Asymmetric synthesis of dihydro-1,3-dioxepines by Rh(II)/Sm(III) relay catalytic three-component tandem [4+3]-cycloaddition

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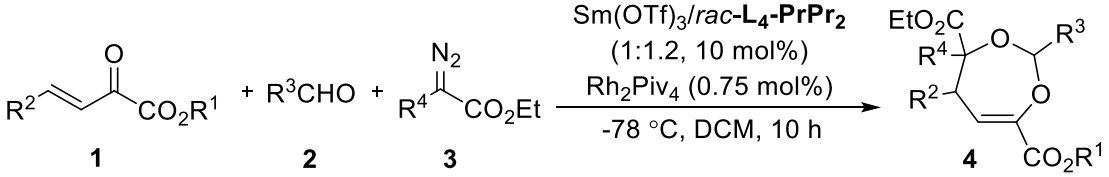
1. General Method

^{1}H NMR spectra were recorded on Bruker AMX-400 (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane (TMS) with the TMS resonance as the internal standard (TMS, δ = 0.00). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C{^{1}H} NMR spectra were collected on Bruker AMX-400 (100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). ^{19}F{^{1}H} NMR spectra were collected on Bruker AMX-400 (376 MHz) with complete proton decoupling. HRMS was recorded on Thermo Q-Exactive Focus (FTMS+c ESI). Enantiomeric excesses (ee) were determined by HPLC and UPC^2 analysis using the corresponding commercial Daicel Chiralcel column as stated in the experimental procedures at 25 °C. Optical rotations were reported as follows: $[\alpha]^T_D$ (*c* g/100 mL, λ = 589 nm, in solvent). IR spectra were recorded on BRUKER TENSOR II IR spectrophotometer. CD spectra were determined by Chirascan CD (DCM as the solvent) which was purchased from Applied photophysics Ltd. Silica gel for thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd. Reagents obtained from commercial sources were used without further purification. Acetonitrile (CH_3CN), CH_2Cl_2, chloroform ($CHCl_3$), ethyl acetate (EA) and 1,2-dichloroethane (DCE) were distilled over CaH_2 before use. THF, toluene and Et_2O were distilled from sodium benzophenone ketyl before use. The *N,N'*-dioxides were prepared according to the methods reported in the literature.[1]

The β,γ-unsaturated α-ketoester **1**[2] and 2-diazo-2-arylacetate **3**[3] were prepared according to the methods reported in the literature. All the liquid aldehydes were freshly distilled prior to use. All the solid aldehydes were used after recrystallization with petroleum ether. Rh_2Piv_4 was weighed in a volumetric flask, and added as a DCM solution.

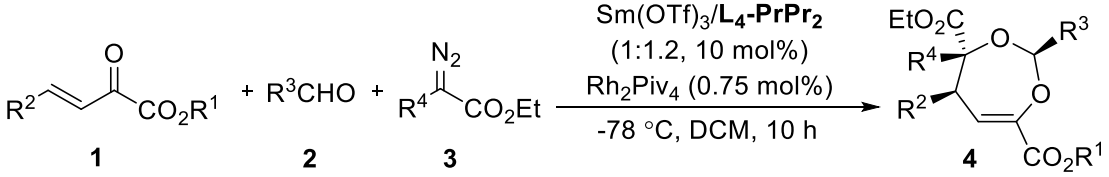
All catalytic reactions were weighed in glovebox.

2. General Procedure for Preparation of the Racemic Products



A dry reaction tube was charged with $Sm(OTf)_3$ (6.0 mg, 0.01 mmol, 10 mol%), Rh_2Piv_4 (dirhodium tetrapivalate) (0.45 mg, 0.75 μmol, 0.75 mol%) and the ligand *rac*-**L_4-PrPr$_2$** (7.6 mg, 0.012 mmol, 12 mol%) in anhydrous DCM (1.0 mL) under nitrogen atmosphere. The mixture was stirred at 35 °C for 30 min and the aldehydes **2** (0.30 mmol) were added. Then the mixture was stirred at −20 °C and 2-diazo-2-arylacetates **3** (0.30 mmol) was added in one port. The reaction mixture was stirred at −20 °C for another 20 min. Next, the mixture was stirred at −78 °C. Then β,γ-unsaturated α-ketoester **1** (0.10 mmol) dissolved in anhydrous DCM was added in one port and the solvent in the reaction mixture was replenished to 2 mL totally. The reaction mixture was stirred at −78 °C for another 10 h. Desired product was purified directly by silica gel column chromatograph.

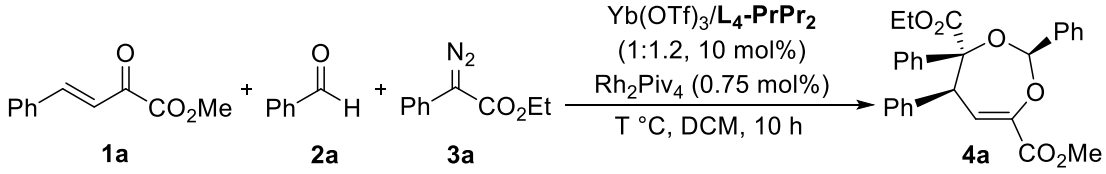
3. Typical Procedure for the Asymmetric Cycloaddition Reaction of β,γ-Unsaturated α-ketoesters 1, Aldehydes 2 and 2-Diazo-2-arylacetates 3



A dry reaction tube was charged with $Sm(OTf)_3$ (6.0 mg, 0.01 mmol, 10 mol%), Rh_2Piv_4 (dirhodium tetrapivalate) (0.45 mg, 0.75 μmol, 0.75 mol%) and the ligand **L_4-PrPr$_2$** (7.6 mg, 0.012 mmol, 12 mol%) in anhydrous DCM (1.0 mL) under nitrogen atmosphere. The mixture was stirred at 35 °C for 30 min and the aldehydes **2** (0.40 mmol) were added. Then the mixture was stirred at −20 °C and 2-diazo-2-arylacetates **3** (0.40 mmol) was added in one port. The reaction mixture was stirred at −20 °C for another 20 min. Next, the mixture was stirred at −78 °C. Then β,γ-unsaturated α-ketoester **1** (0.10 mmol) dissolved in anhydrous DCM was added in one port and the solvent in the reaction mixture was replenished to 2 mL totally. The reaction mixture was stirred at −78 °C for another 10 h. Desired product was purified directly by silica gel column chromatograph.

4. The Optimization of Reaction Conditions

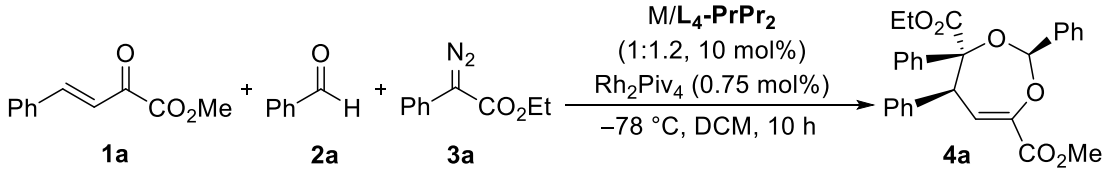
Table S1. Optimization of temperature.



Entry[a]	T (°C)	Yield [%]	ee [%]
1	–20	58	67
2	–40	74	64
3	–60	81	65
4	–78	90	66

[a] The reaction was run with Rh_2Piv_4 (0.75 mol%), $Yb(OTf)_3$/**L_4-PrPr$_2$** (1:1.2, 10 mol%), unsaturated ketoester **1** (0.10 mmol), aldehyde **2a** (3 equiv) and α-diazo ester **3a** (3 equiv) at T °C in DCM (2 mL) for 10 h under an N_2 atmosphere.. Yield was the isolated yield of major diastereomer, ee value was determined by HPLC analysis on a chiral stationary phase.

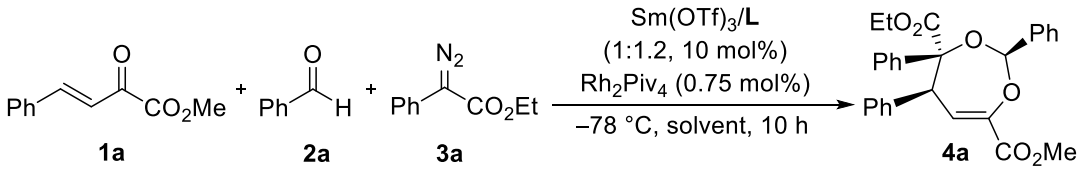
Table S2: Optimization of metal salts.

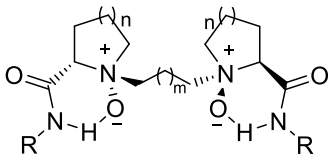


Entry[a]	Metal salt	Yield [%][b]	ee [%][c]
1	$Mg(OTf)_2$	trace	-
2	$Ni(OTf)_2$	trace	-
3	$Zn(OTf)_2$	trace	-
4	$La(OTf)_3$	86	72
5	$Nd(OTf)_3$	89	80
6	$Sm(OTf)_3$	90	84
7	$Ho(OTf)_3$	91	61
8	$Yb(OTf)_3$	90	66

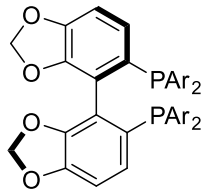
[a] The reaction was run with Rh_2Piv_4 (0.75 mol%), M/**L_4-PrPr$_2$** (1:1.2, 10 mol%), unsaturated ketoester **1** (0.10 mmol), aldehyde **2a** (3 equiv) and α-diazo ester **3a** (3 equiv) at –78 °C in DCM (2 mL) for 10 h under an N_2 atmosphere. Yield was the isolated yield of major diastereomer, ee value was determined by HPLC analysis on a chiral stationary phase.

Table S3: Optimization of the ligands.

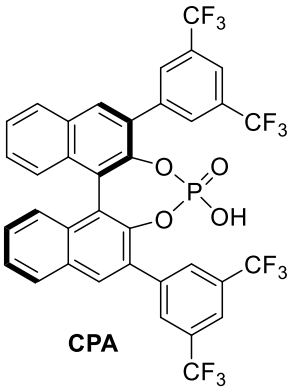




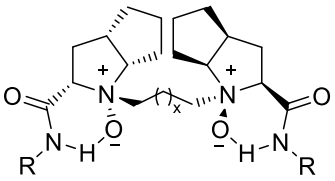
L_3-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1, m = 1
L_4-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1, m = 2
L_5-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1, m = 3
L_4-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2, m = 2
L_4-PrEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 1, m = 2
L_4-PrPr$_3$: R = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, n = 1, m = 2



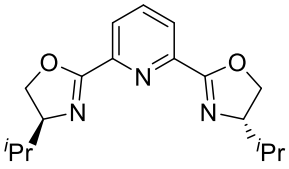
DTBM-SEGPHOS
Ar = 3,5-^{t}Bu$_2$-4-OMeC$_6$H$_2$



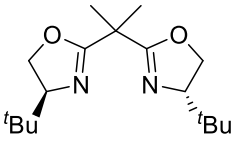
CPA



L_4-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, x = 2



iPr-PyBOX

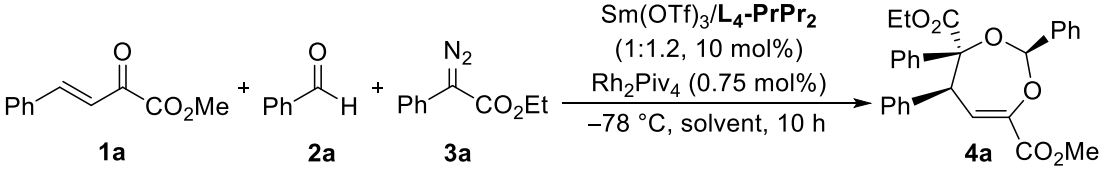


tBu-BOX

Entry[a]	Ligand	Yield [%]	ee [%]
1	**L_3-PrPr$_2$**	38	26
2	**L_4-PrPr$_2$**	90	84
3	**L_5-PrPr$_2$**	85	54
4	**L_4-PiPr$_2$**	68	32
5	**L_4-RaPr$_2$**	50	26
6	**L_4-PrEt$_2$**	86	78
7	**L_4-PrPr$_3$**	90	51
8	***t*Bu-BOX**	56	11
9	***i*Pr-PyBOX**	trace	-
10	**DTBM-SEGPHOS**	57	0
11	**CPA**[b]	trace	-
12	**-**	trace	-
13	**-**[c]	trace	-

[a] Unless otherwise noted, the reaction was run with Rh_2Piv_4 (0.75 mol%), Sm(OTf)$_3$/**L** (1:1.2, 10 mol%), unsaturated ketoester **1** (0.10 mmol), aldehyde **2a** (3 equiv) and α-diazo ester **3a** (3 equiv) at –78 °C in DCM (2 mL) for 10 h under an N_2 atmosphere. Yield was the isolated yield of major diastereomer, ee value was determined by HPLC analysis on a chiral stationary phase. [b] Used as catalyst without Sm(III). [c] Using Rh_2Piv_4 as only catalyst without Sm(OTf)$_3$ and ligand.

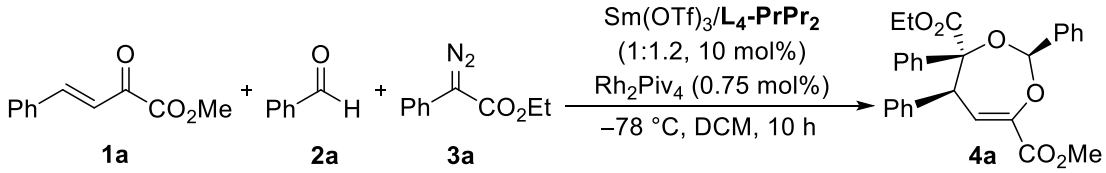
Table S4: Optimization of solvents.



Entry[a]	Solvent	Yield [%]	ee [%]
1	DCM	90	84
2	THF	trace	-
3	Toluene	50	80
4	Et_2O	18	29
5	EA	trace	-

[a] The reaction was run with Rh_2Piv_4 (0.75 mol%), $Sm(OTf)_3$/**L_4-PrPr$_2$** (1:1.2, 10 mol%), unsaturated ketoester **1** (0.10 mmol), aldehyde **2a** (3 equiv) and α-diazo ester **3a** (3 equiv) at –78 °C in solvent (2 mL) for 10 h under an N_2 atmosphere. Yield was the isolated yield of major diastereomer, ee value was determined by HPLC analysis on a chiral stationary phase.

Table S5: Optimization of ratio of substrates.

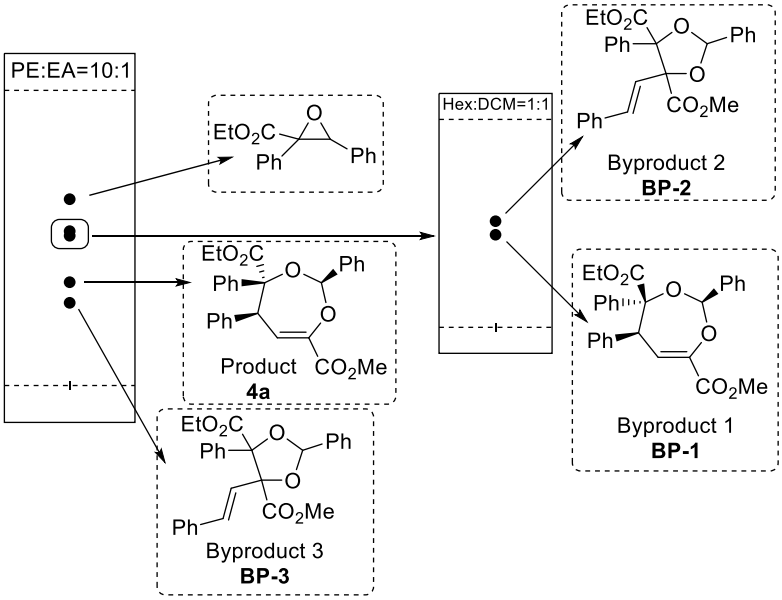


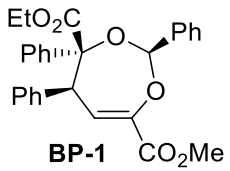
Entry[a]	**1a**:**2a**:**3a**	Yield [%]	ee [%]
1	1:2:2	51	68
2	1:2:3	46	54
3	1:3:2	53	50
4	1:3:3	90	84
5	1:4:4	92	99

[a] The reaction was run with Rh_2Piv_4 (0.75 mol%), $Sm(OTf)_3$/**L_4-PrPr$_2$** (1:1.2, 10 mol%), unsaturated ketoester **1** (0.10 mmol), aldehyde **2a** and α-diazo ester **3a** at –78 °C in DCM (2 mL) for 10 h under an N_2 atmosphere. Yield was the isolated yield of major diastereomer, ee value was determined by HPLC analysis on a chiral stationary phase.

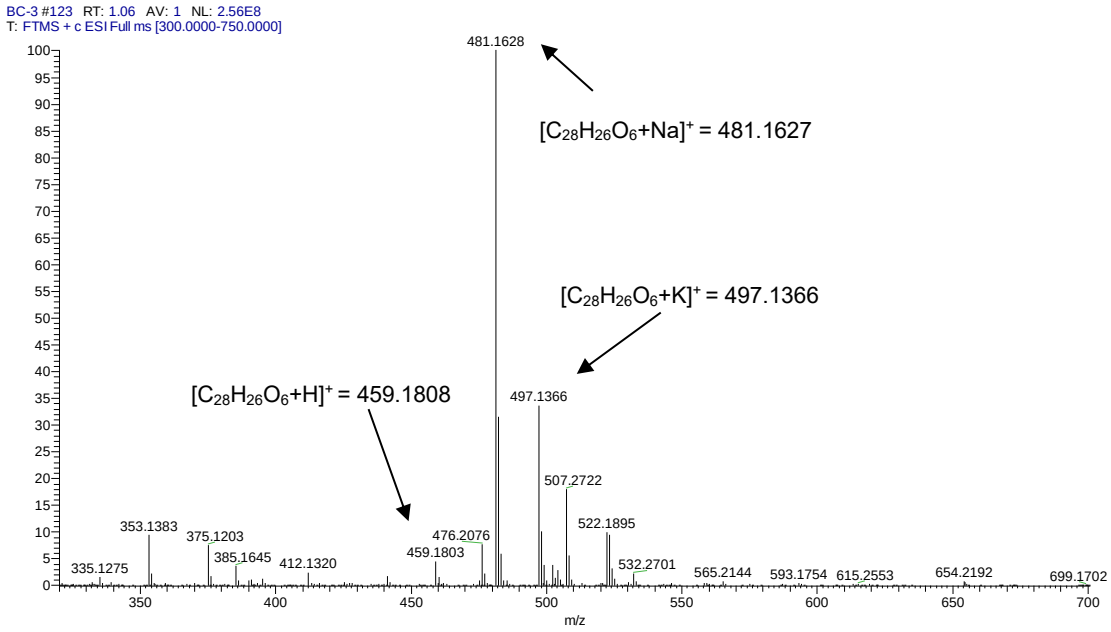
5. Determination of the By-products

Four by-products were found in the reaction system. Three of them are supposed to be regio- or stereo-isomers of major product **4a** according to 2D NMR spectra. Probable structures of them are shown below.

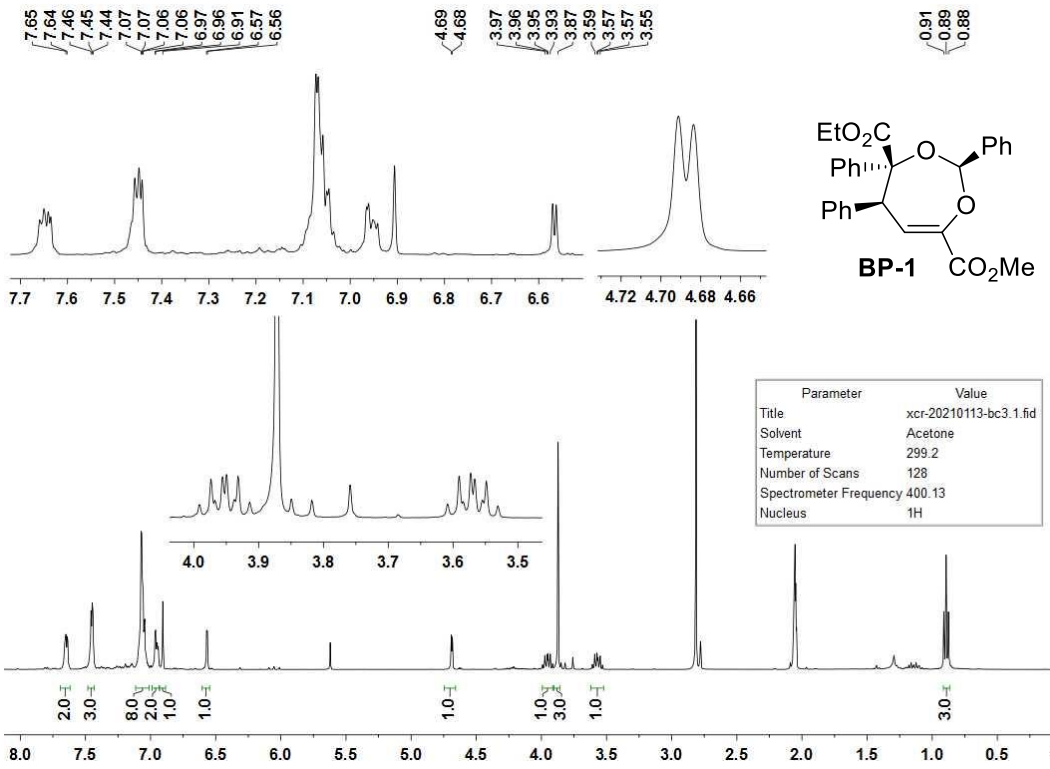


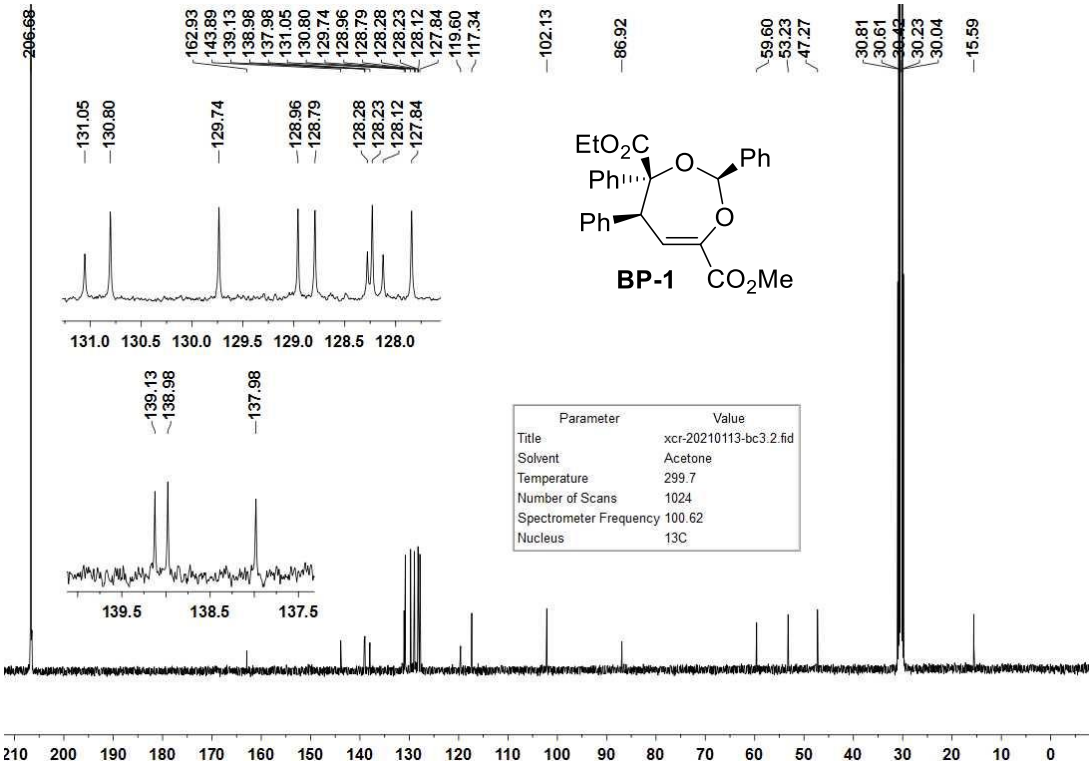


BP-1 was supposed to be a diastereo-isomer of product **4a**. It was determined to be a three component product by HRMS. All of the three molecule weights of the product $+H^+$, $+Na^+$ and $+K^+$ could be found. And the NMR spectrum was shown below.

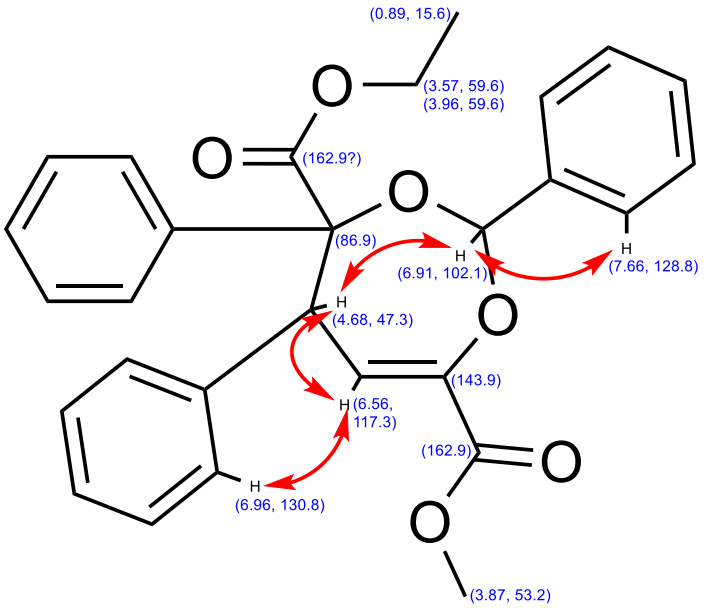


NMR spectrum of **BP-1** in acetone-d_6





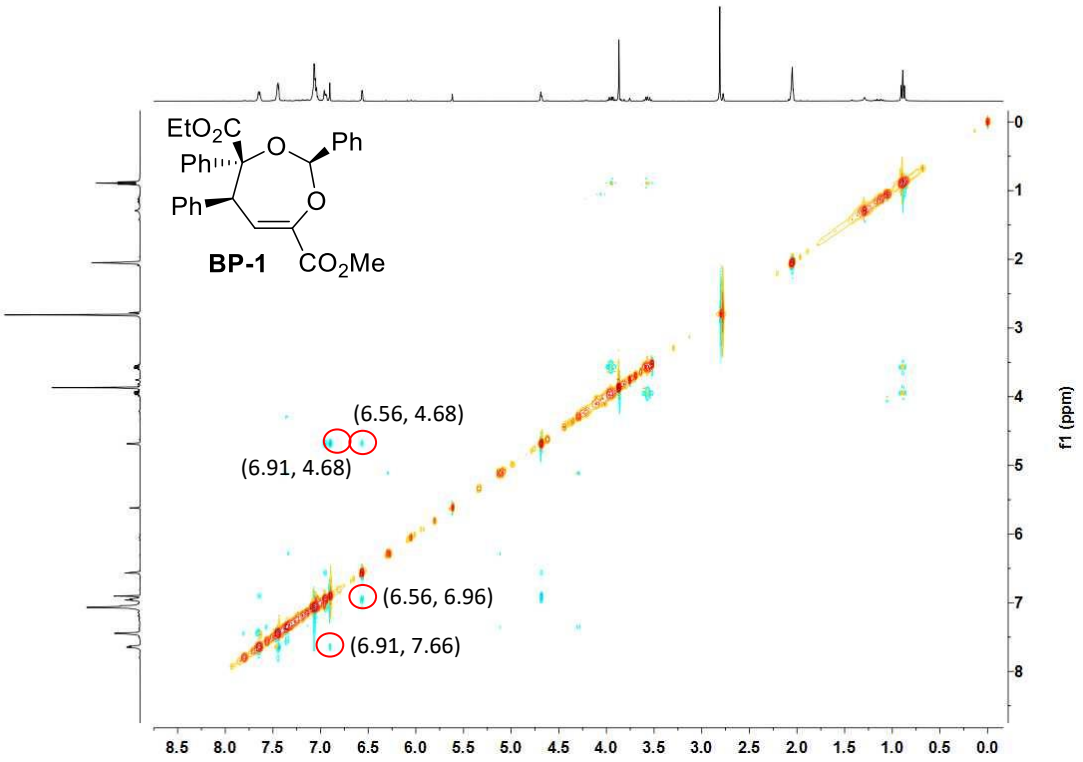
2D **NMR** spectra of **BP-1**:

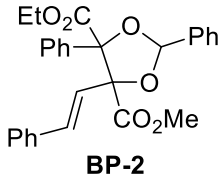


HSQC-Correlation Peak: (0.89, 15.6); (3.57, 59.6); (3.87, 53.2); (3.96, 59.6); (4.68, 47.3); (6.56, 117.3); (6.91, 102.1); (6.96, 130.8); (7.66, 128.8).

HMBC-Correlation Peak: (0.89, 59.6); (3.57, 162.9); (3.87, 162.9); (3.96, 162.9); (4.68, 86.9); (4.68, 117.3); (4.68, 130.8); (4.68, 139.1); (4.68, 143.9); (6.58, 86.9); (6.58, 143.9); (6.58, 162.9); (6.91, 128.8).

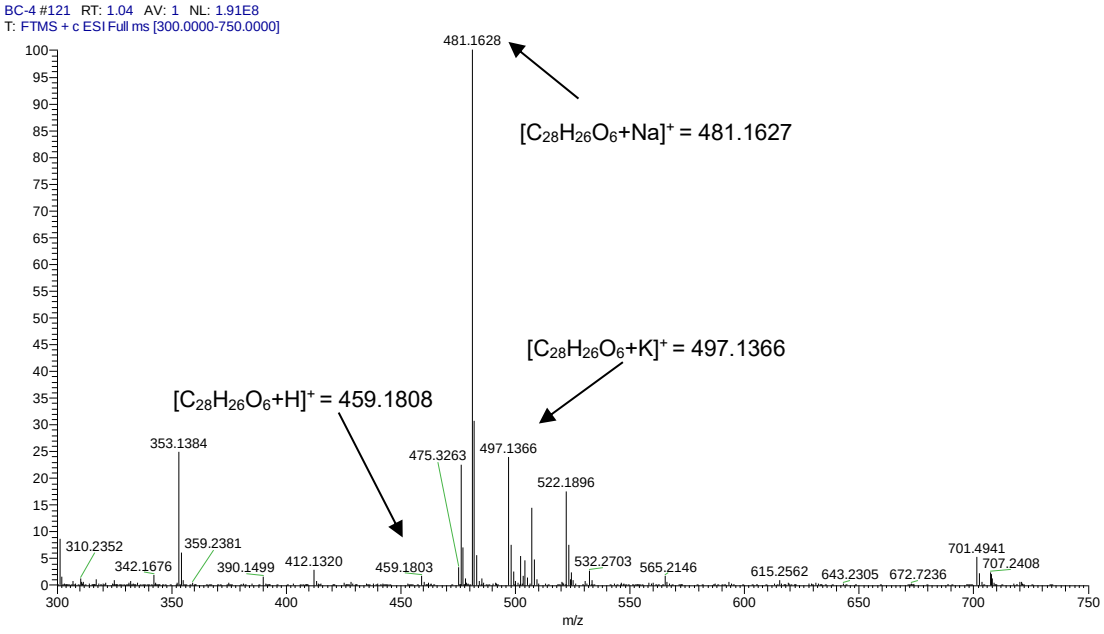
NOESY sprctrum:



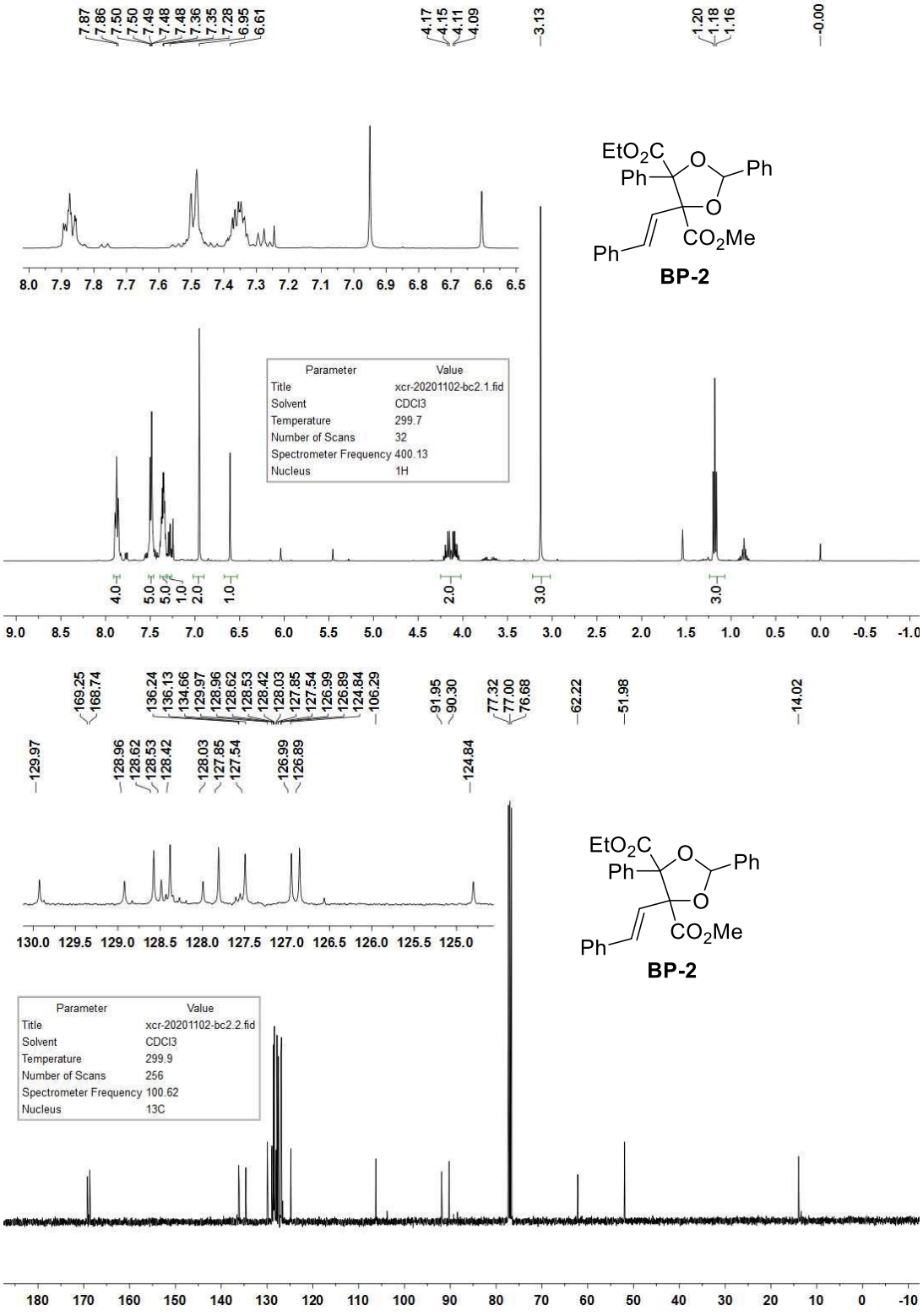


BP-2

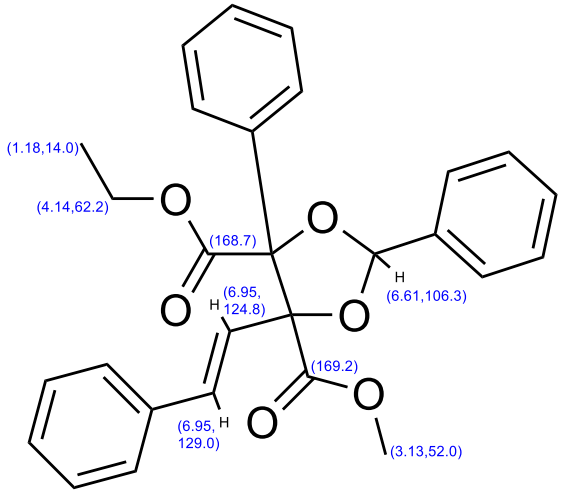
BP-2 was supposed to be a regio-isomer of product **4a**. It was determined to be a three component product by HRMS. All of the three molecule weights of the product $+H^+$, $+Na^+$ and $+K^+$ could be found. And the NMR spectrum was shown below.



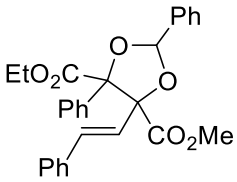
NMR spectrum of **BP-2** in chloroform-*d*



2D **NMR** spectra of **BP-2**:

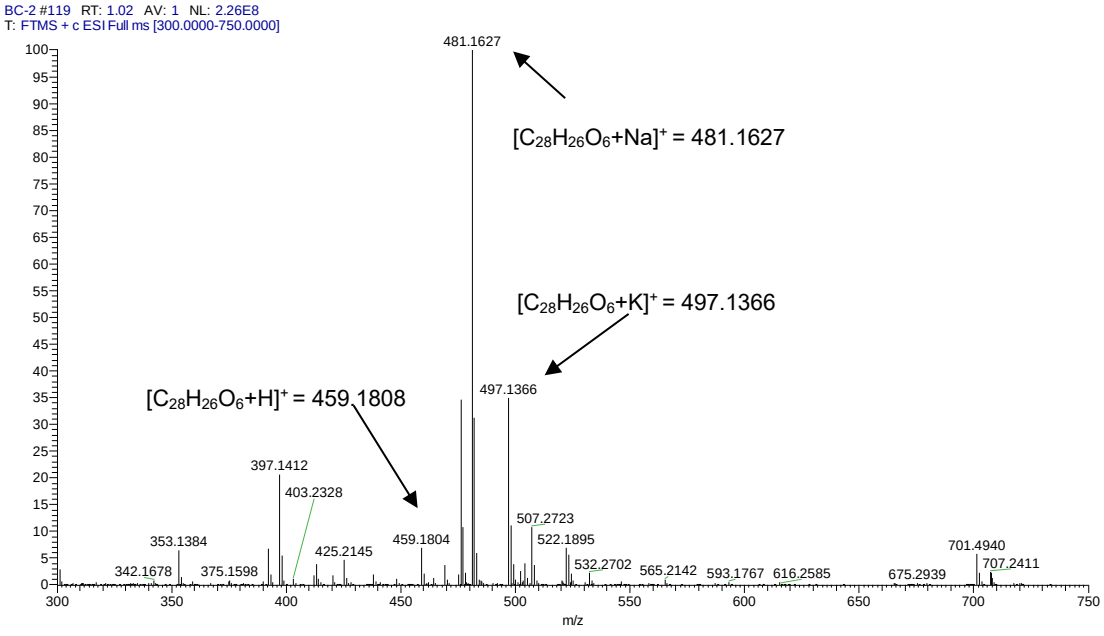


HSQC-Correlation Peak: (1.18, 14.0); (3.13, 52.0); (4.14, 82.2); (6.61, 106.3); (6.95, 124.8); (6.95, 129.0).

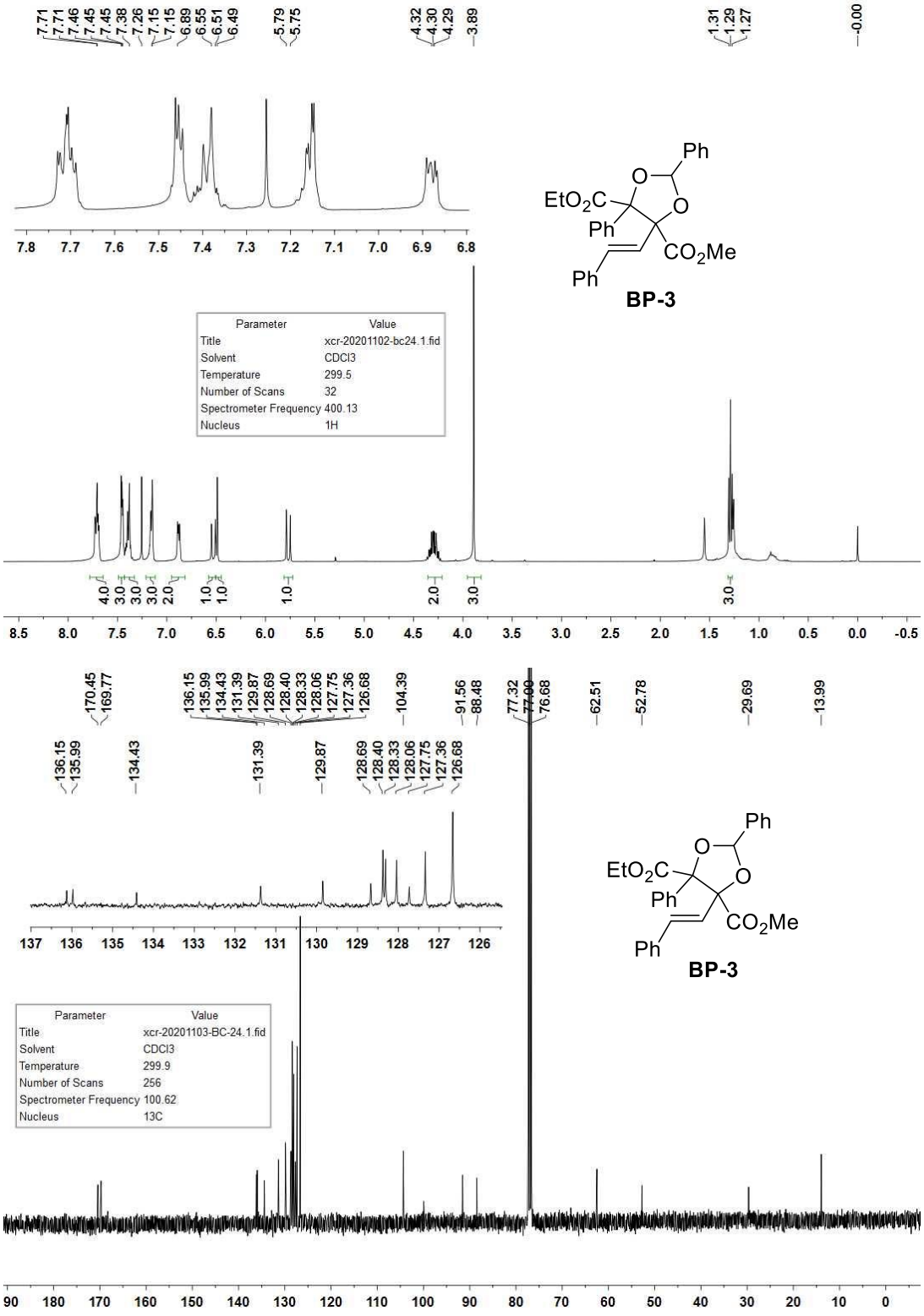


BP-3

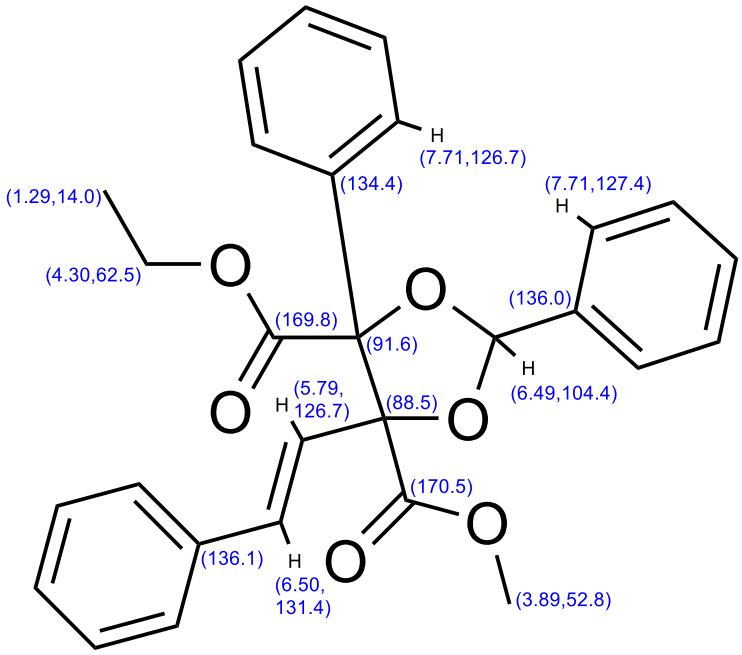
BP-3 was supposed to be a diastereo-isomer of byproduct **BP-2**. It was determined to be a three component product by HRMS. All of the three molecule weights of the product $+H^+$, $+Na^+$ and $+K^+$ could be found. And the NMR spectrum was shown below.



NMR spectrum of **BP-3** in chloroform-*d*



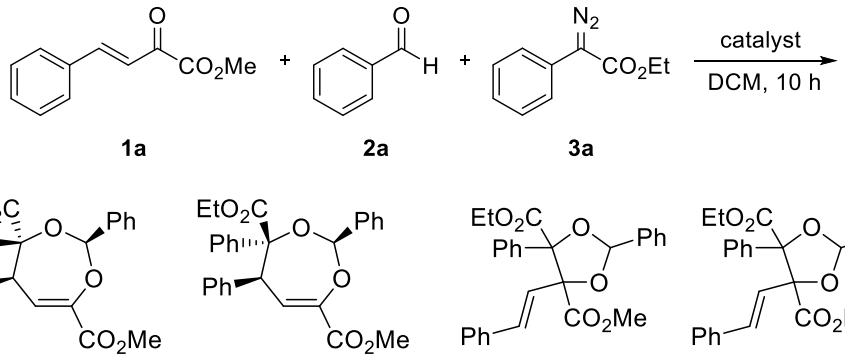
2D **NMR** spectra of **BP-3**:



HSQC-Correlation Peak: (1.29, 14.0); (3.89, 52.8); (4.30, 62.5); (5.79, 126.7); (6.49, 104.4); (6.50, 131.4); (7.71, 126.7); (7.71, 127.4).
HMBC-Correlation Peak: (1.29, 62.5); (3.89, 170.5); (4.30, 14.0); (4.30, 169.8); (5.79, 88.5); (5.79, 136.1); (6.49, 136.0); (6.49, 127.4); (6.50, 88.5); (6.50, 126.7); (7.71, 91.4); (7.71, 104.4).

6. Control experiments and Operando IR Experiments

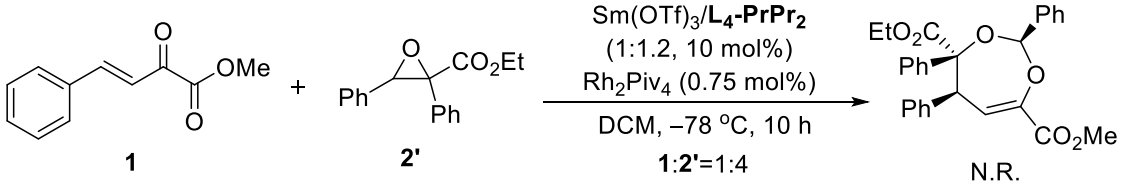
Table S6:



Entry[a]	Catalyst	T (°C)	**1a:2a:3a**	**4a** [%]	**BP-1** [%]	**BP-2** [%]	**BP-3** [%]
1	Rh_2Piv_4 (0.75 mol%)+Yb(OTf)$_3$/**L$_4$-PrPr$_2$** (10 mol%)	–20	1:3:3	64	18	7	0
2	Rh_2Piv_4 (0.75 mol%)+Yb(OTf)$_3$/**L$_4$-PrPr$_2$** (10 mol%)	–78	1:3:3	90	0	<5	0
3	Rh_2Piv_4 (0.75 mol%)+Sm(OTf)$_3$/**L$_4$-PrPr$_2$** (10 mol%)	–78	1:3:3	91	0	<5	0
4	Rh_2Piv_4 (0.75 mol%)+Sm(OTf)$_3$/**L$_4$-PrPr$_2$** (10 mol%)	–78	1:4:4	96	0	0	0
5	Rh_2Piv_4 (0.75 mol%)+Sm(OTf)$_3$/**L$_3$-PrPr$_2$** (10 mol%)	–78	1:4:4	48	10	17	11
6	Rh_2Piv_4 (0.75 mol%)+Sm(OTf)$_3$/**L$_5$-PrPr$_2$** (10 mol%)	–78	1:4:4	97	0	0	0
7	D-(+)-CSA (10 mol%)	–78	1:4:4	0	0	0	0
8	Rh_2Piv_4 (0.75 mol%)	–78	1:4:4	13	9	26	18
9	Rh_2(S-DOSP)$_4$ (0.75 mol%)	–78	1:4:4	<5	<5	36	18
10	Rh_2(*S*-DOSP)$_4$ (0.75 mol%)+Sm(OTf)$_3$/*rac*-**L$_4$-PrPr$_2$** (10 mol%)	–78	1:4:4	95	0	0	0

[a] The reaction was run with catalyst, unsaturated ketoester **1** (0.10 mmol), aldehyde **2a** and α-diazo ester **3a** at −78 °C in DCM (2 mL) for 10 h under an N_2 atmosphere. Yield detected by NMR. CSA = camphorsulfonic acid.

The reaction gives about 3.5:1 dr value and a little regioselective product at −20 °C (entry 1). Turning down the temperature to −78 °C, the better diastereo- and regioselectivity were given (entry 2). Changing the metal salt from $Yb(OTf)_3$ to $Sm(OTf)_3$ did not influence the selectivity significantly except ee value (entry 3). The addition of 0.4 mmol **2a** and **3a** promoted the yield of **4a** slightly (entry 4). *N*,*N'*-dioxide ligand with three-carbon linker gave a complex of the products (entry 5), but five-carbon linker one (entry 6) gave a similar result with entry 4. Without the Rh_2Piv_4, the three components did not react at all, even if camphor sulfonic acid (CSA) capable of carbene generation from diazo compounds in previous report was used (entry 7). Using only Rh(II) as catalyst did not give any selectivity (entry 8). Using Rh_2(S-DOSP)$_4$ without Sm/*N*,*N'*-dioxide ligand gave a complex reaction mixture with trace yield of **4a**, which chould not detected the ee value (entry 8). The use of chiral Rh_2(S-DOSP)$_4$ with Sm/*rac*-*N*,*N'*-dioxide ligand gave rise to racemic product in 95% yield (entry 9).



$Sm(OTf)_3$ (6.0 mg, 0.01 mmol, 10 mol%), **L_4-PrPr$_2$** (7.6 mg, 0.012 mmol, 12 mol%) and Rh_2Piv_4 (0.45 mg, 0.75 μmol, 0.75 mol%) were stirred in 1.0 mL DCM at 35 °C for 0.5 h under an N_2 atmosphere. Then epoxide **2'** (107.2 mg, 0.40 mmol) was stirred at −20 °C for 20 min. Next, β,γ-unsaturated α-ketoester **1** (0.10 mmol) dissolved in DCM (1.0 mL) was added at −78 °C. The mixture was stirred at −78 °C for further 10 h.

No reaction occurred, and most of the β,γ-unsaturated α-ketoester **1** and epoxide **8** were recovered. These results indicated that the reaction does not proceed through the formation of epoxide **8** from 2-diazo-2-arylacetates and aldehydes. Therefore, the carbonyl ylide was supposed to be the real reactive intermediate.

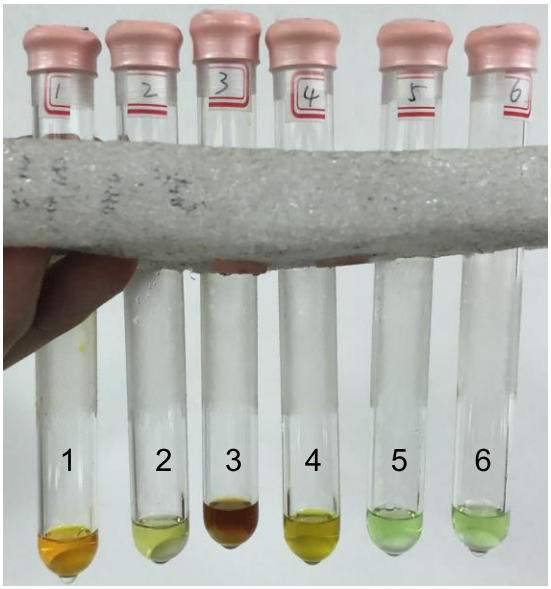


Figure S1. With different catalysts, **2a** and **3a** stirred with catalyst at −20 °C after 20 min. **1)** D(+)-CSA (10 mol%); **2)** Rh_2Piv_4 (0.75 mol%); **3)** Rh_2Piv_4 (0.75 mol%)+$Sm(OTf)_3$ (10 mol%); **4)** Rh_2Piv_4 (0.75 mol%)+**L_4-PrPr$_2$** (10 mol%); **5)** Rh_2Piv_4 (0.75 mol%)+$Sm(OTf)_3$/**L_4-PrPr$_2$** (10 mol%); **6)** Rh_2Piv_4 (0.75 mol%)+$Sm(OTf)_3$/**L_3-PrPr$_2$** (10 mol%)

After stirring the mixture of **2a** and **3a** with catalyst in DCM at −20 °C after 20 min, the difference in color indicated the effect of Sm(III) complex in carbonyl ylide formation and possible interaction of ylide with Sm(III) complex.

A control experiment was also carried out under monitoring by operando IR (Figure S2). A solution of **3a** in DCM was added to a solution of **2a**, $Sm(OTf)_3$/**L_4-PrPr$_2$** and Rh_2Piv_4 in DCM. The peaks at 1170 cm^{-1} are related to the corresponding substrate **3a** (Figure S2a)**.** At the early stage of reaction, the amount of **3a** decreased rapidly. With the consumption of **3a**, the amount of ylide **B** at 1727 cm^{-1} increased quickly (Figure S2b). After the depletion of **3a**, all of the diazo compound was transferred to **B** under the effect of Rh^{2+}. Without the appearance of **1a**, the 1,3-dipole intermediate **B** was stable temporarily in the mixture (Figure S2c).

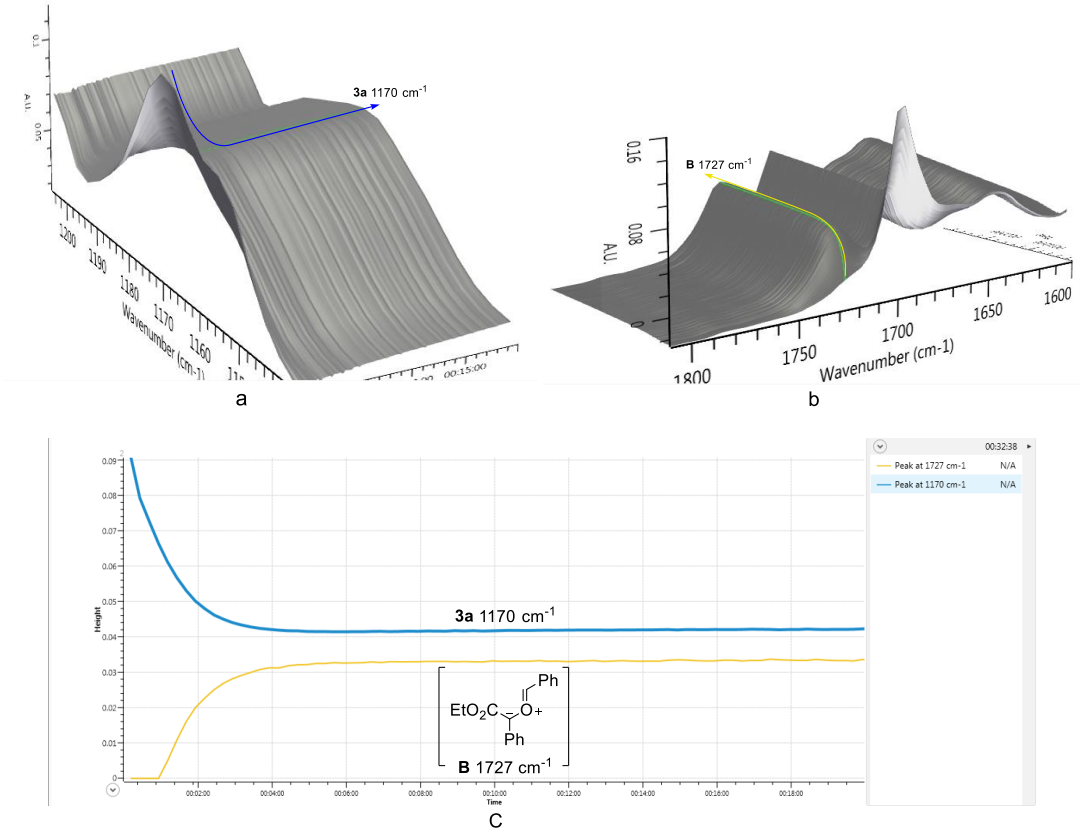


Figure S2. a, b) The operando IR experiment of substrate **3a** and Intermediate **B**. c) The trend of each component (X axes: reaction time; Y axes: absorbance unit). **3a**: peak at 1170 cm^{-1}; **B**: peak at 1727 cm^{-1}

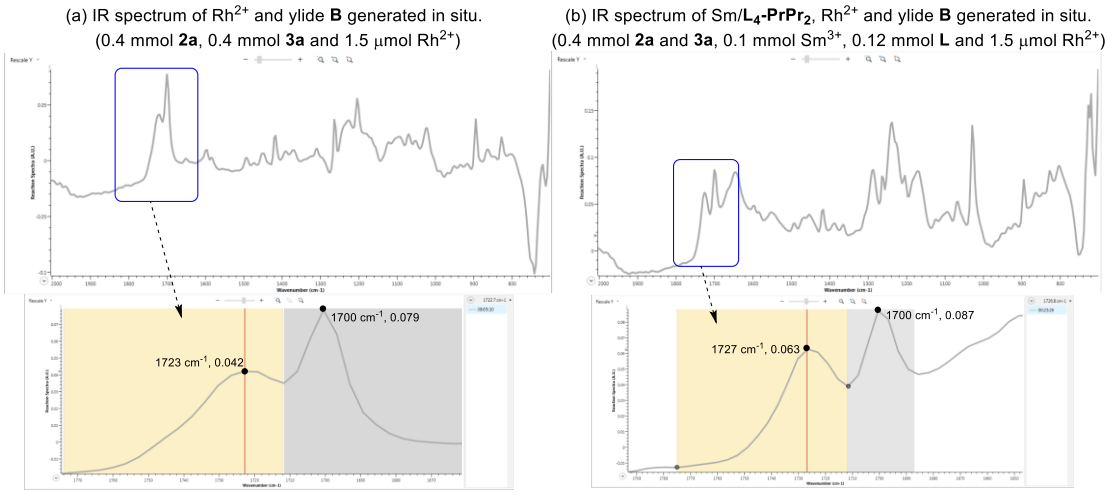
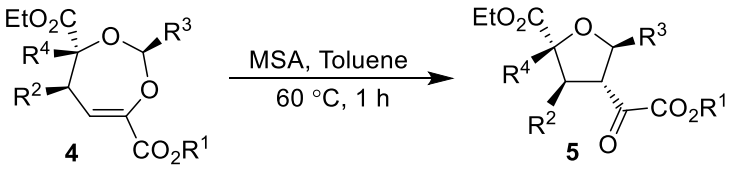


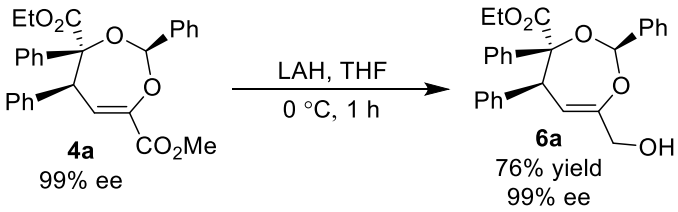
Figure S3. IR sepctra of Rh^{2+} and ylide **B** generated in situ with or without $Sm(OTf)_3$/**L_4-PrPr$_2$**.

The IR spectra of ylide **B** generated in situ also show that **B** has a peak of carbonyl group stretching vibration at 1723 cm^{-1} (Figure S3a), according to figure S2b. But it slightly move to 1727 cm^{-1} in the performance of Sm(III) complex with an obvious intensity change (Figure 3b), which indicated a possible interaction of ylide **B** with the Sm(III) complex.

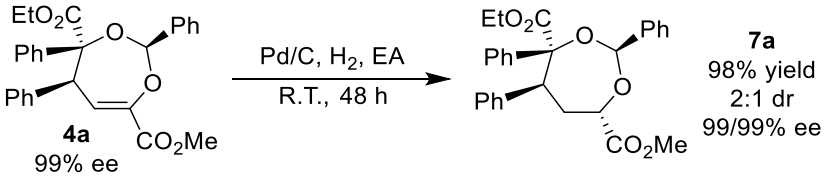
7. Transformations of the Product



Synthesis of **5**: To a solution of **4** (0.1 mmol) in toluene (1.0 mL) was added methanesulfonic acid (0.2 mmol) dissolved in toluene (1 mL) at 60 °C, the solution was stirred at 60 °C for 1 h. After the reaction was completed, 2.0 mL saturated $NaHCO_3$ solution was added. Then, the mixture was extract by DCM, and the aqueous layer was washed with DCM (2 x 2.0 mL). The combined organic phases was washed with brine (5.0 mL), and dried over Na_2SO_4. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with PE/EA = 4:1 to afford product **5** as colourless oil or white solid.



Synthesis of **6a**: To a solution of **4a** (0.1 mmol, 45.8 mg) in THF (1.0 mL) was added $LiAlH_4$ (8.4 mg, 0.22 mmol) at 0 °C, the solution was stirred at 0 °C for 1 h. After the reaction was completed, 10% aqueous solution of NaOH was added. Then, the mixture was extract by EtOAc, and the aqueous layer was washed with EtOAc (2 x 2.0 mL). The combined organic phases was washed with brine (5.0 mL), and dried over Na_2SO_4. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with PE/EA = 4:1. The product **6a** was obtained in 76% yield as a white solid with 99% ee.

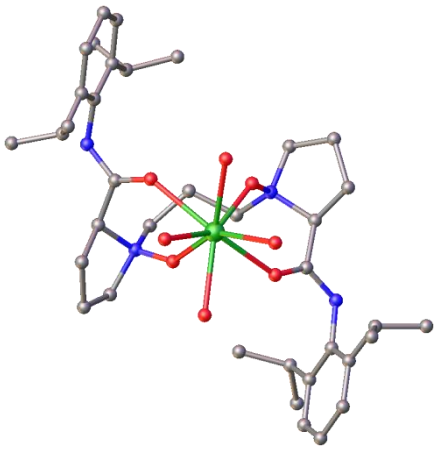


Synthesis of **7a**: To a solution of **4a** (0.1 mmol, 45.8 mg) in EtOAc (2.0 mL) was added 10% palladium on carbon (10.6 mg, 0.01 mmol) at room temperature. The atmosphere above the reaction was replaced with hydrogen gas and the reaction was charged with a H_2 balloon. The solution was stirred at R.T. for 48 h. When the reaction was completed, the reaction mixture was filtered and the filter cake was washed with EtOAc. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with PE/EA = 4:1 to afford product **7a** as a white solid. The product **7a** was obtained in 98% yield with 2:1 dr value and 99/99% ee.

8. Crystal Data of Catalysts and Products

(a) L_3-$PrPr_2$ /$Sm(OTf)_3$:

The structure of the catalyst [**(*S*)-L_3-$PrPr_2$/$Sm(OTf)_3$**] was determined by X-ray chromatography analysis (thermal ellipsoids are shown with a 50% probability level). Single crystals of the catalyst was obtained by slow evaporation at r.t. in Et_2O/EtOH at 25 °C. CCDC 2053510 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.



Crystallographic Data for $C_{44}H_{68}F_9N_4O_{15}S_3Sm$.

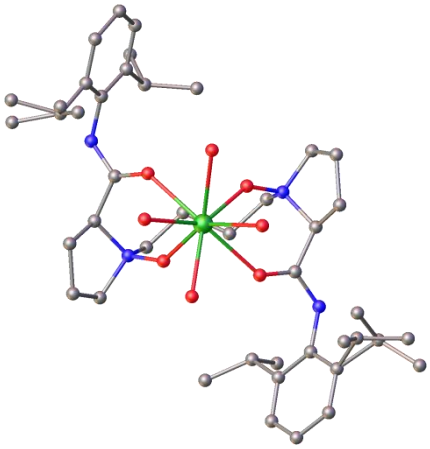
Formula	$C_{88}H_{136}F_{18}N_8O_{30}S_6Sm_2$
Formula mass (amu)	2621.10
Space group	P21
a (Å)	13.6883(9)
b (Å)	20.9229(13)
c (Å)	21.4877(13)
α (deg)	90
β (deg)	103.980(2)
γ (deg)	90
V (Å^3)	5971.8(7)
Z	2
λ (Å)	0.71073
T (K)	148
ρ_{calcd} (g cm^{-3})	1.458
μ (mm^{-1})	1.177
Transmission factors	0.697, 0.888
$2\theta_{max}$ (deg)	25.248
No. of unique data, including $F_o^2 < 0$	21553
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	20675
No. of variables	1461
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0197
$R_w(F_o^2)$ [b]	0.0495
Goodness of fit	1.043

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

(b) L_4-$PrPr_2$ /$Sm(OTf)_3$:

The structure of the catalyst [**(*S*)-L_4-$PrPr_2$/$Sm(OTf)_3$**] was determined by X-ray chromatography analysis (thermal ellipsoids are shown with a 50% probability level). Single crystals of the catalyst was obtained by slow evaporation at r.t. in Et_2O/EtOH at 25 °C. CCDC 2025197 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.



Crystallographic Data for $C_{45}H_{70}F_9N_4O_{15}S_3Sm$.

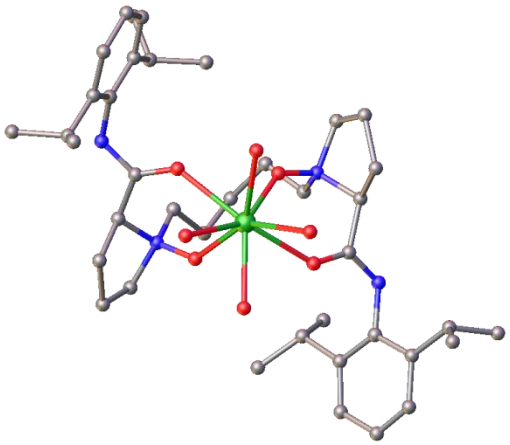
Formula	$C_{45}H_{70}F_9N_4O_{15}S_3Sm$
Formula mass (amu)	1324.58
Space group	P21
a (Å)	10.8034(9)
b (Å)	13.3417(9)
c (Å)	21.6804(17)
α (deg)	90
β (deg)	91.981(3)
γ (deg)	90
V (Å^3)	3123.1(4)
Z	2
λ (Å)	0.71073
T (K)	142
ρ_{calcd} (g cm^{-3})	1.409
μ (mm^{-1})	1.126
Transmission factors	0.786, 0.924
$2\theta_{max}$ (deg)	30.162
No. of unique data, including $F_o^2 < 0$	9586
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	9066
No. of variables	735
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0414
$R_w(F_o^2)$ [b]	0.0975
Goodness of fit	1.056

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

(c) L_5-$PrPr_2$ /$Sm(OTf)_3$:

The structure of the catalyst [**(*S*)-L_5-$PrPr_2$/$Sm(OTf)_3$**] was determined by X-ray chromatography analysis (thermal ellipsoids are shown with a 50% probability level). Single crystals of the catalyst was obtained by slow evaporation at r.t. in THF/^{i}PrOH at 25 °C. CCDC 2055726 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

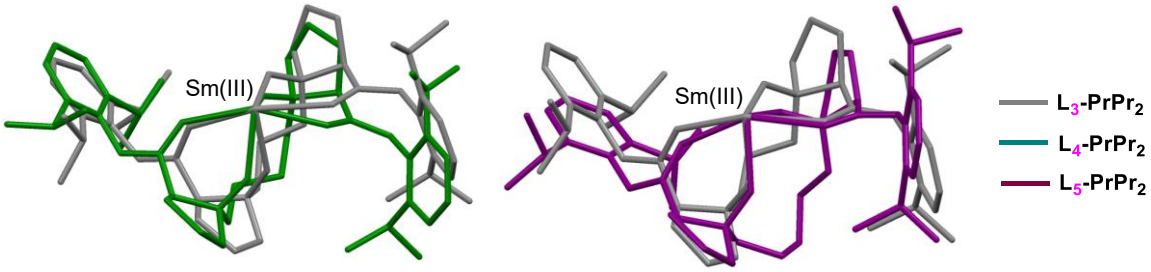


Crystallographic Data for $C_{45}H_{70}F_9N_4O_{15}S_3Sm$.

Formula	$C_{96}H_{152}F_{18}N_8O_{30}S_6Sm_2$
Formula mass (amu)	2733.31
Space group	P21
a (Å)	11.2756(3)
b (Å)	18.6968(5)
c (Å)	36.0442(9)
α (deg)	90
β (deg)	91.416(2)
γ (deg)	90
V (Å^3)	7596.4(3)
Z	2
λ (Å)	1.54178
T (K)	151
ρ_{calcd} (g cm^{-3})	1.195
μ (mm^{-1})	7.214
Transmission factors	0.203, 0.541
$2\theta_{max}$ (deg)	66.250
No. of unique data, including $F_o^2 < 0$	25054
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	23587
No. of variables	1472
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0579
$R_w(F_o^2)$ [b]	0.1531
Goodness of fit	1.045

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.



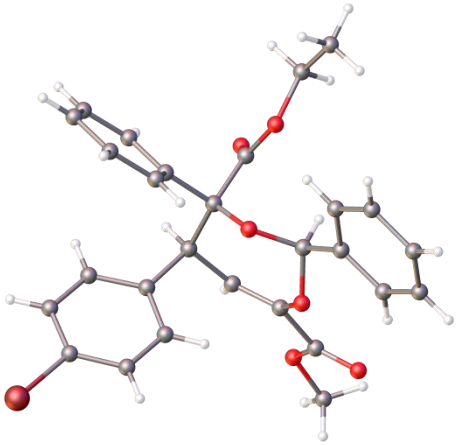
Sm(III)/*N*,*N*′-dioxide complexes with different linker length created slightly different chiral pockets. Further studies are needed to illustrate the effect of catalyst structure on regio-, diastereo- and enantioselectivity.

Comparison of geometry of the three crystals:

Crystal	Angles between O^C-Sm-O^C	Angles between O^N-Sm-O^N	Bond distance of O^C-Sm	Bond distance of O^N-Sm
L_3-PrPr$_2$/Sm	140.659°	88.611°	2.428 and 2.433 Å	2.297 and 2.299 Å
L_4-PrPr$_2$/Sm	138.540°	94.409°	2.393 and 2.423 Å	2.266 and 2.286 Å
L_5-PrPr$_2$/Sm	142.531°	90.500°	2.404 and 2.423 Å	2.284 and 2.316 Å

(d) Product 4m:

The absolute configuration of product **4m** was determined to be (2*S*, 4*S*, 5*S*) by X-ray chromatography analysis (thermal ellipsoids are shown with a 50% probability level). Single crystals of **4m** [$C_{28}H_{25}BrO_6$] was obtained by recrystallization in hexane/CH_2Cl_2 at 25 °C. CCDC 2015654 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.



Crystallographic Data for $C_{28}H_{25}BrO_6$.

Formula	$C_{28}H_{25}BrO_6$
Formula mass (amu)	537.39
Space group	P212121
a (Å)	9.6194(5)
b (Å)	15.9110(9)
c (Å)	16.4920(9)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2524.2(2)
Z	4
λ (Å)	0.71073

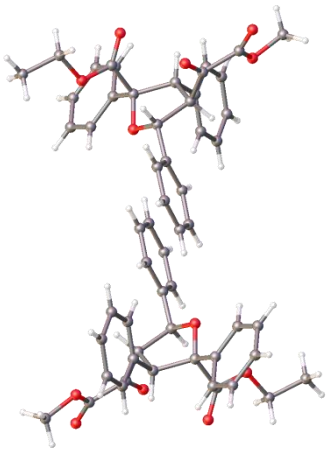
T (K)	170
ρ_{calcd} (g cm^{-3})	1.414
μ (mm^{-1})	1.669
Transmission factors	0.512, 0.712
$2\theta_{max}$ (deg)	33.138
No. of unique data, including $F_o^2 < 0$	9563
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	8101
No. of variables	318
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0318
$R_w(F_o^2)$ [b]	0.0741
Goodness of fit	1.076

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

(e) Racemic 5a:

The relative configuration of racemic **5a** was determined by X-ray chromatography analysis (thermal ellipsoids are shown with a 50% probability level). And the absolute configuration of product **5a** was determined to be (2*S*, 3*S*, 4*R*, 5*R*) by absolute configuration of **4a** and relative configuration of racemic **5a**. Single crystals of **5a** [$C_{28}H_{26}O_6$] was obtained by recrystallization in hexane/CH_2Cl_2 at 25 °C. CCDC 2046337 contains the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.



Crystallographic Data for $C_{28}H_{26}O_6$.

