Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Lewis Acid Catalyzed Nazarov Type Cyclization for the Synthesis of Substituted Indane Framework: Total Synthesis of (±)-Mutisianthol

Dattatraya H. Dethe,*[€] Raghavender Boda[€] and Ganesh M. Murhade[€]

[€]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India

Tel: + 91-512-2596537, Fax**:** + 91-512-2597436.

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General Information

All reactions were carried out under nitrogen or argon atmosphere with dry solvents under anhydrous conditions, unless otherwise mentioned. 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.

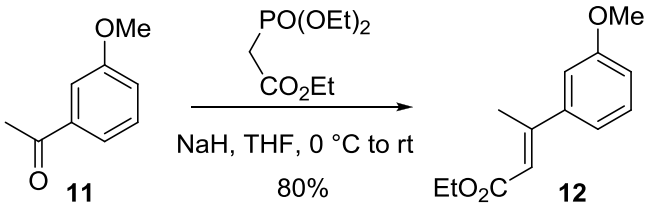
Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and an p-anisaldehyde or ninhydrin stain, and heat as developing agents. Merck silica gel (particle size 100-200 and 230-400 mesh) was used for flash column chromatography.

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. NMR spectra were recorded on either a Bruker Avance 200 (^{1}H: 200 MHz, ^{13}C: 50MHz), Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100MHz), Bruker Avance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz), JEOL ECX 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) Mass spectrometric data were obtained using WATERS-Q-Tof Premier-ESI-MS.

Diastereomeric ratios (dr) were determined by crude ^{1}H NMR.

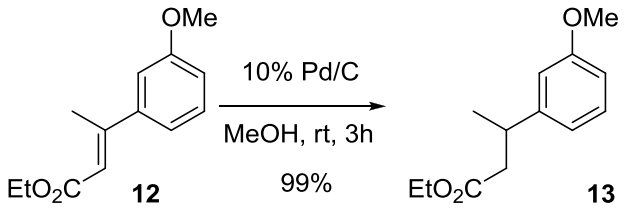
The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dm = doublet of a multiplet, m = multiplet, br = broad.

Synthesis of compound 12



To a suspension of NaH (60% dispersion in mineral oil, 1.6 g, 40 mmol) in dry THF (20 ml) was added drop wise triethylphosphonoacetate (9.6 ml, 48 mmol) at 0 °C under argon atmosphere. After 30 min, the compound **11** (4 g, 26.7 mmol) in dry THF was added to the reaction mixture, which was then allowed to warm to RT and stirred for 24h and then cooled with a water bath. A saturated aqueous NH_4Cl solution (20 ml) was then added drop wise to the cold mixture. The aqueous phase was extracted with EtOAc (2 × 50mL) and the combined organic phase was washed with brine (3 × 50mL), dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column furnished the product **12** (4.7 g, 80%) as a colorless liquid; *Rf* = 0.4 (EtOAc-hexane 1:19); **IR** (neat): ν_{max}/cm^{-1} 2933, 1712, 1627, 1578, 1342, 1291, 1217, 1160, 1043, 853, 781, 692; ^1H NMR (200 MHz, CHLOROFORM-d) δ = 7.29 (t, *J* = 8.0 Hz, 1 H), 7.12 - 7.03 (m, 1 H), 7.00 (t, *J* = 2.1 Hz, 1 H), 6.96 - 6.86 (m, 1 H), 6.14 (d, *J* = 1.3 Hz, 1 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 3.83 (s, 3 H), 2.57 (d, *J* = 1.3 Hz, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 166.7, 159.5, 155.3, 143.6, 129.4, 118.7, 117.2, 114.2, 112.0, 59.8, 55.2, 17.9, 14.2; **HRMS-ESI**: m/z calcd for $C_{13}H_{16}NaO_3$ [M+Na]: 243.0997; found: 243.0997.

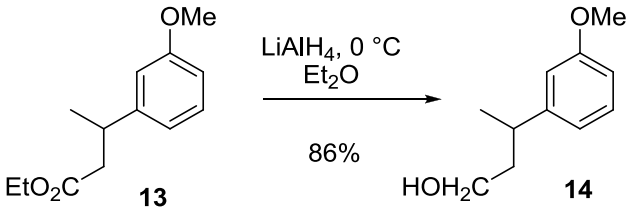
Synthesis of compound 13



Compound **12** (4 g, 18.2 mmol) was dissolved in 20 ml of MeOH and 10% palladium on activated carbon was added. The reaction was stirred under H_2 at RT overnight, whereupon TLC showed the reaction was complete. The solid was filtered off. Evaporation of the solvent

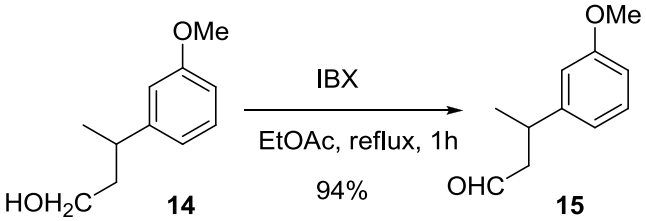
and purification of the residue on silica gel column furnished the product **13** (4.0 g, 99%) as a colorless liquid; *Rf* = 0.4 (EtOAc-hexane 1:19); **IR** (neat): ν_{max}/cm^{-1} 2966, 1733, 1602, 1585, 1488, 1455, 1437, 1369, 1262, 1159, 1070, 1095, 1034, 781, 700; ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.22 (t, *J* = 7.8 Hz, 1 H), 6.83 (d, *J* = 7.8 Hz, 1 H), 6.80 - 6.73 (m, 2 H), 4.10 (q, *J* = 7.1 Hz, 2 H), 3.81 (s, 3 H), 3.26 (sxt, *J* = 7.1 Hz, 1 H), 2.66 - 2.49 (m, 2 H), 1.30 (d, *J* = 7.1 Hz, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (125 MHz, CHLOROFORM-d) δ = 172.3, 159.6, 147.4, 129.4, 119.1, 112.7, 111.4, 60.2, 55.1, 42.9, 36.5, 21.7, 14.1; **HRMS-ESI**: m/z calcd for $C_{13}H_{18}NaO_3$ [M+Na]: 245.1154; found: 245.1159.

Synthesis of compound 14



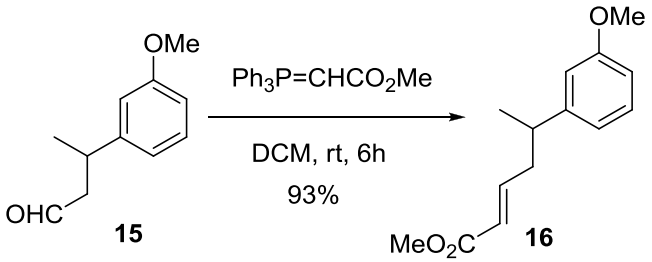
To a cold (0 °C), magnetically stirred solution of ester **13** (3 g, 13.5 mmol) in ether (25 ml) was added $LiAlH_4$ (1 g, 27.0 mmol) portion wise and stirred for 15 min. Progress of the reaction was monitored by TLC. The reaction mixture was then quenched with EtOAc, extracted with ether and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue furnished the product **14** (2.1 g, 86%) as a colorless liquid; *Rf* = 0.3 (EtOAc-hexane 1:4); **IR** (neat): ν_{max}/cm^{-1} 3358, 2958, 2932, 2876, 1608, 1600, 1584, 1486, 1454, 1436, 1317, 1285, 1261, 1159, 1043, 995, 872, 779, 701; ^{1}H NMR (400MHz, CHLOROFORM-d) δ = 7.23 (t, *J* = 7.8 Hz, 1 H), 6.81 (d, *J* = 7.6 Hz, 1 H), 6.78 - 6.73 (m, 2 H), 3.81 (s, 3 H), 3.62 - 3.52 (m, 2 H), 2.87 (sxt, *J* = 7.1 Hz, 1 H), 1.85 (q, *J* = 6.9 Hz, 2 H), 1.28 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, CHLOROFORM-d) δ = 159.7, 148.6, 129.4, 119.3, 112.9, 111.0, 61.1, 55.1, 40.8, 36.5, 22.3; **HRMS-ESI**: m/z calcd for $C_{11}H_{17}O_2$ [M+H]: 181.1229; found: 181.1225.

Synthesis of compound 15



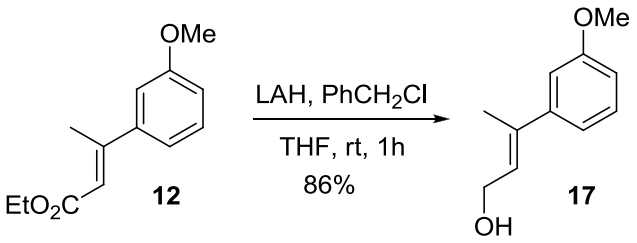
To a solution of alcohol **14** (2 g, 11.1 mmol) in ethyl acetate, was added IBX (3.7 g, 13.3 mmol) and refluxed for 1 h. The reaction mixture was cooled to RT and filtered through sintered funnel. The filter cake was washed with ethyl acetate for 2 to 3 times. Evaporation of the solvent and purification of the residue on silica gel column furnished the product **15** (1.8 g, 94%) as a colorless liquid; *Rf* = 0.4 (EtOAc-hexane 1:6); **IR** (neat): ν_{max}/cm^{-1} 2962, 2929, 2936, 2723, 1723, 1601, 1584, 1487, 1455, 1437, 1318, 1290, 1264, 1160, 1041, 872, 782, 700; ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 9.71 (t, *J* = 2.1 Hz, 1 H), 7.24 (t, *J* = 7.6 Hz, 1 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 6.79 - 6.75 (m, 2 H), 3.81 (s, 3 H), 3.34 (sxt, *J* = 7.1 Hz, 1 H), 2.80 - 2.61 (m, 2 H), 1.32 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, CHLOROFORM-d) δ = 201.7, 159.8, 147.1, 129.6, 119.0, 112.8, 111.4, 55.1, 51.6, 34.3, 22.0; **HRMS-ESI**: m/z calcd for $C_{11}H_{14}O_2$ [M^+]: 178.0994; found: 178.0993.

Synthesis of compound 16



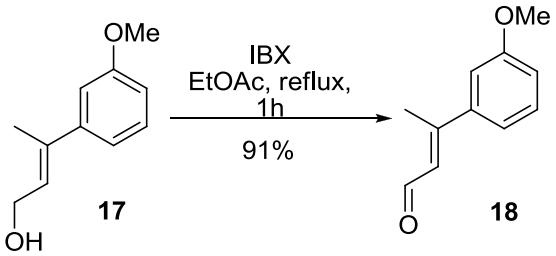
To a solution of aldehyde **15** (1.5 g, 8.42 mmol) in anhydrous CH_2Cl_2, was added dry $Ph_3P{=}CHCO_2Me$ (5.6 g, 16.8 mmol) and stirred magnetically for 6 h at RT. Evaporation of the solvent and purification of the residue on silica gel column furnished the product **16** (1.8 g, 93%) as a colorless liquid; *Rf* = 0.4 (EtOAc-hexane 1:6); **IR** (neat): ν_{max}/cm^{-1} 2958, 2836, 1723, 1656, 1601, 1584, 1487, 1454, 1435, 1314, 1266, 1209, 1158, 1043, 980, 872, 780, 700; ^{1}H NMR (500MHz, CHLOROFORM-d) δ = 7.25 - 7.20 (m, 1 H), 6.88 (td, *J* = 7.6, 15.3 Hz, 1 H), 6.79 (d, *J* = 7.3 Hz, 1 H), 6.77 - 6.72 (m, 2 H), 5.81 (d, *J* = 15.9 Hz, 1 H), 3.81 (s, 3 H), 3.71 (s, 3 H), 2.87 (sxt, *J* = 7.0 Hz, 1 H), 2.57 - 2.49 (m, 1 H), 2.47 - 2.38 (m, 1 H), 1.28 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, CHLOROFORM-d) δ = 166.9, 159.7, 147.7, 147.5, 129.4, 122.2, 119.2, 112.9, 111.3, 55.1, 51.4, 40.8, 39.2, 21.6; **HRMS-ESI**: m/z calcd for $C_{14}H_{22}NO_3$ [M+NH_4]: 252.1600; found: 252.1608.

Synthesis of compound 17



To a stirred suspension of $LiAlH_4$ (0.8g, 20.4 mmol) in dry THF, a solution of BnCl (2.5 ml, 21.8 mmol) in dry THF was added drop wise via syringe at room temperature. After the suspension was stirred for 15 min, a solution of compound **12** (3.0 g, 13.6 mmol) in dry THF was added drop wise to the suspension. The reaction mixture was stirred at room temperature for 1 h. Then the reaction was quenched with water, filtered and the filtrate was dried with Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column furnished the product **17** (2.1 g, 86%) as a colorless liquid; *Rf* = 0.3 (EtOAc-hexane 1:6); **IR** (neat): ν_{max}/cm^{-1} 3351, 2997, 2939, 2835, 1599, 1578, 1485, 1429, 1320. 1288, 1208, 1174, 1046, 997, 857, 777, 695; ^{1}H NMR (500MHz, CHLOROFORM-d) δ = 7.25 (t, *J* = 7.9 Hz, 1 H), 7.03 - 6.99 (m, 1 H), 6.97 - 6.94 (m, 1 H), 6.83 (dd, *J* = 2.1, 7.6 Hz, 1 H), 6.01 - 5.97 (m, 1 H), 4.36 (d, *J* = 6.7 Hz, 2 H), 3.83 (s, 3 H), 2.07 (s, 3 H); ^{13}C NMR (125 MHz ,CHLOROFORM-d) δ = 159.5, 144.4, 137.6, 129.2, 126.7, 118.3, 112.5, 111.7, 59.8, 55.2, 16.0; **HRMS-ESI**: m/z calcd for $C_{11}H_{13}O_2$ [M-H]: 177.0916; found: 177.0915.

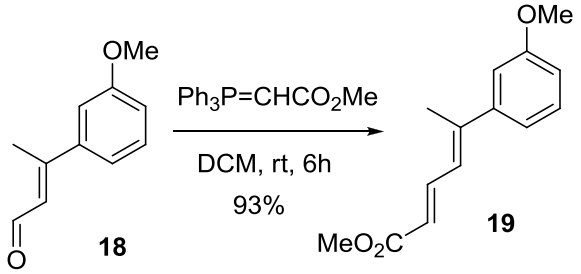
Synthesis of compound 18



To a solution of alcohol **17** (2.0g, 11.2 mmol) in ethyl acetate, was added IBX (3.8g, 13.5 mmol) and refluxed for 1 h. The reaction mixture was cooled to RT and filtered through sintered funnel. The filter cake was washed with ethyl acetate for 2 to 3 times. Evaporation of the solvent and purification of the residue on silicagel column furnished the product **18** (1.8 g, 91%) as a colorless liquid; *Rf* = 0.5 (EtOAc-hexane 1:6); **IR** (neat): ν_{max}/cm^{-1} 3003, 2940, 2838, 1666, 1599, 1577, 1487, 1449, 1432, 1289, 1266, 1138, 1044, 854, 782, 692; ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 10.17 (d, *J* = 7.7 Hz, 1 H), 7.32 (t, *J* = 8.1 Hz, 1 H), 7.12

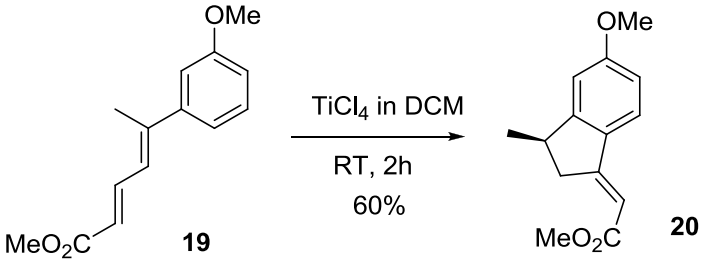
(dd, *J* = 0.8, 7.8 Hz, 1 H), 7.05 (t, *J* = 2.1 Hz, 1 H), 6.96 (dd, *J* = 2.5, 8.1 Hz, 1 H), 6.38 (dd, *J* = 1.1, 7.7 Hz, 1 H), 3.83 (s, 3 H), 2.55 (d, *J* = 1.1 Hz, 3 H); ^{13}C NMR (100 MHz ,CHLOROFORM-d) δ = 191.2, 159.6, 157.5, 141.9, 129.6, 127.2, 118.6, 115.3, 111.9, 55.2, 16.3; **HRMS-ESI**: m/z calcd for $C_{11}H_{13}O_2$ [M+H]: 177.0916; found: 177.0915.

Synthesis of compound 19



To a solution of aldehyde **18** (2.0 g, 11.4 mmol) in anhydrous CH_2Cl_2, was added dry $Ph_3P{=}CHCO_2Me$ (5.7 g, 17.0 mmol) and stirred magnetically for 6 h at RT. Evaporation of the solvent and purification of the residue on silicagel column furnished the product **19** (2.4 g, 93%) as a colorless liquid; *Rf* = 0.4 (EtOAc-hexane 1:9); **IR** (neat): ν_{max}/cm^{-1} 2997, 2949, 1715, 1619, 1575, 1432, 1314, 1294, 1260, 1211, 1142, 1041, 977, 869, 779; ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.67 (dd, *J* = 12.0, 15.0 Hz, 1 H), 7.20 (t, *J* = 8.0 Hz, 1 H), 7.00 (d, *J* = 7.4 Hz, 1 H), 6.93 (t, *J* = 2.3 Hz, 1 H), 6.79 (dd, *J* = 2.3, 8.0 Hz, 1 H), 6.49 (d, *J* = 12.0 Hz, 1 H), 5.91 (d, *J* = 15.0 Hz, 1 H), 3.75 (s, 3 H), 3.70 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR (125 MHz, CHLOROFORM-d): δ = 167.7, 159.6, 145.4, 143.5, 140.8, 129.4, 124.8, 120.9, 118.5, 113.5, 111.9, 55.3, 51.5, 16.7; **HRMS-ESI**: m/z calcd for $C_{14}H_{16}NaO_3$ [M+Na]: 255.0997; found: 255.0998.

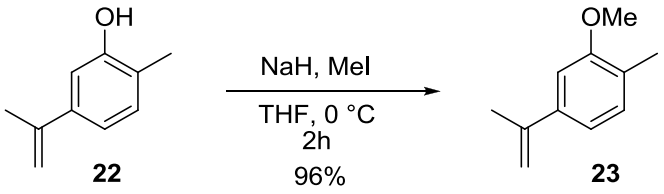
Synthesis of compound 20



To a stirred solution of compound **19** (50 mg, 0.2 mmol) in dry DCM (3 mL) under argon was added $TiCl_4$ (0.2 ml, 1 M sol in DCM, 0.2 mmol) drop wise at 0 °C. The progress of the reaction was followed by TLC. After it was stirred 2h at 0 °C, the reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$. The organic layer was separated, and

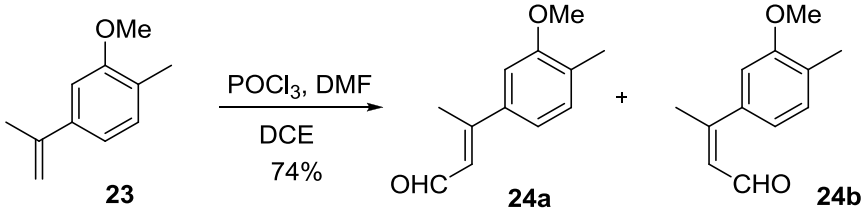
the aqueous layer was extracted with DCM (10 mL). The combined organic extracts were washed with water, brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silicagel column furnished the product **20** (30 mg, 60%) as a semi solid; *Rf* = 0.4 (EtOAc-hexane 1:19); **IR** (neat): v_{max}/cm^{-1} 2955, 2838, 1707, 1633, 1600, 1489, 1354, 1261, 1248, 1189, 1165, 1104, 1049, 847, 818; ^{1}H NMR (500 MHz ,CHLOROFORM-d) δ = 7.50 (d, *J* = 8.8 Hz, 1 H), 6.88 - 6.78 (m, 2 H), 6.16 (s, 1 H), 3.85 (s, 3 H), 3.76 (s, 3 H), 3.66 - 3.57 (m, 1 H), 3.37 - 3.27 (m, 1 H), 2.88 - 2.78 (m, 1 H), 1.32 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (125 MHz, CHLOROFORM-d): δ = 168.2, 162.6, 161.9, 156.6, 132.0, 122.8, 114.3, 108.5, 105.0, 55.4, 50.9, 40.9, 37.4, 21.3; **HRMS-ESI**: m/z calcd for $C_{14}H_{16}O_3$ [M^+]: 232.1099; found: 232.1098.

Synthesis of compound 23



A suspension of NaH (4.0 g, 60% suspension in mineral oil, 101.3 mmol) in dry THF was cooled to 0 °C and added drop wise a solution of compound **22** (10.0 g, 67.6 mmol) in dry THF. After 15 min MeI (8.4 ml, 135.1 mmol) was added slowly, the reaction mixture was allowed to stir at RT for 1 h. The reaction mixture was cooled to 0 °C, water was added to the reaction mixture and extracted with EtOAc. Evaporation of the solvent and purification of the residue on silicagel column furnished the product **23** (10.5 g, 96%) as a colorless liquid; *Rf* = 0.4 (hexane); **IR** (neat): v_{max}/cm^{-1} 2953, 2924, 1462, 1377, 1137, 1045, 886, 852; ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.22 - 7.09 (m, 1 H), 7.07 - 6.94 (m, 2 H), 5.38 (s, 1 H), 5.09 (s, 1 H), 3.90 (s, 3 H), 2.20 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 157.5, 143.4, 140.3, 130.2, 126.0, 117.6, 111.7, 107.2, 55.2, 21.9, 15.9; **HRMS-ESI**: m/z calcd for $C_{11}H_{15}O$ [M+H]: 163.1123; found: 163.1127.

Synthesis of compounds 24a, b



To 1.3 ml (17.0 mmol) of DMF, cooled to 5 °C, was added 1.6 ml (17.0 mmol) of $POCl_3$. 10 ml of ethylene dichloride was then added and the mixture was stirred for 15 min while it was cooled to 5 °C. Compound **23** (7.5 g, 46.3 mmole) dissolved in 10 ml of ethylene dichloride and added drop wise with stirring over the course of 40 min. The mixture was then refluxed for 15 min and cooled to room temperature. A solution of 7.0 gm (85.0 mmol) of anhydrous sodium acetate in 50 ml of water was added to the mixture slowly at first and then rapidly with stirring and cooling. The mixture was refluxed for 15 minutes, cooled and extracted with ether. Organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure. The crude was purified by flash chromatography over silica gel column furnished the major product **24a** (5.4 g, 62%) as a yellow color semi solid type compound; *Rf* = 0.4 (EtOAc-hexane 1:6) and minor product **24b** (1.0 g, 12%) as a yellow color semi solid type compound; *Rf* = 0.5 (EtOAc-hexane 1:6);

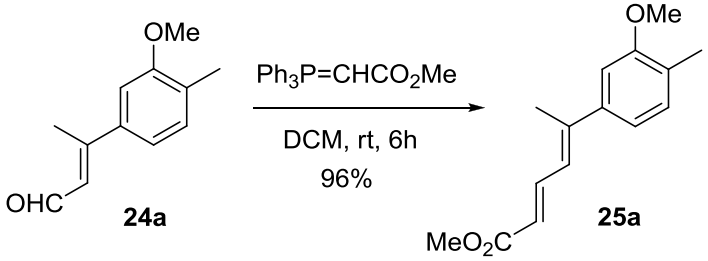
Major aldehyde (24a)

IR (neat): ν_{max}/cm^{-1} 2959, 2905, 1713, 1618, 1432, 1408, 1315, 1292, 1258, 1238, 1171, 1143, 1033, 972, 851, 794; ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 10.17 (d, *J* = 7.9 Hz, 1 H), 7.15 (d, *J* = 7.7 Hz, 1 H), 7.06 (dd, *J* = 1.7, 7.9 Hz, 1 H), 6.97 (d, *J* = 1.5 Hz, 1 H), 6.40 (dd, *J* = 1.0, 7.9 Hz, 1 H), 3.85 (s, 3 H), 2.55 (d, d, *J* = 1.0 Hz, 3 H), 2.24 (s, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 191.2, 157.7, 157.6, 139.1, 130.5, 129.3, 126.4, 118.4, 107.3, 55.1, 16.2, 16.0; **HRMS-ESI**: m/z calcd for $C_{12}H_{15}O_2$ [M+H]: 191.1072; found: 191.1074.

