Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Intramolcular Diels-Alder Reactions Using Chiral Ruthenium Lewis Acid and Application in the Total Synthesis of Ledol

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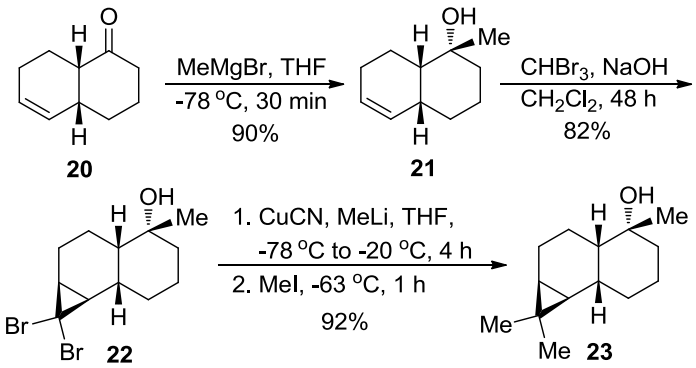
General

Catalysts **1a** and **1b** were prepared by published procedures.[1] ^{1}H-, ^{13}C- and ^{31}P-, NMR spectra were recorded on Bruker ARX-500, AMX-400 or ARX-300 FT spectrometers in the solvent indicated. ^{1}H- and ^{13}C-NMR chemical shifts (δ) are quoted in parts per million (ppm) relative to TMS. Coupling constants (*J*) are in hertz (Hz). ^{31}P-NMR chemical shifts are referenced to H_3PO_4 as external standard. Infrared spectra (IR) were recorded on a Perkin–Elmer Spectrum One spectrophotometer using a diamond ATR Golden Gate sampling. A band is described as strong (*s*), medium (*m*), or weak (*w*) depending on its depth. Electron impact (EI) HRMS mass spectra were obtained using a *Finningan MAT 95* operating at 70eV. Electrospray ionization (ESI) HRMS analyses were measured on a VG analytical 7070E instrument. Optical rotations were measured on a Perkin Elmer 241 Polarimeter using a quartz cell (l = 10 cm) with a Na high-pressure lamp (λ = 589 nm, continuous). UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller (25 ºC). CD spectra were recorded on a JASCO J-815 spectropolarimeter with a thermostated S3cell holder at 25°C in quartz cells with 1 cm light path. Three spectra were averaged, and the spectrum of solvent was subtracted for correction. The reactions were carried out under N_2. Solvents were removed by using a rotary evaporator at a water-aspirator pressure followed by evacuation of the flask to approximate 0.20 mmHg to remove traces of solvents. All glassware and syringes were oven-dried and further dried by placing under vacuum and heating with a heat gun for *ca.* 5 minutes as necessary. Flash column chromatography (FC) was performed by using Brunschwig silica gel (60 Å/32-63 mesh) (Art. 7736). Thin layer chromatography was performed on pre-coated aluminium plates (Fluka silica 60F_{254}), and visualized using UV light or aq. $KMnO_4$. Purification of THF, diethyl ether, toluene and dichloromethane was carried out by passing through activated Al_2O_3 (Solvtek© purification system). Commercial chemicals were used as supplied unless otherwise stated.

Experimental procedures of trienes and adducts

Cyclopropanation of bicyclic 21



1. 1-methyl-1,2,3,4,4a,7,8,8a-octahydronaphthalen-1-ol (21)

To a stirring solution of bicyclic ketone **20** (100 mg, 0.67 mmol, 1 eq) in THF (2 mL) at -78 °C was added dropwise a solution of MeMgBr (3 M in ethers, 0.27 mL, 0.80 mmol, 1.2 eq). After being stirred at -78 °C for 30 min (white suspension was observed), the reaction mixture quenched with sat. NH_4Cl (1 mL) and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phases were brine, dried (anh. $MgSO_4$) and filtrated. Solvents were removed in vacuo. The residue was purified by FC on silica gel (50% Et_2O in pentanes, R_f = 0.36,) to give a colorless viscous oil of alcohol **21** (100 mg, 0.60 mmol, 90% yield). IR (Neat): ν_{max} 3403*m*, 2932*m*, 2860*m*, 1462*m*, 1374*m*, 1255*m* cm^{-1}; MS: *m/z* (%) relative intensity 149.25 (M^+-H_2O); ^1H NMR (400 MHz, $CDCl_3$) δ 5.73–5.57 (m, 2H, C*H*=C*H*), 2.24–2.03 (m, 3H, C*H*COHC*H*H and C*H*HCH=CH), 1.86 (ddd, *J* = 14.7, 9.1, 5.4 Hz, 1H, C*H*HCH=CH), 1.74–1.34 (m, 9H, *H*OCCH*H*CH_2CH_2C*H* and CH_2CH), 1.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0 (CH), 126.5 (CH), 72.6 (C), 45.1 (CH), 35.5 (CH_2), 35.3 (CH), 28.6 (CH_2), 28.0 (CH_3), 26.3 (CH_2), 23.1 (CH_2), 17.5 (CH_2).

2. 1,1-dibromo-4-methyldecahydro-1*H*-cyclopropa[a]naphthalen-4-ol (22)[2]

Bicyclic alcohol **21** (30 mg, 0.18, 1 eq) was dissolved in CH_2Cl_2 (0.1 mL) followed by addition of $CHBr_3$ (0.32 mL, 3.6 eq, 20 eq) and powdered NaOH (115 mg, 2.88 mmol, 16 eq). The reaction mixture was stirred at 50-60 °C for 48 h. This mixture was diluted with water (1 mL) and extracted with CH_2Cl_2 (3 × 2 mL). The combined organic phases were dried (anh. $MgSO_4$) and filtrated. Solvents were removed in vacuo. The residue was chromatographed on silica gel (30% Et_2O in pentanes, R_f = 0.36 in 50% Et_2O in pentanes) to give a colorless solid of gem-

dibromopropane **22** (50 mg, 0.148 mmol, 82% yield). IR (Neat): ν_{max} 3374*m*, 2929*s*, 2863*m*, 1460*m*, 1374*w*, 1121*m*, 728*m* cm^{-1}; MS: *m/z* (%) relative intensity 319.95 (M^+-H_2O); ^1H NMR (400 MHz, $CDCl_3$) δ 2.30 (ddd, *J* = 18.2, 9.5, 4.6 Hz, 1H, HOCC*H*H), 2.12–2.01 (m, 1H, Br_2CC*H*CH), 1.91 (td, *J* = 10.5, 3.7 Hz, 1H, Br_2CC*H*CH_2), 1.79–1.52 (m, 6H, C*H*HC*H*HC*H*CO*H*, CH_2C*H*HCH_2 and Br_2CCHC*H*H), 1.53–1.18 (m, 9H, HOCC*H*HCH*H*C*H*$_2$, Br_2CCHC*H*CHCH*H* and C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.1 (C), 42.1 (CH), 39.7 (C), 35.9 (CH_2), 34.4 (CH), 31.4 (CH), 29.0 (CH_2), 28.2 (CH), 28.1 (CH_3), 22.0 (CH_2), 21.5 (CH_2), 17.9 (CH_2); HSMS (ESI-TOF) calcd for $C_{12}H_{18}Br_2O$; 335.9724 found: 335.9725.

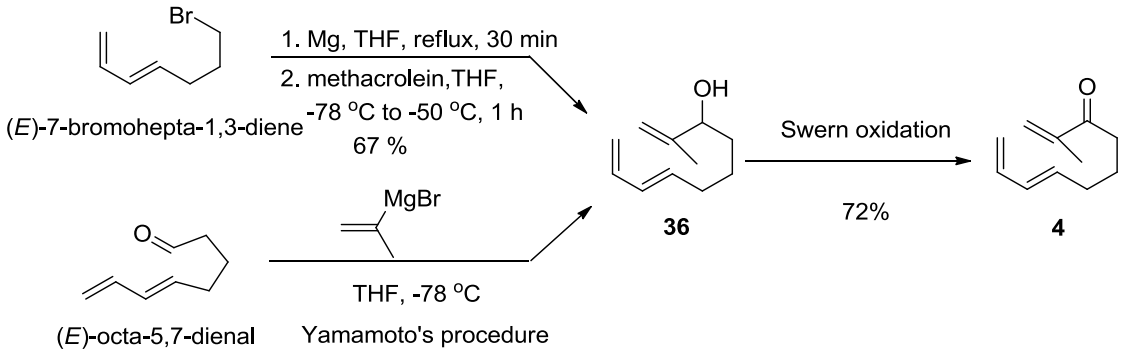
3. 1,1,4-trimethyldecahydro-1*H*-cyclopropa[a]naphthalen-4-ol (23)[3]

A solution of MeLi (1.6 M in ethers, 0.67 mL, 1.07 mmol, 5.1 eq) was added dropwise under N_2 at -78 ^oC to a stirred suspension of CuCN (56 mg, 0.651 mmol, 3.1 eq) in THF. The green suspension became to white turbid solution in 5 min. A solution of dibromopropane (70 mg, 0.21 mmol, 1 eq) in THF (2 mL), was slowly added to the previous mixture at -78 ^oC. The reaction mixture was warmed up to -20 ^oC and stirred for 4 h. MeI (0.25 mL, 4.2 mmol, 20 eq) was then added at -63 ^oC. After being stirred at -63 ^oC for 1 h, the mixture was poured into sat. $NaHCO_3$, extracted with Et_2O (3 × 10 mL) and washed with water (10 mL). The combined organic phases were dried (anh. $MgSO_4$) and filtrated. Solvents were removed in vacuo. The residue was chromatographed on silica gel (20% Et_2O in pentanes, R_f = 0.42) to give a colorless oil of gem-dimethylcyclopropane **23** (40 mg, 0.19 mmol, 92% yield). IR (Neat): ν_{max} 3364*m*, 2929*s*, 2862*m*, 1456*m*, 1373*m*, 1223*w*, 1116*m*, 914*m* cm^{-1}; MS: *m/z* (%) relative intensity 225.1 (M^+-H+NH_4); ^1H NMR (500 MHz, $CDCl_3$) δ 2.02 (ddt, *J* = 14.5, 9.8, 4.5 Hz, 1H, Me_2CCHC*H*H), 1.87–1.78 (m, 1H, Me_2CCHC*H*), 1.74–1.61 (m, 1H, CH_2C*H*HCH_2), 1.59–1.47 (m, 3H, C*H*HCH_2C*H*H and O*H*), 1.46–1.16 (m, 10H, CH*H*C*H*$_2$C*H*, CH*H*CH*H*CH*H*, HOCC*H*$_3$), 1.01 (s, 3H, C*H*$_3$), 0.98 (s, 3H, C*H*$_3$), 0.67 (td, *J* = 9.2, 4.5 Hz, 1H, Me_2CC*H*CH_2), 0.32 (dd, *J* = 9.2, 2.8 Hz, 1H, Me_2CC*H*CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 72.6 (C), 43.8 (CH), 36.7 (CH_2), 30.4 (CH_2), 30.0 (CH_3), 29.6 (CH), 28.0 (CH_3), 26.9 (CH), 21.1 (CH_2), 20.1 (CH), 19.9 (CH_2), 19.3 (CH_2), 18.0 (C), 15.1 (CH_3); HSMS (ESI-TOF) calcd for $C_{14}H_{24}O$; 208.1827 found: 208.1825.

Experimental procedures of trienes and adducts

4. Synthesis of triene 4[4]

(*E*)-7-bromohepta-1,3-diene was prepared according to the literature procedure.[5]



4.1 (*E*)-2-methyldeca-1,7,9-trien-3-ol (36)

In round bottom flask equipped with a magnetic stirring bar and Mg powder (50-150 mesh, 170 mg, 7 mmol, 2 eq), under N_2, was charged with THF (3.5 mL) and heated with heating gun until refluxing. The solution of alkyl bromide (613 mg, 3.5 mmol, 1 eq) in THF (5 mL) was added dropwise around 10% of all solution to refluxed heterogeneous Mg in THF over 30 min. After 15 min, the brown gray solution of Grignard reagent was cannula transferred to dropping funnel that was connected to another one round bottom which was contained a solution of methacrolein (0.23 mL, 2.8 mmol, 0.8 eq) in THF (2.0 mL) at -78 °C. The Grignard reagent was dripped into the solution of methacrolein over 15 min and warmed up to -50 °C for 1 h. The reaction mixture was quenched with sat. NH_4Cl (7 mL), extracted with Et_2O (3 x 10 mL), brine and dried (anh. Na_2SO_4). The crude reaction was purified by FC on silica gel (20% Et_2O in pentanes, R_f = 0.19 in 30 % Et_2O in pentanes) to give a pale yellow oil of alcohol **36** (390 mg, 2.35 mmol, 67% yield). IR (Neat): ν_{max} 3351*br. s*, 2932*s*, 2860*s*, 1454*m*, 1377*w*, 1059*s* cm^{-1}; MS: *m/z* (%) relative intensity 166 (M^+, 2), 151 (3), 148 (3), 133 (4), 123 (5), 97 (16), 94 (14), 80 (100), 79 (45), 71 (32), 69 (14), 67 (21), 55 (13); ^1H NMR (300 MHz, $CDCl_3$): δ 6.31 (td, *J* = 16.9, 10.3 Hz, 1H, CHC*H*=CH_2), 6.06 (dd, *J* = 15.1, 10.3 Hz, 1H, C*H*CH=CH_2), 5.70 (td, *J* = 6.9, 15.1 Hz, 1H, CH_2C*H*=CH), 5.09 (d, *J* = 16.9 Hz, 1H, CHCH=C*H*H), 5.00-4.91 (m, 2H, CHCH=C*H*H and CH_3C=C*H*H), 4.84 (t, *J* = 1.51 Hz, 1H, CH_3C=CH*H*), 4.07 (dd, *J* = 9.93, 6.08 Hz, 1H, C*H*OH), 2.10 (q, *J* = 7.1 Hz, 2H, =CHCH_2), 1.73 (s, 3H, CH_3), 1.49 (m, 5H, CH_2CH_2 and O*H*); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.6 (C), 137.3 (CH), 134.9 (CH), 131.3 (CH), 114.9 (CH_2), 111.1 (CH_2),

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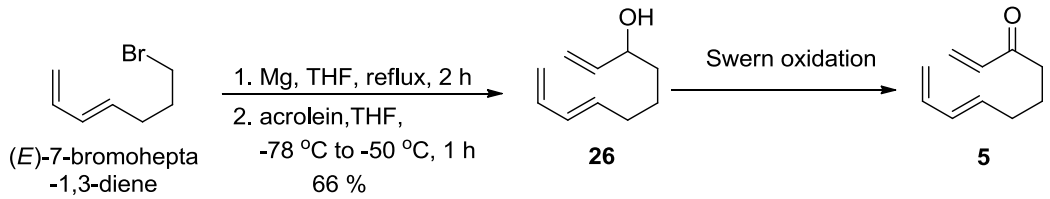
75.9 (CH), 34.4 (CH_2), 32.4 (CH_2), 25.2 (CH_2), 17.6 (CH_3); HSMS (ESI-TOF) calcd for $C_{11}H_{18}O$; 166.1358 found: 166.1356.

4.2 (*E*)-2-methyldeca-1,7,9-trien-3-one (4)

In a 10 mL round-bottom flask equipped with a magnetic stirring bar, under N_2, was charged with a solution of dimethyl sulfoxide (0.052 mL, 0.66 mmol, 1.1 eq) in 20 mL of THF. Oxalyl chloride (0.056 mL, 0.66 mmol, 1.1 eq) was added at -78 ^oC and the mixture was stirred for 15 min. 1,7,9-trienol **36** (100 mg, 0.6 mmol, 1 eq) was then added slowly, and the mixture was allowed to stir for 20 min. NEt_3 (0.23 mL, 1.8 mmol, 3 eq) was then added, and the reaction was allowed to warm to r.t. and stirred for 30 min. 1 M HCl (2 mL) was added, the aqueous and organic phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were then dried (anh. Na_2SO_4) and concentrated in vacuo to afford crude ketone **4** which was purified by FC on silica gel (5% Et_2O in pentanes, R_f = 0.22) to give a pale yellow oil of trienone **4** (72 mg, 0.43 mmol, 72% yield).[6] IR (Neat): ν_{max} 2926*m*, 1676*s*, 1631*w*, 1452*m*, 1369*w*, 1095*m*, 1003*s* cm^{-1}; MS: *m/z* (%) relative intensity 164 (M^+, 17), 149 (15), 139 (17), 121 (15), 112 (16), 111 (34), 109 (17), 97 (38), 95 (27), 93 (30), 85 (48), 83 (39), 81 (37), 71 (71), 69 (84), 57 (100), 55 (85); ^1H NMR (400 MHz, $CDCl_3$) δ 6.32 (td, *J* = 17.0, 10.3 Hz, 1H CHC*H*=CH_2), 6.07 (dd, *J* = 15.2, 10.3 Hz, 1H, C*H*CH=CH_2), 5.96 (s, 1H, CH_3CH=C*H*H), 5.77 (s, 1H, CH_3CH=CH*H*), 5.74-5.63 (td, *J* = 15.2, 6.6 Hz, 1H, C*H*=CH), 5.11 (d, *J* = 17.0 Hz, 1H, CHCH=C*H*H), 4.98 (d, *J* = 10.7 Hz, 1H, CHCH=C*H*H), 2.70 (t, *J* = 7.4 Hz, 2H, CH_2CO), 2.13 (q, *J* = 7.2 Hz, 2H, =CHCH_2), 1.88 (s, 3H, CH_3), 1.74 (p, *J* = 7.4 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.0 (CO), 144.6 (C), 137.1 (CH), 134.4 (CH), 131.7 (CH), 124.5 (CH_2), 115.2 (CH_2), 36.7 (CH_2), 32.0 (CH_2), 23.9 (CH_2), 17.7 (CH_2); HSMS (ESI-TOF) calcd for $C_{11}H_{16}O$; 164.1201 found: 164.1202.

5. Synthesis of triene 5[7]



5.1 (*E*)-deca-1,7,9-trien-3-ol (26)

Obtained in 66% yield as a pale yellow oil according to the procedure in 4.1. IR (Neat): ν_{max} 3347*s*, 2929*s*, 1651*m*, 1603*m*, 1424*m*, 1001*s*, 896*s* cm^{-1}; MS: *m/z* (%) relative intensity 152 (M^+, 1), 134 (3), 111 (4), 91 (6), 83 (15), 80 (100), 79 (38), 70 (11), 67 (25), 57 (32), 55 (19);^{1}H NMR (400 MHz, $CDCl_3$): δ 6.36 (dt, *J* = 17.0, 10.4 Hz, 1H, CHC*H*=CH_2), 6.11 (dd, *J* = 15.2, 10.4 Hz, 1H, CHC*H*=CH_2), 5.91 (ddd, *J* = 17.2, 10.6, 6.4 Hz, 1H, C*H*CH=CH_2), 5.74 (dd, *J* = 15.2, 7.5 Hz, 1H, CH=C*H*CH_2), 5.27 (dt, *J* = 17.2, 1.4 Hz, 1H, CHCH=C*H*H), 5.16 (ddd, *J* = 17.0, 5.9, 4.7 Hz, 2H, CHCH=CH*H* and HOCHCH=C*H*H), 5.01 (d, *J* = 10.1 Hz, 1H, HOCHCH=CH*H*), 4.16 (q, *J* = 5.9 Hz, 1H, C*H*OH), 2.17 (q, *J* = 6.7 Hz, 2H, CH=CHCH_2), 1.68–1.53 (m, 4H, CH_2CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.2 (CH), 137.2 (CH), 134.9 (CH), 131.3 (CH), 115.0 (CH_2), 114.8 (CH_2), 73.2 (CH), 36.5 (CH_2), 32.4 (CH_2), 24.9 (CH_2).

5.2 (*E*)-deca-1,7,9-trien-3-one (5)

In a 50 mL round-bottom flask equipped with a magnetic stirring bar, under N_2 was charged with a solution of dimethyl sulfoxide (0.23 mL, 3.3 mmol, 1.1 eq) in CH_2Cl_2 (18 mL). Oxalyl chloride (0.28 mL, 3.3 mmol, 1.1 eq) was added at -78 ^oC and the mixture was stirred for 15 min. The trienol **26** (3 mmol, 1 eq) was then added slowly, and the mixture was allowed to stir for 20 min. NEt_3 (1.25 mL, 9 mmol, 3 eq) was then added, and the reaction was allowed to warm to r.t. and stirred for 30 min. In the reaction mixture, buffer NaH_2PO_4/Na_2HPO_4 (pH 8, 2 mL) was added, the aqueous and organic phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were then dried (anh. Na_2SO_4) and concentrated in vacuo to afford a 1:0.2 of ketone **5** and its cycloaddition product (15% Et_2O in pentanes, R_f = 0.41 and 0.31, respectively). This mixture cannot be purified by FC on silica gel with 1-2% NEt_3 because IMDA reaction of triene **5** easily performed (The purification was performed to give 60% yield of cycloadduct **20**). IR (Neat): ν_{max} 1702*s*, 1681*s*, 1615*m*, 1401*m*, 1004*s* cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 (m, 2H, COC*H*=C*H*H), 6.22 (d, *J* = 17.6 Hz, 1H, COCH=CH*H*), 6.11 (dd, *J* = 17.0, 10.1 Hz, 1H, CHC*H*=CH_2), 5.84 (d, *J* = 10.5 Hz, 1H, CHCH=C*H*), 5.72 (m, 1H, CH_2C*H*=CH), 5.13 (d, *J* = 17.0 Hz, 1H, CH=C*H*H), 5.00 (d, *J* = 10.1 Hz, 1H, CH=CH*H*), 2.61 (dd, *J* = 14.6, 7.2 Hz, 2H, CH_2CO), 2.15 (q, *J* = 7.2 Hz, 2H, CH_2), 1.74 (m, 2H, CH_2);^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.3 (CO), 137.2 (CH), 136.6 (CH), 134.4 (CH), 131.6 (CH), 127.5 (CH_2), 114.8 (CH_2), 38.7 (CH_2), 31.8 (CH_2), 23.2 (CH_2).

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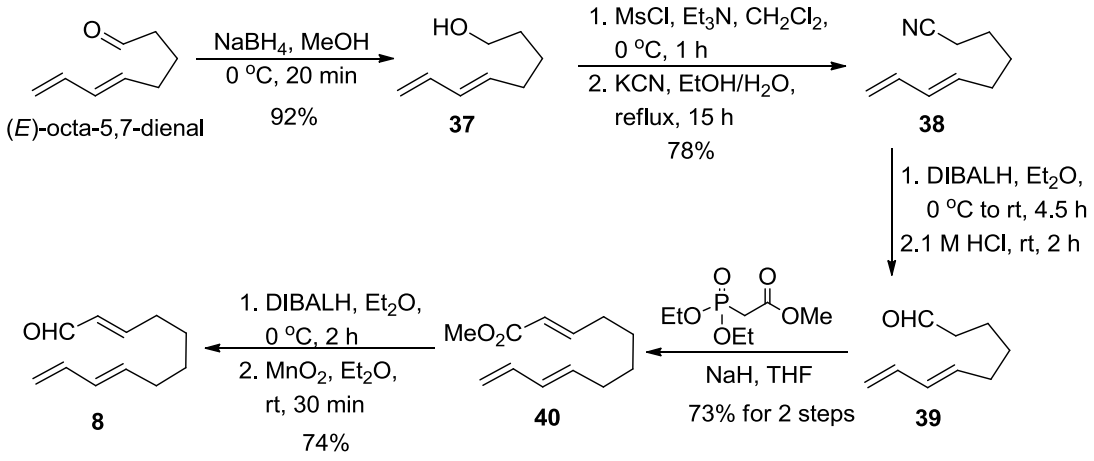
6. Synthesis of triene 8

(*E*)-octa-5,7-dienal was prepared according to the literature procedure.[8]



6.1 (*E*)-octa-5,7-dien-1-ol (37)

A solution of aldehyde (0.90 g, 7.30 mmol) in MeOH (7.3 mL) was added $NaBH_4$ (excess) as solid at 0 °C. After 20 min, the reaction was monitored by TLC which starting material was not observed. The mixture was added with water (7 mL) to destroy the rest of $NaBH_4$ and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried (anh. $MgSO_4$). The solvent was removed in vacuo. The crude product was passed through silica gel plug (40% Et_2O in pentanes, R_f = 0.18) to give a colorless oil of alcohol **37** (0.85 g, 6.75 mmol, 92% yield). IR (Neat): ν_{max} 3330*m*, 2930*m*, 1651*w*, 1603*w*, 1415*m*, 1334*m*, 1002*s* cm^{-1}; MS: *m/z* (%) relative intensity 126.1 (M^+); ^1H NMR (400 MHz, $CDCl_3$) δ 6.31 (dt, *J* = 17.0, 10.2 Hz, 1H, CHC*H*=CH_2), 6.06 (dd, *J* = 15.2, 10.4 Hz, 1H, C*H*CH=CH_2), 5.69 (dt, *J* = 15.2, 7.2 Hz, 1H, C*H*=CHCH), 5.09 (d, *J* = 17.0 Hz, 1H, CH=C*H*H), 4.96 (d, *J* = 10.2 Hz, 1H, CH=CH*H*), 3.64 (t, *J* = 6.5 Hz, 2H, CH_2OH), 2.12 (q, *J* = 7.0 Hz, 2H, CH=CHCH_2), 1.63-1.54 (m, 3H, *H*OCH_2CH_2), 1.52-1.42 (m, 2H, CH_2CH_2);^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3 (CH), 135.0 (CH), 131.3 (CH), 115.0 (CH_2), 62.8 (CH_2), 32.3 ($2CH_2$), 25.3 (CH_2); HSMS (ESI-TOF) calcd for $C_8H_{14}OH$; 126.1045 found: 126.1043.

6.2 (*E*)-nona-6,8-dienenitrile (38)

MsCl (0.70 mL, 9.11 mmol, 1.35 eq) was added dropwise to a 0 °C solution of alcohol **37** (850 mg, 6.75 mmol, 1 eq) and NEt_3 (1.88 mL, 13.50 mmol, 2 eq) in dry CH_2Cl_2 (22 mL). After 1 h, the reaction mixture was poured into a separating funnel which was contained cold 1 M HCl

(10 mL). The aqueous phase was separated and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were washed with sat. $NaHCO_3$ (10 mL), dried (anh. Na_2SO_4), filtrated and evaporated in vacuo to give a crude mesylate. The crude product was then combined with KCN (814 mg, 12.5 mmol, 1.85 eq) and 80:20 mixture of EtOH:H_2O (5.5 mL and 1.4 mL). This mixture was refluxed for 18 h. The cooled mixture was diluted with brine and extracted with Et_2O (3 x 10 mL), dried (anh. Na_2SO_4), filtered and evaporated in vacuo. The residue was purified by FC on silica gel (10% Et_2O in pentanes, R_f = 0.16) to give a pale yellow oil of nitrile **38** (709 mg, 5.25 mmol, 78% yield). IR (Neat): ν_{max} 2935*m*, 1652*w*, 1603*w*, 1460*m*, 1426*m*, 1005*s* cm^{-1}; MS: *m/z* (%) relative intensity 136.11 (M^++H); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29 (dt, *J* = 17.0, 10.2 Hz, 1H, CHC*H*=CH_2), 6.06 (dd, *J* = 15.2, 10.4 Hz, 1H, C*H*CH=CH_2), 5.65 (dt, *J* = 15.2, 7.2 Hz, 1H, C*H*=CHCH), 5.11 (d, *J* = 17.0 Hz, 1H, CH=CH*H*), 4.98 (d, *J* = 10.2 Hz, 1H, CH=C*H*H), 2.34 (t, *J* = 7.0 Hz, 2H, CH_2CN), 2.13 (q, *J* = 7.0 Hz, 2H, CH=CHCH_2), 1.66 (m, 2H, NCCH_2CH_2), 1.61-1.51 (m, 2H, CH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0 (CH), 133.7 (CH), 131.9 (CH), 119.7 (CN), 115.5 (CH_2), 31.6 (CH_2), 28.1 (CH_2), 24.8 (CH_2), 17.1 (CH_2); HSMS (ESI-TOF) calcd for $C_9H_{13}O$; 135.1041 found: 135.1048.