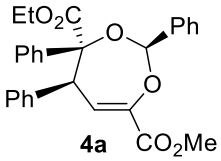
Formula	$C_{28}H_{26}O_6$
Formula mass (amu)	458.49
Space group	R -3:H
a (Å)	34.7546(9)
b (Å)	34.7546(9)
c (Å)	9.9252(4)
α (deg)	90
β (deg)	90
γ (deg)	120

V (Å^3)	10382.3(7)
Z	18
λ (Å)	1.54178
T (K)	148
ρ_{calcd} (g cm^{-3})	1.320
μ (mm^{-1})	0.756
Transmission factors	0.851, 0.966
$2\theta_{max}$ (deg)	68.276
No. of unique data, including $F_o^2 < 0$	4173
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	3758
No. of variables	309
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0365
$R_w(F_o^2)$ [b]	0.0832
Goodness of fit	1.058

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

9. Spectral Characterization Data for the Products



4a

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2,4,5-triphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1a**) scale reaction:

Result: white solid, M.P. 177-181°C, 92% yield (42.1 mg), 99% ee, >19:1 dr; $[\alpha]^{28}_D$ = –352.5 (*c* 0.76, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 9.99 min, $t_{R(minor)}$ = 6.31 min);

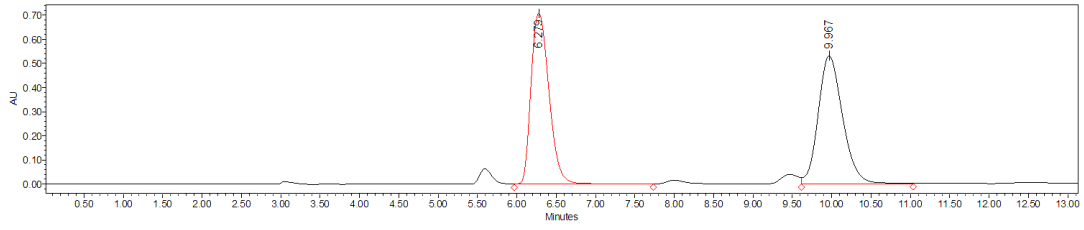
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.81 (m, 2H), 7.46 (m, 3H), 7.28 (m, 2H), 7.21 – 7.16 (m, 2H), 7.16 – 7.06 (m, 3H), 6.97 (m, 4H), 6.02 (s, 1H), 4.60 (d, *J*=8.8 Hz, 1H), 4.26 (m, 2H), 3.79 (s, 3H), 1.15 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.4, 164.0, 146.6, 138.5, 137.9, 137.5, 130.0, 128.9, 128.2, 127.9, 127.8, 127.6, 126.9, 126.6, 125.0, 124.1, 102.0, 86.9, 62.2, 52.9, 52.4, 13.9;

ESI-HRMS calcd for [$C_{28}H_{26}O_6$+Na$^+$]: 481.1627, found 481.1623;

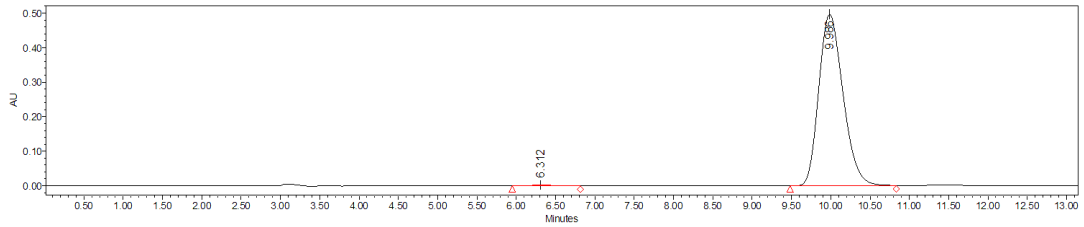
IR (film): $\tilde{\nu}$ (cm^{-1}) 2951, 1727, 1655, 1494, 1446, 1370, 1331, 1260, 1232, 1126, 1062, 1024, 970, 942, 893, 813, 769, 746, 697, 619, 559.

Racemic **4a**:

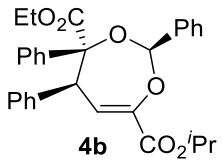


	Retention Time	Area	% Area
1	6.279	11227780	49.59
2	9.967	11412168	50.41

Chiral **4a**:



	Retention Time	Area	% Area
1	6.312	54645	0.51
2	9.986	10670947	99.49



4b

4-Ethyl 7-isopropyl (2*S*,4*S*,5*S*)-2,4,5-triphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1b**) scale reaction:

Result: colourless oil, 88% yield (42.7 mg), 85% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –309.4 (*c* 0.85, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 9.20 min, $t_{R(minor)}$ = 6.76 min);

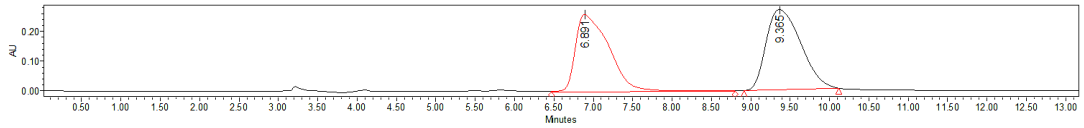
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.85 (m, 2H), 7.49 – 7.38 (m, 3H), 7.28 (m, 2H), 7.22 – 7.16 (m, 2H), 7.16 – 7.06 (m, 3H), 7.03 – 6.94 (m, 3H), 6.91 (d, *J*=8.8 Hz, 1H), 6.01 (s, 1H), 5.17 – 4.99 (m, 1H), 4.59 (d, *J*=8.8 Hz, 1H), 4.23 (m, 2H), 1.31 (dd, *J*=9.6, 6.4 Hz, 6H), 1.14 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.5, 163.1, 147.1, 138.6, 138.1, 137.6, 130.1, 128.8, 128.2, 127.9, 127.7, 127.5, 126.9, 126.7, 125.0, 123.6, 101.9, 86.9, 69.3, 62.2, 52.8, 21.9, 21.8, 13.9;

ESI-HRMS calcd for [$C_{30}H_{30}O_6$+Na^+]: 509.1940, found 509.1939;

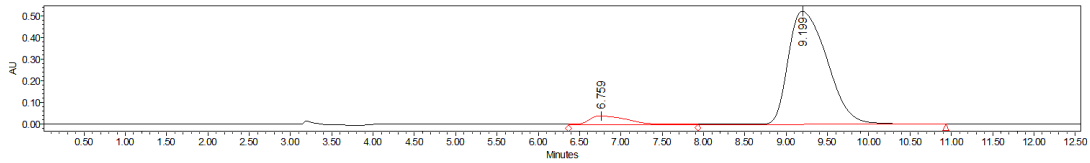
IR (film): $\tilde{\nu}$ (cm^{-1}) 3063, 2980, 1723, 1655, 1600, 1494, 1450, 1373, 1326, 1258, 1231, 1182, 1130, 1104, 1057, 1021, 914, 891, 840, 770, 745, 696, 620, 559, 520.

Racemic **4b**:

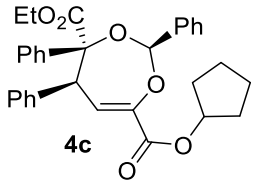


	Retention Time	Area	% Area
1	6.891	7765096	48.54
2	9.365	8231553	51.46

Chiral **4b**:



	Retention Time	Area	% Area
1	6.759	1380234	7.50
2	9.199	17025684	92.50



7-Cyclopentyl 4-ethyl (2*S*,4*S*,5*S*)-2,4,5-triphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1c**) scale reaction:

Result: colourless oil, 84% yield (43.0 mg), 94% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –323.6 (*c* 0.82, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 7.10 min, $t_{R(minor)}$ = 5.67 min);

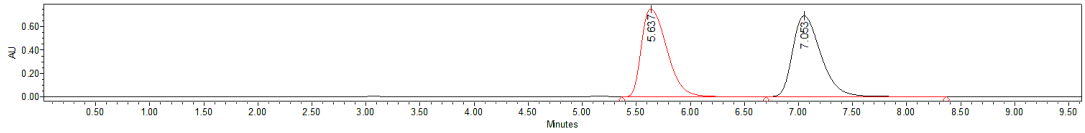
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (m, 2H), 7.45 (m, 3H), 7.29 (m, 2H), 7.22 – 7.16 (m, 2H), 7.16 – 7.08 (m, 3H), 6.98 (m, 3H), 6.89 (d, *J*=8.8 Hz, 1H), 6.00 (s, 1H), 5.25 (m, 1H), 4.58 (d, *J*=8.8 Hz, 1H), 4.23 (m, 2H), 2.00 – 1.85 (m, 2H), 1.85 – 1.71 (m, 4H), 1.61 (m, 2H), 1.14 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.5, 163.4, 147.2, 138.6, 138.1, 137.6, 130.1, 128.8, 128.2, 127.9, 127.7, 127.5, 126.9, 126.7, 125.0 , 123.5, 101.9, 86.9, 78.5 , 62.2, 52.8, 32.7, 32.6, 23.7, 23.7, 13.9;

ESI-HRMS calcd for [$C_{32}H_{32}O_6$+Na^+]: 535.2097, found 535.2094;

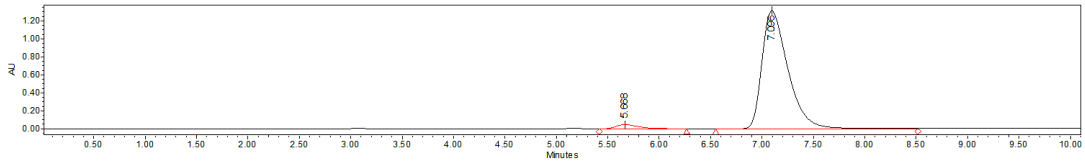
IR (film): $\tilde{\nu}$ (cm^{-1}) 3063, 2966, 1723, 1655, 1600, 1494, 1449, 1374, 1327, 1257, 1231, 1127, 1059, 1023, 961, 892, 843, 769, 745, 697, 620, 555, 514.

Racemic **4c**:

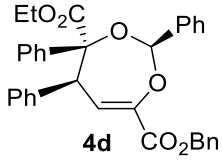


	Retention Time	Area	% Area
1	5.637	12319722	49.46
2	7.053	12591076	50.54

Chiral **4c**:



	Retention Time	Area	% Area
1	5.668	716918	3.02
2	7.096	22991391	96.98



7-Benzyl 4-ethyl (2*S*,4*S*,5*S*)-2,4,5-triphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1d**) scale reaction:

Result: colourless oil, 72% yield (38.4 mg), 94% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –298.4 (*c* 0.83, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 14.06 min, $t_{R(minor)}$ = 12.21 min);

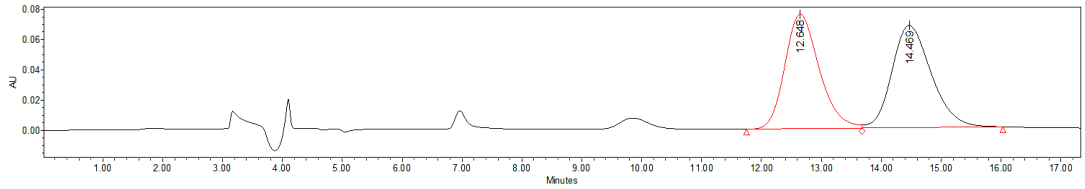
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (m, 2H), 7.48 – 7.32 (m, 8H), 7.31 – 7.27 (m, 2H), 7.20 – 7.16 (m, 2H), 7.15 – 7.08 (m, 3H), 7.01 – 6.93 (m, 4H), 6.02 (s, 1H), 5.22 (s, 2H), 4.59 (d, *J*=8.8 Hz, 1H), 4.22 (m 2H), 1.13 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.4, 163.4, 146.6, 138.5, 137.9, 137.4, 135.5, 130.1, 128.8, 128.5, 128.3, 128.3, 128.2, 127.9, 127.8, 127.6, 126.9, 126.7, 125.0, 124.4, 102.0, 86.9, 67.2, 62.2, 52.9, 13.9;

ESI-HRMS calcd for [$C_{34}H_{30}O_6$+Na^+]: 557.1940, found 557.1945;

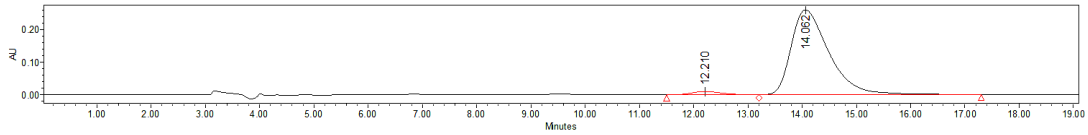
IR (film): $\tilde{\nu}$ (cm^{-1}) 3032, 2981, 1725, 1654, 1601, 1494, 1450, 1383, 1328, 1235, 1125, 1058, 1023, 965, 893, 744, 696, 619, 507.

Racemic **4d**:

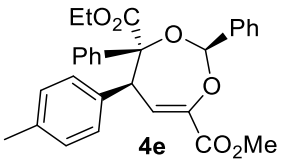


	Retention Time	Area	% Area
1	12.648	3003617	49.45
2	14.469	3070893	50.55

Chiral **4d**:



	Retention Time	Area	% Area
1	12.210	391724	3.02
2	14.062	12560518	96.98



4e

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2,4-diphenyl-5-(p-tolyl)-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1e**) scale reaction:

Result: white solid, M.P. 192-197°C, 87% yield (41.0 mg), 94% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –367.1 (*c* 0.83, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 10.39 min, $t_{R(minor)}$ = 6.66 min);

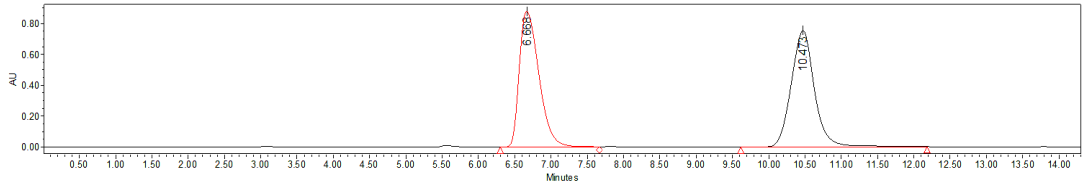
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (m, 2H), 7.46 (m, 3H), 7.30 (m, 2H), 7.10 (m, 5H), 6.94 (d, *J*=8.8 Hz, 1H), 6.78 (d, *J*=8.0 Hz, 2H), 6.00 (s, 1H), 4.58 (d, *J*=8.8 Hz, 1H), 4.22 (m 2H), 3.78 (s, 3H), 2.13 (s, 3H), 1.14 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.4, 164.1, 146.4, 138.6, 138.0, 136.5, 134.3, 129.9, 128.9, 128.5, 128.2, 127.9, 127.5, 126.6, 125.0, 124.4, 102.0, 86.9, 62.2, 52.4, 20.9, 13.9;

ESI-HRMS calcd for $[C_{29}H_{28}O_6+Na^+]$: 495.1784, found 495.1780;

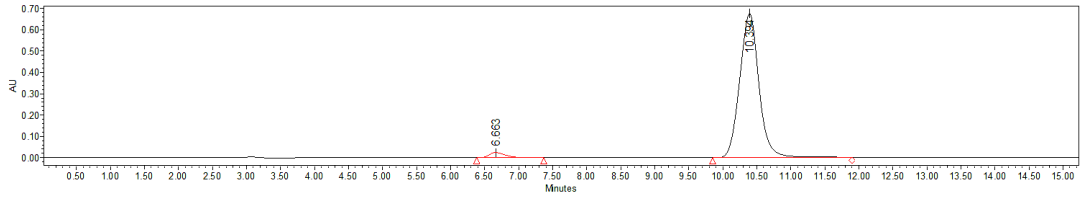
IR (film): $\tilde{\nu}$ (cm^{-1}) 2982, 1727, 1654, 1508, 1444, 1370, 1330, 1250, 1231, 1124, 1063, 1022, 970, 942, 898, 815, 745, 698, 590, 529.

Racemic **4e**:

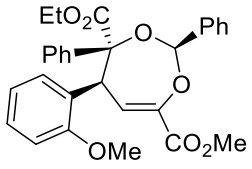


	Retention Time	Area	% Area
1	6.668	16473203	49.72
2	10.473	16658852	50.28

Chiral **4e**:



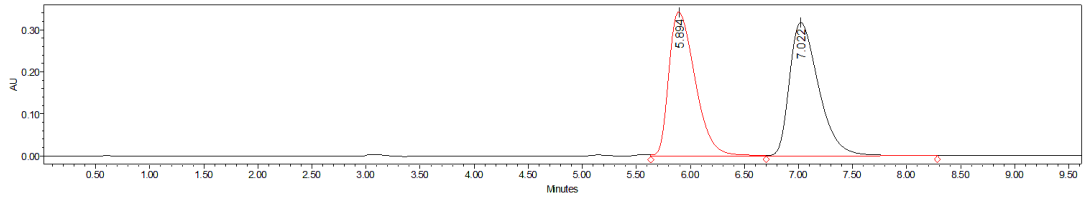
	Retention Time	Area	% Area
1	6.663	399118	2.91
2	10.394	13330793	97.09



4f

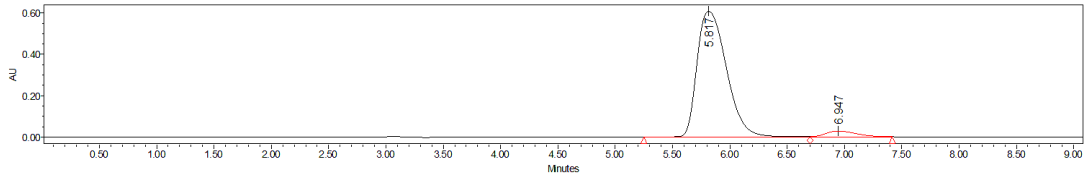
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(2-methoxyphenyl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1f**) scale reaction:
Result: colourless oil, 83% yield (40.5 mg), 91% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –299.0 (*c* 0.79, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 5.82 min, $t_{R(minor)}$ = 6,95 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 2H), 7.85 (m, 1H), 7.46 (m, 3H), 7.37 (m, 2H), 7.13 – 7.03 (m, 3H), 6.97 (m, 1H), 6.91 (d, *J*=8.8 Hz, 1H), 6.68 (m, 1H), 6.47 (s, 1H), 5.99 (s, 1H), 5.50 (d, *J*=8.8 Hz, 1H), 4.21 (m, 2H), 3.77 (s, 3H), 3.56 (s, 3H), 1.13 (t, *J*=7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.5, 164.2, 155.9, 146.9, 138.5, 138.1, 130.5, 128.8, 128.2, 128.1, 127.3, 127.3, 126.7, 126.4, 125.3, 124.1, 120.5, 109.5, 102.1, 86.9, 62.1, 55.0, 52.3, 41.7, 13.9;
ESI-HRMS calcd for [$C_{29}H_{28}O_7$+Na^+]: 511.1733, found 511.1733;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2951, 1728, 1595, 1491, 1443, 1370, 1329, 1236, 1126, 1061, 1026, 970, 941, 899, 810, 750, 697, 619, 583, 510.

Racemic **4f**:

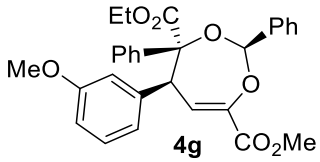


	Retention Time	Area	% Area
1	5.894	5792501	49.27
2	7.022	5963906	50.73

Chiral **4f**:



	Retention Time	Area	% Area
1	5.817	10824773	95.48
2	6.947	512830	4.52



4g

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(3-methoxyphenyl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1g**) scale reaction:

Result: white solid, M.P. 153-157°C, 91% yield (44.4 mg), 95% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –358.8 (*c* 0.83, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 12.16 min, $t_{R(minor)}$ = 7.98 min);

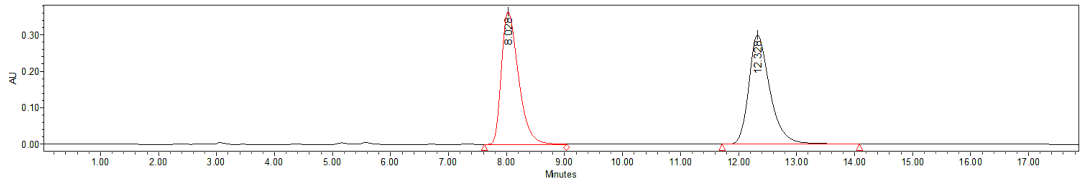
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (m, 2H), 7.45 (m, 3H), 7.30 (m, 2H), 7.14 (m, 3H), 6.94 (m, 2H), 6.84 – 6.72 (m, 2H), 6.55 (m, 1H), 6.01 (s, 1H), 4.58 (d, *J*=8.8 Hz, 1H), 4.23 (m, 2H), 3.79 (s, 3H), 3.57 (s, 3H), 1.15 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.3, 164.0, 158.9, 146.6, 138.8, 138.5, 138.0, 128.9, 128.6, 128.2, 127.9, 127.6, 126.6, 125.0, 124.0, 122.6, 115.5, 112.7, 102.0, 86.8, 62.2, 55.0, 52.7, 52.4, 13.9;

ESI-HRMS calcd for [$C_{29}H_{28}O_7$+Na^+]: 511.1733, found 511.1731;

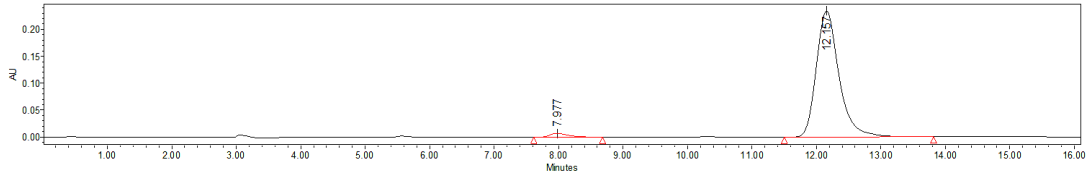
IR (film): $\tilde{\nu}$ (cm^{-1}) 2950, 1727, 1655, 1599, 1489, 1443, 1369, 1330, 1257, 1226, 1125, 1061, 1023, 970, 912, 860, 771, 746, 696, 591.

Racemic **4g**:

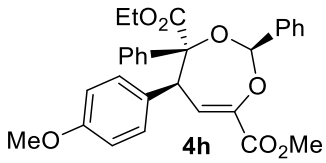


	Retention Time	Area	% Area
1	8.028	7428321	49.49
2	12.328	7580181	50.51

Chiral **4g**:



	Retention Time	Area	% Area
1	7.977	146808	2.49
2	12.157	5738182	97.51



4h

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(4-methoxyphenyl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1h**) scale reaction:

Result: colourless oil, 88% yield (42.9 mg), 99% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –402.4 (*c* 0.72, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 15.10 min, $t_{R(minor)}$ = 9.21 min);

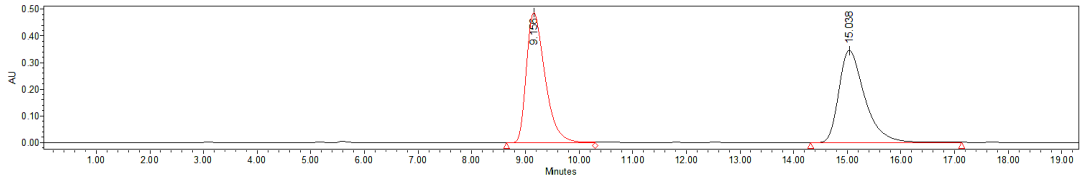
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (m, 2H), 7.46 (m, 3H), 7.29 (m, 2H), 7.20 – 7.04 (m, 5H), 6.95 (d, *J*=8.8 Hz, 1H), 6.51 (d, *J*=8.8 Hz, 2H), 6.00 (s, 1H), 4.55 (d, *J*=8.8 Hz, 1H), 4.22 (m, 2H), 3.79 (s, 3H), 3.63 (s, 3H), 1.15 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.4, 164.1, 158.5, 146.3, 138.6, 138.0 , 131.0, 129.4, 128.9, 128.2, 128.0, 127.5, 126.6, 125.0, 124.6, 113.2, 102.0, 87.0, 62.2, 55.0, 52.4, 52.0, 13.9;

ESI-HRMS calcd for [$C_{29}H_{28}O_7$+Na^+]: 511.1733, found 511.1733;

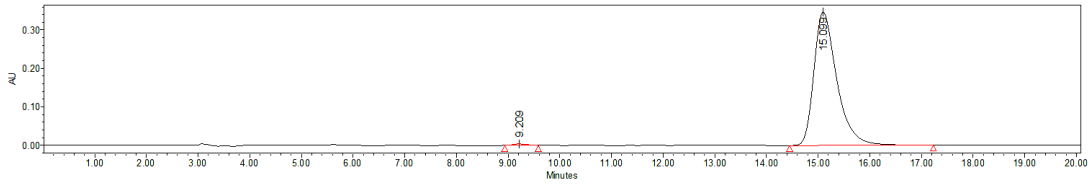
IR (film): $\tilde{\nu}$ (cm^{-1}) 2952, 1726, 1654, 1608, 1509, 1444, 1369, 1330, 1239, 1181, 1124, 1064, 1026, 970, 941, 898, 832, 747, 698, 592, 546.

Racemic **4h**:

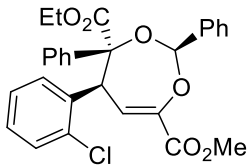


	Retention Time	Area	% Area
1	9.156	11733698	50.38
2	15.038	11555411	49.62

Chiral **4h**:



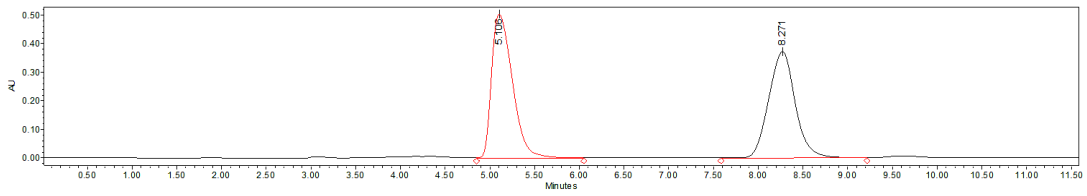
	Retention Time	Area	% Area
1	9.209	73036	0.68
2	15.099	10662077	99.32



4i

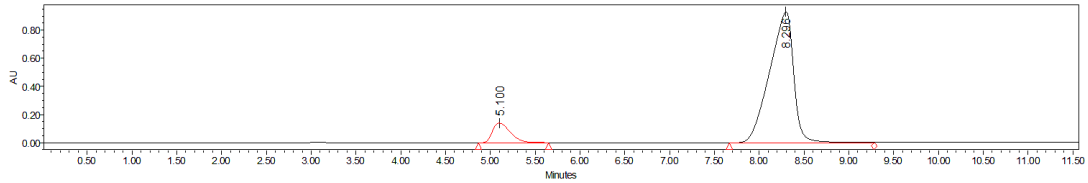
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(2-chlorophenyl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1i**) scale reaction:
Result: white solid, M.P. 151-156°C, 73% yield (36.0 mg), 80% ee, >19:1 dr; $[\alpha]^{30}_{D}$ = –230.4 (*c* 0.81, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 8.30 min, $t_{R(minor)}$ = 5.10 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.97 (m, 1H), 7.96 – 7.88 (m, 2H), 7.52 – 7.42 (m, 5H), 7.14 (m, 4H), 6.98 – 6.87 (m, 3H), 6.02 (s, 1H), 5.55 (d, *J*=8.8 Hz, 1H), 4.22 (m, 2H), 3.78 (s, 3H), 1.15 (t, *J*=7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.0, 163.9, 147.2, 138.0, 137.9, 136.2, 133.6, 130.8, 129.0, 128.7, 128.3, 128.3, 127.9, 127.8, 127.0, 126.6, 125.2, 122.1, 102.3, 86.4, 62.4, 52.4, 46.1, 13.9;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{35}ClO_6+Na^+]$: 515.1237, found 515.1238;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{37}ClO_6+Na^+]$: 517.1208, found 517.1215;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2983, 1729, 1656, 1443, 1370, 1330, 1259, 1230, 1126, 1064, 1030, 969, 942, 900, 813, 747, 695, 619, 566, 506.

Racemic **4i**:

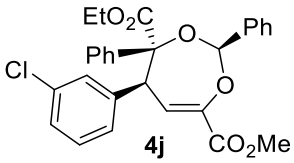


	Retention Time	Area	% Area
1	5.106	8175379	51.52
2	8.271	7692337	48.48

Chiral **4i**:



	Retention Time	Area	% Area
1	5.100	1939914	10.09
2	8.296	17278472	89.91



4j

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(3-chlorophenyl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1j**) scale reaction:

Result: white solid, M.P. 162-166°C, 91% yield (44.9 mg), 99% ee, >19:1 dr; $[\alpha]^{30}_{D}$ = –344.3 (*c* 0.95, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 9.20 min, $t_{R(minor)}$ = 6.57 min);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.79 (m, 2H), 7.46 m, 3H), 7.28 (m, 2H), 7.24 – 7.06 (m, 5H), 6.98 (m, 1H), 6.90 (m, 2H), 6.01 (s, 1H), 4.58 (d, *J*=8.8 Hz, 1H), 4.23 (m, 2H), 3.80 (s, 3H), 1.15 (t, *J*=7.2 Hz, 3H);

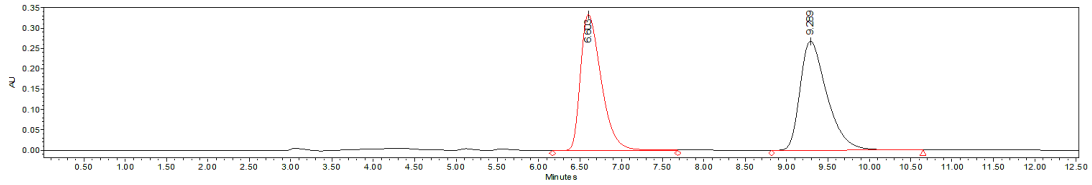
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.1, 163.9, 147.0, 139.5, 138.1, 137.7, 133.4, 130.0, 129.0, 128.3, 128.1, 128.1, 127.8, 127.1, 126.6, 124.9, 123.3, 102.2, 86.6, 62.3, 52.5, 13.9;

ESI-HRMS calcd for $[C_{28}H_{25}{}^{35}ClO_6+Na^+]$: 515.1237, found 515.1238;

ESI-HRMS calcd for $[C_{28}H_{25}{}^{37}ClO_6+Na^+]$: 517.1208, found 517.1214;

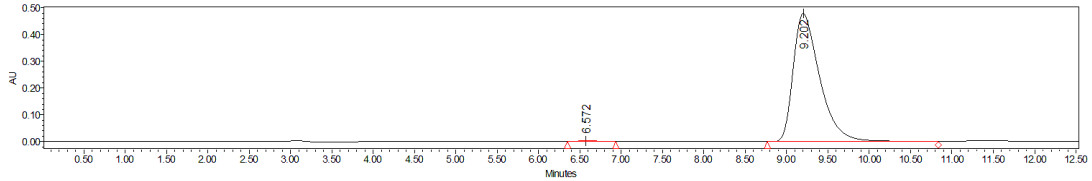
IR (film): $\tilde{\nu}$ (cm^{-1}) 2984, 1728, 1656, 1593, 1474, 1444, 1369, 1331, 1258, 1126, 1064, 1025, 970, 942, 909, 850, 747, 697, 580.

Racemic **4j**:

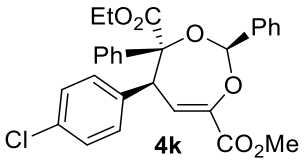


	Retention Time	Area	% Area
1	6.603	5835852	49.17
2	9.289	6033499	50.83

Chiral **4j**:



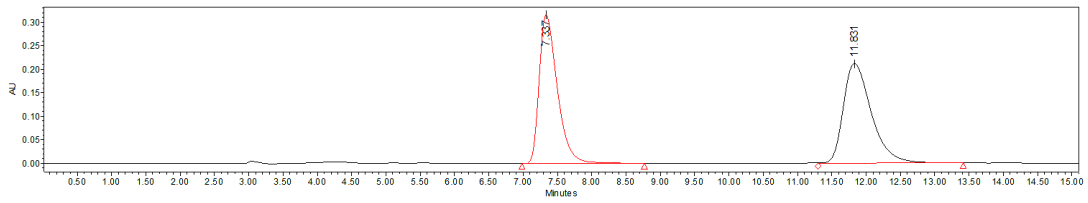
	Retention Time	Area	% Area
1	6.572	64323	0.60
2	9.202	10680040	99.40



4k

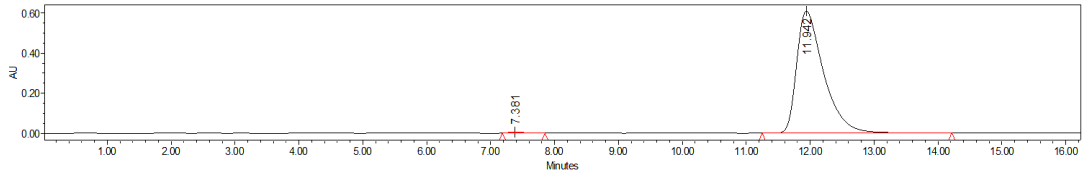
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(4-chlorophenyl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1k**) scale reaction:
Result: white solid, M.P. 200-204°C, 93% yield (45.9 mg), 99% ee, >19:1 dr; $[\alpha]^{30}_{D}$ = –352.4 (*c* 0.83, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 11.94 min, $t_{R(minor)}$ = 7.38 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (m, 2H), 7.47 (m, 3H), 7.28 (m, 2H), 7.19 – 7.07 (m, 5H), 6.93 (m, 3H), 6.01 (s, 1H), 4.58 (d, *J*=8.8 Hz, 1H), 4.23 (m, 2H), 3.80 (s, 3H), 1.14 (t, *J*=7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.1, 163.9, 146.8, 138.2, 137.7, 136.0, 131.3, 129.0, 128.3, 128.1, 127.9, 127.8, 126.6, 124.9, 123.7, 102.1, 86.7, 62.3, 52.5, 52.1, 13.9;
ESI-HRMS calcd for [$C_{28}H_{25}{}^{35}ClO_6$+Na$^+$]: 515.1237, found 515.1237;
ESI-HRMS calcd for [$C_{28}H_{25}{}^{37}ClO_6$+Na$^+$]: 517.1208, found 517.1212;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2983, 1727, 1656, 1491, 1444, 1369, 1330, 1258, 1126, 1063, 1019, 970, 942, 898, 826, 745, 698, 579, 519, 437.

Racemic **4k**:

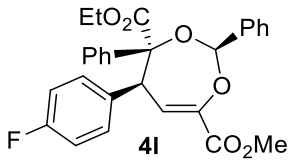


	Retention Time	Area	% Area
1	7.337	5784092	49.14
2	11.831	5985452	50.86

Chiral **4k**:



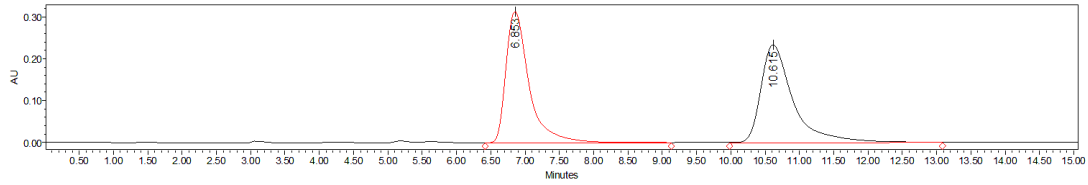
	Retention Time	Area	% Area
1	7.381	103702	0.58
2	11.942	17860217	99.42



4l

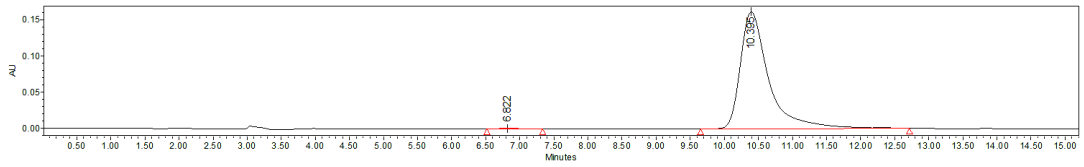
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(4-fluorophenyl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1l**) scale reaction:
Result: white solid, M.P. 162-167°C, 64% yield (30.5 mg), 99% ee, >19:1 dr; $[\alpha]^{30}_{D}$ = –339.7 (*c* 0.63, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 10.40 min, $t_{R(minor)}$ = 6.82 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.80 (m, 2H), 7.46 (m, 3H), 7.27 (m, 2H), 7.21 – 7.07 (m, 5H), 6.94 (d, *J*=8.8 Hz, 1H), 6.66 (m, 2H), 6.01 (s, 1H), 4.58 (d, *J*=8.8 Hz, 1H), 4.23 (m, 2H), 3.81 (s, 3H), 1.15 (t, *J*=7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.2, 164.0, 161.1 (*J*=244.2 Hz), 146.7, 138.4, 137.8, 133.2 (*J*=3.3 Hz), 131.5 (*J*=7.9Hz), 129.0, 128.3, 128.1, 127.7, 126.6, 124.9, 124.0, 114.7, 114.5 (*J*=21.1 Hz), 102.1, 86.9, 62.3, 52.5, 52.1, 13.9;
^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –115.52;
ESI-HRMS calcd for [$C_{28}H_{25}FO_6$+Na$^+$]: 449.1533, found 449.1530;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2953, 1729, 1656, 1602, 1506, 1445, 1370, 1331, 1261, 1230, 1160, 1127, 1064, 1025, 970, 898, 836, 750, 698, 590, 531.

Racemic **4l**:

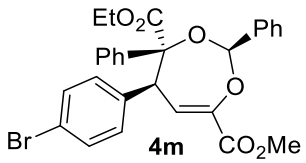


	Retention Time	Area	% Area
1	6.853	7387085	49.15
2	10.615	7643332	50.85

Chiral **4l**:



	Retention Time	Area	% Area
1	6.822	16860	0.36
2	10.395	4672411	99.64



4m

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(4-bromophenyl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1m**) scale reaction:

Result: white solid, M.P. 201-205°C, 94% yield (50.5 mg), 99% ee, >19:1 dr; $[\alpha]^{30}_{D}$ = –341.1 (*c* 1.05, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 13.17 min, $t_{R(minor)}$ = 7.71 min);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.77 (m, 2H), 7.46 (m, 3H), 7.28 (m, 2H), 7.15 (m, 3H), 7.08 (m, 4H), 6.91 (d, *J*=8.8 Hz, 1H), 6.01 (s, 1H), 4.57 (d, *J*=8.8 Hz, 1H), 4.23 (m, 2H), 3.80 (s, 3H), 1.14 (t, *J*=7.2 Hz, 3H);

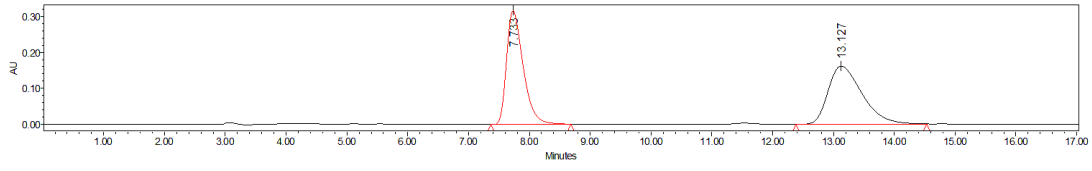
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.1, 163.9, 146.9, 138.2, 137.7, 136.6, 131.6, 130.9, 129.0, 128.3, 128.2, 127.8, 126.6, 124.9, 123.6, 102.1, 86.6, 62.3, 52.5, 52.2, 13.9;

ESI-HRMS calcd for $[C_{28}H_{25}{}^{79}BrO_6+Na^+]$: 559.0732, found 559.0733;

ESI-HRMS calcd for $[C_{28}H_{25}{}^{81}BrO_6+Na^+]$: 561.0712, found 561.0712;

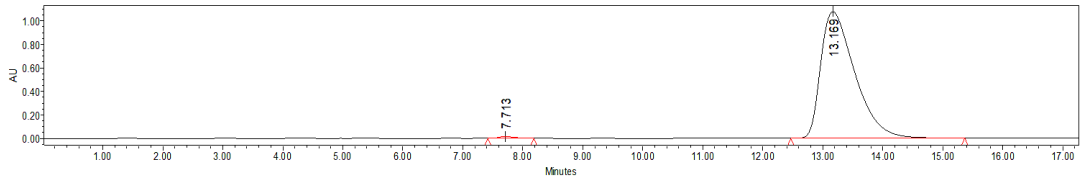
IR (film): $\tilde{\nu}$ (cm^{-1}) 2952, 1727, 1655, 1487, 1444, 1369, 1330, 1258, 1125, 1064, 1010, 969, 942, 897, 821, 743, 697, 647, 570, 517.

Racemic **4m**:

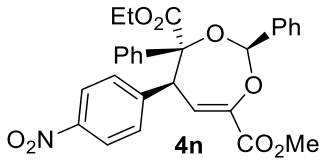


	Retention Time	Area	% Area
1	7.733	5973191	48.90
2	13.127	6241417	51.10

Chiral **4m**:



	Retention Time	Area	% Area
1	7.713	285247	0.67
2	13.169	42464971	99.33



4n

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(4-nitrophenyl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1n**) scale reaction:

Result: colourless oil, 86% yield (43.3 mg), 98% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –364.8 (*c* 0.94, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 20.09 min, $t_{R(minor)}$ = 11.54 min);

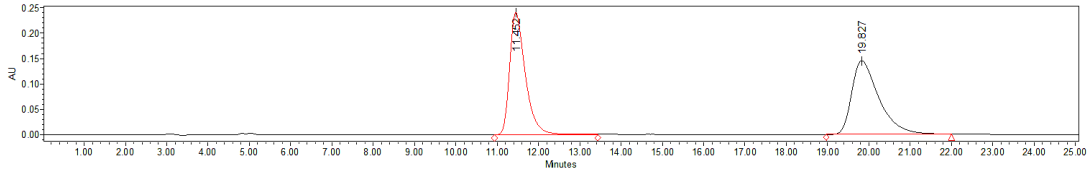
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (m, 4H), 7.48 (m, 3H), 7.38 (m, 2H), 7.29 (m, 2H), 7.16 (m, 3H), 6.91 (d, *J*=8.8 Hz, 1H), 6.05 (s, 1H), 4.75 (d, *J*=8.8 Hz, 1H), 4.25 (m, 2H), 3.82 (s, 3H), 1.16 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.7, 163.6, 147.6, 146.8, 145.3, 137.8, 137.4, 130.8, 129.1, 128.4, 128.34 , 128.1, 126.5, 124.7, 122.9, 122.5, 102.3, 86.4, 62.5, 52.6, 52.5, 13.9;

ESI-HRMS calcd for [$C_{28}H_{25}NO_8$+Na$^+$]: 526.1478, found 526.1479;

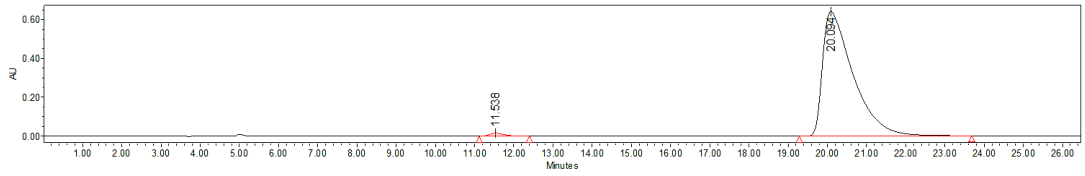
IR (film): $\tilde{\nu}$ (cm^{-1}) 2951, 1728, 1656, 1599, 1519, 1445, 1339, 1260, 1125, 1064, 1024, 970, 901, 853, 816, 746, 697, 578, 514.

Racemic **4n**:

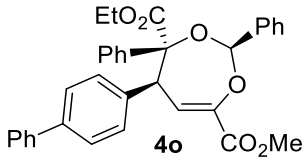


	Retention Time	Area	% Area
1	11.452	6383482	49.08
2	19.827	6621807	50.92

Chiral **4n**:



	Retention Time	Area	% Area
1	11.538	401792	1.15
2	20.094	34583970	98.85

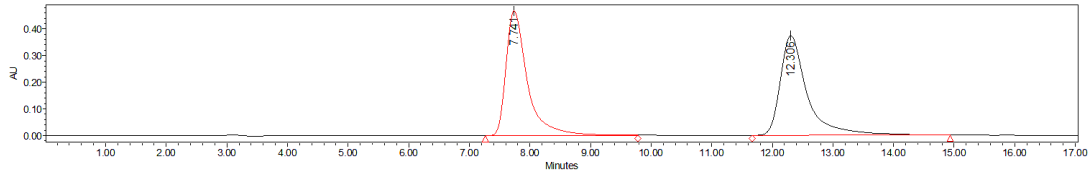


4o

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-([1,1'-biphenyl]-4-yl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

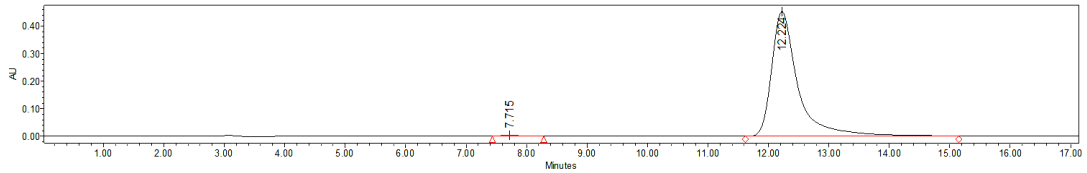
0.1 mmol (**1o**) scale reaction:
Result: colourless oil, 95% yield (50.7 mg), 99% ee, >19:1 dr; $[\alpha]^{30}_{D}$ = –386.6 (*c* 1.07, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 12.22 min, $t_{R(minor)}$ = 7.71 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.83 (m, 2H), 7.42 (m, 5H), 7.38 – 7.30 (m, 4H), 7.23 (m, 5H), 7.18 – 7.06 (m, 3H), 6.98 (d, *J*=8.8 Hz, 1H), 4.66 (d, *J*=8.8 Hz, 1H), 4.24 (m, 2H), 3.80 (s, 3H), 1.16 (t, *J*=7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.3, 164.0, 146.7, 140.6, 139.6, 138.5, 137.9, 136.5, 130.4, 128.9, 128.6, 128.3, 128.0, 127.6, 127.1, 126.8, 126.6, 126.4, 125.0, 124.1, 102.1, 86.9, 62.2, 52.5, 52.4, 13.9;
ESI-HRMS calcd for [$C_{34}H_{30}O_6$+Na^+]: 557.1940, found 557.1939;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3031, 1727, 1654, 1601, 1487, 1444, 1369, 1330, 1258, 1124, 1064, 1023, 970, 942, 898, 839, 741, 697, 619, 578, 511.

Racemic **4o**:

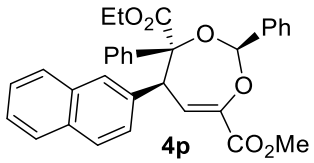


	Retention Time	Area	% Area
1	7.741	11453020	49.84
2	12.306	11526937	50.16

Chiral **4o**:



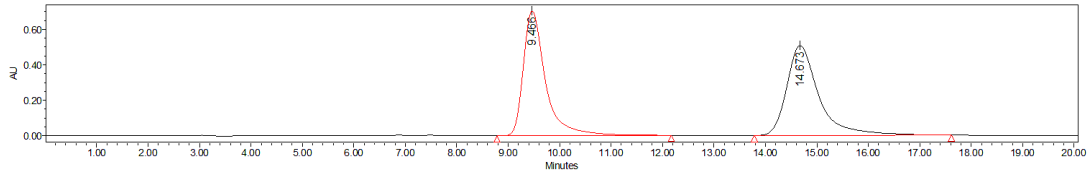
	Retention Time	Area	% Area
1	7.715	79457	0.58
2	12.224	13633024	99.42



4p

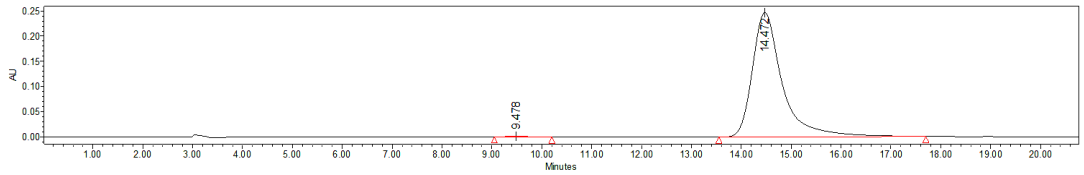
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(naphthalen-2-yl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1p**) scale reaction:
Result: colourless oil, 90% yield (45.7 mg), 99% ee, >19:1 dr; $[\alpha]^{30}_{D}$ = –402.4 (*c* 0.82, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 14.47 min, $t_{R(minor)}$ = 9.48 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.84 (m, 2H), 7.58 (m, 3H), 7.45 (m, 5H), 7.37 – 7.28 (m, 4H), 7.11 – 6.95 (m, 4H), 6.08 (s, 1H), 4.81 (d, *J*=8.8 Hz, 1H), 4.24 (m, 2H), 3.78 (s, 3H), 1.16 (t, *J*=7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.4, 164.0, 146.6, 138.4, 138.0, 135.0, 132.9, 129.2, 128.9, 128.3, 128.0, 127.8, 127.8, 127.6, 127.4, 127.3, 126.7, 125.6, 125.5, 125.0, 123.9, 102.2, 87.0, 62.3, 52.8, 52.4, 13.9;
ESI-HRMS calcd for [$C_{32}H_{28}O_6$+Na^+]: 531.1784, found 531.1786;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2952, 1727, 1655, 1599, 1497, 1444, 1369,1330, 1259, 1231, 1125, 1064, 1022, 970, 909, 857, 817, 745, 699, 585, 529, 478.

Racemic **4p**:

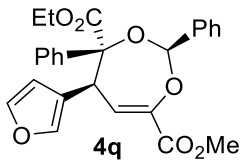


	Retention Time	Area	% Area
1	9.466	21061119	49.00
2	14.673	21918756	51.00

Chiral **4p**:



	Retention Time	Area	% Area
1	9.478	43235	0.42
2	14.472	10287483	99.58



4q

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-5-(furan-3-yl)-2,4-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1q**) scale reaction:

Result: white solid, M.P. 115-119°C, 94% yield (42.1 mg), 99% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –290.0 (*c* 0.86, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 12.88 min, $t_{R(minor)}$ = 7.69 min);

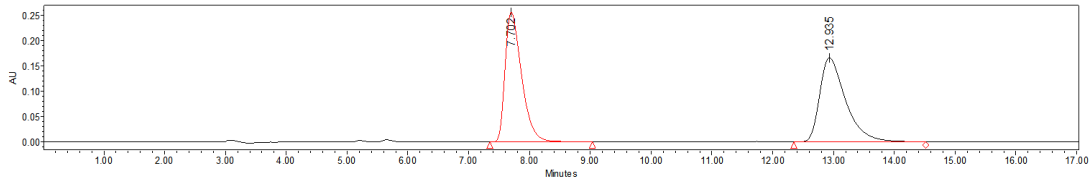
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (m, 2H), 7.51 – 7.39 (m, 5H), 7.25 (m, 3H), 7.07 – 6.98 (m, 2H), 6.95 (d, *J*=8.8 Hz, 1H), 6.21 (m, 1H), 5.96 (s, 1H), 4.53 (d, *J*=8.8 Hz, 1H), 4.22 (m, 2H), 3.80 (s, 3H), 1.16 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.0, 163.9, 147.5, 141.9, 141.3, 138.7, 138.0, 128.9, 128.3, 128.1, 127.9, 126.5, 125.0, 124.7, 120.2, 111.5, 101.9, 85.9, 62.1, 52.4, 43.5, 13.9;

ESI-HRMS calcd for $[C_{26}H_{24}O_7+Na^+]$: 471.1420, found 471.1418;

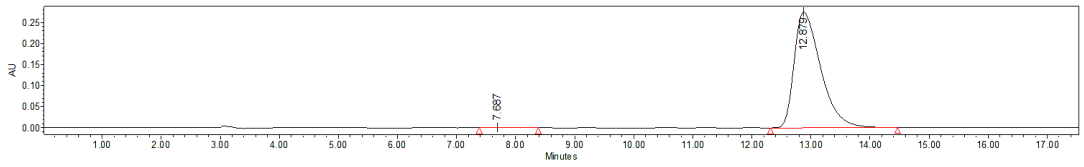
IR (film): $\tilde{\nu}$ (cm^{-1}) 2952, 1727, 1656, 1496, 1444, 1370, 1330, 1255, 1210, 1124, 1066, 1019, 968, 873, 747, 699, 638, 599.

Racemic **4q**:

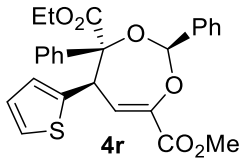


	Retention Time	Area	% Area
1	7.702	4835128	49.45
2	12.935	4943427	50.55

Chiral **4q**:



	Retention Time	Area	% Area
1	7.687	32757	0.38
2	12.879	8569057	99.62



4r

4-Ethyl 7-methyl (2*S*,4*S*,5*R*)-2,4-diphenyl-5-(thiophen-2-yl)-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1r**) scale reaction:

Result: white solid, M.P. 149-154°C, 90% yield (41.8 mg), 98% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –333.2.4 (*c* 0.88, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 14.93 min, $t_{R(minor)}$ = 7.99 min);

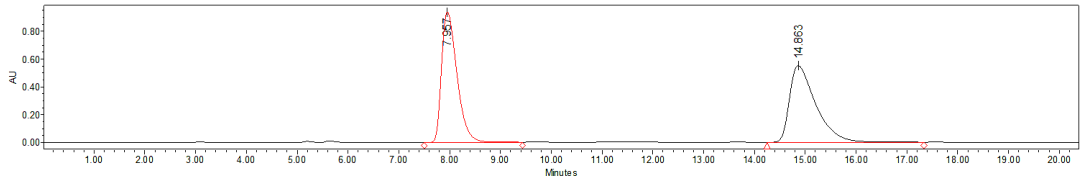
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.81 (m, 2H), 7.52 – 7.37 (m, 5H), 7.20 (m, 3H), 6.99 (d, *J*=8.8 Hz, 1H), 6.94 (m, 1H), 6.76 (m, 1H), 6.67 – 6.60 (m, 1H), 5.99 (s, 1H), 4.92 (d, *J*=8.8 Hz, 1H), 4.23 (m, 2H), 3.79 (s, 3H), 1.17 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.8, 163.8, 147.1, 138.3, 138.2, 137.9, 128.9, 128.3, 128.1, 127.9, 127.8, 126.6, 125.7, 125.3, 125.0, 124.2, 102.1, 86.0, 62.2, 52.4, 47.8, 14.0;

ESI-HRMS calcd for $[C_{26}H_{24}O_6S+Na^+]$:487.1191, found 487.1189;

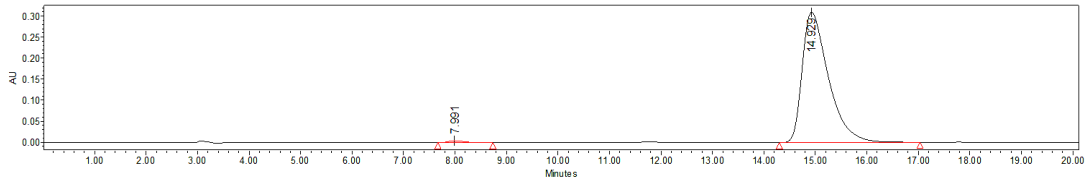
IR (film): $\tilde{\nu}$ (cm^{-1}) 2951, 1727, 1655, 1494, 1443, 1368, 1330, 1242, 1203, 1124, 1062, 1024, 967, 884, 851, 747, 697, 588, 512.

Racemic **4r**:

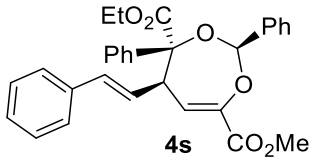


	Retention Time	Area	% Area
1	7.957	19830128	50.06
2	14.863	19782342	49.94

Chiral **4r**:



	Retention Time	Area	% Area
1	7.991	92217	0.83
2	14.929	10976494	99.17

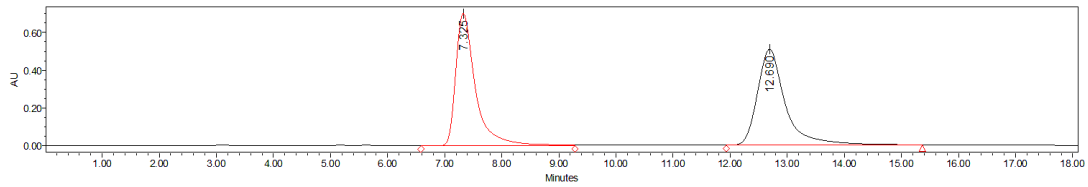


4s

4-Ethyl 7-methyl (2*S*,4*S*,5*R*)-2,4-diphenyl-5-((*E*)-styryl)-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

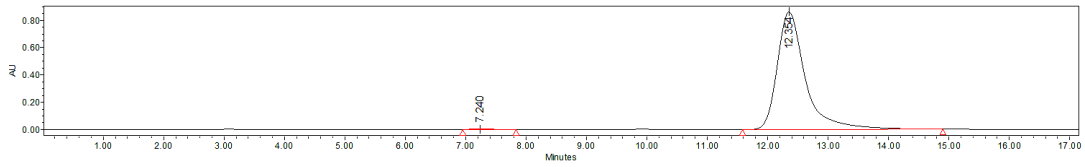
0.1 mmol (**1s**) scale reaction:
Result: colourless oil, 94% yield (45.5 mg), 99% ee, >19:1 dr; $[\alpha]^{26}_{D}$ = –440.5 (*c* 0.87, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 12.35 min, $t_{R(minor)}$ = 7.24 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.79 (m, 2H), 7.56 (m, 2H), 7.47 (m, 3H), 7.31 (m, 2H), 7.25 – 7.06 (m, 6H), 6.88 (d, *J*=8.8 Hz, 1H), 6.09 (m, 2H), 5.92 (s, 1H), 4.30 – 4.08 (m, 3H), 3.81 (s, 3H), 1.16 (t, *J*=7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.9, 163.9, 147.9, 138.6, 138.0, 136.9, 133.9, 128.9, 128.3, 128.2, 128.2, 128.0, 127.3, 126.5, 126.2, 125.2, 124.8, 123.3, 101.9, 85.5, 62.1, 52.4, 50.6, 14.0;
ESI-HRMS calcd for $[C_{30}H_{28}O_6+Na^+]$: 507.1784, found 507.1782;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2952, 1727, 1651, 1494, 1444, 1368, 1328, 1254, 1209, 1126, 1064, 1024, 968, 910, 854, 747, 695, 582, 505.

Racemic **4s**:

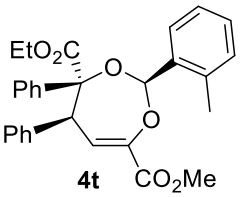


	Retention Time	Area	% Area
1	7.325	16755354	49.25
2	12.690	17264254	50.75

Chiral **4s**:

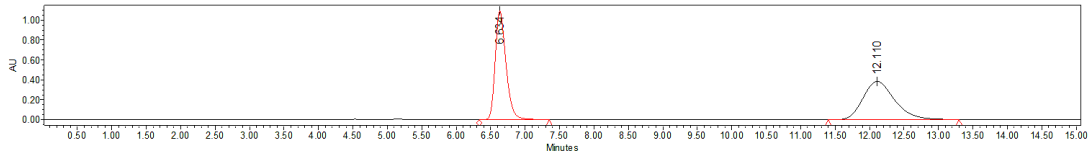


	Retention Time	Area	% Area
1	7.240	135682	0.49
2	12.354	27743722	99.51



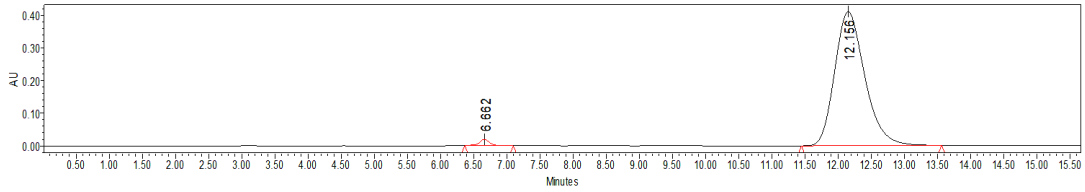
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-4,5-diphenyl-2-(o-tolyl)-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: white solid, M.P. 170-175°C, 93% yield (43.9 mg), 97% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –296.6 (*c* 0.84, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 12.16 min, $t_{R(minor)}$ = 6.66 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.84 (m, 1H), 7.33 – 7.21 (m, 7H), 7.12 (m, 3H), 7.04 (m, 3H), 6.96 (d, *J*=8.8 Hz, 1H), 6.16 (s, 1H), 4.61 (d, *J*=8.8 Hz, 1H), 4.24 (m, 2H), 3.73 (s, 3H), 2.52 (s, 3H), 1.14 (t, *J*=7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.2, 163.9, 146.5, 138.5, 137.3, 136.0, 135.6, 130.6, 130.2, 129.1, 127.9, 127.8, 127.6, 127.0, 126.1, 126.0, 125.0, 124.0, 101.2, 87.2, 62.2, 52.7, 52.3, 19.0, 14.0;
ESI-HRMS calcd for $[C_{29}H_{28}O_6+Na^+]$: 495.1784, found 495.1781;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2952, 1727, 1652, 1493, 1444, 1368, 1326, 1260, 1127, 1063, 1033, 997, 937, 890, 757, 699, 618.

Racemic **4t**:

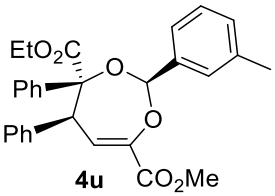


	Retention Time	Area	% Area
1	6.634	11833608	49.17
2	12.110	12233141	50.83

Chiral **4t**:



	Retention Time	Area	% Area
1	6.662	207110	1.58
2	12.156	12942423	98.42



4u

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-4,5-diphenyl-2-(m-tolyl)-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1a**) scale reaction:

Result: colourless oil, 95% yield (44.8 mg), 98% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –327.8 (*c* 1.01, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 8.68 min, $t_{R(minor)}$ = 5.73 min);

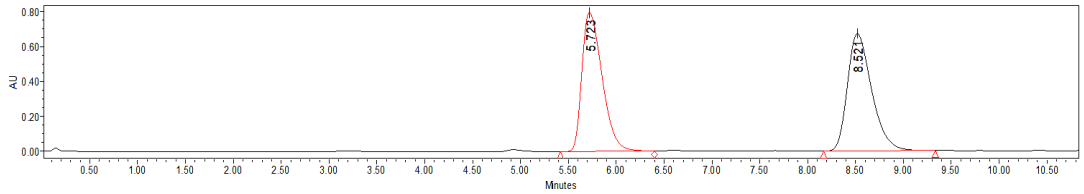
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (m, 2H), 7.35 (m, 1H), 7.32 – 7.26 (m, 2H), 7.24 (m, 1H), 7.21 – 7.16 (m, 2H), 7.12 (m, 3H), 7.03 – 6.89 (m, 4H), 5.99 (s, 1H), 4.59 (d, *J*=8.8 Hz, 1H), 4.23 (m, 2H), 3.79 (s, 3H), 2.43 (s, 3H), 1.16 (t, *J*=7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.4, 164.0, 146.6, 138.5, 137.9, 137.5, 130.0, 129.6, 128.18, 127.9, 127.7, 127.5, 127.1, 126.9, 125.0, 124.1, 123.7, 102.2, 86.9, 62.2, 52.9, 52.4, 21.6, 13.9;

ESI-HRMS calcd for [$C_{29}H_{28}O_6$+Na^+]: 495.1784, found 495.1781;

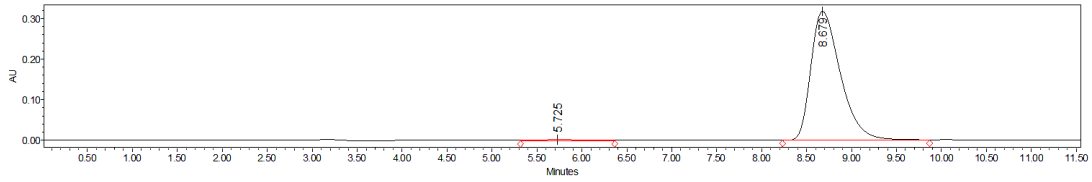
IR (film): $\tilde{\nu}$ (cm^{-1}) 2951, 1727, 1655, 1604, 1492, 1444, 1370, 1330, 1259, 1230, 1162, 1125, 1063, 1027, 890, 854, 763, 698, 619, 557.

Racemic **4u**:

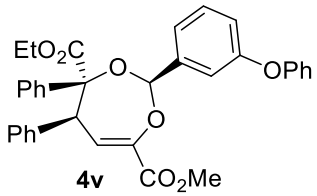


	Retention Time	Area	% Area
1	5.723	11674902	49.78
2	8.521	11779219	50.22

Chiral **4u**:



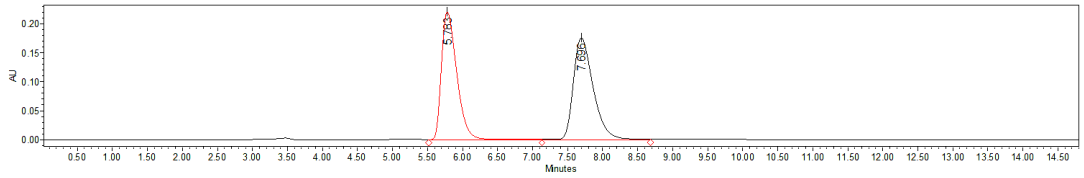
	Retention Time	Area	% Area
1	5.725	84849	1.15
2	8.679	7262262	98.85



4v

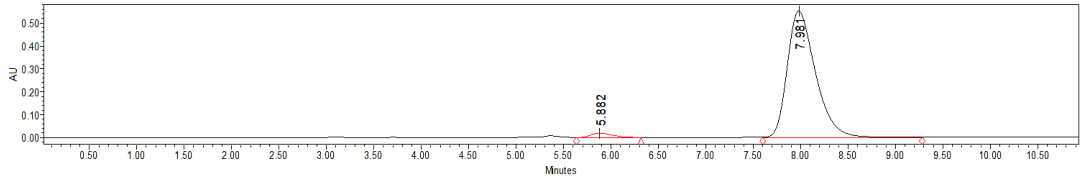
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2-(3-phenoxyphenyl)-4,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: colourless oil, 87% yield (47.9 mg), 95% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –290.7 (*c* 0.93, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 7.98 min, $t_{R(minor)}$ = 5.88 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (m, 1H), 7.53 (m, 1H), 7.42 (m, 1H), 7.34 (m, 2H), 7.24 (m, 2H), 7.19 – 7.15 (m, 2H), 7.09 (m, 7H), 6.96 (m, 4H), 5.97 (s, 1H), 4.60 (d, *J*=8.8 Hz, 1H), 4.19 (m, 2H), 3.74 (s, 3H), 1.10 (t, *J*=7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.2, 163.9, 157.4, 156.9, 146.5, 139.9, 138.3, 137.4, 130.0, 129.7, 129.6, 127.9, 127.8, 127.6, 126.9, 124.9, 124.1, 123.4, 121.3, 119.2, 119.0, 117.1, 101.6, 86.9, 62.2, 52.7, 52.4, 13.9;
ESI-HRMS calcd for $[C_{34}H_{30}O_7+Na^+]$: 573.1889, found 573.1888;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2984, 1728, 1655, 1586, 1487, 1443, 1369, 1329, 1253, 1125, 1064, 1027, 966, 894, 862, 763, 695, 619, 486.

Racemic **4v**:

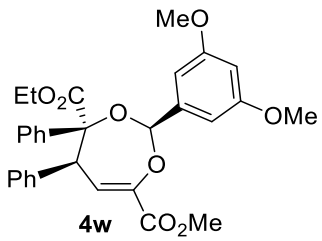


	Retention Time	Area	% Area
1	5.783	3352672	49.36
2	7.696	3439552	50.64

Chiral **4v**:



	Retention Time	Area	% Area
1	5.882	302236	2.57
2	7.981	11449283	97.43

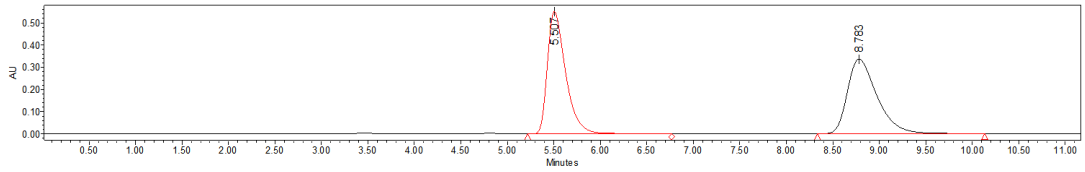


4w

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2-(3,5-dimethoxyphenyl)-4,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:

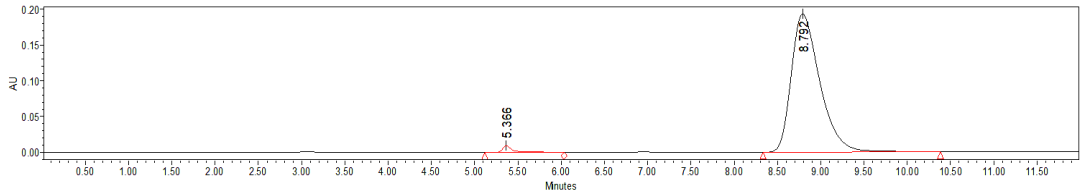
Result: colourless oil, 95% yield (49.2 mg), 96% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –298.1 (*c* 1.07, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 85/15, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 8.79 min, $t_{R(minor)}$ = 5.37 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 2H), 7.20 – 7.15 (m, 2H), 7.11 (m, 3H), 7.07 (m, 2H), 7.03 – 6.90 (m, 4H), 6.52 (s, 1H), 5.95 (s, 1H), 4.60 (d, *J* = 8.8 Hz, 1H), 4.23 (m, 2H), 3.84 (s, 6H), 3.79 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.3, 164.0, 160.7, 146.5, 140.1, 138.5, 137.4, 130.0, 127.9, 127.7, 127.5, 126.9, 124.9, 124.2, 104.8, 101.8, 101.0, 86.8, 62.2, 55.4, 55.3, 52.8, 52.4, 14.0;
ESI-HRMS calcd for $[C_{30}H_{30}O_8+Na^+]$: 541.1838, found 541.1837;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2950, 2842, 1727, 1655, 1600, 1455, 1372, 1332, 1260, 1232, 1202, 1154, 1125, 1062, 1026, 967, 923, 893, 842, 764, 697, 620, 555.

Racemic **4w**:

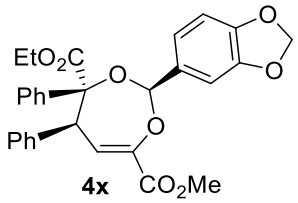


	Retention Time	Area	% Area
1	5.507	7517922	50.35
2	8.783	7414611	49.65

Chiral **4w**:

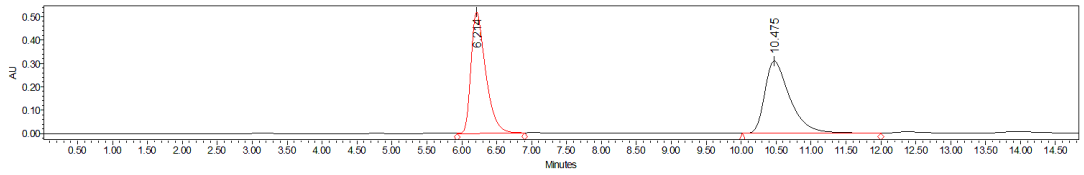


	Retention Time	Area	% Area
1	5.366	89278	1.97
2	8.792	4438357	98.03



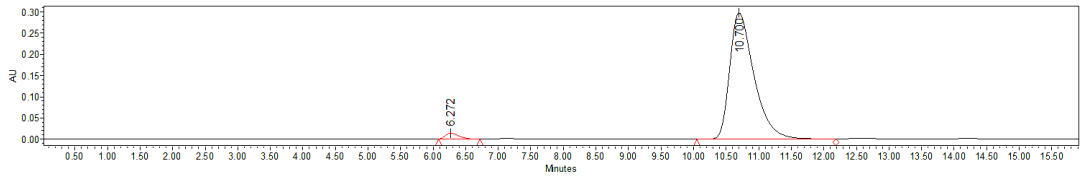
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2-(benzo[d][1,3]dioxol-5-yl)-4,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: colourless oil, 88% yield (44.2 mg), 95% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –296.8 (*c* 0.76, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 85/15, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 10.70 min, $t_{R(minor)}$ = 6.27 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (m, 2H), 7.29 – 7.25 (m, 2H), 7.19 – 7.09 (m, 5H), 7.01 – 6.87 (m, 5H), 6.00 (s, 2H), 5.92 (s, 1H), 4.58 (d, *J* = 8.8 Hz, 1H), 4.23 (m, 2H), 3.79 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.3, 164.0, 148.0, 147.6, 146.4, 138.4, 137.4, 132.0, 130.0, 127.9, 127.8, 127.6, 126.9, 124.9, 124.1, 120.4, 108.0, 107.4, 101.9, 101.2, 86.9, 62.2, 52.8, 52.4, 14.0;
ESI-HRMS calcd for $[C_{29}H_{26}O_8+Na^+]$: 525.1525, found 525.1525;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2900, 1727, 1655, 1495, 1443, 1327, 1247, 1120, 1062, 1033, 934, 890, 860, 810, 765, 699, 619, 557.

