Supporting Information

Catalytic Asymmetric Intra- and Intermolecular Haloetherification of Enones: An Efficient Approach to (−)-Centrolobine

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Table of Contents

1. General remarks

Reactions were carried out using commercial available reagents in over-dried apparatus. *O*-xylene

and toluene were dried over dry molecular sieves and distilled under nitrogen. Enantiomeric excess (*ee*) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 23 ˚C with UV detector at 254 nm or 210 nm. Optical rotations were reported at indicated wavelength as follows: $[\alpha]^{T}_{D}$ (c g/100 mL, in solvent). ^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26, DMSO-d_6, δ = 2.51). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0, DMSO-d_6, δ = 39.5). HRMS was recorded on a commercial apparatus (ESI Source).

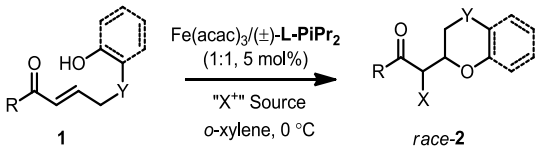
2. General procedure for chiral *N,N'*-dioxide and substrates preparation

The *N,N'*-dioxide chiral ligands **L-PiPr₂**, **L-PrPr₂** and **L-RaPr₂** were synthesized according to the same procedure published on the literatures.[1-3]

The substrates **1a-1s, 3a-3h** were synthesized from diverse diols according to the general procedure reported on the literature.[4-7] Substrate (±)-**13** was synthesized according to the literature[8] using olefin metathesis.

3. Typical procedure for the haloetherification

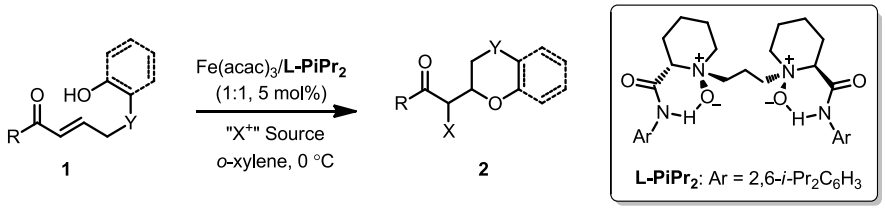
General procedure for the racemic haloetherification products preparation



For bromo- and chlorocyclization: A dry test tube was charged with (+)-**L-PiPr₂** (0.0025 mmol), (-)-**L-PiPr₂** (0.0025 mmol) and $Fe(acac)_3$ (0.005 mmol), under N_2 atmosphere, *o*-xylene (2.0 mL) was added. The mixture was stirred at 35 °C for 15-20 min, followed by the addition of halogen reagent (for *p*-$NsNCl_2$, 0.1 mmol; for BsNMeBr, 0.2 mmol). After stirring for 5 min, the mixture was cooled to 0 °C. Substrate **1** (0.1 mmol) was added under stirring and the reaction mixture was continued stirring at 0 °C for 4 h. The residue was purified by flash chromatography on silica gel to afford the desired racemic product *race*-**2**.

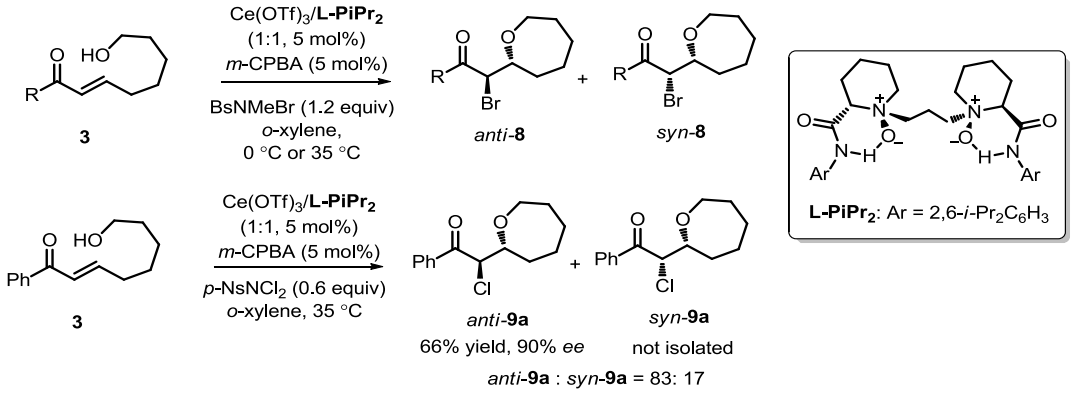
For iodocyclization: A dry test tube was charged with (+)-**L-PiPr₂** (0.0025 mmol), (-)-**L-PiPr₂** (0.0025 mmol) and $Fe(acac)_3$ (0.005 mmol), under N_2 atmosphere, *o*-xylene (2.0 mL) was added. The mixture was stirred at 35 °C for 15-20 min, followed by the addition of NIS (0.2 mmol) in the dark. After stirring for 5 min, the mixture was cooled to 0 °C. Substrate **1a** (0.1 mmol) was added under stirring and the reaction mixture was continued stirring at 0 °C for 4 h. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 15:1) to afford the desired racemic product *race*-**2ca**.

General procedure for the asymmetric halotherification products preparation

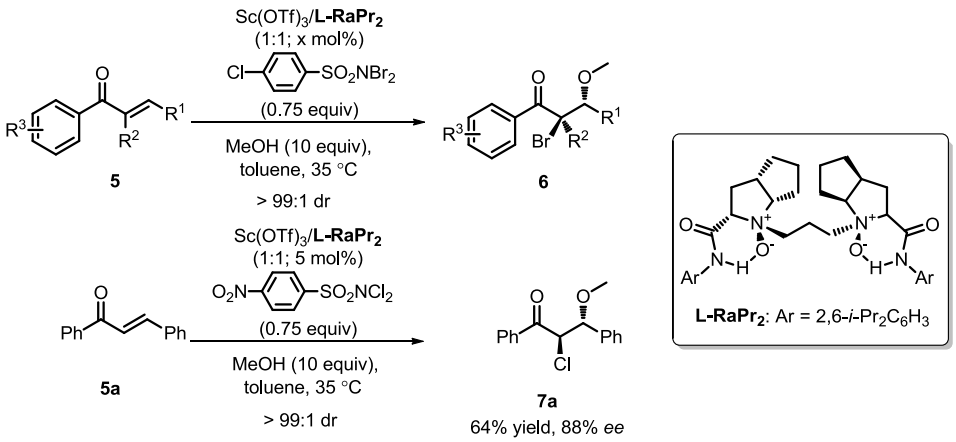


For bromo- and chlorocyclization: A dry reaction tube was charged with **L-PiPr₂** (0.005 mmol) and $Fe(acac)_3$ (0.005 mol). Under N_2 atmosphere, *o*-xylene (2.0 mL) was added. The mixture was stirred at 35 °C for 15-20 min, followed by the addition of halogen reagent (for *p*-$NsNCl_2$, 0.1 mmol; for BsNMeBr, 0.2 mmol). After stirring for 5 min, the mixture was cooled to 0 °C. Substrate **1** (0.1 mmol) was added under stirring and the reaction mixture was continued stirring at 0 °C for 4 h. The residue was purified by flash chromatography on silica gel to afford the desired product **2**. The enantiomeric excess (*ee*) and diastereomeric ratio (dr) was determined by high-performance liquid chromatography (HPLC) using a Chiral-cel column.

For iodocyclization: A dry reaction tube was charged with **L-PiPr₂** (0.005 mmol) and $Fe(acac)_3$ (0.005 mol). Under N_2 atmosphere, *o*-xylene (2.0 mL) was added. The mixture was stirred at 35 °C for 15-20 min, followed by the addition of NIS (0.2 mmol) in the dark. After stirring for 5 min, the mixture was cooled to 0 °C. Substrate **1** (0.1 mmol) was added under stirring and the reaction mixture was continued stirring at 0 °C for 4 h. The residue was purified by flash chromatography on silica gel (petroleum ether : EtOAc = 15:1) to afford the desired product **2ca**. The enantiomeric excess (*ee*) and diastereomeric ratio (dr) was determined by high-performance liquid chromatography (HPLC) using a Chiral-cel column.

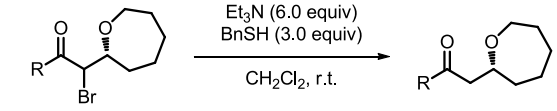


A dry reaction tube was charged with **L-PiPr₂** (0.005 mmol), $Ce(OTf)_3$ (0.005 mol) and *m*-CPBA (0.005 mol). Under N_2 atmosphere, *o*-xylene (2.0 mL) was added. The mixture was stirred at 35 °C for 15-20 min, followed by the addition of halogen reagent (for *p*-$NsNCl_2$, 0.06 mmol; for BsNMeBr, 0.12 mmol). After stirring for 5 min, the mixture was cooled to 0 °C (or remain stay at 35 °C, for details, s*ee* "Characterization of the products"). Substrate **3** (0.1 mmol) was added under stirring and the reaction mixture was continued stirring at 0 °C (or 35 °C) for indicated time. The residue was purified by flash chromatography on silica gel to afford the desired product **8** (or *anti*-**9a**). The diastereomeric ratio (dr) was determined by ^1H NMR of crude product. The enantiomeric excess (*ee*) was determined by high-performance liquid chromatography (HPLC) using a Chiral-cel column.



A dry reaction tube was charged with *x* μL (x mol% loading) catalyst solution (0.02M in THF). After the solvent was removed under vacuo, chalcones **5** (0.1 mmol) were weighed into the tube followed by adding toluene (2.0 mL). The mixture was stirred at 35 °C for 5 min, followed by the addition of halogen reagent 0.075 mmol. After stirring for 5 min, MeOH (1.0 mmol) was added under stirring and the reaction mixture was continued stirring at 35 °C for indicated time. The residue was purified by flash chromatography on silica gel to afford the desired product **6** (or **7a**). The diastereomeric ratio (dr) was determined by ^{1}H NMR and HPLC. The enantiomeric excess (*ee*) was determined by high-performance liquid chromatography (HPLC) using a Chiral-cel column.

4. Typical procedure for the debromination of product

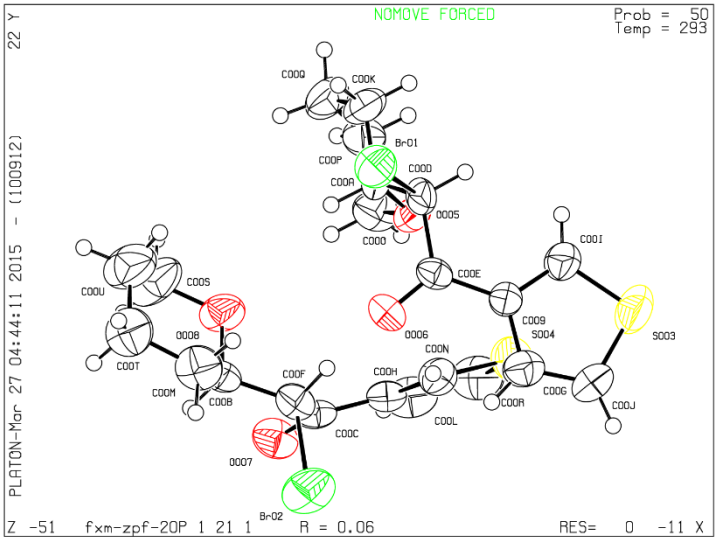


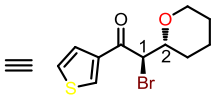
A dried flask was charged with **8** (indicated amount, see "Characterization of the products" for details) and CH_2Cl_2 (1.5 mL). Et_3N (6.0 equiv) and BnSH (3.0 equiv) was added to this solution at ambient temperature, and the mixture was stirred at ambient temperature for indicated time. Purified by flash silica gel chromatography giving the corresponding debromination product **4.**

5. Determination of absolute configuration of 2bn, *anti*-8d and 6a

The absolute configuration of the optically active product **2bn** was determined by its X-ray crystal structure.

Single crystal of $C_{11}H_{13}BrO_2S$ **2bn** was recrystallized from mixed solvents of CH_2Cl_2 and petroleum ether. Both the absolute configuration of C1 and the absolute configuration of C2 are *R*. CCDC 1403958 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

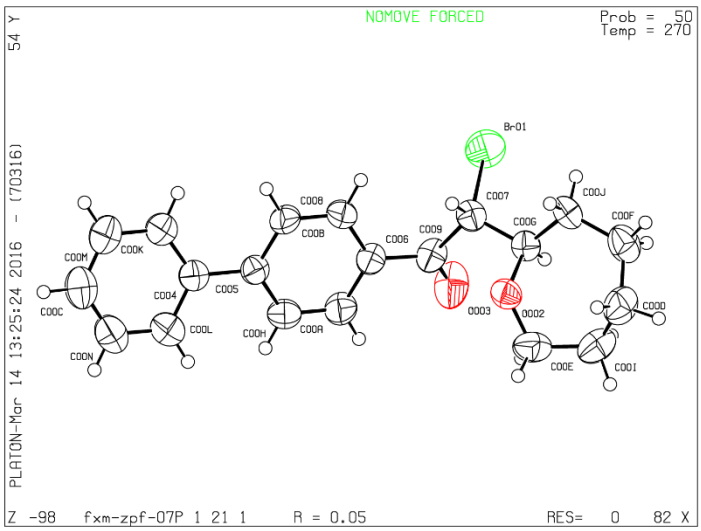


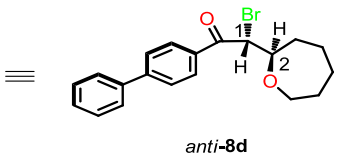


2bn

The absolute configuration of the optically active product *anti*-**8d** was determined by its X-ray crystal structure.

Single crystal of $C_{20}H_{21}BrO_2$ *anti*-**8d** was recrystallized from mixed solvents of CH_2Cl_2 and *n*-hexane. Both the absolute configuration of C1 and the absolute configuration of C2 are *R*. CCDC 1411983 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



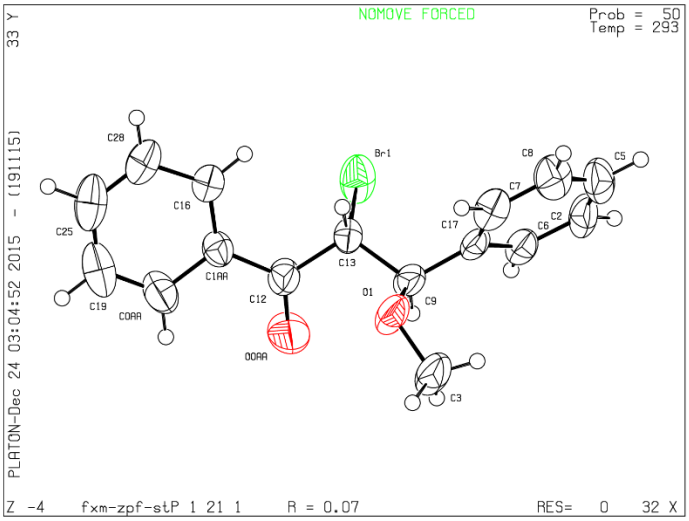


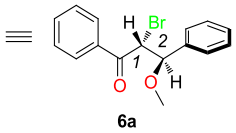
anti-**8d**

The absolute configuration of the optically active product **6a** was determined by its X-ray crystal structure.

Single crystal of $C_{16}H_{15}BrO_2$ **6a** was recrystallized from mixed solvents of CH_2Cl_2 and *n*-hexane. Both the absolute configuration of C1 and the absolute configuration of C2 are *R*. CCDC 1465501 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

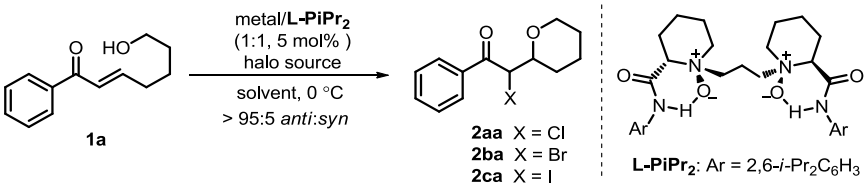




6a

6. Optimization of reaction conditions and substrate scope

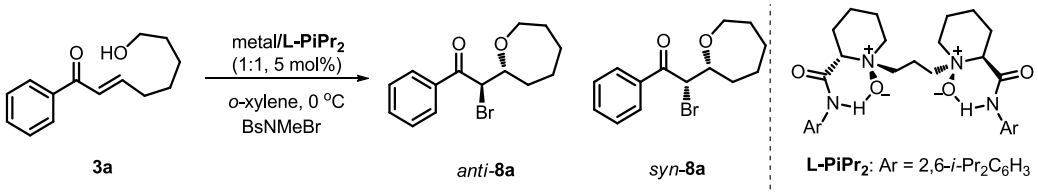
Table S1. **Optimized the reaction conditions of asymmetric haloetherification of enone 1a**[a]



Entry	metal	halo source; solvent	Yield [%][b]	*ee* [%][c]
1	$Sc(OTf)_3$	NBS; CH_2Cl_2	82(**2ba**)	35
2	$Fe(acac)_3$	NBS; CH_2Cl_2	77(**2ba**)	66
3	$Fe(acac)_3$	NBS; toluene	65(**2ba**)	79
4[d]	$Fe(acac)_3$	NBS; toluene	95(**2ba**)	82
5[d]	$Fe(acac)_3$	NBS; *o*-xylene	93(**2ba**)	86
6[d,e]	$Fe(acac)_3$	NBS; *o*-xylene	93(**2ba**)	91
7[e]	$Fe(acac)_3$	$BsNBr_2$; *o*-xylene	94(**2ba**)	92
8[d,e]	**$Fe(acac)_3$**	**BsNMeBr; *o*-xylene**	**97(2ba)**	**96**
9[e]	**$Fe(acac)_3$**	***p*-$NsNCl_2$; *o*-xylene**	**91(2aa)**	**85**
10[d,e]	**$Fe(acac)_3$**	**NIS; *o*-xylene**	**90(2ca)**	**89**

[a] Unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), halogen reagent (0.12 mmol) and $Fe(acac)_3$/**L-PiPr₂** (1:1, 5 mol%) in solvent (0.2 M) at 0 °C for 4 h. [b] Isolated yield. [c] Dr was determined by ^1H NMR (up to 95:5), and the *ee* of the *anti*-**2** was determined by HPLC. [d] 2.0 equiv of halogen reagent (0.2 mmol) was used. [e] Reaction concentration was 0.05 M. Bs = phenylsulfonyl, *p*-Ns = (4-nitrophenyl) sulfonyl.

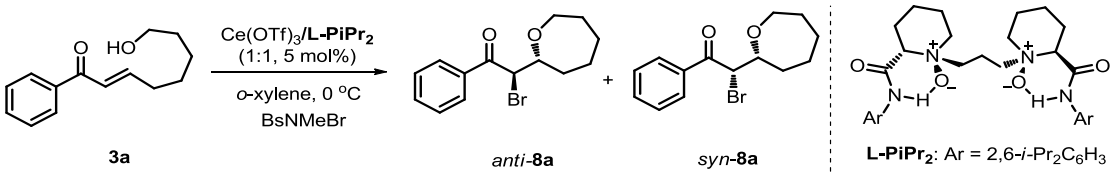
Table S2. **Screening of the metal salts of haloetherification of enone 3a**[a]



Entry	metal	Yield[%][b]	dr (*anti*-**8a**:*syn*-**8a**)[c]	*ee* [%][c]
1	$Fe(acac)_3$	92	85:15	40/--
2	$Fe(acac)_2$	93	85:15	48/--
3	$Ni(OTf)_2$	N.R.	--	--
4	$Co(acac)_3$	N.R.	--	--
5	$Sc(OTf)_3$	76	75:25	-17/--
6	$Mg(OTf)_2$	N.R.	--	--
7	$Yb(OTf)_3$	N.R.	--	--
8	$Lu(OTf)_3$	N.R.	--	--
9	**$Ce(OTf)_3$**	**97**	**48:52**	**87/93**
10	$Gd(OTf)_3$	N.R.	--	--
11	$In(OTf)_3$	N.R.	--	--
12	$Cu(OTf)_2$	N.R.	--	--
13	$Zn(OTf)_2$	N.R.	--	--

[a] Reaction conditions: metal/**L-PiPr$_2$** (1:1, 5 mol%), **3a** (0.1 mmol), and BsNMeBr (0.2 mmol) in *o*-xylene (2.0 mL) at 0 °C for 12 h, and the products were purified by silica gel column chromatography. [b] Total isolated yield of the two diastereoisomers *anti*-**8a** and *syn*-**8a**. [c] Determined by chiral HPLC.

Table S3. **Screening of the additive of haloetherification of enone 3a**[a]



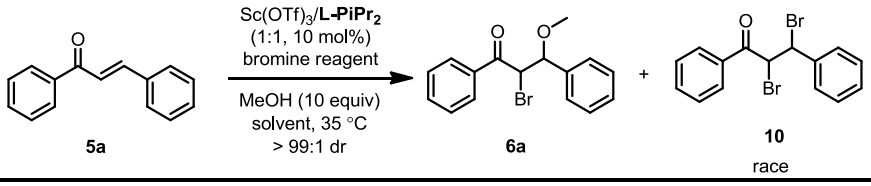
Entry	Additive (5 mol%)	Yield[%][b]	dr (*anti*-**8a**:*syn*-**8a**)[c]	*ee*[%][c]
1	H_2O (3μL)	81	53:47	91/95
2	***m*-CPBA**	**97**	**57:43**	**98/> 99**
3	PhCOOH	41	73:27	95/96
4	*m*-chlorobenzoic acid	93	50:50	96/99
5[d]	***m*-CPBA**	**97**	**57:43**	**98/> 99**
6	PhCOONa	13	53:47	77/87

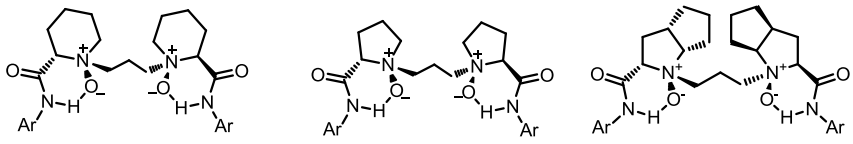
[a] Reaction conditions: $Ce(OTf)_3$/**L-PiPr$_2$** (1:1, 5 mol%), **3a** (0.1 mmol), and BsNMeBr (0.2 mmol) in *o*-xylene (2.0 mL) at 0 °C for 12 h, and the products were purified by silica gel column chromatography. [b] Total isolated yield of the both diastereoisomers. [c] Determined by chiral HPLC. [d] Using 0.12 mmol BsNMeBr.

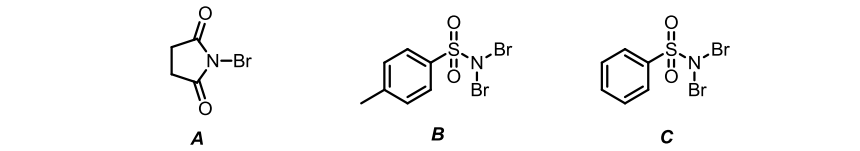
As shown in ***Table S3***, proton additive plays positive effect on the enantioselectivity. Using

PhCOONa as additive, the reactivity and enantioselectivity decreased sharply. We proposed the *m*-CPBA act as a proton additive. However, the real role of *m*-CPBA is still unclear.

Table S4. **Optimization of intermolecular haloetherification**[a]



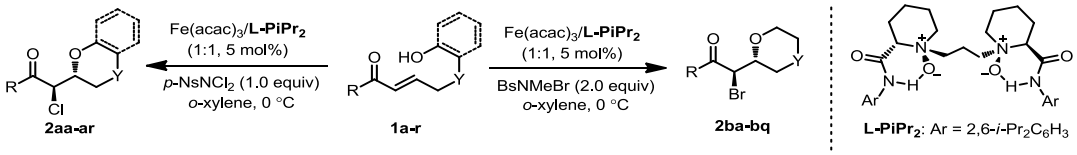


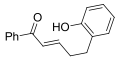


Entry	L	Bromine reagent	Solvent	Yield [%]	*ee* [%]
1[b]	--	***A***	MeOH	92	--
2	**L-PiPr$_2$**	***A***	MeOH	98	6
3	**L-PiPr$_2$**	***A***	CH_2Cl_2	50	50
4[c]	**L-PiPr$_2$**	***A***	CH_2Cl_2	78	50
5[c]	**L-PrPr$_2$**	***A***	CH_2Cl_2	71	77
6[c]	**L-RaPr$_2$**	***A***	CH_2Cl_2	76	86
7[c,d]	**L-RaPr$_2$**	***A***	CH_2Cl_2	78	86
8[c,d]	**L-RaPr$_2$**	***A***	toluene	82	89
9[d,e]	**L-RaPr$_2$**	***B***	toluene	99	91
10[d,e]	**L-RaPr$_2$**	***C***	toluene	98	94
11[d,e]	**L-RaPr$_2$**	***D***	**toluene**	**99**	**95**
12[d,e]	**L-RaPr$_2$**	***E***	toluene	97	92
13[c,d]	**L-RaPr$_2$**	***F***	toluene	98	90
14[c,d]	**L-RaPr$_2$**	***G***	toluene	98	85
14[d-f]	**L-RaPr$_2$**	***D***	**toluene**	**92**	**96**

[a] Reaction conditions: 0.1 mmol **5a,** 10 mol% catalyst loading (metal: ligand = 1:1), 1.0 mmol MeOH, 1.2 equiv bromine reagent, solvent (0.2 M), 35°C. [b] without catalyst. [c] Using 1.5 equiv bromine reagent. [d] reaction contentration: 0.05M. [e] Using 0.75 equiv bromine reagent. [f] catalyst loading: 0.5 mol%.

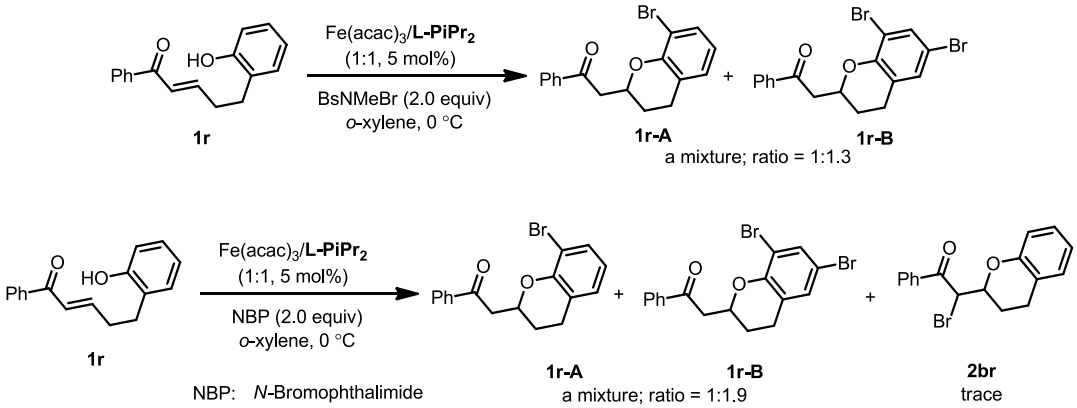
Table S5. **Substrate scope of chloroetherification and bromoetherification**[a]



Entry	Yield [%][b]	*ee* [%][c]	dr[d]	R; Y	Yield [%][b]	*ee* [%][c]	dr [d]
1	91 (**2aa**)	85	> 99:1	Ph; CH_2 (**1a**)	97 (**2ba**)	96	96:4
2	92 (**2ab**)	85	> 99:1	2-FC_6H_4; CH_2 (**1b**)	96 (**2bb**)	95	95:5
3	98 (**2ac**)	86	> 99:1	2-$MeOC_6H_4$; CH_2 (**1c**)	98 (**2bc**)	96	98:2
4	91 (**2ad**)	77	> 99:1	3-ClC_6H_4; CH_2 (**1d**)	89 (**2bd**)	95	95:5
5	95 (**2ae**)	76	> 99:1	3-MeC_6H_4; CH_2 (**1e**)	99 (**2be**)	95	96:4
6	80 (**2af**)	91	> 99:1	4-FC_6H_4; CH_2 (**1f**)	98 (**2bf**)	97	99:1
7	93 (**2ag**)	90	> 99:1	4-ClC_6H_4; CH_2 (**1g**)	90 (**2bg**)	96	93:7
8	97 (**2ah**)	89	> 99:1	4-$MeOC_6H_4$; CH_2 (**1h**)	99 (**2bh**)	97	96:4
9	82 (**2ai**)	87	> 99:1	3,4-$Cl_2C_6H_3$; CH_2 (**1i**)	83 (**2bi**)	95	96:4
10[e]	75 (**2aj**)	92	> 99:1	 ; CH_2 (**1j**)	98 (96) (**2bj**)	97 (93)	96:4
11	94 (**2ak**)	87	> 99:1	2-naphthyl; CH_2 (**1k**)	93 (**2bk**)	94	95:5
12	71 (**2al**)	44	> 99:1	2-furyl; CH_2 (**1l**)	93 (**2bl**)	78	94:6
13	85 (**2am**)	81	> 99:1	2-thienyl; CH_2 (**1m**)	94 (**2bm**)	95	95:5
14[f]	90 (**2an**)	82	> 99:1	3-thienyl; CH_2 (**1n**)	98 (**2bn**)	94 (*R, R*)	96:4
15	54 (**2ao**)	73	88:12	$PhCH_2CH_2$; CH_2 (**1o**)	90 (**2bo**)	93	95:5
16	88 (**2ap**)	87	> 99:1	Ph; O (**1p**)	97 (**2bp**)	95	96:4
17	85 (**2aq**)	40	93:7	Ph; NTs (**1q**)	93 (**2bq**)	77	88:12
18	86 (**2ar**)	90	80:20	 (**1r**)	--	--	--
19	--	--	--	Me; CH_2Cl_2 (**1s**)	68 (**2bs**)	73	94:6

[a] The reaction were performed with **1** (0.1 mmol), halogen reagent (for BsNMeBr 0.2 mmol, for *p*-$NsNCl_2$ 0.1 mmol), and $Fe(acac)_3$/**L-PiPr$_2$** (5 mol%, 1:1) in *o*-xylene (0.05 M) at 0 °C for 4 h, unless otherwise stated. [b] Yield of the isolated product. [c] Determined by HPLC or GC. [d] Determined by HPLC and ^{1}H NMR. [e] The value in the parentheses was conducted on a gram scale (4 mmol of **1j**). [f] The absolute configuration of **2bn** was verified by X-ray crystallography as (2*R,3R*).

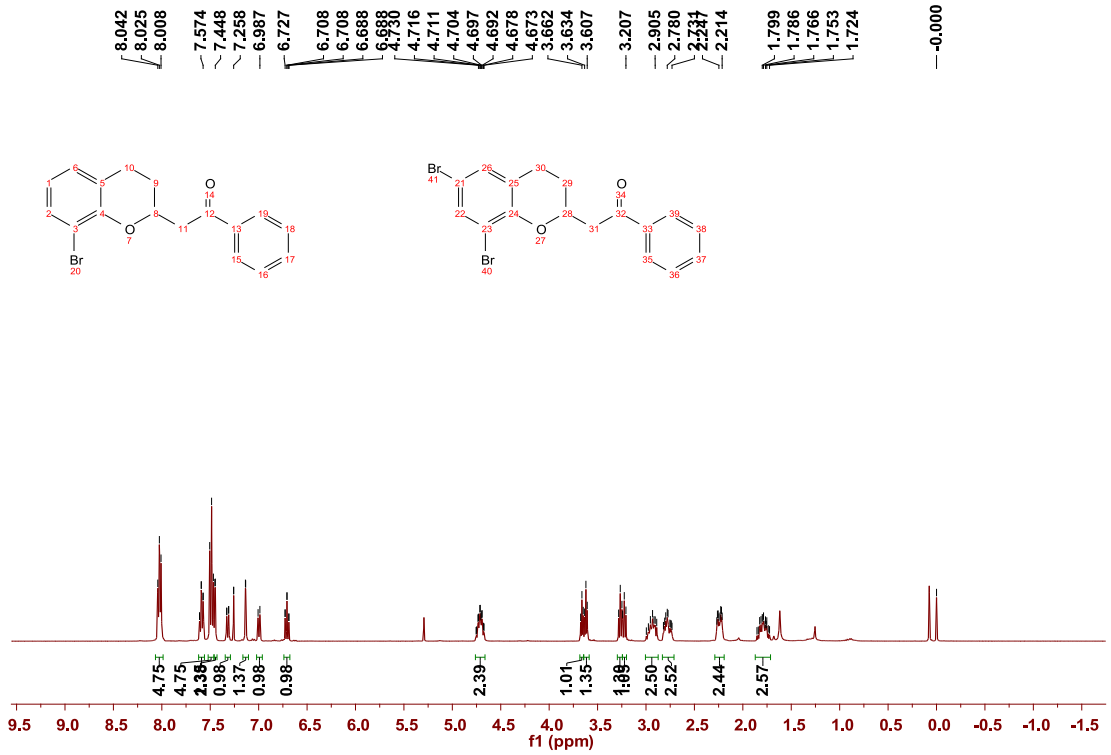
***Scheme S1*. Bromocyclization of 1r.**

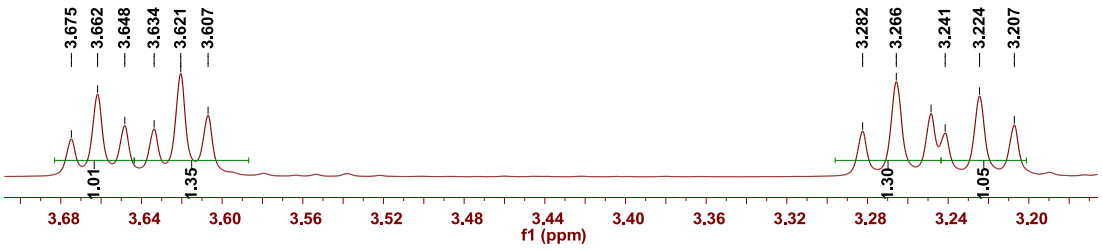


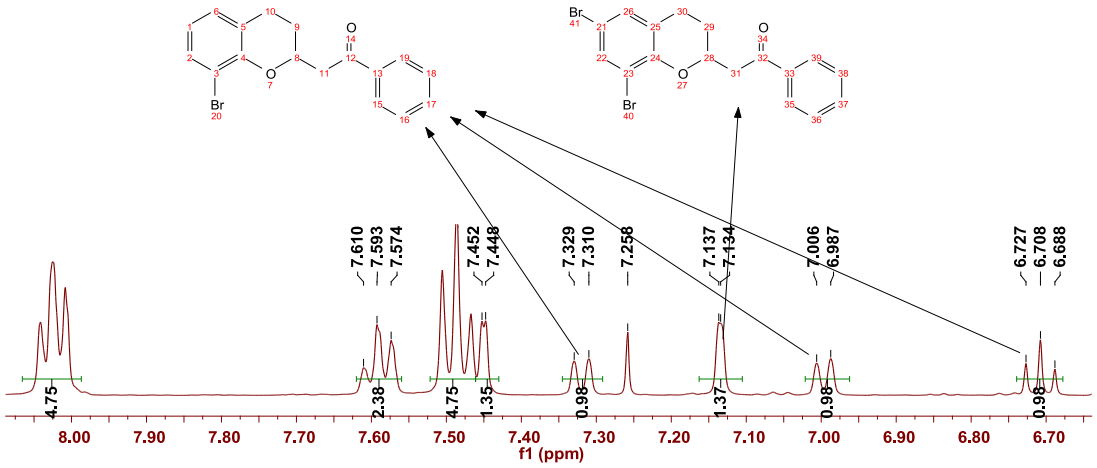
Under standard reaction conditions of bromocyclization, **1r** undergoes oxa-Michael reaction accompanied by direct bromination of phenol unit to give a inseperatable mixture **1r-A** and **1r-B**, the ratio is 1:1.3. When changing the bromine reagent to less reactive NBP, onlytrace amount of bromocyclization product **2br** can be dected.

1r-A: HRMS (ESI-TOF) calcd for $C_{17}H_{15}{}^{78.9183}BrO_2$ ([M]+Na^+) = 353.0153, Found 353.0143; HRMS (ESI-TOF) calcd for $C_{17}H_{15}{}^{80.9163}BrO_2$ ([M]+Na^+) = 355.0133, Found 355.0124.

1r-B: HRMS (ESI-TOF) calcd for $C_{17}H_{14}{}^{78.9183}Br_2O_2$ ([M]+Na^+) = 430.9258, Found 430.9253; HRMS (ESI-TOF) calcd for $C_{17}H_{14}{}^{78.9183}Br^{80.9163}BrO_2$ ([M]+Na^+) = 432.9238, Found 432.9238; HRMS (ESI-TOF) calcd for $C_{17}H_{14}{}^{80.9163}Br_2O_2$ ([M]+Na^+) = 434.9212, Found 434.9217.