6.3 (2*E*,8*E*)-methyl undeca-2,8,10-trienoate (39)

In a 50 mL round-bottom flask equipped with a magnetic stirring bar, under N_2, was charged with a solution of nitrile **38** (0.27 g, 2 mmol, 1 eq) of in dry Et_2O (4 mL). Then, DIBALH solution (1.2 M in toluenes, 2.5 mL, 3 mmol, 1.5 eq) was added dropwise at 0 ^oC. The solution was warmed to r.t. and stirred for 4.5 h. The solution was cooled to 0 ^oC, and then 1.50 mL of methanol was added followed by 7.5 mL of 1 M HCl. This two-phase mixture was stirred for 2 h at r.t. and extracted with Et_2O (3 x 10 mL). The organic extracts were washed with sat. $NaHCO_3$ (10 mL), dried (anh. Na_2SO_4), filtered, and concentrated in vacuo to give aldehyde **39** (5% Et_2O in pentanes, R_f = 0.20).

In a 50 mL round-bottom flask equipped with a magnetic stirring bar, was put with NaH (0.122 g, 3 mmol, 1.5 eq) which was washed with hexanes (3 x 5 mL) and decantation by syringe under N_2. Methyldiethylphosphonoacetate (0.44 mL, 2.4 mmol, 1.2 eq) was added to a 0 ^oC suspension of NaH in THF (5 mL) and the resulting mixture was stirred for 1 h at r.t.. The solution of crude dienal **39** (2 mmol, 1 eq) in THF (1 mL) was then added to the reaction at 0 ^oC. The reaction mixture was slowly warmed to r.t. and stirred for 30 min, the reaction was quenched

with sat. NH_4Cl. The aqueous and organic layers were then separated, the aqueous layer extracted with Et_2O (3 x 10 mL), and the combined organic layers were dried (anh. Na_2SO_4). Following concentration of the organic layers in vacuo, the residue was chromatographed on silica gel (5-10% Et_2O in pentanes, R_f = 0.36 in 10% Et_2O in pentanes) to give ester **40** as colorless oil (0.305 g, 1.46 mmol, 73% yield). IR (Neat): ν_{max} 2932*m*, 1722*s*, 1655*m*, 1603*w*, 1436*m*, 1269*s*, 1196*s*, 1173*s*, 1003*s* cm^{-1}; MS: *m/z* (%) relative intensity 195.0 (M^+); ^1H NMR (400 MHz, $CDCl_3$) δ 7.01 (dt, *J* = 15.4, 7.0 Hz, 1H, C*H*=CHCO$_2$Me), 6.35 (dt, *J* = 16.6, 10.2 Hz, 1H, CHC*H*=CH$_2$), 6.09 (dd, *J* = 15.4, 10.4 Hz, 1H, C*H*CH=CH$_2$), 5.87 (dt, *J* = 15.4, 1.5 Hz, 1H, CH=C*H*CO$_2$Me), 5.74 (t, *J* = 15.4. 7.2 Hz, 1H, C*H*=CHCH), 5.14 (d, *J* = 16.6 Hz, 1H, CH=C*H*H), 5.01 (d, *J* = 10.2 Hz, 1H, CH=CH*H*), 3.77 (s, 3H, CO$_2$CH$_3$), 2.26 (q, *J* = 7.0 Hz, 2H, CH_2CH=CHCO$_2$Me), 2.14 (q, *J* = 6.8 Hz, 2H, CH_2CH=CH), 1.58-1.42 (m, 4H, CH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2 (CO), 149.5 (CH), 137.2 (CH), 134.8 (CH), 131.3 (CH), 121.0 (CH), 115.0 (CH_2), 51.5 (CH_3), 32.3 (CH_2), 32.1 (CH_2), 28.6 (CH_2), 27.6 (CH_2); HSMS (ESI-TOF) calcd for $C_{12}H_{18}O_2$; 194.1307 found: 194.1307.

6.4 (2*E*,8*E*)-undeca-2,8,10-trienal (8)

To the ester **40** (270 mg, 1.4 mmol, 1 eq) solution in dry Et_2O (7.7 mL) was added DIBALH (1.2 M in toluenes, 2.38 mL, 2.86 mmol, 2.2 eq) at 0 ^oC. After 2 h, the reaction was quenched by addition of sat. Rochell's salt (7 mL) and allowed to warm to r.t.. The clear 2 phases were seperated. The aqueous phase was extracted with Et_2O (3 x 10 mL). The combined organic phases were dried (anh. $MgSO_4$). Volatiles were evaporated in vacuo. The crude product was purified by FC (40% Et_2O in pentanes, R_f = 0.27) to give a pale yellow oil of trienal **8**. IR (Neat): ν_{max} 3355*br. m*, 2928*m*, 1652*w*, 1003*s*, 904*s* cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.36 (dt, *J* = 17.0, 10.2 Hz, 1H, CHC*H*=CH$_2$), 6.10 (dd, *J* = 15.1, 10.4 Hz, 1H, C*H*CH=CH$_2$), 5.72 (m, 3H, C*H*=CHCH and C*H*=C*H*CH$_2$OH), 5.14 (d, *J* = 17.0 Hz, 1H, CH=C*H*H), 5.01 (d, *J* = 10.2 Hz, 1H, CH=CH*H*), 4.14 (d, *J* = 4.1 Hz, 2H, CH_2OH), 2.23-2.02 (m, 4H, CH=CHCH_2 and CH_2CH=CHCH$_2$OH), 1.51-1.40 (m, 4H, CH_2CH_2), 1.38 (s, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.32 (CH), 135.29 (CH), 133.29 (CH), 131.08 (CH), 129.05 (CH), 114.83 (CH_2), 63.87 (CH_2), 32.42 (CH_2), 32.09 (CH_2), 28.71 (CH_2), 28.68 (CH_2).

The pure alcohol solution in Et_2O (5 mL) was added MnO_2 (2.26 g, 26 mmol, 20 eq) as one portion. After 30 min, the reaction was monitored by TLC (40% Et_2O in pentanes, R_f = 0.55).

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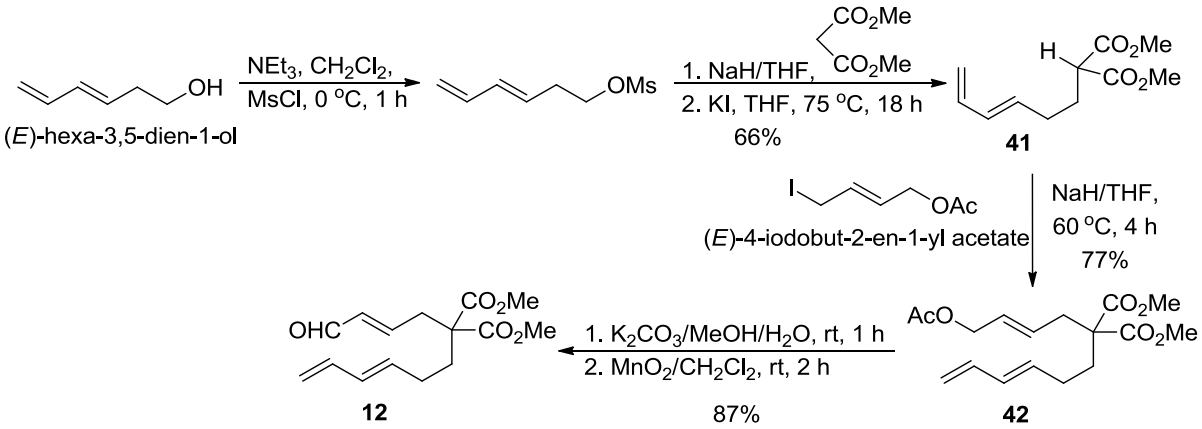
After removing of MnO_2, the solvents were removed in vacuo to give pale yellow oil (170 mg, 1.04 mmol, 74% yield) for 2 steps. IR (Neat): ν_{max} 2931*m*, 1687*s*, 1652*w*, 1637*w*, 1603*w*, 1436*w*, 1122*m*, 1004*s* cm^{-1}; MS: *m/z* (%) relative intensity 165.1 (M^++H); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 7.9 Hz, 1H, C*H*O), 6.85 (dt, *J* = 15.5, 6.8 Hz, 1H, C*H*=CHCHO), 6.31 (dt, *J* = 17.0, 10.3 Hz, 1H, CHC*H*=CH_2), 6.18–5.98 (m, 2H, C*H*CH=CH_2 and CH=C*H*CHO), 5.68 (dt, *J* = 15.2, 7.0 Hz, 1H, C*H*=CHCH), 5.10 (d, *J* = 17.0 Hz, 1H, CH=C*H*H), 4.97 (d, *J* = 10.1 Hz, 1H, CH=CH*H*), 2.35 (q, *J* = 7.0 Hz, 2H, CH_2CH=CHCHO), 2.12 (q, *J* = 7.0 Hz, 2H, CH_2CH=CH), 1.59–1.41 (m, 4H, CH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2 (CHO), 158.7 (CH), 137.1 (CH), 134.6 (CH), 133.1 (CH), 131.2 (CH), 115.2 (CH_2), 32.6 (CH_2), 32.2 (CH_2), 28.6 (CH_2), 27.4 (CH_2); HSMS (ESI-TOF) calcd for $C_{11}H_{16}O$; 164.1201 found: 164.1196.

7. Synthesis of triene 12

(*E*)-hexa-3,5-dien-1-ol[9] and **(*E*)-1-acetoxy-4-iodo-2-butene**[10] were prepared according to the literature procedure.



7.1 (*E*)-dimethyl 2-(hexa-3,5-dienyl)malonate (41)

To a solution of (*E*)-hexa-3,5-dien-1-ol (0.49 g, 5 mmol, 1 eq) and NEt_3 (1.40 mL, 10 mmol, 2 eq) in CH_2Cl_2 (16 mL) at 0 °C was added MsCl (0.41 mL, 5.25 mmol, 1.05 eq). After stirring at 0 °C for 1 h, the mixture was poured into cool 1 M HCl (10 mL), extracted with CH_2Cl_2 (3 x 20 mL) and the extracted were washed with brine and dried (anh. Na_2SO_4) and concentrated under rotary evaporator to give the crude mesylate compound as yellowish oil. To suspension of NaH (0.363 g, 9 mmol, 1.8 eq) in dry DMF (10 mL) were added dropwise a solution of dimethyl malonate (0.86 mL, 10 mmol, 2 eq) in THF (13 mL). The mixture became to clear solution which was added with a solution of crude mesylate in THF (12 mL) followed by adding KI (0.166 g, 1

mmol, 0.2 eq) as solid. The reaction mixture was stirred at 75 ^{o}C. After 18 h, it was quenched with sat. NH_4Cl and extracted with Et_2O (3 x 20 mL). The combined organic layers were dried (anh. Na_2SO_4) and concentrated in vacuo. The residue was chromatographed on silica gel (5-10 % Et_2O in pentanes, R_f = 0.22) to give product **41** (700 mg, 3.3 mmol, 66% yield). IR (Neat): ν_{max} 1733*s*, 1653*w*, 1603*w*, 1435*m*, 1221*s*, 1196*s*, 1153*s*, 1005*s* cm^{-1}; MS: *m/z* (%) relative intensity 213 (M^+, 100), 195 (24, 181 (22), 82 (19), 66 (12); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.28 (td, *J* = 17.0, 10.3 Hz, 1H, CH_2=C*H*), 6.05 (dd, *J* = 15.2, 10.3 Hz, 1H, CHC*H*=CH), 5.62 (dt, *J* = 15.2, 7.6 Hz, 1H, CHCH=C*H*), 5.10 (d, *J* = 17.0 Hz, 1H, CH*H*=CH), 4.98 (d, *J* = 10.3 Hz, 1H, C*H*H=CH), 3.72 (s, 6H, $2CO_2CH_3$), 3.37 (t, *J* = 7.3 Hz, 1H, C*H*CO_2CH_3), 2.12 (dd, *J* = 14.5, 7.12 Hz, 2H, CH_2CH=CH), 2.01 (dd, *J* = 14.5, 7.3 Hz, 2H, CH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8 (2CO), 136.9 (CH), 132.7 (CH), 132.5 (CH), 115.8 (CH_2), 52.6 ($2CH_3$), 50.9 (CH), 30.2 (CH_2), 28.2 (CH_2); HSMS (ESI-TOF) calcd for $C_{11}H_{16}O_4$; 212.1049 found: 212.1049.

7.2 Dimethyl 2-((*E*)-4-acetoxybut-2-enyl)-2-((*E*)-hexa-3,5-dienyl)malonate (42)

A solution of **41** (0.55 g, 2.60 mmol, 1 eq) in dry THF (5.20 mL) was added at r.t. to a suspension of NaH (115 mg of 60% suspension in mineral oil, 2.86 mmol, 1.1 eq) in dry THF (3.00 mL) under N_2. The mixture was stirred at r.t. for 0.5 h, then (*E*)-1-acetoxy-4-iodo-2-butene (0.687 g 2.86 mmol, 1.1 eq) in dry THF (5.20 mL) was added dropwise and the reaction was stirred at 60 ^{o}C for 4 h. Then the mixture was carefully diluted with water and extracted with Et_2O (3 x 15 mL). Combined organic portions were dried (anh. Na_2SO_4). The solvent was evaporated and the residue was chromatographed on silica gel (20% Et_2O in pentanes, R_f = 0.10) to afford product **42** as an viscous clear liquid (0.66 g, 2.04 mmol, 77% yield). IR (Neat): ν_{max} 1729*s*, 1436*m*, 1226*s*, 1199*s*, 1024*m*, 971*m* cm^{-1}; MS: *m/z* (%) relative intensity 324 (M^+, 1), 265 (100), 233 (23), 205 (73), 173 (15), 146 (24); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.32 (td, *J* = 17.0, 10.3 Hz, 1H, C*H*=CH_2), 6.09 (dd, *J* = 15.3, 10.4 Hz, 1H, C*H*CH=CH_2), 5.78-5.60 (m, 3H, C*H*=C*H*CH_2OCOCH_3 and C*H*CH=CH_2), 5.15 (d, *J* = 17.0 Hz, 1H, CH=C*H*H), 5.03 (d, *J* = 10.3 Hz, 1H, CH=CH*H*), 4.53 (d, *J* = 5.4 Hz, 2H, CH_2OCOCH_3), 3.76 (s, 6H, 2CH_3), 2.71 (d, *J* = 6.5 Hz, 2H, CH_2CH=CH), 2.09 (s, 3H, CH_3CO_2), 2.06-1.98 (m, 4H, CH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3 (CO), 170.6 (2CO), 136.8 (CH), 133.2 (CH), 131.6 (CH), 129.3 (CH), 128.4 (CH), 115.6 (CH_2), 64.5 (CH_2), 57.2 (C), 52.4 ($2CH_3$), 35.7 (CH_2), 31.9 (CH_2), 27.0 (CH_2), 20.9 (CH_3); HSMS (ESI-TOF) calcd for $C_{17}H_{24}O_6Na$; 347.1465 found: 347.1463.

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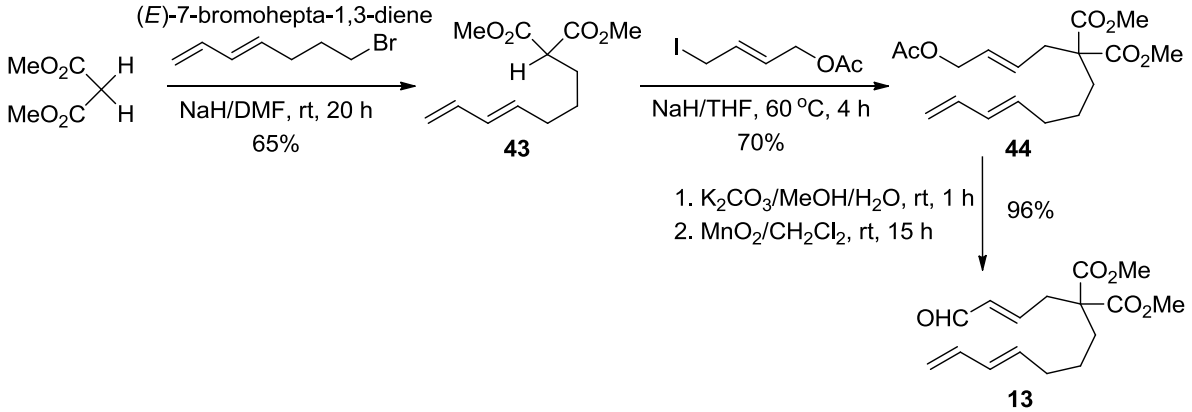
7.3 Dimethyl 2-((*E*)-hexa-3,5-dienyl)-2-((*E*)-4-oxobut-2-enyl)malonate (12)

A solution of **42** (0.60 mg, 1.85 mmol, 1 eq) in MeOH (6.20 mL) was added to a solution of K_2CO_3 (0.563 g, 4.07 mmol, 2.2 eq) in a mixture of MeOH (2.50 mL) and H_2O (6.20 mL) at r.t.. The mixture was stirred at r.t. for 1 h, then MeOH was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (3 x 10 mL), brine and dried (anh. Na_2SO_4). The solvent was evaporated in vacuo and the residue was used in further step. (IR (Neat): ν_{max} 3422*b*, 1728*s*, 1653*w*, 1603*w*, 1435*m*, 1198*s*, 1005*s* cm^{-1}). This crude alcohol was dissolved in CH_2Cl_2 (10 mL) and then was added MnO_2 (4.00 g, 46.25 mmol, 25 eq). The reaction mixture was stirred at r.t. for 2 h. After removing of MnO_2 by filtration, the crude aldehyde was purified on silica gel (40 % Et_2O in pentanes, R_f = 0.27) to give a trienal **12** as a white solid (0.450 g, 1.61 mmol, 87% yield, mp 53-55 ^oC). IR (Neat): ν_{max} 1727*s*, 1436*m*, 1199*s*, 1004*m*, 991*s* cm^{-1}; MS: *m/z* (%) relative intensity 281 (M^++1, 74), 280 (M^+, 70), 263 (74), 243 (100); ^1H NMR (300 MHz, $CDCl_3$): δ 9.49 (d, *J* = 7.8 Hz, 1H, C*H*O), 6.71 (dd, *J* = 15.6, 7.8 Hz, 1H, COCH=C*H*), 6.26 (td, *J* = 17.0, 10.2 Hz, 1H, CH=C*H*CH), 6.18-5.97 (m, 2H, C*H*CHO and C*H*=CH_2), 5.60 (td, *J* = 11.2, 5.2 Hz, 1H, C*H*=CHCH), 5.11 (dd, *J* = 17.0, 1.6 Hz, 1H, CH=C*H*H), 4.99 (dd, *J* = 10.2, 1.58 Hz, 1H, CH=CH*H*), 3.73 (s, 6H, 2OCH_3), 2.90 (dd, *J* = 7.5, 1.4 Hz, 2H, CH_2CH=CHCHO), 2.06-1.97 (m, 4H, CH_2CH=CH and CH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.29 (CO), 170.74 (2CO), 151.55 (CH), 136.63 (CH), 135.74 (CH), 132.53 (CH), 131.96 (CH), 115.90 (CH_2), 57.05 (C), 52.71 ($2CH_3$), 36.20 (CH_2), 32.70 (CH_2), 27.13 (CH_2); HSMS (ESI-TOF) calcd for $C_{15}H_{20}O_5Na$; 303.1202 found: 303.1182.

8. Synthesis of triene 13



8.1 (*E*)-dimethyl 2-(hepta-4,6-dienyl)malonate (43)

To a suspension of NaH (84 mg of 60% in mineral oil, 2.10 mmol, 1.05 eq) in dry DMF (6 mL) at 0 °C a dimethyl malonate (0.172 mL, 2.00 mmol, 1 eq) was added. After 15 min, (*E*)-7-bromohepta-1,3-diene (0.368 g, 2.10 mmol, 1.05 eq) was added dropwise to anion solution. The mixture was stirred at r.t.. After 20 h, the reaction was quenched with sat. NH_4Cl (1 mL), concentrated under vacuum pump (to remove DMF) and extracted with Et_2O (3 x 10 mL). The organic layers were washed with brine, dried (anh. $MgSO_4$) and concentrated in vacuo. The residue was purified by FC on silica gel (12% Et_2O in pentane, R_f = 0.22) to give malonate **43** as a colorless oil (295 mg, 1.30 mmol, 65% yield). IR (Neat): ν_{max} 1733*s*, 1652*w*, 1603*w*, 1435*m*, 1198*m*, 1152*m*, 1005*m* cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.34 (td, *J* = 17.0, 10.3 Hz, 1H, C*H*=CH_2), 6.10 (dd, *J* = 15.2, 10.3 Hz, 1H, C*H*CH=CH_2), 5.70 (dt, *J* = 15.2, 7.3 J Hz, 1H, CH_2C*H*=CH), 5.14 (d, *J* = 17.0 Hz, 1H, CH=C*H*H), 5.02 (d, *J* = 10.3 Hz, 1H, CH=CH*H*), 3.78 (s, 6H, 2CH_3), 3.41 (t, *J* = 7.6 Hz, 1H, C*H*CO_2CH_3), 2.16 (q, *J* = 7.1 Hz, 2H, CH_2CH=CH), 1.95 (m, 2H, CHCH_2), 1.47 (m, 2H, CH_2CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9 (2CO), 137.1 (CH), 134.1 (CH), 131.6 (CH), 115.2 (CH_2), 52.6 (2CH_3), 51.6 (CH), 32.1 (CH_2), 28.4 (CH_2), 26.9 (CH_2); HSMS (ESI-TOF) calcd for $C_{12}H_{18}O_4$; 226.1205 found: 226.1208.

8.2 Dimethyl 2-((*E*)-4-acetoxybut-2-enyl)-2-((*E*)-hepta-4,6-dienyl)malonate (44)

A solution of **43** (0.226 g, 1 mmol, 1 eq) in dry THF (2 mL) was added at r.t. to a suspension of NaH (44 mg of a 60% suspension in mineral oil, 1.1 mmol, 1.1 eq) in dry THF (1 mL) under N_2. The mixture was stirred at r.t. for 0.5 h, then (*E*)-1-acetoxy-4-iodo-2-butene (1.05 mmol, 1.05 eq) in dry THF (2 mL) was added dropwise and the reaction was stirred at 60 °C for 4 h. Then the mixture was carefully diluted with water and extracted with Et_2O (3 x 5 mL). Combined organic portions were dried (anh. Na_2SO_4). The solvent was evaporated and the residue was chromatographed on silica gel (30% EtOAc in pentanes, R_f = 0.38) to afford product **44** as an viscous liquid (237 mg, 0.70 mmol, 70% yield). IR (Neat): ν_{max} 1730*s*, 1652*w*, 1603*w*, 1435*m*, 1365*m*, 1225s, 1199*m*, 1006*m*, 972*m* cm^{-1}; MS: *m/z* (%) relative intensity 278 (10), 218 (27), 192 (13), 187 (14), 177 (15), 164 (28), 145 (29), 105 (27), 80 (100), 67 (44); ^1H NMR (300 MHz, $CDCl_3$): δ 6.33 (td, *J* = 16.9, 10.3 Hz, 1H, C*H*=CH_2), 6.09 (dd, *J* = 15.2, 10.3 Hz, 1H, C*H*CH=CH_2), 5.75-5.62 (m, 3H, C*H*=C*H*CH_2OCOCH_3 and C*H*CH=CH_2), 5.14 (dd, *J* = 16.9, 1.7 Hz, 1H, CH=C*H*H), 5.01 (ddd, *J* = 10.1, 1.1, 0.6 Hz, 1H, CH=CH*H*), 4.53 (d, *J* = 5.0 Hz, 2H, C$H_2$$OCOCH_3$), 3.76 (s, 6H, 2C$H_3$), 2.68 (d, *J* = 6.2 Hz, 2H, CH_2CH=CH), 2.19-2.05 (m, 5H,

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OCOC*H*$_3$ and CH$_2$C*H*$_2$CH=CH), 1.95-1.86 (m, 2H, CH$_2$C*H*$_2$C), 1.38-1.26 (m, 2H, C*H*$_2$CH$_2$C); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 171.8 (2CO), 170.8 (CO), 137.1 (CH), 134.2 (CH), 131.6 (CH), 129.6 (CH), 128.4 (CH), 115.3 (CH$_2$), 64.6 (CH$_2$), 57.6 (C), 52.5 (2CH$_3$), 35.7 (CH$_2$), 32.5 (CH$_2$), 32.2 (CH$_2$), 23.7 (CH$_2$), 21.0 (CH$_3$); HSMS (ESI-TOF) calcd for C$_{18}$H$_{26}$O$_6$Na; 361.1621 found: 361.1632.

8.3 Dimethyl 2-((*E*)-hepta-4,6-dienyl)-2-((*E*)-4-oxobut-2-enyl)malonate (13)

A solution of **44** (100 mg, 0.30 mmol, 1 eq) in MeOH (1 mL) was added to a solution of K$_2$CO$_3$ (92 mg, 0.66 mmol, 2.2 eq) in MeOH (4 mL) and H$_2$O (1 mL) at r.t.. The mixture was stirred at r.t. for 1 h, then MeOH was removed under reduced pressure. The residue was extracted with CH$_2$Cl$_2$ (3 x 5 mL), brine and dried (anh. Na$_2$SO$_4$). The solvent was removed in vacuo and the residue was used in further step. (IR (Neat): ν_{max} 3431*b*, 1730*s*, 1652*w*, 1603*w*, 1435*m*, 1198*s*, 1005s cm^{-1}) This crude alcohol solution in CH$_2$Cl$_2$ (3 mL) was added MnO$_2$ (0.65 g, 7.5 mmol, 25 eq). The reaction mixture was stirred at r.t. for 15 h. After removing of MnO$_2$ by filtration, the crude aldehyde was purified on silica gel to give a triene **13** as a colorless viscous liquid (85 mg, 0.29 mmol, 96% yield). IR (Neat): ν_{max} 2954*m*, 1731*s*, 1688*s*, 1651*w*, 1435*m*, 1251*m*, 1197*m*, 1142*s*, 1006*m* cm^{-1}; MS: *m/z* (%) relative intensity 295 (M$^+$, 1), 250 (70), 193 (11), 190 (11), 161 (14), 145 (16), 113 (13), 93 (20), 81 (19), 80 (100), 79 (53), 67 (42), 59 (25), 53 (16);^{1}H NMR (400 MHz, CDCl$_3$): δ 9.55 (d, *J* = 7.8 Hz, 1H, C*H*O), 6.76 (td, *J* = 15.3, 7.5 Hz, 1H, C*H*=CHCHO), 6.33 (td, *J* = 17.0, 10.3 Hz, 1H, CH=C*H*CH), 6.18 (tdd, *J* = 15.3, 7.8, 1.2 Hz, 1H, C*H*CHO), 6.10 (dd, *J* = 15.2, 10.4 Hz, 1H, C*H*=CH$_2$), 5.68 (d, *J* = 15.1 Hz, 1H, C*H*=CHCH), 5.15 (d, *J* = 17.0 Hz, 1H, CH=C*H*H), 5.04 (d, *J* = 10.4 Hz, 1H, CH=CH*H*), 3.79 (s, 6H, 2OC*H*$_3$), 2.94 (dd, *J* = 7.5, 1.3 Hz, 2H, C*H*$_2$CH=CHCHO), 2.15 (q, *J* = 7.0 Hz, 2H, C*H*$_2$CH=CH), 1.96 (m, 2H, C*H*$_2$CCO$_2$Me), 1.42-1.31 (m, 2H, C*H*$_2$CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 193.5 (CHO), 171.0 (2CO), 151.9 (CH), 137.0 (CH), 135.8 (CH), 133.7 (CH), 131.9 (CH), 115.5 (CH$_2$), 57.4 (C), 52.8 (2CH$_3$), 36.2 (CH$_2$), 32.9 (CH$_2$), 32.4 (CH$_2$), 23.8 (CH$_2$); HSMS (ESI-TOF) calcd for C$_{16}$H$_{22}$O$_5$; 294.1467 found: 294.1465.