Minor aldehyde (24b)

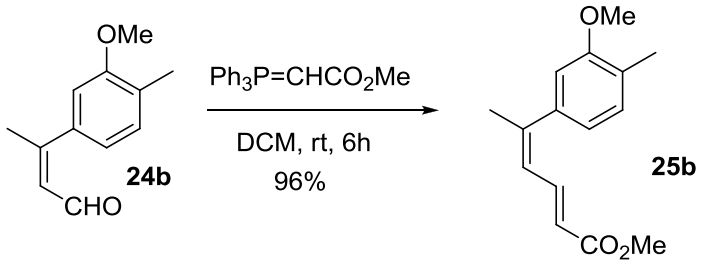
IR (neat): ν_{max}/cm^{-1} 2923, 2853, 1673, 1607, 1571, 1504, 1464, 1387, 1405, 1250, 1174, 1129, 1036, 862, 818; ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 9.45 (d, *J* = 8.1 Hz, 1 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 6.79 - 6.59 (m, 2 H), 6.00 (dd, *J* = 1.2, 8.1 Hz, 1 H), 3.74 (s, 3 H), 2.21 (d, *J* = 1.2 Hz, 3 H), 2.15 (s, 3 H); ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 193.1, 162.0, 157.3, 136.9, 130.2, 128.7, 127.8, 120.4, 109.6, 55.1, 26.1, 15.8; **HRMS-ESI**: m/z calcd for $C_{12}H_{15}O_2$ [M+H]: 191.1072; found: 191.1075.

Synthesis of compound 25a



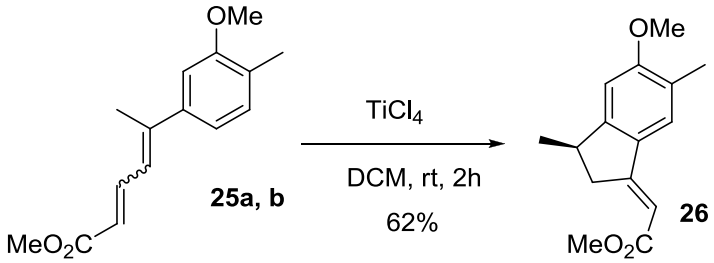
To a solution of aldehyde **24a** (5.4 g, 28.4 mmol) in anhydrous CH_2Cl_2, was added dry $Ph_3P{=}CHCO_2Me$ (14.2 g, 42.63 mmol) and stirred magnetically for 6 h at RT. Evaporation of the solvent and purification of the residue on silicagel column furnished the product **25a** (6.7 g, 96%) as a yellow solid, Mp. 52-54 °C; *Rf* = 0.4 (EtOAc-hexane 1:19); **IR** (KBr): ν_{max}/cm^{-1} 2950, 1713, 1616, 1605, 1516, 1430, 1408, 1317, 1291, 1238, 1206, 1192, 1142, 1132, 971, 887, 851, 794; ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.79 (dd, *J* = 11.6, 15.0 Hz, 1 H), 7.19 - 6.90 (m, 3 H), 6.58 (d, *J* = 11.6 Hz, 1 H), 5.99 (d, *J* = 15.0 Hz, 1 H), 3.87 (s, 3 H), 3.78 (s, 3 H), 2.24 (s, 3 H), 2.29 (s, 3 H); ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 167.5, 157.4, 145.5, 140.7, 140.5, 130.2, 127.0, 123.7, 120.2, 117.9, 107.1, 54.9, 51.2, 16.4, 15.8; **HRMS-ESI**: m/z calcd for $C_{15}H_{19}O_3$ [M+H]: 247.1334; found: 247.1333.

Synthesis of compound 25b



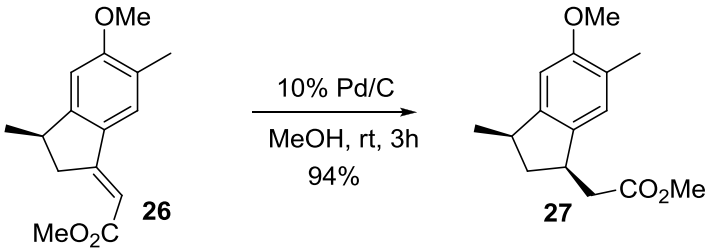
To a solution of aldehyde **24b** (1.0 g, 5.2 mmol) in anhydrous CH_2Cl_2, was added dry $Ph_3P{=}CHCO_2Me$ (2.6 g, 7.9 mmol) and stirred magnetically for 6 h at RT. Evaporation of the solvent and purification of the residue on silicagel column furnished the product **25b** (1.2 g, 96%) as a yellow color liquid; *Rf* = 0.5 (EtOAc-hexane 1:19); **IR** (neat): ν_{max}/cm^{-1} 2948, 2854, 1713, 1616, 1587, 1510, 1436, 1405, 1304, 1252, 1229, 1191, 1168, 1039, 852, 817; ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.47 (dd, *J* = 11.5, 15.3 Hz, 1 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 6.81 - 6.64 (m, 2 H), 6.27 (d, *J* = 11.5 Hz, 1 H), 5.89 (d, *J* = 15.3 Hz, 1 H), 3.84 (s, 3 H), 3.70 (s, 3 H), 2.26 (s, 3 H), 2.22 (s, 3 H); ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 167.5, 157.3, 148.7, 142.5, 138.8, 130.3, 126.4, 124.8, 120.0, 119.4, 109.7, 55.1, 51.1, 25.8, 15.8; **HRMS-ESI**: m/z calcd for $C_{15}H_{18}NaO_3$ [M+Na]: 269.1154; found: 269.1159.

Synthesis of compound 26



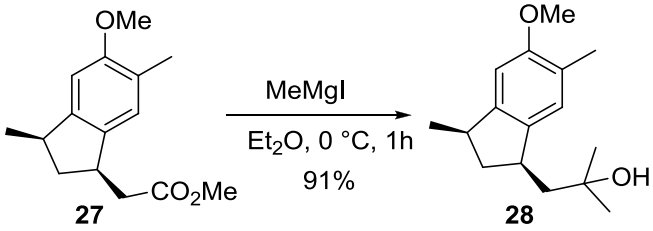
To a stirred solution of compound **25a, b** (200 mg, 0.8 mmol) in dry DCM (5 mL) under argon was added $TiCl_4$ (0.8 ml, 1 M sol in DCM, 0.8 mmol) drop wise at 0 °C. The progress of the reaction was followed by TLC. After it was stirred 2h at 0 °C, the reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with DCM (10 mL). The combined organic extracts were washed with water, brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silicagel column furnished the product **26** (124 mg, 62%) as a yellow solid, Mp. 53-55 °C; *Rf* = 0.4 (EtOAc-hexane 1:19); **IR** (KBr): ν_{max}/cm^{-1} 2952, 2832, 1707, 1684, 1631, 1608, 1578, 1491, 1451, 1436, 1346, 1325, 1262, 1178, 1164, 1116, 1020, 841; ^1H NMR (200 MHz, CHLOROFORM-d) δ = 7.31 (s, 1 H), 6.72 (s, 1 H), 6.12 (t, *J* = 2.4 Hz, 1 H), 3.86 (s, 3 H), 3.74 (s, 3 H), 3.67 - 3.49 (m, 1 H), 3.40 – 3.17 (m, 1 H), 2.89 - 2.71 (m, 1 H), 2.21 (s, 3 H), 1.31 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 168.0, 162.1, 160.7, 154.1, 131.0, 126.1, 123.0, 104.7, 104.2, 55.1, 50.5, 40.7, 37.2, 21.2, 16.3; **HRMS-ESI**: m/z calcd for $C_{15}H_{19}O_3$ [M+H]: 247.1334; found: 247.1338.

Synthesis of compound 27



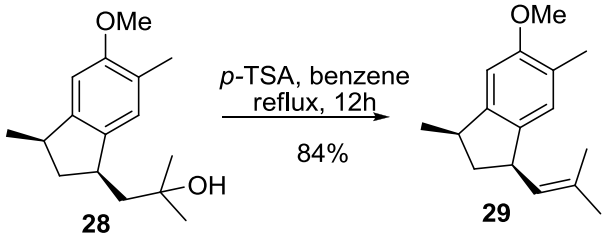
Compound **26** (300 mg, 1.2 mmol) was dissolved in 5 mL of methanol and 10% palladium on activated carbon was added. The reaction was stirred under H_2 at room temperature overnight, whereupon TLC showed the reaction was complete. The solid was filtered off. Evaporation of the solvent and purification of the residue on silicagel column furnished the product **27** (284 mg, 94%) as a colorless liquid; *Rf* = 0.5 (EtOAc-hexane 1:19); **IR** (neat): ν_{max}/cm^{-1} 2953, 2857, 1738, 1493, 1465, 1436, 1408, 1255, 1201, 1155, 1079, 1028, 996, 878; ^1H NMR (200 MHz, CHLOROFORM-d) δ = 6.89 (s, 1 H), 6.66 (s, 1 H), 3.81 (s, 3 H), 3.71 (s, 3 H), 3.53 - 3.31 (m, 1 H), 3.20 - 3.00 (m, 1 H), 2.88 (dd, *J* = 5.2, 15.4 Hz, 1 H), 2.75 - 2.49 (m, 1 H), 2.35 (dd, *J* = 9.3, 15.4 Hz, 1 H), 2.19 (s, 3 H), 1.30 (d, *J* = 6.7 Hz, 3 H); 1.35 - 1.18 (m, 1 H); ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 173.2, 157.1, 146.9, 136.5, 124.8, 124.5, 104.9, 55.2, 51.4, 42.8, 39.9, 39.3, 38.0, 19.7, 16.3; **HRMS-ESI**: m/z calcd for $C_{15}H_{20}NaO_3$ [M+Na]: 271.1310; found: 271.1319.

Synthesis of compound 28



To a cold (0 °C), magnetically stirred solution of the compound **27** (284 mg, 1.1 mmol) in dry ether was added methyl magnesium ioide [prepared from magnesium turnings (140 mg, 5.7 mmol), methyl iodide (0.3 ml, 5.7 mmol) and few crystals of iodine in dry ether] drop wise via syringe and stirred for 0.5 h at 0 °C. The reaction mixture was then quenched with aq NH_4Cl solution and extracted with EtOAc. Organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure. The crude was purified by flash chromatography over silica gel column furnished the product **28** (258 mg, 91%) as a gel type compound; *Rf* = 0.5 (EtOAc-hexane 1:9); **IR** (neat): v_{max}/cm^{-1} 3390, 2957, 2924, 2855, 1613, 1489, 1465, 1406, 1374, 1299, 1278, 1176, 1201, 1176, 1097, 1064, 1028, 909, 879; ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 6.97 (s, 1 H), 6.69 (s, 1 H), 3.85 (s, 3 H), 3.23 - 2.96 (m, 2 H), 2.80 - 2.58 (m, 1 H), 2.33 - 2.18 (m, 1 H), 2.23 (s, 3 H), 1.56 (dd, *J* = 10.0, 14.1 Hz, 1 H), 1.44 - 1.33 (m, 1 H), 1.36 (s, 6 H), 1.34 (d, *J* = 8.1 Hz, 3 H); ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 156.8, 146.6, 138.7, 125.0, 124.4, 105.0, 71.3, 55.4, 49.5, 45.6, 39.1, 38.5, 30.4, 29.7, 19.5, 16.3; **HRMS-ESI**: m/z calcd for $C_{16}H_{28}NO_2$ [M+NH_4]: 266.2120; found: 266.2121.

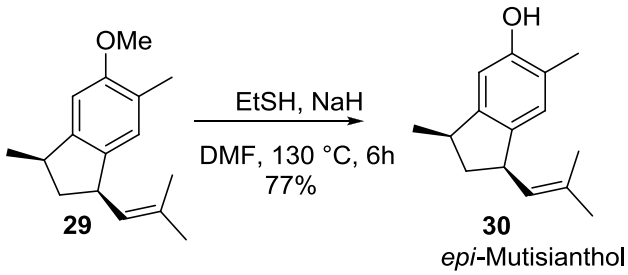
Synthesis of compound 29



A solution of compound **28** (100 mg, 0.4 mmol) and *p*-TSA (18 mg, 0.1 mmol) in dry benzene (3 mL) was refluxed for 12 h, after which it was cooled, washed with saturated $NaHCO_3$, brine and then dried. Removal of solvent followed by chromatography of the residue gave the compound **29** (77.9 mg, 84%) as a gel type compound; *Rf* = 0.5 (hexane); **IR** (neat): v_{max}/cm^{-1} 2953, 2925, 2853, 1613, 1488, 1465, 1405, 1374, 1303, 1278, 1198, 1156, 1095, 1068, 1027, 883, 843, 808; ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 6.82 (s, 1 H), 6.69 (s, 1 H), 5.13 (d, *J* = 9.2 Hz, 1 H), 3.85 (s, 3 H), 3.84 - 3.79 (m, 1 H), 3.14 - 3.05 (m, 1

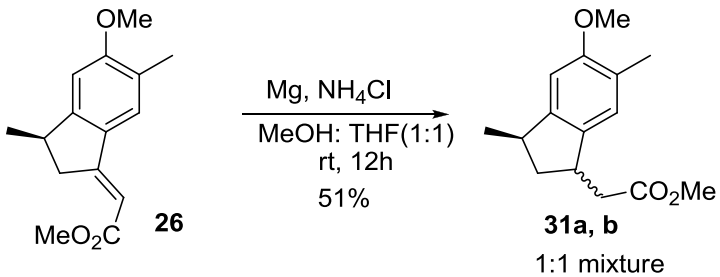
H), 2.46 (td, *J* = 6.9, 12.1 Hz, 1 H), 2.20 (s, 3 H), 1.80 (s, 3 H), 1.78 (s, 3 H), 1.33 (d, *J* = 6.7 Hz, 3 H), 1.35 – 1.29 (m, 1 H); ^{13}C NMR (125 MHz, CHLOROFORM-d) δ = 156.9, 146.8, 138.3, 132.2, 128.5, 125.8, 124.5, 105.1, 55.5, 44.0, 42.4, 38.3, 25.8, 19.4, 18.1, 16.3; **HRMS-ESI**: m/z calcd for $C_{16}H_{23}O$ [M+H]: 231.1749; found: 231.1744.

Synthesis of compound 30



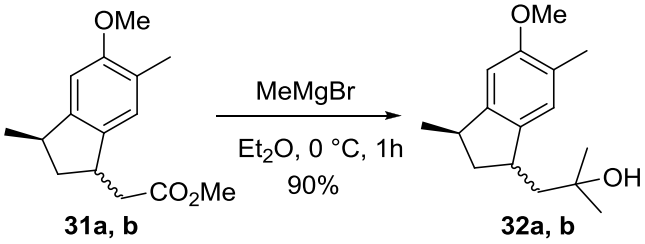
Under N_2, NaH (417.4 mg, 10.4 mmol, 60% in mineral oil) was washed with anhydrous hexanes (3 times). After a few minutes, anhydrous DMF (10 mL) was added. To this mixture was slowly added a solution of EtSH (0.5 mL, 6.8 mmol) in anhydrous DMF (1 mL) at 0 °C, and the resulting yellow solution was stirred for 20 min at rt. A solution of compound **29** (50 mg, 0.22 mmol) in anhydrous DMF (1 mL) was then added dropwise, and the resulting mixture was stirred for 6 h at 130 °C, becoming slightly brown. The mixture was cooled to rt, and a saturated solution of NH_4Cl was added. The mixture was extracted with Et_2O, and the organic phase was washed with H_2O and brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Evaporation of the solvent and purification of the residue on silicagel column furnished the product **30** (36.1 mg, 77%) as a semi solid; *Rf* = 0.5 (EtOAc-hexane 1:9); **IR** (neat): ν_{max}/cm^{-1} 3401, 2955, 2925, 2866, 1488, 1457, 1416, 1375, 1286, 1182, 1150, 1057, 995; ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 6.79 (s, 1 H), 6.62 (s, 1 H), 5.11 (d, *J* = 8.6 Hz, 1 H), 4.57 (s, 1 H), 3.84 - 3.77 (m, 1 H), 3.10 - 3.00 (m, 1 H), 2.48 - 2.41 (m, 1 H), 2.22 (s, 3 H), 1.80 (s, 3 H), 1.77 (s, 3 H), 1.28 (d, *J* = 6.7 Hz, 3 H), 1.25 – 1.28 (m, 1 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 152.7, 147.5, 139.1, 132.3, 128.4, 125.9, 121.2, 109.6, 44.1, 42.4, 38.0, 25.8, 19.2, 18.1, 15.8; **HRMS-ESI**: m/z calcd for $C_{15}H_{20}O$ [M^+]: 216.1514; found: 216.1516.

Synthesis of compound 31a, b



To a solution of compound **26** (400 mg, 1.6 mmol) in 1:1 MeOH (5 mL) and THF (5 mL) at RT was added freshly crushed Mg turnings (1.2 g, 48.8 mmol) and NH_4Cl (172 mg, 3.2 mmol). The resulting mixture was stirred vigorously at rt for 12 h. The reaction was cooled to 0 °C and quenched by saturated aqueous NH_4Cl solution and allowed to warm to RT before being partitioned between H_2O and CH_2Cl_2. The organic phase was isolated and the aqueous phase extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue on silicagel column furnished inseparable mixture of diasteromers (1:1) **31a, b** (205 mg, 51%) as a gel type compound;; **IR** (neat): v_{max}/cm^{-1} 2953, 2857, 1738, 1493, 1465, 1436, 1408, 1255, 1201, 1155, 1079, 1028, 996, 878; ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 6.93 (s, 1 H), 6.89 (s, 1 H), 6.66 (s, 2 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 3.72 (s, 3 H), 3.69 (s, 3 H), 3.59 - 3.50 (m, 1 H), 3.47 - 3.36 (m, 1 H), 3.28 - 3.17 (m, 1 H), 3.14 - 3.02 (m, 1 H), 2.88 (dd, *J* = 5.1, 15.4 Hz, 1 H), 2.66 - 2.53 (m, 2 H), 2.42 - 2.31 (m, 2 H), 2.19 (s, 3 H), 2.18 (s, 3 H), 2.06 – 1.97 (m, 1 H), 1.96 – 1.87 (m, 1 H), 1.30 (d, *J* = 6.7 Hz, 3 H), 1.24 (d, *J* = 7.0 Hz, 3 H), 1.33 - 1.21 (m, 1 H); ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 173.3, 173.2, 157.2, 157.1, 146.9, 146.8, 136.5, 136.4, 125.5, 124.8, 124.7, 124.5, 105.2, 105.0, 55.3, 55.2, 51.4, 51.3, 42.8, 41.1, 40.1, 39.9, 39.3, 39.2, 38.0, 37.5, 20.3, 19.7, 16.3; **HRMS-ESI**: m/z calcd for $C_{15}H_{20}NaO_3$ [M+Na]: 271.1310; found: 271.1319.

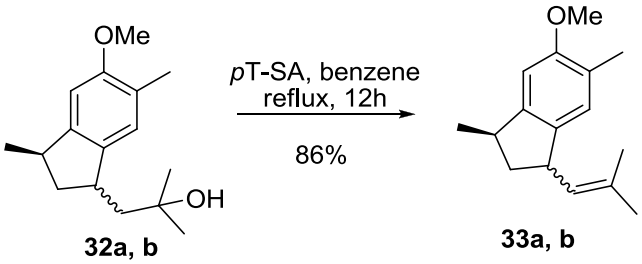
Synthesis of compound 32a, b



According to the procedure for the synthesis of compound **28**, compound **31a, b** (200 mg, 0.8 mmol), magnesium turnings (97 mg, 4.0 mmol) and methyl iodide (0.3 ml, 4.0 mmol) were used to furnish the product **32a, b** (180 mg, 90%) as a colorless liquid; *Rf* = 0.5 (EtOAc-hexane 1:9); **IR** (neat): v_{max}/cm^{-1} 3391, 2957, 2924, 2865, 1613, 1490, 1465, 1406, 1374, 1334, 1298, 1277, 1253, 1201, 1174, 1147, 1096, 1066, 1028, 995, 932, 909, 879, 843; ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 6.97 (s, 2 H), 6.69 (s, 2 H), 3.84 (s, 3 H), 3.85 (s, 3 H), 3.35 - 3.19 (m, 2 H), 3.15 - 3.06 (m, 2 H), 2.71 - 2.65 (m, 1 H), 2.29 - 2.21 (m, 1 H), 2.22 (s, 3 H), 2.21 (s, 3H), 2.16 - 2.08 (m, 1 H), 2.03 - 1.93 (m, 2 H), 1.66 - 1.53 (m, 2 H), 1.37 - 1.32 (m, 1 H), 1.36 (s, 6 H), 1.34 (s, 6 H), 1.33 (d, *J* = 8.8 Hz, 3 H), 1.24 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, CHLOROFORM-d) δ = 156.9, 147.0, 146.6, 138.8, 138.7, 125.5,

125.0, 124.7, 124.4, 105.3, 105.0, 71.4, 55.5, 55.4, 49.8, 49.5, 45.6, 43.3, 39.2, 38.6, 38.2, 30.5, 30.2, 29.9, 29.7, 20.9, 19.6, 16.4; **HRMS-ESI**: m/z calcd for $C_{16}H_{24}NaO_2$ [M+Na]: 271.1674; found: 271.1672.

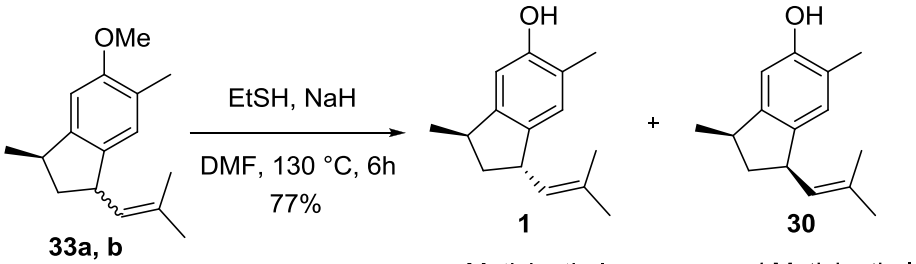
Synthesis of compound 33a, b



32a, b **33a, b**

According to the procedure for the synthesis of compound **29**, compound **32a, b** (100 mg, 0.4 mmol) and *p*-TSA (18 mg, 0.1 mmol) were used to furnish the product **33a, b** (79.7 mg, 86%) as a colorless liquid; *Rf* = 0.5 (hexane); **IR** (neat): ν_{max}/cm^{-1} 2953, 2925, 2855, 1614, 1489, 1465, 1406, 1374, 1300, 1277, 1199, 1168, 1092, 1068, 1027, 883, 843, 808; ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 6.85 (s, 1 H), 6.82 (s, 1 H), 6.69 (s, 2 H), 5.13 (d, *J* = 9.2 Hz, 2 H), 4.04 - 3.97 (m, 1 H), 3.85 (s, 1 H), 3.83 (s, 1 H), 3.85 - 3.83 (m, 1 H), 3.27 – 3.24 (m, 1 H), 3.12 - 3.06 (m, 1 H), 2.50 - 2.44 (m, 1 H), 2.20 (s, 3 H), 2.19 (s, 3 H), 2.02 - 1.92 (m, 2 H),1.80 (s, 6 H), 1.78 (s, 3 H), 1.76 (s, 3 H), 1.33 (d, *J* = 6.3 Hz, 3 H), 1.24 (d, *J* = 6.3 Hz, 3 H), 1.35 – 1.29 (m, 1 H); ^{13}C NMR (125 MHz, CHLOROFORM-d) δ = 157.0, 147.2, 146.8, 138.4, 137.8, 132.2, 131.1, 128.7, 128.5, 126.1, 125.8, 124.8, 124.5, 105.5, 105.1, 55.6, 55.5, 44.1, 42.44, 42.42, 41.5, 38.4, 38.3, 29.7, 25.8, 21.0, 19.4, 18.14, 18.14, 16.34, 16.28;

Synthesis of compounds 1 and 30

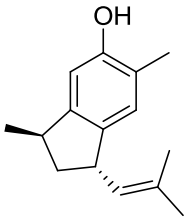


33a, b **1** **30**

Mutisianthol *epi*-Mutisianthol

According to the procedure for the synthesis of compound **30**, compound **33a, b** (79 mg, 0.3 mmol), NaH (659 mg, 16.5 mmol, 60% in mineral oil) and EtSH (0.8 mL, 10.7 mmol) were used to furnish the product **1** (28.5 mg, 38%) as a white solid and product **30** (28.5 mg, 38%), Mp. 97-98 °C; *Rf* = 0.5 (EtOAc-hexane 1:9; **IR** (neat): ν_{max}/cm^{-1} 3331, 2951, 2924, 2857, 1618, 1492, 1446, 1374, 1295, 1190, 1162, 881, 861; ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 6.81 (s, 1 H), 6.61 (s, 1 H), 5.12 (brd, *J* = 10.4 Hz, 1 H), 4.54 (brs, 1 H), 4.02 - 3.92 (m, 1 H), 3.24 - 3.16 (m, 1 H), 2.21 (s, 3 H), 1.98 - 1.89 (m, 2 H), 1.78 (brs, 3 H), 1.74 (brs, 3

H), 1.20 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 152.7, 147.9, 138.6, 131.2, 128.6, 126.3, 121.6, 110.1, 42.4, 41.5, 38.0, 25.8, 20.9, 18.1, 15.8; **HRMS-ESI**: m/z calcd for $C_{15}H_{20}O$ [M^+]:216.1514; found: 216.1515.



