Supplementary Information for

Ruthenium-Catalyzed Formal sp^3-H Activation of Allylsilanes/esters with Olefins: Efficient Access to functionalized 1,3-Dienes

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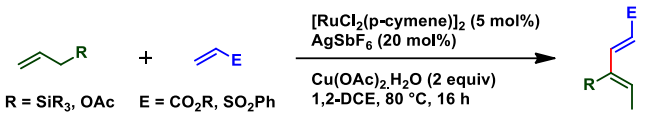
1. General Information:

General Aspects: Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware. Commercial solvents and reagents were used without further purification unless otherwise noted. All the chemicals were purchased commercially, and used without further purification. Yields refer to chromatographically pure compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and an p-anisaldehyde or ninhydrine stain, and heat as developing agents. Merck silica gel (particle size 100-200 and 230-400 mesh) was used for flash column chromatography. Neat compounds were used for record IR spectra. NMR spectra were recorded on either a Bruker Avance 400 (1H, 400 MHz; 13C, 100 MHz), Bruker Avance 500 (1H, 500 MHz; 13C, 125 MHz), or JEOL DELTA (ECX) 500 (1H, 500 MHz; 13C, 125 MHz). Mass spectrometric data were obtained using WATERS-Q-Tof-Premier-HAB213 and WATERS-QTof-Premier-ESI-MS instruments. Optical rotations were measured using a polarimeter (AUTOPOL II) at 30 °C. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, spt= septet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dt = doublet of a triplet, td = triplet of a doublet, m = multiplet, br = broad.

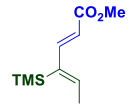
2. Experimental Procedures:

2.1. General procedure for the oxidative coupling reaction of allylsilanes/esters with activated olefins

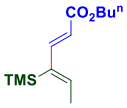


A 8 mL screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 0.01 mmol, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (80 mg, 0.4 mmol, 2.0 equiv), $AgSbF_6$ (14 mg, 0.04 mmol, 20 mol%) and 1,2-dichloroethane (2.0 mL). Then acrylate/vinyl sulfone (0.2 mmol, 1.0 equiv) and allylsilane or allyl ester (0.24 mmol, 1.2 equiv) were added into the solution in sequence. The vial was sealed under N_2 and heated to 80°C with stirring for 16 h. After cooling down, the mixture was diluted with ethyl acetate, filtrated and concentrated to give the crude compound which was directly purified by column chromatography.

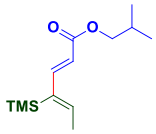
2.1a. Examples with data

Compound 3aa 

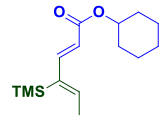
Following general procedure, **3aa** was obtained as a pale yellow oil (30:1::pet ether:EtOAc) (33 mg, 0.16 mmol, 82%).^{1}H NMR (400MHz, $CDCl_3$) δ 7.38 (d, *J* = 15.9 Hz, 1H), 6.56 (q, *J* = 7.2 Hz, 1H), 5.79 (d, *J* = 15.7 Hz, 1H), 3.70 (s, 3H), 1.88 (d, *J* = 7.2 Hz, 3H), 0.21 (s, 9H). ^{13}C NMR (125MHz, $CDCl_3$) δ 167.9, 152.2, 146.2, 138.3, 116.7, 51.4, 18.3, 0.5 (3C).HRMS (ESI) m/z calcd. for $C_{10}H_{18}O_2Si$ $[M+H]^+$199.1154; found 199.1158. IR (neat): ν_{max}/cm^{-1}2970, 2950, 1743, 1712, 1643, 1618, 1432, 1300, 1115, 910, 840.
NOESY shows that H_a (0.21) and H_b (1.88) are correlated and also H_c (6.56) and H_d (7.38) are weakly correlated.

Compound 3ab 

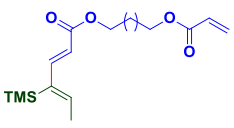
Following general procedure, **3ab** was obtained as a pale yellow oil (30:1::pet ether:EtOAc) (40 mg, 0.168 mmol, 84%).^{1}H NMR (400MHz, $CDCl_3$) δ 7.38 (d, *J* = 15.9 Hz, 1H), 6.57 (q, *J* = 7.2 Hz, 1H), 5.79 (d, *J* = 15.5 Hz, 1H), 4.12 (t, *J* = 6.4 Hz, 2H), 1.89 (d, *J* = 7.2 Hz, 3H), 1.67 - 1.61 (m, 2H), 1.42 - 1.35 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.22 (s, 9H). ^{13}C NMR (100MHz,$CDCl_3$) δ167.6, 151.8, 146.1, 138.3, 117.2, 64.1, 30.9, 19.3, 18.4, 13.8, 0.5(3C).HRMS (ESI) m/z calcd. for $C_{13}H_{24}O_2Si$ $[M+H]^+$241.1624; found 241.1626. IR (neat): ν_{max}/cm^{-1}2975, 2948, 1749, 1716, 1640, 1619, 1430, 1298, 1120, 908, 838.

Compound 3ac 

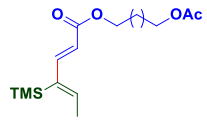
Following general procedure, **3ac** was obtained as a pale yellow oil (30:1::pet ether:EtOAc) (38 mg, 0.158 mmol, 79%).^{1}H NMR (400MHz, $CDCl_3$) δ7.39 (d, *J* = 15.9 Hz, 1H), 6.58 (q, *J* = 7.2 Hz, 1H), 5.81 (d, *J* = 15.3 Hz, 1H), 3.91 (d, *J* = 6.4 Hz, 2H), 2.00 - 1.94 (m, 1H), 1.89 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 6H), 0.23 (s, 9H).^{13}C NMR (125MHz,$CDCl_3$) δ167.5, 151.8, 145.8, 138.4, 117.2, 70.4, 27.9, 19.2 (2C), 18.3, 0.5 (3C).HRMS (ESI) m/z calcd. for $C_{13}H_{24}O_2Si$ $[M+H]^+$241.1624; found 241.1626. IR (neat): ν_{max}/cm^{-1}2978, 2949, 1748, 1716, 1642, 1622, 1431, 1297, 1122, 906, 839.

Compound 3ad 

Following general procedure, **3ad** was obtainedas a pale yellow oil (30:1::pet ether:EtOAc) (42 mg, 0.16 mmol, 80%).^{1}H NMR (400MHz, $CDCl_3$) δ 7.37 (d, *J* = 15.9 Hz, 1H), 6.57 (q, *J* = 7.2 Hz, 1H), 5.78 (d, *J* = 15.3 Hz, 1H), 4.83 - 4.76 (m, 1H), 1.88 (d, *J* = 7.3 Hz, 3H), 1.76 - 1.71 (m, 2H), 1.43 (d, *J* = 9.8 Hz, 2H), 1.38 - 1.34 (m, 2H), 0.22 (s, 9H). ^{13}C NMR (100MHz,$CDCl_3$) δ 166.9, 151.5, 145.9, 138.3, 117.7, 72.3, 31.8 (2C), 25.5, 23.9 (2C), 18.4, 0.5 (3C).HRMS (ESI) m/z calcd. for $C_{15}H_{26}O_2Si$ $[M+H]^+$267.1780; found 267.1783. IR (neat): ν_{max}/cm^{-1}2983, 2953, 1743, 1708, 1636, 1620, 1439, 1293, 1115, 902, 832.

Compound 3ae 

Following general procedure, **3ae** was obtained as a pale yellow oil (30:1::pet ether:EtOAc) (54 mg, 0.150 mmol, 71%).^{1}H NMR (500MHz, $CDCl_3$) δ7.38 (d, *J* = 15.9 Hz, 1H), 6.57 (q, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 6.9 Hz, 1H), 6.11 (dd, *J* = 6.9, 5.2, Hz, 1H), 5.81 - 5.78 (m, 2H), 4.15 - 4.12 (m, 4H), 1.89 (d, *J* = 7.4 Hz, 3H), 1.65 (m, 6H), 1.37 - 1.33 (m, 8H), 0.23 (s, 9H). ^{13}C NMR (125MHz,$CDCl_3$) δ167.6, 166.4, 151.8, 146.0, 130.5, 128.7, 117.2, 64.8, 64.4, 29.5, 29.4, 29.3, 29.2, 28.8, 28.7, 26.0 (2C), 18.4, 0.5 (3C).HRMS (ESI) m/z calcd. for $C_{21}H_{36}O_4Si$ $[M+H]^+$381.2461; found 381.2460. IR (neat): ν_{max}/cm^{-1}2945, 2860, 1769, 1720, 1658, 1629, 1432, 1370, 1259, 1120, 920, 850.

Compound 3af 

Following general procedure, **3af** was obtained as a pale yellow oil (30:1::pet ether:EtOAc) (50 mg, 0.146 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 15.9 Hz, 1H), 6.51 (q, *J* = 7.2 Hz, 1H), 5.79 (d, *J* = 15.7 Hz, 1H), 4.09 (t, *J* = 6.4 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.03 (s, 3H), 1.89 (d, *J* = 7.2 Hz, 3H), 1.65 - 1.59 (m, 6H), 1.34 (m, 4H), 0.22 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ

171.3, 167.5, 151.8, 146.0, 138.4, 117.2, 64.6, 64.2, 29.0, 28.7, 28.6, 25.9, 25.9, 21.1, 18.3, 0.5 (3C).HRMS (ESI) m/z calcd. for $C_{18}H_{32}O_4Si[M+H]^+$341.2148; found 341.2149. IR (neat): ν_{max}/cm^{-1}2935, 2850, 1723, 1638, 1463, 1415, 1370, 1293, 1125, 935. 860

Compound 3ba Following general procedure, **3ba** was obtained as a pale yellow oil (30:1::pet ether:EtOAc) (45 mg, 0.166 mmol, 83%).^{1}H NMR (500 MHz, $CDCl_3$) δ7.37 (d, *J* = 16.0 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 6.9 Hz, 2H), 6.57 (q, *J* = 7.2 Hz, 1H), 5.76 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H), 2.26 (s, 2H), 1.76 (d, *J* = 6.9 Hz, 3H), 0.20 (s, 6H).^{13}C NMR (100MHz, $CDCl_3$) δ167.8, 152.0, 147.0, 139.3, 136.7, 128.3 (2C), 128.2 (2C), 124.4, 117.0, 51.5, 26.1, 18.4, -1.3 (2C).HRMS (ESI) m/z calcd. for $C_{16}H_{22}O_2Si$ $[M+H]^+$275.1467; found 275.1469. IR (neat): ν_{max}/cm^{-1}3033, 2940, 1820, 1765, 1730, 1663, 1615, 1450, 1370, 1260, 1123, 960, 835.

Compound 3bb Following general procedure, **3bb** was obtained as a pale yellow oil (30:1::pet ether:EtOAc) (54 mg, 0.17 mmol, 85%).^{1}H NMR (500 MHz, $CDCl_3$) δ7.35 (d, *J* = 15.5 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.59 (q, *J* = 6.9 Hz, 1H), 5.75 (d, *J* = 16.0 Hz, 1H), 4.12 (t, *J* = 6.4 Hz, 2H), 2.26 (s, 2H), 1.76 (d, *J* = 6.9 Hz, 3H), 1.65 (m, 2H), 1.40 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.20 (s, 6H). ^{13}C NMR (125MHz, $CDCl_3$) δ167.4, 151.5, 146.5, 139.3, 136.8, 128.3 (2C), 128.2 (2C), 124.4, 117.6, 64.1, 30.9, 26.1, 19.3, 18.3, 13.8, -1.3 (2C).HRMS (ESI) m/z calcd. for $C_{19}H_{28}O_2Si$ $[M+H]^+$317.1937; found 317.1938. IR (neat): ν_{max}/cm^{-1}3025, 2930, 1835, 1740, 1715, 1670, 1630, 1425, 1360, 1225, 1115, 930, 840.

Compound 3bc Following general procedure, **3bc** was obtained as a pale yellow oil (30:1::pet ether:EtOAc) (54 mg, 0.164 mmol, 82%).^{1}H NMR (500 MHz, $CDCl_3$) δ7.36 (d, *J* = 16.0 Hz, 1H), 7.16 (t, *J* = 7.4 Hz 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.59 (q, *J* = 7.1 Hz, 1H), 5.75 (d, *J* = 16.0 Hz, 1H), 3.91 (d, *J* = 6.9 Hz, 2H), 2.26 (s, 2H), 1.96 (m, 1H), 1.77 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 6H), 0.20 (s, 6H). ^{13}C NMR (125MHz, $CDCl_3$) δ167.4, 151.5, 146.3, 139.3, 136.8, 128.3 (2C), 128.2(2C), 124.4, 117.6, 70.4, 27.9, 26.1, 19.2 (2C), 18.4, -1.3 (2C).HRMS (ESI) m/z calcd. for $C_{19}H_{28}O_2Si$ $[M+H]^+$317.1937; found 317.1938. IR (neat): ν_{max}/cm^{-1}3026, 2932, 1839, 1742, 1717, 1672, 1632, 1430, 1365, 1229, 1116, 938, 838.

Compound 3cb Following general procedure, **3cb** was obtained as a pale yellow oil (30:1::pet ether:EtOAc) (45 mg, 0.16 mmol, 80%).^{1}H NMR (500 MHz, $CDCl_3$) δ7.43 (d, *J* = 15.9 Hz, 1H), 6.59 (q, *J* = 6.9 Hz, 1H), 5.79 (d, *J* = 15.4 Hz, 1H), 4.12 (t, *J* = 6.7 Hz, 2H), 1.88 (d, *J* = 7.2 Hz, 3H), 1.67 - 1.62 (m, 2H), 1.42 - 1.37 (m, 2H), 0.92 (t, *J* = 6.7 Hz, 3H), 0.91 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (125MHz, $CDCl_3$) δ167.5, 152.8, 145.1, 136.8, 117.3, 64.1, 30.9, 27.0 (3C), 19.3, 19.1, 18.5, 13.8, -3.2 (2C).HRMS (ESI) m/z calcd. for $C_{16}H_{30}O_2Si$ $[M+H]^+$283.2093; found 283.2097. IR (neat): ν_{max}/cm^{-1}2965, 2939, 2872, 1773, 1720, 1643, 1630, 1315, 1173, 1050, 960, 855.

Compound 3ag Following general procedure, **3ag** was obtained as a pale yellow solid (15:1::pet ether:EtOAc) (43 mg, 0.154 mmol, 78%).^{1}H NMR (500 MHz, $CDCl_3$) δ7.87 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 14.9 Hz, 1H), 6.60 - 6.54 (m, 1H), 6.24 (d, *J* = 14.9 Hz, 1H), 1.89 (d, *J* = 7.4 Hz, 3H), 0.19 (s, 9H).^{13}C NMR (125MHz, $CDCl_3$) δ 149.6, 147.6, 141.5, 136.7, 133.1, 129.3 (2C), 127.5 (2C), 125.9, 18.5, 0.3(3C).HRMS (ESI) m/z calcd. for $C_{14}H_{20}O_2SSi$ $[M+H]^+$281.1032; found 281.1035. IR (neat): ν_{max}/cm^{-1}3039, 2945, 1820, 1778, 1715, 1660, 1615, 1472, 1343, 1235, 1132, 1055, 960, 853.

Compound 3bg Following general procedure, **3bg** was obtained as a pale yellow solid (15:1::pet ether:EtOAc) (54 mg, 0.152 mmol, 76%).^{1}H NMR (500 MHz, $CDCl_3$) δ7.82 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 15.5 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 6.9 Hz, 2H), 6.58 (q, *J* = 7.4 Hz, 1H), 6.05 (d, *J* = 14.9 Hz, 1H), 2.21 (s, 2H), 1.80 (d, *J* = 7.4 Hz, 3H), 0.18 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ149.3, 148.0, 141.3, 138.8, 135.3, 133.1, 129.3 (2C), 128.3, 128.2 (3C), 127.5(2C), 126.3, 124.5, 25.9, 18.5, -1.5 (2C).HRMS (ESI) m/z calcd. for $C_{20}H_{24}O_2SSi[M+H]^+$357.1345; found 357.1349. IR (neat): ν_{max}/cm^{-1}3050, 2958, 2936, 2915, 1816, 1780, 1740, 1615, 1602, 1520, 1459, 1368, 1232, 1128, 1059, 960, 856.

Compound 3da Following general procedure, **3da** was obtained as a pale yellow oil (30:1::pet ether:EtOAc)(49 mg, 0.136 mmol, 68%).^{1}H NMR (500 MHz, $CDCl_3$) δ7.55 (d, *J* = 8.0 Hz, 4H), 7.42 - 7.38 (m, 2H), 7.37 - 7.33 (m, 4H), 7.10 (dd, *J* = 10.9, 15.5 Hz, 1H), 6.18 - 6.08 (m, 1H), 5.95 (dd, *J* = 10.9, 14.9 Hz, 1H), 5.59 (d, *J* = 14.9 Hz, 1H), 3.68 (s, 3H), 2.30 (d, *J* = 8.0 Hz, 2H), 1.07 (s, 9H). ^{13}C NMR

(125MHz, $CDCl_3$) δ168.0, 145.6, 141.9, 136.0 (4C), 133.7, 129.5 (2C), 128.5, 127.8 (5C), 117.1, 51.4, 27.9 (3C), 19.4, 18.7. HRMS (ESI) m/z calcd. for $C_{23}H_{28}O_2Si$ $[M+H]^+$ 365.1937; found 365.1938. IR (neat): ν_{max}/cm^{-1}3080, 3032, 2980, 2936, 2915, 1826, 1790, 1745, 1630, 1580, 1523, 1480, 1353, 1238, 1130, 1030, 953, 842.

Compoumd 5aa Following general procedure, **5aa** was obtained as a white solid (8.5:1.5::pet ether:EtOAc) (54 mg, 0.132 mmol, 66%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 15.6 Hz, 1 H), 5.83 (q, *J* = 7.2 Hz, 1 H), 5.75 (d, *J* = 15.6 Hz, 1 H), 3.75 (s, 3 H), 2.54 (t, *J* = 7.6 Hz, 2 H), 1.77 - 1.72 (m, 2 H), 1.69 (d, *J* = 7.2 Hz, 3 H), 1.42 - 1.38 (m, 2 H), 1.27 (s, 26 H), 0.88 (t, *J* = 6.7 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 167.3, 145.7, 139.7, 126.3, 116.7, 52.0, 34.2, 32.3, 30.0(8C), 29.9, 29.8, 29.7, 29.5, 25.4, 23.0, 14.5, 12.6. HRMS (ESI) m/z calcd. for $C_{25}H_{44}O_4$ $[M+NH_4]^+$ 426.3583; found 426.3583. IR (neat): ν_{max}/cm^{-1} 2925, 2854, 1764, 1725, 1652, 1628, 1435, 1306, 1167.

Compound 5ba Following general procedure, **5ba** was obtained as a pale yellow oil (8:2::pet ether:EtOAc) (28 mg, 0.13mmol, 65%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.19 (d, *J* = 15.5 Hz, 1 H), 5.85 - 5.80 (m, 1 H), 5.73 (d, *J* = 15.5 Hz, 1 H), 3.75 (s, 3 H), 2.81 (spt, *J* = 7.0 Hz, 1 H), 1.68 (d, *J* = 7.2 Hz, 3 H), 1.33 (s, 3 H), 1.32 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 167.3, 145.6, 139.7, 126.2, 116.5, 77.1, 52.0, 34.3, 19.5(2C), 12.4. HRMS (ESI) m/z calcd. for $C_{11}H_{16}O_4$ $[M+H]^+$213.1127; found 213.1134. IR (neat): ν_{max}/cm^{-1} 2975, 2950, 1757, 1721, 1652, 1627, 1436, 1306, 1168.

Compound 5ca Following general procedure, **5ca** was obtained as a white solid (8:2::pet ether:EtOAc) (35 mg, 0.136 mmol, 68%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 15.3 Hz, 1 H), 5.82 (q, *J* = 7.3 Hz, 1 H), 5.74 (d, *J* = 15.9 Hz, 1 H), 3.74 (s, 3 H), 2.54 (t, *J* = 7.3 Hz, 2 H), 1.77 - 1.72 (m, 2 H), 1.68 (d, *J* = 7.2 Hz, 3 H), 1.43 - 1.37 (m, 2 H), 1.35 - 1.31 (m, 4 H), 0.89 (t, *J* = 6.7 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 167.3, 145.6, 139.7, 126.3, 116.6, 52.0, 34.2, 31.7, 29.2, 25.3, 22.8, 14.3, 12.6. HRMS (ESI) m/z calcd. for $C_{14}H_{23}O_4$ $[M+H]^+$ 255.1596; found 255.1591. IR (neat): ν_{max}/cm^{-1} 2931, 2859, 1761, 1723, 1652, 1628, 1435, 1308, 1168.

Compound 5da Following general procedure, **5da** was obtained as a pale yellow oil (8:2::pet ether:EtOAc) (32 mg, 0.142mmol, 71%). ^1H NMR (500 MHz, $CDCl_3$):δ 7.17 (d, *J* = 15.5 Hz, 1 H), 5.83 (q, *J* = 7.3 Hz, 1 H), 5.74 (d, *J* = 15.5 Hz, 1 H), 3.74 (s, 3 H), 2.42 (d, *J* = 7.2 Hz, 2 H), 2.27 - 2.18 (m, 1 H), 1.69 (d, *J* = 7.2 Hz, 3 H), 1.05 (s, 3 H), 1.04 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 167.1, 145.4, 139.5, 126.0, 116.4, 51.8, 42.8, 25.7, 22.5(2C), 12.4. HRMS (ESI) m/z calcd. for $C_{12}H_{18}O_4$ $[M+H]^+$ 227.1283; found 227.1280. IR (neat): ν_{max}/cm^{-1} 2959, 2874, 1760, 1723, 1653, 1628, 1466, 1307, 1169.

Compound 5ea Following general procedure, **5ea** was obtained as a white solid (8:2::pet ether:EtOAc) (25mg, 0.086mmol, 43%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 15.9 Hz, 1 H), 6.94 (s, 2 H), 5.98 - 5.88 (m, 2 H), 3.75 (s, 3 H), 2.47 (s, 6 H), 2.33 (s, 3 H), 1.85 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ167.4, 166.8, 145.9, 140.7, 140.1, 136.9(2C), 129.5(2C), 129.1, 126.6, 117.0, 52.1, 21.5, 21.4(2C), 13.3. HRMS (ESI) m/z calcd. for $C_{17}H_{24}NO_4$ $[M+NH_4]^+$ 306.1705; found 306.1705. IR (neat): ν_{max}/cm^{-1} 2923, 2852, 1725, 1612, 1651, 1435, 1307, 1234, 1165, 1052.

Compoumd 5fa Following general procedure, **5fa** was obtained as a white solid (8:2::pet ether:EtOAc) (29 mg, 0.096 mmol, 48%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 15.9 Hz, 1 H), 5.81 (q, *J* = 7.3 Hz, 1 H), 5.70 (d, *J* = 15.9 Hz, 1 H), 3.75 (s, 3 H), 2.09 (br. s., 3 H), 2.07 (br, s, 6 H), 1.77 (br. s, 6 H), 1.66 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.7, 167.4, 145.6, 139.9, 126.2, 116.4, 52.0, 41.6, 39.3(3C), 36.7(3C), 28.2(3C), 12. HRMS (ESI) m/z calcd. for $C_{18}H_{24}O_4$ $[M+NH_4]^+$ 322.2018; found 322.2019. IR (neat): ν_{max}/cm^{-1} 2909, 2853, 1750, 1722, 1651, 1627, 1453, 1435, 1307, 1201, 1180, 1167.

Compound 5ga Following general procedure, **5ga** was obtained as a pale yellow oil (8:2::pet ether:EtOAc) (24 mg, 0.13 mmol, 65%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.17 (d, *J* = 15.6 Hz, 1 H), 5.82 (q, *J* = 7.2 Hz, 1 H), 5.77 (d, *J* = 15.5 Hz, 1 H), 3.75 (s, 3 H), 2.28 (s, 3 H), 1.70 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8, 167.0, 145.4, 139.2, 126.1, 116.5, 51.8, 20.4, 12.3. HRMS (ESI) m/z calcd. for $C_9H_{12}O_4$ $[M+H]^+$ 185.0814; found 185.0818. IR (neat): ν_{max}/cm^{-1} 3058, 2953, 1762, 1723, 1653, 1628, 1436, 1310, 1200, 1171.

NOESY shows that H_a (5.80 - 5.86) and H_b (7.19 - 7.15) are correlated. H_c (5.76 - 5.78) and H_d (1.70) are weakly correlated.

Compound 5gb Following general procedure, **5gb** was obtained as a pale yellow oil (8:2::pet ether:EtOAc) (32 mg, 0.140 mmol, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, *J* = 15.5 Hz, 1 H), 5.82 (q, *J* = 7.3 Hz, 1 H), 5.76 (d, *J* = 15.5 Hz, 1 H), 4.15 (t, *J* = 7.1 Hz, 3 H), 2.28 (s, 3 H), 1.69 (d, *J* = 7.3 Hz, 3 H), 1.66 - 1.63 (m, 2 H), 1.42 - 1.38 (m, 2 H), 0.94 (t, *J* = 7.1 Hz, 3 H).^{13}C NMR (125 MHz, $CDCl_3$): δ 168.1, 166.9, 145.8, 139.1, 126.0, 117.3, 64.8, 31.1, 20.6, 19.5, 14.0, 12.5. HRMS (ESI) m/z calcd. for $C_{12}H_{18}O_4$ $[M+H]^+$ 227.1283; found 227.1281. IR (neat): ν_{max}/cm^{-1} 2960, 2934, 2874, 1765, 1715, 1653, 1627, 1304, 1196, 1170.

Compound 5gc Following general procedure, **5gc** was obtained as a pale yellow oil (8:2::pet ether:EtOAc) (31 mg, 0.136 mmol, 68%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (d, *J* = 15.5 Hz, 1 H), 5.83 (q, *J* = 7.3 Hz, 1 H), 5.77 (d, *J* = 15.6 Hz, 1 H), 3.93 (d, *J* = 6.6 Hz, 2 H), 2.29 (s, 3 H), 2.00 - 1.92 (m, 1 H), 1.70 (d, *J* = 7.2 Hz, 3 H), 0.95 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8, 166.6, 145.4, 138.8, 125.8, 116.9, 70.7, 27.8, 20.4, 19.1(2C), 12.2. HRMS (ESI) m/z calcd. for $C_{12}H_{18}O_4$ $[M+H]^+$ 227.1283; found 227.1282. IR (neat): ν_{max}/cm^{-1} 2962, 2928, 2875, 2854, 1765, 1718, 1627, 1653, 1470, 1371, 1211, 1197, 1168.

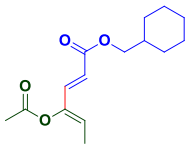
Compound 5gd Following general procedure, **5gd** was obtained as a white solid (8:2::pet ether:EtOAc) (32 mg, 0.128 mmol, 64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, *J* = 15.6 Hz, 1 H), 5.82 (q, *J* = 7.3 Hz, 1 H), 5.74 (d, *J* = 15.5 Hz, 1 H), 4.85 - 4.78 (m, 1 H), 2.28 (s, 3 H), 1.89 - 1.84 (m, 2 H), 1.74 (m, 2 H), 1.69 (d, *J* = 7.3 Hz, 3 H), 1.58 - 1.52 (m, 1 H), 1.44 - 1.36 (m, 4 H), 1.29 - 1.24 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 166.0, 145.5, 138.5, 125.6, 117.5, 72.9, 31.7(2C), 25.4, 23.8(2C), 20.4, 12.2. HRMS (ESI) m/z calcd. for $C_{14}H_{20}O_4$ $[M+H]^+$ 253.1440; found 253.1443. IR (neat): ν_{max}/cm^{-1} 2936, 2859, 1764, 1713, 1653, 1626, 1450, 1371, 1259, 1197, 1173.

Compound 5gh Following general procedure, **5gh** was obtained as a pale yellow oil (8:2::pet ether:EtOAc) (29 mg, 0.144 mmol, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (d, *J* = 15.5 Hz, 1 H), 5.85 - 5.80 (m, 1 H), 5.75 (d, *J* = 15.6 Hz, 1 H), 4.20 (q, *J* = 7.2 Hz, 2 H), 2.28 (s, 3 H), 1.70 (d, *J* = 7.2 Hz, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.1, 166.8, 145.7, 139.2, 126.1, 117.2, 60.9, 20.7, 14.6, 12.5. HRMS (ESI) m/z calcd. for $C_{10}H_{14}O_4$ $[M+NH_4]^+$ 216.1236; found 216.1233. IR (neat): ν_{max}/cm^{-1} 2982, 1764, 1714, 1652, 1628, 1369, 1305, 1197, 1175.

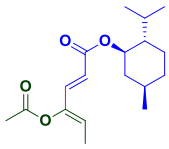
Compound 5gi Following general procedure, **5gi** was obtained as a white solid (8:2::pet ether:EtOAc) (40 mg, 0.148 mmol, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (d, *J* = 15.5 Hz, 1 H), 5.83 (q, *J* = 7.3 Hz, 1 H), 5.76 (d, *J* = 15.6 Hz, 1 H), 4.14 (t, *J* = 6.8 Hz, 2 H), 2.29 (s, 3 H), 1.70 (d, *J* = 7.3 Hz, 3 H), 1.67 - 1.64 (m, 2 H), 1.32 (m, 8 H), 0.89 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 167.0, 145.7, 139.1, 126.1, 117.2, 65.1, 32.1, 29.3, 29.0, 26.2, 22.9, 20.7, 14.4, 12.5. HRMS (ESI) m/z calcd. for $C_{15}H_{24}O_4$ $[M+H]^+$ 269.1753; found 269.1757. IR (neat): ν_{max}/cm^{-1}2925, 2855, 1727, 1651, 1627, 1453, 1435, 1307, 1261, 1180, 1167.

Compound 5ge Following general procedure, **5ge** was obtained as a white solid (8:2::pet ether:EtOAc) (40 mg, 0.108 mmol, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.16 (d, *J* = 15.5 Hz, 1 H), 6.40 (dd, *J* = 1.4, 17.3 Hz, 1 H), 6.12 (dd, *J* = 10.5, 17.3 Hz, 1 H), 5.84 - 5.80 (m, 2 H), 5.75 (d, *J* = 15.5 Hz, 1 H), 4.17 - 4.12 (m, 4 H), 2.28 (s, 3 H), 1.70 (d, *J* = 7.3 Hz, 3 H), 1.68 - 1.63 (m, 4 H), 1.37 - 1.31 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 166.6, 166.4, 145.4, 138.8, 130.5, 128.7, 125.8, 116.9, 64.7, 64.7, 29.4, 29.2(2C), 28.7, 28.6, 25.9(2C), 20.4, 12.2. HRMS (ESI) m/z calcd. for $C_{20}H_{30}O_6$ $[M+H]^+$ 367.2121; found 367.2121. IR (neat): ν_{max}/cm^{-1} 2930,2856, 1725 (br), 1636, 1465, 1408, 1371, 1370, 1302, 1288, 1297, 1272, 1196.

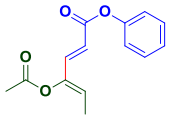
Compound 5gj Following general procedure, **5gj** was obtained as a white solid (8:2::pet ether:EtOAc) (48 mg, 0.156 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 15.3 Hz, 1 H), 5.84 (q, *J* = 7.3 Hz, 1 H), 5.78 (d, *J* = 15.9 Hz, 1 H), 4.97 - 4.92 (m, 1 H), 2.42 - 2.34 (m, 1 H), 2.31 (s, 3 H), 2.01 - 1.93 (m, 1 H), 1.77 (ddd, *J* = 4.0, 7.6, 11.6 Hz, 1 H), 1.70 (d, *J* = 7.3 Hz, 3 H), 1.37 - 1.22 (m, 3 H), 1.01 (dd, *J* = 3.4, 13.7 Hz, 1 H), 0.92 (s, 3 H), 0.88 (s, 3 H), 0.85 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 166.9, 145.4, 138.5, 125.7, 117.4, 80.2, 48.9, 47.9, 44.9, 36.8, 28.0, 27.2, 20.4, 19.7, 18.9, 13.5, 12.2. HRMS (ESI) m/z calcd. for $C_{18}H_{26}O_4$ $[M+NH_4]^+$ 324.2175; found 324.2177. IR (neat): ν_{max}/cm^{-1}2924, 2864, 1750, 1722, 1651, 1627, 1453, 1435, 1307, 1201, 1180, 1167. $[\alpha]_D^{30}$ = -20.68 (c = 0.81 in $CHCl_3$).

Compound 5gk 

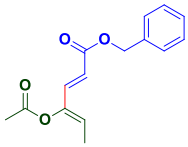
Following general procedure, **5gk** was obtained as a white solid (8:2::pet ether:EtOAc) (42 mg, 0.160 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 15.9 Hz, 1 H), 5.83 (q, *J* = 7.1 Hz, 1 H), 5.76 (d, *J* = 15.3 Hz, 1 H), 3.96 (d, *J* = 6.7 Hz, 2 H), 2.29 (s, 3 H), 1.76 - 1.66 (m, 10 H), 1.28 - 1.21 (m, 3 H), 1.02 - 0.98 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 167.0, 145.8, 139.1, 126.0, 117.3, 70.1, 37.5, 30.1(2C), 26.7, 26.0(2C), 20.7, 12.5. HRMS (ESI) m/z calcd. for $C_{15}H_{22}O_4$ $[M+Na]^+$ 289.1416; found 289.1418. IR (neat): ν_{max}/cm^{-1} 2928, 2854, 1766, 1715, 1651, 1627, 1450, 1370, 1305, 1288, 1196, 1168, 1023.

Compound 5gl 

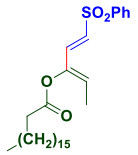
Following general procedure, **5gl** was obtained as a white solid (8:2::pet ether:EtOAc) (43 mg, 0.14 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 15.9 Hz, 1 H), 5.82 (q, *J* = 7.1 Hz, 1 H), 5.75 (d, *J* = 15.3 Hz, 1 H), 4.76 (dt, *J* = 4.3, 10.7 Hz, 1 H), 2.29 (s, 3 H), 2.04 - 1.98 (m, 1 H), 1.91 - 1.84 (m, 1 H), 1.69 [m, 4 H (3H +1H)], 1.55 - 1.45 (m, 1 H), 1.43 - 1.36 (m, 1 H), 1.10 - 0.97 (m, 2 H), 0.92 - 0.88 (m, 8 H), 0.75 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 166.4, 145.8, 138.9, 126.0, 117.6, 74.6, 47.5, 41.3, 34.6, 31.7, 26.5, 23.7, 22.4, 21.1, 20.7, 16.6, 12.5. HRMS (ESI) m/z calcd. for $C_{18}H_{28}O_4$ $[M+Na]^+$ 331.1885; found 331.1889. IR (neat): ν_{max}/cm^{-1} 2956, 2929, 2870, 1766, 1711, 1651, 1626, 1455, 1370, 1302, 1288, 1196, 1171. $[\alpha]_D^{30}$ = -15.78 (c = 0.58 in $CHCl_3$).

Compound 5gm 

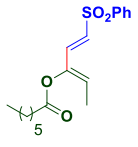
Following general procedure, **5gm** was obtained as a brownish oil (8:2::pet ether:EtOAc) (29 mg, 0.116 mmol, 58%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 - 7.38 (m, 2 H), 7.36 (d, *J* = 15.5 Hz, 1 H), 7.26 - 7.22 (m, 1 H), 7.12 (d, *J* = 7.6 Hz, 2 H), 5.98 - 5.90 (m, 2 H), 2.33 (s, 3 H), 1.75 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.1, 165.3, 151.1, 145.8, 141.0, 129.8(2C), 127.4, 126.2, 121.9(2C), 116.4, 20.7, 12.7. HRMS (ESI) m/z calcd. for $C_{14}H_{14}O_4$ $[M+H]^+$ 247.0970; found 247.0973. IR (neat): ν_{max}/cm^{-1} 2924, 2854, 1762, 1731, 1649, 1626, 1493, 1371, 1290, 1192, 1141.

Compound 5gn 

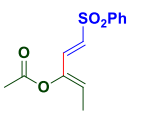
Following general procedure, **5gn** was obtained as a white solid (8:2::pet ether:EtOAc) (36 mg, 0.138 mmol, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 - 7.35 (m, 5 H), 7.21 (d, *J* = 15.5 Hz, 1 H), 5.86 - 5.80 (m, 2 H), 5.20 (s, 2 H), 2.27 (s, 3 H), 1.70 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.7, 166.4, 145.5, 139.5, 136.0, 128.7(2C), 128.4(2C), 128.4, 126.2, 116.6, 66.5, 20.4, 12.3. HRMS (ESI) m/z calcd. for $C_{15}H_{16}O_4$ $[M+NH_4]^+$ 278.1392; found 278.1394. IR (neat): ν_{max}/cm^{-1} 3034, 2938, 1815, 1760, 1723, 1650, 1626, 1455, 1372, 1264, 1198, 1165.

Compound 5ag 

Following general procedure, **5ag** was obtained as a white solid (8:2::pet ether:EtOAc) (43mg, 0.088 mmol, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.3 Hz, 2 H), 7.62 (t, *J* = 7.3 Hz, 1 H), 7.53 (t, *J* = 7.6 Hz, 2 H), 7.19 (d, *J* = 14.6 Hz, 1 H), 6.20 (d, *J* = 14.6 Hz, 1 H), 5.95 (q, *J* = 7.3 Hz, 1 H), 2.47 (t, *J* = 7.6 Hz, 2 H), 1.69 (d, *J* = 7.1 Hz 3 H), 1.68 - 1.63 (m, 2 H), 1.31 - 1.25 (m, 28 H), 0.88 (t, *J* = 6.7 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 143.6, 140.5, 137.8, 133.4, 129.3(2C), 128.8, 127.6(2C), 125.7, 33.8, 31.9, 29.7(6C), 29.6, 29.6, 29.4, 29.4, 29.2, 29.1, 24.9, 22.7, 14.2, 12.6. HRMS (ESI) m/z calcd. for $C_{29}H_{46}O_4S$ $[M+NH_4]^+$ 508.3461; found 508.3463. IR (neat): ν_{max}/cm^{-1} 2923, 2853, 1763, 1652, 1601, 1447, 1308, 1192, 1147, 1112, 1085.

Compound 5cg 

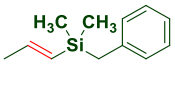
Following general procedure, **5cg** was obtained as a white solid (8:2::pet ether:EtOAc) (34 mg, 0.10 mmol, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.2 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.54 (t, *J* = 7.9 Hz, 2 H), 7.19 (d, *J* = 14.9 Hz, 1 H), 6.20 (d, *J* = 14.9 Hz, 1 H), 5.95 (q, *J* = 7.3 Hz, 1 H), 2.48 (t, *J* = 7.6 Hz, 2 H), 1.70 (d, *J* = 7.2 Hz, 3 H), 1.68 - 1.64 (m, 2 H), 1.34 - 1.27 (m, 6 H), 0.90 - 0.86 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 143.6, 140.5, 137.8, 133.5, 129.3(2C), 128.8, 127.6 (2C), 125.7, 33.8, 31.3, 28.8, 24.9, 22.4, 14.0, 12.6. HRMS (ESI) m/z calcd. for $C_{18}H_{24}O_4S$ $[M+NH_4]^+$ 354.1739; found 354.1737. IR (neat): ν_{max}/cm^{-1} 2923, 2853, 1721, 1650, 1661, 1447, 1308, 1147, 1084, 1025.

Compound 5gg 

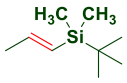
Following general procedure, **5gg** was obtained as a white solid (8:2::pet ether:EtOAc) (28.19 mg, 0.106 mmol, 53%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.2 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.54 (t, *J* = 7.9 Hz, 2 H), 7.19 (d, *J* = 14.9 Hz, 1 H), 6.23 (d, *J* = 14.9 Hz, 1 H), 5.96 (q, *J* = 7.2 Hz, 1 H), 2.23 (s, 3 H), 1.71 (d, *J* = 7.3 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.6, 144.0, 140.8, 137.9, 133.8, 129.7(2C), 129.2, 128.0 (2C), 126.2, 20.6, 12.9. HRMS (ESI) m/z calcd. for $C_{13}H_{14}O_4S$ $[M+NH_4]^+$ 284.0957; found 284.0954. IR (neat): ν_{max}/cm^{-1} 2923, 2852, 1762, 1652, 1600, 1447, 1371, 1306, 1194, 1145, 1085, 1023.

Procedure for Isomerization of Allylsilanes:

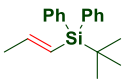
A 8 mL screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 0.01 mmol, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (80 mg, 0.4 mmol, 2.0 equiv), $AgSbF_6$ (14 mg, 0.04 mmol, 20 mol%) and 1,2-dichloroethane (1.5 mL). Then allylsilane (0.2 mmol, 1.0 equiv) was added into the solution. The vial was sealed under N_2 and heated to 80°C with stirring for 12 h. After cooling down, the mixture was diluted with dichloromethane, filtered and concentrated to give the crude compound which was directly purified by column chromatography using only pentane as a eluent.

Compound 6b 

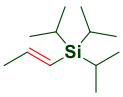
Following general procedure, **6b** was obtained as a colourless oil (using pentane as a eluent) (34 mg, 0.174 mmol, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (t, *J* = 7.2 Hz, 2 H), 7.07 (t, *J* = 6.9 Hz, 1 H), 7.00 (d, *J* = 7.4 Hz, 2 H), 6.12 - 5.99 (m, 1 H), 5.63 (d, *J* = 20 Hz, 1 H), 2.11 (s, 2 H), 1.81 (d, *J* = 6.3 Hz, 3 H), 0.02 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 140.6, 129.8, 128.6, 128.4, 124.2, 26.5, 23.0, -3.0. HRMS (ESI) m/z calcd. for $C_{12}H_{18}Si$ $[M+H]^+$ 191.1256; found 191.1258. IR (neat): ν_{max}/cm^{-1} 3078, 3022, 2988, 2953, 2849, 1799, 1618, 1599, 1492, 1247, 1055, 831, 697.

Compound 6c 

Following general procedure, **6c** was obtained as a colourless oil (using pentane as a eluent) (26 mg, 0.166 mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.05 (qd, *J* = 6.0, 18.5 Hz, 1 H), 5.67 - 5.60 (m, 1 H), 1.85 - 1.79 (m, 3 H), 0.85 (s, 9 H), -0.01 (s, 7 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 128.6, 26.5, 22.8, 16.5, -6.0. HRMS (ESI) m/z calcd. for $C_9H_{20}Si$ $[M+H]^+$ 157.1413; found 157.1416. IR (neat): ν_{max}/cm^{-1} 2923, 2852, 1600, 1371, 1234, 1050, 827, 720.

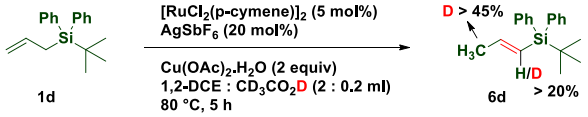
Compound 6d 

Following general procedure, **6d** was obtained as a colourless oil (using pentane as a eluent) (50 mg, 0.18 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.67 - 7.59 (m, 4 H), 7.43 - 7.31 (m, 6 H), 6.17 - 6.00 (m, 2 H), 1.93 (d, *J* = 4.6 Hz, 3 H), 1.09 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 136.4, 135.2, 129.0, 127.6, 124.7, 27.8, 23.1, 18.2. HRMS (ESI) m/z calcd. for $C_{19}H_{24}Si$ $[M+H]^+$ 281.1726; found 281.1723. IR (neat): ν_{max}/cm^{-1} 3082, 3035, 2992, 2949, 2901, 1601, 1592, 1567, 1492, 1282, 1012 845, 693.

Compound 6e 

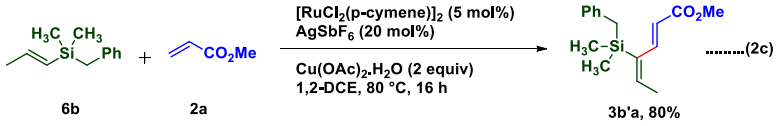
Following general procedure, **6e** was obtained as a colourless oil (using pentane as a eluent) (34 mg, 0.17 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.67 - 7.59 (m, 4 H), 7.43 - 7.31 (m, 6 H), 6.17 - 6.00 (m, 2 H), 1.93 (d, *J* = 4.6 Hz, 3 H), 1.09 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 136.4, 135.2, 129.0, 127.6, 124.7, 27.8, 23.1, 18.2. HRMS (ESI) m/z calcd. for $C_{12}H_{26}Si$ $[M+H]^+$ 199.1882; found 199.1886. IR (neat): ν_{max}/cm^{-1} 2946, 2893, 1593, 1299, 1203, 1001, 819, 725.

Procedure for Deuterium study:



A 8 mL screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (11 mg, 0.017 mmol, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (143 mg, 0.71 mmol, 2.0 equiv), $AgSbF_6$ (24.5 mg, 0.07 mmol, 20 mol%), 1,2-dichloroethane (2 mL) and CD_3CO_2D (0.2 ml). Then Diphenyltertiarybutyl allylsilane **1d** (0.2 mmol, 1.0 equiv) was added into the solution. The vial was sealed under N_2 and heated to 80°C with stirring for 5 h. After cooling down, the mixture was diluted with dichloromethane, filtered and concentrated to give the crude compound which was directly purified by column chromatography using only pentane as a eluent to afford compound **6d**. It was found that deuterium scrambling at the α-position (> 20%) as well as at the methyl group (> 45%) in vinylsilane.

Coupling reaction between vinylsilane 6b and methyl acrylate 2a:

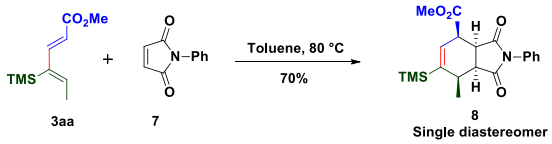


A 8 mL screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (11 mg, 0.017 mmol, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (143 mg, 0.71 mmol, 2.0 equiv), $AgSbF_6$ (24.5 mg, 0.07 mmol, 20 mol%) and 1,2-dichloroethane (2 mL) Then vinylsilane **6b** (70 mg,

0.4 mmol, 1.2 equiv) and methyl acrylate **2a** (30 mg, 0.35 mmol, 1.0 equiv) were added into the solution. The vial was sealed under N_2 and heated to 80°C with stirring for 16 h. After cooling down, the mixture was diluted with dichloromethane, filtered and concentrated to give the crude compound which was directly purified by column chromatography using 30:1 pet::ether:EtOAc as a eluent to afford compound **3b'a** (77 mg, 0.28 mmol, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 15.9 Hz, 1 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.06 (t, *J* = 7.3 Hz, 1 H), 6.96 (d, *J* = 6.7 Hz, 2 H), 6.68 - 6.47 (m, 1 H), 5.75 (d, *J* = 15.9 Hz, 1 H), 3.72 (s, 3 H), 2.25 (s, 2 H), 1.75 (d, *J* = 7.3 Hz, 3 H), 0.19 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 151.9, 146.8, 139.3, 136.8, 128.3, 128.3, 124.4, 117.1, 51.5, 26.1, 18.4, -1.3.

Procedure for Diels-Alder reaction:

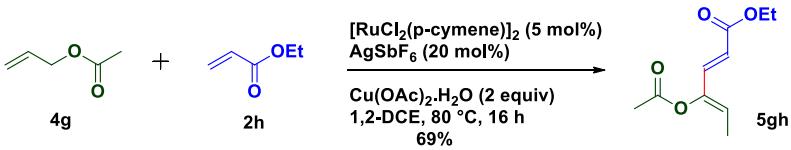


Compound **3aa** (100 mg, 0.5 mmol, 1.0 equiv.,) and N-phenyl maleimide **7** (88 mg, 0.5 mmol, 1.0 equiv.,) were taken in 8 mL screw-cap vial and Toluene (1.5 ml) was added. Then reaction mixture was heated at 80 °C for 15 h. After cooling down, Toluene was removed under reduced pressure and crude compound was directly purified by column chromatography using 0 - 20% EtOAc in Pet ether as a eluent to afford single diastereomer **8** (130 mg, 0.35 mmol) in 70% yield.

Compound 8:
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 - 7.38 (m, 2 H), 7.36 - 7.31 (m, 1 H), 7.19 - 7.13 (m, 2 H), 6.67 (dd, *J* = 2.6, 3.7 Hz, 1 H), 3.80 (s, 3 H), 3.77 - 3.69 (m, 1 H), 3.33 - 3.25 (m, 1 H), 3.23 - 3.15 (m, 1 H), 2.67 (t, *J* = 6.9 Hz, 1 H), 1.56 (d, *J* = 7.4 Hz, 3 H), 0.13 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.5, 176.4, 171.4, 148.0, 135.3, 131.8, 129.1, 128.6, 126.5, 52.4, 44.6, 42.9, 41.1, 35.6, 16.7, -0.1. HRMS (ESI) m/z calcd. for $C_{20}H_{25}NO_4Si$ $[M+H]^+$ 372.1631; found 372.1634. IR (neat): ν_{max}/cm^{-1} 2951, 2922, 2849, 1739, 1709, 1499, 1455, 1382, 1276, 1247, 1201, 1036, 923, 834, 690.

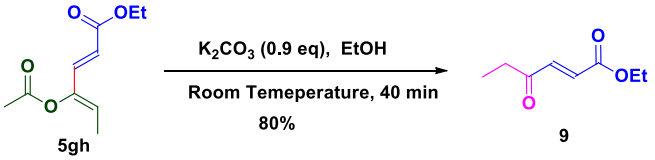
2.2. Gram scale synthesis and its applications

2.2a. Synthesis of compound 3gb



By following the general procedure, A 100 mL seal tube was charged with $[RuCl_2(p\text{-cymene})]_2$ (307 mg, 0.5 mmol, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (4.0 g, 20 mmol, 2.0 equiv), $AgSbF_6$ (685 mg, 2.0 mmol, 20 mol%) and 1,2-dichloroethane (30 mL). Then ethyl acrylate **2h** (1.0g, 1.06ml, 10 mmol, 1.0 equiv) and allyl acetate **4g** (1.2g, 1.3ml, 12mmol, 1.2equiv) were added into the solution in sequence. Then vial was sealed under N_2 and heated to 80 °C with stirring for 16 h. After cooling down, the mixture was diluted with ethyl acetate, filtrated and concentrated to give the crude compound which was directly purified by column chromatography (8:2 petroleum ether/ethyl acetate) to give **5gh** as a colourless oil (1.36 g, 6.9 mmol, 69%).

2.2b. Synthesis of compound 9

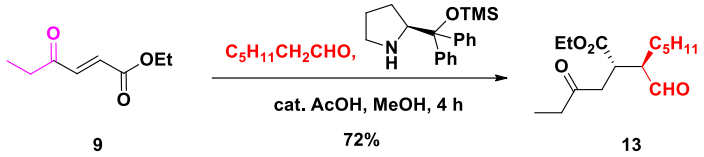


To a solution of **5gh** (1.3 g, 6.5 mmol, 1.0 equiv) in ethanol (15 ml), added potassium carbonate (815 mg, 5.9 mmol, 0.9 equiv) in four portions over 5 min and reaction mixture was allowed to stirred for 40 minutes at room temperature. Then reaction mixture was quenched with water and extracted with ethyl acetate (15 ml X 3), washed with brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography (7:3 petroleum ether/ethyl acetate) furnishing the enone **9** (816 mg, 5.2 mmol, 80%) as a yellow liquid.

(E)-ethyl 4-oxohex-2-enoate (9)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, *J* = 16.5 Hz, 1 H), 6.67 (d, *J* = 15.9 Hz, 1 H), 4.26 (q, *J* = 7.3 Hz, 2 H), 2.67 (q, *J* = 7.3 Hz, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H), 1.13 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.2, 165.6, 139.2, 130.6, 61.4, 34.8, 14.1, 7.6. HRMS (ESI) m/z calcd. for $C_8H_{12}O_3$ $[M+NH_4]^+$ 174.1130; found 174.1139. IR (neat): ν_{max}/cm^{-1} 2982, 2939, 1727, 1704, 1688, 1641, 1304, 1185.

2.2c.Synthesis of compound 13[1]



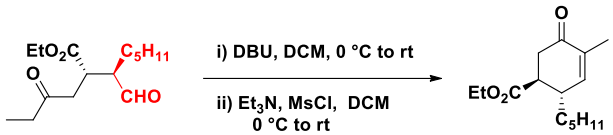
9 72% 13

To a suspension of catalyst (52 mg, 0.16 mmol, 0.1 equiv), enone **9** (250 mg, 1.60 mmol, 1 equiv) and acetic acid (10 µl, 0.16 mmol, 0.1 equiv) in methanol (7 ml) was added heptaldehyde (0.45 ml, 365 mg, 3.2 mmol, 2 equiv) at 0 °C. The reaction mixture was stirred for 1 h at the same temperature and then warmed to room temperature for 3 h. The solution was partitioned between ethyl acetate and saturated $NaHCO_3$. The organic phase was separated and aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. Purification of the residue by flash column chromatography (silica gel) eluting with 10:1 petroleum ether/ethyl acetate afforded the Michael adduct **13** (310 mg, 1.152 mmol, 72%) as a pale-yellow liquid.

