

Enantioselective Baeyer–Villiger Oxidation: Desymmetrization of *meso*-Cyclic Ketones and
Kinetic Resolution of Racemic 2-Aryl-cyclohexanones

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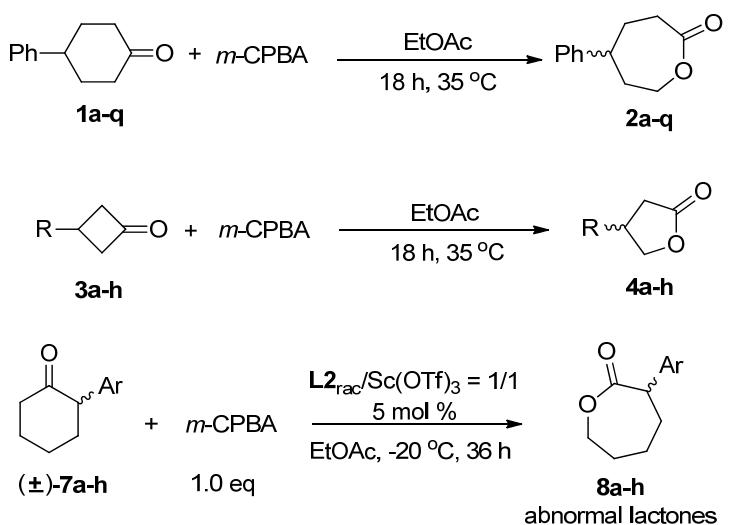
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1. General

¹H NMR spectra were recorded on commercial instruments (300 MHz or 400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : $\delta = 7.26$). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, w = wide), coupling constants (Hz) and integration. ¹³C NMR spectra were collected on commercial instruments (75 MHz or 100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl_3 : $\delta = 77.0$). The enantiomeric excesses were determined by HPLC analysis on chiral Daicel Chiralcel AS-H, AD-H and OD-H columns in comparison with the authentic racemates and chiral GC analysis. ESI-HRMS spectra were recorded on a commercial apparatus and methanol or acetonitrile was used to dissolve the sample. Reagents obtained from commercial sources were used without further purification. CH_2Cl_2 were distilled over CaH_2 before use. THF and other solvents were distilled from sodium benzophenone ketyl before use. The *N,N'*-dioxides were prepared according to the methods reported in the literature.^[1]

2. General procedure for the preparation of the racemic products



Desymmetrization of *meso*-cyclic ketones: The reactions were performed with prochiral ketones **1** or **3** (0.10 mmol) and *m*-chlorobenzoperoxoic acid (*m*-CPBA) (0.12 mmol) in EtOAc (1.0 mL). The mixtures were stirred at 35 °C for 18 h. After that the saturated K_2CO_3 solution (10 mL) was added and the organic layers were extracted with CH_2Cl_2 (3 x 5 mL). Then the organic layers were concentrated in *vacuo* and the crude products were purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 4/1 or 8/1) to afford the corresponding product.

Kinetic resolution of racemic cyclohexanones: The reactions were performed with racemic ketones **7** (0.10 mmol), racemic catalyst solution prepared beforehand (0.005 mmol $\text{Sc}(\text{OTf})_3/\text{L2}_{\text{rac}}$ in 1.0 mL of EtOAc, 5 mol % catalyst loading) in a dry reaction tube. Then *m*-CPBA (0.12 mmol in 1.0 mL of EtOAc) was added at -20 °C. After the reaction mixtures were stirred for 36 h at -20 °C, the saturated K_2CO_3 solution (10 mL) was added and the organic layers were extracted with CH_2Cl_2 (3 x 5 mL). Then the combined organic layers were concentrated in *vacuo* and the crude products were purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to afford the desired products **8**.

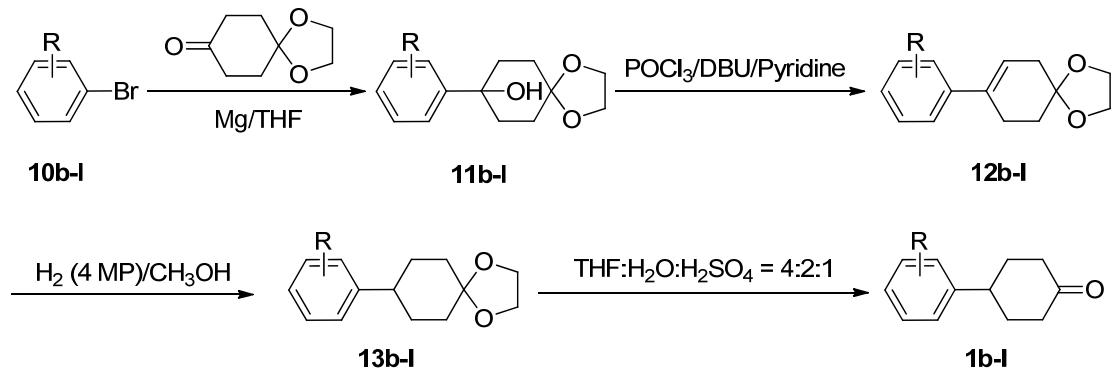
3. General experimental procedures for the catalytic asymmetric Baeyer–Villiger Oxidation

Preparation of the chiral catalyst solution: *N,N'*-dioxide **L3** (39.0 mg, 0.05 mmol) and scandium triflate (24.5 mg, 0.05 mmol) were stirred in 10.0 mL of EtOAc at 35 °C for 30 min.

Desymmetrization of *meso*-cyclic ketones: The reactions were performed with ketones **1** or **3** (0.10 mmol), chiral catalyst solution prepared beforehand (0.005 mmol Sc(OTf)₃/**L** in 1.0 ml of EtOAc, 5 mol % catalyst loading) in a dry reaction tube. Then *m*-CPBA (0.12 mmol in 1.0 ml of EtOAc) was added at -20 or -60 °C. After the reaction mixtures were stirred for 18 h at -20 or -60 °C, the saturated K₂CO₃ solution (10 mL) was added and the organic layers were extracted with CH₂Cl₂ (3 x 5 mL). Then the combined organic layers were concentrated in *vacuo* and the crude products were purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 4/1 or 8/1) to afford the desired products **2** or **4**.

Kinetic resolution of racemic cyclohexanones: The reactions were performed with racemic ketones **7** (0.10 mmol) and Al(O*i*Pr)₃ (0.1 mmol, 20.0 mg, purity: 99.99%) in a dry reaction tube, then the chiral catalyst solution prepared beforehand (0.005 mmol Sc(OTf)₃/**L** in 1.0 ml of EtOAc, 5 mol % catalyst loading) and *m*-CPBA (0.10 mmol in 1.0 ml of EtOAc) was added at the indicated temperature. After the reaction mixtures were stirred for the indicated time, the saturated K₂CO₃ solution (10 mL) was added and the organic layers were extracted with CH₂Cl₂ (3 x 5 mL). Then the combined organic layers were concentrated in *vacuo* and the crude products were purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to afford the desired abnormal lactones **8/9** and recover the unreacted ketones **7**. The lactones **8** and **9** have the same R_f value and could not be separated by chromatography.

4. Experimental procedure for the synthesis of the 4-substituted cyclohexanones



Experimental procedure for the synthesis of the alcohol **11b-I:** The alcohols **11b-I** were prepared according to the methods reported in the literature with a minor modification.^[2] To magnesium turnings (0.60 g, 49.6 mmol) was added a solution of **10b-I** (23.5 mmol) dissolved in THF (40 mL). The suspension was stirred and heated at reflux until the formation of the Grignard began. Then the heat was removed and the reaction continued until all of the Mg had reacted. After the flask was cooled to room temperature, a solution of 1,4-cyclohexanedione monoethylene ketal (3.50 g, 22.4 mmol) in THF (40 mL) was added dropwise, and the reaction mixture was heated at reflux for 24 h. The reaction was quenched by the addition of saturated NH₄Cl (50 mL), and the resultant mixture was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed again with aqueous NaOH (20 mL) and H₂O (50 mL). The organic layers were then dried (MgSO₄) and concentrated to give crude solids. The crude products were purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to afford the desired products **11b-I**.

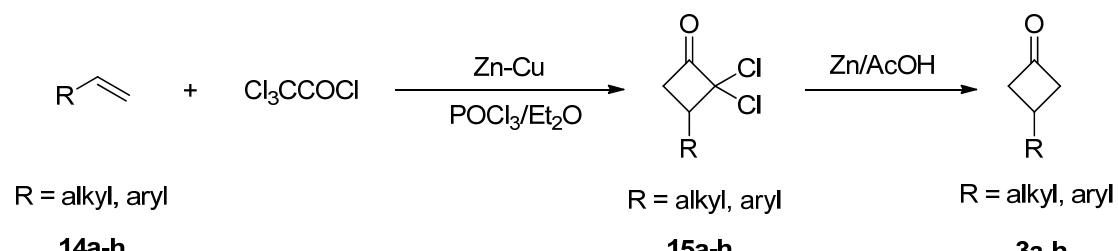
Experimental procedure for the synthesis of the **12b-I:** The products **12b-I** were prepared according to the methods reported in the literature with a minor modification.^[3] To a solution of **11b-I** (15.0 mmol)

in pyridine (85 mL) at 0 °C was added DBU (4.5 mL, 30.0 mmol) (1,8-diazabicyclo[5.4.0]undec-7-ene) followed by POCl₃ (2.7 mL, 29.5 mmol) dropwise. The resultant orange solution was stirred at room temperature for 1 h and at 80 °C for 90 min during which time the orange color darkened. The solution was cooled to 0 °C, and diluted carefully with EtOAc (100 mL) and H₂O (100 mL). The organic phase was washed with H₂O and brine, dried (MgSO₄) and evaporated in *vacuo* to give **12b-I** as orange-brown oil. The crude products were purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 8/1) to afford the desired pure sample **12b-I**.

Experimental procedure for the synthesis of the 13b-l: The pure sample **12b-l** from the above reactions was dissolved in 1:1 MeOH/EtOAc (25 mL). Palladium (10% on carbon, 0.3 g) was added. The mixture was stirred for 5 h under hydrogen (4 MPa) and filtered through a pad of Celite ®. The solvent was evaporated in *vacuo* to afford the crude products. The crude products were purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 8/1) to afford the desired pure sample **13b-l**.

Experimental procedure for the synthesis of the cyclohexanones 1b-l: The cyclohexanones 1b-l were prepared according to the methods reported in the literature with a minor modification.^[3] The pure sample 13b-l was dissolved in a mixture of THF, water and concentrated sulfuric acid (4:2:1, 70 mL). The mixture was stirred for 90 min, diluted with brine (50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic extracts were dried (MgSO_4) and the solvent evaporated in *vacuo*. Chromatography of the residue over silica gel, eluting with petroleum ether/EtOAc = 8/1, gave the desired pure sample 1b-l.

5. Experimental procedure for the synthesis of the 3-substituted cyclobutanones

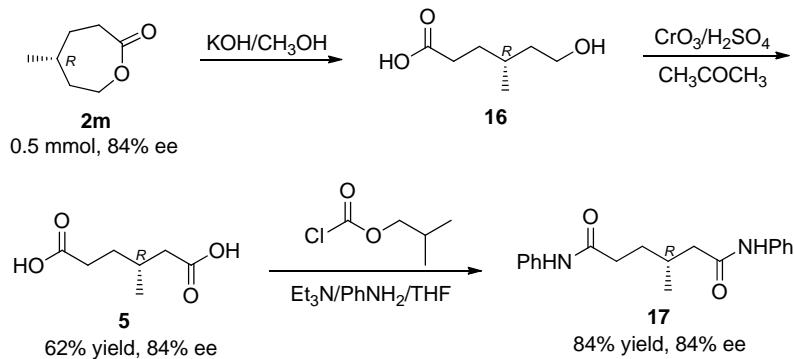


Experimental procedure for the synthesis of the 15a-h: The products **15a-h** were prepared according to the methods reported in the literature with a minor modification.^[4] To a stirred suspension of activated Zn-Cu (1.60 g, 25 mmol) and **14a-h** (10 mmol) in dry Et₂O (20 mL) was added dropwise through an addition funnel, during 2 h at reflux, a solution of trichloroacetic chloride (2.2 mL, 20 mmol) and phosphorus oxychloride (1.9 mL, 20 mmol) in Et₂O (10 mL). The suspension was stirred overnight at reflux. The mixture was cooled to room temperature and then filtered through a pad of Celite. The residue was washed with Et₂O (3 × 15 mL). The organic phase was concentrated in *vacuo* to give crude products **15a-h**, which were routinely used without further purification to the next step.

Experimental procedure for the synthesis of the cyclobutanones 3a-h: The cyclobutanones **3a-h** were prepared according to the methods reported in the literature with a minor modification.^[4] The solution of the previous crude products **15a-h** in acetic acid (10 mL) was added dropwise to a vigorously stirred suspension of zinc dust (2.6 g, 40 mmol) in acetic acid (8 mL) at 0 °C. After the addition, the reaction mixture was heated at 70 °C for 2 h. The mixture was allowed to cool to room temperature and then evacuated to get rid of most of the acetic acid. The residue was dissolved in Et₂O (20 mL) and then poured into a separation funnel containing water (20 mL) and Et₂O (20 mL). The organic layer was washed with water (3 × 10 mL), saturated sodium bicarbonate solution (2 × 10 mL),

brine (50 mL) and dried over MgSO_4 . The solution was then filtered and concentrated, followed by purification with flash chromatography (petroleum ether/EtOAc = 8/1) to afford the desired pure sample products **3a-h**.

6. Experimental procedure for the asymmetric synthesis of adipic acid **5**



Experimental procedure for the synthesis of the compound 16: The reaction was performed with ϵ -lactone **2m** (0.5 mmol), KOH (1.0 mmol) and CH_3OH (1.0 mL) in a dry tube. After the stirring was continued for 24 h at rt., HCl solution (1.0 mol/L, 10 mL) was added. The organic layer was extracted with EtOAc (3×15 mL). The extract was washed with brine, dried over NaSO_4 and concentrated in *vacuo*, affording the crude product **16**. The crude product was not purified and directly used for the next step.

Experimental procedure for the synthesis of the adipic acid 5: The reaction was performed with **16** (0.4 mmol), Jones reagent (4.0 mL) and CH_3COCH_3 (5.0 mL) in a dry tube. After the stirring was continued for 24 h at rt., isopropyl alcohol (5.0 mL) was added and the organic layer was extracted with EtOAc (3×15 mL). The extract was washed with brine, dried over Na_2SO_4 , and concentrated in *vacuo*. The crude product was purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the desired product **5** in 62% overall yield and 84% *ee* value.

Experimental procedure for the synthesis of the compound 17: The reaction was performed with **5** (0.20 mmol), Et_3N (0.44 mmol) and isobutyl carbonochloridate (0.44 mmol) with THF (1.0 mL) in a dry tube. After the stirring was continued for 15 min at 0 °C, the aniline (0.44 mmol) was added. Then stirring was continued for 8 h at 35 °C, the organic layer was extracted with CH_2Cl_2 (3×15 mL). The extract was washed with brine and concentrated in *vacuo*. The crude product was purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the desired product **17** in 84% yield and 84% *ee* value.

7. Extra condition optimizations for the asymmetric Baeyer–Villiger Oxidation

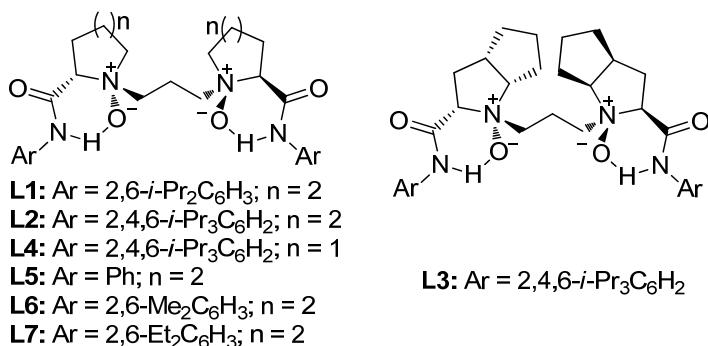
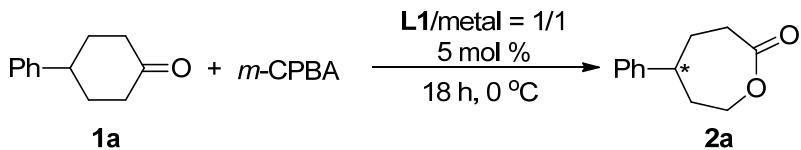


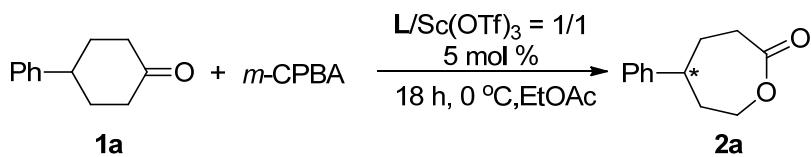
Table 1: Exploring the efficiency of Lewis acids on the asymmetric Baeyer–Villiger Oxidation of 4-phenylcyclohexanone **1a**^[a].



Entry	metal	Solvent	Yield [%] ^[b]	ee [%] ^[c]
1	Cu(OTf) ₂	EtOAc	42	0
2	Mg(OTf) ₂	EtOAc	39	0
3	Ni(OTf) ₂	EtOAc	42	0
4	In(OTf) ₃	EtOAc	91	6
5	Sc(OTf) ₃	EtOAc	84	68
6	Y(OTf) ₃	EtOAc	18	0
7	La(OTf) ₃	CH ₂ Cl ₂	-	-
8	Yb(OTf) ₃	CH ₂ Cl ₂	45	0
9	Gd(OTf) ₃	CH ₂ Cl ₂	32	0
10	Sm(OTf) ₃	CH ₂ Cl ₂	18	0
11	Pr(OTf) ₃	CH ₂ Cl ₂	trace	-
12	Er(OTf) ₃	CH ₂ Cl ₂	44	0
13	Eu(OTf) ₃	CH ₂ Cl ₂	38	0
14	Ho(OTf) ₃	CH ₂ Cl ₂	42	0

[a] Unless otherwise noted, the reactions were performed with **1a** (0.10 mmol), **L1** (5 mol %), metal (5 mol %) in solvent (0.5 mL) at 35 °C for 30 minutes. Then *m*-CPBA (0.12 mmol) was added at 0 °C. The reaction mixture was stirred at 0 °C for 18 hours. [b] Isolated yield. [c] Determined by chiral HPLC (Chiraldak AS-H).

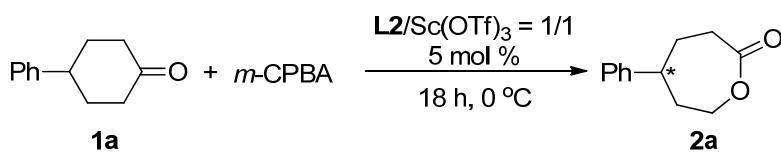
Table 2: Exploring the efficiency of ligands on the asymmetric Baeyer–Villiger Oxidation of 4-phenylcyclohexanone **1a**^[a].



Entry	ligand	Yield [%] ^[b]	ee [%] ^[c]
1	L1	84	68
2	L2	91	86
3	L3	86	88
4	L4	58	50
5	L5	46	0
6	L6	67	34
7	L7	86	64

[a] Unless otherwise noted, the reactions were performed with **1a** (0.10 mmol), **L** (5 mol %), Sc(OTf)₃ (5 mol %) in EtOAc at 35 °C for 30 minutes, then *m*-CPBA was added at 0 °C. The reaction mixture was stirred at 0 °C for 18 hours. [b] Isolated yield. [c] Determined by chiral HPLC (Chiraldak AS-H).

Table 3: Exploring the efficiency of solvent on the asymmetric Baeyer–Villiger Oxidation of 4-phenylcyclohexanone **1a**^[a].

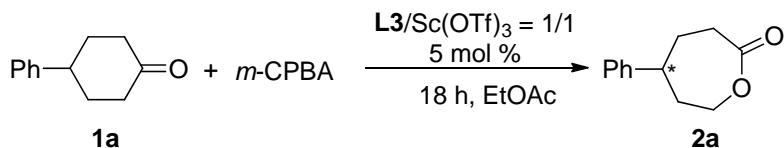


Entry	Solvent	Yield [%] ^[b]	ee [%] ^[c]
1	CH ₂ Cl ₂	81	75
2	THF	81	80
3	PhCH ₃	54	73

4	EtOAc	91	86
5	CH ₃ CN	53	88
6	EtOH	93	82
7	CHCl ₃	57	68
8	MeOAc	69	86
9	n-PrOAc	71	85
10	i-BuOAc	67	84
11	t-BuOAc	74	83

[a] Unless otherwise noted, the reactions were performed with **1a** (0.10 mmol), **L2** (5 mol %), Sc(OTf)₃ (5 mol %) in 0.5 mL of solvent at 35 °C for 30 minutes, then *m*-CPBA was added at 0 °C. The reaction mixture was stirred at 0 °C for 18 hours. [b] Isolated yield. [c] Determined by chiral HPLC (Chiralpak AS-H).

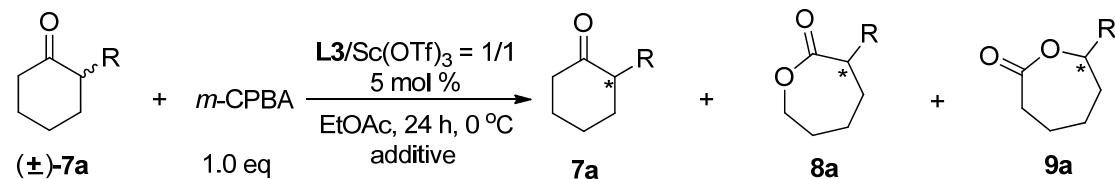
Table 4: Exploring the efficiency of temperature on the asymmetric Baeyer–Villiger Oxidation of 4-phenylcyclohexanone **1a**^[a].



Entry	T [°C]	Yield [%] ^[b]	ee [%] ^[c]
1	35	96	73
2	0	86	88
3	-20	72	91
4	-40	42	94

[a] Unless otherwise noted, the reactions were performed with **1a** (0.10 mmol), **L3** (5 mol %), Sc(OTf)₃ (5 mol %), in EtOAc (0.5 mL) at 35 °C for 30 minutes, then *m*-CPBA was added at the indicated temperature. The reaction mixture was stirred at the indicated temperature for 18 hours. [b] Isolated yield. [c] Determined by chiral HPLC (Chiralpak AS-H).

Table 5: Exploring the efficiency of additive on the asymmetric Baeyer–Villiger Oxidation of 2-phenylcyclohexanone **7a**^[a].



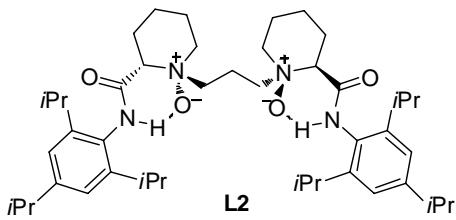
Entry	additive	Yield _{7a} [%] ^[b]	Ee _{7a} [%] ^[c]	Yield _{8a+9a} [%] ^[b]	Ee _{8a} [%] ^[c]	8a/9a ^[c]
1	-	75	23	23	94	12/1
2	K ₂ CO ₃	77	19	22	93	11/1
3	NaHCO ₃	82	14	13	94	9/1
4	Et ₃ N	76	17	14	94	10/1
5	DBU	72	21	27	94	12/1
6	TSOH	93	0	trace	-	-
7	CF ₃ COOH	75	22	24	93	10/1
8	NaBA ₄ F	0	-	99	-	0/1
9	Al(O <i>i</i> Pr) ₃	65	38	30	94	16/1
10	Al(OTf) ₃	37	0	62	-	0/1
11	Sc(O <i>i</i> Pr) ₃	49	-10	51	-	0/1
12 ^[d]	Al(O <i>i</i> Pr) ₃	38	90	59	76	8/1
13 ^[d, e]	Al(O <i>i</i> Pr) ₃	46	94	51	94	18/1

[a] Unless otherwise noted, the reactions were performed with **7a** (0.10 mmol), **L3** (5 mol %), Sc(OTf)₃ (5 mol %), additive (5 mol %) in 1.0 mL of EtOAc at 0 °C, then *m*-CPBA (0.1 mmol in 1.0 mL of EtOAc) was added at 0 °C. The reaction mixture was stirred at 0 °C for 24 hours. [b] Isolated yield. [c] Determined by chiral HPLC

(Chiralpak OD-H). [d] 0.1 mmol of Al(O*i*Pr)₃ (20.0 mg) was added. [e] The reaction was stirred at -40 °C for 36 hours.

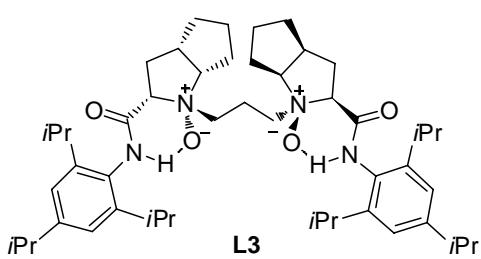
8. Characterization of the *N,N'*-dioxide ligands

chiral *N,N'*-dioxide L2:



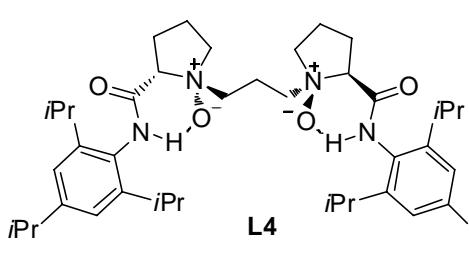
Prepared according to the methods reported in the literature.^[1] ¹H NMR (300 MHz, CDCl₃): δ = 11.80 (s, 1.64H), 7.01 (s, 4H), 3.75–3.24 (m, 8H), 3.12–2.57 (m, 12H), 2.49–2.25 (m, 2H), 2.19–2.08 (m, 2H), 1.99–1.83 (m, 2H), 1.75–1.60 (m, 2H), 1.51–1.35 (m, 2H), 1.27–1.15 (m, 36H). ¹³C NMR (75 MHz, CDCl₃) δ = 167.74, 148.08, 144.54, 128.32, 121.33, 121.23, 76.20, 65.91, 64.83, 34.15, 28.94, 26.40, 23.95, 23.63, 23.56, 22.25, 20.10, 15.99 ppm. ES-HRMS Calcd for C₄₅H₇₂N₄O₄[M + H]⁺ m/z 733.5632, Found: m/z 733.5645.

chiral *N,N'*-dioxide L3:



Prepared according to the methods reported in the literature.^[1] ¹H NMR (300 MHz, CDCl₃): δ = 12.42 (s, 1.91H), 6.99 (s, 4H), 4.01–3.88 (m, 4H), 3.48–3.32 (m, 4H), 3.00–2.64 (m, 14H), 2.02–1.64 (m, 12H), 1.20 (s, 36H). ¹³C NMR (75 MHz, CDCl₃) δ = 166.25, 147.82, 144.51, 128.73, 121.21, 83.90, 80.86, 65.79, 42.53, 34.59, 34.17, 32.11, 28.96, 27.70, 27.09, 23.99, 23.72, 23.34, 18.80 ppm. ES-HRMS Calcd for C₄₉H₇₆N₄O₄[M + H]⁺ m/z 785.5945, Found: m/z 785.5956.

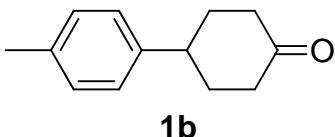
chiral *N,N'*-dioxide L4:



Prepared according to the methods reported in the literature.^[1] ¹H NMR (300 MHz, CDCl₃): δ = 12.45 (s, 1.74H), 7.01 (s, 4H), 3.95–3.31 (m, 10H), 3.08–2.99 (p, J = 6.9 Hz, 4H), 2.92–2.83 (p, J = 6.9 Hz, 4H), 2.76–2.39 (m, 6H), 2.11–2.03 (m, 2H), 1.24–1.16 (m, 36H). ¹³C NMR (75 MHz, CDCl₃) δ = 166.27, 147.96, 144.43, 128.54, 121.25, 76.85, 68.08, 63.92, 34.18, 28.93, 27.40, 23.98, 23.79, 23.17, 20.20, 19.73 ppm. ES-HRMS Calcd for C₄₃H₆₈N₄O₄[M + H]⁺ m/z 705.5319, Found: m/z 705.5313.

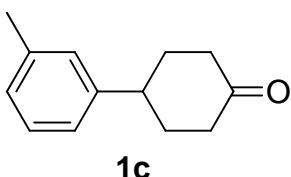
9. Characterization of the prochiral cyclohexanones

4-(*p*-tolyl)cyclohexanone 1b:



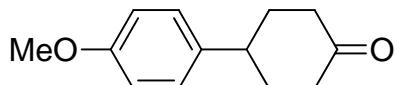
¹H NMR (300 MHz, CDCl₃): δ = 7.14 (s, 4H), 3.00 (tt, J = 12.0 Hz, 3.3 Hz, 1H), 2.57–2.48 (m, 4H), 2.34 (s, 3H), 2.28–2.14 (m, 2H), 2.03–1.83 (m, 2H).

4-(*m*-tolyl)cyclohexanone 1c:



¹H NMR (300 MHz, CDCl₃): δ = 7.25–7.20 (m, 1H), 7.07–7.04 (m, 3H), 3.00 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.60–2.44 (m, 4H), 2.36 (s, 3H), 2.27–2.14 (m, 2H), 2.04–1.86 (m, 2H).

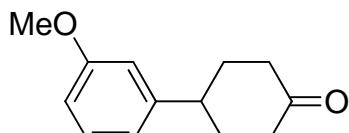
4-(4-methoxyphenyl)cyclohexanone 1d:



1d

¹H NMR (300 MHz, CDCl₃): δ = 7.17 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 2.98 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.60–2.42 (m, 4H), 2.28–2.13 (m, 2H), 2.02–1.80 (m, 2H).

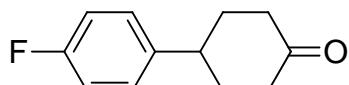
4-(3-methoxyphenyl)cyclohexanone 1e:



1e

¹H NMR (300 MHz, CDCl₃): δ = 7.29–7.20 (m, 1H), 6.85–6.76 (m, 3H), 3.81 (s, 3H), 3.00 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.59–2.44 (m, 4H), 2.29–2.16 (m, 2H), 2.05–1.85 (m, 2H).

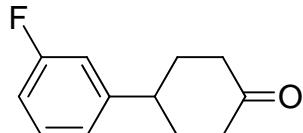
4-(4-fluorophenyl)cyclohexanone 1f:



1f

¹H NMR (400 MHz, CDCl₃): δ = 7.19 (dd, *J* = 8.2, 5.6 Hz, 2H), 6.99 (t, *J* = 8.5 Hz, 2H), 3.01 (tt, *J* = 12.0, 3.2 Hz, 1H), 2.58–2.39 (m, 4H), 2.21–2.18 (w, 2H), 1.97–1.81 (m, 2H).

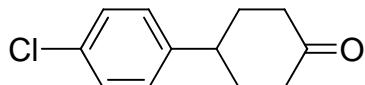
4-(3-fluorophenyl)cyclohexanone 1g:



1g

¹H NMR (300 MHz, CDCl₃): δ = 7.34–7.23 (m, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.99–6.87 (m, 2H), 3.03 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.59–2.45 (m, 4H), 2.29–2.16 (m, 2H), 2.02–1.83 (m, 2H).

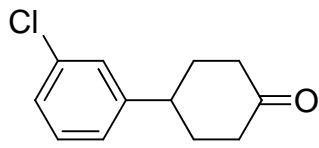
4-(4-chlorophenyl)cyclohexanone 1h:



1h

¹H NMR (300 MHz, CDCl₃): δ = 7.29 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 3.01 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.59–2.42 (m, 4H), 2.27–2.12 (m, 2H), 2.01–1.79 (m, 2H).

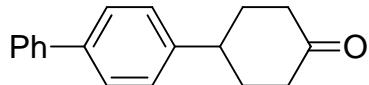
4-(3-chlorophenyl)cyclohexanone 1i:



1i

¹H NMR (300 MHz, CDCl₃): δ = 7.29–7.16 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 1H), 3.00 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.58–2.44 (m, 4H), 2.28–2.14 (m, 2H), 2.01–1.81 (m, 2H).

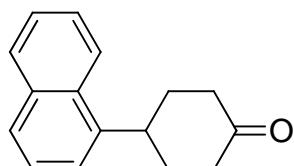
4-([1,1'-biphenyl]-4-yl)cyclohexanone 1j:



1j

¹H NMR (300 MHz, CDCl₃): δ = 7.58 (t, *J* = 7.5 Hz, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 8.1 Hz, 3H), 3.09 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.64–2.45 (m, 4H), 2.35–2.20 (m, 2H), 2.10–1.88 (m, 2H).

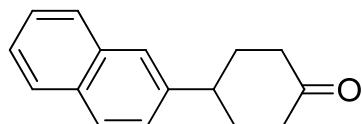
4-(naphthalen-1-yl)cyclohexanone 1k:



1k

¹H NMR (300 MHz, CDCl₃): δ = 8.16 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.62–7.35 (m, 4H), 3.85 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.76–2.52 (m, 4H), 2.45–2.32 (m, 2H), 2.06 (qd, *J* = 12.9, 4.8 Hz, 2H).

4-(naphthalen-2-yl)cyclohexanone 1l:

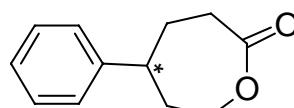


1l

¹H NMR (300 MHz, CDCl₃): δ = 7.87–7.76 (m, 3H), 7.69 (s, 1H), 7.53–7.35 (m, 3H), 3.20 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.66–2.49 (m, 4H), 2.38–2.25 (m, 2H), 2.16–1.97 (m, 2H).

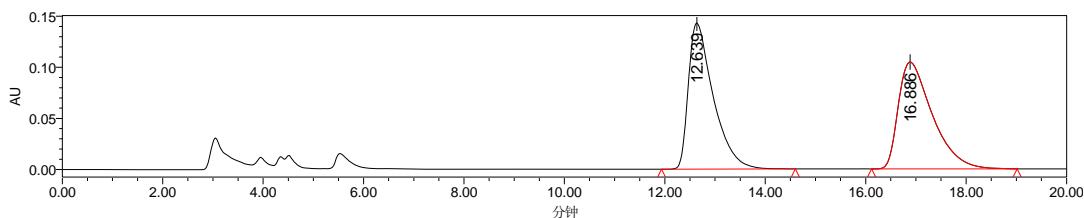
10. Characterization of the products and unreacted ketones

(+)-5-phenyloxepan-2-one 2a:

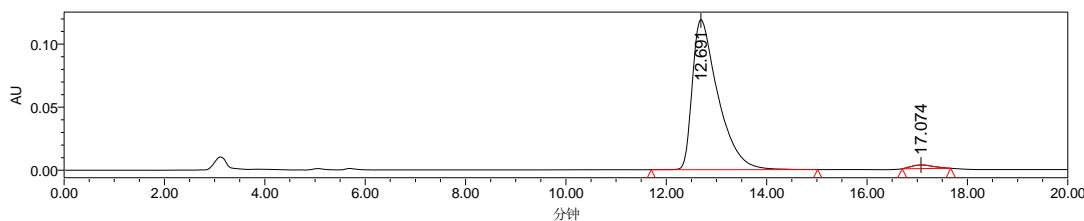


2a

Prepared according to **general procedure**. 86% yield, 95% *ee*. [α]_D²⁰ = +48.1 (c 0.73, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), t_r(major) = 12.69 min, t_r(minor) = 17.07 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (t, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 4.39–4.15 (m, 2H), 2.85–2.62 (m, 3H), 2.14–1.86 (m, 3H), 1.85–1.67 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ = 174.68, 143.94, 127.75, 125.84, 125.59, 67.22, 46.20, 35.70, 32.67, 29.30 ppm. ES-HRMS Calcd for C₁₂H₁₄O₂[M + Na]⁺ m/z 213.0891, Found: m/z 213.0888.

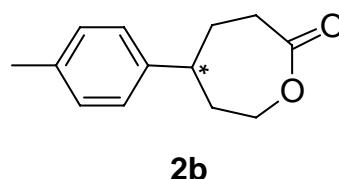


	Retention Time	% Area
1	12.639	48.96
2	16.886	50.04

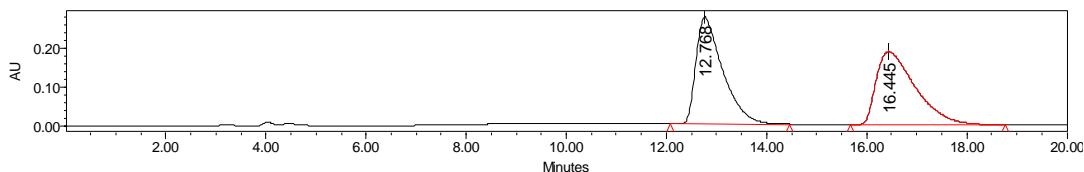


	Retention Time	% Area
1	12.691	97.57
2	17.074	2.43

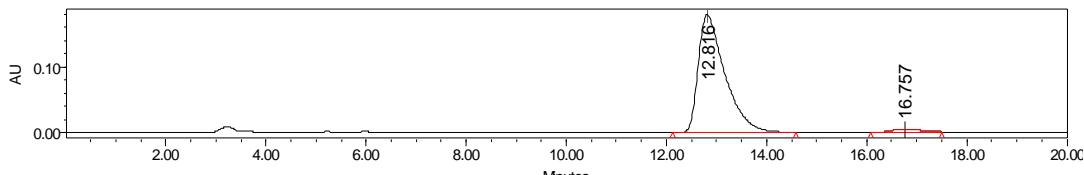
(+)-5-(p-tolyl)oxepan-2-one 2b:



Prepared according to **general procedure**. 90% yield, 95% ee. $[\alpha]_D^{20} = +46.1$ (c 0.80, CHCl_3). The ee was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), $t_r(\text{major}) = 12.82$ min, $t_r(\text{minor}) = 16.76$ min. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.14$ (d, $J = 8.0$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 4.42–4.26 (m, 2H), 2.86–2.69 (m, 3H), 2.33 (s, 3H), 2.18–1.95 (m, 3H), 1.88–1.75 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 175.79, 142.05, 136.48, 129.43, 126.49, 68.31, 46.83, 36.83, 33.72, 30.45, 21.01$ ppm. ES-HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2[\text{M} + \text{NH}_4]^+$ m/z 222.1494, Found: m/z 222.1491.



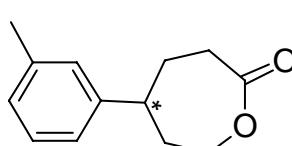
	Retention Time	% Area
1	12.768	50.09
2	16.445	49.91



	Retention Time	% Area
1	12.816	97.52

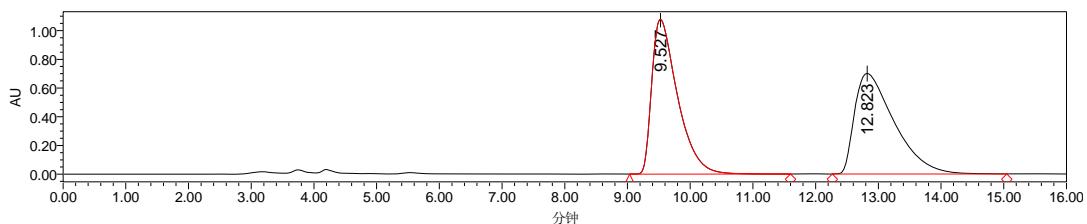
2	16.757	2.48
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(+)-5-(m-tolyl)oxepan-2-one **2c**:

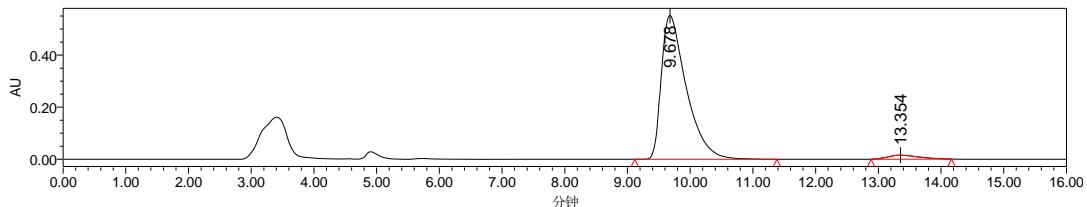


2c

Prepared according to **general procedure**. 84% yield, 94% *ee*. $[\alpha]_D^{20} = +39.5$ (c 0.85, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), t_r(major) = 9.68 min, t_r(minor) = 13.35 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.21 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.99–6.97 (m, 2H), 4.43–4.26 (m, 2H), 2.86–2.69 (m, 3H), 2.34 (s, 3H), 2.16–1.97 (m, 3H), 1.90–1.77 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ = 175.77, 144.97, 138.41, 128.68, 127.61, 127.43, 123.63, 68.31, 47.24, 36.76, 33.74, 30.35, 21.48 ppm. ES-HRMS Calcd for C₁₃H₁₆O₂[M + NH₄]⁺ m/z 222.1494, Found: m/z 222.1491.

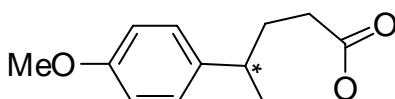


	Retention Time	% Area
1	9.527	49.80
2	12.823	50.20



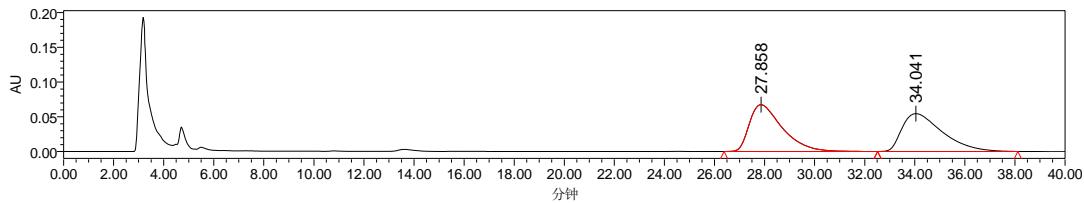
	Retention Time	% Area
1	9.678	96.87
2	13.354	3.13

(+)-5-(4-methoxyphenyl)oxepan-2-one **2d**:

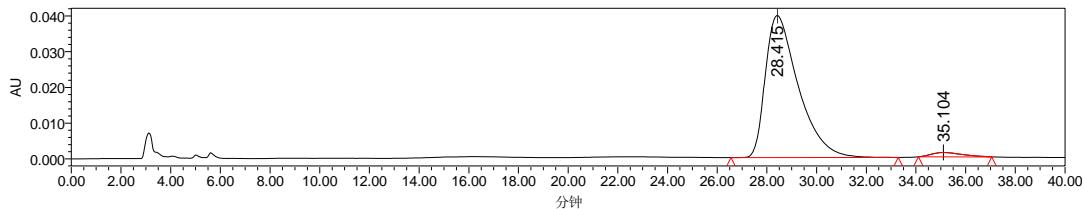


2d

Prepared according to **general procedure**. 81% yield, 95% *ee*. $[\alpha]_D^{20} = +48.0$ (c 0.78, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), t_r(major) = 28.42 min, t_r(minor) = 35.10 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.10 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.42–4.25 (m, 2H), 3.79 (s, 3H), 2.86–2.70 (m, 3H), 2.17–1.93 (m, 3H), 1.86–1.73 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ = 175.79, 158.37, 137.21, 127.55, 114.09, 68.29, 55.30, 46.38, 36.97, 33.69, 30.59 ppm. ES-HRMS Calcd for C₁₃H₁₆O₃[M + Na]⁺ m/z 243.0997, Found: m/z 243.0995.

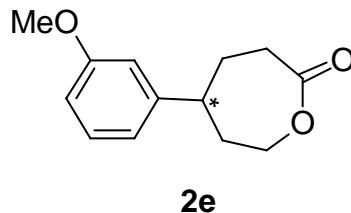


	Retention Time	% Area
1	27.858	49.93
2	34.041	50.07

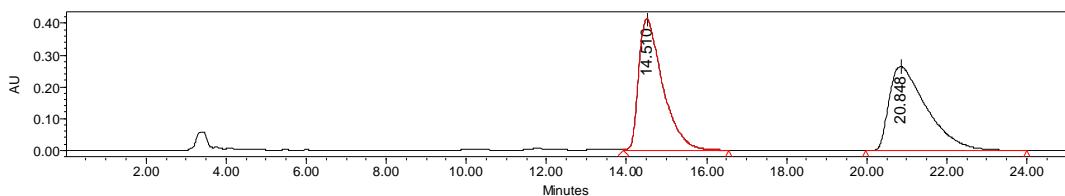


	Retention Time	% Area
1	28.415	97.42
2	35.104	2.58

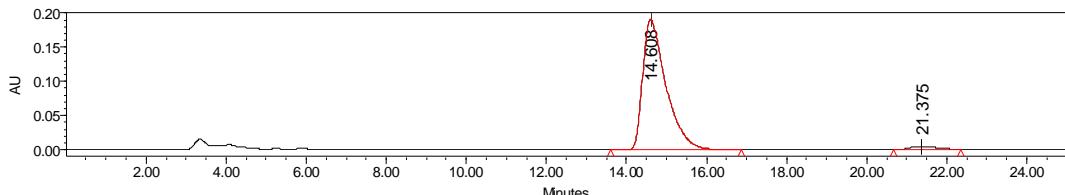
(+)-5-(3-methoxyphenyl)oxepan-2-one 2e:



Prepared according to **general procedure**. 81% yield, 95% *ee*. $[\alpha]_D^{20} = +39.1$ (*c* 0.94, CHCl_3). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), t_r (major) = 14.61 min, t_r (minor) = 21.38 min. ^1H NMR (400 MHz, CDCl_3): δ = 7.22–7.12 (m, 1H), 6.72–6.65 (m, 3H), 4.37–4.18 (m, 2H), 3.73 (s, 3H), 2.81–2.62 (m, 3H), 2.10–1.90 (m, 3H), 1.83–1.69 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ = 175.71, 159.85, 146.62, 129.80, 118.95, 112.73, 111.79, 68.23, 55.22, 47.27, 36.68, 33.67, 30.26 ppm. ES-HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$ [M + NH_4^+] *m/z* 238.1443, Found: *m/z* 238.1449.



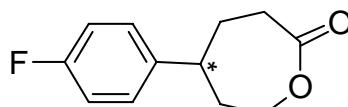
	Retention Time	% Area
1	14.510	49.99
2	20.848	50.01



	Retention Time	% Area
1	14.608	97.12

2	21.375	2.88
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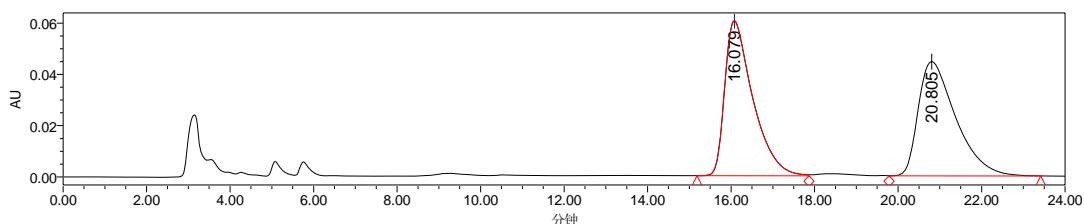
(+)-5-(4-fluorophenyl)oxepan-2-one **2f**:



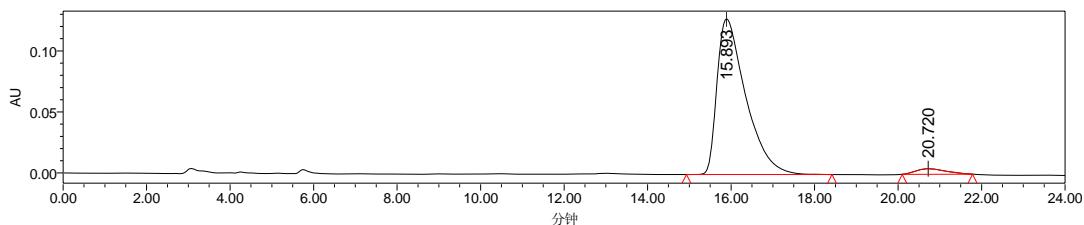
2f

Prepared according to **general procedure**. 71% yield, 92% *ee*. $[\alpha]_D^{20} = +49.2$ (c 0.93, CHCl_3). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), $t_r(\text{major}) = 15.89$ min, $t_r(\text{minor}) = 20.72$ min.

^1H NMR (400 MHz, CDCl_3): $\delta = 7.13$ (dd, $J = 8.4, 5.6$ Hz, 2H), 6.99 (t, $J = 8.4$ Hz, 2H), 4.38 (ddd, $J = 13.2, 5.2, 2.0$ Hz, 1H), 4.34–4.25 (m, 1H), 2.89–2.69 (m, 3H), 2.15–1.92 (m, 3H), 1.85–1.73 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 175.53, 162.83, 160.40, 140.72, 140.69, 128.08, 128.00, 115.65, 115.44, 68.10, 46.47, 36.91, 33.61, 30.49$ ppm. ES-HRMS Calcd for $\text{C}_{12}\text{H}_{13}\text{FO}_2[\text{M} + \text{Na}]^+$ m/z 231.0797, Found: m/z 231.0799.

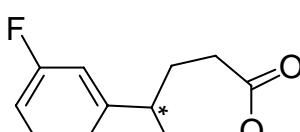


	Retention Time	% Area
1	16.079	49.97
2	20.805	50.03



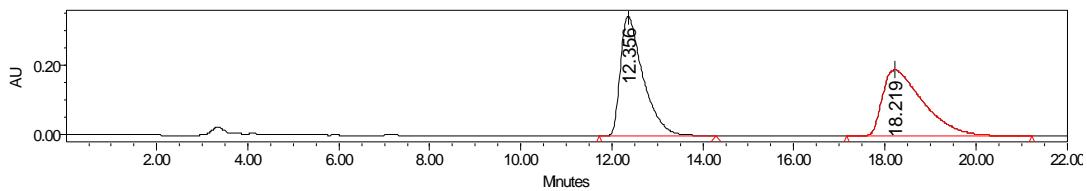
	Retention Time	% Area
1	15.893	95.95
2	20.720	4.05

(+)-5-(3-fluorophenyl)oxepan-2-one **2g**:

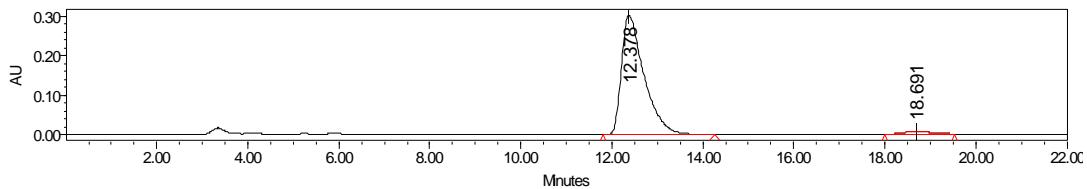


2g

Prepared according to **general procedure**. 84% yield, 94% *ee*. $[\alpha]_D^{20} = +41.8$ (c 0.77, CHCl_3). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), $t_r(\text{major}) = 12.38$ min, $t_r(\text{minor}) = 18.69$ min. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.30$ –7.27 (m, 1H), 7.02–6.84 (m, 3H), 4.46–4.24 (m, 2H), 2.92–2.70 (m, 3H), 2.21–1.94 (m, 3H), 1.89–1.75 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 175.43, 164.22, 161.77, 147.46, 147.39, 130.35, 130.27, 122.27, 122.24, 113.88, 113.76, 113.67, 113.54, 68.02, 46.92, 46.91, 36.59, 33.56, 30.15$ ppm. ES-HRMS Calcd for $\text{C}_{12}\text{H}_{13}\text{FO}_2[\text{M} + \text{Na}]^+$ m/z 231.0797, Found: m/z 231.0801.

