Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2014

Supporting information

Trinuclear $Zn_3(OAc)_4$-3,3'-bis(aminoimino)binaphthoxide Complex for Highly Efficient Catalytic Asymmetric Iodo- and Bromolactonization

Takayoshi Arai,[a]* Noriyuki Sugiyama,[a] Hyuma Masu,[b] Sayaka Kado,[b] Shinnosuke Yabe,[c] and Masahiro Yamanaka[c]

[a]Department of Chemistry, Graduate School of Science, Chiba University
1-33 Yayoi, Inage, Chiba 263-8522, Japan
[b]Center for Analytical Instrumentation, Chiba University
1-33 Yayoi, Inage, Chiba 263-8522, Japan
[c]Department of Chemistry, Rikkyo University
3-34-1 Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8588, Japan

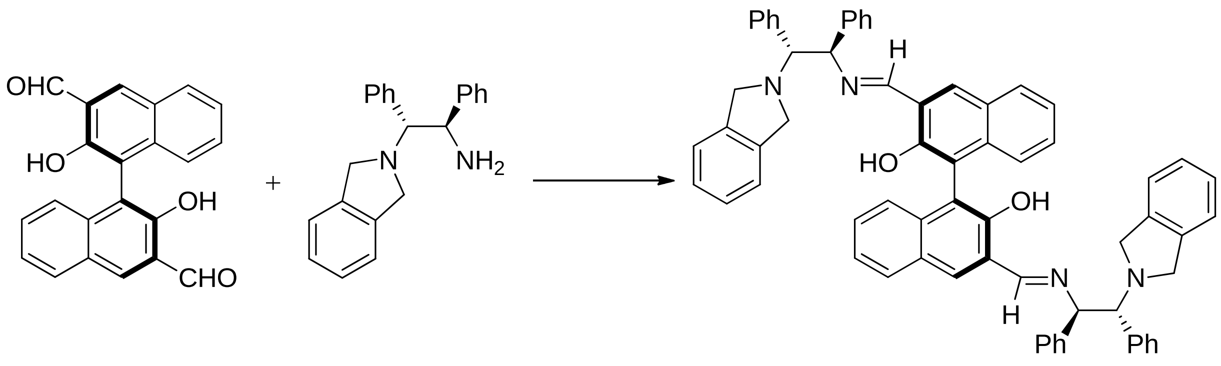
*e-mail: tarai@faculty.chiba-u.jp

Contents

1. General

Dry solvents were purchased from commercial suppliers and used without further purification. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). Silica gel column chromatography was performed on Kanto silica gel 60 (spherical, 100-210 μm). IR spectra were recorded on JASCO FT/IR-4100 using ATR. ^{1}H-NMR spectra were recorded on JEOL ECS-400 (400MHz), ECA-500 (500MHz), ECX-400 (400MHz) spectrometers. Chemical shifts of ^{1}H-NMR spectra were reported relative to tetramethyl silane (δ 0). ^{13}C-NMR spectra were recorded on JEOL ECS-400 (100MHz), ECA-500 (125MHz), ECX-400 (100MHz) spectrometers. Chemical shifts of ^{13}C-NMR spectra were reported relative to $CDCl_3$ (δ 77.0). Splitting patterns were reported as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

2. Synthesis of *(R)*-3,3'-bis((*E*)-(((*1R,2R*)-2-(isoindolin-2-yl)-1,2-diphenylethyl)imino)methyl)-[1,1'-binaphthalene]-2,2'-diol (L3)



L3

A mixture of (*R*)-2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-dicarbaldehyde[1)] (61.0 mg, 0.195 mmol) and (*1R,2R*)-2-(isoindolin-2-yl)-1,2-diphenylethanamine (0.41 mmol)[2)] in ethanol (30 mL) was heated to reflux. After being stirred for 24 hours, the solvent was removed under reduced pressure and the resulting residue was washed with cold ethanol to give **L3** as a yellow brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 2H), 7.96 (s, 2H), 7.88 (d, *J*=7.73 Hz, 2H), 7.37-7.30 (m, 6H), 7.14-7.00 (m, 30 H), 4.95 (d, *J*=7.45 Hz, 2H), 4.25 (d, *J*=7.45 Hz, 2H), 4.05 (d, *J*=11.46 Hz, 4H), 3.98 (d, *J*=11.46 Hz, 4H); ^{13}C NMR (125MHz, $CDCl_3$) δ164.97, 154.57, 139.89, 139.48, 138.02, 135.27, 133.92, 129.54, 128.89, 128.26, 128.11, 127.93, 127.74, 127.62, 127.22, 127.06, 126.58, 124.94, 123.35, 122.12, 121.09, 116.59, 78.70, 77.54, 58.32; HRMS calced for $C_{66}H_{55}O_2N_4$ $(M+H)^+$: 935.4320, found: *m/z* 935.4314; $[\alpha]_D^{20.0}$= +30.6 (c=0.115, $CHCl_3$); IR (neat) 3696, 3028, 2870, 2783, 1628, 1494, 1464, 1451, 1384, 1341, 1316, 1299, 1263, 1176, 1149, 1119, 1073, 1053, 1028, 934 cm^{-1}.

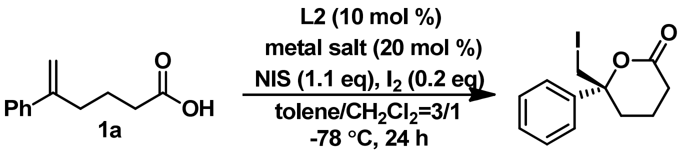
1) Belkon, Y. N.; Chusov, D.; Borkin, D. A.; Yashkina, L. V.; Dmitriev, A. V.; Katayev, D.; North, M. *Tetrahedron: Asymmetry* **2006**, *17*, 2328-2333.

2) Arai, T.; Watanabe, M.; Yanagisawa, A. *Org. Lett*. **2007**, *9*, 3595-3597.

3. Reaction optimization of enantioselective iodolactonization

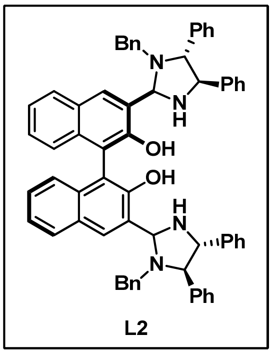
First, the effects of metal salts were investigated using *in situ* prepared-**L2** ligand (Table S1, entry 1~6). By using $Zn(OAc)_2$, we obtained iodolactone in good yield and excellent enantioselectivity. The **L2’** (diastereomer of **L2**) prepared from (*R*)-2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-dicarbaldehyde and (*1S*,*2S*)-*N1*-benzyl-1,2-diphenylethane-1,2-diamine was less effective in the $Zn(OAc)_2$-catalyzed asymmetric iodolactonization than that of **L2**-$Zn(OAc)_2$ catalyst (entry 7).

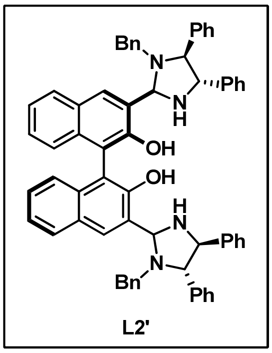
Table S1. Optimization of metal salts



entry	metal salt	yield (%)	ee (%)
1	$Ni(OAc)_2 \bullet 4H_2O$	>99	41
2	$Co(OAc)_2 \bullet 4H_2O$	79	17
3	$Cu(OAc)_2$	93	56
4	$Zn(OAc)_2$	78	98
5	$ZnCl_2$	80	36
6	$Zn(CN)_2$	>99	20
7[a)]	$Zn(OAc)_2$	92	85

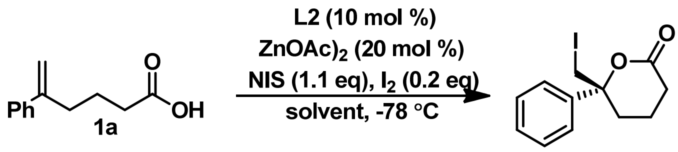
a) L2' was used as a ligand.





In the further optimization, effects of solvents and additives were studied in Table S2. The condition examined in Entry 3 gave the best result, and we selected this as an optimized condition.

Table S2. Optimization of solvents and additives



entry	solvent	x (eq)	y (eq)	time (h)	yield (%)	ee (%)
1	toluene only	1.1	0.2	24	54	88
2	CH_2Cl_2 only	1.1	0.2	3.5	91	69
3	toluene/CH_2Cl_2 =3/1	1.1	0.2	24	75	98
4	toluene/CH_3Cl =3/1	1.1	0.2	24	61	95
5	toluene/CH_2Cl_2 =3/1	1.1	0	24	9	86
6	toluene/CH_2Cl_2 =3/1	0	0.2	24	15	39

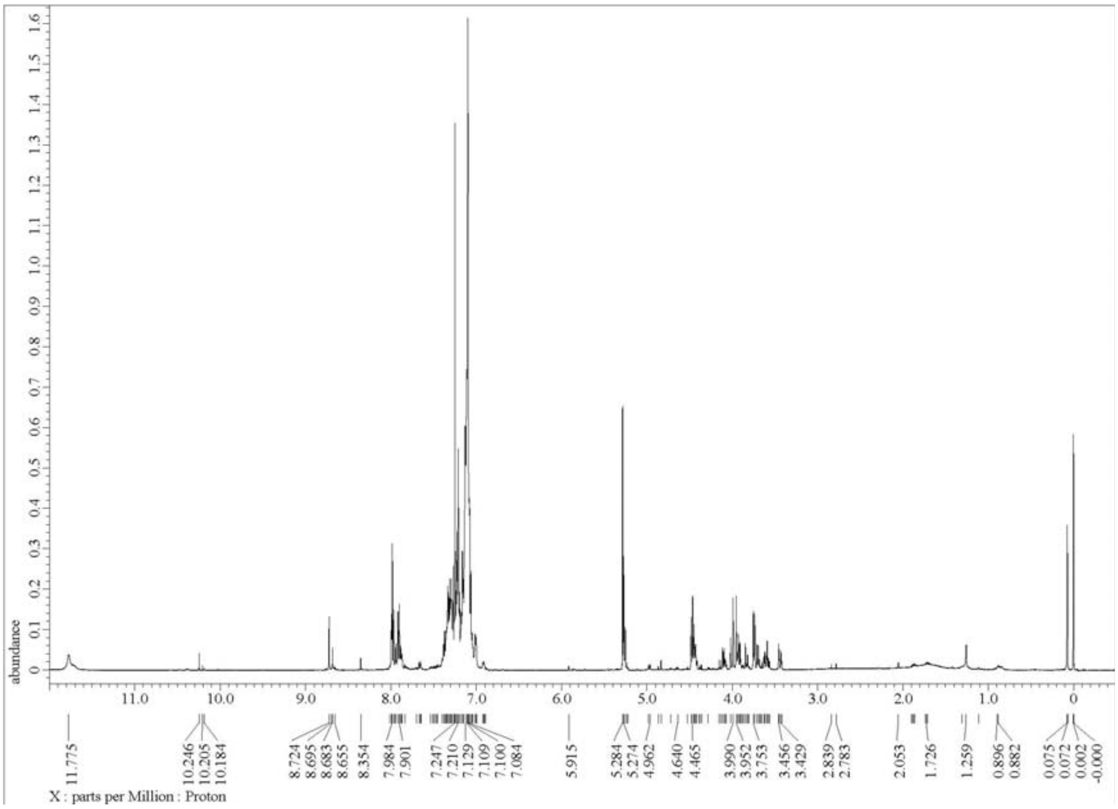
4. General procedure of enantioselective iodolactonization (Table 2, entries 1-14).

A mixture of **L3** (0.001 mmol) and $Zn(OAc)_2$ (0.003 mmol) was stirred for 0.5 hour in anhydrous dichloromethane (1.0 ml) at rt. After cooling the mixture to -78 °C, carboxylic acid (0.1 mmol) in toluene (3.0 ml) was slowly added to the resulting yellow solution and stirred for 0.5 hour at the same temperature. Then, *N*-iodosuccinimide (NIS) (24.6 mg, 0.11 mmol) and I_2 (5.0 mg, 0.02 mmol) were added to the reaction mixture. After being stirred for appropriate time, the reaction mixture was quenched with saturated Na_2SO_3 aq and 1*N* NaOH aq, and then the products were extracted with dichloromethane in 3 times. The collected organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromathography (hexane/acetone=8/1) to afford the iodolactone. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H and Chiralpak AD-H column.

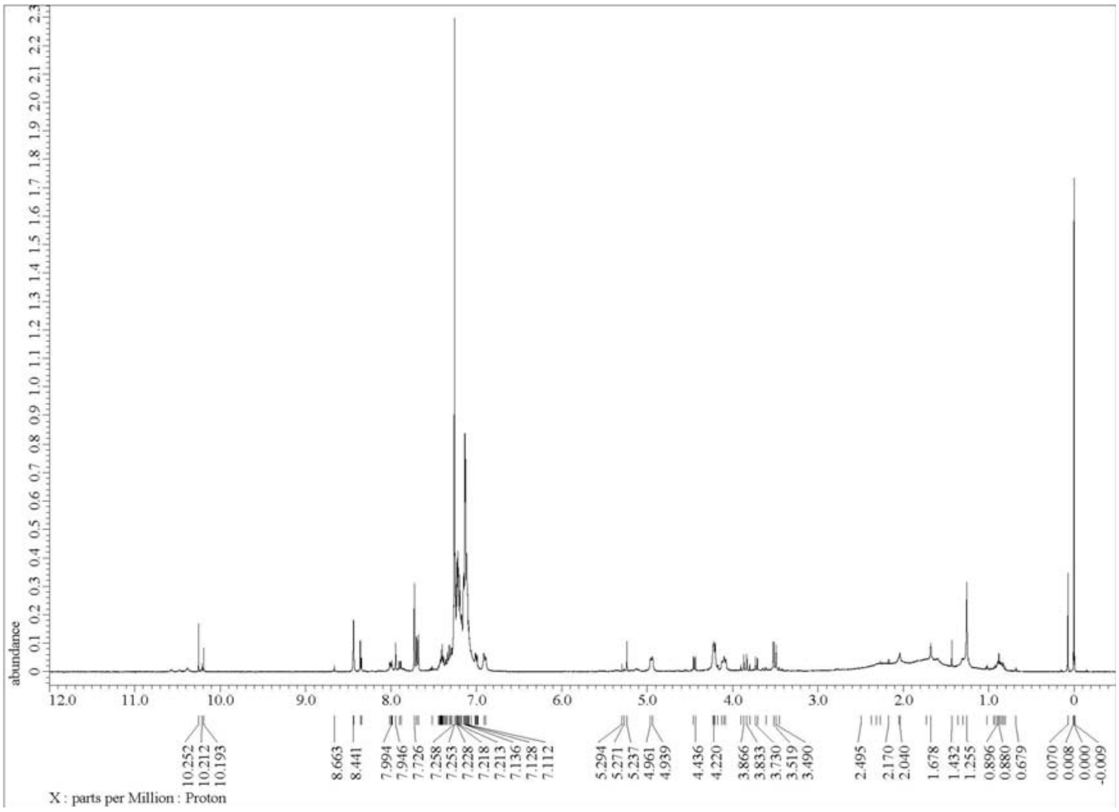
5. ^{1}H-NMR study for ligand-Zn(OAc)$_2$ species

The *in situ* prepared **L2** and *in situ* prepared **L2-**Zn(OAc)$_2$ gave complex ^{1}H-NMR spectra in $CDCl_3$ at room temperature (Figure S1a and S1b). Although **L2** was successfully purified (Figure S1c), the isolated **L2** gave iodolactone **2a** with lower 62% ee in the Zn(OAc)$_2$-catalyzed reaction.

S1a) ***in situ*** **prepared L2**



S1b) *in situ* prepared L2-Zn(OAc)$_2$ complex



S1c) L2

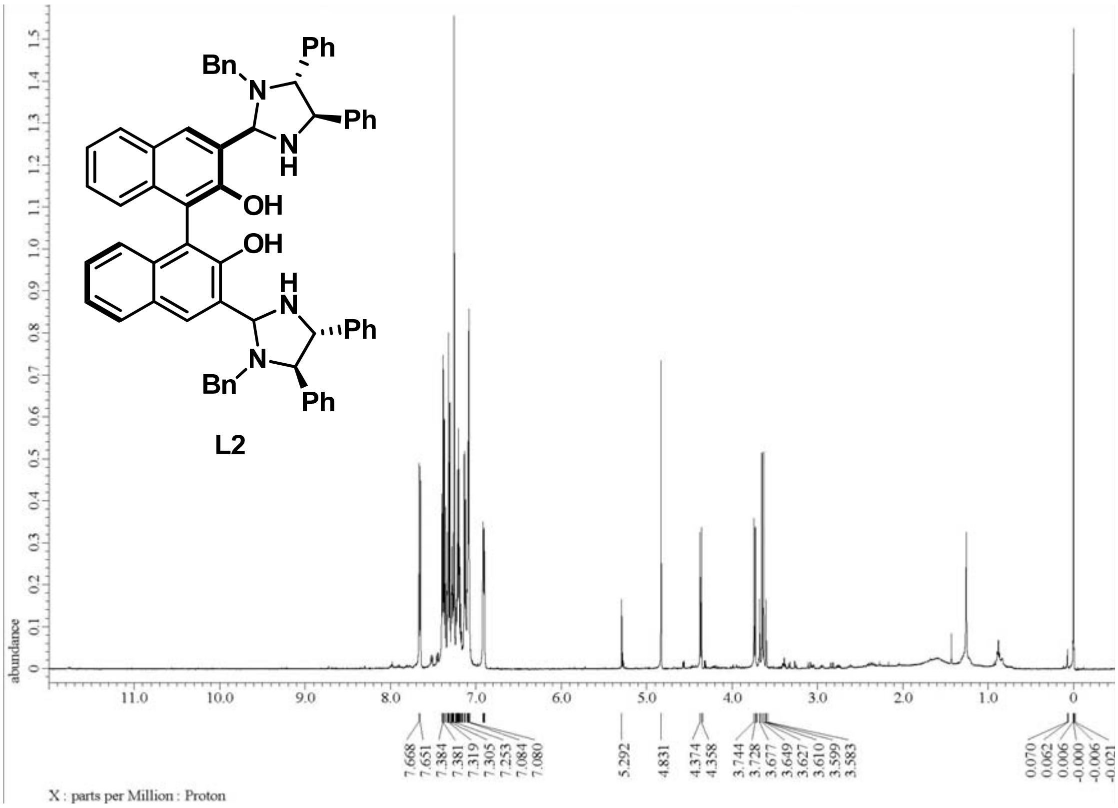
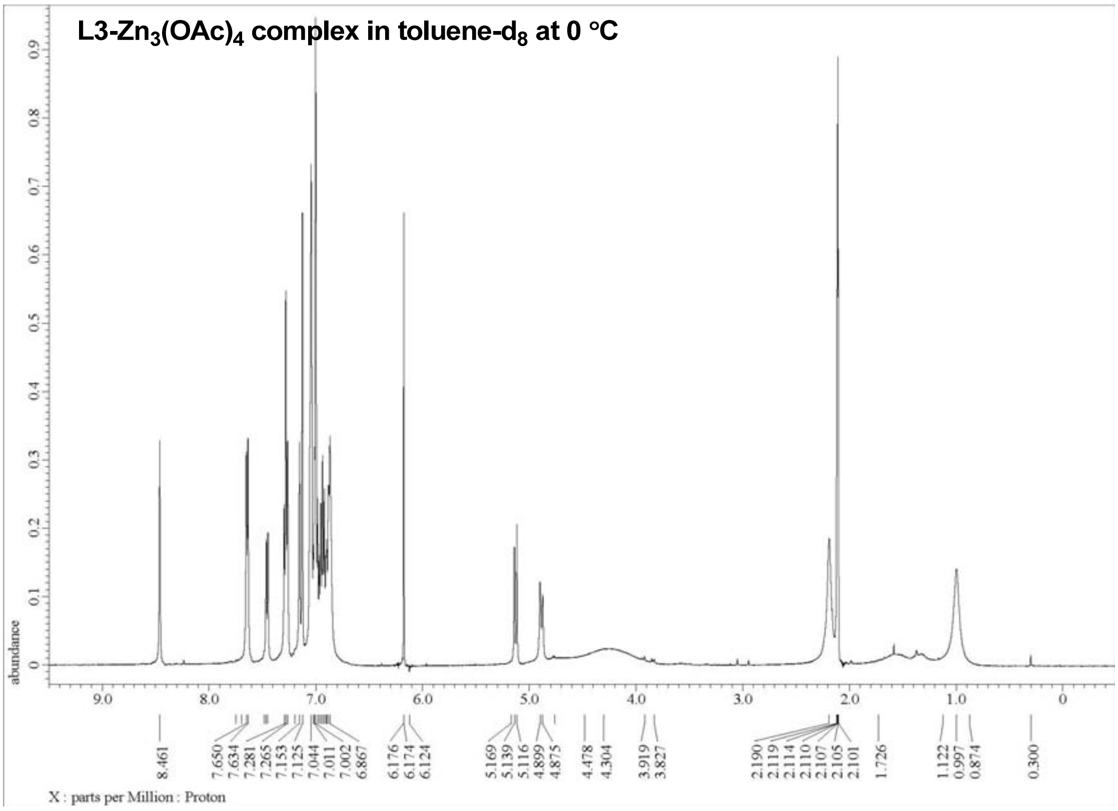


Figure S1. ^{1}H-NMR spectrum of a) *in situ* prepared L2, b) *in situ* prepared L2-Zn (OAc)$_2$ complex, c) L2.

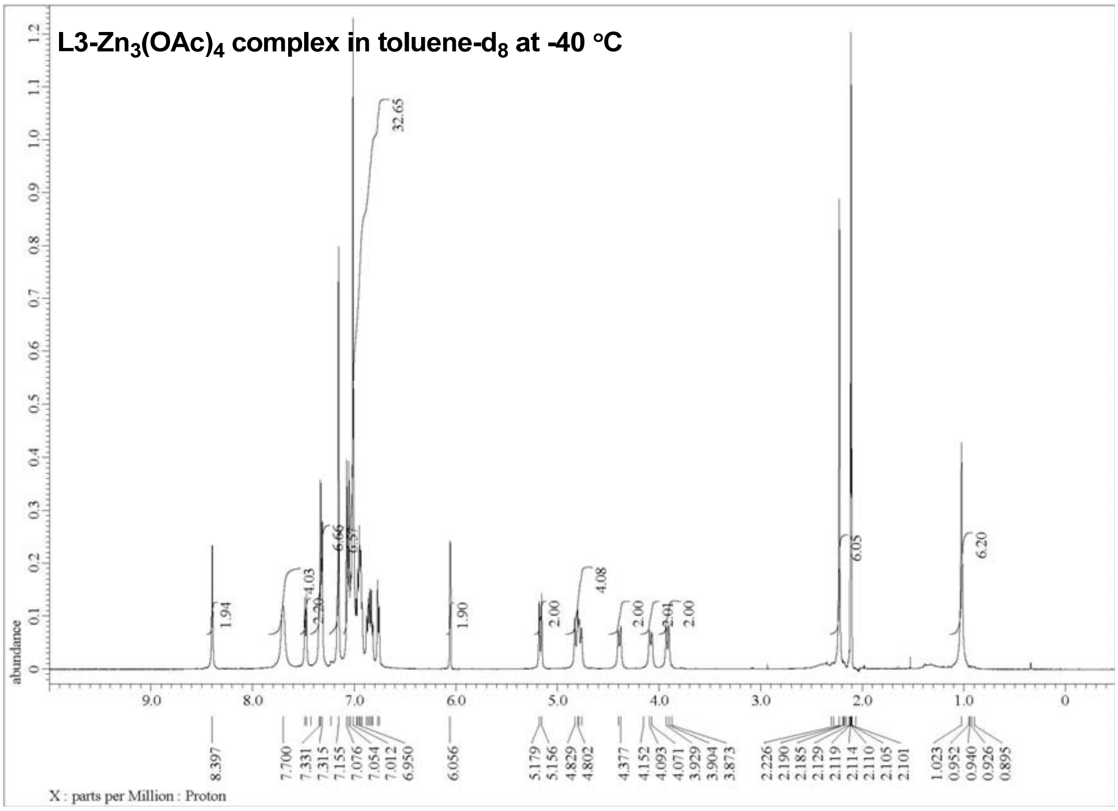
The VT-NMR spectra were shown in Figure S2. Although the ^{1}H-NMR spectra of **L3**-$Zn_3(OAc)_4$ in toluene-d_8 is broad at 0 °C (Figure S2a), the resolution is improved at -40 °C (Figure S2b). The ^{13}C-NMR spectrum of **L3**-$Zn_3(OAc)_4$ in toluene-d_8 at -40 °C is also provided in Figure 2c.