(2R,3S)-ethyl 3-formyl-2-(2-oxobutyl)octanoate (13)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (s, 1 H), 4.13 (q, *J* = 7.3 Hz, 2 H), 3.37 - 3.28 (m, 1 H), 2.97 (dd, *J* = 9.8, 17.7 Hz, 1 H), 2.65 - 2.57 (m, 1 H), 2.51 - 2.44 (m, 2 H), 2.42 - 2.36 (m, 1 H), 1.33 - 1.26 (m, 8 H), 1.23 (s, 3 H), 1.05 (t, *J* = 7.3 Hz, 3 H), 0.87 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 209.0, 202.7, 173.1, 61.1, 52.7, 40.7, 39.6, 36.1, 31.7, 27.1, 26.2, 22.4, 14.1, 13.9, 7.7. HRMS (ESI) m/z calcd. for $C_{15}H_{26}O_4$ $[M-H]^-$ 269.1757; found 269.1753. IR (neat): ν_{max}/cm^{-1} 2957, 2932, 2860, 1725 (br), 1461, 1376, 1212, 1179, 1115. $[\alpha]_D^{30}$ = +12.68 (c = 1.6 in $CHCl_3$).

2.2d. Synthesis of compound 11[1]



13 11

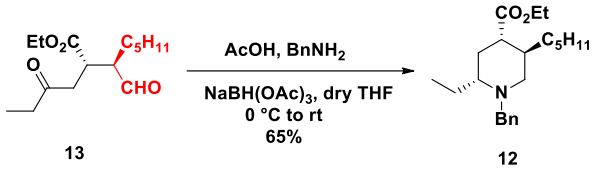
To a solution of Michael adduct **13** (100 mg, 0.37 mmol) in 4 mL of DCM, was added DBU (113 ml, 0.74 mmol, 2.0 equiv) at 0 °C. After it was stirred for 1 h at 0 °C, the solution was warmed to room temperature and stirred for 2h. The reaction mixture was partitioned between ethyl acetate and brine. The organic phase was separated and aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silicagel, 10:1 petroleum ether/ethyl acetate as eluent) to give the corresponding cyclohexanone.

To a solution of aldol reaction product (70 mg, 0.25 mmol) in DCM (3 mL) were added MsCl (60 µl, 0.77 mmol, 3.0 equiv) and Et_3N (0.19 ml, 1.5 mmol, 6.0 equiv) at 0 °C. After the reaction mixture was stirred for 1h at 0 °C, and 6 h at 25 °C, it was partitioned between ethyl acetate and brine. The organic phase was separated and aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The residual oil was purified viaflash column chromatography (silica gel, 20:1 petroleum ether/ethyl acetate as eluent) to afford the corresponding cyclohexenone **11** (38mg, 0.15mmol, 60%).

(1S, 2S)-ethyl 4-methyl-5-oxo-2-pentylcyclohex-3-enecarboxylate (11)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (br. s., 1 H), 4.15 (q, *J* = 6.9 Hz, 2 H), 2.86 - 2.75 (m, 2 H), 2.64 - 2.59 (m, 2 H), 1.77 (s, 3 H), 1.53 - 1.35 (m, 4 H), 1.30 (br. s., 4 H), 1.25 (d, *J* = 7.3 Hz, 3 H), 0.89 (t, *J* = 6.7 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.4, 173.8, 147.8, 135.0, 61.2, 46.1, 39.3, 38.5, 33.5, 32.1, 26.5, 22.8, 16.1, 14.5, 14.3. HRMS (ESI) m/z calcd. for $C_{15}H_{24}O_3$ $[M+H]^+$ 253.1804; found 253.1806. IR (neat): ν_{max}/cm^{-1} 2957, 2928, 2859, 1733, 1682, 1454, 1377, 1276, 1175, 1032. $[\alpha]_D^{30}$ = +68.6 (c = 0.70 in $CHCl_3$).

2.2e. Synthesis of compound 12[1]



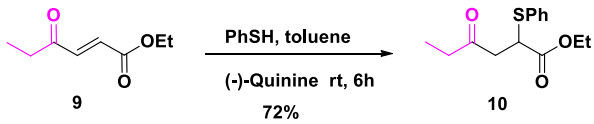
13 12

The Michael adduct **13** (100 mg, 0.37 mmol) was dissolved in 3 mL THF. To this solution $NaBH(OAc)_3$ (235 mg, 1.11 mmol, 3.0 equiv), AcOH (23 µl, 0.37 mmol, 1.0 equiv) and $BnNH_2$ (60 mg, 61 µl, 0.55 mmol, 1.5 equiv) were added at 0 °C. After it was stirred for 1 h at 0 °C, the solution was warmed to rt, and stirred for 2.5hours. Then mixture was partitioned between ethyl acetate and saturated $NaHCO_3$. The organic phase was separated and aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. Purification of the residue by flash column chromatography (silica gel, 20:1 petroleum ether/ethyl acetate as eluent) afforded the corresponding piperidine **12** (82.5 mg, 0.24 mmol, 65%).

(2R,4S,5R)-ethyl 1-benzyl-2-ethyl-5-pentylpiperidine-4-carboxylate (12)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 - 7.28 (m, 3 H), 7.25 (br..s, 2 H), 4.17 - 4.11 (m, 2 H), 2.84 (d, *J* = 13.6 Hz, 1 H), 2.79 (dd, *J* = 2.7, 11.8 Hz, 1 H), 2.51 (td, *J* = 4.1, 13.1 Hz, 1 H), 2.12 - 2.07 (m, 1 H), 1.86 - 1.75 (m, 3 H), 1.73 - 1.61 (m, 4 H), 1.25 - 1.22 (m, 5 H), 1.20 - 1.15 (m, 3 H), 0.98 - 0.94 (m, 3 H), 0.92 - 0.86 (m, 3 H), 0.81 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ175.1, 140.7, 128.8(2C), 128.4(2C), 126.9, 62.0, 60.4, 57.5, 55.6, 46.2, 36.9, 32.3, 28.0, 27.6, 26.9, 26.3, 22.9, 14.6, 14.4, 8.6. HRMS (ESI) m/z calcd. for $C_{22}H_{35}O_2N$ $[M+H]^+$ 346.2746; found 346.2735. IR (neat): ν_{max}/cm^{-1} 2957, 2929, 2873, 2856, 2791, 2754, 1732, 1453, 1377, 1338, 1254, 1237, 1185, 1169. $[\alpha]_D^{30}$ = -29.2 (c = 1.1 in $CHCl_3$).

2.2f. Synthesis of compound 7[2]



9 10

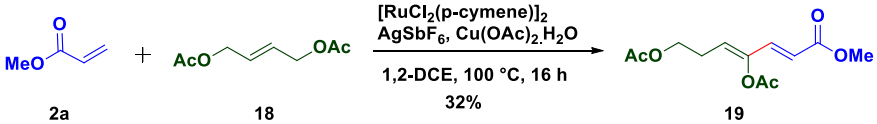
To a solution of thiophenol (39 mg, 36 µl, 0.35 mmol, 1.1 equiv) and Quinine (10.5 mg, 0.032 mmol, 0.1 equiv) in toluene, was added enone **9** (50 mg, 0.32 mmol, 1 equiv) at rt and reaction mixture was allowed stirred for 6 h. Then reaction mixture was quenched with water and extracted with ethyl acetate (15ml X 3), washed with brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography furnishing the product **10**[2](61.2 mg, 0.23 mmol, 72%).

Ethyl 4-oxo-2-(phenylthio)hexanoate (10)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 - 7.45 (m, 2 H), 7.37 - 7.29 (m, 3 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 4.06 (dd, *J* = 4.6, 10.1 Hz, 1 H), 3.10 (dd, *J* = 10.4, 17.7 Hz, 1 H), 2.79 (dd, *J* = 4.6, 18.0 Hz, 1 H), 2.48 - 2.39 (m, 2 H), 1.17 (t, *J* = 7.3 Hz, 3 H), 1.05 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.4, 171.9, 134.0 (2C), 132.7, 129.3 (2C), 128.8, 61.7, 45.1, 44.3, 36.3, 14.3, 7.9. HRMS (ESI) m/z calcd. for $C_{14}H_{18}O_3S$ $[M+Na]^+$ 289.0874; found 289.0878. IR (neat): ν_{max}/cm^{-1} 2979, 2938, 2906, 1731, 1582, 1439, 1369, 1223, 1173, 1153.

2.3. Synthesis of norpyrenophorin (14)

2.3a. Synthesis of compound 19



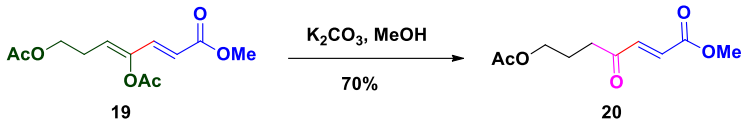
2a 18 19

By following the general procedure, A 50 mL seal tube was charged with $[RuCl_2(p\text{-cymene})]_2$ (179 mg, 5.83 mmol, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2.32 g, 11.6 mmol, 2.0 equiv), $AgSbF_6$ (400 mg, 2.0 mmol, 20 mol%) and 1,2-dichloroethane (20 mL). Then methyl acrylate **2a** (250mg, 0.255ml, 2.90 mmol, 0.5equiv) and diacetate **18** (1.0 g,5.83 mmol, 1.0 equiv) were added into the solution in sequence. Then vial was sealed under N_2 and heated to 100 °C with stirring for 16 h. After cooling down, the mixture was diluted with ethyl acetate, filtrated and concentrated to give the crude compound which was directly purified by column chromatography (3:1:: Pet ether : EtOAc) to give **19** (477 mg, 1.86 mmol, 32%).

(3Z,5E)-7-methoxy-7-oxohepta-3,5-diene-1,4-diyl diacetate (19)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 15.9 Hz, 1 H), 5.83 - 5.73 (m, 2 H), 4.13 (t, *J* = 6.7 Hz, 2 H), 3.75 (s, 3 H), 2.42 (q, *J* = 6.9 Hz, 2 H), 2.28 (s, 3 H), 2.05 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0, 167.8, 166.7, 146.0, 138.7, 125.9, 117.7, 62.3, 51.8, 26.4, 20.9, 20.3. HRMS (ESI) m/z calcd. for $C_{12}H_{16}O_6$ $[M+NH_4]^+$ 274.1291; found 274.1296. IR (neat): ν_{max}/cm^{-1} 2954, 2849, 1765, 1738, 1652, 1627, 1435, 1368, 1309, 1238, 1198, 1172, 1037.

2.3b. Synthesis of compound 20



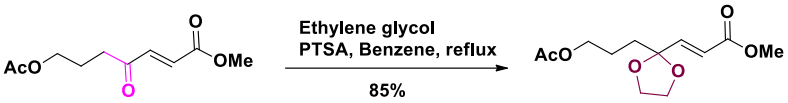
19 20

To a solution of **19** (450 mg, 1.75 mmol, 1.0 equiv) in methanol, added potassium carbonate (218 mg, 1.58 mmol, 0.9 equiv) in four portions over 5 min and reaction mixture was allowed to stirred for 40 minutes at room temperature. Then reaction mixture was quenched with water and extracted with ethyl acetate (15ml X 3), washed with brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography (3 : 1.5 :: Pet ether : EtOAc) furnishing the compound **20** (262mg, 1.22mmol, 70%).

(E)-methyl 7-acetoxy-4-oxohept-2-enoate (20)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 16.0 Hz, 1 H), 6.70 (d, *J* = 16.0 Hz, 1 H), 4.10 (t, *J* = 6.3 Hz, 2 H), 3.82 (s, 3 H), 2.74 (t, *J* = 6.9 Hz, 2 H), 2.04 (s, 3 H), 2.02 - 1.97 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.5, 171.1, 166.0, 139.3, 130.6, 63.4, 52.5, 38.0, 22.7, 21.0. HRMS (ESI) m/z calcd. for $C_{10}H_{14}O_5$ $[M+Na]^+$ 237.0739; found 237.0730. IR (neat): ν_{max}/cm^{-1} 2956, 2853, 1737, 1731, 1703, 1643, 1437, 1366, 1305, 1241, 1176, 1040.

2.3c. Synthesis of compound 21



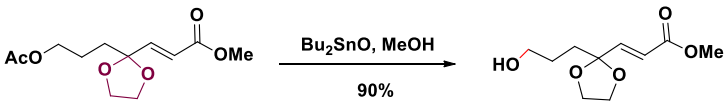
20 21

Using a Dean-Stark trap, ethylene glycol (1.3 ml, 23.36 mmol, 30 equiv.) was refluxed in benzene (5 mL) for 1 hour. Upon cooling, compound **20** (250 mg, 1.16 mmol) in benzene (2 mL) and p-toluene sulfonic acid (10 mg, 0.046 mmol, 0.04 equiv.) were added to the solution and the resulting mixture was heated to reflux under a condenser for 1.5 hours (heating for more than 1.5 hours resulted in decomposition of product). The solution was then cooled and quenched with $NaHCO_3$ (10 mL). The resulting mixture was extracted with EtOAc (3 x 10 mL), washed with water (80 mL) and brine (80 mL), dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography (3 : 1.5:: Pet ether : EtOAc) to obtain of the pure ketal **21** (254 mg, 0.986 mmol, 85% yield) as a yellow liquid.

(E)-methyl 3-(2-(3-acetoxypropyl)-1,3-dioxolan-2-yl)acrylate (21)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (d, *J* = 15.6 Hz, 1 H), 6.09 (d, *J* = 15.8 Hz, 1 H), 4.07 (t, *J* = 6.4 Hz, 2 H), 4.00 - 3.95 (m, 2 H), 3.90 - 3.85 (m, 2 H), 3.76 (s, 3 H), 2.04 (s, 3 H), 1.85 - 1.78 (m, 2 H), 1.78 - 1.70 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.4, 166.9, 146.6, 121.9, 108.2, 65.3 (2C), 64.5, 52.1, 34.4, 22.8, 21.3. HRMS (ESI) m/z calcd. for $C_{12}H_{18}O_6$ $[M+Na]^+$ 281.1001; found 281.1000. IR (neat): ν_{max}/cm^{-1}2955, 2895, 1731 (br.), 1663, 1436, 1387, 1365, 1305, 1243, 1197, 1169, 1036.

2.3d. Synthesis of compound 22



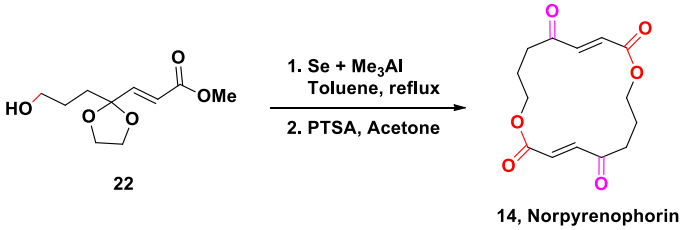
21 22

To a solution of **21** (240 mg, 0.930 mmol, 1.0 equiv) in methanol (8 ml), added dibutyl tin oxide (2.31 g, 5.9 mmol, 0.9 equiv) in one portion and reaction mixture was refluxed for 2 hours. Upon cooling the reaction mixture, concentrated *in vacuo*, solid was removed by filtration, residue washed with ethyl acetate and filterarte was concentrated, purified by column chromatography (3 : 2 :: Pet ether : EtOAc) furnishing theproduct **22** (216 mg, 0.93 mmol, 90%) as a pale brownish liquid.

(E)-methyl 3-(2-(3-hydroxypropyl)-1,3-dioxolan-2-yl)acrylate (22)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (d, *J* = 15.4 Hz, 1 H), 6.07 (d, *J* = 15.4 Hz, 1 H), 4.00 - 3.96 (m, 2 H), 3.89 - 3.85 (m, 2 H), 3.74 (s, 3 H), 3.63 (t, *J* = 5.9 Hz, 2 H), 2.03 (br. s., 1 H), 1.87 - 1.82 (m, 2 H), 1.69 - 1.64 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 146.3, 121.5, 108.1, 64.9 (2C), 62.5, 51.8, 34.1, 26.2. HRMS (ESI) m/z calcd. for $C_{10}H_{16}O_5$ $[M+Na]^+$ 239.0895; found 239.0894. IR (neat): ν_{max}/cm^{-1} 3400 (br.), 2954, 2849, 1765, 1738, 1652, 1627, 1435, 1368, 1309, 1238, 1198, 1172, 1037.

2.3e. Synthesis of norpyrenophorin 14[3]



22

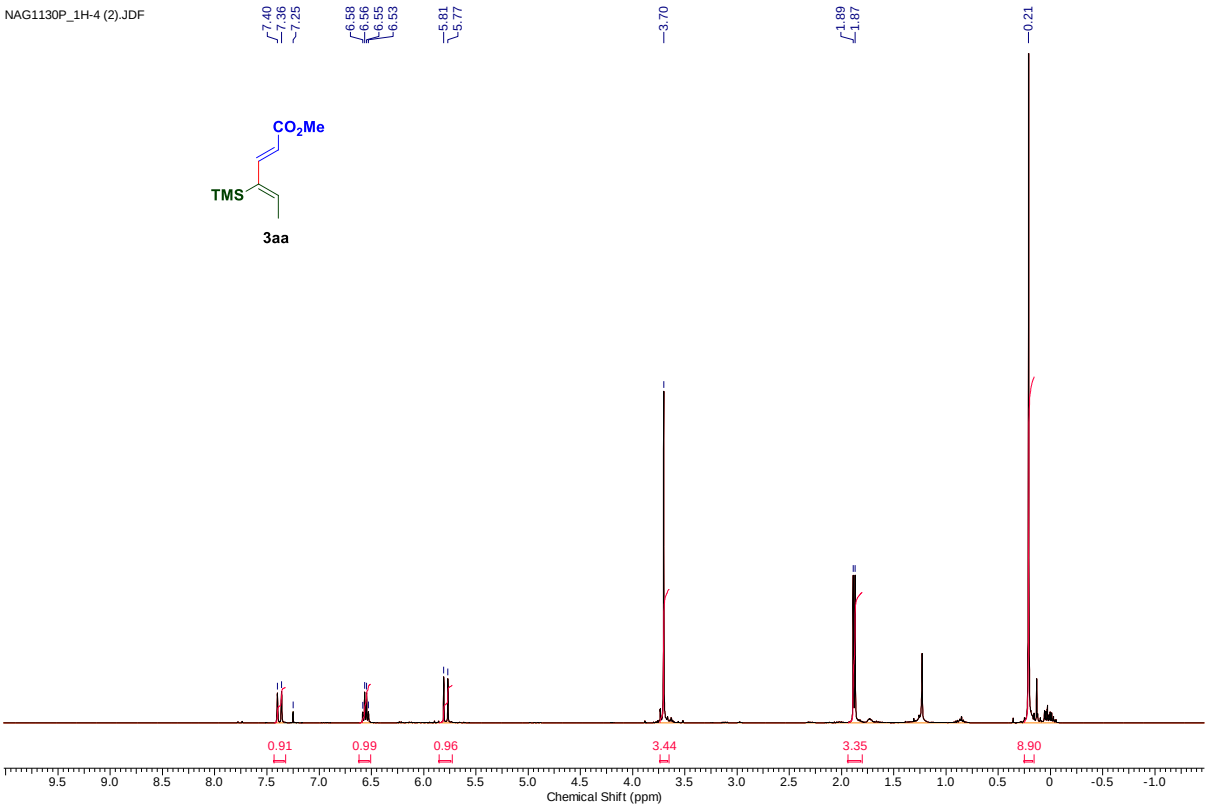
14, Norpyrenophorin

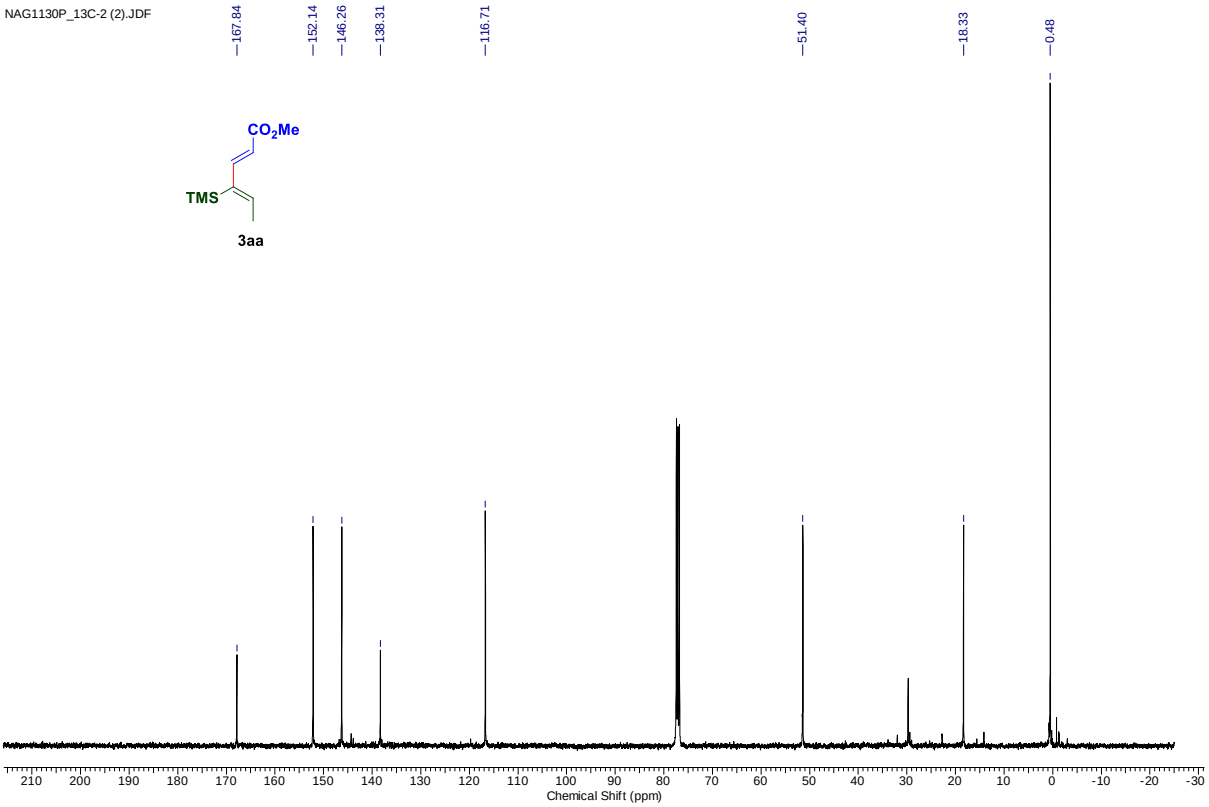
Trimethylaluminium (0.925 mL of a 2 M solution, 1.85 mmol, 10 equiv) in toluene was added to a 5 mL side-arm flask containing selenium powder (150 mg, 1.924 mmol, 10.4 equiv) at 0 °C and refluxed till the selenium powder had reacted completely, the resulting mixture was cooled to room temperature. An aliquot of $Me_2SeAlMe$ (10 µl, 1.1 mmol) was transferred by syringe to a solution containing compound **22** (40 mg, 0.185 mmol) in toluene (1.2 mL) at 0 °C. After 28 h of heating at reflux, the yellow solution was warmed to room temperature over a period of 30 min and treated with sodium sulfate. The solution was then diluted with dichloromethane, washed with water six times and treated with sodium hydrogen carbonate. The solution was then dried with brine and anhydrous magnesium sulfate. The solvent was removed under vacuum from the yellow solution and the residue wasdissolved in acetone (0.75 ml), added p-toluene sulfonic acid (3 mg, 0.0081 mmol, 0.1 equiv) at 0 °C and stirred for 4 hours at room temperature. then reaction mixture was quenched with $NaHCO_3$ solution and extracted with EtOAc, dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography(1:1 :: Pet ether : EtOAc) furnishing the **norpyrenophorin 14**[3](6 mg, 0.0214 mmol, 23% in two steps).

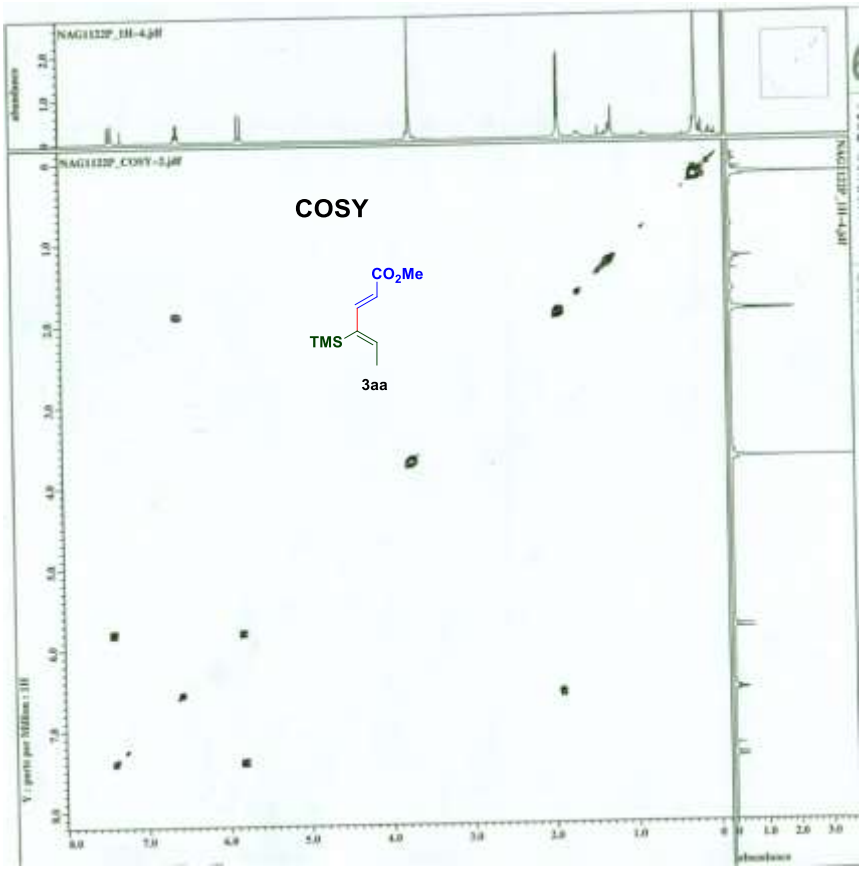
Norpyrenophorin (14)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (d, *J* = 16.3 Hz, 1 H), 6.68 (d, *J* = 16.2 Hz, 1 H), 4.31 (t, *J* = 5.9 Hz, 2 H), 2.85 (t, *J* = 7.0 Hz, 2 H), 2.13 - 2.07 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.5, 165.4, 140.2, 131.2, 64.6, 37.2, 22.4. HRMS (ESI) m/z calcd. for $C_{14}H_{17}O_6$ $[M+H]^+$ 281.1025; found 281.1025. IR (neat): ν_{max}/cm^{-1} 2923, 2852, 1728, 1428, 1258.

3. NMR spectra



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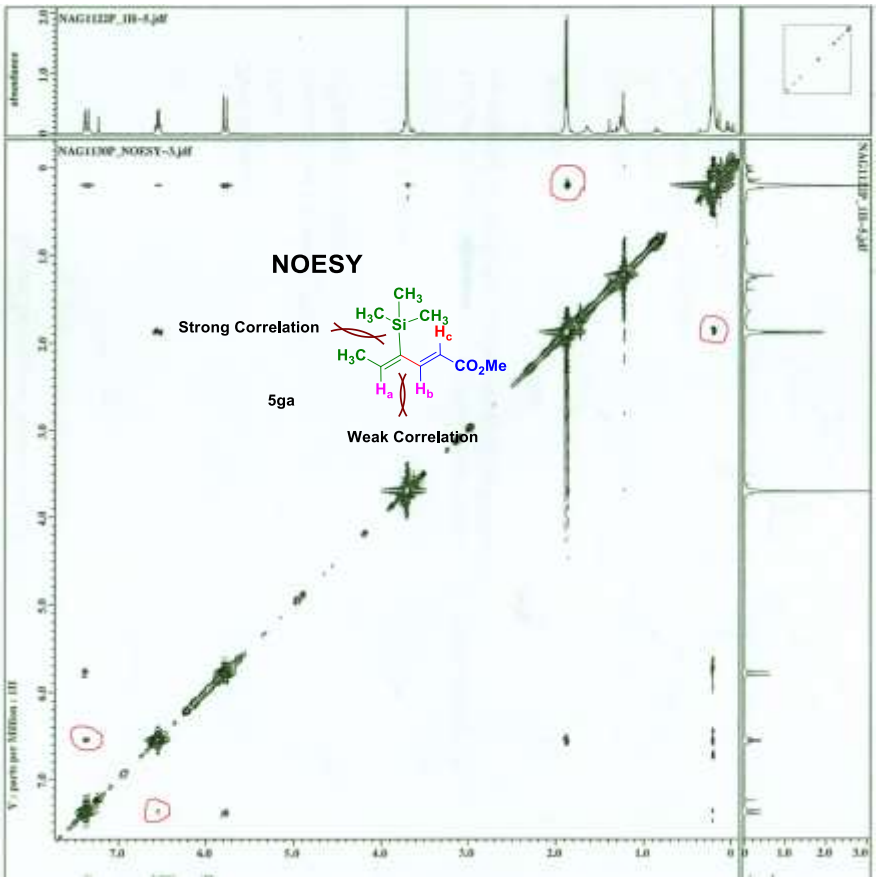
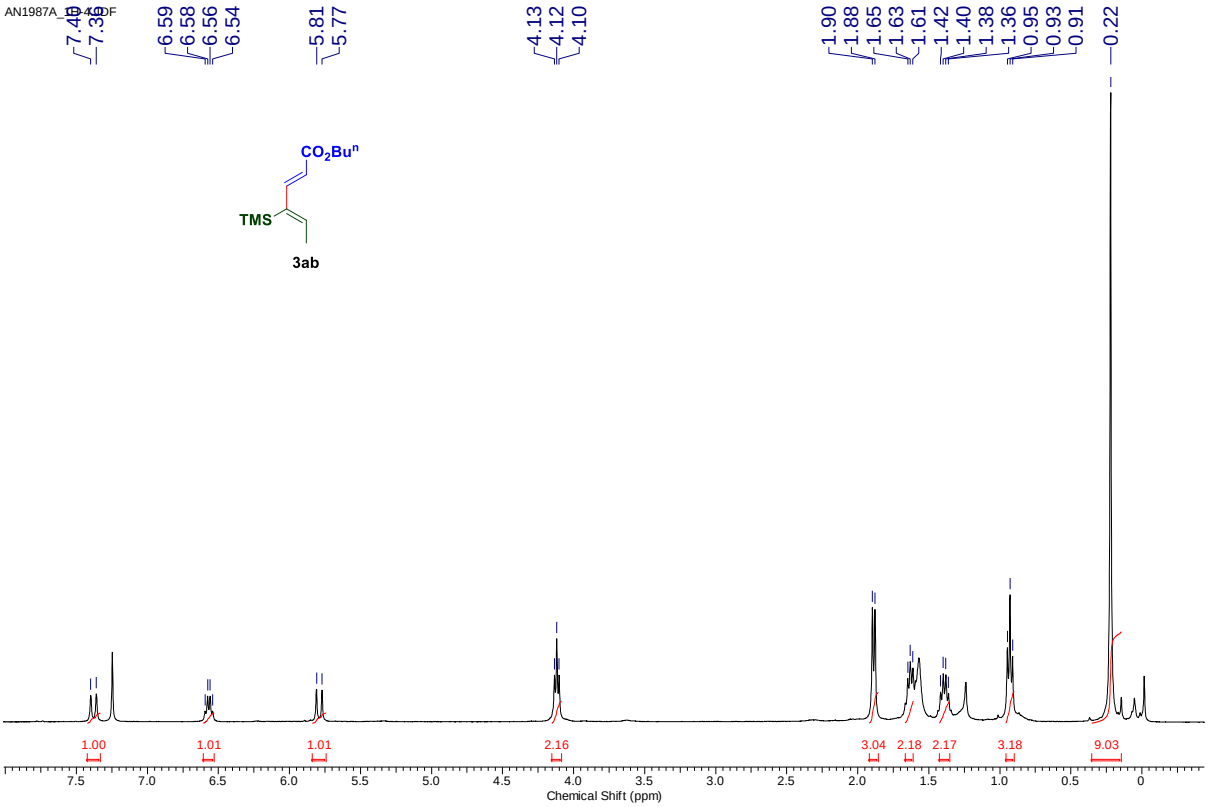
TMS
3aa


