Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

$Hg(OAc)_2$ mediated highly regio- and/or diastereoselective allylic *tert*-acetylation of olefins

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1. General Information

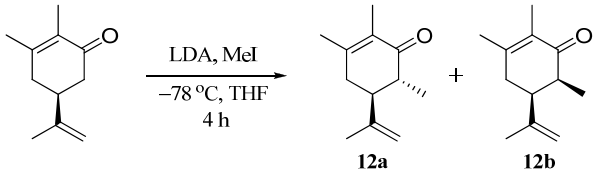
All reactions were carried out under nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise mentioned. All the chemicals were purchased commercially, and used without further purification. Anhydrous THF and diethyl ether were distilled from sodium-benzophenone and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically pure material, unless otherwise stated. Reaction 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 *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.

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. NMR spectra were recorded on Bruker Avance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) in $CDCl_3$ having TMS 0.03% as internal standard. Mass spectrometric data were obtained using WATERS-Q-T of Premier-ESI-MS.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet.

2. Experimental Procedures

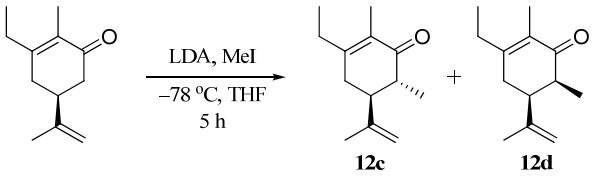
Synthesis of compound 12a and 12b:



To a cold (–78 °C), magnetically stirred solution of diisopropylamine (1.3 mL, 9.15 mmol) in anhydrous THF (10 mL) was slowly added a solution of *n*-BuLi (1.6 M in hexane, 4.6 mL, 7.32 mmol) over a period of 5 min and stirred for 10 min. To LDA thus formed was added drop wise a solution of (*S*)-2,3-dimethyl-5-(prop-1-en-2-yl)cyclohex-2-enone (600 mg, 3.66 mmol) in anhydrous THF (5 mL) over a period of 25 min. and stirred for 1.5 h at the same temperature. The enolate was then treated with methyl iodide (0.9 mL, 14.64 mmol) and stirred for 3 h at rt. The reaction mixture was then diluted with water (15 mL) and extracted with ethyl acetate (2 × 30 mL). The combined organic extract was washed with brine and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using EtOAc-hexane (2:98) as eluent furnished compound **12a** (360 mg, 55%) as a colorless oil; R_f = 0.5 (EtOAc-hexane 1:12); **IR** (neat): ν_{max}/cm^{-1} 2969, 2929, 1664, 1643, 1377; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.83-4.75 (m, 2H), 2.55-2.37 (m, 2H), 2.30-2.15 (m, 2H), 1.91 (s, 3H), 1.76 (s, 3H), 1.70 (s, 3H), 1.04 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 201.3, 153.1, 146.2, 130.4, 113.4, 49.9, 43.6, 38.1, 21.6, 18.1, 13.3, 11.6; **HRMS**: m/z calcd. for $C_{12}H_{19}O$ $[M+H]^+$: 179.1436; found: 179.1436.

Further elution with same solvent system furnished compound **12b** (161 mg, 25%) as a colorless oil; R_f = 0.4 (EtOAc-hexane 1:12); **IR** (neat): ν_{max}/cm^{-1} 2969, 1662, 1635, 1378; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.91 (s, 1H), 4.74 (s, 1H), 2.70-2.62 (m, 2H), 2.57-2.49 (m, 1H), 2.23 (dd, *J* = 18 Hz and 3.8 Hz, 1H), 1.95 (s, 3H), 1.77 (br. s, 3H), 1.69 (br. s, 3H), 0.9 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 203.3, 153.9, 145.5, 129.3, 111.5, 43.9, 42.4, 33.2, 22.2, 21.9, 11.4, 11.0; **HRMS**: m/z calcd. for $C_{12}H_{19}O$ $[M+H]^+$: 179.1436; found: 179.1439.

Synthesis of compound 12c and 12d:



To a cold (–78 °C), magnetically stirred solution of diisopropylamine (1 mL, 7 mmol) in anhydrous THF (10 mL) was slowly added a solution of *n*-BuLi (1.6 M in hexane, 3.6 mL, 5.8 mmol) over a period of 5 min and stirred for 10 min. To LDA thus formed was added drop wise a solution of (*S*)-3-ethyl-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enone (500 mg, 2.8 mmol) in anhydrous THF (5 mL) over a period of 25 min. and stirred for 1.5 h at the same temperature. The enolate was then treated with methyl iodide (0.7 mL, 11.6 mmol) and stirred for 4 h at rt. The reaction mixture was then diluted with water (15 mL) and extracted with ethyl acetate (2 × 30 mL). The combined organic extract was washed with brine and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using EtOAc-hexane (1:99) as eluent furnished compound **12c** (298 mg, 56%) as a colorless oil; R_f = 0.5 (EtOAc-hexane 1:12); **IR** (neat): ν_{max}/cm^{-1} 2969, 2933, 1664, 1640, 1375; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.79 (br. s, 2H), 2.46-2.35 (m, 2H), 2.27-2.15 (m, 4H), 1.75 (s, 3H), 1.68 (s, 3H), 1.07-1.01 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 201.8, 153.8, 146.2, 129.6, 113.4, 50.1, 43.8, 35.6, 28.4, 18.5, 13.3, 12.0, 11.0; **HRMS**: m/z calcd for $C_{13}H_{21}O$ $[M+H]^+$: 193.1592; found: 193.1590.

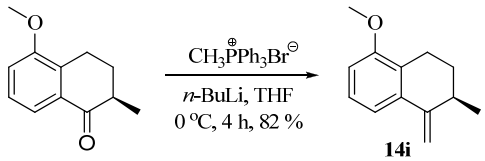
Further elution with same solvent system furnished compound **12d** (137 mg, 25%) as a colorless oil; R_f = 0.4 (EtOAc-hexane 1:12); **IR** (neat): ν_{max}/cm^{-1} 2969, 2934, 1664, 1632; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.91 (s, 1H), 4.75 (s, 1H), 2.68-2.61 (m, 2H), 2.55-2.46 (m, 1H), 2.35-2.23 (m, 3H), 1.78 (s, 3H), 1.70 (s, 3H), 1.09 (t, *J* = 7.8 Hz, 3H), 0.90 (d, *J* = 6.7Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 203.7, 159.2, 145.6, 128.5, 111.5, 44.1, 42.4, 30.6, 28.6, 22.2, 12.1, 11.0, 10.8; **HRMS**: m/z calcd. for $C_{13}H_{21}O$ $[M+H]^+$: 193.1592; found: 193.1594.

General procedure for one carbon Wittig reaction

To a cold (0 °C), magnetically stirred solution of methyltriphenylphosphoniumbromide (2 eq.) in anhydrous THF was slowly added a solution of *n*-BuLi (1.6 M in hexane, 1.8 eq.) over a period of 5 min and stirred for 15 min, followed by dropwise addition of ketone (1 eq.) dissolved in THF and further stirred for 1-5 h at the same temperature. The reaction mixture was then

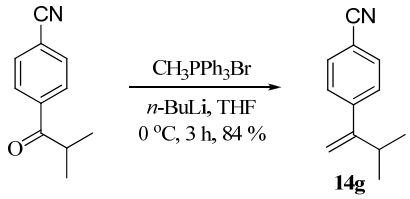
quenched with saturated solution of Ammonium Chloride, diluted with water (20 mL) and extracted with ethyl acetate (2 × 30 mL). The combined organic extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel column using EtOAc-hexane furnished the product.

Synthesis of compound 14i:



According to the general procedure for the Wittig reaction, methyltriphenylphosphoniumbromide (1.87 g, 5.36 mmol), *n*-BuLi (1.6 M in hexane, 2.95 mL, 4.73 mmol) and 5-methoxy-2-methyl-3,4-dihydronaphthalen-1(2H)-one (500 mg, 2.63 mmol) were used to furnish product **14i** (408 mg, 82%), as a colorless liquid; R_f = 0.8 (EtOAc-hexane 1:8); **IR** (neat): ν_{max}/cm^{-1} 2928, 2835, 1574, 1471, 1276, 1064; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8 Hz, 1H), 7.15 (t, *J* = 8 Hz, 1H), 6.75 (d, *J* = 8 Hz, 1H), 5.47 (s, 1H), 5.01 (s, 1H), 3.84 (s, 3H), 2.84 (td, *J* = 5.7 Hz, 17.6 Hz, 1H), 2.76-2.70 (m, 1H), 2.59-2.52 (m, 1H), 2.01-1.95 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 157.5, 149.5, 136.7, 126.4, 125.9, 117.5, 108.8, 107.1, 55.7, 35.3, 31.1, 22.1, 19.2; **HRMS**: m/z calcd. for $C_{13}H_{16}O$ $[M]^{+\cdot}$: 188.1201; found: 188.1204.

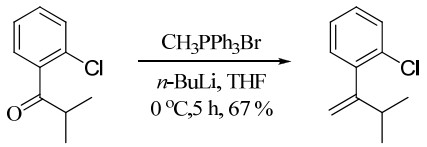
Synthesis of compound 14g:



According to the general procedure for the Wittig reaction, methyltriphenylphosphoniumbromide (1.2 g, 3.35 mmol), *n*-BuLi (1.6 M in hexane, 1.9 mL, 3 mmol) and 4-isobutyrylbenzonitrile (290 mg, 1.67 mmol) were used to furnish product **14g** (240 mg, 84%), as a colorless liquid; R_f = 0.7 (EtOAc-hexane 1:10); **IR** (neat): ν_{max}/cm^{-1} 2965, 2227, 1605, 1503, 906, 850; **^{1}H NMR** (500

MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 5.20 (s, 1H), 5.15 (s, 1H), 2.80 (sep, *J* = 6.5 Hz, 1H), 1.08 (d, *J* = 6.5Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 154.6, 147.8, 132.3, 127.6, 119.3, 112.9, 111.0, 32.4, 22.1; **HRMS**: m/z calcd. for $C_{12}H_{13}N$ $[M]^{+\cdot}$:171.1044; found: 171.1048.

Synthesis of compound 14f:



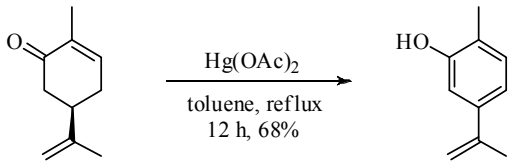
14f

According to the general procedure for the Wittig reaction, methyltriphenylphosphoniumbromide (1.05 g, 11.53 mmol), *n*-BuLi (1.6 M in hexane, 6.5 mL, 10.36 mmol) and 1-(2-chlorophenyl)-2-methylpropan-1-one (1.05 g, 5.75 mmol) were used to furnish product **14f** (698 mg, 67%), as a colorless liquid; R_f = 0.9 (EtOAc-hexane 1:10); **IR** (neat): ν_{max}/cm^{-1} 2963, 2871, 1633, 1471, 1044, 906, 764, 746; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.39-7.35 (m, 1H), 7.23-7.18 (m, 2H), 7.17-7.13 (m, 1H), 5.23 (s, 1H), 4.94 (s, 1H), 2.71 (sep, *J* = 6.8 Hz, 1H), 1.09 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 155.0, 142.9, 132.7, 130.9, 129.8, 128.3, 126. 6, 112.7, 34.0, 21.7; **HRMS**: m/z calcd. for $C_{11}H_{13}Cl$ $[M]^+$: 180.0706; found: 180.0704.

<u>General procedure for allylic oxidation of olefins by Mercury(II)Acetate.</u>

To a magnetically stirred solution of olefin, in toluene (30 mL) was added Mercury(II)acetate (1.2 eq.) (**#Caution: Mercury(II)acetate is highly toxic, handle with care**) and refluxed for 1-12 h. The reaction was monitored by TLC, and after completion of the reaction, the reaction mixture was filtered through celite. Evaporation of the solvent and purification of the residue on a neutral alumina column chromatography afforded corresponding acetate.

Synthesis of compound 3:

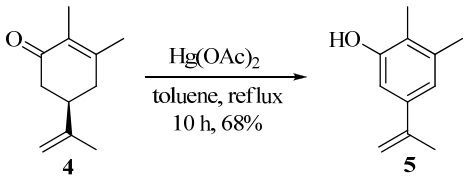


1 **3**

According to the general procedure for Mercury(II)acetate oxidation, carvone **1** (100 mg, 0.66 mmol), Mercury(II)acetate (254 mg, 0.79 mmol) were used to furnish compound **3** (67 mg, 68%), as a colorless liquid; R_f = 0.5 (EtOAc-hexane 1:10).

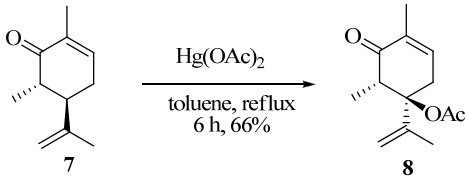
Data were consistent with those previously reported.[1]

Synthesis of compound 5:



According to the general procedure for Mercury(II)acetate oxidation, compound **4** (100 mg, 0.61 mmol), Mercury(II)acetate (232 mg, 0.73 mmol) were used to furnish compound **5** (67 mg, 68%) as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:10); **IR** (neat): ν_{max}/cm^{-1} 3401 (br.), 2956, 1580, 1451, 1301, 1073, 853; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.88 (s, 1H), 6.74 (s, 1H), 5.30 (s, 1H), 5.01 (br. s, 1H), 4.75 (br. s, 1H), 2.28 (s, 3H), 2.15 (s, 3H), 2.10 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.7, 143.2, 139.7, 138.3, 122.1, 120.1, 110.3, 22.1, 22.6, 11.7; **HRMS**: m/z calcd. for $C_{11}H_{15}O$ $[M+H]^+$: 163.1123; found: 163.1126.

Synthesis of compound 8:

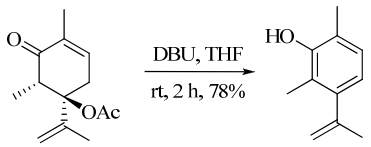


According to the general procedure for Mercury(II)acetate oxidation, compound **7** (100 mg, 0.61 mmol), Mercury(II)acetate (232 mg, 0.73 mmol) were used to furnish compound **8** (89 mg, 66%), as a colorless liquid; R_f = 0.3 (EtOAc-hexane 1:10); $[\alpha]_D^{20}$ −26.3 (*c* 0.3, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 2975, 2926, 1740, 1678, 1633, 1226, 1244, 1023; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.50 (br. s, 1H), 5.10 (br. s, 1H), 5.03 (br. s, 1H), 3.40 (dd, *J* = 5.8 Hz, 19.2 Hz, 1H), 2.81 (td, *J* = 2.3 Hz, 19.2 Hz, 1H), 2.68 (q, *J* = 7.3 Hz, 1H), 1.90 (s, 3H), 1.79 (br. s, 3H), 1.68 (s, 3H), 0.93 (d, *J*

1] Al-Hassan and Mohammed I., *Synthetic Communications*, 1989, **19**, 453.

= 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 201.6, 170.0, 143.1, 139.4, 133.6, 114.5, 88.3, 49.5, 27.9, 20.1, 18.5, 16.0, 12.7; **HRMS**: m/z calcd. for $C_{13}H_{18}NaO_3$ $[M+Na]^+$: 245.1154; found: 245.1159.

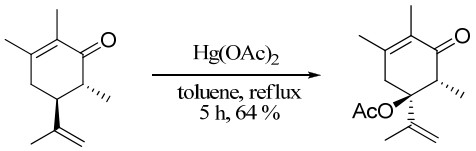
Synthesis of compound 6:



8 **6**

To a magnetically stirred solution of compound **8** (80 mg, 0.36 mmol) in THF was added DBU (650 µL, 0.43 mmol) at room temperature. The reaction was continued at same temperature for 2 h, after the completion of reaction, shown by TLC, quenched by ice cold water and extracted with ethyl acetate (2 × 30 mL). The combined organic extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel column using EtOAc-hexane (1:33) as eluent furnished compound **6** (46 mg, 78%) as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:10); **IR** (neat): ν_{max}/cm^{-1} 3573 (br.), 2965, 2924, 1569, 1445, 1414, 1189, 1046, 898, 814; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.95 (d, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.3 Hz, 1H), 5.19 (br. s, 1H), 4.83 (s, 1H), 4.68 (s, 1H), 2.25 (s, 3H), 2.22 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 152.5, 146.1, 143.7, 128.0, 121.7, 120.2, 120.1, 115.1, 25.0, 16.2, 12.9; **HRMS**: m/z calcd. for $C_{11}H_{15}O$ $[M+H]^+$: 163.1123; found: 163.1125.

Synthesis of compound 13a:

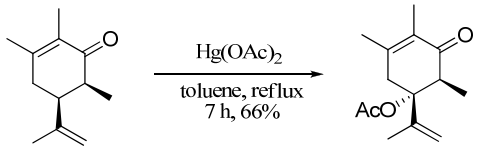


12a **13a**

According to the general procedure for Mercury(II)acetate oxidation, compound **12a** (100 mg, 0.56 mmol), Mercury(II)acetate (214 mg, 0.67 mmol) were used to furnish compound **13a** (85 mg, 64%), as a colorless liquid; R_f = 0.5 (EtOAc-hexane 1:9); $[\alpha]_D^{20}$ +121 (*c* 0.33, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 2925, 1740, 1668, 1367, 1232, 1192, 1022; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.12

(s, 1H), 5.05 (s, 1H), 3.38 (d, *J* = 18.4 Hz, 1H), 2.91 (d, *J* = 18.4 Hz, 1H), 2.68 (q, *J* = 7.3 Hz, 1H), 4.08-4.04 (m, 1H), 1.94 (s, 3H), 1.91 (s, 3H), 1.80 (s, 3H), 1.70 (s, 3H), 0.94 (d, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 201.0, 170.2, 149.1, 143.1, 128.7, 114.4, 87.4, 48.7, 34.7, 22.2, 21.6, 18.5, 13.0, 11.2; **HRMS**: m/z calcd. for $C_{14}H_{20}NaO_3$ $[M+Na]^+$: 259.1310; found: 259.1308.

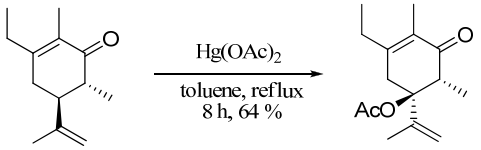
Synthesis of compound *ent*-13a:



12b ***ent*-13a**

According to the general procedure for Mercury(II)acetate oxidation, compound **12b** (100 mg, 0.56 mmol), Mercury(II)acetate (214 mg, 0.67 mmol) were used to furnish compound ***ent*-13a** (88 mg, 66%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:9); $[\alpha]_D^{20}$ −127 (*c* 0.3 in $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 2926, 1740, 1667, 1368, 1232, 1192, 1023; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.12 (s, 1H), 5.05 (s, 1H), 3.38 (d, *J* = 18.4 Hz, 1H), 2.91 (d, *J* = 18.4 Hz, 1H), 2.68 (q, *J* = 7.3 Hz, 1H), 4.08-4.04 (m, 1H), 1.94 (s, 3H), 1.91 (s, 3H), 1.80 (s, 3H), 1.70 (s, 3H), 0.94 (d, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 201.0, 170.2, 149.1, 143.1, 128.7, 114.4, 87.4, 48.7, 34.7, 22.2, 21.6, 18.5, 13.0, 11.2; **HRMS**: m/z calcd. for $C_{14}H_{20}NaO_3$ $[M+Na]^+$: 259.1310; found: 259.1306.

Synthesis of compound 13c:

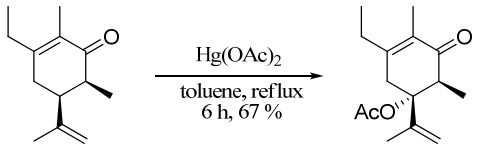


12c **13c**

According to the general procedure for Mercury(II)acetate oxidation, compound **12c** (100 mg, 0.52 mmol), Mercury(II)acetate (198 mg, 0.62 mmol) were used to furnish compound **13c** (83 mg, 64%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:9); $[\alpha]_D^{20}$ +189 (*c* 0.33, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 2924, 1739, 1668, 1367, 1231; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.12 (s, 1H), 5.05 (s, 1H), 3.42 (d, *J* = 18.8 Hz), 2.8 (dd, *J* = 18.8 Hz and 2.1 Hz, 1H), 2.66 (dq, *J* = 7.7 Hz and

1.5 Hz, 1H), 2.43-2.35 (m, 1H), 2.16-2.10 (m, 1H), 1.90 (s, 3H), 1.80 (s, 3H), 1.70 (s, 3H), 1.03 (t, J = 7.5 Hz, 3H), 0.94 (d, J = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 201.5, 170.1, 154.6, 143.3, 128.0, 114.3, 87.5, 48.7, 31.9, 28.3, 22.1, 18.5, 13.0, 11.9, 10.6; **HRMS**: m/z calcd. for $C_{15}H_{22}NaO_3$ $[M+Na]^+$: 273.1467; found: 273.1472.

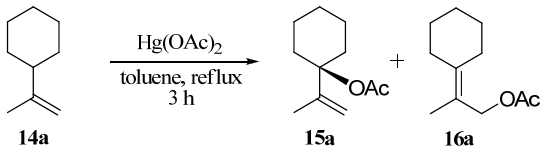
Synthesis of compound *ent*-13c:



12d ***ent*-13c**

According to the general procedure for Mercury(II)acetate oxidation, compound **12d** (100 mg, 0.52 mmol), Mercury(II)acetate (199 mg, 0.62 mmol) were used to furnish compound ***ent*-13c** (87 mg, 67%), as a colorless liquid; R_f = 0.35 (EtOAc-hexane 1:9); $[\alpha]_D^{20}$ −193 (*c* 0.30, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 2926, 1740, 1668, 1366, 1232; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.12 (s, 1H), 5.05 (s, 1H), 3.42 (d, J = 18.8 Hz), 2.8 (dd, J = 18.8 Hz and 2.1 Hz, 1H), 2.66 (dq, J = 7.7 Hz and 1.5 Hz, 1H), 2.43-2.35 (m, 1H), 2.16-2.10 (m, 1H), 1.90 (s, 3H), 1.80 (s, 3H), 1.70 (s, 3H), 1.03 (t, J = 7.5 Hz, 3H), 0.94 (d, J = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 201.5, 170.1, 154.6, 143.3, 128.0, 114.3, 87.5, 48.7, 31.9, 28.3, 22.1, 18.5, 13.0, 11.9, 10.6; **HRMS**: m/z calcd. for $C_{15}H_{22}NaO_3$ $[M+Na]^+$: 273.1467; found: 273.1470.

Synthesis of compound 15a and 16a:

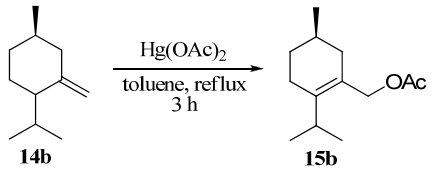


14a **15a** **16a**

According to the general procedure for MercuryII)acetate oxidation, compound **14a** (80 mg, 0.64 mmol), Mercury(II)acetate (246 mg, 0.77 mmol) were used to furnish product **15a** and **16a** (5:1) as a inseparable mixture (79 mg, 67%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:19); **IR** (neat): ν_{max}/cm^{-1} 2931, 2855, 1740, 1260, 1231, 1017; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.89 (s, 1H), 4.87 (s, 1H), 4.59 (s, 0.77H), 2.32-2.27 (m, 2H), 2.23-2.17 (m, 2H), 2.05 (s, 1.18H), 2.04 (s,

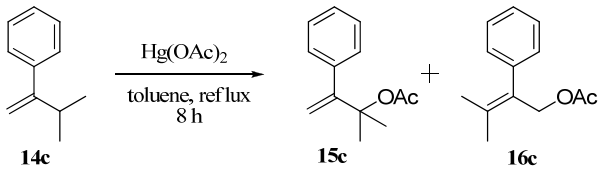
3H), 1.72 (s, 3H), 1.71 (s, 1.18H), 1.69-1.63 (m, 1.27H), 1.58-1.41 (m, 9H), 1.26-1.19 (m, 1.46H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.8, 170.1, 148.7, 140.8, 119.7, 110.6, 84.0, 65.7, 34.5, 31.2, 30.9, 28.6, 28.1, 27.1, 25.8, 22.2, 21.5, 19.0, 16.7; **HRMS**: m/z calcd. for $C_{11}H_{18}NaO_2$ $[M+Na]^+$: 205.1204; found: 205.1202.

Synthesis of compound 15b:



According to the general procedure for Mercury(II)acetate oxidation, compound **14b** (200 mg, 1.31 mmol), Mercury(II)acetate (502 mg, 1.58 mmol) were used to furnish product **15b** (196 mg, 71%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:19); **IR** (neat): ν_{max}/cm^{-1} 3384, 2922, 2822, 1740, 1596, 1232, 1019; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.61 (d, *J* = 12.1 Hz, 1H), 4.49 (d, *J* = 12.1 Hz, 1H), 2.89 (sep, *J* = 6.9 Hz, 1H), 2.13-2.07 (m, 1H), 2.05 (s, 3H), 1.98-1.91 (m, 1H), 1.73-1.56 (m, 4H), 1.14-1.06 (m, 1H), 0.93 (d, *J* = 6.9 Hz, 6H), 0.94 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.8, 142.8, 123.7, 64.7, 37.4, 31.4, 29.6, 29.0, 23.9, 22.2, 21.7, 21.5; **HRMS**: m/z calcd. for $C_{13}H_{22}NaO_2$ $[M+Na]^+$: 233.1517; found: 233.1516.

Synthesis of compound 15c and 16c:



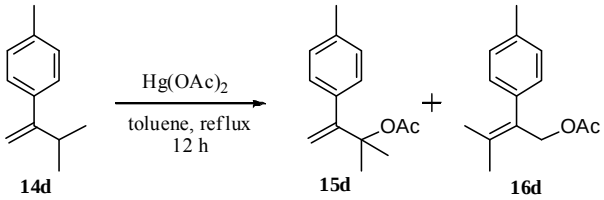
According to the general procedure for Mercury(II)acetate oxidation, compound **14c** (100 mg, 0.68 mmol), Mercury(II)acetate (261 mg, 0.82 mmol) were used to furnish product **15c** (89 mg, 64%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:18).

Data were consistent with those previously reported.[1]

1] J. Jacques, C. Weidmann-Hattier, and A. Horeau, *Bulletin de la Societe Chimique de France*, 1959, 424.

Further elution with same solvent system furnished **16c** (9 mg, 6%) as a colorless oil; R_f = 0.3 (EtOAc-hexane 1:18); **IR** (neat): ν_{max}/cm^{-1} 2916, 1738, 1229, 1022; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.32 (t, *J* = 7.4 Hz, 2H), 7.25-7.21 (m, 1H), 7.14 (d, *J* = 6.8 Hz, 2H), 4.85 (s, 2H), 1.98 (s, 3H), 1.92 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.5, 141.8, 136.3, 130.3, 129.3, 128.4, 126.8, 65.6, 22.9, 21.3, 20.7; **HRMS**: m/z calcd. for $C_{13}H_{20}NO_2$ $[M+NH_4]^+$: 222.1494; found: 222.1497.

Synthesis of compound 15d and 16d:

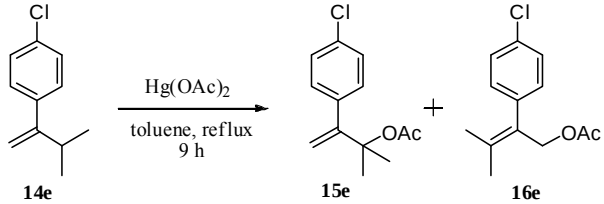


14d **15d** **16d**

According to the general procedure for Mercury(II)acetate oxidation, 1-methyl-4-(3-methylbut-1-en-2-yl)benzene (**14d**) (100 mg, 0.62 mmol), Mercury(II)acetate (238 mg, 0.75 mmol) were used to furnish product **15d** (95 mg, 70%), as a colorless liquid; R_f = 0.5 (EtOAc-hexane 1:10); **IR** (neat): ν_{max}/cm^{-1} 2982, 2926, 1739, 1248; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.5 Hz, 2H), 7.10 (d, 8.5 Hz, 2H), 5.31 (s, 1H), 5.06 (s, 1H), 2.34 (s, 3H), 1.91 (s, 3H), 1.64 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.3, 153.7, 138.2, 137.0, 128.8, 128.7, 114.1, 82.4, 28.1, 22.6, 21.4; **HRMS**: m/z calcd. for $C_{12}H_{15}$ $[M-CH_3COO^-]^+$: 159.1168; found:159.1178.

Further elution with same solvent system furnished **16d** (11 mg, 8%) as a colorless oil; R_f = 0.4 (EtOAc-hexane 1:10); **IR** (neat): ν_{max}/cm^{-1} 2922, 1738, 1228, 1021; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.3 Hz, 2H), 7.03 (d, 8.3 Hz, 2H), 4.84 (s, 2H), 2.34 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H), 1.64 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.6, 138.9, 136.3, 136.1, 130.1, 129.2, 129.1, 65.7, 22.9, 21.5, 21.4, 20.7; **HRMS**: m/z calcd. for $C_{12}H_{15}$ $[M-CH_3COO^-]^+$: 159.1168; found: 159.1183.

Synthesis of compound 15e and 16e:

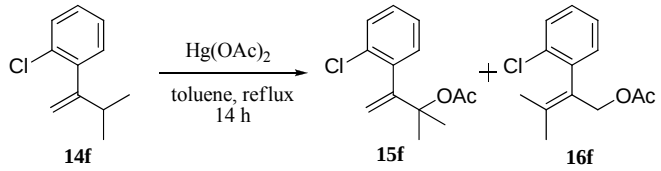


14e **15e** **16e**

According to the general procedure for Mercury(II)acetate oxidation, 1-chloro-4-(3-methylbut-1-en-2-yl)benzene **(14e)** (100 mg, 0.55 mmol), Mercury(II)acetate (211 mg, 0.66 mmol) were used to furnish product **15e** (87 mg, 66%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:20); **IR** (neat): ν_{max}/cm^{-1} 2983, 1737, 1488, 1365, 1249, 1015, 854; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.33 (s, 1H), 5.07 (s, 1H), 1.88 (s, 3H), 1.62 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.2, 152. 9, 139.5, 133.4, 130.2, 128.2, 115.0, 82.1, 28.2, 22.5; **HRMS**: m/z calcd. for $C_{13}H_{15}ClNaO_2$ $[M+Na]^+$: 261.0658; found: 261.0659.

Further elution with the same solvent system furnished **16e** (9 mg, 7%) as a colorless oil; R_f = 0.3 (EtOAc -hexane 1:20); **IR** (neat): ν_{max}/cm^{-1} 2916, 1738, 1228, 1092, 1015; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.81 (s, 2H), 1.96 (s, 3H), 1.90 (s, 3H), 1.61 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.4, 140.1, 136.9, 132.6, 130.7, 129.3, 128.6, 65.2, 22.8, 21.3, 20.7; **HRMS**: m/z calcd. for $C_{13}H_{15}ClNaO_2$ $[M+Na]^+$: 261.0658; found: 261.0656.

