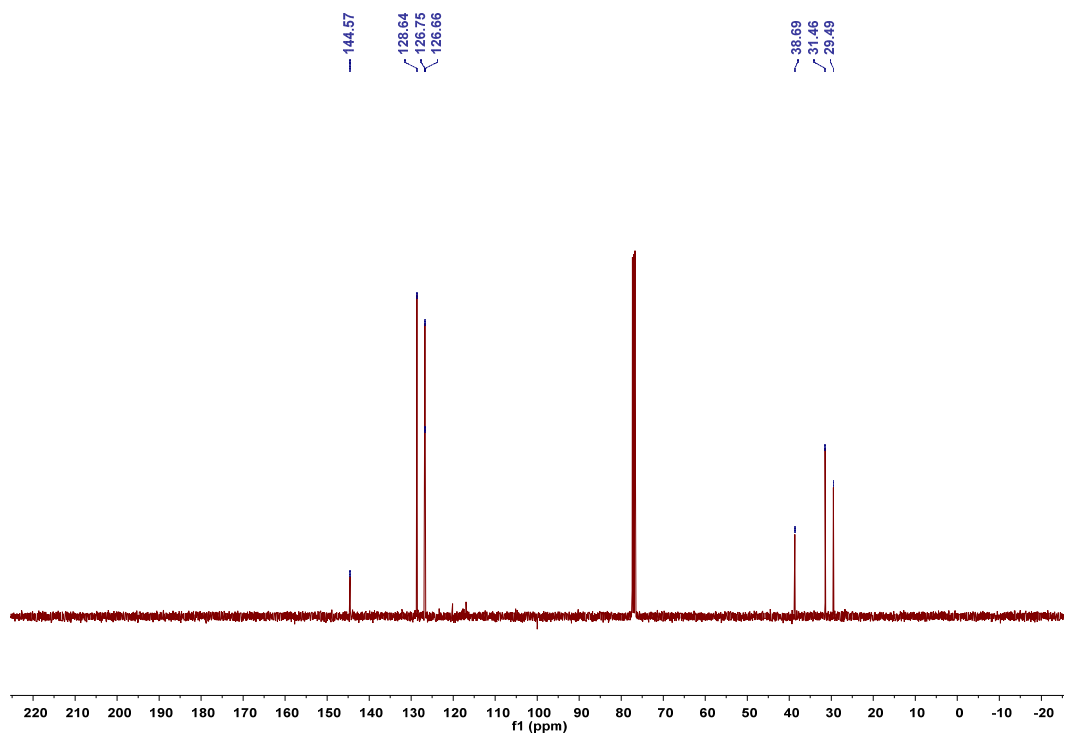
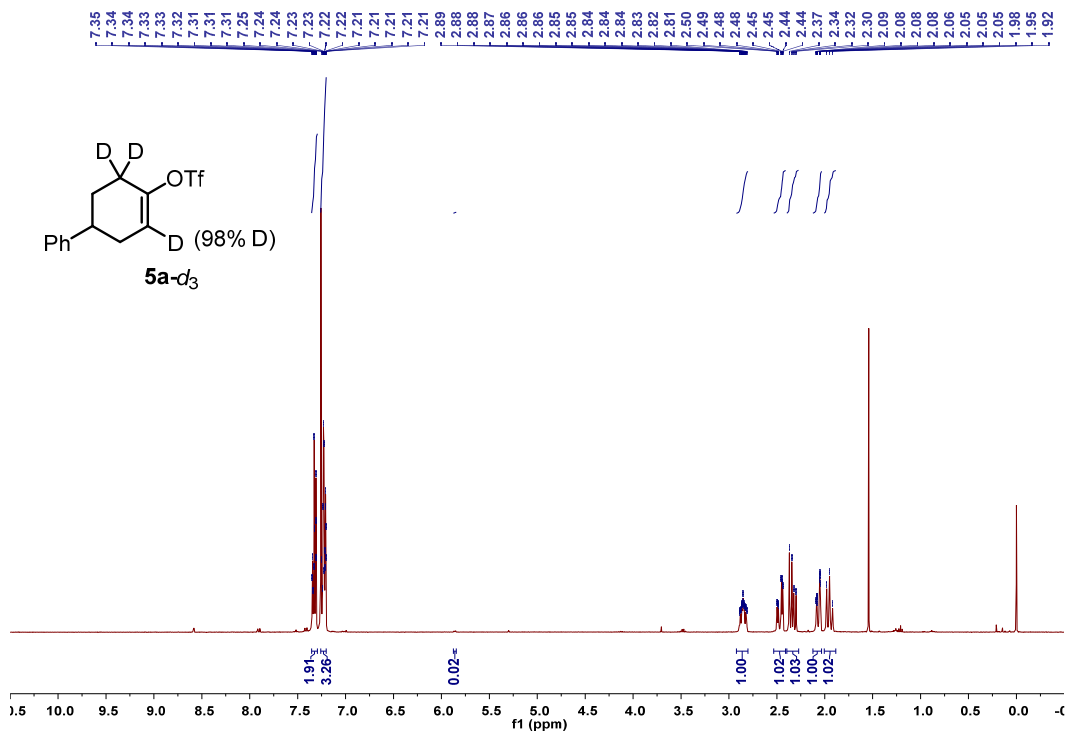


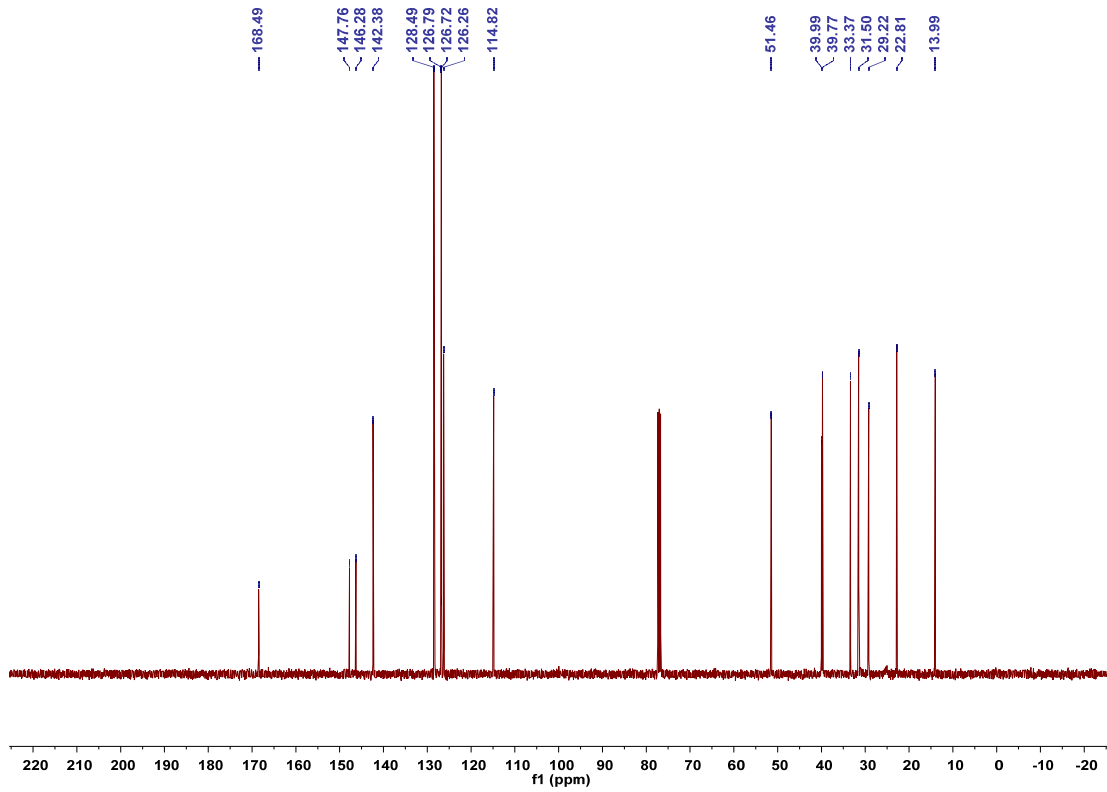
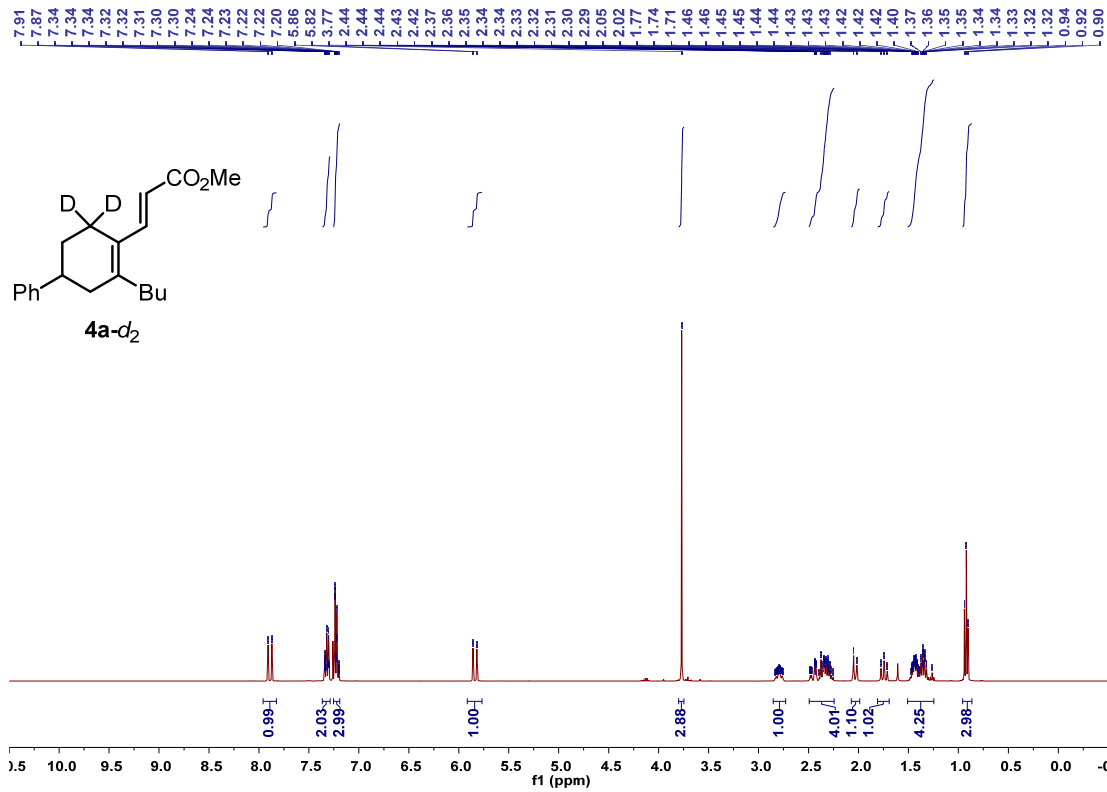


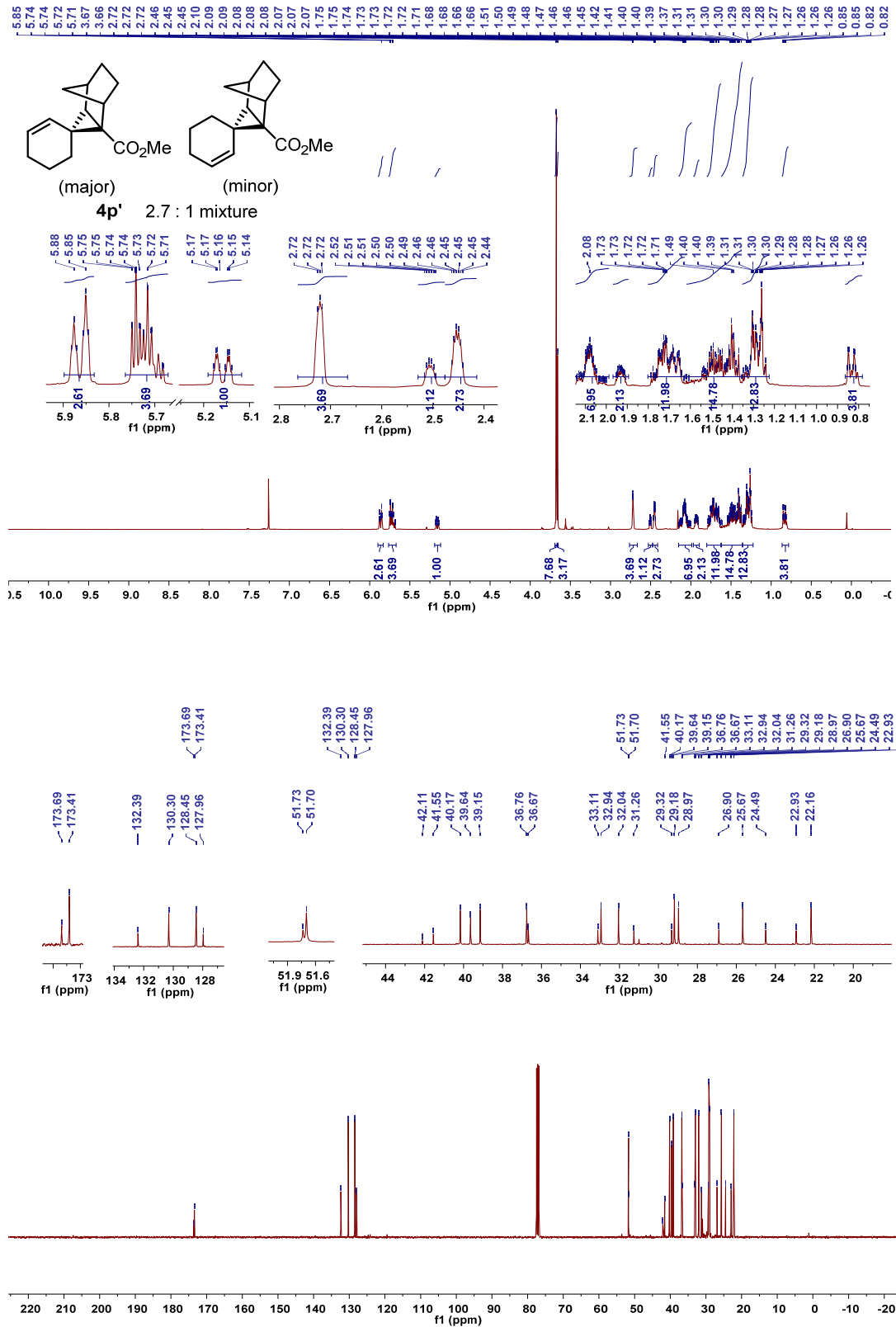




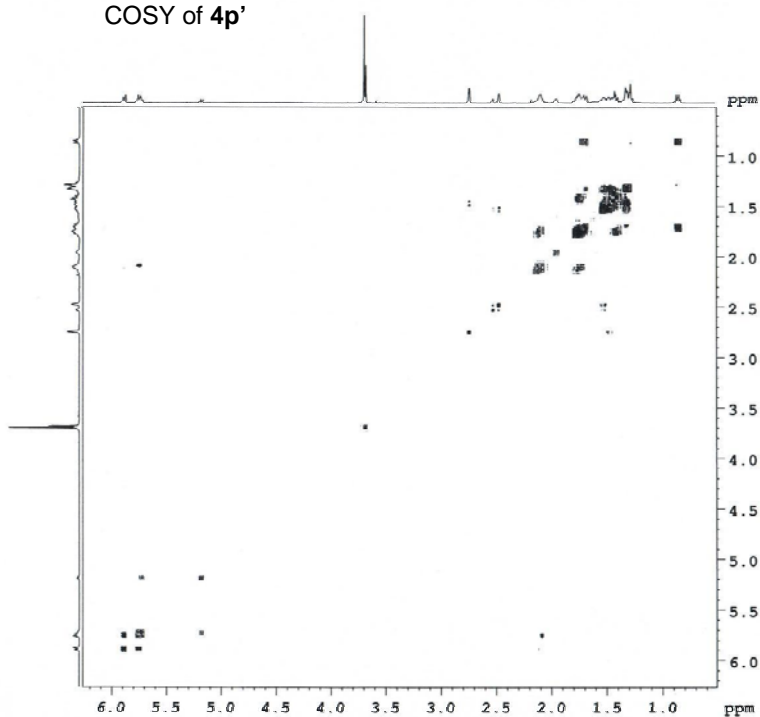








COSY of 4p'



```

Current Data Parameters
NAME      W3-R-63-final
EXPNO    3
PROCNO   1

F2 - Acquisition Parameters
Date_    20190402
Time     20.48
INSTRUM  spect
PROBHD   5 mm F4BBO BB/
PULPROG  cosypprph
TD       32768
SOLVENT  CDCl3
NS       8
DS       4
SWH      2876.870 Hz
FIDRES   1.404722 Hz
AQ       0.3554254 sec
RG       655.65
RW       173.800 usec
DE       6.50 usec
TE       297.4 K
DQ       0.00014107 sec
D1       2.00000000 sec