^{1}H-NMR and ^{13}C-NMR spectra data for **L3**-$Zn_3(OAc)_4$ are shown here. ^{1}H NMR (500 MHz, toluene-d_8 at -40 °C) δ 8.40 (s, 2H), 7.70 (br, 4H), 7.48 (d, *J*= 8.31 Hz, 2H), 7.35-7.32 (m, 6H), 7.23-7.14 (m, 6H), 7.08-6.70 (m, 18H), 6.06 (s, 2H), 5.17 (d, *J*= 11.46 Hz, 2H), 4.83-4.76 (m, 4H), 4.39 (d, *J*= 11.74 Hz, 2H), 4.08 (d, *J*= 11.17 Hz, 2H), 3.92 (d, *J*= 12.31 Hz, 2H), 2.23 (s, 6H), 1.02 (s, 6H); ^{13}C-NMR (125 MHz, toluene-d_8 at -40 °C) 184.95, 176.08, 159.92, 143.85, 138.54, 133.05, 130.94,127.61, 125.54, 123.83, 123.56, 123.21, 71.59, 68.39, 56.66, 54.39, 51.940, 24.95 (Several peaks are not detected because of overlapping with toluene's peaks.)

S2a)



S2b)



S2c)

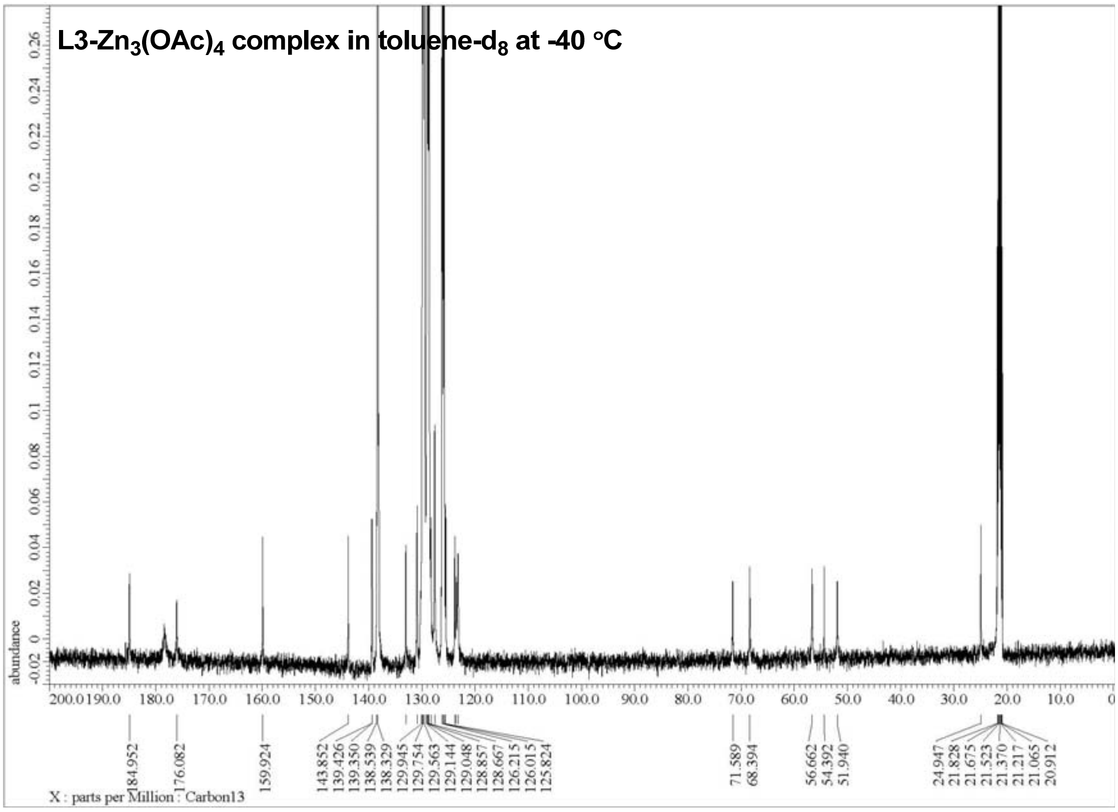
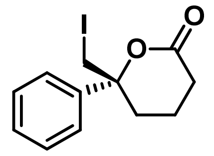


Figure S2. **^{1}H-NMR spectrum of L3-$Zn_3(OAc)_4$ in toluene-d_8 a) at 0 °C, b) at -40 °C, c) ^{13}C-NMR spectrum of L3-$Zn_3(OAc)_4$ in toluene-d_8 at -40 °C.**

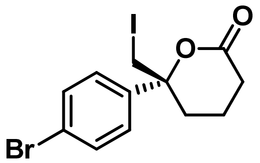
6. Analytical data for product of iodolactonization and bromolactonization

(*R*)-6-(iodomethyl)-6-phenyltetrahydro-*2H*-pyran-2-one (2a)



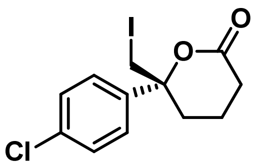
TLC R*f* = 0.40 (hexane : ethyl acetate = 2:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.33 (m, 5H), 3.57 (dd, *J*=11.3, 11.1 Hz, 2H), 2.55-2.30 (m, 4H), 1.87-1.79 (m, 1H), 1.63-1.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 140.1, 129.0, 128.4, 125.1, 84.4, 32.0, 28.9, 17.7, 16.5; HRMS calced for $C_{12}H_{14}O_2I$ $(M+H)^+$: 317.0033, found: *m/z* 317.0031; Enantiomeric excess was determined by HPLC with a Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_r = 14.5 min, major enantiomer t_r = 16.3 min; 99.5% ee; $[\alpha]_D^{22.0}$= -31.6 (c=1.0, $CHCl_3$, 99.5% ee) ; IR (neat) 2956, 2933, 2863, 1734, 1682, 1575, 1388, 1276, 1130, 879 cm^{-1}

(*R*)-6-(4-bromophenyl)-6-(iodomethyl)tetrahydro-2*H*-pyran-2-one (2b)



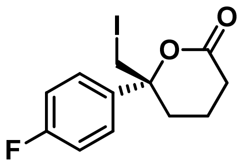
TLC R*f* = 0.33 (hexane : ethyl acetate = 2:1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J*= 8.59 Hz, 2H), 7.25 (d, *J*=8.59 Hz, 2H), 3.54 (s, 2H), 2.54-2.30 (m, 4H), 1.88-1.83 (m, 1H), 1.62-1.55 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 170.0, 139.3, 132.1, 127.0, 122.6, 84.1, 31.9, 28.9, 16.9, 16.5; Enantiomeric excess was determined by HPLC with a Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_r = 17.8 min, major enantiomer t_r = 23.4 min; 99.8% ee; $[\alpha]_D^{22.0}$= -30.4 (c=1.0, $CHCl_3$, 99.8% ee) ; IR (neat) 2957, 2929, 1740, 1489, 1238, 1180, 1132, 1039 cm^{-1}

(*R*)-6-(4-chlorophenyl)-6-(iodomethyl)tetrahydro-2*H*-pyran-2-one (2c)



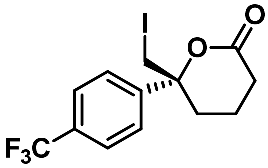
TLC R*f* = 0.33 (hexane : ethyl acetate = 2:1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.31 (m, 4H), 3.54 (s, 2H), 2.48-2.36 (m, 4H), 1.84-1.83 (m, 1H), 1.59-1.57 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 170.0, 138.8, 134.4, 129.1, 126.7, 84.0, 31.9, 29.0, 17.0, 16.5; HRMS calced for $C_{12}H_{13}O_2ClI$ $(M+H)^+$: 350.9643, found: *m/z* 350.9642; Enantiomeric excess was determined by HPLC with a Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_r = 18.0 min, major enantiomer t_r = 20.9 min; 99.8% ee; $[\alpha]_D^{23.0}$= -31.3 (c=1.0, $CHCl_3$, 99.8% ee) ; IR (neat) 2957, 1738, 1492, 1278, 1179, 1094, 1039, 822, 752 cm^{-1}

(*R*)-6-(4-fluorophenyl)-6-(iodomethyl)tetrahydro-2*H*-pyran-2-one (2d)



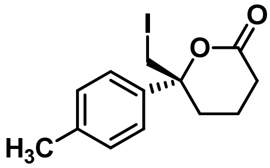
TLC R*f* = 0.32 (hexane : ethyl acetate = 2:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.12-7.05 (m, 2H), 3.54 (dd, *J*=12.6, 10.9 Hz, 2H), 2.55-2.29 (m, 4H), 1.89-1.81 (m, 1H), 1.62-1.57 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 170.2, 162.4 (d, $^{1}J_{CF}$=248.32 Hz), 136.0, 127.2 (d, $^{3}J_{CF}$=8.4 Hz, 2C), 115.9 (d, $^{2}J_{CF}$=21.6 Hz), 84.1, 31.9, 28.9, 17.4, 16.5; HRMS calced for $C_{12}H_{13}O_2FI$ $(M+H)^+$: 334.9941, found: *m/z* 334.9939; Enantiomeric excess was determined by HPLC with a Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_r = 16.9 min, major enantiomer t_r = 19.0 min; 94% ee; $[\alpha]_D^{22.0}$= -14.4 (c=1.0, $CHCl_3$, 94% ee) ; IR (neat) 2962, 2872, 1733, 1603, 1509, 1443, 1411, 1231, 1186, 1038, 936, 841 cm^{-1}

(*R*)-6-(iodomethyl)-6-(4-(trifluoromethyl)phenyl)tetrahydro-2*H*-pyran-2-one (2e)



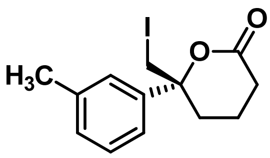
TLC R*f* = 0.33 (hexane : ethyl acetate = 2:1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J*= 8.31 Hz, 2H), 7.52 (d, *J*=8.31 Hz, 2H), 3.57 (s, 2H), 2.57-2.35 (m, 4H), 1.91-1.85(m, 1H), 1.59-1.55 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 169.7, 144.4, 130.7 (q, $^{2}J_{CF}$=32.4 Hz), 126.0 (q, $^{3}J_{CF}$=3.6 Hz), 125.8, 124.8, 84.1, 32.2, 29.0, 16.6, 16.5; HRMS calced for $C_{13}H_{12}O_2F_3INa$ $(M+Na)^+$: 406.9726, found: *m/z* 406.9716; Enantiomeric excess was determined by HPLC with a Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_r = 14.4 min, major enantiomer t_r = 19.0 min; >99.9% ee; $[\alpha]_D^{23.0}$= -17.6 (c=1.0, $CHCl_3$, >99.9% ee) ; IR (neat) 2926, 1741 cm^{-1}

(*R*)-6-(iodomethyl)-6-(p-tolyl)tetrahydro-2*H*-pyran-2-one (2f)



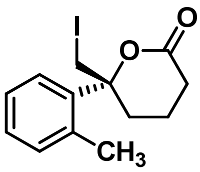
TLC R*f* = 0.47 (hexane : ethyl acetate = 2:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 4H), 3.55 (m, 2H), 2.53-2.29 (m, 7H), 1.86-1.77 (m, 1H), 1.66-1.53 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 170.6, 138.3, 137.1, 129.6, 125.1, 84.4, 31.9, 28.9, 21.0, 17.9, 16.5; HRMS calced for $C_{13}H_{16}O_2I$ $(M+H)^+$: 331.0189, found: *m/z* 331.0190; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_r = 14.1 min, major enantiomer t_r = 16.8 min; 93% ee; $[\alpha]_D^{22.0}$= -34.7 (c=1.0, $CHCl_3$, 93% ee) ; IR (neat) 1724, 1510, 1443, 1259, 1231, 1038, 937, 812, 634 cm^{-1}

(*R*)-6-(iodomethyl)-6-(m-tolyl)tetrahydro-2*H*-pyran-2-one (2g)



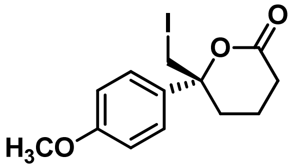
TLC R*f* = 0.41 (hexane : ethyl acetate = 2:1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.14 (m, 4H), 3.56 (s, 2H), 2.52-2.31 (m, 7H), 1.85-1.79 (m, 1H), 1.64-1.52 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 170.5, 140.0, 138.8, 129.1, 128.8, 125.8, 122.2, 84.4, 32.0, 29.0, 21.6, 17.8, 16.5; HRMS calced for $C_{13}H_{15}O_2INa$ $(M+Na)^+$: 353.0009, found: *m/z* 353.0002; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_r = 13.2 min, major enantiomer t_r = 15.1 min; 99.7% ee; $[\alpha]_D^{23.0}$= -33.5 (c=1.0, $CHCl_3$, 99.7% ee) ; IR (neat) 2954, 2921, 1738 cm^{-1}

(*R*)-6-(iodomethyl)-6-(o-tolyl)tetrahydro-2*H*-pyran-2-one (2h)



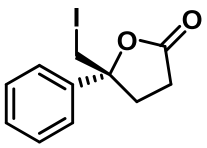
TLC R*f* = 0.41 (hexane : ethyl acetate = 2:1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.20 (m, 4H), 3.68 (dd, *J*=24.06 Hz, *J*=11.17 Hz, 2H), 2.65-2.61 (m, 1H), 2.52-2.45 (m, 4H), 2.33-2.25 (m, 2H), 1.90-1.86 (m, 1H), 1.73-1.67 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 170.8, 137.0, 135.0, 133.6, 128.6, 126.9, 126.4, 85.3, 31.5, 28.4, 22.5, 16.2, 15.6; HRMS calced for $C_{13}H_{15}O_2INa$ $(M+Na)^+$: 353.0009, found: *m/z* 353.0003; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_r = 14.9 min, major enantiomer t_r = 17.0 min; 99.4% ee; $[\alpha]_D^{23.0}$= -2.00 (c=1.0, $CHCl_3$, 99.4% ee) ; IR (neat) 2956, 1736 cm^{-1}

(*R*)-6-(iodomethyl)-6-(4-methoxyphenyl)tetrahydro-2*H*-pyran-2-one (2i)



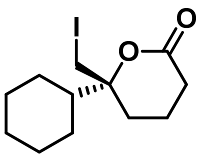
TLC R*f* = 0.34 (hexane : ethyl acetate = 2:1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 2H), 6.92 (m, 2H) 3.82 (s, 3H), 3.54 (m, 2H), 2.50-2.30 (m, 4H), 1.85-1.80 (m, 1H), 1.64-1.58 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 170.5, 159.5, 132.0, 126.5, 114.2, 84.2, 55.3, 31.8, 28.9, 18.1, 16.5; HRMS calced for $C_{12}H_{14}O_2I$ $(M+H)^+$: 347.0139, found: *m/z* 347.0139; Enantiomeric excess was determined by HPLC with a Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_r = 20.4 min, major enantiomer t_r = 24.9 min; 82% ee; $[\alpha]_D^{27.0}$= -23.0 (c=1.0, $CHCl_3$, 82% ee) ; IR (neat) 3031, 1722, 1508, 1443, 1231, 1038, 812 cm^{-1}

(*R*)-5-(iodomethyl)-5-phenyldihydrofuran-2(3*H*)-one (2j)



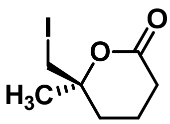
TLC R*f* = 0.40 (hexane : ethyl acetate = 2:1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.33 (m, 5H), 3.63 (dd, *J*=14.9 Hz, 11.2 Hz, 2H) 2.81-2.61 (m, 3H), 2.56-2.47 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 175.3, 140.5, 128.8, 128.5, 124.8, 86.0, 33.9, 29.2, 16.3; HRMS calced for $C_{11}H_{12}O_2I$ $(M+H)^+$: 302.9876, found: *m/z* 302.9879; Enantiomeric excess was determined by HPLC with a Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); major enantiomer t_r = 13.9 min, minor enantiomer t_r = 15.2 min; 87% ee; $[\alpha]_D^{23.0}$= +11.51 (c=1.0, $CHCl_3$, 87% ee) ; IR (neat)3030, 2958, 1779, 1541, 1449, 1154, 1025, 929, 766 cm^{-1}

(*R*)-6-cyclohexyl-6-(iodomethyl)tetrahydro-2*H*-pyran-2-one (2k)



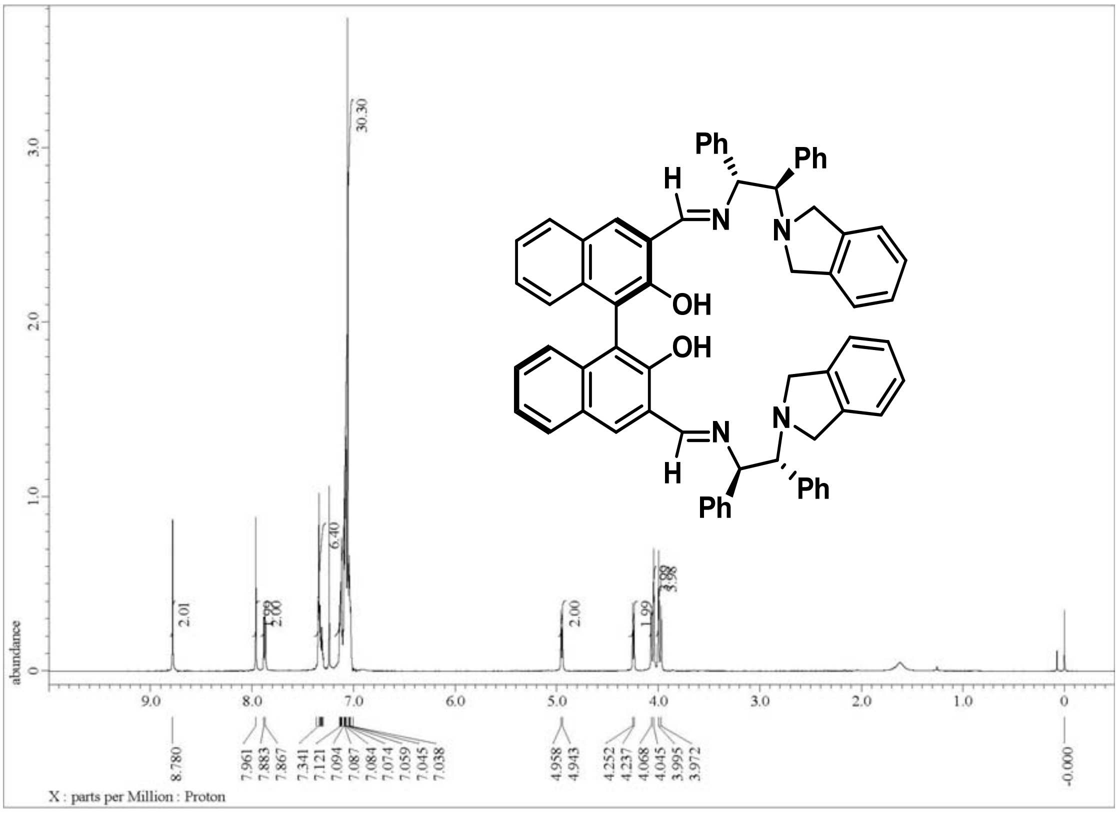
TLC R*f* = 0.40 (hexane : ethyl acetate = 2:1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.45 (dd, *J*=12.6, 10.9 Hz, 2H), 2.58-2.40 (m, 2H), 1.99-1.68 (m, 10 H), 127-1.09 (m, 5H); ^{13}C NMR (125MHz, $CDCl_3$) δ 170.6, 84.7, 45.5, 29.6, 27.1, 26.7, 26.4, 26.3, 26.2, 26.1, 16.8, 13.7; HRMS calced for $C_{12}H_{20}O_2I$ $(M+H)^+$: 323.0504, found: *m/z* 323.0502; Enantiomeric excess was determined by HPLC with a Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); major enantiomer t_r = 10.4 min, minor enantiomer t_r = 11.2 min;_99.3% ee; $[\alpha]_D^{30.0}$= -12.0 (c=1.0, $CHCl_3$, 99.3% ee) ; IR (neat) 2928, 1730 cm^{-1}

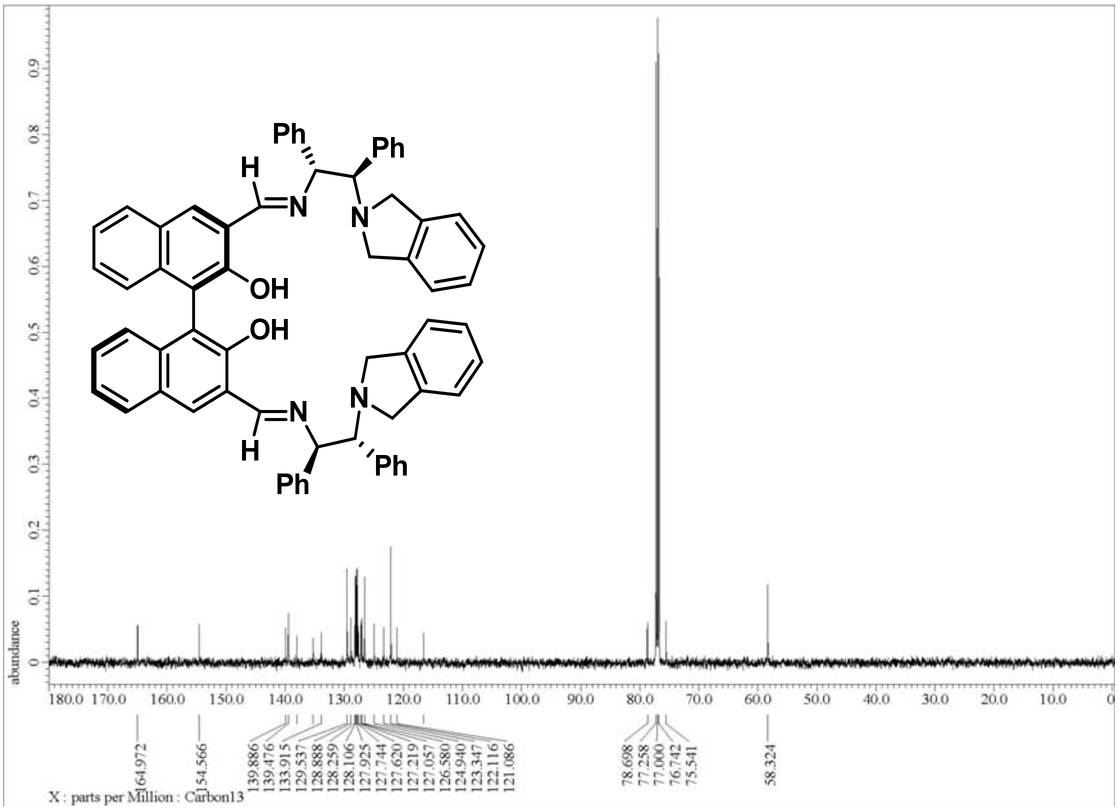
(*S*)-6-(iodomethyl)-6-methyltetrahydro-2*H*-pyran-2-one (2l)