3.675
3.662
3.648
3.634
3.621
3.607
3.282
3.266
3.241
3.224
3.207
1.01
1.35
1.30
1.05
3.68
3.64
3.60
3.56
3.52
3.48
3.44
3.40
3.36
3.32
3.28
3.24
3.20
f1 (ppm)


7.610
7.593
7.574
7.452
7.448
7.329
7.310
7.258
7.137
7.134
7.006
6.987
6.727
6.708
6.688
4.75
2.38
4.75
1.35
0.98
1.37
0.98
0.96
8.00
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
6.70
f1 (ppm)

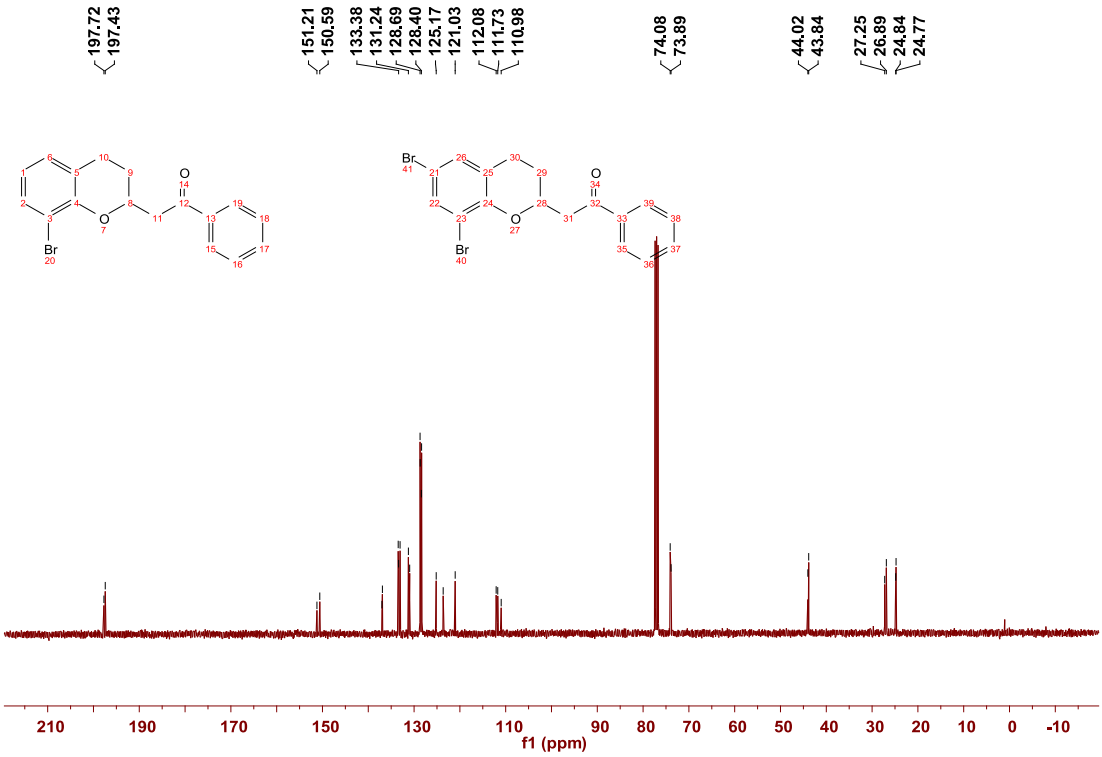
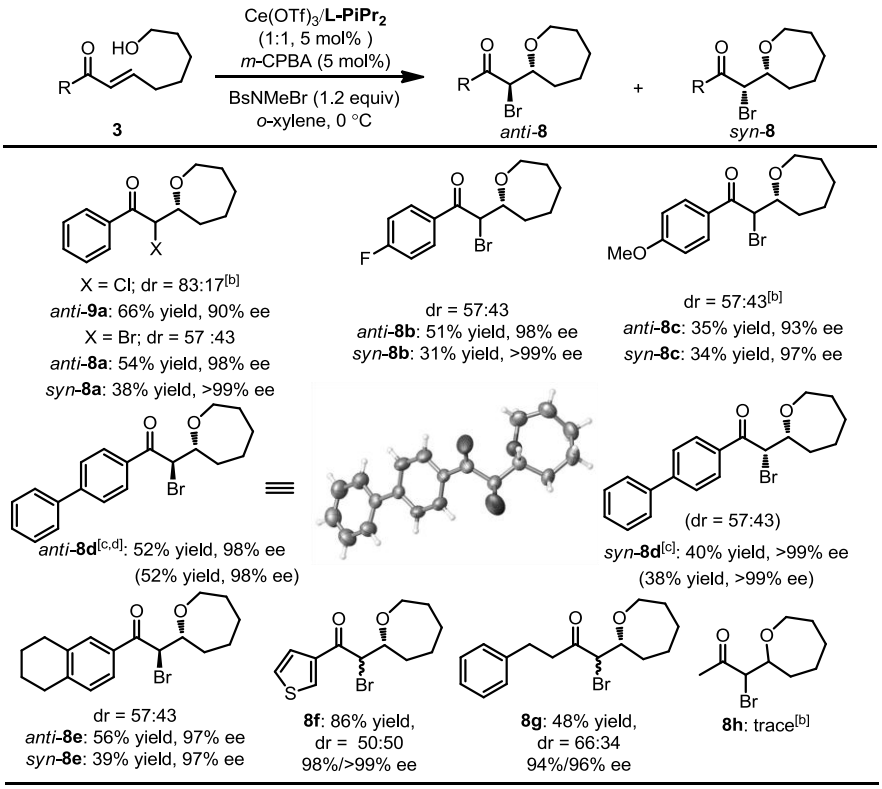
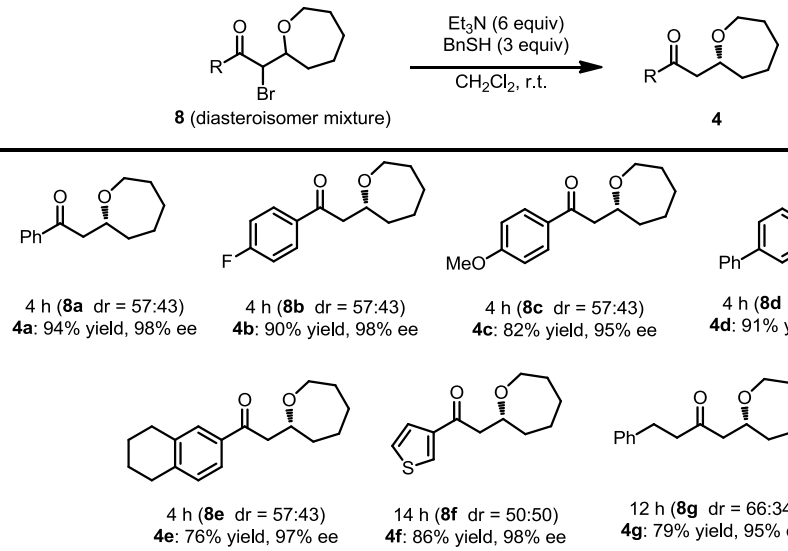

197.72
197.43
151.21
150.59
133.38
131.24
128.69
128.40
125.17
121.03
112.08
111.73
110.98
74.08
73.89
44.02
43.84
27.25
26.89
24.84
24.77
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Table S6. **Substrate scope of seven-membered halocyclization[a]**



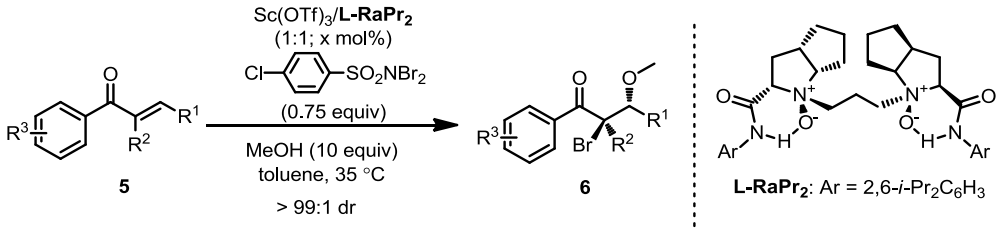
[a] The reactions were run with **3** (0.1 mmol), BsNMeBr (1.2 equiv), and Ce(OTf)$_3$/**L-PiPr$_2$** (5 mol%, 1:1) in *o*-xylene (0.05 M) at 0 °C for 12–36 h, unless otherwise stated. Yield of the isolated isomers. Diastereoselectivities were determined by ^{1}H NMR. Enantioselectivities were determined by HPLC. [b] Conducted at 35 °C for 24 h. [c] The value in the parentheses is conducted on 1.4 mmol scale of **3d**. [d] The absolute configuration of (2*R,3R*)-*anti*-**8d** was verified by X-ray crystallography.

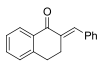
Table S7. **Debromination of diastereoisomer mixture 8**[a]

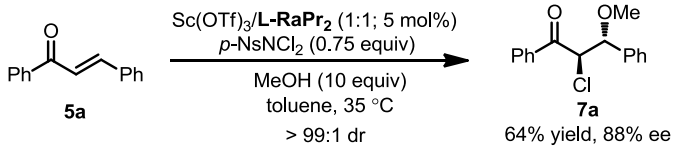


[a] The reactions were run with the catalytic products **8** (indicated amounts), Et_3N (6.0 equiv) and BnSH (3.0 equiv) in CH_2Cl_2 at room temperature. Values in the parentheses were the dr of **8**. Yields after chromatography purification. Enantioselectivities were determined by HPLC.

Table S8. **Substrate scope of intermolecular bromoetherification.**[a]



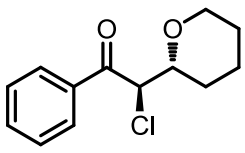
Entry	R^1	R^2; R^3	x	Yield [%][b]	*ee* [%][c]
1[d]	Ph	H; H	0.5	92 (91) (**6a**)	96 (94) (*R*, R)
2	4-MeC_6H_4	H; H	5	81 (**6b**)	94
3	4-FC_6H_4	H; H	1	99 (**6c**)	95
4	4-$F_3CC_6H_4$	H; H	5	90 (**6d**)	95
5	3-ClC_6H_4	H; H	1	97 (**6e**)	94
6	2-naphthyl	H; H	5	80 (**6f**)	92
7	Ph	H; 4-MeO	5	98 (**6g**)	94
8	*i*-Pr	H; H	5	70 (**6h**)	75
9	*i*-Bu	H; H	5	66 (**6i**)	80
10[e]	Ph	CN; H	5	67 (**6j**)	60/60
11			5	64 (**6k**)	96
12			5	messy	--



[a] The reaction were performed with **5** (0.1 mmol), bromine reagent (0.075 mmol) , and $Sc(OTf)_3$/**L-RaPr₂** (x mol%, 1:1) in toluene (0.05 M) at 35 °C for 4-12 h, unless otherwise stated. [b] Yield of the isolated product. [c] Determined by HPLC. [d] The value in the parentheses is conducted on 2 mmol scale of **5a** using 0.5 mol% catalyst, the absolute configuration of **6a** was established as (2*R*, 3*R*). [e] dr = 75: 25.

7. Characterization of the products

2-chloro-1-phenyl-2-(tetrahydro-2H-pyran-2-yl) ethanone (2aa):



2aa

($C_{13}H_{15}ClO_2$) Prepared according to the general procedure. The tittle compound **2aa** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 91% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), t_r (major) = 5.29 min, t_r (minor) = 7.32 min, 85% *ee*; dr > 99:1.

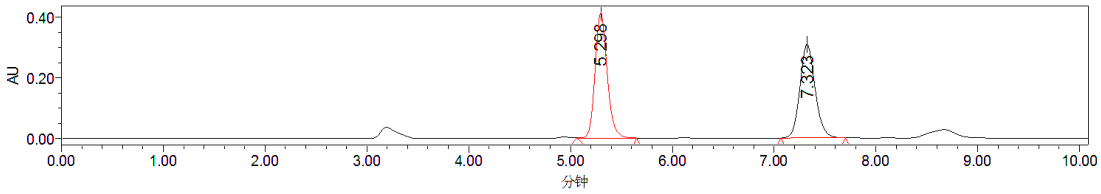
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.96 (m, 2H), 7.63 – 7.56 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 5.00 (d, *J* = 8.0 Hz, 1H), 3.99 – 3.92 (ddd, *J* = 10.4, 8.0, 2.0 Hz 1H), 3.90 (dd, *J* = 10.4, 3.2 Hz, 1H), 3.44 (td, *J* = 11.2, 2.8 Hz, 1H), 2.08 (d, *J* = 13.2 Hz, 1H), 1.93 (ddd, *J* = 8.4, 5.2, 2.8 Hz, 1H), 1.62

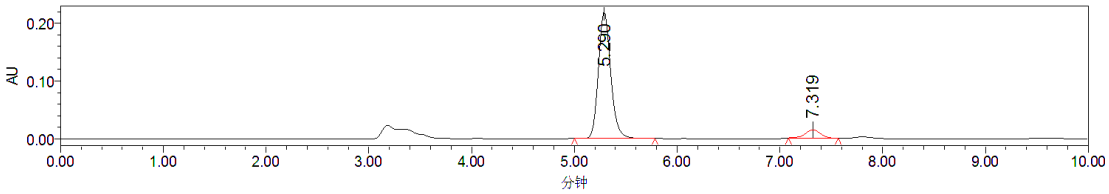
– 1.41 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.70, 135.39, 133.71, 128.91, 128.73, 77.66, 68.98, 58.18, 28.15, 25.71, 22.88.

HRMS (ESI-TOF) calcd for $C_{13}H_{15}{}^{34.9689}ClO_2$ ([M]+Na^+) = 261.0653, Found 261.0661.

HRMS (ESI-TOF) calcd for $C_{13}H_{15}{}^{36.9659}ClO_2$ ([M]+Na^+) = 263.0623, Found 263.0648.

$[\alpha]^{29}_D$ = 3.3 (*c* = 0.39, in CH_2Cl_2); wavelength: 589 nm.

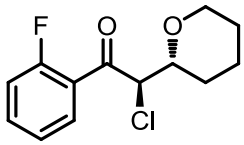




	Retention Time	Area	% Area
1	5.298	3388870	51.59
2	7.323	3179686	48.41

	Retention Time	Area	% Area
1	5.290	1820179	92.56
2	7.319	146390	7.44

2-chloro-1-(2-fluorophenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2ab):



2ab

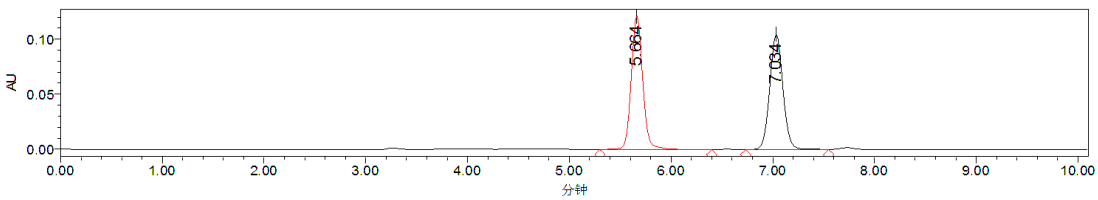
($C_{13}H_{14}ClFO_2$) Prepared according to the general procedure. The tittle compound **2ab** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 92% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 5.61 min, t_r (minor) = 6.95 min, 85% *ee*; dr > 99:1.

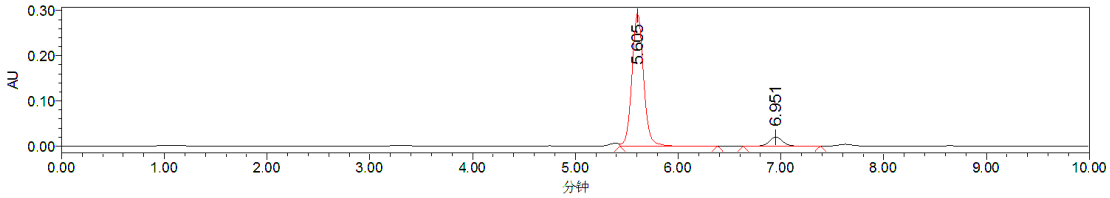
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.80 (m, 1H), 7.60 – 7.51 (m, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.15 (dd, *J* = 11.2, 8.4 Hz, 1H), 5.01 (d, *J* = 7.6 Hz, 1H), 3.93 (m, 2H), 3.45 (t, *J* = 11.2 Hz, 1H), 2.00 (d, *J* = 12.8 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.66 – 1.40 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.31 (d, *J* = 4.0 Hz), 161.39(d, *J* = 54.0 Hz), 135.17 (d, *J* = 9.0 Hz), 131.29 (d, *J* = 2.0 Hz), 124.67 (d, *J* = 3.0 Hz), 124.56, 116.75 (d, *J* = 22.0 Hz), 77.80, 68.96, 62.22 (d, *J* = 8.0 Hz), 27.90, 25.66, 22.86.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{34.9689}ClFO_2$ ([M]+Na^+) = 279.0559, Found 279.0561.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{36.9659}ClFO_2$ ([M]+Na^+) = 281.0529, Found 281.0535.

$[\alpha]^{23}_D$ = -2.4 (*c* = 0.42, in CH_2Cl_2); wavelength: 589 nm.

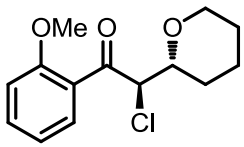




	Retention Time	Area	% Area
1	5.664	955522	50.33
2	7.034	942929	49.67

	Retention Time	Area	% Area
1	5.605	2301520	92.71
2	6.951	181075	7.29

2-chloro-1-(2-methoxyphenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2ac):



2ac

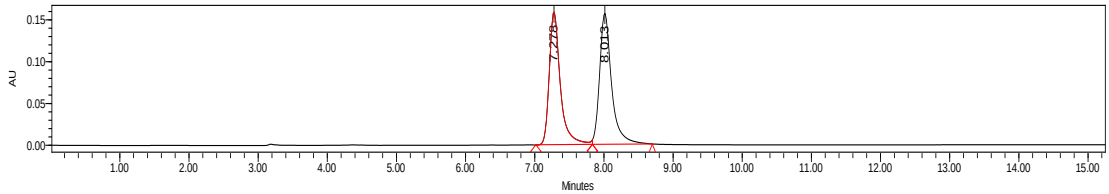
($C_{14}H_{17}ClO_3$) Prepared according to the general procedure. The tittle compound **2ac** was purified by silica gel chromatography (petroleum ether : EtOAc = 10 : 1) to afford a colorless oil in 98% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 254 nm), t_r (minor) = 7.21 min, t_r (major) = 7.94 min, 86% *ee*; dr > 99:1.

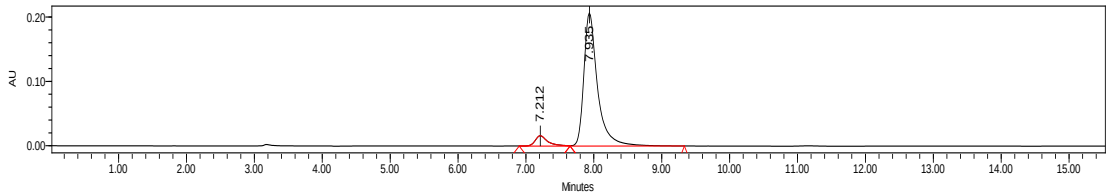
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.33 (d, *J* = 6.4 Hz, 1H), 3.99 – 3.85 (m, 5H), 3.45 (t, *J* = 11.2 Hz, 1H), 1.86 (d, *J* = 9.2 Hz, 2H), 1.62 – 1.42 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.64, 158.38, 134.24, 131.16, 126.80, 121.00, 111.70, 77.86, 69.04, 64.29, 55.79, 27.30, 25.68, 22.91.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{34.9689}ClO_3$ ([M]+H$^+$) = 269.0939, Found 269.0938

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{36.9659}ClO_3$ ([M]+H$^+$) = 271.0909, Found 271.0919.

$[\alpha]^{25}_D$ = -2.2 (*c* = 0.59, in CH_2Cl_2); wavelength: 589 nm.

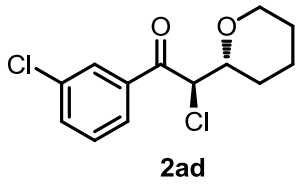




	Retention time	Area	Area%
1	7.278	1761153	48.37
2	8.013	1880140	51.63

	Retention time	Area	Area%
1	7.212	211490	6.81
2	7.935	2892511	93.19

2-chloro-1-(3-chlorophenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2ad):



2ad

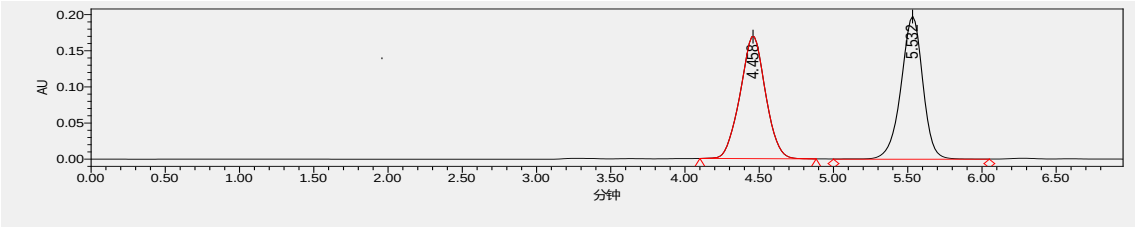
($C_{13}H_{14}Cl_2O_2$) Prepared according to the general procedure. The tittle compound **2ad** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 91% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 4.54 min, t_r (minor) = 5.56 min, 77% *ee*; dr > 99:1.

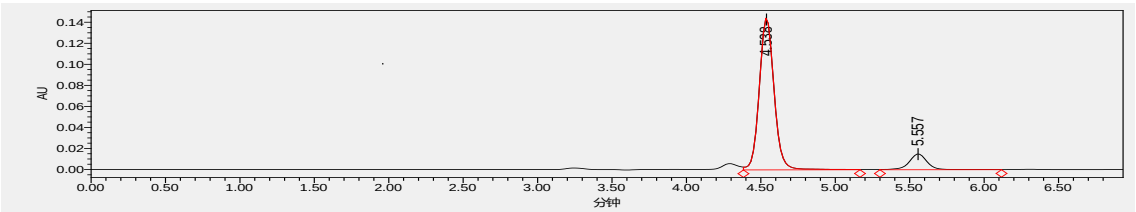
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 4.88 (d, *J* = 8.4 Hz, 1H), 3.99 – 3.80 (m, 2H), 3.50 – 3.36 (m, 1H), 2.10 (d, *J* = 12.0 Hz, 1H), 1.94 (d, *J* = 4.4 Hz, 1H), 1.62 – 1.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.74, 137.00, 135.06, 133.58, 130.02, 128.94, 126.98, 77.71, 68.96, 57.95, 28.28, 25.67, 22.84.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{34.9689}Cl_2O_2$ ([M]+Na^+) = 295.0263, Found 295.0273.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{34.9689}Cl^{36.9659}ClO_2$ ([M]+Na^+) = 297.0234, Found 297.0262.

$[\alpha]^{16}_D$ = 1.1 (*c* = 0.54, in CH_2Cl_2); wavelength: 589 nm.

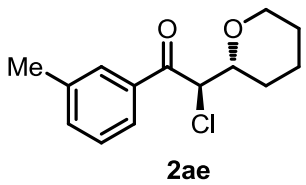




	Retention Time	Area	% Area
1	4.458	2052441	50.43
2	5.532	2017043	49.57

	Retention Time	Area	% Area
1	4.538	1001293	88.66
2	5.557	128118	11.34

2-chloro-2-(tetrahydro-2H-pyran-2-yl)-1-(m-tolyl)ethanone (2ae):



2ae

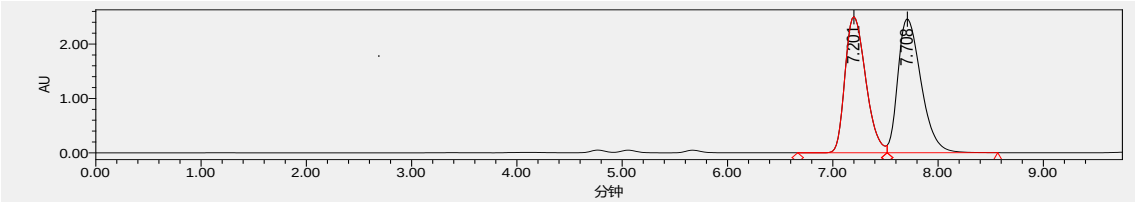
($C_{14}H_{17}ClO_2$) Prepared according to the general procedure. The tittle compound **2ae** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 95% yield. HPLC (Chiralcel ID, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 7.71 min, t_r (minor) = 7.21 min, 76% *ee*; dr > 99:1.

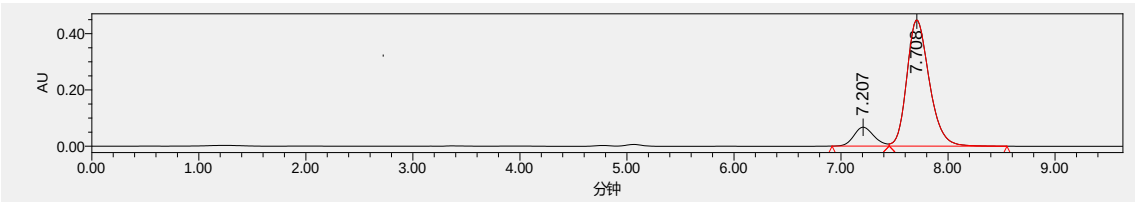
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.8 Hz, 2H), 7.43 – 7.33 (m, 2H), 4.99 (d, *J* = 8.0 Hz, 1H), 4.00 – 3.84 (m, 2H), 3.44 (td, *J* = 11.2, 2.8 Hz, 1H), 2.42 (s, 3H), 2.07 (d, *J* = 12.8 Hz, 1H), 1.93 (dd, *J* = 6.0, 2.8 Hz, 1H), 1.62 – 1.40 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.85, 138.61, 135.43, 134.53, 129.34, 128.61, 126.11, 77.64, 68.97, 58.13, 28.10, 25.71, 22.89, 21.38.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{34.9689}ClO_2$ ([M]+Na^+) = 275.0809, Found 275.0813.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{36.9659}ClO_2$ ([M]+Na^+) = 277.0780, Found 277.0755.

$[\alpha]^{16}_D$ = 1.5 (*c* = 0.54, in CH_2Cl_2); wavelength: 589 nm.

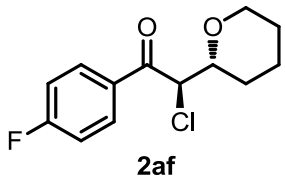




	Retention Time	Area	% Area
1	7.201	33983212	47.47
2	7.708	37605944	52.53

	Retention Time	Area	% Area
1	7.207	877685	11.86
2	7.708	6522464	88.14

2-chloro-1-(4-fluorophenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2af):



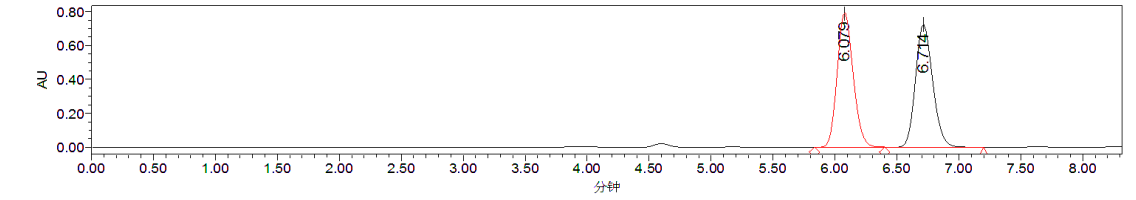
2af

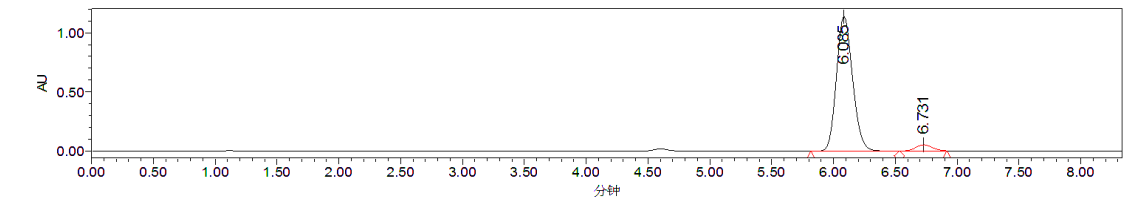
($C_{13}H_{14}ClFO_2$) Prepared according to the general procedure. The tittle compound **2af** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 80% yield. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 6.09 min, t_r (minor) = 6.73 min, 91% *ee*; dr > 99:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.97 (m, 2H), 7.15 (t, *J* = 8.4 Hz, 2H), 4.92 (d, *J* = 8.0 Hz, 1H), 3.97 – 3.84 (m, 2H), 3.43 (td, *J* = 11.2, 2.8 Hz, 1H), 2.10 (d, *J* = 12.0 Hz, 1H), 2.01 – 1.87 (m, 1H), 1.62 – 1.39 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.23, 166.07 (d, *J* = 254.0 Hz), 131.81 (d, *J* = 3.0 Hz), 131.69(d, *J* = 10.0 Hz), 115.90(d, *J* = 22.0 Hz), 77.69, 68.97, 58.00, 28.28, 25.69, 22.86.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{34.9689}ClFO_2$ ([M]+Na$^+$) = 279.0559, Found 279.0564.

$[\alpha]^{16}{}_D$ = 4.8 (*c* = 0.50 in CH_2Cl_2); wavelength: 589 nm.

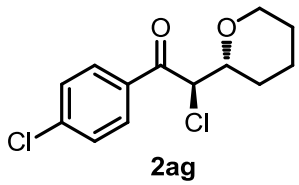




	Retention Time	Area	% Area
1	6.079	7134114	50.58
2	6.714	6971194	49.42

	Retention Time	Area	% Area
1	6.085	10311049	95.65
2	6.731	468410	4.35

2-chloro-1-(4-chlorophenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2ag):



2ag

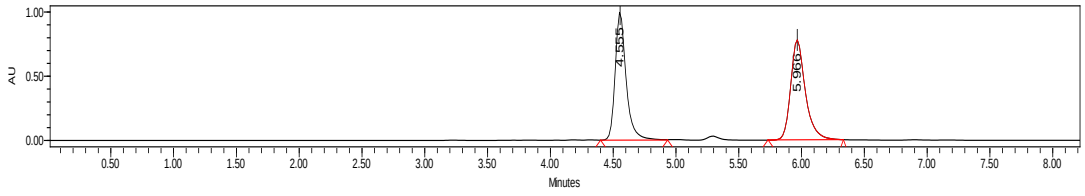
($C_{13}H_{14}Cl_2O_2$) Prepared according to the general procedure. The tittle compound **2ag** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 93% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 4.55 min, t_r (minor) = 6.00 min, 90% *ee*; dr > 99:1.

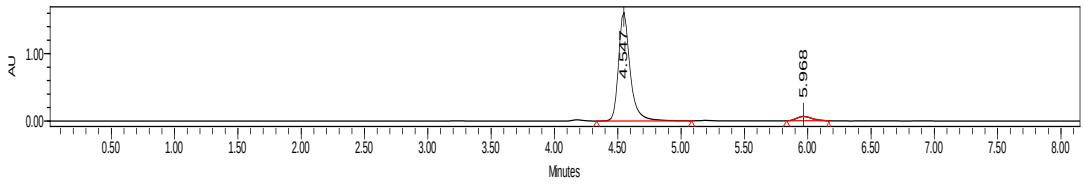
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 4.90 (d, *J* = 8.0 Hz, 1H), 3.91 (m, 2H), 3.41 (m, 1H), 2.10 (d, *J* = 12.4 Hz, 1H), 1.94 (d, *J* = 4.0 Hz, 1H), 1.60 – 1.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.68, 140.23, 133.72, 130.35, 129.05, 77.72, 68.97, 58.03, 28.29, 25.68, 22.85.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{34.9689}Cl_2O_2$ ([M]+Na^+) = 295.0263, Found 295.0275.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{34.9689}Cl^{36.9659}ClO_2$ ([M]+Na^+) = 297.0234, Found 297.0248.

$[\alpha]^{15}_D$ = 1.6 (*c* = 0.50, in CH_2Cl_2); wavelength: 589 nm.

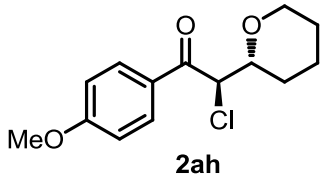




	Retention Time	Area	% Area
1	4.555	6049397	48.99
2	5.966	6299961	51.01

	Retention Time	Area	% Area
1	4.547	10264290	95.04
2	5.968	535507	4.96

2-chloro-1-(4-methoxyphenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2ah)



2ah

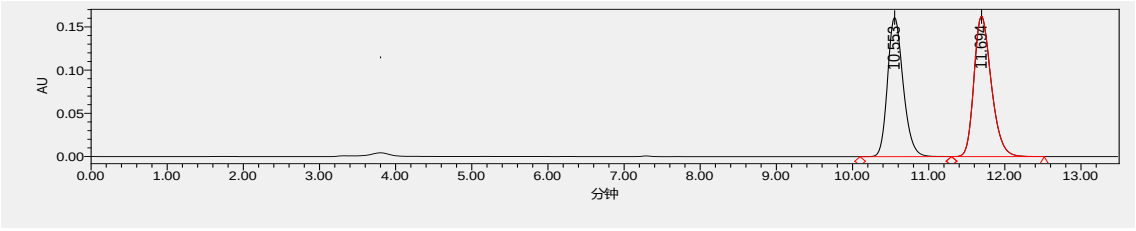
($C_{14}H_{17}ClO_3$) Prepared according to the general procedure. The tittle compound **2ah** was purified by silica gel chromatography (petroleum ether : EtOAc = 10 : 1) to afford a colorless oil in 97% yield. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 10.47 min, t_r (minor) = 11.65 min, 89% *ee*; dr > 99:1.

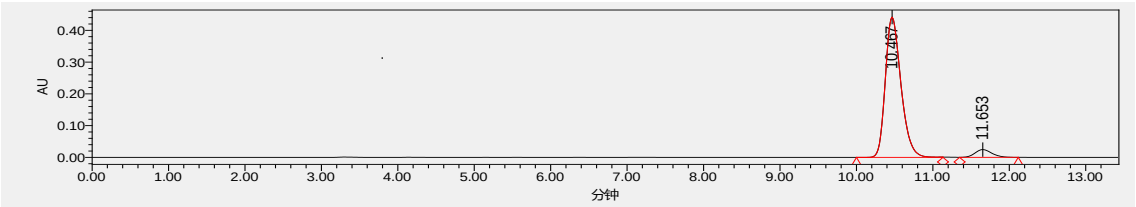
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H), 6.95 (m, 2H), 4.97 (d, *J* = 8.0 Hz, 1H), 3.97 – 3.89 (m, 2H), 3.88 (s, 3H), 3.49 – 3.38 (m, 1H), 2.08 (d, *J* = 12.8 Hz, 1H), 1.93 (dd, *J* = 6.0, 3.2 Hz, 1H), 1.62 – 1.40 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.01, 164.04, 131.34, 128.26, 113.96, 77.64, 68.99, 58.11, 55.55, 28.15, 25.72, 22.91.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{34.9689}ClO_3$ ([M]+H^+) = 269.0939, Found 269.0943.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{36.9659}ClO_3$ ([M]+H^+) = 271.0909, Found 271.0919.

$[\alpha]^{23}_D$ = -1.9 (*c* = 0.52, in CH_2Cl_2); wavelength: 589 nm.

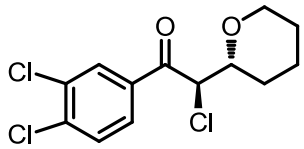




	Retention Time	Area	% Area
1	10.553	2288071	47.20
2	11.694	2559541	52.80

	Retention Time	Area	% Area
1	10.467	6261317	94.35
2	11.653	374743	5.65

2-chloro-1-(3,4-dichlorophenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2ai):



2ai

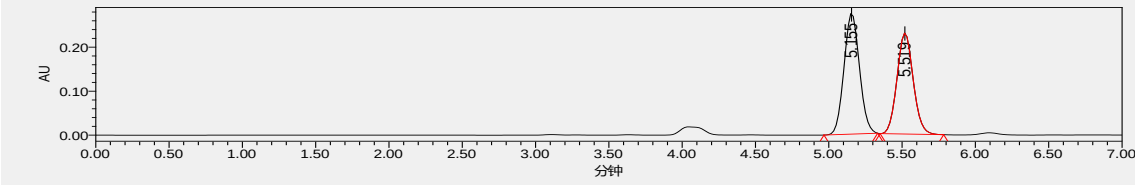
($C_{13}H_{13}Cl_3O_2$) Prepared according to the general procedure. The tittle compound **2ai** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 82% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 5.56 min, t_r (minor) = 5.20 min, 87% *ee*; dr > 99:1.

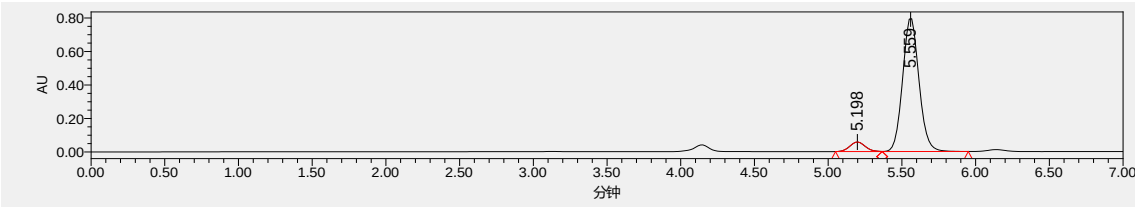
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 4.83 (d, *J* = 8.4 Hz, 1H), 3.96 – 3.84 (m, 2H), 3.41 (td, *J* = 11.2, 3.2 Hz, 1H), 2.11 (d, *J* = 12.4 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.60 – 1.37 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.92, 138.31, 135.01, 133.45, 130.87, 130.79, 127.93, 77.80, 68.96, 57.91, 28.38, 25.64, 22.82.

HRMS (ESI-TOF) calcd for $C_{13}H_{13}{}^{34.9689}Cl_3O_2$ ([M]+Na^+) = 328.9873, Found 328.9876.

HRMS (ESI-TOF) calcd for $C_{13}H_{13}{}^{34.9689}Cl_2{}^{36.9659}ClO_2$ ([M]+Na^+) = 330.9844, Found 330.9870.

$[\alpha]^{25}_D$ = -17.4 (*c* = 0.86, in CH_2Cl_2); wavelength: 589 nm.

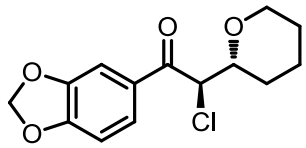




	Retention time	Area	Area%
1	5.155	2014447	53.36
2	5.519	1760970	46.64

	Retention time	Area	Area%
1	5.198	413530	6.30
2	5.559	6152993	93.70

1-(benzo[d][1,3]dioxol-5-yl)-2-chloro-2-(tetrahydro-2H-pyran-2-yl)ethanone (2aj):



2aj

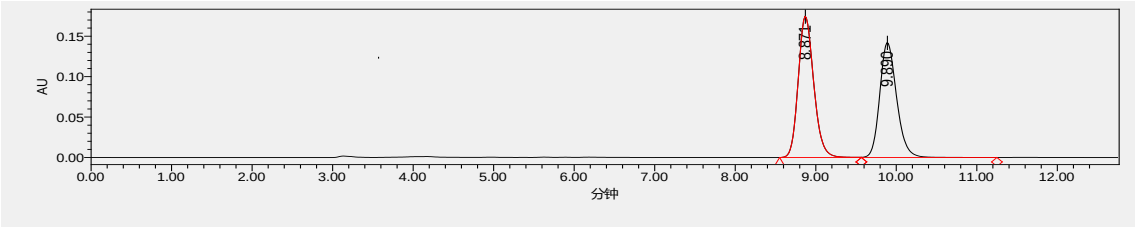
($C_{14}H_{15}ClO_4$) Prepared according to the general procedure. The tittle compound **2aj** was purified by silica gel chromatography (petroleum ether : EtOAc = 8 : 1) to afford a colorless oil in 75% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 9.89 min, t_r (minor) = 8.91 min, 92% *ee*; dr > 99:1.