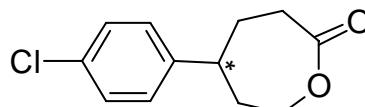


	Retention Time	% Area
1	12.356	50.20
2	18.219	49.80

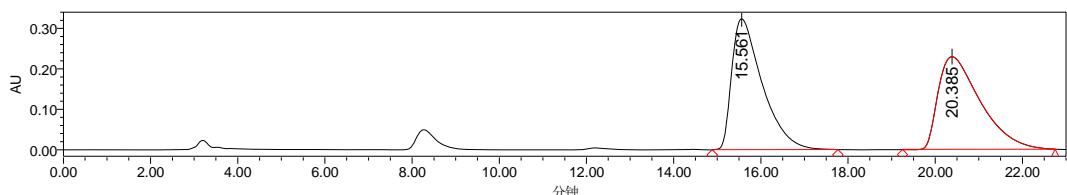


	Retention Time	% Area
1	12.376	96.79
2	18.691	3.21

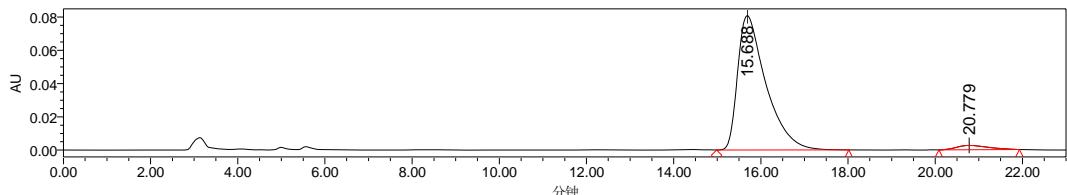
(+)-5-(4-chlorophenyl)oxepan-2-one 2h:



Prepared according to **general procedure**. 82% yield, 94% *ee*. $[\alpha]_D^{20} = +40.2$ (*c* 0.80, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), t_r(major) = 15.69 min, t_r(minor) = 20.78 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.29 (d, *J* = 8.4 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 4.39–4.16 (m, 2H), 2.82–2.62 (m, 3H), 2.06–1.87 (m, 3H), 1.80–1.68 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ = 175.44, 143.35, 132.58, 128.93, 127.98, 68.05, 46.63, 36.70, 33.60, 30.28 ppm. ES-HRMS Calcd for C₁₂H₁₃Cl^{34,9689}O₂[M + Na]⁺ m/z 247.0502, Found: m/z 247.0506.



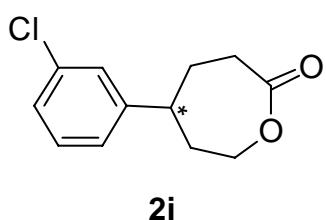
	Retention Time	% Area
1	15.561	50.23
2	20.385	49.77



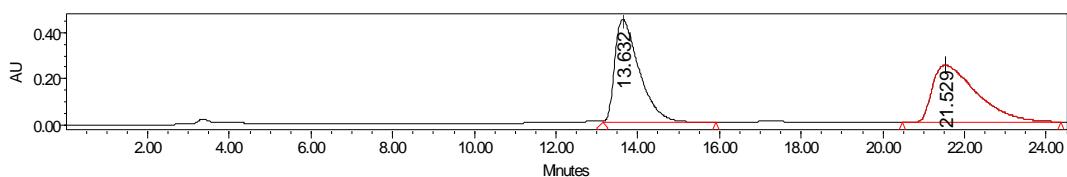
	Retention Time	% Area
1	15.688	96.77

2	20.779	3.23
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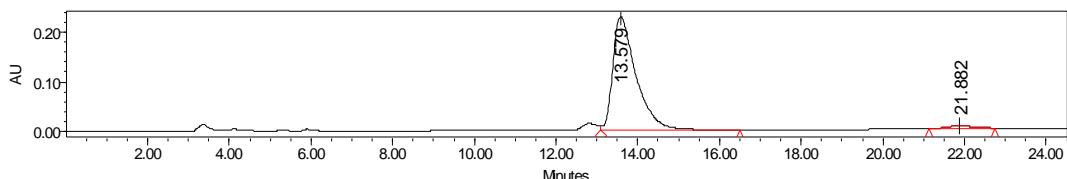
(+)-5-(3-chlorophenyl)oxepan-2-one 2i:



Prepared according to **general procedure**. 81% yield, 94% *ee*. $[\alpha]_D^{20} = +40.8$ (c 0.87, CHCl_3). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), major diastereomer: $t_r(\text{major}) = 13.58$ min, $t_r(\text{minor}) = 21.88$ min. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.30\text{--}7.20$ (m, 2H), 7.18 (s, 1H), 7.08–7.06 (m, 1H), 4.44–4.25 (m, 2H), 2.90–2.70 (m, 3H), 2.18–2.05 (m, 2H), 2.04–1.94 (m, 1H), 1.87–1.57 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 175.38$, 146.88, 134.52, 130.11, 127.08, 126.98, 124.80, 68.00, 46.90, 36.57, 33.57, 30.14 ppm. ES-HRMS Calcd for $\text{C}_{12}\text{H}_{13}\text{Cl}^{34.9689}\text{O}_2[\text{M} + \text{Na}]^+$ m/z 247.0502, Found: m/z 247.0502.

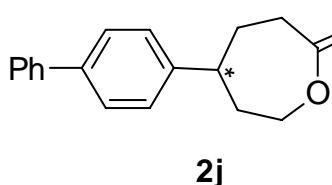


	Retention Time	% Area
1	13.632	49.67
2	21.529	50.33

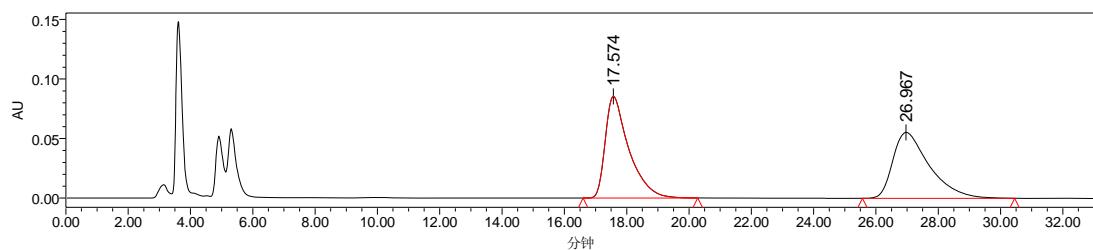


	Retention Time	% Area
1	13.579	96.89
2	21.882	3.11

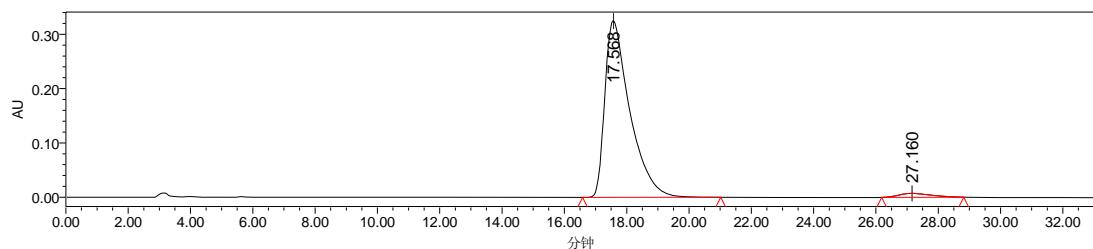
(+)-5-([1,1'-biphenyl]-4-yl)oxepan-2-one 2j:



Prepared according to **general procedure**. 81% yield, 94% *ee*. $[\alpha]_D^{20} = +50.0$ (c 0.47, CHCl_3). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), major diastereomer: $t_r(\text{major}) = 17.57$ min, $t_r(\text{minor}) = 27.16$ min. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.49$ (t, $J = 8.0$ Hz, 4H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.18 (t, $J = 4.0$ Hz, 2H), 4.40–4.20 (m, 2H), 2.82 (tt, $J = 12.0, 3.6$ Hz, 1H), 2.77–2.64 (m, 2H), 2.09–1.94 (m, 3H), 1.90–1.70 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 175.69$, 144.02, 140.68, 139.86, 128.82, 127.50, 127.32, 127.07, 127.03, 68.25, 46.89, 36.75, 33.72, 30.35 ppm. ES-HRMS Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2[\text{M} + \text{Na}]^+$ m/z 289.1204, Found: m/z 289.1201.

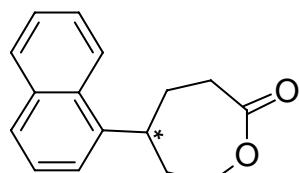


	Retention Time	% Area
1	17.574	49.97
2	26.967	50.03

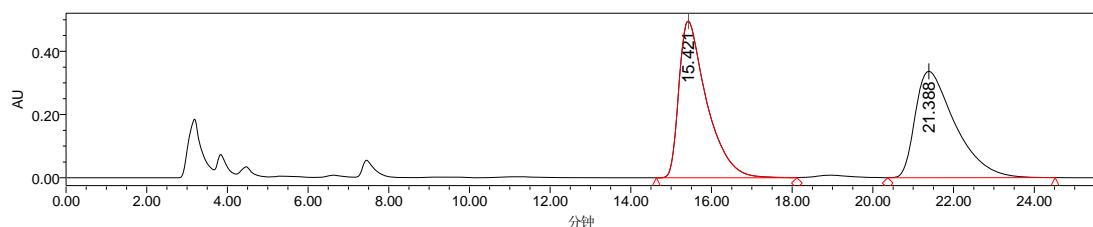


	Retention Time	% Area
1	17.566	97.00
2	27.160	3.00

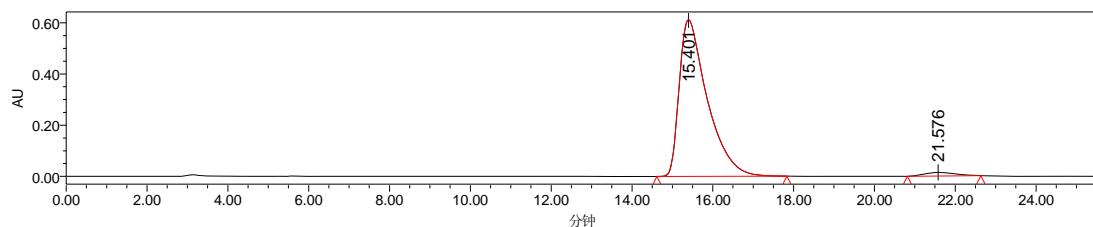
(+)-5-(naphthalen-1-yl)oxepan-2-one 2k:



Prepared according to **general procedure**. 84% yield, 95% *ee*. $[\alpha]_D^{20} = +24.5$ (c 0.86, CHCl_3). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), $t_r(\text{major}) = 15.40$ min, $t_r(\text{minor}) = 21.58$ min. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.05$ (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.59–7.40 (m, 3H), 7.33 (d, $J = 7.2$ Hz, 1H), 4.52–4.37 (m, 2H), 3.68 (tt, $J = 12.0, 3.6$ Hz, 1H), 2.97–2.79 (m, 2H), 2.35–2.07 (m, 3H), 2.03–1.88 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 175.77, 140.66, 134.01, 130.59, 129.34, 127.36, 126.29, 125.68, 125.67, 122.86, 122.27, 68.64, 41.62, 36.35, 34.09, 29.95$ ppm. ES-HRMS Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2[\text{M} + \text{NH}_4]^+$ m/z 258.1494, Found: m/z 258.1493.

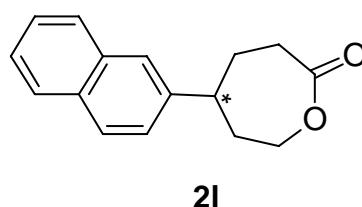


	Retention Time	% Area
1	15.421	50.45
2	21.388	49.55

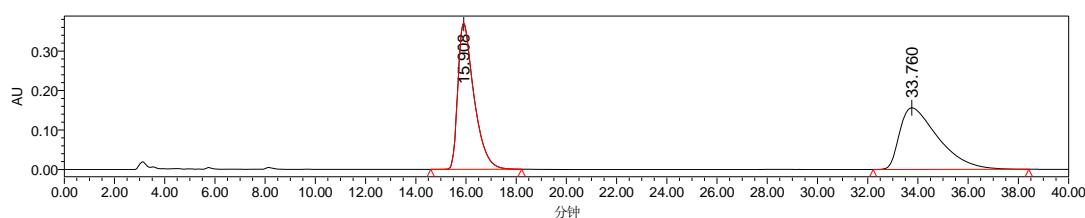


	Retention Time	% Area
1	15.401	97.45
2	21.576	2.55

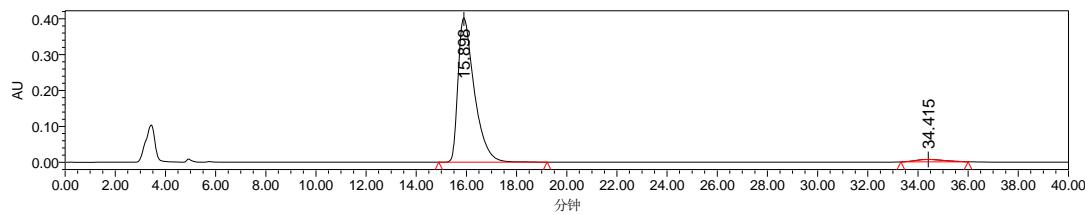
(+)-5-(naphthalen-2-yl)oxepan-2-one 2l:



Prepared according to **general procedure**. 87% yield, 94% *ee*. $[\alpha]_D^{20} = +47.3$ (*c* 0.89, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), *t*_r(major) = 15.90 min, *t*_r(minor) = 34.42 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (t, *J* = 7.6 Hz, 3H), 7.63 (s, 1H), 7.53–7.42 (m, 2H), 7.32 (dd, *J* = 8.8, 1.2 Hz, 1H), 4.49–4.30 (m, 2H), 3.01 (tt, *J* = 12.0, 3.6 Hz, 1H), 2.89–2.75 (m, 2H), 2.28–2.07 (m, 3H), 2.02–1.88 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ = 175.70, 142.37, 133.54, 132.44, 128.50, 127.66, 126.31, 125.76, 125.28, 124.89, 68.27, 47.31, 36.73, 33.75, 30.30 ppm. ES-HRMS Calcd for C₁₆H₁₆O₂[M + NH₄]⁺ m/z 258.1494, Found: m/z 258.1485.

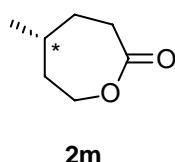


	Retention Time	% Area
1	15.908	49.80
2	33.760	50.20

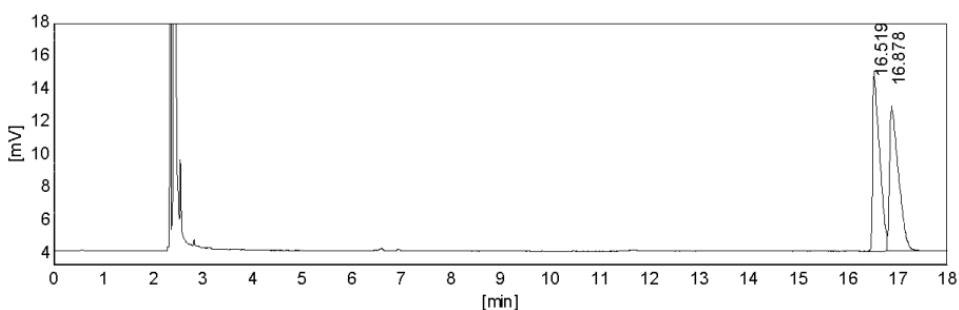


	Retention Time	% Area
1	15.898	96.77
2	34.415	3.23

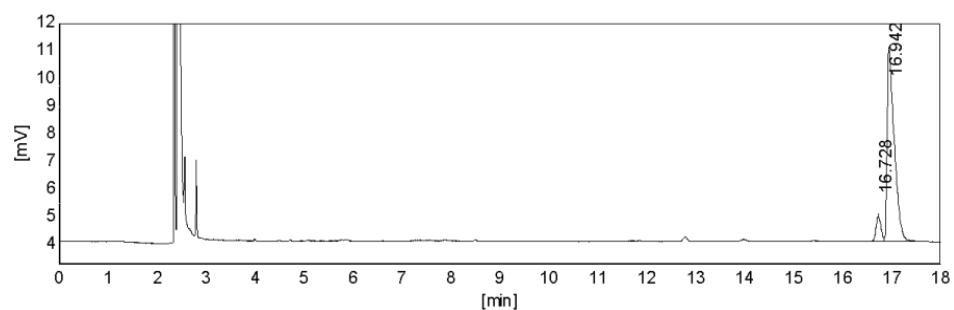
(+)-(R)-5-methyloxepan-2-one 2m:



Prepared according to **general procedure**: 76% yield, 84% *ee*. $[\alpha]_D^{20} = +26.9$ (*c* 0.39, CHCl₃); [Lit.:^[5] $[\alpha]_D^{20} = -45.0$ (*c* 1.40, CHCl₃) for *S*-isomer with 98% *ee*]. The *ee* was determined by GC using a Chiralsil DEX CB column (130 °C); *t*_r(major) = 16.94 min, *t*_r(minor) = 16.73 min. ¹H NMR (400 MHz, CDCl₃): δ = 4.27 (dd, *J* = 11.6, 5.6 Hz, 1H), 4.21–4.12 (m, 1H), 2.70–2.55 (m, 2H), 1.97–1.81 (m, 2H), 1.81–1.70 (m, 1H), 1.49 (dt, *J* = 15.2, 10.8 Hz, 1H), 1.38–1.27 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 3H).



	Retention Time	% Area
1	16.519	49.16
2	16.878	50.84

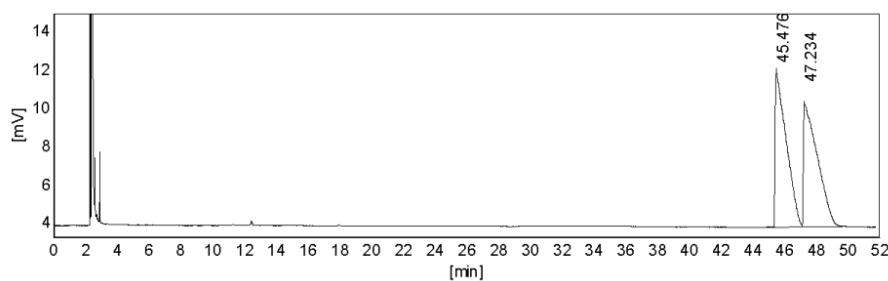


	Retention Time	% Area
1	16.728	8.15
2	16.942	91.85

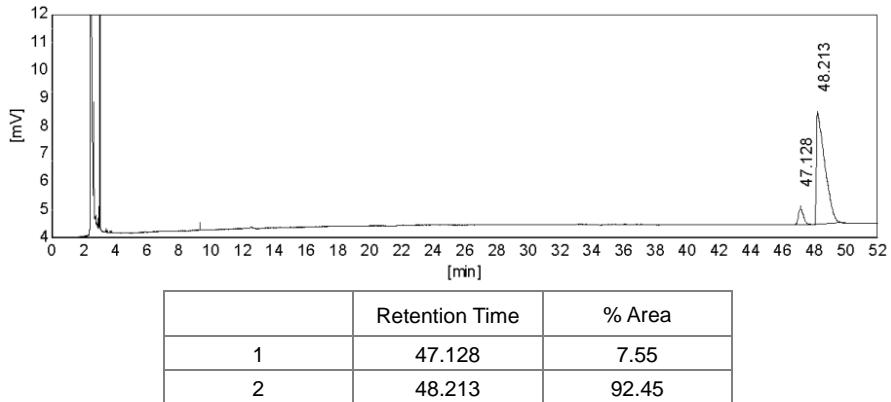
(+)-(R)-5-ethyloxepan-2-one 2n:

2n

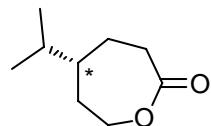
Prepared according to **general procedure**: 72% yield, 85% ee. $[\alpha]_D^{20} = +30.3$ (c 0.45, CHCl₃); [Lit.^[5] $[\alpha]_D^{20} = -29.0$ (c 3.20, CHCl₃) for S-isomer with 98% ee]. The ee was determined by GC using a Chiralsil DEX CB column (120 °C); t_r(major) = 48.21 min, t_r(minor) = 47.22 min. ¹H NMR (400 MHz, CDCl₃): δ = 4.33–4.25 (m, 1H), 4.16 (dd, J = 12.8, 10.0 Hz, 1H), 2.68–2.64 (m, 1H), 2.63–2.53 (m, 1H), 2.03–1.87 (m, 2H), 1.56–1.40 (m, 2H), 1.36–1.22 (m, 3H), 0.90 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 176.18, 68.21, 41.89, 34.96, 33.17, 29.14, 28.52, 11.31 ppm.



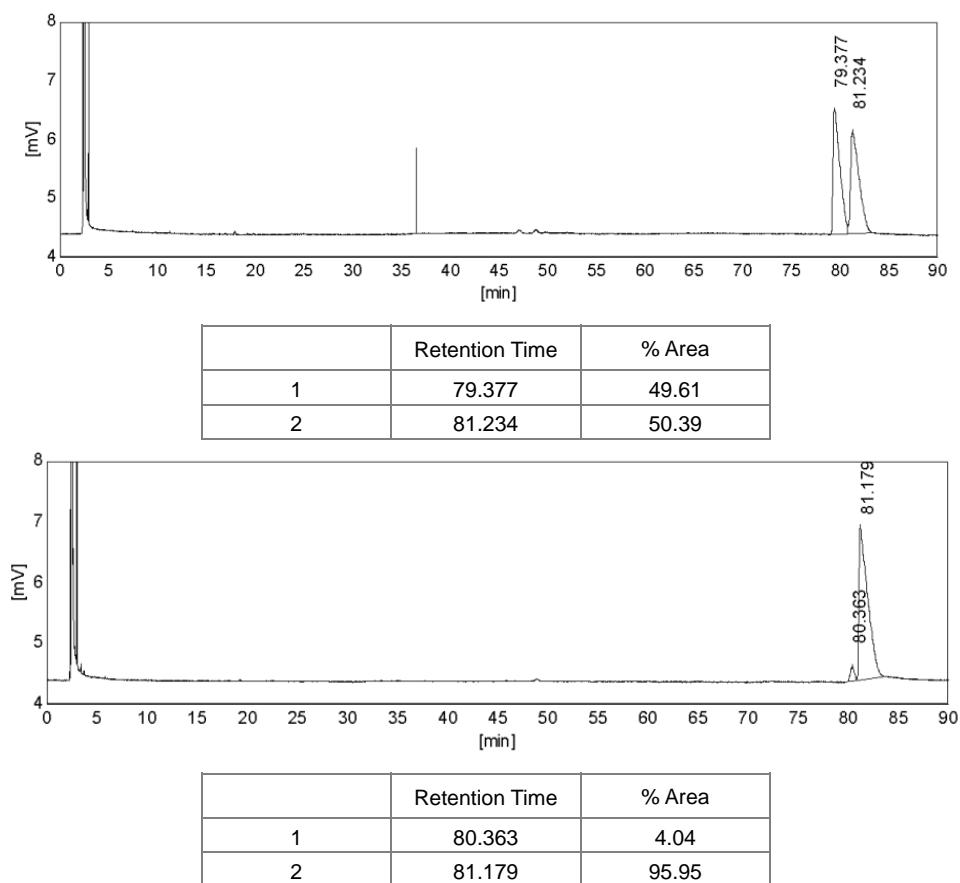
	Retention Time	% Area
1	45.476	49.94
2	47.234	50.06



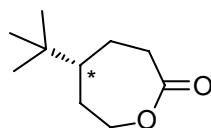
(+)-(R)-5-isopropylloxepan-2-one 2o:



Prepared according to **general procedure**: 75% yield, 92% *ee*. $[\alpha]_D^{20} = +34.8$ (c 0.50, CHCl₃); [Lit.:^[5] $[\alpha]_D^{20} = -27.0$ (c 2.00, CHCl₃) for *S*-isomer with 98% *ee*). The *ee* was determined by GC using a Chiralsil DEX CB column (120 °C); t_r(major) = 81.18 min, t_r(minor) = 80.36 min. ¹H NMR (400 MHz, CDCl₃): δ = 4.32 (ddd, *J* = 12.8, 5.6, 1.2 Hz, 1H), 4.14 (dd, *J* = 12.8, 10.4 Hz, 1H), 2.71–2.66 (m, 1H), 2.60–2.54 (m, 1H), 1.92–1.82 (m, 2H), 1.63–1.22 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 176.24, 68.52, 46.60, 33.41, 32.57, 32.02, 25.69, 19.39, 19.27 ppm.

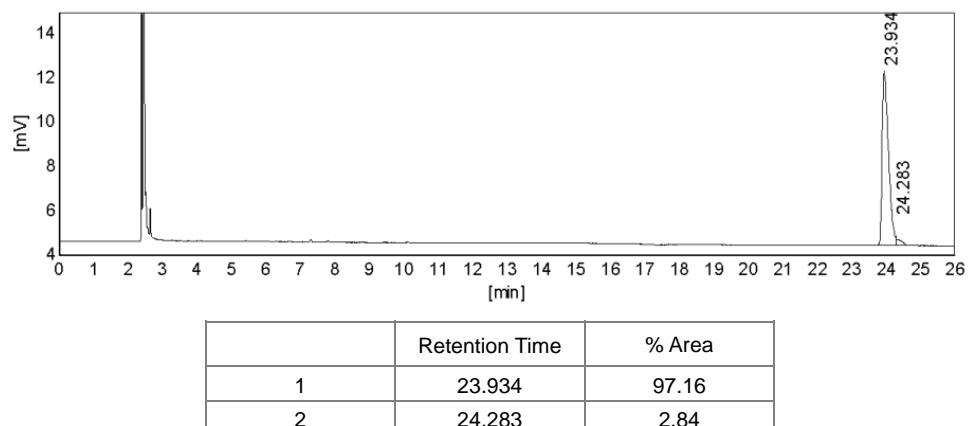
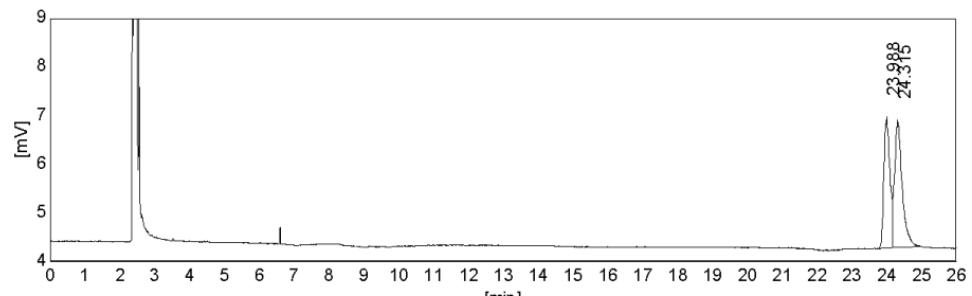


(+)-(R)-5-(tert-butyl)oxepan-2-one 2p:



Prepared according to **general procedure**: 81% yield, 94% *ee*. $[\alpha]_D^{20} = +30.2$ (c 1.06, CHCl₃); [Lit.:^[6] $[\alpha]_D^{20} = -34.9$ (c 0.78, CHCl₃) for *S*-isomer with 98% *ee*].

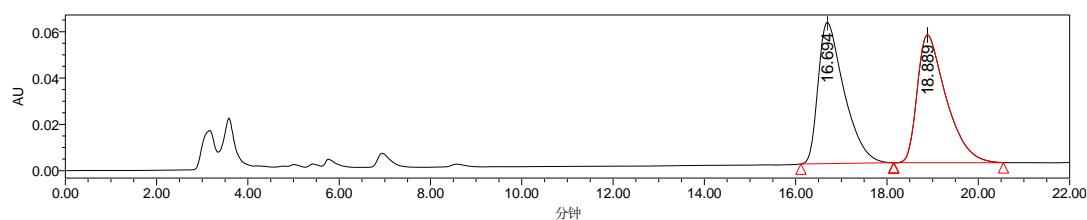
The *ee* was determined by GC using a Chiralsil DEX CB column (150 °C); t_r (major) = 23.93 min, t_r (minor) = 24.28 min. ^1H NMR (400 MHz, CDCl_3): δ = 4.37–4.24 (m, 1H), 4.19–4.05 (m, 1H), 2.68 (dd, J = 14.0, 7.2 Hz, 1H), 2.60–2.48 (m, 1H), 2.11–1.94 (m, 2H), 1.54–1.425 (m, 1H), 1.38–1.25 (m, 2H), 0.87 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ = 176.32, 68.64, 50.76, 33.46, 33.00, 30.34, 27.46, 23.77 ppm.

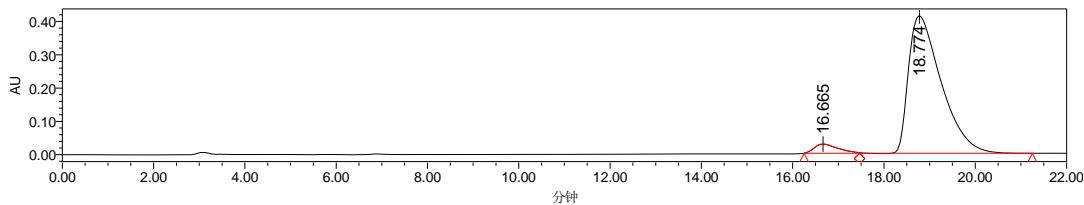


(+)-(S)-4-phenyldihydrofuran-2(3H)-one 4a:

4a

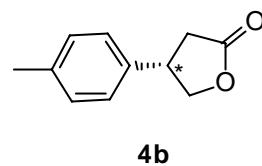
Prepared according to **general procedure**: 82% yield, 91% *ee*. $[\alpha]_D^{20} = +41.0$ (c 0.84, CHCl_3); [Lit.^[7] $[\alpha]_D^{20} = -46.7$ (c 0.48, CHCl_3) for *R*-isomer with 88% *ee*]. The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), t_r (minor) = 16.67 min, t_r (major) = 18.77 min. ^1H NMR (400 MHz, CDCl_3): δ = 7.37 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.24 (d, J = 7.2 Hz, 2H), 4.67 (t, J = 8.4 Hz, 1H), 4.27 (t, J = 8.4 Hz, 1H), 3.77 (p, J = 8.4 Hz, 1H), 2.92 (dd, J = 17.4, 8.8 Hz, 1H), 2.67 (dd, J = 17.6, 9.2 Hz, 1H).



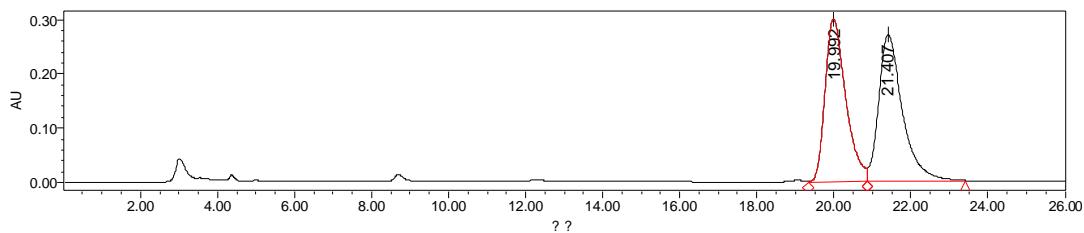


	Retention Time	% Area
1	16.665	4.55
2	18.774	95.45

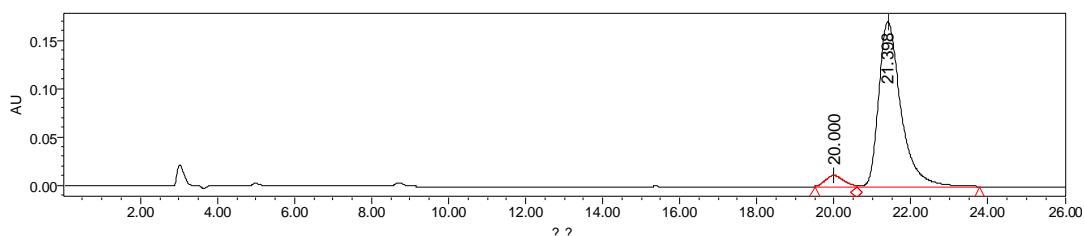
(+)-(S)-4-(p-tolyl)dihydrofuran-2(3H)-one 4b:



Prepared according to **general procedure**: 84% yield, 90% *ee*. $[\alpha]_D^{20} = +37.3$ (*c* 0.64, CHCl₃); [Lit.:^[7] $[\alpha]_D^{20} = -31.3$ (*c* 0.67, CHCl₃) for *R*-isomer with 93% *ee*]. The *ee* was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 92/8, 1.0 mL/min, 210 nm), *t_r*(major) = 21.40 min, *t_r*(minor) = 20.00 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.65 (t, *J* = 8.4 Hz, 1H), 4.24 (t, *J* = 8.4 Hz, 1H), 3.75 (p, *J* = 8.4 Hz, 1H), 2.90 (dd, *J* = 17.6, 8.8 Hz, 1H), 2.65 (dd, *J* = 17.6, 9.2 Hz, 1H), 2.35 (s, 3H).

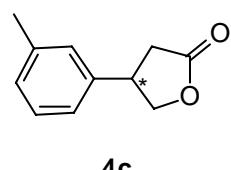


	Retention Time	% Area
1	19.992	48.79
2	21.407	51.21



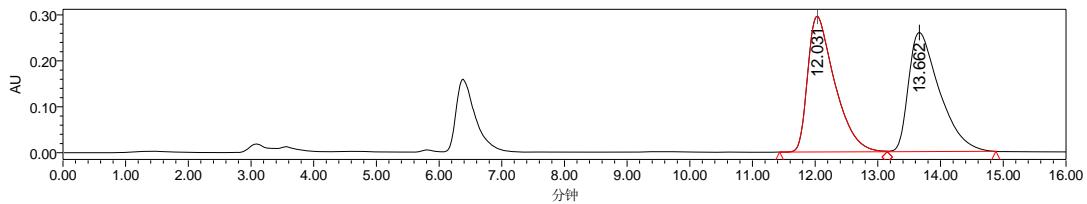
	Retention Time	% Area
1	20.000	5.16
2	21.398	94.84

(+)-4-(m-tolyl)dihydrofuran-2(3H)-one 4c:

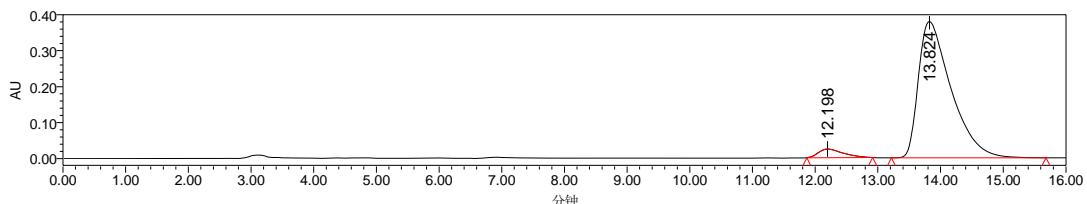


Prepared according to **general procedure**: 80% yield, 91% *ee*. $[\alpha]_D^{20} = +37.6$ (*c* 0.57, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel AS-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), *t_r*(major) = 13.82 min, *t_r*(minor) = 12.20 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.29 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.06–7.04 (m, 2H), 4.68 (t, *J* = 8.4 Hz,

1H), 4.29 (t, J = 8.4 Hz, 1H), 3.77 (p, J = 8.4 Hz, 1H), 2.93 (dd, J = 17.6, 8.8 Hz, 1H), 2.69 (dd, J = 17.5, 9.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 176.54, 139.41, 138.92, 129.03, 128.45, 127.43, 123.72, 74.11, 41.04, 35.72, 21.43 ppm. ES-HRMS Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2[\text{M} + \text{Na}]^+$ m/z 199.0735, Found: m/z 199.0738.

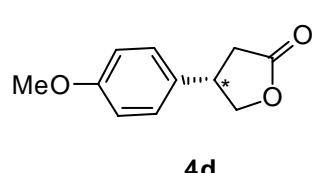


	Retention Time	% Area
1	12.301	49.56
2	13.662	50.44

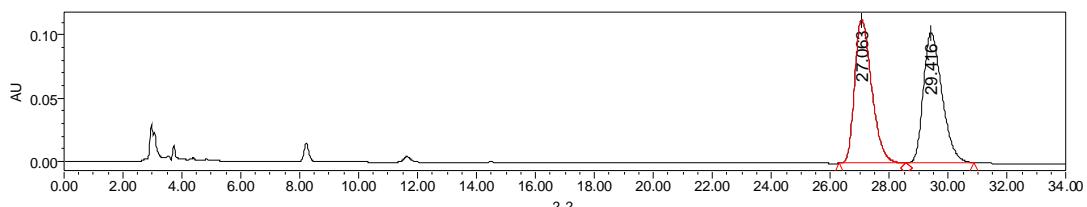


	Retention Time	% Area
1	12.198	4.48
2	13.824	95.52

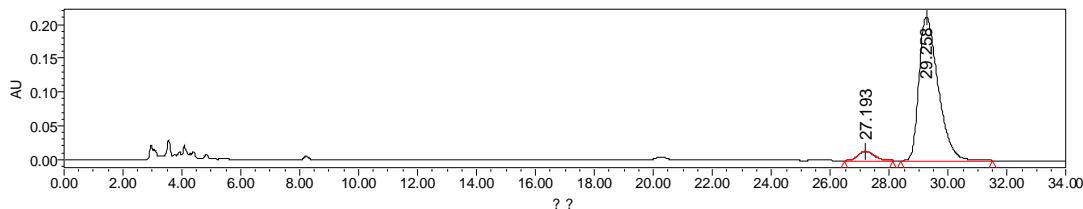
(+)-(S)-4-(4-methoxyphenyl)dihydrofuran-2(3H)-one 4d:



Prepared according to **general procedure**: 78% yield, 91% ee. $[\alpha]_D^{20} = +36.8$ (*c* 0.60, CHCl_3); [Lit.^[7] $[\alpha]_D^{20} = -28.3$ (*c* 0.90, CHCl_3) for *R*-isomer with 85% ee]. The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, 210 nm), $t_r(\text{major}) = 29.26$ min, $t_r(\text{minor}) = 27.19$ min. ^1H NMR (400 MHz, CDCl_3): δ = 7.15 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 4.63 (t, J = 8.4 Hz, 1H), 4.22 (t, J = 8.4 Hz, 1H), 3.80 (s, 3H), 3.72 (p, J = 8.4 Hz, 1H), 2.89 (dd, J = 17.6, 8.4 Hz, 1H), 2.63 (dd, J = 17.6, 9.2 Hz, 1H).

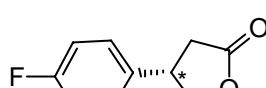


	Retention Time	% Area
1	27.063	50.16
2	29.416	49.84



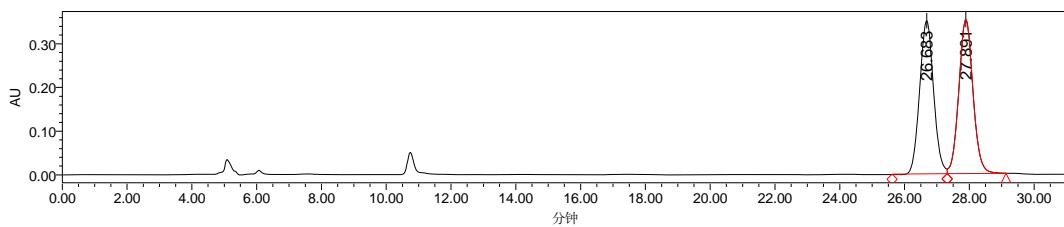
	Retention Time	% Area
1	27.193	4.46
2	29.258	95.54

(+)-(S)-4-(4-fluorophenyl)dihydrofuran-2(3H)-one 4e:

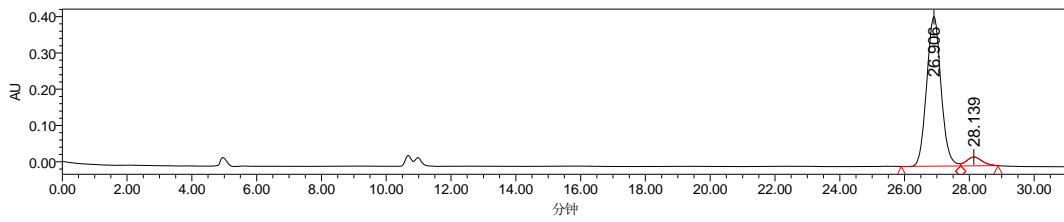


4e

Prepared according to **general procedure**: 71% yield, 87% ee. $[\alpha]_D^{20} = +41.0$ (c 0.52, CHCl₃); [Lit.:^[7] $[\alpha]_D^{20} = -40.2$ (c 0.85, CHCl₃) for R-isomer with 84% ee]. The ee was determined by HPLC analysis using a chiralcel AD-H column (hexane/2-propanol = 95/5, 0.6 mL/min, 210 nm), t_r (major) = 26.91 min, t_r (minor) = 28.14 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.20 (dd, *J* = 8.0, 5.6 Hz, 2H), 7.05 (t, *J* = 8.4 Hz, 2H), 4.65 (t, *J* = 8.4 Hz, 1H), 4.23 (t, *J* = 8.4 Hz, 1H), 3.78 (p, *J* = 8.4 Hz, 1H), 2.92 (dd, *J* = 17.6, 8.8 Hz, 1H), 2.63 (dd, *J* = 17.6, 8.8 Hz, 1H).

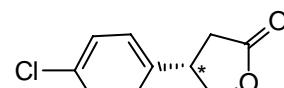


	Retention Time	% Area
1	26.683	49.30
2	27.891	50.70



	Retention Time	% Area
1	26.908	93.44
2	28.139	6.56

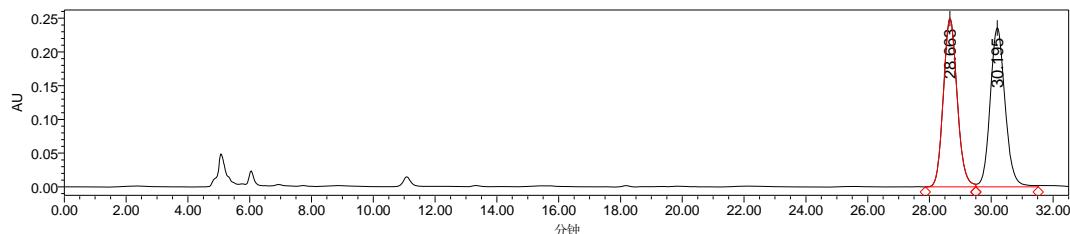
(+)-(S)-4-(4-chlorophenyl)dihydrofuran-2(3H)-one 4f:



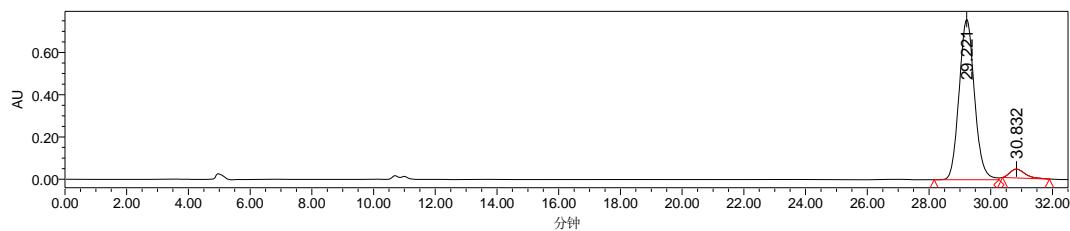
4f

Prepared according to **general procedure**: 83% yield, 87% ee. $[\alpha]_D^{20} = +43.7$ (c 0.59, CHCl₃); [Lit.:^[7] $[\alpha]_D^{20} = -47.2$ (c 0.90, CHCl₃) for R-isomer with 82% ee]. The ee was determined by HPLC analysis using a chiralcel AD-H column (hexane/2-propanol = 95/5, 0.6 mL/min, 210 nm), t_r (major) = 29.22 min, t_r (minor) = 30.83 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.33 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.65 (t, *J* = 8.4 Hz, 1H), 4.23 (t, *J* = 8.4 Hz, 1H),

3.77 (p, $J = 8.0$ Hz, 1H), 2.92 (dd, $J = 17.2, 8.8$ Hz, 1H), 2.62 (dd, $J = 17.2, 8.8$ Hz, 1H).



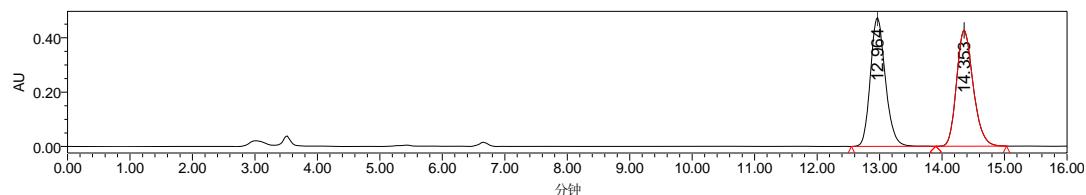
	Retention Time	% Area
1	28.663	49.55
2	30.195	50.45



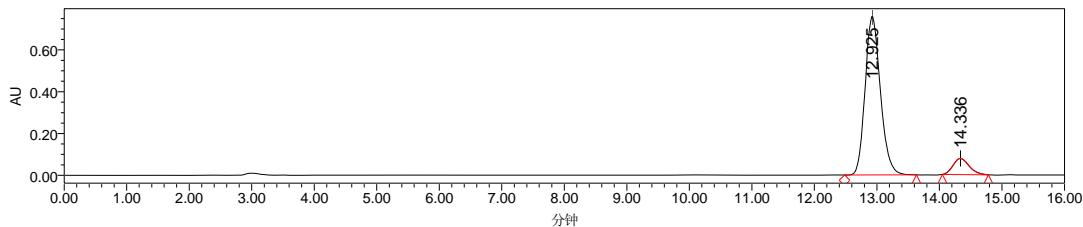
	Retention Time	% Area
1	29.221	93.54
2	30.832	6.46

(+)-(R)-4-(3-methoxybenzyl)dihydrofuran-2(3H)-one 4g:

4g Prepared according to **general procedure**: 99% yield, 80% ee. $[\alpha]_D^{20} = +5.5$ (c 0.77, CHCl_3); [Lit.:^[8] $[\alpha]_D^{20} = -6.5$ (c 1.42, CHCl_3) for S-isomer with 98% ee]. The ee was determined by HPLC analysis using a chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, 210 nm), t_r (major) = 12.93 min, t_r (minor) = 14.34 min. ^1H NMR (400 MHz, CDCl_3): δ = 7.24 (t, $J = 8.0$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.74 (d, $J = 7.6$ Hz, 1H), 6.69 (s, 1H), 4.40–4.27 (m, 1H), 4.03 (dd, $J = 9.2, 6.4$ Hz, 1H), 3.79 (s, 3H), 2.92–2.78 (m, 1H), 2.78–2.66 (m, 2H), 2.60 (dd, $J = 17.6, 7.2$ Hz, 1H), 2.28 (dd, $J = 17.6, 7.2$ Hz, 1H).

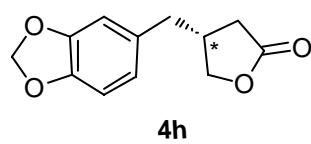


	Retention Time	% Area
1	12.964	50.05
2	14.353	49.95

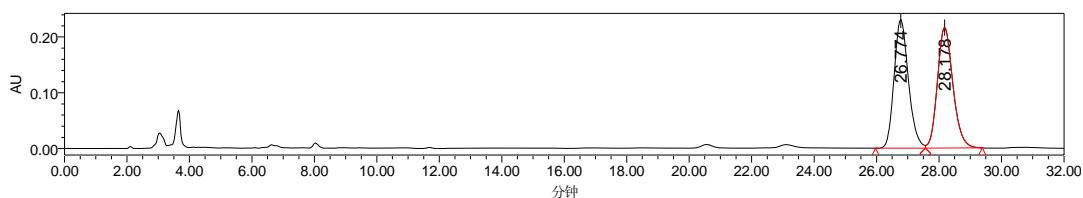


	Retention Time	% Area
1	12.925	90.11
2	14.336	9.89

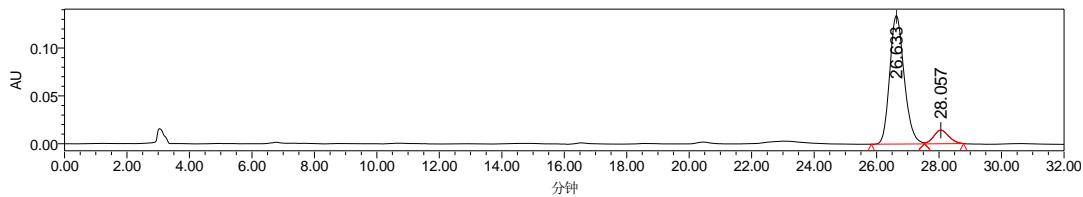
(+)-(R)-4-(benzo[d][1,3]dioxol-5-ylmethyl)dihydrofuran-2(3H)-one **4h**:



Prepared according to **general procedure**: 99% yield, 80% ee. $[\alpha]_D^{20} = +3.9$ (*c* 0.83, CHCl₃); [Lit.:^[8] $[\alpha]_D^{20} = -4.2$ (*c* 0.75, CHCl₃) for S-isomer with 98% ee]. The ee was determined by HPLC analysis using a chiralcel AD-H column (hexane/2-propanol = 95/5, 1.0 mL/min, 210 nm), t_r(major) = 26.63 min, t_r(minor) = 28.06 min. ¹H NMR (400 MHz, CDCl₃): δ = 6.74 (d, *J* = 7.6 Hz, 1H), 6.62 (s, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 4.35–4.28 (m, 1H), 4.01 (dd, *J* = 9.2, 6.4 Hz, 1H), 2.85–2.73 (m, 1H), 2.73–2.63 (m, 2H), 2.58 (dd, *J* = 17.6, 8.0 Hz, 1H), 2.26 (dd, *J* = 17.6, 7.2 Hz, 1H).

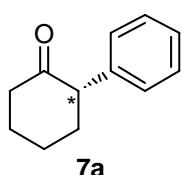


	Retention Time	% Area
1	26.774	49.63
2	28.178	50.37



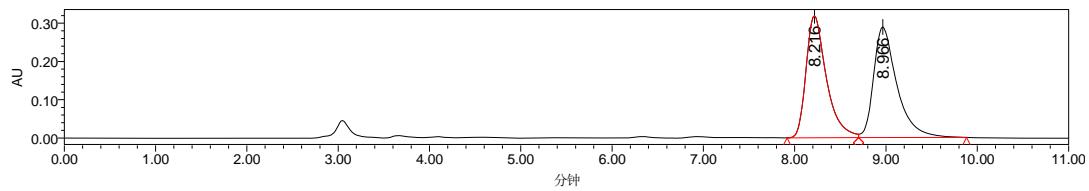
	Retention Time	% Area
1	26.633	89.75
2	28.057	10.25

(-)-(S)-2-phenylcyclohexanone **7a**:

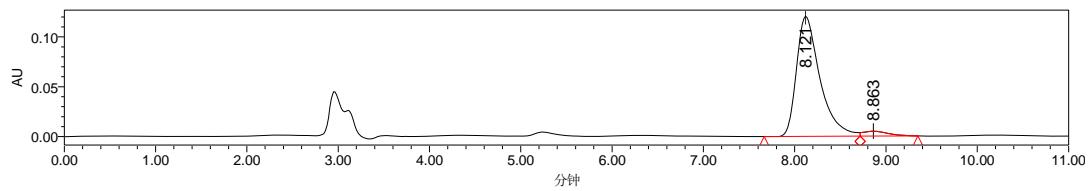


Prepared according to **general procedure**: -40 °C, 36 h, 46% yield, 94% ee. $[\alpha]_D^{20} = -80.5$ (*c* 0.60, CHCl₃), $[\alpha]_D^{20} = -36.0$ (*c* 0.48, C₆H₆) [Lit.:^[9] $[\alpha]_D^{25} = -113.5$ (*c* 0.6, C₆H₆) for S-isomer]. The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 95/5, 1.0 mL/min, 210 nm), t_r(major) = 8.12 min, t_r(minor) = 8.86 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.35–7.12 (m, 5H), 3.60

(dd, $J = 12.4, 5.6$ Hz, 1H), 2.57–2.40 (m, 2H), 2.32–2.22 (m, 1H), 2.20–2.10 (m, 1H), 2.09–1.96 (m, 2H), 1.76–1.75 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 290.24, 137.75, 127.50, 127.32, 125.85, 56.35, 41.15, 34.06, 26.79, 24.29 ppm.



