Supporting Information

Asymmetric Vinylogous Michael Reaction of Cyclic Enones with Silyloxy Furans

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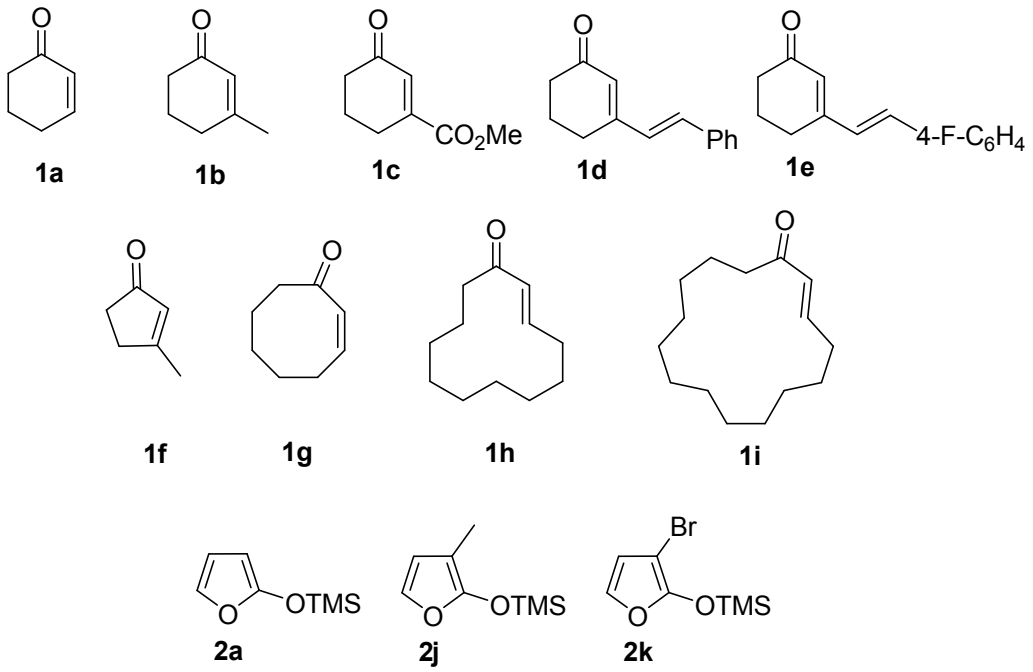
General Information: Bruker AV-300 instrument (300 MHz and 75 MHz, respectively) was used to record ^{1}H and ^{13}C NMR spectra in deuterated solvents with residual protonated solvent signals as internal reference.^{1}H NMR's data is reported as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), integration, coupling constant (Hz). ^{13}C NMR's data is recorded in terms of chemical shift (δ, ppm). IR spectra were recorded on an FT-IR spectrometer by taking solid samples as KBr pellets and liquids as thin films on KBr disks. Mass spectra were recorded on a high-resolution mass spectrometer (ESI-TOF) in positive-ion mode. Specific rotations were recorded on an Autopol III Automatic Polarimeter. Column chromatographic separations were carried out on silica gel (100–200 mesh). High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using a chiral column (AS-H, OJ-H, IA, IC) (250 x 4.6 mm) as noted. UV absorption was monitored at 209 nm, 230 nm or 254 nm.

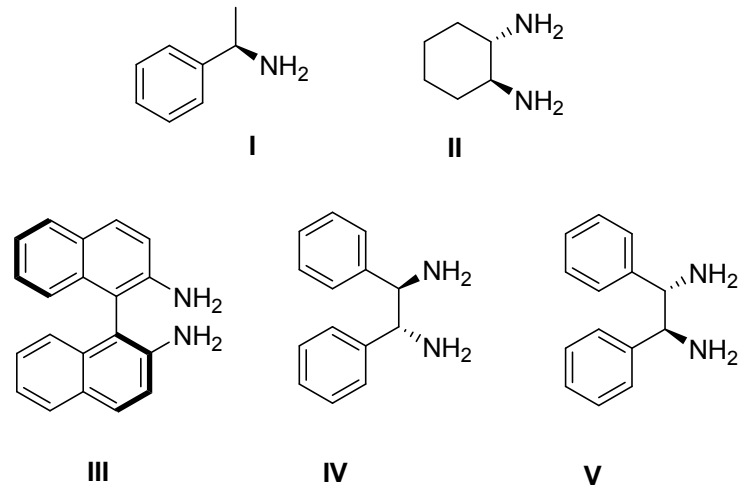
Preparation of the Catalysts: Catalysts **I-IV** were purchased from Sigma Aldrich and used without further purification. Catalyst **V** was prepared according to known literature procedure.[1]

Preparation of the Substrates: Cyclohex-2-enone **(1a),** 3-methylcyclohex-2-enone **(1b)**, 3-methylcyclopent-2-enone **(1f)** were purchased from Sigma Aldrich and used without further purification. Methyl-3-oxocyclohex-1-enecarboxylate **(1c)**, (*E*)-3-styrylcyclohex-2-enone **(1d)**, (*E*)-3-(4-fluorostyryl)cyclohex-2-enone **(1e)**, 2-Cyclooctenone **(1g)**, (*E*)-2-Cyclododecenone **(1h)**, (*E*)-2-Cyclopentadecenone **(1i)** were prepared according to reported

literature procedures.[2] 2-trimethylsilyloxy furan **2a** was purchased from TCI-India and used without further purification. Trimethylsilyloxyfurans **2j** and **2k** were prepared according to reported literature methods.[3]



S-Figure 1. The Sructure of Cyclic Enones 1 and Trimethylsilyloxy furans 2

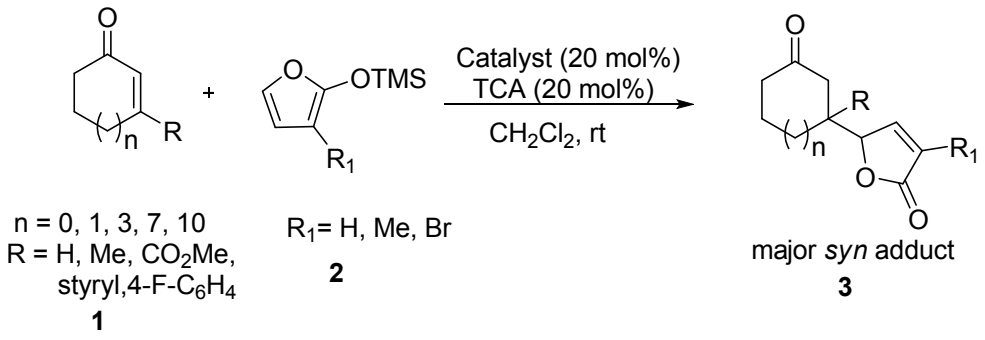


S-Figure 2. The Structure of Catalysts

Preparation of Racemic Michael Adducts:[4] To a solution of cyclic enone (0.20 mmol) in anhydrous methylene chloride, 2-(trimethylsilyloxy) furan (0.30 mmol) was added. The

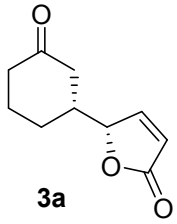
reaction mixture was cooled to -78 °C, stirred at the same temperature for 5 minutes and then $Bi(OTf)_3$ (0.04 mmol) was added all at once. The reaction mixture was stirred at -78 °C and the progress of the reaction was monitored by TLC (usually 2–3 h). After completion of the reaction, it was quenched with aqueous saturated NH_4Cl at –78 °C and the mixture was allowed to warm to room temperature. The resulting biphasic mixture was transferred in separating funnel. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 mL × 3). The organic phases were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was treated by THF/HCl (1 N) (1:1, v/v, 10 $mLmmol^{-1}$) at room temperature for 30 min and then was diluted with H_2O, extracted with EtOAc (3 mL × 3), dried with Na_2SO_4, filtered, and the solvent was evaporated. The crude mixture was purified by silica gel column chromatography by using ethyl acetate/hexane gradient as described below for the corresponding chiral reaction, and subjected to HPLC analysis.

General Procedure for Asymmetric Vinylogous Michael Addition:



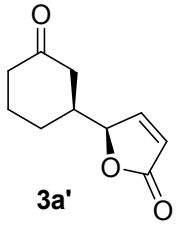
In an ordinary dram vial equipped with a magnetic stirring bar, (1*R*, 2*R*)-1,2-diphenylethylenediamine (8.5 mg, 0.04 mmol) was dissolved in 1 mL of methylene chloride. To the solution trichloroacetic acid (6.5 mg, 0.04 mmol) was added at room temperature and then stirred for 5 minutes at same temperature. In the resulting mixture, cyclic α, β-unsaturated ketones (0.2 mmol), and water (20μL) was added at room temperature and then stirred for the next 10 minutes at same temperature. Subsequently, silyloxyfuran (0.3 mmol) was drop wise added to the reaction mixture. The vial was closed with a cap and stirring was continued for the indicated time (48-96 h) at the room temperature. Once the reaction completed, the reaction mixture was transferred to a 25 mL conical flask with the help of CH_2Cl_2. The resulting solution was dried over Na_2SO_4. The crude solution was concentrated and the resulting organic residue was passed through a short plug of silica gel for the removal of the catalyst and the silica gel plug was washed with ethyl acetate. The eluent was concentrated in vacuo and the residue was subjected to silica gel flash chromatography (eluent: EtOAc/PE = 1/1, v/v) for the individual Michael adduct.

(*R*)-5-((*R*)-3-oxocyclohexyl)furan-2(5H)-one (3a):



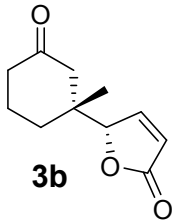
Catalyst **IV**(8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol, 20 mol%) catalysed reaction of cyclohex-2-enone (20 μL, 0.20 mmol) and 2-(trimethylsilyloxy) furan (51 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 48 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 1/1) to give the product as a colourless liquid (33.1 mg, 92% yield). The *syn/anti* ratio (95:5) was determined by HPLC analysis of the purified product. The er of the *syn* diastereomer was determined to be 98:2 [determined by HPLC, Chiralpak AS-H, hexanes:isopropanol = 55:45, 0.5 mL/min, λ= 230 nm, t (minor) = 36.3 min, t (major) = 49.27 min]. R_f= 0.40 (ethyl acetate/hexane = 1/1), $[\alpha]^{D}_{38}$ = -84.91 º (*c* 1.31, $CHCl_3$); **^{1}H-NMR**(300 MHz, $CDCl_3$) δ 1.63-1.82 (m, 2H), 1.94-1.98 (m, 1H), 2.12-2.16 (m, 2H), 2.22-2.25 (m, 2H), 2.28-2.40 (m, 2H), 5.03 (s, 1H), 6.16 (d, *J* = 6.00 Hz, 1H), 7.43 (d, *J* = 6.00 Hz, 1H); **^{13}C-NMR**(75 MHz, $CDCl_3$) δ 24.62, 27.66, 40.92, 41.16, 41.47, 85.43, 122.53, 154.04, 172.45, 209.41; **FTIR** (KBr) cm^{-1}: 2921, 1754, 1711, 1638, 1455, 1023, 818 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{10}H_{12}O_3Na$ 203.0679; found 203.0676.

(*S*)-5-((*S*)-3-oxocyclohexyl)furan-2(5H)-one (3a')



Catalyst **V** (8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol, 20 mol%) catalysed reaction of cyclohex-2-enone (20 μL, 0.20 mmol) and 2-(trimethylsilyloxy) furan (51 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 48 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 1/1) to give the product as a colourless liquid (33.2 mg, 92% yield). The *syn/anti* ratio (92:8) was determined by HPLC analysis of the purified product. The er of the *syn* diastereomer was determined to be 98:2 [determined by HPLC, Chiralpak AS-H, hexanes:isopropanol = 55:45, 0.5 mL/min, λ= 230 nm, t (major) = 27.17 min, t (minor) = 39.64 min]. R_f= 0.40 (ethyl acetate/hexane = 1/1), $[\alpha]^{D}_{38}$ = +89.51 º (*c* 1.31, $CHCl_3$).

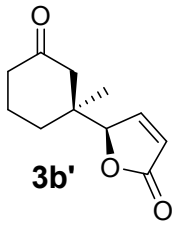
(*S)*-5-((*R*)-1-methyl-3-oxocyclohexyl)furan-2(5H)-one (3b):



Catalyst **IV** (8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol**,** 20 mol%) catalysed reaction of 3-methylcyclohex-2-enone (23 μL,0.20 mmol) and 2-(trimethylsilyloxy) furan (51 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 48 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 1/1) to give the product as a colourless liquid (30.7 mg, 79% yield).The *syn/anti* ratio (99:1) was determined by HPLC

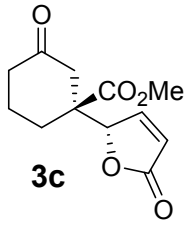
analysis of the purified product. The *er* of the *syn* diastereomer was determined to be 98.1:1.5 [determined by HPLC, Chiralpak AS-H, hexanes:isopropanol = 55:45, 0.5 mL/min, λ= 230 nm, t (minor) = 34.91 min, t (major) = 51.52 min]. R_f= 0.40 (ethyl acetate/hexane = 1/1),[α] $^{D}_{38}$ = -41.66 º (*c* 1.56*,* $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 0.96 (s, 3H), 1.59-1.63 (m, 1H), 1.86-2.01 (m, 4H), 2.25- 2.31 (m, 3H) 4.81 (s, 1H), 6.18 (d, *J* = 6.00 Hz, 1H), 7.46 (d, *J* = 6.00 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 20.24, 21.31, 32.87, 40.67, 42.44, 47.83, 89.42, 123.42, 152.77, 172.32, 209.75; **FTIR**(KBr) cm^{-1}: 2927, 1753, 1708, 1459, 1316, 1097, 824 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{11}H_{14}O_3Na$ 217.0835; found 217.0836.

(*R*)-5-((*S*)-1-methyl-3-oxocyclohexyl)furan-2(5H)-one (3b'):



Catalyst **V** (8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol 20 mol%) catalysed reaction of 3-methylcyclohex-2-enone (23 μL, 0.2 mmol), 2-(trimethylsilyloxy) furan (51 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 48 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 1/1) to give the product as a colourless liquid (31.8 mg, 82% yield). The *syn/anti* ratio (99.9:0.1) was determined by HPLC analysis of the purified product. The er of the *syn* diastereomerwas determined to be 98:02 [determined by HPLC, Chiralpak AS-H, hexanes:isopropanol = 55:45, 0.5 mL/min, λ= 250 nm, t (major) = 38.17 min, t (minor) = 60.00 min]. R_f= 0.40 (ethyl acetate/hexane = 1/1), [α] $^{D}_{37}$ = +81.66 º (*c* 1.50*,* $CHCl_3$); **^{1}H-NMR** (300 MHz, CDCl3) δ 1.00 (s, 3H), 1.89-1.90 (m, 1H), 2.01-2.05 (m, 3H), 2.29- 2.34 (m, 3H) 4.81 (s, 1H), 6.23 (d, *J* = 6.00 Hz, 1H), 7.47 (d, *J* = 6.00 Hz, 1H); **^{13}C-NMR** (75 MHz, CDCl3) δ 20.24, 21.31, 32.87, 40.66, 42.44, 47.83, 89.42, 123.42, 152.76, 172.31, 209.74; **FTIR** (KBr) cm^{-1}: 2927, 1753, 1708, 1459, 1316, 1097, 824 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{11}H_{14}O_3Na$ 217.0835; found 217.0836.

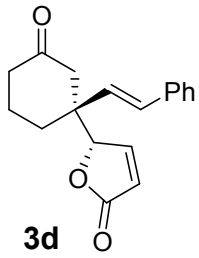
Methyl-3-oxo-1-5-oxo-2,(5-dihydrofuran-2-yl)cyclohexanecarboxylate (3c):



Catalyst **IV** (8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol, 20 mol%) catalysed reaction of methyl 3-oxocyclohex-1-enecarboxylate(27 μL, 0.20 mmol) and 2-(trimethylsilyloxy) furan (51 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 48 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 3/2) to give the product as a colourless liquid (29.5 mg, 62% yield). The *syn/anti* ratio (98:2) was determined by HPLC analysis of the purified product. The *er* of the *syn* diastereomer was determined to be 99.9:0.1 [determined by HPLC, Chiralpak IC, hexanes:isopropanol = 50:50, 1.0 mL/min, λ= 250 nm, t (major) = 38.97 min, t (minor) = 90.37 min]. R_f= 0.40 (ethyl acetate/hexane = 3/2), [α] $^{D}_{38}$ = -91.82 º (*c* 1.59*,* $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 1.61-1.72 (m, 1H), 1.96-2.10 (m, 2H), 2.17-2.23 (m, 3H), 2.29-2.40 (m, 2H), 3.73 (s, 3H), 5.30-5.34 (m, 1H), 6.17 (d, *J* = 6.00 Hz, 1H), 7.26 (d, *J* = 6.00 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 21.36, 31.33, 39.67, 40.92, 52.80, 53.20, 85.12, 123.29, 152.83, 171.75, 172.63, 206.66; **FTIR**(KBr)

cm^{-1}: 2923, 1742, 1457, 1252, 1159, 1097, 819 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{12}H_{14}O_5Na$ 261.0733; found 261.0733.

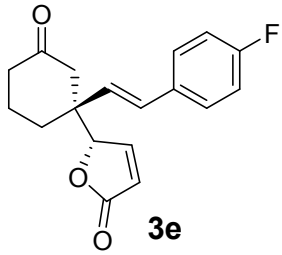
(E)-5-(3-oxo-1-styrylcyclohexyl)furan-2(5H)-one (3d) :



3d

Catalyst **IV**(8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol, 20 mol%) catalysed reaction of (E)-3-styrylcyclohex-2-enone (39.6 mg, 0.20mmol) and 2-(trimethylsilyloxy) furan (51 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 72 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 2/3) to give the product as a colourless liquid (29.0 mg, 51.36% yield). The *syn/anti* ratio (99:1) was determined by HPLC analysis of the purified product. The er of the *syn* diastereomer was determined to be 98:02 [determined by HPLC, Chiralpak IB, hexanes:isopropanol = 80:20, 0.75 mL/min, λ= 205 nm, t (major) = 52.53 min, t (minor) = 61.92 min]. R_f= 0.5 (ethyl acetate/hexane = 2/3),$[\alpha]^{D}{}_{30}$ = -93.33 º (*c* 1.80, $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 1.65-1.74 (m,2H), 1.85-1.89 (m, 2H), 2.15-2.29 (m, 5H), 4.89 (s, 1H), 5.89 (d, *J* = 16.32 Hz, 1H), 6.10 (d, *J* = 4.22 Hz, 1H), 6.40 (d, *J* = 16.51 Hz, 1H), 7.18-7.25 (m, 4H), 7.30-7.31 (m, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ21.05, 32.97, 40.72, 43.19, 48.00, 87.79,123.21, 126.41, 128.33, 128.68, 129.05, 134.56, 135.81, 153.48, 172.43, 209.23; **FTIR** (KBr) cm^{-1}: 2924, 1748, 1636, 1459, 1260, 1078, 890 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{18}H_{18}O_3Na$ 305.1148; found 305.1146.

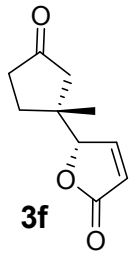
(E)-5-(1-(4-fluorostyryl)-3-oxocyclohexyl)furan-2(5H)-one (3e):



3e

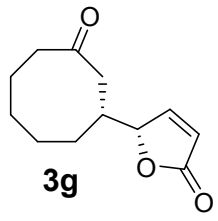
Catalyst **IV**(8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.52 mg, 0.04 mmol, 20 mol%) catalysed reaction of (E)-3-(4-fluorostyryl)cyclohex2-enone (43.2 mg, 0.20mmol) and 2-(trimethylsilyloxy) furan (51 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 72 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 2/3) to give the product as a colourless liquid (33.0 mg, 55.05% yield). The *syn/anti* ratio (96:4) was determined by HPLC analysis of the purified product. The er of the *syn*diastereomerwas determined to be 99:01 [determined by HPLC, Chiralpak IB, hexanes:isopropanol =80:20, 0.75 mL/min, λ= 230 nm, t (major) = 30.17 min, t (minor) =38.79 min]. R_f= 0.5 (ethyl acetate/hexane = 2/3), $[\alpha]^{D}{}_{20}$ = -126.11 º (*c* 1.80, $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 1.70-1.74 (m,1H), 1.85-1.95 (m, 2H), 2.14-2.37 (m, 5H), 4.90 (s, 1H), 5.81 (d, *J* = 16.32 Hz, 1H), 6.10 (d, *J* = 4.22 Hz, 1H), 6.38 (d, *J* = 16.51 Hz, 1H), 6.92-6.98 (m, 2H), 7.21-7.34 (m, 3H); **^{13}C-NMR** (75 MHz, CDCl3)δ 21.10, 32.91, 40.74, 43.37, 48.01, 87.75, 115.47, 115.75, 123.29, 127.95, 128.05, 128.79, 133.41, 153.28, 161.01, 164.30, 172.28, 209.05; **FTIR** (KBr) cm^{-1}: 2924, 2359, 1752, 1643, 1463, 1160, 1032 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{18}H_{17}FO_3Na$ 323.1059; found. 323.1063.

5-(1-methyl-3-oxocyclopentyl)furan-2(5H)-one (3f):



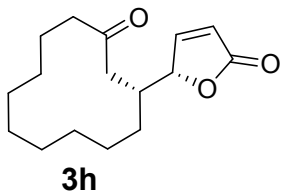
Catalyst **IV** (8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol, 20 mol%) catalysed reaction of 3-methylcyclopent-2-enone (19.8 μL , 0.20mmol) and 2-(trimethylsilyloxy) furan (51 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 72 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 2/3) to give the product as a colourless liquid (18.4 mg, 51.00% yield). The *syn/anti* ratio (93:7) was determined by HPLC analysis of the purified product. The *er* of the *syn* diastereomer was determined to be 92:08 [determined by HPLC, Chiralpak AS-H, hexanes:isopropanol = 55:45, 0.5 mL/min, λ= 250 nm, t (major) = 56.63 min, t (minor) = 106.40 min]. R_f= 0.45 (ethyl acetate/hexane = 2/3), [α] $^{D}{}_{38}$ = -8.88 º (*c* 0.91*,* $CHCl_3$); **^{1}H-NMR**(300 MHz, $CDCl_3$) δ 1.12 (s, 3H), 1.81-1.90 (m, 1H), 1.97-2.03 (m, 1H), 2.18-2.24 (m, 2H), 2.36-2.42 (m, 2H), 4.95 (s, 1H), 6.25 (d, *J* = 6.00 Hz, 1H) 7.49 (d, *J* = 6.00 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 21.90, 31.84, 36.18, 42.74, 47.18, 88.59, 123.43, 153.09, 172.30, 216.45; **FTIR** (KBr) cm^{-1}: 2924, 1746, 1601, 1459, 1164, 1096, 824 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{10}H_{12}O_3Na$ 203.0679; found 203.0681.

5-(3-oxocyclooctyl)furan-2(5H)-one (3g):



Catalyst **IV**(8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol,20 mol%) catalysed reaction of (Z)-cyclooct-2-enone (26.4 μL , 0.20 mmol) and 2-(trimethylsilyloxy) furan (51 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 48 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 2/3) to give the product as a colourless liquid (22.9 mg, 55.0% yield). The *syn/anti* ratio (78:22) was determined by HPLC analysis of the purified product. The *er* of the *syn* diastereomer was determined to be 94:06 [determined by HPLC, Chiralpak ASH, hexanes:isopropanol = 55:45, 0.5 mL/min, λ= 230 nm, t (major) = 39.83min, t (minor) = 63.89 min]. R_f= 0.40 (ethyl acetate/hexane = 2/3),[α] $^{D}{}_{38}$ = +22.22 º (*c* 0.90*,* $CHCl_3$); **^{1}H-NMR** (300 MHz, CDCl3) δ 1.30-1.39 (m, 1H), 1.41-1.55 (m, 2H), 1.62-1.67 (m, 2H), 1.83-1.96 (m, 3H), 2.22-2.59 (m, 5H), 4.99-5.00 (m, 1H), 6.17 (d, *J* = 6.00 Hz, 1H), 7.48 (d, *J* = 6.00 Hz, 1H); **^{13}C-NMR** (75 MHz, CDCl3) δ 22.97, 24.18, 27.35, 29.61, 40.65, 42.63, 42.89, 86.37, 122.65, 154.35, 172.53, 215.04; **FTIR** (KBr) cm^{-1}: 2929, 1753, 1695, 1461, 1331, 1164, 823 cm-1; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{12}H_{16}O_3Na$ 231.0992; found 231.0998.

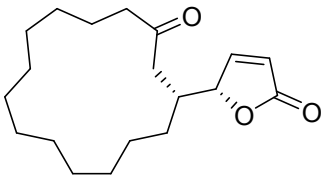
5-(3-oxocyclododecyl)furan-2(5H)-one (3h):



Catalyst **IV** (8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol, 20 mol%) catalysed reaction of (E)-cyclododec-2-enone (40.5 μL , 0.20 mmol), 2-(trimethylsilyloxy) furan (51 μL,0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 48 h. The

catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 1/3) to give the product as a colourless liquid (27.4 mg, 52.00% yield). The *syn/anti* ratio (97:03) was determined by HPLC analysis of the purified product. The *er* of the *syn* diastereomerwas determined to be 92:08 [determined by HPLC, Chiralpak AS-H, hexanes:isopropanol = 55:45, 0.5 mL/min, λ= 230 nm, t (major) = 50.27 min, t (minor) = 56.85 min]. R_f = 0.5 (ethyl acetate/hexane = 1/3), [α] $^{D}_{38}$ = +59.28 º (*c* 1.40*,* $CHCl_3$); **^{1}H-NMR**(300 MHz, CDCl3) δ 1.25-1.49 (m, 14H), 1.55-1.76 (m, 2H), 2.22-2.29 (m, 1H), 2.39-2.52 (m, 3H), 2.70-2.76 (m, 1H), 5.11-5.13 (m, 1H), 6.14 (d, *J* = 6.00 Hz, 1H), 7.53 (d, *J* = 6.00 Hz, 1H); **^{13}C-NMR** (75 MHz, CDCl3) δ 22.12, 22.77, 23.17, 23.81, 25.42, 25.50, 28.17, 36.55, 38.89, 42.85, 85.95, 122.11, 155.59, 172.90, 211.01; **FTIR** (KBr) cm^{-1}: 2923, 1753, 1704, 1465, 1161, 1020, 652 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{16}H_{24}O_3Na$ 287.1618; found 287.1618.

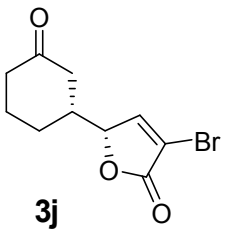
5-(3-oxocyclopentadecyl)furan-2(5H)-one (3i) :



3i

Catalyst **IV** (8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol, 20 mol%) catalysed reaction of (E)-cyclopentadec-2-enone (51.2 μL , 0.20 mmol) and 2-(trimethylsilyloxy) furan (51 μL, 0.30mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 48 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 1/3) to give the product as a white solid (37.9 mg, 62.00% yield). The *syn/anti* ratio (80:20) was determined by HPLC analysis of the purified product. The *er* of the *syn* diastereomer was determined to be 97:3 [determined by HPLC, Chiralpak IC, hexanes:isopropanol = 90:10, 0.75 mL/min, λ= 250 nm, t (major) = 103.61 min, t (minor) = 111.58 min]. R_f= 0.35 (ethyl acetate/hexane = 1/3),[α] $^{D}_{38}$ = +68.66 º (*c* 1.50*,* $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 1.24-1.29 (m, 19H), 1.49-1.52 (m, 2H), 1.73-1.75 (m, 1H), 2.19-2.25 (m, 2H), 2.44-2.51 (m, 3H), 5.08-5.12 (m, 1H), 6.09 (d, *J* = 6.00 Hz, 1H), 7.43 (d, *J* = 6.00 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 22.98, 25.42, 25.65, 26.13, 26.49, 26.66, 27.46, 31.33, 35.84, 40.84, 42.21, 85.92, 121.92, 155.66, 172.93, 209.95; **FTIR** (KBr) cm^{-1}: 2928, 1754, 1703, 1457, 1163, 1097, 830 cm^{-1}**HRMS ESI:** $[M+Na]^+$, Calcd for $C_{19}H_{30}O_3Na$ 329.2087; found 329.2088.