Synthesis of compound 15f and 16f:



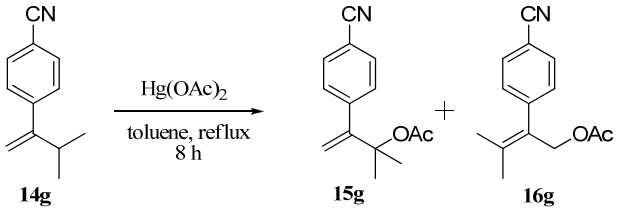
14f **15f** **16f**

According to the general procedure for Mercury(II)acetate oxidation, 1-chloro-2-(3-methylbut-1-en-2-yl)benzene **(14f)** (100 mg, 0.55 mmol), Mercury(II)acetate (211 mg, 0.66 mmol) were used to furnish product **15f** (92 mg, 70%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:20); **IR** (neat): ν_{max}/cm^{-1} 2983, 2930, 1738, 1365, 1247, 1138; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.40-7.36 (m, 1H), 7.35-7.31 (m, 1H), 7.23-7.18 (m, 2H), 5.58 (s, 1H), 5.08 (s, 1H), 2.00 (s, 3H), 1.62 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.4, 150.2, 139.9, 133.5, 132.0, 129.7, 128.7, 126.3, 117.2, 82.7, 27.3, 22.8; **HRMS**: m/z calcd. for $C_{11}H_{14}Cl$ $[M-CH_3CO_2H]^+$: 178.0549; found: 175.0548.

Further elution with same solvent system furnished **16f** (9 mg, 7%) as a colorless oil; R_f = 0.3 (EtOAc-hexane 1:20); **HPLC purity**: 99.86%; **IR** (neat): ν_{max}/cm^{-1} 2920, 2852, 1739, 1373, 1226, 1021, 745; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.38-7.34 (m, 1H), 7.24-7.17 (m, 2H), 7.12-

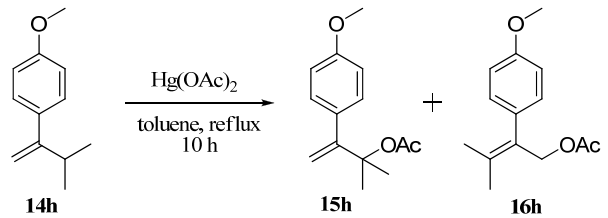
7.08 (m, 1H), 4.92 (d, *J* = 11.8 Hz, 1H), 4.75 (d, *J* = 11.8 Hz, 1H), 1.95 (s, 3H), 1.94 (s, 3H), 1.51 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.4, 140.1, 137.7, 134.0, 131.6, 129.7, 128.5, 127.8, 126.8, 64.4, 22.5, 21.3, 20.2; **HRMS**: m/z calcd. for $C_{11}H_{14}Cl$ $[M\text{-}CH_3CO_2H]^+$: 178.0549; found: 175.0556.

Synthesis of compound 15g and 16g:



According to the general procedure for Mercury(II)acetate oxidation, 4-(3-methylbut-1-en-2-yl)benzonitrile (**14g**) (100 mg, 0.58 mmol), Mercury(II)acetate (223 mg, 0.7 mmol) were used to furnish product **15g** (99 mg, 74%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:20); **IR** (neat): ν_{max}/cm^{-1} 2985, 2933, 2228, 1735, 1367, 1249, 1136; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 5.40 (s, 1H), 5.12 (s, 1H), 1.86 (s, 3H), 1.63 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.1, 152.8, 146.0, 131.9, 129.6, 119.2, 116.0, 111.3, 81.7, 28.3, 22.4; **HRMS**: m/z calcd. for $C_{12}H_{11}N$ $[M\text{-}CH_3CO_2H]^+$: 154.0651; found: 154.0650.
Further elution with same solvent system furnished **16g** (9 mg, 7%) as a colorless oil; R_f = 0.3 (EtOAc-hexane 1:20); **IR** (neat): ν_{max}/cm^{-1} 2917, 2850, 2227, 1738, 1228, 1021; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.83 (br. s, 2H), 1.96 (s, 6H), 1.93 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.0, 146.6, 137.7, 132.1, 123.0, 128.9, 119.1, 110.5, 64.6, 22.6, 21.0, 20.6; **HRMS**: m/z calcd. for $C_{12}H_{11}N$ $[M\text{-}CH_3CO_2H]^+$: 154.0651; found: 154.0651.

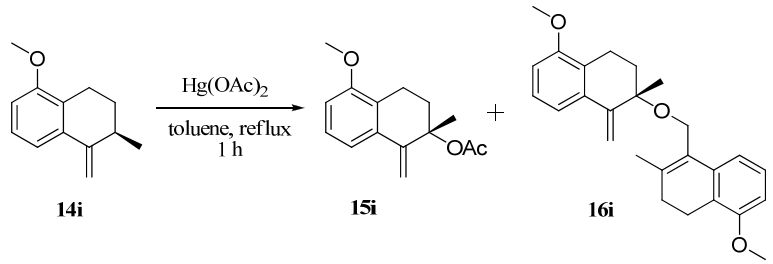
Synthesis of compound 15h and 16h:



According to the general procedure for Mercury(II)acetate oxidation, 1-methoxy-4-(3-methylbut-1-en-2-yl)benzene (**14h**) (100 mg, 0.56 mmol), Mercury(II)acetate (216 mg, 0.68 mmol) were used to furnish product **15h** (84 mg, 64%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:10); **HPLC purity**: 98.32%; **IR** (neat): ν_{max}/cm^{-1} 2981, 2932, 1736, 16.8, 1510, 1247; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9Hz, 2H), 5.29 (s, 1H), 5.05 (s, 1H), 3.80 (s, 3H), 1.89 (s, 3H), 1.63 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.0, 158.7, 153.1, 133.3, 129.7, 113.7, 113.1, 82.3, 55.3, 27.9, 22.3; **HRMS**: m/z calcd. for $C_{14}H_{19}O_3$ $[M+H]^+$: 235.1335; found: 235.1334.

Further elution with same solvent system furnished **16h** (9 mg, 7%) as a colorless oil; R_f = 0.3 (EtOAc-hexane 1:9); **IR** (neat): ν_{max}/cm^{-1} 2916, 2849, 1736, 1510, 1243, 1029; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.05 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.82 (br. s, 2H), 3.80 (s, 3H), 1.97 (s, 3H), 1.90 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.6, 158.4, 136.1, 134.1, 130.4, 129.7, 113.8, 65.7, 55.5, 22.9, 22.4, 20.7; **HRMS**: m/z calcd. for $C_{12}H_{14}O$ $[M-CH_3CO_2H]^+$: 174.1045; found: 174.1041.

Synthesis of compound 15i and 16i:



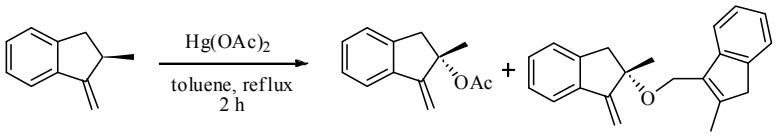
14i **15i** **16i**

According to the general procedure for Mercury(II)acetate oxidation, compound **14i** (100 mg, 0.53 mmol), Mercury(II)acetate (203 mg, 0.64 mmol) were used to furnish product **16i** (13 mg, 12%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:19); **IR** (neat): ν_{max}/cm^{-1} 2926, 1597, 1470, 1305, 1060; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8 Hz, 1H), 6.72 (d, *J* = 8 Hz, 1H), 5.71 (s, 1H), 5.47 (s, 1H), 4.78 (d, *J* = 9.6 Hz, 1H), 3.74 (d, *J* = 9.6 Hz, 1H), 3.83 (s, 3H) 3.81 (s, 3H), 2.9-2.83 (m, 1H), 2.74-2.67 (m, 3H), 2.29-2.24 (m, 1H), 2.20 (t, *J* = 8 Hz, 2H), 1.95 (s, 3H), 1.90-1.85 (m, 1H), 1.53 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 157.2, 156.0, 146.1, 142.2, 137.1, 135.4, 126.8, 126.7, 126.6, 125.0, 123.1, 117.7, 116.6, 111.0, 109.0, 108.9, 81.4,

71.4, 55.9, 55.7, 33.3, 30.6, 23.7, 20.7, 20.5, 20.1; **HRMS**: m/z calcd. for $C_{23}H_{31}O_3$ $[M+H]^+$: 391.2273; found: 391.2278.

Further elution with the same solvent system furnished product **15i** (79 mg, 60%) as a colorless oil; R_f = 0.3 (EtOAc-hexane 1:19); **IR** (neat): ν_{max}/cm^{-1} 2927, 1734, 1576, 1472, 1261, 1059; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.1 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.75 (d, *J* = 8.1Hz, 1H), 5.57 (s, 1H), 5.36 (s, 1H), 3.83 (s, 3H), 2.87-2.80 (m, 1H), 2.77-2.70 (m, 1H), 2.43-2.38 (m, 1H), 2.14-2.08 (m, 1H), 1.93 (s, 3H), 1.72 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.3, 156.8, 146.5, 135.0, 126.7, 124.6, 117.9, 109.2, 108.8, 80.6, 55.4, 33.7, 23.3, 22.4, 20.7; **HRMS**: m/z calcd. for $C_{15}H_{22}NO_3$ $[M+NH_4]^+$: 264.1600; found: 264.1607.

Synthesis of compound 15j and 16j:

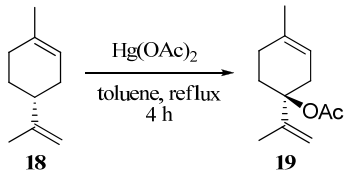


14j **15j** **16j**

According to the general procedure for Mercury(II)acetate oxidation, compound **14j** (100 mg, 0.69 mmol), Mercury(II)acetate (265 mg, 0.83 mmol) were used to furnish product **16j** (5 mg, 9%), as a colorless liquid; R_f = 0.4 (EtOAc-hexane 1:19); **IR** (neat): ν_{max}/cm^{-1} 2877, 1606, 1463, 1101, 1055, 777, 730; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50-7.47 (m, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.26-7.08 (m, 6H), 5.68 (s, 1H), 5.34 (s, 1H), 4.94 (s, 2H), 3.42 (d, *J* = 17.3 Hz, 1H), 3.26 (s, 3H), 2.91 (d, *J* = 17.3 Hz, 1H), 2.05 (s, 3H), 1.55 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 152.3, 146.3, 145.2, 142.6, 142.2, 139.5, 132.0, 129.2, 127.0, 126.5, 125.6, 124.2, 123.5, 121.3, 120.0, 106.6, 89.5, 68.2, 43.4, 42.8, 24.2, 14.5; **HRMS**: m/z calcd. for $C_{22}H_{23}O$ $[M+H]^+$: 303.1749; found: 303.1752.

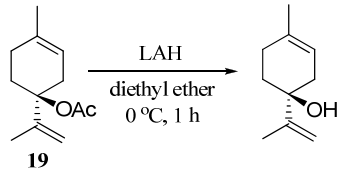
Further elution with same solvent system furnished product **15j** (83 mg, 51%) as a colorless oil; R_f = 0.3 (EtOAc-hexane 1:19); **IR** (neat): ν_{max}/cm^{-1} 2922, 2851, 1732, 1463, 1261, 1165; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 6.5 Hz, 1H), 7.26-7.20 (m, 3H), 5.58 (s, 1H), 5.20 (s, 1H), 3.50 (d, *J* = 18.5 Hz, 1H), 3.21 (d, *J* = 18.5 Hz, 1H), 2.03 (s, 3H), 1.60 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.1, 154.4, 142.0, 138.4, 129.5, 127.3, 125.5, 121.3, 110.5, 86.3, 44.6, 27.5, 22.5; **HRMS**: m/z calcd. for $C_{11}H_{11}NO_3$ $[M-OAc]^+$: 143.0861; found: 143.0856.

Synthesis of compound 19:

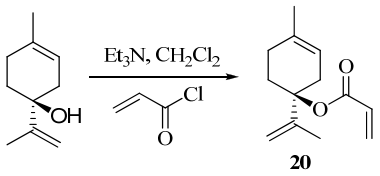


According to the general procedure for Mercury(II)acetate oxidation, limonene **18** (1 g, 7.35 mmol), Mercury(II)acetate (2.81 g, 8.81 mmol) were used to furnish product **19** (980 mg, 69%), as a colorless liquid; R_f = 0.5 (EtOAc-hexane 1:19).
Data were consistent with those previously reported.[1]

Synthesis of compound 20:



To a magnetically stirred solution of compound **19** (500 g, 2.57 mmol) in diethyl ether (10 mL) was added $LiAlH_4$ (98 mg, 2.57 mmol) in 3 portions, at 0 °C, the reaction was continued at same temperature. The reaction was monitored by TLC, and after the completion of reaction, quenched by dropwise addition of ethyl acetate. The reaction mixture was then diluted with water (15 mL) and extracted with ethyl acetate (2 × 30 mL). The combined organic extract was washed with brine, dried (Na_2SO_4) and concentrated in vacuo to afford 4-methyl-1-(prop-1-en-2-yl)cyclohex-3-enol (350 mg, 89%) as a colorless oil; R_f = 0.3 (EtOAc-hexane 1:10). The crude product was used directly for further reaction.

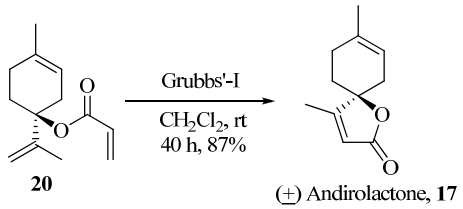


1] A. F. Thomas, W. Bucher, *Helv. Chim. Acta* 1970, **53**, 770.

To a magnetically stirred solution of 4-methyl-1-(prop-1-en-2-yl)cyclohex-3-enol (200 mg, 1.31 mmol) in DCM (10 mL) was added triethylamine (0.9 mL, 6.55 mmol), cooled to 0 ^{o}C, followed by dropwise addition of acryloyl chloride (0.4 mL, 5.26 mmol). The reaction mixture then allowed to come at rt and stirred for 3 hrs at same temperature. Reaction was monitored by TLC, after the completion of reaction, the reaction mixture was diluted with water (15 mL) and extracted with DCM (2 × 30 mL). The combined organic extract was washed with brine and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using EtOAc-hexane (1:10) as eluent furnished product **20** (239 mg, 88%) as a colorless oil; R_f = 0.5 (EtOAc-hexane 1:1)

Data were consistent with those previously reported.[1]

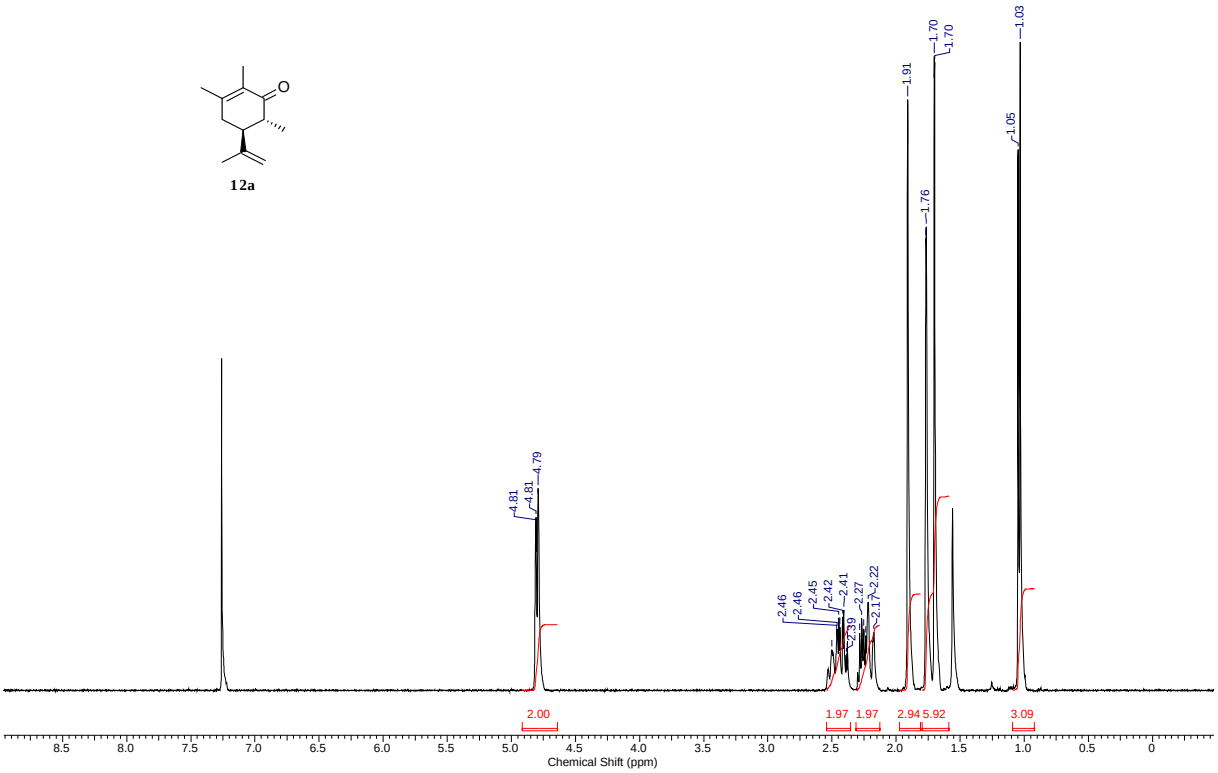
Synthesis of Andirolactone (17):

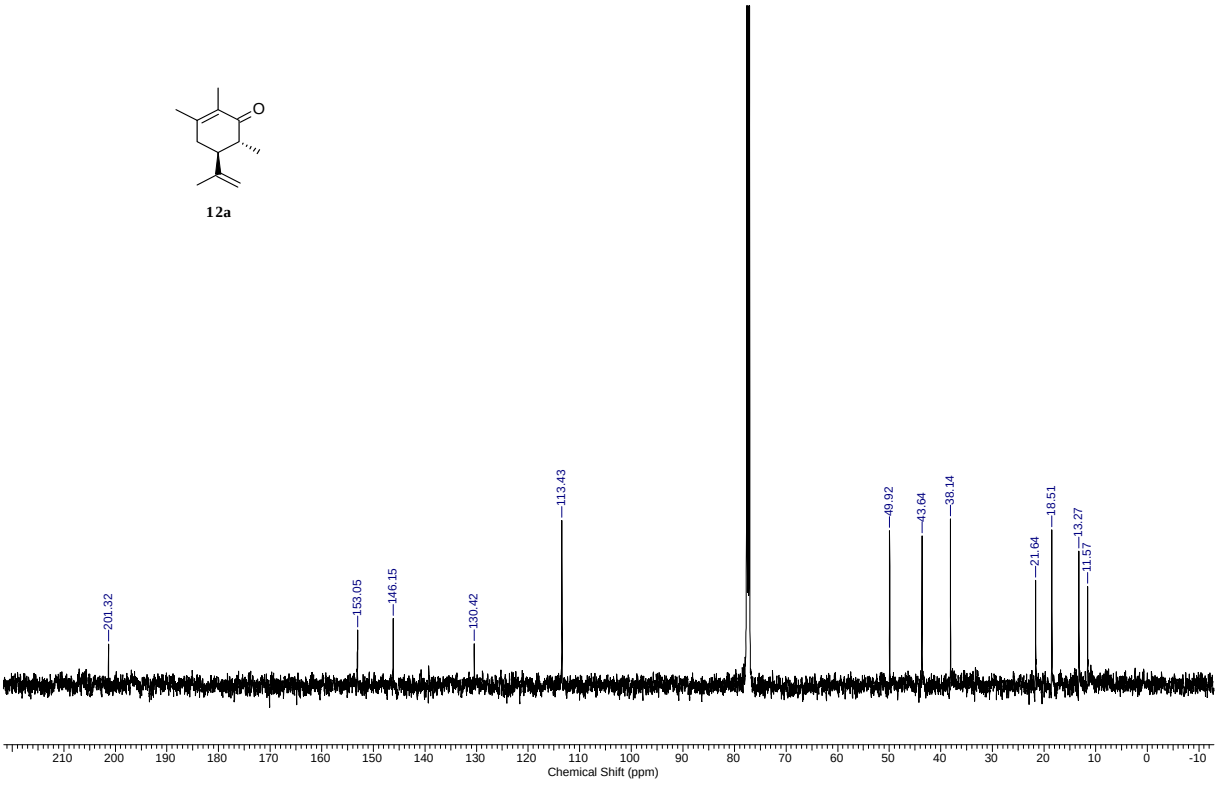


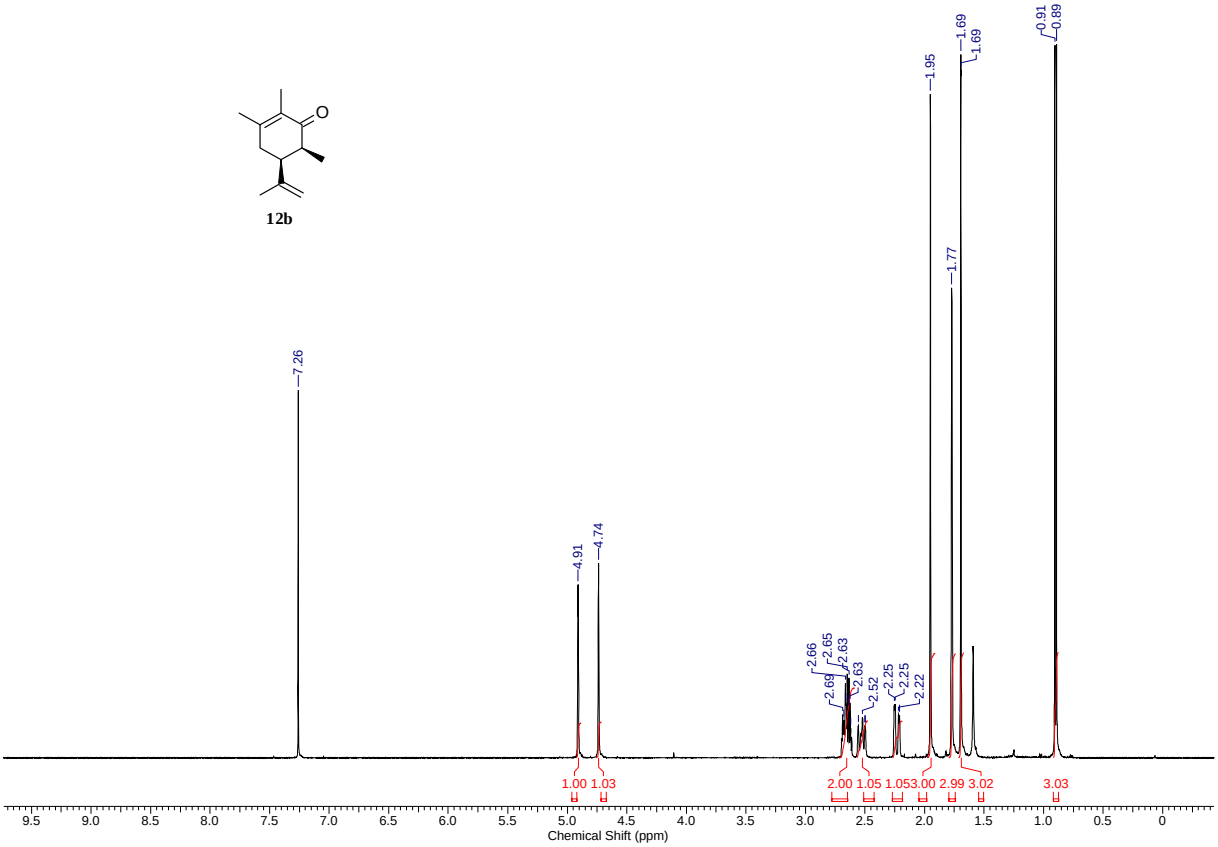
Compound **20** (200 mg, 0.97 mmol) and $Ti(OiPr)_4$ (145 µL, 0.48 mmol, 0.5 eq.) were dissolved in CH_2Cl_2 (25 mL), and the mixture was refluxed for 1 h. The Grubb's first generation catalyst (39 mg, 0.048 mmol) in CH_2Cl_2 (2 mL) was then added, and reflux was continued for 40 h. The mixture was cooled to ambient temperature and filtered through a short pad of silica gel. The solvent was removed in vacuo, and the residue was purified on silica gel column using EtOAc-hexane (1:5) as eluent furnished Andirolactone (**17**) (150 mg, 87%) as a colorless oil; R_f = 0.3 (EtOAc-hexane 1:4); **IR** (neat): ν_{max}/cm^{-1} 2921, 1750, 1437, 962, 939; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.75 (s, 1H), 5.38 (br. s, 1H), 2.52-2.48 (m, 1H), 2.41-2.32 (m, 1H), 2.06 (d, J = 5.5 Hz, 1H), 2.03 (d, J = 1.2 Hz, 3H), 1.96-1.85 (m, 2H), 1.72 (s, 3H), 1.67-1.63 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.6, 172.3, 133.3, 116.5, 116.4, 87.2, 33.1, 29.8, 26.9, 23.3, 13.3; **HRMS**: m/z calcd. for $C_{11}H_{15}O_2$ $[M+H]^+$: 179.1072; found: 179.1076.

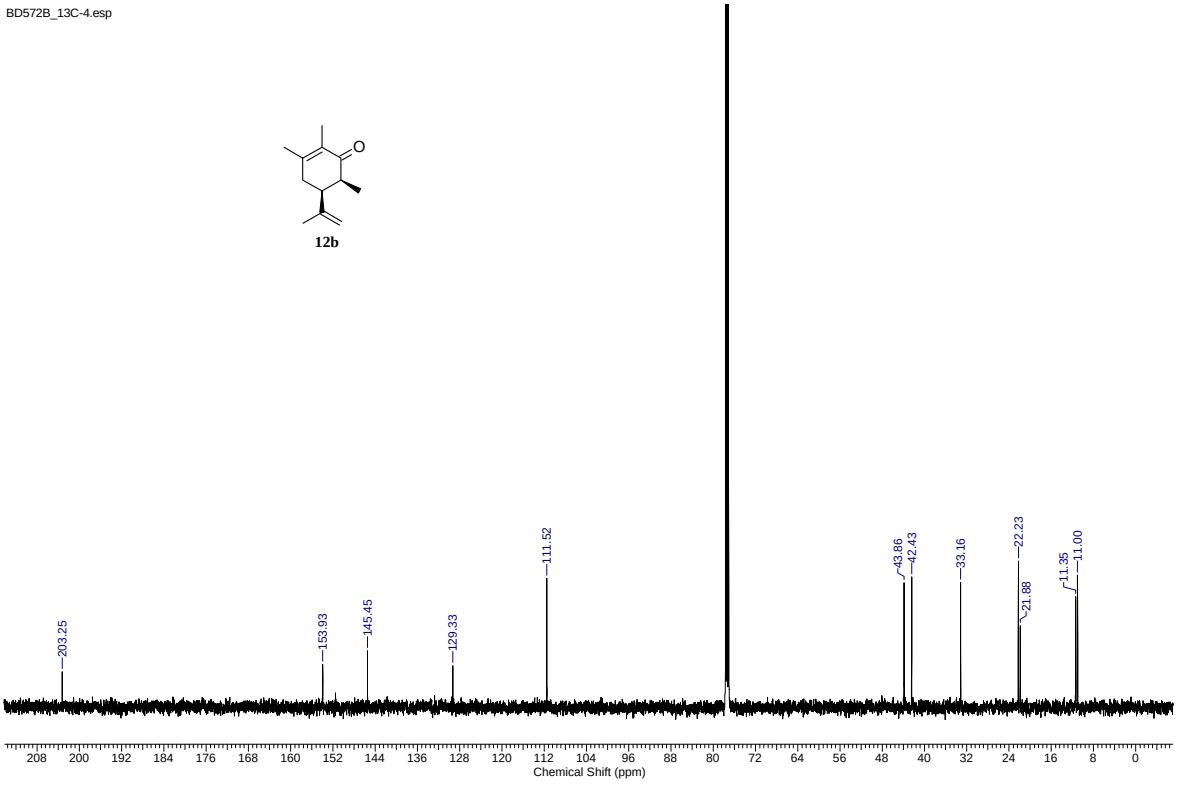
1] Yi Li, Tao Zhang and Yu-Lin Li, *Tetrahedron Lett.*, 2007, **48**, 1503.