9. Synthesis of triene 14

Triene **11** was prepared according to the literature procedure.[10]

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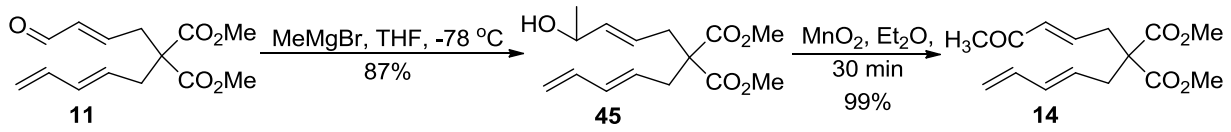

9.1 Dimethyl 2-((*E*)-4-hydroxypent-2-en-1-yl)-2-((*E*)-penta-2,4-dien-1-yl)malonate (45)

To a stirring solution of trienal **11** (310 mg, 1.16 mmol, 1 eq) in THF (1 mL) at -78 °C was added dropwise a solution of MeMgBr (3 M in ethers, 0.43 mL, 1.27 mmol, 1.1 eq). After being stirred at -78 °C for 20 min, the reaction mixture was warmed up to r.t.. Quenching with sat. NH_4Cl (1 mL) and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phased were brine, dried (anh. $MgSO_4$) and filtrated. Solvents were removed in vacuo. The residue was purified by FC on silica gel (50% Et_2O, in pentanes R_f = 0.19) to give a colorless oil of alcohol (250 mg, 0.88 mmol, 87% yield). IR (Neat): ν_{max} 3424*m*, 2955*m*, 1729*s*, 1437*s*, 1237*m*, 1202*m*, 1006*m* cm^{-1}; MS: *m/z* (%) relative intensity 283.3 (M^++H); ^1H NMR (400 MHz, $CDCl_3$) δ 6.28 (tt, *J* = 16.8, 8.4 Hz, 1H, C*H*=CH_2), 6.09 (dd, *J* = 15.1, 10.3 Hz, 1H, C*H*CH=CH_2), 5.60 (dd, *J* = 15.3, 6.2 Hz, 1H, C*H*=CHCHOH), 5.55–5.43 (m, 2H, CH=C*H*CHOH and CH=C*H*CH_2), 5.13 (d, *J* = 16.8 Hz, 1H, CH=C*H*H), 5.03 (d, *J* = 10.3 Hz, 1H, CH=CH*H*), 4.26 (p, *J* = 6.3 Hz, 1H, C*H*OH), 3.72 (s, 6H, $2CO_2CH_3$), 2.66 (d, *J* = 7.6 Hz, 2H, CH_2), 2.60 (d, *J* = 7.1 Hz, 2H, CH_2), 1.85 (m, 1H, OH), 1.24 (d, *J* = 6.3 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2 (CO), 171.1 (CO), 139.2 (CH), 136.5 (CH), 135.2 (CH), 127.6 (CH), 123.7 (CH), 116.7 (CH_2), 68.5 (CH), 58.0 (C), 52.5 ($2CH_3$), 35.9 (CH_2), 35.5 (CH_2), 23.3 (CH_3); HSMS (ESI-TOF) calcd for $C_{15}H_{22}O_5Na$; 305.1360 found: 305.1359.

9.2 Dimethyl 2-((*E*)-4-oxopent-2-en-1-yl)-2-((*E*)-penta-2,4-dien-1-yl)malonate (14)

Alcohol **45** (220 mg, 0.78 mmol, 1 eq) was dissolved in Et_2O (2 mL) and then MnO_2 (1.70 g, 19.5 mmol, 25 eq) was added. The reaction mixture was monitored by TLC (50% Et_2O in pentanes, R_f = 0.28) after stirring at r.t. for 30 min. After removing MnO_2 by filtration, the crude ketone **14** was obtained as pale yellow oil (215 mg, 0.77 mmol, 99% yield). IR (Neat): ν_{max} 2956*m*, 1731*s*, 1699*m*, 1677*s*, 1436*s*, 1361*w*, 1252*s*, 1200*s*, 1164*s*, 1006*m* cm^{-1}; MS: *m/z* (%) relative intensity 298.5 (M^++NH_4^+); ^1H NMR (400 MHz, $CDCl_3$) δ 6.64 (dt, *J* = 15.9, 7.6 Hz, 1H, C*H*=CHCOMe), 6.27 (dt, *J* = 16.8, 10.3 Hz, 1H, C*H*=CH_2), 6.10 (dd, *J* = 15.4, 10.2 Hz, 2H, CH=C*H*COMe and C*H*CH=CH_2), 5.48 (dt, *J* = 15.2, 7.6 Hz, 1H, CH=C*H*CH_2), 5.15 (d, *J* = 16.5

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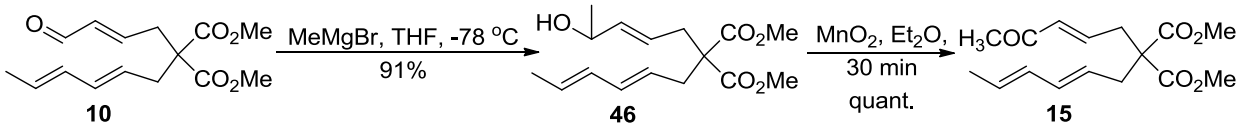
Hz, 1H, CH=C*H*H), 5.05 (d, *J* = 10.2 Hz, 1H, CH=CH*H*), 3.73 (s, *J* = 2.5 Hz, 6H, $2CO_2CH_3$), 2.76 (dd, *J* = 7.6, 1.3 Hz, 2H, CH_2), 2.68 (d, *J* = 7.4 Hz, 2H, CH_2), 2.23 (s, *J* = 4.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0 (CO), 170.6 (2CO), 141.6 (CH), 136.3 (CH), 135.7 (CH), 134.5 (CH), 126.9 (CH), 117.2 (CH_2), 57.6 (C), 52.7 ($2CH_3$), 36.6 (CH_2), 36.0 (CH_2), 27.0 (CH_3); HSMS (ESI-TOF) calcd for $C_{15}H_{21}O_5$; 281.1383 found: 281.1383.

10. Synthesis of triene 15

Triene **10** was prepared according to the literature procedure.[10]



10 **46** **15**

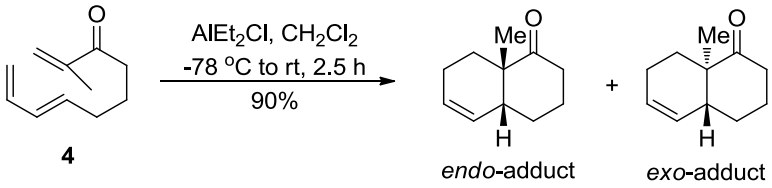
10.1 Dimethyl 2-((2*E*,4*E*)-hexa-2,4-dien-1-yl)-2-((*E*)-4-hydroxypent-2-en-1-yl) malonate (46)

To a stirring solution of trienal **10** (286 mg, 1.02 mmol, 1 eq) in THF (1 mL) at -78 °C was added dropwise a solution of MeMgBr (3 M in ethers, 0.38 mL, 1.12 mmol, 1.1 eq). After being stirred at -78 °C for 20 min, the reaction mixture was warmed up to r.t.. Quenching with sat. NH_4Cl (1 mL) and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phased were brine, dried (anh. $MgSO_4$) and filtrated. Solvents were removed in vacuo. The residue was purified by FC on silica gel (50% Et_2O in pentanes, R_f = 0.12) to give a colorless oil of alcohol (275 mg, 0.92 mmol, 91% yield). IR (Neat): ν_{max} 3448m, 2956*m*, 1729*s*, 1729*s*, 1437*s*, 1237*s*, 1199*s*, 1153*s*, 1102*m*, 1060*s* cm^{-1}; MS: *m/z* (%) relative intensity 314.0 (M^++NH_4^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (app. p, *J* = 10.4 Hz, 2H, C*H*C*H*=CHCH_3), 5.60 (m, 2H, CHCH=C*H*CH_2 and C*H*=CHCHOH), 5.47 (dt, *J* = 15.3, 7.2 Hz, 1H, CH=C*H*CHOH), 5.32 (app. dt, *J* = 14.2, 7.0 Hz, 1H, CH=C*H*CH_3), 4.24 (p, *J* = 6.2 Hz, 1H, C*H*OH), 3.70 (s, 6H, $2CO_2CH_3$), 2.60 (dd, *J* = 13.5, 7.4 Hz, 4H, $2CH_2$), 1.72 (d, *J* = 7.0 Hz, 3H, CH=CHC*H*$_3$), 1.23 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3 (CO), 171.2 (CO), 139.1 (CH), 134.8 (CH), 131.1 (CH), 128.9 (CH), 124.0 (CH), 123.8 (CH), 68.5 (CH), 58.1 (C), 52.5 ($2CH_3$), 35.9 (CH_2), 35.3 (CH_2), 23.3 (CH_3), 18.1 (CH_3); HSMS (ESI-TOF) calcd for $C_{16}H_{24}O_5Na$; 319.1517 found: 319.1516.

10.2 Dimethyl 2-((2*E*,4*E*)-hexa-2,4-dien-1-yl)-2-((*E*)-4-oxopent-2-en-1-yl)malonate (15)

Alcohol **46** (30 mg, 0.1 mmol, 1 eq) was dissolved in Et_2O (0.5 mL) and then MnO_2 (0.174 g, 2.0 mmol, 20 eq) was added. The reaction mixture was monitored by TLC (50% Et_2O in pentanes, R_f = 0.33) after stirring at r.t. for 30 min. After removing MnO_2 by filtration, the crude aldehyde was obtained as pale yellow oil in quantitative yield. IR (Neat): ν_{max} 2955*m*, 1733*s*, 1701*m*, 1679*s*, 1436*m*, 1361*w*, 1251*s*, 1201*s*, 990*m* cm^{-1}; MS: *m/z* (%) relative intensity 295.5 (M^++H); ^1H NMR (400 MHz, $CDCl_3$) δ 6.65 (dtd, *J* = 9.5, 7.6, 1.9 Hz, 1H, C*H*=CHCO), 6.15 – 5.92 (m, 3H, C*H*C*H*=CHCH$_3$ and CH=C*H*CO), 5.65 (td, *J* = 13.4, 7.0 Hz, 1H, CHCH=C*H*CH$_2$), 5.31 (dt, *J* = 14.7, 7.0 Hz, 1H, CH=C*H*CH$_3$), 3.74 and 3.73 (each s, 6H, 2C*H*$_3$), 2.76 (d, *J* = 7.6 Hz, 2H, C*H*$_2$), 2.66 (d, *J* = 7.0 Hz, 2H, C*H*$_2$), 2.24 (d, *J* = 2.2 Hz, 3H, COC*H*$_3$), 1.74 (d, *J* = 7.0 Hz, 3H, CHC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1 (CO), 170.8 (2CO), 141.8 (CH), 135.3 (CH), 134.5 (CH), 130.9 (CH), 129.5 (CH), 123.3 (CH), 57.7 (C), 52.7 (2CH_3), 36.7 (CH_2), 36.0 (CH_2), 27.0 (CH_3), 18.1 (CH_3). HSMS (ESI-TOF) calcd for $C_{16}H_{22}O_5$; 294.1467 found: 294.1467.

11. IMDA of triene 4



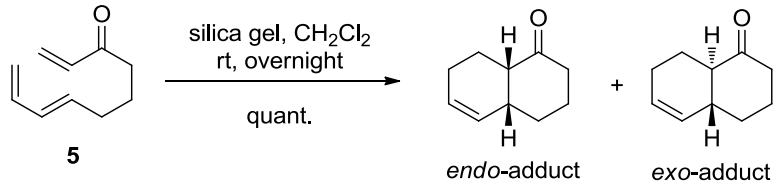
4 *endo*-adduct *exo*-adduct

8a-methyl-2,3,4,4a,8,8a-hexahydronaphthalen-1(7*H*)-one

In a 10 mL round-bottom flask equipped with a magnetic stirring bar, under N_2, was charged with a solution of triene **4** (50 mg, 0.30 mmol, 1 eq) in CH_2Cl_2 (0.3 mL). $AlEt_2Cl$ solution (0.15 mL, 0.15 mmol, 0.5 eq) was added dropwise at -78 °C. The yellow reaction mixture was stirred at -78 °C to r.t. for 2 h and quenched with sat. $NaHCO_3$ (2 mL) and CH_2Cl_2 (2 mL). The organic phase was extracted with Et_2O (5 x 3 mL), brine and dried (anh. Na_2SO_4). A 90:10 mixture of *endo*:*exo* adducts was determined by ^1H NMR and GC. The crude reaction was purified by FC (10% Et_2O in pentanes, R_f = 0.31) to give a colorless oil of adducts (45 mg, 0.274 mmol, 90% yield). Chiral GC (Hydrodex-β, H_2, 100 °C hold 30 min then heating 0.5 °C/min to 120 °C): t_R of *endo* product (min) = 41.13, 43.10 and t_R of *exo* product (min) = 51.59, 52.34. IR (Neat): ν_{max} 1700*s*, 1448*m*, 1429*m*, 1119*m* cm^{-1}; MS: *m/z* (%) relative intensity 164 (M^+, 5), 149 (16), 139 (12), 137 (18), 135

(10), 127 (10), 125 (19), 111 (36), 109 (26), 97 (52), 95 (39), 93 (21), 85 (42), 71 (56), 69 (100), 57 (97), 55 (82); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81-5.71 (m, 1H, C*H*=CH), 5.48 (d, *J* = 10.03 Hz, 1H, CH=C*H*), 2.51-1.53 (m, 9H, C*H* and 4CH_2), 1.32-1.18 (m, 5H, CH_3 and CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.6 (CO), 130.2 (CH), 128.3 (CH), 47.0 (C), 43.5 (CH), 38.8 (CH_2), 30.5 (CH_2), 27.8 (CH_2), 24.6 (CH_3), 23.1 (CH_2), 22.7 (CH_2).

12. IMDA of triene 5

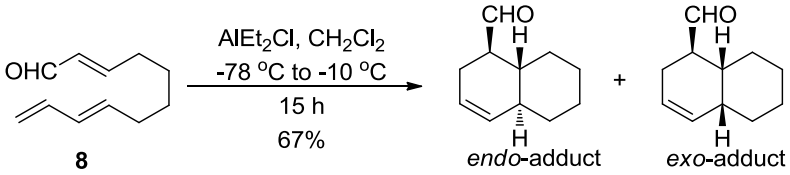


5 *endo*-adduct *exo*-adduct

2,3,4,4a,8,8a-hexahydronaphthalen-1(7*H*)-one

A solution of triene **5** (30 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) was then put silica gel and stirred at r.t. overnight. After removal silica gel by filtration, a 99:1 mixture of *endo:exo* isomers of the corresponding adduct was obtained in quantitative yield. Chiral GC (Hydrodex-β, H_2, 100 °C hold 30 min then heating 0.5 ^{o}C/min to 120 ^{o}C): t_R of *endo* product (min) = 45.93, 48.85. IR (Neat): ν_{max} 1702*s*, 1445*m*, 1430*m*, 1123*m* cm^{-1}; MS: *m/z* (%) relative intensity 150 (M^+, 100), 107 (30), 104 (32), 95 (30), 94 (34), 93 (35), 80 (44), 79 (89), 77 (34), 55 (37); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.79-5.72 (m, 1H, C*H*=CH), 5.58-5.51 (m, 1H, CH=C*H*), 2.80-2.68 (m, 1H, C*H*CO), 2.58-2.50 (m, 1H, C*H*CHCO), 2.45-2.36 (m, 1H, COC*H*H), 2.34-1.67 (m, 8H, COCH*H*, 3CH_2 and C*H*HCH), 1,56 (m, 1H, CH*H*CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.3 (CO), 129.8 (CH), 128.5 (CH), 48.1 (CH), 40.7 (CH_2), 37.3 (CH), 29.6 (CH_2), 23.4 (CH_2), 23.0 (CH_2), 22.3 (CH_2).

13. IMDA of triene 8

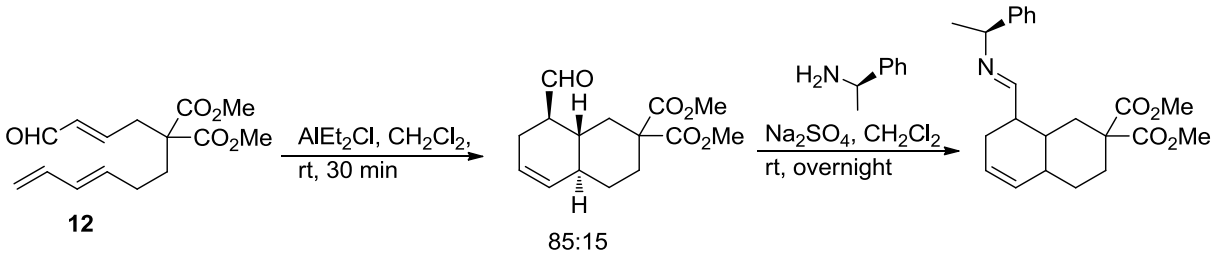


8 *endo*-adduct *exo*-adduct

1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carbaldehyde

In a 10 mL round-bottom flask equipped with a magnetic stirring bar, under N_2, was charged with a solution of triene **8** (32 mg, 0.2 mmol, 1 eq) in CH_2Cl_2 (2 mL). $AlEtCl_2$ solution (1 M in hexanes, 0.2 mL, 0.2 mmol, 1 eq) was added dropwise at r.t. The yellow reaction mixture was stirred at -78 to -10 ^oC and quenched with sat. $NaHCO_3$ (2 mL) and CH_2Cl_2 (2 mL). The organic phase was extracted with CH_2Cl_2 (3 x 5 mL), brine and dried (anh. Na_2SO_4). A 84:16 mixture of *endo*:*exo* adducts was obtained. The crude product was purified by FC (10% Et_2O in pentanes, R_f = 0.47) to give a colorless oil of adducts (22 mg, 0.134 mmol, 67% yield). Chiral GC (Hydrodex-β, H_2, 100 °C hold 30 min then heating 0.5 ^oC/min to 120 ^oC): t_R of *endo* product (min) = 53.52 , 54.93 and t_R of *exo* product (min) = 72.45, 73.26. IR (Neat): ν_{max} 2921*s*, 2852*m*, 1727*s*, 1446*w*, 1067*m* cm^{-1}; MS: *m/z* (%) relative intensity 165.1 (M^++H); ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 4.3 Hz, 1H, C*H*O), 5.64 (tdd, *J* = 9.7, 4.3, 2.4 Hz, 1H, C*H*=CH), 5.49 (dd, *J* = 9.7, 1.5 Hz, 1H, CH=C*H*), 2.43-2.19 (m, 2H, C*H*HC*H*CHO), 2.11 (m, 1H, CH*H*CHCHO), 1.85-1.68 (m, 3H, C*H*CHCHO and C*H*HCH$_2$CH$_2$C*H*H), 1.45 (dt, *J* = 10.0, 4.0 Hz, 1H, CH=CHC*H*), 1.39-1.04 (m, 6H, CH*H*C*H*$_2$C*H*$_2$CH*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.2 (CO), 132.5 (CH), 123.4 (CH), 52.2 (CH), 41.0 (CH), 40.6 (CH), 33.1 (CH_2), 50.5 (CH_2), 26.44 (CH_2), 26.37 (CH_2), 23.4 (CH_2); HSMS (ESI-TOF) calcd for $C_{11}H_{16}O$; 164.1201 found: 164.1199.

14. IMDA of triene 12



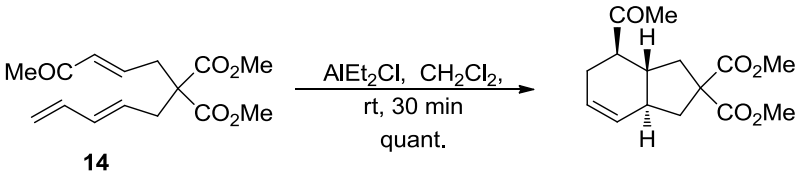
12

85:15

Trienone **12** (28 mg, 0.1 mmol, 1 eq) was placed in dry reaction flask and then CH_2Cl_2 (1 mL) was added under N_2. $AlEt_2Cl$ solution (1 M in hexanes, 0.02 mL, 0.2 eq) was slowly added dropwise at r.t.. After 30 min, the reaction was quenched with water (2 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phases were brine, dried (anh. $MgSO_4$) and filtrated. Solvents were removed in vacuo. The residue was passed through Celite 545 plug to give a yellow oil of bicyclic product (25 mg, 0.089 mmol, 89% yield) with a 85:15 ratio of *endo*:*exo* isomers. To determine enantiomeric ratio, aldehyde adducts were changed to chiral imine derivative (^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.9, 4.3 Hz, CH_{exo}=N), 7.78

(dd, *J* = 8.9, 4.3 Hz, C*H*$_{exo}$=N), 7.67 (d, *J* = 7.1 Hz, C*H*$_{endo}$=N) and 7.64 (d, *J* = 7.1 Hz, C*H*$_{endo}$=N)). IR ($CHCl_3$): ν_{max} 2924*m*, 1727*s*, 1435*s*, 1241*s*, 1205*m*, 1005*m*, 911*m*, 730*s* cm^{-1}; MS: *m/z* (%) relative intensity 281.32 (M^++H^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 4.3 Hz, 1H, C*H*O), 5.64 (m, 1H, C*H*=CH), 5.67 (ddd, *J* = 10.2 Hz, 1H, CH=C*H*), 3.76 (s, 3H, CO_2CH_3), 3.69 (s, 3H, CO_2CH_3), 2.44 (t, *J* = 14.0 Hz, 2H, C*H*HCC*H*H), 2.34-2.20 (m, 2H, C*H*HC*H*CHO), 2.13 (d, *J* = 17.5 Hz, 1H, CH*H*CHCHO), 1.87-1.75 (m, 3H, C*H*C*H*HC*H*H), 1.66-1.48 (m, 2H, C*H*C*H*HC), 1.26 (m, 1H, CHCH*H*CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.0 (CHO), 172.2 (CO), 171.3 (CO), 131.0 (CH), 124.0 (CH), 55.4 (C), 52.8 (CH_3), 52.7 (CH_3), 51.6 (CH), 39.7 (CH), 36.4 (CH), 35.1 (CH_2), 31.3 (CH_2), 29.2 (CH_2), 25.3 (CH_2); HRMS (ESI-TOF) calcd for $C_{15}H_{20}O_5$; 280.1311 found: 280.1313.

15. IMDA of triene 14



14

Dimethyl 7-acetyl-3,3a,7,7a-tetrahydro-1*H*-indene-2,2(6*H*)-dicarboxylate

Trienone **14** (28 mg, 0.1 mmol, 1 eq) was placed in dry reaction flask and then CH_2Cl_2 (1 mL) was added under N_2. $AlEt_2Cl$ solution (1 M in hexanes, 0.02 mL, 0.2 eq) was slowly added dropwise at r.t.. After 30 min, the reaction was monitored by IR (peak at 1677 cm^{-1} of α,β-unsaturated ketone was disappeared). Water (2 mL) was added at r.t.. The aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phases were brine, dried (anh. $MgSO_4$) and filtrated. Solvents were removed in vacuo. The residue was passed through Celite 545 plug to give a yellow oil of bicyclic product in quantitative yield with exclusive *endo* isomer (28 mg, 0.1 mmol). Chiral GC (CP-Chirasil-Dex CB, H_2, 150 °C hold 5 min then heating 0.5 ^{o}C/min to 160 ^{o}C hold 45 min, flow 0.5 mL/min): t_R of *endo* product (min) = 59.22, 60.89. IR (Neat): ν_{max} 2924*m*, 1711*s*, 1729*s*, 1435*s*, 1358*m*, 1252*s*, 1197*m*, 1164*s*, 1100*m* cm^{-1}; MS: *m/z* (%) relative intensity 298.4 (M^++NH_4^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (d, *J* = 9.9 Hz, 1H, C*H*=CH), 5.64 (ddd, *J* = 9.6, 6.5, 2.7 Hz, 1H, CH=C*H*), 3.72 (s, 3H, CO_2CH_3), 3.73 (s, 3H, CO_2CH_3), 2.79–2.51 (m, 3H, C*H*CO and CH*H*CCH*H*), 2.40–2.04 (m, 6H, CH_2CH=CH, $COCH_3$, and C*H*CH=CH), 1.93–1.58 (m, 3H, C*H*HCC*H*H and C*H*CHCOCH_3); ^{13}C NMR (100 MHz, $CDCl_3$)

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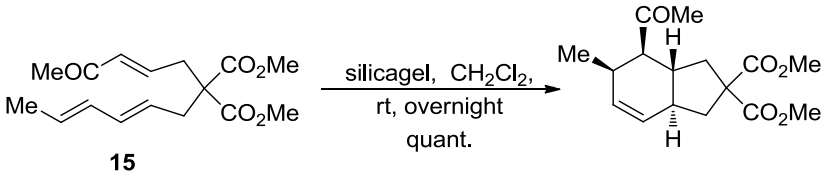
δ 210.4 (CO), 173.1 (CO), 172.7 (CO), 128.0 (CH), 126.5 (CH), 58.3 (C), 52.9 ($2CH_3$), 52.6 (CH), 44.4 (CH), 43.4 (CH), 38.1 (CH_2), 37.6 (CH_2), 29.2 (CH_2), 29.0 (CH_3); HSMS (ESI-TOF) calcd for $C_{15}H_{21}O_5$; 281.1383 found: 281.1381.

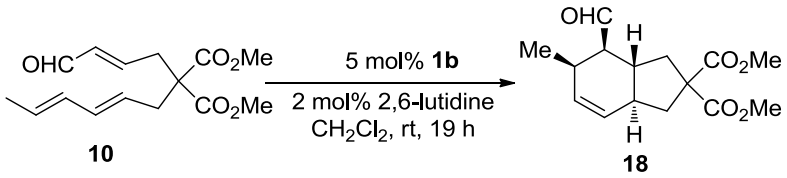
16. IMDA of triene 15



Dimethyl 7-acetyl-6-methyl-3,3a,7,7a-tetrahydro-1*H*-indene-2,2(6*H*)-dicarboxylate

Trienone **15** (29.5 mg, 0.1 mmol, 1 eq) in CH_2Cl_2 (1 mL), silica gel and 1 drops of conc. HCl were added, and then stirred at r.t. for overnight. The reaction was monitored by IR (peak at 1679 cm^{-1} of α,β-unsaturated ketone was disappeared). After filtration through Celite plug, the *endo* adduct was obtained in quantitative yield with exclusive *endo* isomer (29 mg, 0.1 mmol). Chiral GC (CP-Chirasil-Dex CB, H_2, 150 °C 5 min then heating 0.4 °C/min to 160 °C hold 35 min): t_R of *endo* product (min) = 43.64, 65.26; IR (Neat): ν_{max} 2924*m*, 1733*s*, 1713*s*, 1436*m*, 1358*w*, 1252*s*, 1195*m*, 1164*m*, 1110*m* cm^{-1}; MS: *m/z* (%) relative intensity 294.2 (M^+); ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (d, *J* = 9.8 Hz, 1H, C*H*=CH), 5.57 (dt, *J* = 9.8, 3.2 Hz, 1H, CH=C*H*), 3.74 (s, 3H, CO_2CH_3), 3.71 (s, 3H, CO_2CH_3), 2.88–2.74 (m, 3H, C*H*CH=CH and CH*H*CCH*H*), 2.49 (dd, *J* = 12.6, 6.3 Hz, 1H, C*H*CO), 2.15 (s, 3H, $COCH_3$), 2.02 (m, 1H, C*H*HCH=CH), 1.89–1.66 (m, 3H, C*H*HCC*H*H and C*H*CHCOCH_3), 0.85 (d, *J* = 7.0 Hz, 3H, $CHCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2 (CO), 173.4 (CO), 172.9 (CO), 133.1 (CH), 127.2 (CH), 58.6 (C), 56.8 (CH), 52.81 (CH_3), 52.78 (CH_3), 44.0 (CH), 38.9 (CH), 38.0 (CH_2), 37.4 (CH_2), 32.8 (CH), 29.13 (CH_3), 17.10 (CH_3); HSMS (ESI-TOF) calcd for $C_{16}H_{22}O_5$; 294.1467 found: 294.1467.