3-bromo-5-(3-oxocyclohexyl)furan-2(5H)-one (3j):

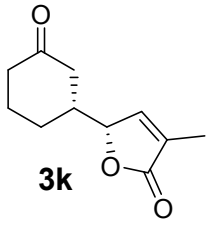


3j

Catalyst **IV** (8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol, 20 mol%) catalysed reaction of cyclohex-2-enone (20 μL, 0.20mmol) and (3-bromofuran-2-yloxy)trimethylsilane (55 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 48 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 2/3) to give the product as a yellow solid (28.3 mg, 55% yield). The *syn/anti* ratio (72:28) was determined by HPLC analysis of the purified product. The er of the *syn* diastereomer was determined to be 99:01[determined by HPLC, Chiralpak AS-H, hexanes:isopropanol = 55:45,

0.5 mL/min, λ= 250 nm, t (minor) = 30.21 min, t (major) = 64.64 min]. R_f= 0.4 (ethyl acetate/hexane = 2/3),[α] $^{D}{}_{38}$ = -102.44 ° (*c* 2.86*,* $CHCl_3$); **^{1}H-NMR**(300 MHz, $CDCl_3$) δ 1.69-1.72 (m, 3H), 1.90-1.99 (m, 1H), 2.11-2.19 (m, 1H), 2.21-2.30 (m, 2H), 2.38-2.45 (m, 2H), 4.87-4.97 (m, 1H), 7.48 (d, *J* = 2.99 Hz, 1H)**; ^{13}C-NMR** (75 MHz, $CDCl_3$) δ 24.58, 27.39, 40.93, 41.38, 41.57, 84.83, 114.14, 150.41, 167.78, 208.76; **FTIR**(KBr) cm^{-1}: 2928, 1766, 1606, 1370, 1223, 991, 515 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{10}H_{11}O_3BrNa$ 280.9784; found 280.9785.

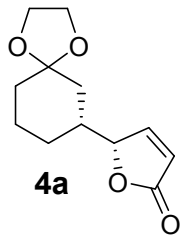
3-methyl-5-(3-oxocyclohexyl)furan-2(5H)-one (3k):



3k

Catalyst **IV**(8.5 mg, 0.04 mmol, 20 mol%) and TCA (6.5 mg, 0.04 mmol, 20 mol%) catalysed reaction of cyclohex-2-enone (20 μL, 0.20 mmol) and (3-methylfuran-2-yloxy)trimethylsilane (52.7 μL, 0.30 mmol) in CH_2Cl_2 and water (20μL) was run at room temperature for 48 h. The catalyst was removed according to the general procedure. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/hexane = 2/3) to give the product as a colourless liquid (17.5 mg, 45.0% yield). The *syn/anti* ratio (65:35) was determined by HPLC analysis of the purified product. The *er* of the *syn* diastereomer was determined to be 92:08 [determined by HPLC, Chiralpak AS-H, hexanes:isopropanol = 55:45, 0.5 mL/min, λ= 250 nm, t (minor) = 19.98 min, t (major) = 33.37 min]. R_f= 0.4 (ethyl acetate/hexane = 2/3), [α] $^{D}{}_{38}$ = +19.42 ° (*c* 1.39*,* $CHCl_3$); **^{1}H-NMR** (300 MHz, CDCl3) δ 1.41-1.50 (m, 1H), 1.62-1.71 (m, 2H), 1.94 (s, 3H), 2.11-2.14 (m, 2H), 2.22-2.43 (m 4H), 4.78-4.88 (m, 1H), 7.00-7.03 (m, 1H); **^{13}C-NMR** (75 MHz, CDCl3) δ 10.68, 24.40, 25.69, 41.11, 41.92, 43.96, 83.16, 131.27, 146.16, 173.58, 209.43**; FTIR** (KBr) cm^{-1}: 2924, 1753, 1646, 1456, 1223, 1030, 861 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{11}H_{14}O_3Na$ 217.0835; found 217.0836.

5-(1,4-dioxaspiro[4.5]decan-7-yl)furan-2(5H)-one (4a):[5a]

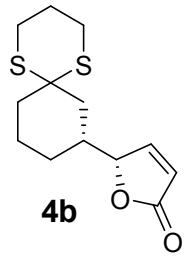


4a

To a solution of Michael adduct **3a** (36 mg, 0.2 mmol) in ethylene glycol (1 ml), 4Å molecular sieves was added at room temperature. In the resulting mixture *p*-TsOH (34.5 mg, 1 eq) was added all at once, and then stirred at room temperature for 30 min. The progress of the reaction was monitored by TLC. Once the reaction completed, it was quenched with saturated aqueous $NaHCO_3$. The resulting biphasic mixture was transferred in separating funnel and extracted with EtOAc (3 mL x 3). The combined organic layers were washed with brine and the brine layer was back-extracted with EtOAc, dried over Na_2SO_4 and concentrated in vacuum. The crude organic residue was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether = 5/95 to 40/60) to give the product **4a** as a pale yellow oil (32.5 mg, 72% yield). The *syn/anti* ratio (98:2) was determined by HPLC analysis of the purified product. The *er* of the *syn* diastereomer was determined to be 99.9:0.1 [determined by HPLC, Chiralpak OJ-H, hexanes:isopropanol = 98:02, 1.00 mL/min, λ= 205 nm, t (minor) = 42.59 min, t (major) = 46.24 min]. R_f = 0.6 (ethyl acetate/hexane = 2/3), [α] $^{D}{}_{28}$ = -79.50 ° (*c* 2.00*,* $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 1.16-1.29 (m, 2H),

1.33-1.46(m, 2H), 1.70-1.74 (m, 4H), 2.01-2.02 (m, 1H), 3.91 (s,4H), 4.89 (d, *J* = 6.00 Hz, 1H), 6.12 (d, *J* = 6.00 Hz, 1H), 7.45 (d, *J* = 6.00 Hz, 1H); **^{13}C-NMR** (75 MHz, CDCl3) δ 22.49, 27.38, 34.58, 36.18, 38.97, 64.26, 86.49, 108.46, 122.01, 154.74, 172.84; **FTIR** (KBr) cm^{-1}: 2924,1753, 1460, 1163, 1323, 1024, 816 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{12}H_{16}O_4Na$ 247.0941; found 247.0936.

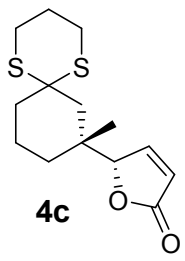
5-(1,5-dithiaspiro[5.5]undecan-8-yl)furan-2(5H)-one (4b):[5b]



4b

To the solution of Michael adduct **3a** (36 mg, 0.2 mmol) and 1,3-propanedithiol (30.0 μL, 0.3mmol) in anhydrous CH_2Cl_2 (0.5 ml), $BF_3.OEt_2$ (2.8 mg, 0.02 mmol) was added at room temperature. The resulting solution was stirred at same temperature for 16 hours. The progress of the reaction was monitored by TLC. Once the reaction was completed, it was quenched with sodium bicarbonate solution. The resulting biphasic mixture was transferred in separating funnel and extracted with CH_2Cl_2 (3 ml x 3). The combined organic layer was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude organic residue was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether = 2/98 to 25/75) to give the product **4b** as a white solid (38.3 mg, 71% yield). The *syn/anti* ratio (91.3:8.7) was determined by HPLC analysis of the purified product. The *er* of the *syn* diastereomer was determined to be 98:02 [determined by HPLC, Chiralpak IA, hexanes:isopropanol = 90:10, 0.5.0 mL/min, λ= 230 nm, t (minor) = 32.55 min, t (major) = 35.49 min]. R_f = 0.5 (ethyl acetate/hexane = 1/3), $[\alpha]_{28}^{D}$ = -58.33 º (*c* 1.20, $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 1.20-1.28 (m, 1H), 1.45-1.69 (m, 3H), 1.78-1.81 (m, 2H), 1.97-2.00 (m, 2H), 2.19-2.31 (m, 2H), 2.47-2.51 (m, 1H), 2.72-2.76 (m, 2H), 2.79-2.87 (m, 1H), 2.91-2.95 (m, 1H), 4.85-4.87 (d, *J* = 6 Hz, 1H), 6.15-6.17 (d, *J* = 6 Hz, 1H), 7.46-7.48 (d, *J* = 6 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 21.06, 25.70, 25.83, 26.10, 28.24, 36.98, 37.64, 38.85, 49.49, 86.62, 122.25, 154.57, 172.78; **FTIR** (KBr) cm^{-1} 2926, 2364, 1750, 1640, 1461, 1095, 822 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{13}H_{18}NaO_2S_2$ 293.0640; found 293.0650.

5-(8-methyl-1,5-dithiaspiro[5.5]undecan-8-yl)furan-2(5H)-one (4c):[5b]

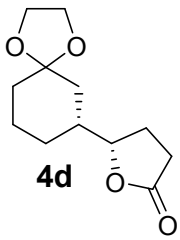


4c

To a solution of Michael adduct **3b** (39 mg, 0.2 mmol) and 1,3-propanedithiol (30.0 μL, 0.3mmol) in anhydrous CH_2Cl_2 (0.5 ml), $BF_3.OEt_2$ (2.8 mg, 0.02 mmol) was added at room temperature. The resulting reaction mixture was stirred at room temperature for 16 hours. The progress of the reaction was monitored by TLC. Once the reaction was completed, it was quenched by aqueous sodium bicarbonate solution. The resulting biphasic mixture was transferred in separating funnel and extracted with CH_2Cl_2 (3 ml x 3). The combined organic layer was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude organic residue was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether = 2/98 to 25/75) to give the product **4c** as a white solid (35

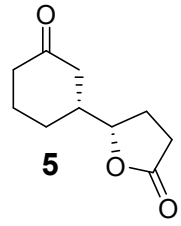
mg, 62% yield). R_f= 0.5 (ethyl acetate/hexane = 1/3), The *syn/anti* ratio (99.9:0.1) was determined by HPLC analysis of the purified product. The *er* of the *syn* diastereomer was determined to be 99:01 [determined by HPLC, Chiralpak IB, hexanes:isopropanol = 95:05, 0.5.0 mL/min, λ= 230 nm, t (minor) = 37.45 min, t (major) = 43.53 min]. $[\alpha]_{23}^{D}$= -80.00 º (*c* 1.20*,* $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 0.91 (s, 3H) 1.39-1.45 (m, 1H), 1.75-1.79 (m, 3H), 1.85-2.04 (m, 5H), 2.39-2.44 (m, 1H), 2.73-2.76(m, 2H), 2.80-3.10 (m, 2H), 5.52 (s, 1H), 6.14-6.16 (d, *J* = 6 Hz, 1H), 7.44-7.46 (d, *J* = 6 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 18.25, 22.30, 25.43, 26.40, 34.52, 38.21, 38.36, 43.73, 48.58, 88.76, 122.54, 153.98, 173.04; **FTIR** (KBr) cm^{-1}: 3459, 2925, 2362, 1750, 1637, 1460, 1094 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{14}H_{20}NaO_2S_2$ 307.0802; found 307.0807.

5-(1,4-dioxaspiro[4.5]decan-7-yl)dihydrofuran-2(3H)-one (4d):[5c]



To a solution of **4a** (44.8 mg, 0.2 mmol) in THF/MeOH=1/1 (2.0 mL) was added $NiCl_2.6H_2O$ (99.8 mg, 0.42 mmol, 2.1 equiv.) and $NaBH_4$ (8.4 mg, 0.22 mmol, 1.1 equiv.) at –78 °C. The reaction mixture was stirred at same temperature for 5 minutes, then warmed at 0°C and stirred at same temperature for 1 h. Subsequently, reaction mixture was warmed to room temperature and stirred at same temperature for 12 h. The progress of the reaction was monitored by TLC. Once the reaction was completed, it was quenched by sat. NH_4Cl (5 mL). The resulting biphasic mixture was transferred in separating funnel and seprated water layer was extracted with ethyl acetate (3 mL x 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether = 5/95 to 50/50) to give the product **4d** (37.1mg, yield 82%), R_f= 0.6 (ethyl acetate/hexane = 2/3), $[\alpha]_{28}^{D}$ = +19.16 º (*c* 2.40*,* $CHCl_3$); **^{1}H-NMR**(300 MHz, $CDCl_3$) δ 1.02-1.10 (m, 1H), 1.25-1.34 (m, 1H), 1.46-1.63 (m, 2H), 1.67-1.72 (m, 4H), 1.78-2.02 (m, 2H), 2.23-2.30 (m, 1H), 2.49-2.55 (m, 2H), 3.92 (s, 4H), 4.20-4.28 (m, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 22.54, 25.92, 26.53, 28.81, 34.84, 37.21, 40.68, 64.30, 84.12, 108.47, 177.00; **FTIR** (KBr) cm^{-1}: 2924, 1769, 1457, 1354, 1083, 915, 812 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{12}H_{18}O_4Na$ 249.1097; found 249.1090.

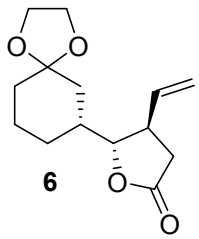
5-(3-oxocyclohexyl)dihydrofuran-2(3H)-one (5):[5d]



To a magnetically stirred solution of **4b** (45.2 mg, 0.2 mmol) in anhydrous acetone (1.5 mL) was added a catalytic amount (6.9 mg, 20 mol %) of *p*-toluene sulfonic acid and stirred at room temperature for 30 h, and then is quenched by the addition of saturated aqueous solution of $NaHCO_3$. The resulting solution was extracted with EtOAc (3mL x 3). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The crude mixture was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether = 5/95 to 45/55) to give the product **3c** as a pale yellow oil (29.8 mg, 82% yield), R_f= 0.4 (ethyl acetate/hexane = 2/3), $[\alpha]_{28}^{D}$ = +41.22 º (*c* 1.14*,* $CHCl_3$);**^{1}H-NMR**(300 MHz, CDCl3) δ 1.53-1.71 (m, 2H), 1.87-2.03 (m, 3H), 2.11-2.27 (m, 2H), 2.20-2.39 (m, 3H), 2.52-2.60 (m, 3H), 4.34-4.42 (m, 1H); **^{13}C-NMR** (75 MHz, CDCl3) δ 24.70, 25.44, 26.92, 28.65,

41.13, 42.91, 43.21, 83.09, 176.46, 209.65; **FTIR**(KBr) cm^{-1}: 2930, 1769, 1709, 1348, 1185, 1017, 807 cm^{-1},**HRMS ESI:** $[M+Na]^+$, Calcd for $C_{10}H_{14}O_3Na$ 205.0835; found 205.0846.

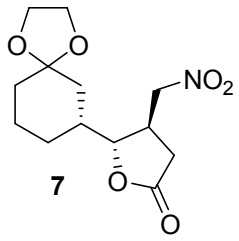
5-(1,4-dioxaspiro[4.5]decan-7-yl)-4-vinyldihydrofuran-2(3H)-one (6):[5e]



6

To a suspension of CuBr.DMS (1 mmol) in THF (0.5 ml), vinyl magnesium bromide (1ml, 1M in THF, 1 mmol) was added at -78 ^oC and the solution was stirred at the same temperature for 30 min. To the resulting mixture was added trimethylsilyl chloride (60 µL) followed by a solution of **4a** (0.2 mmol, 44.8 mg) in dichloromethane (0.5 ml). The reaction mixture was stirred at -78^oC for 2.5 h and the progress of the reaction was monitored by TLC. Once the reaction was completed, it was quenched with saturated NH_4Cl and warmed to room temperature for 1h. The mixture was partitioned between saturated NH_4Cl and dichloromethane. The organic layer was washed with H_2O and combined aqueous layer were extracted with dichloromethane (3mLx3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude organic residue was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether = 5/95 to 30/70) to give the colourless liquid (22.5 mg, yield =44.58 %, R_f= 0.7 (ethyl acetate/hexane = 2/3); $[\alpha]^{D}_{28}$ = + 28.33º (*c* 1.20*,* $CHCl_3$); **^{1}H-NMR**(300 MHz, $CDCl_3$) δ 1.24-1.30 (m, 1 H), 1.33-1.49 (m, 3H), 1.57-1.62 (m ,2H), 1.73-.1.81 (m, 3H), 1.82-1.99 (m, 2H), 2.39-2.48 (m, 1H), 2.67-2.75 (m, 1H), 2.94-3.00 (m, 1H), 3.94 (s, 4H), 4.03-4.08 (m, 1H), 5.14-5.20 (m, 2H), 5.77 (ddd, J1 = 17.6 Hz, J2 = 10.4 Hz, J3 = 7.2 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 22.70, 27.81, 34.76, 35.49, 36.46, 39.41, 42.88, 64.34, 87.82, 108.67, 117.54, 136.85, 175.53; **FTIR**(KBr) cm^{-1}: 2924, 2361, 1776, 1460, 1210, 1015, 922 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{14}H_{20}O_4Na$ 275.1254; found 275.1263.

4-(nitromethyl)-5-(1,4-dioxaspiro[4.5]decan-7-yl)dihydrofuran-2(3H)-one (7):[5f]



7

To a solution of compound **4a** (44.8 mg, 0.2 mmol) in anhydrous nitromethane (0.66 mL, 12.4 mmol, , 62 equiv.) was added distilled DBU (0.04 mmol, 06μL, 0.2 equiv.) and the reaction mixture was stirred at room temperature for 16 h. The solvent was evaporated off under reduced pressure and the crude mixture was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether = 5/95 to 30/70) to give **8** (52.4 mg, 92% yield) as a yellow oil. R_f = 0.6 (ethyl acetate/hexane = 1/3), $[\alpha]^{D}_{30}$ = +06.07 º (*c* 2.80*,* $CHCl_3$); **^{1}H-NMR**(300 MHz, $CDCl_3$) δ 1.24-1.57 (m, 4H), 1.72-1.90 (m, 5H), 2.40 (dd, J_1= 4.95 Hz, J_2 = 18.34 Hz, 1H), 2.82-2.92 (m, 1H), 3.05-3.12(m, 1H), 3.94 (s, 4H), 4.09-4.12 (m, 1H), 4.40-4.56 (m, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 22.42, 27.40, 32.25, 32.39, 34.53, 35.76, 36.08, 39.70, 64.34, 84.94, 108.32, 173.96; **FTIR** (KBr) cm^{-1}: 2923, 1747, 1553, 1460, 1162, 1078, 729 cm^{-1}; **HRMS ESI:** $[M+Na]^+$, Calcd for $C_{13}H_{19}NO_6Na$ 308.1105; found 308.1092.

References:

1. Cooksey, J. P.; Kocieński, P. J.; Schmidt, A. W; Snaddon, T. N.; Kilner, C. A. *Synthesis* **2012**, *44*, 2779.

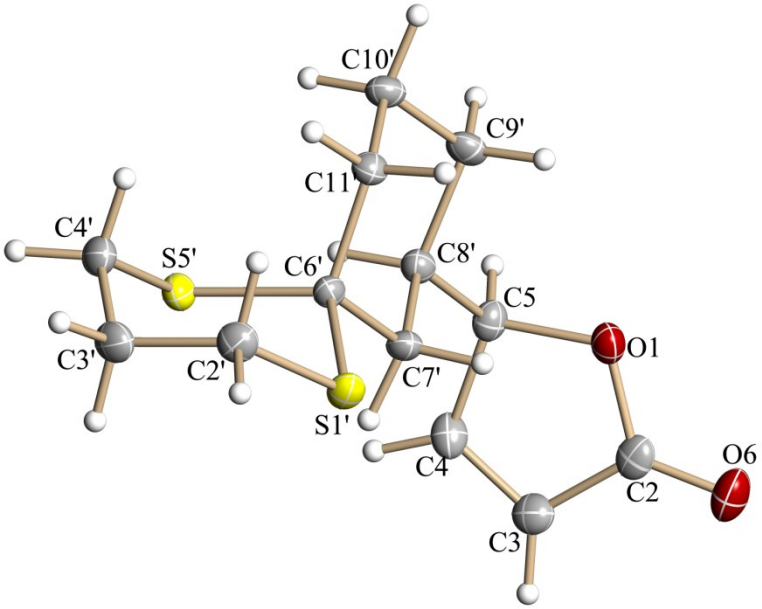
2. (a) Peese, K. M.; Gin, D. Y. *Chem. Eur. J.* **2008**, *14*, 1654. (b) Satoh, N.; Ishiyama, T.; Miyaura, N.; Suzuki, A. *Bull. Chem. Soc. Jpn.*, 60, 3471. (c) Nicolaou, K. C.; Zhong, Y. L.; Baran, P. S. *J. Am. Chem. Soc*., **2000**, *122*, 7596.

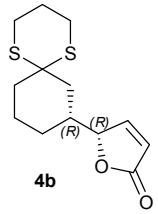
3. (a) Evans, D. A.; Kvarno, L.; Dunn, T. B.; Beauchemin, A.; Raymer, B.; Mulder, J. A.; Olhava, E. J.; Juhl, M.; Kagechika, K.; Favor, D. A. *J. Am. Chem. Soc.*, **2008**, *130*, 16295. (b) Burghart, J.; Brückner, R. *Angew. Chem. Int. Ed.*, **2008**, *47*, 7664.

4. Chabaud, L.; Jousseaume, T.; Retailleau, P.; Guillou, C. *Eur. J. Org. Chem.* **2010**, 5471.

5. (a) Ciceri, P.; Demnitz, F. W. J.; *Tetrahedron Lett.,***1997**, *38*, 389. (b) Luiken, S.; Kirschning, A. *J. Org. Chem.*, **2008**, *73*, 2018. (c) Yin, L.; Takada, H.; Kumagai, N.; Shibasaki, M. *Angew. Chem. Int. Ed.*, **2013**, *52*, 7310. (d) Borrelly, S.; Paquette, L. A. *J. Am. Chem. Soc.* **1996**, *118,* 727. (e) Song, L.; Yao, H.; Zhu, L.; Tong, R. *Org. Lett.* **2012**, *15*, 6. (f) Fournier, J.; Lozano, O.; Menozzi, C.; Arseniyadis, S.; Cossy, J. *Angew. Chem. Int. Ed*,. **2013**, *52*, 1257.

Assignment of the absolute configuration of *syn*-4b by X-ray analysis:





X-Ray data collection, solution, and refinement for Compound *syn*-4b:

X-ray intensity data measurements of compound ***syn*-4b** was carried out on a Bruker SMART Apex2 CCD diffractometer with graphite-monochromatized (MoK_α= 0.71073Å) radiation at 150(2) K. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames (12 frames from each set). The optimized strategy used for data collection consisted of one $\varphi$and fourω scan sets, with 0.5° steps in φorω;completeness achieved was100% with redundancy3.98. Data were collected with a frame time of 15 sec keeping the sample-to-detector distance fixed at 5.00 cm. A total of 1552 frames were collected. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).[1]Final unit cell parameters were obtained from 9923 reflections after integration.

Crystal data of ***syn*-4b:** $C_{13}H_{18}O_2S_2$, M=270.39, colorless plate, 0.45 x 0.36 x 0.29 mm^3, orthorhombic, space group $P2_12_12_1$, a =6.6349(2), b=8.9609(3), c=21.6859(6)Å, V = 1289.33(7)$Å^3$, Z = 4, T = 150(2) K, $2\theta_{max}$=50.00°, D_{calc} (g cm^{-3}) = 1.393, $F(000)$ = 576, μ (mm^{-1}) = 0.400, 8835 reflections collected, 2245 unique reflections (R_{int} = 0.0305), 2215 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.841, T_{max} = 0.893, 154 refined parameters, S = 1.137, $R1$ = 0.0252, $wR2$ = 0.0624 (all data R = 0.0257, $wR2$ = 0.0626), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.30, $\Delta\rho_{min}$= -0.16 ($eÅ^{-3}$).

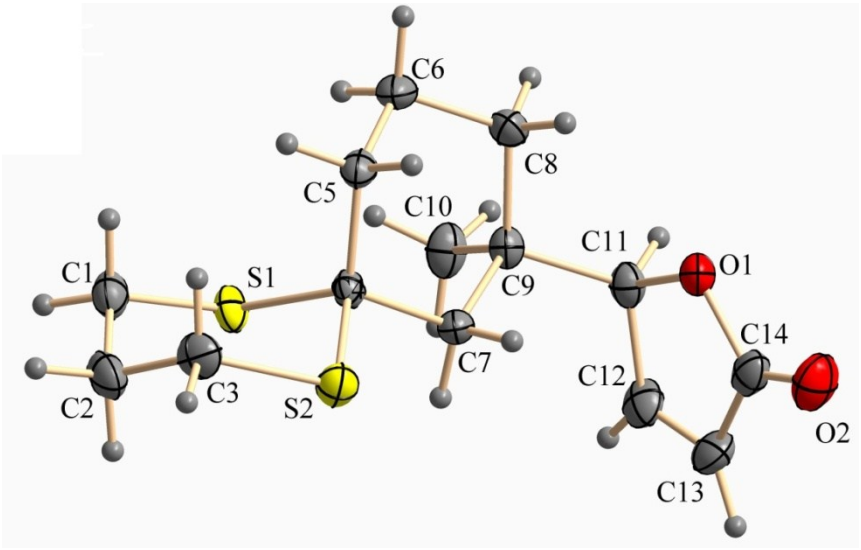
All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Apex2, Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2.[2] All the hydrogen atoms were placed in geometrically idealized positionand constrained to ride on their

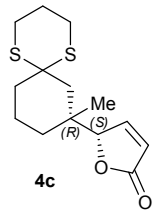
parent atoms. The absolute configuration established by anomalous dispersion effects in diffraction measurements on the crystal which could become possible due to the presence of heavy atom Sin the molecule.The absolute configuration of the molecule was found by using Flack parameter refinement.[3] A value of Flack parameter of 0.03(7) established that the configuration of atoms C5 and C8' is *R*.

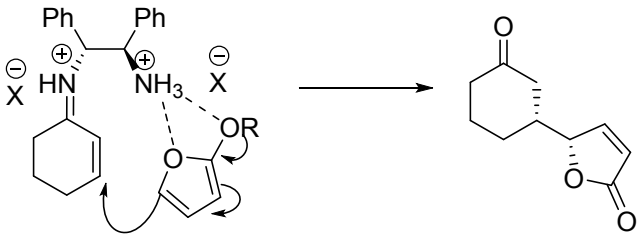
References

(1) Bruker (2006). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
(2) Sheldrick, G. M. *Acta Crystallogr*., **2008**, *A64*, 112.
(3) Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143.