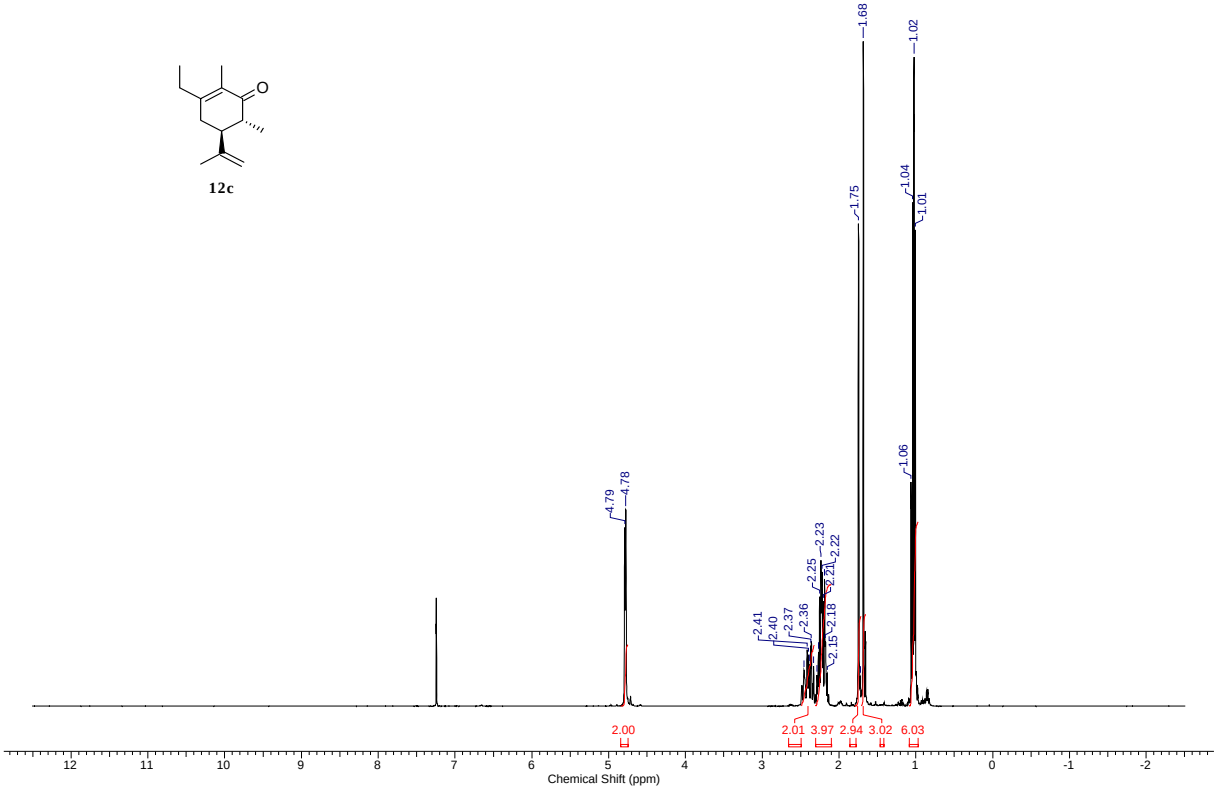
3. NMR Spectras:

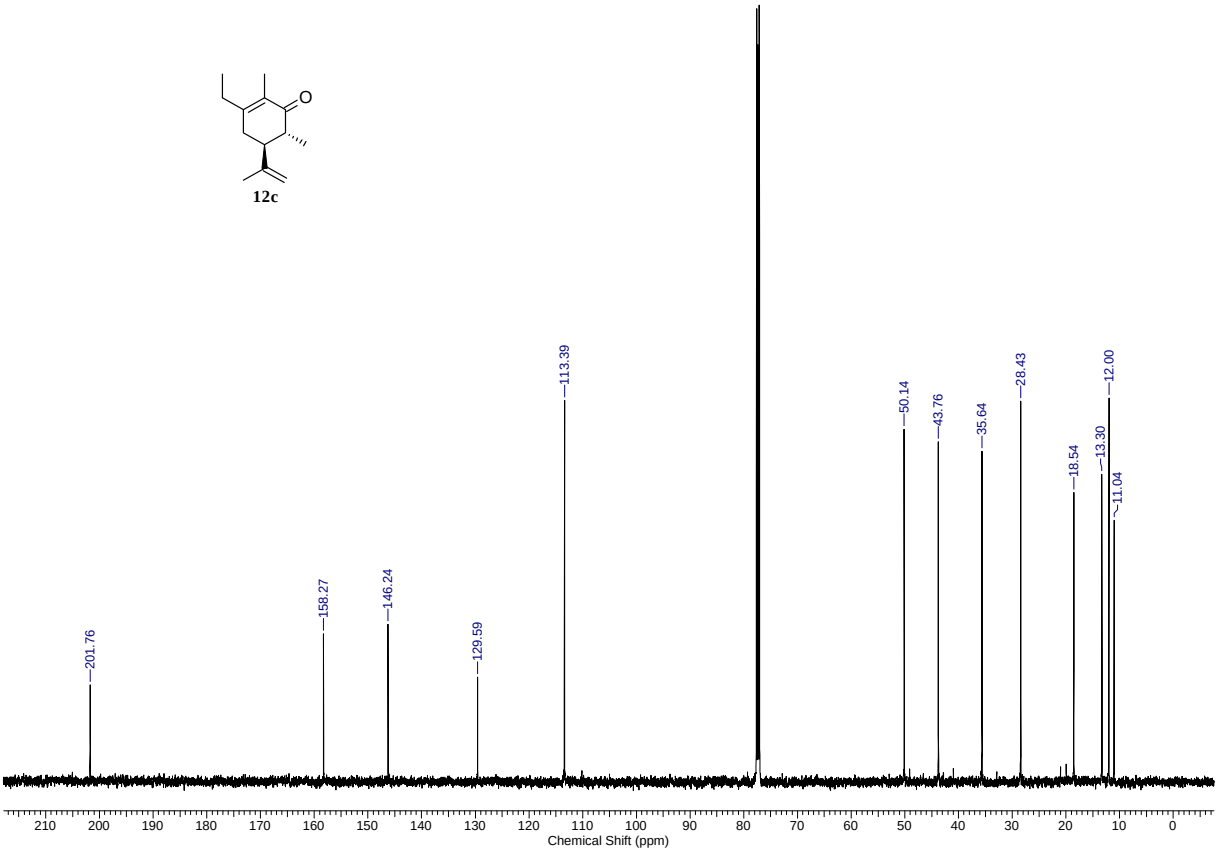


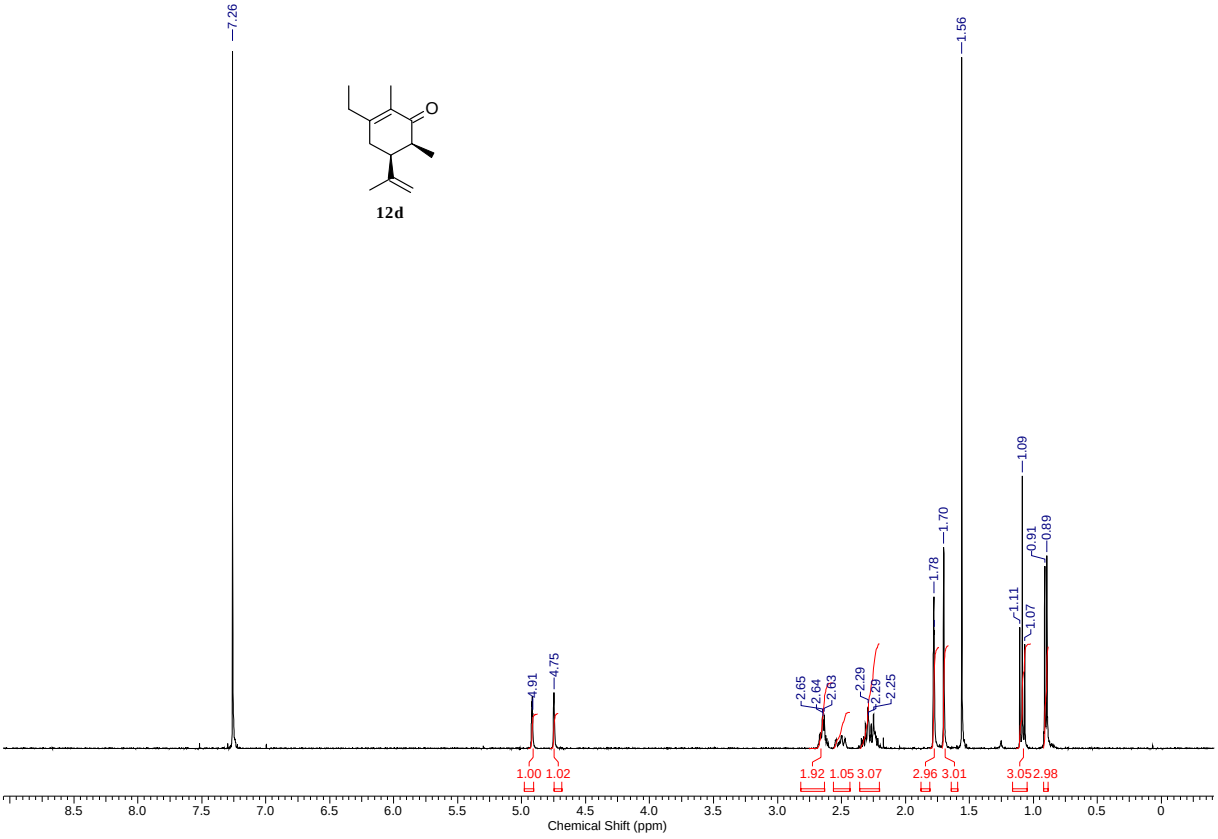



12b
7.26
4.91
4.74
2.66
2.65
2.63
2.63
2.52
2.25
2.25
2.22
1.95
1.69
1.69
1.77
0.91
0.89
1.00 1.03
2.00 1.05 1.05 3.00 2.99 3.02
3.03
Chemical Shift (ppm)

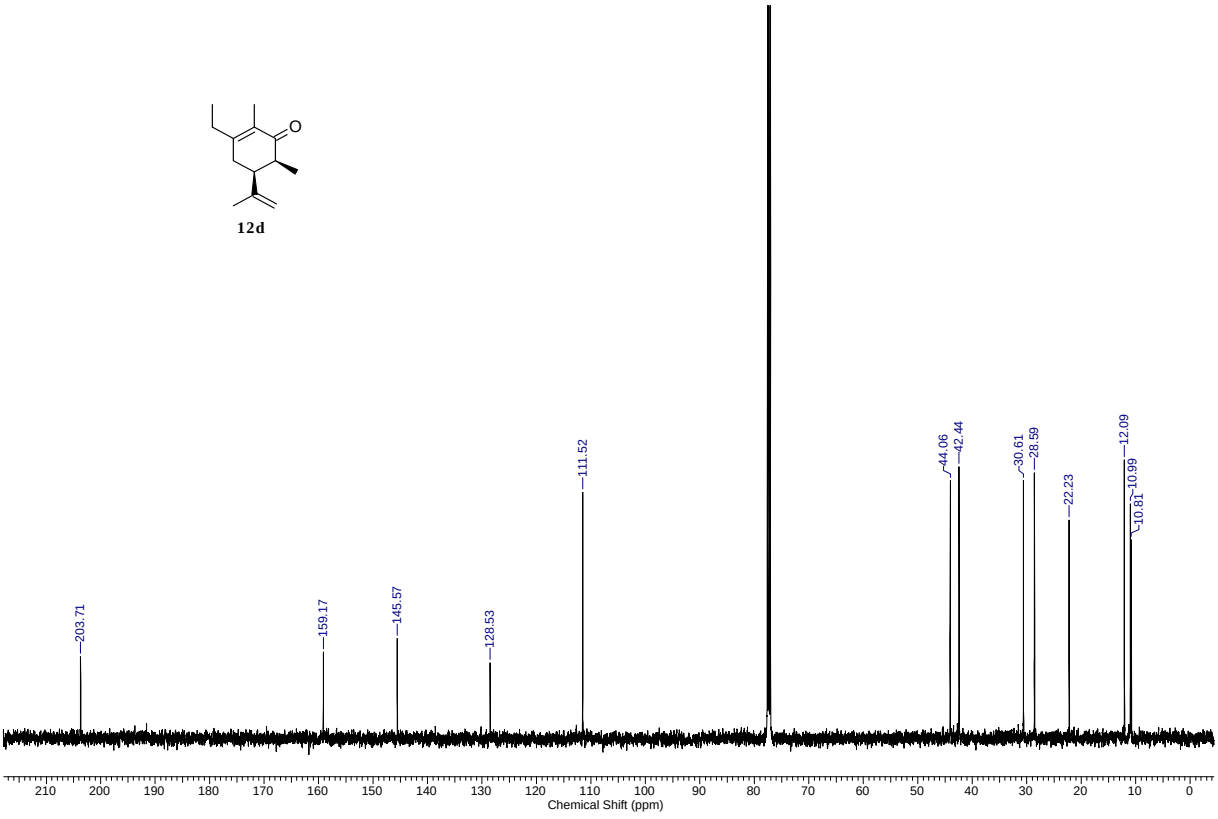

BD572B_13C-4.esp
12b
203.25
153.93
145.45
129.33
111.52
43.86
42.43
33.16
22.23
21.88
11.35
11.00
Chemical Shift (ppm)


12c
1.68
1.02
1.75
1.04
1.01
1.06
4.79
4.78
2.41
2.40
2.37
2.36
2.25
2.23
2.22
2.21
2.18
2.15
2.00
2.01
3.97
2.94
3.02
6.03
Chemical Shift (ppm)

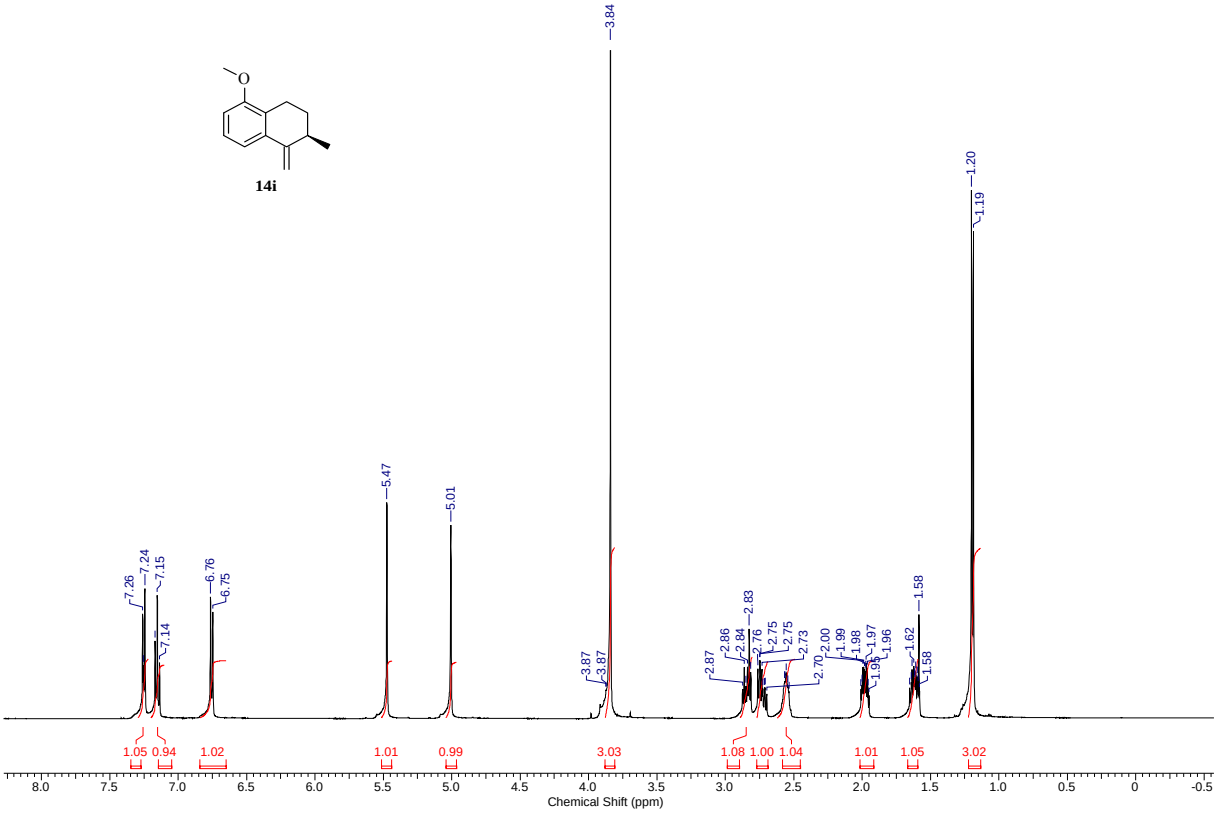

12c
201.76
158.27
146.24
129.59
113.39
50.14
43.76
35.64
28.43
18.54
13.30
12.00
11.04
Chemical Shift (ppm)

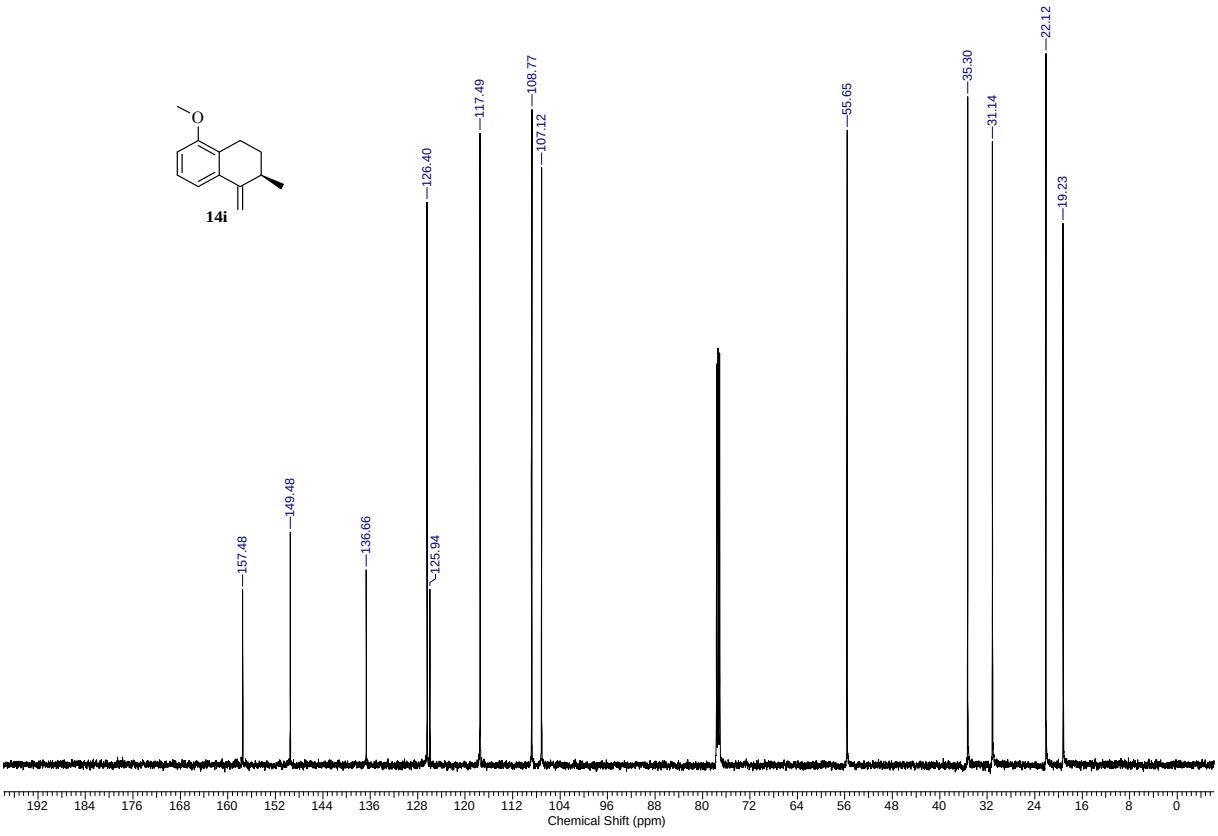

7.26
1.56
1.09
1.70
0.91
0.89
1.78
1.11
1.07
4.91
4.75
2.65
2.64
2.63
2.29
2.29
2.25
1.00 1.02
1.92 1.05 3.07
2.96 3.01
3.05 2.98
Chemical Shift (ppm)

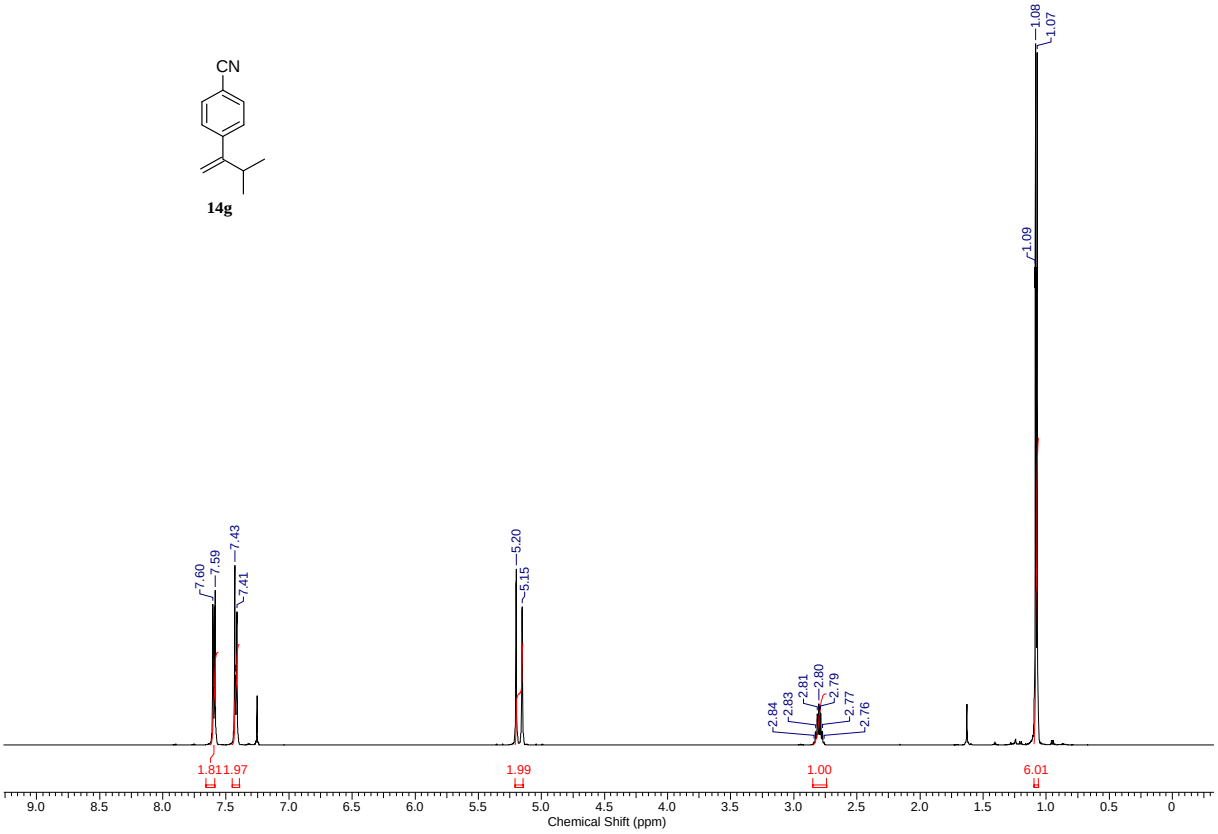
12d

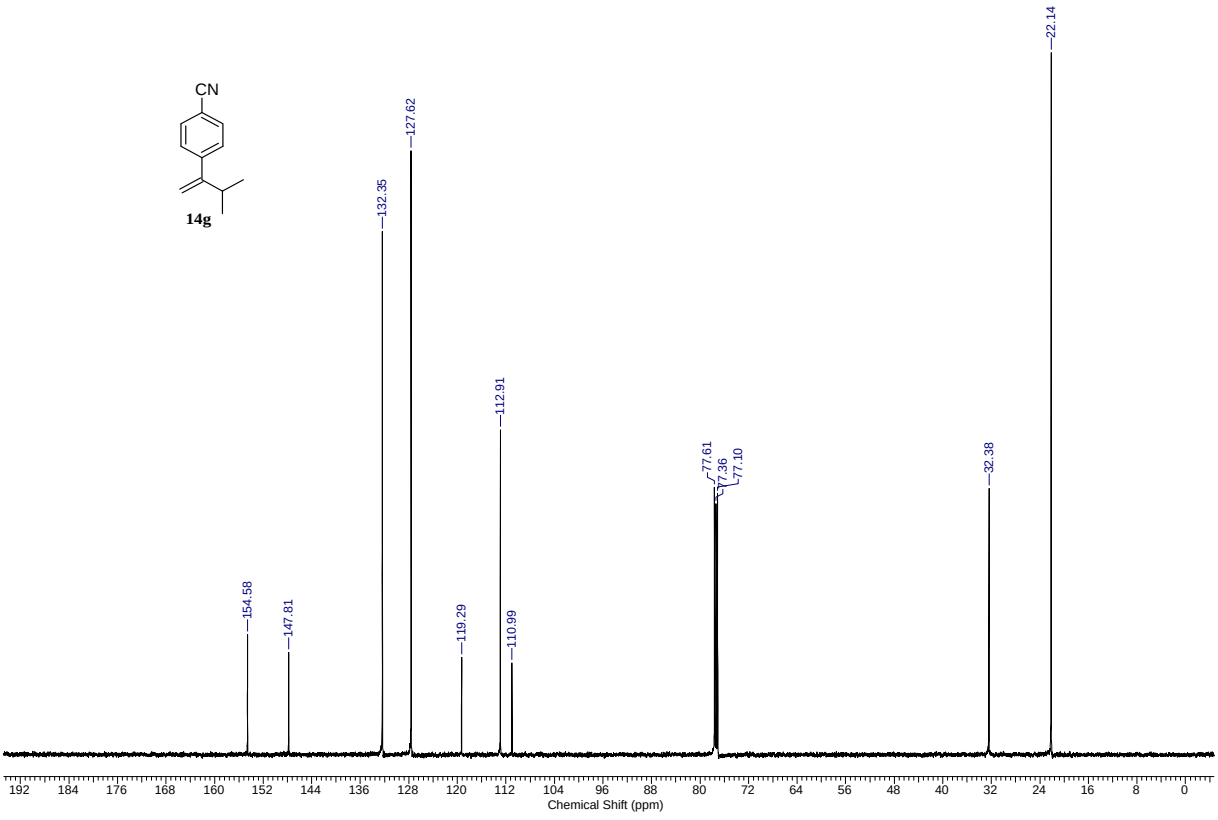

203.71
159.17
145.57
128.53
111.52
44.06
42.44
30.61
28.59
22.23
12.09
10.99
10.81
Chemical Shift (ppm)

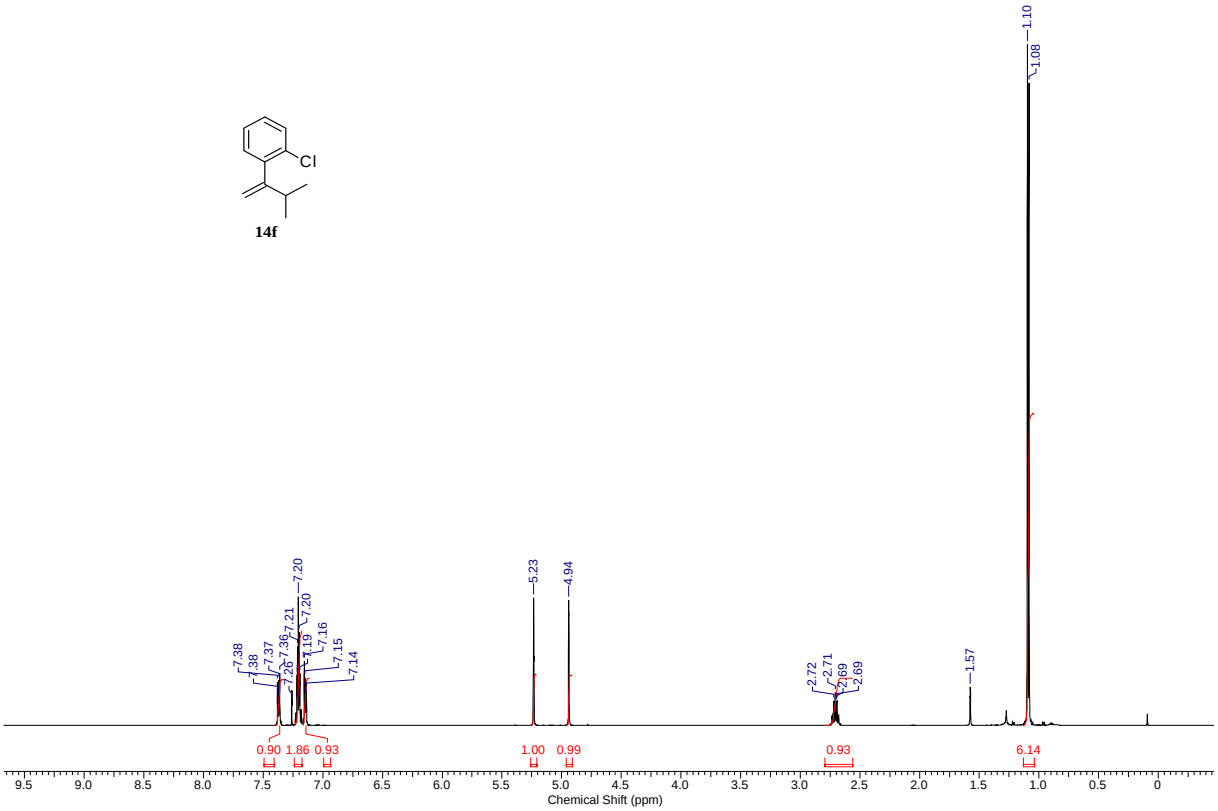
12d

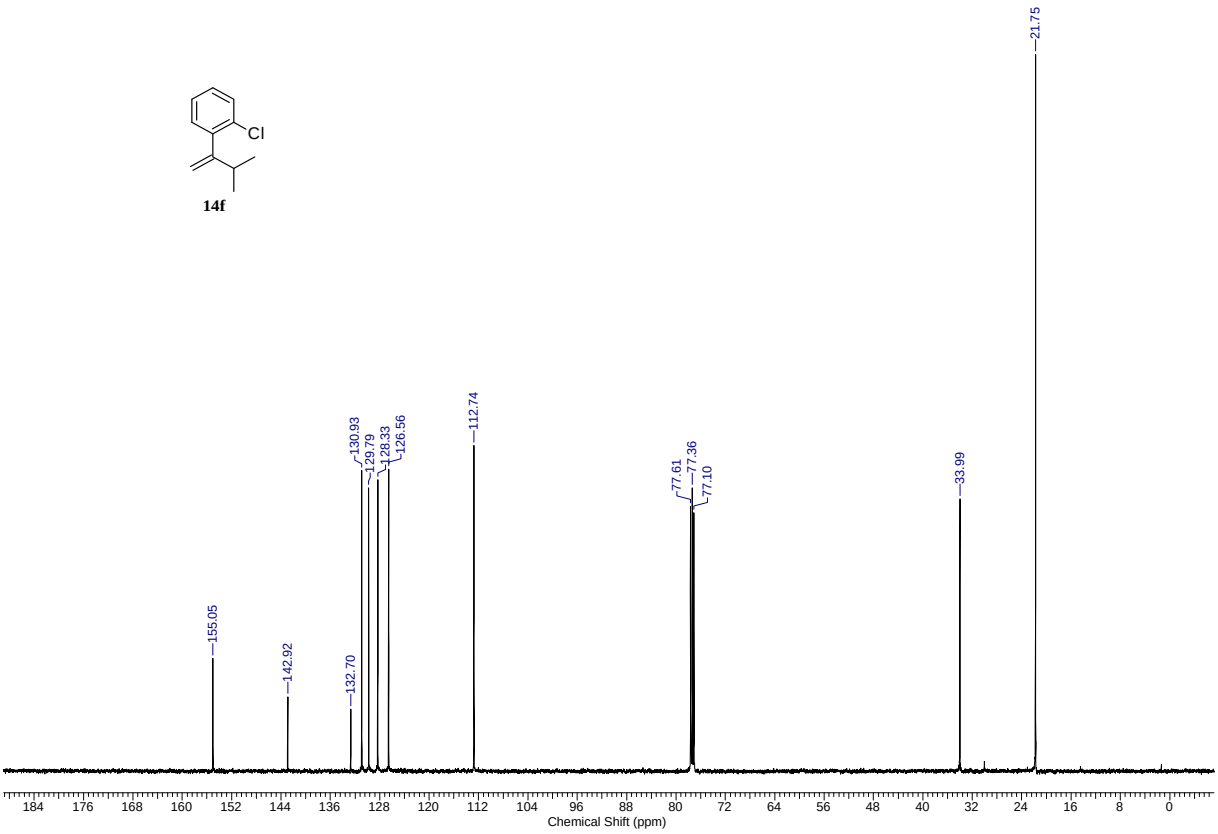

14i
3.84
1.20
1.19
5.47
5.01
7.26
7.24
7.15
6.76
6.75
7.14
3.87
3.87
2.87
2.86
2.84
2.83
2.76
2.75
2.75
2.73
2.70
2.00
1.99
1.98
1.97
1.96
1.94
1.62
1.58
1.58
1.05
0.94
1.02
1.01
0.99
3.03
1.08
1.00
1.04
1.01
1.05
3.02
Chemical Shift (ppm)


14i
157.48
149.48
136.66
126.40
125.94
117.49
108.77
107.12
55.65
35.30
31.14
22.12
19.23
Chemical Shift (ppm)

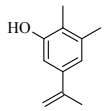

CN
14g
1.08
1.07
1.09
7.60
7.59
7.43
7.41
5.20
5.15
2.84
2.83
2.81
2.80
2.79
2.77
2.76
1.81
1.97
1.99
1.00
6.01
Chemical Shift (ppm)


CN
14g
22.14
132.35
127.62
112.91
77.61
77.36
77.10
32.38
154.58
147.81
119.29
110.99
Chemical Shift (ppm)

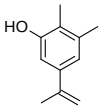

Cl
14f
7.38
7.38
7.37
7.36
7.26
7.21
7.20
7.20
7.19
7.16
7.15
7.14
5.23
4.94
2.72
2.71
2.69
2.69
1.57
1.10
1.08
0.90
1.86
0.93
1.00
0.99
0.93
6.14
Chemical Shift (ppm)