Following IMDA reaction of triene 10 with ReactIR™



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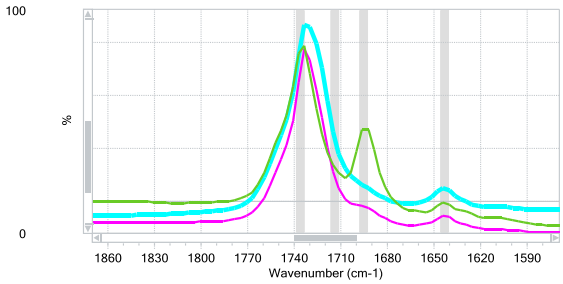

At the start of reaction, there are 2 peaks at ν = 1731 and 1693 cm^{-1} in the IR spectrum corresponding to the ester and aldehyde groups, respectively (green spectrum). After 4 h, the aldehyde peak of triene **10** disappeared and only one peak of aldehyde of adduct **18** was seen at ν = 1731 cm^{-1} as shown in the pink (after 4 h) and blue spectra (after 19 h). The peak at 1647 cm^{-1} corresponds to the acetone complex **1b** indicating catalyst recovery.

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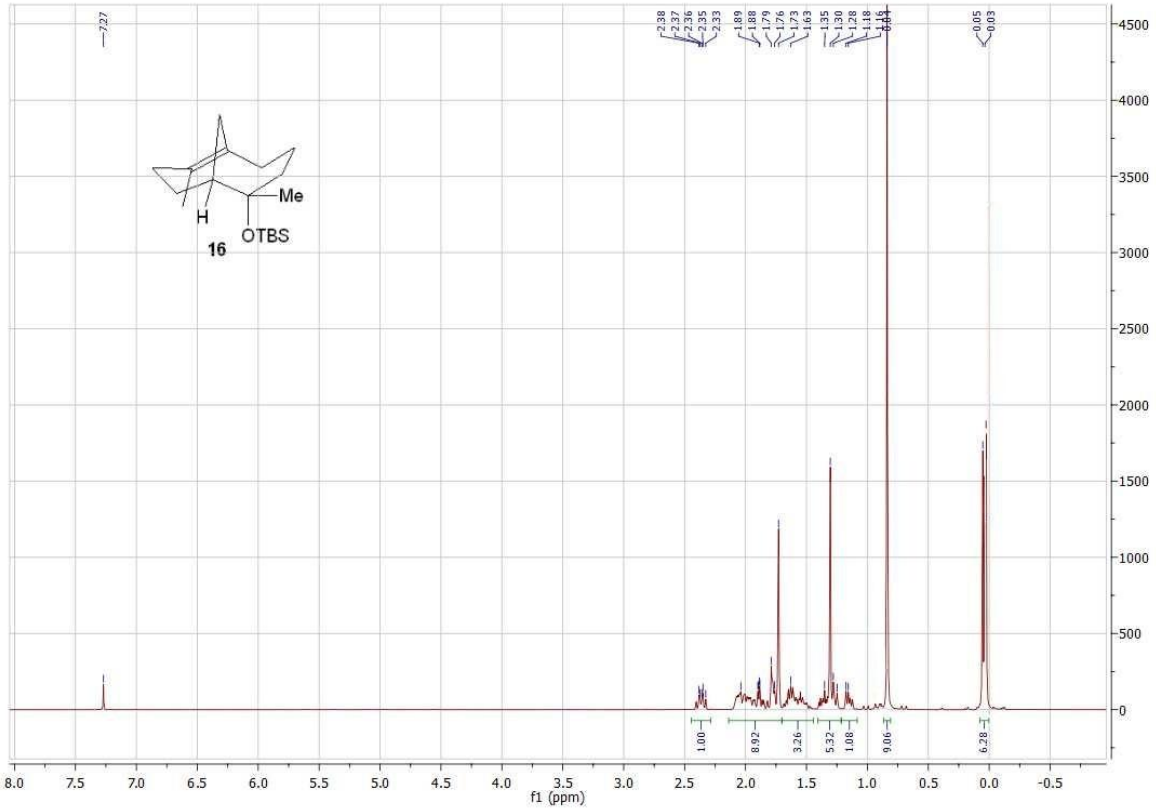
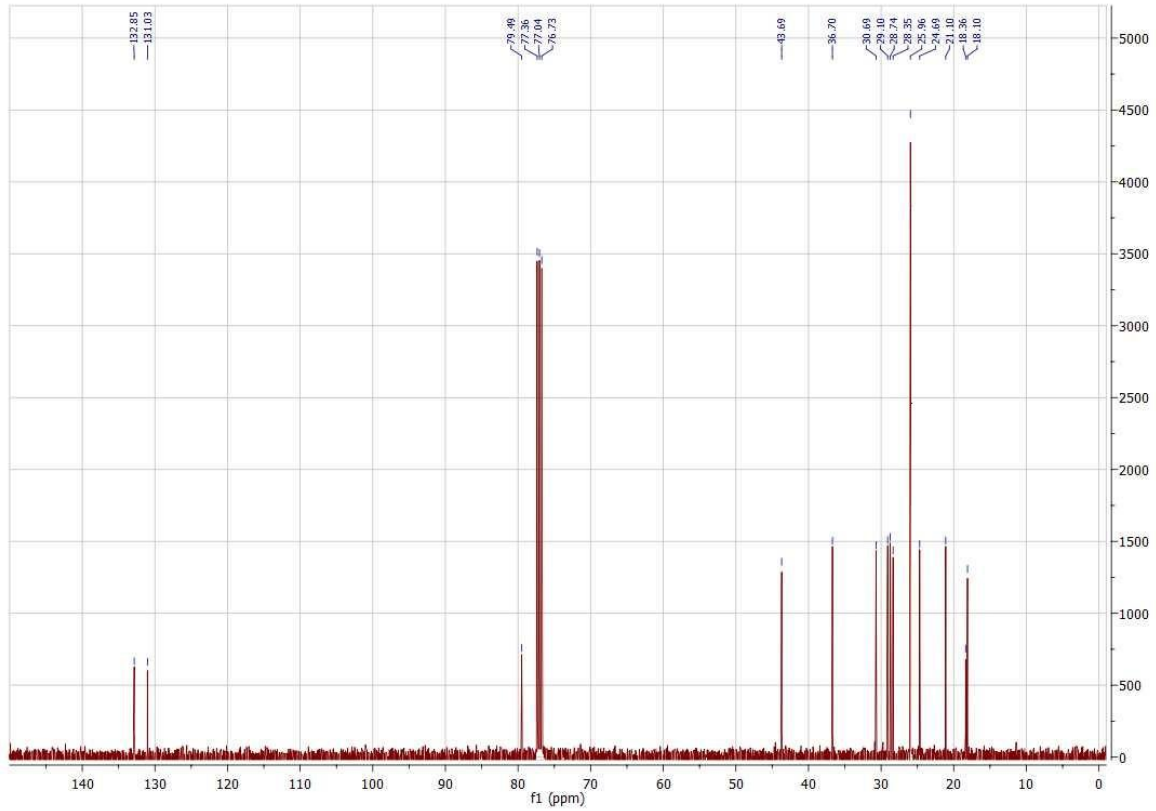
NMR Spectra





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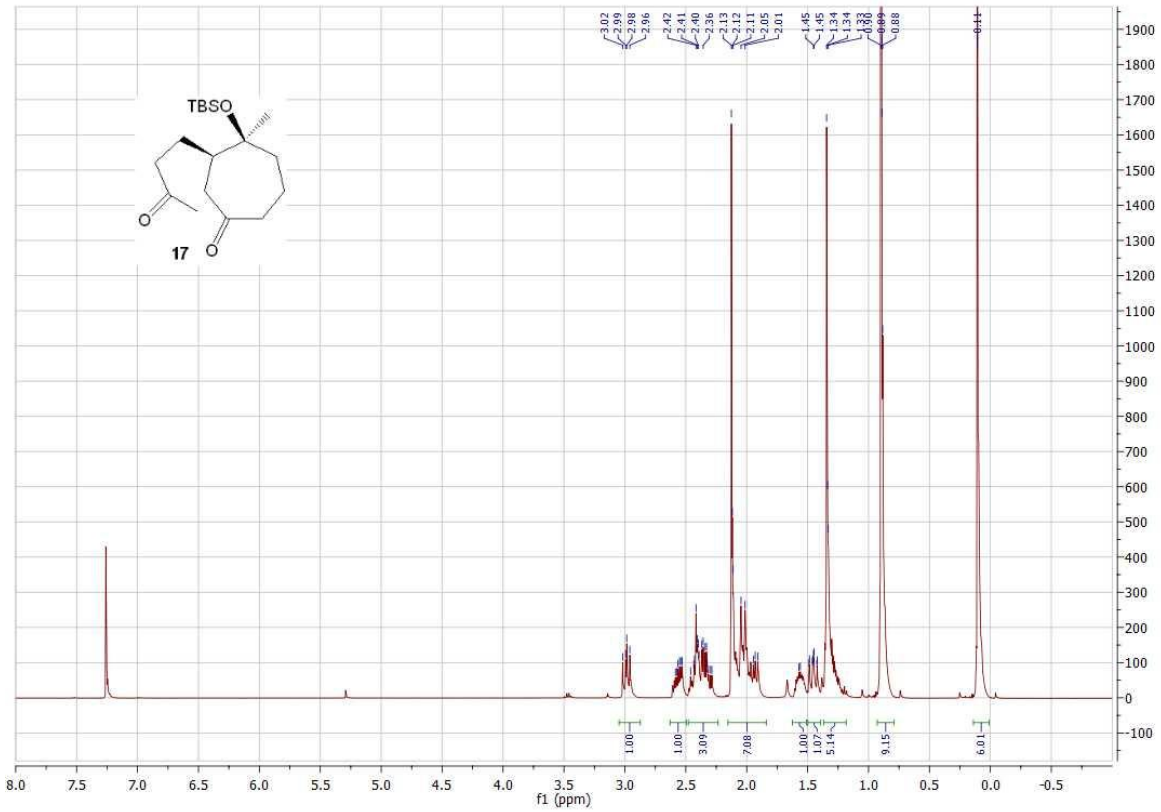

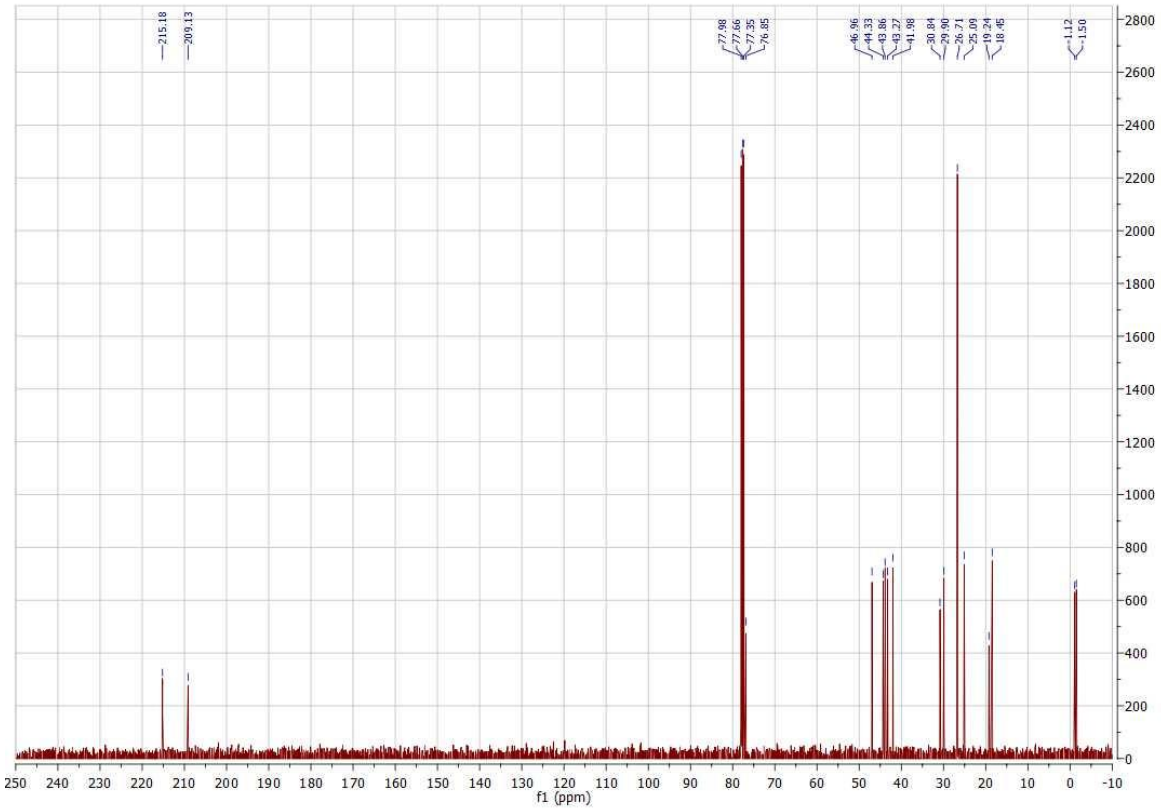

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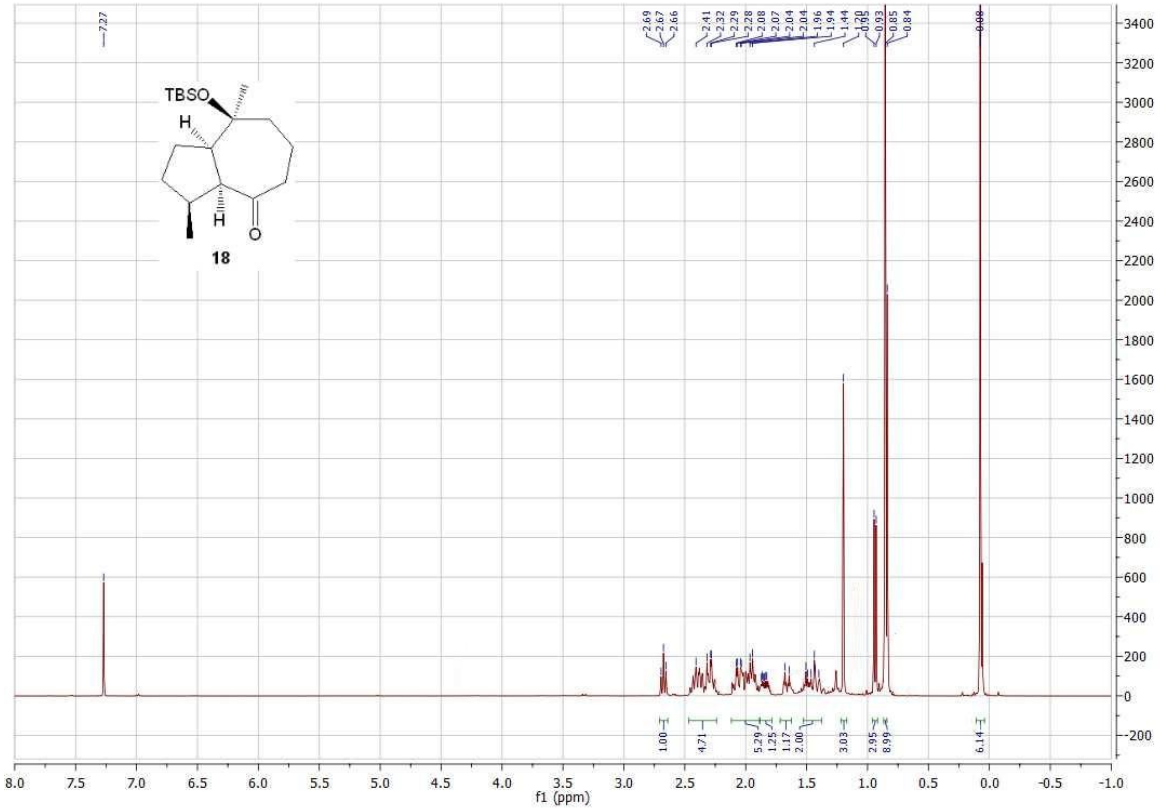

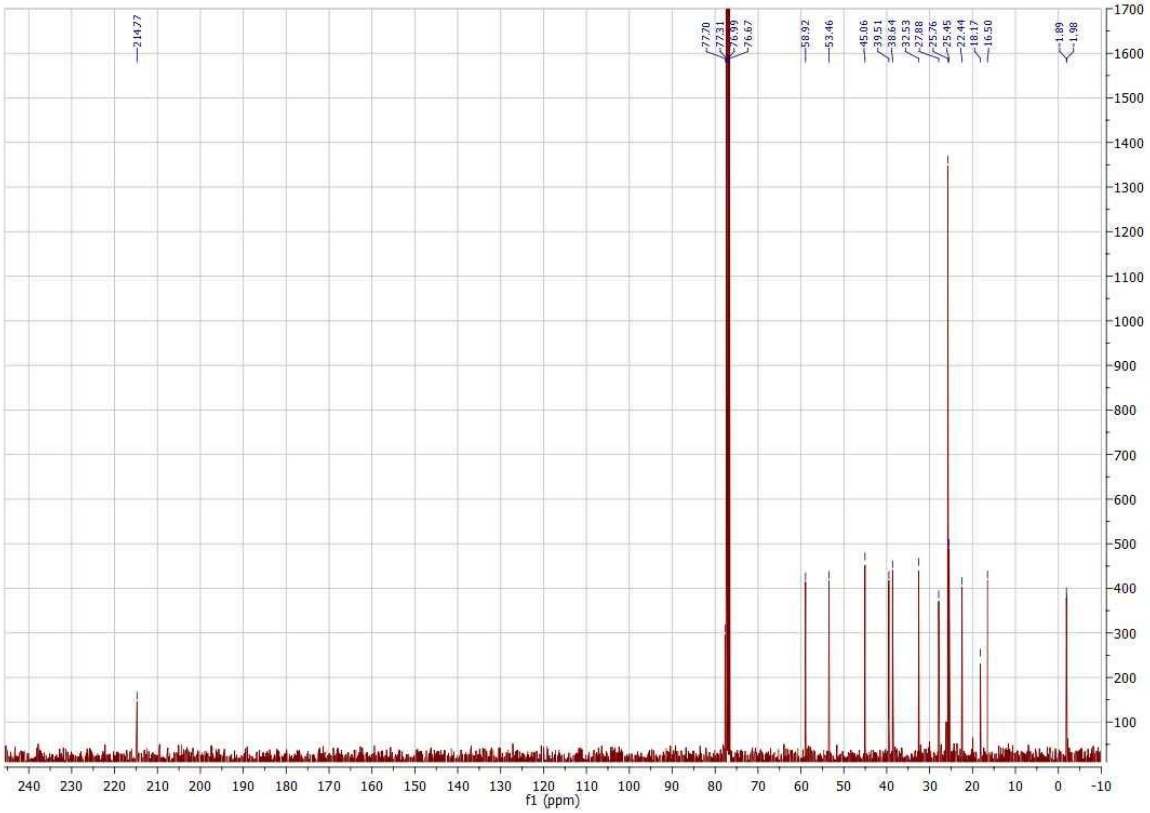

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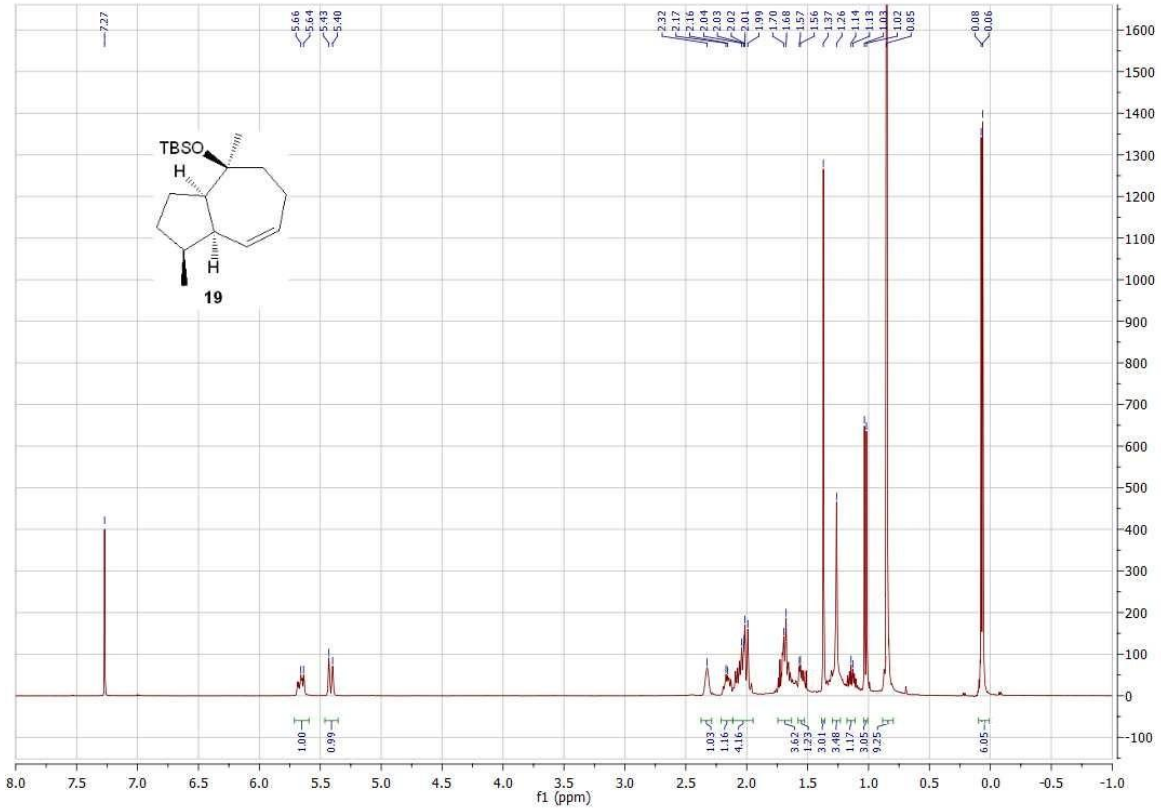

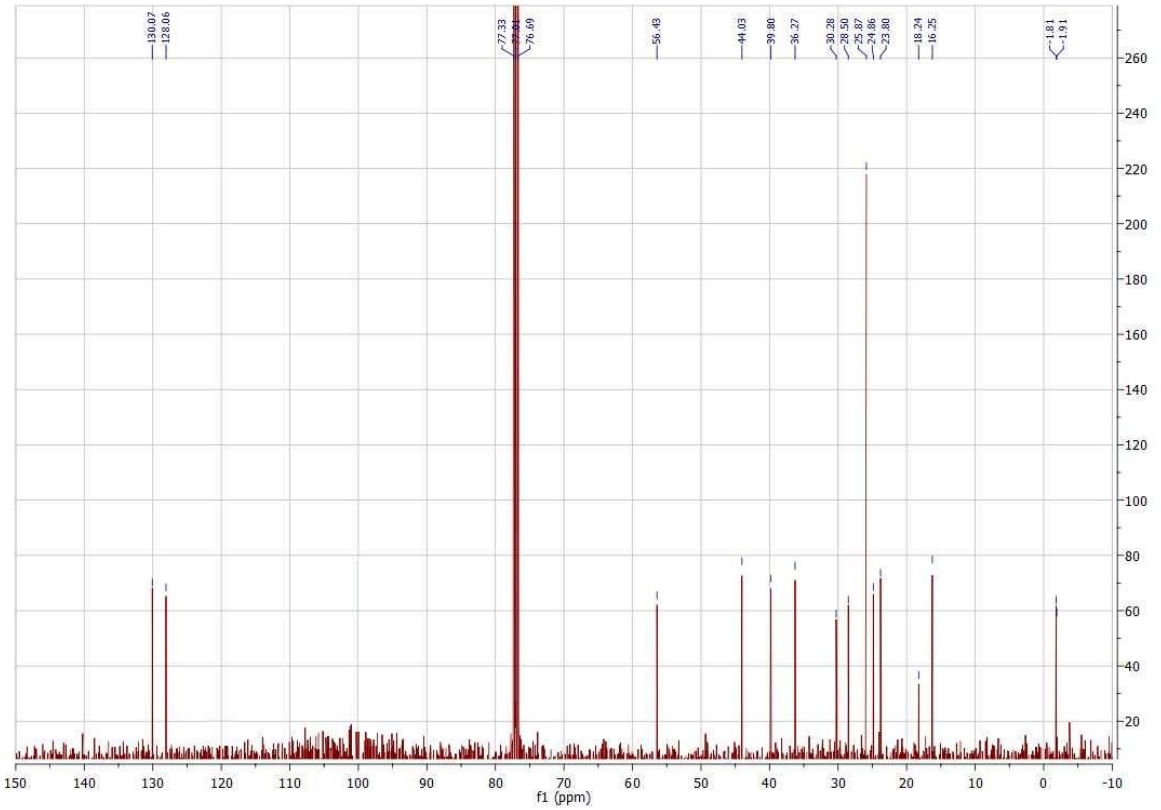

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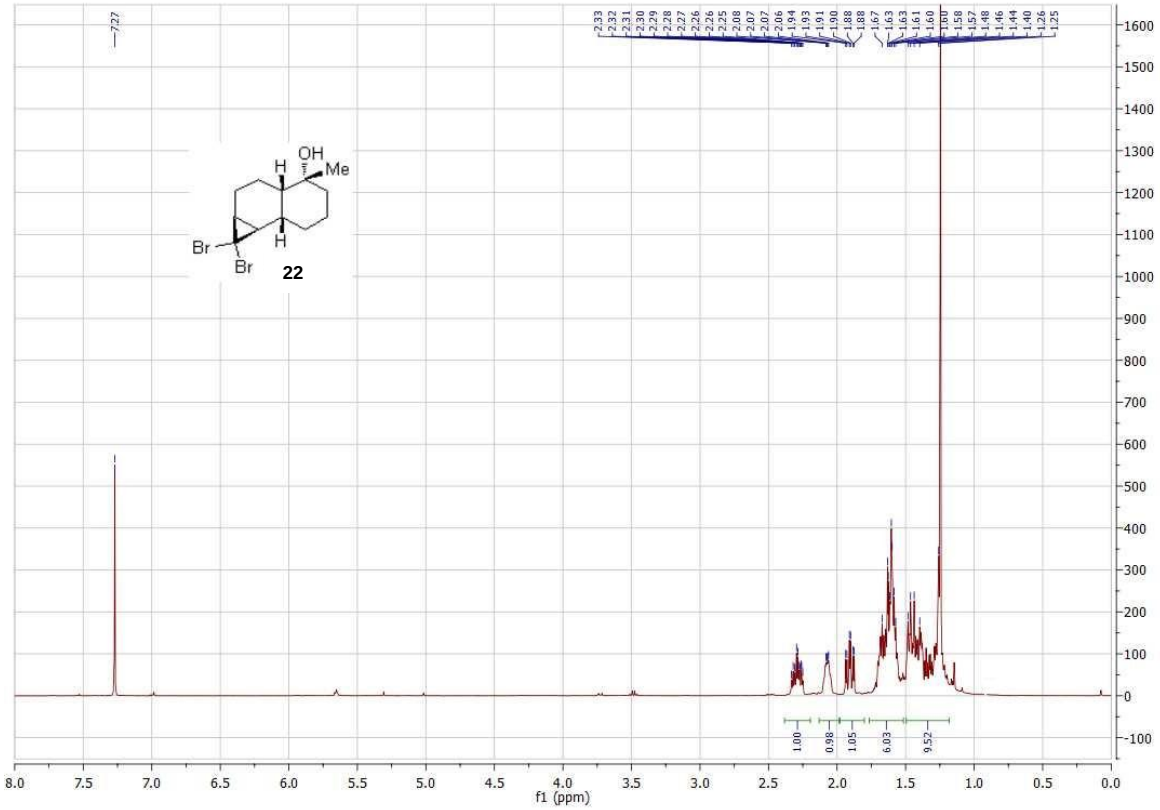