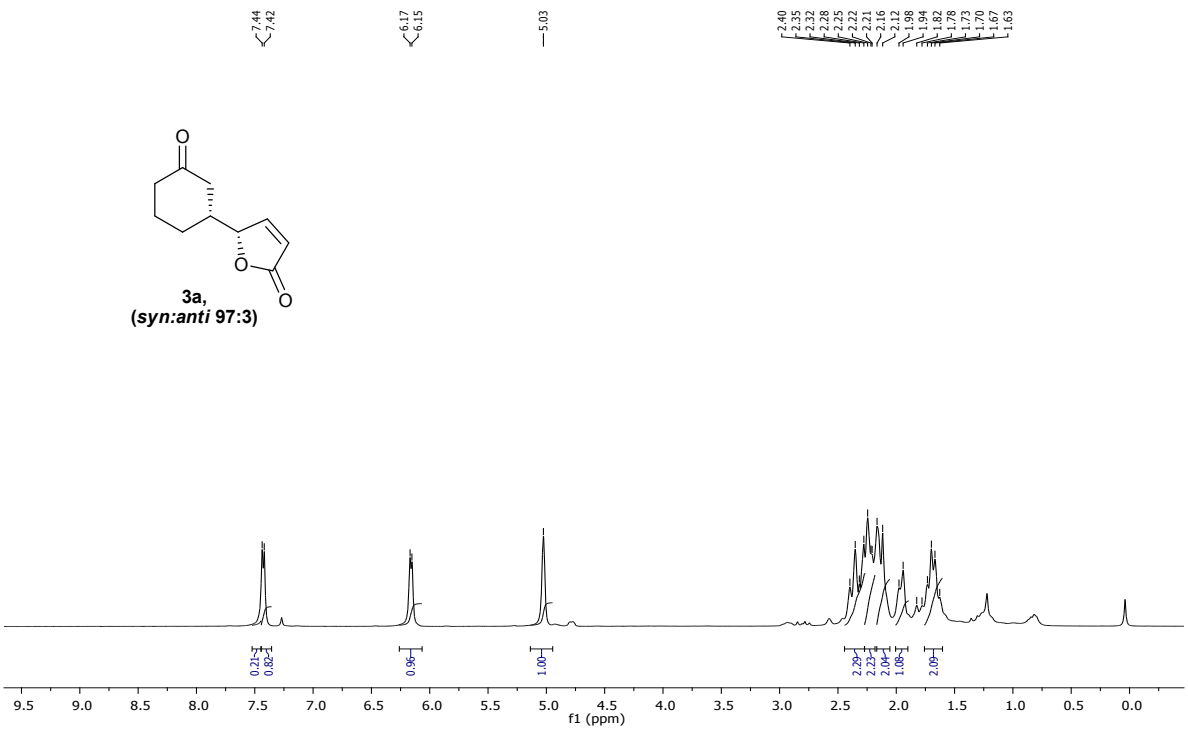
Assignment of the absolute configuration of syn-4c by X-ray analysis:







Scheme S1: A plausible transition state for **IV**-catalysed vinylogous Michael Reaction



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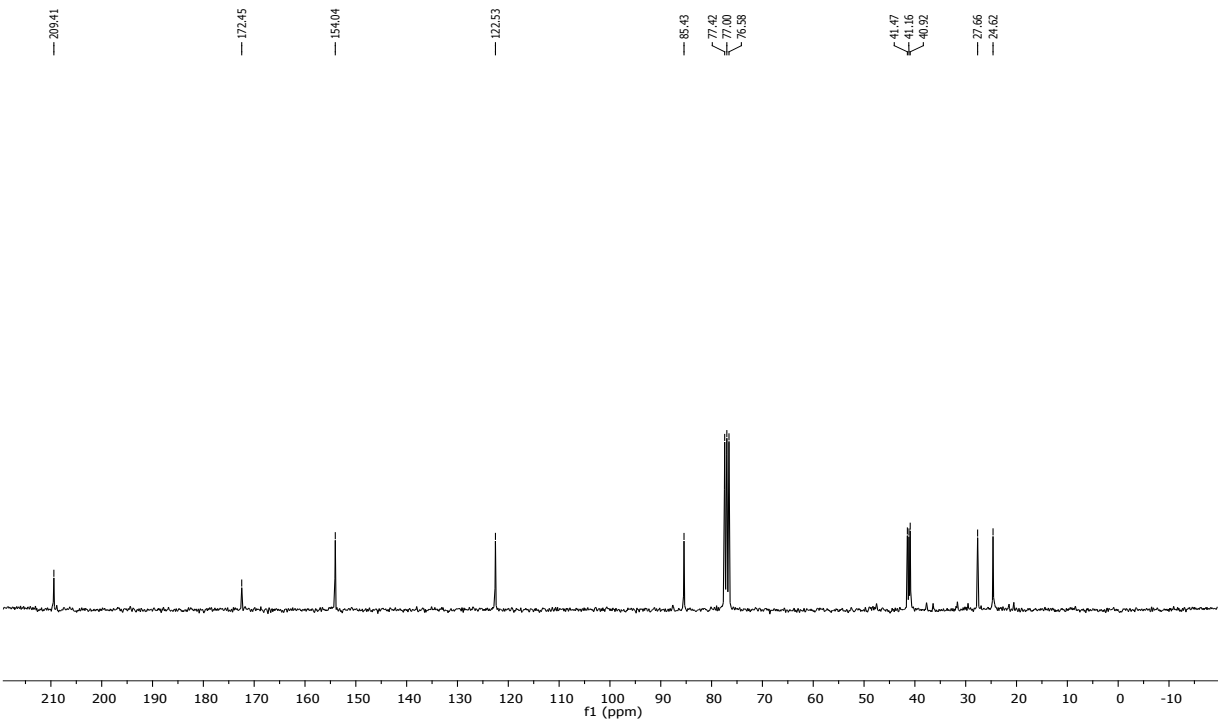

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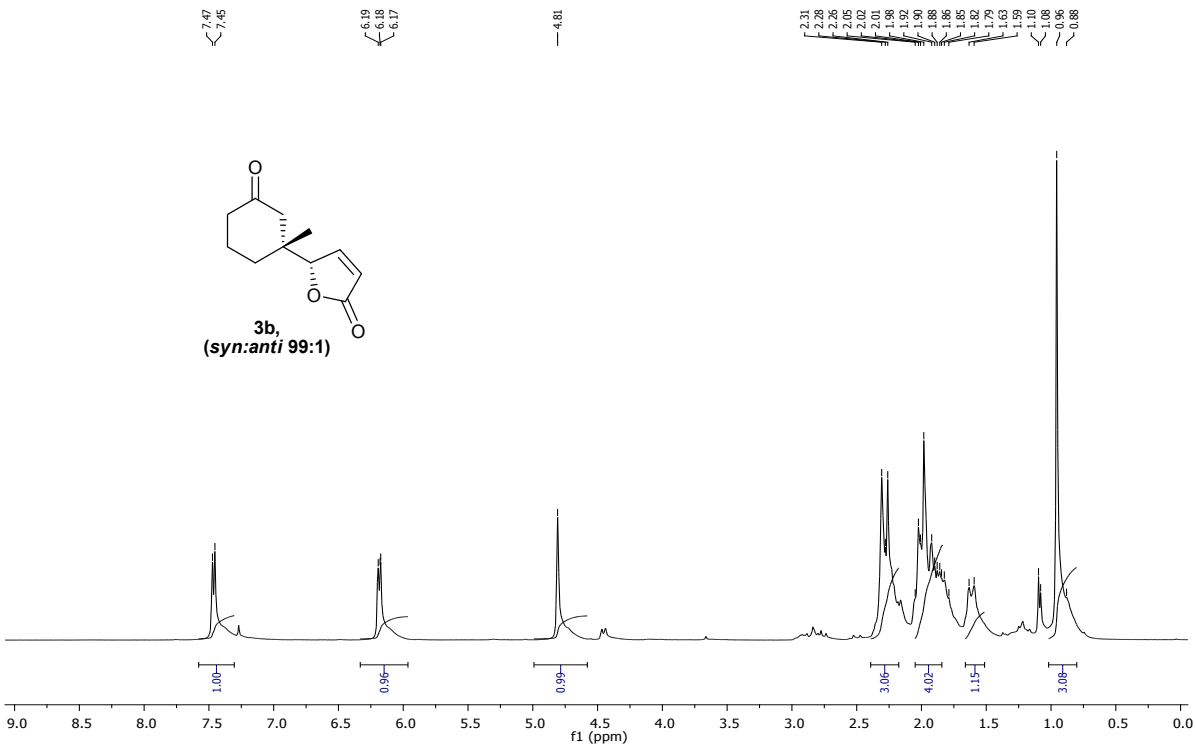
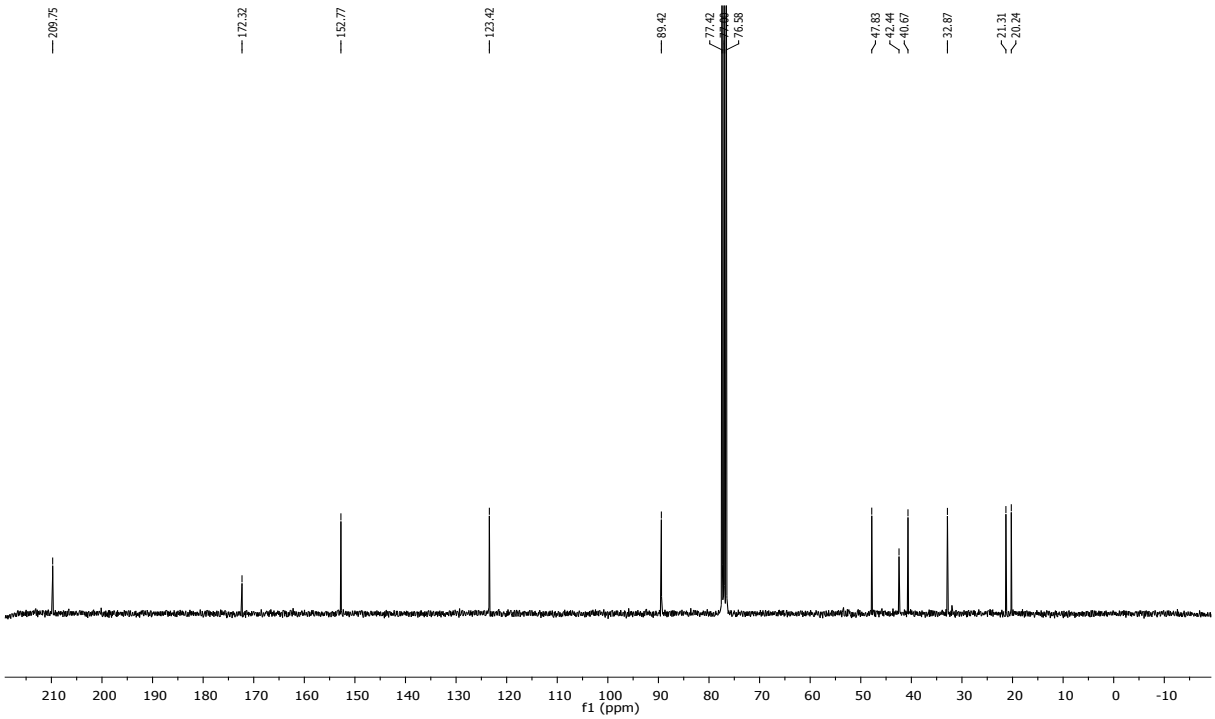


3b,
(*syn:anti* 99:1)



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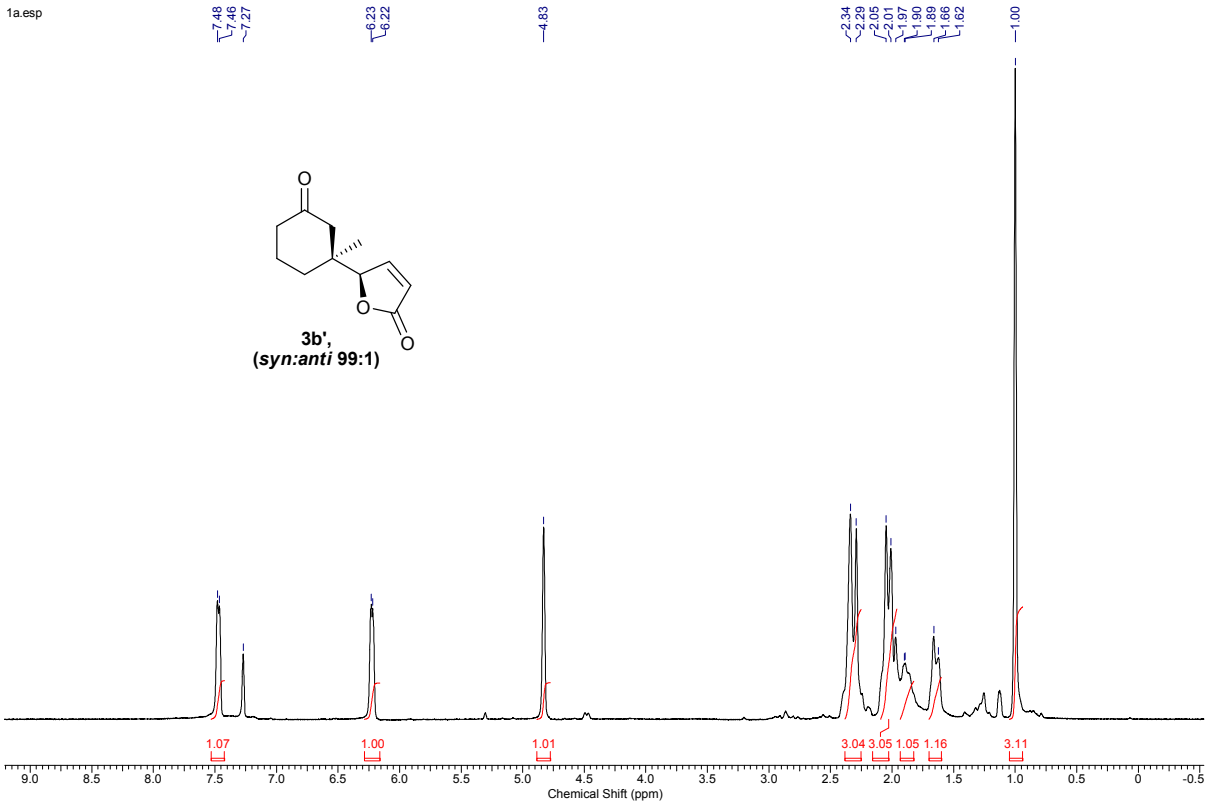

3b',
(*syn:anti* 99:1)

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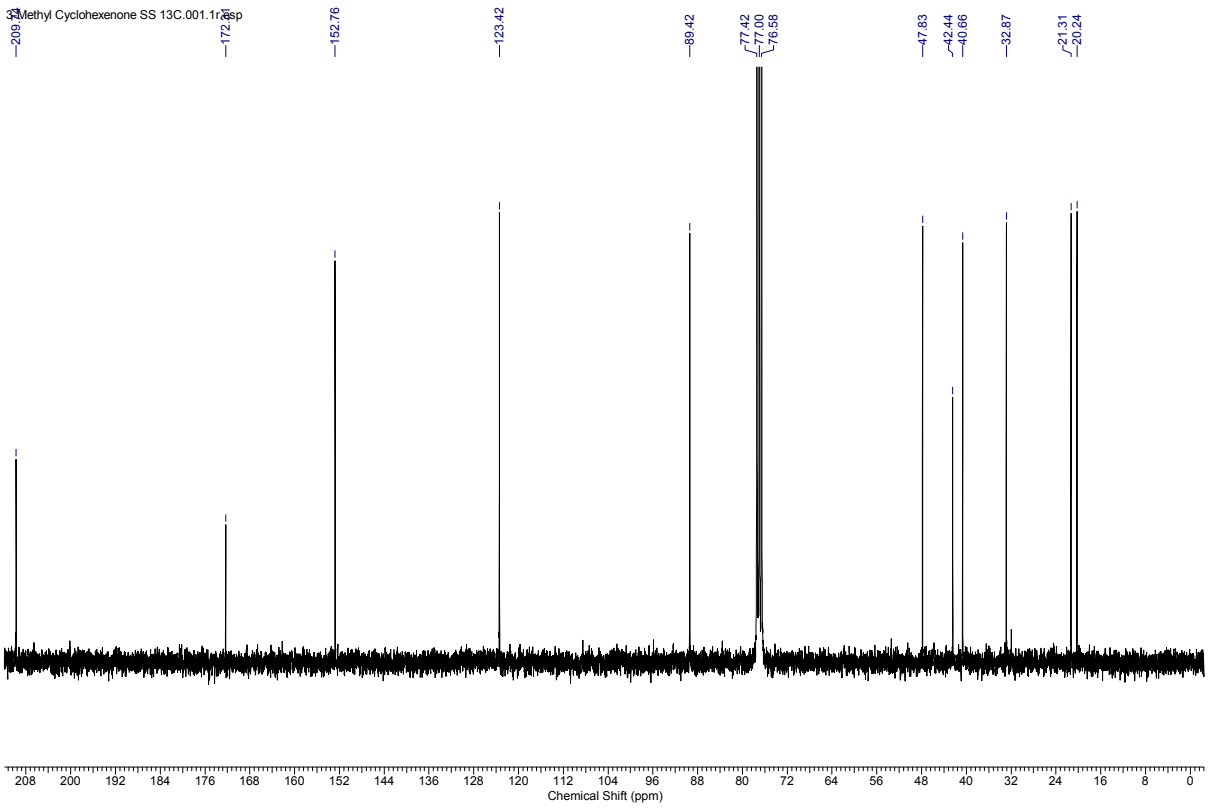

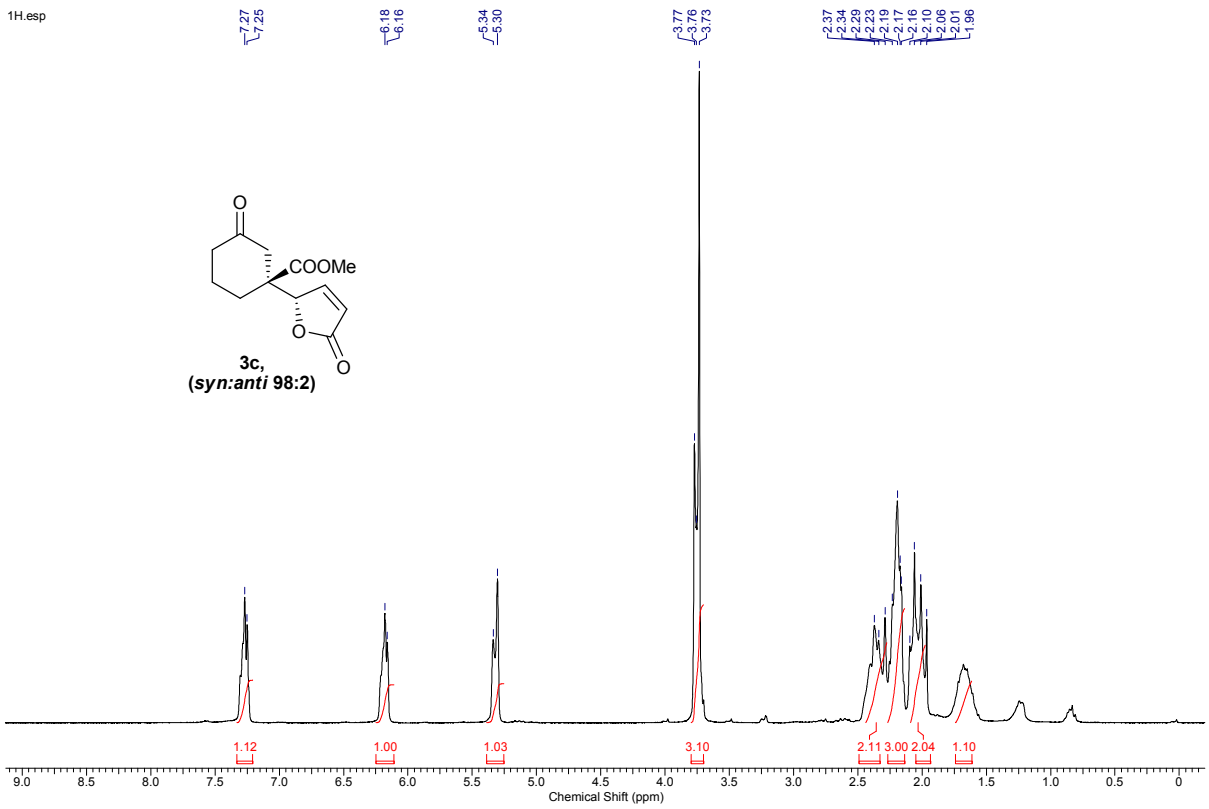

3c,
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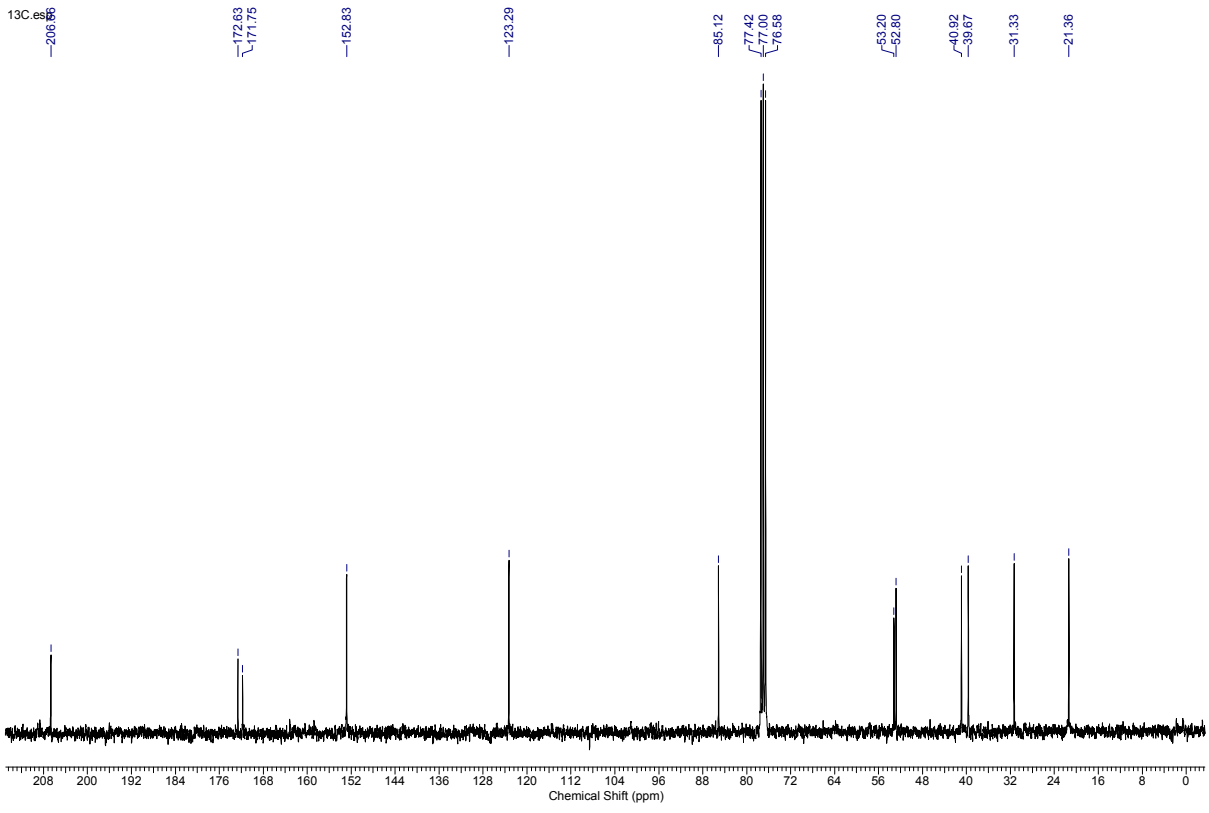