Cl
14f
155.05
142.92
132.70
130.93
129.79
128.33
126.56
112.74
77.61
77.36
77.10
33.99
21.75
Chemical Shift (ppm)

BD822A1_PROTON-4.JDF



5



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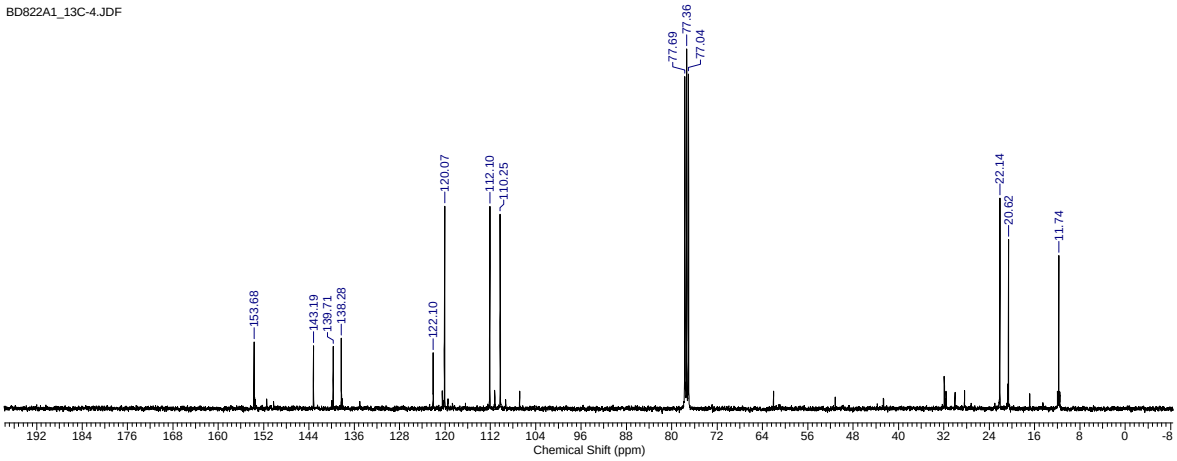
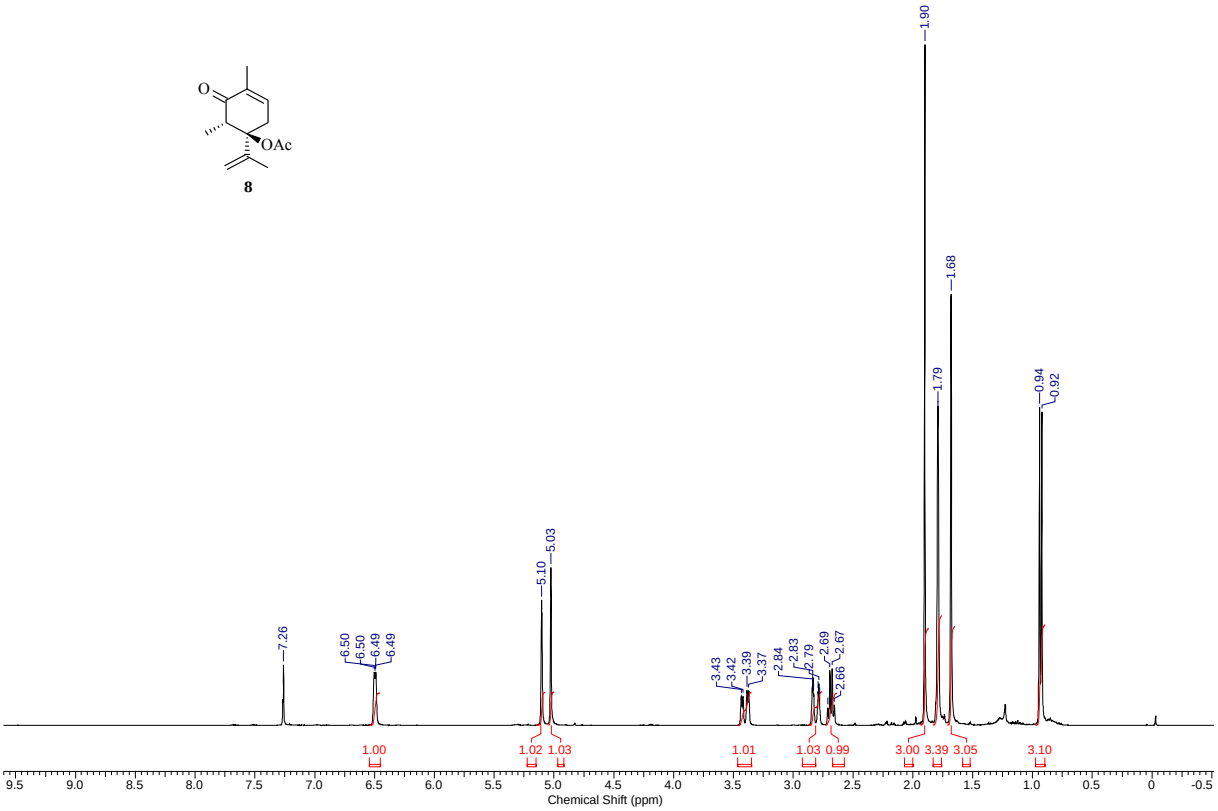
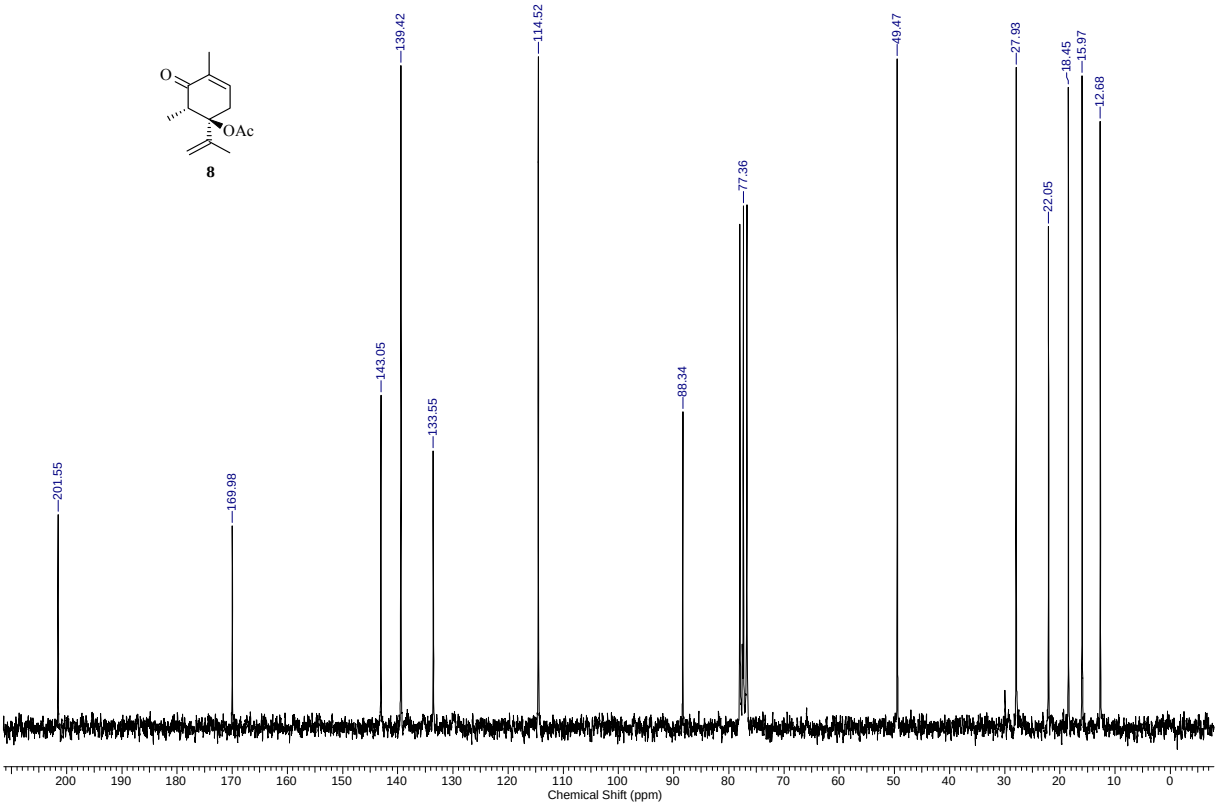
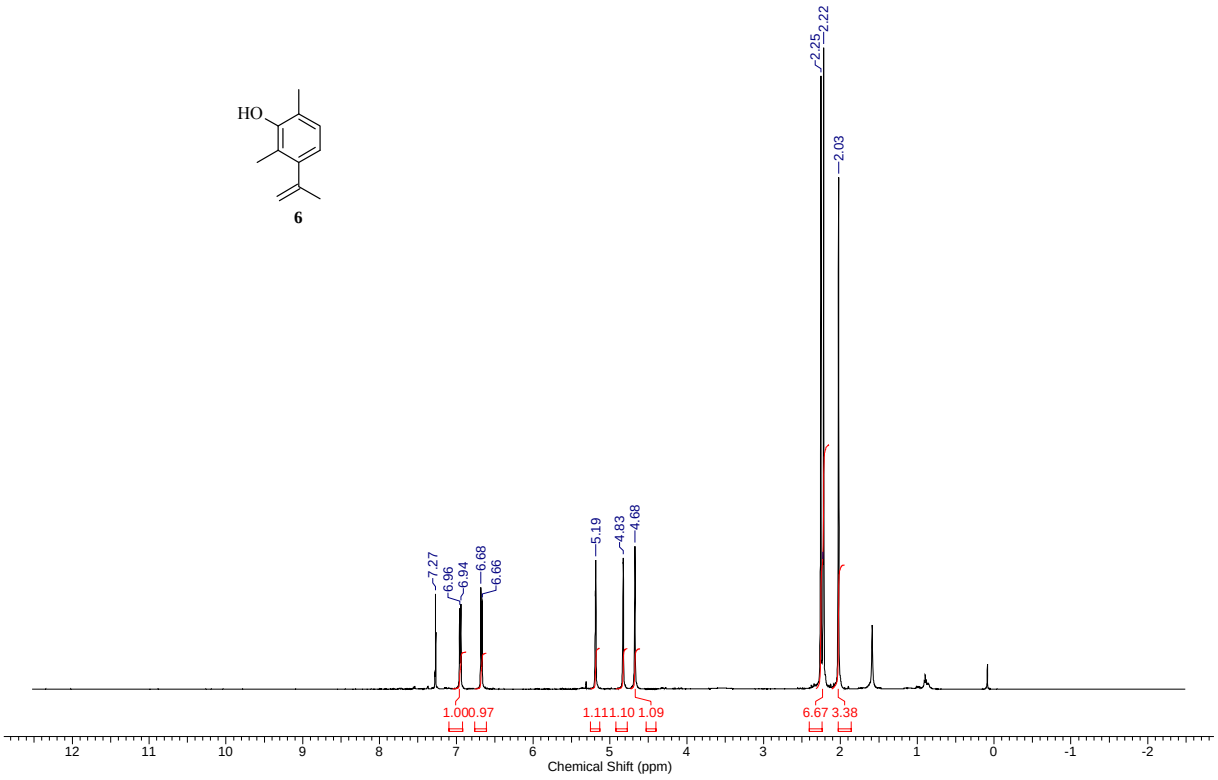
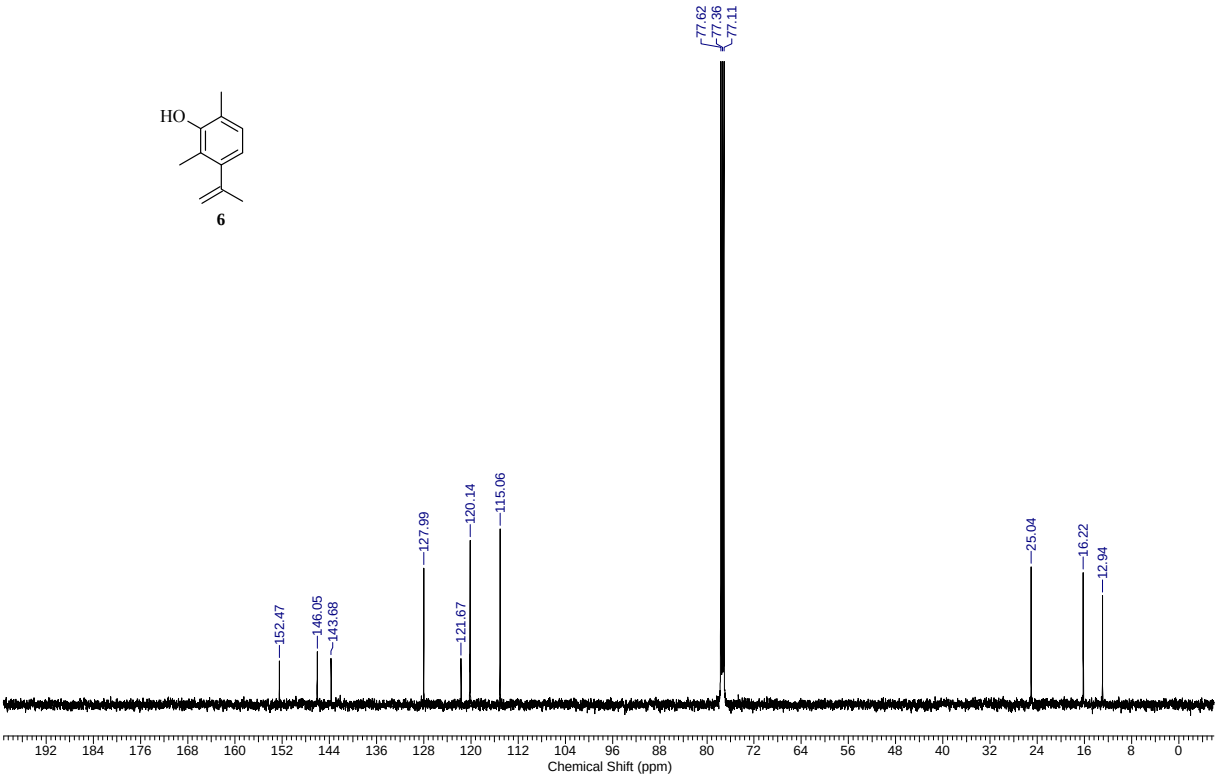
BD822A1_13C-4.JDF




O
OAc
8
1.90
1.68
1.79
0.94
0.92
7.26
6.50
6.50
6.49
6.49
5.10
5.03
3.43
3.42
3.39
3.37
2.84
2.83
2.79
2.69
2.67
2.66
1.00
1.02
1.03
1.01
1.03
0.99
3.00
3.39
3.05
3.10
Chemical Shift (ppm)


O
OAc
8
139.42
114.52
49.47
27.93
18.45
15.97
12.68
77.36
22.05
143.05
133.55
88.34
201.55
169.98
Chemical Shift (ppm)


HO
6
2.25
2.22
2.03
7.27
6.96
6.94
6.68
6.66
5.19
4.83
4.68
1.00 0.97
1.11 1.10 1.09
6.67 3.38
Chemical Shift (ppm)


HO
6
77.62
77.36
77.11
152.47
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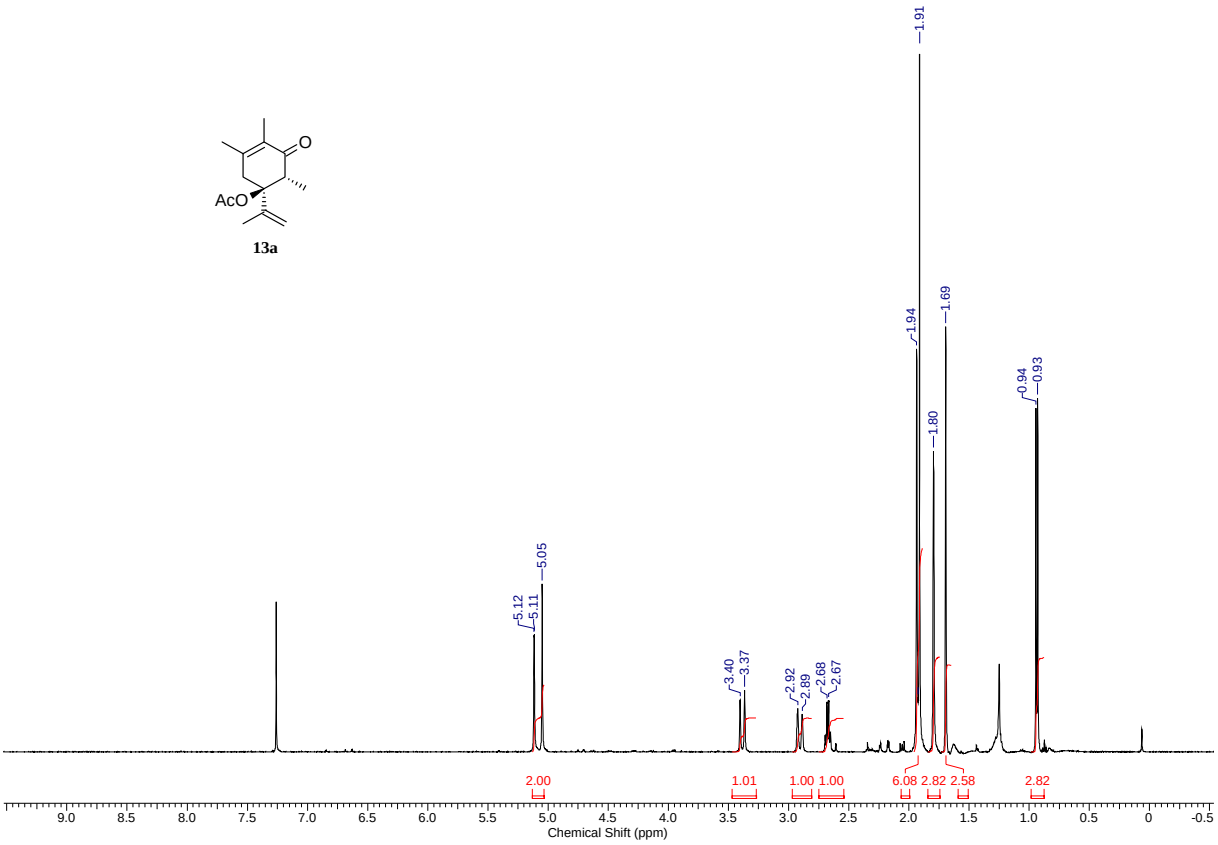
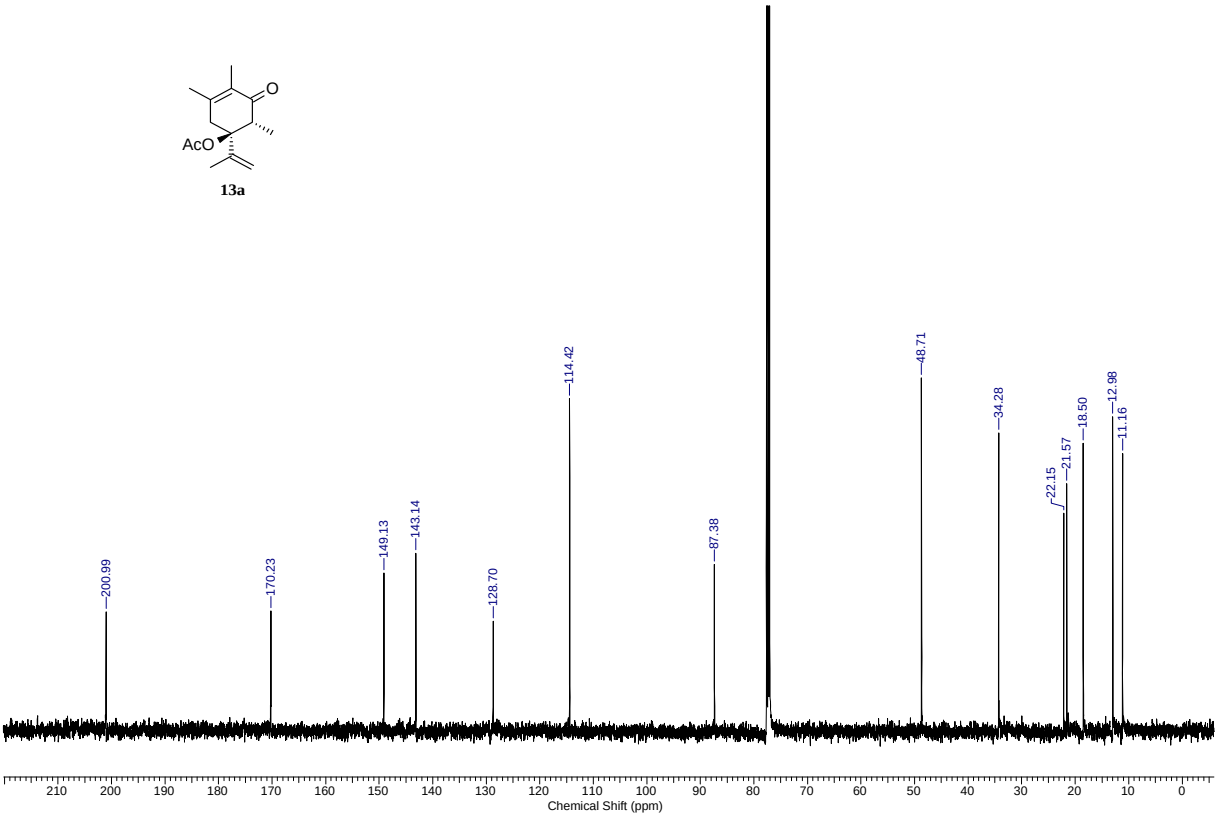
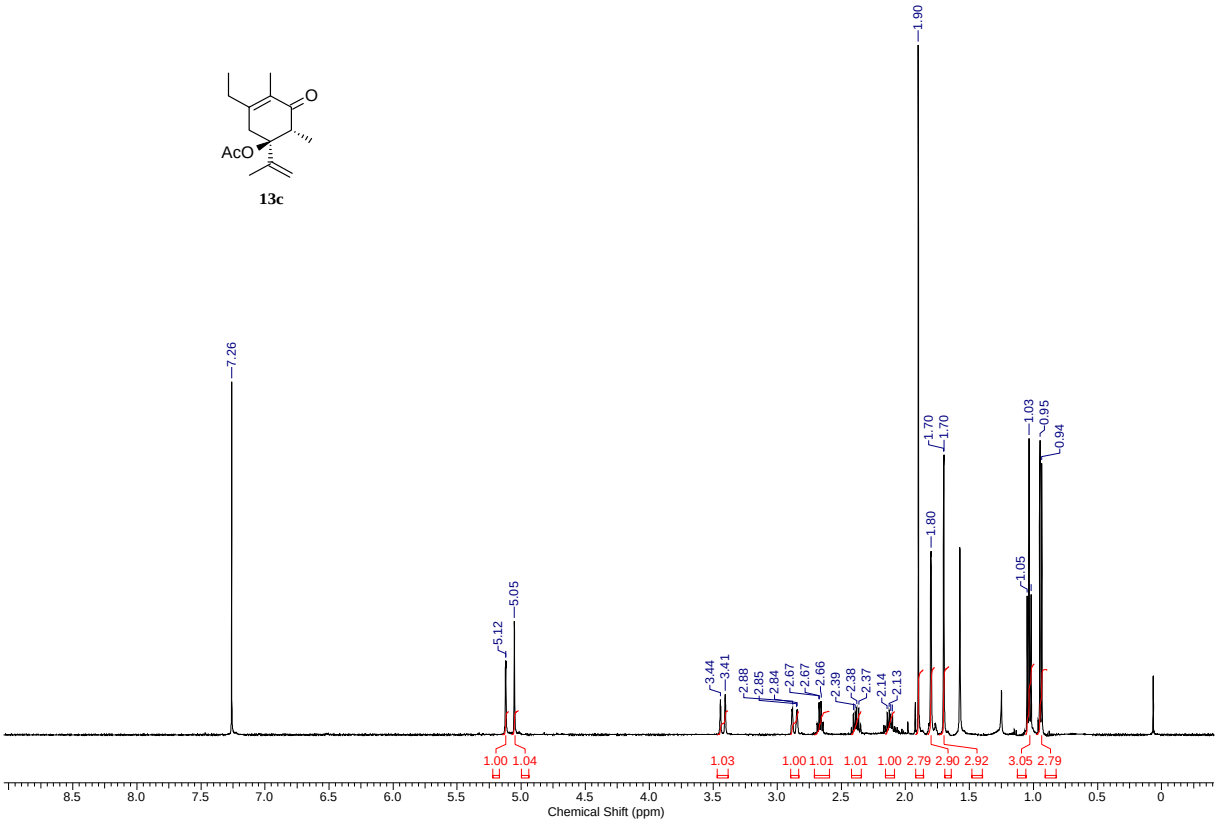
143.68
127.99
121.67
120.14
115.06
25.04
16.22
12.94
Chemical Shift (ppm)


AcO
O
13a
1.91
1.94
1.69
1.80
0.94
0.93
5.12
5.11
5.05
3.40
3.37
2.92
2.89
2.68
2.67
2.00
1.01
1.00
1.00
6.08
2.82
2.58
2.82
Chemical Shift (ppm)


AcO
O
13a
200.99
170.23
149.13
143.14
128.70
114.42
87.38
48.71
34.28
22.15
21.57
18.50
12.98
11.16
Chemical Shift (ppm)


AcO
O
13c
7.26
5.12
5.05
3.44
3.41
2.88
2.85
2.84
2.67
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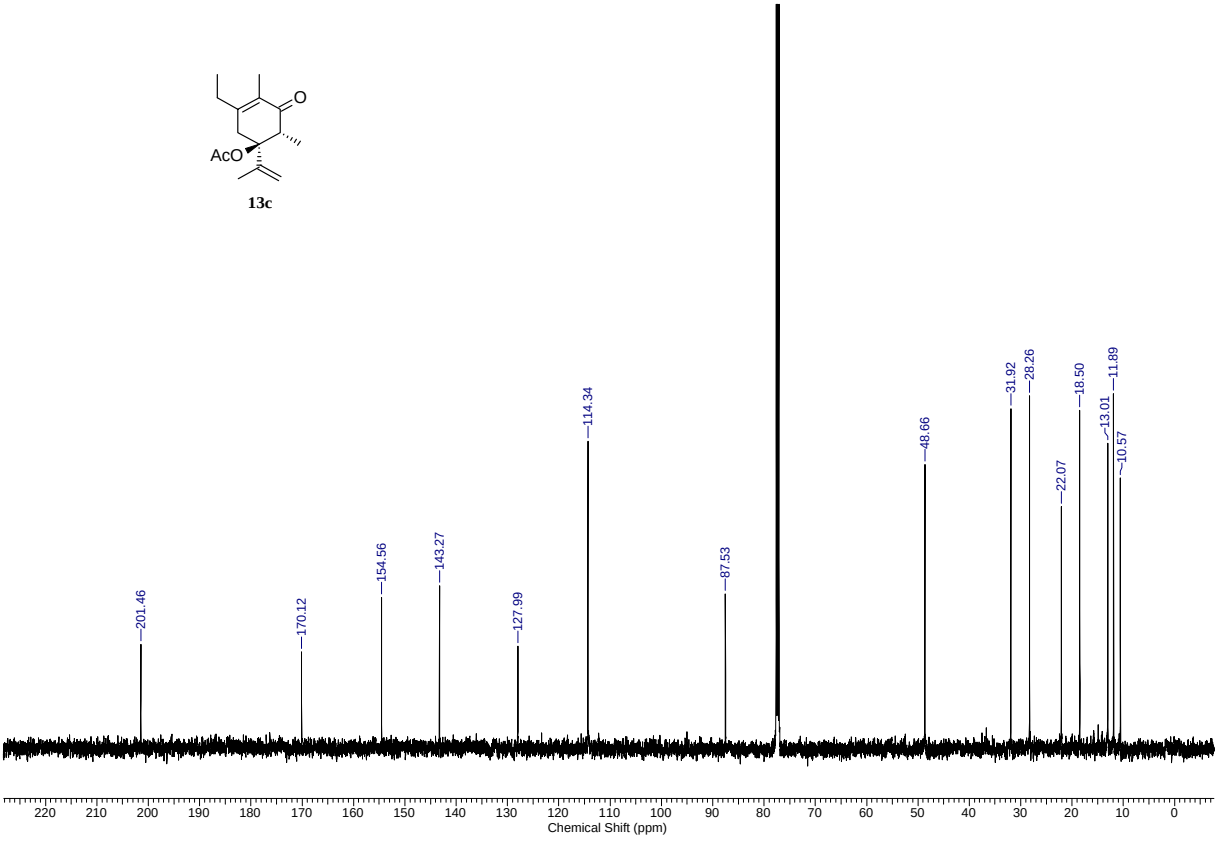
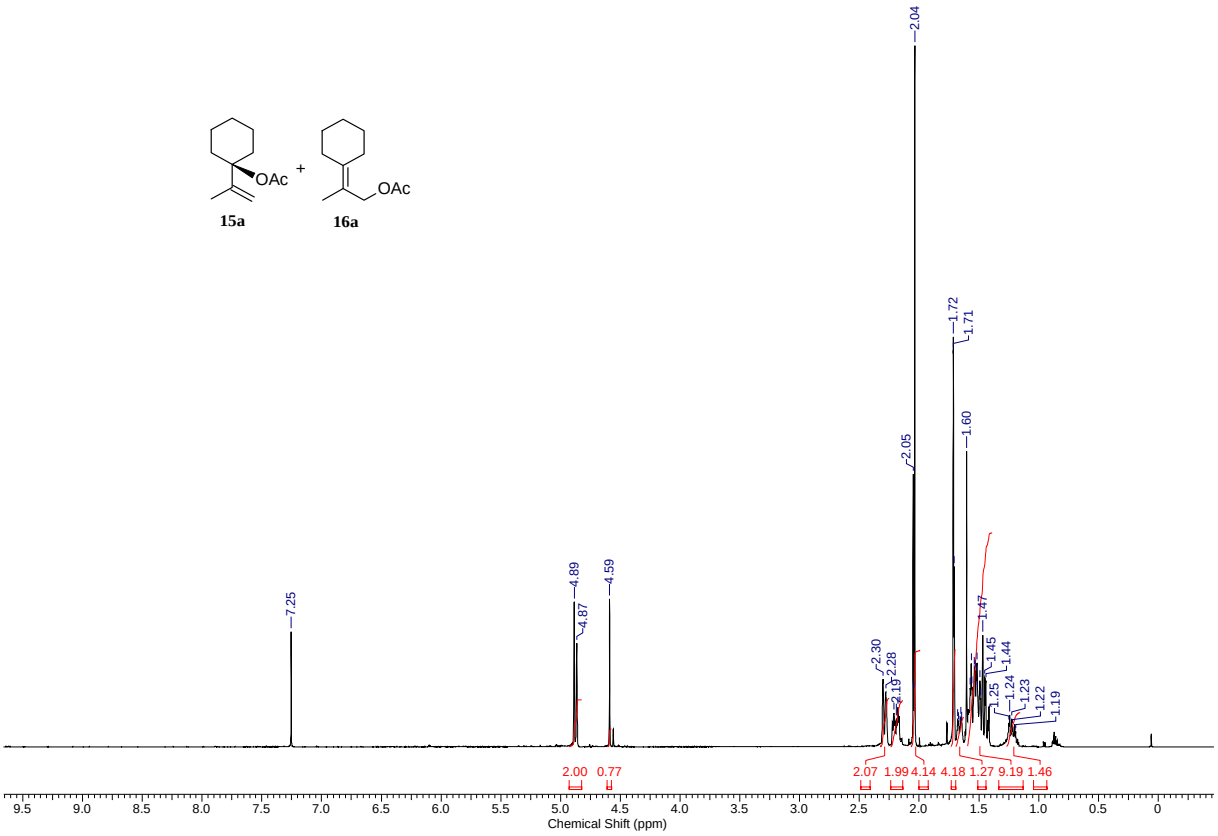
2.66
2.39
2.38
2.37
2.14
2.13
1.90
1.80
1.70
1.70
1.05
1.03
0.95
0.94
1.00 1.04
1.03
1.00 1.01
1.01
1.00
2.79
2.90 2.92
3.05 2.79
Chemical Shift (ppm)