Mutisianthol 1

synthesized Mutisianthol (**1)**	Synthetic Mutisianthol (literature) Ferraz, H. M. C.; Aguilar, A. M.; Silva, L. F. Jr. *Tetrahedron*, **2003**, *59*, 5817.	Isolation
δH (500 MHz, $CDCl_3$)	δH (500 MHz, $CDCl_3$)	δH (270 MHz, $CDCl_3$)
1.20 (d, *J* = 7.0 Hz, 3 H)	1.20 (d, *J* = 7.0 Hz, 3H)	1.20 (d, *J* = 7.0 Hz, 3 H)
1.74 (brs, 3 H)	1.74 (d, *J* = 1.3 Hz, 3H),	1.74 (d, *J* = 10.0 Hz, 3 H)
1.78 (brs, 3 H)	1.77 (d, *J* = 1.3 Hz, 3H)	1.78 (d, *J* = 1.0 Hz, 3 H)
1.89 - 1.98 (m, 2 H),	1.88 – 1.97 (m, 2H),	1.93 (m, 2 H)
2.21 (s, 3 H),	2.21 (s, 3H)	2.20 (s, 3 H)
3.16 - 3.24 (m, 1 H)	3.14 – 3.25 (m, 1H)	3.21 (ddq, *J* = 7.0 Hz, 1 H)
3.92 - 4.02 (m, 1 H),	3.95 – 3.99 (m, 1H)	3.97 (ddd, *J* = 9.0 Hz, 1 H)
4.54 (brs, 1 H),		
5.12 (brd, *J* = 10.4 Hz, 1 H	5.10 – 5.13 (m, 1H)	5.13 (dqq, *J* = 8.0 Hz, 1 H)
6.61 (s, 1 H),	6.61 (s, 1H)	6.61 (s, 1 H)
6.81 (s, 1 H),	6.81 (s, 1H)	6.81 (s, 1 H)

synthesized Mutisianthol (**1)**	Synthetic Mutisianthol (literature) Ferraz, H. M. C.; Aguilar, A. M.; Silva, L. F. Jr. *Tetrahedron*, **2003**, *59*, 5817.
δC (100 MHz, $CDCl_3$)	δC (75 MHz, $CDCl_3$)
15.8	15.8
18.1	18.1
20.9	20.9
25.8	25.8
38.0	38.1
41.5	41.5
42.4	42.4
110.1	110.1
121.6	121.6
126.3	126.3
128.6	128.6
131.2	131.2
138.6	138.7
147.9	147.9
152.7	152.8

X-ray crystallographic data and structure refinement for compound 20

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) compound1

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: compound1

Bond precision: C-C = 0.0058 A Wavelength=0.71073

Cell: a=9.0170(7) b=12.1740(9) c=12.8341(9)
alpha=108.889(2) beta=99.634(2) gamma=109.852(2)
Temperature: 273 K

	Calculated	Reported
Volume	1191.34(16)	1191.34(15)
Space group	P -1	?
Hall group	-P 1	?
Moiety formula	C14 H16 O3	?
Sum formula	C14 H16 O3	C29 H29 O6
Mr	232.27	473.52
Dx,g cm-3	1.295	1.320
Z	4	2
Mu (mm-1)	0.090	0.092
F000	496.0	502.0
F000'	496.26	
h,k,lmax	12,16,17	12,16,17
Nref	5960	5938
Tmin,Tmax		
Tmin'		

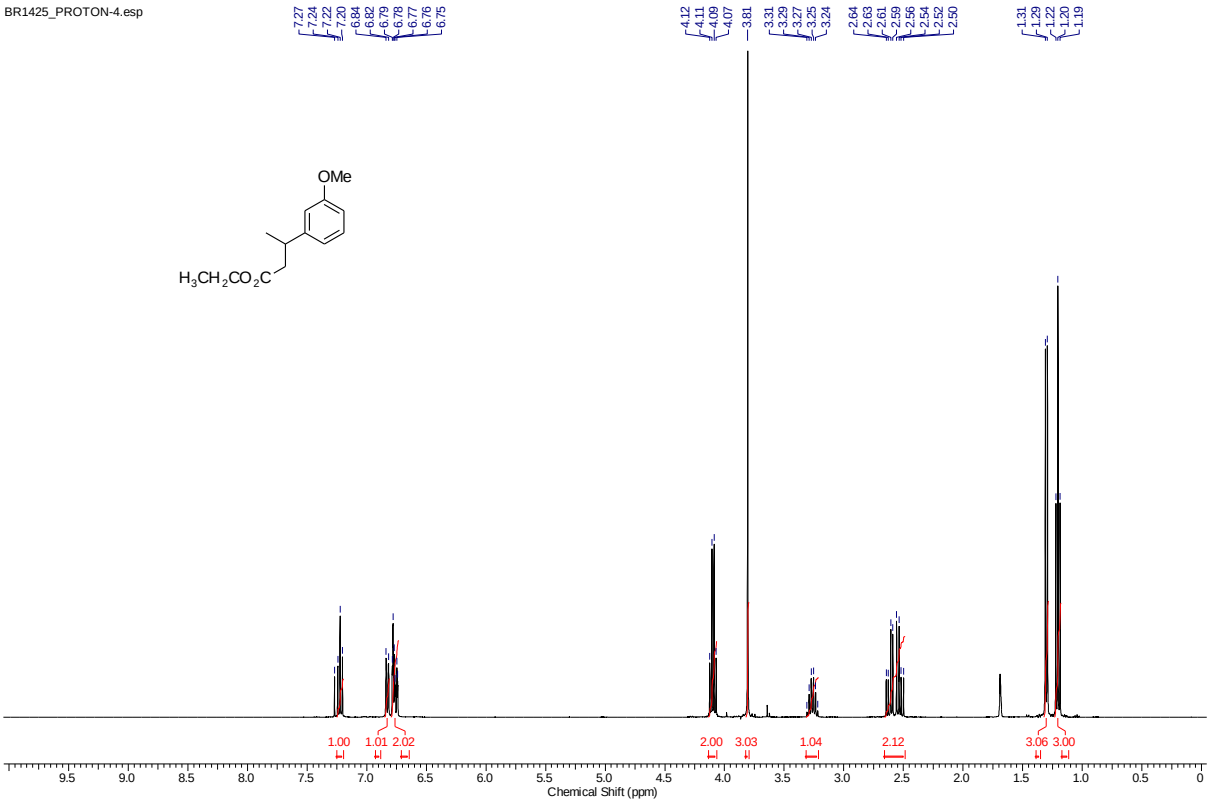
Correction method= Not given

Data completeness= 0.996 Theta(max)= 28.360

R(reflections)= 0.0964(3658) wR2(reflections)= 0.2630(5938)

S = 1.035 Npar= 308

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.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6.78
6.77
6.76
6.75
4.12
4.11
4.09
4.07
3.81
3.31
3.29
3.27
3.25
3.24
2.64
2.63
2.61
2.59
2.56
2.54
2.52
2.50
1.31
1.29
1.22
1.20
1.19
OMe
H3CH2CO2C
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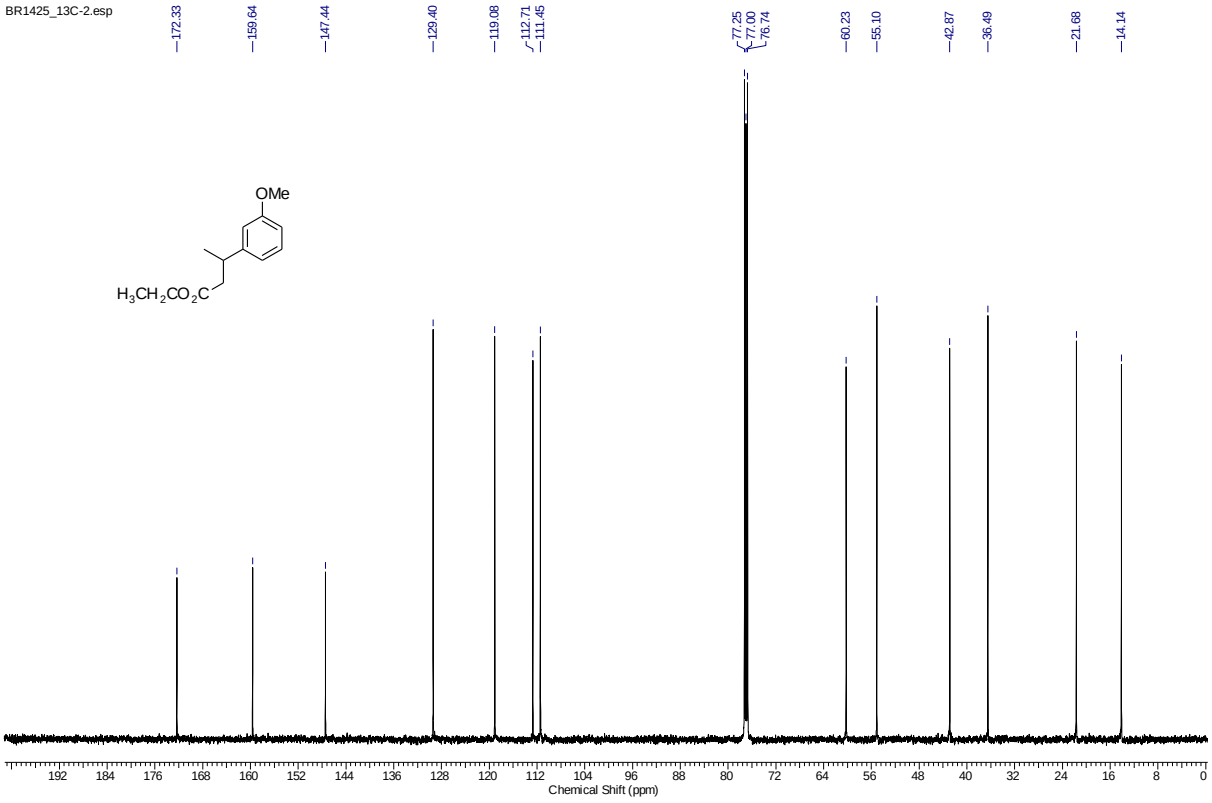
1.01
2.02
2.00
3.03
1.04
2.12
3.06
3.00
Chemical Shift (ppm)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112.71
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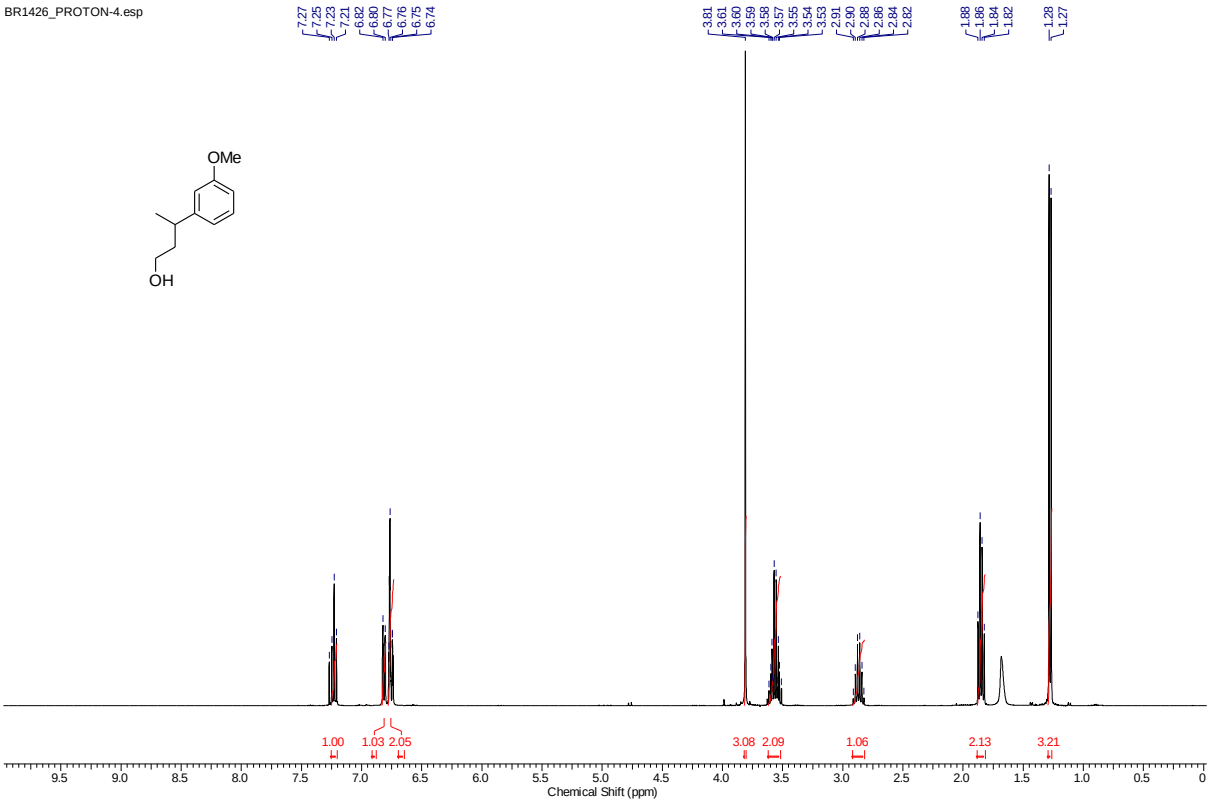
76.74
60.23
55.10
42.87
36.49
21.68
14.14
OMe
H3CH2CO2C
Chemical Shift (ppm)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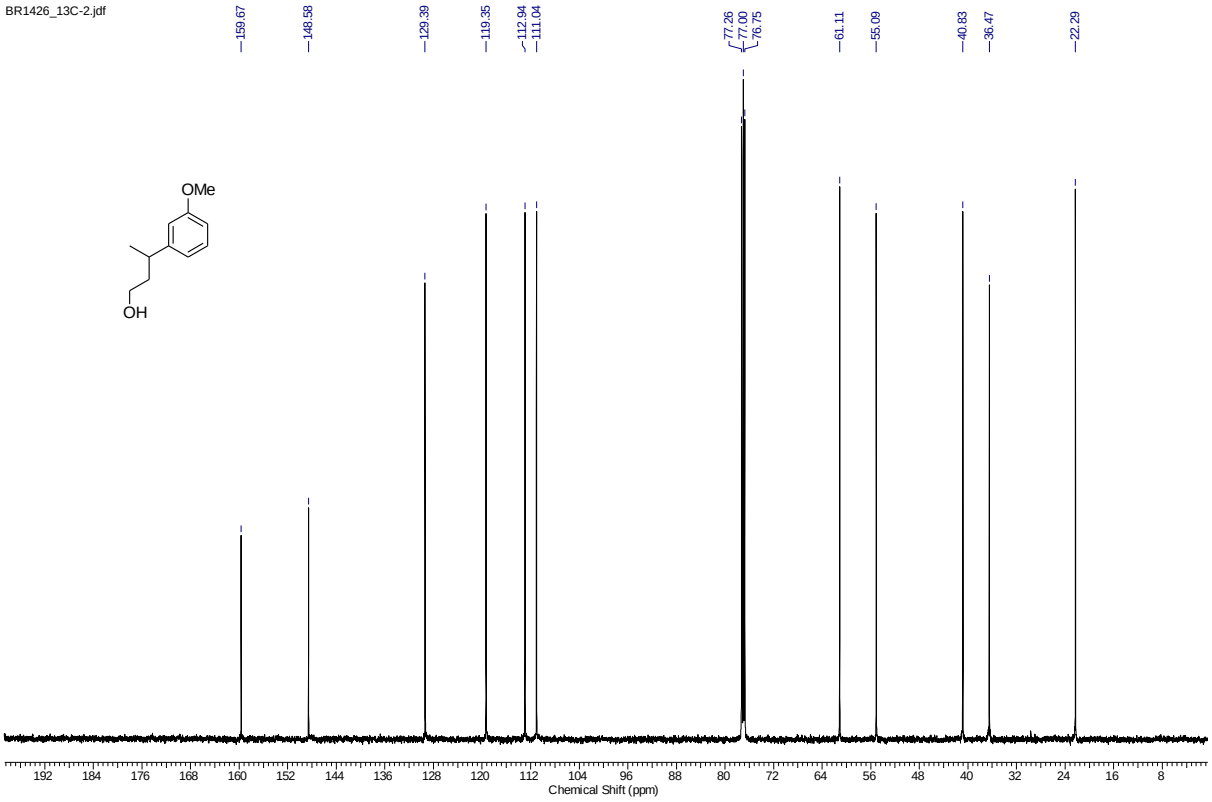
6.76
6.75
6.74
3.81
3.61
3.60
3.59
3.58
3.57
3.55
3.54
3.53
2.91
2.90
2.88
2.86
2.84
2.82
1.88
1.86
1.84
1.82
1.28
1.27
OMe
OH
1.00
1.03
2.05
3.08
2.09
1.06
2.13
3.21
Chemical Shift (ppm)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148.58
129.39
119.35
112.94
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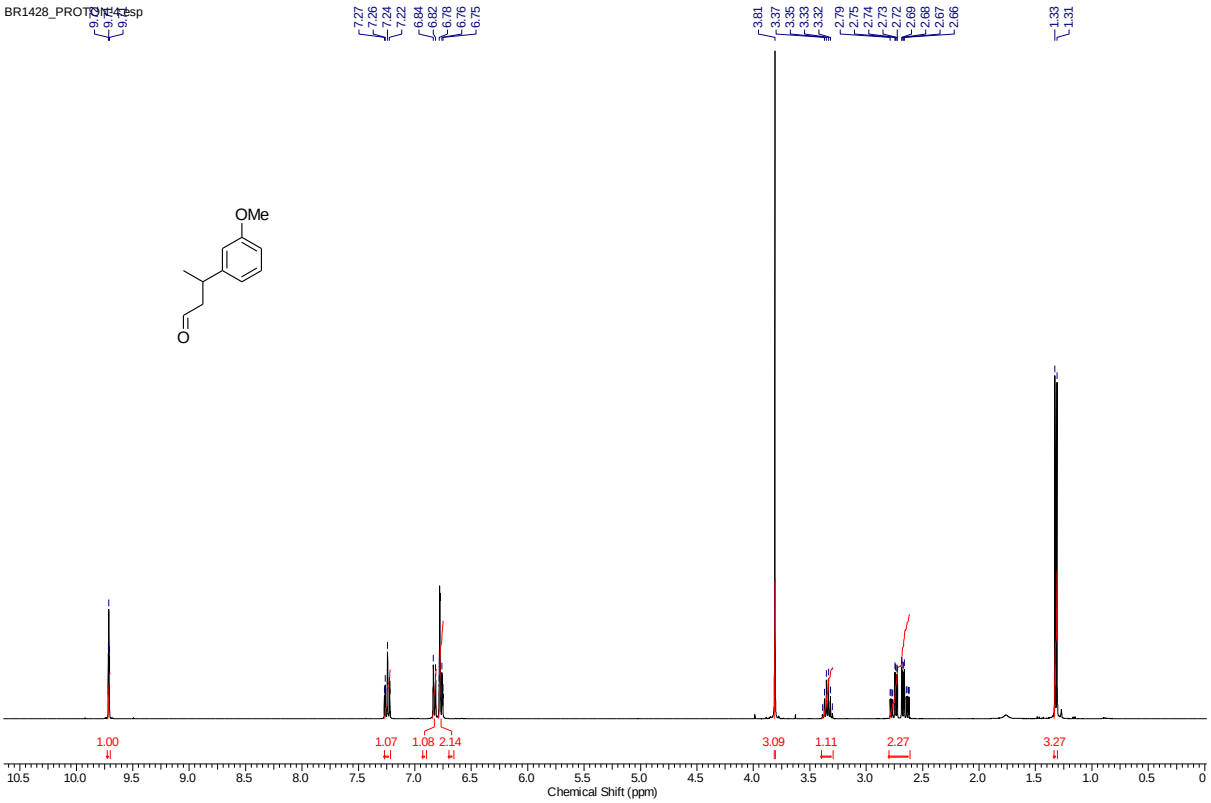
77.26
77.00
76.75
61.11
55.09
40.83
36.47
22.29
OMe
OH
Chemical Shift (ppm)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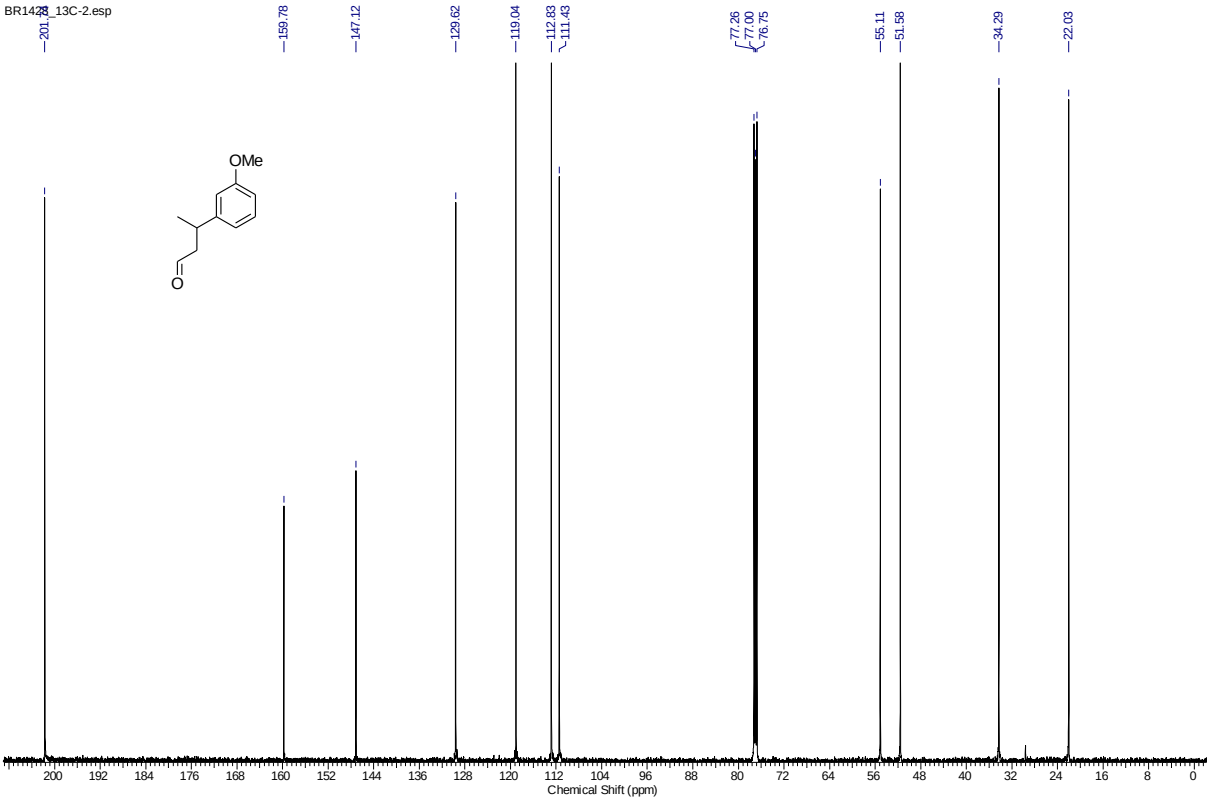
9.76
7.27
7.26
7.24
7.22
6.84
6.82
6.78
6.76
6.75
3.81
3.37
3.35
3.33
3.32
2.79
2.75
2.74
2.73
2.72
2.69
2.68
2.67
2.66
1.33
1.31
OMe
O
1.00
1.07
1.08
2.14
3.09
1.11
2.27
3.27
Chemical Shift (ppm)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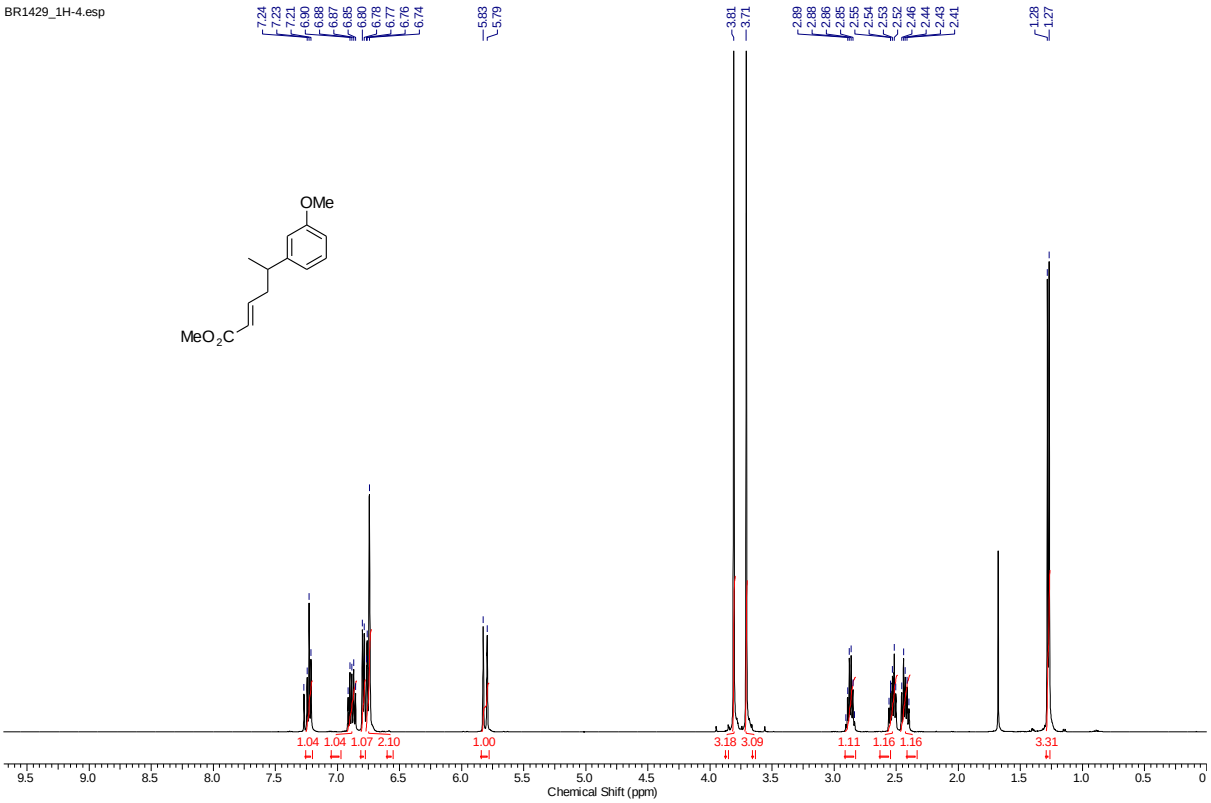
51.58
34.29
22.03
OMe
O
Chemical Shift (ppm)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7.23
7.21
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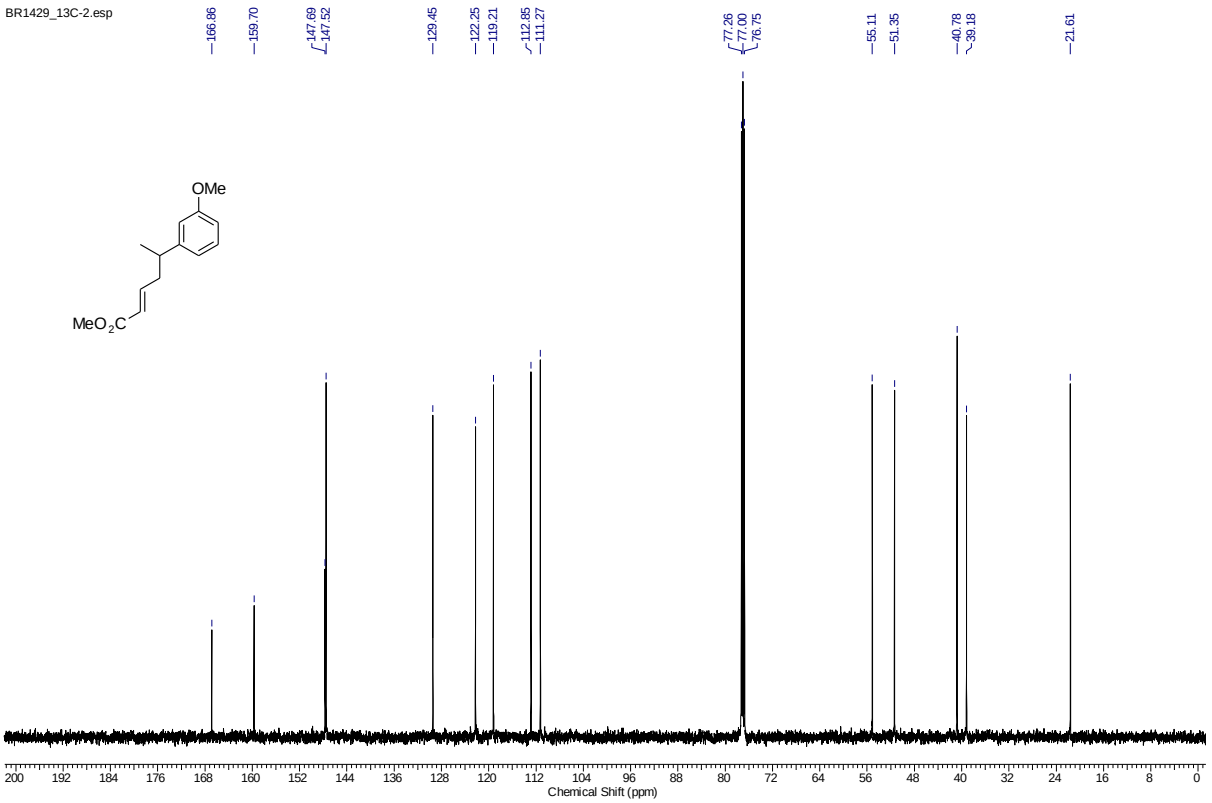
6.88
6.87
6.85
6.80
6.78
6.77
6.76
6.74
5.83
5.79
3.81
3.71
2.89
2.88
2.86
2.85
2.55
2.54
2.53
2.52
2.46
2.44
2.43
2.41
1.28
1.27
OMe
MeO2C
1.04 1.04 1.07 2.10 1.00 3.18 3.09 1.11 1.16 1.16 3.31
Chemical Shift (ppm)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147.52
129.45
122.25
119.21
112.85
111.27
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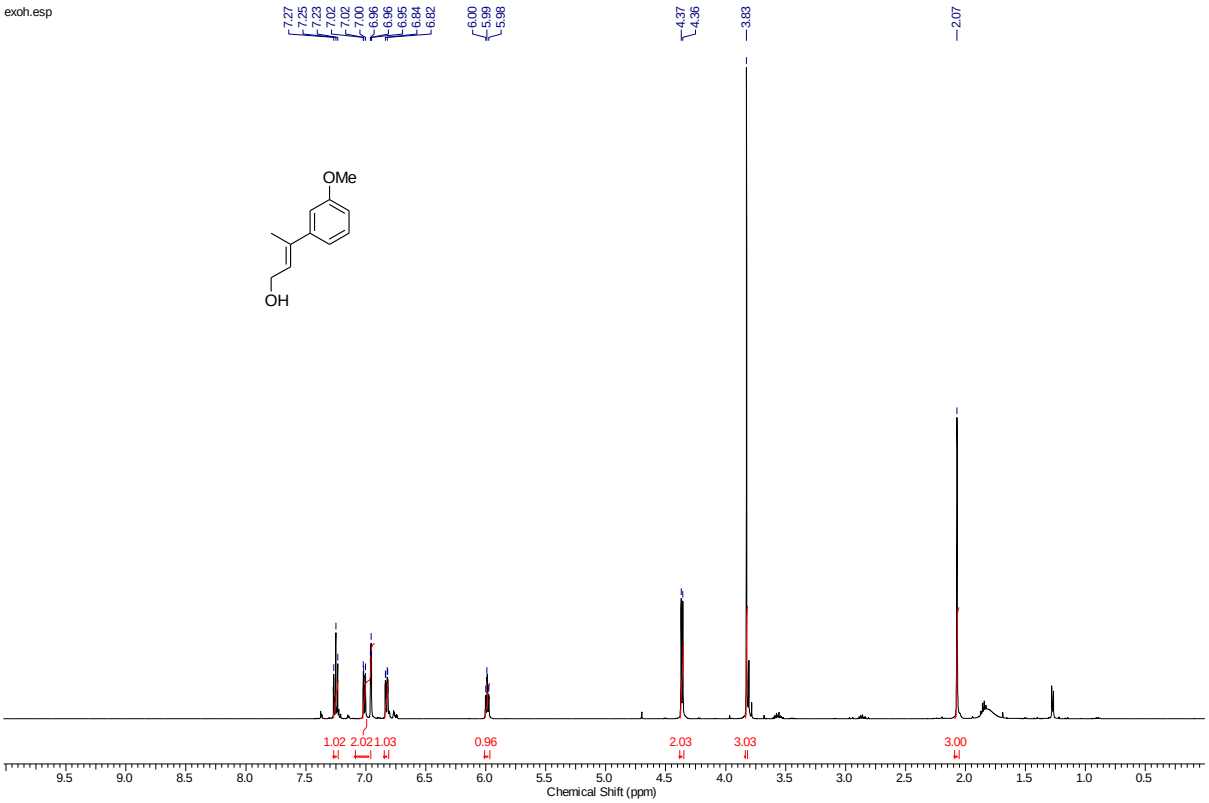
76.75
55.11
51.35
40.78
39.18
21.61
OMe
MeO2C
Chemical Shift (ppm)