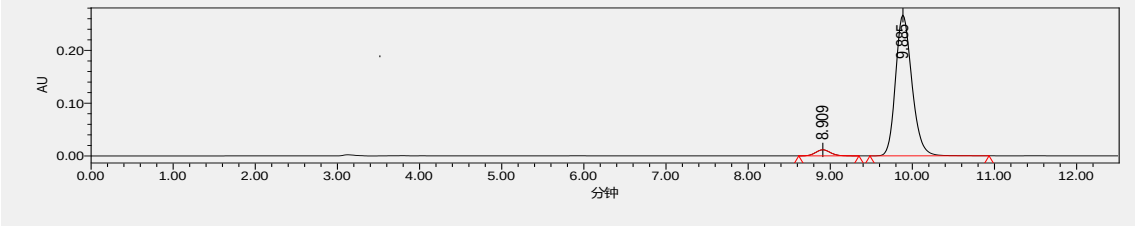
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.06 (s, 2H), 4.90 (d, *J* = 8.0 Hz, 1H), 3.92 (m, 2H), 3.51 – 3.34 (m, 1H), 2.08 (d, *J* = 12.8 Hz, 1H), 1.99 – 1.87 (m, 1H), 1.61 – 1.37 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.74, 152.41, 148.35, 130.09, 125.48, 108.66, 108.04, 102.04, 77.72, 68.97, 57.98, 28.20, 25.71, 22.89.

HRMS (ESI-TOF) calcd for $C_{14}H_{15}{}^{34.9689}ClO_4$ ([M]+H$^+$) = 283.0732, Found 283.0731.

HRMS (ESI-TOF) calcd for $C_{14}H_{15}{}^{36.9659}ClO_4$ ([M]+H$^+$) = 285.0702, Found 285.0706.

$[\alpha]^{24}_D$ = -36.3 (*c* = 1.12, in CH_2Cl_2); wavelength: 589 nm.

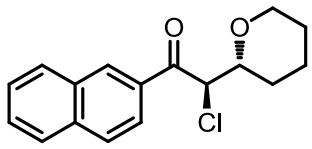




	Retention Time	Area	% Area
1	8.871	2333371	53.04
2	9.890	2065765	46.96

	Retention Time	Area	% Area
1	8.909	144904	3.79
2	9.885	3677139	96.21

2-chloro-1-(naphthalen-2-yl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2ak):



2ak

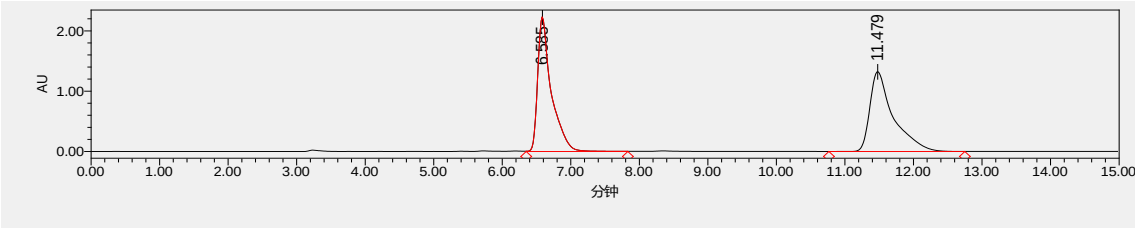
($C_{17}H_{17}ClO_2$) Prepared according to the general procedure. The tittle compound **2ak** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 94% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 6.59 min, t_r (minor) = 11.48 min, 87% *ee*; dr > 99:1.

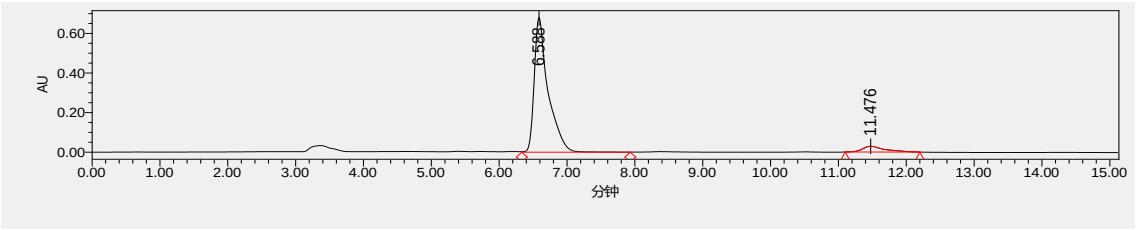
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.05 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (dd, *J* = 13.6, 8.8 Hz, 2H), 7.59 (dt, *J* = 22.4, 7.6 Hz, 2H), 5.17 (d, *J* = 8.0 Hz, 1H), 4.08 – 3.97 (m, *J* = 1H), 3.94 – 3.86 (m, 1H), 3.50 – 3.40 (m, 1H), 2.12 (d, *J* = 11.6 Hz, 1H), 2.00 – 1.89 (m, 1H), 1.62 – 1.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.65, 135.84, 132.72, 132.43, 130.85, 129.81, 128.92, 128.69, 127.81, 126.94, 124.32, 77.77, 69.01, 58.18, 28.21, 25.73, 22.92.

HRMS (ESI-TOF) calcd for $C_{17}H_{17}{}^{34.9689}ClO_2$ ([M]+Na$^+$) = 311.0809, Found 311.0821.

HRMS (ESI-TOF) calcd for $C_{17}H_{17}{}^{36.9659}ClO_2$ ([M]+Na$^+$) = 313.0780, Found 313.0797.

$[\alpha]^{29}_D$ = -14.7 (*c* = 0.44, in CH_2Cl_2); wavelength: 589 nm.

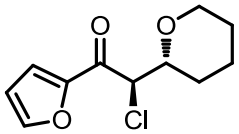




	Retention time	Area	Area%
1	6.585	30833167	49.56
2	11.479	31376485	50.44

	Retention time	Area	Area%
1	6.588	9682194	93.58
2	11.476	663728	6.42

2-chloro-1-(furan-2-yl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2al):



2al

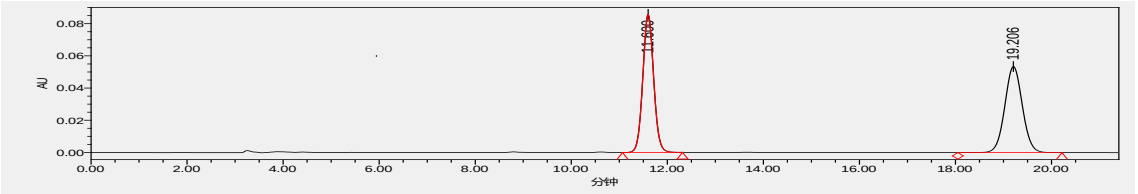
($C_{11}H_{13}ClO_3$) Prepared according to the general procedure. The tittle compound **2al** was purified by silica gel chromatography (petroleum ether : EtOAc = 12 : 1) to afford a white solid in 71% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 11.46 min, t_r (minor) = 18.87 min, 44% *ee*; dr > 99:1.

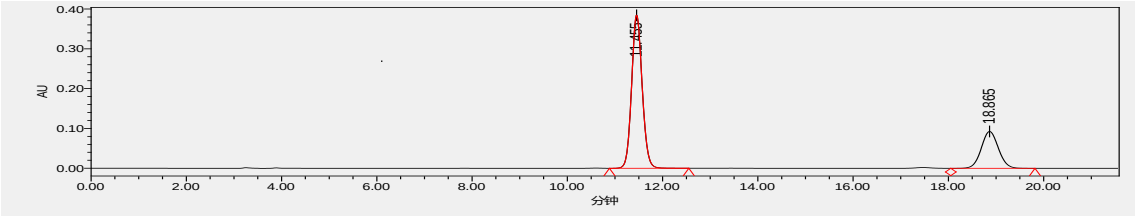
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.27 (d, *J* = 3.6 Hz, 1H), 6.52 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.74 (d, *J* = 8.4 Hz, 1H), 3.89 – 3.78 (m, 2H), 3.30 – 3.40 (m, 1H), 2.00 (d, *J* = 12.4 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.54 – 1.30 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.46, 151.13, 147.44, 119.43, 112.79, 77.59, 68.96, 58.59, 28.22, 25.63, 22.84.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}{}^{34.9689}ClO_3$ ([M]+Na^+) = 251.0445, Found 251.0452.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}{}^{36.9659}ClO_3$ ([M]+Na^+) = 253.0416, Found 253.0428.

$[\alpha]^{25}_D$ = 5.3 (*c* = 0.34, in CH_2Cl_2); wavelength: 589 nm.

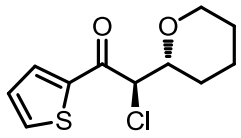




	Retention time	Area	Area%
1	11.600	1350365	49.92
2	19.206	1354515	50.08

	Retention time	Area	Area%
1	11.455	5942440	72.01
2	18.865	2310062	27.99

2-chloro-2-(tetrahydro-2H-pyran-2-yl)-1-(thiophen-2-yl)ethanone (2am)



2am

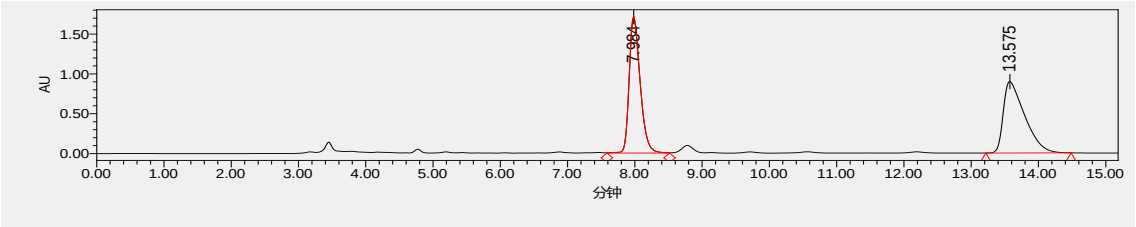
($C_{11}H_{13}ClO_2S$) Prepared according to the general procedure. The tittle compound **2am** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 85% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 8.03 min, t_r (minor) = 13.84 min, 81% *ee*; dr > 99:1.

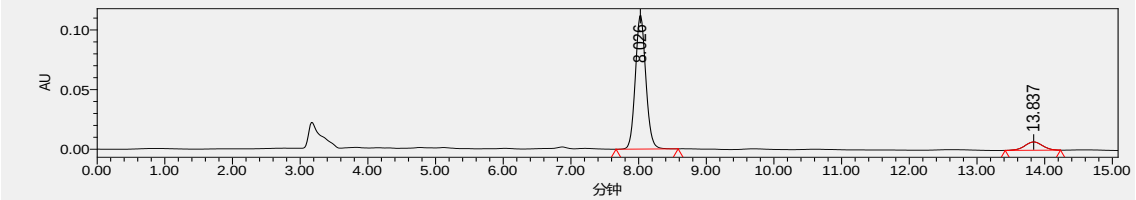
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 4.0, 0.8 Hz, 1H), 7.73 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.17 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.79 (d, *J* = 8.0 Hz, 1H), 3.97 – 3.85 (m, 2H), 3.48 – 3.37 (m, 1H), 2.16 – 2.03 (m, 1H), 1.99 – 1.87 (m, 1H), 1.62 – 1.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.56, 142.20, 135.34, 133.43, 128.37, 77.76, 69.01, 59.64, 28.24, 25.65, 22.86.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}{}^{34.9689}ClO_2S$ ([M]+Na^+) = 267.0222, Found 267.0224.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}{}^{36.9659}ClO_2S$ ([M]+Na^+) = 269.0193, Found 269.0196.

$[\alpha]^{25}_D$ = 69.1 (*c* = 0.63, in CH_2Cl_2); wavelength: 589 nm.

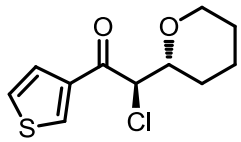




	Retention time	Area	Area%
1	7.984	19415831	49.62
2	13.575	19713017	50.38

	Retention time	Area	Area%
1	8.026	1207682	90.49
2	13.837	126853	9.51

2-chloro-2-(tetrahydro-2H-pyran-2-yl)-1-(thiophen-3-yl)ethanone (2an)



2an

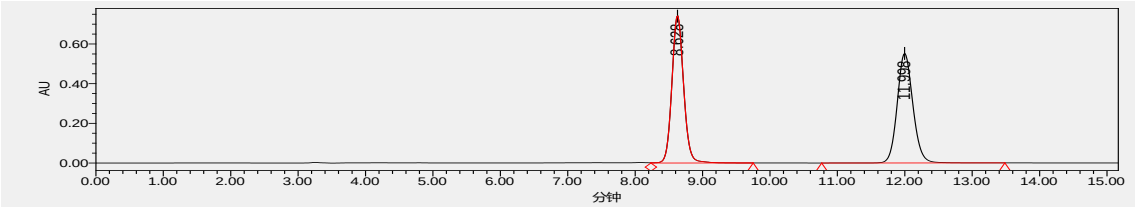
($C_{11}H_{13}ClO_2S$) Prepared according to the general procedure. The tittle compound **2an** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 90% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 8.62 min, t_r (minor) = 11.98 min, 82% *ee*; dr > 99:1.

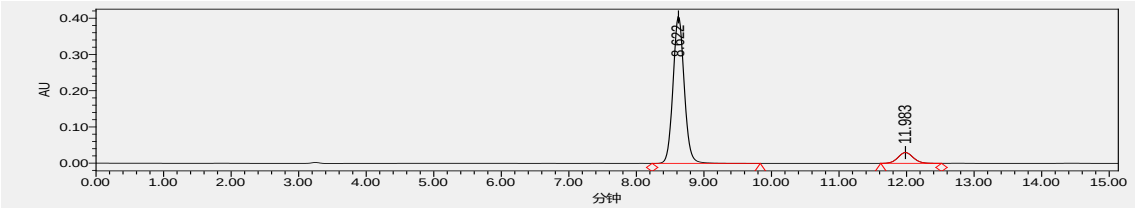
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.60 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.34 (dd, *J* = 5.2, 2.8 Hz, 1H), 4.78 (d, *J* = 8.0 Hz, 1H), 3.97 – 3.83 (m, 2H), 3.49 – 3.34 (m, 1H), 2.14 – 2.04 (m, 1H), 1.98 – 1.88 (dd, *J* = 5.5, 3.0 Hz, 1H), 1.64 – 1.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.75, 140.07, 133.87, 127.51, 126.58, 77.63, 68.99, 60.15, 28.20, 25.67, 22.86.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}{}^{34.9689}ClO_2S$ ([M]+Na^+) = 267.0217, Found 267.0217.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}{}^{36.9659}ClO_2S$ ([M]+Na^+) = 269.0187, Found 269.0187.

$[\alpha]^{16}_D$ = 4.4 (*c* = 0.64, in CH_2Cl_2); wavelength: 589 nm.

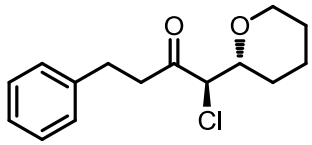




	Retention Time	Area	% Area
1	8.628	8968263	50.13
2	11.998	8921589	49.87

	Retention Time	Area	% Area
1	8.622	4669540	90.90
2	11.983	467705	9.10

1-chloro-4-phenyl-1-(tetrahydro-2H-pyran-2-yl)butan-2-one (2ao)



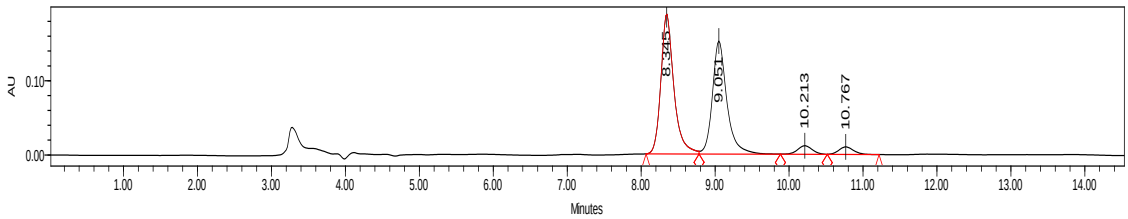
2ao

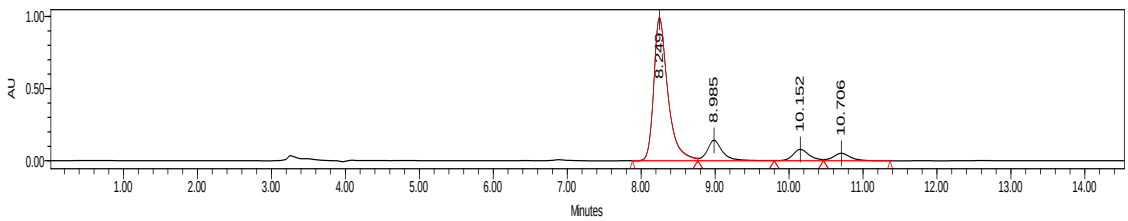
($C_{15}H_{19}ClO_2$) Prepared according to the general procedure. The tittle compound **2ao** was purified by silica gel chromatography (petroleum ether : EtOAc = 20 : 1) to afford colorless oil in 54% yield. HPLC (Chiralcel OJ-H, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 210 nm), t_{r1} (*anti*) = 8.25 min, t_{r2} (*anti*) = 8.99 min, t_{r3} (*syn*) = 10.15 min, t_{r4} (*syn*) = 10.71 min, 73% *ee*; dr = 88:12.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 5H), 4.05 (d, *J* = 7.6 Hz, 1H), 3.92 (d, *J* = 11.2 Hz, 1H), 3.71 – 3.61 (m, 1H), 3.36 (td, *J* = 11.2, 2.4 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.97 – 2.85 (m, 3H), 1.87 (d, *J* = 9.6 Hz, 2H), 1.57 – 1.28 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.76, 140.84, 128.45, 128.40, 126.13, 78.43, 68.89, 64.33, 41.05, 29.41, 28.20, 25.52, 22.78.

HRMS (ESI-TOF) calcd for $C_{15}H_{19}{}^{34.9689}ClO_2$ ([M]+Na^+) = 289.0966, Found 289.0981.

HRMS (ESI-TOF) calcd for $C_{15}H_{19}{}^{36.9659}ClO_2$ ([M]+Na^+) = 291.0936, Found 291.0948.

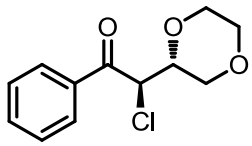




	Retention time	Area	Area%
1	8.345	2291949	49.13
2	9.051	2068863	44.35
3	10.213	161580	3.46
4	10.767	142227	3.05

	Retention time	Area	Area%
1	8.249	13120102	76.12
2	8.985	2052433	11.91
3	10.152	1217770	7.07
4	10.706	845467	4.91

2-chloro-2-(1,4-dioxan-2-yl)-1-phenylethanone (2ap):



2ap

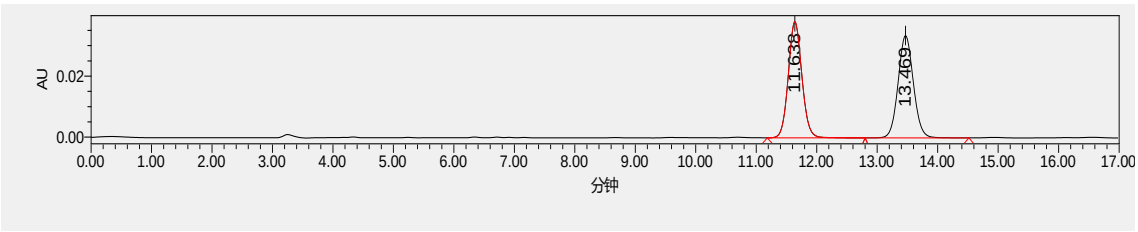
($C_{12}H_{13}ClO_3$) Prepared according to the general procedure. The tittle compound **2ap** was purified by silica gel chromatography (petroleum ether : EtOAc = 10 : 1) to afford a colorless oil in 88% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 11.55 min, t_r (minor) = 13.43 min, 87% *ee*; dr > 99:1.

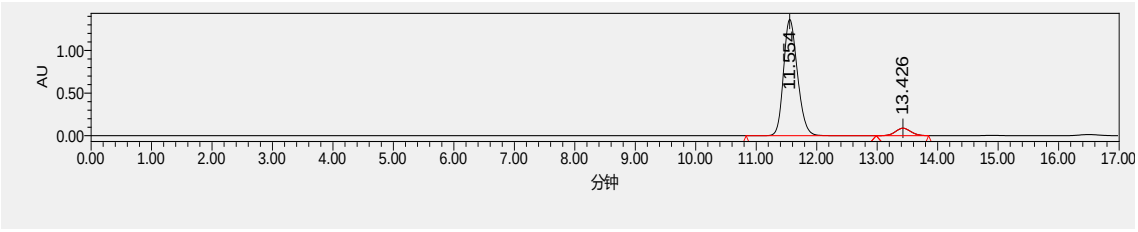
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.96 (m, 2H), 7.66 – 7.58 (m, 1H), 7.55 – 7.46 (m, 2H), 5.05 (d, *J* = 8.4 Hz, 1H), 4.28 (ddd, *J* = 9.6, 8.4, 2.8 Hz, 1H), 4.21 (dd, *J* = 11.6, 2.8 Hz, 1 H), 3.77 – 3.69 (m, 3H), 3.67 – 3.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.27, 134.84, 134.05, 128.97, 128.86, 74.29, 68.59, 66.73, 66.38, 54.08.

HRMS (ESI-TOF) calcd for $C_{12}H_{13}{}^{34.9689}ClO_3$ ([M]+Na^+) = 263.0445, Found 263.0446.

HRMS (ESI-TOF) calcd for $C_{12}H_{13}{}^{36.9659}ClO_3$ ([M]+Na^+) = 265.0416, Found 265.0420.

$[\alpha]^{15}_D$ = -9.6 (*c* = 0.56, in CH_2Cl_2); wavelength: 589 nm.

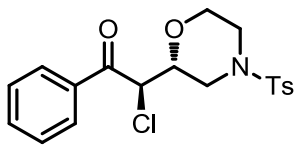




	Retention time	Area	Area%
1	11.638	592693	50.20
2	13.469	587863	49.80

	Retention time	Area	Area%
1	11.554	21883625	93.48
2	13.426	1526220	6.52

2-chloro-1-phenyl-2-(4-tosylmorpholin-2-yl)ethanone (2aq):



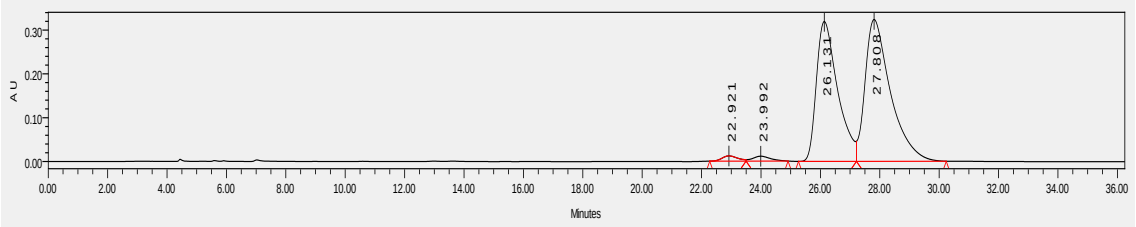
2aq

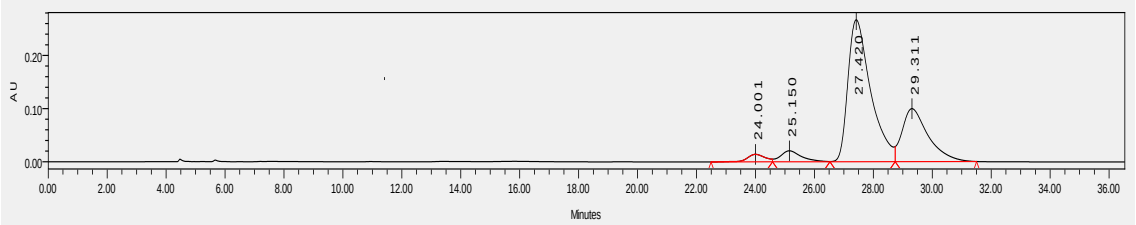
($C_{19}H_{20}ClNO_4S$) Prepared according to the general procedure. The tittle compound **2aq** was purified by silica gel chromatography (petroleum ether : EtOAc = 8 : 1) to afford a white solid in 85% yield. HPLC (Chiralcel ID, hexane/ *i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*syn*) = 24.00 min, t_{r2} (*syn*) = 25.15 min, t_{r3} (*anti*) = 27.42 min, t_{r4} (*anti*) = 29.31 min, 40% *ee*; dr = 93:7.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 4.97 (d, *J* = 8.0 Hz, 1H), 4.23 (ddd, *J* = 10.4, 8.0, 2.4 Hz, 1H), 4.04 (d, *J* = 11.6 Hz, 1H), 3.87 – 3.80 (m, 1H), 3.67 (td, *J* = 11.2, 2.8 Hz, 1H), 3.53 (d, *J* = 11.2 Hz, 1H), 2.52 – 2.39 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.69, 144.15, 134.67, 134.12, 132.28, 129.91, 128.91, 128.88, 127.88, 74.67, 66.16, 54.74, 47.64, 45.36, 21.60.

HRMS (ESI-TOF) calcd for $C_{19}H_{20}{}^{34.9689}ClNO_4S$ ([M]+Na^+) = 416.0694, Found 416.0691.

HRMS (ESI-TOF) calcd for $C_{19}H_{20}{}^{36.9659}ClNO_4S$ ([M]+Na^+) = 418.0664, Found 418.0674.

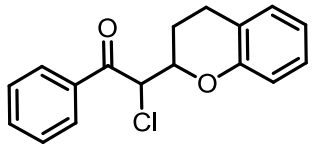




	Retention Time	Area	% Area
1	22.921	437807	1.22
2	23.992	459649	1.28
3	26.131	15880269	44.19
4	27.808	19156798	53.31

	Retention Time	Area	% Area
1	24.001	591824	2.68
2	25.150	1017760	4.61
3	27.420	14357412	65.00
4	29.311	6121150	27.71

2-chloro-2-(chroman-2-yl)-1-phenylethanone (2ar)

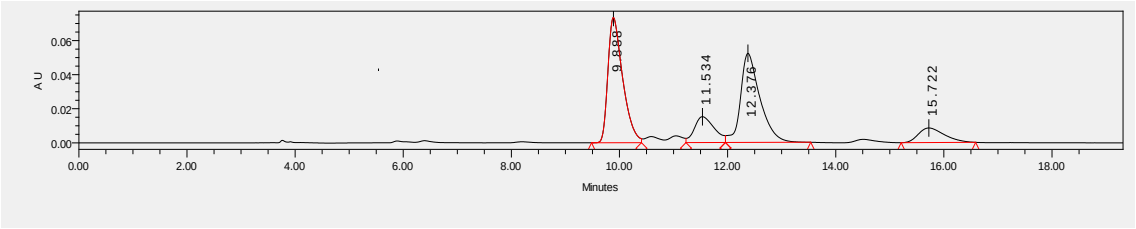


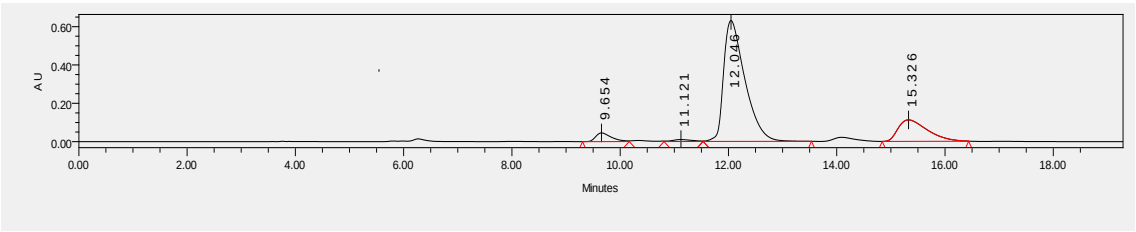
2ar

($C_{17}H_{15}ClO_2$) Prepared according to the general procedure. The tittle compound **2ar** was purified by silica gel chromatography (petroleum ether : EtOAc = 20 : 1) to afford colorless oil in 86% yield. HPLC (Chiralcel ID, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} = 9.65 min, t_{r2} = 11.12 min, t_{r3} = 12.05 min, t_{r4} = 15.33 min, 90% *ee*; dr = 80:20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.08 – 6.94 (m, 2H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 5.25 (d, *J* = 7.6 Hz, 1H), 4.76 – 4.67 (m, 1H), 2.97 – 2.81 (m, 2H), 2.49 – 2.38 (m, 1H), 2.14 – 1.97 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.83, 153.67, 135.16, 133.92, 129.48, 128.96, 128.82, 127.41, 121.69, 120.78, 116.82, 75.33, 56.83, 23.69, 23.62.

HRMS (ESI-TOF) calcd for $C_{17}H_{15}{}^{34.9689}ClO_2$ ([M]+Na^+) = 309.0653, Found 309.0654.

HRMS (ESI-TOF) calcd for $C_{17}H_{15}{}^{36.9659}ClO_2$ ([M]+Na^+) = 311.0623, Found 311.0631.

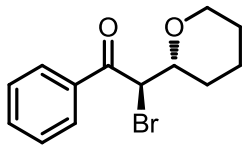




	Retention Time	Area	% Area
1	9.888	1389991	41.31
2	11.534	386254	11.48
3	12.376	1302406	38.71
4	15.722	286202	8.51

	Retention Time	Area	% Area
1	9.654	910570	4.04
2	11.121	248533	1.10
3	12.046	17197920	76.29
4	15.326	4186826	18.57

2-bromo-1-phenyl-2-(tetrahydro-2H-pyran-2-yl) ethanone (2ba):



2ba

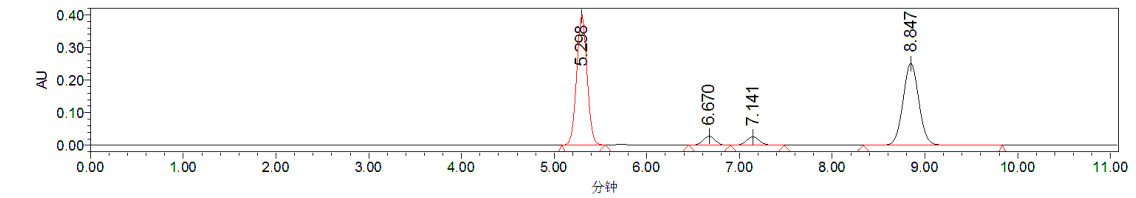
($C_{13}H_{15}BrO_2$) Prepared according to the general procedure. The tittle compound **2ba** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 97% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 5.31 min, t_{r2} (*syn*) = 6.68 min, t_{r3} (*syn*) = 7.15 min t_{r4} (*anti*) = 8.84 min, 96% *ee*; dr = 96:4.

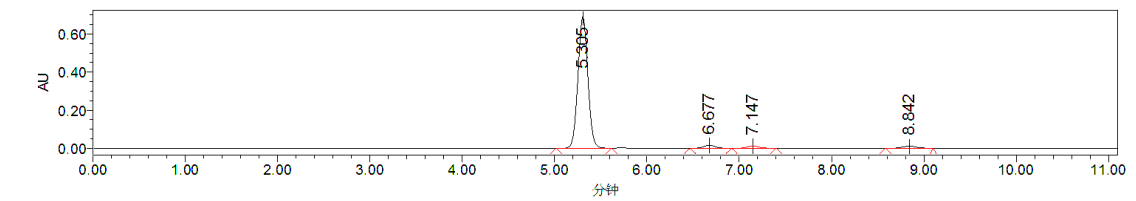
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.99 (d, *J* = 8.4 Hz, 1H), 3.99 (t, *J* = 9.2 Hz, 1H), 3.89 (d, *J* = 10.0 Hz, 1H), 3.46 (dd, *J* = 11.2, 9.2 Hz, 1H), 2.23 (d, *J* = 12.4 Hz, 1H), 1.93 (s, 1H), 1.62 – 1.36 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.36, 135.19, 133.64, 128.85, 128.74, 77.09, 69.08, 47.97, 29.28, 25.65, 23.14.

HRMS (ESI-TOF) calcd for $C_{13}H_{15}{}^{78.9183}BrO_2$ ([M]+Na^+) = 305.0148, Found 305.0159.

HRMS (ESI-TOF) calcd for $C_{13}H_{15}{}^{80.9163}BrO_2$ ([M]+Na^+) = 307.0127, Found 307.0124.

$[\alpha]^{15}{}_D$ = 21.0 (*c* = 0.59, in CH_2Cl_2), wavelength: 589 nm.

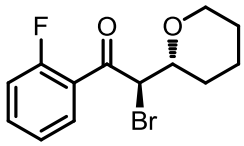




	Retention time	Area	% Area
1	5.298	3120720	47.27
2	6.670	247720	3.75
3	7.141	251588	3.81
4	8.847	2982127	45.17

	Retention time	Area	% Area
1	5.305	5157101	93.93
2	6.677	130495	2.38
3	7.147	98316	1.79
4	8.842	104212	1.90

2-bromo-1-(2-fluorophenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2bb):



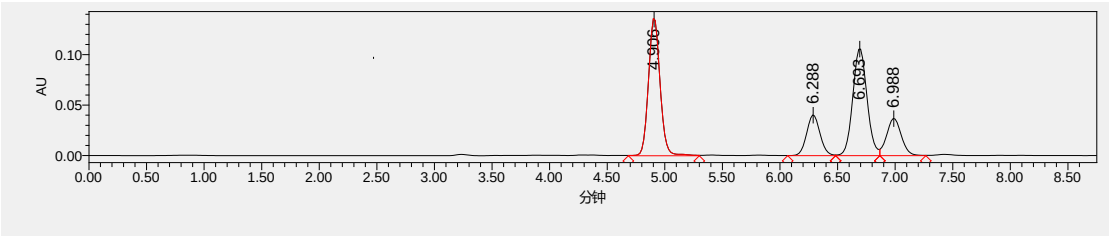
2bb

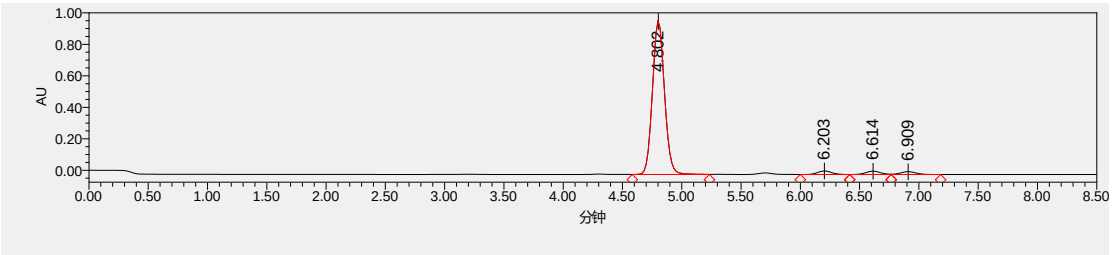
($C_{13}H_{14}BrFO_2$) Prepared according to the general procedure. The tittle compound **2bb** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 96% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 4.80 min, t_{r2} (*syn*) = 6.20 min, t_{r3} (*anti*) = 6.61 min t_{r4} (*syn*) = 6.91 min, 95% *ee*; dr = 95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, *J* = 7.2 Hz, 1H), 7.55 (dd, *J* = 13.2, 6.4 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.15 (dd, *J* = 11.2, 8.4 Hz, 1H), 5.00 (d, *J* = 8.4 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.92 – 3.82 (m, 1H), 3.47 (dd, *J* = 10.8, 2.0 Hz, 1H), 2.17 (d, *J* = 12.4 Hz, 1H), 1.98 – 1.86 (m, 1H), 1.61 – 1.36 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.73 (d, *J* = 4.0 Hz), 161.34 (d, *J* = 254.0 Hz), 135.14 (d, *J* = 9.0 Hz), 131.48 (d, *J* = 2.0 Hz), 124.66 (d, *J* = 4.0 Hz), 124.29 (d, *J* = 12.0 Hz), 116.81 (d, *J* = 23.0 Hz), 77.24, 69.06, 52.32 (d, *J* = 9.0 Hz), 29.10, 25.63, 23.10.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{78.9183}BrFO_2$ ([M]+Na^+) = 323.0059, Found 323.0053.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{80.9163}BrFO_2$ ([M]+Na^+) = 325.0038, Found 325.0034.

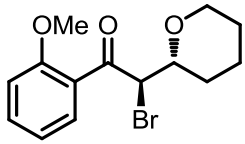




	Retention Time	Area	% Area
1	4.906	955188	37.92
2	6.288	326982	12.98
3	6.693	911034	36.17
4	6.988	325694	12.93

	Retention Time	Area	% Area
1	4.802	6881005	92.74
2	6.203	187632	2.53
3	6.614	183860	2.48
4	6.909	167514	2.26

2-bromo-1-(2-methoxyphenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2bc):



2bc

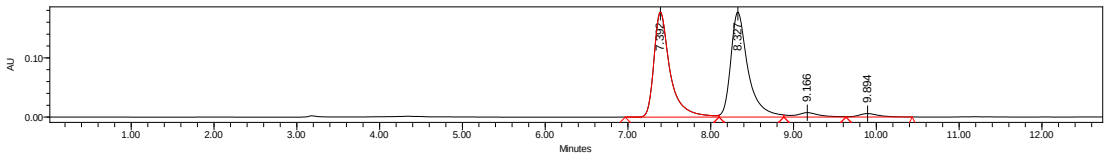
($C_{14}H_{17}BrO_3$) Prepared according to the general procedure. The tittle compound **2bc** was purified by silica gel chromatography (petroleum ether : EtOAc = 3 : 1) to afford a colorless oil in 98% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 7.40 min, t_{r2} (*anti*) = 8.33 min, t_{r3} (*syn*) = 9.15 min t_{r4} (*syn*) = 9.91 min, 96% *ee*; dr = 98:2.

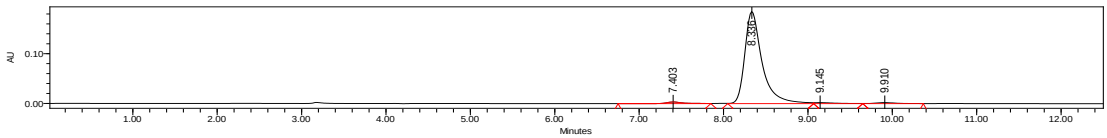
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 5.31 (d, *J* = 7.2 Hz, 1H), 3.93 – 3.88 (m, 5H), 3.53 – 3.42 (m, 1H), 2.09 (d, *J* = 13.2 Hz, 1H), 1.90 (d, *J* = 5.6 Hz, 1H), 1.62 – 1.39 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.18, 158.42, 134.24, 131.44, 126.52, 120.95, 111.72, 77.49, 69.07, 55.78, 54.64, 28.93, 25.69, 23.12.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{78.9183}BrO_3$ ([M]+H$^+$) = 313.0434, Found 313.0440.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{80.9163}BrO_3$ ([M]+H$^+$) = 315.0413, Found 315.0413.

$[\alpha]^{15}_D$ = -19.3 (*c* = 0.69, in CH_2Cl_2), wavelength: 589 nm.