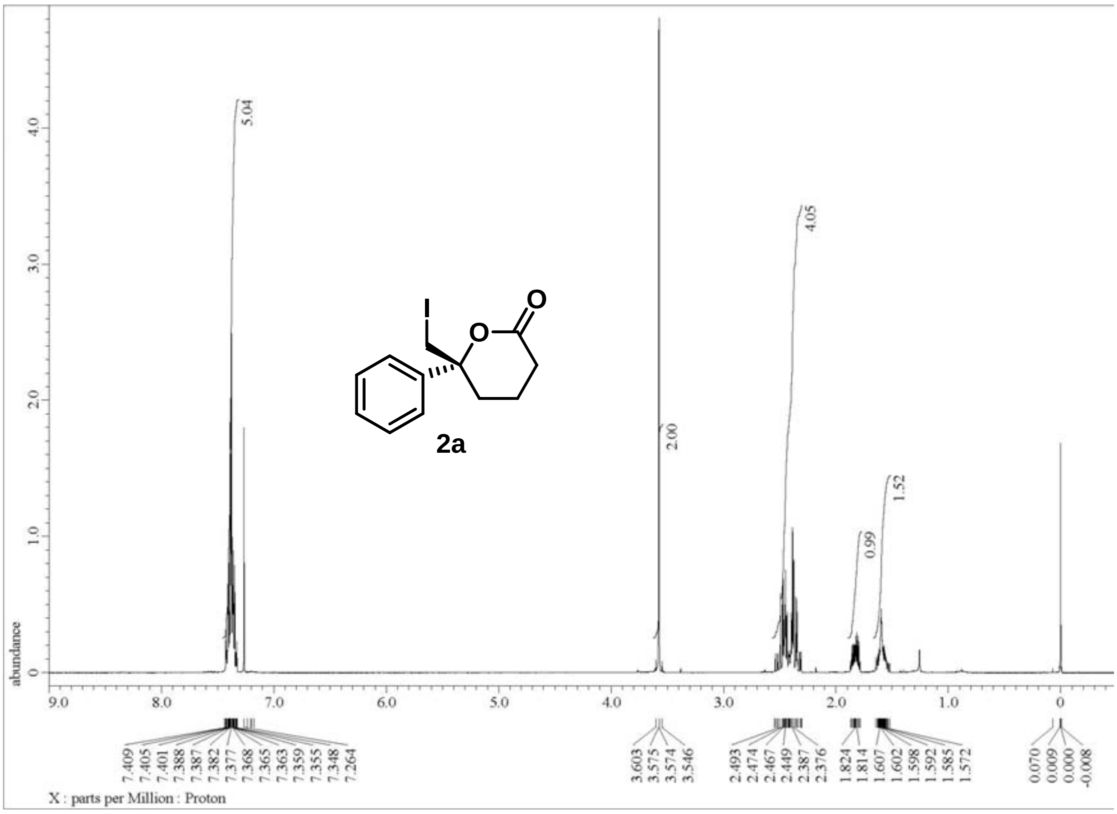


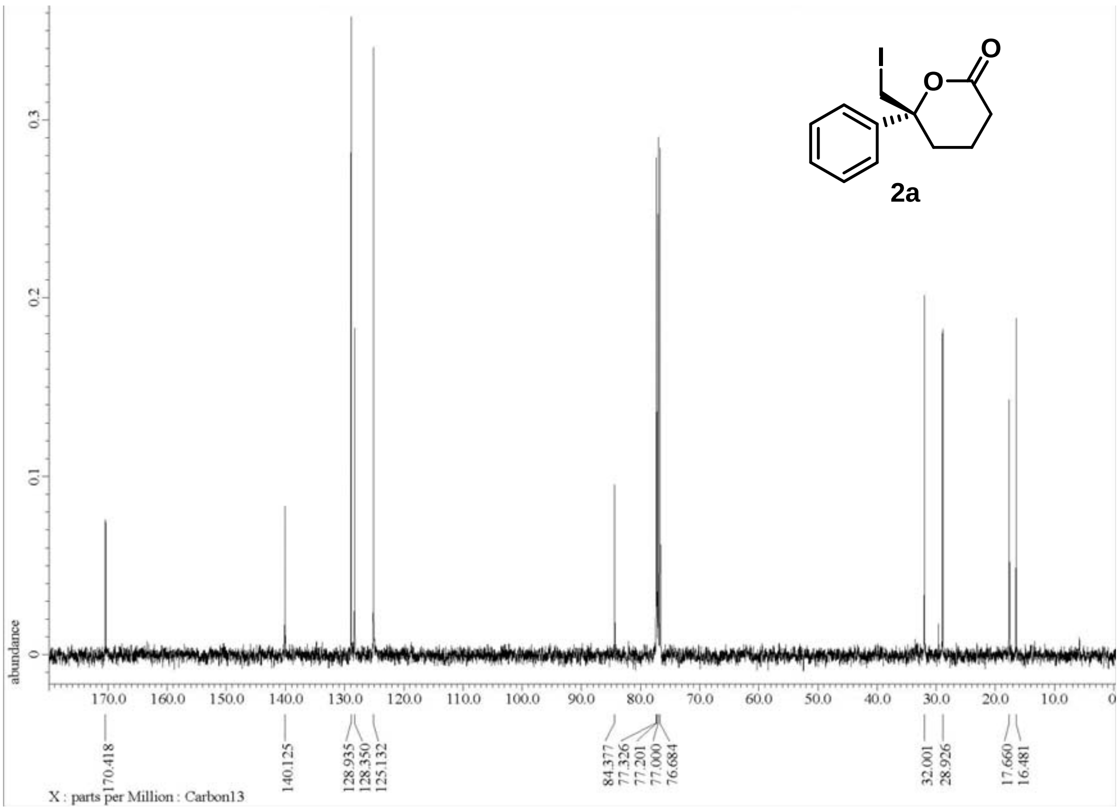
TLC R*f* = 0.30 (hexane : ethyl acetate = 2:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42-3.35 (m, 2H), 2.59-2.42 (m, 2H), 2.13-2.02 (m, 1H) 1.92-1.82 (m, 3H) 1.57 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 170.1, 81.6, 31.6, 29.1, 26.2, 16.6, 15.1; HRMS calced for $C_7H_{12}O_2I$ $(M+H)^+$: 254.9876, found: *m/z* 254.9875; Enantiomeric excess was determined by HPLC with a Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); major enantiomer t_r = 11.4 min, minor enantiomer t_r = 13.6 min; 94% ee; $[\alpha]_D^{27.0}$= -45.6 (c=1.0, $CHCl_3$, 94% ee) ; IR (neat) 2955, 1725 cm^{-1}

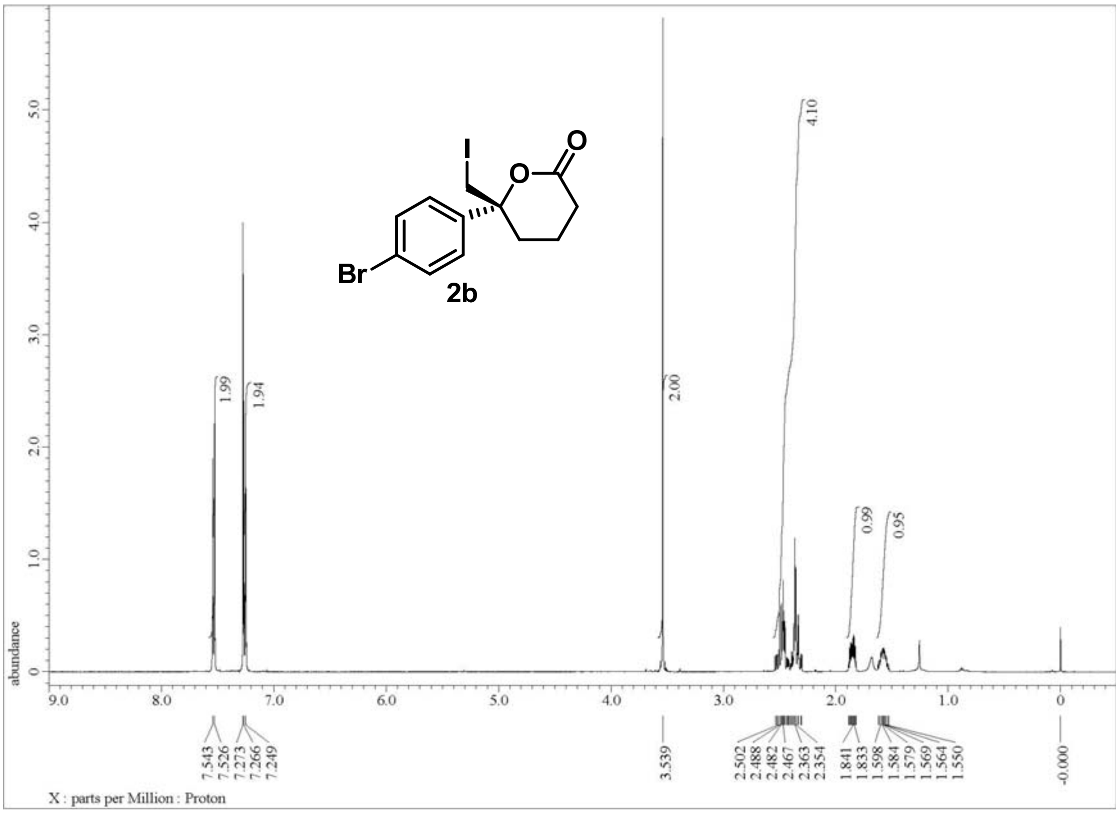
7. ^{1}H-NMR and ^{13}C-NMR spectra



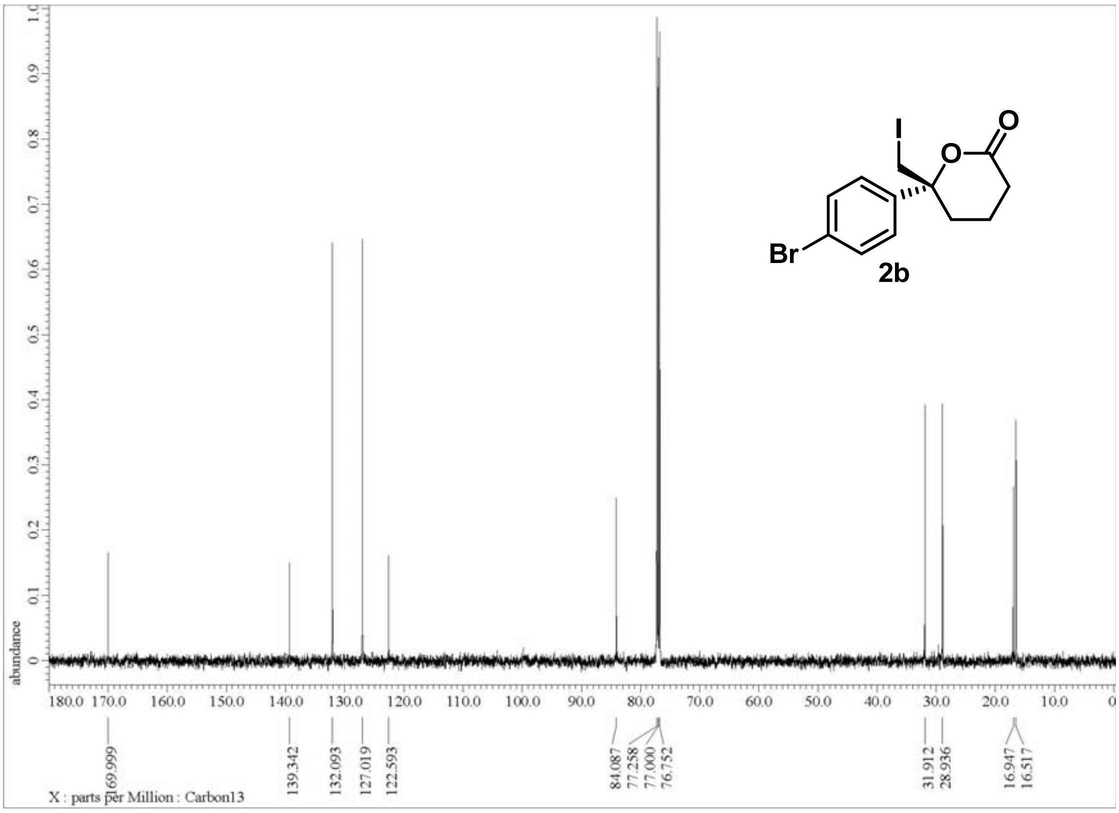



2a
5.04
4.05
2.00
0.99
1.52
abundance
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.409 7.405 7.401 7.388 7.387 7.382 7.377 7.368 7.365 7.363 7.359 7.355 7.348 7.264
3.603 3.575 3.574 3.546
2.493 2.474 2.467 2.449 2.387 2.376
1.824 1.814 1.607 1.602 1.598 1.592 1.585 1.572
0.070 0.009 0.000 -0.008
X : parts per Million : Proton

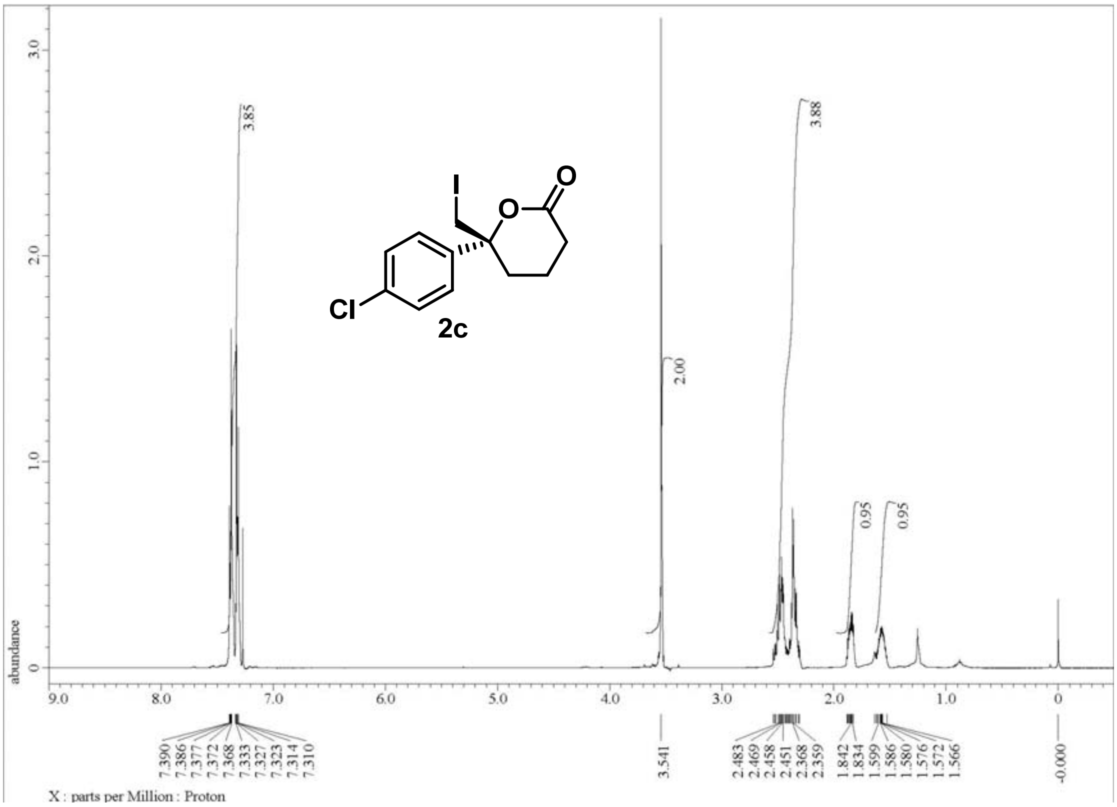

2a
abundance
170.418
140.125
128.935 128.350 125.132
84.377 77.326 77.201 77.000 76.684
32.001 28.926
17.660 16.481
X : parts per Million : Carbon13



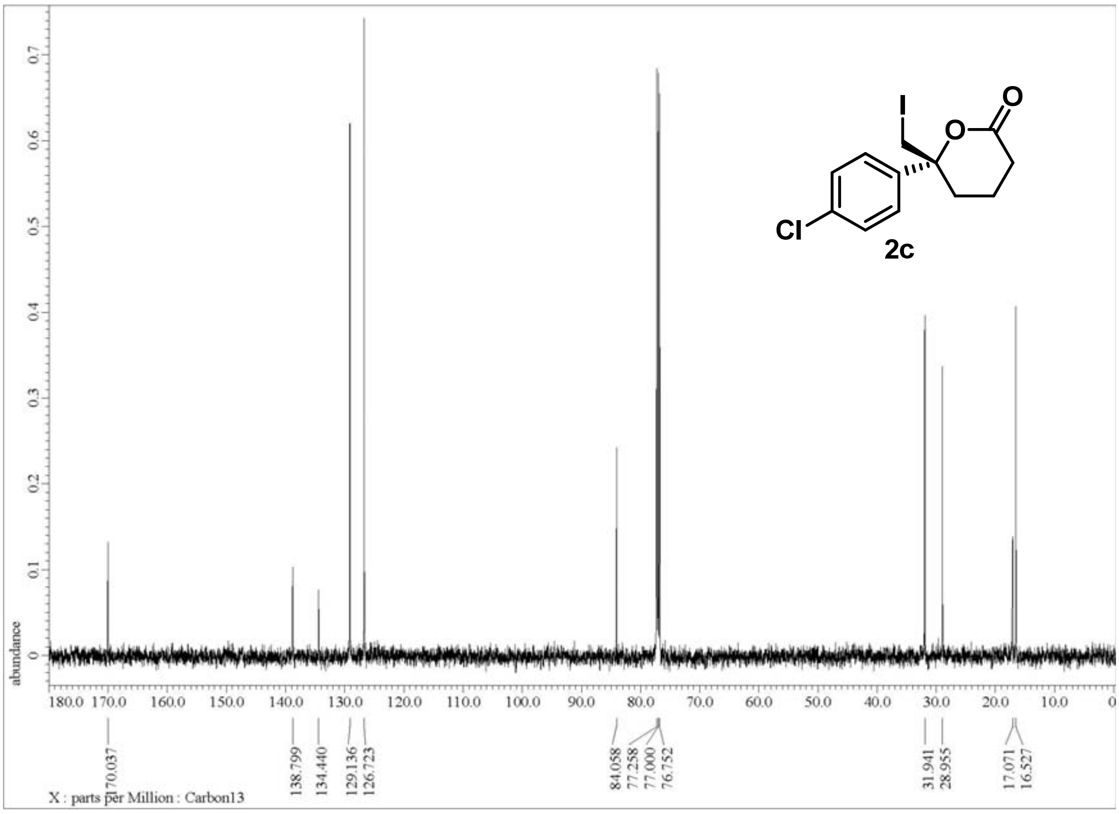
2b
abundance
X : parts per Million : Proton
1.99
1.94
2.00
4.10
0.99
0.95
7.543
7.526
7.273
7.266
7.249
3.539
2.502
2.488
2.482
2.467
2.363
2.354
1.841
1.833
1.598
1.584
1.579
1.569
1.564
1.550
-0.000



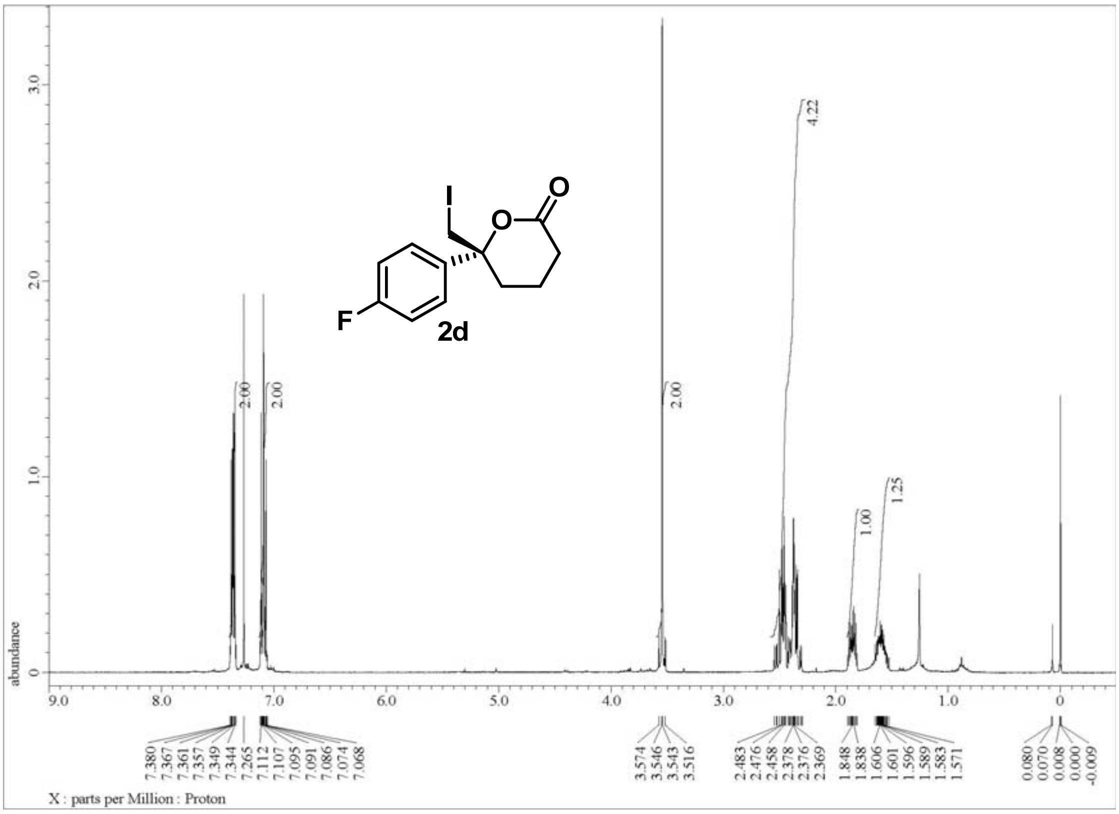
2b
abundance
X : parts per Million : Carbon13
169.999
139.342
132.093
127.019
122.593
84.087
77.258
77.000
76.752
31.912
28.936
16.947
16.517

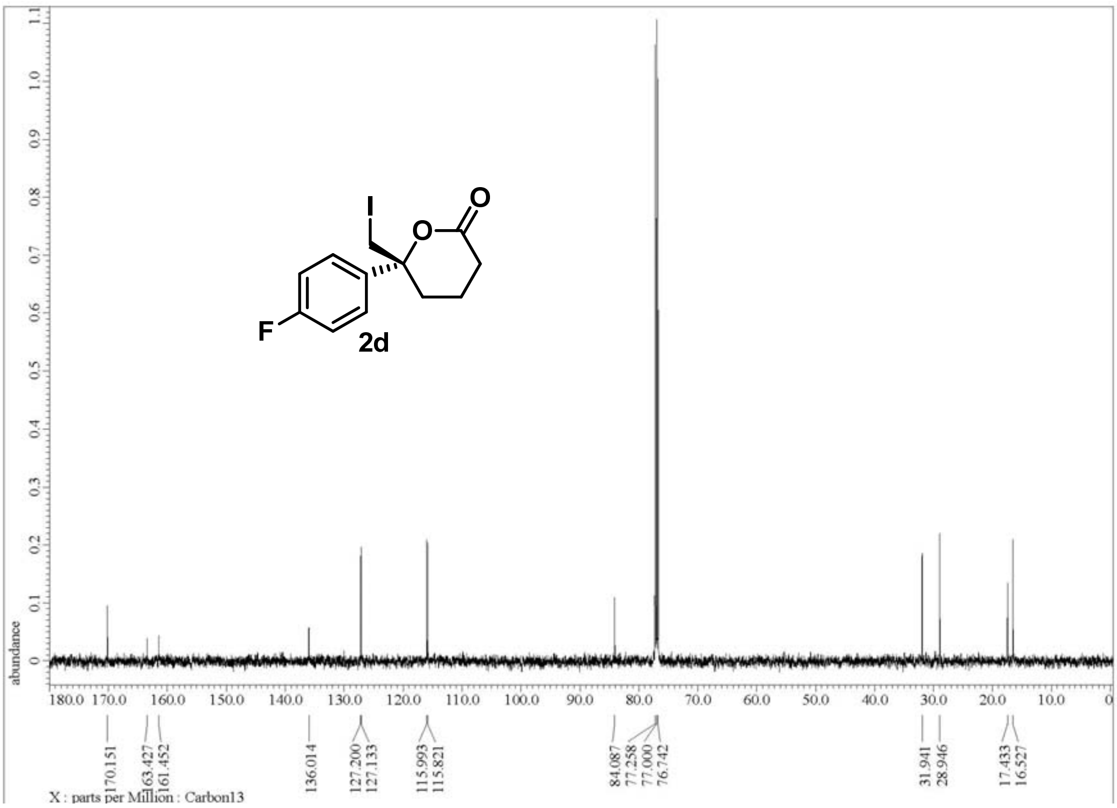


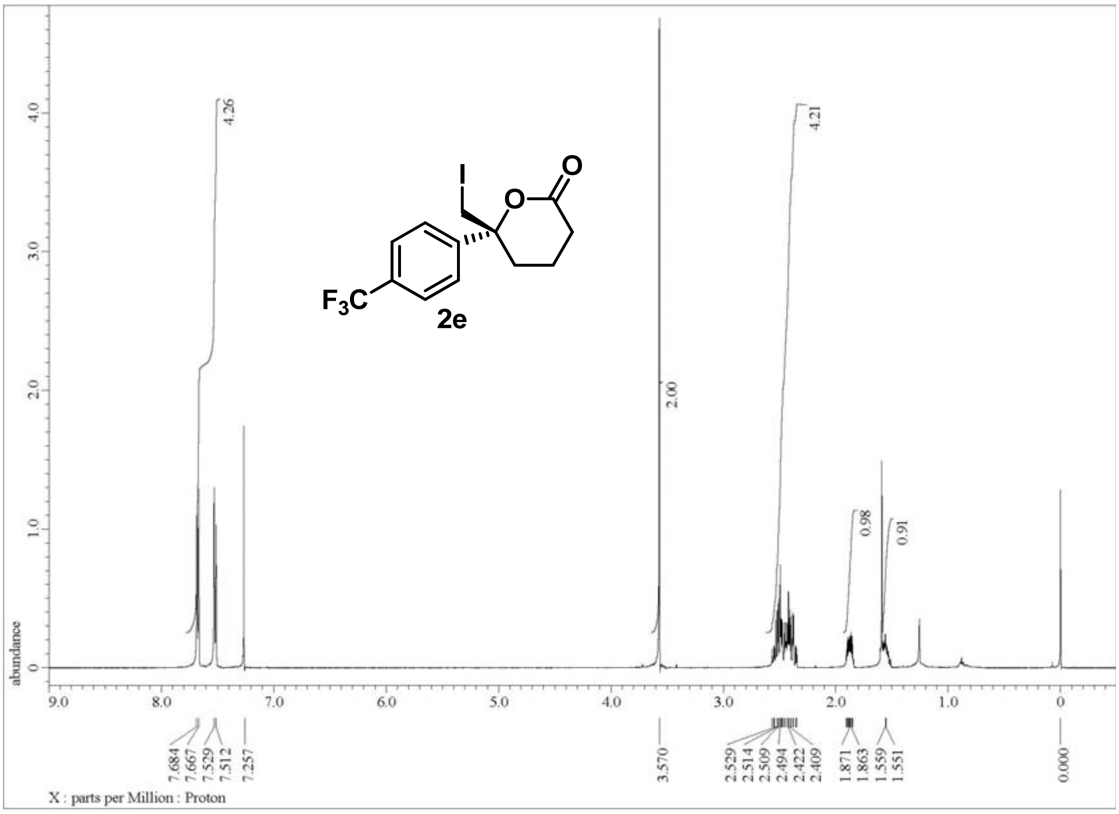
O
I
O
Cl
2c
3.85
2.00
3.88
0.95
0.95
abundance
7.390
7.386
7.377
7.372
7.368
7.333
7.327
7.323
7.314
7.310
3.541
2.483
2.469
2.458
2.451
2.368
2.359
1.842
1.834
1.599
1.586
1.580
1.576
1.572
1.566
-0.000
X : parts per Million : Proton

