Asymmetric Baeyer-Villiger oxidation: classical and parallel kinetic resolution of 3-substituted cyclohexanones and desymmetrization of *meso*-disubstituted cycloketones

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Index

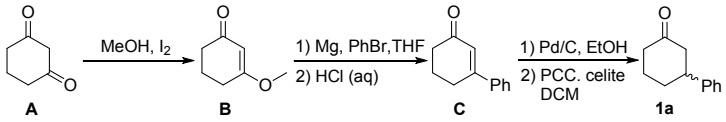
1. General information.

Reactions were carried out using commercial available reagents in oven-dried apparatus. EtOAc were dried and distilled from calcium hydride under nitrogen just before use. Molecular sieves were dried at 500 °C for 3 h and restored under nitrogen before use. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR and ^{19}F NMR data were collected with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomeric excesses (ee) were determined by chiral HPLC analysis on Daicel Chiralcel IA/AD-H/OD-H/AS-H and chiral SFC OX-3/OJ-3/AYH-3/AD-3/AS-3/IC-3 in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ = (c: g/100 mL, in solvent). ESI-HRMS spectra were recorded on a commercial apparatus and methanol was used to dissolve the sample. The *N*,*N*′-dioxides were prepared according to the methods reported in the literature.[1]

2. Methods for the preparation of 3-substituted cycloketones.

2.1 Synthesis of 3-substituted cycloketones.

The synthesis of 3-phenylcyclohexanone (**1a**) was selected as a model for the synthesis of 3-substituted cyclohexanones, 3-phenyl cyclopentanone and 3-phenyl cycloheptanone.



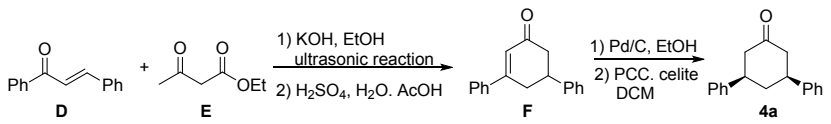
(a) Synthesis of 3-methoxycyclohex-2-enone (**B**). To a dry flask were added 1,3-cyclohexanedione (**A**) and MeOH (1.0 M). I_2 (5 mol%) was added portion-wise with stirring. The reaction was stirred at room temperature and was monitored via TLC. After the complete consumption of **A**, the reaction mixture was concentrated and DCM was added to the residue. The mixture was washed with Na_2SO_3 (aq.). The organic phase concentrated and the residue was purified by flash column chromatography to give **B**. (yellow oil, 87% yield).

(b) Synthesis of 3-phenylcyclohex-2-enone (**C**). To an oven-dry three-necked flask were added Mg chips (1.25 equiv.) and half a grain of I_2. The flask was evacuated and flushed with nitrogen gas for three times. Anhydrous THF was added (1.0 M) and the mixture was heated to 65 °C. One-third of bromobenzene solution (1.0 M in anhydrous THF) was added. When the color of the reaction solution turned from yellow to pale yellow, the rest of bromobenzene solvent was added drop-wise for 15 min whilst the reaction mixture was heated to micro-boiling. The reaction was stirred at 65 °C until the complete consumption of Mg chips. Subsequently, a solution of **B** was added portion-wise (1.0 M in THF) to the reaction mixture and stirred for 30 min. After cooling to room temperature, 10 mL HCl (aq., 2N) was added and the reaction mixture was monitored by TLC. The mixture was extracted by EtOAc, then the combined organic phase was concentrated and the residue was purified by flash column chromatography to give **C** (pale yellow oil, 76% yield).

(c) Synthesis of 3-phenylcyclohexanone (**1a**).To a dry flask were added **C** and 10% Pd/C (20% *w*/*w*). The flask was evacuated and flushed with hydrogen gas for three times. EtOH (0.2 M) was added to the reaction. T, the mixture was stirred at room temperature and monitored by TLC. After the complete consumption of **C**, the reaction mixture was filtered and the filtrate was concentrated. Then celite and pyridinium chlorochromate (PCC) were added after the residue was dissolved in DCM (1 M). The mixture was stirred for 30 min and filtered and the filtrate was concentrated. Purification was conducted by flash column chromatography to give (±)-**1a** (colorless oil, 89% yield).

2.2 Synthesis of *cis*-3,5-diarylcyclohexanones.

The synthesis of *cis*-3,5-diphenylcyclohexaone (**4a**) was selected as a model for synthesis of *cis*-3,5-diarylcyclohexanones.

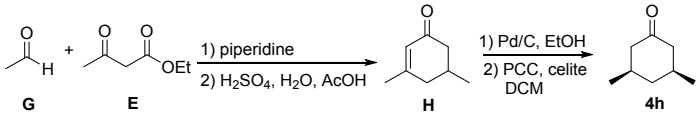


(a) Synthesis of 3,5-diphenylcyclohex-2-enone (**F**). To a dry flask were added EtOH (1.0 M), KOH (0.2 equiv.), chalcone (**D**, 1.0 equiv.) and ethyl acetoacetate (**E**, 1.2 equiv.). After stirred to a homogenous state, the mixture underwent unltrasonic reaction at 50 °C for 5 h and the reaction was monitored via TLC. The reaction mixture was concentrated, and the residue was dissolved in EtOAc and washed with water. The organic phase was concentrated and the residue was dissolved in a mixed solvent of AcOH, H_2SO_4 and water (*V*:*V*:*V* = 1:1:1,

0.3 M). The solution was heated to reflex and stirred for 8 h. After cooling to room temperature, EtOAc was added to the reaction mixture, then the organic phase was washed with water, Na_2CO_3 (aq., sat.) and water in sequence. The organic phase was dried with Na_2SO_4 and concentrated. The residue was purified by flash column chromatography and recrystallization in EtOH to give **F** (white solid, 60% yield).

(b) Synthesis of *cis*-3,5-diphenylcyclohexanone (**4a**). To a dry flask was added **F** and 10% Pd/C (20% *w*/*w*), the flask was evacuated and flushed with hydrogen gas for three times. EtOAc (0.2 M) was added to the reaction was stirred at room temperature. The reaction was monitored by TLC. After the complete consumption of **F**, the reaction mixture was filtered and the filtrate was concentrated. Then celite and pyridinium chlorochromate (PCC) were added after the residue was dissolved in DCM (1 M). The mixture was filtered and filtrate was concentrated. Purification was conducted by flash column chromatography and recrystallization in MeOH to give **4a** (white solid, 64% yield).

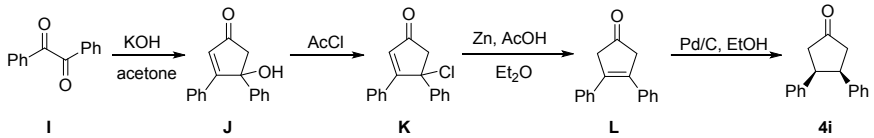
2.3 Synthesis of *cis*-3,5-dimethylcyclohexanone.



(a) Synthesis of 3,5-dimethylcyclohex-2-enone (**H**). To a dry flask were added ethyl acetoacetate (**E**, 1.0 equiv.), ethanal (**G**, 2.5 equiv., freshly distillated from paraldehyde and concentrated sulfuric acid), piperidine (0.2 equiv.) and MeOH (1.0 M). The reaction mixture was stirred at room temperature for 2 h. Then the reaction mixture was concentrated and extracted with EtOAc and water. The combined organic phase was concentrated and the residue was dissolved in a mixed solvent of AcOH, H_2SO_4 and water (*V*:*V*:*V* = 1:1:1, 0.3 M). The solution was heated to reflux and stirred for 6 h. After cooling to room temperature, EtOAc was added and the organic phase was washed with water, Na_2CO_3 (aq., sat.) and water in sequence. The organic phase was dried with Na_2SO_4, concentrated and the residue was purified by flash column chromatography to give **H** (colorless oil, 67% yield).

(b) Synthesis of *cis*-3,5-dimethylcyclohexanone (**4h**). To a dry flask was added **H** and 10% Pd/C (20% *w*/*w*), and the flask was evacuated and flushed with hydrogen gas for three times. EtOAc (0.2 M) was added, then the mixture was stirred at room temperature and monitored by TLC. After the complete consumption of **H**, the reaction mixture was filtered and the filtrate was concentrated. Then celite and pyridinium chlorochromate (PCC) was added after the residue was dissolved in DCM (1 M). The mixture was filtered and the filtrate was concentrated. Purification was conducted by flash column chromatography and recrystallization in MeOH to give **4h** (white oil, 80% yield).

2.4 Synthesis of *cis*-3,5-diphenylcyclopentanones.



(a) Synthesis of 4-hydroxy-3,4-diphenylcyclopent-2-enone (**J**). To a dry flask were added benzil (**I**, 1.0 equiv.), acetone (2.5 equiv.), KOH (0.03 equiv., 7.5 mol/L in water) and the reaction mixture was stirred at room temperature for 5 min. KOH (0.6 equiv., 7.5 mol/L in water) was then added to reaction mixture before the reaction was heated to 60 °C for 1 h and the reaction was monitored by TLC. The reaction mixture was concentrated and extracted with DCM and water. The combined organic phase was dried with Na_2SO_4 and concentrated, then the residue was purified by flash column chromatography and recrystallization to give **J** (white solid, 51% yield).

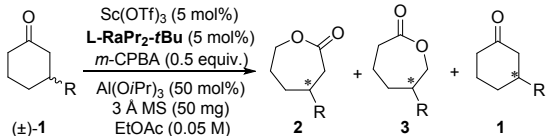
(b) Synthesis of 4-chloro-3,4-diphenylcyclopent-2-enone (**K**). To a dry flask were added **J** in AcCl as solvent (1.0 M). The reaction mixture was stirred at 60 °C and monitored by TLC. Then AcCl was evaporated and the residue was purified by flash column chromatography to give **K** (yellow solid, 91% yield).

(c) Synthesis of 3,4-diphenylcyclopent-3-enone (**L**). Zn powder (3.0 equiv.) was evenly dispersed in AcOH solution (10 equiv., 1.0 M in Et_2O) under vigorous stirring. To the mixture were added **K** (1.0 equiv. 0.1 M in Et_2O) drop-wise at room temperature and the reaction mixture was stirred at room temperature for 30 min. EtOAc was added to the reaction mixture and the organic phase was washed with water, Na_2CO_3 (aq., sat.) and water in sequence. The combined organic phase was dried with Na_2SO_4 and concentrated. Then the residue was purified by flash column chromatography and recrystallization with EtOAc and petroleum ether to give **L** (white solid, 69% yield).

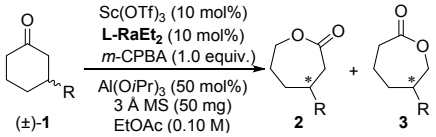
(d) Synthesis of *cis*-3,4-diphenylcyclopentanone (**4i**). To a dry flask was added **L** and 10% Pd/C (20% *w*/*w*), and the flask was evacuated and flushed with hydrogen gas for three times. EtOAc (0.2 M) was added and the mixture was stirred at room temperature. After the

complete consumption of **L**, the reaction mixture was filtered and the filtrate was concentrated. Purification was conducted by flash column chromatography and recrystallization in MeOH to give **4i** (white solid, 94% yield).

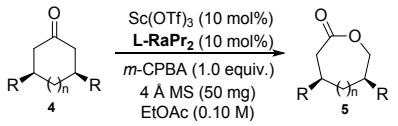
3 General procedures of asymmetric Baeyer-Villiger oxidation.



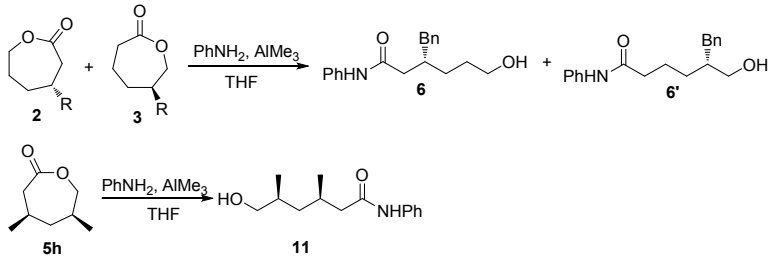
(a) Classical kinetic resolution. Chiral *N*,*N*′-dioxide **L-RaPr$_2$-*t*Bu** (0.05 equiv.), Sc(OTf)$_3$ (0.05 equiv.), 4 Å MS (50 mg), Al(O*i*Pr)$_3$ (0.5 equiv.), 3-substituted cyclohexanone **1** (0.20 mmol, 1.0 equiv.) and EtOAc (1 mL) was added under the air atmosphere. The mixture was stirred at 30 °C for 30 min. Then the reaction mixture was cooled to −20 °C and stirred vigorously. *m*-Chloro peroxobenzoic acid (*m*-CPBA) (0.5 equiv.) dissolved in EtOAc (1 mL) was added to the reaction mixture at −20 °C. The reaction was monitored by TLC. After consumption of *m*-CPBA, one drop of HCl (aq. 2 N) was added and the mixture was purified by column chromatography on silica gel with a pad of celite on top to afford the desired product **2**. The yields of **2** were calculated according to the amount of **1**.



(b) Parallel kinetic resolution. Chiral *N*,*N*′-dioxide **L-RaEt$_2$** (0.10 equiv.), Sc(OTf)$_3$ (0.10 equiv.), 4 Å MS (50 mg), Al(O*i*Pr)$_3$ (0.5 equiv.), 3-substituted cyclohexanone **1** (0.10 mmol, 1.0 equiv.) and EtOAc (1 mL) was added in air. The mixture was stirred at 30 °C for 30 min. The reaction was stirred vigorously at −20 °C and *m*-chloro peroxobenzoic acid (*m*-CPBA) (1.0 equiv.) was desolved in EtOAc (1 mL) and the solution was added to the reaction mixture. The reaction was monitored by TLC. After complete consumption of **1**, 1 drop of HCl (aq. 2 M) was added to the reaction mixture and the mixture was purified by column chromatography on silica gel with a pad of celite on top to afford the desired product **2** and **3**. The yields of **2** and **3** were calculated according to the amount of **1**.

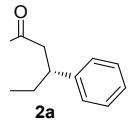


(c) Desymmetrization. Chiral *N*,*N*′-dioxide **L-RaPr$_2$** (0.10 equiv.), Sc(OTf)$_3$ (0.10 equiv.), 3 Å MS (50 mg), disubstituted cycloketone **4** (0.10 mmol, 1.0 equiv.) and EtOAc (1 mL) was added in air. The mixture was stirred at 30 °C for 30 min. The reaction was stirred vigorously at −20 °C and *m*-chloro peroxobenzoic acid (*m*-CPBA) (1.0 equiv.) was desolved in EtOAc (1 mL) and the solution was added to the reaction mixture. The reaction was monitored by TLC. After consumption of **4**, the mixture was purified by column chromatography on silica gel with a pad of celite on top to afford the desired product **5**. The yields of **5** were calculated according to the amount of **4**.



(d) The mixture of lactones **2** and **3** as well as aniline (2.0 equiv.) were added in a reaction tube, and the reaction tube was evacuated and flushed with nitrgen gas for three times. Then, THF (0.1 M) and $AlMe_3$ (1.0 M solution in heptanes, 2.0 equiv.) were added in the reaction tube in sequence. The reaction was stirred vigorously at room temperature and monitored by TLC. The reaction mixture was concentrated and extracted with DCM and water. The combined organic phase was dried with Na_2SO_4 and concentrated, and then the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product**s**. For **2g**, **2i**, **2j**, **2l**, **3g**, **3i**, **3j, 3l** and **5h**, ee values were determined according to the ee values of **6g**, **6i**, **6j**, **6l**, **6'g**, **6'i**, **6'j**, **6'l** and **11**, respectively.

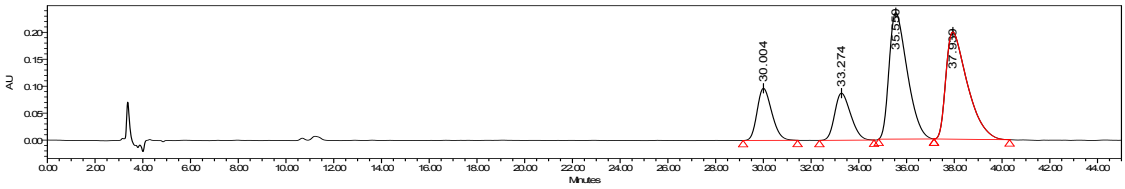
4 Characterization of the products in CKR.



2a

(*R*)-4-phenyloxepan-2-one **(2a)**

Prepared according to general procedure using (±)-**1a** (0.2 mmol, 34.8 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as colorless oil in 48% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **HPLC**: Chiralcel OD-H, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 30.3 min, t_{r2}= 34.0 min, t_{r3}= 36.2 min, t_{r4}= 37.6 min, **2a**/**3a** = 95/5, 93% ee for **2a**, 91% ee for **3a**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.26 – 7.16 (m, 3H), 4.45 – 4.22 (m, 2H), 3.06 (dd, *J* = 13.1, 11.7 Hz, 1H), 2.96 (dd, *J* = 11.9, 3.1 Hz, 1H), 2.83 (dt, *J* = 13.2, 1.5 Hz, 1H), 2.18 – 2.03 (m, 2H), 1.99 – 1.87 (m, 1H), 1.86 – 1.75 (m, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 174.5, 145.5, 128.8, 126.8, 126.2, 69.1, 41.4, 40.6, 37.8, 29.0. **HRMS** (ESI-TOF) Calculated for $C_{12}H_{14}O_2$ ([M]+Na$^+$) = 213.0886, found 213.0883. $[\alpha]_D^{28}$ = −115.7 (*c* = 0.250, in CH_2Cl_2).



	Retention Time	Area	% Area
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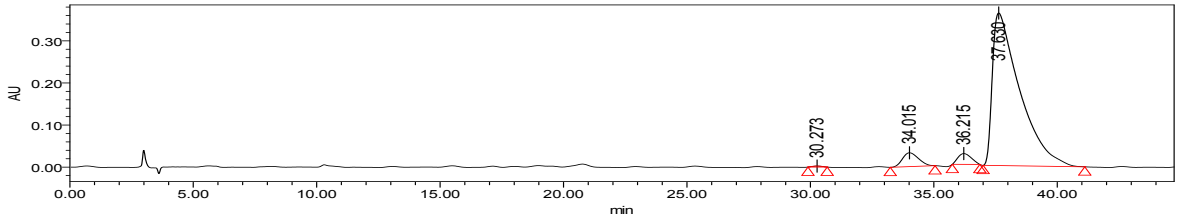
2	33.274	4065870	12.35
3	35.550	12335995	37.46
4	37.939	12408321	37.68



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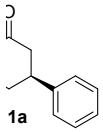
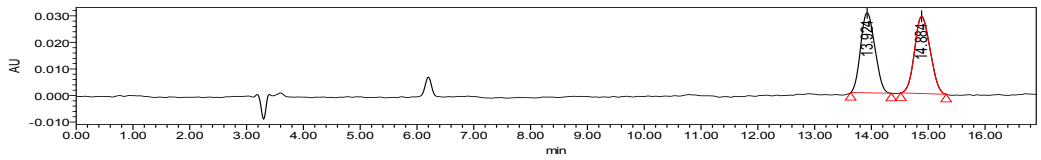
3	36.215	967011	3.19
4	37.630	27845501	91.72



1a

(*S*)-3-phenylcyclohexanone **(1a)**

1a (recovered): colorless oil in 48% recovery yield. **HPLC**: Chiralcel IC, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 13.8 min, t_{r2}= 14.8 min, 82% ee. $[\alpha]_D^{28}$ = −28.7 (*c* = 0.192, in $CHCl_3$). {Lit.[2] $[\alpha]_D^{20}$ = −22 (*c* = 0.208, in $CHCl_3$), conf. (*S*)}.



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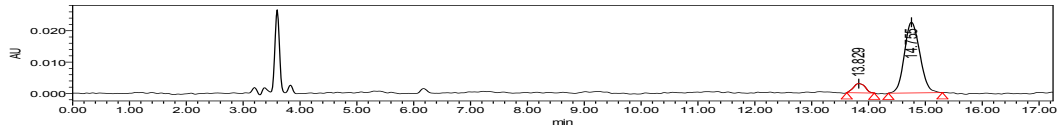
2	14.884	552709	51.30



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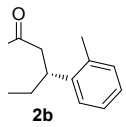
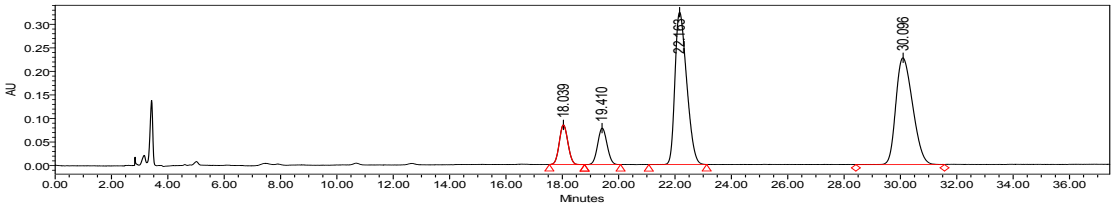
2	14.755	425788	90.89



2b

(*R*)-4-(2-methylphenyl)oxepan-2-one (**2b**)

Prepared according to general procedure using (±)-**1b** (0.2 mmol, 38.0 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 48% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel AYH-3, CO_2/EtOH = 95/05, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 18.1 min, t_{r2}= 19.7 min, t_{r3}= 22.4 min, t_{r4}= 30.0 min, **2b**/**3b** = 90/10, 88% ee for **2b**, 99% ee for **3b**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.17 – 6.98 (m, 4H), 4.39 – 4.18 (m, 2H), 3.07 (td, *J* = 11.6, 2.8 Hz, 1H), 2.95 (td, *J* = 12.4, 11.6, 2.5 Hz, 1H), 2.66 (d, *J* = 13.3 Hz, 1H), 2.27 (d, *J* = 2.4 Hz, 3H), 2.07 – 1.95 (m, 2H), 1.92 – 1.81 (m, 1H), 1.72 (ddt, *J* = 17.2, 11.8, 2.8 Hz, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 174.7, 143.6, 134.7, 130.7, 126.5, 126.4, 124.4, 69.1, 41.2, 36.6, 35.9, 29.2, 19.3. **HRMS** (ESI-TOF) Calculated for $C_{13}H_{16}O_2$ ([M]+Na$^+$) = 227.1048, found 227.1042. $[\alpha]_D^{28}$ = −97.2 (*c* = 0.250, in CH_2Cl_2). **M.P.**: 118 – 125 °C.



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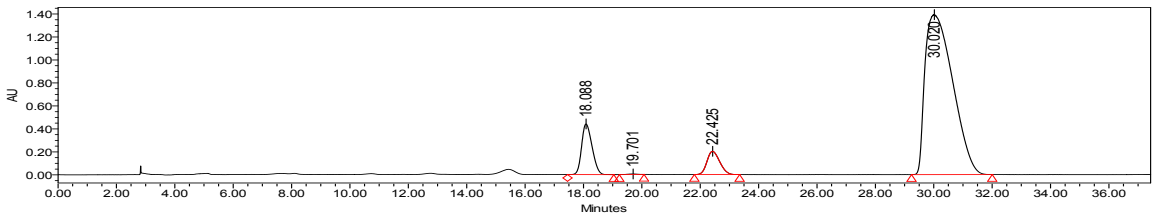
3	22.163	9312661	41.80
4	30.096	9377565	42.09



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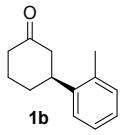
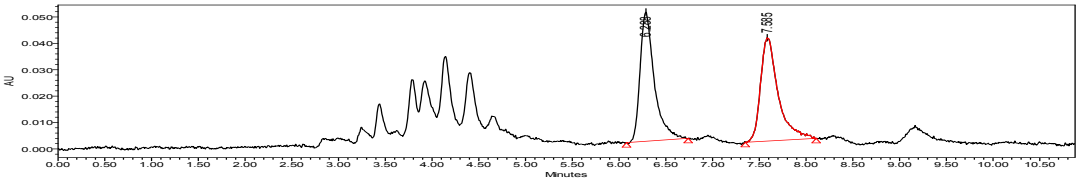


1b

(*S*)-3-(2-methylphenyl)cyclohexanone (**1b**)

1b (recovered): colorless oil in 48% recovery yield. **HPLC**: Chiralcel AD-H, hexane/*i*-PrOH = 97/03, flow rate 1.0 mL/min, λ = 220 nm, t_{r1}= 6.3 min, t_{r2}= 7.6 min, 72% ee. $[\alpha]_D^{28}$ = −121.6 (*c* = 0.226, in CH_2Cl_2). {Lit.[2] $[\alpha]_D^{20}$ = −45 (*c* = 0.168, in $CHCl_3$), conf. (*S*)}.



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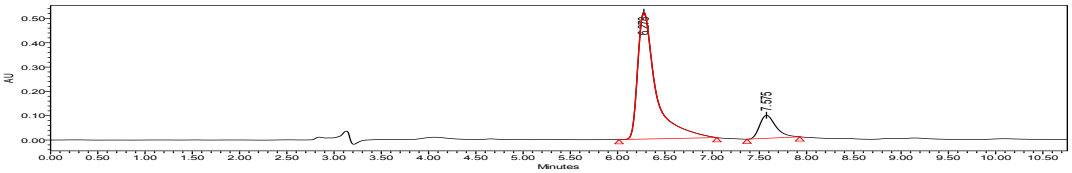
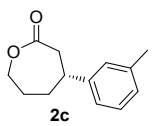


	Retention Time	Area	% Area
1	6.278	6953542	86.02
2	7.575	1130015	13.98

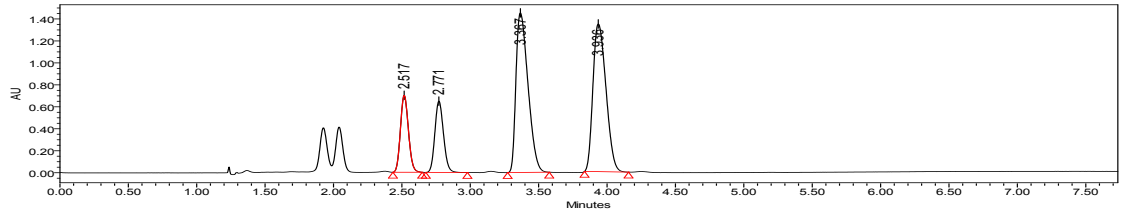


2c

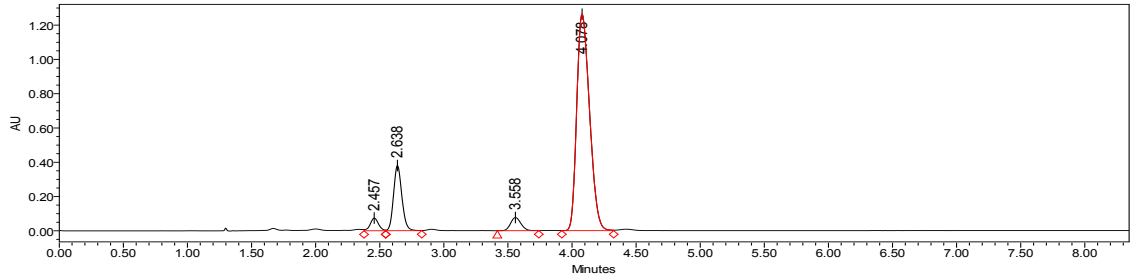
(*R*)-4-(3-methylphenyl)oxepan-2-one (**2c**)

Prepared according to general procedure using (±)-**1c** (0.2 mmol, 38.0 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 49% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel AS-3, CO_2/MeOH = 90/10, flow

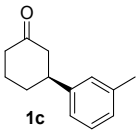
rate 1.0 mL/min, λ = 210 nm, t_{r1}= 2.5 min, t_{r2}= 2.6 min, t_{r3}= 3.6 min, t_{r4}= 4.1 min, **2b**/**3b** = 82/18, 91% ee for **2b**, 68% ee for **3b**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 1H), 7.11 – 6.88 (m, 3H), 4.43 – 4.19 (m, 2H), 3.02 (d, *J* = 12.6 Hz, 1H), 2.91 (dd, *J* = 11.7, 2.8 Hz, 1H), 2.81 (d, *J* = 13.3 Hz, 1H), 2.34 (s, 3H), 2.18 – 2.02 (m, 2H), 2.00 – 1.86 (m, 1H), 1.86 – 1.73 (m, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 174.5, 145.5, 138.8, 128.6, 127.5, 127.1, 123.2, 69.0, 41.5, 40.6, 37.7, 29.0, 21.4. **HRMS** (ESI-TOF) Calculated for $C_{13}H_{16}O_2$ ([M+Na$^+$) = 227.1042, found 227.1050. $[\alpha]_D^{28}$ = −112.8 (*c* = 0.234, in CH_2Cl_2). **M.P.**: 54 – 57 °C.



	Retention Time	Area	% Area
1	2.517	2852269	12.15
2	2.771	2842670	12.11
3	3.367	8890009	37.87
4	3.936	8889912	37.87

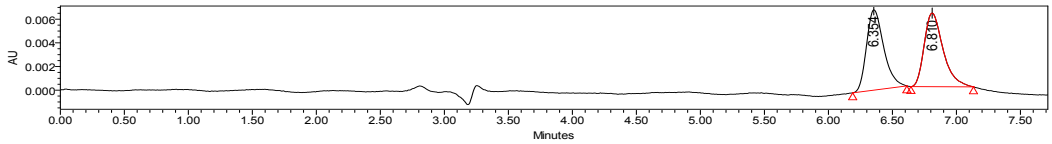


	Retention Time	Area	% Area
1	2.457	333723	2.96
2	2.638	1724295	15.29
3	3.558	430498	3.82
4	4.078	8788652	77.93

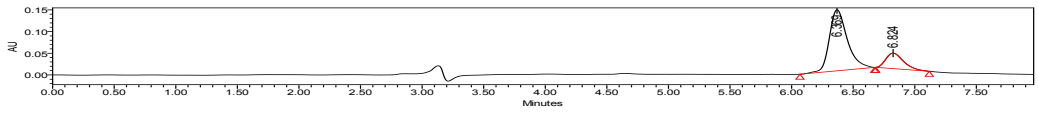


(*S*)-3-(3-methylphenyl)cyclohexanone (**1c**)

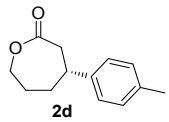
1c (recovered): colorless oil in 46% recovery yield. **HPLC**: Chiralcel AD-H, hexane/*i*-PrOH = 97/03, flow rate 1.0 mL/min, λ = 220 nm, t_{r1}= 6.4 min, t_{r2}= 6.8 min, 67% ee. $[\alpha]_D^{28}$ = −64.7 (*c* = 0.150, in CH_2Cl_2). {Lit.[2] $[\alpha]_D^{20}$ = −22 (*c* = 0.116, in $CHCl_3$), conf. (*S*)}.



	Retention Time	Area	% Area
1	6.356	640032	49.61
2	6.811	650053	50.39



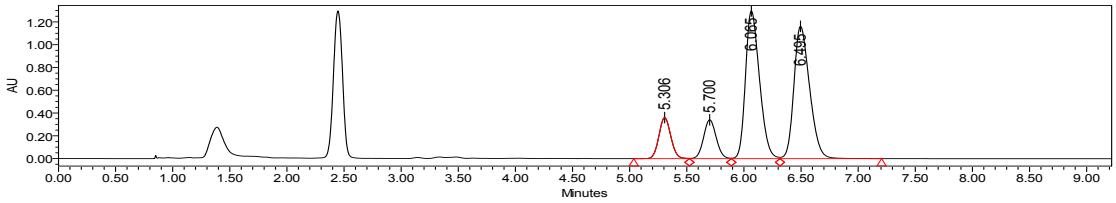
	Retention Time	Area	% Area
1	6.369	1119590	83.33
2	6.824	224028	16.67



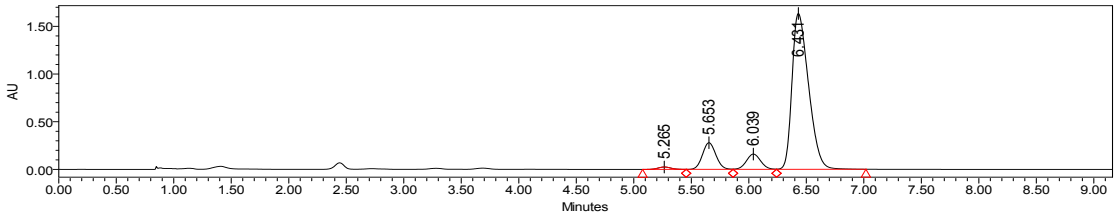
2d

(*R*)-4-(4-methylphenyl)oxepan-2-one (**2d**)

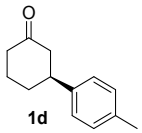
Prepared according to general procedure using (±)-**1d** (0.2 mmol, 38.0 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 47% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel IC-3, CO_2/MeOH = 90/10, flow rate 1.5 mL/min, λ = 210 nm, t_{r1}= 5.3 min, t_{r2}= 5.7 min, t_{r3}= 6.0 min, t_{r4}= 6.4 min, **2b**/**3b** = 88/12, 85% ee for **2b**, 90% ee for **3b**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.13 – 6.91 (m, 4H), 4.36 – 4.12 (m, 2H), 2.95 (dd, *J* = 13.2, 11.7 Hz, 1H), 2.84 (d, *J* = 3.0 Hz, 1H), 2.73 (dt, *J* = 13.2, 1.5 Hz, 1H), 2.25 (s, 3H), 2.10 – 1.94 (m, 2H), 1.85 (dd, *J* = 12.6, 2.6 Hz, 1H), 1.77 – 1.68 (m, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 174.6, 142.5, 136.4, 129.4, 126.1, 69.1, 41.6, 40.2, 37.8, 29.0, 21.0, 20.9. **HRMS** (ESI-TOF) Calculated for $C_{13}H_{16}O_3$ ([M]+Na$^+$) = 227.1042, found 227.1051. $[\alpha]_D^{28}$ = −121.3 (*c* = 0.244, in CH_2Cl_2). **M.P.**: 50 – 53 °C.



	Retention Time	Area	% Area
1	5.306	2622166	9.56
2	5.700	2622116	9.56
3	6.065	11052130	40.30
4	6.495	11129777	40.58



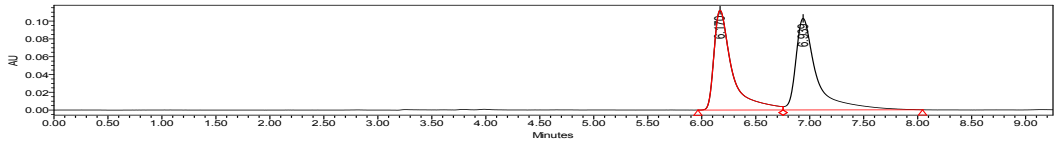
	Retention Time	Area	% Area
1	5.265	190822	0.95
2	5.653	2253676	11.19
3	6.039	1375702	6.83
4	6.431	16315276	81.03



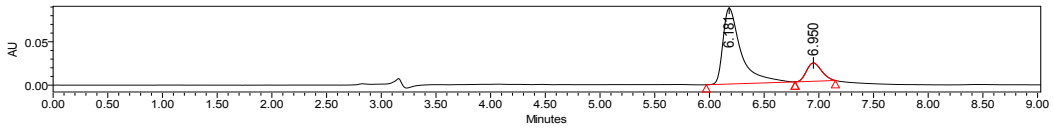
1d

(*S*)-3-(4-methylphenyl)cyclohexanone (**1d**)

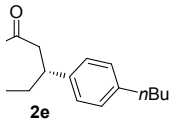
1d (recovered): colorless oil in 49% recovery yield. **HPLC**: Chiralcel AD-H, hexane/*i*-PrOH = 97/03, flow rate 1.0 mL/min, λ = 220 nm, t_{r1}= 6.2 min, t_{r2}= 7.0 min, 72% ee. $[\alpha]_D^{28}$ = −70.1 (*c* = 0.292, in CH_2Cl_2). {Lit.[2] $[\alpha]_D^{20}$ = −30 (*c* = 0.108, in $CHCl_3$), conf. (*S*)}.



	Retention Time	Area	% Area
1	6.170	1318801	48.82
2	6.939	1382306	51.18



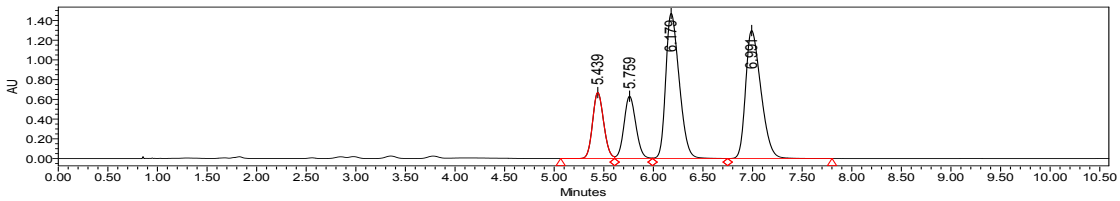
	Retention Time	Area	% Area
1	6.181	1228184	83.37
2	6.950	245026	16.63



2e

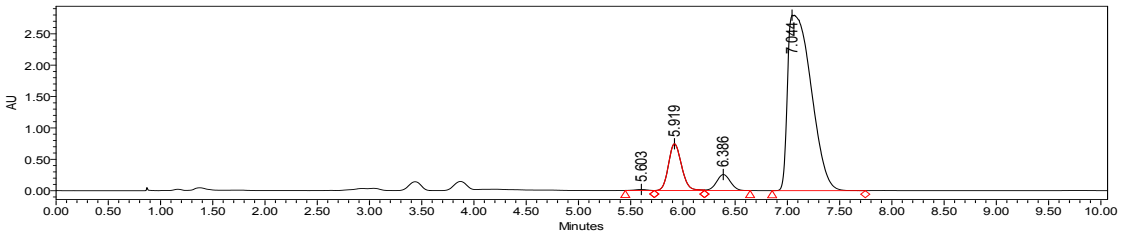
(*R*)-4-(4-*n*-butylphenyl)oxepan-2-one (**2e**)

Prepared according to general procedure using (±)-**1e** (0.2 mmol, 46.1 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as colorless oil in 45% yield. **TLC**: R_f = 0.4 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel IC-3, CO_2/MeOH = 90/10, flow rate 1.5 mL/min, λ = 210 nm, t_{r1}= 5.6 min, t_{r2}= 5.9 min, t_{r3}= 6.4 min, t_{r4}= 7.0 min, **2e**/**3e** = 88/12, 90% ee for **2e**, 96% ee for **3e**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.08 – 6.97 (m, 4H), 4.39 – 4.17 (m, 2H), 3.02 – 2.90 (m, 1H), 2.84 (td, *J* = 11.8, 3.0 Hz, 1H), 2.74 (d, *J* = 13.2 Hz, 1H), 2.51 (t, *J* = 7.8 Hz, 2H), 2.07 – 1.94 (m, 2H), 1.90 – 1.79 (m, 1H), 1.77 – 1.68 (m, 1H), 1.55 – 1.46 (m, 2H), 1.28 (q, *J* = 7.4 Hz, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 174.6, 142.7, 141.4, 128.7, 126.0, 69.0, 41.6, 40.2, 37.8, 35.2, 33.6, 29.0, 22.4, 13.9. **HRMS** (ESI-TOF) Calculated for $C_{16}H_{22}O_2$ ([M]+Na^+) = 269.1512, found 269.1506. $[\alpha]_D^{26}$ = −101.4 (*c* = 0.296, in CH_2Cl_2).

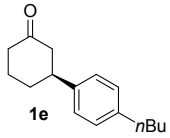


	Retention Time	Area	% Area
1	5.439	5201510	13.61
2	5.759	5235198	13.70

3	6.179	13880278	36.31
4	6.991	13907921	36.38

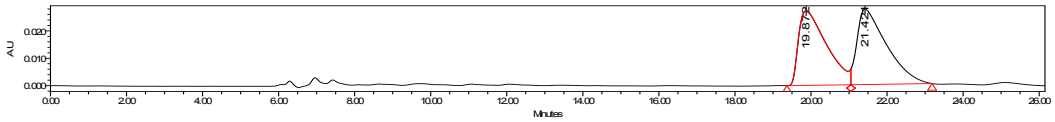


	Retention Time	Area	% Area
1	5.603	115619	0.22
2	5.919	6452751	12.22
3	6.386	2338091	4.43
4	7.044	43911442	83.14

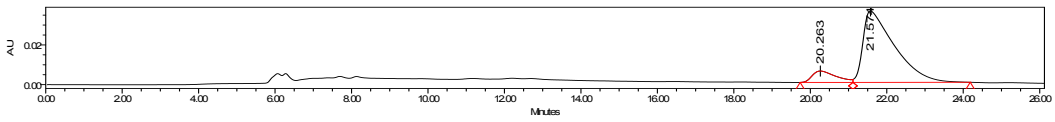


(*S*)-3-(4-*n*-butylphenyl)cyclohexanone (**1e**)

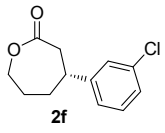
1e (recovered): colorless oil in 42% recovery yield. **HPLC**: Chiralcel AS-H, hexane/*i*-PrOH = 95/05, flow rate 0.5 mL/min, λ = 220 nm, t_{r1}= 20.3 min, t_{r2}= 21.6 min, 79% ee. $[\alpha]_D^{28}$ = −86.3 (*c* = 0.258, in CH_2Cl_2).



	Retention Time	Area	% Area
1	19.872	4836954	49.15
2	21.421	5005113	50.85

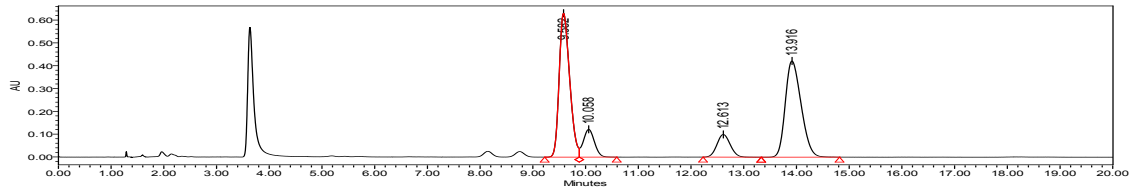


	Retention Time	Area	% Area
1	20.263	247387	10.74
2	21.574	2056036	89.26

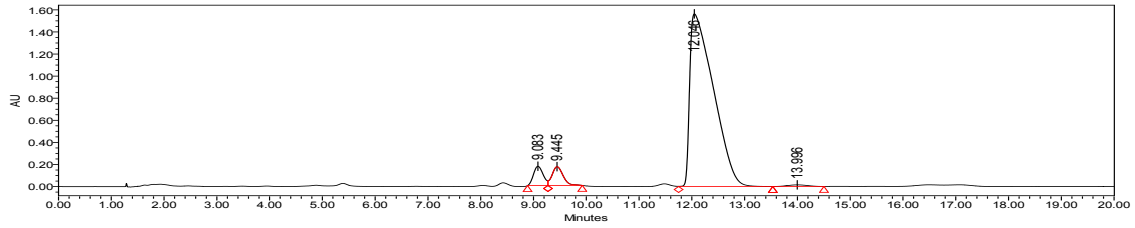


(*R*)-4-(3-chlorophenyl)oxepan-2-one (**2f**)

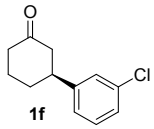
Prepared according to general procedure using (±)-**1f** (0.2 mmol, 41.7 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 49% yield. **TLC**: R_f = 0.25 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel AD-3, CO_2/MeOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 9.1 min, t_{r2}= 9.4 min, t_{r3}= 12.0 min, t_{r4}= 14.0 min, **2f**/**3f** = 90/10, 90% ee for **2f**, 75% ee for **3f**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.21 – 7.08 (m, 3H), 7.05 – 6.90 (m, 1H), 4.39 – 4.15 (m, 2H), 2.96 (dd, *J* = 13.1, 11.8 Hz, 1H), 2.90 – 2.81 (m, 1H), 2.72 (dt, *J* = 13.2, 1.6 Hz, 1H), 2.09 – 1.95 (m, 2H), 1.92 – 1.80 (m, 1H), 1.77 – 1.67 (m, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 174.0, 147.3, 134.5, 130.1, 127.0, 126.4, 124.6, 69.0, 41.2, 40.3, 37.5, 28.9. **HRMS** (ESI-TOF) Calculated for $C_{18}H_{16}{}^{34.9689}ClO_2$ ([M+Na$^+$) = 247.0496, found 247.0492. Calculated for $C_{18}H_{16}{}^{36.9659}ClO_2$ ([M+Na$^+$) = 249.0467, found 249.0460. $[\alpha]_D^{26}$ = −108.1 (*c* = 0.210, in CH_2Cl_2). **M.P.**: 74 – 92 °C.



	Retention Time	Area	% Area
1	9.582	8729162	41.51
2	10.058	1783800	8.48
3	12.613	1744239	8.29
4	13.916	8771670	41.71



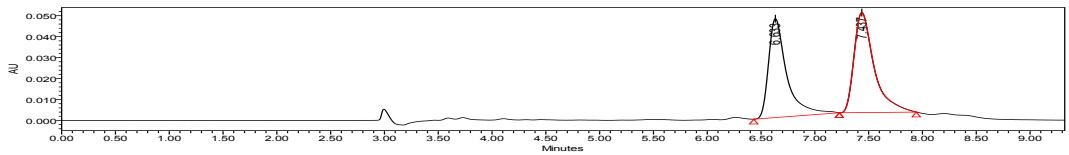
	Retention Time	Area	% Area
1	9.083	2218120	4.14
2	9.445	2468360	4.61
3	12.046	48480470	90.56
4	13.996	365936	0.68



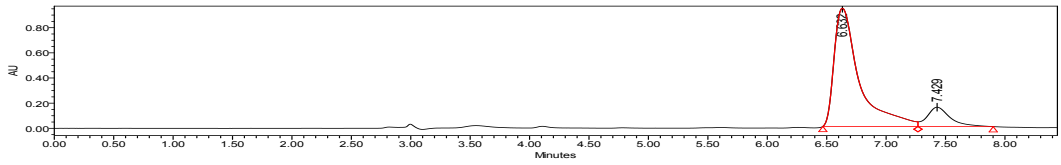
1f

(*S*)-3-(3-chlorophenyl)cyclohexanone (**1f**)

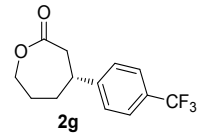
1f (recovered): colorless oil in 49% recovery yield. **HPLC**: Chiralcel AD-H, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 220 nm, t_{r1}= 6.6 min, t_{r2}= 7.4 min, 74% ee. $[\alpha]_D^{28}$ = −87.1 (*c* = 0.256, in CH_2Cl_2). {Lit.[2] $[\alpha]_D^{20}$ = −8 (*c* = 0.136, in $CHCl_3$), conf. (*S*)}.



	Retention Time	Area	% Area
1	6.633	554627	47.33
2	7.437	617135	52.67



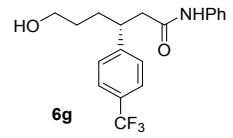
	Retention Time	Area	% Area
1	6.632	13781256	86.96
2	7.429	2065992	13.04



2g

(*R*)-4-(4-trifluoromethylphenyl)oxepan-2-one (**2g**)

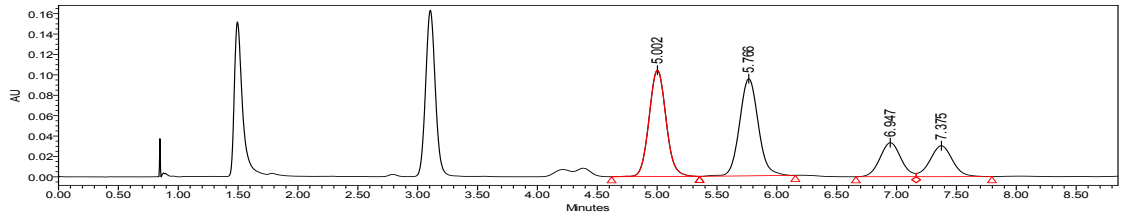
Prepared according to general procedure using (±)-**1g** (0.2 mmol, 48.4 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 45% yield. **TLC**: R_f = 0.3 (petroleum ether:EtOAc = 3:1) [UV]. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.30 – 7.21 (m, 2H), 4.36 – 4.19 (m, 2H), 3.05 – 2.89 (m, 2H), 2.78 – 2.70 (m, 1H), 2.09 – 1.99 (m, 2H), 1.94 – 1.82 (m, 1H), 1.79 – 1.70 (m, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 173.9, 149.2, 129.2 (q, J_{CF} = 32.3 Hz), 126.7, 125.8 (q, J_{CF} = 4.0 Hz), 124.0 (q, J_{CF} = 272.0 Hz). 77.3, 77.0, 76.7, 69.0, 41.1, 40.4, 37.5, 28.9. **^{19}F NMR**: (376 MHz, $CDCl_3$) δ −62.5. **HRMS** (ESI-TOF) Calculated for $C_{13}H_{13}F_3O_2$ ([M]+Na$^+$) = 281.0760, found 281.0768. $[\alpha]_D^{26}$ = −105.2 (*c* = 0.446, in CH_2Cl_2). **M.P.**: 97 – 106 °C.



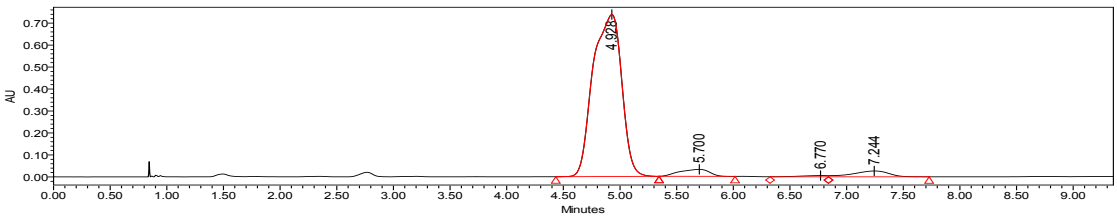
6g

(*R*)-6-hydroxy-*N*-phenyl-3-(4-(trifluoromethyl)phenyl)hexanamide (**6g**)

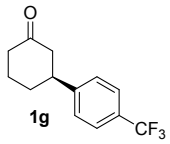
Prepared according to general procedure using **2g** (0.1 mmol), anniline (0.2 mmol), $AlMe_3$ (0.2 mmol). **SFC**: Chiralcel OX-3, CO_2/MeOH = 90/10, flow rate 1.5 mL/min, λ = 240 nm, t_{r1}= 4.9 min, t_{r2}= 5.7 min, t_{r3}= 6.8 min, t_{r4}= 7.2 min, **7g**/**7'g** = 95/5, 95% ee for **2g**, 73% ee for **3g**. $[\alpha]_D^{26}$ = −93.2 (*c* = 0.424, in CH_2Cl_2).



	Retention Time	Area	% Area
1	5.002	1027839	35.91
2	5.766	1036166	36.20
3	6.947	405354	14.16
4	7.375	392763	13.72

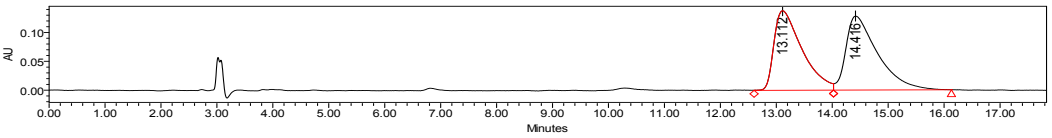


	Retention Time	Area	% Area
1	4.928	12965271	91.20
2	5.700	585369	4.12
3	6.770	88970	0.63
4	7.244	576996	4.06

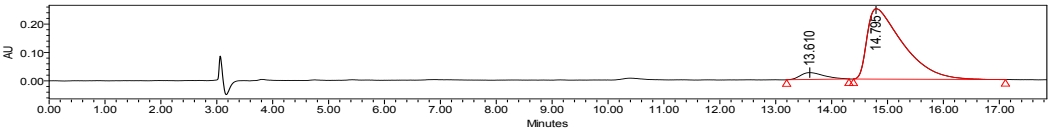


(*S*)-3-(4-trifluoromethylphenyl)cyclohexanone (**1g**)

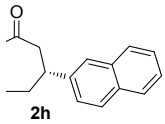
1g (recovered): white solid in 43% recovery yield. **HPLC**: Chiralcel AS-H, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 220 nm, t_{r1}= 13.6 min, t_{r2}= 14.8 min, 88% ee. $[\alpha]_D^{28}$ = −83.1 (*c* = 0.242, in CH_2Cl_2). {Lit.[3] $[\alpha]_D^{24}$ = +14.6 (*c* = 1.30, in $CHCl_3$), conf. (*R*)}. **M.P.**: 62 – 65 °C.



	Retention Time	Area	% Area
1	13.112	4810456	48.72
2	14.416	5063078	51.28



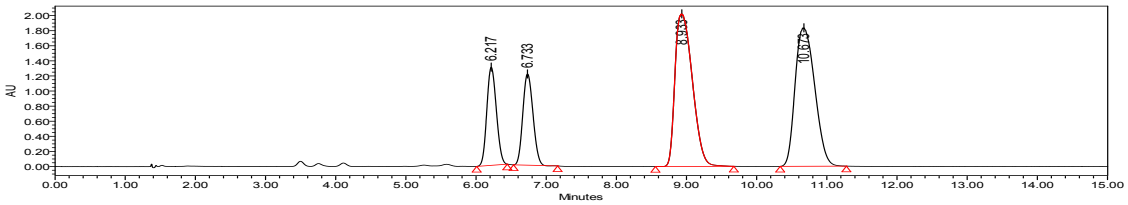
	Retention Time	Area	% Area
1	13.610	711272	6.07
2	14.795	11012931	93.93



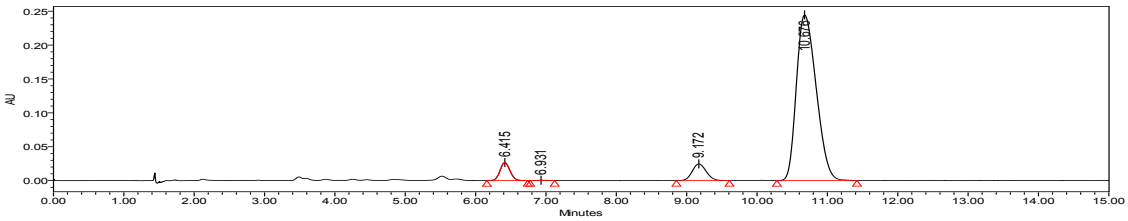
(*R*)-4-(naphthalen-2-yl)oxepan-2-one (**2h**)

Prepared according to general procedure using (±)-**1h** (0.2 mmol, 44.9 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc:DCM = 7:1:1) to give the title compound as white solid in 50% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel AS-3, CO_2/MeOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 6.4 min, t_{r2}= 6.9 min, t_{r3}= 9.2 min, t_{r4}= 10.7 min, **2h**/**3h** = 95/5, 87% ee for **2h**, 98% ee for **3h**. **^{1}H**

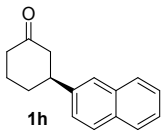
NMR: (400 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 6H), 7.64 – 7.58 (m, 2H), 7.52 – 7.41 (m, 4H), 7.36 – 7.28 (m, 2H), 4.47 – 4.27 (m, 4H), 3.22 – 3.05 (m, 4H), 2.98 – 2.86 (m, 2H), 2.25 – 2.17 (m, 2H), 2.16 – 2.08 (m, 2H), 2.04 – 1.88 (m, 4H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 174.5, 142.8, 133.4, 132.3, 128.6, 127.6, 127.6, 126.3, 125.7, 124.9, 124.5, 69.1, 41.5, 40.7, 37.6, 29.1 **HRMS** (ESI-TOF) Calculated for $C_{16}H_{16}O_2$ ([M]+Na^+) = 263.1042, found 263.1039. $[\alpha]_D^{28}$ = −148.4 (*c* = 0.306, in CH_2Cl_2). **M.P.**: 88 – 96 °C.



	Retention Time	Area	% Area
1	6.217	12281777	12.95
2	6.733	12185964	12.85
3	8.933	34705903	36.60
4	10.673	35655584	37.60



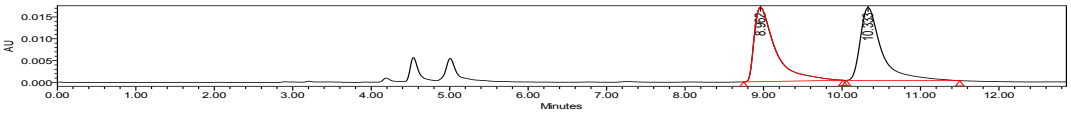
	Retention Time	Area	% Area
1	6.415	259245	4.83
2	6.931	3700	0.07
3	9.172	332892	6.21
4	10.676	4768314	88.89



1h

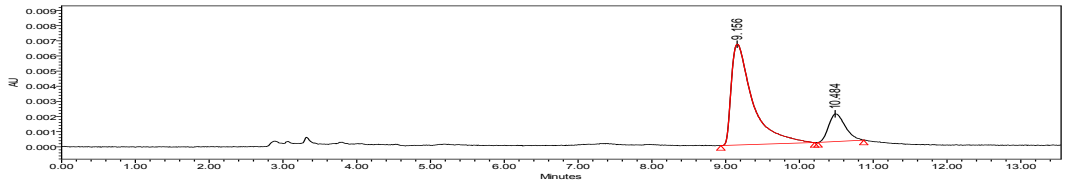
(*S*)-3-(naphthalen-2-yl)cyclohexanone (**1h**)

1h (recovered): white solid in 49% recovery yield. **HPLC**: Chiralcel AD-H, hexane/*i*-PrOH = 99/01, flow rate 1.0 mL/min, λ = 220 nm, t_{r1}= 9.2 min, t_{r2}= 10.5 min, 72% ee. $[\alpha]_D^{28}$ = −89.3 (*c* = 0.294, in CH_2Cl_2). {Lit.[2] $[\alpha]_D^{20}$ = −3 (*c* = 0.108, in $CHCl_3$), conf. (*S*)}. **M.P.**: 58 – 64 °C.

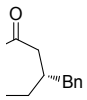


	Retention Time	Area	% Area
1	8.962	313660	49.86

2	10.333	315383	50.14



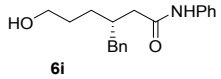
	Retention Time	Area	% Area
1	9.157	1159337	81.21
2	10.495	268237	18.79



2i

(*S*)-4-benzyloxepan-2-one **(2i)**

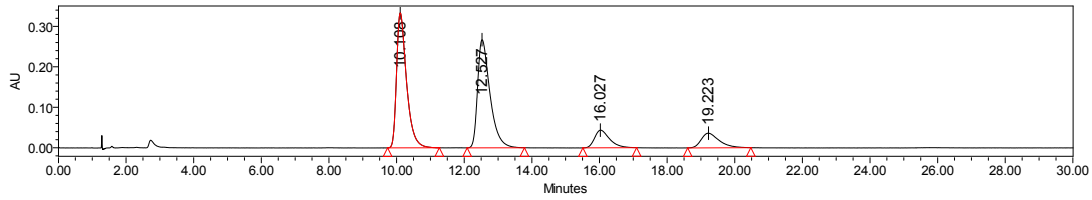
Prepared according to general procedure using (±)-**1h** (0.2 mmol, 38.0 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 48% yield. **TLC**: R_f = 0.4 (petroleum ether:EtOAc = 4:1) [UV]. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 2H), 7.17 – 7.12 (m, 1H), 7.11 – 7.04 (m, 2H), 4.22 – 4.15 (m, 1H), 4.15 – 4.07 (m, 1H), 4.01 – 3.91 (m, 0H), 2.67 – 2.54 (m, 2H), 2.54 – 2.46 (m, 2H), 2.05 – 1.94 (m, 1H), 1.94 – 1.86 (m, 1H), 1.86 – 1.76 (m, 1H), 1.70 – 1.59 (m, 1H), 1.42 – 1.28 (m, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 175.8, 174.8, 139.1, 138.9, 129.1, 129.0, 128.5, 128.4, 126.4, 71.8, 69.1, 42.6, 40.4, 40.0, 38.0, 35.7, 34.5, 34.4, 34.3, 27.8, 21.1. **HRMS** (ESI-TOF) Calculated for $C_{13}H_{16}O_2$ ([M]+Na^+) = 227.1042, found 227.1041. $[\alpha]_D^{26}$ = −108.9 (*c* = 0.342, in CH_2Cl_2). **M.P.**: 47 – 55 °C.



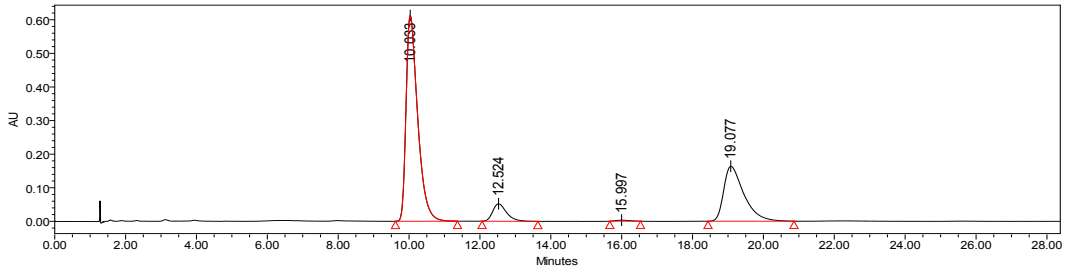
6i

(*S*)-3-benzyl-6-hydroxy-*N*-phenylhexanamide (**6i**)

Prepared according to general procedure using **2h** (0.1 mmol), anniline (0.2 mmol), $AlMe_3$ (0.2 mmol). **SFC**: Chiralcel OJ-3, CO_2/MeOH = 90/10, flow rate 1.0 mL/min, λ = 240 nm, t_{r1}= 10.0 min, t_{r2}= 12.5 min, t_{r3}= 16.0 min, t_{r4}= 19.1 min, **7g/7'g** = 70/30, 95% ee for **2f**, 73% ee for **3f**. $[\alpha]_D^{26}$ = −71.1 (*c* = 0.284, in CH_2Cl_2).