Racemic **4x**:

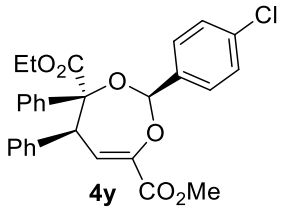


	Retention Time	Area	% Area
1	6.214	7627717	49.67
2	10.475	7729210	50.33

Chiral **4x**:

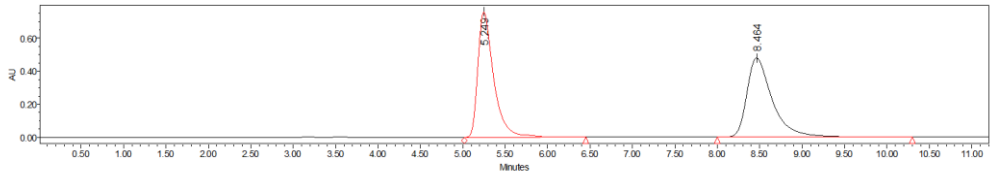


	Retention Time	Area	% Area
1	6.272	203291	2.56
2	10.700	7751938	97.44



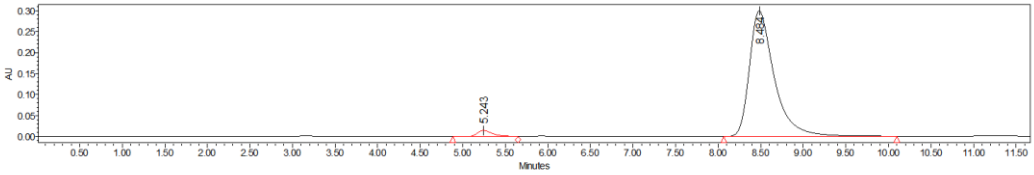
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2-(4-chlorophenyl)-4,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: colourless oil, 81% yield (39.9 mg), 94% ee, >19:1 dr; $[\alpha]^{19}_{D}$ = –312.5 (*c* 0.80, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 8.48 min, $t_{R(minor)}$ = 5.24 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J*=8.4 Hz, 2H), 7.43 (d, *J*=8.4 Hz, 2H), 7.25 (m, 2H), 7.18 – 7.07 (m, 5H), 7.03 – 6.92 (m, 4H), 5.97 (s, 1H), 4.60 (d, *J* = 8.8 Hz, 1H), 4.23 (m, 2H), 3.79 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.2, 163.9, 146.4, 138.3, 137.3, 136.4, 134.9, 130.0, 128.4, 128.2, 128.0, 127.8, 127.7, 127.0, 124.9, 124.2, 101.4, 87.0, 62.3, 52.8, 52.5, 14.0;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{35}ClO_6+Na^+]$: 515.1237, found 515.1238;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{37}ClO_6+Na^+]$: 517.1208, found 517.1213;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2984, 1729, 1655, 1601, 1492, 1444, 1369, 1331, 1262, 1232, 1128, 1064, 1023, 971, 893, 817, 763, 698, 621, 504.

Racemic **4y**:

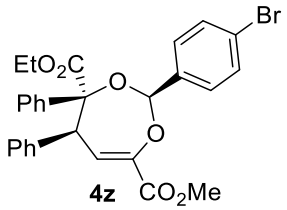


	Retention Time	Area	% Area
1	5.249	9835793	49.80
2	8.464	9913377	50.20

Chiral **4y**:

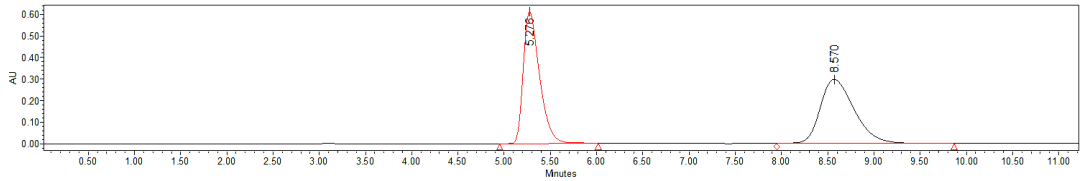


	Retention Time	Area	% Area
1	5.243	180581	2.89
2	8.484	6060830	97.11



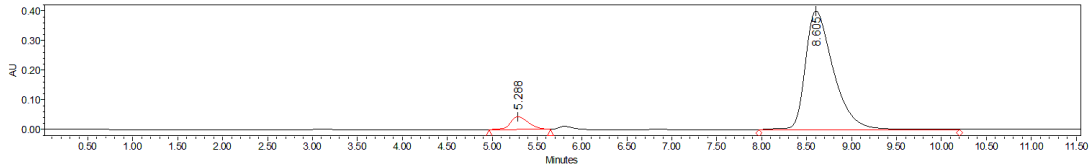
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2-(4-bromophenyl)-4,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: colourless oil, 81% yield (43.5 mg), 87% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –275.8 (*c* 0.85, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 8.61 min, $t_{R(minor)}$ = 5.29 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J*=8.4 Hz, 2H), 7.59 (d, *J*=8.4 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.18 – 7.08 (m, 5H), 7.03 – 6.91 (m, 4H), 5.95 (s, 1H), 4.60 (d, *J* = 8.8 Hz, 1H), 4.23 (m, 2H), 3.79 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.2, 163.9, 146.4, 138.3, 137.3, 136.9, 131.4, 130.0, 128.5, 128.0, 127.8, 127.7, 127.0, 124.9, 124.2, 123.2, 101.4, 87.0, 62.3, 52.8, 52.5, 14.0;
ESI-HRMS calcd for [$C_{28}H_{25}{}^{79}BrO_6$+Na$^+$]: 559.0732, found 559.0732;
ESI-HRMS calcd for [$C_{28}H_{25}{}^{81}BrO_6$+Na$^+$]: 561.0712, found 561.0713;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2984, 1729, 1655, 1597, 1490, 1444, 1371, 1330, 1261, 1232, 1127, 1065, 1019, 971, 893, 814, 764, 698, 664, 621, 501.

Racemic **4z**:

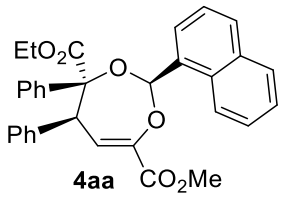


	Retention Time	Area	% Area
1	5.276	7514383	49.63
2	8.570	7625047	50.37

Chiral **4z**:



	Retention Time	Area	% Area
1	5.288	600785	6.49
2	8.605	8655837	93.51



4aa

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2-(naphthalen-1-yl)-4,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1a**) scale reaction:

Result: colourless oil, 90% yield (45.7 mg), 99% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –269.1 (*c* 0.90, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 85/15, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 9.39 min, $t_{R(minor)}$ = 6.09 min);

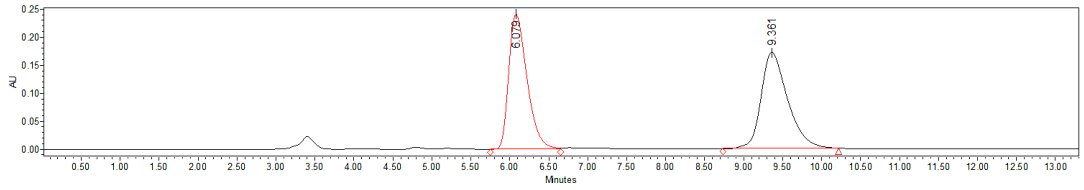
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (m, 1H), 8.07 (m, 1H), 7.96 – 7.87 (m, 2H), 7.54 (m, 3H), 7.27 (m, 4H), 7.15 – 7.01 (m, 7H), 6.62 (s, 1H), 4.69 (d, *J* = 8.8 Hz, 1H), 4.24 (m, 2H), 3.72 (s, 3H), 1.08 (t, *J* = 7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.2, 164.0, 146.8, 138.5, 137.1, 134.0, 133.3, 130.3, 130.2, 130.0, 128.6, 128.0, 127.8, 127.7, 127.0, 126.1, 125.7, 125.1, 125.0, 124.7, 124.4, 124.2, 101.8, 87.6, 62.2, 52.8, 52.4, 13.9;

ESI-HRMS calcd for [$C_{32}H_{28}O_6$+Na$^+$]: 531.1784, found 531.1783;

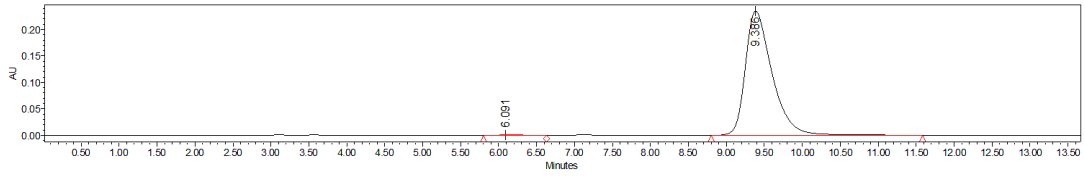
IR (film): $\tilde{\nu}$ (cm^{-1}) 2983, 1726, 1653, 1599, 1493, 1443, 1323, 1260, 1123, 1066, 1033, 1000, 892, 855, 800, 768, 699, 618.

Racemic **4aa**:

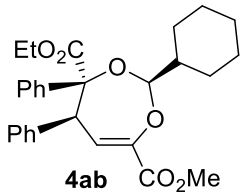


	Retention Time	Area	% Area
1	6.079	3910254	49.10
2	9.361	4053991	50.90

Chiral **4aa**:



	Retention Time	Area	% Area
1	6.091	26343	0.46
2	9.386	5751249	99.54



4ab

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2-cyclohexyl-4,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate

0.1 mmol (**1a**) scale reaction:

Result: white solid, M.P. 51-56°C, 76% yield (35.3 mg), 80% ee, >19:1 dr; $[\alpha]^{19}_{D}$ = –298.3 (*c* 0.60, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 11.58 min, $t_{R(minor)}$ = 7.09 min);

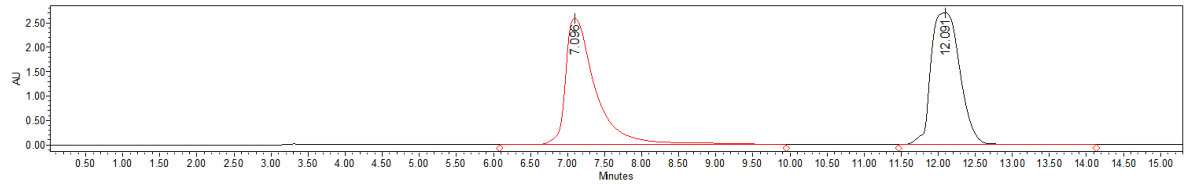
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.36 – 7.31 (m, 2H), 7.31 – 7.25 (m, 2H), 7.16 (m, 2H), 7.13 – 7.07 (m, 1H), 7.04 – 6.98 (m, 3H), 6.79 (d, *J* = 8.8 Hz, 1H), 4.87 (d, *J* = 5.2 Hz, 1H), 4.63 (d, *J* = 8.8 Hz, 1H), 4.21 (m, 2H), 3.70 (s, 3H), 2.20 (m, 1H), 2.16 – 2.08 (m, 1H), 2.04 – 1.95 (m, 1H), 1.88 – 1.79 (m, 2H), 1.71 (m, 1H), 1.53 – 1.43 (m, 1H), 1.43 – 1.32 (m, 3H), 1.30 – 1.22 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Acetone-d_6) δ 171.9, 164.6. 147.6, 140.4, 139.6, 131.0, 128.8, 128.6, 128.3, 127.7, 126.0, 124.7, 107.0, 86.9, 62.7, 53.0, 52.5, 44.7, 28.7, 28.6, 27.4, 26.8, 26.7, 14.4;

ESI-HRMS calcd for [$C_{28}H_{32}O_6$+Na$^+$]: 487.2097, found 487.2091;

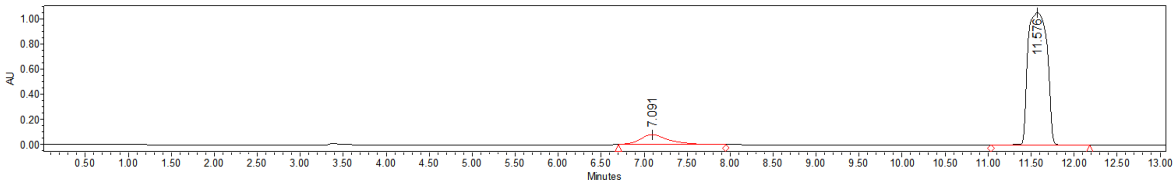
IR (film): $\tilde{\nu}$ (cm^{-1}) 2929, 2853, 1727, 1655, 1493, 1448, 1331, 1260, 1233, 1131, 1061, 1033, 962, 888, 766, 731, 697, 621, 558.

Racemic **4ab**:

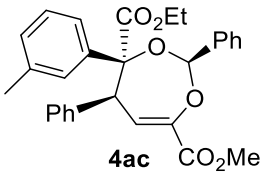


	Retention Time	Area	% Area
1	7.096	73623605	50.03
2	12.091	73547197	49.97

Chiral **4ab**:

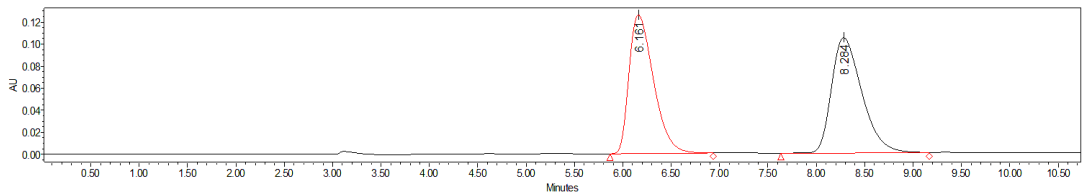


	Retention Time	Area	% Area
1	7.091	1803949	10.01
2	11.576	16224960	89.99



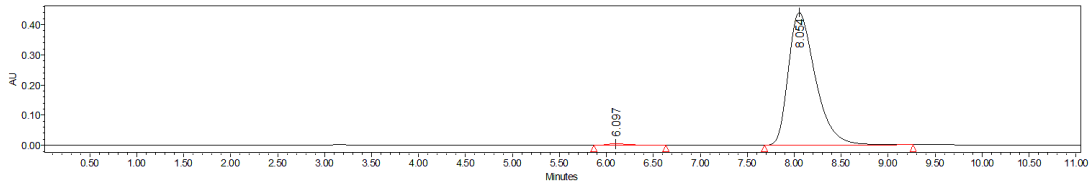
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2,5-diphenyl-4-(m-tolyl)-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: white solid, M.P. 130-134°C, 94% yield (44.4 mg), 98% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –363.4 (*c* 0.92, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 8.05 min, $t_{R(minor)}$ = 6.10 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (m, 2H), 7.46 (m, 3H), 7.17 (m, 2H), 7.06 (m, 2H), 7.04 – 6.86 (m, 6H), 6.00 (s, 1H), 4.57 (d, *J* = 8.8 Hz, 1H), 4.24 (m, 2H), 3.79 (s, 3H), 2.18 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.5, 164.1, 146.5, 138.4, 138.0, 137.5, 137.5, 130.0, 128.9, 128.3, 128.2, 127.8, 127.7, 126.9, 126.6, 125.6, 124.2, 122.1, 102.1, 87.0, 62.2, 52.9, 52.4, 21.4, 13.9;
ESI-HRMS calcd for [$C_{29}H_{28}O_6$+Na^+]: 495.1784, found 495.1782;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2951, 1727, 1655, 1604, 1491, 1445, 1370, 1329, 1260, 1230, 1186, 1124, 1063, 1011, 888, 851, 748, 697, 621, 557, 444.

Racemic **4ac**:

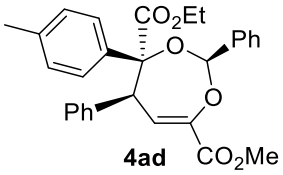


	Retention Time	Area	% Area
1	6.161	2210402	49.12
2	8.284	2289204	50.88

Chiral **4ac**:



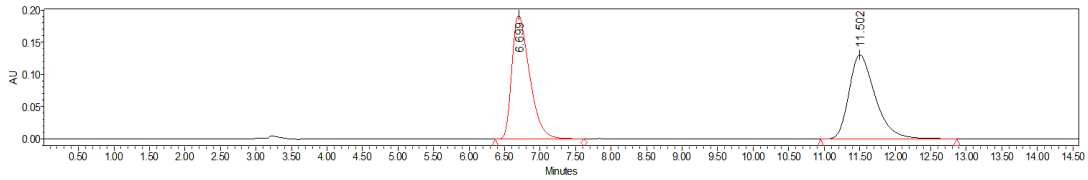
	Retention Time	Area	% Area
1	6.097	78179	0.88
2	8.054	8781375	99.12



4ad

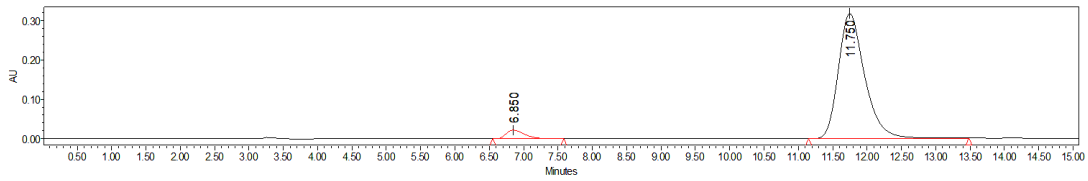
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2,5-diphenyl-4-(p-tolyl)-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: white solid, M.P. 146-160°C, 89% yield (42.0 mg), 91% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –340.5 (*c* 0.86, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 11.75 min, $t_{R(minor)}$ = 6.85 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (m, 2H), 7.45 (m, 3H), 7.17 (m, 4H), 7.03 – 6.90 (m, 6H), 6.00 (s, 1H), 4.60 (d, *J* = 8.8 Hz, 1H), 4.22 (m, 2H), 3.79 (s, 3H), 2.20 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.5, 164.1, 146.5, 138.0, 137.6, 137.2, 135.6, 130.1, 128.8, 128.6, 128.2, 127.8, 126.9, 126.6, 124.9, 124.3, 102.0, 86.9, 62.1, 52.7, 52.3, 20.9, 13.9;
ESI-HRMS calcd for $[C_{29}H_{28}O_6+Na^+]$: 495.1784, found 495.1782;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2951, 1727, 1655, 1493, 1445, 1370, 1329, 1259, 1230, 1124, 1061, 1014, 971, 941, 893, 818, 743, 698, 658, 612, 582, 513.

Racemic **4ad**:

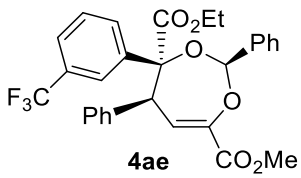


	Retention Time	Area	% Area
1	6.699	3331461	49.92
2	11.502	3341763	50.08

Chiral **4ad**:



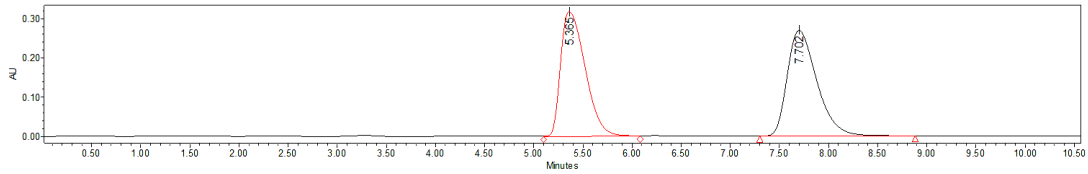
	Retention Time	Area	% Area
1	6.850	395515	4.48
2	11.750	8426033	95.52



4ae

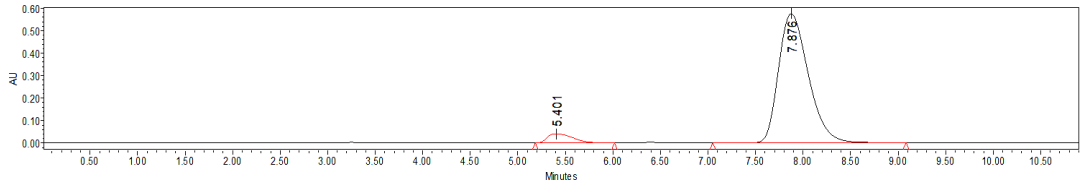
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2,5-diphenyl-4-(3-(trifluoromethyl)phenyl)-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: colourless oil, 95% yield (50.0 mg), 89% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –287.0 (*c* 1.01, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 7.88 min, $t_{R(minor)}$ = 5.40 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.82 (m, 2H), 7.53 – 7.41 (m, 5H), 7.36 (m, 1H), 7.24 (m, 1H), 7.18 – 7.10 (m, 2H), 7.04 – 6.90 (m, 4H), 6.04 (s, 1H), 4.59 (d, *J* = 8.8 Hz, 1H), 4.27 (m, 2H), 3.80 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.9, 163.9, 146.7, 139.7, 137.6, 137.0, 130.2 (*J*=32.1 Hz), 129.9, 129.0, 128.4 (*J*=5.6 Hz), 128.3, 128.0, 127.2, 126.5, 124.4 (*J*=3.8 Hz), 123.5, 122.5 (*J*=270.8 Hz), 122.2 (*J*=3.9 Hz), 102.1, 86.6, 62.6, 52.9, 13.9;
^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –62.78;
ESI-HRMS calcd for [$C_{29}H_{25}F_3O_6$+Na^+]: 549.1501, found 549.1501;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2953, 1729, 1656, 1493, 1443, 1327, 1260, 1232, 1165, 1123, 1069, 1022, 980, 894, 748, 698, 654, 615, 559, 519.

Racemic **4ae**:

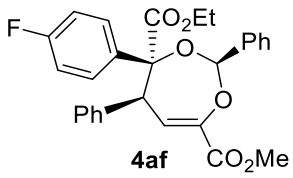


	Retention Time	Area	% Area
1	5.365	5512605	49.52
2	7.702	5620159	50.48

Chiral **4ae**:



	Retention Time	Area	% Area
1	5.401	747270	5.63
2	7.876	12515720	94.37

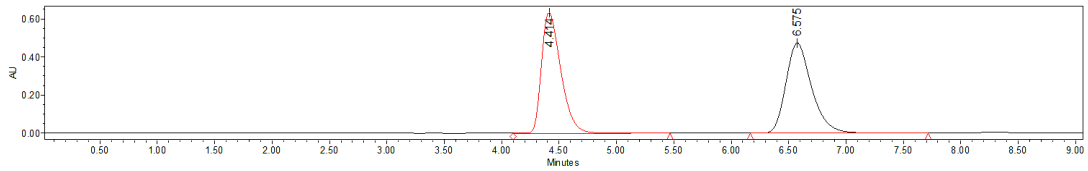


4af

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-4-(4-fluorophenyl)-2,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: white solid, M.P. 215-220°C, 97% yield (46.2 mg), 99% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –350.0 (*c* 0.96, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 6.64 min, $t_{R(minor)}$ = 4.42 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.79 (m, 2H), 7.46 (m, 3H), 7.25 (m, 2H), 7.17 (m, 2H), 7.00 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.82 (m, 2H), 6.01 (s, 1H), 4.58 (d, *J* = 8.8 Hz, 1H), 4.24 (m, 2H), 3.79 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.2, 163.9, 160.8 (*J*=245.4 Hz), 146.6, 137.8, 137.3, 134.4 (*J*=3.2 Hz), 130.0, 129.0, 128.3, 127.9, 127.1, 126.9 (*J*=8.2 Hz), 126.6, 123.8, 114.7 (*J*=21.5 Hz), 102.1, 86.5, 62.3, 52.8, 52.4, 13.9;
^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –114.49;
ESI-HRMS calcd for [$C_{28}H_{25}FO_6$+Na^+]: 449.1533, found 449.1530;

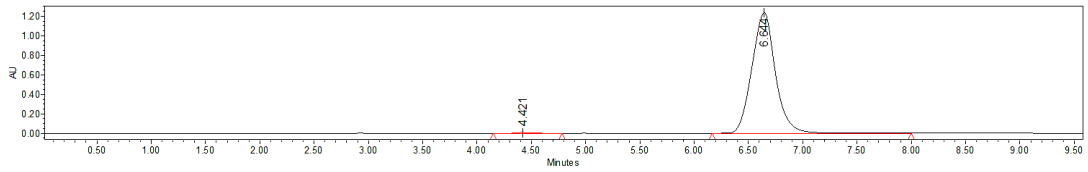
IR (film): $\tilde{\nu}$ (cm^{-1}) 2984, 1728, 1655, 1603, 1505, 1446, 1369, 1330, 1260, 1228, 1160, 1127, 1061, 1013, 970, 893, 836, 812, 747, 699, 611, 520.

Racemic **4af**:

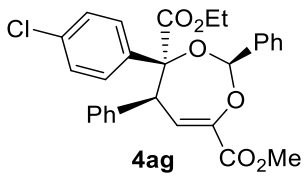


	Retention Time	Area	% Area
1	4.414	7407888	50.05
2	6.575	7392969	49.95

Chiral **4af**:



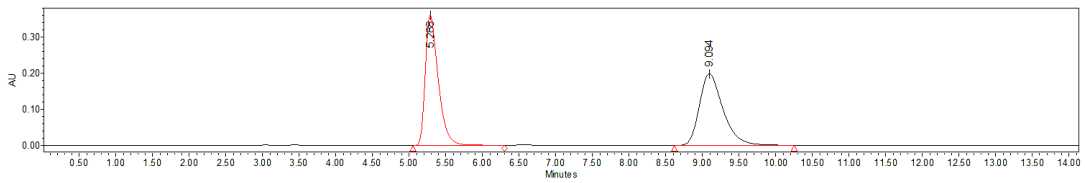
	Retention Time	Area	% Area
1	4.421	95917	0.51
2	6.644	18562310	99.49



4ag

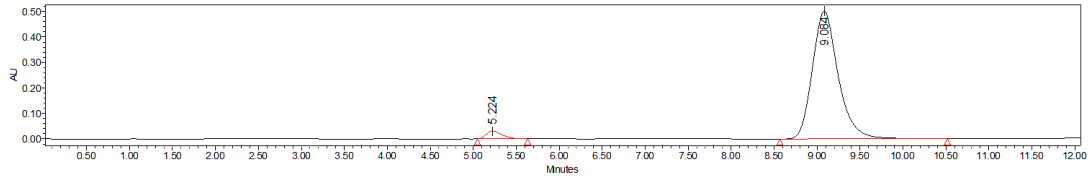
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-4-(4-chlorophenyl)-2,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: white solid, M.P. 213-218°C, 95% yield (46.8 mg), 93% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –344.7 (*c* 0.95, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 9.08 min, $t_{R(minor)}$ = 5.22 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (m, 2H), 7.46 (m, 3H), 7.25 – 7.17 (m, 4H), 7.11 (m, 2H), 7.01 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.00 (s, 1H), 4.57 (d, *J* = 8.8 Hz, 1H), 4.23 (m, 2H), 3.79 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.1, 163.9, 146.6, 137.7, 137.2, 137.2, 133.5, 130.0, 129.0, 128.3, 128.1, 128.0, 127.2, 126.5, 126.5, 123.8, 102.1, 86.5, 62.4, 52.6, 13.9;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{35}ClO_6+Na^+]$: 515.1237, found 515.1242;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{37}ClO_6+Na^+]$: 517.1208, found 517.1217;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2984, 1728, 1656, 1491, 1445, 1398, 1330, 1261, 1232, 1128, 1089, 1062, 1011, 970, 893, 830, 751, 699, 621, 513.

Racemic **4ag**:

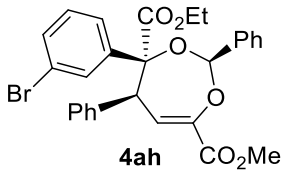


	Retention Time	Area	% Area
1	5.288	4439142	50.08
2	9.094	4424577	49.92

Chiral **4ag**:



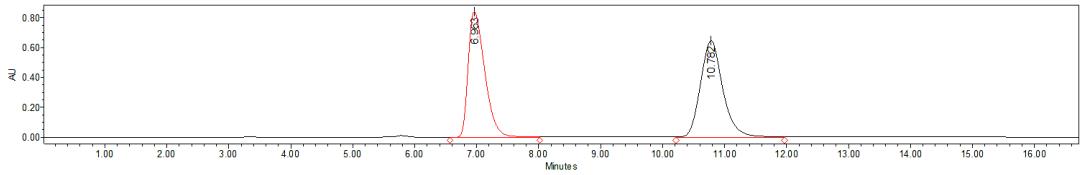
	Retention Time	Area	% Area
1	5.224	385338	3.55
2	9.084	10460766	96.45



4ah

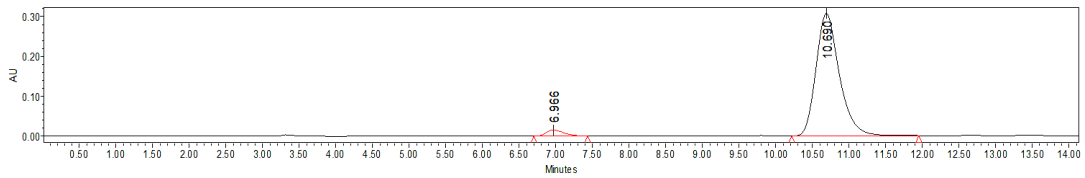
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-4-(3-bromophenyl)-2,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: colourless oil, 94% yield (50.5 mg), 93% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –319.8 (*c* 0.98, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 10.69 min, $t_{R(minor)}$ = 6.97 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (m, 2H), 7.45 (m, 4H), 7.25 – 7.14 (m, 4H), 7.09 – 6.96 (m, 4H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.00 (s, 1H), 4.56 (d, *J* = 8.8 Hz, 1H), 4.25 (m, 2H), 3.79 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.9, 163.9, 146.6, 140.8, 137.7, 137.1, 130.7, 129.9, 129.4, 129.0, 128.3, 128.3, 127.9, 127.2, 126.6, 123.7, 122.2, 102.1, 86.4, 62.5, 52.8, 52.4, 13.9;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{79}BrO_6+Na^+]$: 559.0732, found 559.0735;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{81}BrO_6+Na^+]$: 561.0712, found 561.0714;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2951, 1729, 1656, 1568, 1446, 1370, 1331, 1261, 1233, 1127, 1063, 1026, 976, 886, 773, 751, 697, 620.

Racemic **4ah**:

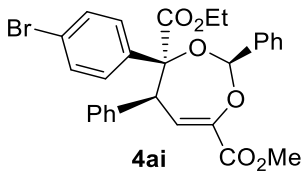


	Retention Time	Area	% Area
1	6.963	15594934	49.17
2	10.782	16118775	50.83

Chiral **4ah**:



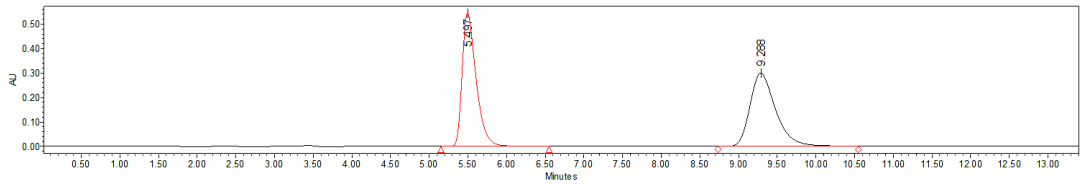
	Retention Time	Area	% Area
1	6.966	248860	3.53
2	10.690	6810469	96.47



4ai

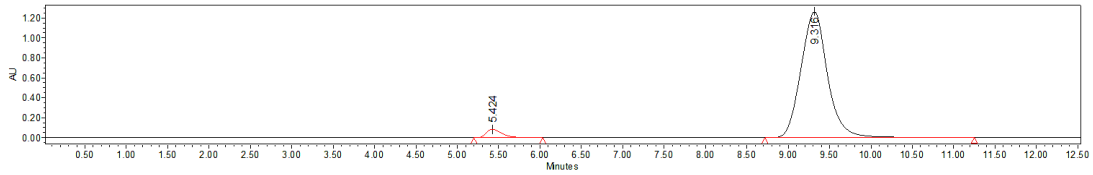
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-4-(4-bromophenyl)-2,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: white solid, M.P. 209-214°C, 94% yield (50.5 mg), 92% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –349.4 (*c* 0.97, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 9.32 min, $t_{R(minor)}$ = 5.42 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (m, 2H), 7.46 (m, 3H), 7.26 (m, 2H), 7.17 (m, 4H), 7.02 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.00 (s, 1H), 4.57 (d, *J* = 8.8 Hz, 1H), 4.23 (m, 2H), 3.79 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.0, 163.9, 146.6, 137.7, 137.7, 137.2, 131.1, 130.0, 129.0, 128.3, 128.0, 127.2, 126.8, 126.5, 123.8, 121.8, 102.0, 86.6, 62.4, 52.6, 52.4, 13.9;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{79}BrO_6+Na^+]$: 559.0732, found 559.0730;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{81}BrO_6+Na^+]$: 561.0712, found 561.0712;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2984, 1728, 1656, 1488, 1445, 1393, 1330, 1260, 1232, 1127, 1063, 1031, 1007, 942, 893, 826, 749, 698, 621, 511.

Racemic **4ai**:

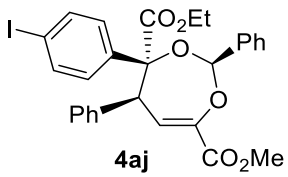


	Retention Time	Area	% Area
1	5.497	6819895	49.71
2	9.288	6899907	50.29

Chiral **4ai**:



	Retention Time	Area	% Area
1	5.424	1090688	3.75
2	9.316	28031168	96.25

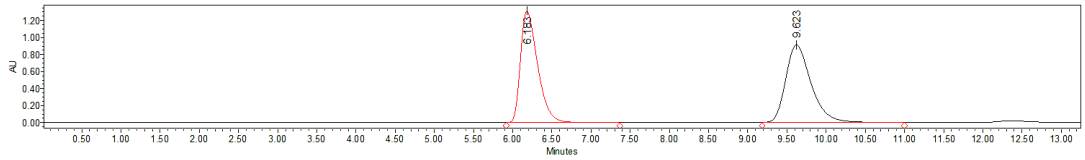


4aj

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-4-(4-iodophenyl)-2,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: white solid, M.P. 184-188°C, 88% yield (51.4 mg), 91% ee, >19:1 dr; $[\alpha]^{29}_{D}$ = –325.0 (*c* 0.93, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 9.76 min, $t_{R(minor)}$ = 6.26 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.79 (m, 2H), 7.54 – 7.37 (m, 5H), 7.19 (m, 2H), 7.09 – 6.96 (m, 5H), 6.93 (d, *J* = 8.8 Hz, 1H), 5.99 (s, 1H), 4.56 (d, *J* = 8.8 Hz, 1H), 4.23 (m, 2H), 3.79 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.0, 163.9, 146.6, 138.4, 137.7, 137.1, 137.0, 129.9, 129.0, 128.3, 128.0, 127.2, 127.0, 126.5, 123.8, 102.0, 93.5, 86.6, 62.4, 52.5, 52.4, 13.9;
ESI-HRMS calcd for $[C_{28}H_{25}IO_6+Na^+]$: 607.0594, found 607.0591;

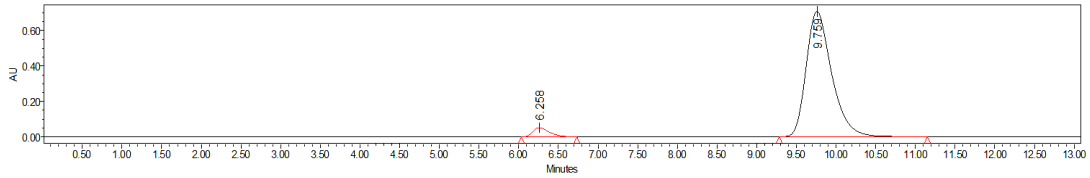
IR (film): $\tilde{\nu}$ (cm^{-1}) 2950, 1727, 1655, 1486, 1445, 1390, 1329, 1259, 1231, 1126, 1061, 1029, 1002, 941, 893, 822, 745, 698, 650, 620, 593, 562, 509.

Racemic **4aj**:

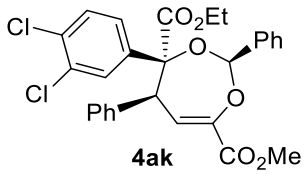


	Retention Time	Area	% Area
1	6.183	19913784	49.19
2	9.623	20567959	50.81

Chiral **4aj**:



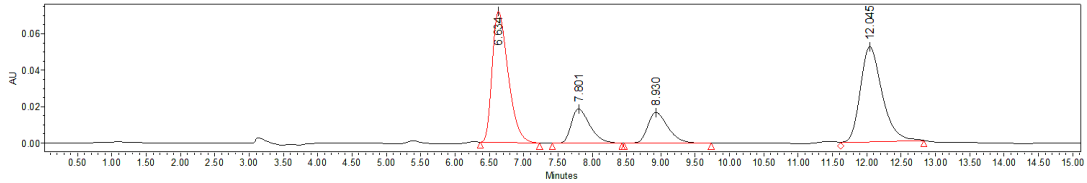
	Retention Time	Area	% Area
1	6.258	747818	4.54
2	9.759	15716894	95.46



4ak

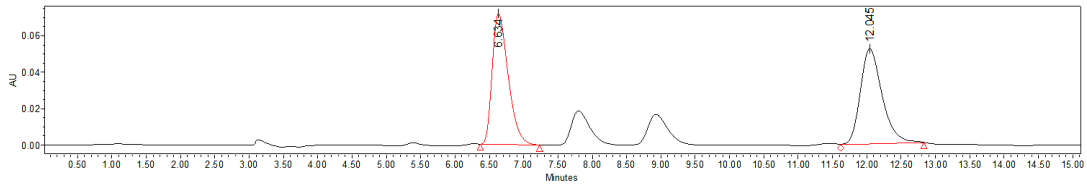
4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-4-(3,4-dichlorophenyl)-2,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: white solid, M.P. 146-150°C, 95% yield (50.1 mg), 96% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –317.4 (*c* 1.12, λ = 589 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 12.01 min, $t_{R(minor)}$ = 6.58 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.80 (m, 2H), 7.47 (m, 3H), 7.39 (m, 1H), 7.24 – 7.16 (m, 3H), 7.14 (m, 1H), 7.04 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 1H), 5.99 (s, 1H), 4.56 (d, *J* = 8.8 Hz, 1H), 4.26 (m, 2H), 3.79 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.7, 163.8, 146.7, 138.8, 137.5, 136.9, 132.3, 129.9, 129.9, 129.1, 128.4, 128.1, 127.4, 127.3, 126.5, 124.5, 123.5, 102.1, 86.1, 62.7, 52.5, 52.4, 13.9;
ESI-HRMS calcd for $[C_{28}H_{24}{}^{35}Cl_2O_6+Na^+]$: 549.0848, found 549.0847;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{35}Cl^{37}ClO_6+Na^+]$: 551.0818, found 551.0819;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{37}Cl_2O_6+Na^+]$: 553.0789, found 553.0806;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2984, 1728, 1656, 1470, 1383, 1330, 1261, 1232, 1127, 1063, 1024, 980, 886, 821, 751, 698, 624, 499.

Racemic **4ak**:



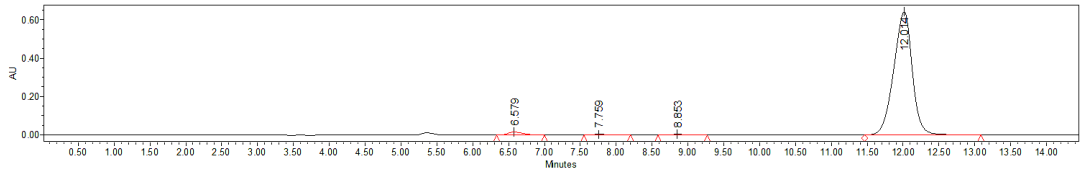
	Retention Time	Area	% Area
1	6.634	1161509	38.51
2	7.801	355340	11.78

3	8.930	347177	11.51
4	12.045	1152262	38.20

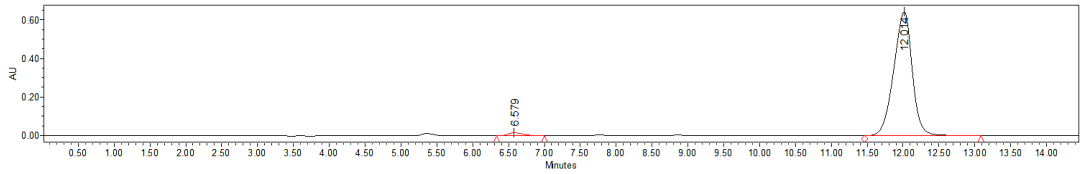


	Retention Time	Area	% Area
1	6.634	1161509	50.20
2	12.045	1152262	49.80

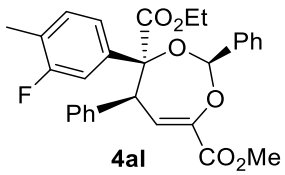
Chiral **4ak**:



	Retention Time	Area	% Area
1	6.579	241250	2.02
2	7.759	70803	0.59
3	8.853	69847	0.59
4	12.014	11552096	96.80



	Retention Time	Area	% Area
1	6.579	241250	2.05
2	12.014	11552096	97.95

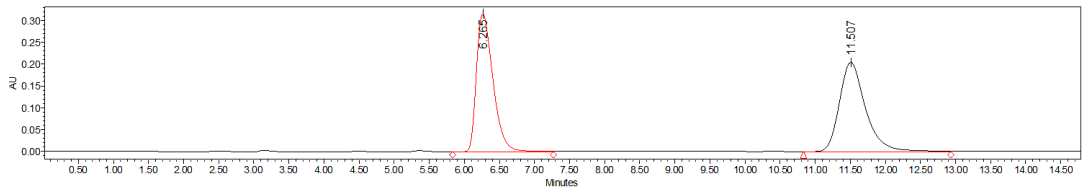


4al

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-4-(3-fluoro-4-methylphenyl)-2,5-diphenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1a**) scale reaction:
Result: colourless oil, 95% yield (46.6 mg), 99% ee, >19:1 dr; $[\alpha]^{28}_{D}$ = –346.6 (*c* 1.02, λ = 589 nm, CH_2Cl_2) HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 11.58 min, $t_{R(minor)}$ = 6.26 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (m, 2H), 7.46 (m, 3H), 7.22 (m, 2H), 7.08 – 6.88 (m, 7H), 5.99 (s, 1H), 4.58 (d, *J* = 8.8 Hz, 1H), 4.23 (m, 2H), 3.79 (s, 3H), 2.12 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.1, 164.0, 159.8 (*J*=242.8 Hz), 146.6, 138.3 (*J*=7.5 Hz), 137.8, 137.3, 130.9 (*J*=5.4 Hz), 129.9, 128.9, 128.3, 127.9, 127.1, 126.6, 124.0 (*J*=17.1 Hz), 123.9, 120.3, 120.3, 112.3, 112.1 (*J*=24.9 Hz), 102.1, 86.3 (*J*=1.4 Hz), 62.4, 52.6, 52.4, 14.1, 13.9;
^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –117.00;

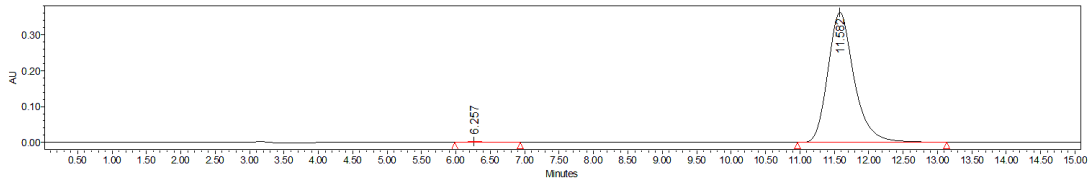
ESI-HRMS calcd for [$C_{29}H_{27}FO_6$+Na^+]: 513.1689 found 513.1688;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2984, 1728, 1655, 1580, 1500, 1445, 1412, 1330, 1233, 1121, 1061, 1004, 877, 819, 748, 698, 661, 618, 557, 517.

Racemic **4al**:

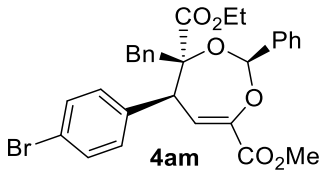


	Retention Time	Area	% Area
1	6.265	5152532	49.42
2	11.507	5273908	50.58

Chiral **4al**:



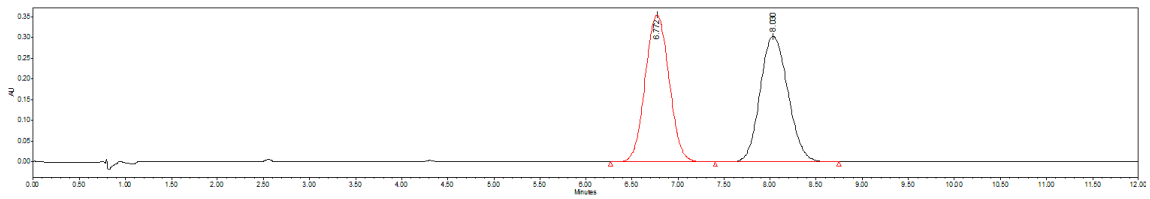
	Retention Time	Area	% Area
1	6.257	55226	0.57
2	11.582	9553144	99.43



4am

4-Ethyl 7-methyl (2*S*,4*R*,5*S*)-4-benzyl-5-(4-bromophenyl)-2-phenyl-4,5-dihydro-1,3-dioxepine-4,7-dicarboxylate
0.1 mmol (**1m**) scale reaction:
Result: white solid, M.P. 51-56°C, 31% yield (17.1 mg), 84% ee, >19:1 dr; $[\alpha]^{19}_D$ = –110.7 (*c* 0.20, λ = 589 nm, CH_2Cl_2); UPC^2 (Daicel chiralcel OX-3, CO_2/MeOH 95/5, 1.5 mL/min, λ = 254 nm, $t_{R(major)}$ = 7.91 min, $t_{R(minor)}$ = 6.77 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (m, 2H), 7.60 – 7.51 (m, 2H), 7.43 (m, 5H), 7.23 (m, 3H), 7.10 – 6.96 (m, 2H), 6.73 (d, *J* = 8.8 Hz, 1H), 6.01 (s, 1H), 4.34 (d, *J* = 8.8 Hz, 1H), 3.97 (m, 2H), 3.76 (s, 3H), 2.86 – 2.66 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.2, 163.9, 147.5, 137.9, 137.5, 135.3, 131.8, 131.8, 130.3, 128.7, 128.1, 127.8, 127.1, 126.5, 123.0, 121.9, 102.0, 85.2, 61.7, 52.5, 50.5, 45.3, 13.7;
ESI-HRMS calcd for [$C_{29}H_{27}{}^{79}BrO_6$+Na^+]: 573.0889, found 573.0900;
ESI-HRMS calcd for [$C_{29}H_{27}{}^{81}BrO_6$+Na^+]: 575.0868, found 575.0881;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2956, 2361, 1727, 1654, 1489, 1451, 1330, 1262, 1194, 1123, 1096, 1076, 1011, 955, 899, 804, 746, 698, 648, 516.

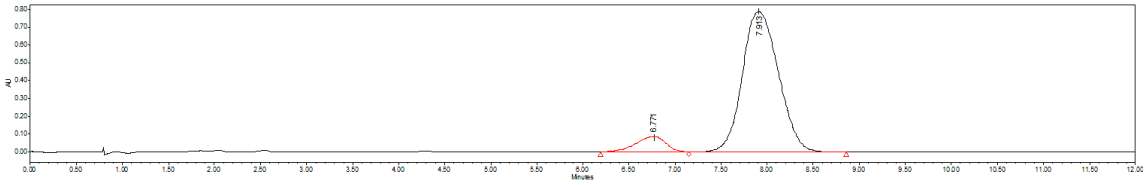
Racemic **4am**:



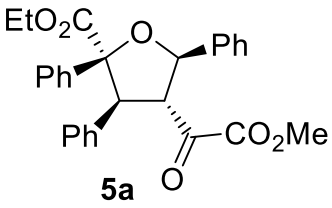
	Retention Time	Area	% Area
1	6.772	6397253	50.11

2	8.030	6369811	49.89

Chiral **4am**:



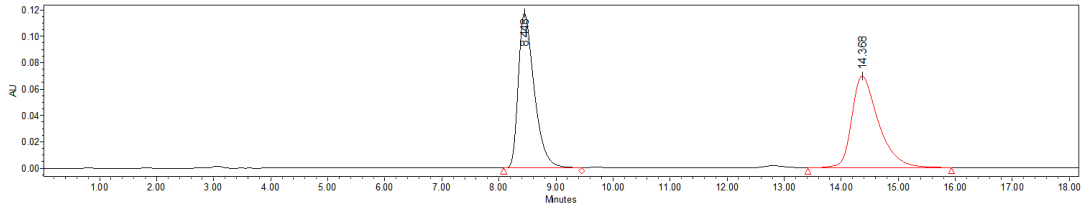
	Retention Time	Area	% Area
1	6.771	1901067	8.16
2	7.913	21405960	91.84



5a

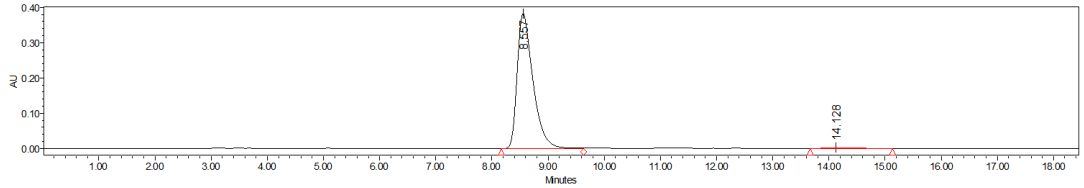
Ethyl (2*S*,3*S*,4*R*,5*R*)-4-(2-methoxy-2-oxoacetyl)-2,3,5-triphenyltetrahydrofuran-2-carboxylate
0.1 mmol (**4a**) scale reaction:
Result: white solid, M.P. 111-116°C, 93% yield (42.6 mg), 98% ee, >19:1 dr; $[\alpha]^{25}$ = +272.9 (*c* 0.82, λ = 405 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 8.56 min, $t_{R(minor)}$ = 14.13 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.54 (m, 2H), 7.43 (m, 2H), 7.35 (m, 1H), 7.28 (m, 2H), 7.08 (m, 3H), 7.01 (m, 5H), 5.59 (d, *J* = 8.8 Hz, 1H), 4.70 (d, *J* = 6.4 Hz, 1H), 4.26 (m, 2H), 4.14 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.67 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 192.2, 172.8, 160.8, 138.9, 138.7, 136.7, 129.2, 128.7, 128.3, 127.9, 127.6, 127.4, 126.9, 126.0, 126.0, 90.7, 80.0, 63.4, 62.4, 56.3, 53.0, 14.0;
ESI-HRMS calcd for [$C_{28}H_{26}O_6$+Na^+]: 481.1627, found 481.1621;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3033, 1727, 1603, 1495, 1451, 1369, 1240, 1074, 1029, 855, 721, 700, 507.

Racemic **5a**:



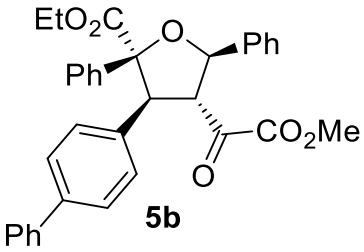
	Retention Time	Area	% Area
1	8.448	2273534	50.11
2	14.368	2263376	49.89

Chiral **5a**:



	Retention Time	Area	% Area

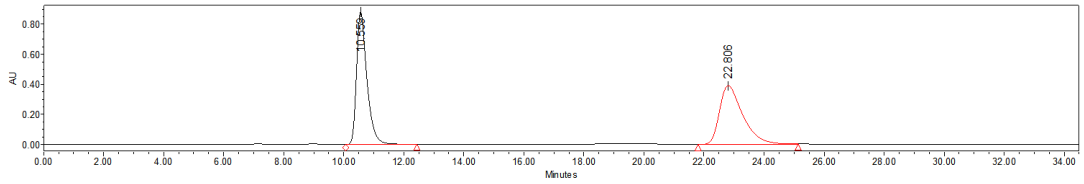
1	8.557	7432013	98.93
2	14.128	80755	1.07



5b

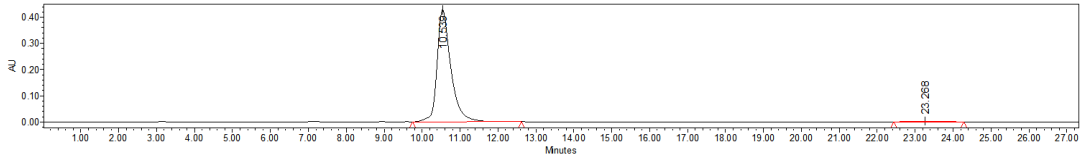
Ethyl (2*S*,3*S*,4*R*,5*R*)-3-([1,1'-biphenyl]-4-yl)-4-(2-methoxy-2-oxoacetyl)-2,5-diphenyltetrahydrofuran-2-carboxylate
0.065 mmol (**4o**) scale reaction:
Result: colourless oil, 85% yield (29.5 mg), 97% ee, >19:1 dr; $[\alpha]^{25}$ = +593.9 (*c* 0.52, λ = 405 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 10.54 min, $t_{R(minor)}$ = 23.27 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (m, 2H), 7.44 (m, 4H), 7.39 – 7.26 (m, 8H), 7.09 (m, 5H), 5.62 (d, *J* = 8.4 Hz, 1H), 4.75 (d, *J* = 6.4 Hz, 1H), 4.27 (m, 2H), 4.17 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.69 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 192.1, 172.8, 160.9, 140.4, 139.5, 138.7, 137.9, 136.7, 129.6, 128.7, 128.6, 128.3, 127.7, 127.5, 127.2, 126.8, 126.5, 126.1, 126.0, 90.7, 80.1, 63.3, 62.4, 56.1, 53.0, 14.0;
ESI-HRMS calcd for [$C_{34}H_{30}O_6$+Na^+]: 557.1940, found 557.1943;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3032, 1727, 1602, 1489, 1449, 1370, 1242, 1082, 1028, 849, 742, 700, 506.

Racemic **5b**:

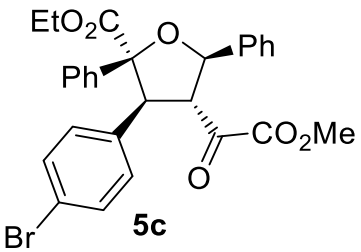


	Retention Time	Area	% Area
1	10.559	21099467	50.25
2	22.806	20889376	49.75

Chiral **5b**:



	Retention Time	Area	% Area
1	10.539	10832645	98.41
2	23.268	175218	1.59

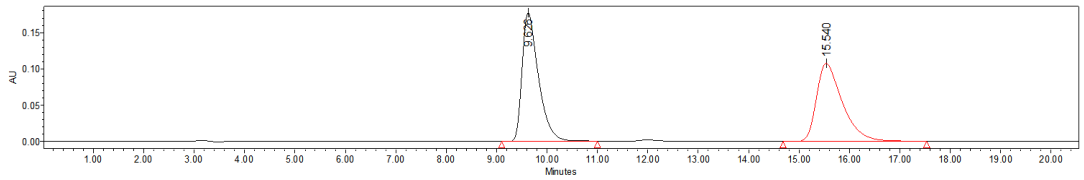


5c

Ethyl (2*S*,3*S*,4*R*,5*R*)-3-(4-bromophenyl)-4-(2-methoxy-2-oxoacetyl)-2,5-diphenyltetrahydrofuran-2-carboxylate

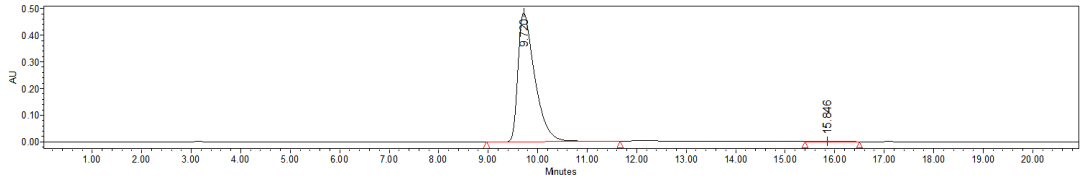
0.077 mmol (**4m**) scale reaction:
Result: white solid, M.P. 222-227°C, 84% yield (34.7 mg), 99% ee, >19:1 dr; $[\alpha]^{25}$ = +329.9 (*c* 0.70, λ = 405 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 9.72 min, $t_{R(minor)}$ = 15.85 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (m, 2H), 7.43 (m, 2H), 7.39 – 7.34 (m, 1H), 7.27 (m, 2H), 7.13 (m, 5H), 6.89 (m, 2H), 5.59 (d, *J* = 8.4 Hz, 1H), 4.67 (d, *J* = 6.4 Hz, 1H), 4.25 (m, 2H), 4.05 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.72 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 191.7, 172.6, 160.8, 138.6, 138.1, 136.4, 131.0, 130.8, 128.7, 128.4, 127.9, 127.7, 125.9, 125.9, 120.9, 90.6, 79.9, 63.3, 62.5, 55.6, 53.1, 14.0;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{79}BrO_6+Na^+]$: 559.0732, found 559.0728;
ESI-HRMS calcd for $[C_{28}H_{25}{}^{81}BrO_6+Na^+]$: 561.0712, found 561.0706;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2983, 1729, 1491, 1450, 1370, 1244, 1074, 1030, 840, 737, 700, 513.

Racemic **5c**:

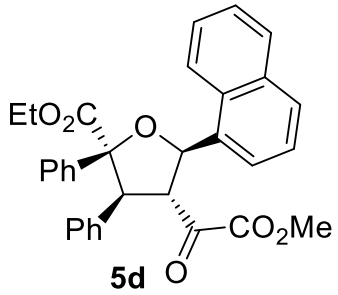


	Retention Time	Area	% Area
1	9.626	3995576	50.97
2	15.540	3844262	49.03

Chiral **5c**:



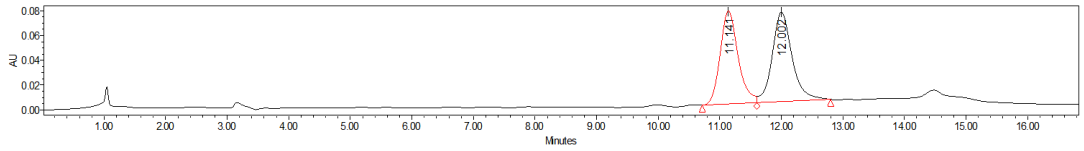
	Retention Time	Area	% Area
1	9.720	11349240	99.39
2	15.846	69178	0.61



5d

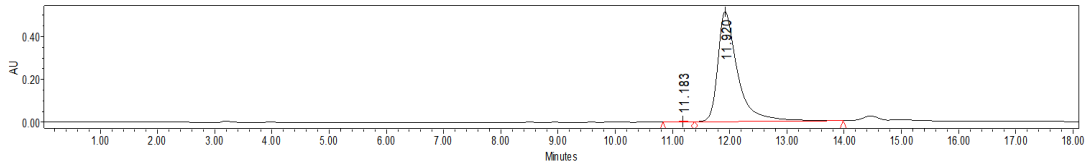
Ethyl (2*S*,3*S*,4*R*,5*R*)-4-(2-methoxy-2-oxoacetyl)-5-(naphthalen-1-yl)-2,3-diphenyltetrahydrofuran-2-carboxylate
0.076 mmol (**4aa**) scale reaction:
Result: colourless oil, 88% yield (34.0 mg), 99% ee, >19:1 dr; $[\alpha]^{26}$ = +360.2 (*c* 0.61, λ = 405 nm, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 11.92 min, $t_{R(minor)}$ = 11.18 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.13 (m, 1H), 8.01 (m, 1H), 7.88 (m, 2H), 7.53 (m, 3H), 7.31 (m, 2H), 7.06 (m, 8H), 6.34 (d, *J* = 8.4 Hz, 1H), 4.76 (d, *J* = 6.4 Hz, 1H), 4.52 (dd, *J* = 8.4, 6.4 Hz, 1H), 4.36 (m, 2H), 3.62 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 192.2, 172.9, 160.8, 138.7, 136.7, 133.8, 129.3, 129.2, 128.8, 127.9, 127.6, 127.4, 126.9, 126.6, 126.3, 125.9, 125.2, 123.8, 123.6, 90.9, 77.7, 62.4, 60.8, 57.2, 53.0, 14.1;
ESI-HRMS calcd for $[C_{32}H_{28}O_6+Na^+]$: 531.1784, found 531.1787;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2983, 1728, 1600, 1495, 1450, 1236, 1067, 1028, 858, 776, 724, 700, 591, 506.

Racemic **5d**:

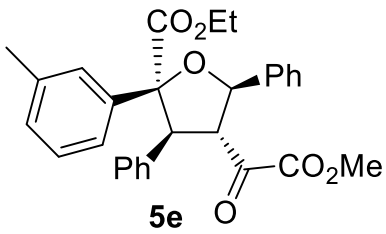


	Retention Time	Area	% Area
1	11.141	1513294	48.34
2	12.002	1616925	51.66

Chiral **5d**:



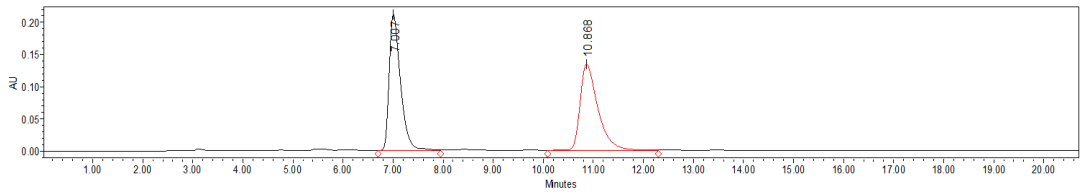
	Retention Time	Area	% Area
1	11.183	44431	0.36
2	11.920	12331867	99.64



5e

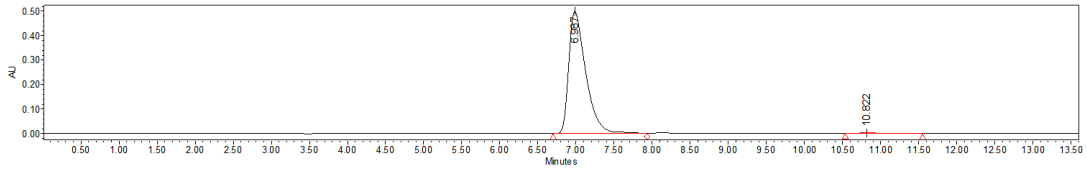
Ethyl (2*S*,3*S*,4*R*,5*R*)-4-(2-methoxy-2-oxoacetyl)-3,5-diphenyl-2-(m-tolyl)tetrahydrofuran-2-carboxylate
0.083 mmol (**4ac**) scale reaction:
Result: colourless oil, 85% yield (33.3 mg), 99% ee, >19:1 dr; $[\alpha]^{25}$ = +278.3 (*c* 0.58, λ = 405 nm, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 6.99 min, $t_{R(minor)}$ = 10.82 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.55 (m, 2H), 7.43 (m, 2H), 7.35 (m, 1H), 7.07 (m, 2H), 7.02 (m, 6H), 6.87 (m, 1H), 5.57 (d, *J* = 8.4 Hz, 1H), 4.68 (d, *J* = 6.4 Hz, 1H), 4.26 (m, 2H), 4.13 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.67 (s, 3H), 2.16 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 192.2, 172.9, 160.9, 138.9, 138.7, 137.1, 136.6, 129.2, 128.7, 128.3, 128.1, 127.8, 127.4, 126.8, 126.7, 126.1, 123.1, 90.7, 80.0, 63.4, 62.3, 56.3, 53.0, 21.3, 14.0;
ESI-HRMS calcd for $[C_{29}H_{28}O_6+Na^+]$: 495.1784, found 495.1782;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3729, 3033, 1972, 1729, 1605, 1493, 1453, 1231, 1081, 1029, 881, 754, 699, 512, 431.

Racemic **5e**:

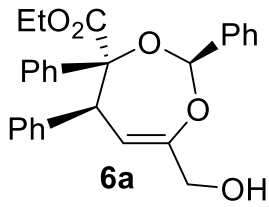


	Retention Time	Area	% Area
1	7.007	3321807	50.25
2	10.868	3288214	49.75

Chiral **5e**:



	Retention Time	Area	% Area
1	6.987	7743197	99.43
2	10.822	44359	0.57



6a

Ethyl (2*S*,4*S*,5*S*)-7-(hydroxymethyl)-2,4,5-triphenyl-4,5-dihydro-1,3-dioxepine-4-carboxylate

0.1 mmol (**4a**) scale reaction:

Result: white solid, M.P. 56-60°C, 76% yield (32.7 mg), 99% ee, >19:1 dr; $[\alpha]^{25}$ = –956.2 (*c* 0.69, λ = 405 nm, CH_2Cl_2); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm, $t_{R(major)}$ = 14.29 min, $t_{R(minor)}$ = 12.26 min);

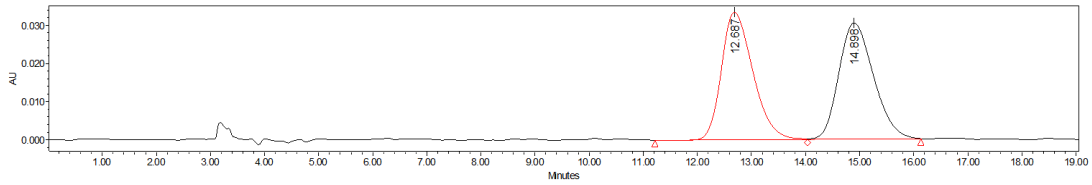
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.84 (m, 2H), 7.47 (m, 3H), 7.37 (m, 2H), 7.30 (m, 2H), 7.13 (m, 3H), 6.96 (m, 3H), 6.12 (s, 1H), 5.69 (d, *J* = 8.8 Hz, 1H), 4.61 (d, *J* = 8.8 Hz, 1H), 4.29 (m, 1H), 4.19 (m, 2H), 4.09 (m, 1H), 4.03 (m, 1H), 1.16 (t, *J* = 7.2 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Acetone-d_6) δ 172.1, 158.9, 141.6, 140.7, 140.3, 131.0, 129.5, 129.0, 128.7, 128.3, 128.2, 127.5, 127.0, 126.3, 110.1, 102.4, 87.7, 63.2, 62.5, 52.8, 14.4;

ESI-HRMS calcd for $[C_{27}H_{26}O_5+Na^+]$: 453.1678, found 453.1669;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3398, 3063, 2929, 1729, 1600, 1493, 1450, 1331, 1232, 1176, 1096, 1022, 880, 829, 753, 698, 615, 552.

Racemic **6a**:



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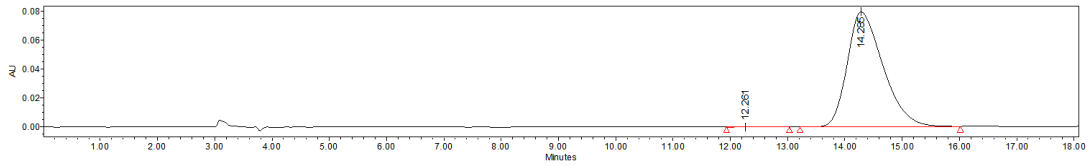
2	14.898	1353241	50.10

Chiral **6a**:



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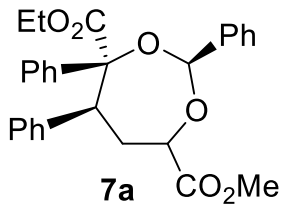
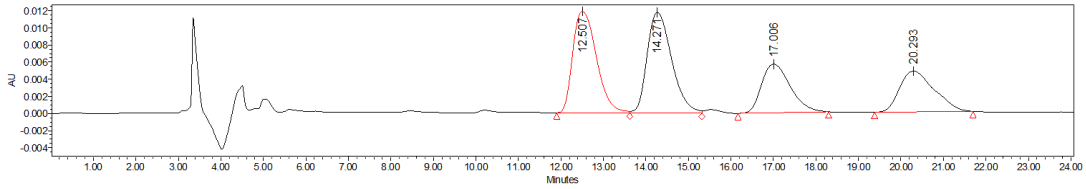


7a

4-Ethyl 7-methyl (2*S*,4*S*,5*S*)-2,4,5-triphenyl-1,3-dioxepane-4,7-dicarboxylate
0.1 mmol (**4a**) scale reaction:
Result: white solid, 98% yield (45.1 mg), 2:1 dr, 99/99% ee, HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, λ = 254 nm, t_{R1} = 12.51 min, t_{R2} = 14.27 min, t_{R3} = 17.01 min, t_{R4} = 20.29 min);
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (m, 2H), 7.43 (m, 6H), 7.14 (m, 2H), 7.09 – 7.01 (m, 5H), 6.44 (s, 1H), 4.61 (m, 2H), 4.18 (m, 2H), 3.71 (s, 3H), 2.93 – 2.72 (m, 1H), 2.55 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 173.5, 172.4, 139.2, 137.6, 130.0, 128.4, 128.1, 127.9, 127.3, 127.1, 126.9, 126.5, 125.8, 96.0, 86.6, 79.0, 72.8, 62.1, 52.0, 49.8, 36.1, 34.9, 13.9;
ESI-HRMS calcd for [$C_{28}H_{28}O_6$+Na^+]: 483.1784, found 483.1779;
IR (film): $\tilde{\nu}$ (cm^{-1}) 2952, 1728, 1494, 1448, 1364, 1234, 1149, 1119, 1026, 747, 699, 569.

Racemic **7a**:



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1	12.507	458773	31.31
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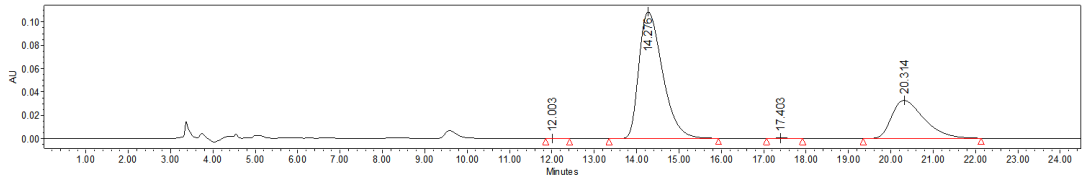
3	17.006	266227	18.17
4	20.293	268756	18.34

Chiral **7a**:



	Retention Time	Area	% Area
1	12.003	3595	0.06
2	14.276	4193693	70.73
3	17.403	7821	0.13
4	20.314	1723980	29.08

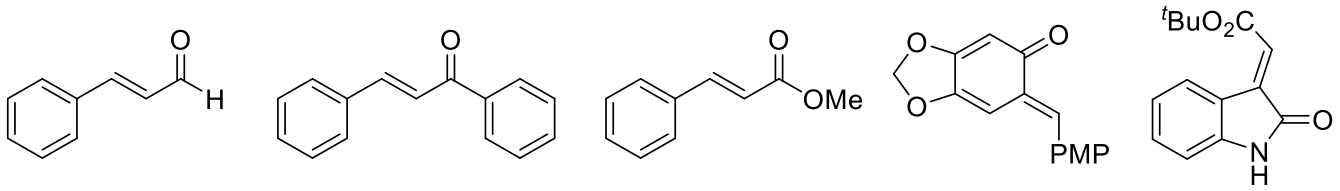
	Retention Time	Area	% Area
1	12.003	3595	0.09
2	14.276	4193693	99.91

	Retention Time	Area	% Area
1	17.403	7831	0.45

2	20.314	1723980	99.55

10. Other α,β-unsaturated carbonyl compounds

Other α,β-unsaturated carbonyl compounds have been tested in this catalytic system, but no desired products were obtained. They are listed below. β,γ-Unsaturated α-ketoester was a proper 1,4-dipolarophile with suitable reactivity in this [4+3]-cycloaddition.[4]



11. References

1 Synthetic method of chiral *N*,*N*′ -dioxide ligands :(a) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett,* 2005, 2445; (b) Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie and X. M. Feng, *Angew. Chem. Int. Ed.,* 2008, **47**, 1308; (c) K. Zheng, B. Qin, X. H. Liu and X. M. Feng, *J. Org. Chem.,* 2007, **72**, 8478; (d) X. Zhang, D. H. Chen, X. H. Liu and X. M. Feng, *J. Org. Chem.,* 2007, **72**, 5227; (e) X. Zhou, D. J. Shang, Q. Zhang, L. L. Lin, X. H. Liu and X. M. Feng, *Org. Lett.,* 2009, **11**, 1401.

2 (a) B. W. Hu, J. Li, W. D. Cao, Q. C. Lin, J. Yang, L. L. Lin, X. H. Liu and X. M. Feng, *Adv. Synth. Catal.,* 2018, **360**, 2831; (b) S. L. Ge, W. D. Cao, T. F. Kang, B. W. Hu, H. Zhang, Z. S. Su, X. H. Liu and X. M. Feng, *Angew. Chem. Int. Ed.,* 2019, **58**, 4017.

3 (a) J. Yang, P. R. Ruan, W. Yang, X. M. Feng and X. H. Liu, *Chem. Sci.,* 2019, **10**, 10305; b) M. Y. Hu, C. F. Ni, L. C. Li, Y. X. Han and J. B. Hu, *J. Am. Chem. Soc.,* 2015, **137**, 14496.

4 For selected reviews on β,γ-unsaturated α-ketoesters: (a) G. Desimoni, G. Faita and P. Quadrelli, *Chem. Rev.,* 2013, **113**, 5924; (b) B. Eftekhari-Sis and M. Zirak, *Chem. Rev.,* 2015, **115**, 151; for selected examples of β,γ-unsaturated α-ketoesters as 1,4-dipolarophile: (c) X. Y. Hao, X. H. Liu, W. Li, F. Tan, Y. Y. Chu, X. H. Zhao, L. L. Lin and X. M. Feng, *Org. Lett.*, 2014, **16**, 134; (d) S. L. Ge, W. D. Cao, T. F. Kang, B. W. Hu, H. Zhang, Z. S. Su, X. H. Liu and X. M. Feng, *Angew. Chem. Int. Ed.* 2019, **58**, 4017; (e) J. Li, L. L. Lin, B. W. Hu, X. J. Lian, G. Wang, X. H. Liu and X. M. Feng, *Angew. Chem. Int. Ed.* 2016, **55**, 6075.