exoh.esp
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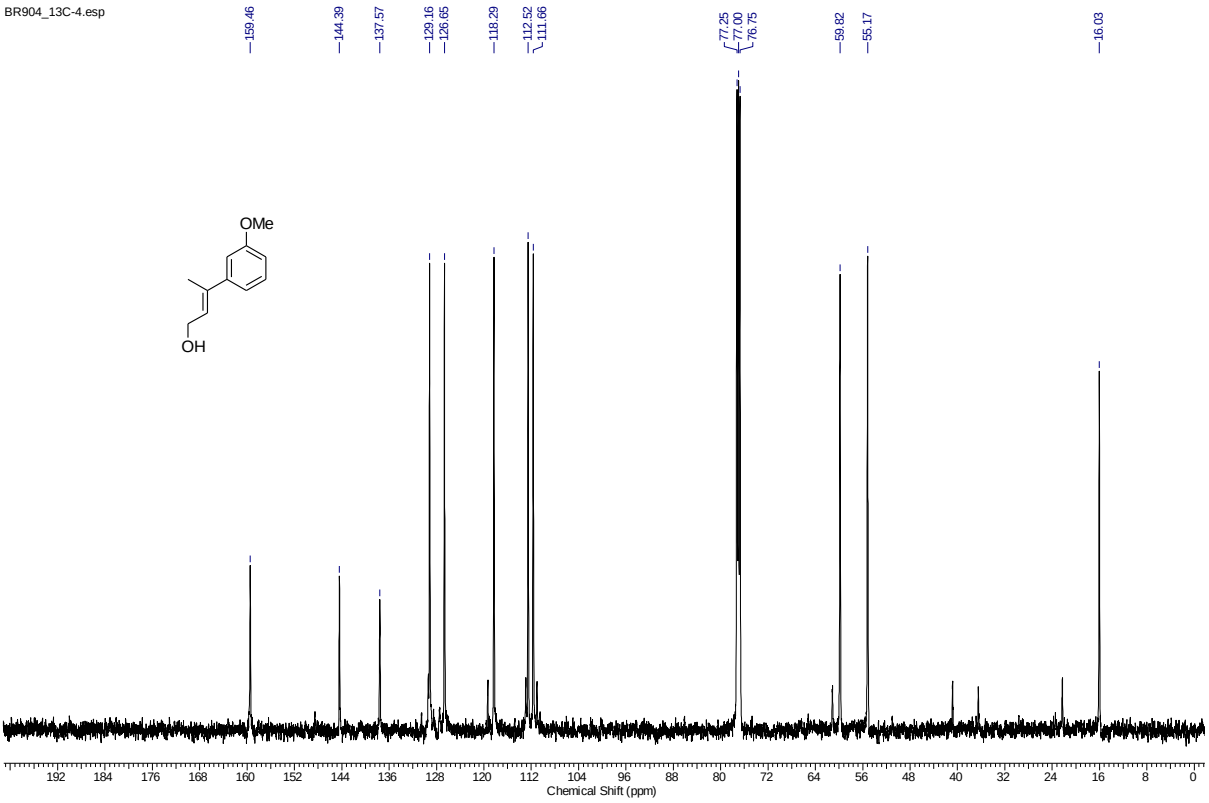
7.25
7.23
7.02
7.02
7.00
6.96
6.96
6.95
6.84
6.82
6.00
5.99
5.98
4.37
4.36
3.83
2.07
OMe
OH
1.02
2.02
1.03
0.96
2.03
3.03
3.00
Chemical Shift (ppm)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159.46
144.39
137.57
129.16
126.65
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111.66
77.25
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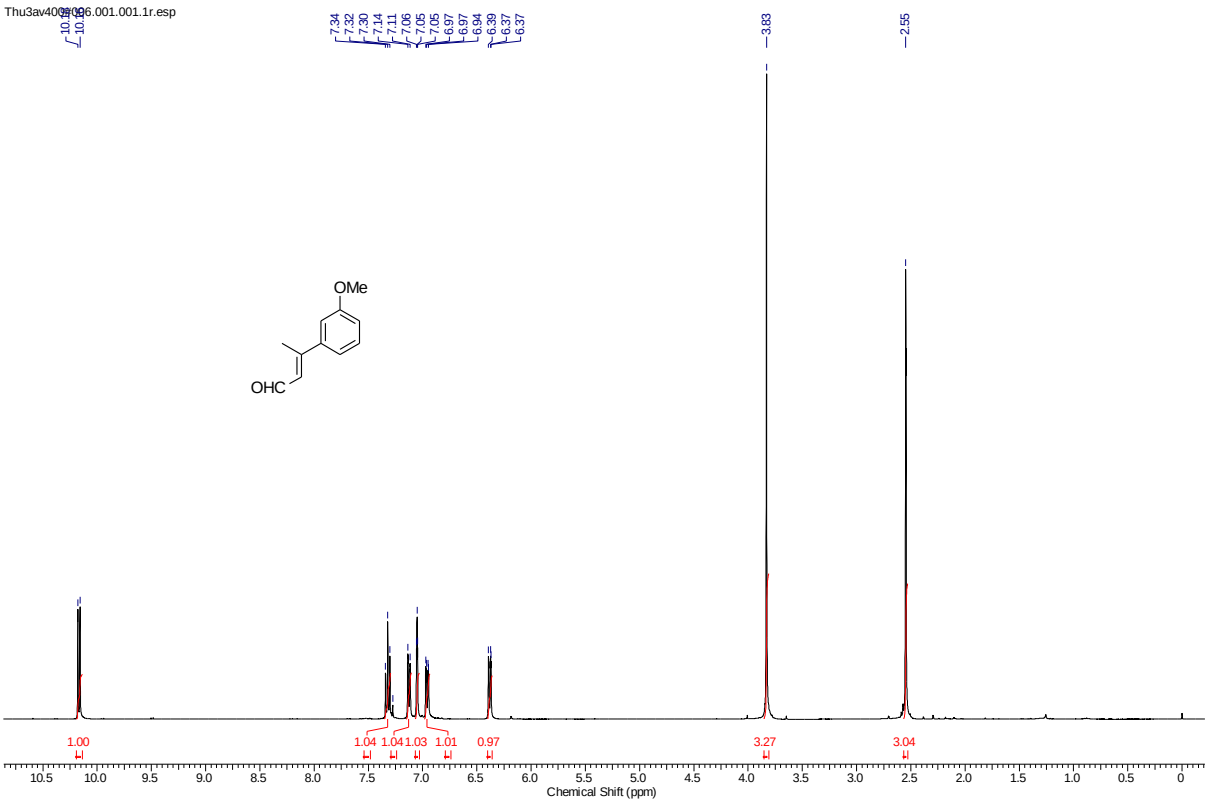
59.82
55.17
16.03
OMe
OH
Chemical Shift (ppm)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10.19
7.34
7.32
7.30
7.14
7.11
7.06
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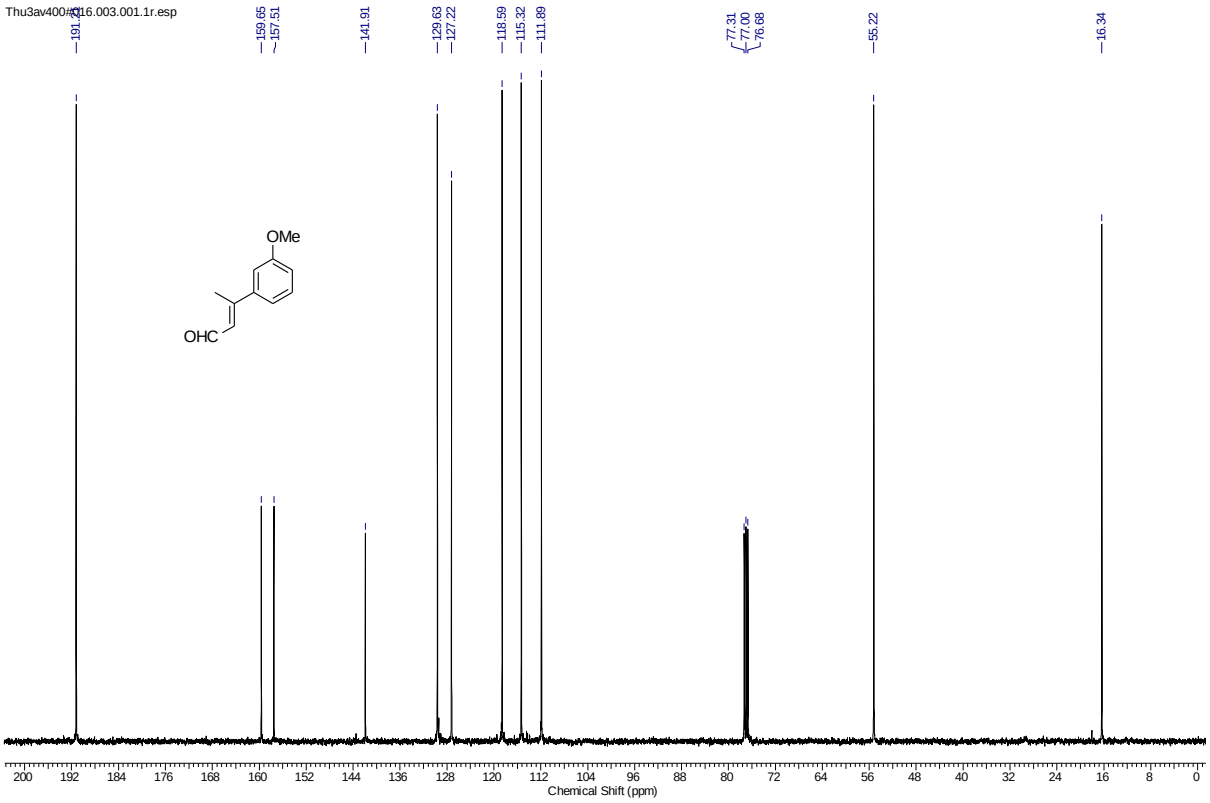
6.97
6.94
6.39
6.37
6.37
3.83
2.55
OMe
OHC
1.00
1.04
1.04
1.03
1.01
0.97
3.27
3.04
Chemical Shift (ppm)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191.21
159.65
157.51
141.91
129.63
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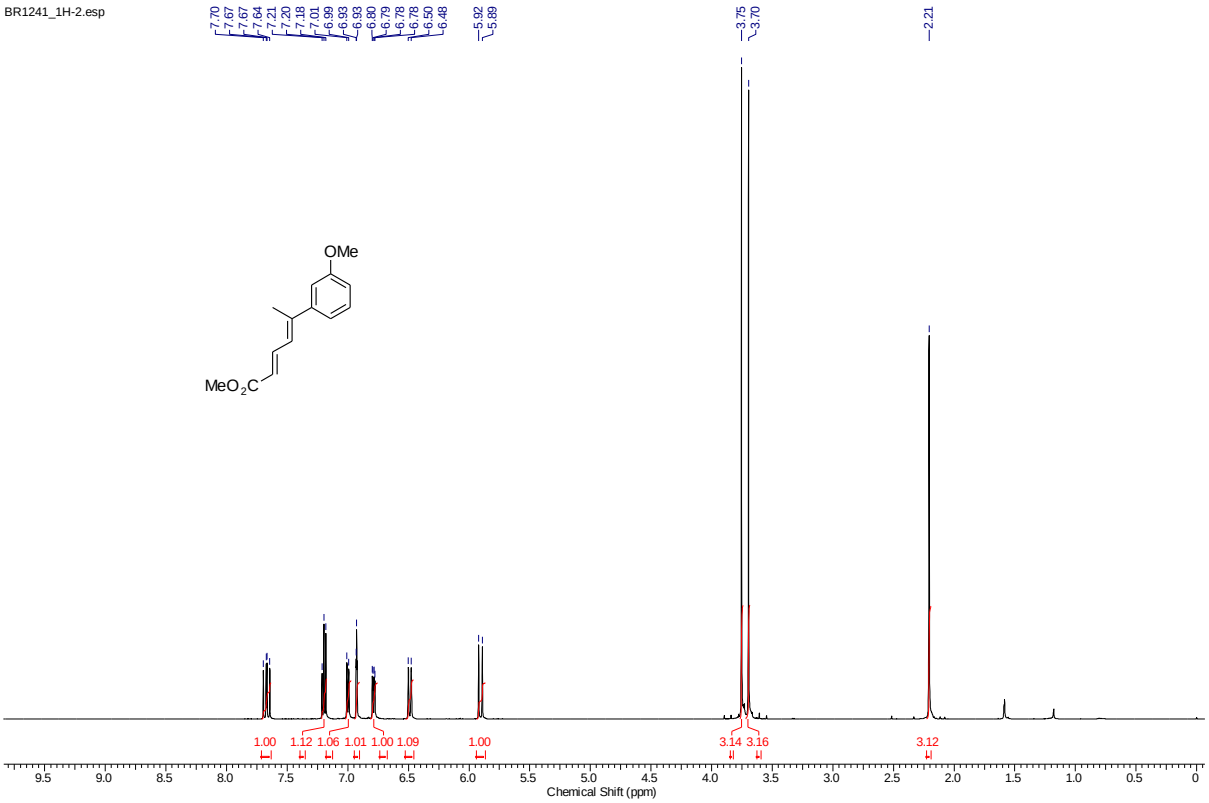
77.31
77.00
76.68
55.22
16.34
OMe
OHC
Chemical Shift (ppm)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7.70
7.67
7.67
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7.21
7.20
7.18
7.01
6.99
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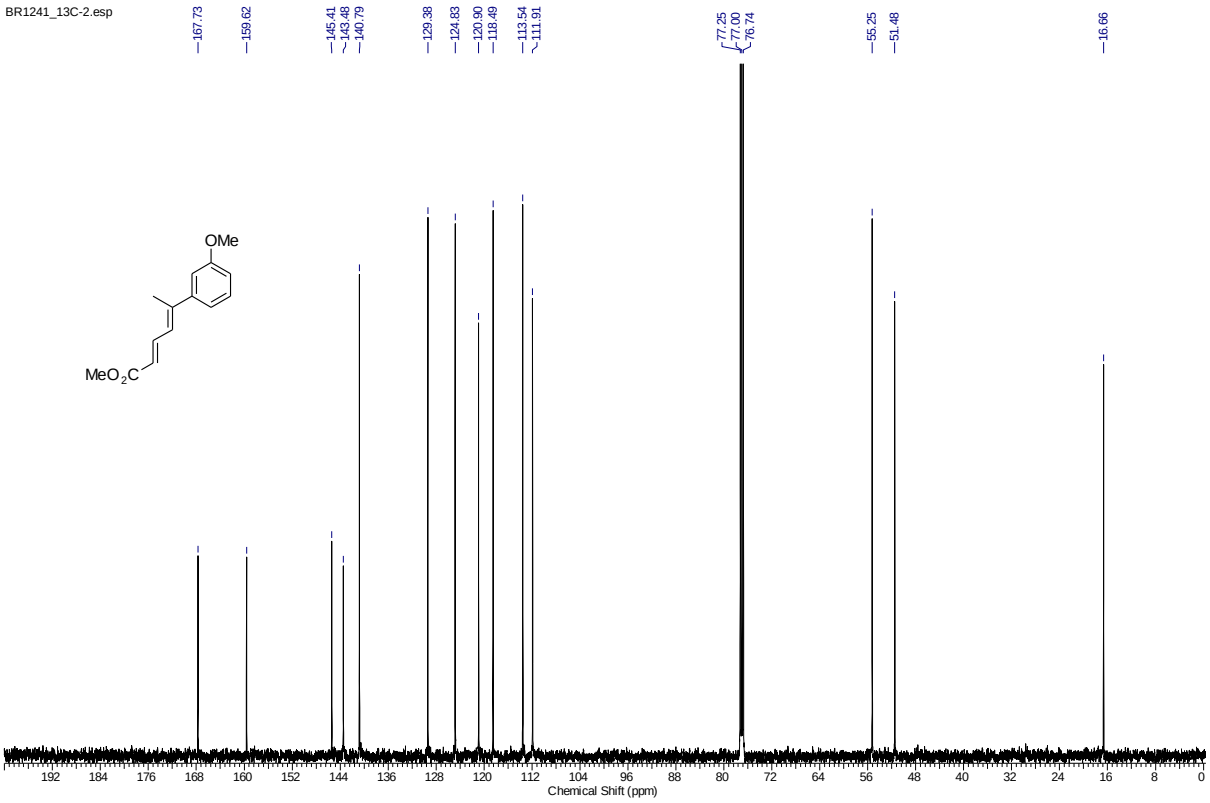
6.93
6.80
6.79
6.78
6.78
6.50
6.48
5.92
5.89
3.75
3.70
2.21
OMe
MeO2C
1.00
1.12
1.06
1.01
1.00
1.09
1.00
3.14
3.16
3.12
Chemical Shift (ppm)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129.38
124.83
120.90
118.49
113.54
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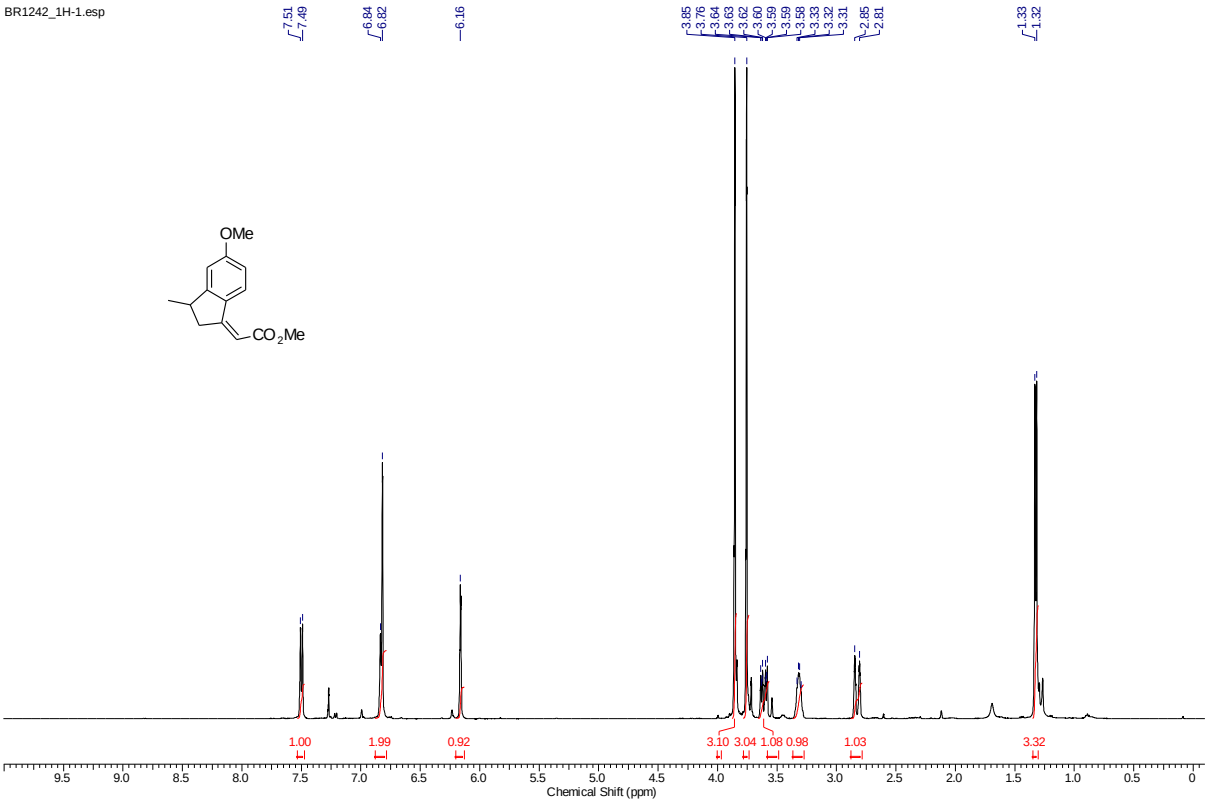
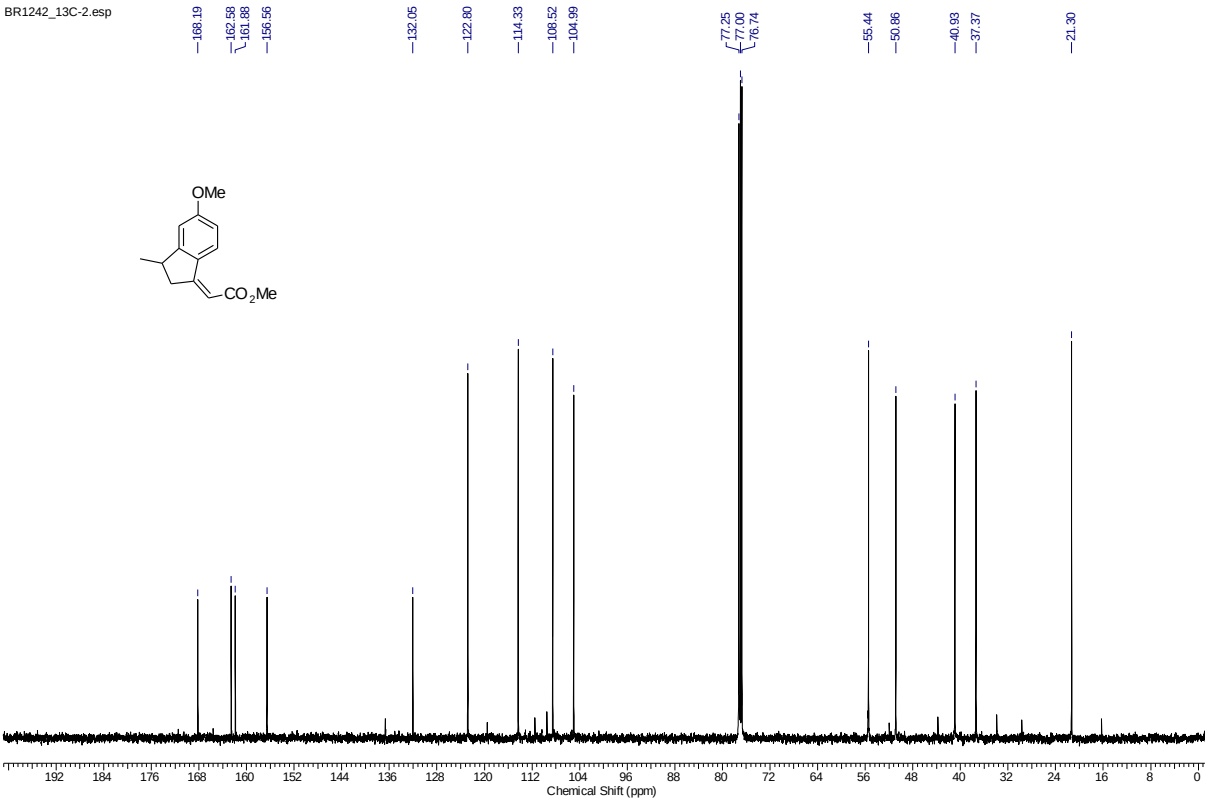
77.25
77.00
76.74
55.25
51.48
16.66
OMe
MeO2C
Chemical Shift (ppm)


