Supporting Information

Regioselective and Enantioselective Intermolecular Buchner Ring Expansions in Flow

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1. General Methods and Starting Materials

^{1}H NMR spectra were recorded at 500 MHz at ambient temperature with CDCl3 as a solvent unless otherwise stated. ^{13}C NMR spectra were recorded at 500 MHz at ambient temperature with CDCl3 as a solvent unless otherwise stated. Chemical shifts are reported in parts per million relative to CDCl3 (^{1}H, δ 7.24; ^{13}C, δ 77.0). Data for ^{1}H NMR are reported as follows: chemical shift, multiplicity, integration (app=apparent, par obsc=partially obscure, ovrlp=overlapping, br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet) and coupling constants are reported as values in hertz. All ^{13}C NMR spectra were recorded with complete proton decoupling. Infrared spectra were recorded on a Nicolet FT-IR with ATR. High-resolution mass spectra were obtained on a Waters QTof API US at the Boston University Chemical Instrumentation Center. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm at 24°C and are reported as $[\alpha]^{D}$ (concentration, g/100 mL). The enantiomeric excess (*ee*) of the products was determined by chiral stationary phase HPLC analysis performed using a Waters 1525 Binary HPLC Pump with a Waters 2487 diode array detector. Chiral columns include Chiralpak®AD-H (Chiral Technologies Inc., 150 x 4.6 mm I.D.) and (R,R) Whelk-0®1 (Regis Technologies, Inc.). Dichloroethane was dried by passage through columns of neutral alumina. Flash chromatography was performed using Silicycle UltraPure silica gel (particle size 40- 63μm). Unless otherwise noted commercially available reagents were used without further purification. Yields refer to quantitative ^{1}H NMR yields obtained using crude material and benzyl benzoate as a standard. Chemical names were generated using ChemBioDraw Ultra (version 14.0.0.117).

Disubstituted diazo substrates were prepared following reported procedures.[1]

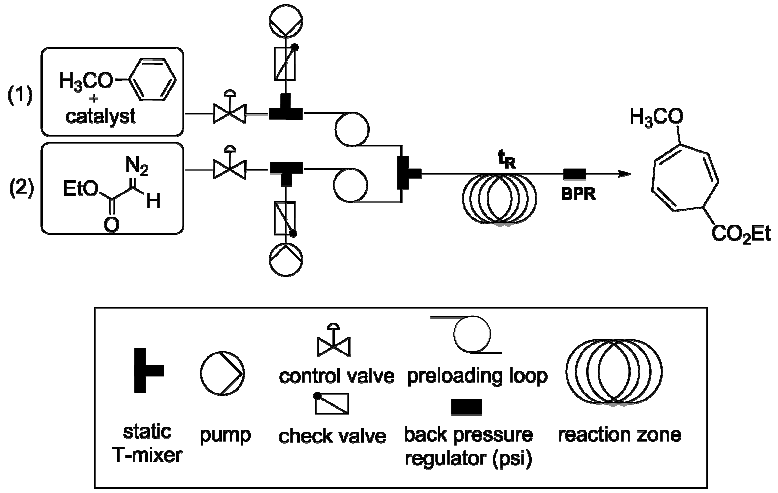
[1] Davis, O. A.; Croft, R. A.; Bull, J. A.; *Chem. Commun.* **2015**, *51*, 15446-15449.

2. Rhodium(II) Catalyzed Buchner Ring Expansion

2.1 General Procedure for Intermolecular Buchner Reactions

A solution of rhodium (II) catalyst (0.5 mol %, 0.05 mmol) and aromatic substrate (10 equivalents, 10 mmol) in dichloroethane was prepared in vial 1 and brought to a volume of 3 mL. A solution of ethyl diazoacetate (1 equivalent, 1 mmol) in dichloroethane was prepared in vial 2 and brought to a final volume of 3 mL. The solutions were taken into separate syringes and each injected into 3 mL loading loops. The switches were then closed to the syringes and the reaction mixtures were pushed through the PTFE tubing reactor by HPLC pumps with dichloroethane. The two solutions were mixed at a T-joint connection and subsequently reacted in a 20 mL reactor at 1 mL/min. The crude mixture exiting the flow system was collected over 4 Å molecular sieves, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by flash chromatography (SiO_2) using 2% ethyl acetate in hexanes unless otherwise stated.

Figure S1. Flow Chemistry Platform



Two single piston delivery HPLC pumps were used to pump solvent through the system. PTFE tubing was used for all tubing of the reactor (1/32" ID, 1/16" OD). A Zaiput Flow Technology membrane back pressure regulator connected to a nitrogen tank was used to control the back pressure induced on the system.

2.2 General Procedure for Calculation of Quantitative NMR Yields

The concentrated crude reaction mixture was weighed and a small aliquot (~10-25 mg) was weighed and added to a tared vial, along with a weighed amount of benzyl benzoate and 0.700 mL of $CDCl_3$. The sample was analyzed by ^1H NMR using the following settings:

Number of scans: 8
Relaxation time: 25 seconds

The crude ^1H NMR spectra data was processed using MestReNova v10.0.2 and the baseline was manually inspected before integration. The ratios were measured by integration of the ^1H NMR peaks resulting from the indicated hydrogens below from representative classes of cycloheptatrienes.

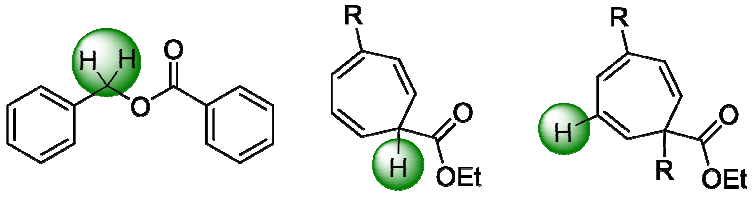
The purity of the desired product in the crude reaction mixture was determined using equation 1.

Equation 1. Quantitative yield determination

$$P_{Sample} = \frac{I_{analyte}}{I_{CRM}} x \frac{N_{CRM}}{N_{analyte}} x \frac{M_{analyte}}{M_{CRM}} x \frac{m_{analyte}}{m_{CRM}} x P_{CRM}$$

P: purity, mass fraction
I: integral
N: number of protons
M: molecular mass
m: mass

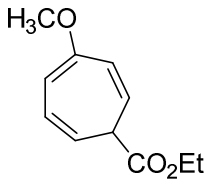
Figure S2. Yield determination proton



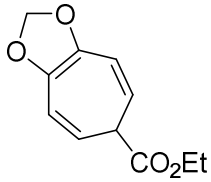
Protons circled were used to calculate proton ratios to determine yield

2.3 Characterization Data for Cycloheptatrienes

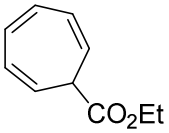
All prepared using the general intermolecular Buchner protocol on a 1 mmol scale unless otherwise noted.



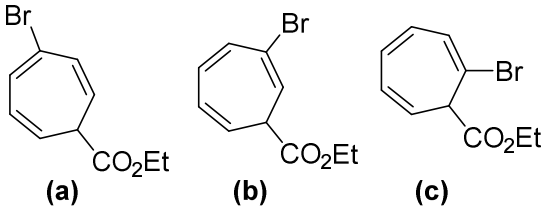
Ethyl 4-methoxycyclohepta-2,4,6-triene-1-carboxylate (3).
Yield: Obtained in 81% yield (qNMR) using $Rh_2(oct)_4$ and 71% (qNMR) yield using $Rh_2(tfa)_4$. Obtained in 79% isolated yield (153 mg) using $Rh_2(oct)_4$.
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.19 (dd, *J* = 8.0, 7.1 Hz, 1H), 6.06 (d, *J* = 9 Hz, 1H), 5.85 (dd, *J* = 6.7, 1.6 Hz, 1H), 5.60 (dd, *J* = 9.8, 5.9 Hz, 1H), 5.25 (dd, *J* = 9.16, 5.2 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 2.68 (dd, *J* = 5.5, 5.5 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 172.9, 159.9, 124.8, 122.1, 119.9, 113.3, 104.8, 71.3, 61.0, 54.7, 44.0, 14.2;
IR (thin film): νmax 2982, 2833, 2253, 1733, 1631, 1551, 1465, 1416, 1393, 1368, 1302, 1228, 1197, 1171, 1114, 1037, 1014, 1037, 1014, 905, 861, 812, 727, 649, 615, 519, 472;
HRMS calculated for $C_{11}H_{15}O_3$ (M+H): 195.1021. Found: 195.1014.



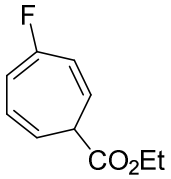
Ethyl 6H-cyclohepta[*d*][1,3]dioxole-6-carboxylate (4).
Yield: Obtained in 76% yield (qNMR) using $Rh_2(oct)_4$ and 48% (qNMR) using $Rh_2(tfa)_4$.
Physical appearance: yellow oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.33 (d, *J* = 9.5 Hz, 1H), 5.86 (d, *J* = 1.6 Hz, 1H), 5.68 (d, *J* = 1.6 Hz, 1H), 5.15 (dd, *J* = 9.5 Hz, *J* = 5.9 Hz, 1H) 4.27 (q, *J* = 7.1 Hz, 2H), 2.62 (dd, *J* = 5.9 Hz, *J* = 5.9 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 142.0, 115.5, 110.3, 98.6, 61.2, 45.3, 14.2;
IR (thin film): νmax 2982, 2873, 1735, 1625, 1600, 1550, 1446, 1402, 1368, 1301, 1227, 1183, 1117, 1039, 973, 939, 914, 861, 824, 779, 743, 703, 616, 523;
HRMS calculated for $C_{11}H_{13}O_4$ (M+H): 209.0814 Found: 209.0813.



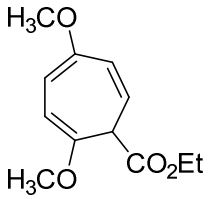
Ethyl cyclohepta-2,4,6-triene-1-carboxylate (5).
Yield: Obtained in 40% yield (qNMR) using $Rh_2(oct)_4$ and 64% yield (qNMR) using $Rh_2(tfa)_4$.
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.65 (dd, *J* = 3.6, 2.8 Hz, 2H), 6.26 (m, 2H), 5.44 (m, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.54 (ddd, *J* = 5.6, 2.6, 1.3 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 173.0, 130.9, 125.6, 117.3, 61.1, 44.1, 14.2;
IR (thin film): νmax 3071, 2983, 1764, 1446, 1395, 1368, 1301, 1215, 1190, 1165, 1107, 1039, 1001, 861, 783, 746, 698, 591;
HRMS calculated for $C_{10}H_{12}O_2Na$ (M+Na): 187.0735. Found: 187.0742.



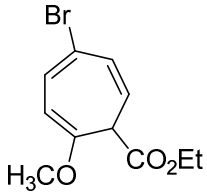
Ethyl 4-bromocyclohepta-2,4,6-triene-1-carboxylate (7).
Yield: Obtained in 42% yield (qNMR) using $Rh_2(oct)_4$ and isolated as a mixture of regioisomers (13:2:1) and in 82% yield using $Rh_2(tfa)_4$ and isolated as a mixture of regioisomers (8:2:1).
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): **(a)** δ 7.04 (d, *J* = 6.3 Hz, 1H), 6.35 (d, *J* = 9.6 Hz, 1H), 6.15 (dd, *J* = 6.9 Hz, 9.1 Hz, 1H), 5.54 (dd, *J* = 5.5 Hz, 9.2 Hz, 1H) 5.45 (dd, *J* = 6.1 Hz, 9.6 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.75 (dd, *J* = 5.8 Hz, 5.8 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); **(b)** δ 6.64 (ovrlp, d, *J* = 10.9 Hz, 1H), 6.50 (dd, *J* = 6.02 Hz, 10.8 Hz, 1H), 6.24 (dd, *J* = 5.3 Hz, 8.1 Hz, 1H), 5.47 (ovrlp, 1H), 5.28 (M, 1H), 4.25 (ovrlp, 2H), 2.53 (dd, *J* = 5.9 Hz, 5.9 Hz, 1H), 1.29 (ovrlp, 3H) **(c)** δ 6.68 (d, *J* = 6.4 Hz, 1H), 6.63 (ovrlp, 1H), 6.41-6.31 (ovrlp, 2H), 5.78 (dd, *J* = 8.25 Hz, 9.4 Hz, 1H), 4.24 (ovrlp, 2H), 3.52 (d, *J* = 7.6 Hz, 1H), 1.30 (ovrlp, 3H)
^{13}C NMR (125 MHz, $CDCl_3$): δ **(a)** 127.0, 133.5, 129.1, 125.5, 125.1, 120.2, 119.2, 61.4, 44.2, 14.2;
IR (thin film): νmax 2982, 1736, 1598, 1531, 1465, 1445, 1394, 1368, 1302, 1267, 1192, 1174, 1113, 1096, 1039, 950, 907, 877, 808, 728, 592;
HRMS calculated for $C_{10}H_{12}BrO_2$ (M+H): 243.0021. Found: 243.0024.



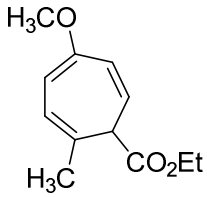
Ethyl 4-fluorocyclohepta-2,4,6-triene-1-carboxylate (8).
Yield: Obtained in 11% yield (qNMR) as a single regioisomer using $Rh_2(oct)_4$ and 66% yield (qNMR) as a mixture of regioisomers (0:1:6) using $Rh_2(tfa)_4$.
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.39 (ddd, *J* = 2.0 Hz, 6.7 Hz, 16.0 Hz, 1H), 6.23 (M, 2H), 5.68 (ddd, *J* = 5.6 Hz, 10.5 Hz, 16.0 Hz, 1H), 5.37 (dd, *J* = 5.4 Hz, 9.2 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H) 2.69 (ddd, *J* = 1.2 Hz, 6.2 Hz, 6.2 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 172.17, 123.4, 122.3, 120.0, 120.0, 116.6, 112.1, 61.3, 44.7, 14.2;
IR (thin film): νmax 2981, 2931, 1736, 1633, 1612, 1560, 1465, 1447, 1414, 1391, 1369, 1300, 1267, 1192, 1148, 1101, 1039, 867, 814, 769, 717, 602;
HRMS calculated for $C_{10}H_{11}FO_2$ (M+H): 183.0821. Found: 183.0814 (M+H).



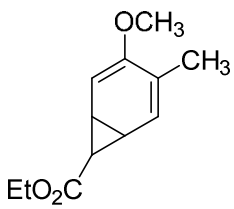
Ethyl 2,5-dimethoxycyclohepta-2,4,6-triene-1-carboxylate (10).
Yield: Obtained in 70% yield (qNMR) using $Rh_2(oct)_4$ and 41% yield (qNMR) using $Rh_2(tfa)_4$. Obtained in 55% isolated yield (123 mg) using $Rh_2(oct)_4$.
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.14 (d, *J* = 9.9 Hz, 1H), 5.81 (dd, *J* = 9.9 Hz, 7.3 Hz, 1H), 5.72 (dd, *J* = 7.4 Hz, 1.6 Hz, 1H), 5.35 (d, *J* = 7.4 Hz, 1H) 4.21 (m, 2H), 3.62 (s, 3H), 3.59 (s, 3H), 3.28 (d, *J* = 7.3 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 155.4, 146.0, 123.8, 120.7, 102.3, 94.7, 61.0, 56.5, 55.1, 48.4, 14.2;
IR (thin film): νmax 2936, 2833, 1740, 1625, 1464, 1416, 1369, 1326, 1311, 1260, 1216, 1193, 1169, 1095, 1076, 1035, 905, 797, 726, 649, 621;
HRMS calculated for $C_{12}H_{15}O_4$ (M+H): 223.0990. Found: 223.0981.



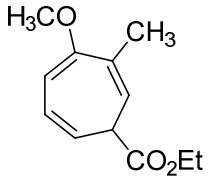
Ethyl 5-bromo-2-methoxycyclohepta-2,4,6-triene-1-carboxylate (11).
Yield: Obtained in 42% yield (qNMR) using $Rh_2(oct)_4$ and 36% yield (qNMR) using $Rh_2(tfa)_4$.
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.84 (d, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 9.5 Hz, 1H), 5.61 (dd, *J* = 7.5 Hz, *J* = 9.5 Hz, 1H), 5.37 (d, *J* = 7.3 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 3H), 3.32 (d, *J* = 7.3 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 149.9, 133.6, 130.5, 129.9, 119.7, 117.6, 97.2, 61.2, 48.6, 14.1;
IR (thin film): νmax 2962, 2933, 2858, 1741, 1614, 1530, 1463, 1396, 1369, 1320, 1265, 1223, 1162, 1095, 1076, 1033, 981, 906, 791, 731, 649;
HRMS calculated for $C_{11}H_{14}BrO_3$ (M+H): 273.0126. Found: 273.0134.



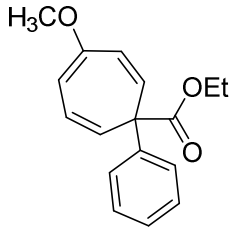
Ethyl 5-methoxy-2-methylcyclohepta-2,4,6-triene-1-carboxylate (12).
Yield: Obtained in 70% yield (qNMR) using $Rh_2(oct)_4$ and 66% yield (qNMR) as a mixture of 1:0:1 mixture of regioisomers using $Rh_2(tfa)_4$.
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.23 (d, *J* = 6.9 Hz, 1H), 6.11 (d, *J* = 9.0 Hz, 1H), 5.63 (dd, *J* = 7.5 Hz, 9.5 Hz, 1H), 5.38 (d, *J* = 6.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 3H), 3.30 (d, *J* = 7.5 Hz, 1H), 2.01 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 148.2, 133.3, 129.8, 125.0, 117.4, 96.8, 60.9, 56.4, 48.6, 23.7, 14.2;
IR (thin film): νmax 2979, 2936, 2253, 1740, 1616, 1548, 1464, 1368, 1315, 1263, 1222, 1192, 1155, 1080, 1035, 903, 802, 726, 649, 598;
HRMS calculated for $C_{12}H_{17}O_3$ (M+H): 209.1178. Found: 209.1183.



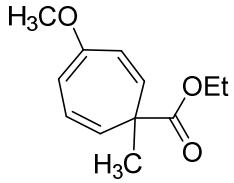
Ethyl 3-methoxy-4-methylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (13).
Yield: Obtained in 59% yield (qNMR) using $Rh_2(oct)_4$.
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.05 (d, *J* = 7.6 Hz, 1H), 5.70 (d, *J* = 8.1 Hz, 1H), 4.27 (m, 1H), 4.21 (q, *J* = 7.1 Hz, 2H) 4.04 (m, 2H), 3.61 (s, 3H), 1.89 (s, 3H), 1.67 (dd, *J* = 4.9 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 174.5, 154.8, 127.3, 125.5, 109.1, 103.1, 60.8, 56.5, 44.2, 34.6, 16.6, 14.3;
IR (thin film): νmax 2891, 2935, 1736, 1715, 1655, 1622, 1581, 1454, 1403, 1377, 1304, 1256, 1228, 1188, 1159, 1096, 1069, 1056, 1041, 1004, 905, 839, 795, 728, 649;
MS calculated for $C_{12}H_{17}O_3$ (M+H): 209.1172. Found: 207.1174.



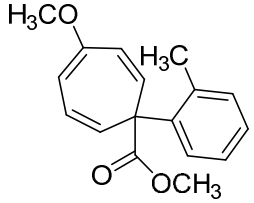
Ethyl 4-methoxy-3-methylcyclohepta-2,4,6-triene-1-carboxylate (14).
Yield: Obtained in 30% yield (qNMR) using $Rh_2(oct)_4$.
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.15 (ddd, *J* = 9.0 Hz. *J* = 6.4 Hz, *J* = 1.4 H, 1H), 5.78 (d, *J* = 6.4 Hz, 1H), 5.48 (d, *J* = 6.3 Hz, 1H), 5.44 (dd, *J* = 9.2 Hz, 5.4 Hz, 1H) 4.24 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 3H), 2.71 (dd, *J* = 6.1 Hz, 6.1 Hz, 1H), 1.93 (t, *J* = 1.3 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 173.2, 161.4, 130.5, 124.3, 119.3, 117.5, 103.1, 60.9, 54.6, 44.2, 18.6, 14.2;
IR (thin film): νmax 2979, 2957, 2929, 2833, 1735, 1676, 1636, 1552, 1453, 1408, 1367, 1319, 1278, 1225, 1200, 1172, 1151, 1112, 1041, 1027, 967, 836, 798, 738, 695;
HRMS calculated for $C_{12}H_{17}O_3$ (M+H): 209.1178. Found: 209.1188.



Ethyl 4-methoxy-1-phenylcyclohepta-2,4,6-triene-1-carboxylate (20).
Yield: Obtained in 73% yield (qNMR) with 93% ee using Rh_2(*S*-PTAD)$_4$ and 71% yield (qNMR) with 91% *ee* using Rh_2(*R*-PTAD)$_4$.
Physical appearance: yellow oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 7.23-7.14 (m, 5H), 6.25 (dd, *J* = 8.1 Hz, *J* = 8.1 Hz, 1H), 5.63 (dd, *J* = 1.8 Hz, *J* = 8.1 Hz, 1H), 5.58 (dd, *J* = 2.1 Hz, *J* = 8.6 Hz, 1H), 4.56 (m, 1H), 4.37 (m, 1H) 4.09 (q, *J* = 7.1 Hz, 2H), 3.42 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 175.0, 157.2, 145.3, 133.0, 130.8, 128.4, 128.2, 127.1, 126.7, 126.1, 68.6, 61.4, 54.5, 33.9, 25.2, 14.1;
IR (thin film): νmax 3026, 2981, 2906, 2831, 1730, 1707, 1649, 1582, 1556, 1494, 1446, 1422, 1391, 1366, 1230, 1175, 1095, 1056, 1020, 831, 781, 758, 745, 730, 699, 675, 643, 556, 521, 419;
HRMS calculated for $C_{17}H_{18}O_3Na$ (M+Na): 293.1154. Found: 293.1160.
$[\alpha]_D^{24}$ = 47.5° (*c*= 1.3)

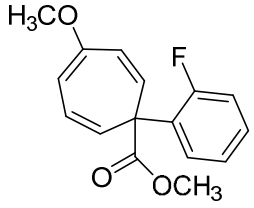


Ethyl-4-methoxy-1-methylcyclohepta-2,4,6-triene-1-carboxylate (21).
Yield: Obtained in 55% yield (qNMR) with 49% ee using Rh_2(*R*-PTAD)$_4$ and 41% yield (qNMR) with 50% *ee* using Rh_2(*S*-PTAD)$_4$.
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.12 (dd, *J* = 8.3 Hz, *J* = 8.3 Hz, 1H), 5.84 (d, *J* = 8.3 Hz, 1H), 5.63 (d, *J* = 8.3 Hz, 1H), 4.44 (br m, 1H), 4.20 (br m, 1H), 4.12 (m, 2H), 3.61 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.15 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 176.5, 157.6, 125.2, 111.9, 110.0, 60.9, 54.5, 29.7, 17.3, 16.5, 14.2;
IR (thin film): νmax 2979, 2933, 1729, 1709, 1646, 1581, 1563, 1448, 1420, 1389, 1367, 1300, 1245, 1226, 1166, 1110, 1022, 989, 957, 934, 859, 801, 733, 659;
HRMS calculated for $C_{12}H_{17}O_3$ (M+H): 209.1178. Found: 209.1183.

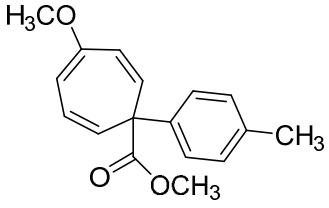


Methyl 4-methoxy-1-(o-tolyl)cyclohepta-2,4,6-triene-1-carboxylate (22).

Yield: Obtained in 35% yield (qNMR) with 94% *ee* using Rh_2(*S*-PTAD)$_4$ and 36% yield (qNMR) with 93% *ee* using Rh_2(*R*-PTAD)$_4$. Obtained in 35% isolated yield (49 mg) using Rh_2(*R*-PTAD)$_4$.
Physical appearance: yellow oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 7.21-6.91 (m, 5H), 6.20 (dd, *J* = 5.4 Hz, *J* = 9.7 Hz, 1H), 5.57 (d, *J* = 9.7 Hz, 1H), 5.12 (d, *J* = 5.3 Hz, 1H), 3.64 (s, 3H), 3.42 (s, 3H), 3.10 (m, 1H), 3.03 (m, 1H), 2.25 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 177.0, 154.9, 139.4, 134.2, 130.46, 130.0, 127.2, 126.4, 124.5, 124.1, 92.3, 54.3, 52.8, 36.5, 35.5, 30.0, 19.5;
IR (thin film): νmax 3054, 2253, 1708, 1649, 1608, 1422, 1264, 1232, 1166, 1103, 1029, 906, 807, 727, 649, 451;
HRMS calculated for $C_{17}H_{19}O_3$ (M+H): 271.1334. Found: 271.1322.
$[\alpha]_D^{24}$ = 63.9° (*c*= 0.7)

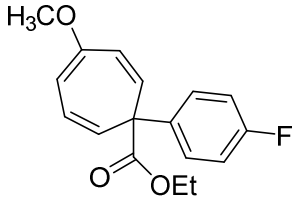


Methyl 1-(2-fluorophenyl)-4-methoxycyclohepta-2,4,6-triene-1-carboxylate (23).
Yield: Obtained in 54% yield (qNMR) with 96% *ee* using Rh_2(*S*-PTAD)$_4$ and 48% yield (qNMR) with 98% *ee* using Rh_2(*R*-PTAD)$_4$.
Physical appearance: white-yellow solid;
^{1}H NMR (125 MHz, $CDCl_3$): δ 7.18 (m, 1H), 6.99 (ddd, *J* = 1.4 Hz, *J* = 7.8 Hz, *J* = 9.4 Hz, 1H), 6.93(d, 1H), 6.91 (m, ovrlp, 1H), 6.21 (dd, *J* = 5.5 Hz, *J* = 9.8 Hz, 1H), 5.56 (dd, *J* = 2.0 Hz, *J* = 9.8 Hz, 1H), 5.12 (d, *J* = 5.9 Hz, 1H), 3.64 (s, 3H), 3.42 (s, 3H), 3.17 (dd, *J* = 6.0 Hz, *J* = 8.8 Hz, 1H), 3.08 (dd, *J* = 5.5 Hz, *J* = 8.8 Hz, 1H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 176.0, 163.5, 161.5, 154.9, 135.4, 129.2, 126.8, 124.1, 122.5, 115.1, 92.8, 54.3, 52.9, 37.2, 36.0, 21.5;
IR (thin film): νmax 2953, 2252, 1708, 1649, 1585, 1495, 1453, 1435, 1422, 1341, 1251, 1232, 1166, 1107, 1030, 973, 903, 833, 811, 722, 649, 573, 520, 498, 453;
HRMS calculated for $C_{16}H_{15}FO_3Na$ (M+Na): 297.0939. Found: 297.0939.
$[\alpha]_D^{24}$ = 63.9° (*c*= 0.8)

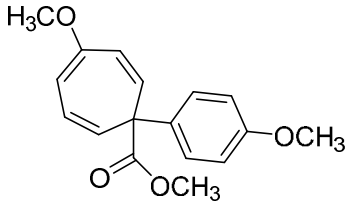


Methyl 4-methoxy-1-(p-tolyl)cyclohepta-2,4,6-triene-1-carboxylate (24).

Yield: Obtained in 41% yield (qNMR) with 96% *ee* using Rh_2(*R*-PTAD)$_4$ and 35% yield (qNMR) with 89% *ee* using Rh_2(*S*-PTAD)$_4$.
Physical appearance: yellow oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 7.06 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.21 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 5.58 (dd, *J* = 1.8 Hz, *J* = 8.8 Hz, 1H), 5.50 (brd d, *J* = 7.6 Hz, 1H), 4.25 (brd m, 1H), 4.08 (brd m, 1H), 3.63 (s, 3H), 3.44 (s, 3H), 2.27 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 176.1, 156.7, 144.6, 136.3, 133.7, 132.8, 131.2, 130.2, 129.6, 129.6, 129.1, 128.9, 128.0, 126.3, 54.5, 52.8, 21.2;
IR (thin film): νmax 2952, 2252, 1718, 1649, 1606, 1514, 1434, 1335, 1232, 1166, 1108, 1062, 1021, 969, 905, 820, 801, 725, 648, 586, 521, 479, 456, 411;
HRMS calculated for $C_{17}H_{19}O_3$ (M+H): 271.1334. Found: 271.1328.
$[\alpha]_D^{24}$ = 163.3° (*c*= 1.0)

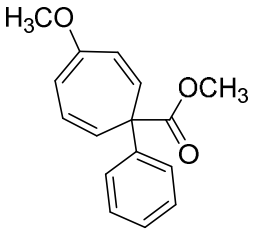


Ethyl 1-(4-fluorophenyl)-4-methoxycyclohepta-2,4,6-triene-1-carboxylate (25).
Yield: Obtained in 76% yield (qNMR) with 95% *ee* using Rh_2(*S*-PTAD)$_4$ and 76% yield (qNMR) with 95% *ee* using Rh_2(*R*-PTAD)$_4$.
Physical appearance: white-yellow solid;
^{1}H NMR (125 MHz, $CDCl_3$): δ 7.14 (dd, *J* = 5.5 Hz, *J* = 8.6 Hz, 2H), 6.84 (dd, *J* = 8.6 Hz, *J* = 8.6 Hz, 2H), 6.23 (dd, *J* = 7.9 Hz, *J* = 8.6 Hz, 1H), 5.58 (dd, *J* = 2.0 Hz, *J* = 8.8 Hz, 1H), 5.52 (dd, *J* = 1.7 Hz, *J* = 7.7 Hz, 1H), 4.33 (br dd, *J* = 6.3 Hz, *J* = 6.3 Hz, 1H), 4.15 (br dd, *J* = 6.8 Hz, *J* = 6.8 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.43 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 175.0, 162.5, 160.5, 156.9, 132.9, 131.2, 130.1, 129.5, 126.2, 116.8, 114.1, 113.9, 110.0, 104.6, 61.5, 54.5, 14.1;
IR (thin film): νmax 2980, 2832, 1730, 1705, 1648, 1600, 1554, 1510, 1445, 1421, 1366, 1335, 1297, 1219, 1157, 1094, 1056, 1018, 955, 838, 813, 787, 757, 734, 711, 667, 631, 608, 586, 552, 523, 478, 443, 411;
MS calculated for $C_{17}H_{18}FO_3$ (M+H): 289.1240. Found: 289.1245.
$[\alpha]_D^{24}$ = 23.1° (*c*= 1.1)

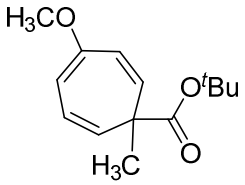


Methyl 4-methoxy-1-(4-methoxyphenyl)cyclohepta-2,4,6-triene-1-carboxylate (26).
Yield: Obtained in 43% yield (qNMR) with 89% *ee* using Rh_2(*R*-PTAD)$_4$ and 25% yield (qNMR) with 86% *ee* using Rh_2(*S*-PTAD)$_4$.