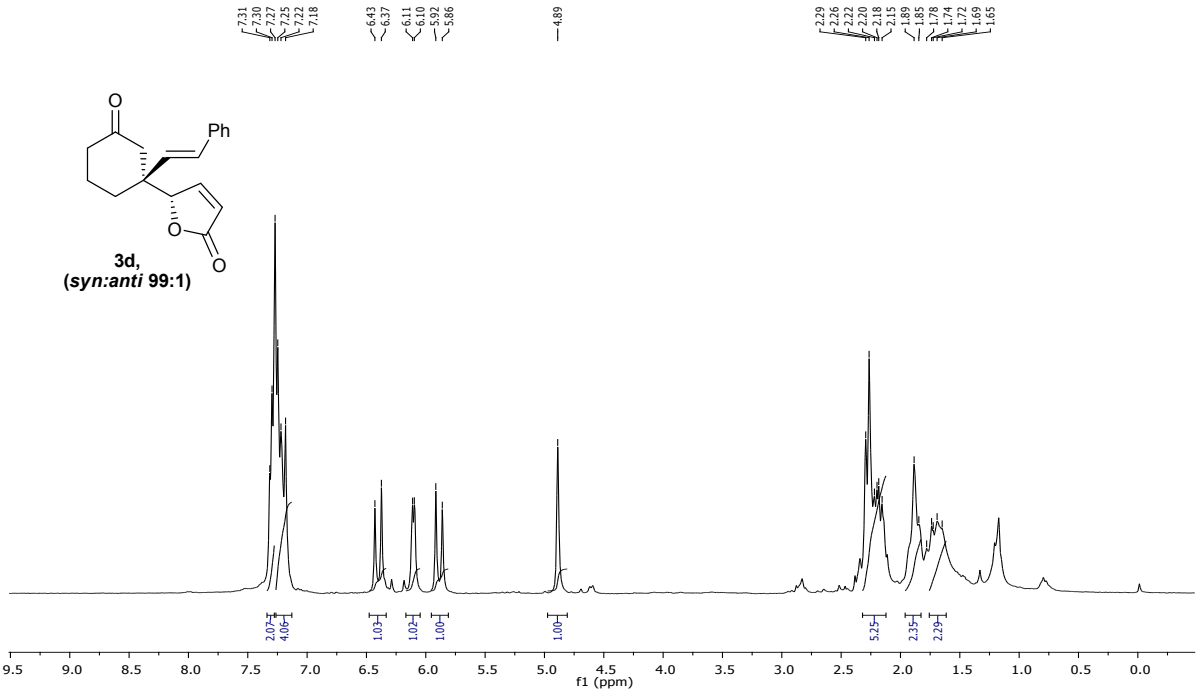
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2.29
2.26
2.22
2.20
2.18
2.15
1.89
1.85
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1.74
1.72
1.69
1.65
O
Ph
O
O
3d,
(syn:anti 99:1)
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1.02
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1.00
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2.29
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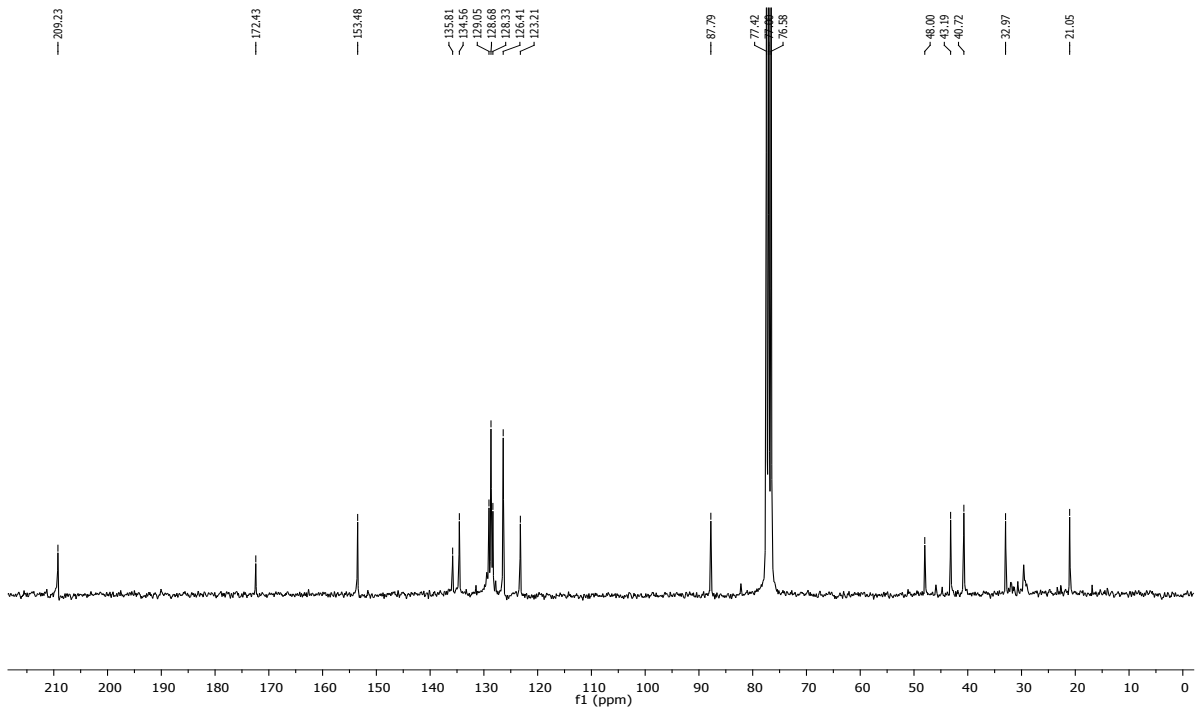
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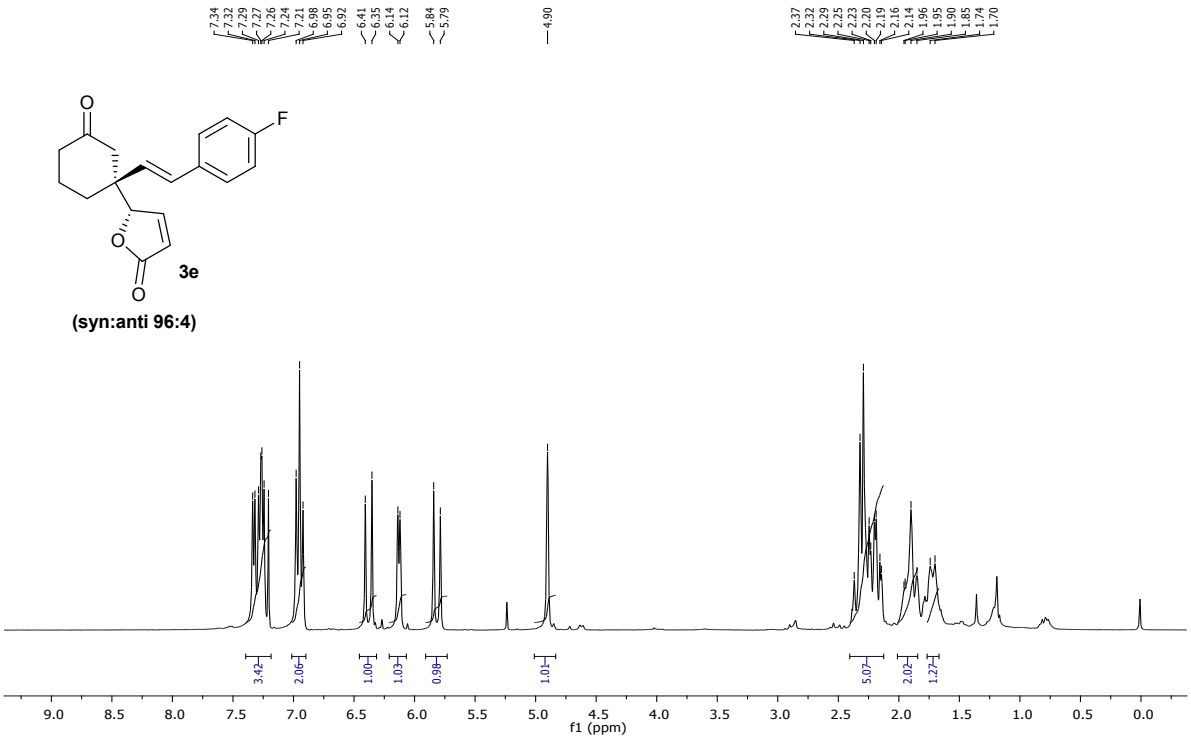
f1 (ppm)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2.16
2.14
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1.95
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1.85
1.74
1.70
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F
O
O
3e
(syn:anti 96:4)
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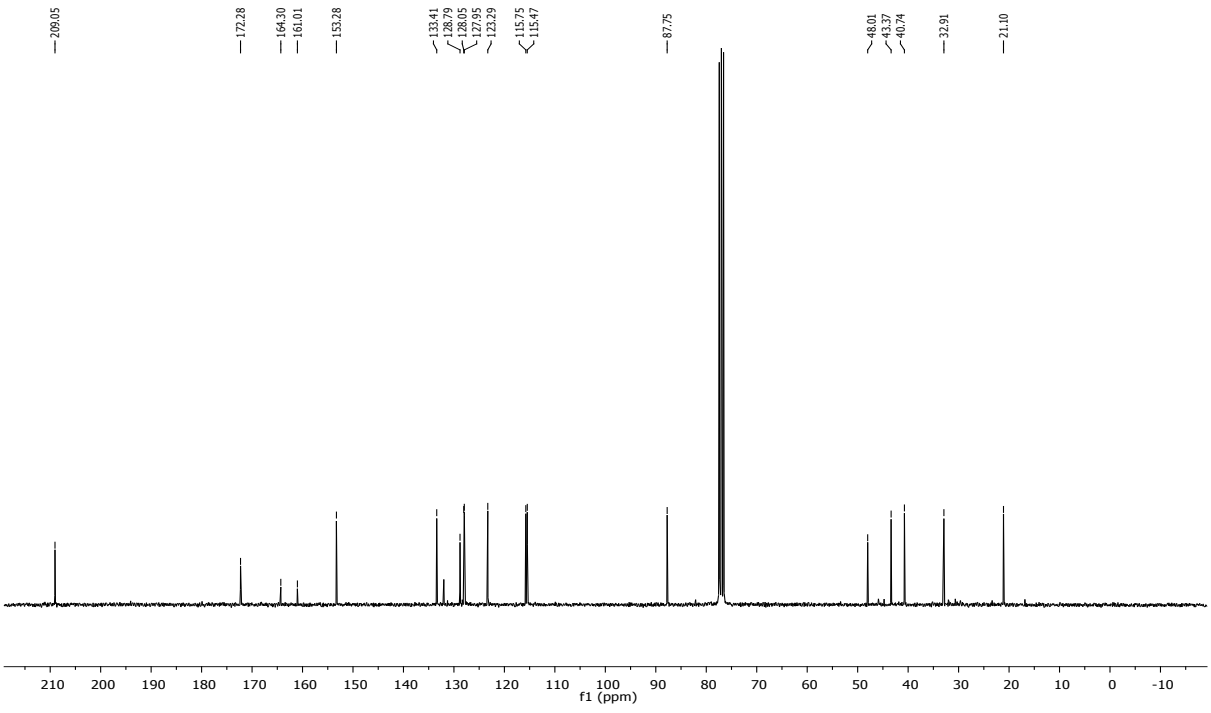
f1 (ppm)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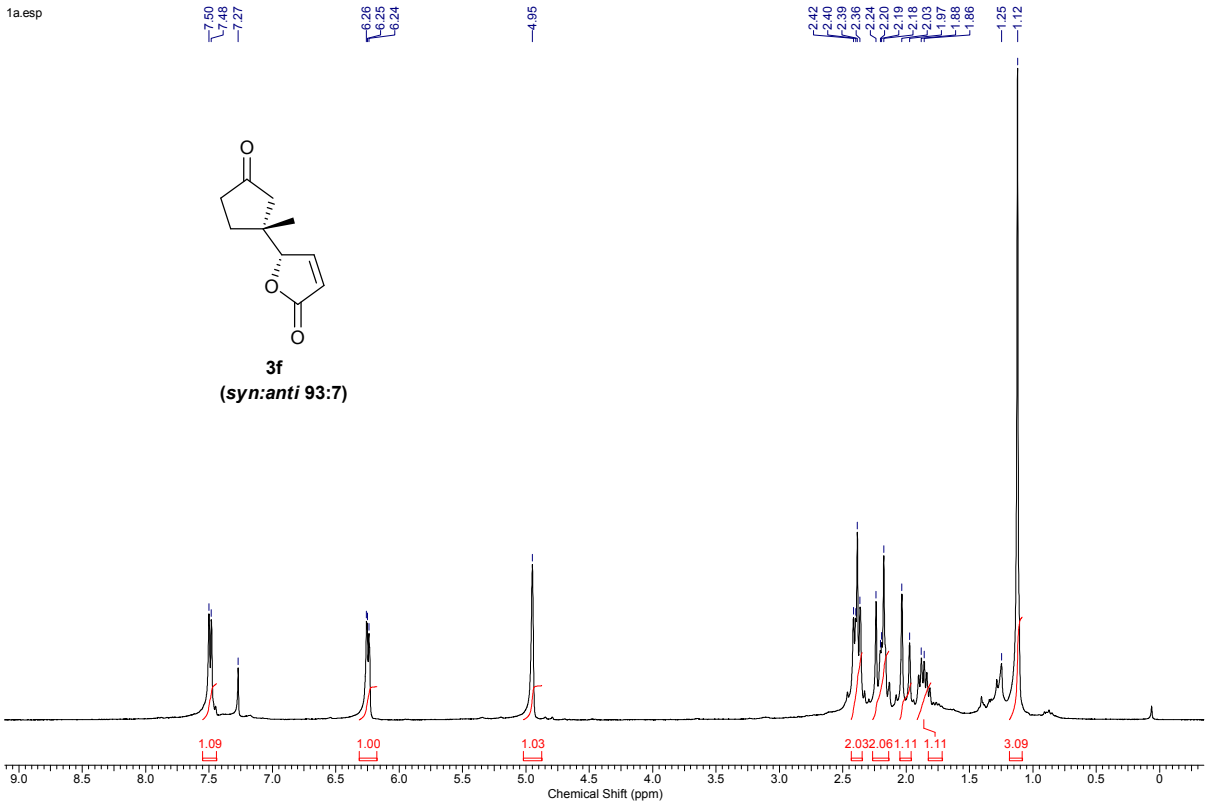
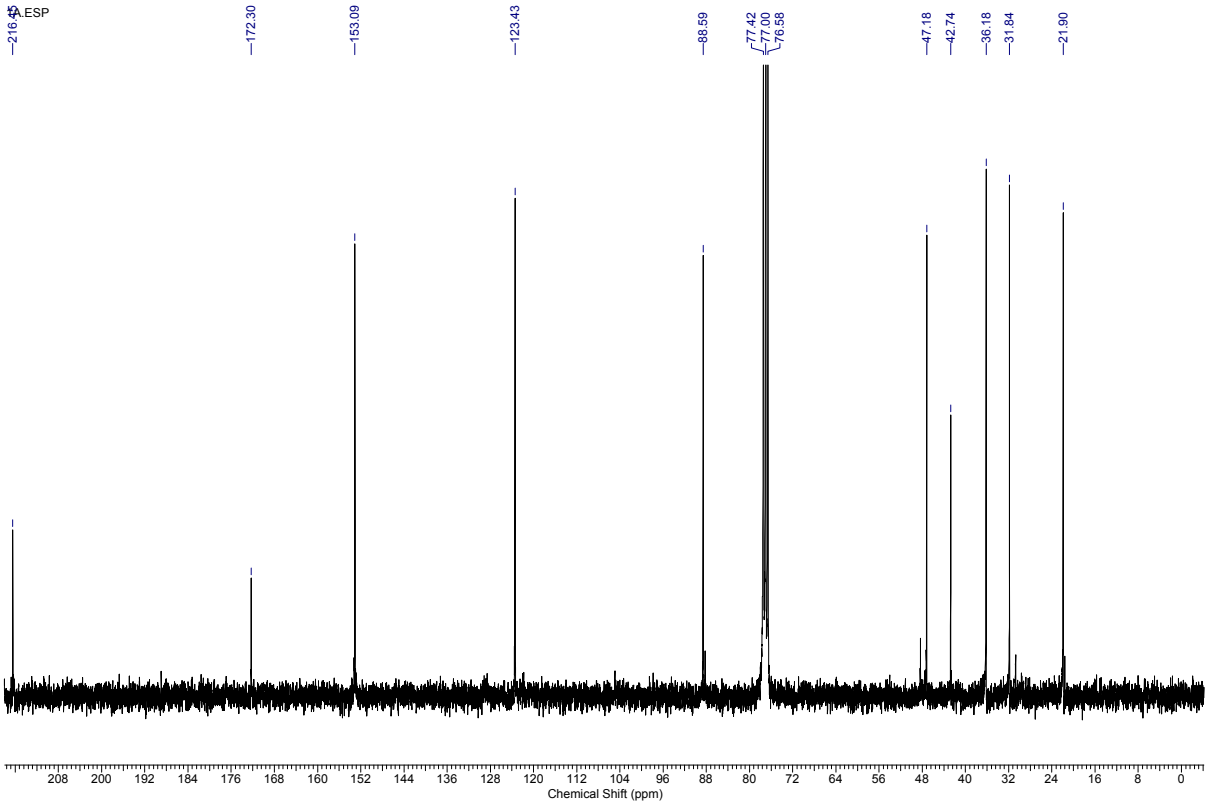
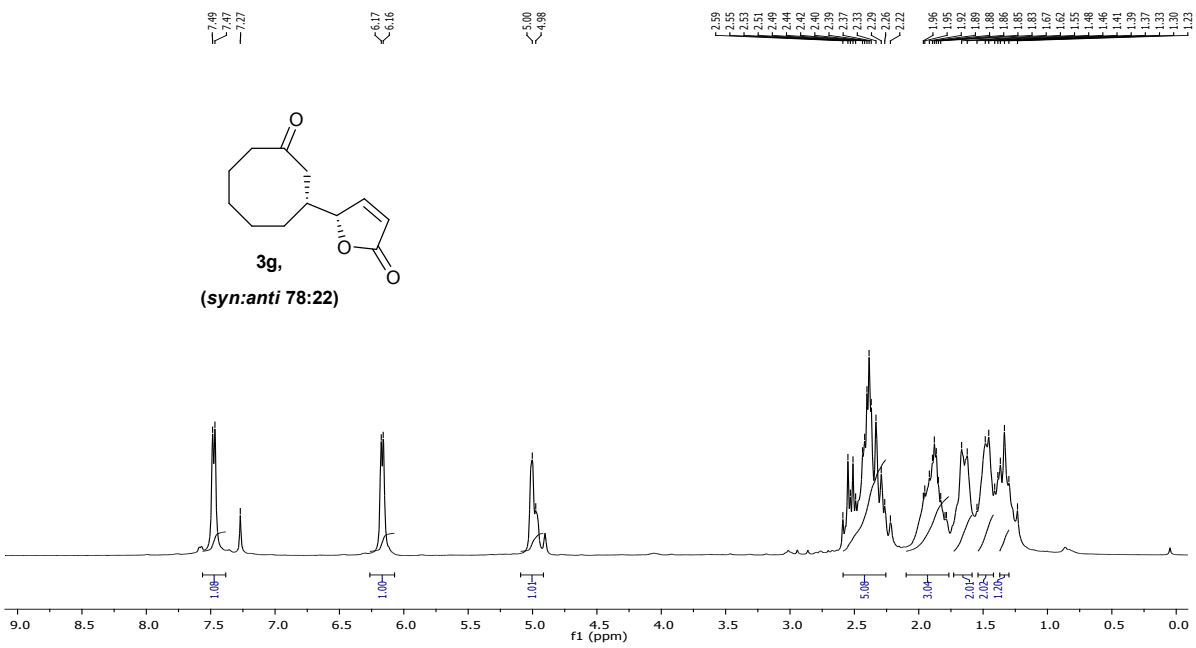
21.10
f1 (ppm)



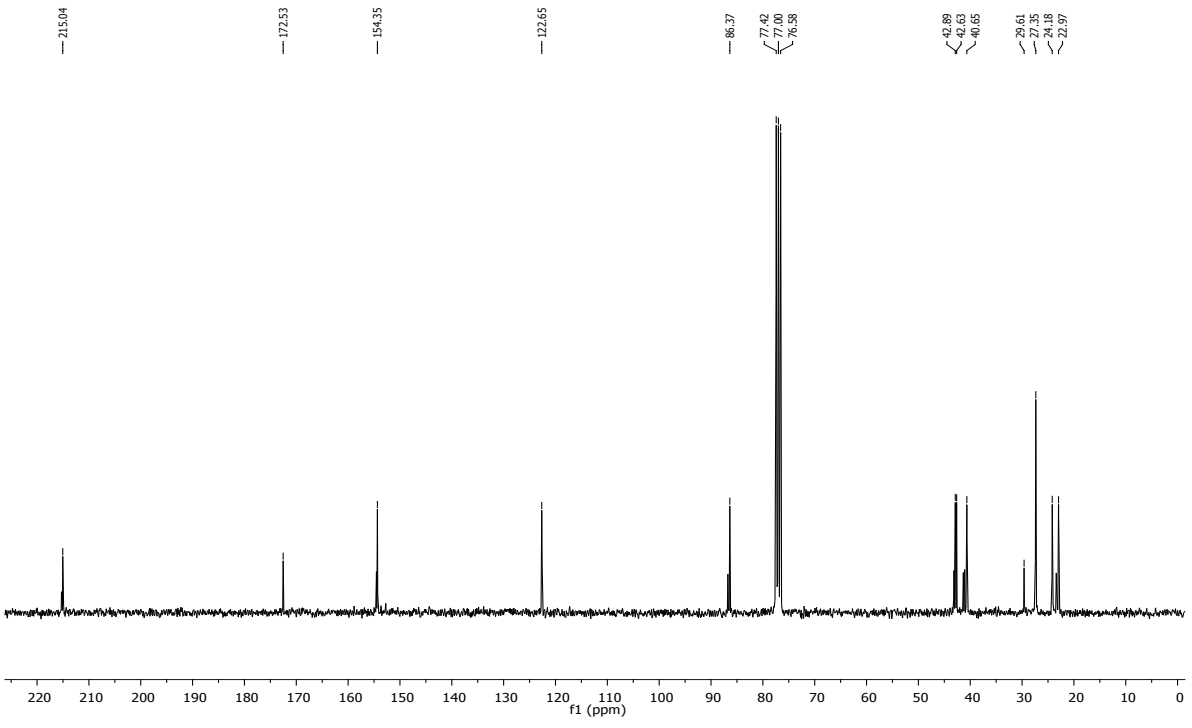
3f
(*syn:anti* 93:7)

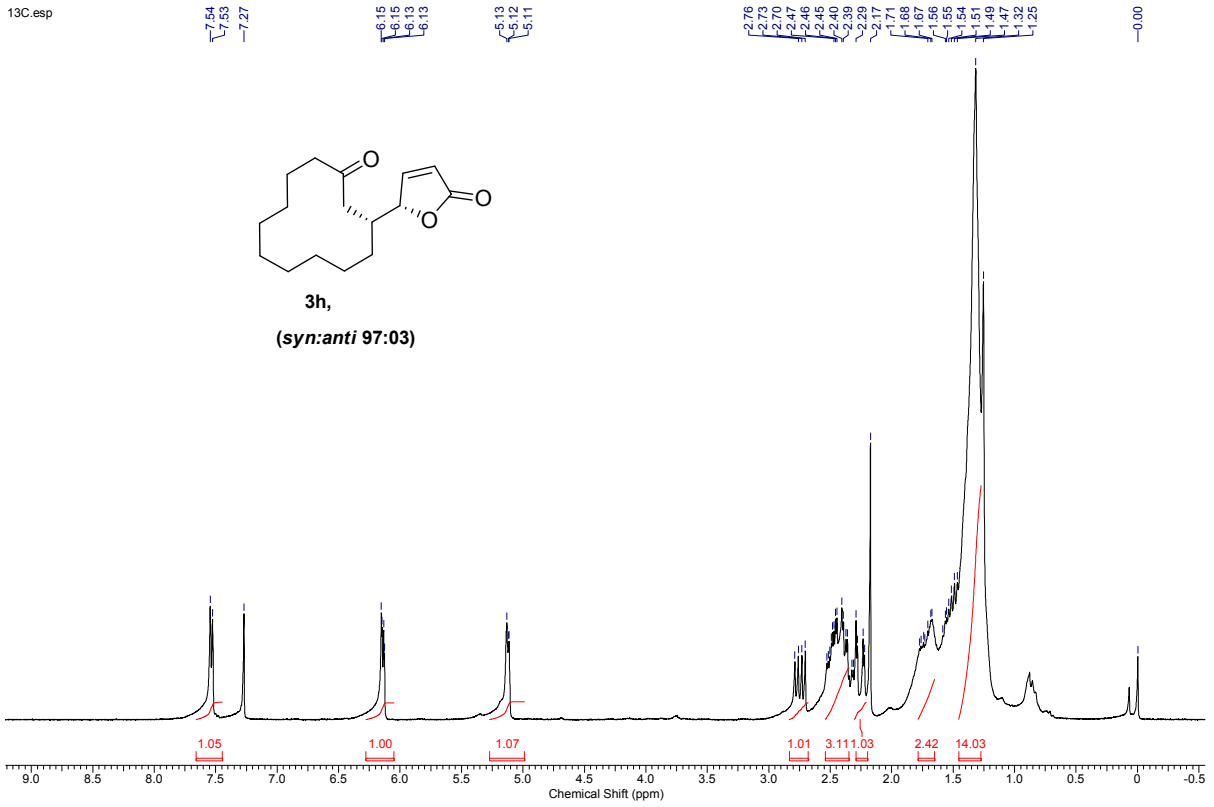




3g,

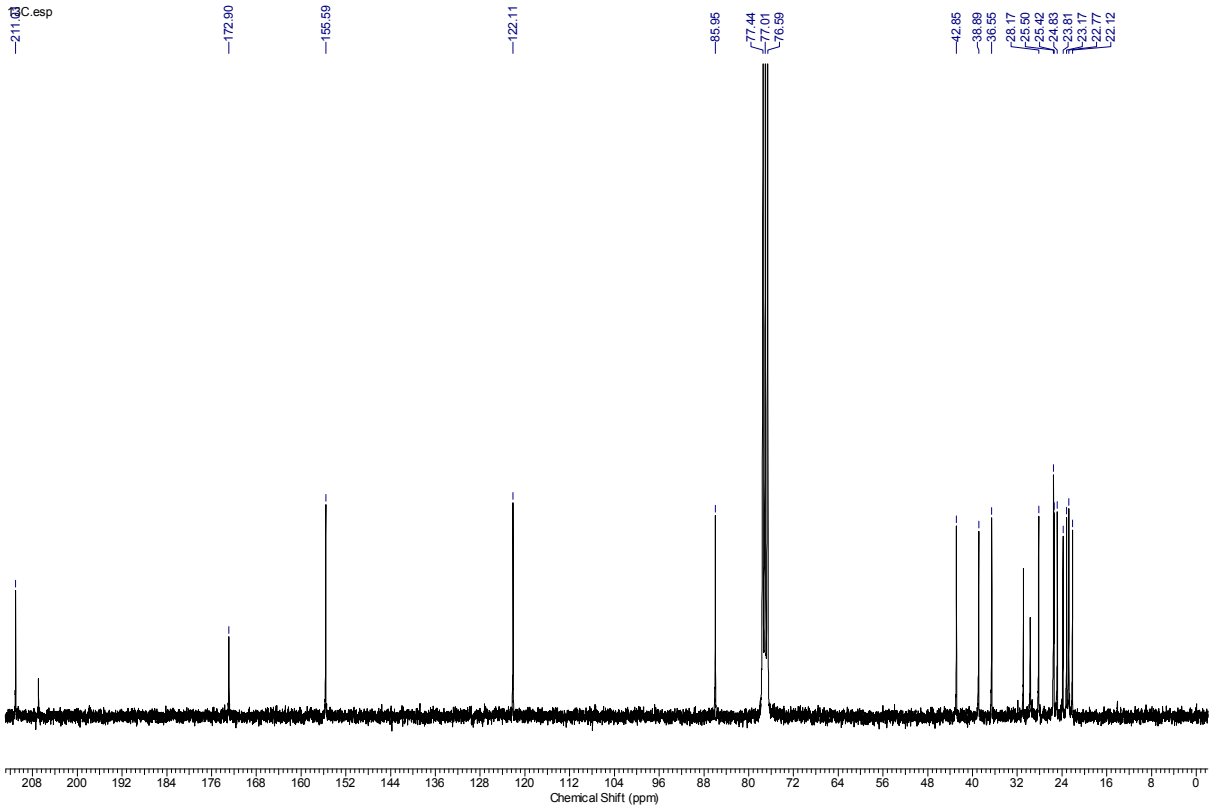
(***syn*:*anti* 78:22**)

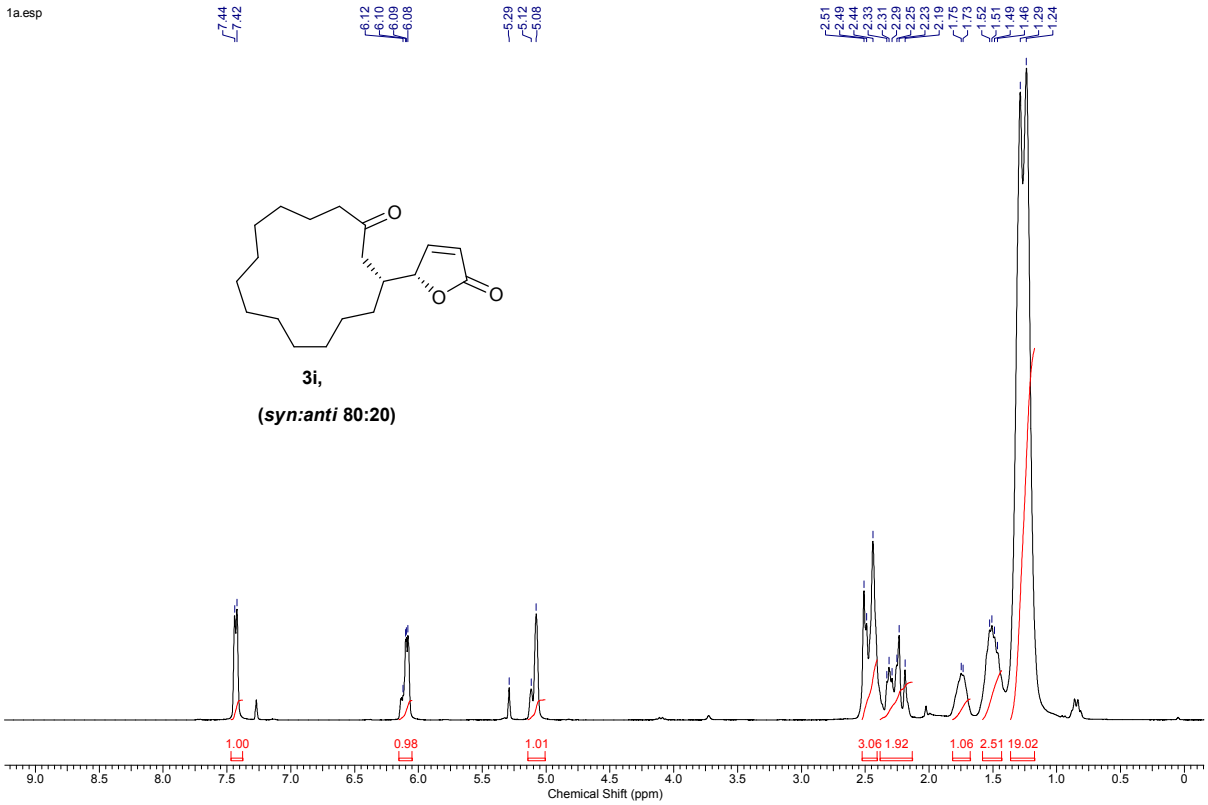




3h,

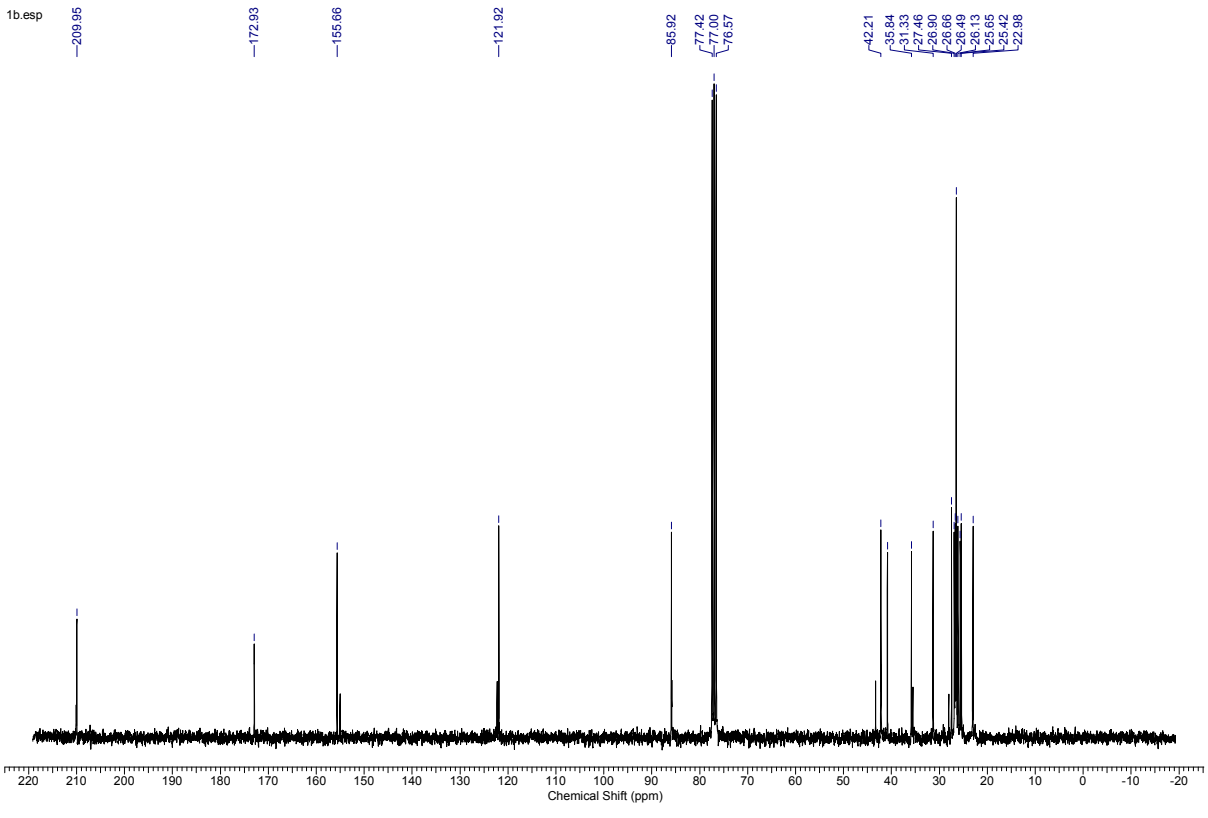
(*syn:anti* 97:03)