NOESY
Strong Correlation
CH3
H3C
Si
CH3
Hc
H3C
CO2Me
Ha
Hb
5ga
Weak Correlation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6.58
6.56
6.54
5.81
5.77
4.13
4.12
4.10
1.90
1.88
1.65
1.63
1.61
1.42
1.40
1.38
1.36
0.95
0.93
0.91
0.22
CO2Bun
TMS
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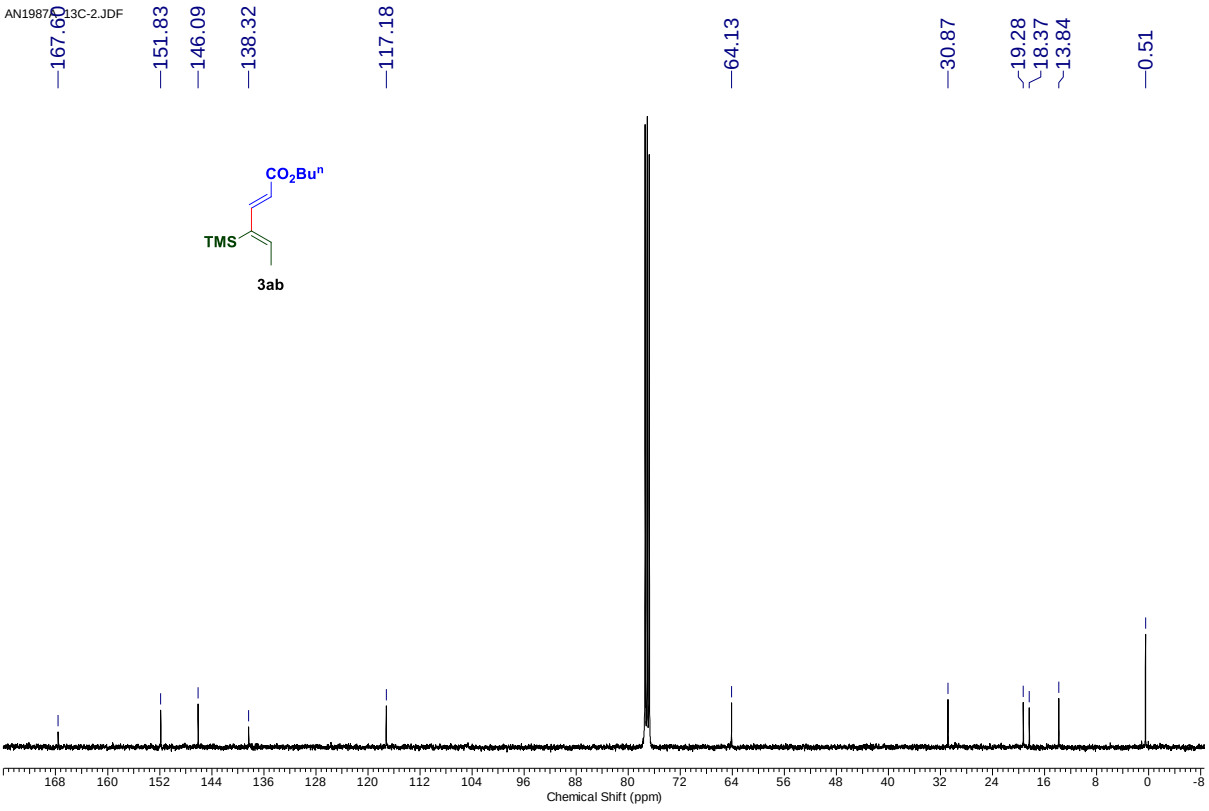
1.01
1.01
2.16
3.04
2.18
2.17
3.18
9.03
Chemical Shift (ppm)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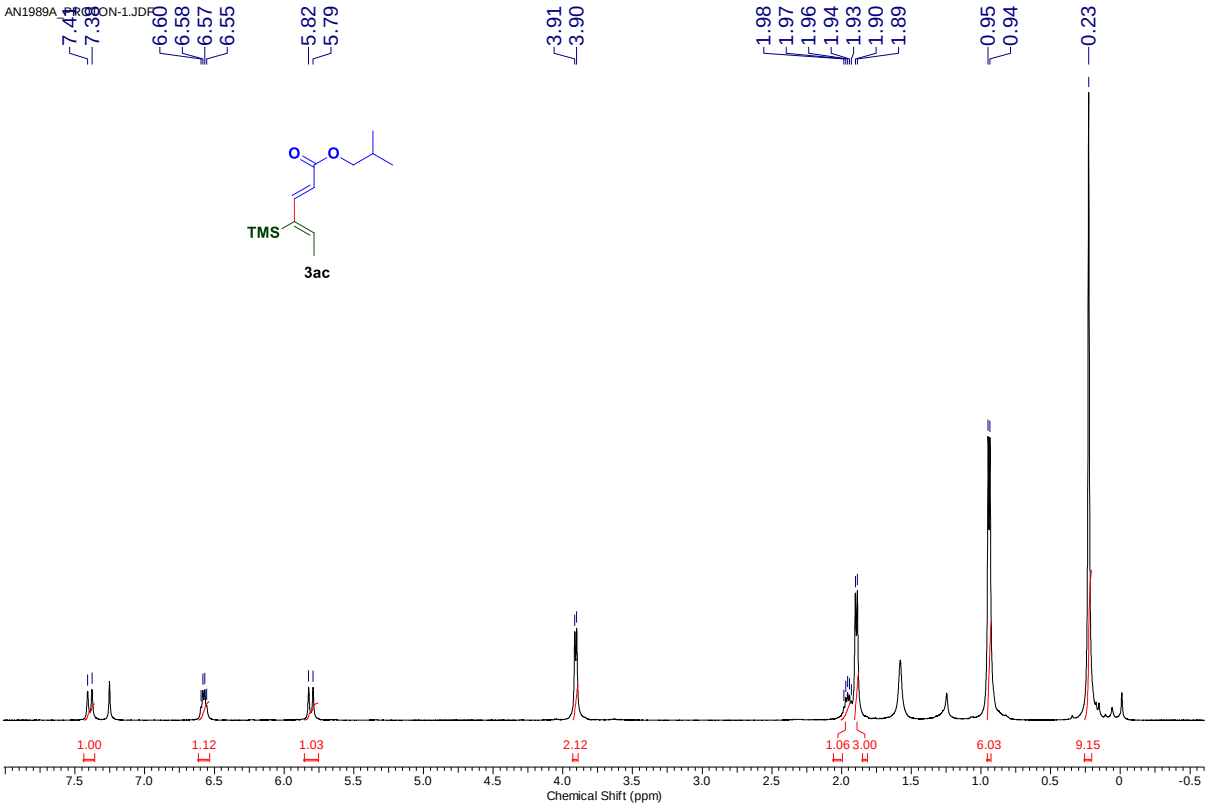
TMS
3ab
Chemical Shift (ppm)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1.94
1.93
1.90
1.89
0.95
0.94
0.23
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O
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1.12
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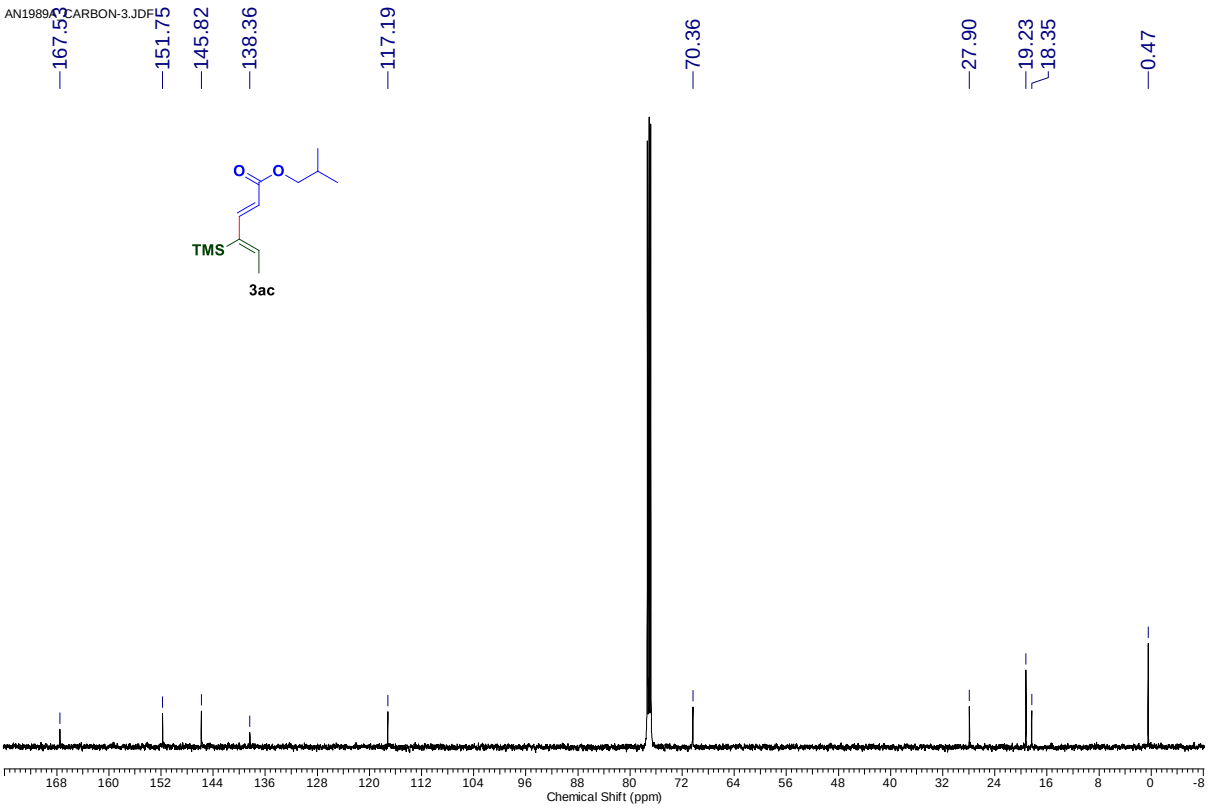
3.00
6.03
9.15
Chemical Shift (ppm)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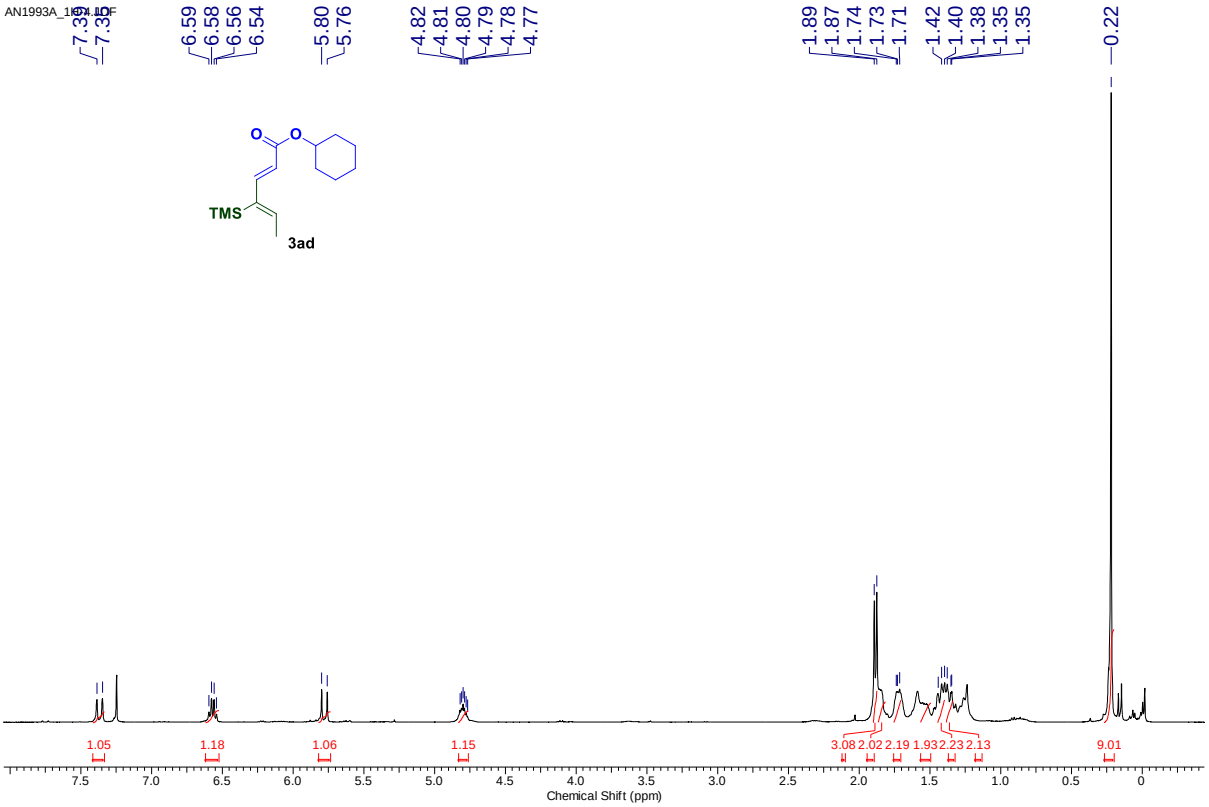
O
TMS
3ac
Chemical Shift (ppm)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4.77
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1.87
1.74
1.73
1.71
1.42
1.40
1.38
1.35
1.35
0.22
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3ad
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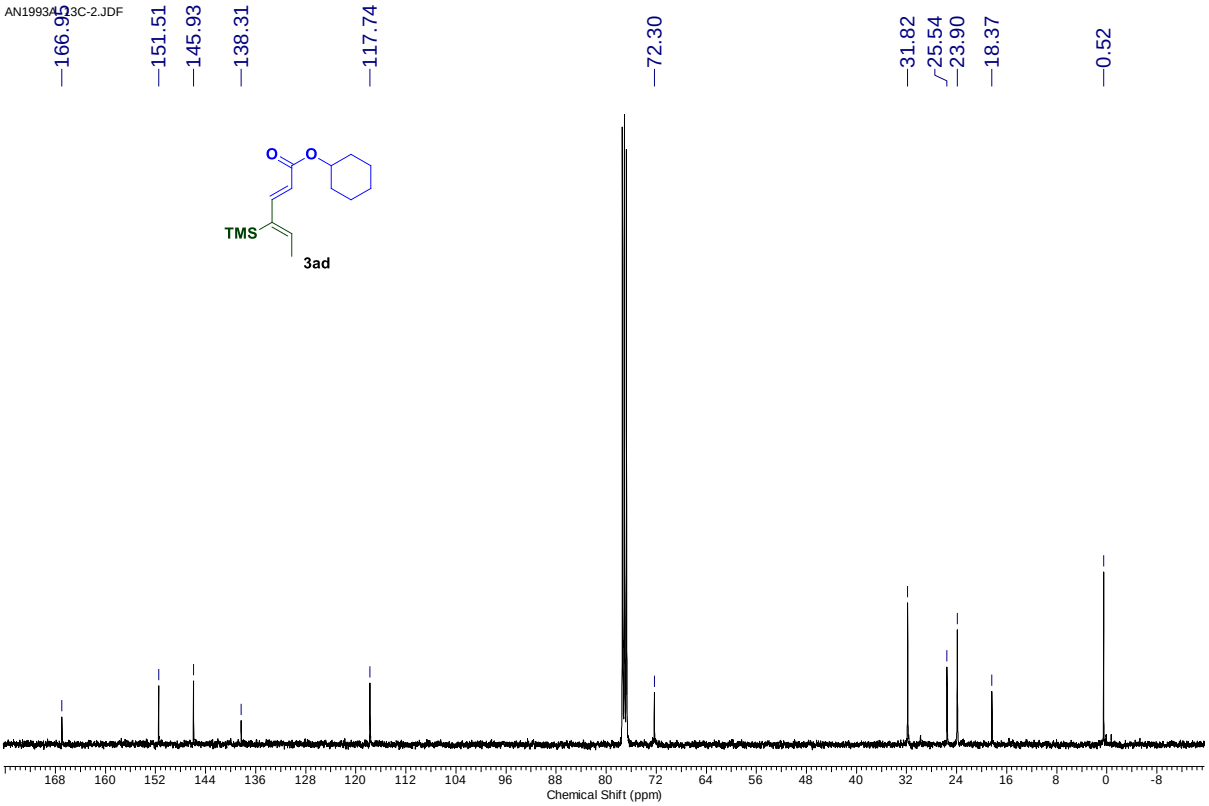
Chemical Shift (ppm)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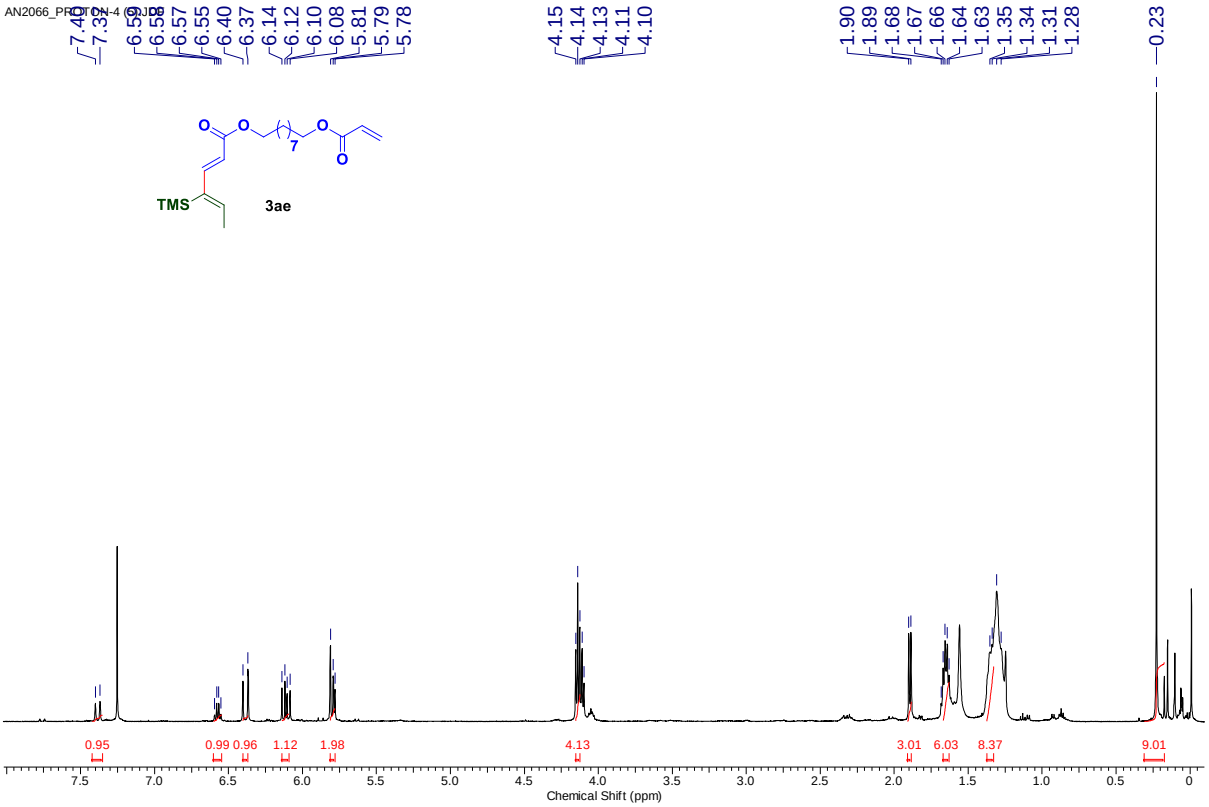
TMS
3ad
Chemical Shift (ppm)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4.10
1.90
1.89
1.68
1.67
1.66
1.64
1.63
1.35
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1.28
0.23
TMS
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6.03
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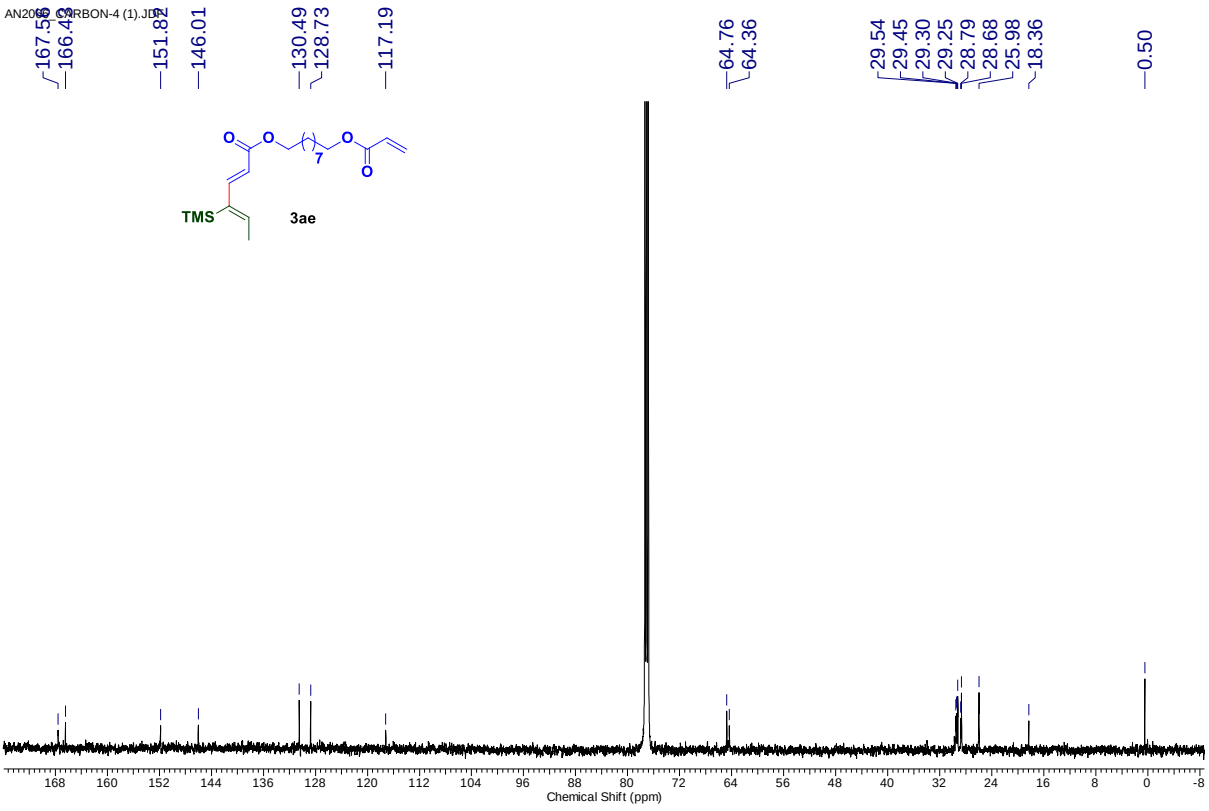
Chemical Shift (ppm)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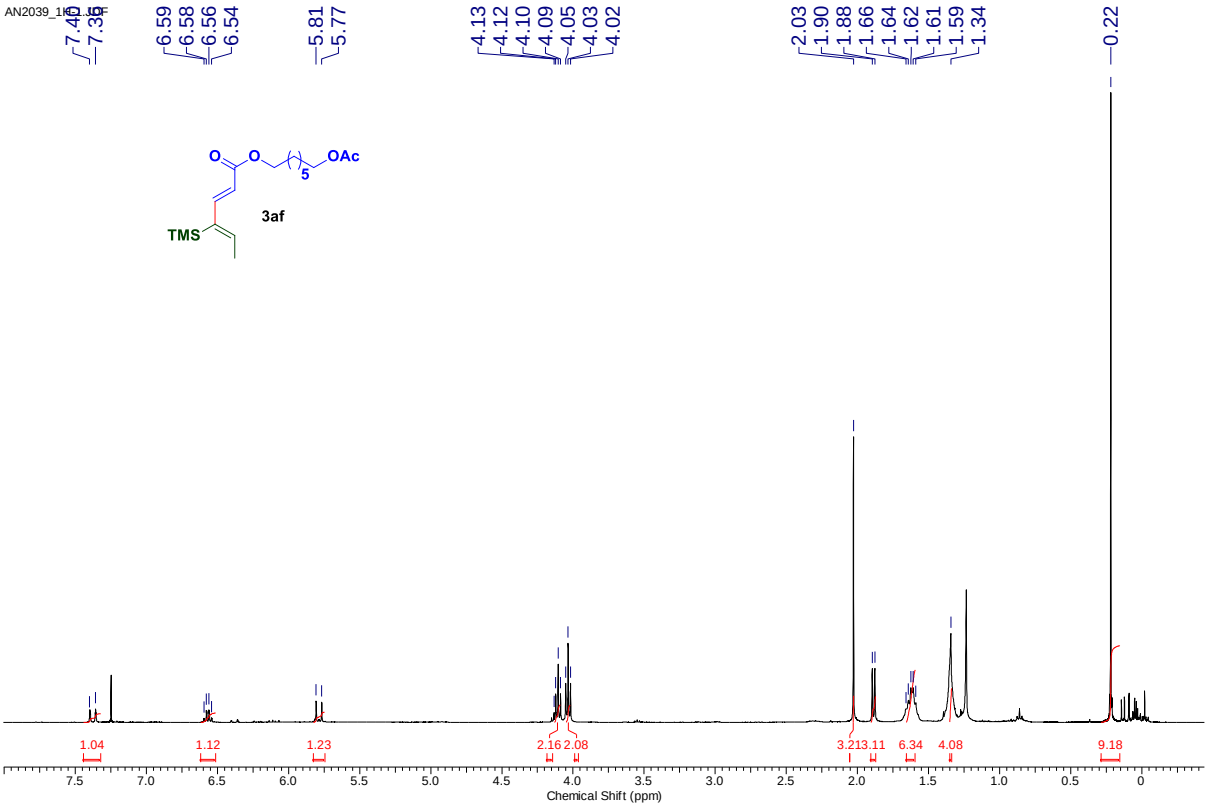
18.36
0.50
TMS
3ae
Chemical Shift (ppm)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4.02
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1.88
1.66
1.64
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1.61
1.59
1.34
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O
O
5
OAc
TMS
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2.08
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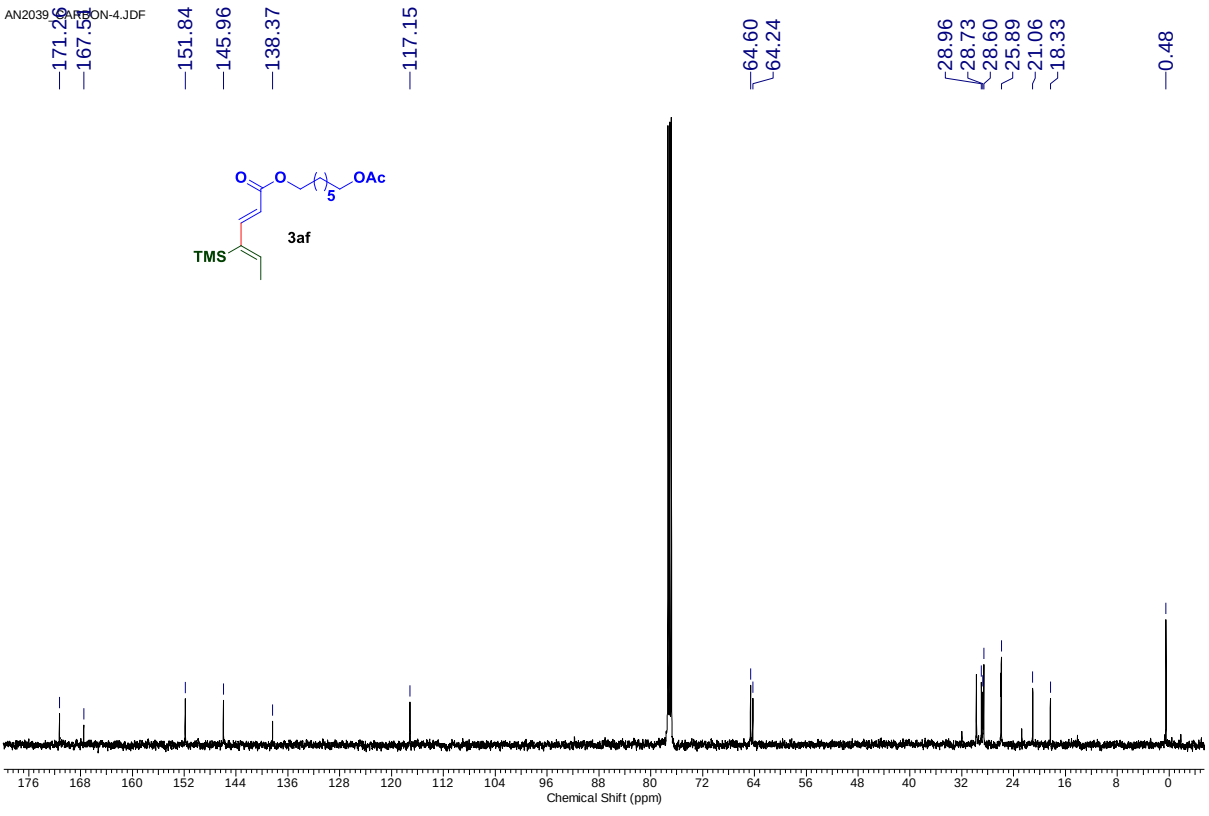
3.11
6.34
4.08
9.18
Chemical Shift (ppm)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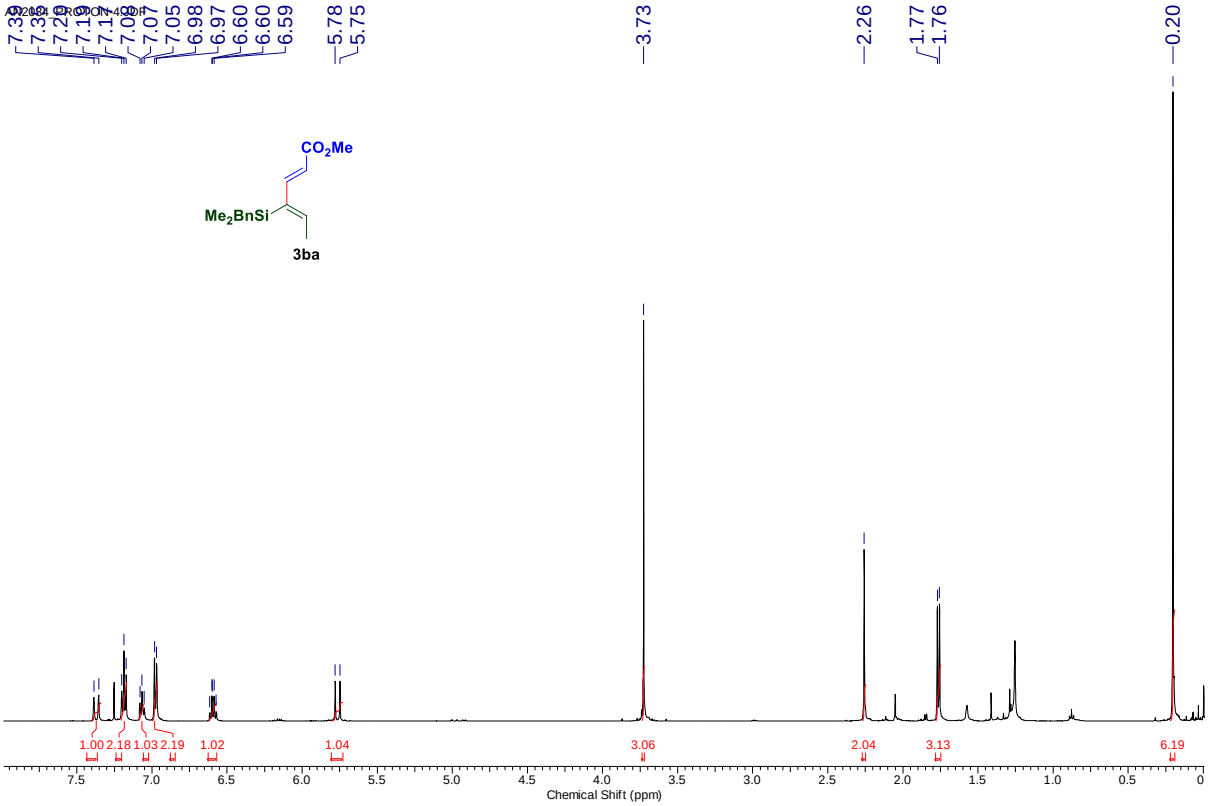
Chemical Shift (ppm)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1.76
0.20
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Me2BnSi
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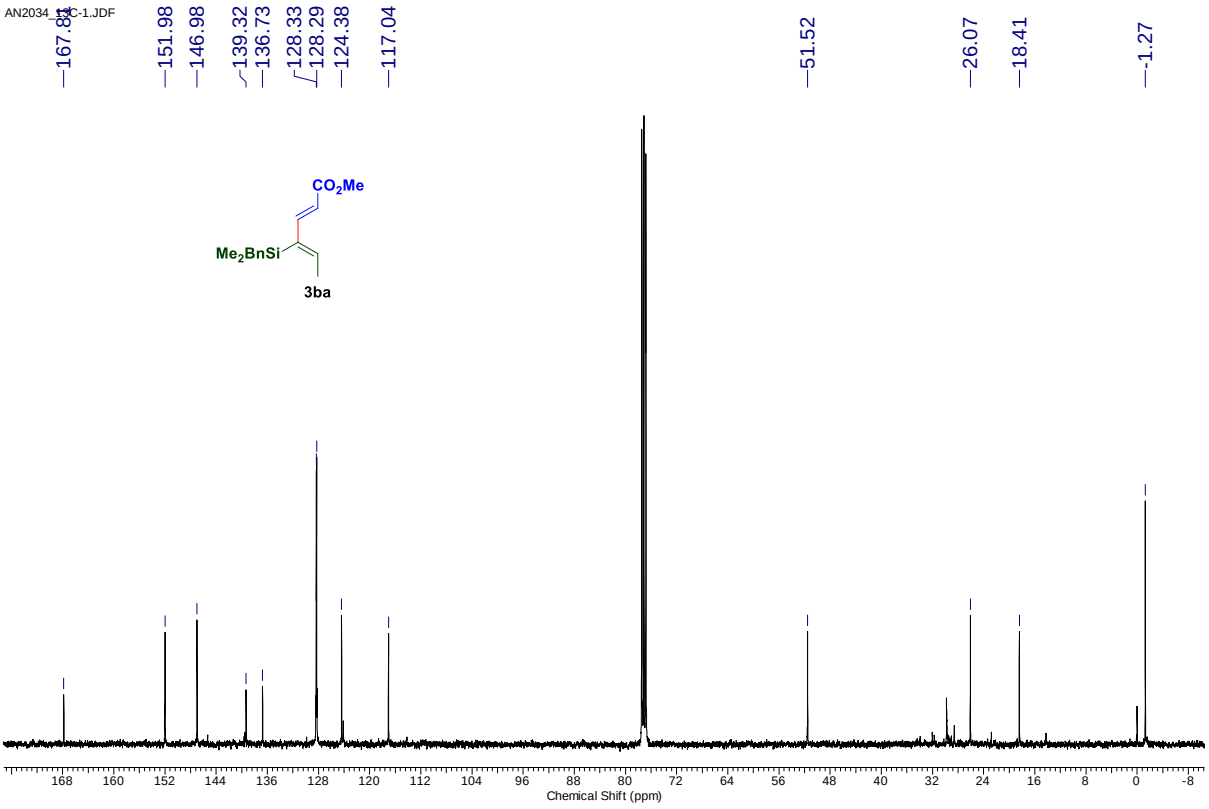
2.04
3.13
6.19
Chemical Shift (ppm)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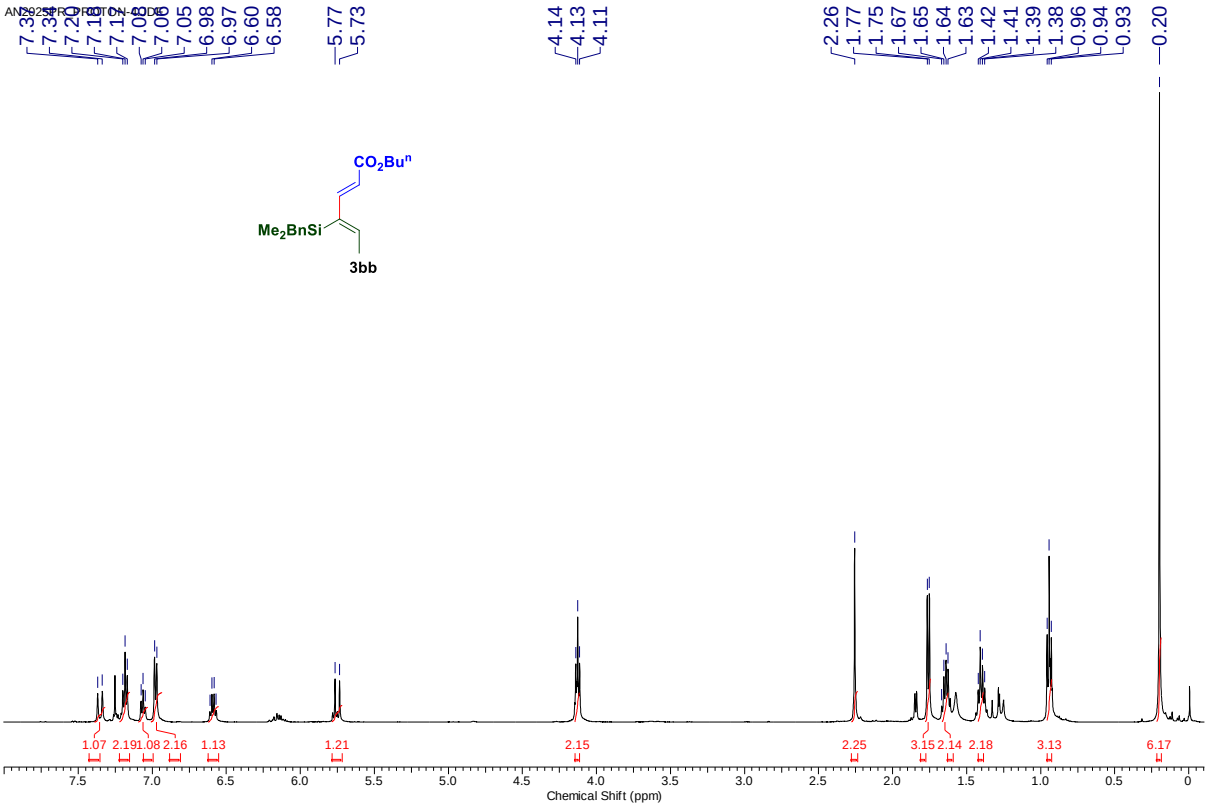
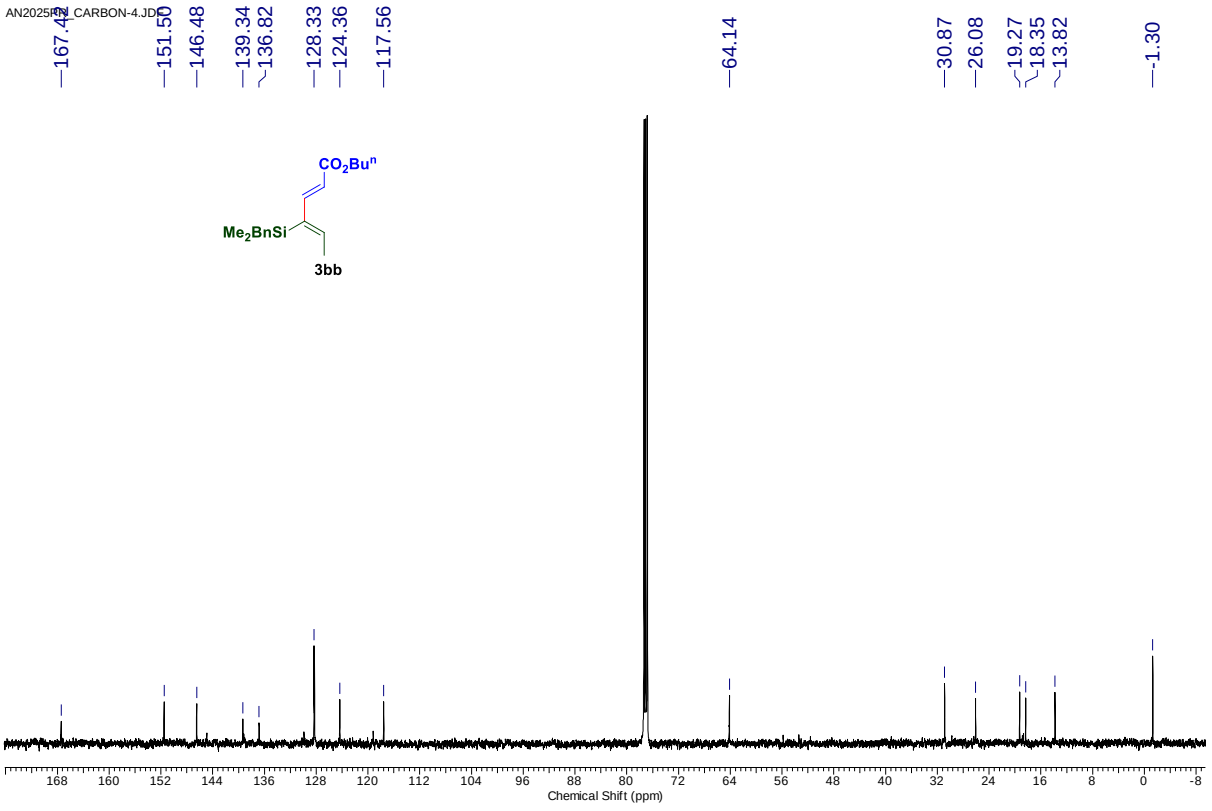
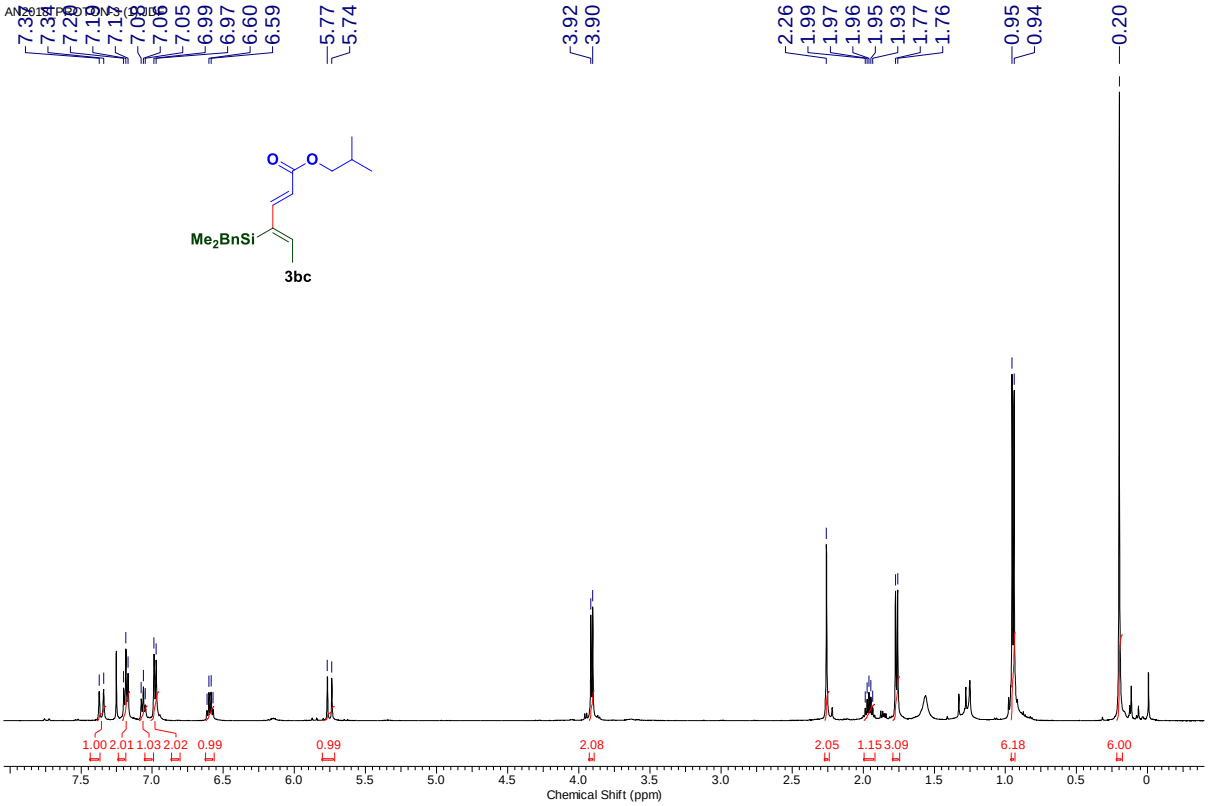
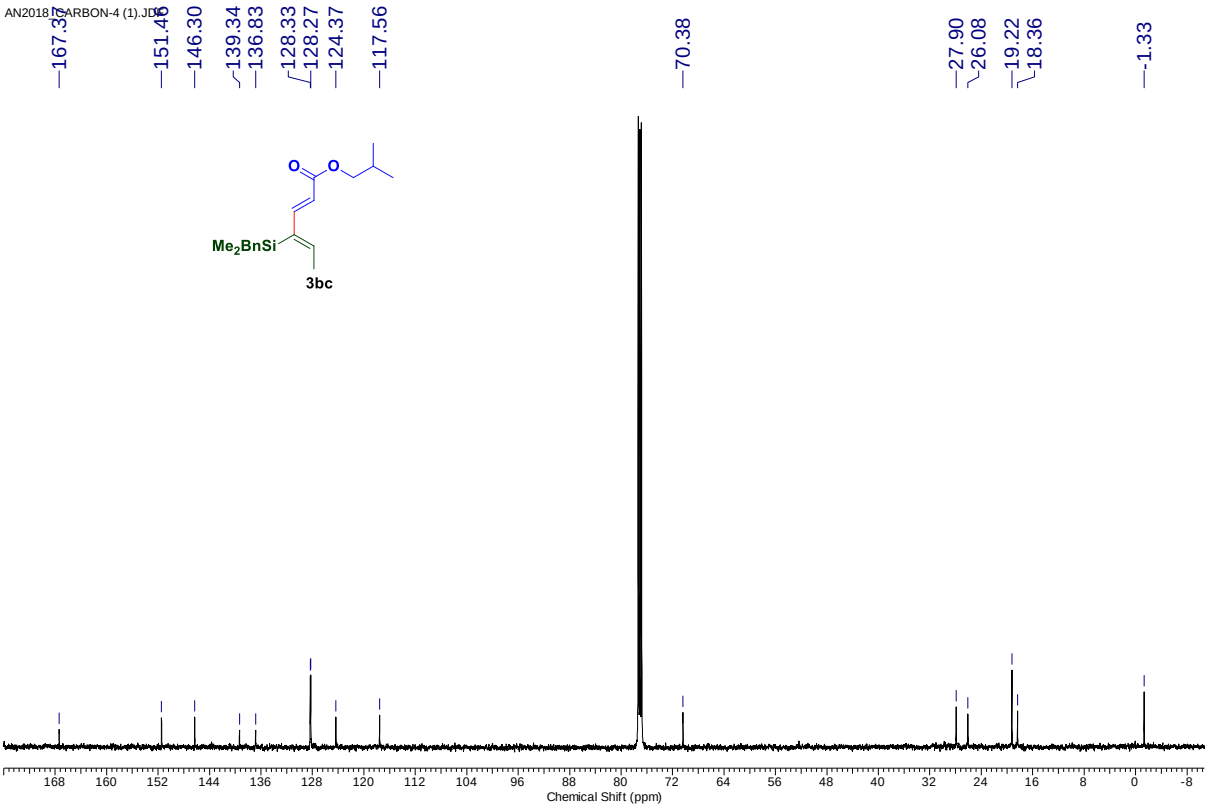
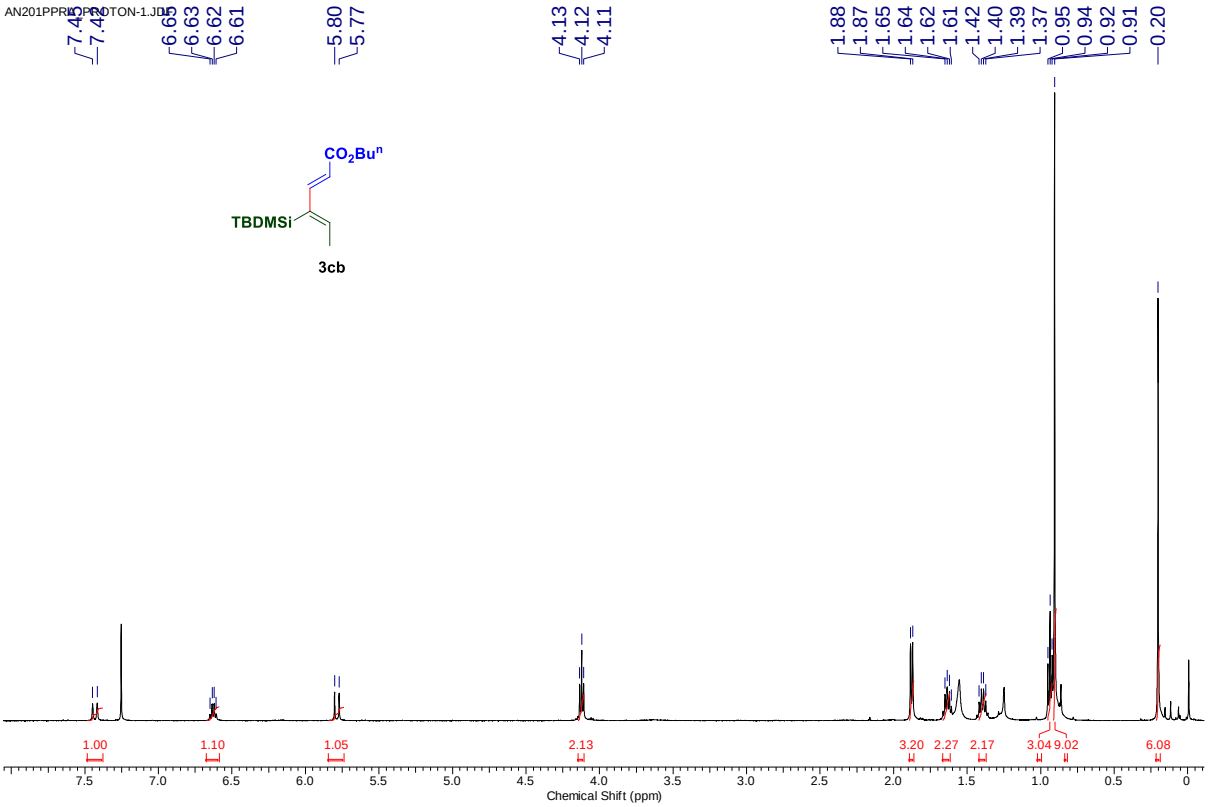
CO2Me
Me2BnSi
3ba
Chemical Shift (ppm)

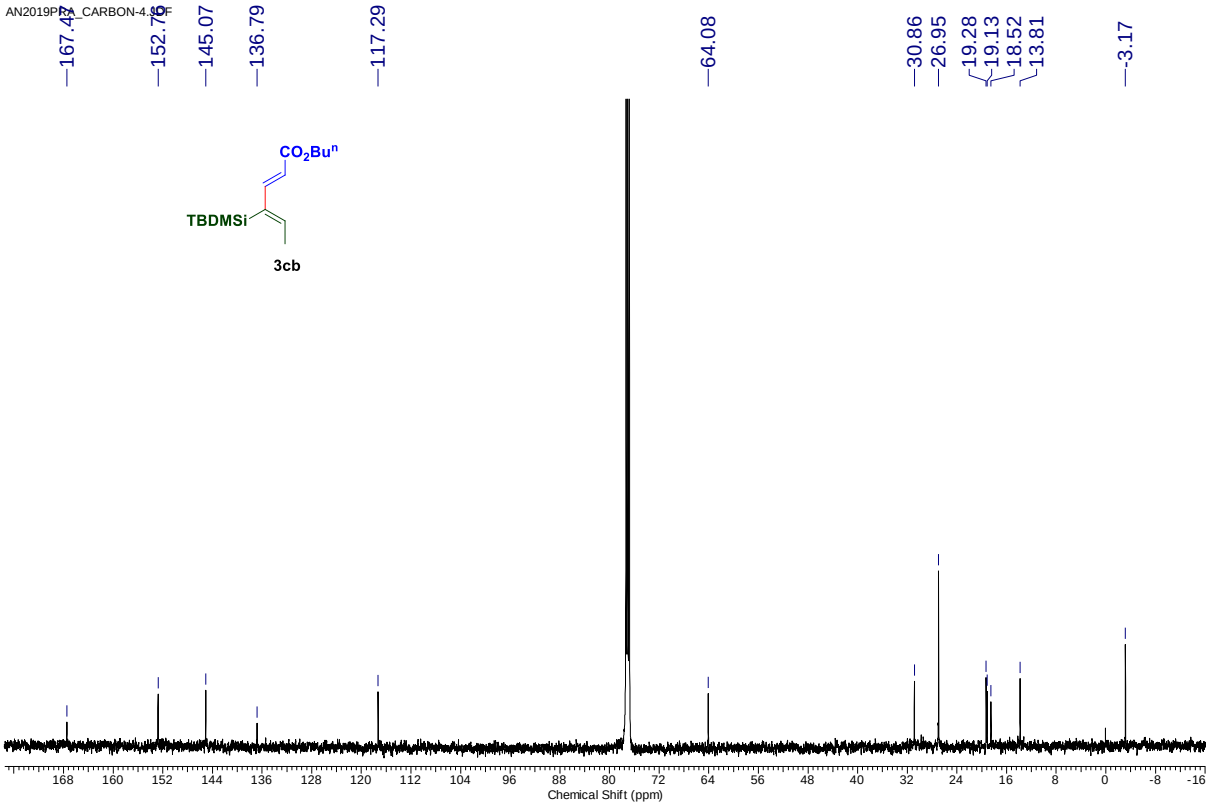

7.36
7.35
7.22
7.18
7.16
7.00
7.06
7.05
6.98
6.97
6.60
6.58
5.77
5.73
4.14
4.13
4.11
2.26
1.77
1.75
1.67
1.65
1.64
1.63
1.42
1.41
1.39
1.38
0.96
0.94
0.93
0.20
CO2Bun
Me2BnSi
3bb
1.07
2.19
1.08
2.16
1.13
1.21
2.15
2.25
3.15
2.14
2.18
3.13
6.17
Chemical Shift (ppm)

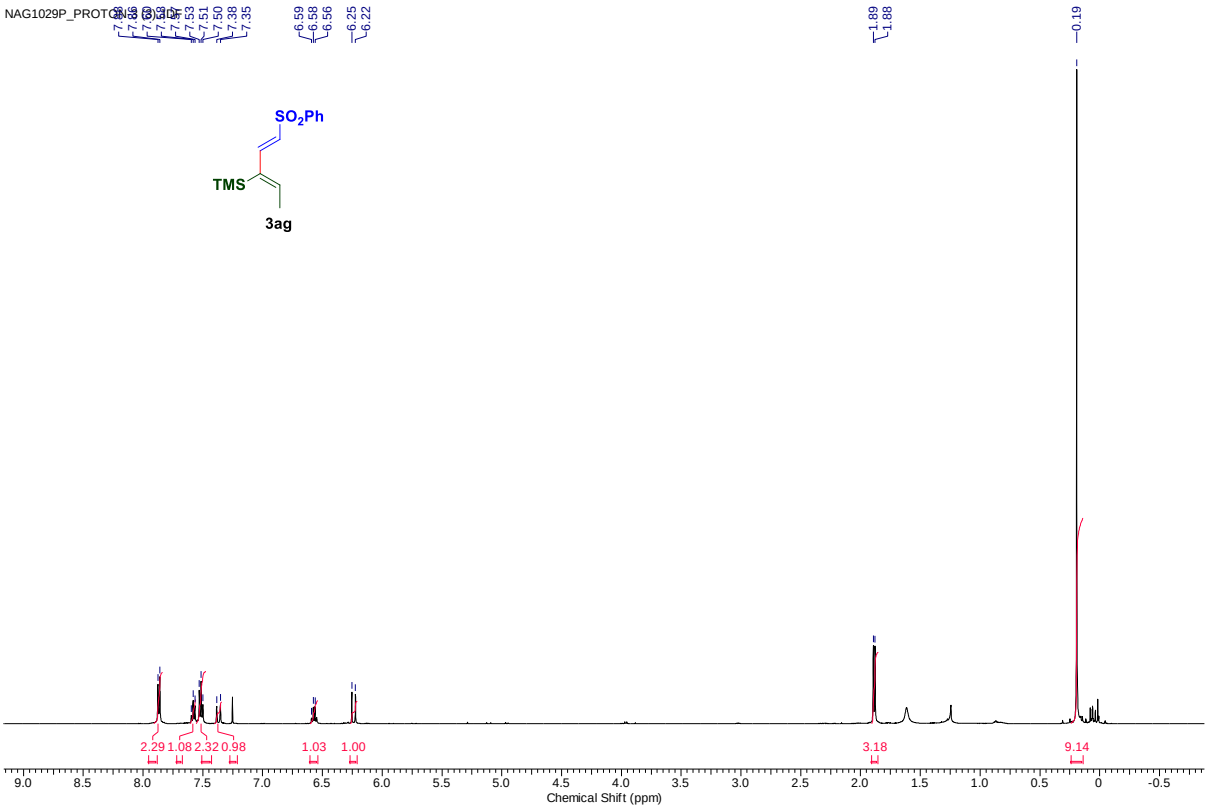

167.42
151.50
146.48
139.34
136.82
128.33
124.36
117.56
64.14
30.87
26.08
19.27
18.35
13.82
1.30
CO2Bun
Me2BnSi
3bb
Chemical Shift (ppm)

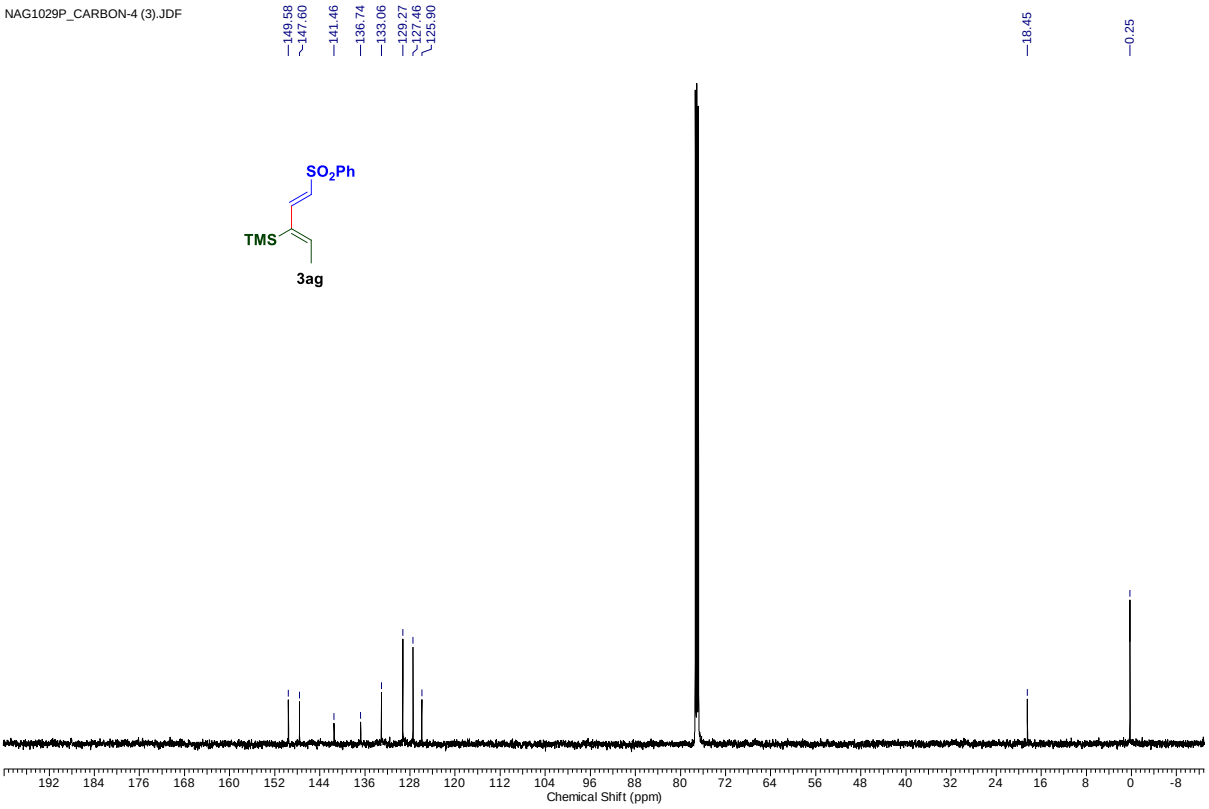

7.31
7.22
7.15
7.12
7.00
7.06
7.05
6.99
6.97
6.60
6.59
5.77
5.74
3.92
3.90
2.26
1.99
1.97
1.96
1.95
1.93
1.77
1.76
0.95
0.94
0.20
Me2BnSi
3bc
1.00 2.01 1.03 2.02 0.99 0.99 2.08 2.05 1.15 3.09 6.18 6.00
Chemical Shift (ppm)

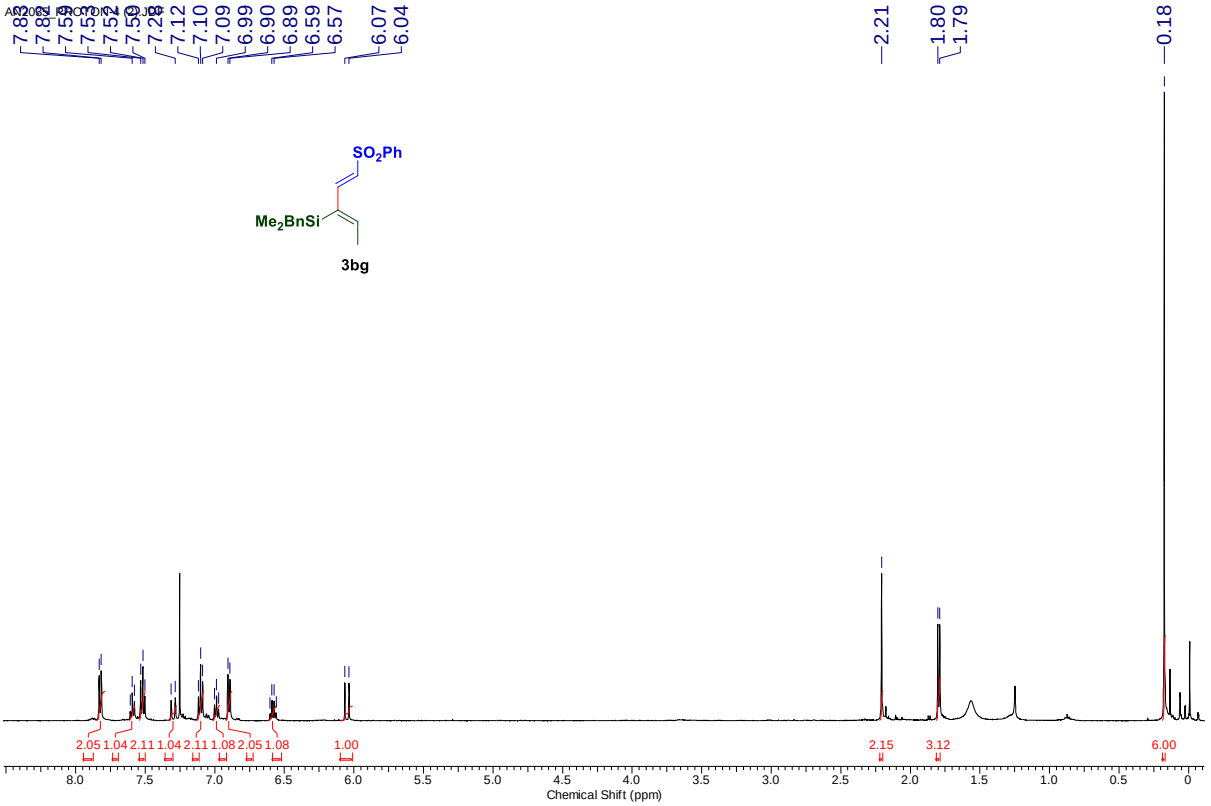

167.31
151.46
146.30
139.34
136.83
128.33
128.27
124.37
117.56
70.38
27.90
26.08
19.22
18.36
-1.33
Me2BnSi
3bc
Chemical Shift (ppm)

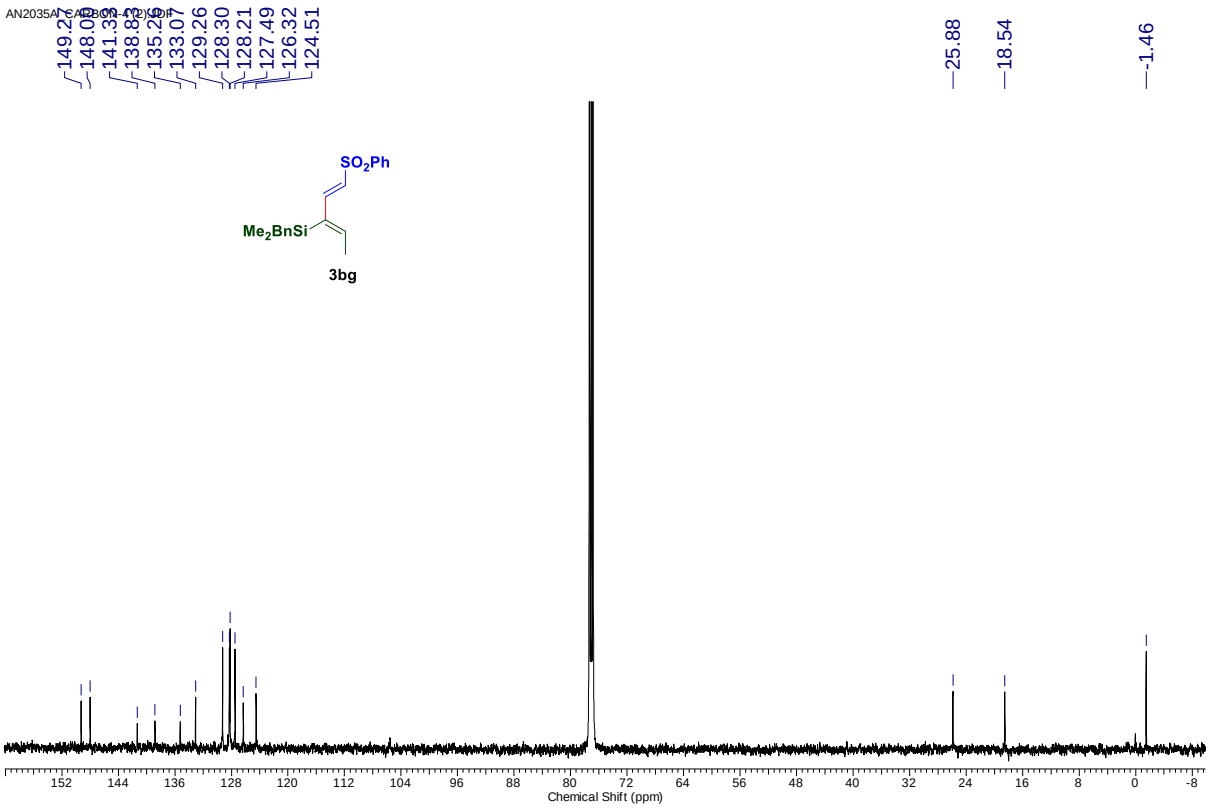

AN201PPRIOPROTON-1.JDF
7.46
7.44
6.65
6.63
6.62
6.61
5.80
5.77
4.13
4.12
4.11
1.88
1.87
1.65
1.64
1.62
1.61
1.42
1.40
1.39
1.37
0.95
0.94
0.92
0.91
0.20
CO2Bun
TBDMSi
3cb
1.00
1.10
1.05
2.13
3.20
2.27
2.17
3.04
9.02
6.08
Chemical Shift (ppm)

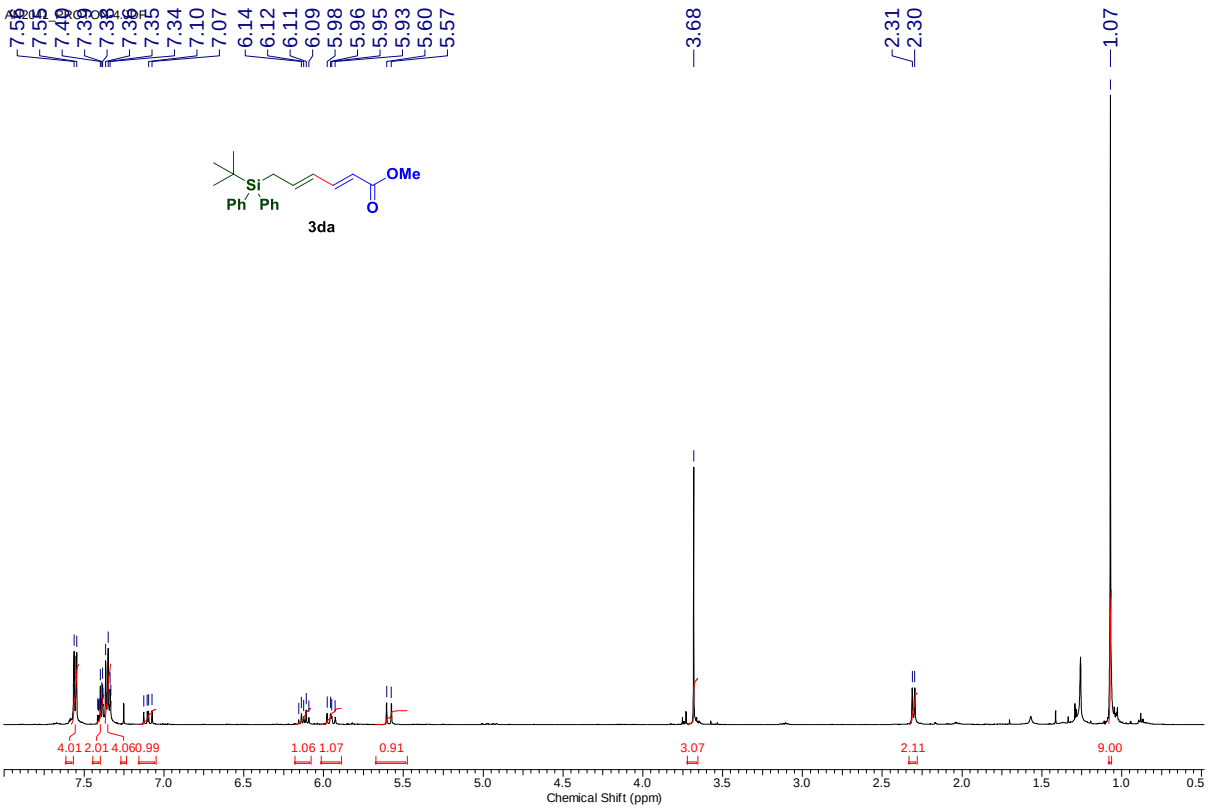

AN2019PRA_CARBON-4.1DF
167.46
152.70
145.07
136.79
117.29
64.08
30.86
26.95
19.28
19.13
18.52
13.81
-3.17
CO2Bun
TBDMSi
3cb
Chemical Shift (ppm)

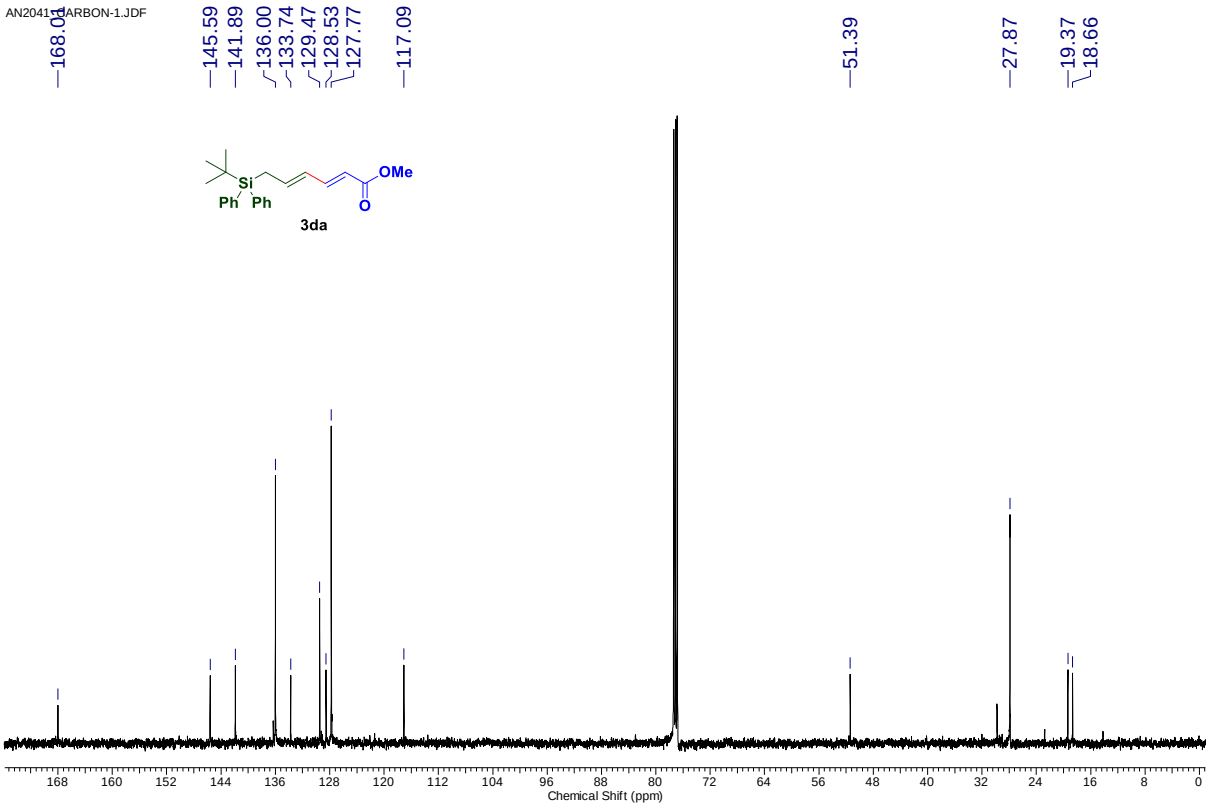

NAG1029P_PROTON-3 (3).JDF
7.38
7.35
6.59
6.58
6.56
6.25
6.22
1.89
1.88
0.19
SO2Ph
TMS
3ag
2.29
1.08
2.32
0.98
1.03
1.00
3.18
9.14
Chemical Shift (ppm)