AcO
O
13c
201.46
170.12
154.56
143.27
127.99
114.34
87.53
48.66
31.92
28.26
22.07
18.50
13.01
11.89
10.57
Chemical Shift (ppm)


OAc
OAc
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16a
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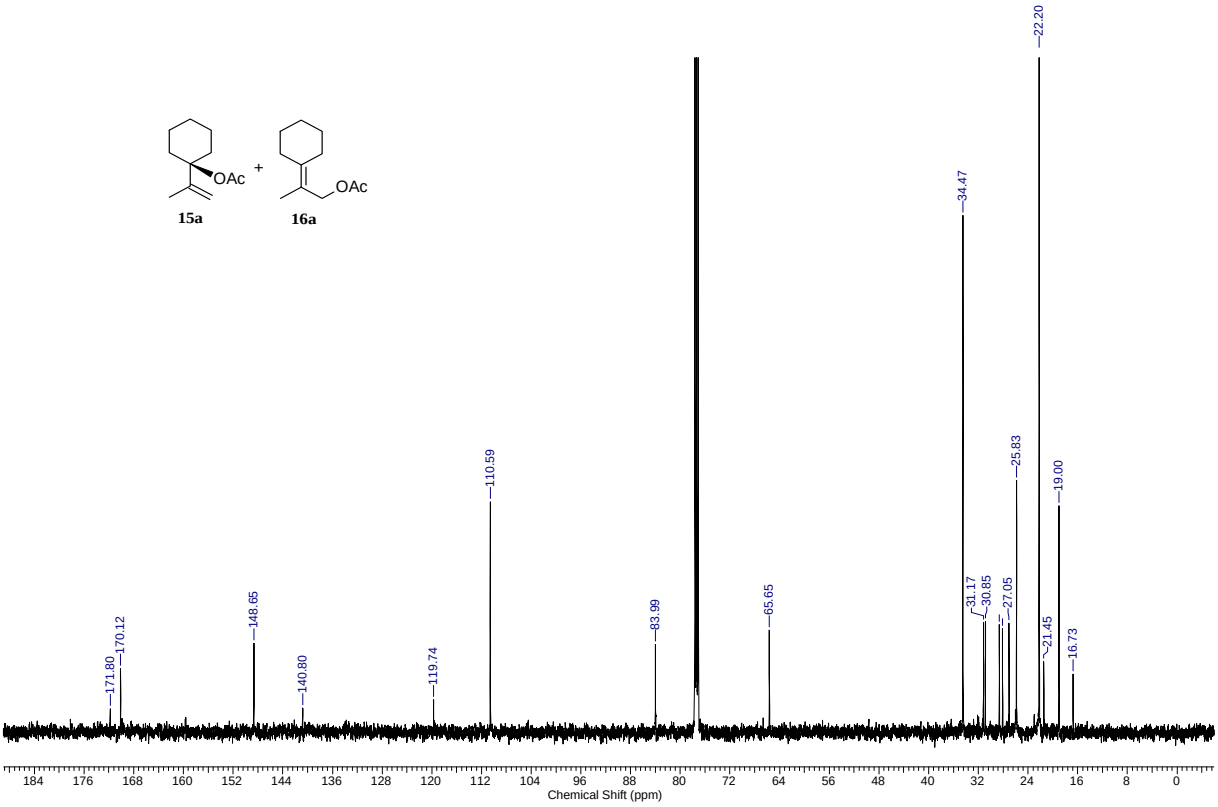
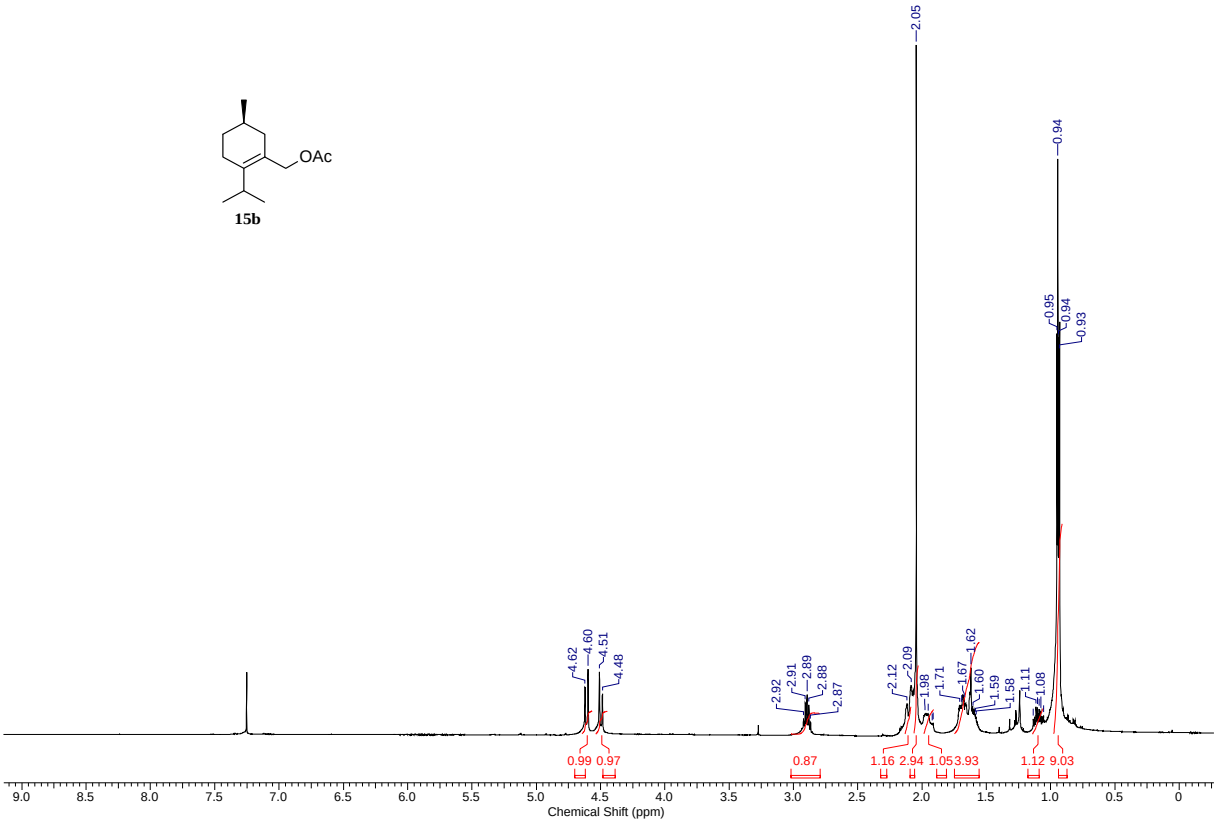
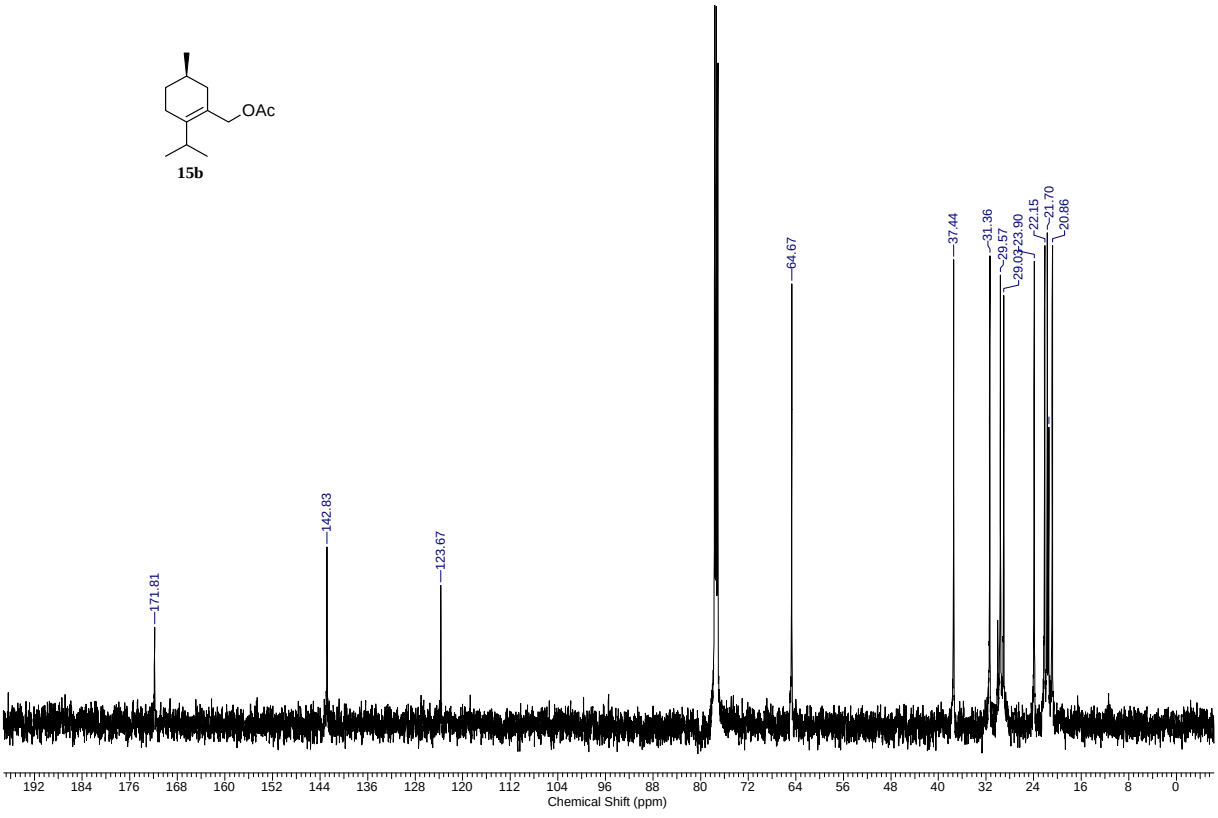
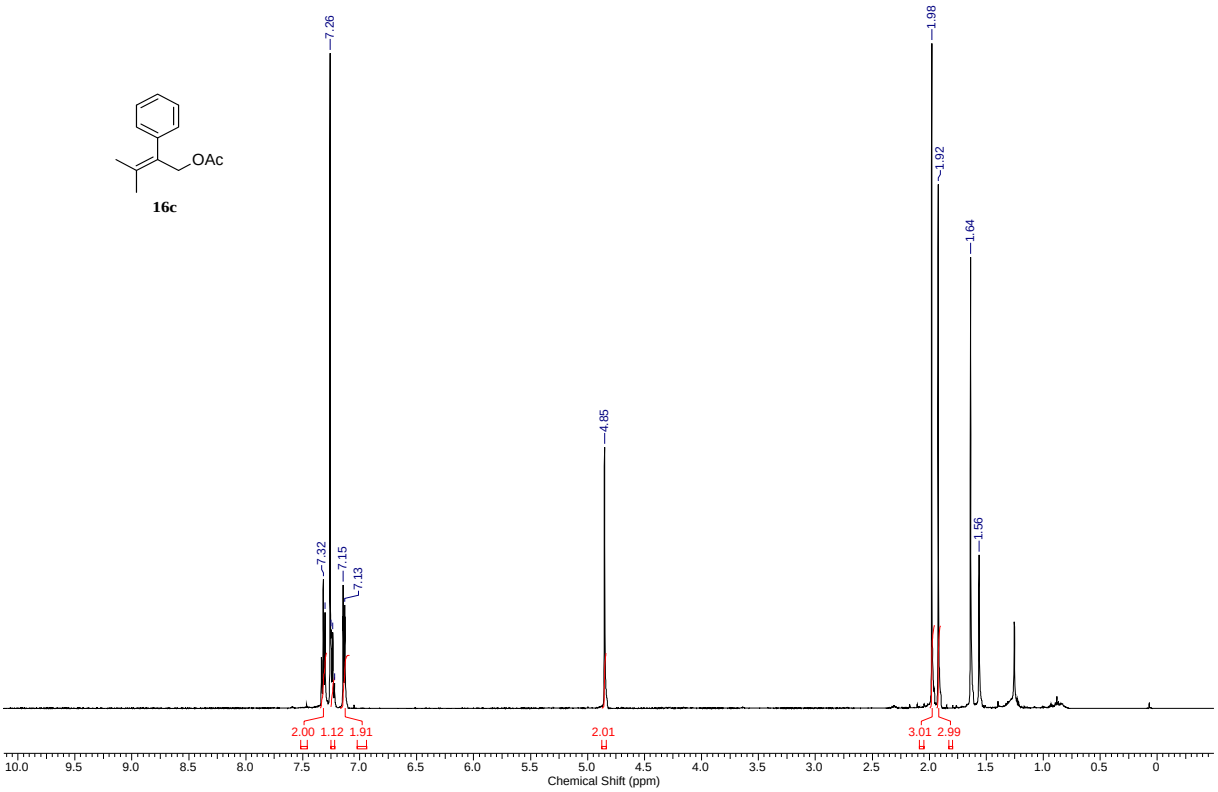
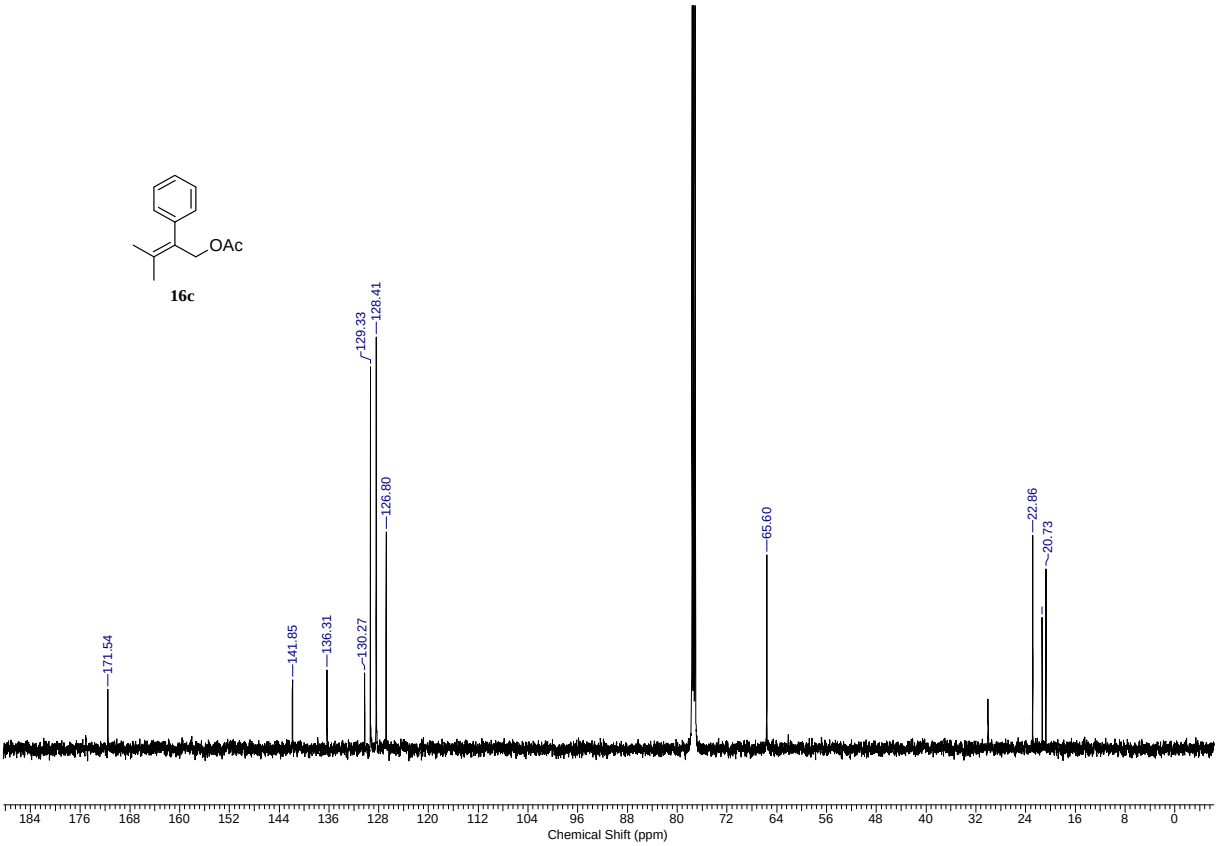
1.72
1.71
2.05
1.60
7.25
4.89
4.87
4.59
2.30
2.28
1.47
1.45
1.44
1.25
1.24
1.23
1.22
1.19
2.00
0.77
2.07
1.99
4.14
4.18
1.27
9.19
1.46
Chemical Shift (ppm)

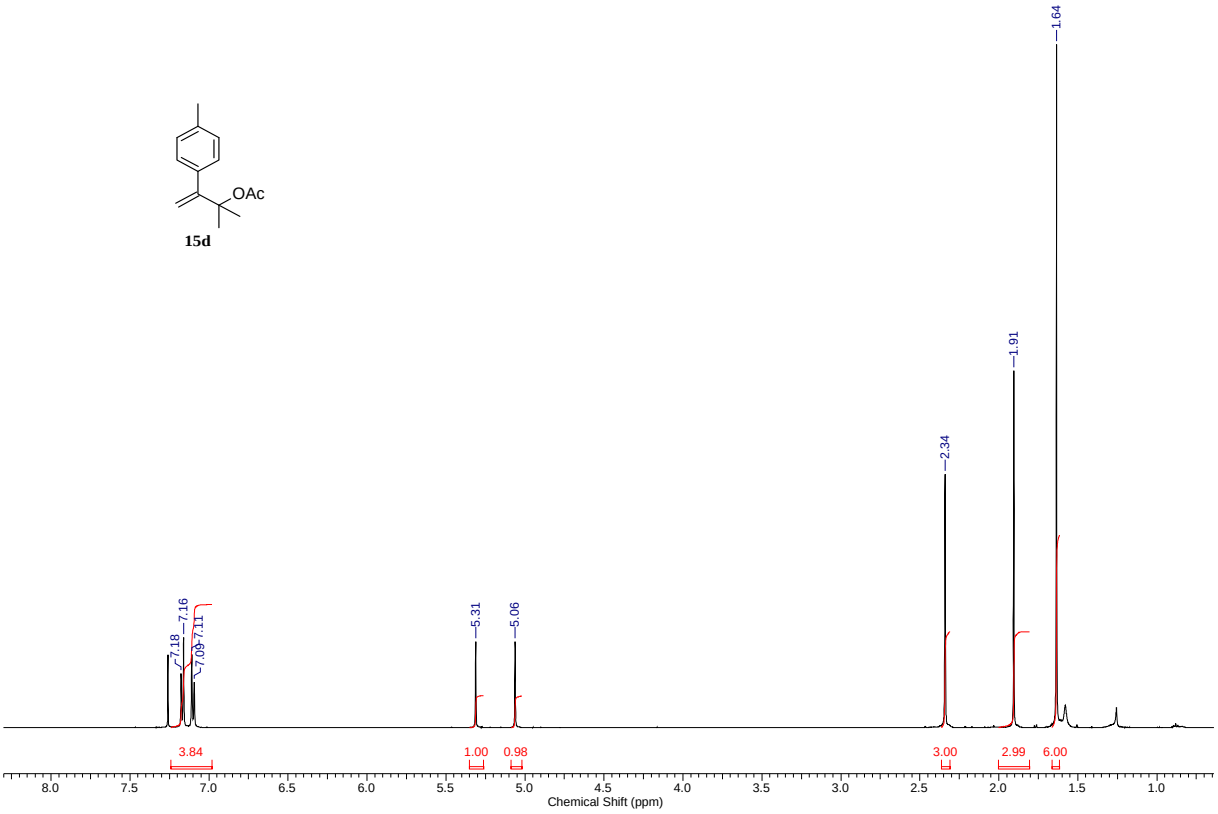

OAc
OAc
15a
16a
22.20
34.47
110.59
25.83
19.00
148.65
171.80
170.12
140.80
119.74
83.99
65.65
31.17
30.85
27.05
21.45
16.73
Chemical Shift (ppm)

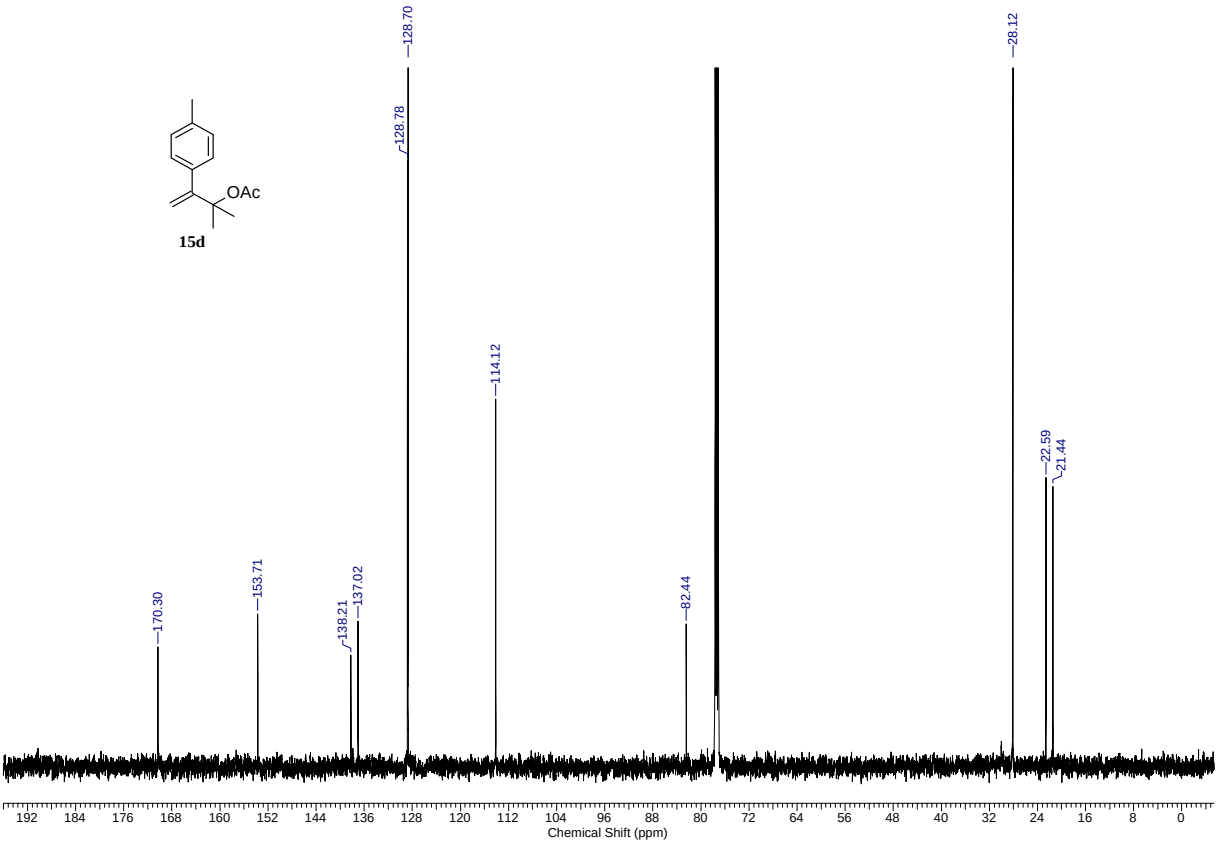

OAc
15b
2.05
0.94
0.95
0.94
0.93
4.62
4.60
4.51
4.48
2.92
2.91
2.89
2.88
2.87
2.12
2.09
1.98
1.71
1.67
1.62
1.60
1.59
1.58
1.11
1.08
0.99
0.97
0.87
1.16
2.94
1.05
3.93
1.12
9.03
Chemical Shift (ppm)

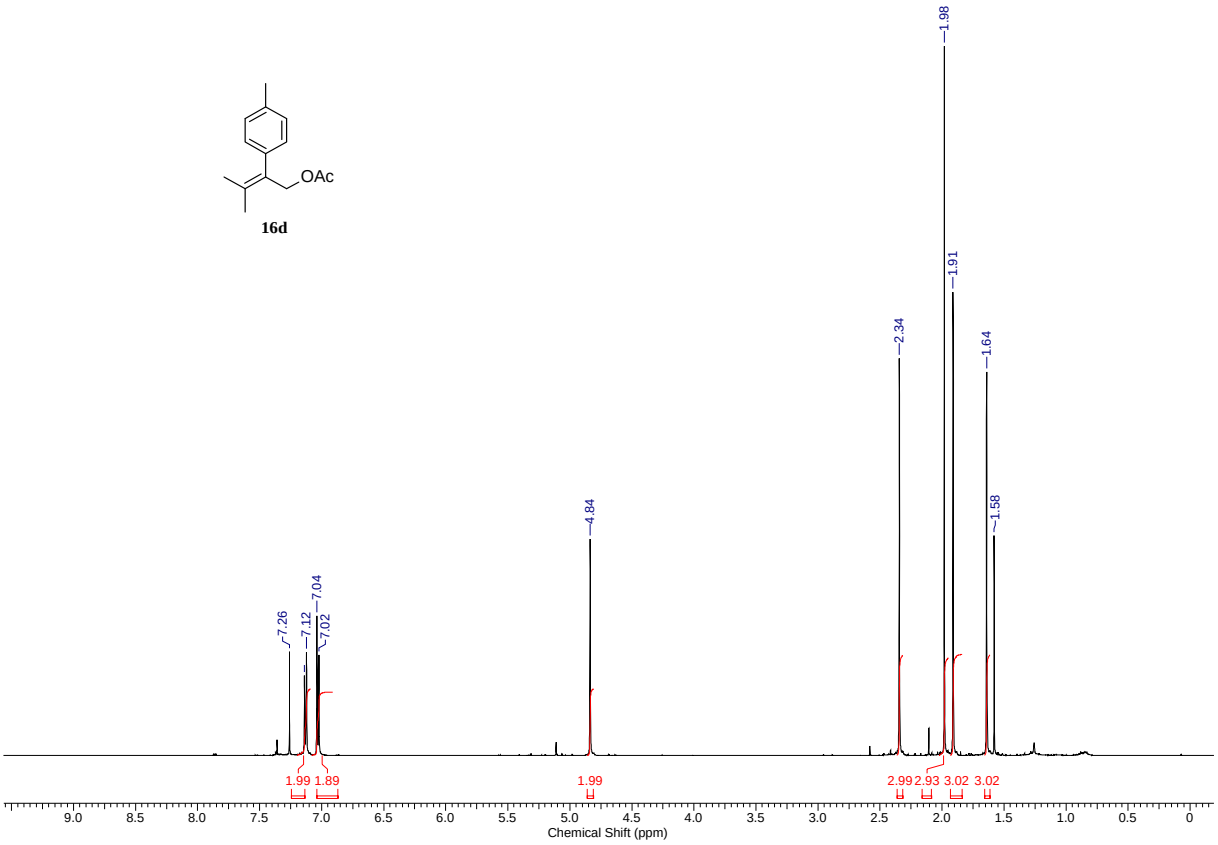

OAc
15b
171.81
142.83
123.67
64.67
37.44
31.36
29.57
29.03
23.90
22.15
21.70
20.86
Chemical Shift (ppm)

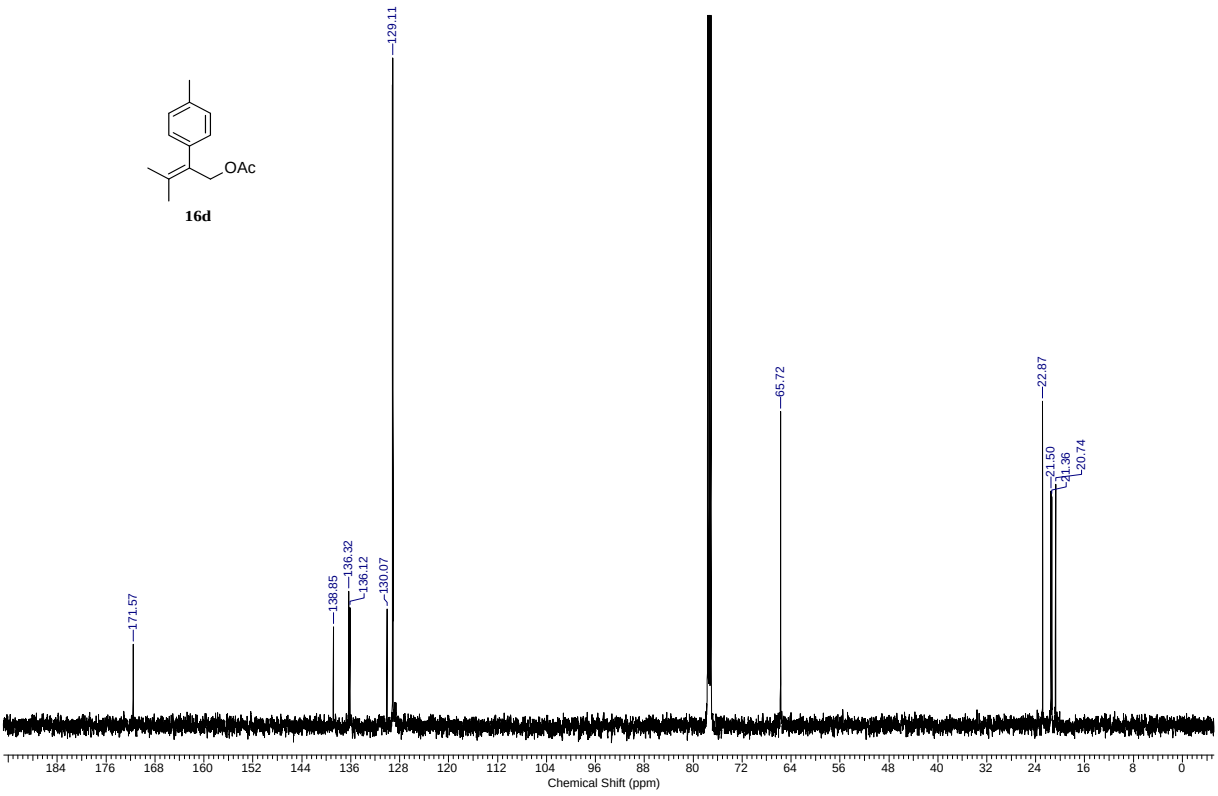

OAc
16c
7.26
1.98
1.92
1.64
4.85
7.32
7.15
7.13
1.56
2.00
1.12
1.91
2.01
3.01
2.99
Chemical Shift (ppm)