D11      0.00000000 sec
D12      0.00000000 sec
D16      0.00000000 sec
RG1      0.00034760 sec

***** CHANNEL f1 *****
SFO1     499.871934 MHz
NUC1     1H
P1       18.00 usec
P2       20.00 usec
PLW1    18.20000000 W

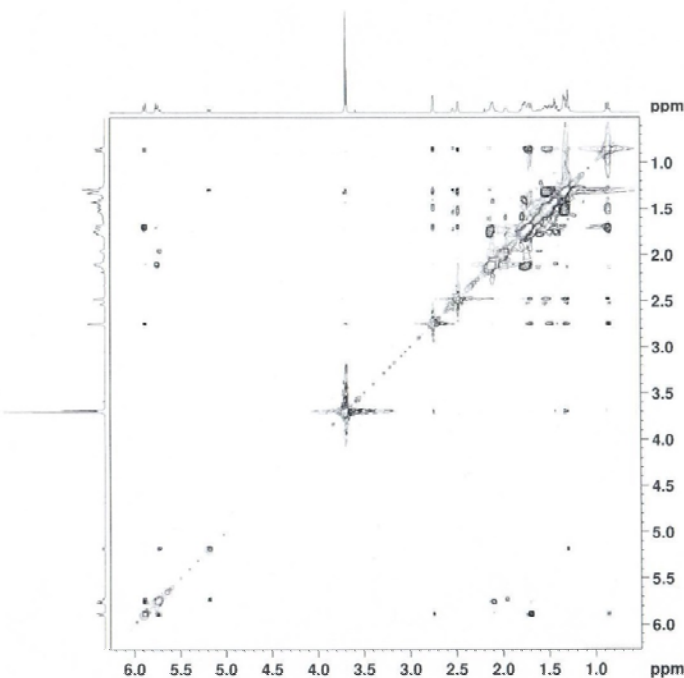
***** GRADIENT CHANNEL *****
GPRAM1[1] SMSQ10.100
GPRAM1[2] SMSQ10.100
GP1      10.00 %
GP2      20.00 %
P16      1000.00 usec

F1 - Acquisition parameters
TD       128
SFO1     499.8717 MHz
FIDRES   22.475544 Hz
SW       5.755 ppm
F2MODE   States-TPPI

F2 - Processing parameters
SI       1024
SF       499.8700000 MHz
WDW      QFIRM
SSB      0
LB       0 Hz
GB       0
PC       0.60

F1 - Processing parameters
SI       1024
MC2      States-TPPI