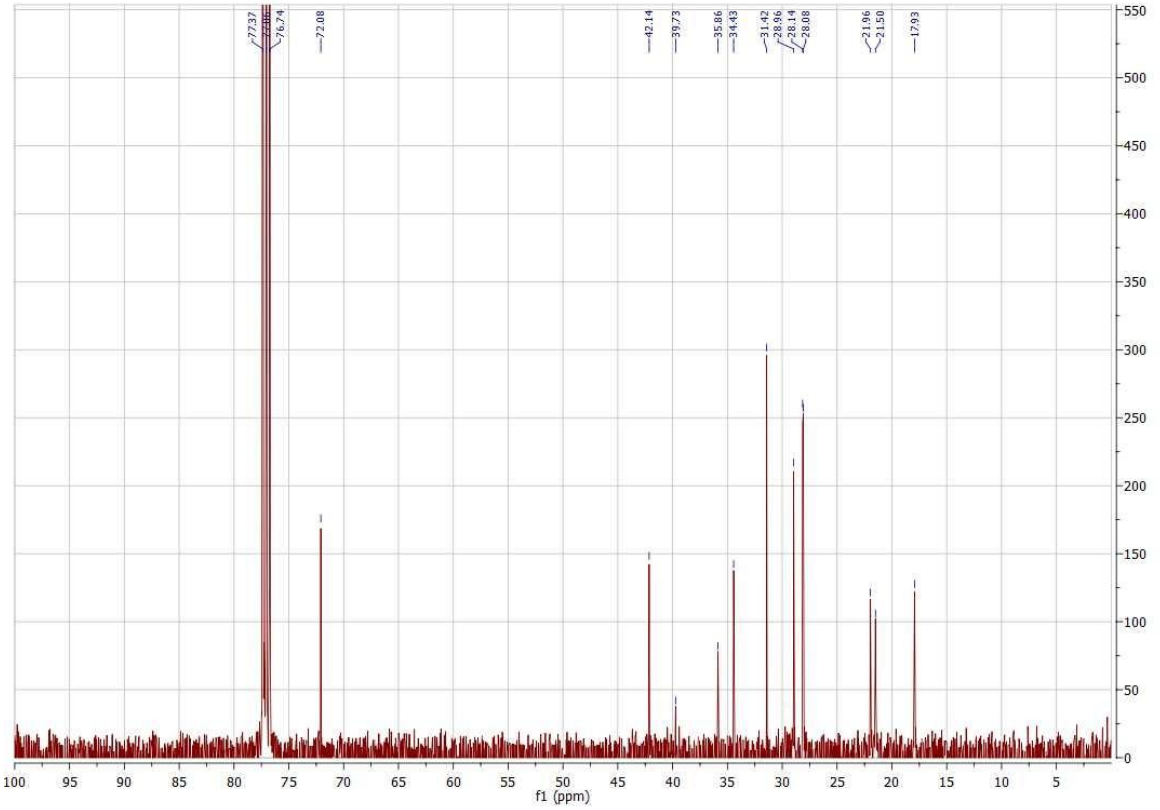

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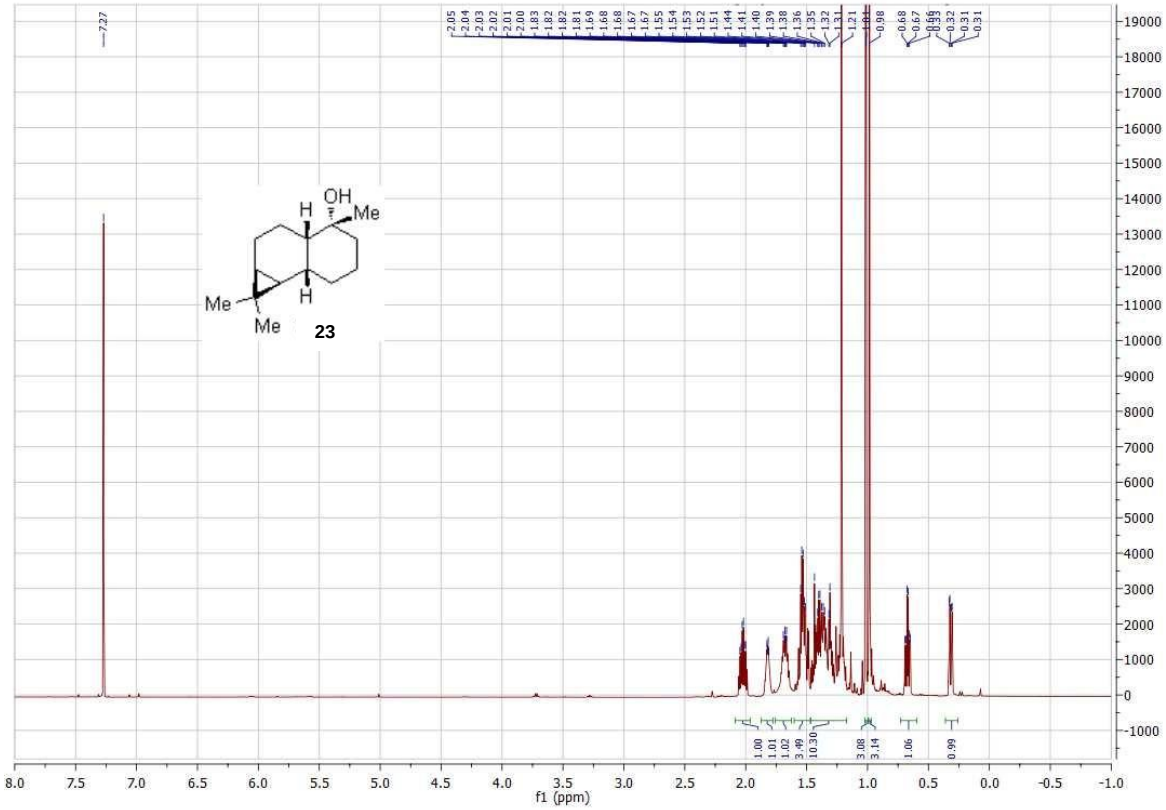

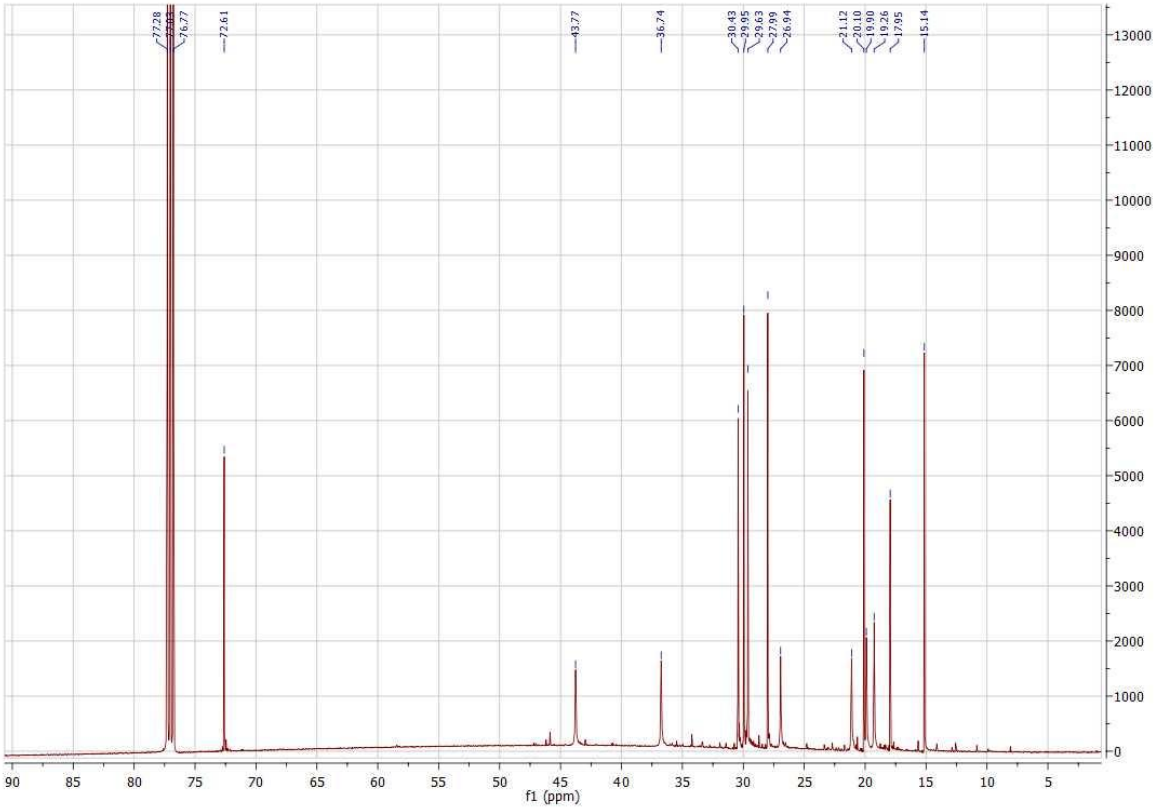

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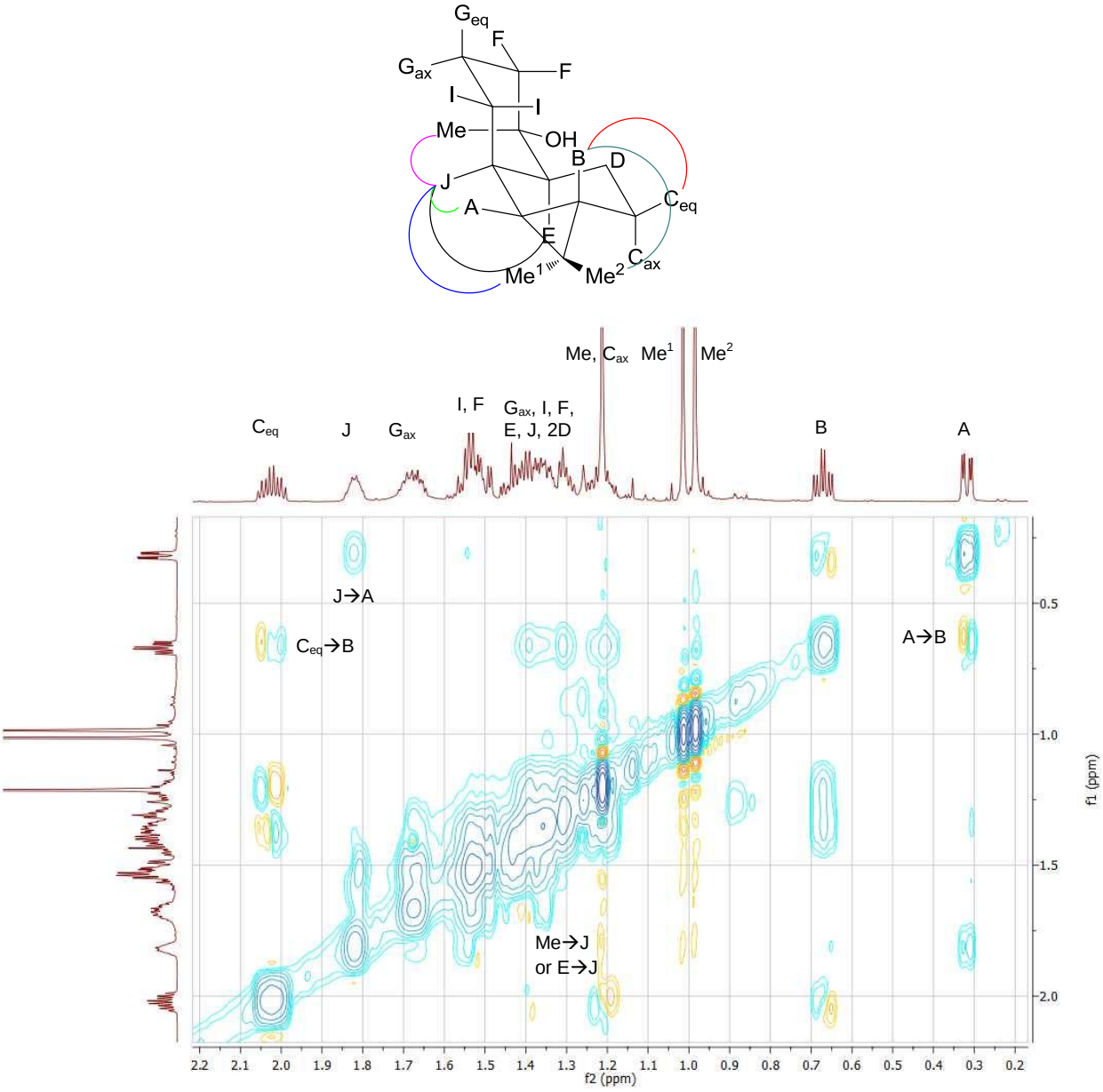

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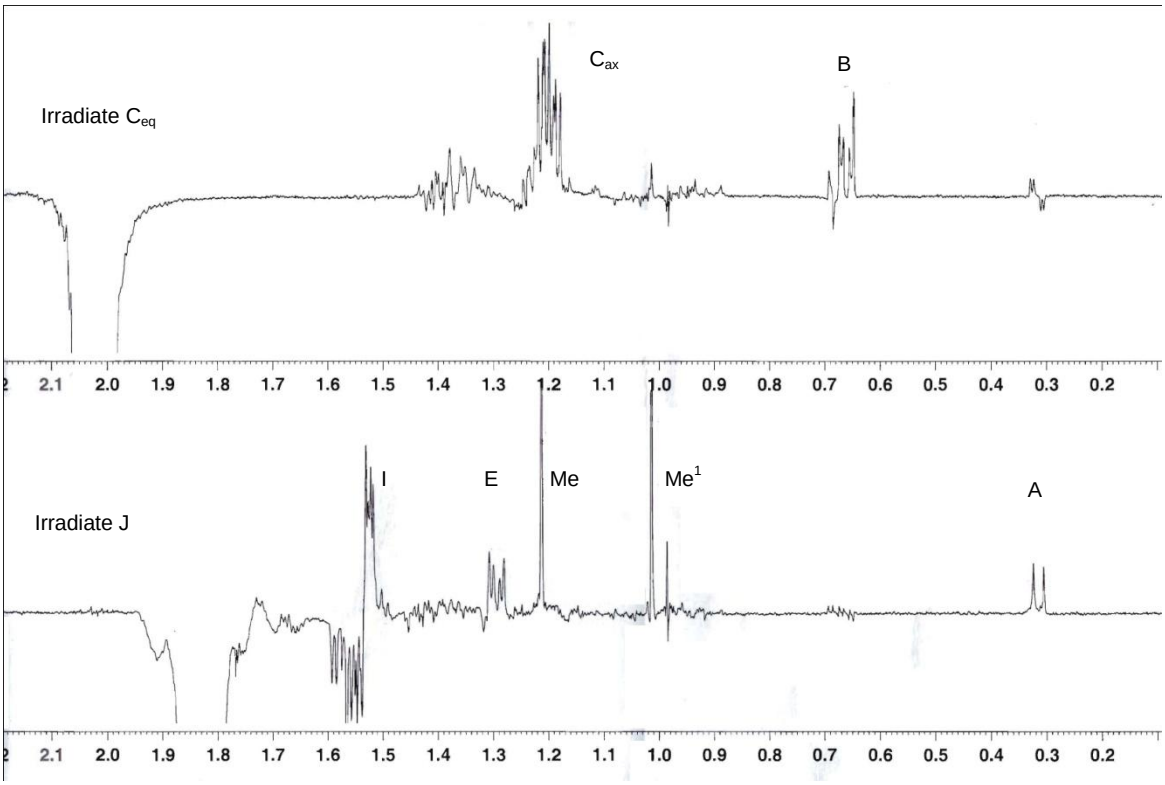

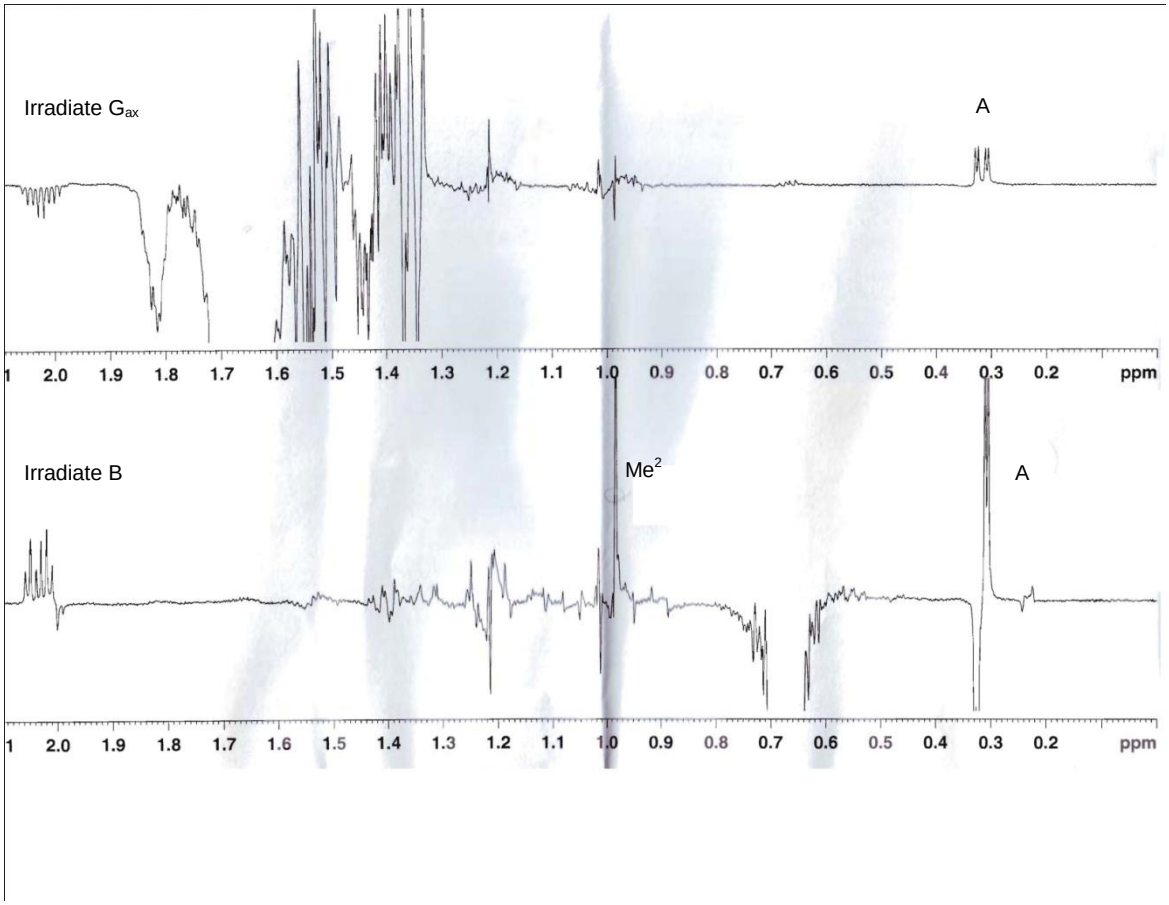

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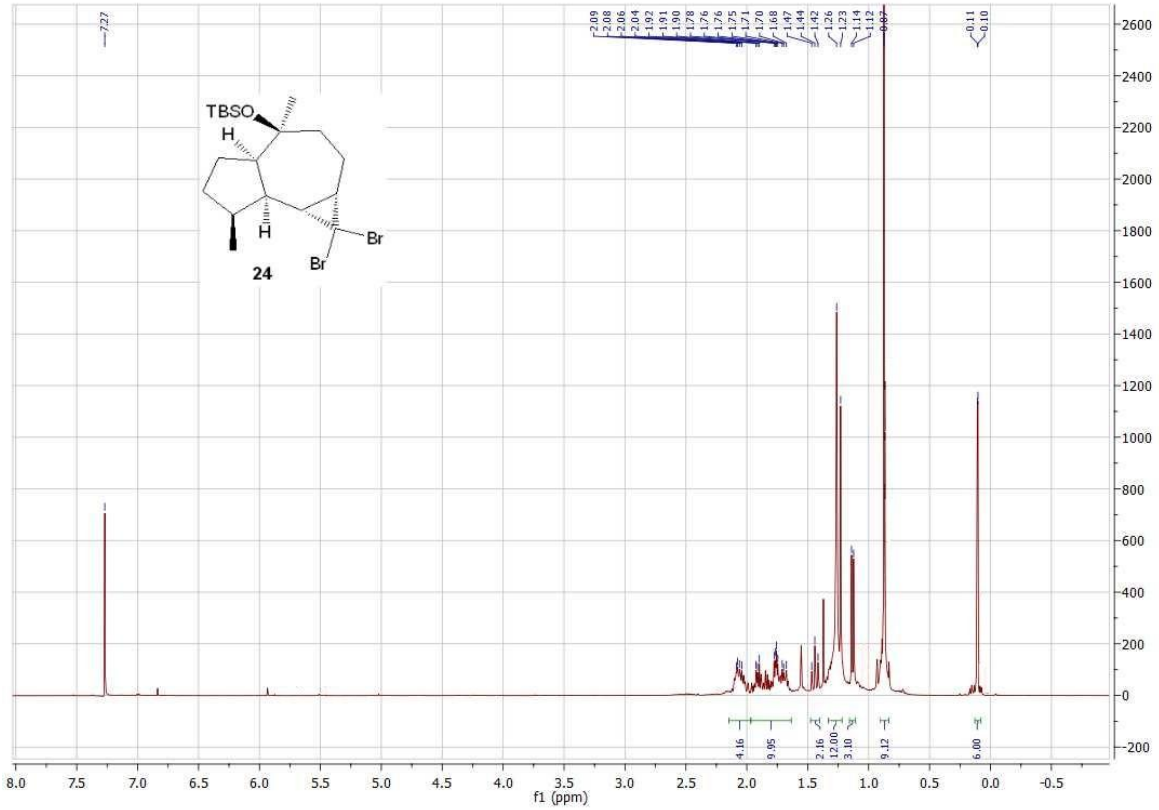

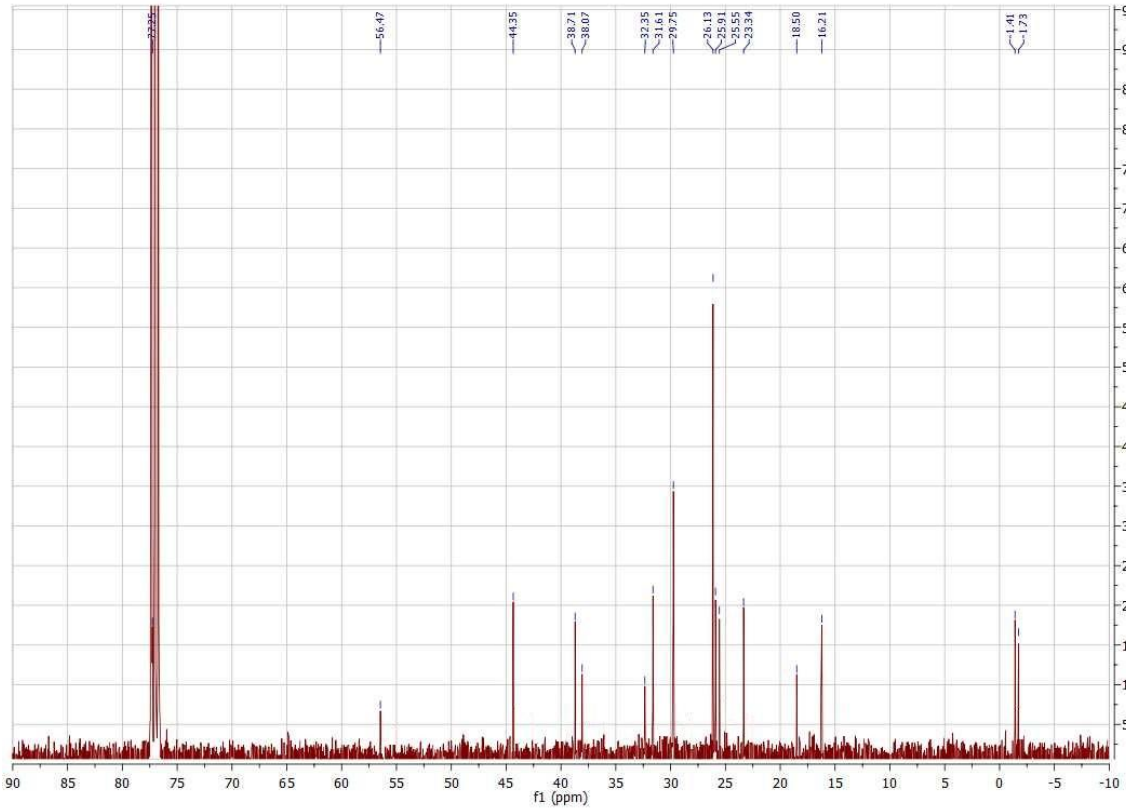

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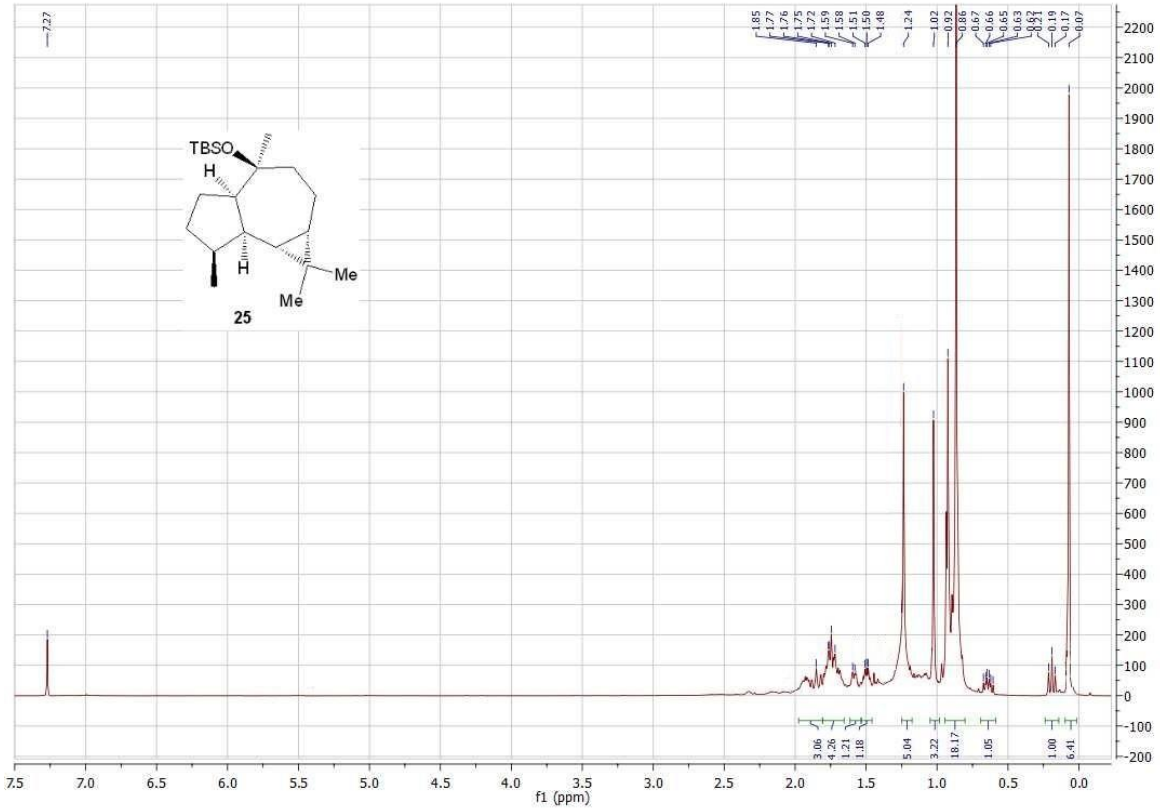