	Retention Time	Area	% Area
1	10.108	6822055	41.90
2	12.527	6780553	41.65
3	16.027	1342155	8.24
4	19.223	1336788	8.21

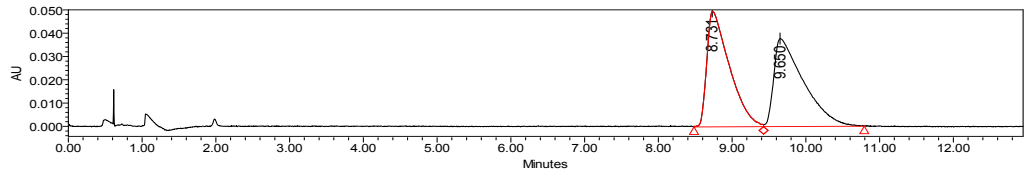


	Retention Time	Area	% Area
1	10.033	13930746	63.72
2	12.524	1404199	6.42
3	15.997	81004	0.37
4	19.077	6445857	29.48

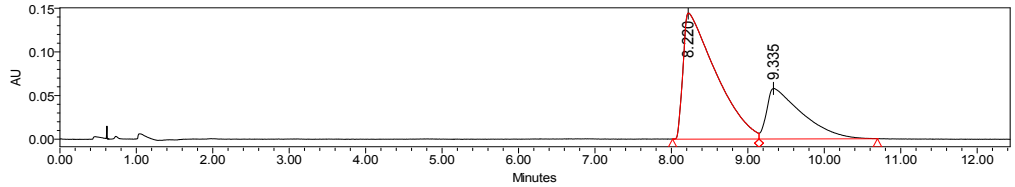
1i

(*R*)-3-benzylcyclohexanone **(1i)**

1i (recovered): colorless oil in 43% recovery yield. **SFC**: Chiralcel AD-3, CO_2/*i*-PrOH = 99.5/0.5, flow rate 2.0 mL/min, λ = 220 nm, t_{r1}= 8.2 min, t_{r2}= 9.3 min, 40% ee. $[\alpha]_D^{28}$ = −83.1 (*c* = 0.242, in CH_2Cl_2). {Lit.[4] $[\alpha]_D$ = +20 (*c* = 1, in $CHCl_3$), conf. (*S*)}.



	Retention Time	Area	% Area
1	8.731	1053516	49.99
2	9.650	1053789	50.01

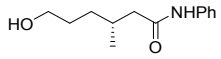


	Retention Time	Area	% Area
1	8.220	4280184	69.77
2	9.335	1854532	30.23

2j

(*R*)-4-methyloxepan-2-one **(2j)**

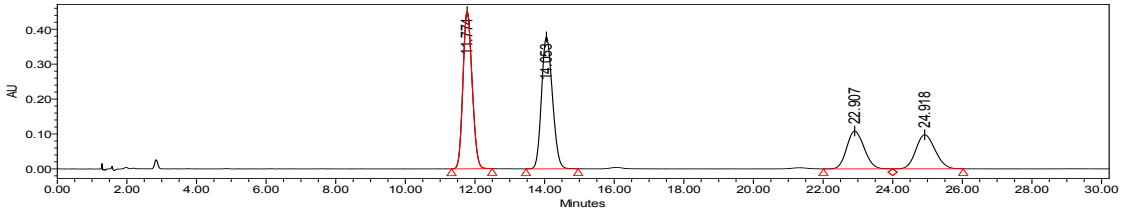
Prepared according to general procedure using (±)-**1j** (0.2 mmol, 22.4 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as colorless oil in 44% yield. **TLC**: R_f = 0.4 (petroleum ether:EtOAc = 4:1) [UV]. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 4.26 – 3.95 (m, 2H), 2.65 – 2.53 (m, 2H), 1.96 – 1.75 (m, 4H), 1.68 – 1.62 (m, 0H), 1.45 – 1.34 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 2H), 0.95 (d, *J* = 7.0 Hz, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 175.9, 175.0, 73.9, 69.2, 41.8, 37.2, 36.9, 34.4, 33.8, 29.2, 27.8, 22.3, 21.6, 17.7. **HRMS** (ESI-TOF) Calculated for $C_{12}H_{14}O_2$ ([M]+Na$^+$) = 151.0735, found 151.0733. $[\alpha]_D^{26}$ = −85.2 (*c* = 0.148, in CH_2Cl_2).



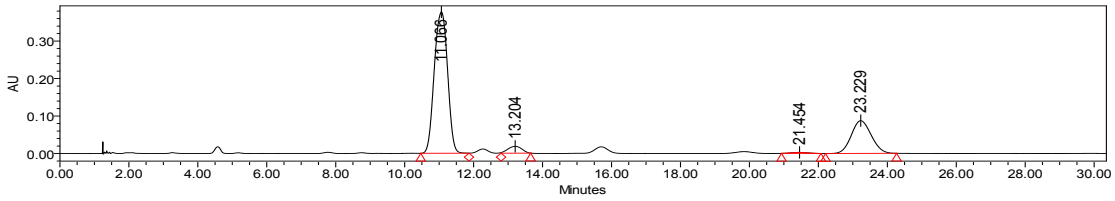
6j

(*R*)-6-hydroxy-3-methyl-N-phenylhexanamide (**6j**)

Prepared according to general procedure using **2j** (0.1 mmol), anniline (0.2 mmol), $AlMe_3$ (0.2 mmol). **SFC**: Chiralcel AD-3, CO_2/MeOH = 90/10, flow rate 1.0 mL/min, λ = 240 nm, t_{r1}= 11.1 min, t_{r2}= 13.2 min, t_{r3}= 21.4 min, t_{r4}= 23.2 min, **7j**/**7'j** = 74/26, 90% ee for **7j**, 95% ee for **7'j**. $[\alpha]_D^{26}$ = −53.3 (*c* = 0.174, in CH_2Cl_2).



	Retention Time	Area	% Area
1	11.774	8241167	34.32
2	14.053	8248551	34.35
3	22.907	3767019	15.69
4	24.918	3754119	15.64



	Retention Time	Area	% Area
1	11.066	10082596	71.10
2	13.204	508801	3.59
3	21.454	87904	0.62
4	23.229	3501629	24.69

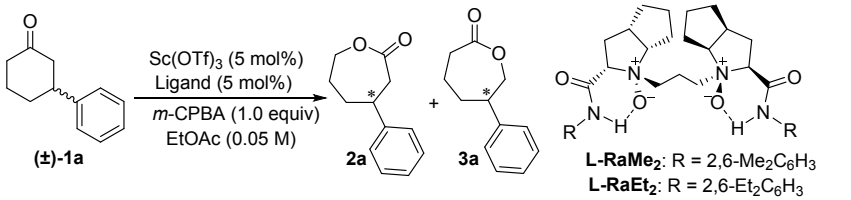
1j

(*S*)-3-methylcyclohexanone **(1j)**

1j (recovered): colorless oil in 40% recovery yield, $[\alpha]_D^{19}$ = −7.9 (*c* = 0.140, in $CHCl_3$). {Lit.[5] $[\alpha]_D^{23}$ = −11.6 (*c* = 1, in $CHCl_3$), conf. (*S*)}. The ee value of **1j** (55% ee) was determined by specific rotation in comparision with enantiopure **(*R*)-1j**, $[\alpha]_D^{19}$ = +14.3 (*c* = 0.140, in $CHCl_3$).

5 Condition optimization of PKR Baeyer-Villiger oxidation

Table S1. Conditition optimization of PKR Baeyer-Villiger oxidation reaction.

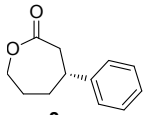


entry[a]	ligand	yield (%)[b]		ee (%)[c]	
		2a + **3a**	**2a**:**3a**[c]	**2a**	**3a**
1	**L-RaPr$_2$-*t*Bu**	86	89:11	74	94
2	**L-RaEt$_2$**	88	57:43	75	91
3	**L-RaEt$_2$-Me**	88	59:41	70	94
4	**L-RaMe$_2$**	n.d.	–	–	–
5[d]	**L-RaEt$_2$**	68	58:42	78	95
6[d,e]	**L-RaEt$_2$**	81	54:46	77	98
7[d,e,f]	**L-RaEt$_2$**	98	55:45	81	97

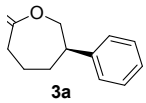
[a]Unless otherwise noticed, the reactions were performed with $Sc(OTf)_3$ (10 mol%), ligand (10 mol%), **1a** (0.10 mmol) and *m*-CPBA (1.0 equiv) in EtOAc (0.05 M) in air at 0 °C for 24 h. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase. [d]$Al(OiPr)_3$ (50 mol%) was added. [e]3 Å MS (50 mg) was added.[f]At -20 °C for 48h.

Subsequently, we turned our attention to the parallel kinetic resolution of racemic 3-substituted cyclohexanones. Under the same reaction conditions (Table S1, entry 1) with the use of one equivalent *m*-CPBA, desired lactones **2a** and **3a** were given in 86% mixed yield, 74% ee of **2a**, 94% ee of **3a** with 89:11 rr. In the process of the screening of different ligands, we were pleased to find that with **L-RaEt$_2$**–$Sc(OTf)_3$ complex (10 mol%), quantitative yield of both **2a** and **3a** were obtained in approximately 1:1 ratio, and the ee of **2a** was moderate while ee of **3a** excellent (Table S1, entry 2). When we attached a methyl group on the *para*- position of the phenyl group on the ligand, and a parallel result was obtained (Table S1, entry 3). Further reducing steric hindrance on the 2,6-position of the phenyl group on the ligand resulted in an drastic decrease of the reactivity (Table S1, entry 4). Adding of $Al(OiPr)_3$ proved effective for promotion of ee value of both **2a** and **3a** yet the reactivity was slightly depressed (Table S1, entry 5). When extra 3 Å MS was utilized, the reactivity of the reaction was increased with selectivity stayed intact (Table S1, entry 6). At −20 °C for 48 h, the reaction achieved quantitative yield, good enantioselectitity for **2a** and excellent enantioselectivity for **3a** (Table S1, entry 7).

6 Characterization of the Products in PKR.



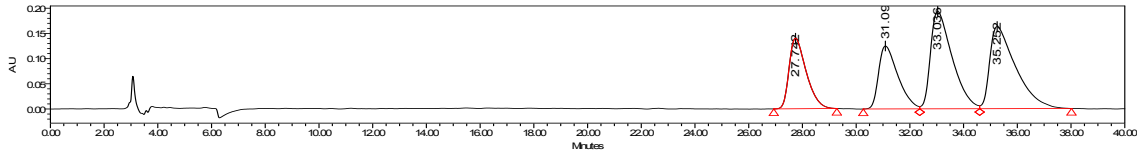
2a



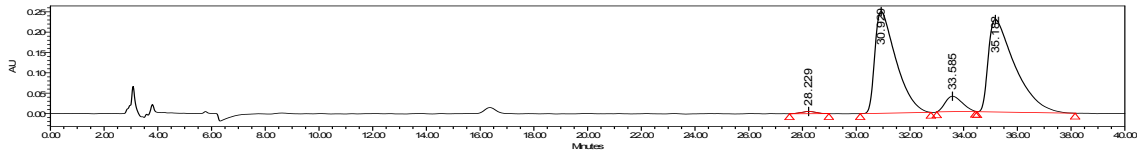
3a

(*R*)-4-phenyloxepan-2-one (**2a**);
(*R*)-6-phenyloxepan-2-one (**3a**)

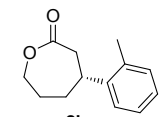
Prepared according to general procedure using (±)-**1a** (0.1 mmol, 17.4 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as colorless oil in 98% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **HPLC**: Chiralcel OD-H, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 28.2 min, t_{r2}= 30.9 min, t_{r3}= 33.6 min, t_{r4}= 35.3 min, **2a**/**3a** = 55/45, 81% ee for **2a**, 97% ee for **3a**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.27 – 7.15 (m, 6H), 4.61 – 4.46 (m, 1H), 4.44 – 4.28 (m, 1H), 3.27 – 3.08 (m, 3H), 2.97 – 2.86 (m, 1H), 2.35 – 2.22 (m, 1H), 2.15 – 2.00 (m, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 173.9, 145.2, 141.8, 129.0, 128.8, 127.2, 126.9, 126.8, 126.2, 73.2, 46.0, 45.8, 41.2, 40.6. **HRMS** (ESI-TOF) Calculated for $C_{12}H_{14}O_2$ ([M]+Na$^+$) = 213.0886, found 213.0881.



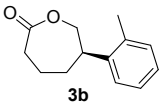
	Retention Time	Area	% Area
1	27.742	6209495	18.13
2	31.090	6235692	18.20
3	33.036	10862364	31.71
4	35.252	10950203	31.96



	Retention Time	Area	% Area
1	28.229	215105	0.69
2	30.929	13719843	43.90
3	33.585	1644575	5.26
4	35.182	15672651	50.15



2b

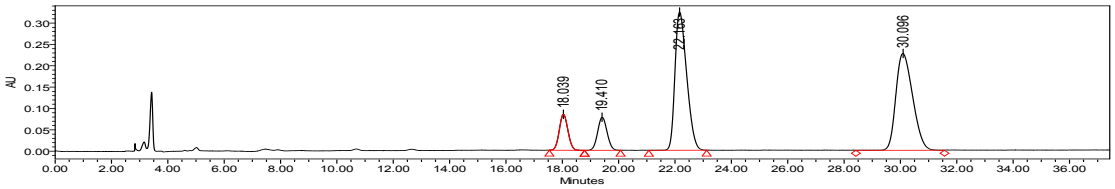


3b

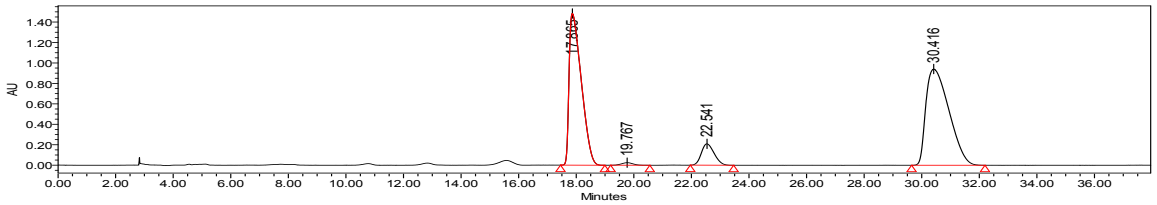
(*R*)-4-(2-methylphenyl)oxepan-2-one (**2b**);

(*R*)-6-(2-methylphenyl)oxepan-2-one (**3b**)

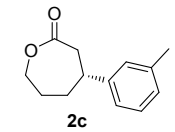
Prepared according to general procedure using (±)-**1b** (0.1 mmol, 19.0 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as colorless oil in 94% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel AYH-3, CO_2/EtOH = 95/05, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 17.9 min, t_{r2}= 19.8 min, t_{r3}= 22.5 min, t_{r4}= 30.4 min, **2b**/**3b** = 56/44, 80% ee for **2b**, 93% ee for **3b**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.24 – 7.02 (m, 8H), 4.43 – 4.28 (m, 3H), 4.24 – 4.15 (m, 1H), 3.23 – 3.10 (m, 2H), 3.07 – 2.99 (m, 1H), 2.82 – 2.68 (m, 3H), 2.40 – 2.28 (m, 6H), 2.16 – 2.03 (m, 4H), 1.99 – 1.75 (m, 4H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 175.6, 174.7, 143.6, 140.5, 135.1, 134.7, 130.9, 130.7, 126.8, 126.6, 126.4, 126.4, 125.2, 124.4, 73.1, 69.1, 41.6, 41.2, 36.6, 36.0, 35.9, 34.4, 29.2, 23.1, 19.4, 19.3. **HRMS** (ESI-TOF) Calculated for $C_{13}H_{16}O_2$ ([M]+Na$^+$) = 227.1042, found 227.1042.

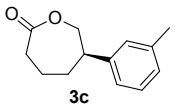


	Retention Time	Area	% Area
1	18.039	1795740	8.06
2	19.410	1795059	8.06
3	22.163	9312661	41.80
4	30.096	9377565	42.09



	Retention Time	Area	% Area
1	17.865	43452286	42.24
2	19.767	683355	0.66
3	22.541	6450179	6.27
4	30.416	52280286	50.82

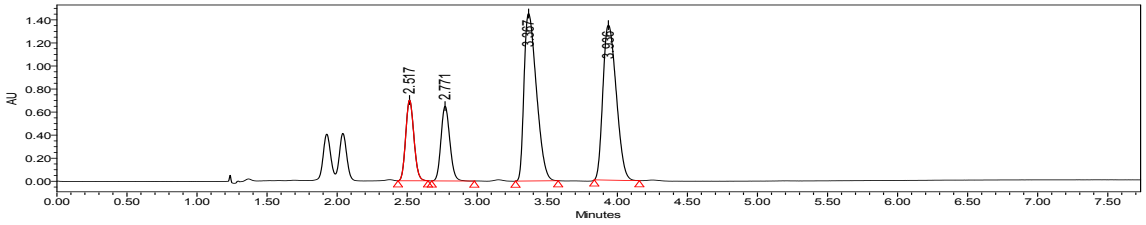

2c


3c

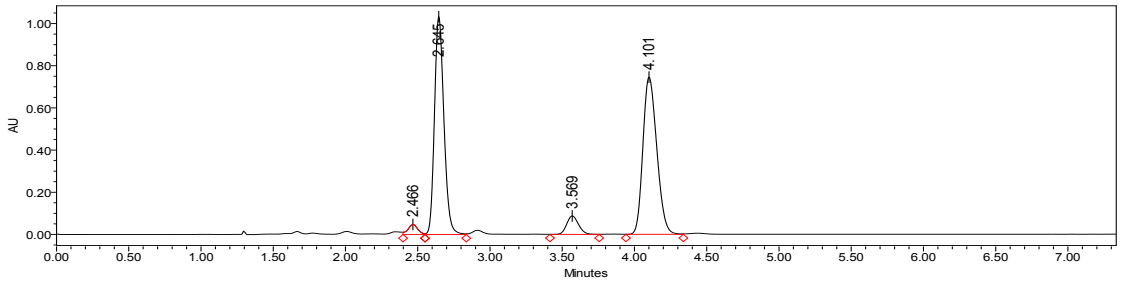
(*R*)-4-(3-methylphenyl)oxepan-2-one (**2c**);
(*R*)-6-(3-methylphenyl)oxepan-2-one (**3c**)

Prepared according to general procedure using (±)-**1c** (0.2 mmol, 38.0 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$-*t*Bu** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as colorless oil in 97% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel AS-3, CO_2/MeOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 2.5 min, t_{r2}= 2.6 min, t_{r3}= 3.6 min, t_{r4}= 4.1 min, **2b**/**3b** = 53/47, 82% ee for **2b**, 91% ee for **3b**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 2H), 7.07 – 6.80 (m, 6H), 4.41 – 4.10 (m, 4H), 3.05 – 2.64 (m, 6H), 2.27 (s, 6H), 2.13 – 1.92 (m, 4H), 1.92 – 1.60 (m, 4H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 175.5, 174.5, 145.5, 142.2, 138.6, 138.4, 128.8, 128.6, 127.8, 127.6, 127.5, 127.1, 123.8,

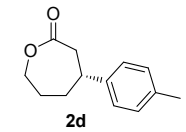
123.2, 73.4, 69.0, 46.0, 41.5, 40.6, 37.7, 36.6, 34.4, 29.0, 22.7, 21.4. **HRMS** (ESI-TOF) Calculated for $C_{13}H_{16}O_2$ ([M]+Na^+) = 227.1042, found 227.1043.

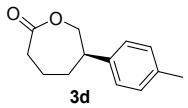


	Retention Time	Area	% Area
1	2.517	2852269	12.15
2	2.771	2842670	12.11
3	3.367	8890009	37.87
4	3.936	8889912	37.87



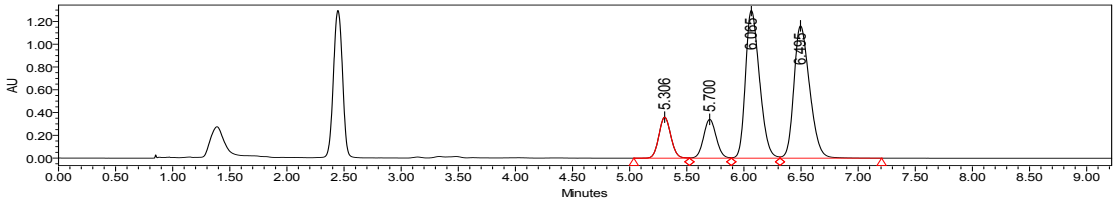
	Retention Time	Area	% Area
1	2.466	223405	2.15
2	2.645	4689092	45.11
3	3.569	501068	4.82
4	4.101	4981462	47.92


2d

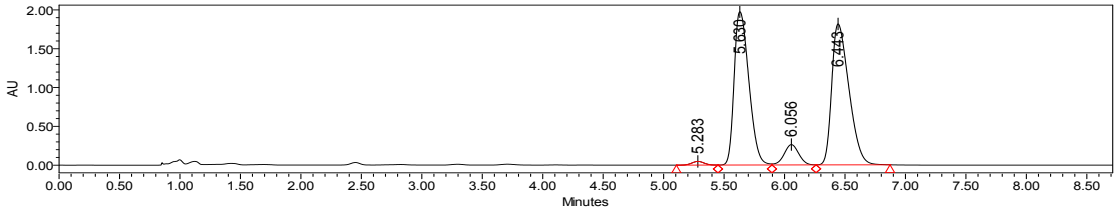

3d

(*R*)-4-(4-methylphenyl)oxepan-2-one (**2d**);
(*R*)-6-(2-methylphenyl)oxepan-2-one (**3d**)

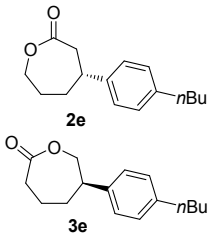
Prepared according to general procedure using (±)-**1d** (0.1 mmol, 19.0 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as colorless oil in 97% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel IC-3, CO_2/MeOH = 90/10, flow rate 1.5 mL/min, λ = 210 nm, t_{r1}= 5.3 min, t_{r2}= 5.7 min, t_{r3}= 6.0 min, t_{r4}= 6.4 min, **2b**/**3b** = 55/45, 80% ee for **2b**, 96% ee for **3b**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 4H), 7.11 – 7.02 (m, 4H), 4.43 – 4.19 (m, 4H), 3.04 – 2.87 (m, 3H), 2.84 – 2.68 (m, 3H), 2.33 (s, 6H), 2.18 – 2.02 (m, 4H), 1.98 – 1.75 (m, 4H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 175.6, 174.6, 142.5, 139.2, 136.8, 136.4, 129.5, 129.4, 126.7, 126.1, 73.5, 69.1, 45.6, 41.6, 40.2, 37.8, 36.6, 34.4, 29.0, 22.7, 21.0. **HRMS** (ESI-TOF) Calculated for $C_{13}H_{16}O_2$ ([M]+Na^+) = 227.1042, found 227.1048.



	Retention Time	Area	% Area
1	5.306	2622166	9.56
2	5.700	2622116	9.56
3	6.065	11052130	40.30
4	6.495	11129777	40.58



	Retention Time	Area	% Area
1	5.265	190822	0.95
2	5.653	2253676	11.19
3	6.039	1375702	6.83
4	6.431	16315276	81.03

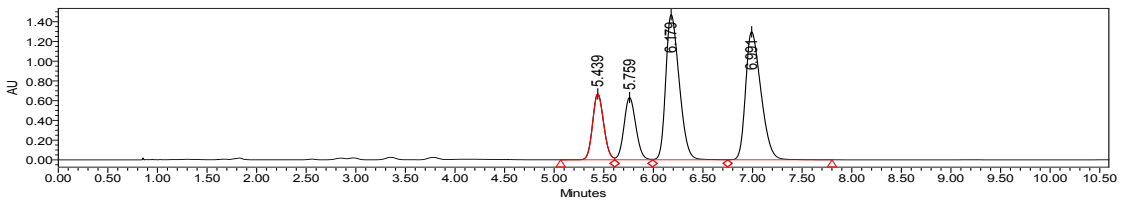


2e

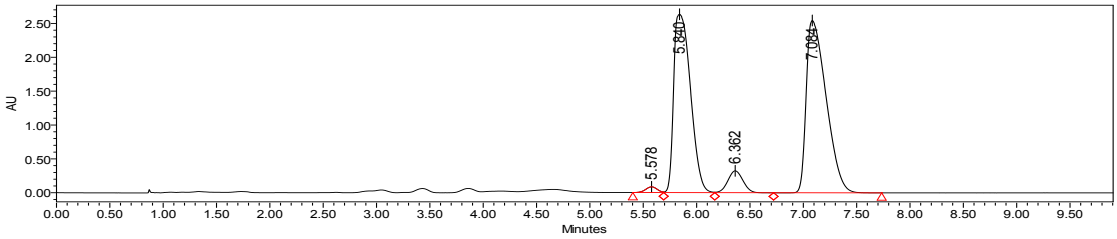
3e

(*R*)-4-(4-*n*-butylphenyl)oxepan-2-one (**2e**);
(*R*)-6-(4-*n*-butylphenyl)oxepan-2-one (**3e**)

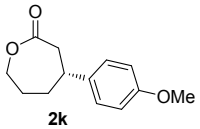
Prepared according to general procedure using (±)-**1e** (0.1 mmol, 23.1 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as colorless oil in 98% yield. **TLC**: R_f = 0.4 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel IC-3, CO_2/MeOH = 90/10, flow rate 1.5 mL/min, λ = 210 nm, t_{r1}= 5.6 min, t_{r2}= 5.9 min, t_{r3}= 6.4 min, t_{r4}= 7.0 min, **2e**/**3e** = 55/45, 83% ee for **2e**, 95% ee for **3e**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.14 – 6.91 (m, 8H), 4.37 – 4.10 (m, 4H), 2.96 – 2.79 (m, 3H), 2.76 – 2.62 (m, 3H), 2.55 – 2.46 (m, 4H), 2.12 – 1.95 (m, 4H), 1.87 – 1.67 (m, 4H), 1.55 – 1.45 (m, 4H), 1.32 – 1.23 (m, 4H), 0.89 – 0.80 (m, 6H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 175.6, 174.6, 142.7, 141.8, 141.4, 139.3, 128.8, 128.7, 126.7, 126.0, 73.5, 69.0, 45.6, 41.6, 40.2, 37.8, 36.6, 35.2, 34.4, 33.6, 29.0, 22.6, 22.3, 13.9. **HRMS** (ESI-TOF) Calculated for $C_{16}H_{22}O_2$ ([M]+Na$^+$) = 269.1512, found 269.1512.



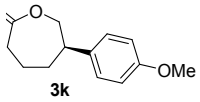
	Retention Time	Area	% Area
1	5.439	5201510	13.61
2	5.759	5235198	13.70
3	6.179	13880278	36.31
4	6.991	13907921	36.38



	Retention Time	Area	% Area
1	5.578	631225	0.96
2	5.840	28816914	43.98
3	6.362	3159909	4.82
4	7.084	32913913	50.23



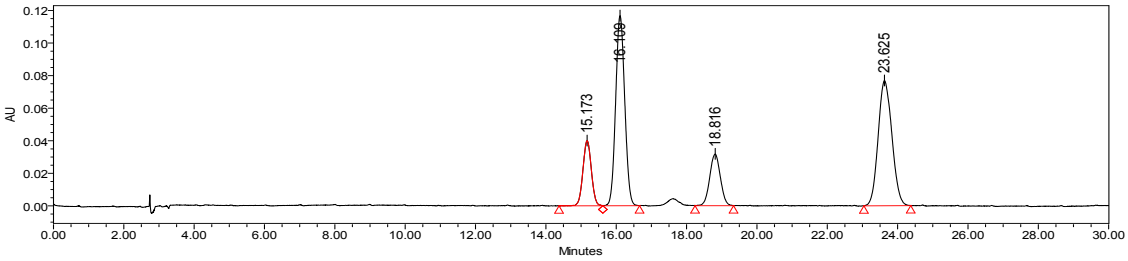
2k



3k

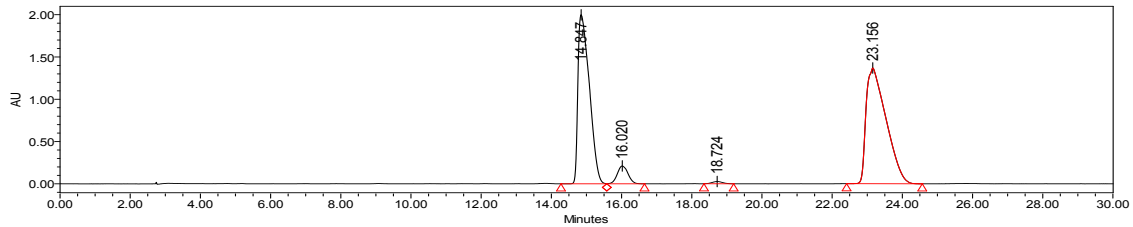
(*R*)-4-(4-methoxylphenyl)oxepan-2-one (**2k**);
(*R*)-6-(4-methoxyphenyl)oxepan-2-one (**3k**)

Prepared according to general procedure using (±)-**1k** (0.1 mmol, 20.4 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as colorless oil in 92% yield. **TLC**: R_f = 0.25 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel AYH-3, CO_2/MeOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 14.8 min, t_{r2}= 16.0 min, t_{r3}= 18.7 min, t_{r4}= 23.1 min, **2k**/**3k** = 52/48, 83% ee for **2k**, 97% ee for **3k**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.18 – 7.01 (m, 8H), 6.95 – 6.76 (m, 8H), 4.44 – 4.17 (m, 8H), 3.80 (s, 12H), 3.03 – 2.86 (m, 6H), 2.84 – 2.65 (m, 6H), 2.18 – 2.02 (m, 6H), 1.98 – 1.74 (m, 6H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 175.6, 174.6, 158.5, 158.3, 137.7, 134.2, 127.8, 127.2, 114.2, 114.0, 73.6, 69.1, 55.2, 45.2, 41.8, 39.8, 37.9, 36.6, 34.4, 29.0, 22.6. **HRMS** (ESI-TOF) Calculated for $C_{13}H_{16}O_3$ ([M]+Na$^+$) = 243.0991, found 243.0990.

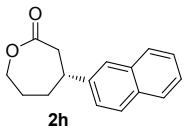


	Retention Time	Area	% Area
1	15.173	666415	12.07
2	16.109	2096022	37.97

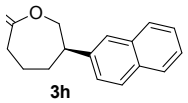
3	18.816	667690	12.10
4	23.625	2089398	37.85



	Retention Time	Area	% Area
1	14.847	45223599	43.36
2	16.020	4485203	4.30
3	18.724	555606	0.53
4	23.156	54031675	51.81



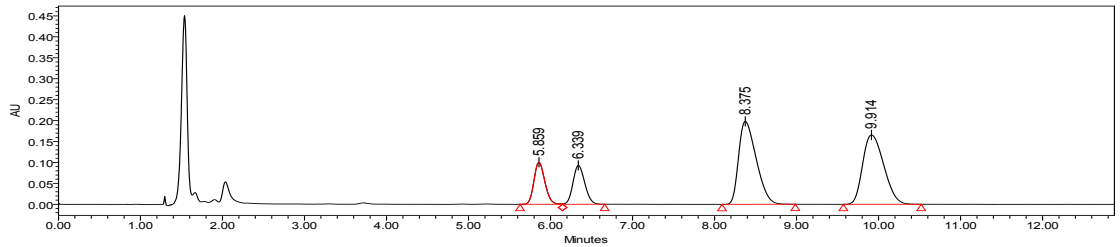
2h



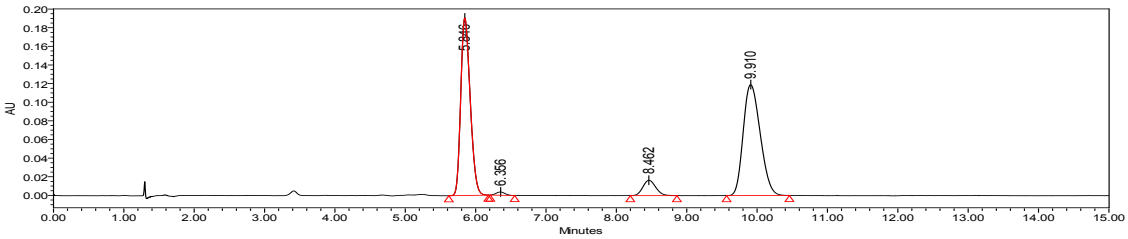
3h

(*R*)-4-(naphthalen-2-yl)oxepan-2-one (**2h**);
(*R*)-6-(naphthalen-2-yl)oxepan-2-one (**3h**)

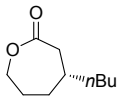
Prepared according to general procedure using (±)-**1h** (0.2 mmol, 44.9 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc:DCM = 7:1:1) to give the title compound as colorless oil in 94% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel AS-3, CO_2/MeOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 5.8 min, t_{r2}= 6.4 min, t_{r3}= 8.5 min, t_{r4}= 9.9 min, **2b**/**3b** = 55/45, 81% ee for **2b**, 96% ee for **3b**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 6H), 7.54 (s, 2H), 7.46 – 7.32 (m, 4H), 7.31 – 7.18 (m, 2H), 4.43 – 4.20 (m, 4H), 3.11 – 2.98 (m, 3H), 2.85 – 2.67 (m, 3H), 2.21 – 2.07 (m, 2H), 2.06 – 1.98 (m, 2H), 1.92 – 1.84 (m, 2H), 1.82 – 1.68 (m, 2H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 175.5, 174.5, 142.8, 139.5, 133.4, 132.4, 132.3, 128.6, 128.5, 127.6, 127.6, 126.3, 126.3, 125.8, 125.7, 125.4, 125.2, 124.9, 124.4, 73.3, 69.1, 46.1, 41.5, 40.7, 37.6, 36.4, 34.3, 29.0, 22.6. **HRMS** (ESI-TOF) Calculated for $C_{16}H_{16}O_2$ ([M]+Na$^+$) = 263.1042, found 263.1041.



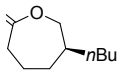
	Retention Time	Area	% Area
1	5.859	928589	11.95
2	6.339	924942	11.90
3	8.375	2956397	38.04
4	9.914	2962085	38.11



	Retention Time	Area	% Area
1	5.846	1777925	44.17
2	6.356	30709	0.76
3	8.462	210789	5.24
4	9.910	2006095	49.83



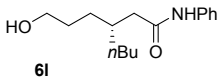
2l



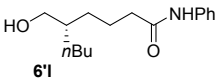
3l

(*R*)-4-butyloxepan-2-one (**2l**);
(*S*)-6-butyloxepan-2-one (**3l**)

Prepared according to general procedure using (±)-**1l** (0.1 mmol, 15.4 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as colorless oil in 84% yield. **TLC**: R_f = 0.4 (petroleum ether:EtOAc = 4:1) [UV]. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 4.28 – 4.10 (m, 3H), 4.08 – 3.94 (m, 1H), 2.70 – 2.45 (m, 4H), 1.99 – 1.83 (m, 4H), 1.82 – 1.59 (m, 5H), 1.48 – 1.39 (m, 2H), 1.37 – 1.20 (m, 13H), 0.93 – 0.83 (m, 6H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 176.0, 175.2, 72.8, 69.2, 40.1, 38.5, 35.6, 34.9, 34.8, 34.3, 33.9, 31.2, 29.0, 29.0, 27.7, 22.7, 22.6, 21.3, 14.0, 13.9. **HRMS** (ESI-TOF) Calculated for $C_{10}H_{18}O_2$ ([M]+Na$^+$) = 193.1204, found 193.1200.



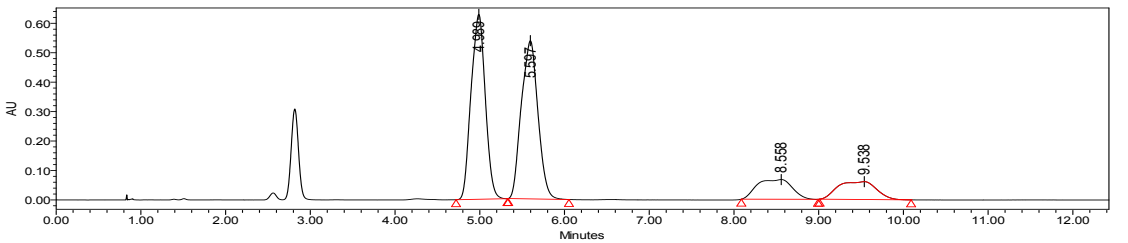
6l



6'l

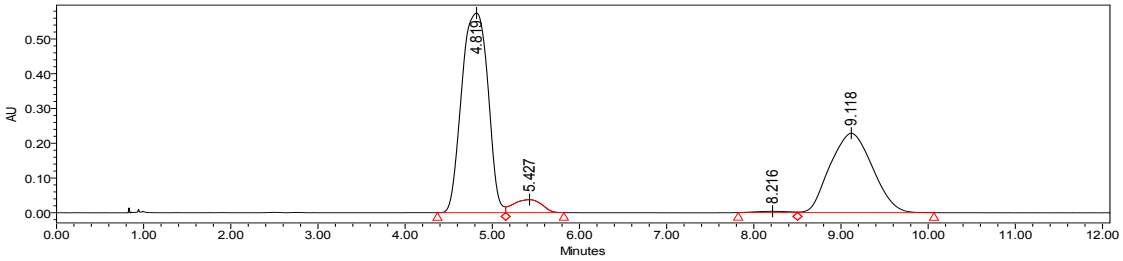
(*R*)-3-(3-hydroxypropyl)-*N*-phenylheptanamide (**6l**);
(*S*)-5-(hydroxymethyl)-*N*-phenylnonanamide (**6'l**)

Prepared according to general procedure using **2j** (0.1 mmol), anniline (0.2 mmol), $AlMe_3$ (0.2 mmol). **SFC**: Chiralcel AD-3, CO_2/MeOH = 90/10, flow rate 1.0 mL/min, λ = 240 nm, t_{r1}= 11.1 min, t_{r2}= 13.2 min, t_{r3}= 21.4 min, t_{r4}= 23.2 min, **7l**/**7'l** = 62/38, 87% ee for **7l**, 97% ee for **7'l**. $[\alpha]_D^{20}$ = −43.1 (*c* = 0.378, in CH_2Cl_2).



	Retention Time	Area	% Area

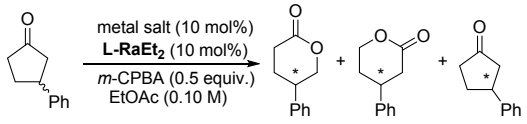
1	4.989	7315409	39.60
2	5.597	7311391	39.58
3	8.558	1929737	10.45
4	9.538	1915324	10.37



	Retention Time	Area	% Area
1	4.819	12053626	58.23
2	5.427	844223	4.08
3	8.216	96778	0.47
4	9.118	7706968	37.23

7 Optimization of conditions for Baeyer-Villiger oxidation of other ketones.

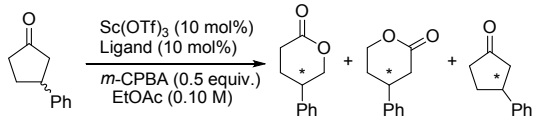
Table S2. Screening of metal salts for BV oxidation of 3-phenyl cyclopentanone.



entry[a]	metal salt	yield (%)[b]			ee (%)[c]		
		12	**13** + **14**	**13**:**14**[c]	**12**	**13**	**14**
1	$Sc(OTf)_3$	52	33	62:38	92	19	30
2	$Y(OTf)_3$	n.d.	n.r.	–	–	–	–
3	$La(OTf)_3$	n.d.	n.r.	–	–	–	–
4	$Yb(OTf)_3$	n.d.	n.r.	–	–	–	–
5	$Mg(OTf)_2$	n.d.	n.r.	–	–	–	–
6	$Fe(OTf)_3$	n.d.	n.r.	–	–	–	–
7	$Fe(OTf)_3$	n.d.	n.r.	–	–	–	–
8	$Al(OTf)_3$	n.d.	n.r.	–	–	–	–
9	$Ga(OTf)_3$	n.d.	n.r.	–	–	–	–
10	$In(OTf)_3$	n.d.	n.r.	–	–	–	–

[a]Unless otherwise noticed, the reactions were performed with metal salt (10 mol%), **L-RaEt$_2$** (10 mol%), (±)-**12** (0.10 mmol), *m*-CPBA (0.5 equiv.), in solvent (0.10 M) in air at 30 °C. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase.

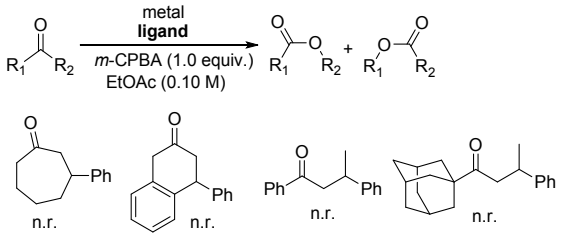
Table S3. Screening of ligands for BV oxidation of 3-phenyl cyclopentanone.



entry[a]	T (°C)	ligand	yield (%)[b]			ee (%)[c]		
			12	**13** + **14**	**13**:**14**[c]	**12**	**13**	**14**
1	30	**L-PrPr$_2$**	56	34	59:41	13	25	29
2	30	**L-PiPr$_2$**	48	48	62:38	19	19	29
3	30	**L-RaPr$_2$**	44	44	62:38	16	14	30
4	30	**L-PiEt$_2$**	70	27	62:38	9	23	28
5	30	**L-PiEt$_3$**	60	37	62:38	10	17	33
6	30	**L-RaPr$_2$-*t*Bu**	35	37	28:72	5	−16	33
7	0	**L-RaPr$_2$-Ad**	55	40	25:75	5	33	39
8	30	**L-RaEt$_2$**	52	33	62:38	92	19	30

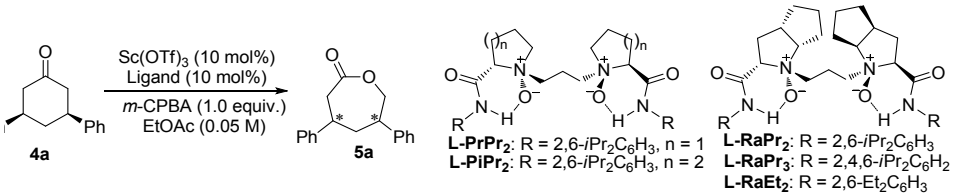
[a]Unless otherwise noticed, the reactions were performed with Sc(OTf)$_3$ (10 mol%), ligand (10 mol%), (±)-**12** (0.10 mmol), *m*-CPBA (1.0 equiv.), in solvent (0.10 M) in air. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase.

Scheme S1. Unsuccessful attempts for BV oxidation.



8 Condition optimization of desymmetrization Baeyer-Villiger oxidation.

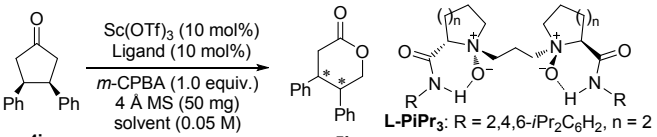
Table S4. Optimization of conditions for desymmetrization BV oxidation of *cis*-3,5-diphenyl cyclohexanone (**4a**).



entry[a]	T (°C)	ligand	additive	yield (%)[b]	ee (%)[c]
1	0	**L-PrPr$_2$**	–	53	44
2	0	**L-PiPr$_2$**	–	93	73
3	0	**L-RaPr$_2$**	–	84	92
4	0	**L-RaEt$_2$**	–	63	92
5	0	**L-RaPr$_3$**	–	47	92
6	0	**L-RaPr$_2$**	3 Å MS (50 mg)	92	92
7	0	**L-RaPr$_2$**	4 Å MS (50 mg)	99	92
8	0	**L-RaPr$_2$**	5 Å MS (50 mg)	98	92
9	0	**L-RaPr$_2$**	Al(O*i*Pr$_3$) (0.5 equiv.)	87	91
10	−20	**L-RaPr$_2$**	4 Å MS (50 mg)	99	96

aUnless otherwise noticed, the reactions were performed with $Sc(OTf)_3$ (10 mol%), ligand (10 mol%), **4a** (0.10 mmol), *m*-CPBA (1.0 equiv.), in EtOAc (0.05 M) in air. bYields of the isolated products. cDetermined by HPLC analysis using a chiral stationary phase.

Table S5. Optimization of conditions for desymmetrization BV oxidation of cis-3,4-diphenyl cyclopentanone (**4i**)**.**

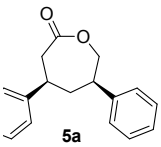


L-PiPr$_3$: R = 2,4,6-*i*Pr$_2$C$_6$H$_2$, n = 2
L-PiEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 2
L-PiEt$_3$: R = 2,4,6-Et$_3$C$_6$H$_2$, n = 2

entry[a]	T (°C)	solvent	ligand	yield (%)[b]	ee (%)[c]
1	35	EtOAc	**L-PrPr$_2$**	85	85
2	35	EtOAc	**L-PiPr$_2$**	96	88
3	35	EtOAc	**L-RaPr$_2$**	97	87
4	35	EtOAc	**L-RaEt$_2$**	80	86
5	35	EtOAc	**L-RaPr$_3$**	87	88
6	35	EtOAc	**L-PiEt$_2$**	44	87
7	35	EtOAc	**L-PiEt$_3$**	98	91
8	35	EtOAc	**L-PiPr$_3$**	80	90
9	0	EtOAc	**L-PiEt$_2$**	99	95
10	0	DCM	**L-PiPr$_2$**	62	70
11	0	THF	**L-PiPr$_2$**	99	92
12	0	Et_2O	**L-PiPr$_2$**	93	93

[a]Unless otherwise noticed, the reactions were performed with $Sc(OTf)_3$ (10 mol%), ligand (10 mol%), **4i** (0.10 mmol), *m*-CPBA (1.0 equiv.), in solvent (0.05 M) in air. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase.

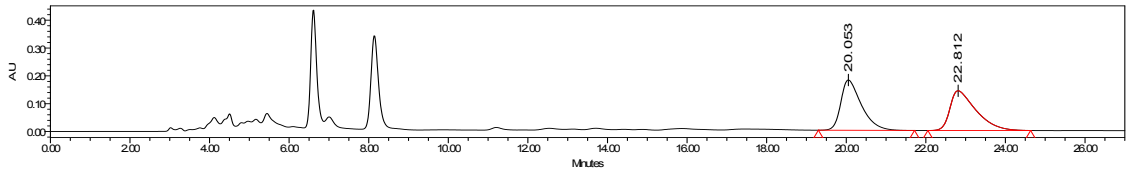
9 Characterization of the products in desymmetrization.



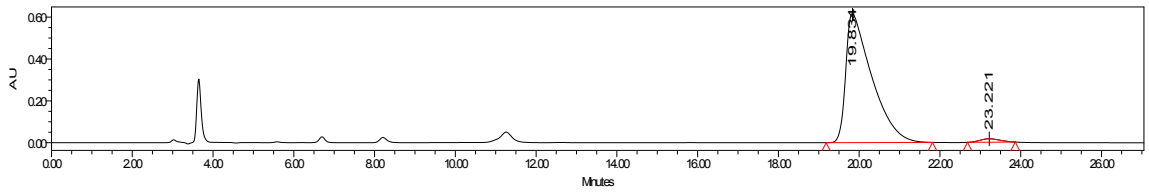
5a

(4*R*,6*R*)-4,6-diphenyloxepan-2-one **(5a)**

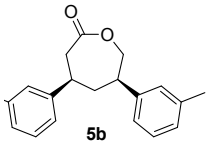
Prepared according to general procedure using **4a** (0.1 mmol, 25.0 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$** (0.010 mmol) and $Sc(OTf)_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 97% yield. **TLC**: R_f = 0.3 (petroleum ether:EtOAc = 4:1) [UV]. **HPLC**: Chiralcel AD-H, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 19.8 min, t_{r2}= 23.2 min, 96% ee. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.27 – 7.15 (m, 6H), 4.53 (dd, *J* = 12.6, 9.5 Hz, 1H), 4.35 (dt, *J* = 12.6, 1.9 Hz, 1H), 3.27 – 3.08 (m, 3H), 2.93 (dd, *J* = 12.6, 1.7 Hz, 1H), 2.35 – 2.22 (m, 1H), 2.08 (dt, *J* = 13.9, 11.9 Hz, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 173.9, 145.2, 141.8, 128.9, 128.8, 127.2, 126.9, 126.8, 126.2, 73.2, 46.0, 45.8, 41.2, 40.6. **HRMS** (ESI-TOF) Calculated for $C_{18}H_{18}O_2$ ([M]+Na$^+$) = 289.1199, found 289.1199. $[\alpha]_D^{27}$ = −49.5 (*c* = 0.444, in CH_2Cl_2).



	Retention Time	Area	% Area
1	20.053	6490261	50.04
2	22.812	6479048	49.96



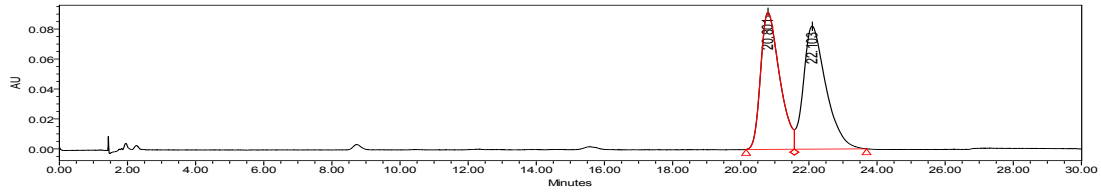
	Retention Time	Area	% Area
1	19.834	27520163	97.98
2	23.221	568353	2.02



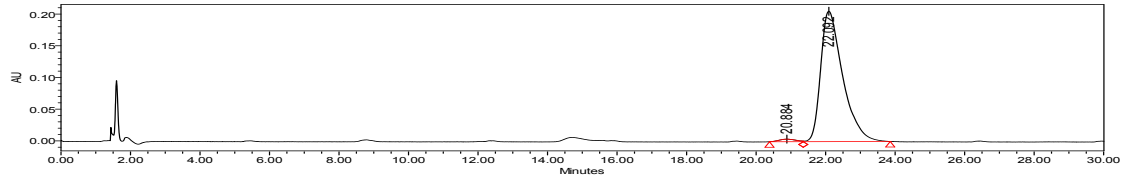
5b

(4*R*,6*R*)-4,6-di(3-methylphenyl)oxepan-2-one (**5b**)

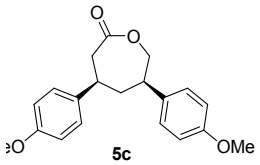
Prepared according to general procedure using **4b** (0.1 mmol, 27.8 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 98% yield. **TLC**: R_f = 0.35 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel OX-3, CO_2/MeOH = 98/02, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 20.9 min, t_{r2}= 22.1 min, 97% ee. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.20 – 7.06 (m, 4H), 6.95– 6.74 (m, 4H), 4.46 (dd, *J* = 12.6, 9.6 Hz, 1H), 4.30 (dt, *J* = 12.6, 1.9 Hz, 1H), 3.78 (d, *J* = 1.7 Hz, 6H), 3.20 – 3.02 (m, 3H), 2.88 (dd, *J* = 12.5, 1.8 Hz, 1H), 2.29 – 2.19 (m, 1H), 2.06 – 1.94 (m, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 174.1, 158.6, 158.4, 137.5, 134.0, 127.8, 127.2, 114.3, 114.2, 73.5, 55.3, 46.1, 45.1, 41.6, 39.8. **HRMS** (ESI-TOF) Calculated for $C_{20}H_{22}O_2$ ([M]+Na$^+$) = 317.1512, found 317.1508. $[\alpha]_D^{27}$ = −43.0 (*c* = 0.460, in CH_2Cl_2).



	Retention Time	Area	% Area
1	20.801	3534188	48.42
2	22.103	3764766	51.58



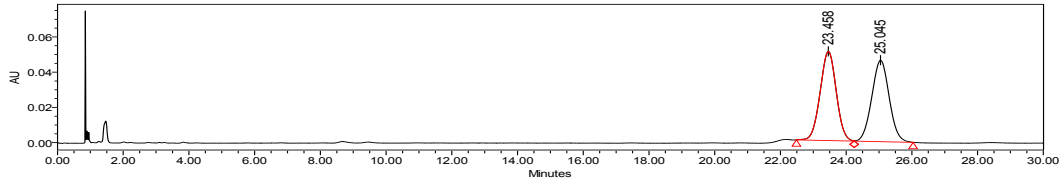
	Retention Time	Area	% Area
1	20.884	136949	1.49
2	22.092	9042443	98.51



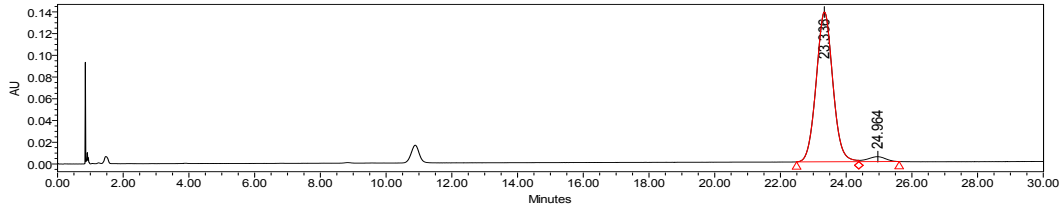
5c

(4*R*,6*R*)-4,6-di(4-methoxyphenyl)oxepan-2-one (**5c**)

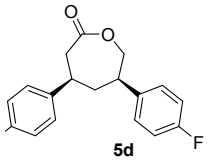
Prepared according to general procedure using **4c** (0.1 mmol, 31.0 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 96% yield. **TLC**: R_f = 0.3 (petroleum ether:EtOAc = 2:1) [UV]. **SFC**: Chiralcel OX-3, CO_2/MeOH = 90/10, flow rate 1.5 mL/min, λ = 220 nm, t_{r1}= 23.3 min, t_{r2}= 25.0 min, 93% ee. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ7.18 – 7.01 (m, 4H), 6.95 – 6.76 (m, 4H), 4.44 – 4.17 (m, 4H), 3.80 (s, 6H), 3.03 – 2.86 (m, 3H), 2.84 – 2.65 (m, 3H), 2.18 – 2.02 (m, 4H), 1.98 – 1.74 (m, 4H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 175.6, 174.6, 158.5, 158.3, 137.7, 134.2, 127.8, 127.2, 114.2, 114.0, 73.6, 69.1, 55.2, 45.2, 41.8, 39.8, 37.9, 36.6, 34.36, 29.0, 22.6. **HRMS** (ESI-TOF) Calculated for $C_{20}H_{22}O_4$ ([M]+Na$^+$) = 349.1410, found 349.1418. $[\alpha]_D^{27}$ = −66.2 (*c* = 0.336, in CH_2Cl_2).



	Retention Time	Area	% Area
1	23.458	1718817	50.26
2	25.045	1700783	49.74



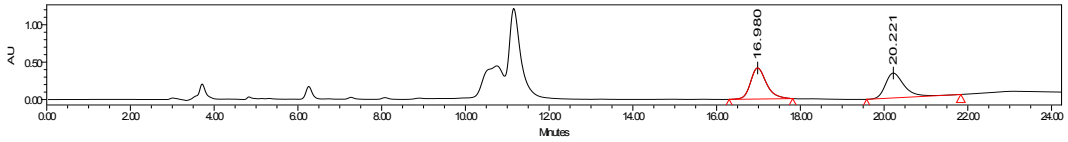
	Retention Time	Area	% Area
1	23.336	4837491	96.56
2	24.964	172091	3.44



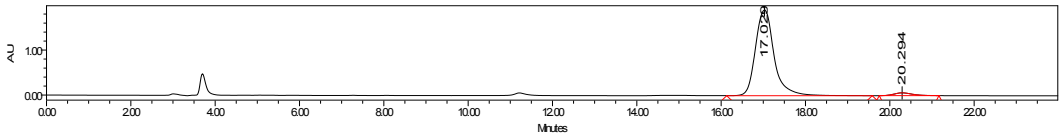
5d

(4*R*,6*R*)-4,6-di(4-fluorophenyl)oxepan-2-one (**5d**)

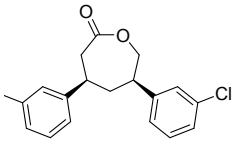
Prepared according to general procedure using **4d** (0.1 mmol, 28.6 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 98% yield. **TLC**: R_f = 0.25 (petroleum ether:EtOAc = 4:1) [UV]. **HPLC**: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 17.0 min, t_{r2}= 20.3 min, 94% ee. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 4H), 7.06 – 6.92 (m, 4H), 4.49 (dd, *J* = 12.6, 9.5 Hz, 1H), 4.37 – 4.23 (m, 1H), 3.22 – 3.06 (m, 3H), 2.89 (d, *J* = 12.4 Hz, 1H), 2.28 – 2.19 (m, 1H), 2.01 (q, *J* = 12.1 Hz, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 173.6, 163.0 (d, J_{CF} = 19.7 Hz), 160.5 (d, J_{CF} = 19.1 Hz), 140.9 (d, J_{CF} = 3.3 Hz), 137.5 (d, J_{CF} = 3.3 Hz), 128.3 (d, J_{CF} = 8.0 Hz), 127.7 (d, J_{CF} = 8.0 Hz), 115.9 (d, J_{CF} = 16.7 Hz), 115.7 (d, J_{CF} = 16.7 Hz), 77.4, 77.1, 76.7, 73.1, 46.0, 45.2, 41.3, 39.8. **^{19}F NMR**: (376 MHz, $CDCl_3$) δ −114.9, −115.5. **HRMS** (ESI-TOF) Calculated for $C_{18}H_{16}F_2O_2$ ([M]+Na$^+$) = 325.1010, Found 325.1009. $[\alpha]_D^{27}$ = −9.8 (*c* = 0.446, in CH_2Cl_2).



	Retention Time	Area	% Area
1	16.980	10974867	51.69
2	20.221	10257606	48.31



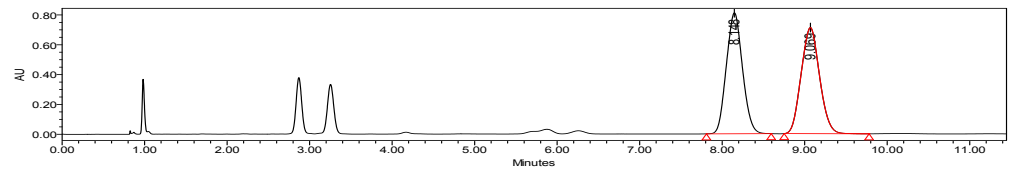
	Retention Time	Area	% Area
1	17.029	58558542	96.87
2	20.294	1892766	3.13



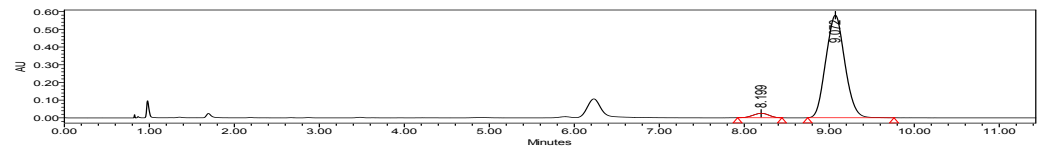
5e

(4*R*,6*R*)-4,6-di(3-chlorophenyl)oxepan-2-one (**5e**)

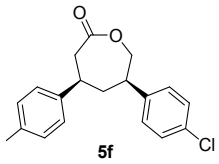
Prepared according to general procedure using **4e** (0.1 mmol, 31.9 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 98% yield. **TLC**: R_f = 0.25 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel OJ-3, CO_2/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 8.2 min, t_{r2}= 9.1 min, 93% ee. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.23 – 7.09 (m, 6H), 7.05 – 6.97 (m, 2H), 4.51 – 4.38 (m, 1H), 4.31 – 4.20 (m, 1H), 3.19 – 2.97 (m, 3H), 2.88 – 2.78 (m, 1H), 2.24 – 2.13 (m, 1H), 2.02 – 1.88 (m, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 173.2, 146.8, 143.4, 134.8, 134.6, 130.3, 130.2, 127.6, 127.3, 126.9, 126.4, 125.1, 124.5, 72.6, 45.6, 45.3, 40.8, 40.1. **HRMS** (ESI-TOF) Calculated for $C_{18}H_{16}{}^{34.9689}Cl_2O_2$ ([M+Na$^+$) = 357.0419, Found 357.0415. Calculated for $C_{18}H_{16}{}^{36.9659}Cl^{34.9689}ClO_2$ ([M+Na$^+$) = 359.0390, Found 359.0381. $[\alpha]_D^{27}$ = −30.3 (*c* = 0.524, in CH_2Cl_2).