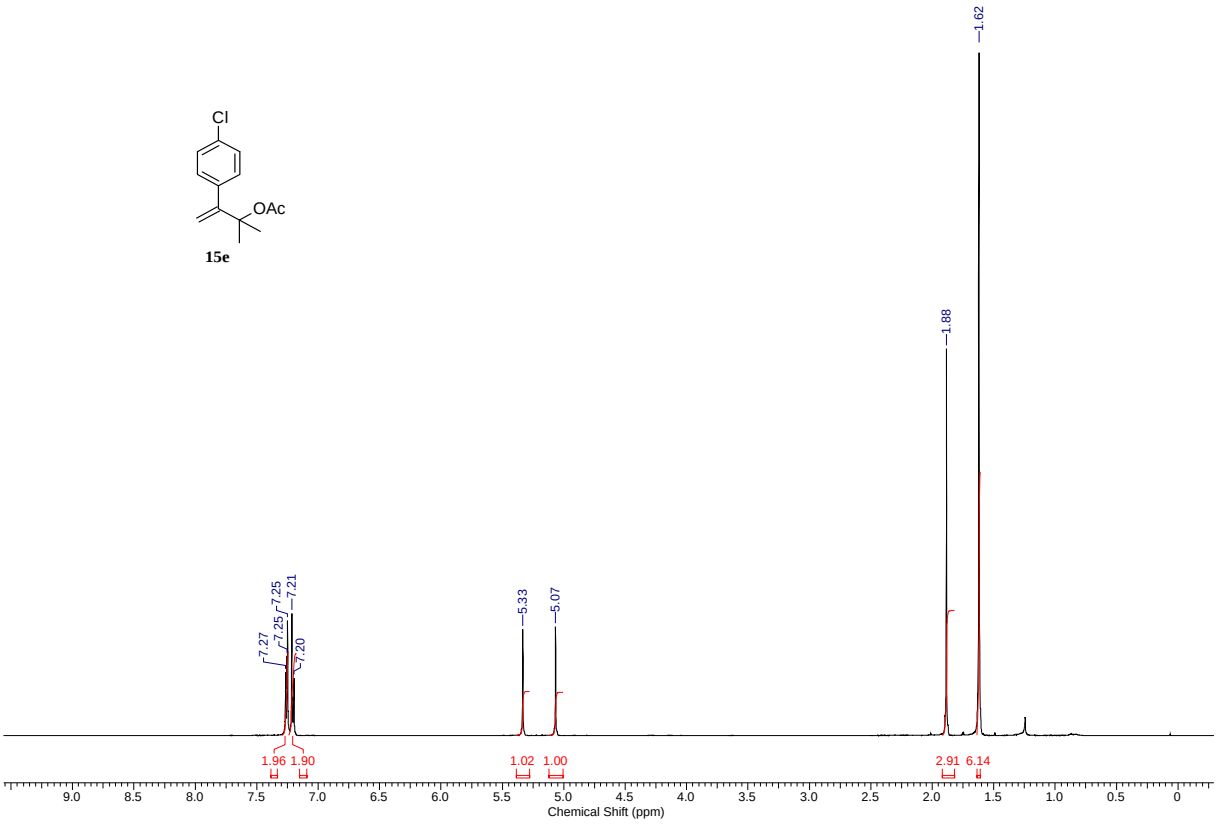

OAc
16c
129.33
128.41
126.80
65.60
22.86
20.73
171.54
141.85
136.31
130.27
Chemical Shift (ppm)

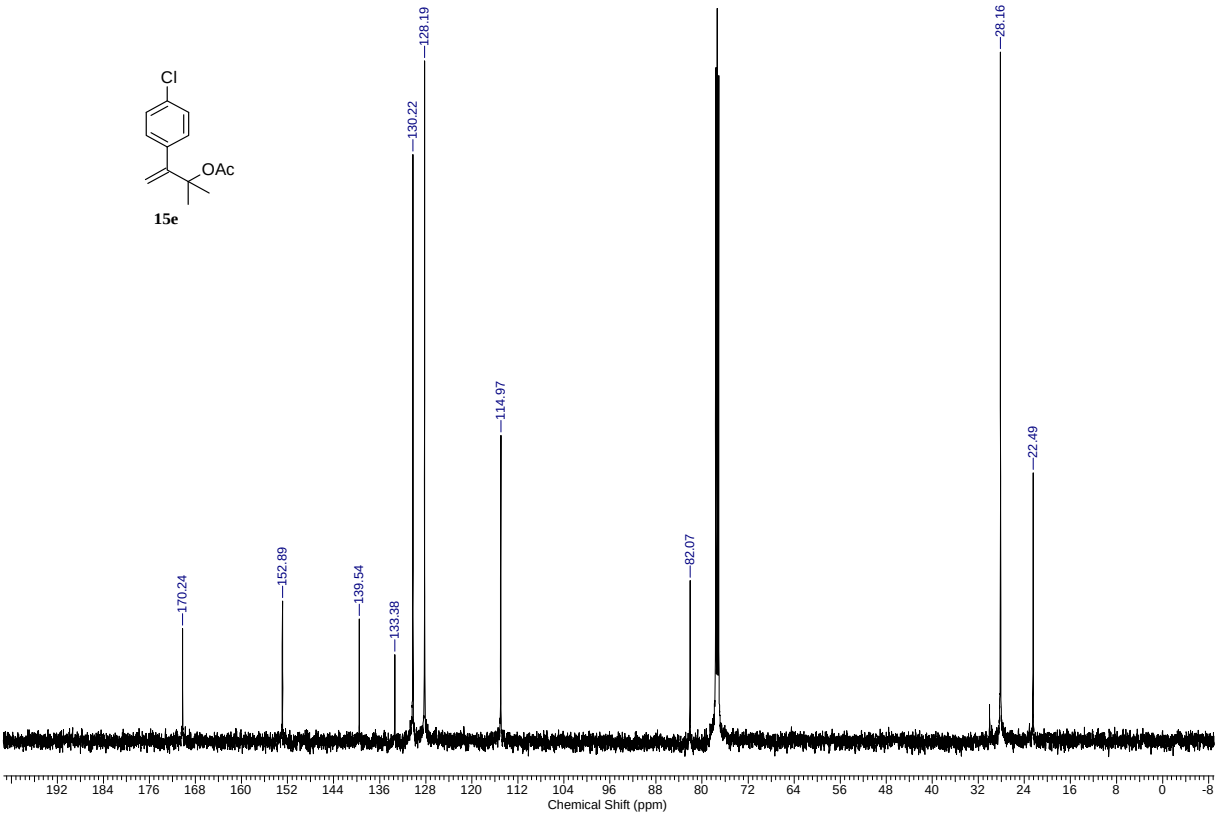

OAc
15d
1.64
1.91
2.34
5.31
5.06
7.16
7.18
7.11
7.09
3.84
1.00
0.98
3.00
2.99
6.00
Chemical Shift (ppm)

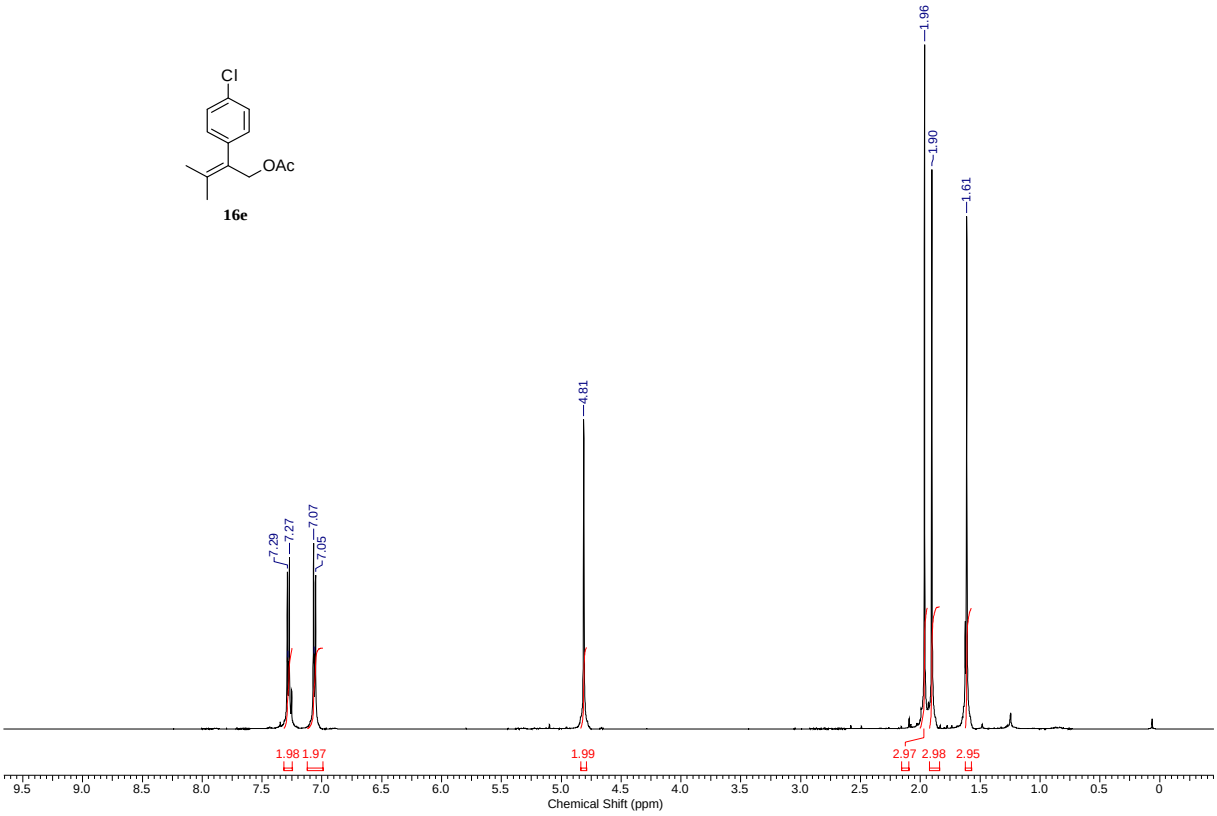

OAc
15d
128.70
128.78
114.12
28.12
22.59
21.44
170.30
153.71
138.21
137.02
82.44
Chemical Shift (ppm)

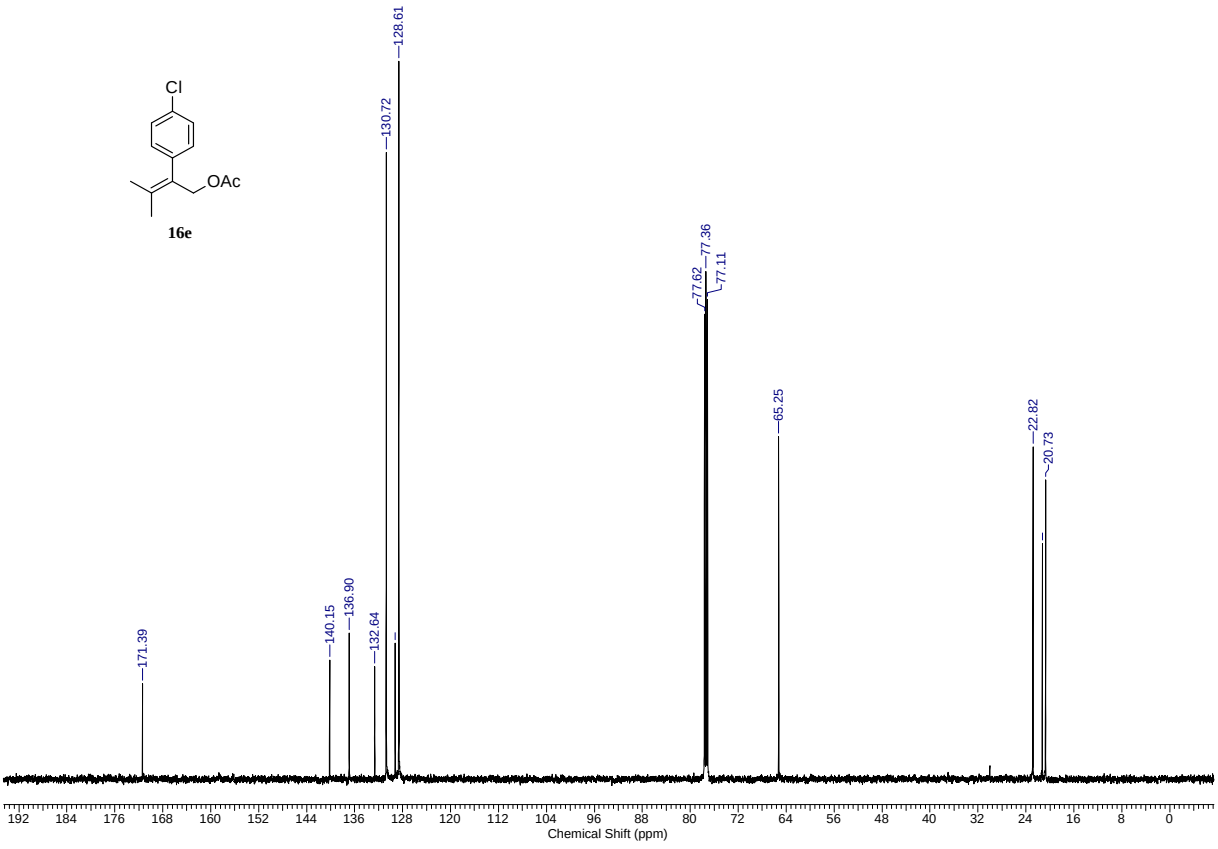

OAc
16d
1.98
1.91
2.34
1.64
1.58
4.84
7.26
7.12
7.04
7.02
1.99 1.89
1.99
2.99 2.93 3.02 3.02
Chemical Shift (ppm)

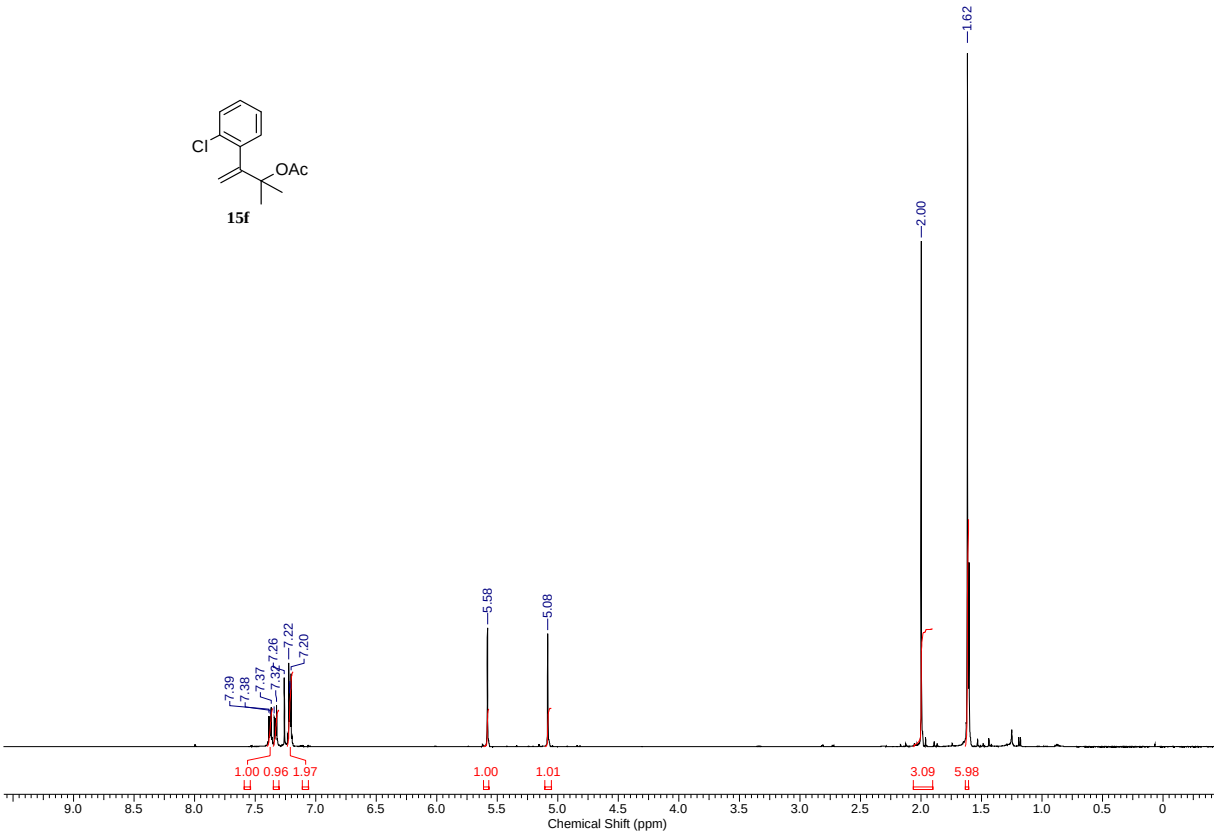

OAc
16d
129.11
65.72
22.87
21.50
21.36
20.74
171.57
138.85
136.32
136.12
130.07
Chemical Shift (ppm)

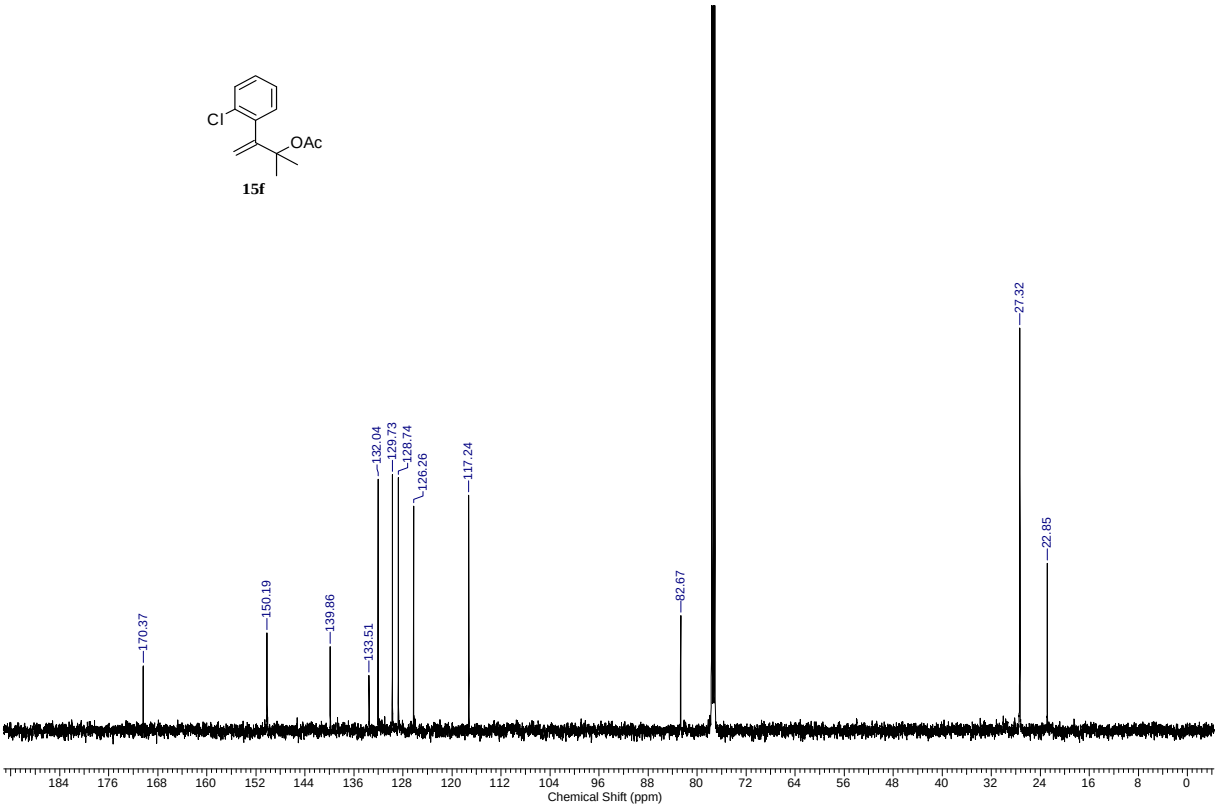

Cl
OAc
15e
1.62
1.88
7.27
7.25
7.25
7.21
7.20
5.33
5.07
1.96
1.90
1.02
1.00
2.91
6.14
Chemical Shift (ppm)

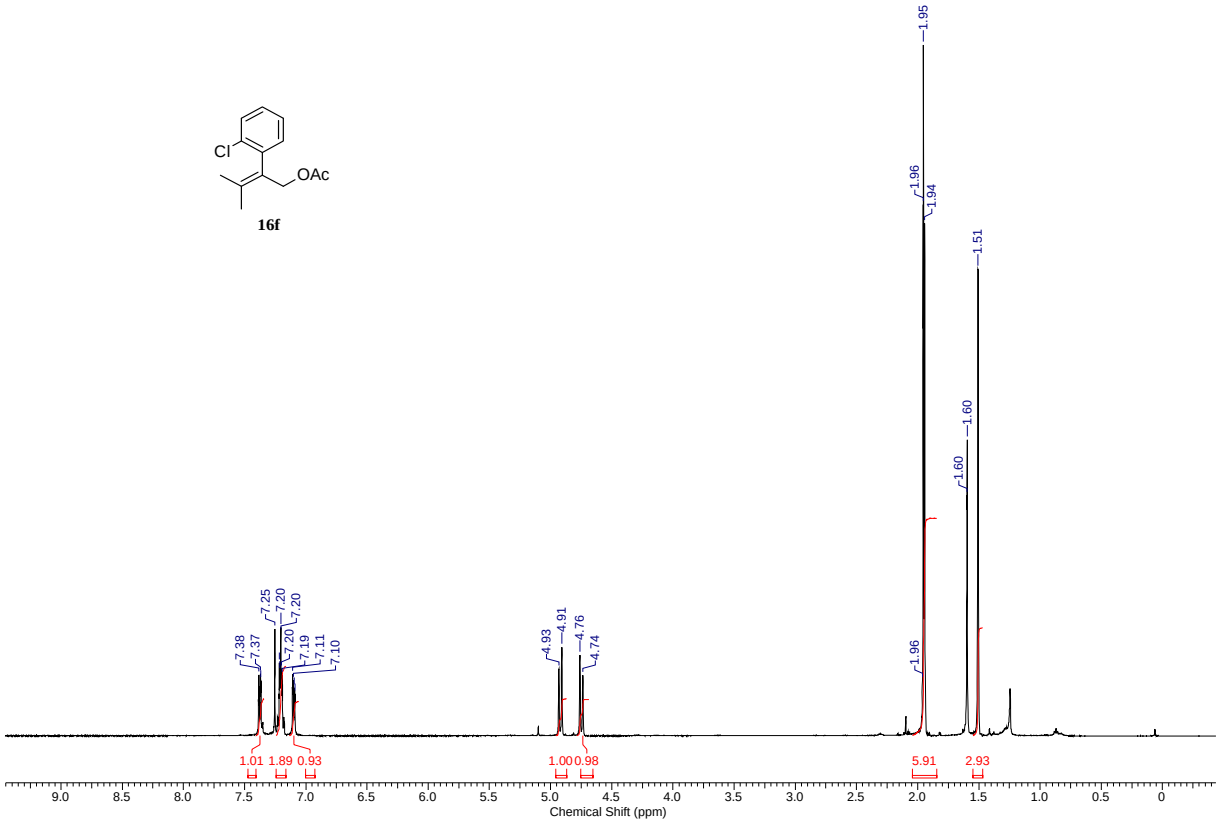

Cl
OAc
15e
128.19
130.22
28.16
114.97
22.49
82.07
170.24
152.89
139.54
133.38
Chemical Shift (ppm)

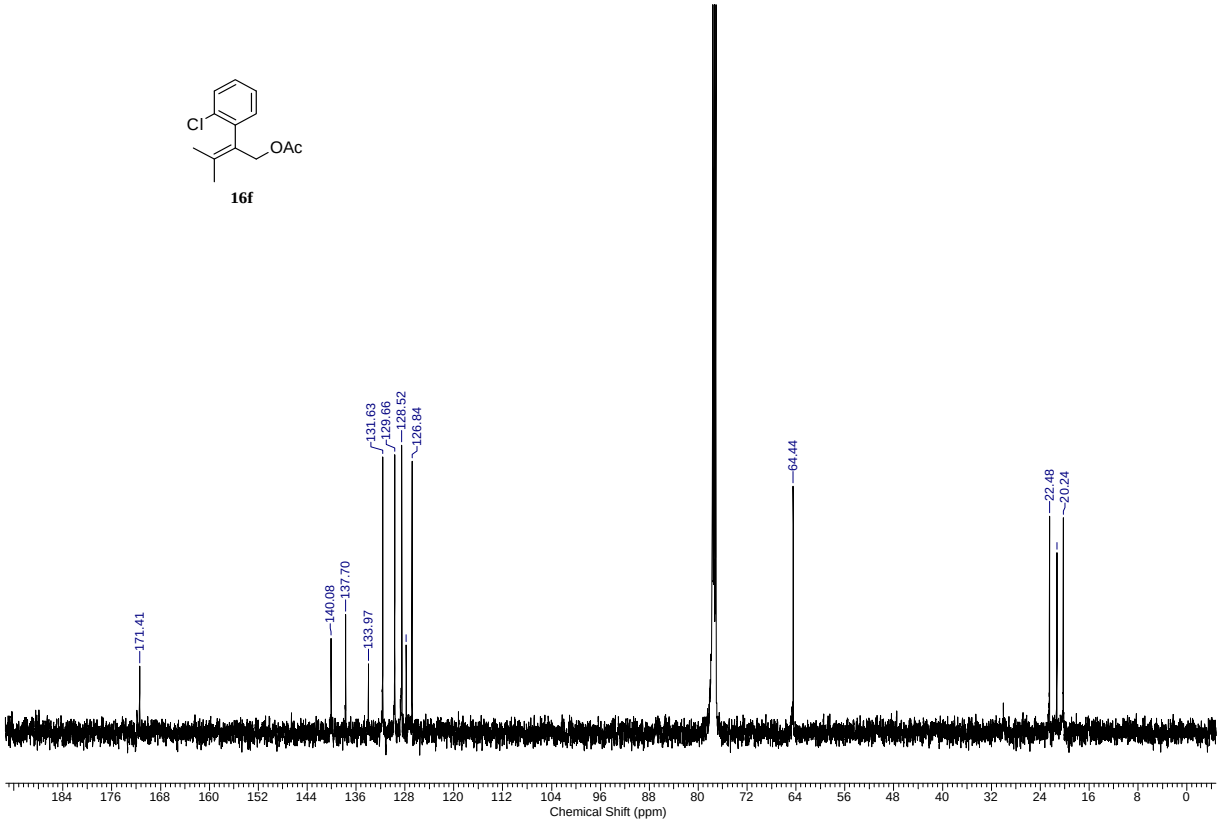

Cl
OAc
16e
1.96
1.90
1.61
4.81
7.29
7.27
7.07
7.05
1.98
1.97
1.99
2.97
2.98
2.95
Chemical Shift (ppm)

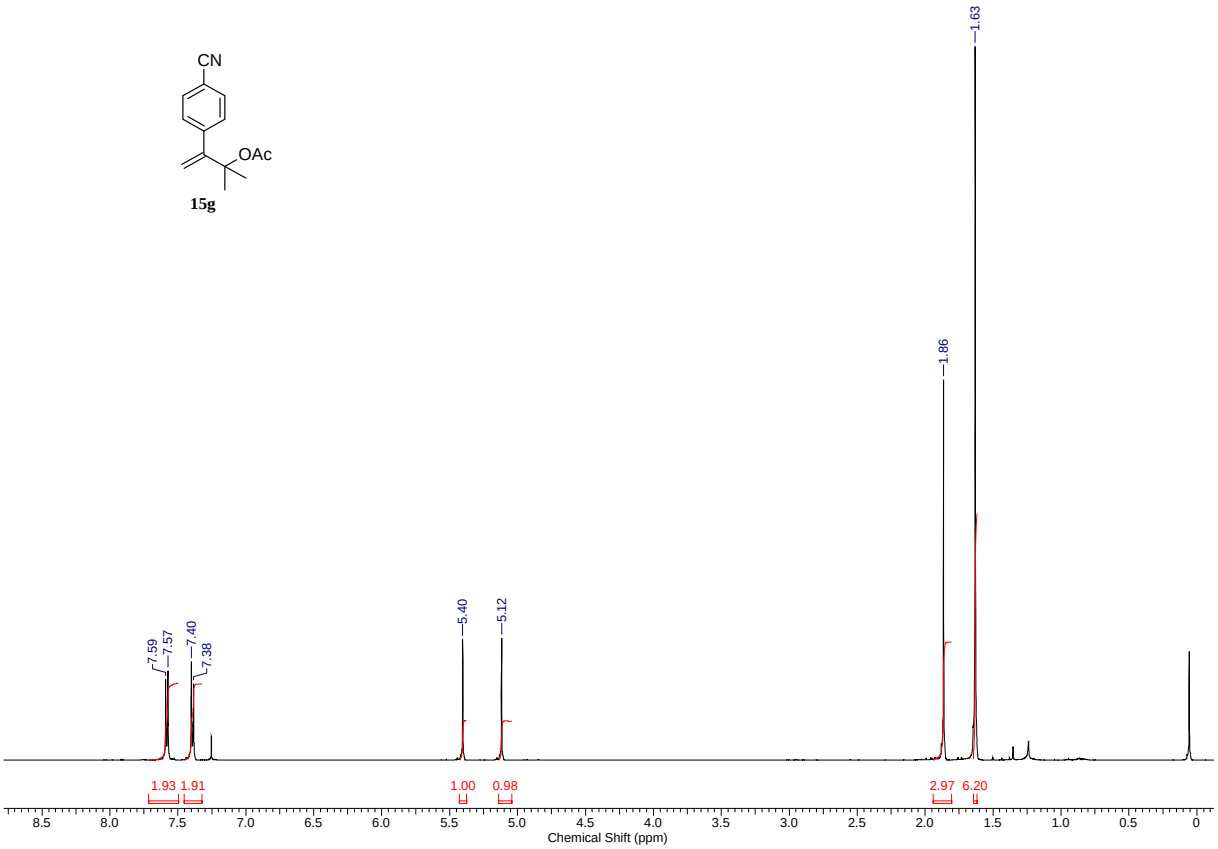

Cl
OAc
16e
128.61
130.72
77.62
77.36
77.11
65.25
22.82
20.73
171.39
140.15
136.90
132.64
Chemical Shift (ppm)