12. Author Contributions

Chaoran Xu: data curation (lead), formal analysis (lead), investigation (lead), writing of original draft (lead)

Jianglin Qiao: data curation (supporting)

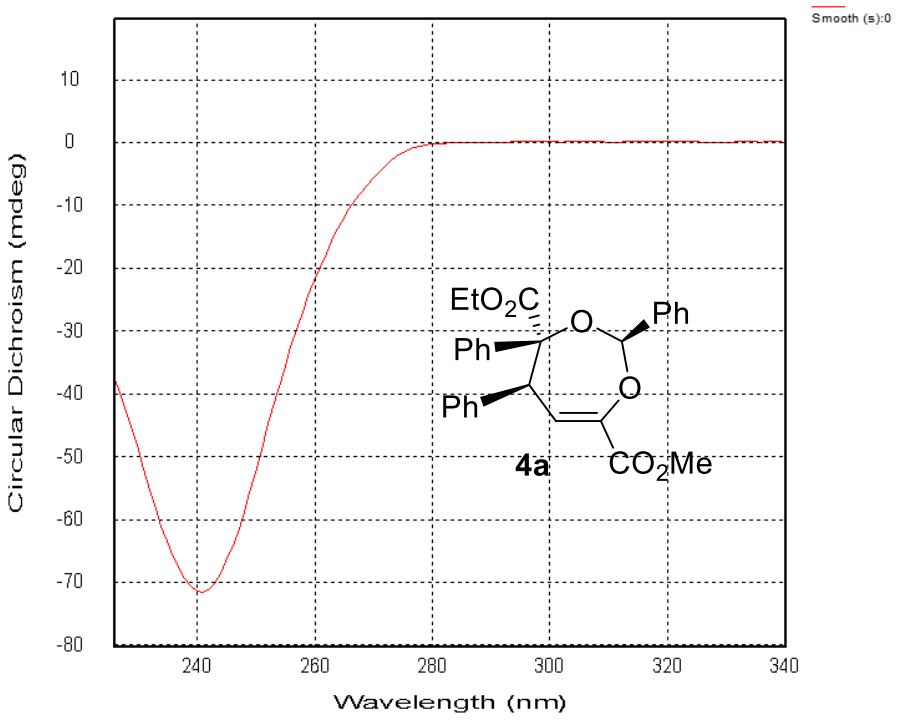
Shunxi Dong*: writing – review & editing (lead)

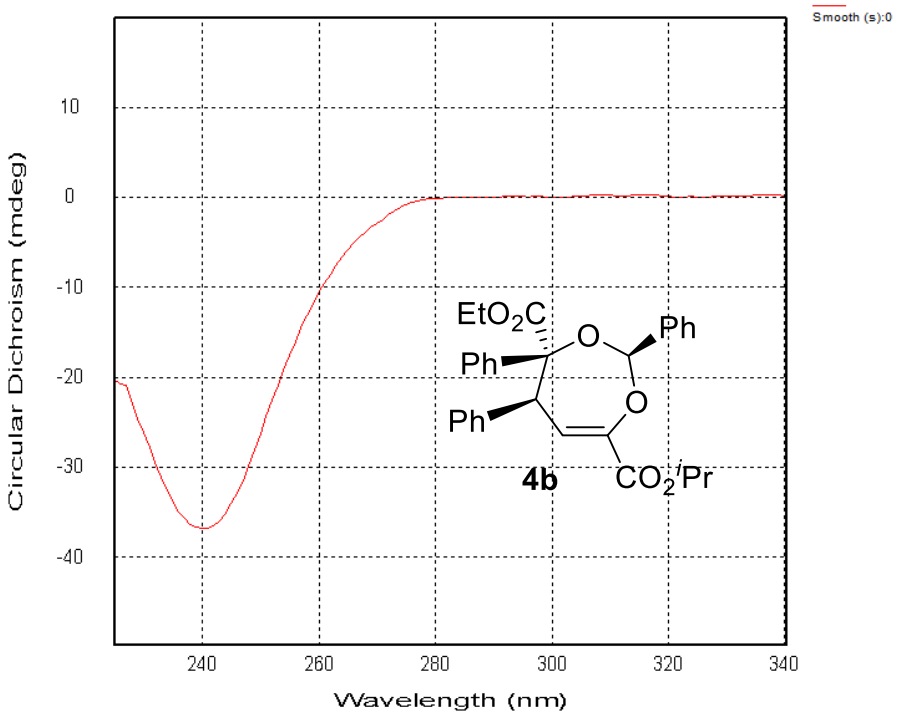
Yuqiao Zhou: X-ray diffraction crystal analysis (lead)

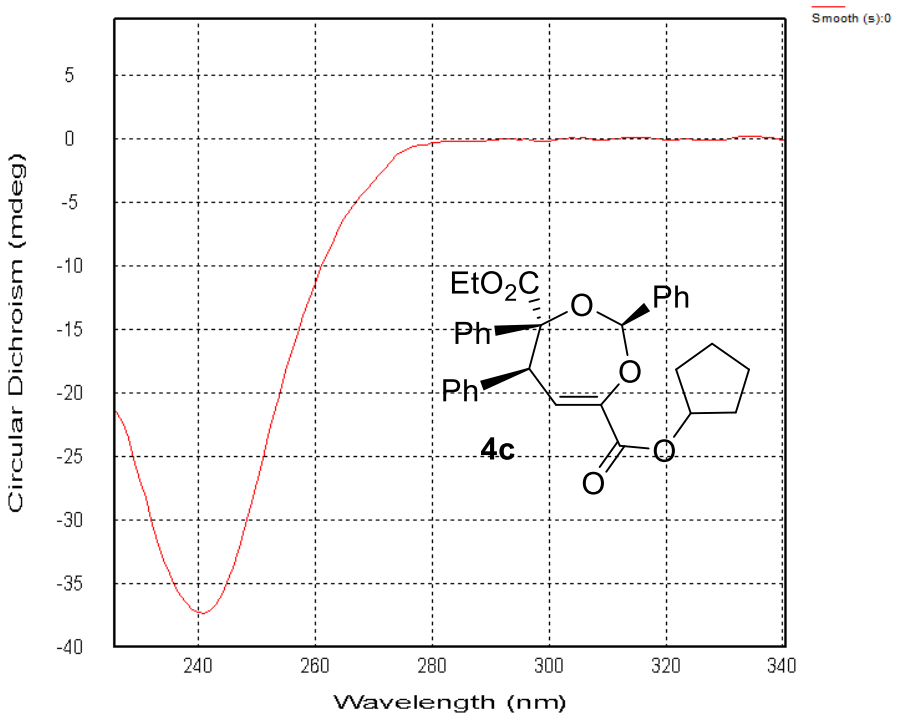
Xiaohua Liu: project administration (equal)

Xiaoming Feng*: funding acquisition (lead), project administration (equal)

13. Copies of CD Spectra for the Products in DCM



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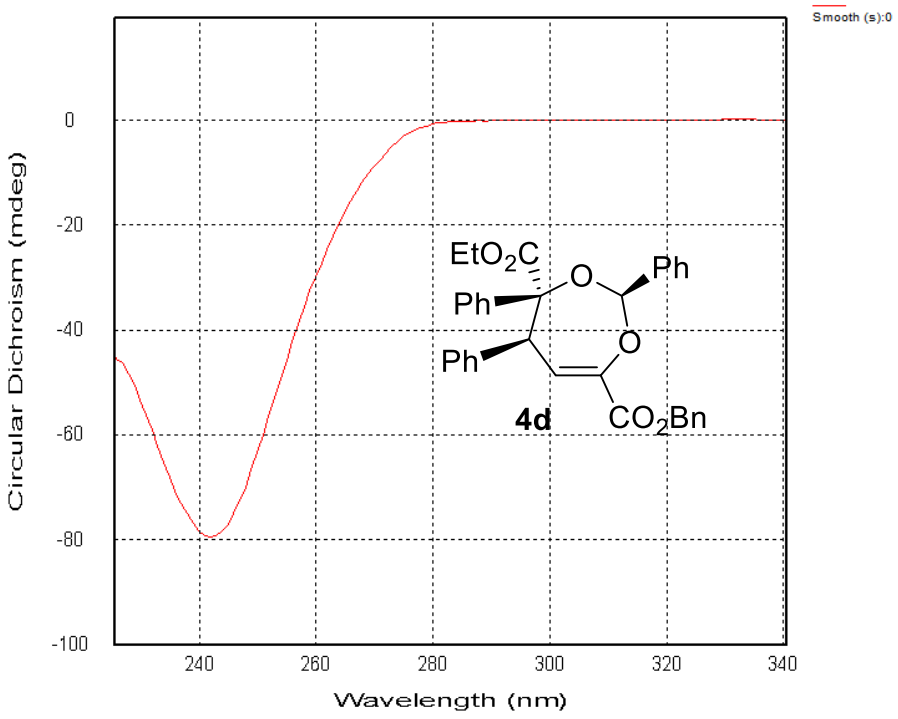
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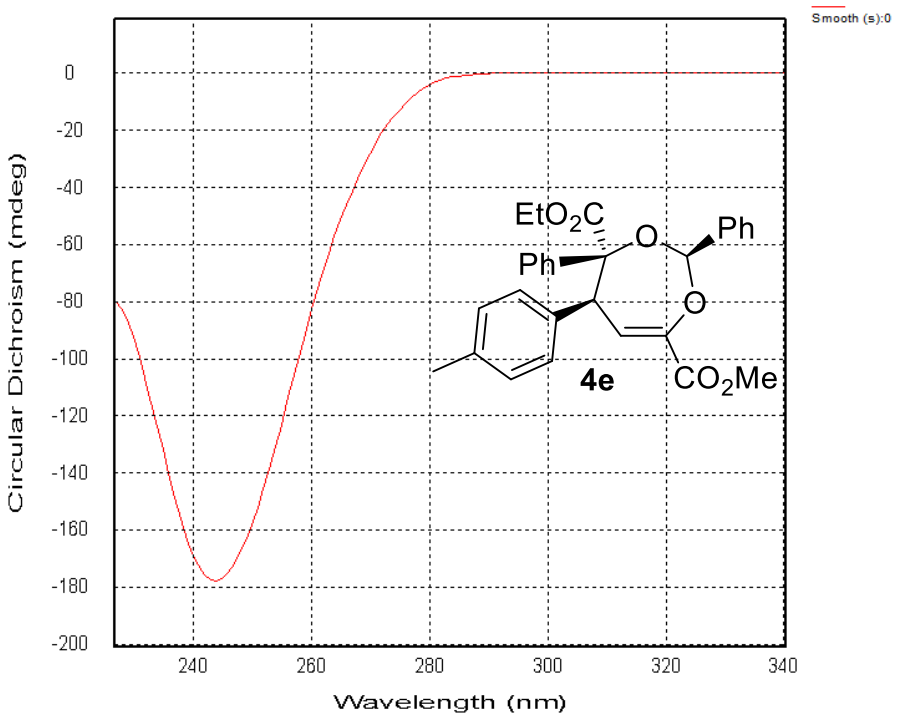
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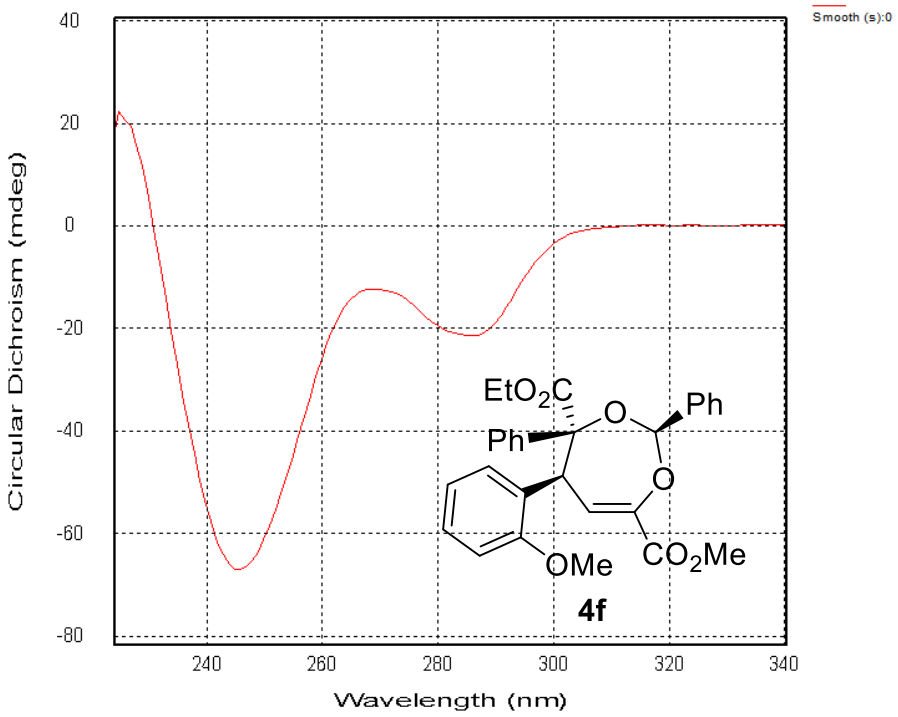
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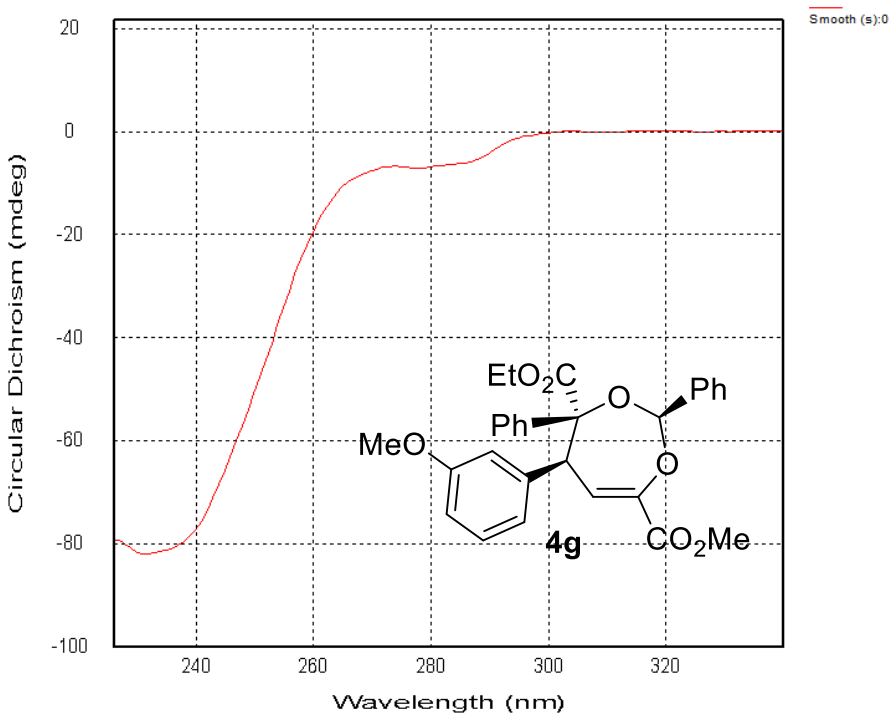
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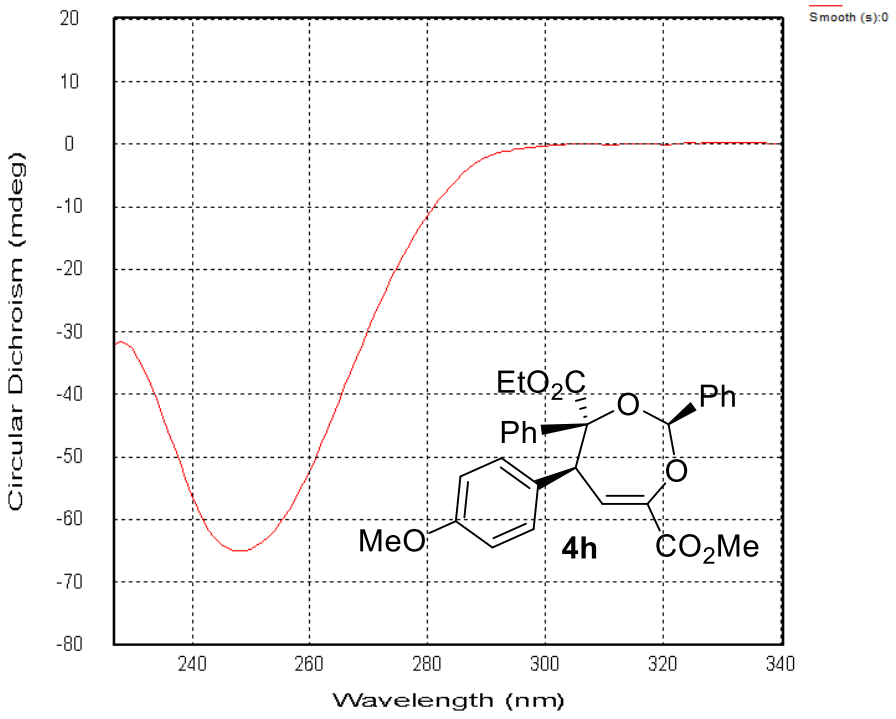
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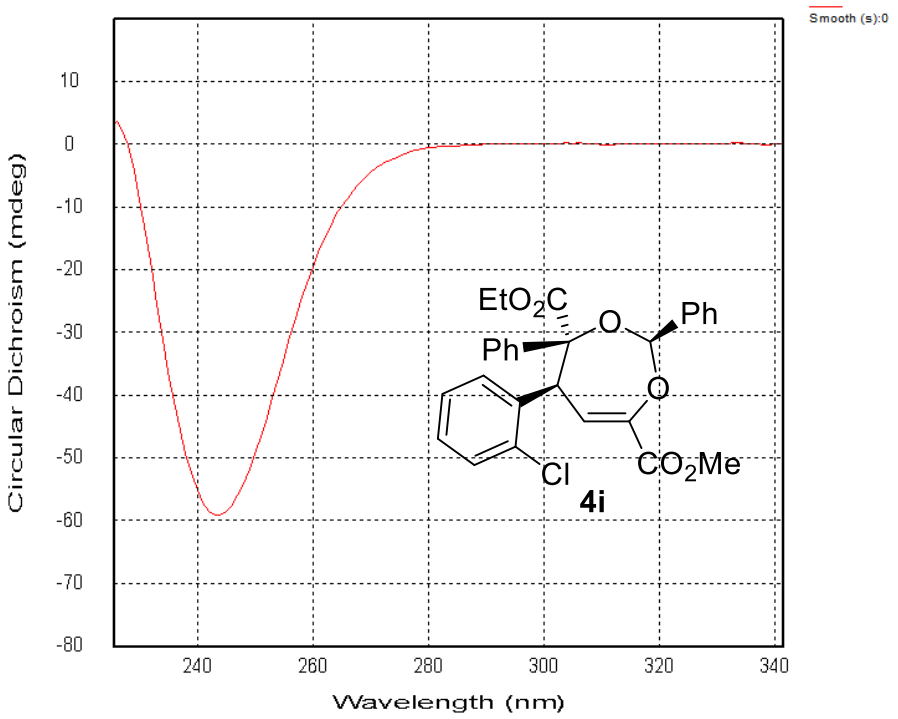
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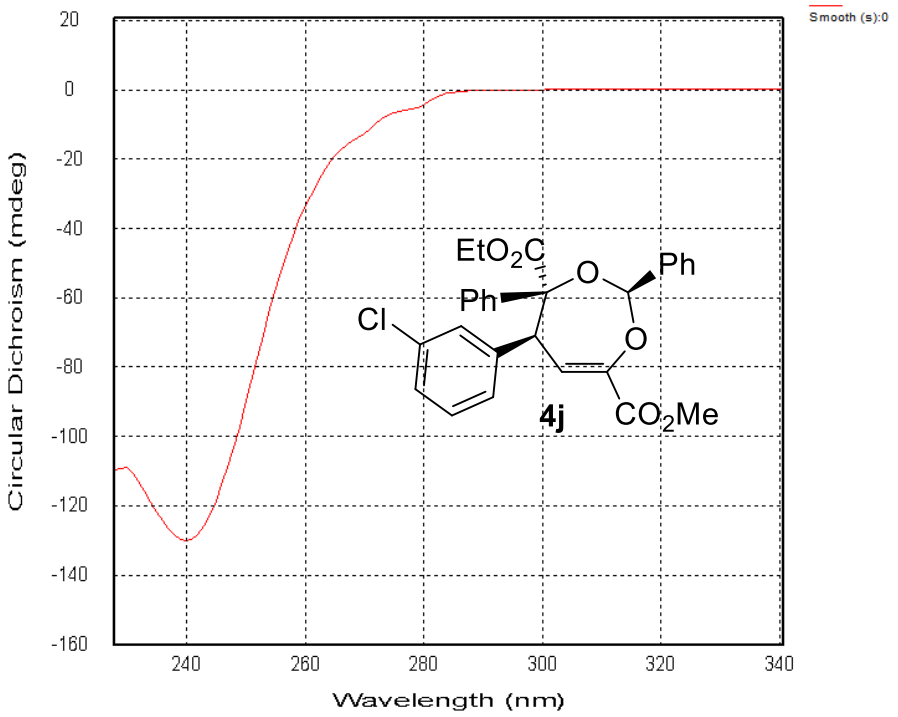
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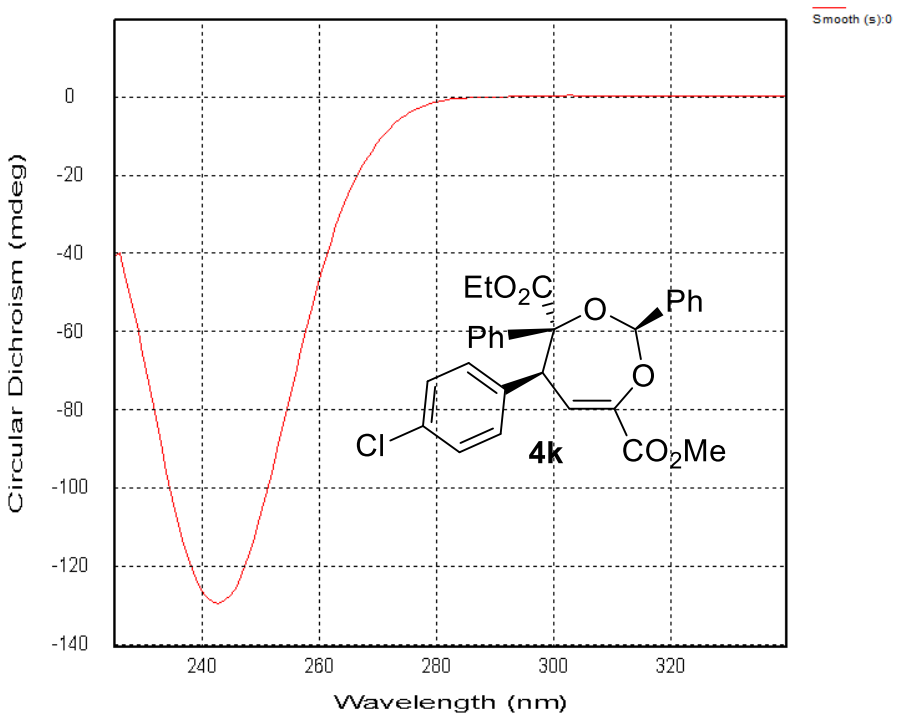
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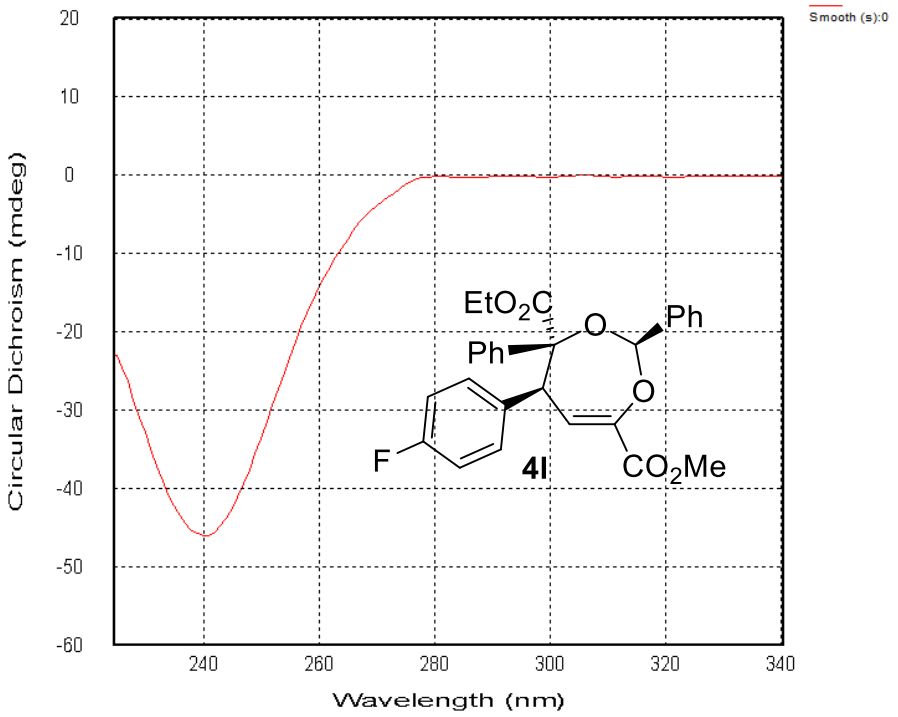
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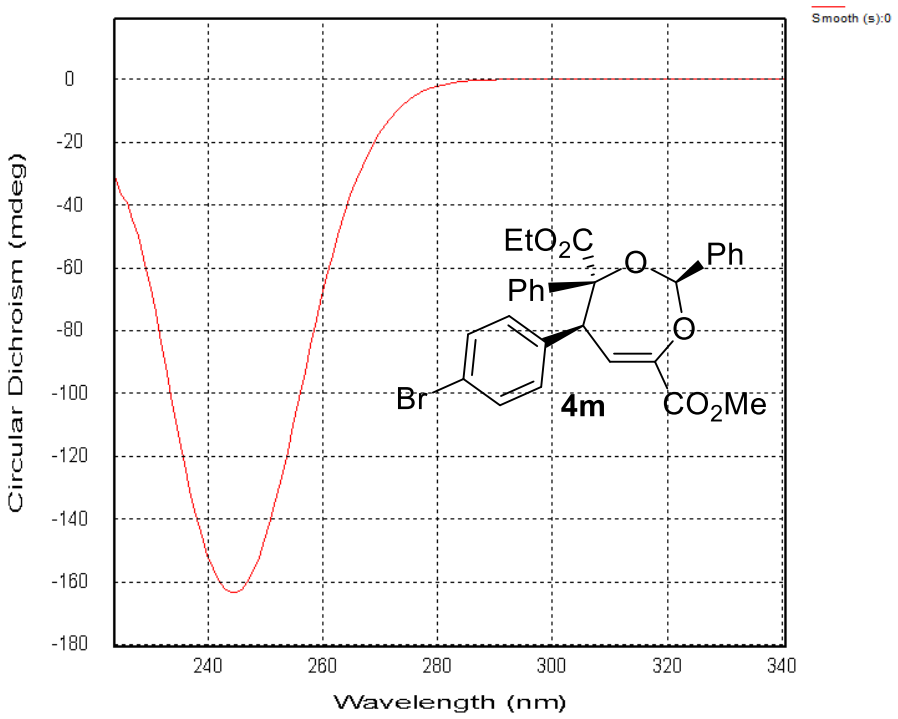
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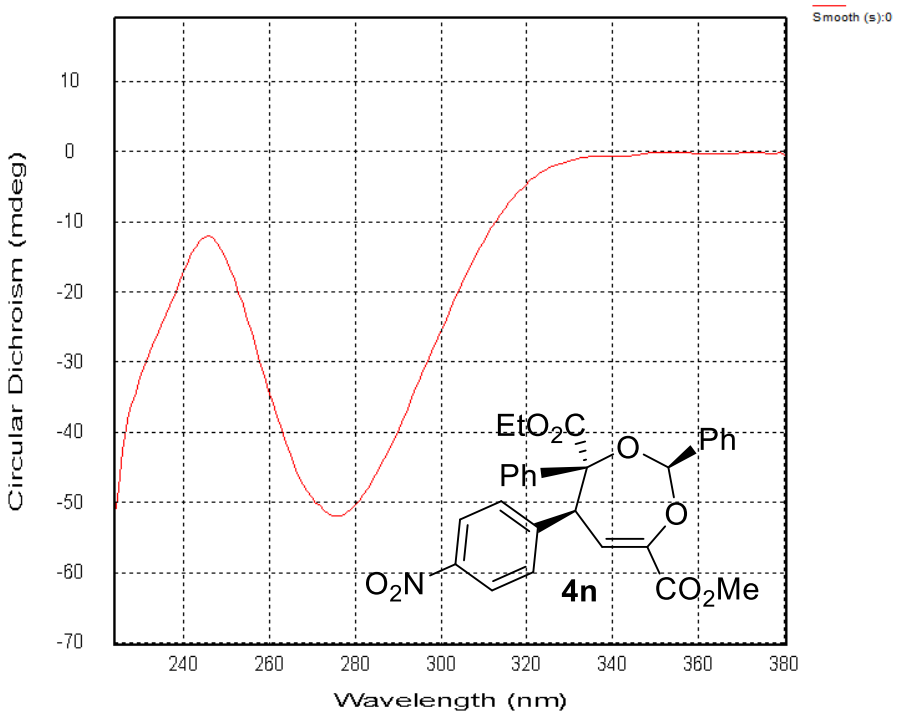
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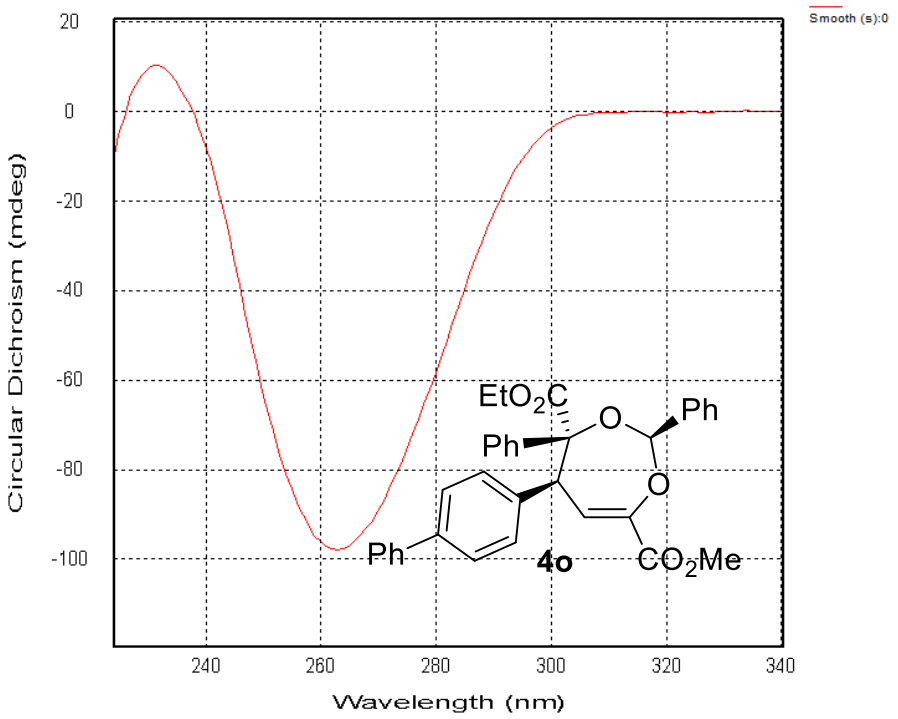
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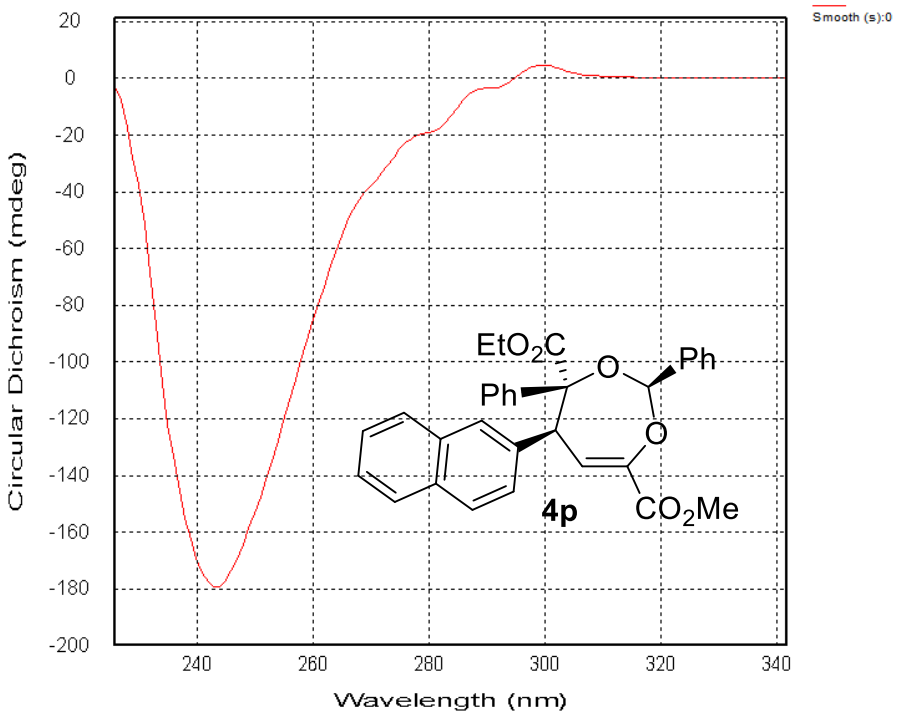
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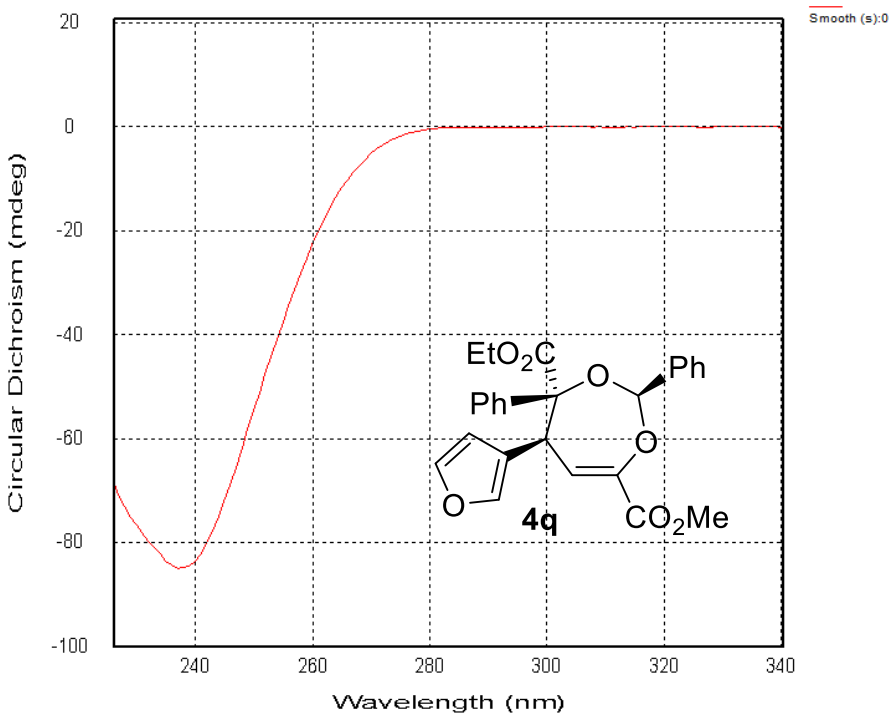
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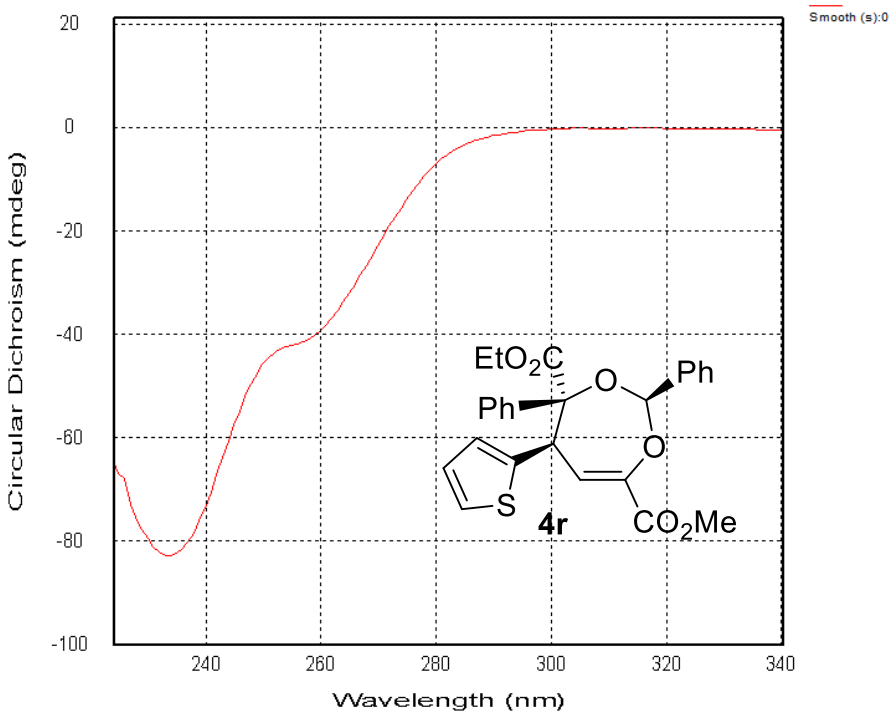
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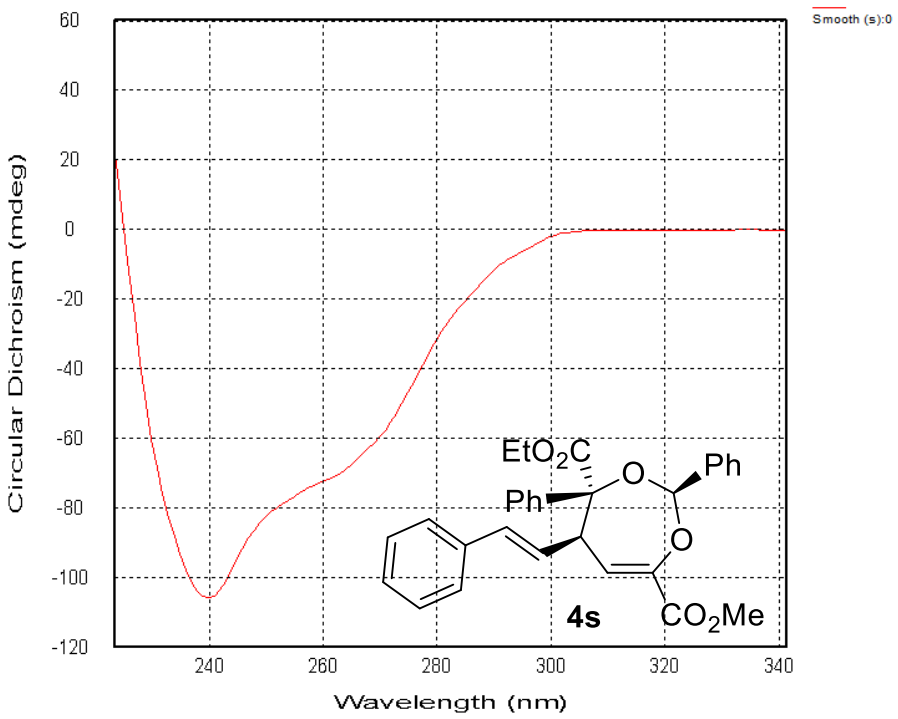
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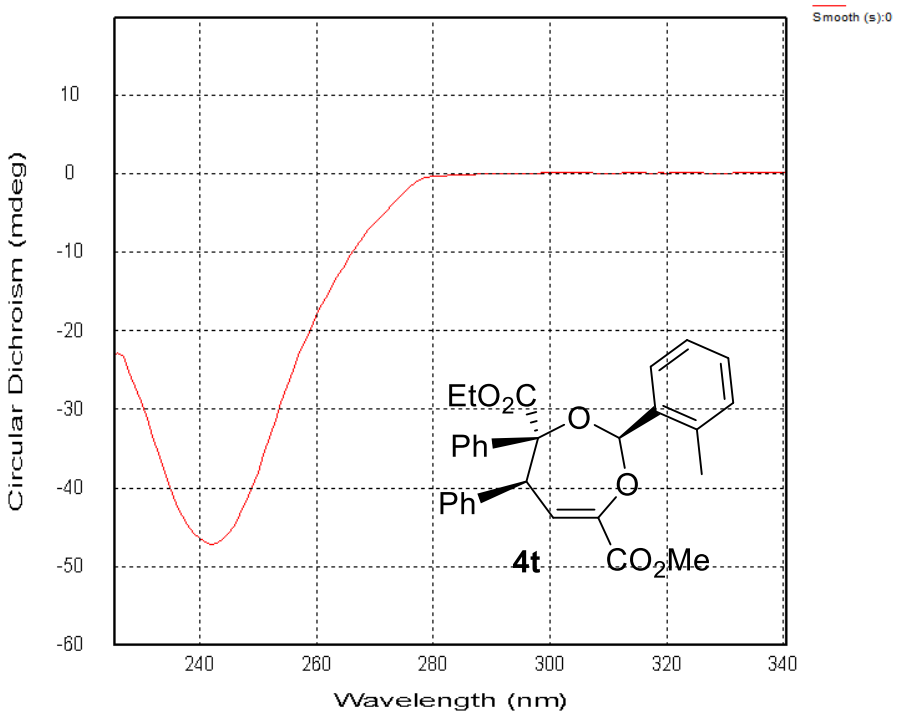
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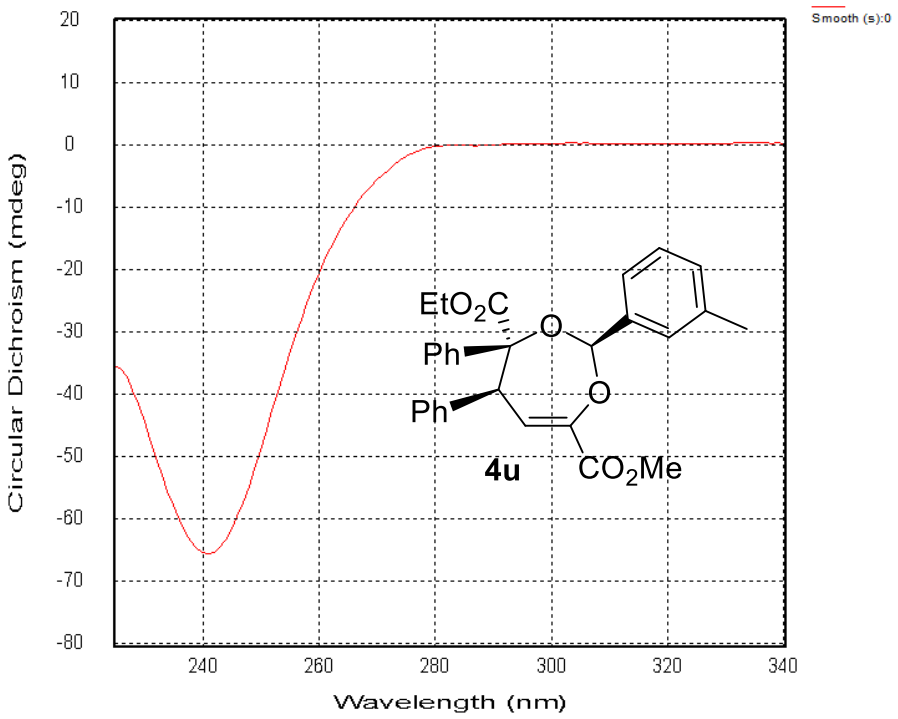
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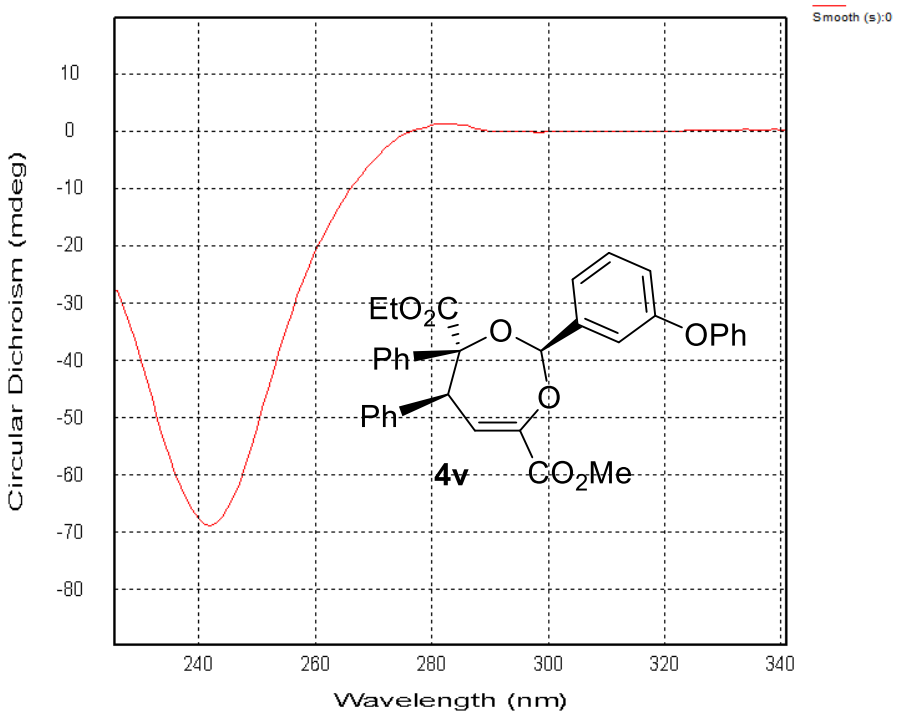
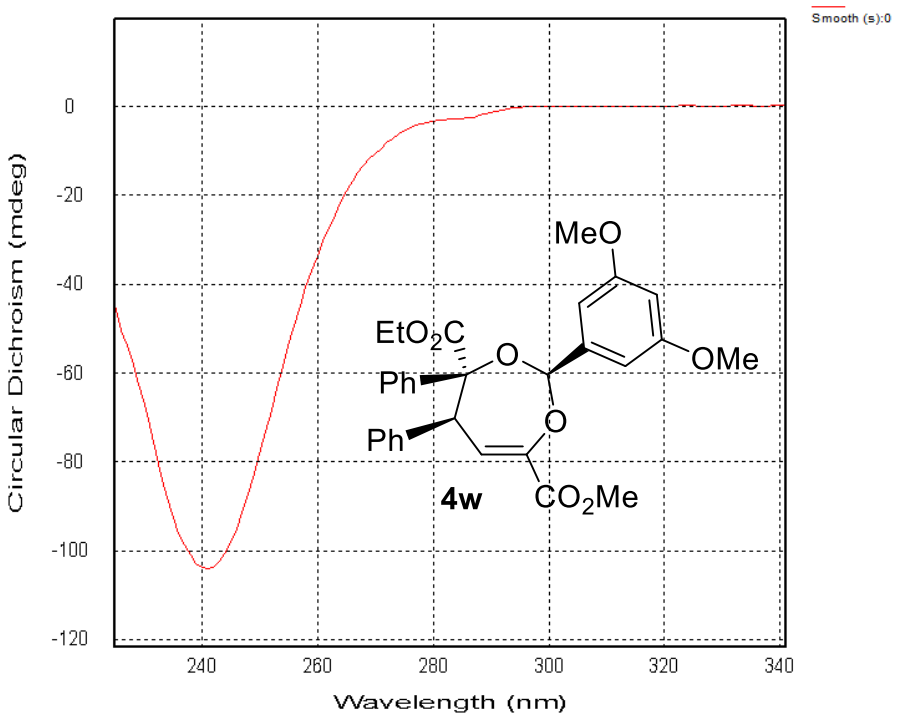
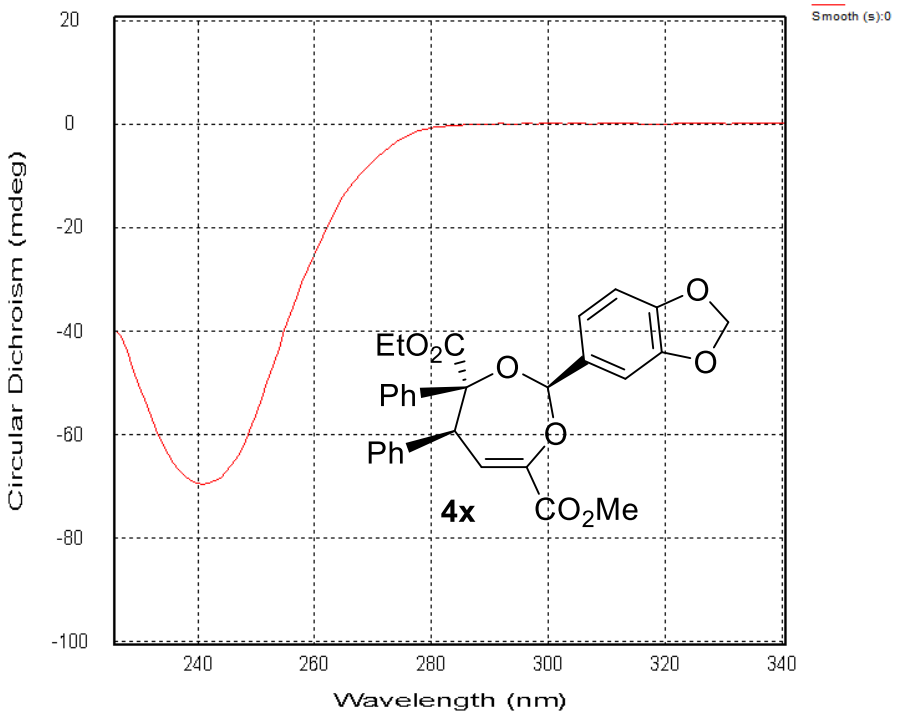
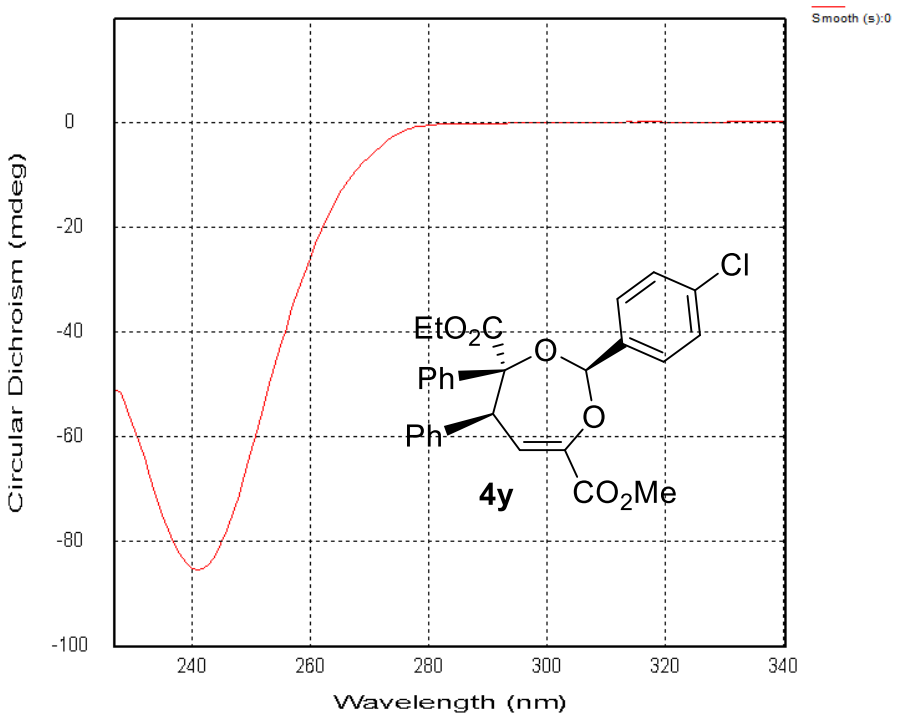
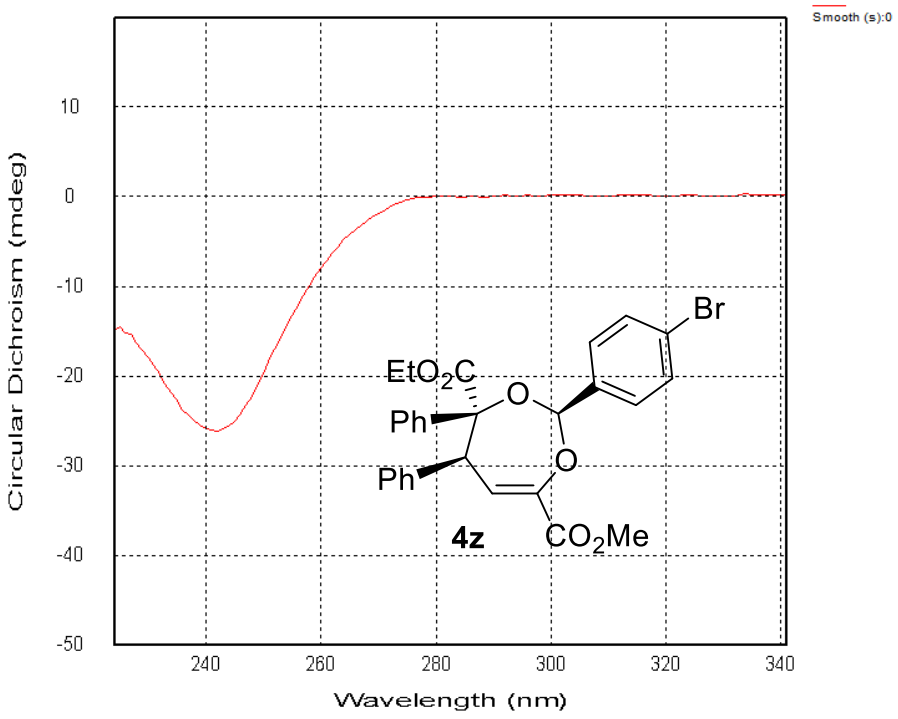
CO2Me

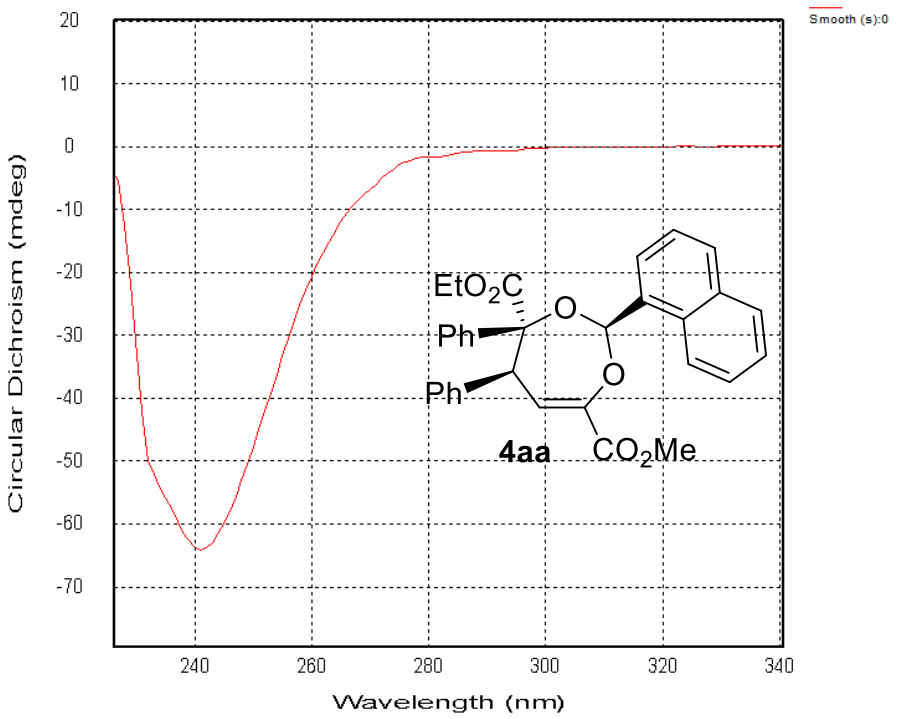

Smooth (s):0
Circular Dichroism (mdeg)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
240
260
280
300
320
340
Wavelength (nm)
EtO2C
Ph
Ph
O
O
OPh
4v
CO2Me


Smooth (s):0
Circular Dichroism (mdeg)
0
-20
-40
-60
-80
-100
-120
240
260
280
300
320
340
Wavelength (nm)
MeO
OMe
EtO2C
Ph
Ph
O
O
4w
CO2Me


Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
240
260
280
300
320
340
Wavelength (nm)
O
O
EtO2C
Ph
Ph
O
O
4x
CO2Me


Smooth (s):0
Circular Dichroism (mdeg)
0
-20
-40
-60
-80
-100
240
260
280
300
320
340
Wavelength (nm)
Cl
EtO2C
O
Ph
O
Ph
4y
CO2Me


Smooth (s):0
Circular Dichroism (mdeg)
10
0
-10
-20
-30
-40
-50
240
260
280
300
320
340
Wavelength (nm)
Br
EtO2C
O
Ph
O
Ph
4z
CO2Me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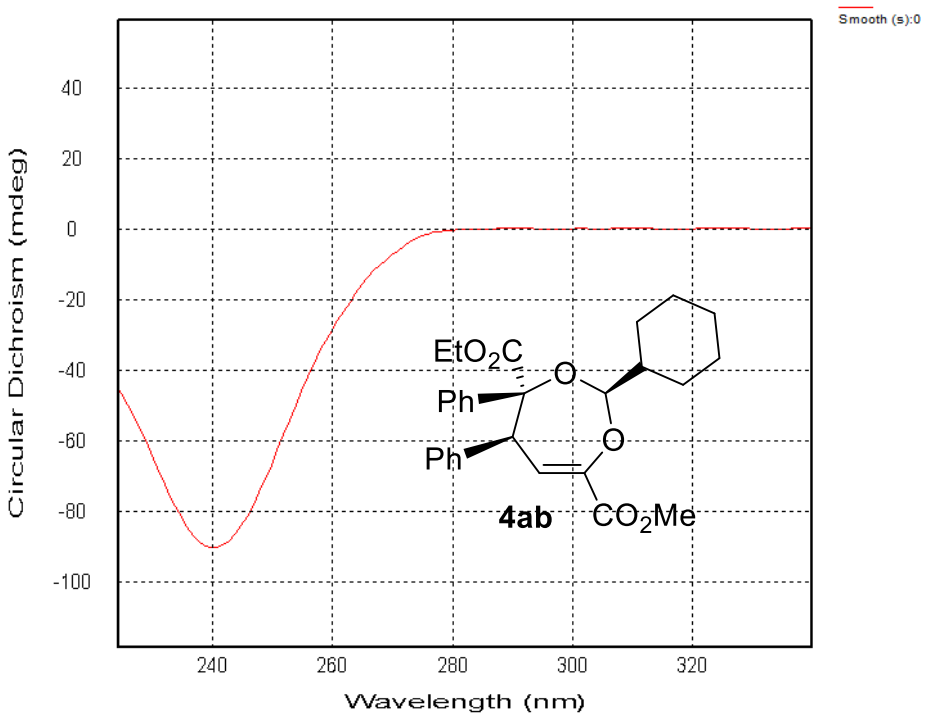
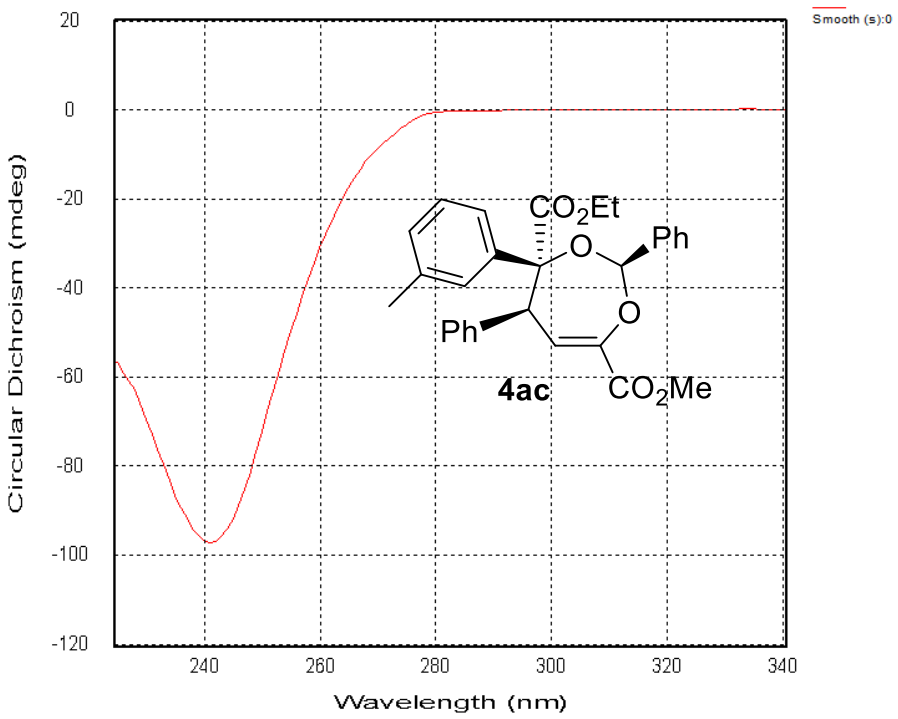
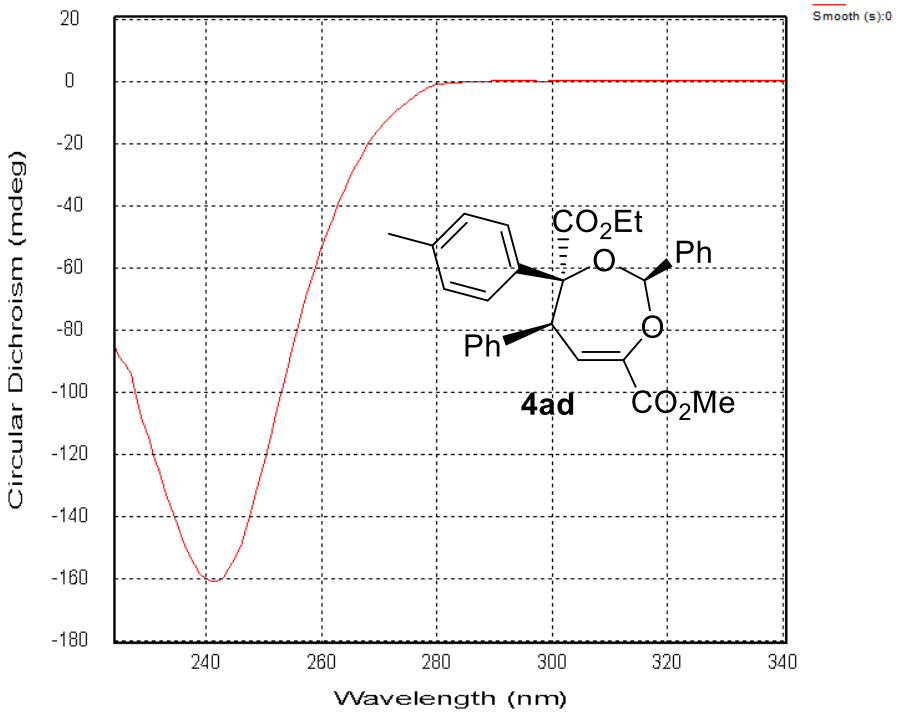
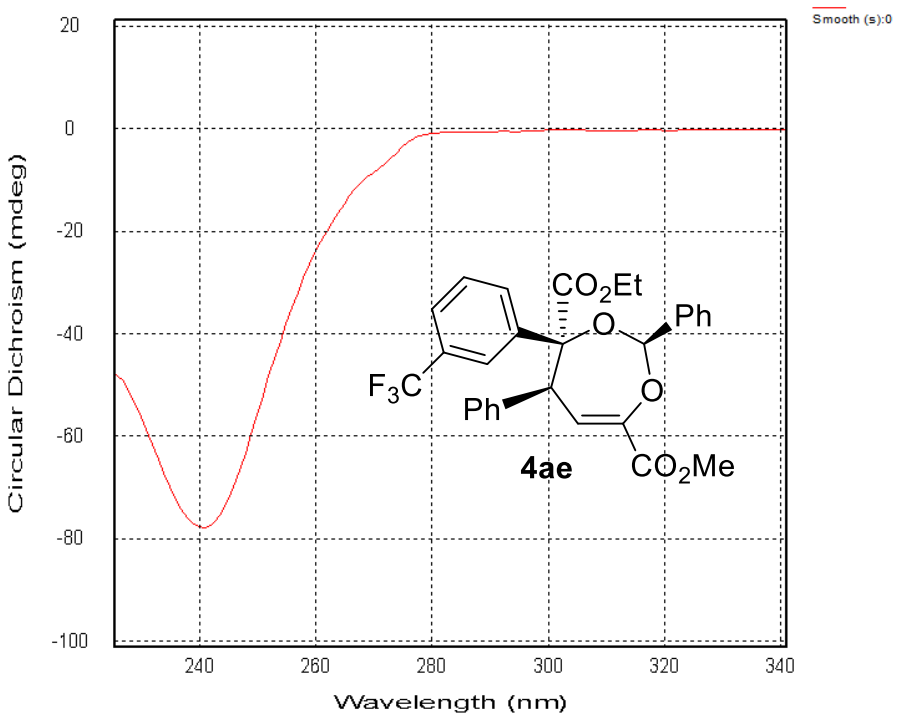
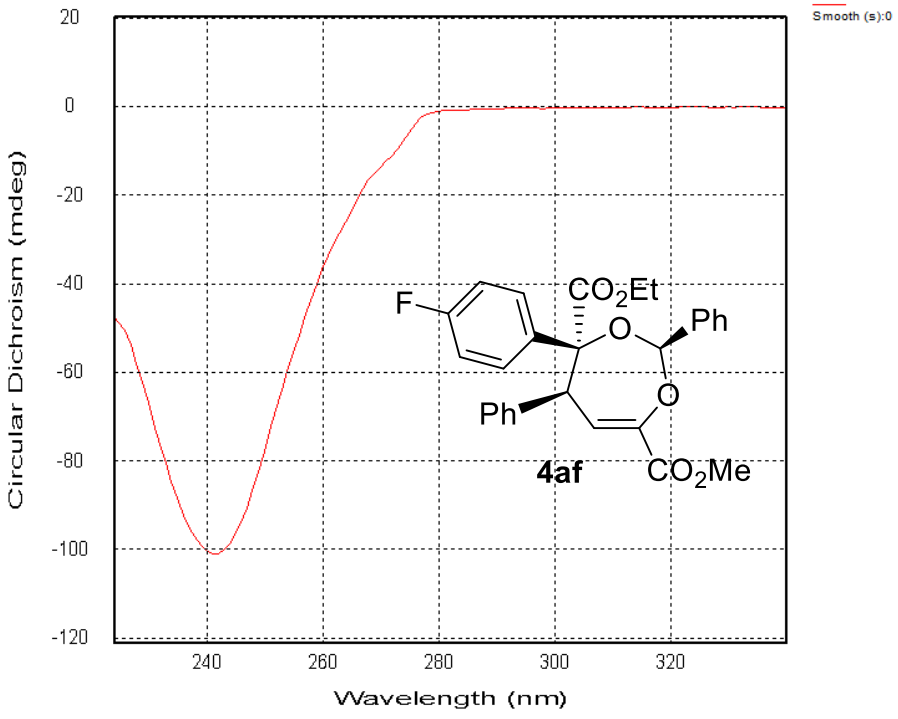
Circular Dichroism (mdeg)
20
10
0
-10
-20
-30
-40
-50
-60
-70
240
260
280
300
320
340
Wavelength (nm)
EtO2C
Ph
Ph
O
O
4aa
CO2Me

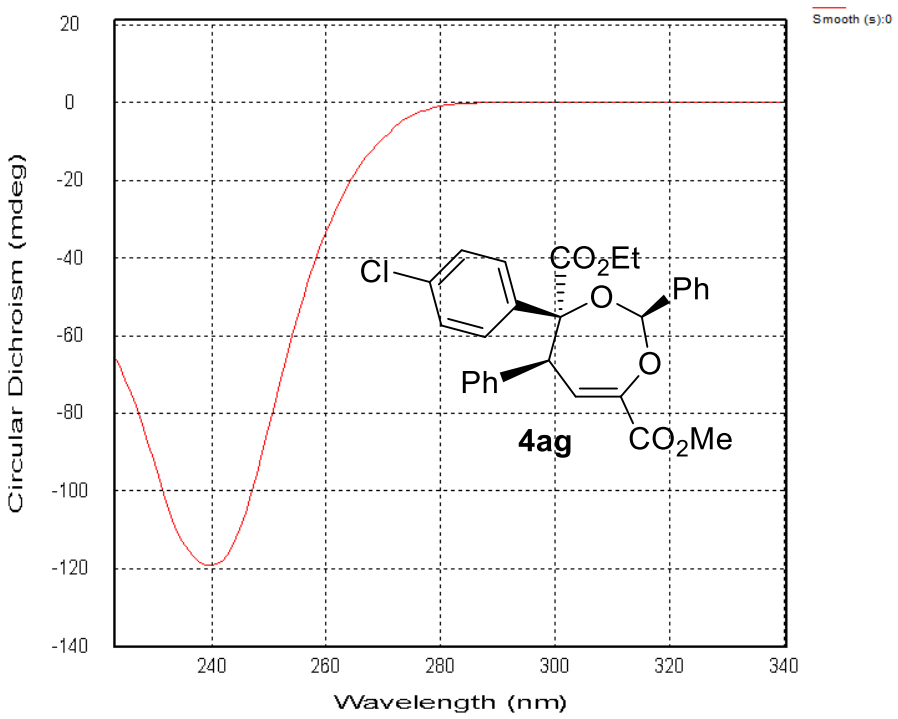

Smooth (s):0
Circular Dichroism (mdeg)
40
20
0
-20
-40
-60
-80
-100
240
260
280
300
320
Wavelength (nm)
EtO2C
Ph
Ph
O
O
4ab
CO2Me

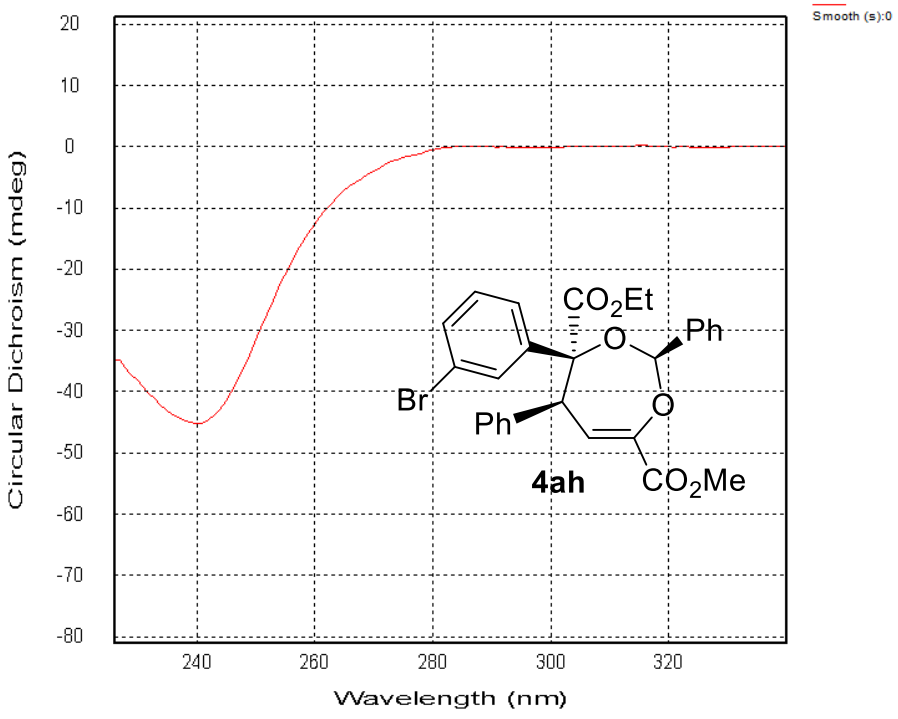

Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
-120
240
260
280
300
320
340
Wavelength (nm)
CO2Et
O
Ph
O
Ph
4ac
CO2Me

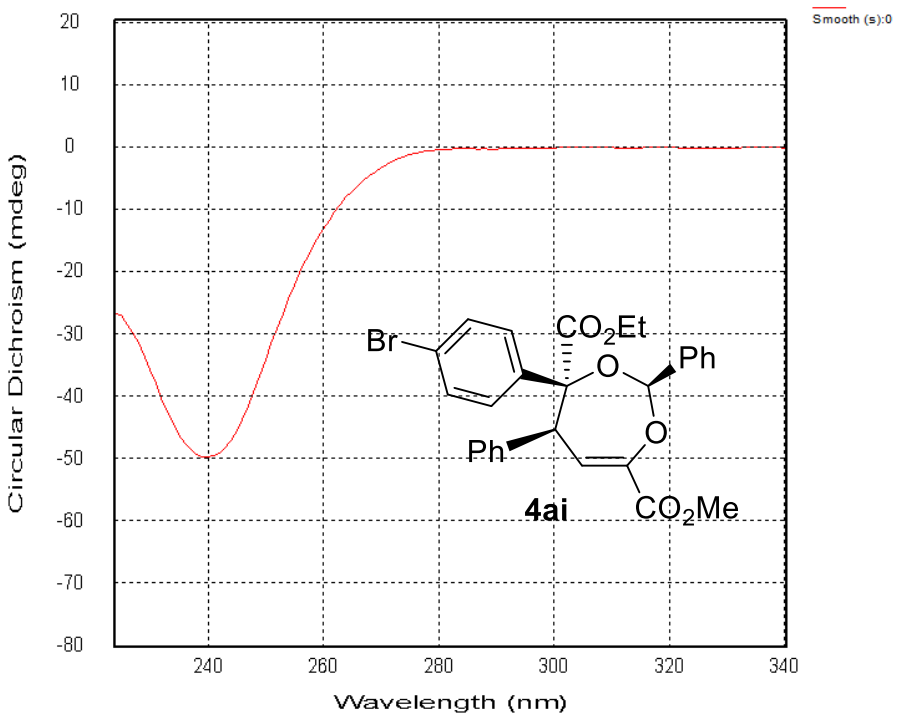

Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
240
260
280
300
320
340
Wavelength (nm)
CO2Et
O
Ph
O
Ph
4ad
CO2Me