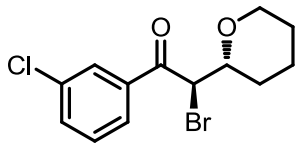




	Retention Time	Area	% Area
1	7.392	2403940	46.12
2	8.327	2564585	49.20
3	9.166	148552	2.85
4	9.894	95171	1.83

	Retention Time	Area	% Area
1	7.403	47328	1.73
2	8.336	2631429	95.92
3	9.145	33759	1.23
4	9.910	30785	1.12

2-bromo-1-(3-chlorophenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2bd):



2bd

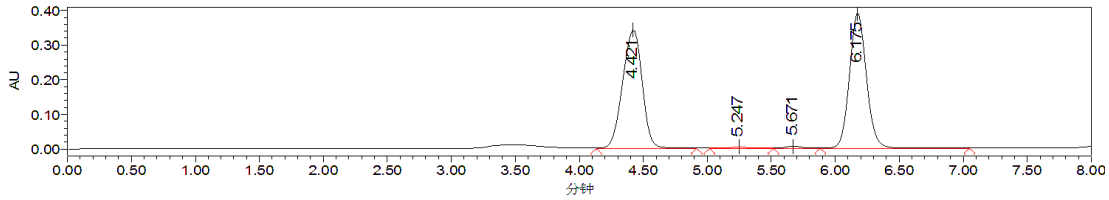
($C_{13}H_{14}BrClO_2$) Prepared according to the general procedure. The tittle compound **2bd** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless in 89% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 4.44 min, t_{r2} (*syn*) = 5.26 min, t_{r3} (*syn*) = 5.67 min t_{r4} (*anti*) = 6.18 min, 95% *ee*; dr = 95:5 (determined by ^{1}H NMR).

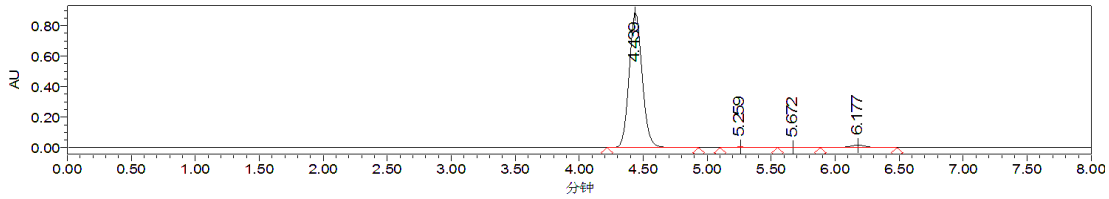
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 4.89 (d, *J* = 8.7 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.93 – 3.85 (m, 1H), 3.50 – 3.41 (m, 1H), 2.23 (d, *J* = 12.8 Hz, 1H), 1.95 (d, *J* = 6.8 Hz, 1H), 1.63 – 1.37 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.30, 136.79, 135.08, 133.53, 130.04, 128.89, 126.90, 77.08, 69.08, 47.63, 29.26, 25.60, 23.09.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{78.9183}Br^{34.9689}ClO_2$ ([M]+Na$^+$) = 338.9758, Found 338.9771.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{80.9163}Br^{34.9689}ClO_2$ ([M]+Na$^+$) = 340.9737, Found 340.9765.

$[\alpha]^{16}_D$ = 34.4 (*c* = 0.46, in CH_2Cl_2), wavelength: 589 nm.

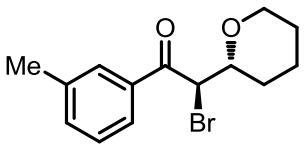




	Retention time	Area	% Area
1	4.421	3674287	49.29
2	5.247	70242	0.94
3	5.671	70196	0.94
4	6.175	3639481	48.82

	Retention time	Area	Area%
1	4.439	6295484	96.61
2	5.259	52916	0.81
	5.672	13593	0.21
	6.177	154560	2.37

2-bromo-2-(tetrahydro-2H-pyran-2-yl)-1-(m-tolyl)ethanone (2be):



2be

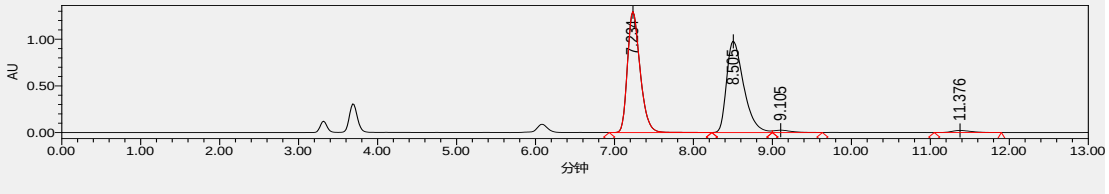
($C_{14}H_{17}BrO_2$) Prepared according to the general procedure. The tittle compound **2be** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 99% yield. HPLC (Chiralcel ID, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 7.21 min, t_{r2} (*anti*) = 8.47 min, t_{r3} (*syn*) = 9.08 min t_{r4} (*syn*) = 10.86 min, 95% *ee*; dr = 96:4.

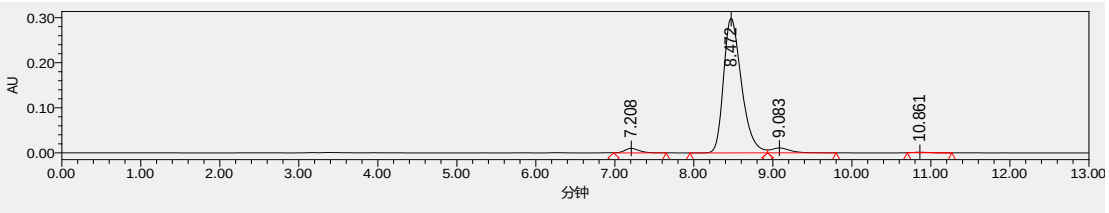
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 2H), 7.41 – 7.34 (m, 2H), 4.99 (d, *J* = 8.4 Hz, 1H), 3.98 (ddd, *J* = 10.8, 8.8, 2.0 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.46 (td, *J* = 11.6, 2.4 Hz, 1H), 2.41 (s, 3H), 2.23 (d, *J* = 12.8 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.65 – 1.37 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.55, 138.60, 135.21, 134.47, 129.31, 128.62, 126.04, 77.10, 69.08, 47.96, 29.25, 25.66, 23.15, 21.38.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{78.9183}BrO_2$ ([M]+H$^+$) = 297.0485, Found 297.0487.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{80.9163}BrO_2$ ([M]+H$^+$) = 299.0464, Found 299.0485.

$[\alpha]^{25}_D$ = 14.1 (*c* = 0.68, in CH_2Cl_2), wavelength: 589 nm.

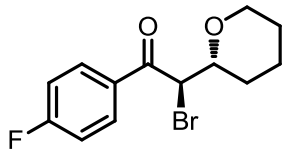




	Retention Time	Area	% Area
1	7.234	14419398	48.28
2	8.505	14698320	49.21
	9.105	378309	1.27
	11.376	371870	1.25

	Retention Time	Area	% Area
1	7.208	127852	2.54
2	8.472	4701541	93.56
	9.083	181576	3.61
	10.861	14025	0.28

2-bromo-1-(4-fluorophenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2bf):



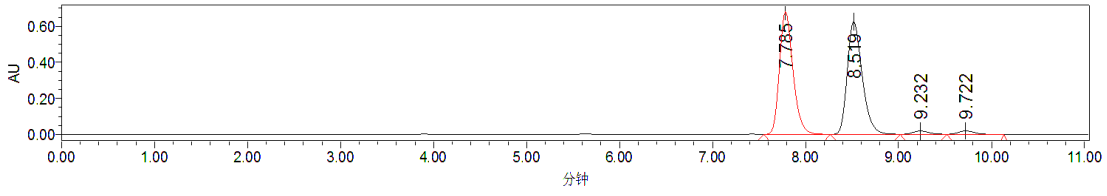
2bf

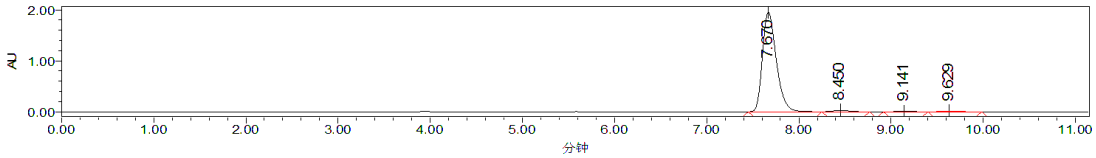
($C_{13}H_{14}BrFO_2$) Prepared according to the general procedure. The tittle compound **2bf** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 98% yield. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 7.67 min, t_{r2} (*anti*) = 8.45 min, t_{r3} (*syn*) = 9.14 min t_{r4} (*syn*) = 9.63 min, 97% *ee*; dr = 99:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.96 (m, 2H), 7.19 – 7.10 (m, 2H), 4.92 (d, *J* = 8.4 Hz, 1H), 3.97 (ddd, *J* = 10.8, 8.8, 2.0 Hz, 1H), 3.89 (td, *J* = 11.2, 2.0 Hz, 1H), 3.45 (td, *J* = 11.2, 2.8 Hz, 1H), 2.24 (d, *J* = 12.8 Hz, 1H), 1.95 (m, 1H), 1.62 – 1.36 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 191.86, 166.03 (d, *J* = 254.0 Hz), 131.61 (d, *J* = 9.0 Hz), 131.58, 115.91 (d, *J* = 22.0 Hz), 77.08, 69.09, 47.75, 29.31, 25.63, 23.11.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{78.9183}BrFO_2$ ([M]+Na^+) = 323.0053, Found 323.0057.

$[\alpha]^{16}_D$ = 15.9 (*c* = 0.66, in CH_2Cl_2), wavelength: 589 nm.

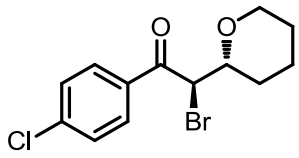




	Retention Time	Area	% Area
1	7.785	6890639	47.91
2	8.519	7000134	48.67
3	9.232	246762	1.72
4	9.722	244642	1.70

	Retention Time	Area	% Area
1	7.670	20440709	97.22
2	8.450	329764	1.57
3	9.141	87360	0.42
4	9.629	167636	0.80

2-bromo-1-(4-chlorophenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2bg):

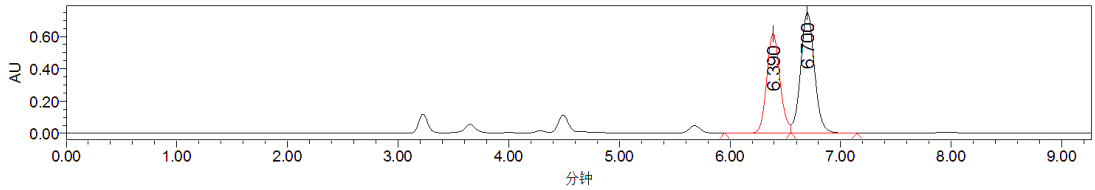


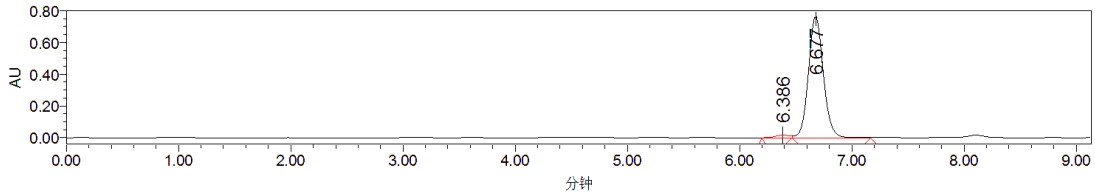
2bg

($C_{13}H_{14}BrClO_2$) Prepared according to the general procedure. The tittle compound **2bg** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 90% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 6.68 min, t_r (minor) = 6.39 min, 96% *ee*; dr = 93:7 (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.46 (t, *J* = 8.4 Hz, 2H), 4.91 (d, *J* = 8.4 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.92 – 3.84 (m, 1H), 3.49 – 3.40 (m, 1H), 2.23 (d, *J* = 12.8 Hz, 1H), 2.00 – 1.87 (m, 1H), 1.63 – 1.35 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.26, 140.15, 133.50, 130.28, 129.07, 77.05, 69.09, 47.73, 29.30, 25.62, 23.10.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{78.9183}Br^{34.9689}ClO_2$ ([M]+Na^+) = 338.9758, Found 338.9754.

HRMS (ESI-TOF) calcd for $C_{13}H_{14}{}^{80.9163}Br^{34.9689}ClO_2$ ([M]+Na^+) = 340.9737, Found 340.9741.

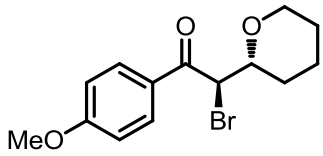




	Retention Time	Area	% Area
1	6.390	5155092	44.02
2	6.700	6554635	55.98

	Retention Time	Area	% Area
1	6.386	140057	1.95
2	6.677	7048431	98.05

2-bromo-1-(4-methoxyphenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2bh):



2bh

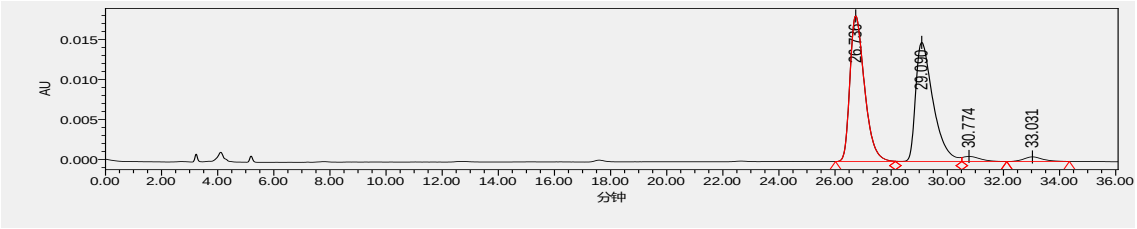
($C_{14}H_{17}BrO_3$) Prepared according to the general procedure. The tittle compound **2bh** was purified by silica gel chromatography (petroleum ether : EtOAc = 10 : 1) to afford a colorless oil in 99% yield. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 26.12 min, t_{r2} (*anti*) = 29.03 min, t_{r3} (*syn*) = 30.36 min, t_{r4} (*syn*) = 32.58 min, 97% *ee*; dr = 96:4.

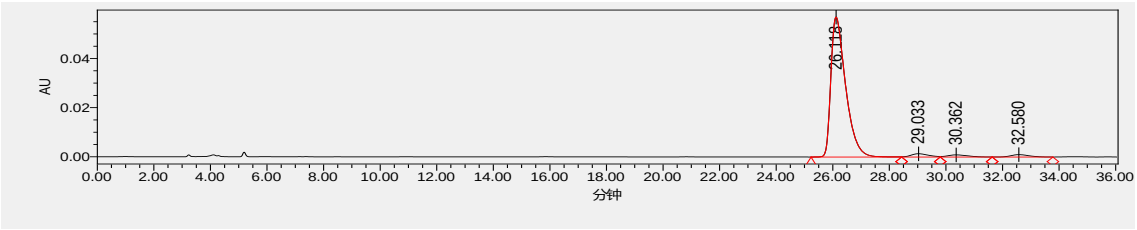
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.2 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.97 (d, *J* = 8.4 Hz, 1H), 3.97 (ddd, *J* = 10.4, 8.4, 2.0 Hz, 1H), 3.93 – 3.88 (m, 1H), 3.87 (s, 3H), 3.46 (td, *J* = 11.2, 2.4 Hz, 1H), 2.23 (d, *J* = 12.8 Hz, 1H), 1.94 (m, 1H), 1.62 – 1.36 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 191.77, 163.99, 131.27, 128.01, 113.96, 77.08, 69.09, 55.55, 48.00, 29.31, 25.67, 23.16.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{78.9183}BrO_3$ ([M]+Na^+) = 335.0253, Found 335.0261.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{80.9163}BrO_3$ ([M]+Na^+) = 337.0233, Found 337.0243.

$[\alpha]^{15}{}_D$ = -3.4 (*c* = 0.59, in CH_2Cl_2), wavelength: 589 nm.

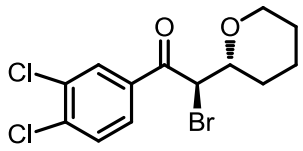




	Retention Time	Area	% Area
1	26.736	657646	48.49
2	29.090	644716	47.54
3	30.774	26829	1.98
4	33.031	27073	2.00

	Retention Time	Area	% Area
1	26.118	2060071	93.63
2	29.033	56761	2.58
	30.362	42086	1.91
	32.580	41325	1.88

2-bromo-1-(3,4-dichlorophenyl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2bi):



2bi

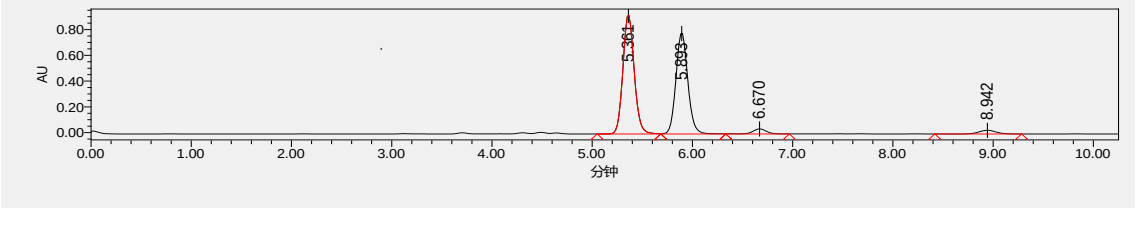
($C_{13}H_{13}Cl_2BrO_2$) Prepared according to the general procedure. The tittle compound **2bi** was purified by silica gel chromatography (petroleum ether : EtOAc = 4 : 1) to afford a colorless oil in 83% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 5.39 min, t_{r2} (*anti*) = 5.94 min, t_{r3} (*syn*) = 6.70 min, t_{r4} (*syn*) = 8.98 min, 95% *ee*; dr = 96:4.

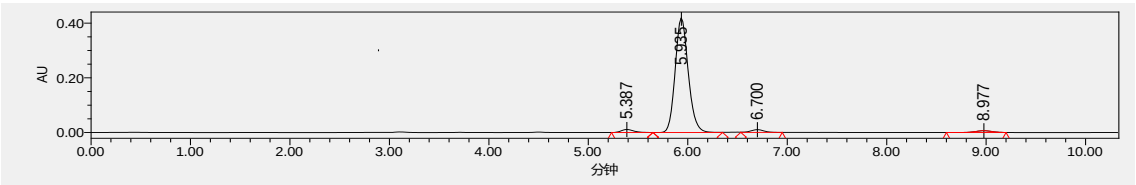
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.0 Hz, 1H), 7.81 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 4.84 (d, *J* = 8.4 Hz, 1H), 3.96 (ddd, *J* = 10.8, 8.8, 2.0 Hz, 1H), 3.90 – 3.86 (m, 1H), 3.44 (td, *J* = 11.2, 2.4 Hz, 1H), 2.23 (d, *J* = 12.8 Hz, 1H), 2.02 – 1.87 (m, 1H), 1.64 – 1.33 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.41, 138.25, 134.79, 133.47, 130.81, 130.79, 127.83, 77.10, 69.08, 47.49, 29.28, 25.58, 23.07.

HRMS (ESI-TOF) calcd for $C_{13}H_{13}{}^{34.9689}Cl_2{}^{78.9183}BrO_2$ ([M]+Na^+) = 372.9368, Found 373.9373.

HRMS (ESI-TOF) calcd for $C_{13}H_{13}{}^{34.9689}Cl_2{}^{80.9163}BrO_2$ ([M]+Na^+) = 374.9348, Found 374.9354.

$[\alpha]^{25}_D$ = 7.8 (*c* = 0.66, in CH_2Cl_2), wavelength: 589 nm.

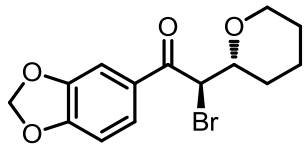




	Retention time	Area	Area%
1	5.361	7240222	50.14
2	5.893	6467375	44.79
	6.670	381656	2.64
	8.942	350681	2.43

	Retention time	Area	Area%
1	5.387	94766	2.32
3	5.935	3820785	93.50
2	6.700	95752	2.34
4	8.977	74891	1.83

1-(benzo[d][1,3]dioxol-5-yl)-2-bromo-2-(tetrahydro-2H-pyran-2-yl)ethanone (2bj):



2bj

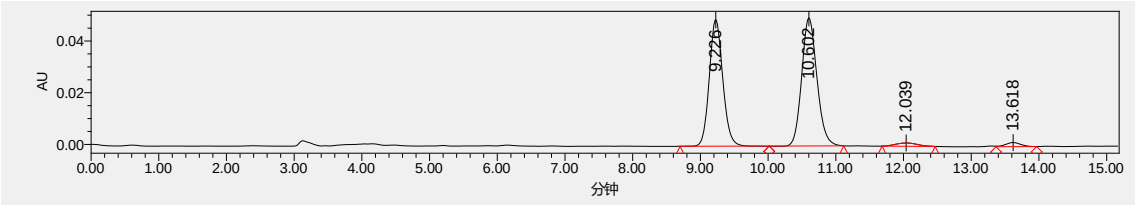
($C_{14}H_{15}BrO_4$) Prepared according to the general procedure. The tittle compound **2bj** was purified by silica gel chromatography (petroleum ether : EtOAc = 8 : 1) to afford a colorless oil in 98% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 9.30 min, t_{r2} (*anti*) = 10.63 min, t_{r3} (*syn*) = 11.95 min, t_{r4} (*syn*) = 13.65 min, 97% *ee*; dr = 96:4.

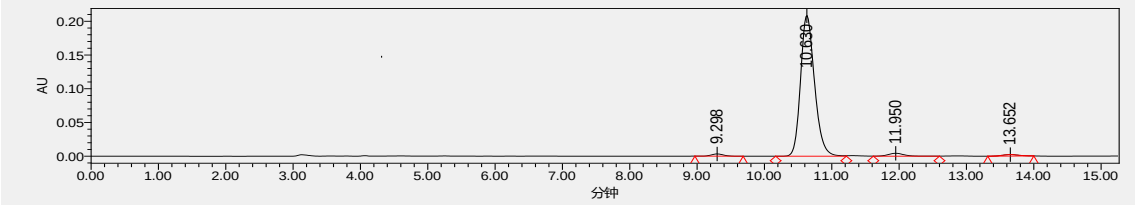
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.05 (s, 2H), 4.91 (d, *J* = 8.4 Hz, 1H), 3.96 (ddd, *J* = 10.8, 8.8, 2.0 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.45 (td, *J* = 11.6, 2.8 Hz, 1H), 2.22 (d, *J* = 12.8 Hz, 1H), 1.94 – 1.92 (m, 1H), 1.66 – 1.35 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.48, 152.35, 148.37, 129.85, 125.34, 108.66, 108.04, 102.03, 77.16, 69.08, 47.84, 29.30, 25.65, 23.14.

HRMS (ESI-TOF) calcd for $C_{14}H_{15}{}^{78.9183}BrO_4$ ([M]+H$^+$) = 327.0226, Found 327.0230.

HRMS (ESI-TOF) calcd for $C_{14}H_{15}{}^{80.9163}BrO_4$ ([M]+H$^+$) = 329.0206, Found 329.0217.

$[\alpha]^{25}_D$ = 2.4 (*c* = 0.72, in CH_2Cl_2), wavelength: 589 nm.

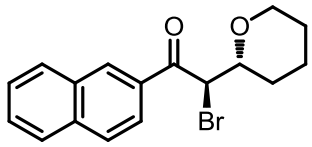




	Retention time	Area	Area%
1	9.226	678454	45.02
2	10.602	775459	51.45
3	12.039	28043	1.86
4	13.618	25141	1.67

	Retention time	Area	Area%
1	9.298	41027	1.30
2	10.630	3004366	95.12
3	11.950	75558	2.39
4	13.652	37641	1.19

2-bromo-1-(naphthalen-2-yl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (2bk):



2bk

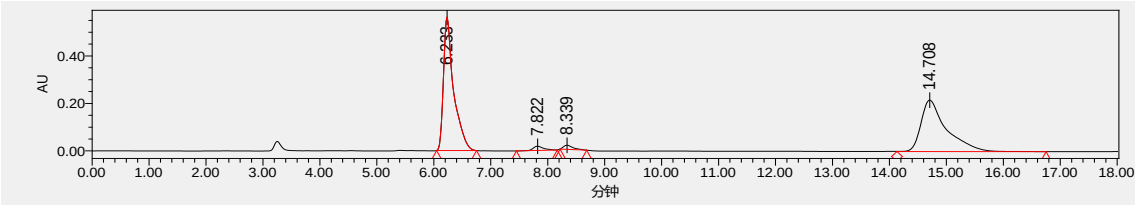
($C_{17}H_{17}BrO_2$) Prepared according to the general procedure. The tittle compound **2bk** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 93% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 6.23 min, t_{r2} (*syn*) = 7.83 min, t_{r3} (*syn*) = 8.34 min, t_{r4} (*anti*) = 14.8 min, 94% *ee*; dr = 95:5.

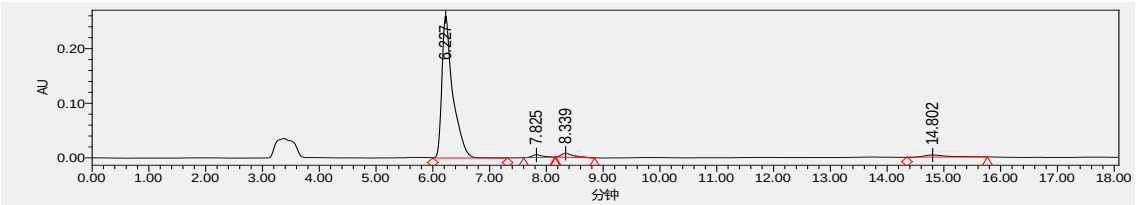
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.05 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.58 (dt, *J* = 22.4, 7.2 Hz, 2H), 5.17 (d, *J* = 8.4 Hz, 1H), 4.05 (ddd, *J* = 12.0, 8.4, 1.6 Hz, 1H), 3.94 – 3.84 (m, 1H), 3.48 (td, *J* = 11.6, 2.4 Hz, 1H), 2.36 – 2.20 (m, 1H), 2.03 – 1.89 (m, 1H), 1.66 – 1.41 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.33, 135.82, 132.49, 132.45, 130.69, 129.79, 128.87, 128.69, 127.80, 126.92, 124.36, 77.20, 69.12, 47.99, 29.33, 25.67, 23.18.

HRMS (ESI-TOF) calcd for $C_{17}H_{17}{}^{78.9183}BrO_2$ ([M]+Na^+) = 355.0304, Found 355.0320.

HRMS (ESI-TOF) calcd for $C_{17}H_{17}{}^{80.9163}BrO_2$ ([M]+Na^+) = 357.0284, Found 357.0298.

$[\alpha]^{29}_D$ = -41.2 (*c* = 0.50, in CH_2Cl_2), wavelength: 589 nm.

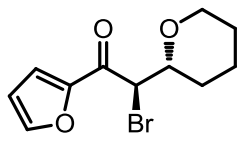




	Retention time	Area	Area%
1	6.233	6977689	49.48
2	7.822	221610	1.57
3	8.339	207020	1.47
4	14.708	6695293	47.48

	Retention time	Area	Area%
1	6.227	3469388	92.43
2	7.825	64265	1.71
3	8.339	112192	2.99
4	14.802	107492	2.86

2-bromo-2-(tetrahydro-2H-pyran-2-yl)-1-(thiophen-3-yl)ethanone (2bl)



2bl

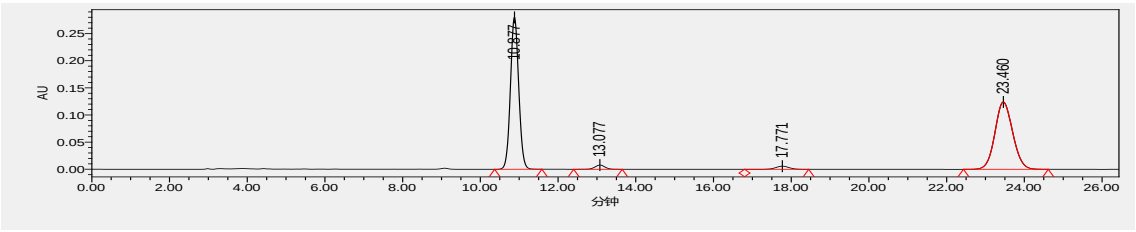
($C_{11}H_{13}BrO_3$) Prepared according to the general procedure. The tittle compound **2bl** was purified by silica gel chromatography (petroleum ether : EtOAc = 12 : 1) to afford a white solid in 93% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 10.87 min, t_{r2} (*syn*) = 13.07 min, t_{r3} (*syn*) = 17.76 min, t_{r4} (*anti*) = 23.50 min, 78% *ee*; dr = 94:6.

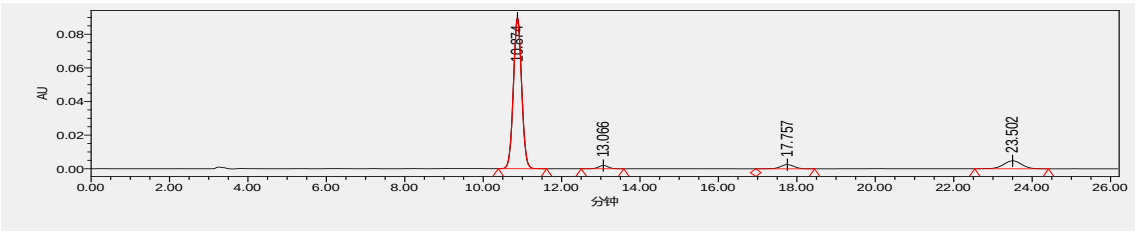
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.33 (d, *J* = 3.2 Hz, 1H), 6.58 (s, 1H), 4.83 (d, *J* = 8.8 Hz, 1H), 3.96 (t, *J* = 9.6 Hz, 1H), 3.89 (d, *J* = 10.4 Hz, 1H), 3.49 – 3.39 (m, 1H), 2.21 (d, *J* = 12.4 Hz, 1H), 1.93 (s, 1H), 1.63 – 1.32 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.26, 150.88, 147.26, 119.18, 112.84, 76.94, 69.05, 48.14, 29.20, 25.57, 23.08.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}^{78.9183}BrO_3$ ([M]+Na^+) = 294.9940, Found 294.9951.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}^{80.9163}BrO_3$ ([M]+Na^+) = 296.9920, Found 296.9929.

$[\alpha]^{15}_D$ = 18.6 (*c* = 0.57, in CH_2Cl_2), wavelength: 589 nm.

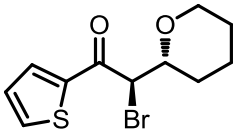




	Retention time	Area	Area%
1	10.877	4168567	49.70
2	13.077	138059	1.65
3	17.771	137347	1.64
4	23.460	3943867	47.02

	Retention time	Area	Area%
1	10.874	1316870	84.15
2	13.066	34521	2.21
3	17.757	60575	3.87
4	23.502	152944	9.77

2-bromo-2-(tetrahydro-2H-pyran-2-yl)-1-(thiophen-3-yl)ethanone (2bm)



2bm

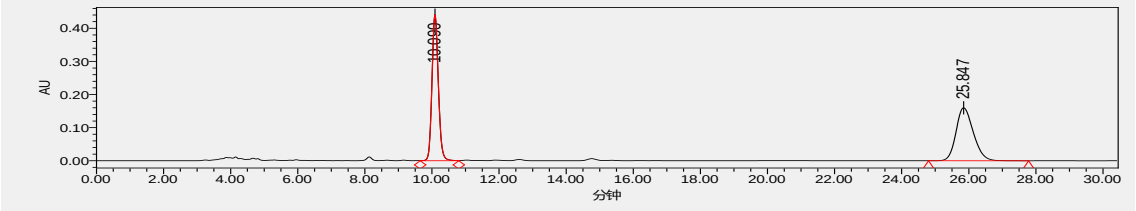
($C_{11}H_{13}BrO_2S$) Prepared according to the general procedure. The tittle compound **2bm** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 94% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 10.12 min, t_r (minor) = 26.18 min, 95% *ee*, dr = 95:5 (determined by ^{1}H NMR).

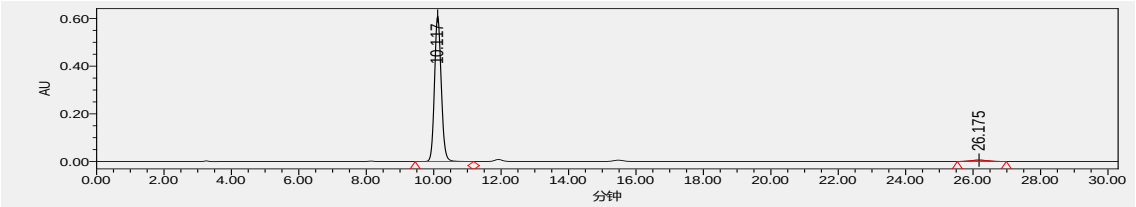
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.71 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.15 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.82 (d, *J* = 8.8 Hz, 1H), 3.95 (ddd, *J* = 10.8, 8.8, 2.0 Hz, 1H), 3.93 – 3.86 (m, 1H), 3.45 (td, *J* = 11.2, 2.8 Hz, 1H), 2.29 – 2.15 (m, 1H), 2.01 – 1.86 (m, 1H), 1.64 – 1.34 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.33, 142.02, 135.27, 133.16, 128.36, 77.16, 69.12, 49.16, 29.24, 25.59, 23.11.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}^{78.9183}BrO_2S$ ([M]+Na^+) = 310.9712, Found 310.9720.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}^{80.9163}BrO_2S$ ([M]+Na^+) = 312.9691, Found 312.9691.

$[\alpha]^{29}_D$ = 19.7 (*c* = 0.58, in CH_2Cl_2), wavelength: 589 nm.

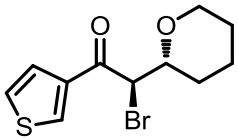




	Retention time	Area	Area%
1	10.090	5779834	50.24
2	25.847	5725015	49.76

	Retention time	Area	Area%
1	10.117	8431885	97.69
2	26.175	199240	2.31

(*R*)-2-bromo-2-((*R*)-tetrahydro-2H-pyran-2-yl)-1-(thiophen-3-yl)ethanone (2bn)



2bn

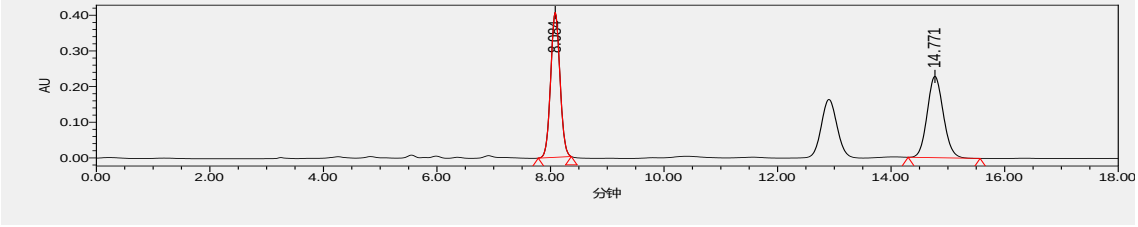
($C_{11}H_{13}BrO_2S$) Prepared according to the general procedure. The tittle compound **2bn** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 98% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 8.08 min, t_r (minor) = 14.75 min, 94% *ee*; dr = 96:4 (by ^{1}H NMR).

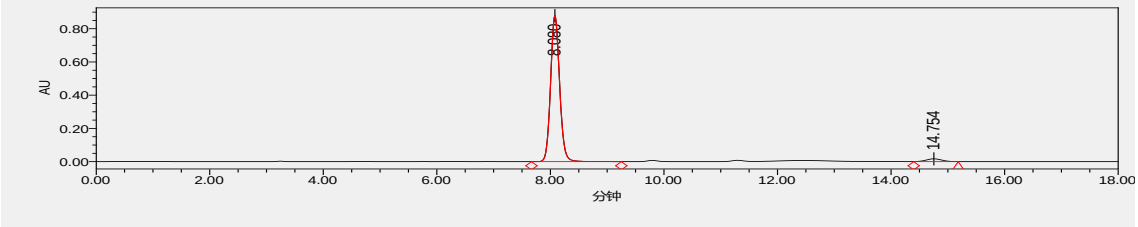
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.60 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.33 (dd, *J* = 5.2, 2.8 Hz, 1H), 4.79 (d, *J* = 8.4 Hz, 1H), 3.95 (ddd, *J* = 10.8, 8.4, 2.4 Hz, 1H), 3.92 – 3.86 (m, 1H), 3.45 (td, *J* = 11.6, 2.8 Hz, 1H), 2.26 –2.17 (m, 1H), 1.99 – 1.90 (m, 1H), 1.64 – 1.34 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.45, 139.92, 133.64, 127.50, 126.64, 77.00, 69.10, 49.82, 29.27, 25.62, 23.11.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}{}^{78.9183}BrO_2S$ ([M]+Na^+) = 310.9712, Found 310.9722.

HRMS (ESI-TOF) calcd for $C_{11}H_{13}{}^{80.9163}BrO_2S$ ([M]+Na^+) = 312.9691, Found312.9687.

$[\alpha]^{29}_D$ = 8.9 (*c* = 0.62, in CH_2Cl_2), wavelength: 589 nm.

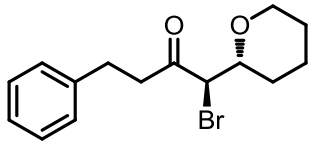




	Retention time	Area	Area%
1	8.084	4832610	50.72
2	14.771	4696135	49.28

	Retention time	Area	Area%
1	8.080	9736103	96.84
2	14.754	317641	3.16

1-bromo-4-phenyl-1-(tetrahydro-2H-pyran-2-yl)butan-2-one (2bo)



2bo

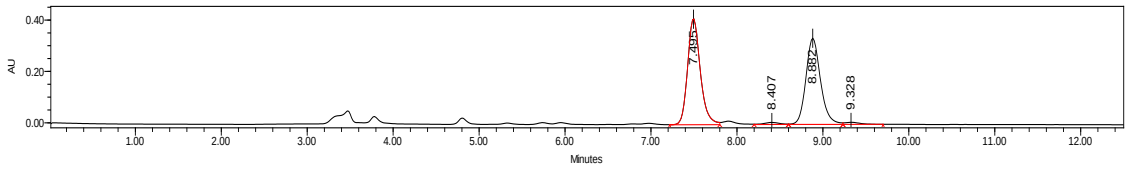
($C_{15}H_{19}BrO_2$) Prepared according to the general procedure. The tittle compound **2bo** was purified by silica gel chromatography (petroleum ether : EtOAc = 20 : 1) to afford a colorless oil in 90% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 210 nm), t_{r1} (*anti*) = 7.43 min, t_{r2} (*syn*) = 8.29 min, t_{r3} (*anti*) = 8.74 min, t_{r4} (*syn*) = 9.19 min, 93% *ee*; dr = 95:5.