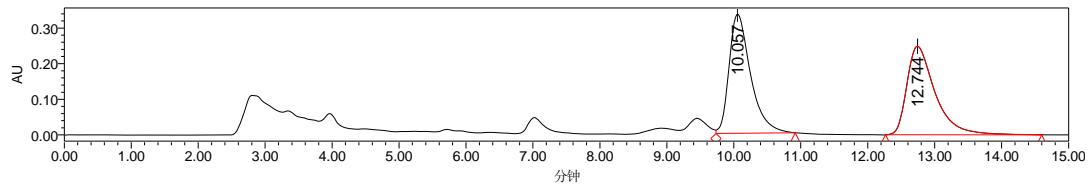
	Retention Time	% Area
1	8.216	49.06
2	8.966	50.94



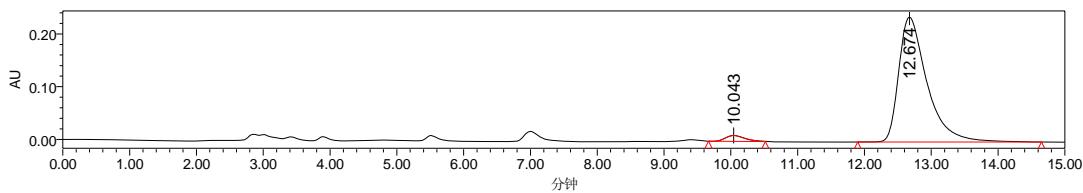
	Retention Time	% Area
1	8.121	96.78
2	8.863	3.22

(+)-(R)-3-phenyloxepan-2-one 8a:

Prepared according to **general procedure**: -40 °C, 36 h, 51% yield, 94% ee. $[\alpha]_D^{20} = +80.6$ (c 0.37, CHCl_3 , **8a/9a** = 17/1). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), t_r (major) = 12.67 min, t_r (minor) = 10.04 min. ^1H NMR (400 MHz, CDCl_3): δ = 7.36–7.20 (m, 5H), 4.41–4.28 (m, 2H), 3.88 (d, $J = 8.0$ Hz, 1H), 2.18–1.85 (m, 4H), 1.84–1.68 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 174.72, 138.97, 127.42, 127.19, 126.15, 67.81, 48.19, 30.25, 27.82, 27.10 ppm. ES-HRMS Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2[\text{M} + \text{Na}]^+$ m/z 213.0891. Found: m/z 213.0899.

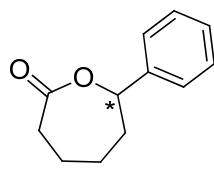


	Retention Time	% Area
1	10.057	50.66
2	12.744	49.34



	Retention Time	% Area
1	10.043	3.05
2	12.674	96.95

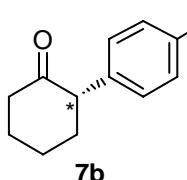
7-phenyloxepan-2-one 9a:



9a

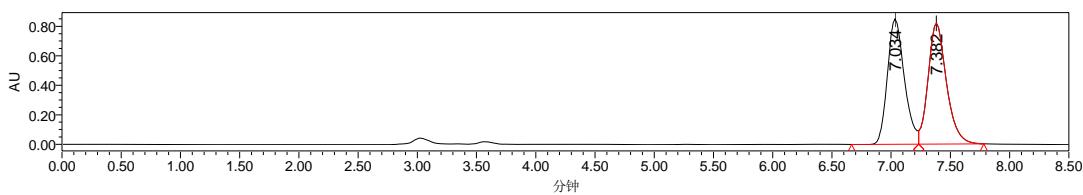
¹H NMR (400 MHz, CDCl₃): δ = 7.33–7.18 (m, 5H), 5.21 (d, *J* = 9.6 Hz, 1H), 2.73–2.65 (m, 2H), 2.10–1.87 (m, 4H), 1.73–1.58 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 173.89, 139.79, 127.55, 127.08, 124.84, 81.08, 36.45, 33.94, 27.59, 21.83 ppm.

(−)-(S)-2-(4-chlorophenyl)cyclohexanone 7b:

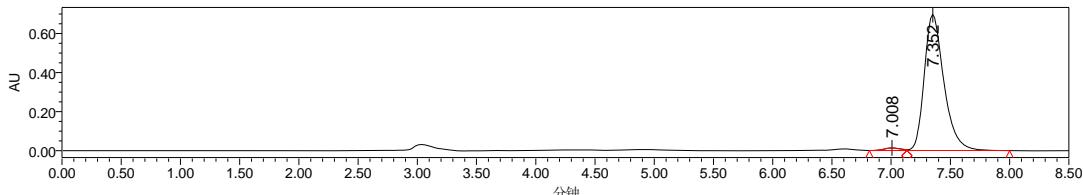


7b

Prepared according to **general procedure**: -40 °C, 41 h, 47% yield, 97% ee. [α]_D²⁰ = -77.2 (c 0.80, CHCl₃). The ee was determined by HPLC analysis using a chiralcel AD-H column (hexane/2-propanol = 95/5, 1.0 mL/min, 210 nm), t_r(major) = 7.35 min, t_r(minor) = 7.00 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.27 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.58 (dd, *J* = 12.0, 5.2 Hz, 1H), 2.60–2.38 (m, 2H), 2.32–2.20 (m, 1H), 2.19–2.10 (m, 1H), 2.05–1.91 (m, 2H), 1.87–1.77 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 208.74, 136.23, 131.64, 128.92, 127.44, 55.76, 41.16, 34.23, 26.75, 24.33 ppm.



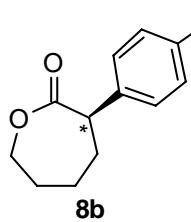
	Retention Time	% Area
1	7.034	49.13
2	7.382	50.87



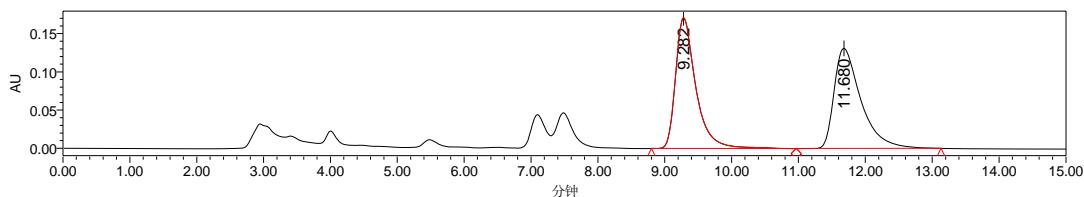
	Retention Time	% Area
	S28	

1	7.008	1.53
2	7.352	98.47

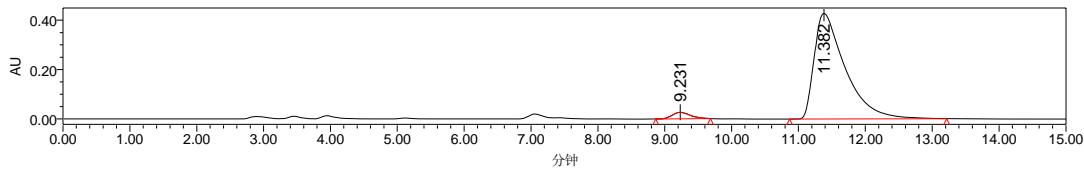
(+)-(R)-3-(4-chlorophenyl)oxepan-2-one 8b:



Prepared according to **general procedure**: -40 °C, 41 h, 53% yield, 93% *ee*. $[\alpha]_D^{20} = +78.5$ (c 0.32, CHCl₃, **8b/9b** >19/1). The *ee* was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), t_r(major) = 11.38 min, t_r(minor) = 9.23 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.37–4.28 (m, 2H), 3.84 (d, *J* = 10.0 Hz, 1H), 2.20–1.81 (m, 4H), 1.85–1.69 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 175.38, 138.63, 122.99, 129.66, 128.56, 68.93, 48.59, 31.46, 28.77, 28.22 ppm. ES-HRMS Calcd for C₁₂H₁₃Cl^{34.9689}O₂[M + Na]⁺ m/z 247.0502, Found: m/z 247.0503.

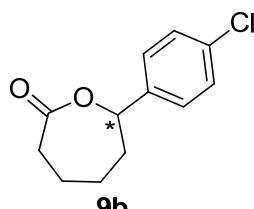


	Retention Time	% Area
1	9.282	49.71
2	11.680	50.29



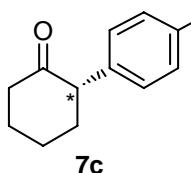
	Retention Time	% Area
1	9.231	3.50
2	11.382	96.50

7-(4-chlorophenyl)oxepan-2-one 9b:



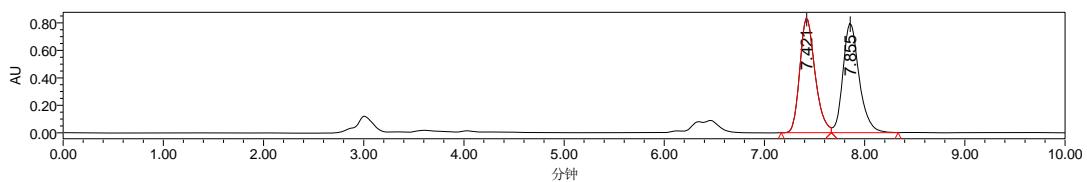
¹H NMR (400 MHz, CDCl₃): δ = 7.31 (s, 4H), 5.25 (d, *J* = 9.6 Hz, 1H), 2.79–2.69 (m, 2H), 2.10–1.90 (m, 4H), 1.81–1.60 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 173.60, 138.34, 132.77, 127.70, 126.26, 80.25, 36.48, 33.88, 27.53, 21.75 ppm.

(-)-(S)-2-(4-bromophenyl)cyclohexanone 7c:

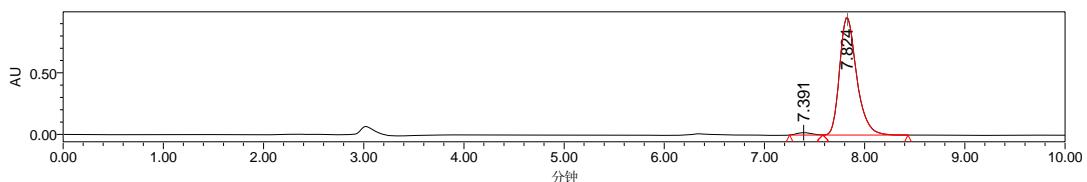


Prepared according to **general procedure**: -40 °C, 41 h, 47% yield, 97% *ee*. $[\alpha]_D^{20} = -54.4$ (c 0.94, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel AD-H column (hexane/2-propanol = 95/5, 1.0 mL/min, 210 nm), t_r(major) = 7.82 min, t_r(minor) = 7.39 min. ¹H NMR (400 MHz, CDCl₃): δ =

7.45 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 3.57 (dd, $J = 12.0, 5.6$ Hz, 1H), 2.57–2.40 (m, 2H), 2.31–2.22 (m, 1H), 2.19–2.10 (m, 1H), 2.05–1.91 (m, 2H), 1.87–1.77 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 208.63, 136.74, 130.39, 129.31, 119.79, 55.83, 41.16, 34.18, 26.75, 24.32 ppm. ES-HRMS Calcd for $\text{C}_{12}\text{H}_{13}\text{Br}^{78,9183}\text{O}[\text{M} + \text{Na}]^+$ m/z 275.0047, Found: m/z 275.0051.



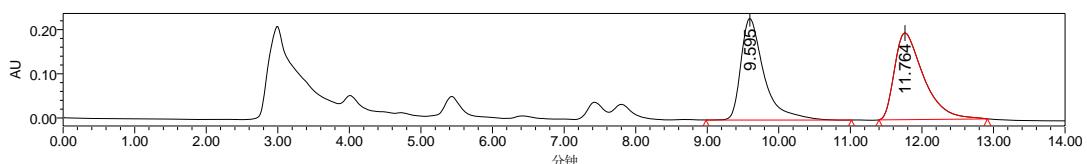
	Retention Time	% Area
1	7.421	49.61
2	7.855	50.39



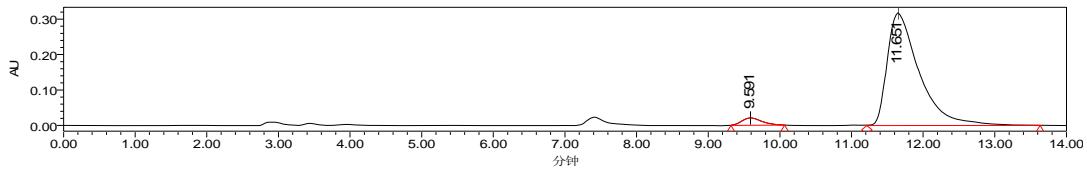
	Retention Time	% Area
1	7.391	1.49
2	7.824	98.51

(+)-(R)-3-(4-bromophenyl)oxepan-2-one 8c:

Prepared according to general procedure: -40 °C, 41 h, 53% yield, 92% ee. m.p. = 155–156 °C (single crystal). $[\alpha]_D^{20} = +62.9$ (c 0.56, CHCl_3 , **8c/9c** > 19/1). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), $t_r(\text{major}) = 11.65$ min, $t_r(\text{minor}) = 9.59$ min. ^1H NMR (400 MHz, CDCl_3): δ = 7.46 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 4.38–4.33 (m, 2H), 3.84 (d, $J = 10.0$ Hz, 1H), 2.12–1.86 (m, 4H), 1.85–1.69 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 174.26, 138.14, 130.47, 129.02, 120.08, 67.91, 47.62, 30.36, 27.73, 27.17 ppm. ES-HRMS Calcd for $\text{C}_{12}\text{H}_{13}\text{Br}^{78,9183}\text{O}_2[\text{M} + \text{Na}]^+$ m/z 290.9997, Found: m/z 290.9998.

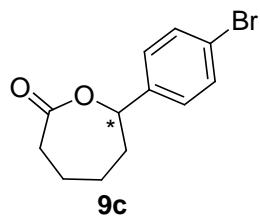


	Retention Time	% Area
1	9.595	49.01
2	11.764	50.99



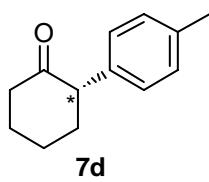
	Retention Time	% Area
1	9.591	3.87
2	11.651	96.13

7-(4-bromophenyl)oxepan-2-one 9c:

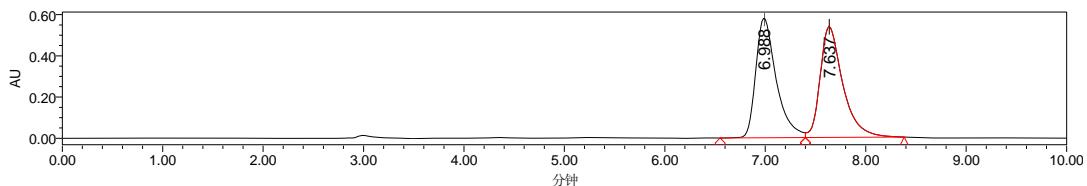


¹H NMR (400 MHz, CDCl₃): δ = 7.48 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.25 (d, *J* = 9.2 Hz, 1H), 2.80–2.65 (m, 2H), 2.10–1.90 (m, 4H), 1.83–1.62 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 173.57, 138.85, 130.66, 126.57, 120.90, 80.26, 36.46, 33.88, 27.52, 21.74 ppm.

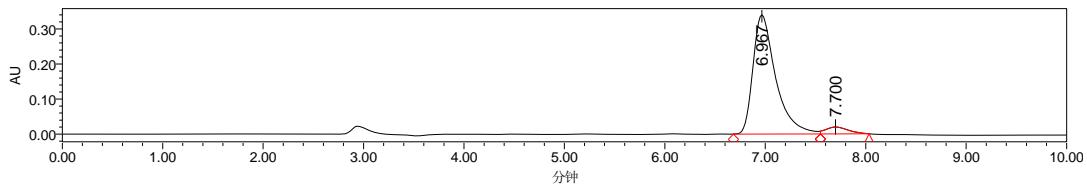
(−)-(S)-2-(p-tolyl)cyclohexanone 7d:



Prepared according to **general procedure**: -40 °C, 43 h, 51% yield, 89% *ee*. [α]_D²⁰ = -61.6 (c 0.87, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 95/5, 1.0 mL/min, 210 nm), t_r(major) = 6.97 min, t_r(minor) = 7.70 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.16 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.59 (dd, *J* = 12.0, 5.2 Hz, 1H), 2.57–2.40 (m, 2H), 2.35 (s, 3H), 2.31–2.22 (m, 1H), 2.19–2.11 (m, 1H), 2.10–1.94 (m, 2H), 1.90–1.75 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 209.38, 135.40, 134.71, 128.06, 127.33, 55.97, 41.13, 34.05, 26.80, 24.30, 20.05 ppm.



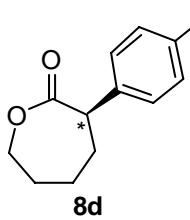
	Retention Time	% Area
1	6.988	49.42
2	7.637	50.58



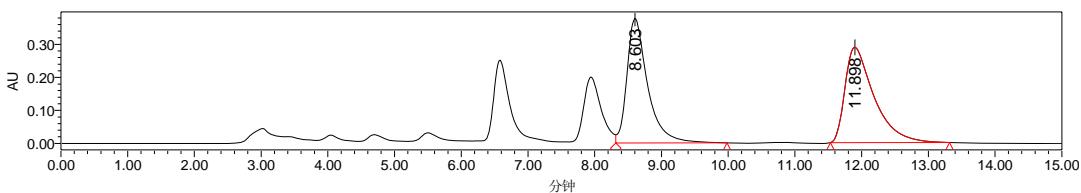
	Retention Time	% Area
1	6.967	94.61

2	7.700	5.39
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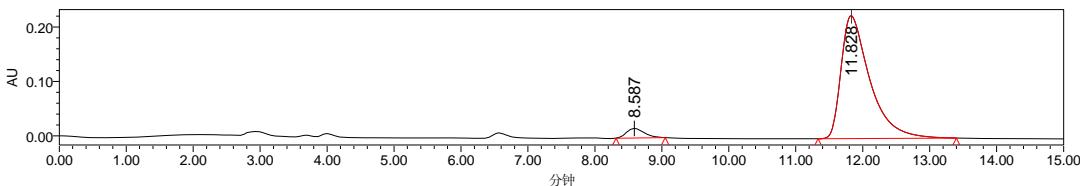
(+)-(R)-3-(p-tolyl)oxepan-2-one 8d:



Prepared according to **general procedure**: -40 °C, 43 h, 48% yield, 91% *ee*. $[\alpha]_D^{20} = +40.7$ (c 0.60, CHCl₃, **8d/9d** = 12/1). The *ee* was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), *t*_r(major) = 11.83 min, *t*_r(minor) = 8.59 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.15 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 4.40–4.34 (m, 2H), 3.86 (d, *J* = 8.8 Hz, 1H), 2.34 (s, 3H), 2.18–1.82 (m, 4H), 1.80–1.69 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 174.97, 135.99, 135.71, 128.12, 126.99, 67.77, 47.77, 30.23, 27.82, 27.06, 20.05 ppm. ES-HRMS Calcd for C₁₃H₁₆O₂[M + Na]⁺ m/z 227.1048, Found: m/z 227.1048.

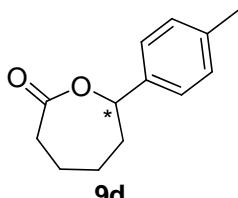


	Retention Time	% Area
1	8.603	49.34
2	11.898	50.66



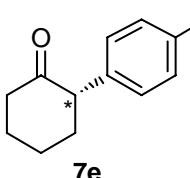
	Retention Time	% Area
1	8.587	4.57
2	11.828	95.43

7-(p-tolyl)oxepan-2-one 9d:



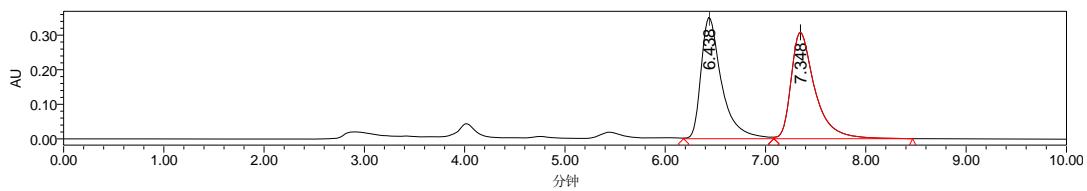
¹H NMR (400 MHz, CDCl₃): δ = 7.19 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.19 (d, *J* = 9.2 Hz, 1H), 2.70–2.63 (m, 2H), 2.26 (s, 3H), 2.07–1.85 (m, 4H), 1.70–1.55 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 173.98, 136.88, 136.81, 128.18, 124.78, 81.02, 36.41, 33.95, 27.57, 21.85, 20.10 ppm.

(-)-(S)-2-(4-methoxyphenyl)cyclohexanone 7e:

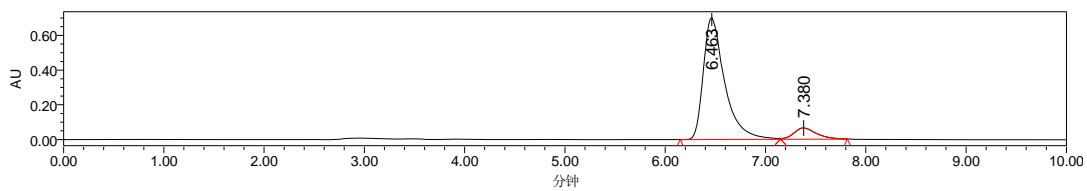


Prepared according to **general procedure**: -40 °C, 48 h, 44% yield, 82% *ee*. $[\alpha]_D^{20} = -65.4$ (c 0.73, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min,

210 nm), t_r (major) = 6.46 min, t_r (minor) = 7.38 min. ^1H NMR (400 MHz, CDCl_3): δ = 7.06 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 3.80 (s, 3H), 3.57 (dd, J = 12.0, 5.6 Hz, 1H), 2.57–2.40 (m, 2H), 2.31–2.22 (m, 1H), 2.19–2.11 (m, 1H), 2.07–1.94 (m, 2H), 1.90–1.79 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 209.64, 157.43, 129.86, 128.42, 112.80, 55.53, 54.19, 41.14, 34.25, 26.83, 24.35 ppm.



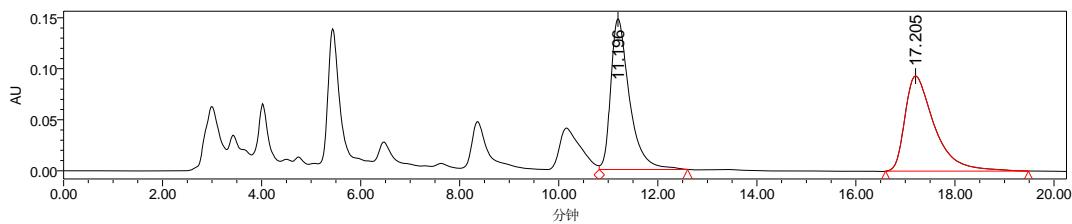
	Retention Time	% Area
1	6.438	49.69
2	7.348	50.31



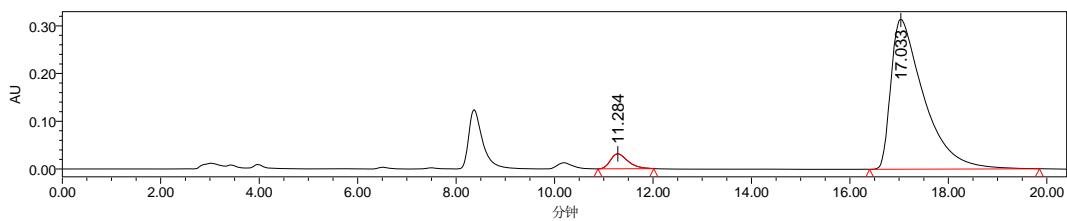
	Retention Time	% Area
1	6.463	91.09
2	7.380	8.91

(+)-(R)-3-(4-methoxyphenyl)oxepan-2-one 8e:

8e Prepared according to **general procedure**: -40 °C, 48 h, 56% yield, 90% ee. $[\alpha]_D^{20} = +101.3$ (c 0.38, CHCl_3 , **8e/9e** = 5.6/1). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), t_r (major) = 17.03 min, t_r (minor) = 11.28 min. ^1H NMR (400 MHz, CDCl_3): δ = 7.14 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.39–4.31 (m, 2H), 3.83 (dd, J = 8.8 Hz, 3.2 Hz, 1H), 3.79 (s, 3H), 2.06–1.95 (m, 4H), 1.86–1.65 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 175.11, 157.60, 131.24, 128.14, 112.84, 67.76, 54.23, 47.31, 30.49, 27.81, 27.10 ppm. ES-HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3[\text{M} + \text{Na}]^+$ m/z 243.0997, Found: m/z 243.0997.

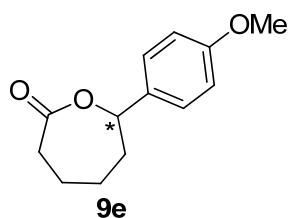


	Retention Time	% Area
1	11.198	50.01
2	17.205	49.99



	Retention Time	% Area
1	11.284	5.00
2	17.033	95.00

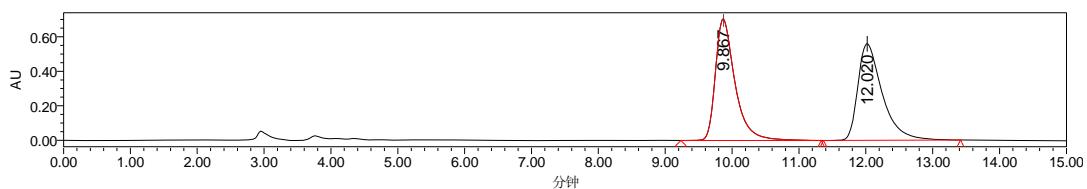
7-(4-methoxyphenyl)oxepan-2-one 9e:



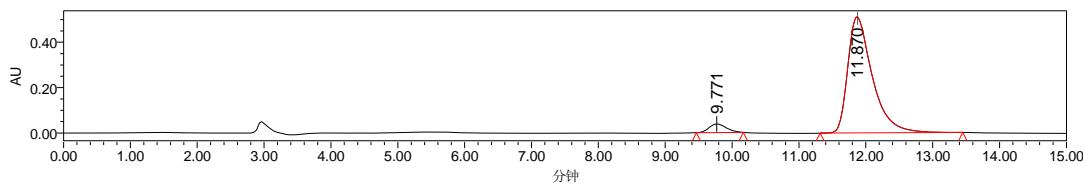
¹H NMR (400 MHz, CDCl₃): δ = 7.29 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.24 (d, *J* = 9.2 Hz, 1H), 3.79 (s, 3H), 2.83–2.65 (m, 2H), 2.15–1.91 (m, 4H), 1.81–1.65 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 174.00, 158.37, 132.07, 126.21, 112.87, 80.86, 54.28, 36.29, 33.95, 27.53, 21.84 ppm.

(−)-(S)-2-([1,1'-biphenyl]-4-yl)cyclohexanone 7f:

7f Prepared according to **general procedure**: -40 °C, 48 h, 44% yield, 90% ee. [α]_D²⁰ = -58.9 (c 0.76, CHCl₃). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 95/5, 1.0 mL/min, 210 nm), t_r(major) = 11.87 min, t_r(minor) = 9.77 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.57 (t, *J* = 8.8 Hz, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.64 (dd, *J* = 12.0, 5.6 Hz, 1H), 2.55–2.30 (m, 2H), 2.29–2.15 (m, 1H), 2.14–1.99 (m, 1H), 1.98–1.85 (m, 2H), 1.84–1.67 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 209.25, 139.98, 138.78, 136.82, 127.91, 127.67, 126.10, 126.07, 56.05, 41.19, 34.13, 26.79, 24.32 ppm. ES-HRMS Calcd for C₁₈H₁₈O[M + Na]⁺ m/z 273.1255, Found: m/z 273.1252.



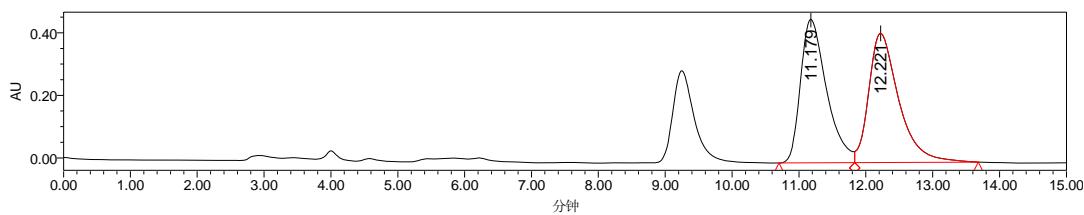
	Retention Time	% Area
1	9.867	50.24
2	12.020	49.76



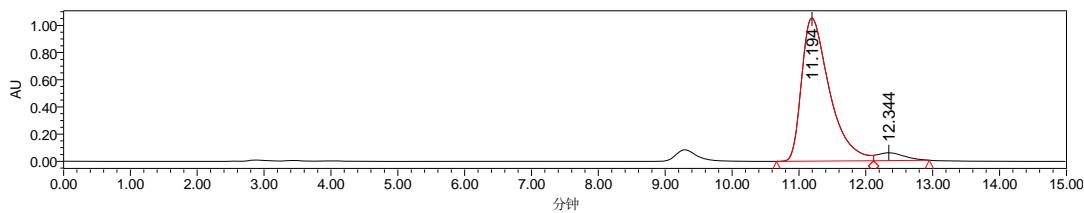
	Retention Time	% Area
1	9.771	5.01
2	11.870	94.99

(+)-(R)-3-([1,1'-biphenyl]-4-yl)oxepan-2-one 8f:

Ph Prepared according to **general procedure**: -40 °C, 48 h, 53% yield, 90% *ee*. $[\alpha]_D^{20} = +72.7$ (*c* 0.80, CHCl₃, **8f/9f** = 16.5/1). The *ee* was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), *t*_r(major) = 11.19 min, *t*_r(minor) = 12.34 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.57 (t, *J* = 6.8 Hz, 4H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.40–4.31 (m, 2H), 3.91 (d, *J* = 9.6 Hz, 1H), 2.18–1.80 (m, 4H), 1.79–1.65 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 174.76, 139.80, 139.03, 138.06, 127.70, 127.60, 126.19, 126.15, 126.06, 67.85, 47.84, 30.31, 27.79, 27.11 ppm. ES-HRMS Calcd for C₁₈H₁₈O₂[M + Na]⁺ m/z 289.1204, Found: m/z 289.1207.

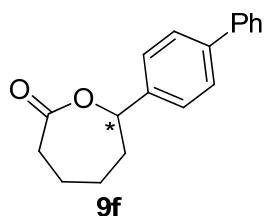


	Retention Time	% Area
1	11.179	49.13
2	12.221	50.87



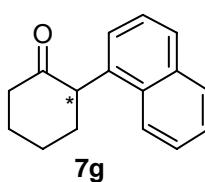
	Retention Time	% Area
1	11.194	95.04
2	12.344	4.96

7-([1,1'-biphenyl]-4-yl)oxepan-2-one 9f:

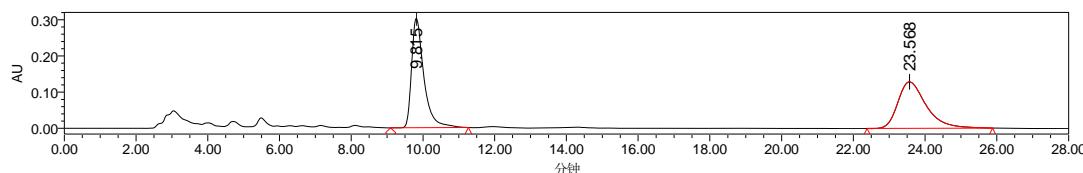


¹H NMR (400 MHz, CDCl₃): δ = 7.60–7.33 (m, 9H), 5.34 (d, *J* = 8.4 Hz, 1H), 2.84–2.68 (m, 2H), 2.21–1.94 (m, 4H), 1.85–1.65 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 174.91, 141.04, 140.62, 139.84, 128.84, 127.45, 127.30, 127.11, 126.36, 81.86, 37.47, 34.99, 28.63, 22.88 ppm.

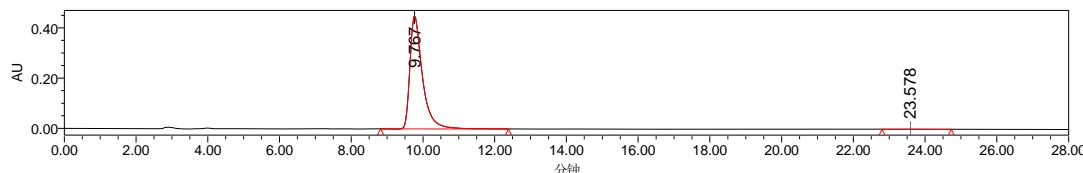
(-)-2-(naphthalen-1-yl)cyclohexanone 7g:



Prepared according to **general procedure**: -20 °C, 27 h, 49% yield, 99% *ee*. [α]_D²⁰ = -5.1 (c 0.88, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), t_r(major) = 9.77 min, t_r(minor) = 23.58 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.70–7.61 (m, 3H), 7.40–7.27 (m, 3H), 7.26 (d, *J* = 7.2 Hz, 1H), 4.28–4.20 (m, 1H), 2.66–2.44 (m, 2H), 2.37–2.25 (m, 1H), 2.24–2.07 (m, 2H), 2.06–1.93 (m, 1H), 1.92–1.75 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 208.96, 134.21, 132.81, 130.80, 127.99, 126.61, 124.85, 124.35, 124.31, 124.29, 122.26, 52.32, 41.60, 33.28, 26.86, 24.90 ppm. ES-HRMS Calcd for C₁₆H₁₆O[M + Na]⁺ m/z 247.1099, Found: m/z 247.1101.

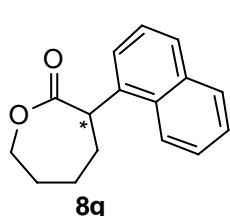


	Retention Time	% Area
1	9.815	50.37
2	23.568	49.63



	Retention Time	% Area
1	9.767	99.55
2	23.578	0.45

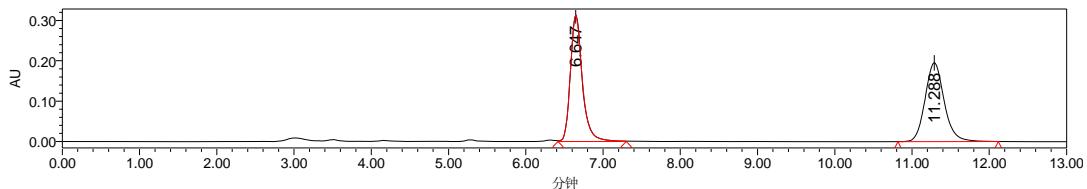
(+)-3-(naphthalen-1-yl)oxepan-2-one 8g:



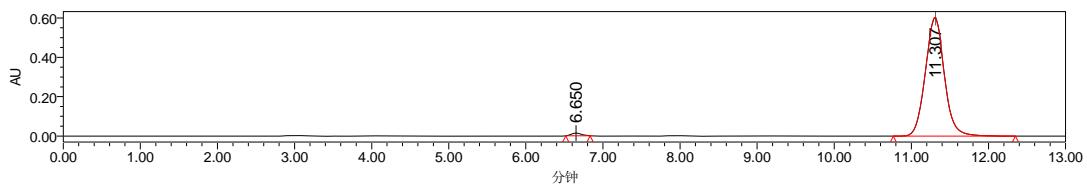
Prepared according to **general procedure**: -20 °C, 27 h, 51% yield, 98% *ee*. [α]_D²⁰ = +50.7 (c 0.59, CHCl₃, **8g/9g** >19/1). The *ee* was determined by HPLC analysis using a chiralcel AD-H column (hexane/2-propanol = 70/30, 1.0 mL/min, 210 nm), t_r(major) = 11.31 min, t_r(minor) = 6.65 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.90–7.75 (m, 4H), 7.70–7.40 (m, 3H), 4.68–4.46 (m, 3H), 2.43–2.21 (m, 2H), 2.20–2.12 (m, 1H), 2.10–2.00 (m, 1H), 1.98–1.72 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ = 174.59, 135.07, 132.68, 130.26, 128.09, 126.85, 125.25, 124.46,

124.43, 124.42, 121.37, 67.06, 43.28, 29.17, 27.85, 27.68 ppm. ES-HRMS Calcd for C₁₆H₁₆O₂[M + Na]⁺ m/z 263.1048, Found: m/z 263.1045.

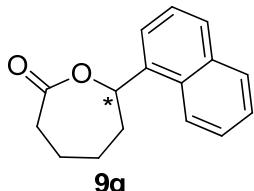


	Retention Time	% Area
1	6.647	50.34
2	11.288	49.66



	Retention Time	% Area
1	6.650	1.11
2	11.307	98.89

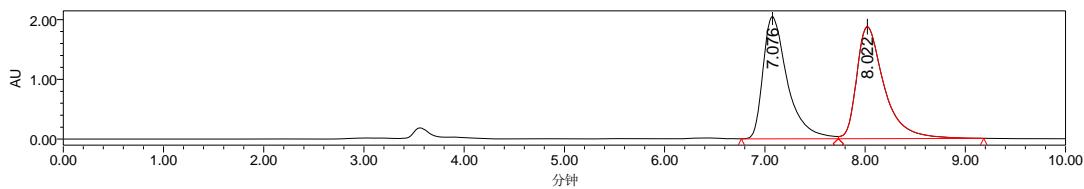
7-(naphthalen-1-yl)oxepan-2-one **9g**:



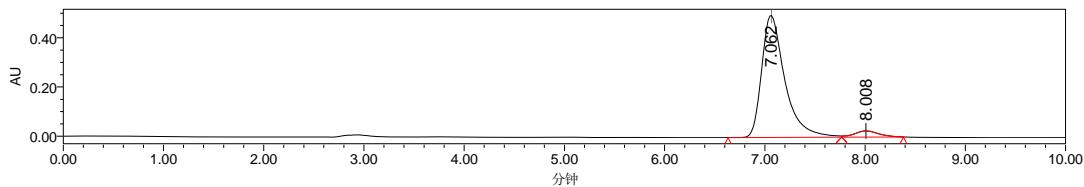
¹H NMR (400 MHz, CDCl₃): δ = 7.91–7.75 (m, 4H), 7.61–7.42 (m, 3H), 6.03 (d, *J* = 9.2 Hz, 1H), 2.97–2.82 (m, 2H), 2.34–1.24 (m, 1H), 2.16–1.99 (m, 3H), 1.98–1.73 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 173.88, 135.19, 132.75, 128.42, 128.19, 127.42, 125.35, 124.57, 124.46, 122.22, 121.28, 77.75, 36.20, 33.99, 27.74, 22.06 ppm.

(−)-2-(naphthalen-2-yl)cyclohexanone **7h**:

Prepared according to **general procedure**: -20 °C, 15 h, 45% yield, 90% *ee*. [α]_D²⁰ = -76.9 (c 0.58, CHCl₃). The *ee* was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), t_r(major) = 7.06 min, t_r(minor) = 8.00 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.83–7.78 (m, 3H), 7.61 (s, 1H), 7.49–7.42 (m, 2H), 7.31–7.27 (m, 1H), 3.79 (dd, *J* = 12.0 Hz, 5.6 Hz, 1H), 2.63–2.46 (m, 2H), 2.41–2.27 (m, 1H), 2.25–2.12 (m, 2H), 2.10–1.96 (m, 1H), 1.95–1.82 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 209.39, 135.38, 132.46, 131.52, 126.78, 126.70, 126.60, 125.96, 125.95, 124.86, 122.58, 56.43, 41.21, 34.01, 26.79, 24.28 ppm. ES-HRMS Calcd for C₁₆H₁₆O[M + Na]⁺ m/z 247.1099, Found: m/z 247.1099.

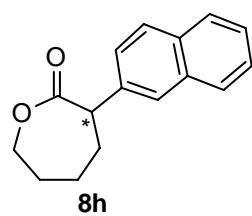


	Retention Time	% Area
1	7.076	49.23
2	8.022	50.77

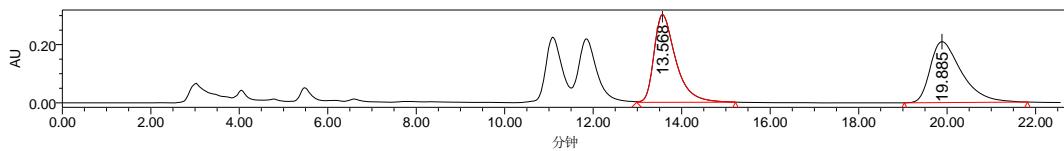


	Retention Time	% Area
1	7.062	94.94
2	8.008	5.06

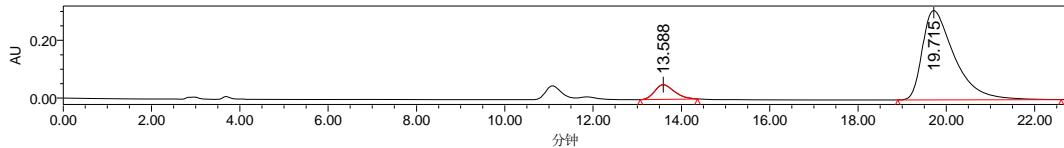
(+)-3-(naphthalen-2-yl)oxepan-2-one 8h:



Prepared according to **general procedure**: -20 °C, 15 h, 54% yield, 82% ee. $[\alpha]_D^{20} = +65.2$ (c 0.87, CHCl₃, **8h/9h** = 9/1). The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 210 nm), *t*_r(major) = 19.72 min, *t*_r(minor) = 13.59 min. ¹H NMR (400 MHz, CDCl₃): δ = 7.81–7.68 (m, 3H), 7.54 (s, 1H), 7.48–7.22 (m, 3H), 4.32–4.19 (m, 2H), 3.94 (d, *J* = 10.4 Hz, 1H), 2.20–1.80 (m, 4H), 1.79–1.65 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 174.79, 136.43, 131.57, 127.08, 126.74, 126.60, 125.59, 125.52, 125.02, 124.79, 67.86, 48.31, 30.24, 27.82, 27.09 ppm. ES-HRMS Calcd for C₁₆H₁₆O₂[M + Na]⁺ m/z 263.1048, Found: m/z 263.1050.

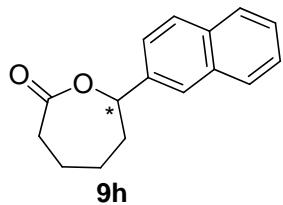


	Retention Time	% Area
1	13.568	49.99
2	19.885	50.01



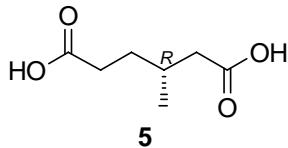
	Retention Time	% Area
1	13.588	9.01
2	19.715	90.99

7-(naphthalen-2-yl)oxepan-2-one 9h:



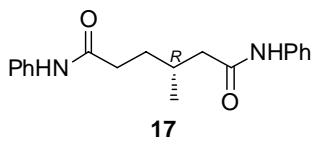
¹H NMR (400 MHz, CDCl₃): δ = 7.89–7.80 (m, 4H), 7.58–7.42 (m, 3H), 5.45 (d, *J* = 9.2 Hz, 1H), 2.92–2.70 (m, 2H), 2.25–1.97 (m, 4H), 1.89–1.69 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 173.90, 137.11, 132.01, 127.43, 127.05, 126.63, 125.31, 125.15, 123.61, 122.76, 81.09, 36.55, 33.97, 27.63, 21.85 ppm.

(+)-(R)-3-methylhexanedioic acid 5:

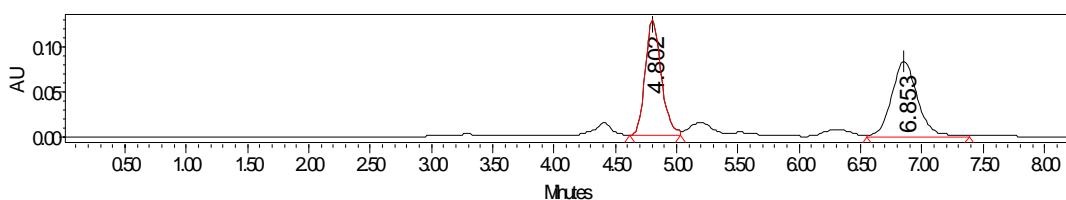


62% yield, 84% ee. [α]_D²⁰ = +7.1 (c 0.67, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 10.92 (w, 2H), 2.40–2.27 (m, 3H), 2.15 (dd, *J* = 15.6, 8.0 Hz, 1H), 2.02–1.88 (m, 1H), 1.76–1.60 (m, 1H), 1.54–1.45 (m, 1H), 0.93 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 180.13, 179.43, 41.20, 31.69, 31.06, 29.54, 19.26 ppm; ES-HRMS Calcd for C₁₆H₁₆O₂[M + Na]⁺ m/z 183.0633, Found: m/z 183.0637.

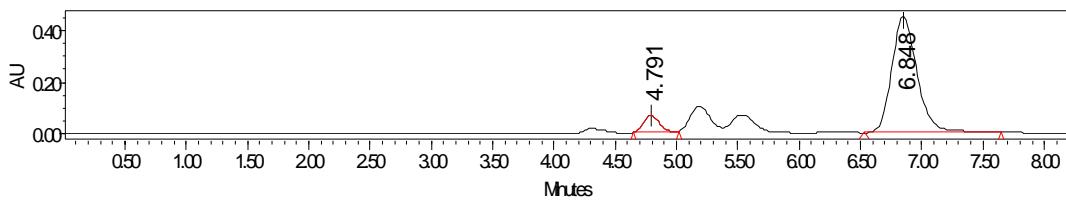
(R)-3-methyl-N¹,N⁶-diphenylhexanediamide 17:



84% yield, 84% ee. The ee was determined by HPLC analysis using a chiralcel AD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, 254 nm), t_r(major) = 6.85 min, t_r(minor) = 4.79 min. ¹H NMR (400 MHz, DMSO): δ = 9.87 (w, 2H), 7.59 (dd, *J* = 7.6, 4.0 Hz, 4H), 7.28 (t, *J* = 7.6 Hz, 4H), 7.02 (t, *J* = 7.2 Hz, 2H), 2.44–2.26 (m, 3H), 2.16 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.04–1.93 (m, 1H), 1.78–1.66 (m, 1H), 1.53–1.44 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, DMSO) δ = 171.22, 170.50, 139.30, 139.22, 128.60, 122.97, 122.91, 119.09, 119.01, 43.88, 34.23, 32.01, 30.03, 19.23 ppm.