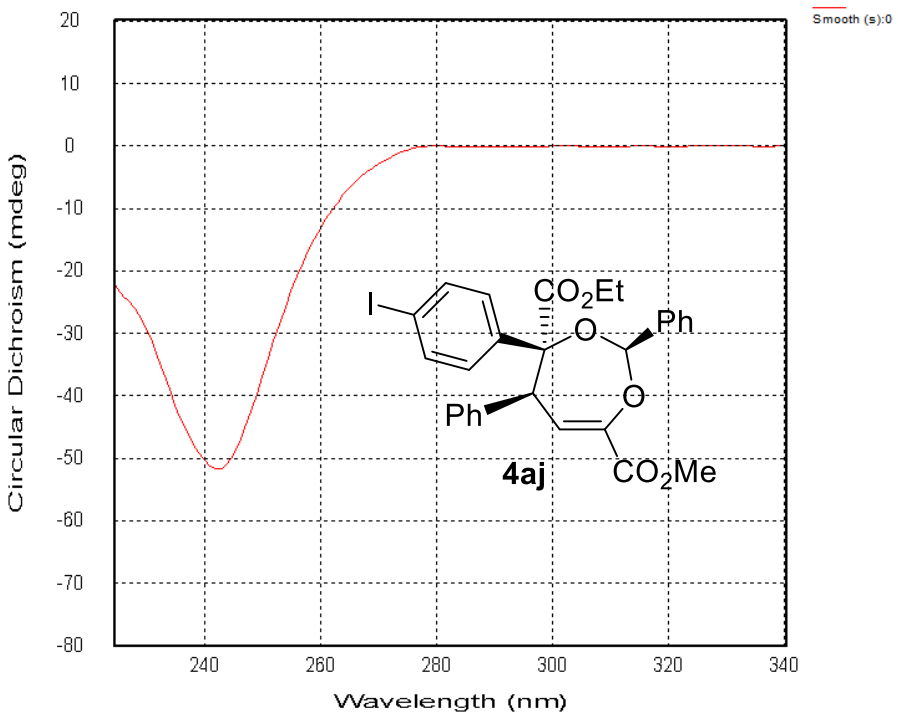

Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
240
260
280
300
320
340
Wavelength (nm)
CO2Et
O
Ph
F3C
Ph
O
4ae
CO2Me

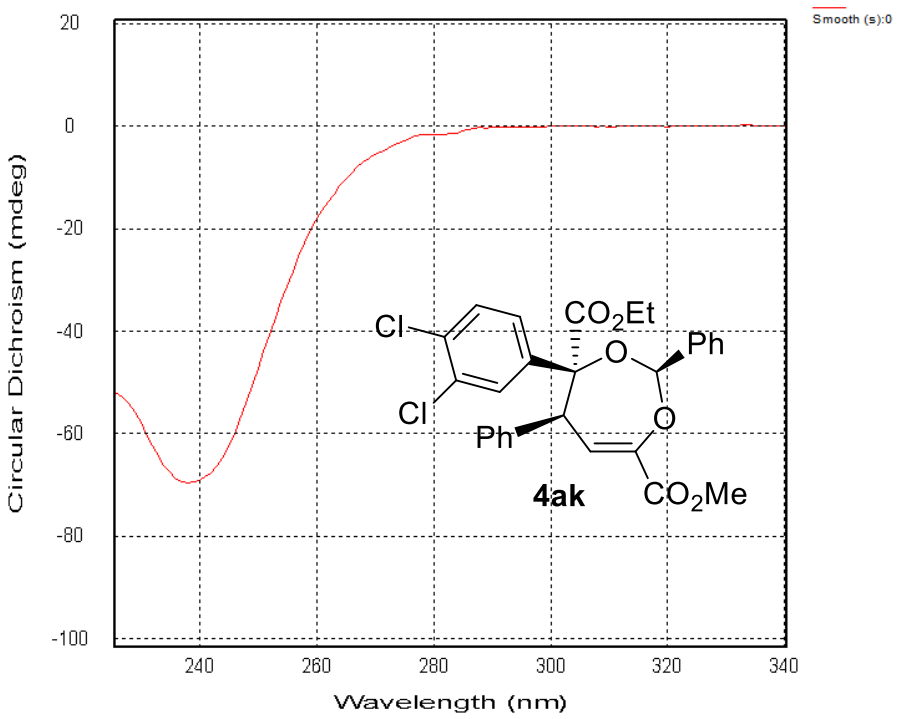

Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
-120
240
260
280
300
320
Wavelength (nm)
F
CO2Et
O
Ph
Ph
O
4af
CO2Me


Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
-120
-140
240
260
280
300
320
340
Wavelength (nm)
Cl
CO2Et
O
Ph
Ph
O
4ag
CO2Me


Smooth (s):0
Circular Dichroism (mdeg)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
240
260
280
300
320
Wavelength (nm)
CO2Et
O
Ph
Br
Ph
O
4ah
CO2Me


Smooth (s):0
Circular Dichroism (mdeg)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
240
260
280
300
320
340
Wavelength (nm)
Br
CO2Et
O
Ph
O
Ph
4ai
CO2Me


Smooth (s):0
Circular Dichroism (mdeg)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
240
260
280
300
320
340
Wavelength (nm)
I
CO2Et
O
Ph
O
Ph
4aj
CO2Me


Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
240
260
280
300
320
340
Wavelength (nm)
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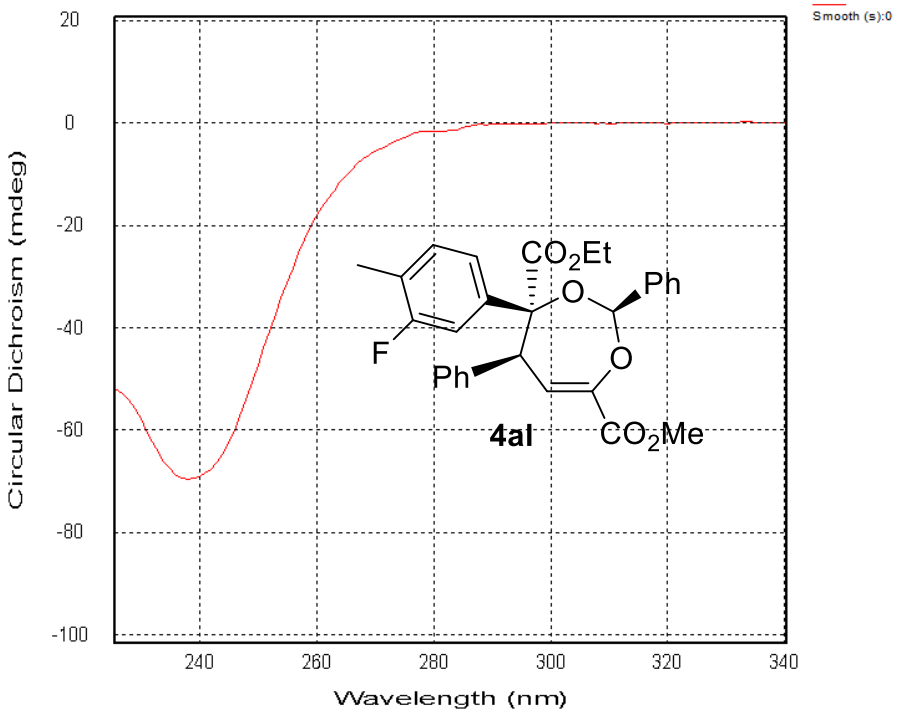
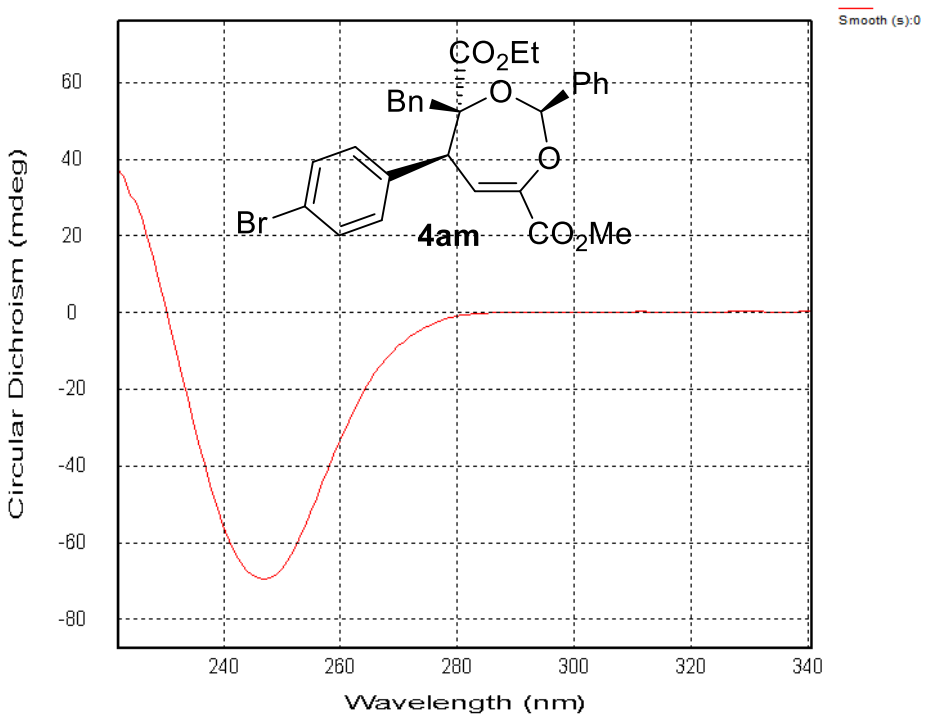
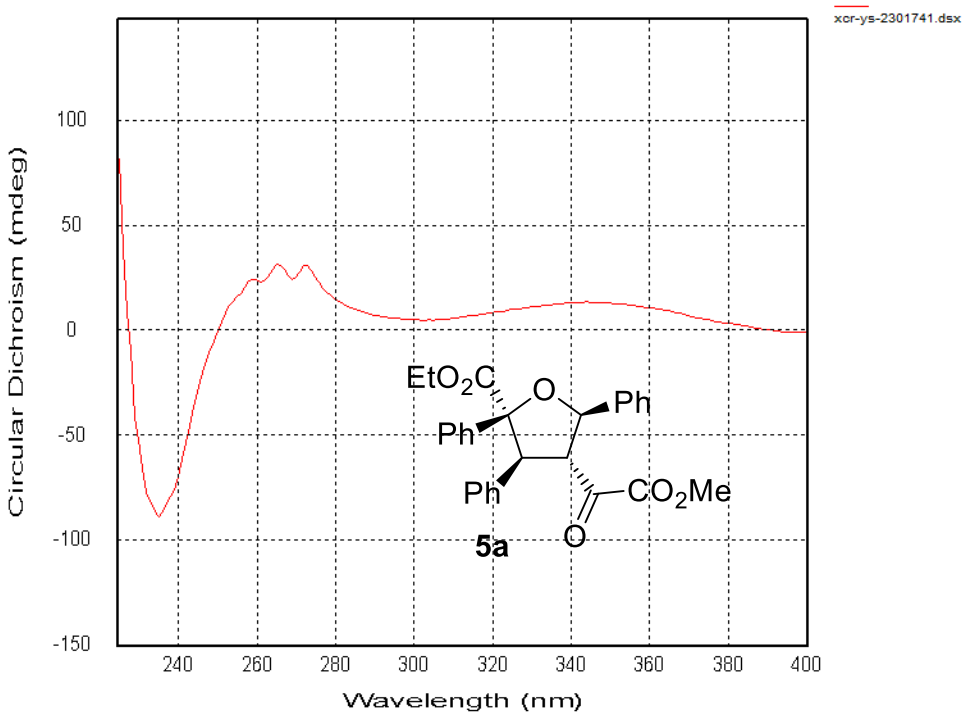
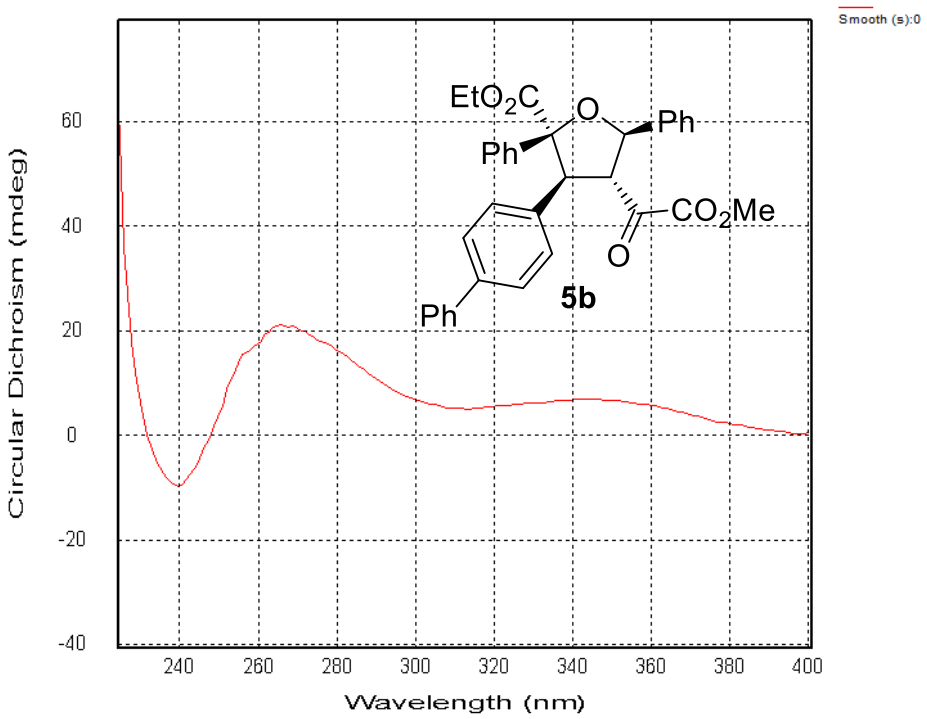
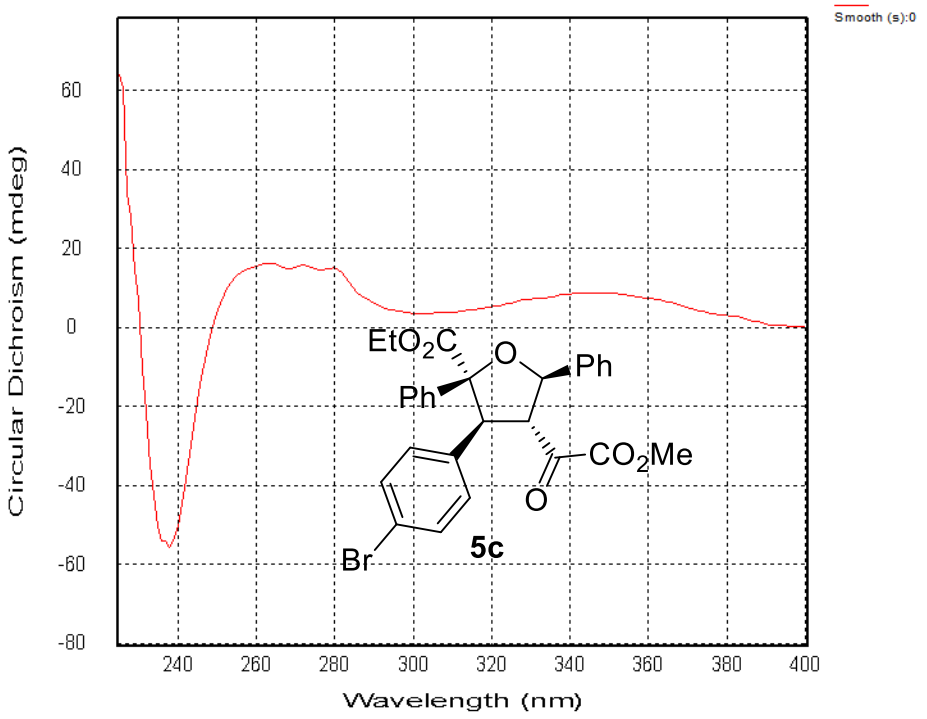
Cl
CO2Et
O
Ph
Ph
O
4ak
CO2Me

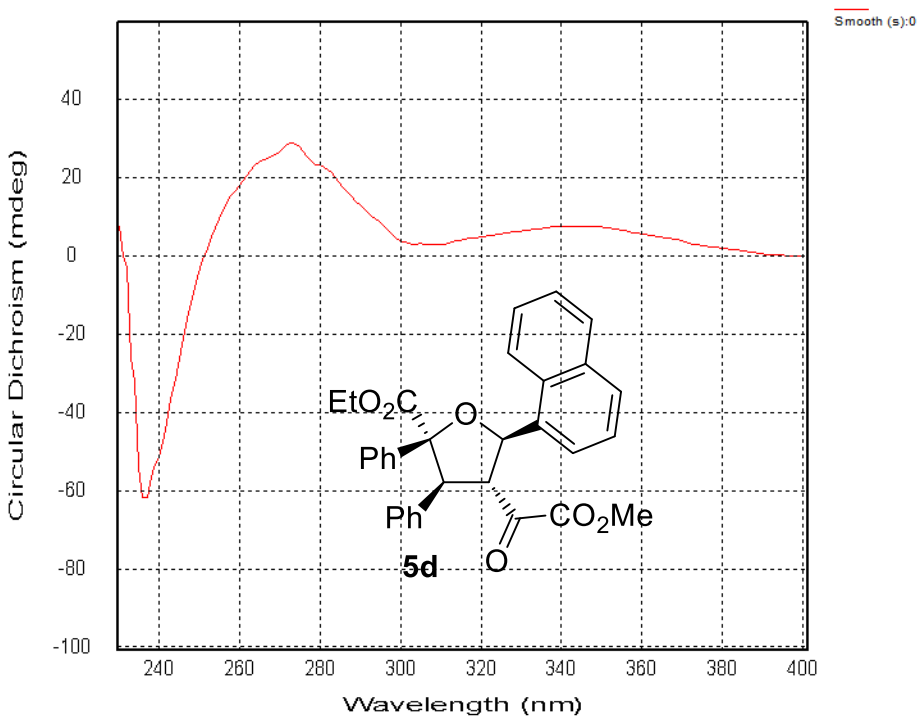

Smooth (s):0
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
240
260
280
300
320
340
Wavelength (nm)
F
CO2Et
O
Ph
Ph
O
4al
CO2Me

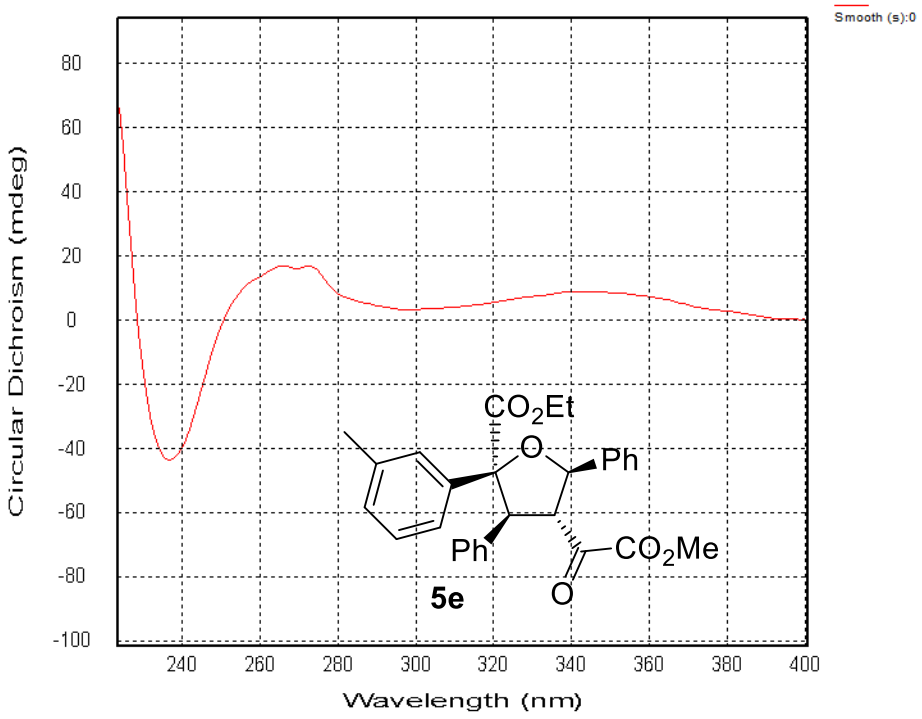

Smooth (s):0
Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
-80
240
260
280
300
320
340
Wavelength (nm)
CO2Et
Bn
O
Ph
O
Br
4am
CO2Me


xcr-ys-2301741.dsx
Circular Dichroism (mdeg)
100
50
0
-50
-100
-150
240
260
280
300
320
340
360
380
400
Wavelength (nm)
EtO2C
O
Ph
Ph
Ph
CO2Me
O
5a

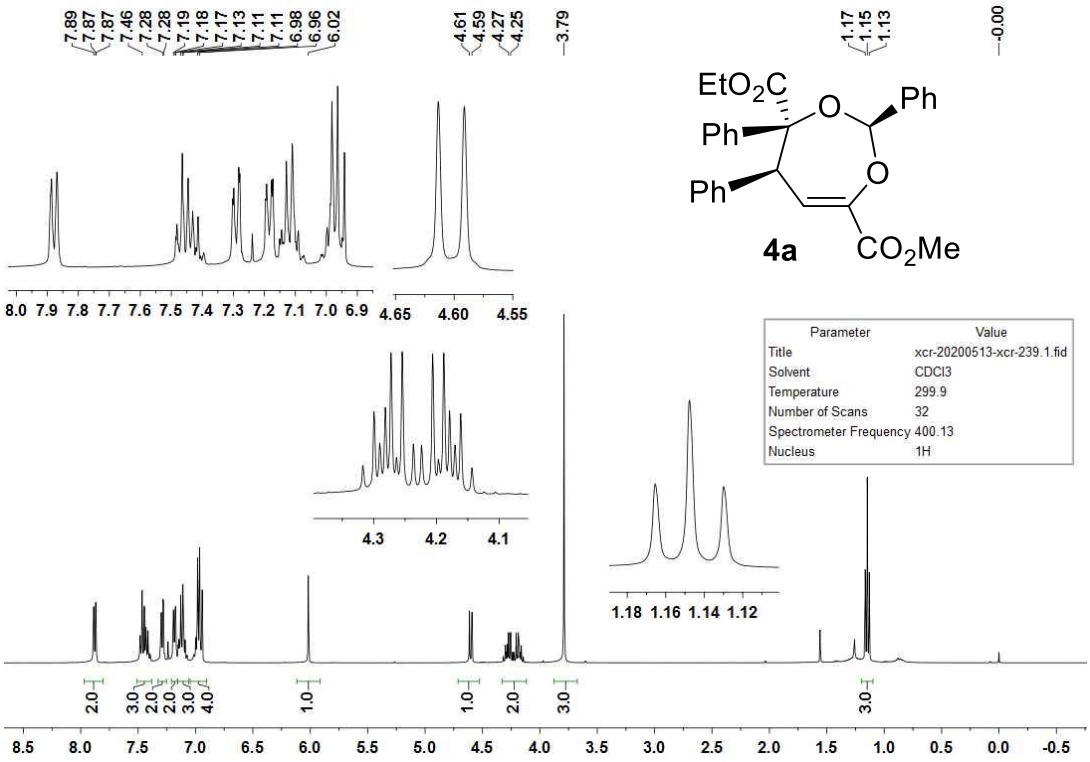

Smooth (s):0
Circular Dichroism (mdeg)
60
40
20
0
-20
-40
240
260
280
300
320
340
360
380
400
Wavelength (nm)
EtO2C
O
Ph
Ph
CO2Me
O
Ph
5b

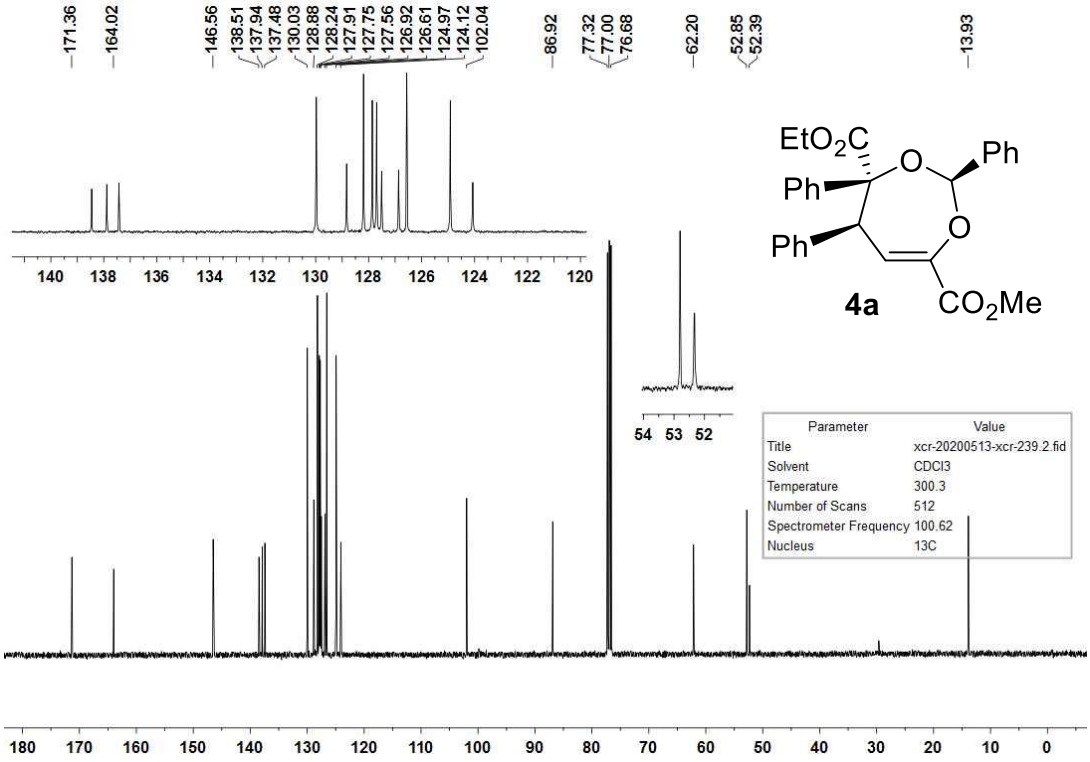

Smooth (s):0
Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
-80
240
260
280
300
320
340
360
380
400
Wavelength (nm)
EtO2C
O
Ph
Ph
CO2Me
O
Br
5c

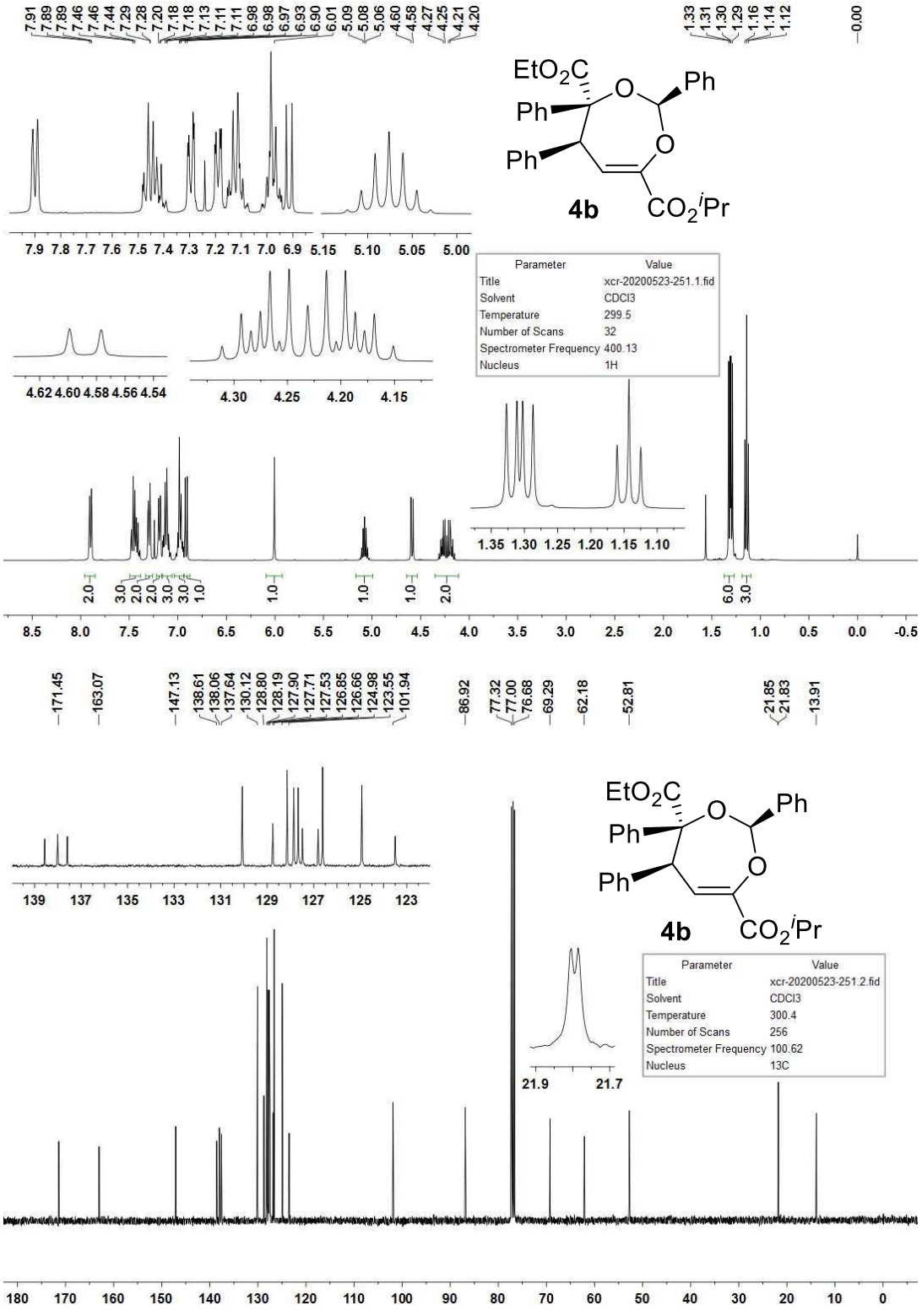

Smooth (s):0
Circular Dichroism (mdeg)
40
20
0
-20
-40
-60
-80
-100
240
260
280
300
320
340
360
380
400
Wavelength (nm)
EtO2C
O
Ph
Ph
CO2Me
O
5d

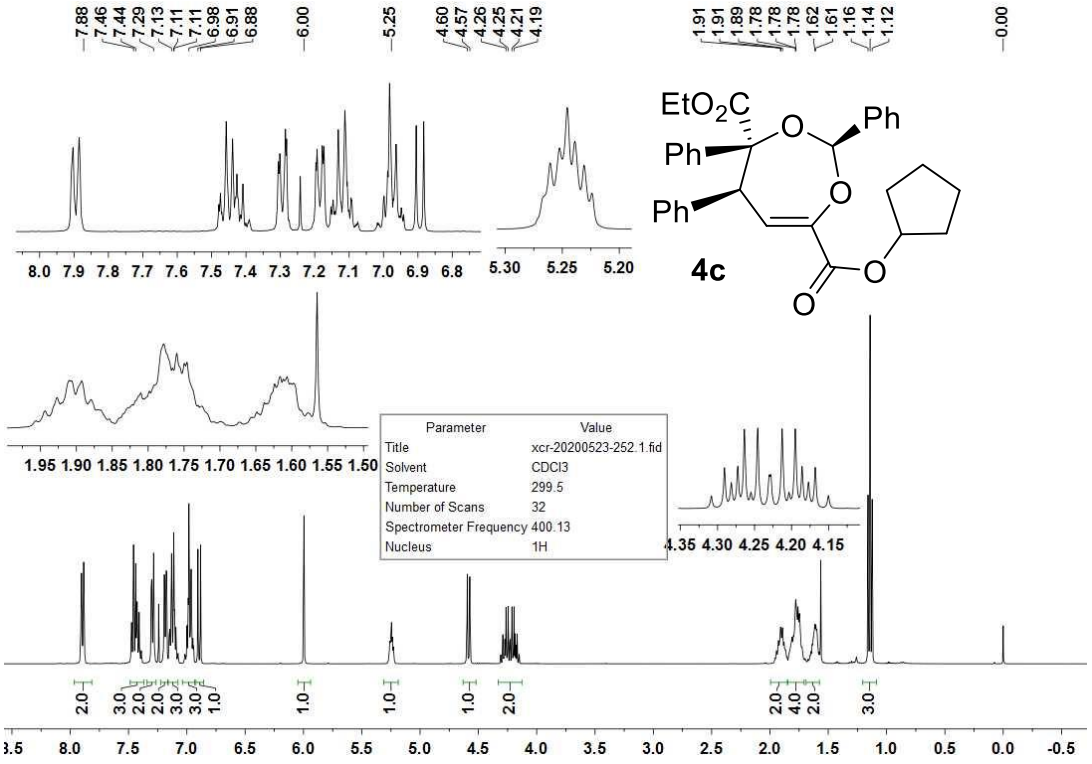

Smooth (s):0
Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
-80
-100
240
260
280
300
320
340
360
380
400
Wavelength (nm)
CO2Et
O
Ph
Ph
CO2Me
O
5e

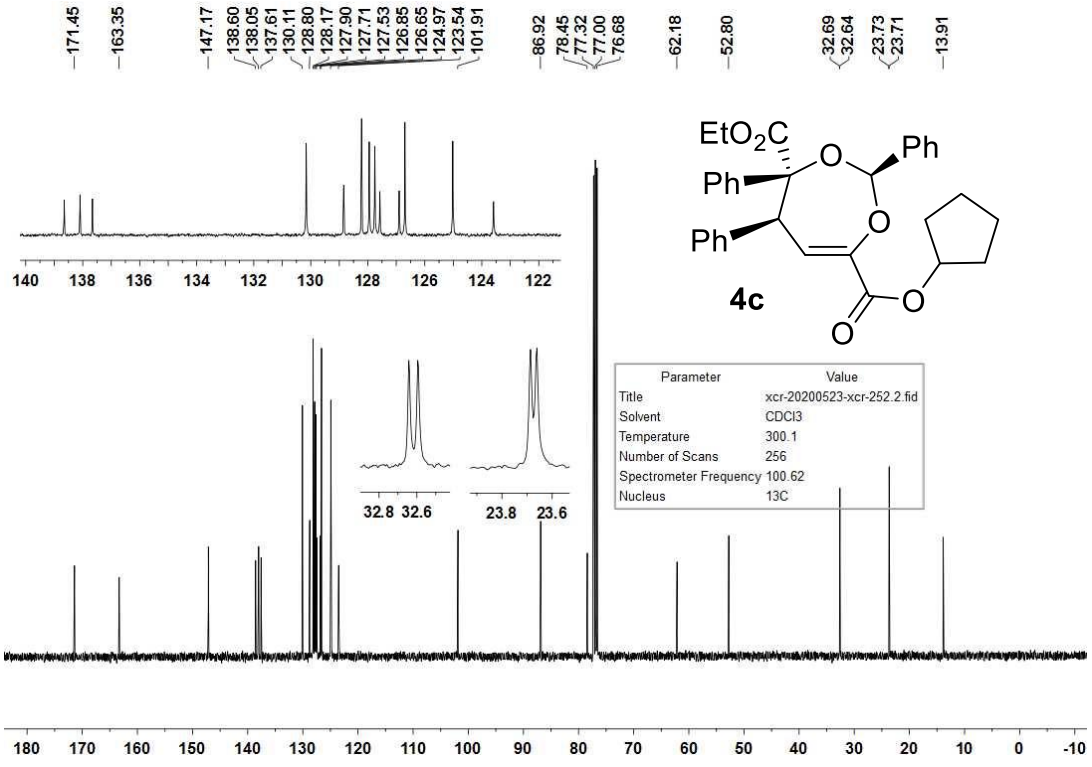
14. Copies of NMR Spectra for the Reaction Products

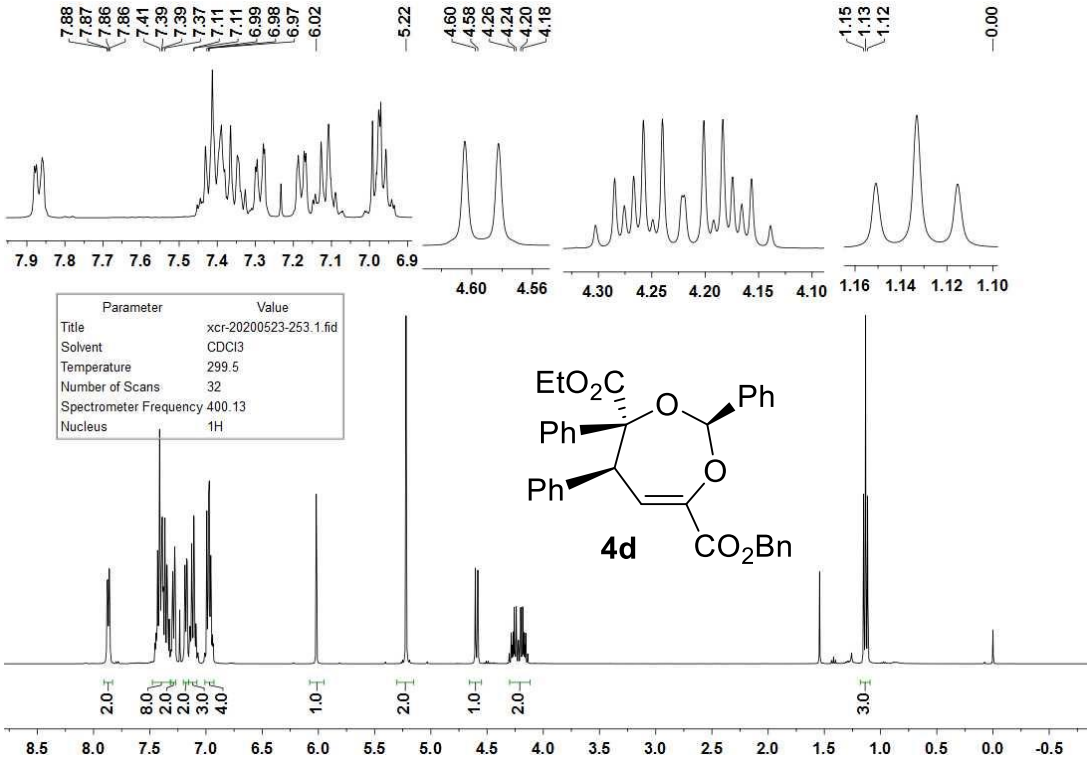


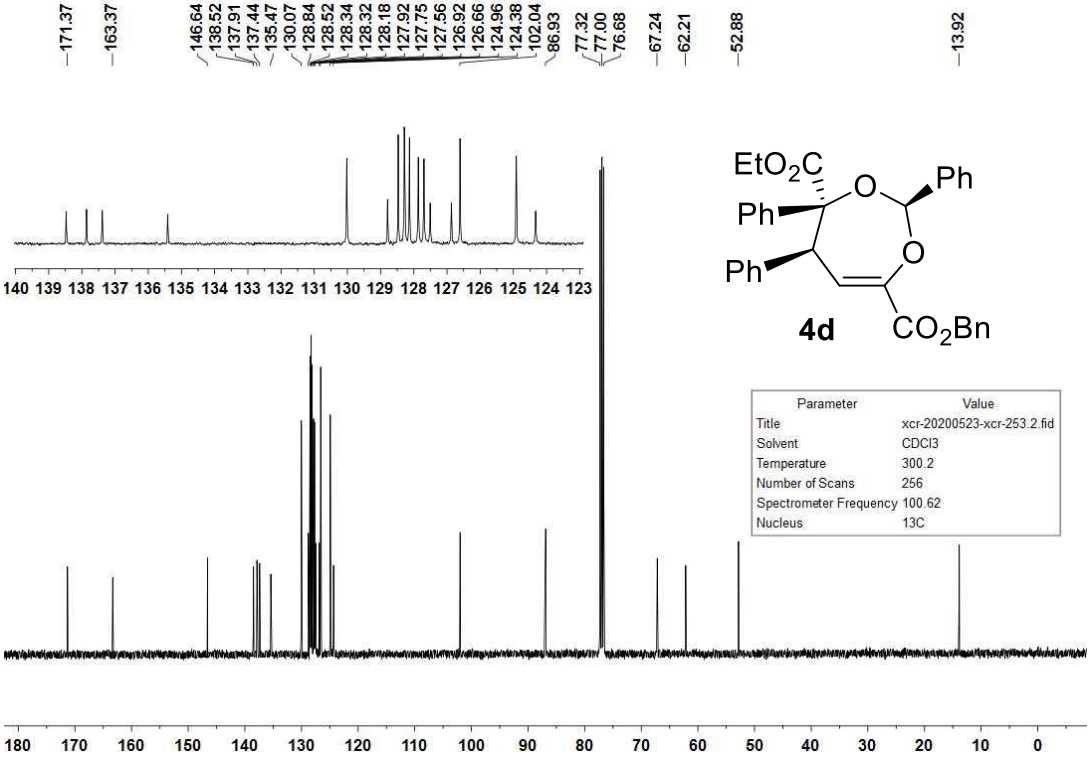


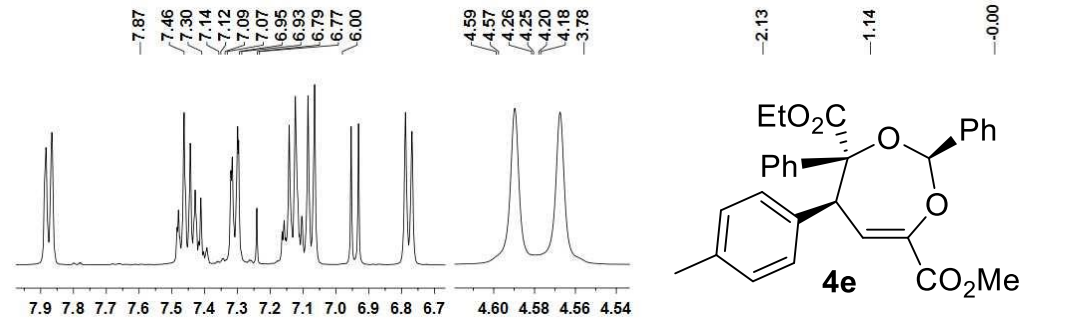

7.91 7.89 7.89 7.46 7.46 7.44 7.29 7.28 7.20 7.18 7.18 7.13 7.11 7.11 6.98 6.98 6.97 6.93 6.90 6.01 5.09 5.08 5.06 4.60 4.58 4.27 4.25 4.21 4.20
1.33 1.31 1.30 1.29 1.16 1.14 1.12 0.00
EtO2C
Ph
Ph
O
Ph
O
4b
CO2iPr
Parameter Value
Title xcr-20200523-251.1.fid
Solvent CDCl3
Temperature 299.5
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
171.45 163.07 147.13 138.61 138.06 137.64 130.12 128.80 128.19 127.90 127.71 127.53 126.85 126.66 124.98 123.55 101.94 86.92 77.32 77.00 76.68 69.29 62.18 52.81 21.85 21.83 13.91
Parameter Value
Title xcr-20200523-251.2.fid
Solvent CDCl3
Temperature 300.4
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C

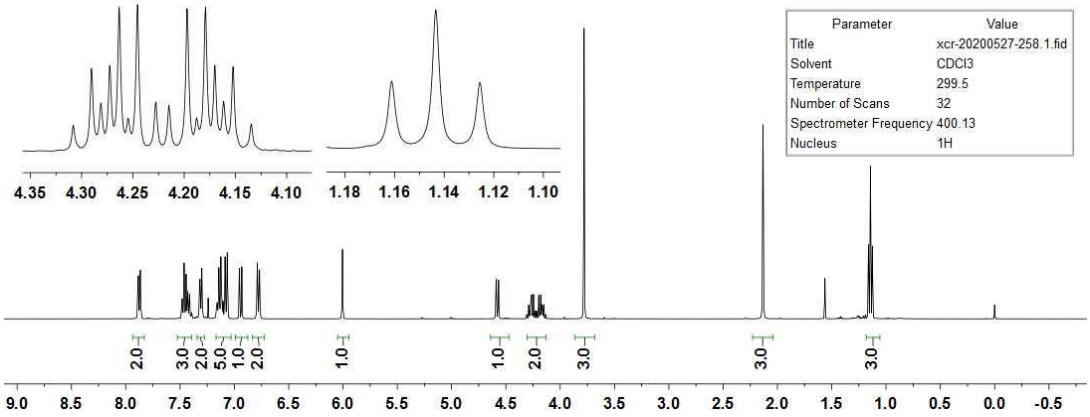

7.88 7.46 7.44 7.29 7.13 7.11 7.11 6.98 6.91 6.88 6.00 5.25 4.60 4.57 4.26 4.25 4.21 4.19 1.91 1.91 1.89 1.78 1.78 1.78 1.62 1.61 1.16 1.14 1.12 0.00
EtO2C
Ph
Ph
Ph
O
O
O
O
O
4c
Parameter Value
Title xcr-20200523-252.1.fid
Solvent CDCl3
Temperature 299.5
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0 3.0 2.0 3.0 1.0 1.0 1.0 1.0 2.0 2.0 4.0 2.0 3.0


171.45 163.35 147.17 138.60 138.05 137.61 130.11 128.80 128.17 127.90 127.71 127.53 126.85 126.65 124.97 123.54 101.91 86.92 78.45 77.32 77.00 76.68 62.18 52.80 32.69 32.64 23.73 23.71 13.91
EtO2C
Ph
Ph
Ph
O
O
O
O
O
4c
Parameter Value
Title xcr-20200523-xcr-252.2.fid
Solvent CDCl3
Temperature 300.1
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C


7.88 7.87 7.86 7.86 7.41 7.39 7.39 7.37 7.11 7.11 6.99 6.98 6.97 6.02 5.22 4.60 4.58 4.26 4.24 4.20 4.18 1.15 1.13 1.12 0.00
Parameter Value
Title xcr-20200523-253.1.fid
Solvent CDCl3
Temperature 299.5
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
EtO2C
Ph
Ph
Ph
O
O
4d
CO2Bn
2.0 8.0 2.0 2.0 3.0 4.0 1.0 2.0 1.0 2.0 3.0


171.37 163.37 146.64 138.52 137.91 137.44 135.47 130.07 128.84 128.52 128.34 128.32 128.18 127.92 127.75 127.56 126.92 126.66 124.96 124.38 102.04 86.93 77.32 77.00 76.68 67.24 62.21 52.88 13.92
EtO2C
Ph
Ph
Ph
O
O
4d
CO2Bn
Parameter Value
Title xcr-20200523-xcr-253.2.fid
Solvent CDCl3
Temperature 300.2
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C


7.87
7.46
7.30
7.14
7.12
7.09
7.07
6.95
6.93
6.79
6.77
6.00
4.59
4.57
4.26
4.25
4.20
4.18
3.78
2.13
1.14
0.00
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
4.60 4.58 4.56 4.54
EtO2C
Ph
Ph
O
O
4e
CO2Me


4.35 4.30 4.25 4.20 4.15 4.10
1.18 1.16 1.14 1.12 1.10
Parameter Value
Title xcr-20200527-258.1.fid
Solvent CDCl3
Temperature 299.5
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0 3.0 2.0 5.0 1.0 2.0 1.0 1.0 2.0 3.0 3.0 3.0
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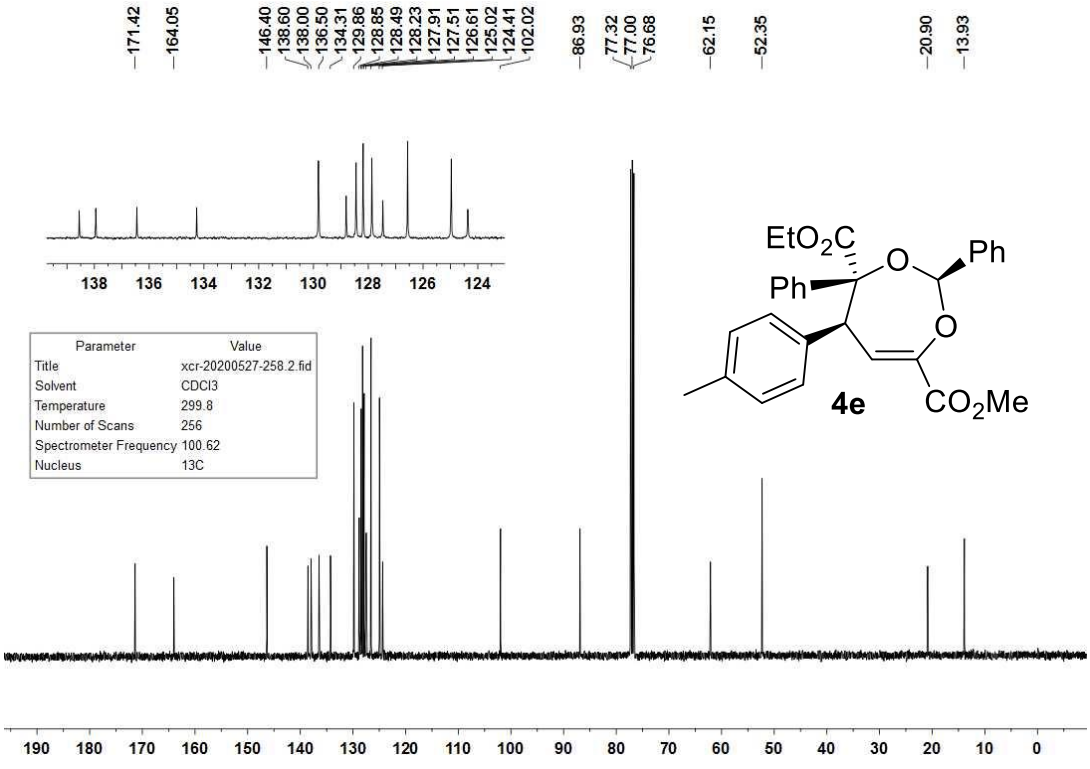
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164.05
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128.49
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126.61
125.02
124.41
102.02
86.93
77.32
77.00
76.68
62.15
52.35
20.90
13.93
138 136 134 132 130 128 126 124
Parameter Value
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Temperature 299.8
Number of Scans 256
Spectrometer Frequency 100.62
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Ph
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4e
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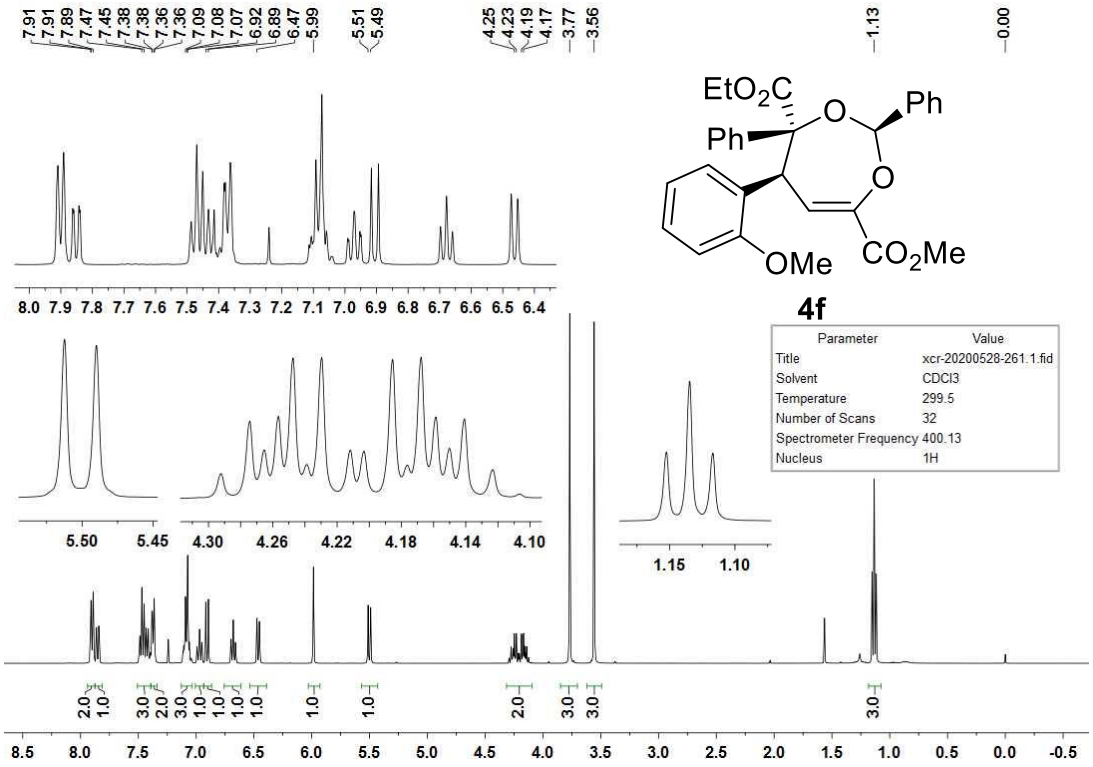
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EtO2C
Ph
O
Ph
O
OMe
CO2Me
4f
Parameter Value
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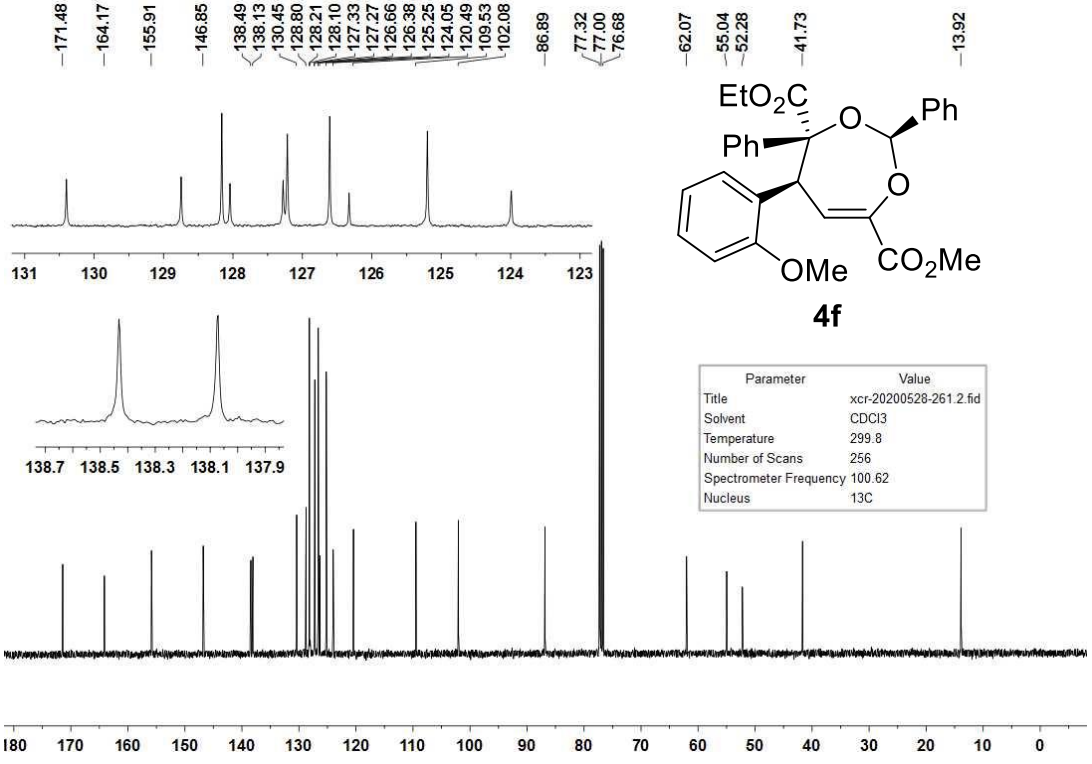
Solvent CDCl3
Temperature 299.5
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H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EtO2C
Ph
O
Ph
O
OMe
CO2Me
4f
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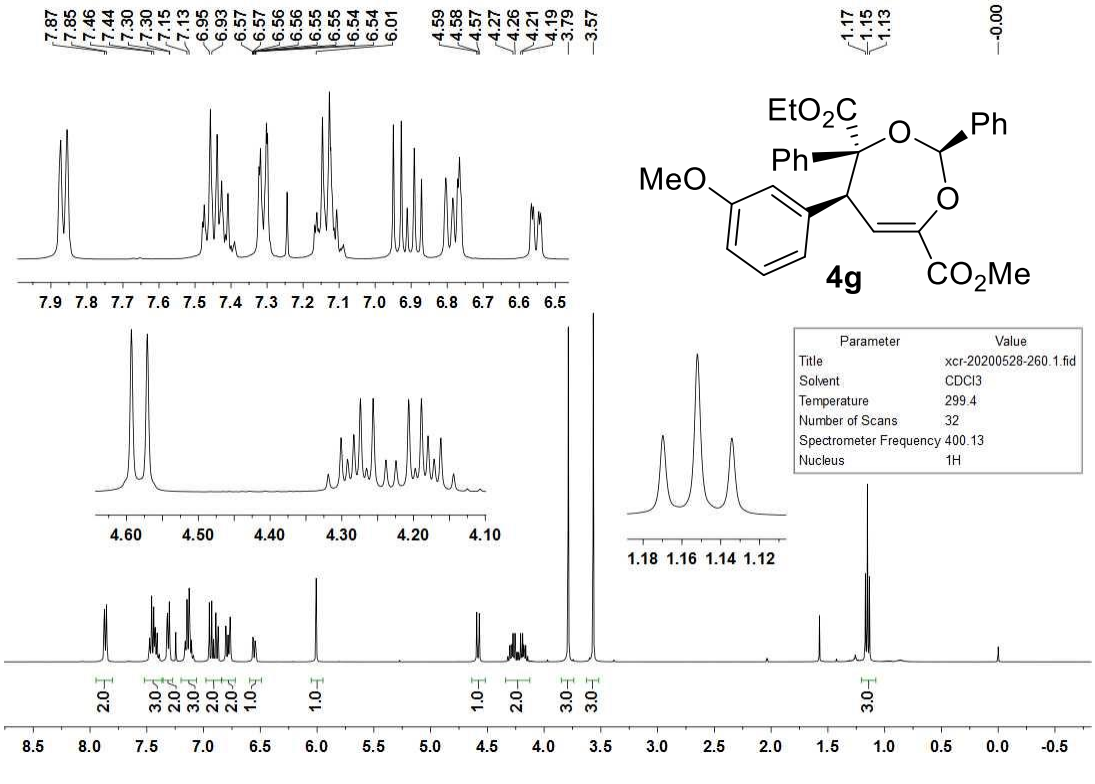
Temperature 299.8
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C