Physical appearance: yellow oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.21 (dd, *J* = 7.1 Hz, *J* = 8.0 Hz, 2H), 5.58 (dd, *J* = 1.4 Hz, *J* = 8.9 Hz, 1H), 5.58 (dd, *J* = 1.4 Hz, *J* = 7.7 Hz, 1H), 5.46 (dd, 1H), 4.16 (br m, 1H), 4.01 (br m, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 3.43 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 176.2, 158.2, 156.7, 132.7, 132.5, 128.5, 127.1, 126.3, 117.7, 114.2, 114.0, 112.6, 55.6, 55.0, 54.45, 52.78, 29.7;
IR (thin film): νmax 2953.3. 2253.0. 2160.2 ,1706.9, 1648.8, 1600.0, 1514.4, 1463.9, 1245.68, 1164.6, 1032.6, 903.6, 802.2, 726.6, 649.7, 544.1, 421.7;
HRMS calculated for $C_{17}H_{19}O_4$ (M+H): 287.1283. Found: 287.1272.
$[\alpha]_D^{24}$ = 68.5° (*c*= 0.3)

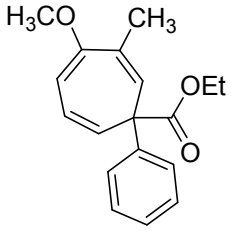


Methyl 4-methoxy-1-phenylcyclohepta-2,4,6-triene-1-carboxylate (27).
Yield: Obtained in 72% yield (qNMR) with 91% *ee* using Rh_2(*R*-PTAD)$_4$ and 81% yield (qNMR) with 93% *ee* using Rh_2(*S*-PTAD)$_4$.
Physical appearance: white solid;
^{1}H NMR (125 MHz, $CDCl_3$): δ 7.22-7.13 (m, 5H), 6.23 (dd, *J* = 8.3 Hz, *J* = 7.3 Hz, 1H), 5.57 (dd, *J* = 8.9, *J* = 2.1 Hz, 1H), 5.50 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 1H), 4.24 (m, 1H), 4.07 (m, 1H), 3.63 (s, 3H), 3.42 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 175.9, 156.7, 135.3, 131.5, 129.7, 128.6, 127.1, 126.8, 126.3, 117.33, 113.9, 103.8, 54.44, 52.8;
IR (thin film): νmax 3025, 2951, 2833, 1732, 1708, 1647, 1608, 1552, 1511, 1495, 1458, 1433, 1422, 1361, 1229, 1180, 1165, 1076, 1057, 1030, 1014, 990, 970, 946, 910, 810, 779, 760, 731, 699, 649, 553, 520;
HRMS calculated for $C_{16}H_{17}O_3$ (M+H): 257.1178. Found: 257.1181.
$[\alpha]_D^{24}$ = 100.1° (*c*= 0.7)

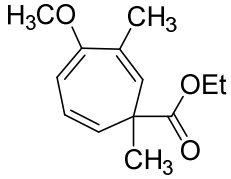


***tert*-butyl 4-methoxy-1-methylcyclohepta-2,4,6-triene-1-carboxylate (28).**
Yield: Obtained in 21% yield (qNMR) with 89% *ee* using Rh_2(*R*-PTAD)$_4$ and 31% yield (qNMR) with 90% *ee* using Rh_2(*S*-PTAD)$_4$.
Physical appearance: yellow oil;

^{1}H NMR (125 MHz, $CDCl_3$): δ 6.12 (dd, *J* = 8.3 Hz, *J* = 8.3 Hz, 1H), 5.80 (dd, *J* = 2.17 Hz, 8.0 Hz, 1H), 5.71 (dd, *J* = 2.3 Hz, *J* = 9.5 Hz, 1H), 4.68 (br m, 1H), 4.42 (br m, 1H), 3.61 (s, 3H), 1.41 (s, 9H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 175.4, 168.7, 158.0, 81.5, 80.4, 54.5, 31.6, 28.1, 27.8, 22.6, 14.1;
IR (thin film): νmax 2980, 2253, 1718, 1646, 1550, 1455, 1420, 1392, 1368, 1254, 1227, 1165, 1131, 1019, 904, 846, 801, 724, 649, 470;
MS calculated for $C_{14}H_{21}O_3$ (M+H): 237.1419. Found: 237.1515.
$[\alpha]_D^{24}$ = 36.6° (*c*= 0.5)

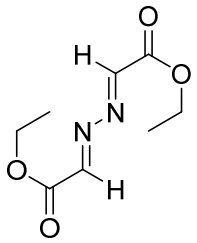


Ethyl 3-methyl-4-methoxy-1-phenylcyclohepta-2,4,6-triene-1-carboxylate (29).
Yield: Obtained in 81% yield (qNMR) with 93% ee using Rh_2(*R*-PTAD)$_4$ and 62% yield (qNMR) with 96% *ee* using Rh_2(*S*-PTAD)$_4$.
Physical appearance: yellow oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 7.25-7.23 (m, 2H), 7.18-7.13 (m, 3H), 6.21 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 5.57 (d, *J* = 7.8 Hz, 1H), 5.10-5.04 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.26 (s, 2H), 2.03 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 174.8, 144.0, 134.1, 129.2, 127.9, 127.2, 126.7, 124.3, 109.7, 61.4, 55.5, 37.3, 29.7, 25.6, 21.8, 18.4, 14.0;
IR (thin film): νmax 2955, 2926, 1731, 1650, 1635, 1556, 1495, 1447, 1413, 1388, 1366, 1231, 1152, 1125, 1095, 1026, 840, 759, 725, 697;
HRMS calculated for $C_{18}H_{21}O_3$ (M+H): 285.1491. Found: 285.1485.



Ethyl-4-methoxy-1,3-dimethylcyclohepta-2,4,6-triene-1-carboxylate (30).
Yield: Obtained in 60% yield (qNMR) with 50% ee using Rh_2(*R*-PTAD)$_4$ and 56% yield (qNMR) with 19% *ee* using Rh_2(*S*-PTAD)$_4$.
Physical appearance: yellow oil;

^{1}H NMR (125 MHz, $CDCl_3$): δ 6.11 (dd, *J* = 7.3 Hz, *J* = 9.0 Hz, 1H), 5.73 (d, *J* = 7.3 Hz, 1H) 5.04 (br s, 1H), 4.99 (d, *J* = 8.9 Hz, 1H), 4.13-3.98 (m, 2H), 3.61 (s, 3H), 1.94 (s, 3H), 1.35 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 176.2, 159.3, 123.9, 105.0, 71.3, 60.7, 55.0, 42.6, 21.9, 19.0, 17.3, 14.2;
IR (thin film): νmax 2977, 2932, 2833, 1730, 1637, 1552, 1452, 1413, 1393, 1367, 1301, 1239, 1220, 1181, 1134, 1090, 1028, 837, 801, 777, 739, 689;
HRMS calculated for $C_{13}H_{18}O_3$ (M+H): 223.1334. Found: 223.1338.
$[\alpha]_D^{24}$ = 6.8° (*c*= 0.7)

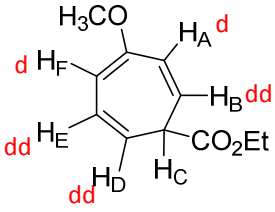


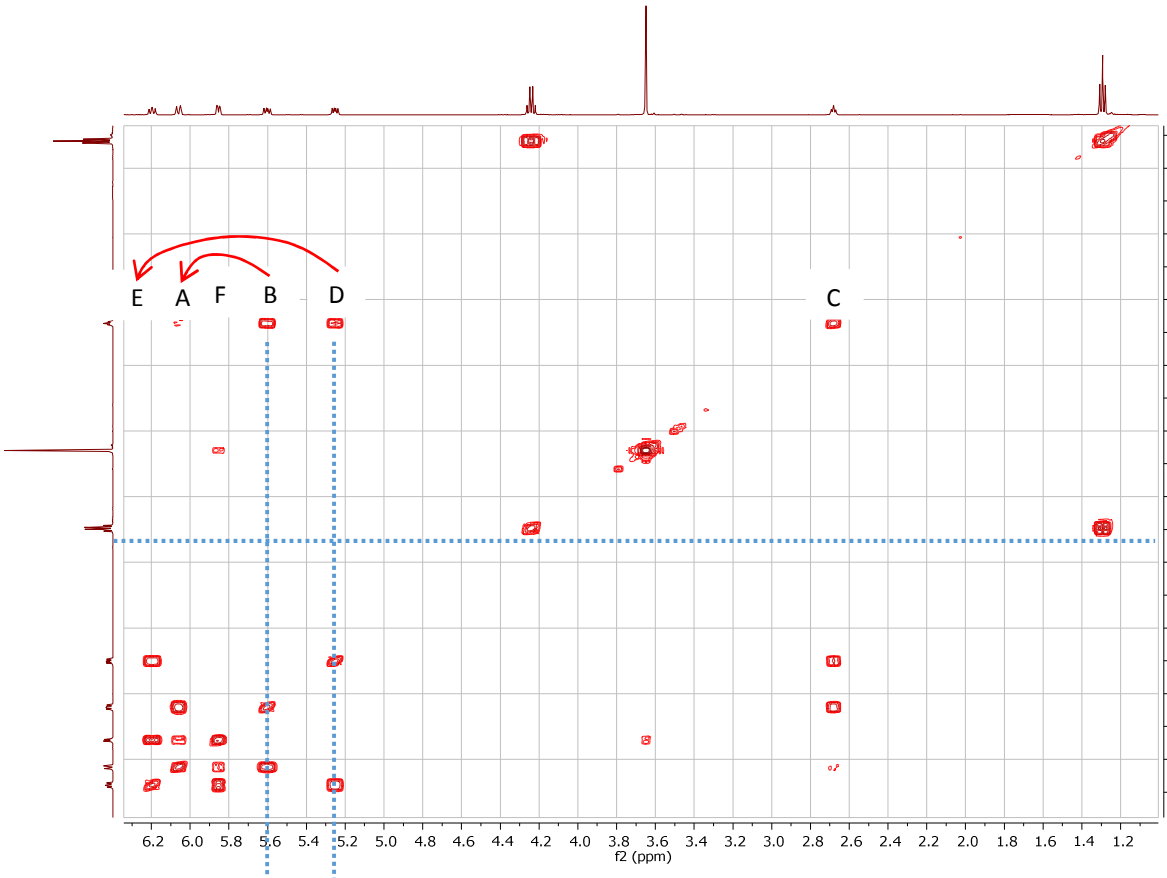
Diethyl 2,2'-(hydrazine-1,2-diylidene)(2E,2'E)-diacetate (S31).
Obtained as a side product in all intermolecular Buchner reactions run with ethyl diazoacetate.
Physical appearance: clear oil;
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.84 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 165.0, 133.6, 61.3, 14.1;
IR (thin film): νmax 2984, 2937, 1719, 1646, 1466, 1447, 1393, 1368, 1298, 1260, 1225, 115, 1096, 1035, 979, 907, 860, 775, 730, 668, 649;
HRMS calculated for $C_8H_{12}N_2O_4Na$ (M+Na): 223.0695 Found: 223.0705.

2.3 Elucidation of Regioisomers

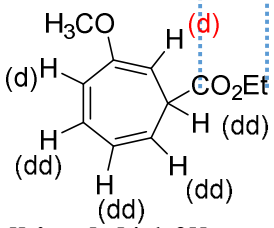
The major regioisomer was confirmed using a combination of 2D NMR experiments. Below are representative critical COSY analyses:

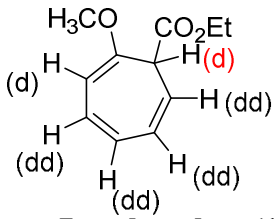
Ethyl 4-methoxycyclohepta-2,4,6-triene-1-carboxylate (3).
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.19 (dd, J = 8.0, 7.1 Hz, 1H), 6.06 (d, J = 9 Hz, 1H), 5.85 (dd, J = 6.7, 1.6 Hz, 1H), 5.60 (dd, J = 9.8, 5.9 Hz, 1H), 5.25 (dd, J = 9.16, 5.2 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.65 (s, 3H), 2.68 (dd, J = 5.5, 5.5 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H).



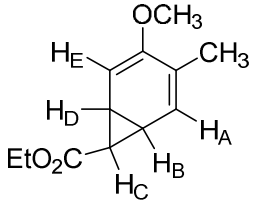


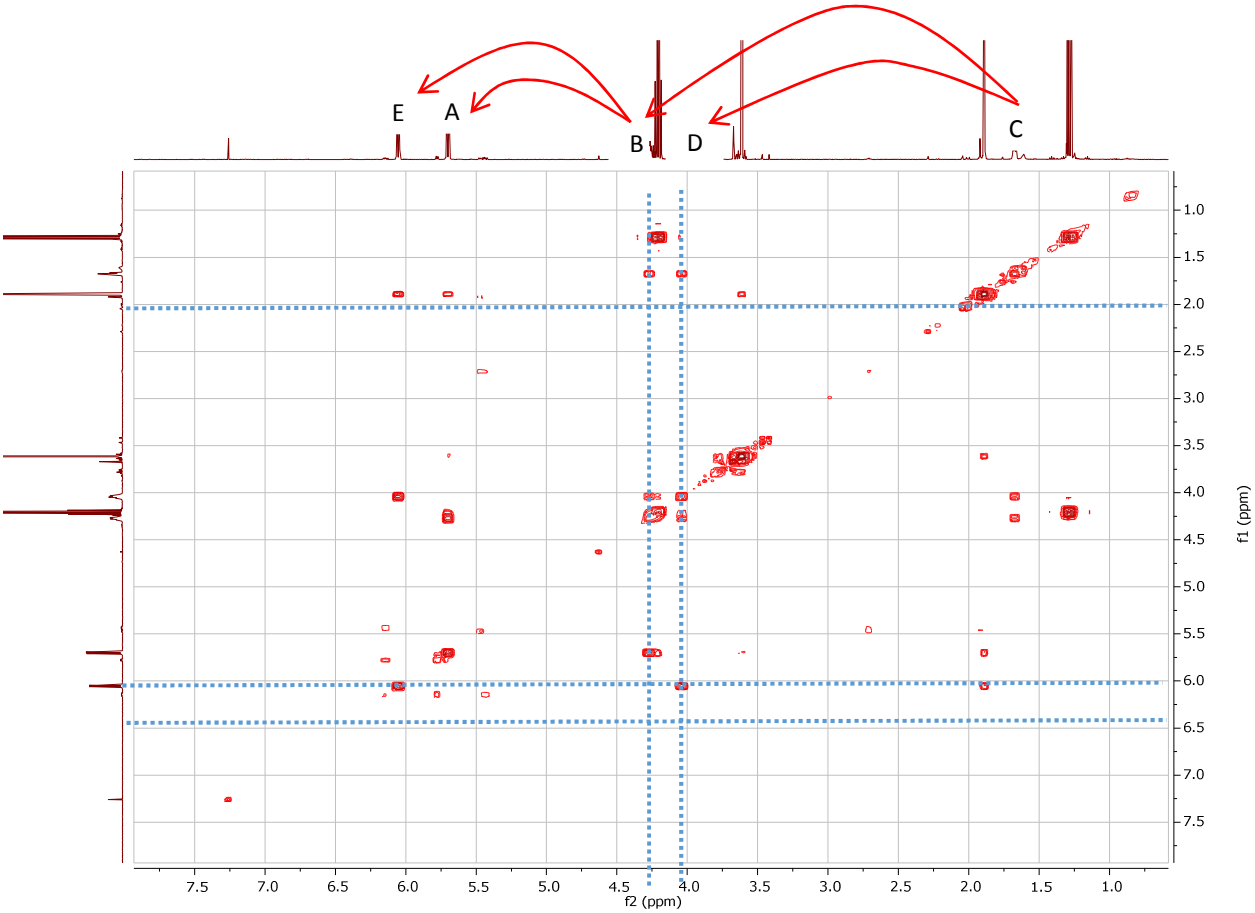
Compared to:



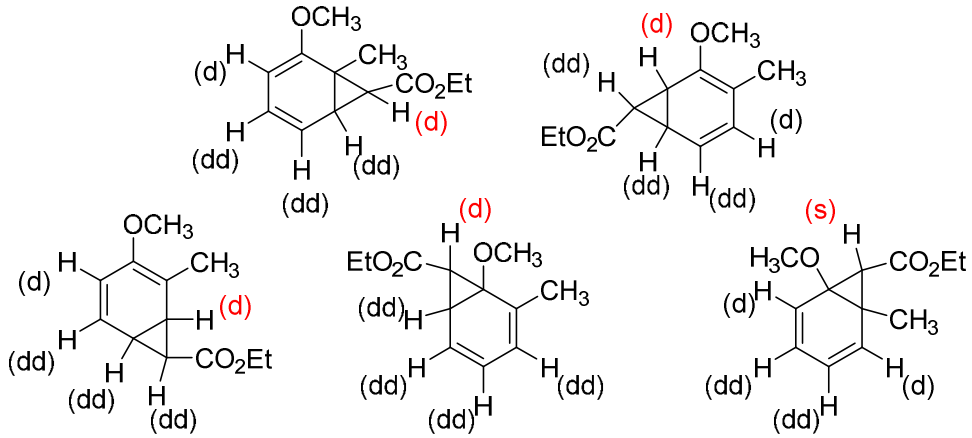


Ethyl 3-methoxy-4-methylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (13).
^{1}H NMR (125 MHz, $CDCl_3$): δ 6.05 (d, J = 7.6 Hz, 1H), 5.70 (d, J = 8.1 Hz, 1H), 4.27 (m, 1H), 4.21 (q, J = 7.1 Hz, 2H) 4.04 (m, 2H), 3.61 (s, 3H), 1.89 (s, 3H), 1.67 (dd, J = 4.9 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H).



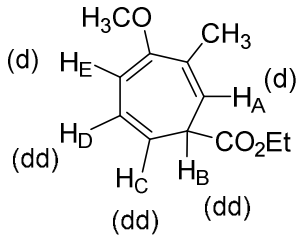


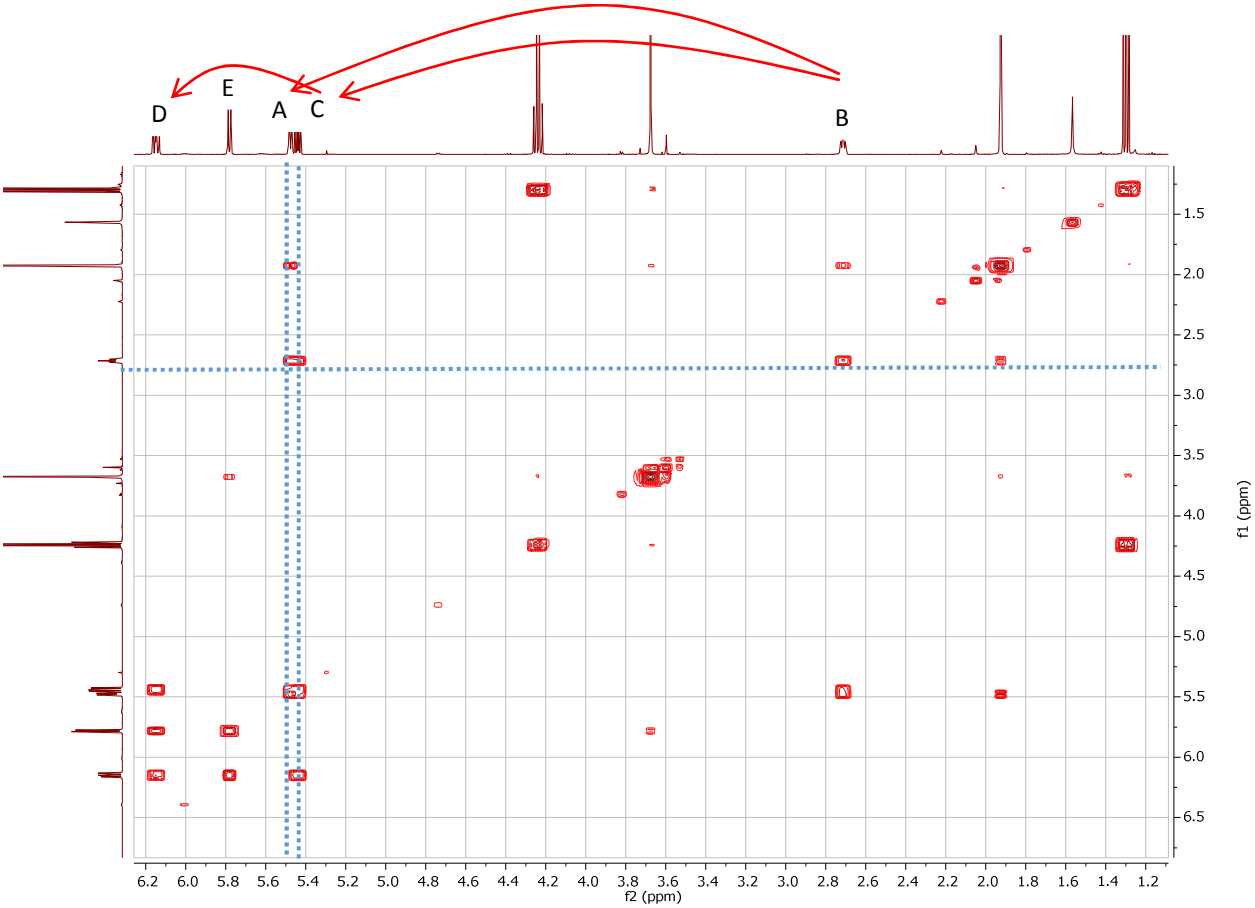
Compared to (also see CHTs on S7):



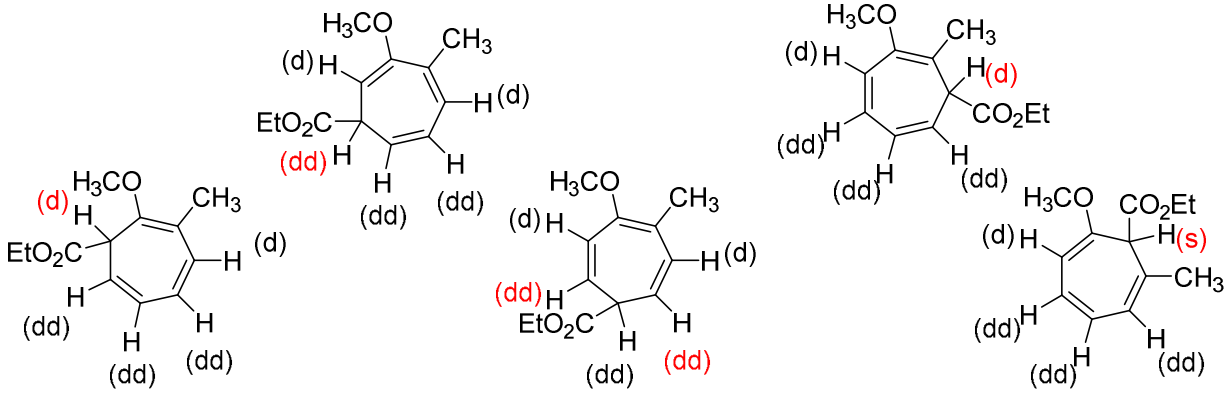
Ethyl 4-methoxy-3-methylcyclohepta-2,4,6-triene-1-carboxylate (14).

^{1}H NMR (125 MHz, $CDCl_3$): δ 6.15 (ddd, J = 9.0 Hz. J = 6.4 Hz, J = 1.4 H, 1H), 5.78 (d, J = 6.4 Hz, 1H), 5.48 (d, J = 6.3 Hz, 1H), 5.44 (dd, J = 9.2 Hz, 5.4 Hz, 1H) 4.24 (q, J = 7.1 Hz, 2H), 3.68 (s, 3H), 2.71 (dd, J = 6.1 Hz, 6.1 Hz, 1H), 1.93 (t, J = 1.3 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H).

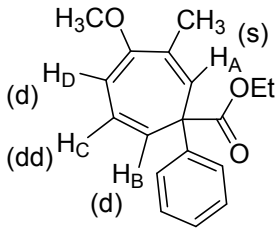


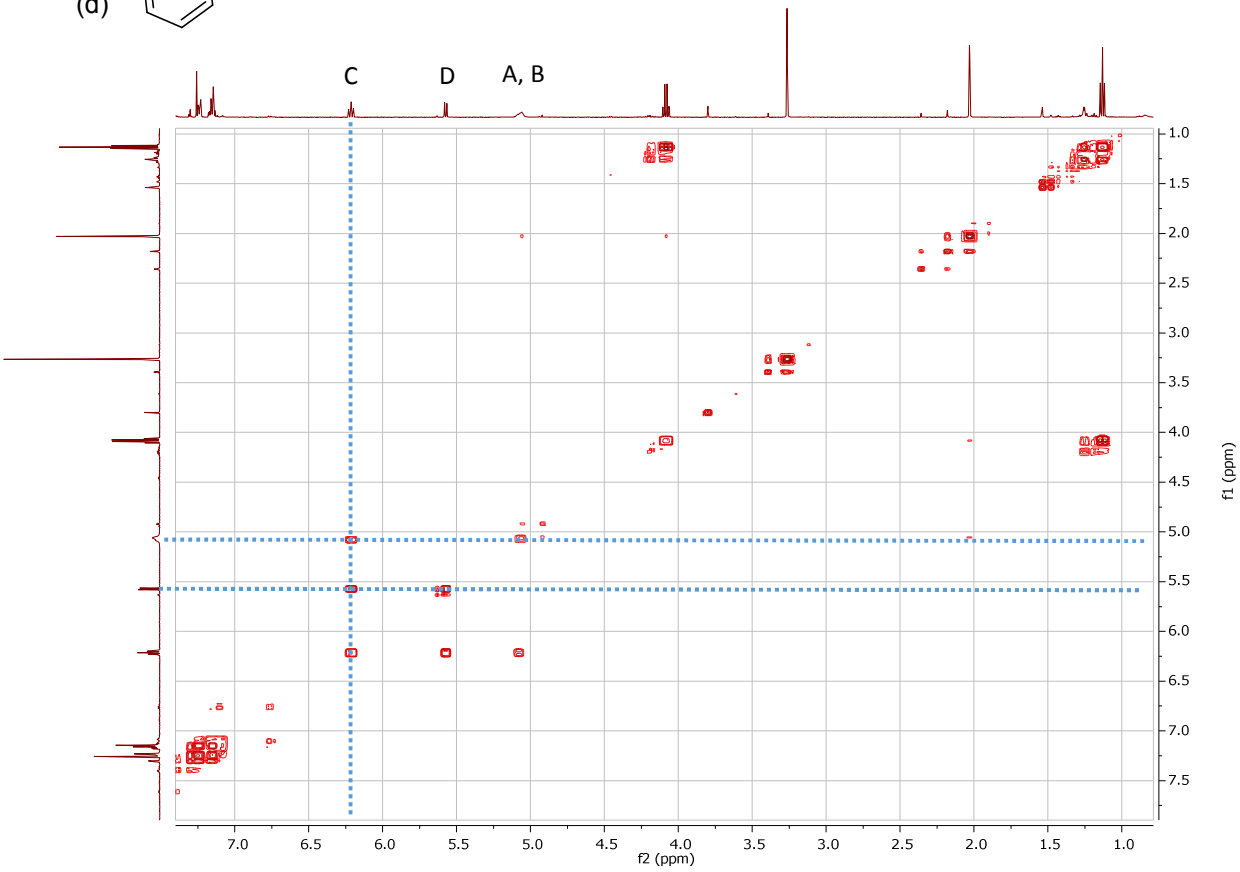


Compared to (also see NCDs on S6):

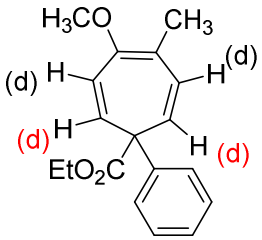


Ethyl 3-methyl-4-methoxy-1-phenylcyclohepta-2,4,6-triene-1-carboxylate (30).
^{1}H NMR (125 MHz, $CDCl_3$): δ 7.25-7.23 (m, 2H), 7.18-7.13 (m, 3H), 6.21 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 5.57 (d, *J* = 7.8 Hz, 1H), 5.10-5.04 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.26 (s, 2H), 2.03 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H);

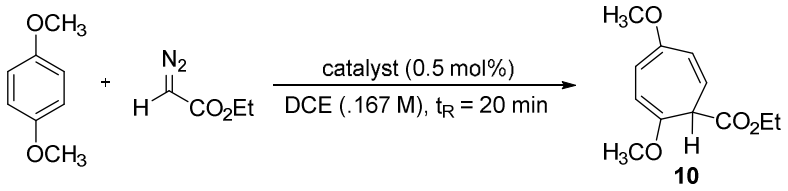




Compared to:



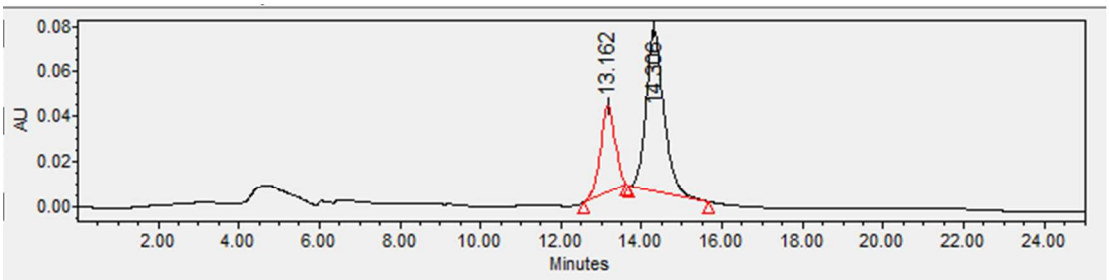
3. Chiral HPLC Traces



10

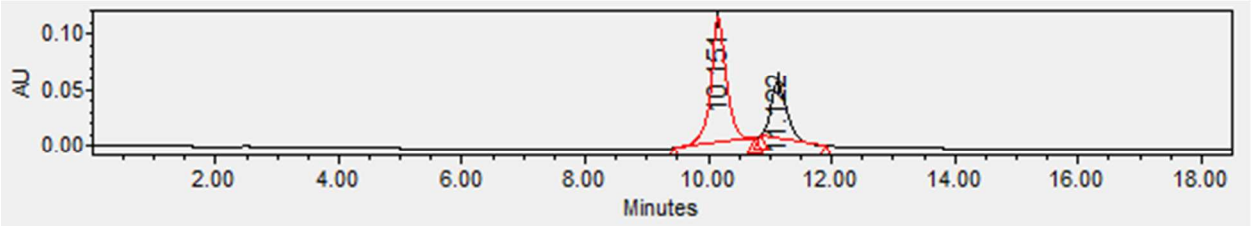
Column data: Whelko® column, Hexane : IPA = 99 : 1, 1 mL/min, 254 nm.

Catalyzed by Rh_2(R-PTAD)$_4$: 75% yield, 30.3 : 69.7 e.r., 40% *ee*



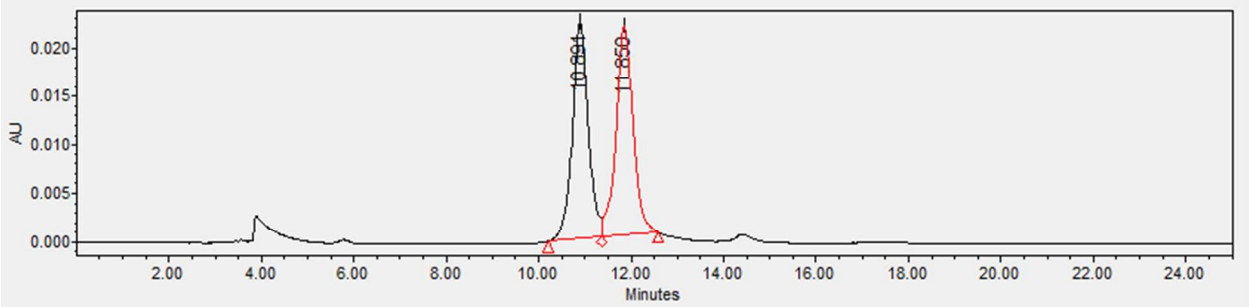
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		13.162	954806	30.29	37982	bb			Unknown	
2		14.306	2197902	69.71	71474	bb			Unknown	

Catalyzed by Rh_2(S-PTAD)$_4$: % yield, 70.4 : 30.6 e.r.; 41% *ee*

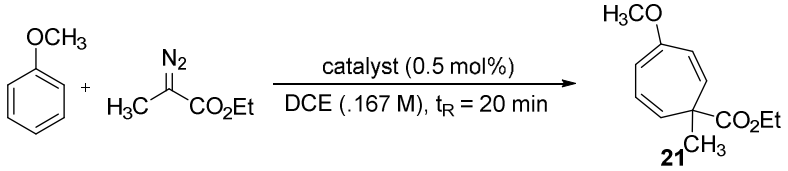


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		10.151	1998668	70.44	112244	bb			Unknown	
2		11.122	838676	29.56	49633	bb			Unknown	

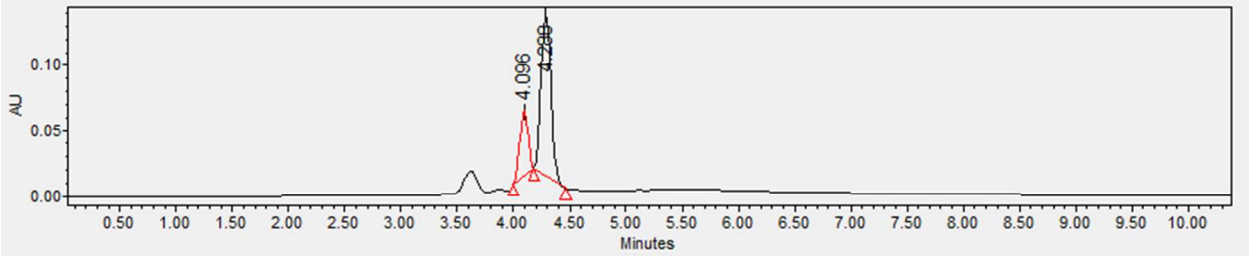
Racemic mixture:



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		10.891	538927	49.31	22289	BV			Unknown	
2		11.850	553912	50.69	21495	Vb			Unknown	



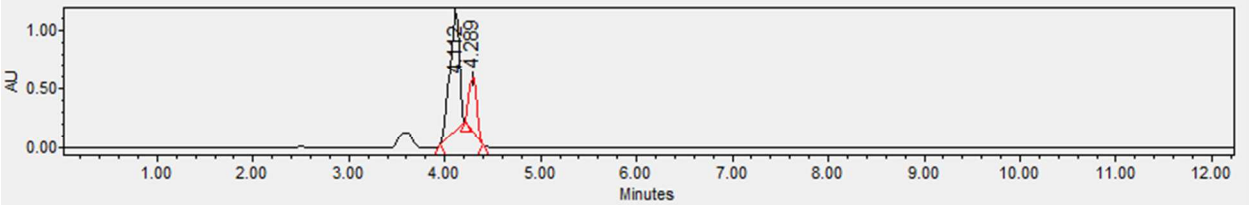
Column data: Chiralpak® AD column, Hexane : IPA = 99 : 1, 1 mL/min, 254 nm.