	Retention Time	Area	% Area
1	8.148	10990617	50.01
2	9.069	10986934	49.99



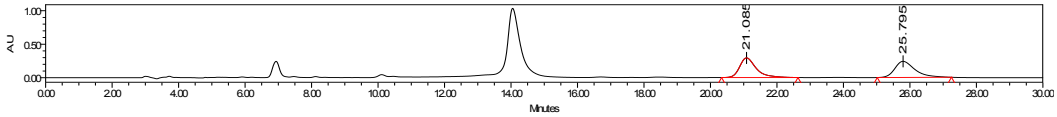
	Retention Time	Area	% Area
1	8.199	327058	3.52
2	9.072	8969564	96.48



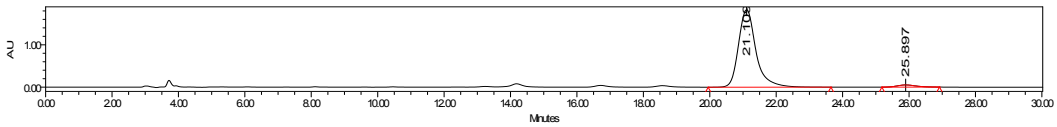
5f

(4*R*,6*R*)-4,6-di(4-chlorophenyl)oxepan-2-one (**5f**)

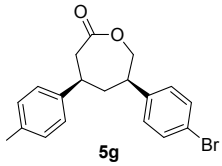
Prepared according to general procedure using **4f** (0.1 mmol, 31.9 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 98% yield. **TLC**: R_f = 0.25 (petroleum ether:EtOAc = 4:1) [UV]. **HPLC**: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 21.1 min, t_{r2}= 25.9 min, 94% ee. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ7.31 – 7.25 (m, 4H), 7.18 – 7.07 (m, 4H), 4.49 (dd, *J* = 12.7, 9.5 Hz, 1H), 4.35 – 4.23 (m, 1H), 3.23 – 3.06 (m, 3H), 2.93 – 2.83 (m, 1H), 2.27 – 2.17 (m, 1H), 2.01 (dt, *J* = 13.4, 11.9 Hz, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 173.4, 143.4, 140.0, 133.1, 132.8, 129.2, 129.0, 128.2, 127.6, 72.8, 45.5, 45.3, 41.0, 39.9. **HRMS** (ESI-TOF) Calculated for $C_{18}H_{16}^{34.9689}Cl_2O_2$ ([M]+Na$^+$) = 357.0419, Found 357.0409. Calculated for $C_{18}H_{16}{}^{36.9659}Cl^{34.9689}ClO_2$ ([M]+Na$^+$) = 359.0390, Found 325.0384. $[\alpha]_D^{27}$ = −12.8 (*c* = 0.454, in CH_2Cl_2).



	Retention Time	Area	% Area
1	21.085	10198497	50.02
2	25.795	10191053	49.98



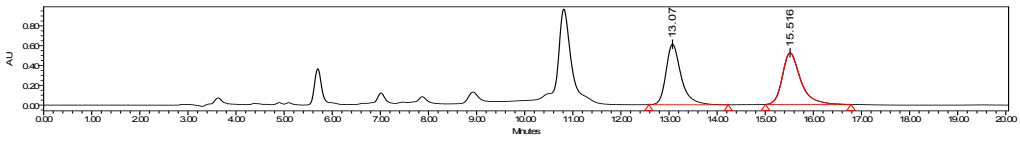
	Retention Time	Area	% Area
1	21.109	66626686	97.05
2	25.897	2027957	2.95



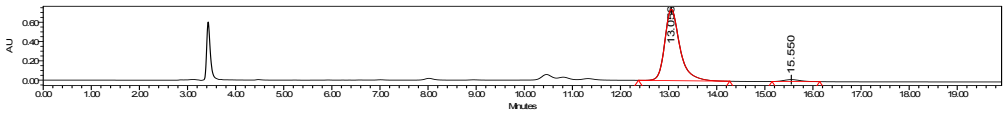
5g

(4*R*,6*R*)-4,6-di(4-bromophenyl)oxepan-2-one (**5g**)

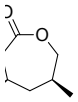
Prepared according to general procedure using **4g** (0.1 mmol, 40.8 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 99% yield. **TLC**: R_f = 0.25 (petroleum ether:EtOAc = 4:1) [UV]. **HPLC**: Chiralcel IA, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 13.1 min, t_{r2}= 15.6 min, 94% ee. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.52 – 7.35 (m, 4H), 7.14 – 6.97 (m, 4H), 4.48 (dd, *J* = 12.7, 9.5 Hz, 1H), 4.34 – 4.21 (m, 1H), 3.20 – 3.04 (m, 3H), 2.87 (dd, *J* = 12.7, 1.7 Hz, 1H), 2.26 – 2.16 (m, 1H), 2.05 – 1.94 (m, 1H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ173.4, 144.0, 140.5, 132.1, 132.0, 128.5, 128.0, 121.2, 120.8, 72.7, 45.4, 45.3, 41.0, 39.9. **HRMS** (ESI-TOF) Calculated for $C_{18}H_{16}^{78.9183}Br_2O_2$ ([M]+Na$^+$) = 446.9389, Found 446.9391. Calculated for $C_{18}H_{16}{}^{80.9163}Br^{78.9183}BrO_2$ ([M]+Na$^+$) = 444.9409, found 444.9412. $[\alpha]_D^{27}$ = −11.1 (*c* = 0.552, in CH_2Cl_2).



	Retention Time	Area	% Area
1	13.073	13294093	49.13
2	15.516	13763949	50.87



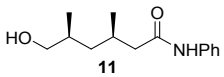
	Retention Time	Area	% Area
1	13.056	16131320	97.11
2	15.550	480318	2.89



5h

(4*R*,6*S*)-4,6-dimethyloxepan-2-one **(5h)**

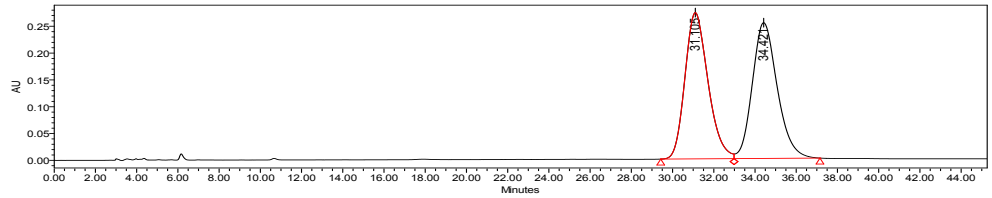
Prepared according to general procedure using **4h** (0.1 mmol, 12.6 mg), *m*-CPBA (0.10 mmol), **L-RaPr$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 99% yield. **TLC**: R_f = 0.6 (petroleum ether:EtOAc = 4:1) [UV]. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 4.06 – 3.90 (m, 2H), 2.58 – 2.44 (m, 2H), 2.00 – 1.83 (m, 3H), 1.25 (s, 1H), 1.04 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 6.9 Hz, 3H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 174.9, 74.3, 46.9, 42.2, 34.0, 29.8, 24.2, 18.9. **HRMS** (ESI-TOF) Calculated for $C_8H_{14}O_2$ ([M]+Na$^+$) = 165.0891, found 165.0890. $[\alpha]_D^{27}$ = −16.3 (*c* = 0.286, in CH_2Cl_2). {Lit.[6] $[\alpha]_D^{2}$ = −12.69 (*c* = 2.45, in $CHCl_3$), conf. (4*R*,6*S*)}.



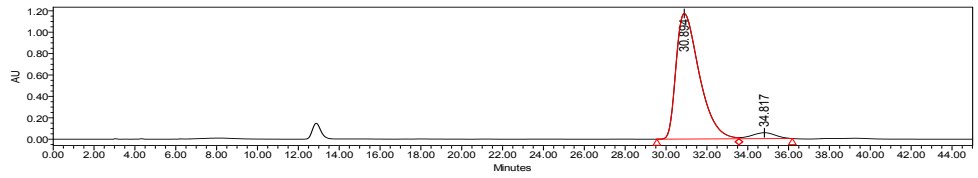
11

(3*R*,5*S*)-6-hydroxy-3,5-dimethyl-*N*-phenylhexanamide (**11**)

Prepared according to general procedure using **5h** (0.1 mmol), anniline (0.2 mmol), $AlMe_3$ (0.2 mmol). **HPLC**: Chiralcel IA, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 240 nm, t_{r1}= 30.9 min, t_{r2}= 34.8 min, 91% ee. Calculated for $C_{14}H_{21}NO_2$ ([M]+Na$^+$) = 258.1464, found 258.1462. $[\alpha]_D^{27}$ = −20.0 (*c* = 0.400, in CH_2Cl_2).

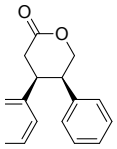


	Retention Time	Area	% Area
1	31.105	21155797	49.88
2	34.421	21259790	50.12



	Retention Time	Area	% Area

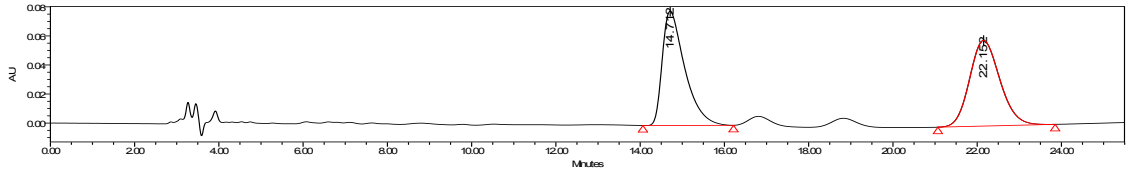
1	30.894	92570629	95.34
2	34.817	4520078	4.66



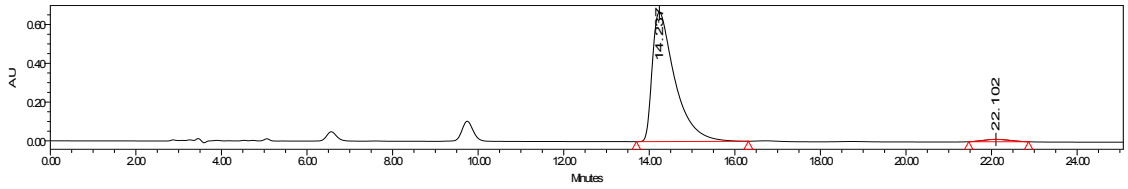
5i

(4*S*,5*R*)-4,5-diphenyltetrahydro-2H-pyran-2-one (**5i**)

Prepared according to general procedure using **4i** (0.1 mmol, 23.6 mg), *m*-CPBA (0.10 mmol), **L-PiEt$_3$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol).The crude mixture was purified by column chromatography on silica gel (petroleum ether:EtOAc = 6:1) to give the title compound as white solid in 99% yield. **TLC**: R_f = 0.3 (petroleum ether:EtOAc = 4:1) [UV]. **HPLC**: Chiralcel OD-H, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 14.2 min, t_{r2}= 22.1 min, 96% ee. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 6H), 6.82 – 6.75 (m, 2H), 6.75 – 6.69 (m, 2H), 4.77 – 4.64 (m, 2H), 3.68 – 3.60 (m, 1H), 3.51 (dt, *J* = 7.0, 4.4 Hz, 1H), 3.01 – 2.85 (m, 2H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 170.4, 138.6, 137.0, 128.4, 128.2, 128.2, 128.2, 127.4, 127.3, 71.3, 43.6, 42.3, 33.8. **HRMS** (ESI-TOF) Calculated for $C_{17}H_{16}O_2$ ([M]+Na^+) = 275.1042, Found 275.1034. $[\alpha]_D^{27}$ = −32.6 (*c* = 0.432, in CH_2Cl_2).



	Retention Time	Area	% Area
1	14.712	2909456	49.79
2	22.152	2934271	50.21



	Retention Time	Area	% Area
1	14.237	24484710	97.89
2	22.102	527251	2.11

10 Determination of the absolute configuration of the products.

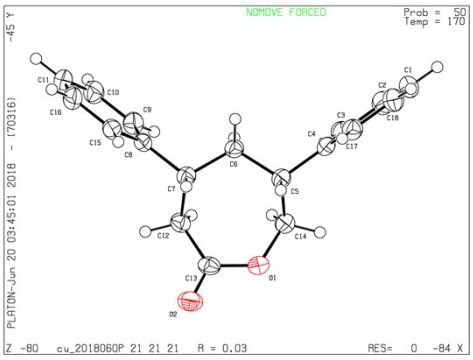
(a) Classical kinetic resolution. Absolute configuration of recovered **1** was determined by comparison of literature. Absolute configuration of product **2** was determined by recovered **1**. Owing to a high ratio of **2**/**3**, product **2** can be considered as the sole product from the kinetic resolution of **1**

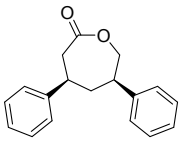
Additionally, absolute configuration of **2a** and **3a** can also be determined by comparison of HPLC analysis of products obtained from BV oxidation of (*S*)-**1a** with **L-RaPr$_2$-*t*Bu** as catalyst. (See section **14** in this SI for more details)

(b) Parallel kinetic resolution. Absolute configuration of product **2** was determined by comparison with chiral HPLC in the classical kinetic resolution. Absolute configuration of product **3** was determined by product **2** due to a high conversion of **1** and good to excellent ee value of product **2** and **3**.

(c) Desymmetrization. Absolute configuration of product **5a** was determined by X-ray crystallography.

Figure S1. Absolute configuration of product of **5a**.

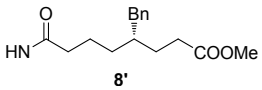




(4*R*,6*R*)-**5a**

Single crystal of $C_{18}H_{22}O_2$ **5a** was recrystallized from mixed solvents of *i*PrOH and *n*-hexane. Both the absolute configuration of C5 and C7 are *R*. CCDC 1848335 contains the supplementary crystallographic data which can be obtained Free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
The absolute configuration of **5h** can be determined in comparison with literature.
The absolute configuration of **5b**-**5i** can be determined by specific rotation in comparision with **5a** and **5h**.

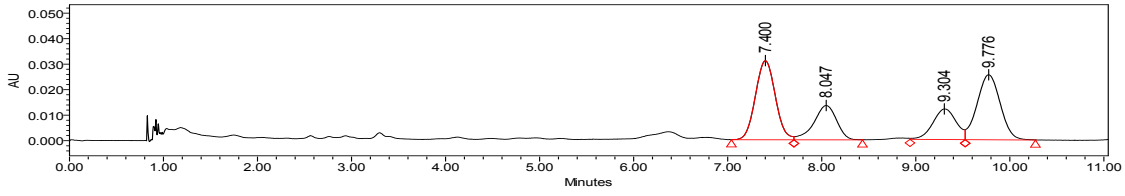
11 The derivation of the BV oxidation products



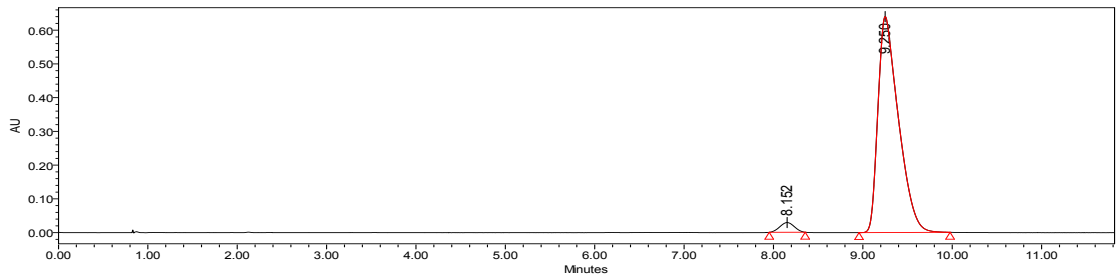
8'

(*S*)-methyl 4-benzyl-8-oxo-8-(phenylamino)octanoate (**8'**)

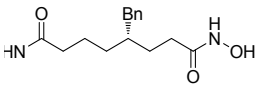
Synthesis of (*S*)-methyl 4-benzyl-8-oxo-8-(phenylamino)octanoate (**8'**). To a dry flask was added a mixture of **7**, **7'** (0.43 mmol) and 10% Pd/C (20% *w*/*w*), and the flask was evacuated and flushed with hydrogen gas for three times. Methanol (15 mL) was added, then the mixture was stirred at room temperature and monitored by TLC. After the complete consumption of **7** and **7'**, the reaction mixture was filtered and the filtrate was concentrated. The reaction mixture was filtered and the filtrate was concentrated. The residue was purified by flash column chromatography. **8'** were seperated (colorless oil, 44% yield for **8'**, 66.0 mg). **TLC**: R_f = 0.20 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel AS-3, CO_2/MeOH = 90/10, flow rate 1.5 mL/min, λ = 240 nm, t_{r2}= 8.2 min, t_{r3}= 9.3 min. (t_{r1}= 7.4 min, t_{r4}= 9.8 min for **9'**, not detected after colum chromatography.) 94% ee for **9**. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 2H), 7.33 – 7.25 (m, 5H), 7.22 – 7.15 (m, 3H), 7.12 – 7.05 (m, 1H), 3.65 (s, 3H), 2.66 (dd, *J* = 20.4, 6.8 Hz, 2H), 2.30 (t, *J* = 7.2 Hz, 2H), 2.27 – 2.20 (m, 2H), 1.71 – 1.56 (m, 4H), 1.41 (q, *J* = 4.8, 2.8 Hz, 3H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 174.3, 170.7, 140.1, 137.9, 129.3, 128.9, 128.3, 126.1, 124.1, 119.7, 41.6, 40.2, 37.1, 33.8, 33.1, 26.0, 24.9. **HRMS** (ESI-TOF) Calculated for $C_{22}H_{27}NO_3$ ([M]+Na^+) = 376.1883, found 376.1889.



	Retention Time	Area	% Area
1	7.400	455253	34.38
2	8.047	226257	17.09
3	9.304	207217	15.65
4	9.776	435266	32.88



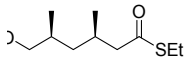
	Retention Time	Area	% Area
1	--	--	--
2	8.152	322518	3.07
3	9.250	10195080	96.93
4	--	--	--



(*S*)-C4-benzyl SAHA analog

(*S*)-C4-benzyl-SAHA analog

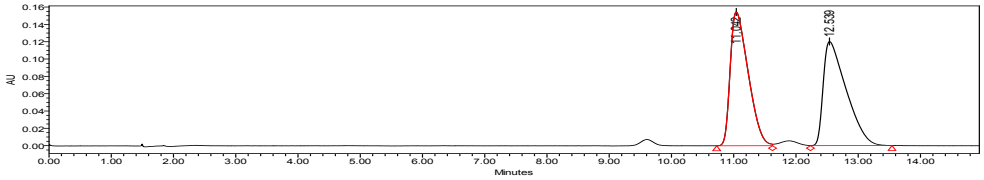
Synthesis of (*S*)-C4-benzyl-SAHA analog. To a dry flask were added methanol (0.3 mL) and hydroxylamine hydrochloride (33.2 mg) and the reaction temperature was dropped to 0 °C. A mixture of methanol (0.3 mL) and KOH (52.1 mg) were added to the reaction before a vigorous stirring for 10 min. Then, a mixture of methanol (0.3 mL) and 8′ (16.4 mg) were added to the reaction, and the reaction was conducted at room temperature for 2 h. The organic phase was concentrated and the residue was extracted with DCM and NH4Cl (aq. sat.). The organic phase was dried with Na_2SO_4 and concentrated. The residue was purified by flash column chromatography to give (*S*)-C4-benzyl-SAHA analog (yellow solid, 90% yield, 14.6 mg). TLC: R_f = 0.2 (DCM:acetone = 3:1) [UV]. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.29 (s, 1H), 7.49 (s, 2H), 7.33 – 6.92 (m, 9H), 2.53 (s, 2H), 2.21 (s, 3H), 2.05 (s, 3H), 1.47 (s, 2H), 1.32 – 1.19 (m, 4H). ^{13}C NMR: (101 MHz, $CDCl_3$) δ 172.0, 171.7, 140.1, 137.9, 129.2, 128.8, 128.3, 126.0, 124.3, 120.2, 41.2, 40.2, 37.0, 32.6, 32.3, 29.7, 25.3. HRMS (ESI-TOF) Calculated for $C_{22}H_{27}NO_3$ ([M]+Na$^+$) = 377.1835, found 377.1831. $[\alpha]_D^{27}$ = +5.6 (*c* = 0.156, in $CHCl_3$). NMR purity analysis 95.3%. Impurity: EtOAc. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.12 (q), 2.05 (s), 1.26 (t). ^{13}C NMR: (101 MHz, $CDCl_3$) δ 171.22, 60.41, 21.04, 14.16.



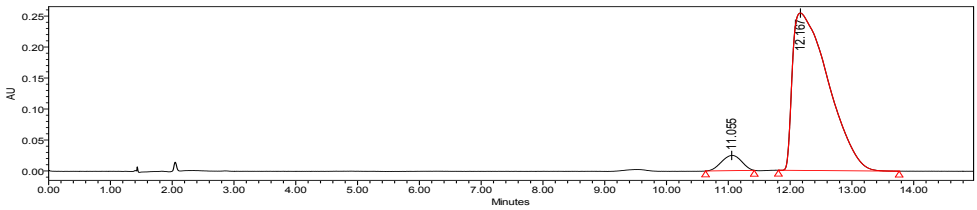
9

(3*R*,5*S*)-S-ethyl 6-hydroxy-3,5-dimethylhexanethioate (**9**)

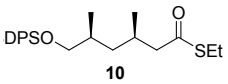
Prepared using **5h** (0.1 mmol), EtSH (0.2 mmol) and $AlMe_3$ (1 M in heptane, 0.2 mmol) in THF (2 mL). **TLC**: R_f = 0.6 (petroleum ether:EtOAc = 4:1) [UV]. **SFC**: Chiralcel OJ-3, CO_2/MeOH = 95/5, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 11.1 min, t_{r2}= 12.2 min, 90% ee. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ 3.48 (t, *J* = 5.6 Hz, 2H), 2.87 (q, *J* = 7.4 Hz, 2H), 2.54 (dd, *J* = 14.8, 6.1 Hz, 1H), 2.34 (dd, *J* = 14.8, 7.7 Hz, 1H), 2.16 – 2.06 (m, 1H), 1.75 – 1.66 (m, 1H), 1.40 (dd, *J* = 13.7, 6.8 Hz, 1H), 1.24 (t, *J* = 7.4 Hz, 3H), 1.02 (dd, *J* = 14.0, 7.1 Hz, 1H), 0.95 (dd, *J* = 8.8, 6.7 Hz, 6H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 199.5, 67.8, 51.0, 40.4, 33.0, 28.4, 23.3, 20.3, 17.3, 14.8. **HRMS** (ESI-TOF) Calculated for $C_8H_{14}O_2$ ([M]+Na$^+$) = 165.0891, found 165.0890 Calculated for $C_{10}H_{20}O_2S$ ([M]+Na$^+$) = 227.1076, found 227.1075. $[\alpha]_D^{27}$ = +1.9 (*c* = 0.214, in CH_2Cl_2).



	Retention Time	Area	% Area
1	11.042	3085085	50.07
2	12.539	3075944	49.93



	Retention Time	Area	% Area
1	11.055	553023	5.14
2	12.167	10196458	94.86



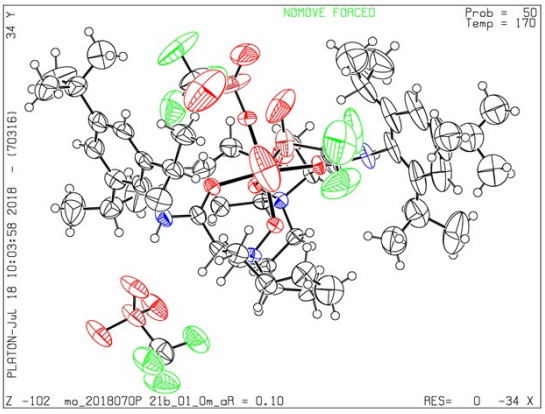
10

(3*R*,5*S*)-S-ethyl 6-((tert-butyldiphenylsilyl)oxy)-3,5-dimethylhexanethioate (**10**)

Prepared using **9** (0.10 mmol), NaH (0.24 mmol), TBDPSCl (0.40 mmol) in EtOAc at room temperature for 15 h. **TLC**: R_f = 0.6 (petroleum ether:EtOAc = 4:1) [UV]. **HPLC**: Chiralcel IA, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 240 nm, t_{r1}= 30.9 min, t_{r2}= 34.8 min, 91% ee. **^{1}H NMR**: (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.61 (m, 4H), 7.48 – 7.33 (m, 6H), 3.57 – 3.37 (m, 2H), 2.87 (q, *J* = 7.4 Hz, 2H), 2.52 (dd, *J* = 14.3, 5.1 Hz, 1H), 2.25 (dd, *J* = 14.3, 8.8 Hz, 1H), 2.08 (ddd, *J* = 8.8, 6.9, 5.1 Hz, 1H), 1.77 – 1.65 (m, 1H), 1.40 (ddd, *J* = 13.6, 7.3, 6.2 Hz, 1H), 1.24 (t, *J* = 7.4 Hz, 4H), 1.06 (s, 9H), 0.93 (dd, *J* = 13.0, 6.6 Hz, 6H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 199.2, 135.6, 134.0, 133.9, 129.5, 127.6, 68.7, 51.2, 40.8, 33.2, 28.7, 26.9, 23.2, 20.3, 19.3, 17.4, 14.8. **HRMS** (ESI-TOF) Calculated for $C_8H_{14}O_2$ ([M]+Na^+) = 165.0891, found 165.0890 Calculated for $C_{10}H_{20}O_2S$ ([M]+Na^+) = 227.1076, found 227.1075. $[\alpha]_D^{27}$ = −5.3 (*c* = 0.704, in CH_2Cl_2).

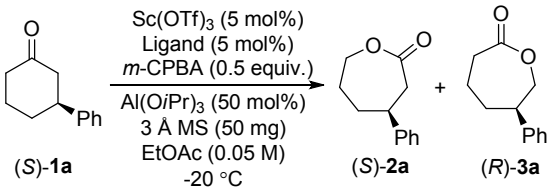
12 The Characterization of L-RaPr$_2$-*t*Bu/Sc(OTf)$_3$

Figure S2. Structure of **L-RaPr$_2$-*t*Bu**/Sc(OTf)$_3$ complex.



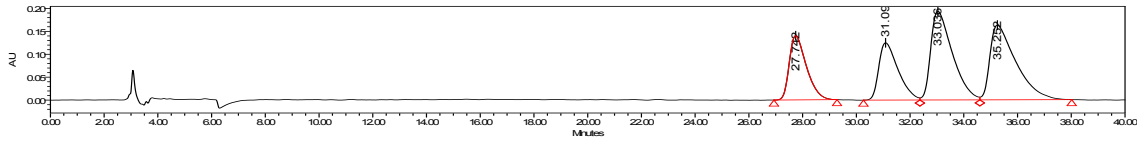
Single crystal of **L-RaPr$_2$-*t*Bu**/Sc(OTf)$_3$ complex was recrystallized from mixed solvents of EtOAc and *n*-hexane in a 5 mm diameter tube. CCDC 1856535 contains the supplementary crystallographic data which can be obtained Free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

13 Control experiments

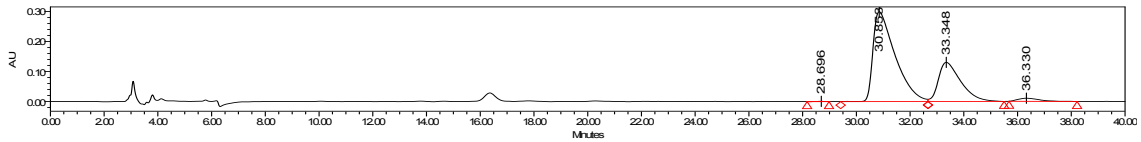


L-RaPr$_2$-tBu: 2a+3a: 85% yield
(*S*)-**2a**:(*R*)-**3a** = 1:2.3

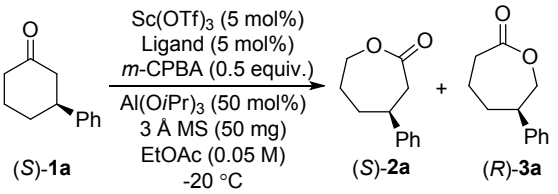
Prepared according to general procedure using (*S*)-**1a** (0.2 mmol, 34.8 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol). **HPLC**: Chiralcel OD-H, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 28.7 min ((*S*)-**3a**), t_{r2}= 30.9 min ((*R*)-**3a**), t_{r3}= 32.8 min ((*S*)-**2a**), t_{r4}= 36.3 min ((*R*)-**2a**), (*S*)-**2a**:(*R*)-**3a** = 1:2.3.



	Retention Time	Area	% Area
1	27.742	6209495	18.13
2	31.090	6235692	18.20
3	33.036	10862364	31.71
4	35.252	10950203	31.96

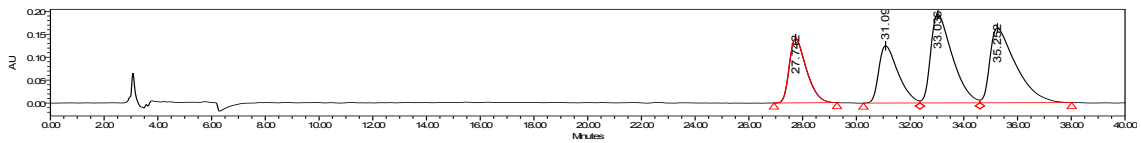


	Retention Time	Area	% Area
1	28.696	20842	0.08
2	30.853	17090439	67.82
3	33.348	7502429	29.77
4	36.330	585505	2.32



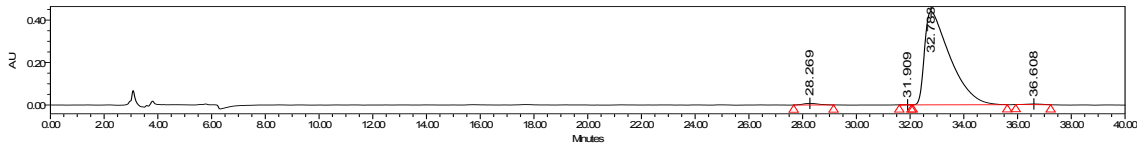
ent-**L-RaPr$_2$-tBu: 2a+3a**: 99% yield
(*S*)-**2a**:(*R*)-**3a** > 99:1

Prepared according to general procedure using (*S*)-**1a** (0.2 mmol, 34.8 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol). **HPLC**: Chiralcel OD-H, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 28.3 min ((*S*)-**3a**), t_{r2}= 31.9 min ((*R*)-**3a**), t_{r3}= 32.7 min ((*S*)-**2a**), t_{r4}= 36.6 min ((*R*)-**2a**), (*S*)-**2a**:(*R*)-**3a** > 99:1.

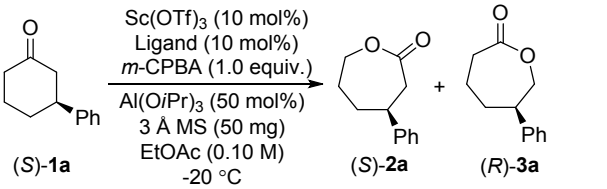


	Retention Time	Area	% Area
1	27.742	6209495	18.13

2	31.090	6235692	18.20
3	33.036	10862364	31.71
4	35.252	10950203	31.96

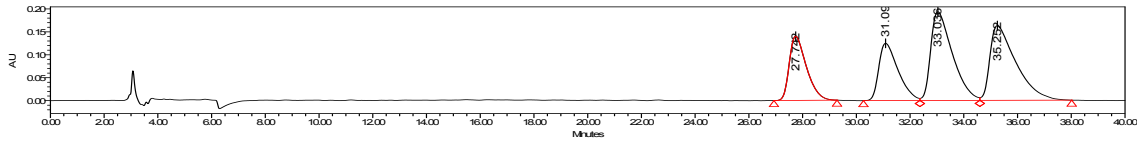


	Retention Time	Area	% Area
1	28.269	290722	0.99
2	31.909	3314	0.01
3	32.783	28867613	98.55
4	36.608	131375	0.45

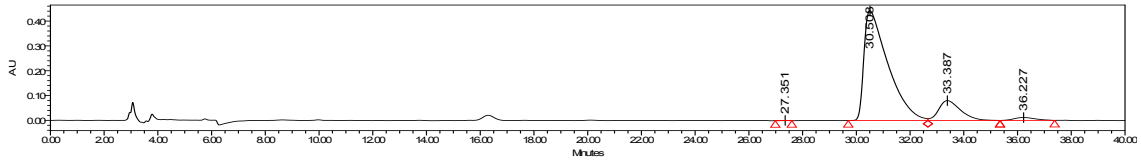


L-RaEt$_2$: 2a+**3a**: 99% yield
(*S*)-**2a**:(*R*)-**3a** = 1:6.1

Prepared according to general procedure using (*S*)-**1a** (0.2 mmol, 34.8 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and Sc(OTf)$_3$ (0.010 mmol). **HPLC**: Chiralcel OD-H, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 27.3 min ((*S*)-**3a**), t_{r2}= 30.5 min ((*R*)-**3a**), t_{r3}= 33.4 min ((*S*)-**2a**), t_{r4}= 36.2 min ((*R*)-**2a**), (*S*)-**2a**:(*R*)-**3a** = 1:6.1.

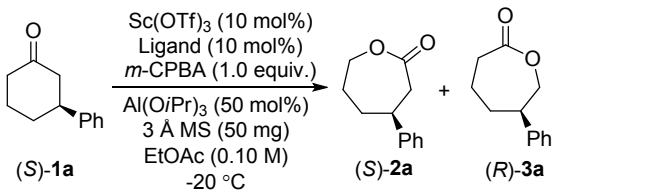


	Retention Time	Area	% Area
1	27.742	6209495	18.13
2	31.090	6235692	18.20
3	33.036	10862364	31.71
4	35.252	10950203	31.96

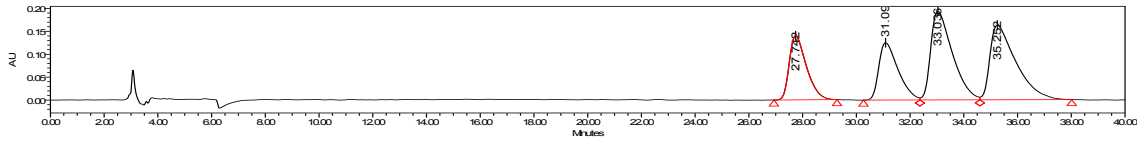


	Retention Time	Area	% Area
1	27.351	15144	0.05
2	30.508	27416242	84.18
3	33.387	4514498	13.86

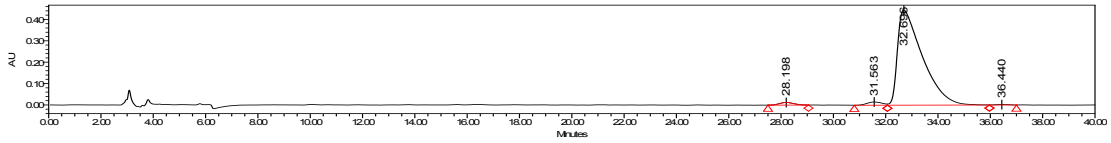
4	36.227	624457	1.92



Prepared according to general procedure using (*S*)-**1a** (0.2 mmol, 34.8 mg), *m*-CPBA (0.10 mmol), **L-RaEt$_2$** (0.010 mmol) and $Sc(OTf)_3$ (0.010 mmol). **HPLC**: Chiralcel OD-H, hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 210 nm, t_{r1}= 28.2 min ((*S*)-**3a**), t_{r2}= 31.6 min ((*R*)-**3a**), t_{r3}= 32.7 min ((*S*)-**2a**), t_{r4}= 36.4 min ((*R*)-**2a**), (*S*)-**2a**:(*R*)-**3a** = 48:1.



	Retention Time	Area	% Area
1	27.742	6209495	18.13
2	31.090	6235692	18.20
3	33.036	10862364	31.71
4	35.252	10950203	31.96



	Retention Time	Area	% Area
1	28.198	476182	1.56
2	31.563	599498	1.97
3	32.696	29354817	96.22
4	36.440	76274	0.25

14 Computational details.

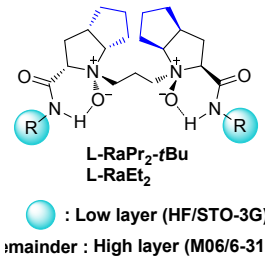
All calculations in this work were performed using Gaussian 09 program package.[7] Geometries of transition states were optimized at the ONIOM[8] (M06/6-31G*:HF/STO-3G) theoretical level, and characterized by frequency analysis at 298 K. The high and low layers in ONIOM method were depicted in Scheme S2. The core region was treated with the M06[9] functional and 6-31G* basis set.[10] The low layer was optimized at the HF/STO-3G level. The bonds between atoms in the core and the outer layers were broken and saturated with hydrogen atoms (link atoms). The intrinsic reaction coordinate (IRC) path was traced to check the energy profiles connecting each transition state to two associated minima of the proposed mechanism.[11]

Table S6. Comparison of the electronic energy corrected by zero-point vibration effect (*E*) and Gibbs Free energy (*G*) of transition states in alkyl group migration step.

entry	Transition states	*E* (Hartree)	Δ*E* (kcal mol^{-1})[a]	*G* (Hartree)	Δ*G* (kcal mol^{-1})[a]
1	**L-RaPr$_2$-*t*Bu**-TS-(*R*)-**2a**	−5621.59101	0.0	−5621.72364	0.0
2	**L-RaPr$_2$-*t*Bu**-TS-(*S*)-**3a**	−5621.58540	3.5	−5621.71737	3.9
3	**L-RaPr$_2$-*t*Bu**-TS-(*R*)-**3a**	−5621.58562	3.4	−5621.71697	4.2
4	**L-RaPr$_2$-*t*Bu**-TS-(*S*)-**2a**	−5621.57323	11.2	−5621.70484	11.8
5	**L-RaEt$_2$**-TS-(*R*)-**2a**	−5159.04231	0.0	−5159.15953	0.0
6	**L-RaEt$_2$**-TS-(*S*)-**3a**	−5159.03894	2.1	−5159.15532	2.6
7	**L-RaEt$_2$**-TS-(*R*)-**3a**	−5159.04343	−0.7	−5159.15849	0.7
8	**L-RaEt$_2$**-TS-(*S*)-**2a**	−5159.03462	4.8	−5159.15091	5.4

[a] The energy of transition states **L-RaPr$_2$-*t*Bu**-TS-(*R*)-**2a** or **L-RaEt$_2$**-TS-(*R*)-**2a** were set to zero.

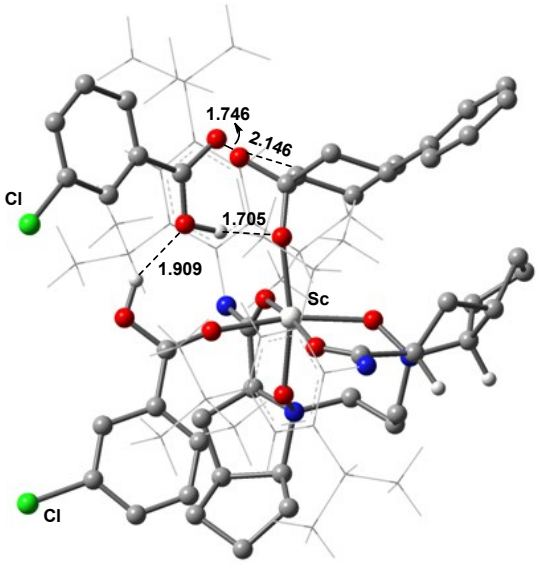
Scheme S2. Layering of the *N*,*N*′-dioxide ligand in ONIOM calculations.



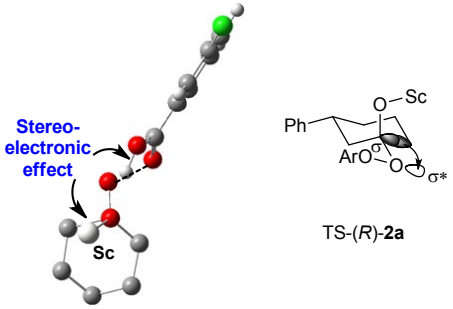
To provide further information about the chiral recognition of the reaction, ONIOM (M06/6-31G*: HF/STO-3G) calculations were performed. The transition states in alkyl group migration step in the CKR and PKR were optimized and their Gibbs free energies were calculated. In **L-RaPr$_2$-*t*Bu**-TS-(*R*)-**2a** and **L-RaEt$_2$**-TS-(*R*)-**2a**, **1a** was placed away from the aniline groups, while in **L-RaPr$_2$-*t*Bu**-TS-(*R*)-**3a** and **L-RaEt$_2$**-TS-(*R*)-**3a**, **1a** was placed between the aniline group and bicyclic ring backbone of the ligand. For **L-RaPr$_2$-*t*Bu** with bulky *iso*-propyl and *tert*-butyl groups on the aniline group, the larger steric hindrance between the ligand and **1a** resulted in a larger energy difference between **L-RaPr$_2$-*t*Bu**-TS-(*R*)-**3a** and **L-RaPr$_2$-*t*Bu**-TS-(*R*)-**2a** (Figure 2a, ΔG = 4.2 kcal mol^{-1}). Meanwhile, owing to a less bulky aniline group, energy difference between **L-RaEt$_2$**-TS-(*R*)-**3a** and **L-RaEt$_2$**-TS-(*R*)-**2a** was significantly smaller (Figure 2b, ΔG = 0.7 kcal mol^{-1}).

Listed bellow are cartesian coordinates and the corresponding optimized geometries of all transition states.

(a) **L-RaPr$_2$-*t*Bu**-TS-(*R*)-**2a**



L-RaPr$_2$-*t*Bu-TS-(*R*)-**2a**



TS-(*R*)-**2a**

Zero-point correction = 1.84070 a.u.
Thermal correction to Gibbs Free Energy = 1.70808 a.u.
Sum of electronic and zero-point Energies = −5621.59101 a.u.
Sum of electronic and thermal Free Energies = −5621.72364 a.u.
Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	1	−0.354245	−1.150763	−0.201503
2	6	2.074654	−0.358009	−2.979935
3	6	1.241607	0.609937	−2.395676
4	6	2.966189	0.036809	−3.961068
5	6	1.296124	1.953073	−2.804142
6	6	2.198986	2.324296	−3.787401
7	6	3.033542	1.373724	-4.367297
8	1	2.022319	-1.403251	−2.684249
9	1	3.743765	1.658527	−5.140424
10	1	2.260483	3.360645	−4.108377
11	1	0.643124	2.686523	−2.338562
12	6	0.300973	0.225276	−1.370082
13	8	−0.659562	0.993637	−1.073286

14	8	0.442411	−0.937376	−0.786070
15	17	4.002962	−1.133649	−4.697295
16	6	−5.815417	0.145257	−0.270509
17	6	−6.860014	0.978657	0.130944
18	6	−7.942318	1.219089	−0.712311
19	6	−7.997826	0.631250	−1.969585
20	6	−6.959865	−0.198445	−2.386012
21	6	−5.882580	−0.435542	−1.542870
22	1	−6.991063	−0.654844	−3.373454
23	1	−5.067498	−1.080227	−1.883031
24	1	−8.842622	0.823422	−2.626754
25	1	−8.745207	1.874395	−0.381832
26	1	−6.845637	1.453227	1.110503
27	21	−1.671700	−3.223289	1.440762
28	8	−2.295191	−4.417829	−0.239126
29	8	−3.655403	−3.526000	1.913643
30	8	−1.144173	−4.890804	2.588353
31	8	−0.987103	−2.286536	3.290188
32	7	−4.450736	−4.623882	1.702681
33	7	−1.252282	−5.078598	3.937561
34	7	0.122876	−1.896721	5.232442
35	1	0.520511	−2.361353	6.048803
36	7	−3.580491	−5.404972	−1.825882
37	1	−4.517062	−5.766373	−2.004685
38	6	−3.395941	−4.873060	−0.627305
39	6	−4.665332	−4.854047	0.214430
40	1	−5.134057	−5.848829	0.153861
41	6	−5.697271	−3.807629	−0.169608
42	1	−6.120434	−3.991541	−1.163779
43	1	−5.231142	−2.815219	−0.188498
44	6	−6.722831	−3.929191	0.954355
45	6	−7.480832	−2.662645	1.371328
46	1	−7.428475	−4.733988	0.705303
47	6	−5.910126	−4.353227	2.202235
48	6	−6.079634	−3.247096	3.229864
49	1	−6.250192	−5.321030	2.591188
50	6	−3.879513	−5.870340	2.334149
51	1	−2.936704	−6.081147	1.822974
52	1	−4.591828	−6.672087	2.104621
53	6	−3.690950	−5.804765	3.838847

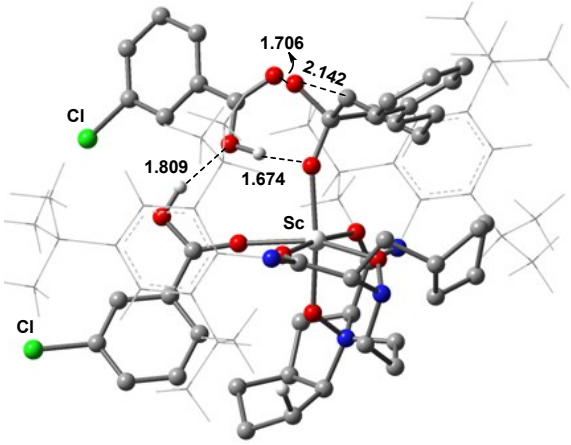
54	1	−3.464052	−6.830259	4.162621
55	1	−4.646291	−5.563834	4.325948
56	6	−2.664007	−4.850196	4.418301
57	1	−2.912430	−3.810780	4.182622
58	1	−2.642211	−4.967235	5.509048
59	6	−0.702911	−6.481813	4.342889
60	6	0.811283	−6.270703	4.606345
61	6	1.072353	−4.788052	4.345795
62	1	1.868427	−4.369213	4.970795
63	1	1.326043	−4.598731	3.292652
64	6	−0.279987	−4.169970	4.665095
65	1	−0.496323	−4.317011	5.734986
66	6	−0.426574	−2.697121	4.330724
67	6	−2.584018	−5.633101	−2.879529
68	6	1.526244	−7.291647	3.719398
69	6	−0.815652	−7.579756	3.297430
70	6	−7.478954	−2.718750	2.899273
71	1	−8.246778	−3.416544	3.262018
72	1	−7.682482	−1.750853	3.370467
73	1	−8.486574	−2.615227	0.942310
74	1	−6.946801	−1.767473	1.020218
75	1	−5.972782	−3.589287	4.266536
76	1	−5.333439	−2.462671	3.046510
77	1	−1.244375	−6.726411	5.265888
78	1	1.010471	−6.488833	5.664811
79	6	0.474847	−8.378656	3.509290
80	1	−1.725288	−8.184663	3.392290
81	1	0.392962	−9.012124	4.403481
82	1	0.699769	−9.044436	2.668734
83	1	1.786328	−6.833226	2.753066
84	1	2.452740	−7.665220	4.166855
85	1	−0.798784	−7.118720	2.300341
86	6	−2.144094	−6.951315	−3.091717
87	6	−2.175930	−4.583807	−3.698891
88	6	−1.269565	−4.866684	−4.720240
89	6	−0.790287	−6.147255	−4.953003
90	6	−1.253412	−7.175889	−4.124873
91	6	−2.701470	−8.116995	−2.248525
92	6	−2.738767	−3.157217	−3.555302
93	1	−0.957715	−4.055590	−5.357773

94	6	−3.645795	−2.804160	−4.761445
95	6	−1.613967	−2.108723	−3.388991
96	6	−3.999329	−8.672389	−2.893099
97	6	−1.685235	−9.263881	−2.038169
98	1	−3.354495	−3.121009	−2.659683
99	1	−2.956254	−7.722902	−1.265019
100	1	−2.047449	−1.128674	−3.212195
101	1	−4.077106	−1.816451	−4.628243
102	1	−4.750625	−7.896686	−3.006773
103	1	−3.787814	−9.081478	−3.876095
104	1	−2.065560	−9.954344	−1.291461
105	1	−1.526304	−9.821843	−2.954405
106	1	−4.454443	−3.522617	−4.855845
107	1	−0.973907	−2.364854	−2.550051
108	1	−1.000528	−2.047644	−4.281610
109	1	−3.077871	−2.806750	−5.686097
110	1	−0.728374	−8.880719	−1.700224
111	1	−4.414806	−9.464363	−2.276968
112	6	0.171150	−0.429895	5.227923
113	6	−0.739096	0.266358	6.042055
114	6	1.165988	0.229894	4.508792
115	6	1.211076	1.621210	4.580963
116	6	0.319126	2.352460	5.352477
117	6	−0.644434	1.645721	6.080398
118	6	−1.751755	−0.492563	6.925364
119	6	2.243084	−0.528431	3.708994
120	1	1.985310	2.131497	4.031697
121	6	3.619439	−0.420325	4.413882
122	6	2.339702	−0.035717	2.245341
123	6	−1.106501	−0.841214	8.293087
124	6	−3.077189	0.273404	7.148589
125	1	1.969410	−1.580979	3.682208
126	1	−1.996087	−1.427129	6.421305
127	1	3.064440	−0.635462	1.702397
128	1	4.362695	−1.000360	3.874843
129	1	−0.199905	−1.425259	8.166754
130	1	−0.850391	0.065261	8.832661
131	1	−2.930640	1.135665	7.789799
132	1	−3.500631	0.612207	6.208777
133	1	3.560218	−0.796772	5.430643

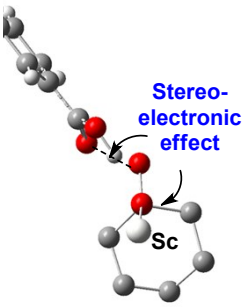
134	1	1.377272	−0.114272	1.748386
135	1	2.663184	0.998499	2.199353
136	1	3.953058	0.611625	4.451471
137	1	−3.795569	−0.381078	7.632730
138	1	−1.801590	−1.413682	8.900135
139	6	0.368151	3.903789	5.456550
140	6	−0.992912	4.490851	4.986762
141	6	1.491051	4.515699	4.579765
142	6	0.627873	4.307631	6.935486
143	1	1.474071	5.595789	4.682156
144	1	−0.966854	5.574059	5.050254
145	1	−1.811937	4.137672	5.604041
146	1	2.470146	4.166521	4.890858
147	1	1.349671	4.276588	3.530674
148	1	−1.194238	4.216405	3.955454
149	1	−1.330200	2.193629	6.707463
150	6	0.206412	−6.481066	−6.099530
151	6	1.490842	−7.112849	−5.492227
152	6	0.617400	−5.221709	−6.905153
153	1	1.317573	−5.509132	−7.682646
154	1	2.197102	−7.341484	−6.284050
155	1	1.268279	−8.033786	−4.964141
156	1	−0.240836	−4.760648	−7.382856
157	1	1.103975	−4.487251	−6.271471
158	1	1.967435	−6.424425	−4.800597
159	1	−0.914714	−8.183901	−4.305931
160	6	−2.099425	−0.020418	0.807115
161	6	−2.261577	0.465196	2.354884
162	6	−3.344188	0.408512	0.034973
163	1	−1.385134	0.123101	2.909251
164	1	−2.312015	1.557895	2.368898
165	1	−3.190011	0.081603	−1.003428
166	1	−3.387753	1.507076	0.027925
167	8	−1.792707	−1.346572	0.692112
168	6	−3.558881	−0.137985	2.878282
169	6	−4.770639	0.278732	2.066008
170	6	−4.628694	−0.170125	0.615417
171	1	−3.481463	−1.235403	2.920444
172	1	−3.651463	0.214616	3.915403
173	1	−4.496368	−1.267733	0.635751

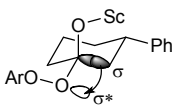
174	1	−4.879737	1.374300	2.112051
175	6	3.247001	−5.442188	0.124440
176	6	1.876419	−5.167782	0.214876
177	6	3.671006	−6.762280	0.070455
178	6	0.939698	−6.208264	0.233317
179	6	1.383391	−7.520603	0.148627
180	6	2.743901	−7.804866	0.074417
181	1	3.977328	−4.638049	0.095601
182	1	3.096648	−8.831725	0.010403
183	1	0.668215	−8.339802	0.138335
184	1	−0.123058	−5.977487	0.282453
185	6	1.415334	−3.782837	0.246443
186	8	0.269673	−3.428654	0.572794
187	8	2.311886	−2.892785	−0.109230
188	1	1.890279	−2.007389	−0.152003
189	8	−1.043517	0.797883	0.619319
190	1	1.568969	3.894100	7.285284
191	1	−0.165829	3.958009	7.586798
192	1	0.679639	5.388784	7.016360
193	6	−0.460010	−7.490643	−7.076508
194	1	−1.366988	−7.070650	−7.500817
195	1	0.222291	−7.719247	−7.889110
196	1	−0.711626	−8.419258	−6.575712
197	1	−5.685336	−0.140904	2.511165
198	17	5.358464	−7.114285	−0.020915

(b) **L-RaPr$_2$-*t*Bu**-TS-(*S*)-**3a**



L-RaPr$_2$-*t*Bu-TS-(*S*)-**3a**





TS-(*S*)-**3a**

Zero-point correction = 1.84109 a.u.
Thermal correction to Gibbs Free Energy = 1.70912 a.u.
Sum of electronic and zero-point Energies = −5621.58540 a.u.
Sum of electronic and thermal Free Energies = −5621.71737 a.u.
Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	21	−1.222265	−3.524144	1.703646
2	8	−2.083533	−4.535500	0.011225
3	8	−3.191362	−3.754269	2.342201
4	8	−0.684027	−5.238305	2.793837
5	8	−0.522873	−2.626099	3.567297
6	7	−4.043987	−4.810654	2.112961
7	7	−0.722123	−5.471377	4.139556
8	7	0.180189	−2.309754	5.708473
9	1	0.512653	−2.810166	6.532418
10	7	−3.578973	−5.168981	−1.571263
11	1	−4.558848	−5.415589	−1.702856
12	6	−3.246853	−4.842725	−0.330230
13	6	−4.420672	−4.887407	0.640794
14	1	−4.913585	−5.866181	0.529403
15	6	−5.463885	−3.797861	0.490552
16	1	−6.001508	−3.857309	−0.463177
17	1	−4.985763	−2.812767	0.533395
18	6	−6.374243	−4.027159	1.693955
19	6	−6.991087	−2.751489	2.276883
20	1	−7.136517	−4.771821	1.430806
21	6	−5.442090	−4.581983	2.794901
22	6	−5.447409	−3.564339	3.929183
23	1	−5.738826	−5.583544	3.124608
24	6	−3.454395	−6.126089	2.568835
25	1	−2.559135	−6.293350	1.968359

26	1	−4.197069	−6.889553	2.307523
27	6	−3.153687	−6.238906	4.054213
28	1	−2.879419	−7.288986	4.227645
29	1	−4.075704	−6.094661	4.635319
30	6	−2.117105	−5.326387	4.682802
31	1	−2.387031	−4.274884	4.543650
32	1	−2.056553	−5.536403	5.757992
33	6	−0.051454	−6.834416	4.467941
34	6	1.465413	−6.523678	4.432797
35	6	1.597466	−4.997379	4.389383
36	1	2.389064	−4.606854	5.037465
37	1	1.780688	−4.636676	3.369020
38	6	0.229007	−4.535363	4.862274
39	1	0.109844	−4.788359	5.926491
40	6	−0.087064	−3.067375	4.655249
41	6	−2.696353	−5.470060	−2.708749
42	6	1.997954	−7.319688	3.243382
43	6	−0.302818	−7.970656	3.483966
44	6	−5.960209	−2.273822	3.294713
45	1	−6.373135	−1.573779	4.029197
46	1	−5.129150	−1.771241	2.785041
47	1	−7.939512	−2.988400	2.775866
48	1	−7.210991	−2.008434	1.498124
49	1	−6.161454	−3.927401	4.681978
50	1	−4.477403	−3.449545	4.423943
51	1	−0.404422	−7.065436	5.481575
52	1	1.910654	−6.911038	5.359537
53	6	1.096445	−8.548966	3.226985
54	1	−1.011292	−8.713927	3.867143
55	1	1.377040	−9.238166	4.035170
56	1	1.151404	−9.114762	2.290367
57	1	1.858069	−6.740020	2.316748
58	1	3.062225	−7.560436	3.333069
59	1	−0.701998	−7.556779	2.549817
60	6	−2.625034	−6.805908	−3.126437
61	6	−2.036384	−4.450062	−3.400691
62	6	−1.270117	−4.807912	−4.501644
63	6	−1.155879	−6.124253	−4.944194
64	6	−1.850820	−7.103663	−4.240280
65	6	−3.443864	−7.907849	−2.420566

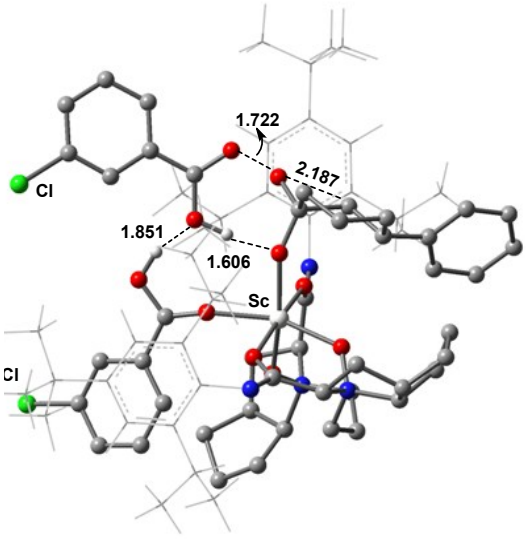
66	6	−2.189558	−2.962166	−3.033651
67	1	−0.765020	−4.026435	−5.048140
68	6	−3.051700	−2.231131	−4.094547
69	6	−0.819214	−2.262157	−2.867276
70	6	−4.844331	−8.038080	−3.076741
71	6	−2.738882	−9.284808	−2.404521
72	1	−2.709717	−2.897158	−2.081095
73	1	−3.583634	−7.606274	−1.382996
74	1	−0.963029	−1.235721	−2.544046
75	1	−3.194839	−1.192300	−3.812317
76	1	−5.382420	−7.094787	−3.060119
77	1	−4.748135	−8.350266	−4.111901
78	1	−3.278620	−9.960221	−1.747676
79	1	−2.719467	−9.729945	−3.393136
80	1	−4.026682	−2.700292	−4.185188
81	1	−0.212541	−2.776057	−2.128412
82	1	−0.271598	−2.241690	−3.803277
83	1	−2.569482	−2.257045	−5.066395
84	1	−1.718731	−9.197051	−2.046423
85	1	−5.437343	−8.780656	−2.551039
86	6	0.015010	−0.859104	5.862848
87	6	−1.098371	−0.387934	6.559117
88	6	1.028304	0.002094	5.414091
89	6	0.872250	1.356080	5.652460
90	6	−0.236411	1.877266	6.327904
91	6	−1.201485	0.984879	6.774325
92	6	−2.148773	−1.349050	7.152640
93	6	2.307666	−0.555675	4.756813
94	1	1.644770	2.032370	5.322833
95	6	3.333548	−0.964279	5.846552
96	6	2.962922	0.425200	3.756521
97	6	−1.893263	−1.544533	8.669915
98	6	−3.604743	−0.887498	6.903365
99	1	2.035958	−1.452053	4.200429
100	1	−2.027896	−2.316199	6.667982
101	1	3.747346	−0.087354	3.207850
102	1	4.221458	−1.388974	5.387432
103	1	−0.887867	−1.913021	8.851428
104	1	−2.010879	−0.605000	9.200486
105	1	−3.825274	0.030162	7.437304

106	1	−3.786540	−0.722284	5.846216
107	1	2.912138	−1.700059	6.524223
108	1	2.235311	0.809018	3.048297
109	1	3.415785	1.266764	4.268962
110	1	3.631929	−0.098668	6.429855
111	1	−4.292868	−1.649965	7.255817
112	1	−2.601023	−2.258585	9.080465
113	6	−0.330428	3.410927	6.571429
114	6	−0.318067	4.147296	5.202011
115	6	0.888992	3.868250	7.420961
116	1	0.824575	4.935157	7.609862
117	1	−0.391092	5.218531	5.360724
118	1	−1.160944	3.836830	4.591584
119	1	0.903624	3.353438	8.376865
120	1	1.825023	3.671792	6.909359
121	1	0.596823	3.950335	4.653517
122	1	−2.054684	1.350166	7.322079
123	6	−0.295108	−6.440934	−6.200826
124	6	1.168278	−5.979823	−5.949029
125	6	−0.879210	−5.677559	−7.423123
126	1	−0.295538	−5.903983	−8.309796
127	1	1.776828	−6.198554	−6.820709
128	1	1.595247	−6.503276	−5.098782
129	1	−1.906667	−5.977386	−7.605995
130	1	−0.855850	−4.604229	−7.268304
131	1	1.221497	−4.912817	−5.760973
132	1	−1.803740	−8.128264	−4.569508
133	6	−1.295713	−0.303251	0.907818
134	6	−1.273583	0.370196	2.273808
135	6	−2.649887	0.062714	0.121407
136	1	−0.358506	0.035921	2.780929
137	1	−1.189595	1.452668	2.106135
138	1	−2.650144	−0.502480	−0.813911
139	1	−2.665383	1.134145	−0.106063
140	8	−1.057345	−1.656489	0.941755
141	6	−2.509030	0.064716	3.096977
142	6	−3.763645	0.462336	2.339023
143	6	−3.853695	−0.289572	1.017595
144	1	−2.544856	−1.009184	3.350269
145	1	−2.447586	0.607953	4.047455