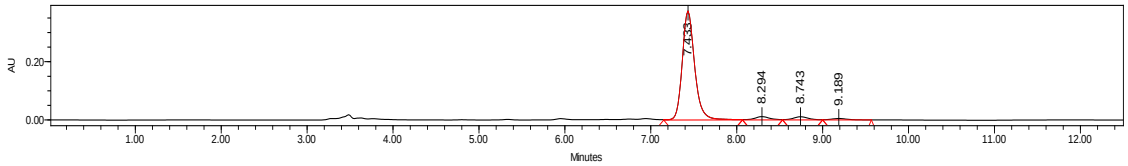
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.14 (m, 5H), 4.04 (d, *J* = 8.8 Hz, 1H), 3.96 – 3.85 (m, 1H), 3.77 – 3.63 (m, 1H), 3.46 – 3.31 (m, 1H), 3.15 – 2.86 (m, 4H), 2.04 (d, *J* = 12.4 Hz, 1H), 1.94 – 1.81 (m, 1H), 1.58 – 1.41 (m, 3H), 1.32 – 1.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.93, 140.87, 128.46, 128.41, 126.14, 77.82, 68.96, 54.26, 40.72, 29.68, 29.02, 25.49, 22.94.

HRMS (ESI-TOF) calcd for $C_{15}H_{19}{}^{78.9183}BrO_2$ ([M]+Na^+) = 333.0461, Found 333.0457.

HRMS (ESI-TOF) calcd for $C_{15}H_{19}{}^{80.9163}BrO_2$ ([M]+Na^+) = 335.0440, Found 335.0439.

$[\alpha]^{29}_D$ = 4.8 (*c* = 0.62, in CH_2Cl_2), wavelength: 589 nm.

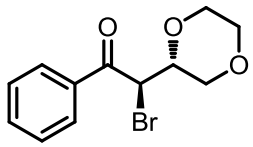




	Retention time	Area	Area%
1	7.495	4227160	50.47
2	8.407	100630	1.20
3	8.882	3952677	47.20
4	9.328	94376	1.13

	Retention time	Area	Area%
1	7.433	3742698	91.58
2	8.294	143013	3.50
3	8.743	136925	3.35
4	9.189	64044	1.57

2-bromo-2-(1,4-dioxan-2-yl)-1-phenylethanone (2bp)



2bp

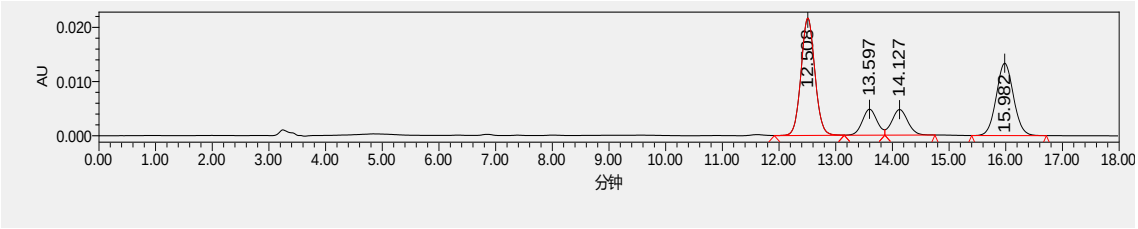
($C_{12}H_{13}BrO_3$) Prepared according to the general procedure. The tittle compound **2bp** was purified by silica gel chromatography (petroleum ether : EtOAc = 10 : 1) to afford a colorless oil in 97% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 12.49 min, t_{r2} (*syn*) = 13.60 min, t_{r3} (*syn*) = 14.13 min, t_{r4} (*anti*) = 15.98 min, 95% *ee*; dr = 96:4.

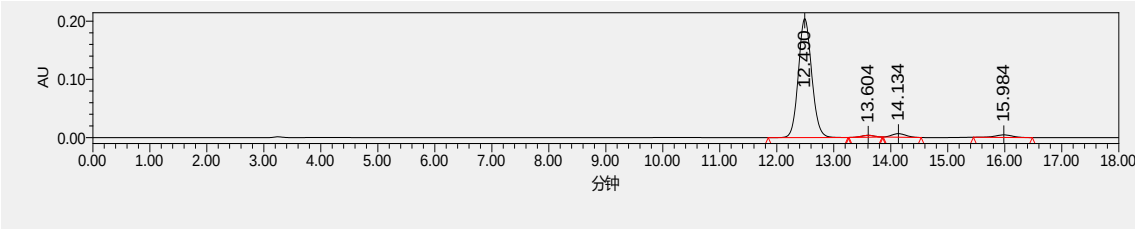
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.99 (m, 2H), 7.66 – 7.58 (m, 1H), 7.52 – 7.48 (m, *J* = 10.6, 4.8 Hz, 2H), 5.04 (d, *J* = 8.4 Hz, 1H), 4.36 – 4.26 (m, 2H), 3.77 – 3.68 (m, 3H), 3.65 – 3.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.93, 134.62, 133.98, 128.90, 128.87, 73.70, 69.58, 66.70, 66.36, 43.00.

HRMS (ESI-TOF) calcd for $C_{12}H_{13}{}^{78.9183}BrO_3$ ([M]+Na^+) = 306.9940, Found 306.9949.

HRMS (ESI-TOF) calcd for $C_{12}H_{13}{}^{80.9163}BrO_3$ ([M]+Na^+) = 308.9920, Found 308.9931.

$[\alpha]^{15}_D$ = 1.7 (*c* = 0.58, in CH_2Cl_2), wavelength: 589 nm.

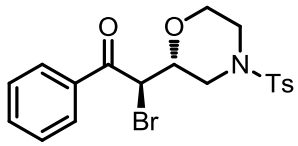




	Retention time	Area	Area%
1	12.508	367649	44.44
2	13.597	86631	10.47
3	14.127	91617	11.07
4	15.982	281370	34.01

	Retention time	Area	Area%
1	12.490	3316091	93.12
2	13.604	49110	1.38
3	14.134	103904	2.92
4	15.984	91839	2.58

2-bromo-1-phenyl-2-(4-tosylmorpholin-2-yl)ethanone (2bq)



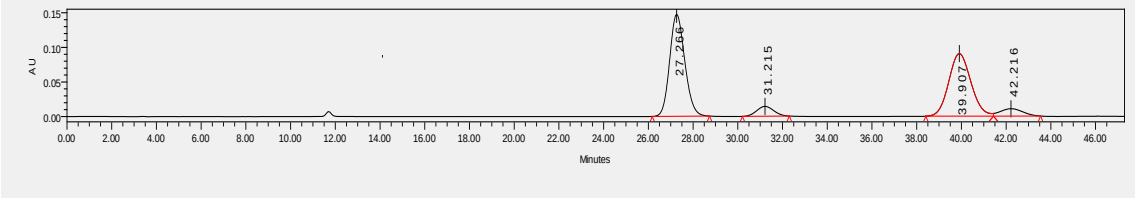
2bq

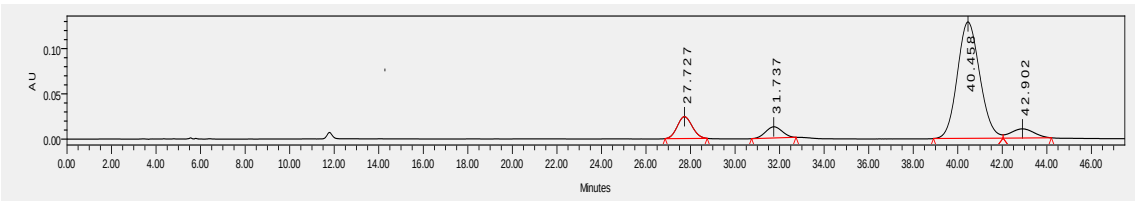
($C_{19}H_{20}BrNO_4S$) Prepared according to the general procedure. The tittle compound **2bq** was purified by silica gel chromatography (petroleum ether : EtOAc = 4 : 1) to afford a white solid in 93% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} (*anti*) = 27.73 min, t_{r2} (*syn*) = 31.74 min, t_{r3} (*anti*) = 40.46 min, t_{r4} (*syn*) = 42.90 min, 77% *ee*; dr = 88:12.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.71 – 7.57 (m, 3H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 4.97 (d, *J* = 8.4 Hz, 1H), 4.30 – 3.60 (m, 4H), 3.49 (d, *J* = 11.6 Hz, 1H), 2.66 (d, *J* = 5.6 Hz, 1H), 2.53 – 2.40 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.50, 144.15, 134.50, 134.04, 132.34, 129.92, 128.88, 128.83, 127.87, 74.20, 66.16, 48.63, 45.32, 43.76, 21.60.

HRMS (ESI-TOF) calcd for $C_{19}H_{20}{}^{78.9183}BrNO_4S$ ([M]+Na^+) = 460.0189, Found 460.0185.

HRMS (ESI-TOF) calcd for $C_{19}H_{20}{}^{80.9163}BrNO_4S$ ([M]+Na^+) = 462.0168, Found 462.0172.

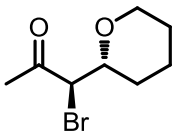




	Retention Time	Area	% Area
1	27.266	6927335	47.26
2	31.215	753211	5.14
3	39.907	6232543	42.52
4	42.216	746361	5.09

	Retention Time	Area	% Area
1	27.727	1147102	9.97
2	31.737	640355	5.57
3	40.458	8987327	78.11
4	42.902	731201	6.35

1-bromo-1-(tetrahydro-2H-pyran-2-yl)propan-2-one (2bs)

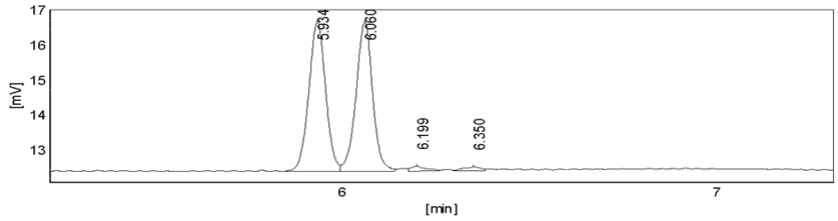


2bs

($C_8H_{13}BrO_2$) Prepared according to the general procedure. The tittle compound **2bs** was purified by silica gel chromatography (petroleum ether : EtOAc = 20 : 1) to afford a colorless oil in 68% yield. GC (CHIRALSIL-DEX CB column, T = 120 °C), t_{r1}= 5.95 min, t_{r2} = 6.08 min, t_{r3}= 6.21 min, t_{r4} = 6.37 min, 73% *ee*; dr = 94:6.

1H NMR (400 MHz, CDCl3) δ 4.02 (d, *J* = 8.8 Hz, 1H), 4.00 – 3.93 (m, 1H), 3.70 (ddd, *J* = 10.8, 8.4, 2.0 Hz, 1H), 3.48 – 3.39 (m, 1H), 2.33 (s, 3H), 2.12 – 2.03 (m, 1H), 1.94 – 1.85 (m, 1H), 1.59 – 1.46 (m, 3H), 1.35 – 1.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.62, 77.89, 68.98, 54.76, 28.92, 26.07, 25.50, 22.90.

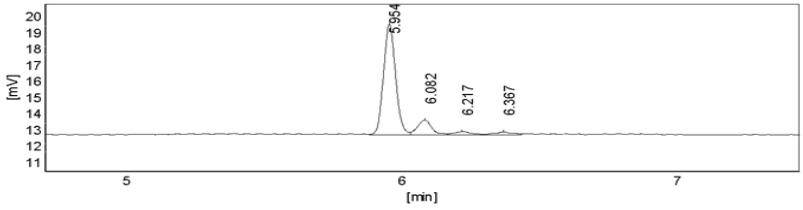
HRMS (ESI-TOF) calcd for $C_8H_{13}{}^{78.9183}BrO_2$ ([M]+K^+) = 242.9991, Found 242.9992.



Analysis Table

分析结果表

No.	峰号	组分名	峰型	height 峰高 [uV]	Retention Time 保留时间 [min]	Area 峰面积 [uV*s]	Area% 面积%	含量 [%]
1			BV	4265	5.934	13407	49.19267	49.19267
2			VV	4267	6.060	13078	47.98531	47.98531
3			XV	131	6.199	396	1.45265	1.45265
4			VV	111	6.350	373	1.36937	1.36937
总计：				8774		27255	100.00000	100.00000

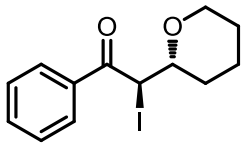


Analysis Table

分析结果表

No.	峰号	组分名	峰型	height 峰高 [uV]	Retention Time 保留时间 [min]	Area 峰面积 [uV*s]	Area% 面积%	含量 [%]
1			VV	6836	5.954	20936	80.97604	80.97604
2			VV	909	6.082	3254	12.58688	12.58688
3			VV	205	6.217	868	3.35613	3.35613
4			VV	170	6.367	797	3.08095	3.08095
总计：				8120		25854	100.00000	100.00000

2-iodo-1-phenyl-2-((R)-tetrahydro-2H-pyran-2-yl)ethanone (2ca):



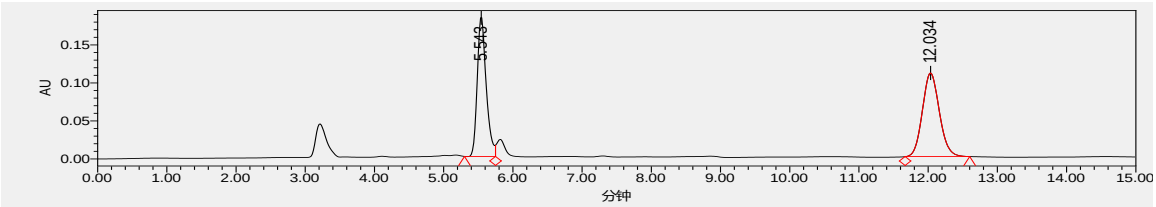
2ca

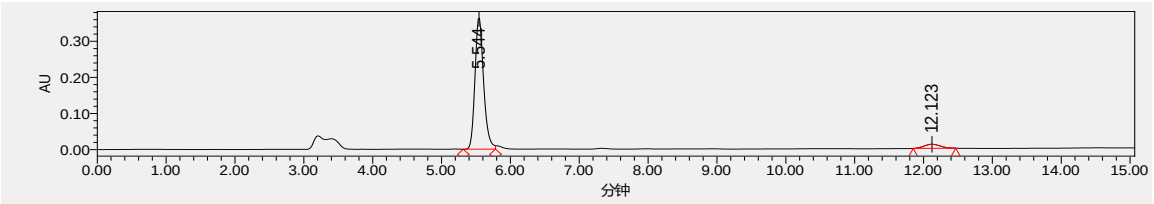
($C_{13}H_{15}IO_2$) Prepared according to the general procedure. The tittle compound **2ca** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a pale yellow oil in 90% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 5.54 min, t_r (minor) = 12.12 min, 89% *ee*; dr > 99:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.93 (m, 2H), 7.61 – 7.53 (m, 1H), 7.52 – 7.40 (m, 2H), 5.21 (d, *J* = 8.8 Hz, 1H), 3.97 – 3.80 (m, 2H), 3.48 (td, *J* = 12.0, 2.8 Hz, 1H), 2.38 (d, *J* = 12.8 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.67 – 1.30 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.52, 134.64, 133.49, 128.73, 128.70, 77.50, 69.18, 31.26, 28.37, 25.51, 23.62.

HRMS (ESI-TOF) calcd for $C_{13}H_{15}IO_2$ ([M]+Na^+) = 353.0014, Found 353.0005.

$[\alpha]^{29}_D$ = 26.2 (*c* = 0.45, in CH_2Cl_2).

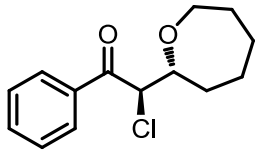




	Retention Time	Area	% Area
1	5.543	1650756	46.92
2	12.034	1867779	53.08

	Retention Time	Area	% Area
1	5.544	3161024	94.54
2	12.123	182677	5.46

2-chloro-2-(oxepan-2-yl)-1-phenylethanone (*anti*-9a)



anti-**9a**

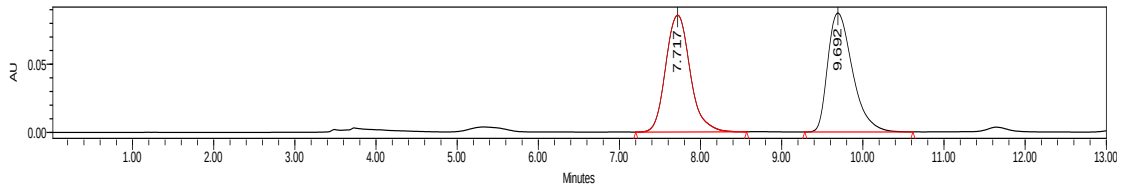
($C_{14}H_{17}ClO_2$) Prepared according to the general procedure at 35 °C for 24 h. The tittle compound *anti*-**9a** was purified by silica gel chromatography (petroleum ether : EtOAc = 30 : 1) to afford a colorless oil in 66% yield. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 7.81 min, t_r (minor) = 9.86 min, 90% *ee*; dr = *anti*-**9a**:*syn*-**9a** = 83:17 (by ^{1}H NMR of crude product).

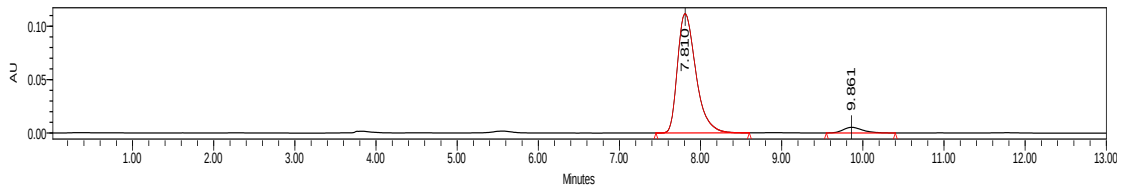
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.94 (m, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 4.93 (d, *J* = 8.8 Hz, 1H), 4.14 (td, *J* = 9.6, 2.8 Hz, 1H), 3.70 (ddd, *J* = 12.4, 7.2, 5.6 Hz, 1H), 3.60 – 3.50 (m, 1H), 2.33 – 2.21 (m, 1H), 1.91 – 1.80 (m, 1H), 1.80 – 1.49 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.82, 135.60, 133.61, 128.82, 128.73, 78.94, 69.62, 57.26, 31.94, 30.74, 26.62, 25.70.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{34.9689}ClO_2$ ([M]+Na^+) = 275.0815, Found 275.0810.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{36.9659}ClO_2$ ([M]+Na^+) = 277.0785, Found 277.0780.

$[\alpha]^{15}_D$ = 12.6 (*c* = 0.27, in CH_2Cl_2), wavelength: 589 nm.

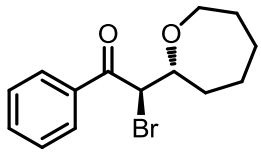




	Retention time	Area	Area%
1	7.717	1787662	49.21
2	9.692	1845408	50.79

	Retention time	Area	Area%
1	7.810	1752603	95.27
2	9.861	87081	4.73

2-bromo-2-(oxepan-2-yl)-1-phenylethanone (*anti*-8a):



anti-**8a**

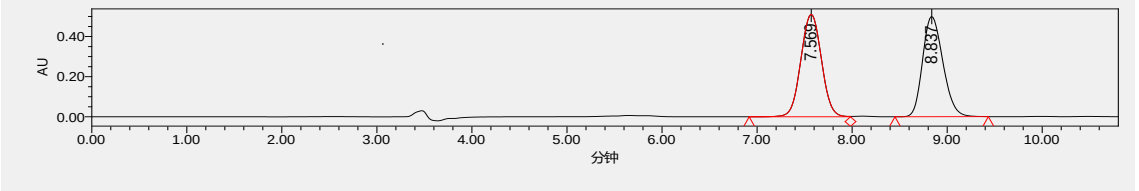
($C_{14}H_{17}BrO_2$) Prepared according to the general procedure at 0 °C for 12 h. The tittle compound *anti*-**8a** was purified by silica gel chromatography (petroleum ether : EtOAc = 30 : 1) to afford a white solid in 54% yield. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 7.62 min, t_r (minor) = 8.97 min, 98% *ee*; dr = *anti*-**8a**:*syn*-**8a** = 57:43 (determined by ^{1}H NMR of crude product).

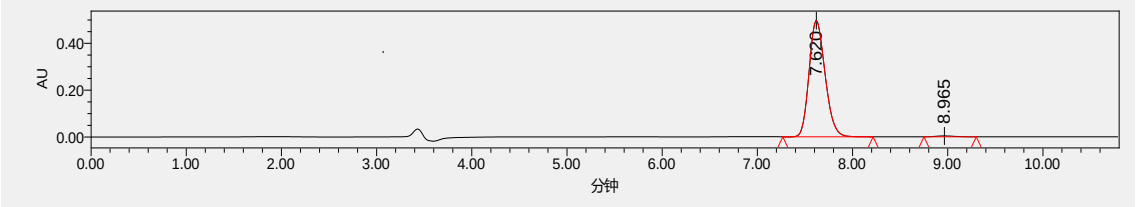
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.96 (d, *J* = 9.6 Hz, 1H), 4.22 (td, *J* = 9.6, 2.8 Hz, 1H), 3.76 – 3.51 (m, 2H), 2.46 – 2.35 (m, 1H), 1.90 – 1.76 (m, 1H), 1.79 – 1.50 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.45, 135.34, 133.58, 128.76, 128.75, 78.44, 69.78, 47.35, 32.63, 30.84, 26.81, 25.50.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{78.9183}BrO_2$ ([M]+Na^+) = 319.0304, Found 319.0300.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{80.9163}BrO_2$ ([M]+Na^+) = 321.0284, Found 321.0281.

$[\alpha]^{30}_D$ = 33.3 (*c* = 0.26, in CH_2Cl_2), wavelength: 589 nm.

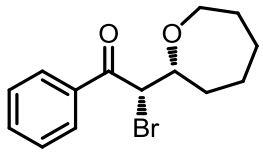




	Retention time	Area	Area%
1	7.569	7674990	50.82
2	8.837	7427943	49.18

	Retention time	Area	Area%
1	7.620	5787704	99.13
2	8.965	50545	0.87

2-bromo-2-(oxepan-2-yl)-1-phenylethanone (*syn*-8a):



syn-**8a**

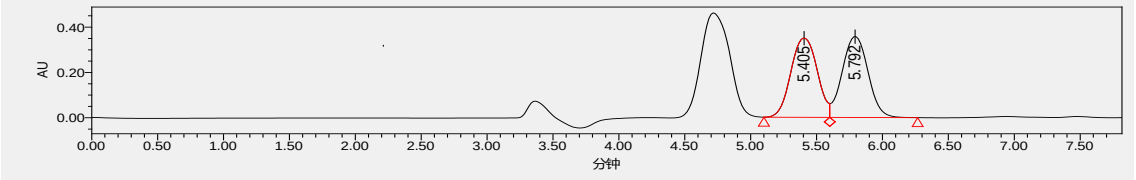
($C_{14}H_{17}ClO_2$) Prepared according to the general procedure at 0 °C for 12 h. The tittle compound *syn*-**8a** was purified by silica gel chromatography (petroleum ether : EtOAc = 30 : 1) to afford a colorless oil in 38% yield. HPLC (Chiralcel IB, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 5.81 min, t_r (minor) = 5.43 min, >99% *ee*; dr = *anti*-**8a***: syn*-**8a** = 57:43 (determined by ^{1}H NMR of crude product).

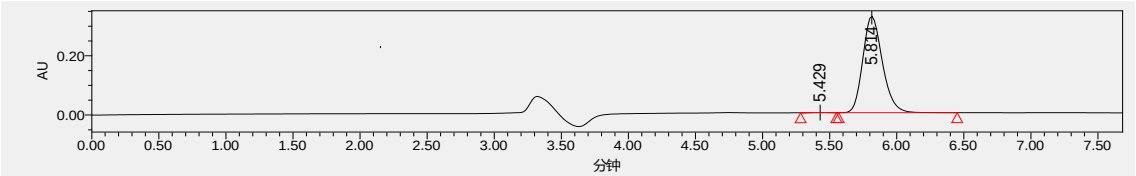
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 5.12 (d, *J* = 8.8 Hz, 1H), 4.04 – 4.13 (m, 1H), 3.98 (td, *J* = 12.0, 6.0 Hz, 1H), 3.72 (td, *J* = 11.2, 5.2 Hz, 1H), 1.92 – 1.37 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.27, 134.81, 133.92, 128.89, 128.86, 78.90, 70.15, 50.89, 33.39, 30.69, 26.63, 25.93.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{78.9183}BrO_2$ ([M]+Na^+) = 319.0304, Found 319.0300.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}{}^{80.9163}BrO_2$ ([M]+Na^+) = 321.0284, Found 321.0288.

$[\alpha]^{29}_D$ = 37.5 (*c* = 0.22, in CH_2Cl_2), wavelength: 589 nm.

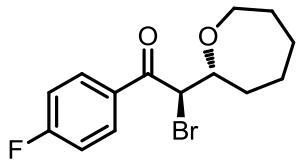




	Retention time	Area	Area%
1	5.405	4855733	49.88
2	5.792	4878410	50.12

	Retention time	Area	Area%
1	5.429	8252	0.25
2	5.814	3308868	99.75

2-bromo-1-(4-fluorophenyl)-2-(oxepan-2-yl)ethanone (*anti*-8b)



anti-**8b**

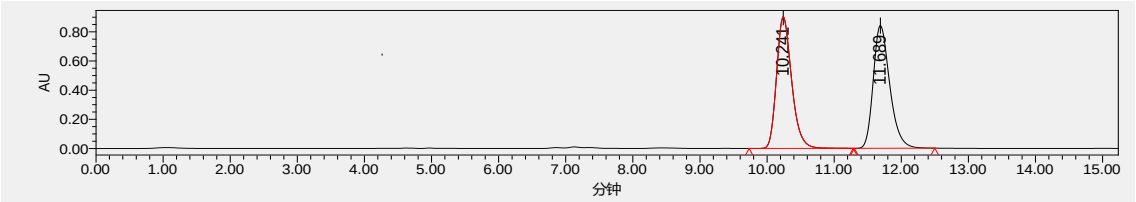
($C_{14}H_{16}BrFO_2$) Prepared according to the general procedure at 0 °C for 12 h. The tittle compound *anti*-**8b** was purified by silica gel chromatography (petroleum ether : EtOAc = 30 : 1) to afford a colorless oil in 51% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 10.12 min, t_r (minor) = 26.18 min, 98% *ee*; dr = *anti*-**8b***:syn*-**8b** = 57:43 (determined by ^{1}H NMR of crude product).

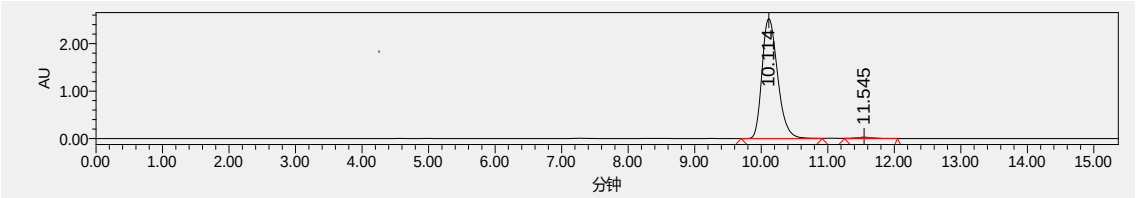
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.98 (m, 2H), 7.20 – 7.10 (m, 2H), 4.90 (d, *J* = 9.6 Hz, 1H), 4.20 (td, *J* = 10.0, 2.8 Hz, 1H), 3.75 – 3.66 (m, 1H), 3.62 – 3.54 (m, 1H), 2.46 – 2.35 (m, 1H), 1.88 – 1.51 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.90, 165.99 (d, *J* = 254.0 Hz), 131.70 (d, *J* = 3.0 Hz), 131.51 (d, *J* = 9.0 Hz), 115.93 (d, *J* = 22.0 Hz), 78.43, 69.82, 47.22, 32.63, 30.82, 26.78, 25.47.

HRMS (ESI-TOF) calcd for $C_{14}H_{16}{}^{78.9183}BrFO_2$ ([M]+Na^+) = 337.0210, Found 337.0206.

HRMS (ESI-TOF) calcd for $C_{14}H_{16}{}^{80.9163}BrFO_2$ ([M]+Na^+) = 337.0189, Found 337.0190.

$[\alpha]^{30}_D$ = 21.4 (*c* = 0.71, in CH_2Cl_2), wavelength: 589 nm.

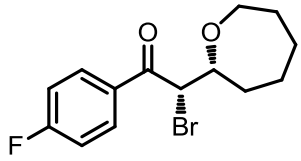




	Retention time	Area	Area%
1	10.241	14056151	49.44
2	11.689	14375491	50.56

	Retention time	Area	Area%
1	10.114	41214594	98.93
2	11.545	446052	1.07

2-bromo-1-(4-fluorophenyl)-2-(oxepan-2-yl)ethanone (*syn*-8b):



syn-**8b**

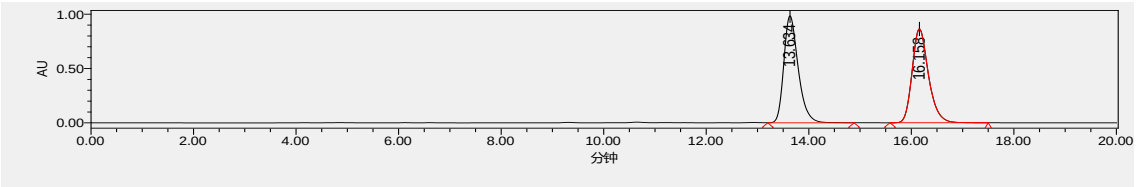
($C_{14}H_{16}BrFO_2$) Prepared according to the general procedure at 0 °C for 12 h. The tittle compound *syn*-**8b** was purified by silica gel chromatography (petroleum ether : EtOAc = 30: 1) to afford a white solid in 31% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 8.03 min, t_r (minor) = 13.84 min, >99% *ee*; dr = *anti*-**8b**:*syn*-**8b** = 57:43 (determined by ^{1}H NMR of crude product).

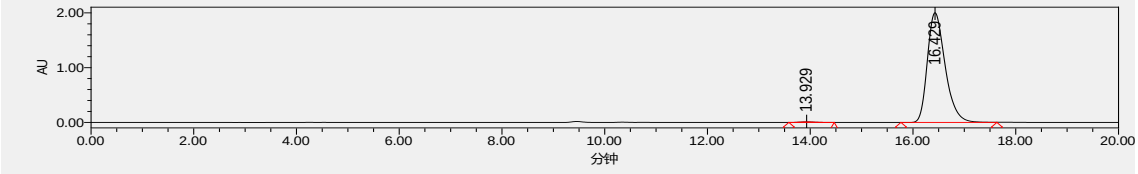
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.96 (m, 2H), 7.17 (t, *J* = 8.8 Hz, 2H), 5.05 (d, *J* = 8.8 Hz, 1H), 4.07 (td, *J* = 9.2, 3.2 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.77 – 3.65 (m, 1H), 1.92 – 1.37 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.73, 166.16 (d, *J* = 255.0 Hz), 131.65 (d, *J* = 10.0 Hz), 131.19 (d, *J* = 3.0 Hz), 116.08(d, *J* = 22.0 Hz) 78.84, 70.18, 50.79, 33.36, 30.66, 26.61, 25.91.

HRMS (ESI-TOF) calcd for $C_{14}H_{16}{}^{78.9183}BrFO_2$ ([M]+Na^+) = 337.0210, Found 337.0210.

HRMS (ESI-TOF) calcd for $C_{14}H_{16}{}^{80.9163}BrFO_2$ ([M]+Na^+) = 337.0189, Found 337.0195.

$[\alpha]^{25}_D$ = 32.5 (*c* = 0.56, in CH_2Cl_2).

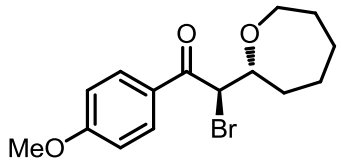




	Retention time	Area	Area%
1	5.405	4855733	49.88
2	5.792	4878410	50.12

	Retention time	Area	Area%
1	5.429	8252	0.25
2	5.814	3308868	99.75

2-bromo-1-(4-methoxyphenyl)-2-(oxepan-2-yl)ethanone (*anti*-8c):



anti-**8c**

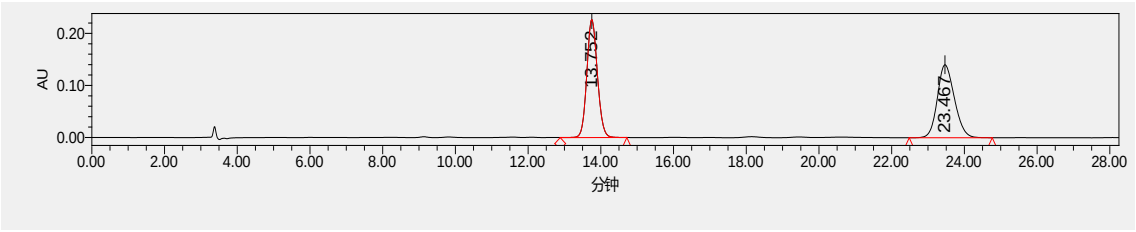
($C_{15}H_{19}BrO_3$) Prepared according to the general procedure at 35 °C for 24 h. The tittle compound *anti*-**8c** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 35% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 13.67 min, t_r (minor) = 23.41 min, 93% *ee*; dr = *anti*-**8c**:*syn*-**8c** = 57:43 (determined by ^{1}H NMR of crude product).

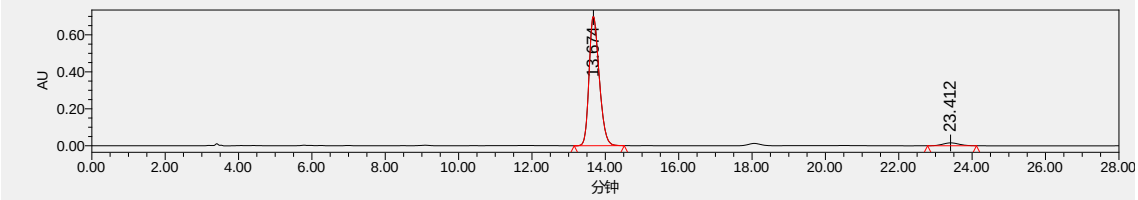
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.05 – 6.83 (m, 2H), 4.94 (d, *J* = 9.6 Hz, 1H), 4.21 (td, *J* = 9.6, 2.8 Hz, 1H), 3.88 (s, 3H), 3.76 – 3.66 (m, 1H), 3.63 – 3.55 (m, 1H), 2.47 – 2.35 (m, 1H), 1.90 – 1.55 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.86, 163.93, 131.17, 128.17, 113.97, 78.43, 69.77, 55.54, 47.38, 32.66, 30.86, 26.81, 25.52.

HRMS (ESI-TOF) calcd for $C_{15}H_{19}{}^{78.9183}BrO_3$ ([M]+Na^+) = 349.0410, Found 349.0406.

HRMS (ESI-TOF) calcd for $C_{15}H_{19}{}^{80.9163}BrO_3$ ([M+2]+Na^+) = 351.0389, Found 351.0394.

$[\alpha]^{29}_D$ = -15.0 (*c* = 0.23, in CH_2Cl_2), wavelength: 405 nm.

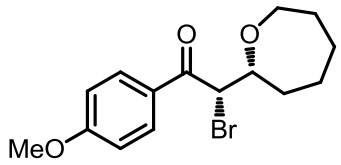




	Retention time	Area	Area%
1	13.752	4580364	50.09
2	23.467	4563877	49.91

	Retention time	Area	Area%
1	13.674	13465779	96.58
2	23.412	476567	3.42

2-bromo-1-(4-methoxyphenyl)-2-(oxepan-2-yl)ethanone (*syn*-8c):



syn-**8c**

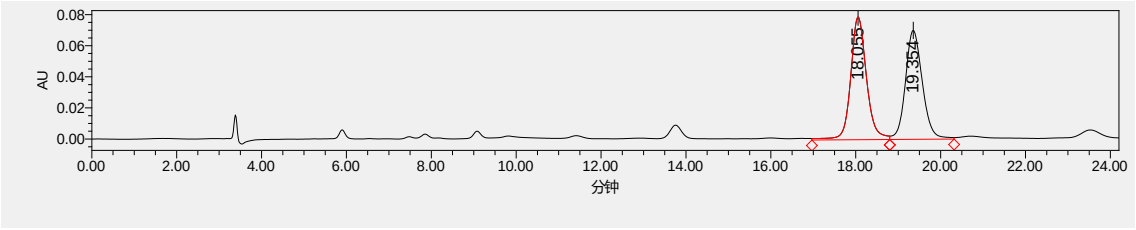
($C_{15}H_{19}BrO_3$) Prepared according to the general procedure at 35 °C for 24 h. The tittle compound *syn*-**8c** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 34% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 18.15 min, t_r (minor) = 19.65 min, 97% *ee*; dr = *anti*-**8c**:*syn*-**8c** = 57:43 (determined by ^{1}H NMR of crude product).

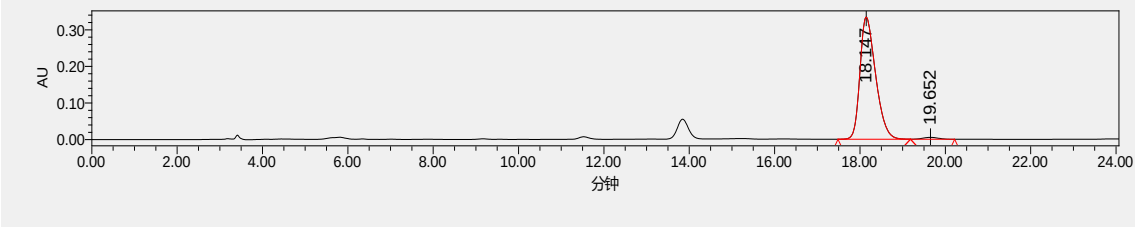
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.89 (m, 2H), 7.04 – 6.88 (m, 2H), 5.08 (d, *J* = 8.8 Hz, 1H), 4.07 (td, *J* = 9.6, 3.2 Hz, 1H), 3.98 (ddd, *J* = 12.4, 7.2, 5.6 Hz, 1H), 3.88 (s, 3H), 3.72 (ddd, *J* = 11.6, 6.4, 4.8 Hz, 1H), 1.91 – 1.79 (m, 2H), 1.71 (m, 3H), 1.60 – 1.35 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.84, 164.19, 131.29, 127.70, 114.11, 79.09, 70.12, 55.59, 50.78, 33.33, 30.69, 26.63, 25.92.