Catalyzed by Rh_2(R-PTAD)$_4$: 55% yield, 25.7 : 74.2 e.r., 49% *ee*

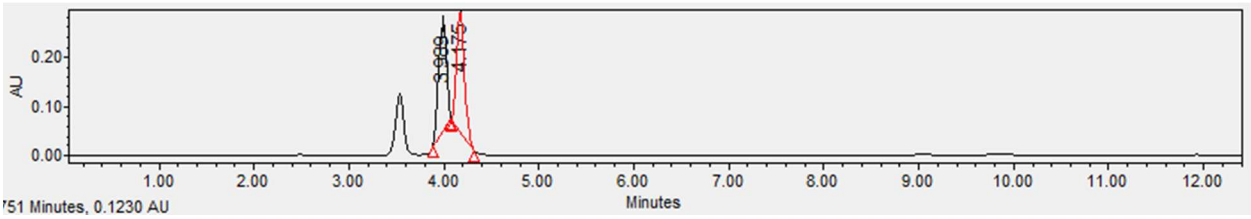
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		4.096	261064	25.74	50034	bb			Unknown	
2		4.288	753218	74.26	124561	bb			Unknown	

Catalyzed by Rh_2(S-PTAD)$_4$: 41% yield, 75.1 : 24.9 e.r., 50% *ee*

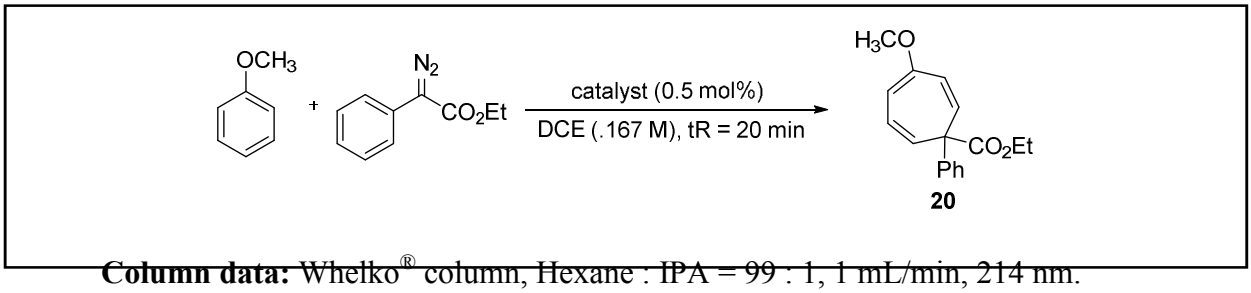


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		4.112	6932180	75.10	986344	bb			Unknown	
2		4.289	2298774	24.90	445722	bb			Unknown	

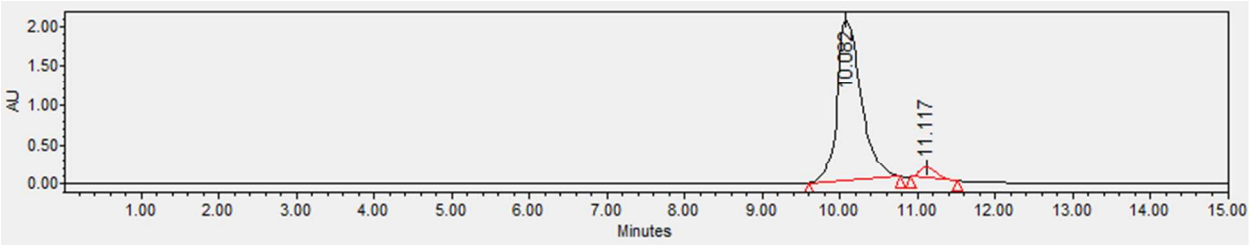
Mixture of R- and S-catalyzed reactions:



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		3.989	1184698	45.57	217146	bb			Unknown	
2		4.175	1414925	54.43	244101	bb			Unknown	



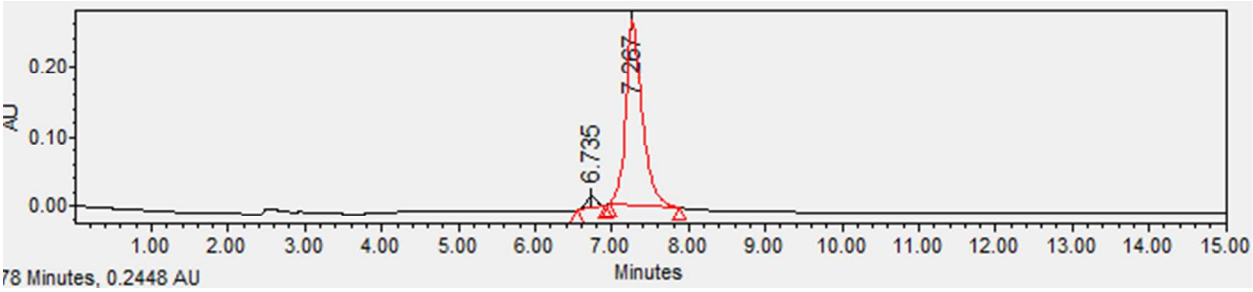
Column data: Whelko® column, Hexane : IPA = 99 : 1, 1 mL/min, 214 nm.



Catalyzed by Rh_2(R-PTAD)$_4$: 71% yield, 95.4 : 4.6 e.r., 91% *ee*

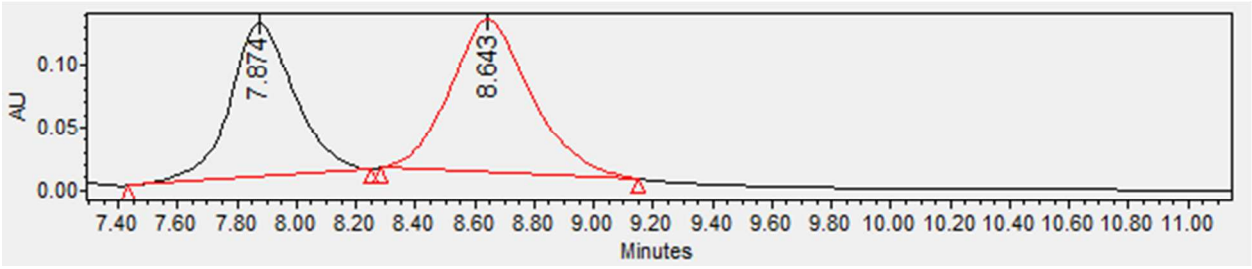
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		10.082	43994179	95.43	2034999	bb			Unknown	
2		11.117	2108517	4.57	144554	bb			Unknown	

Catalyzed by Rh_2(S-PTAD)$_4$: 73% yield, 3.7 : 96.3 e.r., 93% *ee*

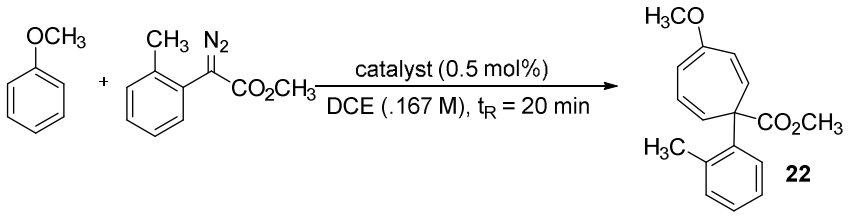


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		6.735	148591	3.66	15838	bb			Unknown	
2		7.267	3914788	96.34	262828	bb			Unknown	

Mixture of R- and S-catalyzed reactions:

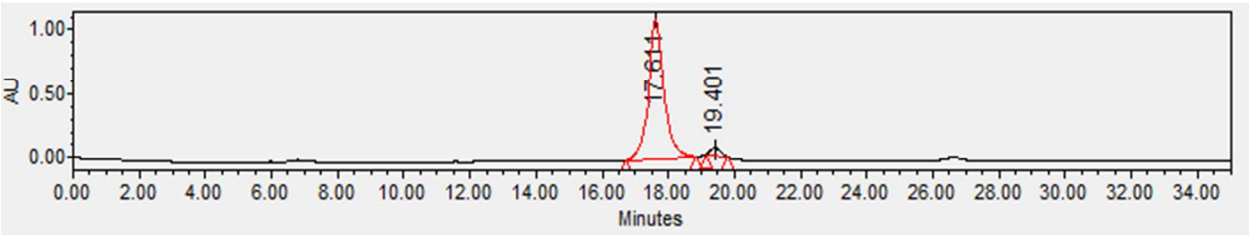


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.874	1846615	44.30	122410	bb			Unknown	
2		8.643	2322098	55.70	121708	bb			Unknown	



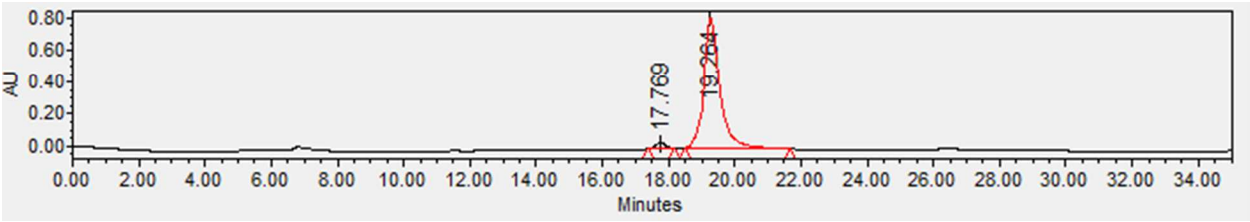
Column data: Whelko® column, Hexane : IPA = 99 : 1, 1 mL/min, 214 nm.

Catalyzed by Rh_2(R-PTAD)$_4$: 36% yield, 96.7 : 3.3 e.r., 93% *ee*



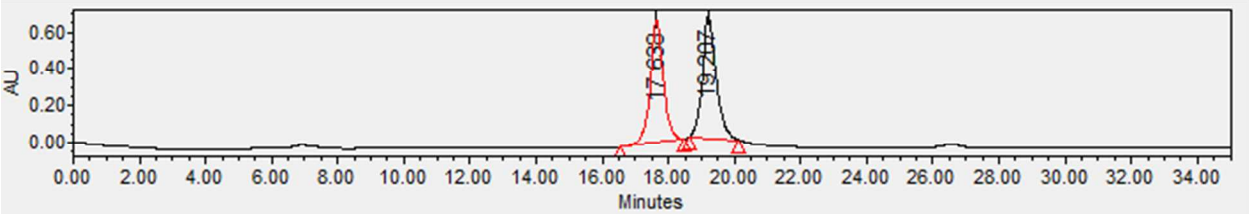
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.611	35292182	96.72	1089116	bb			Unknown	
2		19.401	1195683	3.28	56388	bb			Unknown	

Catalyzed by Rh_2(S-PTAD)$_4$: 35% yield, 2.8 : 97.2 e.r., 94% *ee*

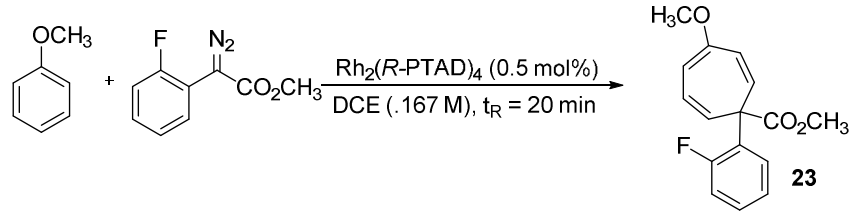


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.769	810643	2.83	37290	bb			Unknown	
2		19.264	27814140	97.17	817895	bb			Unknown	

Mixture of R- and S-catalyzed reactions:

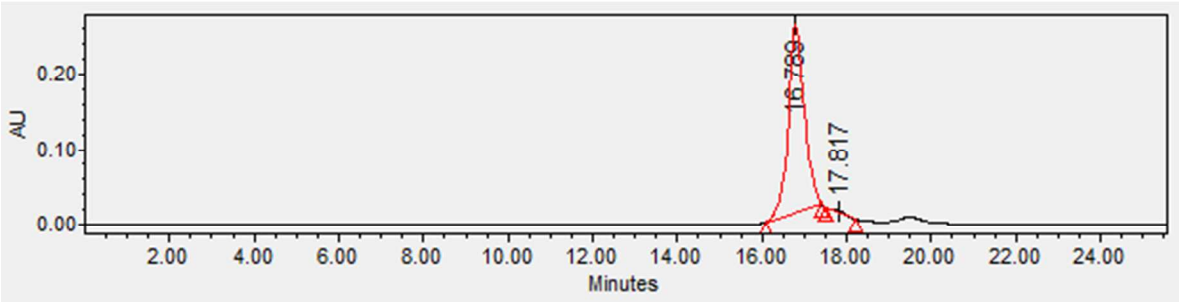


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.638	18221653	48.80	666647	bb			Unknown	
2		19.207	19119042	51.20	663402	bb			Unknown	

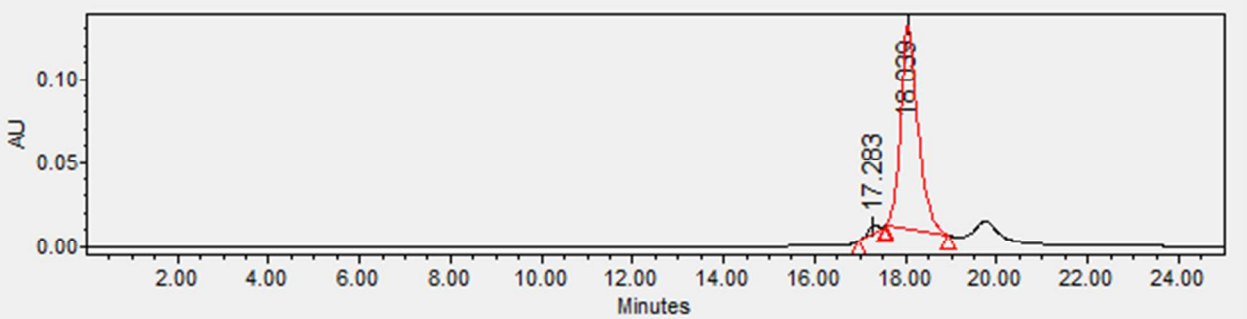


Column data: Whelko® column, Hexane : IPA = 99 : 1, 1 mL/min, 254 nm.

Catalyzed by Rh_2(R-PTAD)$_4$: 48% yield, 99.0 : 1.0 e.r., 99% *ee*

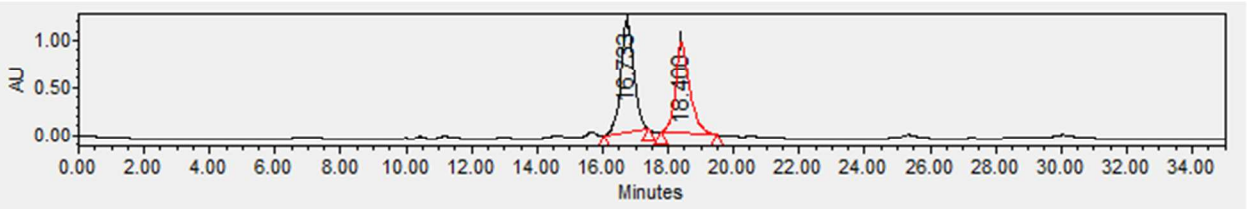


Catalyzed by Rh_2(S-PTAD)$_4$: 48% yield, 2.8 : 97.2 e.r., 98% *ee*

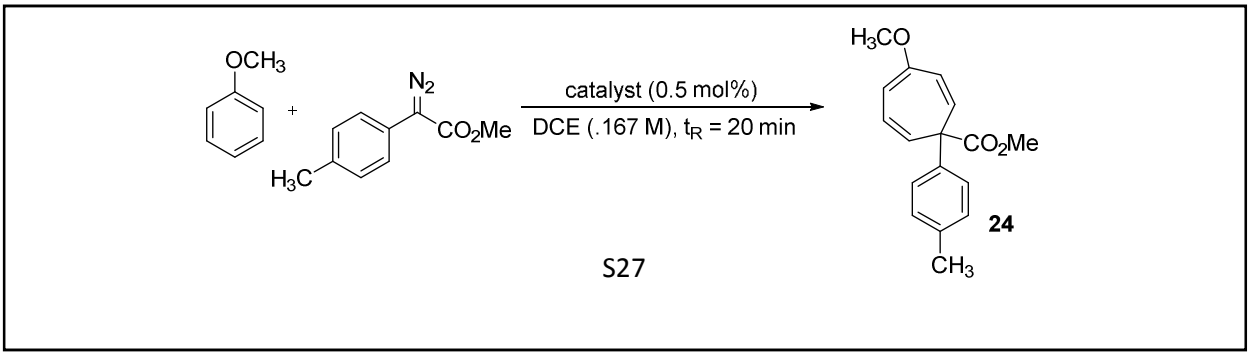


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.283	69393	2.12	4623	bb			Unknown	I08
2		18.039	3200901	97.88	121098	bb			Unknown	

Mixture of R- and S-catalyzed reactions:

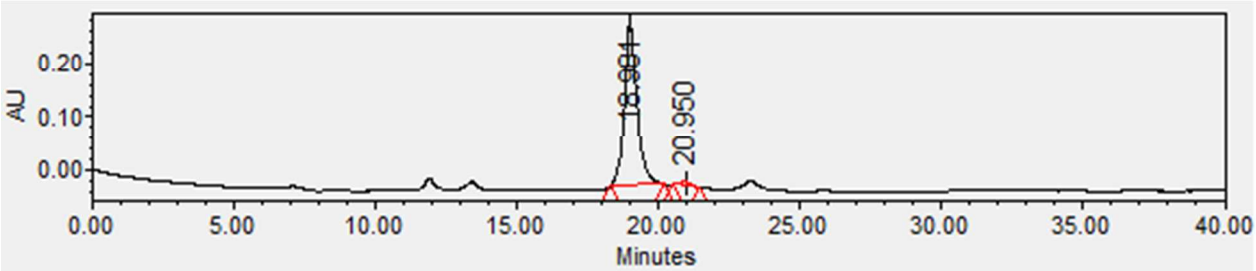


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.733	32629230	53.23	1180274	bb			Unknown	
2		18.400	28670001	46.77	958057	bb			Unknown	



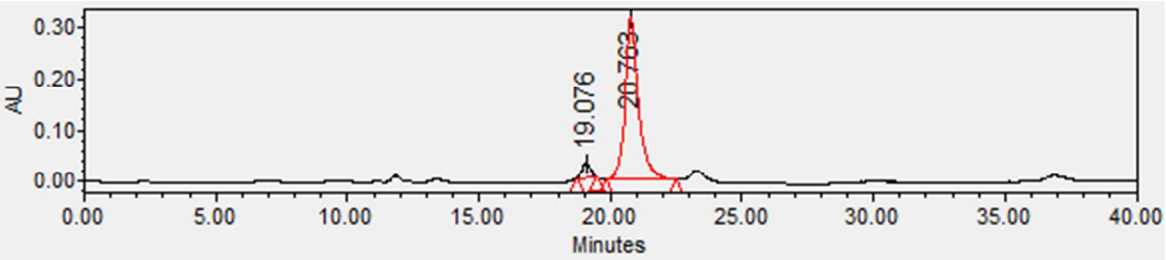
Column data: Whelko® column, Hexane : IPA = 99 : 1, 1 mL/min, 214 nm.

Catalyzed by Rh_2(R-PTAD)$_4$: 41% yield, 97.9 : 2.1 e.r., 96% *ee*



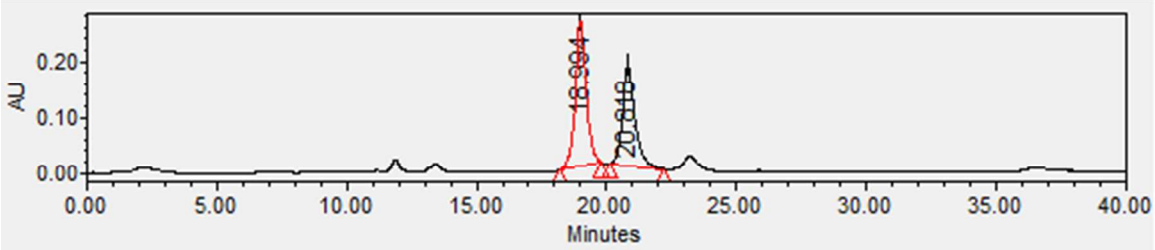
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		18.981	9391356	97.93	304800	bb			Unknown	
2		20.950	198733	2.07	7405	bb			Unknown	I08

Catalyzed by Rh_2(S-PTAD)$_4$: 35% yield, 5.5 : 94.5 e.r., 89% *ee*

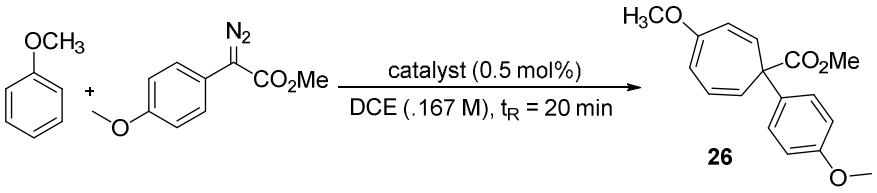


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		19.076	651067	5.48	29196	bb			Unknown	
2		20.763	11231546	94.52	315835	bb			Unknown	

Mixture of R- and S-catalyzed reactions:

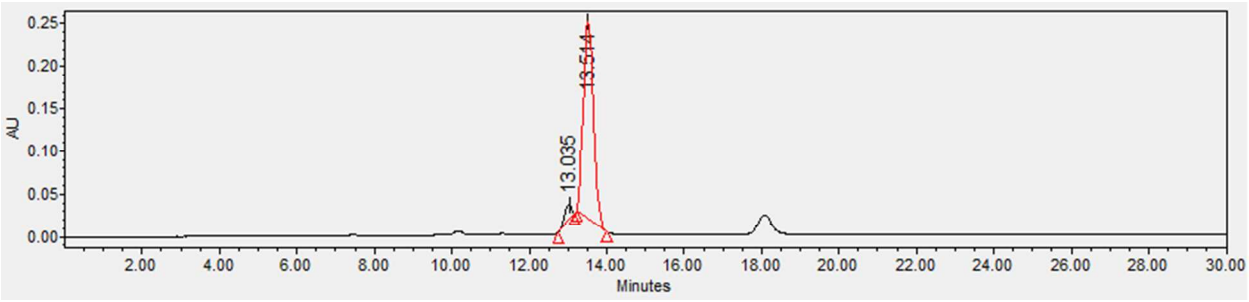


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		18.994	7567834	55.73	259640	bb			Unknown	
2		20.818	6010638	44.27	180177	bb			Unknown	



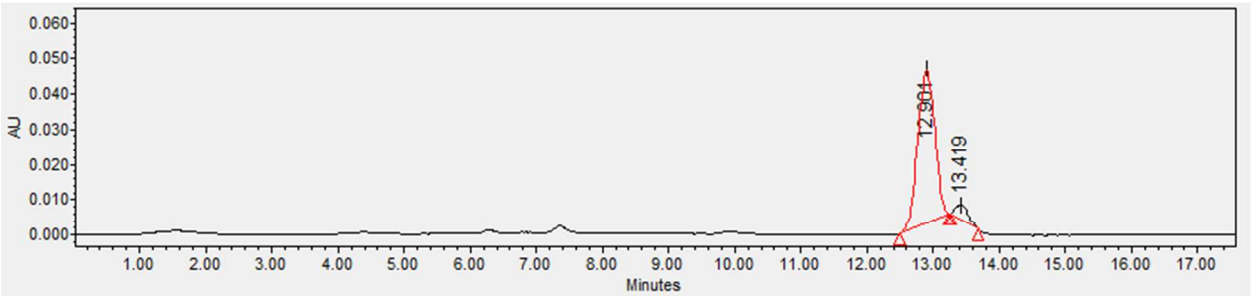
Column data: Chiralpak® AD column, Hexane : IPA = 99 : 1, 1 mL/min, 254 nm.

Catalyzed by Rh_2(R-PTAD)$_4$: 43% yield, 5.3 : 94.7 e.r., 89% *ee*

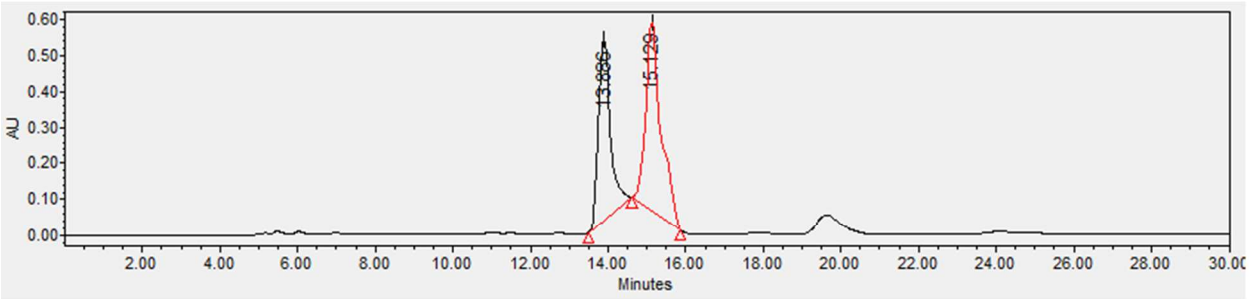


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		13.035	234673	5.31	18304	bb			Unknown	
2		13.514	4181378	94.69	230603	bb			Unknown	

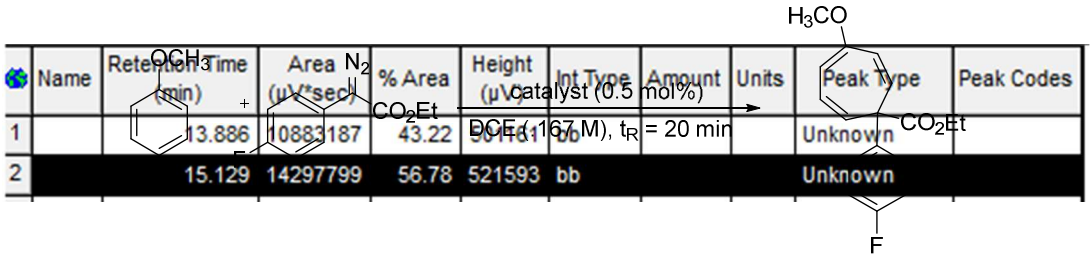
Catalyzed by Rh_2(S-PTAD)$_4$: 25% yield, 93.0 : 7.0 e.r., 86% *ee*



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.901	770712	93.04	43392	bb			Unknown	
2		13.419	57682	6.96	4232	bb			Unknown	



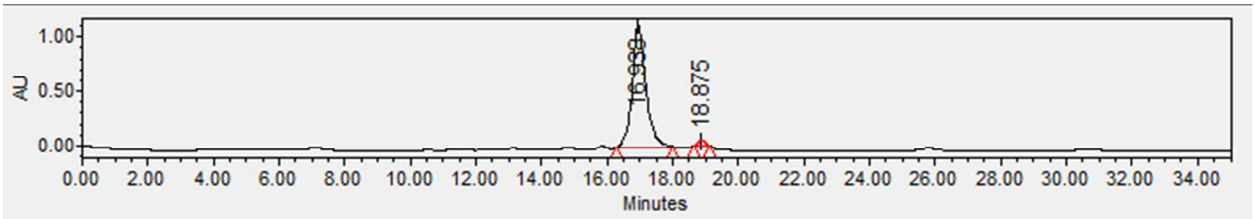
Mixture of R- and S-catalyzed reactions:



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		13.886	10883187	43.22	501161	bb			Unknown	
2		15.129	14297799	56.78	521593	bb			Unknown	

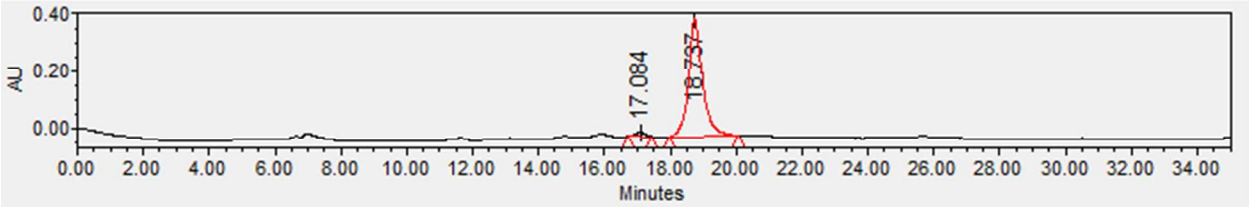
Column data: Whelko® column, Hexane : IPA = 99 : 1, 1 mL/min, 214 nm

Catalyzed by Rh_2(R-PTAD)$_4$: 76% yield, 97.7 : 2.3 e.r., 95% *ee*



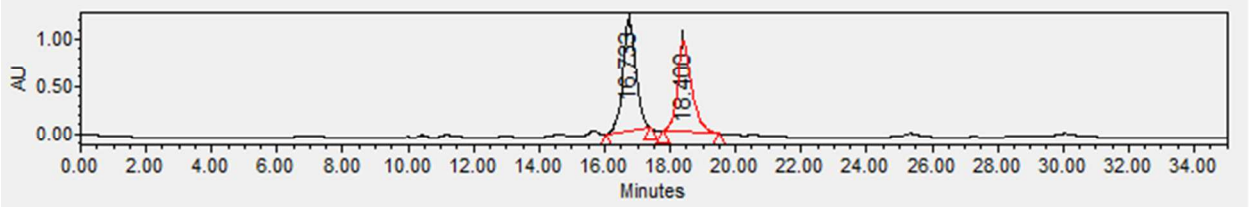
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.938	32345609	97.68	1115500	bb			Unknown	
2		18.875	768196	2.32	47321	bb			Unknown	

Catalyzed by Rh_2(S-PTAD)$_4$: 76% yield, 2.41 : 97.6 e.r., 95% *ee*

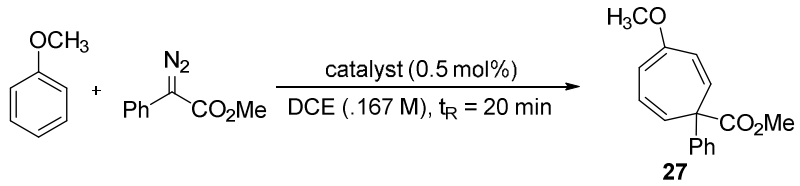


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.084	302008	2.41	15237	bb			Unknown	
2		18.737	12220694	97.59	412163	bb			Unknown	

Mixture of R- and S-catalyzed reactions



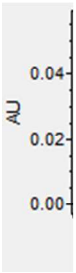
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.733	32629230	53.23	1180274	bb			Unknown	
2		18.400	28670001	46.77	958057	bb			Unknown	



27

Column data: Chiralpak® AD column, Hexane : IPA = 99 : 1, 1 mL/min, 254 nm

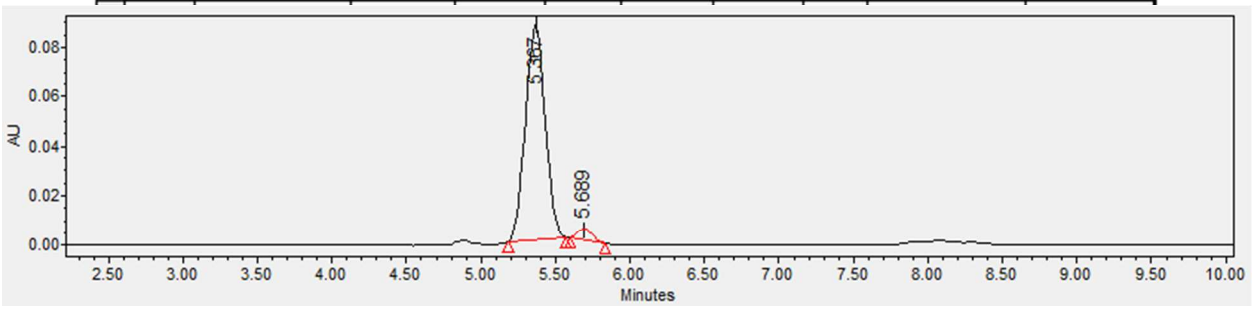
Catalyzed by Rh_2(R-PTAD)$_4$: 72% yield, 4.5 : 95.5 e.r., 91% *ee*

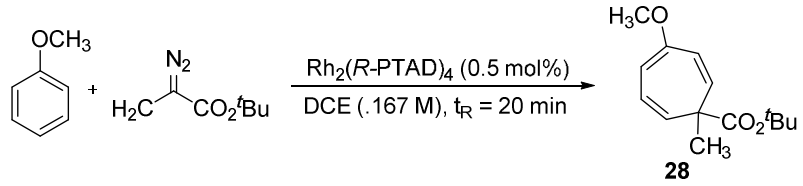


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.426	27013	4.54	3474	bb			Unknown	
2		5.747	568456	95.46	53425	bb			Unknown	

Catalyzed by Rh_2(S-PTAD)$_4$: 81% yield, 96.3 : 3.7 e.r., 93% *ee*

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.367	794013	96.34	86396	bb			Unknown	
2		5.689	30169	3.66	4291	bb			Unknown	

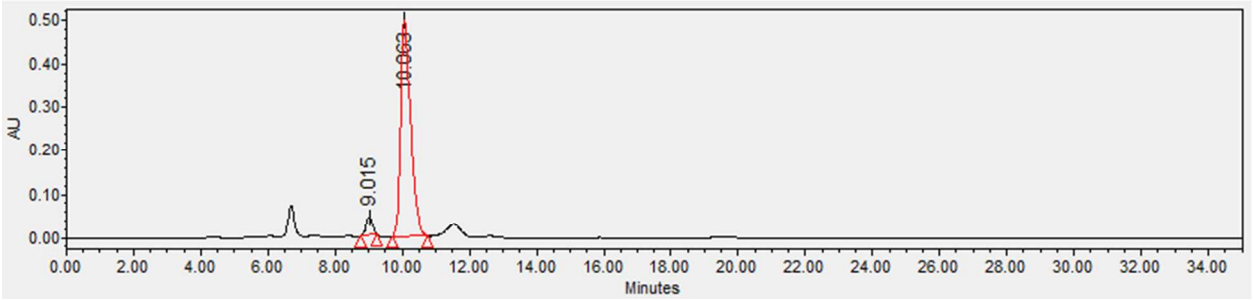




28

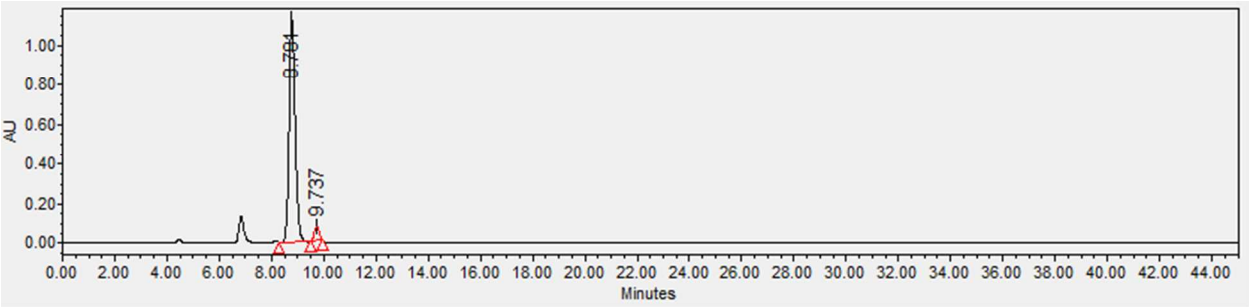
Column data: Chiralpak® AD column, Hexane : IPA = 100 : 0, 1 mL/min, 214 nm.