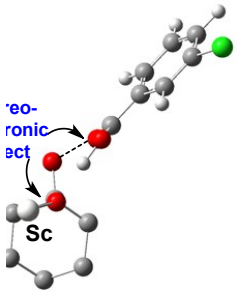
146	6	−5.117202	−0.036658	0.221903
147	1	−3.772288	−1.371617	1.234689
148	6	−5.348076	−0.750673	−0.962207
149	6	−6.511915	−0.571001	−1.696990
150	6	−7.471624	0.341554	−1.264940
151	6	−7.251135	1.069133	−0.101035
152	6	−6.082833	0.886640	0.633177
153	1	−7.990793	1.790272	0.239406
154	1	−5.935357	1.473459	1.537016
155	1	−8.382170	0.492746	−1.839848
156	1	−6.667829	−1.129297	−2.618091
157	1	−4.599547	−1.461927	−1.320425
158	1	−3.749118	1.546568	2.141982
159	6	2.230605	−6.556220	−1.458114
160	6	1.297760	−6.048295	−0.545082
161	6	2.219211	−7.911791	−1.753677
162	6	0.360742	−6.895569	0.055160
163	6	0.362511	−8.247982	−0.254613
164	6	1.289806	−8.762745	−1.156048
165	1	2.959903	−5.904266	−1.930964
166	1	1.300662	−9.822022	−1.402579
167	1	−0.360308	−8.918993	0.206677
168	1	−0.341481	−6.479939	0.773189
169	6	1.306561	−4.625387	−0.212601
170	8	0.563527	−4.077660	0.623439
171	8	2.199566	−3.923316	−0.869468
172	1	2.107233	−2.975468	−0.630969
173	8	−0.531174	0.346449	−0.018899
174	6	−1.626078	3.807396	7.325240
175	1	−2.512286	3.524001	6.766680
176	1	−1.667862	3.348059	8.307332
177	1	−1.644625	4.883966	7.459349
178	6	−0.277122	−7.955060	−6.534310
179	1	0.137265	−8.536146	−5.716842
180	1	−1.273448	−8.322346	−6.757259
181	1	0.342807	−8.119359	−7.409522
182	1	−4.654470	0.272044	2.950776
183	1	0.510650	−1.575670	0.360373
184	6	4.232495	−0.820875	−0.086732
185	6	3.227128	0.159114	−0.122678

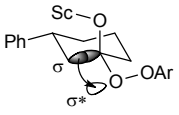
186	6	5.532516	−0.453774	−0.384415
187	6	3.530933	1.493432	−0.440471
188	6	4.839146	1.835019	−0.744917
189	6	5.840363	0.869647	−0.717935
190	1	4.015648	−1.851034	0.186100
191	1	6.869311	1.131295	−0.954966
192	1	5.087418	2.859426	−1.009423
193	1	2.738904	2.236896	−0.469996
194	6	1.855125	−0.190238	0.162749
195	8	1.045143	0.717704	0.518035
196	8	1.479973	−1.436016	0.083269
197	17	6.788042	−1.639752	−0.340811
198	17	3.365774	−8.549582	−2.877402

(c) **L-RaPr$_2$-*t*Bu**-TS-(*R*)-**3a**



L-RaPr$_2$-*t*Bu-TS-(*R*)-**3a**





TS-(*R*)-**3a**

Zero-point correction = 1.84163 a.u.
Thermal correction to Gibbs Free Energy = 1.71028 a.u.
Sum of electronic and zero-point Energies = −5621.58562 a.u.
Sum of electronic and thermal Free Energies = −5621.71697 a.u.
Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	0.657334	−0.378272	5.037382
2	6	−0.039713	0.535789	5.840231
3	6	1.670594	0.031367	4.165734
4	6	1.936316	1.392649	4.068286
5	6	1.245471	2.338537	4.817264
6	6	0.269224	1.880121	5.702629
7	6	−1.048008	0.054473	6.904081
8	6	2.544043	−0.994072	3.414188
9	1	2.721778	1.713655	3.405854
10	6	3.736668	−1.428543	4.306463
11	6	3.066433	−0.479106	2.052869
12	6	−0.300983	−0.312903	8.214130
13	6	−2.159592	1.085810	7.206638
14	1	1.937155	−1.875218	3.213267
15	1	−1.527504	−0.847265	6.524183
16	1	3.529134	−1.295257	1.505814
17	1	4.332841	−2.182152	3.800189
18	1	0.455514	−1.072537	8.042925
19	1	0.188887	0.562449	8.629270
20	1	−1.763273	1.947857	7.731877
21	1	−2.639962	1.424667	6.294414
22	1	3.389394	−1.839794	5.249031
23	1	2.256603	−0.072886	1.455921
24	1	3.814659	0.294811	2.182678
25	1	4.375269	−0.578179	4.524451
26	1	−2.912011	0.628907	7.841119
27	1	−1.003893	−0.690508	8.950734
28	6	1.540911	3.863220	4.728775
29	6	0.242627	4.611698	4.313889
30	6	2.643802	4.188659	3.688677
31	6	2.015294	4.372787	6.119156
32	1	2.799852	5.262059	3.658932
33	1	0.439905	5.676550	4.241294
34	1	−0.548868	4.465351	5.040900
35	1	3.587123	3.721927	3.952676
36	1	2.357648	3.864127	2.693402
37	1	−0.108800	4.264345	3.346774

38	1	−0.254593	2.595106	6.316723
39	1	2.914669	3.850744	6.431642
40	1	1.251639	4.227077	6.875439
41	1	2.238423	5.433610	6.064334
42	21	−1.662941	−3.219559	1.634556
43	8	−2.348919	−4.360531	−0.052390
44	8	−3.649762	−3.586683	2.208930
45	8	−0.984981	−4.867619	2.769292
46	8	−0.924697	−2.255194	3.426922
47	7	−4.389288	−4.723519	1.961577
48	7	−1.085130	−5.056845	4.121649
49	7	0.401045	−1.815055	5.216874
50	1	0.839277	−2.252879	6.026879
51	7	−3.719407	−5.154219	−1.674450
52	1	−4.670794	−5.477678	−1.848827
53	6	−3.472686	−4.756611	−0.436218
54	6	−4.683892	−4.847389	0.479078
55	1	−5.113218	−5.855895	0.362989
56	6	−5.797101	−3.833994	0.268456
57	1	−6.249935	−3.909310	−0.726462
58	1	−5.402175	−2.814180	0.387861
59	6	−6.764601	−4.213025	1.388447
60	6	−7.631089	−3.082108	1.944687
61	1	−7.371302	−5.062785	1.047347
62	6	−5.849152	−4.640958	2.557417
63	6	−6.046747	−3.624596	3.673716
64	1	−6.050401	−5.667092	2.882618
65	6	−3.694077	−5.949322	2.497507
66	1	−2.753400	−6.050776	1.952759
67	1	−4.338214	−6.800368	2.244748
68	6	−3.471130	−5.926385	4.002052
69	1	−3.160744	−6.941580	4.282434
70	1	−4.429361	−5.776872	4.519366
71	6	−2.506778	−4.914601	4.598301
72	1	−2.814681	−3.890854	4.370676
73	1	−2.484462	−5.041061	5.687850
74	6	−0.481178	−6.436340	4.541493
75	6	1.026998	−6.176479	4.763786
76	6	1.227915	−4.676960	4.574230
77	1	1.981226	−4.254534	5.247098

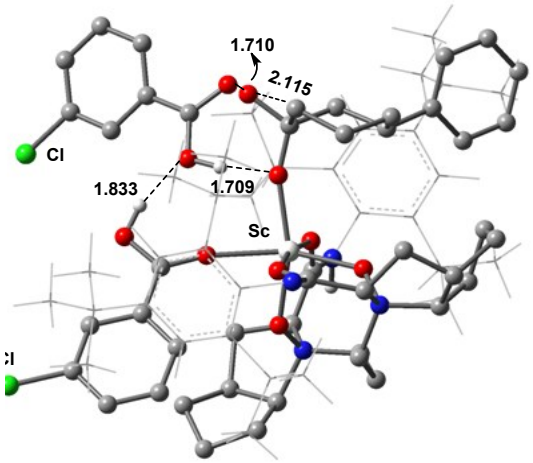
78	1	1.531062	−4.443517	3.544461
79	6	−0.155689	−4.095982	4.842922
80	1	−0.397246	−4.198981	5.912491
81	6	−0.283481	−2.634973	4.433764
82	6	−2.760279	−5.334799	−2.773360
83	6	1.742522	−7.111698	3.789498
84	6	−0.591469	−7.563603	3.523931
85	6	−6.758091	−2.443115	3.017217
86	1	−7.313295	−1.831004	3.736868
87	1	−6.013134	−1.791630	2.549098
88	1	−8.545270	−3.500559	2.385142
89	1	−7.947290	−2.379912	1.162835
90	1	−6.697001	−4.088295	4.428806
91	1	−5.115410	−3.338044	4.172895
92	1	−0.992788	−6.669305	5.483987
93	1	1.274324	−6.454437	5.797586
94	6	0.763587	−8.270427	3.639286
95	1	−1.443539	−8.229883	3.702056
96	1	0.787262	−8.914418	4.529410
97	1	0.977333	−8.910582	2.776217
98	1	1.865280	−6.605301	2.819078
99	1	2.734193	−7.416460	4.138651
100	1	−0.685761	−7.124525	2.522009
101	6	−2.314612	−6.639737	−3.046383
102	6	−2.398267	−4.254131	−3.573976
103	6	−1.540350	−4.494926	−4.646519
104	6	−1.057920	−5.761539	−4.941512
105	6	−1.468166	−6.820536	−4.124587
106	6	−2.818014	−7.840728	−2.219005
107	6	−2.975277	−2.842075	−3.357568
108	1	−1.269003	−3.662495	−5.274401
109	6	−4.059593	−2.536813	−4.422844
110	6	−1.878191	−1.751665	−3.369325
111	6	−4.134083	−8.395969	−2.825449
112	6	−1.775375	−8.976032	−2.090359
113	1	−3.453586	−2.814763	−2.380661
114	1	−3.036130	−7.484013	−1.212786
115	1	−2.322500	−0.783909	−3.158655
116	1	−4.499340	−1.560624	−4.241120
117	1	−4.901388	−7.629507	−2.878397

118	1	−3.959846	−8.766923	−3.830630
119	1	−2.110270	−9.695233	−1.349018
120	1	−1.650135	−9.503402	−3.029607
121	1	−4.849705	−3.280980	−4.391579
122	1	−1.120423	−1.959084	−2.619611
123	1	−1.394143	−1.688932	−4.337682
124	1	−3.629835	−2.538092	−5.419524
125	1	−0.810170	−8.586529	−1.784606
126	1	−4.509507	−9.215937	−2.220314
127	6	−0.112967	−6.046444	−6.143775
128	6	1.207194	−6.677169	−5.617335
129	6	0.242609	−4.757870	−6.929370
130	1	0.908009	−5.012098	−7.747878
131	1	1.877794	−6.871890	−6.448261
132	1	1.022315	−7.616491	−5.107391
133	1	−0.643428	−4.294920	−7.351211
134	1	0.749843	−4.035767	−6.297698
135	1	1.707208	−6.002621	−4.928570
136	1	−1.125652	−7.817767	−4.351819
137	6	−2.020689	−0.004240	0.994677
138	6	−2.654826	0.355741	2.419728
139	6	−2.907634	0.567197	−0.109594
140	1	−2.025394	−0.077249	3.202163
141	1	−2.673837	1.445701	2.531734
142	1	−2.437296	0.305009	−1.066270
143	1	−2.888657	1.662163	−0.022479
144	8	−1.774726	−1.351537	0.837290
145	6	−4.088133	−0.210672	2.450527
146	6	−4.930423	0.377871	1.324577
147	6	−4.327750	0.047474	−0.031134
148	1	−4.007502	−1.298506	2.283285
149	1	−4.324967	−1.044172	−0.193502
150	1	−4.986981	1.472780	1.431181
151	6	3.077546	−5.595854	−0.030907
152	6	1.724353	−5.296665	0.170630
153	6	3.479046	−6.923620	−0.069250
154	6	0.781049	−6.320647	0.310665
155	6	1.198447	−7.642476	0.237792
156	6	2.543733	−7.950560	0.057106
157	1	3.812894	−4.805299	−0.153768

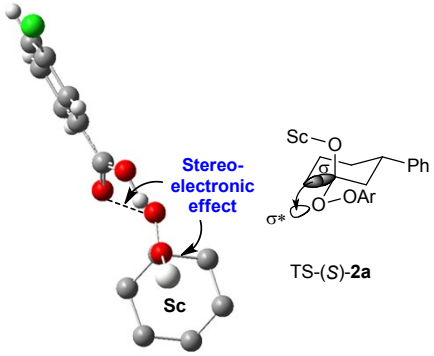
158	1	2.876659	−8.984800	0.005193
159	1	0.474272	−8.449971	0.322689
160	1	−0.268738	−6.068740	0.449244
161	6	1.293135	−3.901765	0.205642
162	8	0.195719	−3.509146	0.636464
163	8	2.167220	−3.043505	−0.263927
164	1	1.759323	−2.149955	−0.268490
165	8	−0.886607	0.728852	1.189737
166	6	−0.811852	−7.036127	−7.118384
167	1	−1.743367	−6.616852	−7.486525
168	1	−0.166053	−7.230507	−7.968839
169	1	−1.027209	−7.982787	−6.634762
170	1	−5.965203	0.011516	1.393964
171	17	5.148359	−7.305155	−0.289814
172	6	−4.649312	−0.005492	3.836266
173	6	−4.312308	−0.919923	4.840878
174	6	−5.537534	1.026538	4.145779
175	6	−4.893980	−0.850809	6.099138
176	1	−3.599944	−1.716308	4.602721
177	6	−6.111656	1.108740	5.410771
178	1	−5.811734	1.762855	3.392506
179	6	−5.804250	0.165033	6.385073
180	1	−4.644852	−1.586547	6.862227
181	1	−6.812794	1.910187	5.631793
182	1	−6.265737	0.226034	7.367893
183	1	−4.924854	0.486548	−0.839216
184	1	−0.437624	−1.159979	−0.031057
185	6	2.159457	−0.228900	−2.626875
186	6	1.627600	0.718400	−1.737236
187	6	3.148756	0.169056	−3.509451
188	6	2.075729	2.049126	−1.745139
189	6	3.069526	2.421565	−2.636216
190	6	3.607379	1.489412	−3.518407
191	1	1.797492	−1.254231	−2.647782
192	1	4.385547	1.777289	−4.221823
193	1	3.433170	3.445508	−2.649740
194	1	1.653727	2.769322	−1.049202
195	6	0.582779	0.323323	−0.815152
196	8	−0.132318	1.218456	−0.279227
197	8	0.391453	−0.947344	−0.596075

198	17	3.816518	−0.977795	−4.617100

(d) **L-RaPr$_2$-*t*Bu**-TS-(*S*)-**2a**



L-RaPr$_2$-*t*Bu-TS-(*S*)-**2a**



TS-(*S*)-**2a**

Zero-point correction = 1.84115 a.u.
Thermal correction to Gibbs Free Energy = 1.70954 a.u.
Sum of electronic and zero-point Energies = −5621.57323 a.u.
Sum of electronic and thermal Free Energies = −5621.70484 a.u.
Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	1	0.799259	−1.415538	0.895144
2	6	4.453822	−0.354265	1.006900
3	6	3.387408	0.541664	0.820705
4	6	5.748930	0.120519	0.913025
5	6	3.626178	1.900944	0.555401
6	6	4.932817	2.352883	0.461665
7	6	5.994220	1.470899	0.639229
8	1	4.281160	−1.403351	1.236053
9	1	7.022214	1.819572	0.567017

10	1	5.134112	3.398369	0.243761
11	1	2.790160	2.578768	0.406384
12	6	2.024410	0.075481	0.886006
13	8	1.074313	0.903031	1.040546
14	8	1.786095	−1.207043	0.802261
15	17	7.075782	−0.962603	1.137708
16	6	−3.790283	0.965530	3.417825
17	6	−4.062199	0.448583	4.683423
18	6	−4.093940	2.306486	3.165370
19	6	−4.648944	1.238070	5.668294
20	1	−3.817534	−0.596579	4.890783
21	6	−4.673269	3.100710	4.147127
22	1	−3.887269	2.744821	2.187995
23	6	−4.960249	2.565623	5.399118
24	1	−4.869506	0.816900	6.646811
25	1	−4.909241	4.140425	3.931551
26	1	−5.426301	3.184211	6.162398
27	6	−0.088052	−1.029874	6.370070
28	6	−1.145422	−0.879584	7.270246
29	6	0.698048	0.056140	5.960828
30	6	0.358779	1.308771	6.442284
31	6	−0.705816	1.513049	7.325022
32	6	−1.436270	0.402508	7.728026
33	6	−1.897400	−2.104924	7.831426
34	6	1.953972	−0.161880	5.092586
35	1	0.954527	2.156980	6.147026
36	6	3.127589	−0.672431	5.970584
37	6	−1.253065	−2.549030	9.171656
38	1	1.724366	−0.931859	4.355487
39	1	−1.783635	−2.920591	7.119263
40	1	4.004799	−0.856782	5.357408
41	1	−1.743567	−3.442159	9.547380
42	1	−0.195303	−2.763248	9.049513
43	1	2.866428	−1.594347	6.479518
44	1	3.387348	0.067030	6.721780
45	1	−1.353577	−1.766839	9.917460
46	1	−2.242434	0.521231	8.432923
47	21	−1.084289	−3.425486	1.909403
48	8	−1.974591	−4.472058	0.230146
49	8	−3.021633	−3.710277	2.598734

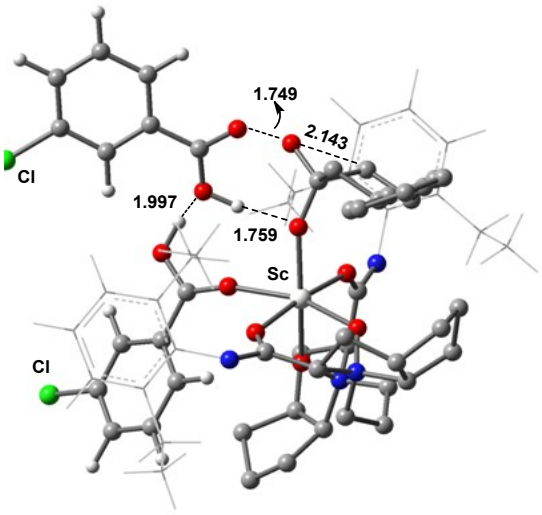
50	8	−0.485629	−5.170512	2.893072
51	8	−0.426430	−2.576490	3.813135
52	7	−3.865023	−4.775070	2.378543
53	7	−0.465433	−5.459250	4.227300
54	7	0.281600	−2.397680	5.979228
55	1	0.679921	−2.958222	6.731120
56	7	−3.498140	−5.228978	−1.280412
57	1	−4.488841	−5.451666	−1.366322
58	6	−3.142090	−4.804953	−0.075019
59	6	−4.298689	−4.811770	0.924592
60	1	−4.804984	−5.783983	0.816925
61	6	−5.364538	−3.734098	0.851285
62	1	−5.920735	−3.760291	−0.092776
63	1	−4.911305	−2.743075	0.955153
64	6	−6.233338	−4.064590	2.064329
65	6	−6.916341	−2.858975	2.714607
66	1	−6.950217	−4.848918	1.788361
67	6	−5.236980	−4.587813	3.124166
68	6	−5.221659	−3.566878	4.258396
69	1	−5.491801	−5.595846	3.467942
70	6	−3.238324	−6.100422	2.758104
71	1	−2.358740	−6.226101	2.123132
72	1	−3.980126	−6.861938	2.489087
73	6	−2.882956	−6.272631	4.224046
74	1	−2.588746	−7.324799	4.344092
75	1	−3.782127	−6.163414	4.847164
76	6	−1.836376	−5.366467	4.839703
77	1	−2.137646	−4.318219	4.752497
78	1	−1.719446	−5.614517	5.901966
79	6	0.250821	−6.815967	4.465334
80	6	1.760647	−6.459836	4.428051
81	6	1.842552	−4.928291	4.372795
82	1	2.664513	−4.513956	4.965841
83	1	1.939115	−4.561705	3.342533
84	6	0.494085	−4.524895	4.941892
85	1	0.449325	−4.844098	5.994153
86	6	0.069498	−3.066454	4.855644
87	6	−2.672507	−5.742857	−2.386784
88	6	2.328346	−7.261693	3.257074
89	6	0.019032	−7.901588	3.423647

90	6	−5.867040	−2.310466	3.674568
91	1	−6.286883	−1.651808	4.442041
92	1	−5.112081	−1.722341	3.135052
93	1	−7.803798	−3.190377	3.269235
94	1	−7.261501	−2.127638	1.973100
95	1	−5.849056	−3.971681	5.064792
96	1	−4.224019	−3.390079	4.675191
97	1	−0.076451	−7.119888	5.468466
98	1	2.212998	−6.813956	5.364800
99	6	1.420211	−8.487211	3.204516
100	1	−0.715704	−8.650115	3.741724
101	1	1.673311	−9.186606	4.013271
102	1	1.497306	−9.042653	2.263251
103	1	2.232212	−6.686923	2.322296
104	1	3.386460	−7.510473	3.387917
105	1	−0.327145	−7.439800	2.489449
106	6	−2.755957	−7.119532	−2.643551
107	6	−1.926128	−4.890997	−3.204627
108	6	−1.245865	−5.456926	−4.275544
109	6	−1.293258	−6.818104	−4.565392
110	6	−2.060324	−7.627507	−3.731759
111	6	−3.652711	−8.043340	−1.791245
112	6	−1.880957	−3.365485	−3.001210
113	1	−0.677172	−4.804992	−4.920383
114	6	−2.691454	−2.646458	−4.109777
115	6	−5.071517	−8.138791	−2.412967
116	1	−2.347413	−3.135104	−2.046308
117	1	−3.746771	−7.598469	−0.801446
118	1	−2.693552	−1.574095	−3.938488
119	1	−5.527192	−7.158570	−2.519773
120	1	−5.021571	−8.593191	−3.397437
121	1	−3.719889	−2.994727	−4.119693
122	1	−2.258474	−2.833951	−5.087076
123	1	−5.715467	−8.750657	−1.788119
124	1	−2.134179	−8.682467	−3.936838
125	6	−1.210655	−0.282907	0.805366
126	6	−1.810138	0.544535	1.933337
127	6	−2.193056	−0.218615	−0.485538
128	1	−1.121397	0.476550	2.789522
129	1	−1.827836	1.593426	1.605533

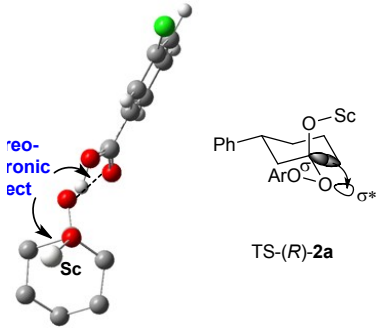
130	1	−1.744487	−0.803359	−1.289409
131	1	−2.300985	0.822789	−0.803394
132	8	−0.885918	−1.563571	1.138778
133	6	−3.209141	0.084826	2.335563
134	6	−4.124801	0.028169	1.107147
135	6	−3.521012	−0.788129	−0.019656
136	1	−3.115645	−0.941711	2.740862
137	1	−3.358617	−1.831576	0.287990
138	1	−4.316221	1.048361	0.740348
139	6	2.921402	−6.269516	−0.773664
140	6	1.755163	−5.775683	−0.174649
141	6	2.998652	−7.616467	−1.098448
142	6	0.673551	−6.625948	0.082141
143	6	0.766615	−7.967400	−0.258652
144	6	1.925450	−8.469724	−0.844257
145	1	3.762422	−5.614108	−0.982149
146	1	2.004856	−9.521182	−1.111086
147	1	−0.065115	−8.641066	−0.063218
148	1	−0.223624	−6.226961	0.550020
149	6	1.683323	−4.369522	0.213363
150	8	0.754091	−3.854524	0.859693
151	8	2.712851	−3.645416	−0.160751
152	1	2.566762	−2.711219	0.103887
153	8	−0.242898	0.356318	0.097708
154	1	−5.110303	−0.366393	1.398426
155	17	4.434982	−8.238539	−1.826453
156	1	−4.185113	−0.805298	−0.896953
157	6	−0.994783	2.948845	7.849582
158	6	−1.264405	3.893312	6.644555
159	1	−0.404433	3.952610	5.986372
160	1	−2.117197	3.546968	6.068794
161	1	−1.480604	4.893891	7.005244
162	6	0.242984	3.456048	8.642914
163	1	0.049102	4.452435	9.027325
164	1	0.453590	2.801814	9.483568
165	1	1.125009	3.502686	8.013237
166	6	−2.227508	2.993067	8.788783
167	1	−3.123157	2.650004	8.281499
168	1	−2.071370	2.387069	9.675118
169	1	−2.394060	4.016067	9.109797

170	6	−0.520167	−7.369998	−5.797243
171	6	−0.686612	−8.903368	−5.955995
172	1	−1.726045	−9.174044	−6.109698
173	1	−0.123747	−9.234774	−6.822413
174	1	−0.309644	−9.435142	−5.088396
175	6	0.993991	−7.057376	−5.632334
176	1	1.174546	−5.989329	−5.574573
177	1	1.386697	−7.523377	−4.733469
178	1	1.544046	−7.446093	−6.483454
179	6	−1.057223	−6.683989	−7.085172
180	1	−0.534395	−7.073217	−7.953084
181	1	−2.117749	−6.880987	−7.209684
182	1	−0.907480	−5.610156	−7.054241
183	6	−0.424498	−2.841376	−2.956240
184	1	−0.414807	−1.769856	−2.784331
185	1	0.132774	−3.324693	−2.159895
186	1	0.089332	−3.027175	−3.892837
187	6	−3.065144	−9.461235	−1.594091
188	1	−2.038309	−9.414570	−1.246634
189	1	−3.654232	−9.998109	−0.856659
190	1	−3.089928	−10.031562	−2.515958
191	6	−3.414667	−1.873115	8.021237
192	1	−3.874356	−1.524362	7.102824
193	1	−3.889352	−2.805680	8.311251
194	1	−3.609431	−1.146457	8.801990
195	6	2.395856	1.103752	4.323169
196	1	2.756982	1.869110	5.000769
197	1	3.210698	0.851914	3.652804
198	1	1.579139	1.518243	3.740158

(e) **L-RaEt$_2$**-TS-(*R*)-**2a**



L-RaEt$_2$-TS-(*R*)-**2a**



TS-(*R*)-**2a**

Zero-point correction = 1.43606 a.u.
Thermal correction to Gibbs Free Energy = 1.31884 a.u.
Sum of electronic and zero-point Energies = −5159.04231 a.u.
Sum of electronic and thermal Free Energies = −5159.15953 a.u.
Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	1	−0.264217	−1.286397	−0.244484
2	6	2.028656	−0.800404	−3.194795
3	6	1.193717	0.214360	−2.698352
4	6	2.866093	−0.512682	−4.256944
5	6	1.194140	1.496733	−3.273295
6	6	2.042533	1.760689	−4.336138
7	6	2.878037	0.763486	−4.830723
8	1	2.021908	−1.799120	−2.764396
9	1	3.546947	0.964881	−5.664670
10	1	2.063170	2.749960	−4.785521
11	1	0.543838	2.269637	−2.872069
12	6	0.311565	−0.056724	−1.588828
13	8	−0.643166	0.732919	−1.330075

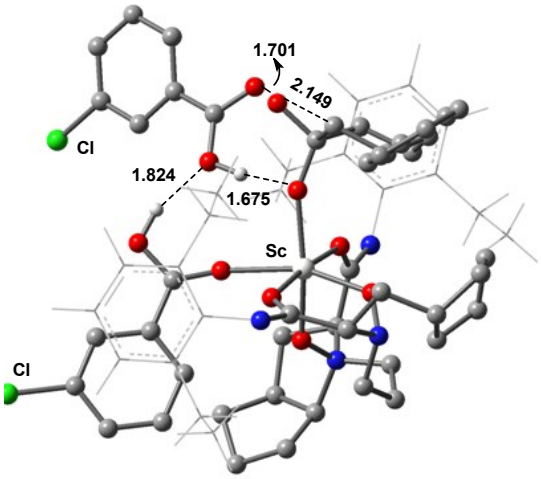
14	8	0.499430	−1.142963	−0.883043
15	6	−5.779337	0.170247	−0.088288
16	6	−6.850363	0.934255	0.376742
17	6	−8.012566	1.067685	−0.379754
18	6	−8.125045	0.439521	−1.613791
19	6	−7.061480	−0.319727	−2.095469
20	6	−5.903927	−0.448280	−1.338369
21	1	−7.134098	−0.801698	−3.068704
22	1	−5.073718	−1.040654	−1.730996
23	1	−9.032402	0.548205	−2.203274
24	1	−8.832818	1.673557	−0.000982
25	1	−6.792896	1.442891	1.337221
26	21	−1.663156	−3.206969	1.531531
27	8	−2.233690	−4.364855	−0.168294
28	8	−3.669094	−3.539076	1.970186
29	8	−1.103222	−4.881708	2.668949
30	8	−1.053431	−2.276867	3.390899
31	7	−4.417118	−4.661723	1.698275
32	7	−1.249375	−5.082174	4.013567
33	7	0.076510	−1.865142	5.306933
34	1	0.484993	−2.299313	6.134646
35	7	−3.459062	−5.194435	−1.866223
36	1	−4.377891	−5.539389	−2.143123
37	6	−3.329517	−4.769769	−0.619392
38	6	−4.607008	−4.822109	0.199019
39	1	−5.050148	−5.823567	0.075302
40	6	−5.666565	−3.782224	−0.122151
41	1	−6.062312	−3.882921	−1.139426
42	1	−5.241005	−2.774319	−0.028068
43	6	−6.718430	−4.065683	0.950027
44	6	−7.548161	−2.863758	1.408262
45	1	−7.353521	−4.891984	0.603351
46	6	−5.904269	−4.503290	2.189577
47	6	−6.123409	−3.446836	3.266619
48	1	−6.173265	−5.509718	2.528573
49	6	−3.800314	−5.902603	2.297116
50	1	−2.833999	−6.048402	1.807746
51	1	−4.463447	−6.730997	2.019516
52	6	−3.656995	−5.874897	3.810658
53	1	−3.401357	−6.899892	4.112241

54	1	−4.633340	−5.682461	4.277909
55	6	−2.681000	−4.900686	4.446905
56	1	−2.946673	−3.864607	4.216783
57	1	−2.697427	−5.035382	5.535783
58	6	−0.673241	−6.470902	4.429008
59	6	0.841234	−6.228556	4.649942
60	6	1.058854	−4.726144	4.473250
61	1	1.818902	−4.313842	5.145438
62	1	1.346408	−4.481295	3.440769
63	6	−0.320677	−4.152452	4.769808
64	1	−0.557586	−4.304281	5.834581
65	6	−0.481311	−2.683227	4.427630
66	6	−2.362308	−5.308477	−2.834505
67	6	1.542507	−7.166967	3.668486
68	6	−0.798697	−7.589369	3.403712
69	6	−6.722136	−2.247690	2.532112
70	1	−7.310415	−1.597292	3.188920
71	1	−5.915198	−1.644100	2.106126
72	1	−8.516555	−3.211912	1.790551
73	1	−7.756480	−2.160499	0.590379
74	1	−6.847838	−3.857646	3.983673
75	1	−5.212075	−3.201861	3.823479
76	1	−1.190992	−6.700332	5.369369
77	1	1.087063	−6.515858	5.681586
78	6	0.548454	−8.312623	3.511045
79	1	−1.658796	−8.245842	3.579791
80	1	0.565997	−8.963215	4.396480
81	1	0.752486	−8.949437	2.643047
82	1	1.671613	−6.655471	2.702098
83	1	2.530008	−7.487768	4.015263
84	1	−0.888495	−7.142407	2.404571
85	6	−1.784258	−6.567197	−3.032298
86	6	−1.960606	−4.180740	−3.556743
87	6	−0.932571	−4.333595	−4.480259
88	6	−0.336002	−5.567758	−4.683499
89	6	−0.761768	−6.675562	−3.968411
90	6	−2.277580	−7.817123	−2.296139
91	6	−2.652646	−2.822171	−3.411537
92	1	−0.607125	−3.477371	−5.056698
93	6	−3.871490	−2.691700	−4.355251

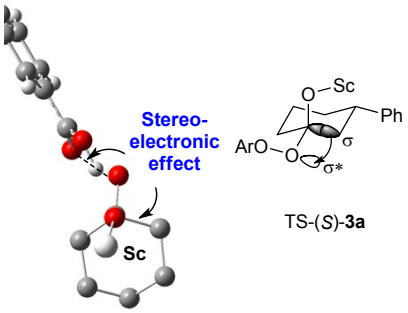
94	6	−3.421758	−8.530358	−3.055048
95	1	−2.969194	−2.664854	−2.383149
96	1	−2.612897	−7.555303	−1.294894
97	1	−4.319275	−1.707313	−4.255942
98	1	−4.283172	−7.879660	−3.172271
99	1	−3.089755	−8.833910	−4.043158
100	1	−4.625039	−3.437949	−4.122822
101	1	−3.567252	−2.826245	−5.388793
102	1	−3.732752	−9.417700	−2.511418
103	6	0.143434	−0.402863	5.216566
104	6	−0.789725	0.352540	5.933581
105	6	1.169952	0.187433	4.470389
106	6	1.235083	1.575223	4.440164
107	6	0.315218	2.344948	5.136050
108	6	−0.686296	1.738988	5.876591
109	6	−1.872511	−0.296138	6.802263
110	6	2.236454	−0.638660	3.744098
111	1	2.022132	2.056938	3.874330
112	6	3.431919	−0.986370	4.662171
113	6	−1.397180	−0.521286	8.257108
114	1	1.801757	−1.555091	3.351182
115	1	−2.180832	−1.244779	6.368796
116	1	4.174322	−1.556586	4.111318
117	1	−0.535288	−1.181015	8.292019
118	1	−1.120538	0.422596	8.716801
119	1	3.110578	−1.574119	5.516606
120	1	3.902221	−0.080194	5.031544
121	1	−2.195096	−0.966388	8.844275
122	1	−1.395165	2.346246	6.425263
123	1	−0.301277	−7.639885	−4.141979
124	6	−1.988253	−0.030845	0.723159
125	6	−2.000277	0.569673	2.239968
126	6	−3.263716	0.393363	−0.001193
127	1	−1.118649	0.177162	2.751705
128	1	−1.952693	1.661279	2.188016
129	1	−3.190686	−0.037205	−1.010305
130	1	−3.252931	1.486838	−0.112465
131	8	−1.743707	−1.372902	0.702174
132	6	−3.305871	0.127778	2.891163
133	6	−4.526806	0.579884	2.115631

134	6	−4.523192	−0.057478	0.727726
135	1	−3.328785	−0.967402	3.021011
136	1	−3.295503	0.569277	3.898756
137	1	−4.413129	−1.149940	0.877527
138	1	−4.530139	1.677767	2.020421
139	6	3.057991	−5.711003	0.063220
140	6	1.723114	−5.309846	0.202689
141	6	3.348903	−7.063686	−0.052259
142	6	0.690696	−6.255807	0.202842
143	6	1.000206	−7.600031	0.053501
144	6	2.324673	−8.011419	−0.065118
145	1	3.861587	−4.978728	0.047783
146	1	2.574094	−9.064382	−0.178565
147	1	0.207013	−8.344543	0.024449
148	1	−0.342860	−5.926464	0.285761
149	6	1.396488	−3.890267	0.309053
150	8	0.308904	−3.438626	0.704959
151	8	2.359937	−3.075689	−0.060164
152	1	2.018372	−2.157328	−0.074777
153	8	−0.915936	0.719292	0.397308
154	1	−5.433047	0.315728	2.674888
155	17	3.905019	−1.742634	−4.885712
156	17	4.990937	−7.573135	−0.201092
157	1	0.385387	3.426652	5.106726
158	1	2.602667	−0.064131	2.896123
159	1	−2.745065	0.353286	6.815403
160	1	−1.937122	−2.039977	−3.654787
161	1	−1.445839	−8.509553	−2.189525
162	1	0.459776	−5.669404	−5.413073

(f) **L-RaEt$_2$**-TS-(*S*)-**3a**



L-RaEt$_2$-TS-(*S*)-**3a**



TS-(*S*)-**3a**

Zero-point correction = 1.43655 a.u.
Thermal correction to Gibbs Free Energy = 1.32017 a.u.
Sum of electronic and zero-point Energies = −5159.03894 a.u.
Sum of electronic and thermal Free Energies = −5159.15532 a.u.
Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	21	−1.353235	−3.503253	1.738616
2	8	−2.168666	−4.496755	0.030519
3	8	−3.332987	−3.768159	2.337211
4	8	−0.810253	−5.240926	2.797426
5	8	−0.600931	−2.653136	3.592206
6	7	−4.167357	−4.833795	2.084866
7	7	−0.857948	−5.490890	4.140253
8	7	0.360227	−2.341480	5.619225
9	1	0.727674	−2.823491	6.439265
10	7	−3.566349	−5.231903	−1.577787
11	1	−4.517230	−5.545043	−1.769509
12	6	−3.308233	−4.861258	−0.331886
13	6	−4.506414	−4.917491	0.603160

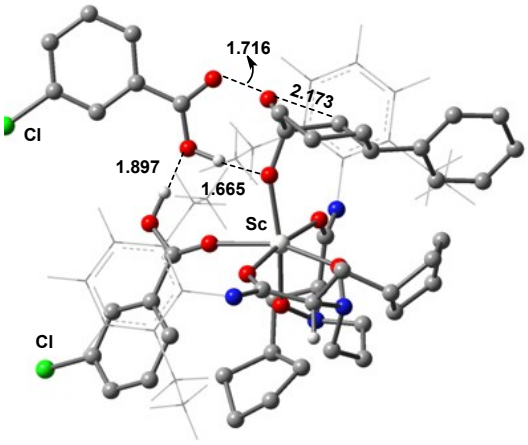
14	1	−4.990572	−5.899429	0.480991
15	6	−5.551628	−3.833387	0.424230
16	1	−6.059061	−3.896914	−0.545669
17	1	−5.081314	−2.844925	0.483596
18	6	−6.493605	−4.072945	1.602123
19	6	−7.139412	−2.806213	2.173171
20	1	−7.240840	−4.824117	1.315347
21	6	−5.587392	−4.622252	2.727821
22	6	−5.632666	−3.610037	3.865476
23	1	−5.882175	−5.628395	3.045205
24	6	−3.574431	−6.137999	2.563171
25	1	−2.667546	−6.304645	1.979873
26	1	−4.305778	−6.911701	2.299875
27	6	−3.298816	−6.223675	4.055729
28	1	−3.047857	−7.274488	4.256949
29	1	−4.226825	−6.047298	4.618168
30	6	−2.251858	−5.319028	4.681232
31	1	−2.506010	−4.264386	4.536658
32	1	−2.197204	−5.524337	5.757735
33	6	−0.235340	−6.882325	4.453713
34	6	1.291770	−6.628079	4.441676
35	6	1.477700	−5.109058	4.410807
36	1	2.278762	−4.752004	5.066686
37	1	1.682925	−4.749964	3.393433
38	6	0.121453	−4.592167	4.870693
39	1	−0.019479	−4.823748	5.937402
40	6	−0.093929	−3.110416	4.640374
41	6	−2.565083	−5.455249	−2.629390
42	6	1.813028	−7.433480	3.253205
43	6	−0.513343	−7.994332	3.448748
44	6	−6.141735	−2.323437	3.221035
45	1	−6.579746	−1.628364	3.945708
46	1	−5.301442	−1.814260	2.734775
47	1	−8.098806	−3.055697	2.644313
48	1	−7.345377	−2.061008	1.392614
49	1	−6.360662	−3.983251	4.599659
50	1	−4.675494	−3.486743	4.383146
51	1	−0.607749	−7.116595	5.459627
52	1	1.709942	−7.037393	5.371603
53	6	0.865593	−8.626866	3.211603

54	1	−1.261474	−8.712028	3.804499
55	1	1.105099	−9.333209	4.018256
56	1	0.913101	−9.187680	2.271635
57	1	1.712648	−6.840541	2.329033
58	1	2.865710	−7.715526	3.358038
59	1	−0.870584	−7.552370	2.510526
60	6	−2.276911	−6.783241	−2.972121
61	6	−1.968026	−4.373396	−3.280831
62	6	−1.035577	−4.649664	−4.277099
63	6	−0.726222	−5.953505	−4.623434
64	6	−1.348495	−7.012092	−3.979370
65	6	−2.985864	−7.970061	−2.310735
66	6	−2.343686	−2.916041	−2.999262
67	1	−0.560346	−3.827419	−4.796434
68	6	−3.417881	−2.404173	−3.987897
69	6	−4.282159	−8.369181	−3.055498
70	1	−2.702659	−2.805369	−1.980274
71	1	−3.216814	−7.739272	−1.273021
72	1	−3.642414	−1.359959	−3.791675
73	1	−4.996446	−7.551305	−3.075020
74	1	−4.059063	−8.646411	−4.081185
75	1	−4.334905	−2.978087	−3.894379
76	1	−3.064390	−2.491215	−5.010716
77	1	−4.746900	−9.219541	−2.565048
78	6	0.378840	−0.875703	5.644868
79	6	−0.644551	−0.205780	6.321580
80	6	1.452658	−0.199681	5.054068
81	6	1.472806	1.186797	5.137958
82	6	0.463024	1.873540	5.795638
83	6	−0.583972	1.183438	6.383110
84	6	−1.783365	−0.950621	7.025823
85	6	2.613097	−0.939268	4.380362
86	1	2.294815	1.733671	4.694467
87	6	3.702448	−1.367142	5.391915
88	6	−1.446387	−1.273858	8.500670
89	1	2.246412	−1.815319	3.849393
90	1	−2.011931	−1.871411	6.494198
91	1	4.514821	−1.871763	4.876916
92	1	−0.569154	−1.909818	8.573539
93	1	−1.250350	−0.360880	9.054549

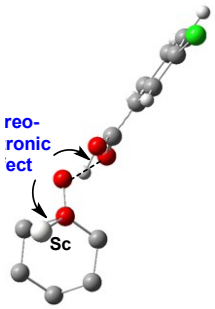
94	1	3.298157	−2.041844	6.140128
95	1	4.107869	−0.498917	5.902445
96	1	−2.281869	−1.785087	8.969904
97	1	−1.363073	1.725296	6.904361
98	1	−1.114643	−8.030006	−4.264396
99	6	−1.458063	−0.260645	1.038163
100	6	−1.498427	0.364286	2.427261
101	6	−2.780761	0.116777	0.209848
102	1	−0.594032	0.028895	2.951843
103	1	−1.426498	1.452983	2.298773
104	1	−2.735217	−0.413698	−0.745369
105	1	−2.802755	1.195505	0.019877
106	8	−1.209041	−1.613099	1.033578
107	6	−2.759763	0.016628	3.193218
108	6	−3.984306	0.428366	2.394538
109	6	−4.011688	−0.284183	1.048136
110	1	−2.796631	−1.065440	3.411774
111	1	−2.745039	0.529419	4.162338
112	6	−5.251100	−0.030974	0.216972
113	1	−3.916844	−1.371209	1.233734
114	6	−5.440472	−0.740627	−0.976704
115	6	−6.579746	−0.562109	−1.749020
116	6	−7.556407	0.345250	−1.344512
117	6	−7.377282	1.067418	−0.170045
118	6	−6.233211	0.886100	0.601666
119	1	−8.130872	1.783813	0.149255
120	1	−6.119468	1.468979	1.512788
121	1	−8.447874	0.496356	−1.948590
122	1	−6.703275	−1.116945	−2.677049
123	1	−4.676130	−1.446653	−1.310090
124	1	−3.966064	1.518023	2.230059
125	6	2.094030	−6.394363	−1.519448
126	6	1.180448	−5.927240	−0.565478
127	6	2.085934	−7.738397	−1.864572
128	6	0.266003	−6.804823	0.027829
129	6	0.269112	−8.144440	−0.333711
130	6	1.177205	−8.617892	−1.276461
131	1	2.806138	−5.719037	−1.985978
132	1	1.189214	−9.667229	−1.562267
133	1	−0.440471	−8.837379	0.115952

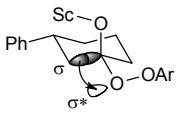
134	1	−0.421744	−6.424371	0.778890
135	6	1.186379	−4.515902	−0.186492
136	8	0.449873	−4.000619	0.675860
137	8	2.068751	−3.785825	−0.826954
138	1	1.982583	−2.848958	−0.545905
139	8	−0.654952	0.427581	0.172799
140	1	−4.899807	0.220206	2.961847
141	1	0.377944	−1.502313	0.509102
142	6	4.112457	−0.709163	0.293129
143	6	3.101780	0.265720	0.255608
144	6	5.423638	−0.317674	0.089551
145	6	3.410591	1.617240	0.026760
146	6	4.730111	1.983118	−0.186257
147	6	5.737162	1.023768	−0.155195
148	1	3.889816	−1.754494	0.495044
149	1	6.775067	1.303723	−0.321649
150	1	4.982669	3.021446	−0.384209
151	1	2.614472	2.356108	−0.007999
152	6	1.719358	−0.104975	0.445037
153	8	0.885334	0.780280	0.803679
154	8	1.356496	−1.345788	0.276922
155	17	6.686069	−1.496013	0.139961
156	17	3.207997	−8.325766	−3.038345
157	1	−0.003974	−6.148159	−5.408442
158	1	−1.451851	−2.300621	−3.098910
159	1	−2.310287	−8.822219	−2.308715
160	1	0.498569	2.955551	5.857674
161	1	3.063940	−0.278773	3.643300
162	1	−2.676231	−0.329897	6.998004

(g) **L-RaEt$_2$**-TS-(*R*)-**3a**



L-RaEt$_2$-TS-(*R*)-**3a**





TS-(*R*)-**3a**

Zero-point correction = 1.43695 a.u.
Thermal correction to Gibbs Free Energy = 1.32190 a.u.
Sum of electronic and zero-point Energies = −5159.04343 a.u.
Sum of electronic and thermal Free Energies = −5159.15849 a.u.
Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	0.333055	−0.375285	5.116647
2	6	−0.399317	0.360040	6.052521
3	6	1.109814	0.239264	4.126829
4	6	1.105842	1.626077	4.065569
5	6	0.366195	2.376414	4.968456
6	6	−0.372338	1.749159	5.956500
7	6	−1.165850	−0.307938	7.197962
8	6	2.007495	−0.557547	3.175450
9	1	1.700943	2.125889	3.312501
10	6	3.379607	−0.888985	3.808963
11	6	−0.298270	−0.450873	8.471108
12	1	1.516622	−1.478632	2.869767
13	1	−1.523083	−1.286914	6.887907
14	1	3.997890	−1.438981	3.105224
15	1	0.580226	−1.061504	8.284037

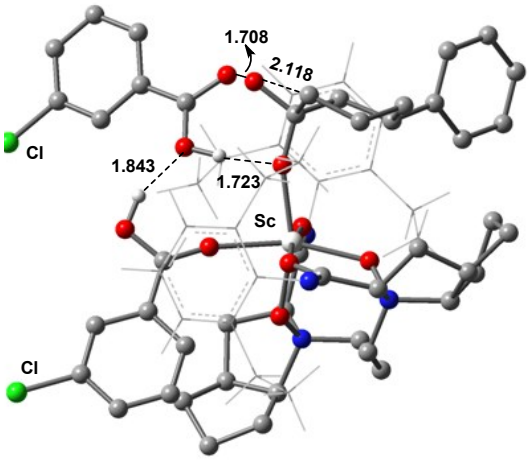
16	1	0.033883	0.523418	8.816306
17	1	3.259709	−1.490810	4.704321
18	1	3.900981	0.023527	4.081474
19	1	−0.876804	−0.915270	9.264296
20	1	−0.933304	2.339782	6.669915
21	21	−1.648142	−3.245020	1.624489
22	8	−2.419829	−4.323362	−0.054902
23	8	−3.604762	−3.620418	2.255279
24	8	−0.941299	−4.907474	2.712546
25	8	−1.017599	−2.304936	3.473981
26	7	−4.369157	−4.742531	2.031630
27	7	−0.996130	−5.117813	4.063949
28	7	0.332134	−1.837944	5.227525
29	1	0.841883	−2.247632	6.009915
30	7	−3.822151	−5.116669	−1.633120
31	1	−4.764738	−5.463610	−1.809606
32	6	−3.553840	−4.729810	−0.396114
33	6	−4.731420	−4.840786	0.561423
34	1	−5.167399	−5.845897	0.441798
35	6	−5.849233	−3.819850	0.417671
36	1	−6.353701	−3.888254	−0.552596
37	1	−5.445831	−2.803291	0.523385
38	6	−6.759729	−4.189827	1.587858
39	6	−7.570134	−3.041158	2.192141
40	1	−7.400752	−5.026707	1.279816
41	6	−5.790314	−4.637214	2.705138
42	6	−5.906945	−3.616753	3.833430
43	1	−5.993929	−5.659846	3.039781
44	6	−3.667290	−5.989328	2.510832
45	1	−2.752776	−6.087254	1.922751
46	1	−4.333858	−6.825091	2.264990
47	6	−3.374818	−6.015858	4.002722
48	1	−3.033896	−7.035308	4.229083
49	1	−4.309829	−5.904616	4.569897
50	6	−2.402416	−5.009218	4.591989
51	1	−2.728349	−3.982944	4.403912
52	1	−2.339124	−5.166285	5.675891
53	6	−0.336201	−6.482119	4.433489
54	6	1.174233	−6.175929	4.578515
55	6	1.320384	−4.663616	4.412551

56	1	2.089148	−4.230306	5.061263
57	1	1.564933	−4.392557	3.375790
58	6	−0.067891	−4.146072	4.769948
59	1	−0.246685	−4.299933	5.846025
60	6	−0.308667	−2.683336	4.434131
61	6	−2.847383	−5.211117	−2.727297
62	6	1.862877	−7.077999	3.554034
63	6	−0.465199	−7.600401	3.408293
64	6	−6.626952	−2.419777	3.215256
65	1	−7.132354	−1.796664	3.961981
66	1	−5.893570	−1.779357	2.713323
67	1	−8.465473	−3.442095	2.684620
68	1	−7.918293	−2.333062	1.429352
69	1	−6.527394	−4.070007	4.619219
70	1	−4.946766	−3.347208	4.287462
71	1	−0.791000	−6.742365	5.398029
72	1	1.485216	−6.463271	5.592437
73	6	0.913898	−8.267387	3.448977
74	1	−1.289112	−8.291932	3.619567
75	1	1.004243	−8.912576	4.333983
76	1	1.099527	−8.897384	2.572095
77	1	1.914599	−6.559645	2.583404
78	1	2.882560	−7.352254	3.842740
79	1	−0.615326	−7.156838	2.414842
80	6	−2.293730	−6.464896	−3.009389
81	6	−2.542901	−4.073639	−3.480509
82	6	−1.635415	−4.210634	−4.525340
83	6	−1.063304	−5.439182	−4.813797
84	6	−1.393499	−6.557306	−4.064598
85	6	−2.690027	−7.726204	−2.235115
86	6	−3.215445	−2.721400	−3.229462
87	1	−1.385973	−3.345679	−5.126330
88	6	−4.564065	−2.594752	−3.976332
89	6	−3.920278	−8.431603	−2.853829
90	1	−3.374200	−2.573101	−2.164675
91	1	−2.896489	−7.480161	−1.195676
92	1	−5.003185	−1.618597	−3.792434
93	1	−4.790163	−7.781635	−2.852629
94	1	−3.715120	−8.720148	−3.880158
95	1	−5.265663	−3.354865	−3.646502

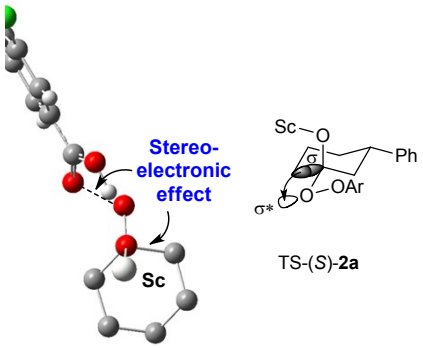
96	1	−4.418550	−2.707972	−5.046330
97	1	−4.159952	−9.327462	−2.288445
98	1	−0.954160	−7.517144	−4.304733
99	6	−1.914143	−0.062551	0.811758
100	6	−2.542092	0.411769	2.210287
101	6	−2.837966	0.327306	−0.335726
102	1	−1.882464	0.070257	3.014827
103	1	−2.607439	1.505371	2.225385
104	1	−2.358791	−0.014261	−1.263372
105	1	−2.889025	1.424086	−0.373784
106	8	−1.593085	−1.399411	0.805971
107	6	−3.948591	−0.206572	2.329935
108	6	−4.828093	0.193914	1.150370
109	6	−4.219063	−0.269502	−0.164029
110	1	−3.825119	−1.302091	2.304969
111	1	−4.134058	−1.370607	−0.178020
112	1	−4.941548	1.288962	1.119492
113	6	2.901115	−5.921204	−0.119233
114	6	1.593751	−5.469141	0.103087
115	6	3.119524	−7.272905	−0.345812
116	6	0.517202	−6.364043	0.083517
117	6	0.754133	−7.708977	−0.159489
118	6	2.050952	−8.169829	−0.371194
119	1	3.740912	−5.231242	−0.115084
120	1	2.243958	−9.223159	−0.563855
121	1	−0.072570	−8.415597	−0.188554
122	1	−0.491465	−5.987431	0.241606
123	6	1.343726	−4.054174	0.352655
124	8	0.245312	−3.574902	0.679705
125	8	2.390772	−3.270616	0.209612
126	1	2.098943	−2.336527	0.284022
127	8	−0.827645	0.752008	0.919584
128	1	−5.842410	−0.212241	1.280742
129	17	4.726454	−7.846217	−0.606622
130	6	−4.499639	0.147987	3.689298
131	6	−4.138721	−0.638820	4.789593
132	6	−5.387673	1.207396	3.887432
133	6	−4.689380	−0.409150	6.043104
134	1	−3.425830	−1.456864	4.639728
135	6	−5.932230	1.446990	5.145004

136	1	−5.681858	1.845255	3.055746
137	6	−5.593378	0.635915	6.222712
138	1	−4.423131	−1.044180	6.885968
139	1	−6.633208	2.267350	5.280690
140	1	−6.030343	0.818214	7.201778
141	1	−4.855695	0.014223	−1.010510
142	1	−0.057828	−1.226473	0.184006
143	6	2.842992	−0.466170	−2.125130
144	6	2.015163	0.536615	−1.593427
145	6	3.913236	−0.095199	−2.919182
146	6	2.253039	1.892794	−1.872258
147	6	3.332645	2.239265	−2.668475
148	6	4.163313	1.253462	−3.192704
149	1	2.649364	−1.520022	−1.937945
150	1	5.012387	1.519967	−3.818366
151	1	3.537076	3.284359	−2.885666
152	1	1.602641	2.655938	−1.453370
153	6	0.888886	0.173265	−0.765141
154	8	−0.045346	1.011060	−0.585161
155	8	0.839257	−1.023528	−0.250941
156	17	4.948048	−1.309394	−3.583172
157	1	−2.038218	0.297147	7.432922
158	1	−2.549321	−1.932912	−3.571941
159	1	−0.362724	−5.528805	−5.636539
160	1	−1.851375	−8.418355	−2.244417
161	1	2.172172	0.034674	2.278399
162	1	0.379437	3.458973	4.908605

(h) **L-RaEt$_2$**-TS-(*S*)-**2a**



L-RaEt$_2$-TS-(*S*)-**2a**



TS-(*S*)-**2a**

Zero-point correction = 1.43613 a.u.
Thermal correction to Gibbs Free Energy = 1.31983 a.u.
Sum of electronic and zero-point Energies = −5159.03462 a.u.
Sum of electronic and thermal Free Energies = −5159.15091 a.u.
Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	1	0.592473	−1.387640	0.660592
2	6	4.302323	−0.503534	0.771937
3	6	3.266723	0.446609	0.783341
4	6	5.612144	−0.063454	0.718037
5	6	3.552196	1.822637	0.748520
6	6	4.872057	2.239702	0.690199
7	6	5.902561	1.304931	0.675931
8	1	4.097506	−1.570675	0.816449
9	1	6.941110	1.625513	0.630374
10	1	5.108052	3.299711	0.649541
11	1	2.739942	2.544223	0.745806
12	6	1.887140	0.028223	0.824179
13	8	0.984286	0.858693	1.151707
14	8	1.582564	−1.211876	0.544354

15	17	6.902602	−1.211711	0.706567
16	6	−3.740116	0.857119	3.768890
17	6	−4.015640	0.182652	4.957957
18	6	−3.942262	2.239349	3.725805
19	6	−4.504325	0.861195	6.070852
20	1	−3.853325	−0.897515	5.005418
21	6	−4.418552	2.923445	4.837754
22	1	−3.733565	2.797687	2.811933
23	6	−4.707948	2.234733	6.011952
24	1	−4.736524	0.317238	6.984476
25	1	−4.573398	3.998752	4.784666
26	1	−5.093939	2.768710	6.877137
27	6	0.501089	−0.898677	5.732051
28	6	−0.499164	−0.366492	6.549809
29	6	1.468825	−0.098530	5.116204
30	6	1.388369	1.275557	5.300069
31	6	0.386750	1.829490	6.084022
32	6	−0.542446	1.015545	6.709754
33	6	−1.485314	−1.256554	7.312123
34	6	2.633501	−0.698538	4.323881
35	1	2.126248	1.918062	4.837465
36	6	3.785396	−1.171774	5.241791
37	6	−0.942778	−1.669237	8.701177
38	1	2.289447	−1.532045	3.714336
39	1	−1.712898	−2.146780	6.730265
40	1	4.600991	−1.571006	4.645698
41	1	−1.672982	−2.284791	9.218377
42	1	−0.018792	−2.233065	8.613594
43	1	3.449393	−1.945404	5.924911
44	1	4.165900	−0.342345	5.830098
45	1	−0.746511	−0.790699	9.308110
46	1	−1.308908	1.453047	7.336890
47	21	−1.290868	−3.376776	1.725828
48	8	−2.272158	−4.292745	0.039275
49	8	−3.226075	−3.645065	2.463094
50	8	−0.678107	−5.140006	2.683823
51	8	−0.448089	−2.576303	3.571784
52	7	−4.087611	−4.697279	2.247570
53	7	−0.644400	−5.439048	4.017586
54	7	0.576584	−2.355140	5.584147

55	1	0.989543	−2.877489	6.355915
56	7	−3.799893	−5.059103	−1.439980
57	1	−4.763987	−5.375282	−1.541412
58	6	−3.436021	−4.666062	−0.228100
59	6	−4.555165	−4.720705	0.801789
60	1	−5.066506	−5.689944	0.689910
61	6	−5.607874	−3.627934	0.759315
62	1	−6.184351	−3.642371	−0.172374
63	1	−5.133427	−2.644063	0.853214
64	6	−6.453944	−3.950775	1.989530
65	6	−7.098046	−2.738910	2.667863
66	1	−7.193567	−4.716525	1.721349
67	6	−5.446924	−4.509657	3.020437
68	6	−5.404808	−3.518520	4.178115
69	1	−5.706721	−5.523747	3.342301
70	6	−3.462268	−6.023200	2.614788
71	1	−2.596502	−6.155679	1.961366
72	1	−4.211227	−6.784863	2.366234
73	6	−3.081288	−6.177082	4.077197
74	1	−2.811804	−7.233256	4.215286
75	1	−3.965786	−6.033724	4.713882
76	6	−1.998499	−5.287785	4.656974
77	1	−2.266630	−4.231379	4.560947
78	1	−1.868592	−5.524449	5.720314
79	6	−0.010223	−6.841233	4.241755
80	6	1.518304	−6.588607	4.196334
81	6	1.702142	−5.067899	4.163100
82	1	2.543066	−4.716599	4.770556
83	1	1.844736	−4.699731	3.138645
84	6	0.376800	−4.564366	4.716001
85	1	0.304512	−4.841614	5.778861
86	6	0.115465	−3.075506	4.572414
87	6	−2.912809	−5.239386	−2.596701
88	6	2.019671	−7.405928	3.005295
89	6	−0.321128	−7.902756	3.195469
90	6	−6.026253	−2.236032	3.627960
91	1	−6.419913	−1.582201	4.413259
92	1	−5.261856	−1.659442	3.090609
93	1	−7.990079	−3.055283	3.223760
94	1	−7.427875	−1.984826	1.942117

95	1	−6.037121	−3.930911	4.977071
96	1	−4.402051	−3.375423	4.594851
97	1	−0.347943	−7.128026	5.246460
98	1	1.953572	−6.989972	5.121988
99	6	1.037670	−8.572065	2.952395
100	1	−1.097156	−8.607258	3.516451
101	1	1.256704	−9.294111	3.751243
102	1	1.067637	−9.122204	2.005431
103	1	1.946750	−6.811218	2.080217
104	1	3.062373	−7.720837	3.116479
105	1	−0.650371	−7.410094	2.271246
106	6	−2.535534	−6.545143	−2.932297
107	6	−2.521911	−4.132785	−3.354965
108	6	−1.698370	−4.355901	−4.453778
109	6	−1.295127	−5.637163	−4.791929
110	6	−1.717045	−6.723288	−4.041009
111	6	−3.043360	−7.766038	−2.158386
112	6	−3.022165	−2.717105	−3.059150
113	1	−1.383029	−3.514562	−5.057480
114	6	−4.367372	−2.420947	−3.763147
115	6	−4.383153	−8.299337	−2.719572
116	1	−3.133921	−2.574522	−1.988246
117	1	−3.161195	−7.521624	−1.104783
118	1	−4.684233	−1.403635	−3.552852
119	1	−5.164287	−7.547167	−2.661774
120	1	−4.269303	−8.588298	−3.759865
121	1	−5.142857	−3.100342	−3.422528
122	1	−4.266378	−2.531467	−4.838516
123	1	−4.703163	−9.170923	−2.156005
124	1	−1.414393	−7.724033	−4.321861
125	6	−1.362661	−0.168036	0.879837
126	6	−1.862791	0.539810	2.130879
127	6	−2.396208	0.085334	−0.344761
128	1	−1.136243	0.332114	2.931150
129	1	−1.840487	1.620546	1.933382
130	1	−2.014645	−0.434622	−1.226656
131	1	−2.462266	1.158371	−0.549184
132	8	−1.085260	−1.491759	1.037207
133	6	−3.263836	0.102190	2.548997
134	6	−4.233578	0.253961	1.371323