7.87 7.85 7.46 7.44 7.30 7.30 7.15 7.13 6.95 6.93 6.57 6.57 6.56 6.56 6.55 6.55 6.54 6.54 6.01
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1.17 1.15 1.13
0.00
EtO2C
Ph
O
Ph
MeO
O
4g
CO2Me
Parameter Value
Title xcr-20200528-260.1.fid
Solvent CDCl3
Temperature 299.4
Number of Scans 32
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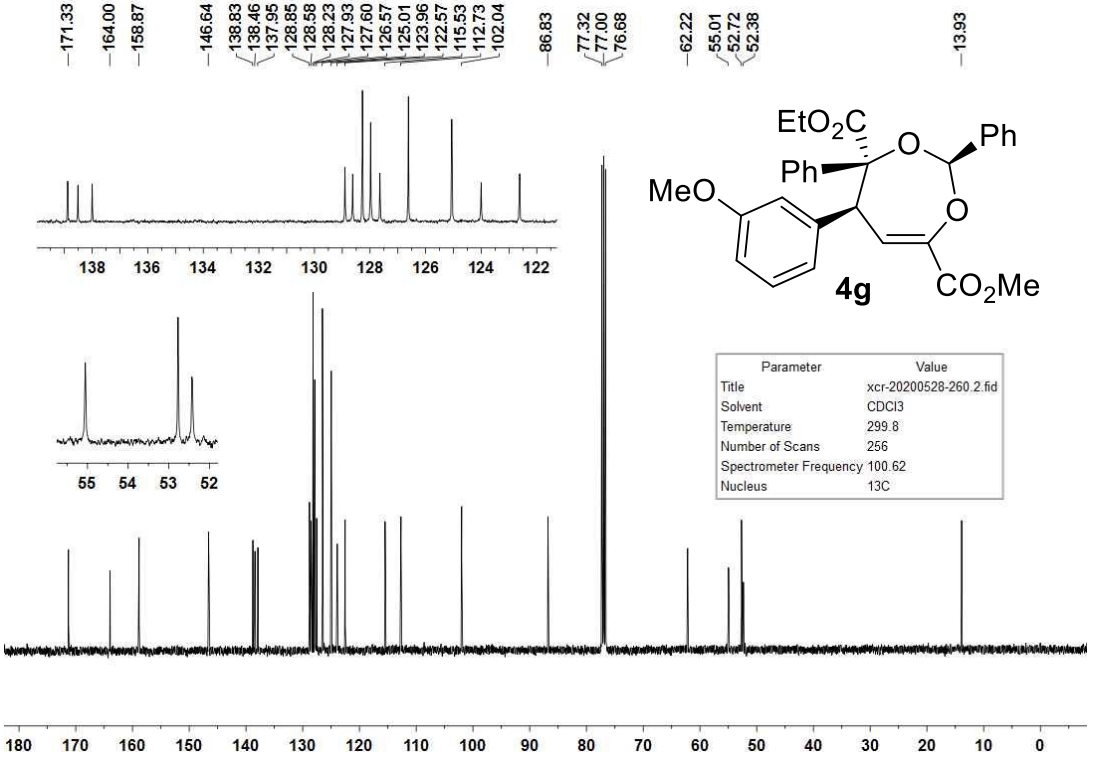
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77.32 77.00 76.68
62.22
55.01 52.72 52.38
13.93
EtO2C
Ph
O
Ph
MeO
O
4g
CO2Me
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Solvent CDCl3
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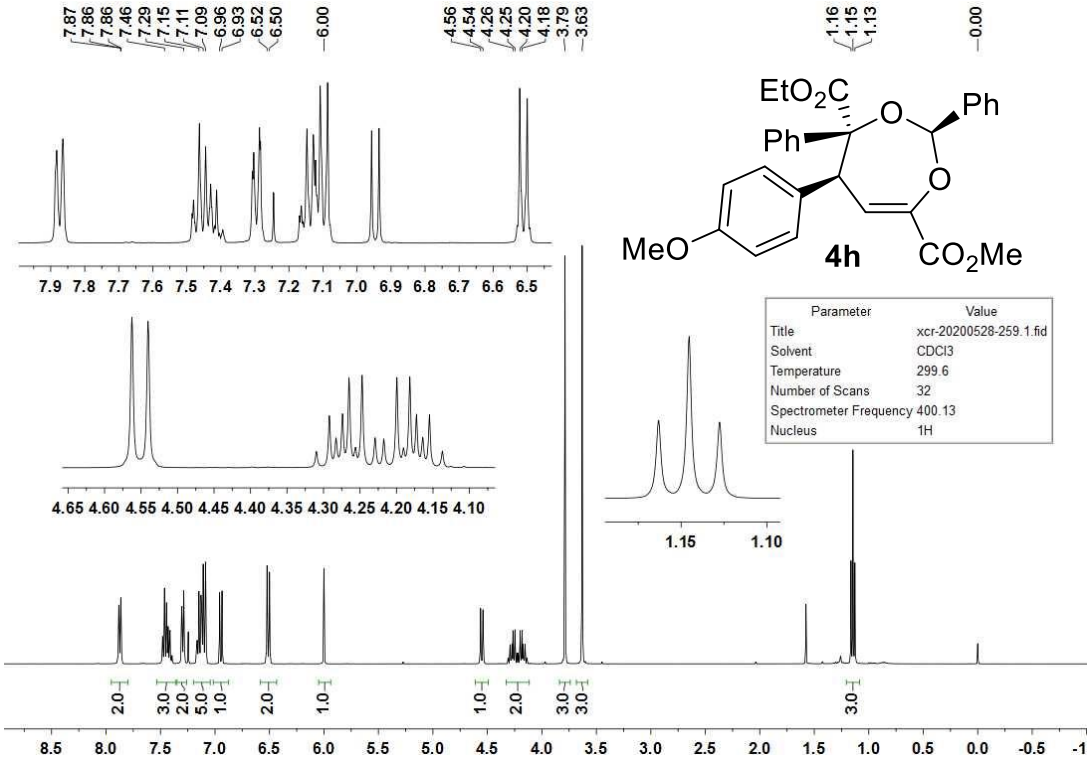
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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4.56 4.54 4.26 4.25 4.20 4.18 3.79 3.63
1.16 1.15 1.13 0.00
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Ph
O
Ph
O
MeO
4h
CO2Me
Parameter Value
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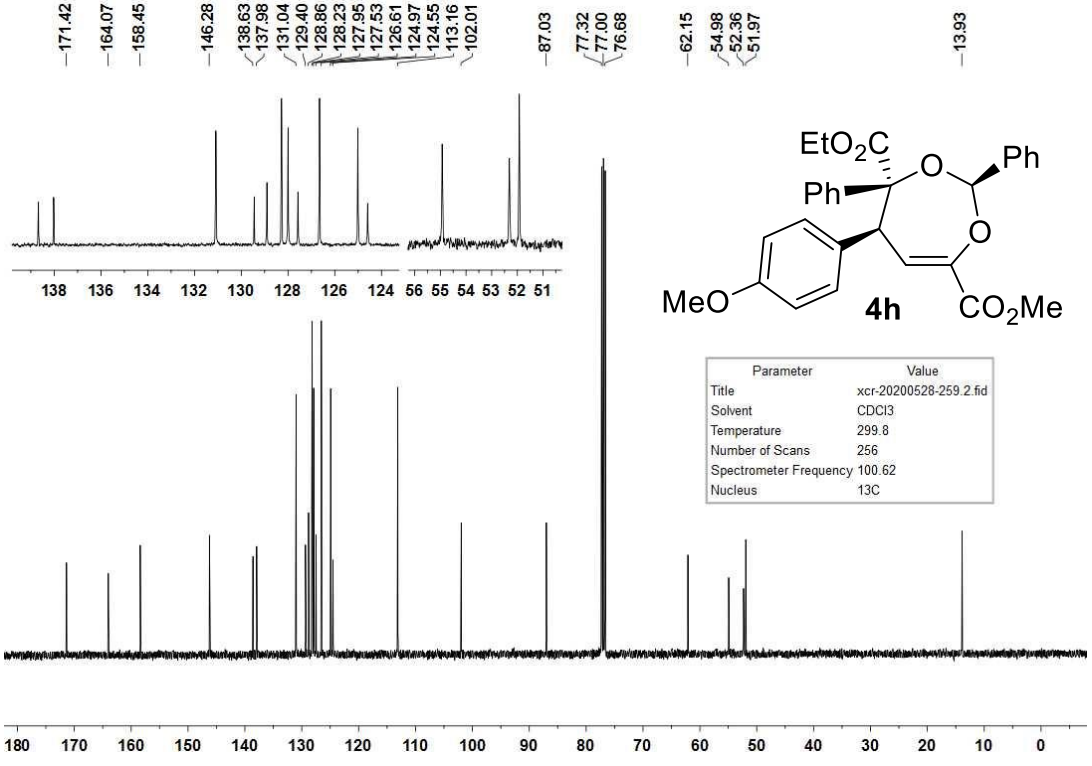
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87.03 77.32 77.00 76.68 62.15 54.98 52.36 51.97 13.93
EtO2C
Ph
O
Ph
O
MeO
4h
CO2Me
Parameter Value
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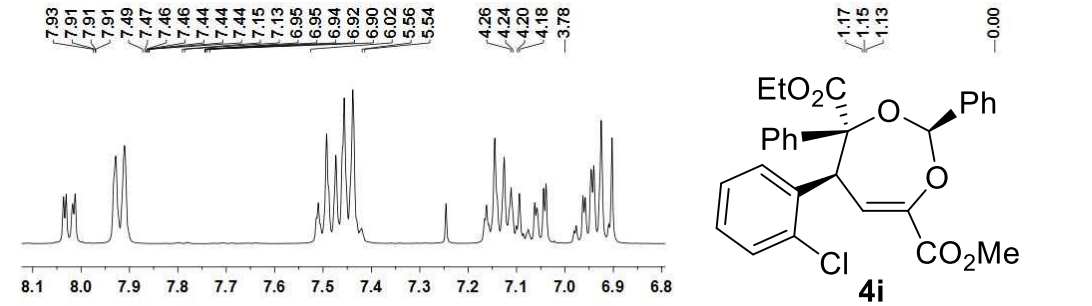
Solvent CDCl3
Temperature 299.8
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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4.26 4.24 4.20 4.18 3.78
1.17 1.15 1.13
0.00
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
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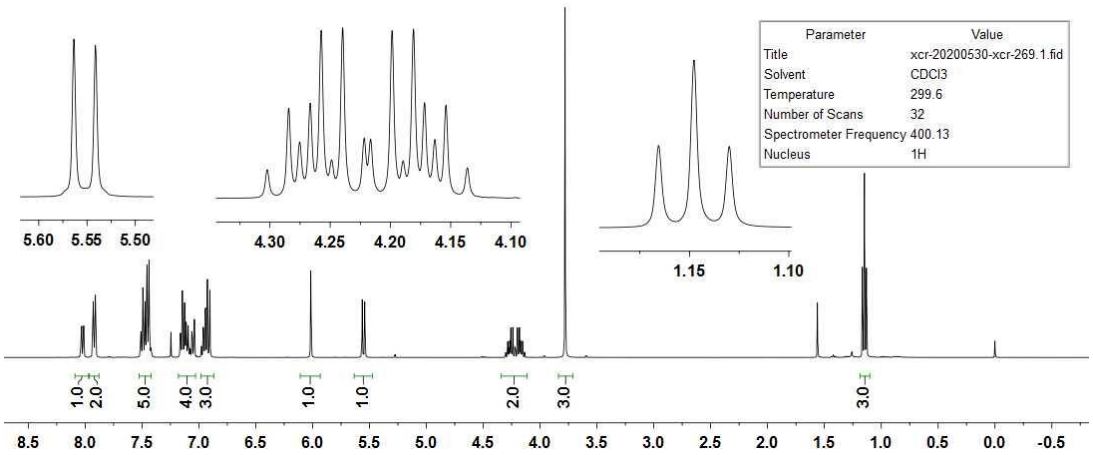
Cl
CO2Me
4i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4.30 4.25 4.20 4.15 4.10
1.15 1.10
1.0 2.0 5.0 4.0 3.0 1.0 1.0 2.0 3.0 3.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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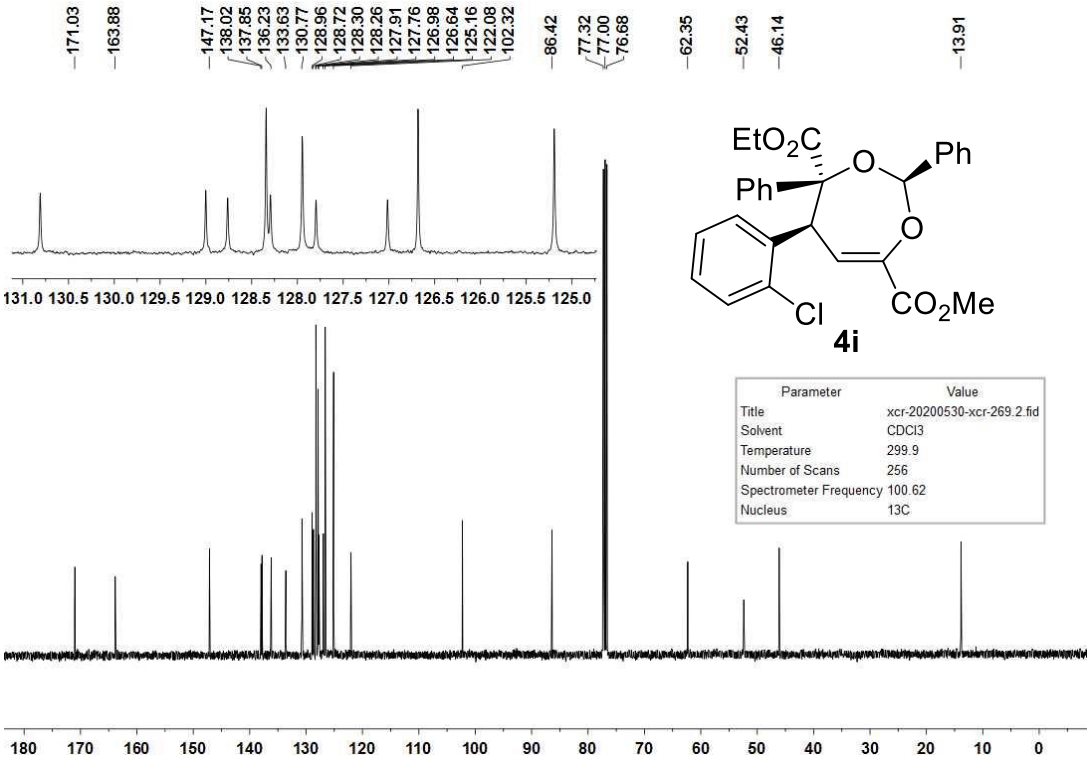
Solvent CDCl3
Temperature 299.6
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H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131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0
EtO2C
Ph
O
Ph
O
Cl
CO2Me
4i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
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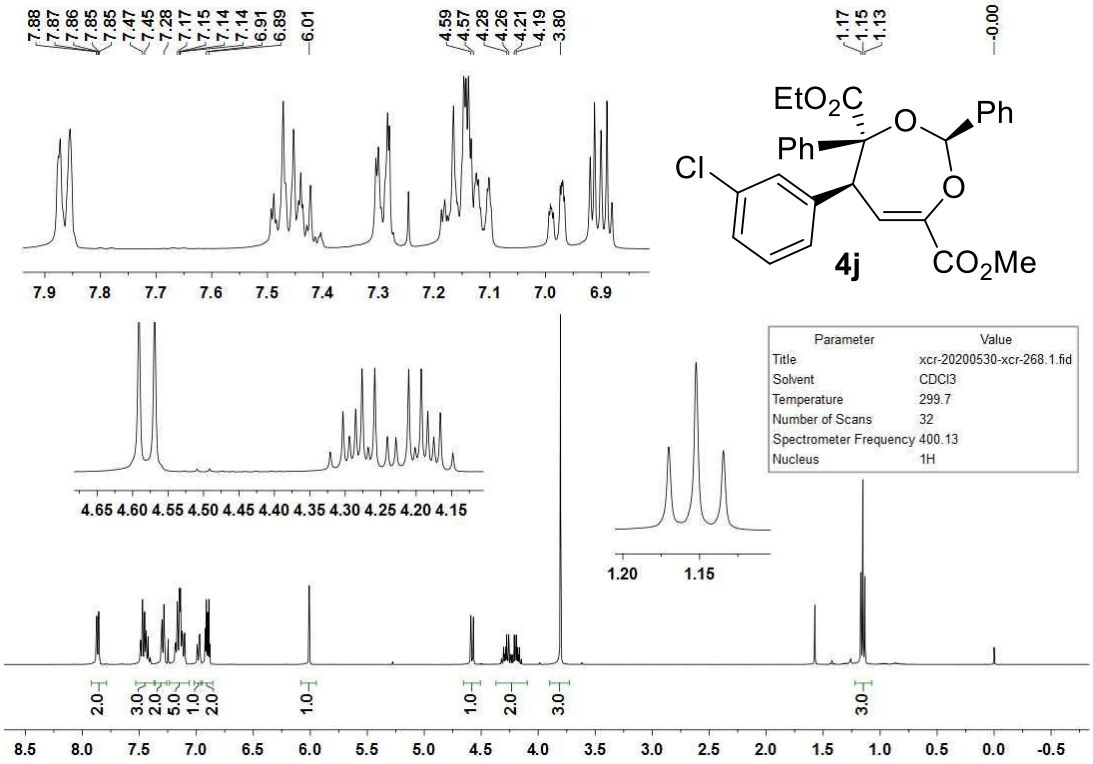
Solvent CDCl3
Temperature 299.9
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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7.14
7.14
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6.89
6.01
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4.26
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4.19
3.80
1.17
1.15
1.13
0.00
EtO2C
Ph
O
Ph
Cl
O
CO2Me
4j
Parameter Value
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Solvent CDCl3
Temperature 299.7
Number of Scans 32
Spectrometer Frequency 400.13
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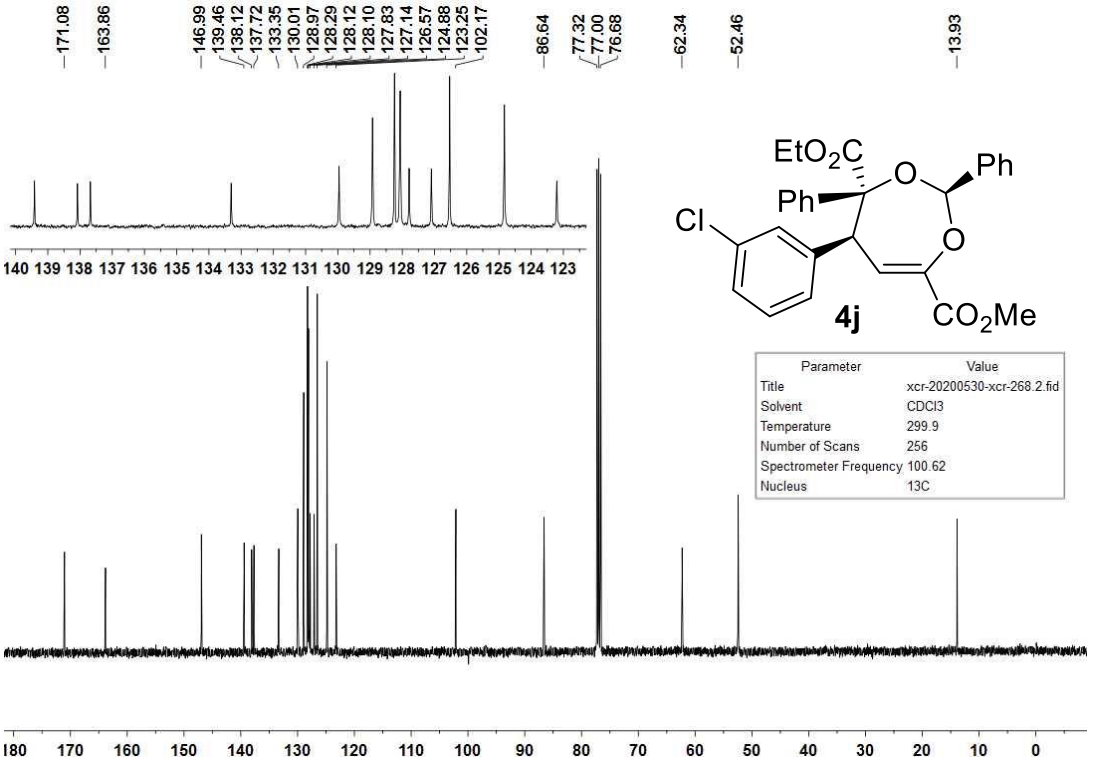
3.0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127.83
127.14
126.57
124.88
123.25
102.17
86.64
77.32
77.00
76.68
62.34
52.46
13.93
EtO2C
Ph
O
Ph
Cl
O
CO2Me
4j
Parameter Value
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Number of Scans 256
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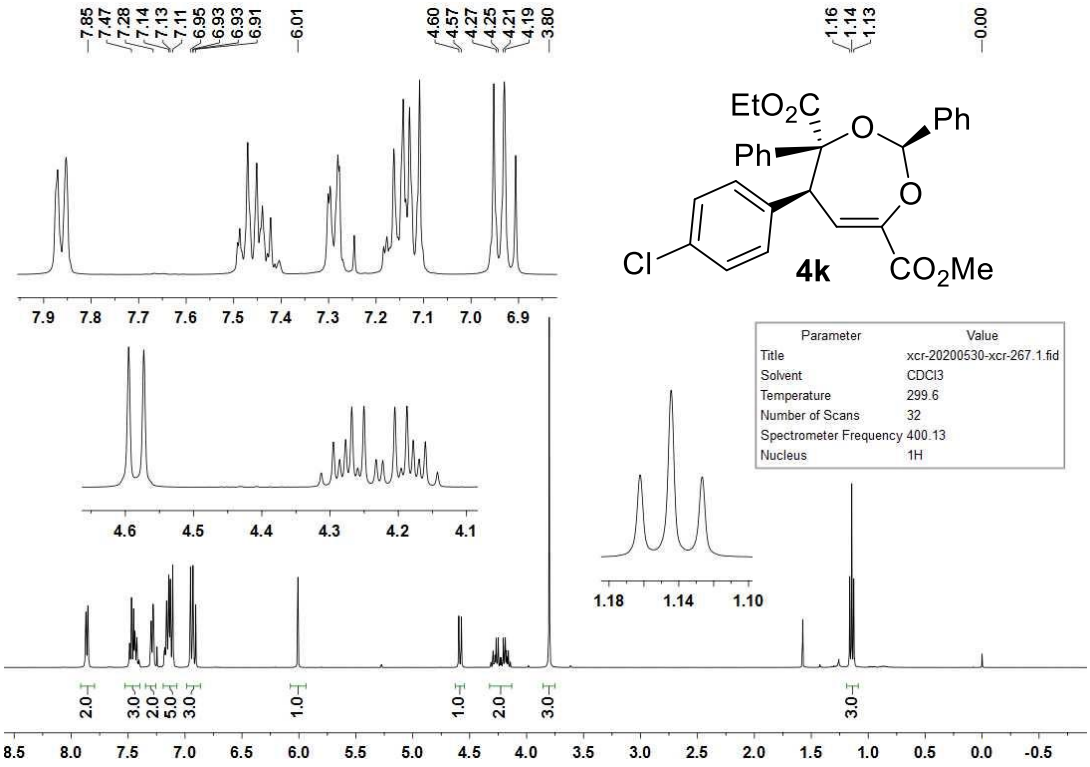
Nucleus 13C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6.01
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4.27
4.25
4.21
4.19
3.80
1.16
1.14
1.13
0.00
EtO2C
Ph
Ph
O
O
Cl
4k
CO2Me
Parameter Value
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Solvent CDCl3
Temperature 299.6
Number of Scans 32
Spectrometer Frequency 400.13
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3.0
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3.0
1.0
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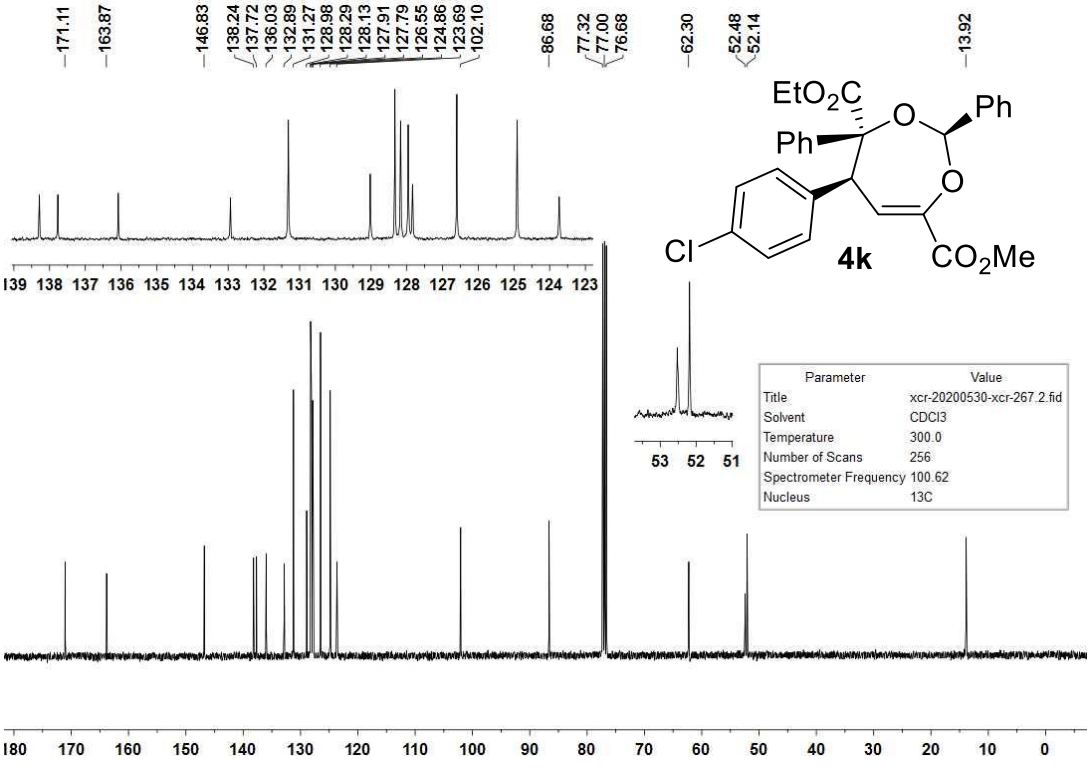
3.0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128.29
128.13
127.91
127.79
126.55
124.86
123.69
102.10
86.68
77.32
77.00
76.68
62.30
52.48
52.14
13.92
EtO2C
Ph
Ph
O
O
Cl
4k
CO2Me
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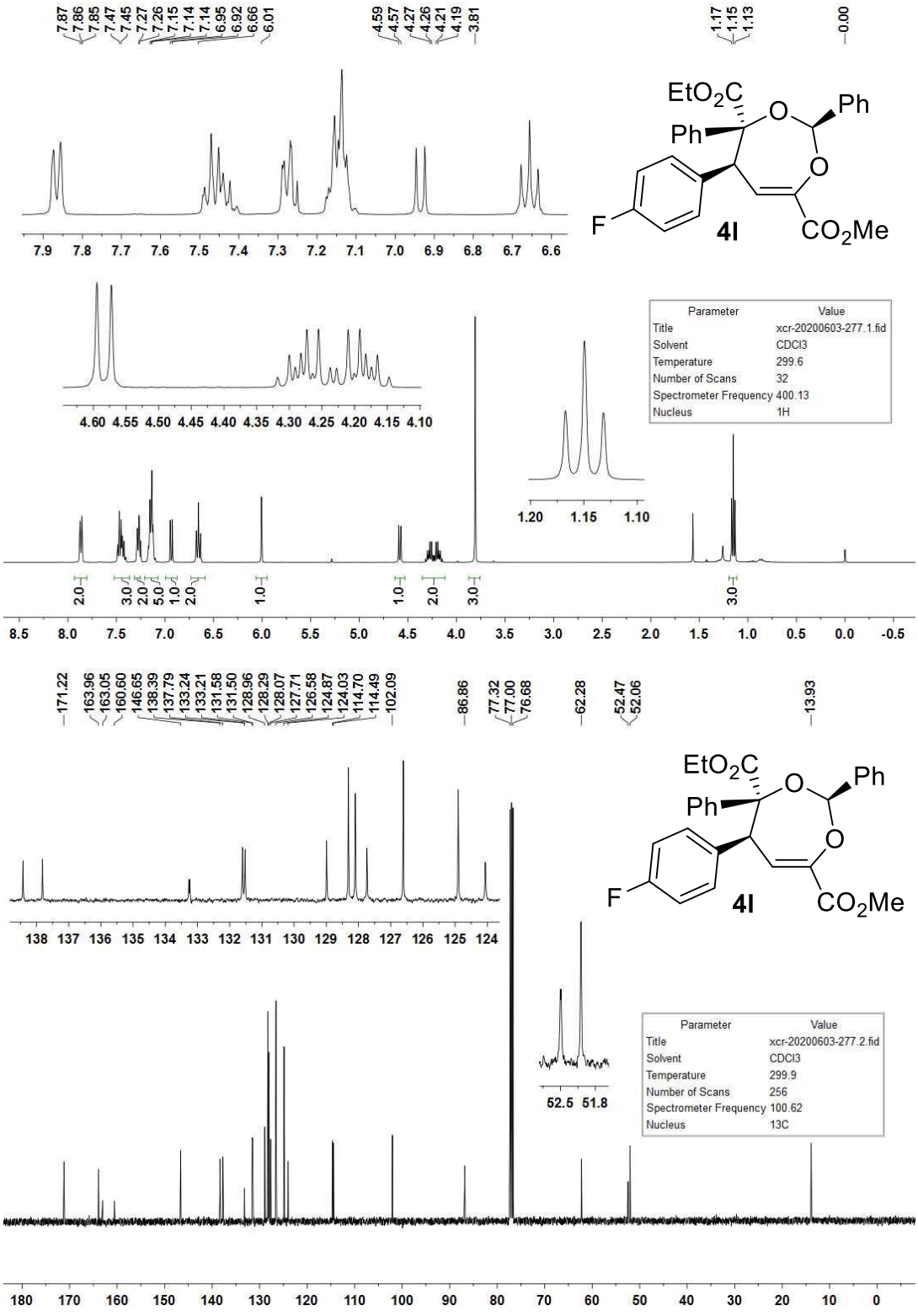
Solvent CDCl3
Temperature 300.0
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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4.59 4.57 4.27 4.26 4.21 4.19 3.81
1.17 1.15 1.13
0.00
EtO2C
Ph
O
Ph
O
F
4l
CO2Me
Parameter Value
Title xcr-20200603-277.1.fid
Solvent CDCl3
Temperature 299.6
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
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171.22 163.96 163.05 160.60 146.65 138.39 137.79 133.24 133.21 131.58 131.50 128.96 128.29 128.07 127.71 126.58 124.87 124.03 114.70 114.49 102.09
86.86
77.32 77.00 76.68
62.28
52.47 52.06
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Temperature 299.9
Number of Scans 256
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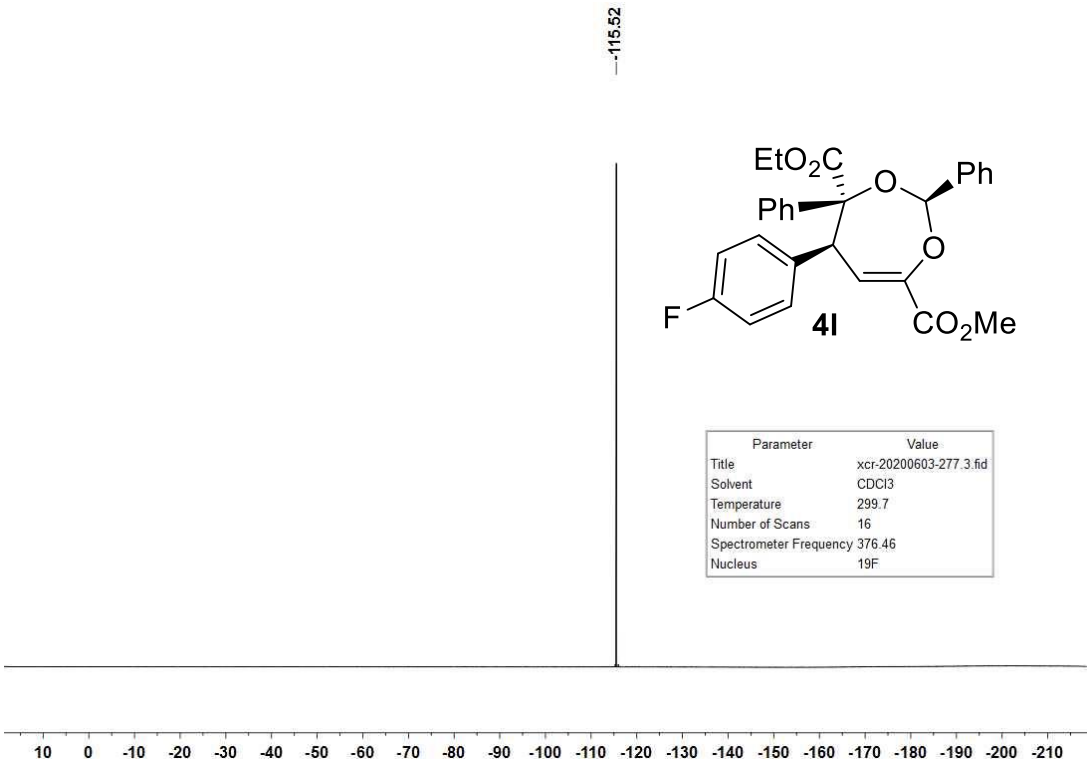
Nucleus 13C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Solvent
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Temperature
299.7
Number of Scans
16
Spectrometer Frequency
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Nucleus
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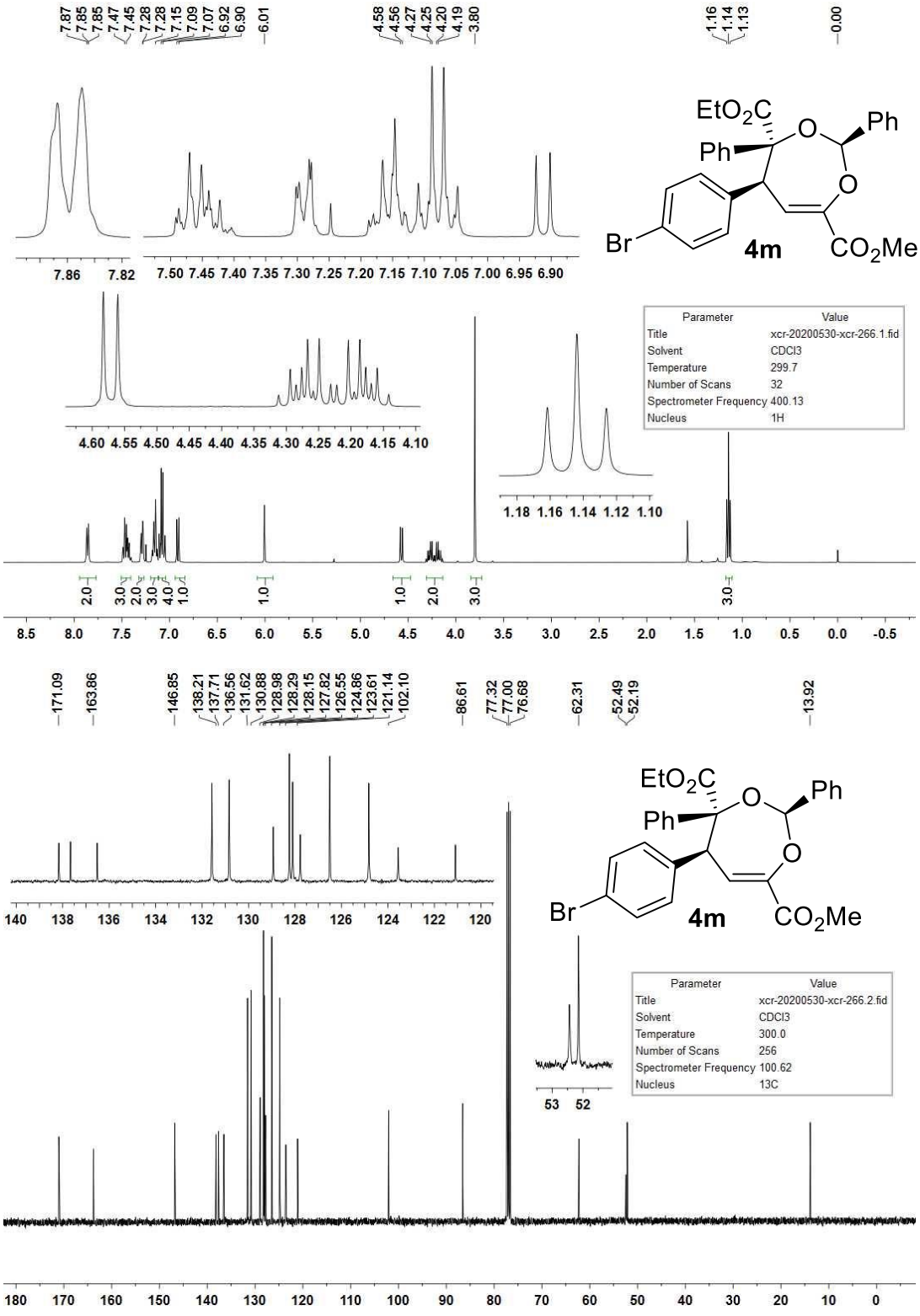
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1.16 1.14 1.13 0.00
EtO2C
Ph
O
Ph
O
Br
4m
CO2Me
7.86 7.82
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10
1.18 1.16 1.14 1.12 1.10
Parameter Value
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Solvent CDCl3
Temperature 299.7
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0 3.0 2.0 3.0 4.0 1.0 1.0 1.0 2.0 3.0 3.0
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 -0.5
171.09 163.86 146.85 138.21 137.71 136.56 131.62 130.88 128.98 128.29 128.15 127.82 126.55 124.86 123.61 121.14 102.10
86.61 77.32 77.00 76.68 62.31 52.49 52.19 13.92
EtO2C
Ph
O
Ph
O
Br
4m
CO2Me
140 138 136 134 132 130 128 126 124 122 120
53 52
Parameter Value
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Spectrometer Frequency 100.62
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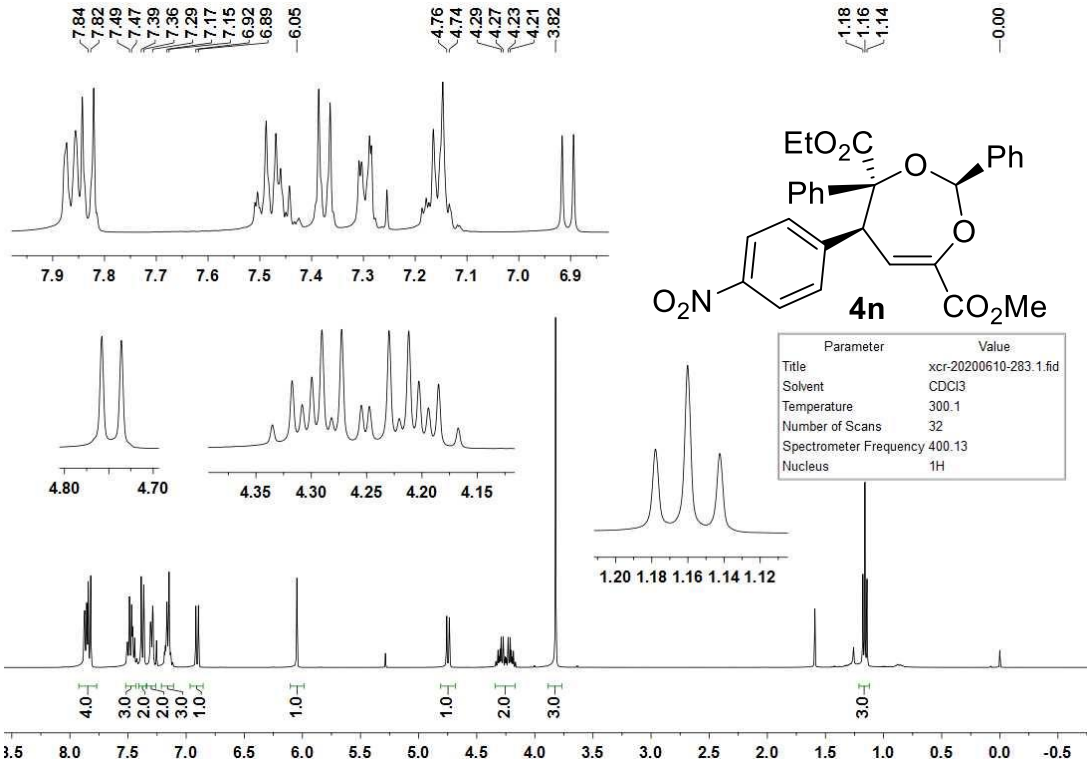
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4.76 4.74 4.29 4.27 4.23 4.21 3.82
1.18 1.16 1.14
0.00
EtO2C
Ph
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Ph
O
O2N
4n
CO2Me
Parameter Value
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Solvent CDCl3
Temperature 300.1
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
4.80 4.70
4.35 4.30 4.25 4.20 4.15
1.20 1.18 1.16 1.14 1.12
4.0 3.0 2.0 2.0 3.0 1.0 1.0 1.0 2.0 3.0 3.0
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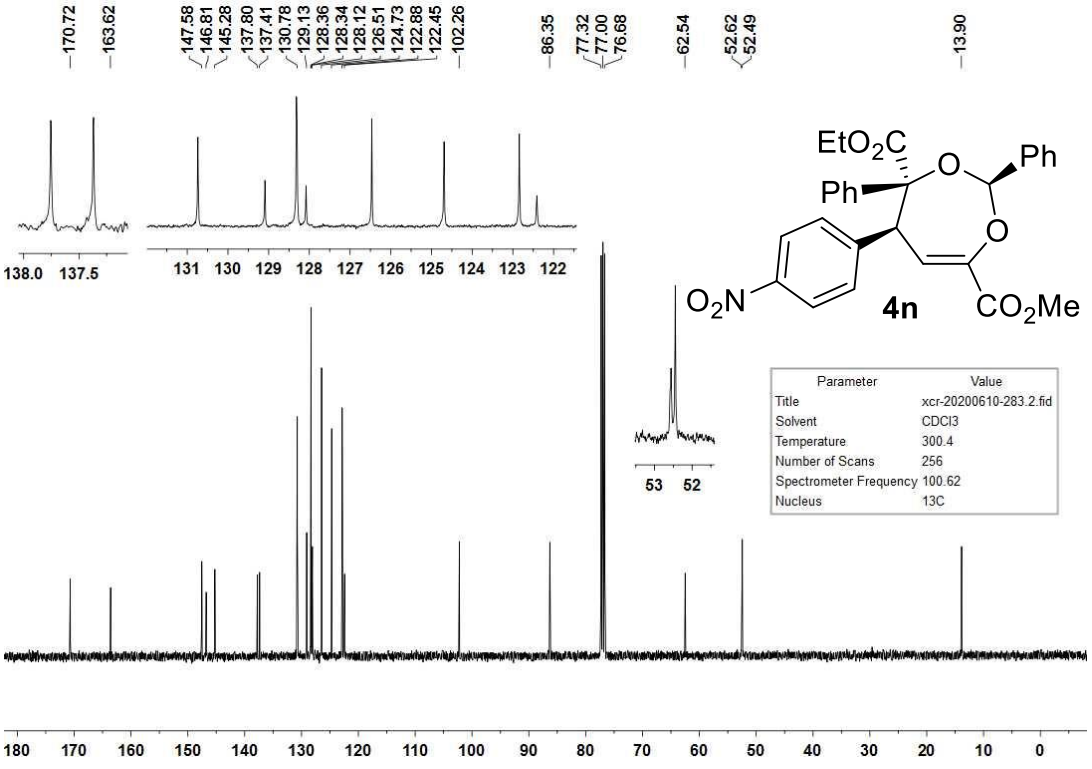
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EtO2C
Ph
O
Ph
O
O2N
4n
CO2Me
Parameter Value
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Solvent CDCl3
Temperature 300.4
Number of Scans 256
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131 130 129 128 127 126 125 124 123 122
53 52
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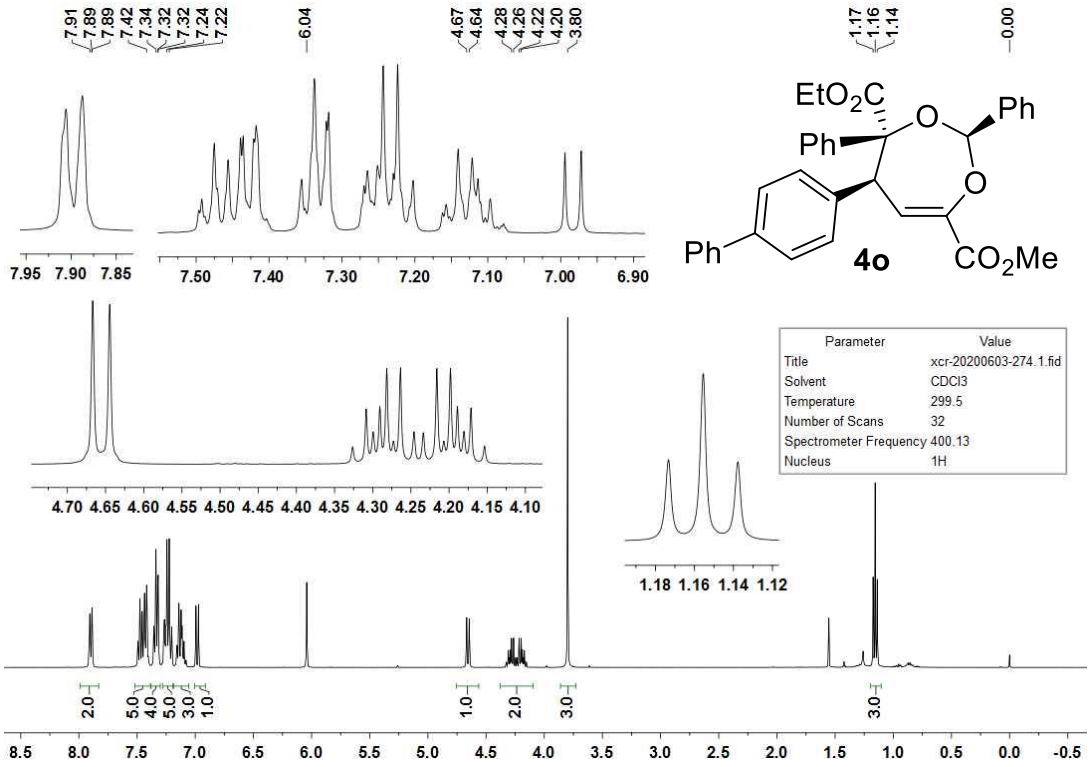
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6.04
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0.00
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Ph
Ph
O
O
Ph
CO2Me
4o
Parameter Value
Title xcr-20200603-274.1.fid
Solvent CDCl3
Temperature 299.5
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Spectrometer Frequency 400.13
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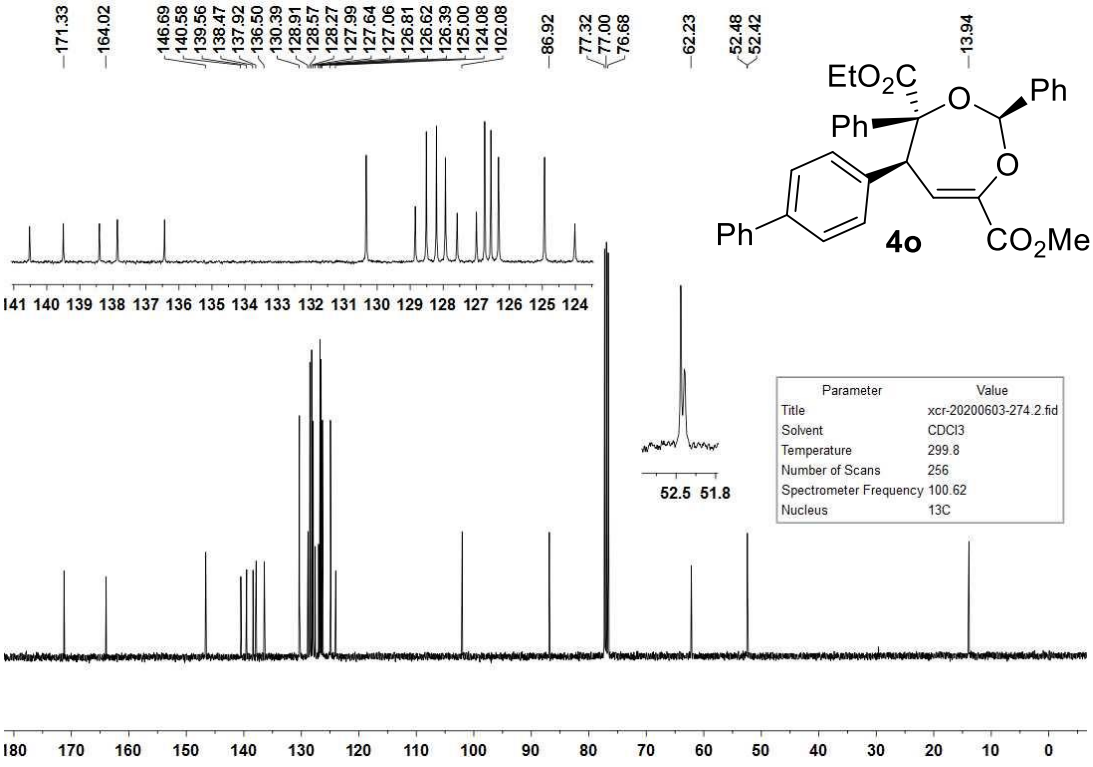
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86.92
77.32 77.00 76.68
62.23
52.48 52.42
13.94
EtO2C
Ph
Ph
O
O
Ph
CO2Me
4o
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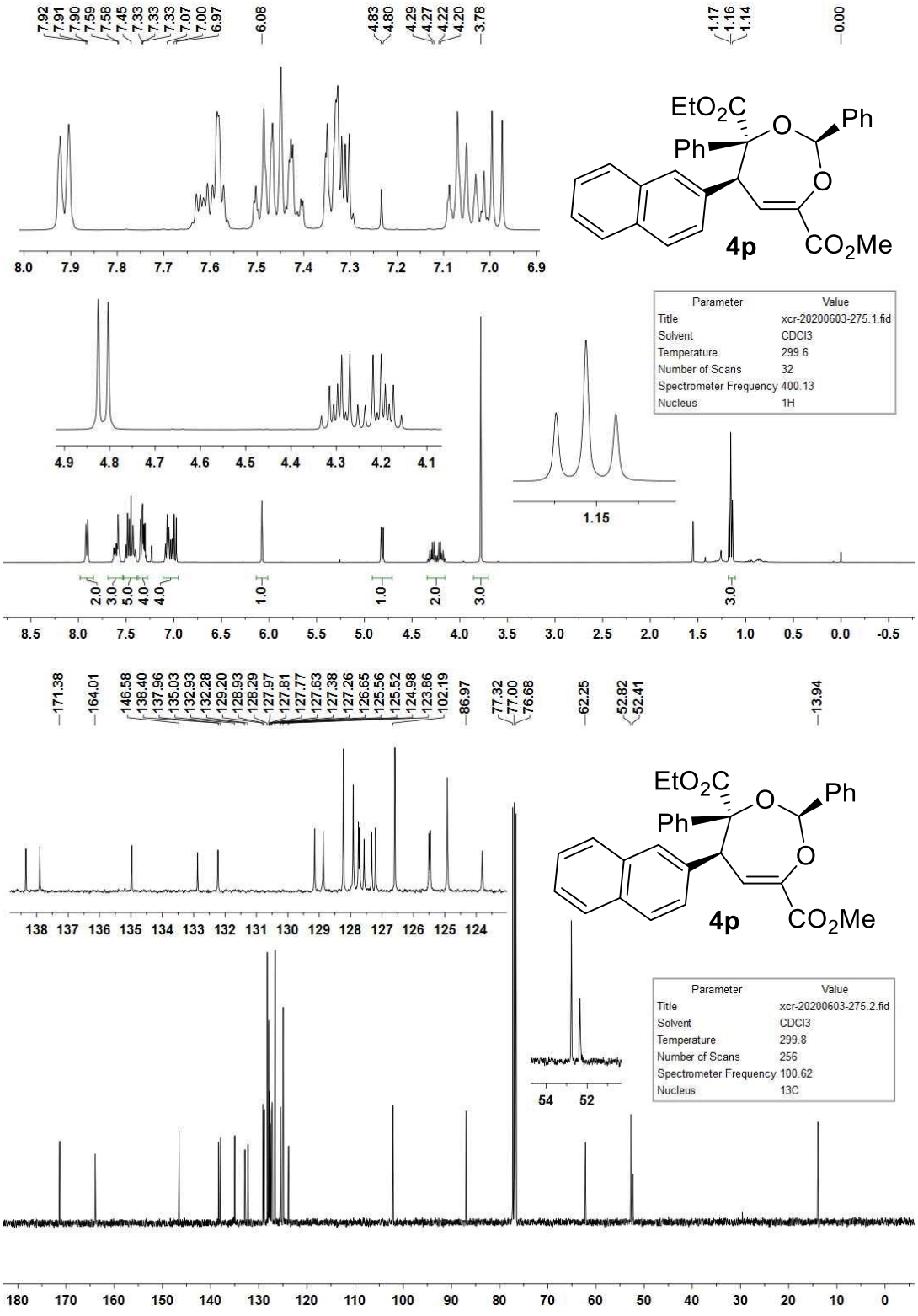
Temperature 299.8
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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EtO2C
Ph
O
Ph
O
4p
CO2Me
Parameter Value
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Temperature 299.6
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
1.15
2.0 3.0 5.0 4.0 4.0 1.0 1.0 2.0 3.0 3.0
171.38 164.01 146.58 138.40 137.96 135.03 132.93 132.28 129.20 128.93 128.29 127.97 127.81 127.77 127.63 127.38 127.26 126.65 125.56 125.52 124.98 123.86 102.19 86.97 77.32 77.00 76.68 62.25 52.82 52.41 13.94
4p
Parameter Value
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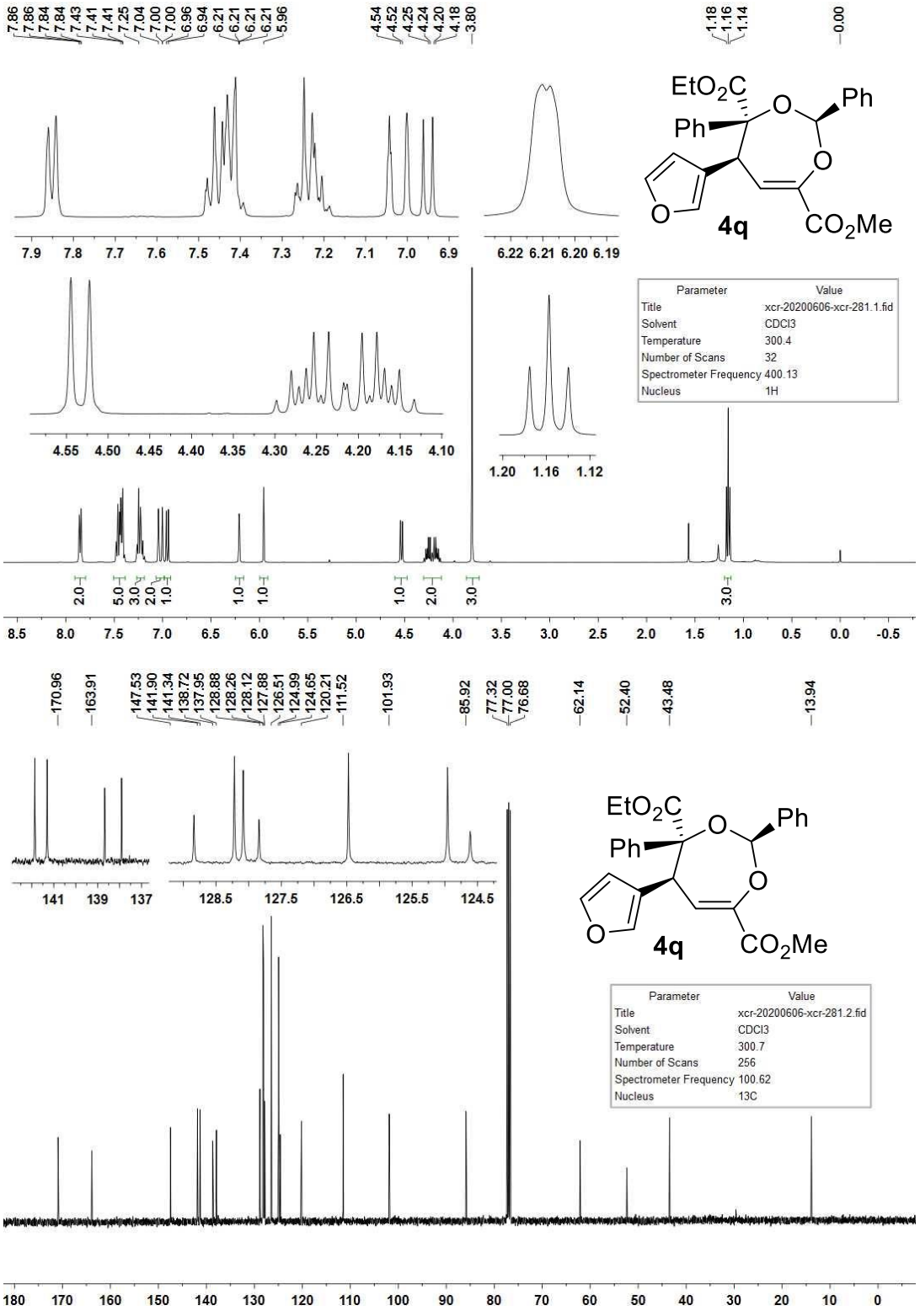
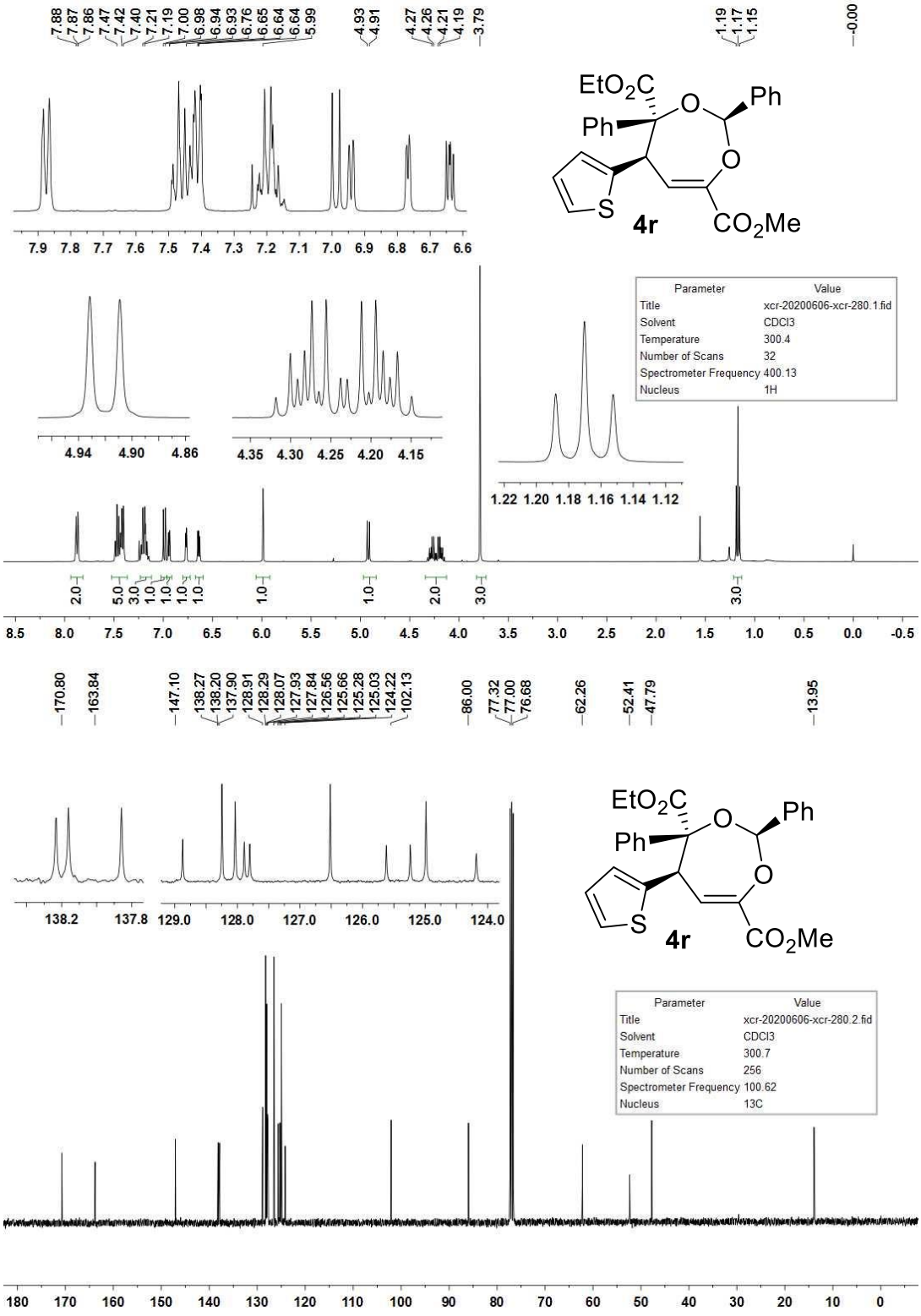
Solvent CDCl3
Temperature 299.8
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C


7.86 7.86 7.84 7.84 7.43 7.41 7.41 7.25 7.04 7.00 7.00 6.96 6.94 6.21 6.21 6.21 5.96
4.54 4.52 4.25 4.24 4.20 4.18 3.80
1.18 1.16 1.14
0.00
EtO2C
Ph
O
Ph
O
O
4q
CO2Me
Parameter Value
Title xcr-20200606-xcr-281.1.fid
Solvent CDCl3
Temperature 300.4
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0 5.0 3.0 2.0 1.0 1.0 1.0 1.0 2.0 3.0 3.0
170.96 163.91 147.53 141.90 141.34 138.72 137.95 128.88 128.26 128.12 127.88 126.51 124.99 124.65 120.21 111.52 101.93 85.92 77.32 77.00 76.68 62.14 52.40 43.48 13.94
EtO2C
Ph
O
Ph
O
O
4q
CO2Me
Parameter Value
Title xcr-20200606-xcr-281.2.fid
Solvent CDCl3
Temperature 300.7
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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EtO2C
Ph
O
Ph
O
S
4r
CO2Me
Parameter Value
Title xcr-20200606-xcr-280.1.fid
Solvent CDCl3
Temperature 300.4
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0 5.0 3.0 1.0 1.0 1.0 1.0 1.0 2.0 3.0 3.0
170.80 163.84 147.10 138.27 138.20 137.90 128.91 128.29 128.07 127.93 127.84 126.56 125.66 125.28 125.03 124.22 102.13 86.00 77.32 77.00 76.68 62.26 52.41 47.79 13.95
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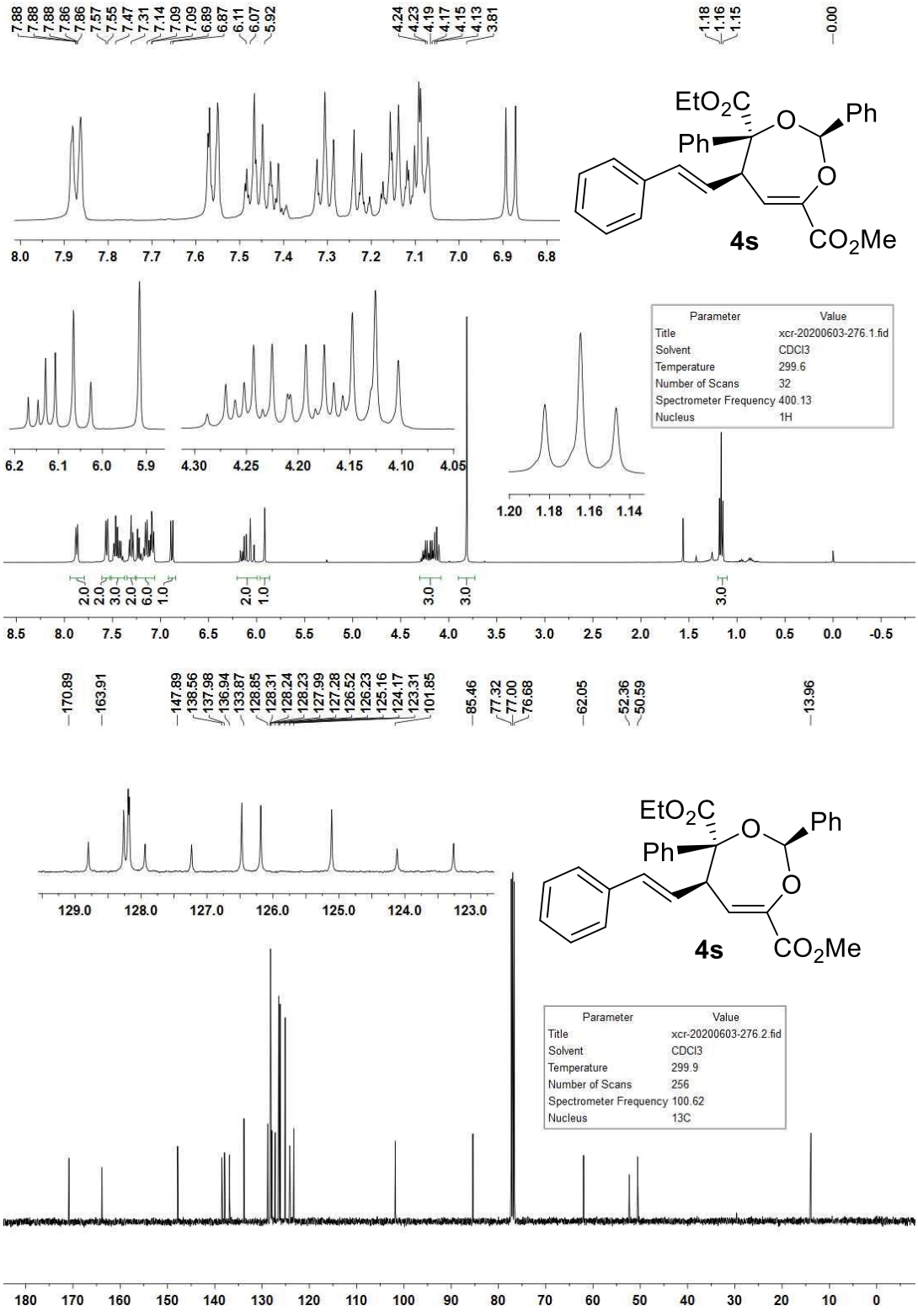
Temperature 300.7
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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7.88
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7.86
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7.47
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7.14
7.09
7.09
6.89
6.87
6.11
6.07
5.92
4.24
4.23
4.19
4.17
4.15
4.13
3.81
1.18
1.16
1.15
0.00
EtO2C
Ph
O
Ph
O
4s
CO2Me
Parameter Value
Title xcr-20200603-276.1.fid
Solvent CDCl3
Temperature 299.6
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0
2.0
3.0
2.0
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3.0
3.0
3.0
170.89
163.91
147.89
138.56
137.98
136.94
133.87
128.85
128.31
128.24
128.23
127.99
127.28
126.52
126.23
125.16
124.17
123.31
101.85
85.46
77.32
77.00
76.68
62.05
52.36
50.59
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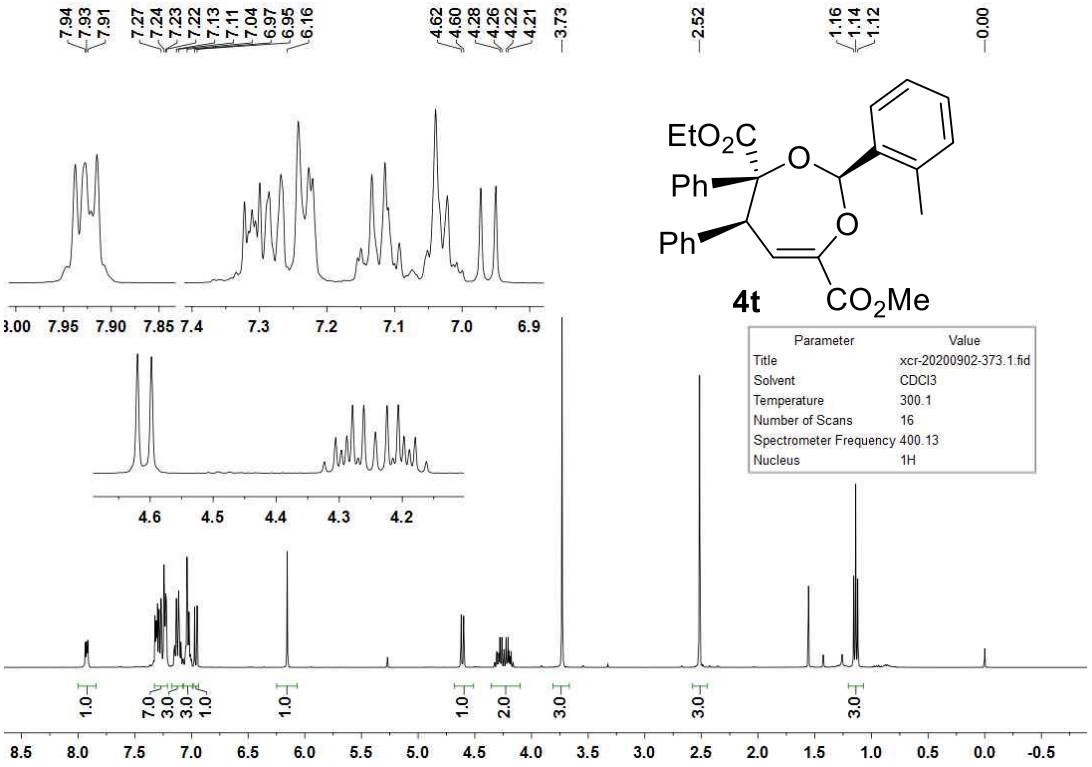
Solvent CDCl3
Temperature 299.9
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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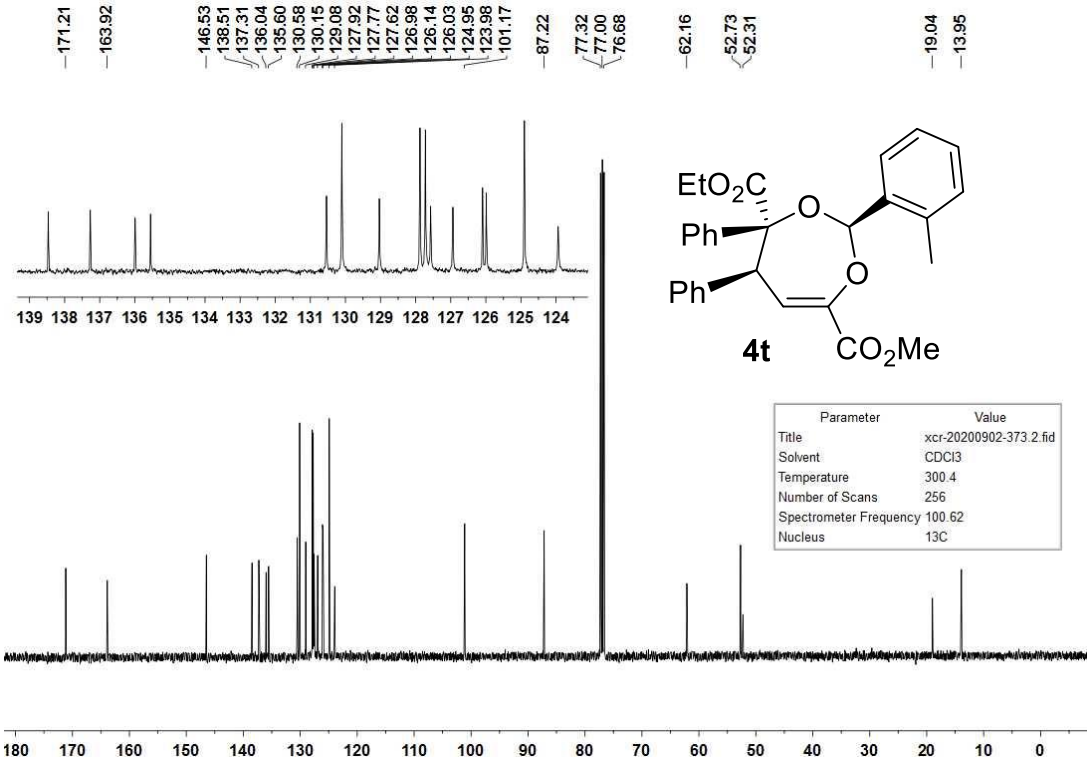
7.91
7.27
7.24
7.23
7.22
7.13
7.11
7.04
6.97
6.95
6.16
4.62
4.60
4.28
4.26
4.22
4.21
3.73
2.52
1.16
1.14
1.12
0.00
EtO2C
Ph
Ph
O
O
CO2Me
4t
Parameter Value
Title xcr-20200902-373.1.fid
Solvent CDCl3
Temperature 300.1
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H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163.92
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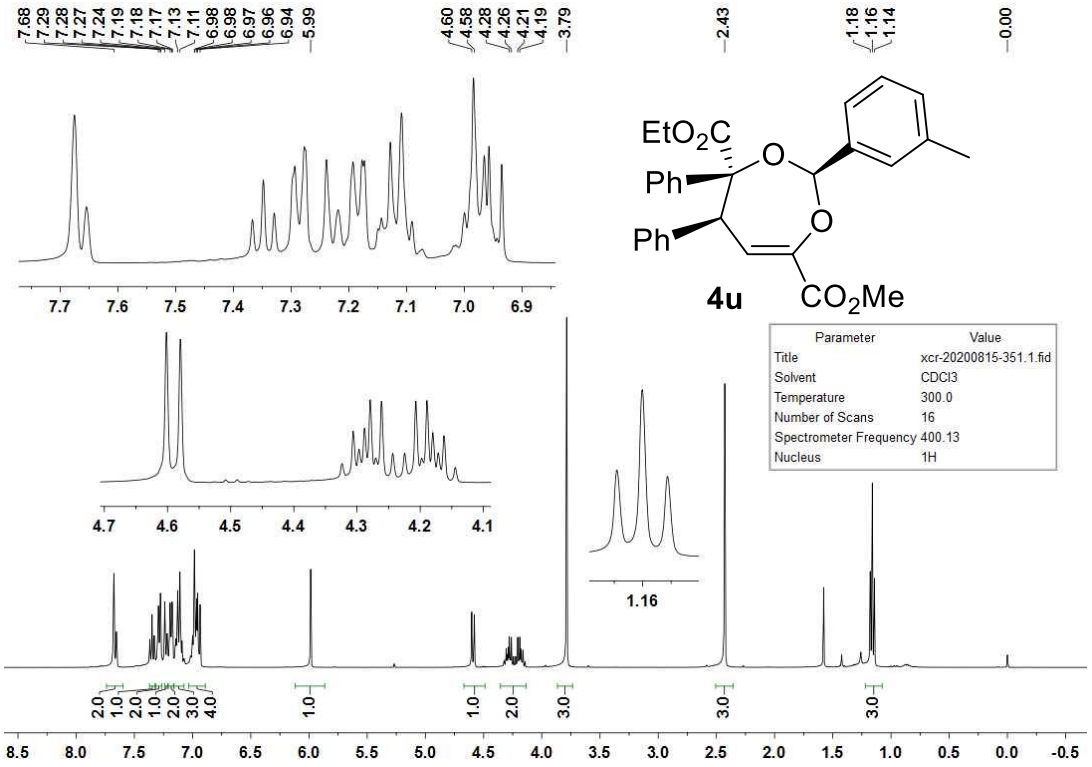
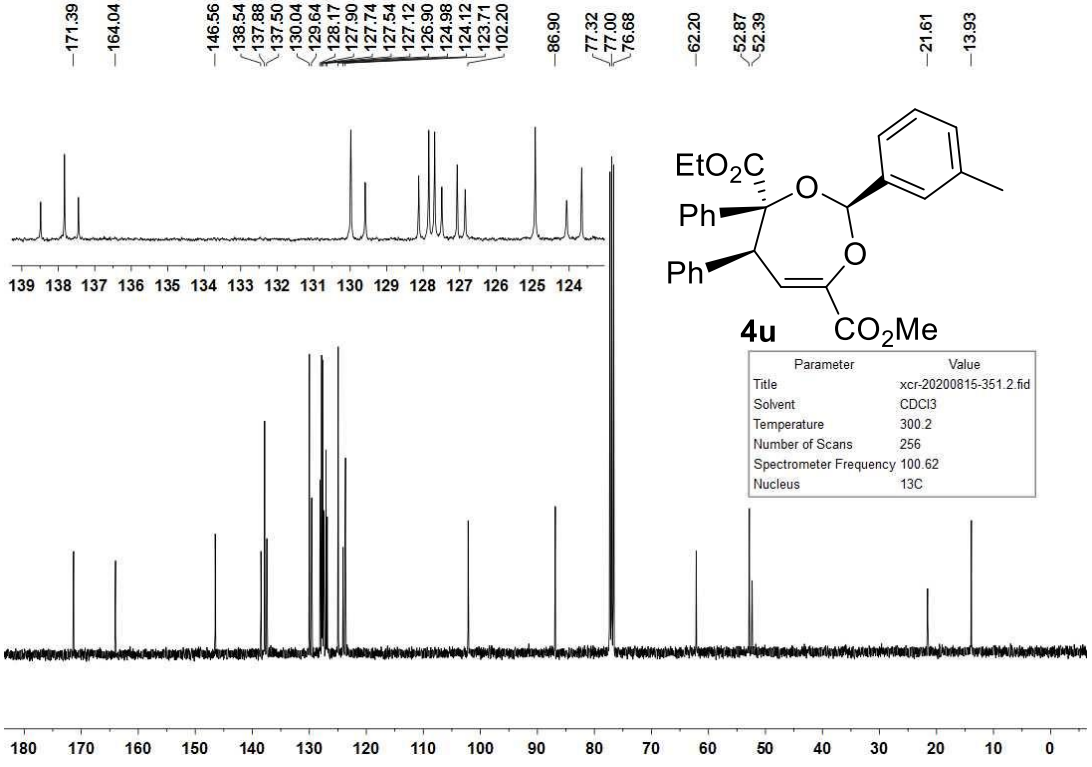
138.51
137.31
136.04
135.60
130.58
130.15
129.08
127.92
127.77
127.62
126.98
126.14
126.03
124.95
123.98
101.17
87.22
77.32
77.00
76.68
62.16
52.73
52.31
19.04
13.95
EtO2C
Ph
Ph
O
O
CO2Me
4t
Parameter Value
Title xcr-20200902-373.2.fid
Solvent CDCl3
Temperature 300.4
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C


7.68 7.29 7.28 7.27 7.24 7.19 7.18 7.17 7.13 7.11 6.98 6.98 6.97 6.96 6.94 5.99
4.60 4.58 4.28 4.26 4.21 4.19 3.79
2.43
1.18 1.16 1.14
0.00
EtO2C
Ph
Ph
O
O
4u
CO2Me
Parameter Value
Title xcr-20200815-351.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
1.16
2.0 1.0 2.0 1.0 2.0 3.0 4.0 1.0 1.0 2.0 3.0 3.0 3.0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86.90
77.32 77.00 76.68
62.20
52.87 52.39
21.61 13.93
EtO2C
Ph
Ph
O
O
4u
CO2Me
Parameter Value
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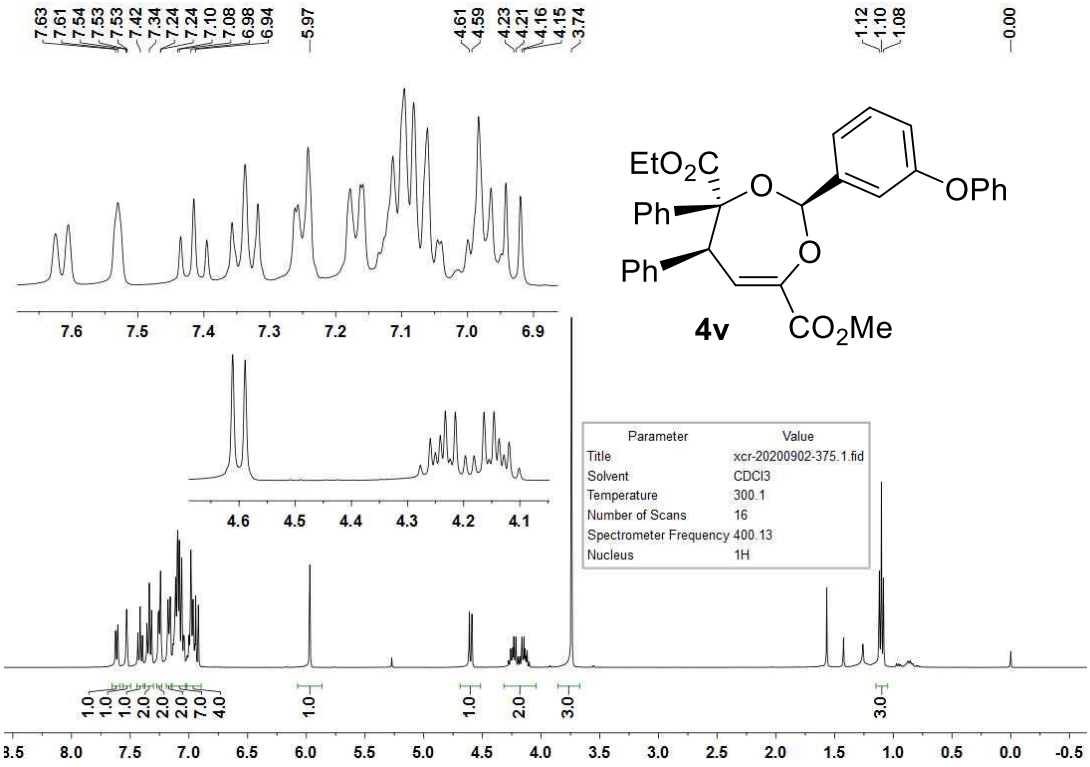
Solvent CDCl3
Temperature 300.2
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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EtO2C
Ph
Ph
O
O
OPh
CO2Me
4v
Parameter Value
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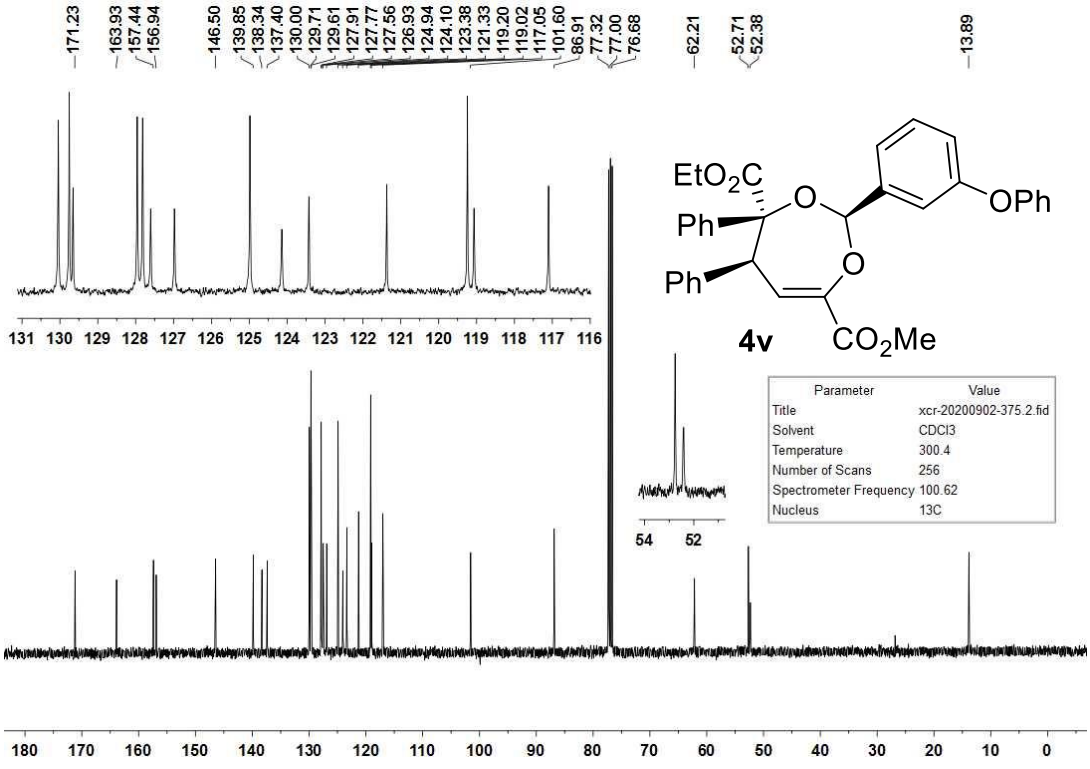
Solvent CDCl3
Temperature 300.1
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H