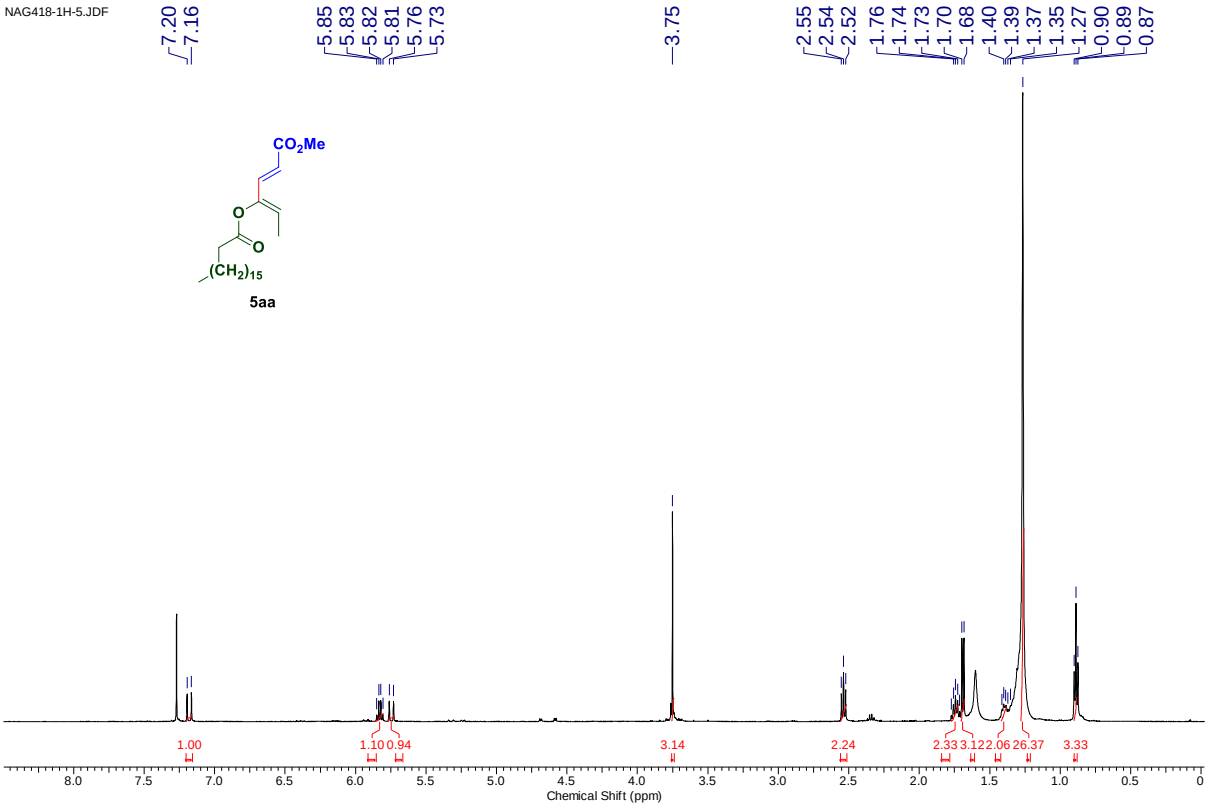

NAG1029P_CARBON-4 (3).JDF
149.58
147.60
141.46
136.74
133.06
129.27
127.46
125.90
18.45
0.25
SO2Ph
TMS
3ag
Chemical Shift (ppm)

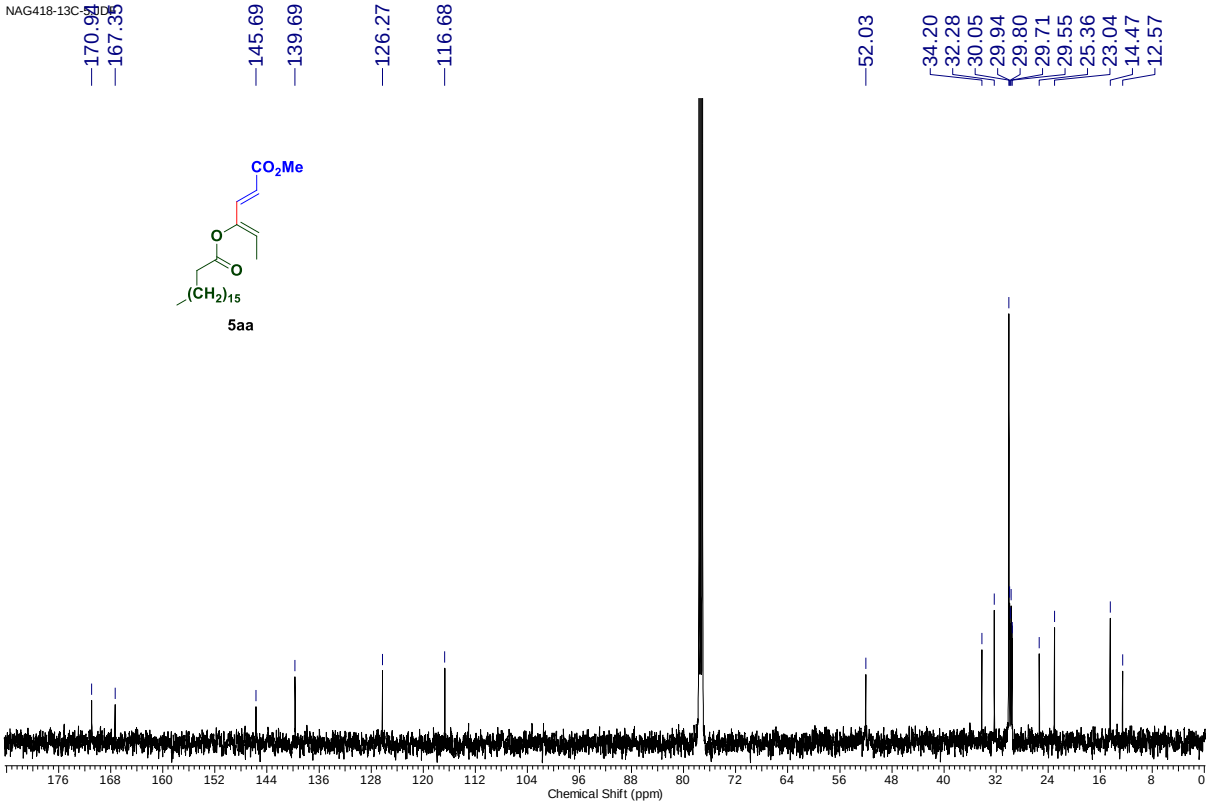

7.82
7.81
7.55
7.53
7.52
7.51
7.50
7.24
7.12
7.10
7.09
6.99
6.90
6.89
6.59
6.57
6.07
6.04
2.21
1.80
1.79
0.18
SO2Ph
Me2BnSi
3bg
2.05 1.04 2.11 1.04 2.11 1.08 2.05 1.08 1.00 2.15 3.12 6.00
Chemical Shift (ppm)

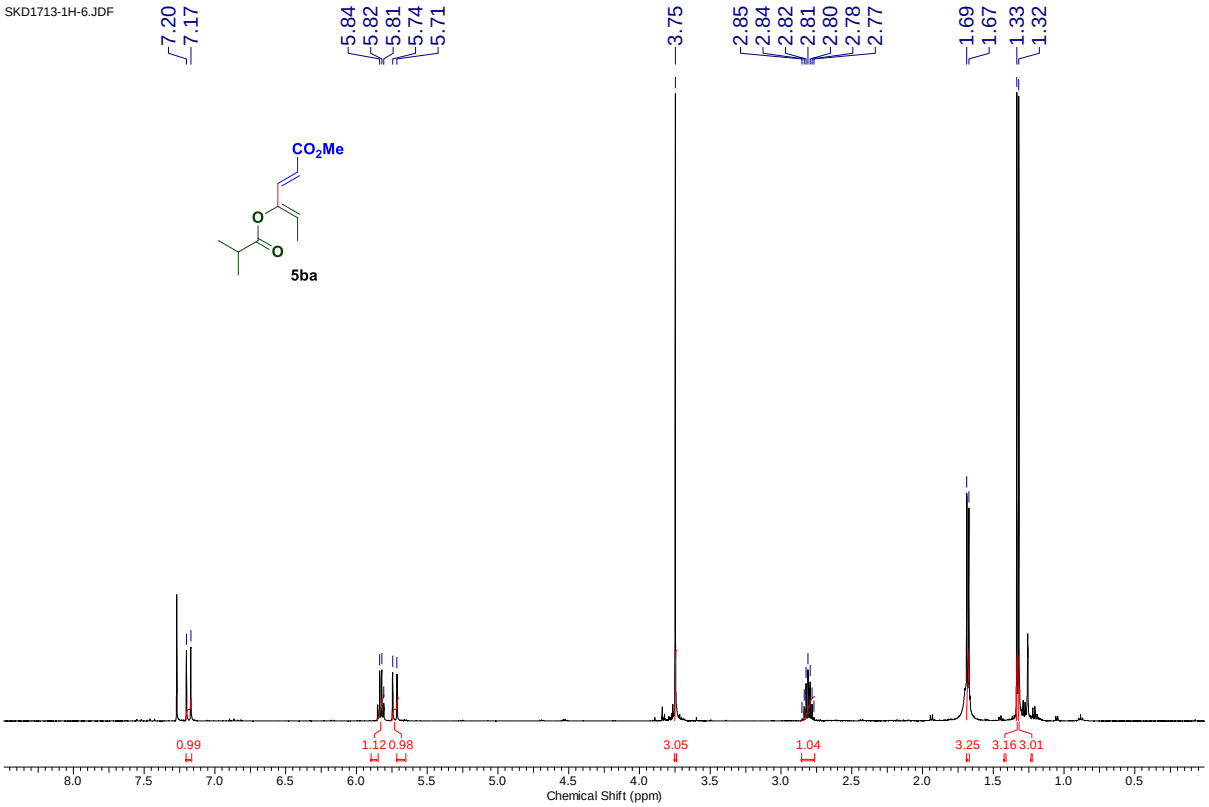

149.21
148.08
141.39
138.82
135.25
133.07
129.26
128.30
128.21
127.49
126.32
124.51
25.88
18.54
-1.46
SO2Ph
Me2BnSi
3bg
Chemical Shift (ppm)

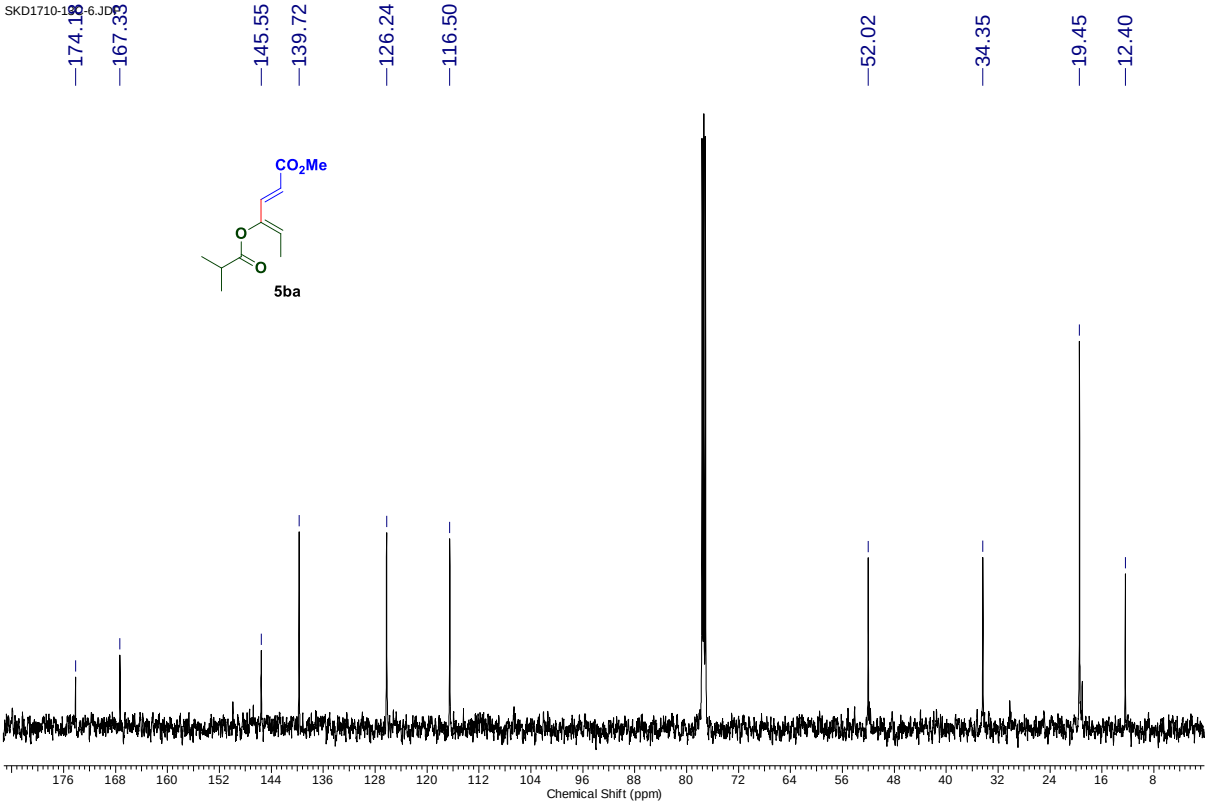

7.56
7.55
7.49
7.39
7.38
7.36
7.35
7.34
7.10
7.07
6.14
6.12
6.11
6.09
5.98
5.96
5.95
5.93
5.60
5.57
3.68
2.31
2.30
1.07
Si
Ph
Ph
OMe
O
3da
4.01
2.01
4.06
0.99
1.06
1.07
0.91
3.07
2.11
9.00
Chemical Shift (ppm)

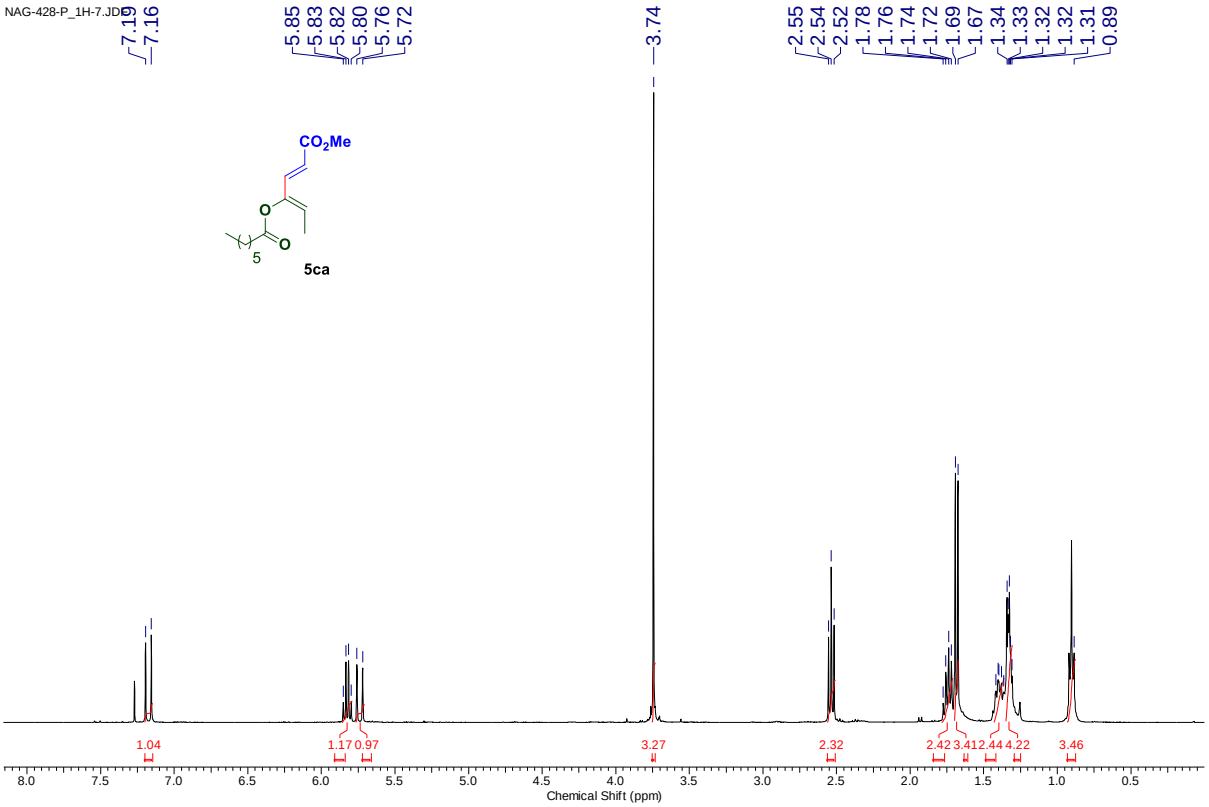

AN2041-CARBON-1.JDF
168.01
145.59
141.89
136.00
133.74
129.47
128.53
127.77
117.09
51.39
27.87
19.37
18.66
Si
Ph
Ph
OMe
O
3da
Chemical Shift (ppm)

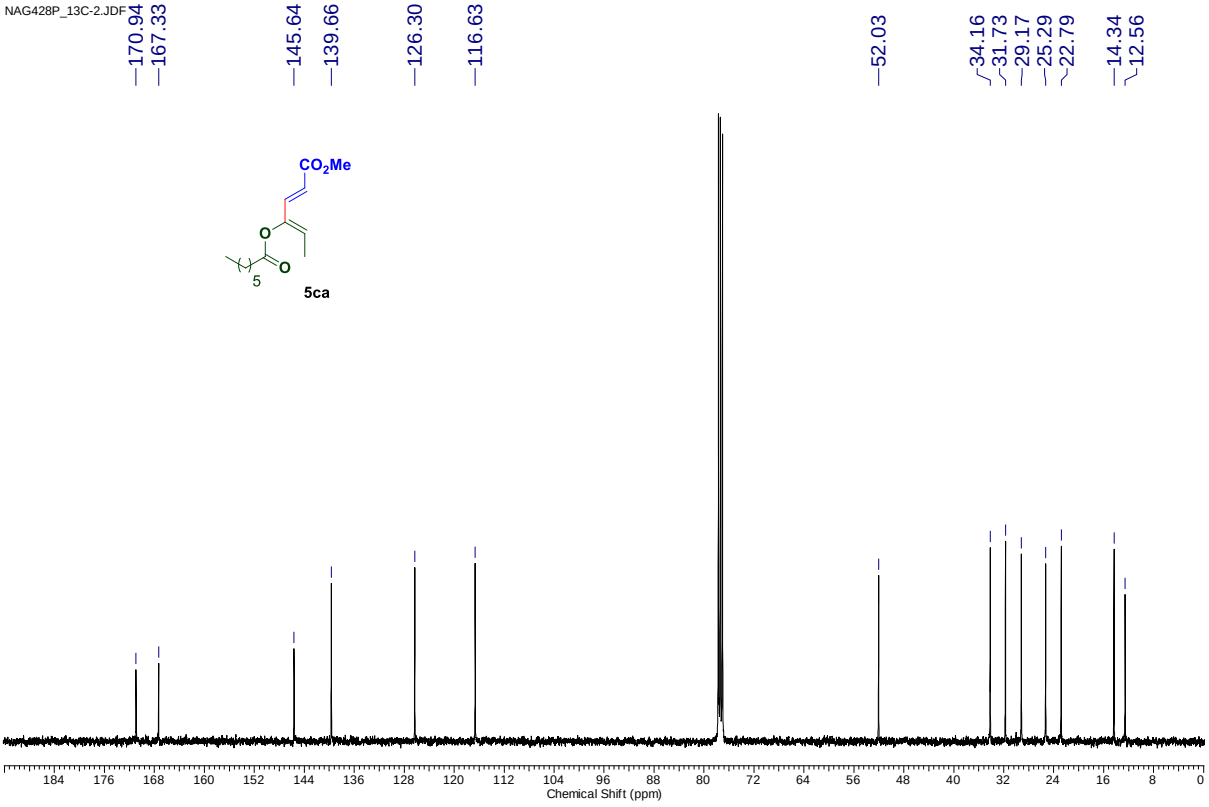

NAG418-1H-5.JDF
7.20
7.16
5.85
5.83
5.82
5.81
5.76
5.73
3.75
2.55
2.54
2.52
1.76
1.74
1.73
1.70
1.68
1.40
1.39
1.37
1.35
1.27
0.90
0.89
0.87
CO2Me
O
O
(CH2)15
5aa
1.00
1.10
0.94
3.14
2.24
2.33
3.12
2.06
6.37
3.33
Chemical Shift (ppm)

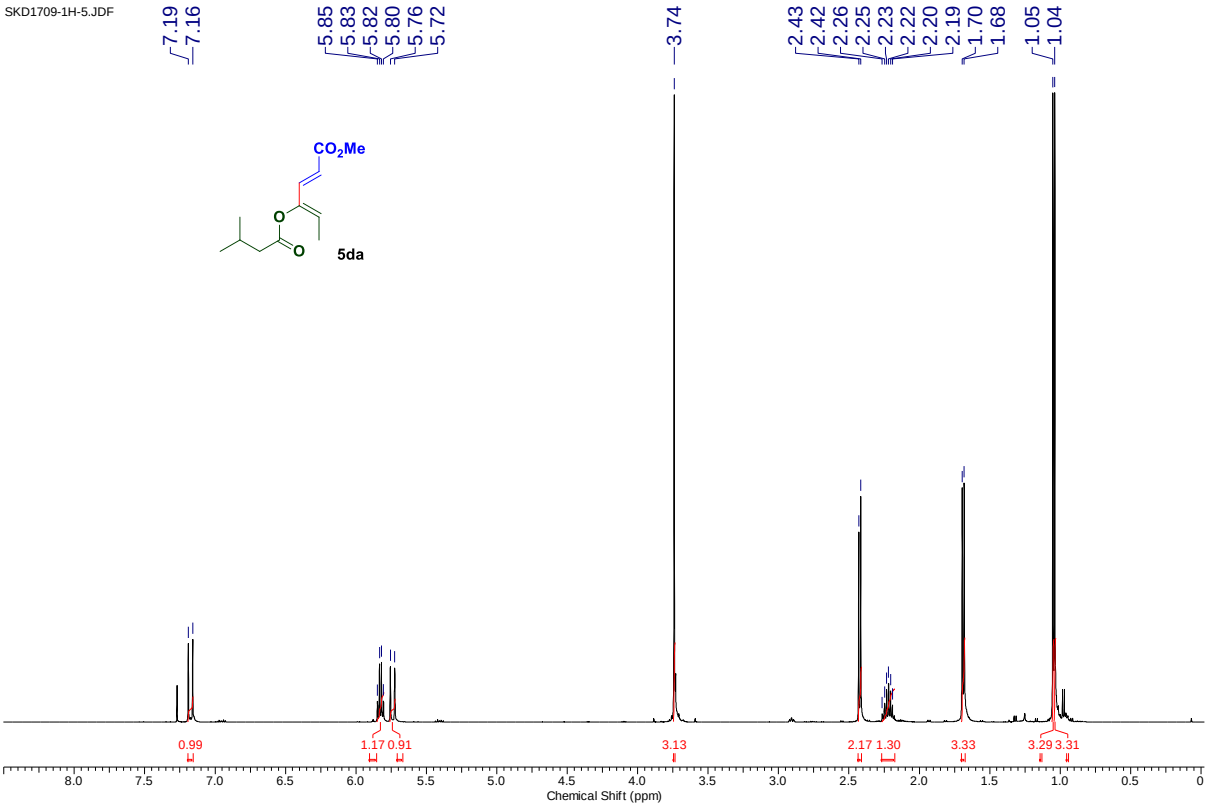

NAG418-13C-5.JDF
170.90
167.35
145.69
139.69
126.27
116.68
52.03
34.20
32.28
30.05
29.94
29.80
29.71
29.55
25.36
23.04
14.47
12.57
CO2Me
O
O
(CH2)15
5aa
Chemical Shift (ppm)

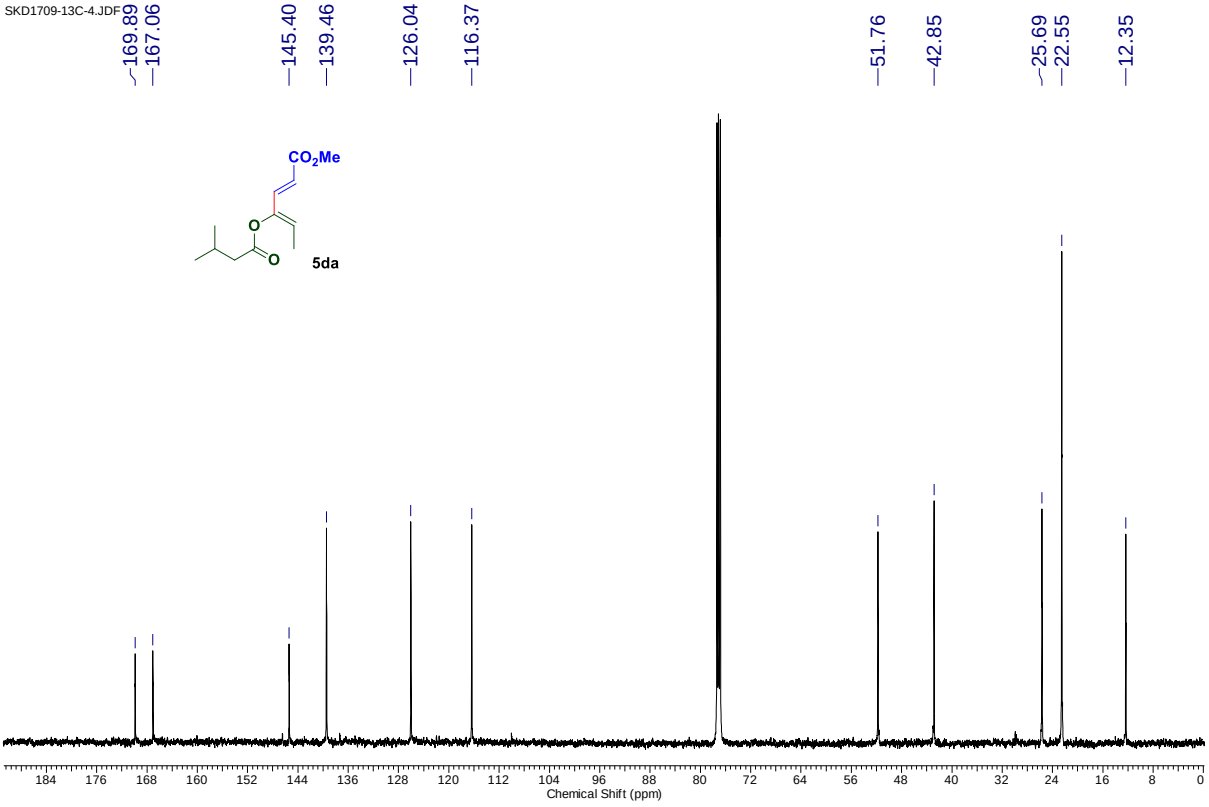

SKD1713-1H-6.JDF
7.20
7.17
5.84
5.82
5.81
5.74
5.71
3.75
2.85
2.84
2.82
2.81
2.80
2.78
2.77
1.69
1.67
1.33
1.32
CO2Me
O
O
5ba
0.99
1.12
0.98
3.05
1.04
3.25
3.16
3.01
Chemical Shift (ppm)

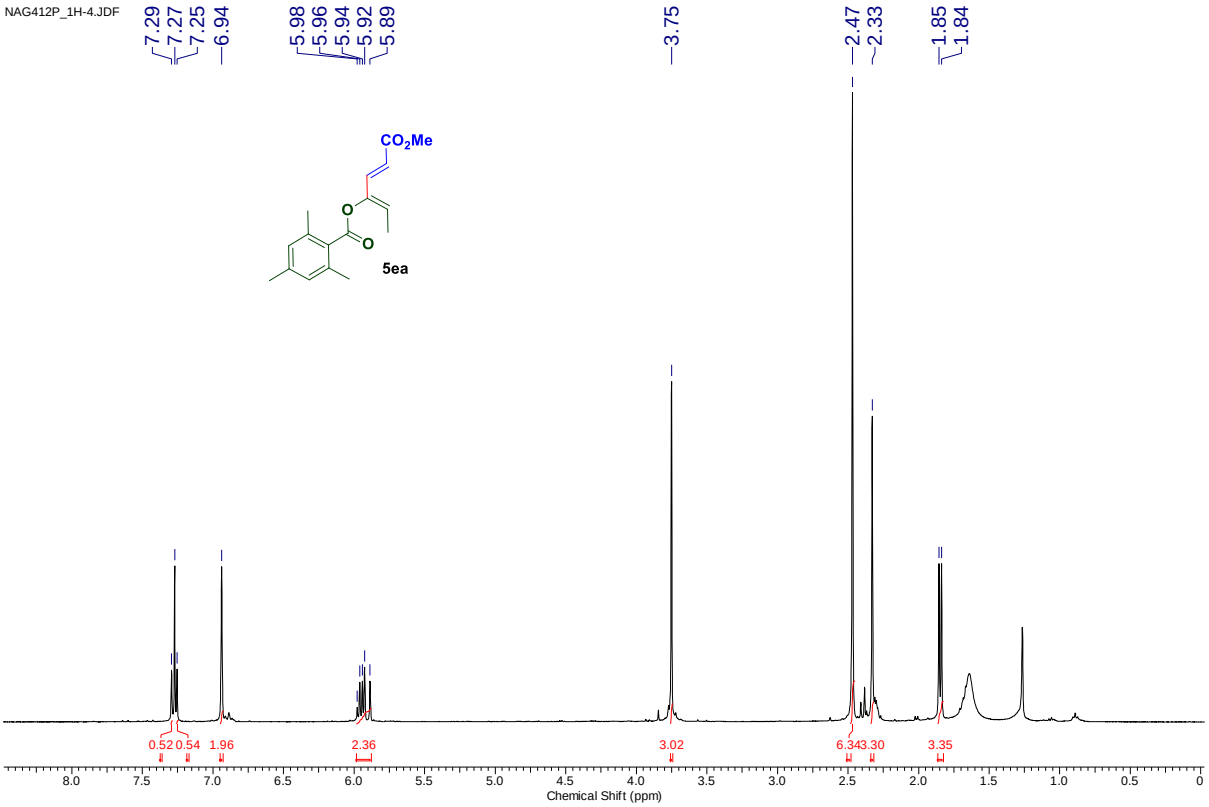

SKD1710-13C-6.JDF
174.19
167.33
145.55
139.72
126.24
116.50
52.02
34.35
19.45
12.40
CO2Me
O
O
5ba
Chemical Shift (ppm)

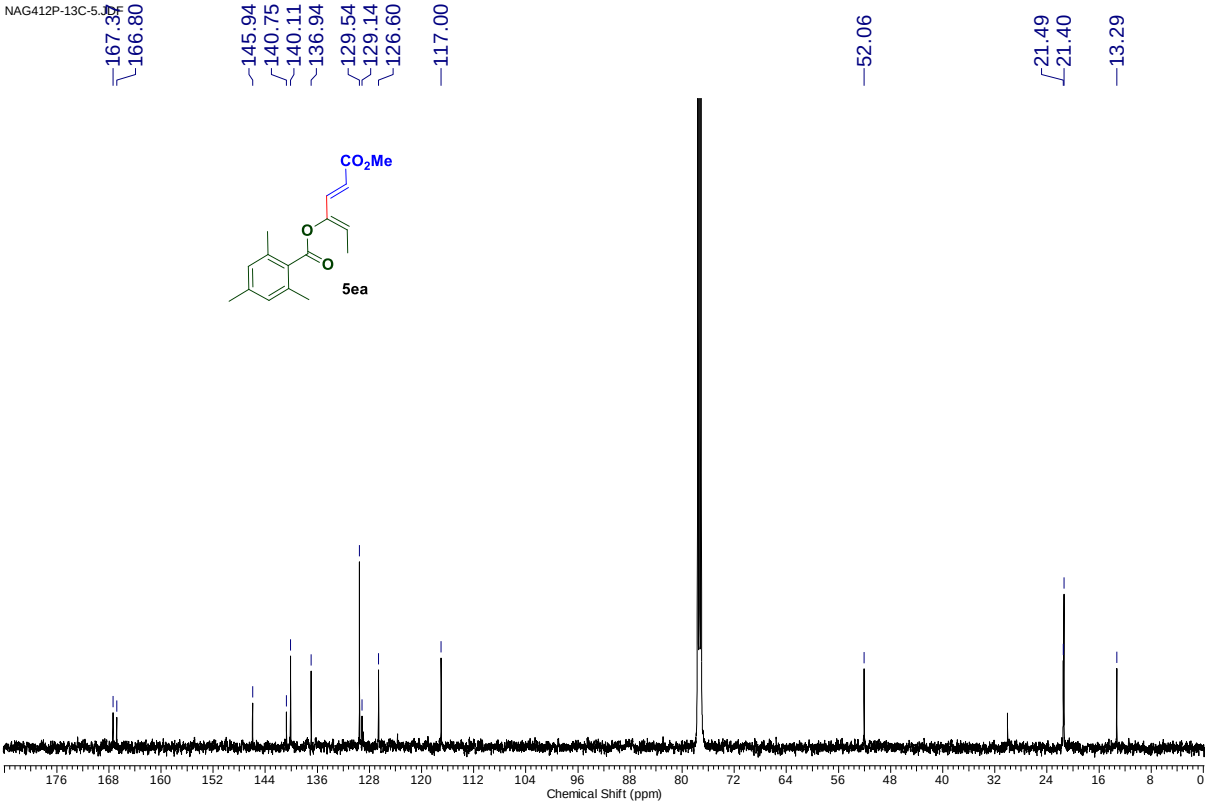

NAG-428-P_1H-7.JDF
7.19
7.16
5.85
5.83
5.82
5.80
5.76
5.72
3.74
2.55
2.54
2.52
1.78
1.76
1.74
1.72
1.69
1.67
1.34
1.33
1.32
1.32
1.31
0.89
CO2Me
O
O
5
5ca
1.04
1.17
0.97
3.27
2.32
2.42
3.41
2.44
4.22
3.46
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

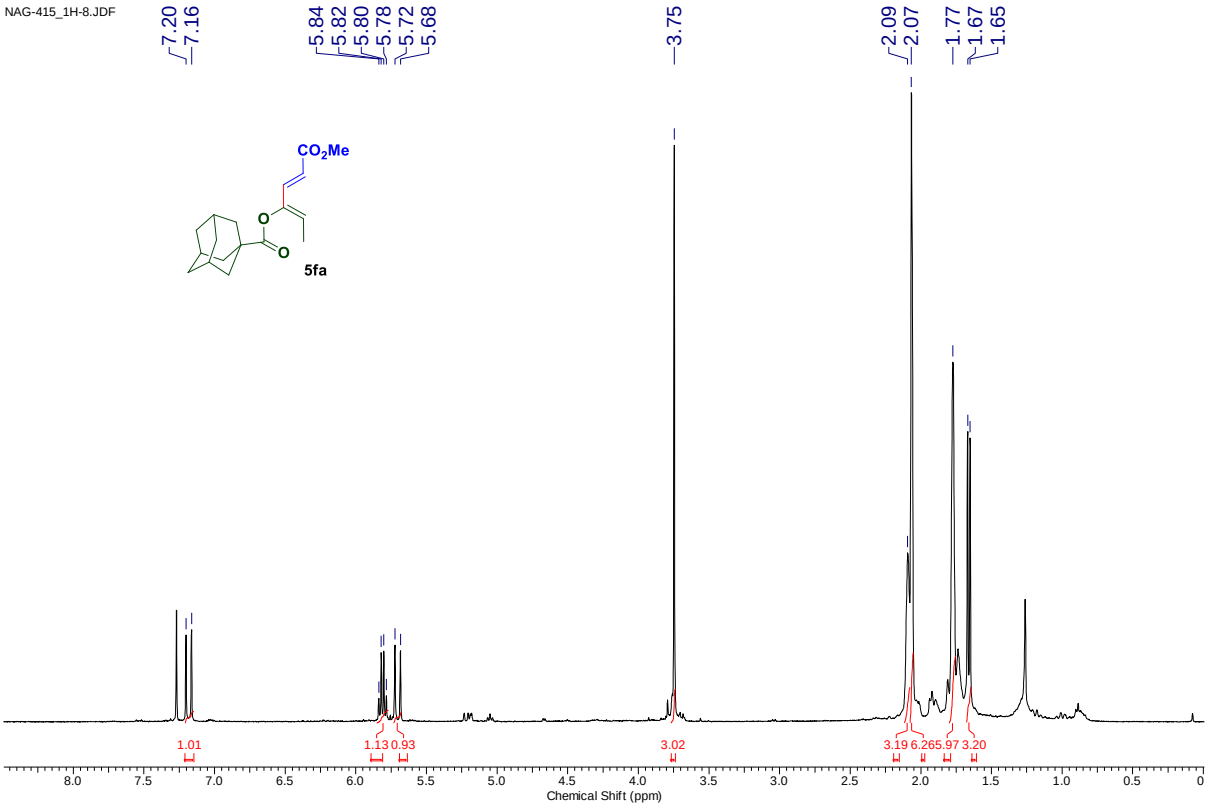

NAG428P_13C-2.JDF
170.94
167.33
145.64
139.66
126.30
116.63
52.03
34.16
31.73
29.17
25.29
22.79
14.34
12.56
CO2Me
O
O
5
5ca
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

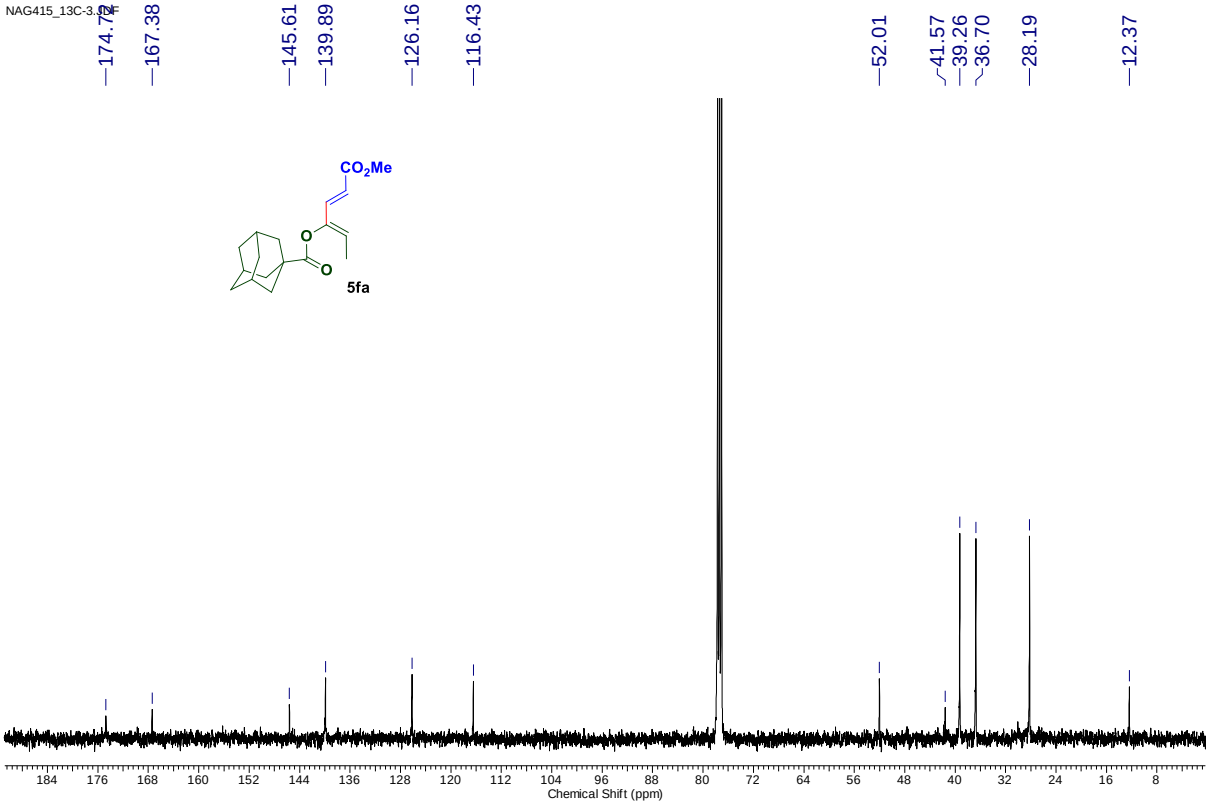

SKD1709-1H-5.JDF
7.19
7.16
5.85
5.83
5.82
5.80
5.76
5.72
3.74
2.43
2.42
2.26
2.25
2.23
2.22
2.20
2.19
1.70
1.68
1.05
1.04
CO2Me
O
O
5da
0.99
1.17
0.91
3.13
2.17
1.30
3.33
3.29
3.31
Chemical Shift (ppm)

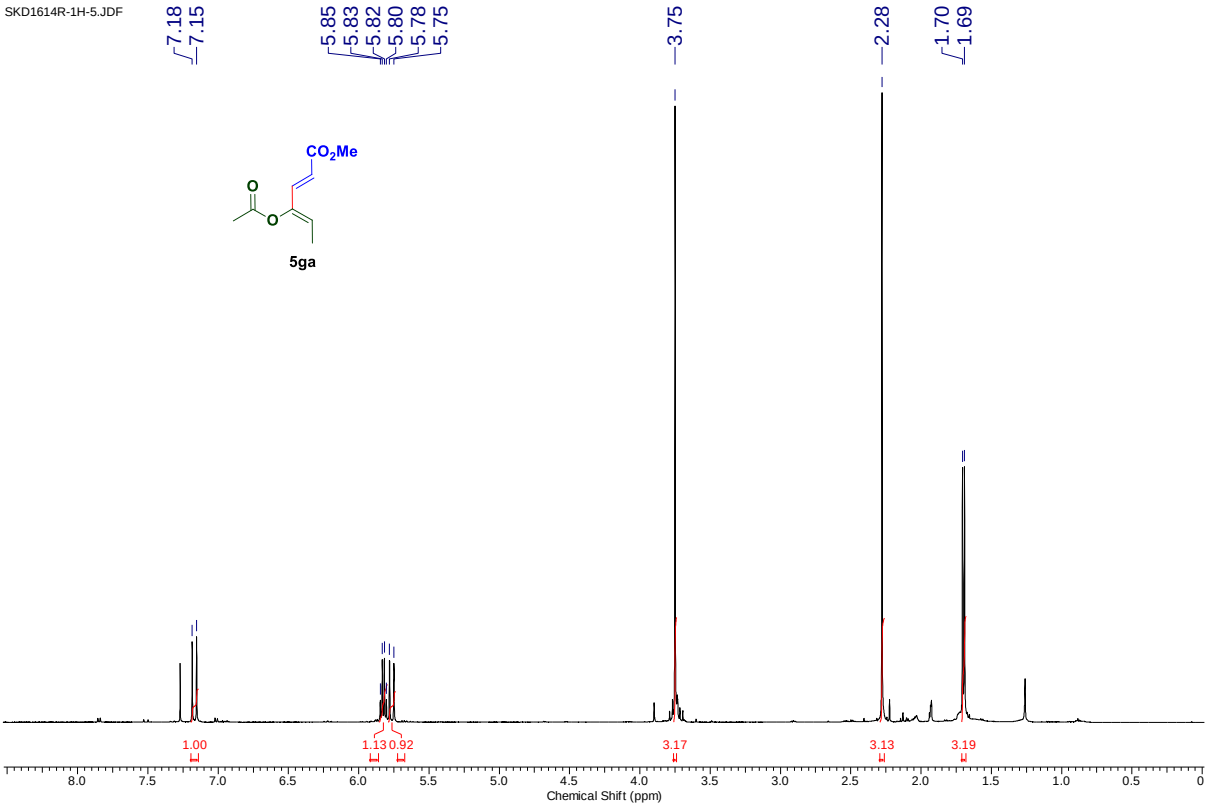

SKD1709-13C-4.JDF
169.89
167.06
145.40
139.46
126.04
116.37
51.76
42.85
25.69
22.55
12.35
CO2Me
O
O
5da
Chemical Shift (ppm)

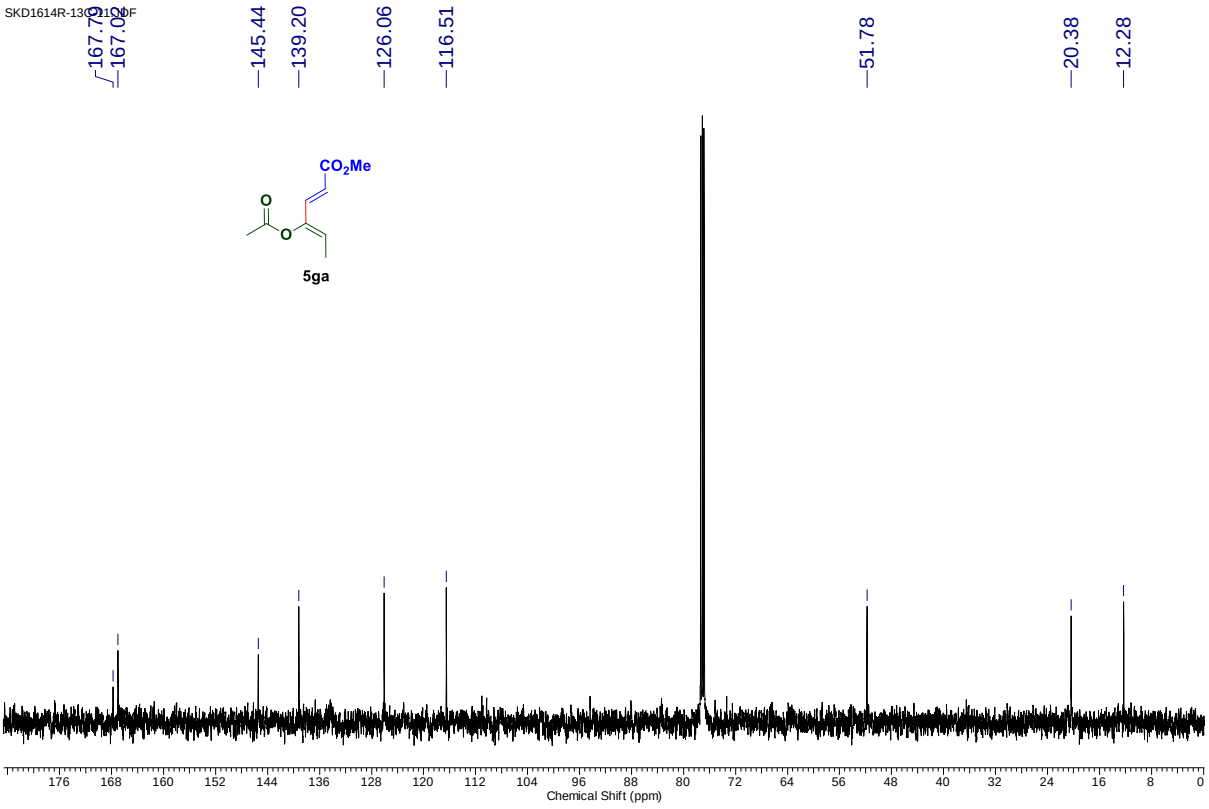

NAG412P_1H-4.JDF
7.29
7.27
7.25
6.94
5.98
5.96
5.94
5.92
5.89
3.75
2.47
2.33
1.85
1.84
CO2Me
O
O
5ea
0.52
0.54
1.96
2.36
3.02
6.34
3.30
3.35
Chemical Shift (ppm)

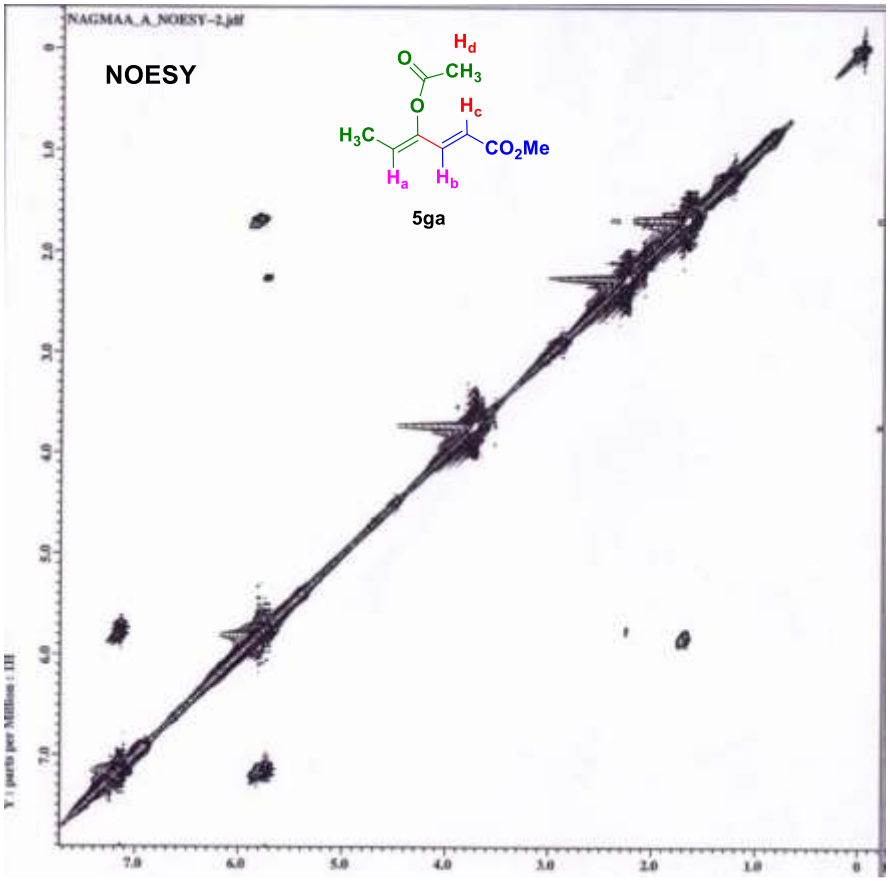

NAG412P-13C-5.JDF
167.39
166.80
145.94
140.75
140.11
136.94
129.54
129.14
126.60
117.00
52.06
21.49
21.40
13.29
CO2Me
O
O
5ea
Chemical Shift (ppm)

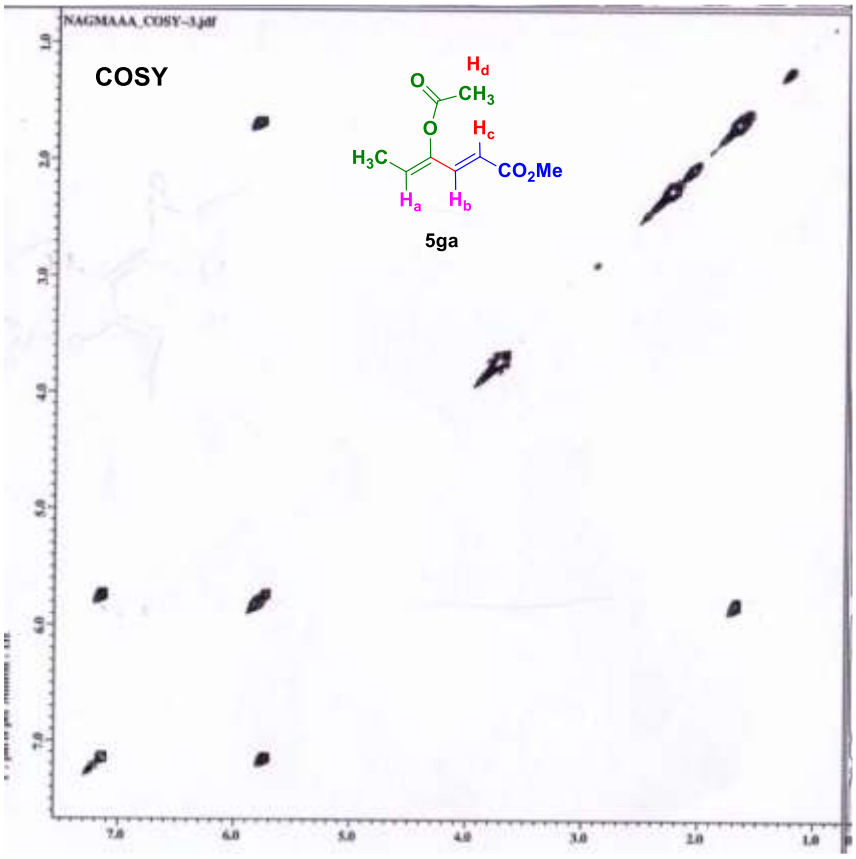

NAG-415_1H-8.JDF
7.20
7.16
5.84
5.82
5.80
5.78
5.72
5.68
3.75
2.09
2.07
1.77
1.67
1.65
CO2Me
O
O
5fa
1.01
1.13
0.93
3.02
3.19
6.26
5.97
3.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