135	6	−3.733127	−0.461731	0.130246
136	1	−3.213609	−0.971956	2.813088
137	1	−3.618386	−1.541036	0.315553
138	1	−4.368635	1.322305	1.140500
139	6	2.601479	−6.322292	−0.969758
140	6	1.424573	−5.787713	−0.429988
141	6	2.665578	−7.681543	−1.243551
142	6	0.317645	−6.608678	−0.186313
143	6	0.396481	−7.962567	−0.478120
144	6	1.567230	−8.505752	−1.000495
145	1	3.460758	−5.688678	−1.171603
146	1	1.635653	−9.566882	−1.229757
147	1	−0.456798	−8.613456	−0.298017
148	1	−0.593881	−6.173104	0.217348
149	6	1.364379	−4.367371	−0.095731
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151	8	2.385019	−3.660370	−0.522516
152	1	2.260197	−2.719373	−0.271608
153	8	−0.396130	0.510949	0.208127
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155	17	4.115279	−8.354007	−1.895707
156	1	−4.438946	−0.343976	−0.705073
157	1	−2.414926	−0.710516	7.447851
158	1	−2.277874	−2.005043	−3.408368
159	1	−0.658616	−5.792816	−5.655856
160	1	−2.300052	−8.556616	−2.227009
161	1	3.020150	0.060987	3.649804
162	1	0.341647	2.904189	6.220853

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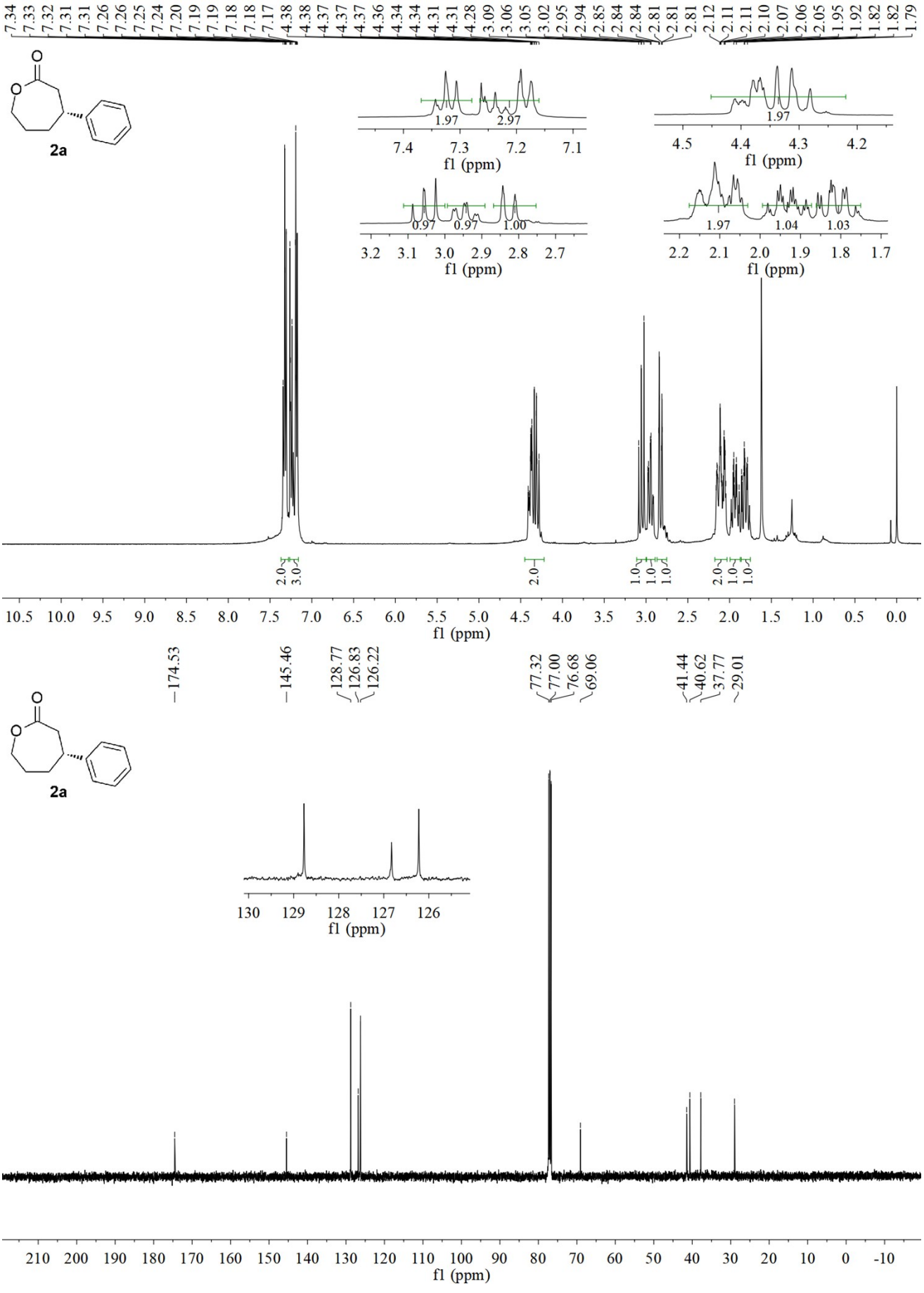
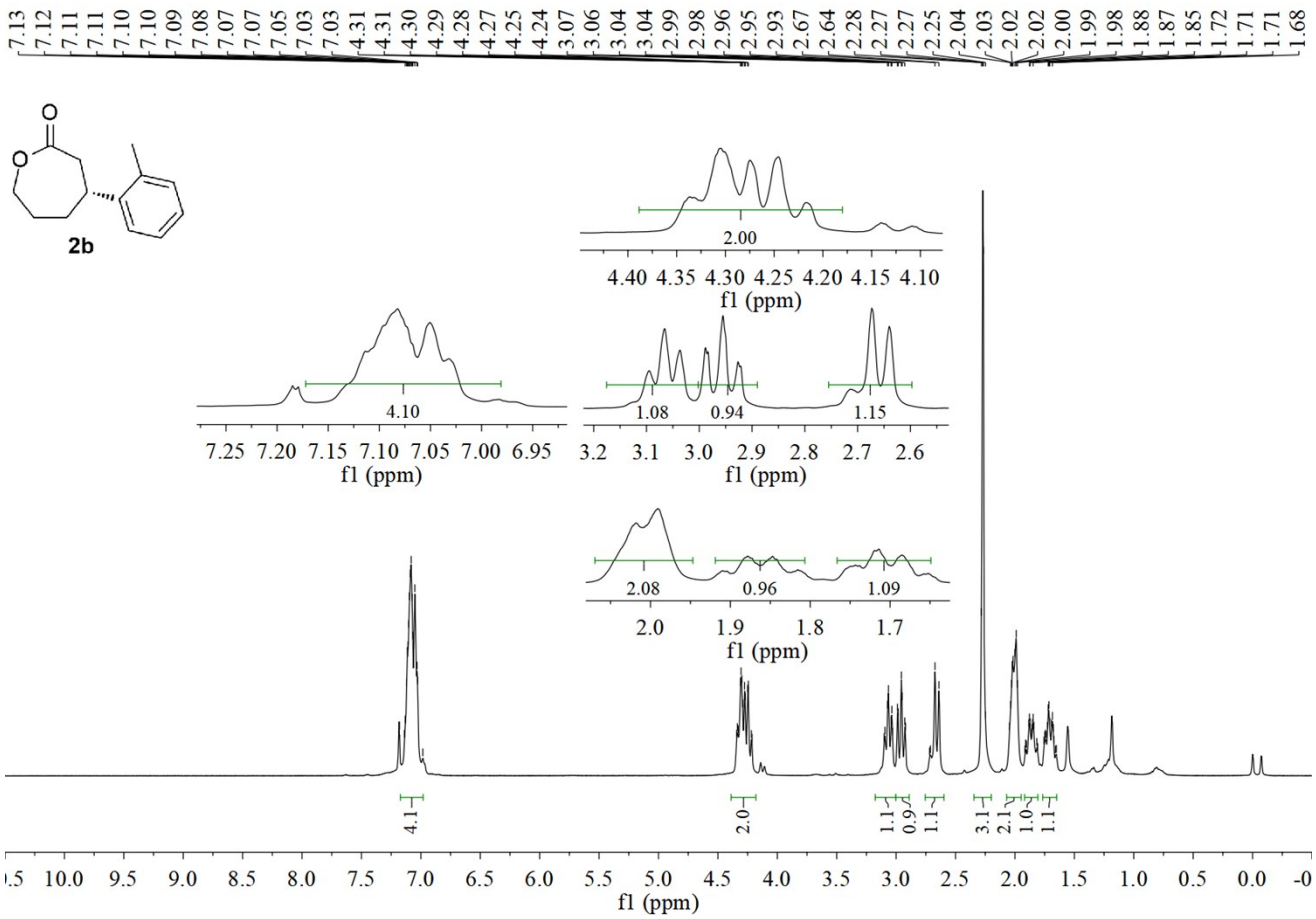
16 Copy of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR.

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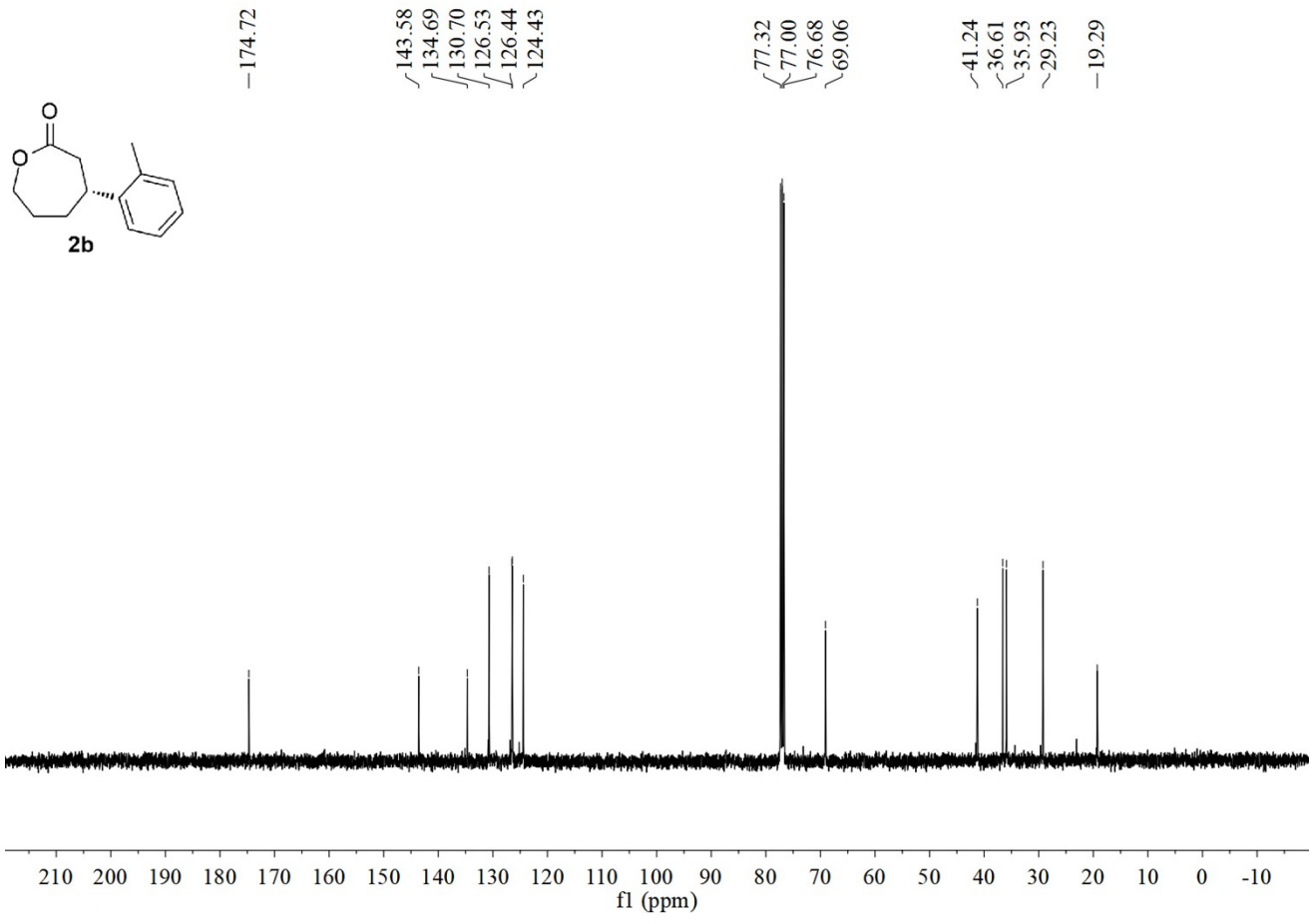
2b
2.00
4.40 4.35 4.30 4.25 4.20 4.15 4.10
f1 (ppm)
4.10
7.25 7.20 7.15 7.10 7.05 7.00 6.95
f1 (ppm)
1.08 0.94 1.15
3.2 3.1 3.0 2.9 2.8 2.7 2.6
f1 (ppm)
2.08 0.96 1.09
2.0 1.9 1.8 1.7
f1 (ppm)
4.1 2.0 1.1 0.9 1.1 3.1 2.1 1.0 1.1
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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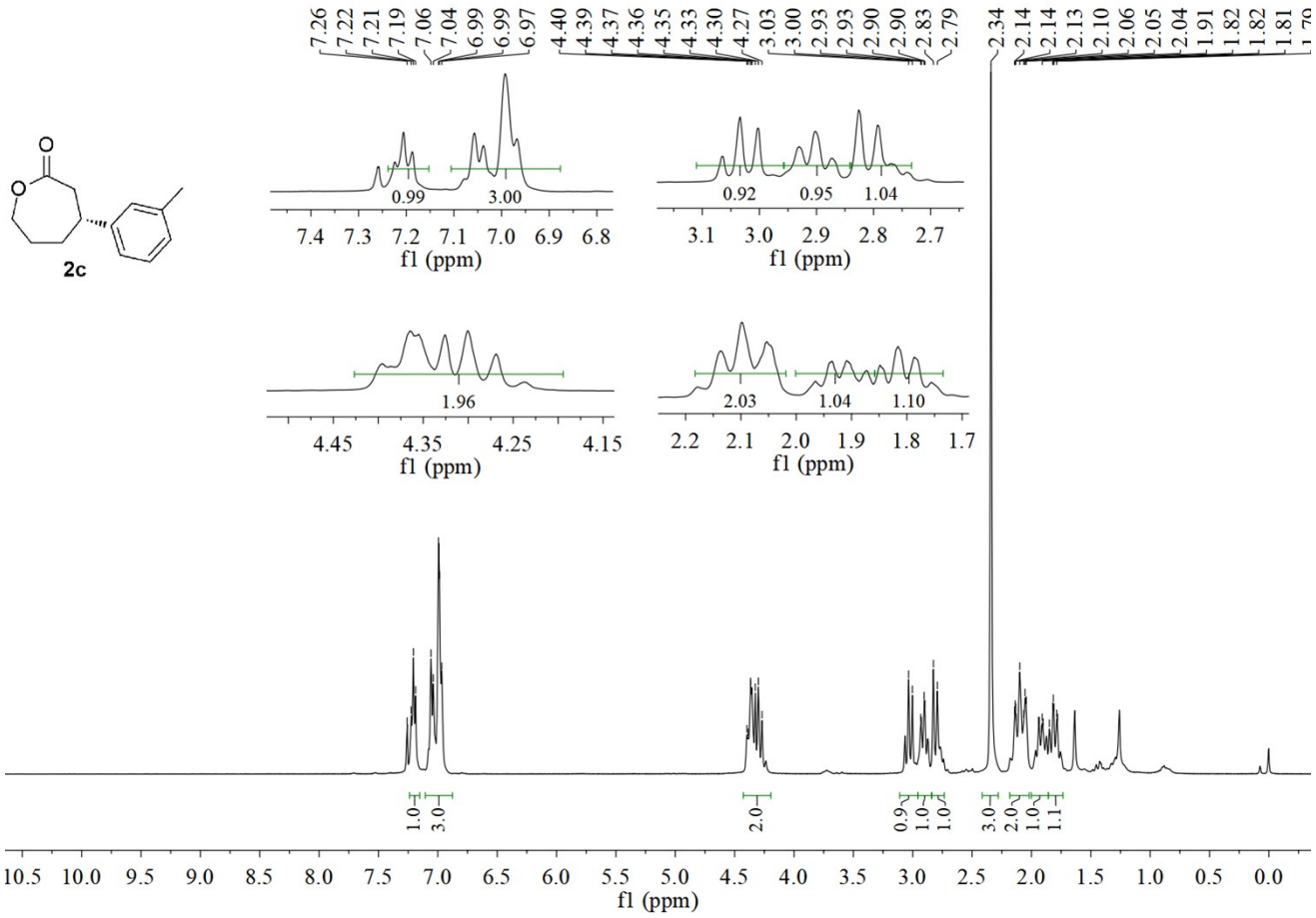
f1 (ppm)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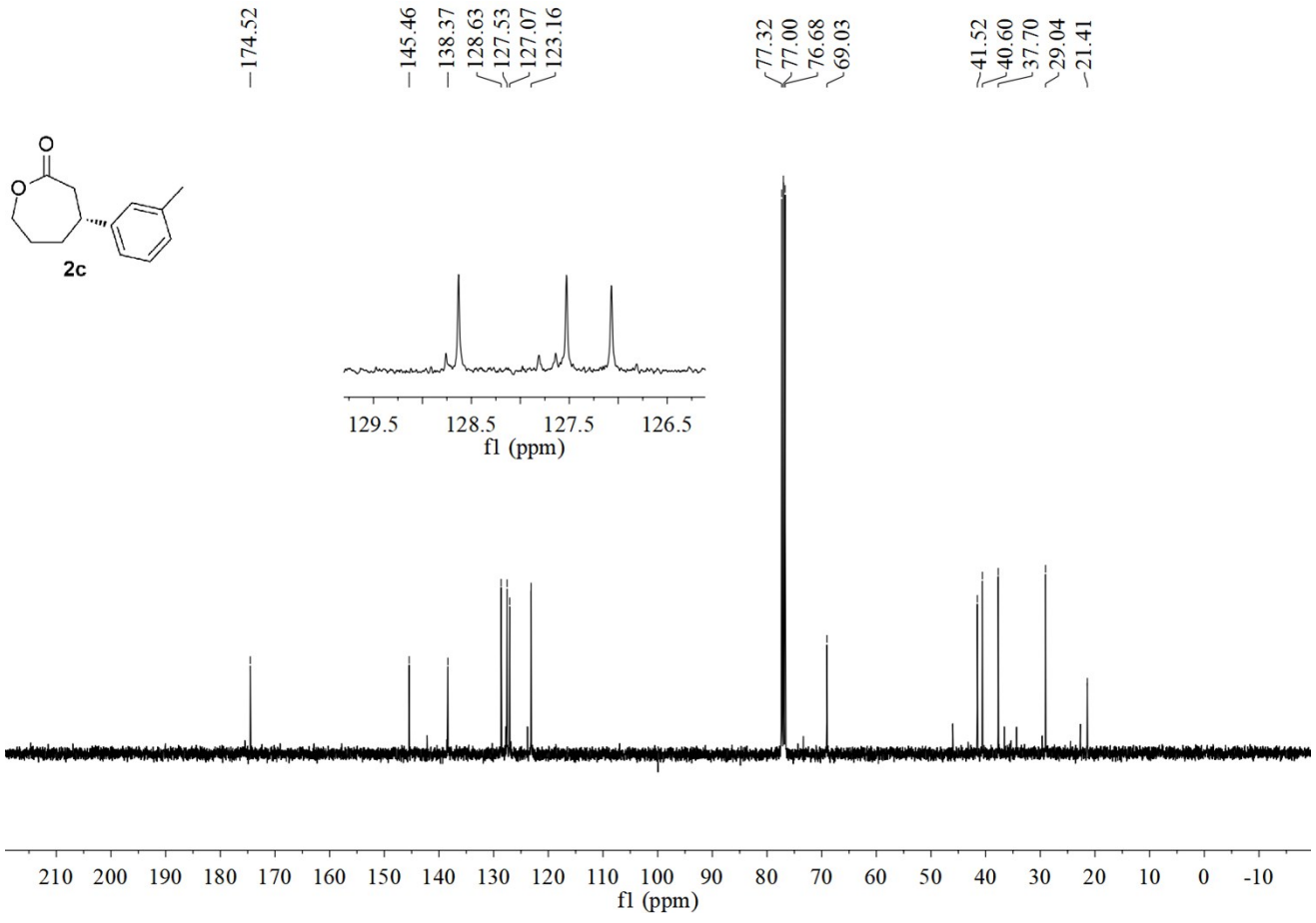
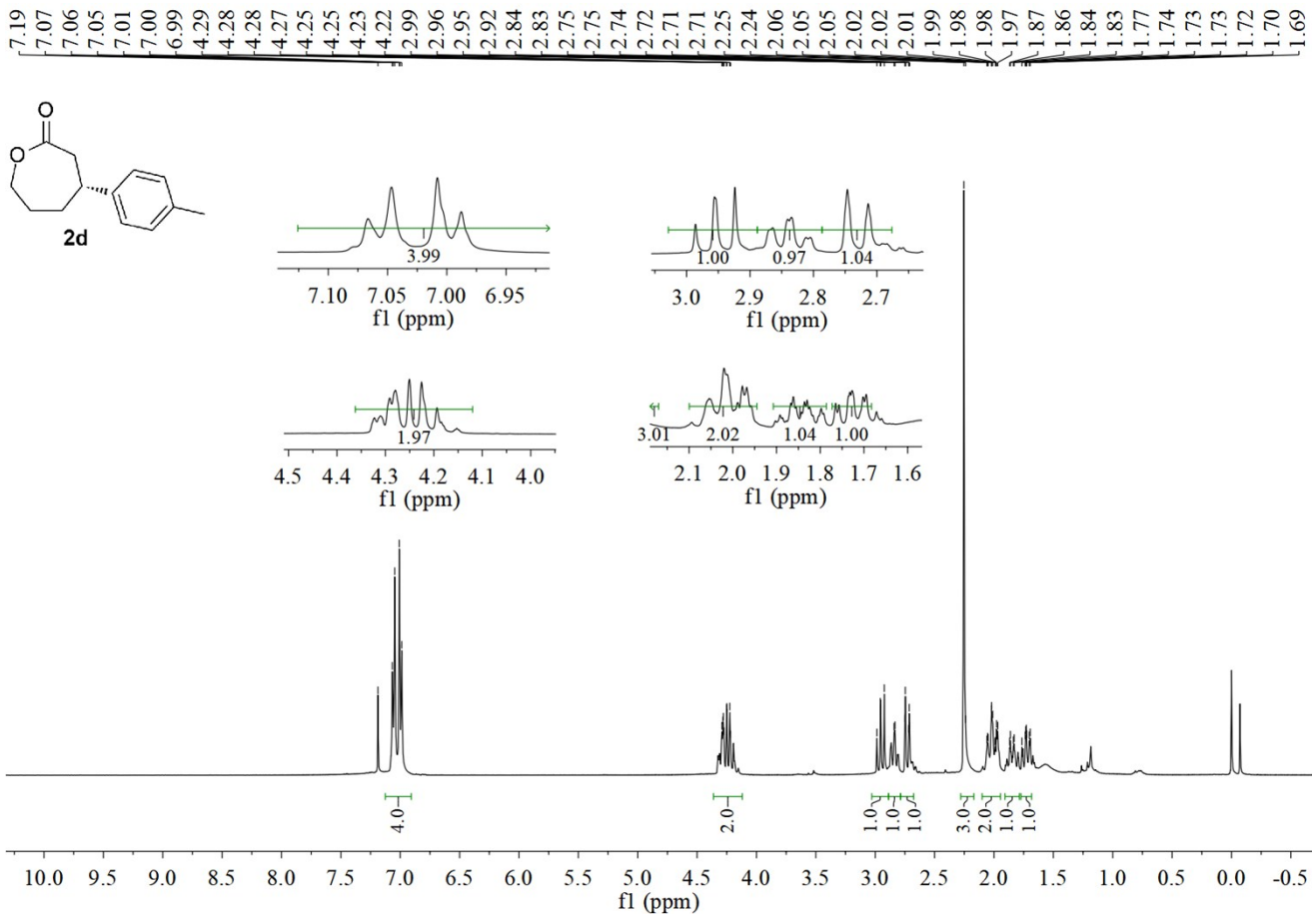
0.99 3.00
0.92 0.95 1.04
1.96
2.03 1.04 1.10
fl (ppm)
1.0 3.0 2.0 0.9 1.0 1.0 3.0 2.0 1.0 1.1
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
fl (ppm)


174.52 145.46 138.37 128.63 127.53 127.07 123.16 77.32 77.00 76.68 69.03 41.52 40.60 37.70 29.04 21.41
2c
129.5 128.5 127.5 126.5
fl (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
fl (ppm)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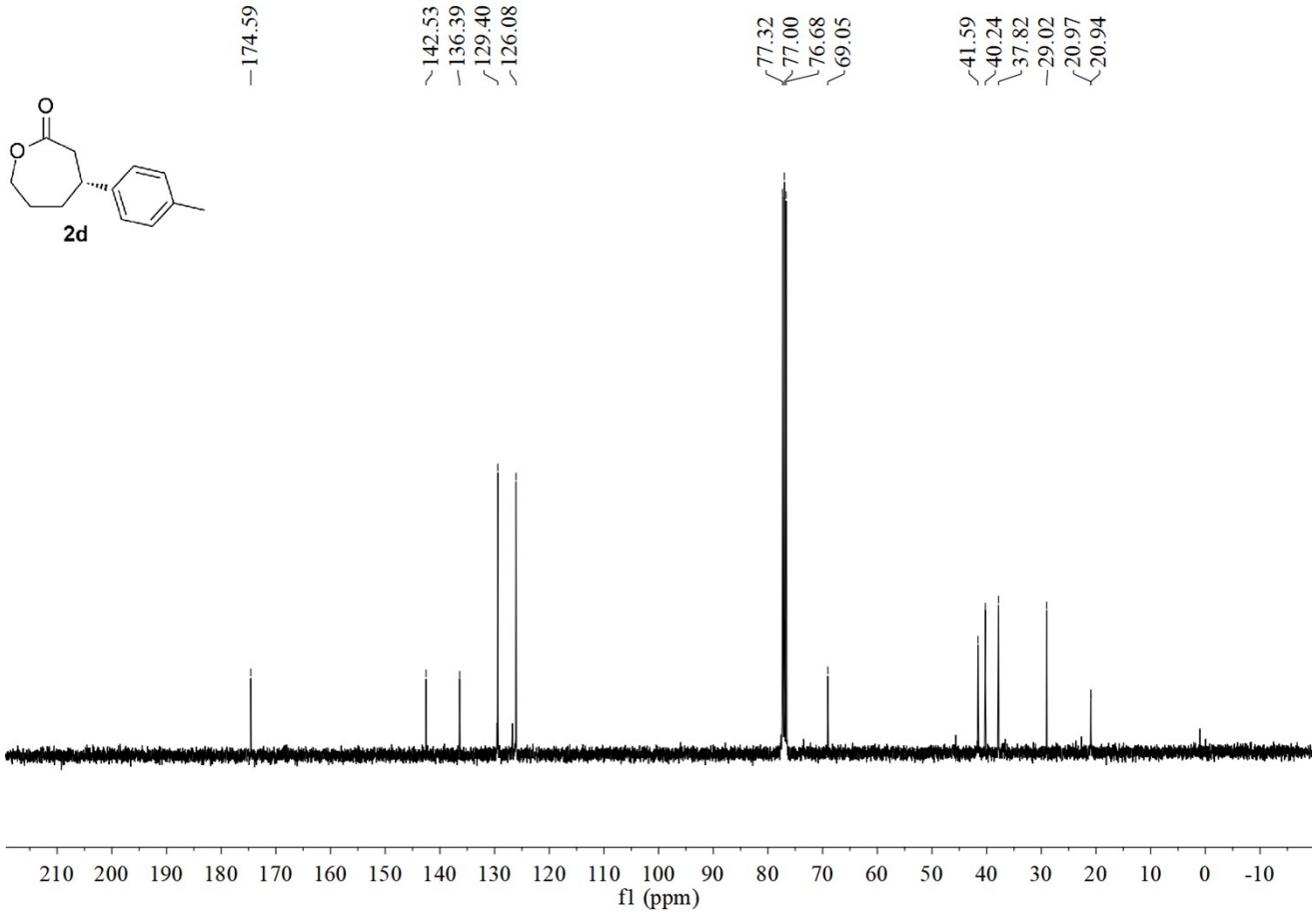
2d
3.99
7.10 7.05 7.00 6.95
f1 (ppm)
1.00 0.97 1.04
3.0 2.9 2.8 2.7
f1 (ppm)
1.97
4.5 4.4 4.3 4.2 4.1 4.0
f1 (ppm)
3.01 2.02 1.04 1.00
2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)
4.0 2.0 1.0 1.0 1.0 3.0 2.0 1.0 1.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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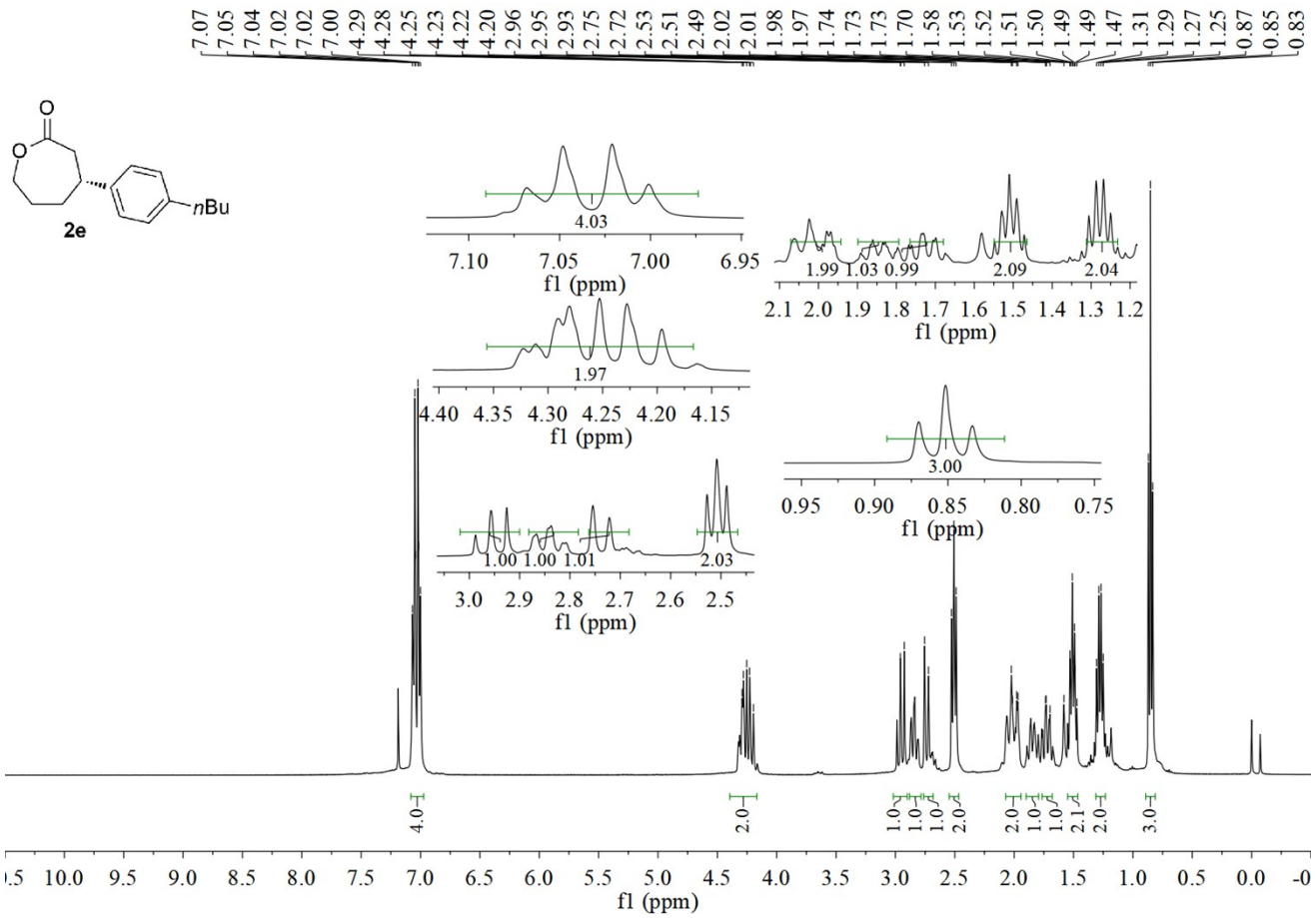
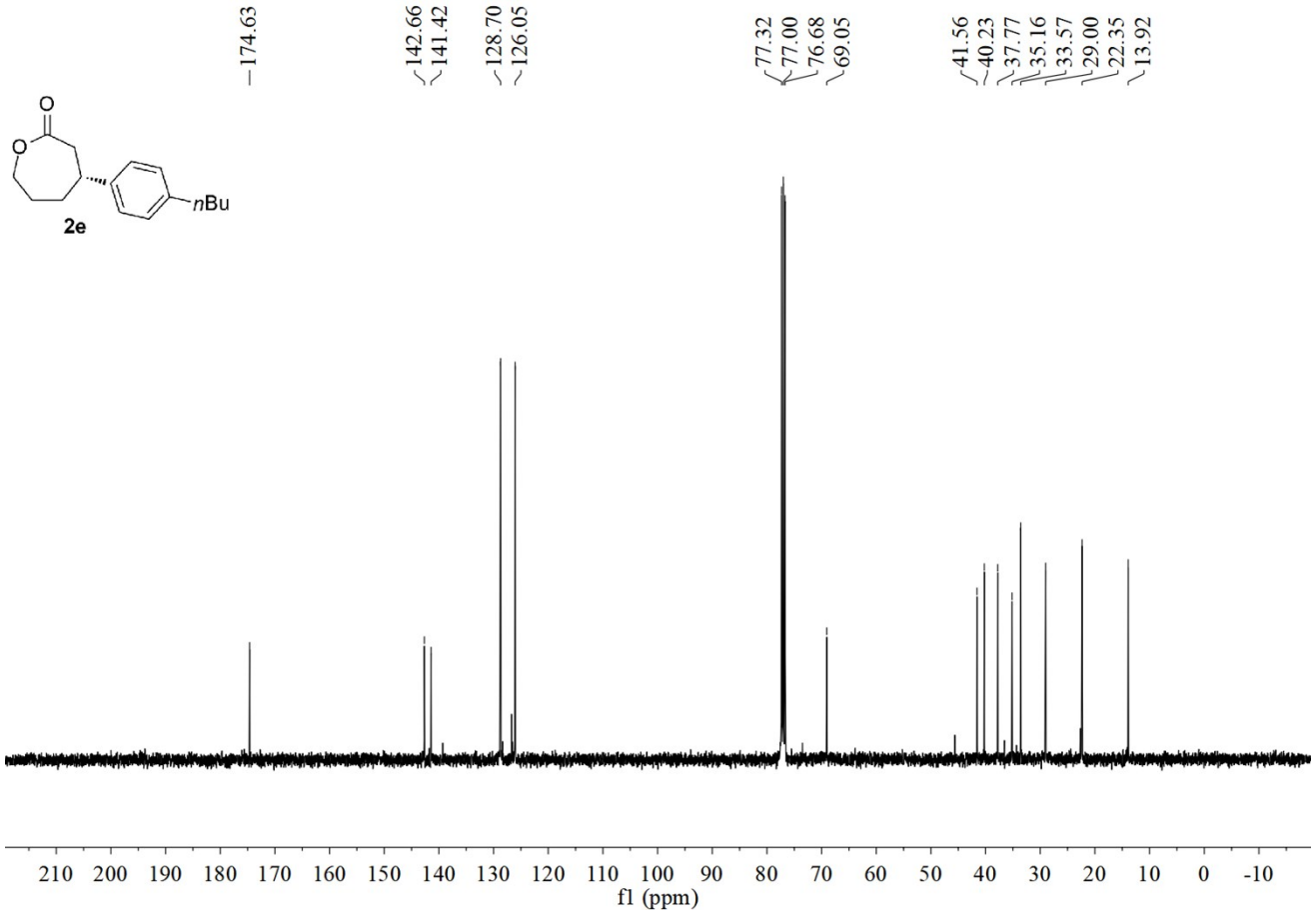
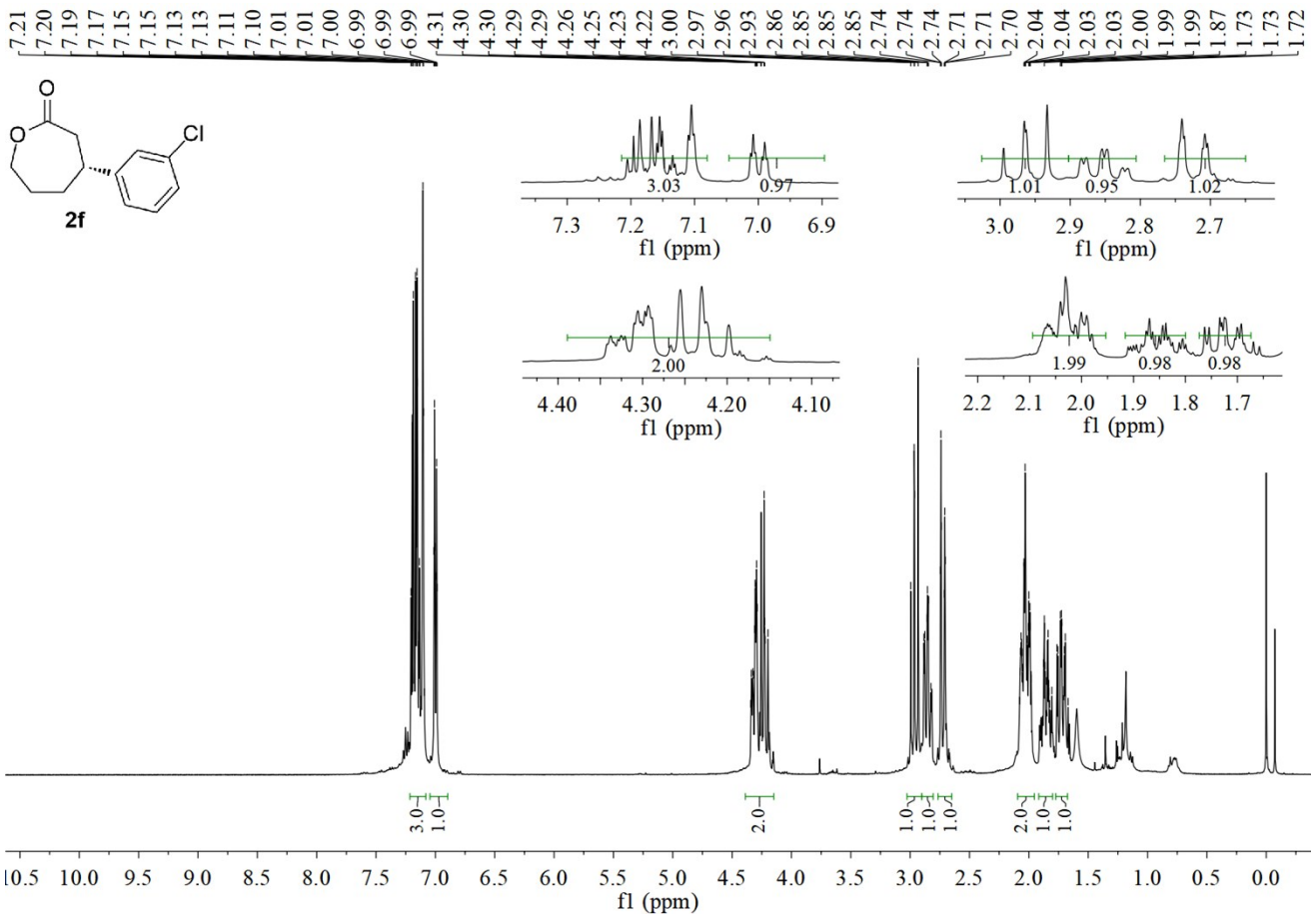
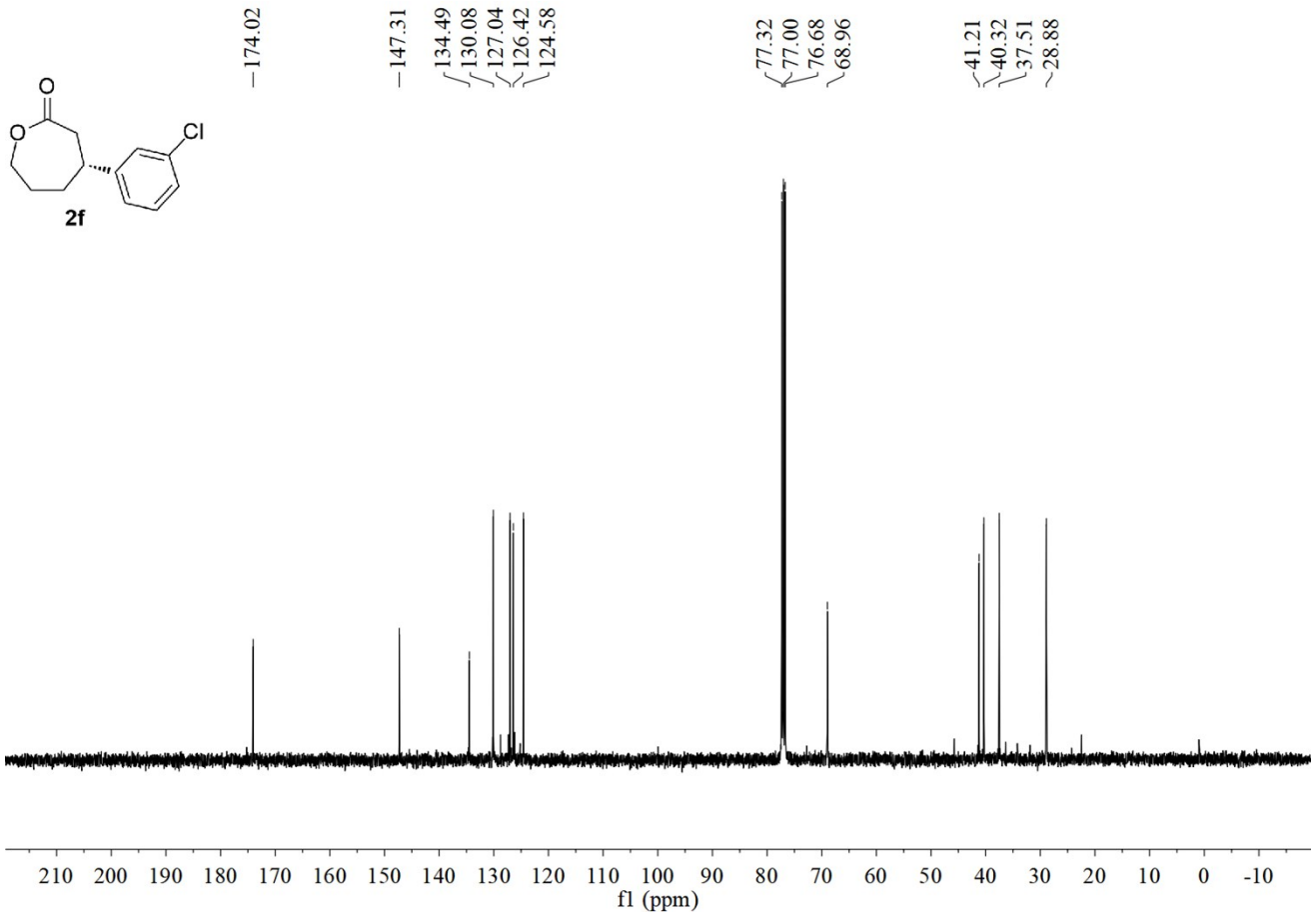
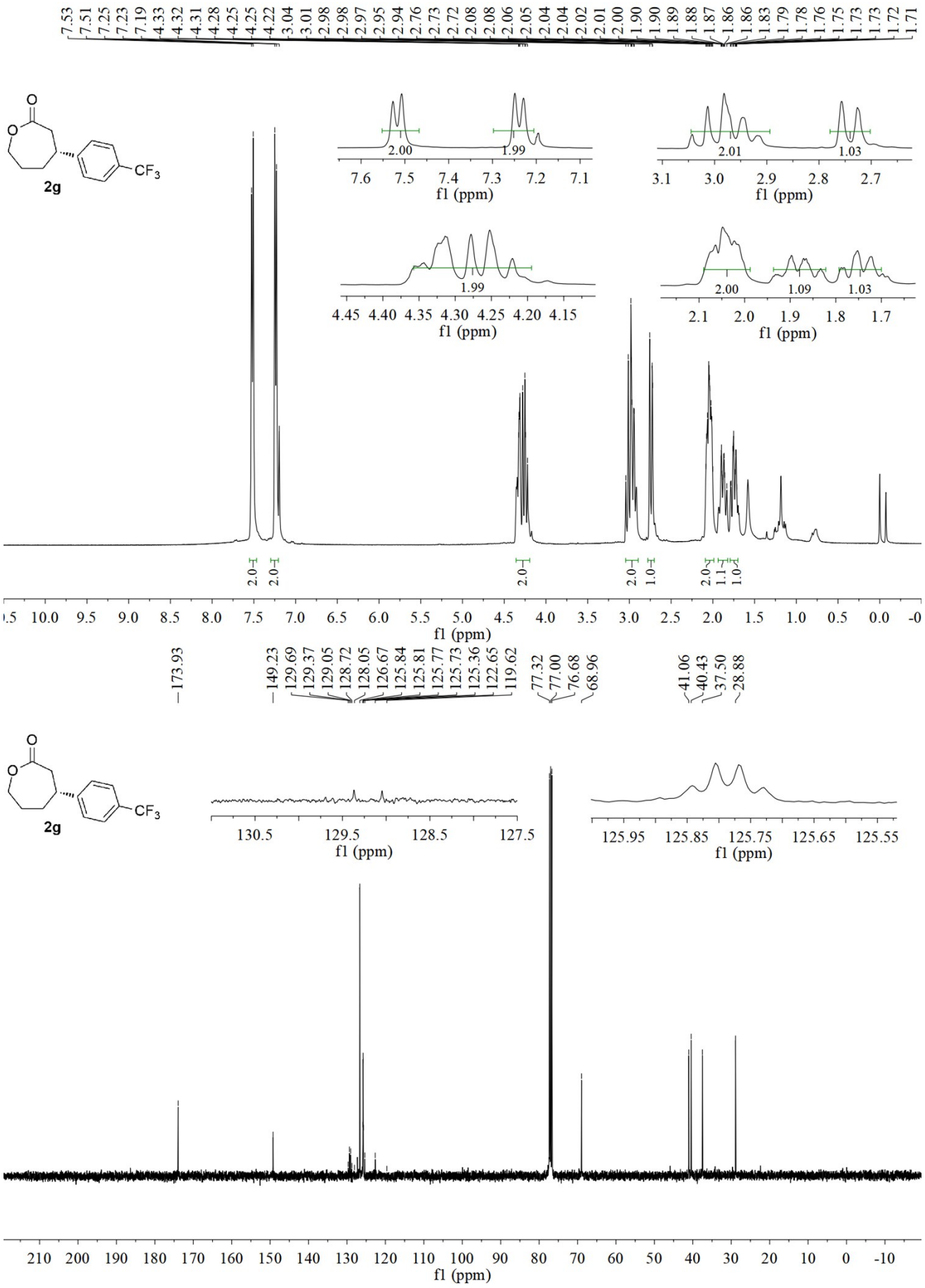
142.53 136.39 129.40 126.08
77.32 77.00 76.68 69.05
41.59 40.24 37.82 29.02 20.97 20.94
2d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

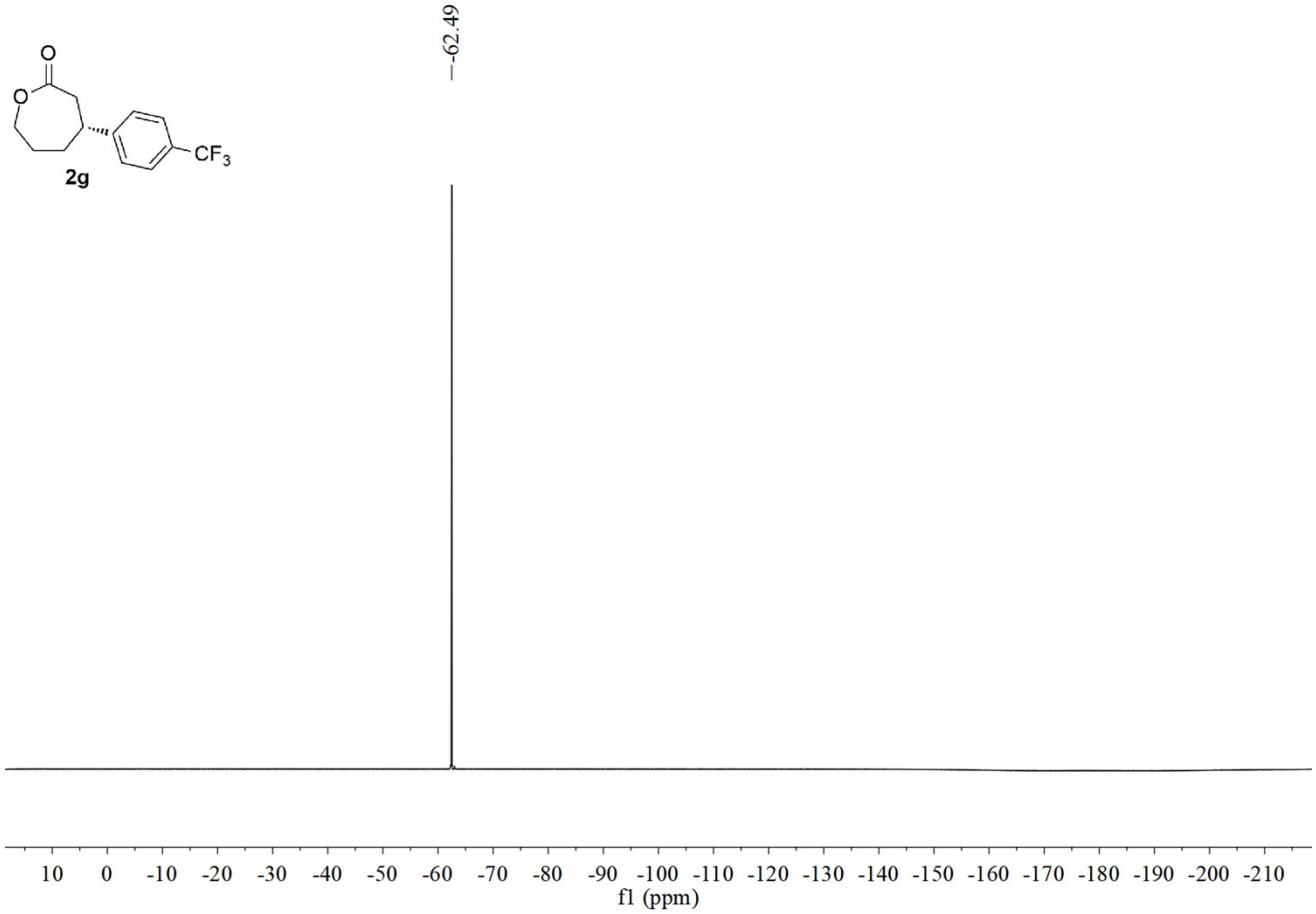

7.07 7.05 7.04 7.02 7.02 7.00 4.29 4.28 4.25 4.23 4.22 4.20 2.96 2.95 2.93 2.75 2.72 2.53 2.51 2.49 2.02 2.01 1.98 1.97 1.74 1.73 1.73 1.70 1.58 1.53 1.52 1.51 1.50 1.49 1.49 1.47 1.31 1.29 1.27 1.25 0.87 0.85 0.83
O
O
nBu
2e
4.03
7.10 7.05 7.00 6.95
f1 (ppm)
1.99 1.03 0.99 2.09 2.04
2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2
f1 (ppm)
1.97
4.40 4.35 4.30 4.25 4.20 4.15
f1 (ppm)
3.00
0.95 0.90 0.85 0.80 0.75
f1 (ppm)
1.00 1.00 1.01 2.03
3.0 2.9 2.8 2.7 2.6 2.5
f1 (ppm)
4.0 2.0 1.0 1.0 1.0 2.0 2.0 1.0 2.1 2.0 3.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

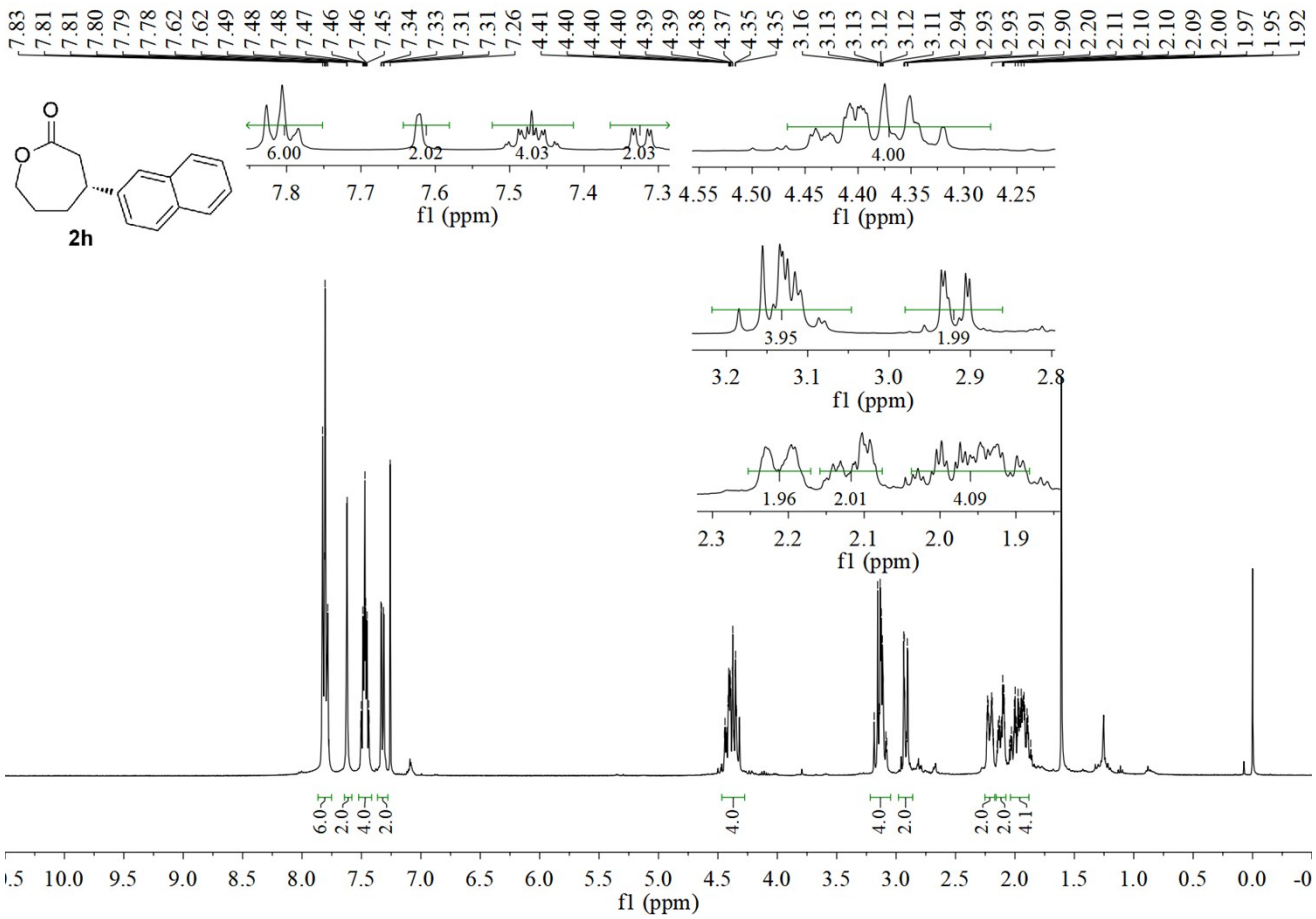

174.63
142.66 141.42 128.70 126.05
77.32 77.00 76.68 69.05
41.56 40.23 37.77 35.16 33.57 29.00 22.35 13.92
O
O
nBu
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

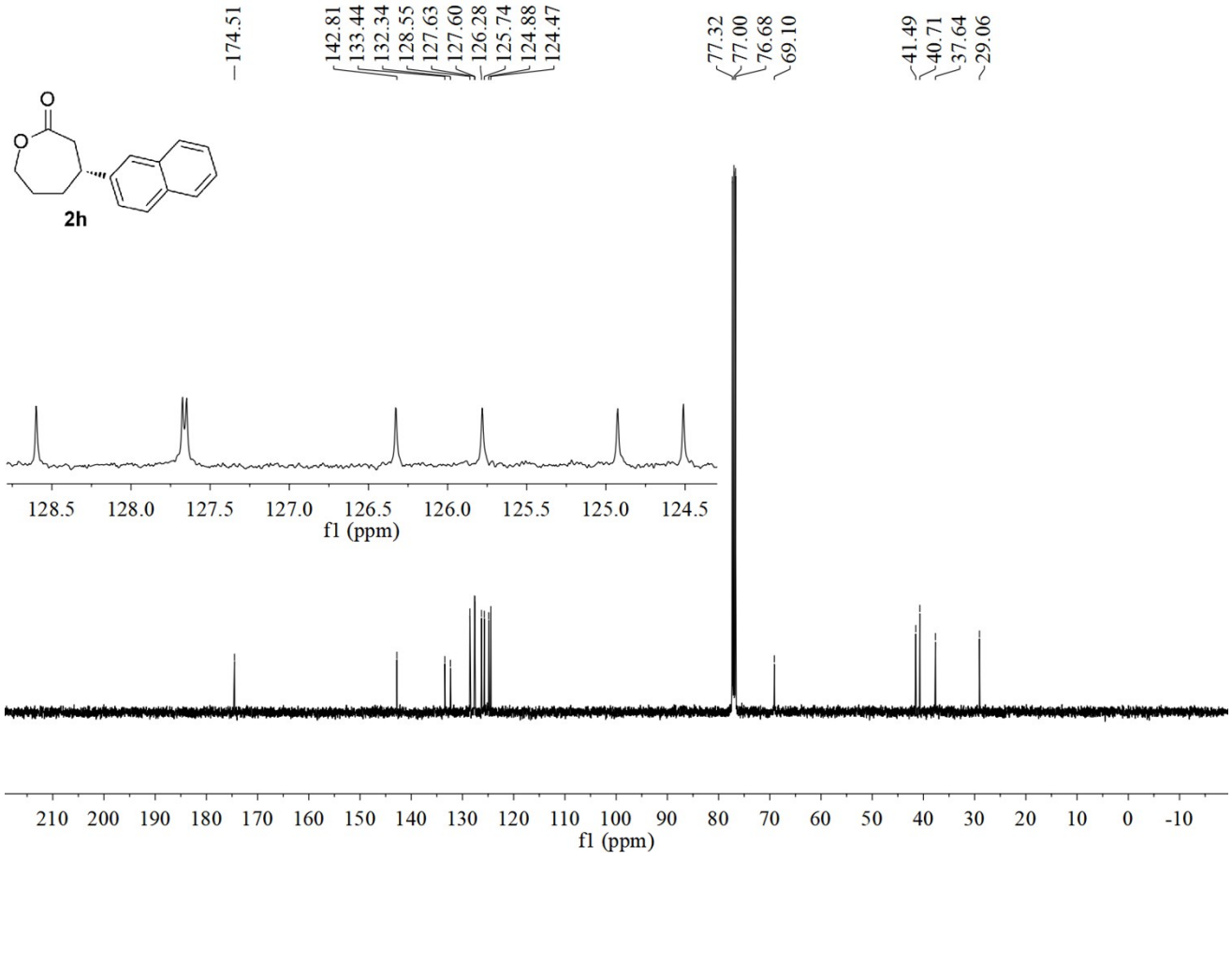

7.21 7.20 7.19 7.17 7.15 7.15 7.13 7.13 7.11 7.10 7.01 7.01 7.00 6.99 6.99 6.99 4.31 4.30 4.30 4.29 4.29 4.26 4.25 4.23 4.22 3.00 2.97 2.96 2.93 2.86 2.85 2.85 2.85 2.74 2.74 2.74 2.71 2.71 2.70 2.04 2.04 2.03 2.03 2.00 1.99 1.99 1.87 1.73 1.73 1.72
O
O
Cl
2f
3.03
0.97
7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.01
0.95
1.02
3.0 2.9 2.8 2.7
f1 (ppm)
2.00
4.40 4.30 4.20 4.10
f1 (ppm)
1.99
0.98
0.98
2.2 2.1 2.0 1.9 1.8 1.7
f1 (ppm)
3.0
1.0
2.0
1.0
1.0
1.0
2.0
1.0
1.0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