Catalyzed by Rh_2(R-PTAD)$_4$: 21% yield, 5.3 : 94.7 e.r., 89% *ee*

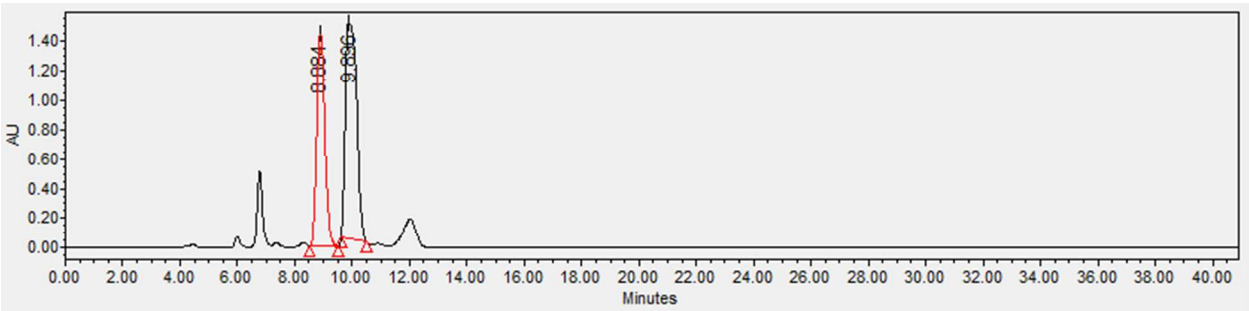


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		9.015	570740	5.27	42274	bb			Unknown	
2		10.063	10255217	94.73	496978	bb			Unknown	

Catalyzed by Rh_2(S-PTAD)$_4$: 31% yield, 95.1 : 4.9 e.r., 90% *ee*

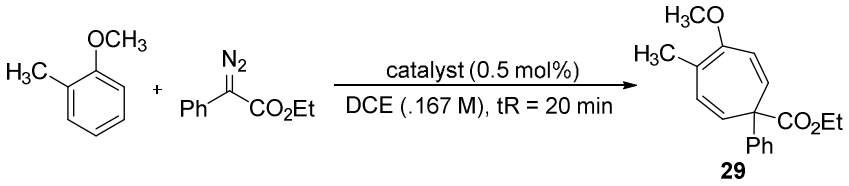


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.781	18432243	95.07	1120725	bb			Unknown	
2		9.737	956494	4.93	71812	bb			Unknown	



Mixture of R- and S-catalyzed reactions:

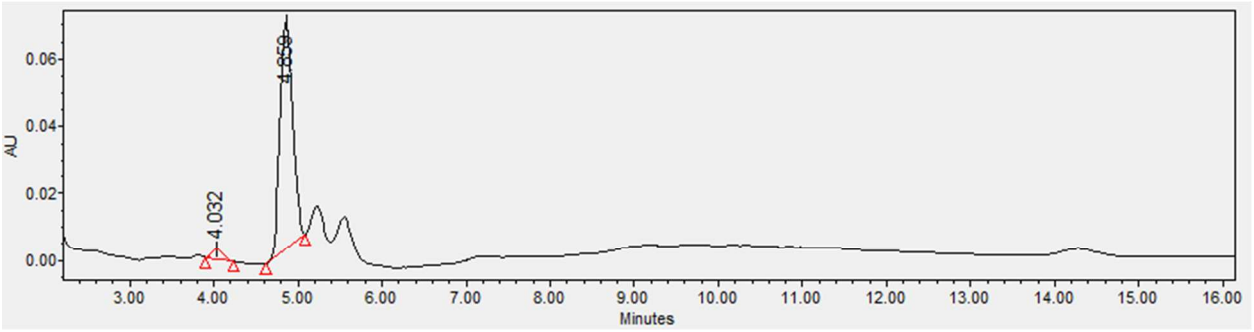
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.884	28743902	41.57	1432403	bb			Unknown	
2		9.896	40400379	58.43	1454943	bb			Unknown	



29

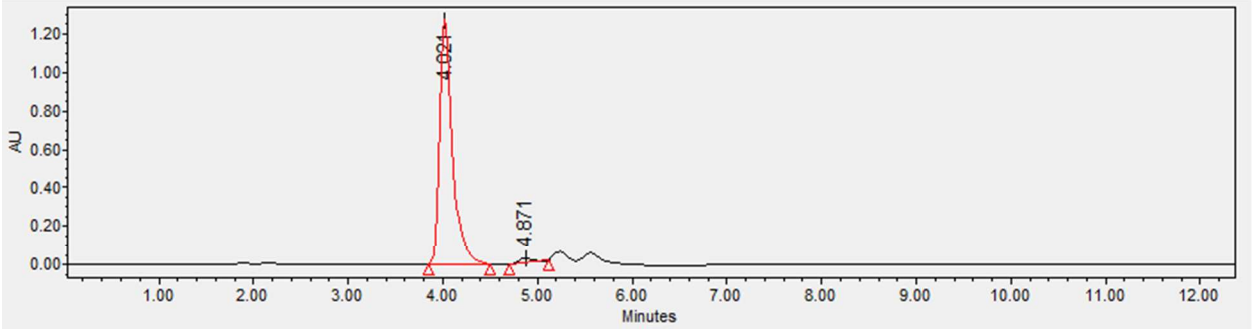
Column data: Chiralpak® AD column, Hexane : IPA = 99 : 1, 1 mL/min, 214 nm.

Catalyzed by Rh_2(R-PTAD)$_4$: 81% yield, 3.5 : 96.5 e.r., 93% *ee*



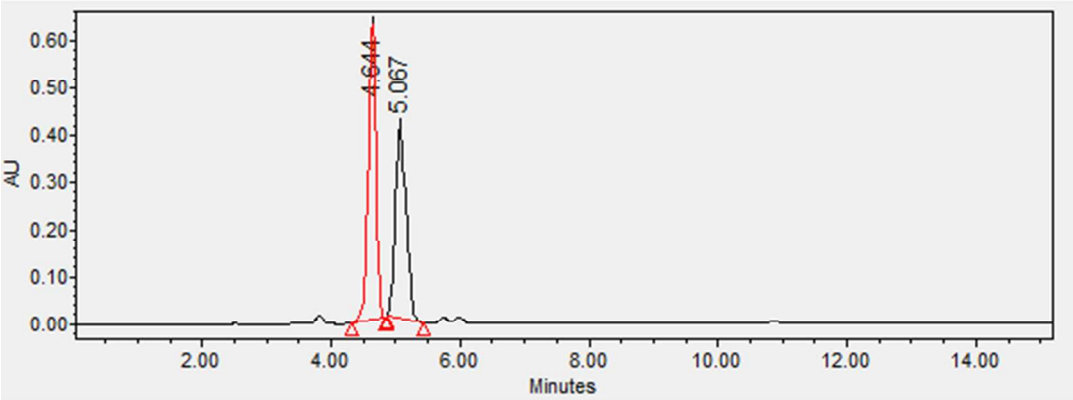
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		4.032	24912	3.50	3020	bb			Unknown	
2		4.859	687342	96.50	67289	bb			Unknown	

Catalyzed by Rh_2(S-PTAD)$_4$: 62% yield, 98.2 : 2.0 e.r., 96% *ee*

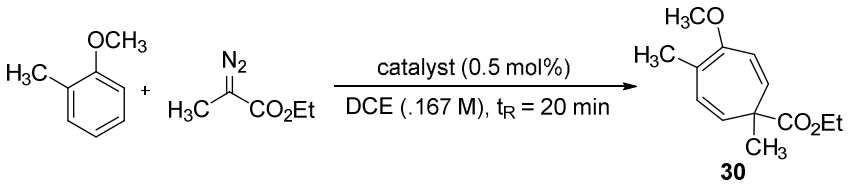


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		4.021	12387016	98.00	1271500	bb			Unknown	
2		4.871	253049	2.00	26013	bb			Unknown	

Mixture of R- and S-catalyzed reactions:



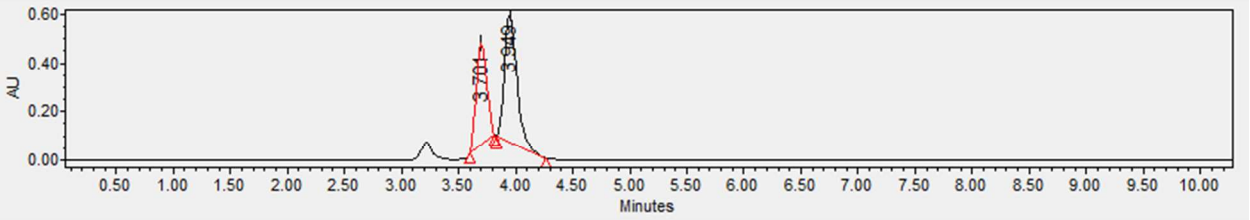
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		4.644	5217626	52.21	626056	bb			Unknown	
2		5.067	4775233	47.79	405255	bb			Unknown	



30

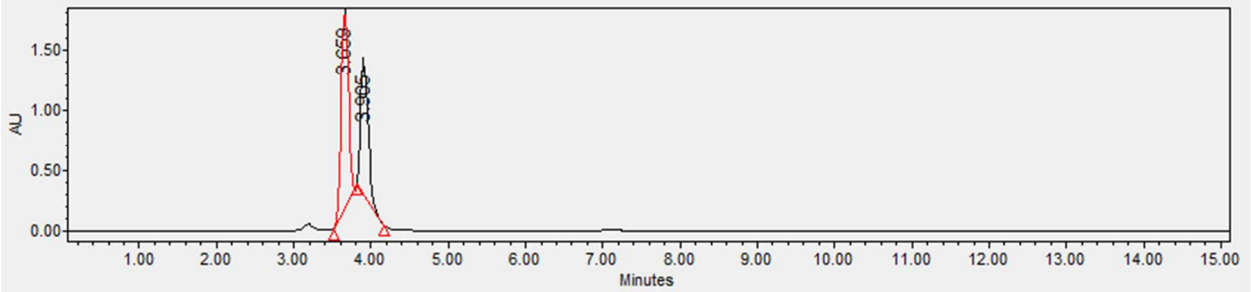
Column data: Chiralpak® AD column, Hexane : IPA = 99 : 1, 1 mL/min, 254 nm.

Catalyzed by Rh_2(R-PTAD)$_4$: 60% yield, 39.8 : 60.3 e.r., 21% *ee*



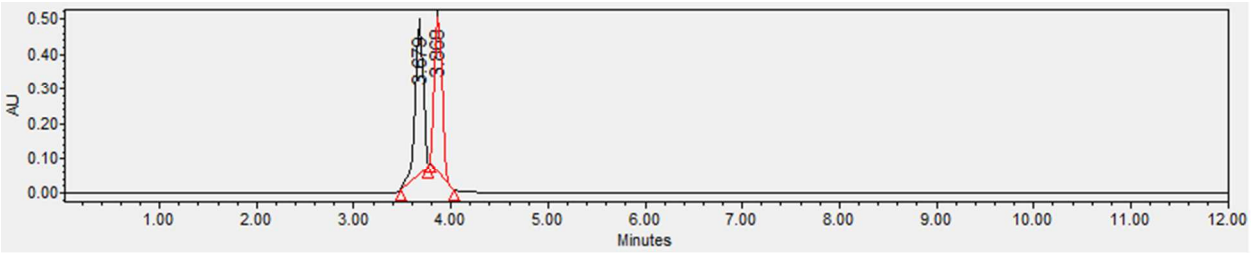
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		3.701	2637685	39.75	413517	bb			Unknown	
2		3.949	3998192	60.25	526227	bb			Unknown	

Catalyzed by Rh_2(S-PTAD)$_4$: 56% yield, 59.3 : 40.7 e.r., 19% *ee*



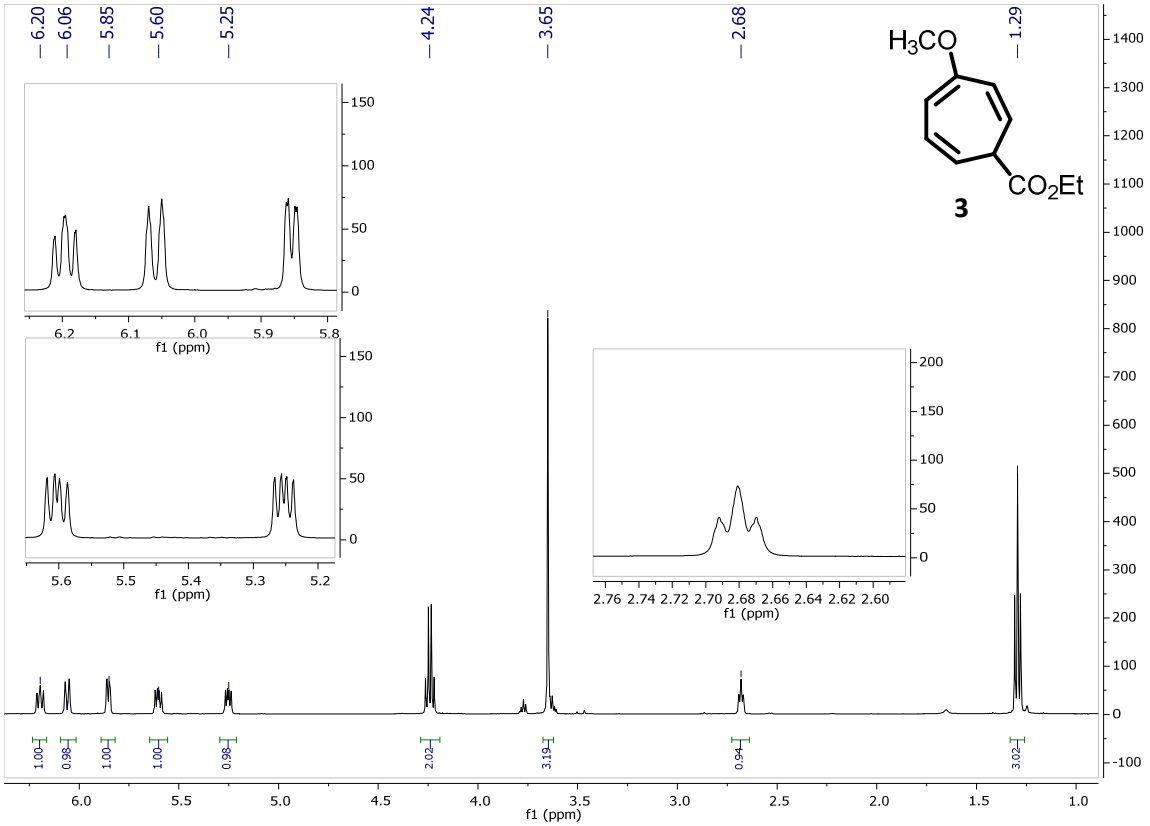
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		3.659	10947299	59.30	1605100	bb			Unknown	
2		3.905	7514046	40.70	1086422	bb			Unknown	

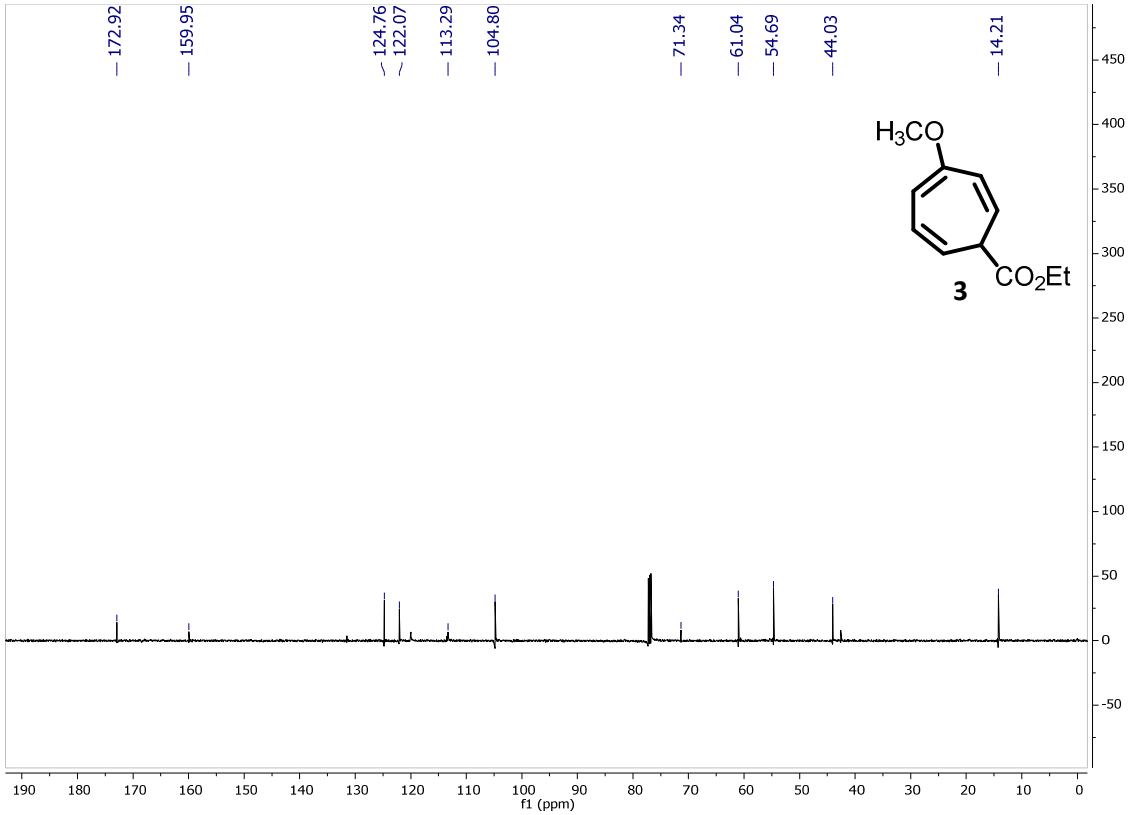
Mixture of R- and S-catalyzed reactions:

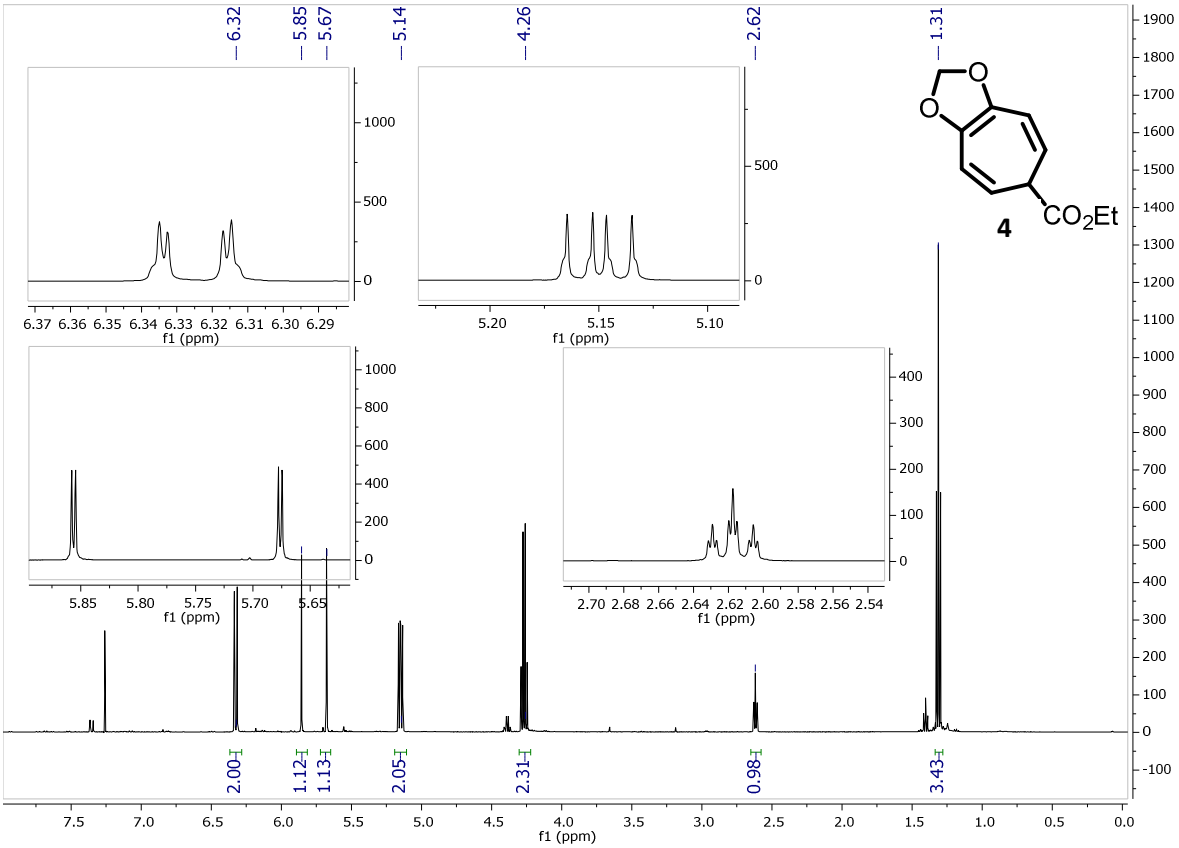


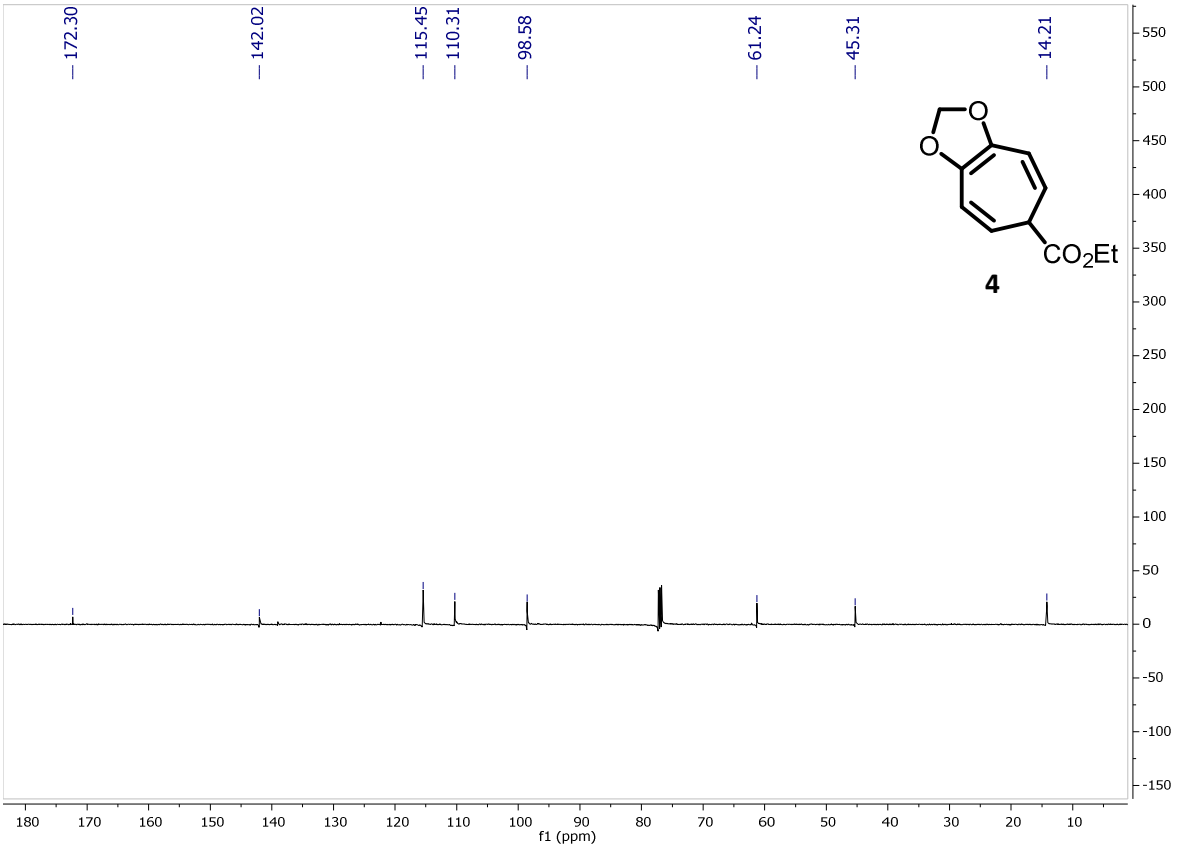
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		3.679	2464593	51.28	429456	bb			Unknown	
2		3.868	2341893	48.72	438602	bb			Unknown	