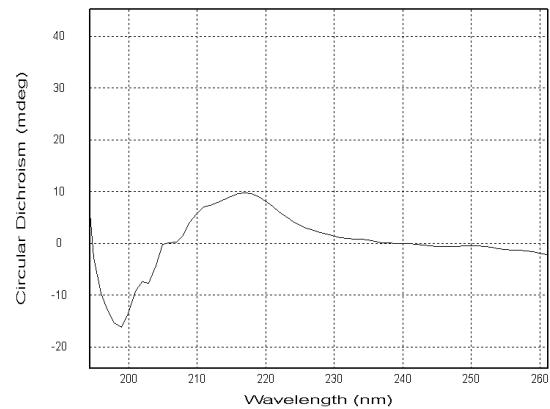
	Retention Time	% Area
1	4.802	49.91
2	6.853	50.09



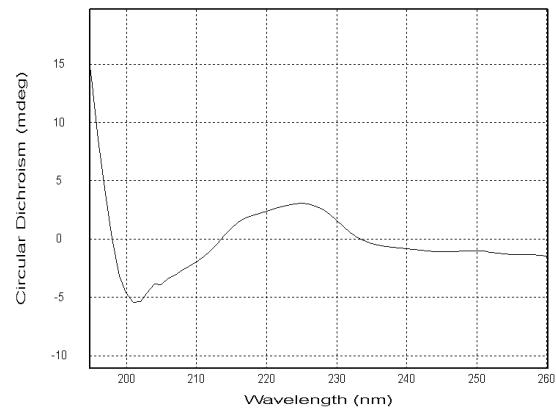
	Retention Time	% Area
1	4.791	8.17
2	6.848	91.83

11. CD spectra:

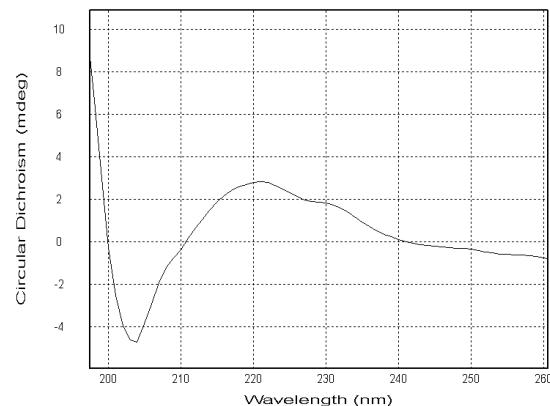
a. CD spectra for the unreacted ketones 7a-f in methanol, (S)-7a is an authentic sample
(S)-7a:



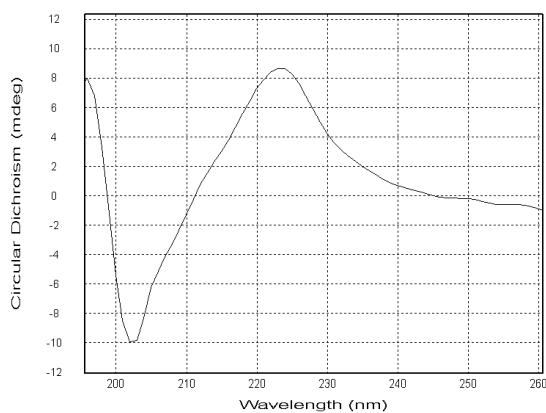
(S)-7b:



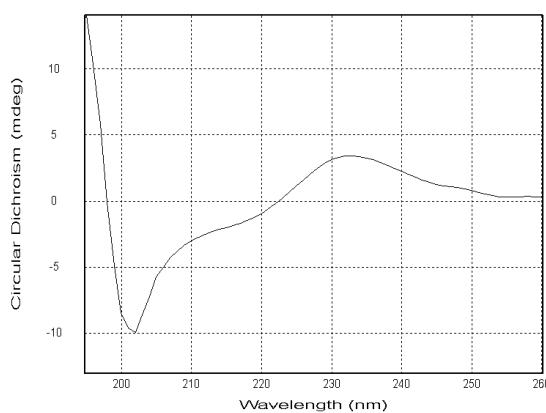
(S)-7c:



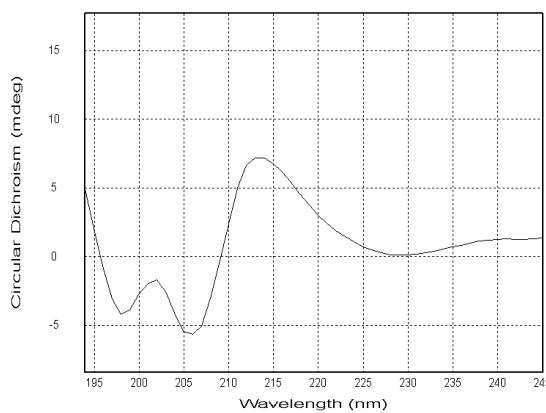
(S)-7d:



(S)-7e:

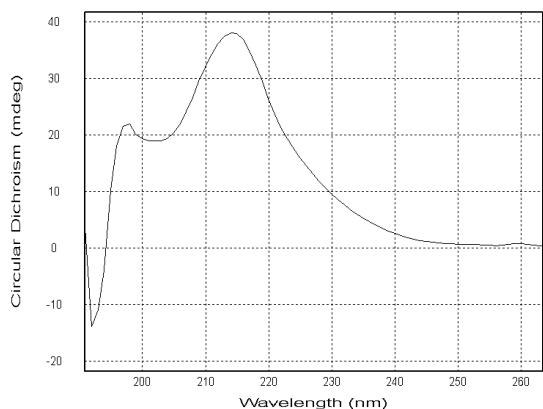


(S)-7f:

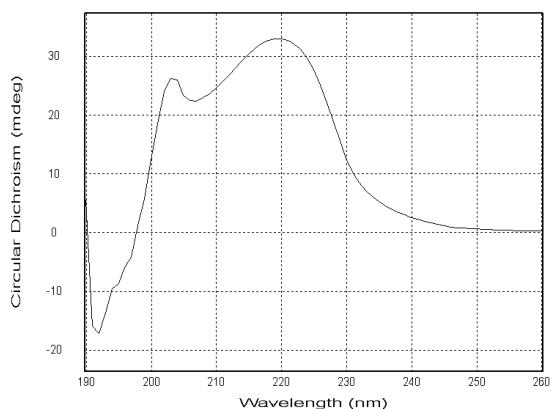


b. CD spectra for the abnormal lactones 8a-f in methanol, (R)-8c is an authentic sample

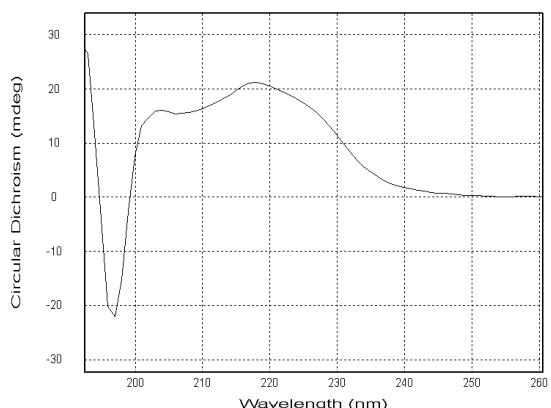
(R)-8a:



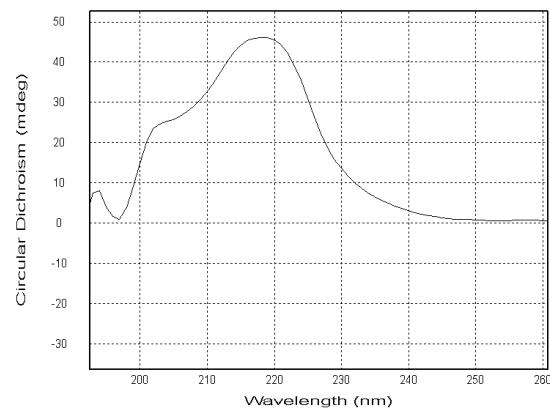
(R)-8b:



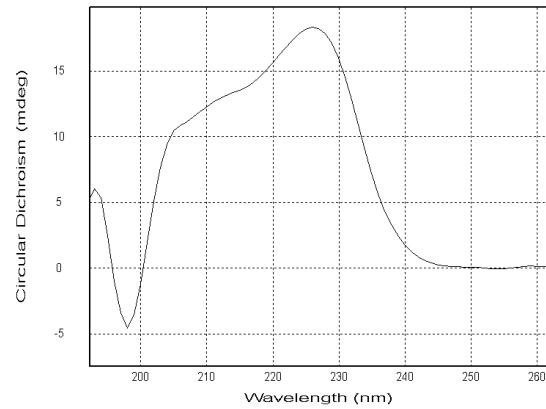
(R)-8c:



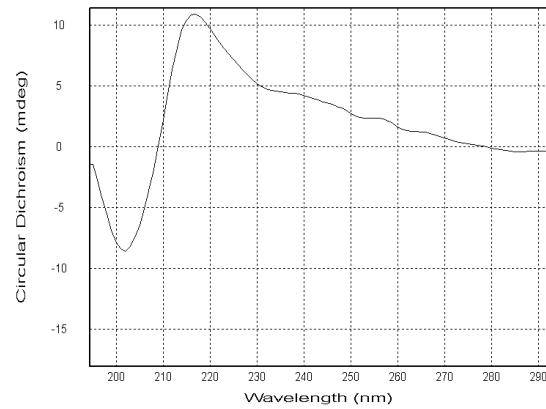
(R)-8d:



(R)-8e:



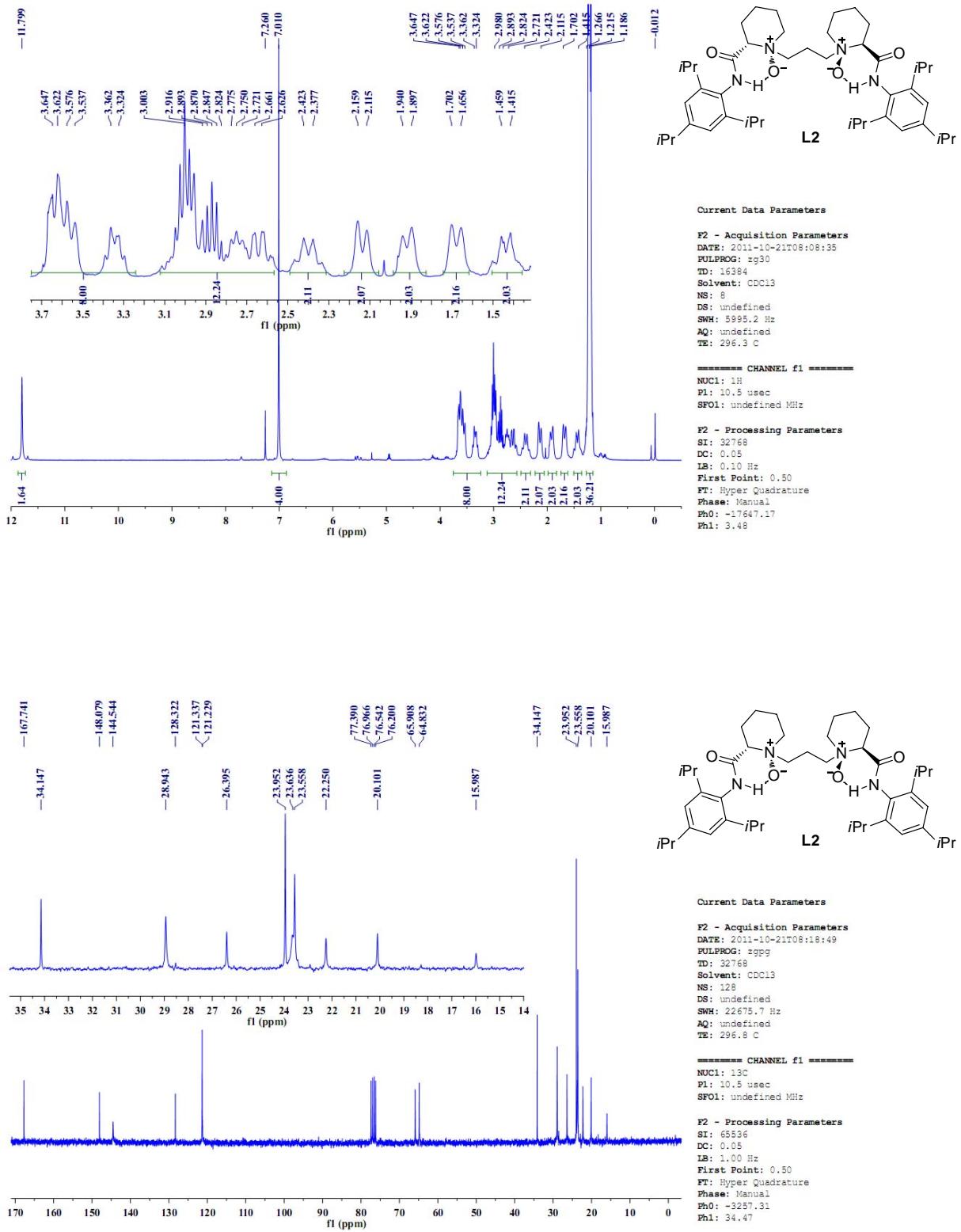
(R)-8f:

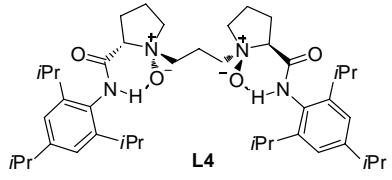
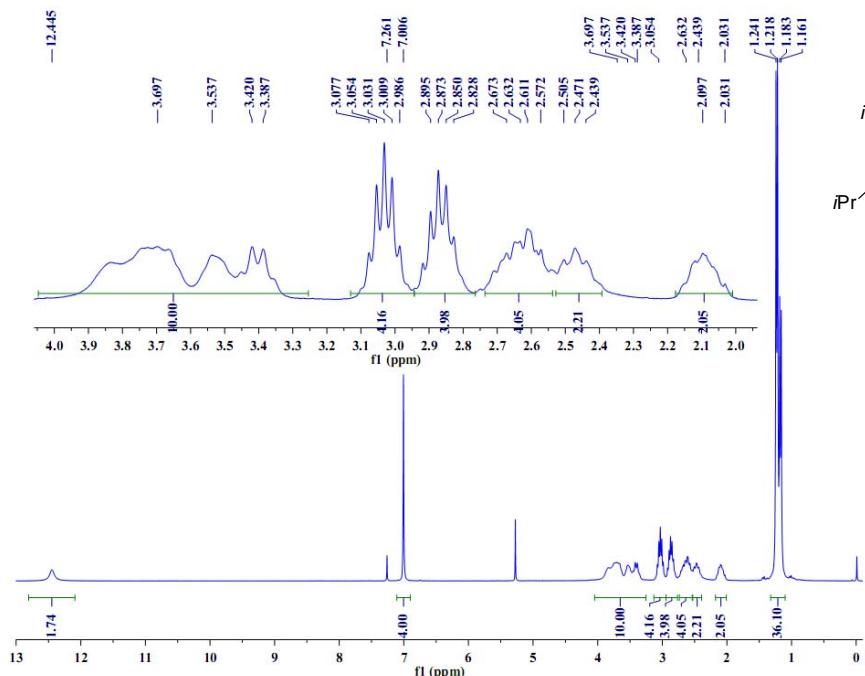


12. Reference:

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- [7] Xu, S.; Wang, Z.; Zhang, X.; Zhang, X. M.; Ding, K. *Angew. Chem. Int. Ed.* **2008**, 47, 2840.
- [8] Rudroff, F.; Rydz, J.; Ogink, F. H.; Fink, M.; Mihovilovic, M. D. *Adv. Synth. Catal.* **2007**, 349, 1436.
- [9] Berti, G.; Macchia, B.; Macchia, F.; Monti, L. *J. Chem. Soc. C* **1971**, 3371.

13. Copy of ^1H NMR and ^{13}C NMR spectra for the ligands:



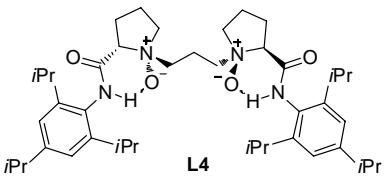
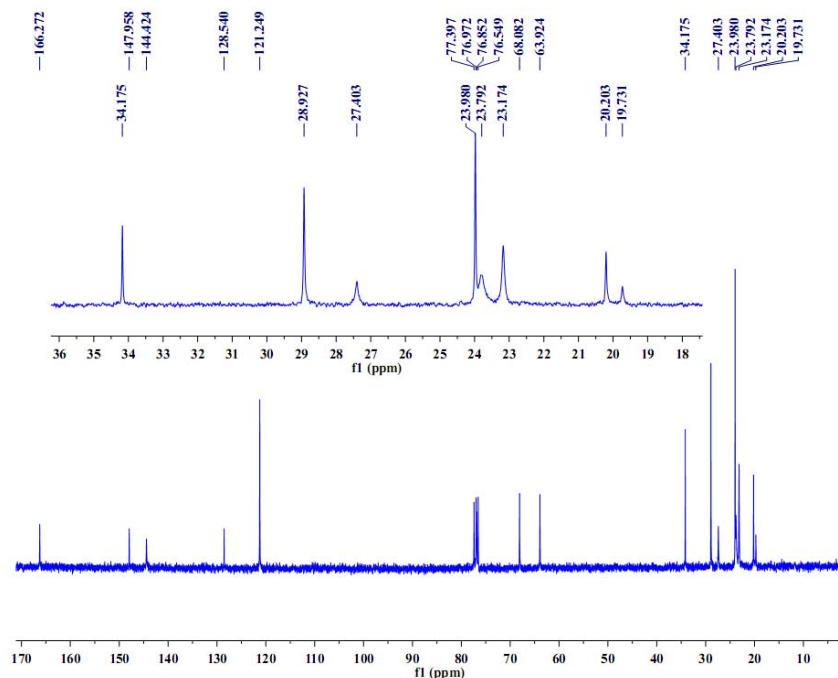


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-10-21T07:52:55
PULPROG: zg30
TD: 16384
Solvent: CDCl3
NS: 8
DS: undefined
SWH: 5995.2 Hz
AQ: undefined
TE: 296.2 C

===== CHANNEL f1 =====
NUC1: 1H
P1: 10.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 32768
DC: 0.05
LB: 0.10 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -17649.08
Ph1: 2.84



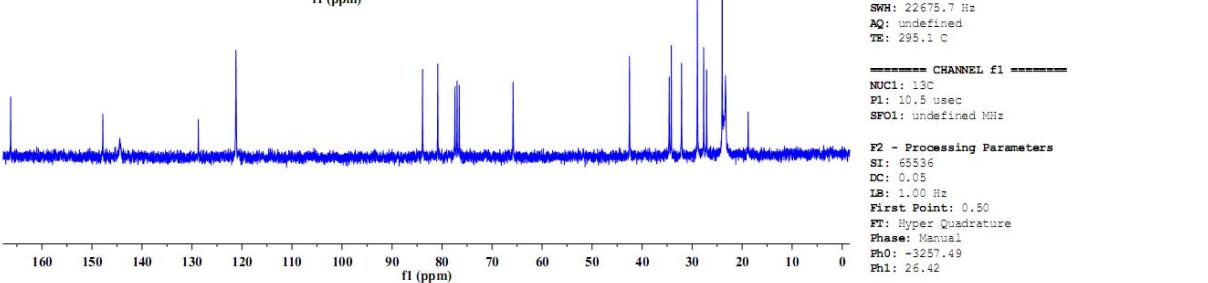
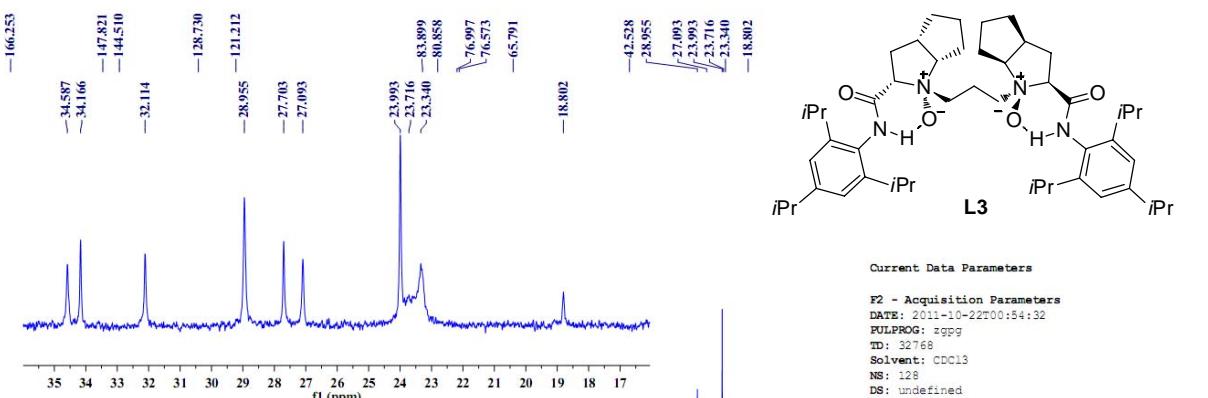
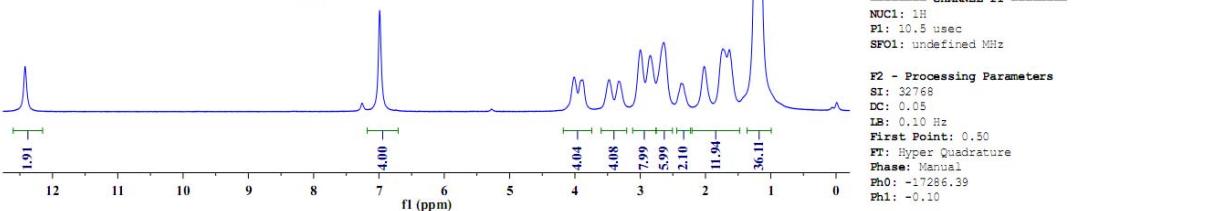
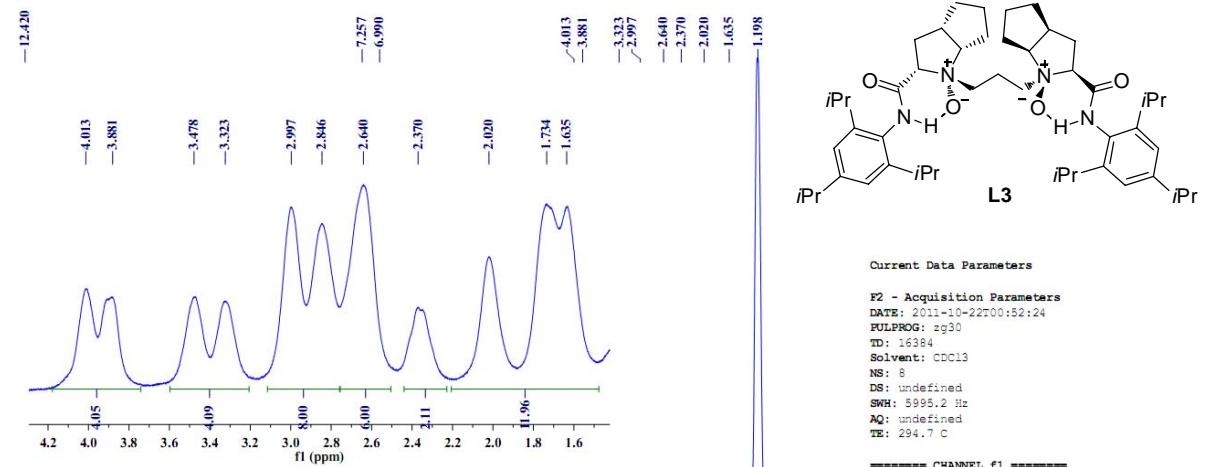
Current Data Parameters

P2 - Acquisition Parameters
DATE: 2011-10-21T08:02:55
FULPROG: zgpg
TD: 32768
Solvent: CDCl3
NS: 128
DS: undefined
SWH: 22675.7 Hz
AQ: undefined
TE: 296.7 C

===== CHANNEL f1 =====
NUC1: 13C
P1: 10.5 usec
SFO1: undefined MHz

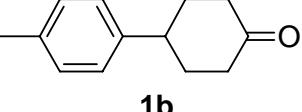
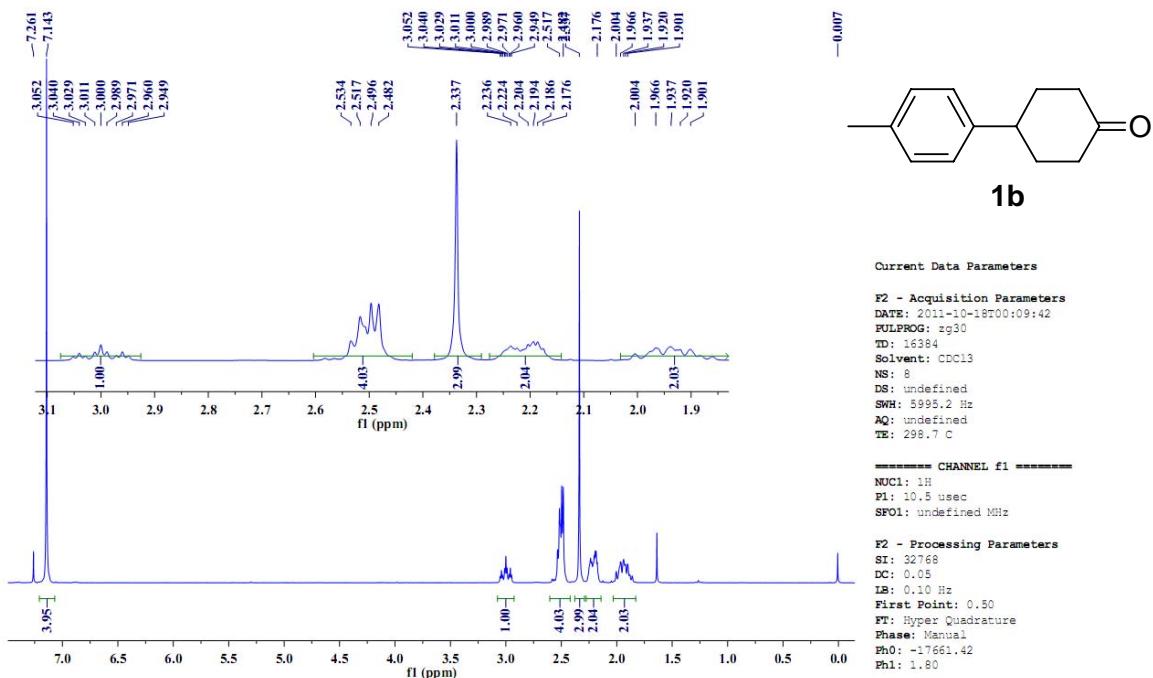
P2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -3253.19
Ph1: 24.24

¹³C NMR (75 MHz, CDCl₃) δ 166.27, 147.96, 144.43, 128.54, 121.25, 77.40, 76.97, 76.85, 76.55, 68.08, 63.92, 34.18, 28.93, 27.40, 23.98, 23.79, 23.17, 20.20, 19.73.



¹³C NMR (75 MHz, CDCl₃) δ 166.25, 147.82, 144.51, 128.73, 121.21, 83.90, 80.86, 77.42, 77.00, 76.57, 65.79, 42.53, 34.59, 34.17, 32.11, 28.96, 27.70, 27.09, 23.99, 23.72, 23.34, 18.80.

14. Copy of ^1H NMR and ^{13}C NMR spectra for the substrates:



1b

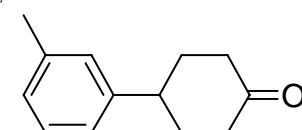
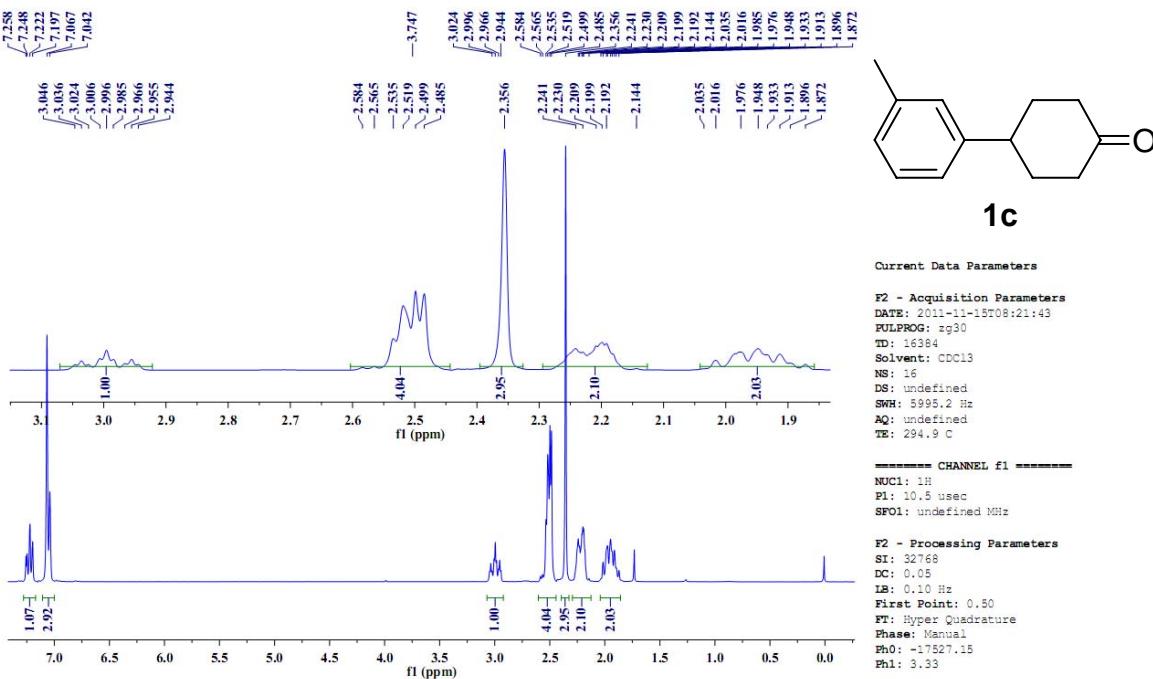
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-10-18T00:09:42
PULPROG: zg30
TD: 16384
Solvent: CDCl3
NS: 8
DS: undefined
SWH: 5995.2 Hz
AQ: undefined
TE: 298.7 C

===== CHANNEL f1 =====

P1: 10.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 32768
DC: 0.05
LB: 0.10 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -17661.42
Ph1: 1.80



1c

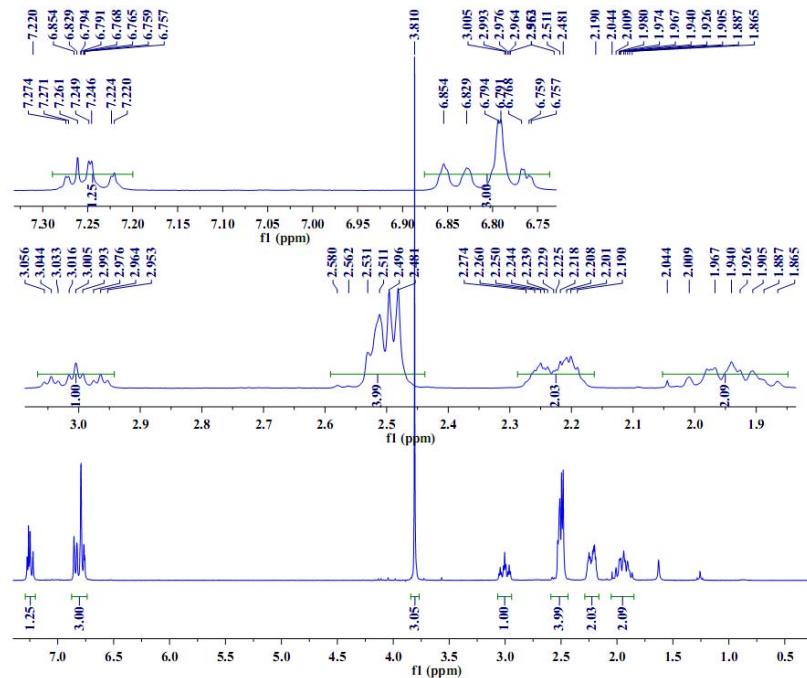
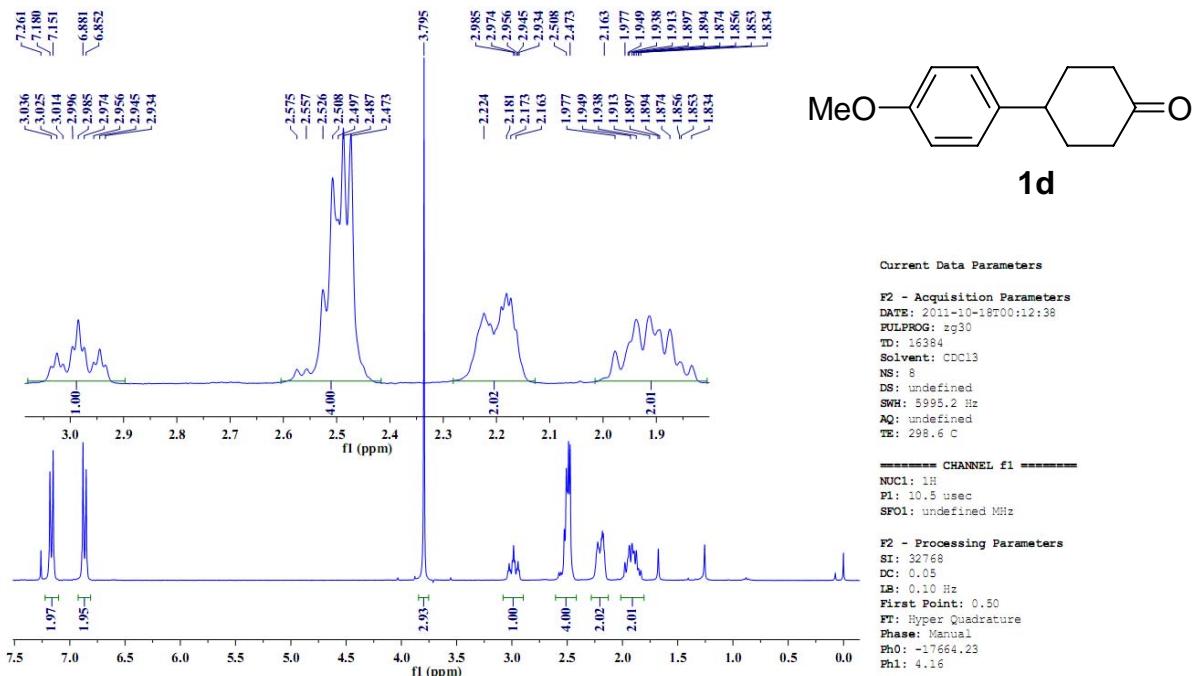
Current Data Parameters

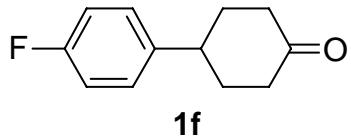
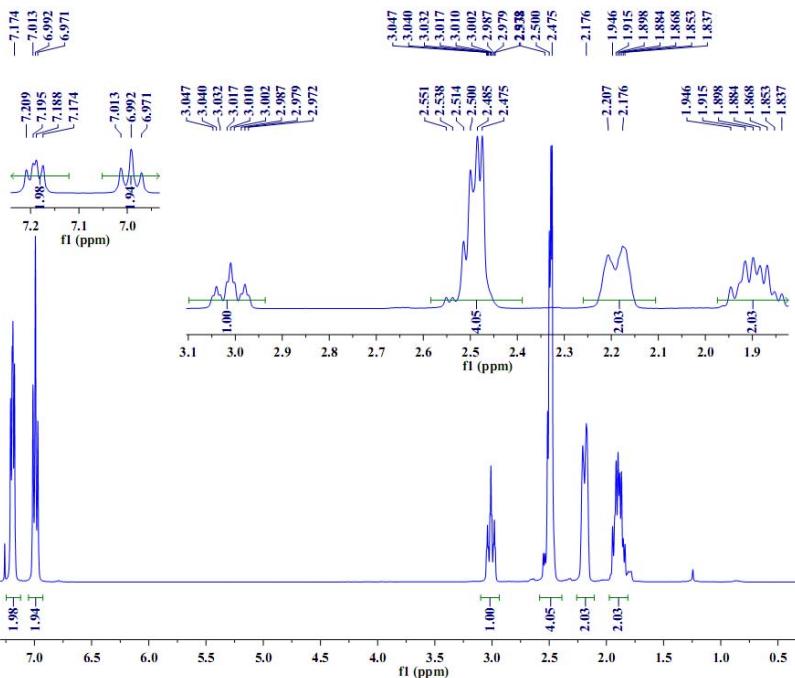
P2 - Acquisition Parameters
DATE: 2011-11-15T08:21:43
PULPROG: zg30
TD: 16384
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 5995.2 Hz
AQ: undefined
TP: 204.0 s

----- CHANNEL f1 -----

NUC1: 1H
P1: 10.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 32768
DC: 0.05
LB: 0.10 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -17527.15



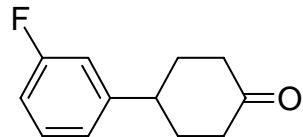
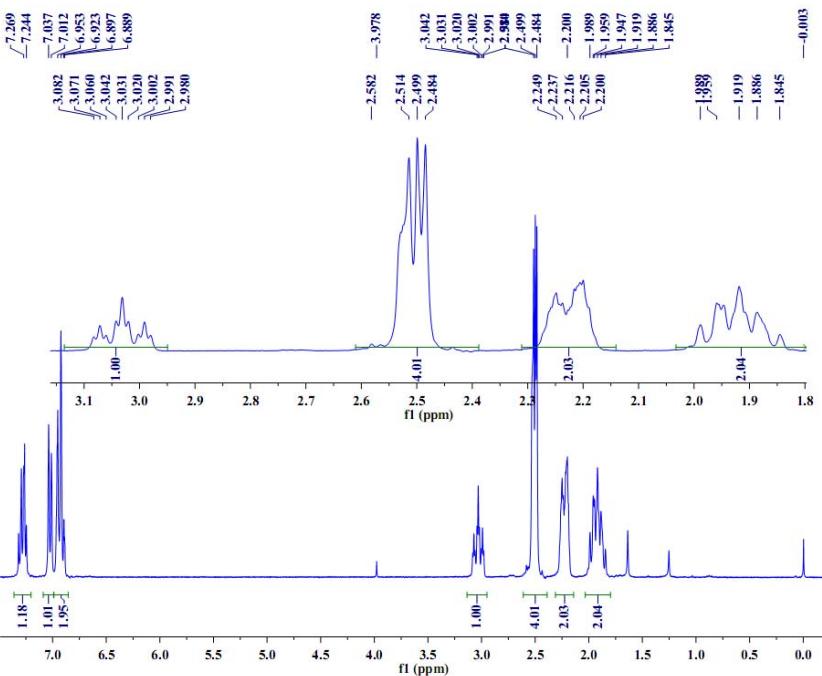


Current Data Parameters

F2 - Acquisition Parameters
 DATE: 2011-11-11T22:20:55
 PULPROG: zg30
 TD: 32768
 Solvent: CDCl3
 NS: 16
 DS: undefined
 SWH: 8223.7 Hz
 AQ: undefined
 TE: 295.7 C

===== CHANNEL f1 ======
 NUC1: 1H
 PI: 13.3 used
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 65536
 DC: 0.05
 LB: 0.60 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: -210.64
 Ph1: 24.32

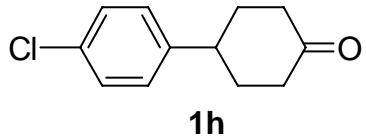
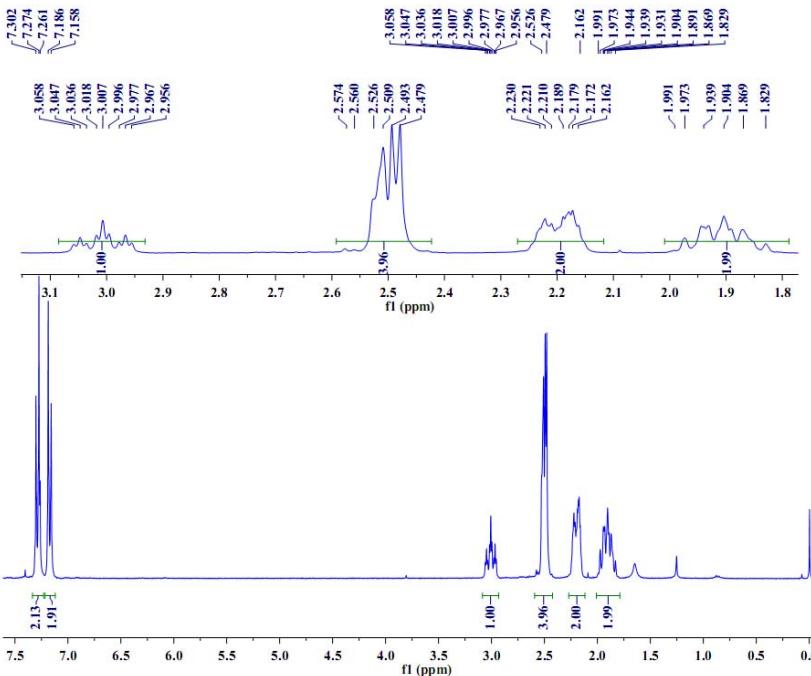


Current Data Parameters

F2 - Acquisition Parameters
 DATE: 2011-10-18T00:15:00
 PULPROG: zg30
 TD: 16384
 Solvent: CDCl3
 NS: 8
 DS: undefined
 SWH: 5995.2 Hz
 AQ: undefined
 TE: 298.4 C

===== CHANNEL f1 ======
 NUC1: 1H
 PI: 10.5 used
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 32768
 DC: 0.05
 LB: 0.10 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: -17664.51
 Ph1: 4.64

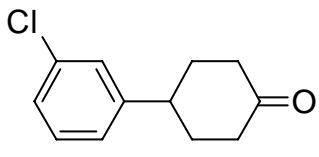
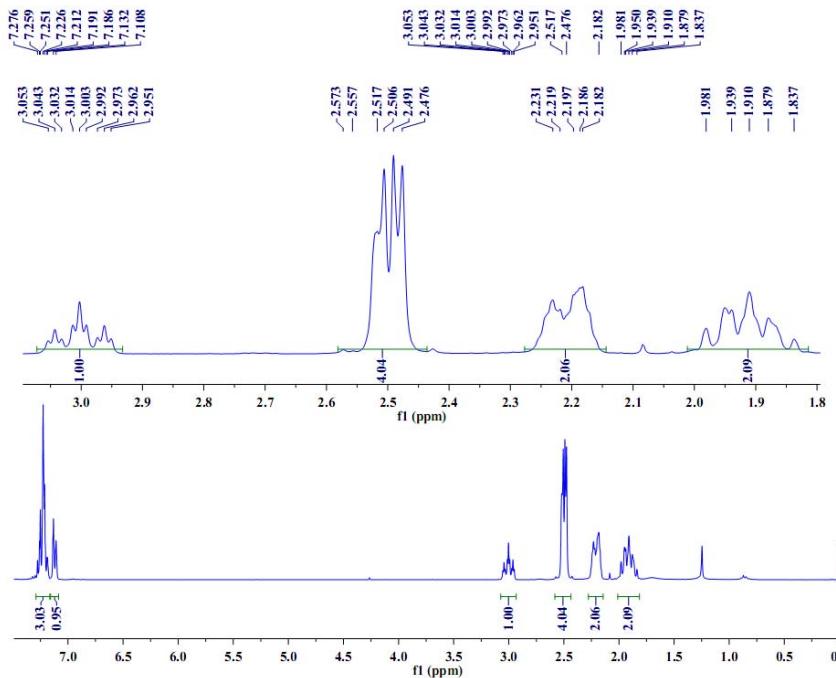


Current Data Parameters

F2 - Acquisition Parameters
 DATE: 2011-10-18T00:17:33
 PULPROG: zg30
 TD: 16384
 Solvent: CDCl3
 NS: 8
 DS: undefined
 SWH: 5995.2 Hz
 AQ: undefined
 TE: 298.4 °C

===== CHANNEL f1 ======
 NUC1: 1H
 PI: 10.5 usec
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 32768
 DC: 0.05
 LB: 0.10 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: -17663.31
 Ph1: 4.66

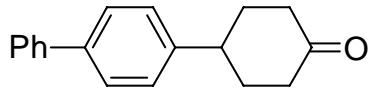
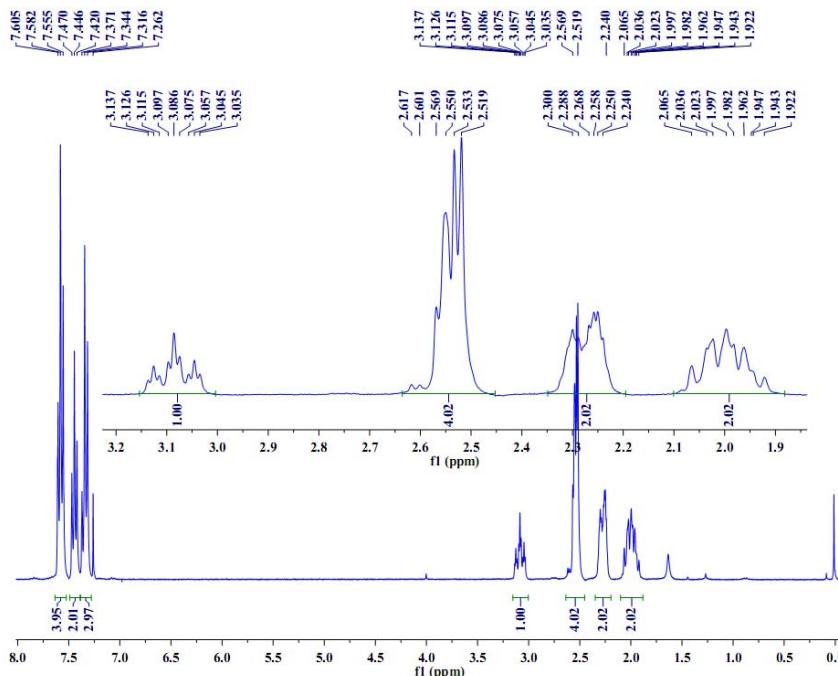


Current Data Parameters

F2 - Acquisition Parameters
 DATE: 2011-11-15T08:24:11
 PULPROG: zg30
 TD: 16384
 Solvent: CDCl3
 NS: 16
 DS: undefined
 SWH: 5995.2 Hz
 AQ: undefined
 TE: 295 °C

===== CHANNEL f1 ======
 NUC1: 1H
 PI: 10.5 usec
 SFO1: undefined MHz

F2 - Processing Parameters
 SI: 32768
 DC: 0.05
 LB: 0.10 Hz
 First Point: 0.50
 FT: Hyper Quadrature
 Phase: Manual
 Ph0: -17525.84
 Ph1: 1.12



1 j

Current Data Parameters

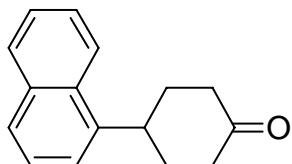
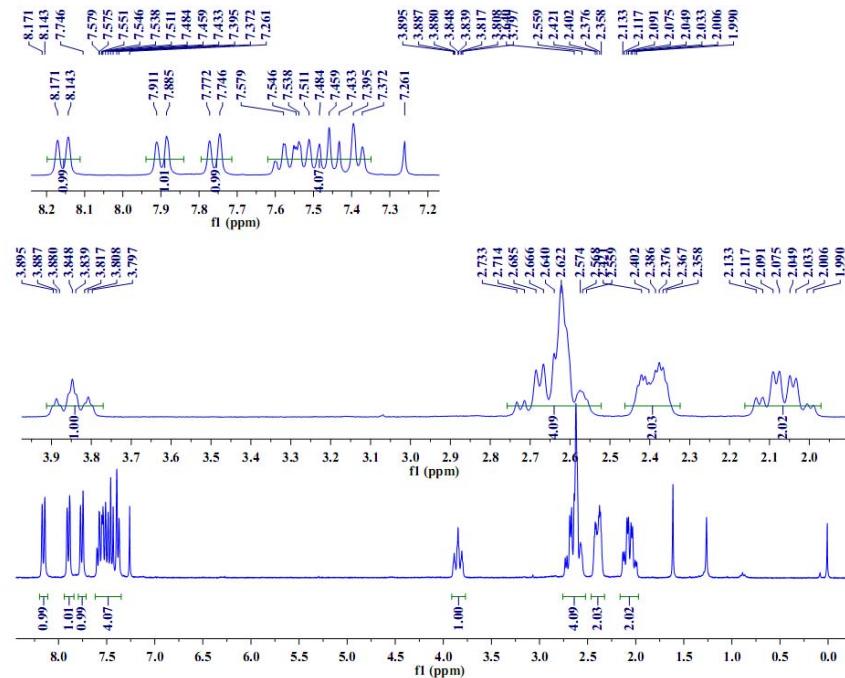
F2 - Acquisition Parameters
DATE: 2011-10-18T00:21:43
PULPROG: zg30
TD: 16384
Solvent: CDCl3
NS: 8
DS: undefined
SWH: 5995.2 Hz
AQ: undefined
TE: 298.2 C

----- CHANNEL f1 -----

NUC1: 1H
P1: 10.5 usec
SFO1: undefined MHz

F2 - Processing Parameters

SI: 32768
DC: 0.05
LB: 0.10 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -17665.77
Ph1: 5.89



1k

Current Data Parameters

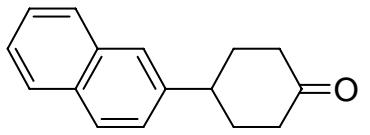
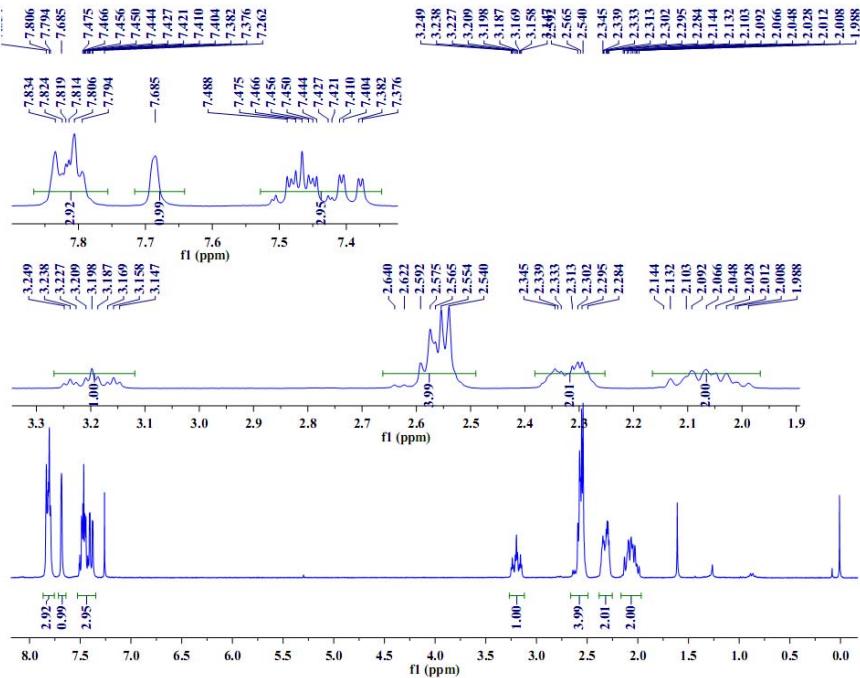
F2 - Acquisition Parameters
DATE: 2011-10-18T00:24:25
PULPROG: zg30
TD: 16384
Solvent: CDCl3
NS: 8
DS: undefined
SWH: 5995.2 Hz
AQ: undefined
TEC:

----- CHANNEL f1 -----

NUC1: 1H
P1: 10.5 usec
SEQ1: undefined MHz

F2 - Processing Parameters

SI: 32768
DC: 0.05
LB: 0.10 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -17665.86



11

Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-10-18T00:26:19
FULPROG: zg30
TD: 16384
Solvent: CDCl3
NS: 8
DS: undefined
SWH: 5995.2 Hz
AQ: undefined
TE: 298 C

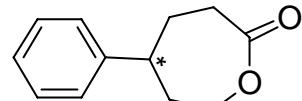
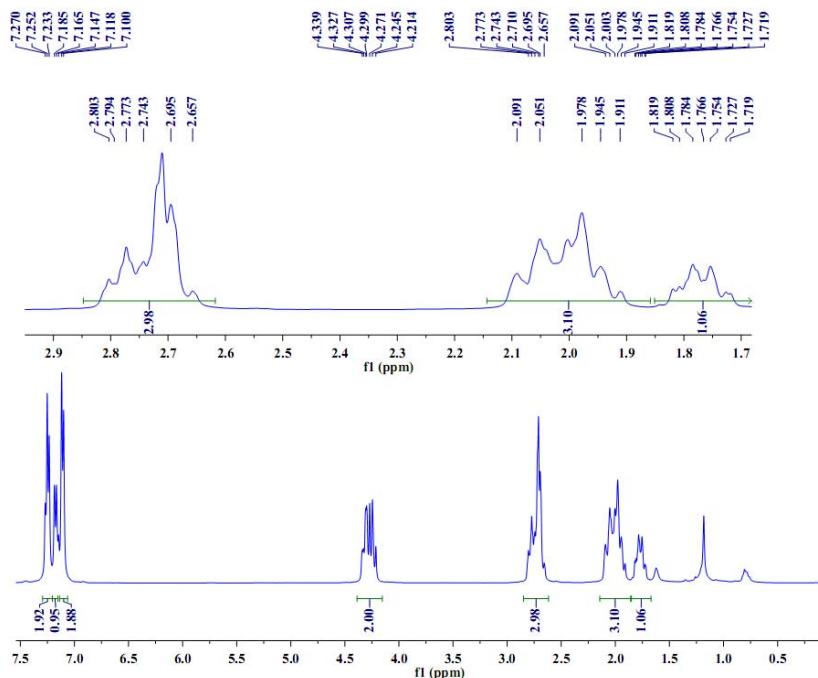
----- CHANNEL f1 -----

NUC1: 1H
P1: 10.5 usec
SFO1: undefined MHz

F2 - Processing Parameters

SI: 32768
DC: 0.05
LB: 0.10 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -17665.94
Ph1: 6.44

15. Copy of ^1H NMR and ^{13}C NMR spectra for the products:



2a

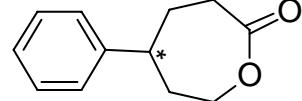
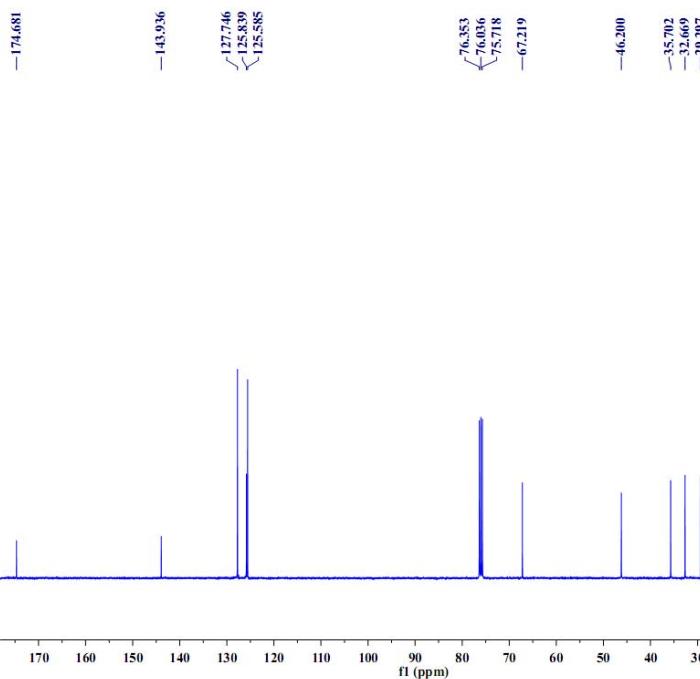
Current Data Parameters

F1 - Acquisition Parameters
DATE: 2012-03-05T10:48:26
PULPROG: zg30
TD: 32768
Solvent: CDCl₃
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 294.7 C

===== CHANNEL f1 =====

NUC1: 1H
PI: 9.93 used
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 80.48
Ph1: 17.70



2a

Current Data Parameters

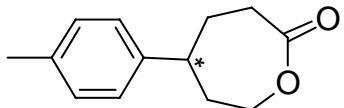
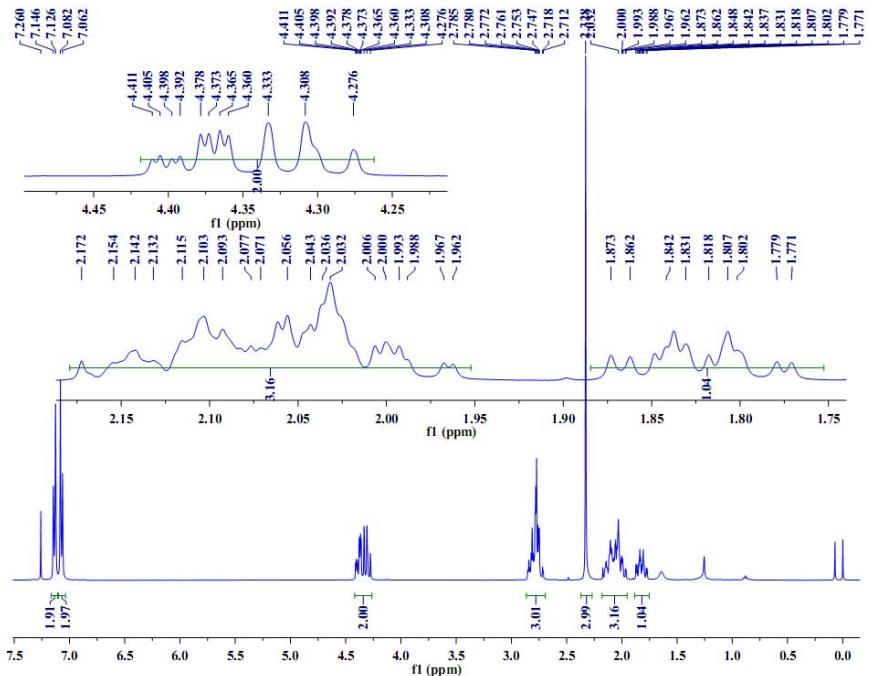
F2 - Acquisition Parameters
DATE: 2012-03-05T13:38:16
PULPROG: zgpg30
TD: 32768
Solvent: CDCl₃
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 295.3 C

===== CHANNEL f1 =====

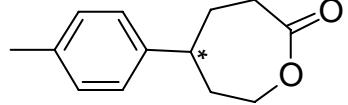
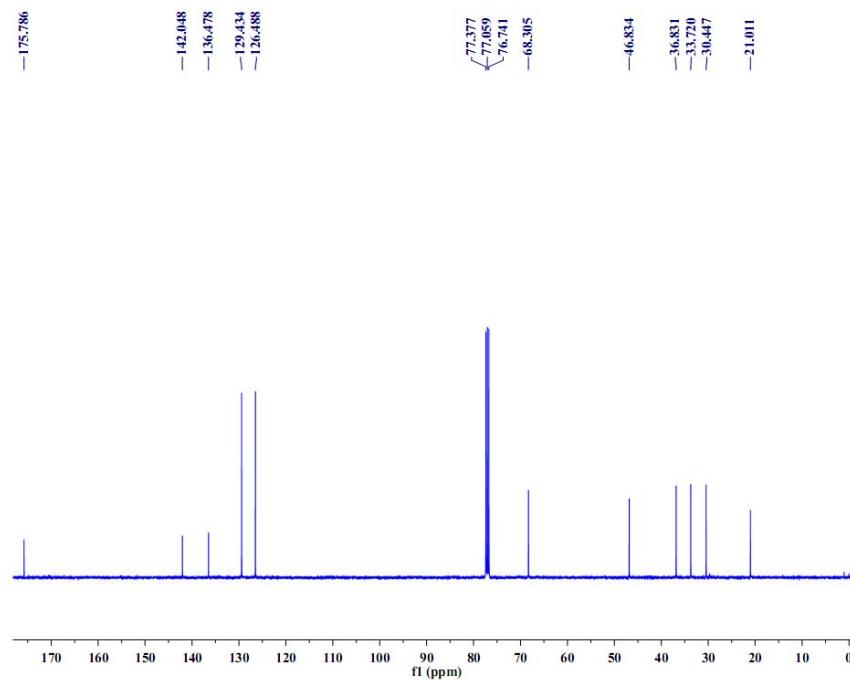
NUC1: 13C
PI: 9.63 used
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -57.05
Ph1: 43.68

^{13}C NMR (101 MHz, CDCl₃) δ 174.68, 143.94, 127.75, 125.84, 125.59, 76.35, 76.04, 75.72, 67.22, 46.20, 35.70, 32.67, 29.30.