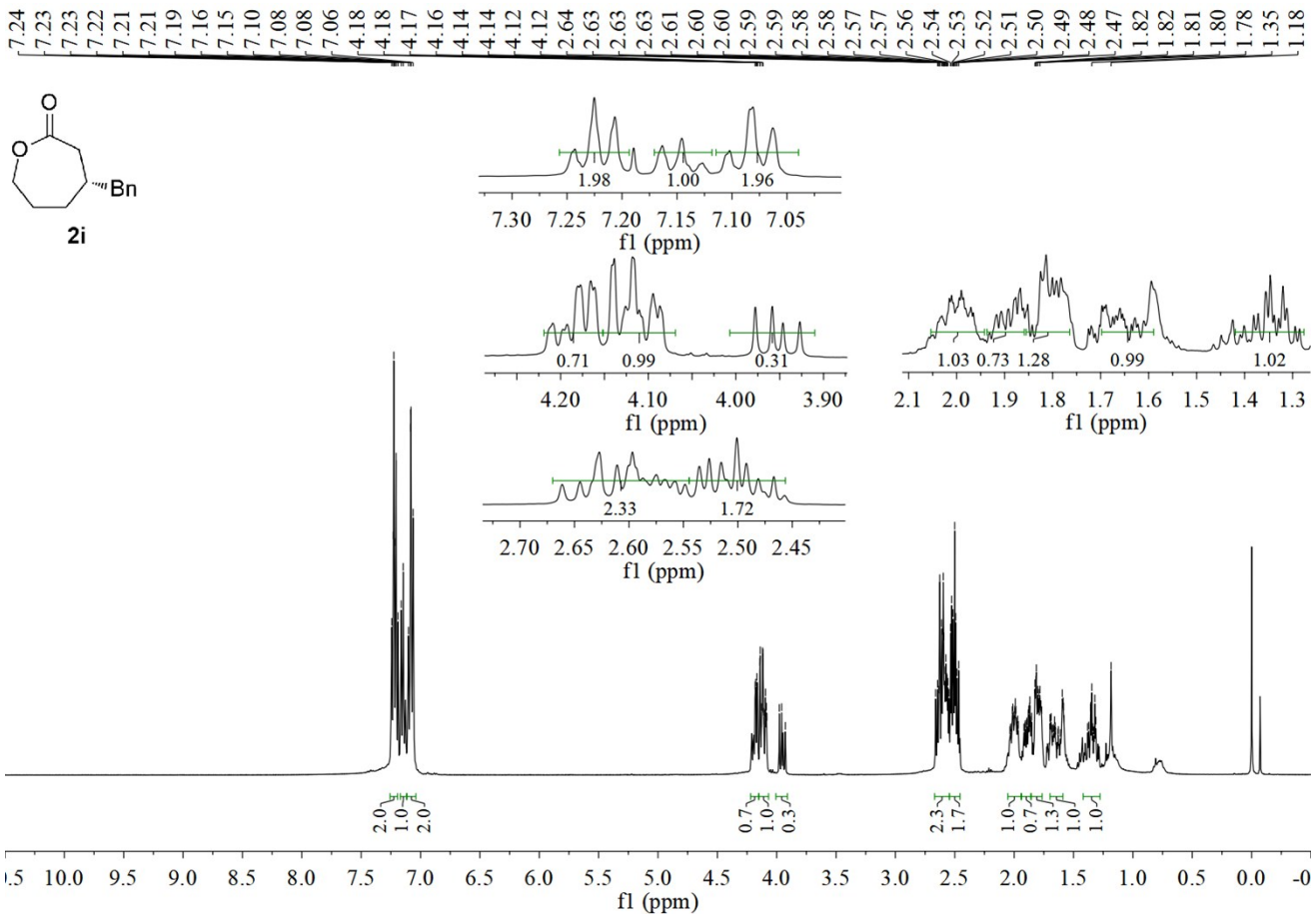

174.02
147.31
134.49
130.08
127.04
126.42
124.58
77.32
77.00
76.68
68.96
41.21
40.32
37.51
28.88
O
O
Cl
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

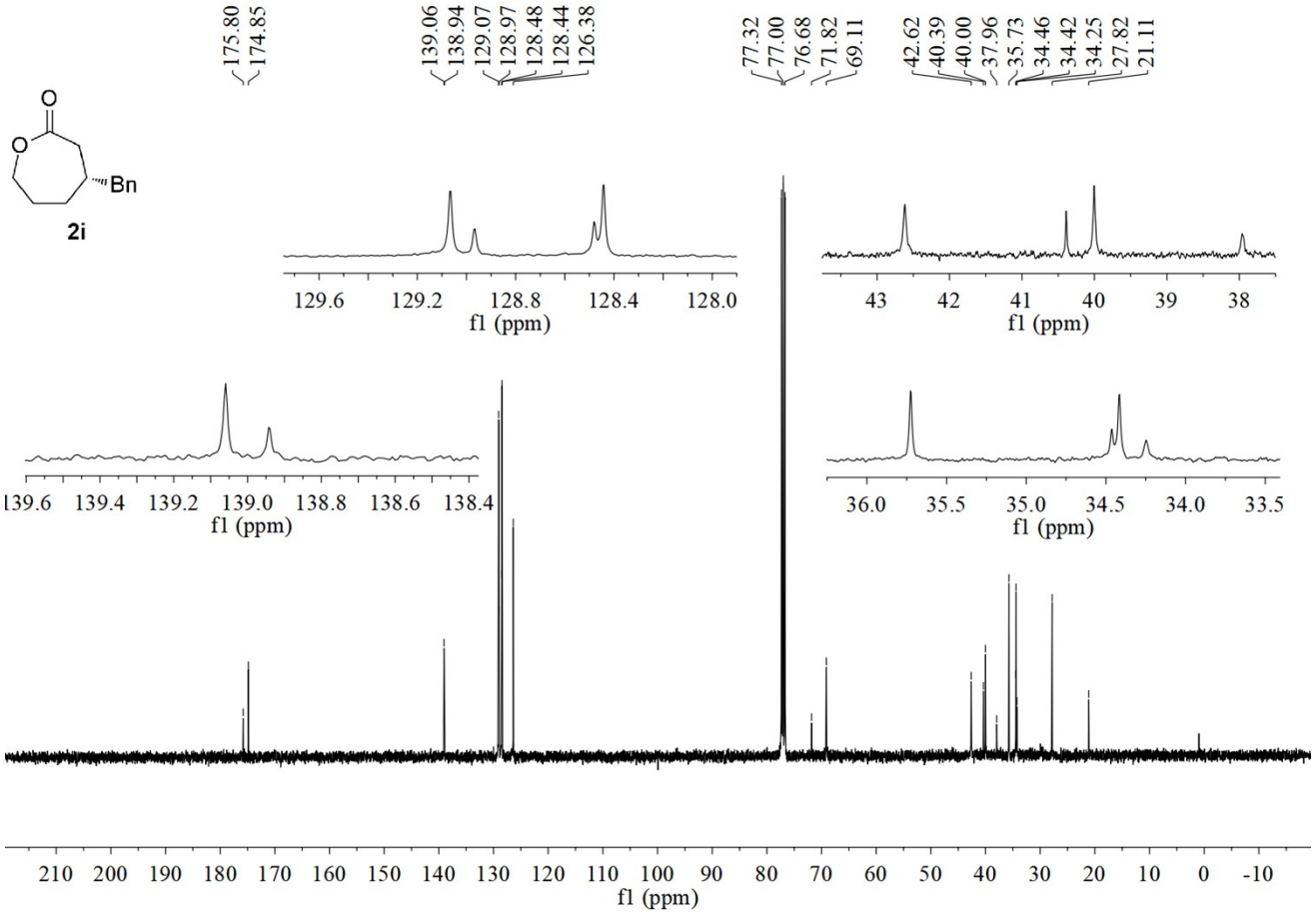

7.53 7.51 7.25 7.23 7.19 4.33 4.32 4.31 4.28 4.25 4.25 4.22 3.04 3.01 2.98 2.98 2.97 2.95 2.94 2.76 2.73 2.72 2.08 2.08 2.06 2.05 2.04 2.04 2.02 2.01 2.00 1.90 1.90 1.89 1.88 1.87 1.86 1.86 1.83 1.79 1.78 1.76 1.75 1.73 1.73 1.72 1.71
O
O
CF3
2g
2.00
1.99
f1 (ppm)
2.01
1.03
f1 (ppm)
1.99
f1 (ppm)
2.00
1.09
1.03
f1 (ppm)
2.0
2.0
2.0
2.0
1.0
2.0
1.1
1.0
f1 (ppm)
173.93
149.23
129.69
129.37
129.05
128.72
128.05
126.67
125.84
125.81
125.77
125.73
125.36
122.65
119.62
77.32
77.00
76.68
68.96
41.06
40.43
37.50
28.88
O
O
CF3
2g
f1 (ppm)
f1 (ppm)
f1 (ppm)

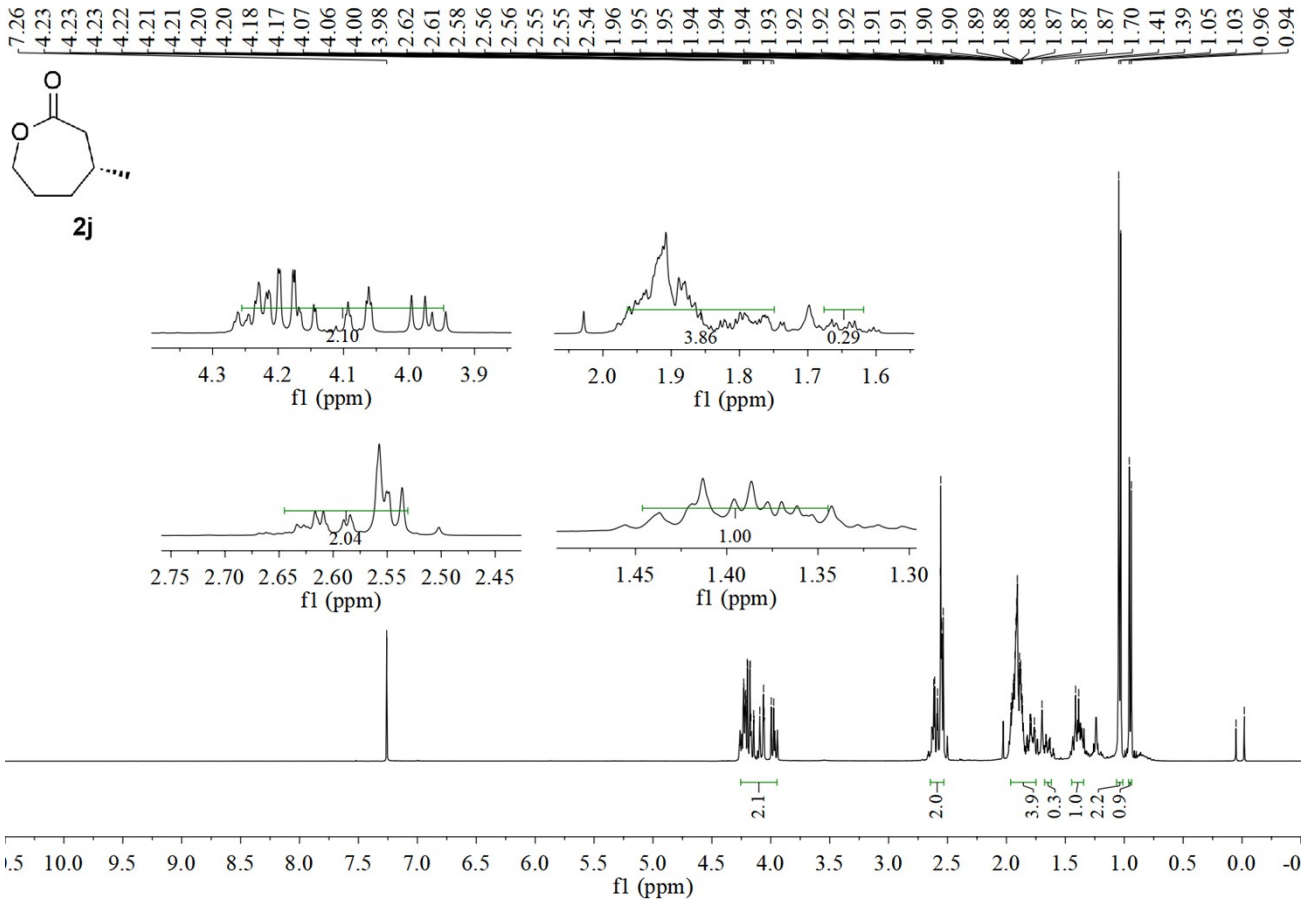

O
O
CF3
2g
-62.49
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

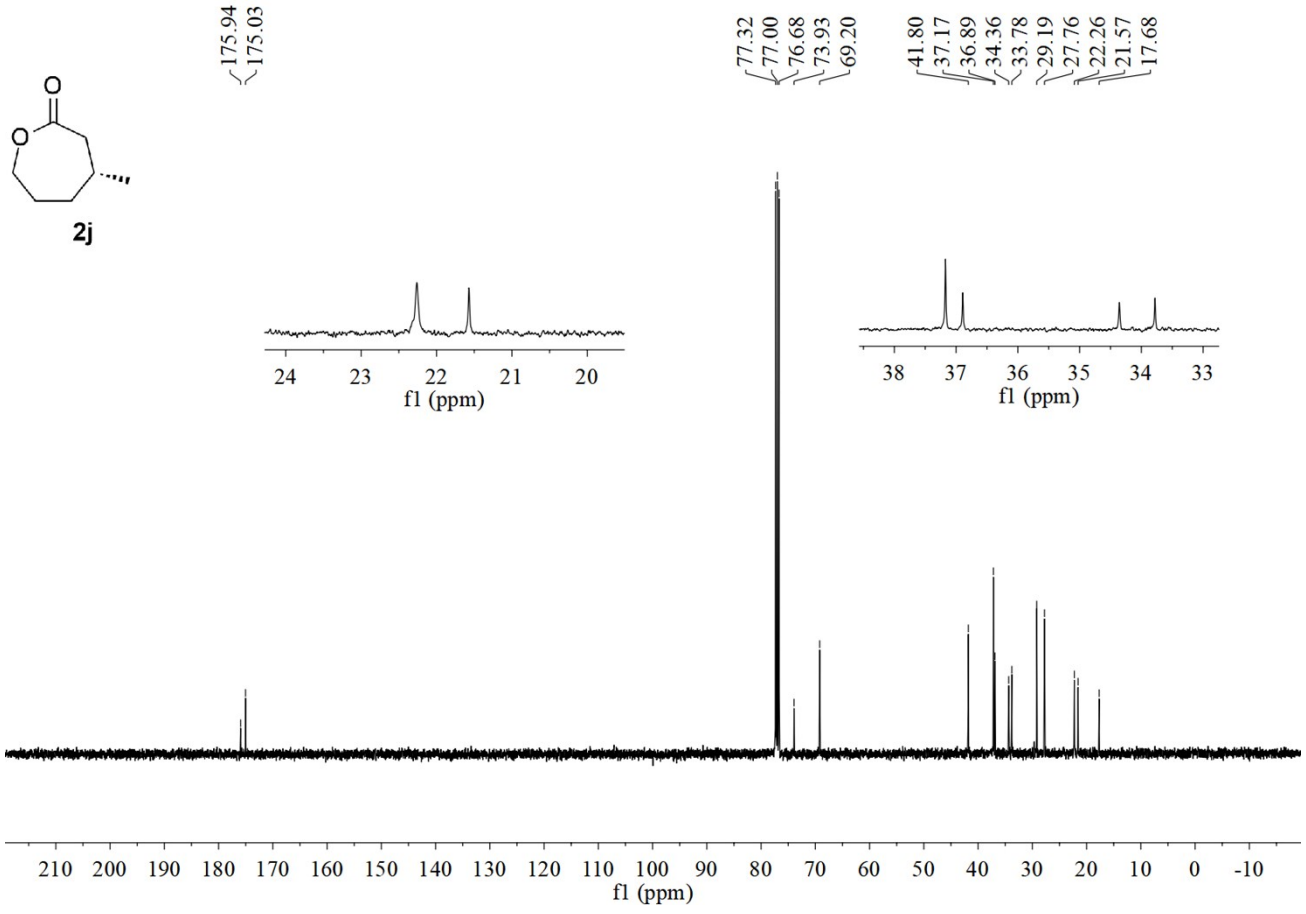

7.83 7.81 7.81 7.80 7.79 7.78 7.62 7.62 7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.34 7.33 7.31 7.31 7.26
4.41 4.40 4.40 4.40 4.39 4.39 4.38 4.37 4.35 4.35
3.16 3.13 3.13 3.12 3.12 3.11 2.94 2.93 2.93 2.91 2.90 2.20 2.11 2.10 2.10 2.09 2.00 1.97 1.95 1.92
2h
6.00
2.02
4.03
2.03
4.00
3.95
1.99
1.96
2.01
4.09
f1 (ppm)

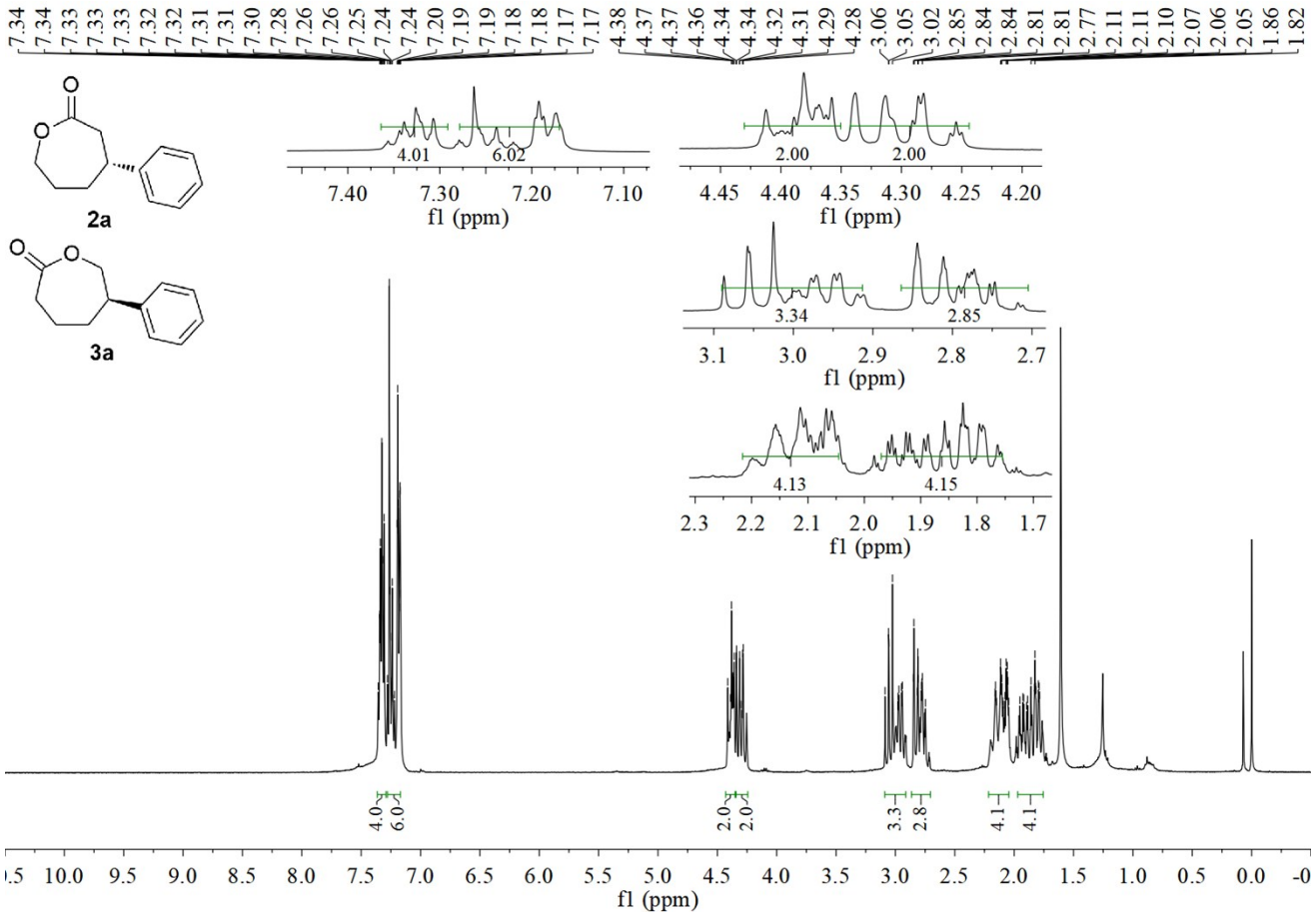

174.51
142.81 133.44 132.34 128.55 127.63 127.60 126.28 125.74 124.88 124.47
77.32 77.00 76.68 69.10
41.49 40.71 37.64 29.06
2h
f1 (ppm)

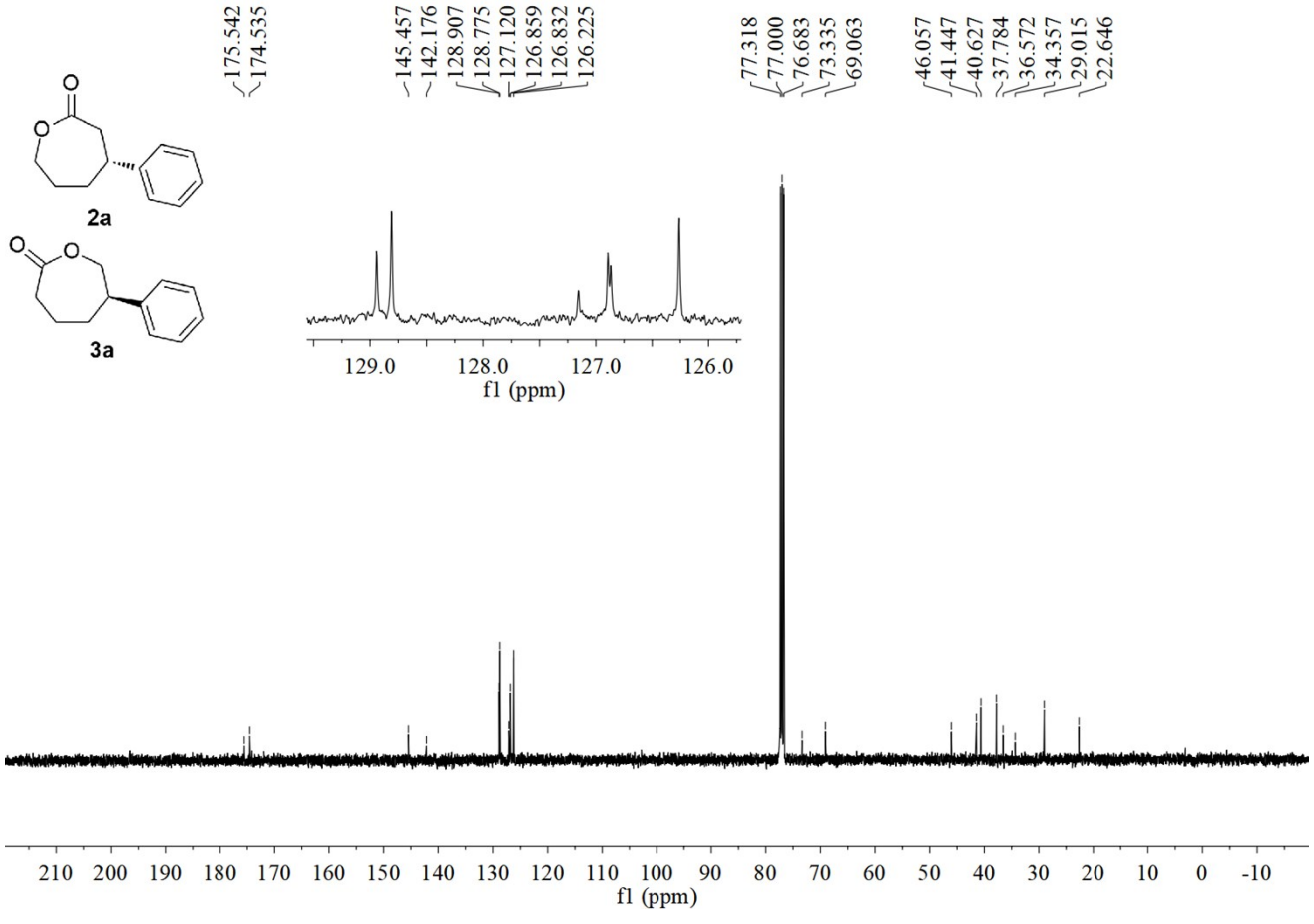

7.24 7.23 7.23 7.22 7.21 7.21 7.19 7.16 7.15 7.10 7.08 7.08 7.06 4.18 4.18 4.17 4.16 4.14 4.14 4.12 4.12 2.64 2.63 2.63 2.63 2.61 2.60 2.60 2.59 2.59 2.58 2.58 2.57 2.57 2.56 2.54 2.53 2.52 2.51 2.50 2.49 2.48 2.47 1.82 1.82 1.81 1.80 1.78 1.35 1.18
O
O
Bn
2i
1.98 1.00 1.96
7.30 7.25 7.20 7.15 7.10 7.05
f1 (ppm)
0.71 0.99 0.31
4.20 4.10 4.00 3.90
f1 (ppm)
1.03 0.73 1.28 0.99 1.02
2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3
f1 (ppm)
2.33 1.72
2.70 2.65 2.60 2.55 2.50 2.45
f1 (ppm)
2.0 1.0 2.0 0.7 1.0 0.3 2.3 1.7 1.0 0.7 1.3 1.0 1.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


175.80 174.85 139.06 138.94 129.07 128.97 128.48 128.44 126.38 77.32 77.00 76.68 71.82 69.11 42.62 40.39 40.00 37.96 35.73 34.46 34.42 34.25 27.82 21.11
O
O
Bn
2i
129.6 129.2 128.8 128.4 128.0
f1 (ppm)
43 42 41 40 39 38
f1 (ppm)
139.6 139.4 139.2 139.0 138.8 138.6 138.4
f1 (ppm)
36.0 35.5 35.0 34.5 34.0 33.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 4.23 4.23 4.23 4.22 4.21 4.21 4.20 4.20 4.18 4.17 4.07 4.06 4.00 3.98 2.62 2.61 2.58 2.56 2.56 2.55 2.55 2.54 1.96 1.95 1.95 1.94 1.94 1.94 1.93 1.92 1.92 1.92 1.91 1.91 1.90 1.90 1.89 1.88 1.88 1.87 1.87 1.87 1.70 1.41 1.39 1.05 1.03 0.96 0.94
O
O
2j
2.10
4.3 4.2 4.1 4.0 3.9
f1 (ppm)
3.86
0.29
2.0 1.9 1.8 1.7 1.6
f1 (ppm)
2.04
2.75 2.70 2.65 2.60 2.55 2.50 2.45
f1 (ppm)
1.00
1.45 1.40 1.35 1.30
f1 (ppm)
2.1
2.0
3.9
0.3
1.0
2.2
0.9
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


175.94
175.03
77.32
77.00
76.68
73.93
69.20
41.80
37.17
36.89
34.36
33.78
29.19
27.76
22.26
21.57
17.68
O
O
2j
24 23 22 21 20
f1 (ppm)
38 37 36 35 34 33
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.28 7.26 7.26 7.25 7.24 7.24 7.20 7.19 7.19 7.18 7.18 7.17 7.17 4.38 4.37 4.37 4.36 4.34 4.34 4.32 4.31 4.29 4.28 3.06 3.05 3.02 2.85 2.84 2.84 2.81 2.81 2.77 2.11 2.10 2.07 2.06 2.05 1.86 1.82
2a
3a
4.01
6.02
7.40 7.30 7.20 7.10
f1 (ppm)
2.00
2.00
4.45 4.40 4.35 4.30 4.25 4.20
f1 (ppm)
3.34
2.85
3.1 3.0 2.9 2.8 2.7
f1 (ppm)
4.13
4.15
2.3 2.2 2.1 2.0 1.9 1.8 1.7
f1 (ppm)
4.0
6.0
2.0
2.0
3.3
2.8
4.1
4.1
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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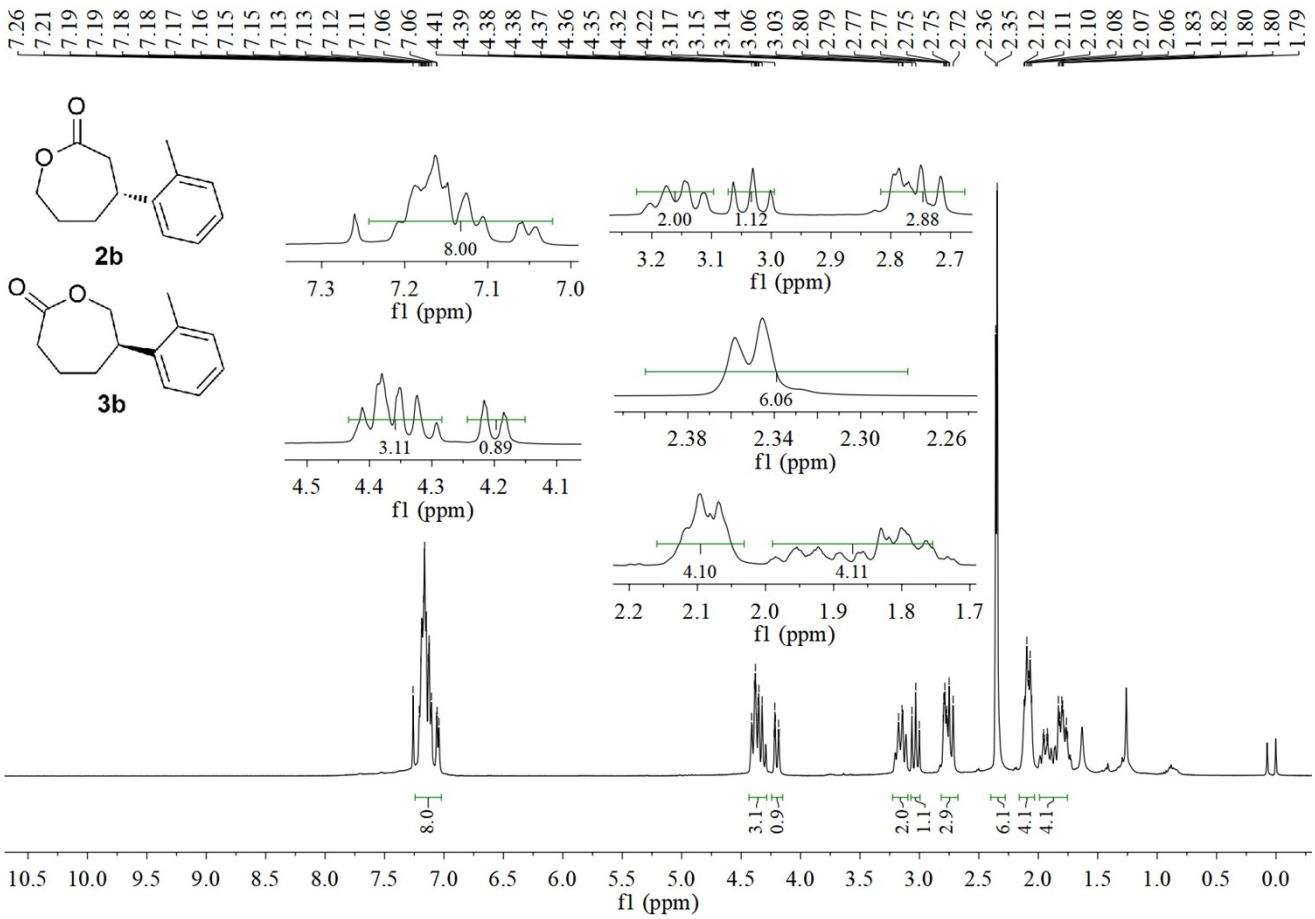
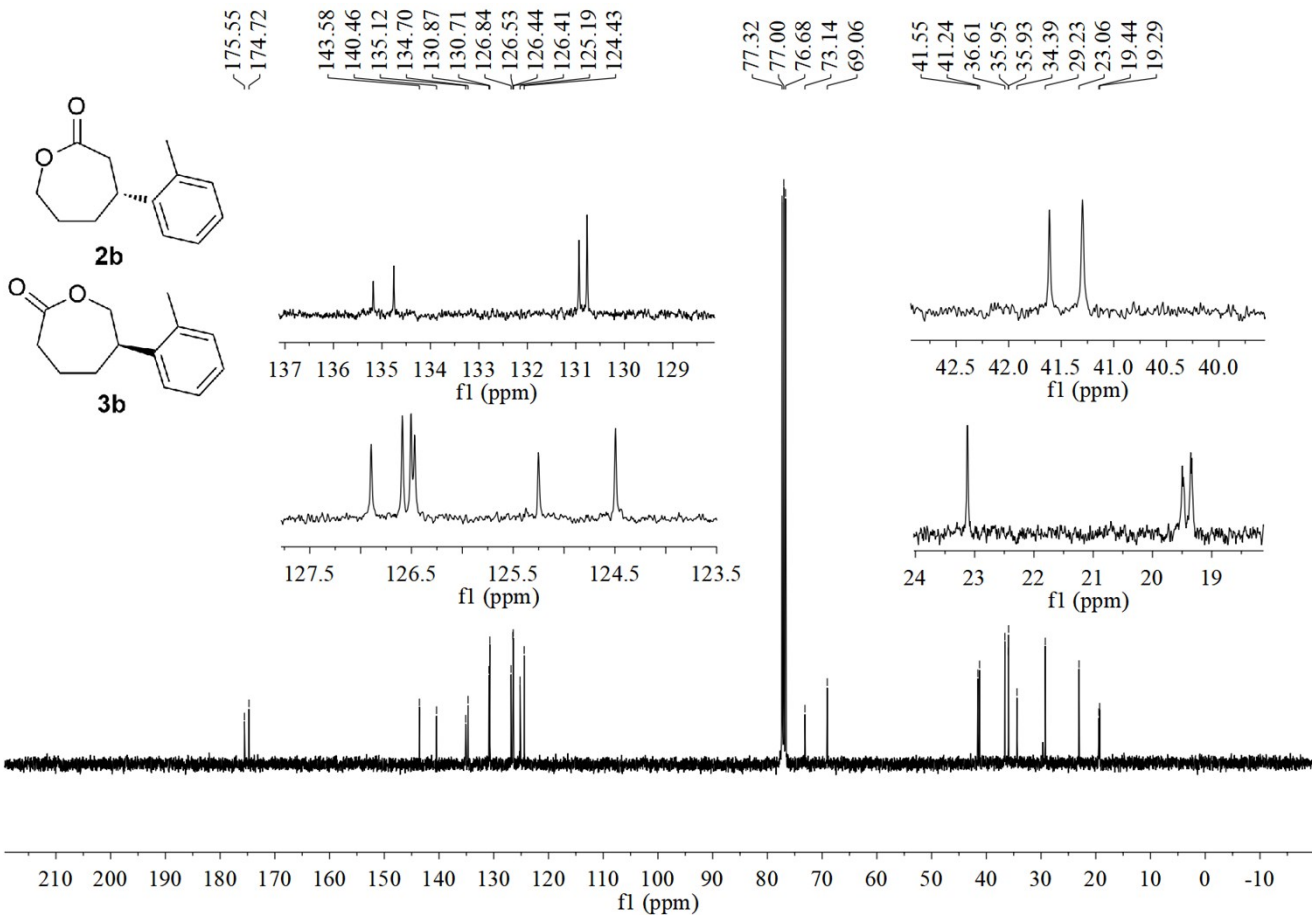
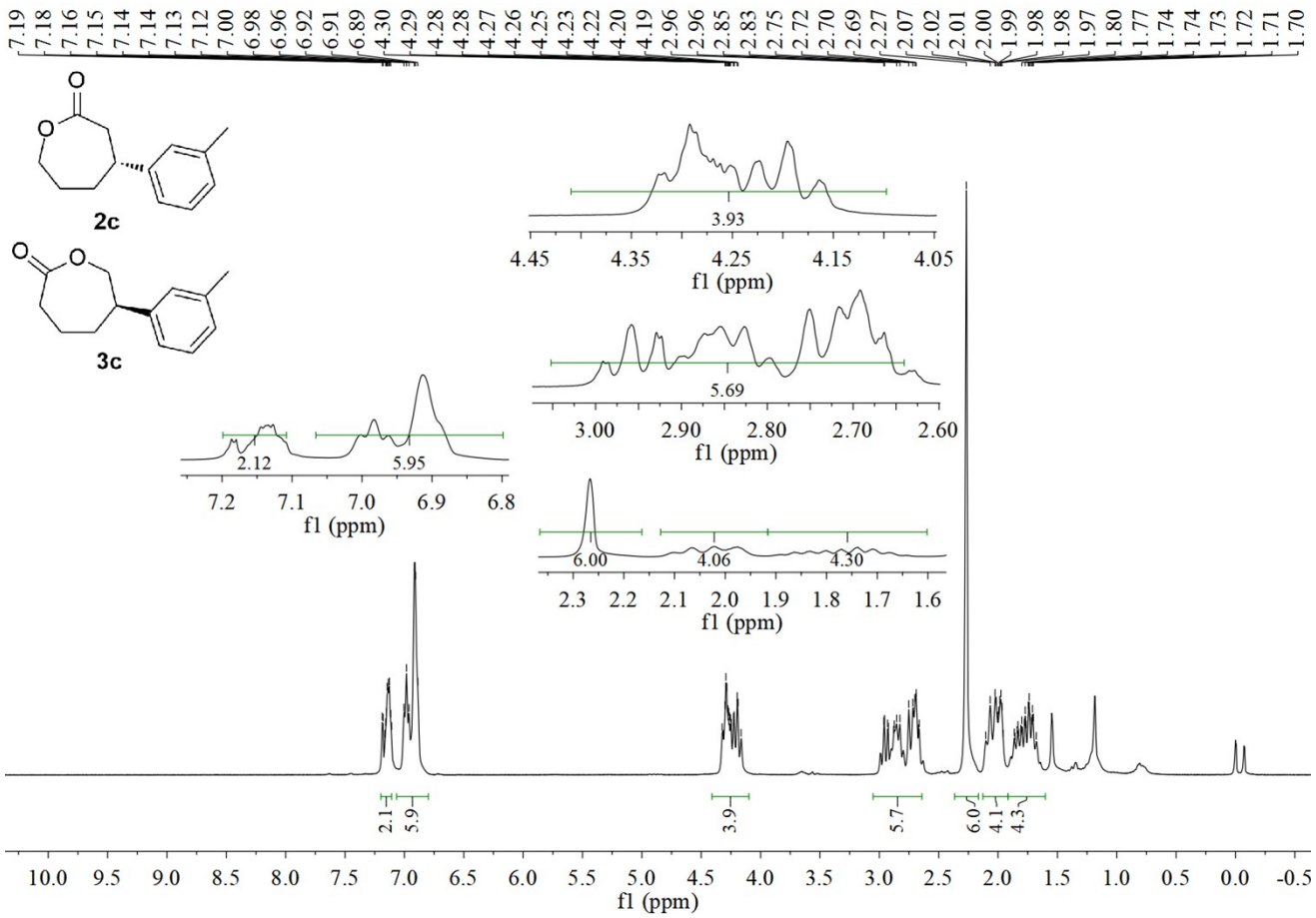
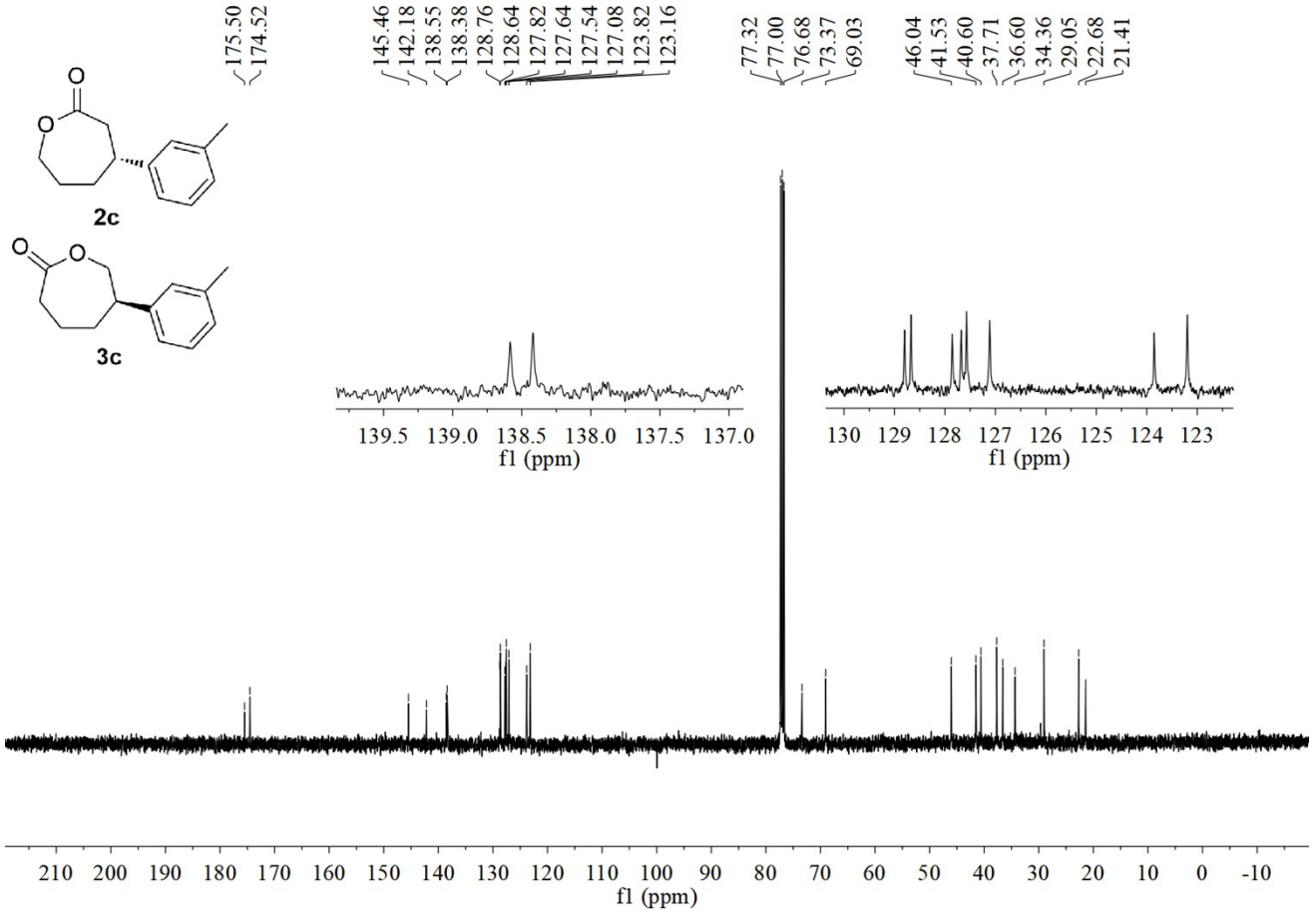
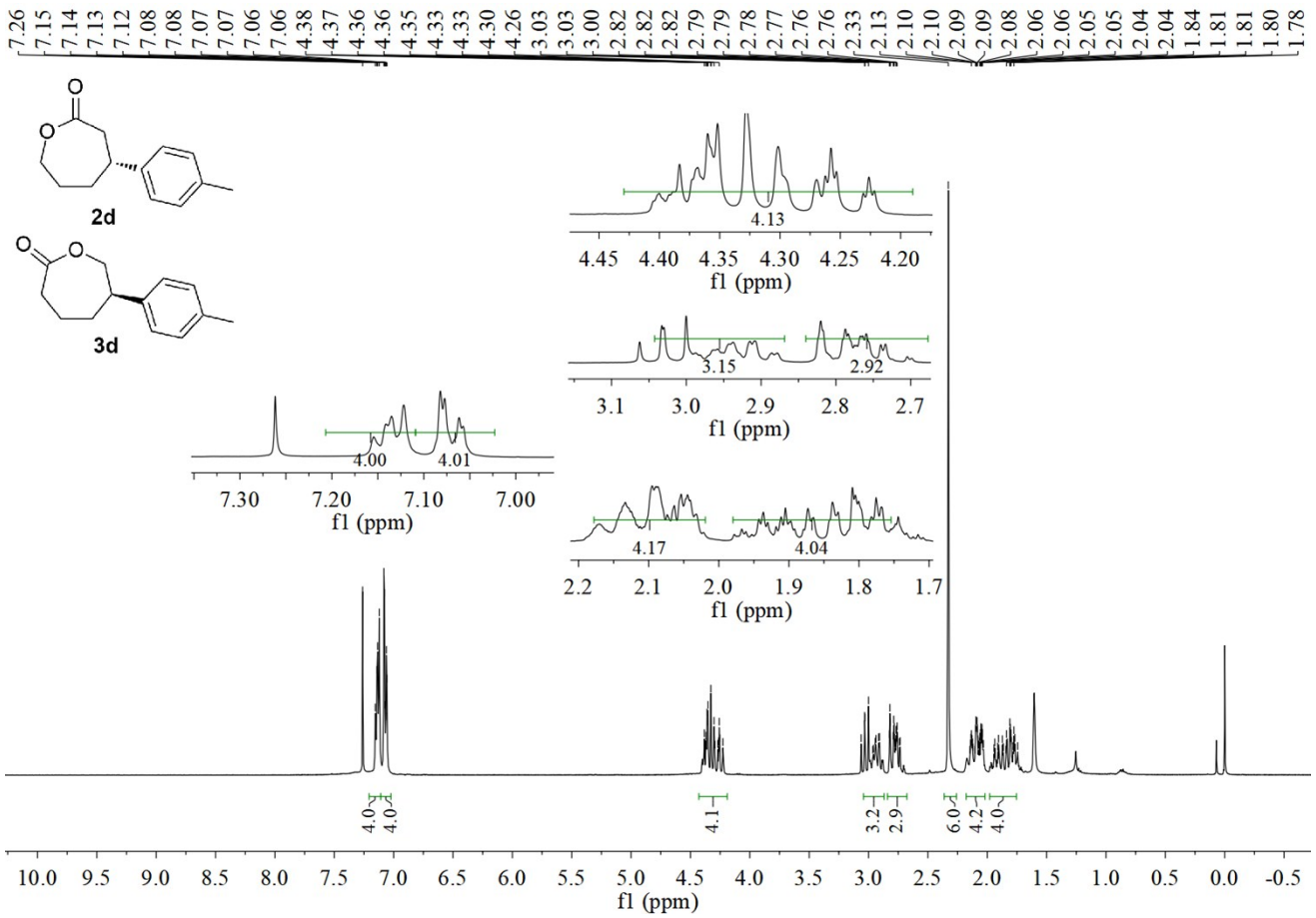
2a
3a
129.0 128.0 127.0 126.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

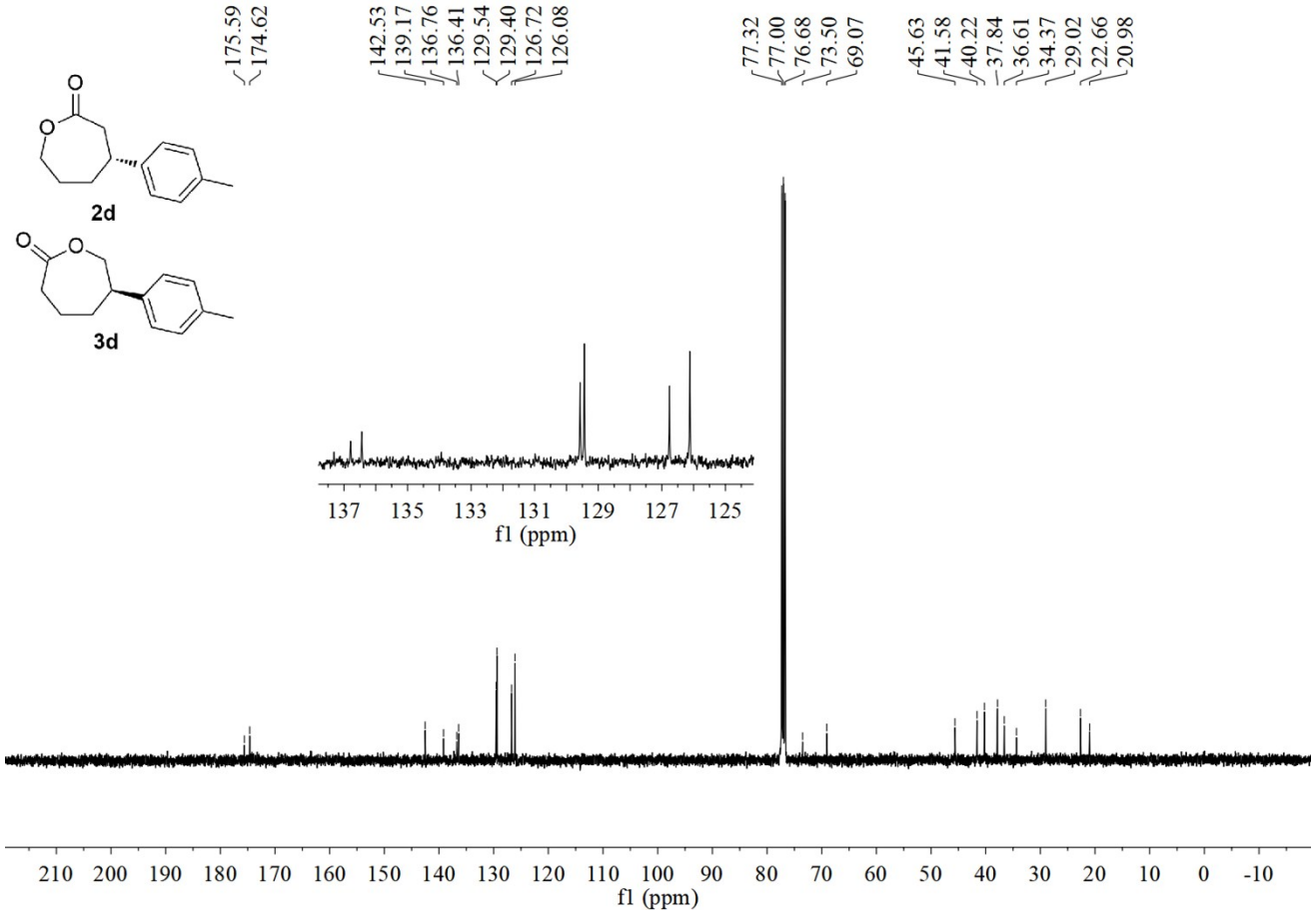

7.26 7.21 7.19 7.19 7.18 7.18 7.17 7.16 7.15 7.15 7.13 7.13 7.12 7.11 7.06 7.06 4.41 4.39 4.38 4.38 4.37 4.36 4.35 4.32 4.22 3.17 3.15 3.14 3.06 3.03 2.80 2.79 2.77 2.77 2.75 2.75 2.72 2.36 2.35 2.12 2.11 2.10 2.08 2.07 2.06 1.83 1.82 1.80 1.80 1.79
2b
3b
8.00
2.00 1.12 2.88
6.06
3.11 0.89
4.10 4.11
f1 (ppm)
8.0 3.1 0.9 2.0 1.1 2.9 6.1 4.1 4.1

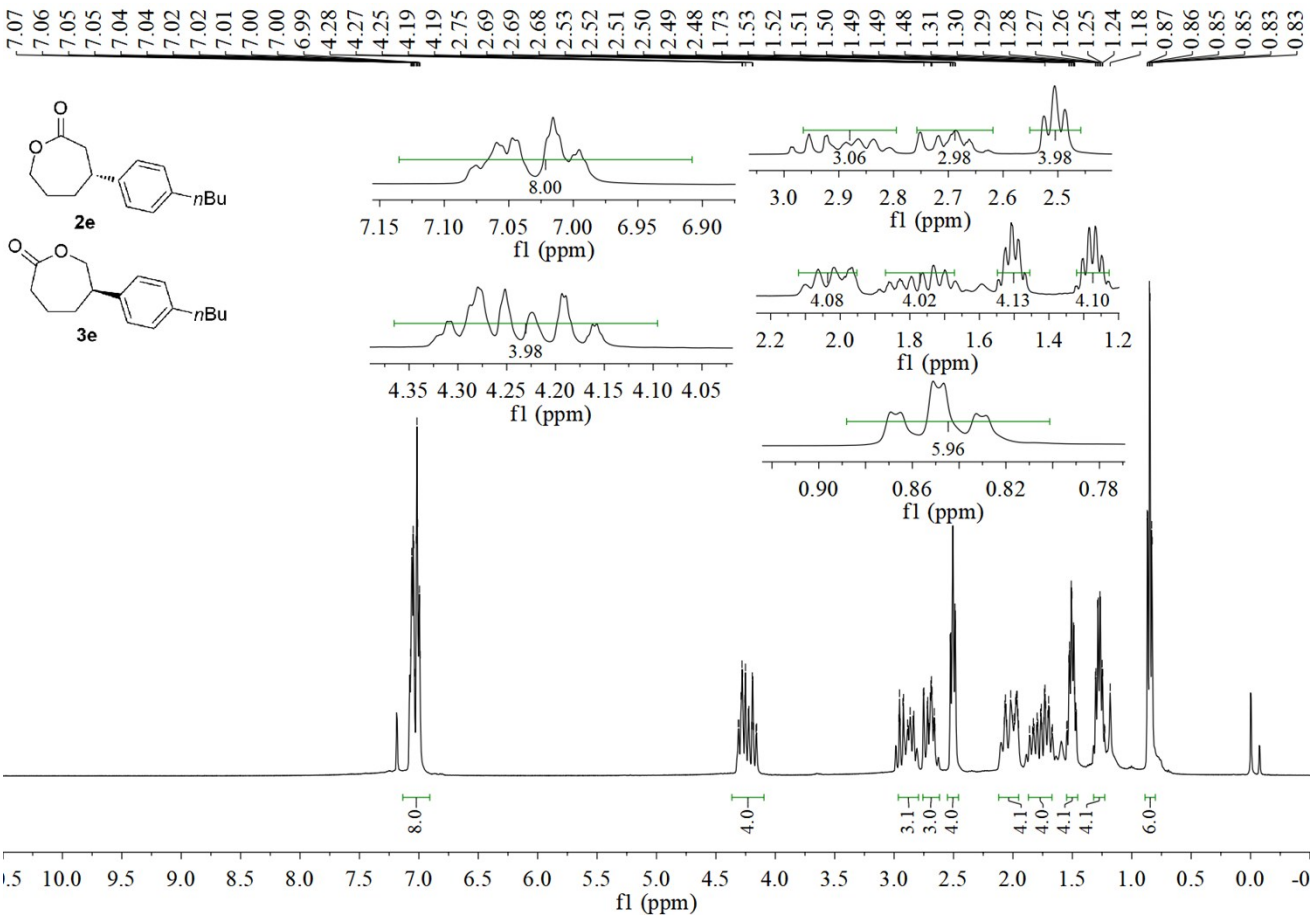

175.55 174.72 143.58 140.46 135.12 134.70 130.87 130.71 126.84 126.53 126.44 126.41 125.19 124.43 77.32 77.00 76.68 73.14 69.06 41.55 41.24 36.61 35.95 35.93 34.39 29.23 23.06 19.44 19.29
2b
3b
f1 (ppm)

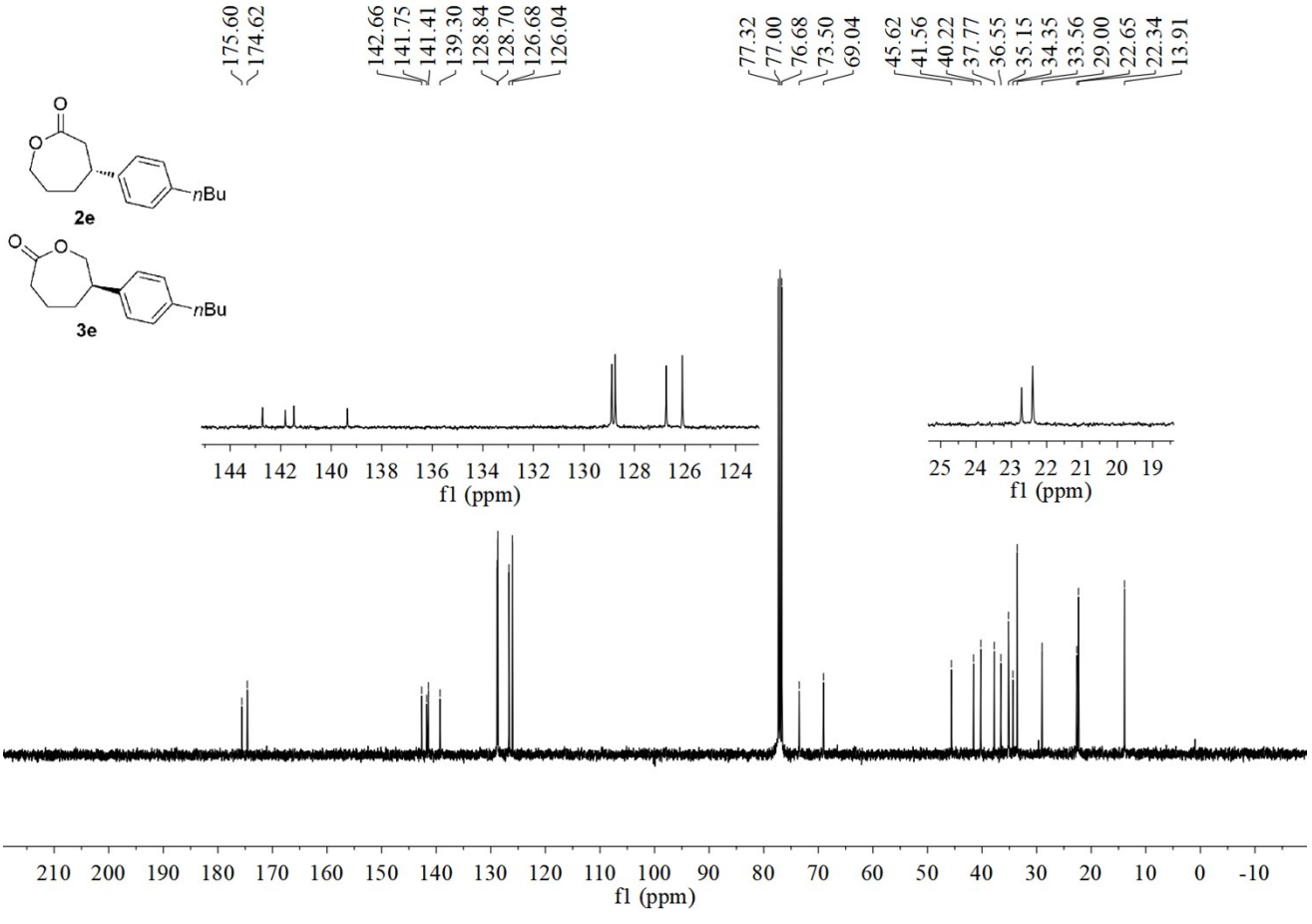

7.19 7.18 7.16 7.15 7.14 7.14 7.13 7.12 7.00 6.98 6.96 6.92 6.91 6.89 4.30 4.29 4.28 4.28 4.27 4.26 4.25 4.23 4.22 4.20 4.19 2.96 2.96 2.85 2.83 2.75 2.72 2.70 2.69 2.27 2.07 2.02 2.01 2.00 1.99 1.98 1.98 1.97 1.80 1.77 1.74 1.74 1.73 1.72 1.71 1.70
2c
3c
3.93
5.69
2.12
5.95
6.00
4.06
4.30
f1 (ppm)
2.1
5.9
3.9
5.7
6.0
4.1
4.3

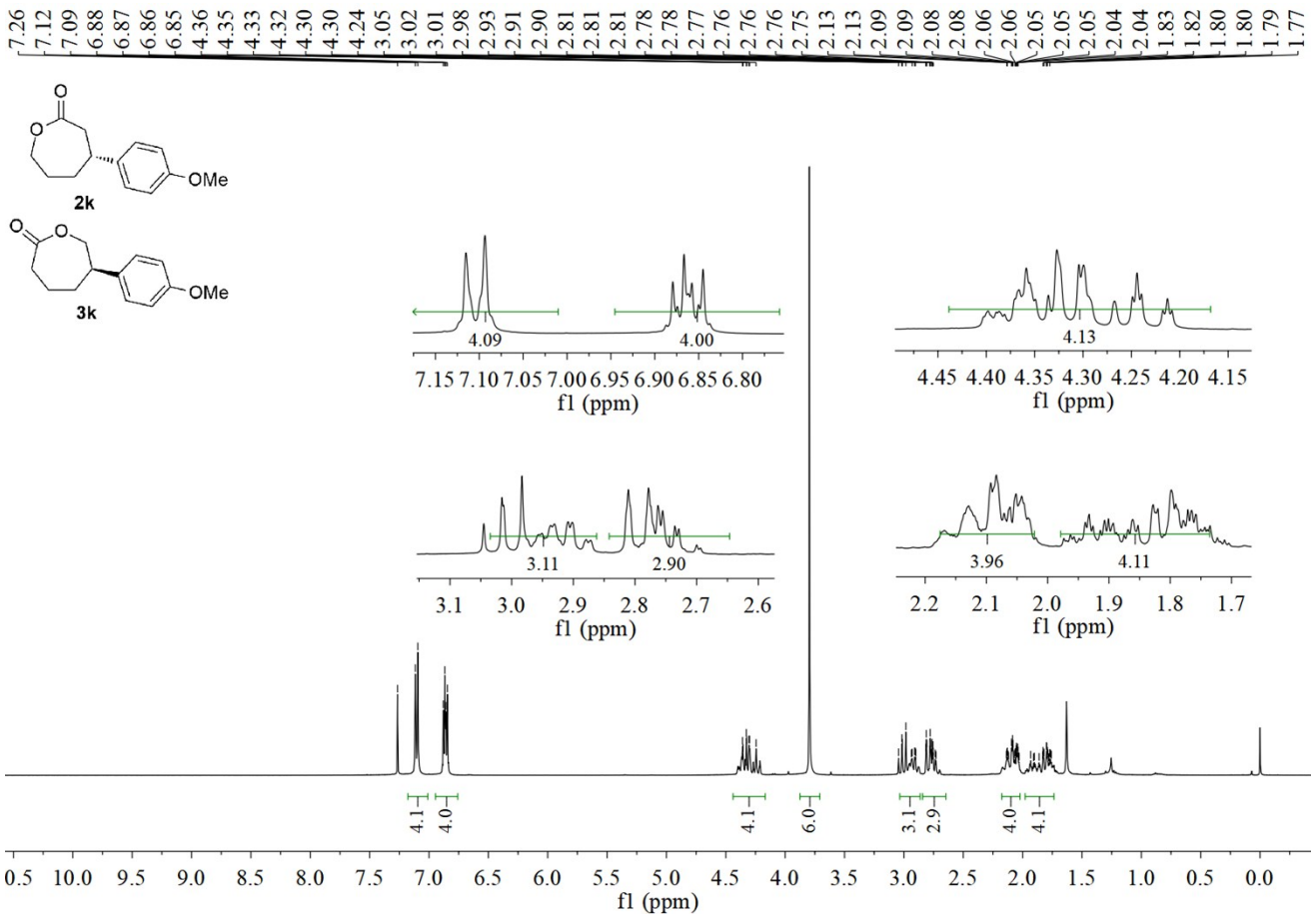

175.50 174.52 145.46 142.18 138.55 138.38 128.76 128.64 127.82 127.64 127.54 127.08 123.82 123.16 77.32 77.00 76.68 73.37 69.03 46.04 41.53 40.60 37.71 36.60 34.36 29.05 22.68 21.41
2c
3c
f1 (ppm)