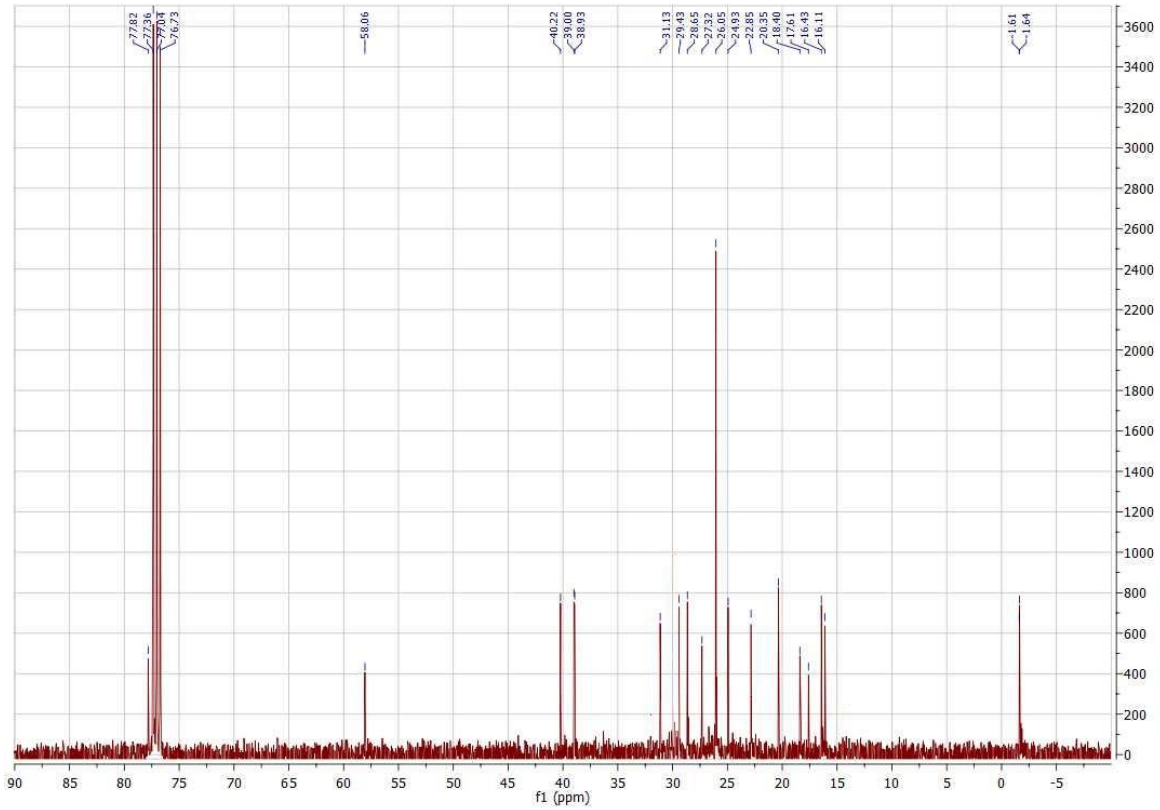

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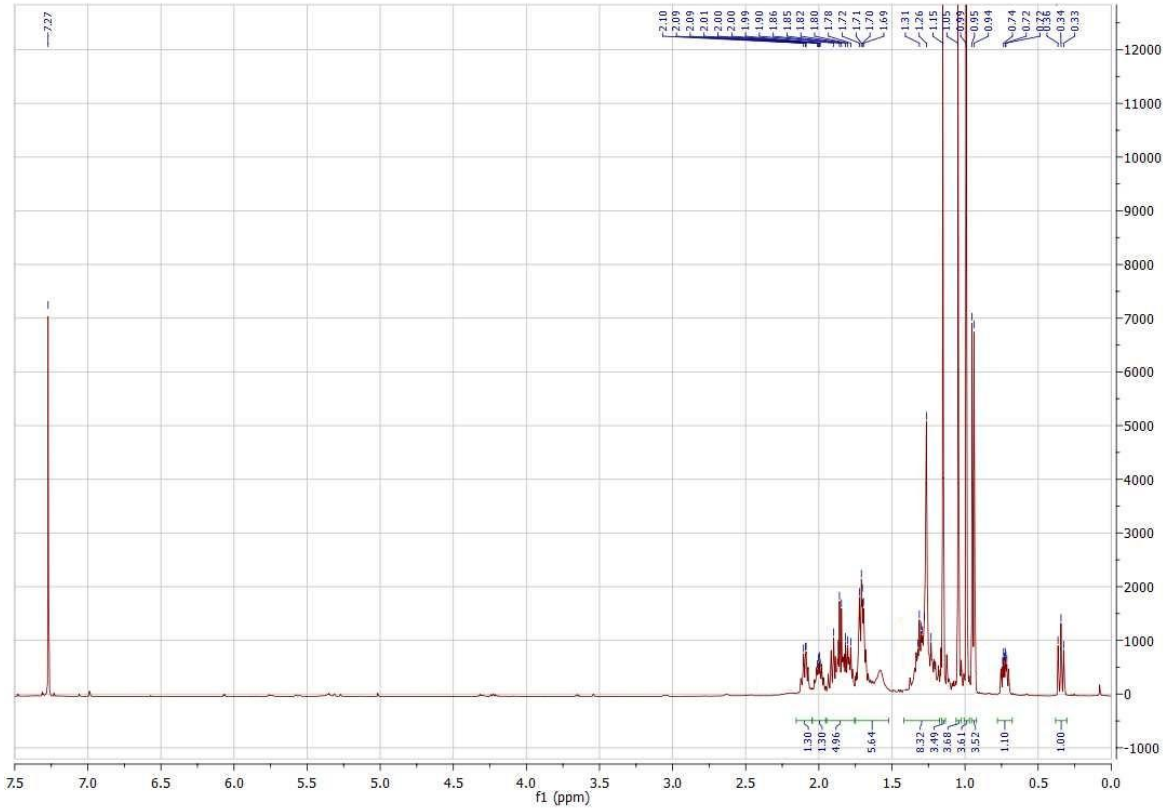

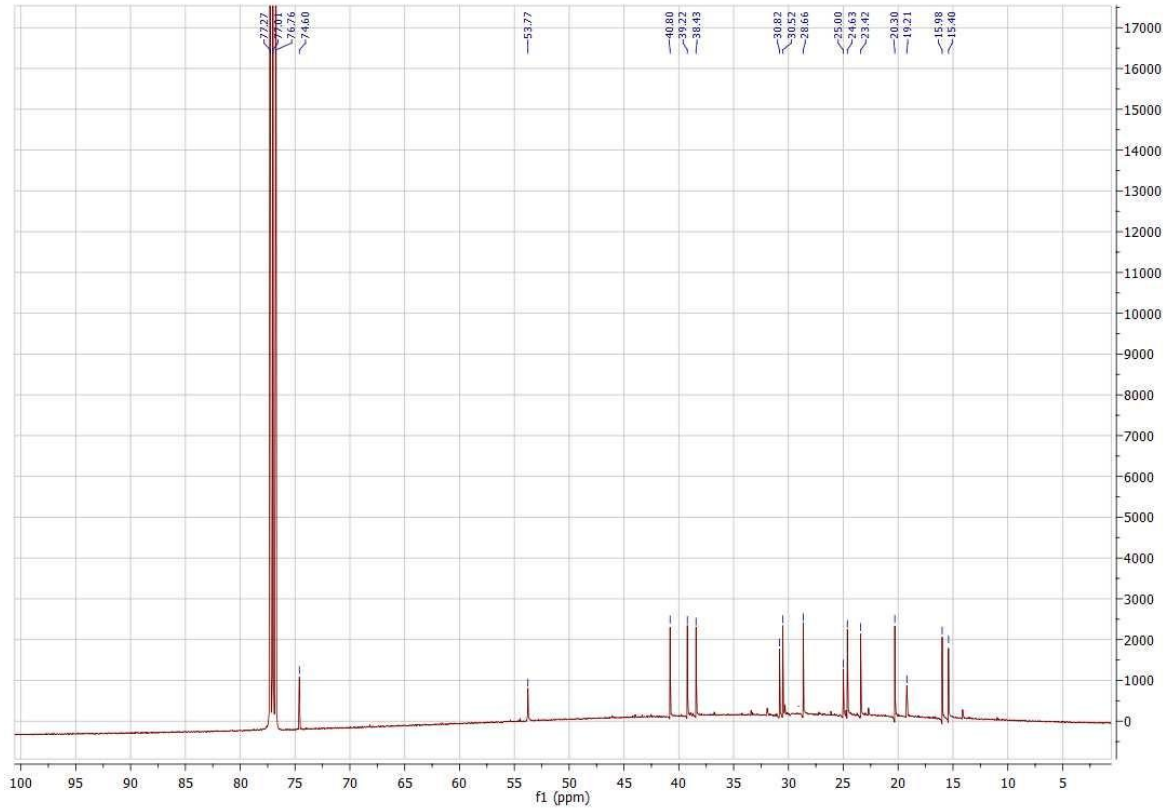

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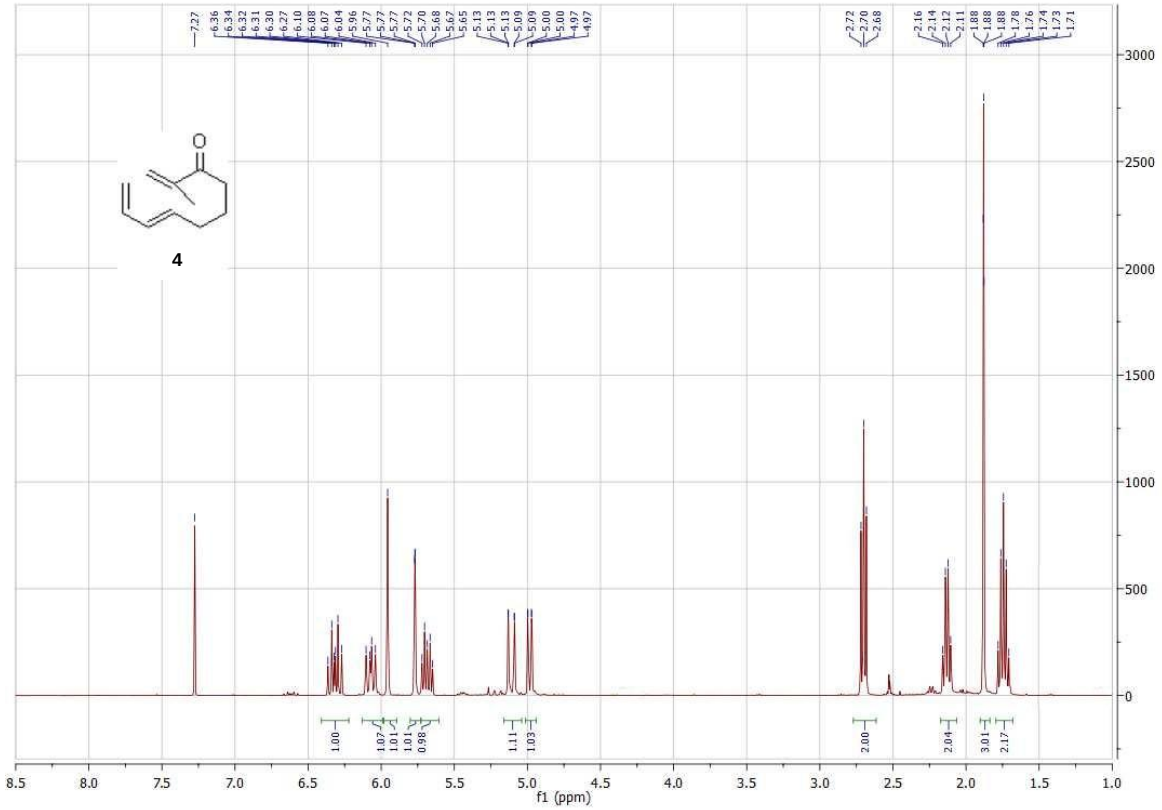

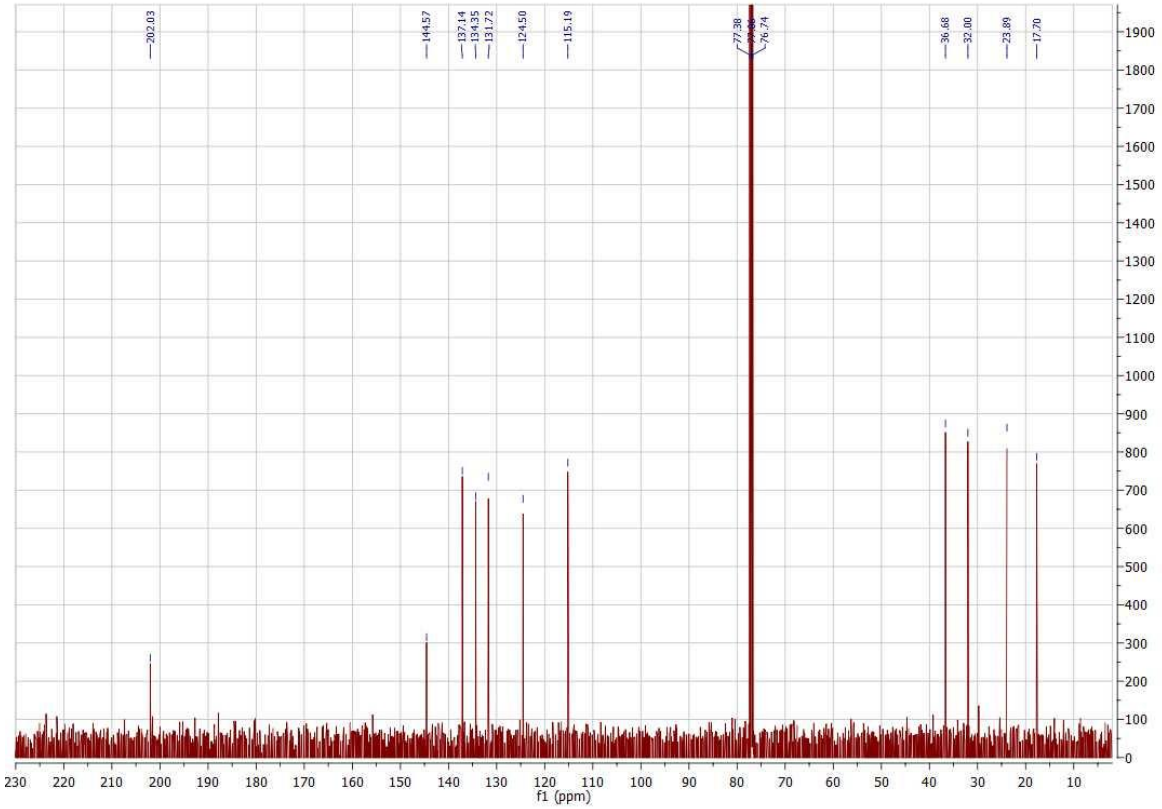

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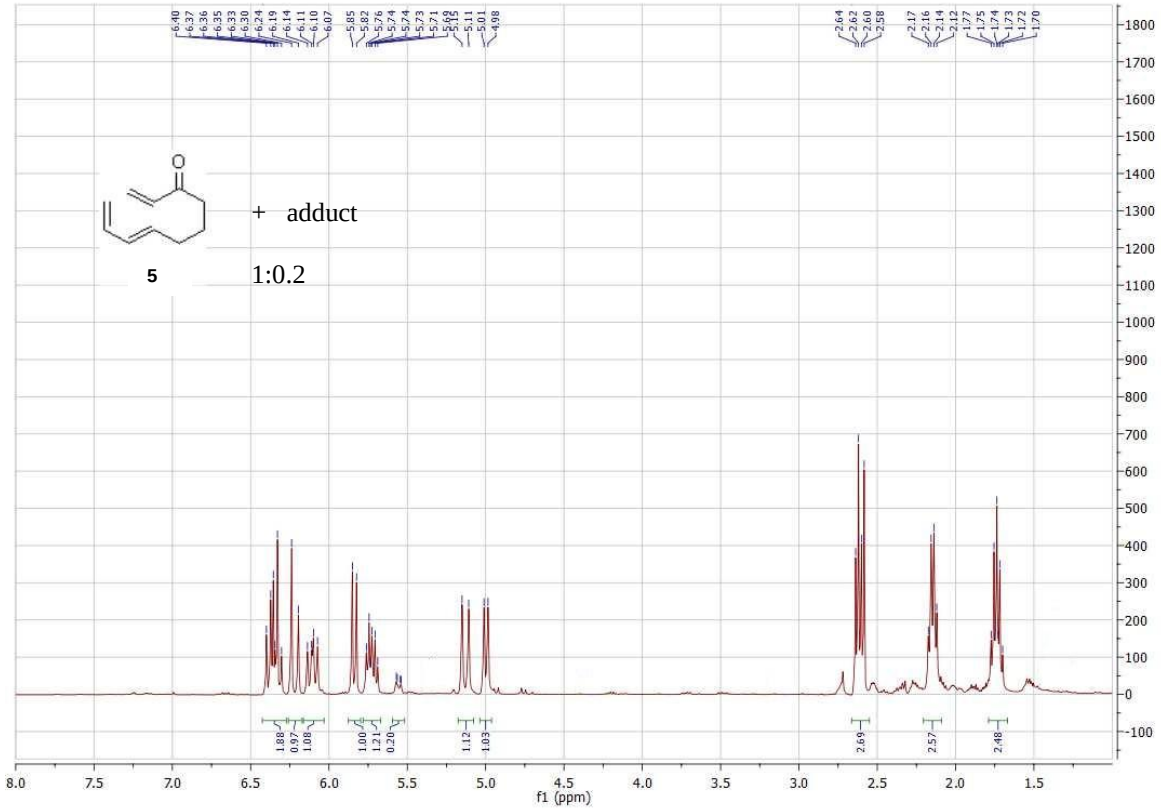

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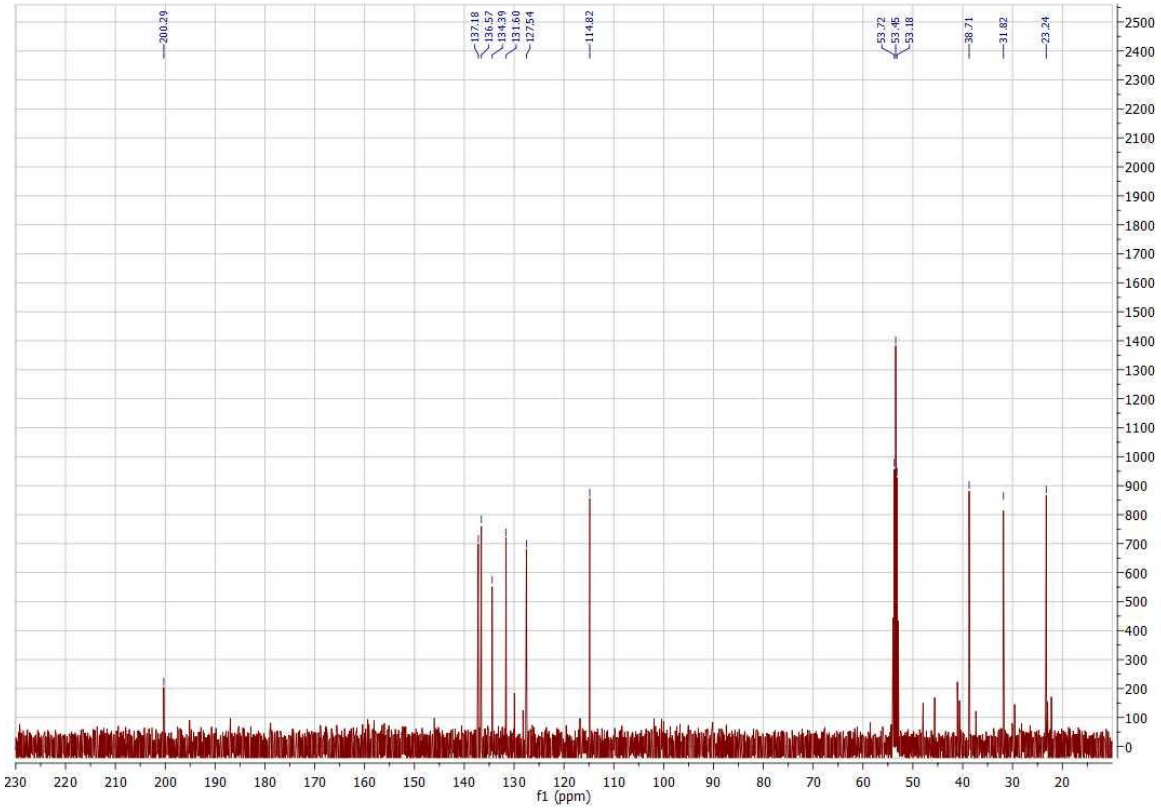

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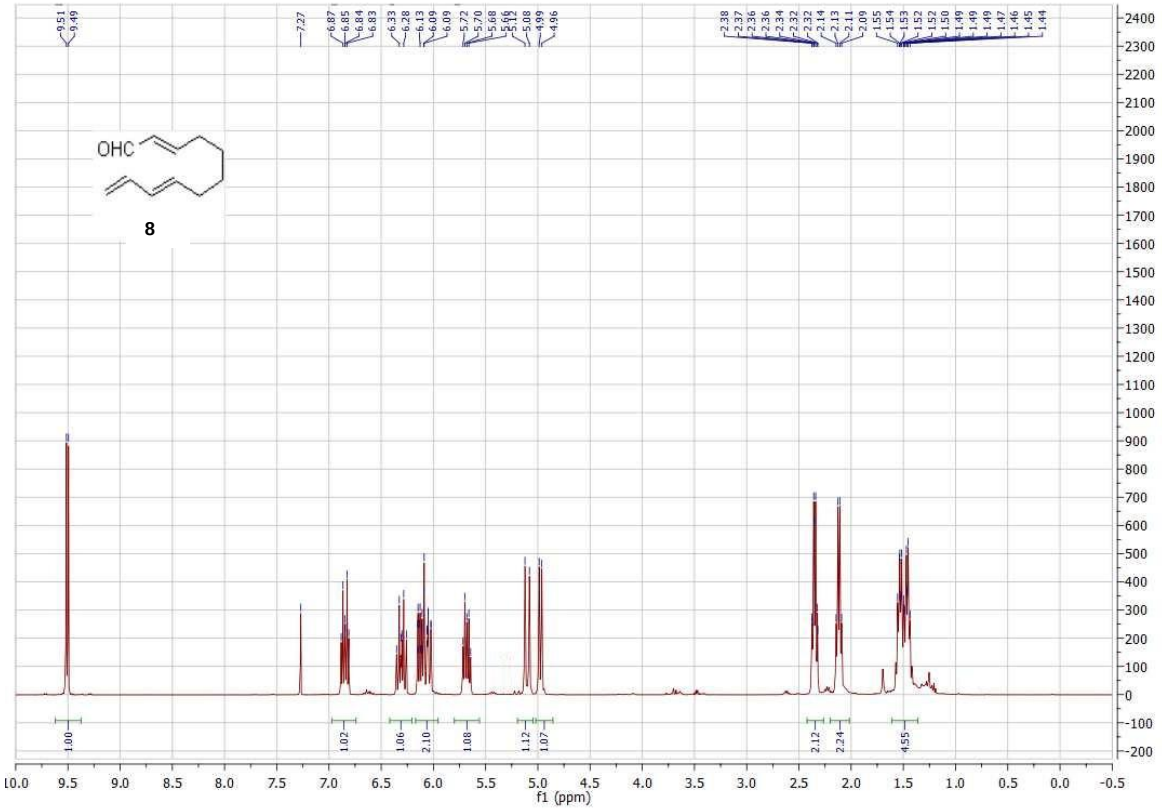