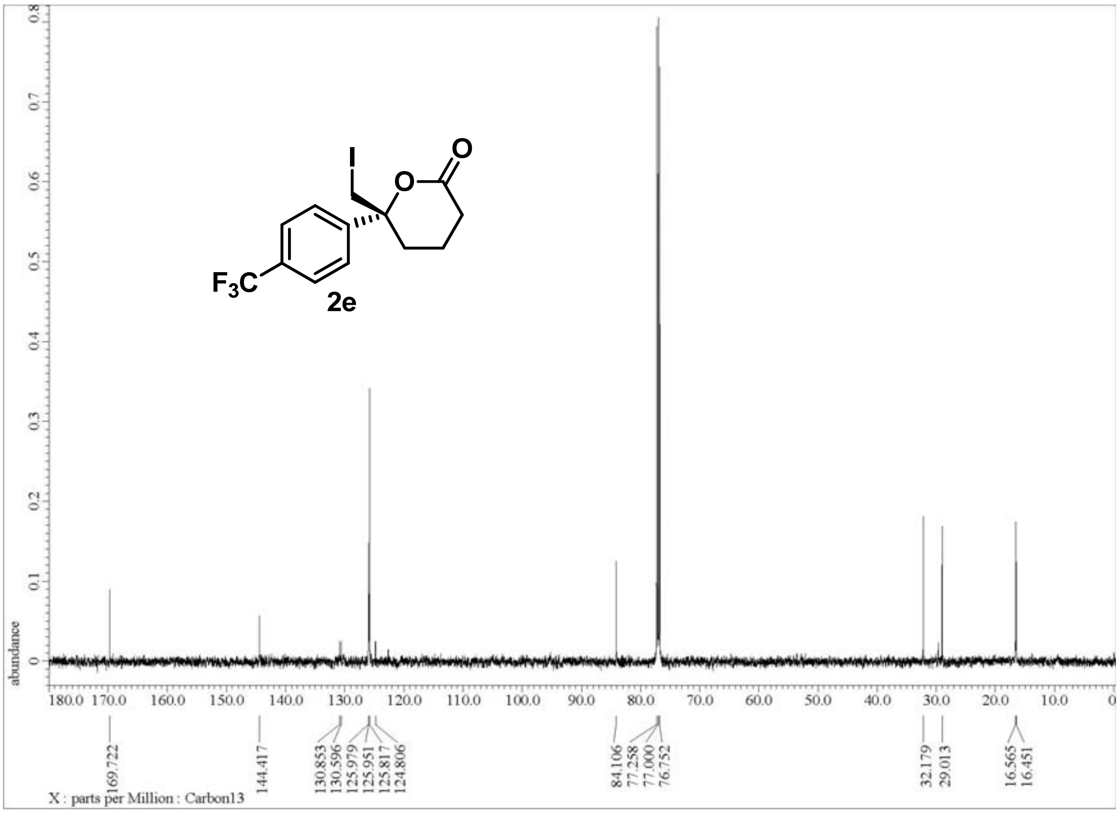


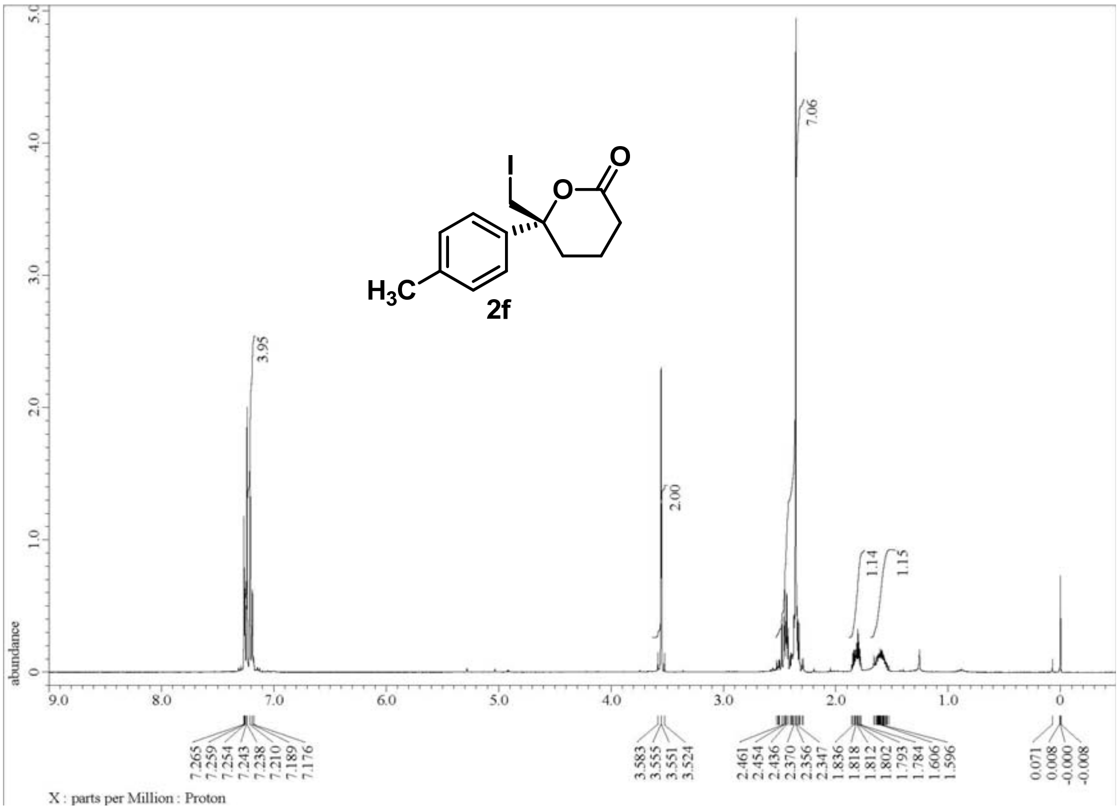
O
I
O
Cl
2c
abundance
170.037
138.799
134.440
129.136
126.723
84.058
77.258
77.000
76.752
31.941
28.955
17.071
16.527
X : parts per Million : Carbon13


F
I
O
O
2d
abundance
2.00
2.00
2.00
4.22
1.00
1.25
7.380 7.367 7.361 7.357 7.349 7.344 7.265 7.112 7.107 7.095 7.091 7.086 7.074 7.068
3.574 3.546 3.543 3.516
2.483 2.476 2.458 2.378 2.376 2.369
1.848 1.838 1.606 1.601 1.596 1.589 1.583 1.571
0.080 0.070 0.008 0.000 -0.009
X : parts per Million : Proton

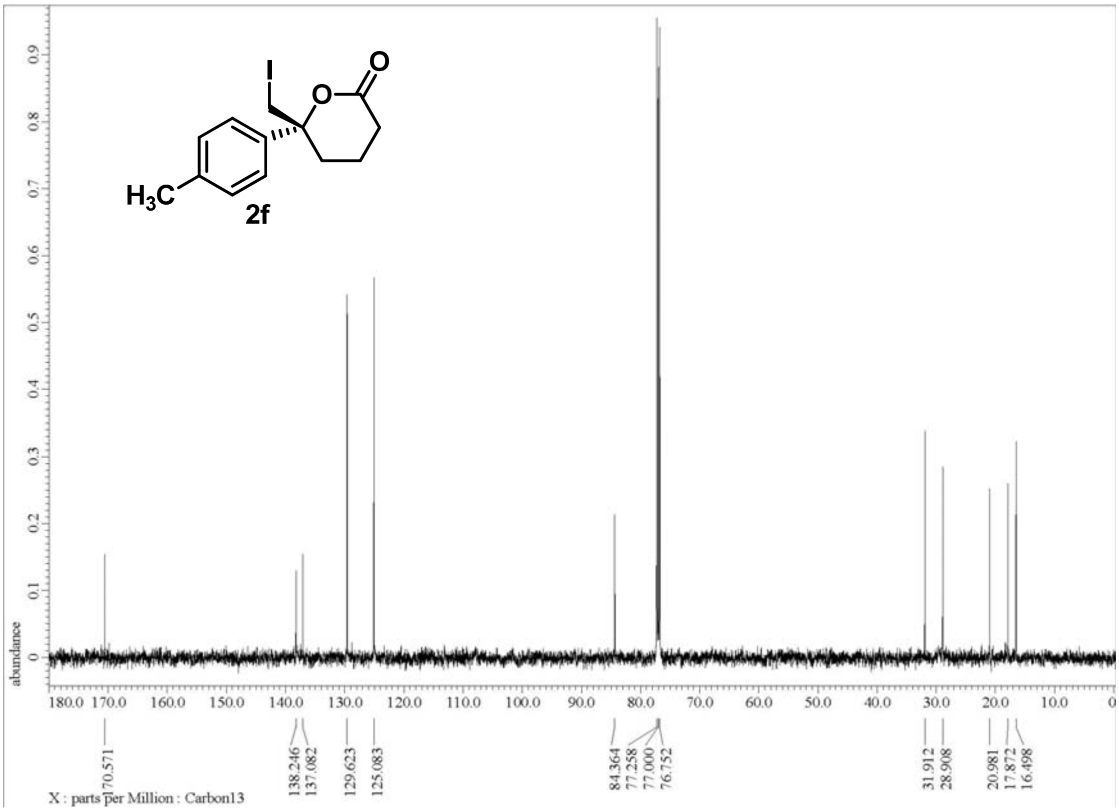

F
I
O
O
2d
abundance
170.151
163.427 161.452
136.014
127.200 127.133
115.993 115.821
84.087 77.258 77.000 76.742
31.941 28.946
17.433 16.527
X : parts per Million : Carbon13


F3C
2e
abundance
X : parts per Million : Proton

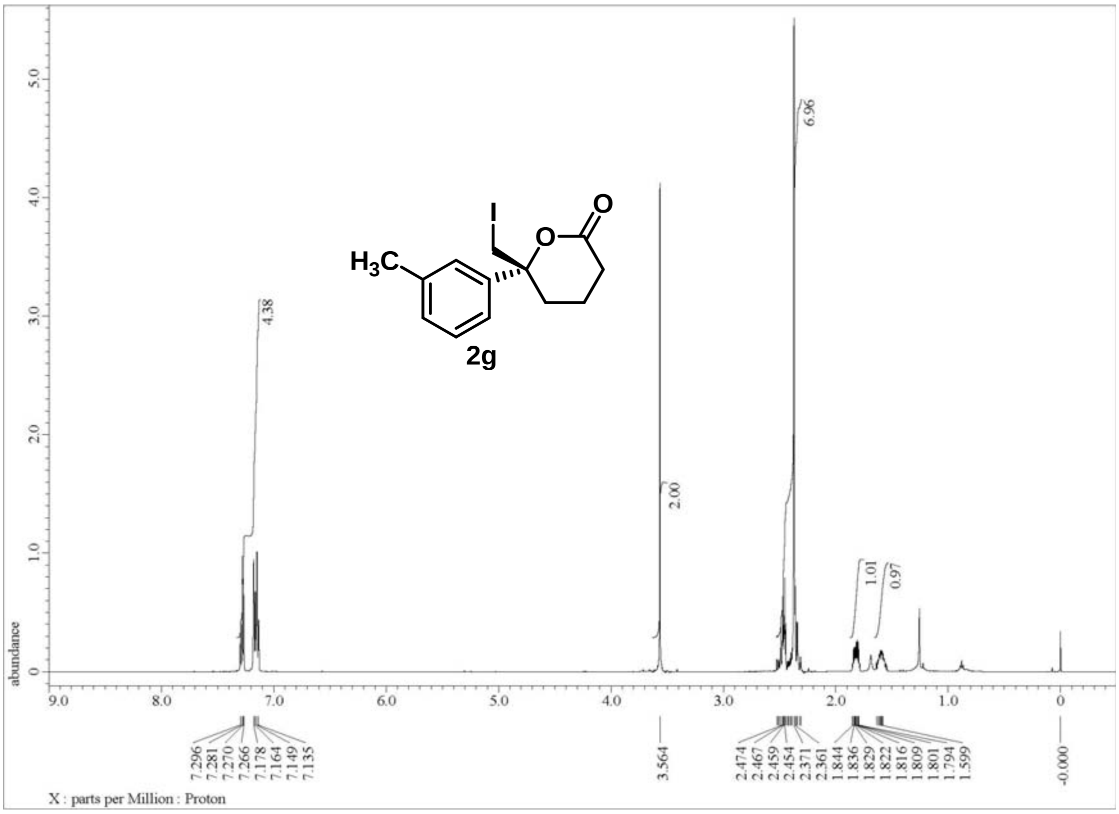

F3C
2e
abundance
X : parts per Million : Carbon13



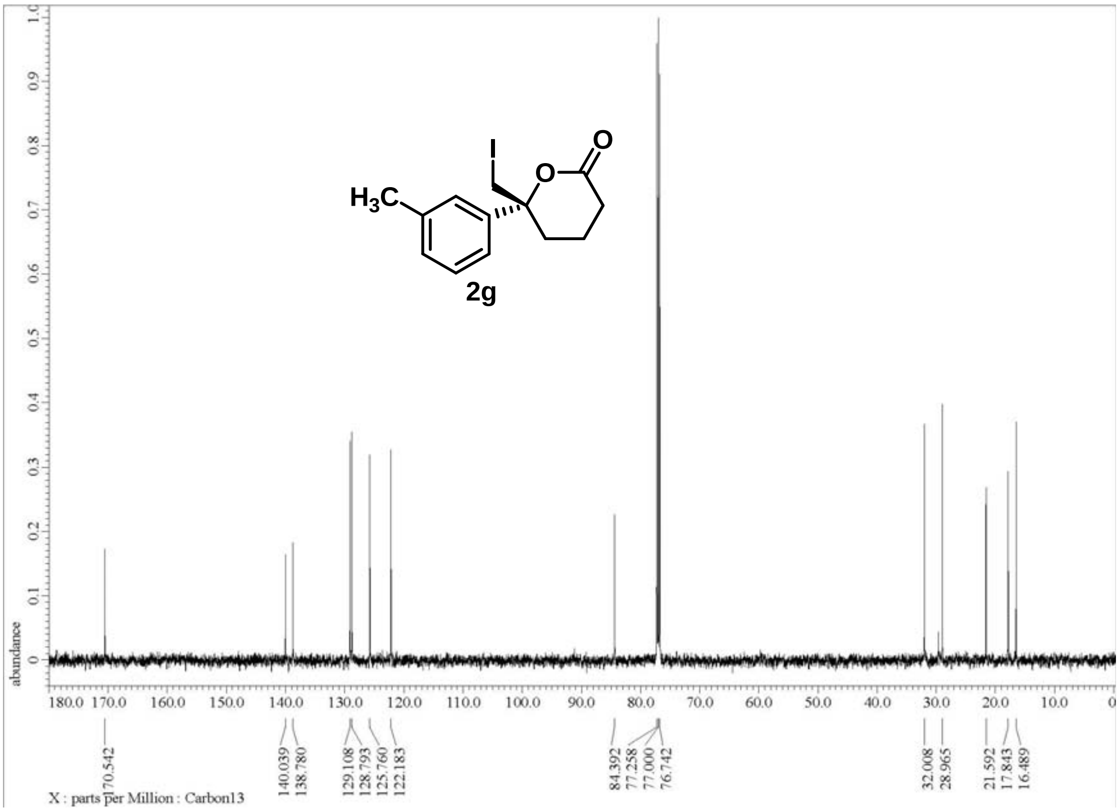
H3C
2f
I
O
O
abundance
X : parts per Million : Proton
3.95
2.00
7.06
1.14
1.15



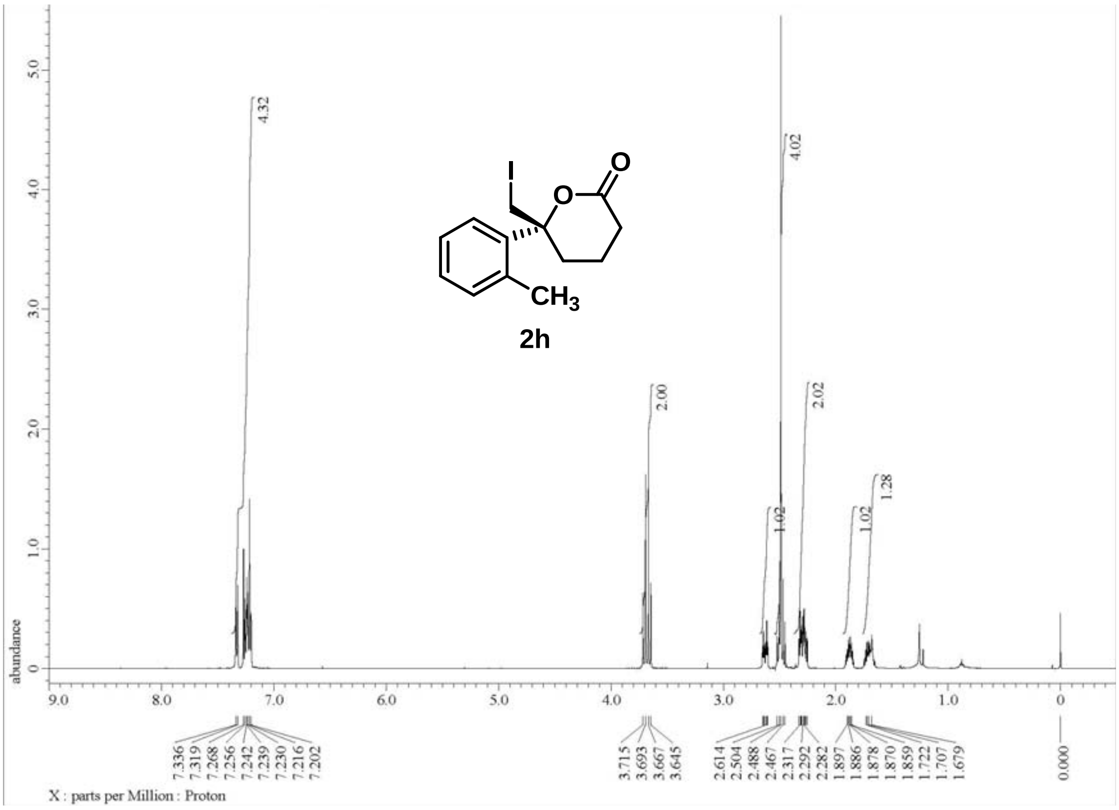
H3C
2f
I
O
O
abundance
X : parts per Million : Carbon13
170.571
138.246
137.082
129.623
125.083
84.364
77.258
77.000
76.752
31.912
28.908
20.981
17.872
16.498

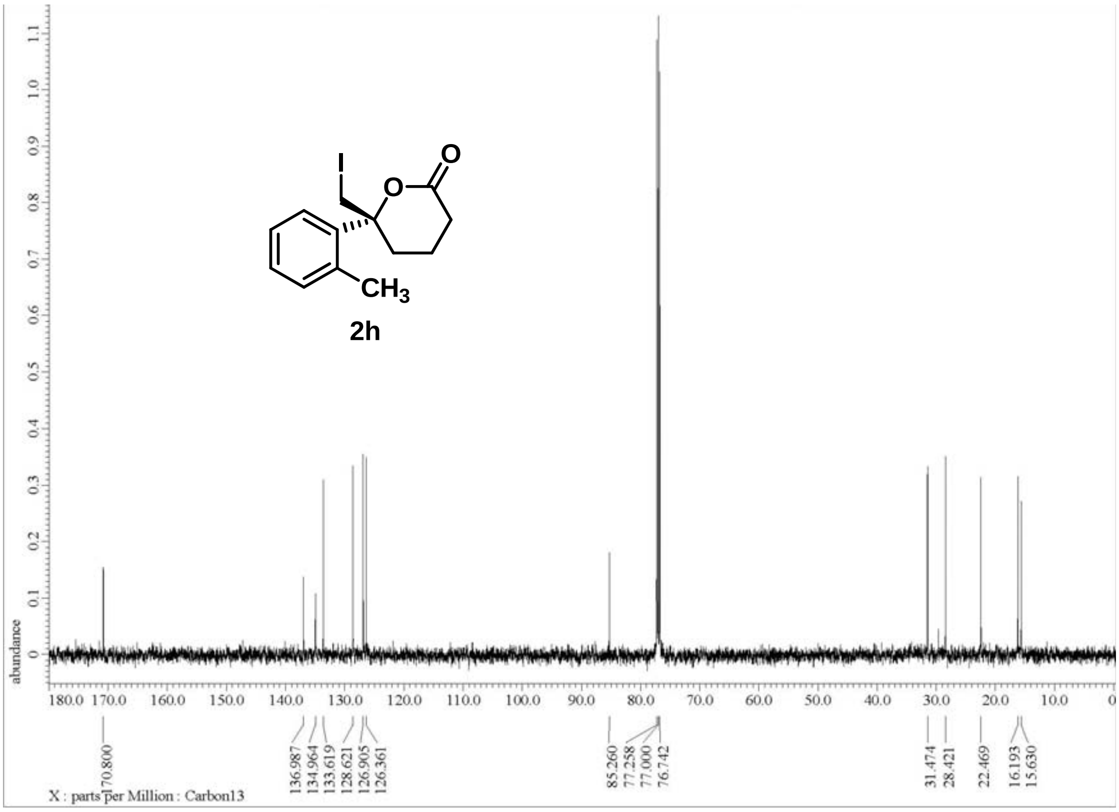


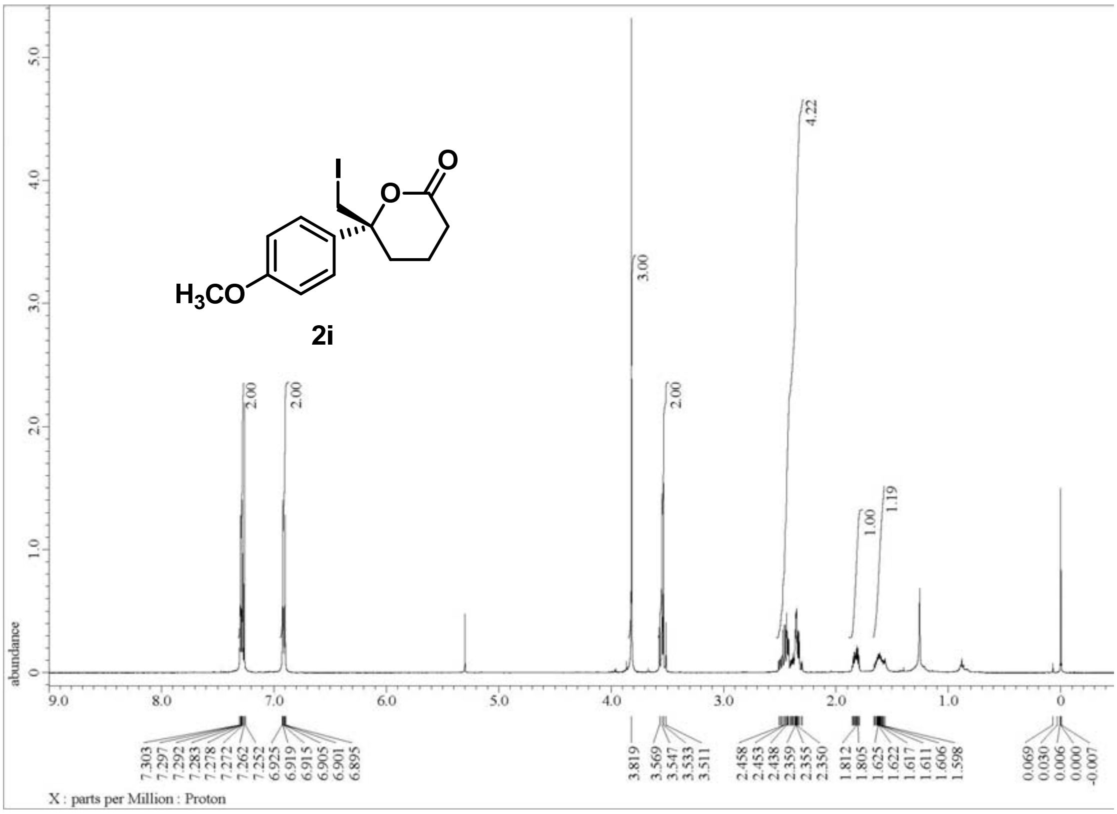
H3C
I
O
O
2g
4.38
2.00
6.96
1.01
0.97
7.296
7.281
7.270
7.266
7.178
7.164
7.149
7.135
3.564
2.474
2.467
2.459
2.454
2.371
2.361
1.844
1.836
1.829
1.822
1.816
1.809
1.801
1.794
1.599
-0.000
abundance
X : parts per Million : Proton