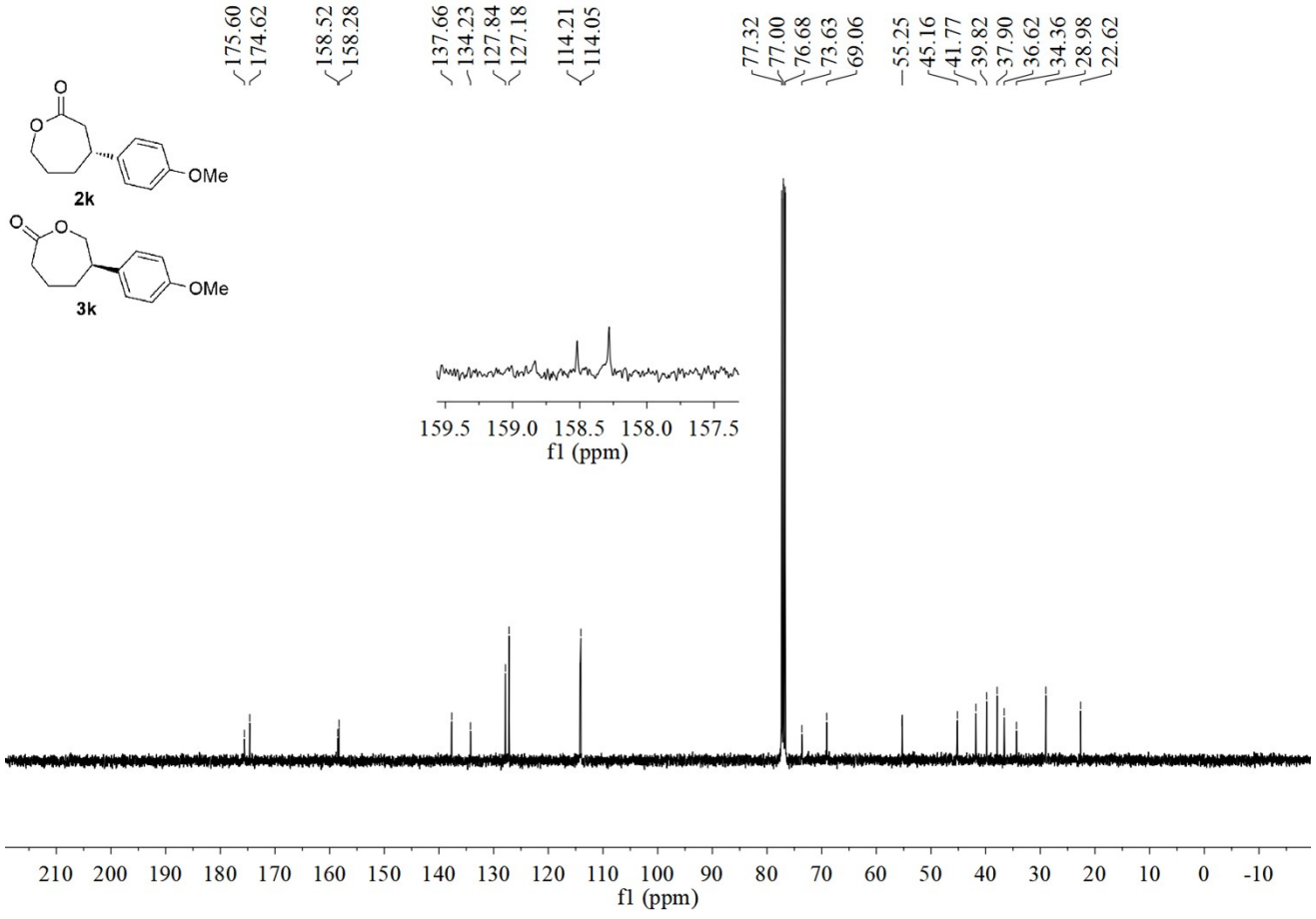

7.26 7.15 7.14 7.13 7.12 7.08 7.08 7.07 7.07 7.06 7.06 4.38 4.37 4.36 4.36 4.35 4.33 4.33 4.30 4.26 3.03 3.03 3.00 2.82 2.82 2.82 2.79 2.79 2.78 2.77 2.76 2.76 2.33 2.13 2.10 2.10 2.09 2.09 2.08 2.06 2.06 2.05 2.05 2.04 2.04 1.84 1.81 1.81 1.80 1.78
2d
3d
4.13
4.45 4.40 4.35 4.30 4.25 4.20
f1 (ppm)
3.15 2.92
3.1 3.0 2.9 2.8 2.7
f1 (ppm)
4.00 4.01
7.30 7.20 7.10 7.00
f1 (ppm)
4.17 4.04
2.2 2.1 2.0 1.9 1.8 1.7
f1 (ppm)
4.0 4.0 4.1 3.2 2.9 6.0 4.2 4.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

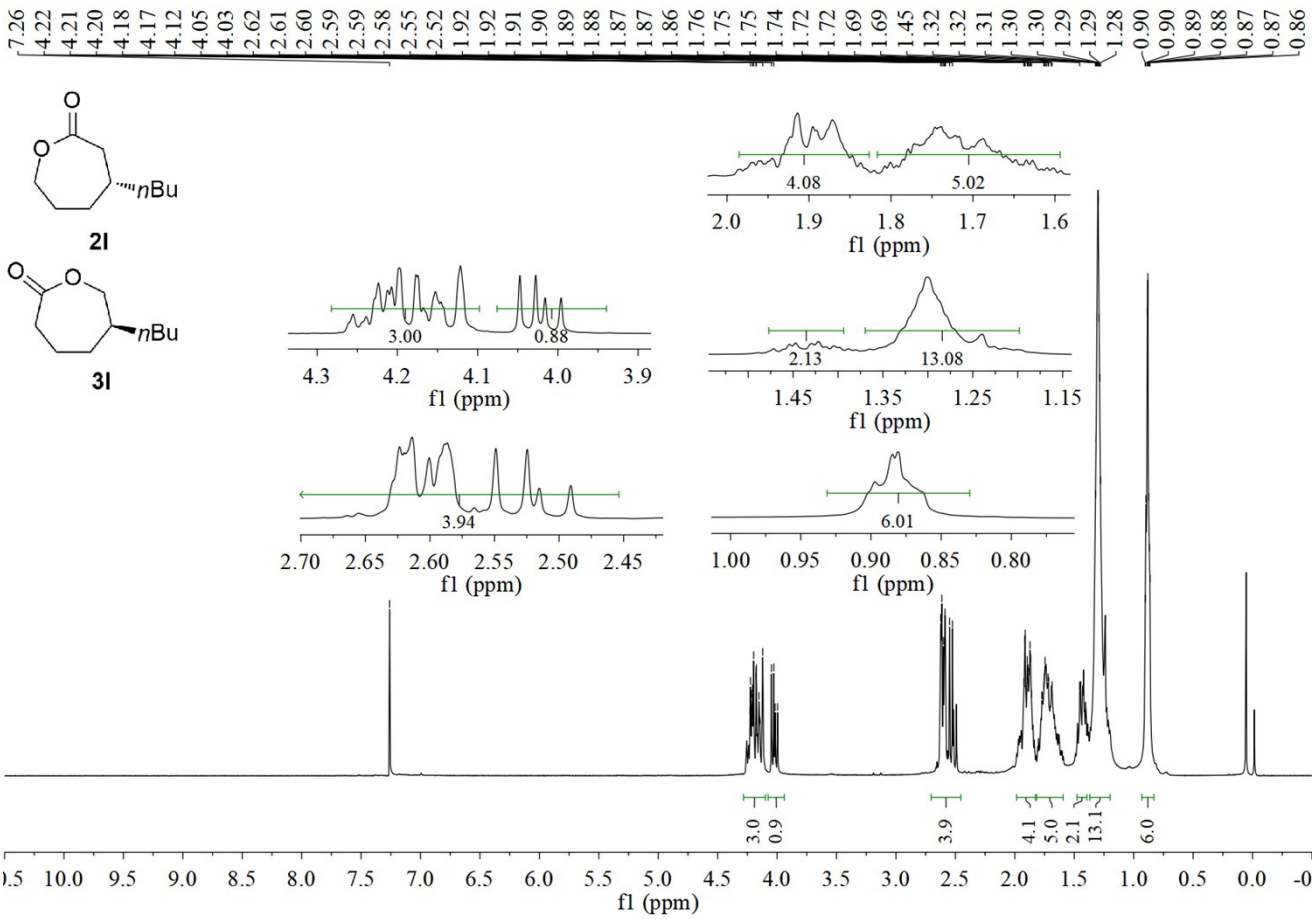

175.59 174.62 142.53 139.17 136.76 136.41 129.54 129.40 126.72 126.08 77.32 77.00 76.68 73.50 69.07 45.63 41.58 40.22 37.84 36.61 34.37 29.02 22.66 20.98
2d
3d
137 135 133 131 129 127 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

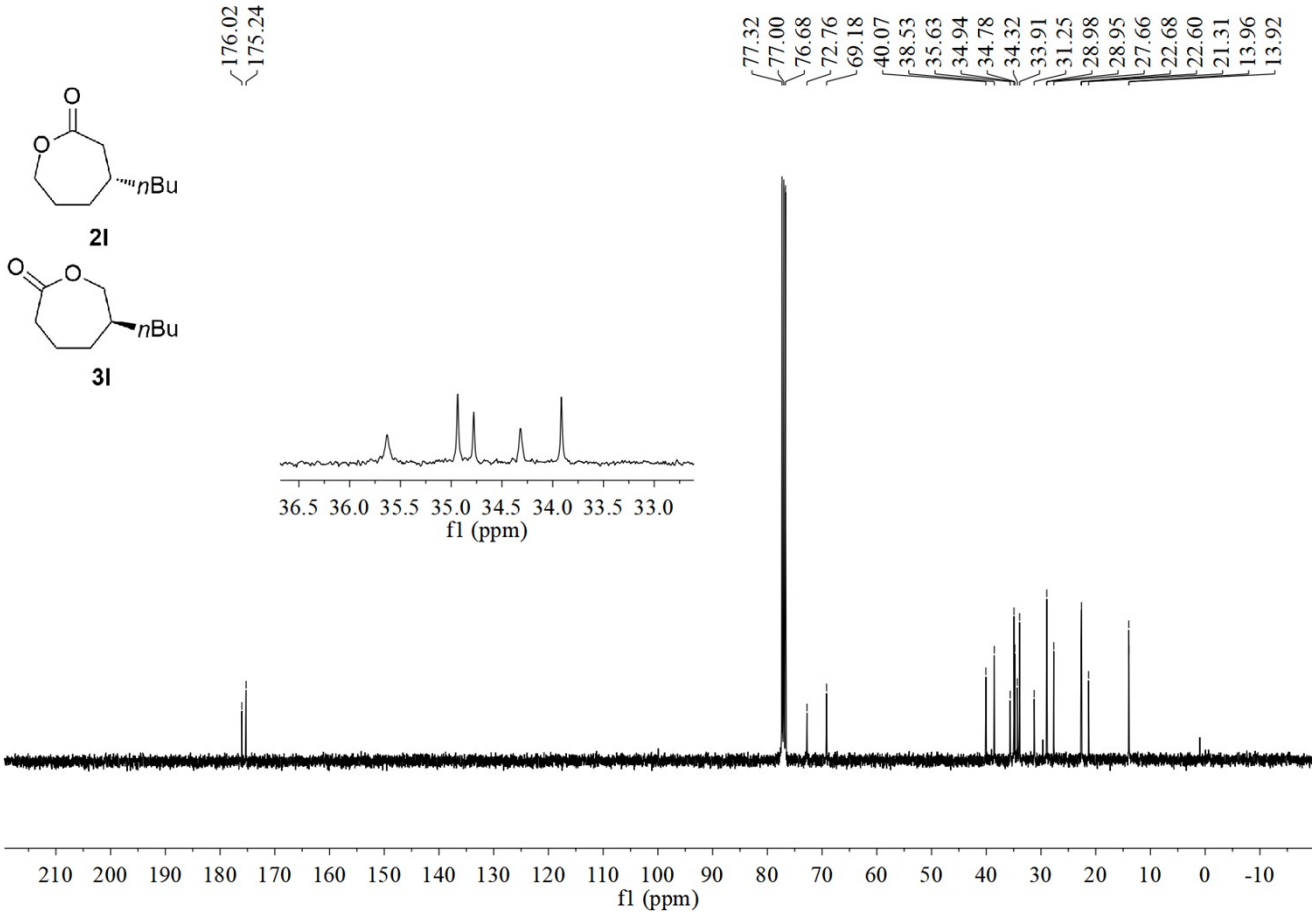

7.07 7.06 7.05 7.05 7.04 7.04 7.02 7.02 7.01 7.00 7.00 6.99 4.28 4.27 4.25 4.19 4.19 2.75 2.69 2.69 2.68 2.53 2.52 2.51 2.50 2.49 2.48 1.73 1.53 1.52 1.51 1.50 1.49 1.49 1.48 1.31 1.30 1.29 1.28 1.27 1.26 1.25 1.24 1.18 0.87 0.86 0.85 0.85 0.83 0.83
2e
3e
nBu
8.00
3.06
2.98
3.98
3.98
4.08
4.02
4.13
4.10
5.96
8.0
4.0
3.1
3.0
4.0
4.1
4.0
4.1
4.1
6.0
f1 (ppm)

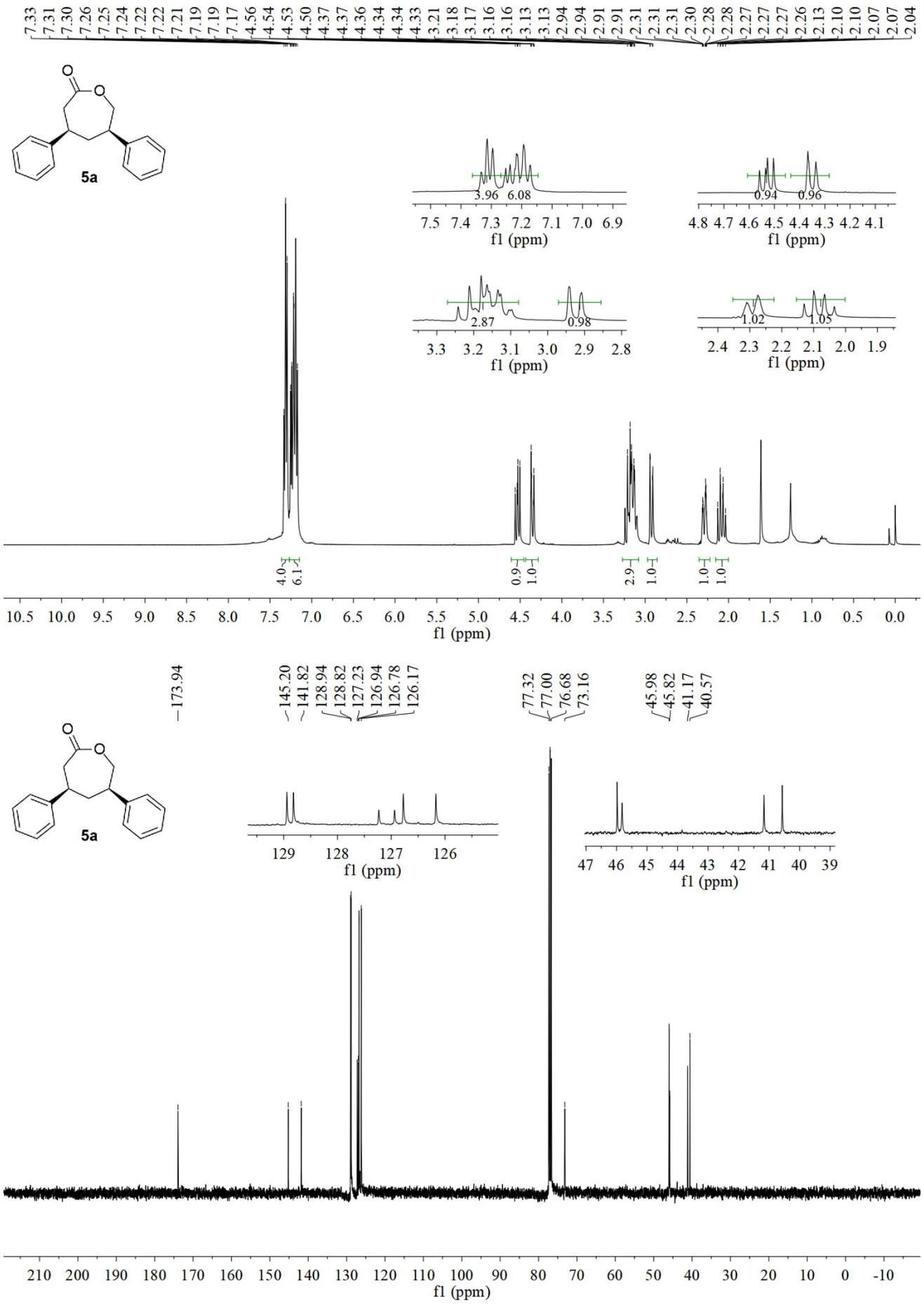

175.60 174.62 142.66 141.75 141.41 139.30 128.84 128.70 126.68 126.04 77.32 77.00 76.68 73.50 69.04 45.62 41.56 40.22 37.77 36.55 35.15 34.35 33.56 29.00 22.65 22.34 13.91
2e
3e
nBu
f1 (ppm)

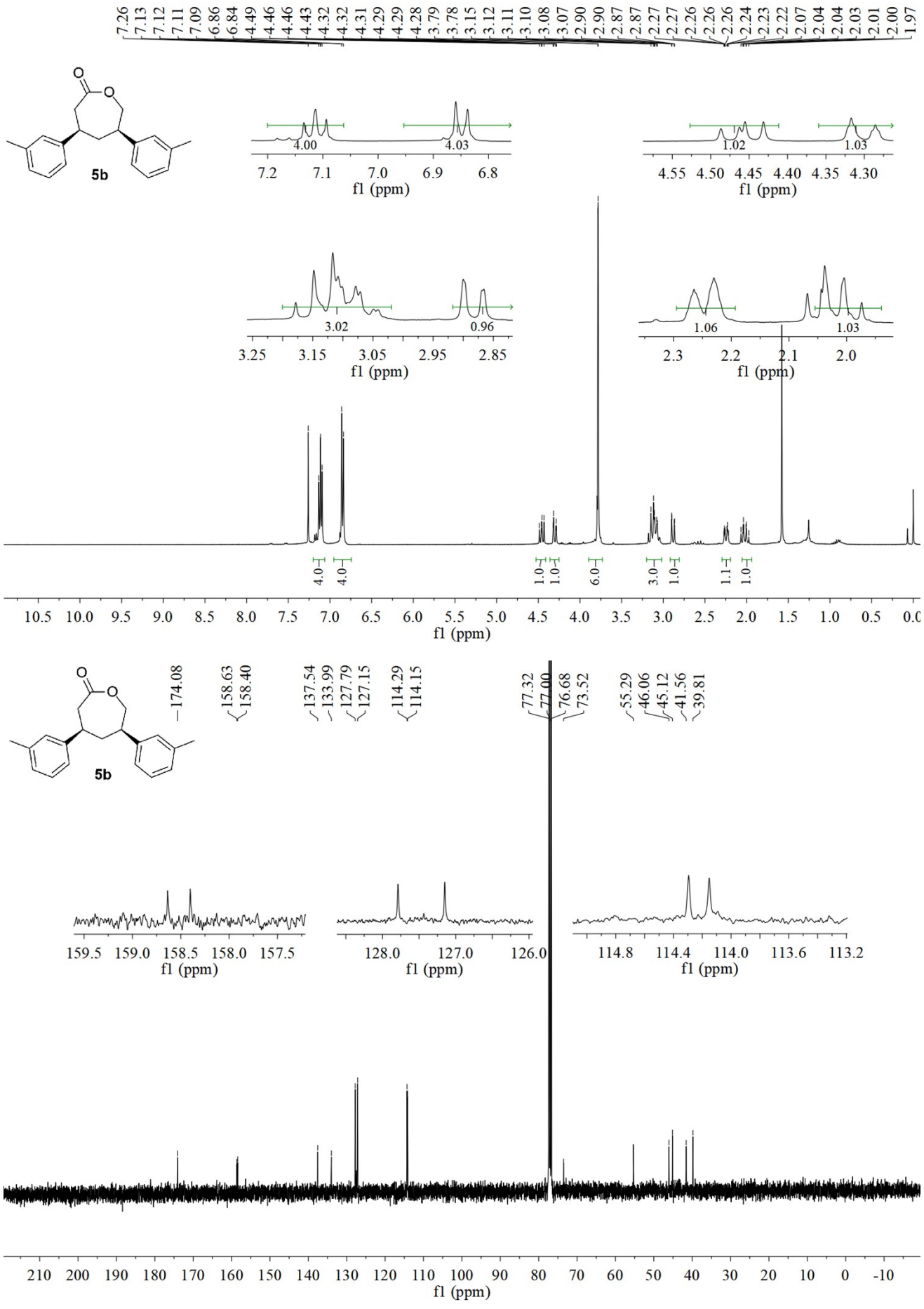

7.26 7.12 7.09 6.88 6.87 6.86 6.85 4.36 4.35 4.33 4.32 4.30 4.30 4.24 3.05 3.02 3.01 2.98 2.93 2.91 2.90 2.81 2.81 2.81 2.78 2.78 2.77 2.76 2.76 2.76 2.75 2.13 2.13 2.09 2.09 2.08 2.08 2.06 2.06 2.05 2.05 2.05 2.04 2.04 1.83 1.82 1.80 1.80 1.79 1.77
2k
3k
OMe
4.09
4.00
7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80
f1 (ppm)
4.13
4.45 4.40 4.35 4.30 4.25 4.20 4.15
f1 (ppm)
3.11
2.90
3.1 3.0 2.9 2.8 2.7 2.6
f1 (ppm)
3.96
4.11
2.2 2.1 2.0 1.9 1.8 1.7
f1 (ppm)
4.1
4.0
4.1
6.0
3.1
2.9
4.0
4.1
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

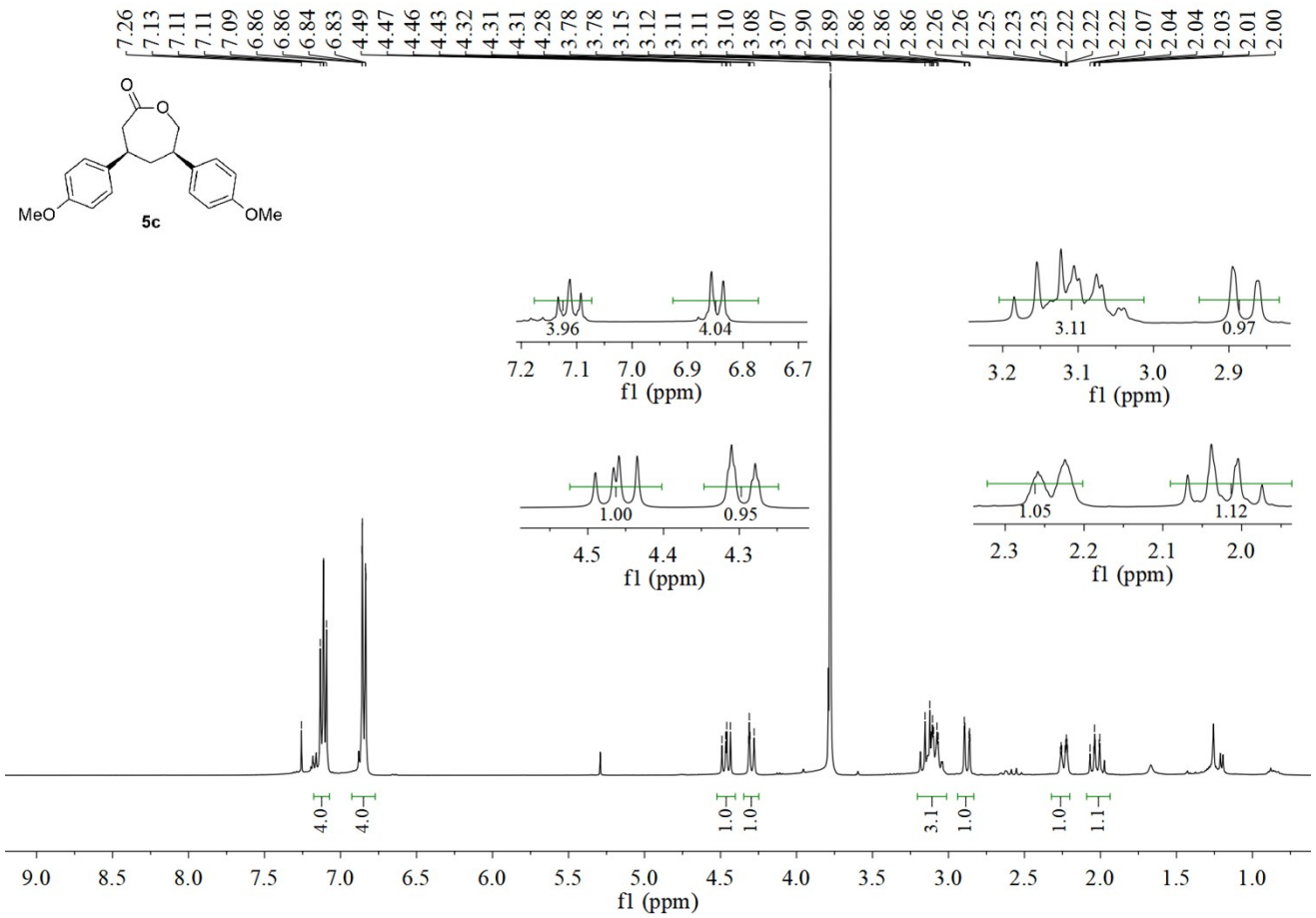

175.60 174.62 158.52 158.28 137.66 134.23 127.84 127.18 114.21 114.05 77.32 77.00 76.68 73.63 69.06 55.25 45.16 41.77 39.82 37.90 36.62 34.36 28.98 22.62
2k
3k
OMe
159.5 159.0 158.5 158.0 157.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

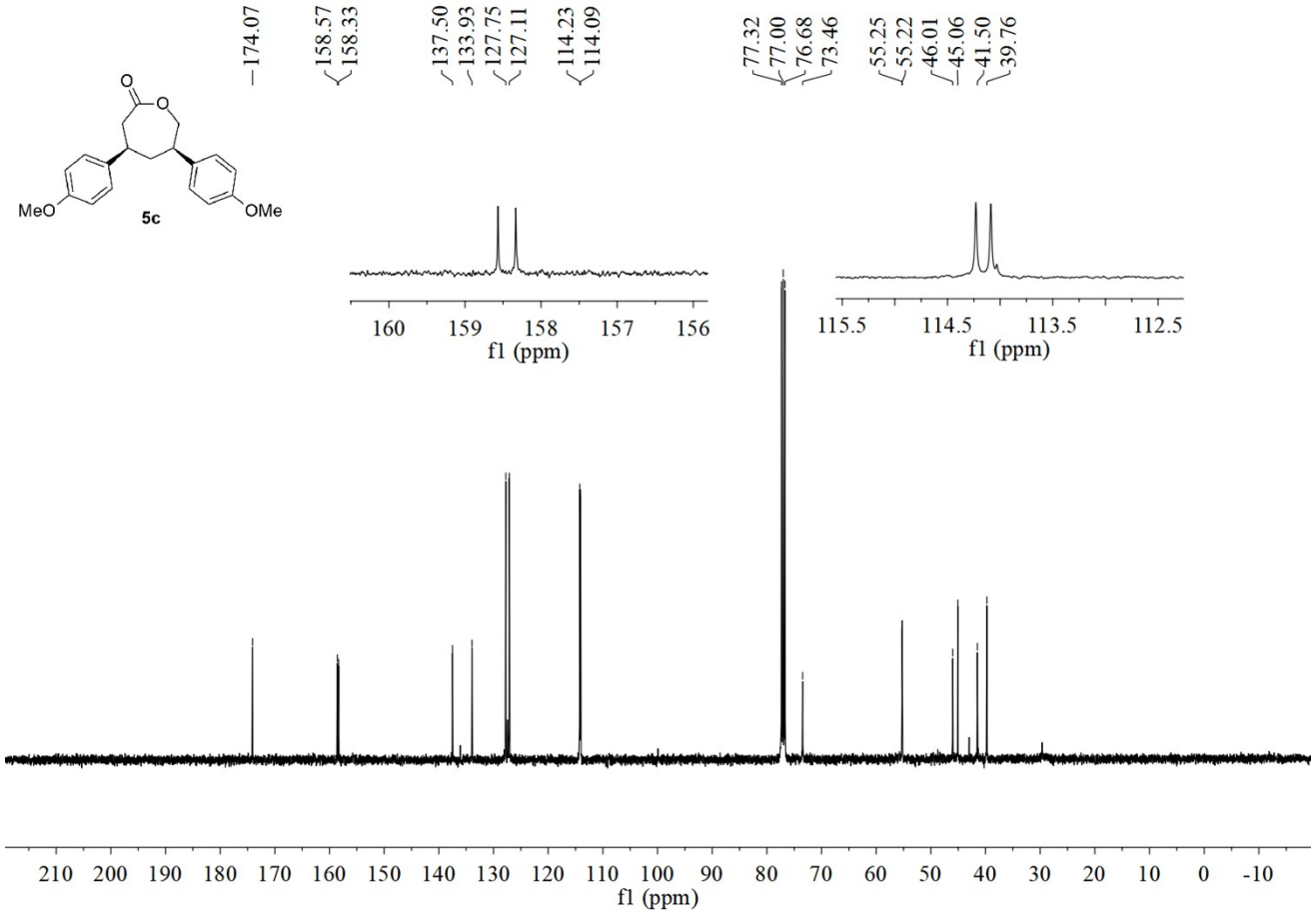

7.26 4.22 4.21 4.20 4.18 4.17 4.12 4.05 4.03 2.62 2.61 2.60 2.59 2.59 2.58 2.55 2.52 1.92 1.92 1.91 1.90 1.89 1.88 1.87 1.87 1.86 1.76 1.75 1.75 1.74 1.72 1.72 1.69 1.69 1.45 1.32 1.32 1.31 1.30 1.30 1.29 1.29 1.28 0.90 0.90 0.89 0.88 0.87 0.87 0.86
nBu
2l
nBu
3l
4.08
5.02
3.00
0.88
2.13
13.08
3.94
6.01
f1 (ppm)
3.0 0.9 3.9 4.1 5.0 2.1 13.1 6.0

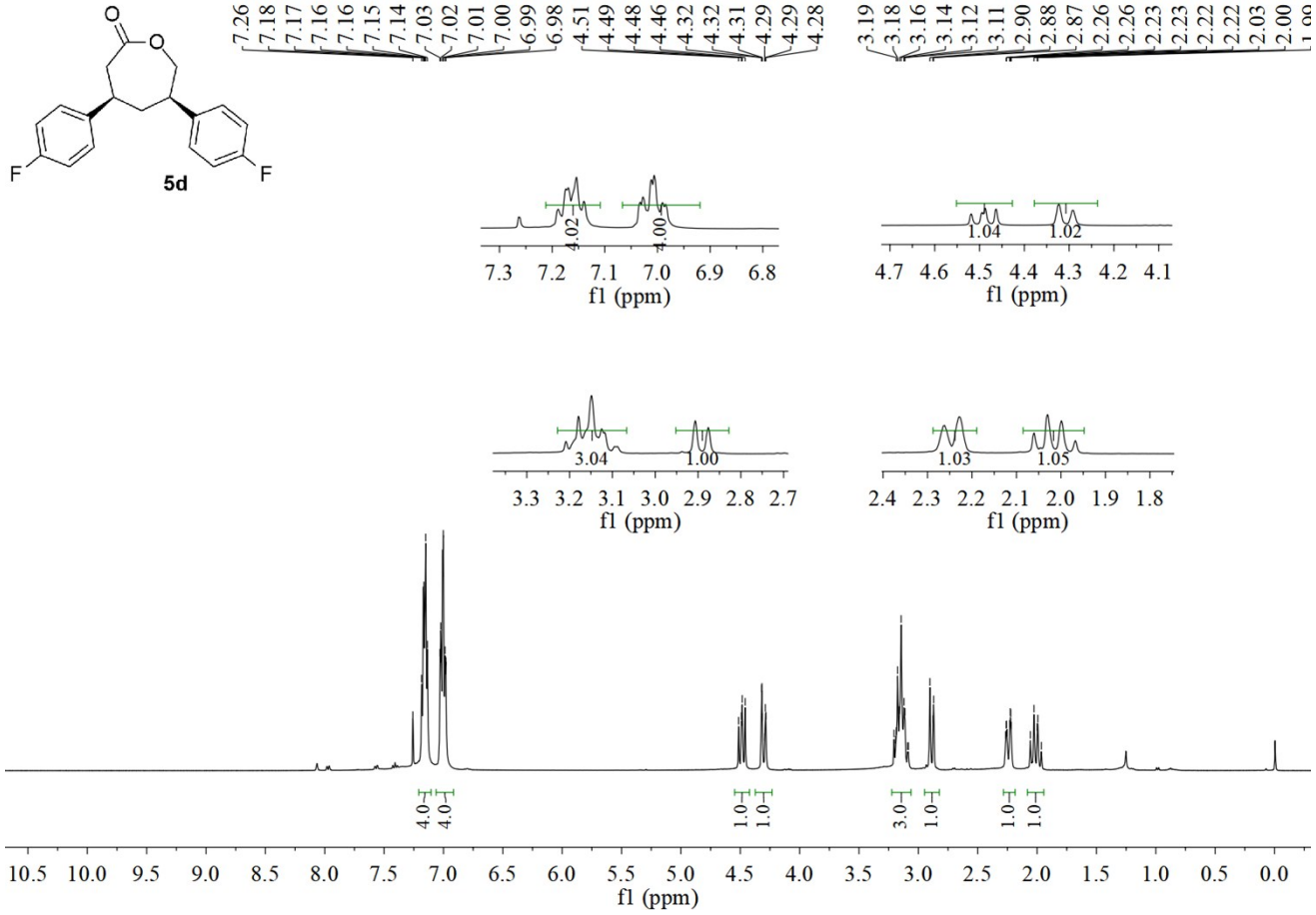

176.02
175.24
77.32 77.00 76.68 72.76 69.18 40.07 38.53 35.63 34.94 34.78 34.32 33.91 31.25 28.98 28.95 27.66 22.68 22.60 21.31 13.96 13.92
nBu
2l
nBu
3l
f1 (ppm)

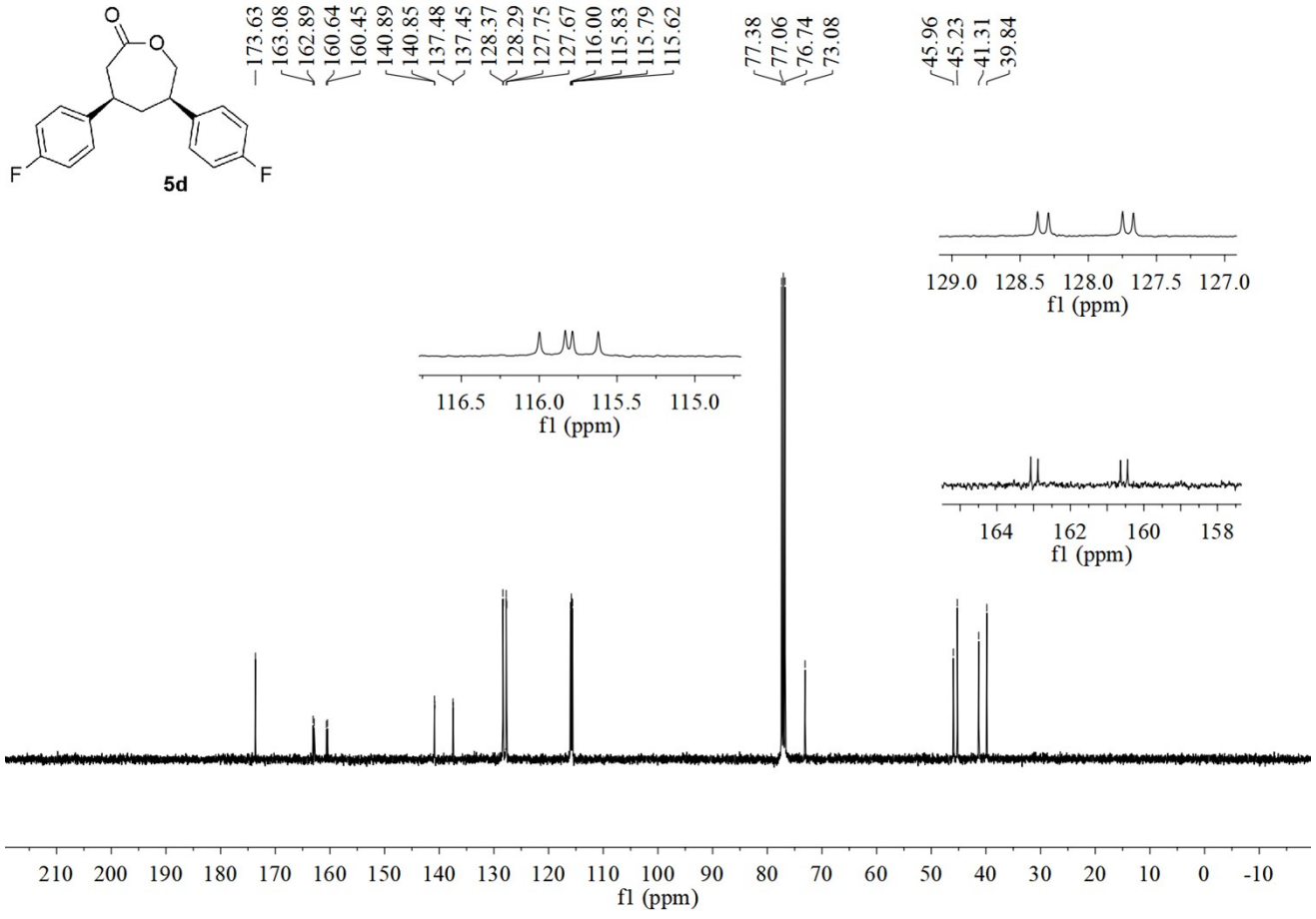

7.33 7.31 7.30 7.26 7.25 7.24 7.22 7.22 7.21 7.19 7.19 7.17 4.56 4.54 4.53 4.50 4.37 4.37 4.36 4.34 4.34 4.33 3.21 3.18 3.17 3.16 3.16 3.13 3.13 2.94 2.94 2.91 2.91 2.31 2.31 2.31 2.30 2.28 2.28 2.27 2.27 2.27 2.26 2.13 2.10 2.10 2.07 2.07 2.04
5a
3.96 6.08
0.94 0.96
2.87 0.98
1.02 1.05
f1 (ppm)
4.0 6.1 0.9 1.0 2.9 1.0 1.0 1.0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
173.94
145.20 141.82 128.94 128.82 127.23 126.94 126.78 126.17
77.32 77.00 76.68 73.16
45.98 45.82 41.17 40.57
5a
129 128 127 126
47 46 45 44 43 42 41 40 39
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

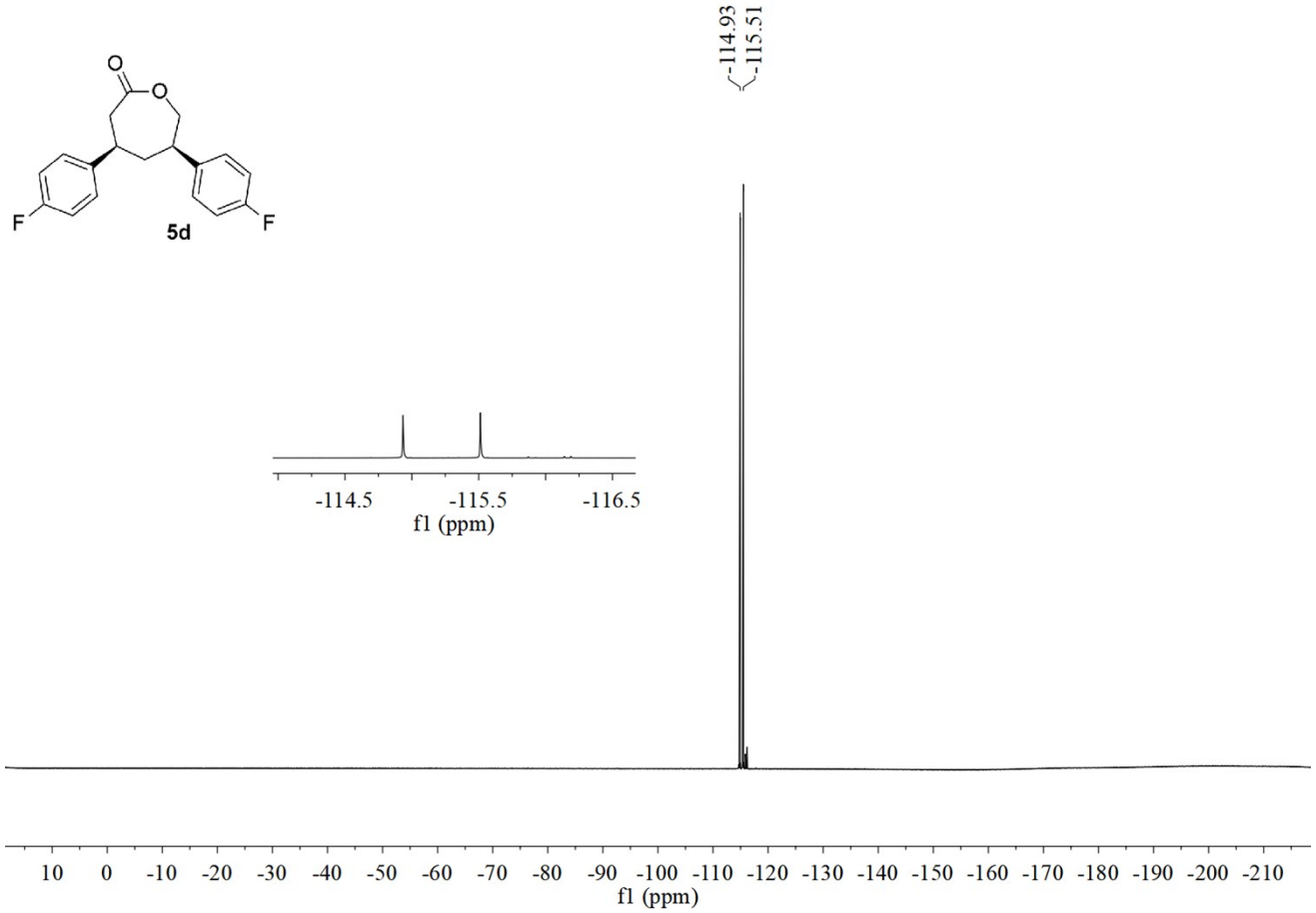

7.26 7.13 7.12 7.11 7.09 6.86 6.84 4.49 4.46 4.46 4.43 4.32 4.32 4.31 4.29 4.29 4.28 3.79 3.78 3.15 3.12 3.11 3.10 3.08 3.07 2.90 2.90 2.87 2.87 2.27 2.27 2.26 2.26 2.26 2.24 2.23 2.22 2.07 2.04 2.04 2.03 2.01 2.00 1.97
5b
4.00
4.03
1.02
1.03
3.02
0.96
1.06
1.03
f1 (ppm)
4.0 4.0 1.0 1.0 6.0 3.0 1.0 1.1 1.0
174.08
158.63
158.40
137.54
133.99
127.79
127.15
114.29
114.15
77.32
77.00
76.68
73.52
55.29
46.06
45.12
41.56
39.81

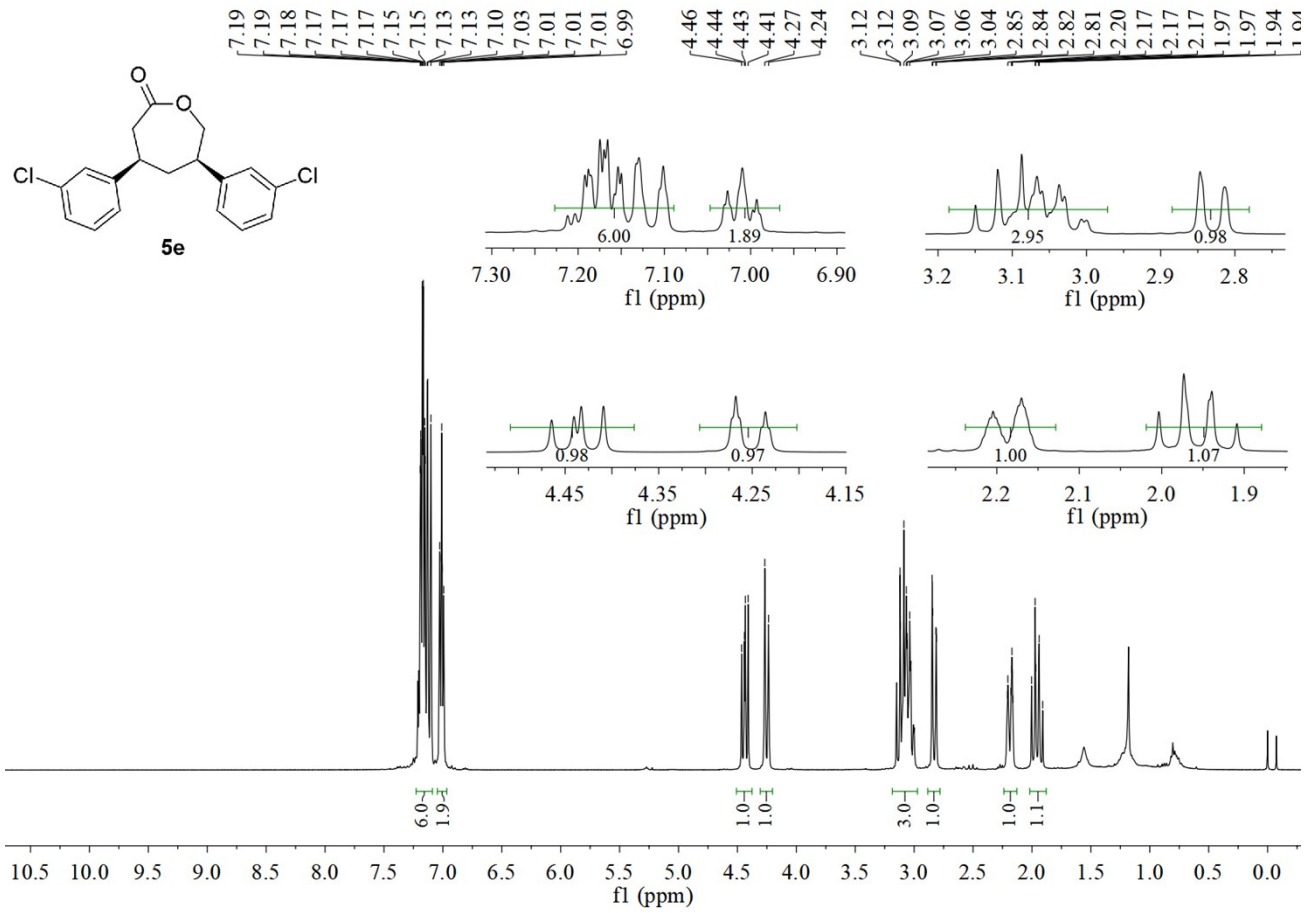

7.26 7.13 7.11 7.11 7.09 6.86 6.86 6.84 6.83 4.49 4.47 4.46 4.43 4.32 4.31 4.31 4.28 3.78 3.78 3.15 3.12 3.11 3.11 3.10 3.08 3.07 2.90 2.89 2.86 2.86 2.86 2.26 2.26 2.25 2.23 2.23 2.22 2.22 2.22 2.07 2.04 2.04 2.03 2.01 2.00
MeO
OMe
5c
3.96
4.04
f1 (ppm)
3.11
0.97
f1 (ppm)
1.00
0.95
f1 (ppm)
1.05
1.12
f1 (ppm)
4.0
4.0
1.0
1.0
3.1
1.0
1.0
1.1
f1 (ppm)

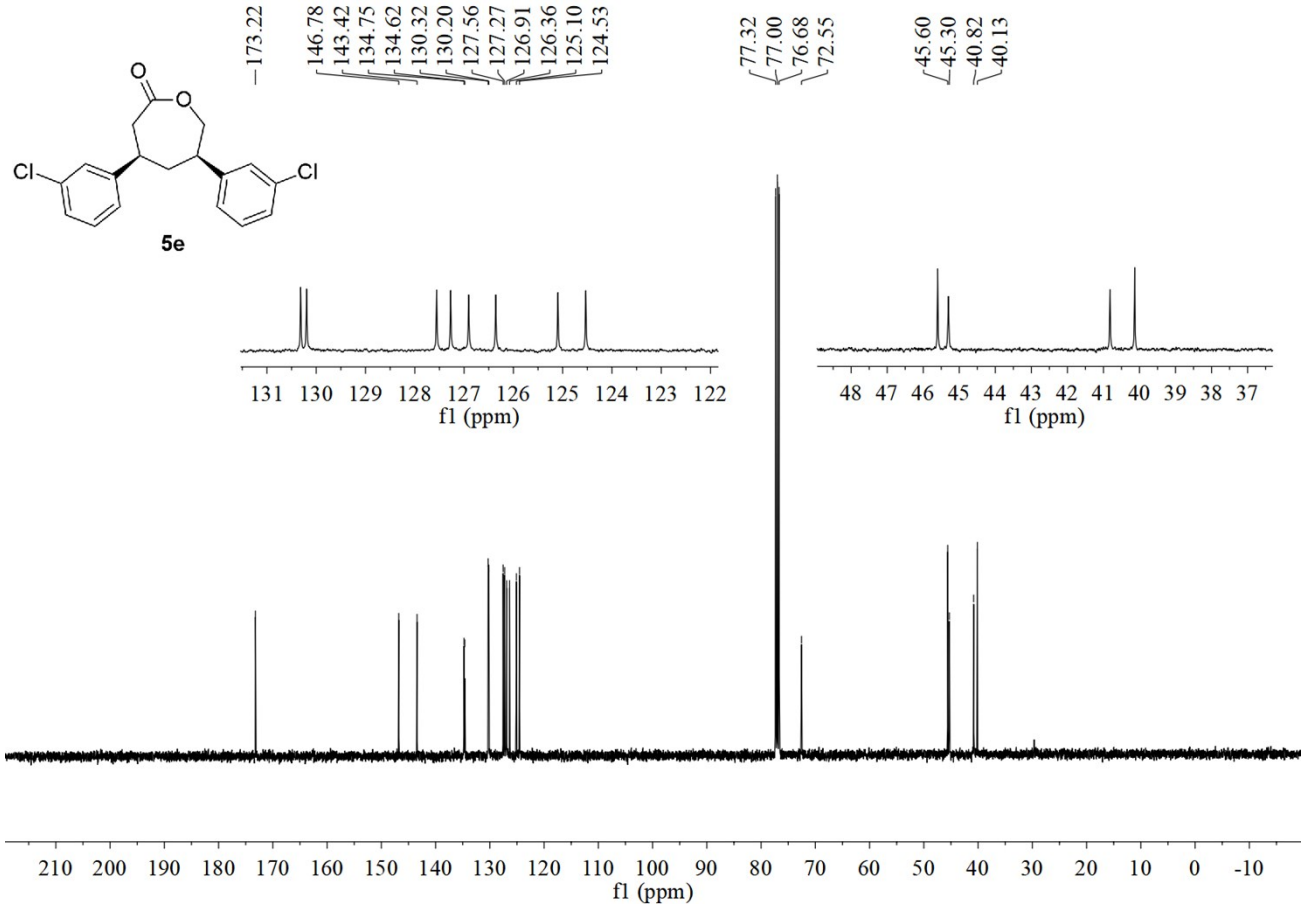

174.07
158.57
158.33
137.50
133.93
127.75
127.11
114.23
114.09
77.32
77.00
76.68
73.46
55.25
55.22
46.01
45.06
41.50
39.76
MeO
OMe
5c
f1 (ppm)
f1 (ppm)
f1 (ppm)

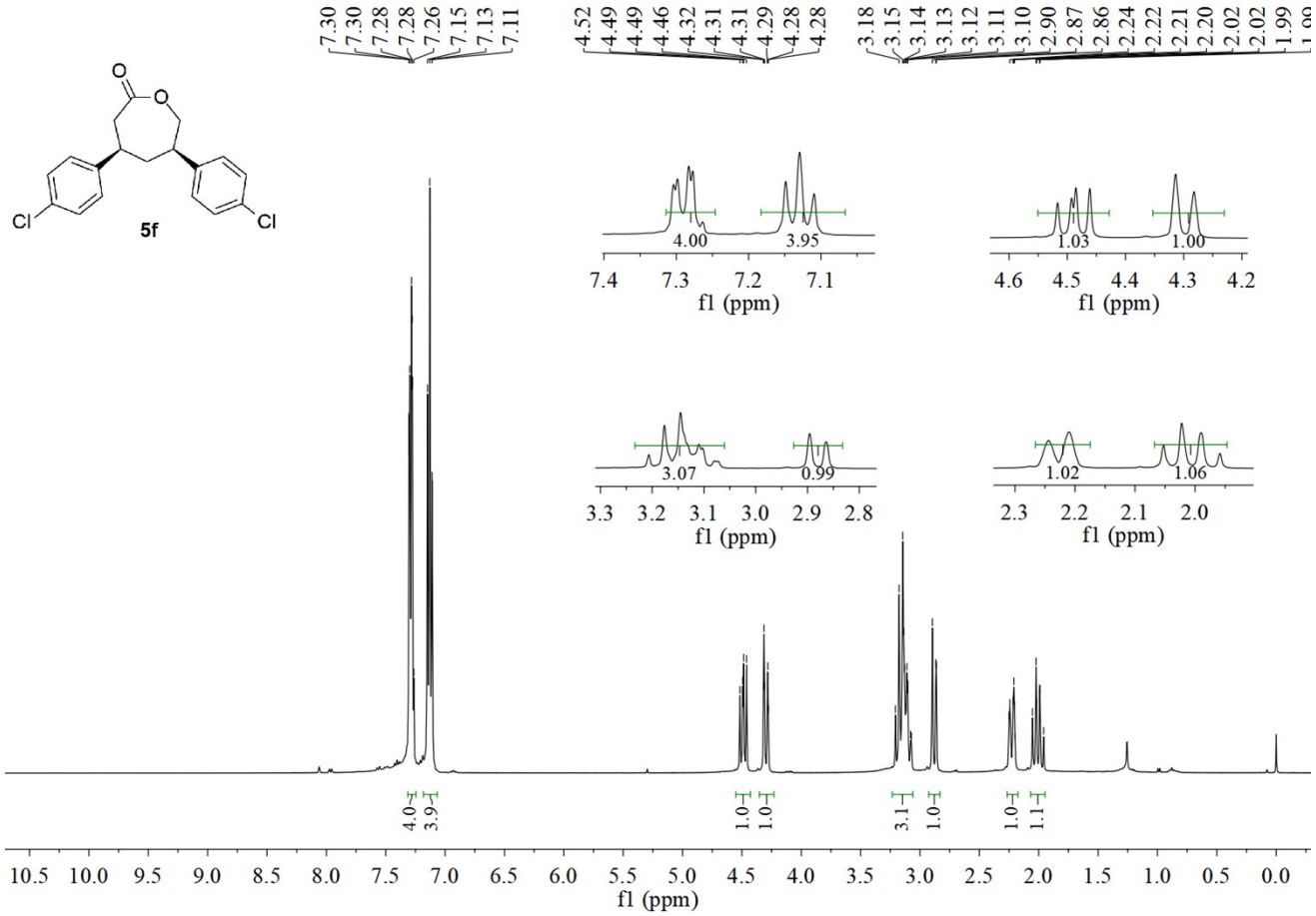

5d
F
F
O
O
7.26 7.18 7.17 7.16 7.16 7.15 7.14 7.03 7.02 7.01 7.00 6.99 6.98 4.51 4.49 4.48 4.46 4.32 4.32 4.31 4.29 4.29 4.28 3.19 3.18 3.16 3.14 3.12 3.11 2.90 2.88 2.87 2.26 2.26 2.23 2.23 2.22 2.22 2.03 2.00
4.02
4.00
7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.04
1.02
4.7 4.6 4.5 4.4 4.3 4.2 4.1
f1 (ppm)
3.04
1.00
3.3 3.2 3.1 3.0 2.9 2.8 2.7
f1 (ppm)
1.03
1.05
2.4 2.3 2.2 2.1 2.0 1.9 1.8
f1 (ppm)
4.0
4.0
1.0
1.0
3.0
1.0
1.0
1.0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

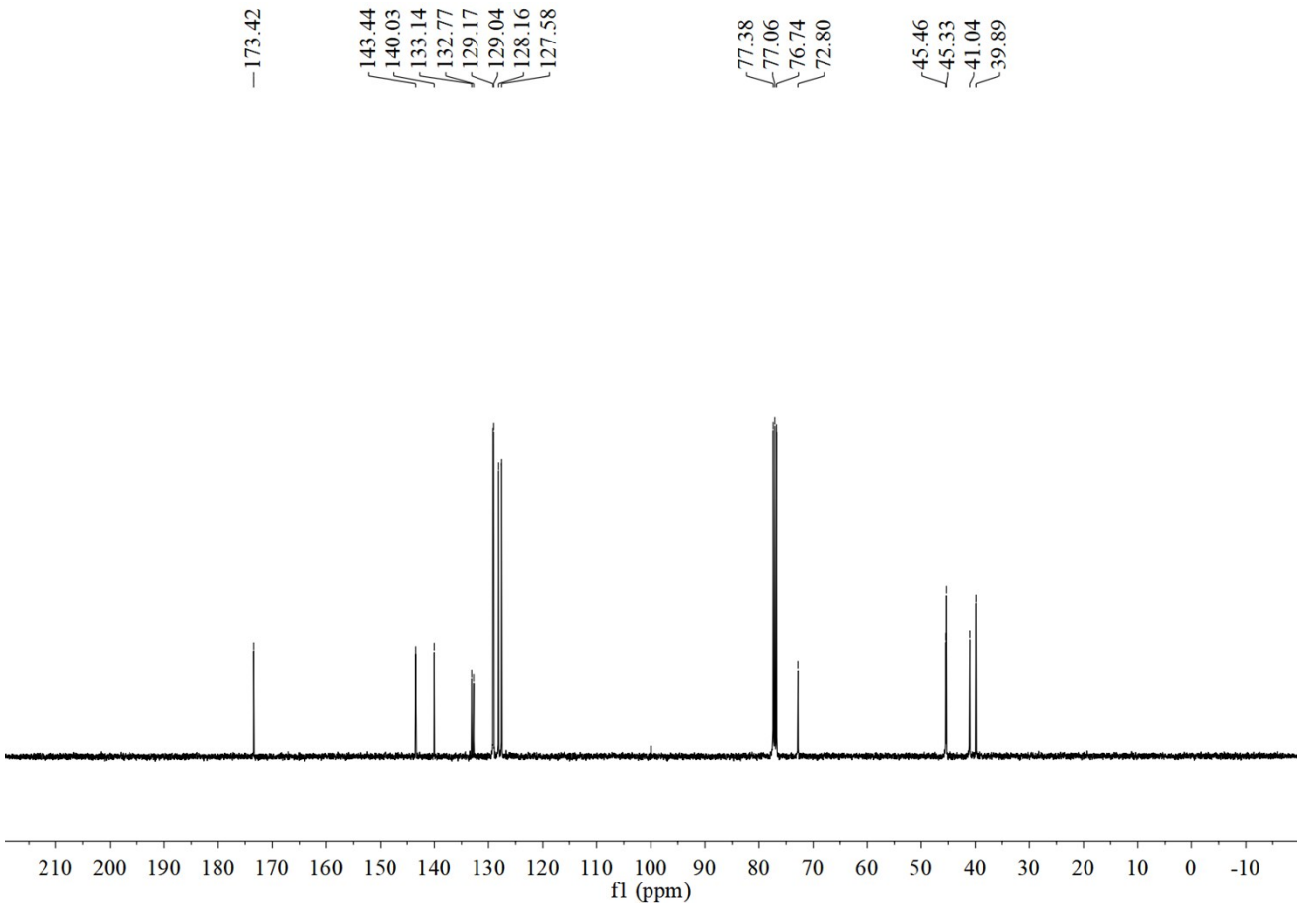

5d
F
F
O
O
173.63 163.08 162.89 160.64 160.45 140.89 140.85 137.48 137.45 128.37 128.29 127.75 127.67 116.00 115.83 115.79 115.62 77.38 77.06 76.74 73.08 45.96 45.23 41.31 39.84
129.0 128.5 128.0 127.5 127.0
f1 (ppm)
116.5 116.0 115.5 115.0
f1 (ppm)
164 162 160 158
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