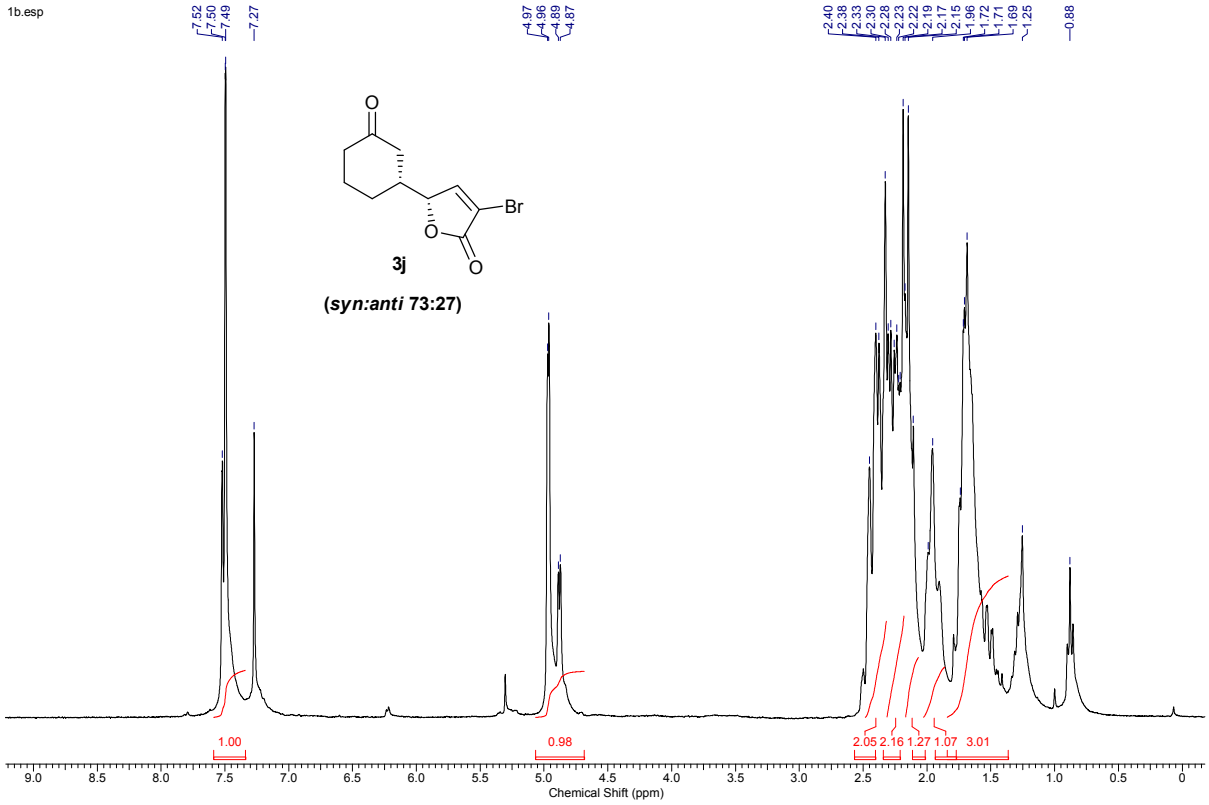




3i,

(*syn:anti* 80:20)

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2.17
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Br
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(syn:anti 73:27)
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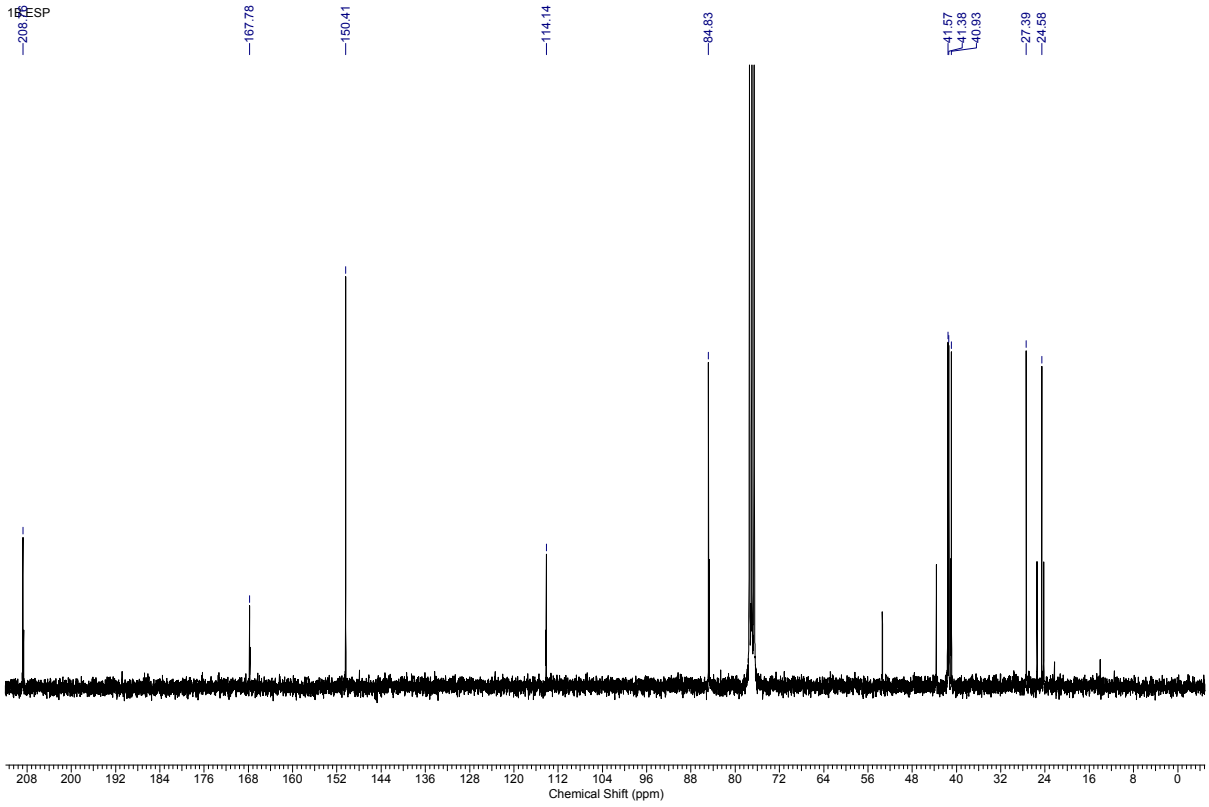
3.01
Chemical Shift (ppm)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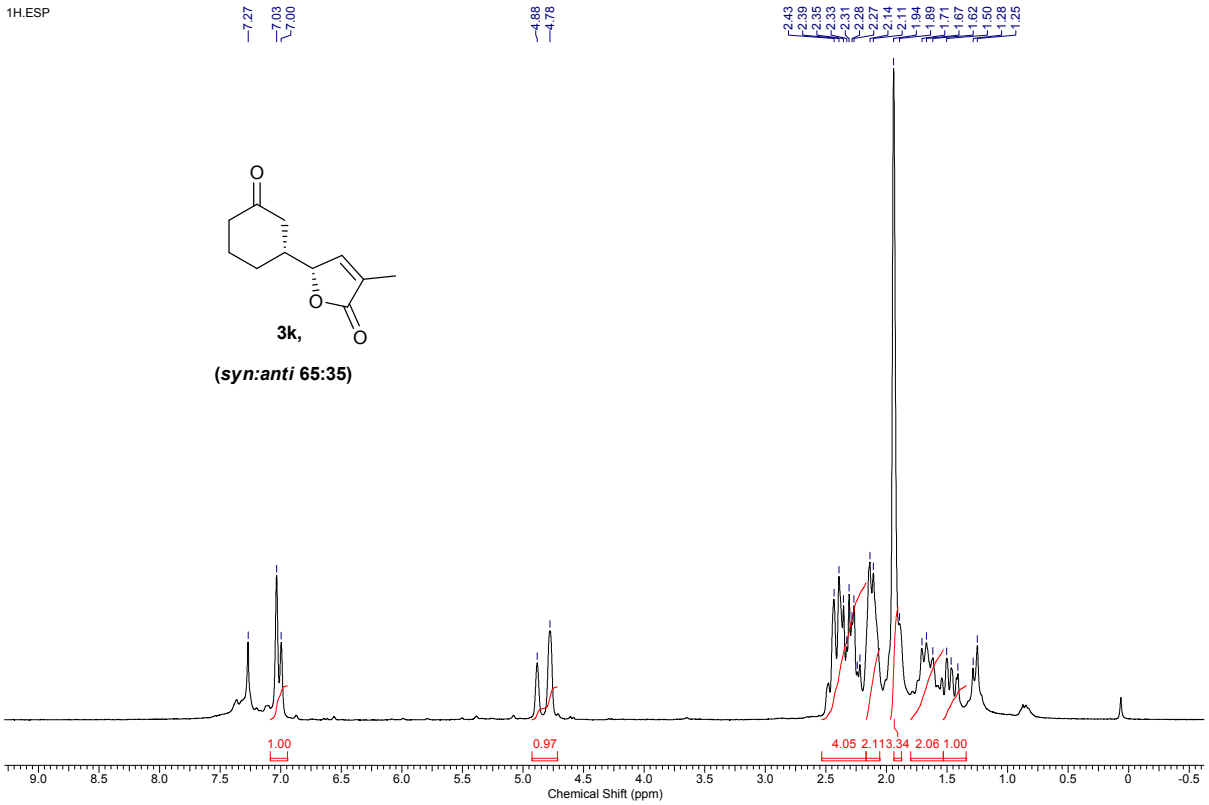
Chemical Shift (ppm)

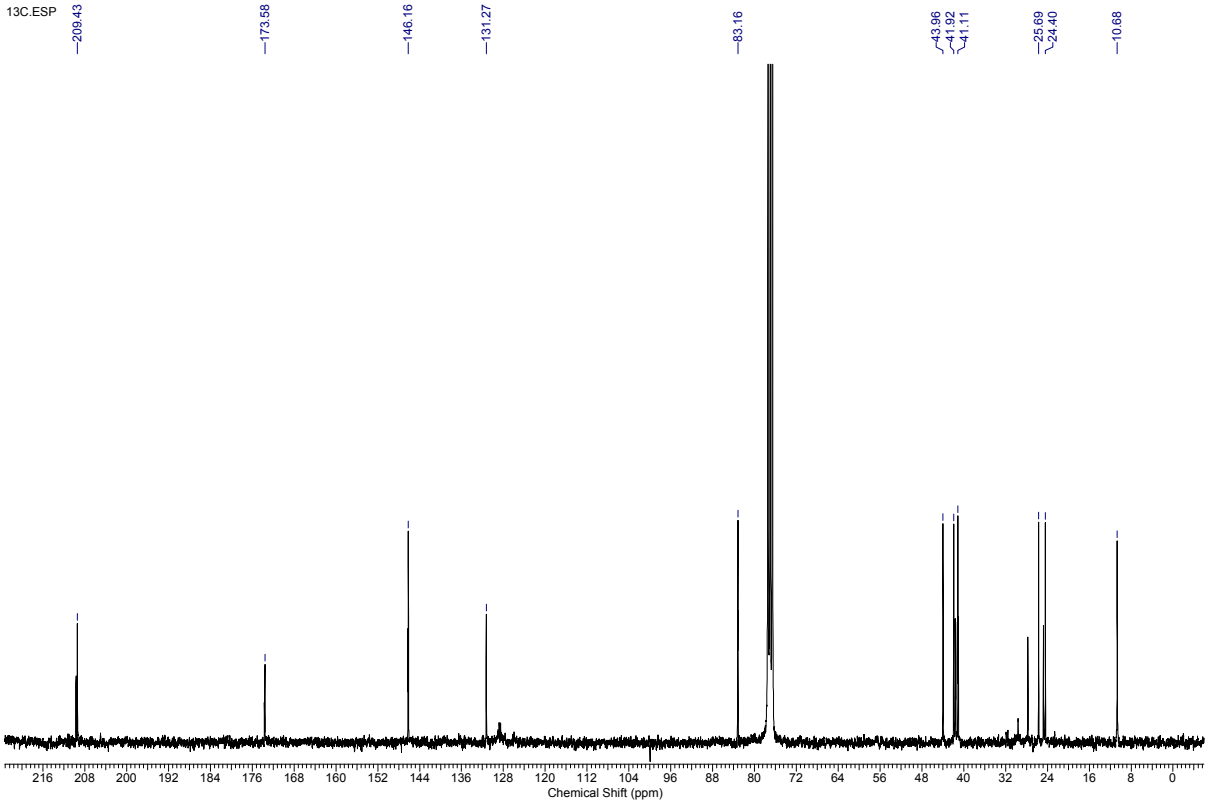
1H.ESP

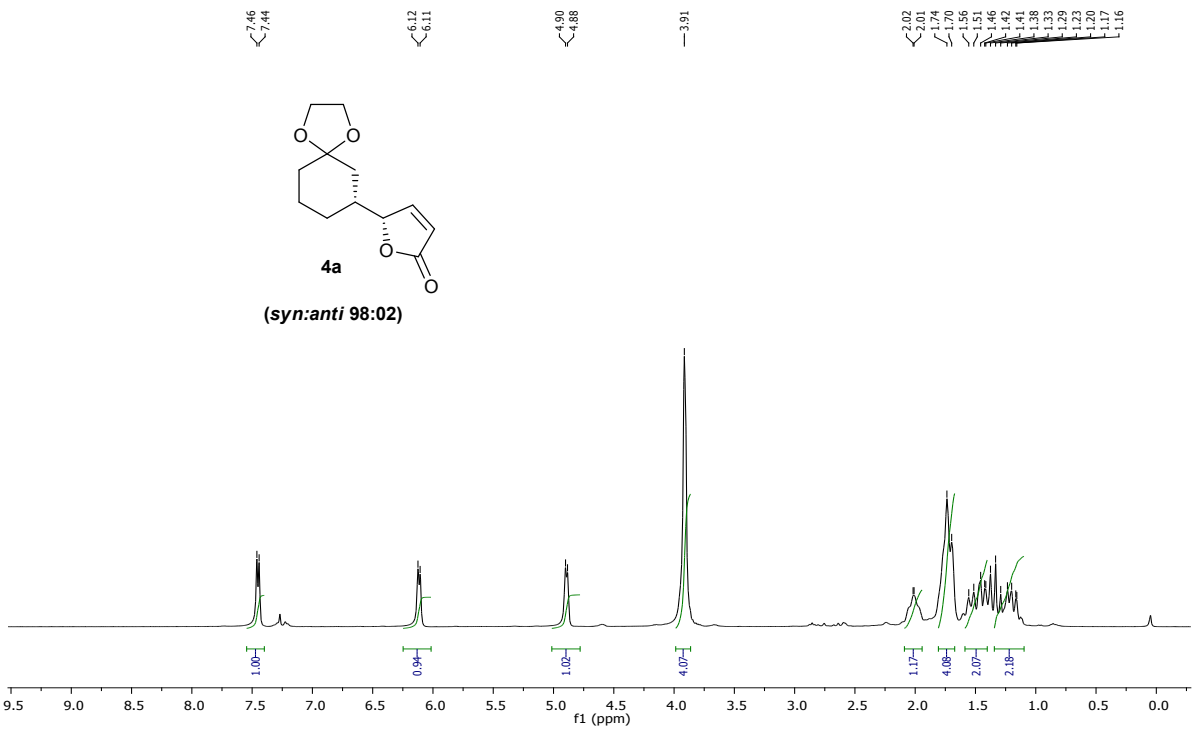


3k,

(*syn:anti* 65:35)

13C.ESP

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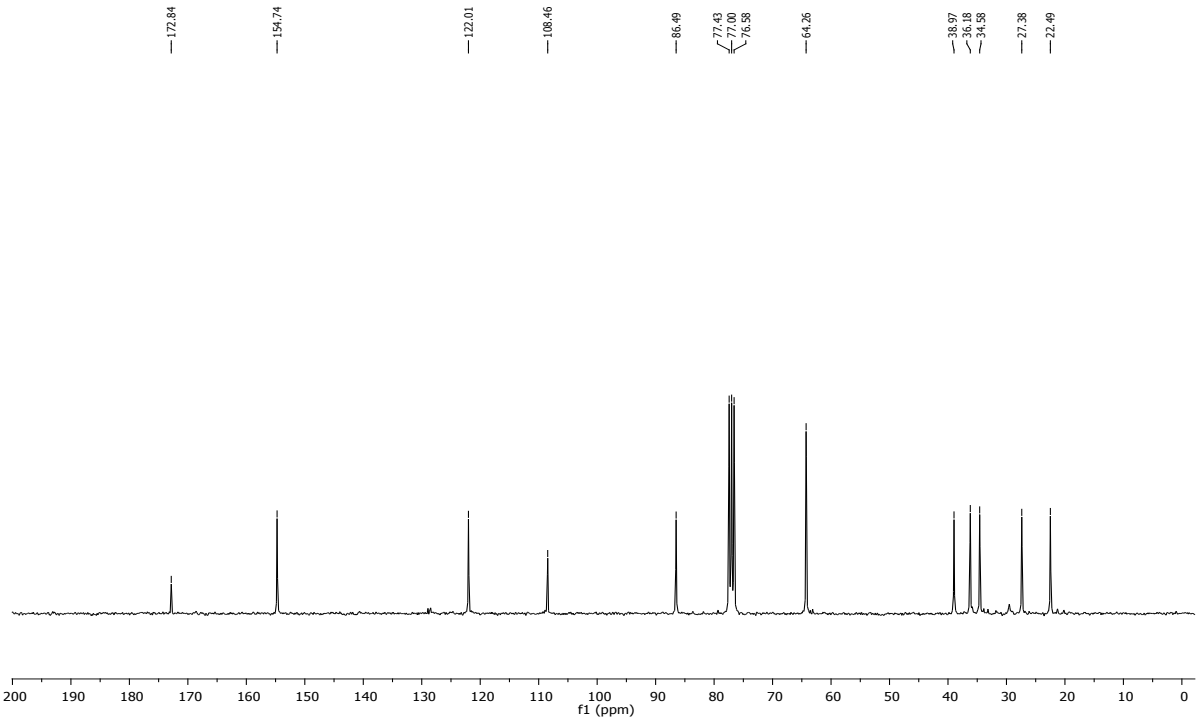
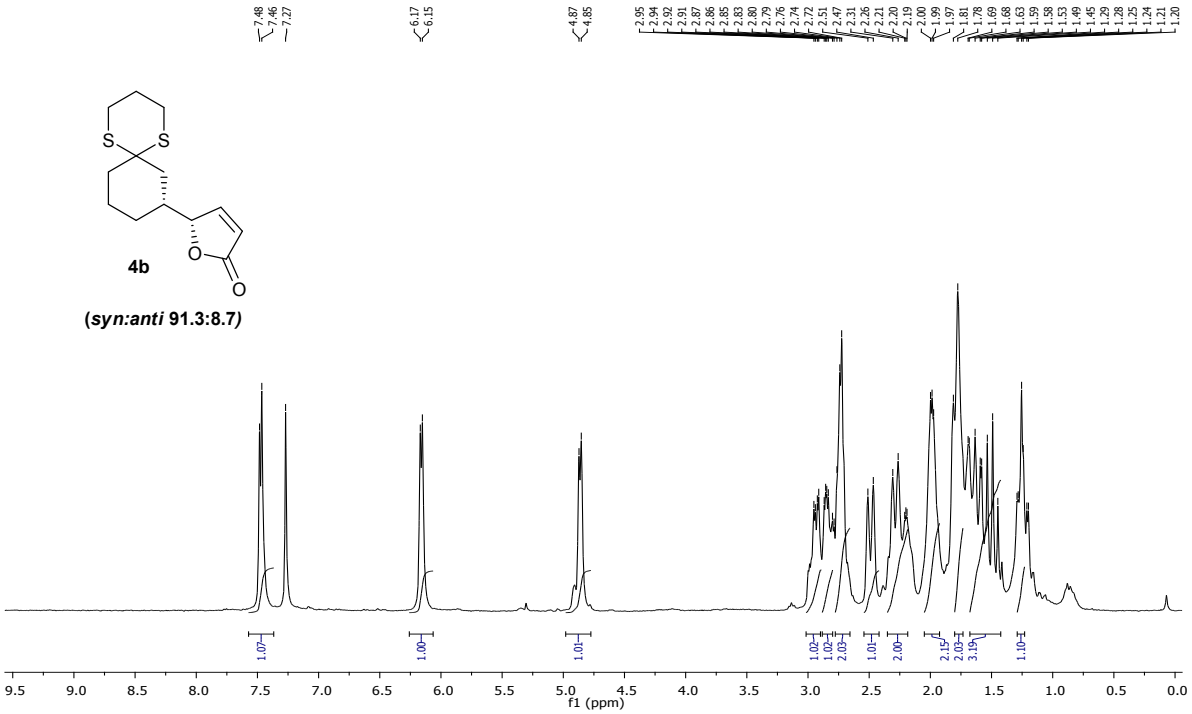
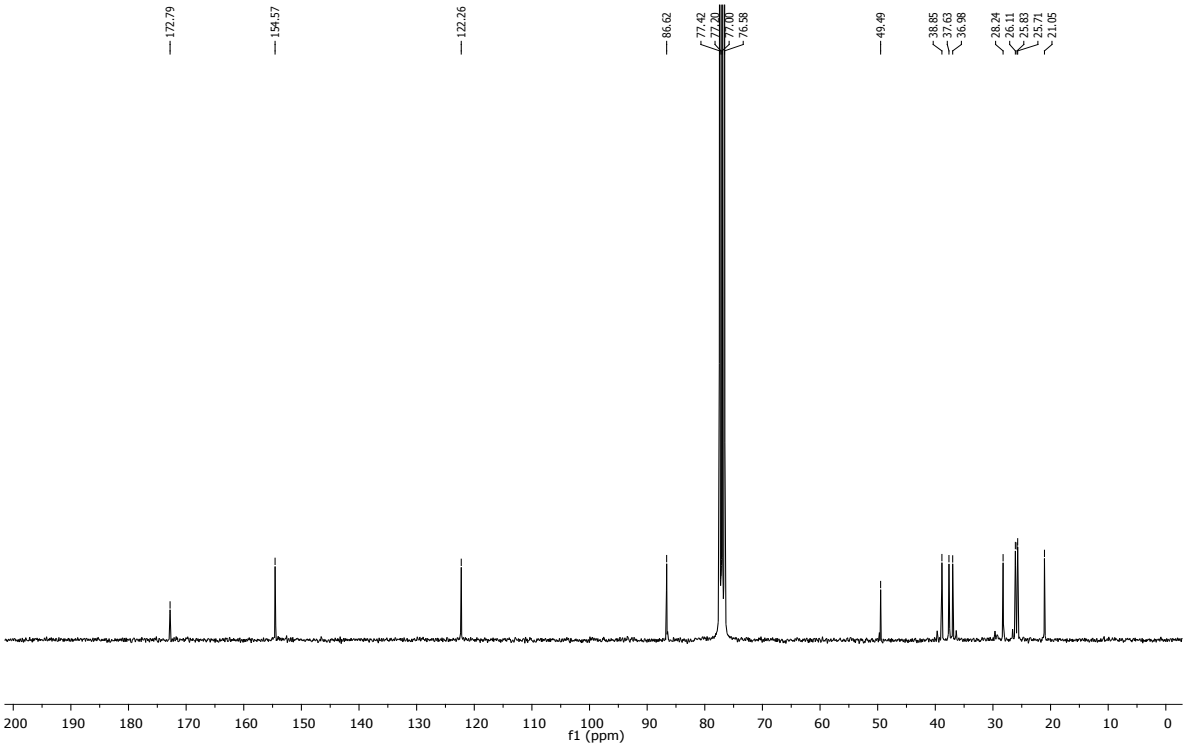
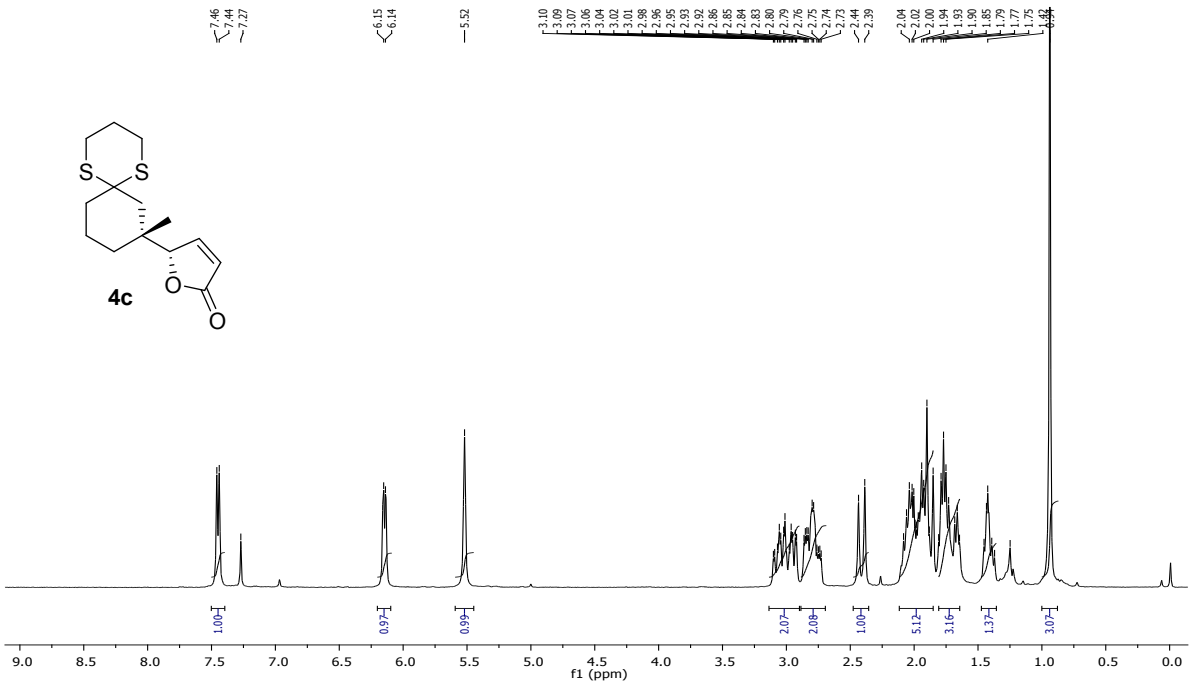
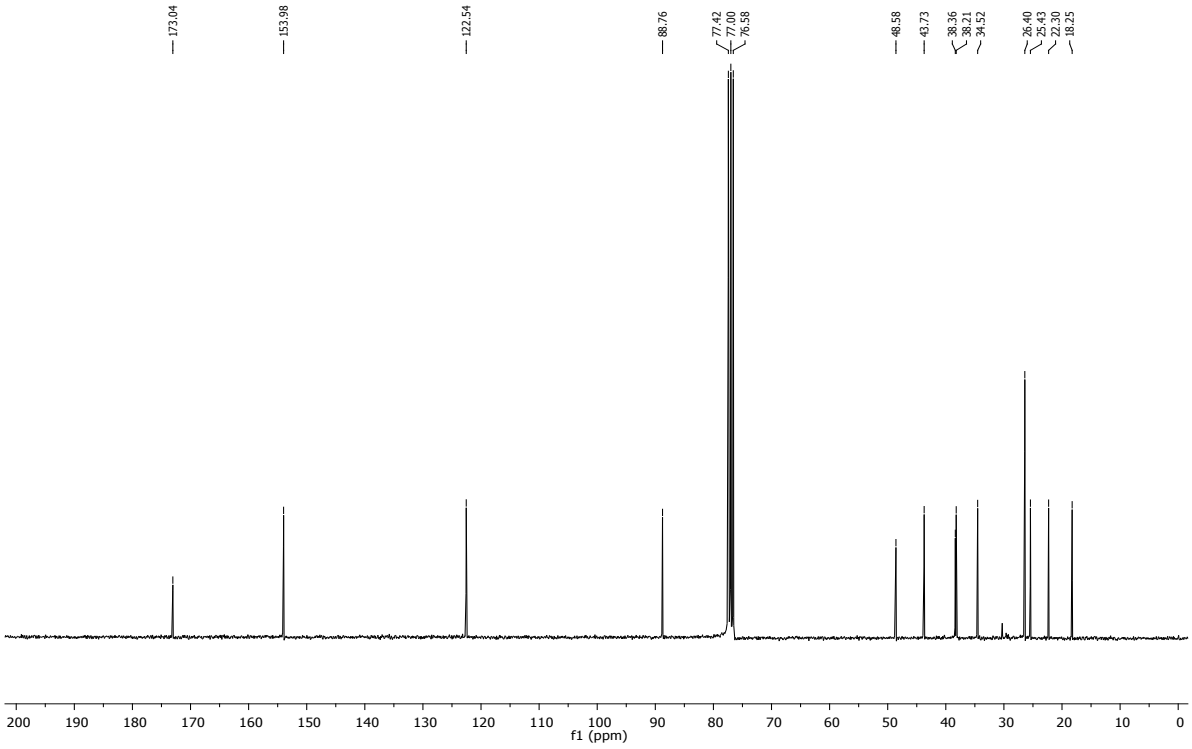
1.33
1.29
1.23
1.20
1.17
1.16
O
O
O
O
4a
(syn:anti 98:02)
1.00
0.94
1.02
4.07
1.17
4.08
2.07
2.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