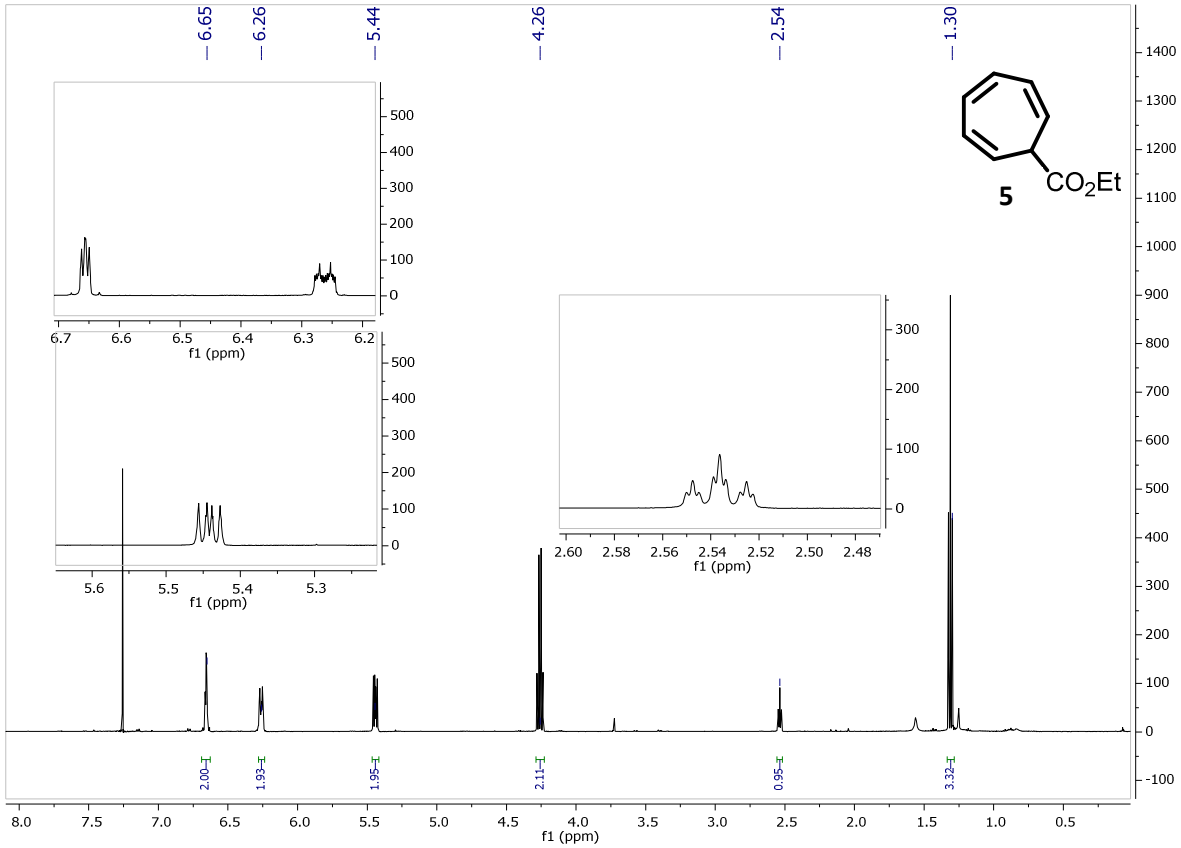
4. ^{1}H and ^{13}C NMR Spectra

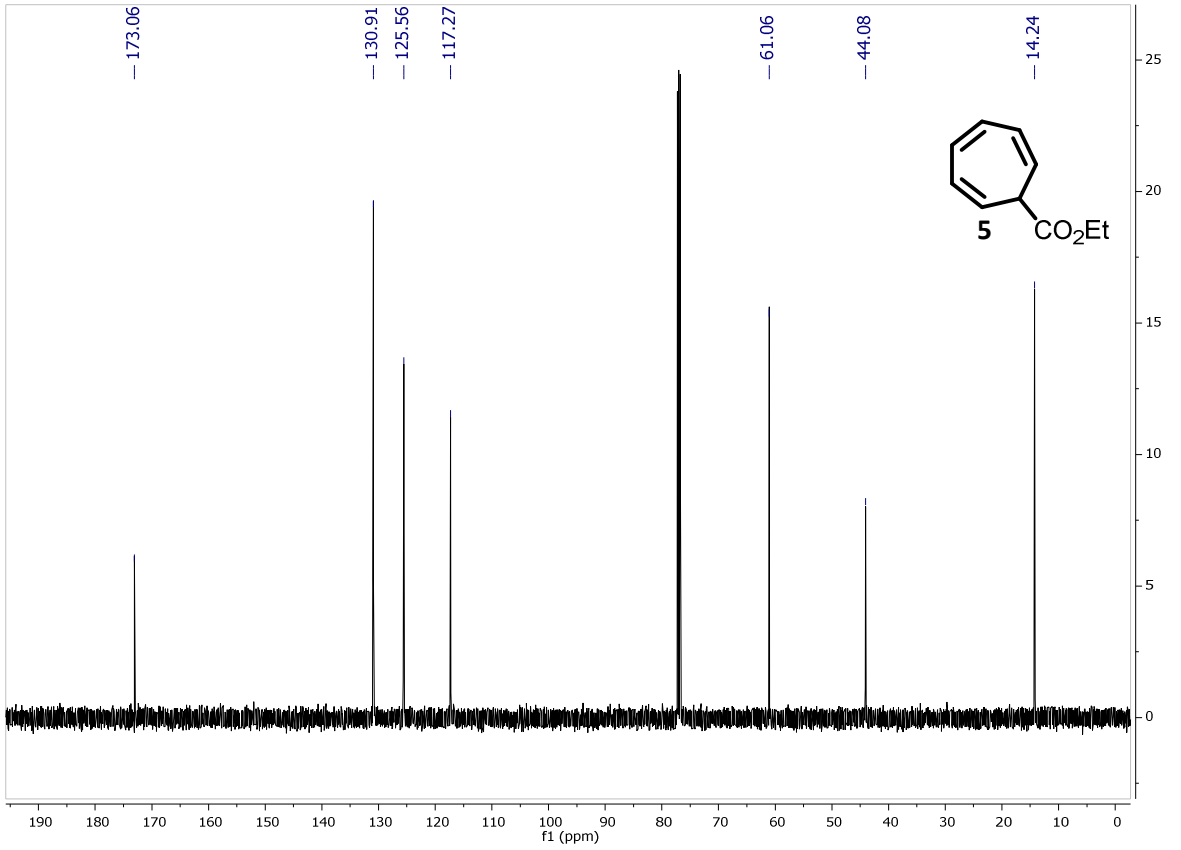


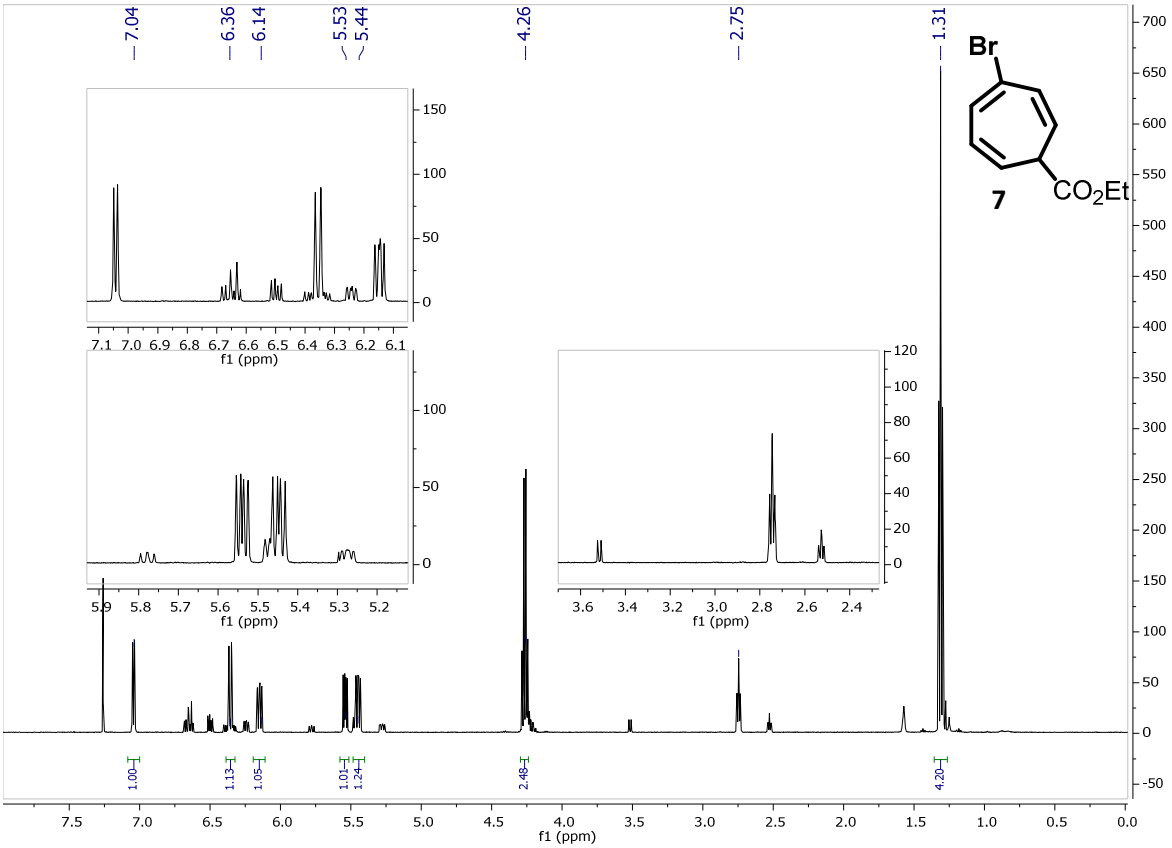


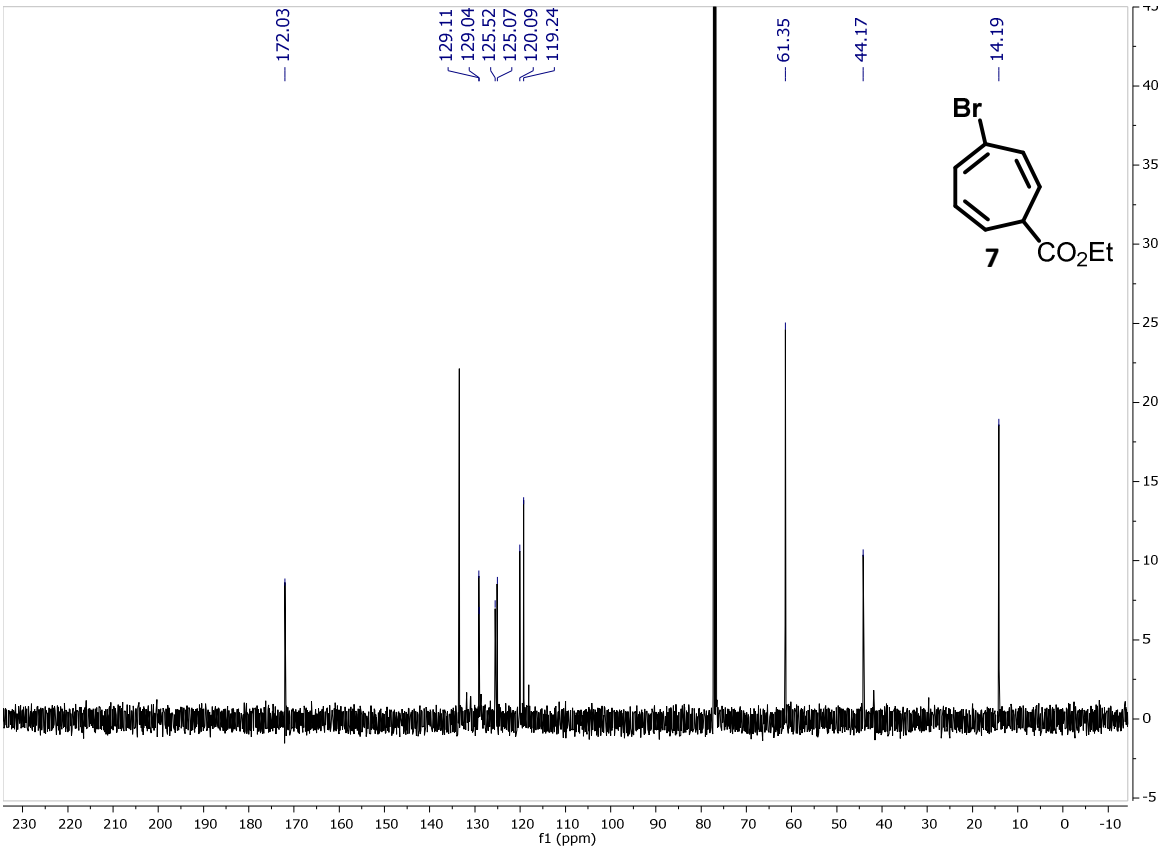

6.32
5.85
5.67
5.14
4.26
2.62
1.31
2.00
1.12
1.13
2.05
2.31
0.98
3.43
f1 (ppm)
4
CO2Et

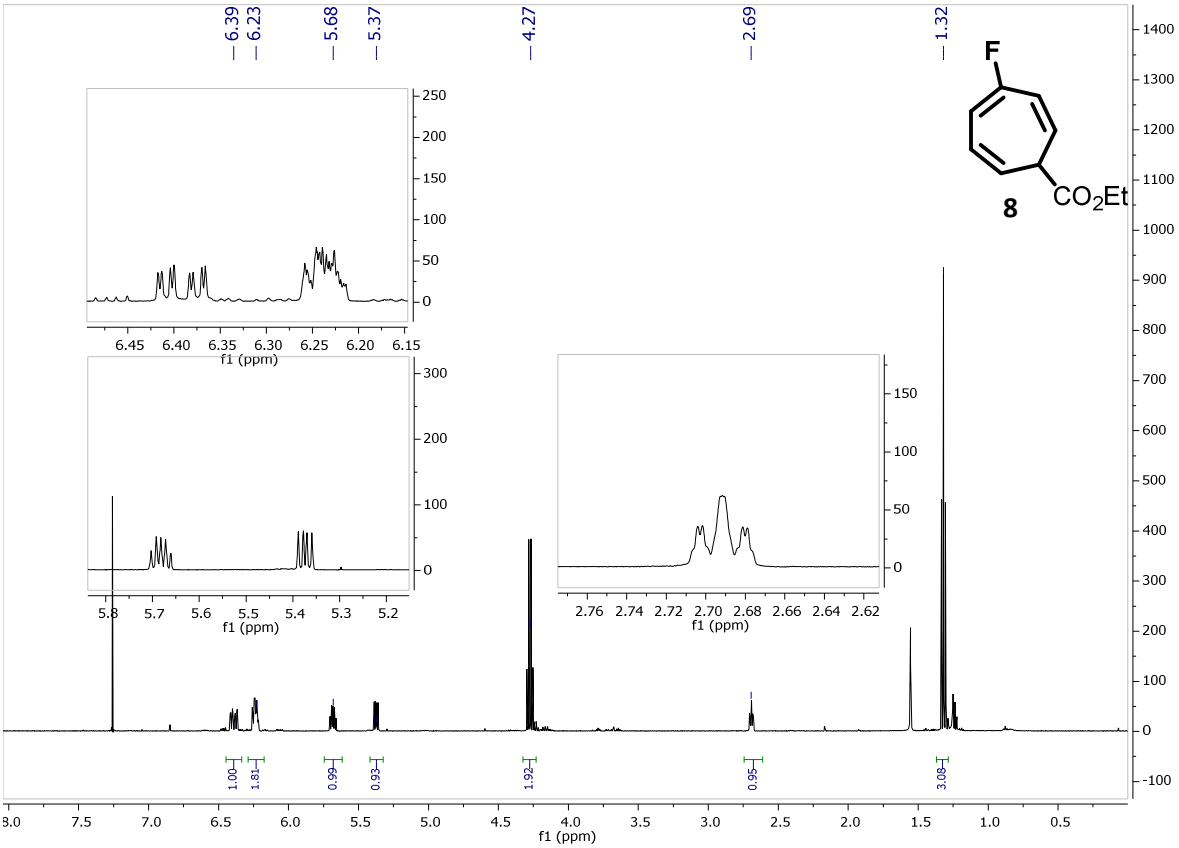

172.30
142.02
115.45
110.31
98.58
61.24
45.31
14.21
f1 (ppm)
4
CO2Et

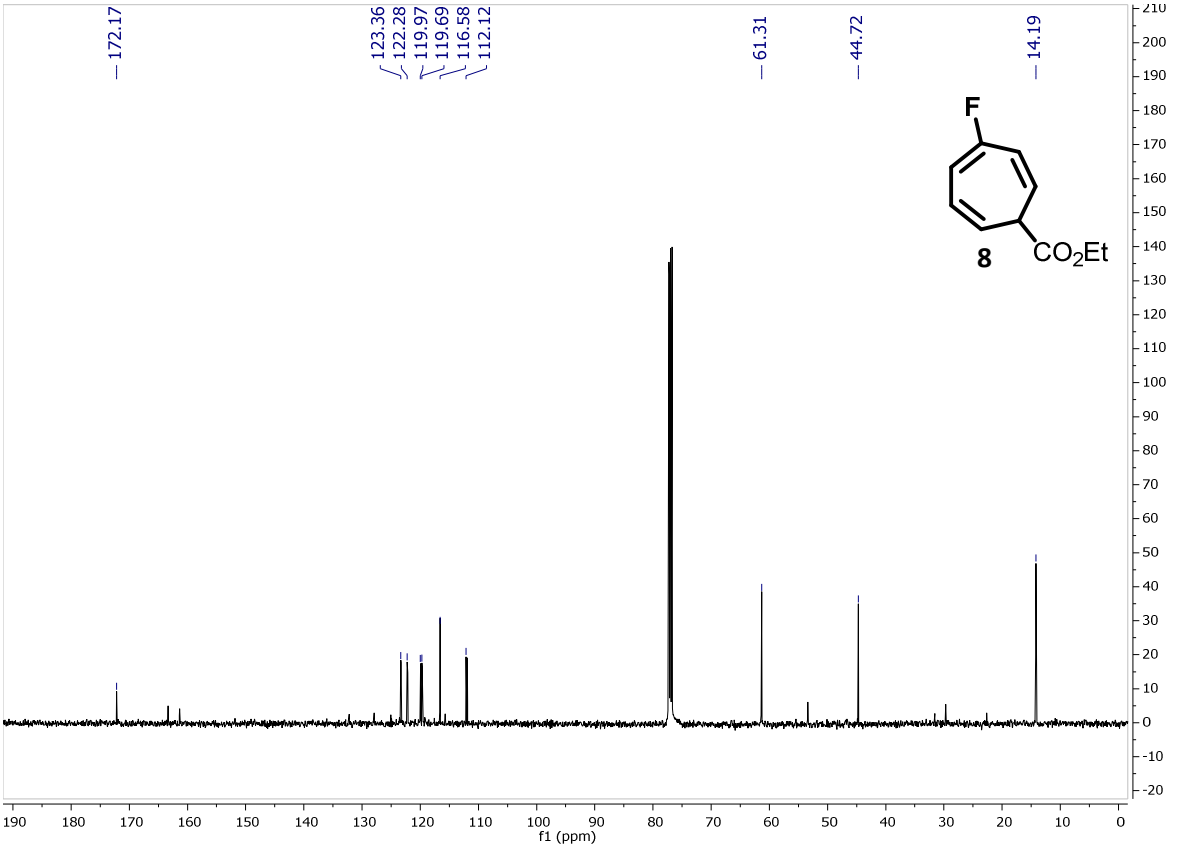

6.65
6.26
5.44
4.26
2.54
1.30
5
CO2Et
f1 (ppm)
2.00
1.93
1.95
2.11
0.95
3.32

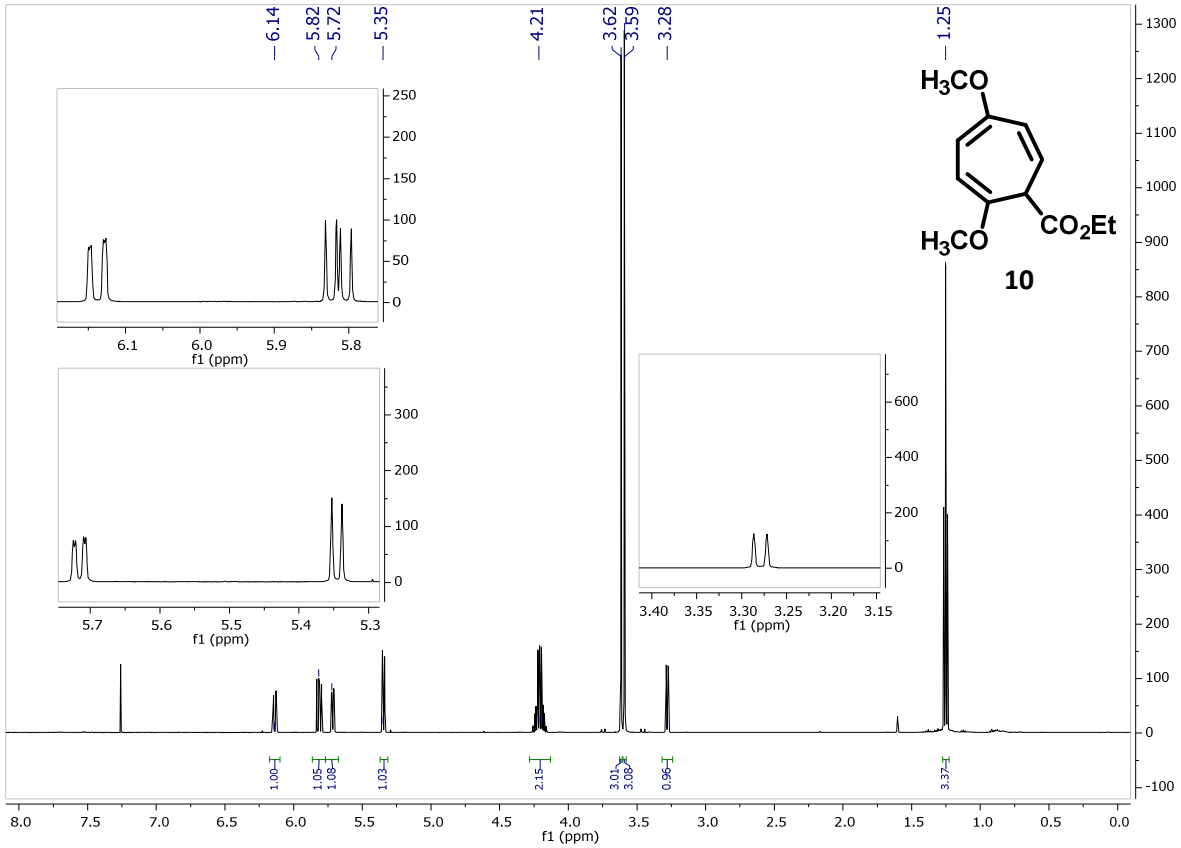

173.06
130.91
125.56
117.27
61.06
44.08
14.24
5
CO2Et
f1 (ppm)

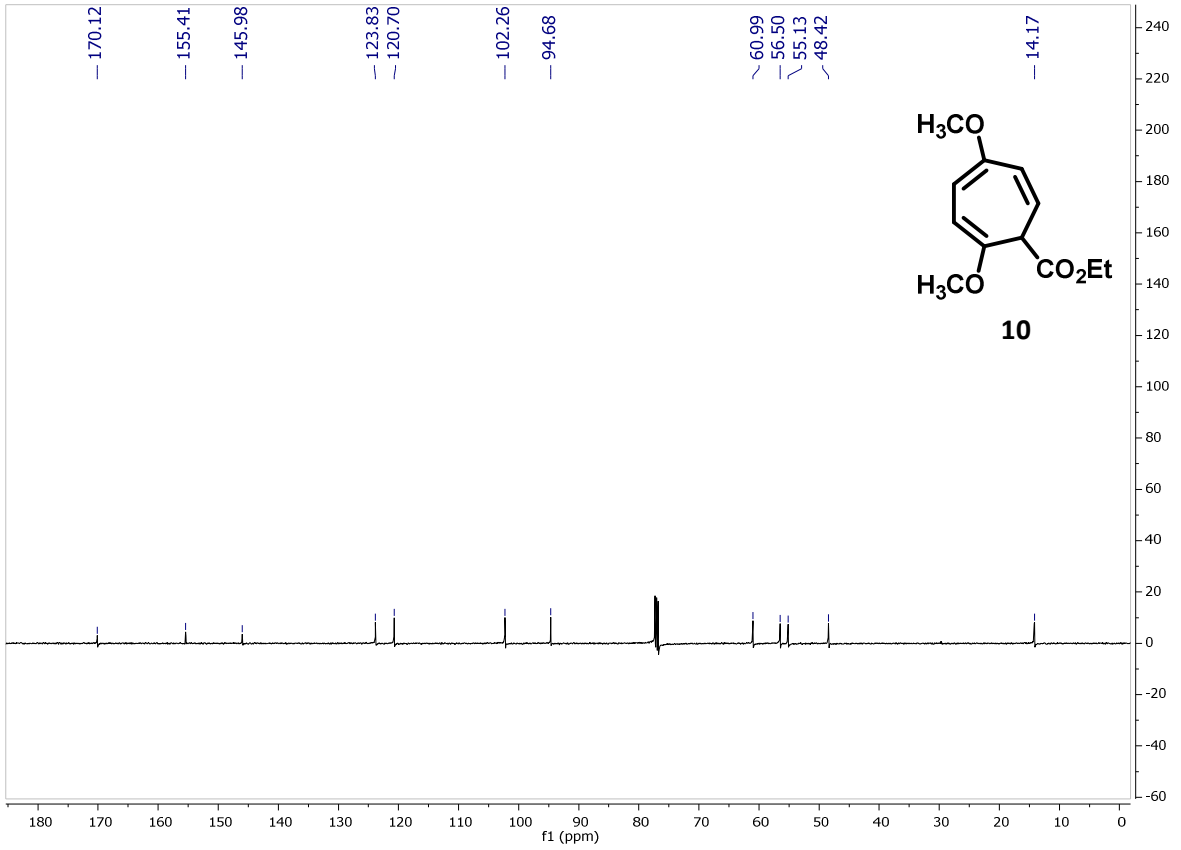

7.04
6.36
6.14
5.53
5.44
4.26
2.75
1.31
Br
CO2Et
7
f1 (ppm)

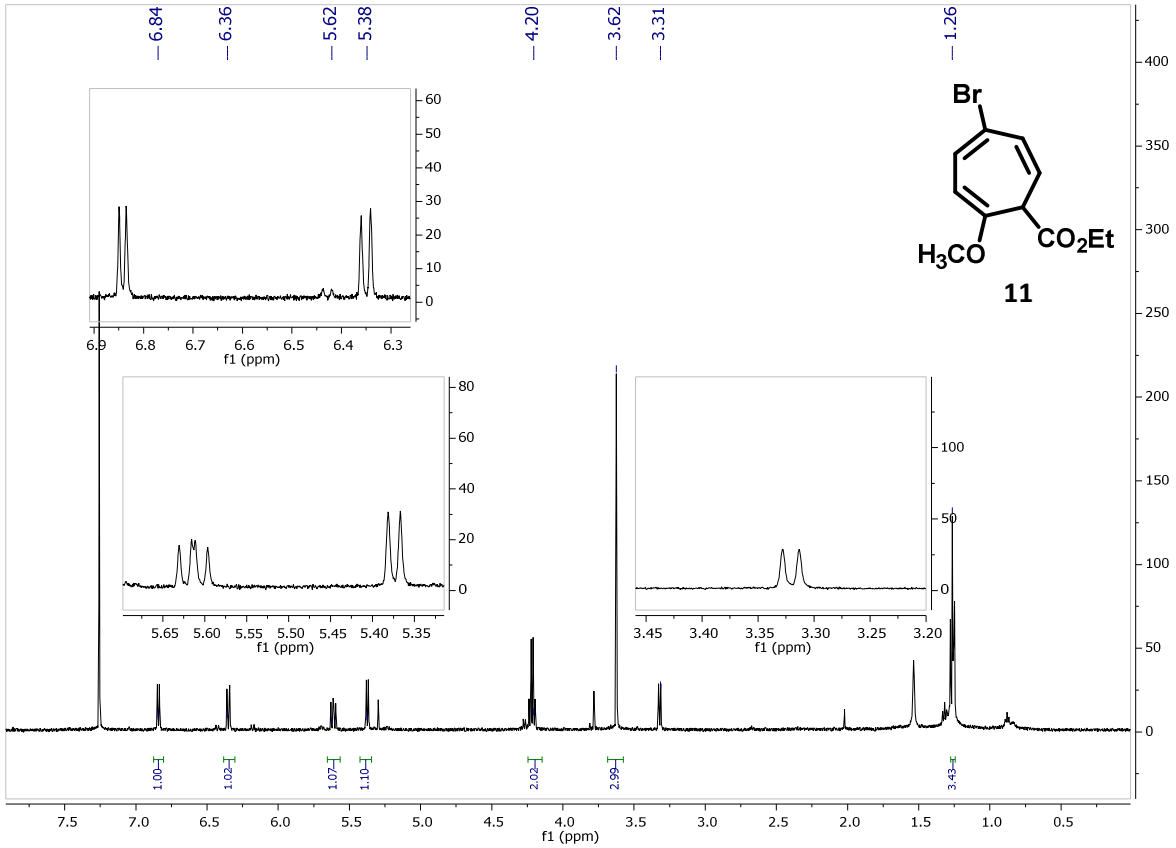

172.03
129.11
129.04
125.52
125.07
120.09
119.24
61.35
44.17
14.19
Br
CO2Et
7
f1 (ppm)

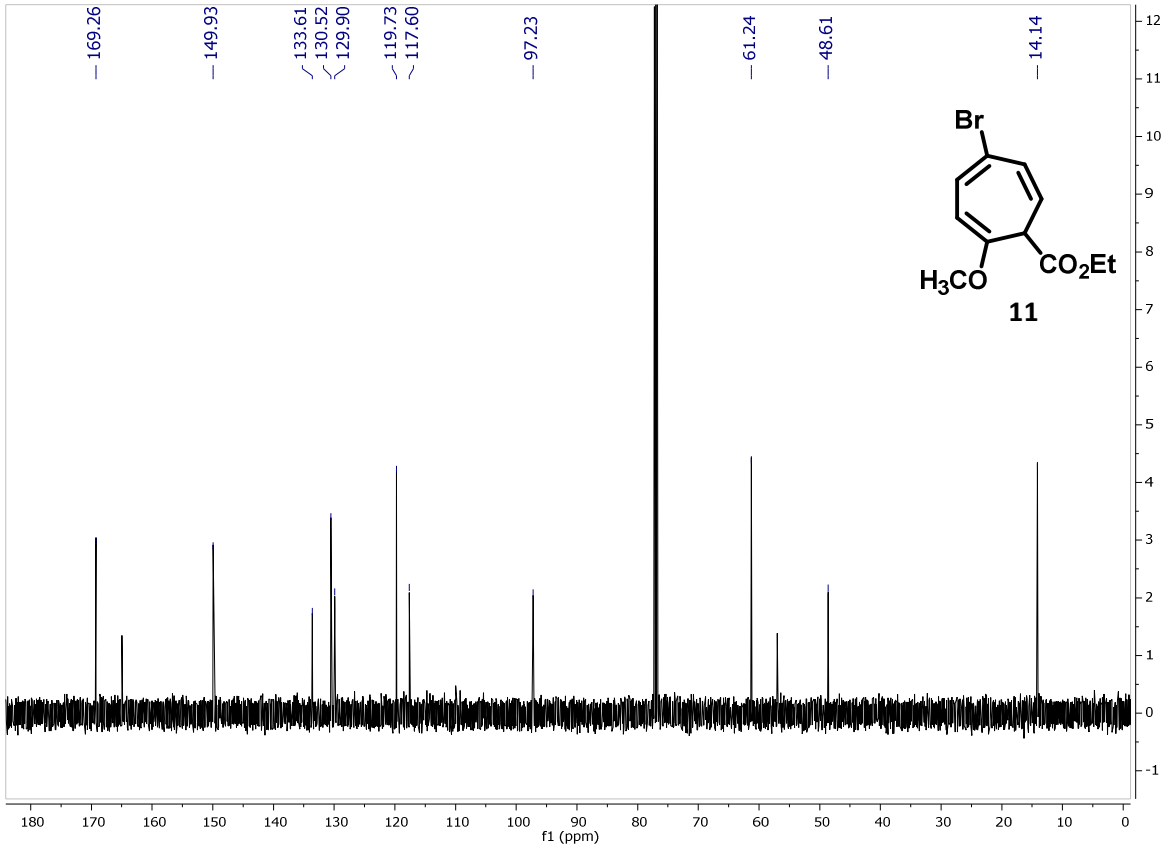

6.39
6.23
5.68
5.37
4.27
2.69
1.32
F
CO2Et
8
f1 (ppm)

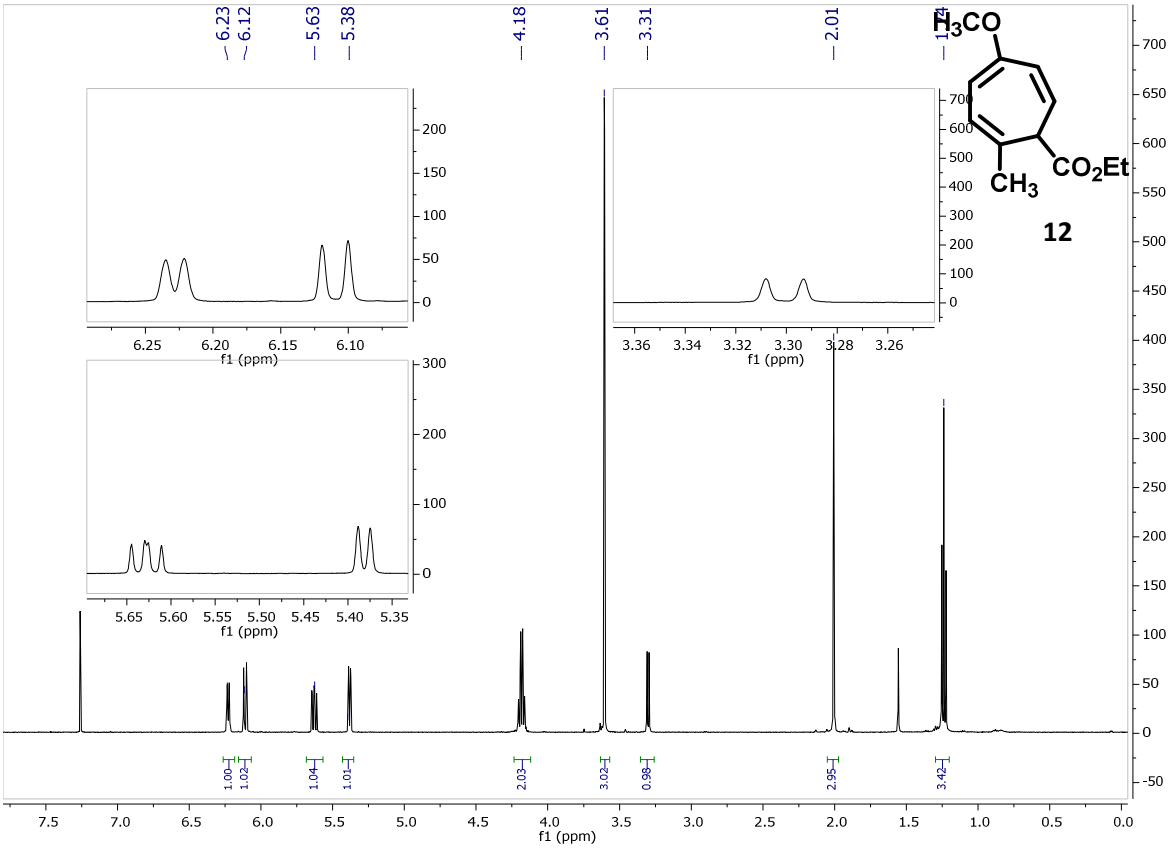

172.17
123.36
122.28
119.97
119.69
116.58
112.12
61.31
44.72
14.19
F
CO2Et
8
f1 (ppm)