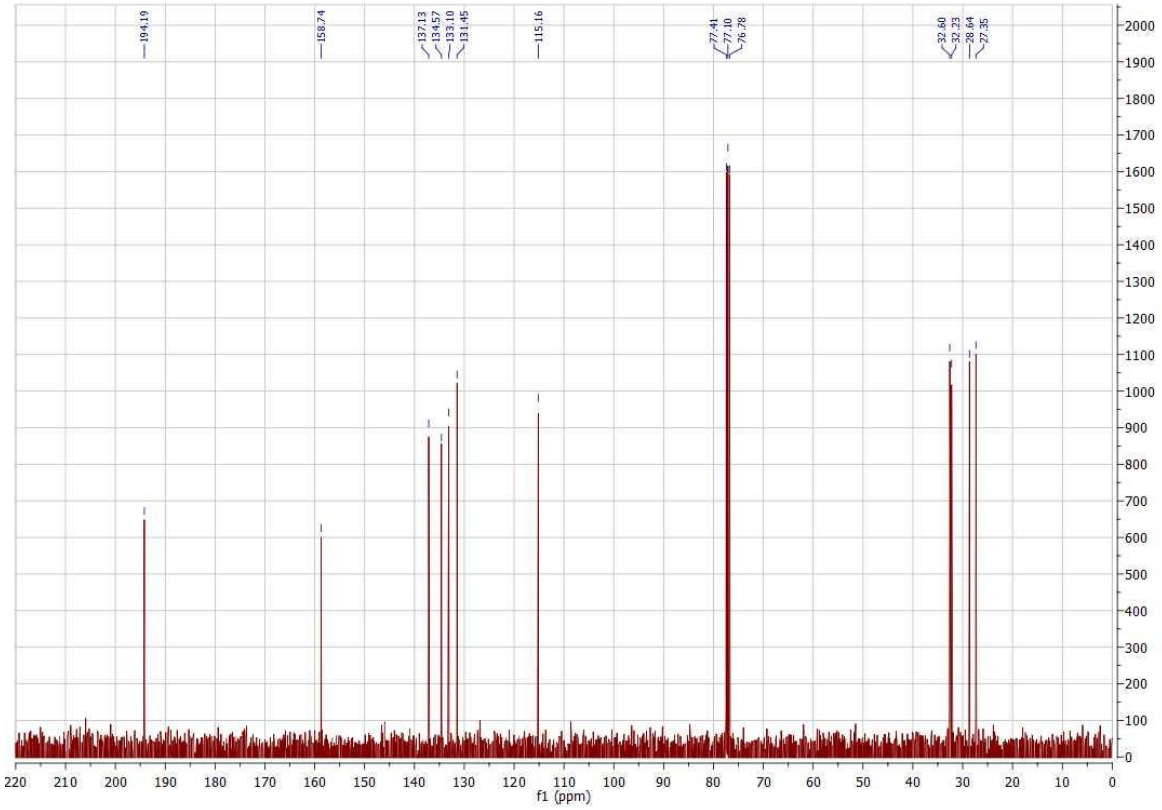

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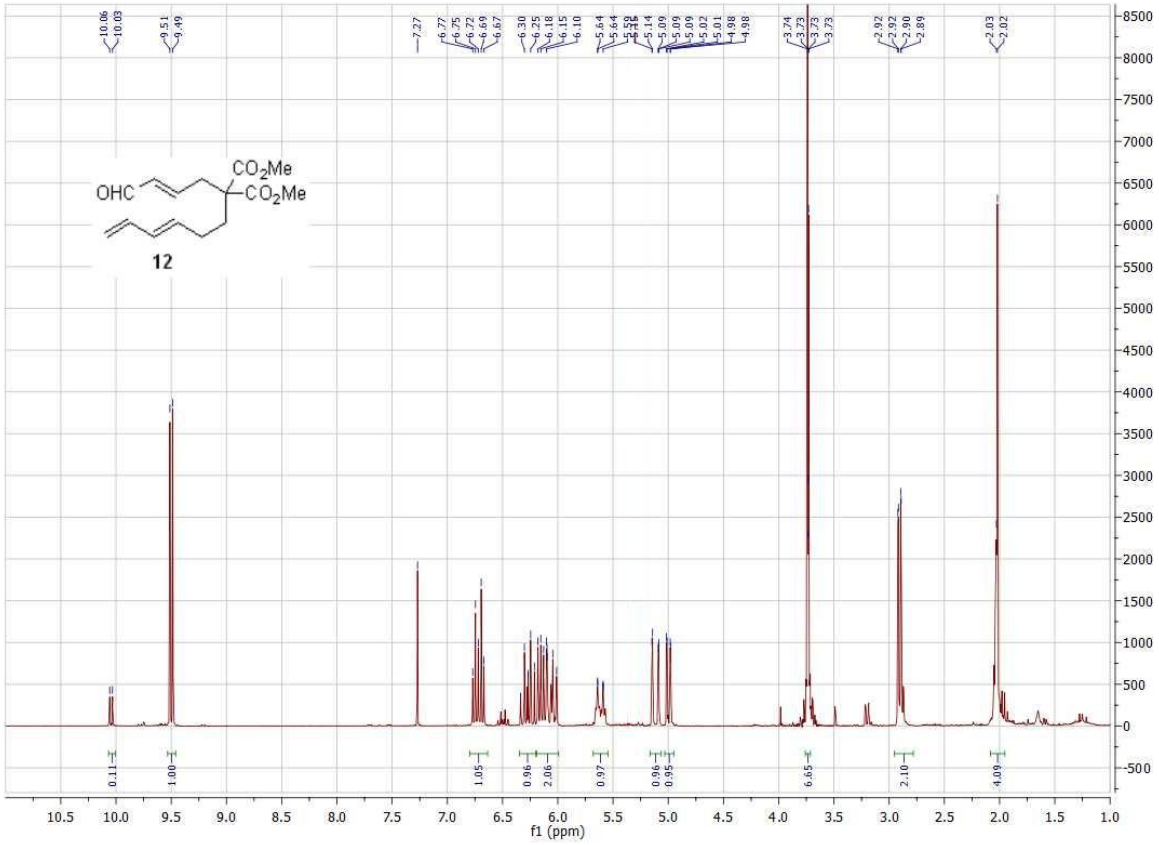

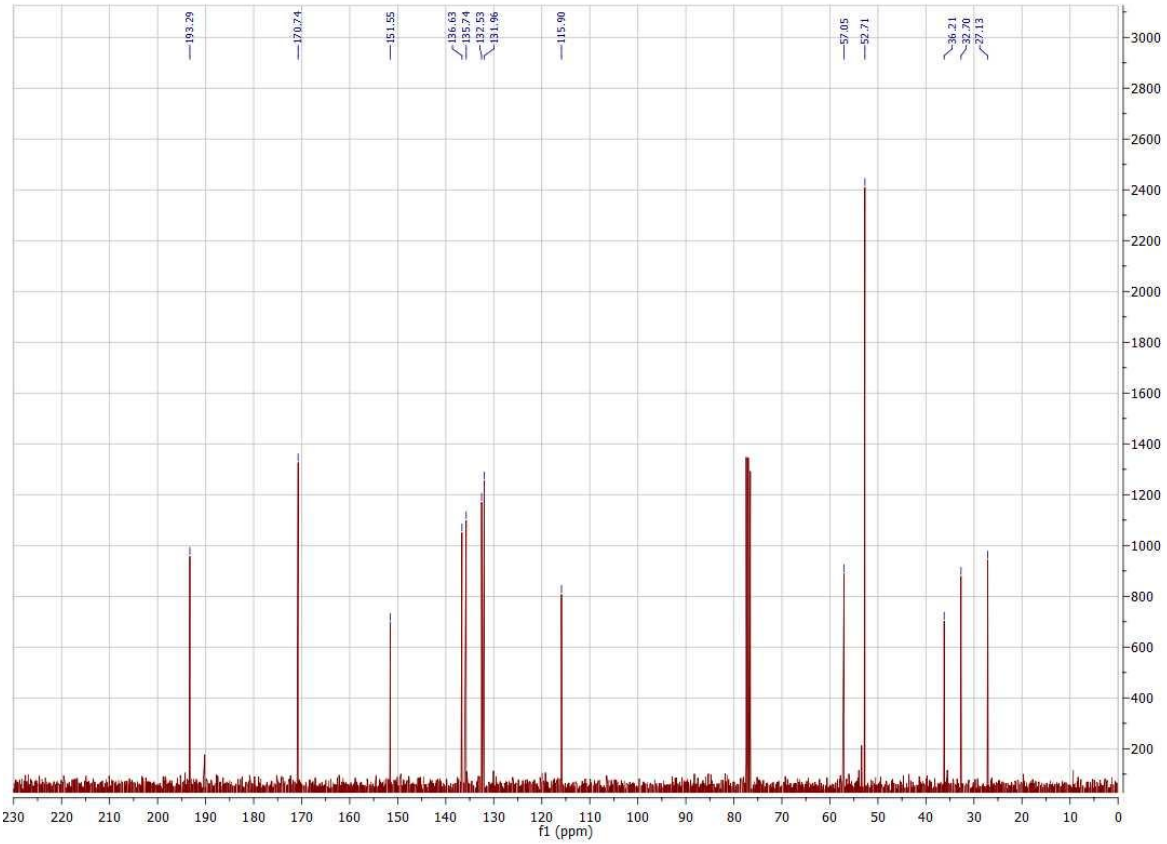

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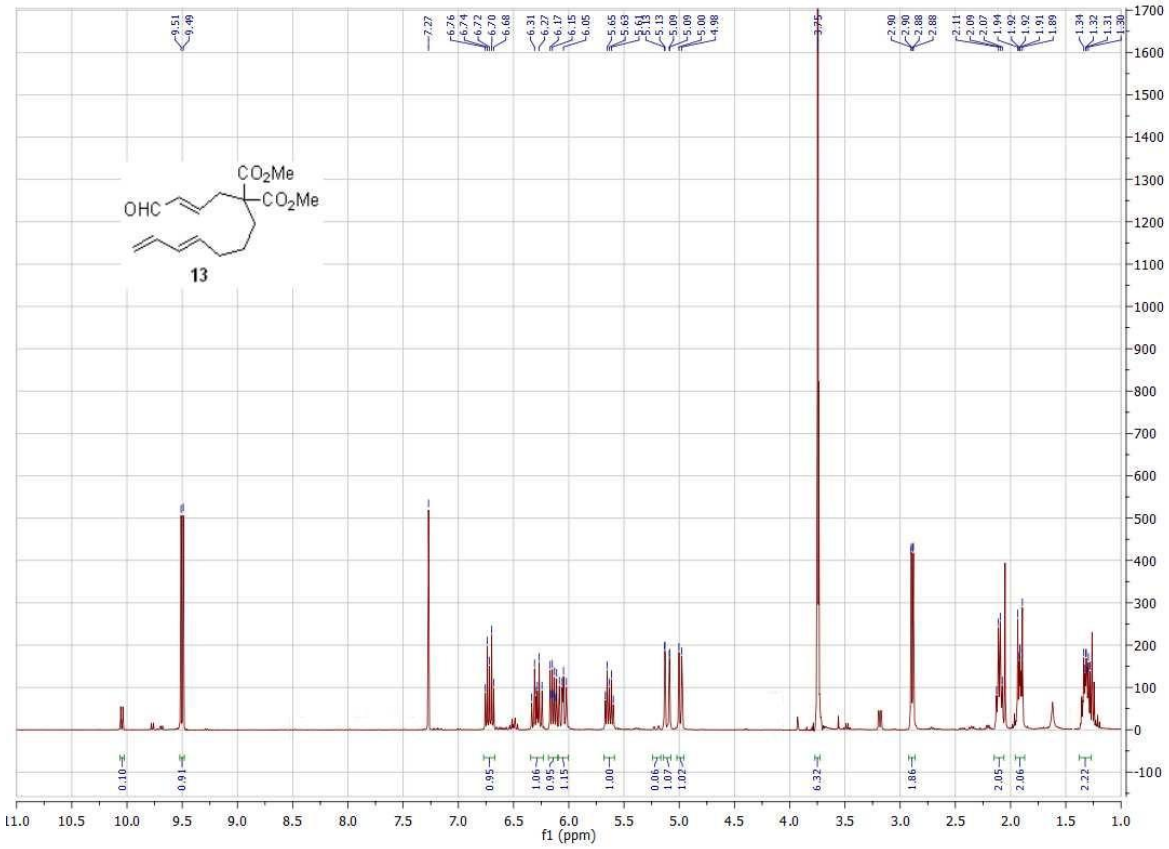

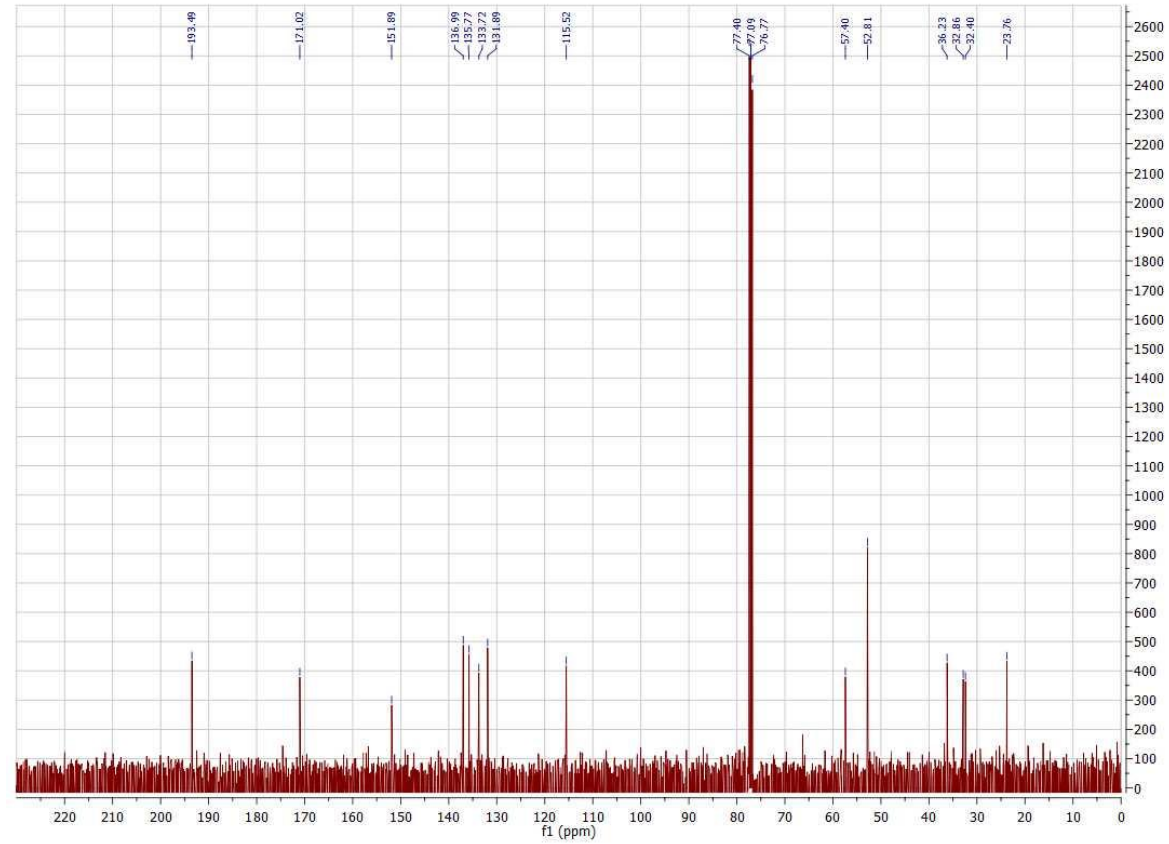

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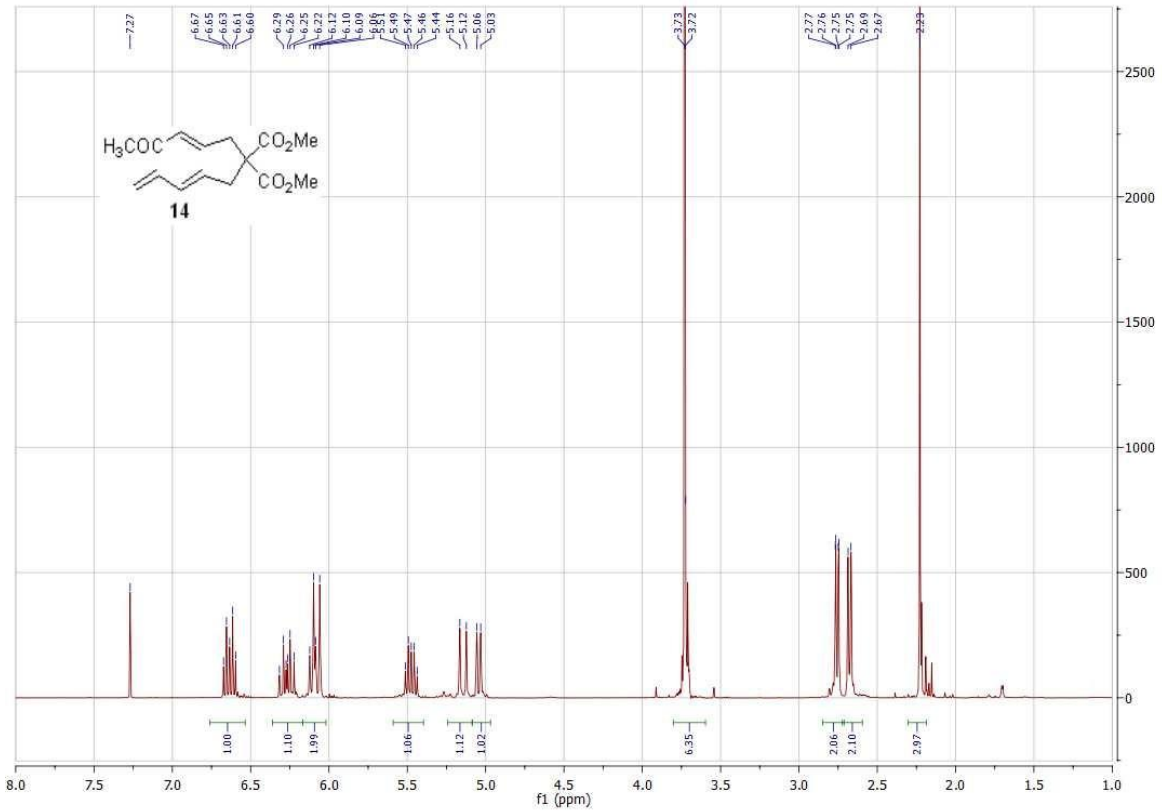

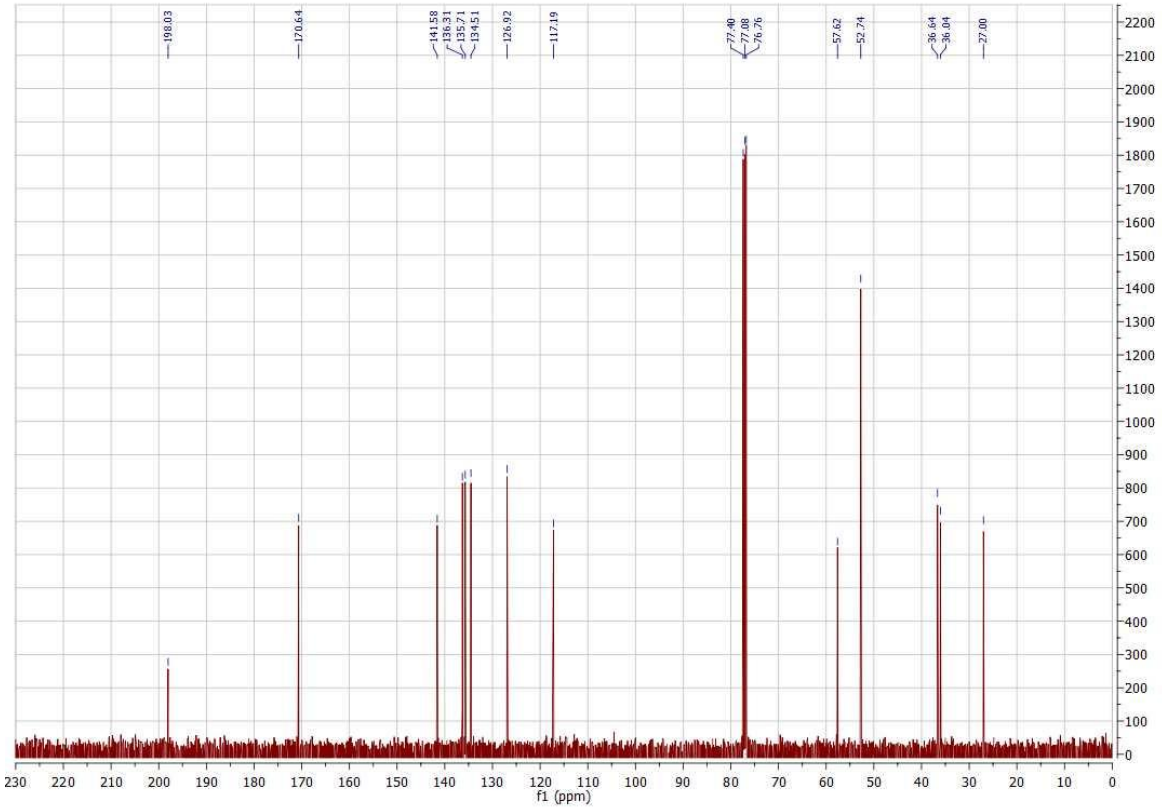

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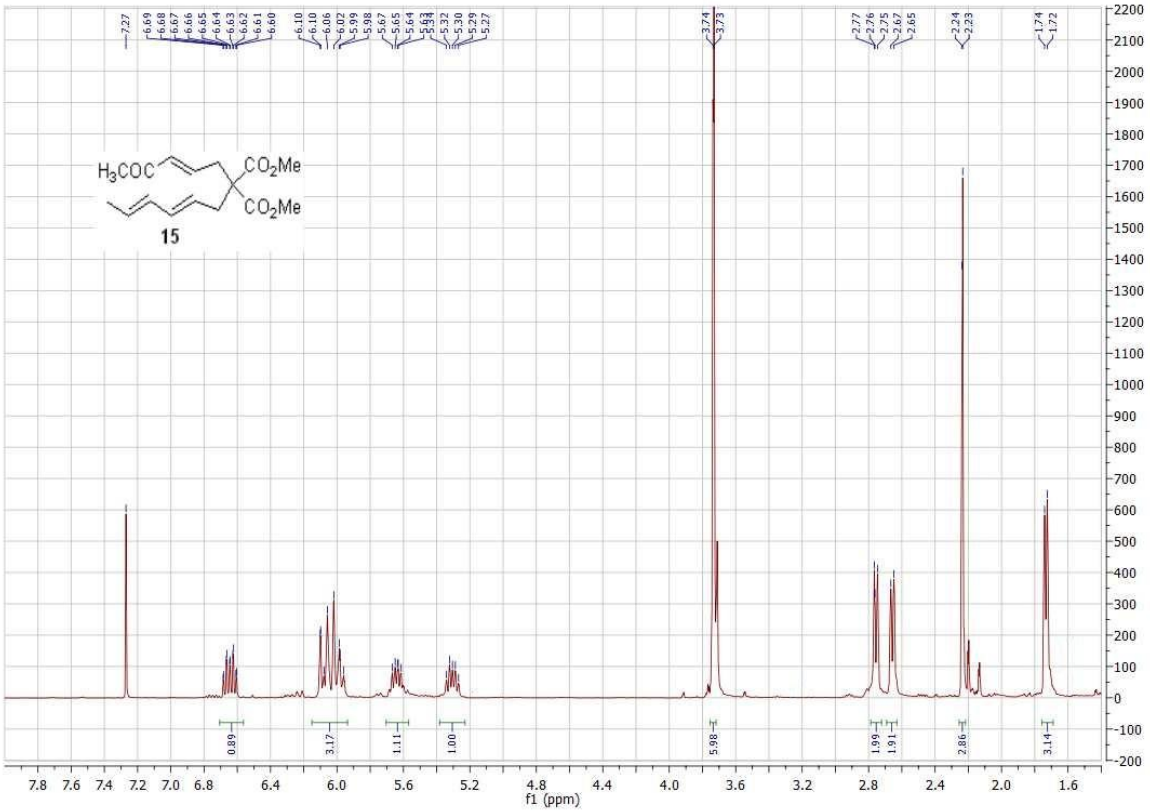

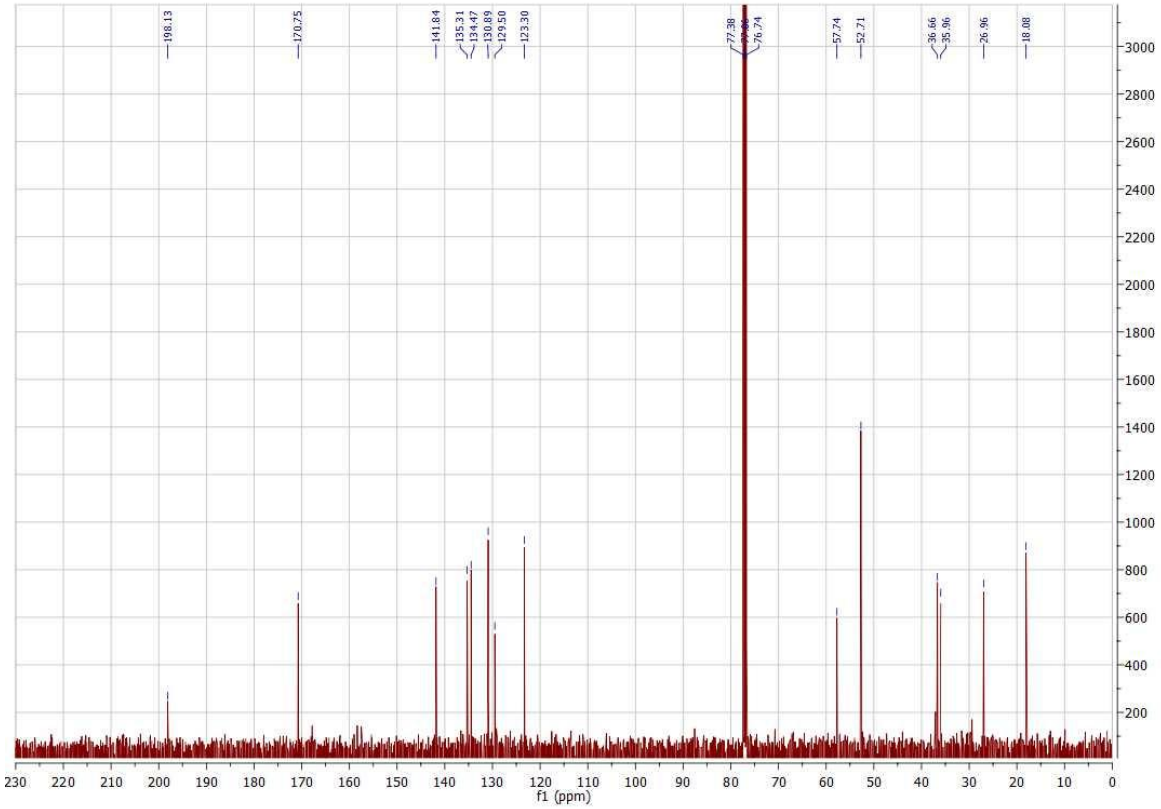

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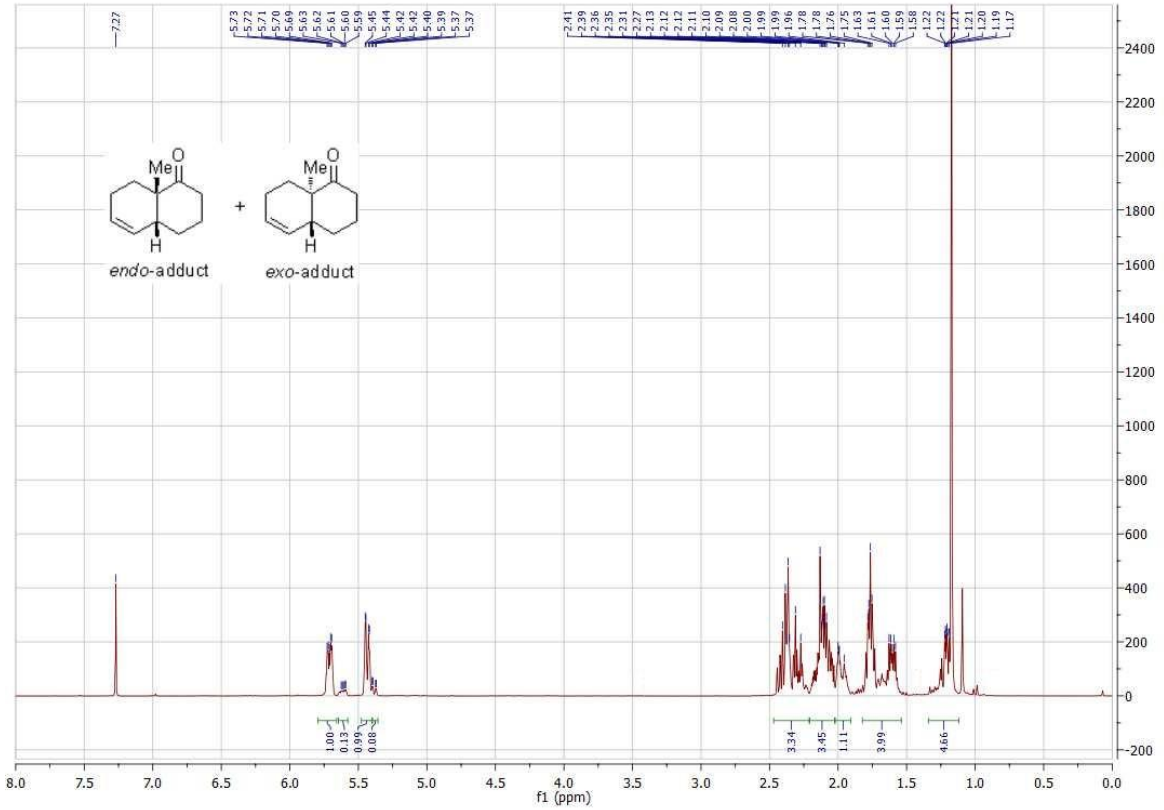