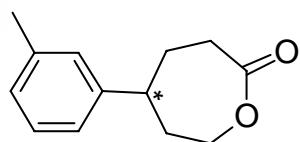
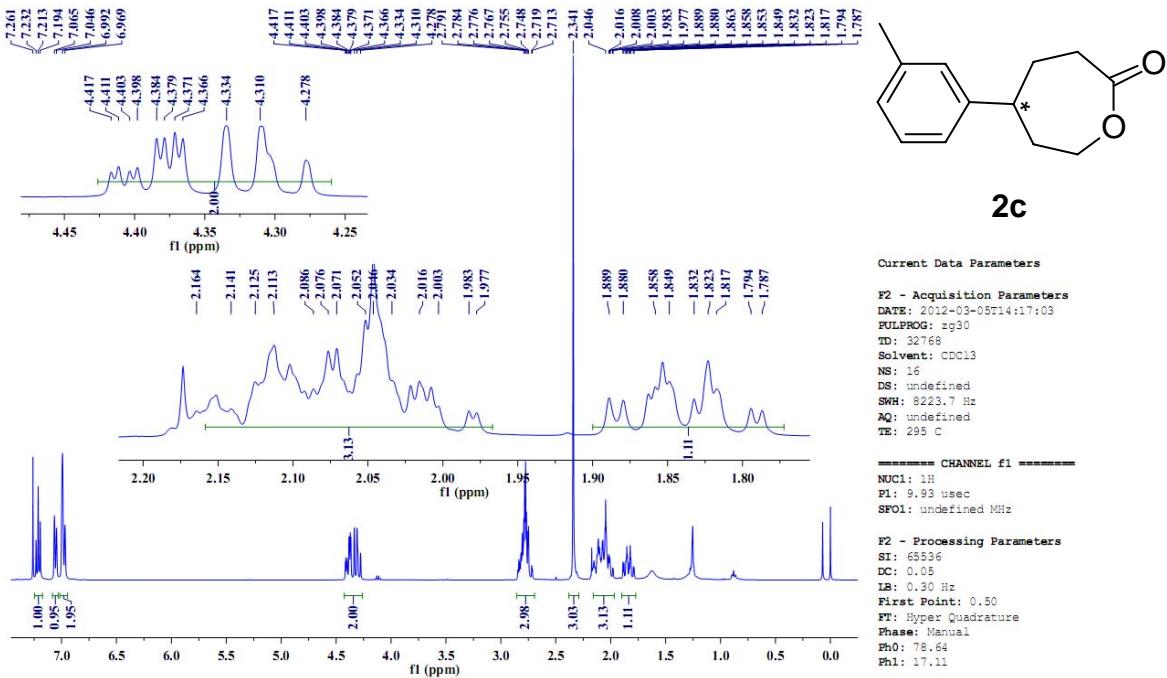


2b



2b

¹³C NMR (101 MHz, CDCl₃) δ 175.79, 142.05, 136.48, 129.43, 126.49, 77.38, 77.06, 76.74, 68.31, 46.83, 36.83, 33.72, 30.45, 21.01.



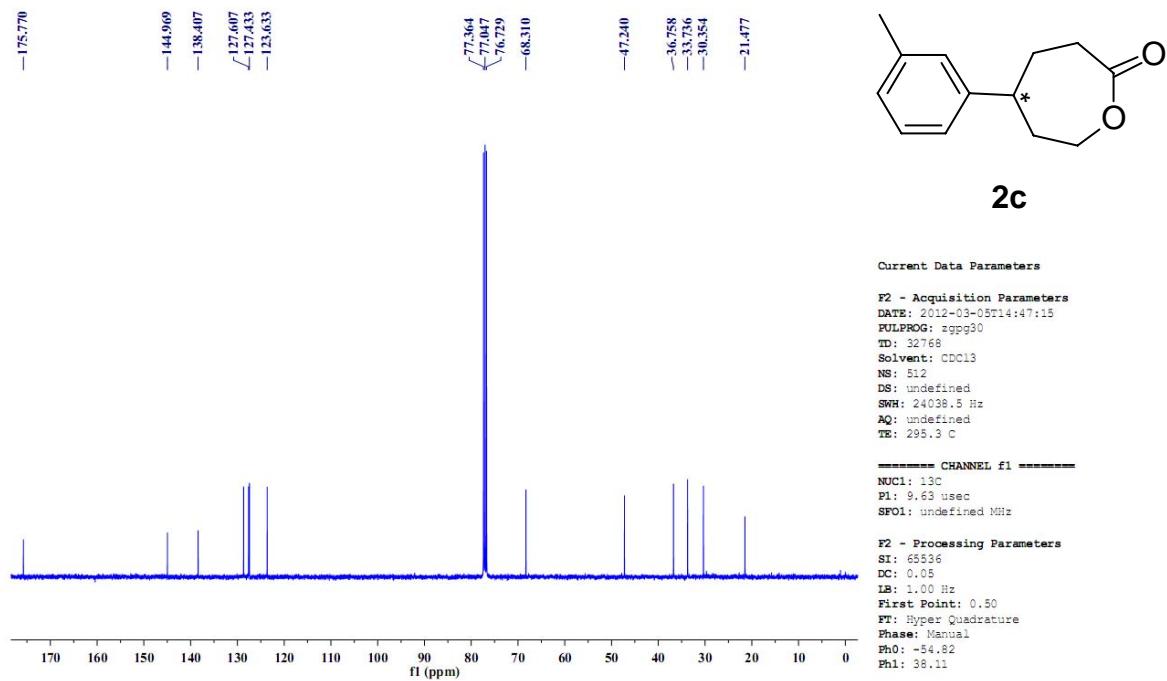
2c

Current Data Parameters

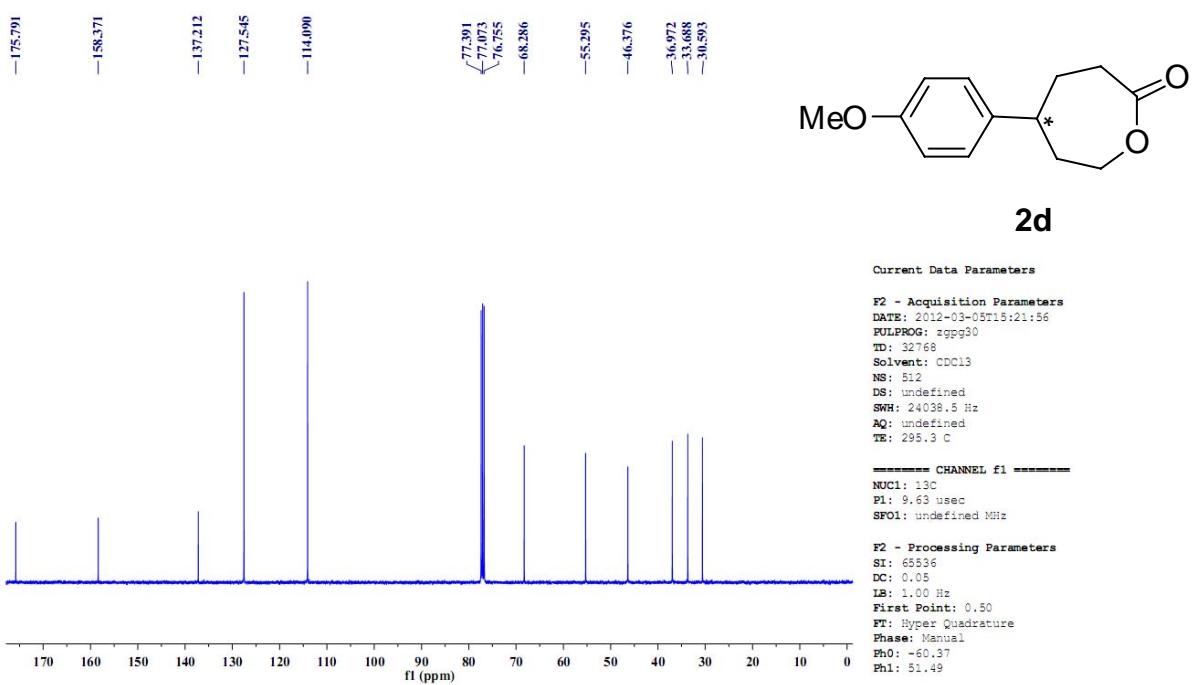
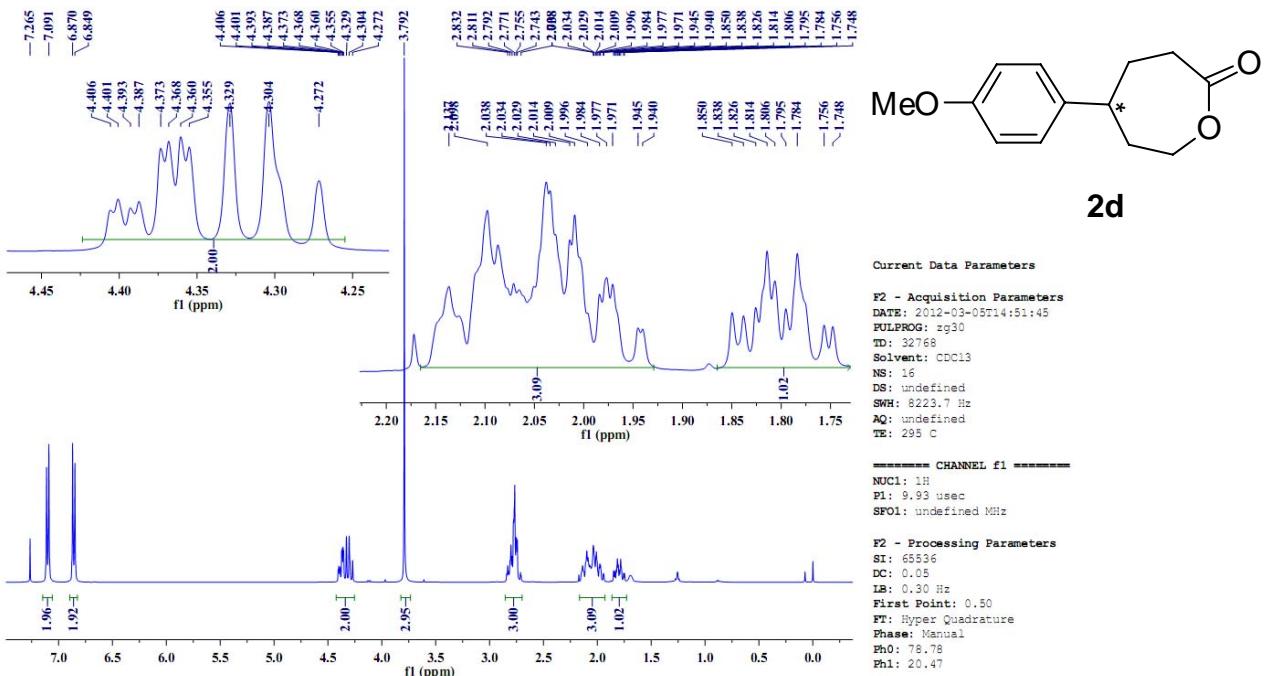
F2 - Acquisition Parameters
DATE: 2012-03-05T14:17:03
FUPROG: zg30
TD: 32768
Solvent: CDQ13
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295 C

===== CHANNEL f1 =====
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

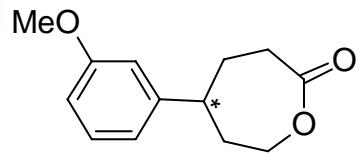
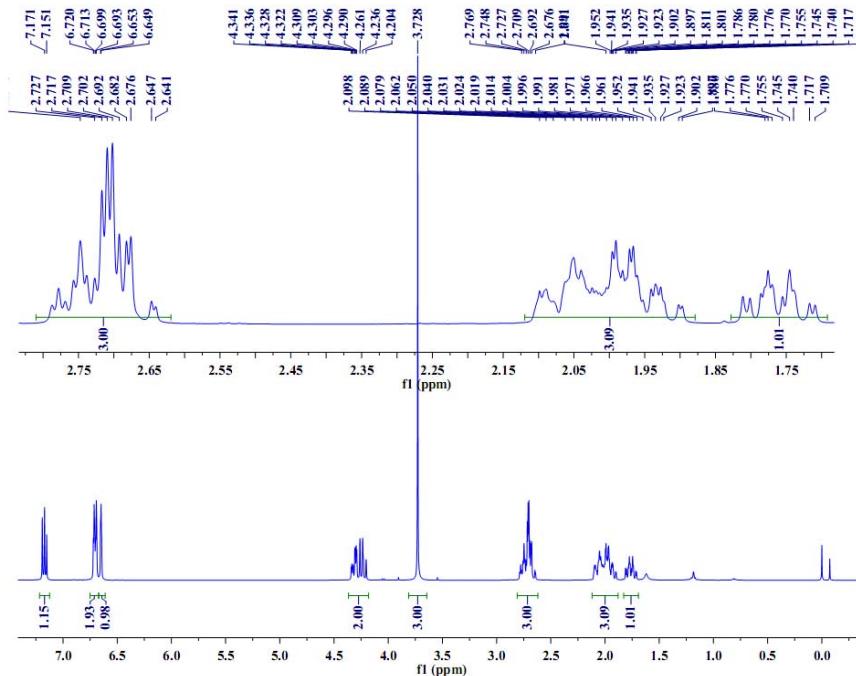
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 78.64
Ph1: 17.11



¹³C NMR (101 MHz, CDCl₃) δ 175.77, 144.97, 138.41, 128.68, 127.61, 127.43, 123.63, 77.36, 77.05, 76.73, 68.31, 47.24, 36.76, 33.74, 30.35, 21.48.



¹³C NMR (101 MHz, CDCl₃) δ 175.79, 158.37, 137.21, 127.55, 114.09, 77.39, 77.07, 76.76, 68.29, 55.30, 46.38, 36.97, 33.69, 30.59.



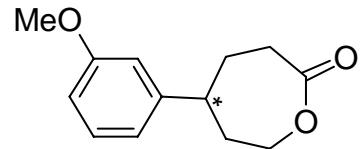
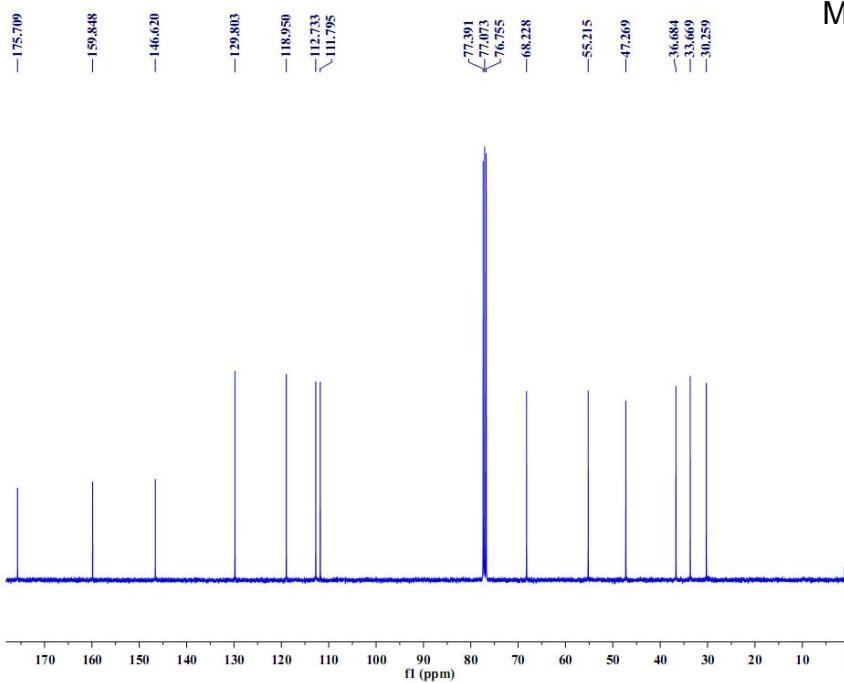
2e

Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-03-05T15:27:40
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 294.9 °C

===== CHANNEL f1 =====
NUC1: 1H
PL: 9.93 used
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 80.32
Ph1: 18.86



2e

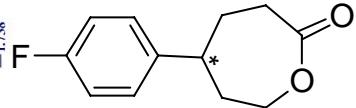
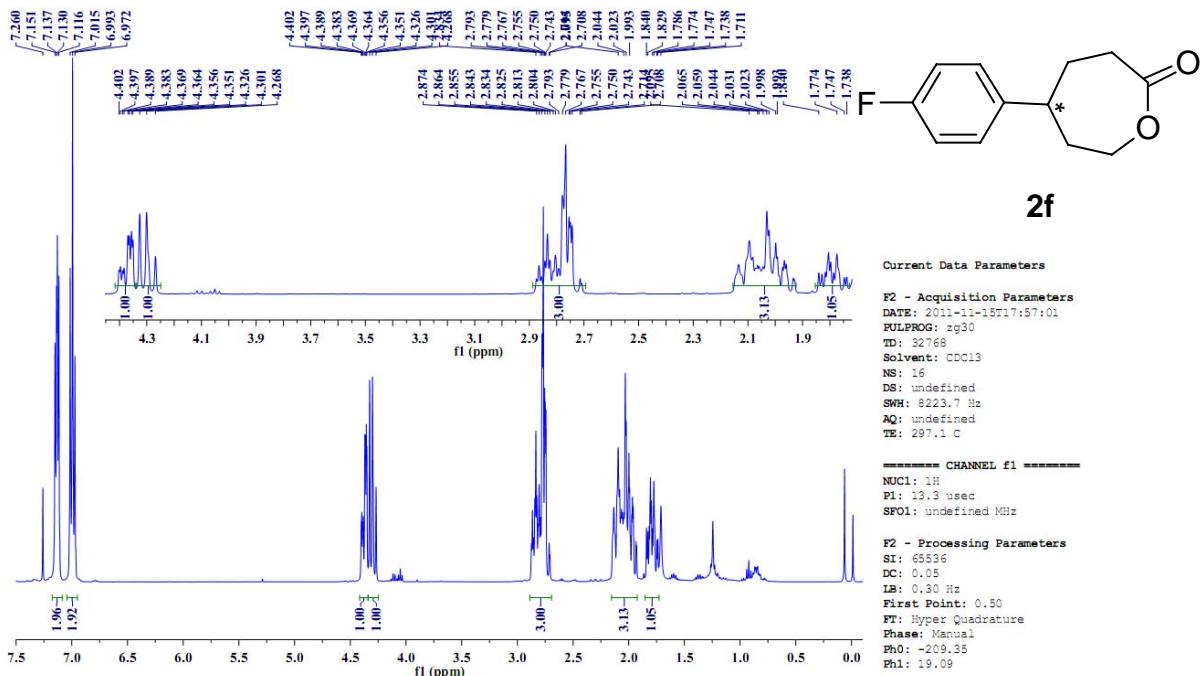
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-03-05T15:57:51
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 295.3 °C

===== CHANNEL f1 =====
NUC1: 13C
PL: 9.63 used
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -66.96
Ph1: 61.61

¹³C NMR (101 MHz, CDCl₃) δ 175.71, 159.85, 146.62, 129.80, 118.95, 112.73, 111.79, 77.39, 77.07, 76.76, 68.23, 55.22, 47.27, 36.68, 33.67, 30.26.



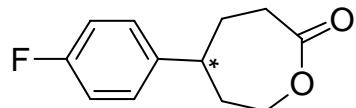
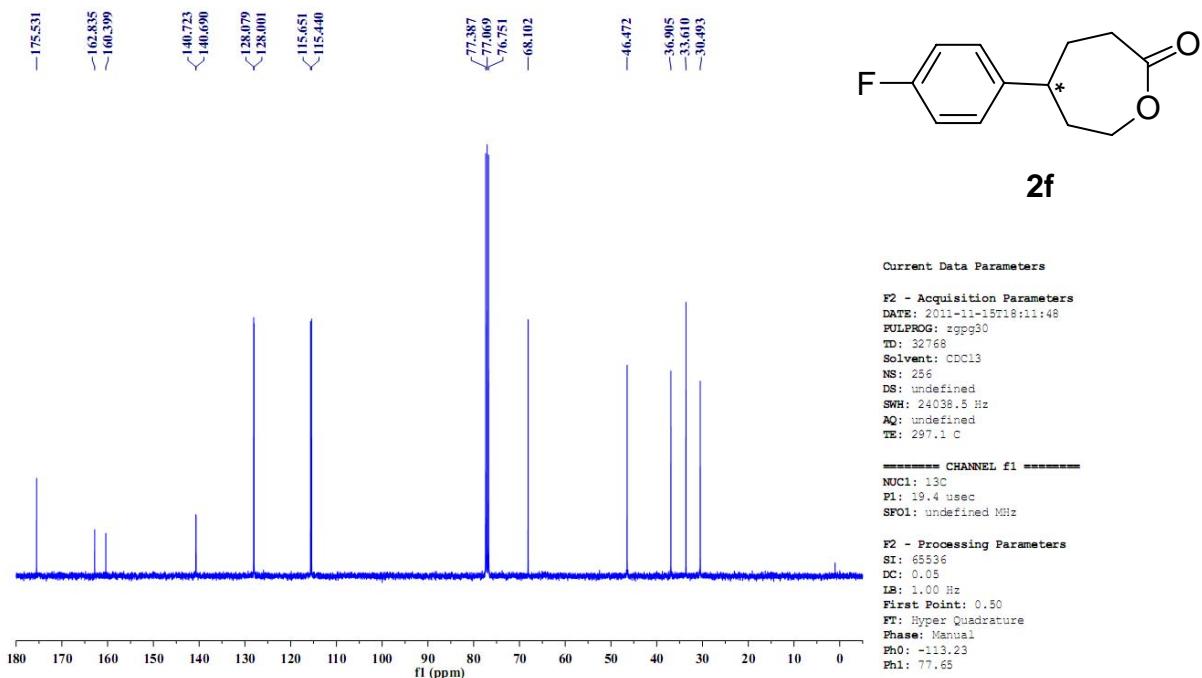
2f

Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-11-15T17:57:01
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 297.1 C

===== CHANNEL f1 =====
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -209.35
Ph1: 19.09



2f

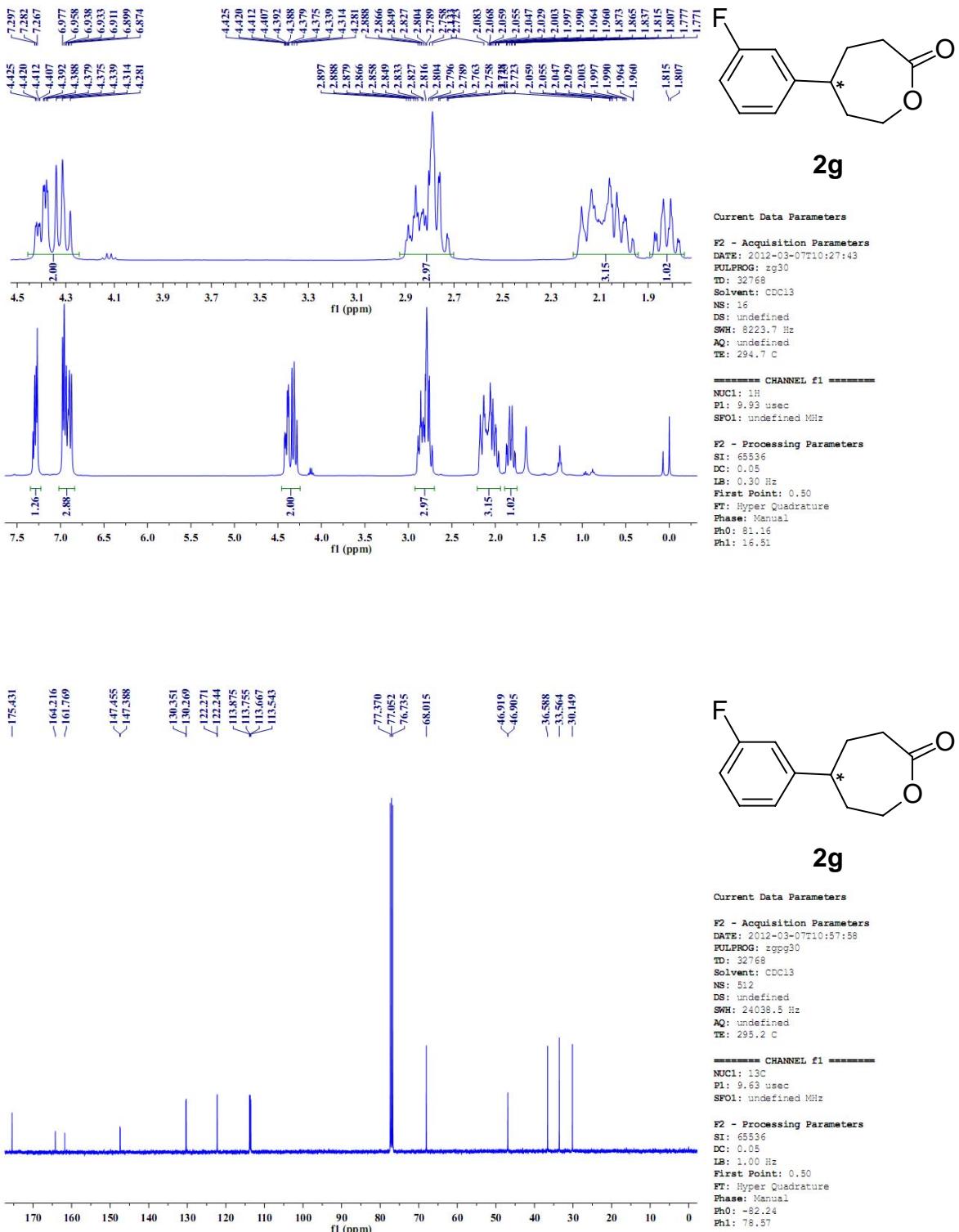
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-11-15T18:11:48
FULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297.1 ms

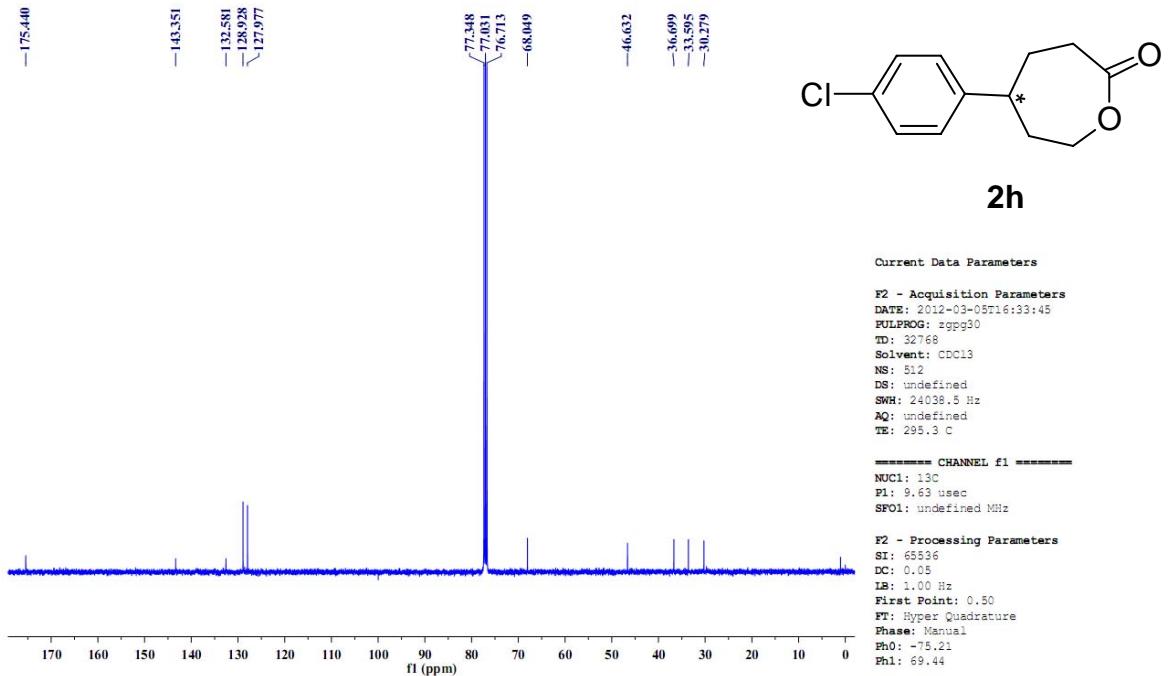
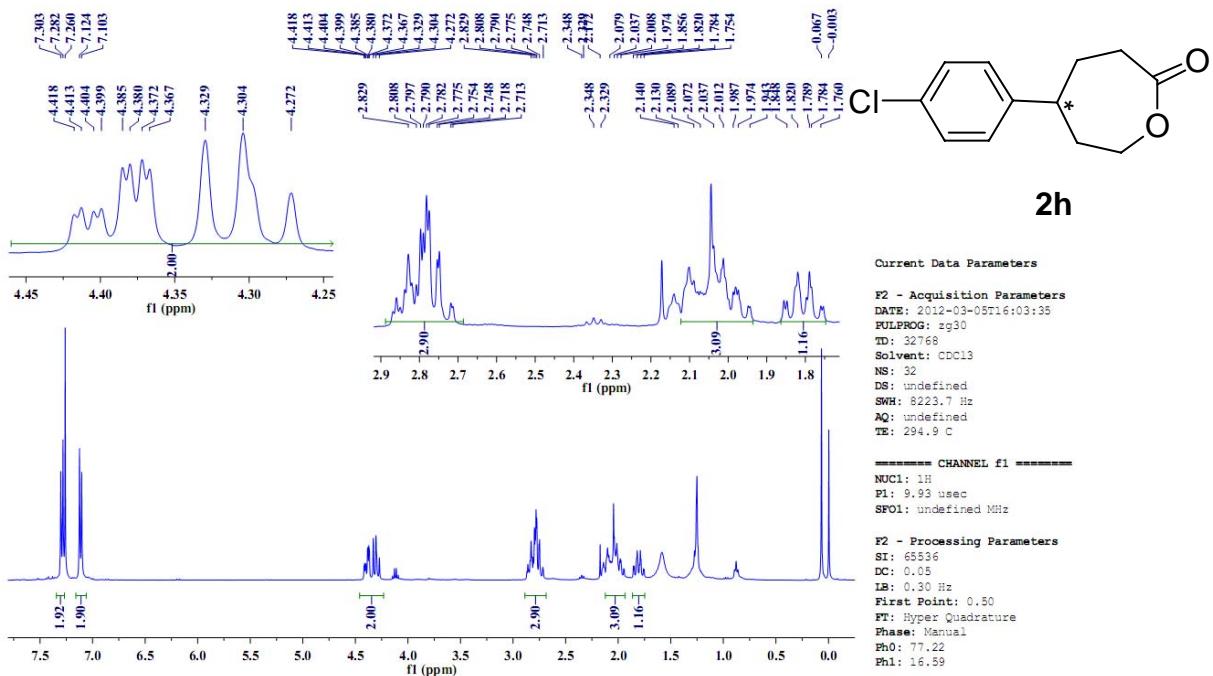
===== CHANNEL f1 =====
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -113.23
Ph1: 77.65

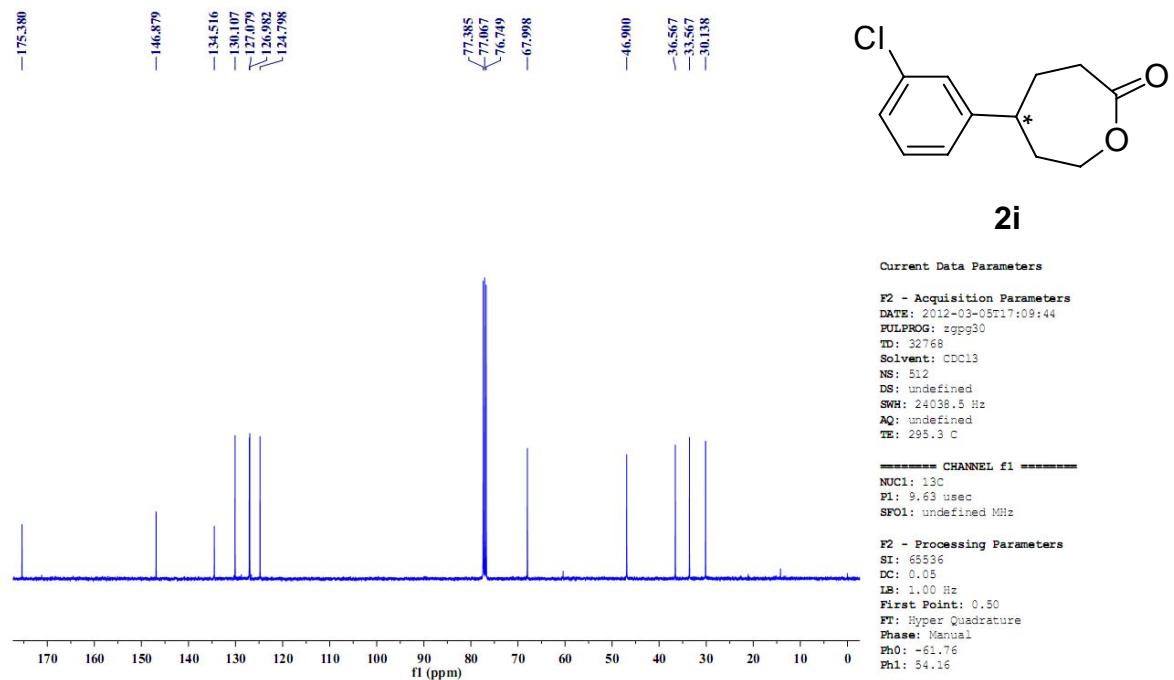
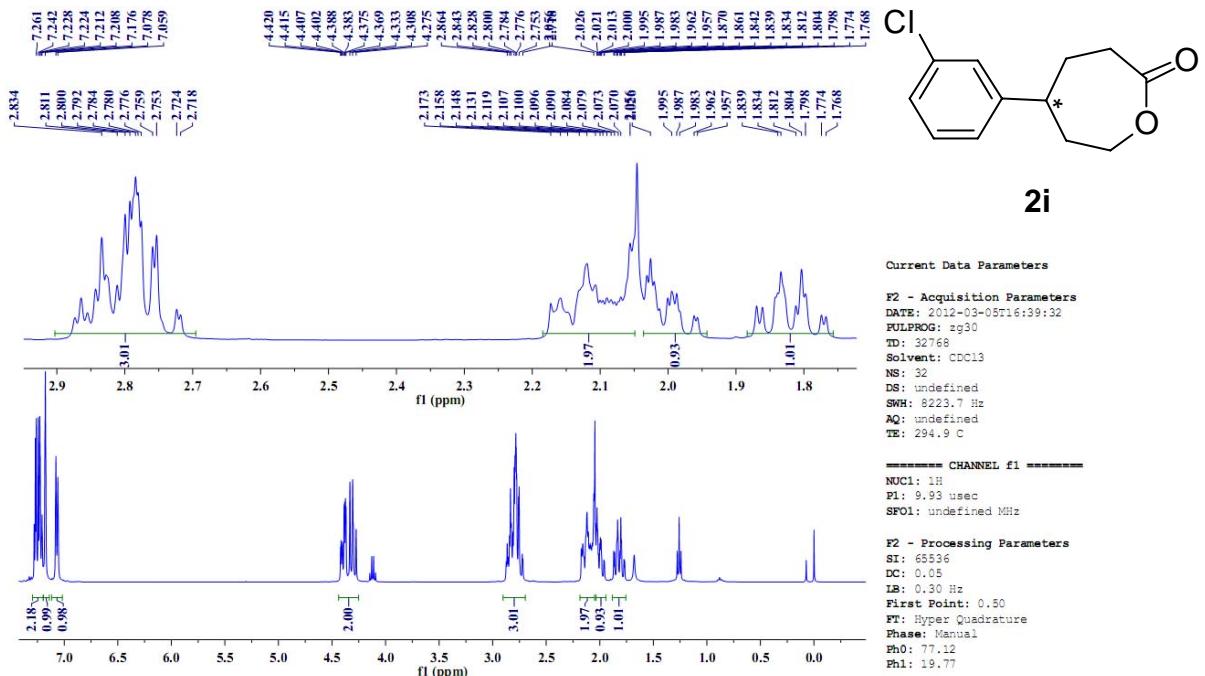
¹³C NMR (101 MHz, CDCl₃) δ 175.53, 162.83, 160.40, 140.72, 140.69, 128.08, 128.00, 115.65, 115.44, 77.39, 77.07, 76.75, 68.10, 46.47, 36.91, 33.61, 30.49.



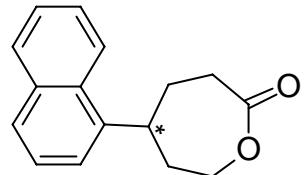
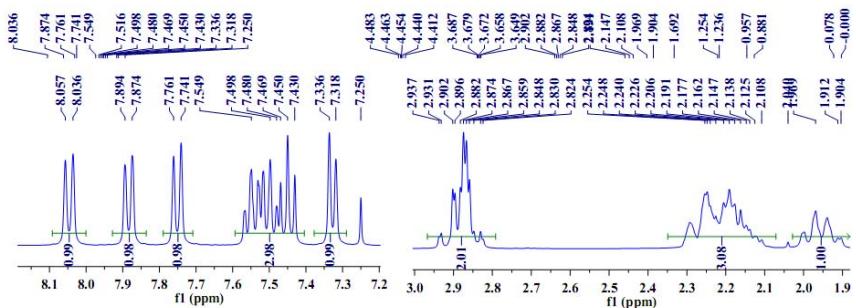
¹³C NMR (101 MHz, CDCl₃) δ 175.43, 164.22, 161.77, 147.46, 147.39, 130.35, 130.27, 122.27, 122.24, 113.88, 113.76, 113.67, 113.54, 77.37, 77.05, 76.73, 68.02, 46.92, 46.91, 36.59, 33.56, 30.15.



¹³C NMR (101 MHz, CDCl₃) δ 175.44, 143.35, 132.58, 128.93, 127.98, 77.35, 77.03, 76.71, 68.05, 46.63, 36.70, 33.60, 30.28.



¹³C NMR (101 MHz, CDCl₃) δ 175.38, 146.88, 134.52, 130.11, 127.08, 126.98, 124.80, 77.38, 77.07, 76.75, 68.00, 46.90, 36.57, 33.57, 30.14.



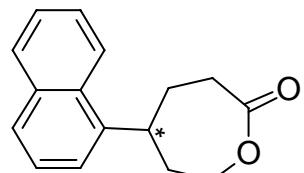
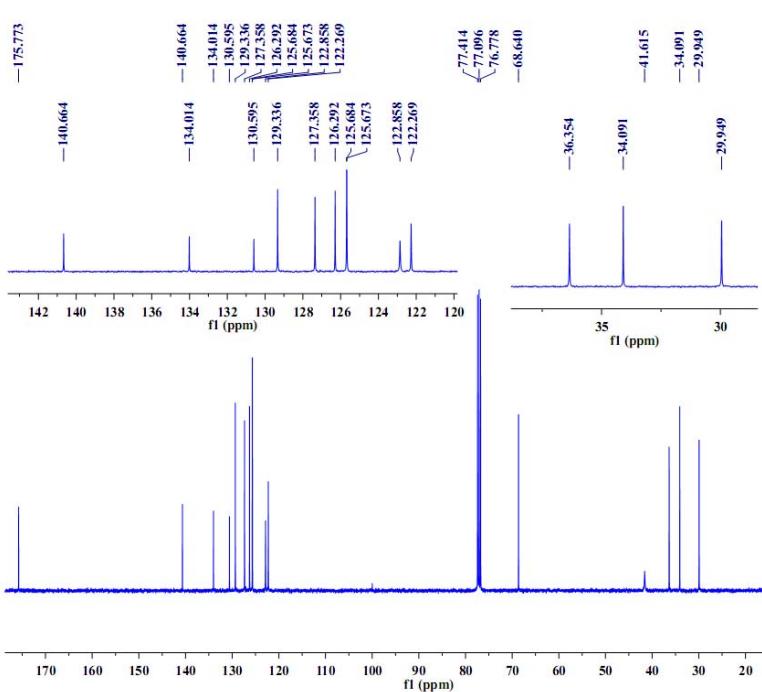
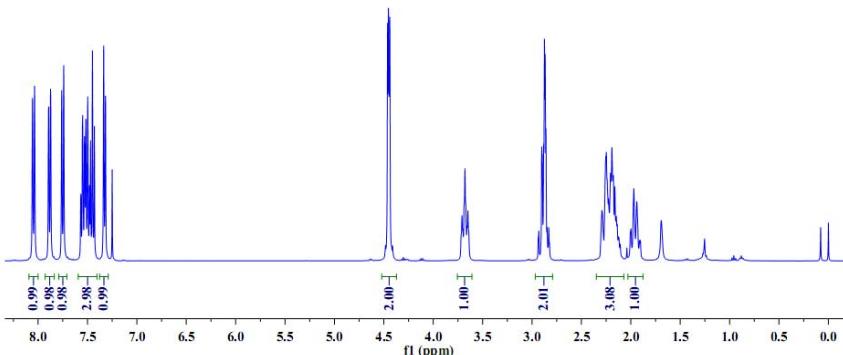
2k

Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-03-07T11:37:16
PULPROG: zg30
TD: 32768
SOLVENT: CDCl₃
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 294.9 °C

===== CHANNEL f1 =====
NUC1: 1H
PL: 9.93 used
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 79.92
Ph1: 21.00



2k

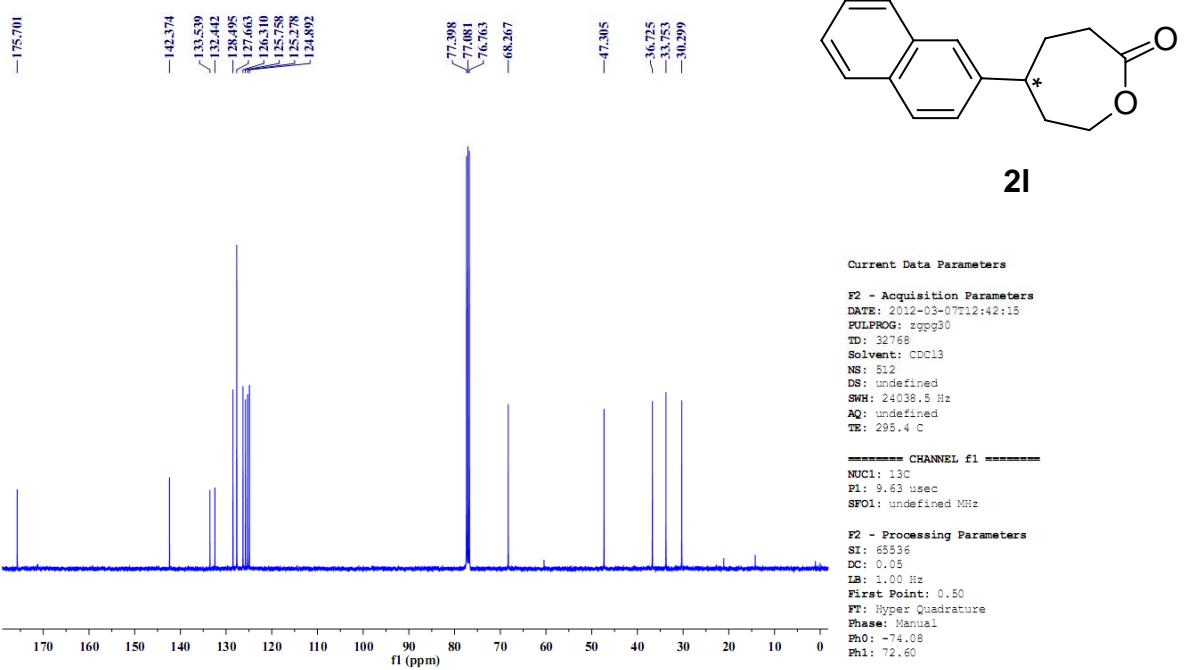
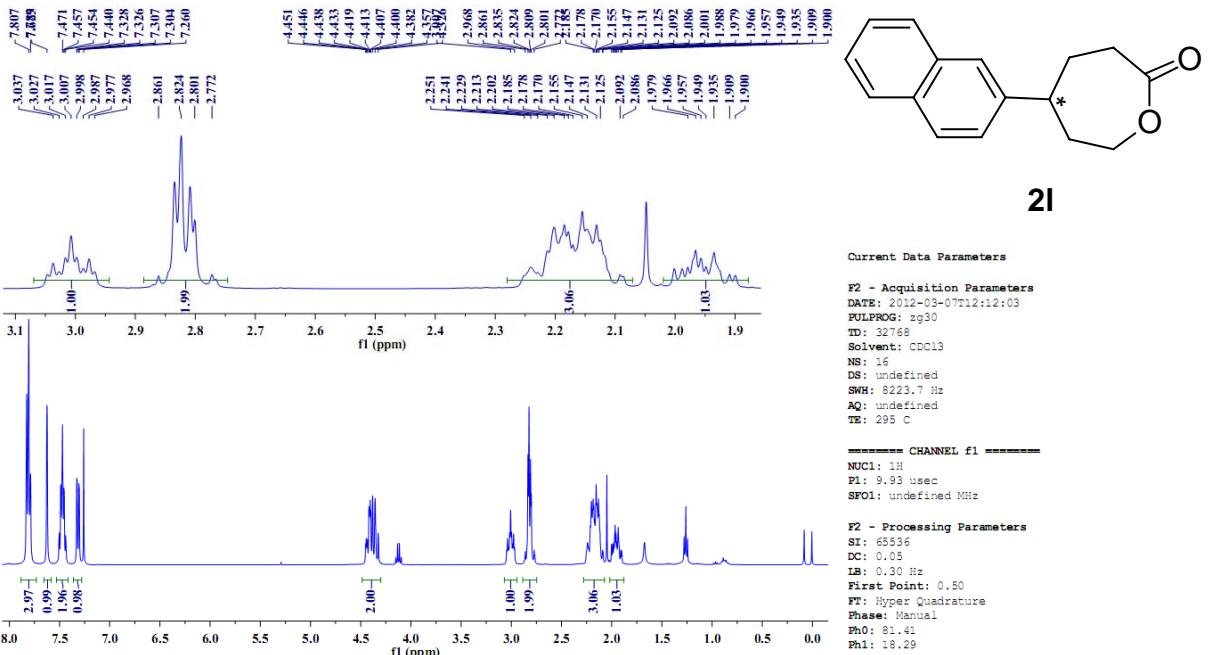
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-03-07T12:07:28
PULPROG: zgpg30
TD: 32768
SOLVENT: CDCl₃
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 295.4 °C

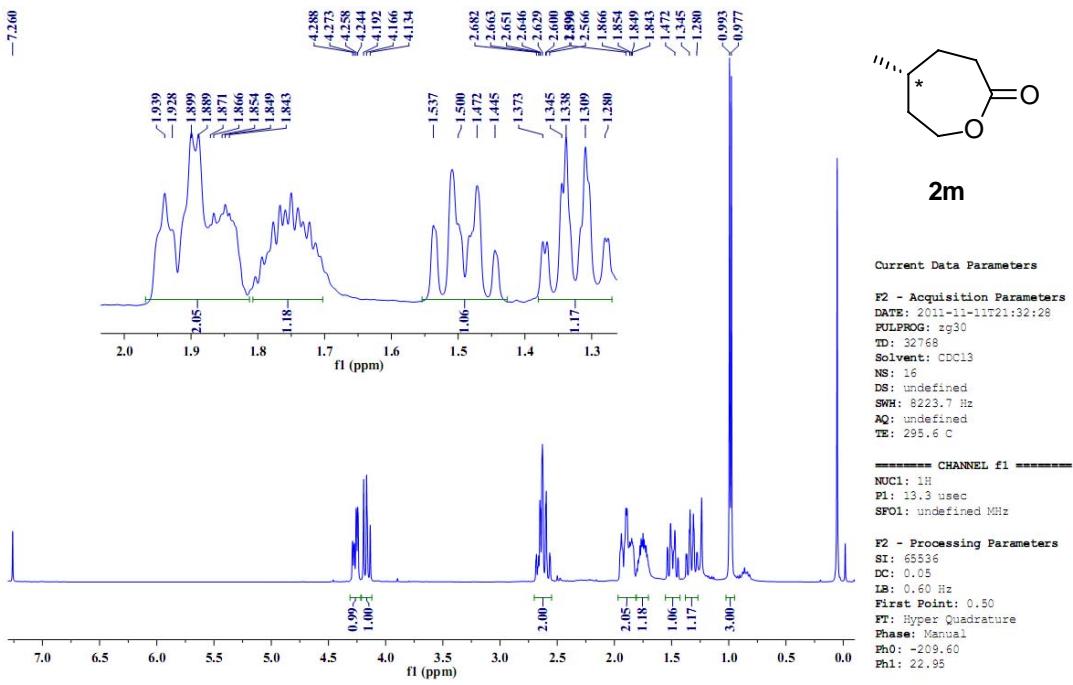
===== CHANNEL f1 =====
NUC1: 13C
PL: 9.63 used
SFO1: undefined MHz

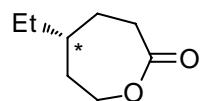
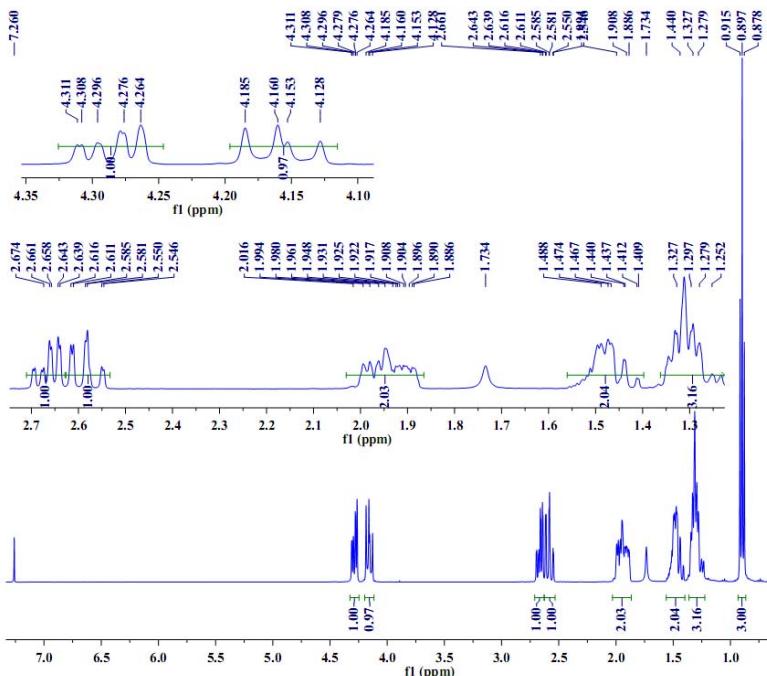
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -69.21
Ph1: 63.19

¹³C NMR (101 MHz, CDCl₃) δ 175.77, 140.66, 134.01, 130.59, 129.34, 127.36, 126.29, 125.68, 125.67, 122.86, 122.27, 77.41, 77.10, 76.78, 68.64, 41.62, 36.35, 34.09, 29.95.