HRMS (ESI-TOF) calcd for $C_{15}H_{19}{}^{78.9183}BrO_3$ ([M]+Na^+) = 349.0410, Found 349.0406.

HRMS (ESI-TOF) calcd for $C_{15}H_{19}{}^{80.9163}BrO_3$ ([M]+Na^+) = 351.0389, Found 351.0394.

$[\alpha]^{29}_{D}$ = 194.2 (*c* = 0.24, in CH_2Cl_2), wavelength: 405 nm.

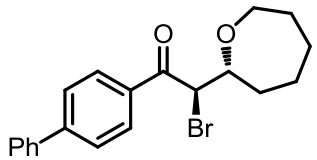




	Retention Time	Area	% Area
1	18.055	2047336	51.36
2	19.354	1938742	48.64

	Retention Time	Area	% Area
1	18.147	8484150	98.44
2	19.652	134834	1.56

(*R*)-1-([1,1'-biphenyl]-4-yl)-2-bromo-2-((*R*)-oxepan-2-yl)ethanone (*anti*-8d):



anti-**8d**

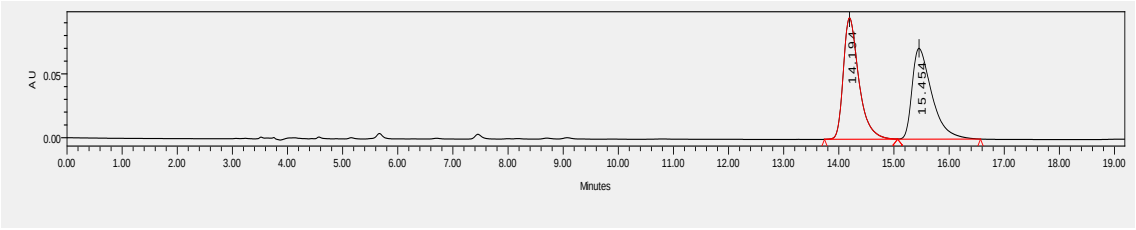
($C_{20}H_{21}BrO_2$) Prepared according to the general procedure at 0 °C for 12 h. The tittle compound *anti*-**8d** was purified by silica gel chromatography (petroleum ether : EtOAc = 30 : 1) to afford a white solid in 52% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 15.45 min, t_r (minor) = 14.19 min, 98% *ee*; dr = *anti*-**8d***: syn*-**8d** = 57:43 (determined by ^{1}H NMR of crude product).

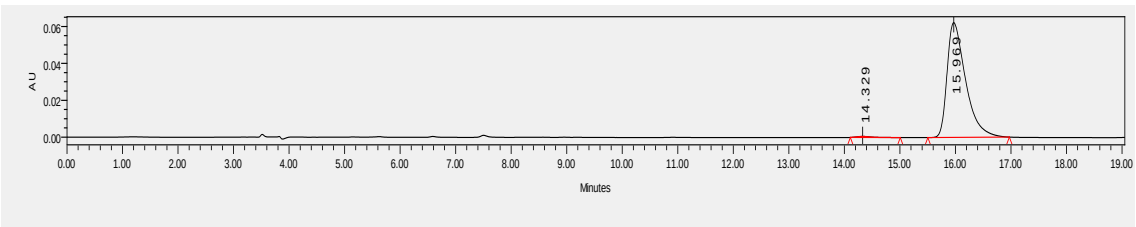
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.59 (m, 2H), 7.52 – 7.44 (m, 2H), 7.44 – 7.38 (m, 1H), 5.00 (d, *J* = 9.6 Hz, 1H), 4.24 (td, *J* = 9.6, 2.4 Hz, 1H), 3.78 – 3.56 (m, 2H), 2.50 – 2.35 (m, 1H), 1.90 – 1.52 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.99, 146.30, 139.77, 133.99, 129.39, 129.00, 128.37, 127.41, 127.32 78.48, 69.81, 47.45, 32.67, 30.87, 26.82, 25.53.

HRMS (ESI-TOF) calcd for $C_{20}H_{21}{}^{78.9183}BrO_2$ ([M]+Na^+) = 395.0617, Found 395.0615.

HRMS (ESI-TOF) calcd for $C_{20}H_{21}{}^{80.9163}BrO_2$ ([M]+Na^+) = 397.0597, Found 397.0603.

$[\alpha]^{29}_{D}$ = -57.1 (*c* = 0.34, in CH_2Cl_2), wavelength: 405 nm.

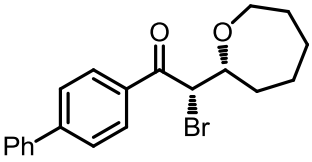




	Retention Time	Area	% Area
1	14.194	1864492	51.30
2	15.454	1770116	48.70

	Retention Time	Area	% Area
1	14.329	10283	0.71
2	15.969	1438494	99.29

2-bromo-1-(4-fluorophenyl)-2-(oxepan-2-yl)ethanone (*syn*-8d):



syn-**8d**

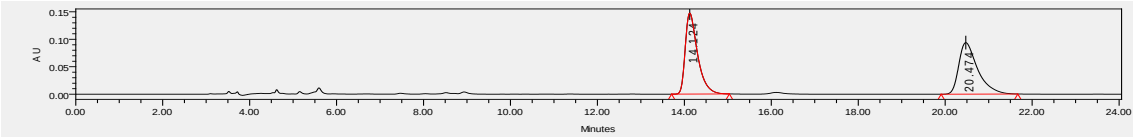
($C_{20}H_{21}BrO_2$) Prepared according to the general procedure at 0 °C for 12 h. The tittle compound *syn*-**8d** was purified by silica gel chromatography (petroleum ether : EtOAc = 30 : 1) to afford a white solid in 40% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 20.48 min, t_r (minor) = 14.21 min, >99% *ee*; dr = *anti*-**8d***: syn*-**8d** = 57:43 (determined by ^{1}H NMR of crude product).

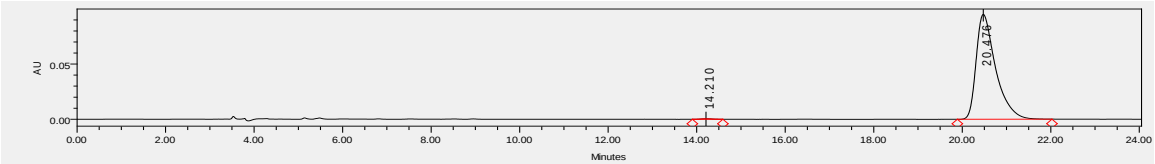
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.60 (m, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H), 5.15 (d, *J* = 8.8 Hz, 1H), 4.11 (td, *J* = 9.6, 3.2 Hz, 1H), 4.00 (ddd, *J* = 12.0, 7.2, 5.6 Hz, 1H), 3.73 (ddd, *J* = 11.6, 6.0, 4.8 Hz, 1H), 1.94 – 1.86 (m, 1H), 1.86 – 1.41 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.84, 146.65, 139.60, 133.47, 129.49, 129.03, 128.49, 127.51, 127.32, 78.97, 70.17, 50.96, 33.41, 30.70, 26.64, 25.95.

HRMS (ESI-TOF) calcd for $C_{20}H_{21}{}^{78.9183}BrO_2$ ([M]+Na^+) = 395.0617, Found 395.0622.

HRMS (ESI-TOF) calcd for $C_{20}H_{21}{}^{80.9163}BrO_2$ ([M]+Na^+) = 397.0597, Found 397.0608.

$[\alpha]^{29}_D$ = 241.9 (*c* = 0.27, in CH_2Cl_2), wavelength: 405 nm.

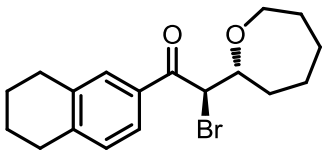




	Retention Time	Area	% Area
1	14.124	2902200	50.72
2	20.474	2819350	49.28

	Retention Time	Area	% Area
1	14.210	7845	0.27
2	20.476	2896667	99.73

2-bromo-1-(4-fluorophenyl)-2-(oxepan-2-yl)ethanone (*anti*-8e):



anti-**8e**

($C_{18}H_{23}BrO_2$) Prepared according to the general procedure at 0 °C for 12 h. The tittle compound *anti*-**8e** was purified by silica gel chromatography (petroleum ether : EtOAc = 30 : 1) to afford a white solid in 56% yield, 97% *ee* (determined by the *ee* of **4e**). dr = *anti*-**8e***: syn*-**8e** = 57:43 (determined by ^{1}H NMR of crude product).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 2H), 7.18 – 7.13 (m, 1H), 4.96 (d, *J* = 9.2 Hz, 1H), 4.21 (td, *J* = 9.6, 2.8 Hz, 1H), 3.79 – 3.52 (m, 2H), 2.82 (d, *J* = 4.8 Hz, 4H), 2.47 – 2.35 (m, 1H), 1.88 – 1.53 (m, 11H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.27, 143.98, 137.73, 132.72, 129.64,

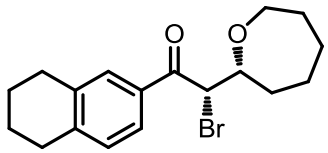
129.52, 125.81, 78.43, 69.76, 47.35, 32.62, 30.87, 29.71, 29.38, 26.84, 25.50, 22.91, 22.77.

HRMS (ESI-TOF) calcd for $C_{18}H_{23}{}^{78.9183}BrO_2$ ([M]+Na^+) = 373.0774, Found 373.0776.

HRMS (ESI-TOF) calcd for $C_{20}H_{21}{}^{80.9163}BrO_2$ ([M]+Na^+) = 375.0753, Found 375.0760.

$[\alpha]^{29}_D$ = 15.0 (*c* = 0.42, in CH_2Cl_2), wavelength: 405 nm.

2-bromo-1-(4-fluorophenyl)-2-(oxepan-2-yl)ethanone (*syn*-8e):



syn-**8e**

($C_{18}H_{23}BrO_2$) Prepared according to the general procedure at 0 °C for 12 h. The tittle compound *syn*-**8e** was purified by silica gel chromatography (petroleum ether : EtOAc = 30 : 1) to afford a white solid in 39% yield, 97% *ee* (determined by the *ee* of **4e**). dr = *anti*-**8e**:*syn*-**8e** = 57:43 (determined by ^{1}H NMR of crude product).

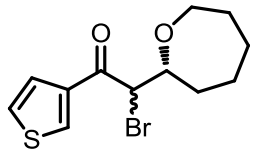
^{1}H NMR (400 MHz, CDCl3) δ 7.63 – 7.74 (m, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 5.10 (d, *J* = 8.8 Hz, 1H), 4.07 (td, J = 9.6, 3.2 Hz, 1H), 3.98 (ddd, *J* = 12.0, 6.8, 5.2 Hz, 1H), 3.71 (ddd, *J* = 12.0, 6.4, 5.2 Hz, 1H), 2.82 (s, 4H), 1.89 – 1.60 (m, 10H), 1.56 – 1.36 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 193.21, 144.42, 137.91, 132.29, 129.75, 129.64, 125.86, 79.07, 70.09, 50.84, 33.34, 30.71, 29.73, 29.38, 26.61, 25.95, 22.86, 22.72.

HRMS (ESI-TOF) calcd for $C_{18}H_{23}{}^{78.9183}BrO_2$ ([M]+Na^+) = 373.0774, Found 373.0778.

HRMS (ESI-TOF) calcd for $C_{20}H_{21}{}^{80.9163}BrO_2$ ([M]+Na^+) = 375.0753, Found 375.0759.

$[\alpha]^{29}_D$ = 4 (*c* = 0.26, in CH_2Cl_2), wavelength: 589 nm.

2-bromo-1-(4-fluorophenyl)-2-(oxepan-2-yl)ethanone (8f):



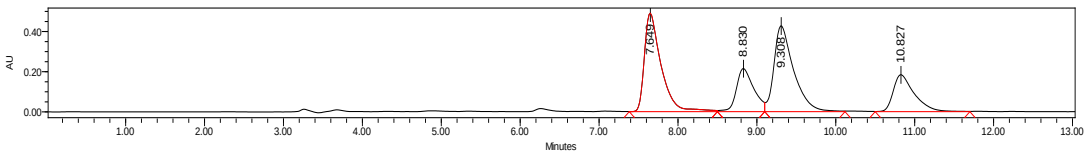
8f

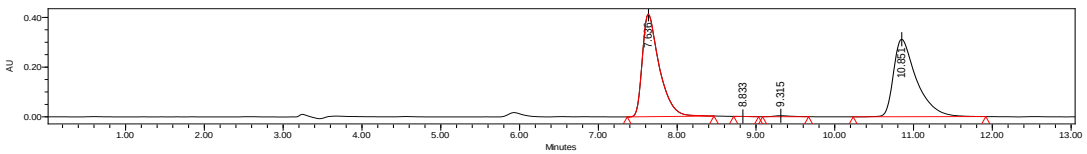
($C_{12}H_{15}BrO_2S$) Prepared according to the general procedure at 0 °C for 12 h. The tittle compound **8f** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a white solid in 86% yield. HPLC (Chiralcel ID, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} = 7.64 min, t_{r2} = 8.83 min, t_{r3} = 9.32 min, t_{r4} = 10.85 min, > 99% *ee*/98% *ee*; dr = *anti*-**8f** : *syn*-**8f** = 50:50.

^{1}H NMR (400 MHz, CDCl3) δ 8.18 (dd, J = 2.8, 1.0 Hz, 1H), 8.16 (dd, J = 2.8, 1.0 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.37 – 7.35 (m, 1H), 7.35 – 7.32 (m, 1H), 4.91 (d, J = 8.7 Hz, 1H, *syn*-**8f**), 4.76 (d, J = 9.4 Hz, 1H,*anti*-**8f**), 4.18 (td, J = 9.7, 2.9 Hz, 1H, *anti*-**8f**), 4.04 (td, J = 9.2, 3.2 Hz, 1H, *syn*-**8f**), 3.96 (ddd, J = 12.3, 7.0, 5.4 Hz, 1H), 3.77 – 3.65 (m, 2H), 3.62 – 3.54 (m, 1H), 2.39 (ddd, J = 12.9, 6.4, 3.1 Hz, 1H), 1.92 – 1.40 (m, 15H) (two diasteroisomers mixture of **8f**). ^{13}C NMR (101 MHz, CDCl3) δ 187.45 (187.42), 140.05 (139.76), 133.37 (133.87), 127.45 (127.44), 126.62 (126.85), 78.37 (78.84), 69.79 (70.07), 49.36 (52.83), 32.65 (33.27), 30.84 (30.68), 26.73 (26.58), 25.54 (25.93) (two diasteroisomers mixture of **8f**).

HRMS (ESI-TOF) calcd for $C_{12}H_{15}{}^{78.9183}BrO_2S$ ([M]+Na^+) = 324.9868, Found 324.9876.

HRMS (ESI-TOF) calcd for $C_{12}H_{15}{}^{80.9163}BrO_2S$ ([M]+Na^+) = 326.9848, Found 326.9861.

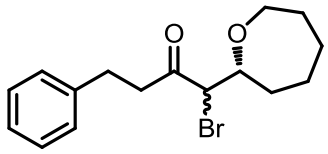




	Retention Time	Area	% Area
1	7.649	7187013	33.78
2	8.830	3284004	15.44
3	9.308	7395414	34.76
4	10.827	3409501	16.03

	Retention Time	Area	% Area
1	7.636	6148054	49.11
2	8.833	3154	0.03
3	9.315	58851	0.47
4	10.851	6308503	50.39

2-bromo-1-(4-fluorophenyl)-2-(oxepan-2-yl)ethanone (8g):



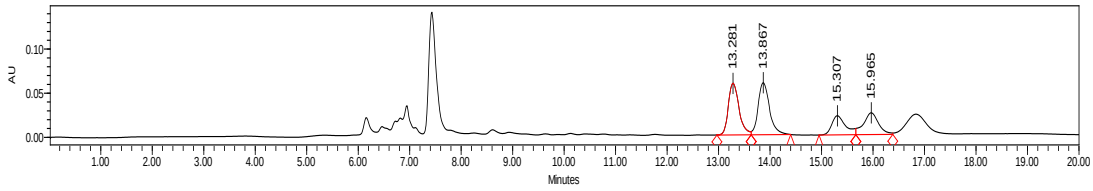
8g

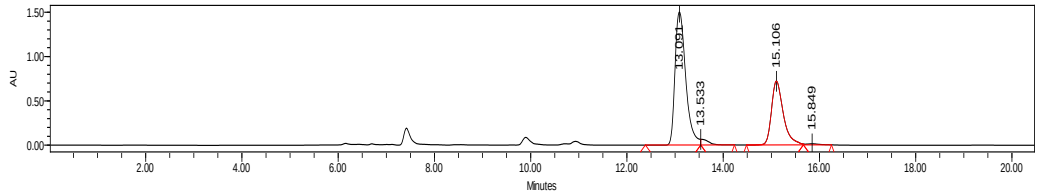
($C_{16}H_{21}BrO_2$) Prepared according to the general procedure at 35 °C for 24 h. The tittle compound **8g** was purified by silica gel chromatography (petroleum ether : EtOAc = 15 : 1) to afford a colorless oil in 48% yield. HPLC (series connection of Chiralcel IE and Phenomenex chiralpakLux 5u Cellulose-2, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 210 nm), t_{r1} = 13.09 min, t_{r2} = 13.53 min, t_{r3} = 15.11 min, t_{r4} = 15.85 min, 94% *ee*/96% *ee*; dr = *anti*-**8g** : *syn*-**8g** =66:34.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.16 (m, 5H), 4.06 (d, *J* = 9.6 Hz, 1H), 4.00 – 3.68 (m, 2H), 3.60 – 3.44 (m, 1H), 3.06 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.02 – 2.88 (m, 3H), 2.29 – 2.00 (m, 1H), 1.82 – 1.44 (m, 7H). For *anti*-**8g**: ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.76, 140.84, 128.46, 128.40, 126.14, 79.16, 69.31, 53.74, 41.21, 32.53, 30.78, 29.65, 26.18, 26.03. For *syn*-**8g**: ^{13}C NMR (101 MHz, CDCl3) δ 203.56, 140.62, 128.51, 128.44, 126.22, 78.52, 69.87, 58.94, 42.38, 33.56, 30.62, 29.87, 26.37, 25.97.

HRMS (ESI-TOF) calcd for $C_{16}H_{21}{}^{78.9183}BrO_2$ ([M]+Na^+) = 347.0617, Found 347.0629.

HRMS (ESI-TOF) calcd for $C_{16}H_{21}{}^{80.9163}BrO_2$ ([M]+Na^+) = 349.0597, Found 349.0612.

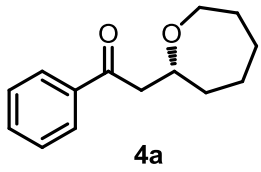




	Retention Time	Area	% Area
1	13.281	849355	31.90
2	13.867	907868	34.09
3	15.307	407247	15.29
4	15.965	498465	18.72

	Retention Time	Area	% Area
1	13.091	23205009	63.66
2	13.533	713399	1.96
3	15.106	12300264	33.74
4	15.849	233553	0.64

2-(oxepan-2-yl)-1-phenylethanone (4a):



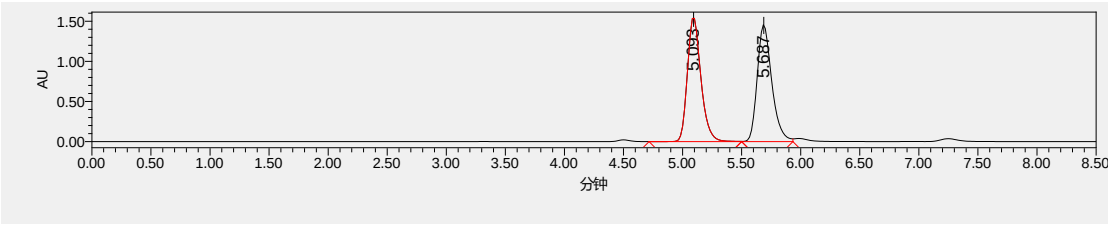
4a

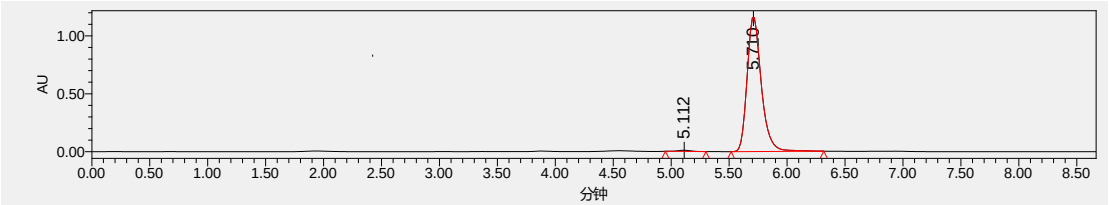
($C_{14}H_{18}O_2$) Prepared according to the general procedure using 0.085 mmol **8a** as substrate. The tittle compound **4a** was purified by silica gel chromatography (petroleum ether : EtOAc = 10 : 1) to afford a colorless oil in 94% yield (debromination step). HPLC (Chiralcel IA, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 5.71 min, t_r (minor) = 5.11 min, 98% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.89 (m, 2H), 7.51 – 7.57 (m, 4.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.23 – 4.12 (m, 1H), 3.86 – 3.76 (m, 1H), 3.59 (ddd, *J* = 11.6, 6.8, 4.0 Hz, 1H), 3.33 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.90 (dd, *J* = 16.0, 5.2 Hz, 1H), 1.93 – 1.84 (m, 1H), 1.80 – 1.52 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.81, 137.39, 132.99, 128.54, 128.24, 75.86, 69.01, 45.68, 35.94, 30.97, 26.27, 26.10.

HRMS (ESI-TOF) calcd for $C_{14}H_{18}O_2$ ([M]+Na^+) = 241.1199, Found 241.1211.

$[\alpha]^{29}_D$ = -6.8 (*c* = 0.37, in CH_2Cl_2), wavelength: 405 nm.

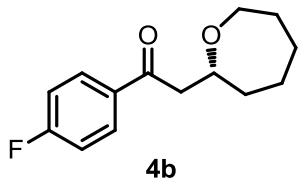




	Retention Time	Area	% Area
1	5.093	12291776	49.62
2	5.687	12479192	50.38

	Retention Time	Area	% Area
1	5.112	75602	0.76
2	5.710	9911539	99.24

1-(4-fluorophenyl)-2-(oxepan-2-yl)ethanone (4b)



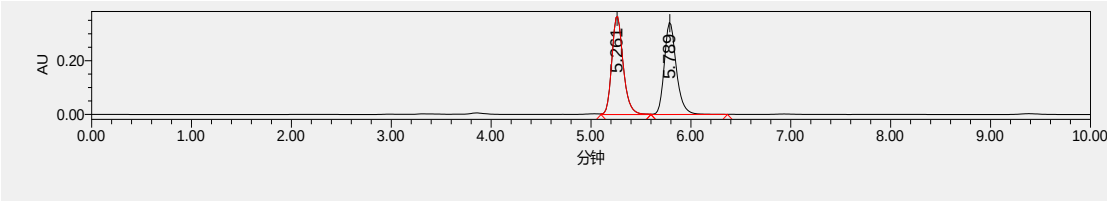
4b

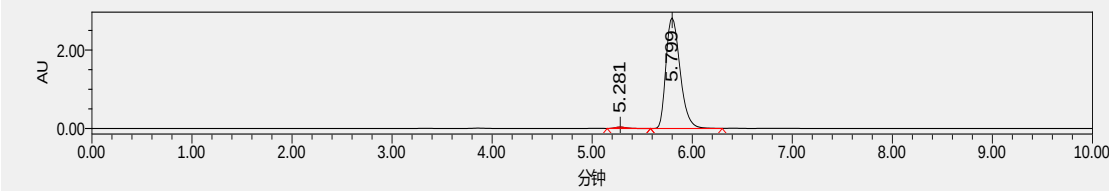
($C_{14}H_{17}FO_2$) Prepared according to the general procedure using 0.084 mmol **8b** as substrate. The tittle compound **4b** was purified by silica gel chromatography (petroleum ether : EtOAc = 10 : 1) to afford a colorless oil in 90% yield (debromination step). HPLC (Chiralcel IA, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 5.80 min, t_r (minor) = 5.28 min, 98% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.91 (m, 2H), 7.17 – 7.05 (m, 2H), 4.20 – 4.10 (m, 1H), 3.87 – 3.73 (m, 1H), 3.58 (ddd, *J* = 12.0, 7.2, 4.4 Hz, 1H), 3.30 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.84 (dd, *J* = 16.0, 4.8 Hz, 1H), 1.88 (ddd, *J* = 13.6, 6.8, 3.6 Hz, 1H), 1.80 – 1.52 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.27, 166.71 (d, *J* = 53.5 Hz), 133.86 (d, *J* = 3.0 Hz), 130.91 (d, *J* = 9.0 Hz), 115.60 (d, *J* = 22.0 Hz), 75.91, 69.06, 45.58, 35.96, 30.95, 26.22, 22.09.

HRMS (ESI-TOF) calcd for $C_{14}H_{17}FO_2$ ([M]+Na^+) = 259.1105, Found 259.1106.

$[\alpha]^{29}_D$ = 8.4 (*c* = 0.37, in CH_2Cl_2), wavelength: 589 nm.

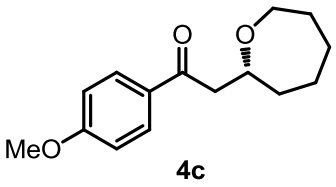




	Retention Time	Area	% Area
1	5.261	2874766	50.05
2	5.789	2869430	49.95

	Retention Time	Area	% Area
1	5.281	298477	1.06
2	5.799	27761285	98.94

1-(4-methoxyphenyl)-2-(oxepan-2-yl)ethanone (4c)

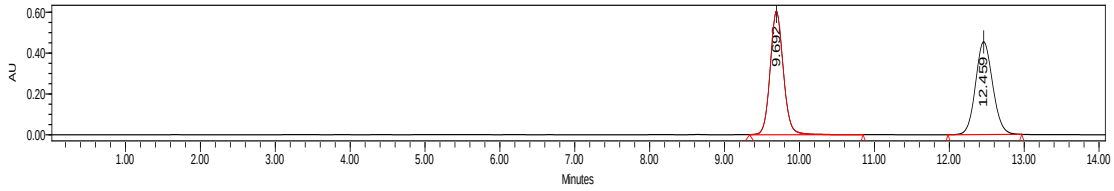


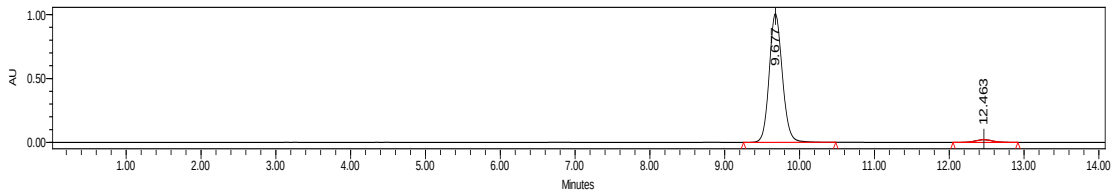
4c

($C_{15}H_{20}O_3$) Prepared according to the general procedure using 0.070 mmol **8c** as substrate. The tittle compound **4c** was purified by silica gel chromatography (petroleum ether : EtOAc = 8 : 1) to afford a colorless oil in 82% yield (debromination step). HPLC (Chiralcel IC, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 9.68 min, t_r (minor) = 12.46 min, 95% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.87 (m, 2H), 7.06 – 6.81 (m, 2H), 4.21 – 4.11 (m, 1H), 3.87 (s, 3H), 3.84 – 3.76 (m, 1H), 3.59 (ddd, *J* = 12.0, 7.2, 4.4 Hz, 1H), 3.28 (dd, *J* = 15.8, 7.6 Hz, 1H), 2.84 (dd, *J* = 15.8, 5.2 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.81 – 1.52 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.33, 163.43, 130.55, 130.54, 113.67, 76.04, 68.99, 55.46, 45.34, 35.95, 30.98, 26.28, 26.09. HRMS (ESI-TOF) calcd for $C_{15}H_{20}O_3$ ([M]+Na^+) = 271.1305, Found 271.1305.

$[\alpha]^{29}_D$ = 22.8 (*c* = 0.30, in CH_2Cl_2), wavelength: 405 nm.

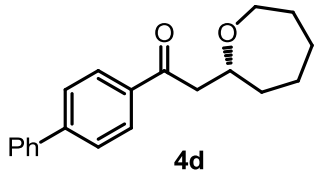




	Retention Time	Area	% Area
1	9.692	7366478	50.49
2	12.459	7224707	49.51

	Retention Time	Area	% Area
1	9.677	12229452	97.33
2	12.463	335230	2.67

1-([1,1'-biphenyl]-4-yl)-2-(oxepan-2-yl)ethanone (4d)



4d

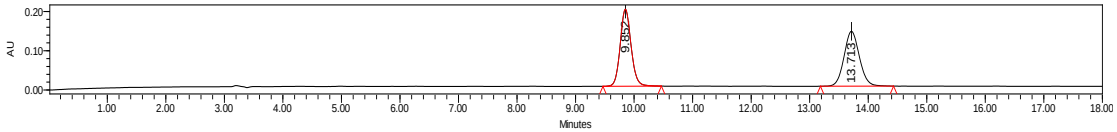
($C_{20}H_{22}O_2$) Prepared according to the general procedure using 0.094 mmol **8d** as substrate. The tittle compound **4d** was purified by silica gel chromatography (petroleum ether: EtOAc = 10: 1) to afford a white solid in 91% yield (debromination step). HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 9.64 min, t_r (minor) = 13.35 min, 99% *ee*.

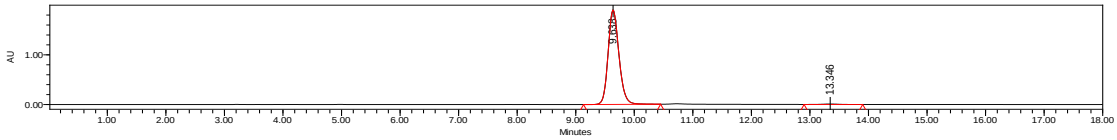
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.98 (m, 2H), 7.73 – 7.65 (m, 2H), 7.65 – 7.57 (m, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.35 (m, 1H), 4.26 – 4.15 (m, 1H), 3.89 – 3.77 (m, 1H), 3.61 (ddd, *J* = 12.0, 7.2, 4.4 Hz, 1H), 3.36 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.92 (dd, *J* = 16.0, 5.2 Hz, 1H), 1.94 – 1.86 (m, 1H), 1.81 – 1.53 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.43, 145.66, 139.92, 136.11, 128.95, 128.87, 128.21, 127.28, 127.21, 75.97, 69.04, 45.71, 35.97, 30.99, 26.29, 26.12.

HRMS (ESI-TOF) calcd for $C_{20}H_{22}O_2$ ([M]+Na^+) = 317.1512, Found 317.1510.

$[\alpha]^{29}_D$ = 16.5 (*c* = 0.50, in CH_2Cl_2), wavelength: 405 nm.

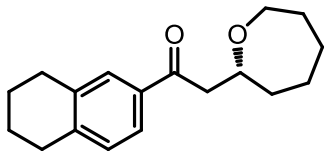




	Retention Time	Area	% Area
1	9.852	2536351	49.89
2	13.713	2547488	50.11

	Retention Time	Area	% Area
1	9.638	24380404	99.36
2	13.346	157723	0.64

2-(oxepan-2-yl)-1-(5,6,7,8-tetrahydronaphthalen-2-yl)ethanone (4e)



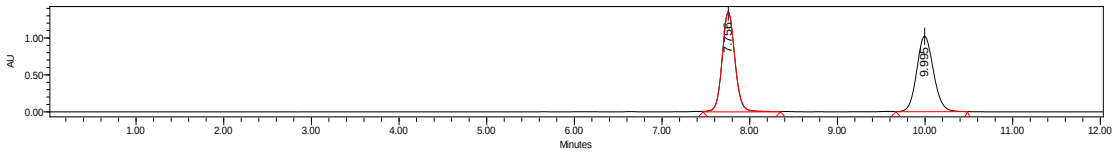
4e

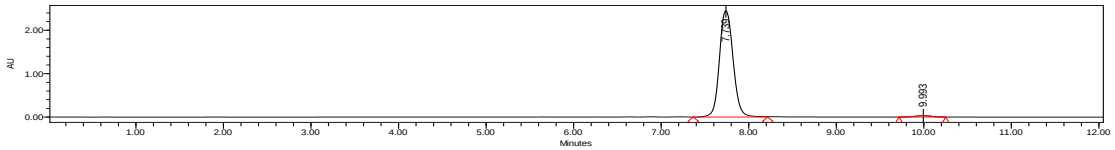
($C_{18}H_{24}O_2$) Prepared according to the general procedure using 0.1 mmol **8e** as substrate. The tittle compound **4e** was purified by silica gel chromatography (petroleum ether : EtOAc = 10 : 1) to afford a colorless oil in 76% yield (debromination step). HPLC (Chiralcel IC, hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 7.74 min, t_r (minor) = 10.00 min, 97% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, *J* = 4.6 Hz, 2H), 7.16 – 7.08 (m, 1H), 4.24 – 4.12 (m, 1H), 3.88 – 3.74 (m, 1H), 3.59 (ddd, *J* = 12.0, 7.2, 4.4 Hz, 1H), 3.29 (dd, *J* = 16.0, 7.2 Hz, 1H), 2.86 (dd, *J* = 16.0, 5.2 Hz, 1H), 2.75 – 2.83 (m, 4H), 1.91 – 1.51 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.72, 143.10, 137.39, 134.91, 129.29, 129.15, 125.35, 75.96, 68.93, 45.52, 35.89, 31.00, 29.63, 29.39, 26.32, 26.08, 22.98, 22.84.

HRMS (ESI-TOF) calcd for $C_{18}H_{24}O_2$ ([M]+Na^+) = 295.1669, Found 295.1664.

$[\alpha]^{29}_D$ = 14.6 (*c* = 0.38, in CH_2Cl_2), wavelength: 405 nm.

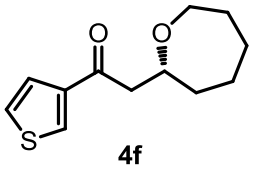




	Retention Time	Area	% Area
1	7.756	13640461	50.24
2	9.995	13508644	49.76

	Retention Time	Area	% Area
1	7.739	26619610	98.47
2	9.993	412864	1.53

2-(oxepan-2-yl)-1-(thiophen-3-yl)ethanone (4f)



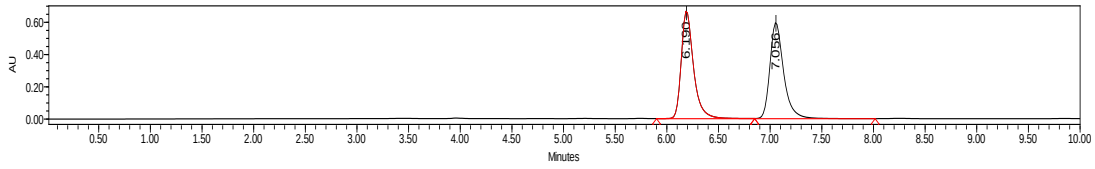
4f

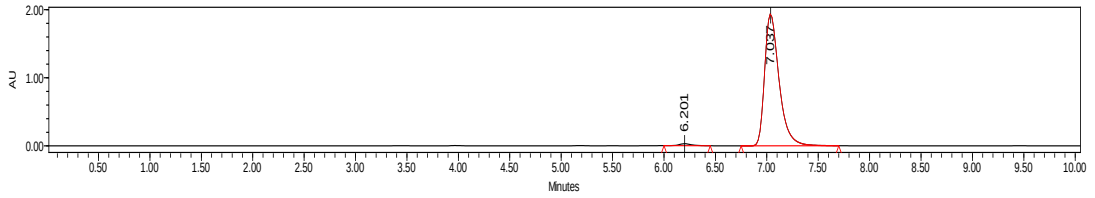
($C_{12}H_{16}O_2S$) Prepared according to the general procedure using 0.064 mmol **8f** as substrate. The tittle compound **4f** was purified by silica gel chromatography (petroleum ether : EtOAc = 8 : 1) to afford colorless oil in 86% yield (debromination step). HPLC (Chiralcel IA, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 7.04 min, t_r (minor) = 6.20 min, 98% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.56 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.30 (dd, *J* = 5.2, 2.8 Hz, 1H), 4.22 – 4.07 (m, 1H), 3.87 – 3.75 (m, 1H), 3.58 (ddd, *J* = 12.0, 7.2, 4.4 Hz, 1H), 3.22 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.81 (dd, *J* = 15.6, 5.2 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.80 – 1.51 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.01, 142.84, 132.38, 127.04, 126.25, 75.84, 69.05, 47.04, 35.92, 30.96, 26.24, 26.07.

HRMS (ESI-TOF) calcd for $C_{12}H_{16}O_2S$ ([M]+Na^+) = 247.0763, Found 247.0766.

$[\alpha]^{29}_D$ = 17.7 (*c* = 0.26, in CH_2Cl_2), wavelength: 405nm.

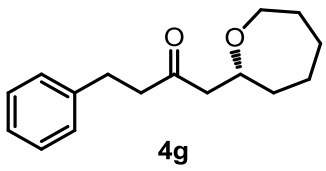




	Retention Time	Area	% Area
1	6.190	5514709	50.04
2	7.056	5504941	49.96

	Retention Time	Area	% Area
1	6.201	238243	1.24
2	7.037	18900684	98.76

1-(oxepan-2-yl)-4-phenylbutan-2-one (4g)



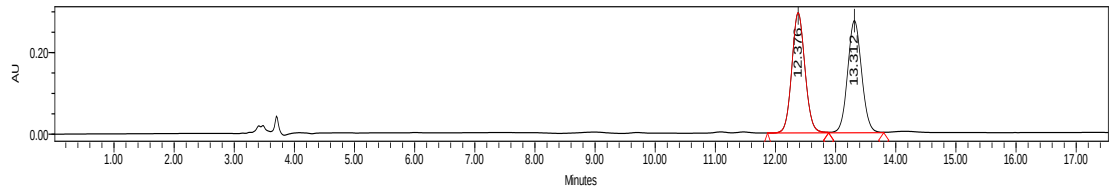
4g

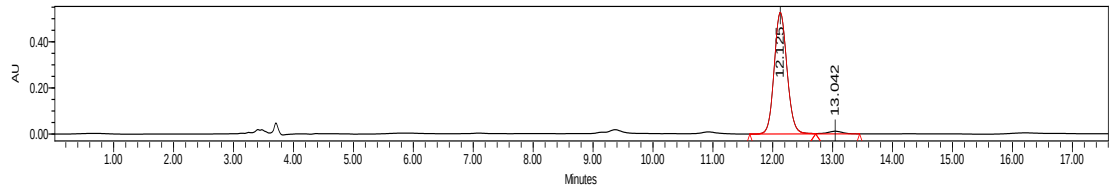
($C_{16}H_{22}O_2$) Prepared according to the general procedure using 0.068 mmol **8g** as substrate. The title compound **4g** was purified by silica gel chromatography (Petroleum ether : EtOAc = 15:1) to afford a colorless oil in 79% yield (debromination step). HPLC (Chiralcel IA, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 210 nm), t_r (major) = 12.13 min, t_r (minor) = 13.04 min, 95% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.14 (m, 5H), 4.04 – 3.91 (m, 1H), 3.83 – 3.72 (m, 1H), 3.52 (ddd, *J* = 12.0, 7.2, 4.4 Hz, 1H), 2.95 – 2.74 (m, 4H), 2.70 (dd, *J* = 15.6, 8.8 Hz, 1H), 2.35 (dd, *J* = 15.6, 4.4 Hz, 1H), 1.80 – 1.63 (m, 5H), 1.59 – 1.41 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.70, 141.19, 128.45, 128.34, 126.02, 75.88, 69.00, 49.93, 45.34, 35.92, 30.90, 29.45, 26.20, 25.98.