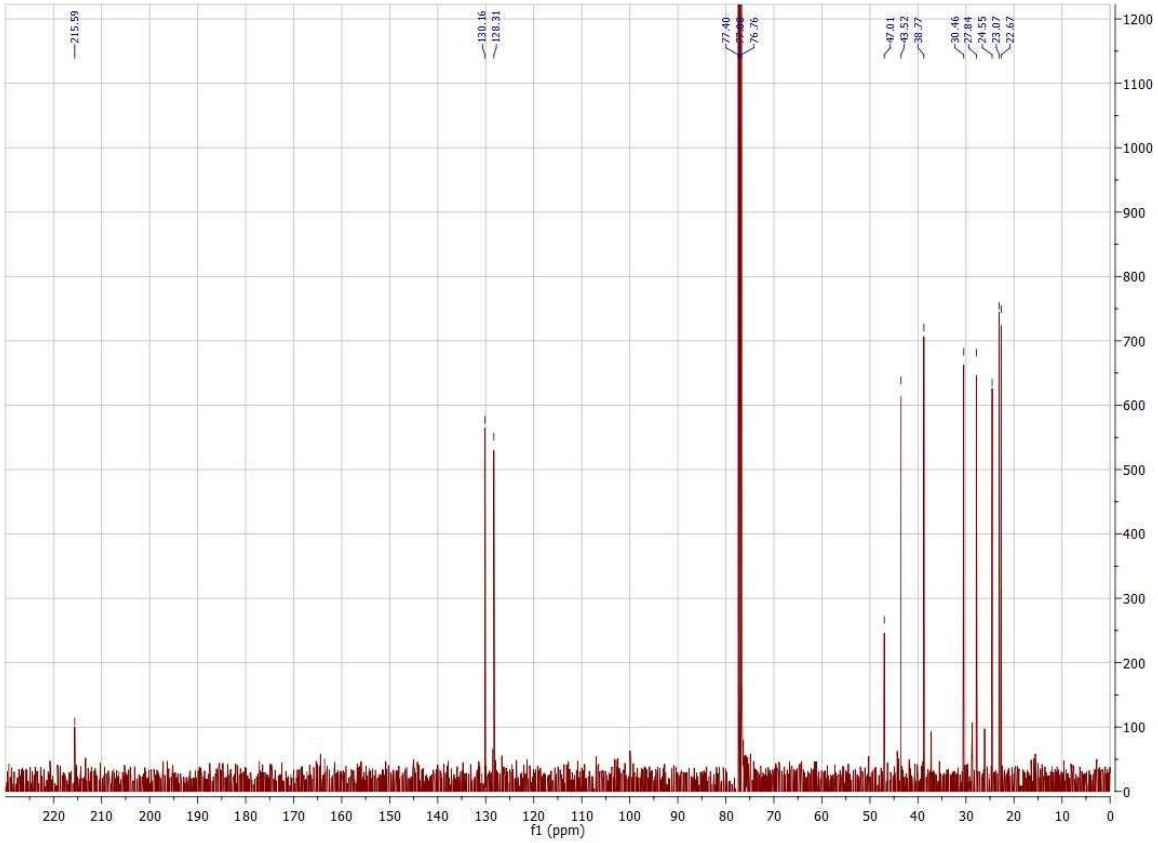

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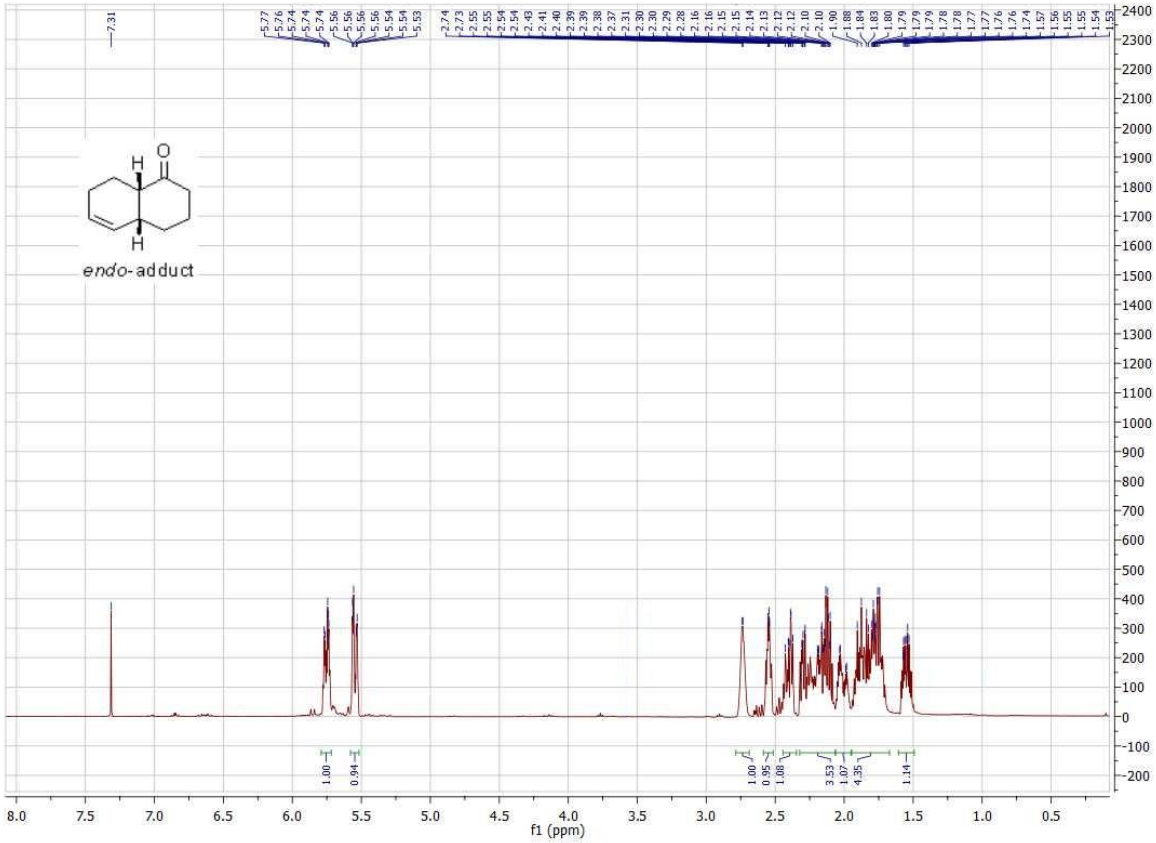

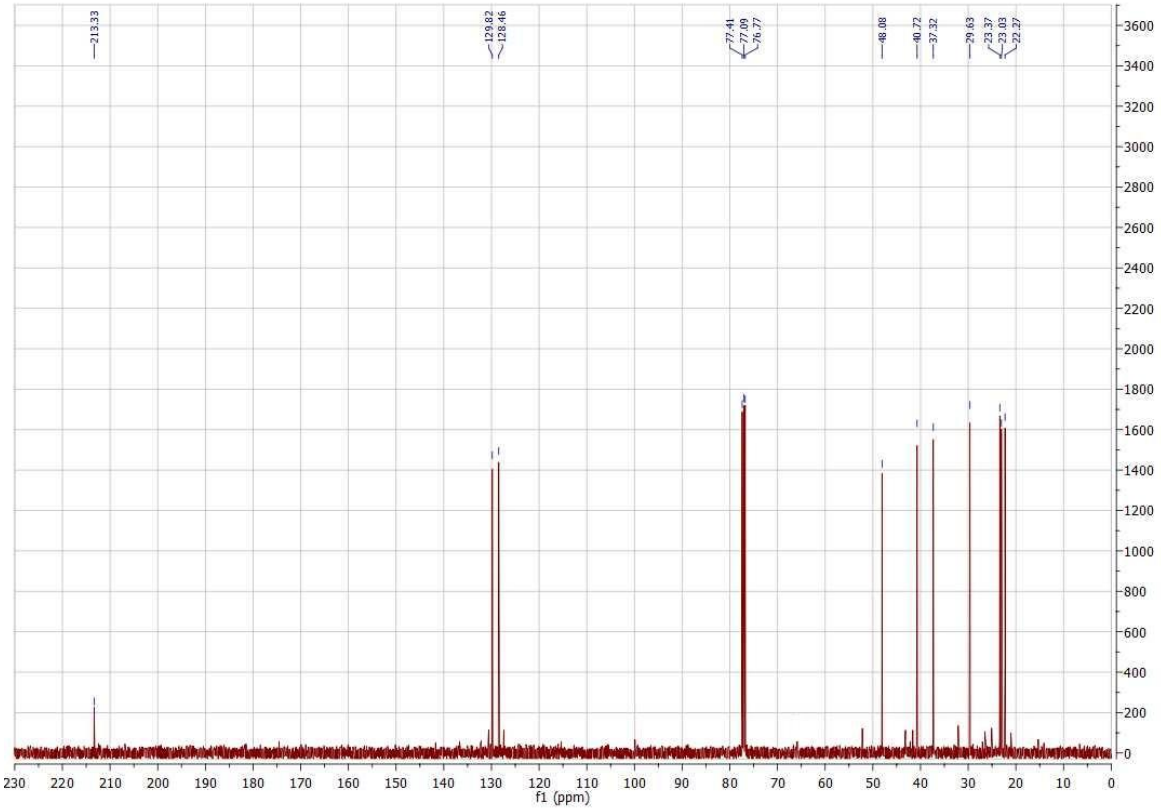

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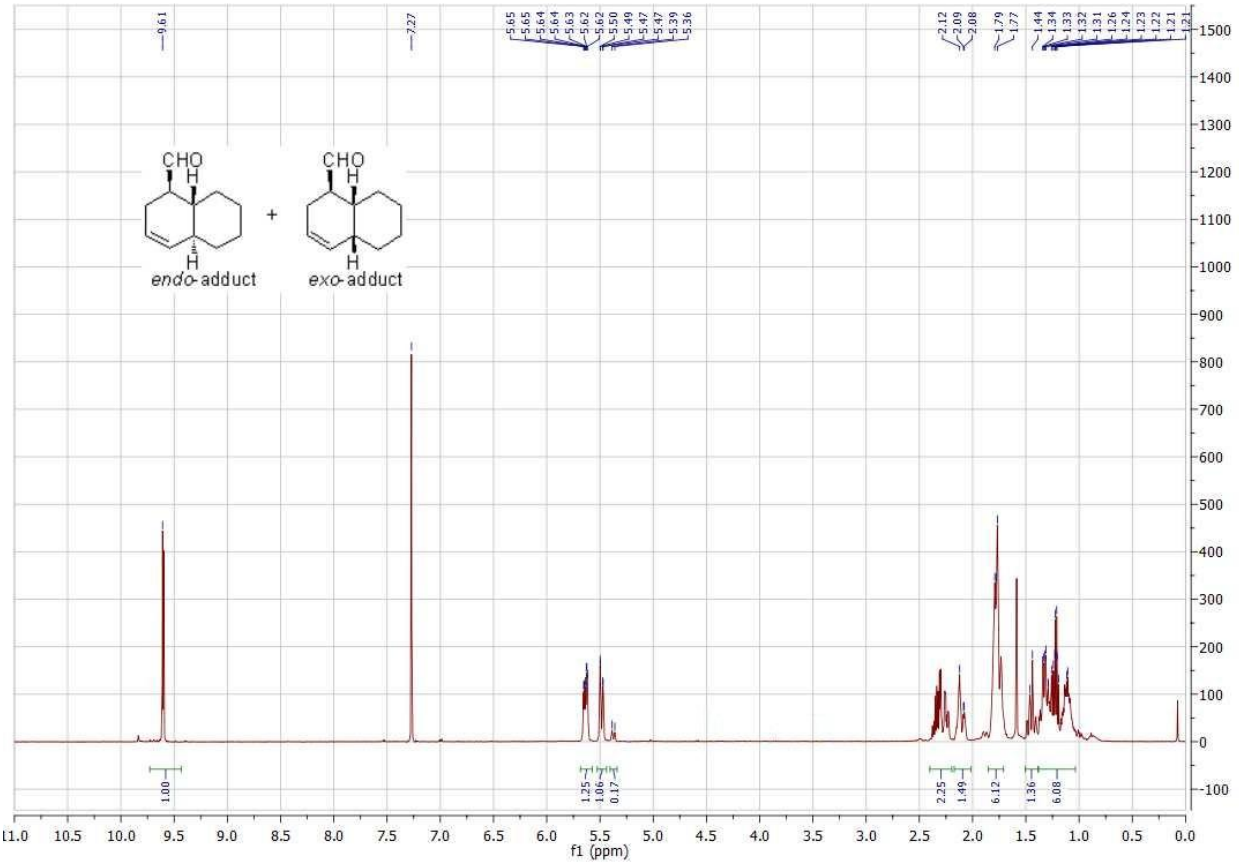

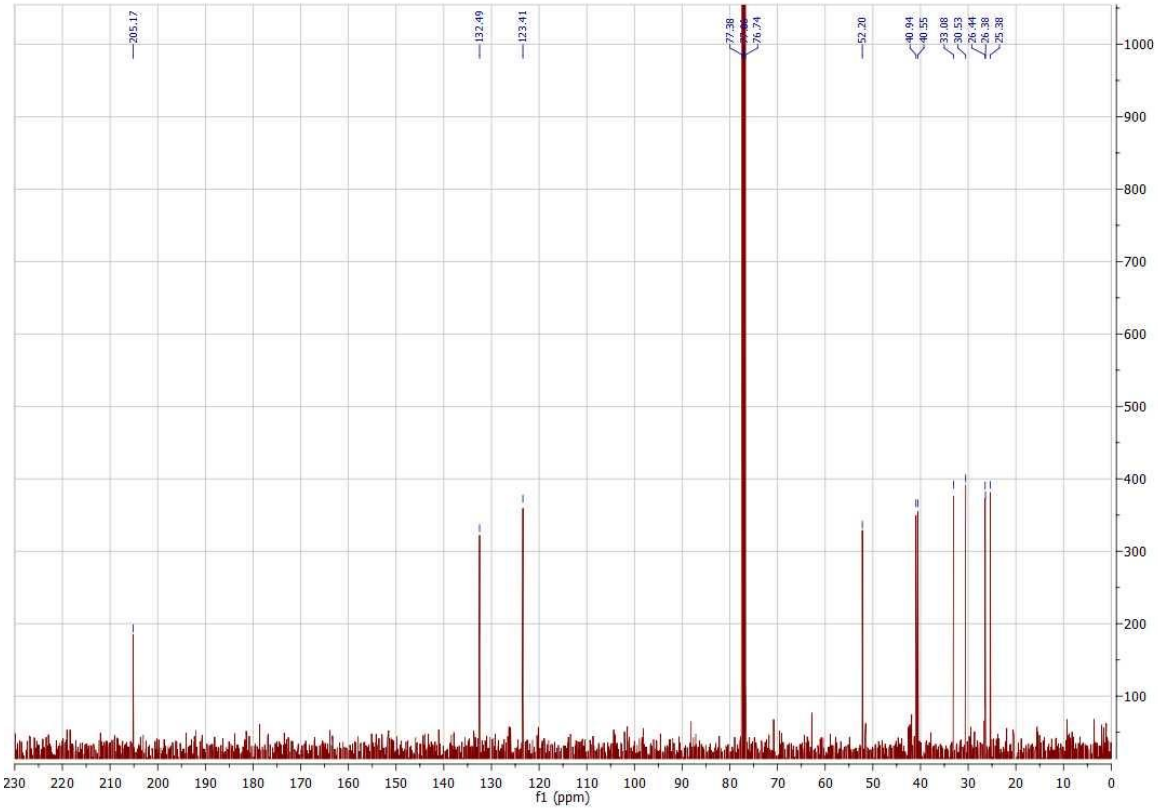

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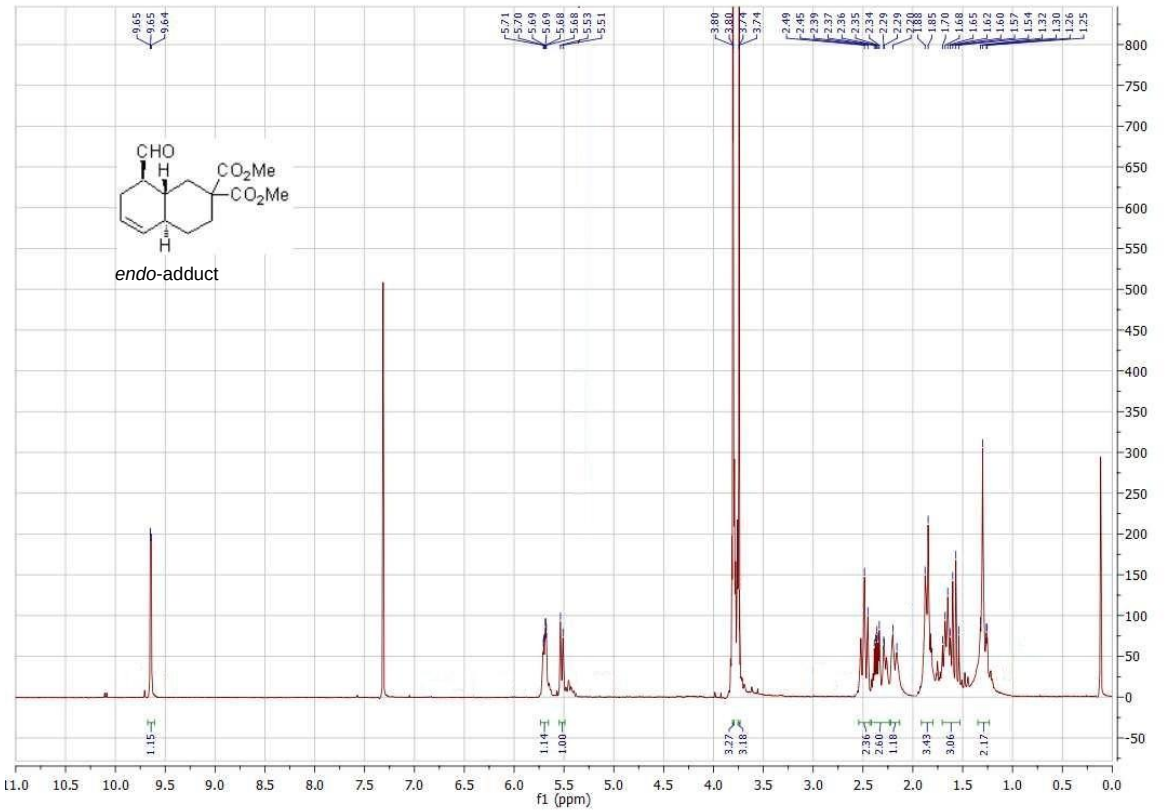

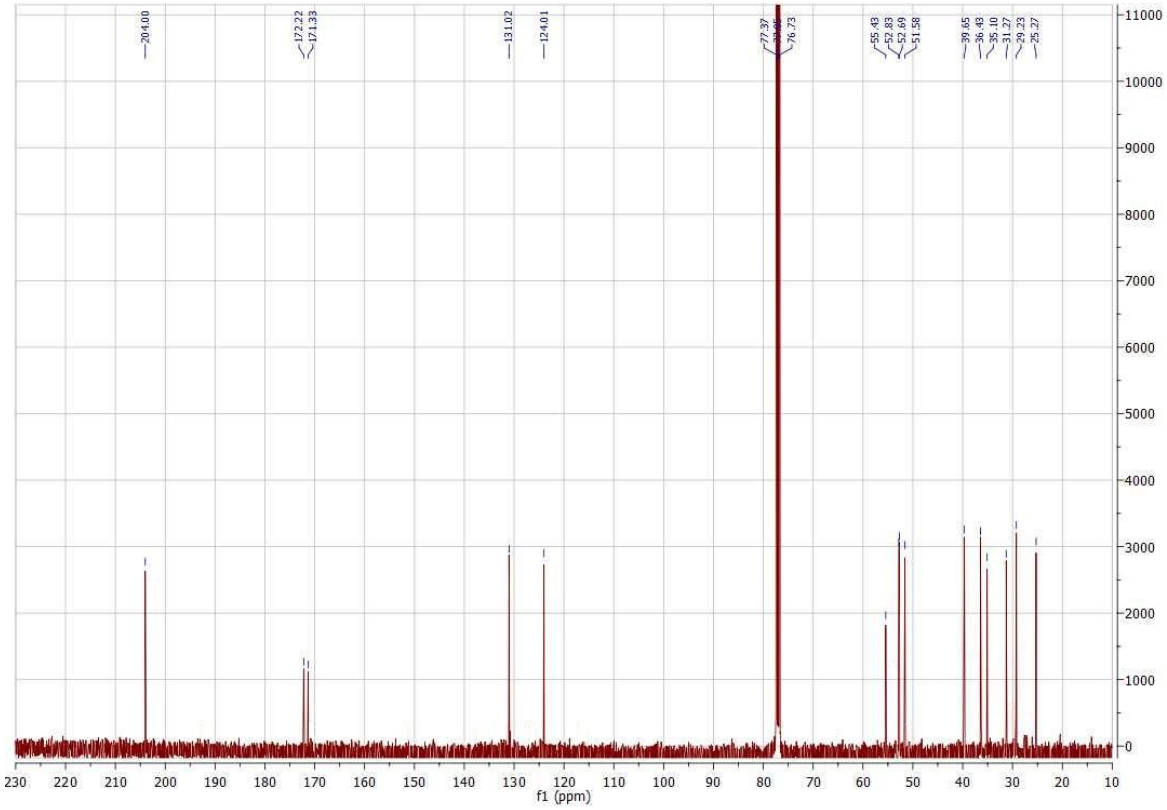

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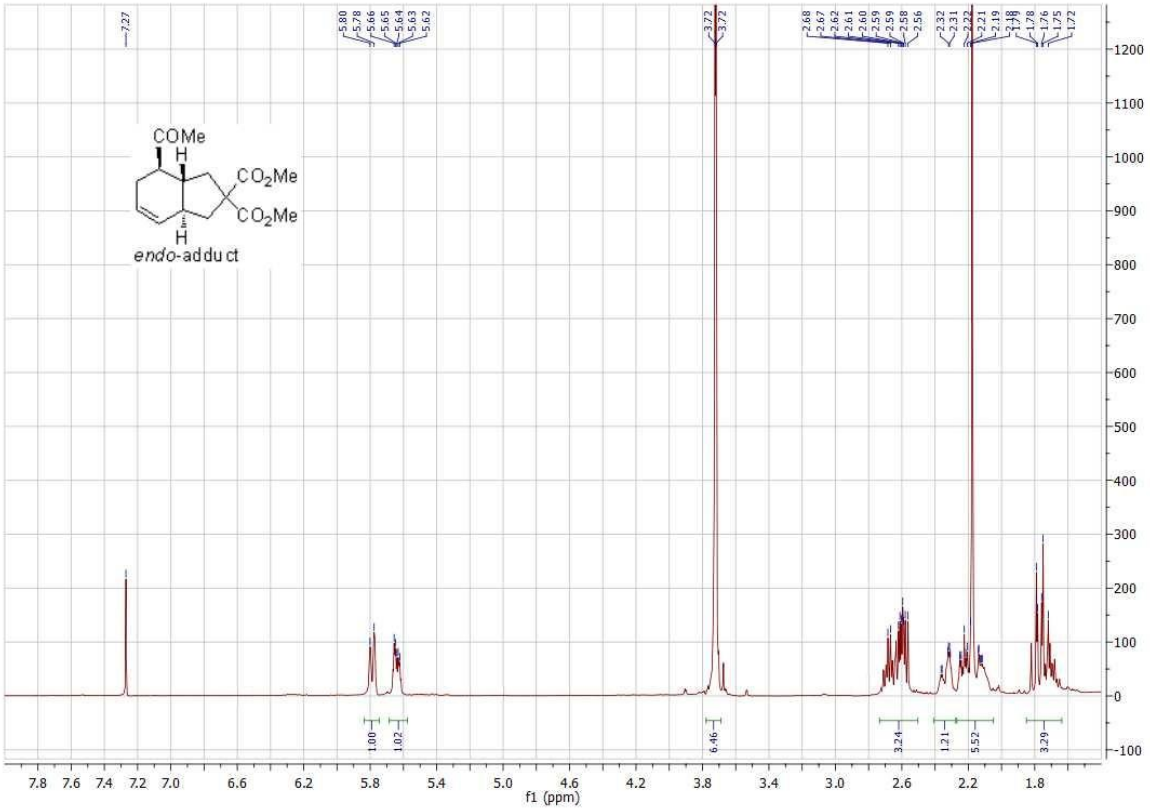

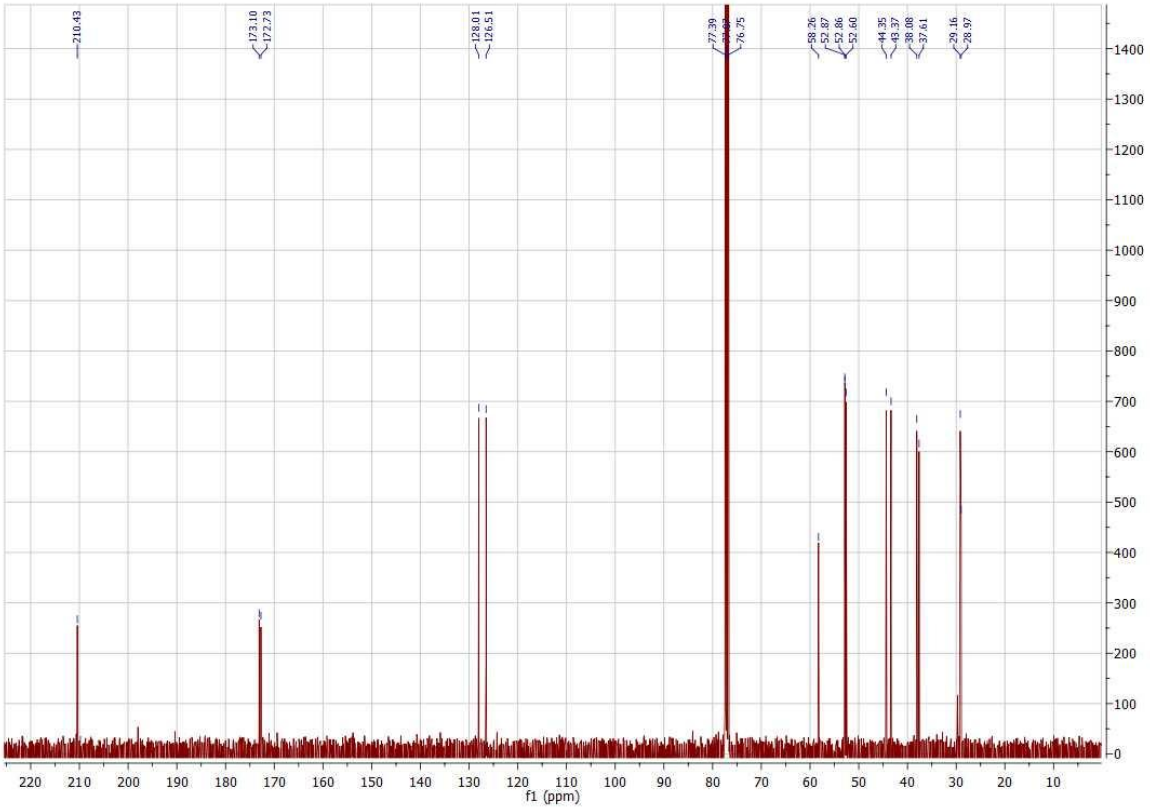

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