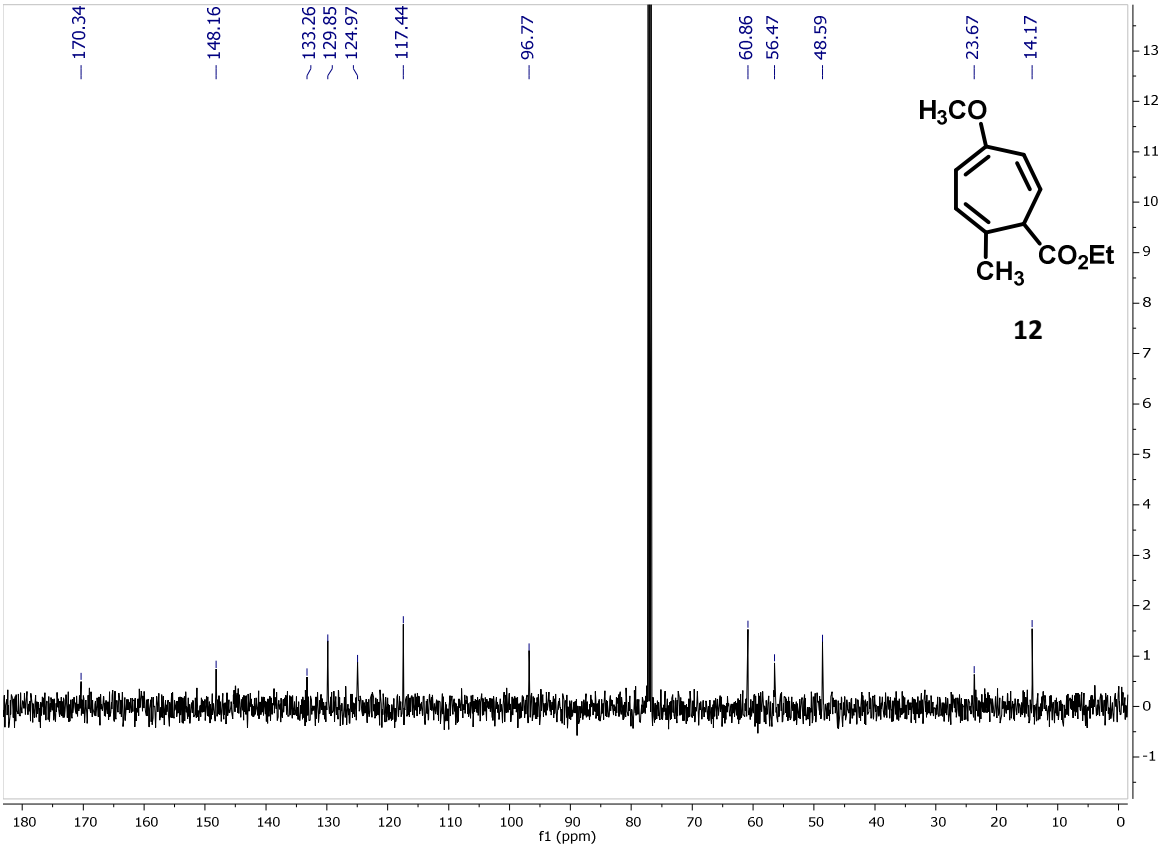

6.14
5.82
5.72
5.35
4.21
3.62
3.59
3.28
1.25
H3CO
CO2Et
H3CO
10
f1 (ppm)

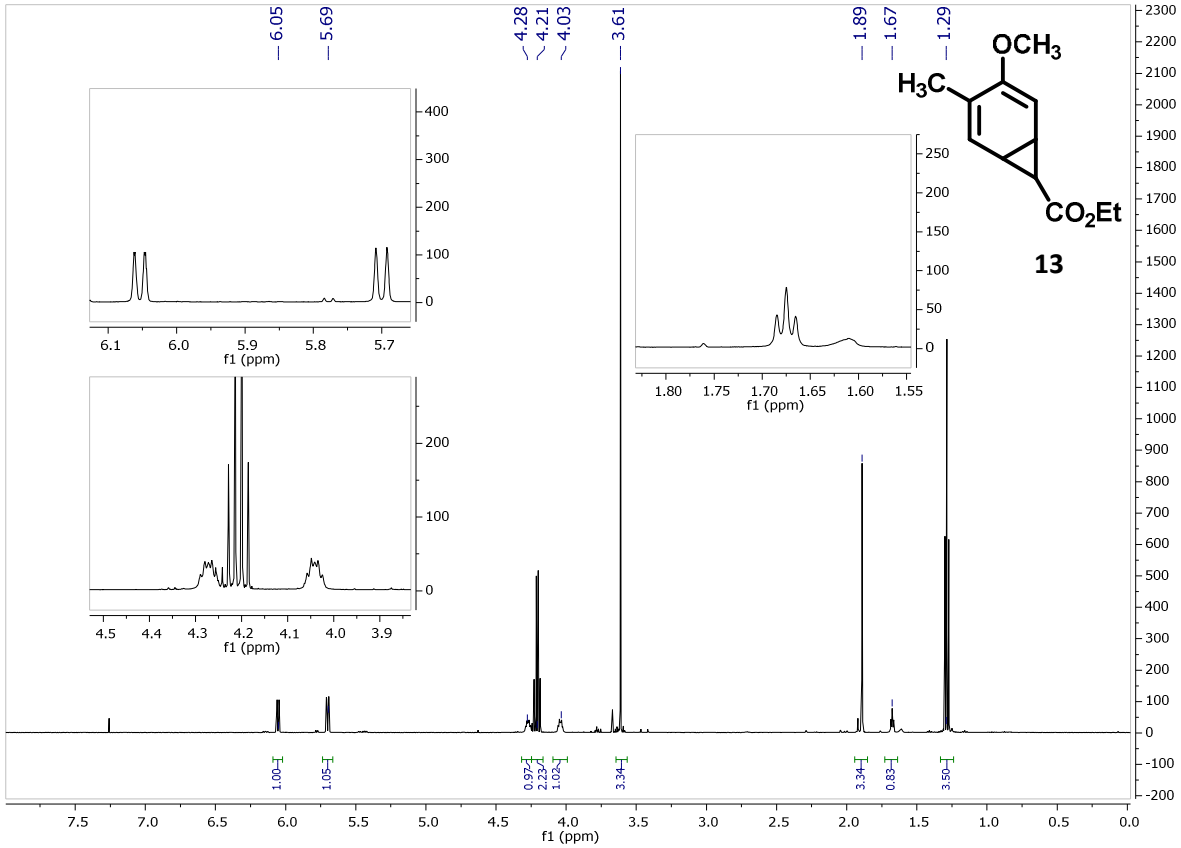

170.12
155.41
145.98
123.83
120.70
102.26
94.68
60.99
56.50
55.13
48.42
14.17
H3CO
CO2Et
H3CO
10
f1 (ppm)

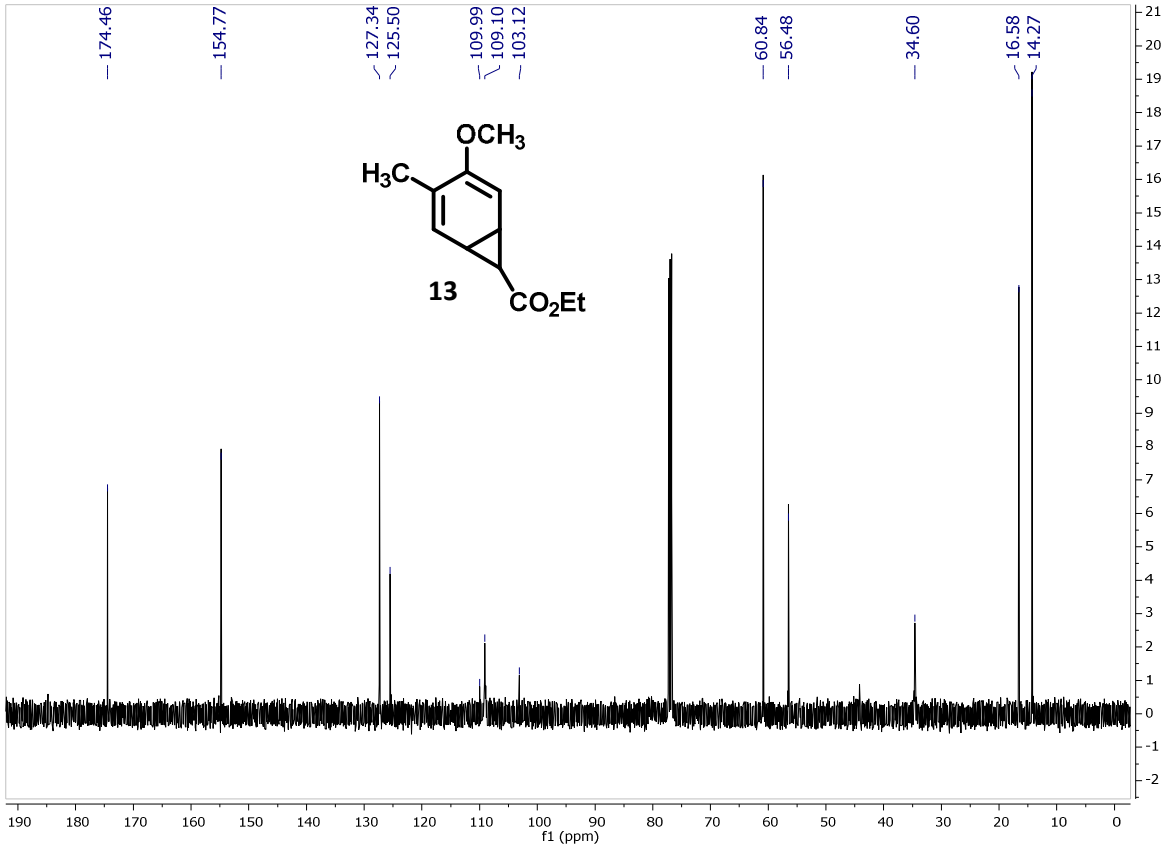

6.84
6.36
5.62
5.38
4.20
3.62
3.31
1.26
Br
H3CO
CO2Et
11
f1 (ppm)
1.00
1.02
1.07
1.10
2.02
2.99
3.43

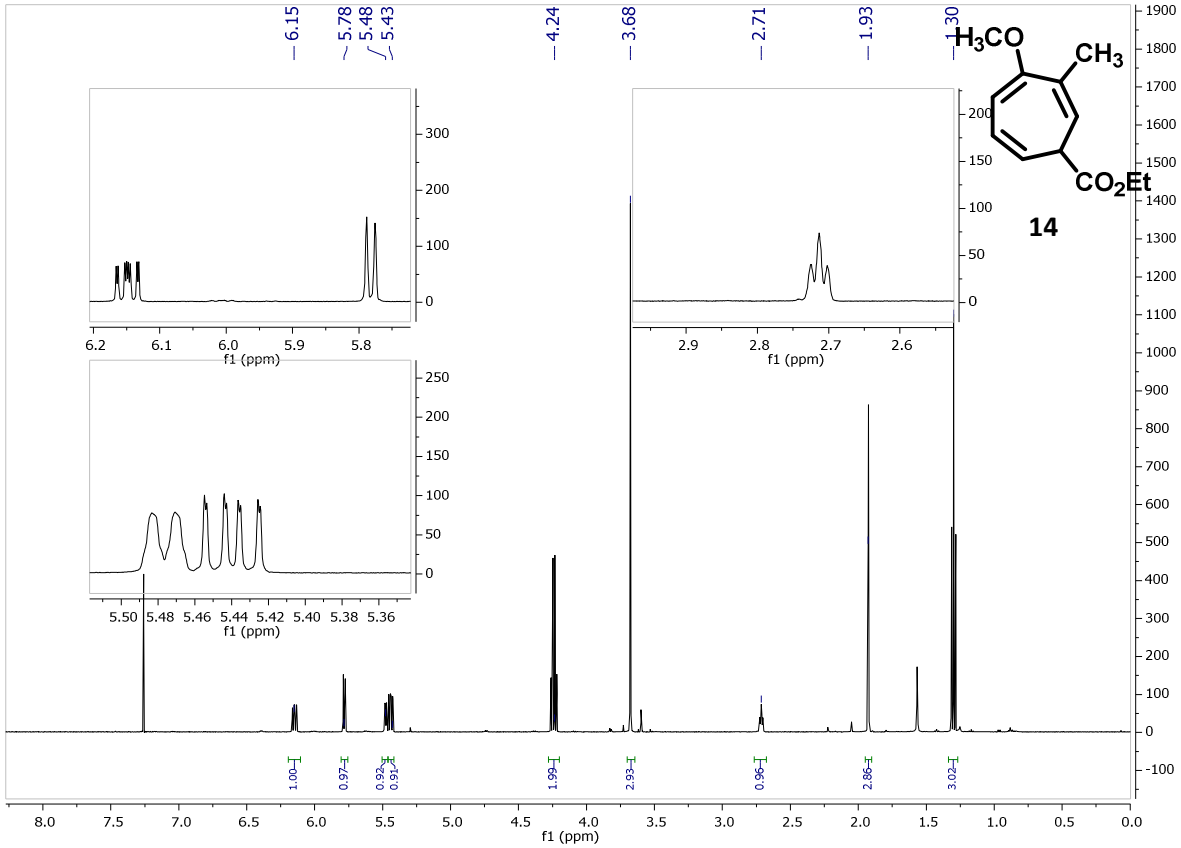

169.26
149.93
133.61
130.52
129.90
119.73
117.60
97.23
61.24
48.61
14.14
Br
H3CO
CO2Et
11
f1 (ppm)

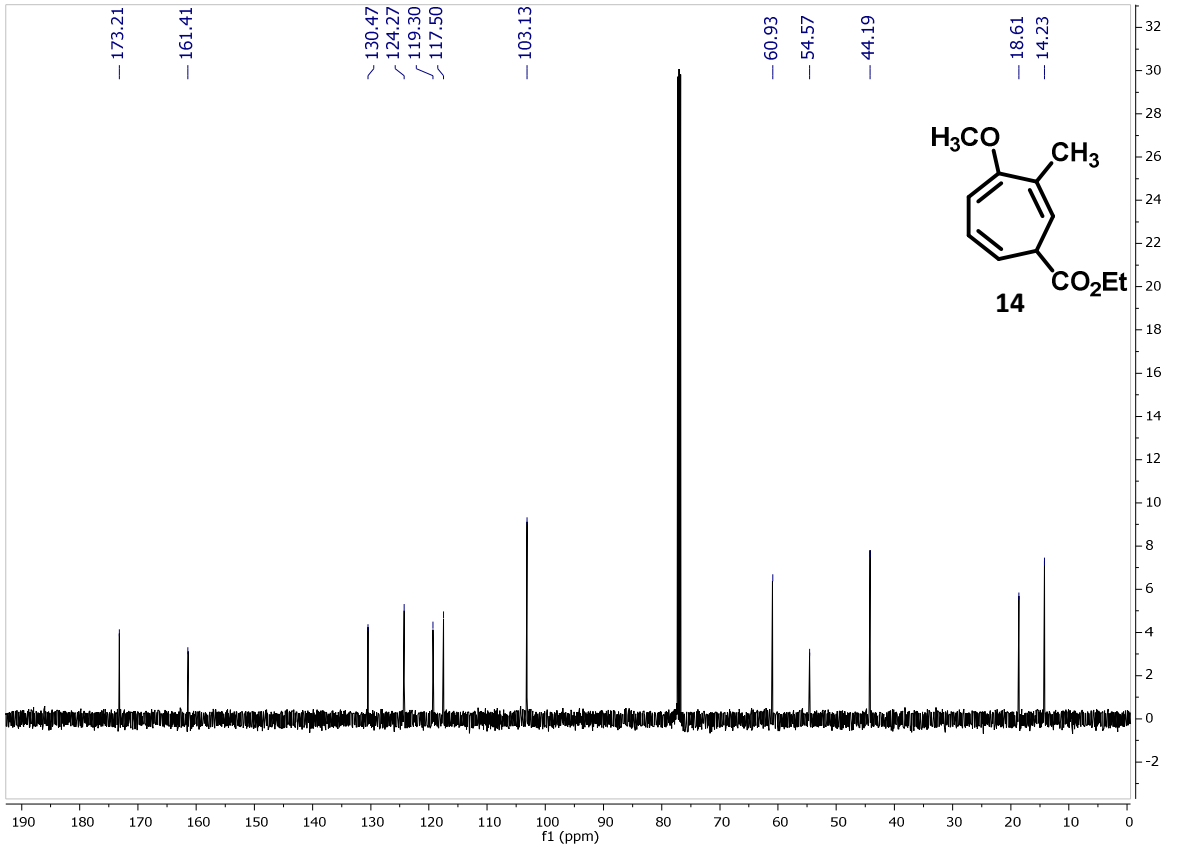

6.23
6.12
5.63
5.38
4.18
3.61
3.31
2.01
1.24
H3CO
CO2Et
CH3
12
f1 (ppm)

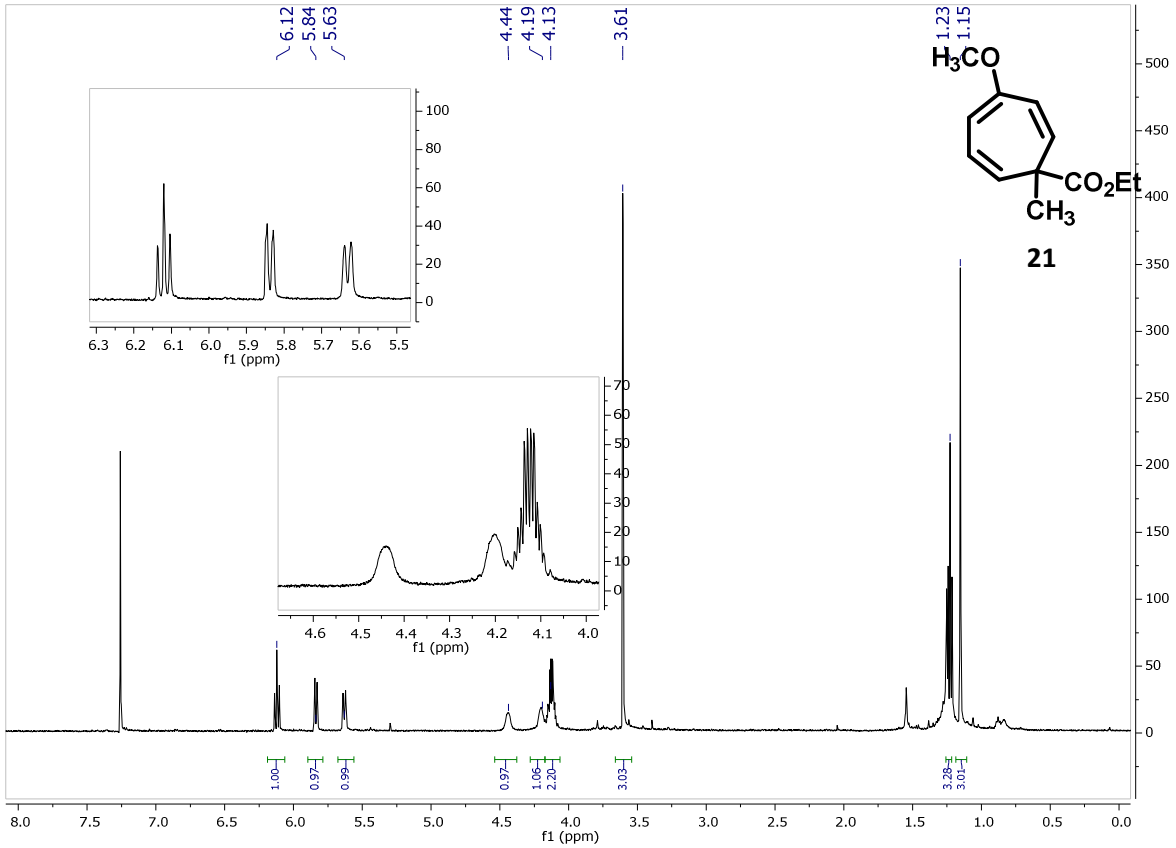

170.34
148.16
133.26
129.85
124.97
117.44
96.77
60.86
56.47
48.59
23.67
14.17
H3CO
CO2Et
CH3
12
f1 (ppm)

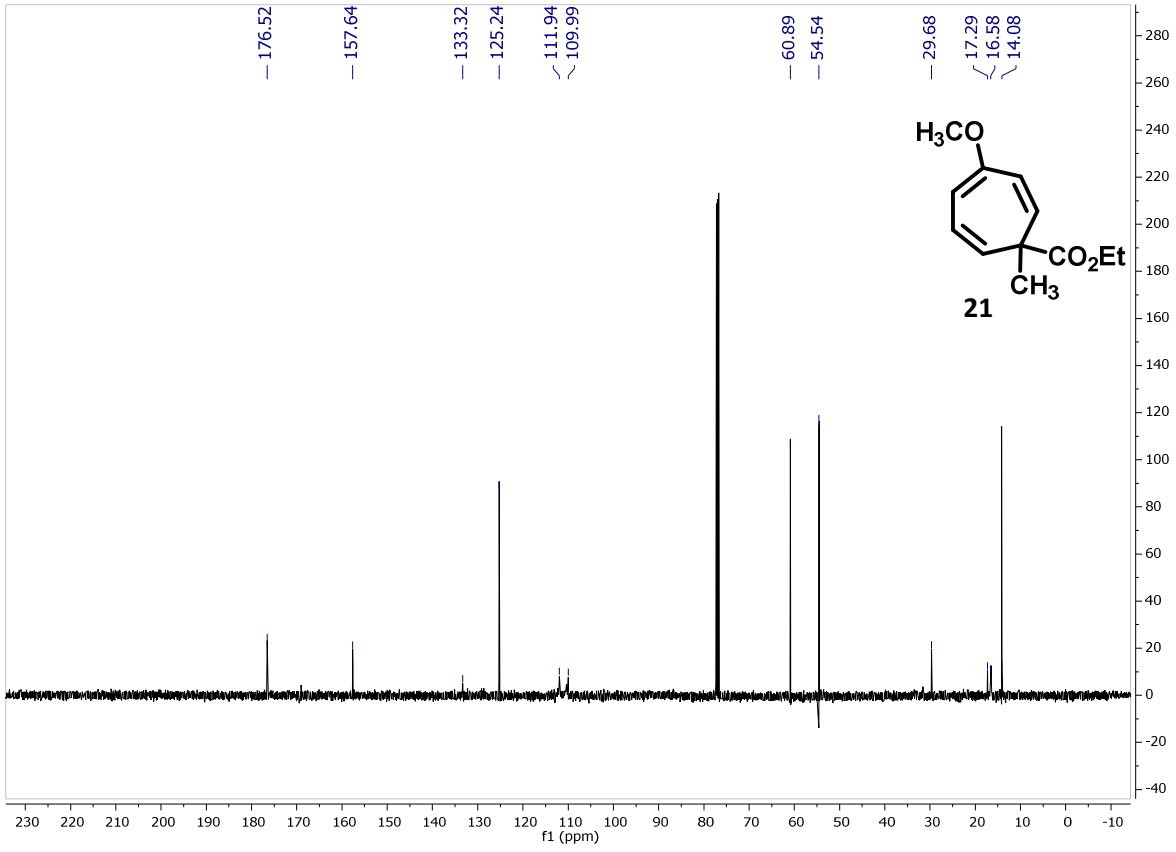

6.05
5.69
4.28
4.21
4.03
3.61
1.89
1.67
1.29
OCH3
H3C
CO2Et
13
f1 (ppm)

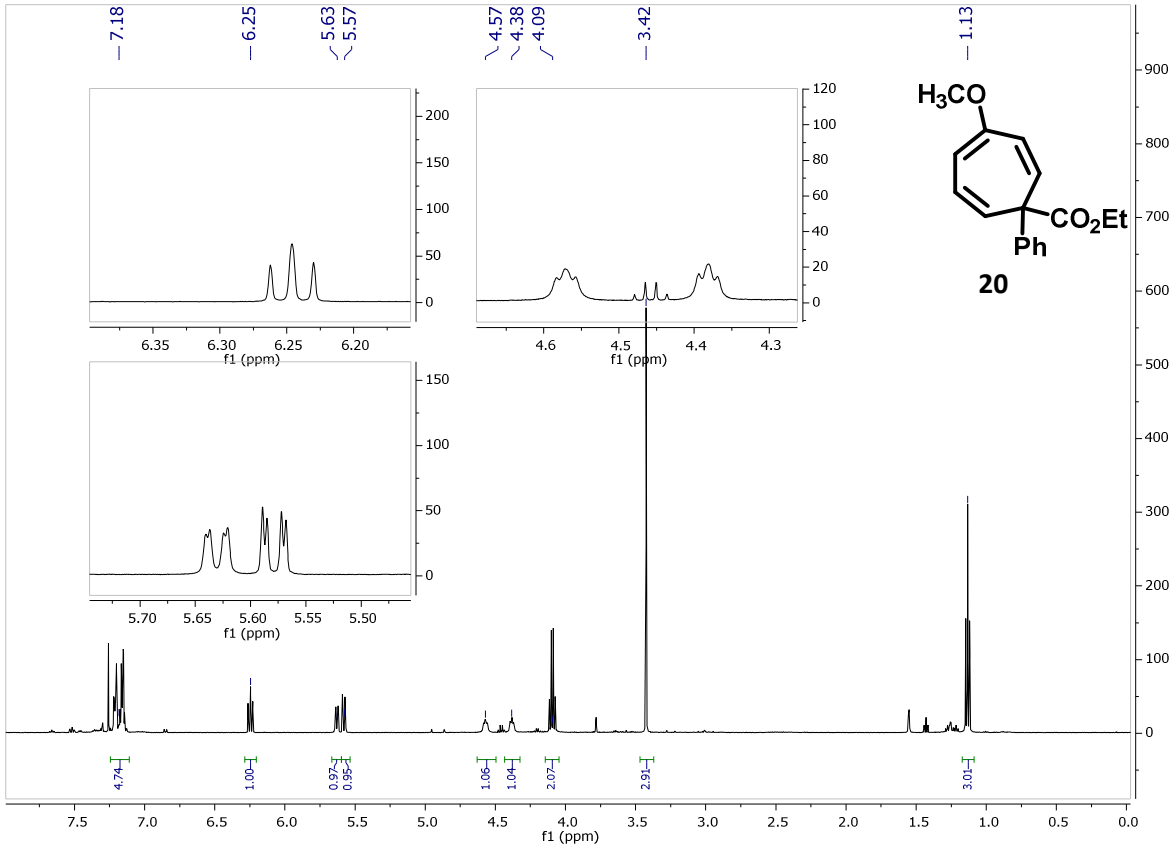

174.46
154.77
127.34
125.50
109.99
109.10
103.12
60.84
56.48
34.60
16.58
14.27
OCH3
H3C
13
CO2Et
f1 (ppm)

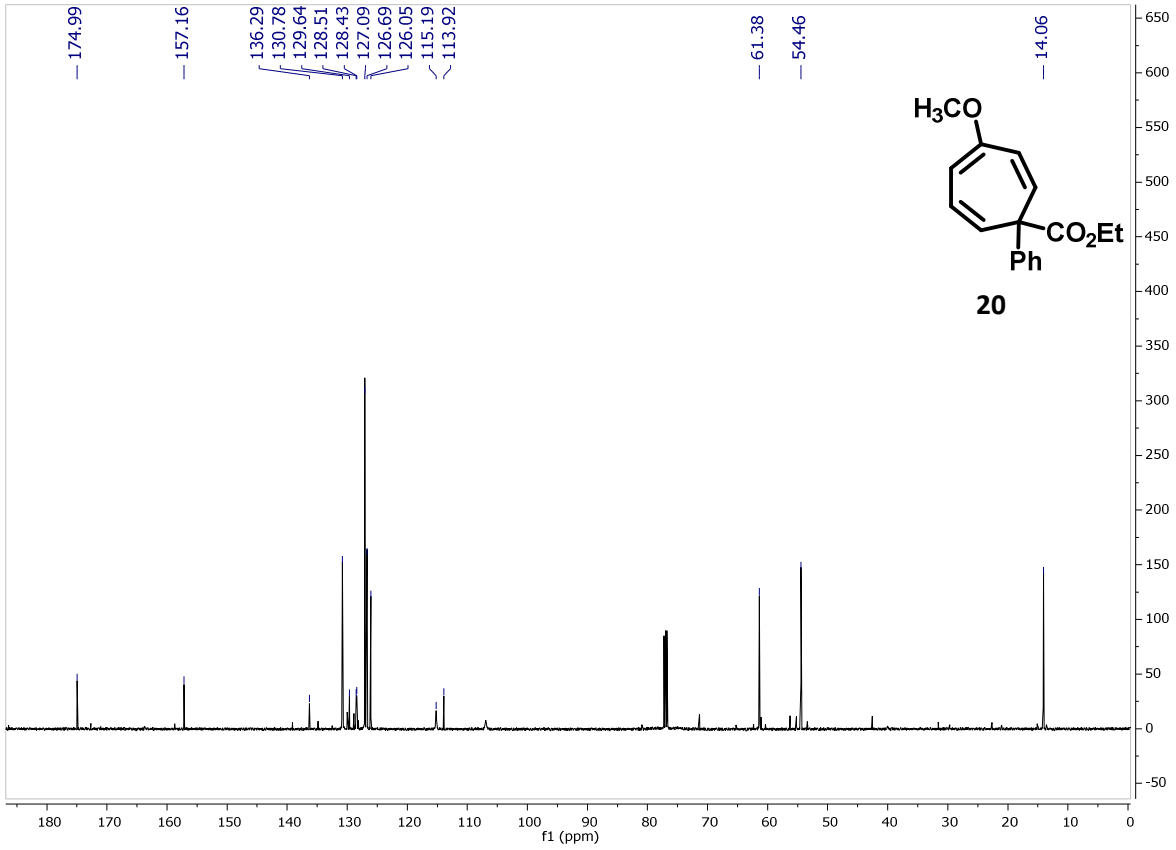

6.15
5.78
5.48
5.43
4.24
3.68
2.71
1.93
1.30
H3CO
CH3
CO2Et
14
f1 (ppm)
1.00
0.97
0.92
0.91
1.99
2.93
0.96
2.86
3.02

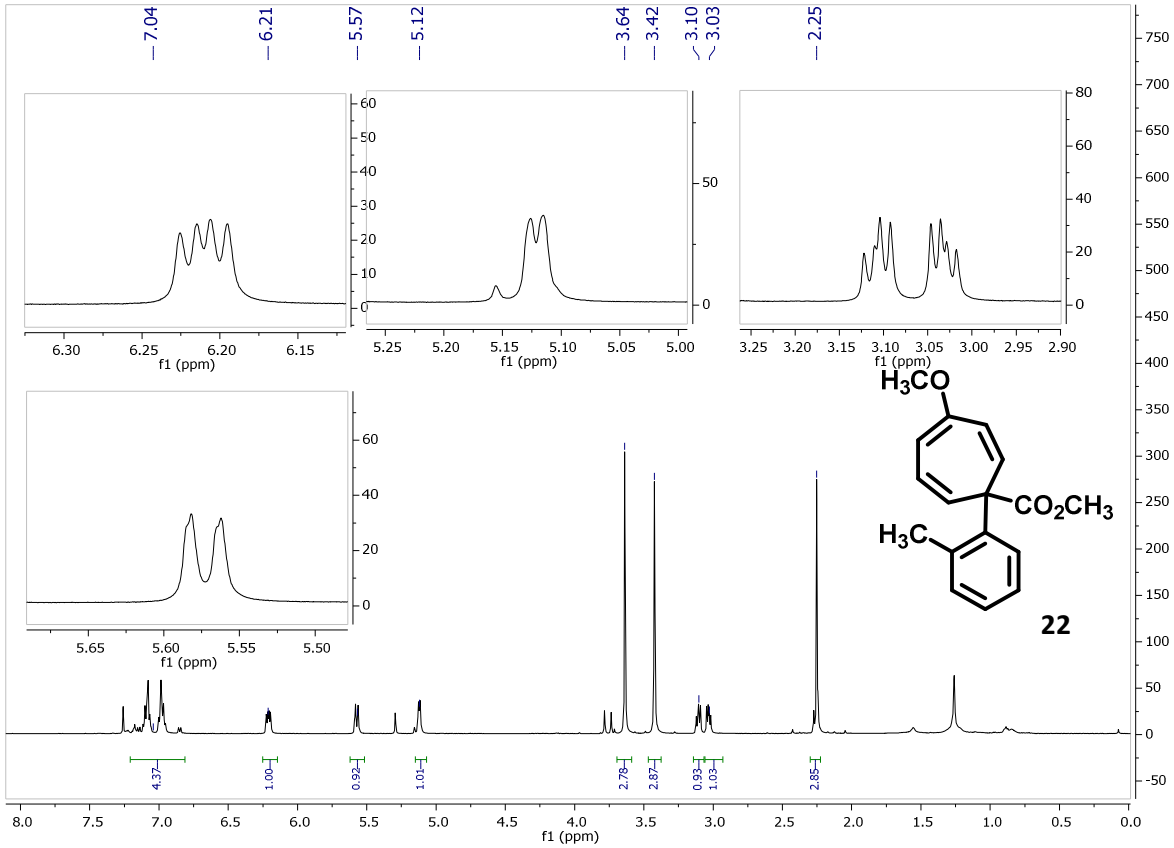

173.21
161.41
130.47
124.27
119.30
117.50
103.13
60.93
54.57
44.19
18.61
14.23
H3CO
CH3
CO2Et
14
f1 (ppm)