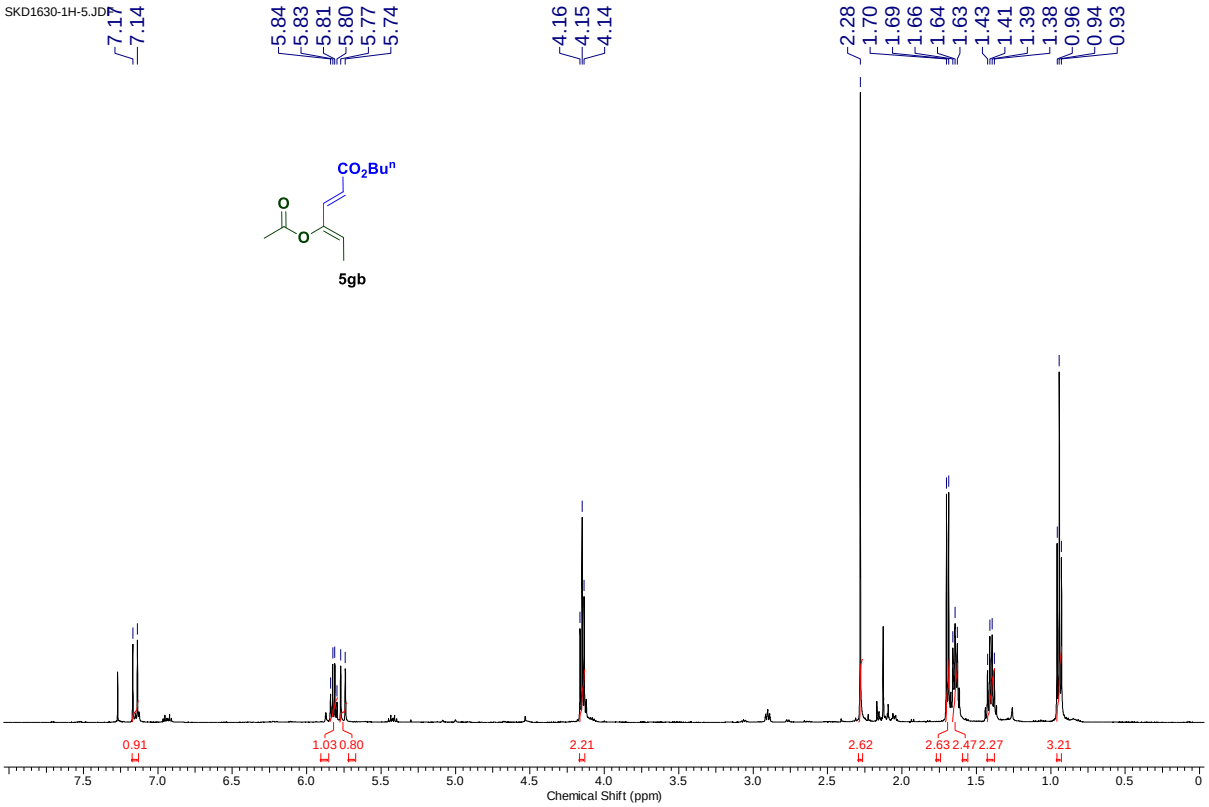

NAG415_13C-3.1F
174.79
167.38
145.61
139.89
126.16
116.43
52.01
41.57
39.26
36.70
28.19
12.37
CO2Me
O
O
5fa
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

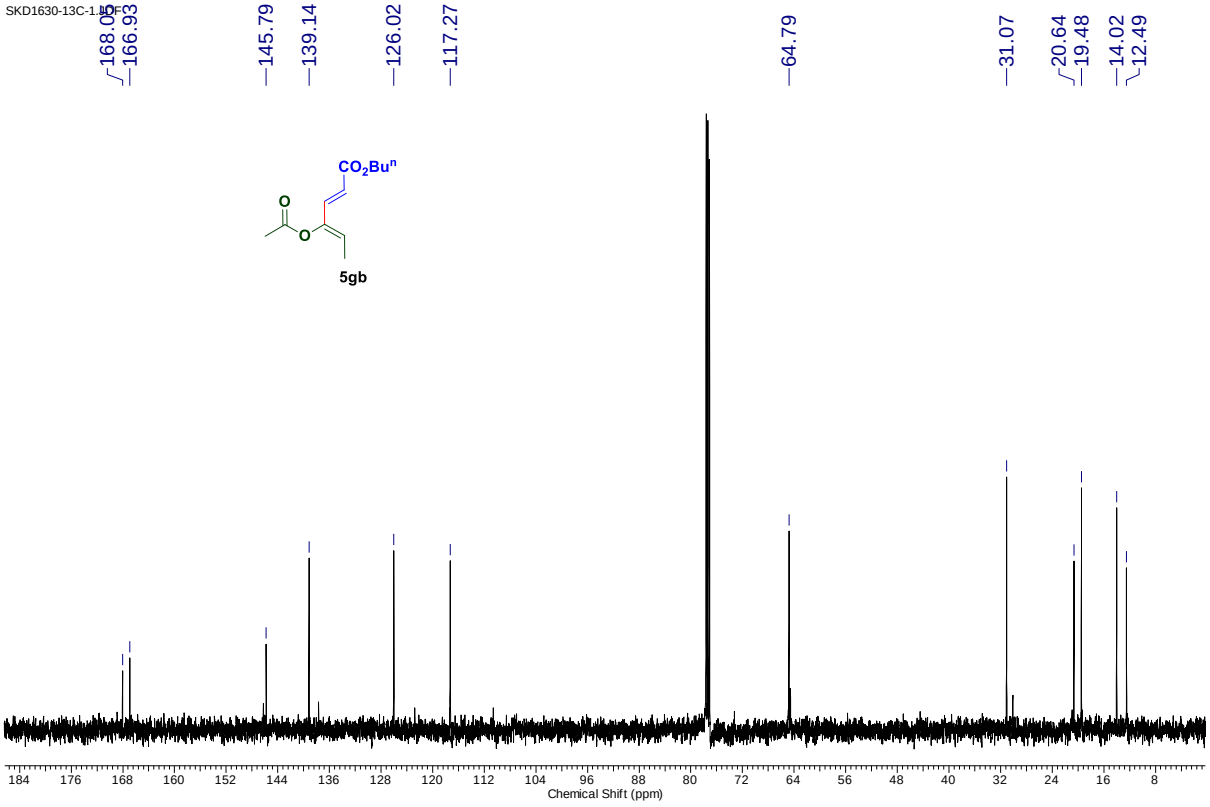

SKD1614R-1H-5.JDF
7.18
7.15
5.85
5.83
5.82
5.80
5.78
5.75
3.75
2.28
1.70
1.69
CO2Me
O
O
5ga
1.00
1.13
0.92
3.17
3.13
3.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

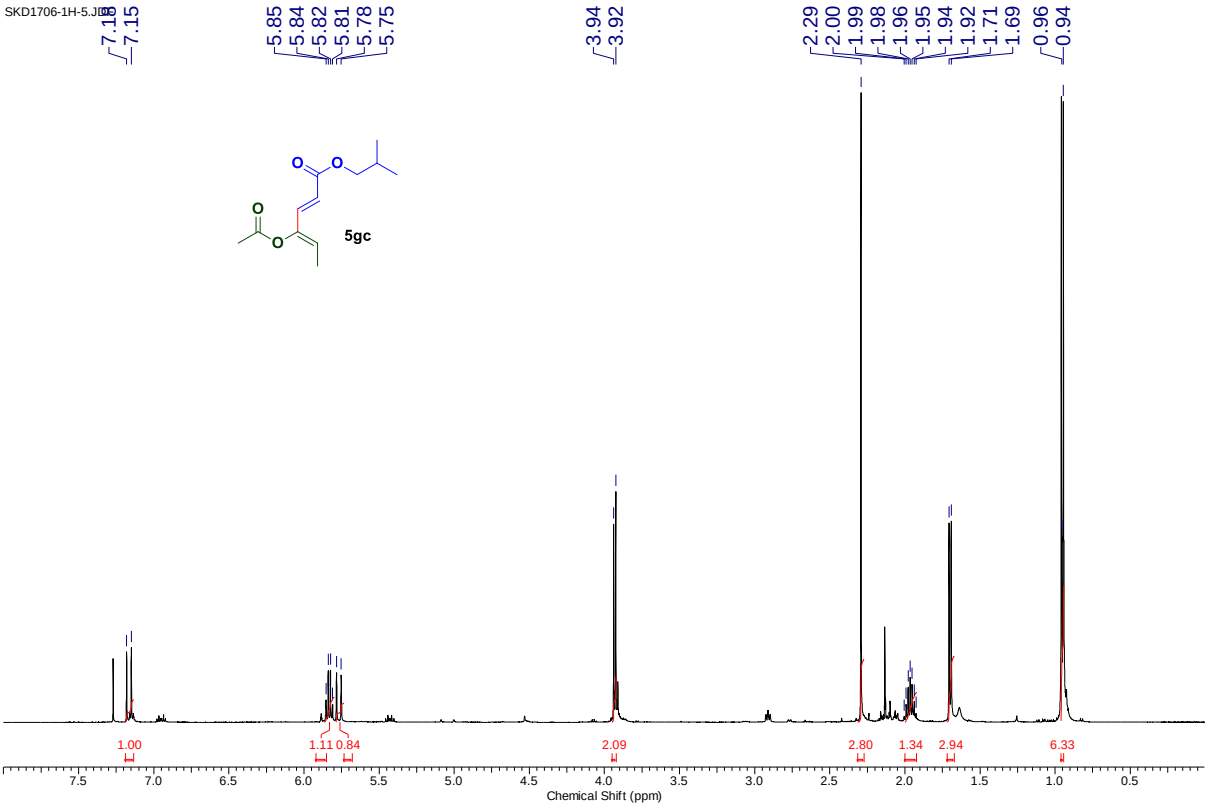

SKD1614R-13C-21.JDF
167.72
167.00
145.44
139.20
126.06
116.51
51.78
20.38
12.28
CO2Me
O
O
5ga
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

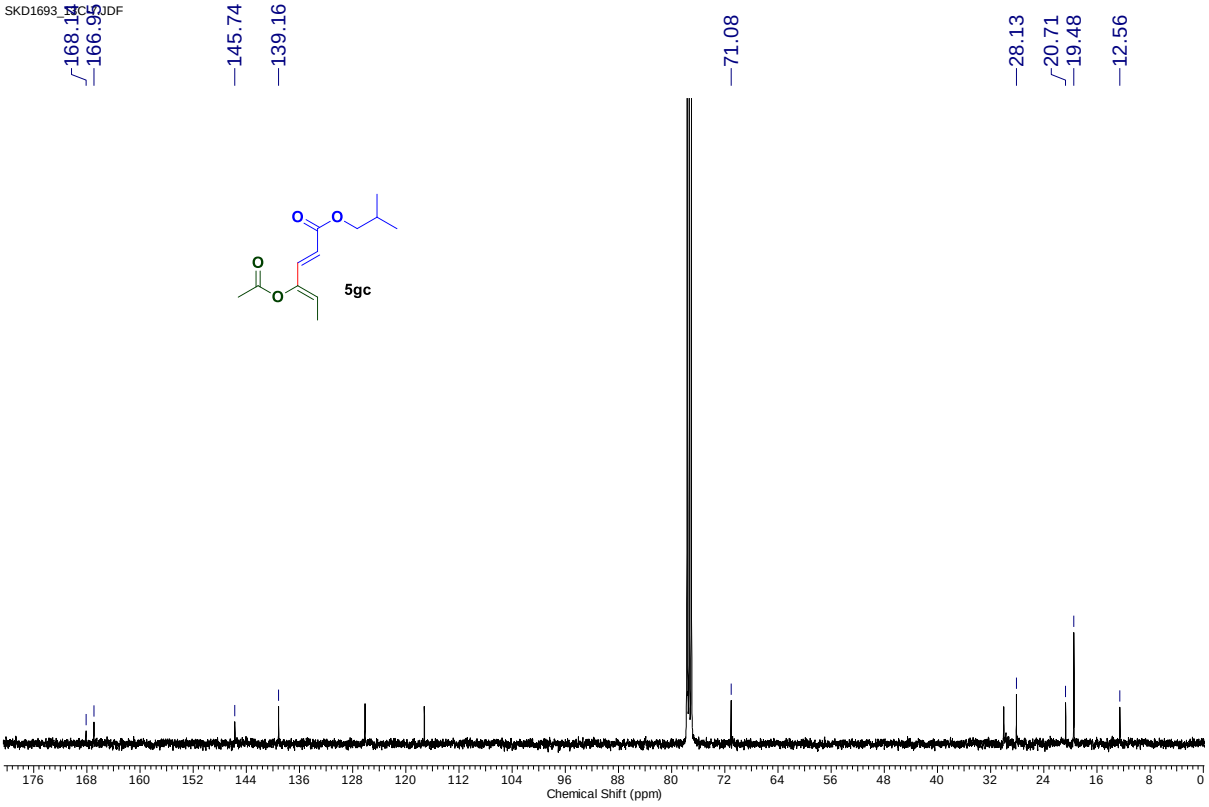

NAGMAA_A_NOESY-2.jdf
NOESY
Hd
O
CH3
O
Hc
H3C
CO2Me
Ha
Hb
5ga

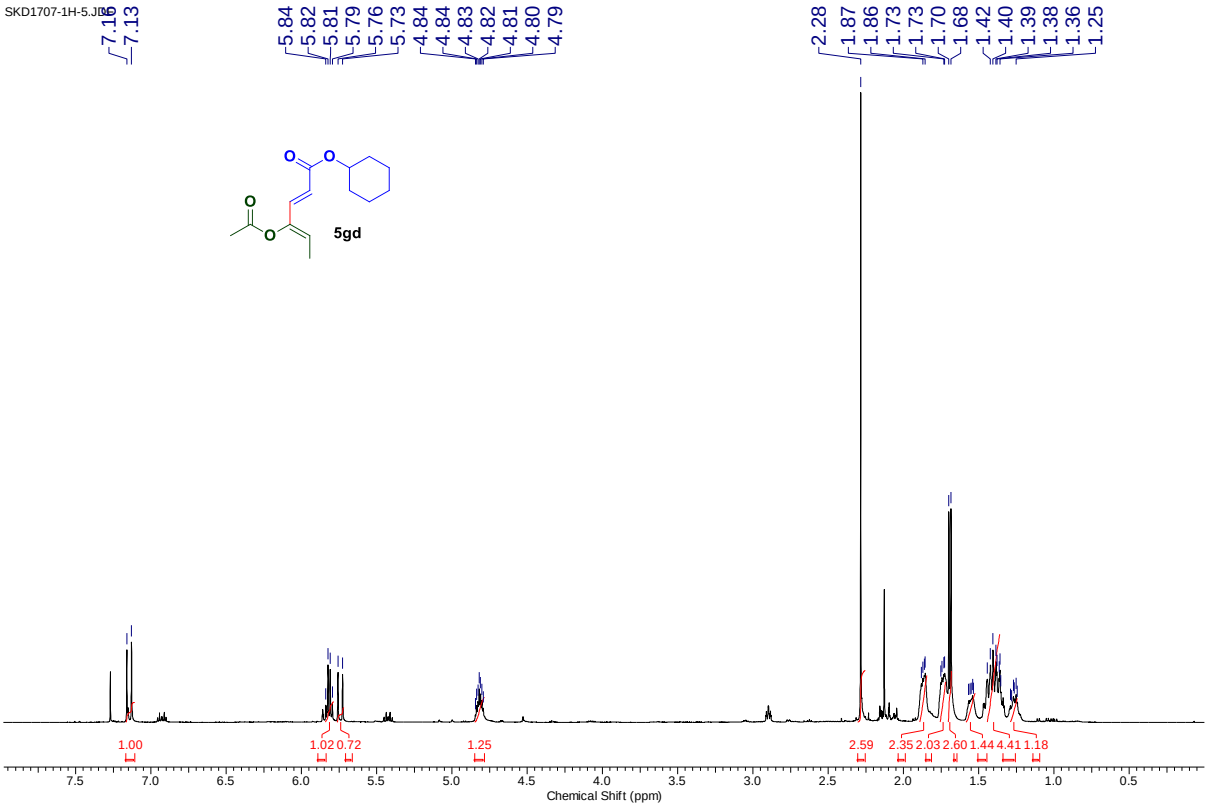

NAGMAAA_COSY-3.jdf
COSY
Hd
O
CH3
O
Hc
H3C
CO2Me
Ha
Hb
5ga

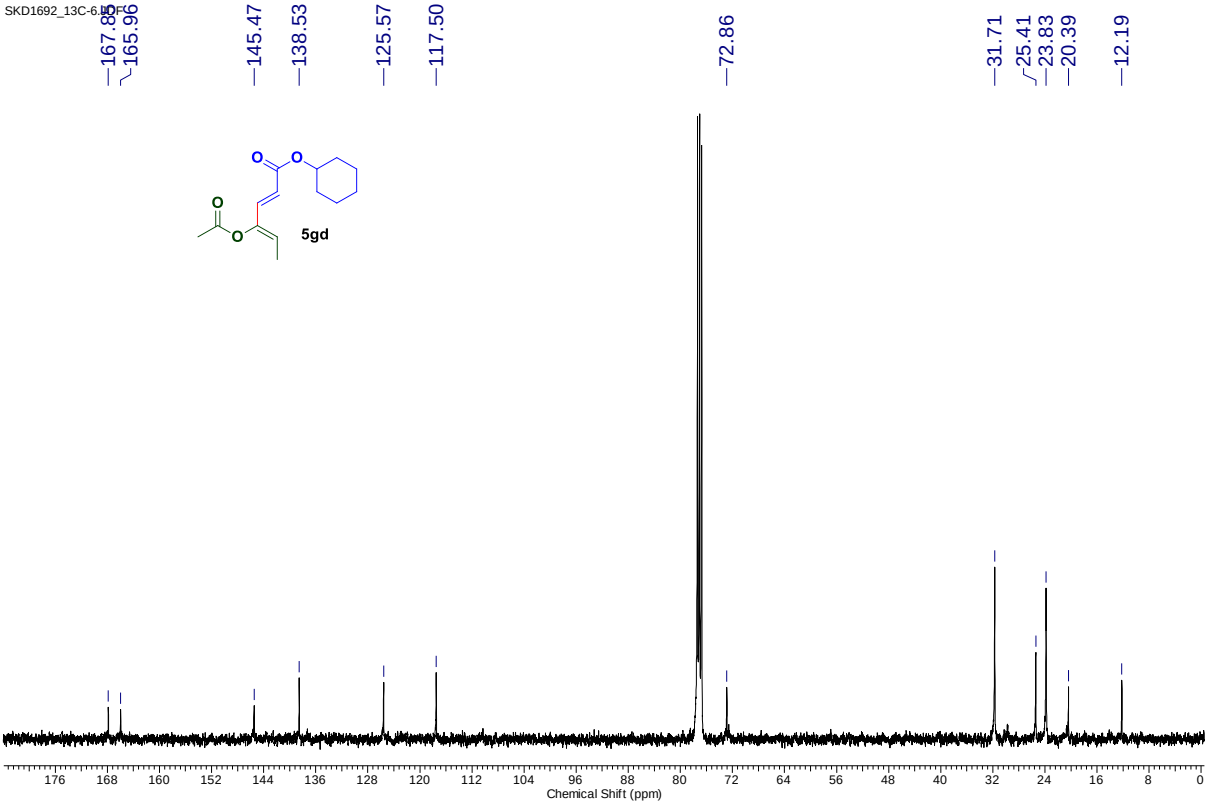

SKD1630-1H-5.JDF
7.17
7.14
5.84
5.83
5.81
5.80
5.77
5.74
4.16
4.15
4.14
2.28
1.70
1.69
1.66
1.64
1.63
1.43
1.41
1.39
1.38
0.96
0.94
0.93
CO2Bun
O
O
5gb
0.91
1.03
0.80
2.21
2.62
2.63
2.47
2.27
3.21
Chemical Shift (ppm)

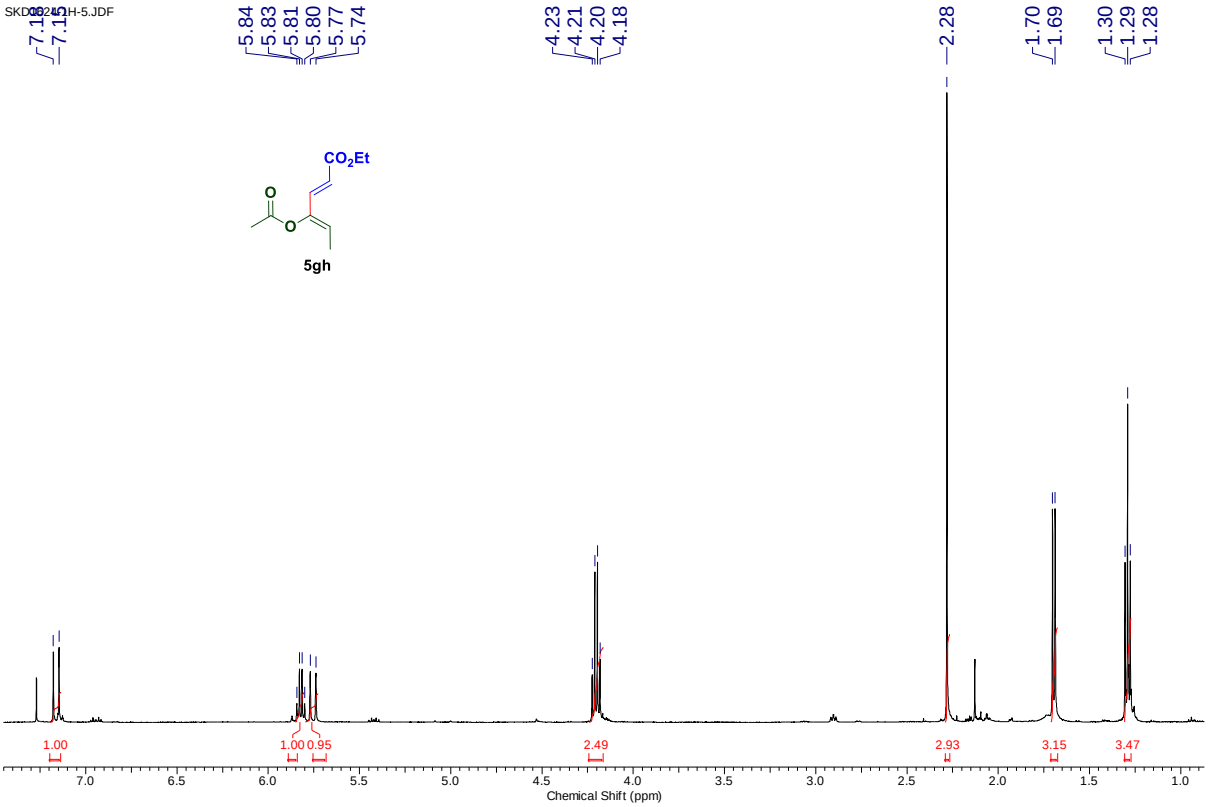

SKD1630-13C-1.JDF
168.05
166.93
145.79
139.14
126.02
117.27
64.79
31.07
20.64
19.48
14.02
12.49
CO2Bun
O
O
5gb
Chemical Shift (ppm)

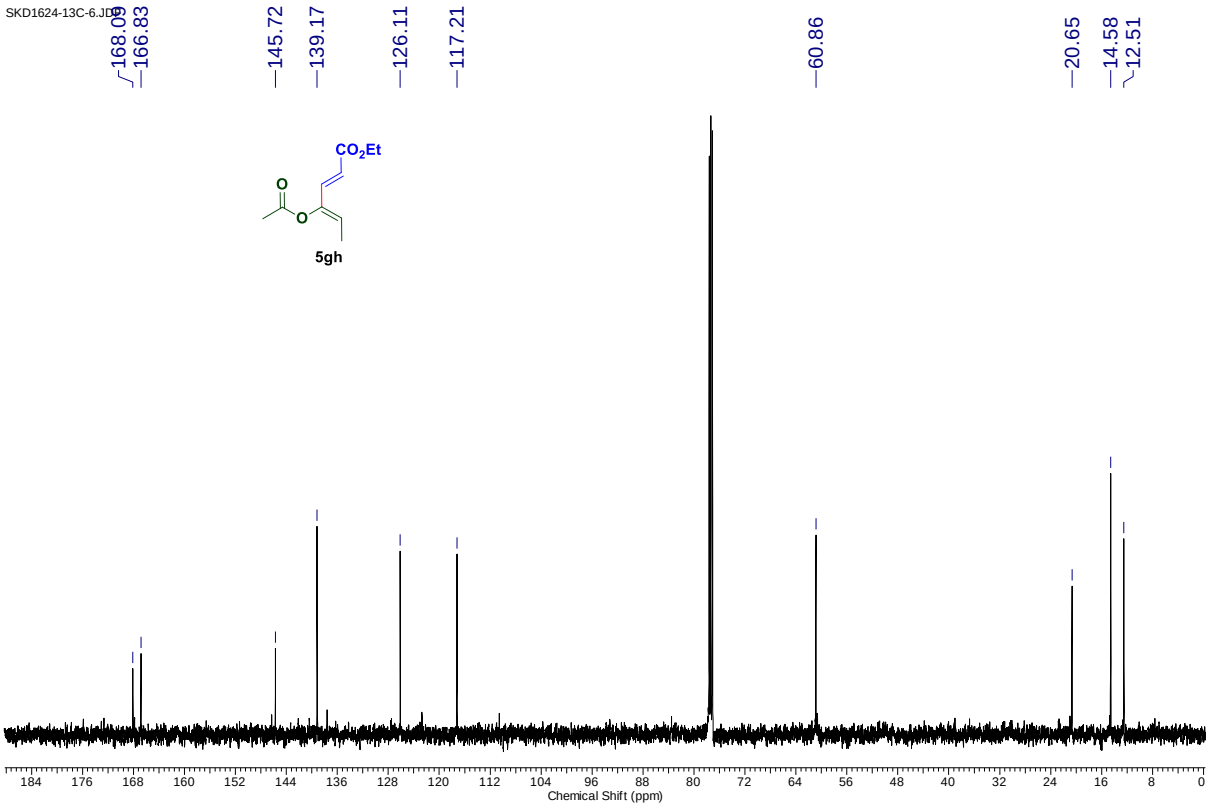

SKD1706-1H-5.JDF
7.18
7.15
5.85
5.84
5.82
5.81
5.78
5.75
3.94
3.92
2.29
2.00
1.99
1.98
1.96
1.95
1.94
1.92
1.71
1.69
0.96
0.94
5gc
1.00
1.11
0.84
2.09
2.80
1.34
2.94
6.33
Chemical Shift (ppm)

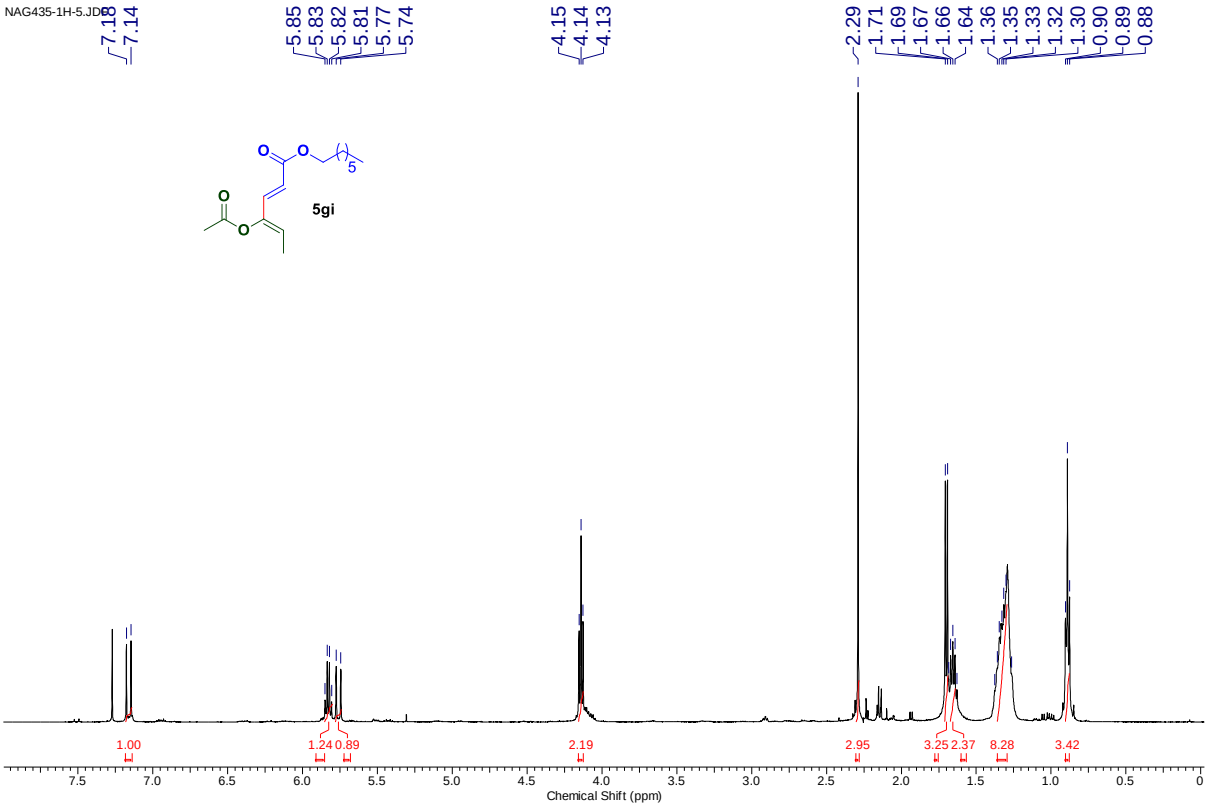

SKD1693_13CCLJDF
168.11
166.95
145.74
139.16
71.08
28.13
20.71
19.48
12.56
5gc
Chemical Shift (ppm)

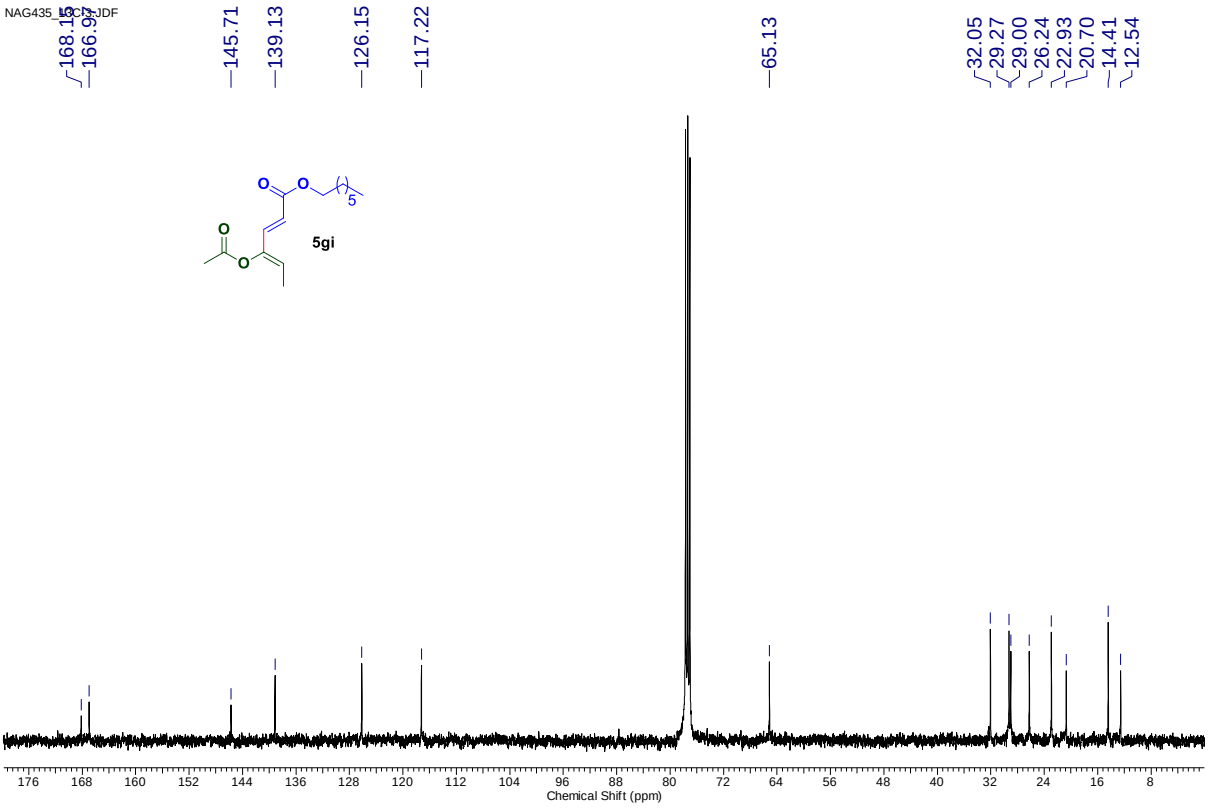

SKD1707-1H-5.JDF
7.16
7.13
5.84
5.82
5.81
5.79
5.76
5.73
4.84
4.84
4.83
4.82
4.81
4.80
4.79
2.28
1.87
1.86
1.73
1.73
1.70
1.68
1.42
1.40
1.39
1.38
1.36
1.25
5gd
1.00
1.02
0.72
1.25
2.59
2.35
2.03
2.60
1.44
4.41
1.18
Chemical Shift (ppm)

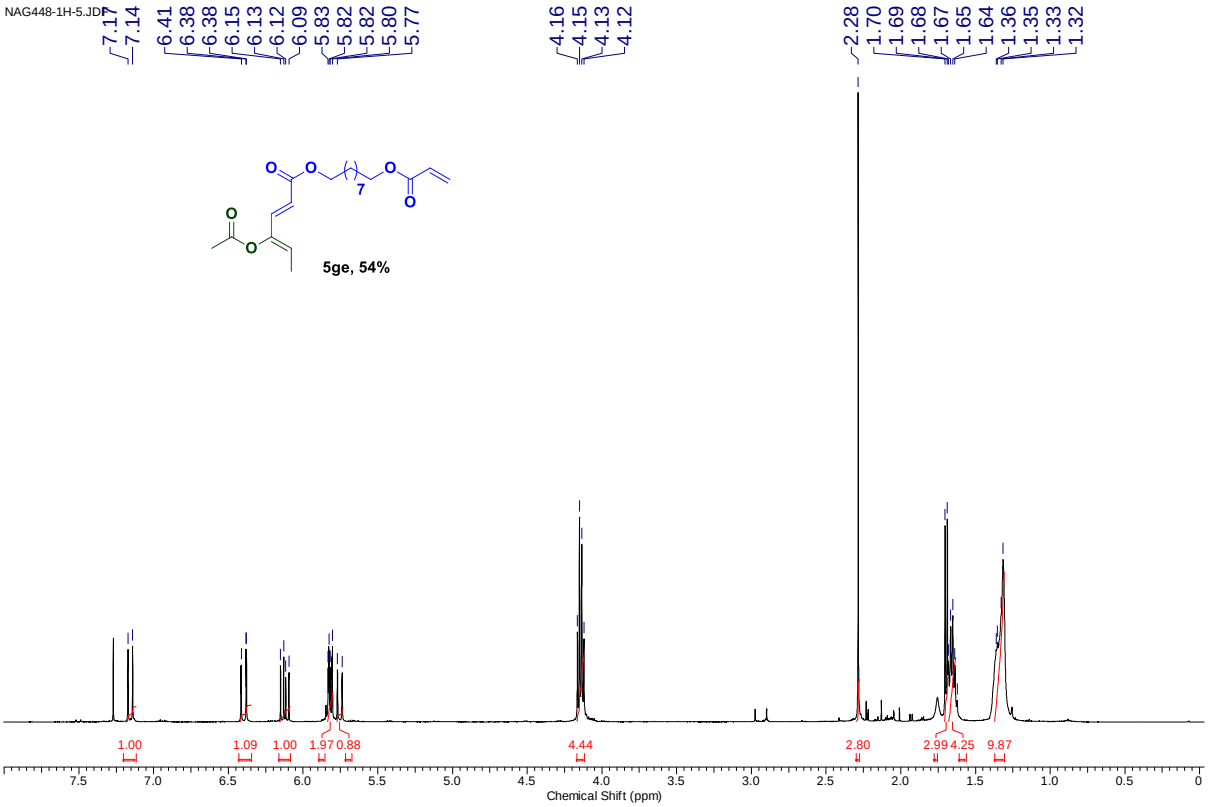

SKD1692_13C-6.JDF
167.80
165.96
145.47
138.53
125.57
117.50
72.86
31.71
25.41
23.83
20.39
12.19
5gd
Chemical Shift (ppm)

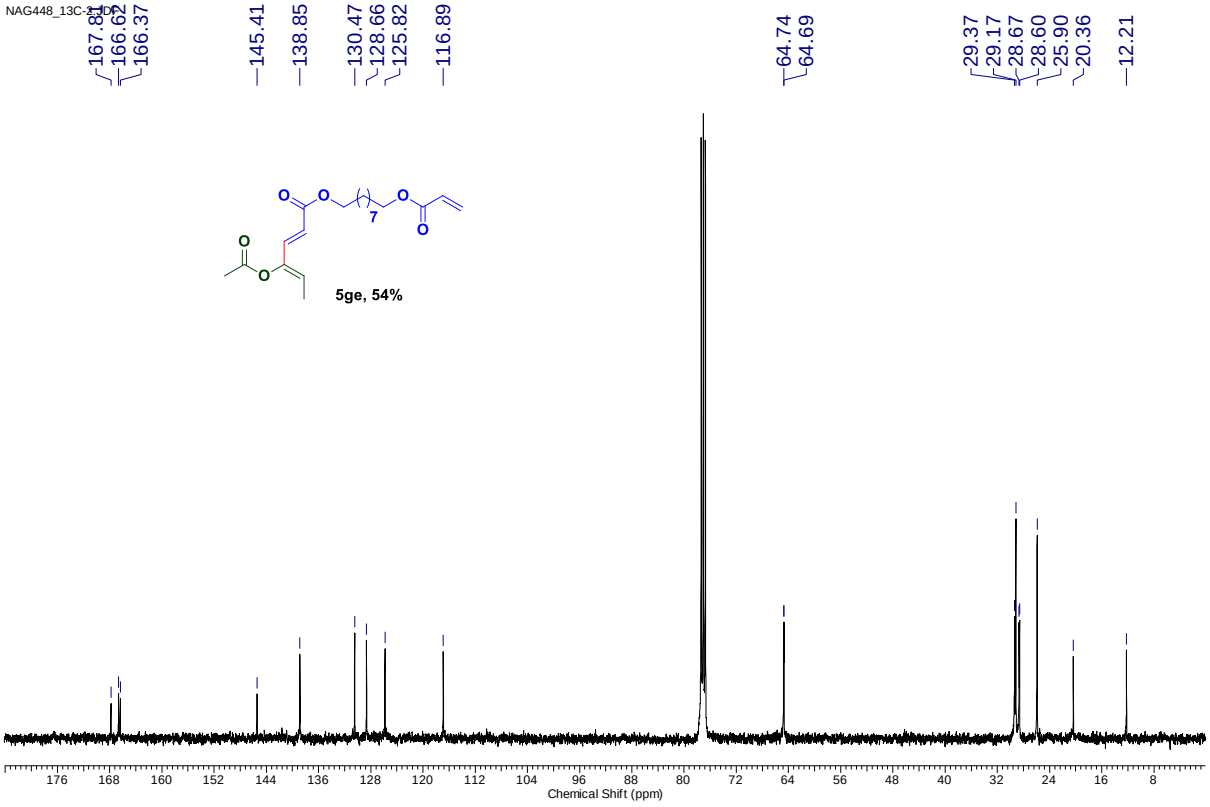

SKD1624-1H-5.JDF
7.15
7.13
5.84
5.83
5.81
5.80
5.77
5.74
4.23
4.21
4.20
4.18
2.28
1.70
1.69
1.30
1.29
1.28
CO2Et
O
O
5gh
1.00
1.00
0.95
2.49
2.93
3.15
3.47
Chemical Shift (ppm)

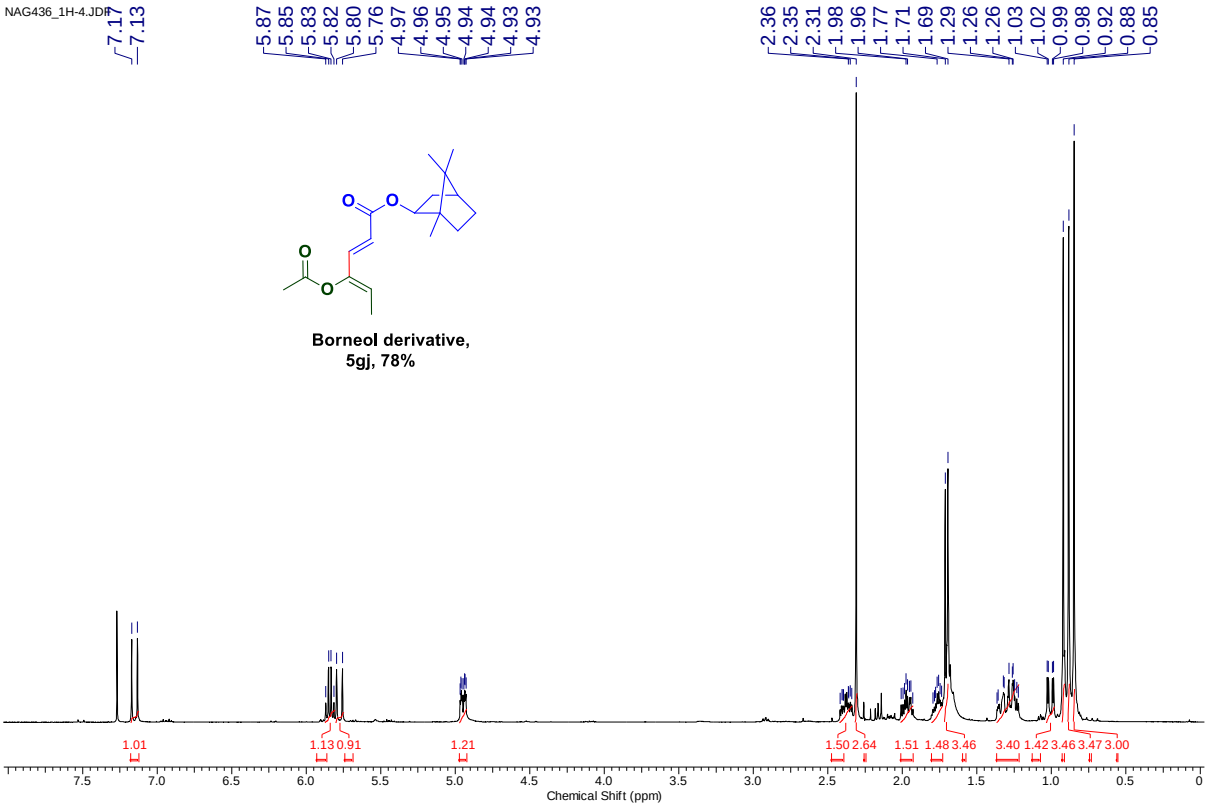

SKD1624-13C-6.JDF
168.09
166.83
145.72
139.17
126.11
117.21
60.86
20.65
14.58
12.51
CO2Et
O
O
5gh
Chemical Shift (ppm)

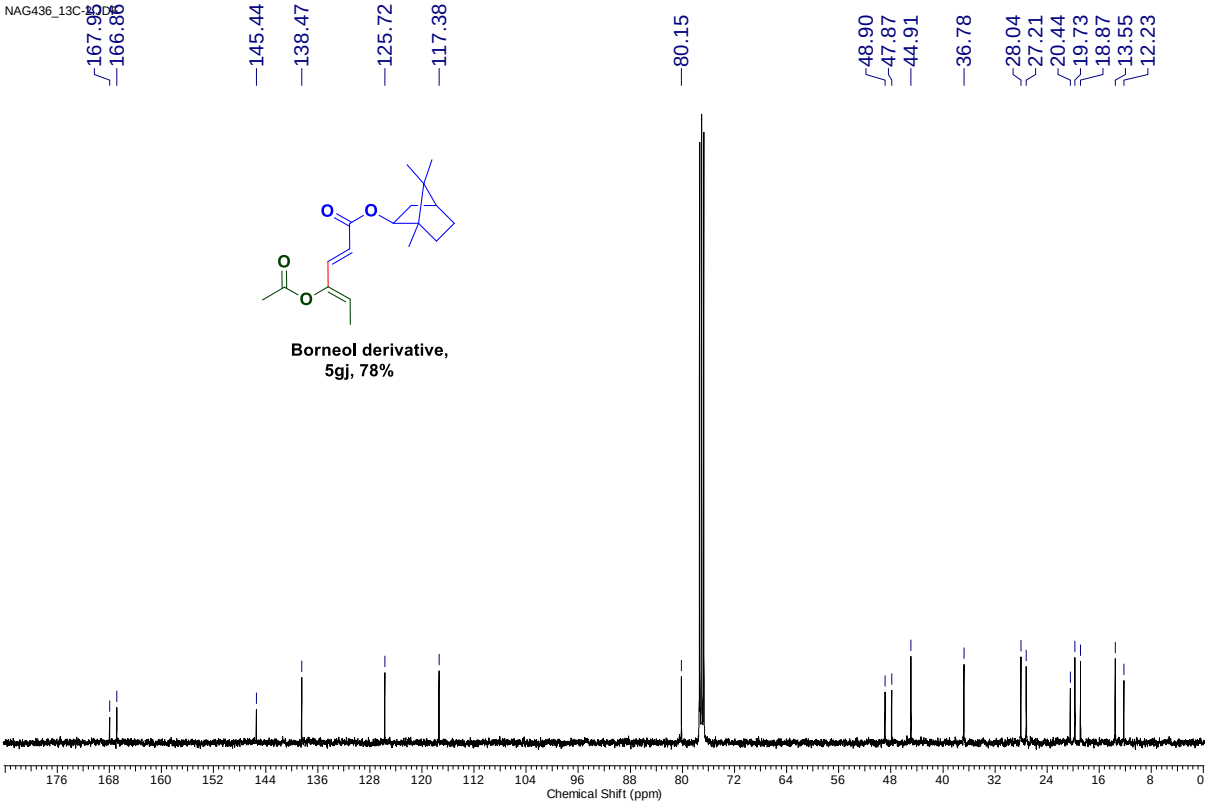

NAG435-1H-5.JDF
7.18
7.14
5.85
5.83
5.82
5.81
5.77
5.74
4.15
4.14
4.13
2.29
1.71
1.69
1.67
1.66
1.64
1.36
1.35
1.33
1.32
1.30
0.90
0.89
0.88
5gi
1.00
1.24
0.89
2.19
2.95
3.25
2.37
8.28
3.42
Chemical Shift (ppm)

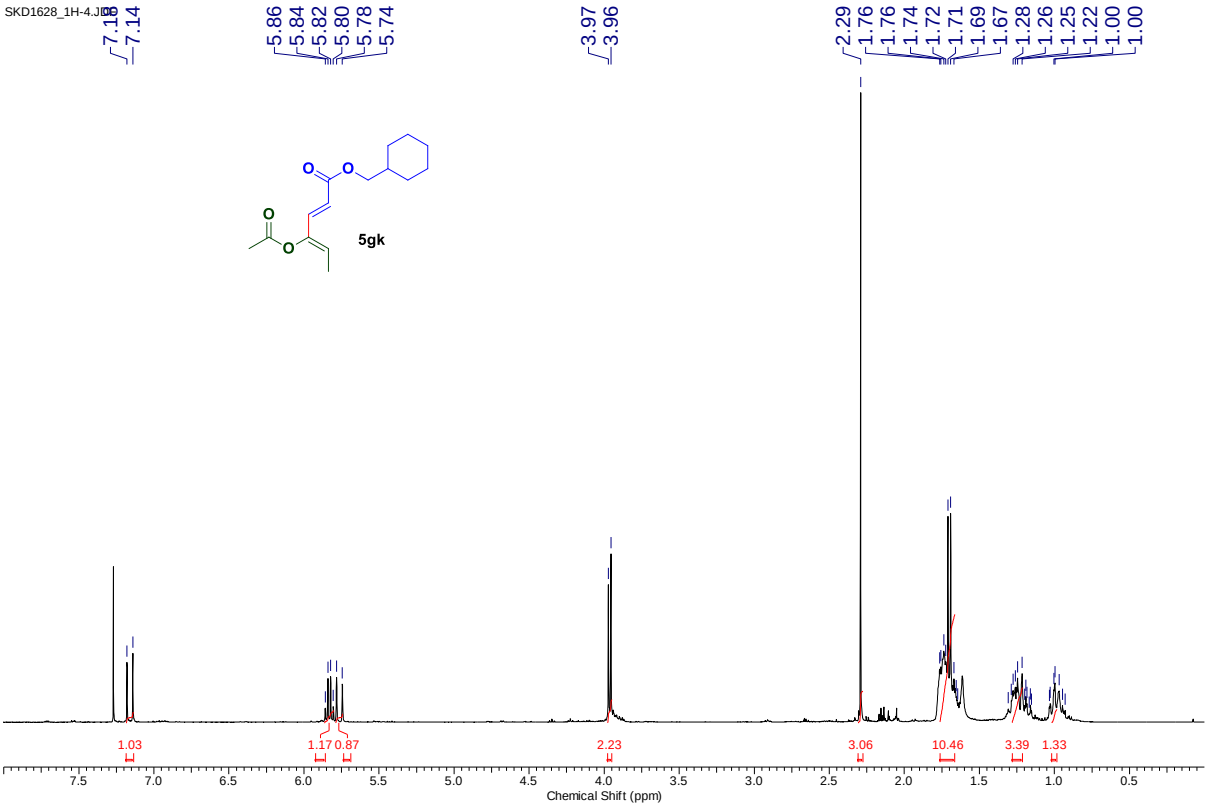

NAG435_CDCl3.JDF
168.10
166.92
145.71
139.13
126.15
117.22
65.13
32.05
29.27
29.00
26.24
22.93
20.70
14.41
12.54
5gi
Chemical Shift (ppm)

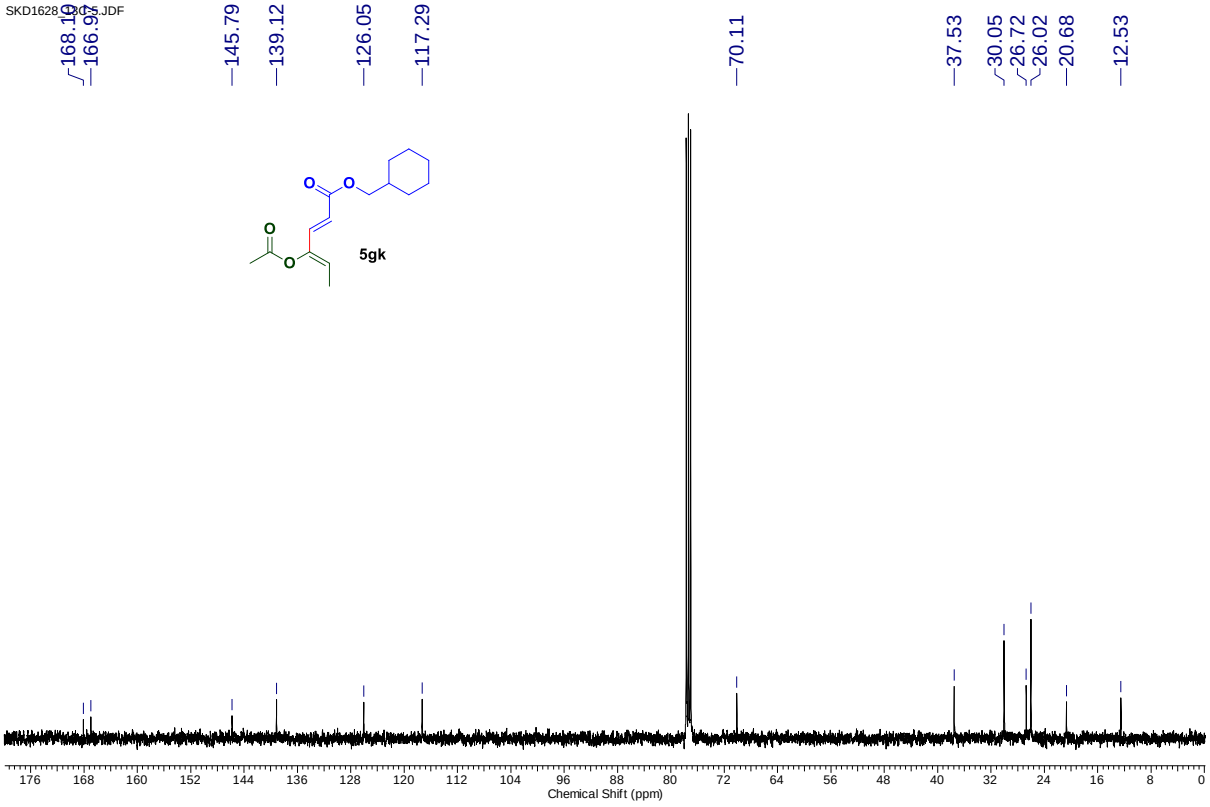

NAG448-1H-5.JDF
7.17
7.14
6.41
6.38
6.38
6.15
6.13
6.12
6.09
5.83
5.82
5.82
5.80
5.77
4.16
4.15
4.13
4.12
2.28
1.70
1.69
1.68
1.67
1.65
1.64
1.36
1.35
1.33
1.32
5ge, 54%
1.00
1.09
1.00
1.97
0.88
4.44
2.80
2.99
4.25
9.87
Chemical Shift (ppm)