BR1242_1H-1.esp
7.51
7.49
6.84
6.82
6.16
3.85
3.76
3.64
3.63
3.62
3.60
3.59
3.59
3.58
3.33
3.32
3.31
2.85
2.81
1.33
1.32
OMe
CO2Me
1.00
1.99
0.92
3.10
3.04
1.08
0.98
1.03
3.32
Chemical Shift (ppm)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161.88
156.56
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122.80
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108.52
104.99
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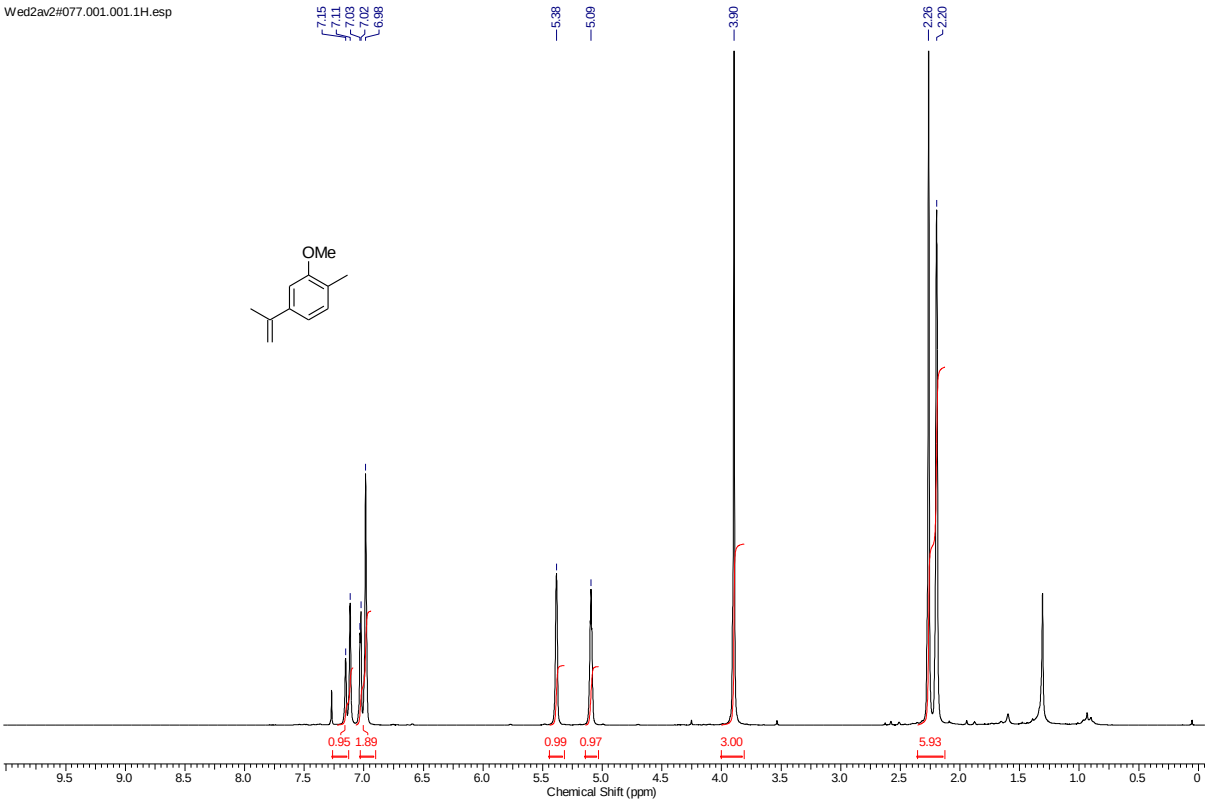
77.00
76.74
55.44
50.86
40.93
37.37
21.30
OMe
CO2Me
Chemical Shift (ppm)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7.11
7.03
7.02
6.98
5.38
5.09
3.90
2.26
2.20
OMe
0.95
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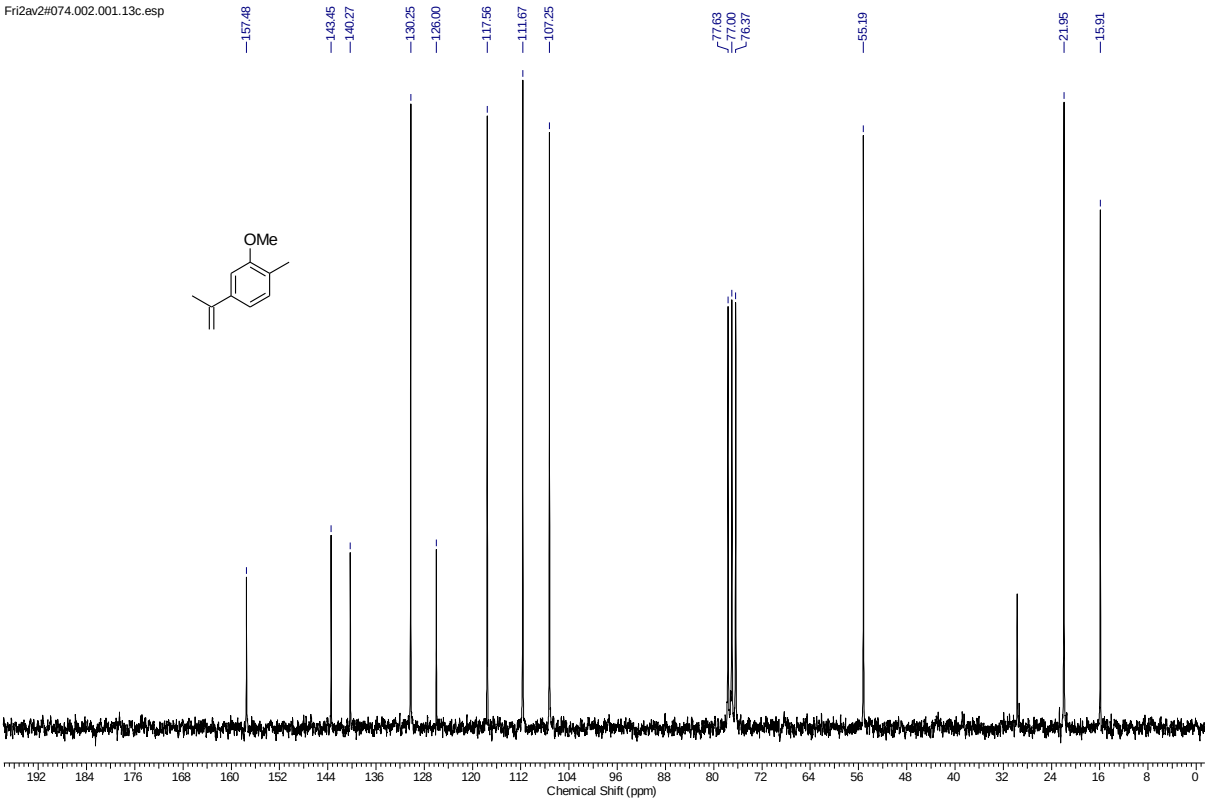
0.99
0.97
3.00
5.93
Chemical Shift (ppm)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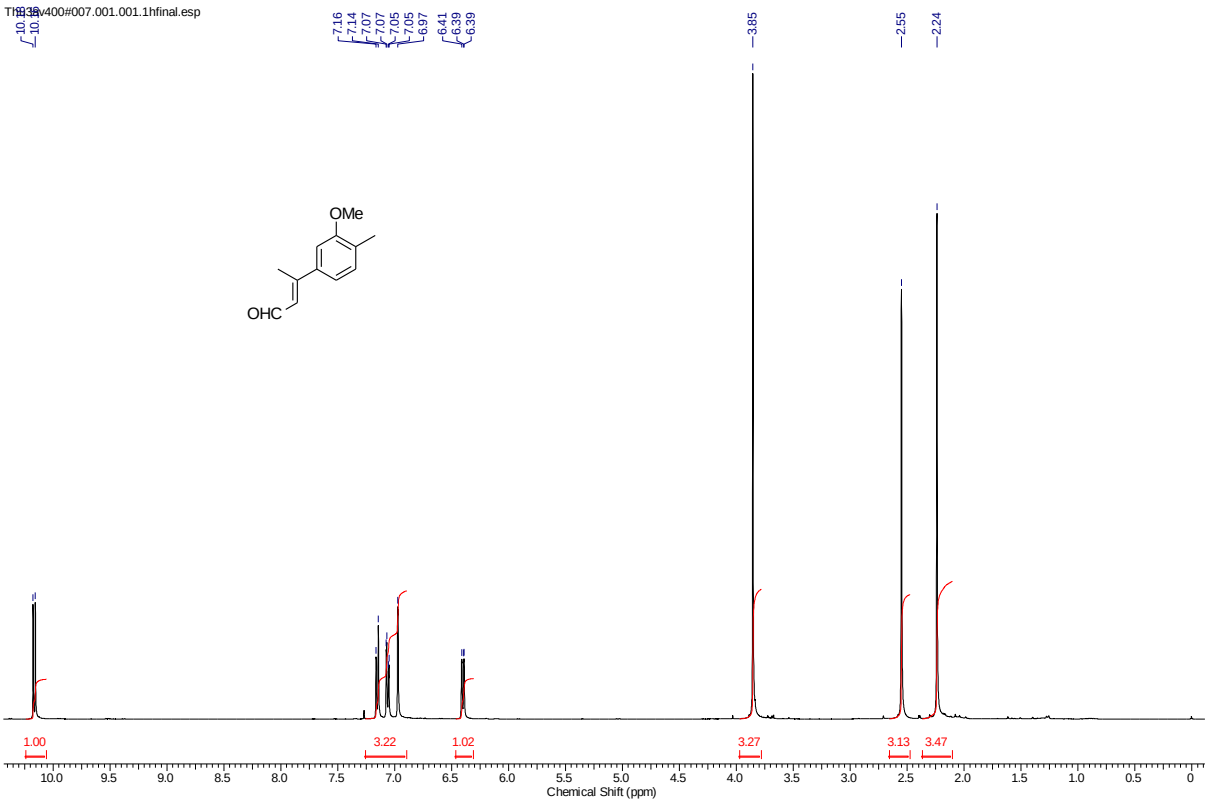
77.00
76.37
55.19
21.95
15.91
OMe
Chemical Shift (ppm)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7.05
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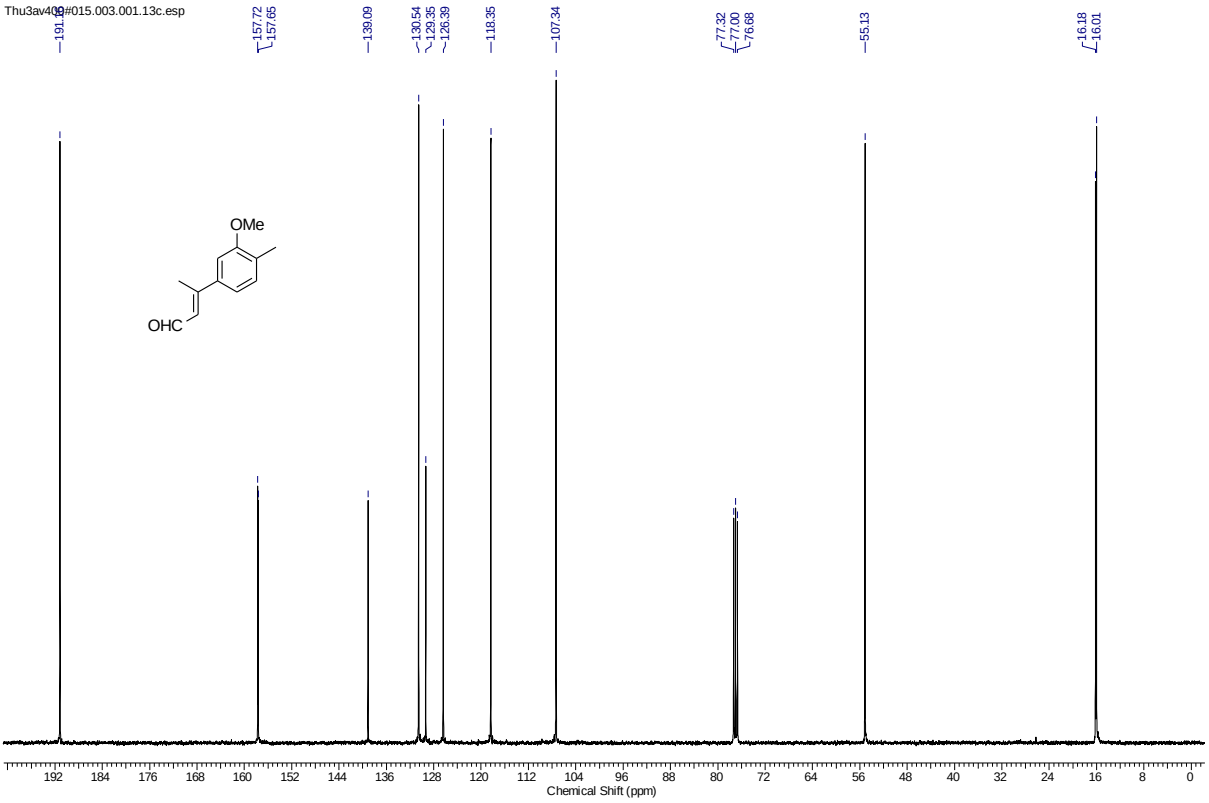
6.39
6.39
3.85
2.55
2.24
OMe
OHC
1.00
3.22
1.02
3.27
3.13
3.47
Chemical Shift (ppm)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139.09
130.54
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126.39
118.35
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77.32
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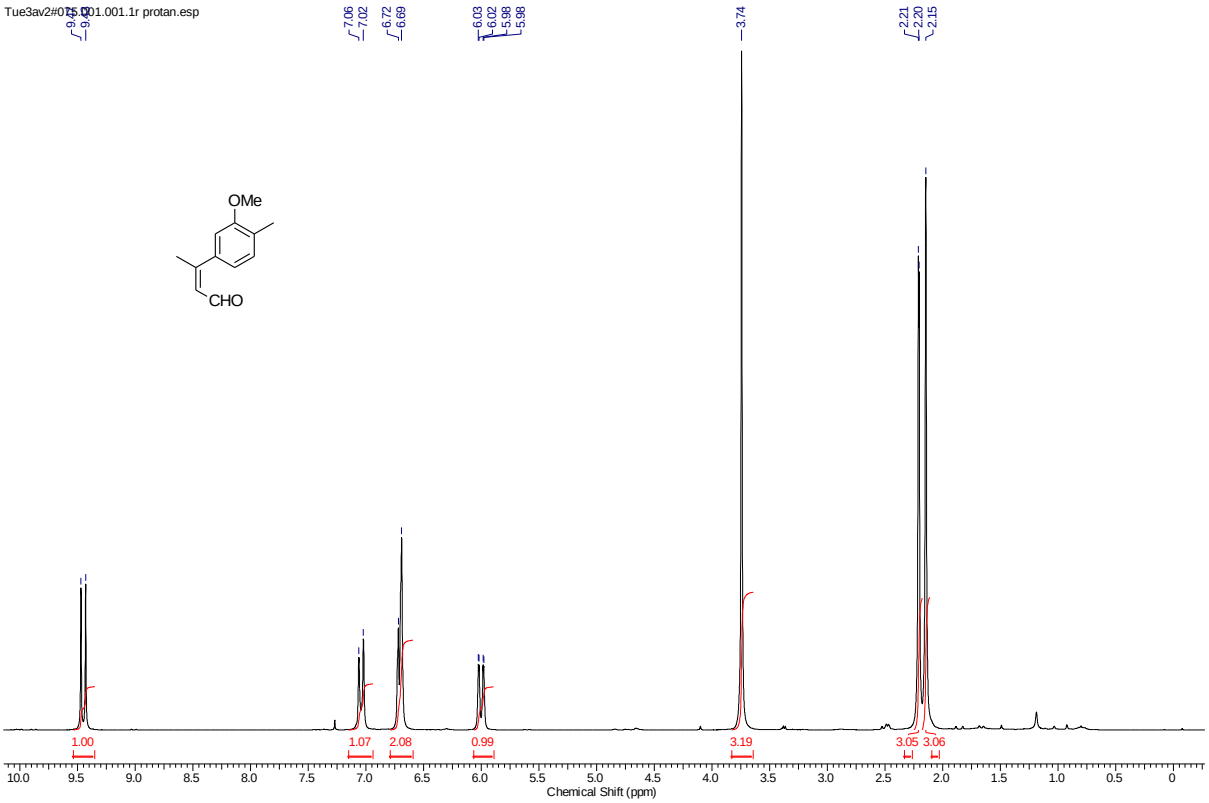
76.68
55.13
16.18
16.01
OMe
OHC
Chemical Shift (ppm)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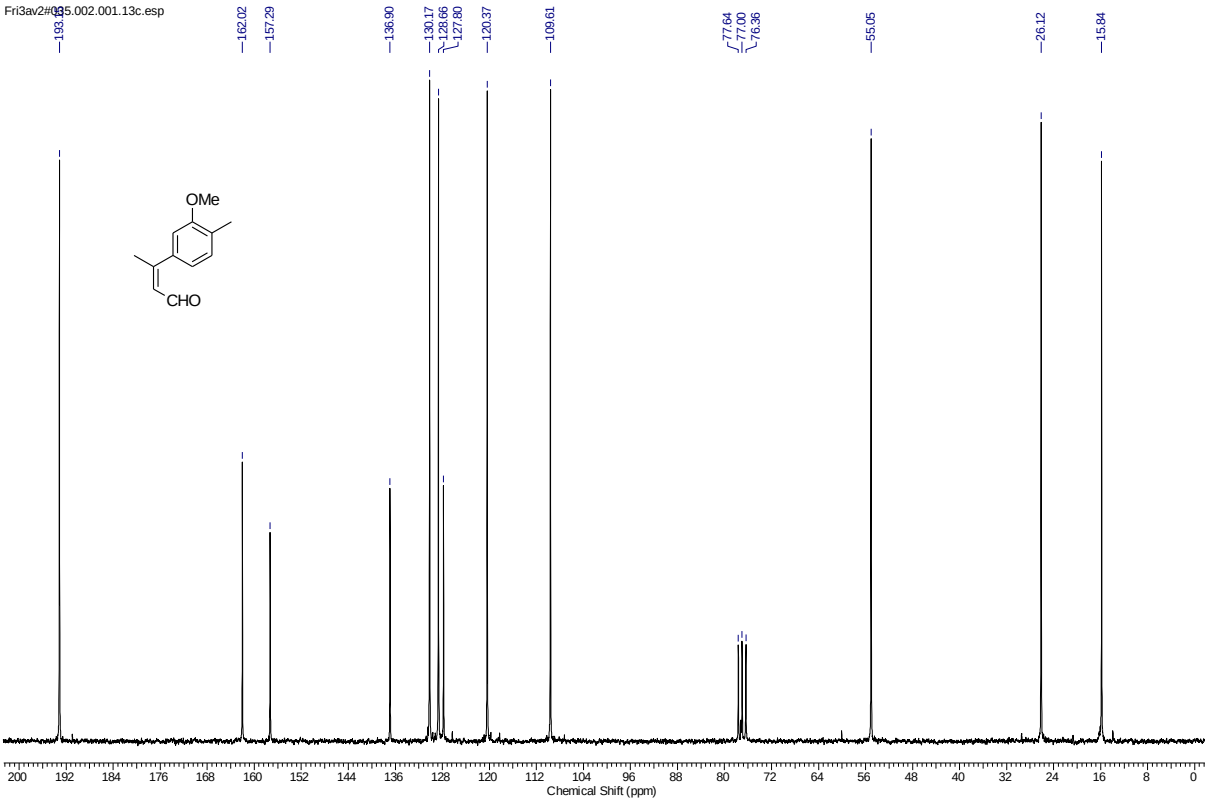
9.52
7.06
7.02
6.72
6.69
6.03
6.02
5.98
5.98
3.74
2.21
2.20
2.15
OMe
CHO
1.00
1.07
2.08
0.99
3.19
3.05
3.06
Chemical Shift (ppm)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26.12
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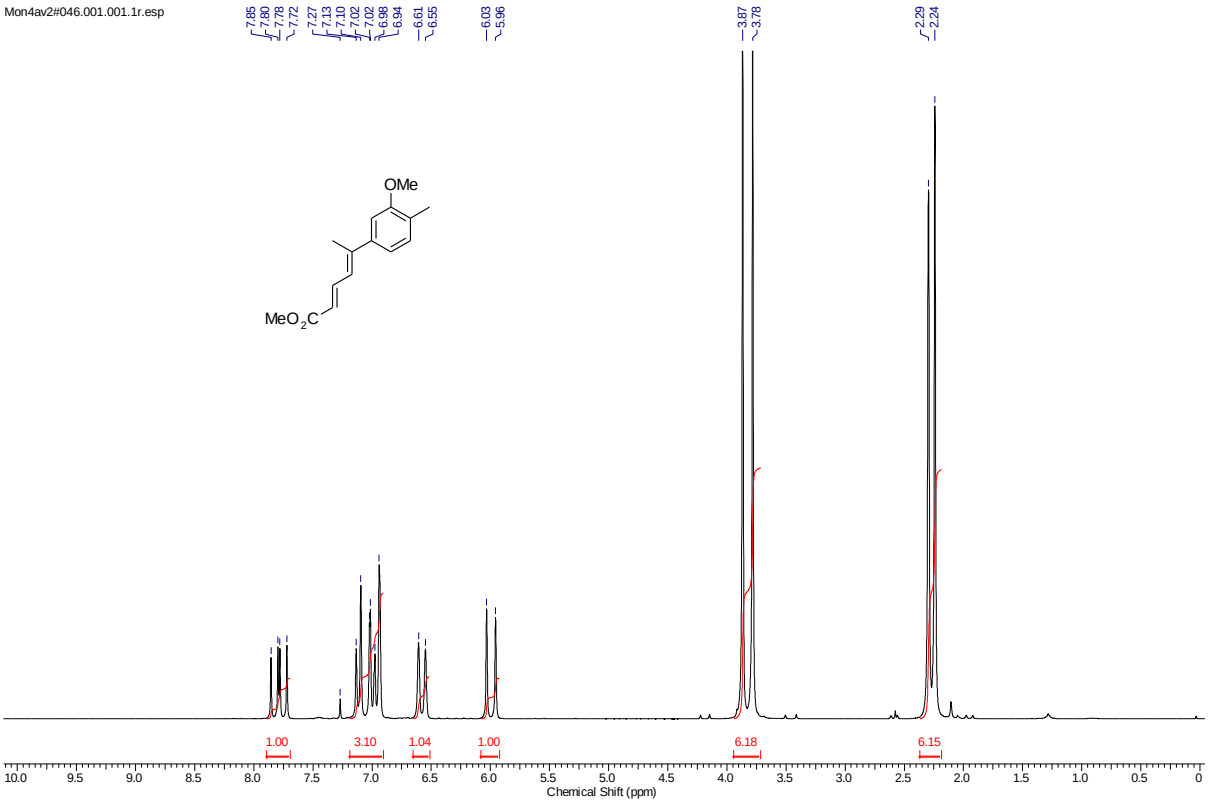
OMe
CHO
Chemical Shift (ppm)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7.27
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7.10
7.02
7.02
6.98
6.94
6.61
6.55
6.03
5.96
3.87
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OMe
MeO2C
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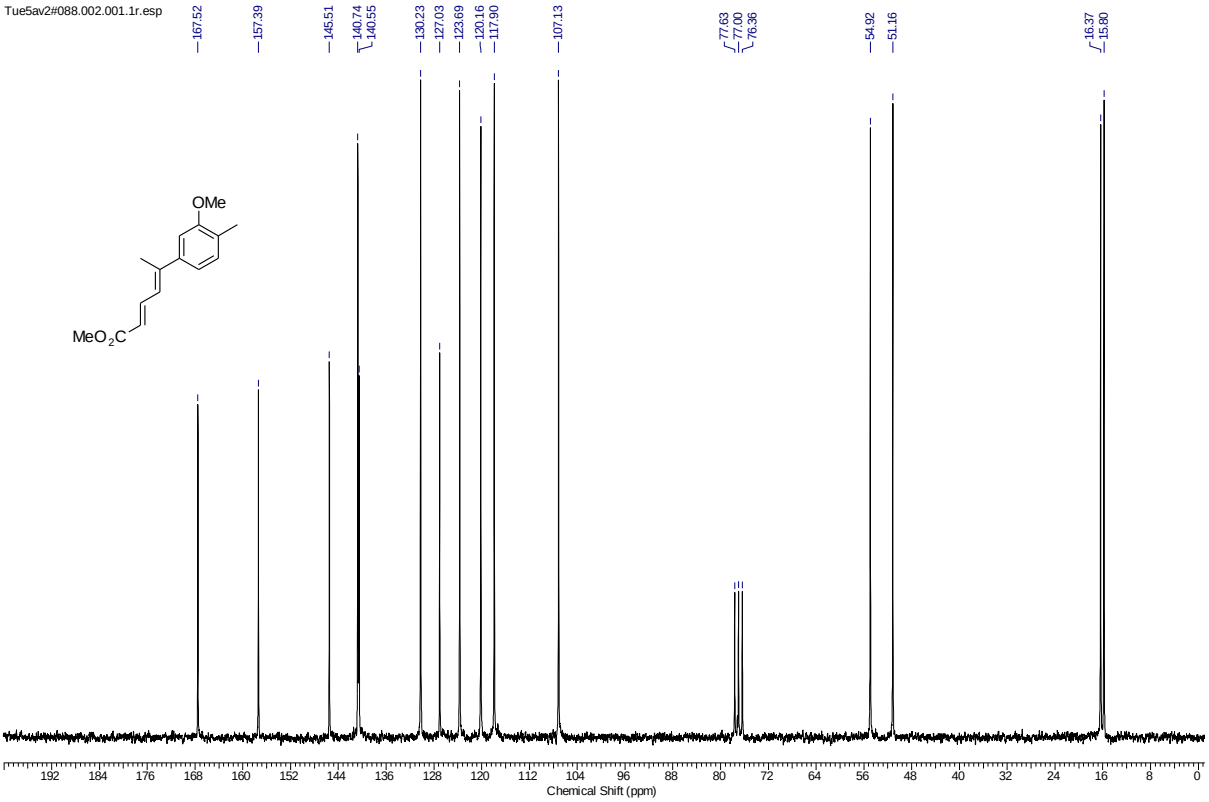
1.00
6.18
6.15
Chemical Shift (ppm)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130.23
127.03
123.69
120.16
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76.36
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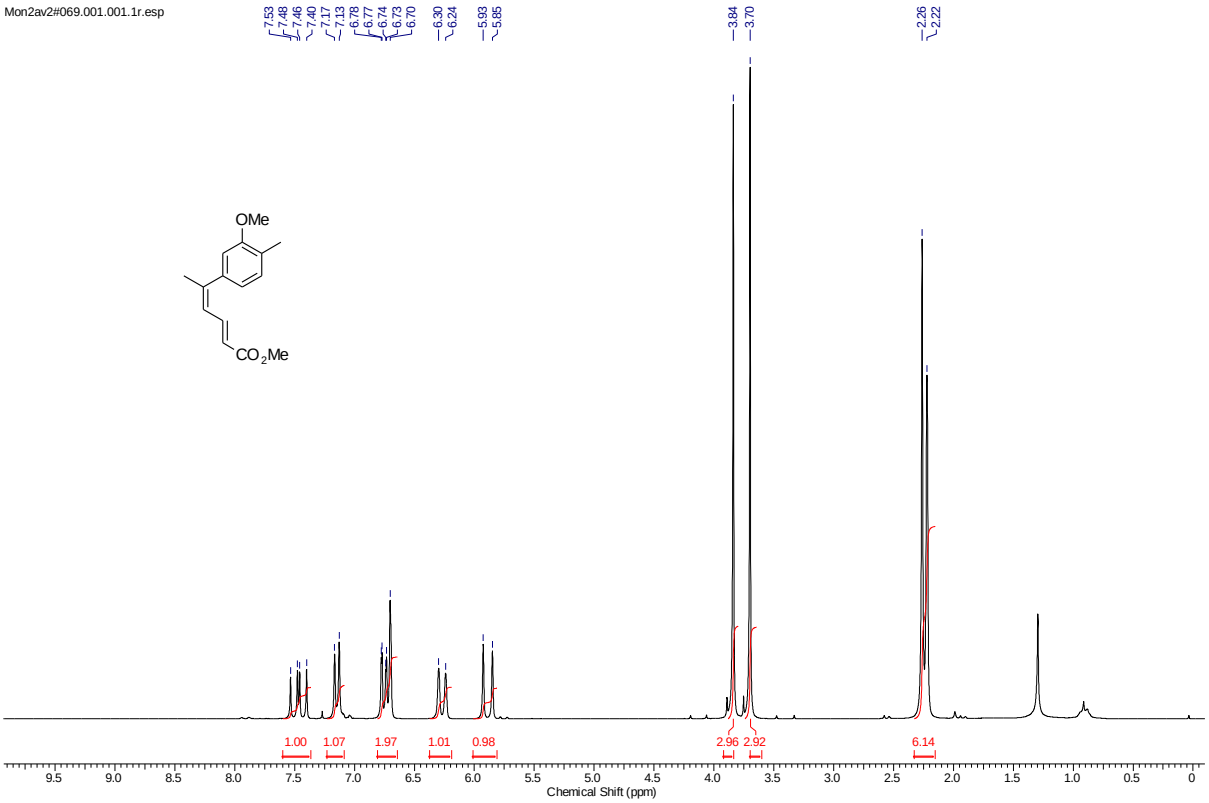
51.16
16.37
15.80
OMe
MeO2C
Chemical Shift (ppm)