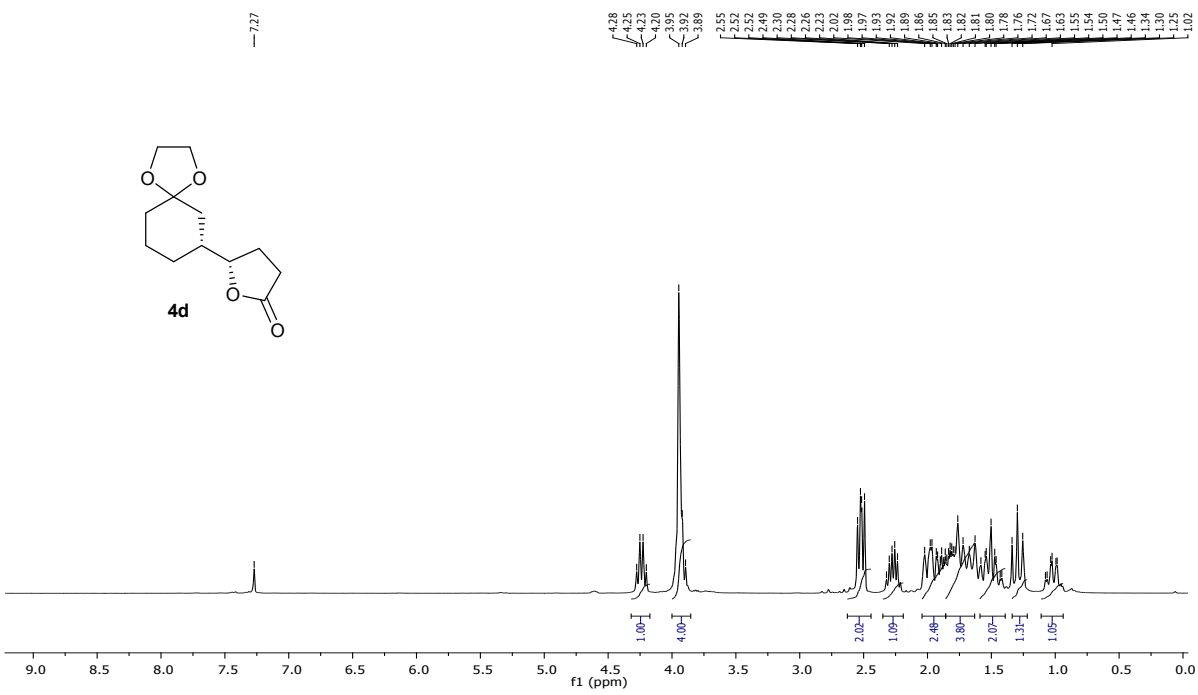

172.84
154.74
122.01
108.46
86.49
77.43
77.00
76.58
64.26
38.97
36.18
34.58
27.38
22.49
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

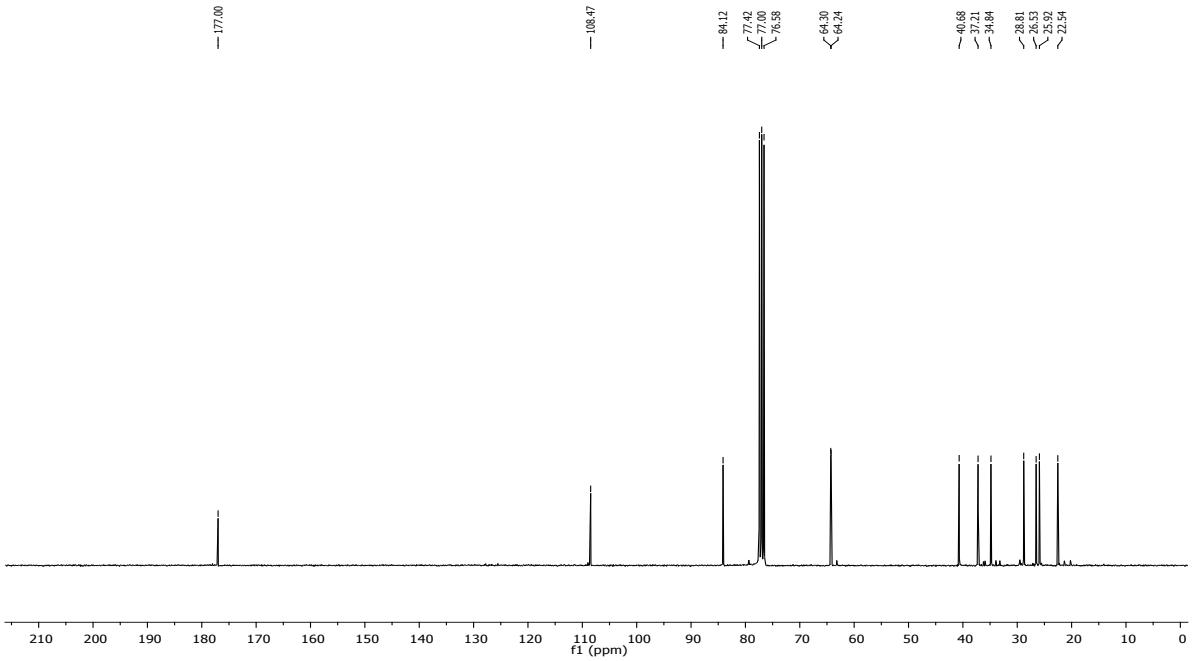

7.48
7.46
7.27
6.17
6.15
4.87
4.85
2.95
2.94
2.92
2.91
2.87
2.86
2.85
2.83
2.80
2.79
2.76
2.74
2.72
2.51
2.47
2.31
2.26
2.21
2.20
2.19
2.00
1.99
1.97
1.81
1.78
1.69
1.68
1.63
1.59
1.58
1.53
1.49
1.45
1.29
1.28
1.25
1.24
1.21
1.20
S
S
O
O
4b
(syn:anti 91.3:8.7)
1.07
1.00
1.01
1.02
1.02
2.05
1.01
2.00
2.15
2.03
3.19
1.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

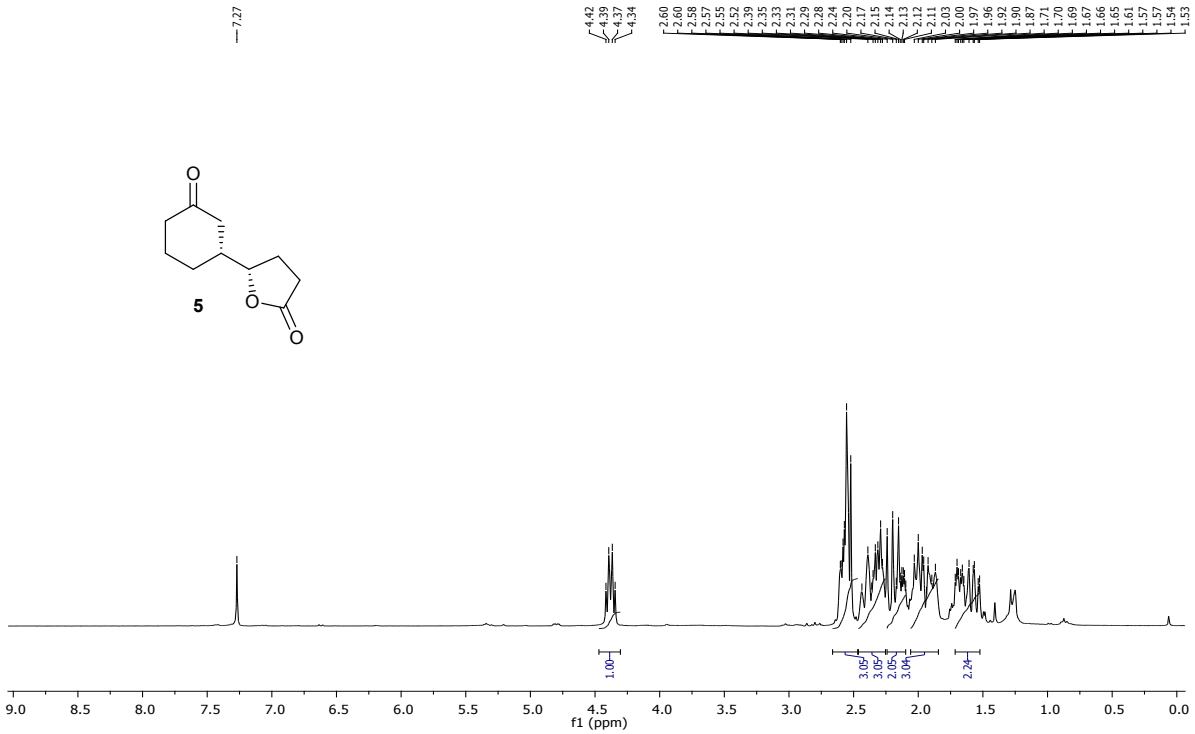

172.79
154.57
122.26
86.62
77.42
77.20
77.00
76.58
49.49
38.85
37.63
36.98
28.24
26.11
25.83
25.71
21.05
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

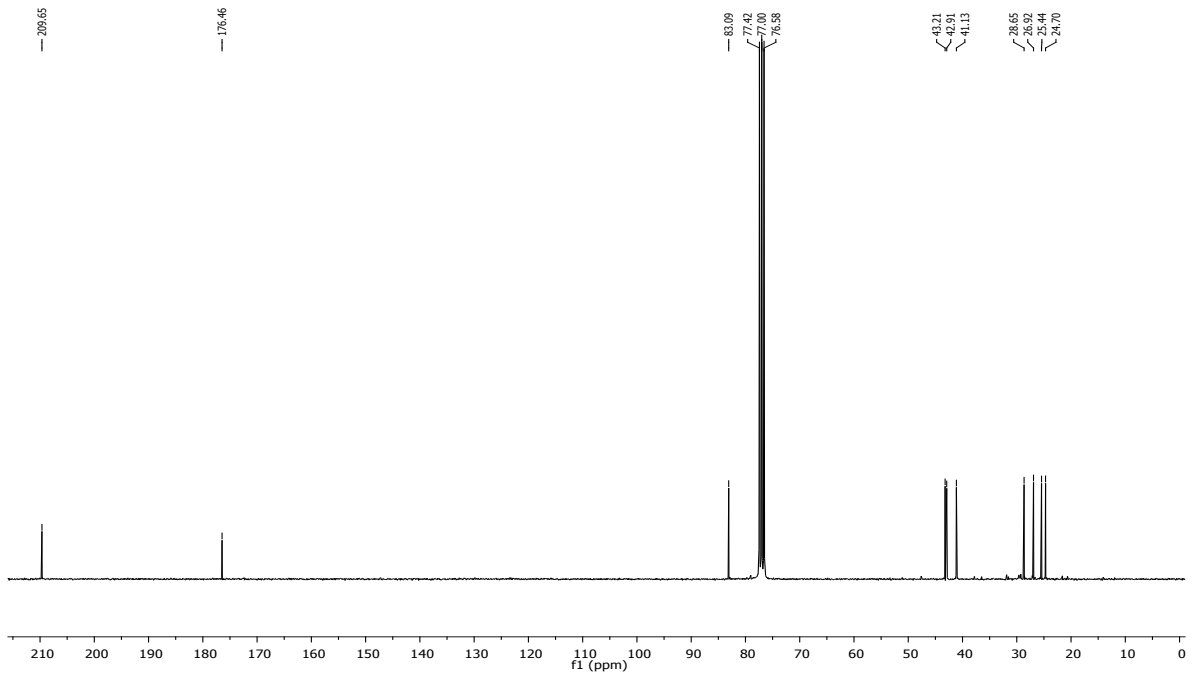

7.46
7.44
7.27
6.15
6.14
5.52
3.10
3.09
3.07
3.06
3.04
3.02
3.01
2.98
2.96
2.95
2.93
2.92
2.86
2.85
2.84
2.83
2.80
2.79
2.76
2.75
2.74
2.73
2.44
2.39
2.04
2.02
2.00
1.94
1.93
1.90
1.85
1.79
1.77
1.75
1.42
0.94
S
S
O
O
4c
1.00
0.97
0.99
2.07
2.08
1.00
5.12
3.16
1.37
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.04
153.98
122.54
88.76
77.42
77.00
76.58
48.58
43.73
38.36
38.21
34.52
26.40
25.43
22.30
18.25
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

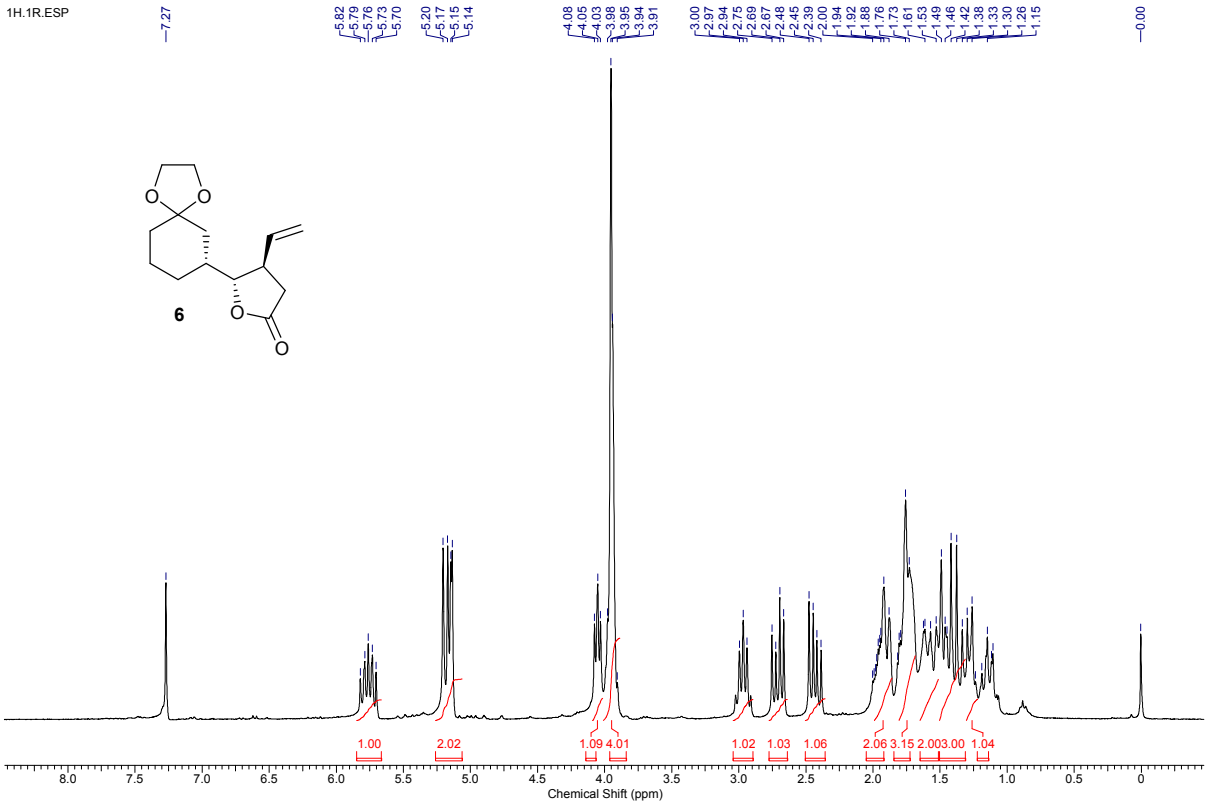

7.27
4.28
4.25
4.23
4.20
3.95
3.92
3.89
2.55
2.52
2.52
2.49
2.30
2.28
2.26
2.23
2.02
1.98
1.97
1.93
1.92
1.89
1.86
1.85
1.83
1.82
1.81
1.80
1.78
1.76
1.72
1.67
1.63
1.55
1.54
1.50
1.47
1.46
1.34
1.30
1.25
1.02
4d
1.00
4.00
2.02
1.09
2.49
3.80
2.07
1.31
1.05
f1 (ppm)


177.00
108.47
84.12
77.42
77.00
76.58
64.30
64.24
40.68
37.21
34.84
28.81
26.53
25.92
22.54
f1 (ppm)


7.27
4.42
4.39
4.37
4.34
2.60
2.60
2.58
2.57
2.55
2.52
2.39
2.35
2.33
2.31
2.29
2.28
2.24
2.20
2.17
2.15
2.14
2.13
2.12
2.11
2.03
2.00
1.97
1.96
1.92
1.90
1.87
1.71
1.70
1.69
1.67
1.66
1.65
1.61
1.57
1.57
1.57
1.54
1.53
O
O
O
5
1.00
3.05
3.05
2.05
3.04
2.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

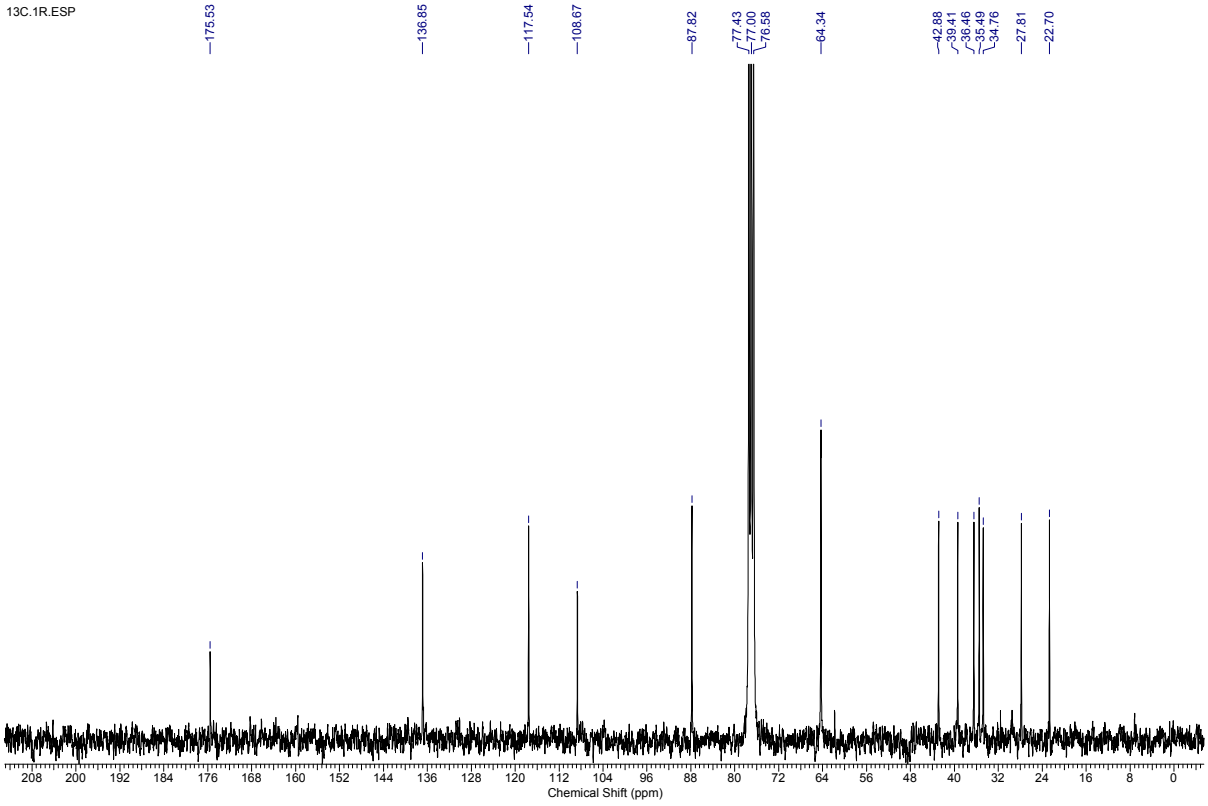

209.65
176.46
83.09
77.42
77.00
76.58
43.21
42.91
41.13
28.65
26.92
25.44
24.70
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

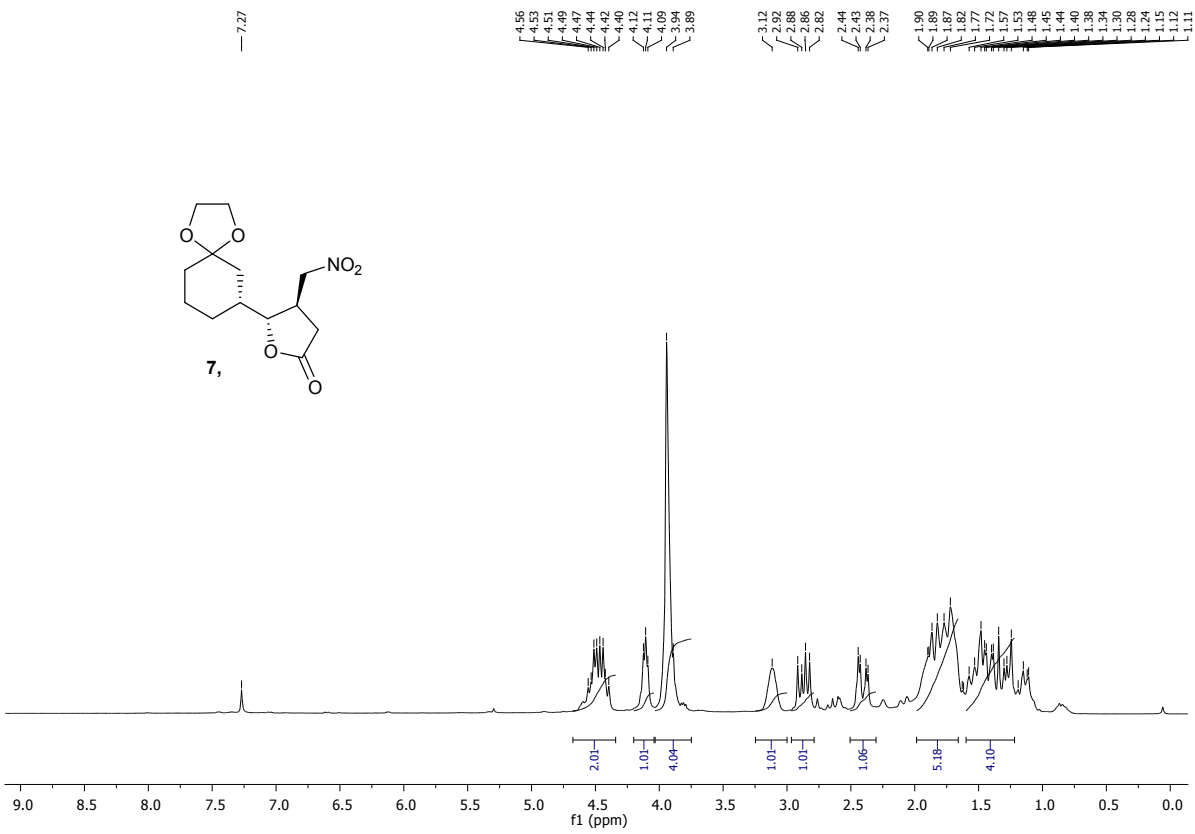
1H.1R.ESP

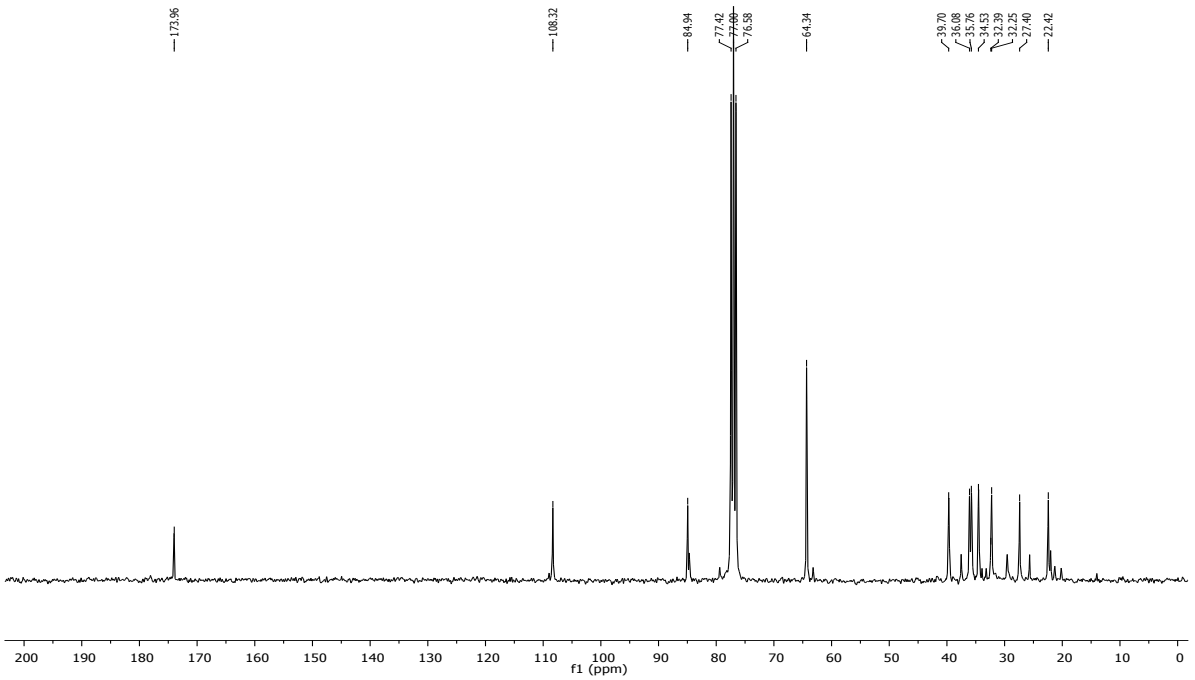


6

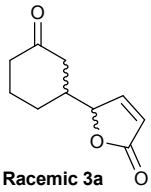
13C.1R.ESP



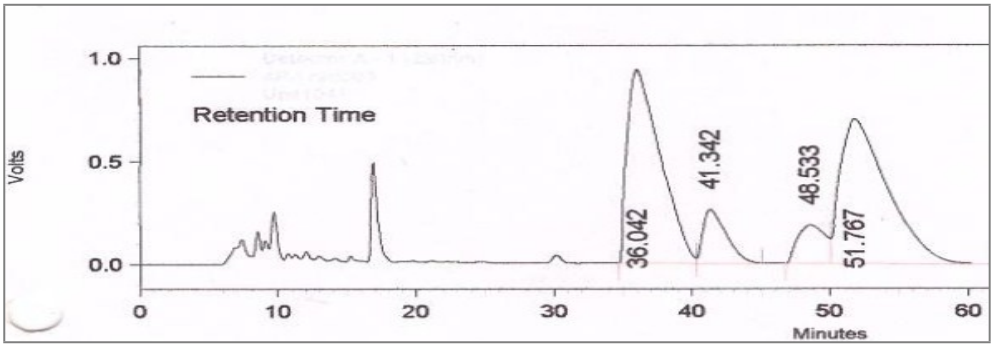

7.27
4.56
4.53
4.51
4.49
4.47
4.44
4.42
4.40
4.12
4.11
4.09
3.94
3.89
3.12
2.92
2.88
2.86
2.82
2.44
2.43
2.38
2.37
1.90
1.89
1.87
1.82
1.77
1.72
1.57
1.53
1.48
1.45
1.44
1.40
1.38
1.34
1.30
1.28
1.24
1.15
1.12
1.11
O
O
NO2
O
O
7,
2.01
1.01
4.04
1.01
1.01
1.06
5.18
4.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.96
108.32
84.94
77.42
77.00
76.58
64.34
39.70
36.08
35.76
34.53
32.39
32.25
27.40
22.42
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

HPLC, Chiralpak AS-H, hexanes: isopropanol = 55:45, 0.5 mL/min, λ= 230 nm.