HRMS (ESI-TOF) calcd for $C_{16}H_{22}O_2$ ([M]+Na^+) = 269.1512, Found 269.1519.

$[\alpha]^{29}_D$ = -4.0 (*c* = 0.20, in CH_2Cl_2), wavelength: 405 nm.

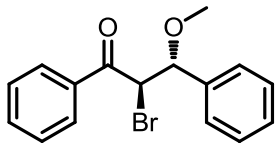




	Retention Time	Area	% Area
1	12.376	4480946	50.19
2	13.312	4446659	49.81

	Retention Time	Area	% Area
1	12.125	7842750	97.49
2	13.042	201514	2.51

(*2R,3R*)-2-bromo-3-methoxy-1,3-diphenylpropan-1-one (6a):



6a

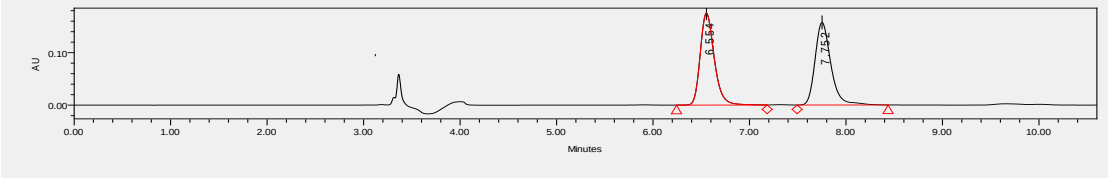
($C_{16}H_{15}BrO_2$) Prepared according to the general procedure using 0.5 mol% catalyst for 4h. The tittle compound **6a** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a white solid in 92% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 6.60 min, t_r (minor) = 7.79 min, 96% *ee*; dr > 99:1.

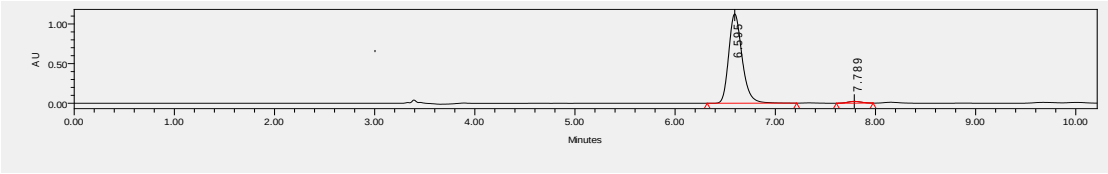
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 2H), 7.65 – 7.59 (m, 1H), 7.46 – 7.28 (m, 7H), 5.06 (d, *J* = 9.6 Hz, 1H), 4.78 (d, *J* = 9.6 Hz, 1H), 3.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.15, 137.83, 135.24, 133.78, 128.88, 128.84, 128.41, 128.26, 83.31, 57.74, 47.26.

HRMS (ESI-TOF) calcd for $C_{16}H_{15}{}^{78.9183}BrO_2$ ([M]+Na^+) = 341.0153, Found 341.0156.

HRMS (ESI-TOF) calcd for $C_{16}H_{15}{}^{80.9163}BrO_2$ ([M]+Na^+) = 343.0127, Found 343.0130.

$[\alpha]^{22}_D$ = -89.3 (*c* = 0.60, in CH_2Cl_2), wavelength: 589 nm.

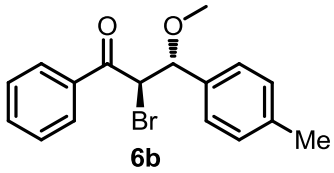




	Retention Time	Area	% Area
1	6.554	1772320	49.78
2	7.752	1787848	50.22

	Retention Time	Area	% Area
1	6.595	10457824	98.04
2	7.789	208725	1.96

2-bromo-3-methoxy-1-phenyl-3-(p-tolyl)propan-1-one (6b):



6b

($C_{17}H_{17}BrO_2$) Prepared according to the general procedure using 5 mol% catalyst for 12h. The tittle compound **6b** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a white solid in 81% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 6.90 min, t_r (minor) = 8.92 min, 94% *ee*; dr > 99:1.

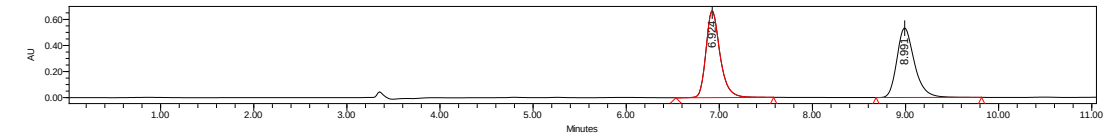
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H), 7.66 – 7.58 (m, 1H), 7.55 – 7.46 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.14 (d, *J* = 9.6 Hz, 1H), 4.83 (d, *J* = 10.0 Hz, 1H), 3.19 (s, 3H), 2.40 (s, 3H).

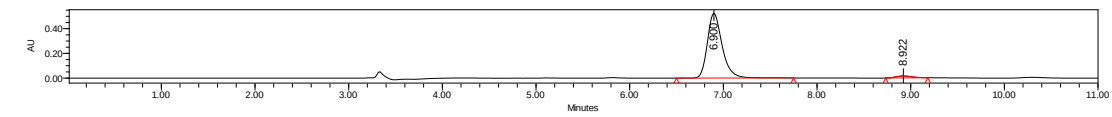
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.26, 138.64, 135.29, 134.77, 133.74, 129.14, 128.87, 128.82, 128.14, 83.16, 57.61, 47.40, 21.34.

HRMS (ESI-TOF) calcd for $C_{17}H_{17}{}^{78.9183}BrO_2$ ([M]+Na^+) = 355.0310, Found 355.0306.

HRMS (ESI-TOF) calcd for $C_{17}H_{17}{}^{80.9163}BrO_2$ ([M]+Na^+) = 357.0284, Found 357.0286.

$[\alpha]^{29}_D$ = -94.9 (*c* = 0.49, in CH_2Cl_2), wavelength: 589 nm.

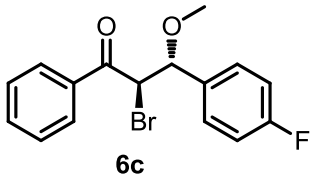




	Retention Time	Area	% Area
1	6.924	6979516	50.03
2	8.991	6970049	49.97

	Retention Time	Area	% Area
1	6.900	5746275	96.96
2	8.922	180162	3.04

2-bromo-3-(4-fluorophenyl)-3-methoxy-1-phenylpropan-1-one (6c):



6c

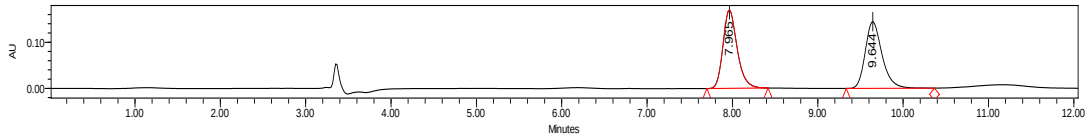
($C_{16}H_{14}BrFO_2$) Prepared according to the general procedure using 1 mol% catalyst for 4h. The tittle compound **6c** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a white solid in 99% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 7.91 min, t_r (minor) = 9.56 min, 95% *ee*; dr > 99:1.

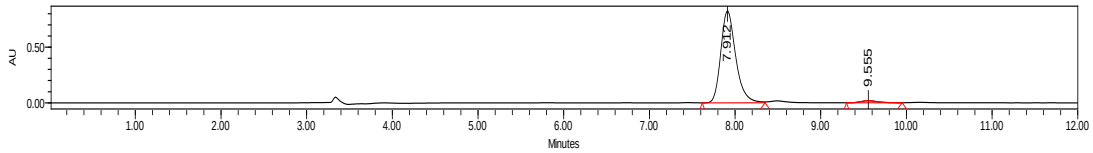
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.00 (m, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.17 – 7.07 (m, 2H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.95, 162.97 (d, *J* = 246.0 Hz), 135.12, 133.85, 133.67 (d, *J* = 3.0 Hz), 129.92, 129.84, 128.86, 115.49, 115.27, 82.59, 57.72, 47.30.

HRMS (ESI-TOF) calcd for $C_{16}H_{14}{}^{78.9183}BrFO_2$ ([M]+Na^+) = 359.0059, Found 359.0062.

HRMS (ESI-TOF) calcd for $C_{16}H_{14}{}^{80.9163}BrFO_2$ ([M]+Na^+) = 361.0033, Found 361.0024.

$[\alpha]^{22}_D$ = -92.1 (*c* = 0.65, in CH_2Cl_2), wavelength: 589 nm.

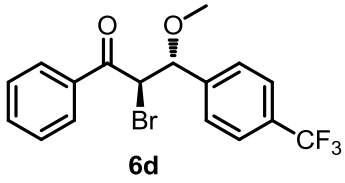




	Retention Time	Area	% Area
1	7.965	1951648	49.66
2	9.644	1978154	50.34

	Retention Time	Area	% Area
1	7.912	9987100	97.62
2	9.555	243266	2.38

2-bromo-3-methoxy-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (6d):



6d

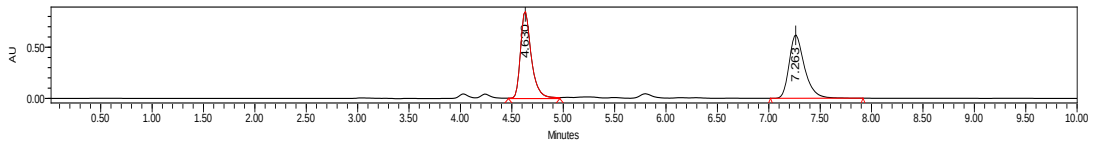
($C_{17}H_{14}BrF_3O_2$) Prepared according to the general procedure using 5 mol% catalyst for 12 h. The tittle compound **6d** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a white solid in 90% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 4.62 min, t_r (minor) = 7.22 min, 95% *ee*; dr > 99:1.

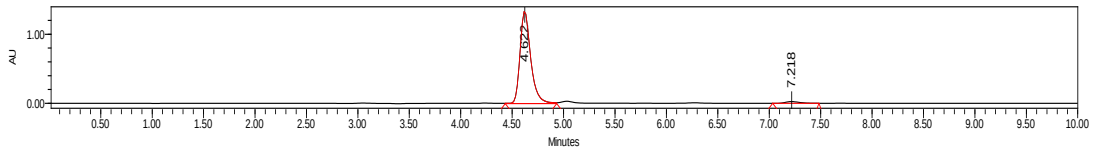
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.00 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.67 – 7.58 (m, 3H), 7.52 (t, *J* = 7.6 Hz, 2H), 5.10 (d, *J* = 10.0 Hz, 1H), 4.93 (d, *J* = 9.6 Hz, 1H), 3.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.58, 142.02, 134.97, 133.95, 130.95 (q, *J* = 32.0 Hz), 128.90, 128.87, 128.66, 125.37 (q, *J* = 4 Hz), 124.04 (q, *J* = 270 Hz), 82.63, 58.02, 46.63.

HRMS (ESI-TOF) calcd for $C_{17}H_{14}{}^{78.9183}BrF_3O_2$ ([M]+Na^+) = 409.0027, Found 409.0026

HRMS (ESI-TOF) calcd for $C_{17}H_{14}{}^{80.9163}BrF_3O_2$ ([M]+Na^+) = 411.0001, Found 410.9991.

$[\alpha]^{22}_D$ = -85.7 (*c* = 0.72, in CH_2Cl_2), wavelength: 589 nm.

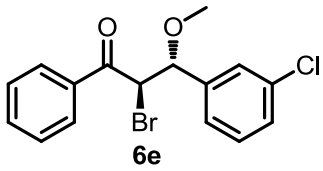




	Retention Time	Area	% Area
1	4.630	6234920	49.30
2	7.263	6411138	50.70

	Retention Time	Area	% Area
1	4.622	9669737	97.66
2	7.218	231600	2.34

2-bromo-3-(3-chlorophenyl)-3-methoxy-1-phenylpropan-1-one (6e):



6e

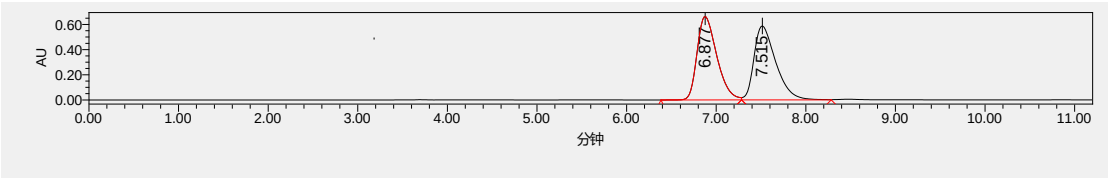
($C_{16}H_{14}BrClO_2$) Prepared according to the general procedure using 1 mol% catalyst for 4 h. The tittle compound **6e** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a white solid in 97% yield. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 6.52 min, t_r (minor) = 7.18 min, 94% *ee*; dr > 99:1.

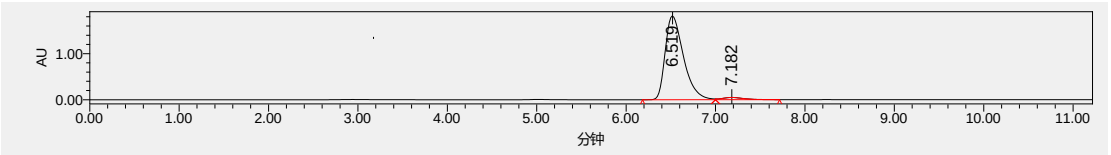
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.66 – 7.59 (m, 1H), 7.55 – 7.46 (m, 3H), 7.36 (d, *J* = 1.2 Hz, 3H), 5.08 (d, *J* = 10.0 Hz, 1H), 4.83 (d, *J* = 9.6 Hz, 1H), 3.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.73, 140.12, 135.03, 134.45, 133.90, 129.62, 129.02, 128.88, 128.06, 126.77, 82.68, 57.96, 46.80.

HRMS (ESI-TOF) calcd for $C_{16}H_{14}{}^{78.9183}Br^{34.9689}ClO_2$ ([M]+Na^+) = 374.9763, Found 374.9757.

HRMS (ESI-TOF) calcd for $C_{16}H_{14}{}^{80.9163}Br^{34.9689}ClO_2$ ([M]+Na^+) = 376.9737, Found 376.9742.

$[\alpha]^{23}_D$ = -83.6 (*c* = 0.69, in CH_2Cl_2), wavelength: 589 nm.

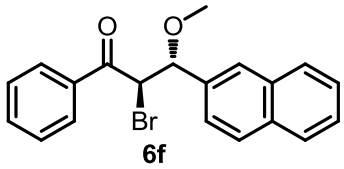




	Retention Time	Area	% Area
1	6.877	10132465	50.54
2	7.515	9916560	49.46

	Retention Time	Area	% Area
1	6.519	25826413	96.99
2	7.182	800472	3.01

2-bromo-3-methoxy-3-(naphthalen-2-yl)-1-phenylpropan-1-one (6f):



6f

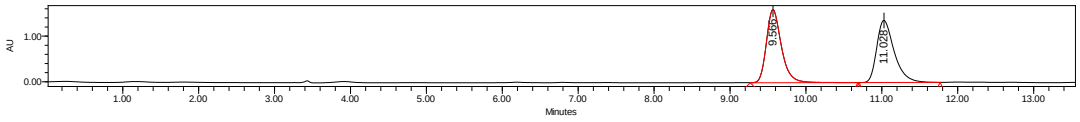
($C_{20}H_{17}BrO_2$) Prepared according to the general procedure using 5 mol% catalyst for 12 h. The tittle compound **6f** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a white solid in 80% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 9.57 min, t_r (minor) = 11.06 min, 92% *ee*; dr > 99:1.

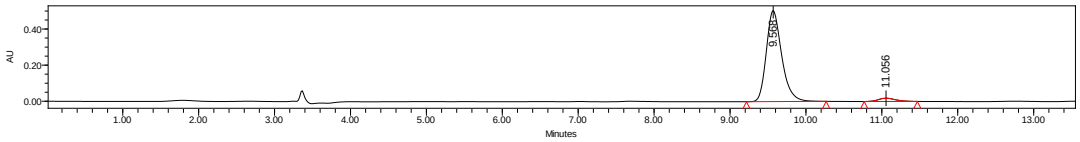
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 2H), 8.00 – 7.86 (m, 4H), 7.69 – 7.60 (m, 2H), 7.59 – 7.50 (m, 4H), 5.27 (d, *J* = 10.0 Hz, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 3.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.13, 135.25, 135.16, 133.82, 133.67, 132.95, 128.92, 128.86, 128.48, 128.46, 128.17, 127.85, 126.43, 126.41, 124.86, 83.52, 57.80, 47.07.

HRMS (ESI-TOF) calcd for $C_{20}H_{17}^{78.9183}BrO_2$ ([M]+Na^+) = 391.0304, Found 391.0314.

HRMS (ESI-TOF) calcd for $C_{20}H_{17}^{80.9163}BrO_2$ ([M]+Na^+) = 393.0284, Found 393.0284.

$[\alpha]^{23}_D$ = -105.7 (*c* = 0.58, in CH_2Cl_2), wavelength: 589 nm.

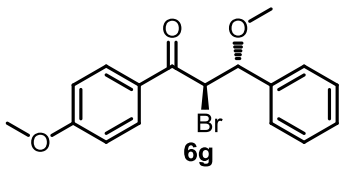




	Retention Time	Area	% Area
1	9.566	21921442	50.24
2	11.028	21709540	49.76

	Retention Time	Area	% Area
1	9.568	7073959	96.17
2	11.056	281712	3.83

2-bromo-3-methoxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one (6g):



6g

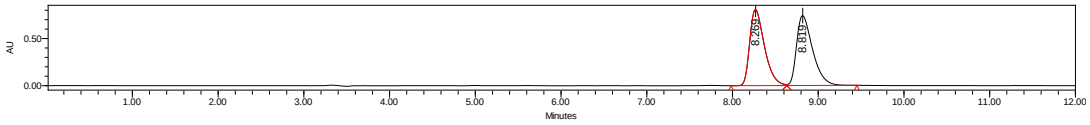
($C_{17}H_{17}BrO_3$) Prepared according to the general procedure using 5 mol% catalyst for 12 h. The tittle compound **6g** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a white solid in 98% yield. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 8.35 min, t_r (minor) = 8.95 min, 94% *ee*; dr > 99:1.

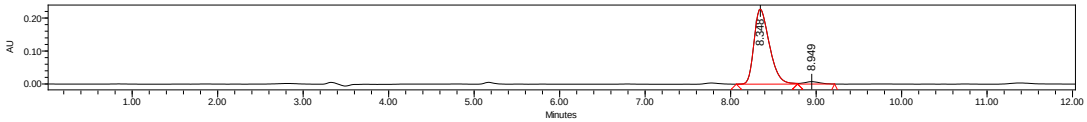
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.94 (m, 2H), 7.52 – 7.34 (m, 5H), 7.02 – 6.92 (m, 2H), 5.12 (d, *J* = 10.0 Hz, 1H), 4.86 (d, *J* = 9.6 Hz, 1H), 3.89 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.55, 164.10, 138.01, 131.30, 128.77, 128.36, 128.27, 128.06, 114.06, 83.29, 57.74, 55.60, 47.18.

HRMS (ESI-TOF) calcd for $C_{17}H_{17}^{78.9183}BrO_3$ ([M]+Na^+) = 371.0253, Found 371.0250.

HRMS (ESI-TOF) calcd for $C_{17}H_{17}^{80.9163}BrO_3$ ([M]+Na^+) = 373.0233, Found 373.0224.

$[\alpha]^{23}_D$ = -148.2 (*c* = 0.56, in CH_2Cl_2), wavelength: 589 nm.

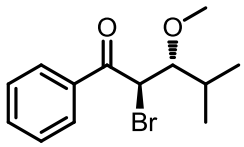




	Retention Time	Area	% Area
1	8.269	9617591	50.05
2	8.819	9597075	49.95

	Retention Time	Area	% Area
1	8.348	2840401	96.92
2	8.949	90282	3.08

2-bromo-3-methoxy-4-methyl-1-phenylpentan-1-one (6h):



6h

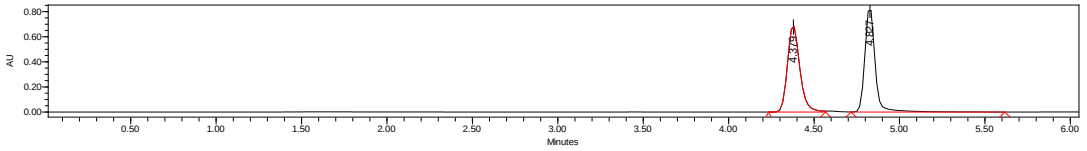
($C_{13}H_{17}BrO_2$) Prepared according to the general procedure using 5 mol% catalyst for 8 h. The tittle compound **6h** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a colorless oil in 70% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 4.23 min, t_r (minor) = 4.54 min, 75% *ee*; dr > 99:1.

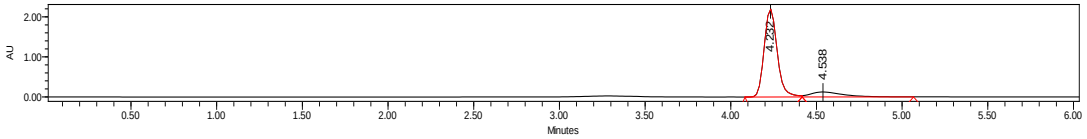
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.96 (m, 2H), 7.60 (ddd, *J* = 6.8, 2.4, 1.2 Hz, 1H), 8.06 – 7.96 (m, 2H), 5.01 (d, *J* = 10.0 Hz, 1H), 3.90 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.37 (s, 3H), 2.49 – 2.32 (m, 1H), 1.11 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.97, 135.54, 133.65, 128.78, 84.27, 61.79, 44.48, 29.58, 20.26, 14.42.

HRMS (ESI-TOF) calcd for $C_{13}H_{17}{}^{78.9183}BrO_2$ ([M]+Na^+) = 307.0304, Found 307.0302.

HRMS (ESI-TOF) calcd for $C_{13}H_{17}{}^{80.9163}BrO_2$ ([M]+Na^+) = 309.0284, Found 309.0274.

$[\alpha]^{21}_D$ = -51.9 (*c* = 0.37, in CH_2Cl_2), wavelength: 589 nm.

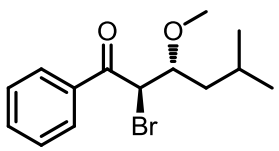




	Retention Time	Area	% Area
1	4.379	3466858	50.09
2	4.827	3453946	49.91

	Retention Time	Area	% Area
1	4.232	11634132	87.56
2	4.538	1653005	12.44

2-bromo-3-methoxy-5-methyl-1-phenylhexan-1-one (6i):



6i

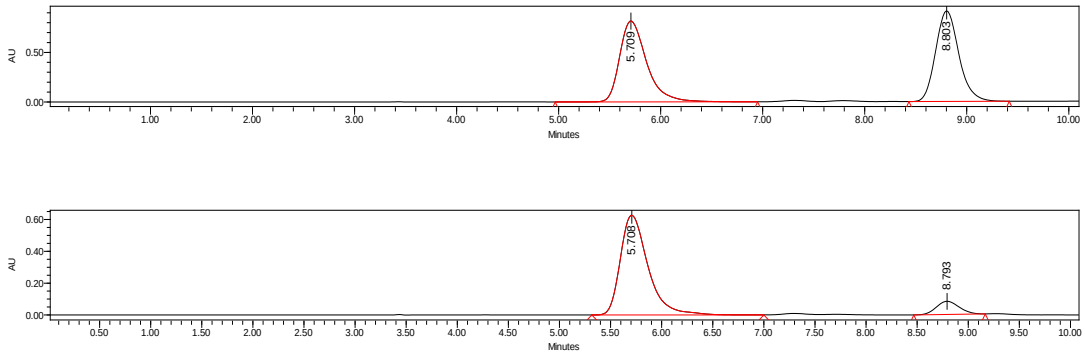
($C_{14}H_{19}BrO_2$) Prepared according to the general procedure using 5 mol% catalyst for 8 h. The tittle compound **6i** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a colorless oil in 66% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 5.71 min, t_r (minor) = 8.79 min, 80% *ee*; dr > 99:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.92 (m, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 5.07 (d, *J* = 8.4 Hz, 1H), 3.97 (td, *J* = 9.2, 2.4 Hz, 1H), 3.38 (s, 3H), 1.97 – 1.85 (m, 1H), 1.85 – 1.76 (m, 1H), 1.67 – 1.55 (m, 1H), 0.99 (dd, *J* = 6.4, 2.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.78, 135.34, 133.70, 128.82, 128.75, 79.48, 59.64, 47.98, 42.07, 24.51, 24.05, 21.90.

HRMS (ESI-TOF) calcd for $C_{14}H_{19}{}^{78.9183}BrO_2$ ([M]+Na^+) = 321.0461, Found 321.0462.

HRMS (ESI-TOF) calcd for $C_{14}H_{19}{}^{80.9163}BrO_2$ ([M]+Na^+) = 323.0440, Found 323.0414.

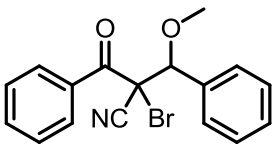
$[\alpha]^{21}{}_D$ = -18.0 (*c* = 0.37, in CH_2Cl_2), wavelength: 589 nm.



	Retention Time	Area	% Area
1	5.709	14952887	50.86
2	8.803	14449751	49.14

	Retention Time	Area	% Area
1	5.708	11778371	90.19
2	8.793	1280447	9.81

2-benzoyl-2-bromo-3-methoxy-3-phenylpropanenitrile (6j):



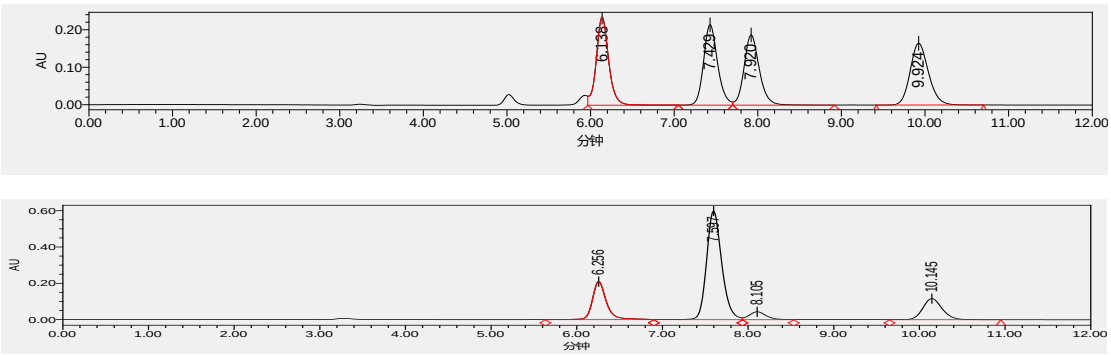
6j

($C_{17}H_{14}BrNO_2$) Prepared according to the general procedure using 5 mol% catalyst for 12 h. The tittle compound **6j** was purified by silica gel chromatography (petroleum ether: CH_2Cl_2 = 3.25 : 1.75) to afford a white solid in 67% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} = 6.26 min, t_{r2} = 7.60 min, t_{r3} = 8.11 min, t_{r4} = 10.15 min, dr = 75:25; 60%/60% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 7.85 (m, 2H), 7.69 – 7.32 (m, 8H), 5.09 (s, 1H), 3.27 (s, 3H). For major isomer: ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.86, 134.04, 133.57, 133.39, 129.78, 129.49, 129.36, 128.59, 128.28, 115.92, 83.92, 58.17, 48.48. For minor isomer: ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.81, 134.06, 133.53, 133.29, 129.81, 129.71, 129.21 (s, 4H), 128.62, 128.51, 115.73, 84.15, 57.95.

HRMS (ESI-TOF) calcd for $C_{17}H_{14}{}^{78.9183}BrNO_2$ ([M]+Na^+) = 366.0100, Found 366.0092.

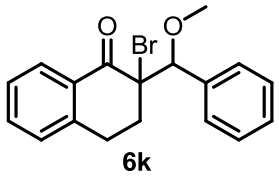
HRMS (ESI-TOF) calcd for $C_{17}H_{14}{}^{80.9163}BrNO_2$ ([M]+Na^+) = 368.0080, Found 368.0076.



	Retention Time	Area	% Area
1	6.138	2421943	24.69
2	7.429	2498760	25.48
3	7.920	2372060	24.18
4	9.924	2515434	25.65

	Retention Time	Area	% Area
1	6.256	2232283	18.74
2	7.597	7318980	61.45
3	8.105	545996	4.58
4	10.145	1812830	15.22

2-bromo-2-(methoxy(phenyl)methyl)-3,4-dihydronaphthalen-1(2H)-one (6k):



6k

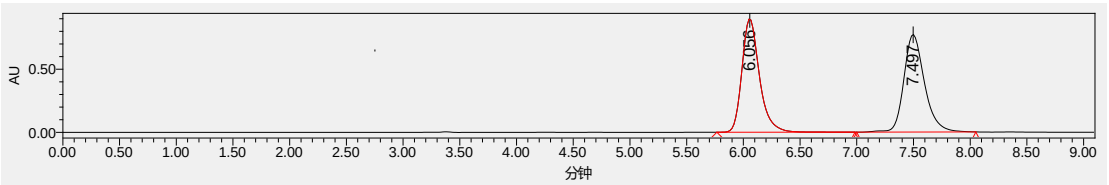
($C_{18}H_{17}BrO_2$) Prepared according to the general procedure using 5 mol% catalyst for 12 h. The tittle compound **6k** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a white solid in 64% yield. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 6.00 min, t_r (minor) = 7.41 min, 96% *ee*; dr > 99:1.

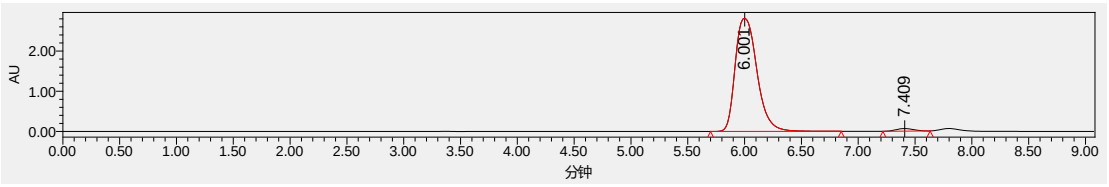
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.48 (m, 3H), 7.47 – 7.33 (m, 4H), 7.30 – 7.20 (m, 1H), 5.34 (s, 1H), 3.26 (s, 3H), 3.14 (ddd, *J* = 16.8, 12.4, 4.4 Hz, 1H), 2.93 – 2.82 (m, 1H), 2.74 (ddd, *J* = 16.8, 12.4, 4.8 Hz, 1H), 2.09 (ddd, *J* = 14.8, 4.4, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.17, 143.10, 135.74, 133.86, 130.45, 129.77, 129.11, 128.66, 128.34, 127.64, 126.98, 84.13, 67.06, 58.12, 29.52, 25.85.

HRMS (ESI-TOF) calcd for $C_{18}H_{17}^{78.9183}BrO_2$ ([M]+Na^+) = 367.0304, Found 367.0304.

HRMS (ESI-TOF) calcd for $C_{18}H_{17}^{80.9163}BrO_2$ ([M]+Na^+) = 369.0284, Found 369.0288.

$[\alpha]^{21}_D$ = -7.8 (*c* = 0.46, in CH_2Cl_2), wavelength: 589 nm.

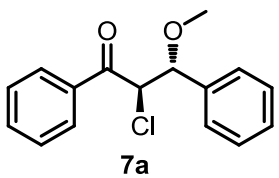




	Retention Time	Area	% Area
1	6.056	9638837	49.67
2	7.497	9768032	50.33

	Retention Time	Area	% Area
1	6.001	37330962	98.21
2	7.409	679529	1.79

2-chloro-3-methoxy-1,3-diphenylpropan-1-one (7a):



7a

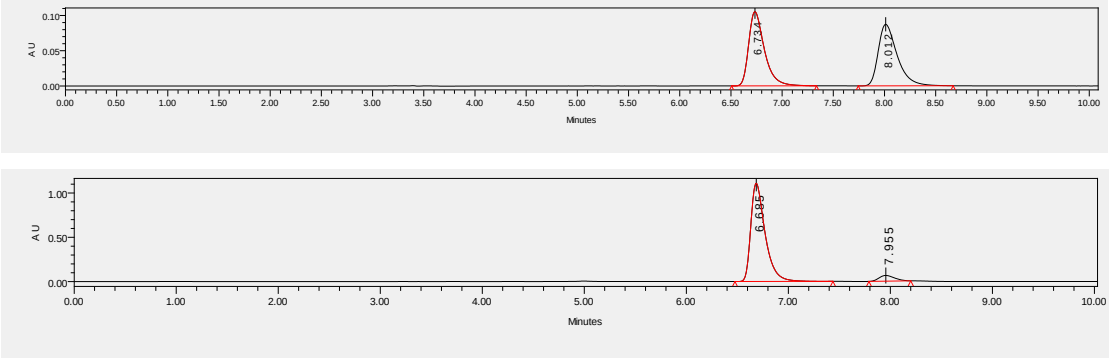
($C_{16}H_{15}ClO_2$) Prepared according to the general procedure using 5 mol% catalyst for 12h. The tittle compound **7a** was purified by silica gel chromatography (petroleum ether : CH_2Cl_2 = 3.25 : 1.75) to afford a white solid in 64% yield. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 6.69 min, t_r (minor) = 8.00 min, 88% *ee*; dr > 99:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.49 – 7.37 (m, 5H), 5.10 (d, *J* = 9.6 Hz, 1H), 4.77 (d, *J* = 9.2 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.47, 137.45, 135.51, 133.81, 128.93, 128.83, 128.81, 128.44, 128.18, 83.66, 57.47, 56.90.

HRMS (ESI-TOF) calcd for $C_{16}H_{15}{}^{34.9689}ClO_2$ ([M]+Na^+) = 297.0658, Found 297.0628.

HRMS (ESI-TOF) calcd for $C_{16}H_{15}{}^{36.9659}ClO_2$ ([M]+Na^+) = 299.0623, Found 299.0616.

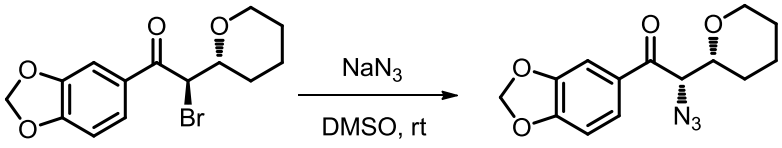
$[\alpha]^{21}_D$ = -101.4 (*c* = 0.35, in CH_2Cl_2), wavelength: 589 nm.



	Retention Time	Area	% Area
1	6.734	1123355	49.99
2	8.012	1123696	50.01

	Retention Time	Area	% Area
1	6.685	10779518	94.10
2	7.955	676375	5.90

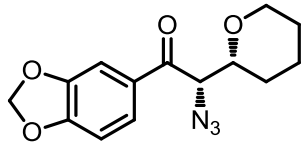
8. Further transformation of the products



2bj **10**

A flame-dried flask under N_2 atmosphere was charged with **2bj** (0.1 mmol) and DMSO (1.5 mL), NaN_3 (0.24 mmol) was added to this solution, and the mixture was stirred at room temperature for 4 h. The mixture was diluted by saturated $NaHCO_3$ and extracted by Et_2O. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Purified by flash silica gel chromatography (eluent: Petroleum ether : EtOAc = 8:1) giving the product **10** as white solid in 49% yield.

2-azido-1-(benzo[d][1,3]dioxol-5-yl)-2-(tetrahydro-2H-pyran-2-yl)ethanone (10)



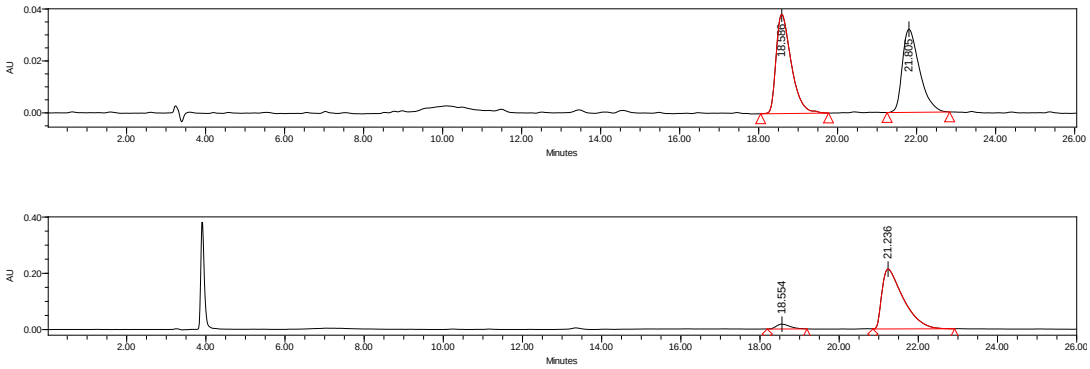
10

($C_{14}H_{15}N_3O_4$) Prepared according to the general procedure. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 21.24 min, t_r (minor) = 18.55 min, 90% ee, dr> 99:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 1H), 7.42 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 2H), 4.42 (d, *J* = 6.0 Hz, 1H), 4.07 – 3.99 (m, 1H), 3.88 – 3.80 (m, 1H), 3.38 (t, *J* = 11.2 Hz, 1H), 1.86 (s, 1H), 1.63 – 1.45 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.41, 152.57, 148.49, 130.02, 125.25, 108.43, 108.12, 102.13, 77.97, 68.81, 66.46, 28.66, 25.51, 22.93.