Mon2av2#069.001.001.1r.esp
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7.17
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6.78
6.77
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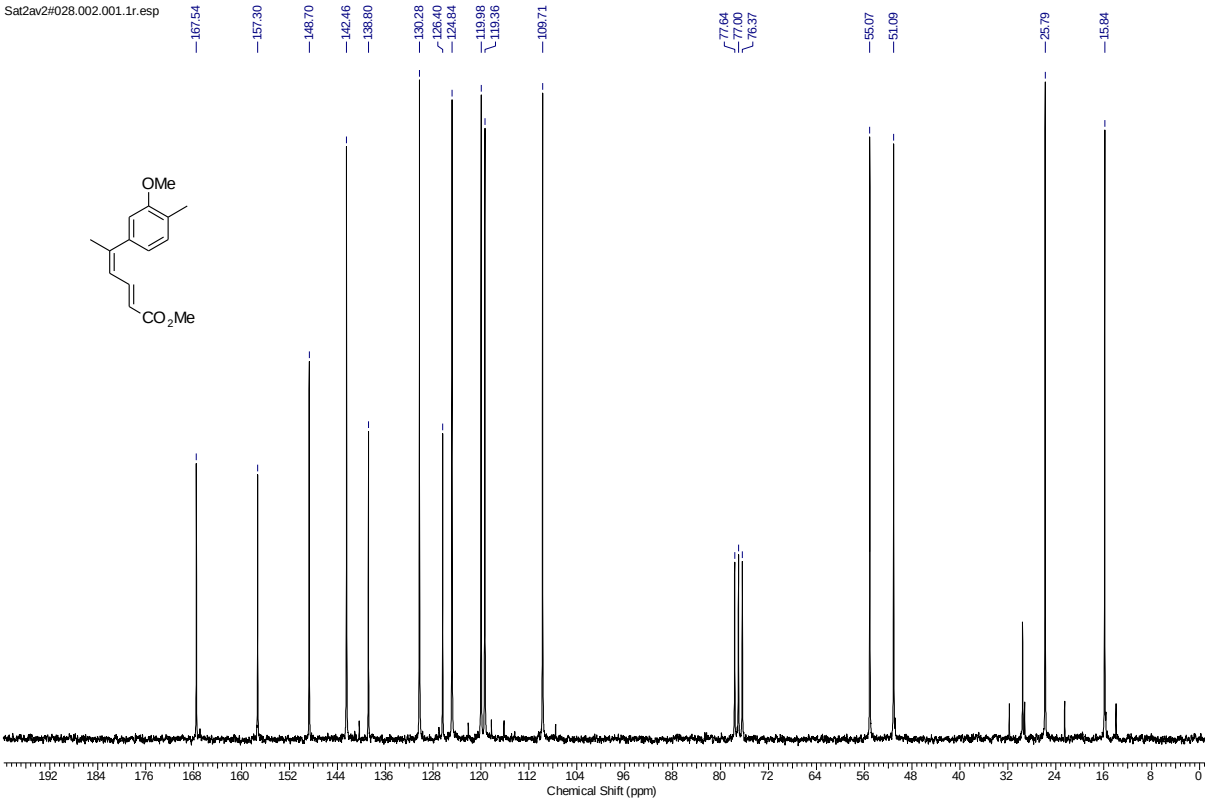
6.70
6.30
6.24
5.93
5.85
3.84
3.70
2.26
2.22
OMe
CO2Me
1.00
1.07
1.97
1.01
0.98
2.96
2.92
6.14
Chemical Shift (ppm)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126.40
124.84
119.98
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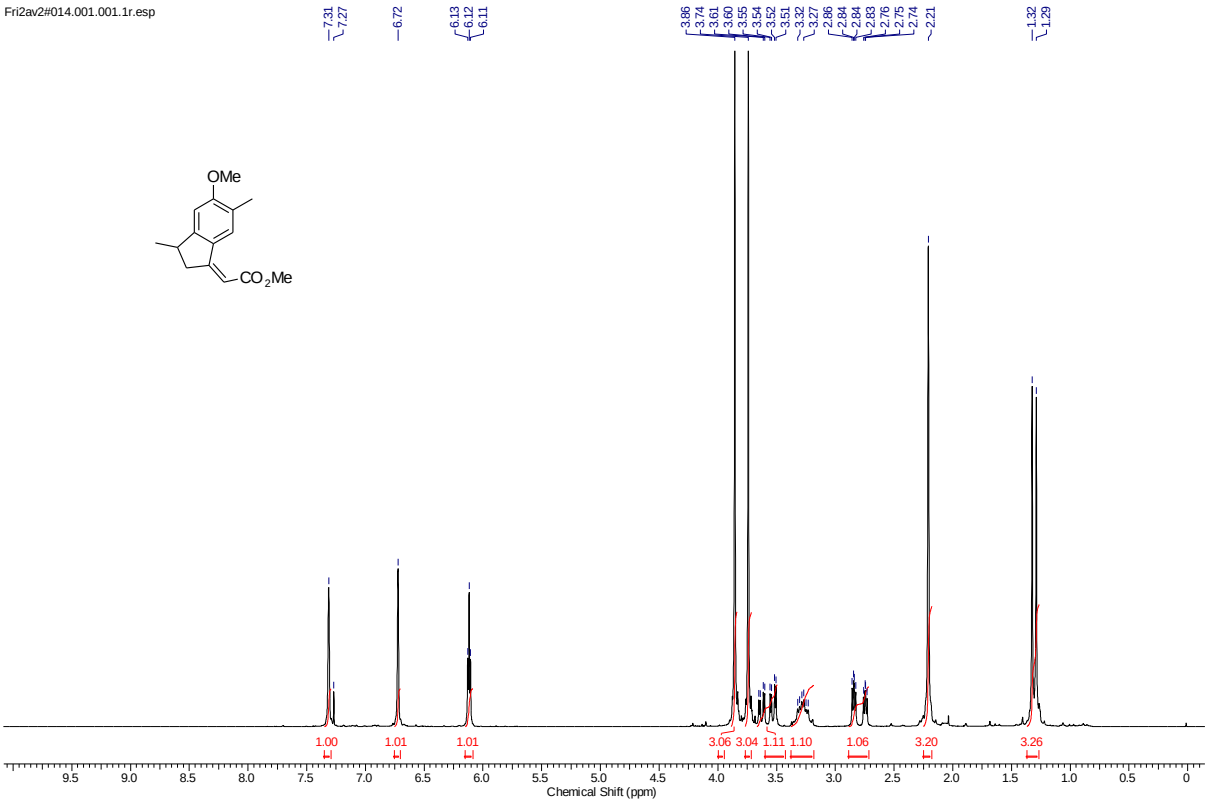
77.00
76.37
55.07
51.09
25.79
15.84
OMe
CO2Me
Chemical Shift (ppm)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6.12
6.11
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3.74
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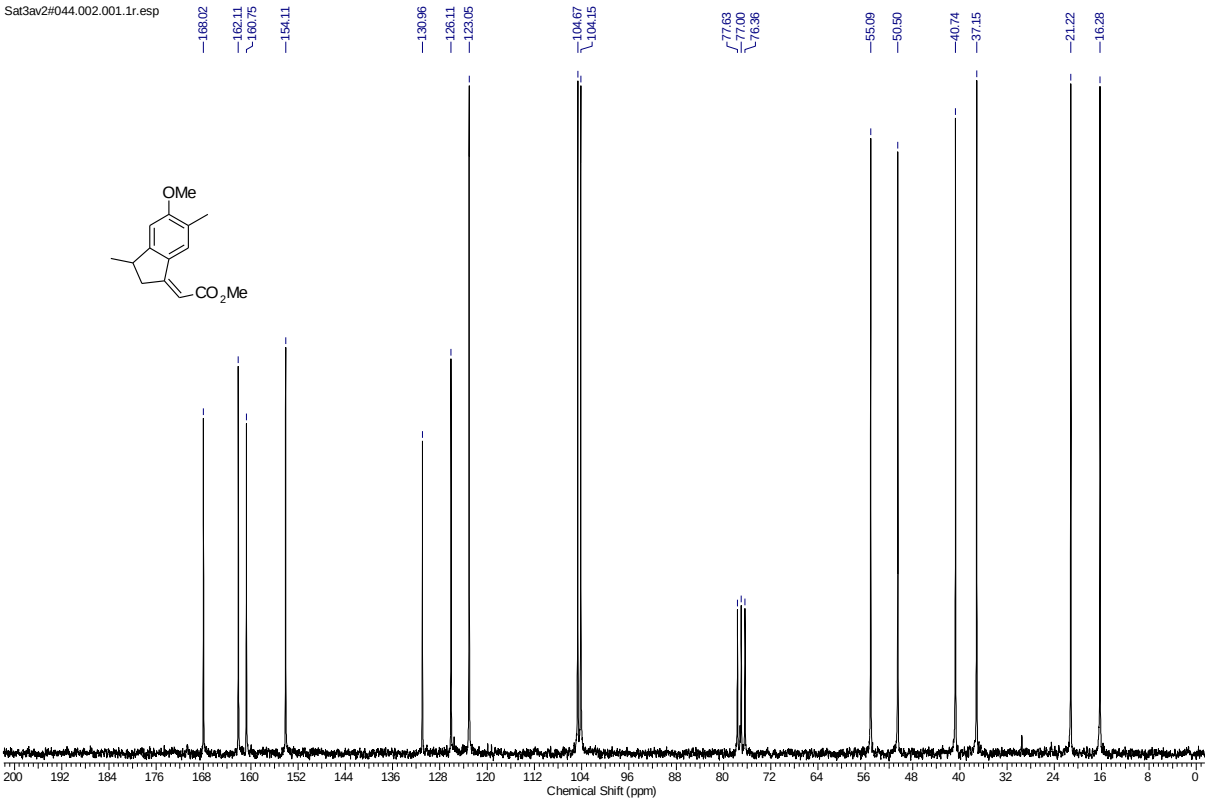
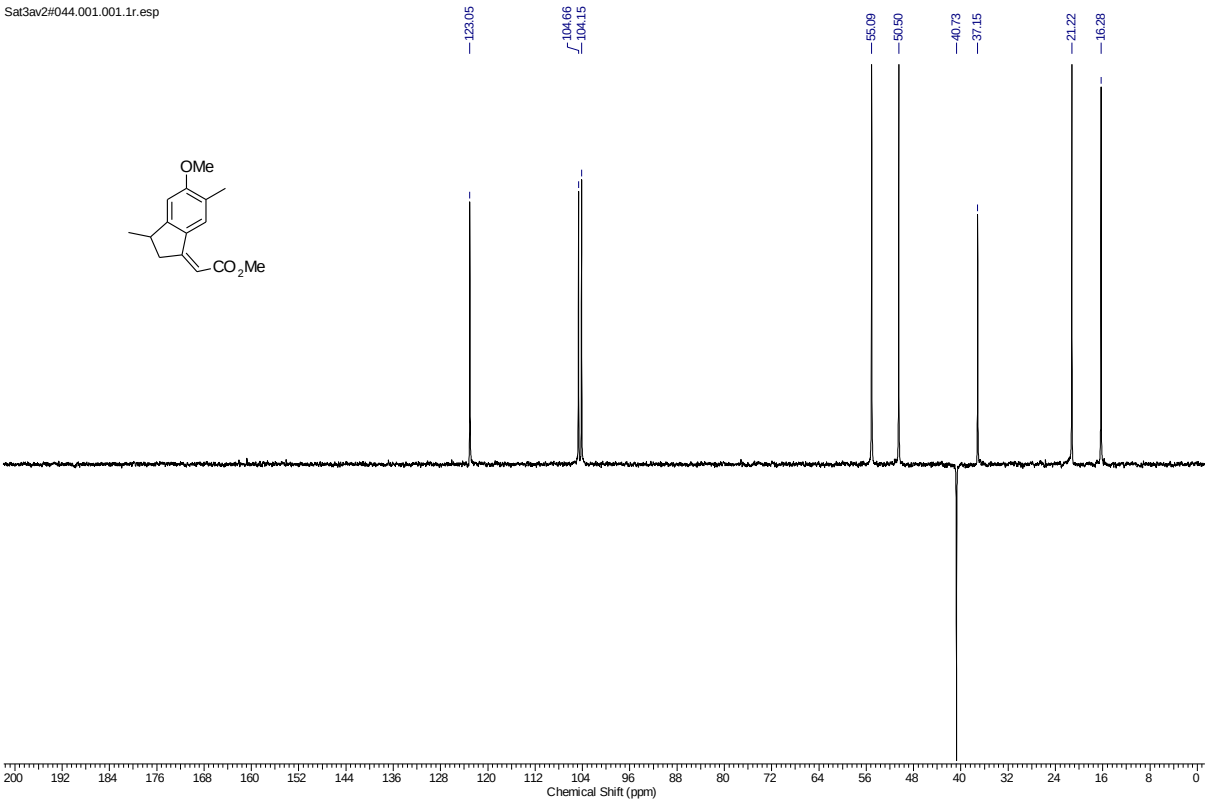
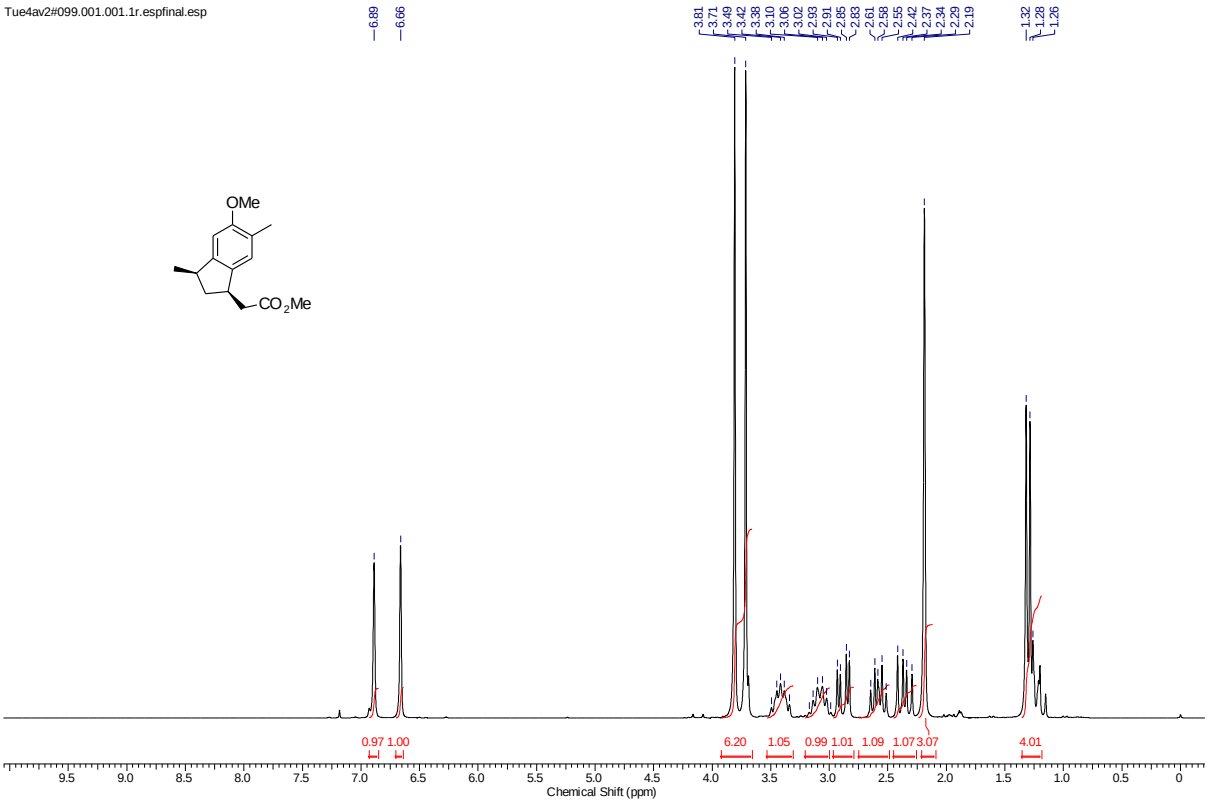
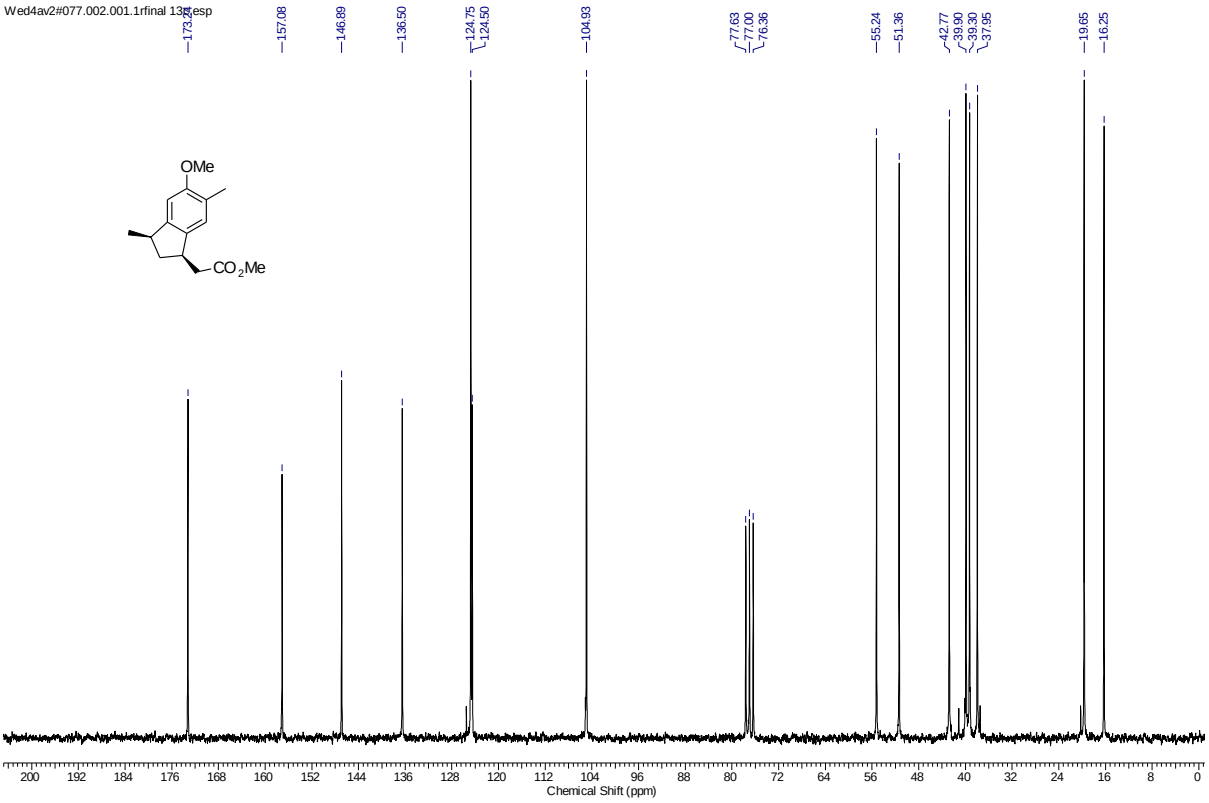
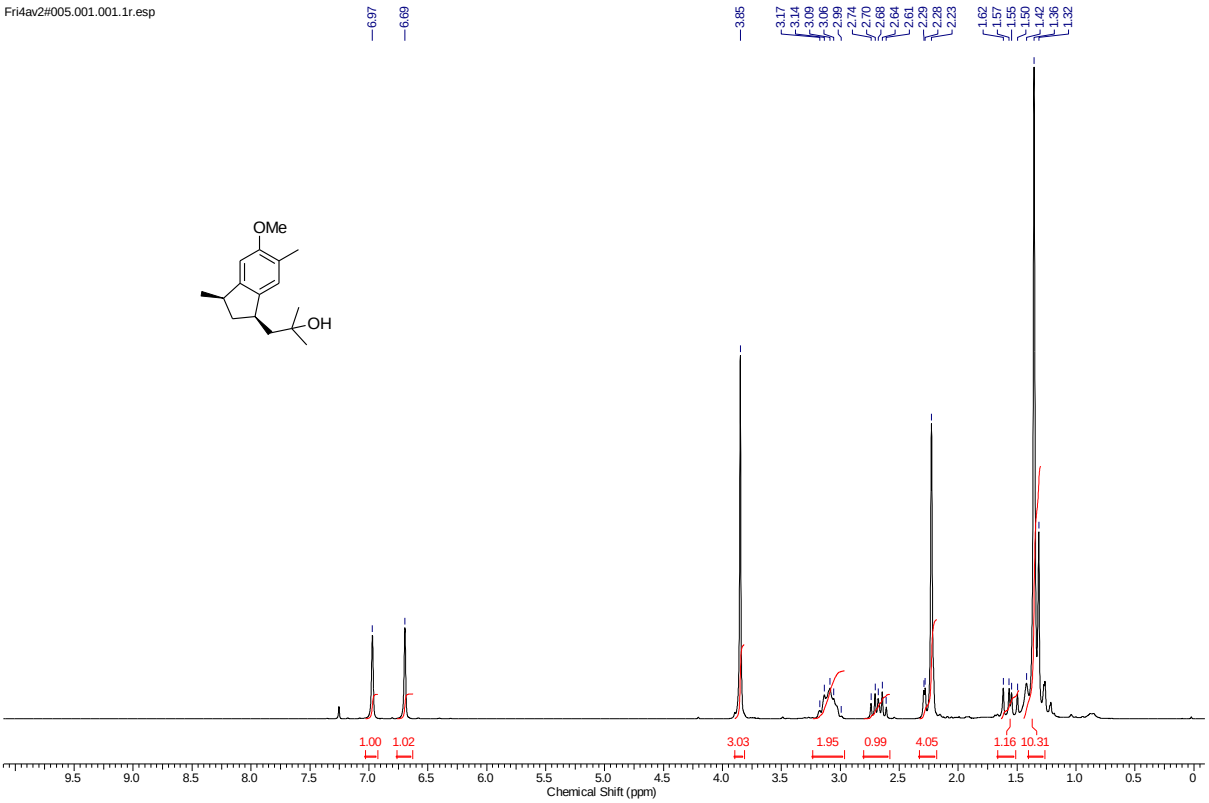
3.51
3.32
3.27
2.86
2.84
2.84
2.83
2.76
2.75
2.74
2.21
1.32
1.29
OMe
CO2Me
1.00
1.01
1.01
3.06
3.04
1.11
1.10
1.06
3.20
3.26
Chemical Shift (ppm)