SF       499.8700000 MHz
WDW      QFIRM
SSB      0
LB       0 Hz
GB       0
    
```

NOESY of 4p'



```

Current Data Parameters
NAME      W3-R-63-final
EXPNO    3
PROCNO   1

F2 - Acquisition Parameters
Date_    20190402
Time     21.45
INSTRUM  spect
PROBHD   5 mm F4BBO BB/
PULPROG  noesygq3dpo
TD       32768
SOLVENT  CDCl3
NS       8
DS       4
SWH      2876.870 Hz
FIDRES   1.404722 Hz
AQ       0.3554254 sec
RG       655.65
RW       173.800 usec
DE       6.50 usec
TE       297.4 K
DQ       0.00014107 sec
D1       2.00000000 sec
D11      1.95000005 sec
D12      0.00000000 sec
D16      0.00000000 sec
RG1      0.00034760 sec

***** CHANNEL f1 *****
SFO1     499.8716934 MHz
NUC1     1H
P1       18.00 usec
P2       20.00 usec
PLW1    18.20000000 W
PLW10   2.49970012 W

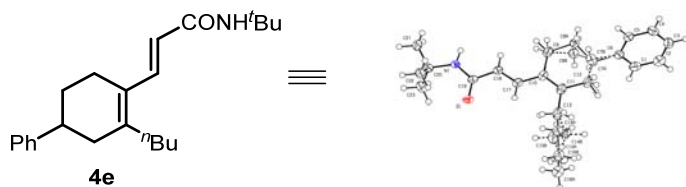
***** GRADIENT CHANNEL *****
GPRAM1[1] SMSQ10.100
GPRAM1[2] SMSQ10.100
GP1      10.00 %
GP2      20.00 %
P16      1000.00 usec

F1 - Acquisition parameters
TD       100
SFO1     499.8717 MHz
FIDRES   28.768700 Hz
SW       5.755 ppm
F2MODE   States-TPPI

F2 - Processing parameters
SI       1024
SF       499.8700000 MHz
WDW      QFIRM
SSB      0
LB       0 Hz
GB       0
PC       1.00

F1 - Processing parameters
SI       1024
MC2      States-TPPI
SF       499.8700000 MHz
WDW      QFIRM
SSB      0
LB       0 Hz
GB       0
    
```

V. X-ray Data



Identification code	4e (CCDC # 1908383)