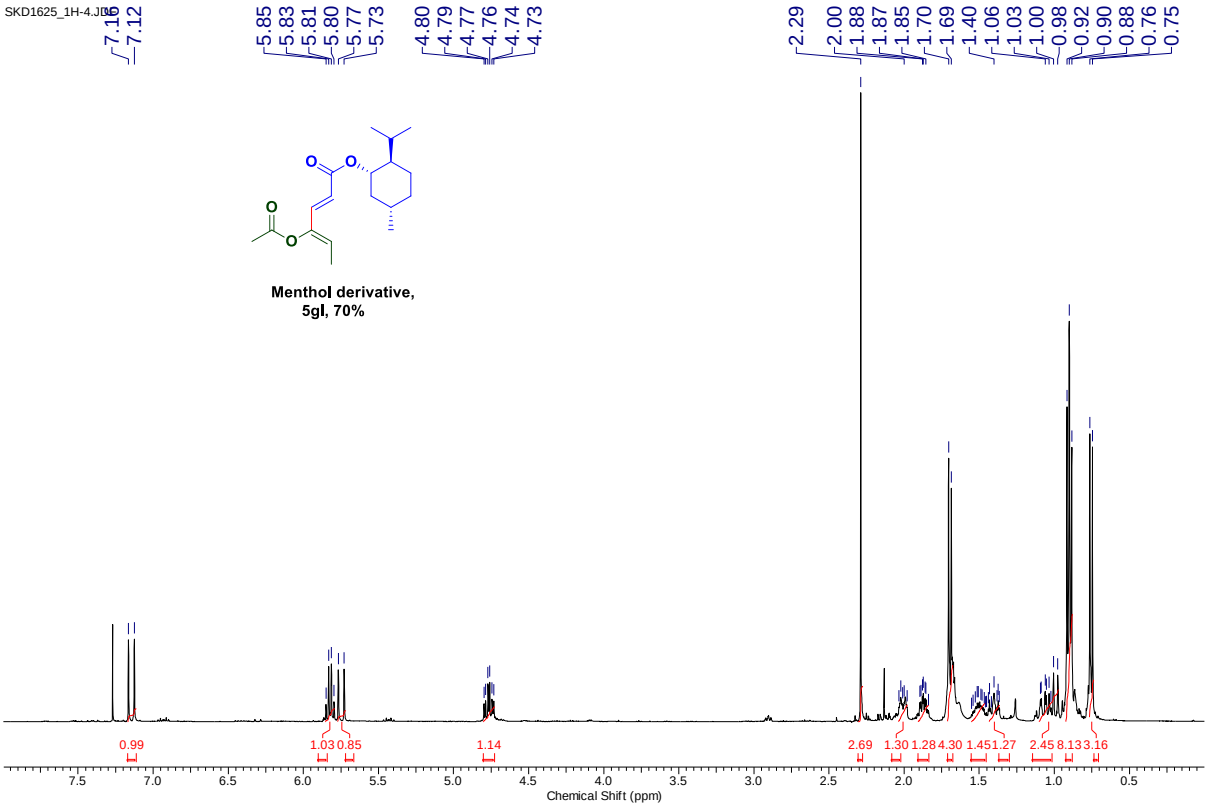

NAG448_13C-1.JDF
167.85
166.62
166.37
145.41
138.85
130.47
128.66
125.82
116.89
64.74
64.69
29.37
29.17
28.67
28.60
25.90
20.36
12.21
5ge, 54%
Chemical Shift (ppm)

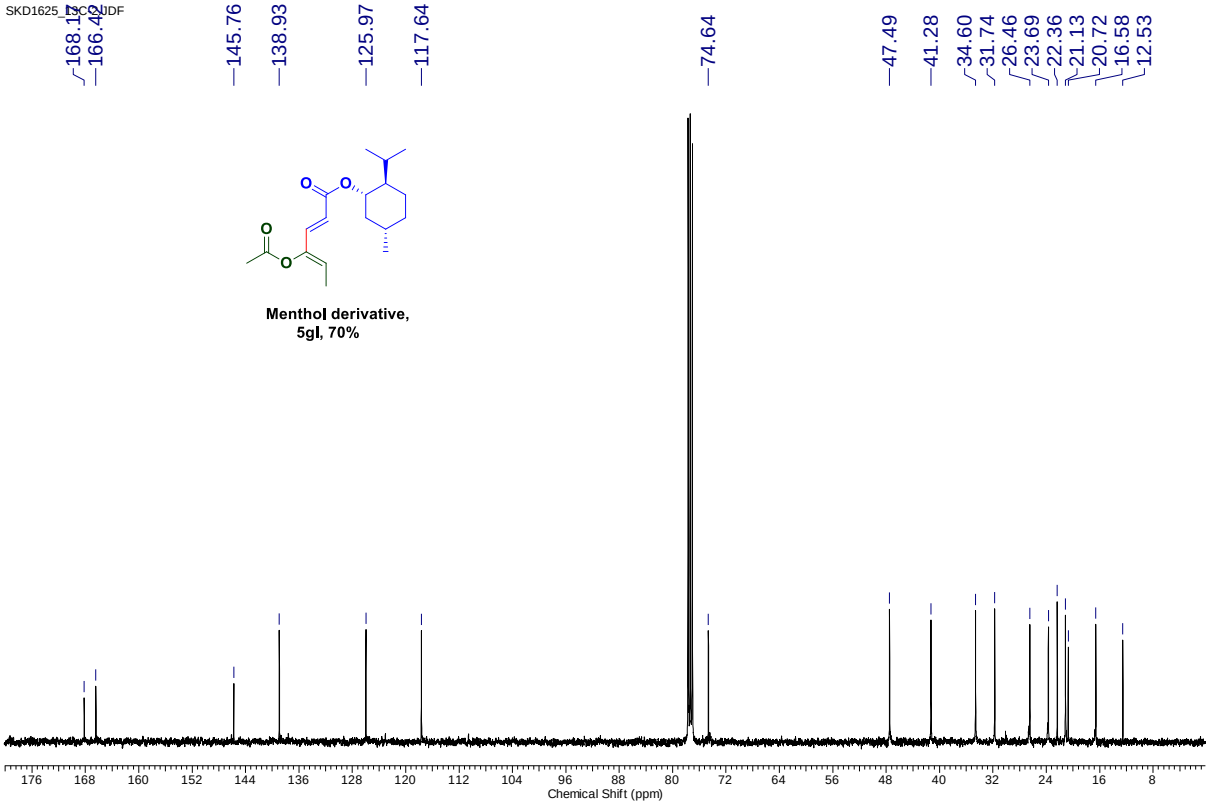

NAG436_1H-4.JDF
7.17
7.13
5.87
5.85
5.83
5.82
5.80
5.76
4.97
4.96
4.95
4.94
4.94
4.93
4.93
2.36
2.35
2.31
1.98
1.96
1.77
1.71
1.69
1.29
1.26
1.26
1.03
1.02
0.99
0.98
0.92
0.88
0.85
Borneol derivative,
5gj, 78%
1.01
1.13
0.91
1.21
1.50
2.64
1.51
1.48
3.46
3.40
1.42
3.46
3.47
3.00
Chemical Shift (ppm)

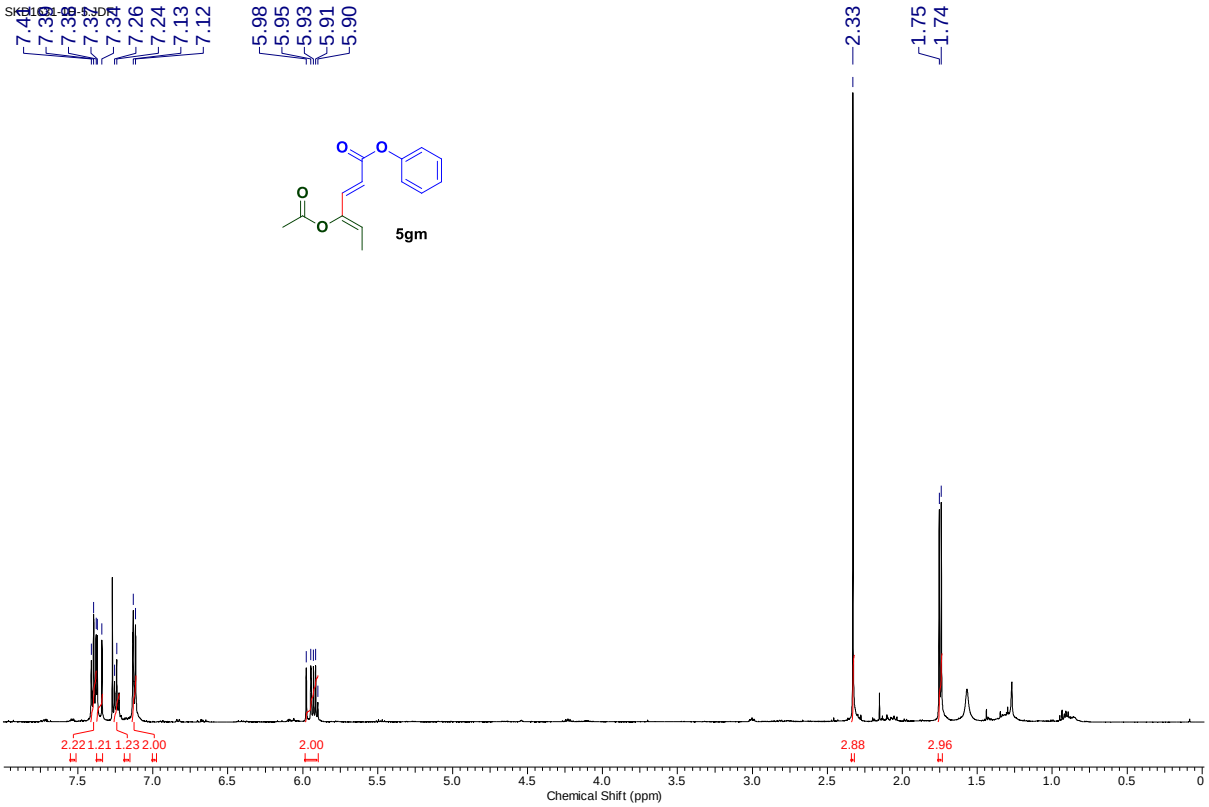

NAG436_13C-1.JDF
167.90
166.86
145.44
138.47
125.72
117.38
80.15
48.90
47.87
44.91
36.78
28.04
27.21
20.44
19.73
18.87
13.55
12.23
Borneol derivative,
5gj, 78%
Chemical Shift (ppm)

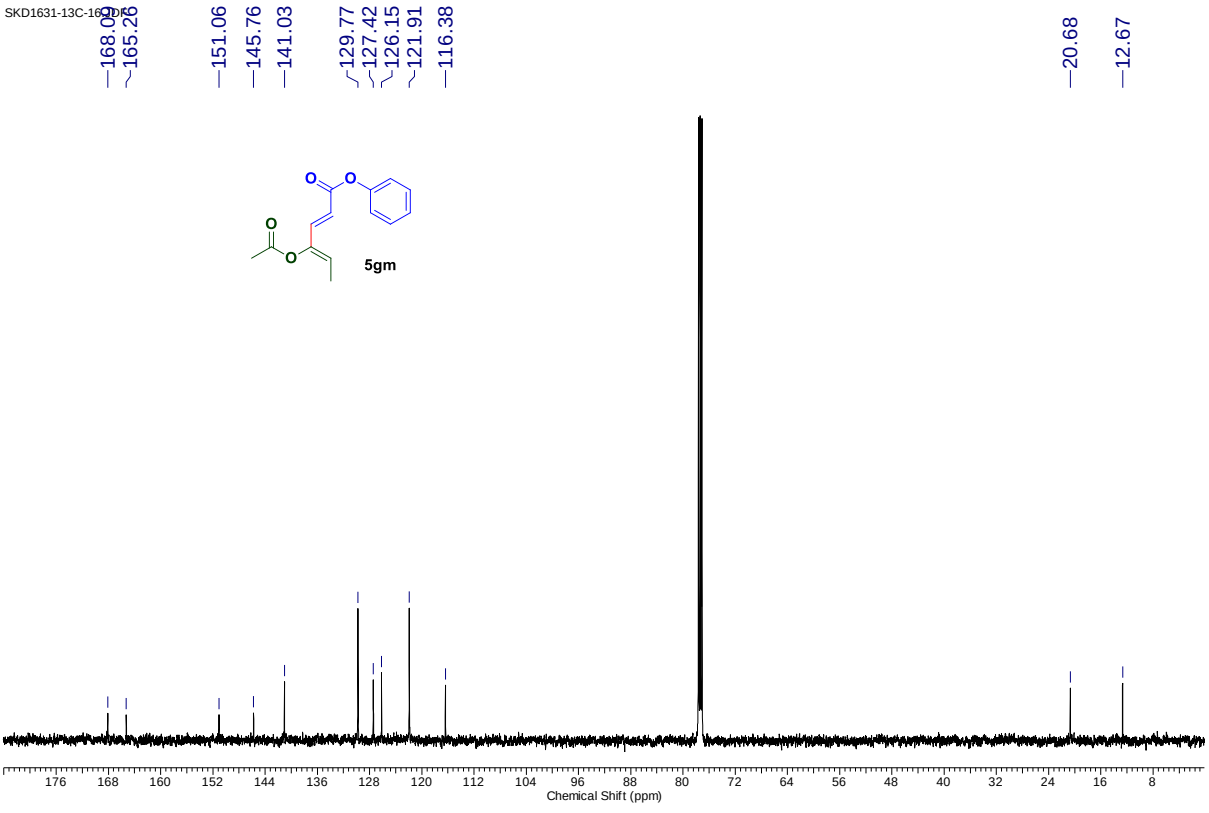

SKD1628_1H-4.JDF
7.15
7.14
5.86
5.84
5.82
5.80
5.78
5.74
3.97
3.96
2.29
1.76
1.76
1.74
1.72
1.71
1.69
1.67
1.28
1.26
1.25
1.22
1.00
1.00
5gk
1.03
1.17
0.87
2.23
3.06
10.46
3.39
1.33
Chemical Shift (ppm)

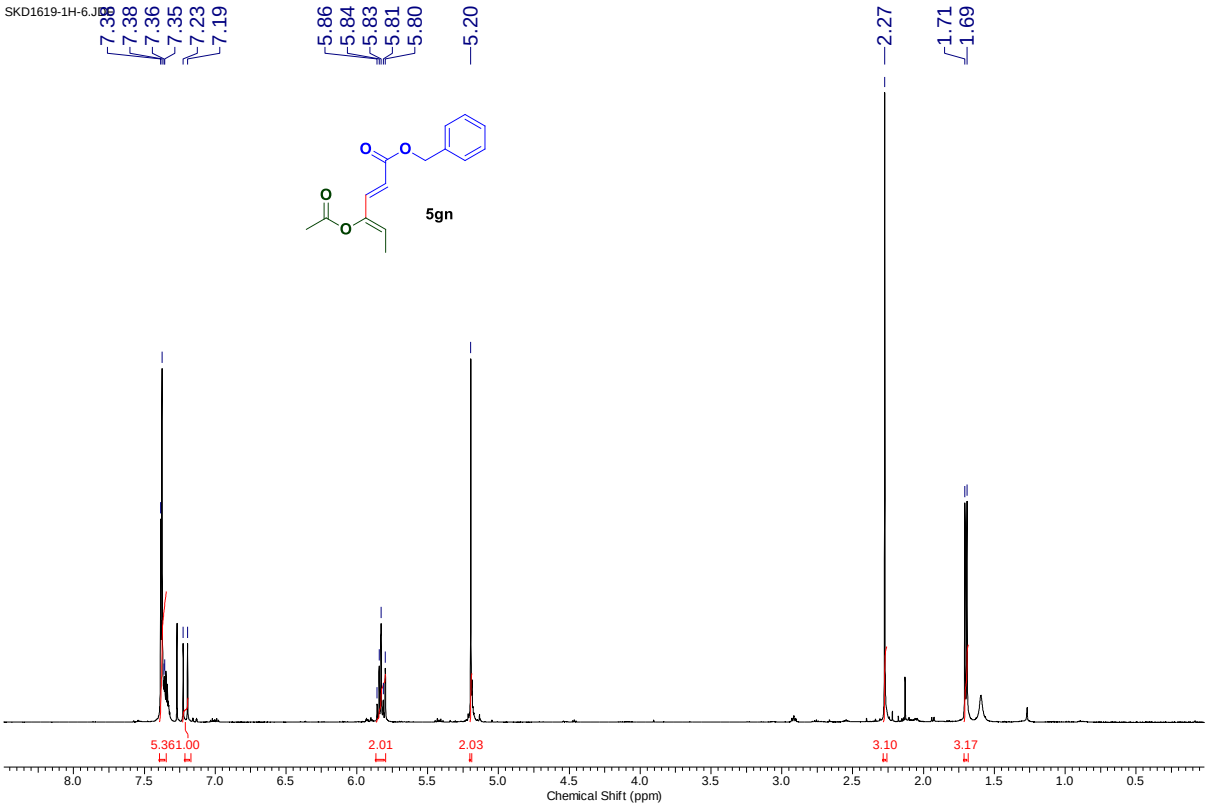

SKD1628_13C-5.JDF
168.13
166.90
145.79
139.12
126.05
117.29
70.11
37.53
30.05
26.72
26.02
20.68
12.53
5gk
Chemical Shift (ppm)

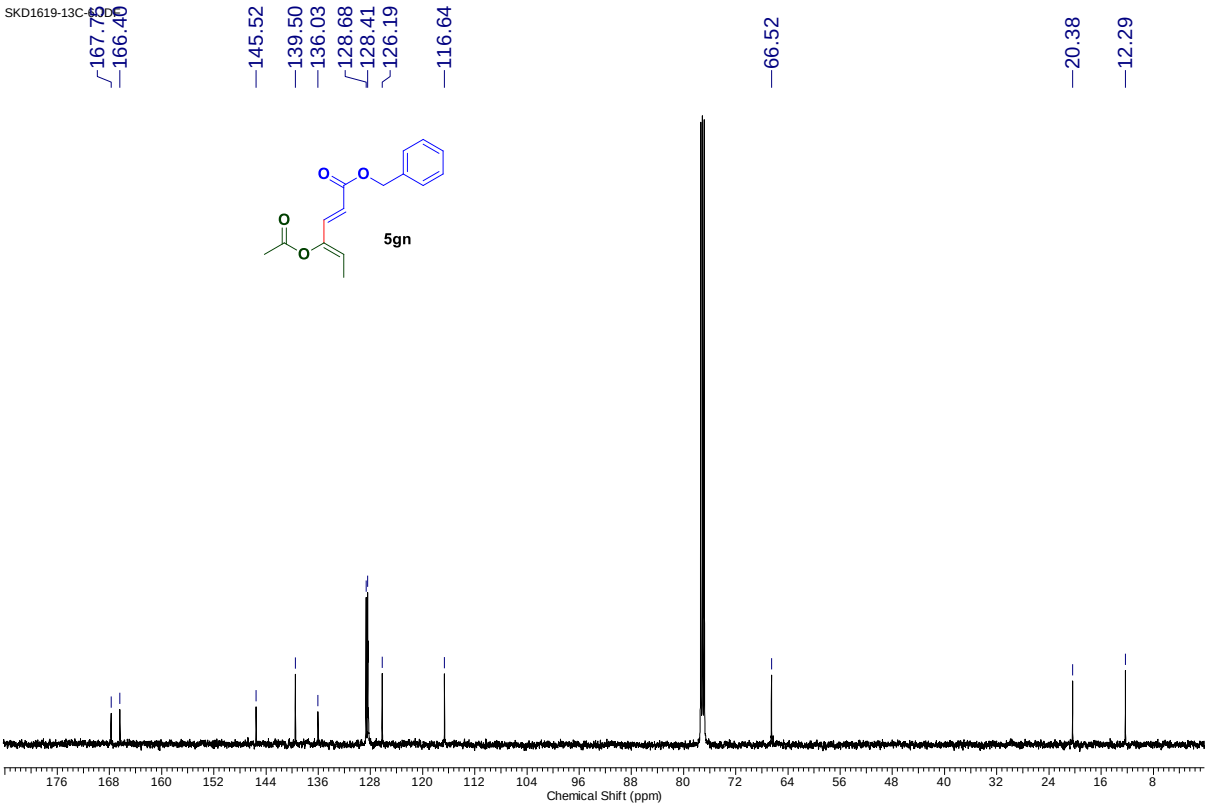

SKD1625_1H-4.JDF
7.15
7.12
5.85
5.83
5.81
5.80
5.77
5.73
4.80
4.79
4.77
4.76
4.74
4.73
2.29
2.00
1.88
1.87
1.85
1.70
1.69
1.40
1.06
1.03
1.00
0.98
0.92
0.90
0.88
0.76
0.75
Menthol derivative,
5gl, 70%
0.99
1.03
0.85
1.14
2.69
1.30
1.28
4.30
1.45
1.27
2.45
8.13
3.16
Chemical Shift (ppm)

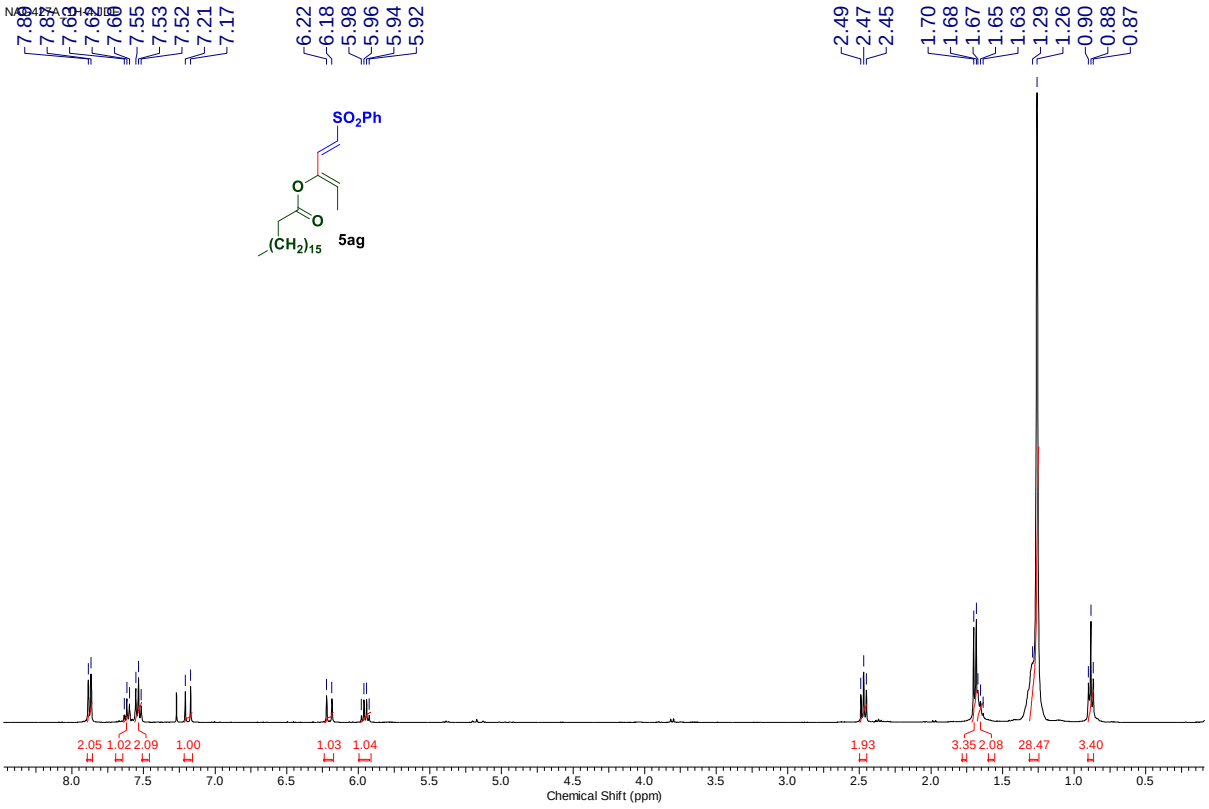

SKD1625_13CCPDF
168.15
166.40
145.76
138.93
125.97
117.64
74.64
47.49
41.28
34.60
31.74
26.46
23.69
22.36
21.13
20.72
16.58
12.53
Menthol derivative,
5gl, 70%
Chemical Shift (ppm)

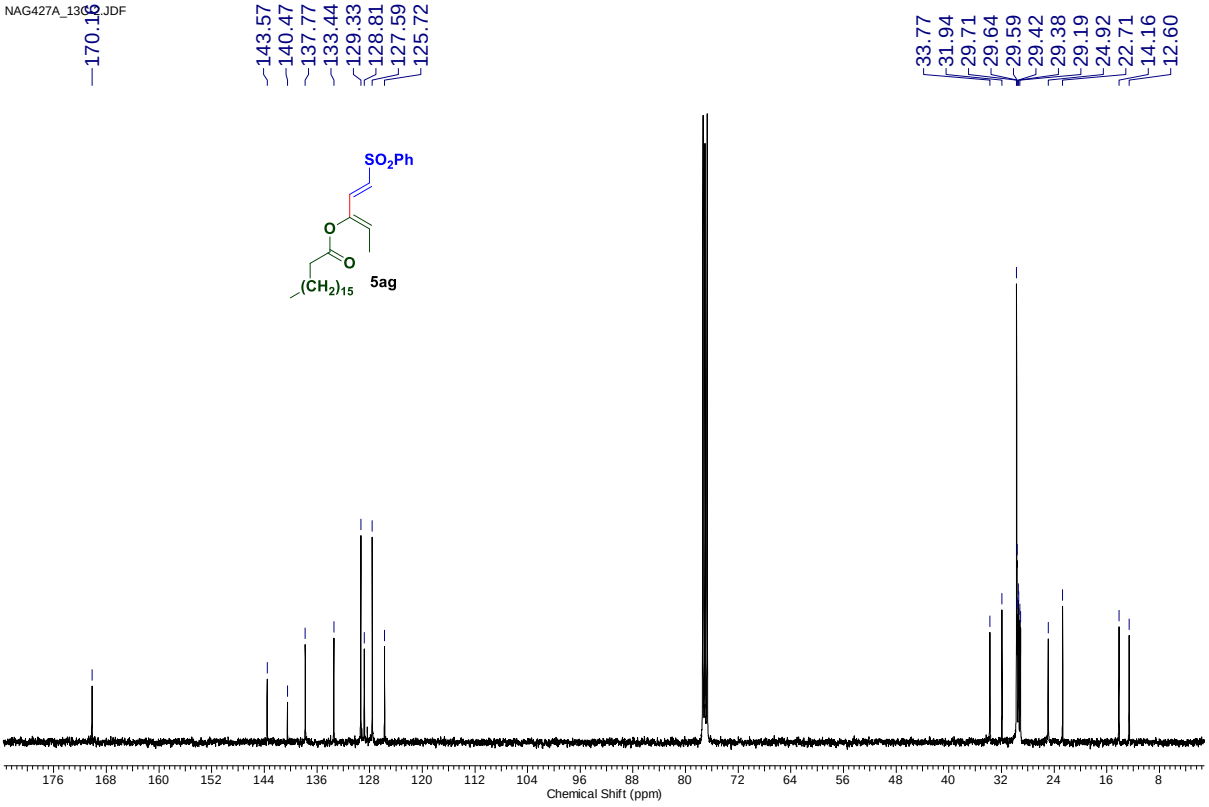

7.41
7.39
7.38
7.37
7.37
7.26
7.24
7.13
7.12
5.98
5.95
5.93
5.91
5.90
2.33
1.75
1.74
5gm
2.22 1.21 1.23 2.00
2.00
2.88
2.96
Chemical Shift (ppm)

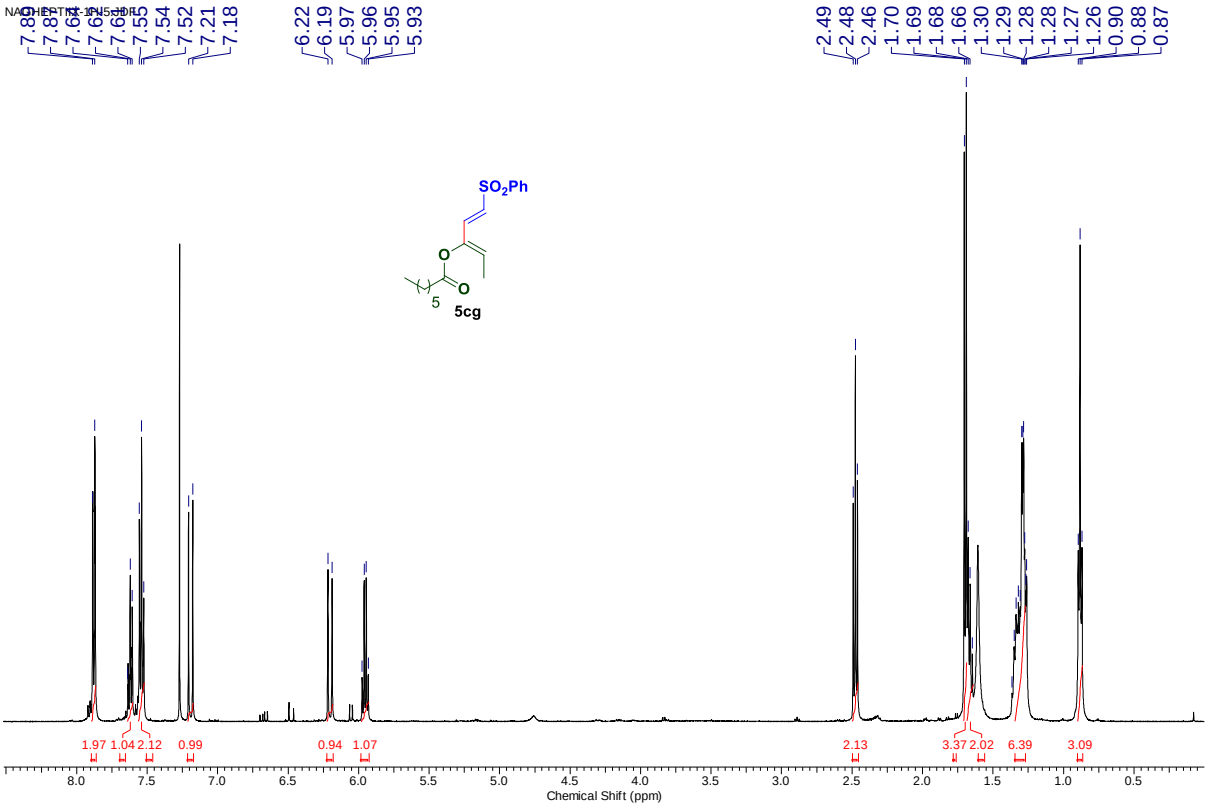

168.02
165.26
151.06
145.76
141.03
129.77
127.42
126.15
121.91
116.38
20.68
12.67
5gm
Chemical Shift (ppm)

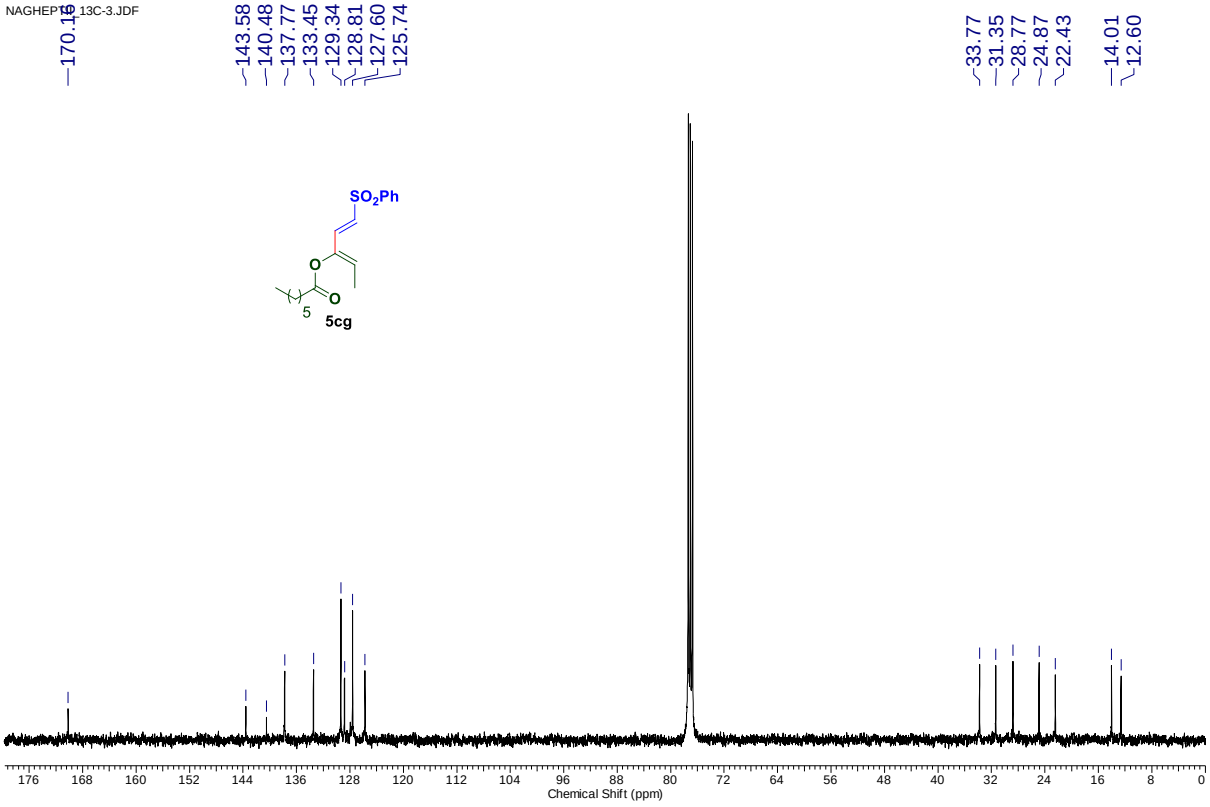

SKD1619-1H-6.JDF
7.38
7.38
7.36
7.35
7.23
7.19
5.86
5.84
5.83
5.81
5.80
5.20
2.27
1.71
1.69
5gn
5.36
1.00
2.01
2.03
3.10
3.17
Chemical Shift (ppm)

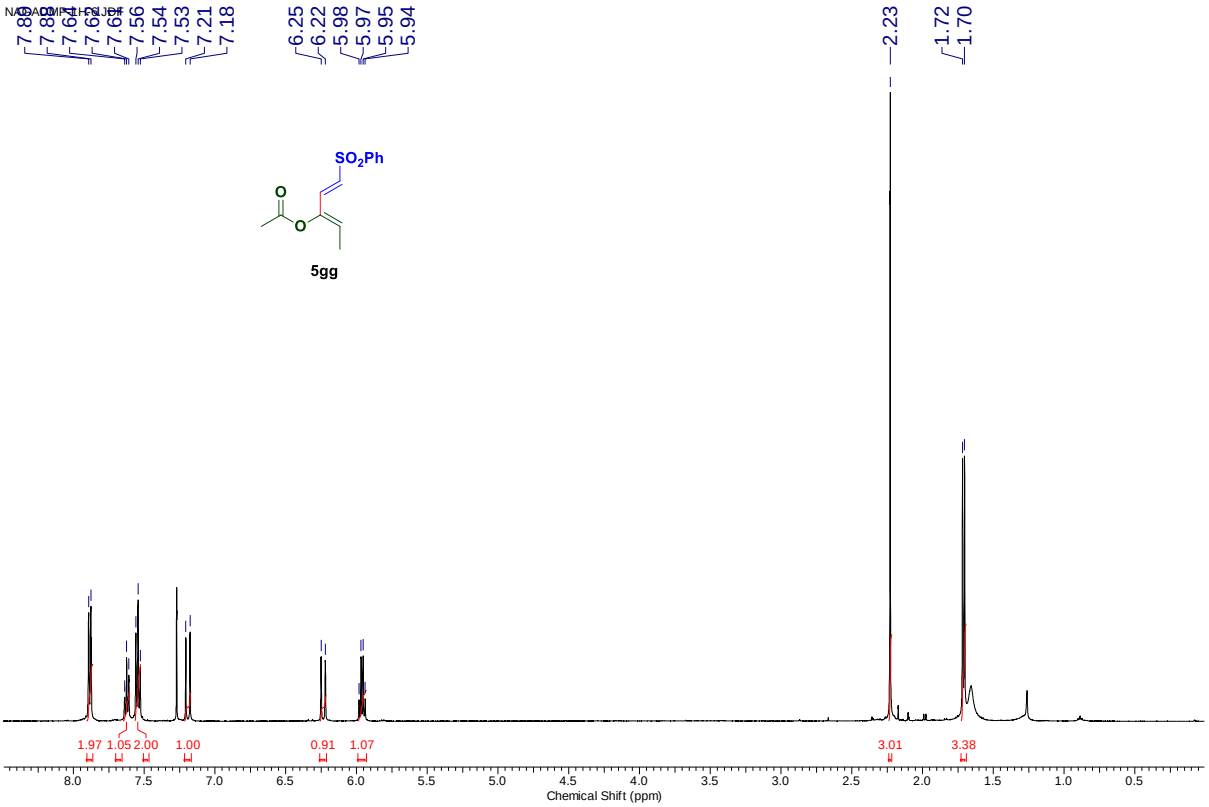

SKD1619-13C-6.JDF
167.70
166.40
145.52
139.50
136.03
128.68
128.41
126.19
116.64
66.52
20.38
12.29
5gn
Chemical Shift (ppm)

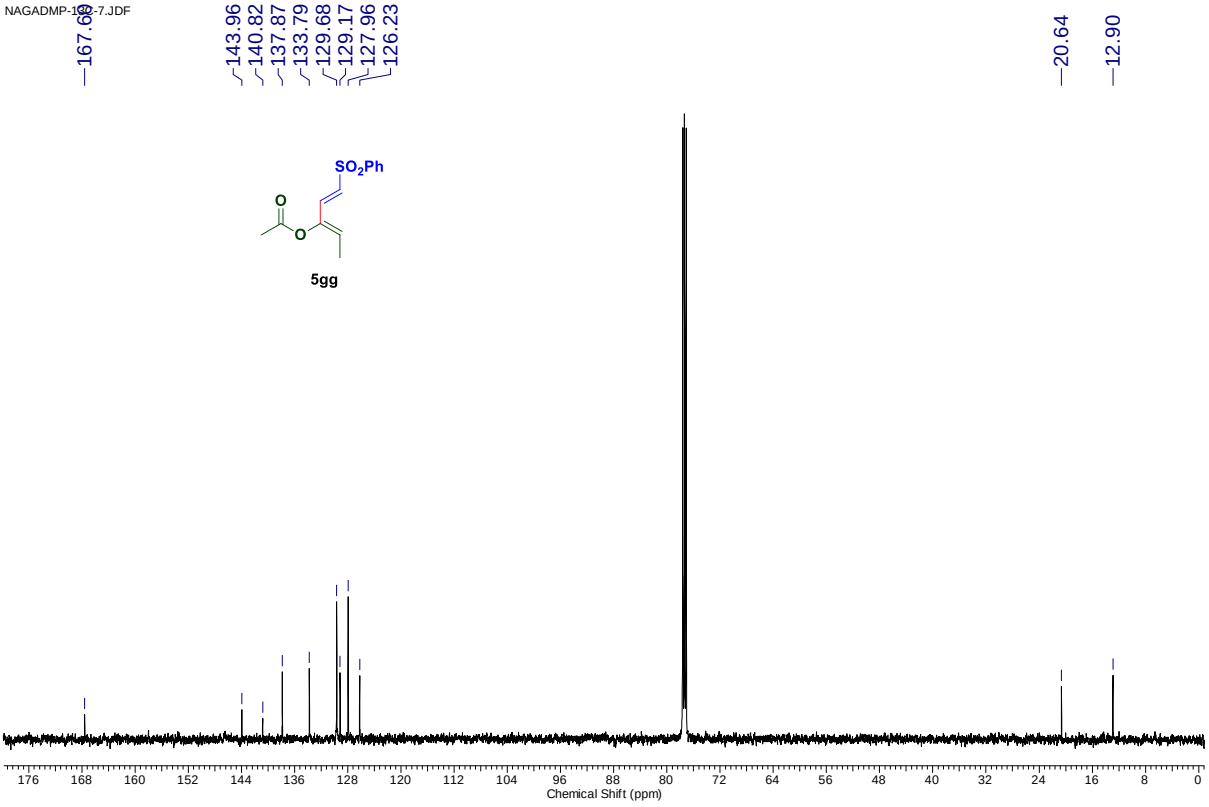

7.80
7.81
7.61
7.60
7.55
7.53
7.52
7.21
7.17
6.22
6.18
5.98
5.96
5.94
5.92
2.49
2.47
2.45
1.70
1.68
1.67
1.65
1.63
1.29
1.26
0.90
0.88
0.87
SO2Ph
O
O
(CH2)15
5ag
2.05
1.02
2.09
1.00
1.03
1.04
1.93
3.35
2.08
28.47
3.40
Chemical Shift (ppm)


170.12
143.57
140.47
137.77
133.44
129.33
128.81
127.59
125.72
33.77
31.94
29.71
29.64
29.59
29.42
29.38
29.19
24.92
22.71
14.16
12.60
SO2Ph
O
O
(CH2)15
5ag
Chemical Shift (ppm)

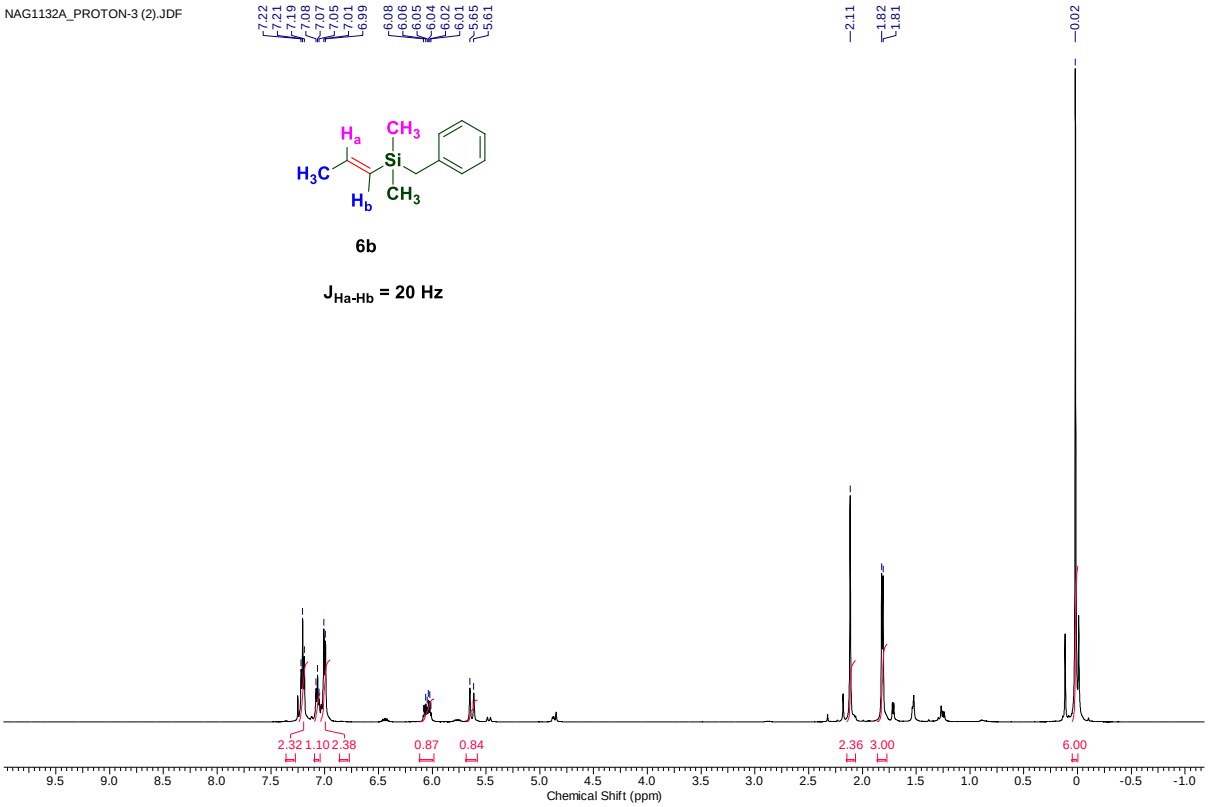

7.88
7.81
7.66
7.65
7.55
7.54
7.52
7.21
7.18
6.22
6.19
5.97
5.96
5.95
5.93
2.49
2.48
2.46
1.70
1.69
1.68
1.66
1.30
1.29
1.28
1.28
1.27
1.26
0.90
0.88
0.87
SO2Ph
O
O
5
5cg
1.97
1.04
2.12
0.99
0.94
1.07
2.13
3.37
2.02
6.39
3.09
Chemical Shift (ppm)


170.14
143.58
140.48
137.77
133.45
129.34
128.81
127.60
125.74
33.77
31.35
28.77
24.87
22.43
14.01
12.60
SO2Ph
O
O
5
5cg
Chemical Shift (ppm)


7.82
7.81
7.66
7.65
7.56
7.54
7.53
7.21
7.18
6.25
6.22
5.98
5.97
5.95
5.94
2.23
1.72
1.70
SO2Ph
O
O
5gg
1.97
1.05
2.00
1.00
0.91
1.07
3.01
3.38
Chemical Shift (ppm)


167.60
143.96
140.82
137.87
133.79
129.68
129.17
127.96
126.23
20.64
12.90
SO2Ph
O
O
5gg
Chemical Shift (ppm)