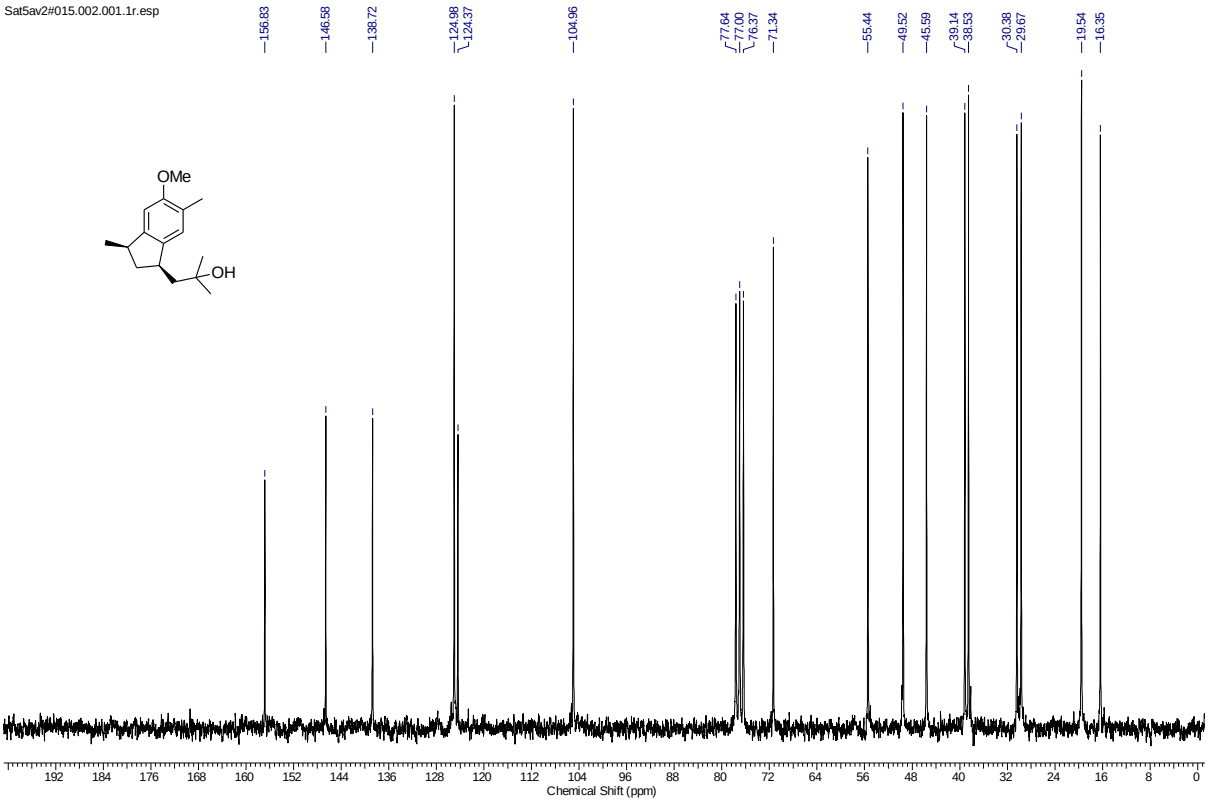

Sat3av2#044.002.001.1r.esp
168.02
162.11
160.75
154.11
130.96
126.11
123.05
104.67
104.15
77.63
77.00
76.36
55.09
50.50
40.74
37.15
21.22
16.28
OMe
CO2Me
Chemical Shift (ppm)

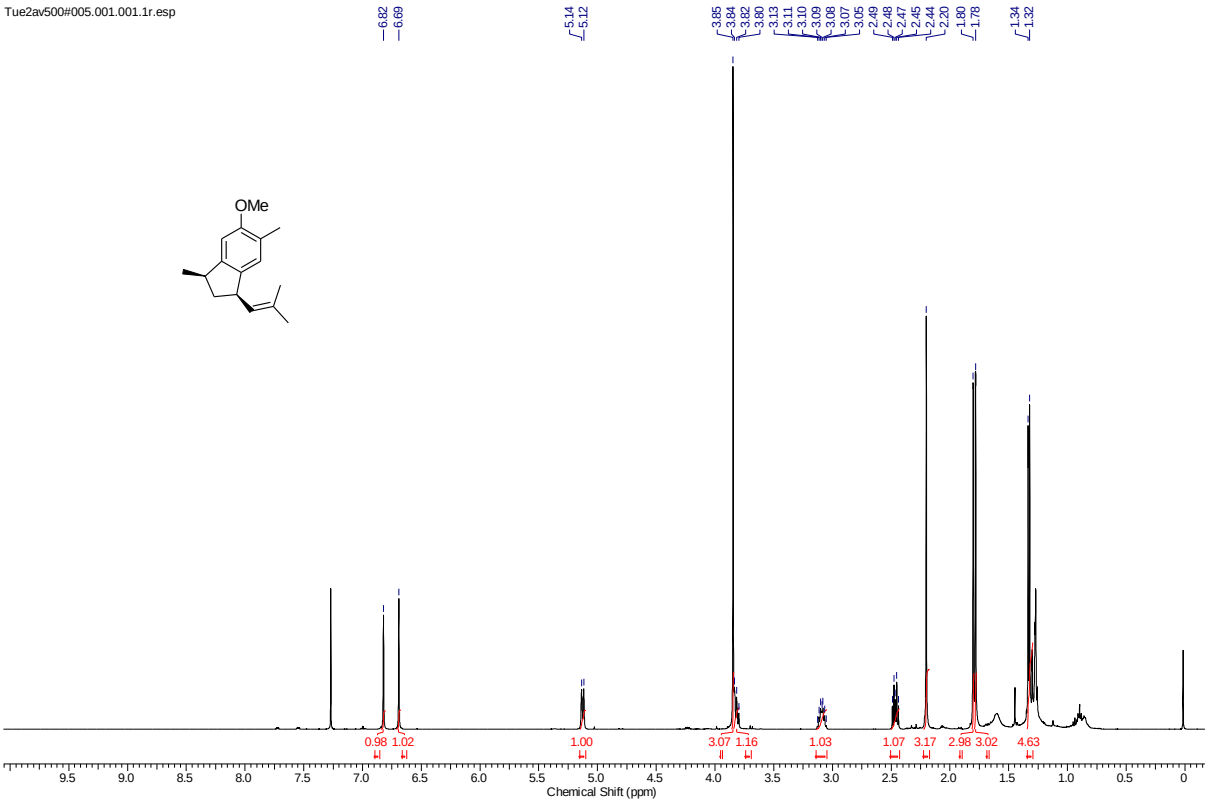

Sat3av2#044.001.001.1r.esp
123.05
104.66
104.15
55.09
50.50
40.73
37.15
21.22
16.28
OMe
CO2Me
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

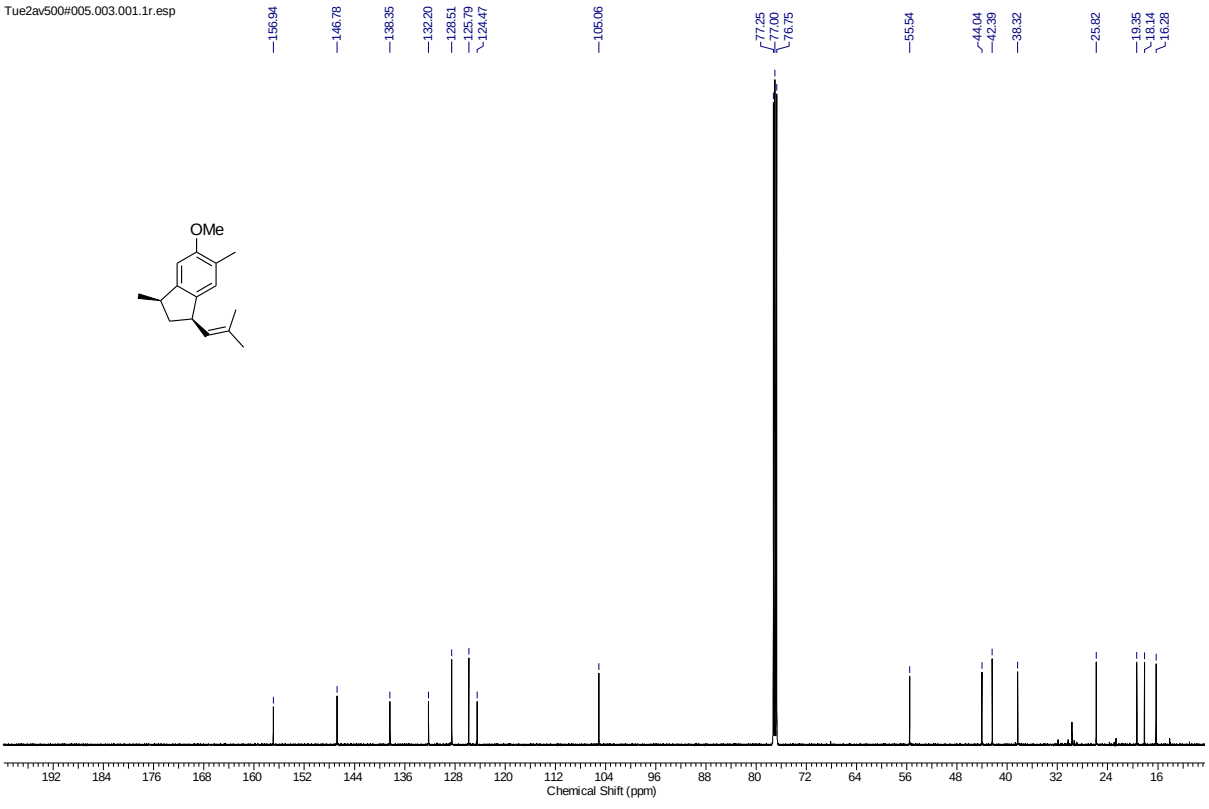

Tue4av2#099.001.001.1r.espfinal.esp
6.89
6.66
3.81
3.71
3.49
3.42
3.38
3.10
3.06
3.02
2.93
2.91
2.85
2.83
2.61
2.58
2.55
2.42
2.37
2.34
2.29
2.19
1.32
1.28
1.26
OMe
CO2Me
0.97 1.00
6.20
1.05
0.99 1.01
1.09
1.07 3.07
4.01
Chemical Shift (ppm)

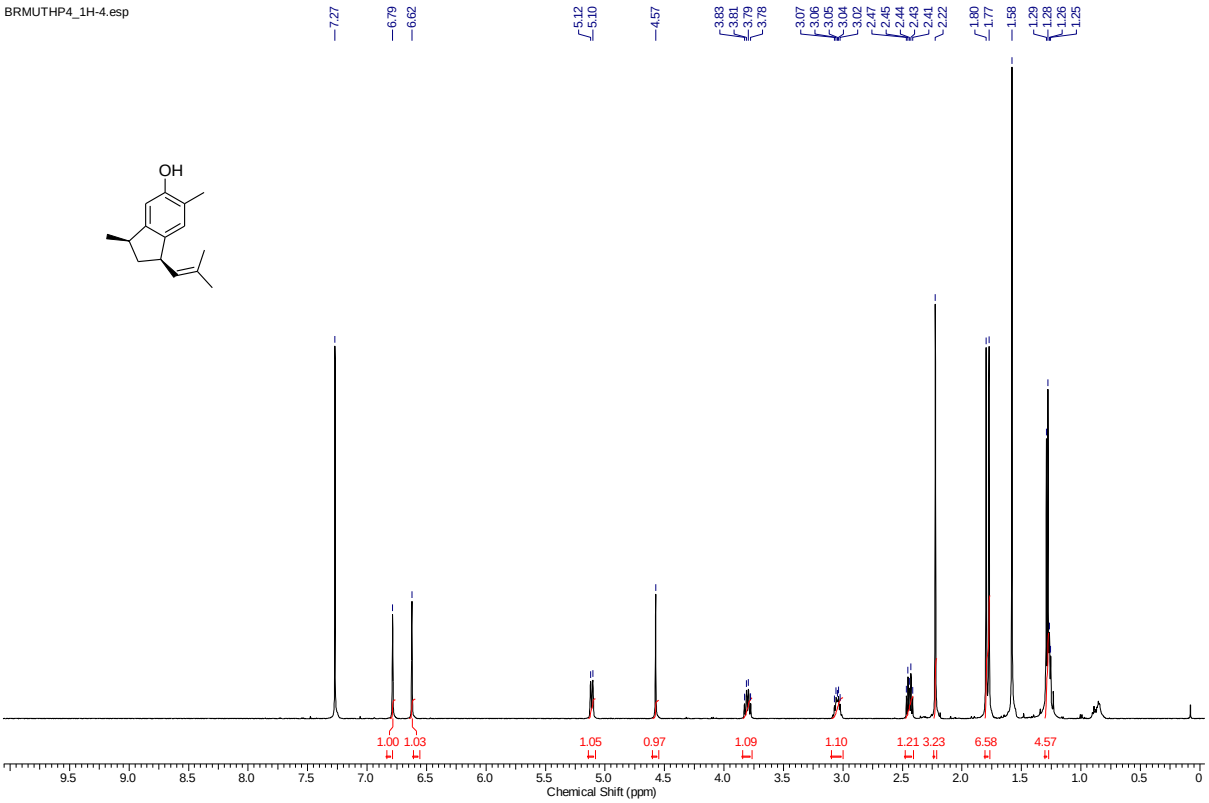

Wed4av2#077.002.001.1rfinal 13c.esp
173.46
157.08
146.89
136.50
124.75
124.50
104.93
77.63
77.00
76.36
55.24
51.36
42.77
39.90
39.30
37.95
19.65
16.25
OMe
CO2Me
Chemical Shift (ppm)

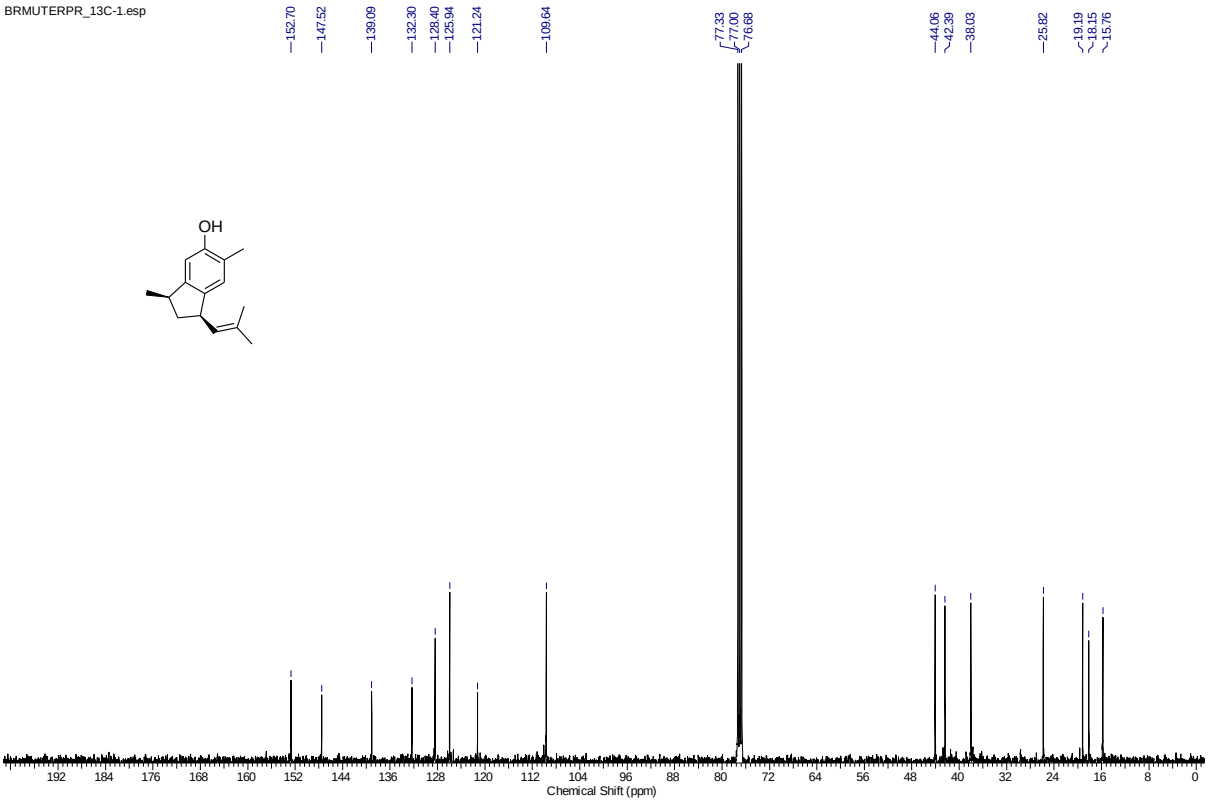

Fri4av2#005.001.001.1r.esp
6.97
6.69
3.85
3.17
3.14
3.09
3.06
2.99
2.74
2.70
2.68
2.64
2.61
2.29
2.28
2.23
1.62
1.57
1.55
1.50
1.42
1.36
1.32
OMe
OH
1.00
1.02
3.03
1.95
0.99
4.05
1.16
10.31
Chemical Shift (ppm)