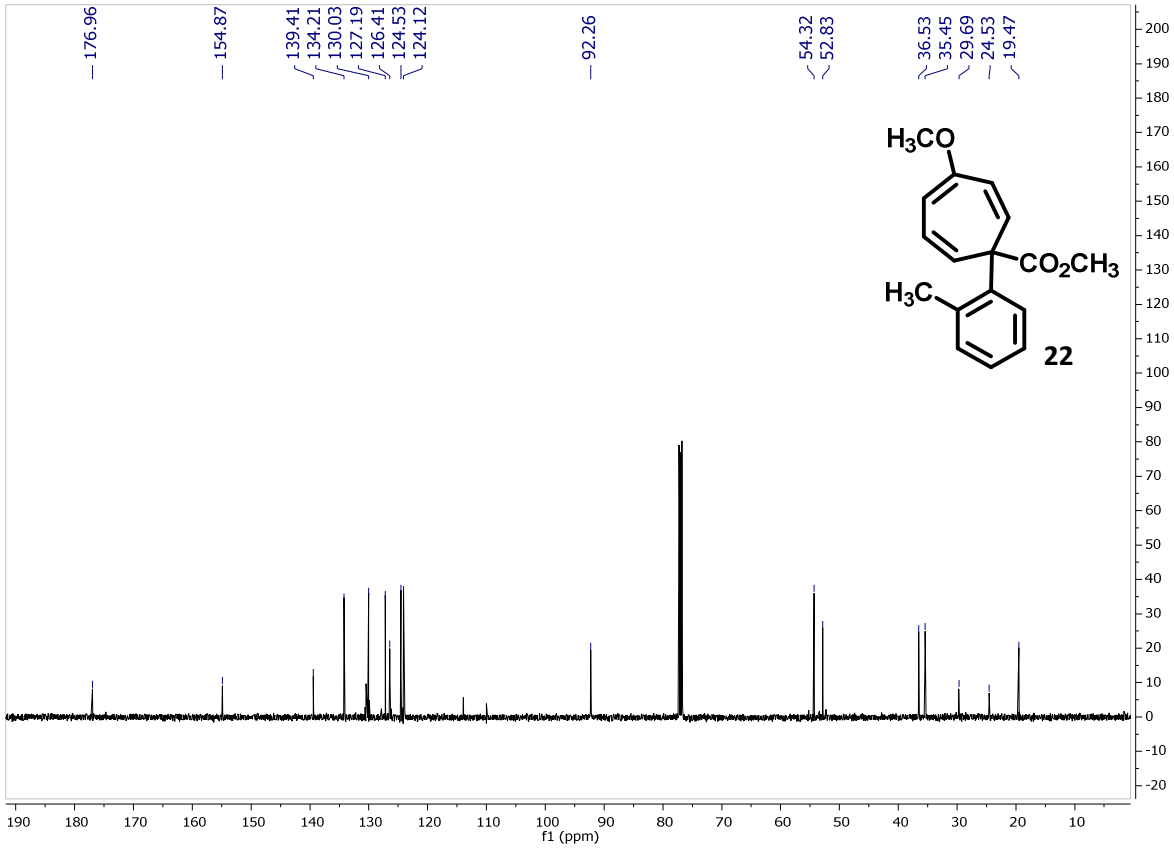

6.12
5.84
5.63
4.44
4.19
4.13
3.61
1.23
1.15
H3CO
CO2Et
CH3
21
f1 (ppm)

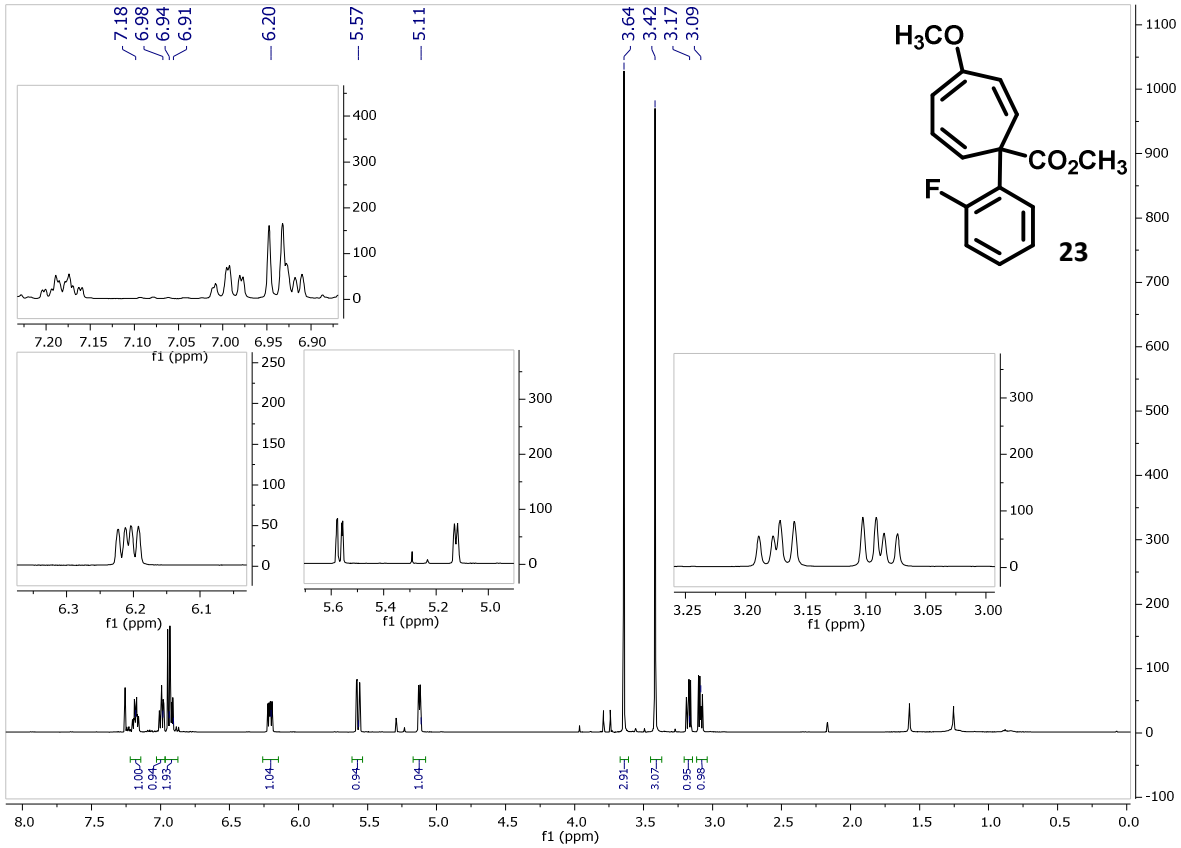

176.52
157.64
133.32
125.24
111.94
109.99
60.89
54.54
29.68
17.29
16.58
14.08
H3CO
CO2Et
CH3
21
f1 (ppm)

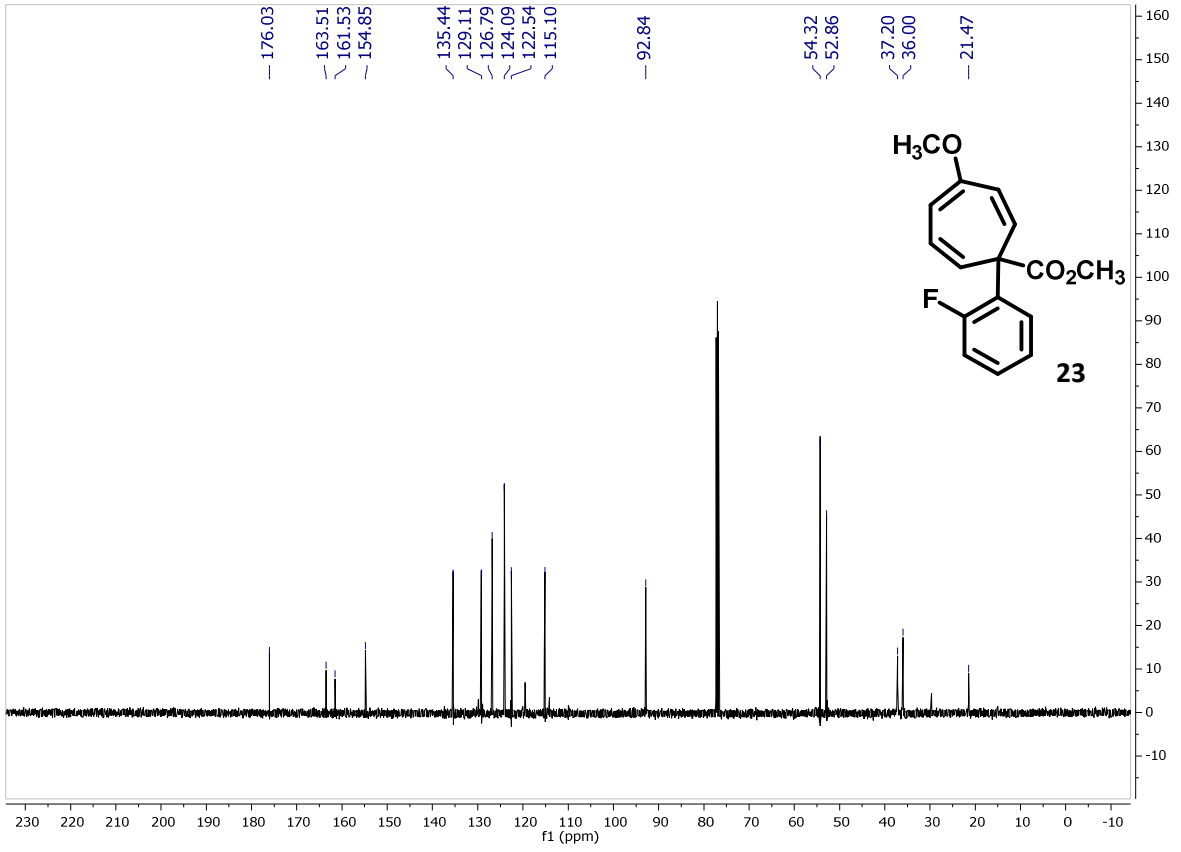

7.18
6.25
5.63
5.57
4.57
4.38
4.09
3.42
1.13
H3CO
CO2Et
Ph
20
f1 (ppm)

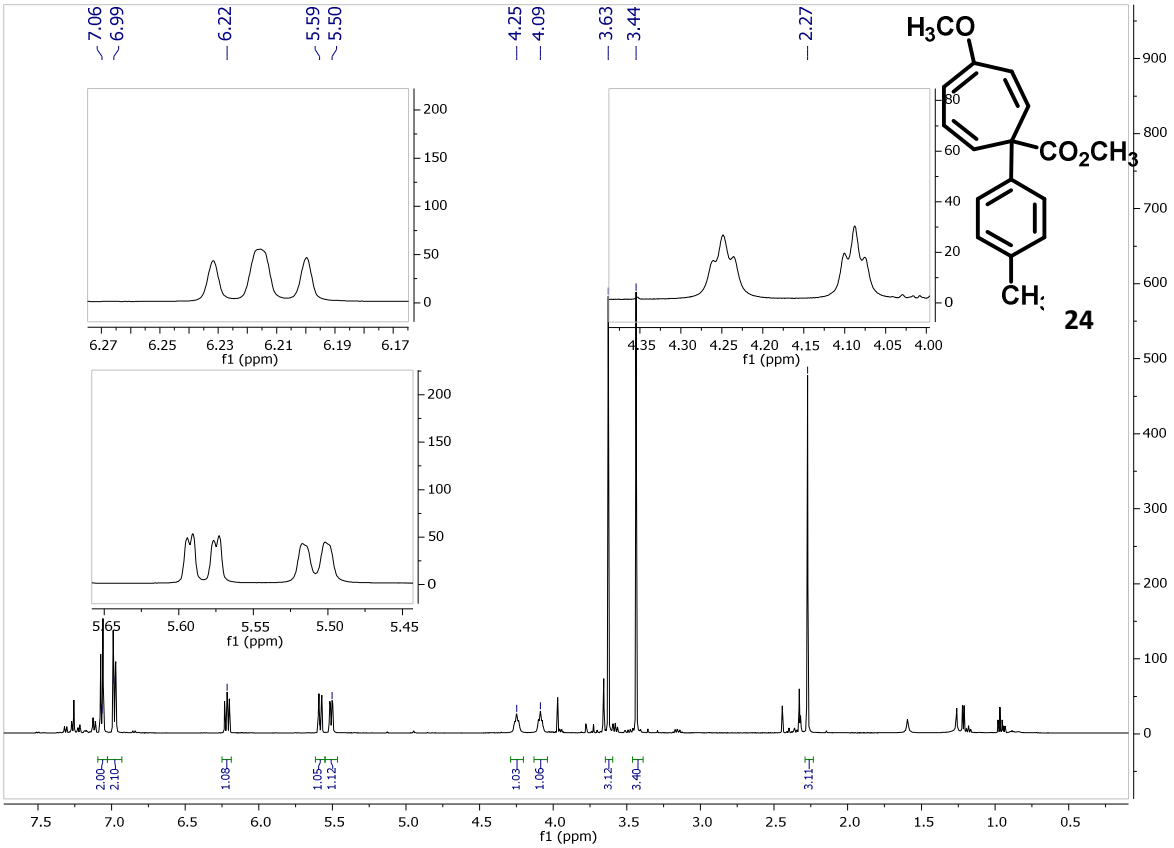

174.99
157.16
136.29
130.78
129.64
128.51
128.43
127.09
126.69
126.05
115.19
113.92
61.38
54.46
14.06
H3CO
CO2Et
Ph
20
f1 (ppm)

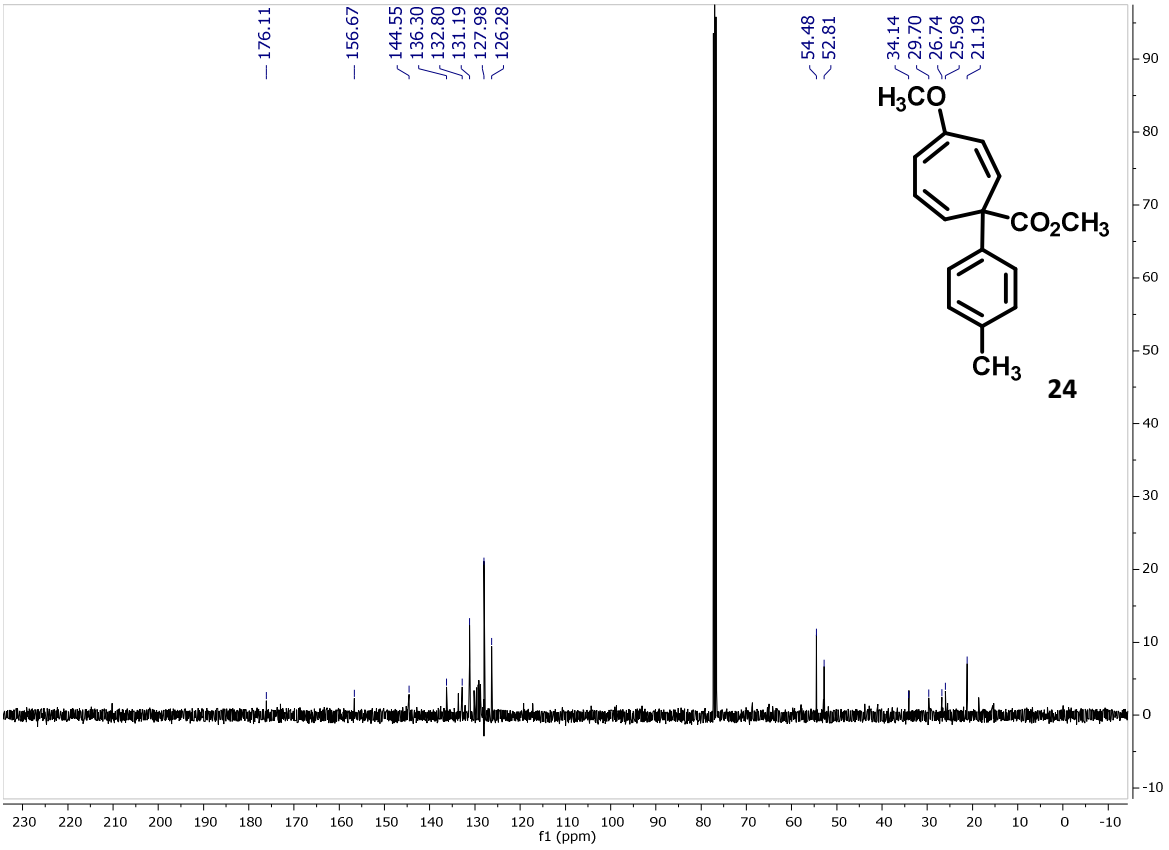

7.04
6.21
5.57
5.12
3.64
3.42
3.10
3.03
2.25
f1 (ppm)
H3CO
CO2CH3
H3C
22

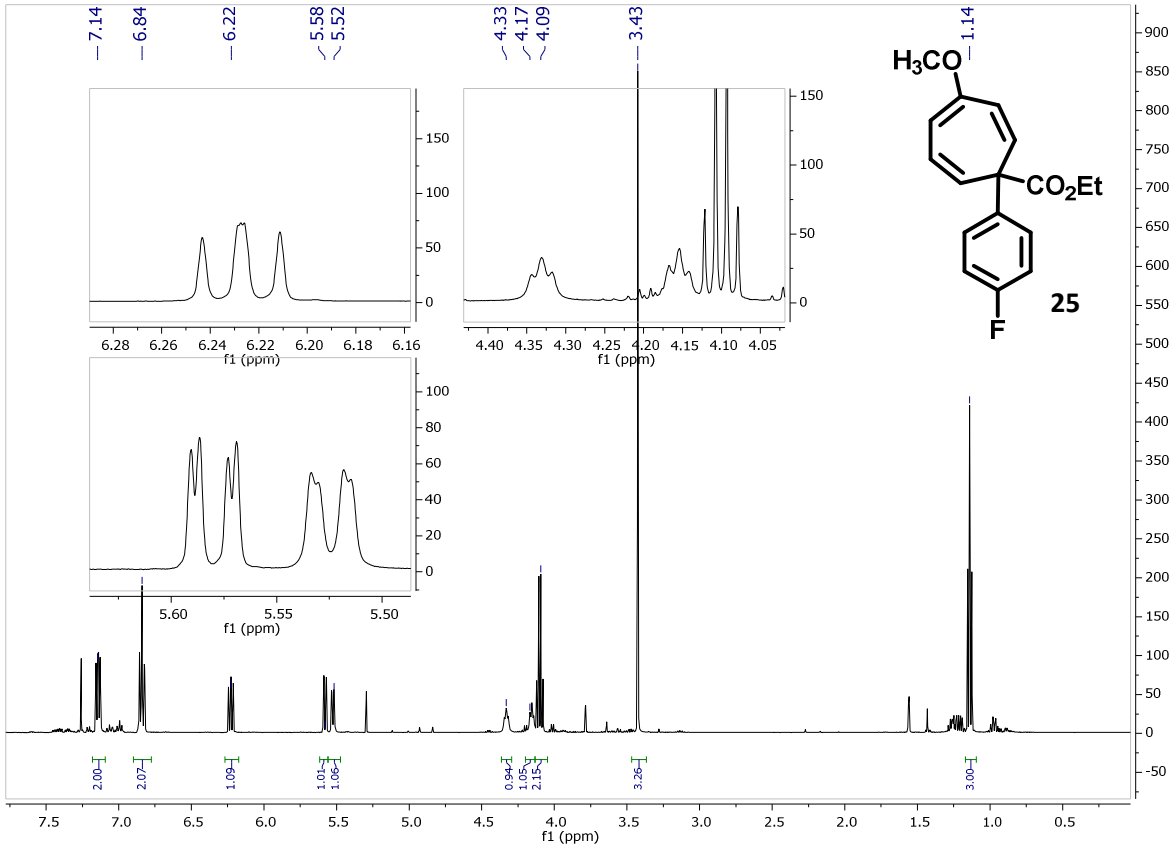

176.96
154.87
139.41
134.21
130.03
127.19
126.41
124.53
124.12
92.26
54.32
52.83
36.53
35.45
29.69
24.53
19.47
f1 (ppm)
H3CO
CO2CH3
H3C
22

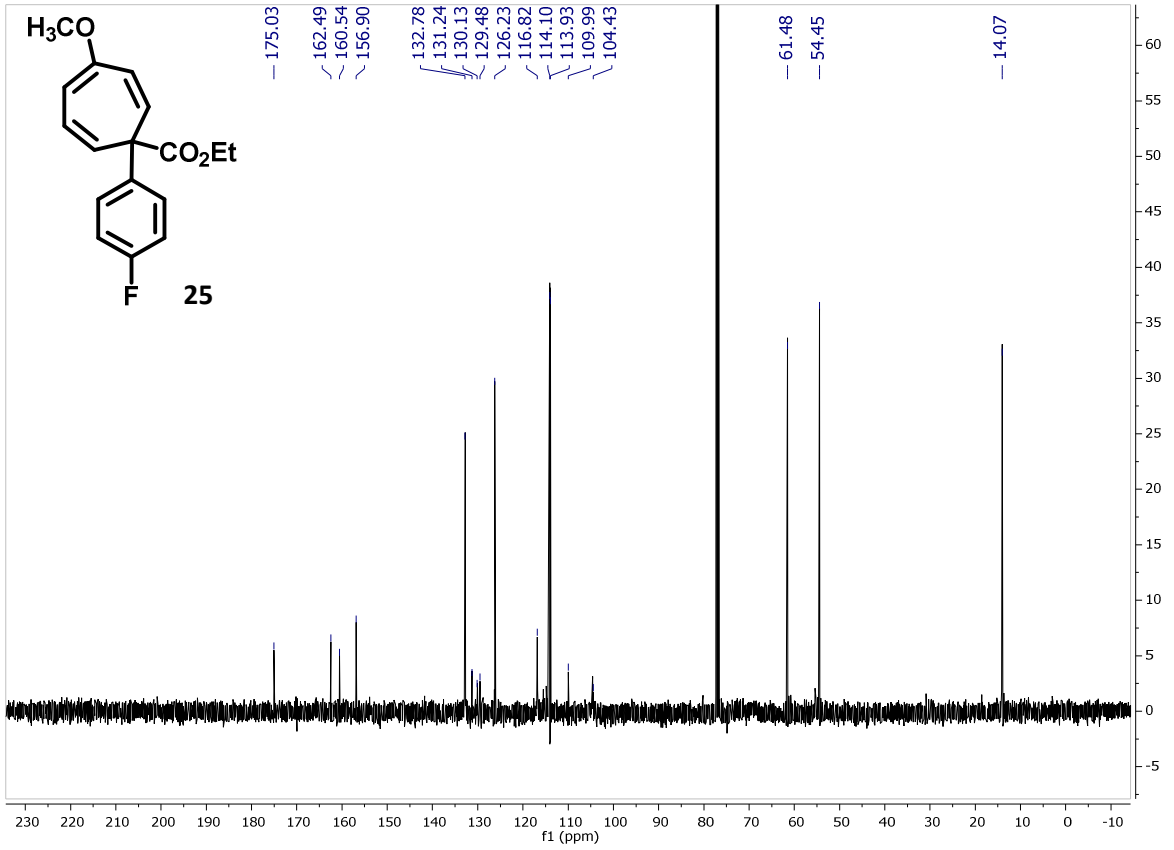

7.18
6.98
6.94
6.91
6.20
5.57
5.11
3.64
3.42
3.17
3.09
H3CO
CO2CH3
F
23
f1 (ppm)

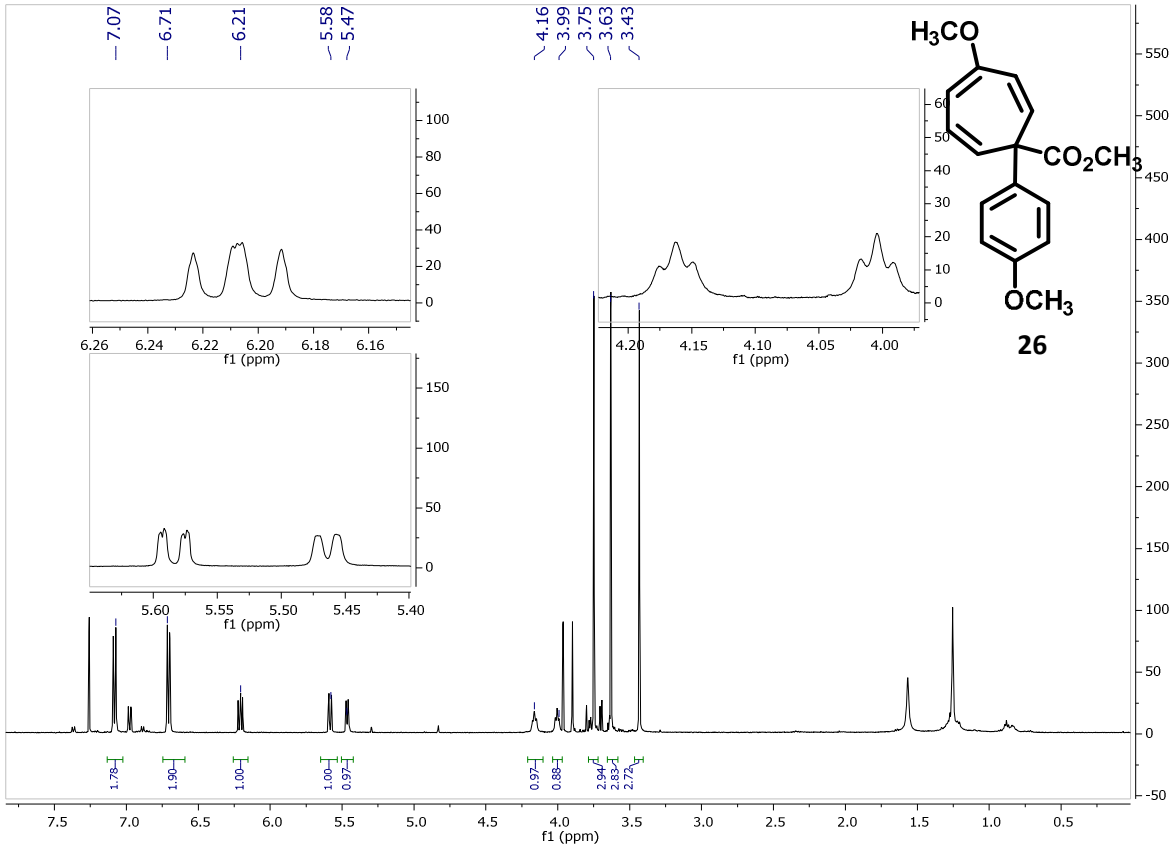

176.03
163.51
161.53
154.85
135.44
129.11
126.79
124.09
122.54
115.10
92.84
54.32
52.86
37.20
36.00
21.47
H3CO
CO2CH3
F
23
f1 (ppm)

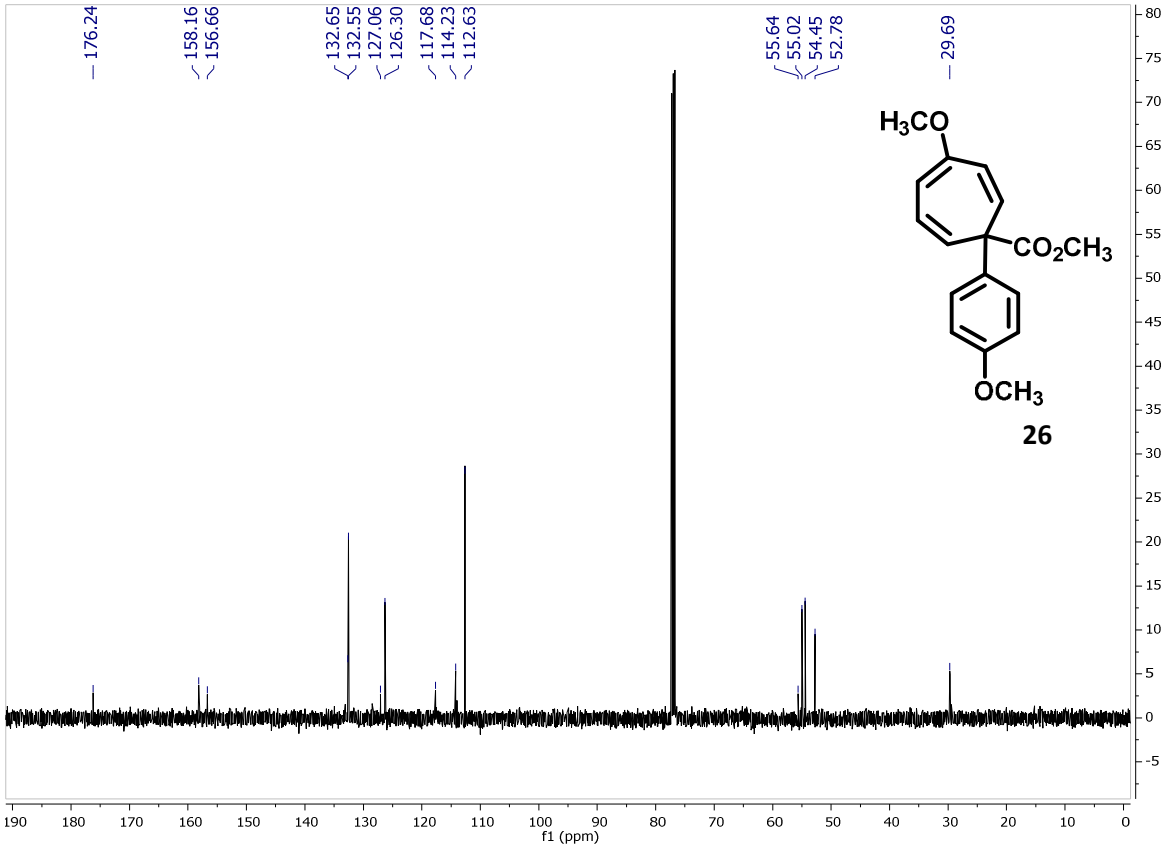

7.06
6.99
6.22
5.59
5.50
4.25
4.09
3.63
3.44
2.27
H3CO
CO2CH3
CH3
24
f1 (ppm)

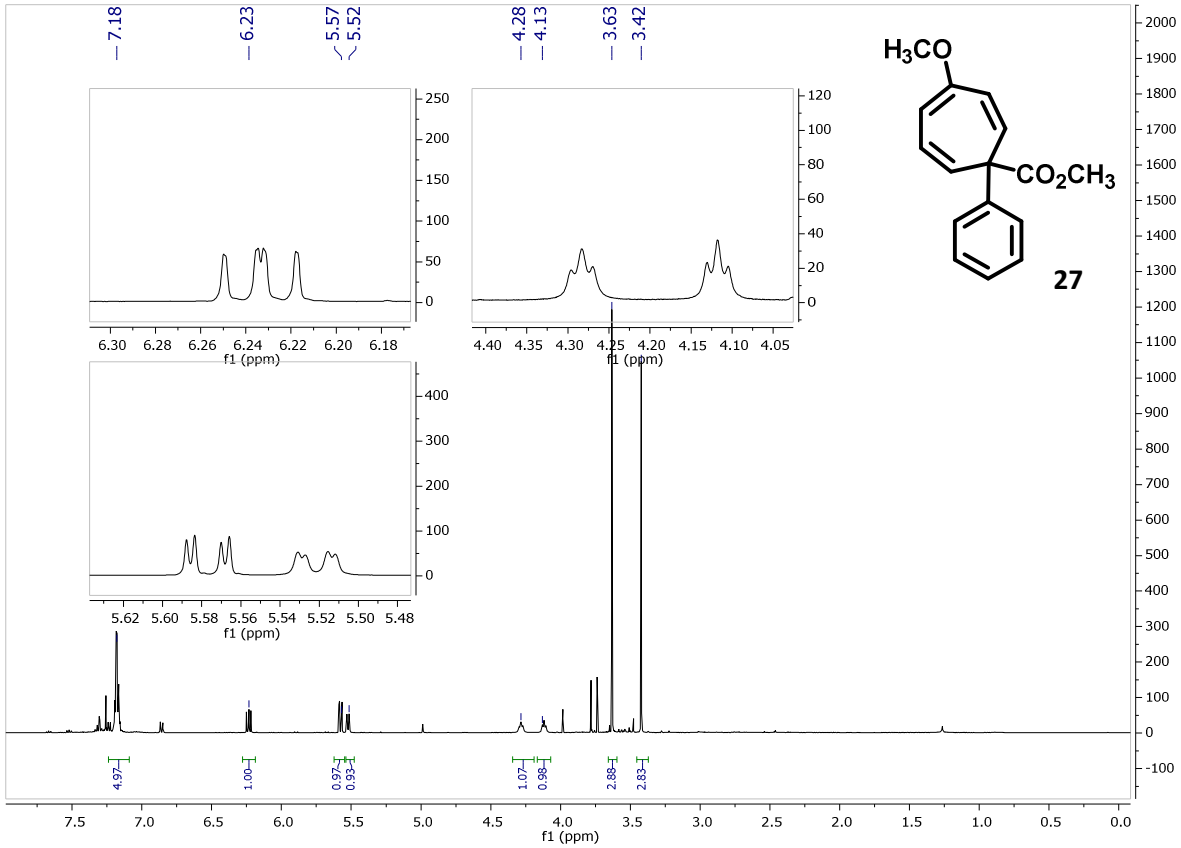

176.11
156.67
144.55
136.30
132.80
131.19
127.98
126.28
54.48
52.81
34.14
29.70
26.74
25.98
21.19
H3CO
CO2CH3
CH3
24
f1 (ppm)