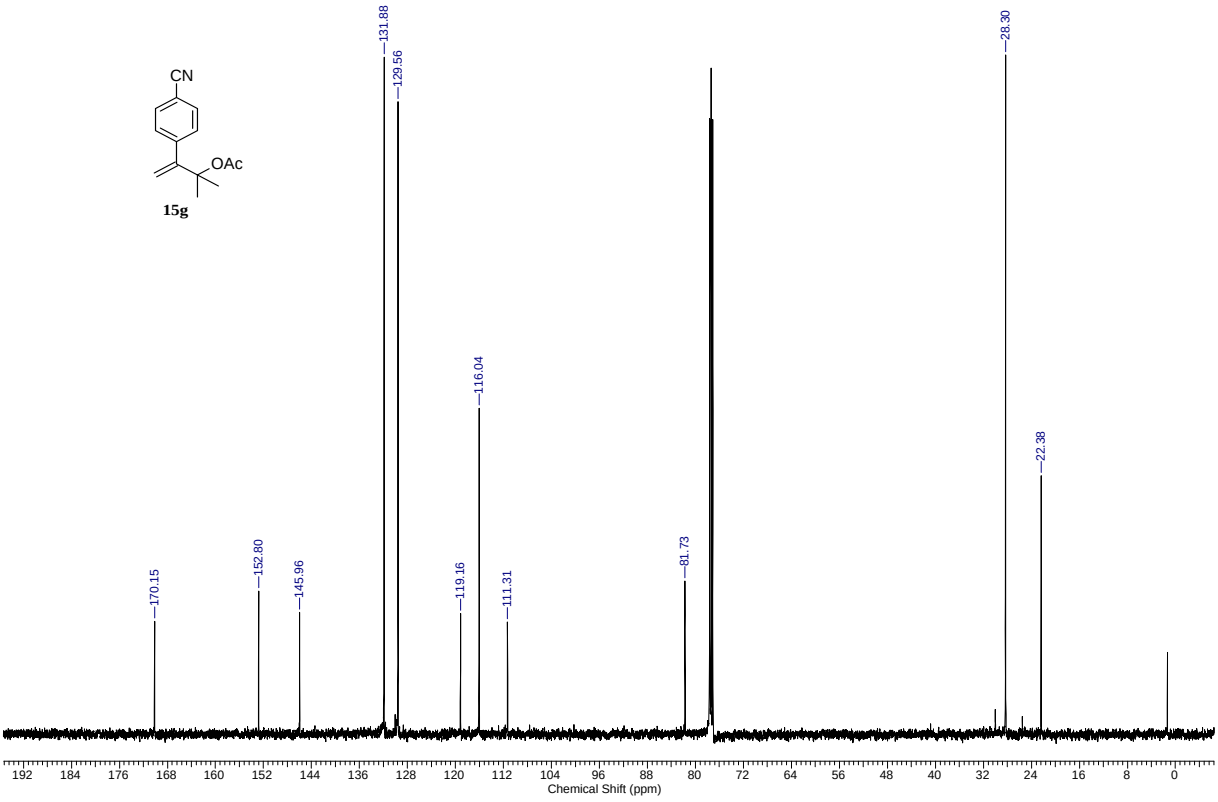

Cl
OAc
15f
1.62
2.00
5.58
5.08
7.39
7.38
7.37
7.32
7.26
7.22
7.20
1.00
0.96
1.97
1.00
1.01
3.09
5.98
Chemical Shift (ppm)

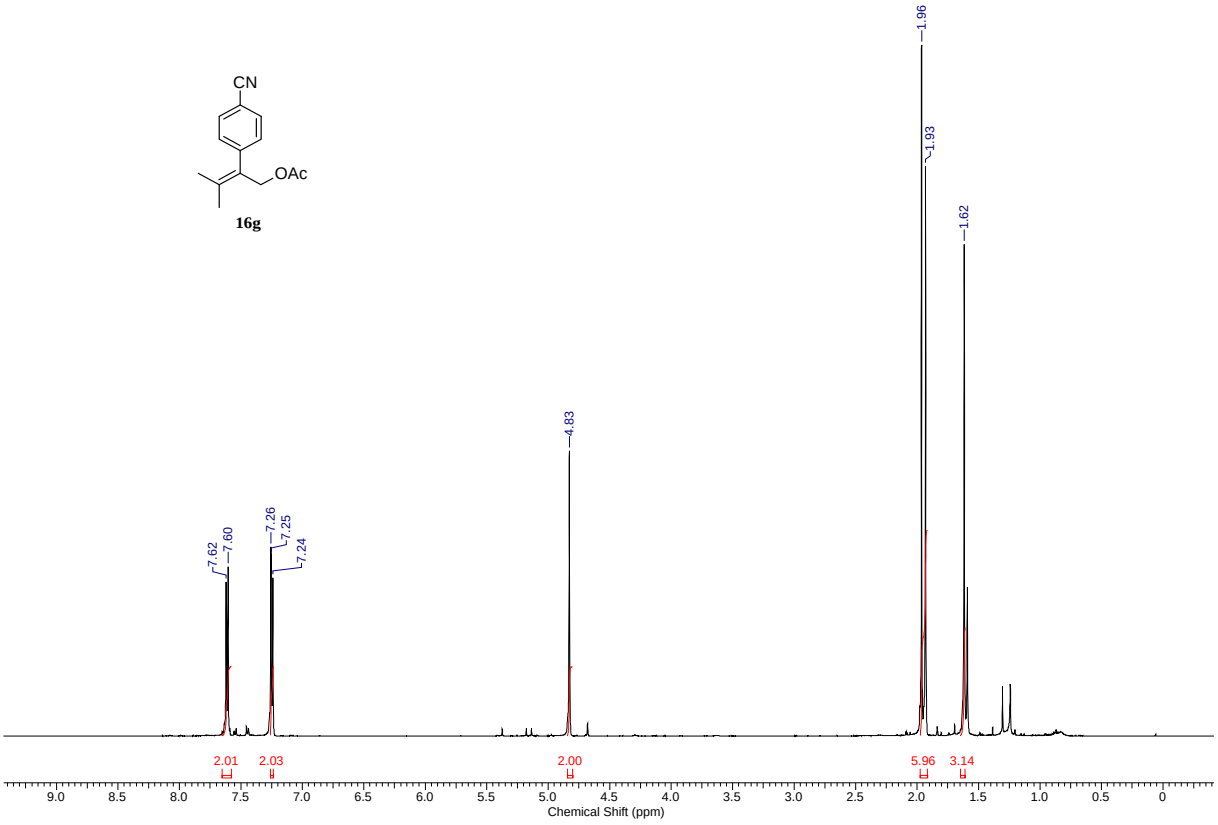

Cl
OAc
15f
170.37
150.19
139.86
133.51
132.04
129.73
128.74
126.26
117.24
82.67
27.32
22.85
Chemical Shift (ppm)

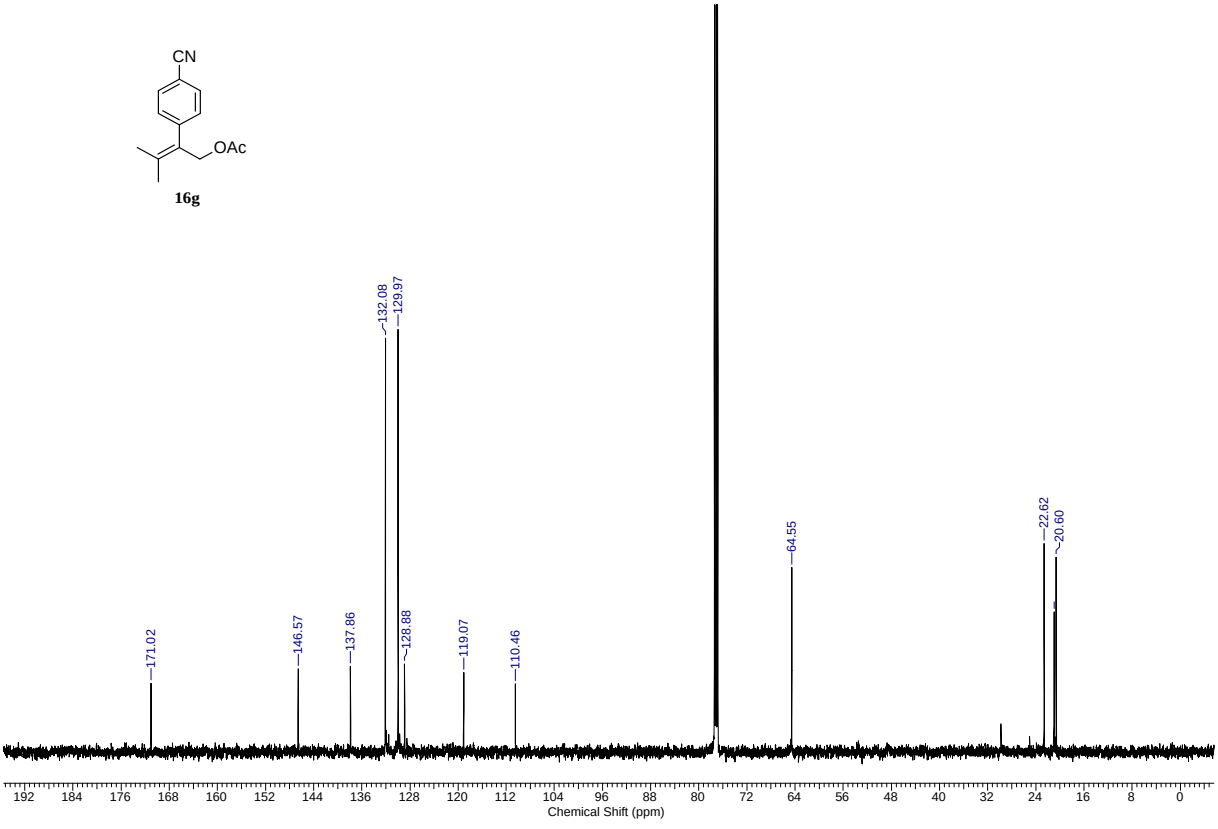

Cl
OAc
16f
7.38
7.37
7.25
7.20
7.20
7.20
7.19
7.11
7.10
4.93
4.91
4.76
4.74
1.96
1.95
1.94
1.60
1.60
1.51
1.01 1.89 0.93
1.00 0.98
5.91
2.93
Chemical Shift (ppm)

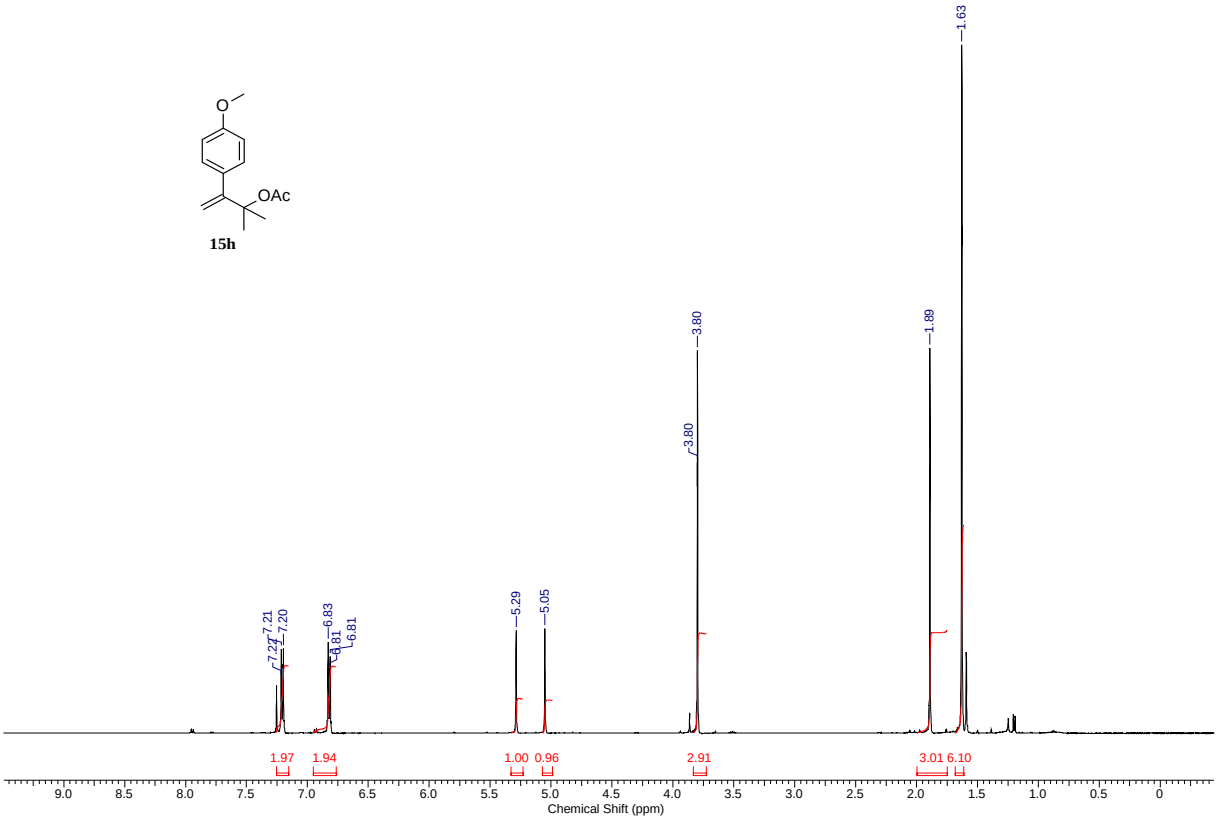

Cl
OAc
16f
171.41
140.08
137.70
133.97
131.63
129.66
128.52
126.84
64.44
22.48
20.24
Chemical Shift (ppm)

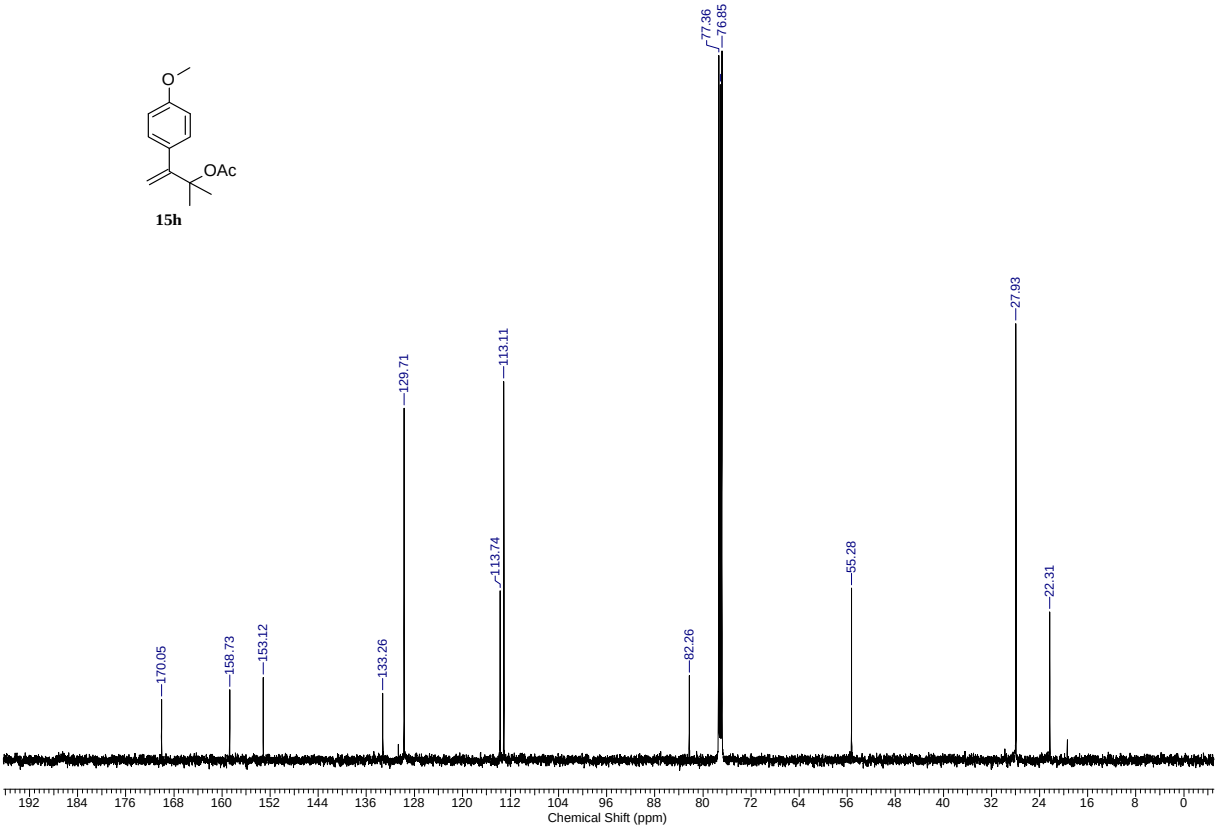

CN
OAc
15g
1.63
1.86
7.59
7.57
7.40
7.38
5.40
5.12
1.93
1.91
1.00
0.98
2.97
6.20
Chemical Shift (ppm)

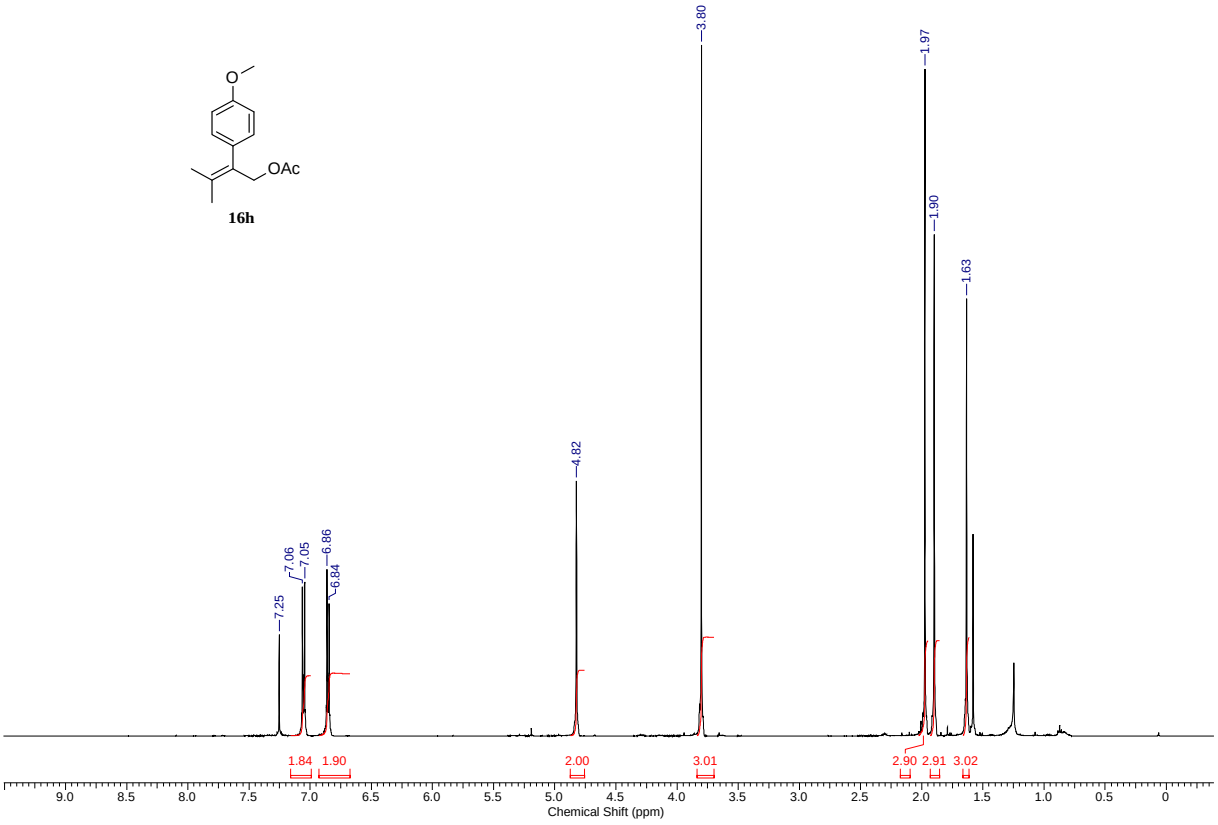

CN
OAc
15g
131.88
129.56
116.04
28.30
22.38
170.15
152.80
145.96
119.16
111.31
81.73
Chemical Shift (ppm)

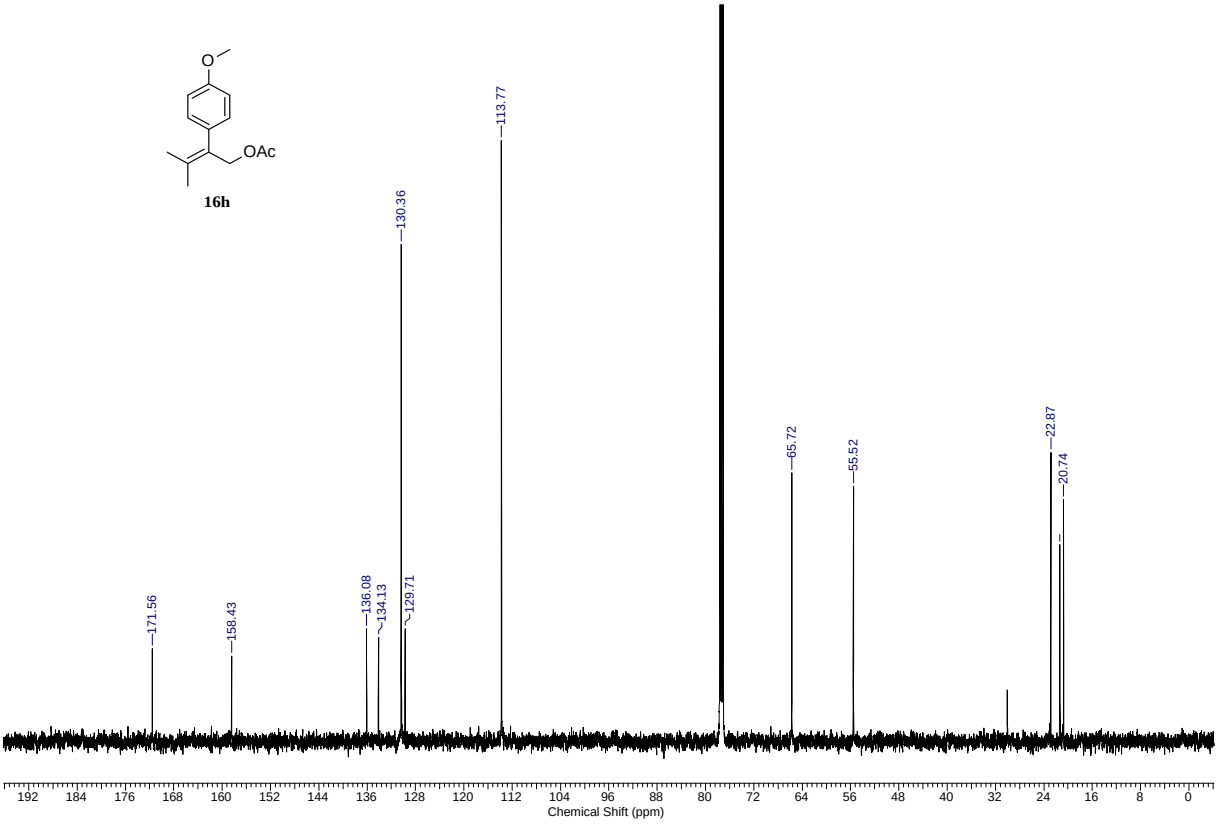

CN
OAc
16g
1.96
1.93
1.62
4.83
7.62
7.60
7.26
7.25
7.24
2.01
2.03
2.00
5.96
3.14
Chemical Shift (ppm)

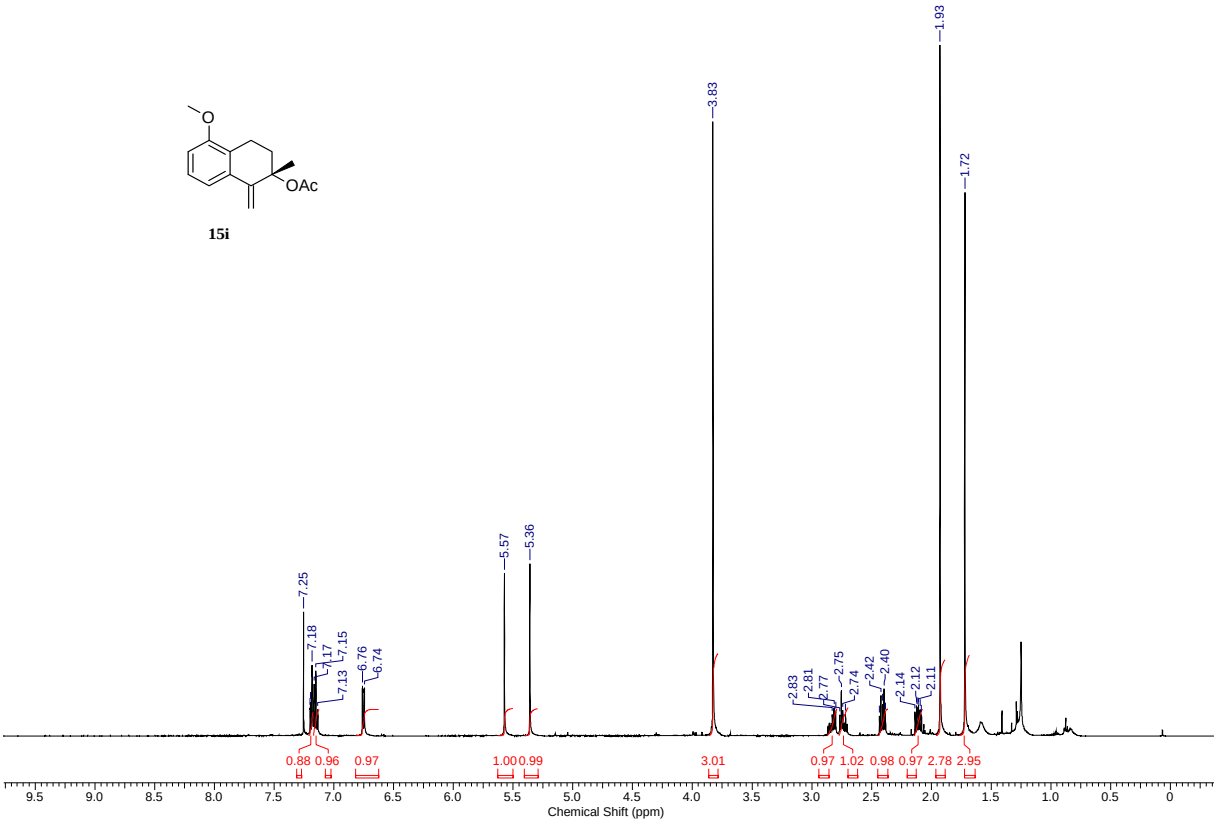

CN
OAc
16g
132.08
129.97
171.02
146.57
137.86
128.88
119.07
110.46
64.55
22.62
20.60
Chemical Shift (ppm)

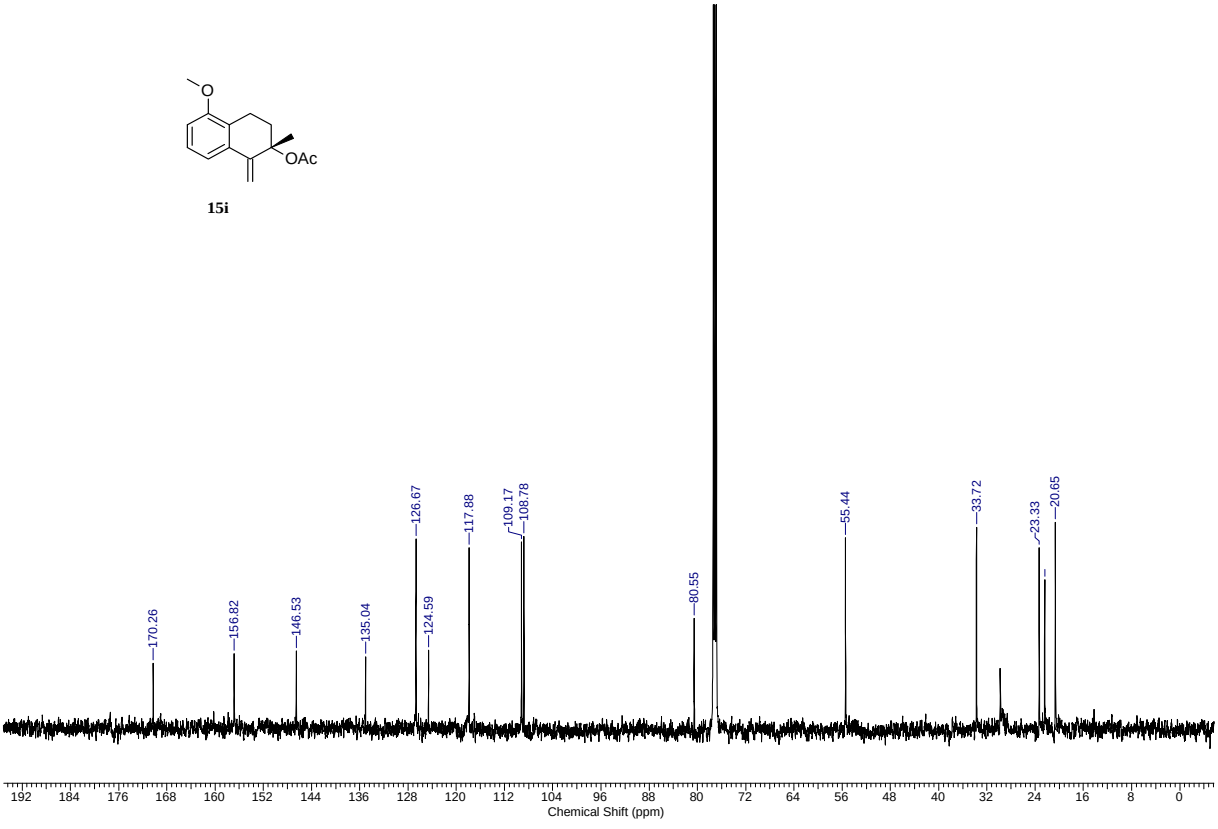

O
OAc
15h
1.63
3.80
1.89
3.80
7.21
7.20
6.83
6.81
6.81
5.29
5.05
1.97
1.94
1.00
0.96
2.91
3.01
6.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

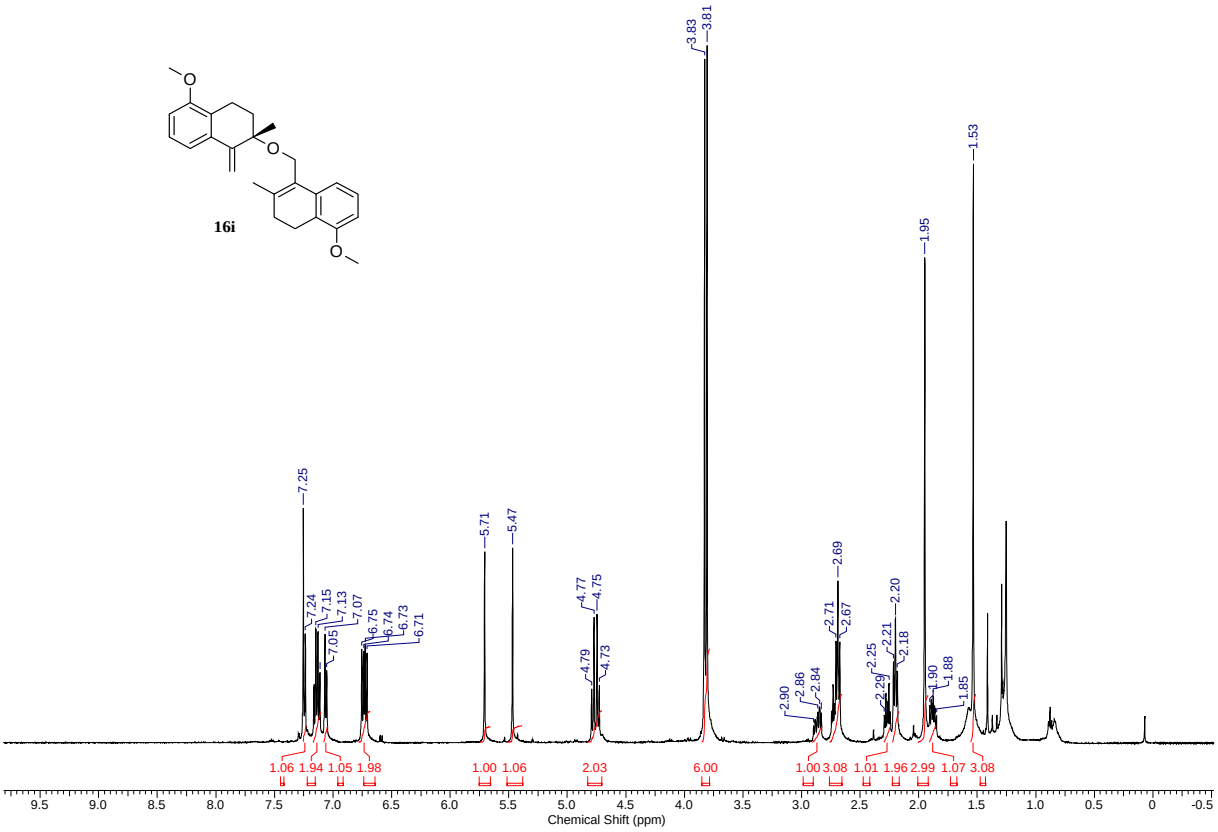

O
OAc
15h
77.36
76.85
27.93
129.71
113.11
113.74
55.28
22.31
170.05
158.73
153.12
133.26
82.26
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