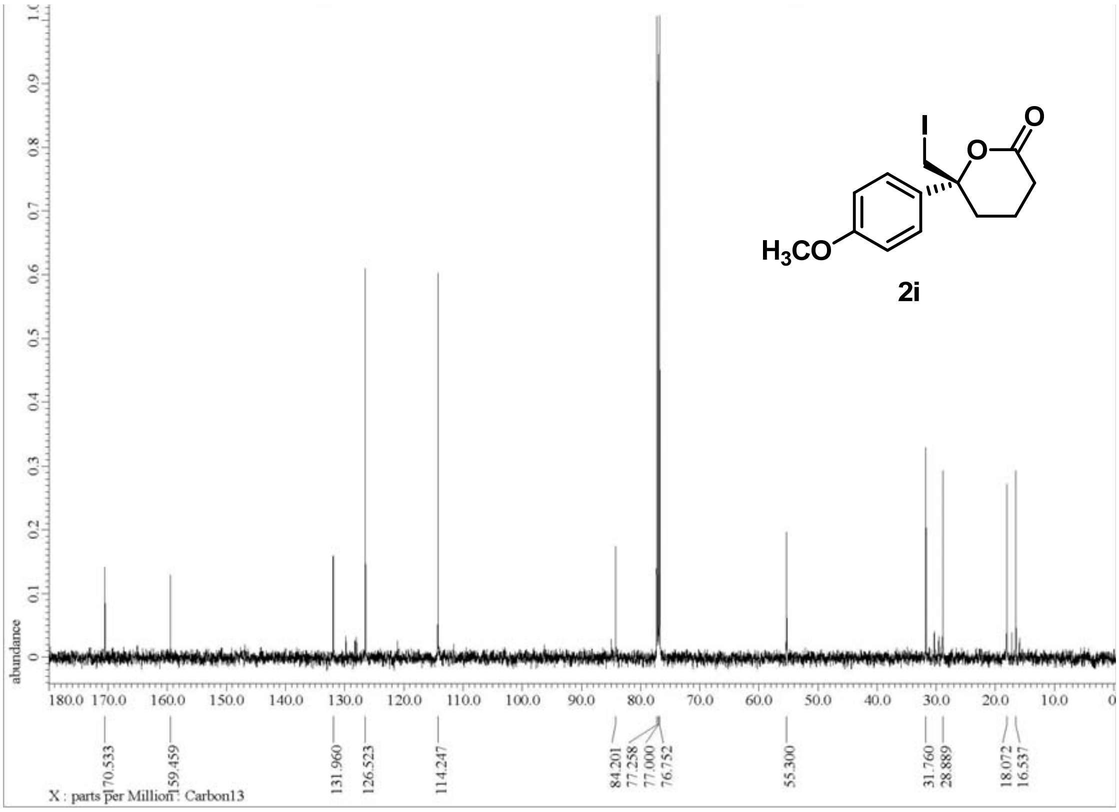
H3C
I
O
O
2g
170.542
140.039
138.780
129.108
128.793
125.760
122.183
84.392
77.258
77.000
76.742
32.008
28.965
21.592
17.843
16.489
abundance
X : parts per Million : Carbon13



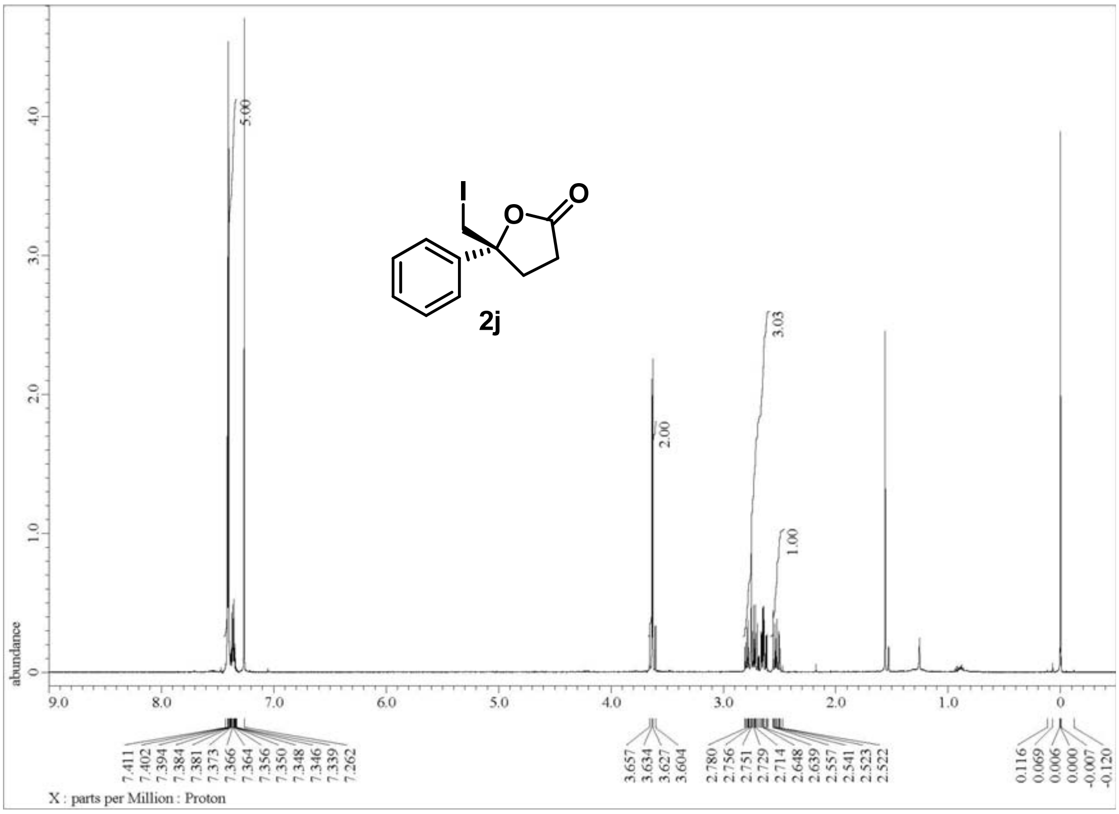


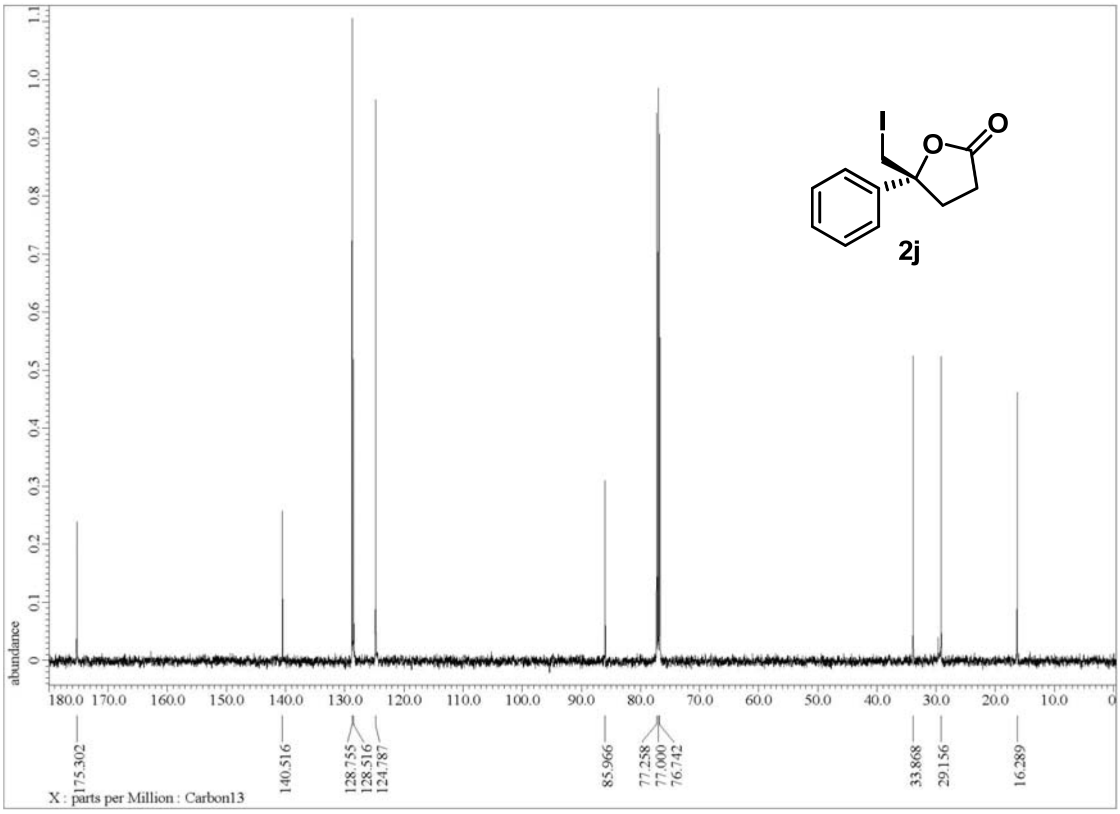


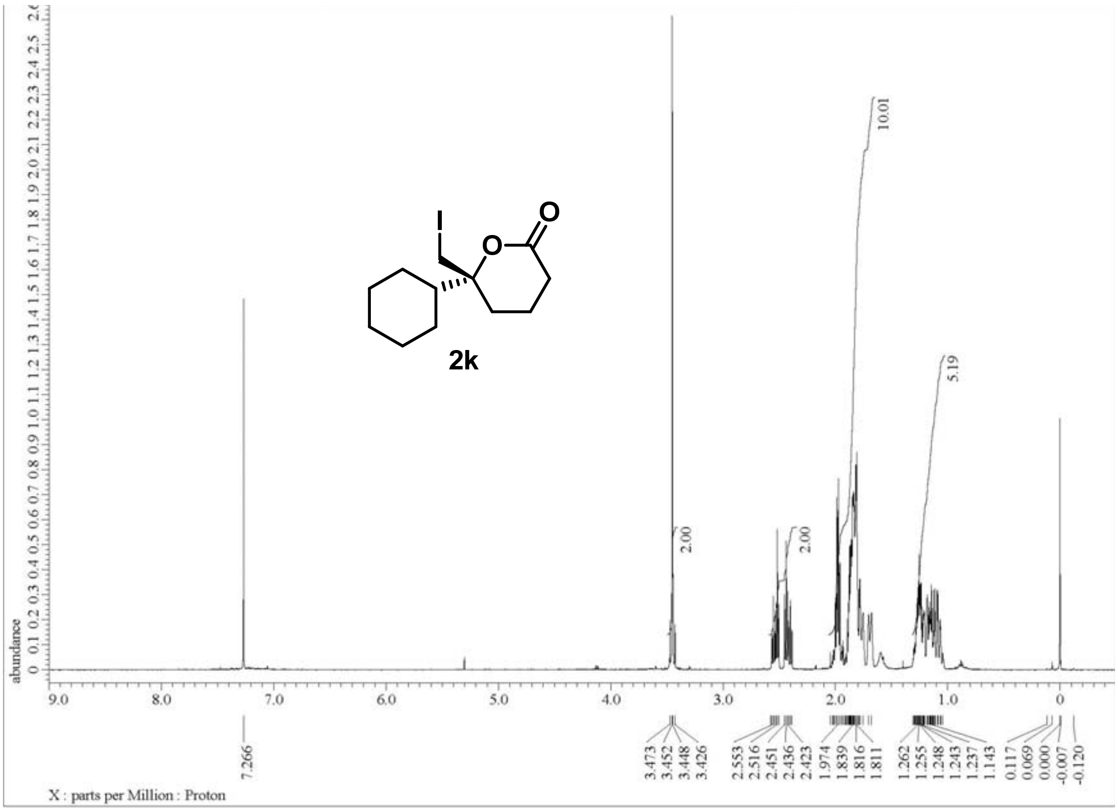
H3CO
2i
3.00
2.00
2.00
2.00
4.22
1.00
1.19
abundance
X : parts per Million : Proton

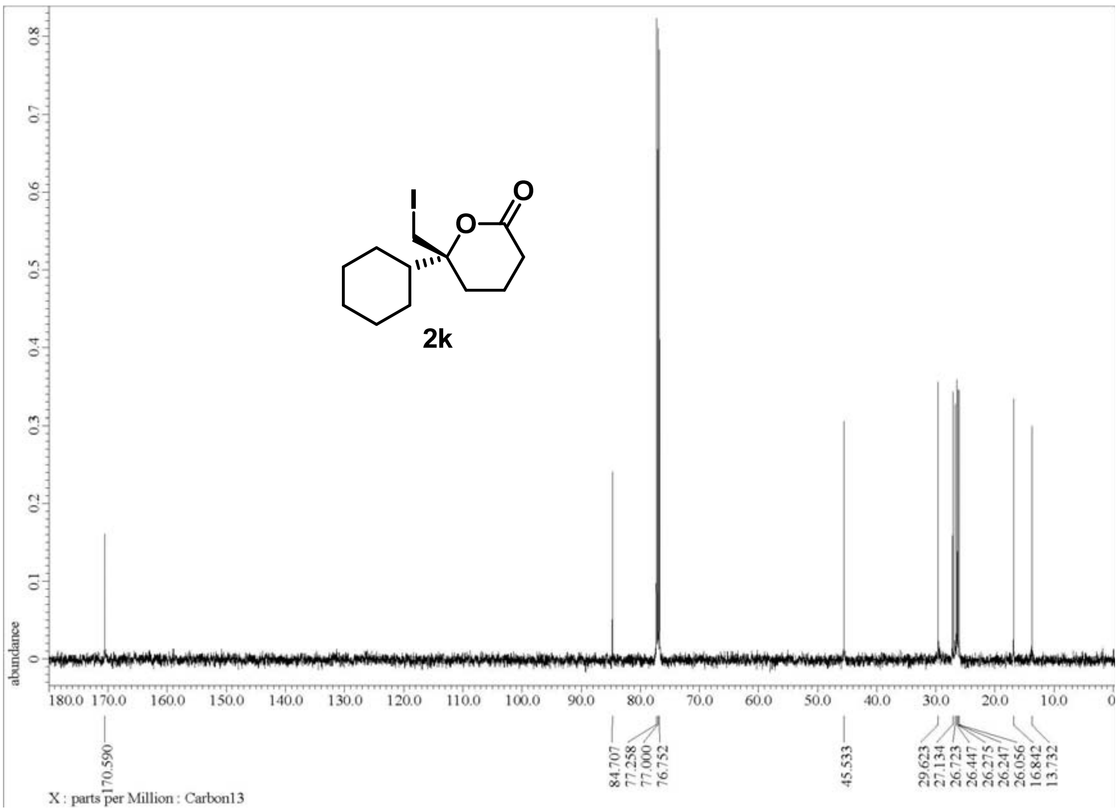


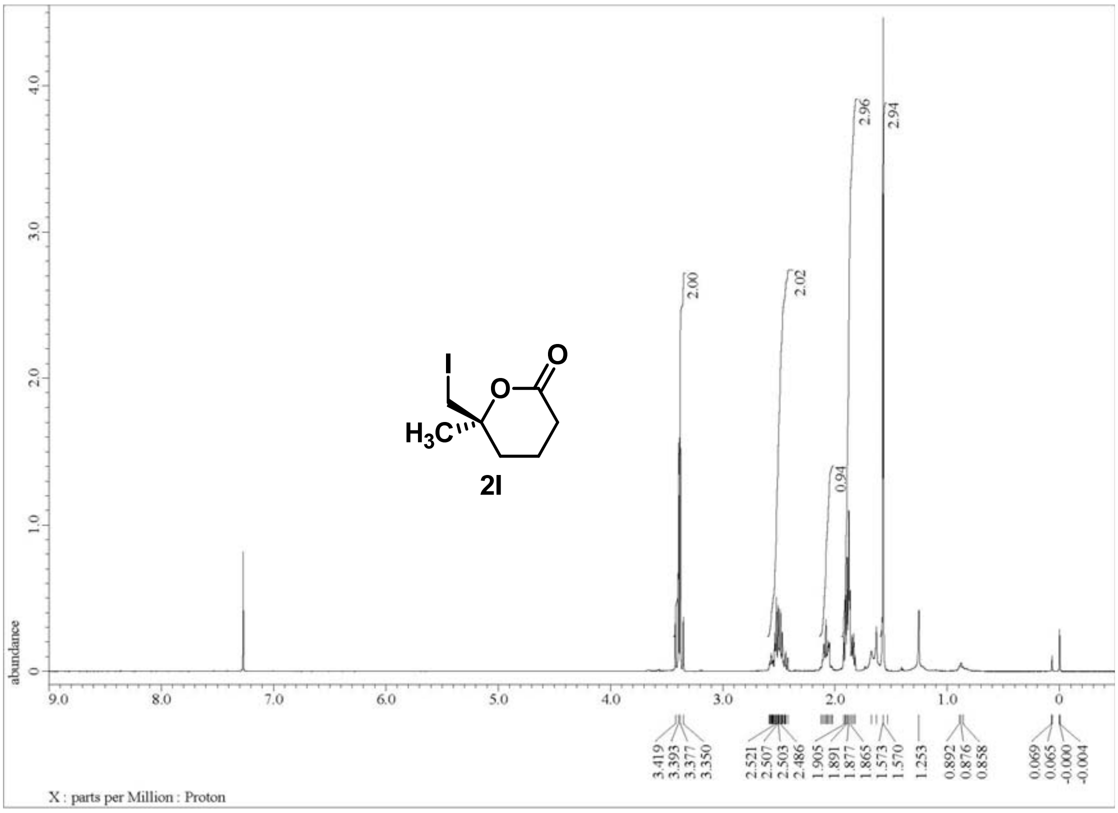
H3CO
2i
abundance
170.533
159.459
131.960
126.523
114.247
84.201
77.258
77.000
76.752
55.300
31.760
28.889
18.072
16.537
X : parts per Million : Carbon13

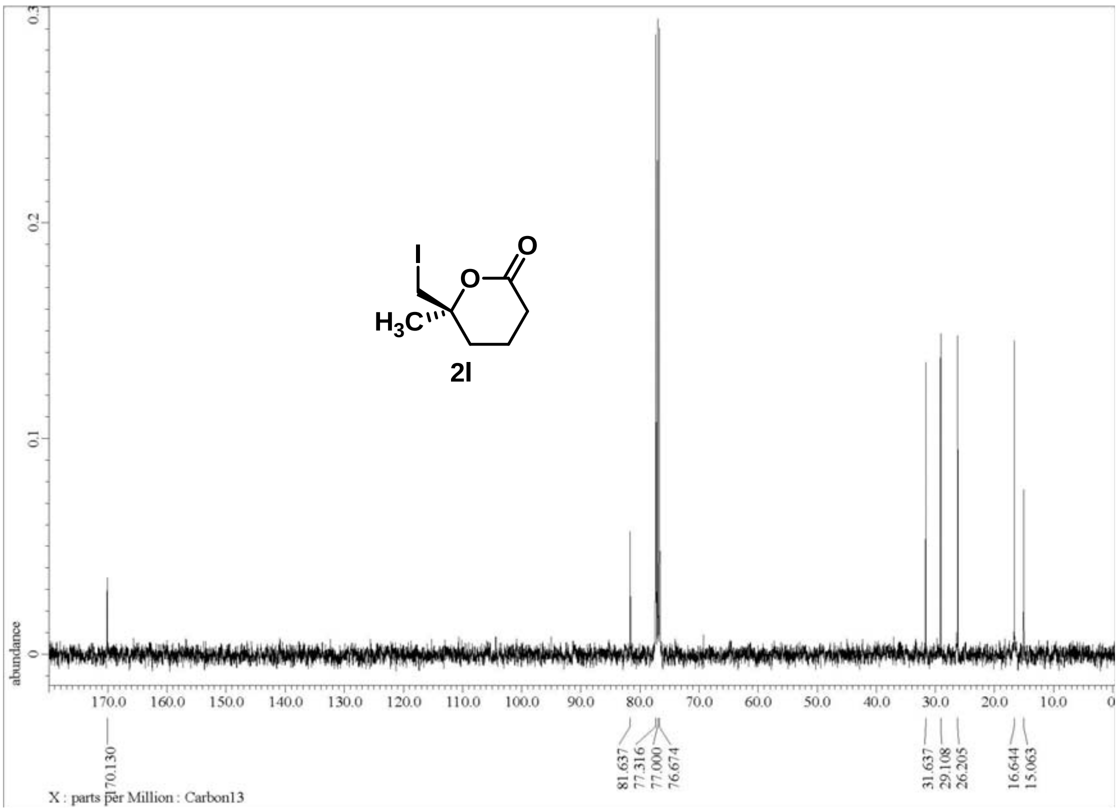

2j
5.00
2.00
3.03
1.00
7.411 7.402 7.394 7.384 7.381 7.373 7.366 7.364 7.356 7.350 7.348 7.346 7.339 7.262
3.657 3.634 3.627 3.604
2.780 2.756 2.751 2.729 2.714 2.648 2.639 2.557 2.541 2.523 2.522
0.116 0.069 0.006 0.000 -0.007 -0.120
abundance
X : parts per Million : Proton


2j
175.302
140.516
128.755 128.516 124.787
85.966
77.258 77.000 76.742
33.868
29.156
16.289
abundance
X : parts per Million : Carbon13

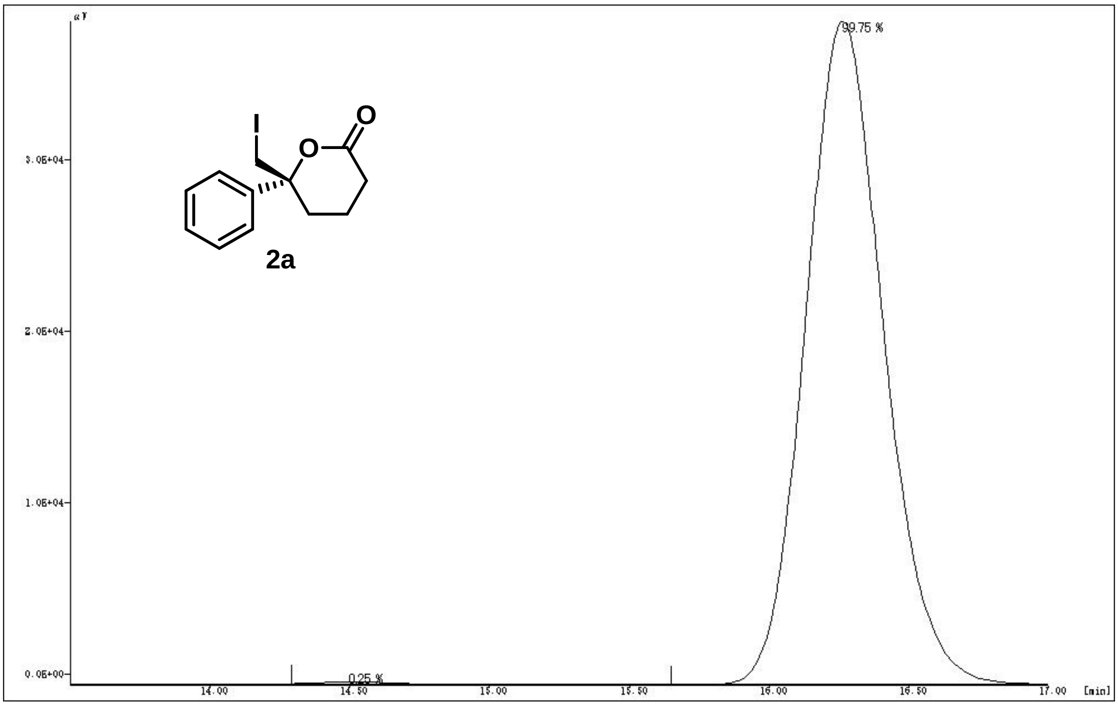

2k
abundance
X : parts per Million : Proton
10.01
5.19
2.00
2.00
7.266
3.473
3.452
3.448
3.426
2.553
2.516
2.451
2.436
2.423
1.974
1.839
1.816
1.811
1.262
1.255
1.248
1.243
1.237
1.143
0.117
0.069
0.000
-0.007
-0.120