¹³C NMR (101 MHz, CDCl₃) δ 175.70, 142.37, 133.54, 132.44, 128.50, 127.66, 126.31, 125.76, 125.28, 124.89, 77.40, 77.08, 76.76, 68.27, 47.31, 36.73, 33.75, 30.30.





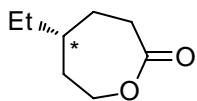
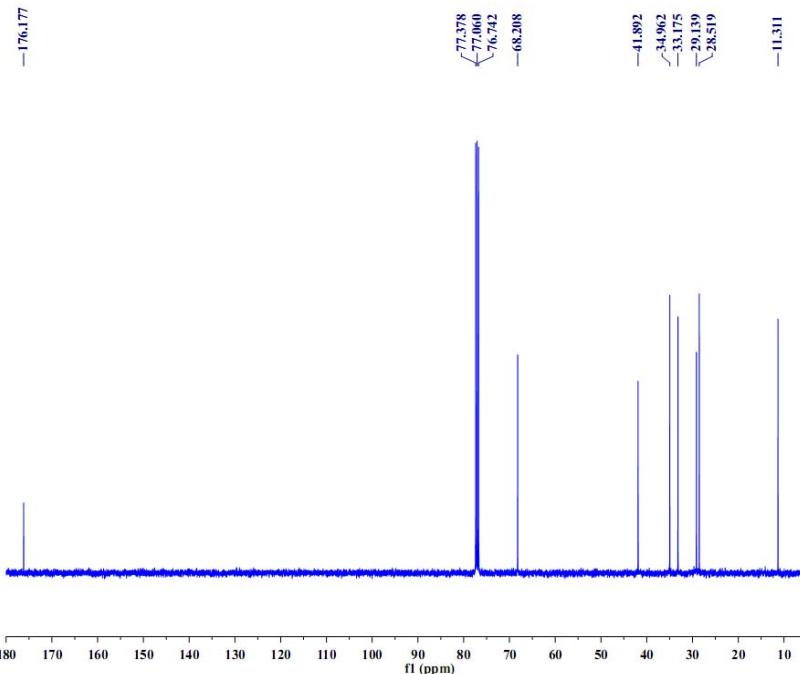
2n

Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-11-15T17:34:39
FUPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.3 C

===== CHANNEL f1 =====
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -204.74
M1: 15.00



2n

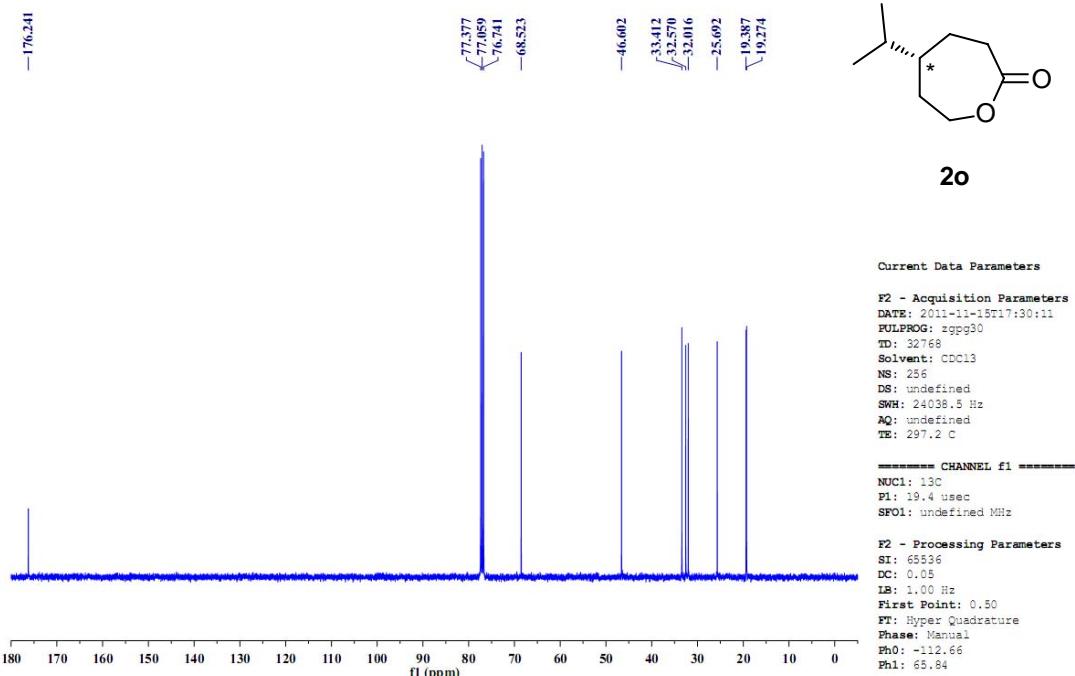
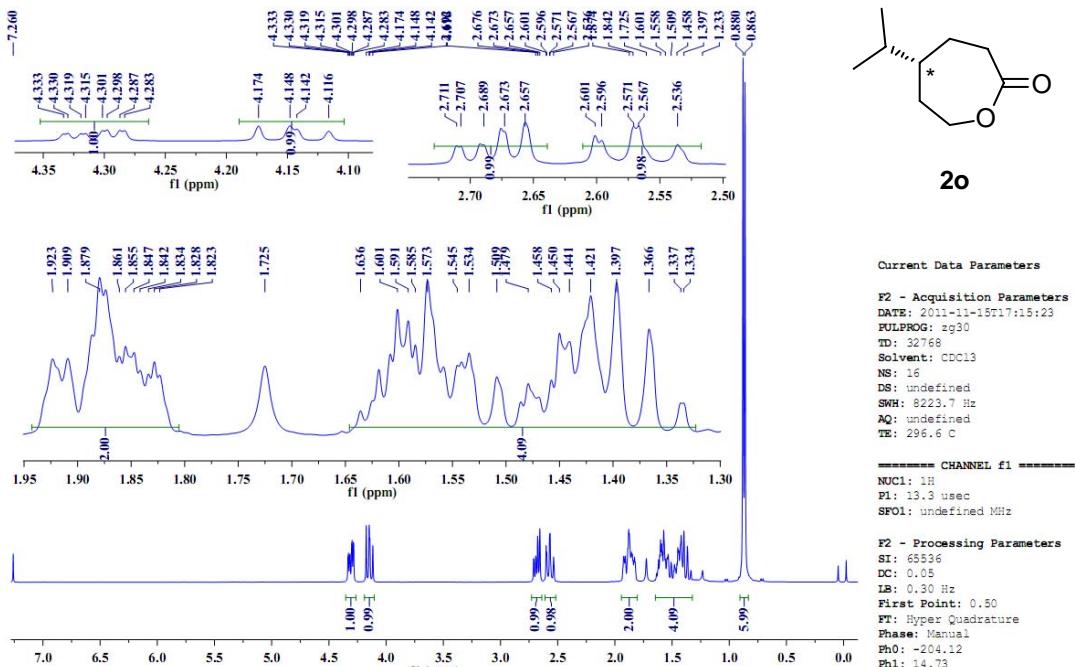
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-11-15T17:49:26
FUPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297.4 C

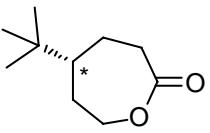
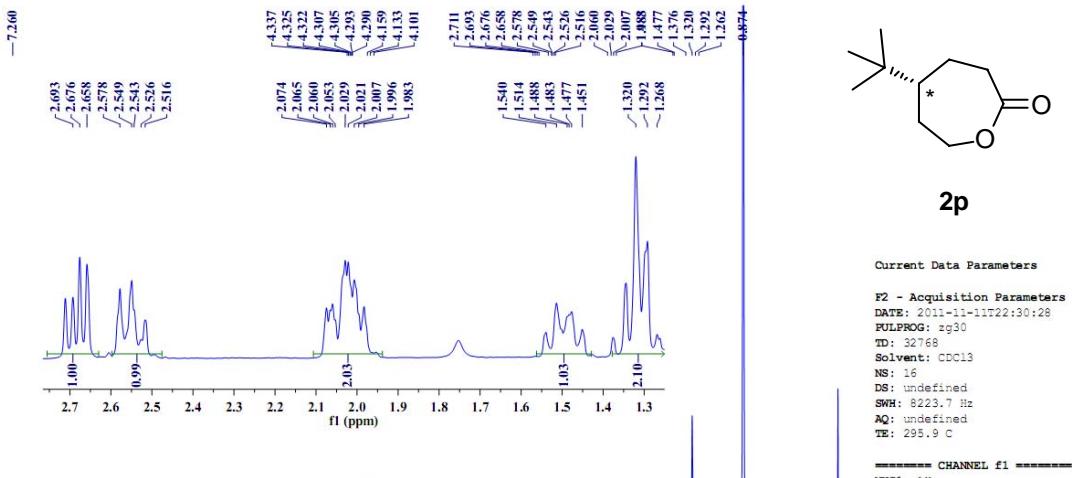
===== CHANNEL f1 =====
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -119.63
Ph1: 82.18

¹³C NMR (101 MHz, CDCl₃) δ 176.18, 77.38, 77.06, 76.74, 68.21, 41.89, 34.96, 33.17, 29.14, 28.52, 11.31.



¹³C NMR (101 MHz, CDCl₃) δ 176.24, 77.38, 77.06, 76.74, 68.52, 46.60, 33.41, 32.57, 32.02, 25.69, 19.39, 19.27.



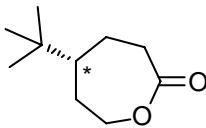
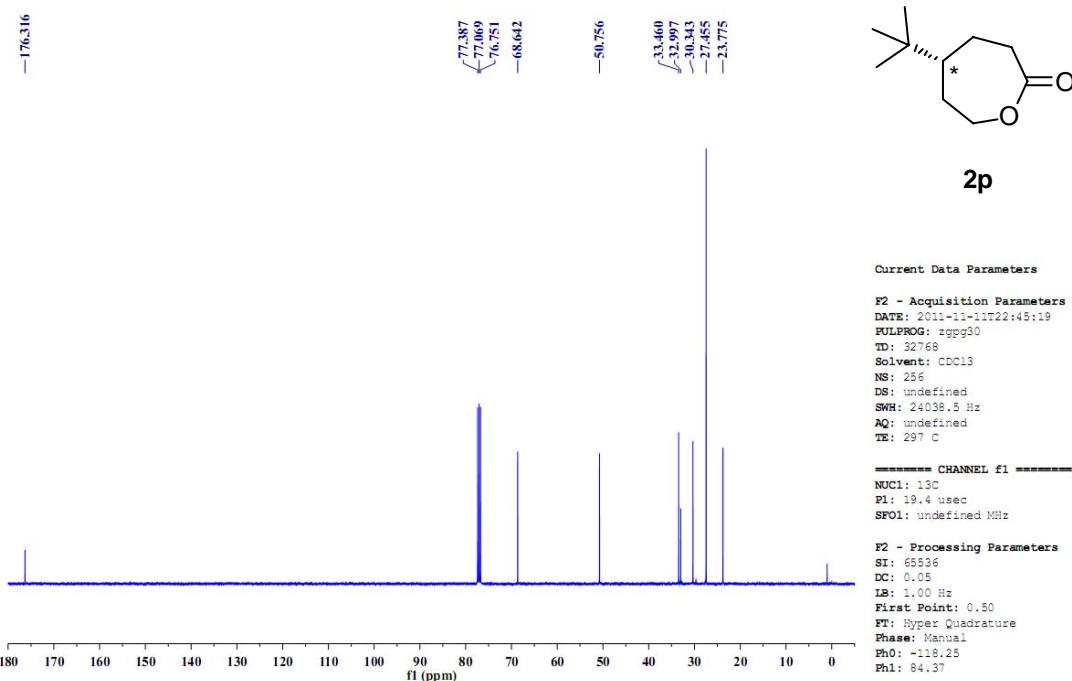
2p

Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-11-11T22:30:28
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.9 C

===== CHANNEL f1 =====
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -209.72
Ph1: 22.95



2p

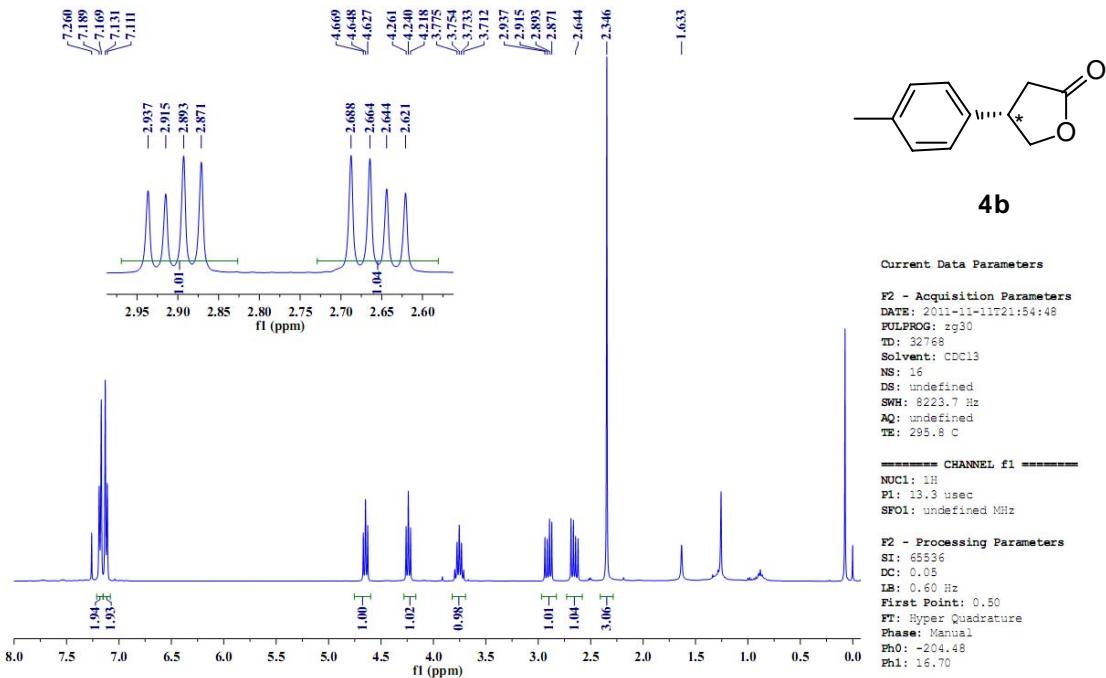
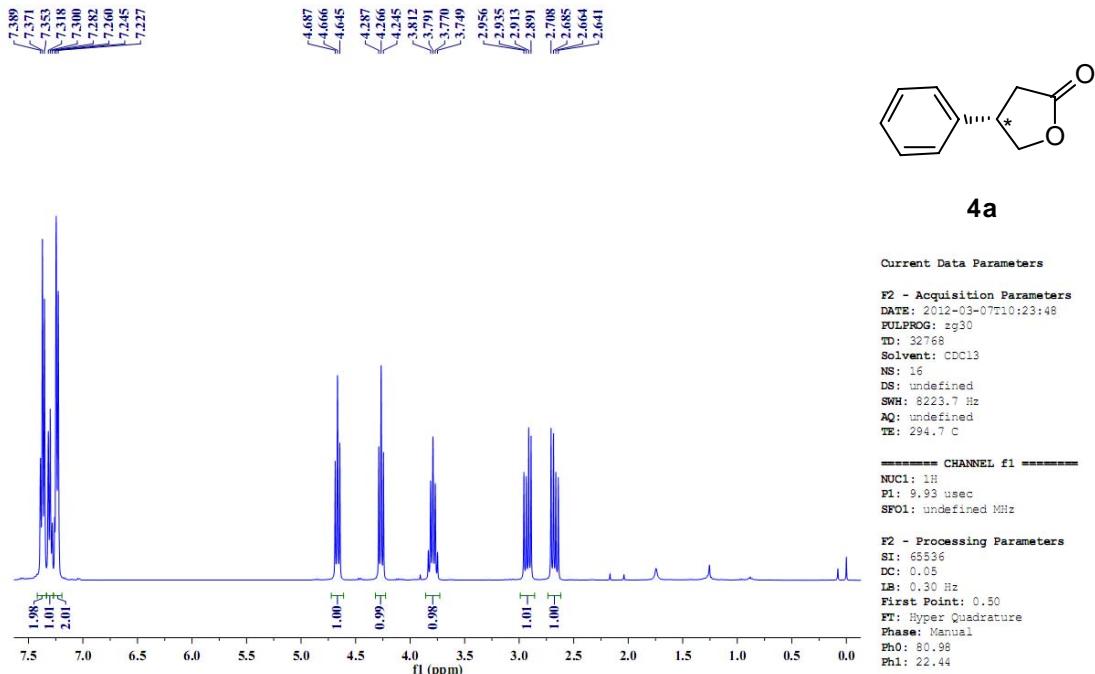
Current Data Parameters

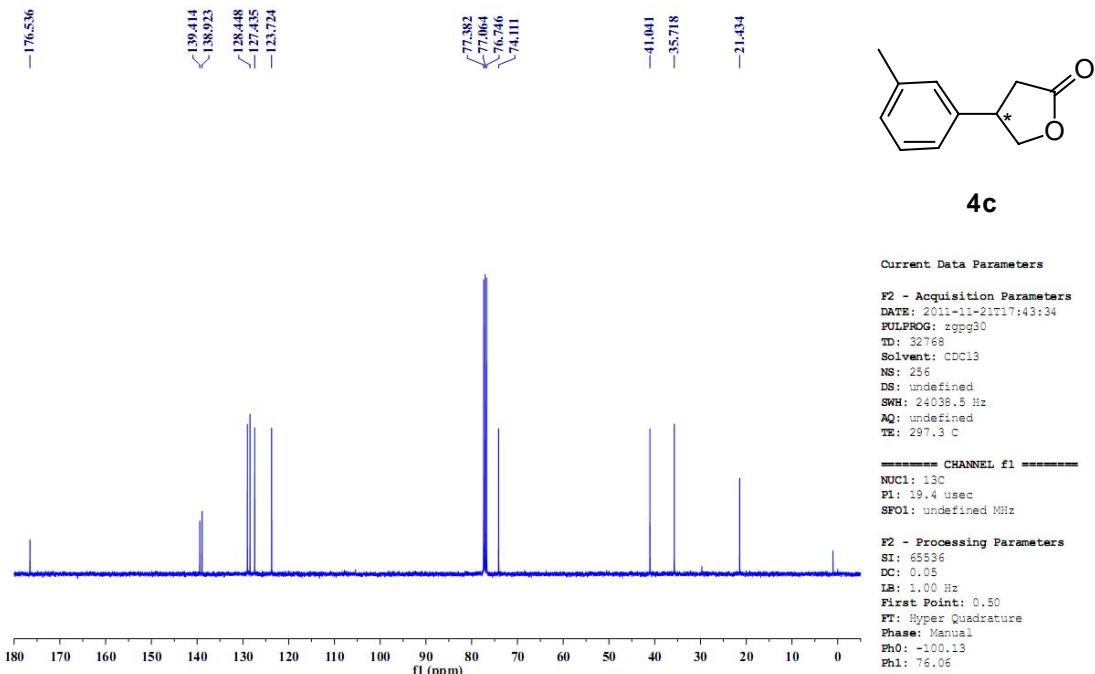
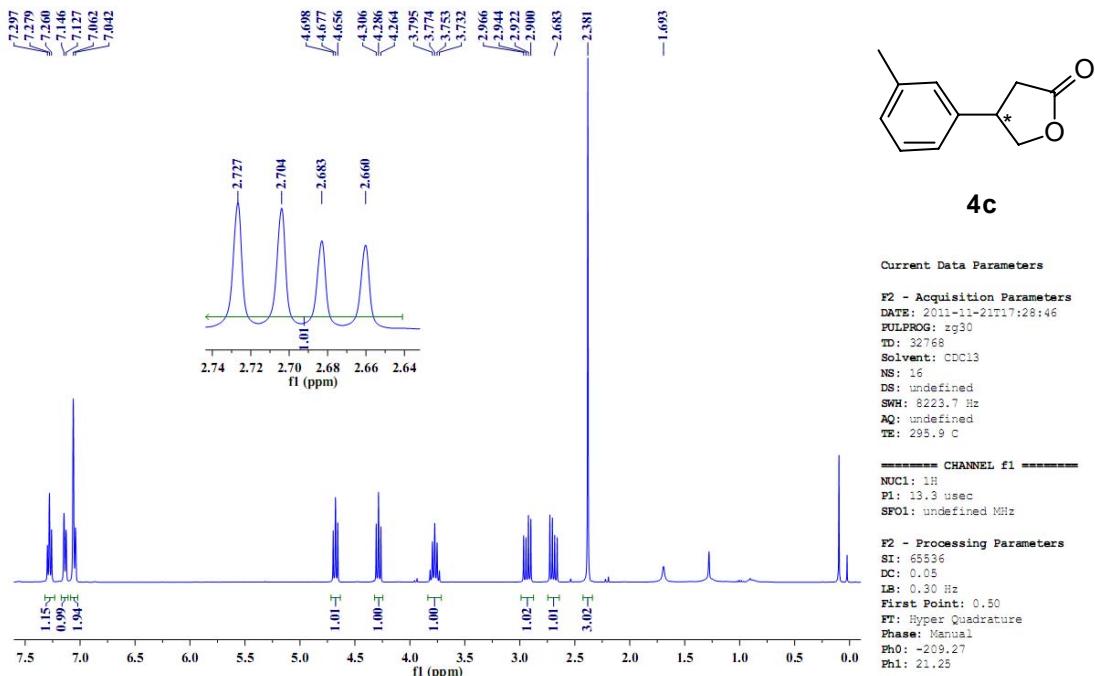
F2 - Acquisition Parameters
DATE: 2011-11-11T22:45:19
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297.0

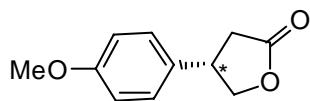
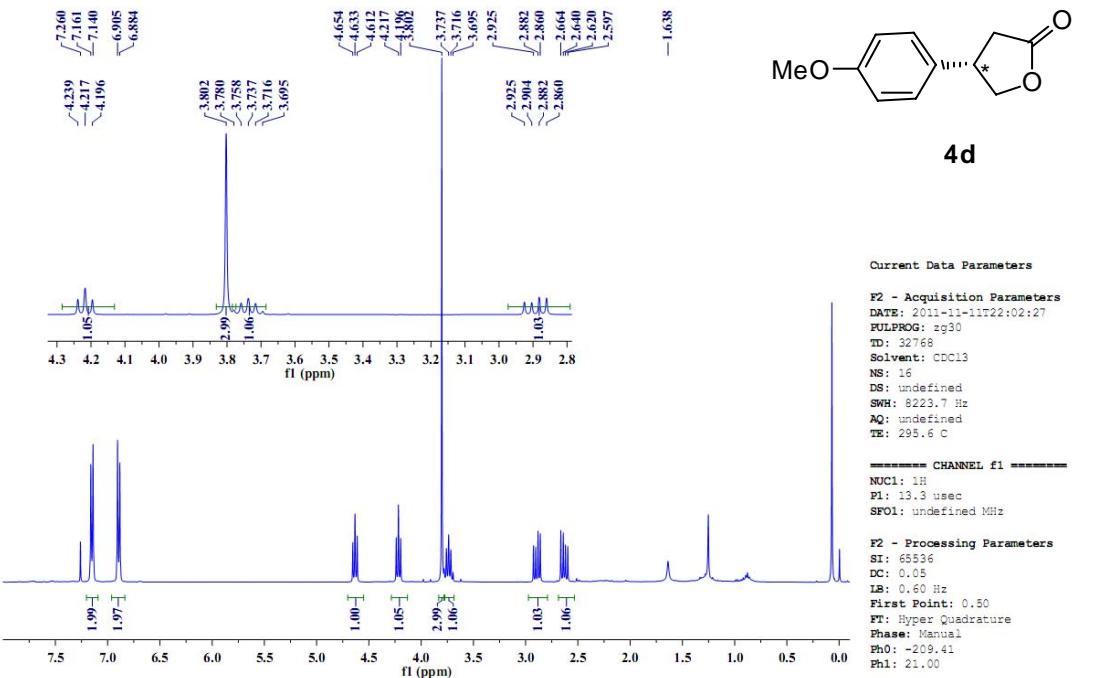
===== CHANNEL f1 =====
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

P2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -118.25
Ph1: 84.37

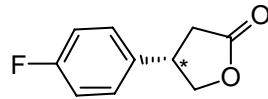
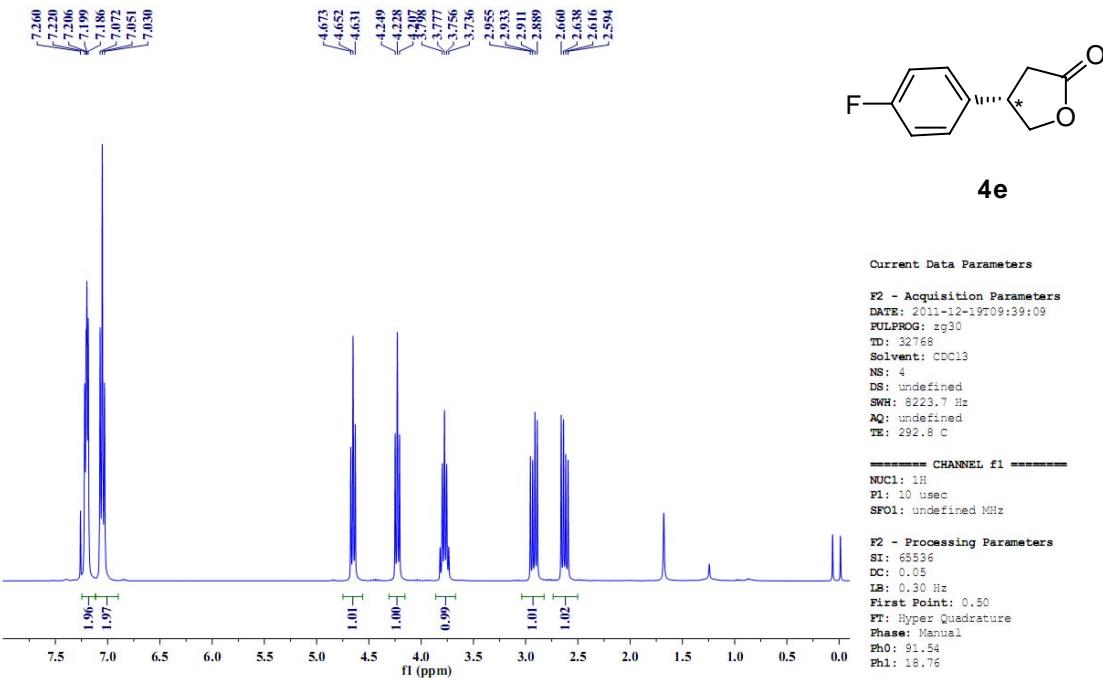
¹³C NMR (101 MHz, CDCl₃) δ 176.32, 77.39, 77.07, 76.75, 68.64, 50.76, 33.46, 33.00, 30.34, 27.46, 23.77.







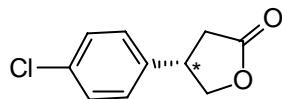
4d



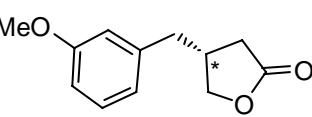
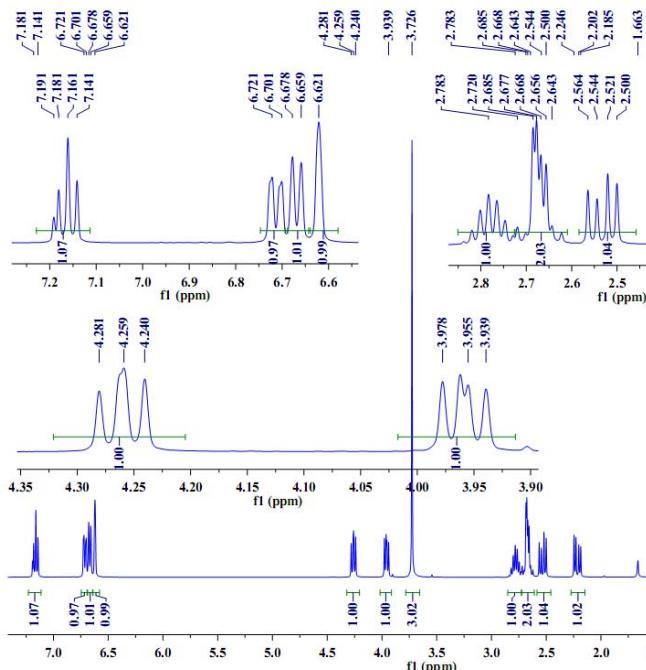
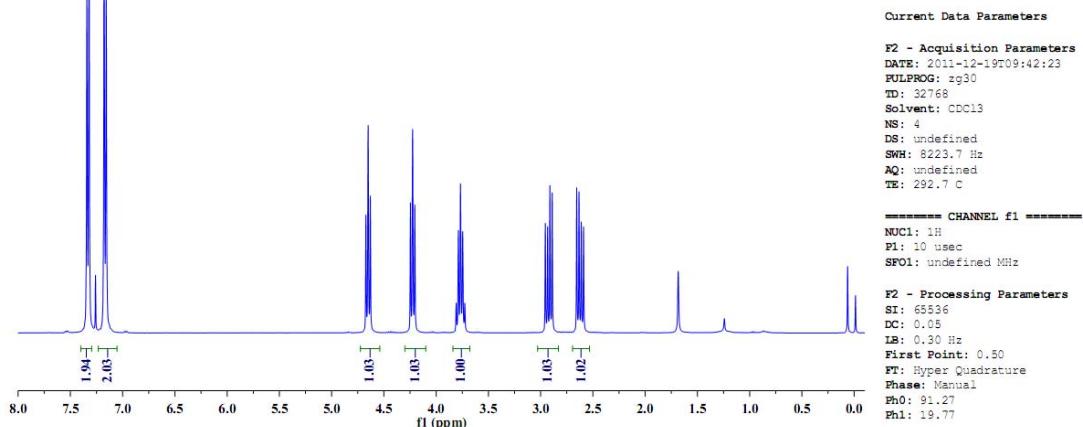
4e

7.342
7.322
7.260
7.178
7.157

4.672
4.651
4.630
4.246
4.225
4.214
3.767
3.746
3.726
2.955
2.912
2.890
2.655
2.633
2.612
2.590



4f



4g

Current Data Parameters

F2 - Acquisition Parameters

DATE: 2011-12-19T09:45:29

PULPROG: zg30

TD: 32768

Solvent: CDCl₃

NS: 4

DS: undefined

SWH: 8223.7 Hz

AQ: undefined

TE: 292.7 °C

===== CHANNEL f1 =====

NUC1: 1H

PL: 10 usec

SFO1: undefined MHz

F2 - Processing Parameters

SI: 65536

DC: 0.05

LB: 0.30 Hz

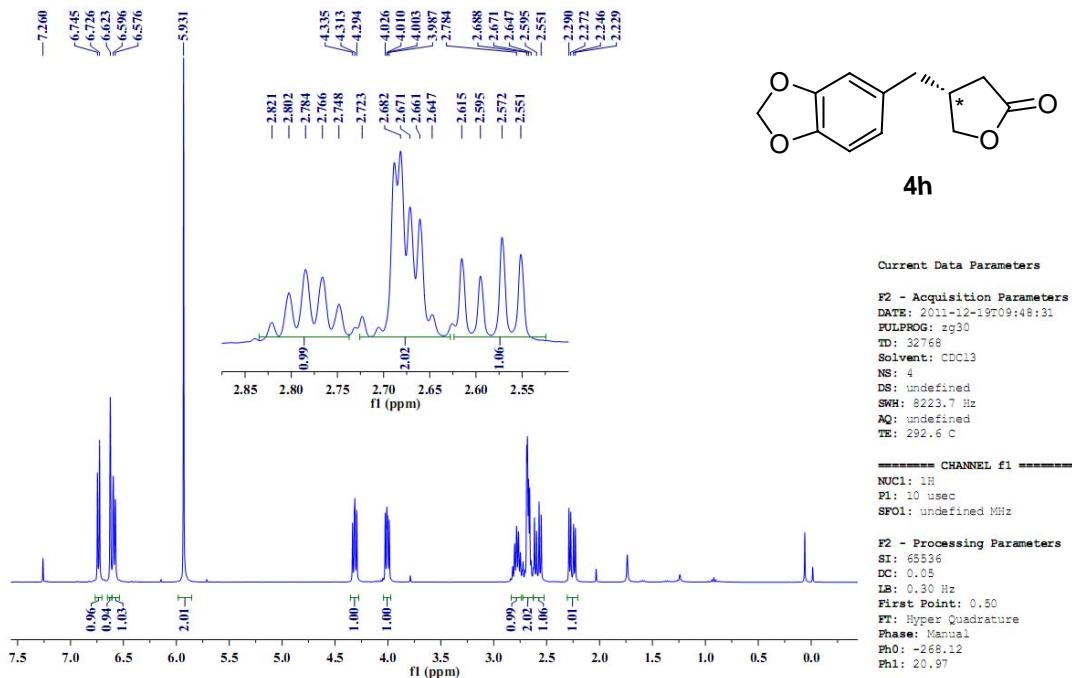
First Point: 0.50

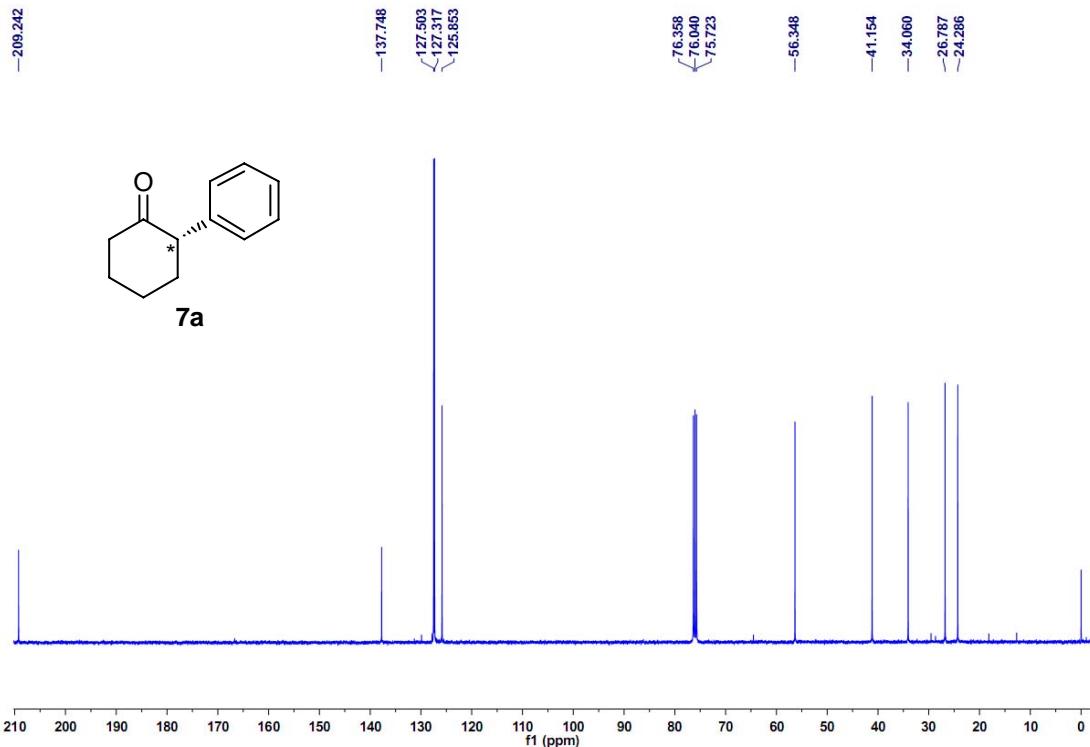
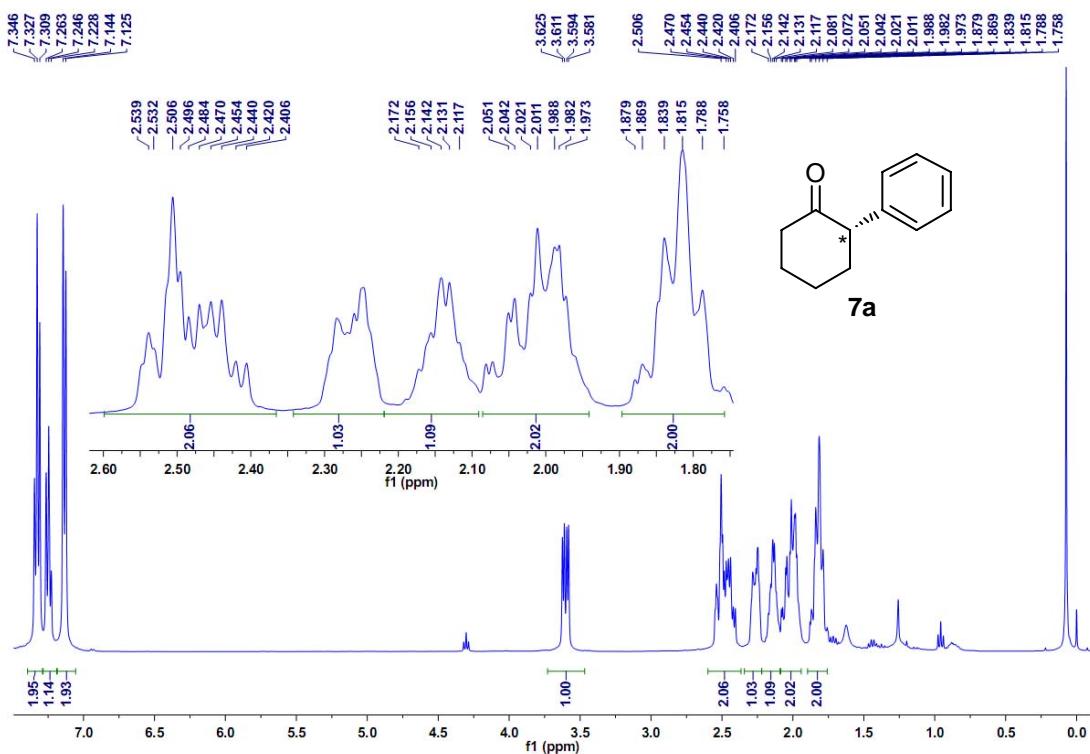
FT: Hyper Quadrature

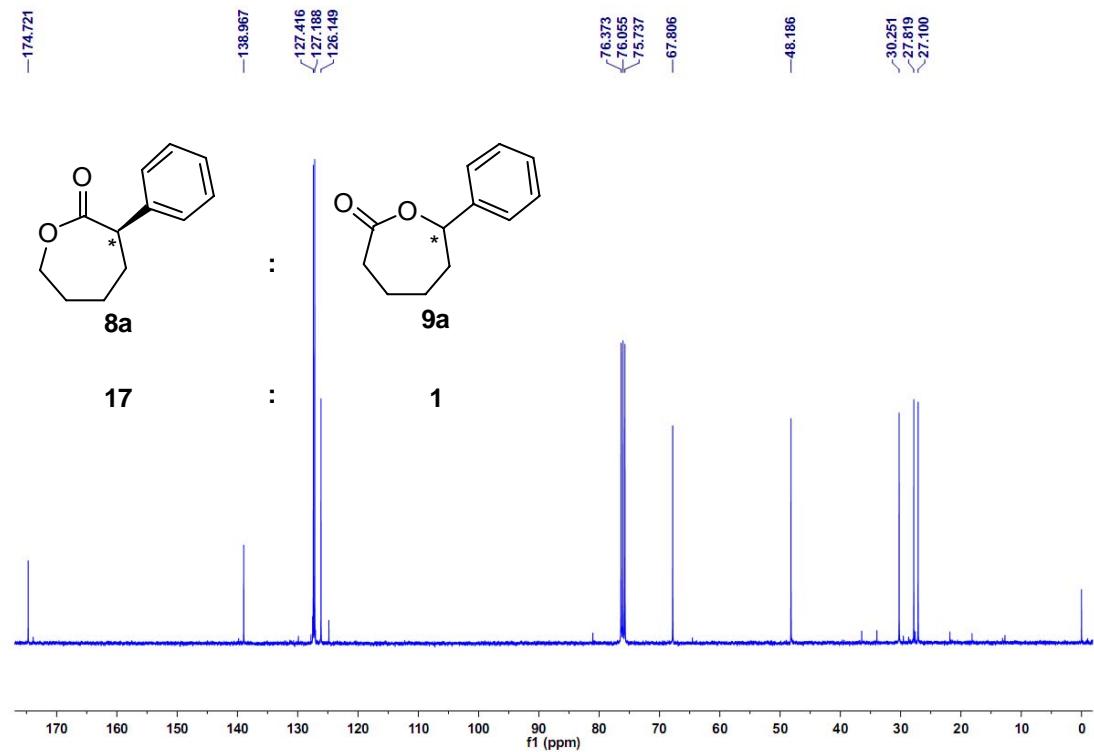
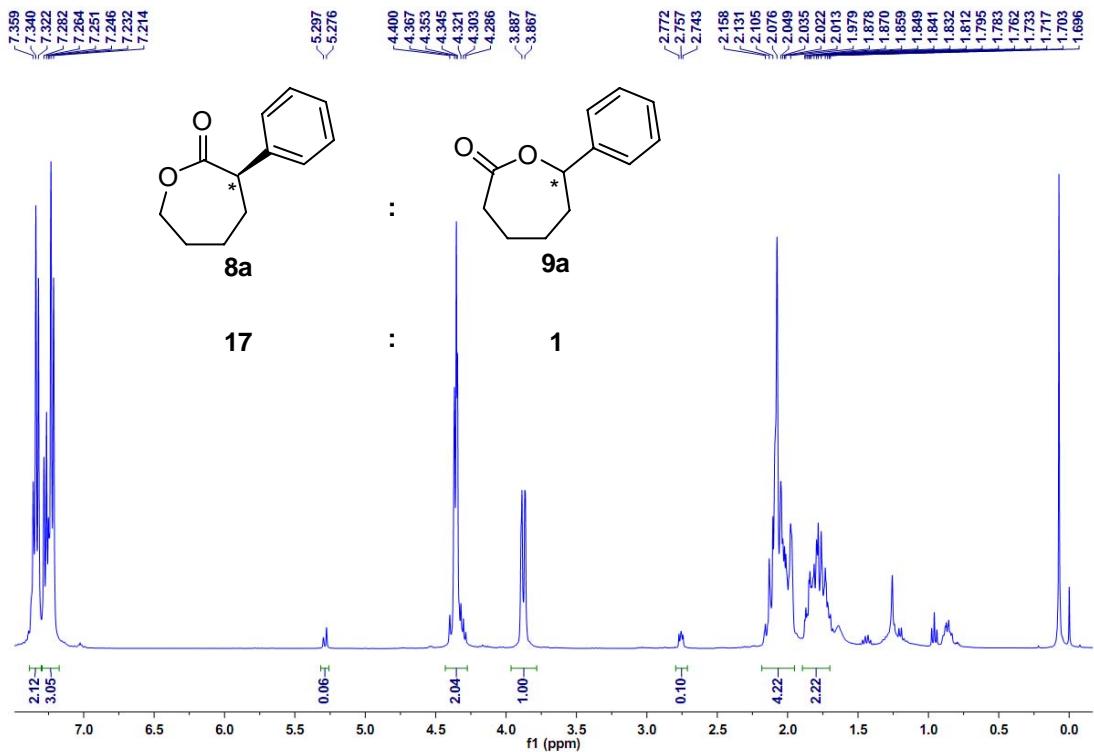
Phase: Manual