171.23 163.93 157.44 156.94 146.50 139.85 138.34 137.40 130.00 129.71 129.61 127.91 127.77 127.56 126.93 124.94 124.10 123.38 121.33 119.20 119.02 117.05 101.60 86.91 77.32 77.00 76.68 62.21 52.71 52.38 13.89
EtO2C
Ph
Ph
O
O
OPh
CO2Me
4v
Parameter Value
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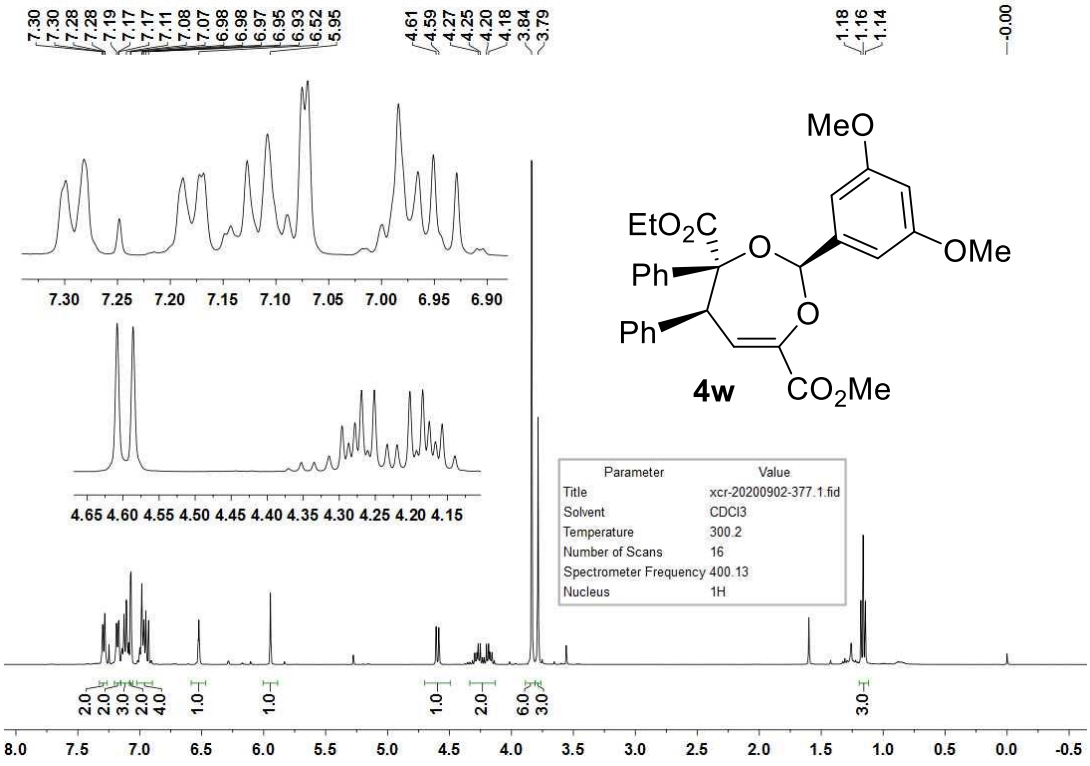
Solvent CDCl3
Temperature 300.4
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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OMe
Ph
O
Ph
4w
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Parameter Value
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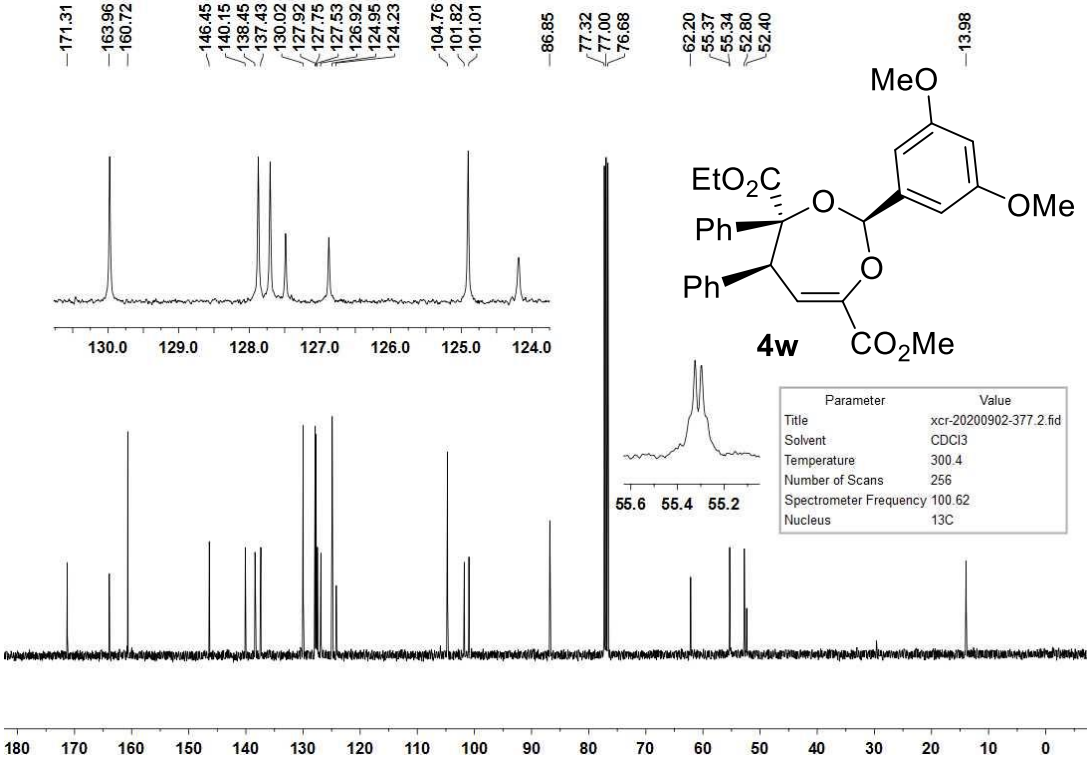
Solvent CDCl3
Temperature 300.2
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H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EtO2C
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OMe
Ph
O
Ph
4w
CO2Me
Parameter Value
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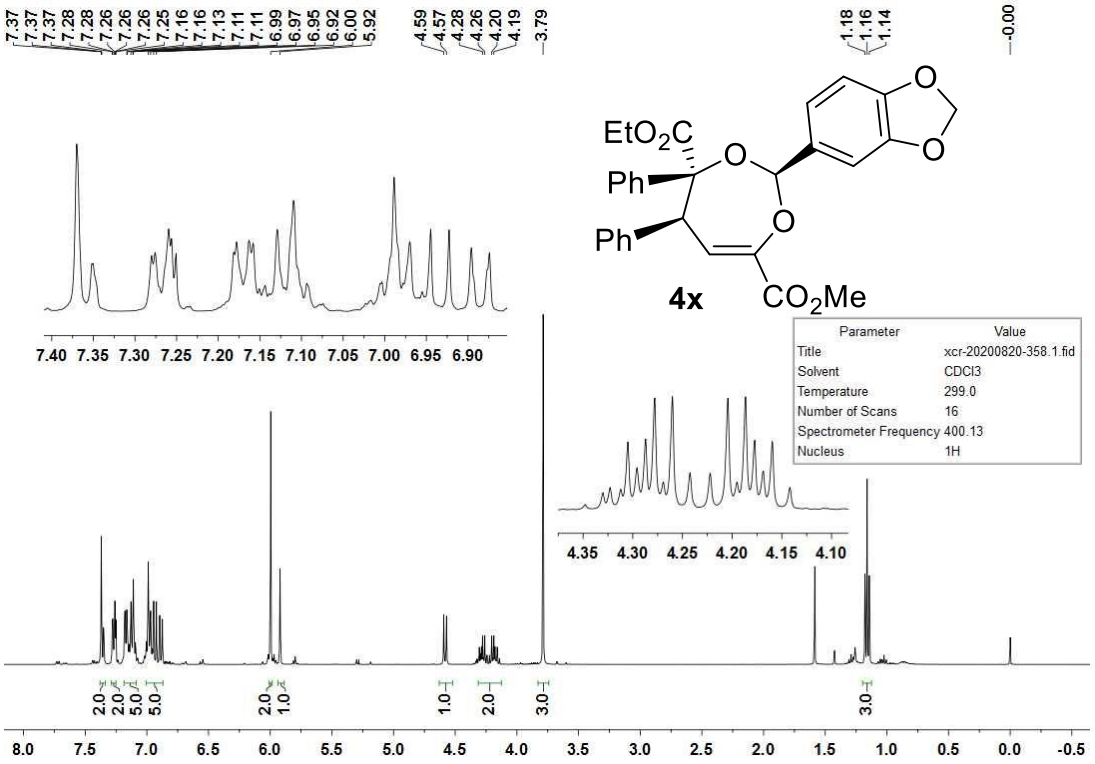
Solvent CDCl3
Temperature 300.4
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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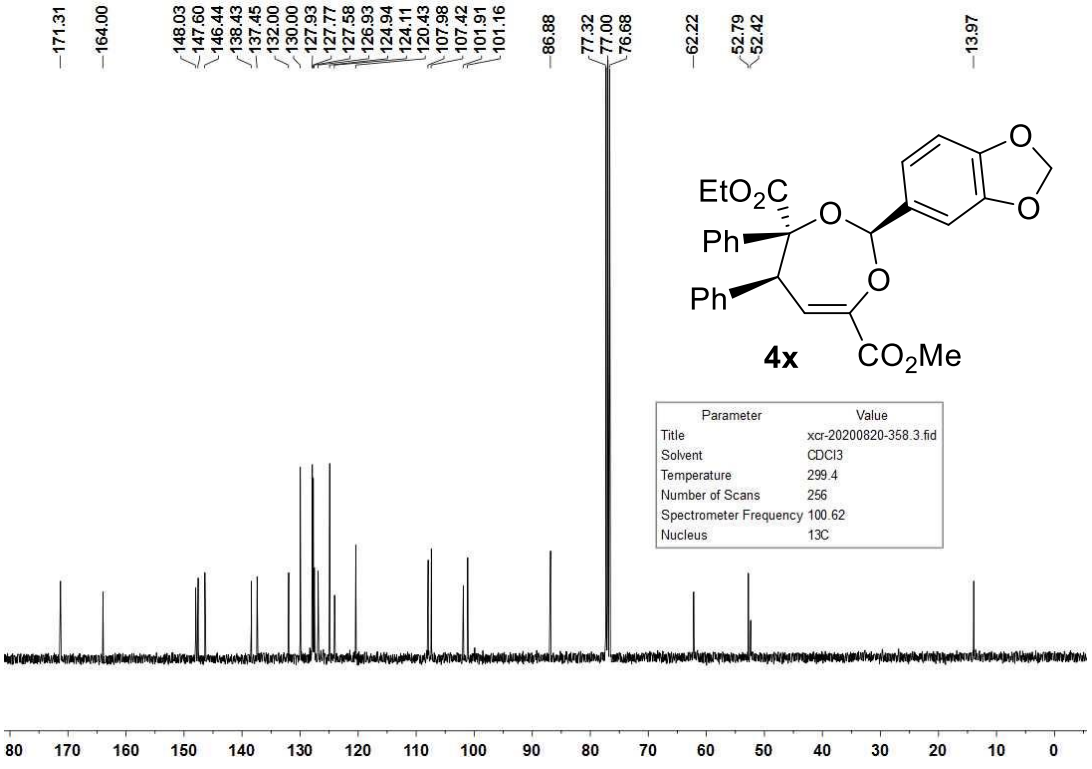
4.59 4.57 4.28 4.26 4.20 4.19 3.79
1.18 1.16 1.14
-0.00
EtO2C
Ph
Ph
O
O
O
O
O
4x
CO2Me
7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
4.35 4.30 4.25 4.20 4.15 4.10
Parameter Value
Title xcr-20200820-358.1.fid
Solvent CDCl3
Temperature 299.0
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
2.0 2.0 5.0 5.0 2.0 1.0 1.0 2.0 3.0 3.0
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 -0.5


171.31 164.00 148.03 147.60 146.44 138.43 137.45 132.00 130.00 127.93 127.77 127.58 126.93 124.94 124.11 120.43 107.98 107.42 101.91 101.16 86.88 77.32 77.00 76.68 62.22 52.79 52.42 13.97
EtO2C
Ph
Ph
O
O
O
O
O
4x
CO2Me
Parameter Value
Title xcr-20200820-358.3.fid
Solvent CDCl3
Temperature 299.4
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C
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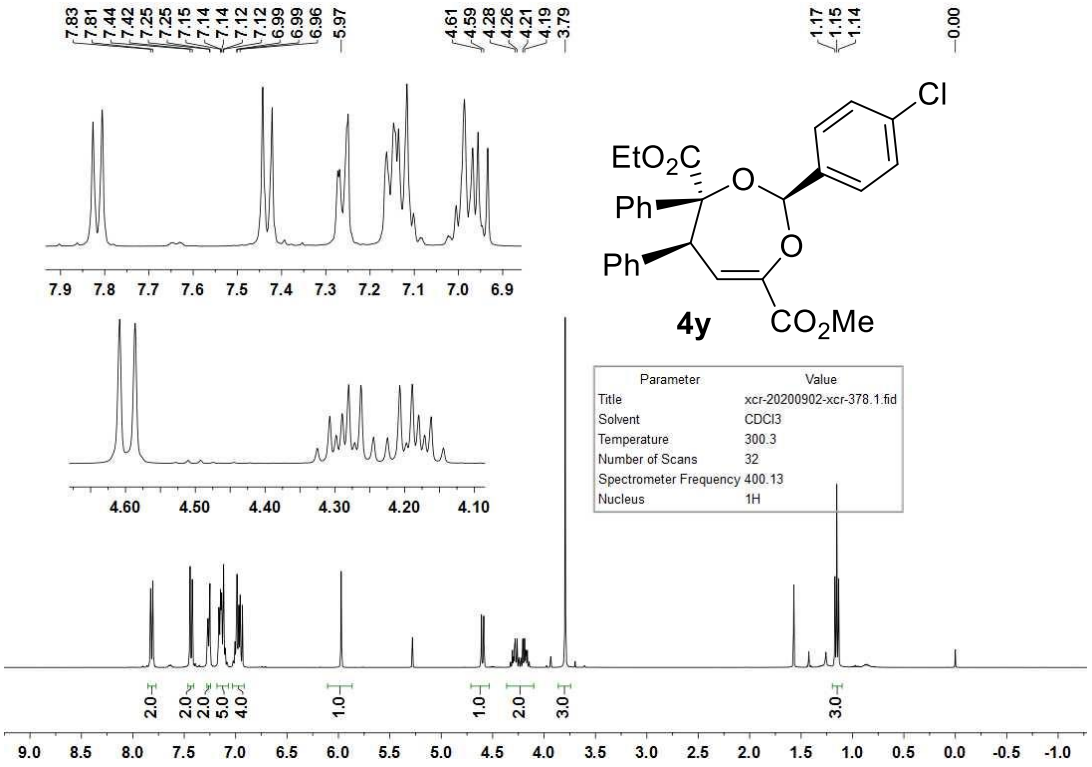
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7.14
7.12
7.12
6.99
6.99
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5.97
4.61
4.59
4.28
4.26
4.21
4.19
3.79
1.17
1.15
1.14
0.00
Cl
EtO2C
O
Ph
Ph
O
4y
CO2Me
Parameter Value
Title xcr-20200902-xcr-378.1.fid
Solvent CDCl3
Temperature 300.3
Number of Scans 32
Spectrometer Frequency 400.13
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2.0
2.0
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1.0
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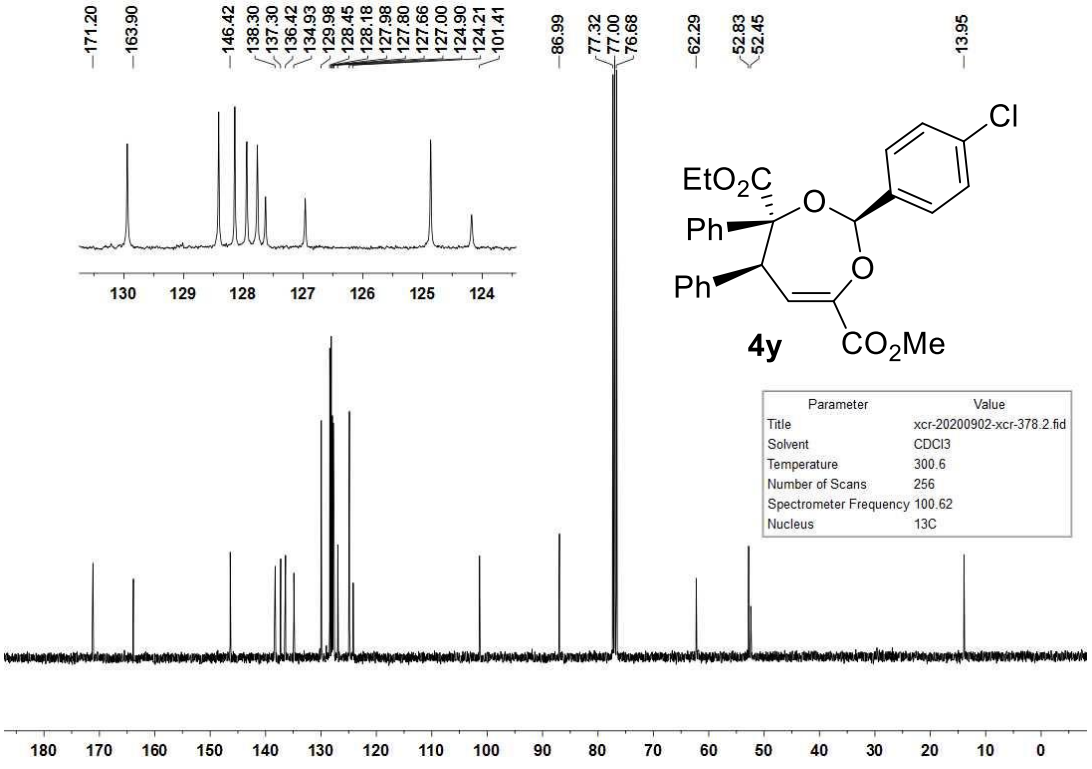
3.0
3.0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136.42
134.93
129.98
128.45
128.18
127.98
127.80
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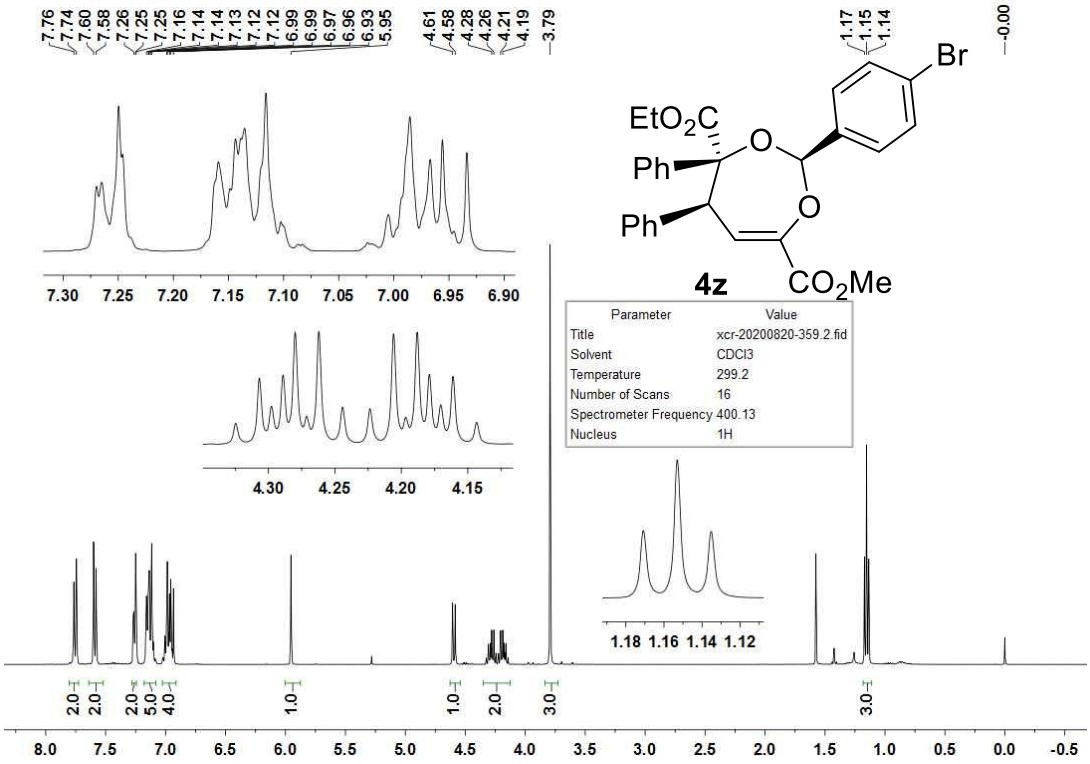
127.00
124.90
124.21
101.41
86.99
77.32
77.00
76.68
62.29
52.83
52.45
13.95
Cl
EtO2C
O
Ph
Ph
O
4y
CO2Me
Parameter Value
Title xcr-20200902-xcr-378.2.fid
Solvent CDCl3
Temperature 300.6
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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4.61 4.58 4.28 4.26 4.21 4.19
3.79
1.17 1.15 1.14
-0.00
Br
EtO2C
O
Ph
Ph
O
CO2Me
4z
Parameter Value
Title xcr-20200820-359.2.fid
Solvent CDCl3
Temperature 299.2
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
4.30 4.25 4.20 4.15
1.18 1.16 1.14 1.12
2.0 2.0 2.0 5.0 4.0 1.0 1.0 2.0 3.0 3.0
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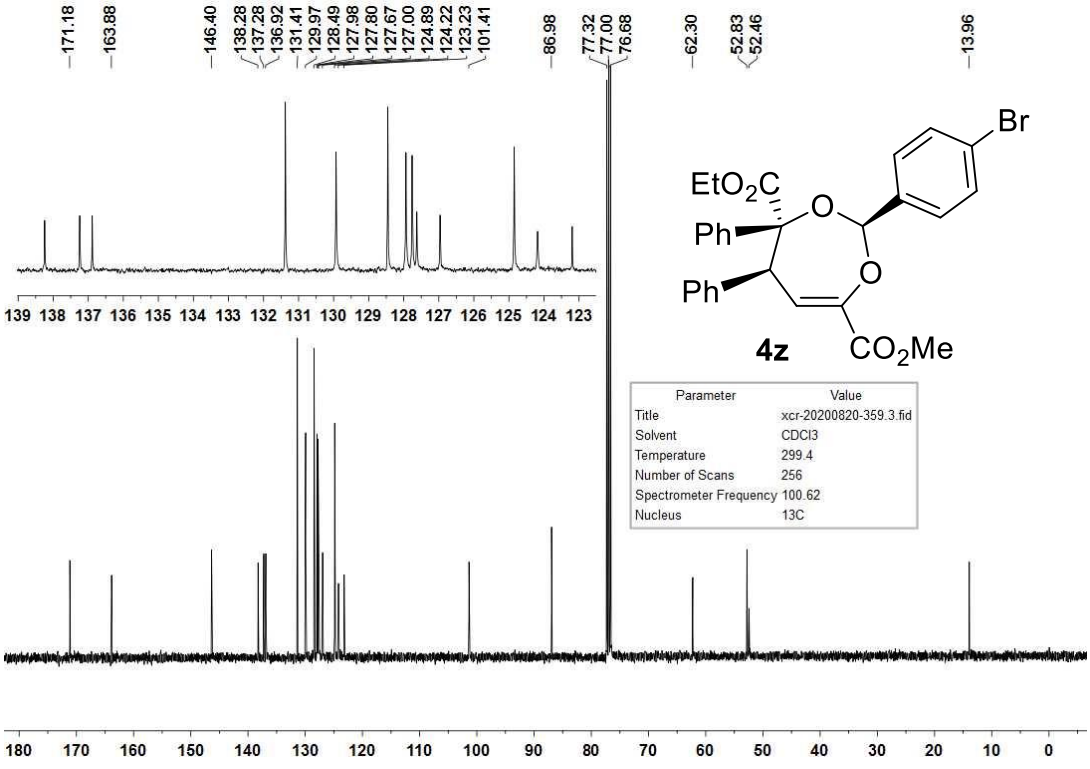
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86.98
77.32 77.00 76.68
62.30
52.83 52.46
13.96
Br
EtO2C
O
Ph
Ph
O
CO2Me
4z
Parameter Value
Title xcr-20200820-359.3.fid
Solvent CDCl3
Temperature 299.4
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C
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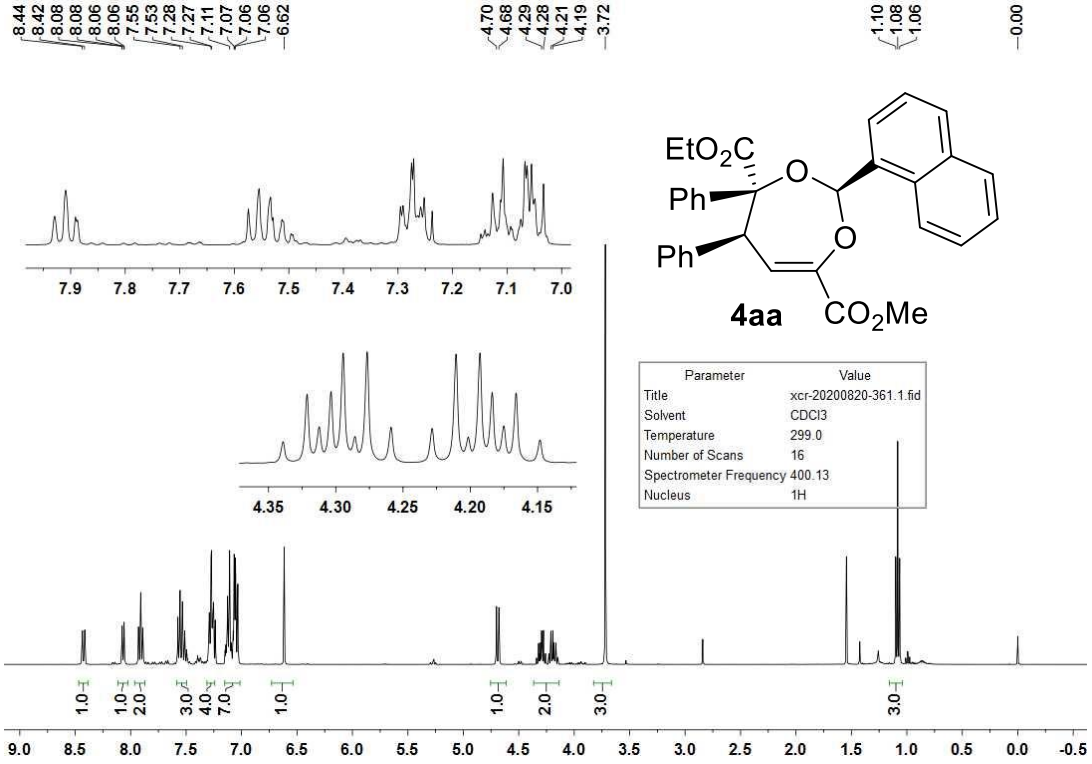
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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8.06
8.06
7.55
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7.27
7.11
7.07
7.06
7.06
6.62
4.70
4.68
4.29
4.28
4.21
4.19
3.72
1.10
1.08
1.06
0.00
EtO2C
Ph
Ph
O
O
CO2Me
4aa
Parameter Value
Title xcr-20200820-361.1.fid
Solvent CDCl3
Temperature 299.0
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
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1.0
2.0
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4.0
7.0
1.0
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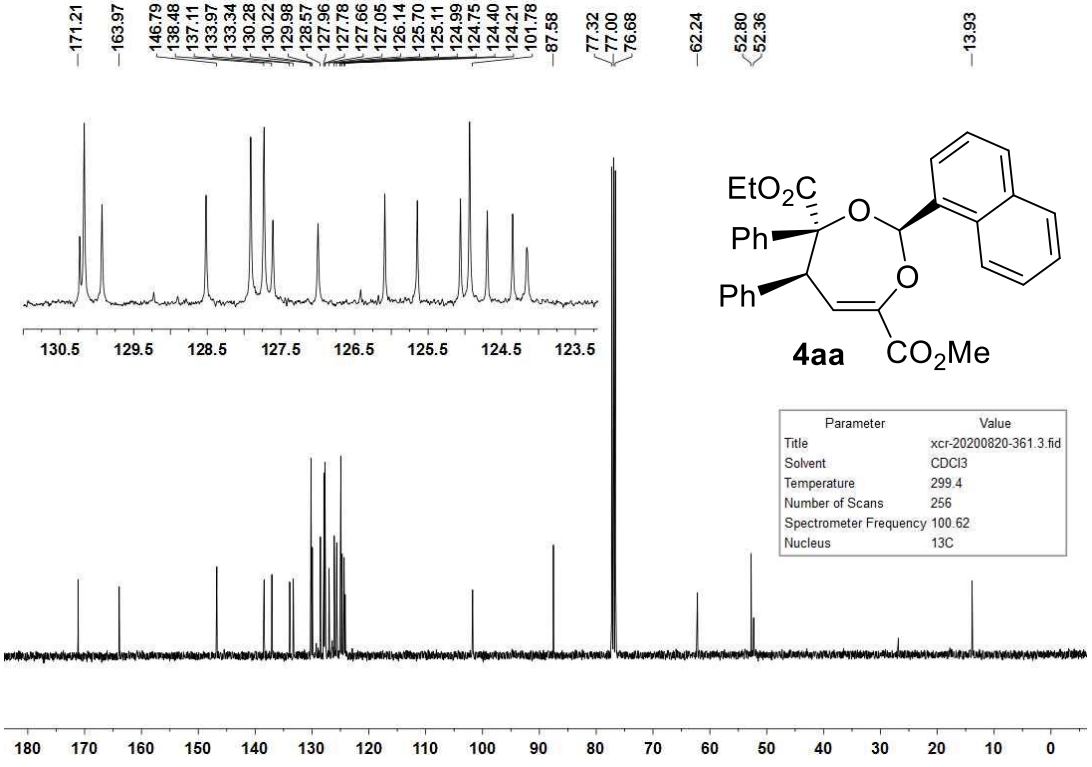
3.0
3.0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130.28
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129.98
128.57
127.96
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127.66
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77.00
76.68
62.24
52.80
52.36
13.93
EtO2C
Ph
Ph
O
O
CO2Me
4aa
Parameter Value
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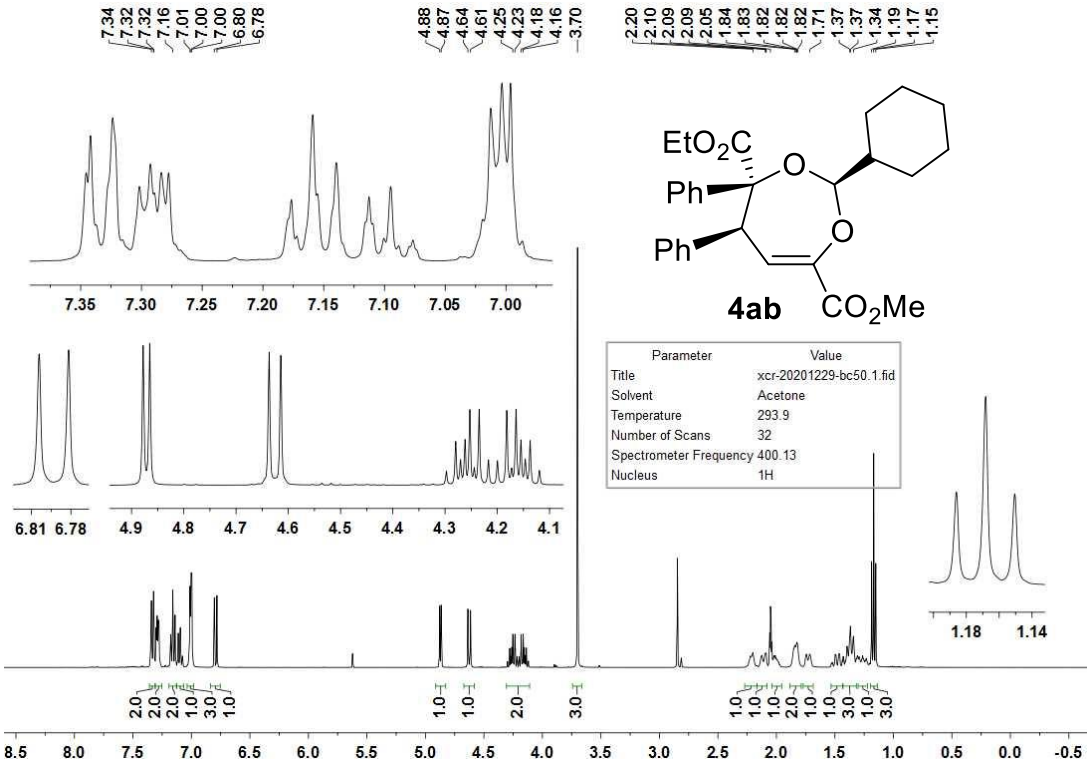
Solvent CDCl3
Temperature 299.4
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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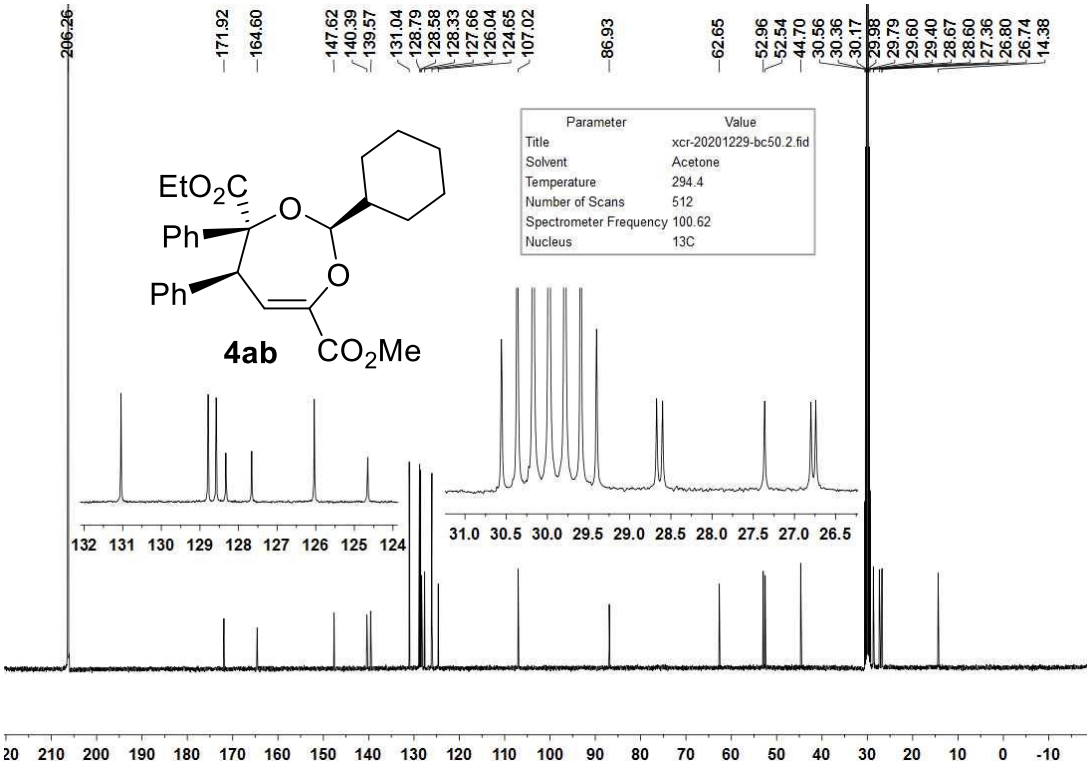
4.88 4.87 4.64 4.61 4.25 4.23 4.18 4.16 3.70
2.20 2.10 2.09 2.09 2.05 1.84 1.83 1.82 1.82 1.82 1.71 1.37 1.37 1.34 1.19 1.17 1.15
EtO2C
Ph
Ph
O
O
CO2Me
4ab
Parameter Value
Title xcr-20201229-bc50.1.fid
Solvent Acetone
Temperature 293.9
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
6.81 6.78
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1
1.18 1.14
2.0 2.0 2.0 1.0 3.0 1.0
1.0 1.0 2.0 3.0
1.0 1.0 2.0 1.0 3.0 1.0 3.0
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 -0.5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107.02
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52.96
52.54
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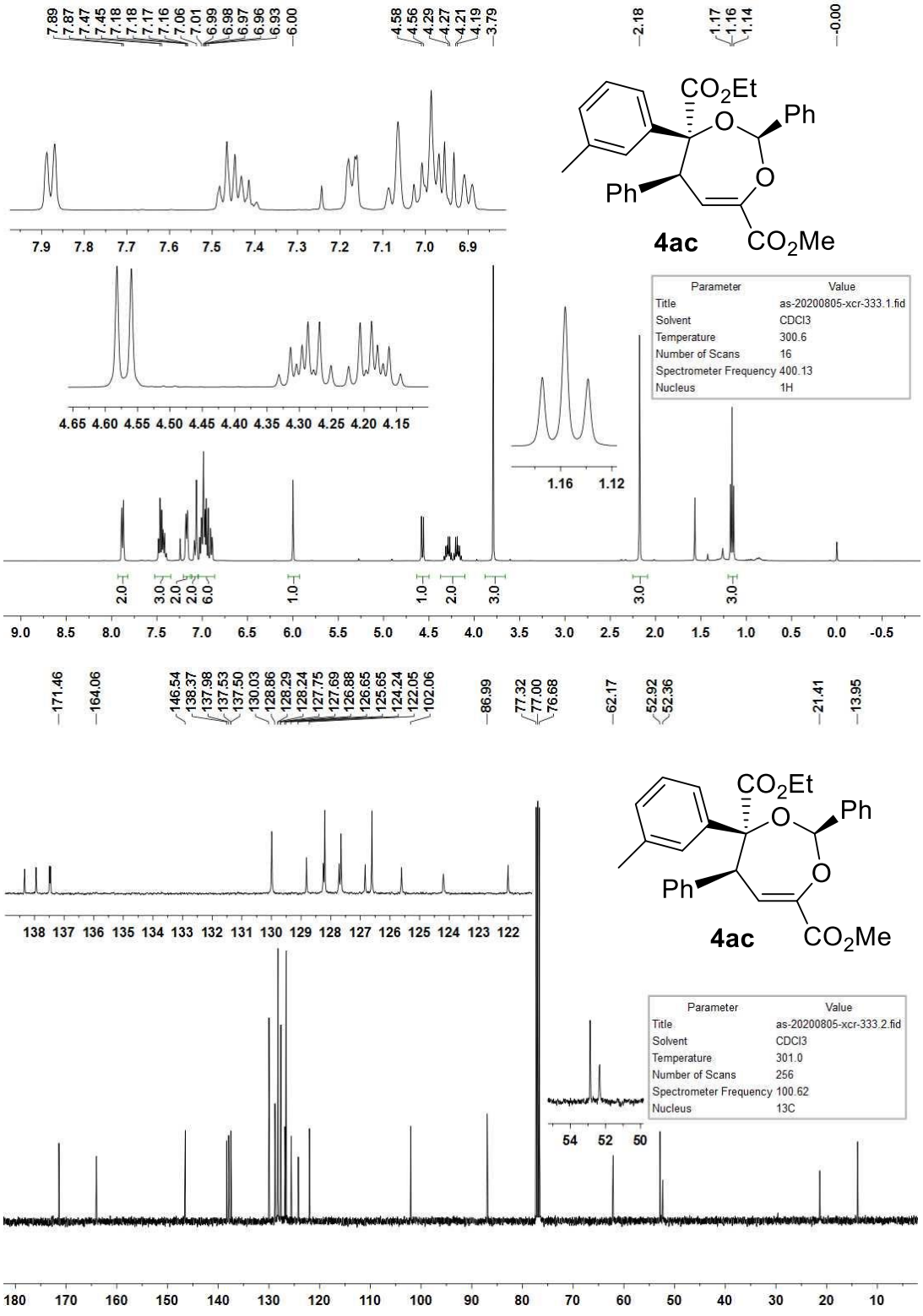
30.17
29.98
29.79
29.60
29.40
28.67
28.60
27.36
26.80
26.74
14.38
EtO2C
Ph
Ph
O
O
CO2Me
4ab
Parameter Value
Title xcr-20201229-bc50.2.fid
Solvent Acetone
Temperature 294.4
Number of Scans 512
Spectrometer Frequency 100.62
Nucleus 13C
132 131 130 129 128 127 126 125 124
31.0 30.5 30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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4.58 4.56 4.29 4.27 4.21 4.19 3.79
2.18
1.17 1.16 1.14
-0.00
CO2Et
O
Ph
Ph
O
4ac
CO2Me
Parameter Value
Title as-20200805-xcr-333.1.fid
Solvent CDCl3
Temperature 300.6
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
2.0 3.0 2.0 2.0 6.0 1.0 1.0 2.0 3.0 3.0 3.0
171.46 164.06 146.54 138.37 137.98 137.53 137.50 130.03 128.86 128.29 128.24 127.75 127.69 126.88 126.65 125.65 124.24 122.05 102.06
86.99 77.32 77.00 76.68 62.17 52.92 52.36 21.41 13.95
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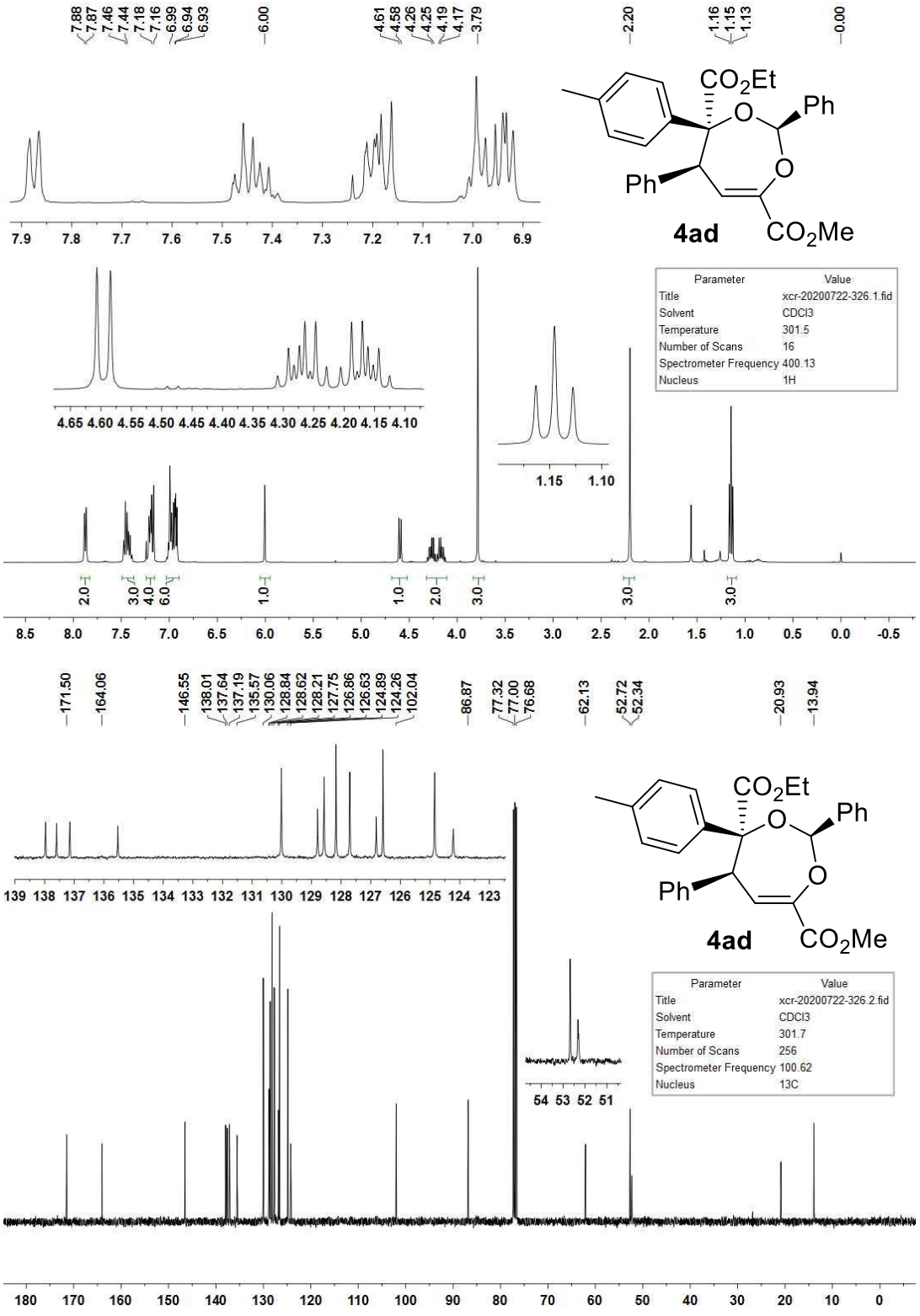
Temperature 301.0
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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4.25
4.19
4.17
3.79
2.20
1.16
1.15
1.13
0.00
CO2Et
O
Ph
Ph
O
CO2Me
4ad
Parameter Value
Title xcr-20200722-326.1.fid
Solvent CDCl3
Temperature 301.5
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
2.0
3.0
4.0
6.0
1.0
1.0
2.0
3.0
3.0
3.0
171.50
164.06
146.55
138.01
137.64
137.19
135.57
130.06
128.84
128.62
128.21
127.75
126.86
126.63
124.89
124.26
102.04
86.87
77.32
77.00
76.68
62.13
52.72
52.34
20.93
13.94
CO2Et
O
Ph
Ph
O
CO2Me
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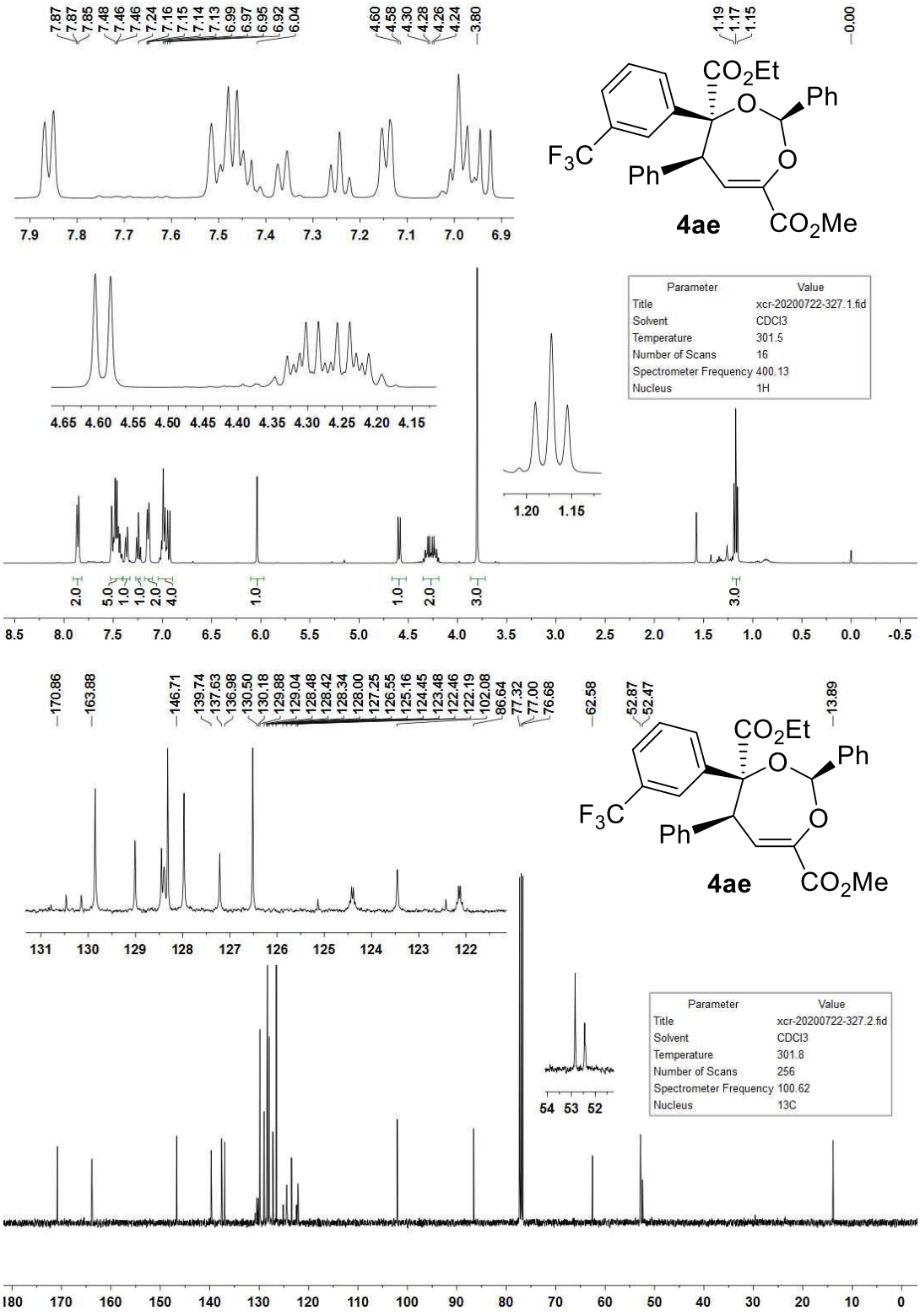
Solvent CDCl3
Temperature 301.7
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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6.95
6.92
6.04
4.60
4.58
4.30
4.28
4.26
4.24
3.80
1.19
1.17
1.15
0.00
CO2Et
O
Ph
F3C
Ph
O
4ae
CO2Me
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15
1.20 1.15
Parameter Value
Title xcr-20200722-327.1.fid
Solvent CDCl3
Temperature 301.5
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
2.0 5.0 1.0 1.0 2.0 4.0 1.0 1.0 2.0 3.0 3.0
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 -0.5
170.86
163.88
146.71
139.74
137.63
136.98
130.50
130.18
129.88
129.04
128.48
128.42
128.34
128.00
127.25
126.55
125.16
124.45
123.48
122.46
122.19
102.08
86.64
77.32
77.00
76.68
62.58
52.87
52.47
13.89
CO2Et
O
Ph
F3C
Ph
O
4ae
CO2Me
131 130 129 128 127 126 125 124 123 122
54 53 52
Parameter Value
Title xcr-20200722-327.2.fid
Solvent CDCl3
Temperature 301.8
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C
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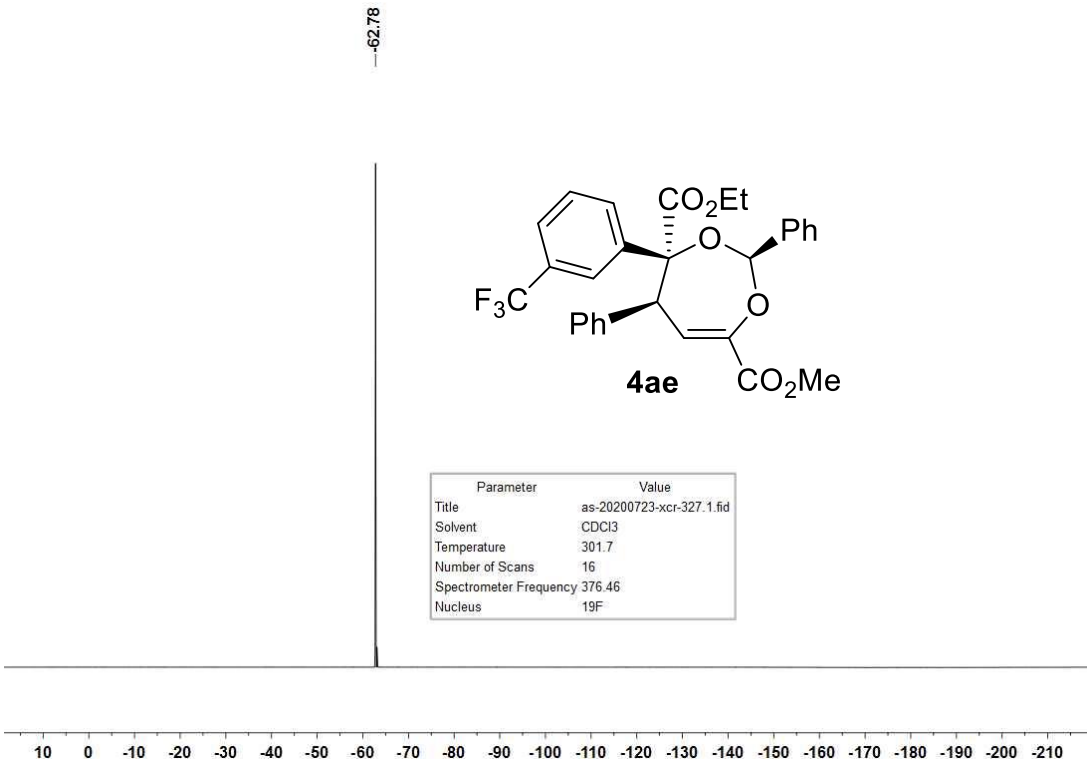
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O
Ph
F3C
Ph
O
4ae
CO2Me
Parameter Value
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Solvent CDCl3
Temperature 301.7
Number of Scans 16
Spectrometer Frequency 376.46
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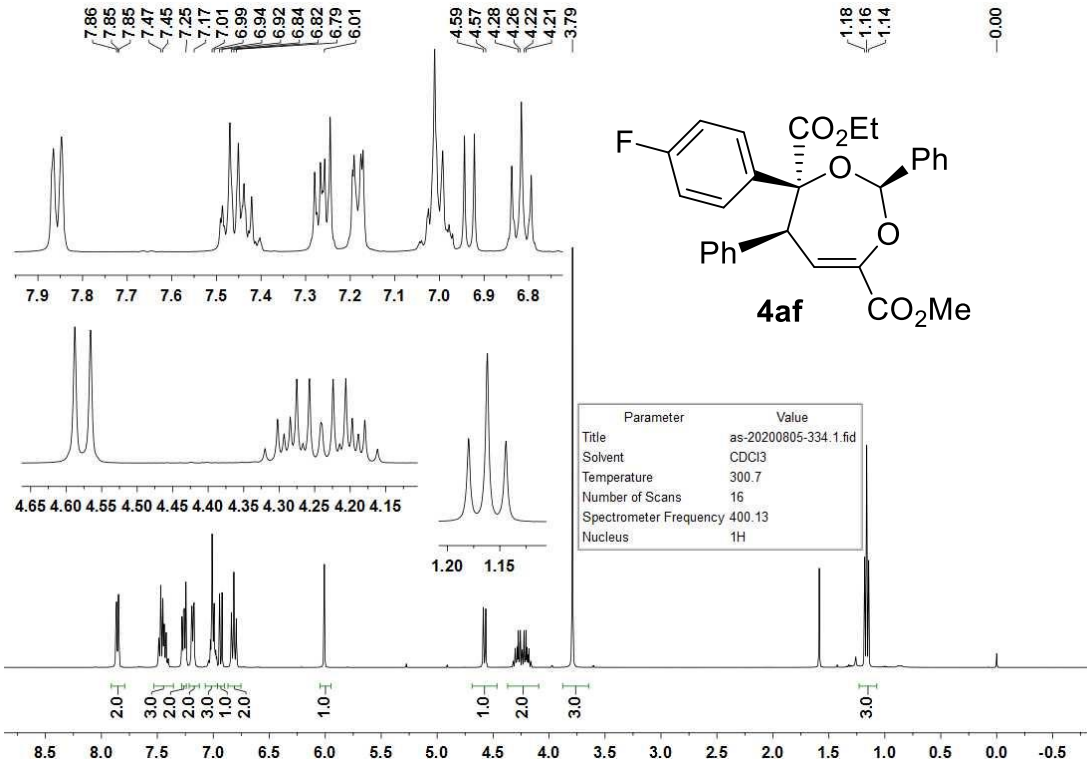
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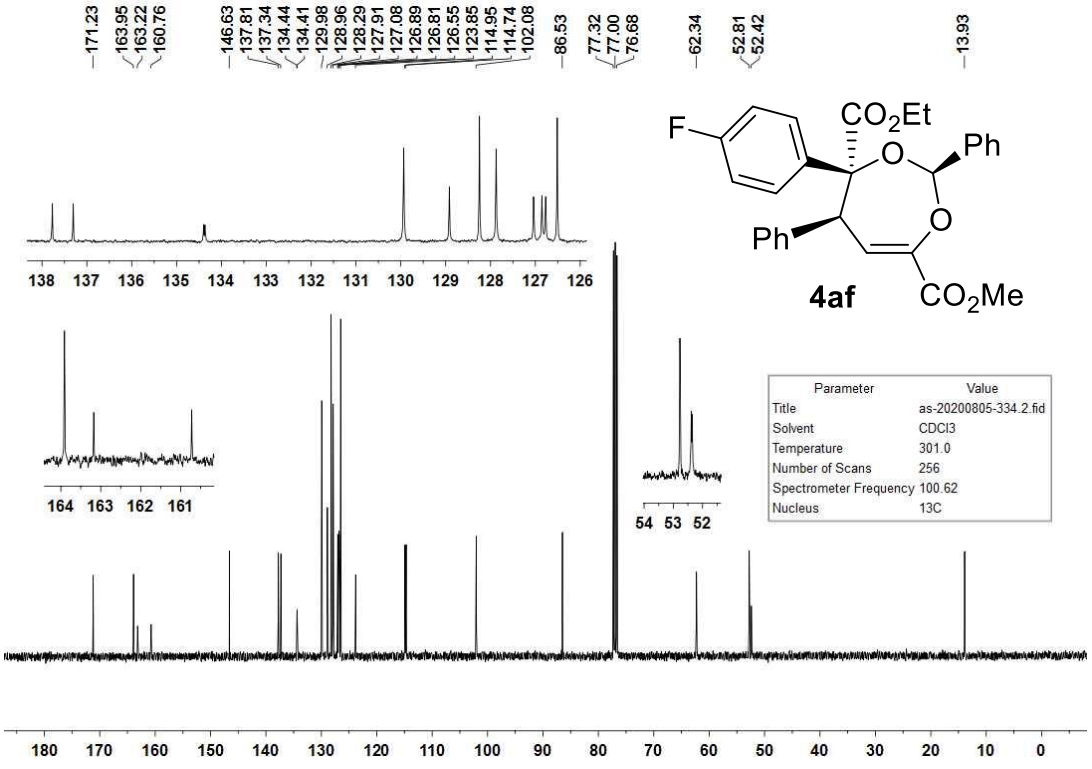
4.59 4.57 4.28 4.26 4.22 4.21 3.79
1.18 1.16 1.14
0.00
F
CO2Et
O
Ph
Ph
O
4af
CO2Me
Parameter Value
Title as-20200805-334.1.fid
Solvent CDCl3
Temperature 300.7
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
2.0 3.0 2.0 2.0 3.0 1.0 2.0 1.0 2.0 3.0 3.0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146.63 137.81 137.34 134.44 134.41 129.98 128.96 128.29 127.91 127.08 126.89 126.81 126.55 123.85 114.95 114.74 102.08
86.53
77.32 77.00 76.68
62.34
52.81 52.42
13.93
F
CO2Et
O
Ph
Ph
O
4af
CO2Me
Parameter Value
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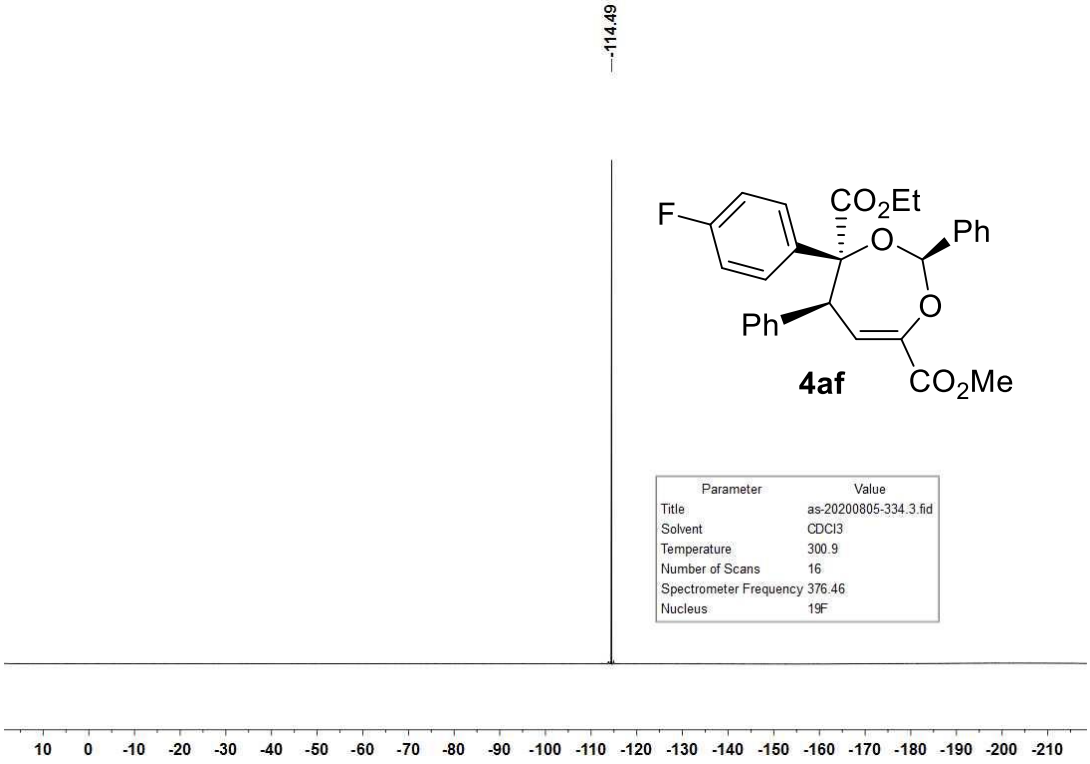
Solvent CDCl3
Temperature 301.0
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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Temperature 300.9
Number of Scans 16
Spectrometer Frequency 376.46
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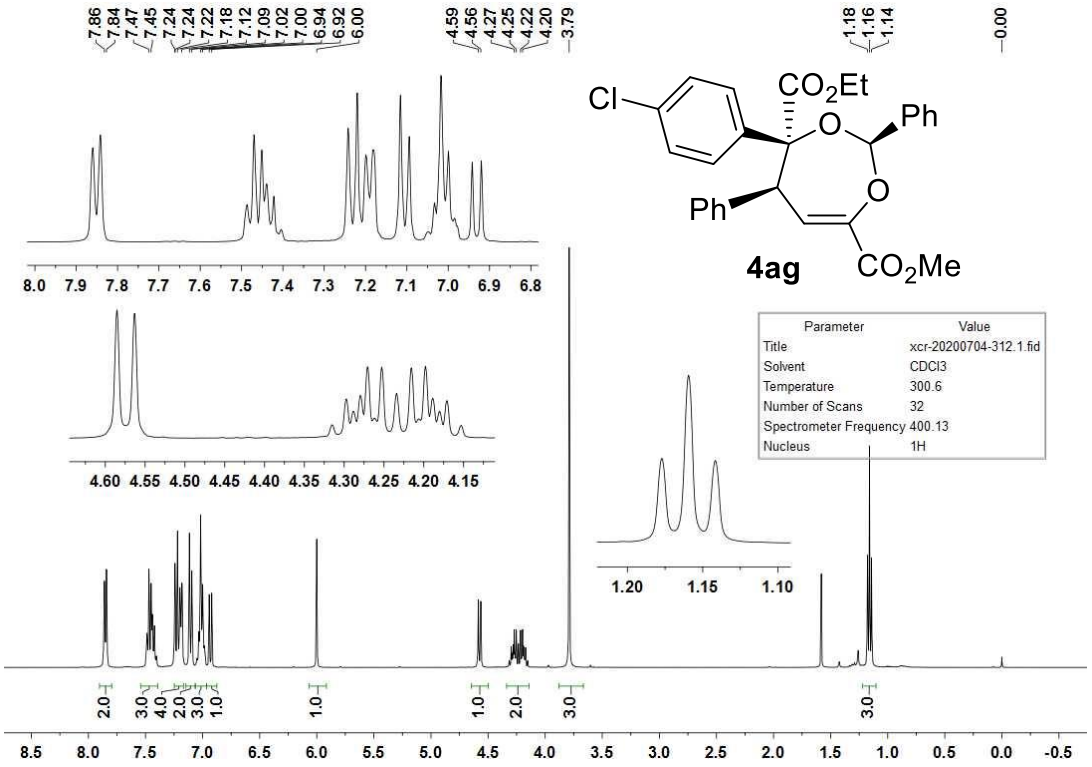
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210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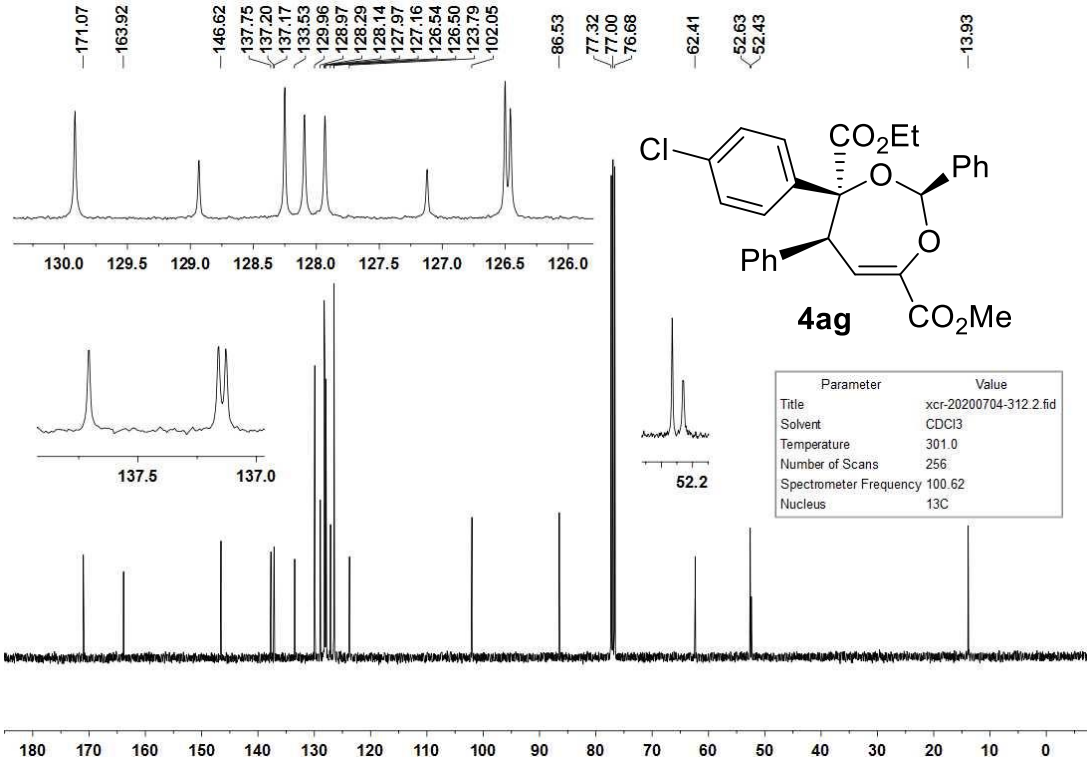
4.59 4.56 4.27 4.25 4.22 4.20 3.79
1.18 1.16 1.14
0.00
Cl
CO2Et
O
Ph
Ph
O
4ag
CO2Me
Parameter Value
Title xcr-20200704-312.1.fid
Solvent CDCl3
Temperature 300.6
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0 3.0 4.0 2.0 3.0 1.0 1.0 1.0 2.0 3.0 3.0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86.53 77.32 77.00 76.68 62.41 52.63 52.43 13.93
Cl
CO2Et
O
Ph
Ph
O
4ag
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Parameter Value
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Solvent CDCl3
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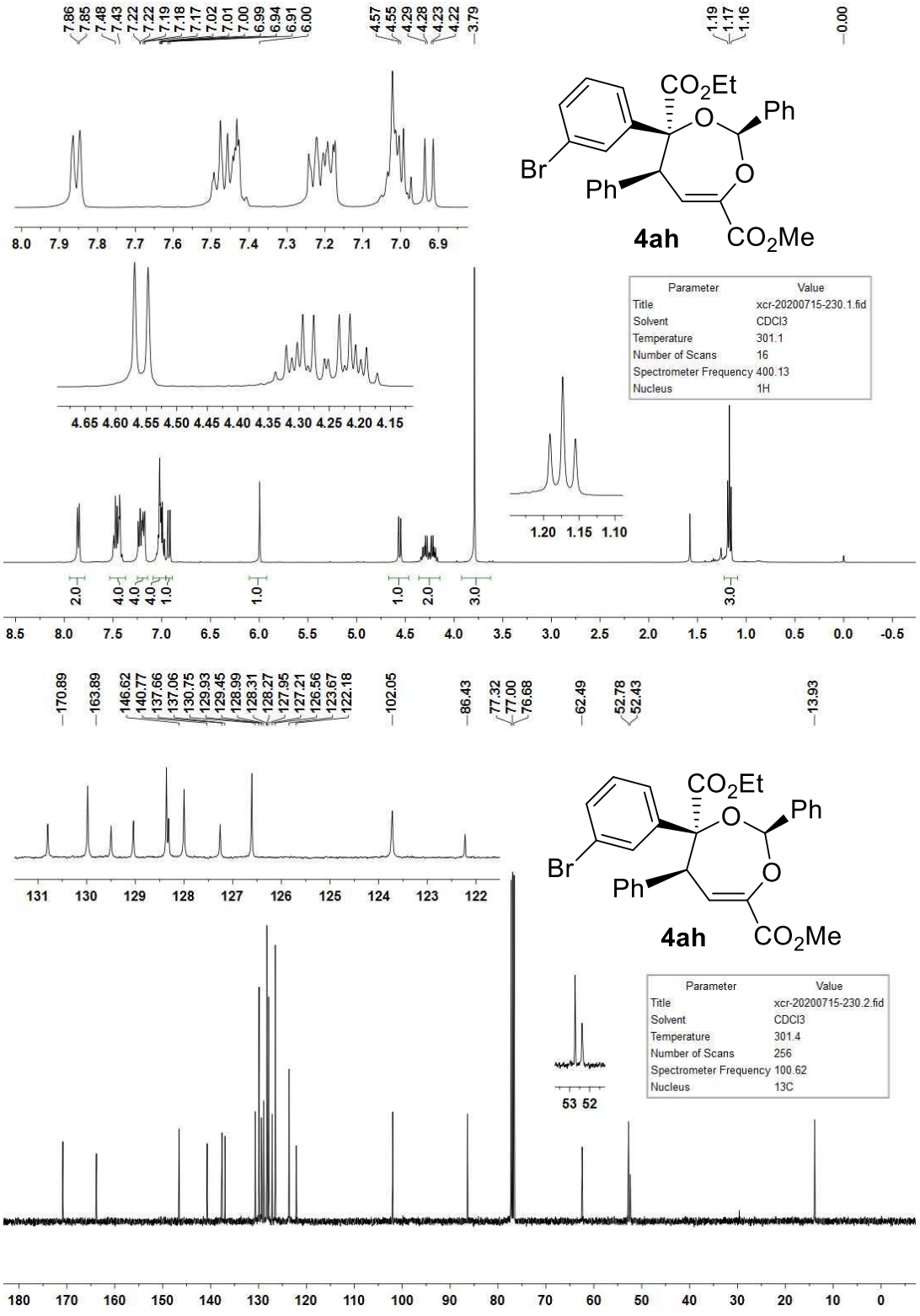
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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4.57 4.55 4.29 4.28 4.23 4.22 3.79
1.19 1.17 1.16
0.00
CO2Et
O
Ph
Br
Ph
O
4ah
CO2Me
Parameter Value
Title xcr-20200715-230.1.fid
Solvent CDCl3
Temperature 301.1
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
2.0 4.0 4.0 4.0 1.0 1.0 1.0 2.0 3.0 3.0
170.89 163.89 146.62 140.77 137.66 137.06 130.75 129.93 129.45 128.99 128.31 128.27 127.95 127.21 126.56 123.67 122.18
102.05
86.43
77.32 77.00 76.68
62.49
52.78 52.43
13.93
CO2Et
O
Ph
Br
Ph
O
4ah
CO2Me
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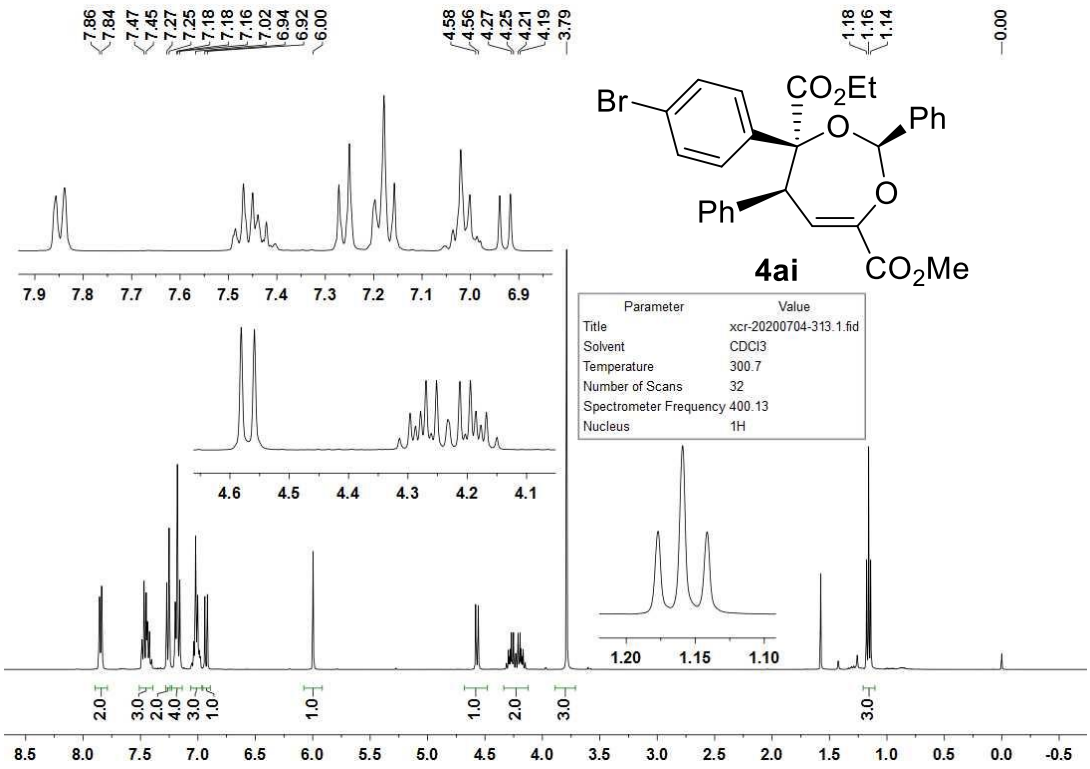
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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7.45
7.27
7.25
7.18
7.18
7.16
7.02
6.94
6.92
6.00
4.58
4.56
4.27
4.25
4.21
4.19
3.79
1.18
1.16
1.14
0.00
Br
CO2Et
O
Ph
Ph
O
CO2Me
4ai
Parameter Value
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Solvent CDCl3
Temperature 300.7
Number of Scans 32
Spectrometer Frequency 400.13
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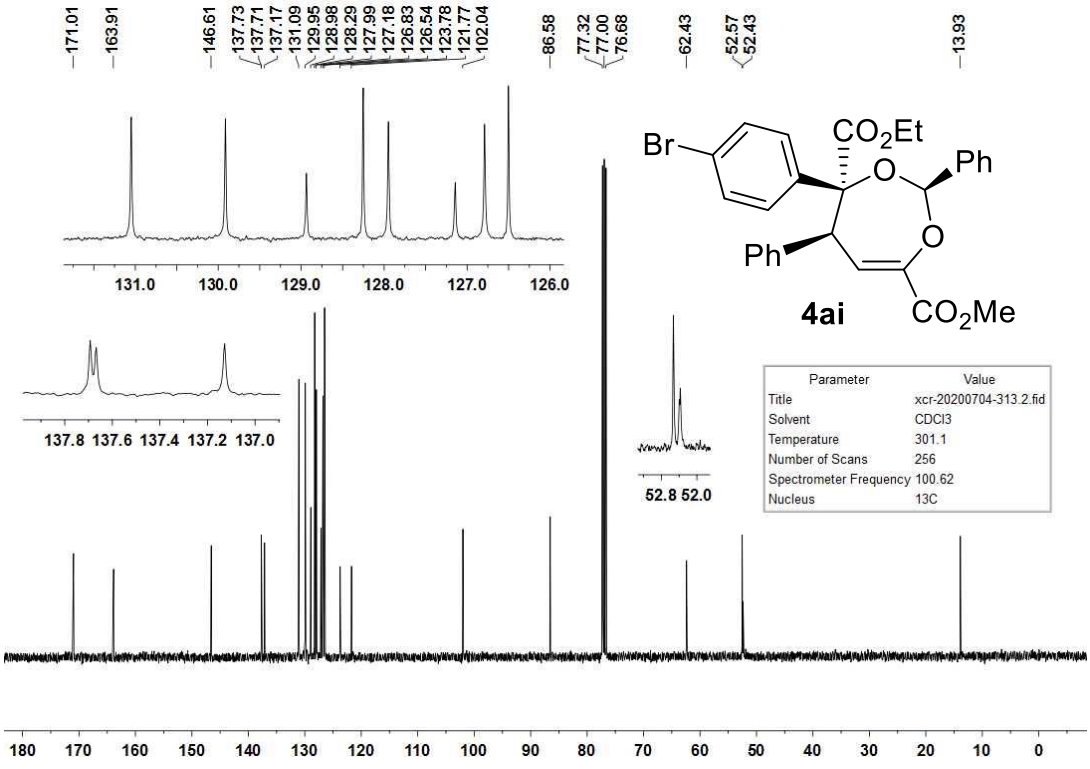
3.0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127.18
126.83
126.54
123.78
121.77
102.04
86.58
77.32
77.00
76.68
62.43
52.57
52.43
13.93
Br
CO2Et
O
Ph
Ph
O
CO2Me
4ai
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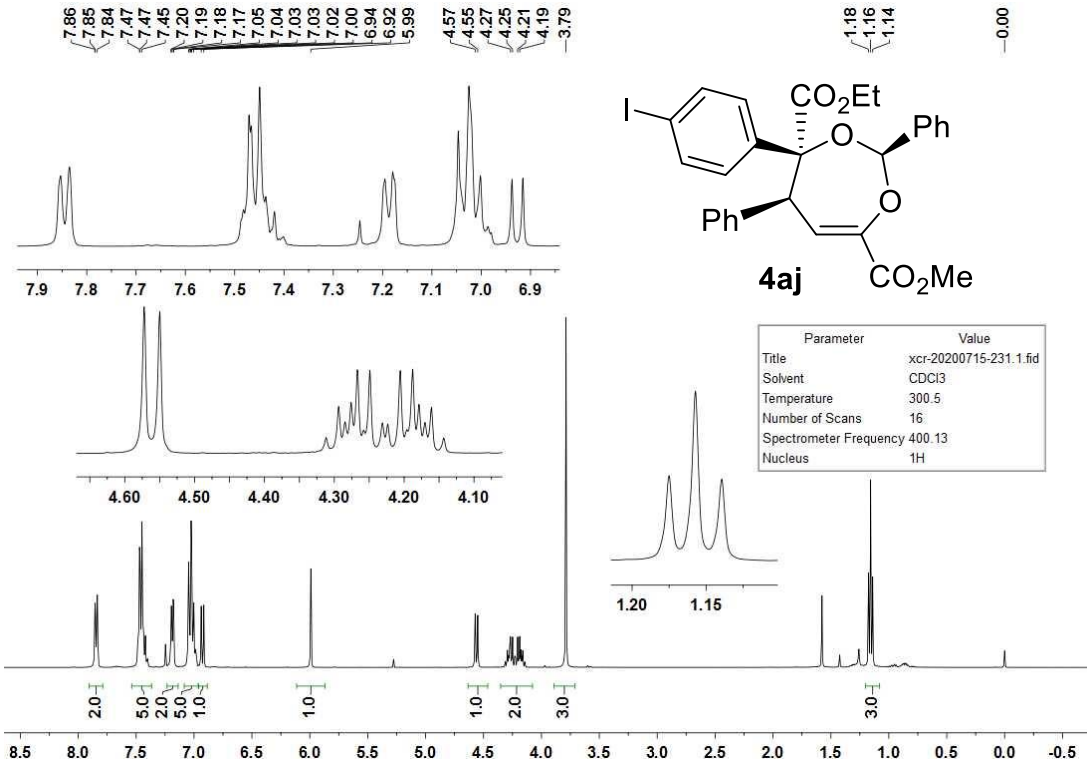
Solvent CDCl3
Temperature 301.1
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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4.57 4.55 4.27 4.25 4.21 4.19 3.79
1.18 1.16 1.14
0.00
I
CO2Et
O
Ph
Ph
O
CO2Me
4aj
Parameter Value
Title xcr-20200715-231.1.fid
Solvent CDCl3
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Spectrometer Frequency 400.13
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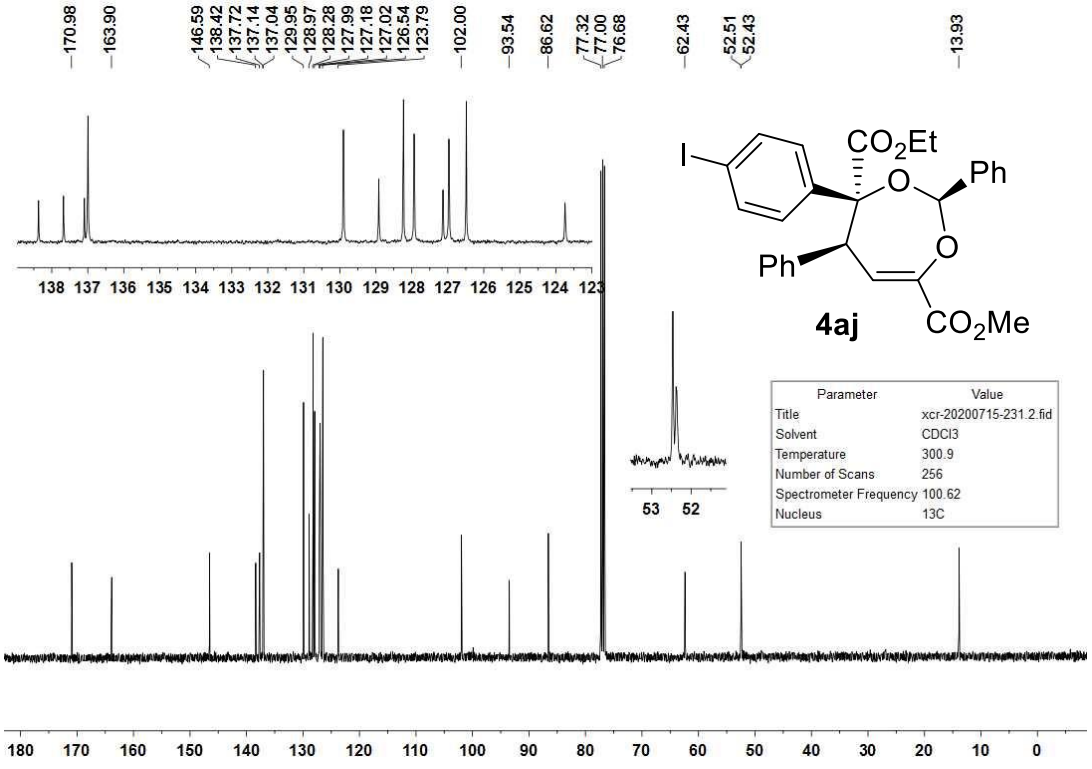
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I
CO2Et
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Ph
Ph
O
CO2Me
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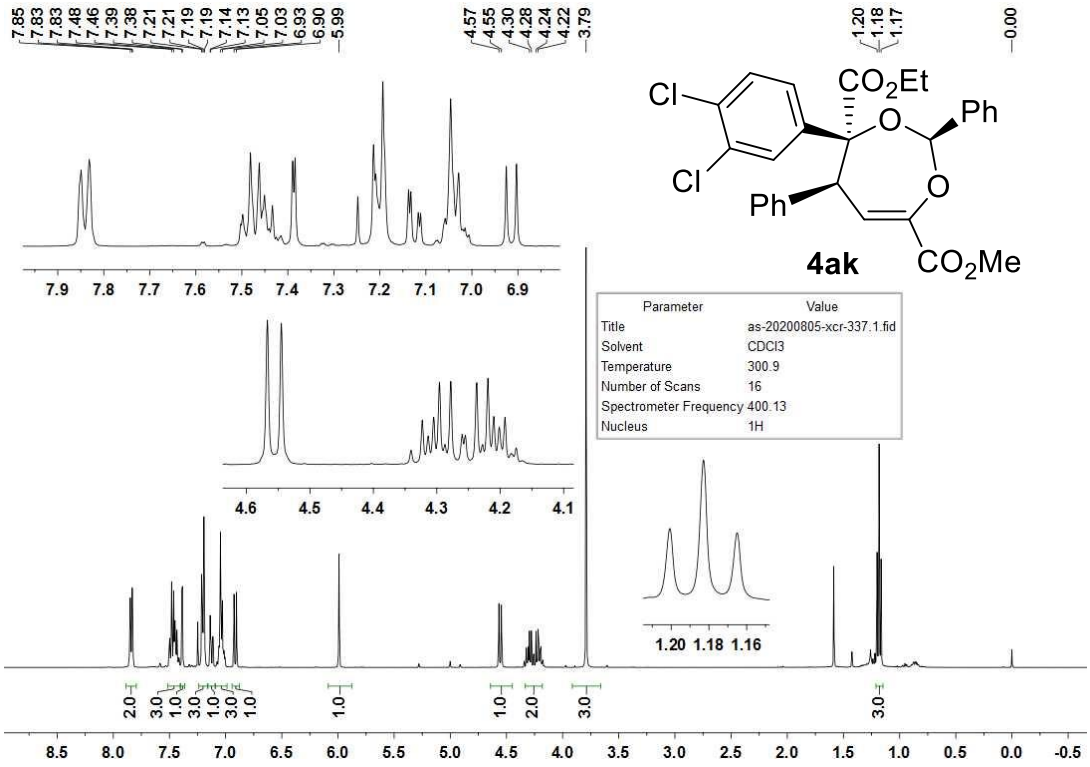
Solvent CDCl3
Temperature 300.9
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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1.20 1.18 1.17
0.00
Cl
Cl
CO2Et
O
Ph
Ph
O
4ak
CO2Me
Parameter Value
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Solvent CDCl3
Temperature 300.9
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Nucleus 1H
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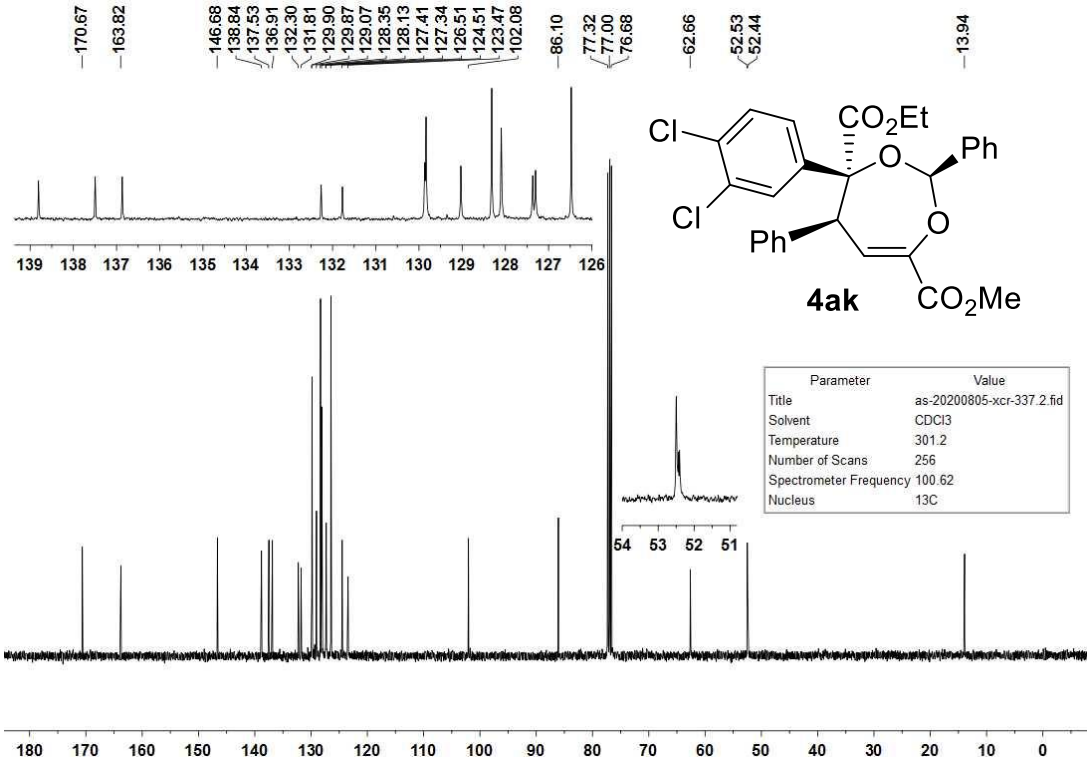
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Cl
Cl
CO2Et
O
Ph
Ph
O
4ak
CO2Me
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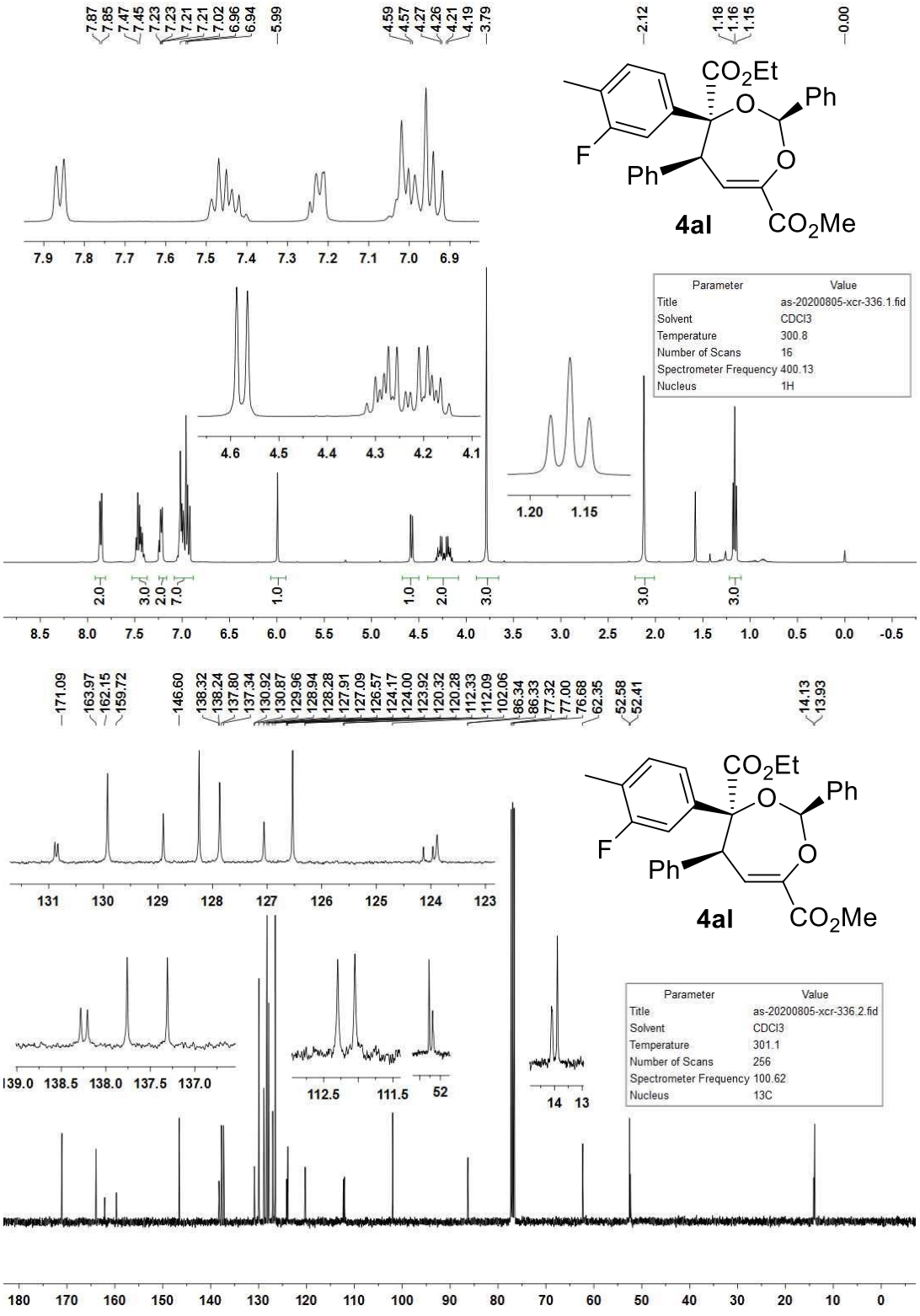
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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4.27
4.26
4.21
4.19
3.79
2.12
1.18
1.16
1.15
0.00
CO2Et
O
Ph
F
Ph
O
4al
CO2Me
Parameter Value
Title as-20200805-xcr-336.1.fid
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Temperature 300.8
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
2.0
3.0
2.0
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1.0
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2.0
3.0
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163.97
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CO2Et
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CO2Me
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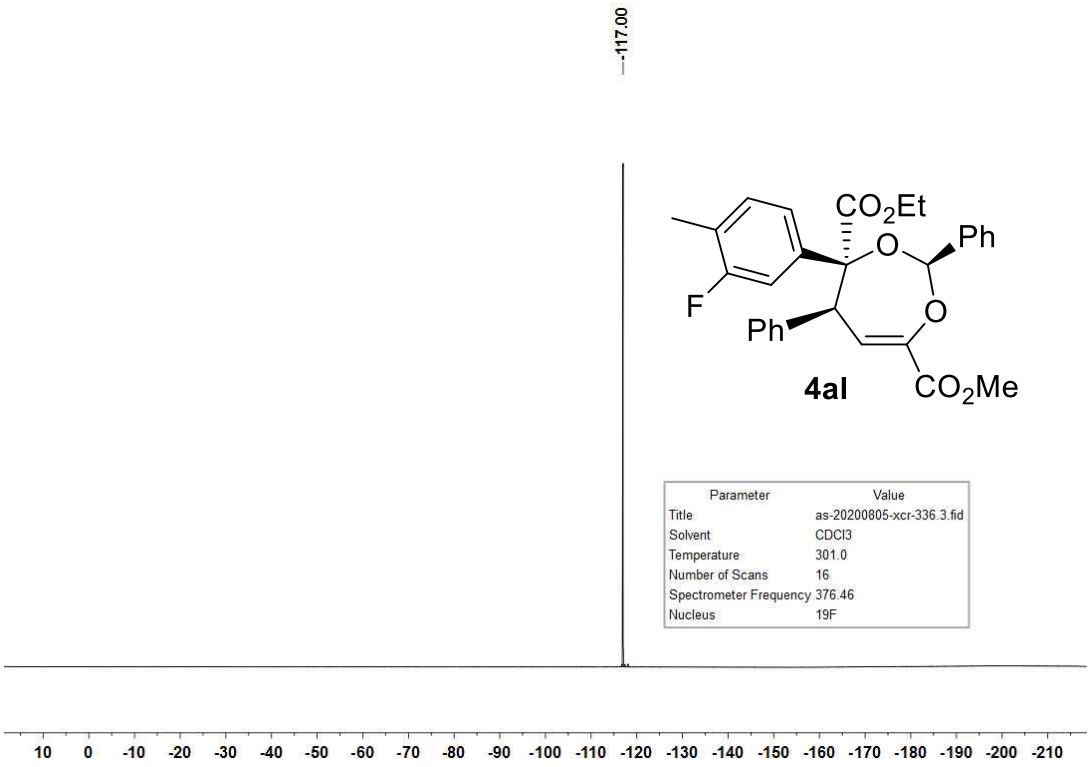
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C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Parameter
Value
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Solvent
CDCl3
Temperature
301.0
Number of Scans
16
Spectrometer Frequency
376.46
Nucleus
19F
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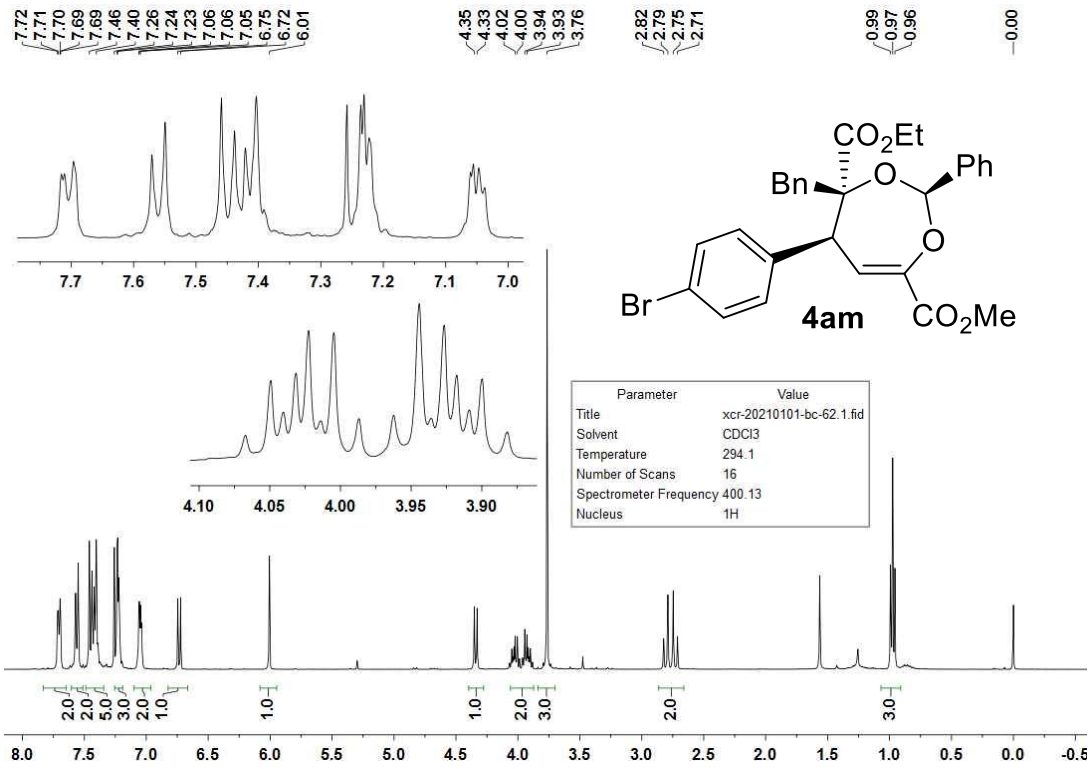
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2.82 2.79 2.75 2.71
0.99 0.97 0.96
0.00
CO2Et
Bn
O
Ph
O
Br
4am
CO2Me
Parameter Value
Title xcr-20210101-bc-62.1.fid
Solvent CDCl3
Temperature 294.1
Number of Scans 16
Spectrometer Frequency 400.13
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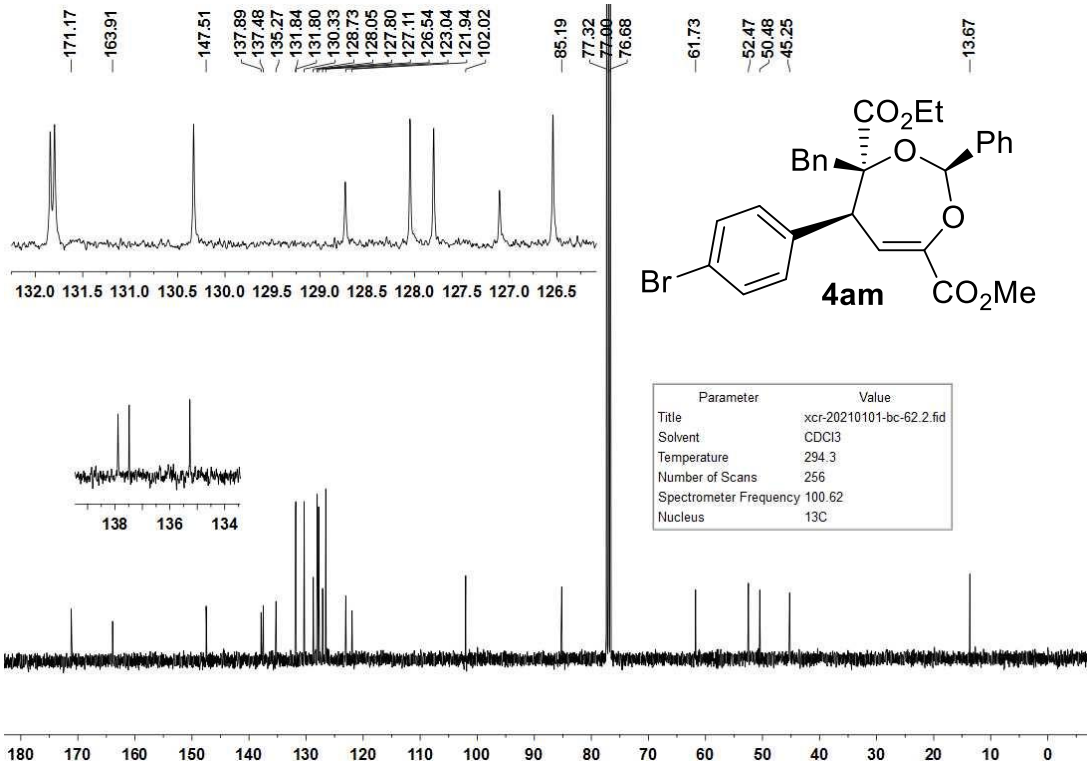
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61.73
52.47 50.48 45.25
13.67
CO2Et
Bn
O
Ph
O
Br
4am
CO2Me
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Solvent CDCl3
Temperature 294.3
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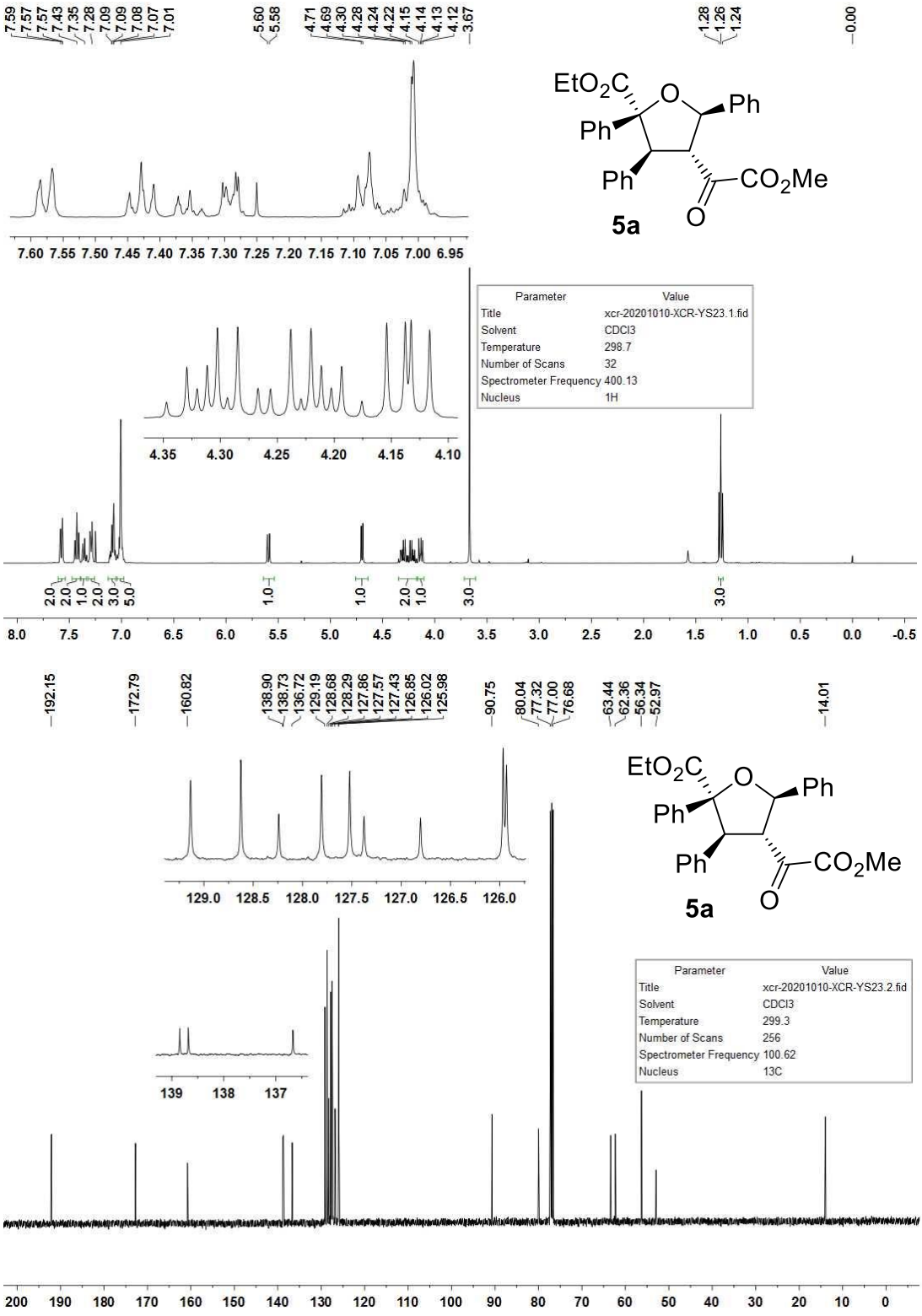
Spectrometer Frequency 100.62
Nucleus 13C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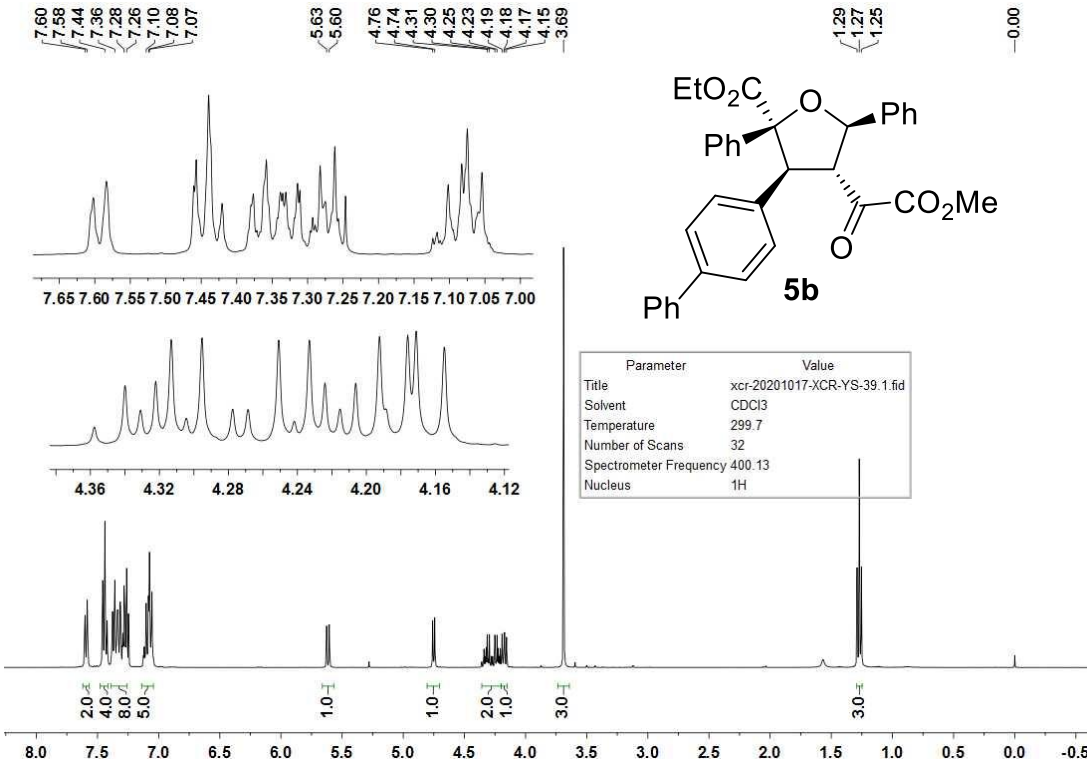
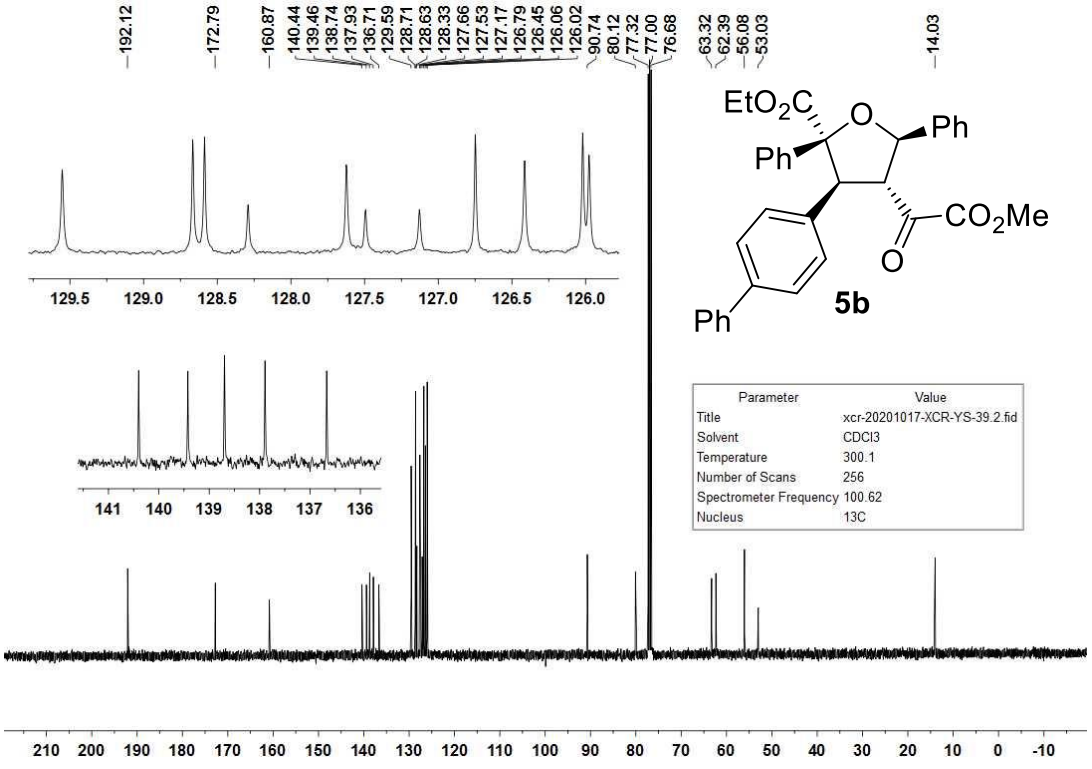
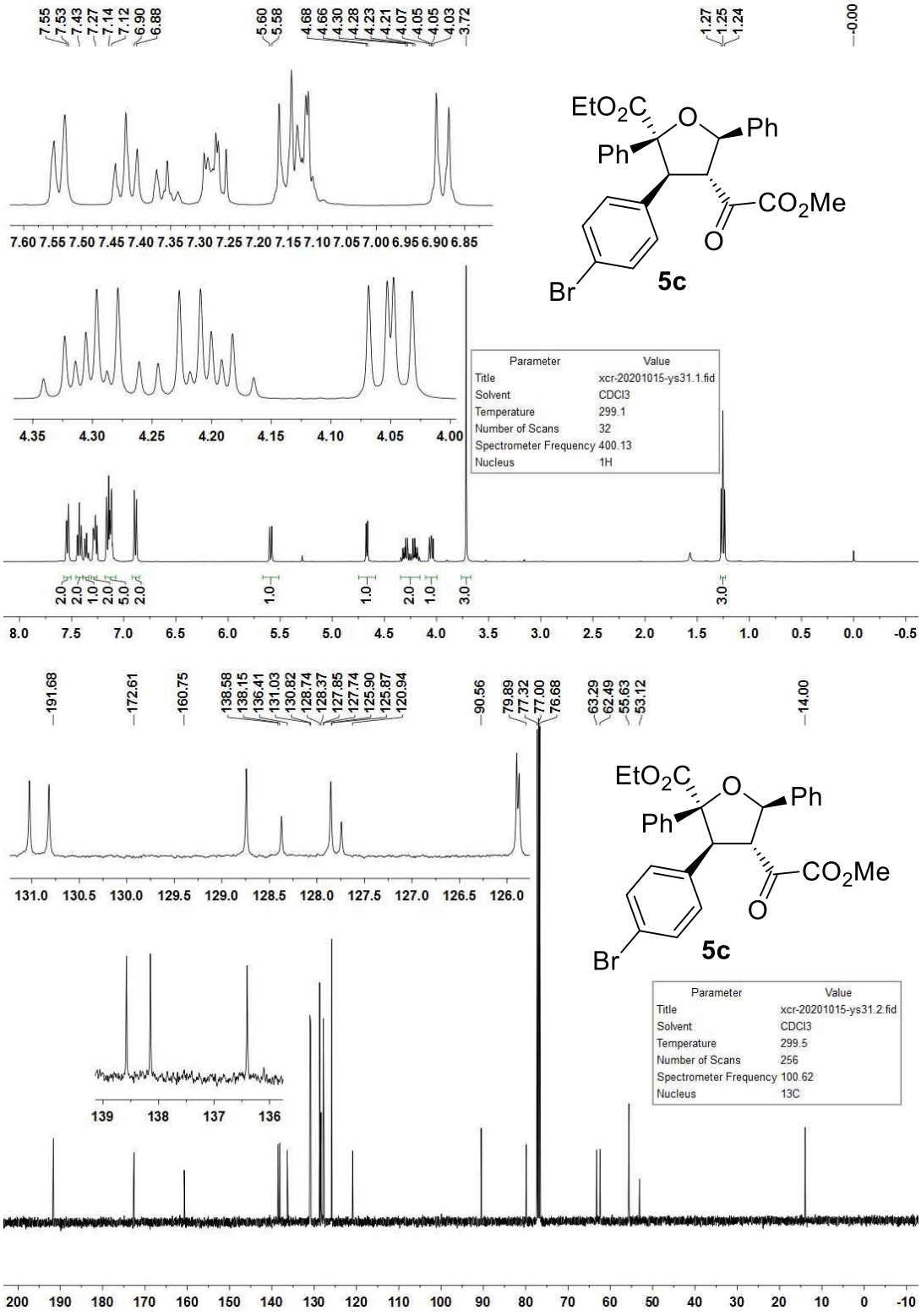
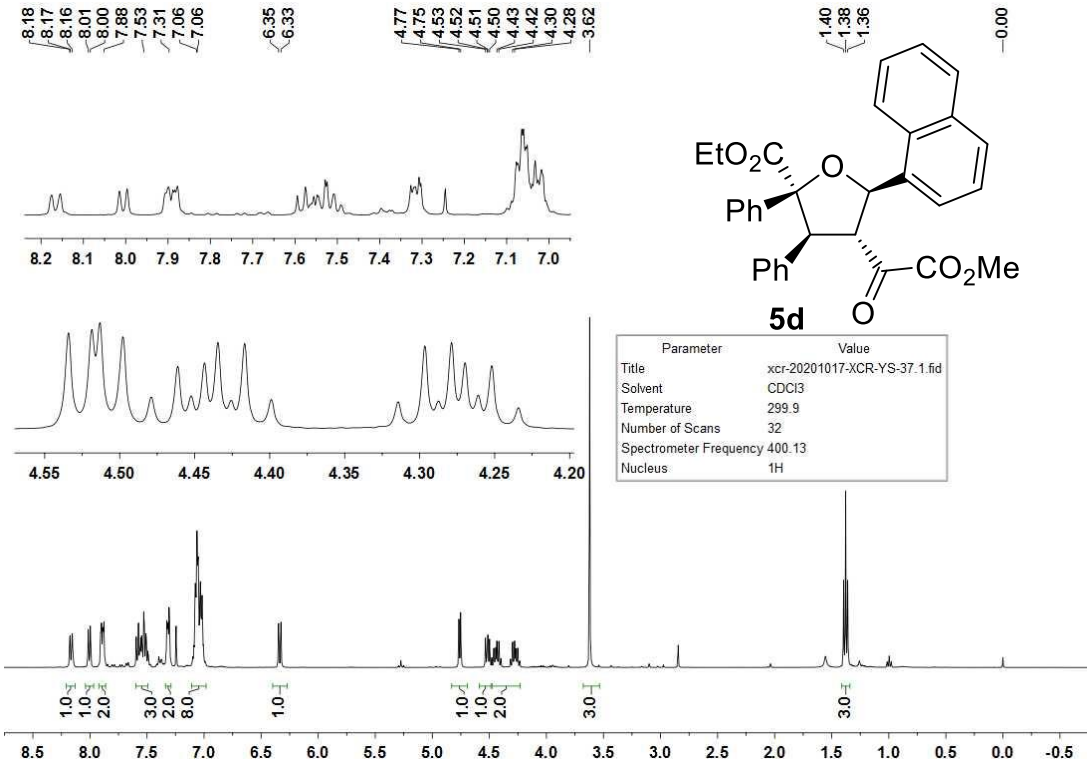
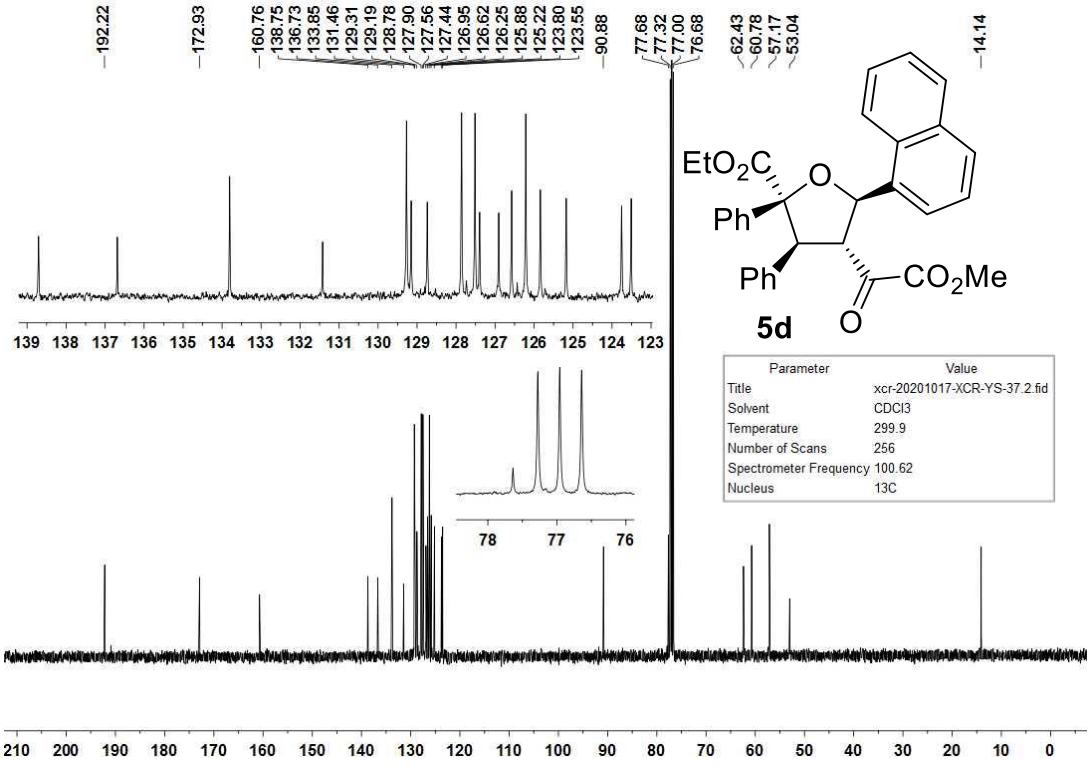
5.60 5.58
4.71 4.69 4.30 4.28 4.24 4.22 4.15 4.14 4.13 4.12 3.67
1.28 1.26 1.24
0.00
EtO2C
O
Ph
Ph
Ph
CO2Me
O
5a
7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95
Parameter Value
Title xcr-20201010-XCR-YS23.1.fid
Solvent CDCl3
Temperature 298.7
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
4.35 4.30 4.25 4.20 4.15 4.10
2.0 2.0 1.0 2.0 3.0 5.0 1.0 1.0 2.0 1.0 3.0 3.0
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 -0.5
192.15
172.79
160.82
138.90 138.73 136.72 129.19 128.68 128.29 127.86 127.57 127.43 126.85 126.02 125.98
90.75
80.04 77.32 77.00 76.68
63.44 62.36 56.34 52.97
14.01
EtO2C
O
Ph
Ph
Ph
CO2Me
O
5a
129.0 128.5 128.0 127.5 127.0 126.5 126.0
Parameter Value
Title xcr-20201010-XCR-YS23.2.fid
Solvent CDCl3
Temperature 299.3
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C
139 138 137
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