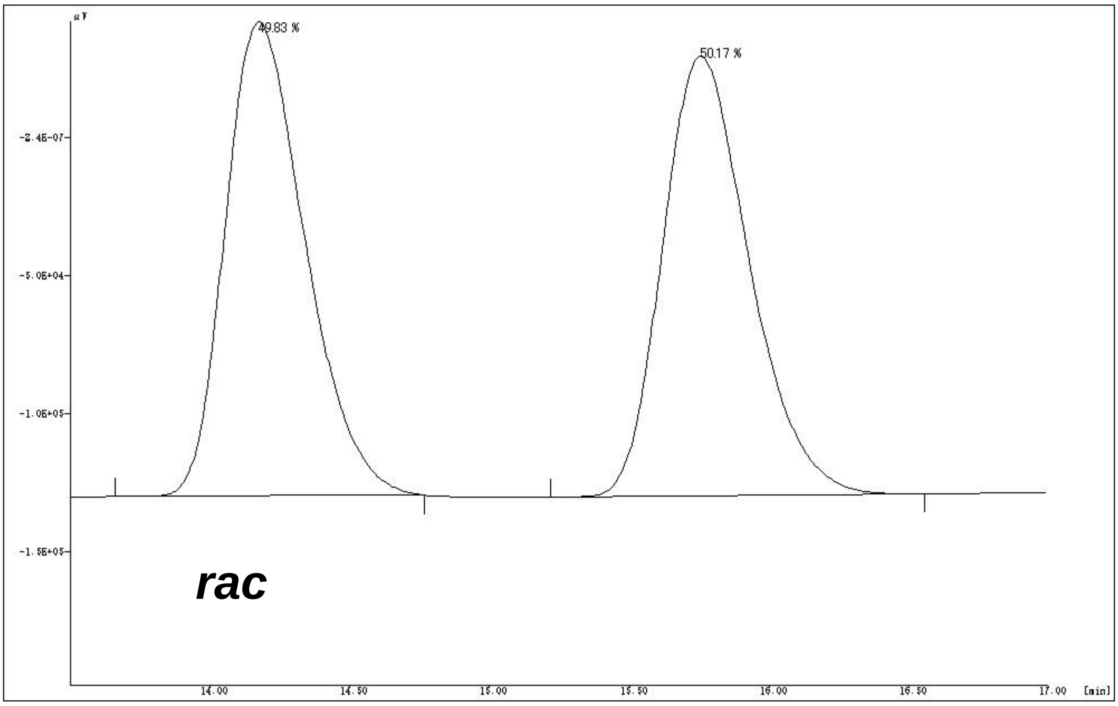

2k
abundance
X : parts per Million : Carbon13
170.590
84.707
77.258
77.000
76.752
45.533
29.623
27.134
26.723
26.447
26.275
26.247
26.056
16.842
13.732


2l
X : parts per Million : Proton
abundance

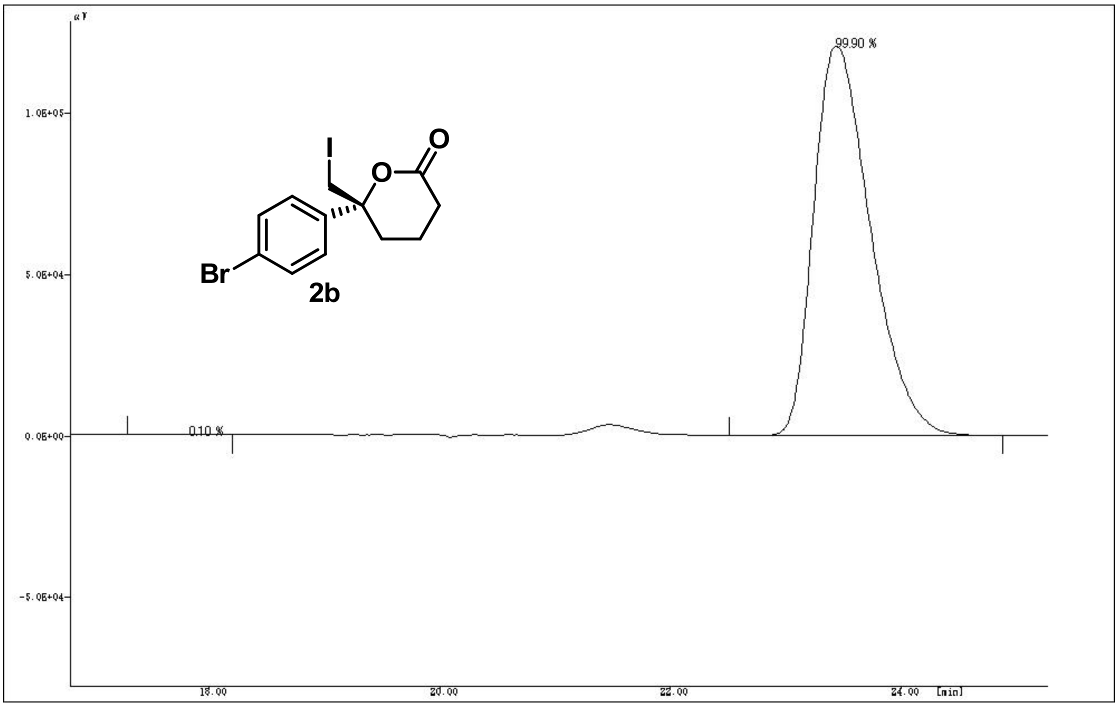

2l
X : parts per Million : Carbon13
abundance

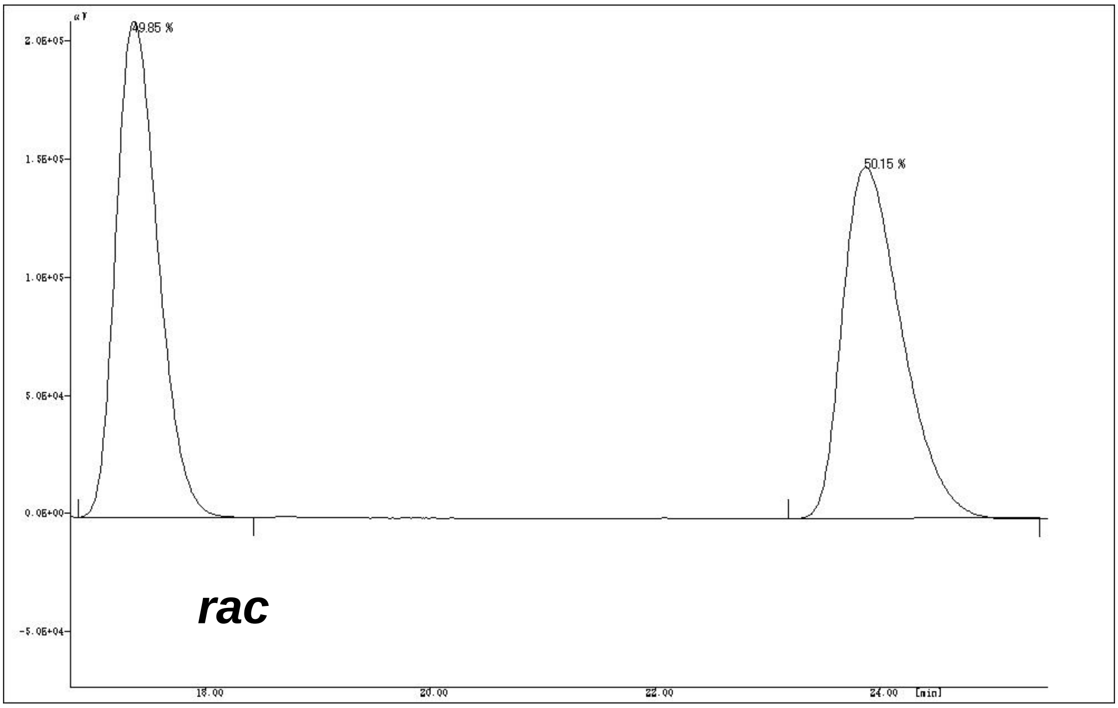
8. HPLC spectra



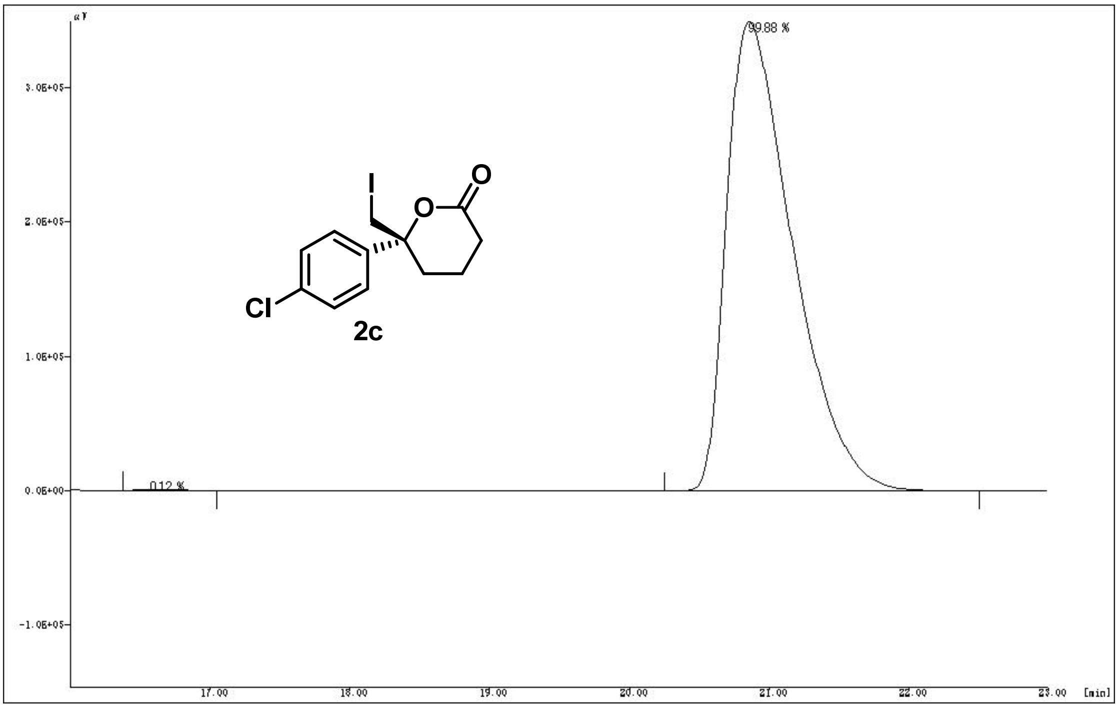


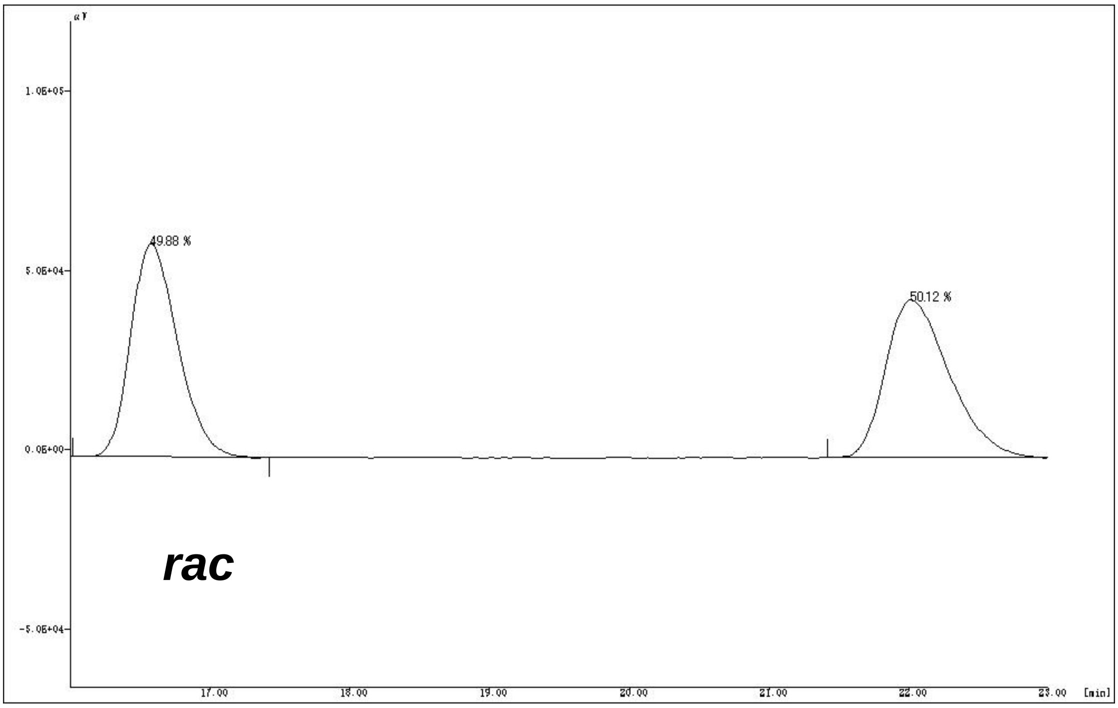
Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)



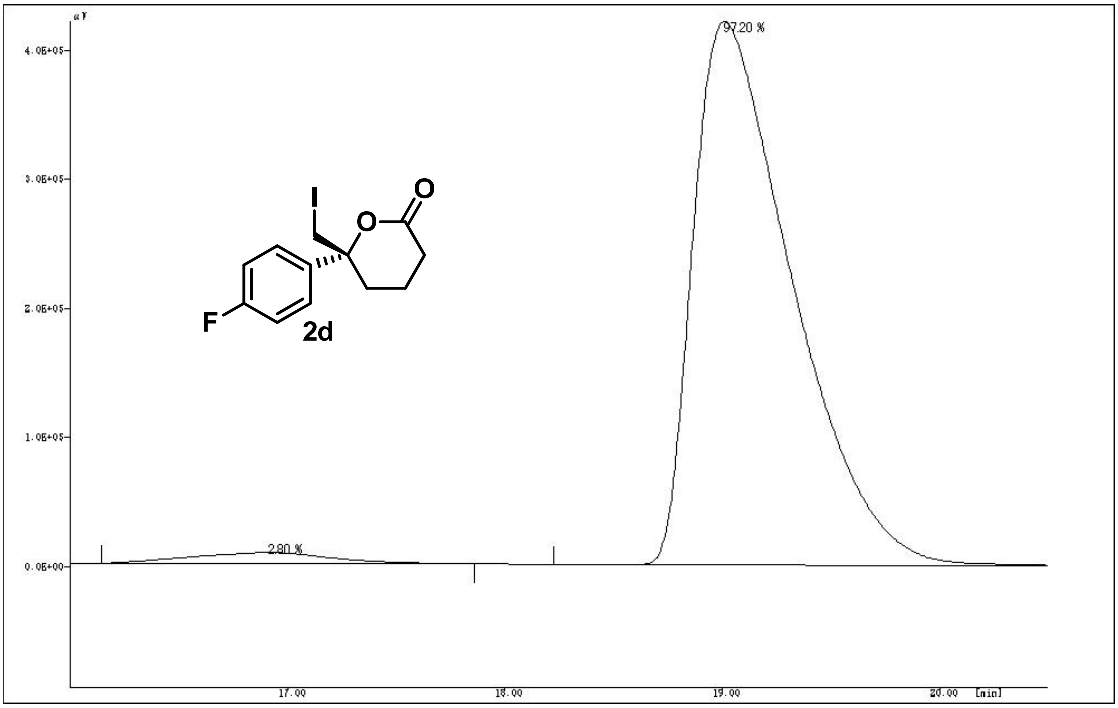


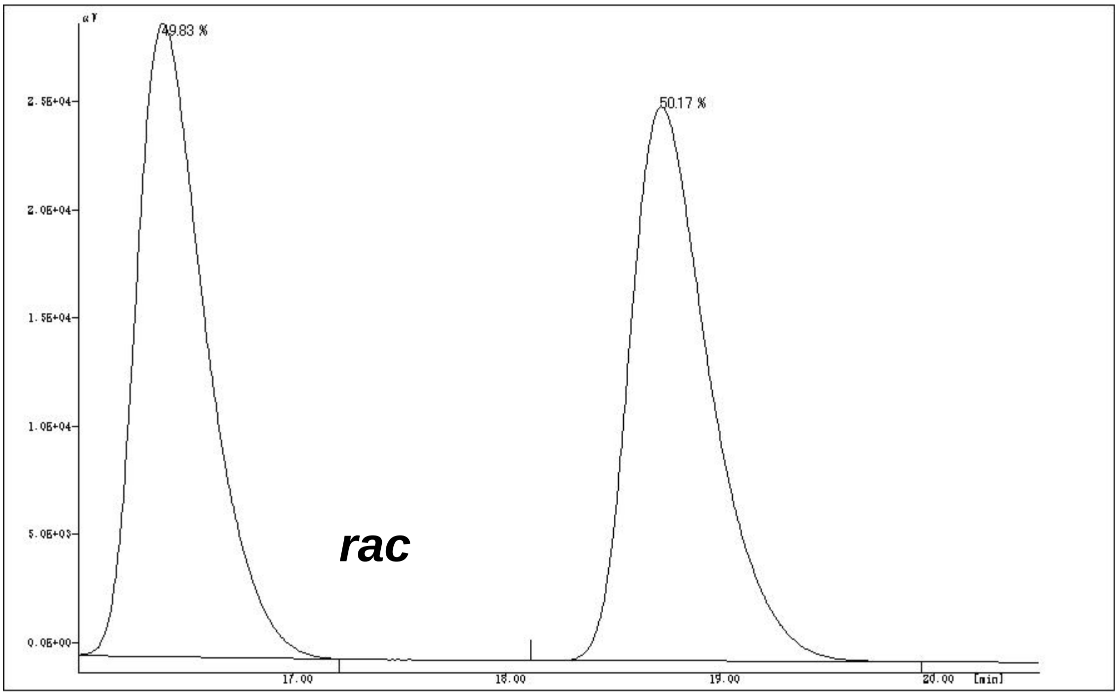
Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)



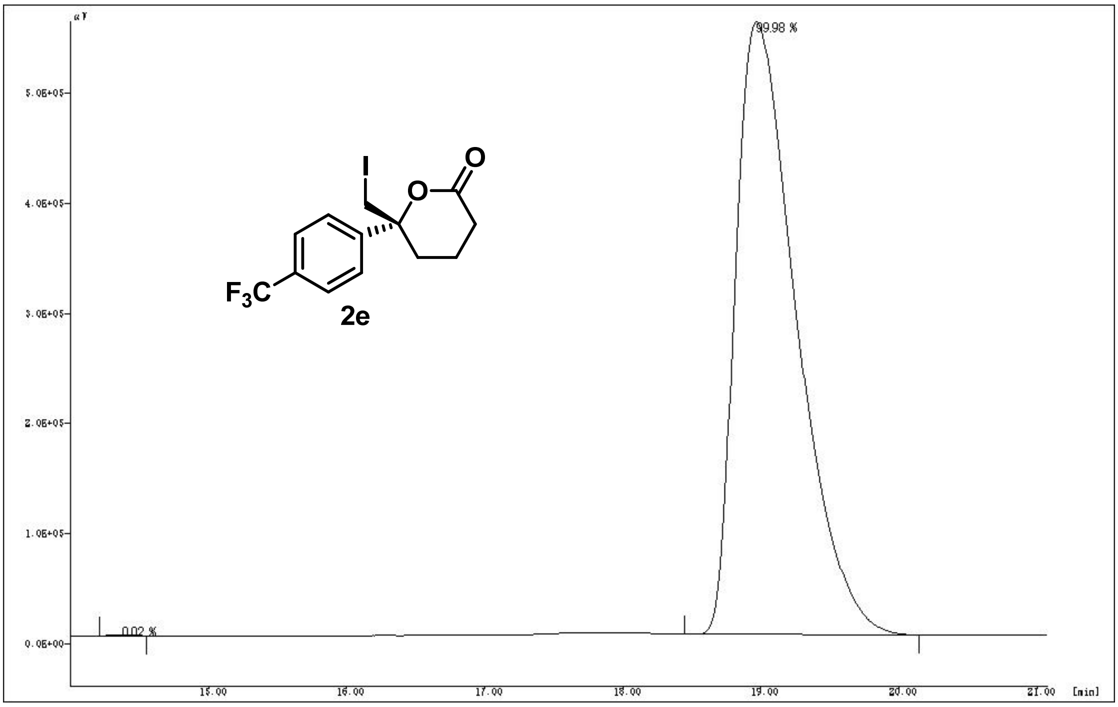


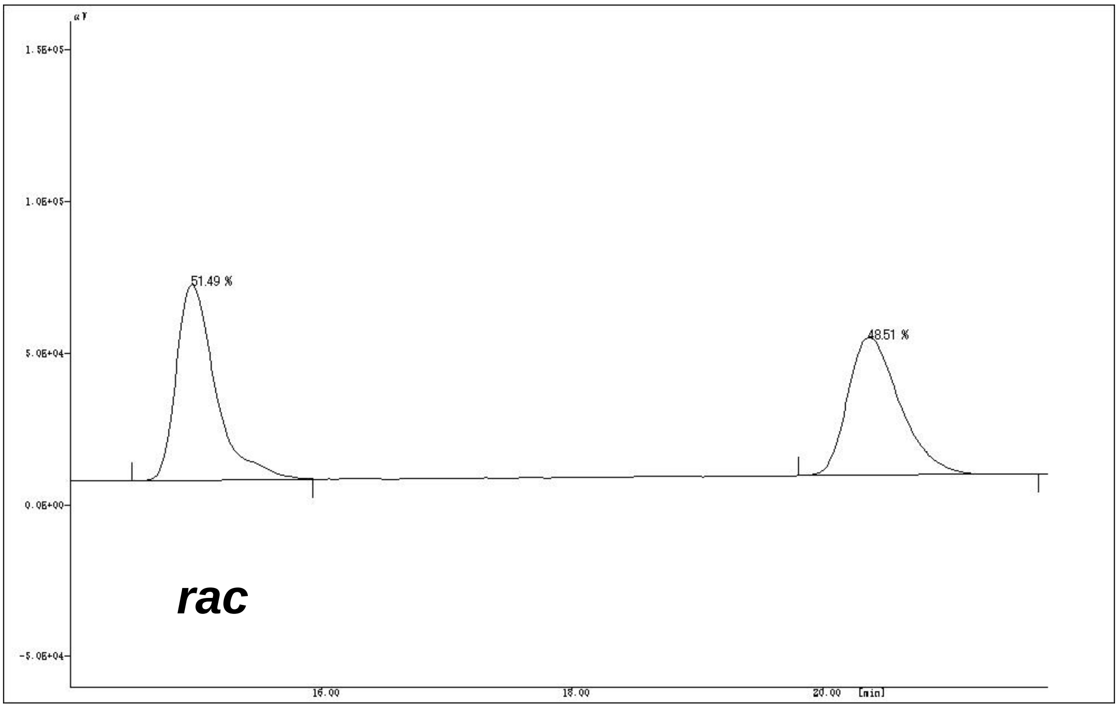
Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)