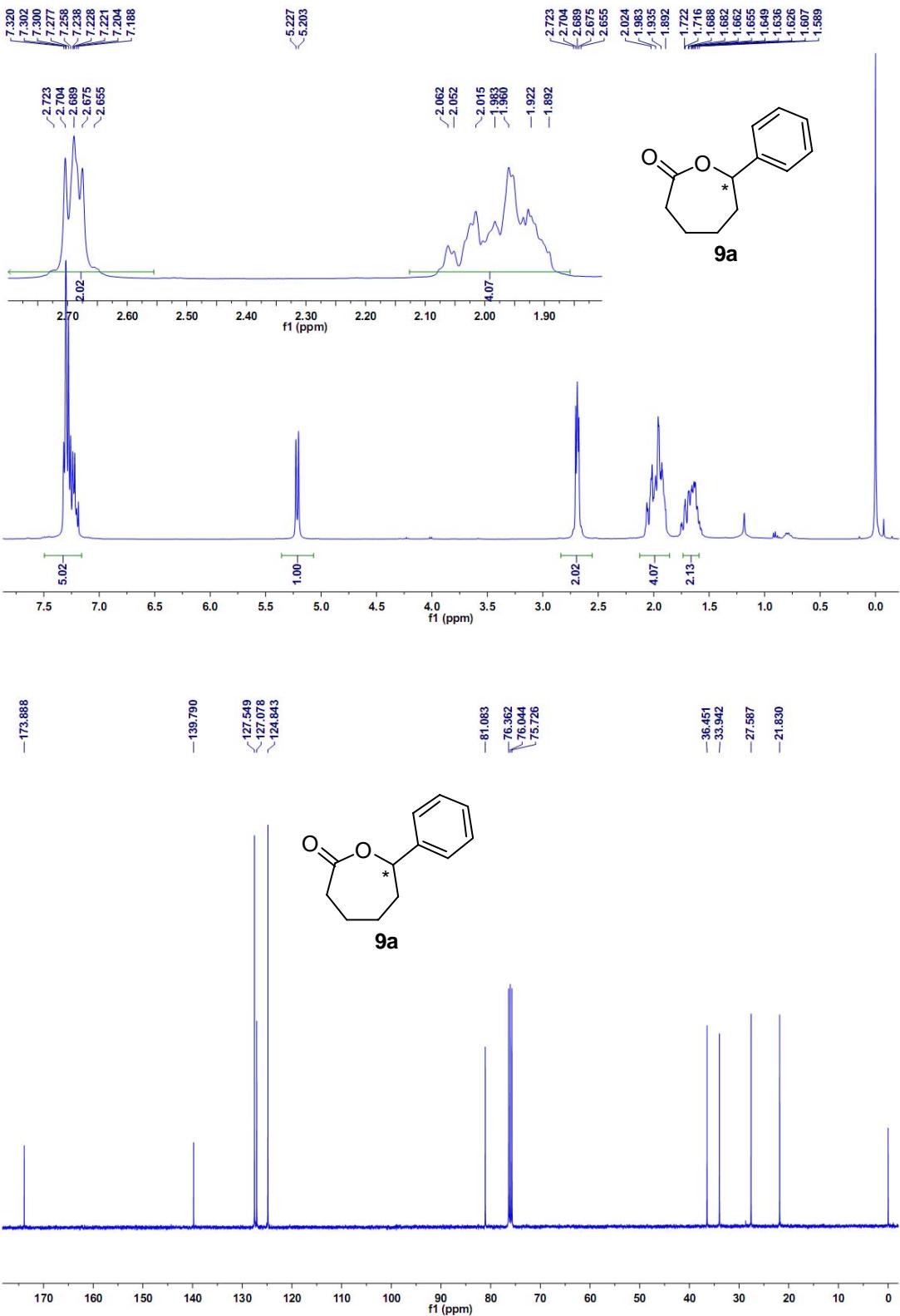
Ph0: -265.93

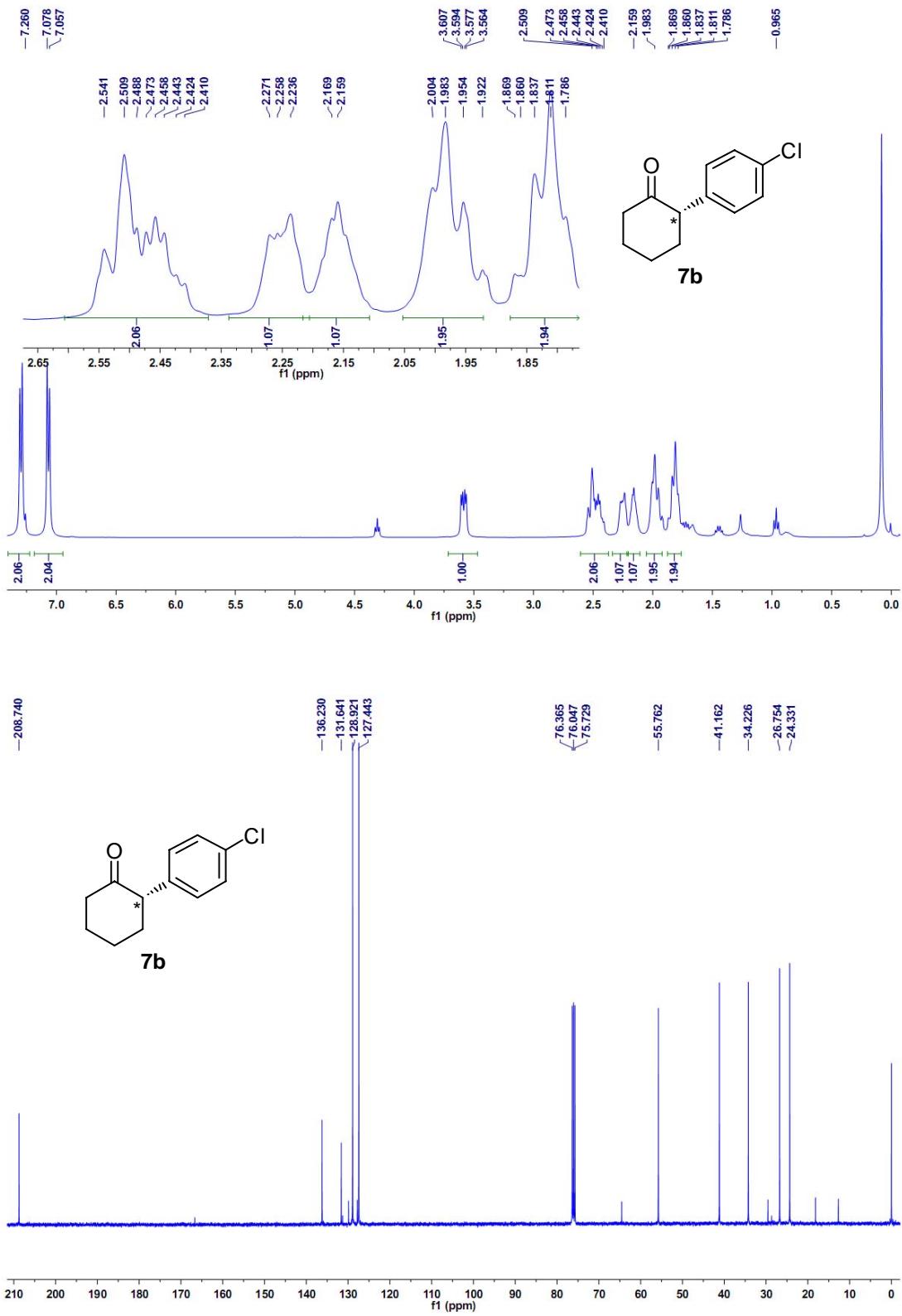
Ph1: 16.96

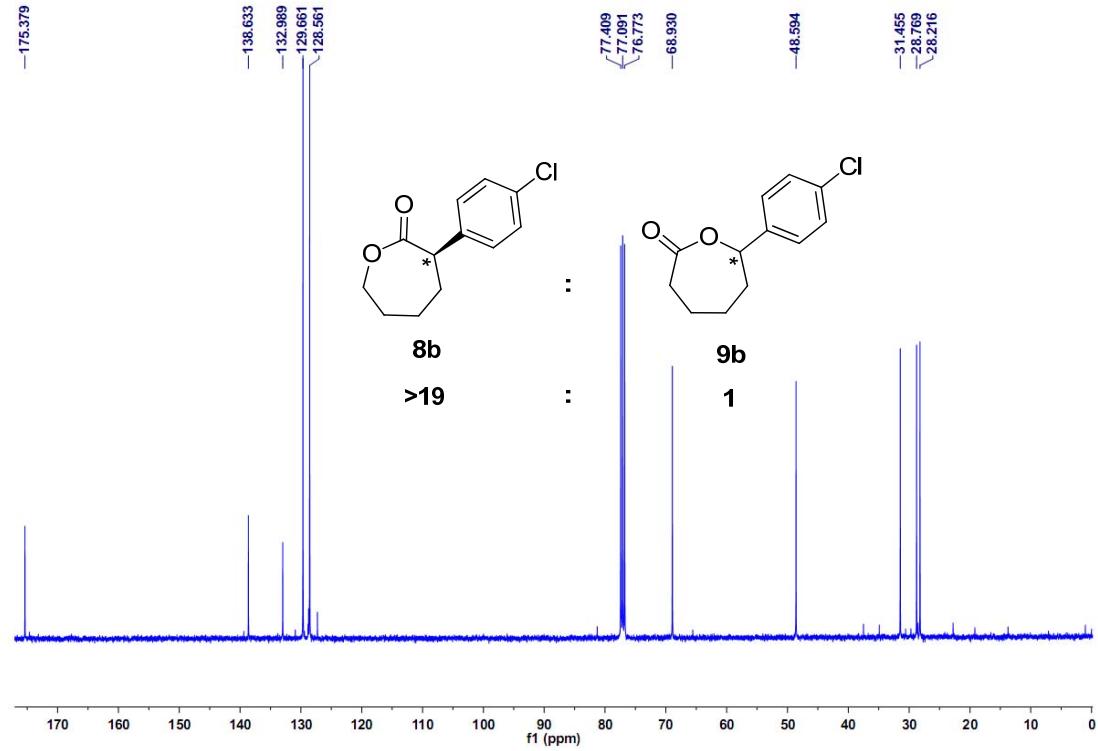
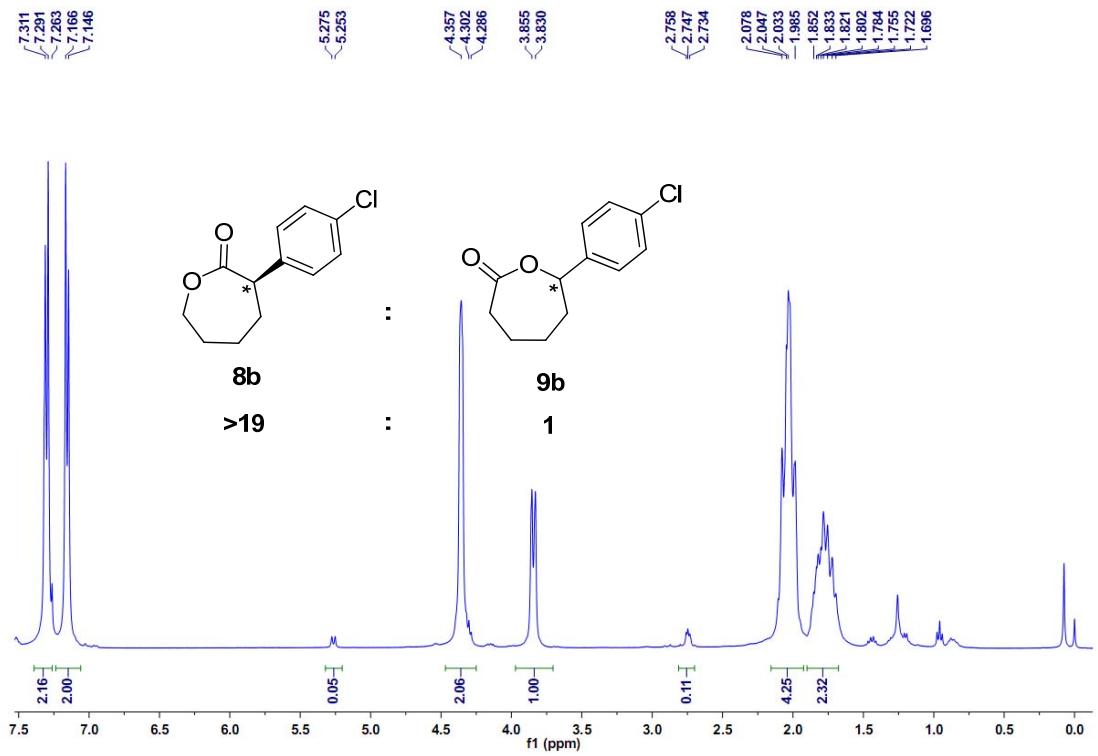


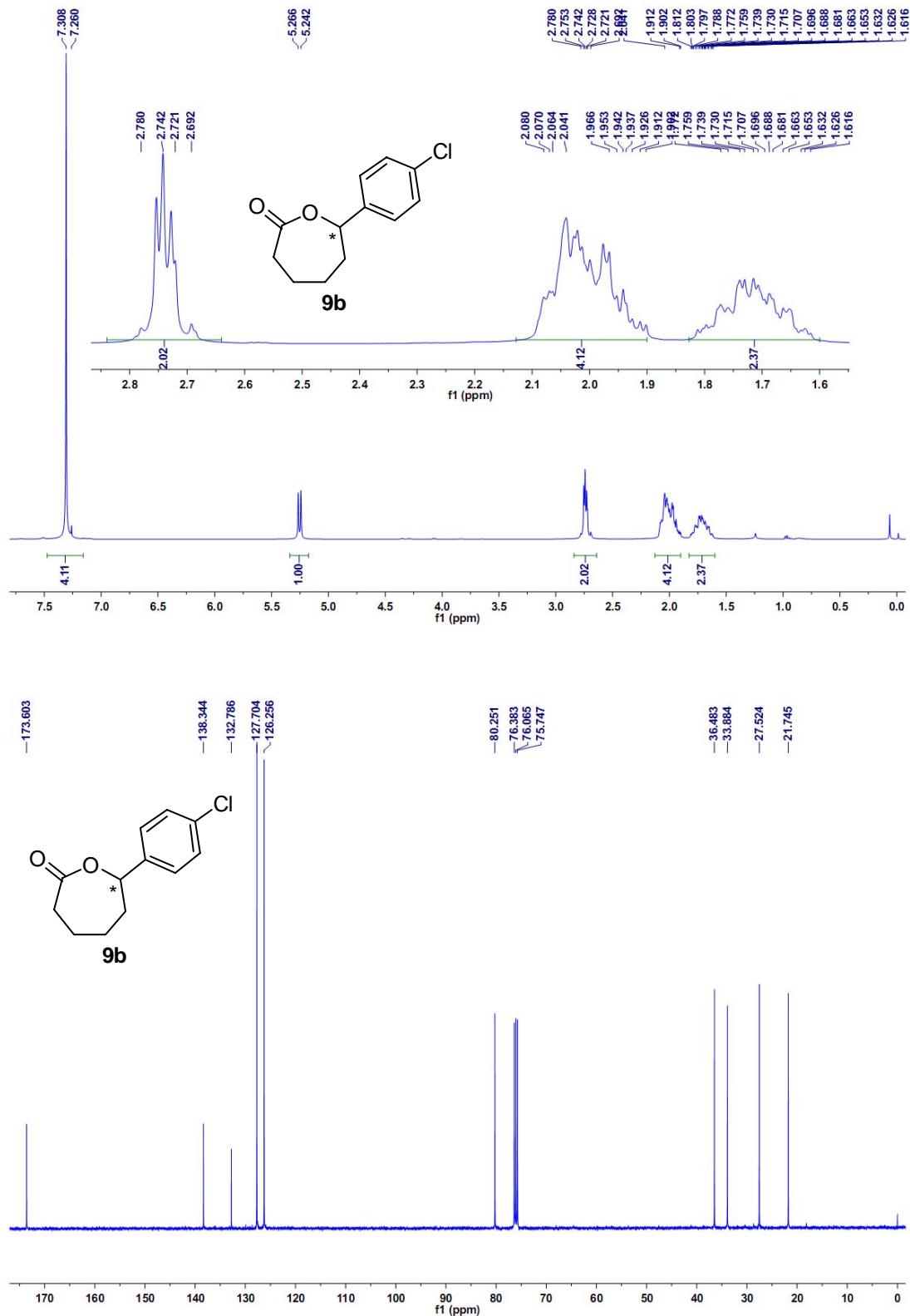


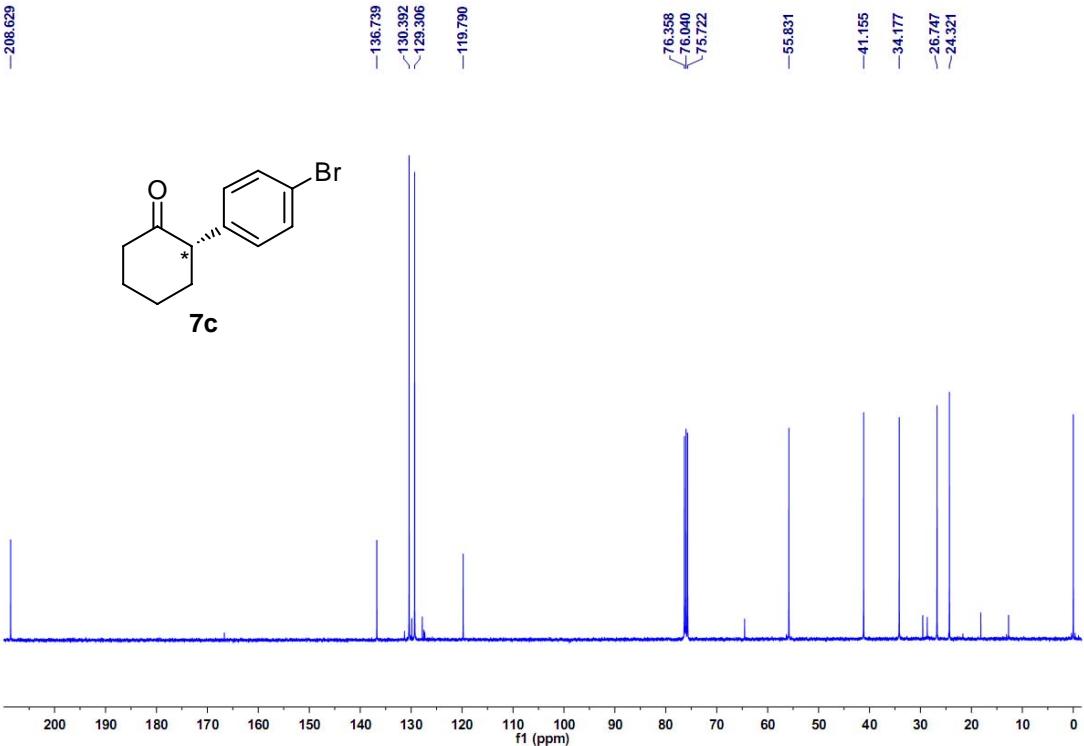
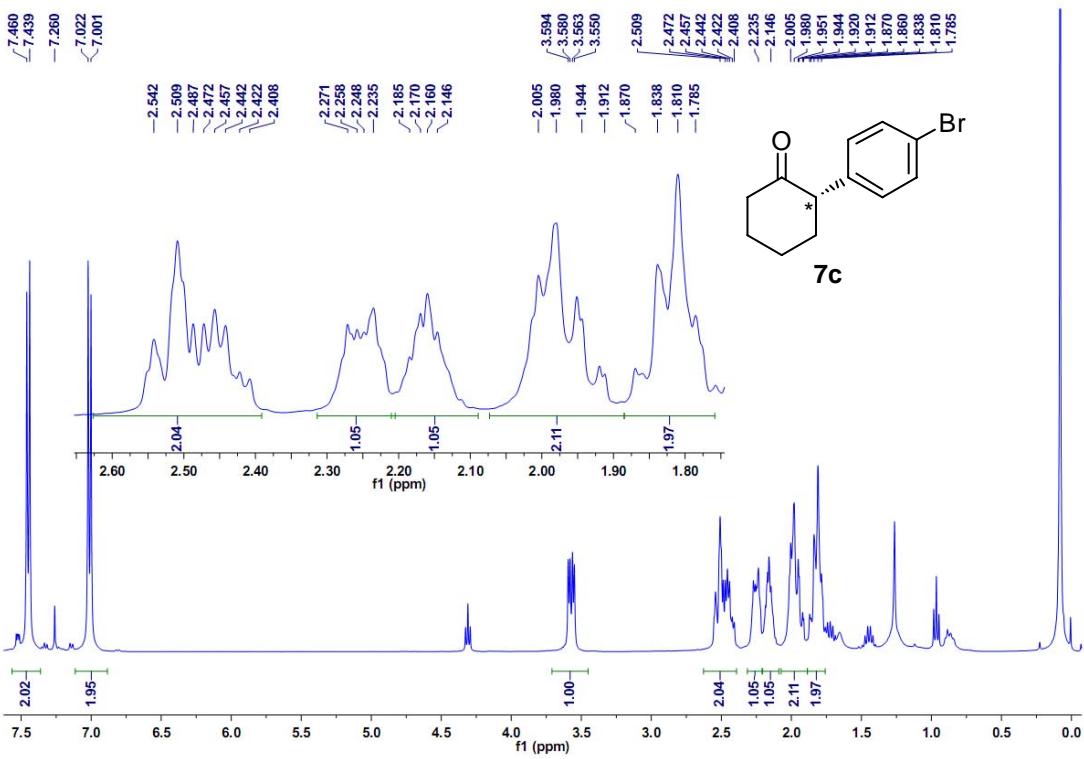


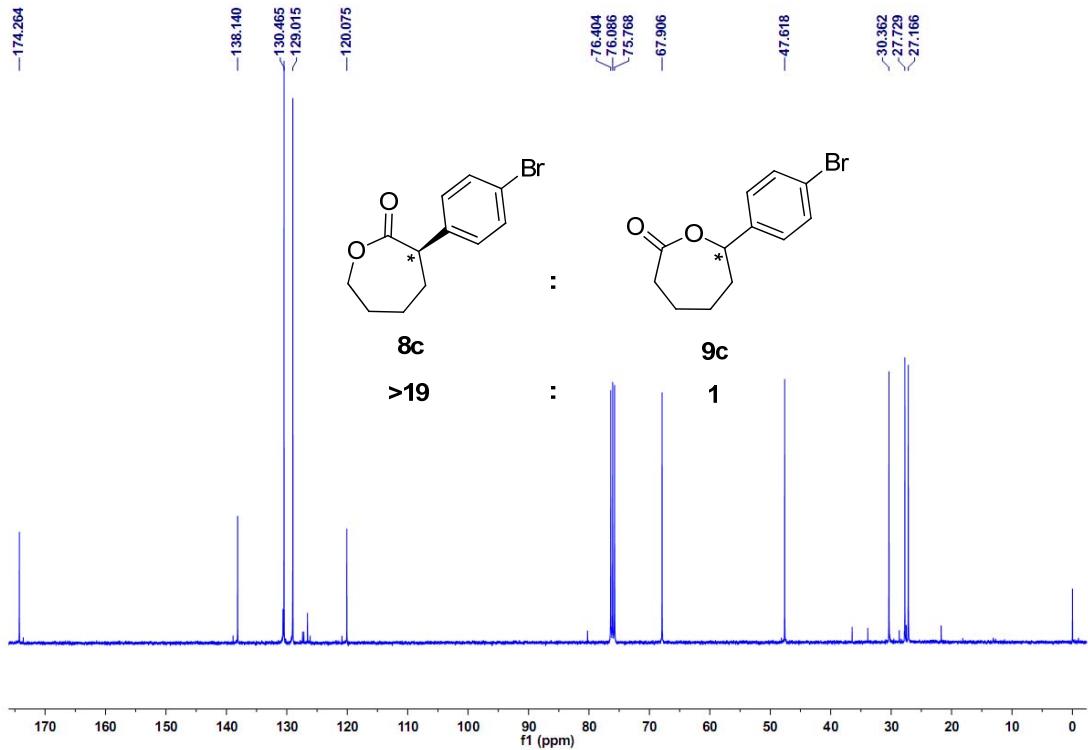
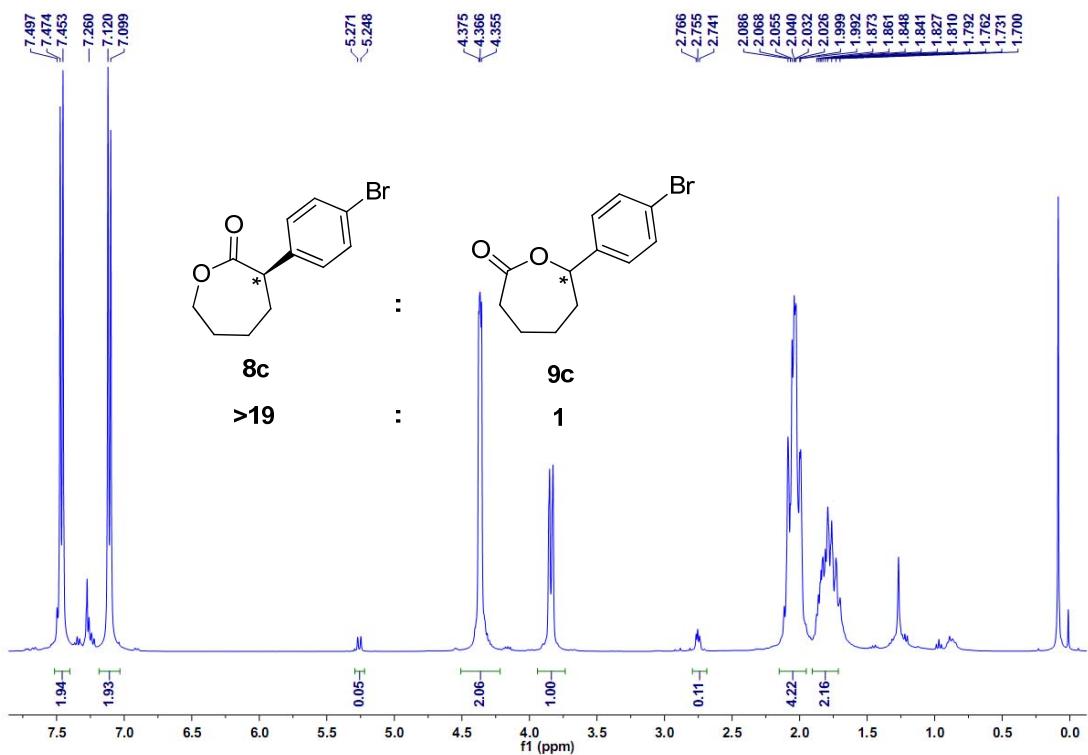


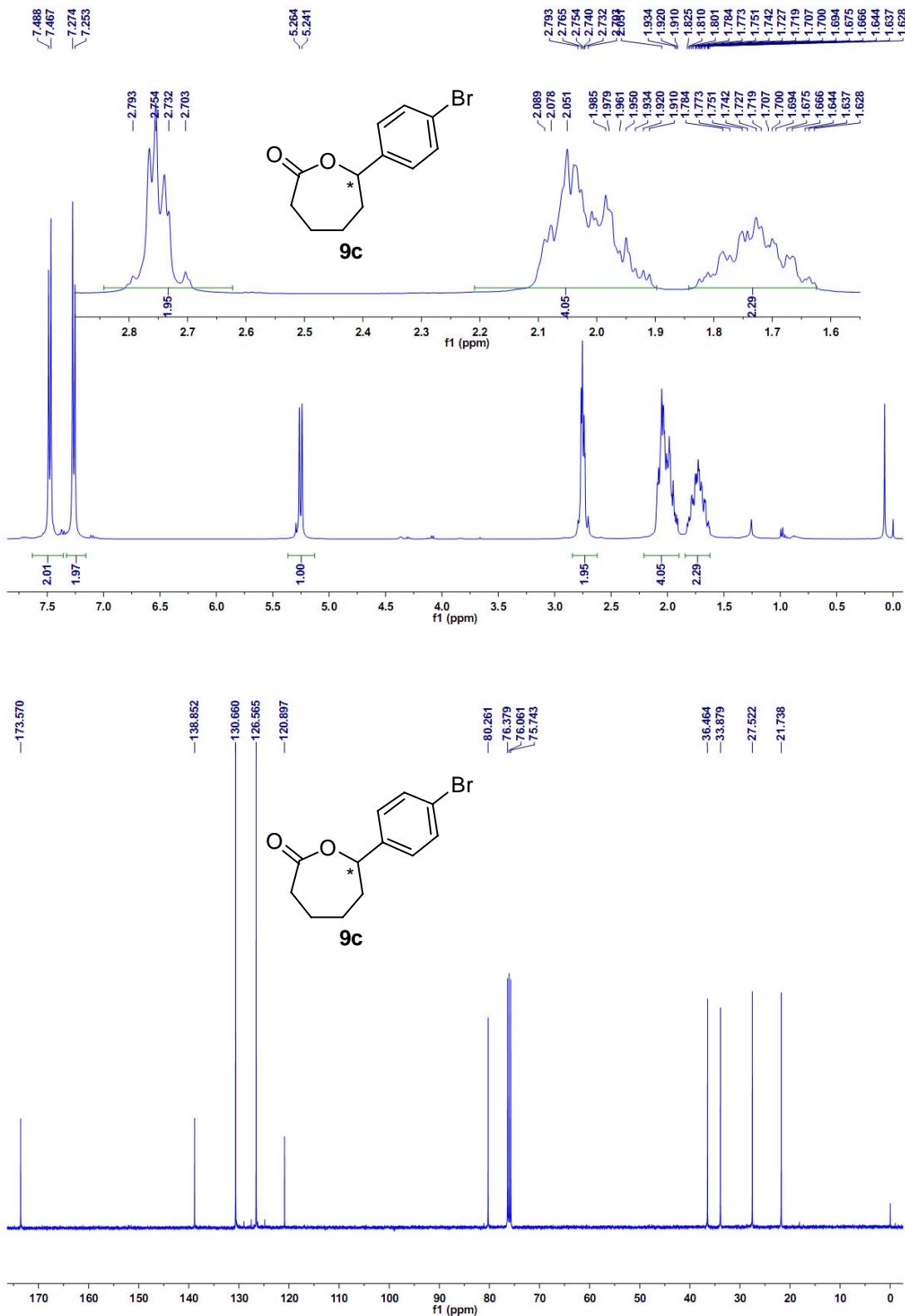


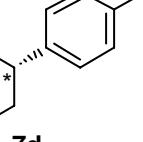
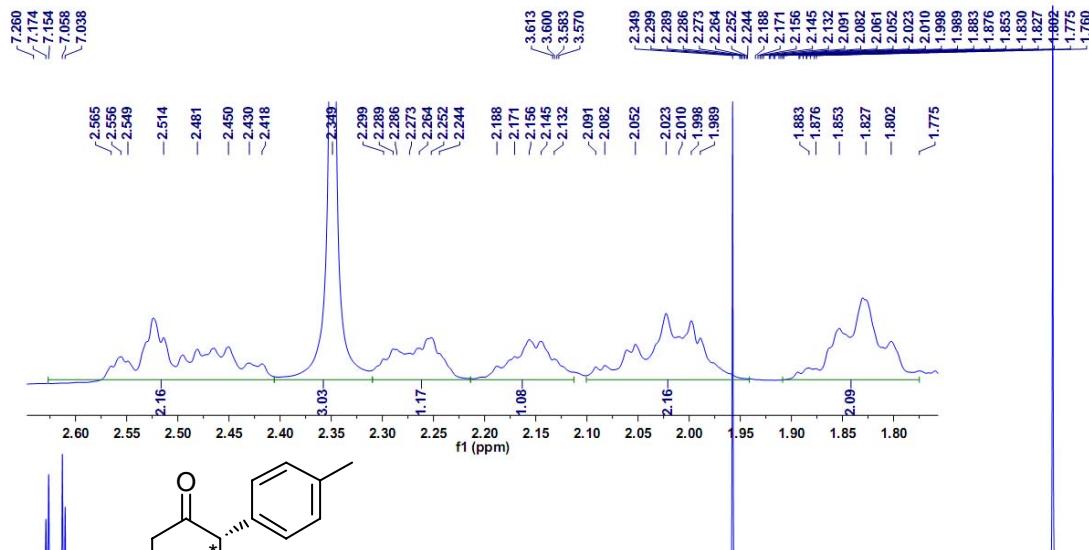




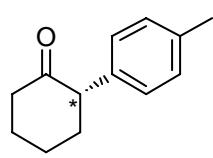
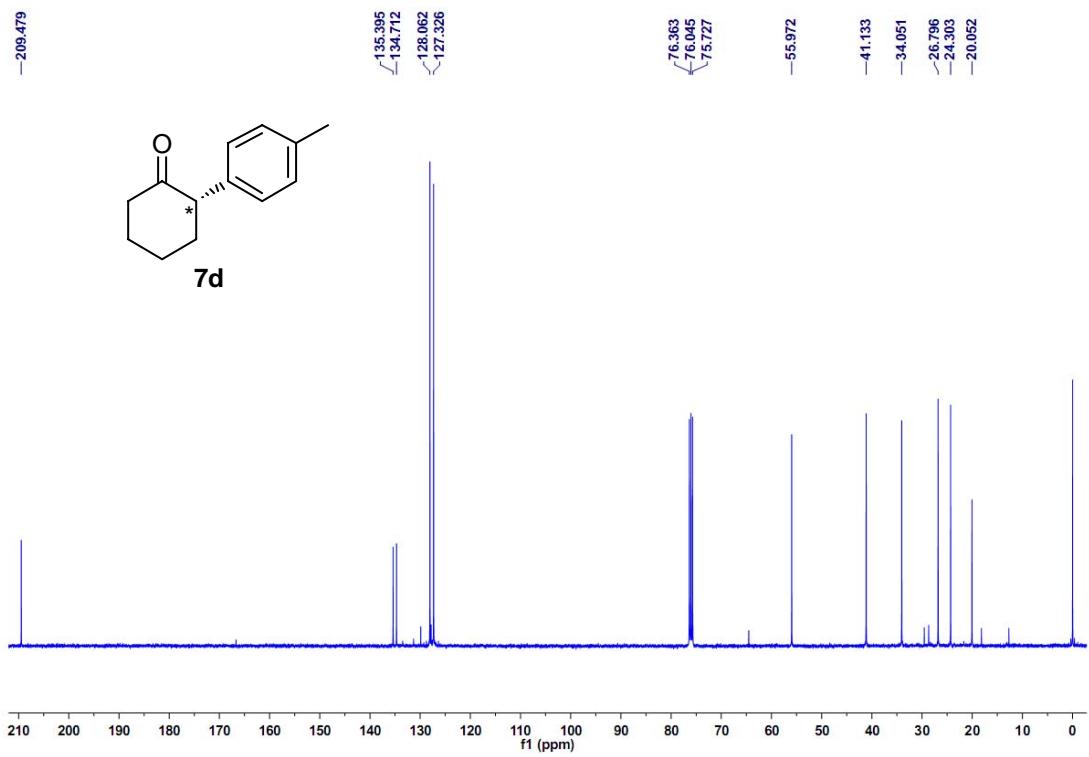




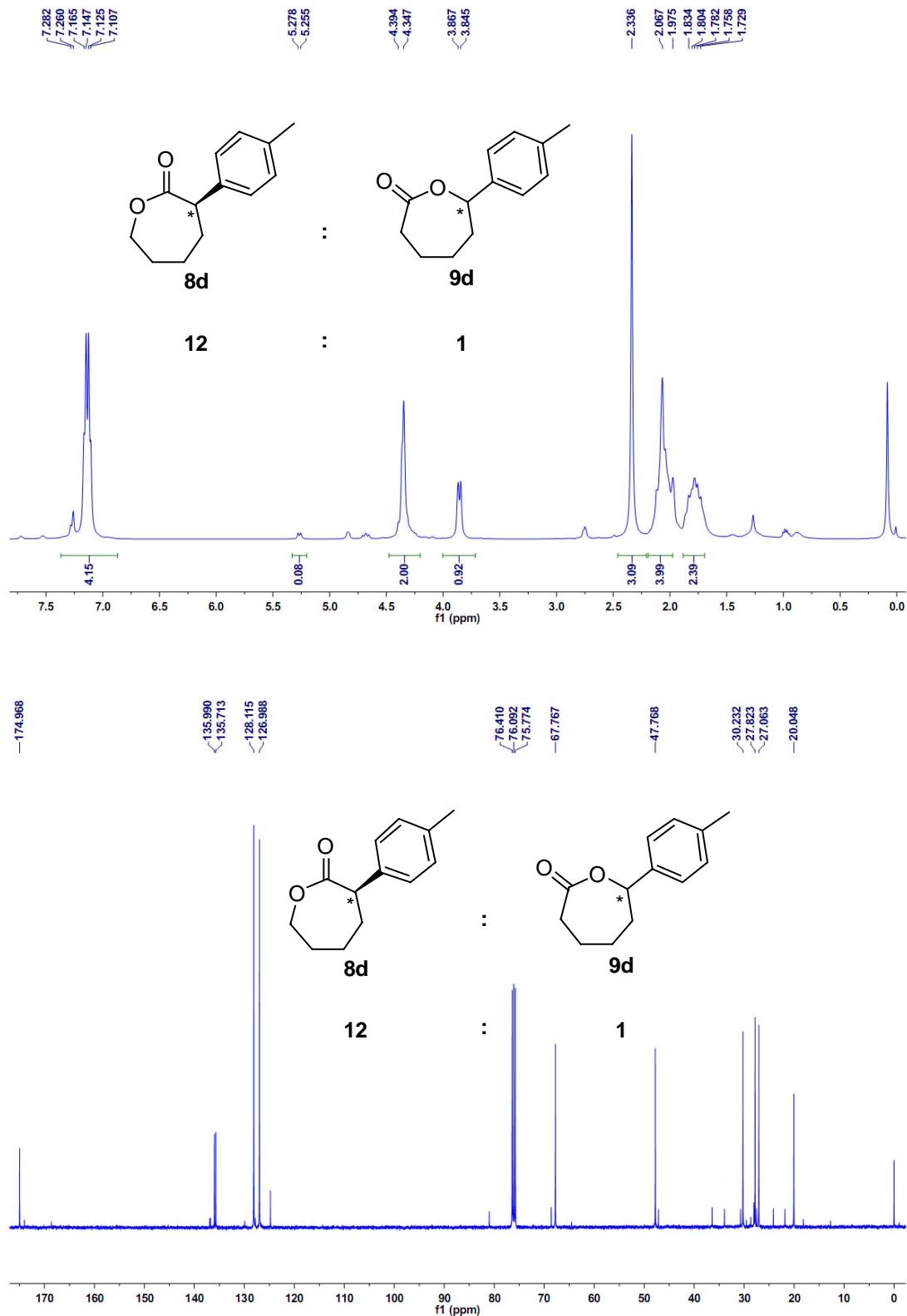


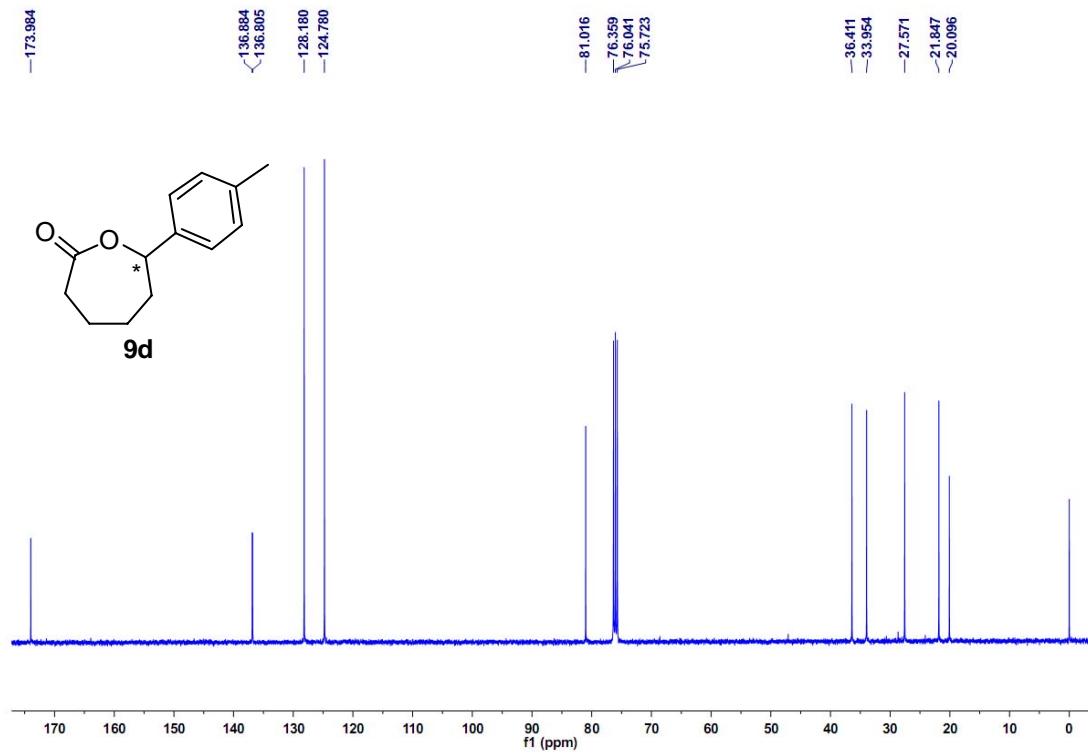
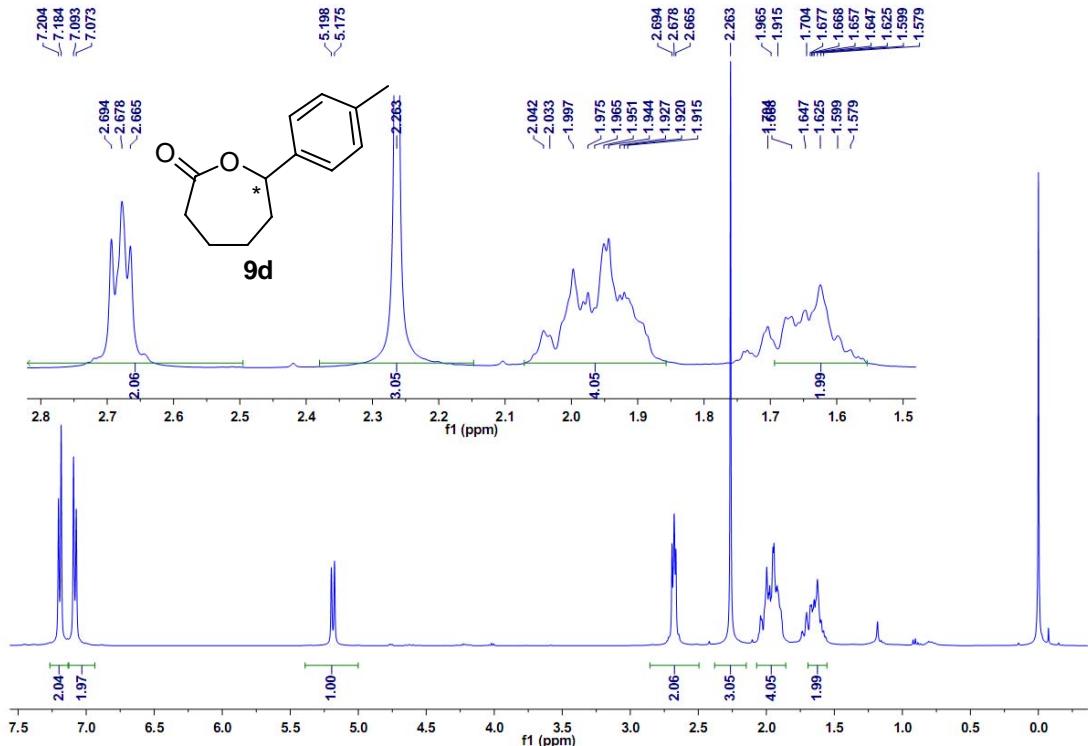


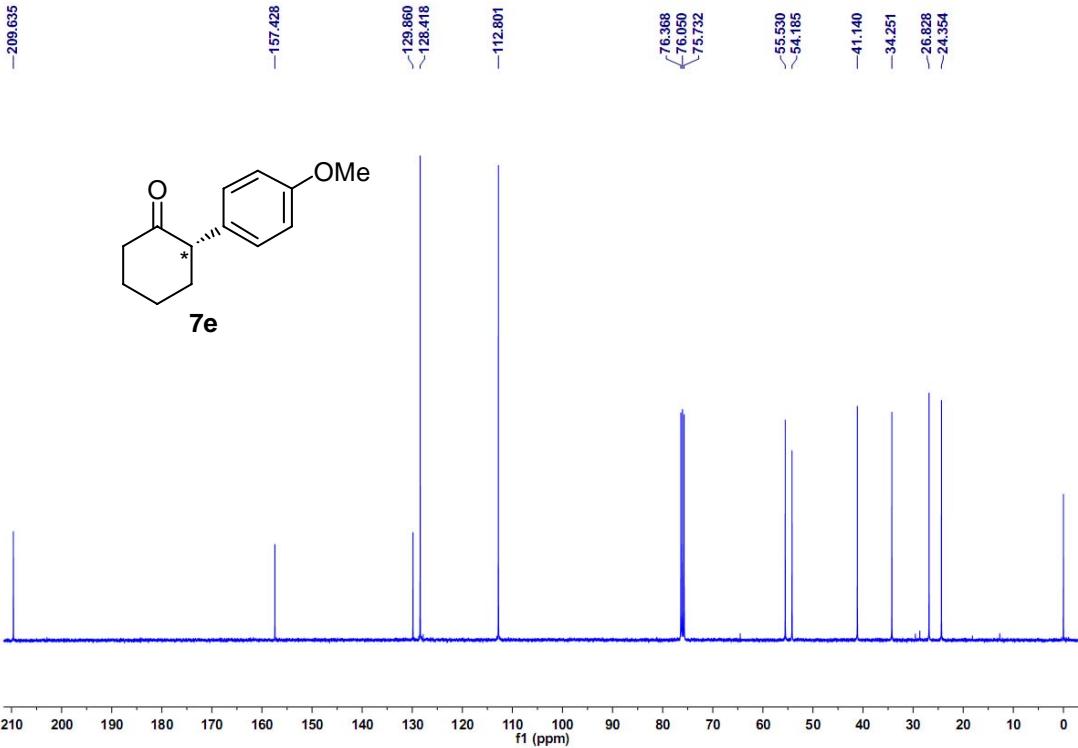
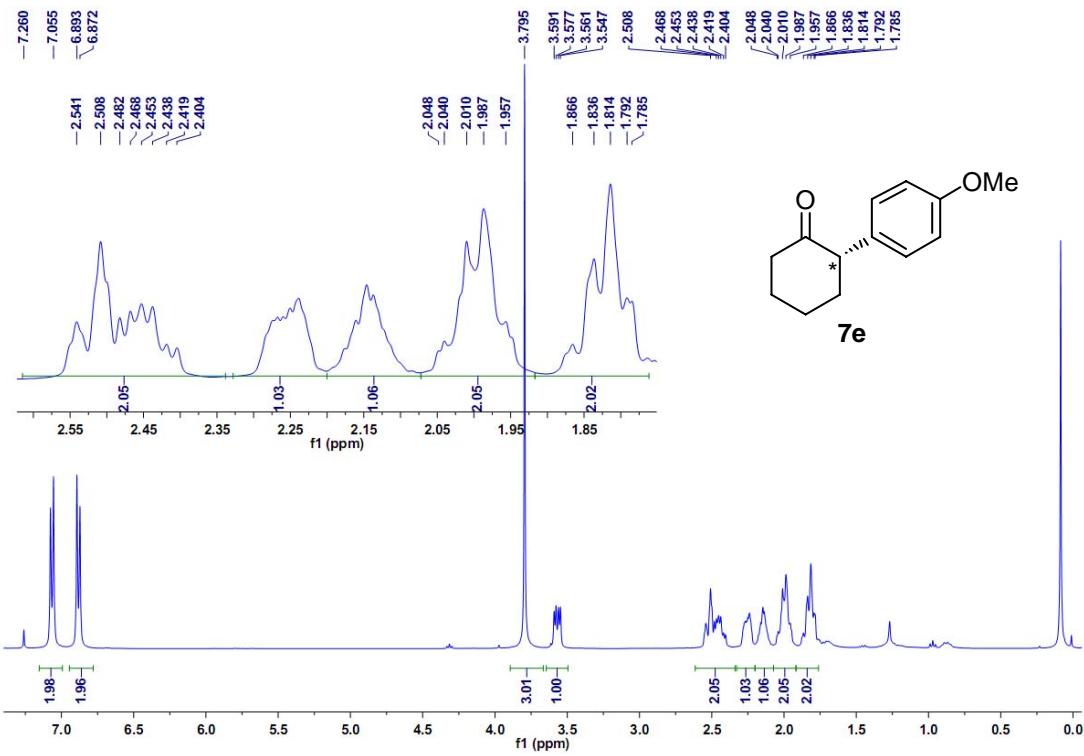
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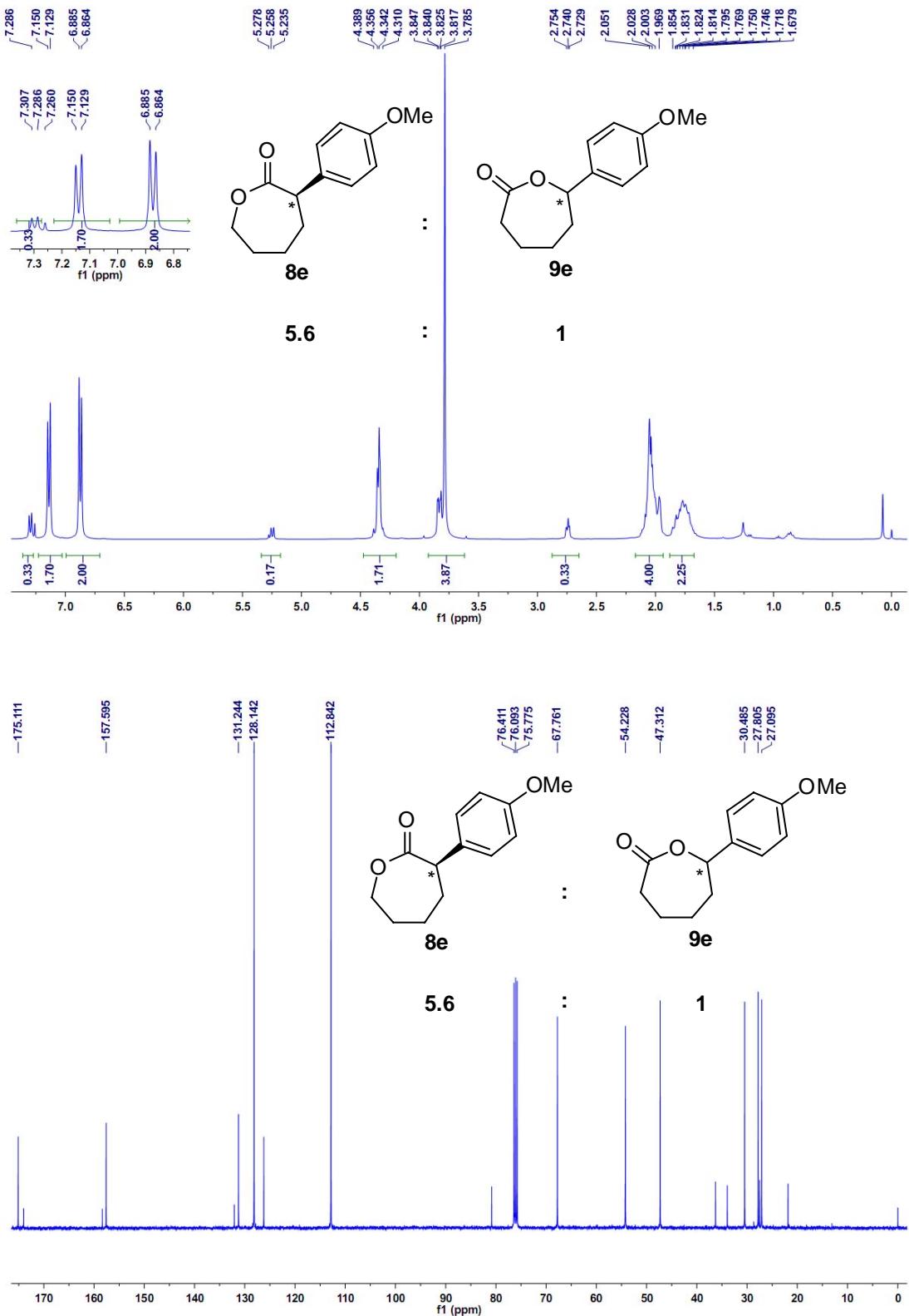