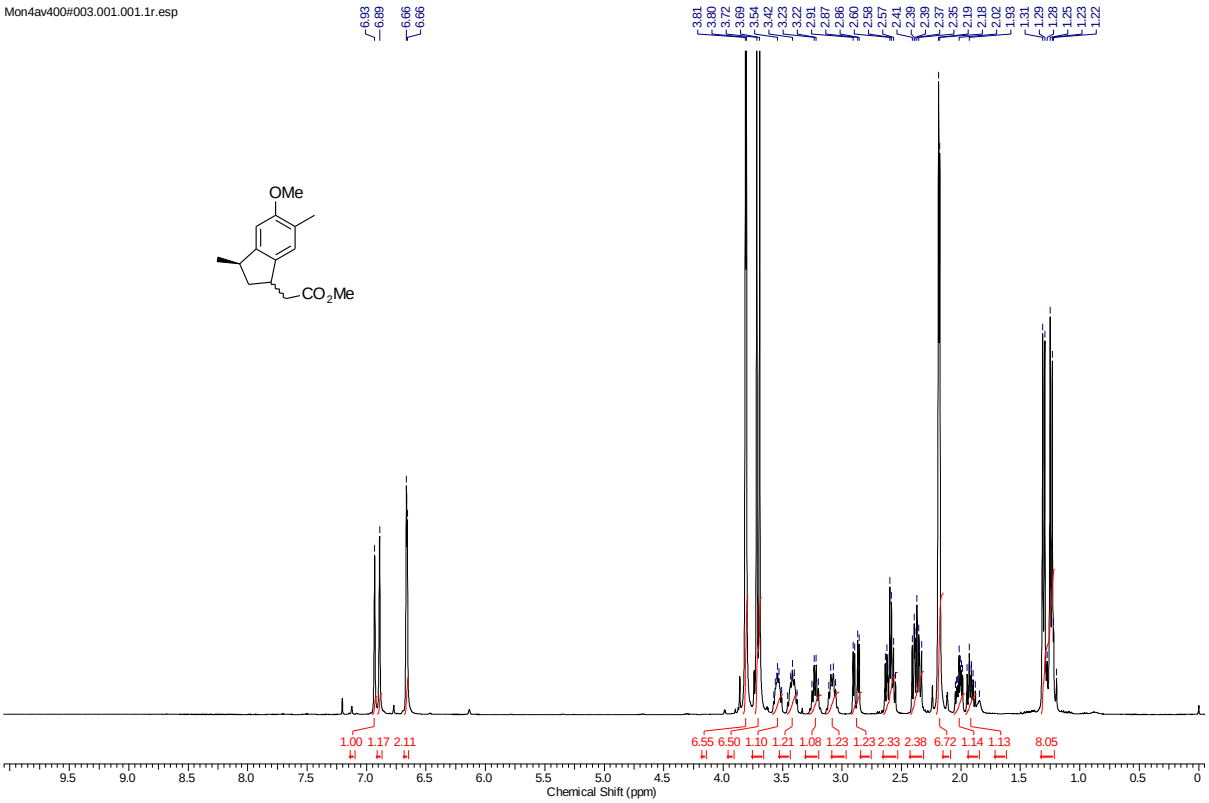

Sat5av2#015.002.001.1r.esp
156.83
146.58
138.72
124.98
124.37
104.96
77.64
77.00
76.37
71.34
55.44
49.52
45.59
39.14
38.53
30.38
29.67
19.54
16.35
OMe
OH
Chemical Shift (ppm)

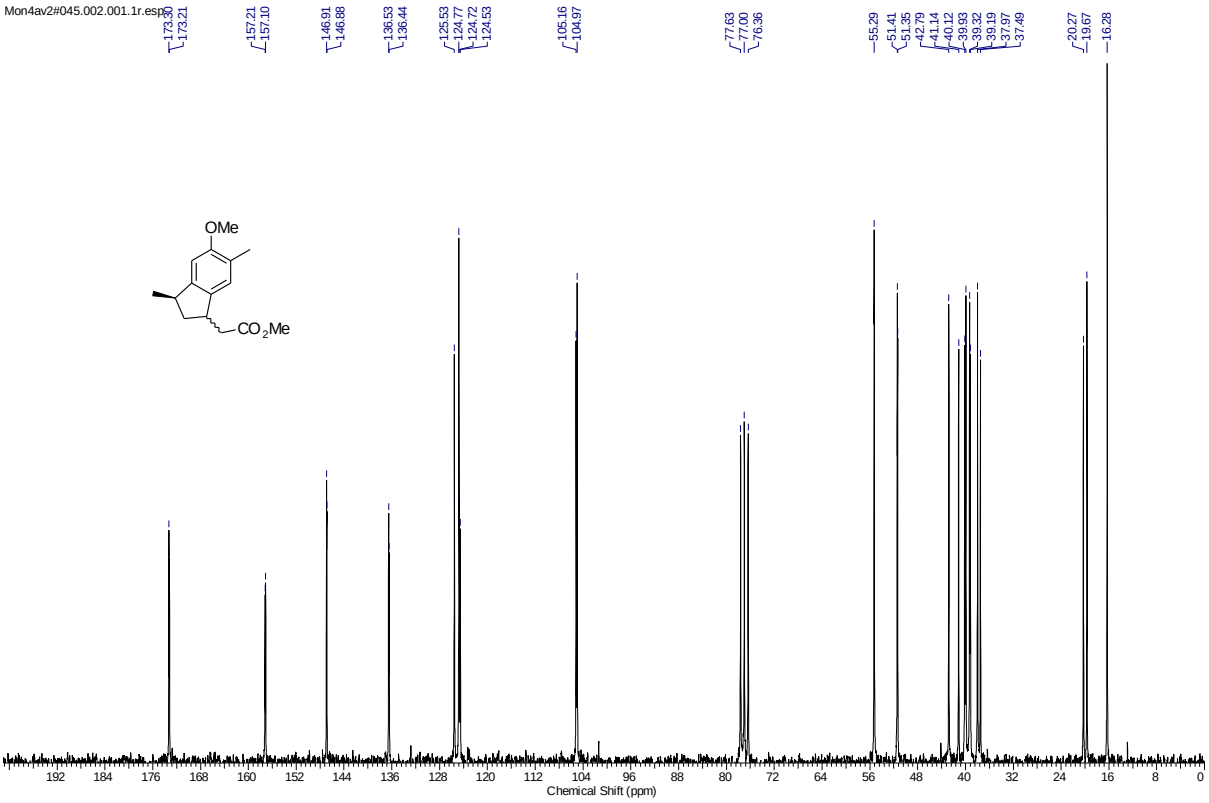

Tue2av500#005.001.001.1r.esp
6.82
6.69
5.14
5.12
3.85
3.84
3.82
3.80
3.13
3.11
3.10
3.09
3.08
3.07
3.05
2.49
2.48
2.47
2.45
2.44
2.20
1.80
1.78
1.34
1.32
OMe
0.98
1.02
1.00
3.07
1.16
1.03
1.07
3.17
2.98
3.02
4.63
Chemical Shift (ppm)

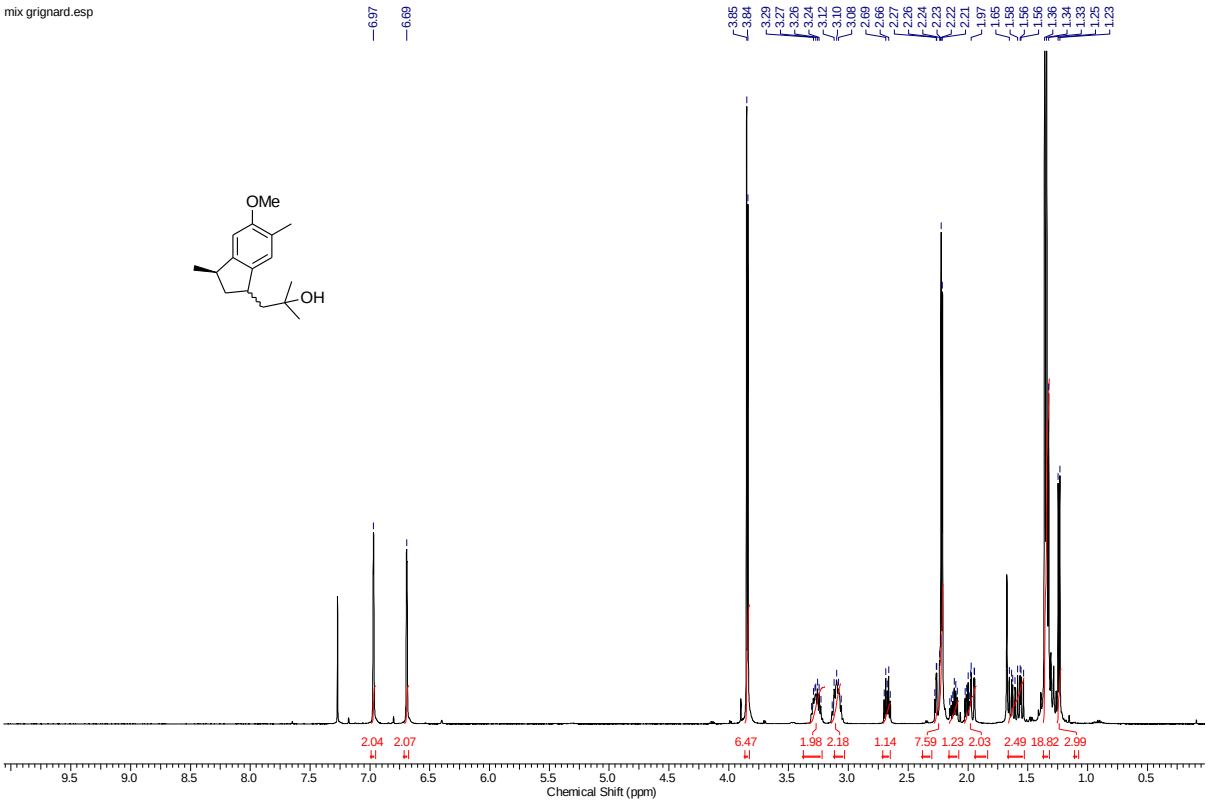

Tue2av500#005.003.001.1r.esp
156.94
146.78
138.35
132.20
128.51
125.79
124.47
105.06
77.25
77.00
76.75
55.54
44.04
42.39
38.32
25.82
19.35
18.14
16.28
OMe
Chemical Shift (ppm)

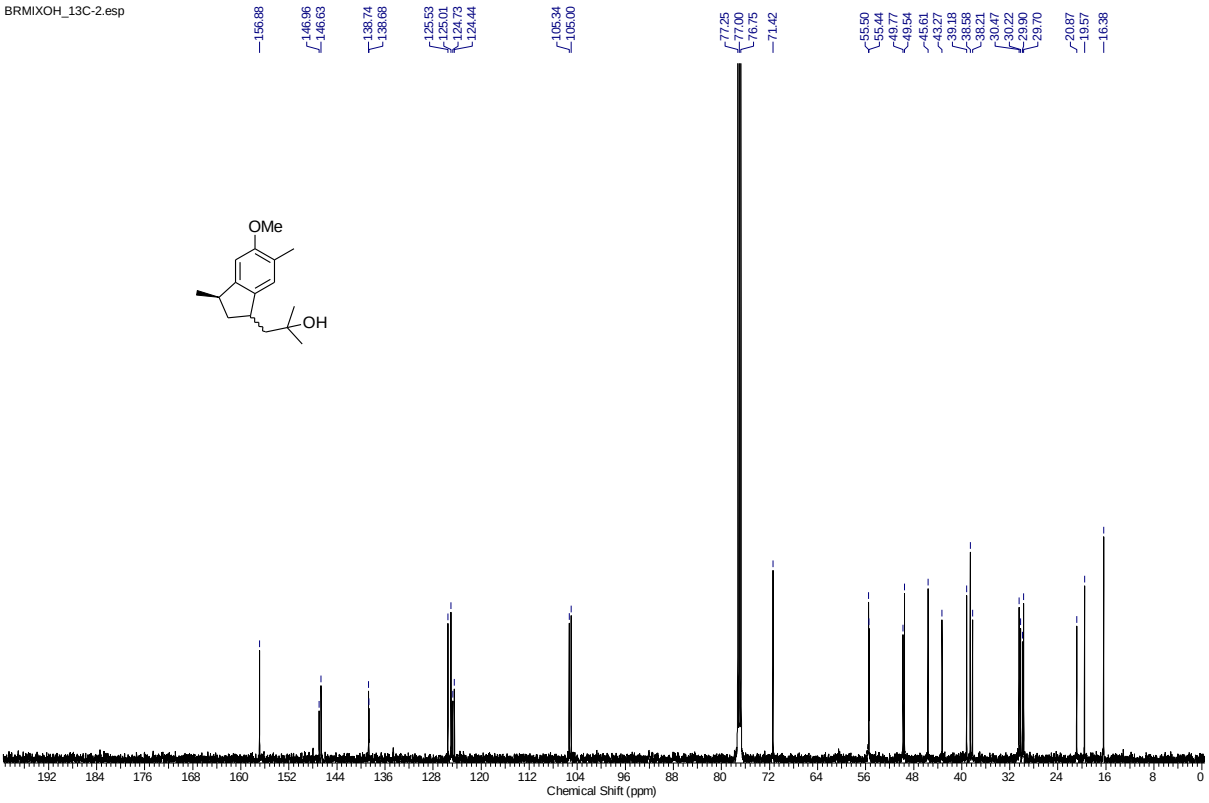

BRMUTHP4_1H-4.esp
7.27
6.79
6.62
5.12
5.10
4.57
3.83
3.81
3.79
3.78
3.07
3.06
3.05
3.04
3.02
2.47
2.45
2.44
2.43
2.41
2.22
1.80
1.77
1.58
1.29
1.28
1.26
1.25
OH
1.00 1.03 1.05 0.97 1.09 1.10 1.21 3.23 6.58 4.57
Chemical Shift (ppm)


BRMUTERPR_13C-1.esp
152.70
147.52
139.09
132.30
128.40
125.94
121.24
109.64
77.33
77.00
76.68
44.06
42.39
38.03
25.82
19.19
18.15
15.76
OH
Chemical Shift (ppm)

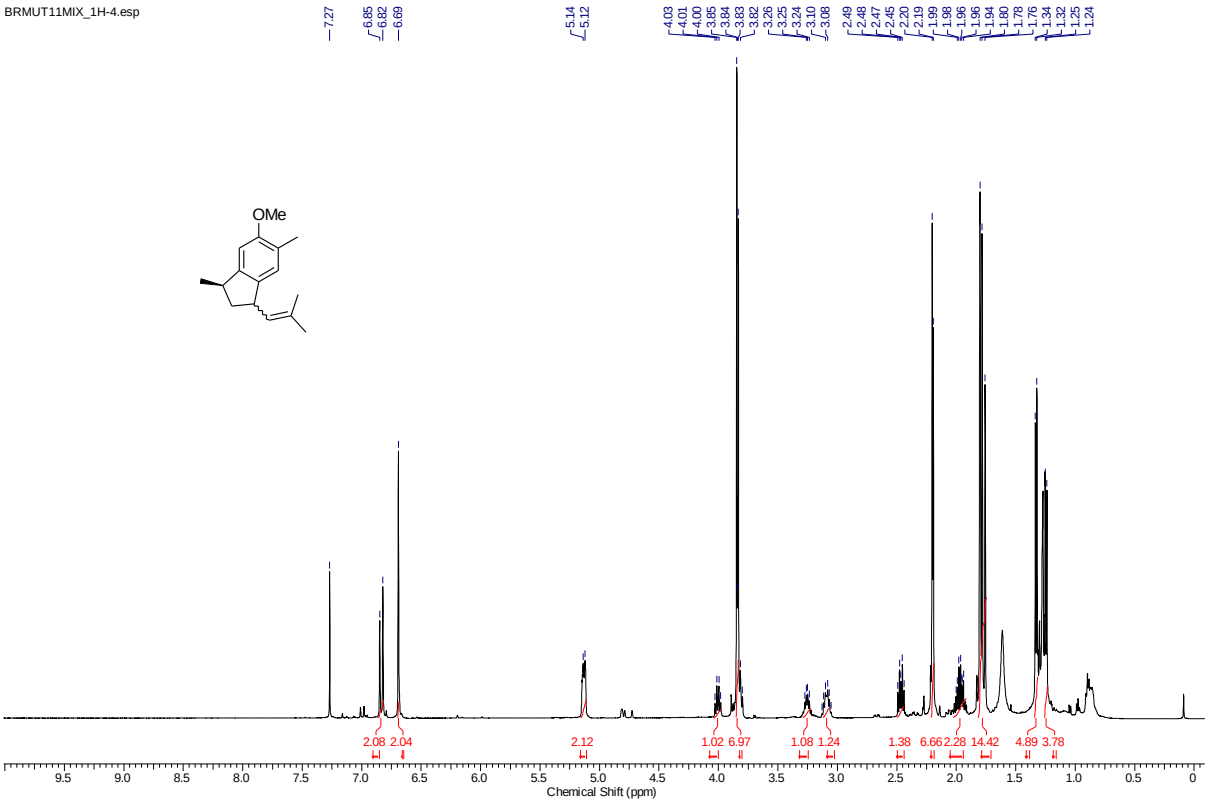

Mon4av400#003.001.001.1r.esp
OMe
CO2Me
Chemical Shift (ppm)


Mon4av2#045.002.001.1r.esp
OMe
CO2Me
Chemical Shift (ppm)

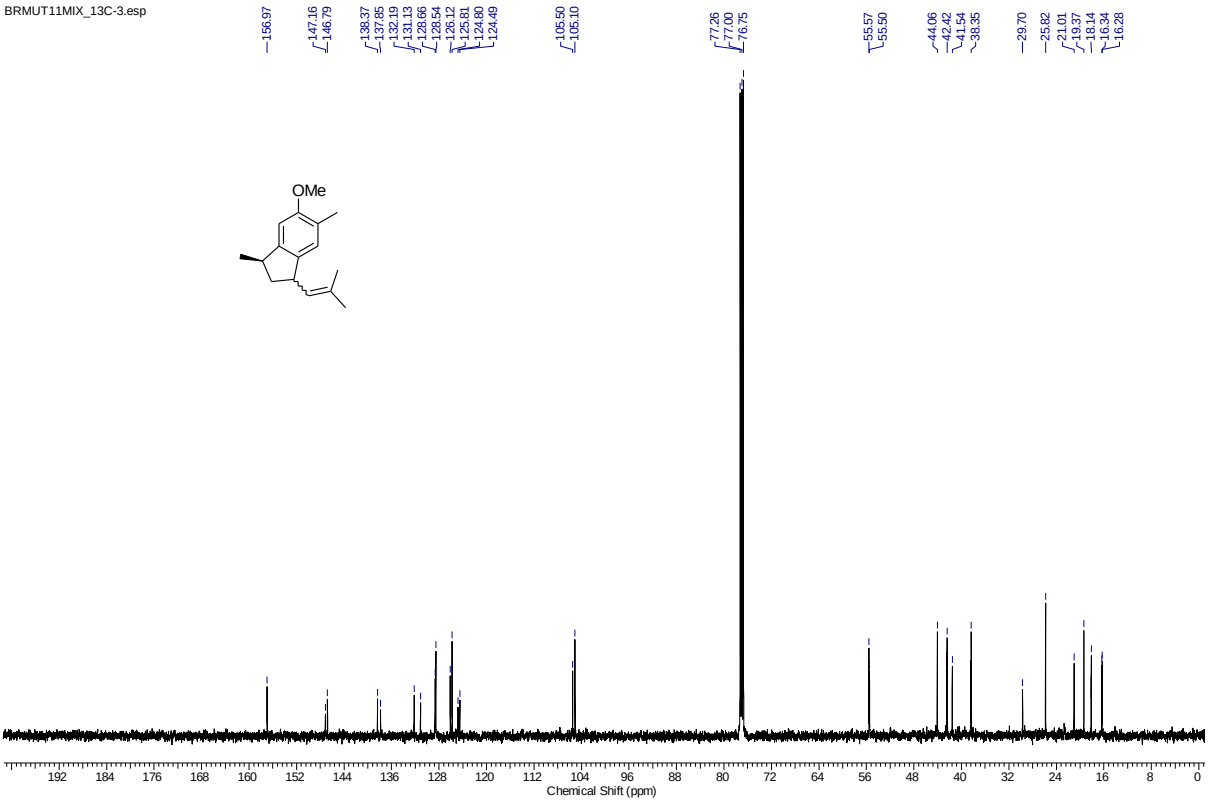

mix grignard.esp
OMe
OH
Chemical Shift (ppm)


BRMIXOH_13C-2.esp
OMe
OH
Chemical Shift (ppm)

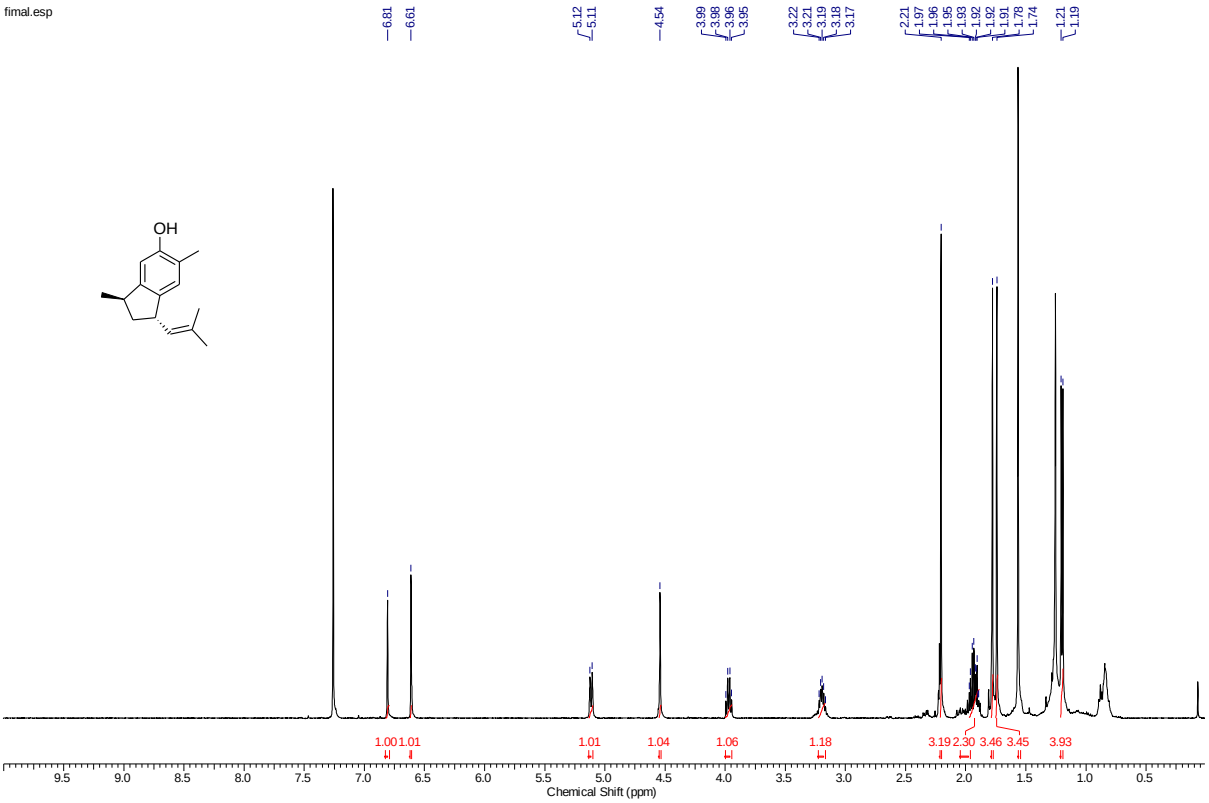
BRMUT11MIX_1H-4.esp



BRMUT11MIX_13C-3.esp



fimal.esp



BRMUTHP2_13C-1.esp