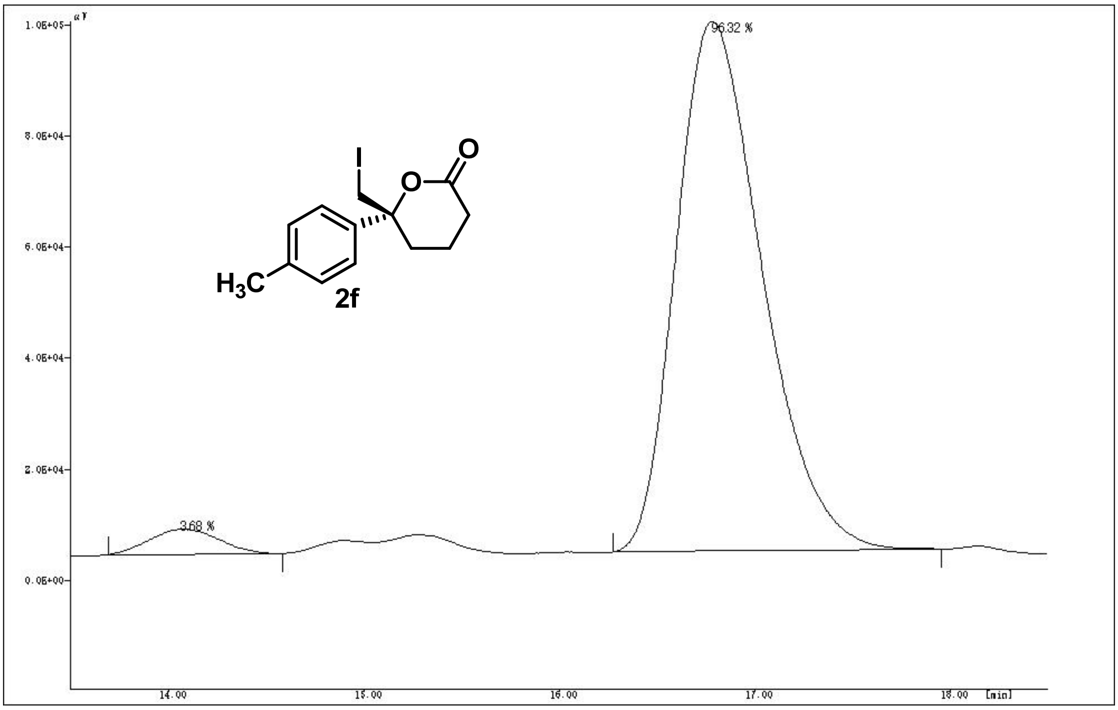


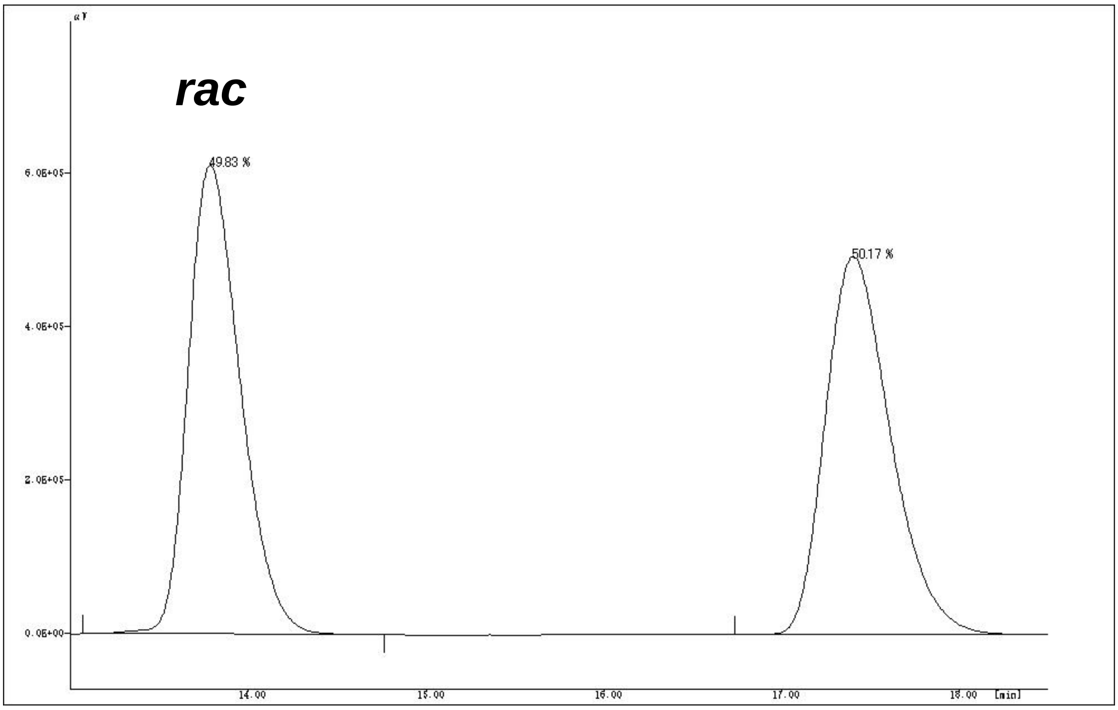
Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)



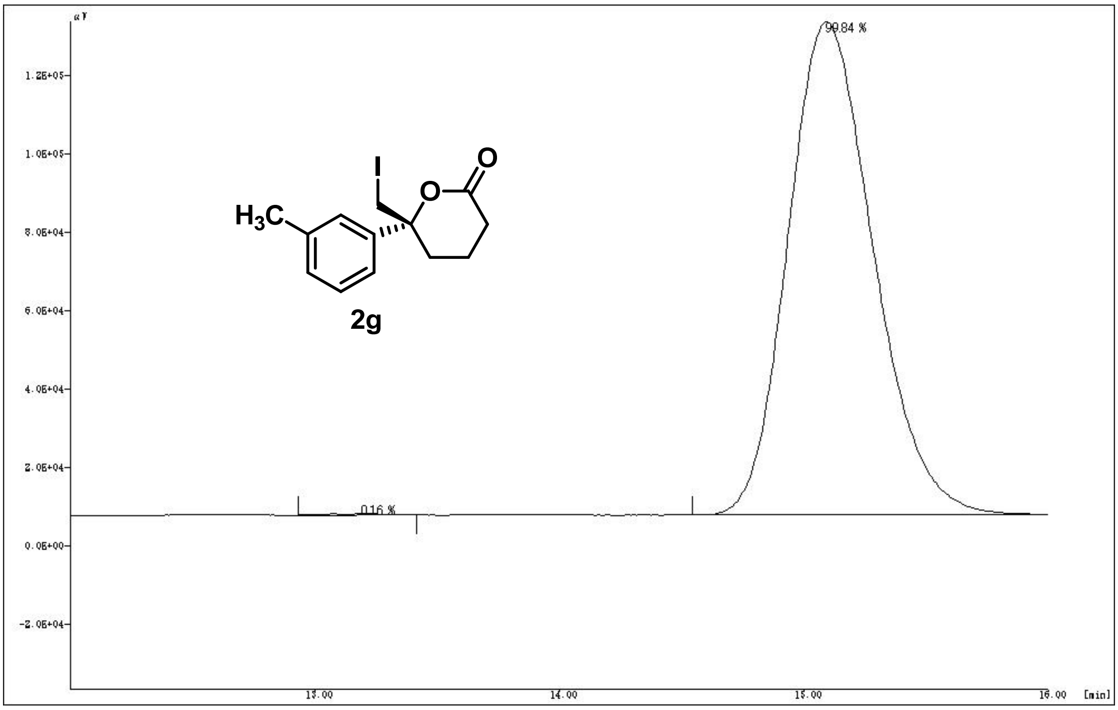


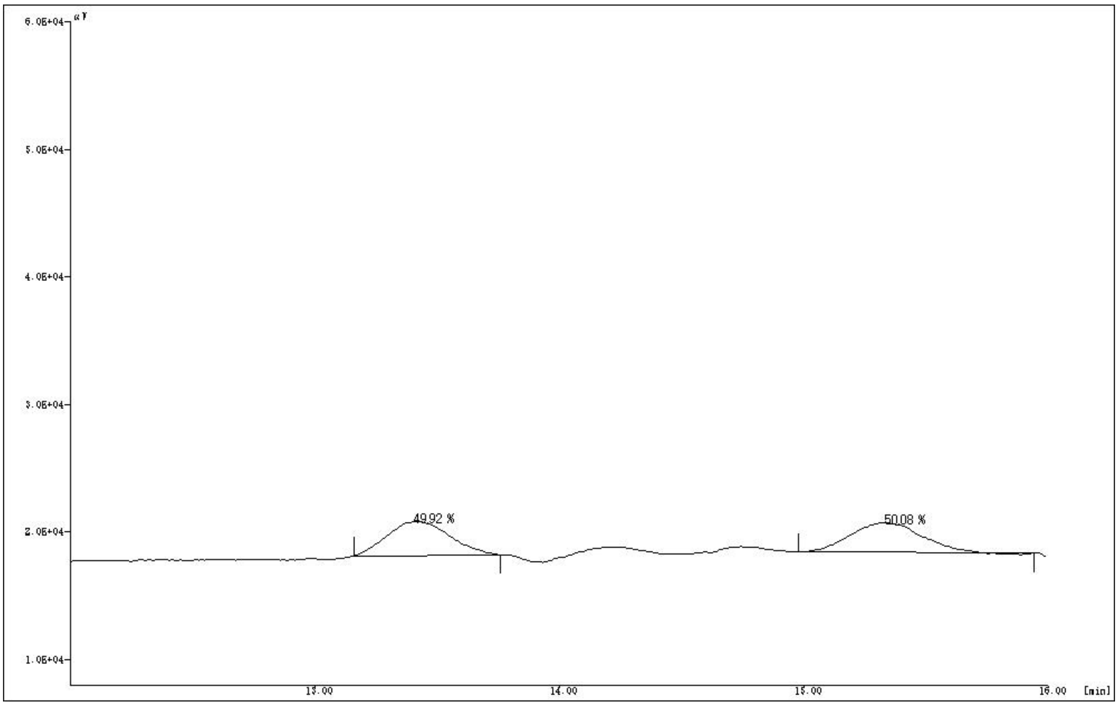
Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)



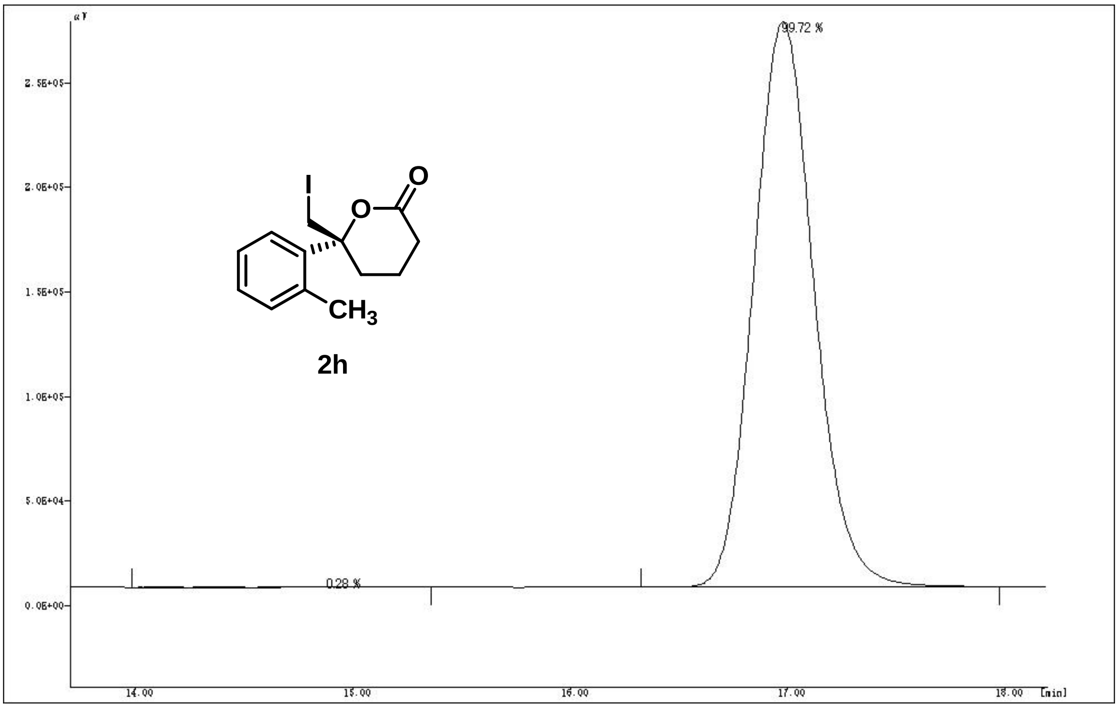


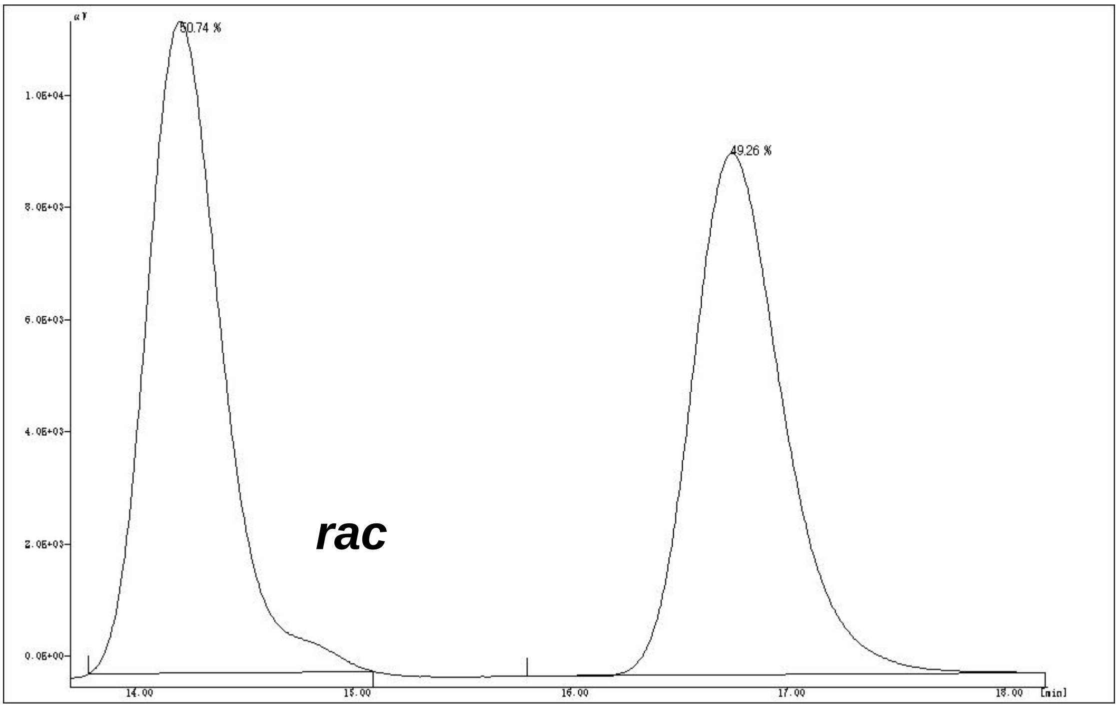
Chiralcel OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)



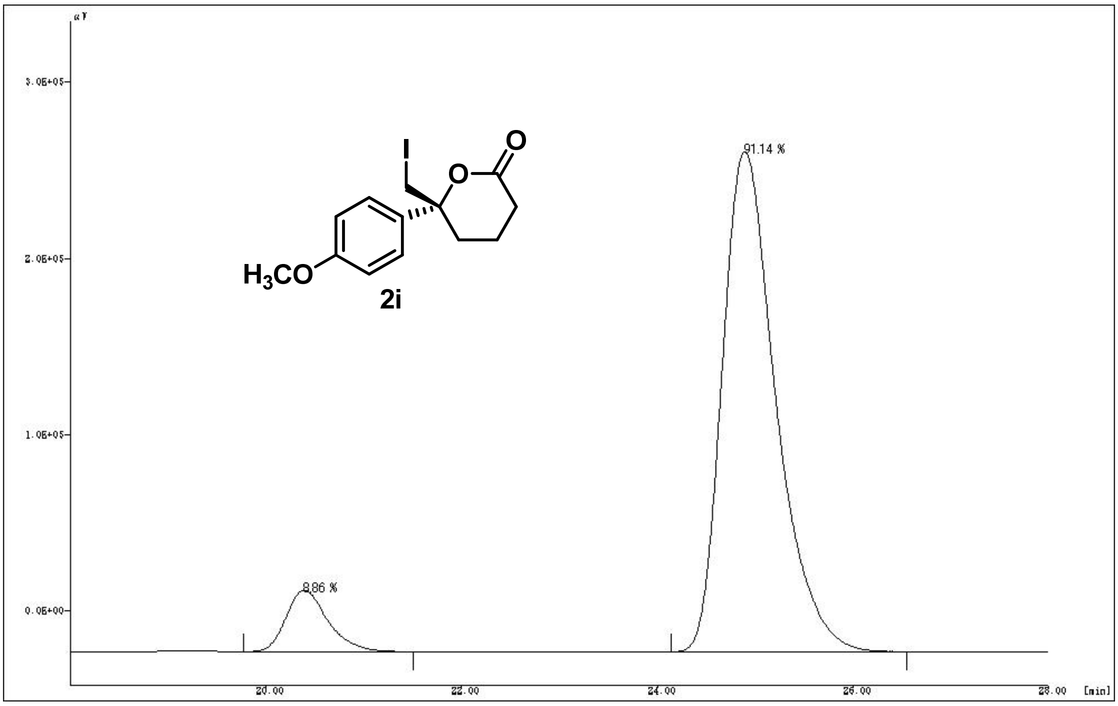


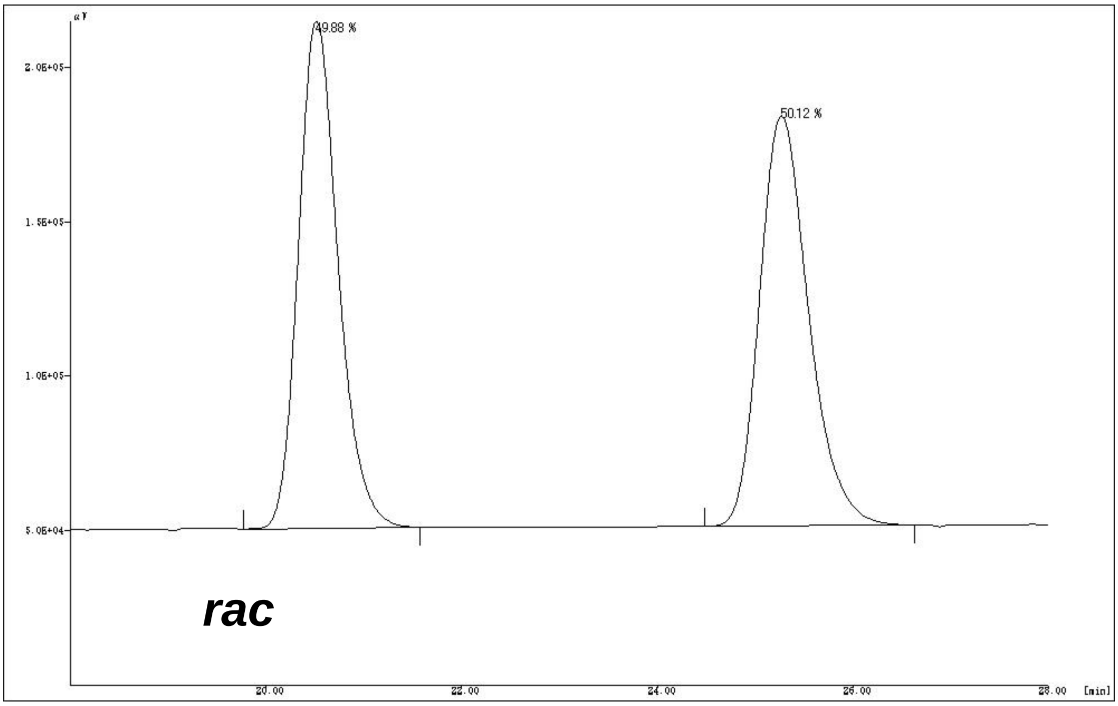
Chiralcel OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)



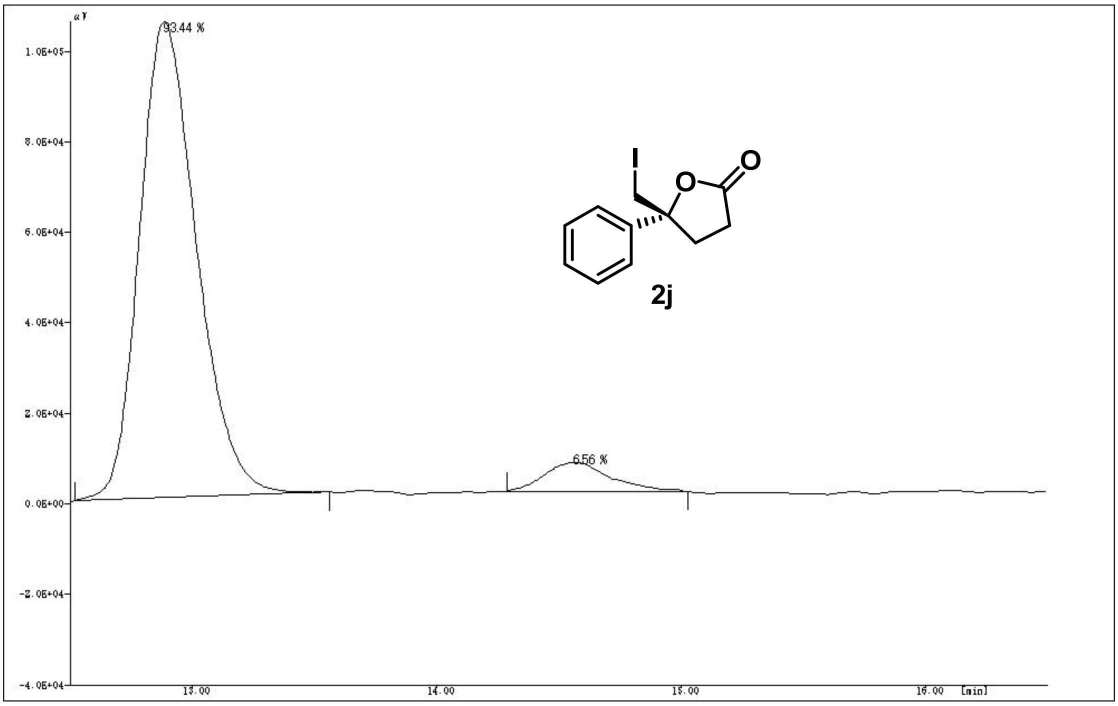


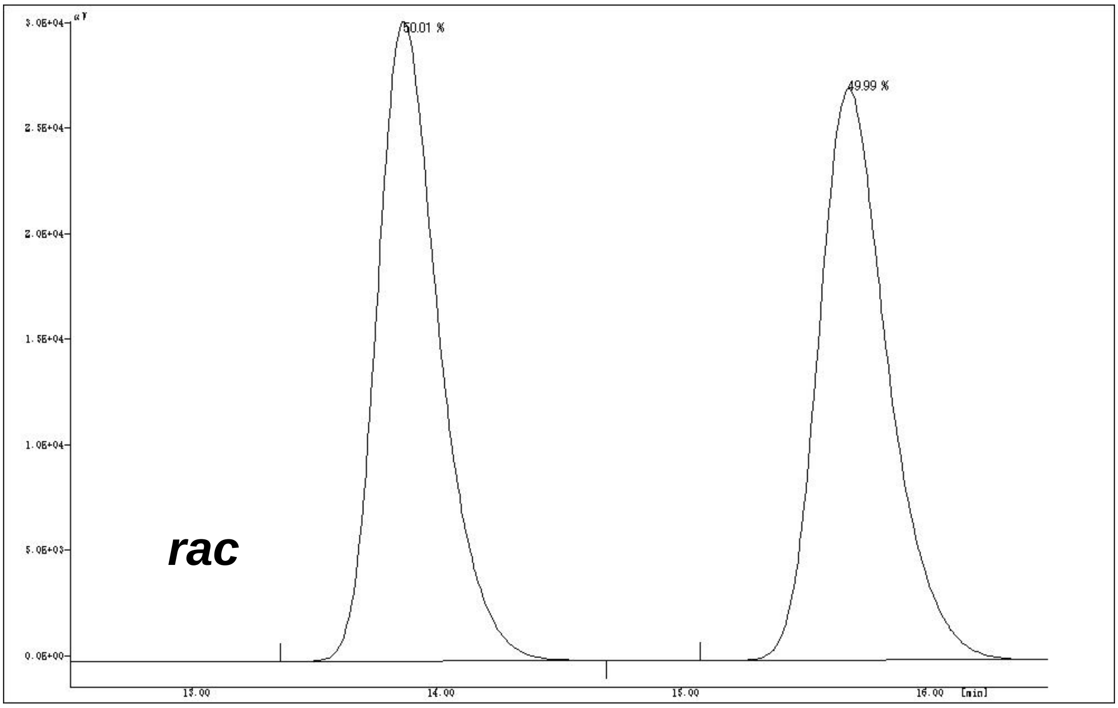
Chiralcel OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)