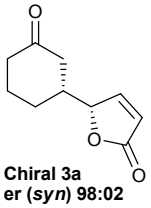


Racemic 3a

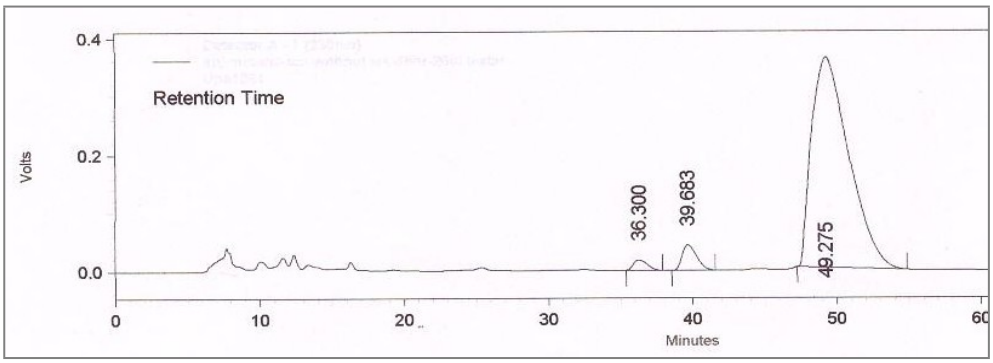


Detector A - 1 (230nm)

Retention Time	C Area	Area %
36.042	157992397	41.564
41.342	30136720	7.928
48.533	25800321	6.787
51.767	166185906	43.720
Totals	380115344	100.000



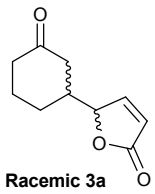
Chiral 3a
er (*syn*) 98:02



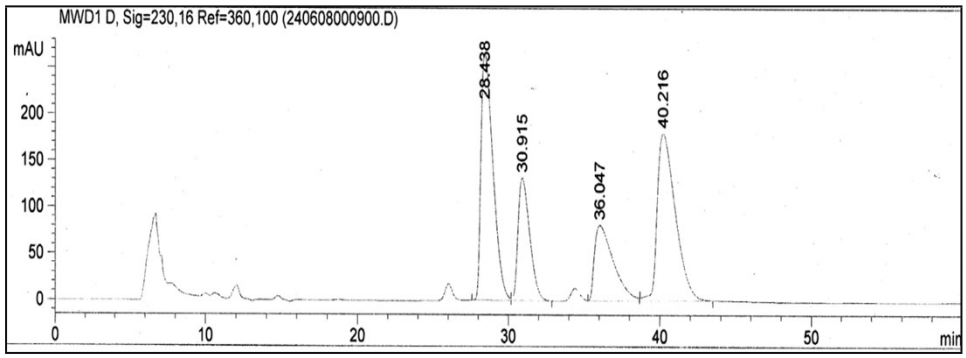
Detector A - 1 (230nm)

Pk #	Retention Time	Area	Area %
1	36.300	1164307	1.693
2	39.683	3023329	4.395
3	49.275	64604411	93.913
Totals		68792047	100.000

HPLC, Chiralpak AS-H, hexanes: isopropanol = 55:45, 0.5 mL/min, λ= 230 nm.

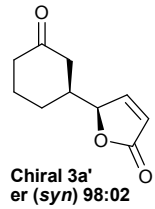


Racemic 3a

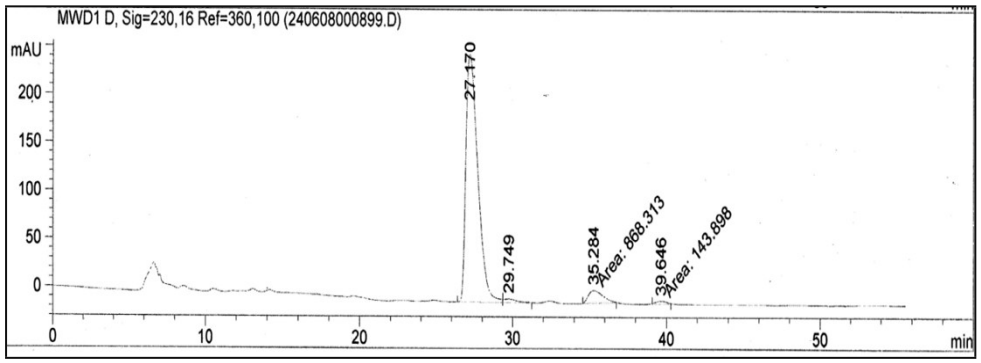


Signal 2: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.438	BV	0.8574	1.47296e4	266.25772	33.4784
2	30.915	VB	0.8387	7136.96582	132.01074	16.2214
3	36.047	VB	1.2835	7109.73779	81.52364	16.1595
4	40.216	BB	1.2628	1.50210e4	180.14224	34.1407
Totals :				4.39973e4	659.93434	



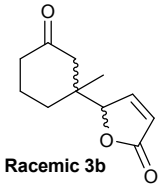
Chiral 3a'
er (*syn*) 98:02



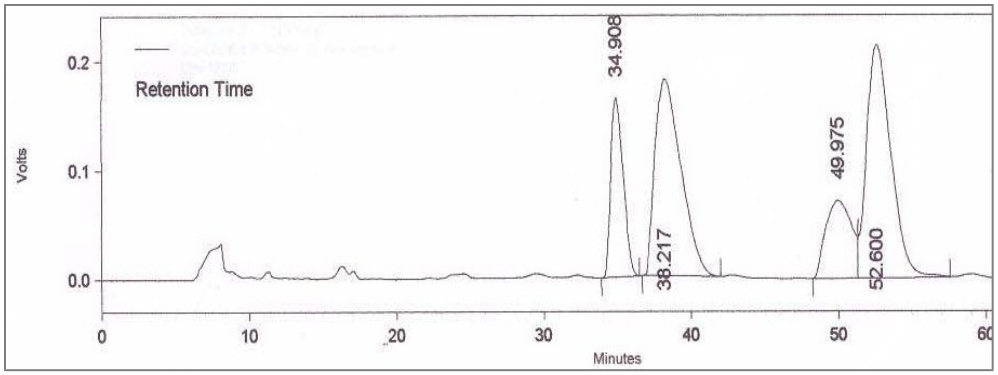
Signal 2: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.170	BB	0.8356	1.39482e4	257.64597	91.9030
2	29.749	BB	0.6841	216.67851	3.77219	1.4277
3	35.284	MM	1.1030	868.31262	13.12024	5.7212
4	39.646	MM	0.8297	143.89787	2.89068	0.9481
Totals :				1.51771e4	277.42907	

HPLC, Chiralpak AS-H, hexanes: isopropanol = 55:45, 0.5 mL/min, λ= 230 nm.

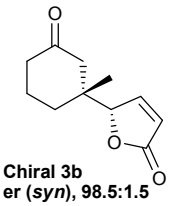


Racemic 3b

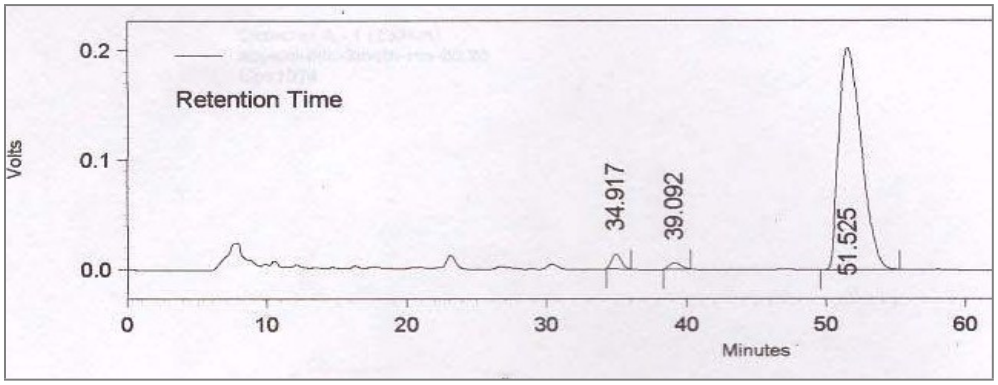


Detector A - 1 (230nm)

Pk #	Retention Time	Area	Area %
1	34.908	9612379	14.769
2	38.217	22194381	34.100
3	49.975	8567708	13.163
4	52.600	24712403	37.968
Totals		65086871	100.000



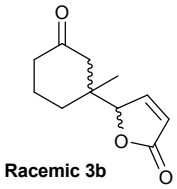
Chiral 3b
er (*syn*), 98.5:1.5



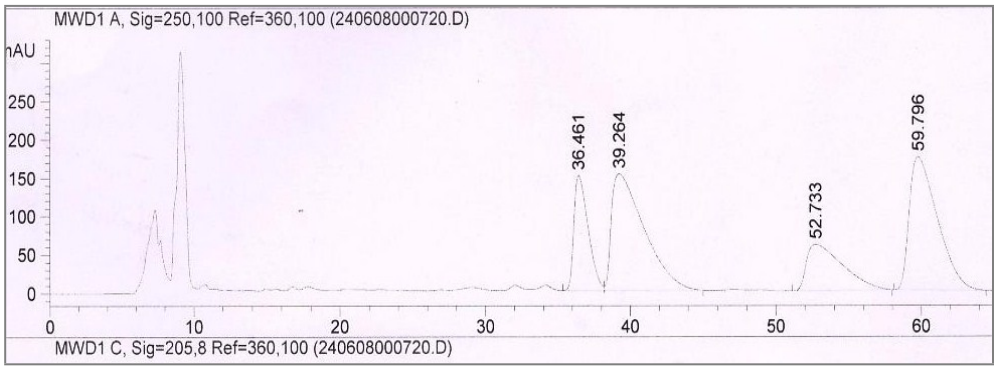
Detector A - 1 (230nm)

Retention Time	C Area	Area %
34.917	630038	2.654
39.092	339020	1.428
51.525	22766384	95.917
Totals	23735442	100.000

HPLC, Chiralpak AS-H, hexanes: isopropanol = 55:45, 0.5 mL/min, λ= 250 nm.

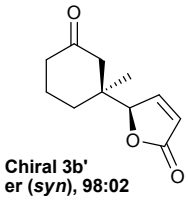


Racemic 3b

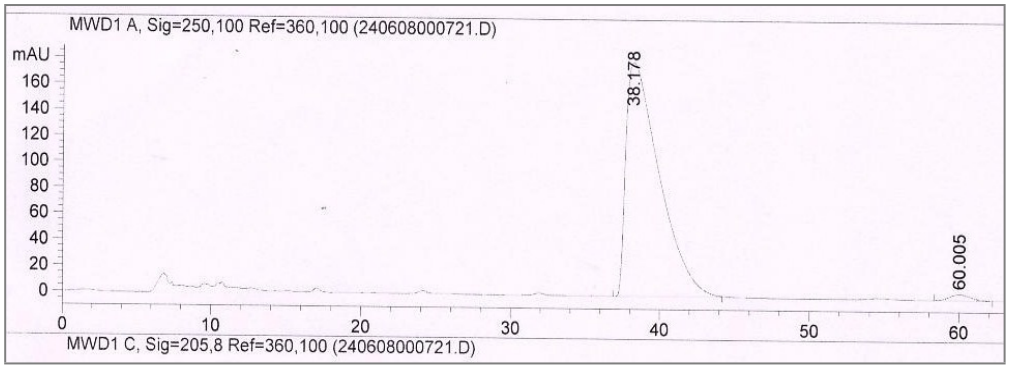


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.461	BV	0.9998	1.01929e4	149.81084	15.0740
2	39.264	VB	1.8400	2.37528e4	152.09416	35.1274
3	52.733	VB	2.0382	1.02612e4	59.85107	15.1750
4	59.796	BB	1.5916	2.34121e4	173.58260	34.6236



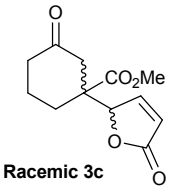
Chiral 3b'
er (*syn*), 98:02



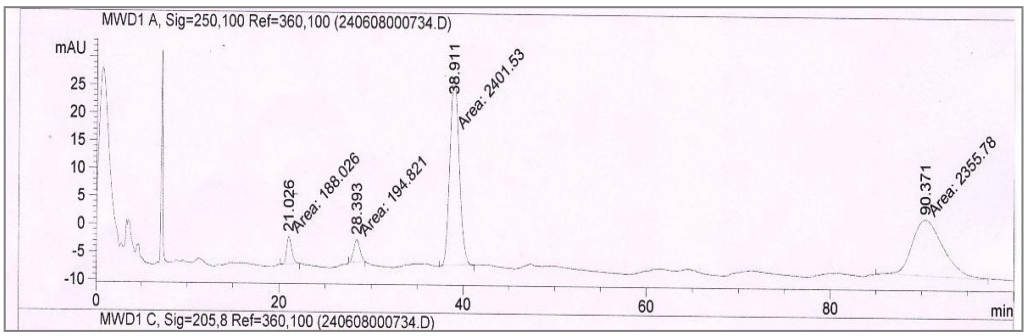
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.178	BB	1.8222	2.78234e4	179.51802	98.4033
2	60.005	BV	1.1337	451.45950	4.67069	1.5967
Totals :				2.82749e4	184.18871	

HPLC, Chiralpak IC, hexanes: isopropanol = 50:50, 1.0 mL/min, λ= 250 nm

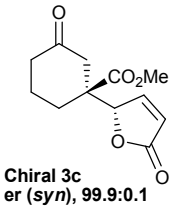


Racemic 3c

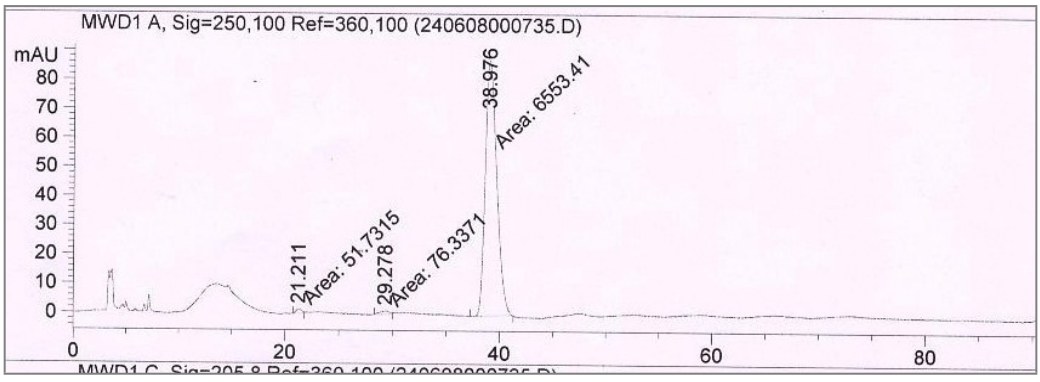


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.026	MM	0.6368	188.02611	4.92089	3.6580
2	28.393	MM	0.8025	194.82098	4.04593	3.7902
3	38.911	MM	1.1788	2401.52832	33.95399	46.7210
4	90.371	MM	3.9254	2355.77661	10.00234	45.8309



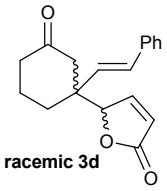
Chiral 3c
er (*syn*), 99.9:0.1



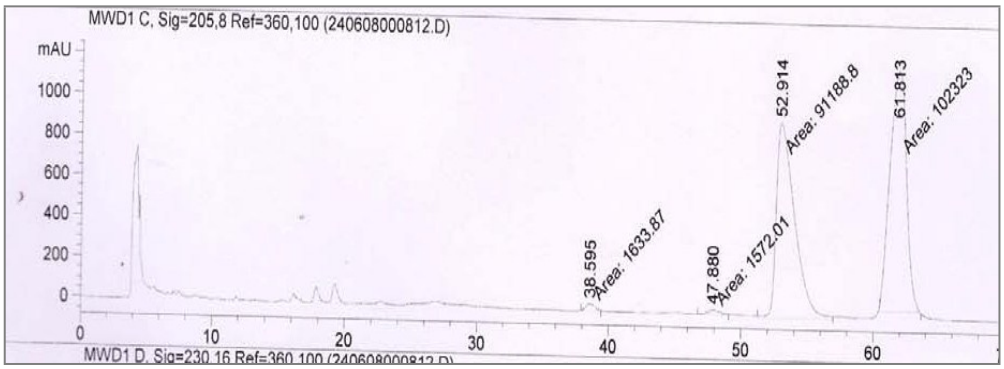
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.211	MM	0.6155	51.73147	1.40069	0.7743
2	29.278	MM	1.0612	76.33709	1.19891	1.1425
3	38.976	MM	1.2472	6553.40576	87.57661	98.0832
Totals :				6681.47432	90.17620	

HPLC, Chiralpak IB, hexanes: isopropanol = 80:20, 0.75 mL/min, λ= 205 nm

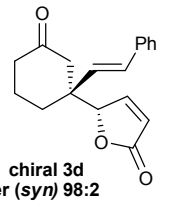


racemic 3d

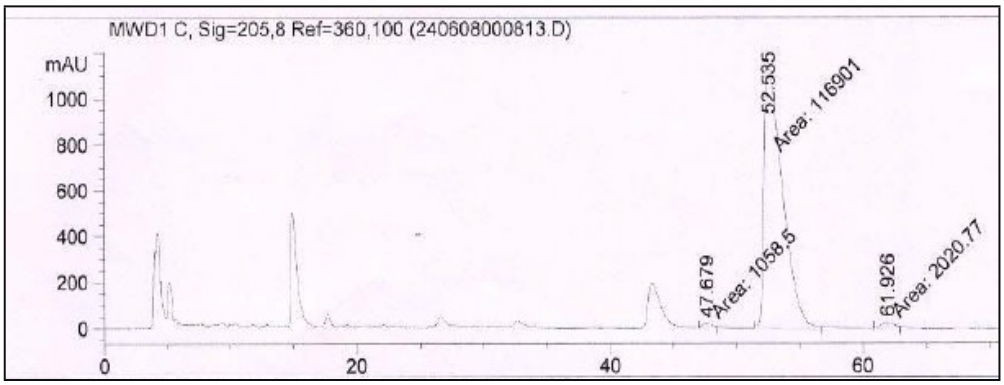


Signal 1: MWD1 C, Sig=205,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.595	MM	0.7966	1633.87012	34.18604	0.8306
2	47.880	MM	1.0948	1572.00635	23.93109	0.7991
3	52.914	MM	1.5901	9.11888e4	955.79211	46.3552
4	61.813	MM	1.4541	1.02323e5	1172.84753	52.0151



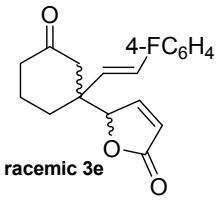
chiral 3d
er (*syn*) 98:2



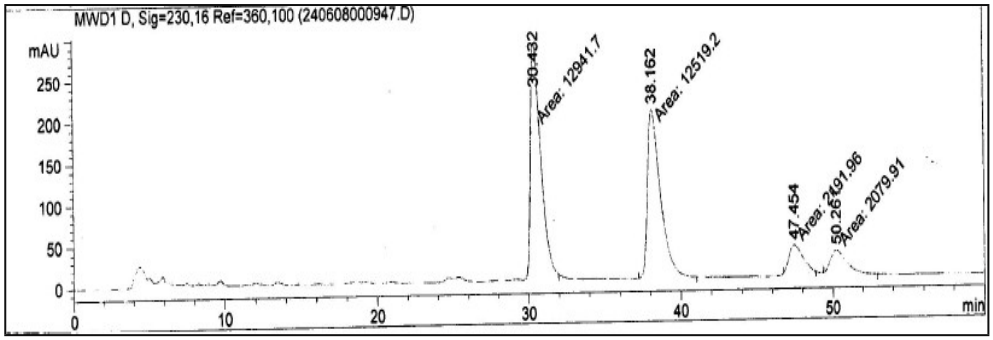
Signal 1: MWD1 C, Sig=205,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.679	MM	0.8877	1058.49683	19.87263	0.8822
2	52.535	MM	1.6946	1.16901e5	1149.74170	97.4335
3	61.926	MM	1.2228	2020.76501	27.54384	1.6842
Totals :				1.19980e5	1197.15817	

HPLC, Chiralpak IB, hexanes: isopropanol = 75:25, 0.75 mL/min, λ= 230 nm

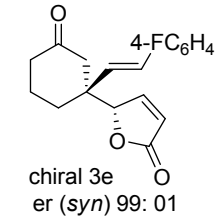


racemic 3e

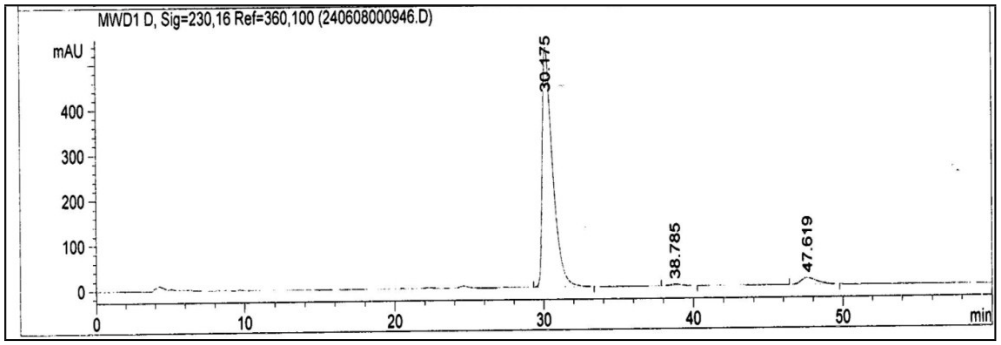


Signal 2: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.432	MM	0.7655	1.29417e4	281.75568	43.5267
2	38.162	MM	1.0131	1.25192e4	205.95340	42.1057
3	47.454	MM	1.0768	2191.95874	33.92660	7.3722
4	50.261	MM	1.2566	2079.90918	27.58698	6.9954



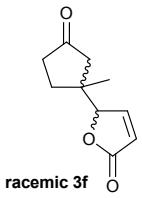
chiral 3e
er (*syn*) 99: 01



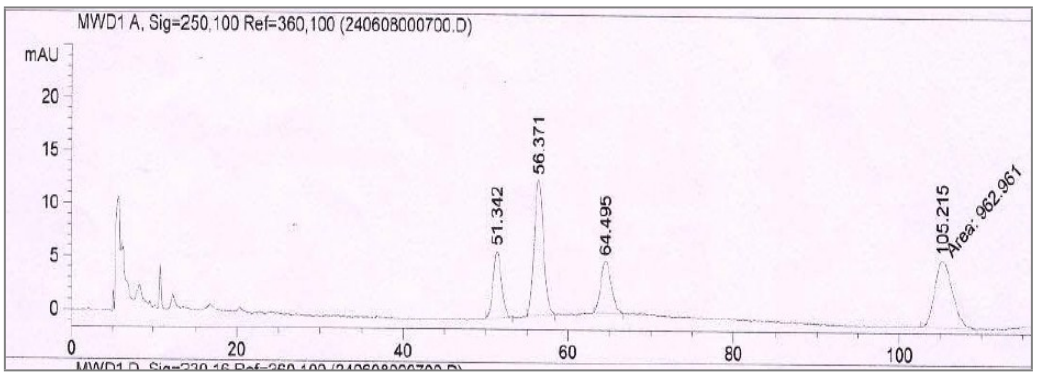
Signal 2: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.175	BB	0.7102	2.53831e4	530.52264	94.9235
2	38.785	BB	0.6922	199.10754	3.52932	0.7446
3	47.619	BB	1.0413	1158.37488	15.47507	4.3319

HPLC, Chiralpak AS-H, hexanes: isopropanol = 55:45, 0.5 mL/min, λ= 250 nm

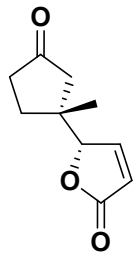


racemic 3f

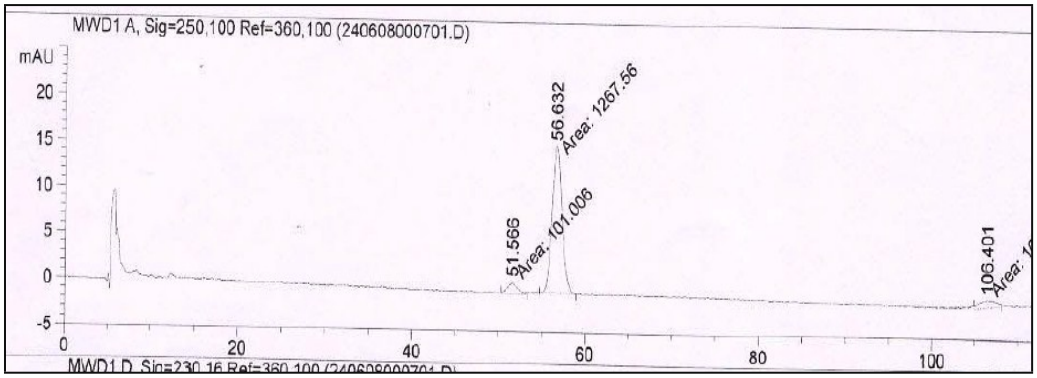


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.342	BB	0.8787	433.34631	6.19052	15.4430
2	56.371	BB	1.1003	980.63953	12.70753	34.9467
3	64.495	BB	1.0567	429.15427	4.85773	15.2936
4	105.215	MM	2.5398	962.96130	6.31909	34.3167