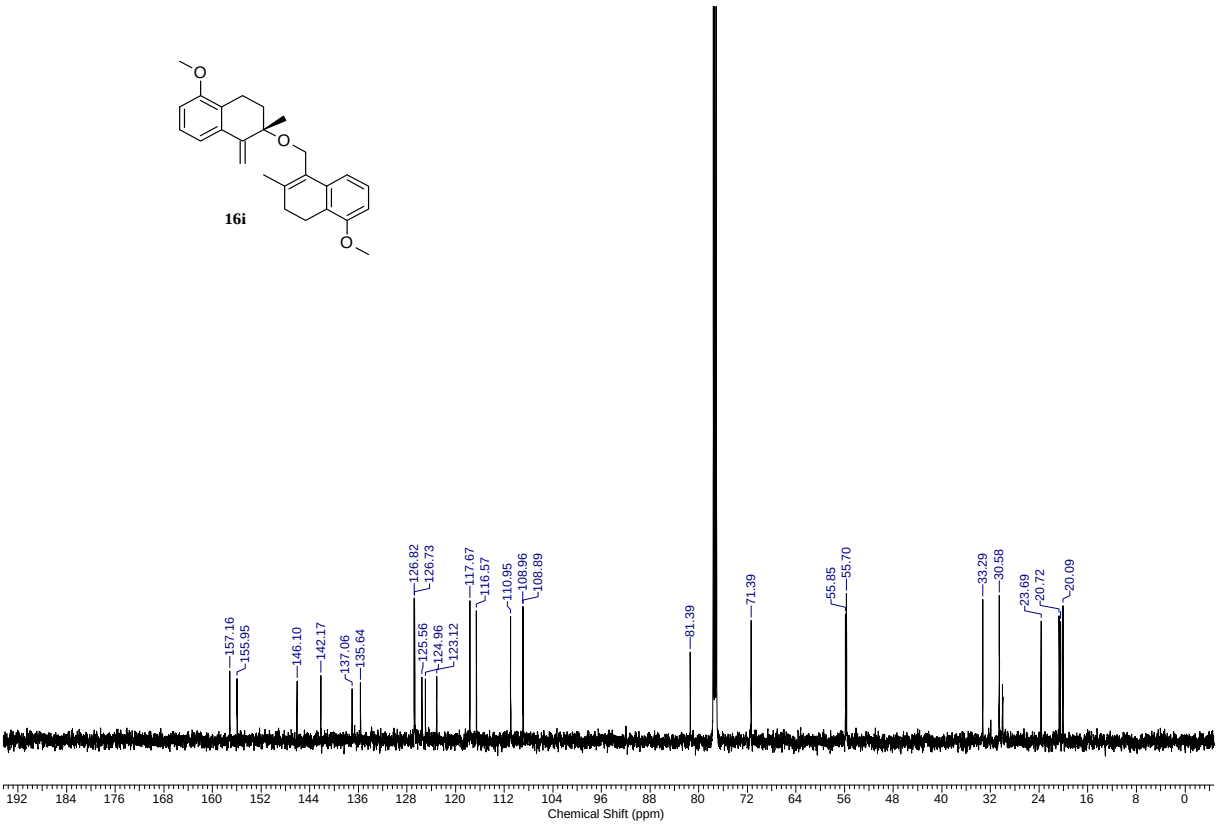

O
OAc
16h
3.80
1.97
1.90
1.63
4.82
7.06
7.05
6.86
6.84
7.25
1.84
1.90
2.00
3.01
2.90
2.91
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

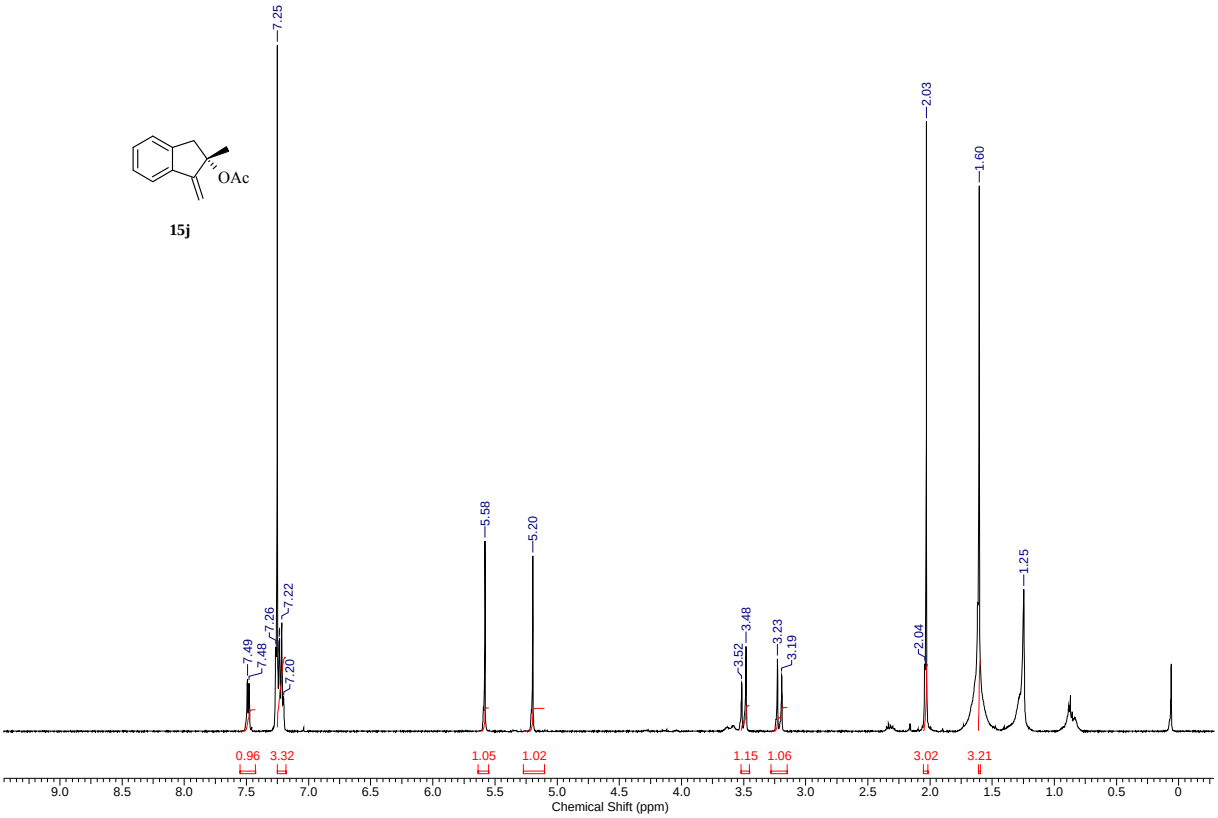

O
OAc
16h
113.77
130.36
65.72
55.52
22.87
20.74
171.56
158.43
136.08
134.13
129.71
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

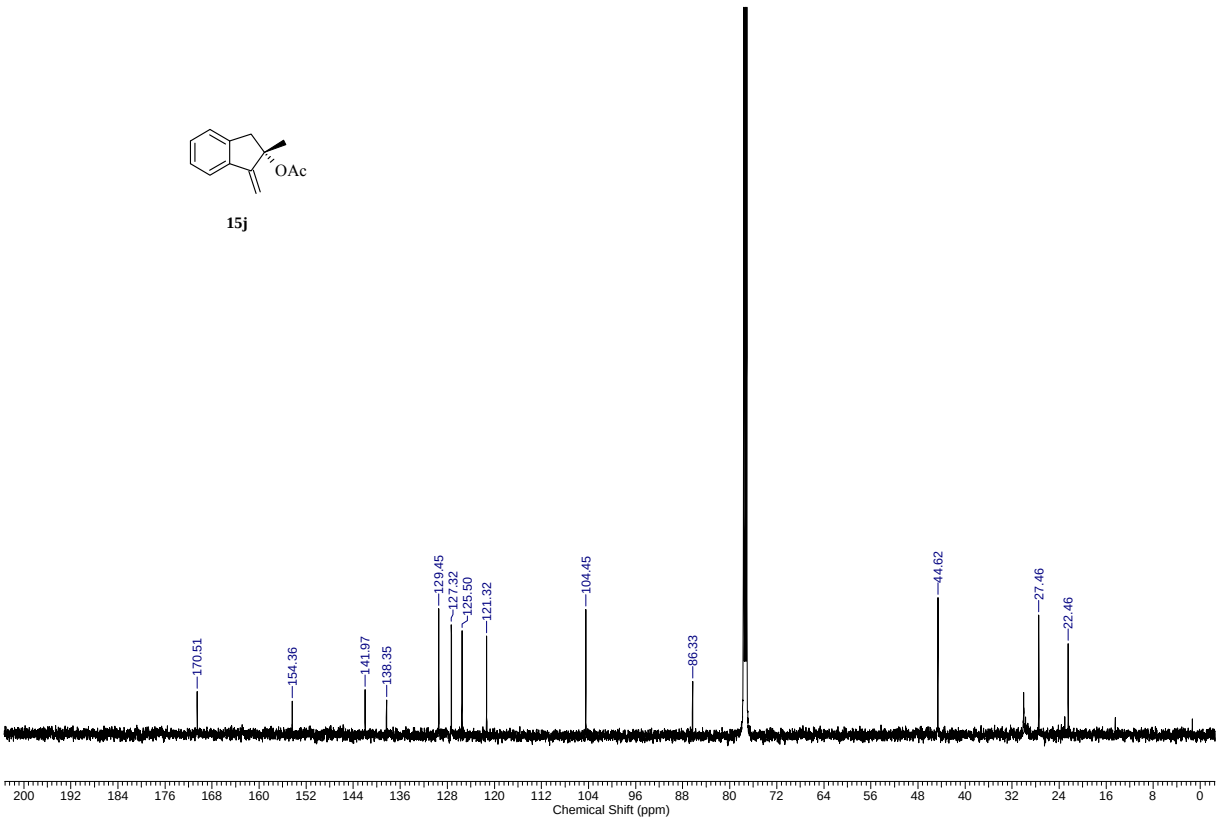

O
OAc
15i
1.93
3.83
1.72
5.57
5.36
7.25
7.18
7.17
7.15
7.13
6.76
6.74
2.83
2.81
2.77
2.75
2.74
2.42
2.40
2.14
2.12
2.11
0.88 0.96 0.97 1.00 0.99 3.01 0.97 1.02 0.98 0.97 2.78 2.95
Chemical Shift (ppm)

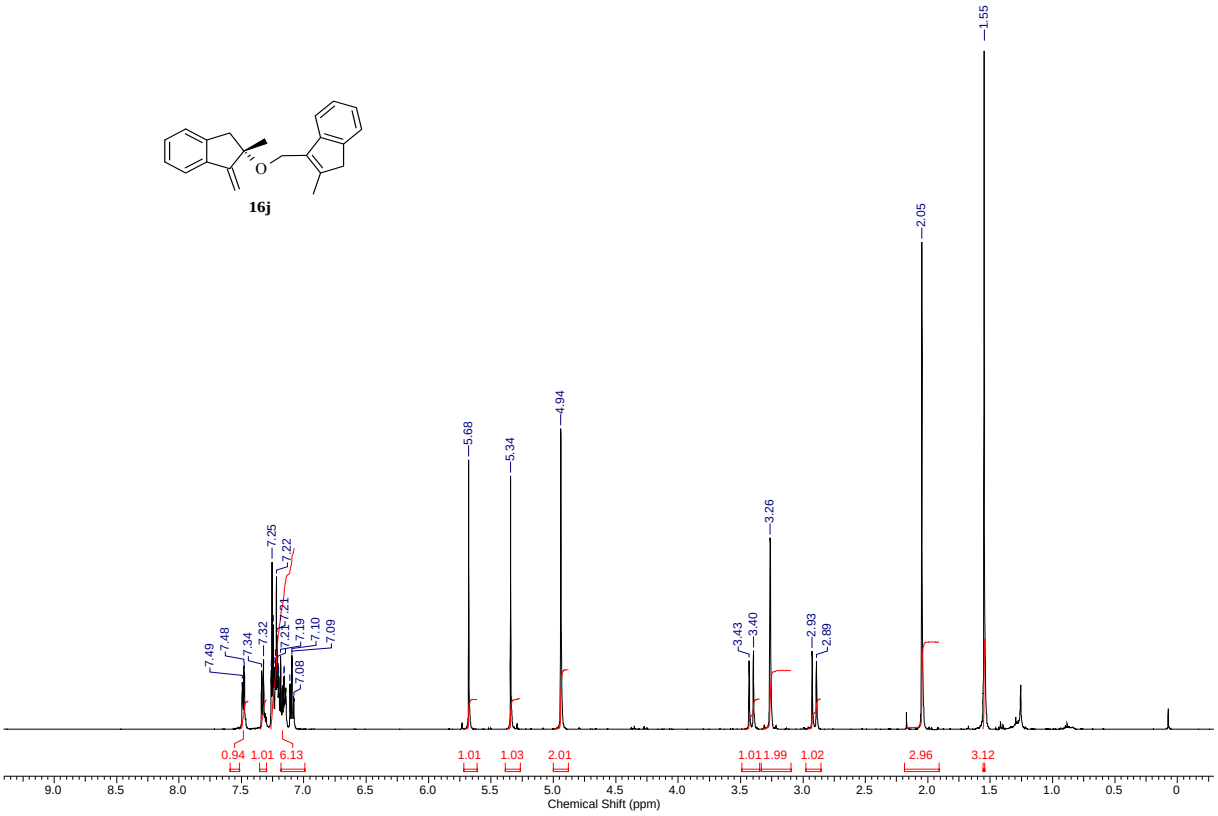

O
OAc
15i
170.26
156.82
146.53
135.04
126.67
124.59
117.88
109.17
108.78
80.55
55.44
33.72
23.33
20.65
Chemical Shift (ppm)

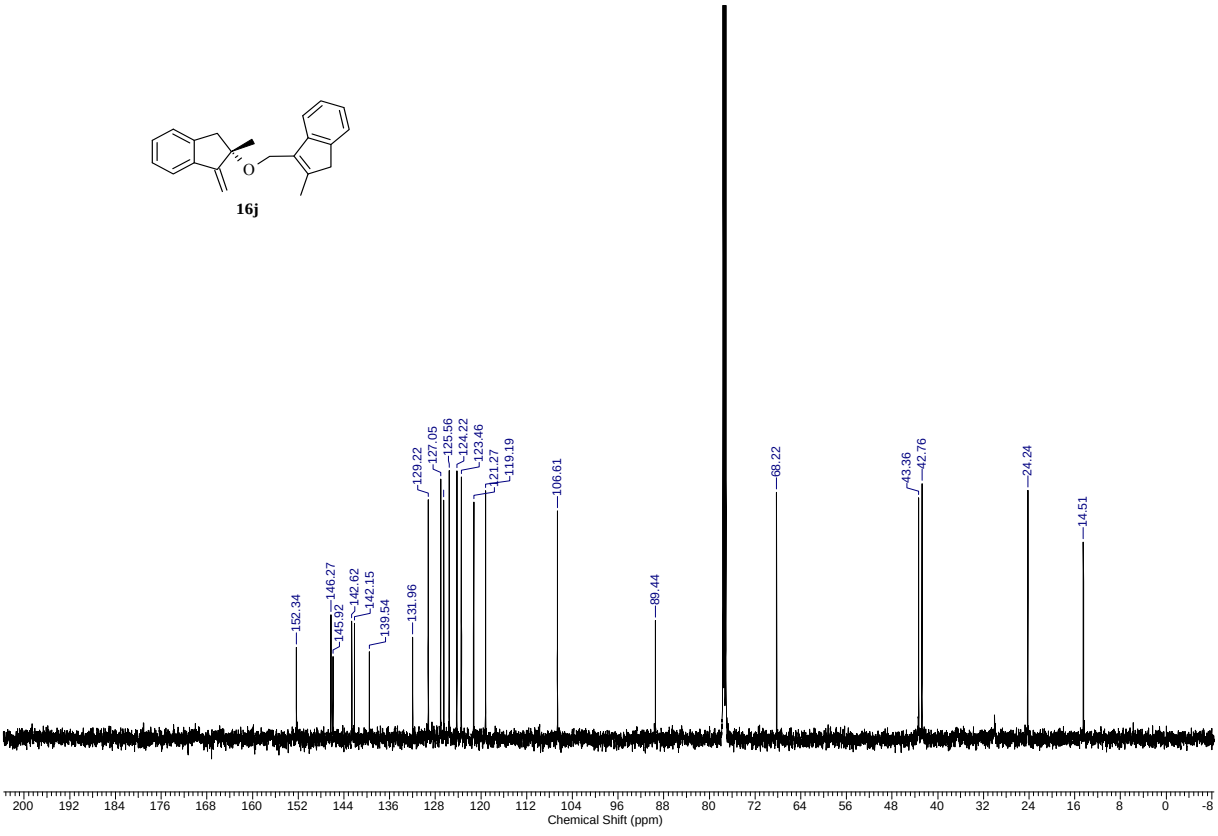

16i
3.83
3.81
1.53
1.95
7.25
5.71
5.47
2.69
4.77
4.75
2.20
7.24
7.15
7.13
7.07
6.75
6.74
6.73
6.71
7.05
2.71
2.67
2.25
2.21
2.18
4.79
4.73
2.90
2.86
2.84
2.29
1.90
1.88
1.85
1.06 1.94 1.05 1.98
1.00 1.06
2.03
6.00
1.00 3.08 1.01 1.96 2.99 1.07 3.08
Chemical Shift (ppm)

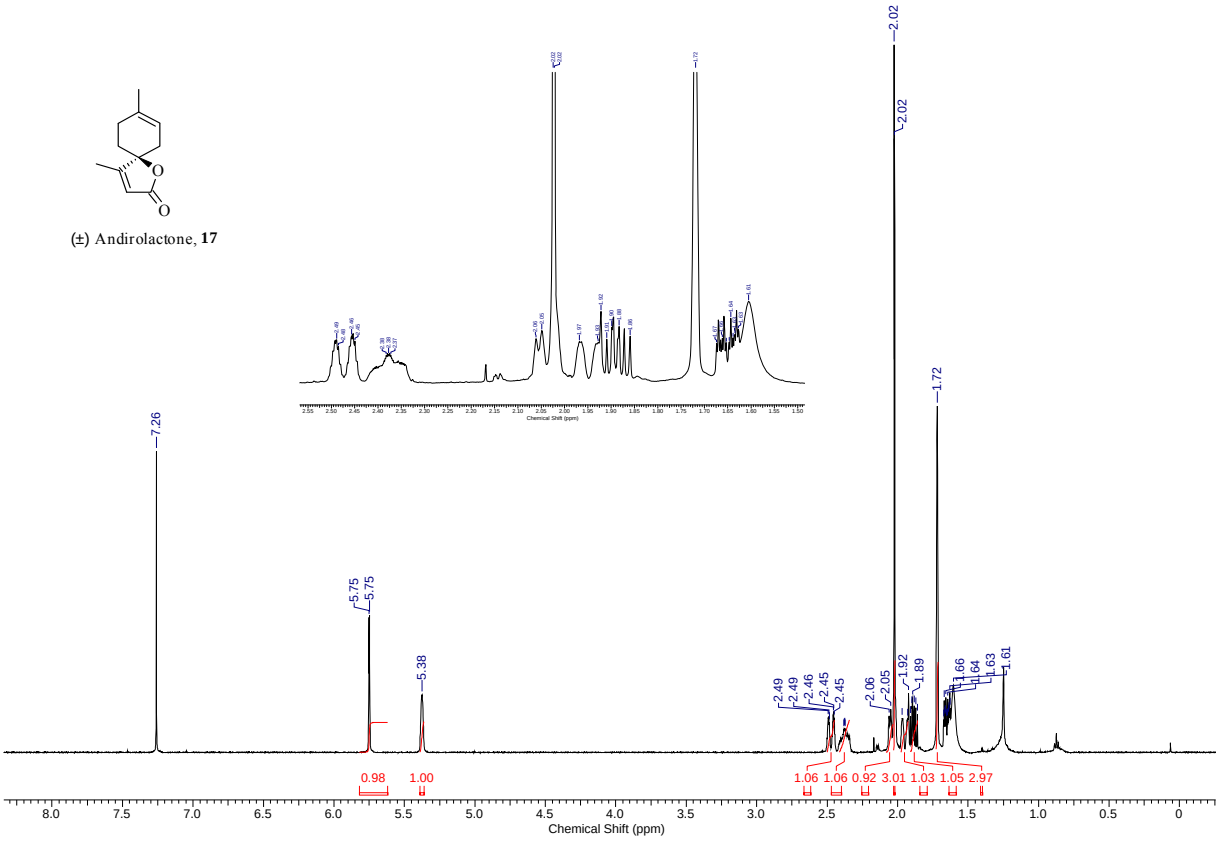

16i
157.16
155.95
146.10
142.17
137.06
135.64
126.82
126.73
125.56
124.96
123.12
117.67
116.57
110.95
108.96
108.89
81.39
71.39
55.85
55.70
33.29
30.58
23.69
20.72
20.09
Chemical Shift (ppm)

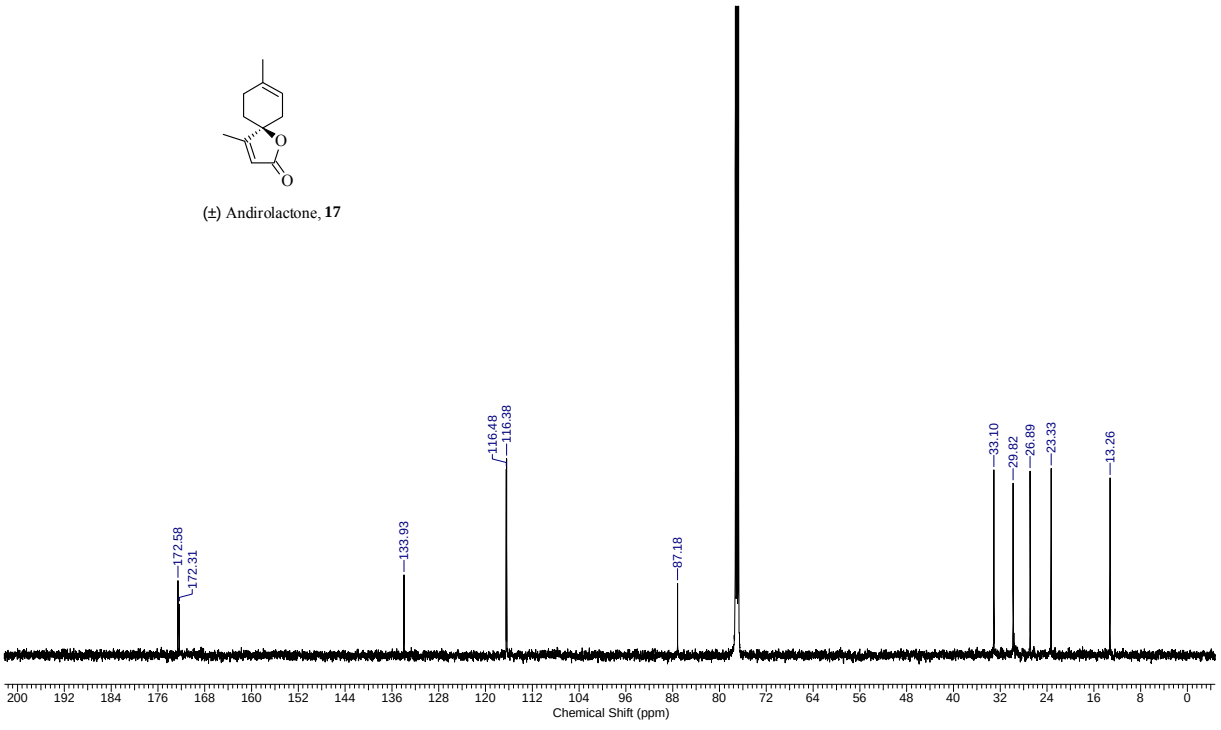

OAc
15j
7.25
2.03
1.60
5.58
5.20
1.25
7.49
7.48
7.26
7.22
7.20
3.48
3.52
3.23
3.19
2.04
0.96
3.32
1.05
1.02
1.15
1.06
3.02
3.21
Chemical Shift (ppm)


OAc
15j
170.51
154.36
141.97
138.35
129.45
127.32
125.50
121.32
104.45
86.33
44.62
27.46
22.46
Chemical Shift (ppm)


16j
1.55
2.05
4.94
5.68
5.34
3.26
7.25
7.22
7.49
7.48
7.34
7.32
7.21
7.19
7.10
7.09
7.08
3.43
3.40
2.93
2.89
0.94
1.01
6.13
1.01
1.03
2.01
1.01
1.99
1.02
2.96
3.12
Chemical Shift (ppm)

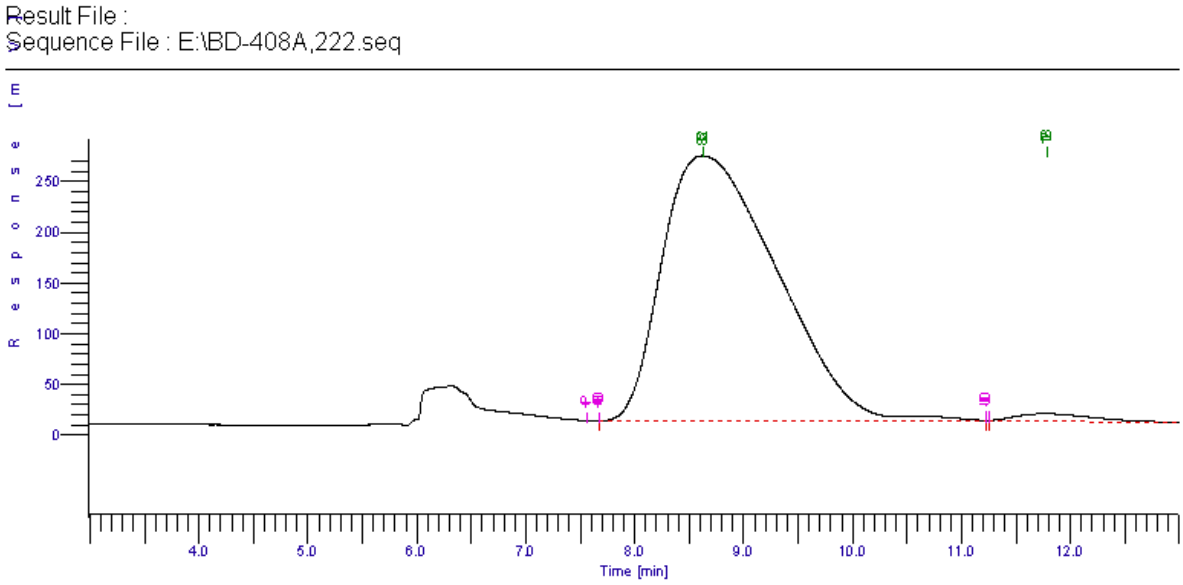

16j
152.34
146.27
145.92
142.62
142.15
139.54
131.96
129.22
127.05
125.56
124.22
123.46
121.27
119.19
106.61
89.44
68.22
43.36
42.76
24.24
14.51
Chemical Shift (ppm)


(±) Andirolactone, 17
7.26
5.75
5.75
5.38
2.49
2.49
2.46
2.45
2.45
2.06
2.05
1.92
1.89
1.72
1.66
1.64
1.63
1.61
2.02
2.02
0.98
1.00
1.06
1.06
0.92
3.01
1.03
1.05
2.97
Chemical Shift (ppm)


(±) Andirolactone, 17
172.58
172.31
133.93
116.48
116.38
87.18
33.10
29.82
26.89
23.33
13.26
Chemical Shift (ppm)

4. HPLC Spectras:

4.1) Compound **15h:**

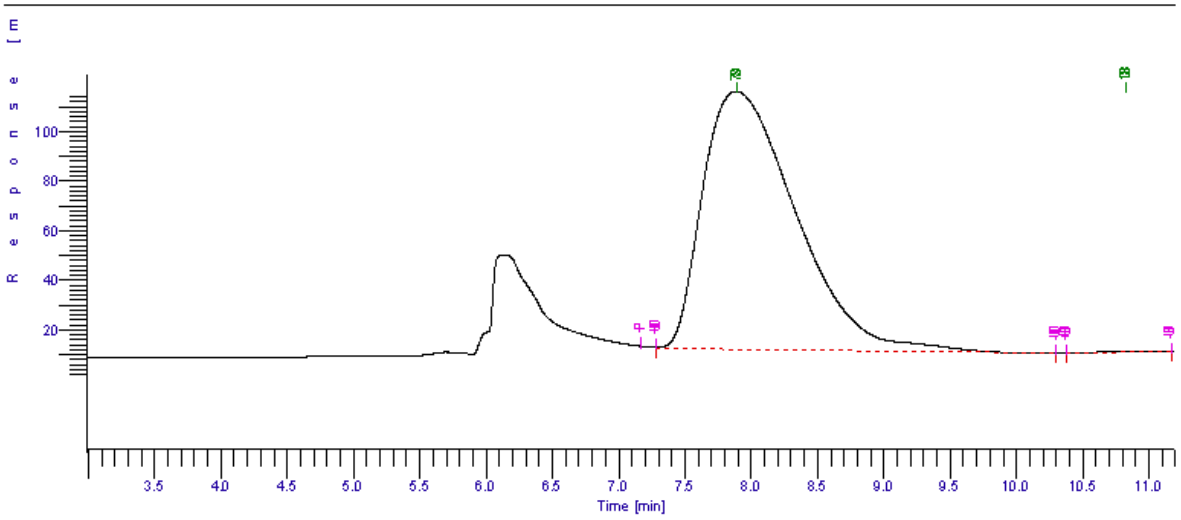


BD-408A C8 95-5 hexane/IPA 0.5 mL/min

Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
19142136.26	262039.78	98.32	98.32			MM	19.1421	19.1421
327393.47	7062.91	1.68	1.68			MM	0.3274	0.3274
19469529.72	269102.69	100.00	100.00				19.4695	19.4695

4.2) Compound **16f:**

Result File :
Sequence File : E:\BD-423B.seq



BD-423B C8 95-5 hexane/IPA 0.5 mL/min

Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
5056944.28	103995.17	99.86	99.86			MM	5.0569	5.0569
7213.08	349.54	0.14	0.14			MM	0.0072	0.0072
5064157.36	104344.71	100.00	100.00				5.0642	5.0642