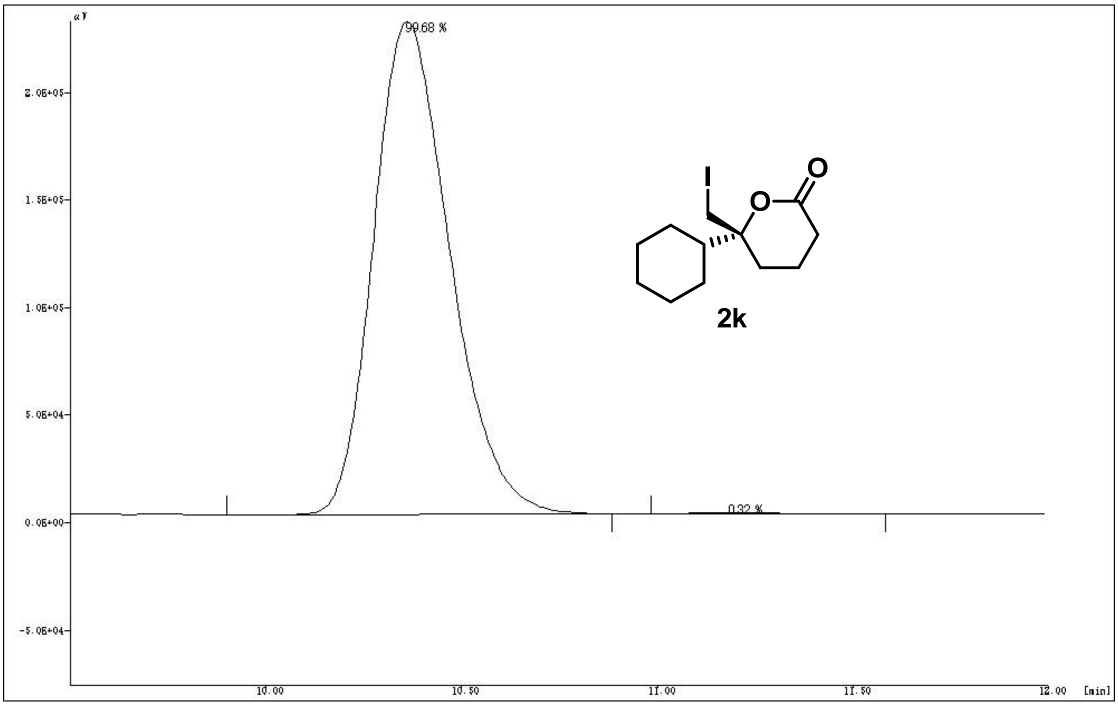


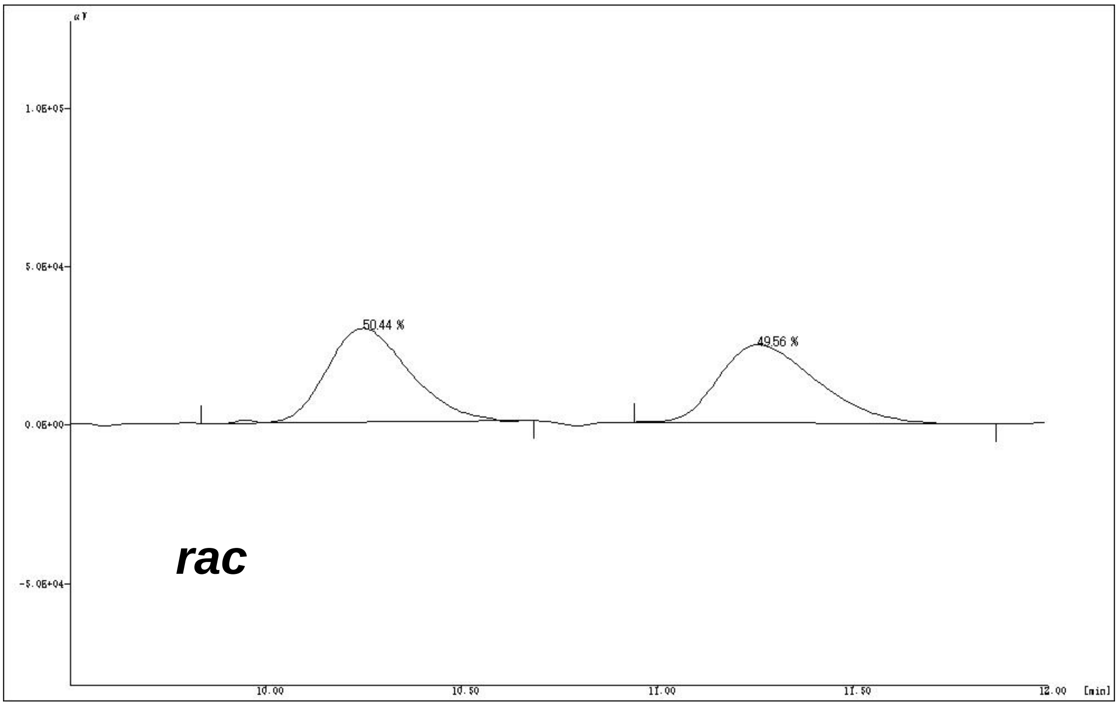
Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)



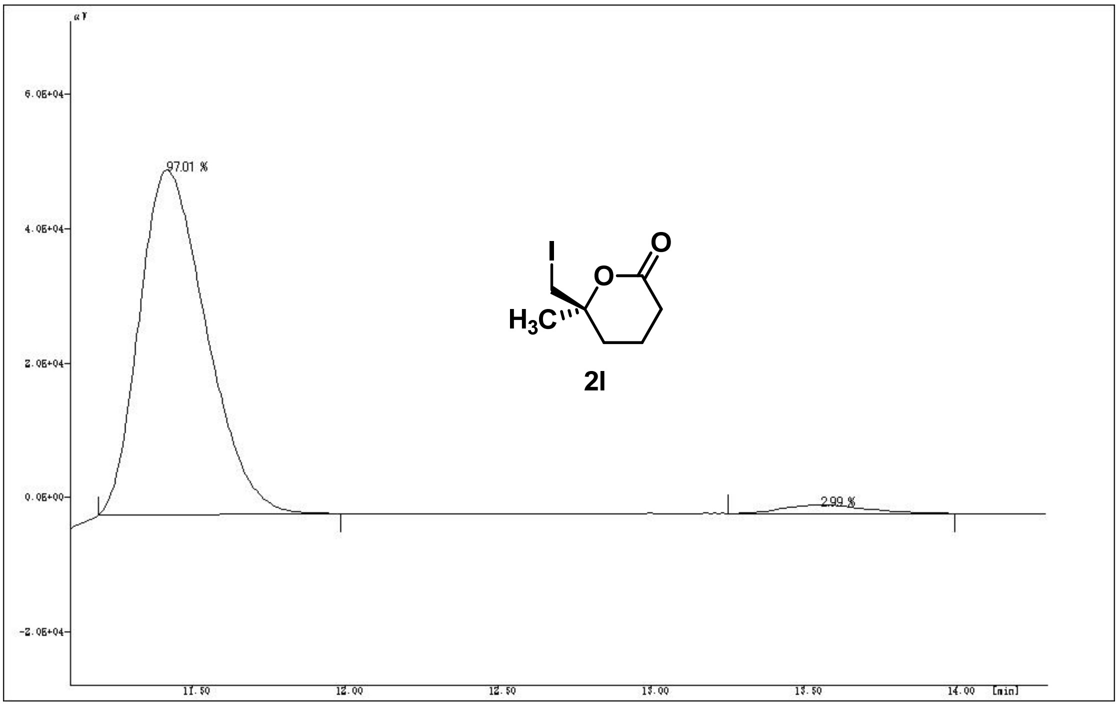


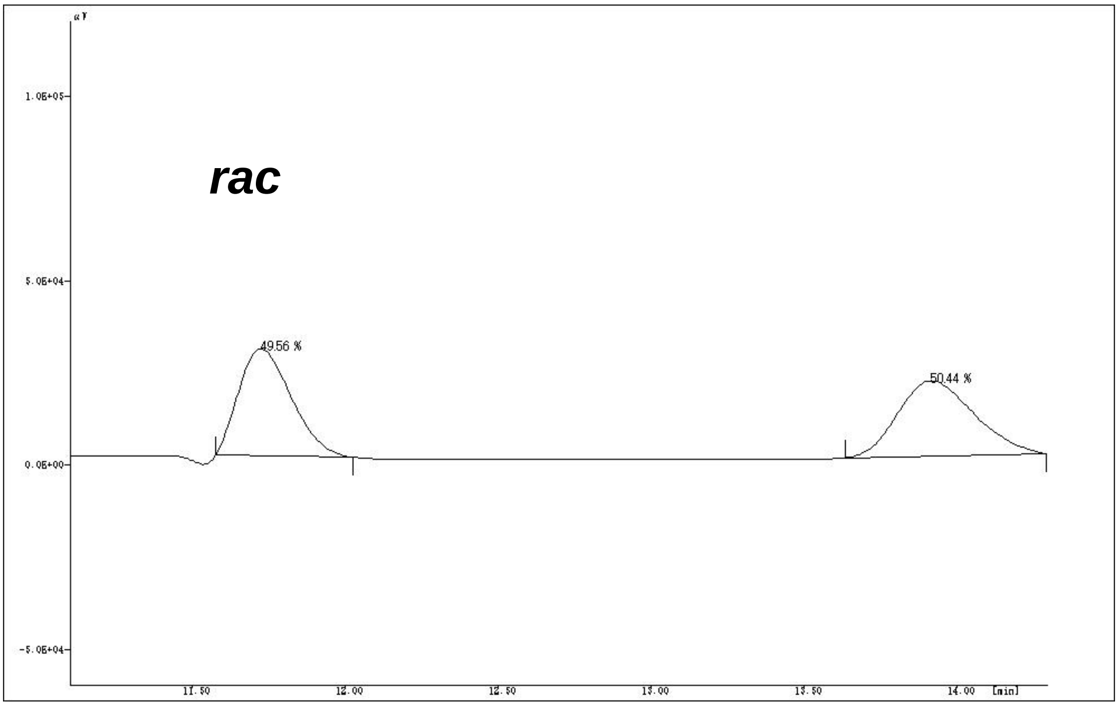
Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)





Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)





Chiralpack AD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm)

9. X-ray crystallography of **L3-Zn$_3$(OAc)$_4$** (CCDC 956608).

Crystallographic data were collected on a CCD diffractometer with Mo Kα (λ = 0.71073 Å) radiation. Data collections were carried out at low temperature (173 K) using liquid nitrogen. All of the crystal structures were solved by direct methods with SHELXS-97 and refined with full-matrix least-squares SHELXL-97.* All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at their calculated positions. The positions of hydrogen atoms included in the water molecules were not calculated. One water molecule is located in disordered two positions (O18A and O18B).

L3-Zn$_3$(OAc)$_4$: $C_{74}H_{64}N_4O_{10}Zn_3$, 2($CH_4O$), 6(O), M_r = 1525.49, Monoclinic, $P2_1$, a = 11.1670(16), b = 22.145(3), c = 16.594(2) Å, β = 108.310(2)°, V = 3896.0(9) Å^3, Z = 2, D_c = 1.300 Mg m^{-3}, 2θ_{max} = 54.94°, T = 173 K, 20839 reflections measured, 15718 unique (R_{int} = 0.1230), μ = 0.984 mm^{-1}. The final R_1 and wR_2 were 0.0464 and 0.1093 ($I > 2\sigma(I)$), 0.0552 and 0.1139 (all data). Flack parameter is 0.019(12).

* A short history of SHELX. Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112–122.

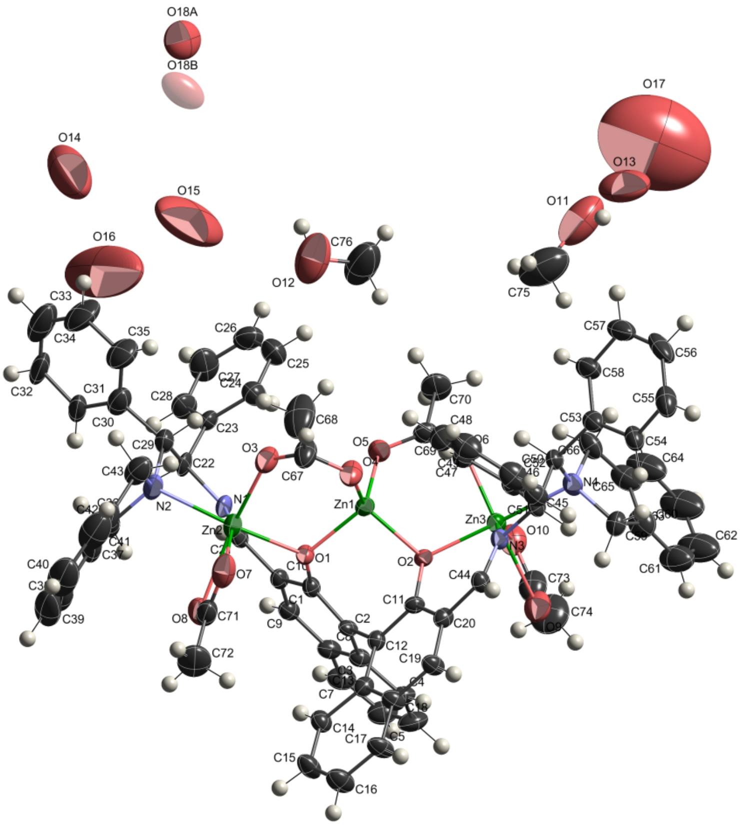


Figure S3. Thermal ellipsoid model of **L3**-Zn$_3$(OAc)$_4$. All atoms in an expanded structure are indicated in the model. The ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level while isotropic hydrogen atoms are represented by spheres of arbitrary size. The labels of non-water hydrogen atoms are omitted for clarity.

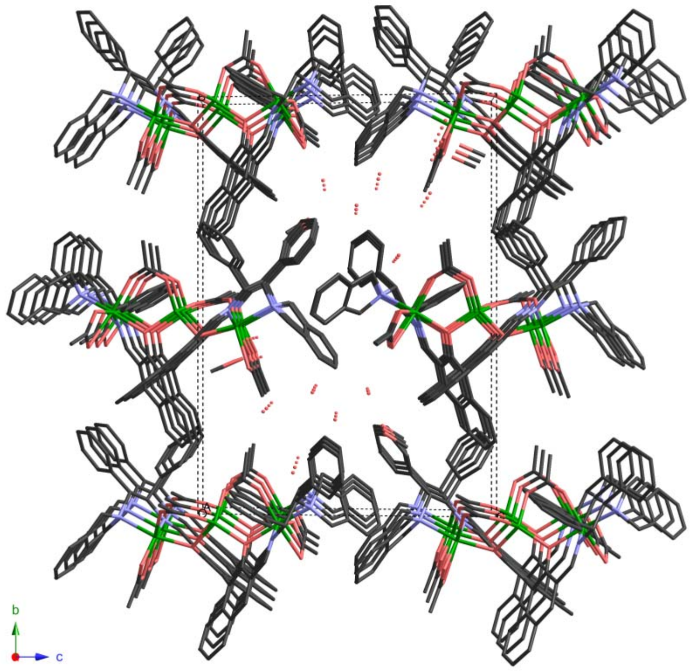


Figure S4. Packing diagram of **L3-**$Zn_3(OAc)_4$ along the *a* axis. Hydrogen atoms are omitted for clarity.

10. DFT-GIAO calculation of **L3-$Zn_3(OAc)_4$**

Computational method

All calculations were performed with the Gaussian 09 package.[i] Geometry of L3-$Zn_3(OAc)_4$ was fully optimized at the B3LYP/ 6-31G*level. The ^{1}H NMR chemical shifts were calculated by the GIAO (gauge independent atomic orbitals) method[ii] at the same computational level for the geometry optimization and referenced to TMS.

Cartesian coordination

L3-$Zn_3(OAc)_4$

SCF Done: E(RB3LYP) = -4026.84494442 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.697058	3.594574	-1.096969
2	6	0	1.174442	5.003048	0.739821
3	6	0	2.502378	4.783604	1.458437
4	6	0	2.775492	3.562712	2.094940
5	6	0	3.985841	3.373542	2.761533
6	6	0	4.942115	4.391689	2.798151
7	6	0	4.683463	5.602420	2.155783
8	6	0	3.471036	5.793550	1.489234
9	6	0	0.000019	5.151597	1.750360
10	6	0	0.205310	6.297925	2.739002
11	6	0	0.579991	7.595110	2.352345
12	6	0	0.726807	8.613252	3.295928
13	6	0	0.507183	8.356062	4.650045
14	6	0	0.146222	7.070105	5.053399
15	6	0	0.000000	6.056090	4.105698
16	6	0	-1.542008	6.291423	0.069931
17	6	0	-3.044494	6.396853	0.027348
18	6	0	-3.857352	7.073158	-0.878374
19	6	0	-5.242182	7.050764	-0.683338
20	6	0	-5.796294	6.361291	0.400478
21	6	0	-4.974903	5.682181	1.305660
22	6	0	-3.597284	5.705958	1.106271

23	6	0	-2.497537	5.095432	1.933374
24	6	0	-2.105718	0.991969	1.785065
25	6	0	-3.469191	1.123219	2.428103
26	6	0	-3.032816	3.433274	-1.850982
27	6	0	-4.118763	3.469973	-2.904529
28	1	0	2.622003	4.180542	-1.174800
29	1	0	1.249729	5.929024	0.152994
30	1	0	2.061902	2.744956	2.044742
31	1	0	4.183631	2.422223	3.248278
32	1	0	5.885024	4.238231	3.316309
33	1	0	5.423315	6.398441	2.168470
34	1	0	3.275810	6.740764	0.992431
35	1	0	-0.025833	4.222615	2.331697
36	1	0	0.778650	7.821279	1.309152
37	1	0	1.018916	9.608210	2.970521
38	1	0	0.623444	9.149031	5.383761
39	1	0	-0.017136	6.852433	6.105499
40	1	0	-0.270406	5.054083	4.430758
41	1	0	-1.103550	6.054333	-0.903510
42	1	0	-1.109427	7.232279	0.437682
43	1	0	-3.429084	7.602988	-1.725498
44	1	0	-5.893043	7.568043	-1.383211
45	1	0	-6.874428	6.346917	0.536115
46	1	0	-5.409267	5.141108	2.142603
47	1	0	-2.667393	4.054188	2.218529
48	1	0	-2.334799	5.681894	2.850044
49	1	0	-4.125277	1.632775	1.712956
50	1	0	-3.405337	1.743025	3.327915
51	1	0	-3.889374	0.146174	2.672393
52	1	0	-4.164211	4.461490	-3.363312
53	1	0	-5.087826	3.205393	-2.477253
54	1	0	-3.867753	2.748217	-3.690943
55	7	0	0.844044	3.896210	-0.178726
56	7	0	-1.308162	5.165027	1.026529
57	8	0	-3.236688	2.824670	-0.751317
58	8	0	-0.280625	1.457469	-1.008875
59	8	0	-1.716999	-0.166808	1.431123
60	8	0	-1.406638	2.037231	1.607999

61	8	0	-1.911578	3.984687	-2.089032
62	30	0	-1.200071	3.163735	-0.199716
63	6	0	0.581842	1.489933	-2.025883
64	6	0	0.546539	0.511064	-3.025169
65	6	0	1.587723	2.526207	-2.076038
66	6	0	1.558936	0.483167	-4.036266
67	6	0	2.544747	2.507181	-3.082706
68	6	0	1.632513	-0.544967	-5.021458
69	6	0	2.568289	1.505651	-4.070740
70	1	0	3.307716	3.283419	-3.105830
71	6	0	2.622348	-0.545766	-5.979522
72	1	0	0.899341	-1.342929	-5.000453
73	6	0	3.571831	1.479887	-5.079725
74	6	0	3.601729	0.479045	-6.020464
75	1	0	2.653995	-1.345759	-6.714826
76	1	0	4.320625	2.269006	-5.085134
77	1	0	4.372436	0.463650	-6.785962
78	6	0	-0.546539	-0.511064	-3.025169
79	6	0	-0.581842	-1.489933	-2.025883
80	6	0	-1.558936	-0.483167	-4.036266
81	8	0	0.280625	-1.457469	-1.008875
82	6	0	-1.587723	-2.526207	-2.076038
83	6	0	-1.632513	0.544967	-5.021458
84	6	0	-2.568289	-1.505651	-4.070740
85	30	0	1.200071	-3.163735	-0.199716
86	6	0	-1.697058	-3.594574	-1.096969
87	6	0	-2.544747	-2.507181	-3.082706
88	6	0	-2.622348	0.545766	-5.979522
89	1	0	-0.899341	1.342929	-5.000453
90	6	0	-3.571831	-1.479887	-5.079725
91	7	0	-0.844044	-3.896210	-0.178726
92	7	0	1.308162	-5.165027	1.026529
93	8	0	3.236688	-2.824670	-0.751317
94	8	0	1.406638	-2.037231	1.607999
95	8	0	1.911578	-3.984687	-2.089032
96	1	0	-2.622003	-4.180542	-1.174800
97	1	0	-3.307716	-3.283419	-3.105830
98	6	0	-3.601729	-0.479045	-6.020464

99	1	0	-2.653995	1.345759	-6.714826
100	1	0	-4.320625	-2.269006	-5.085134
101	6	0	-1.174442	-5.003048	0.739821
102	6	0	-0.000019	-5.151597	1.750360
103	6	0	1.542008	-6.291423	0.069931
104	6	0	2.497537	-5.095432	1.933374
105	6	0	3.032816	-3.433274	-1.850982
106	6	0	2.105718	-0.991969	1.785065
107	1	0	-4.372436	-0.463650	-6.785962
108	1	0	-1.249729	-5.929024	0.152994
109	6	0	-2.502378	-4.783604	1.458437
110	1	0	0.025833	-4.222615	2.331697
111	6	0	-0.205310	-6.297925	2.739002
112	1	0	1.103550	-6.054333	-0.903510
113	1	0	1.109427	-7.232279	0.437682
114	6	0	3.044494	-6.396853	0.027348
115	6	0	3.597284	-5.705958	1.106271
116	1	0	2.667393	-4.054188	2.218529
117	1	0	2.334799	-5.681894	2.850044
118	6	0	4.118763	-3.469973	-2.904529
119	6	0	3.469191	-1.123219	2.428103
120	8	0	1.716999	0.166808	1.431123
121	6	0	-2.775492	-3.562712	2.094940
122	6	0	-3.471036	-5.793550	1.489234
123	6	0	-0.579991	-7.595110	2.352345
124	6	0	0.000000	-6.056090	4.105698
125	6	0	3.857352	-7.073158	-0.878374
126	6	0	4.974903	-5.682181	1.305660
127	1	0	4.164211	-4.461490	-3.363312
128	1	0	5.087826	-3.205393	-2.477253
129	1	0	3.867753	-2.748217	-3.690943
130	1	0	4.125277	-1.632775	1.712956
131	1	0	3.405337	-1.743025	3.327915
132	1	0	3.889374	-0.146174	2.672393
133	1	0	-2.061902	-2.744956	2.044742
134	6	0	-3.985841	-3.373542	2.761533
135	6	0	-4.683463	-5.602420	2.155783
136	1	0	-3.275810	-6.740764	0.992431

137	1	0	-0.778650	-7.821279	1.309152
138	6	0	-0.726807	-8.613252	3.295928
139	6	0	-0.146222	-7.070105	5.053399
140	1	0	0.270406	-5.054083	4.430758
141	1	0	3.429084	-7.602988	-1.725498
142	6	0	5.242182	-7.050764	-0.683338
143	6	0	5.796294	-6.361291	0.400478
144	1	0	5.409267	-5.141108	2.142603
145	1	0	-4.183631	-2.422223	3.248278
146	6	0	-4.942115	-4.391689	2.798151
147	1	0	-5.423315	-6.398441	2.168470
148	1	0	-1.018916	-9.608210	2.970521
149	6	0	-0.507183	-8.356062	4.650045
150	1	0	0.017136	-6.852433	6.105499
151	1	0	5.893043	-7.568043	-1.383211
152	1	0	6.874428	-6.346917	0.536115
153	1	0	-5.885024	-4.238231	3.316309
154	1	0	-0.623444	-9.149031	5.383761
155	30	0	0.000000	0.000000	0.372207

----

[i] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.

[ii] (a) R. McWeeny, *Phys. Rev*. **1962**, *126*, 1028. (b) R. Dichfield, *Mol. Phys.* **1974**, *27*, 789. (c) J. L. Dodds, R. McWeeny, A. J. Sadlej, *Mol. Phys.* **1980**, *41*, 1419. (d) K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251.