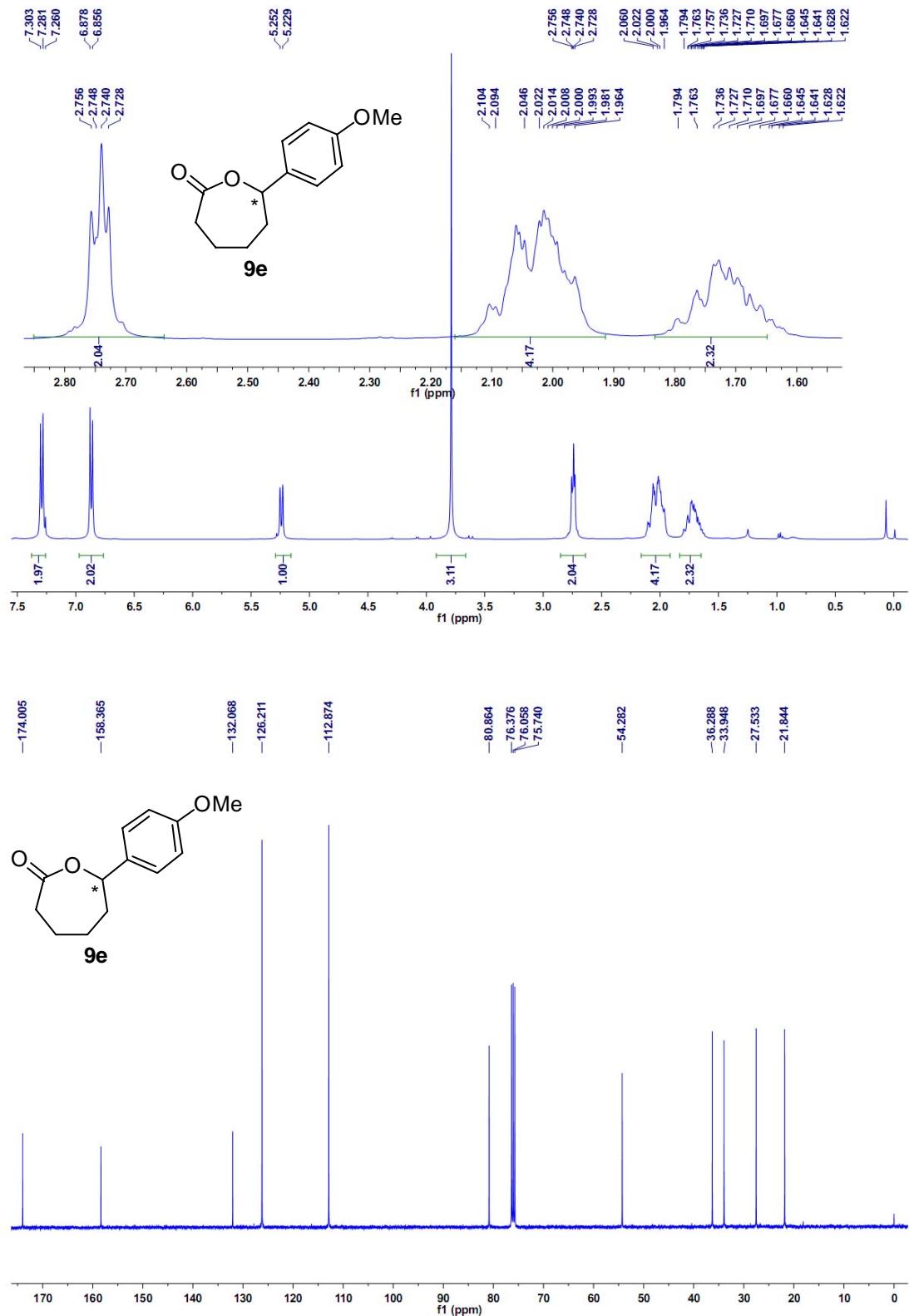
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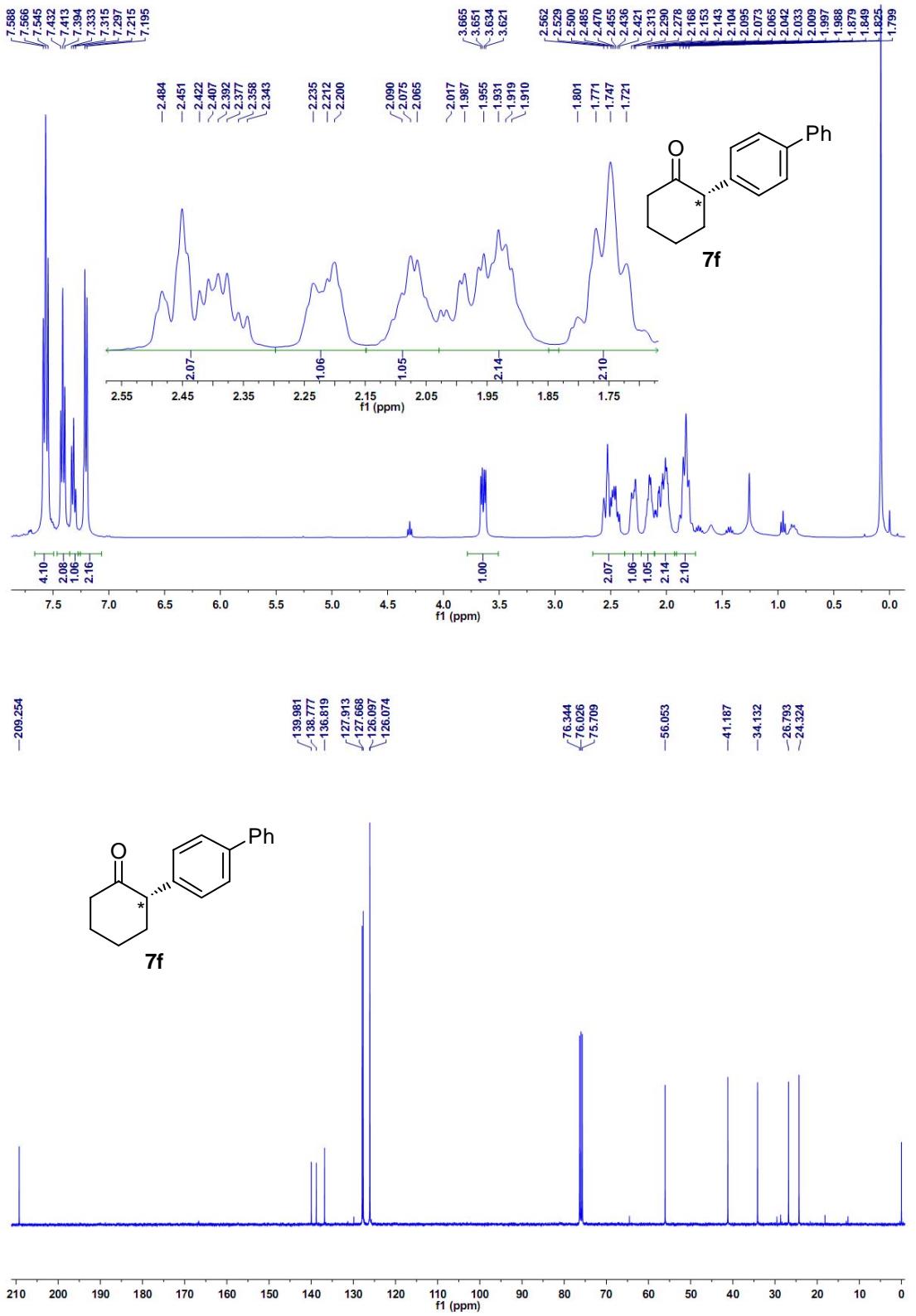


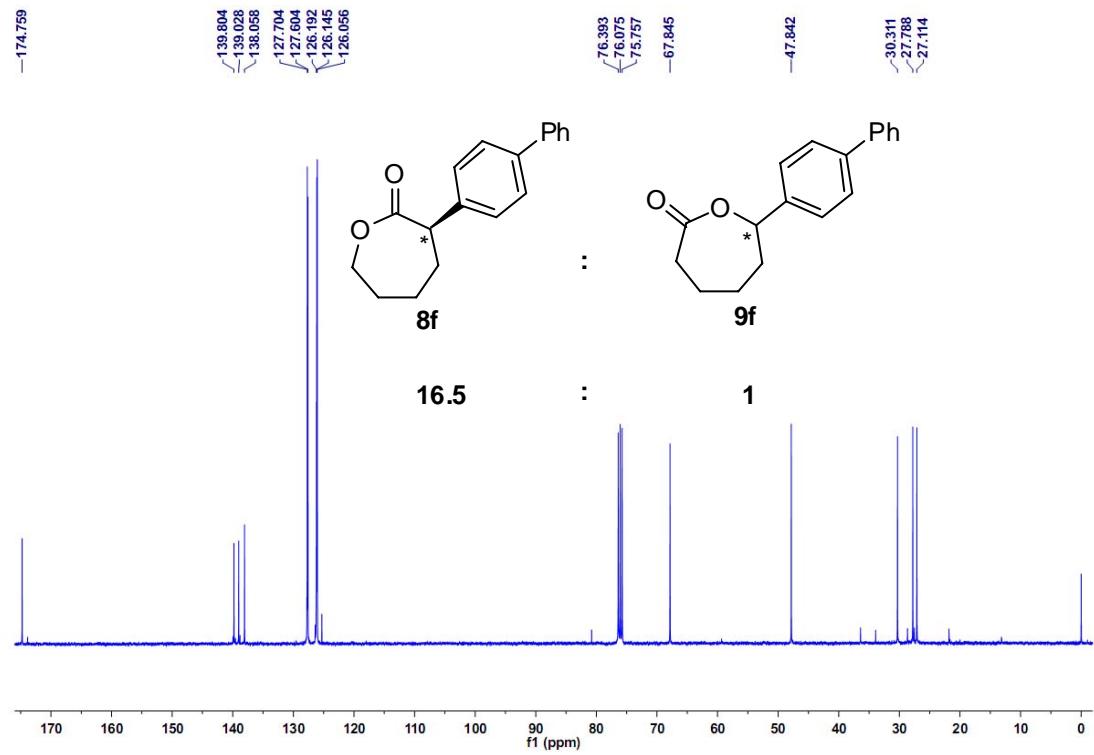
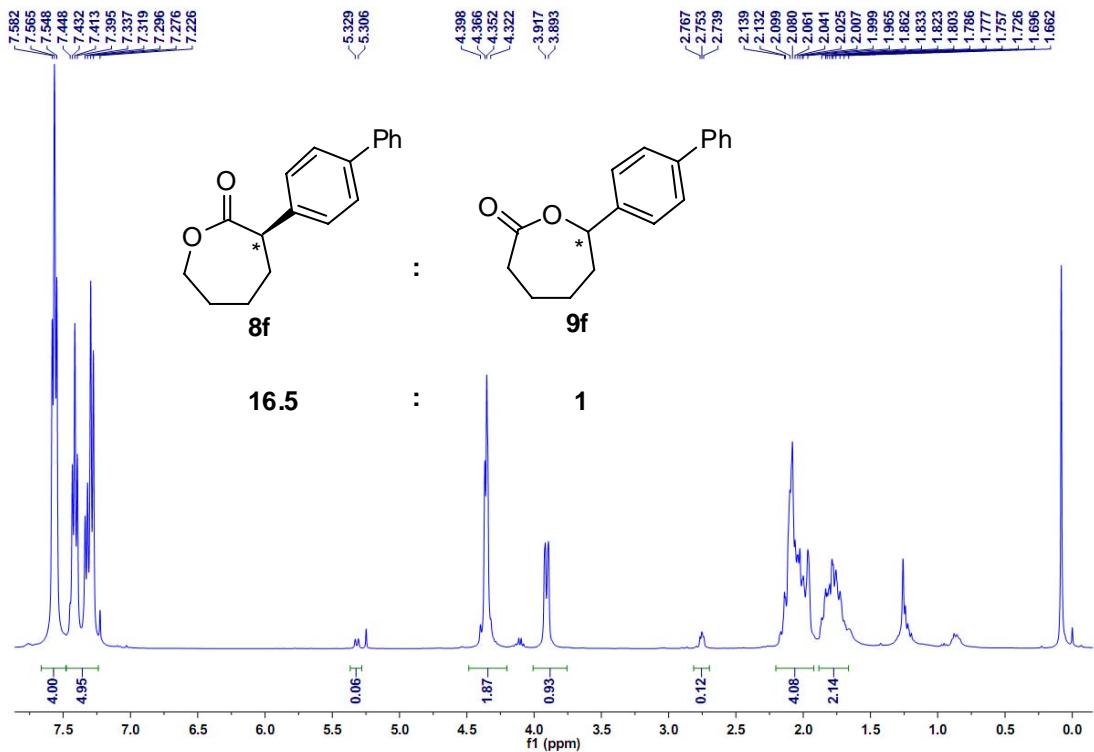


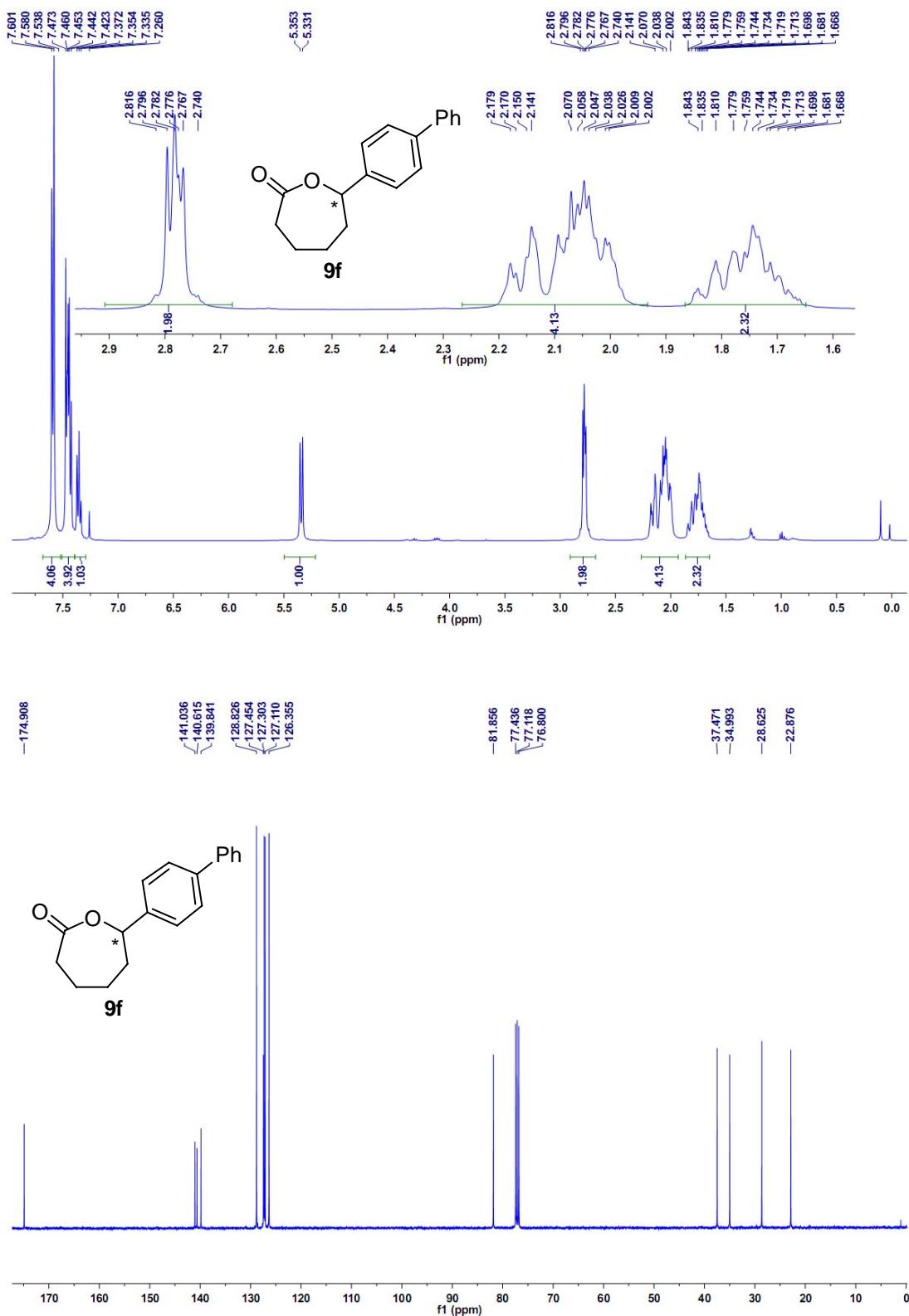


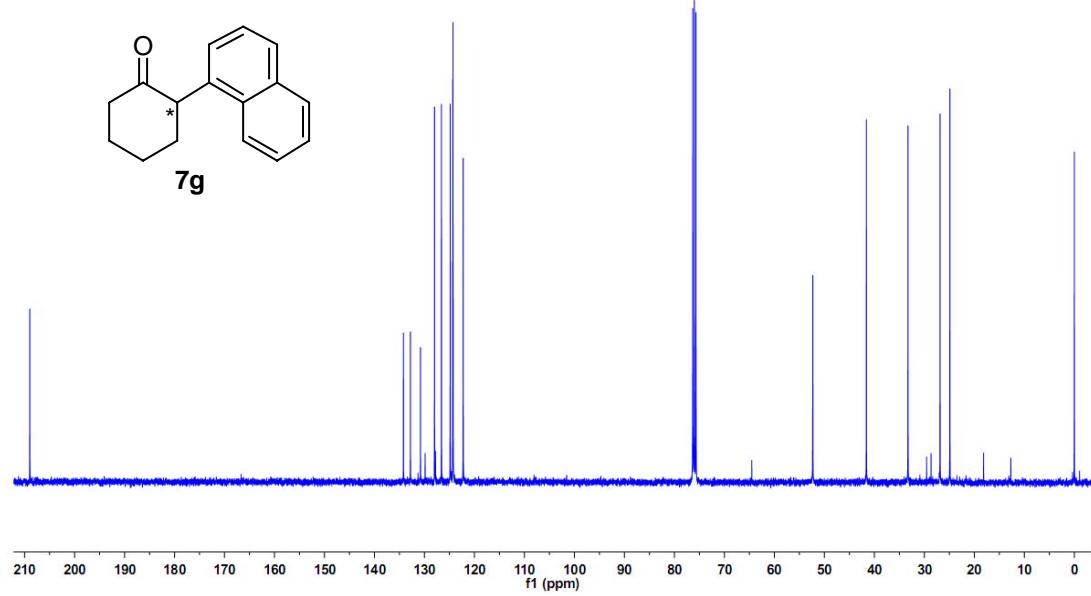
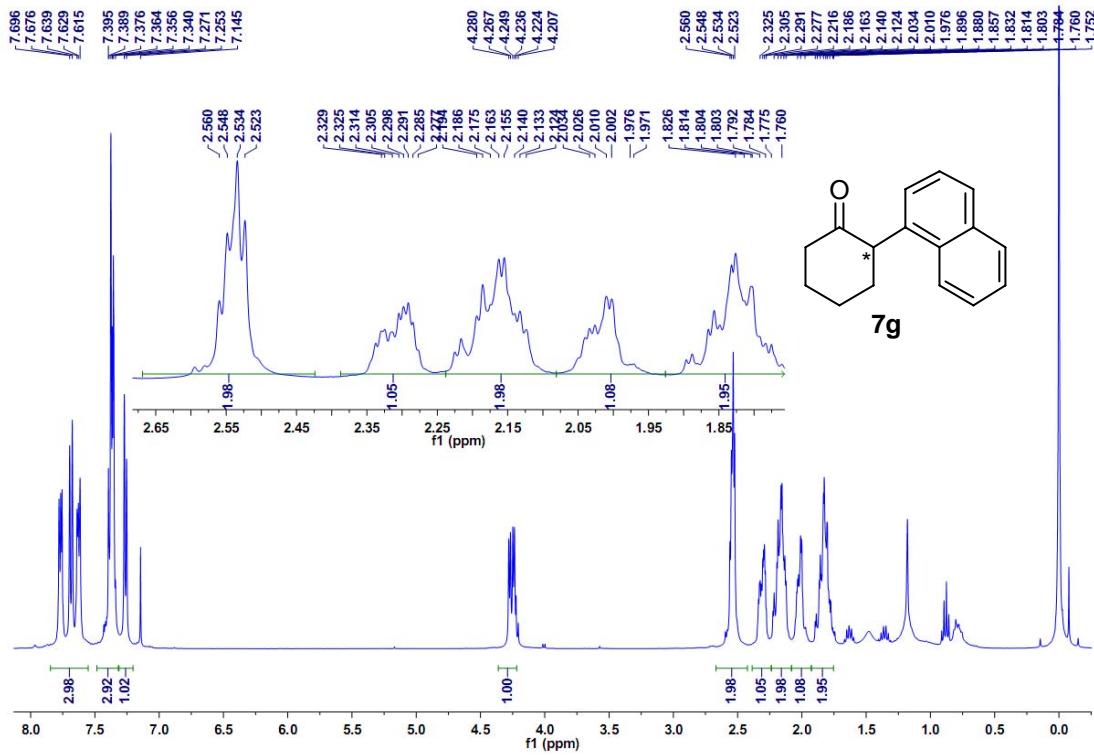


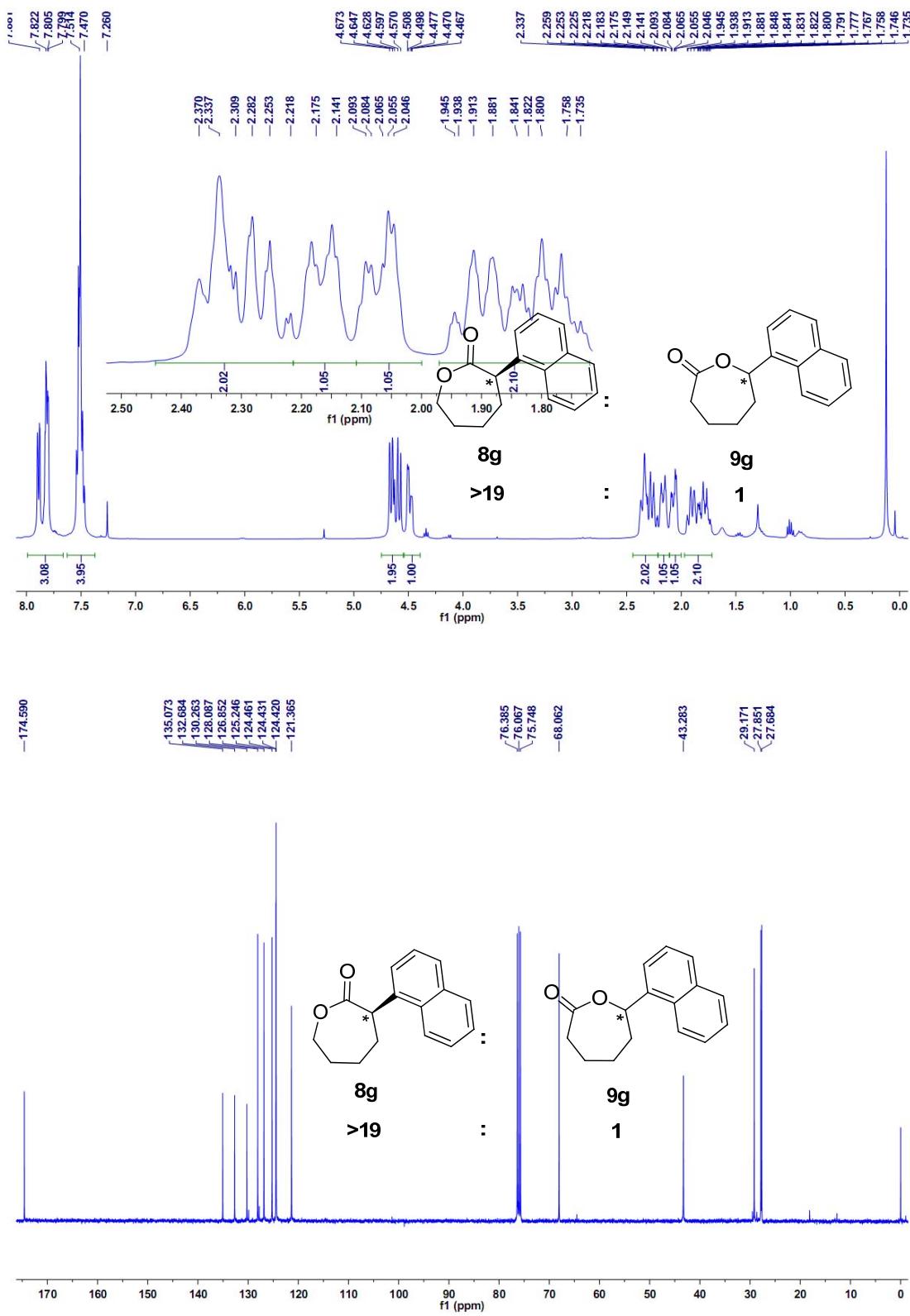


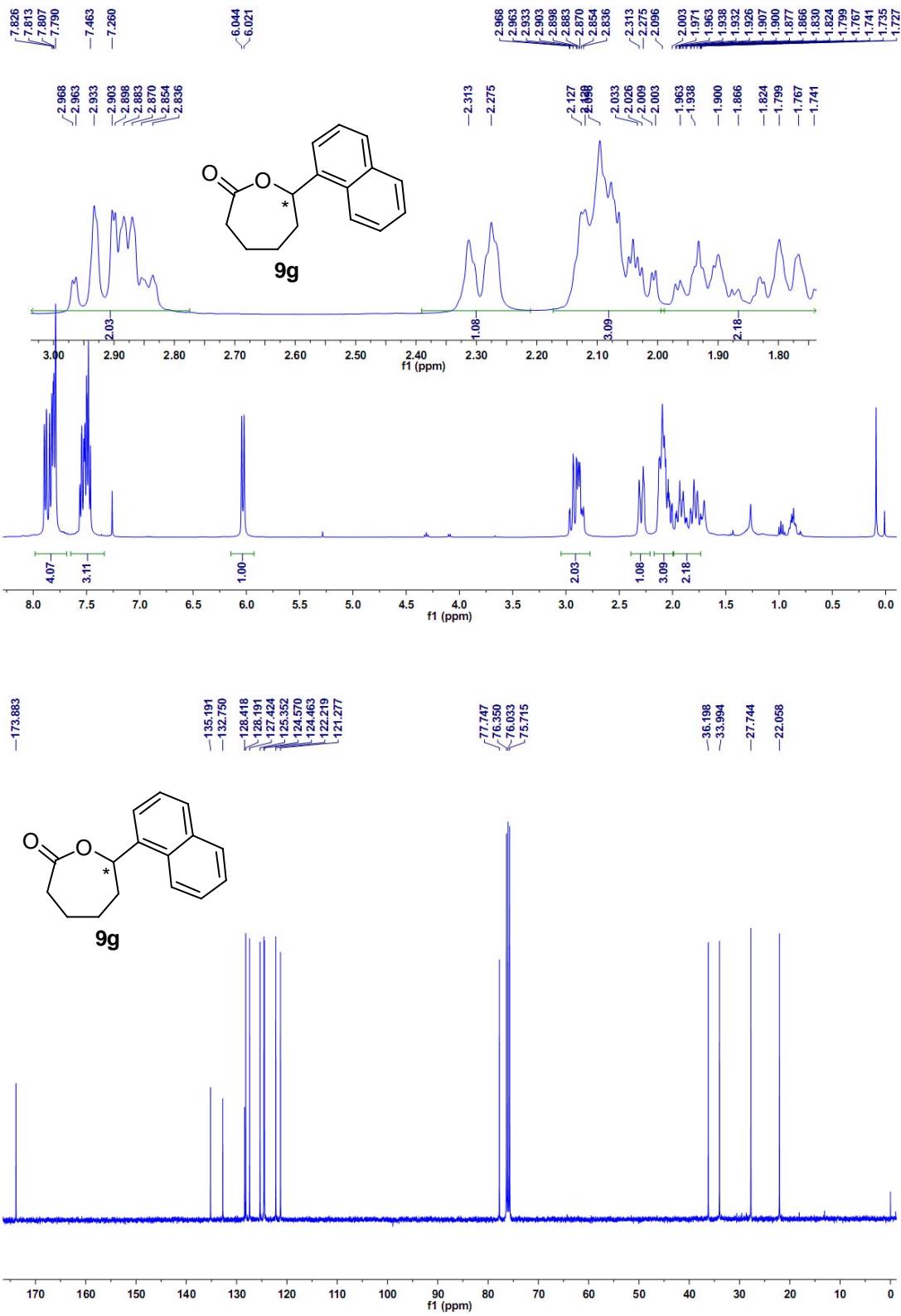


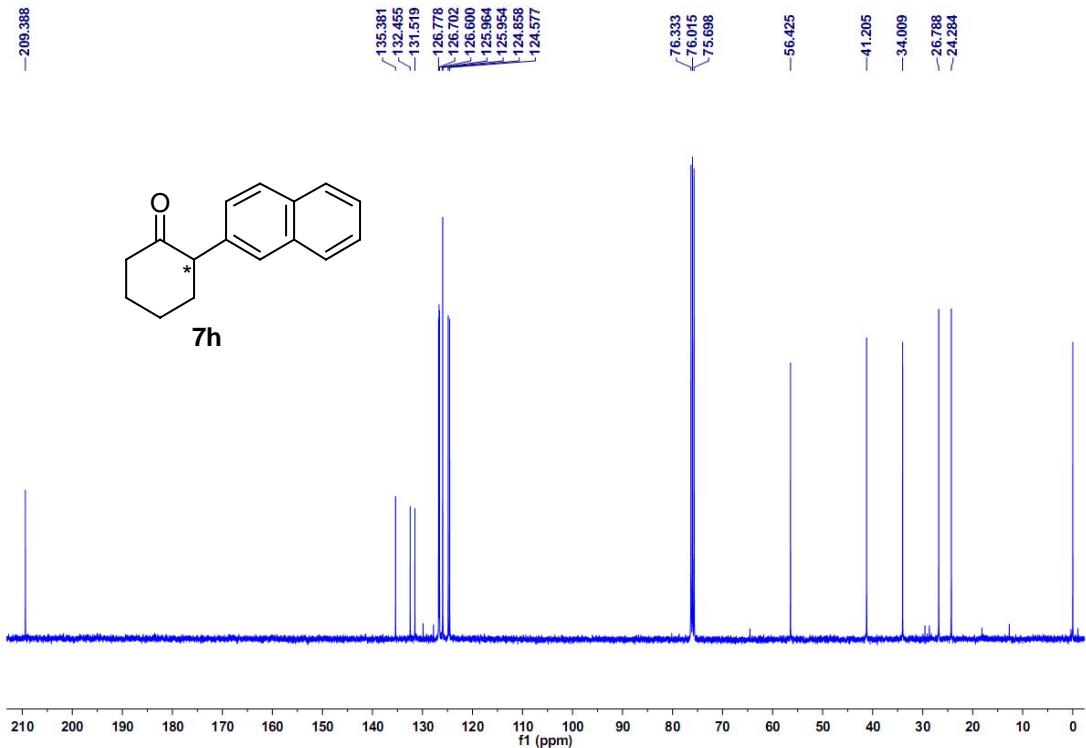
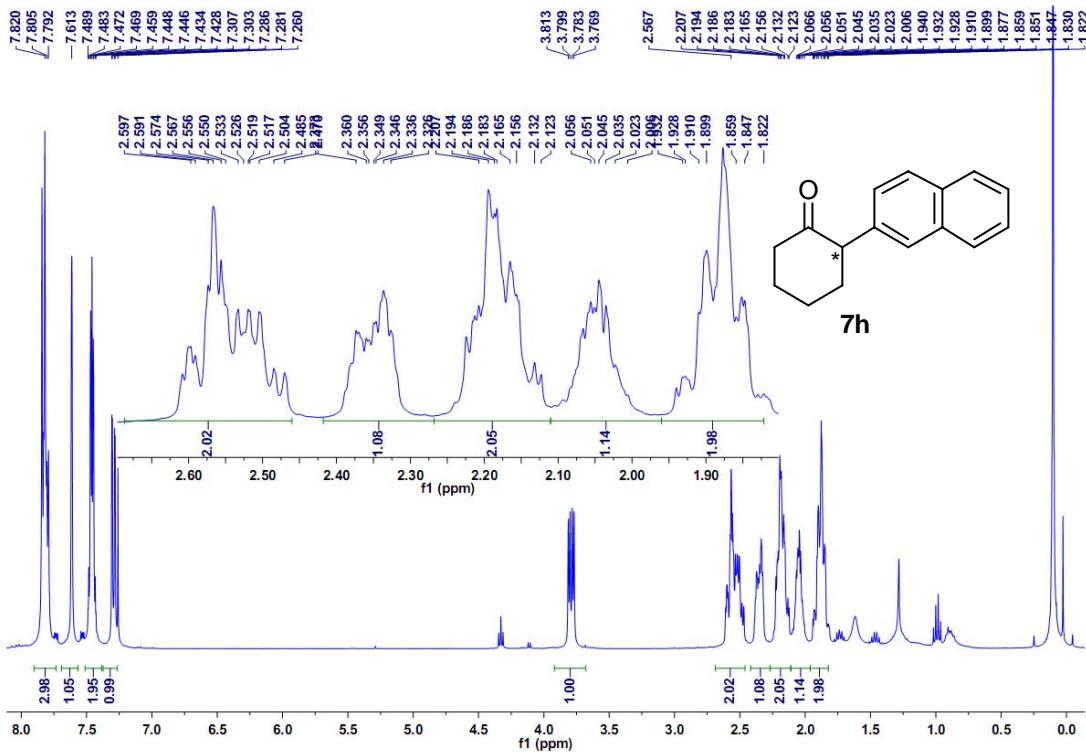


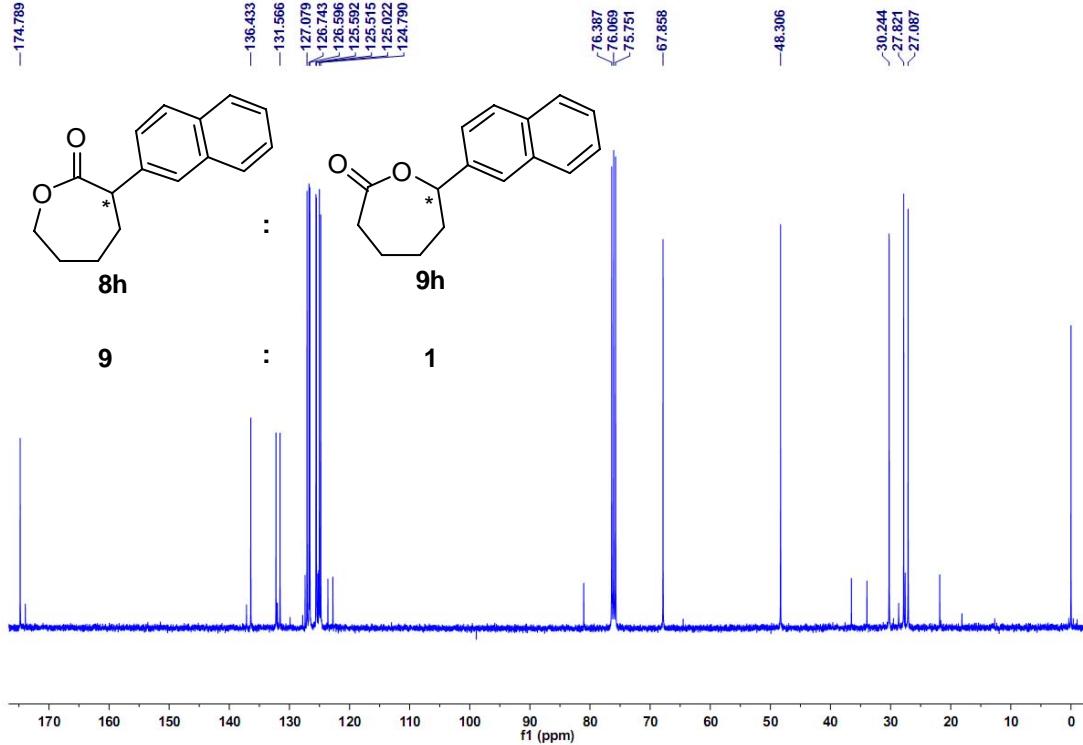
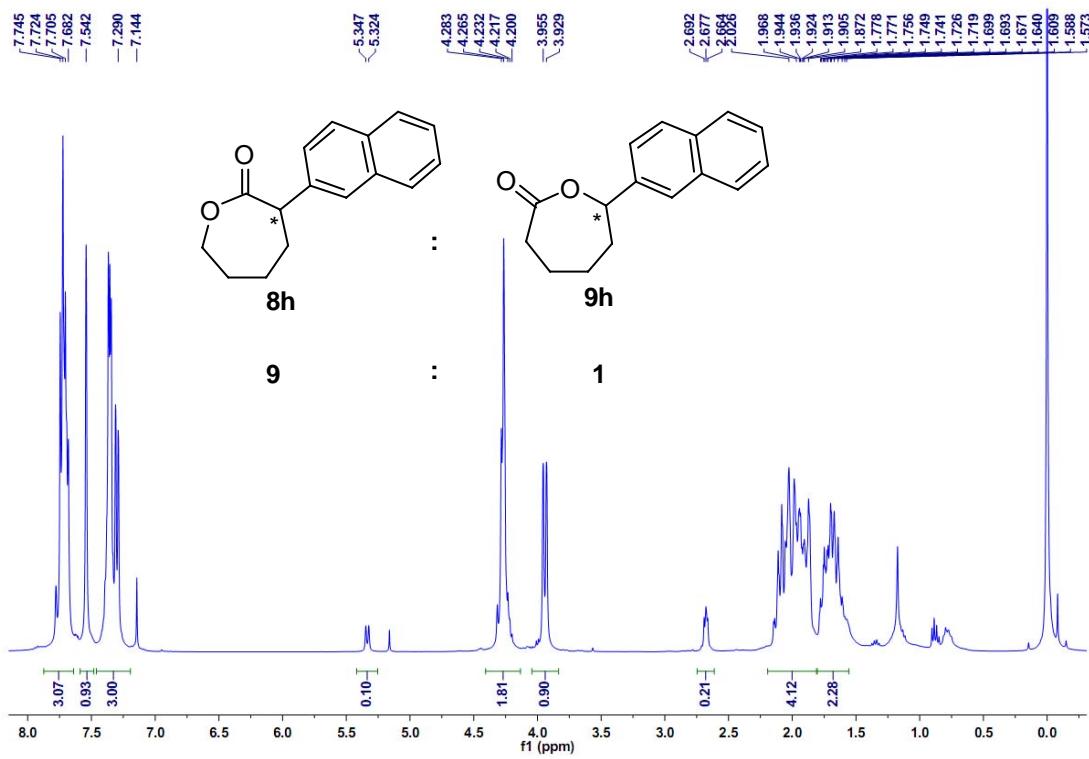


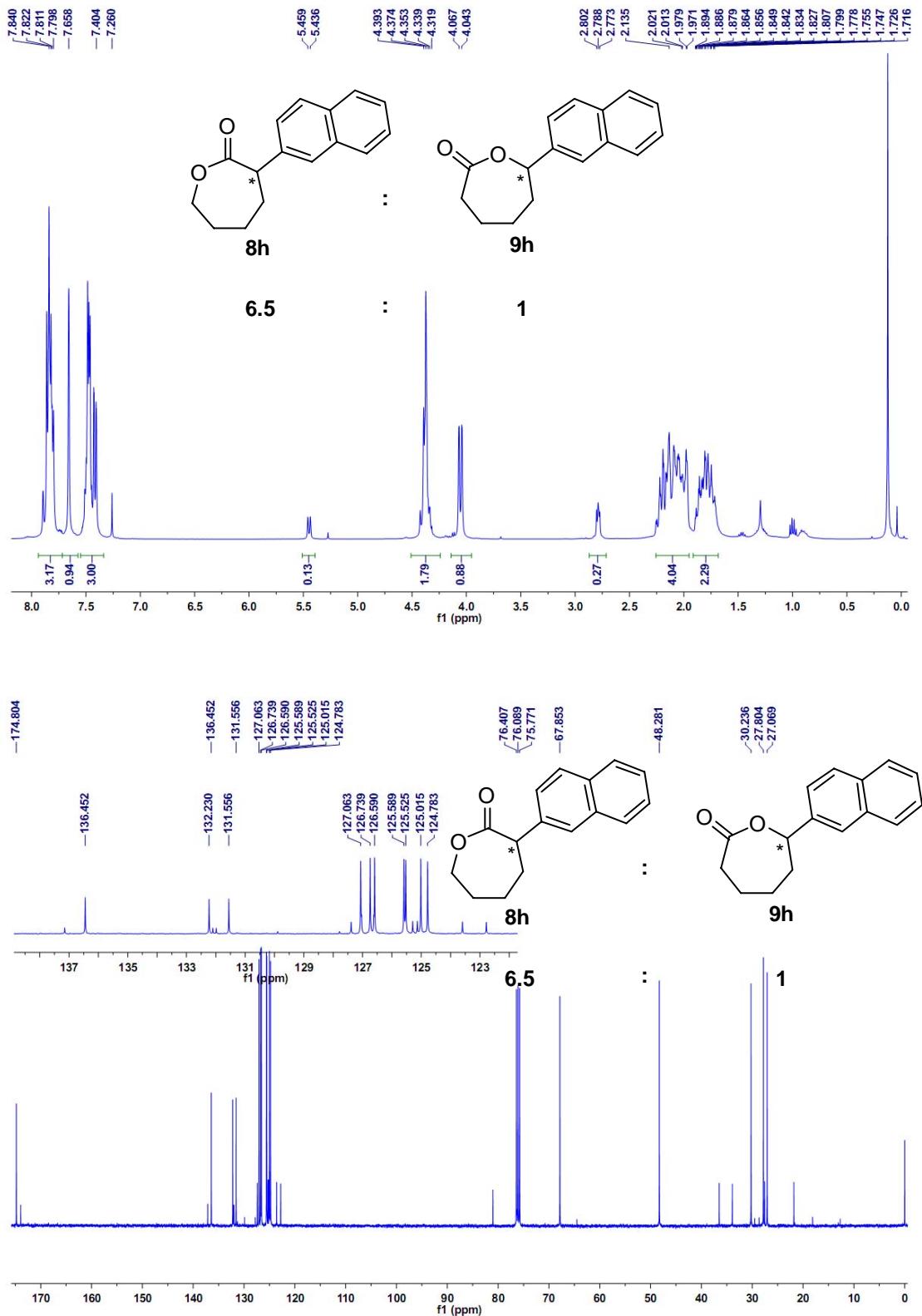


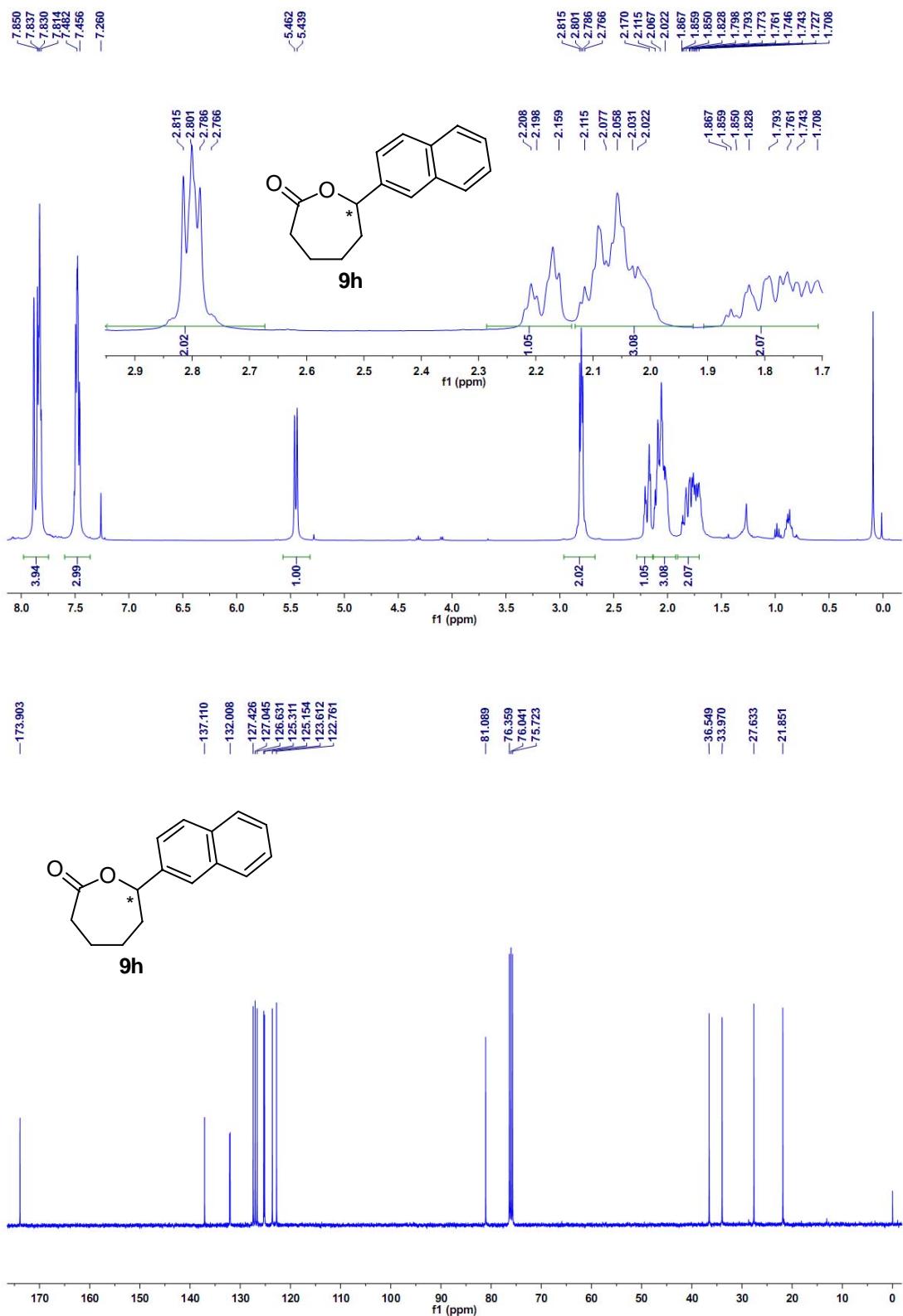


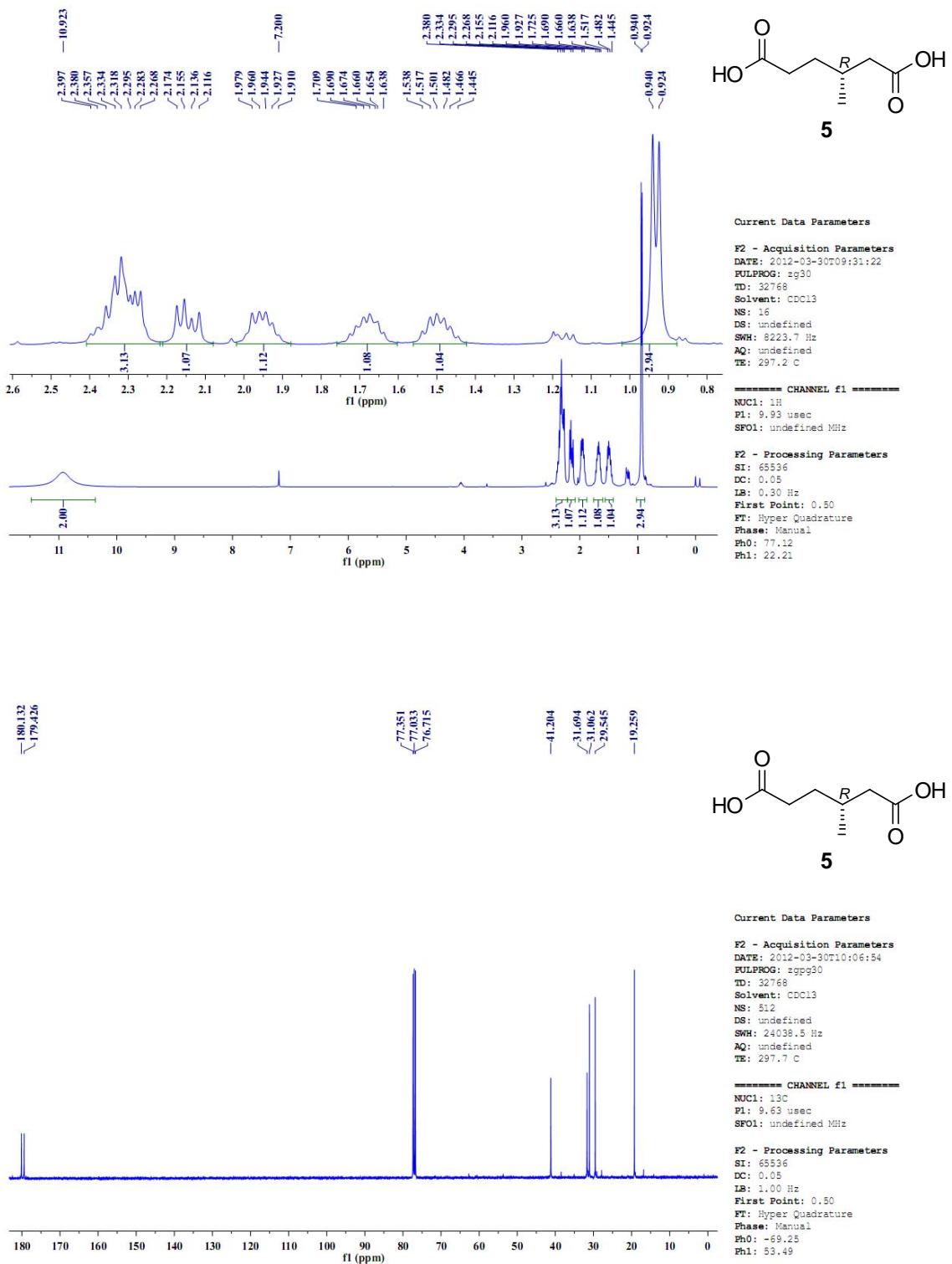


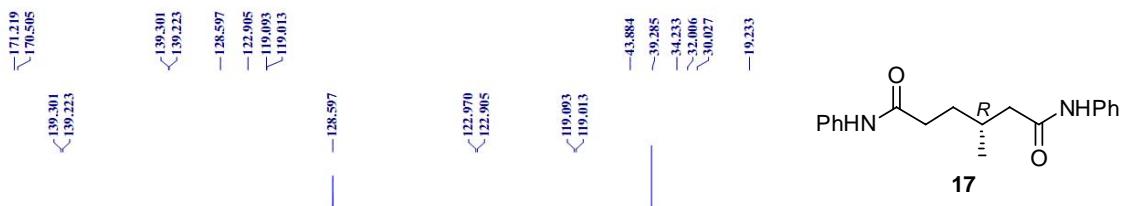
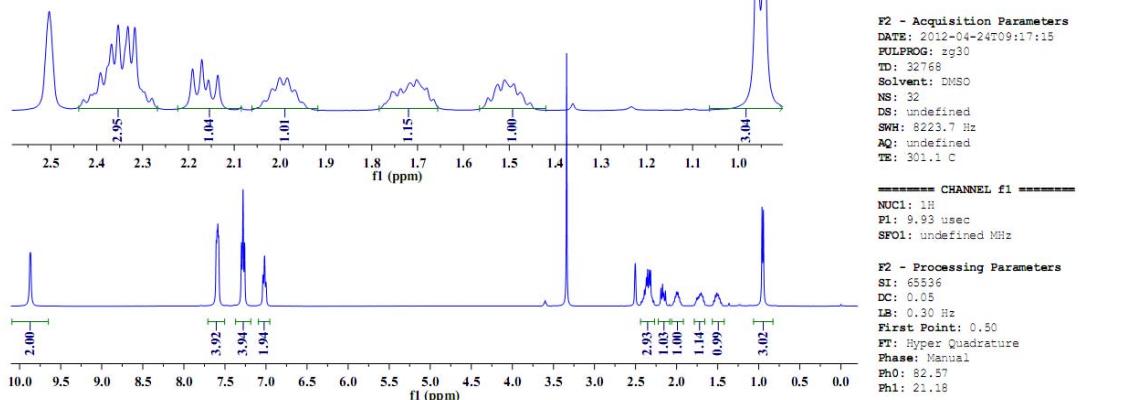
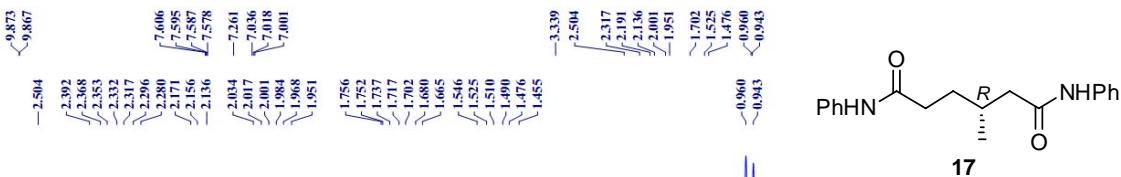












¹³C NMR (101 MHz, DMSO) δ 171.22, 170.50, 139.30, 139.22, 128.60, 122.97, 122.91, 119.09, 119.01, 43.88, 40.12, 39.91, 39.70, 39.49, 39.29, 39.08, 38.87, 34.23, 32.01, 30.03, 19.23.