Empirical formula	C ₂₃ H ₃₃ NO
Formula weight	339.50
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	Pbcn
a/Å	20.2170(10)
b/Å	9.4653(4)
c/Å	22.0972(11)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	4228.5(3)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.067
μ/mm^{-1}	0.064
F(000)	1488.0
Crystal size/mm ³	0.06 × 0.06 × 0.04
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.752 to 54.97
Index ranges	-24 ≤ h ≤ 26, -10 ≤ k ≤ 12, -25 ≤ l ≤ 28
Reflections collected	22244
Independent reflections	4611 [R_{int} = 0.0348, R_{sigma} = 0.0361]
Data/restraints/parameters	4611/59/276
Goodness-of-fit on F ²	1.028
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0491, wR_2 = 0.1091
Final R indexes [all data]	R_1 = 0.0842, wR_2 = 0.1228

One B-Alert: PLAT410_Alert_2_B Type_2 Test for short non-bonding intra H..H contacts. Author response: The atom H13D is included in the disordered *n*-butyl group. Because of low occupancy [22%] and thermal motion of the *n*-butyl group, the short contact of H17...H13D is unavoidable in the crystal.

VI. References

- (1) Dong, Z.; Wang, J.; Ren, Z.; Dong, G. *Angew. Chem. Int. Ed.* **2015**, *54*, 12664-12668.
- (2) Wang, J.; Li, R.; Dong, Z.; Liu, P.; Dong, G. *Nat. Chem.* **2018**, *10*, 866-872.
- (3) La, D. S.; Sattely, E. S.; Ford, J. G.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 7767-7778.
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