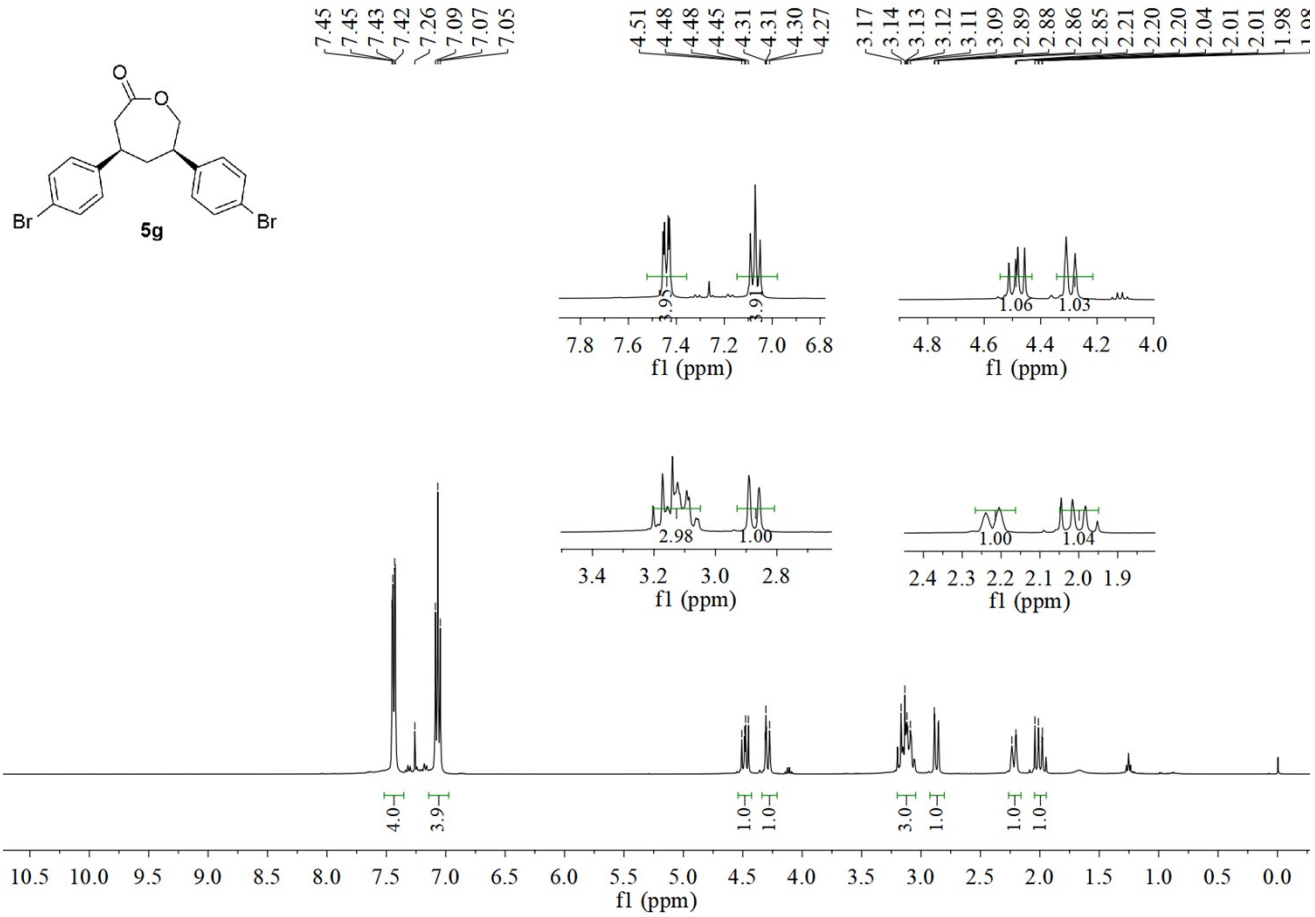

-114.93
-115.51
O
O
F
F
5d
-114.5
-115.5
-116.5
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

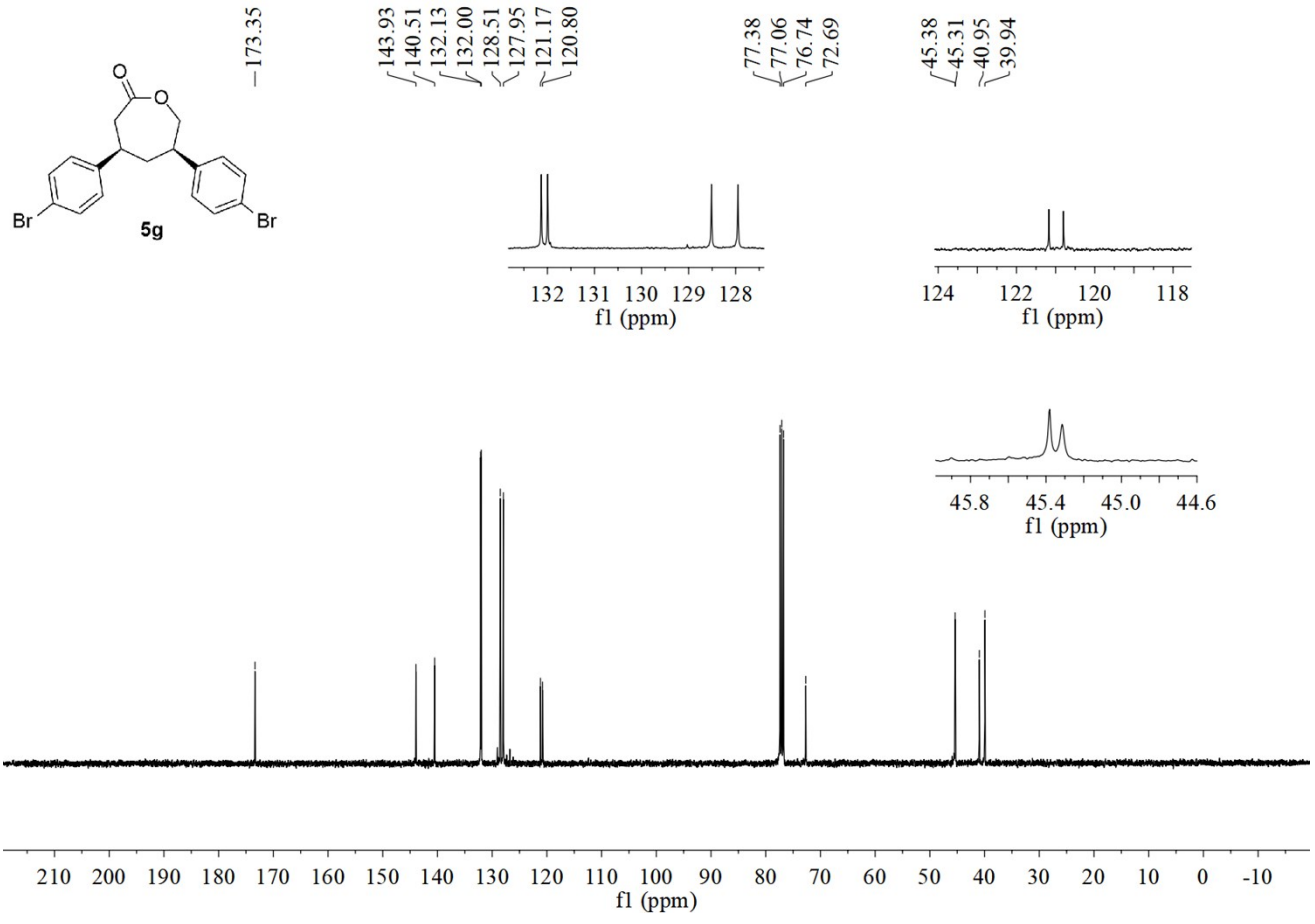

7.19 7.19 7.18 7.17 7.17 7.17 7.15 7.15 7.13 7.13 7.10 7.03 7.01 7.01 7.01 6.99
4.46 4.44 4.43 4.41 4.27 4.24
3.12 3.12 3.09 3.07 3.06 3.04 2.85 2.84 2.82 2.81 2.20 2.17 2.17 1.97 1.97 1.94
O
O
Cl
Cl
5e
6.00
1.89
f1 (ppm)
2.95
0.98
f1 (ppm)
0.98
0.97
f1 (ppm)
1.00
1.07
f1 (ppm)
6.0
1.9
1.0
1.0
3.0
1.0
1.0
1.1
f1 (ppm)

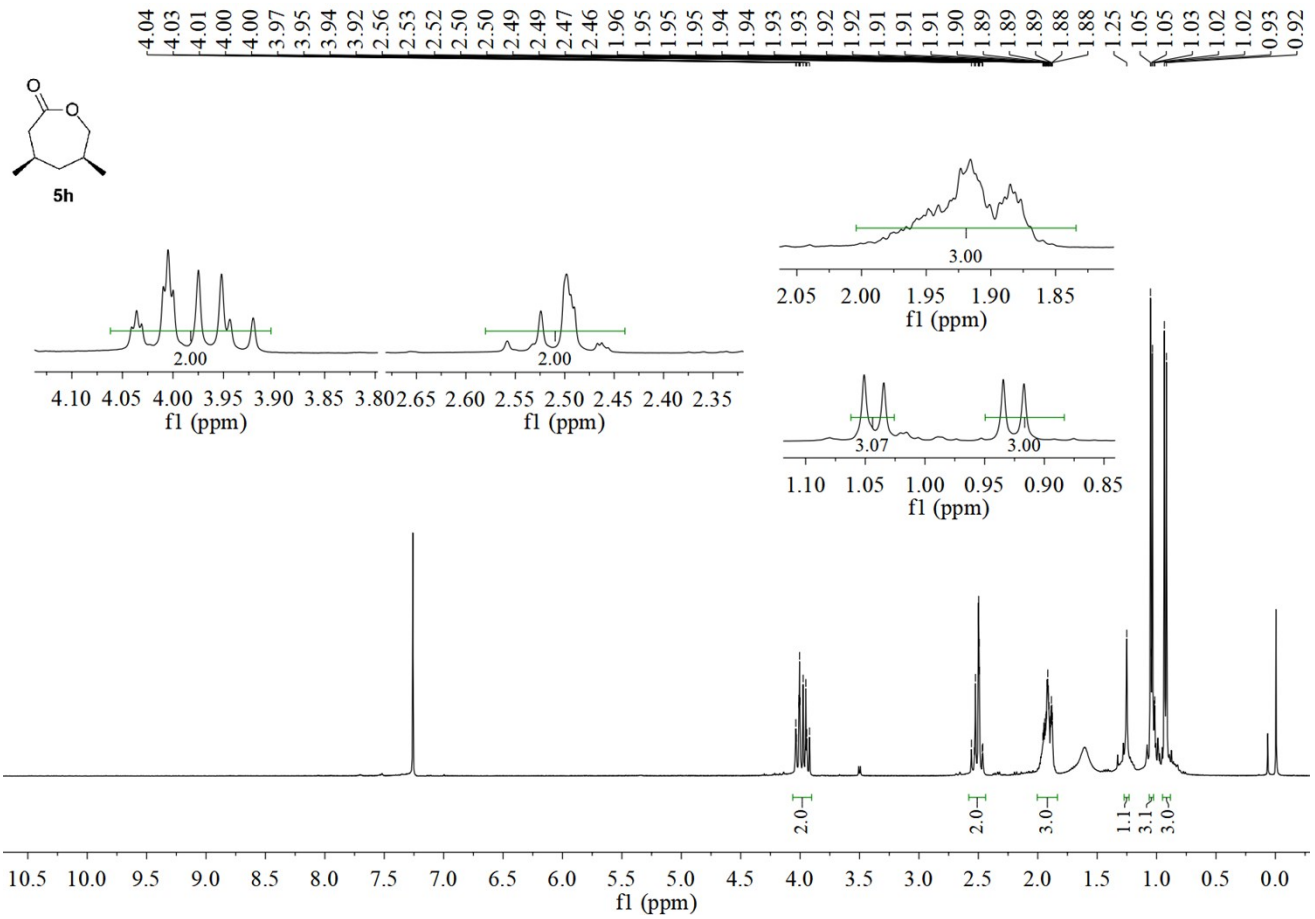

173.22
146.78 143.42 134.75 134.62 130.32 130.20 127.56 127.27 126.91 126.36 125.10 124.53
77.32 77.00 76.68 72.55
45.60 45.30 40.82 40.13
O
O
Cl
Cl
5e
f1 (ppm)
f1 (ppm)
f1 (ppm)

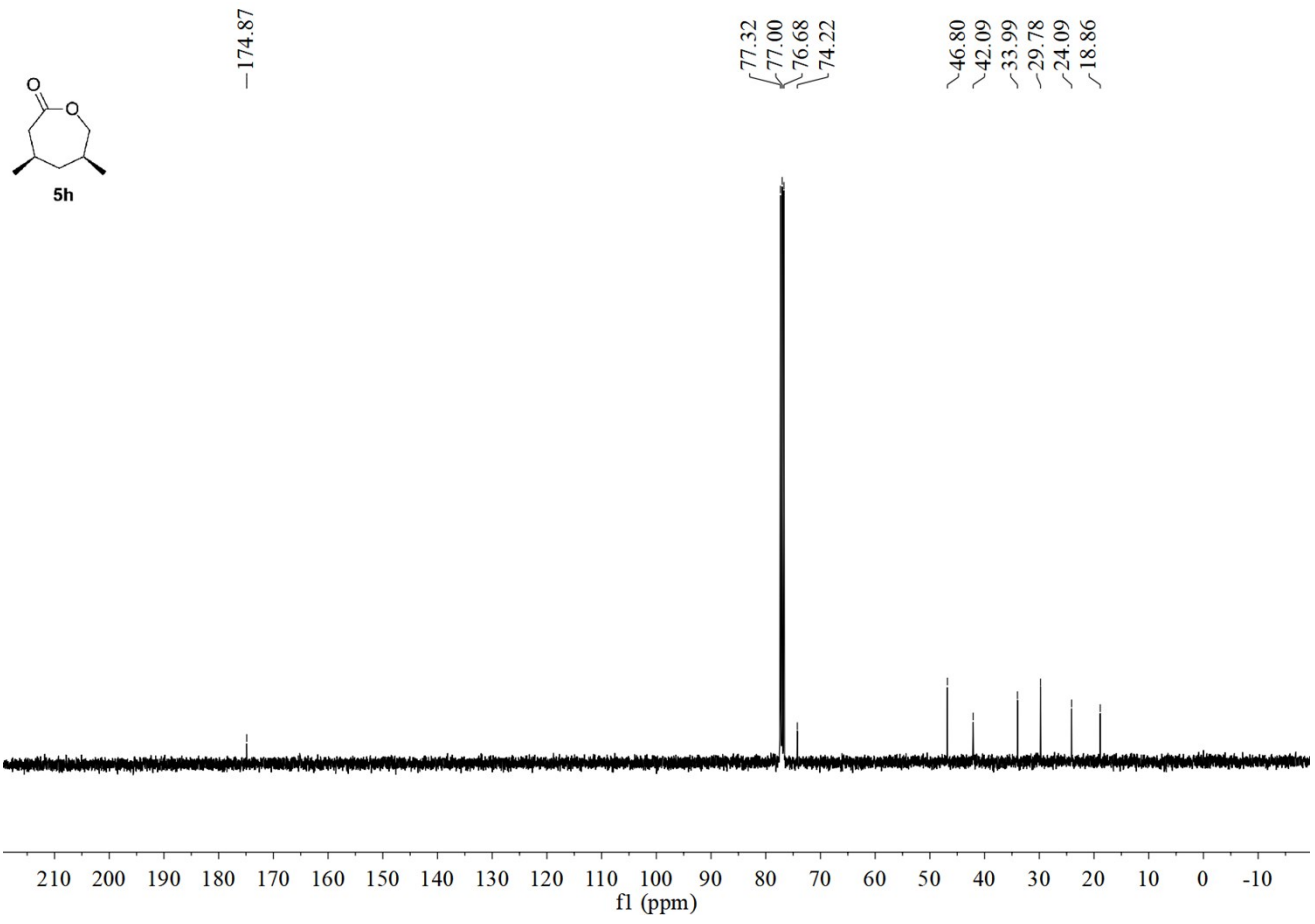

7.30
7.30
7.28
7.28
7.26
7.15
7.13
7.11
4.52
4.49
4.49
4.46
4.32
4.31
4.31
4.29
4.28
4.28
3.18
3.15
3.14
3.13
3.12
3.11
3.10
2.90
2.87
2.86
2.24
2.22
2.21
2.20
2.02
2.02
1.99
O
O
Cl
Cl
5f
4.00
3.95
1.03
1.00
3.07
0.99
1.02
1.06
fl (ppm)
4.0
3.9
1.0
1.0
3.1
1.0
1.0
1.1

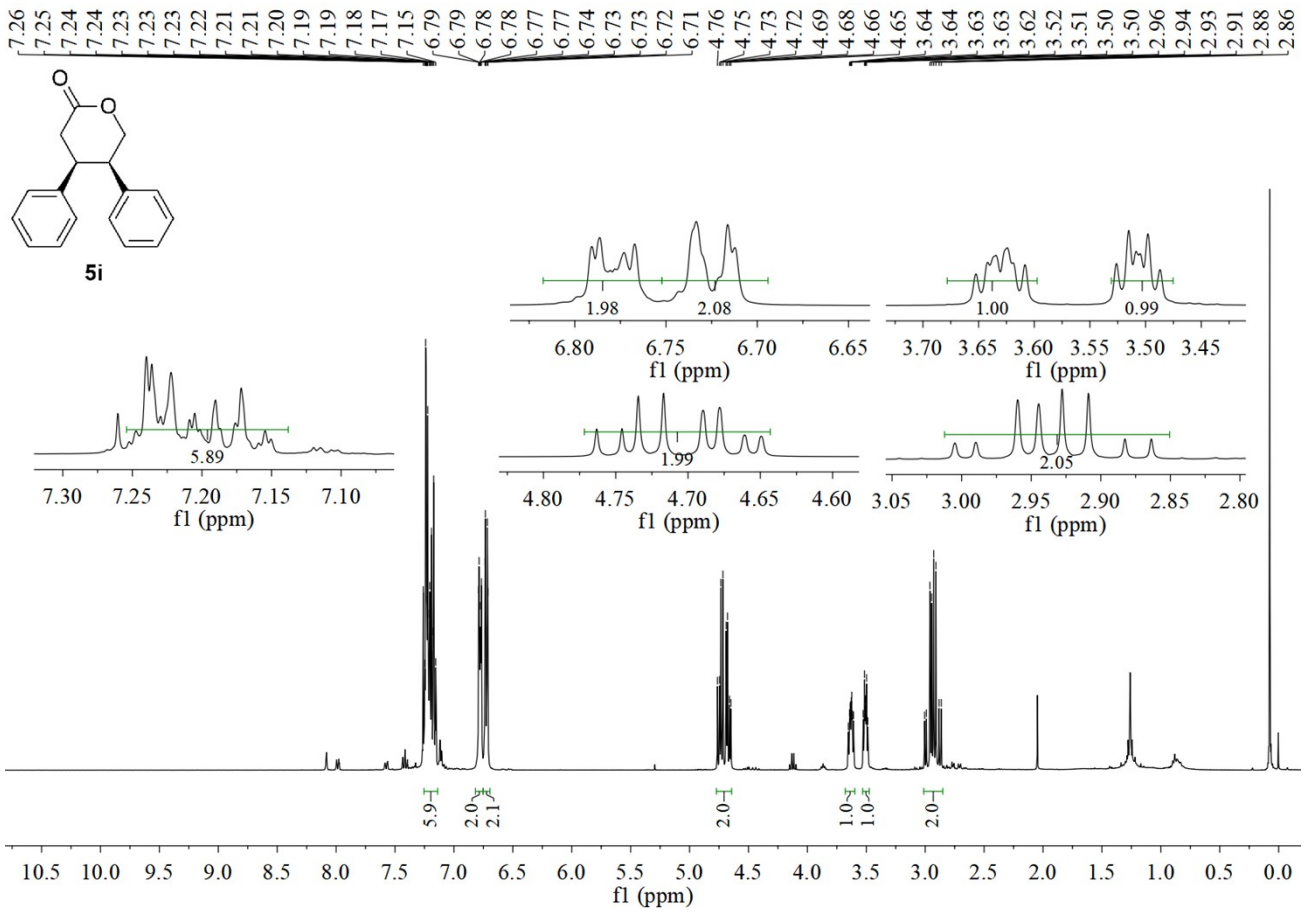

173.42
143.44
140.03
133.14
132.77
129.17
129.04
128.16
127.58
77.38
77.06
76.74
72.80
45.46
45.33
41.04
39.89
fl (ppm)

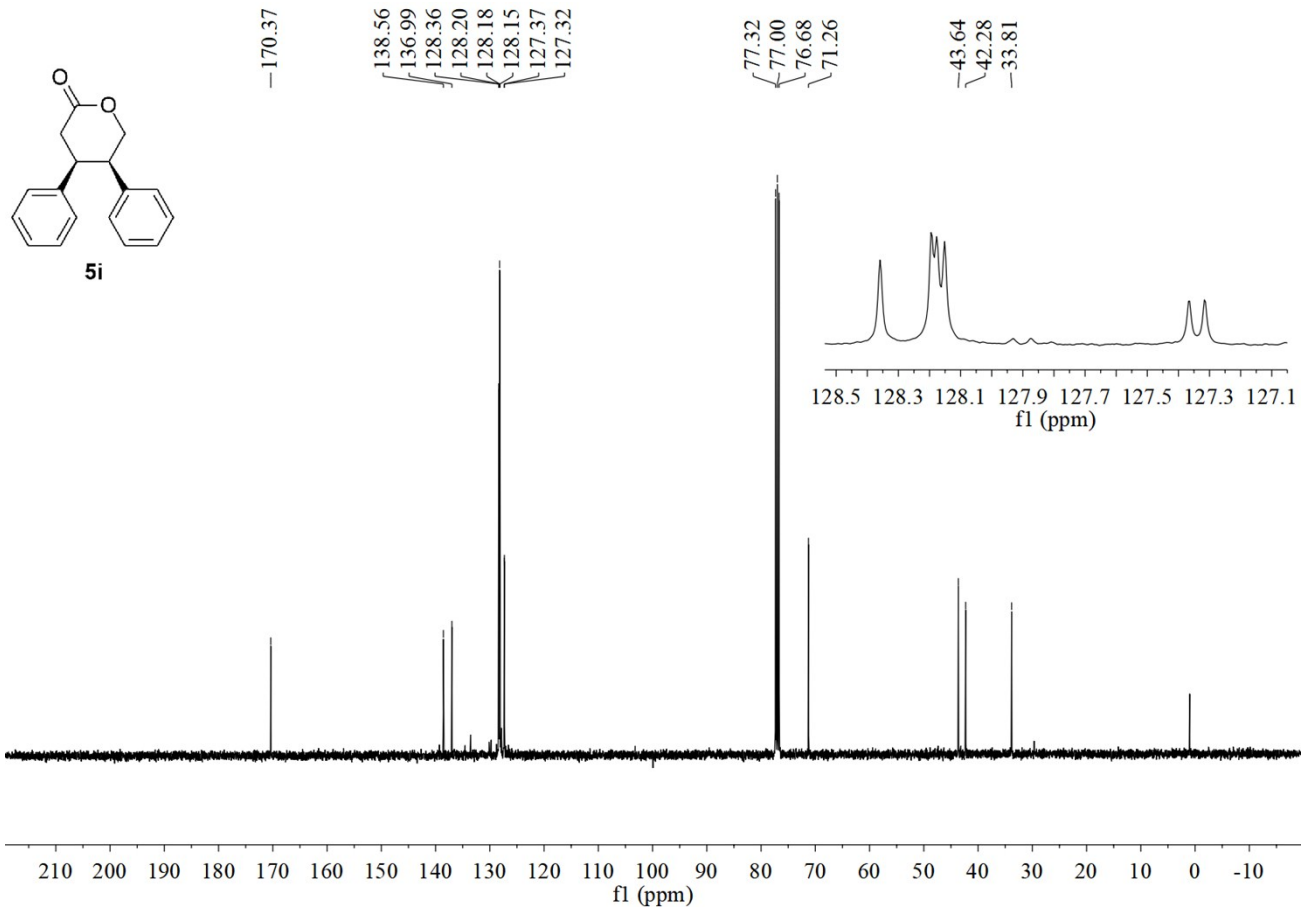

7.45
7.45
7.43
7.42
7.26
7.09
7.07
7.05
4.51
4.48
4.48
4.45
4.31
4.31
4.30
4.27
3.17
3.14
3.13
3.12
3.11
3.09
2.89
2.88
2.86
2.85
2.21
2.20
2.20
2.04
2.01
2.01
1.98
Br
Br
5g
3.95
3.91
1.06
1.03
7.8 7.6 7.4 7.2 7.0 6.8
f1 (ppm)
4.8 4.6 4.4 4.2 4.0
f1 (ppm)
2.98
1.00
1.00
1.04
3.4 3.2 3.0 2.8
f1 (ppm)
2.4 2.3 2.2 2.1 2.0 1.9
f1 (ppm)
4.0
3.9
1.0
1.0
3.0
1.0
1.0
1.0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

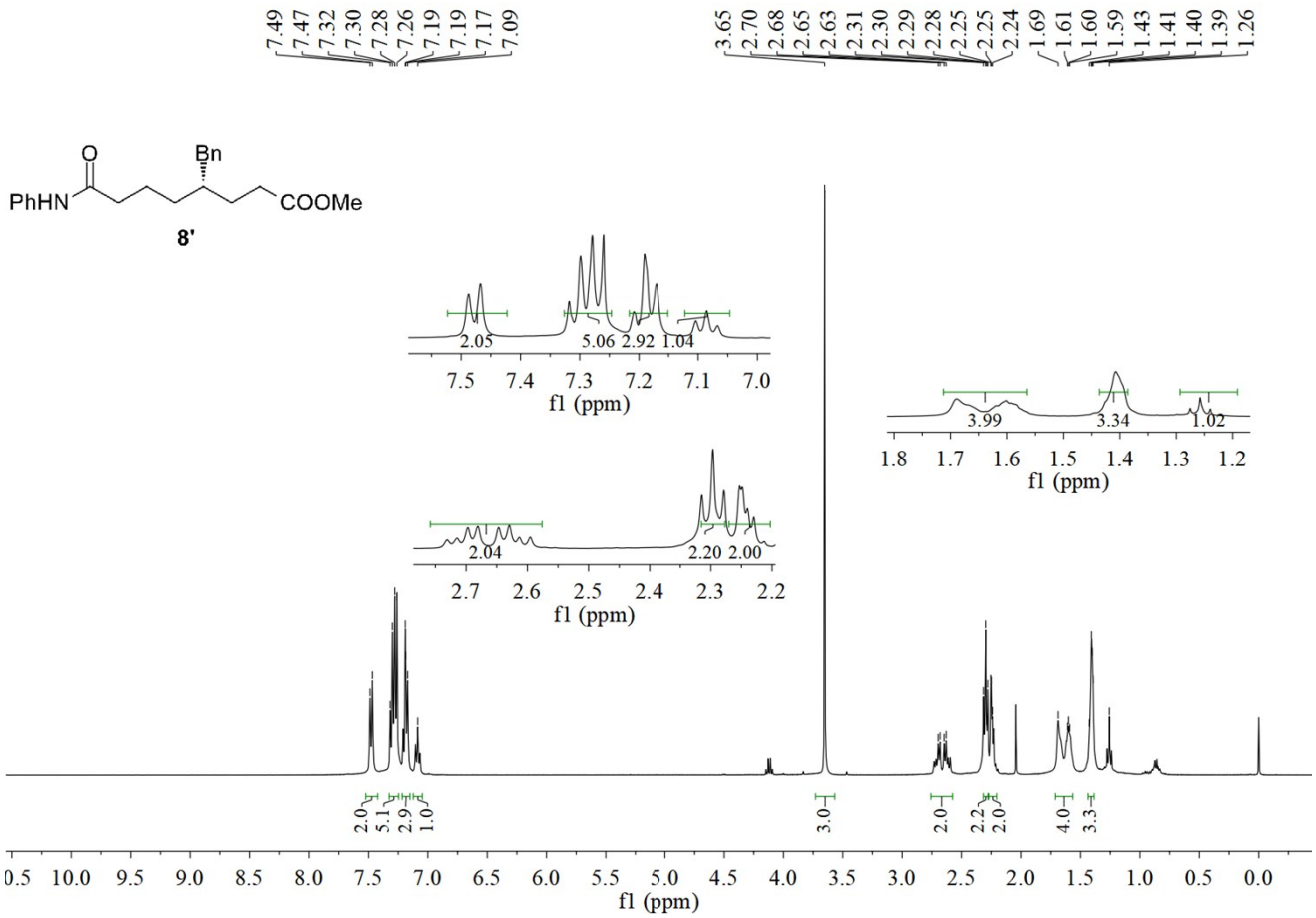

173.35
143.93
140.51
132.13
132.00
128.51
127.95
121.17
120.80
77.38
77.06
76.74
72.69
45.38
45.31
40.95
39.94
Br
Br
5g
132 131 130 129 128
f1 (ppm)
124 122 120 118
f1 (ppm)
45.8 45.4 45.0 44.6
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

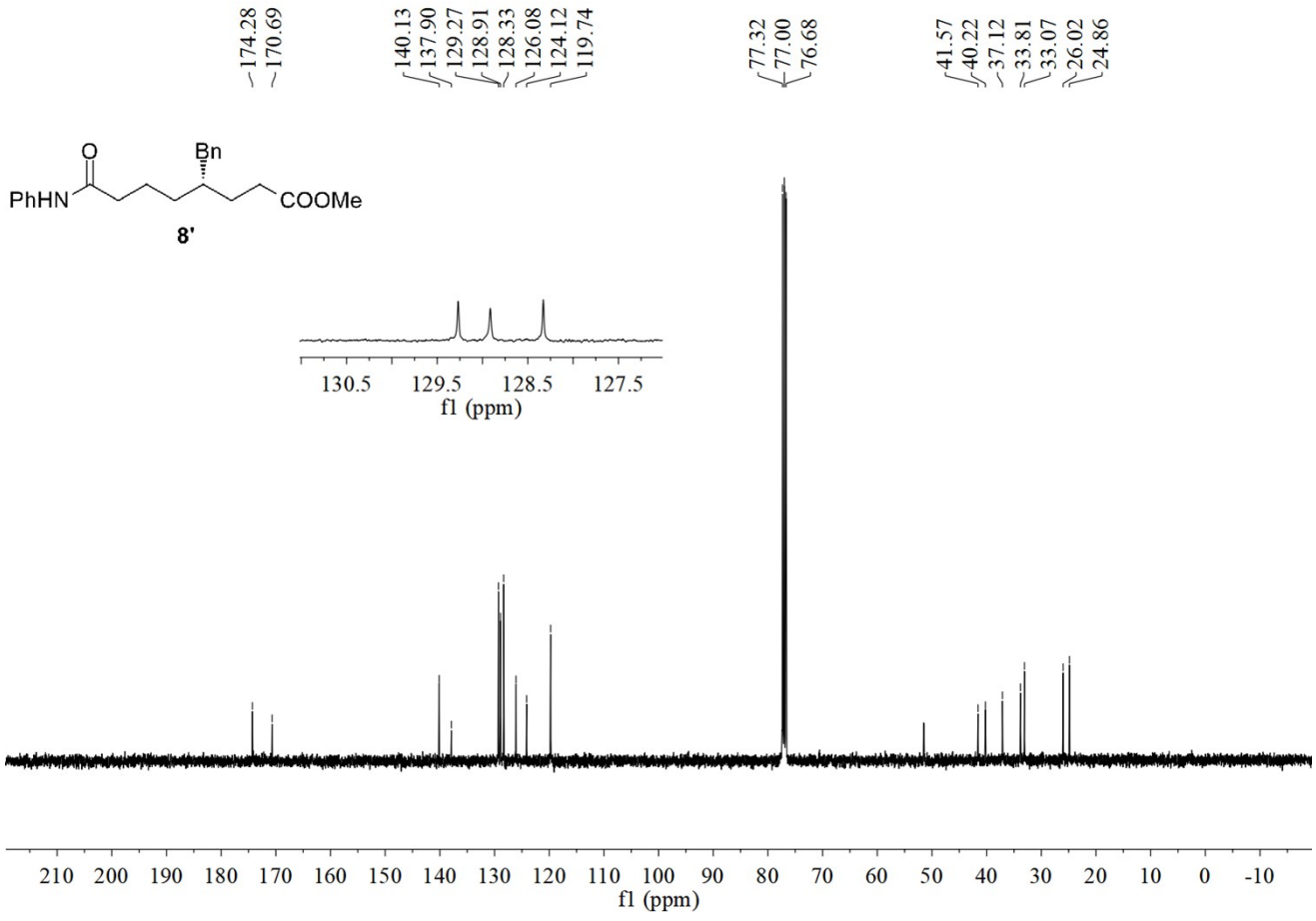

4.04 4.03 4.01 4.00 4.00 3.97 3.95 3.94 3.92 2.56 2.53 2.52 2.50 2.50 2.49 2.49 2.47 2.46 1.96 1.95 1.95 1.95 1.94 1.94 1.93 1.93 1.92 1.92 1.91 1.91 1.91 1.90 1.89 1.89 1.89 1.88 1.88 1.25 1.05 1.05 1.03 1.02 1.02 0.93 0.92
5h
2.00
2.00
3.00
3.07
3.00
2.0
2.0
3.0
1.1
3.1
3.0
fl (ppm)

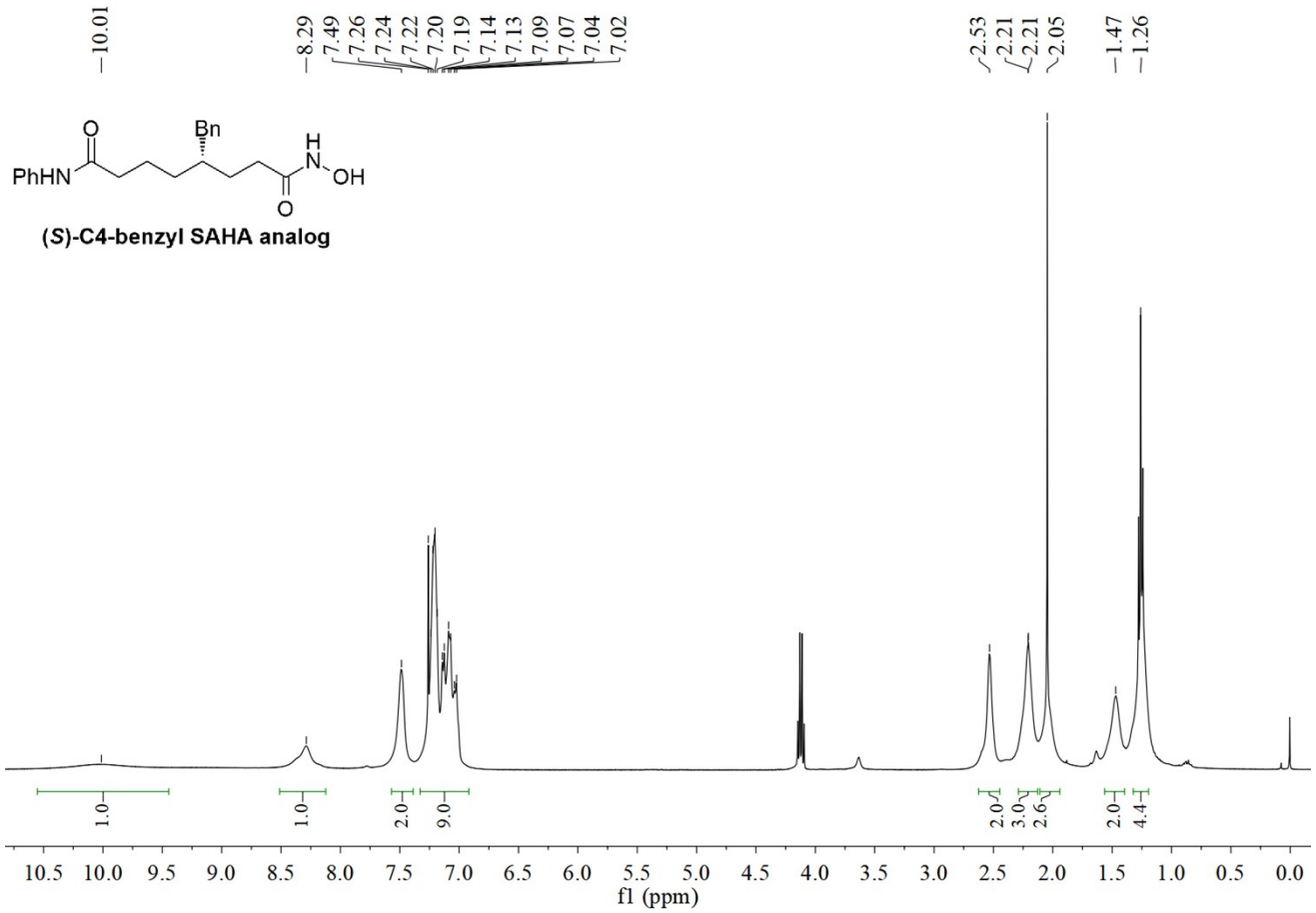

174.87
77.32
77.00
76.68
74.22
46.80
42.09
33.99
29.78
24.09
18.86
5h
fl (ppm)

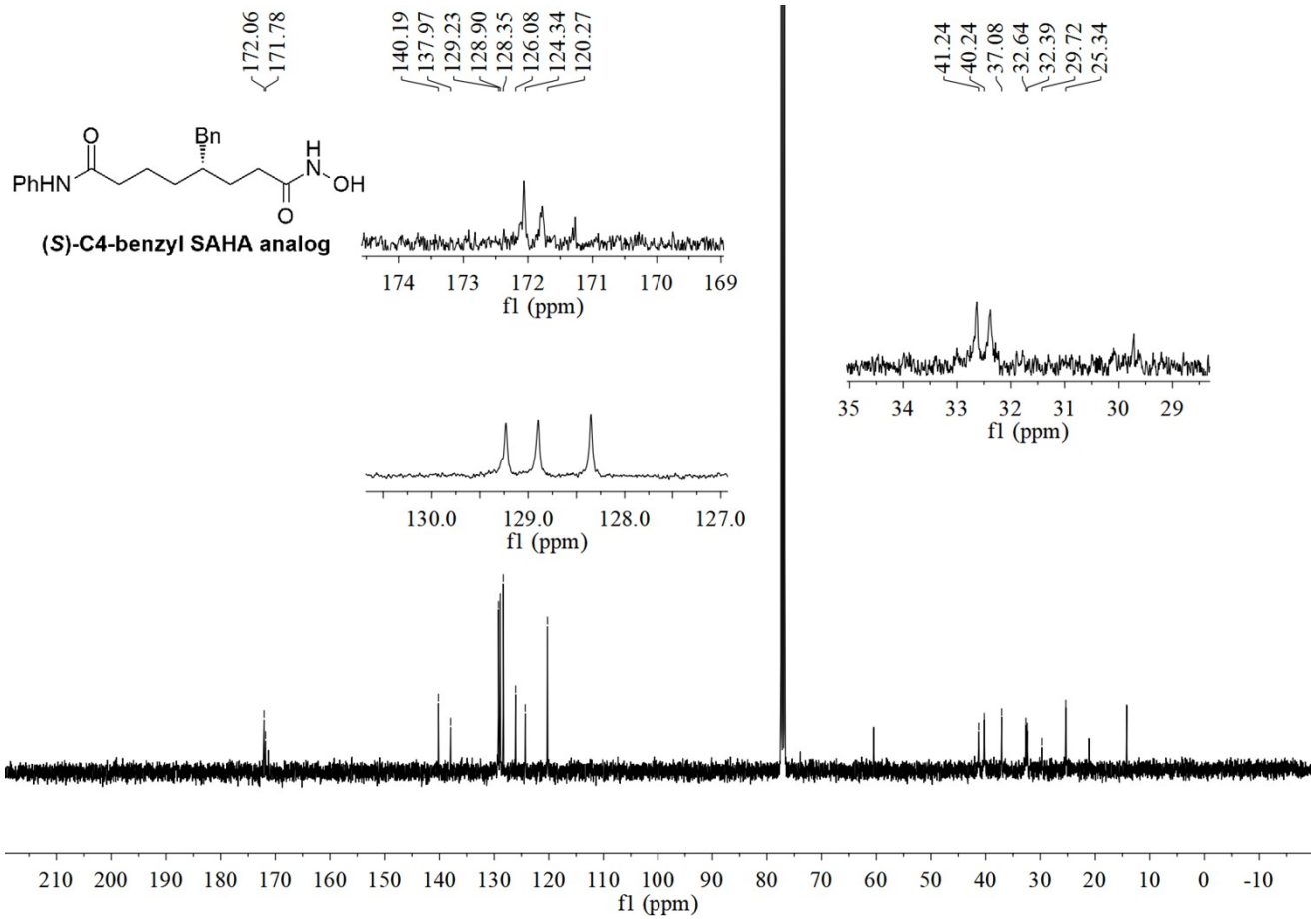

7.26 7.25 7.24 7.24 7.23 7.23 7.23 7.22 7.21 7.21 7.20 7.19 7.19 7.18 7.17 7.15 6.79 6.79 6.78 6.78 6.77 6.77 6.74 6.73 6.73 6.72 6.71 4.76 4.75 4.73 4.72 4.69 4.68 4.66 4.65 3.64 3.64 3.63 3.63 3.62 3.52 3.51 3.50 3.50 2.96 2.94 2.93 2.91 2.88 2.86
5i
1.98 2.08
6.80 6.75 6.70 6.65
f1 (ppm)
1.00 0.99
3.70 3.65 3.60 3.55 3.50 3.45
f1 (ppm)
5.89
7.30 7.25 7.20 7.15 7.10
f1 (ppm)
1.99
4.80 4.75 4.70 4.65 4.60
f1 (ppm)
2.05
3.05 3.00 2.95 2.90 2.85 2.80
f1 (ppm)
5.9 2.0 2.1 2.0 1.0 1.0 2.0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

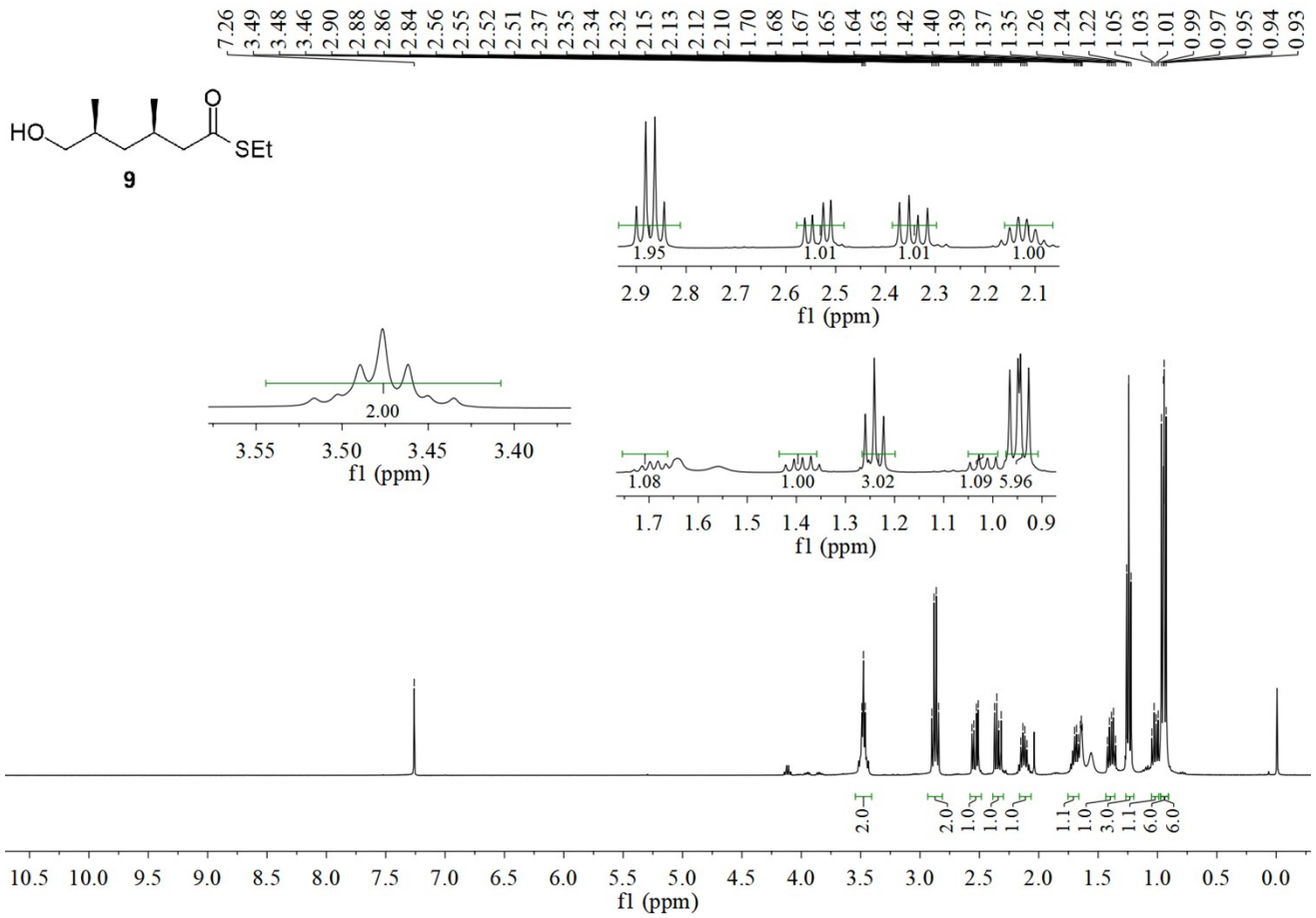

170.37
138.56 136.99 128.36 128.20 128.18 128.15 127.37 127.32
77.32 77.00 76.68 71.26
43.64 42.28 33.81
5i
128.5 128.3 128.1 127.9 127.7 127.5 127.3 127.1
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

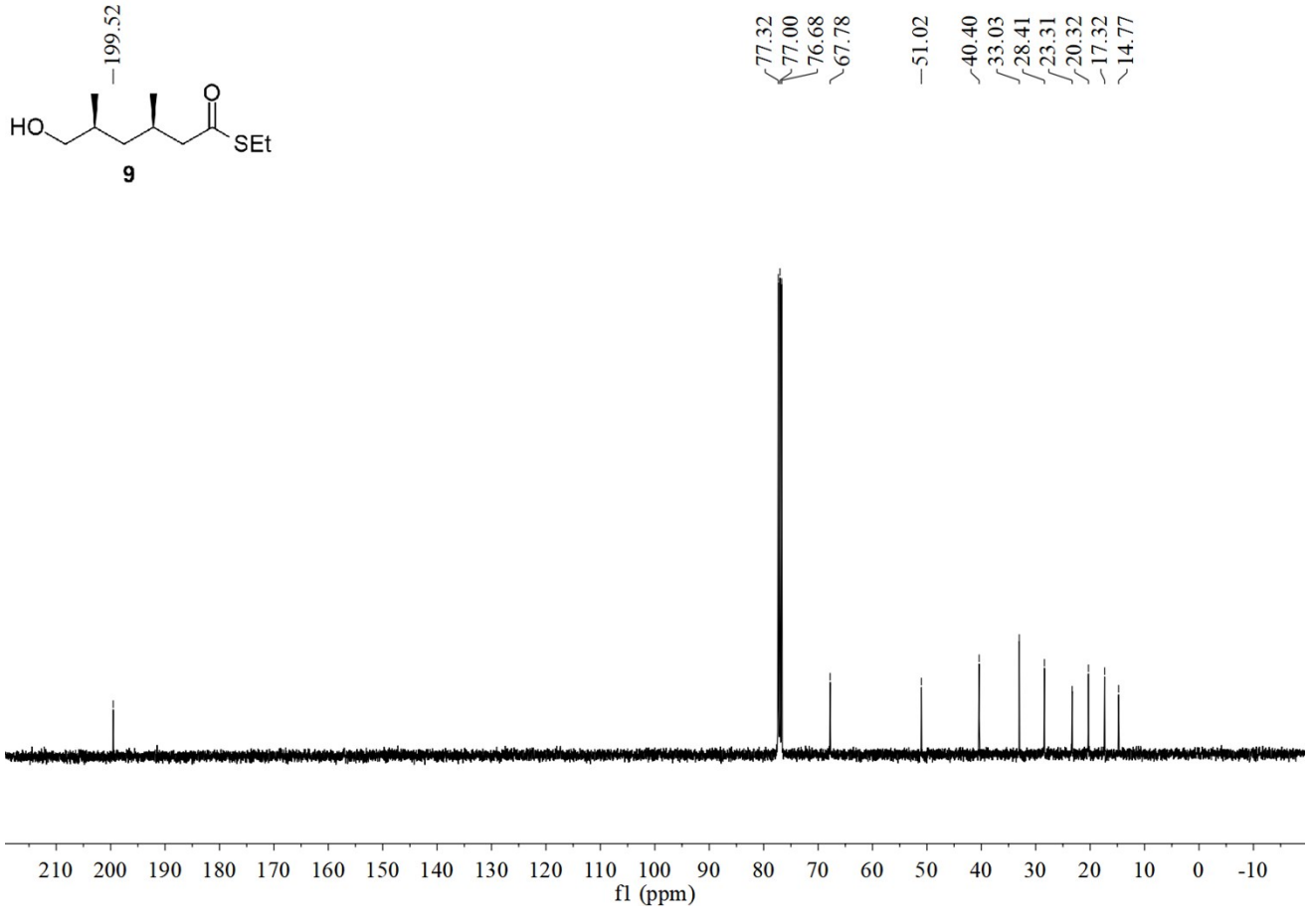

7.49 7.47 7.32 7.30 7.28 7.26 7.19 7.19 7.17 7.09
3.65 2.70 2.68 2.65 2.63 2.31 2.30 2.29 2.28 2.25 2.25 2.24 1.69 1.61 1.60 1.59 1.43 1.41 1.40 1.39 1.26
O
Bn
PhHN
COOMe
8'
2.05 5.06 2.92 1.04
7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
3.99 3.34 1.02
1.8 1.7 1.6 1.5 1.4 1.3 1.2
f1 (ppm)
2.04 2.20 2.00
2.7 2.6 2.5 2.4 2.3 2.2
f1 (ppm)
2.0 5.1 2.9 1.0 3.0 2.0 2.2 2.0 4.0 3.3
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

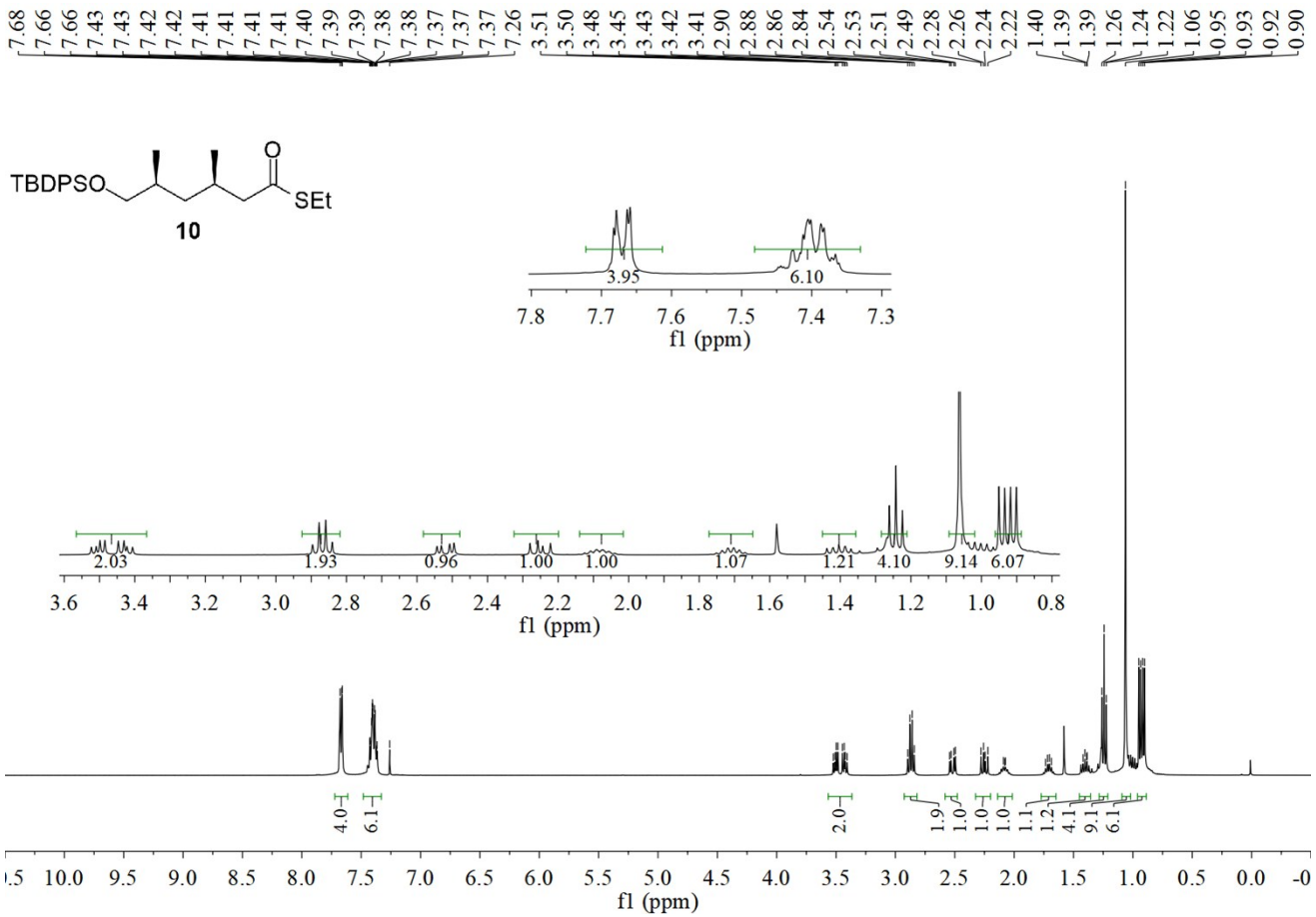

174.28 170.69
140.13 137.90 129.27 128.91 128.33 126.08 124.12 119.74
77.32 77.00 76.68
41.57 40.22 37.12 33.81 33.07 26.02 24.86
O
Bn
PhHN
COOMe
8'
130.5 129.5 128.5 127.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

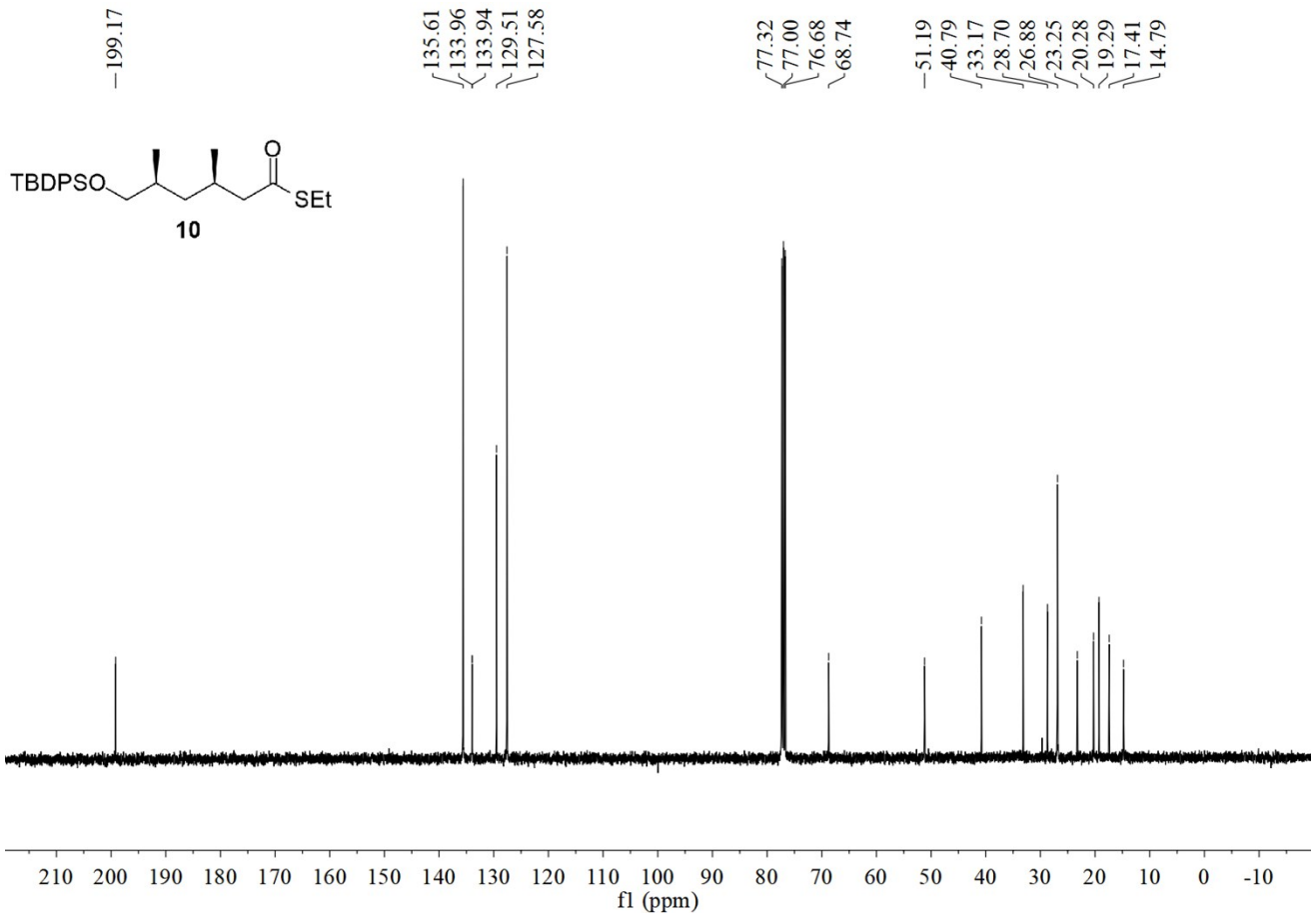

10.01
8.29
7.49
7.26
7.24
7.22
7.20
7.19
7.14
7.13
7.09
7.07
7.04
7.02
2.53
2.21
2.21
2.05
1.47
1.26
Bn
PhHN
H
N
OH
O
O
(S)-C4-benzyl SAHA analog
1.0
1.0
2.0
9.0
2.0
3.0
2.6
2.0
4.4
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.06
171.78
140.19
137.97
129.23
128.90
128.35
126.08
124.34
120.27
41.24
40.24
37.08
32.64
32.39
29.72
25.34
Bn
PhHN
H
N
OH
O
O
(S)-C4-benzyl SAHA analog
174 173 172 171 170 169
f1 (ppm)
35 34 33 32 31 30 29
f1 (ppm)
130.0 129.0 128.0 127.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 3.49 3.48 3.46 2.90 2.88 2.86 2.84 2.56 2.55 2.52 2.51 2.37 2.35 2.34 2.32 2.15 2.13 2.12 2.10 1.70 1.68 1.67 1.65 1.64 1.63 1.42 1.40 1.39 1.37 1.35 1.26 1.24 1.22 1.05 1.03 1.01 0.99 0.97 0.95 0.94 0.93
HO
SEt
O
9
1.95 1.01 1.01 1.00
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1
f1 (ppm)
2.00
3.55 3.50 3.45 3.40
f1 (ppm)
1.08 1.00 3.02 1.09 5.96
1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9
f1 (ppm)
2.0 2.0 1.0 1.0 1.0 1.1 1.0 3.0 1.1 6.0 6.0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


199.52
HO
SEt
O
9
77.32 77.00 76.68 67.78 51.02 40.40 33.03 28.41 23.31 20.32 17.32 14.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.68 7.66 7.66 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.41 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.26
3.51 3.50 3.48 3.45 3.43 3.42 3.41 2.90 2.88 2.86 2.84 2.54 2.53 2.51 2.49 2.28 2.26 2.24 2.22
1.40 1.39 1.39 1.26 1.24 1.22 1.06 0.95 0.93 0.92 0.90
TBDPSO
O
SEt
10
3.95
6.10
7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
2.03 1.93 0.96 1.00 1.00 1.07 1.21 4.10 9.14 6.07
3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)
4.0 6.1 2.0 1.9 1.0 1.0 1.0 1.1 1.2 4.1 9.1 6.1
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


199.17
135.61 133.96 133.94 129.51 127.58
77.32 77.00 76.68 68.74
51.19 40.79 33.17 28.70 26.88 23.25 20.28 19.29 17.41 14.79
TBDPSO
O
SEt
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)