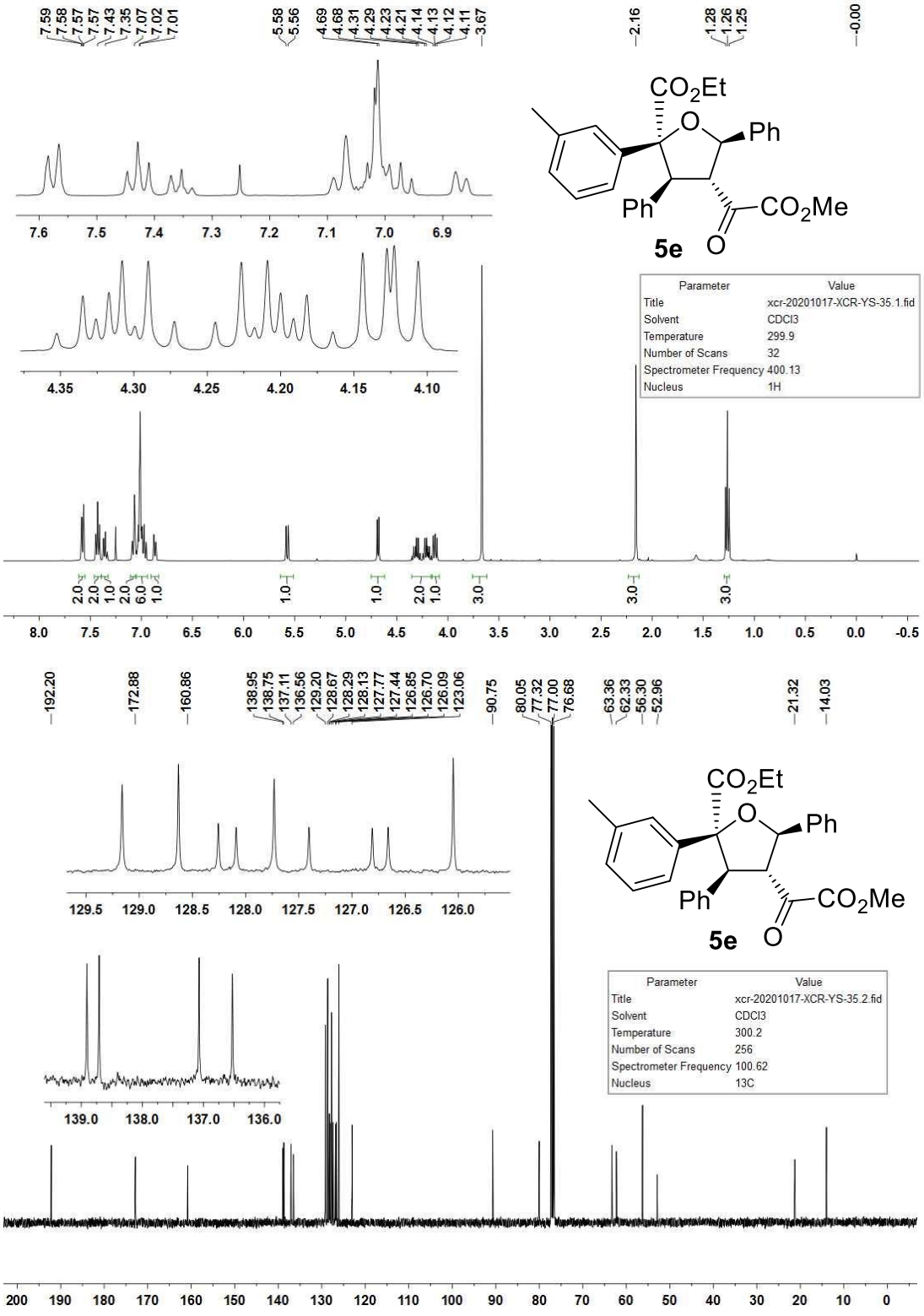

7.60 7.58 7.44 7.36 7.28 7.26 7.10 7.08 7.07
5.63 5.60
4.76 4.74 4.31 4.30 4.25 4.23 4.19 4.18 4.17 4.15 3.69
1.29 1.27 1.25
0.00
EtO2C
O
Ph
Ph
CO2Me
O
Ph
5b
Parameter Value
Title xcr-20201017-XCR-YS-39.1.fid
Solvent CDCl3
Temperature 299.7
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0 4.0 8.0 5.0 1.0 1.0 2.0 1.0 3.0 3.0

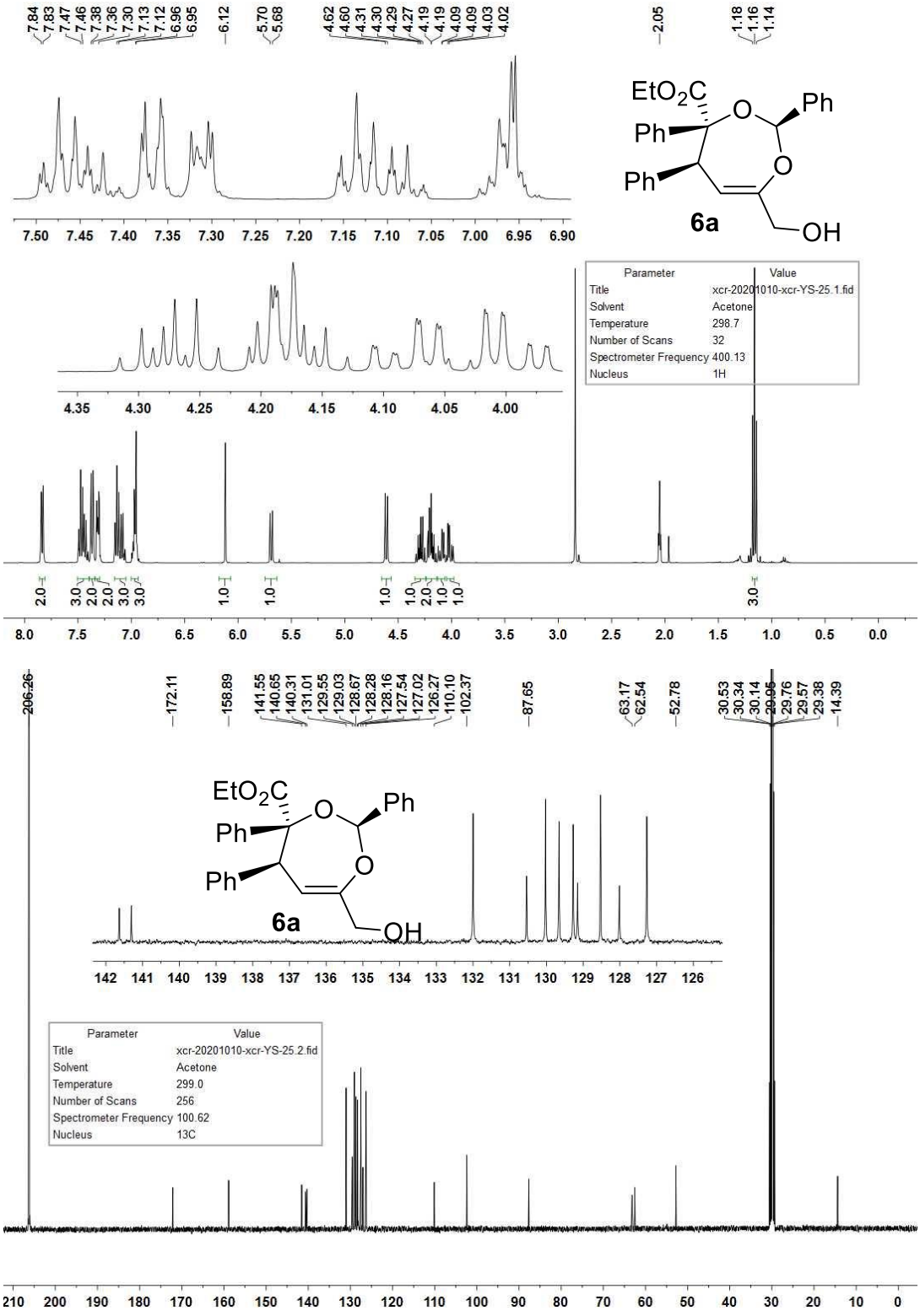

192.12 172.79 160.87 140.44 139.46 138.74 137.93 136.71 129.59 128.71 128.63 128.33 127.66 127.53 127.17 126.79 126.45 126.06 126.02 90.74 80.12 77.32 77.00 76.68 63.32 62.39 56.08 53.03 14.03
EtO2C
O
Ph
Ph
CO2Me
O
Ph
5b
Parameter Value
Title xcr-20201017-XCR-YS-39.2.fid
Solvent CDCl3
Temperature 300.1
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C

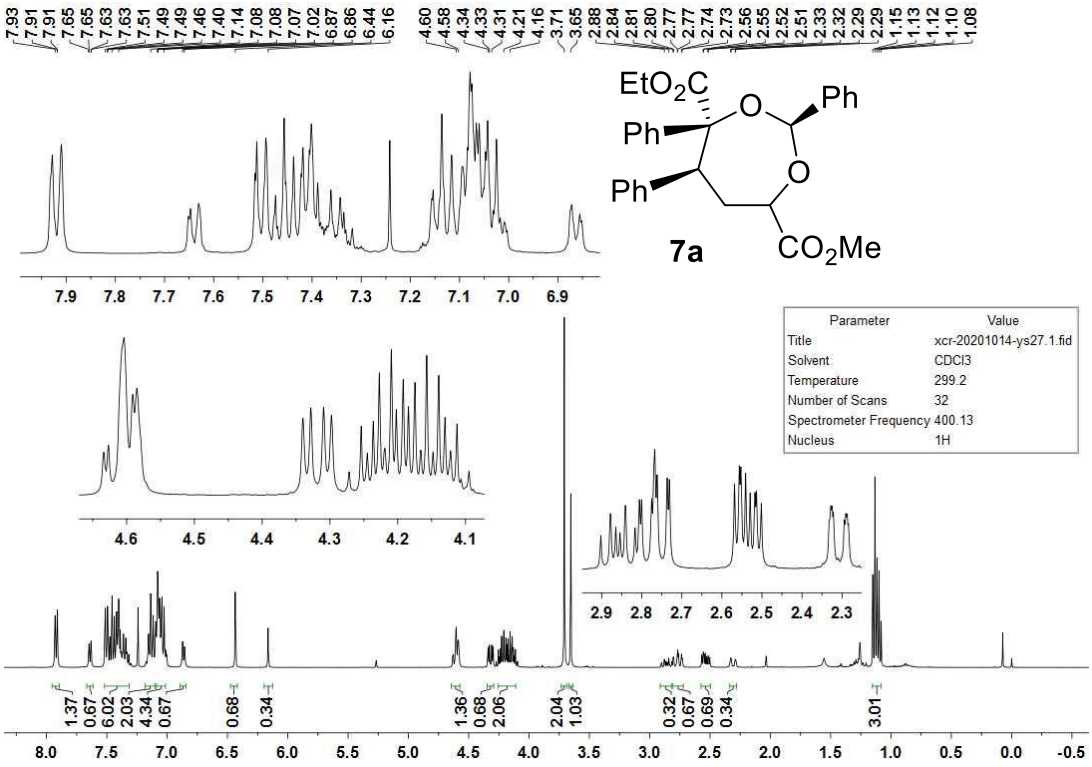

7.55 7.53 7.43 7.27 7.14 7.12 6.90 6.88
5.60 5.58
4.68 4.66 4.30 4.28 4.23 4.21 4.07 4.05 4.05 4.03 3.72
1.27 1.25 1.24
0.00
EtO2C
O
Ph
Ph
CO2Me
O
Br
5c
Parameter Value
Title xcr-20201015-ys31.1.fid
Solvent CDCl3
Temperature 299.1
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0 2.0 1.0 2.0 5.0 2.0 1.0 1.0 2.0 1.0 3.0 3.0
191.68 172.61 160.75
138.58 138.15 136.41 131.03 130.82 128.74 128.37 127.85 127.74 125.90 125.87 120.94
90.56 79.89 77.32 77.00 76.68
63.29 62.49 55.63 53.12
14.00
EtO2C
O
Ph
Ph
CO2Me
O
Br
5c
Parameter Value
Title xcr-20201015-ys31.2.fid
Solvent CDCl3
Temperature 299.5
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C

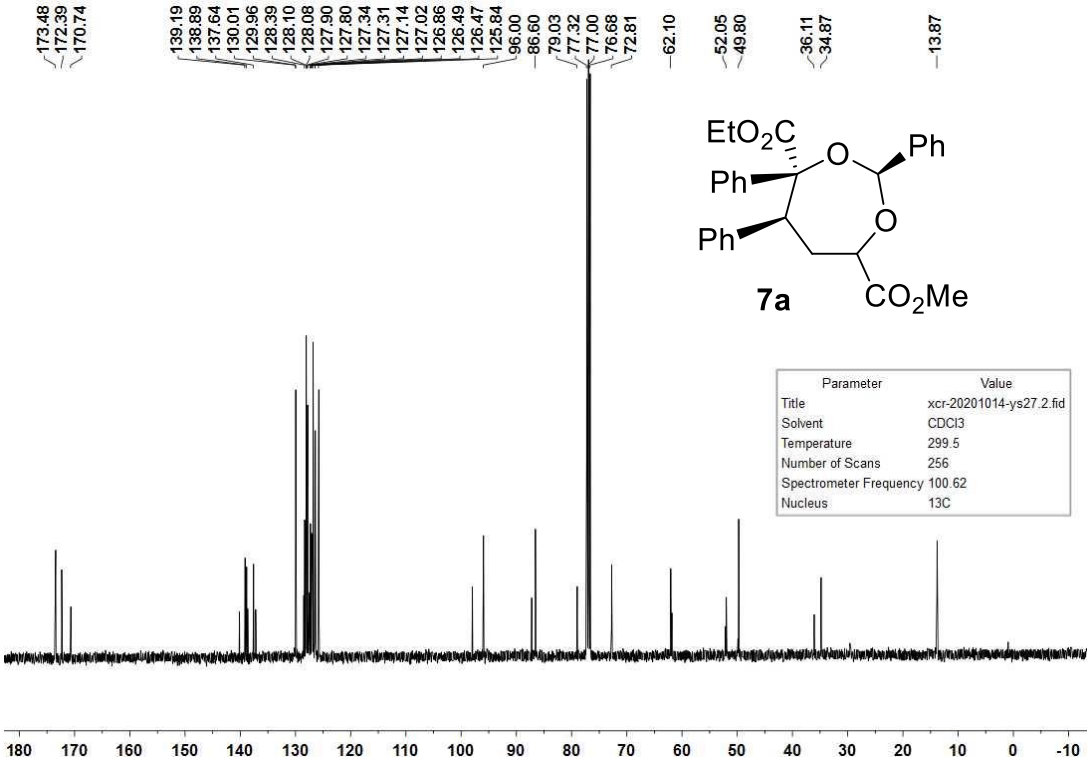

8.18
8.17
8.16
8.01
8.00
7.88
7.53
7.31
7.06
7.06
6.35
6.33
4.77
4.75
4.53
4.52
4.51
4.50
4.43
4.42
4.30
4.28
3.62
1.40
1.38
1.36
0.00
EtO2C
O
Ph
Ph
CO2Me
O
5d
Parameter Value
Title xcr-20201017-XCR-YS-37.1.fid
Solvent CDCl3
Temperature 299.9
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
1.0
1.0
2.0
3.0
2.0
8.0
1.0
1.0
1.0
2.0
3.0
3.0

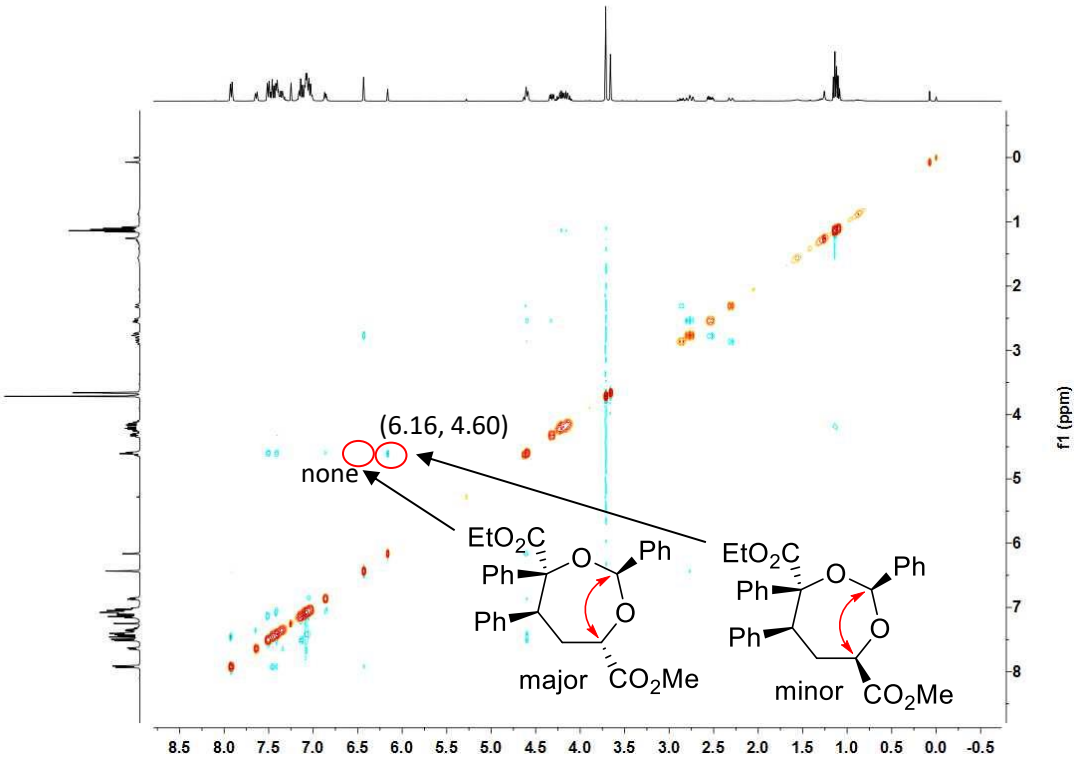

192.22
172.93
160.76
138.75
136.73
133.85
131.46
129.31
129.19
128.78
127.90
127.56
127.44
126.95
126.62
126.25
125.88
125.22
123.80
123.55
90.88
77.68
77.32
77.00
76.68
62.43
60.78
57.17
53.04
14.14
EtO2C
O
Ph
Ph
CO2Me
O
5d
Parameter Value
Title xcr-20201017-XCR-YS-37.2.fid
Solvent CDCl3
Temperature 299.9
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C


7.59 7.58 7.57 7.57 7.43 7.35 7.07 7.02 7.01
5.58 5.56
4.69 4.68 4.31 4.29 4.23 4.21 4.14 4.13 4.12 4.11
3.67
2.16
1.28 1.26 1.25
0.00
CO2Et
O
Ph
Ph
CO2Me
O
5e
Parameter Value
Title xcr-20201017-XCR-YS-35.1.fid
Solvent CDCl3
Temperature 299.9
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0 2.0 1.0 2.0 6.0 1.0 1.0 1.0 2.0 1.0 3.0 3.0 3.0
192.20 172.88 160.86 138.95 138.75 137.11 136.56 129.20 128.67 128.29 128.13 127.77 127.44 126.85 126.70 126.09 123.06 90.75 80.05 77.32 77.00 76.68 63.36 62.33 56.30 52.96 21.32 14.03
CO2Et
O
Ph
Ph
CO2Me
O
5e
Parameter Value
Title xcr-20201017-XCR-YS-35.2.fid
Solvent CDCl3
Temperature 300.2
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C


7.84 7.83 7.47 7.46 7.38 7.36 7.30 7.13 7.12 6.96 6.95 6.12 5.70 5.68 4.62 4.60 4.31 4.30 4.29 4.27 4.19 4.19 4.09 4.09 4.03 4.02 2.05 1.18 1.16 1.14
EtO2C
Ph
O
Ph
Ph
O
6a
OH
Parameter Value
Title xcr-20201010-xcr-YS-25.1.fid
Solvent Acetone
Temperature 298.7
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
206.26 172.11 158.89 141.55 140.65 140.31 131.01 129.55 129.03 128.67 128.28 128.16 127.54 127.02 126.27 110.10 102.37 87.65 63.17 62.54 52.78 30.53 30.34 30.14 29.95 29.76 29.57 29.38 14.39
Parameter Value
Title xcr-20201010-xcr-YS-25.2.fid
Solvent Acetone
Temperature 299.0
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C

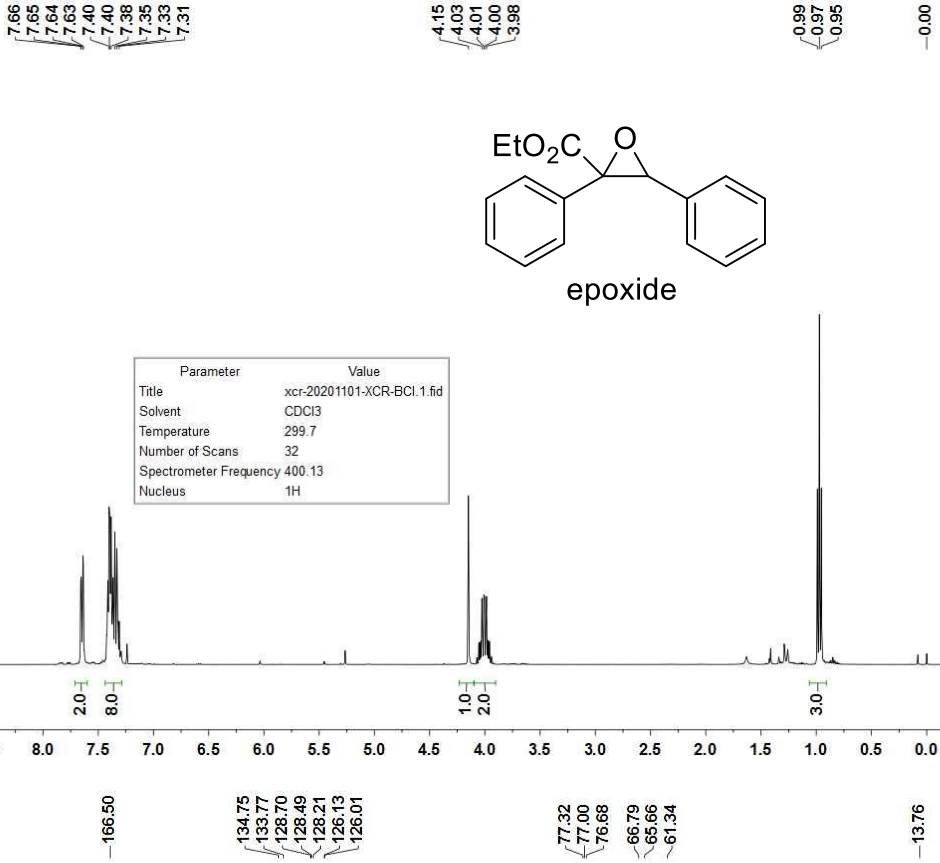

7.93 7.91 7.91 7.65 7.65 7.63 7.63 7.51 7.49 7.49 7.46 7.40 7.14 7.08 7.08 7.07 7.02 6.87 6.86 6.44 6.16
4.60 4.58 4.34 4.33 4.31 4.21 4.16 3.71 3.65 2.88 2.84 2.81 2.80 2.77 2.77 2.74 2.73 2.56 2.55 2.52 2.51 2.33 2.32 2.29 2.29 1.15 1.13 1.12 1.10 1.08
EtO2C
Ph
Ph
Ph
O
O
CO2Me
7a
Parameter Value
Title xcr-20201014-ys27.1.fid
Solvent CDCl3
Temperature 299.2
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
1.37 0.67 6.02 2.03 4.34 0.67 0.68 0.34 1.36 0.68 2.06 2.04 1.03 0.32 0.67 0.69 0.34 3.01

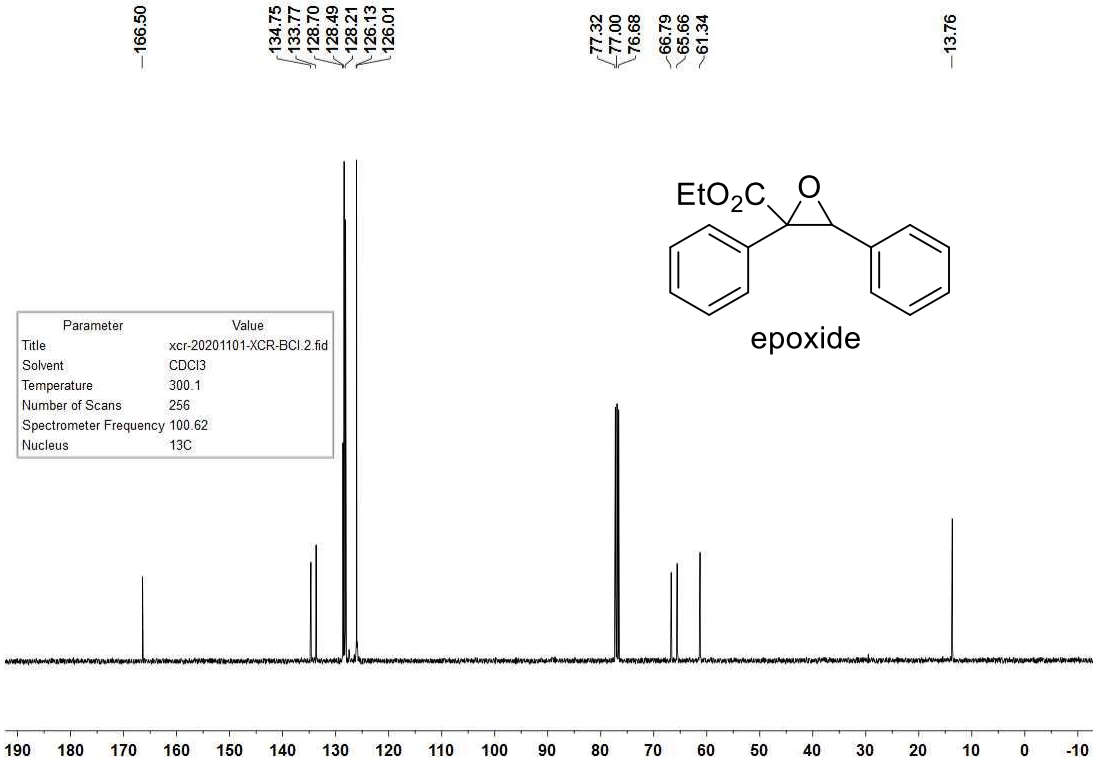

173.48 172.39 170.74
139.19 138.89 137.64 130.01 129.96 128.39 128.10 128.08 127.90 127.80 127.34 127.31 127.14 127.02 126.86 126.49 126.47 125.84 96.00 86.60 79.03 77.32 77.00 76.68 72.81 62.10 52.05 49.80 36.11 34.87 13.87
EtO2C
Ph
Ph
Ph
O
O
CO2Me
7a
Parameter Value
Title xcr-20201014-ys27.2.fid
Solvent CDCl3
Temperature 299.5
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C

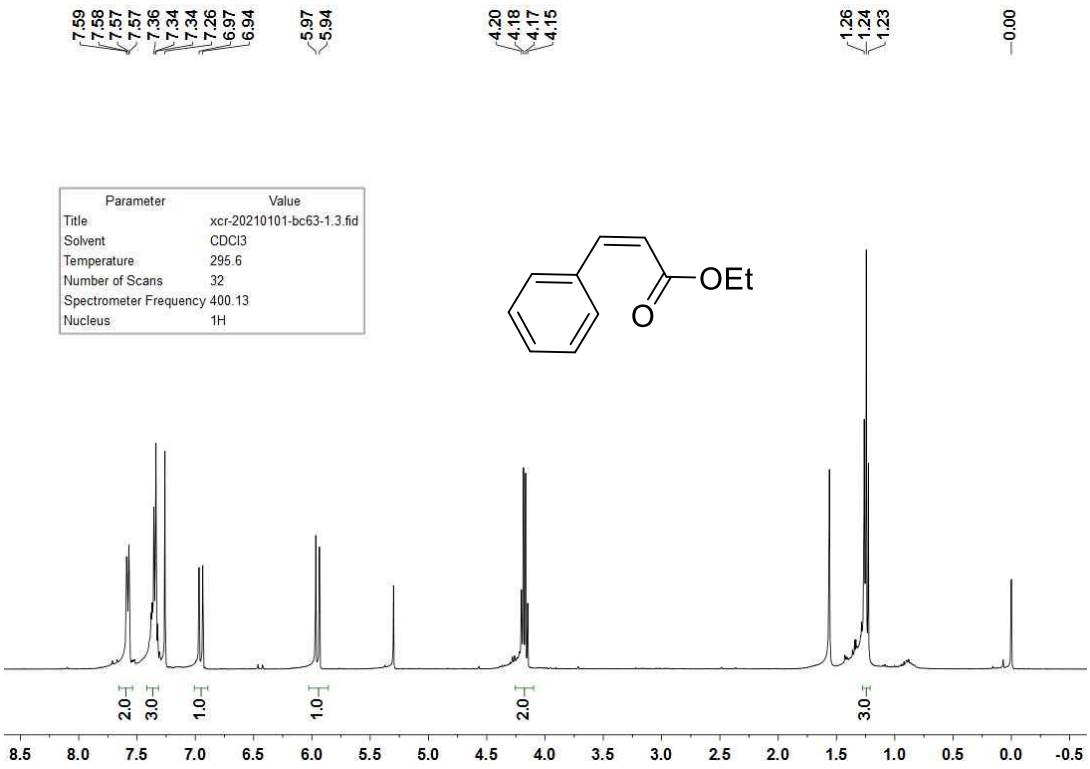


NOESY spectrum of **7a**

The interaction between these two H of minor diastereoisomer can be found in the **NOESY** pectrum, but not in the major isomer.


7.66
7.65
7.64
7.63
7.40
7.40
7.38
7.35
7.33
7.31
4.15
4.03
4.01
4.00
3.98
0.99
0.97
0.95
0.00
EtO2C
O
epoxide
Parameter Value
Title xcr-20201101-XCR-BCl.1.fid
Solvent CDCl3
Temperature 299.7
Number of Scans 32
Spectrometer Frequency 400.13
Nucleus 1H
2.0
8.0
1.0
2.0
3.0
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 -0.5 -1.0


166.50
134.75
133.77
128.70
128.49
128.21
126.13
126.01
77.32
77.00
76.68
66.79
65.66
61.34
13.76
EtO2C
O
epoxide
Parameter Value
Title xcr-20201101-XCR-BCl.2.fid
Solvent CDCl3
Temperature 300.1
Number of Scans 256
Spectrometer Frequency 100.62
Nucleus 13C
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.59
7.58
7.57
7.57
7.36
7.34
7.34
7.26
6.97
6.94
5.97
5.94
4.20
4.18
4.17
4.15
1.26
1.24
1.23
0.00
Parameter
Value
Title
xcr-20210101-bc63-1.3.fid
Solvent
CDCl3
Temperature
295.6
Number of Scans
32
Spectrometer Frequency
400.13
Nucleus
1H
OEt
O
2.0
3.0
1.0
1.0
2.0
3.0
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
-0.5