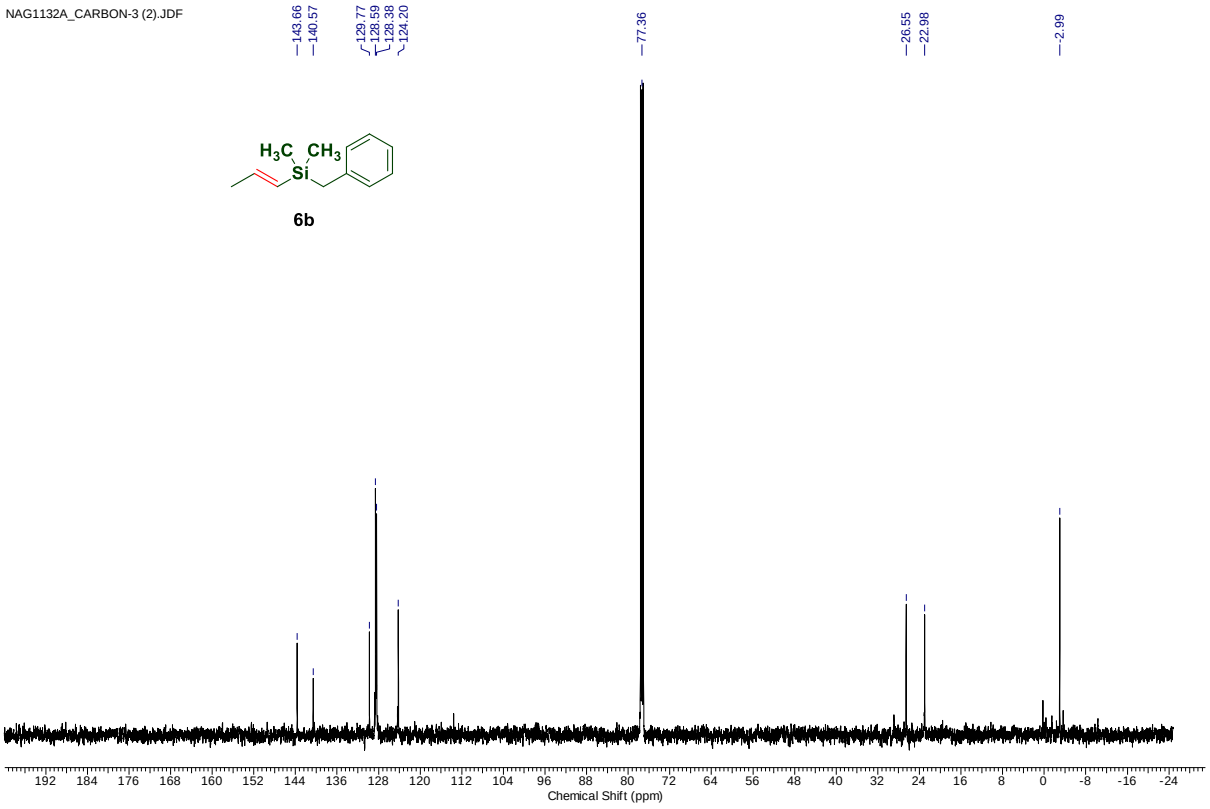
NAG1132A_PROTON-3 (2).JDF



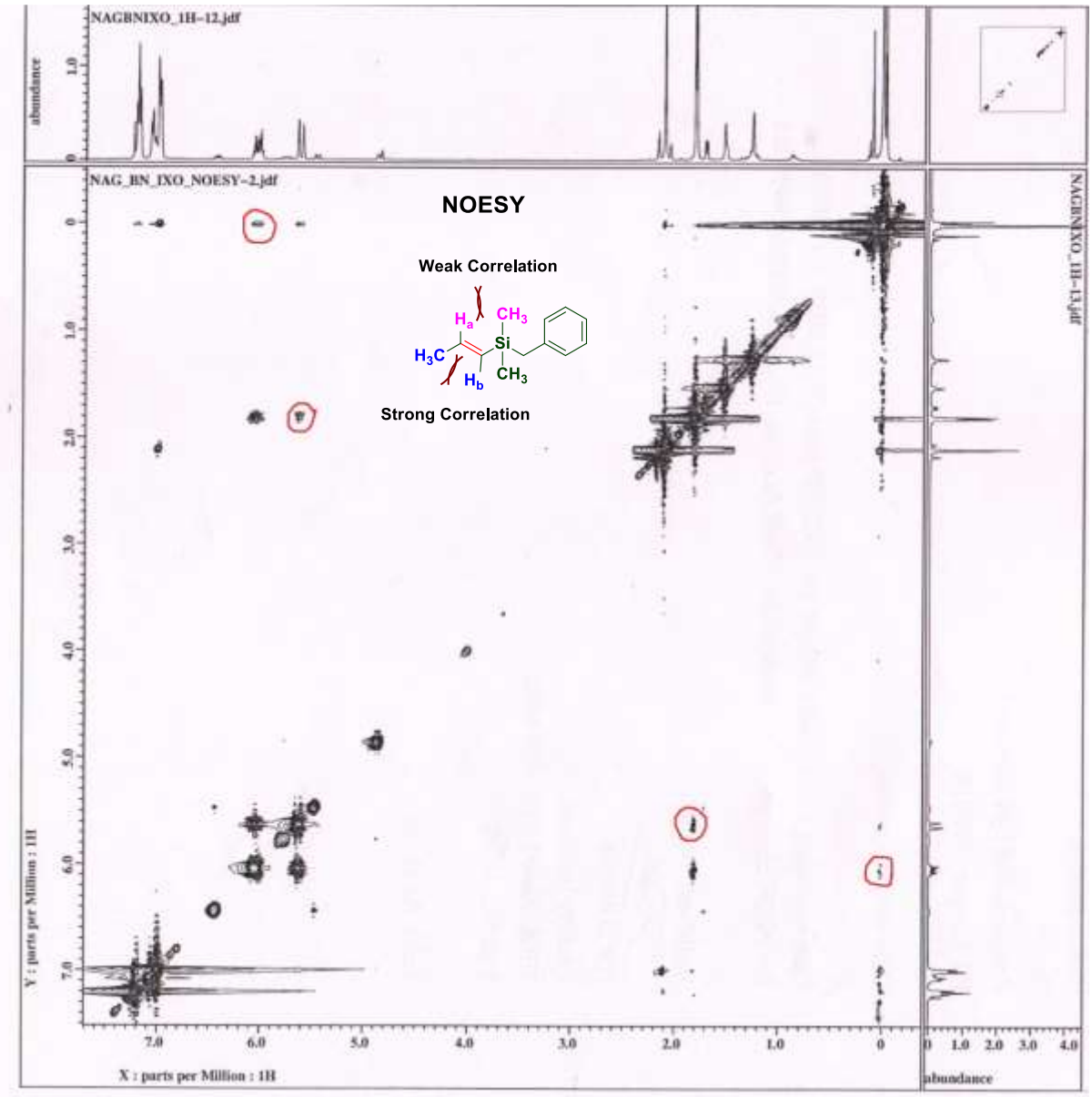
6b

J_{Ha-Hb} = 20 Hz

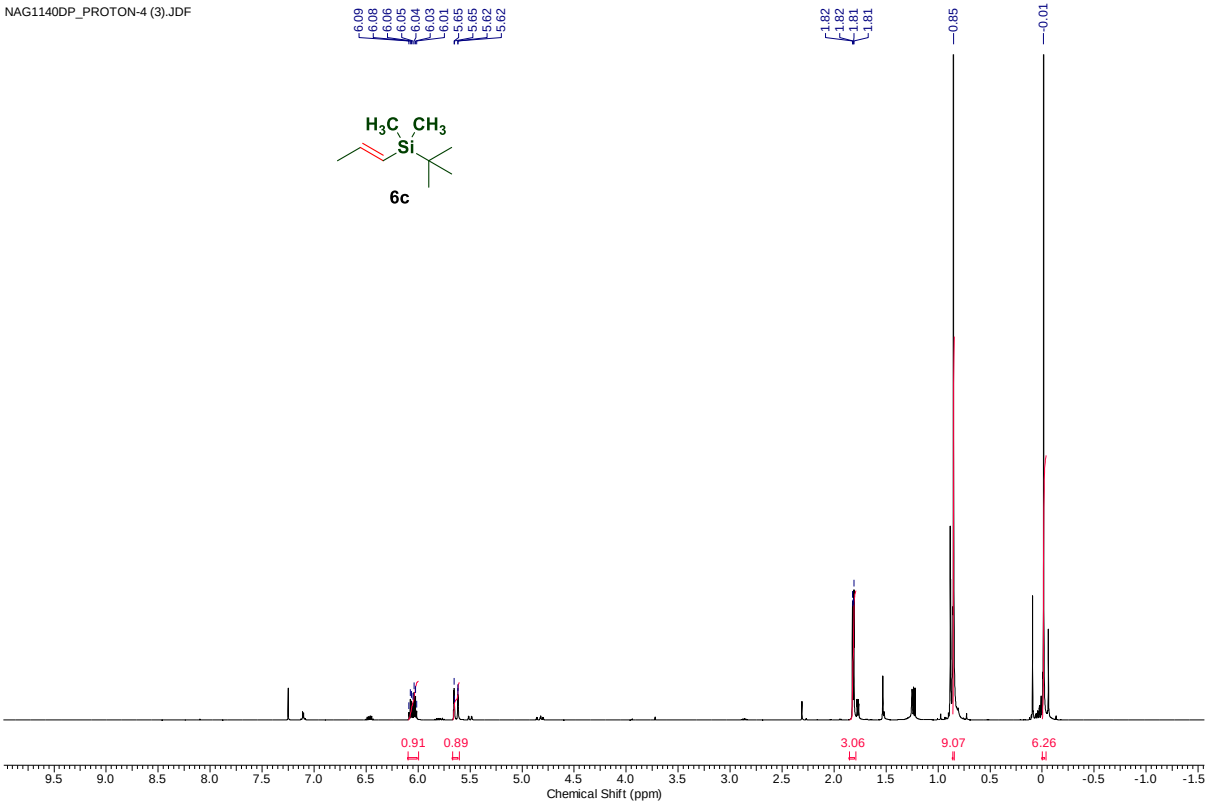
NAG1132A_CARBON-3 (2).JDF



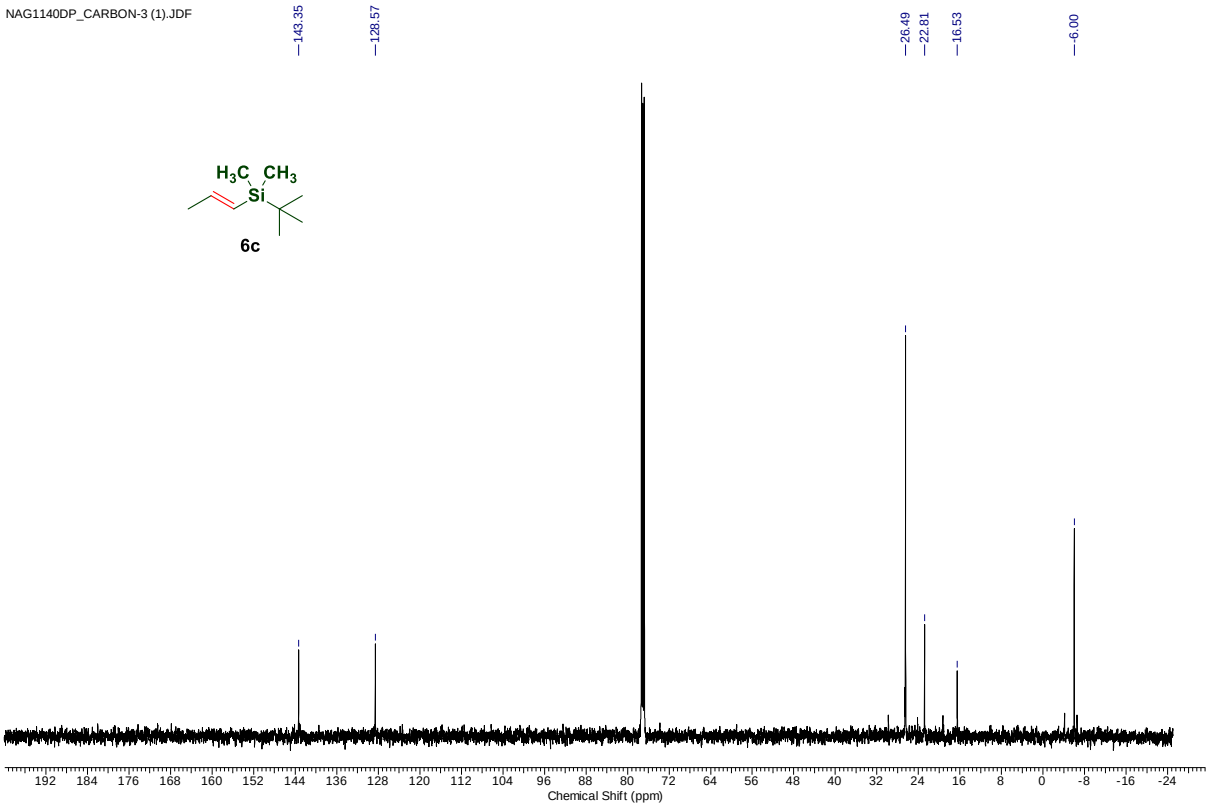
6b

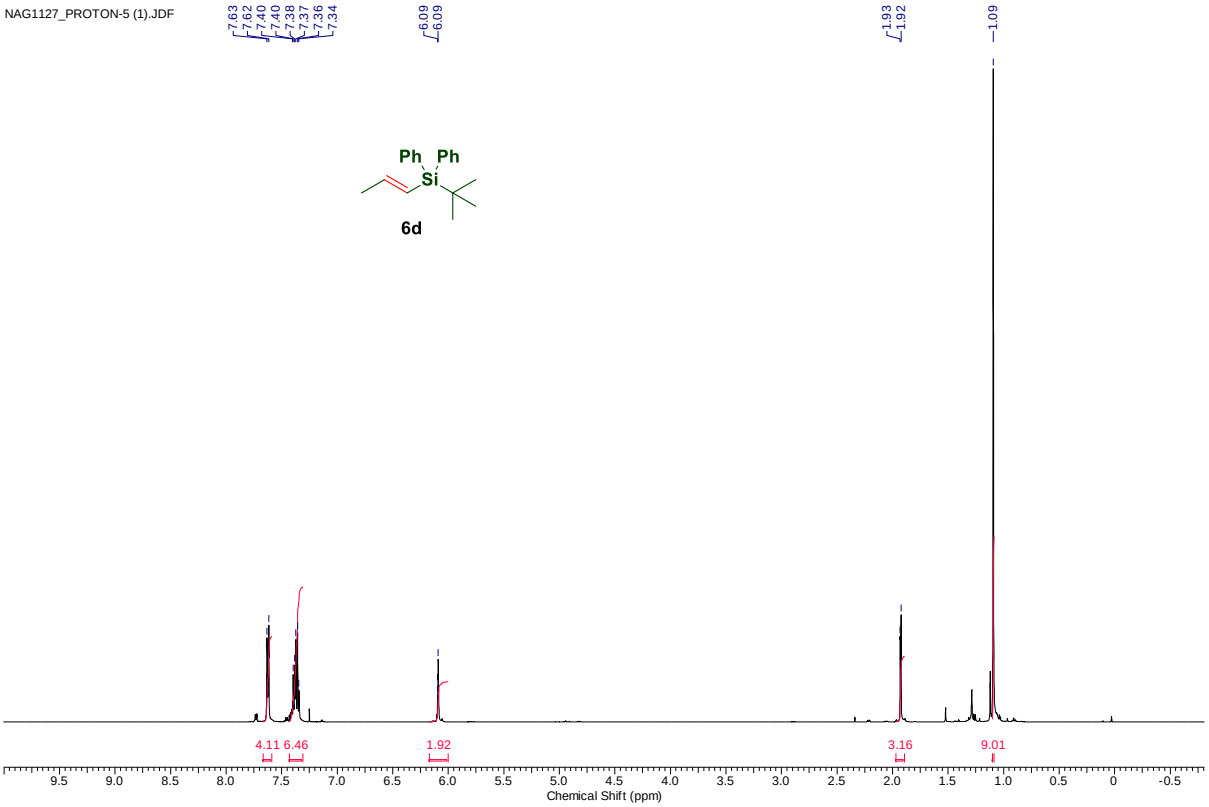

NAGBNIXO_1H-12.jdf
abundance
NAG_BN_IXO_NOESY-2.jdf
NOESY
Weak Correlation
Strong Correlation
NAGBNIXO_1H-13.jdf
Y : parts per Million : 1H
X : parts per Million : 1H
abundance

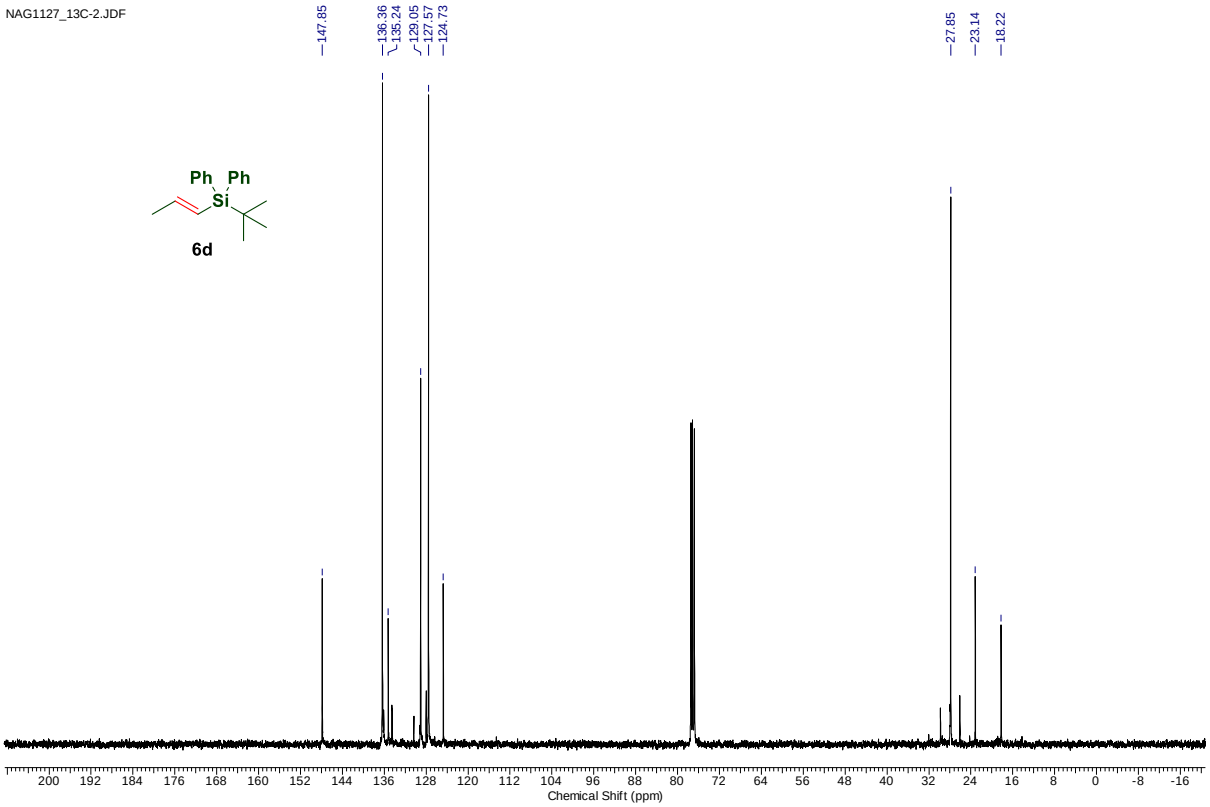
NAG1140DP_PROTON-4 (3).JDF



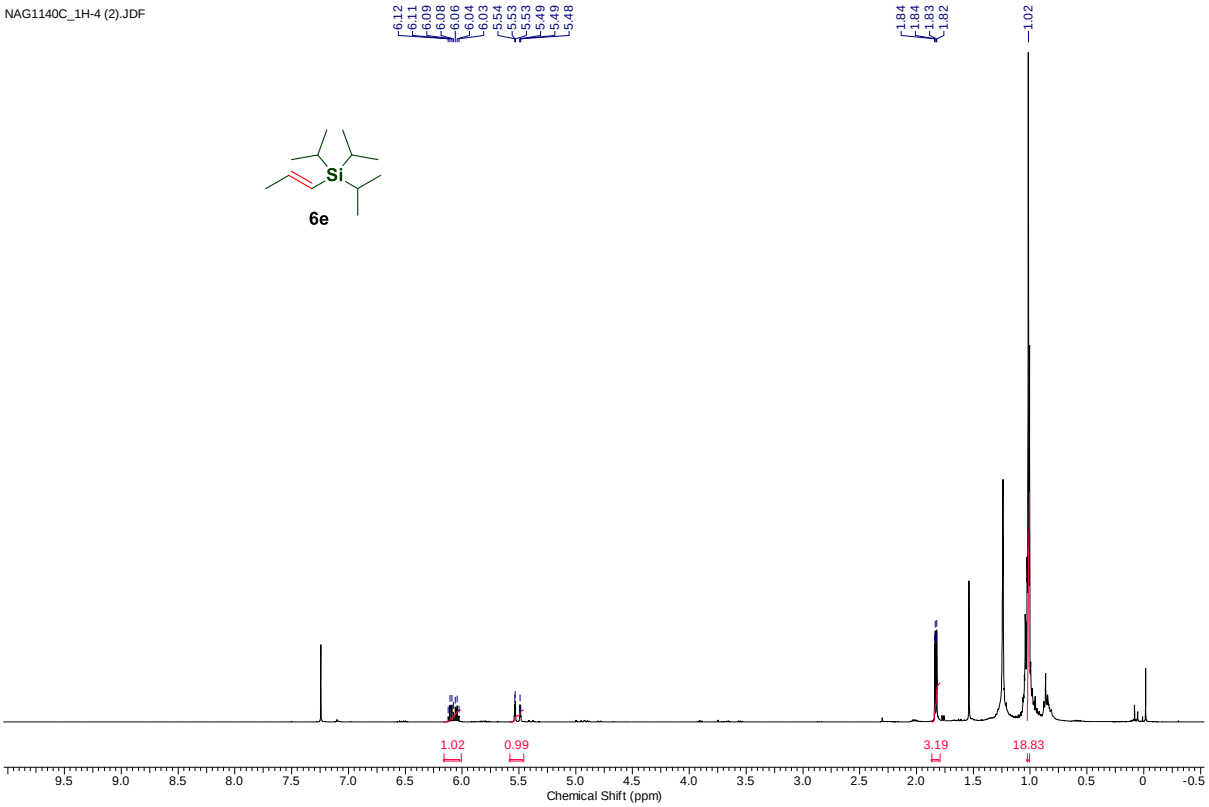
NAG1140DP_CARBON-3 (1).JDF




NAG1127_PROTON-5 (1).JDF
7.63
7.62
7.40
7.40
7.38
7.37
7.36
7.34
6.09
6.09
1.93
1.92
1.09
Ph Ph
Si
6d
4.11 6.46
1.92
3.16
9.01
Chemical Shift (ppm)

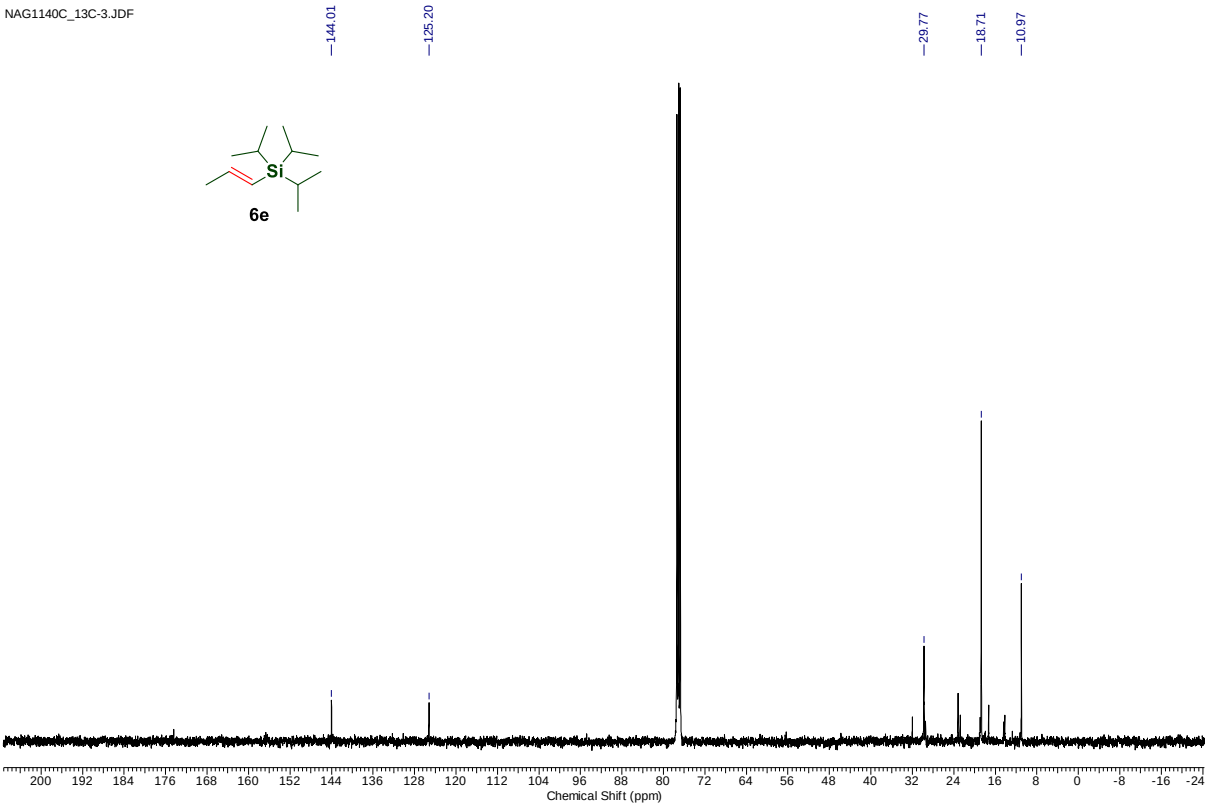

NAG1127_13C-2.JDF
147.85
136.36
135.24
129.05
127.57
124.73
27.85
23.14
18.22
Ph Ph
Si
6d
Chemical Shift (ppm)

NAG1140C_1H-4 (2).JDF

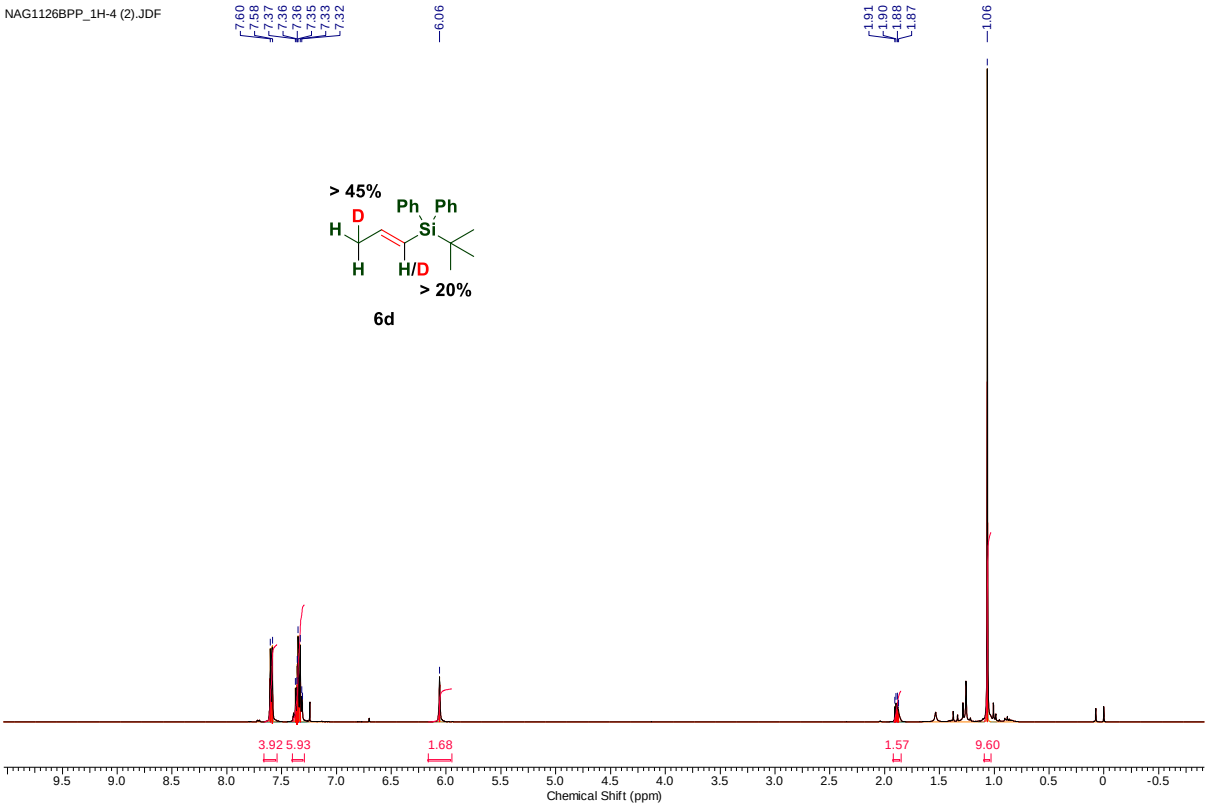


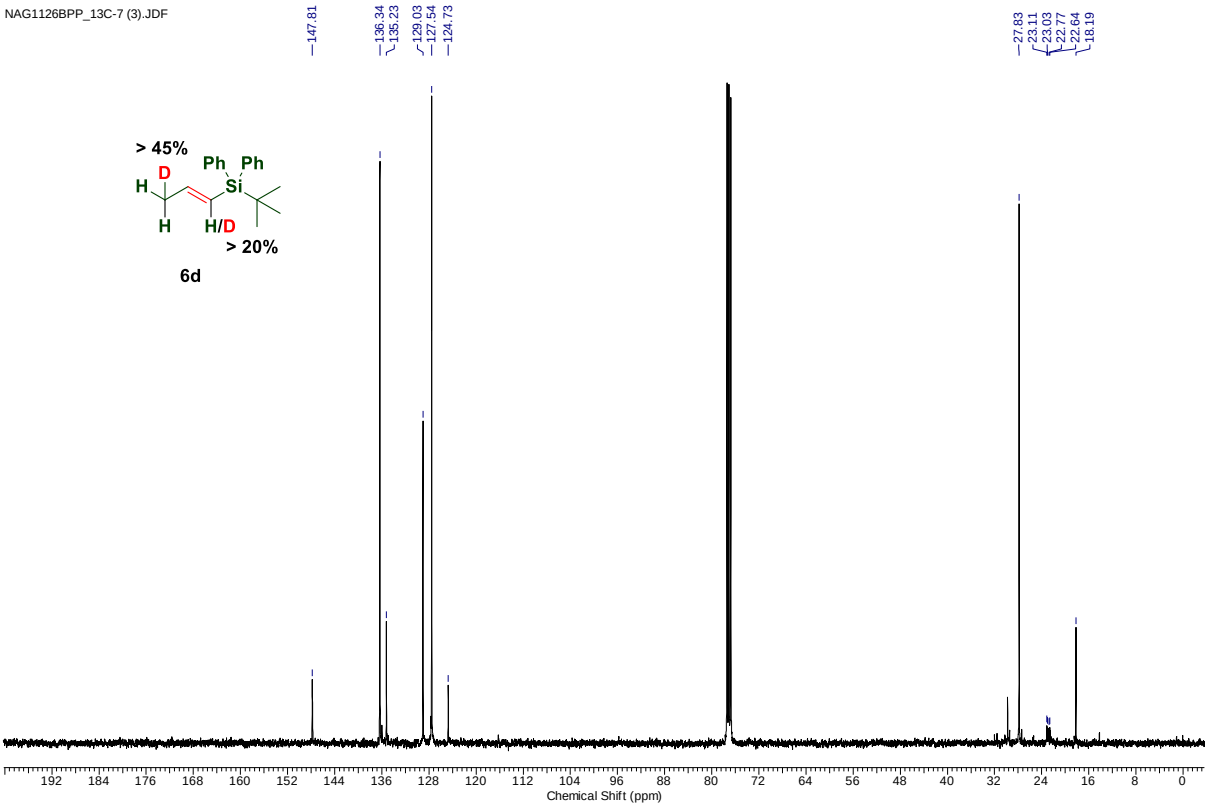
6e

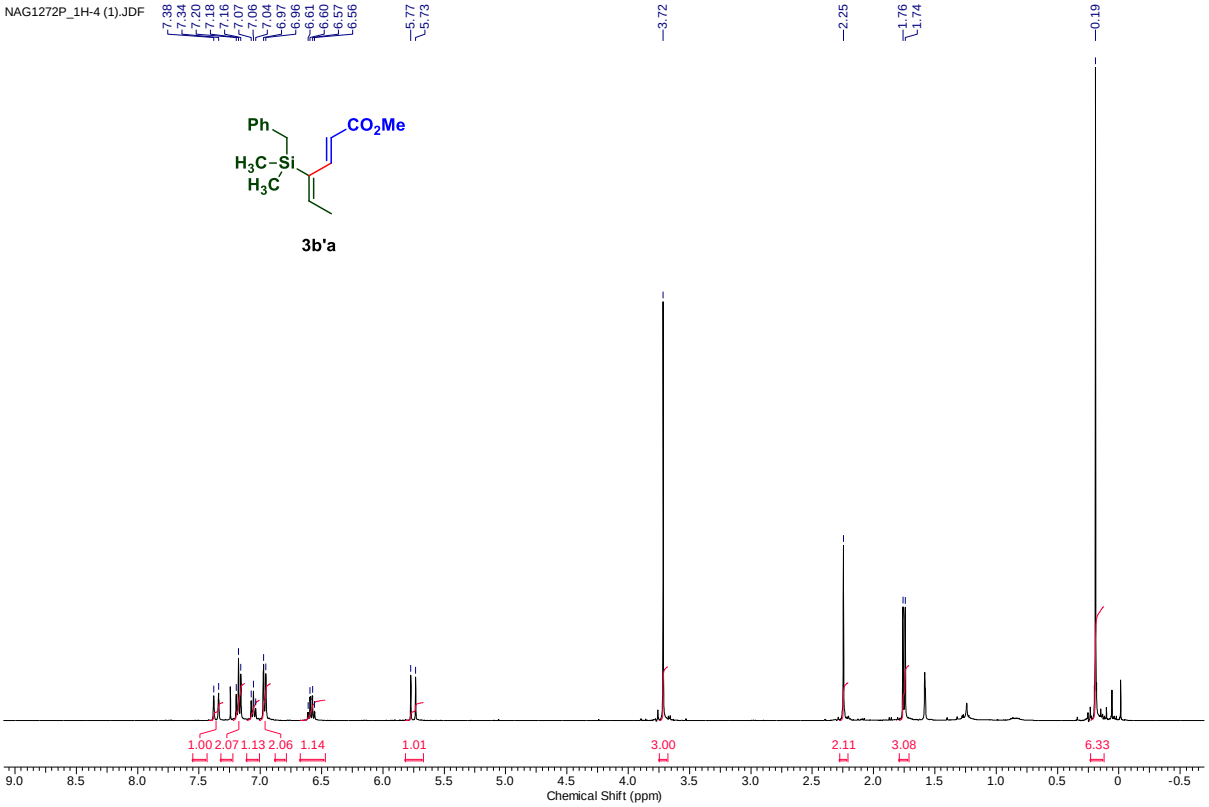
NAG1140C_13C-3.JDF



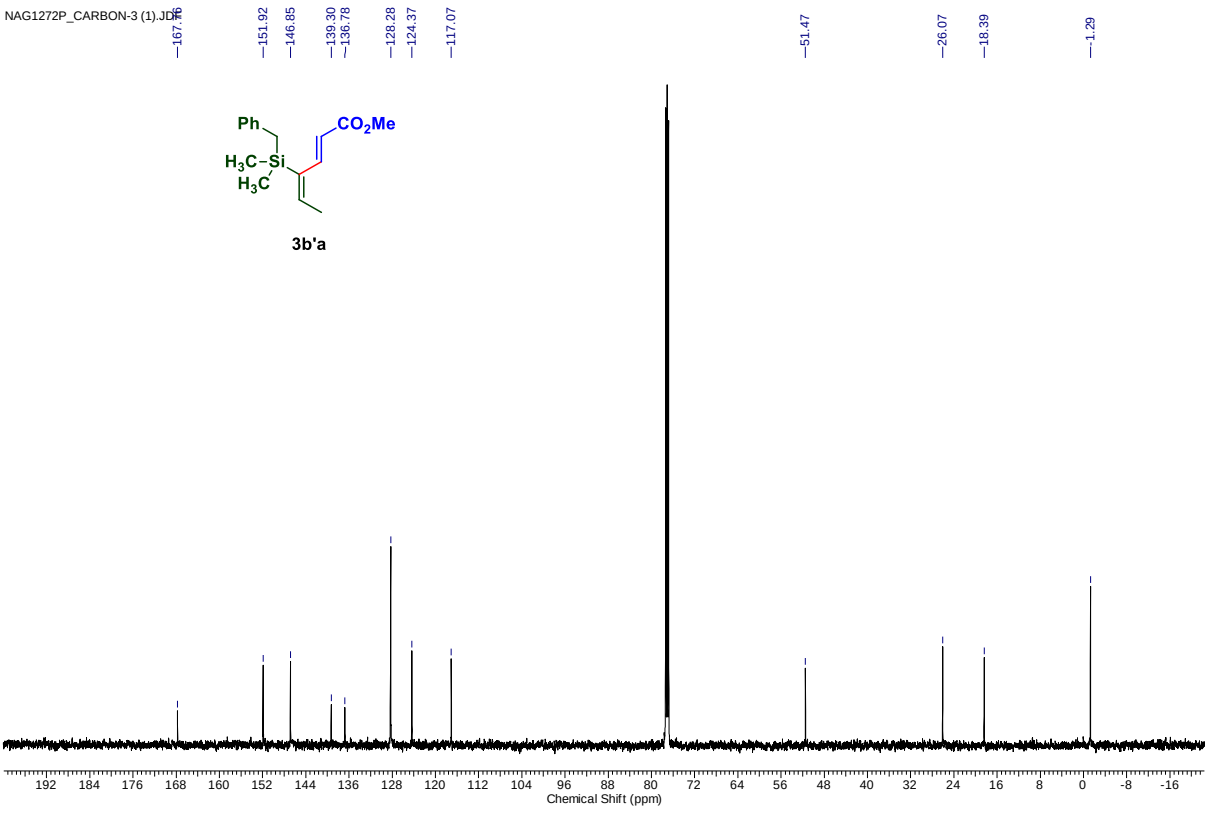
6e


NAG1126BPP_1H-4 (2).JDF
7.60
7.58
7.37
7.36
7.36
7.35
7.33
7.32
6.06
1.91
1.90
1.88
1.87
1.06
> 45%
Ph Ph
D
Si
H
H
H/D
> 20%
6d
3.92 5.93
1.68
1.57
9.60
Chemical Shift (ppm)


NAG1126BPP_13C-7 (3).JDF
147.81
136.34
135.23
129.03
127.54
124.73
27.83
23.11
23.03
22.77
22.64
18.19
> 45%
Ph Ph
D
Si
H
H
H/D
> 20%
6d
Chemical Shift (ppm)

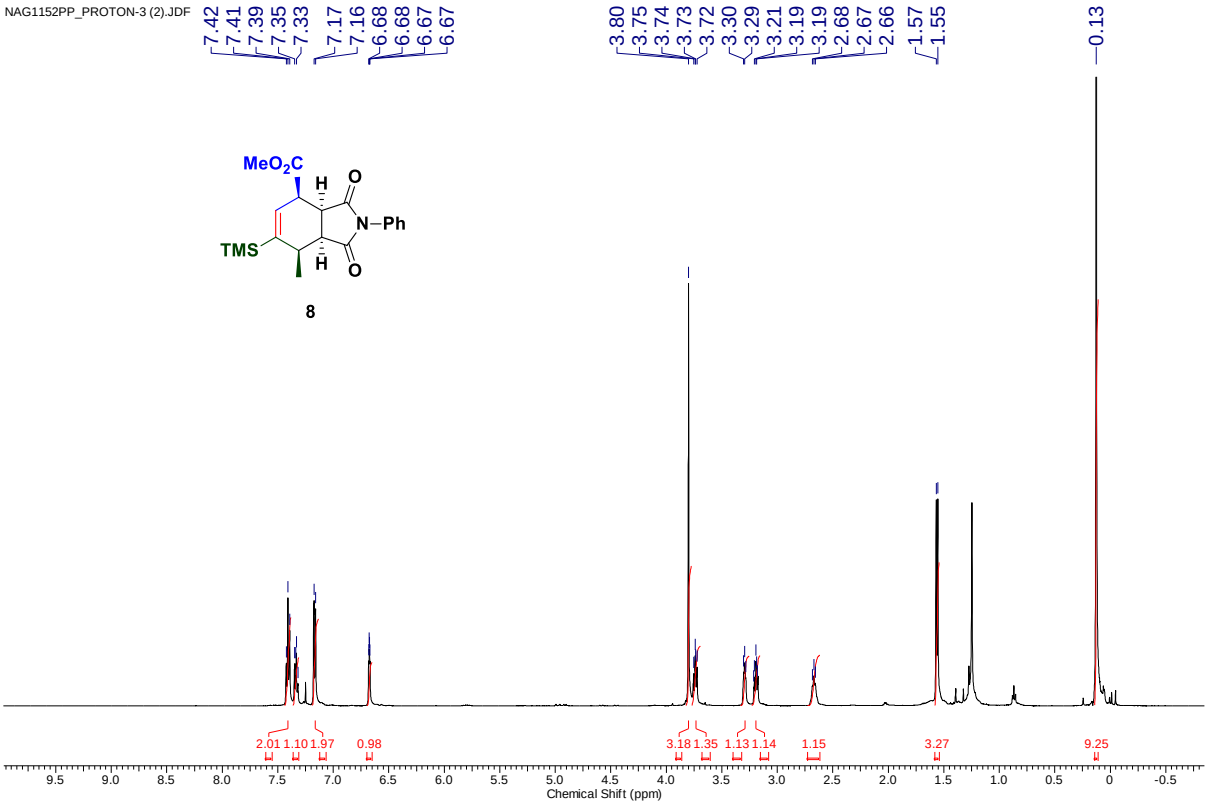

NAG1272P_1H-4 (1).JDF
7.38
7.34
7.20
7.18
7.16
7.07
7.06
7.04
6.97
6.96
6.61
6.60
6.57
6.56
5.77
5.73
3.72
2.25
1.76
1.74
0.19
Ph
CO2Me
H3C–Si
H3C
1.00 2.07 1.13 2.06 1.14 1.01 3.00 2.11 3.08 6.33
Chemical Shift (ppm)

3b'a


NAG1272P_CARBON-3 (1).JDF
167.76
151.92
146.85
139.30
136.78
128.28
124.37
117.07
51.47
26.07
18.39
1.29
Ph
CO2Me
H3C–Si
H3C
Chemical Shift (ppm)

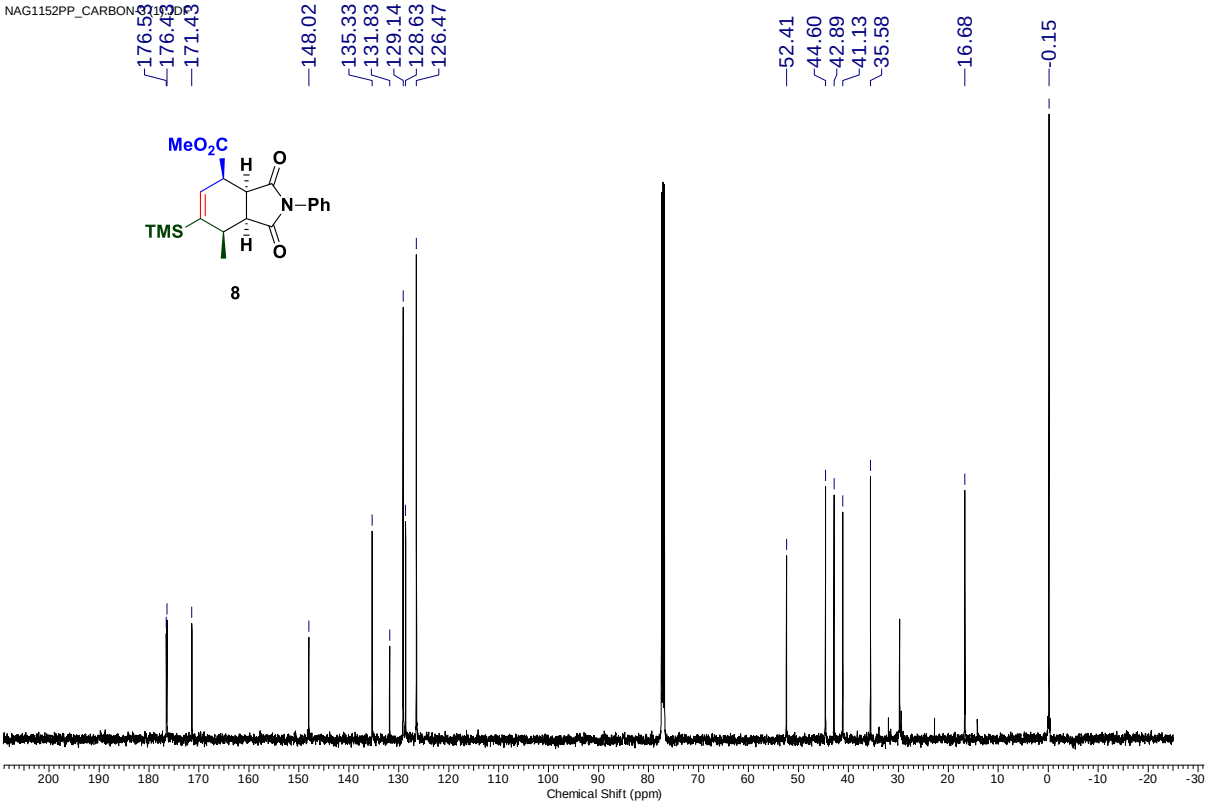
3b'a

NAG1152PP_PROTON-3 (2).JDF

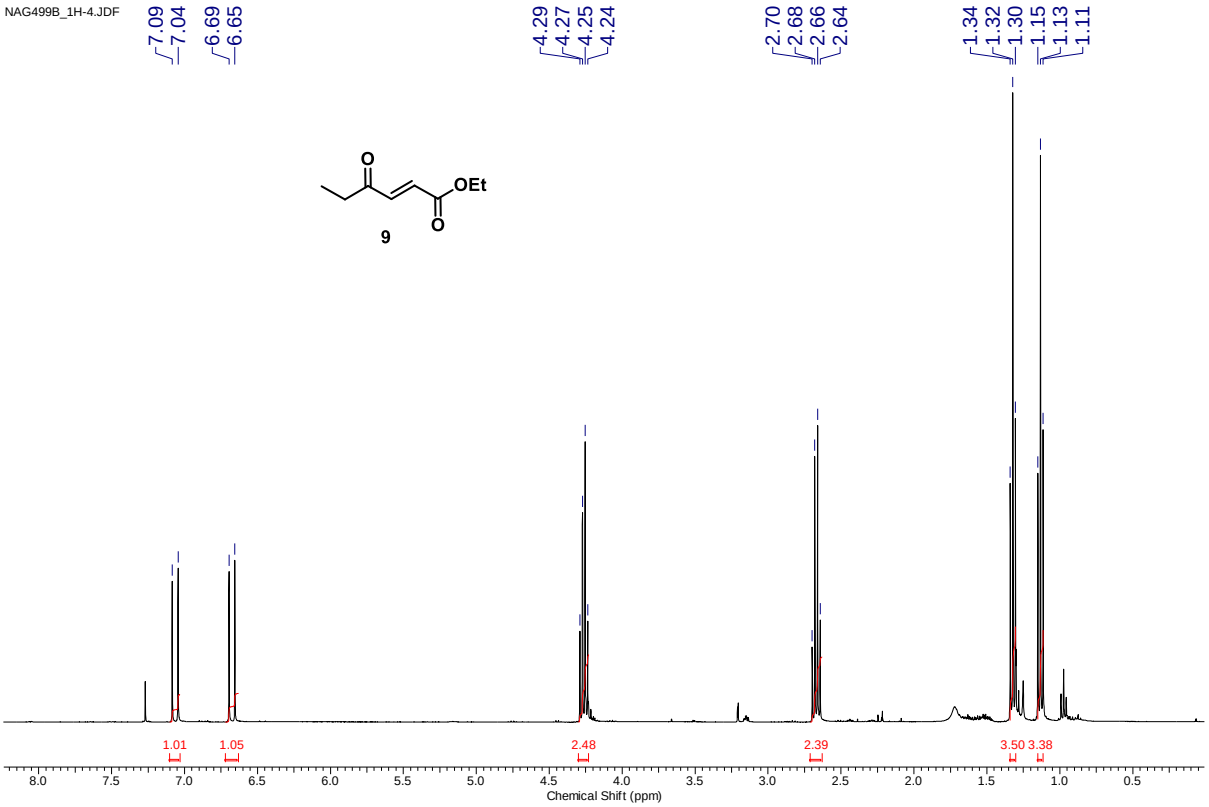


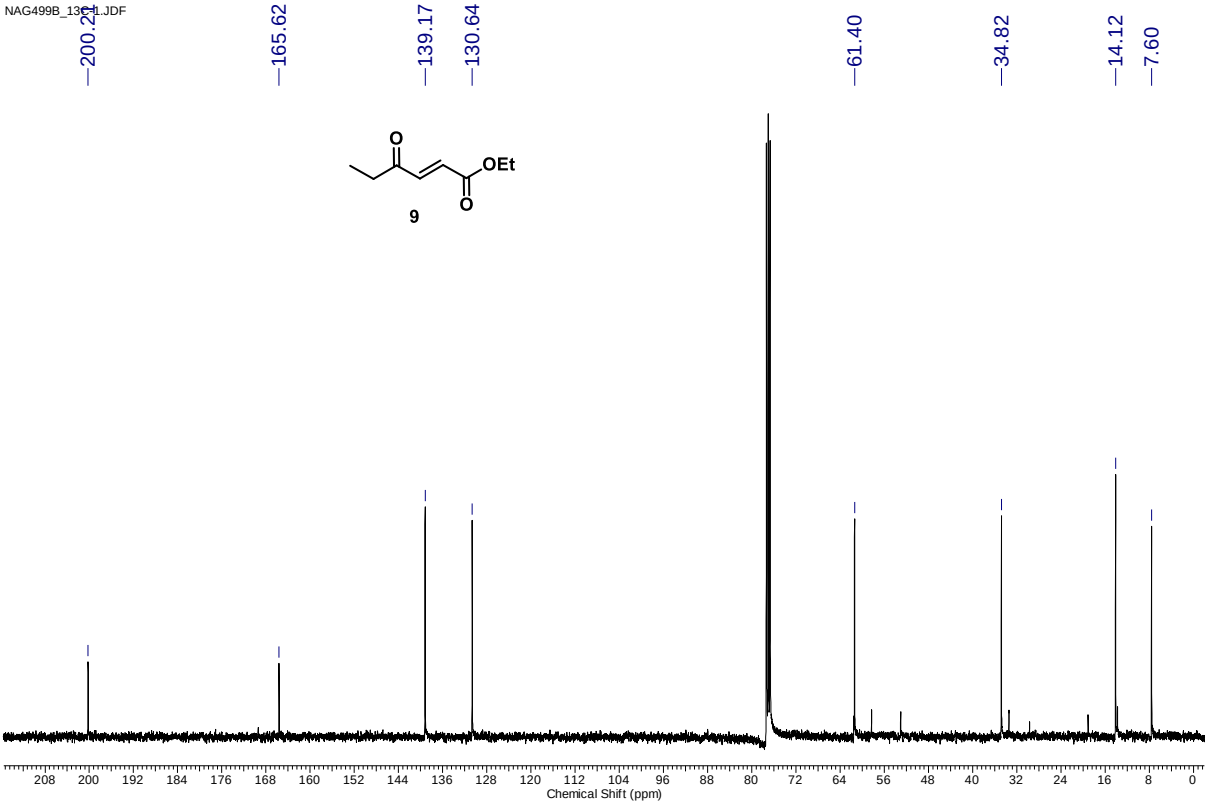
8

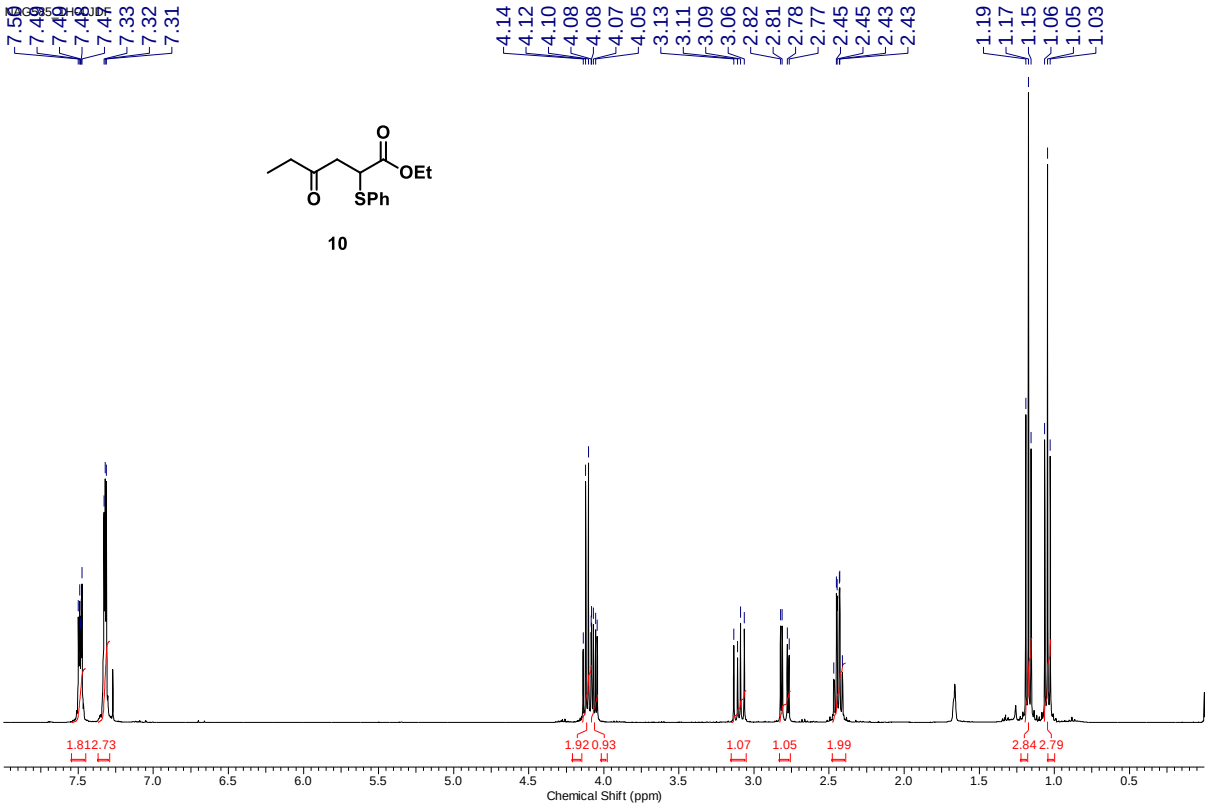
NAG1152PP_CARBON-3 (2).JDF

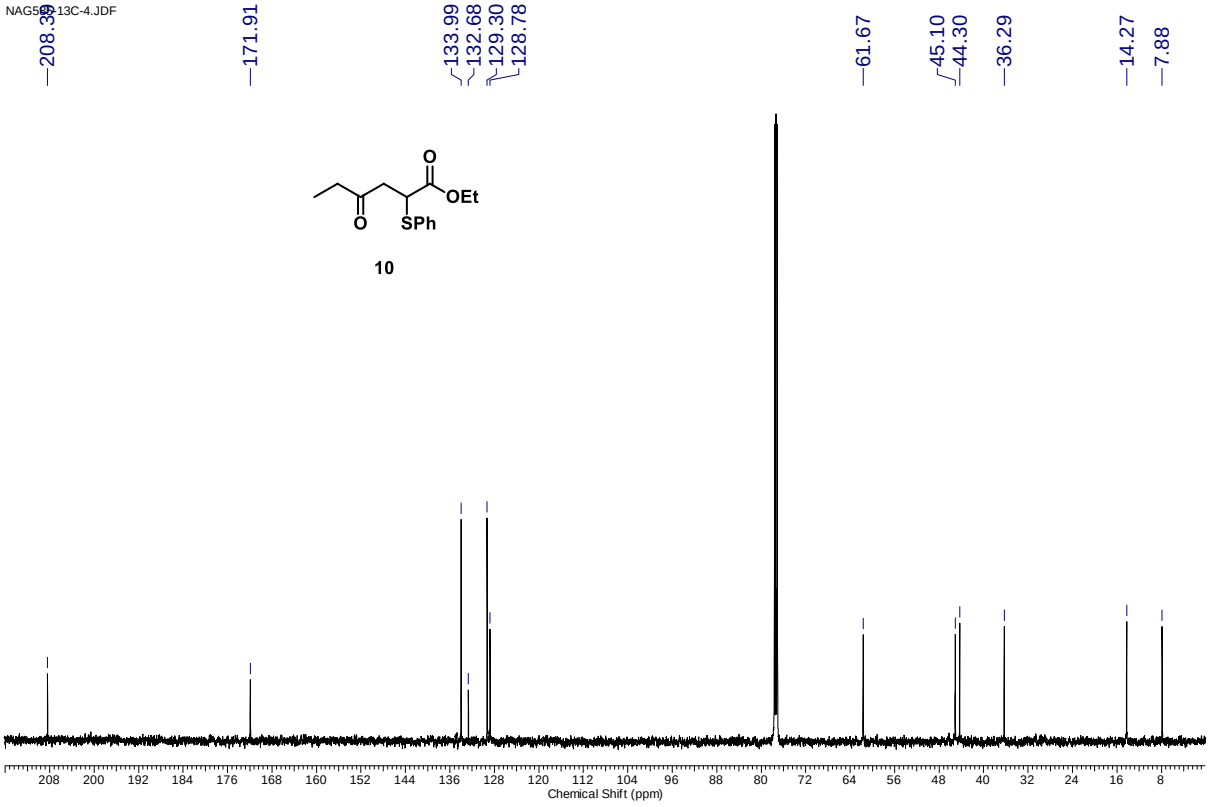


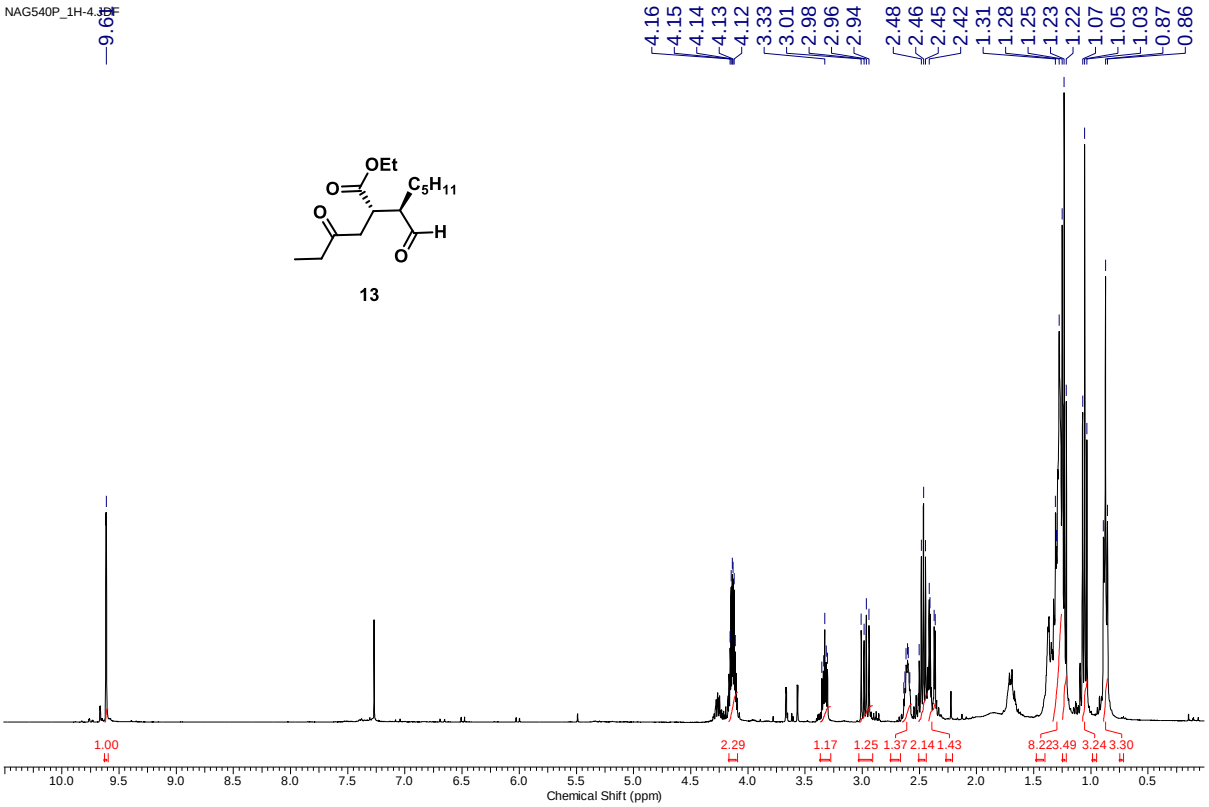
8

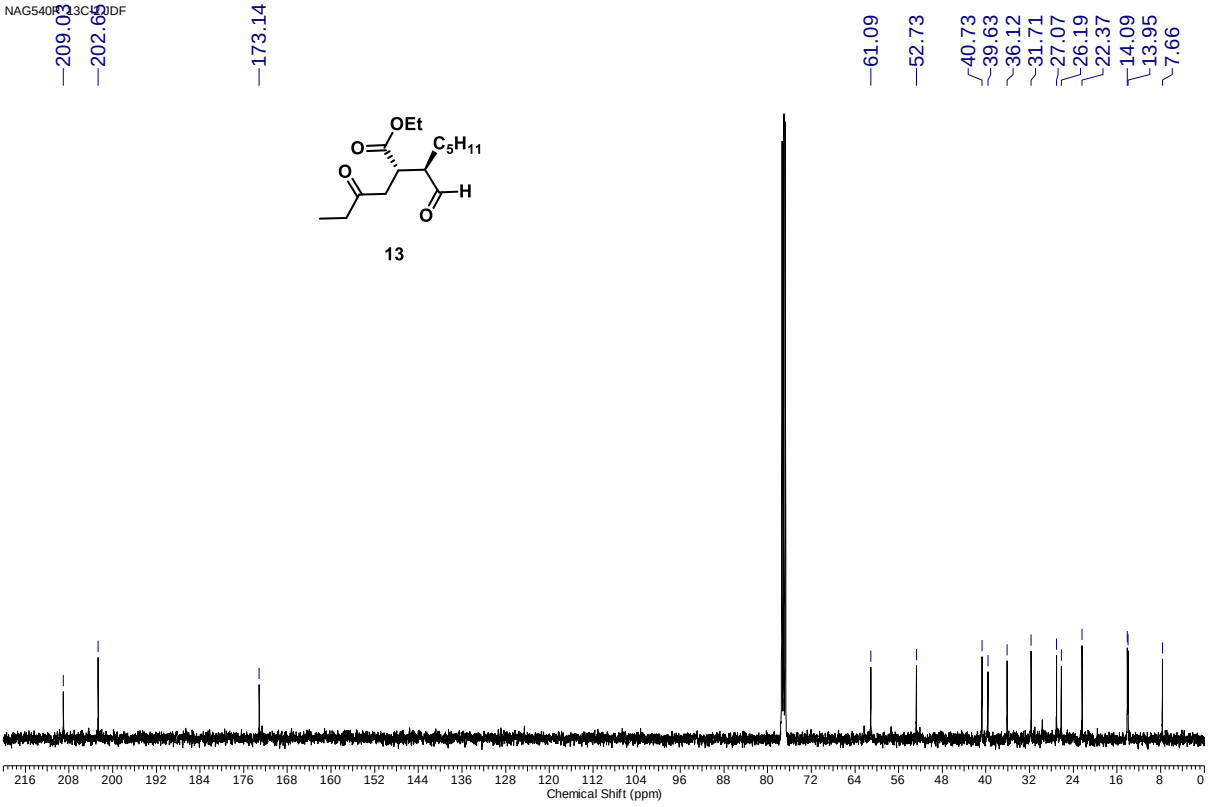

NAG499B_1H-4.JDF
7.09
7.04
6.69
6.65
4.29
4.27
4.25
4.24
2.70
2.68
2.66
2.64
1.34
1.32
1.30
1.15
1.13
1.11
O
OEt
O
9
1.01
1.05
2.48
2.39
3.50
3.38
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