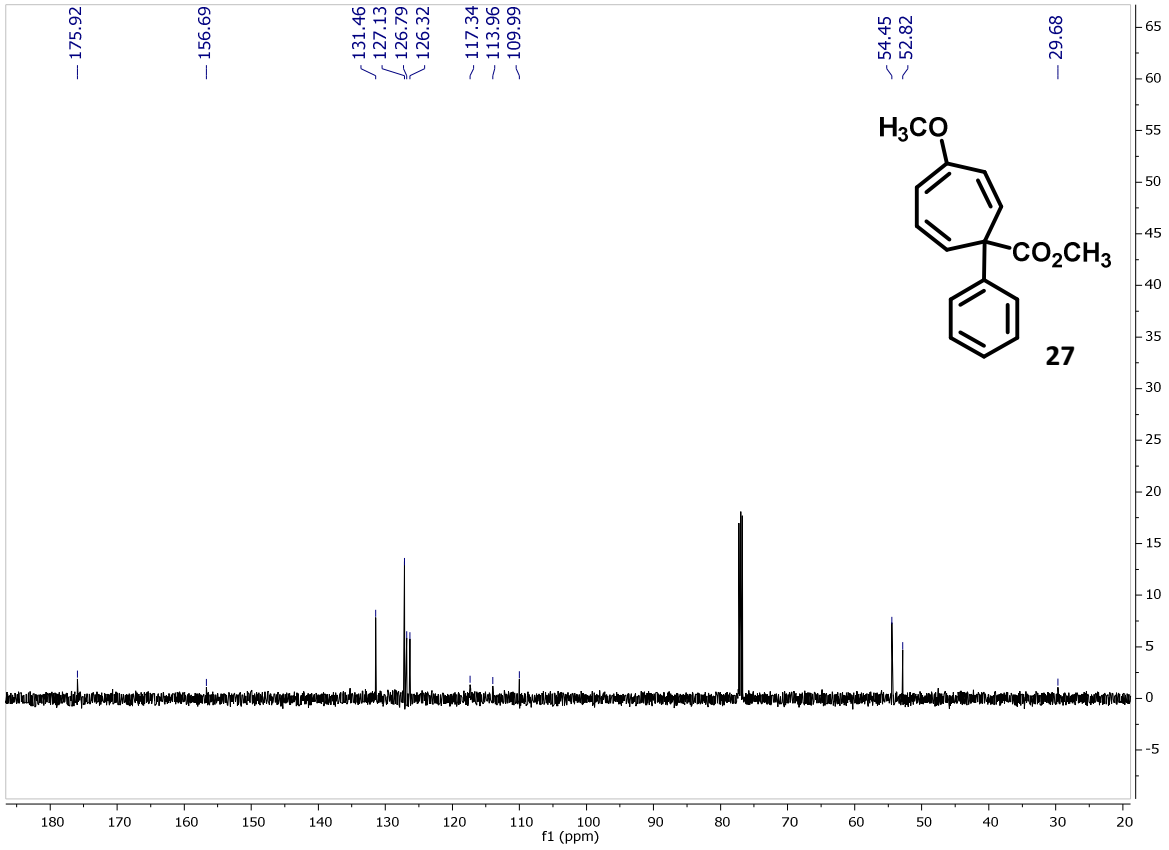

7.14
6.84
6.22
5.58
5.52
4.33
4.17
4.09
3.43
1.14
H3CO
CO2Et
F
25
f1 (ppm)

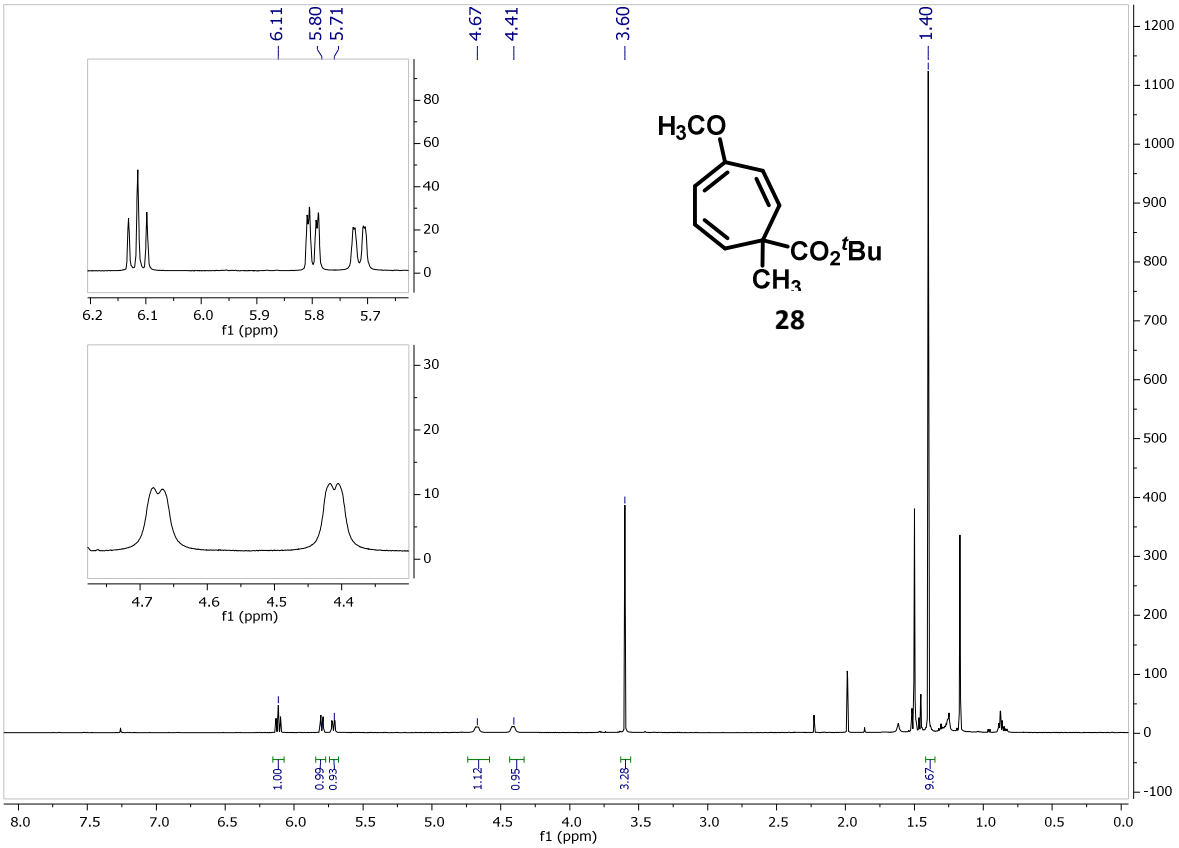

H3CO
CO2Et
F
25
175.03
162.49
160.54
156.90
132.78
131.24
130.13
129.48
126.23
116.82
114.10
113.93
109.99
104.43
61.48
54.45
14.07
f1 (ppm)

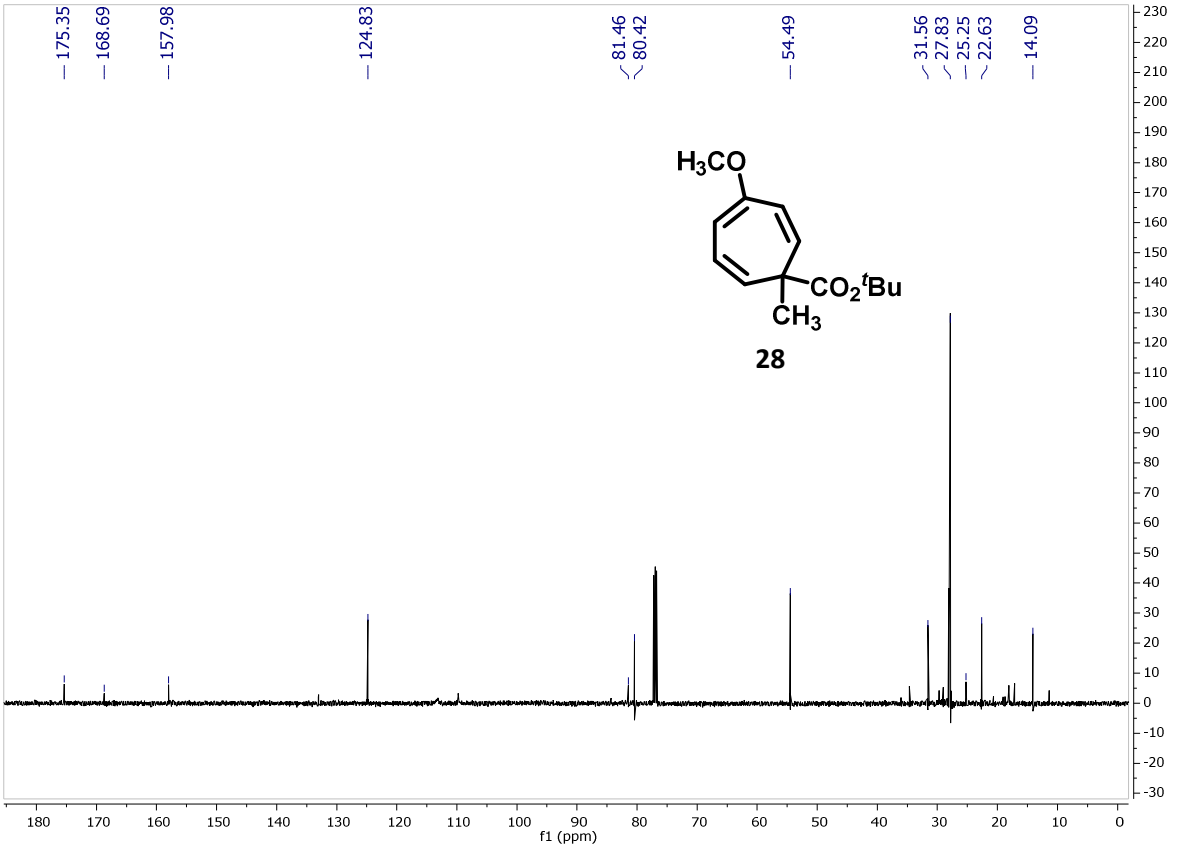

7.07
6.71
6.21
5.58
5.47
4.16
3.99
3.75
3.63
3.43
H3CO
CO2CH3
OCH3
26
f1 (ppm)

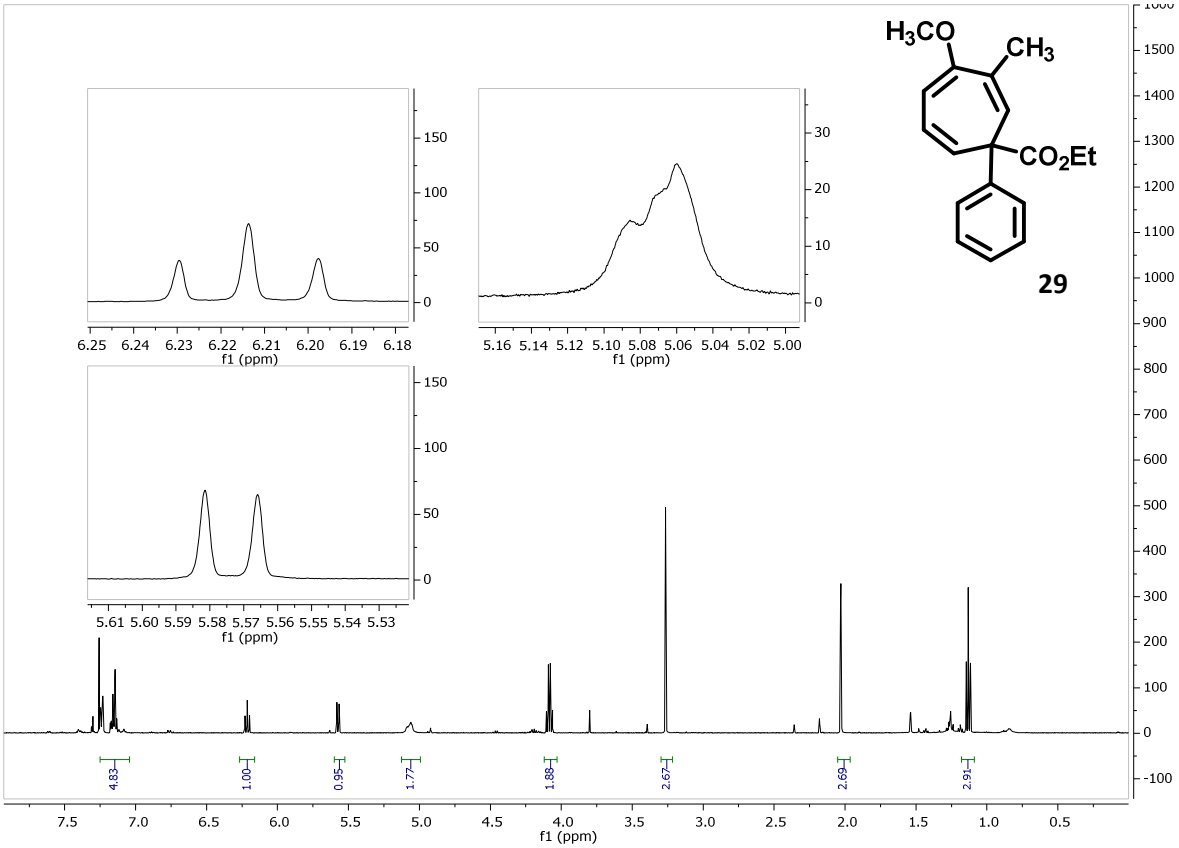

176.24
158.16
156.66
132.65
132.55
127.06
126.30
117.68
114.23
112.63
55.64
55.02
54.45
52.78
29.69
H3CO
CO2CH3
OCH3
26
f1 (ppm)

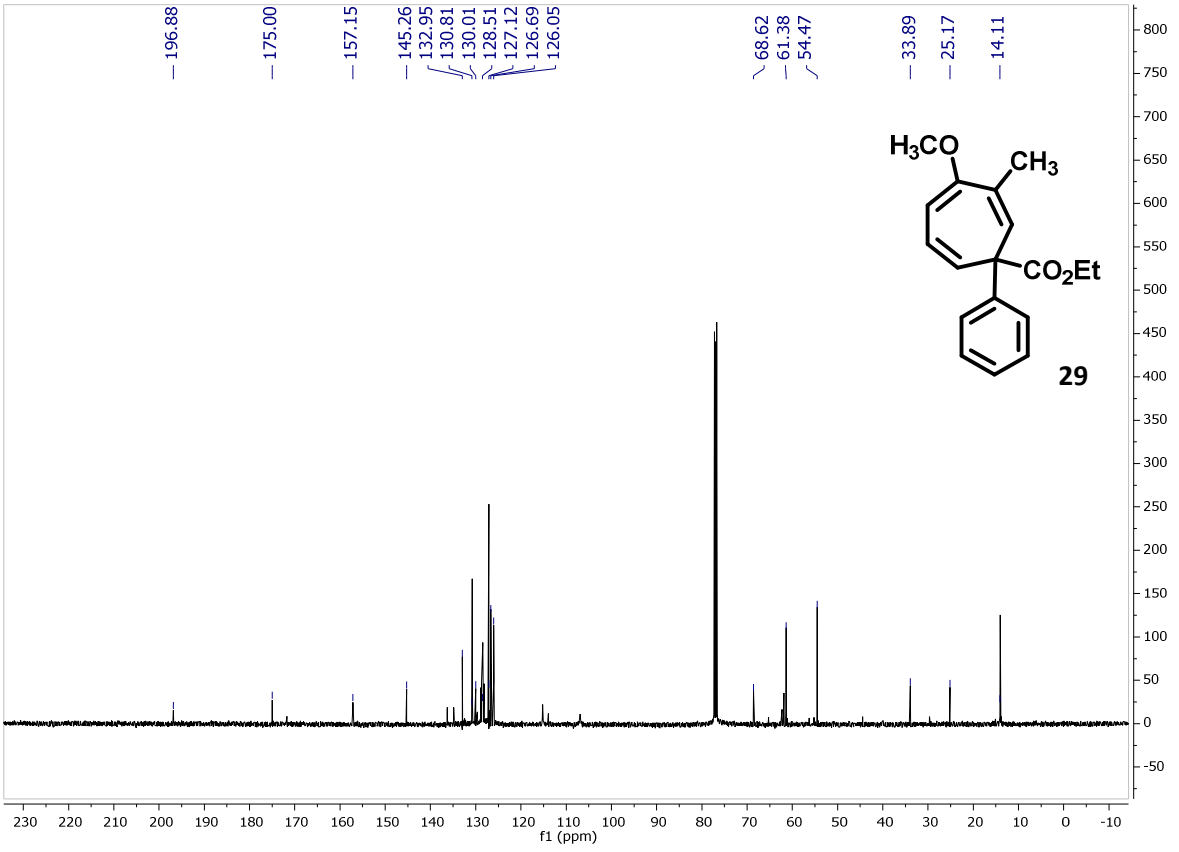

7.18
6.23
5.57
5.52
4.28
4.13
3.63
3.42
H3CO
CO2CH3
27
f1 (ppm)

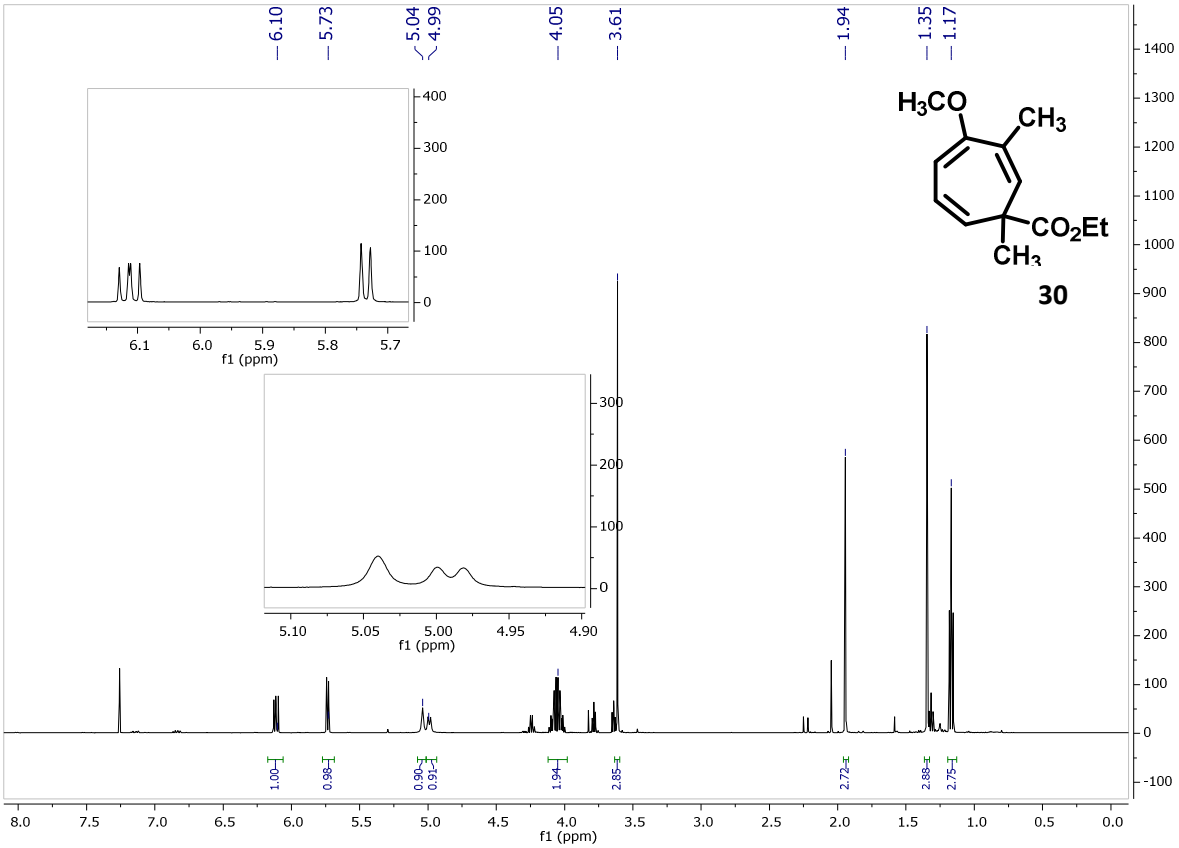

175.92
156.69
131.46
127.13
126.79
126.32
117.34
113.96
109.99
54.45
52.82
29.68
H3CO
CO2CH3
27
f1 (ppm)

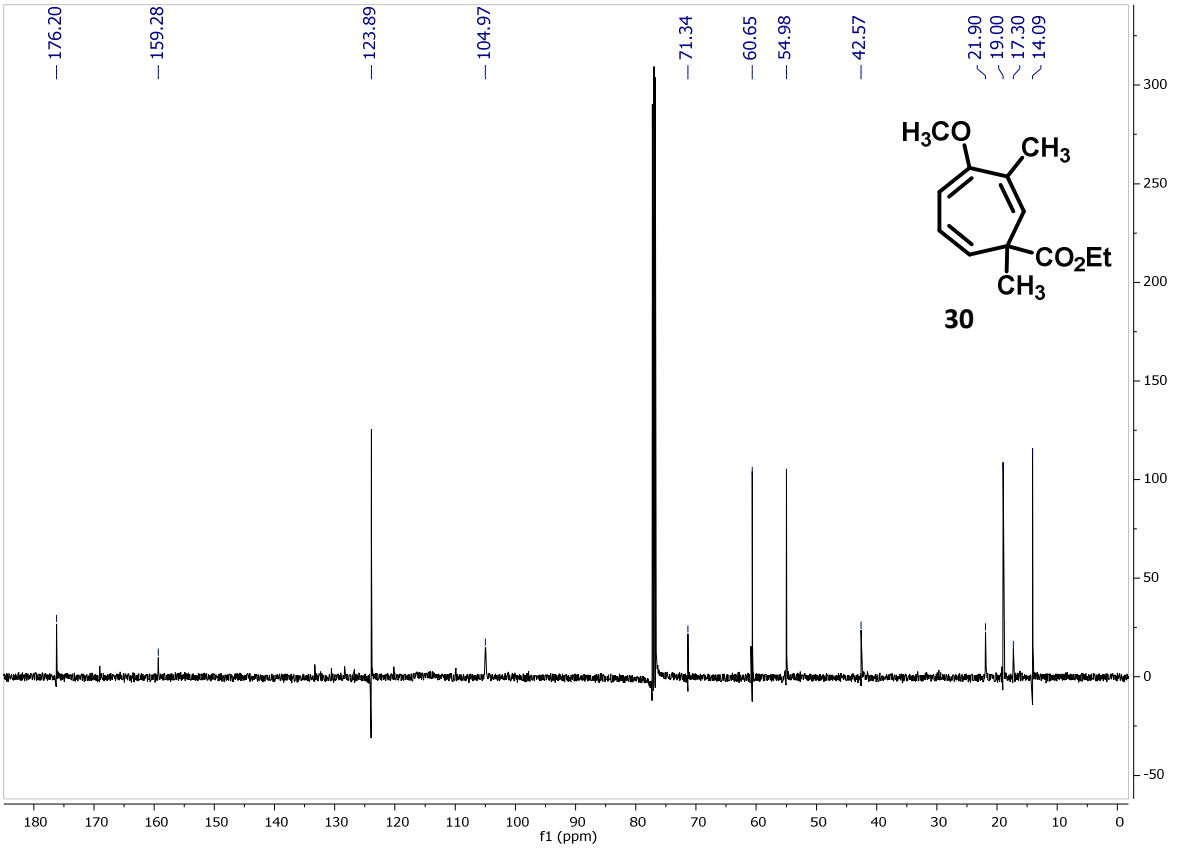

6.11
5.80
5.71
4.67
4.41
3.60
1.40
H3CO
CO2tBu
CH3
28
f1 (ppm)
1.00
0.99
0.93
1.12
0.95
3.28
9.67

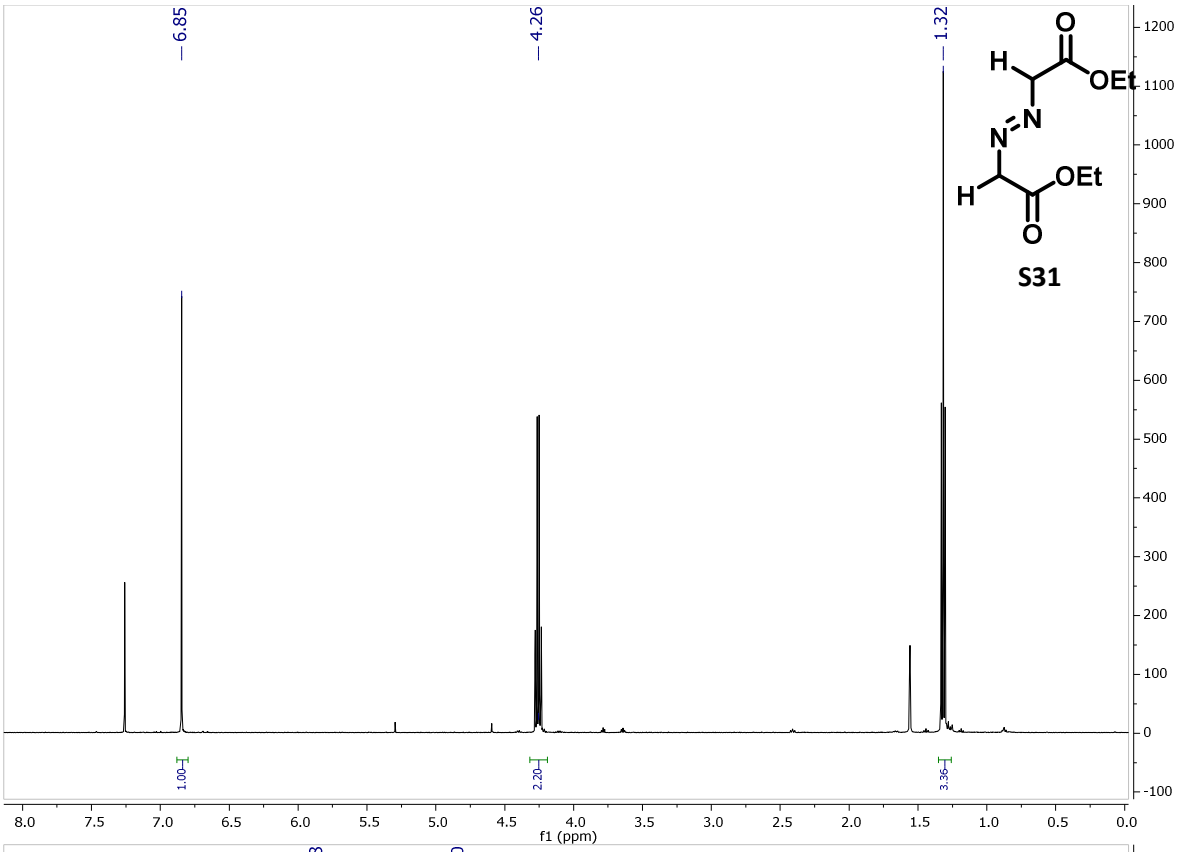

175.35
168.69
157.98
124.83
81.46
80.42
54.49
31.56
27.83
25.25
22.63
14.09
H3CO
CO2tBu
CH3
28
f1 (ppm)

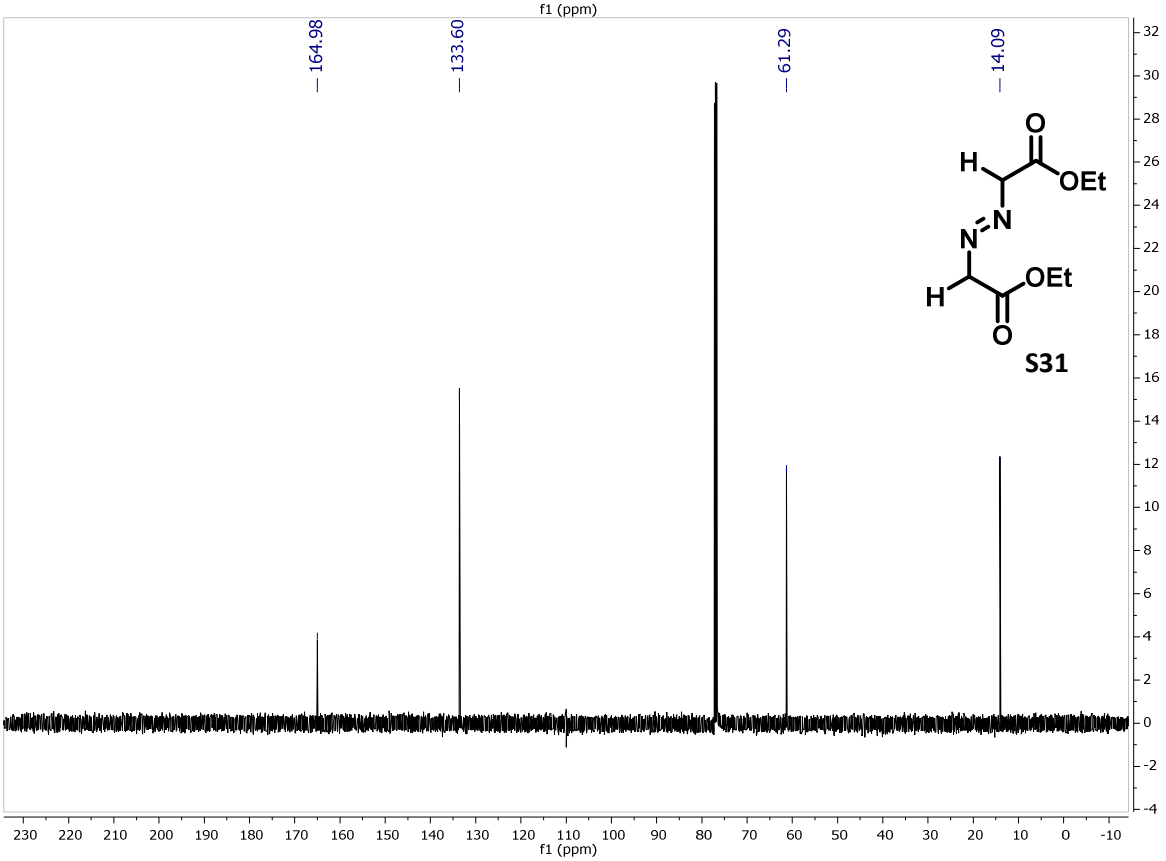

H3CO
CH3
CO2Et
29
f1 (ppm)
4.83
1.00
0.95
1.77
1.88
2.67
2.69
2.91


196.88
175.00
157.15
145.26
132.95
130.81
130.01
128.51
127.12
126.69
126.05
68.62
61.38
54.47
33.89
25.17
14.11
H3CO
CH3
CO2Et
29
f1 (ppm)


6.10
5.73
5.04
4.99
4.05
3.61
1.94
1.35
1.17
H3CO
CH3
CO2Et
CH3
30
f1 (ppm)
1.00
0.98
0.90
0.91
1.94
2.85
2.72
2.88
2.75


176.20
159.28
123.89
104.97
71.34
60.65
54.98
42.57
21.90
19.00
17.30
14.09
H3CO
CH3
CO2Et
CH3
30
f1 (ppm)


6.85
4.26
1.32
1.00
2.20
3.36
f1 (ppm)
S31


164.98
133.60
61.29
14.09
f1 (ppm)
S31