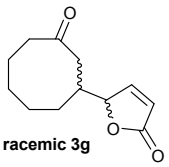
chiral 3f
er (*syn*) 92:08



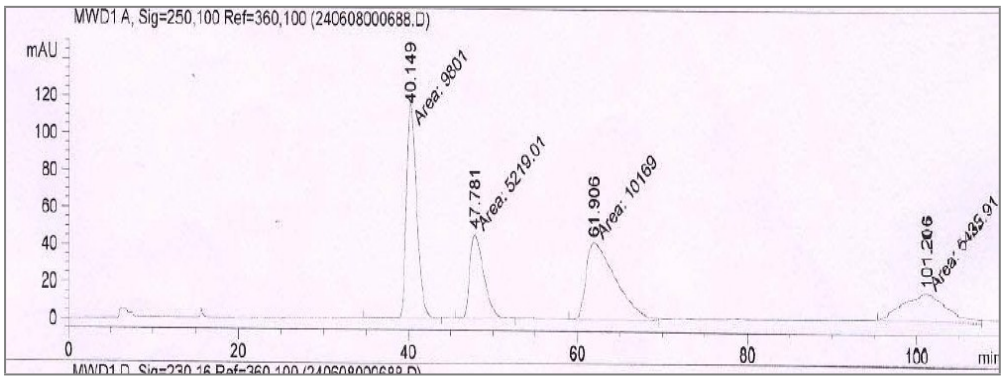
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.566	MM	1.3762	101.00626	1.22322	6.8447
2	56.632	MM	1.3274	1267.55945	15.91500	85.8964
3	106.401	MM	2.2729	107.11916	7.85466e-1	7.2589
Totals :				1475.68487	17.92369	

HPLC, Chiralpak ASH, hexanes: isopropanol = 55:45, 0.5 mL/min, λ= 250 nm

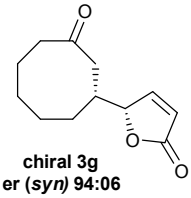


racemic 3g

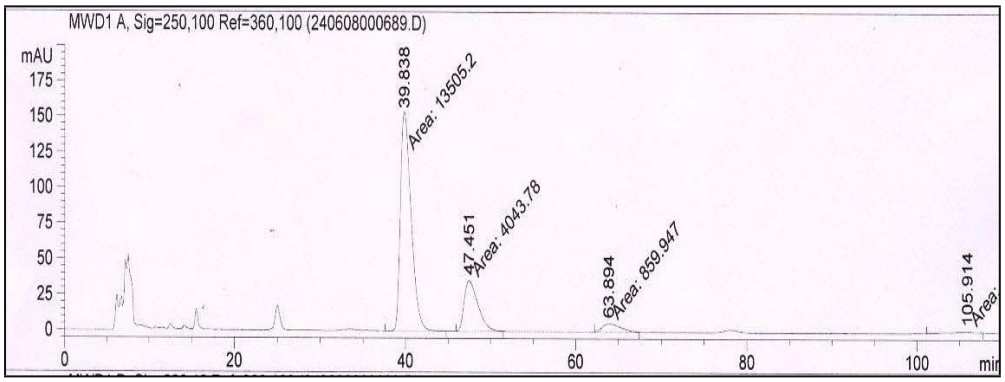


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.149	MM	1.4093	9801.00000	115.91172	32.0034
2	47.781	MM	1.9300	5219.01172	45.07021	17.0417
3	61.906	MM	4.0926	1.01690e4	41.41167	33.2049
4	101.206	MM	6.1684	5435.91309	14.68755	17.7500



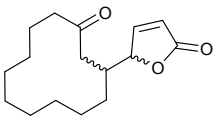
chiral 3g
er (*syn*) 94:06



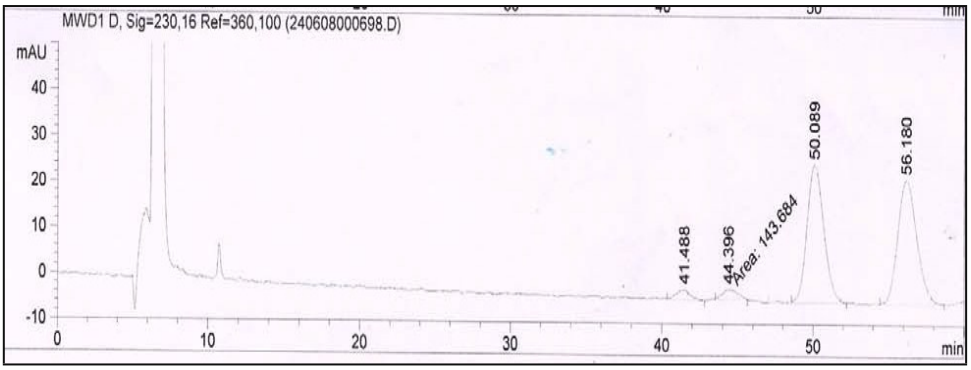
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.838	MM	1.4601	1.35052e4	154.15355	72.7762
2	47.451	MM	1.9022	4043.78052	35.43146	21.7910
3	63.894	MM	2.4829	859.94727	5.77245	4.6341
4	105.914	MM	5.4874	148.23796	4.50236e-1	0.7988

HPLC, Chiralpak AS-H, hexanes: isopropanol = 55:45, 0.5 mL/min, λ= 230 nm

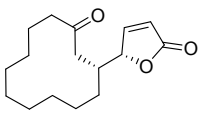


racemic 3h

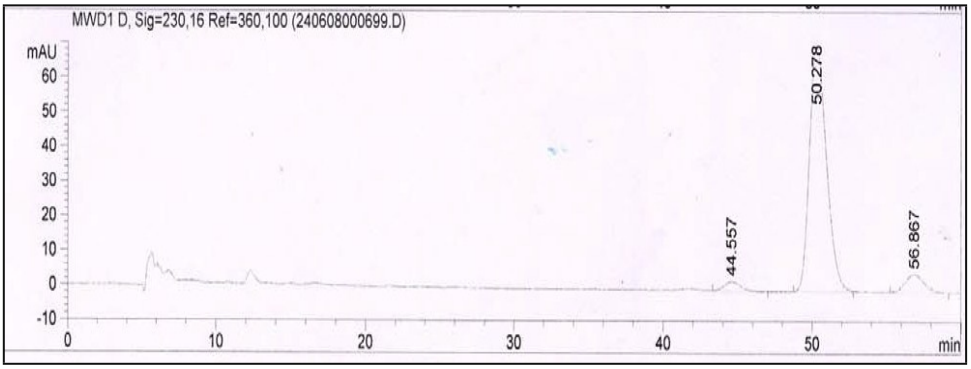


Signal 2: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.488	BV	0.8195	137.52922	2.15814	2.7779
2	44.396	MM	1.1333	143.68394	2.11308	2.9023
3	50.089	BB	1.2181	2336.46411	30.08223	47.1940
4	56.180	BB	1.2993	2333.08569	26.96896	47.1258



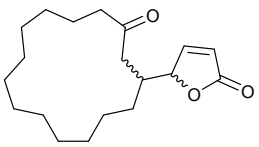
chiral 3h
er (*syn*) 92:08



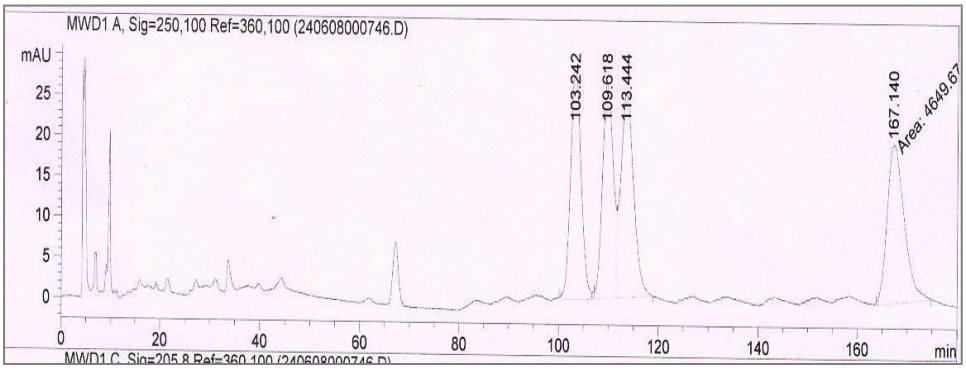
Signal 2: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.557	BB	0.8749	200.21703	2.75828	3.1732
2	50.278	BB	1.2021	5648.50000	71.00803	89.5224
3	56.867	BB	1.0679	460.87833	5.26191	7.3044

HPLC, Chiralpak IC, hexanes: isopropanol = 90:10, 0.75 mL/min, λ= 250 nm

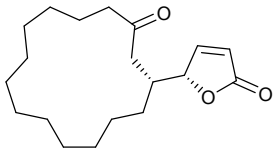


racemic 3i

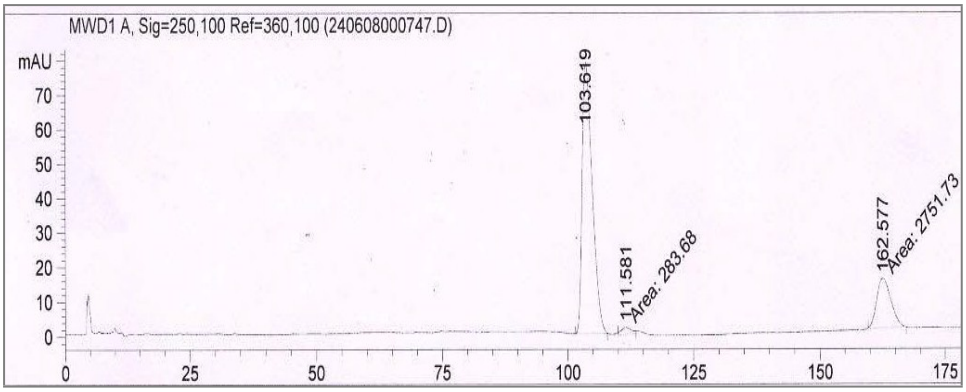


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	103.242	BV	1.7255	4186.48242	28.60506	24.1498
2	109.618	BV	1.7719	4010.39087	26.52486	23.1340
3	113.444	VB	2.1039	4488.90527	25.17976	25.8944
4	167.140	MM	3.9765	4649.67383	19.48808	26.8218



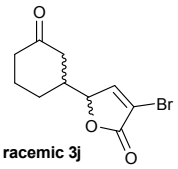
chiral 3i
er (*syn*) 97:03



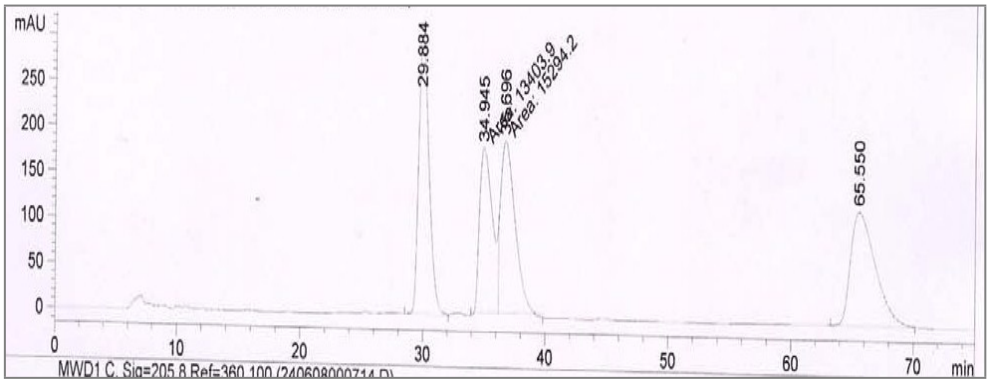
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	103.619	BB	1.6461	1.09711e4	78.61786	78.3286
2	111.581	MM	2.3675	283.68021	1.99707	2.0253
3	162.577	MM	3.2405	2751.72803	14.15280	19.6461

HPLC, Chiralpak IC, hexanes: isopropanol = 55:45, 0.5 mL/min, λ= 250 nm

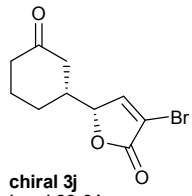


racemic 3j

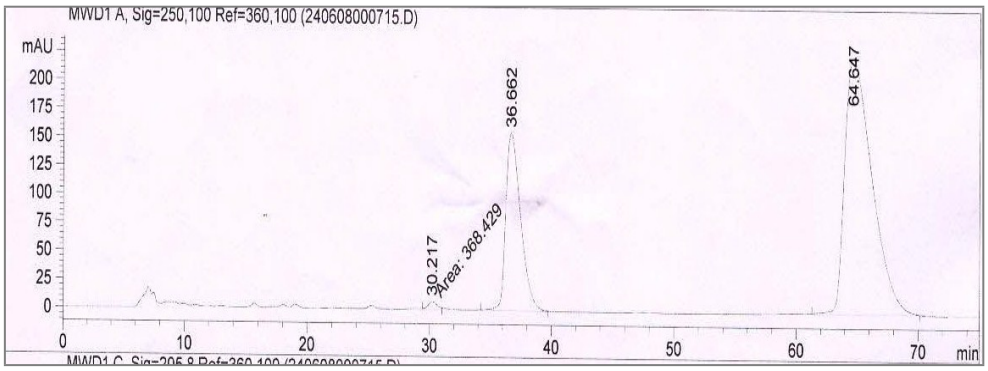


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.884	BB	0.8915	1.78486e4	305.54382	27.8687
2	34.945	MF	1.2412	1.34039e4	179.99023	20.9288
3	36.696	FM	1.3547	1.52942e4	188.15746	23.8803
4	65.550	VB	1.6947	1.74986e4	124.12759	27.3222



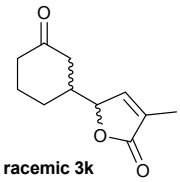
chiral 3j
er (*syn*) 99:01



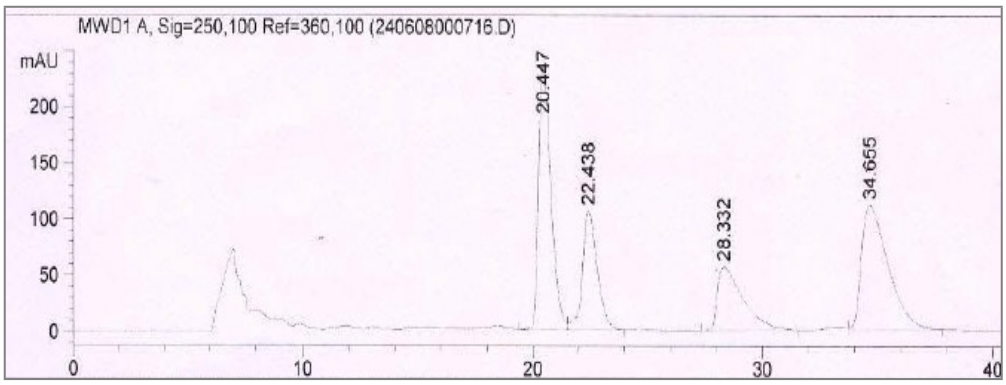
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.217	MM	0.8868	368.42874	6.92428	0.7567
2	36.662	VB	1.2345	1.31734e4	155.47176	27.0576
3	64.647	BB	1.8778	3.51448e4	224.81435	72.1857

HPLC, Chiralpak AS-H, hexanes: isopropanol = 55:45, 0.5 mL/min, λ= 250 nm

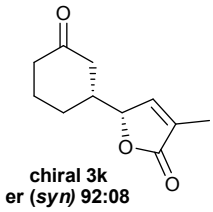


racemic 3k

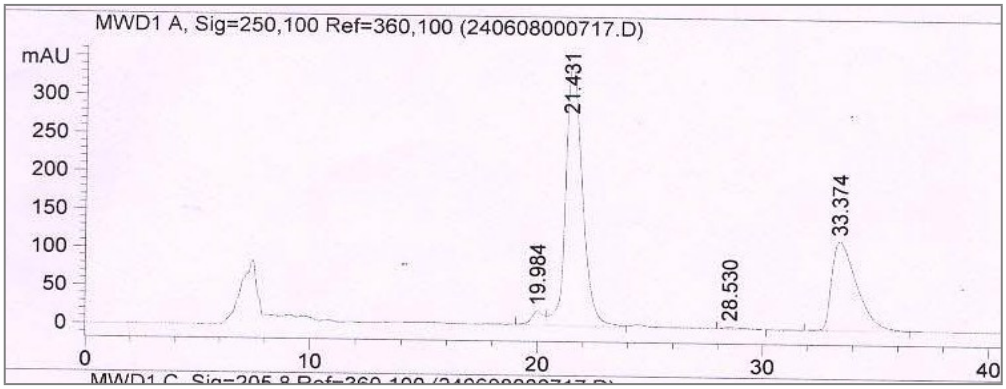


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.447	VV	0.5781	8840.79004	236.51538	33.0170
2	22.438	VB	0.6652	4677.38818	105.50858	17.4683
3	28.332	VB	1.0511	4342.83398	56.10549	16.2188
4	34.655	VV	1.1052	8915.45508	110.97950	33.2959



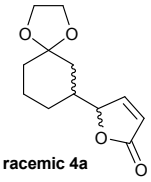
chiral 3k
er (*syn*) 92:08



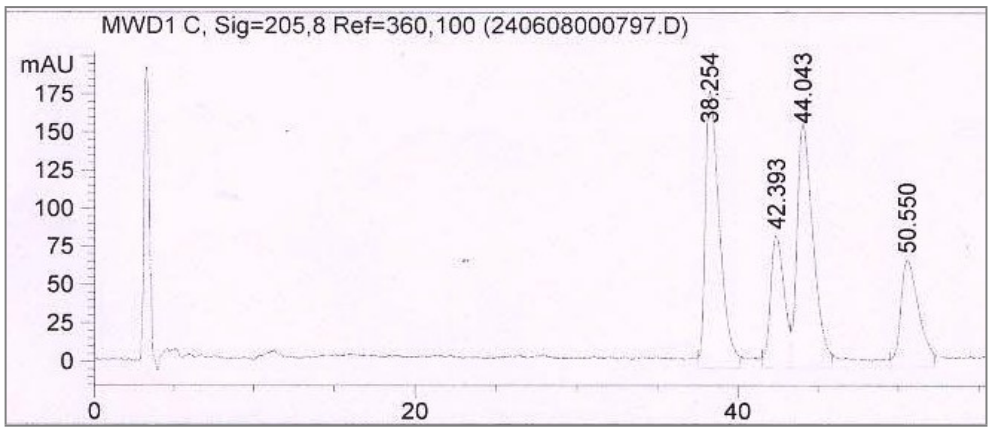
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.984	VV	0.5433	733.34247	18.30739	2.6624
2	21.431	VV	0.7615	1.77220e4	341.46387	64.3402
3	28.530	BV	0.7671	139.87605	2.17253	0.5078
4	33.374	VB	1.0703	8948.99316	116.22198	32.4895

HPLC, Chiralpak OJ-H, hexanes: isopropanol = 98:02, 1.0 mL/min, λ= 205 nm

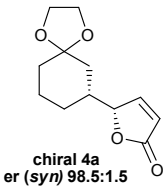


racemic 4a

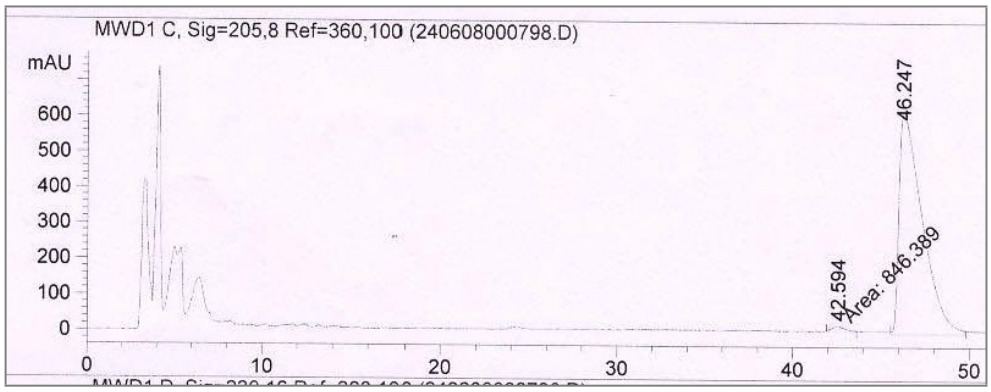


Signal 1: MWD1 C, Sig=205,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.254	VV	0.7513	1.12149e4	181.39926	33.8307
2	42.393	VV	0.7456	5127.30664	86.23753	15.4669
3	44.043	VV	0.8928	1.12111e4	159.73976	33.8191
4	50.550	VV	0.9422	5596.83691	69.89775	16.8833



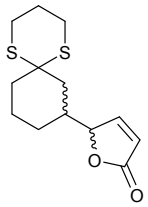
chiral 4a
er (*syn*) 98.5:1.5



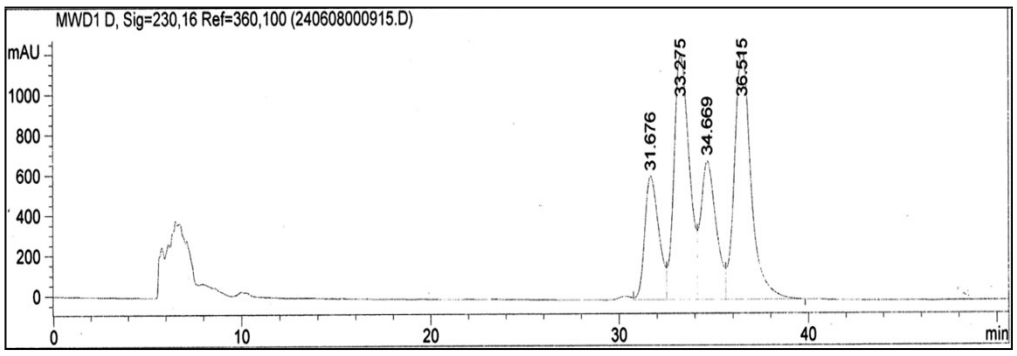
Signal 1: MWD1 C, Sig=205,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.594	MM	0.9899	846.38910	14.25003	1.4729
2	46.247	VV	1.1540	5.66158e4	623.10657	98.5271

HPLC, Chiralpak IA, Hexanes: Isopropanol = 90:10, 0.5 mL/min, λ= 230 nm

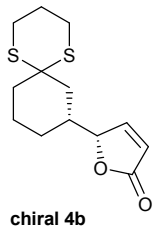


racemic 4b

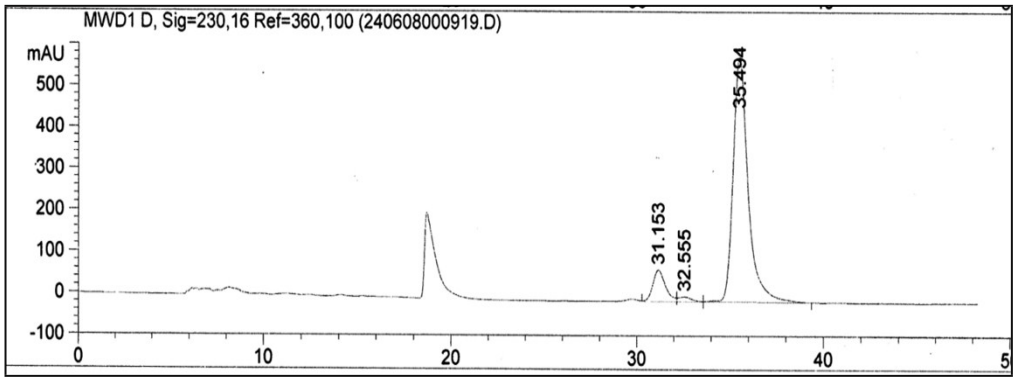


Signal 2: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.676	VV	0.7942	3.15658e4	613.53864	14.7593
2	33.275	VV	0.8615	6.84307e4	1214.32422	31.9963
3	34.669	VV	0.8329	3.87050e4	687.41852	18.0974
4	36.515	VB	0.9274	7.51695e4	1236.16870	35.1471
Totals :				2.13871e5	3751.45007	



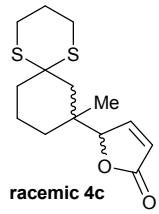
chiral 4b
er (*syn*) 98:02



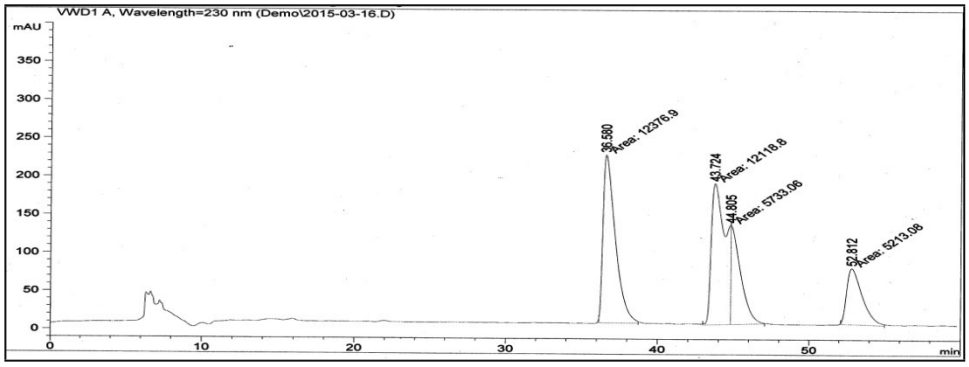
Signal 2: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.153	VV	0.7234	3643.55029	76.53427	9.7181
2	32.555	VV	0.6946	598.65045	11.82635	1.5967
3	35.494	VB	0.8367	3.32501e4	590.72949	88.6852
Totals :				3.74923e4	679.09012	

HPLC, Chiralpak IB, Hexanes: Isopropanol = 95:05, 0.5 mL/min, λ= 230 nm

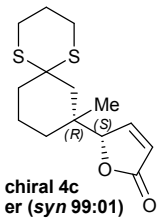


racemic 4c

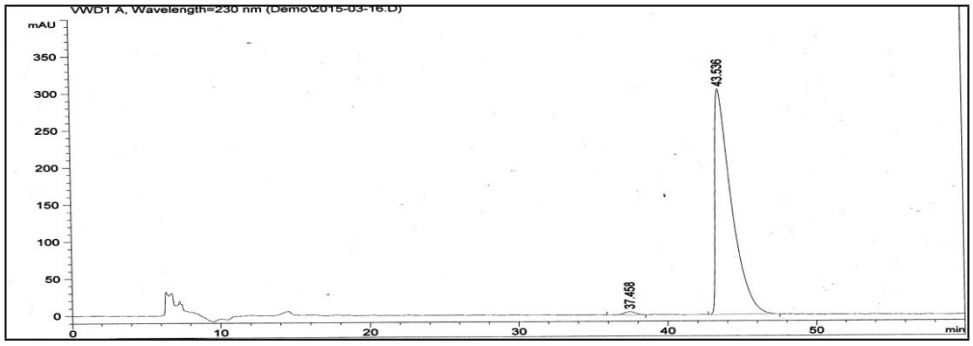


Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.580	MM	0.9384	1.23769e4	219.82452	34.9217
2	43.724	MF	1.0956	1.21188e4	184.34987	34.1934
3	44.805	FM	0.7381	5733.06445	129.45093	16.1760
4	52.812	MM	1.1832	5213.07764	73.43285	14.7088



chiral 4c
er (*syn* 99:01)



Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.458	BB	0.8219	227.72086	4.19115	0.9798
2	43.536	BB	1.0916	2.30128e4	304.55499	99.0202
Totals :				2.32405e4	308.74615	