NAG499B_13C-1.JDF
200.21
165.62
139.17
130.64
61.40
34.82
14.12
7.60
O
OEt
O
9
208
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

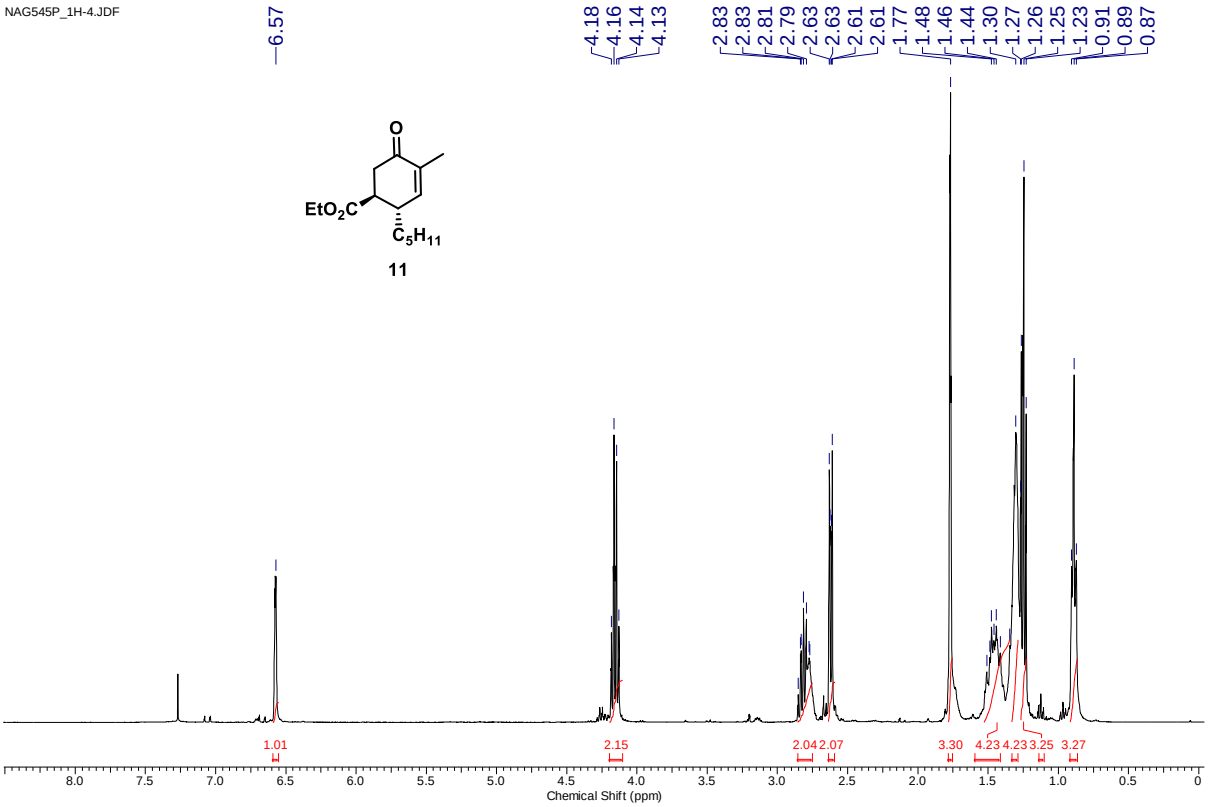

7.51
7.46
7.40
7.41
7.33
7.32
7.31
4.14
4.12
4.10
4.08
4.07
4.05
3.13
3.11
3.09
3.06
2.82
2.81
2.78
2.77
2.45
2.43
1.19
1.17
1.15
1.06
1.05
1.03
O
OEt
O
SPh
10
1.81
2.73
1.92
0.93
1.07
1.05
1.99
2.84
2.79
Chemical Shift (ppm)


208.38
171.91
133.99
132.68
129.30
128.78
61.67
45.10
44.30
36.29
14.27
7.88
O
OEt
O
SPh
10
Chemical Shift (ppm)

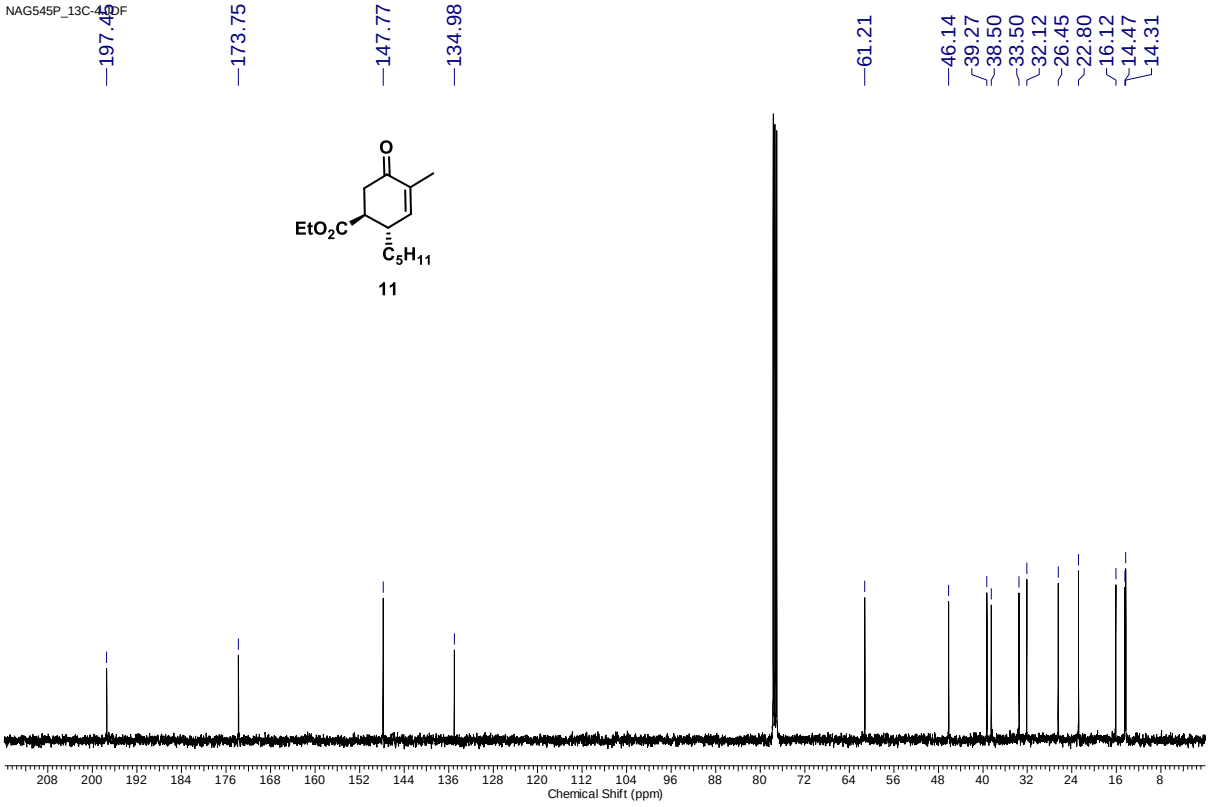

NAG540P_1H-4.10.1.pdf
9.63
4.16
4.15
4.14
4.13
4.12
3.33
3.01
2.98
2.96
2.94
2.48
2.46
2.45
2.42
1.31
1.28
1.25
1.23
1.22
1.07
1.05
1.03
0.87
0.86
OEt
O
O
C5H11
H
O
13
1.00
2.29
1.17
1.25
1.37
2.14
1.43
8.22
3.49
3.24
3.30
Chemical Shift (ppm)

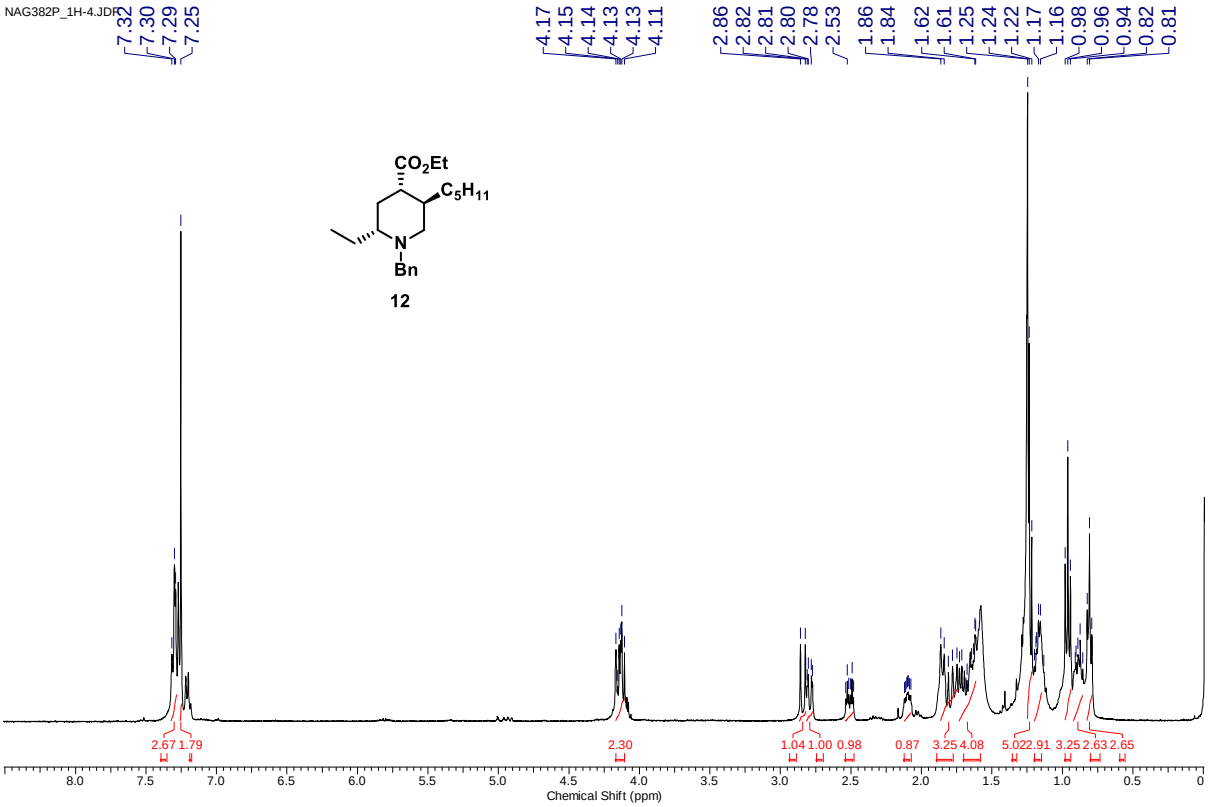

NAG540P_13C-10.1.pdf
209.01
202.66
173.14
61.09
52.73
40.73
39.63
36.12
31.71
27.07
26.19
22.37
14.09
13.95
7.66
OEt
O
O
C5H11
H
O
13
Chemical Shift (ppm)

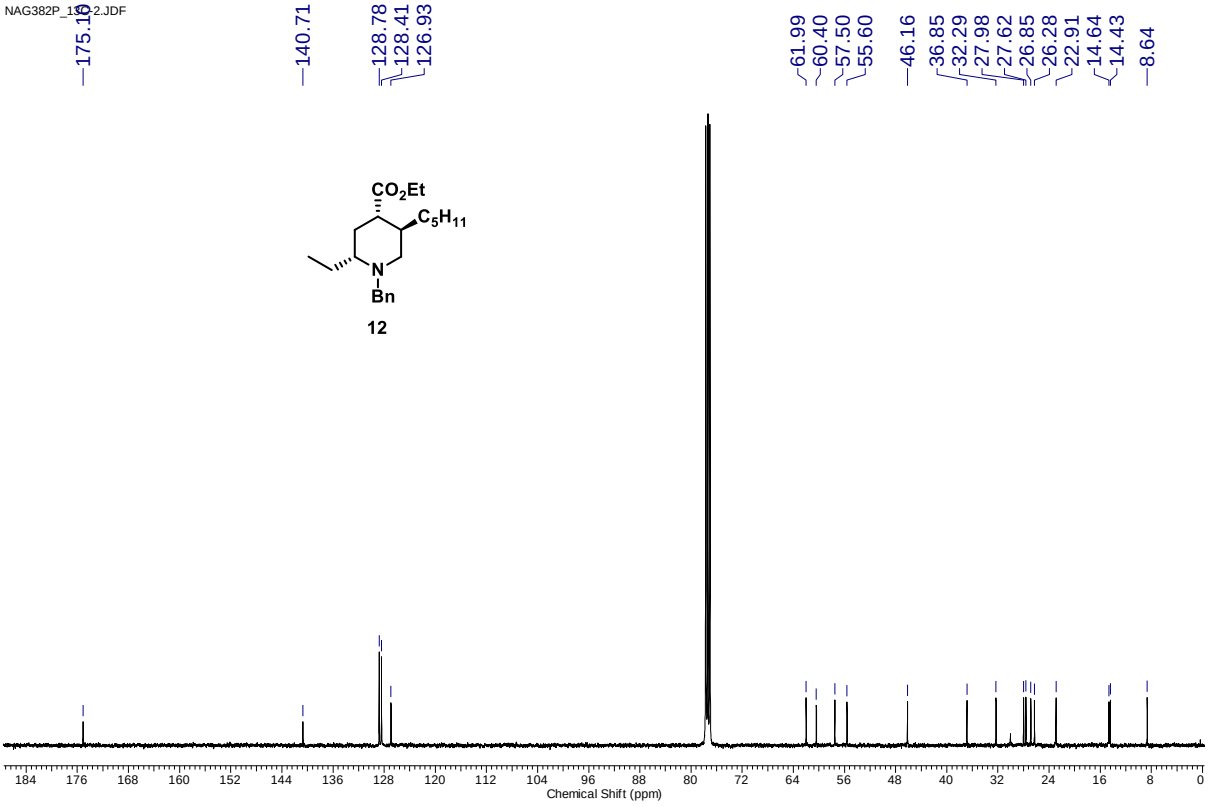
NAG545P_1H-4.JDF

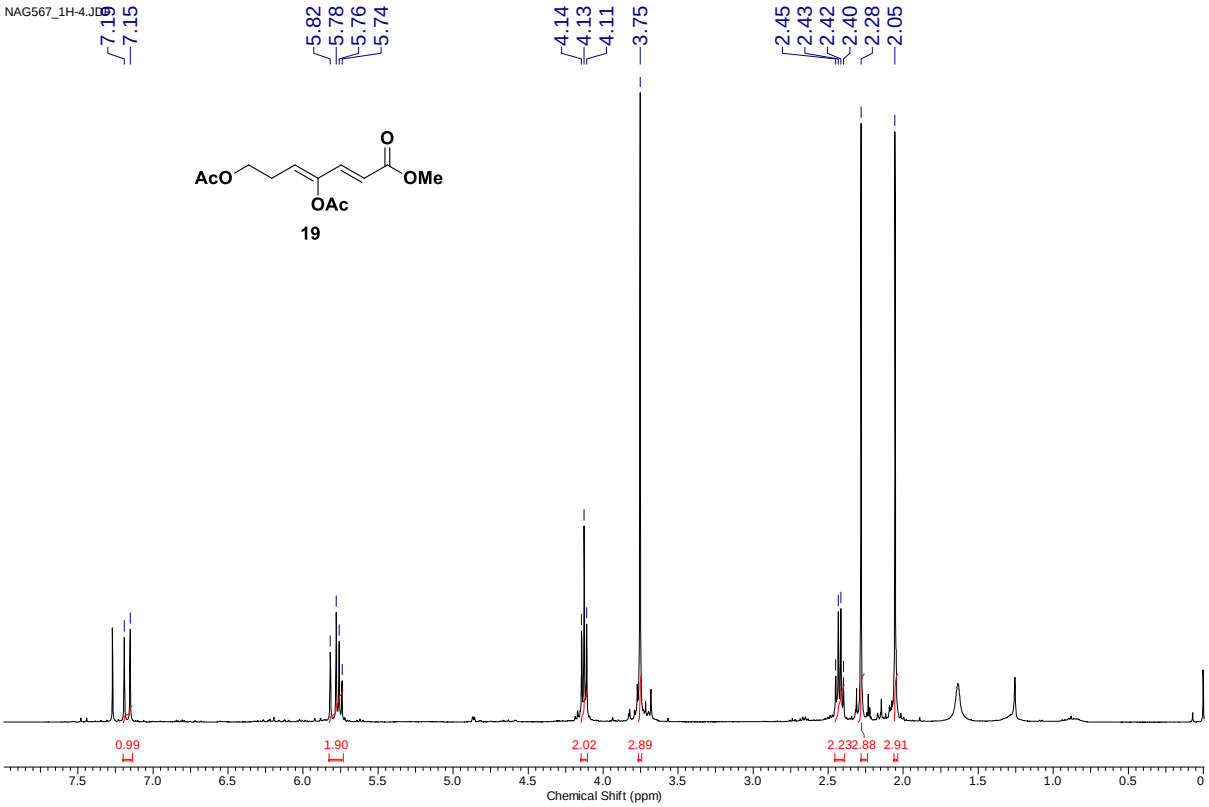


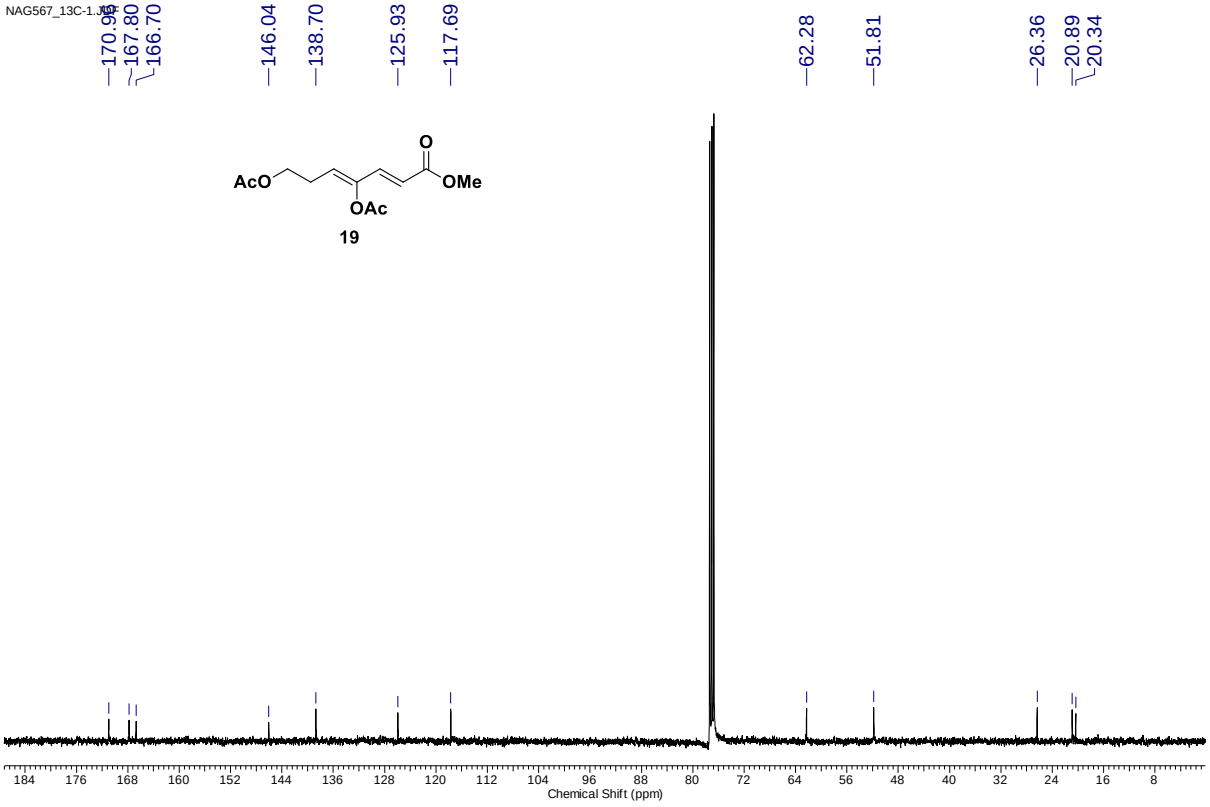
NAG545P_13C-4.JDF

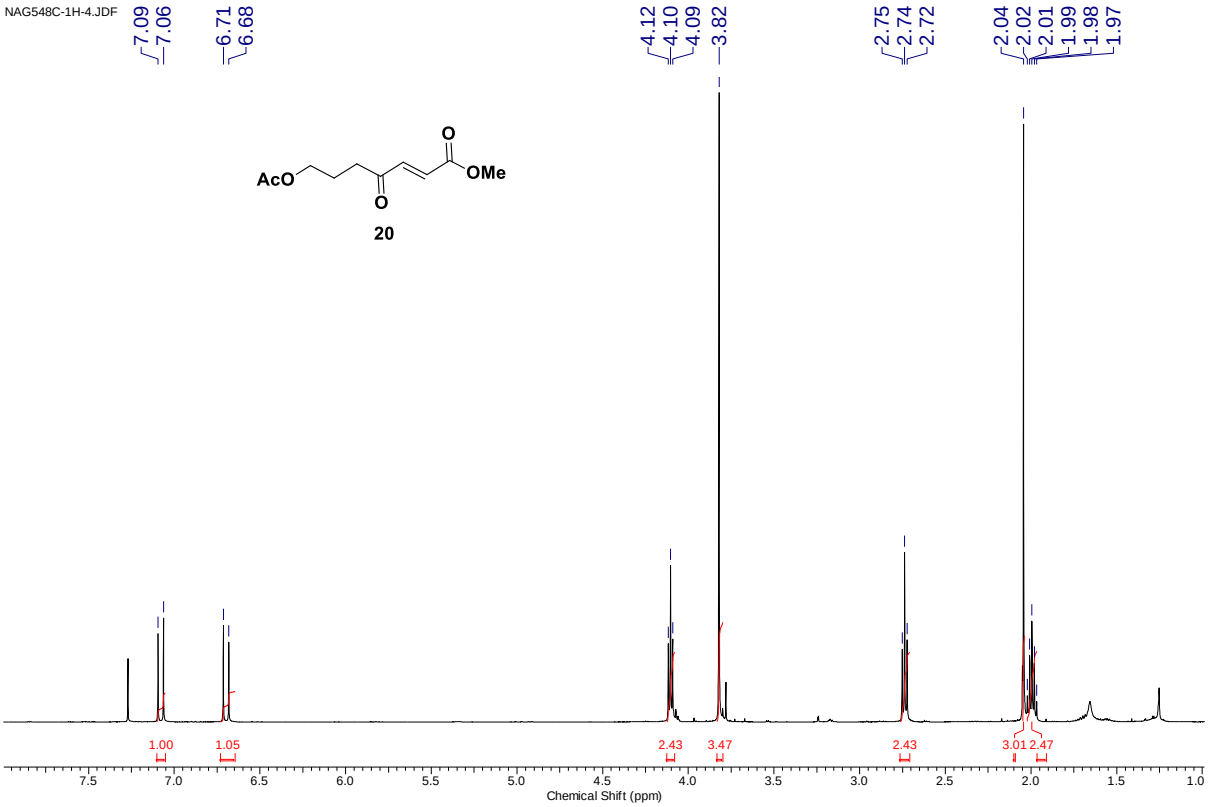


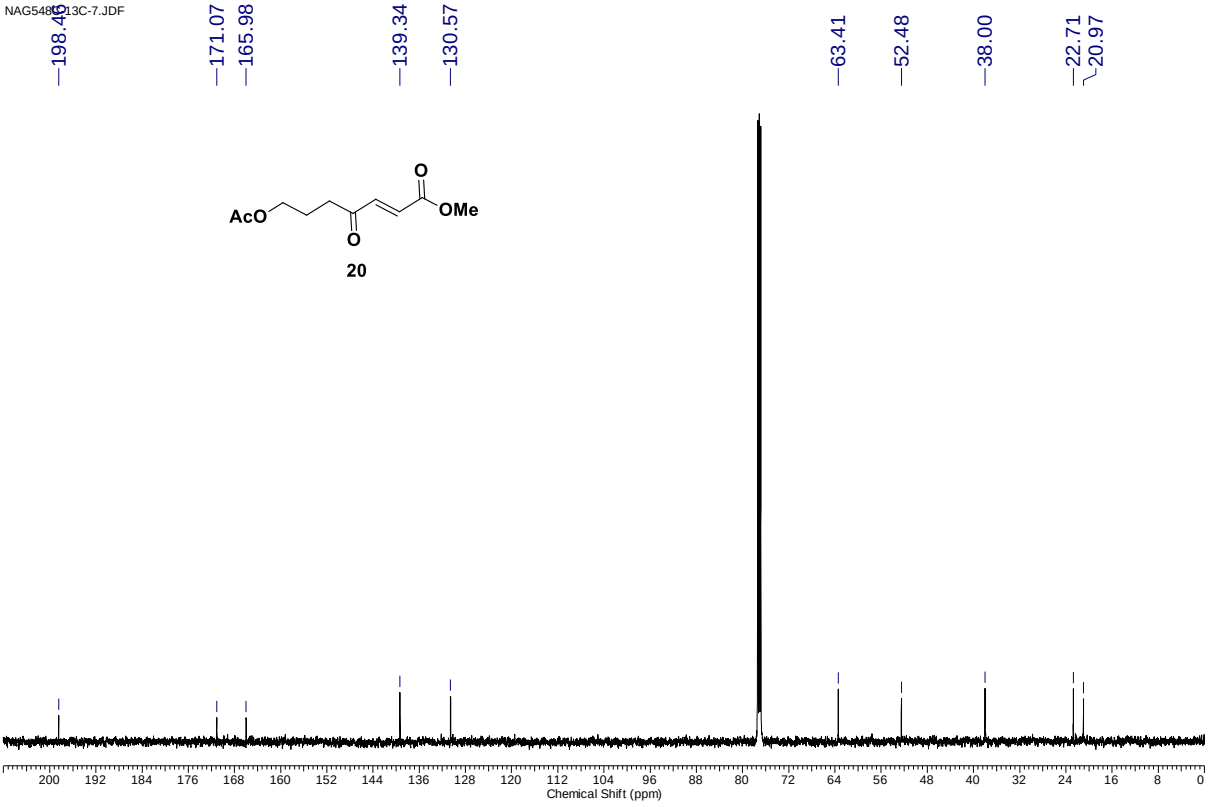

NAG382P_1H-4.JDF
7.32
7.30
7.29
7.25
4.17
4.15
4.14
4.13
4.13
4.11
2.86
2.82
2.81
2.80
2.78
2.53
1.86
1.84
1.62
1.61
1.25
1.24
1.22
1.17
1.16
0.98
0.96
0.94
0.82
0.81
CO2Et
C5H11
N
Bn
12
2.67
1.79
2.30
1.04
1.00
0.98
0.87
3.25
4.08
5.02
2.91
3.25
2.63
2.65
Chemical Shift (ppm)


NAG382P_13C-2.JDF
175.16
140.71
128.78
128.41
126.93
61.99
60.40
57.50
55.60
46.16
36.85
32.29
27.98
27.62
26.85
26.28
22.91
14.64
14.43
8.64
CO2Et
C5H11
N
Bn
12
Chemical Shift (ppm)

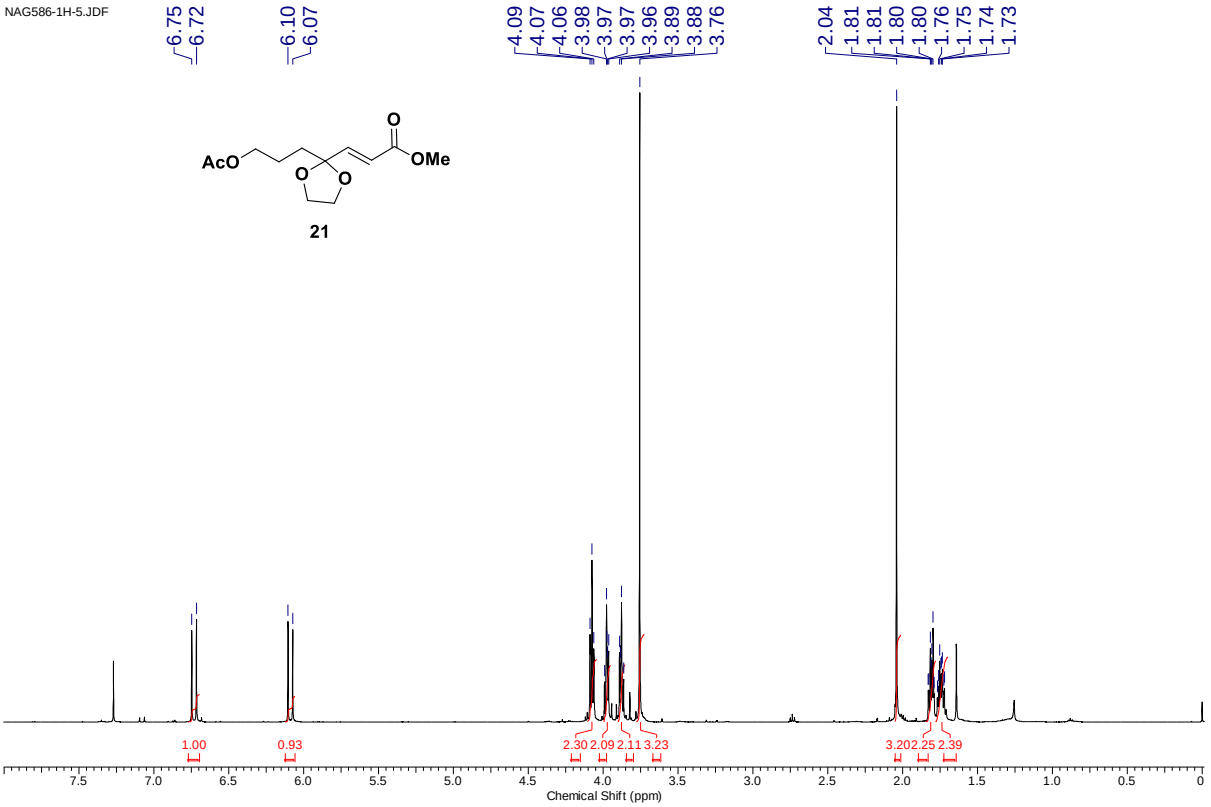

NAG567_1H-4.JDF
7.19
7.15
5.82
5.78
5.76
5.74
4.14
4.13
4.11
3.75
2.45
2.43
2.42
2.40
2.28
2.05
AcO
OAc
O
OMe
19
0.99
1.90
2.02
2.89
2.23
2.88
2.91
Chemical Shift (ppm)


NAG567_13C-1.JDF
170.99
167.80
166.70
146.04
138.70
125.93
117.69
62.28
51.81
26.36
20.89
20.34
AcO
OAc
O
OMe
19
Chemical Shift (ppm)


NAG548C-1H-4.JDF
7.09
7.06
6.71
6.68
4.12
4.10
4.09
3.82
2.75
2.74
2.72
2.04
2.02
2.01
1.99
1.98
1.97
AcO
O
OMe
O
20
1.00
1.05
2.43
3.47
2.43
3.01
2.47
Chemical Shift (ppm)

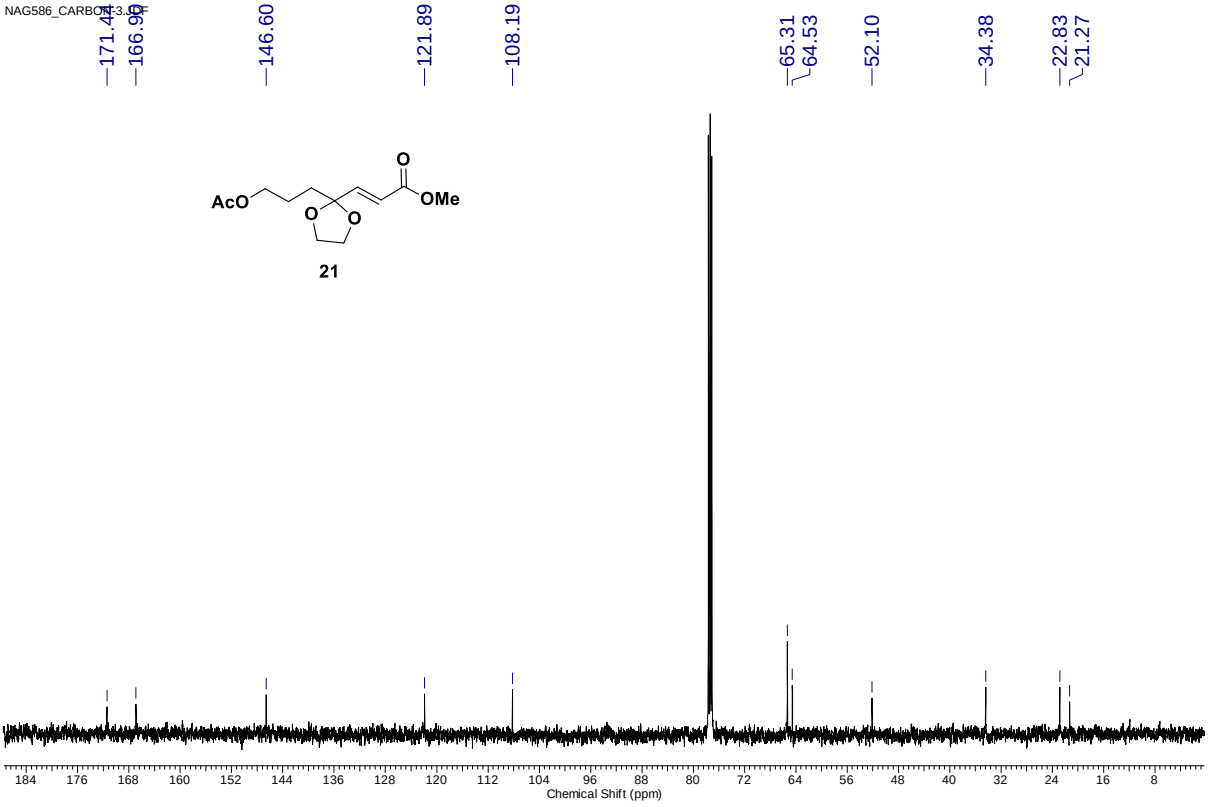

NAG548C-13C-7.JDF
198.40
171.07
165.98
139.34
130.57
63.41
52.48
38.00
22.71
20.97
AcO
O
OMe
O
20
Chemical Shift (ppm)

NAG586-1H-5.JDF

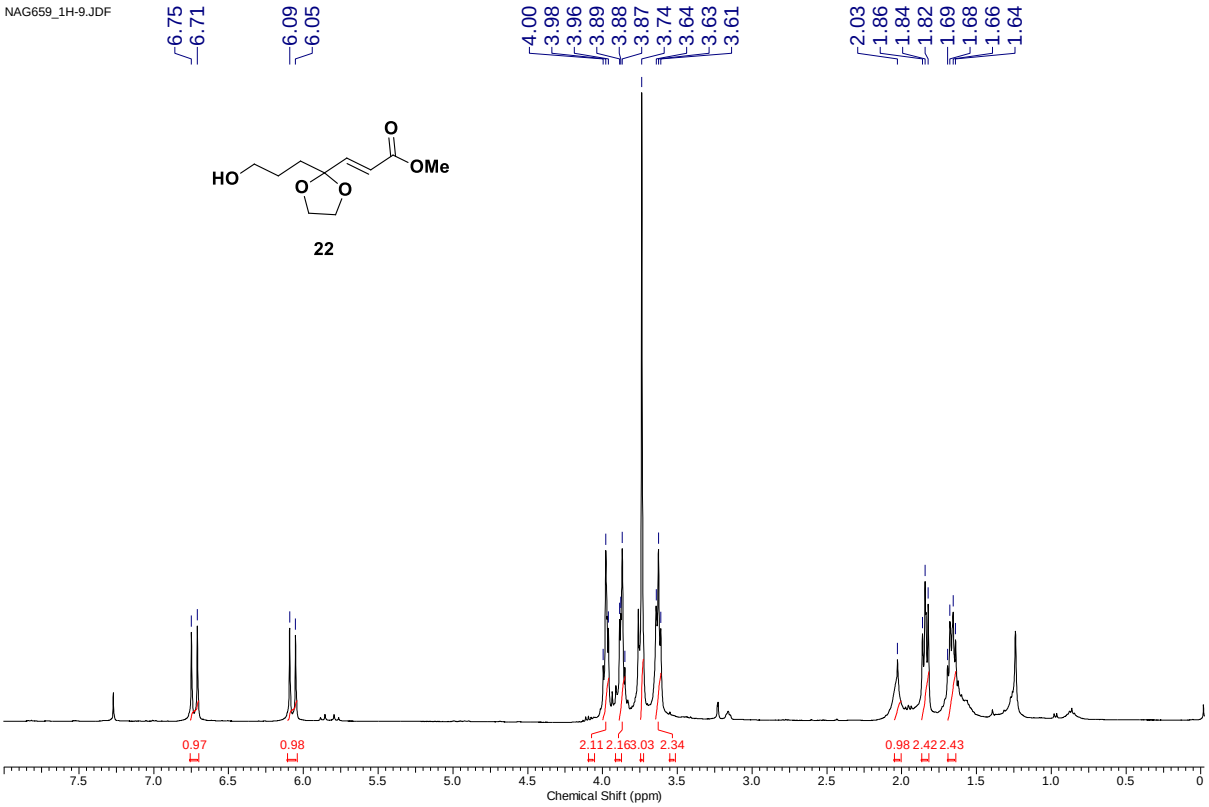


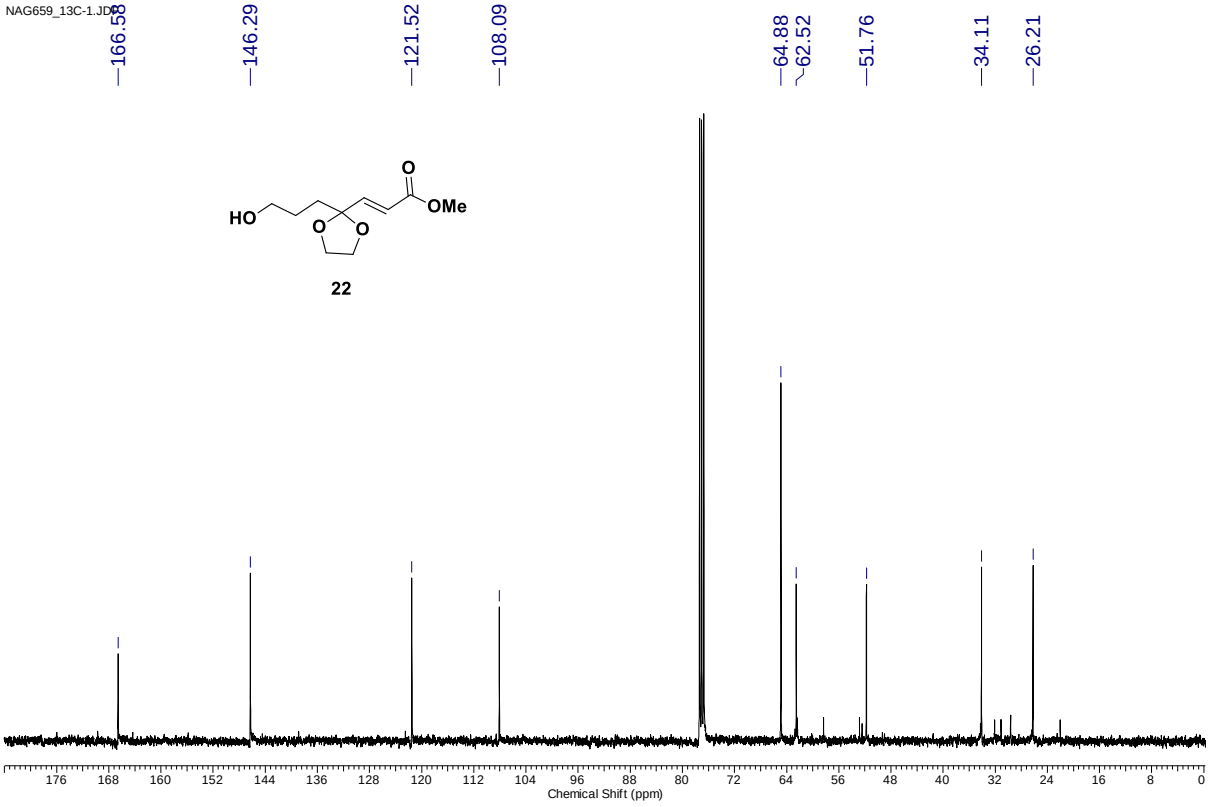
21

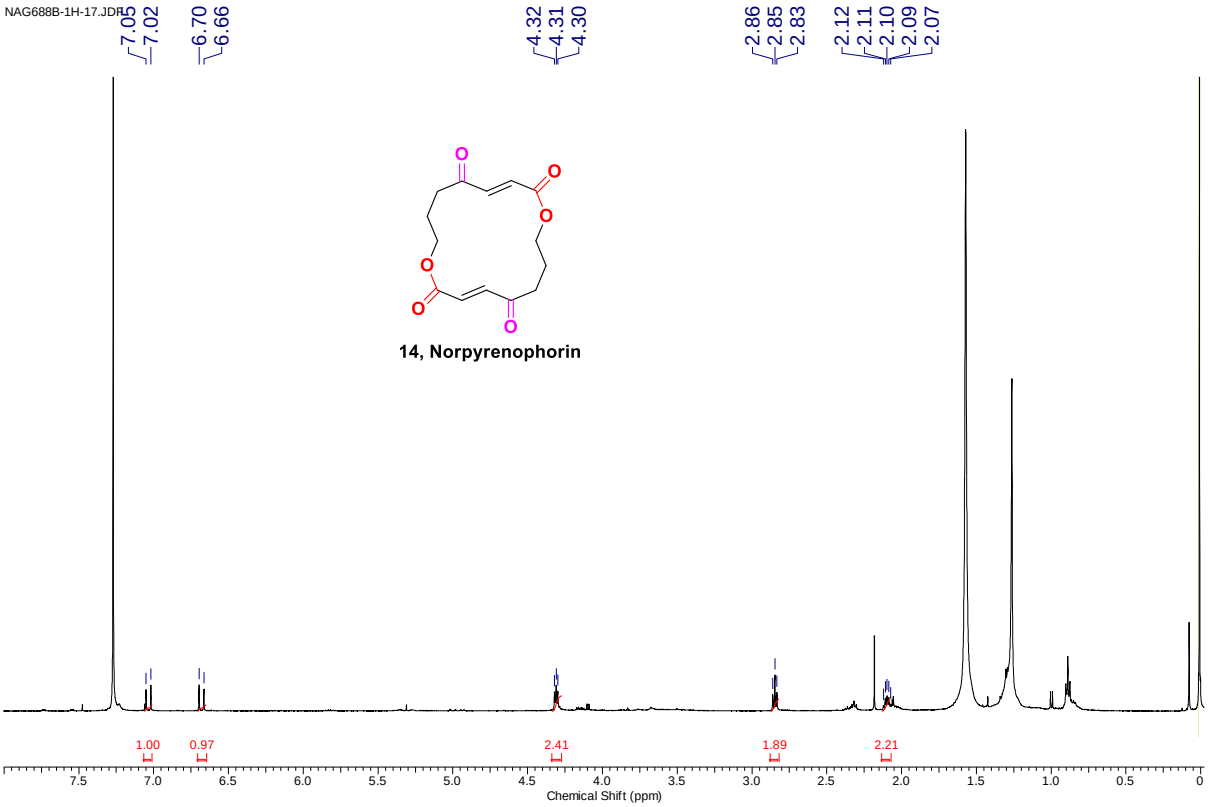
NAG586_CARBON-3.JDF

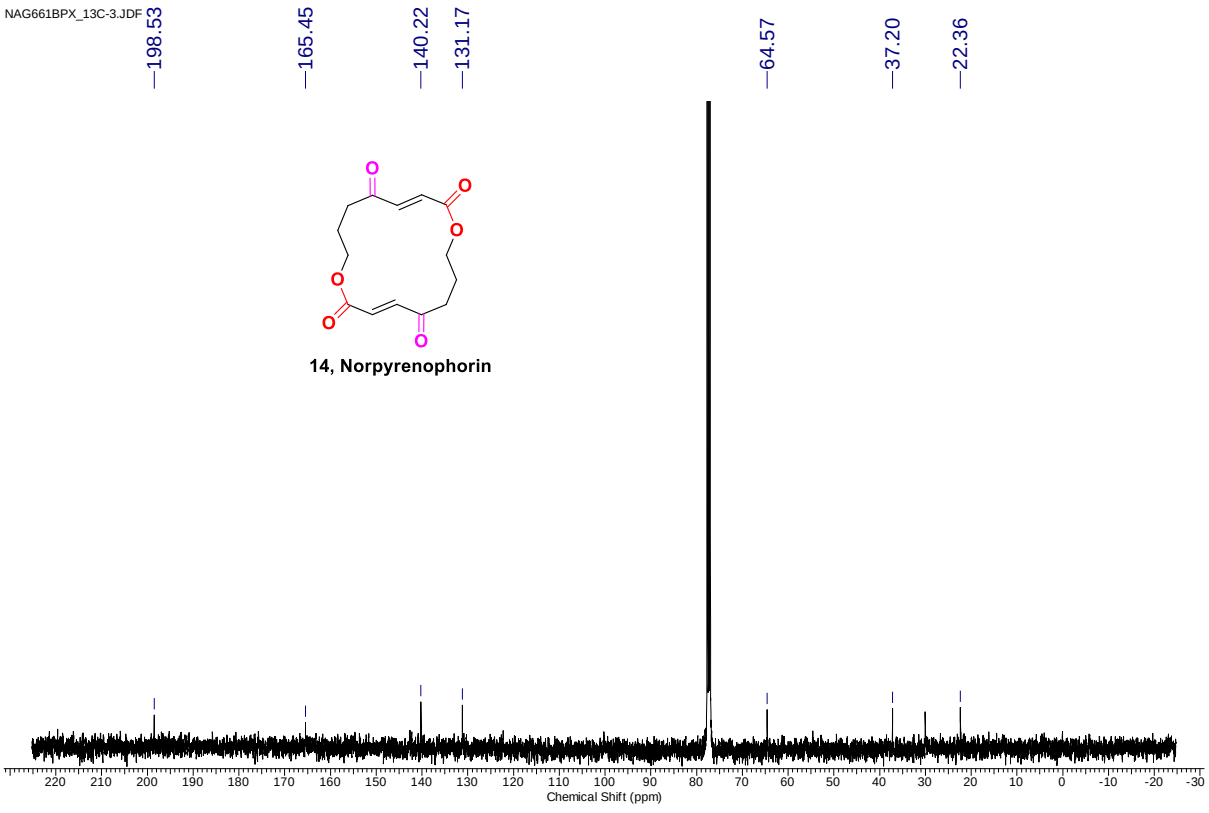


21


NAG659_1H-9.JDF
6.75
6.71
6.09
6.05
4.00
3.98
3.96
3.89
3.88
3.87
3.74
3.64
3.63
3.61
2.03
1.86
1.84
1.82
1.69
1.68
1.66
1.64
HO
O
OMe
O
O
22
0.97
0.98
2.11
2.16
3.03
2.34
0.98
2.42
2.43
Chemical Shift (ppm)


NAG659_13C-1.JDF
166.58
146.29
121.52
108.09
64.88
62.52
51.76
34.11
26.21
HO
O
OMe
O
O
22
Chemical Shift (ppm)


NAG688B-1H-17.JDF
7.05
7.02
6.70
6.66
4.32
4.31
4.30
2.86
2.85
2.83
2.12
2.11
2.10
2.09
2.07
14, Norpyrenophorin
1.00
0.97
2.41
1.89
2.21
Chemical Shift (ppm)


NAG661BPX_13C-3.JDF
198.53
165.45
140.22
131.17
64.57
37.20
22.36
14, Norpyrenophorin
Chemical Shift (ppm)

4. References

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