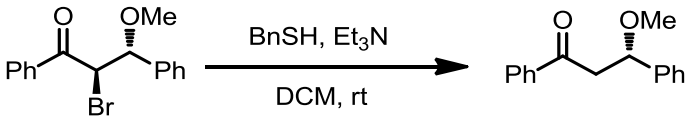
HRMS (ESI-TOF) calcd for $C_{14}H_{15}N_3O_4$ ([M]+Na^+) = 312.0955, Found 312.0952.

$[\alpha]^{30}_D$ = 323.3 (*c* = 0.35, in CH_2Cl_2). wavelength: 589 nm.



	Retention Time	Area	% Area
1	18.586	1018463	51.29
2	21.805	967260	48.71

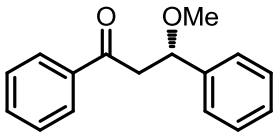
	Retention Time	Area	% Area
1	18.554	417340	4.98
2	21.236	7970019	95.02



6a **11**

To a solution of **6a** (0.1 mmol) in DCM (1.0 mL) was added Et_3N (0.6 mmol) and $AgNO_3$ (0.3 mmol) successively at room temperature. Then the mixture was stirred at same temperature for 2h (monitored by TLC). After the reaction was complete, the residue was purified by flash silica gel chromatography (eluent: Petroleum ether : EtOAc = 20:1) giving the product **11** as colorless oil in 95% yield.

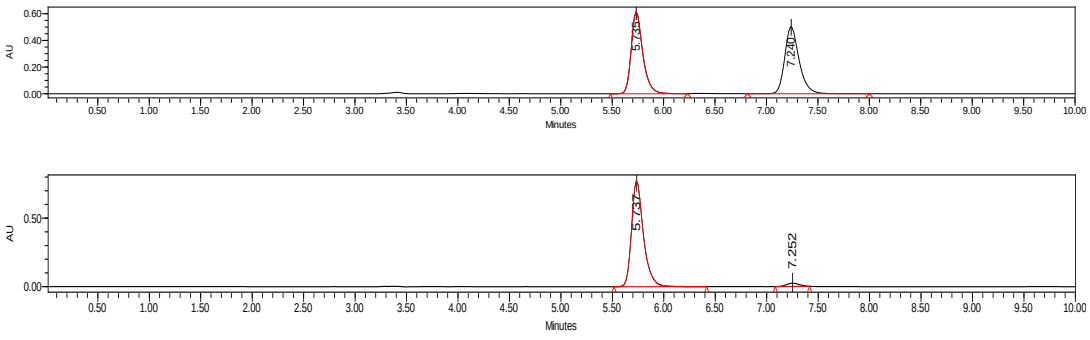
(*S*)-3-methoxy-1,3-diphenylpropan-1-one (11)



11

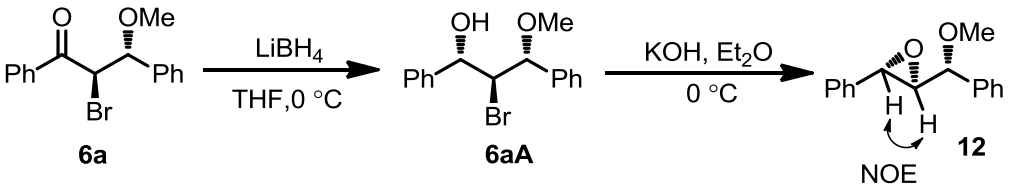
($C_{16}H_{16}O_2$) Prepared according to the general procedure. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_{r1} = 5.74 min, t_{r2} = 7.25 min, 94% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.27 (m, 7H), 4.89 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.59 (dd, *J* = 16.4, 8.4 Hz, 1H), 3.24 (s, 3H), 3.08 (dd, *J* = 16.4, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.73, 141.46, 137.20, 133.12, 128.61, 128.56, 128.25, 127.89, 126.68, 79.58, 56.92, 47.18.



	Retention Time	Area	% Area
1	5.735	4808756	49.66
2	7.240	4874604	50.34

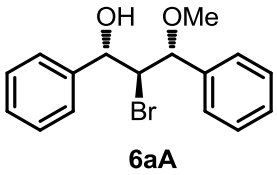
	Retention Time	Area	% Area
1	5.737	6196370	96.74
2	7.252	208765	3.26



To a solution of **6a** (0.5 mmol) in THF (5.0 mL) was added $LiBH_4$ (500 µL, 2.0 M in THF) at 0 °C. Then the mixture was stirred at same temperature for 2h (monitored by TLC). The reaction was quenched by the addition of a saturated aqueous ammonium chloride solution. The aqueous layer was extracted with Ethyl acetate, and the combined organic extracts were dried over sodium sulfate. Concentration in vacuo afforded a crude oil, which was purified via flash silica gel chromatography (eluent: Petroleum ether : EtOAc = 10:1) giving the product **6aA** as a white solid in 58% yield.

A dry test tube was charged with **6aA** (0.14 mmol) and Et_2O (1 mL). The resulting solution was cooled to 0 °C and freshly-powdered KOH (2.8 mmol) was added in small portions. The resulting suspension was allowed to stir at same temperature for 3h, filtered it through short Celite pad and theAfter stirring the resulting suspension for 3h at the same temperature, the mixture was filtered through a Celite pad and washed with DCM. Remove of the most solvents, the residue was purified by flash silica gel chromatography (eluent: Petroleum ether: EtOAc = 10:1) giving the epoxy product **12** as a colorless oil in 91% yield.

2-bromo-3-methoxy-1,3-diphenylpropan-1-ol (6aA)



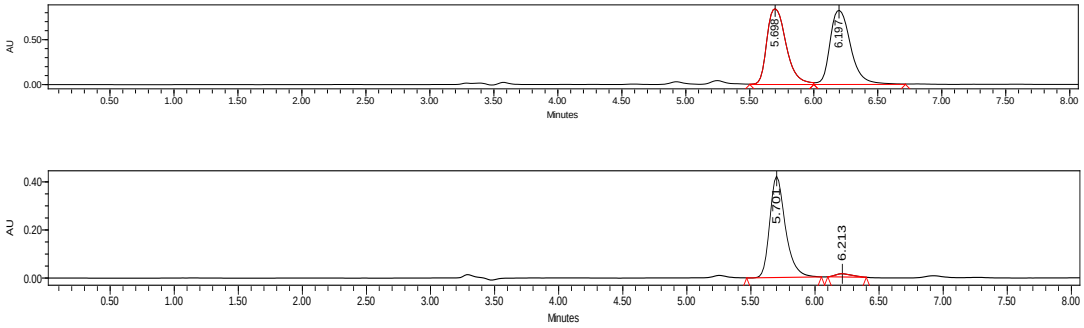
($C_{16}H_{17}BrO_2$) Prepared according to the general procedure. HPLC (Chiralcel IC, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), t_r (major) = 5.70 min, t_r (minor) = 6.21 min, 94% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.22 (m, 10H), 5.14 (d, *J* = 4.0 Hz, 1H), 4.64 (d, *J* = 6.4 Hz, 1H), 4.29 (dd, *J* = 6.4, 1.6 Hz, 1H), 3.57 (d, *J* = 5.2 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.30, 138.33, 128.72, 128.68, 128.11, 127.59, 127.38, 126.04, 86.20 70.98, 64.07, 58.18.

HRMS (ESI-TOF) calcd for $C_{16}H_{17}{}^{78.9183}BrO_2$ ([M]+Na^+) = 343.0304, Found 343.0300.

HRMS (ESI-TOF) calcd for $C_{16}H_{17}{}^{80.9163}BrO_2$ ([M]+Na^+) = 345.0284, Found 345.0323.

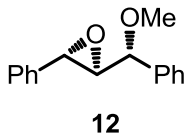
$[\alpha]^{25}_D$ = -22.1 (*c* = 1.12, in CH_2Cl_2). wavelength: 589 nm.



	Retention Time	Area	% Area
1	5.698	8833508	48.73
2	6.197	9292210	51.27

	Retention Time	Area	% Area
1	5.701	3567808	96.74
2	6.213	120413	3.26

2-bromo-3-methoxy-1,3-diphenylpropan-1-ol (12)

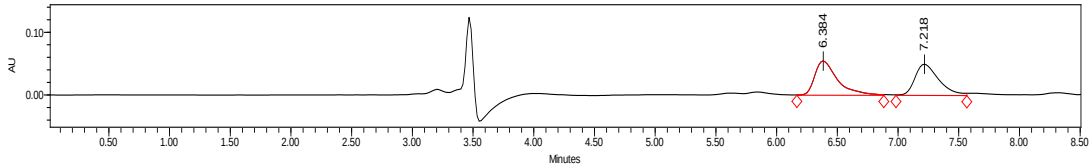


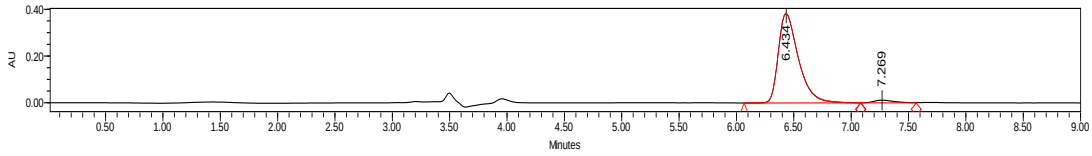
12

($C_{16}H_{16}O_2$) Prepared according to the general procedure. HPLC (Chiralcel ADH, hexane/ *i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 210 nm), t_r (major) = 6.43 min, t_r (minor) = 7.23 min, 94% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.18 (m, 8H), 6.81 – 6.73 (m, 2H), 4.06 (d, *J* = 4.4 Hz, 1H), 3.76 (d, *J* = 8.4 Hz, 1H), 3.41 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.43, 134.93, 128.37, 128.21, 128.20, 127.95, 126.73, 126.52, 81.40, 62.21, 56.88, 55.94.

HRMS (ESI-TOF) calcd for $C_{16}H_{16}O_2$ ([M]+Na^+) = 263.1043, Found 263.1047.

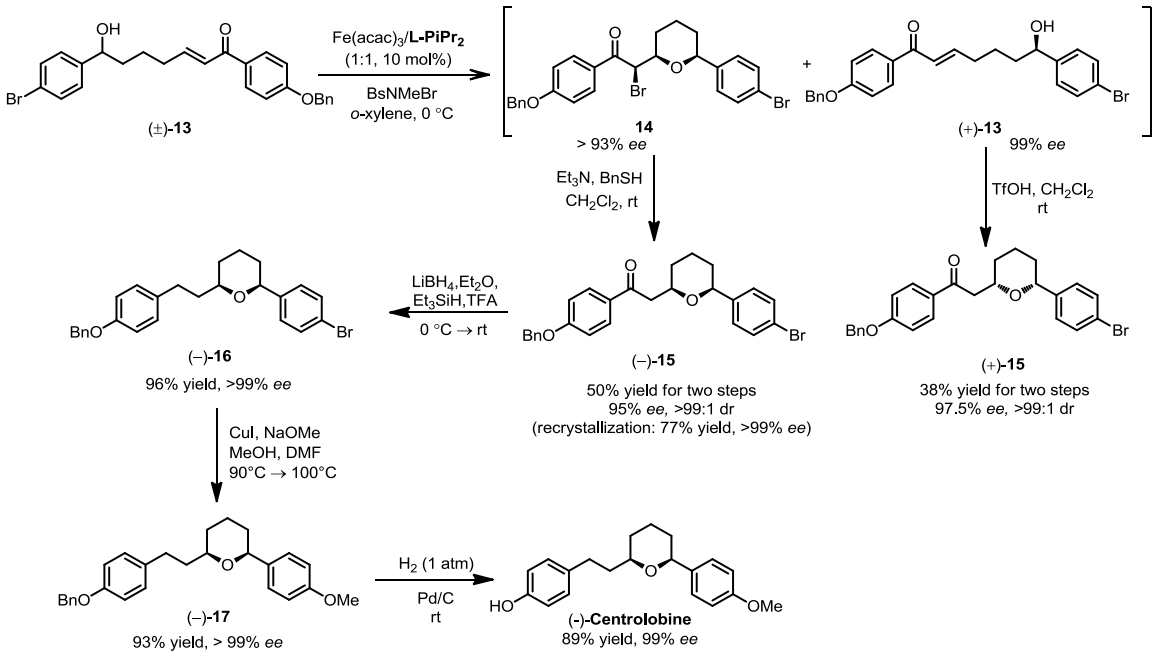




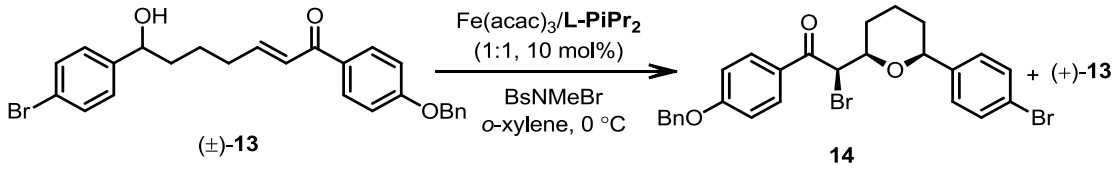
	Retention Time	Area	% Area
1	6.384	715988	51.17
2	7.218	683157	48.83

	Retention Time	Area	% Area
1	6.434	4655898	96.92
2	7.269	148102	3.08

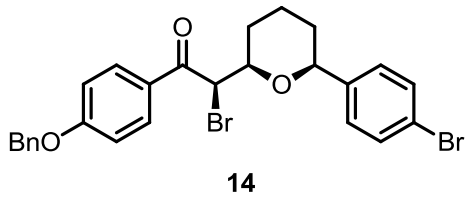
9. Catalytic asymmetric synthesis of (–)-Centrobine[9]



A dry reaction tube was charged with **L-PiPr$_2$** (0.01 mmol) and Fe(acac)$_3$ (0.01 mol). Under N_2 atmosphere, *o*-xylene (2.0 mL) was added. The mixture was stirred at 35 °C for 15-20 min, followed by the addition of BsNMeBr (0.2 mmol). After stirring for 5 min, the mixture was cooled to 0 °C. Substrate (±)-**13** (0.1 mmol) was added under stirring and the reaction mixture was continued stirring at 0 °C for 20 min. The residue was purified by flash chromatography on silica gel to afford the desired product **14** and the recovered starting material (+)-**13**. The enantiomeric excess (*ee*) and diastereomeric ratio (dr) was determined by high-performance liquid chromatography (HPLC) using a Chiral-cel column.



(*R*)-1-(4-(benzyloxy)phenyl)-2-bromo-2-((2*R*,6*S*)-6-(4-bromophenyl)tetrahydro-2*H*-pyran-2-yl)ethanone (14):



14

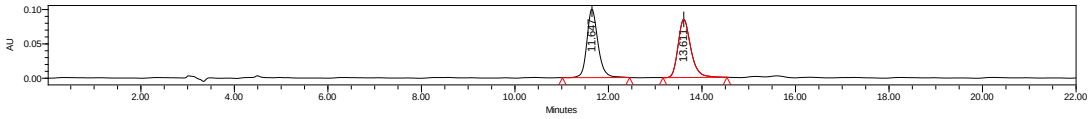
($C_{26}H_{24}Br_2O_3$) Prepared according to the general procedure at 0 °C for 20 min. The tittle compound **14** was purified by silica gel chromatography (petroleum ether : ethyl acetate = 9 : 1) to afford a colorless oil. HPLC (Chiralcel IE, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 13.46 min, t_r (minor) = 11.54 min, > 93% *ee*; dr > 99:1 .

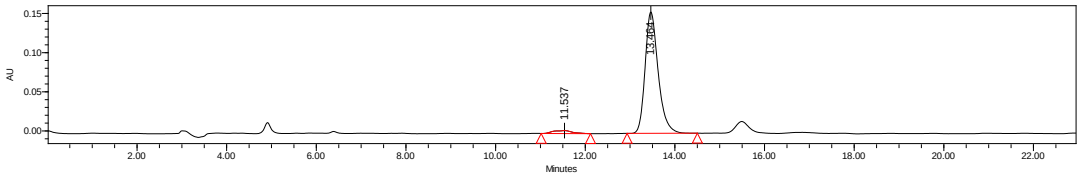
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.45 – 7.39 (m, 4H), 7.39 – 7.35 (m, 1H), 7.34 – 7.30 (m, 2H), 7.05 – 6.99 (m, 4H), 5.14 (s, 2H), 5.09 (d, *J* = 8.4 Hz, 1H), 4.38 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.17 (ddd, *J* = 10.8, 8.4, 1.6 Hz, 1H), 2.29 (d, *J* = 13.2 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.90 – 1.69 (m, 2H), 1.54 – 1.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.91, 163.11, 141.55, 136.03, 131.25, 131.13, 128.76, 128.39, 128.35, 127.51, 127.26, 120.88, 114.78, 79.11, 77.87, 70.23, 48.41, 32.93, 28.72, 23.46.

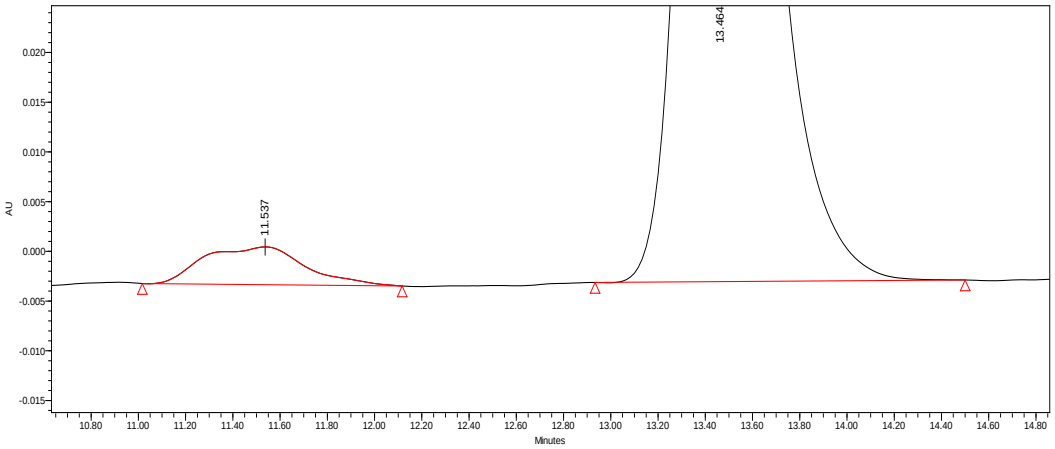
HRMS (ESI-TOF) calcd for $C_{26}H_{24}{}^{78.9183}Br_2O_3$ ([M]+Na^+) = 564.9984, Found 564.9981.

HRMS (ESI-TOF) calcd for $C_{26}H_{24}{}^{78.9183}Br^{80.9163}BrO_3$ ([M]+Na^+) = 566.9964, Found566.9973.

HRMS (ESI-TOF) calcd for $C_{26}H_{24}{}^{80.9163}Br_2O_3$ ([M]+Na^+) = 568.9943, Found 568.9961.



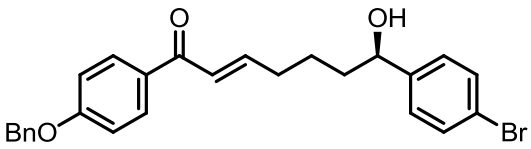




	Retention Time	Area	% Area
1	11.647	1642348	50.70
2	13.611	1597112	49.30

	Retention Time	Area	% Area
1	11.537	113100	3.48
2	13.464	3135506	96.52

(*R,E*)-1-(4-(benzyloxy)phenyl)-7-(4-bromophenyl)-7-hydroxyhept-2-en-1-one ((+)-**13):**



(+)-**13**

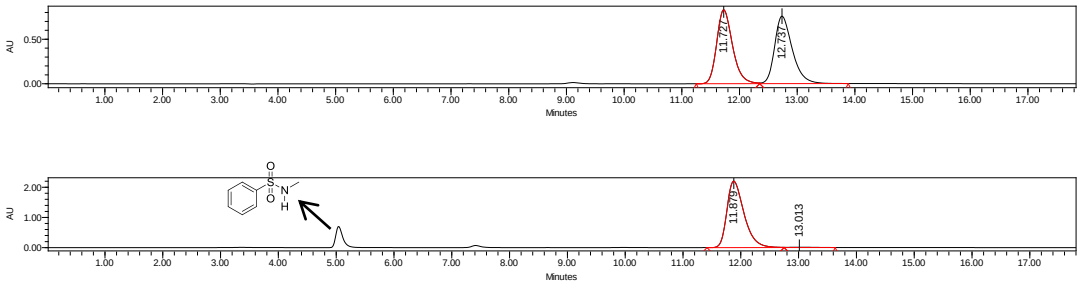
($C_{26}H_{25}BrO_3$) The recovered starting material (+)-**13** couldn't purified because of the byproduct **BsNMeH**. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 15.86 min, t_r (minor) = 13.34 min, 99% *ee*.

^{1}H NMR (400 MHz, DMSO) δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.49 (t, *J* = 8.8 Hz, 4H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.35 (dd, *J* = 8.4, 5.6 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 16.0 Hz, 1H), 6.97 – 6.84 (m, 1H), 5.31 (d, *J* = 4.4 Hz, 1H), 5.21 (s, 2H), 4.62 – 4.50 (m, 1H), 2.30 (dd, *J* = 13.2, 6.4 Hz, 2H), 1.69 – 1.40 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 187.46,

162.12, 148.23, 145.69, 136.43, 130.79, 130.64, 130.25, 128.46, 128.00, 127.77, 125.37, 119.47, 114.75, 71.27, 69.48, 38.66, 31.78, 23.95.

HRMS (ESI-TOF) calcd for $C_{26}H_{25}{}^{78.9183}BrO_3$ ([M]+Na^+) = 487.0879, Found 487.0891.

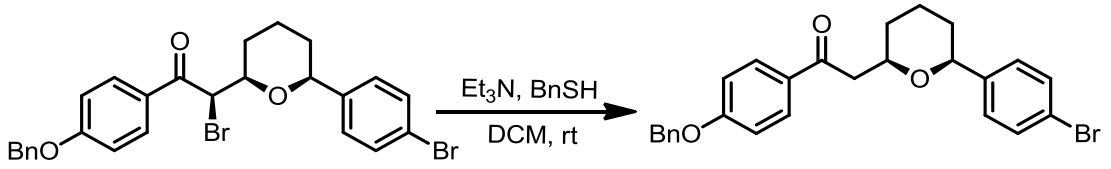
HRMS (ESI-TOF) calcd for $C_{26}H_{25}{}^{80.9163}BrO_3$ ([M]+Na^+) = 489.0859, Found 489.0869.



	Retention Time	Area	% Area
1	11.727	15827983	49.57
2	12.737	16104341	50.43

	Retention Time	Area	% Area
1	11.879	45284487	99.27
2	13.013	332454	0.73

To the solution of **14** in CH_2Cl_2 (1 mL) was added Et_3N (0.3 mmol, 42 μL) and BnSH (0.015 mmol, 27μL) at room temperature. The reaction mixture was stirred at room temperature for 8h. The residue was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 7 : 1) to afford the desired product (−)-**15** in 50% yield (two steps from **13**). The (−)-**15** can be obtained in 77% yield with >99% *ee* after recrystallization from CH_2Cl_2/petroleum ether.



14

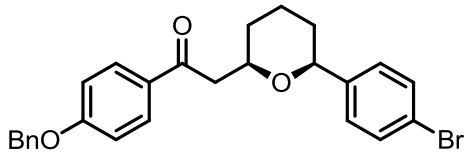
(−)-15

50% yield for two steps

95% *ee*, >99:1 dr

(recrystallization: 77% yield, >99% *ee*)

1-(4-(benzyloxy)phenyl)-2-((2*R*,6*S*)-6-(4-bromophenyl)tetrahydro-2*H*-pyran-2-yl)ethanone ((−)-15)



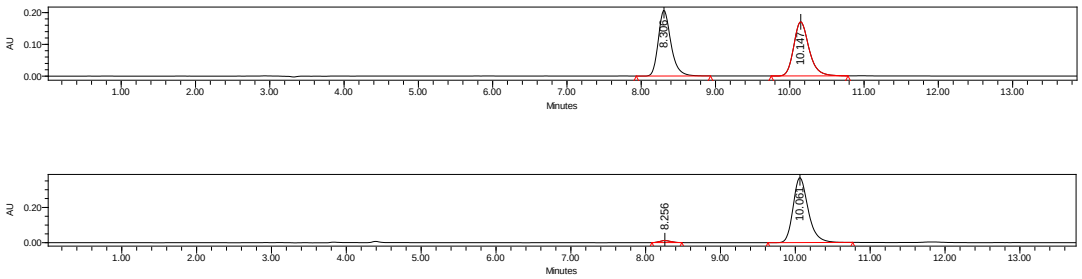
(−)-15

($C_{26}H_{25}BrO_3$) White solid, 50% yield for two steps of halocyclization and debromination. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 10.06 min, t_r (minor) = 8.26 min, 95% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.29 (m, 7H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 5.13 (s, 2H), 4.37 (d, *J* = 11.2 Hz, 1H), 4.14 (dt, *J* = 11.2, 6.0 Hz, 1H), 3.34 (dd, *J* = 15.6, 6.0 Hz, 1H), 2.97 (dd, *J* = 15.6, 6.0 Hz, 1H), 1.94 (d, *J* = 13.2 Hz, 1H), 1.82 (d, *J* = 13.2 Hz, 2H), 1.76 – 1.65 (m, 1H), 1.51 – 1.29 (td, *J* = 24.2, 11.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.05, 162.66, 142.23, 136.19, 131.21, 130.73, 130.69, 128.73, 128.28, 127.52, 127.49, 120.85, 114.51, 79.02, 75.23, 70.15, 45.11, 33.25, 31.30, 23.75.

HRMS (ESI-TOF) calcd for $C_{26}H_{25}{}^{78.9183}BrO_3$ ([M]+Na^+) = 487.0879, Found 487.0883.

HRMS (ESI-TOF) calcd for $C_{26}H_{25}{}^{80.9163}BrO_3$ ([M]+Na^+) = 489.0859, Found 489.0872.

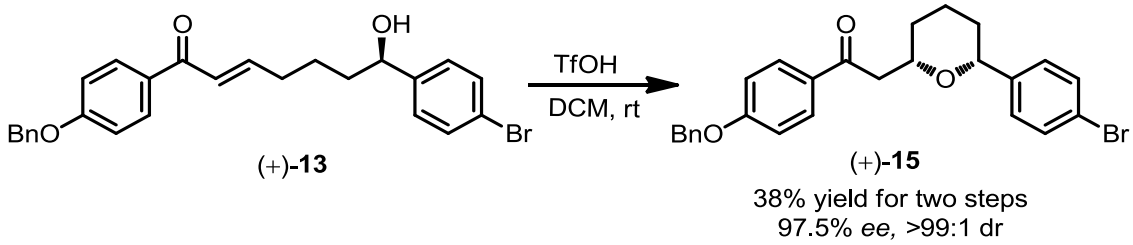
$[\alpha]^{26}_D$ = -47.1 (*c* = 0.42, in CH_2Cl_2), wavelength: 589 nm.



	Retention Time	Area	% Area
1	8.306	2434497	50.03
2	10.147	2431984	49.97

	Retention Time	Area	% Area
1	8.256	120691	2.29
2	10.061	5139116	97.71

To the solution of (+)-**13** in CH_2Cl_2 (1 mL) was added TfOH (one drop) at room temperature. The reaction mixture was stirred at room temperature for 1h. The residue was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 7 : 1) to afford the desired product (+)-**15** in 38% yield (two steps from **13**).



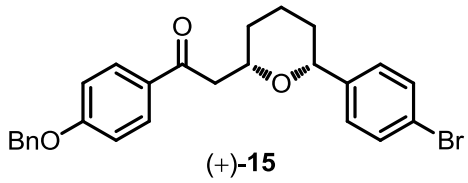
(+)-**13**

(+)-**15**

38% yield for two steps

97.5% *ee*, >99:1 dr

1-(4-(benzyloxy)phenyl)-2-((2*S*,6*R*)-6-(4-bromophenyl)tetrahydro-2*H*-pyran-2-yl)ethanone ((+)**15**)

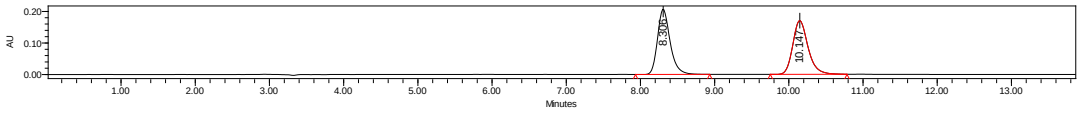


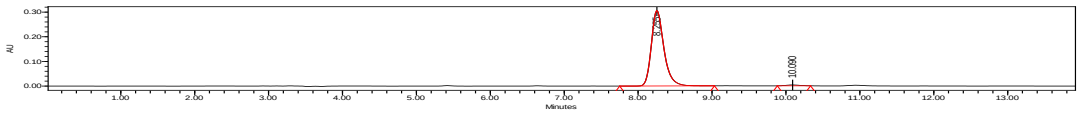
(+)-**15**

($C_{26}H_{25}BrO_3$) White solid, 38% yield for two steps. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 8.23 min, t_r (minor) = 10.09 min, 97.5% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 2H), 7.50 – 7.28 (m, 7H), 7.15 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 5.13 (s, 2H), 4.37 (d, J = 11.2 Hz, 1H), 4.13 (dt, J = 11.2, 6.0 Hz, 1H), 3.34 (dd, J = 15.6, 6.0 Hz, 1H), 2.97 (dd, J = 15.6, 6.0 Hz, 1H), 1.94 (d, J = 13.2 Hz, 1H), 1.82 (d, J = 13.2 Hz, 2H), 1.77 – 1.66 (m, 1H), 1.51 – 1.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.06, 162.66, 142.23, 136.18, 131.21, 130.73, 130.69, 128.73, 128.28, 127.51, 127.49, 120.85, 114.51, 79.02, 75.23, 70.15, 45.11, 33.25, 31.30, 23.74.

$[\alpha]^{26}_D$ = 56.5 (*c* = 0.35, in CH_2Cl_2), wavelength: 589 nm.

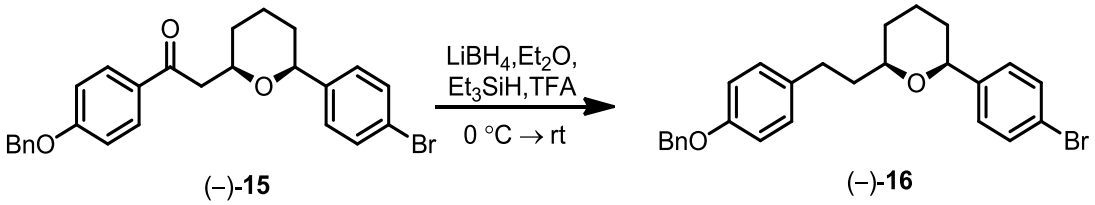




	Retention Time	Area	% Area
1	8.306	2434497	50.03
2	10.147	2431984	49.97

	Retention Time	Area	% Area
1	8.255	3597705	98.77
2	10.090	44657	1.23

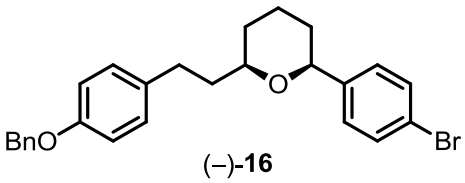
To the solution of (−)-**15** (46.5 mg) in dry Et_2O (0.5 mL) under N_2 atomsphere was added $LiBH_4$ (190 μL, 2.0 M in THF) at 0 ℃. The reaction mixture was stirred at 0 ℃ for 1h before stirred at room temperature for another 1.5 h. Then, the solution was cooled to 0 ℃, and Et_3SiH (0.5 mL) and TFA (0.5 mL) were added. The solution stirred at 0 ℃ for 10 min and warmed to room temperature slowly (ca. 4 h). Then the residue was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford the desired product (−)-**16** in 96% yield as white solid.



(−)-**15** (−)-**16**

96% yield, >99% *ee*

2-(4-(benzyloxy)phenethyl)-6-(4-bromophenyl)tetrahydro-2*H*-pyran ((−)-**16**)



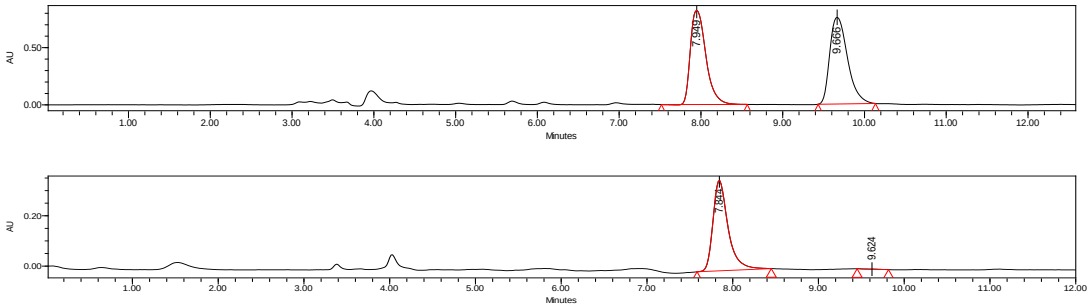
(−)-**16**

($C_{26}H_{27}BrO_2$) White solid, 96% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 98/02, flow rate 1.0 mL/min, λ = 210 nm), t_r (major) = 7.84 min, t_r (minor) = 9.62 min, >99% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 4H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.26 – 7.22 (m, 2H), 7.13 – 7.05 (m, 2H), 6.92 – 6.84 (m, 2H), 5.02 (s, 2H), 4.29 (dd, *J* = 11.2, 2.0 Hz, 1H), 3.49 – 3.37 (m, 1H), 2.79 – 2.59 (m, 2H), 1.96 – 1.85 (m, 2H), 1.85 – 1.78 (m, 1H), 1.77 – 1.70 (m, 1H), 1.67 – 1.56 (m, 2H), 1.48 – 1.38 (m, 1H), 1.38 – 1.28 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.97, 142.74, 137.28, 134.78, 131.28, 129.43, 128.59, 127.92, 127.56, 127.53, 120.81, 114.72, 78.70, 77.16, 70.08, 38.26, 33.60, 31.18, 30.79, 23.97.

HRMS (ESI-TOF) calcd for $C_{26}H_{27}{}^{80.9163}BrO_2$ ([M]+Na^+) = 473.1087, Found 473.1094.

HRMS (ESI-TOF) calcd for $C_{26}H_{27}{}^{80.9163}BrO_2$ ([M]+Na^+) = 475.1066, Found 475.1076.

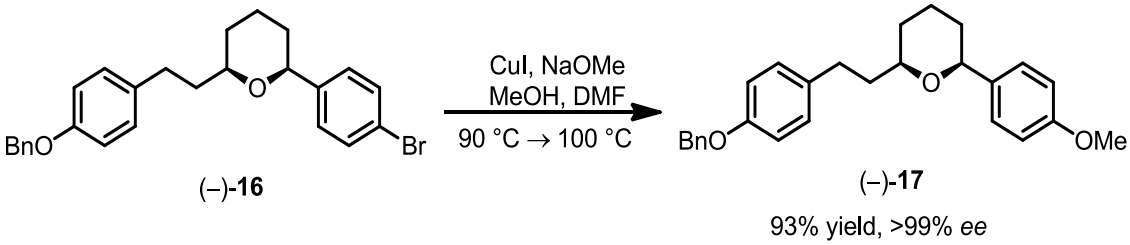
$[\alpha]^{27}_D$ = -80.2 (*c* = 0.84, in CH_2Cl_2), wavelength: 589 nm.



	Retention Time	Area	% Area
1	7.949	10825624	48.65
2	9.666	11426354	51.35

	Retention Time	Area	% Area
1	7.844	4408037	99.89
2	9.624	4965	0.11

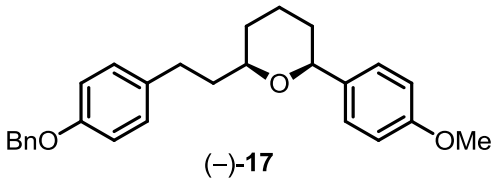
To the solution of NaOMe (0.6 mL,) in dry DMF (0.3 mL) was added CuI (53 mg). The reaction mixture was stirred at 90 ℃ for 3.5h before added (−)-**16** (37.7 mg). Then, the solution was stirred at 100 ℃ for 5.5 h. Finally, the residue was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 30 : 1) to afford the desired product (−)-**17** in 93% yield as white solid.



(−)-**16** (−)-**17**

93% yield, >99% *ee*

(2*R*,6*S*)-2-(4-(benzyloxy)phenethyl)-6-(4-methoxyphenyl)tetrahydro-2*H*-pyran ((−)-**17**)



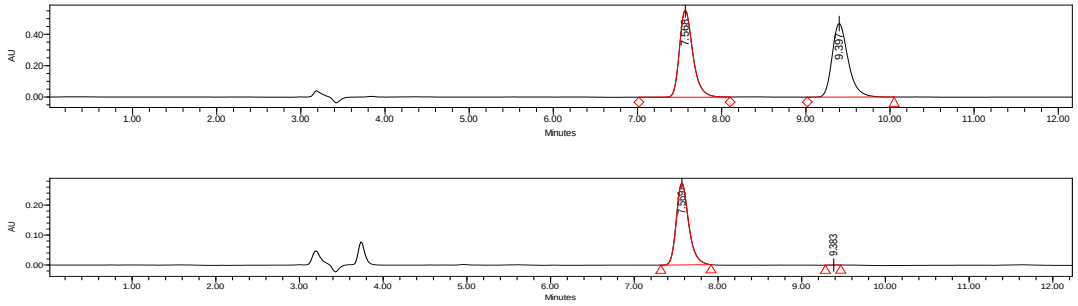
(−)-**17**

($C_{27}H_{30}O_3$) White solid, 93% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 210 nm), t_r (major) = 7.57 min, t_r (minor) = 9.38 min, >99% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.34 – 7.26 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.88 (dd, *J* = 8.4, 4.0 Hz, 4H), 5.03 (s, 2H), 4.29 (d, *J* = 10.4 Hz, 1H), 3.79 (s, 3H), 3.52 – 3.35 (m, 1H), 2.81 – 2.57 (m, 2H), 1.97 – 1.86 (m, 2H), 1.85 – 1.78 (m, 1H), 1.78 – 1.58 (m, 3H), 1.55 – 1.43 (m, 1H), 1.39 – 1.26 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.73, 156.92, 137.29, 135.93, 134.92, 129.45, 128.59, 127.91, 127.53, 127.10, 114.67, 113.62, 79.06, 77.16, 70.06, 55.31, 38.32, 33.36, 31.30, 30.80, 24.09.

HRMS (ESI-TOF) calcd for $C_{27}H_{30}O_3$ ([M]+Na^+) = 425.2087, Found 425.2089.

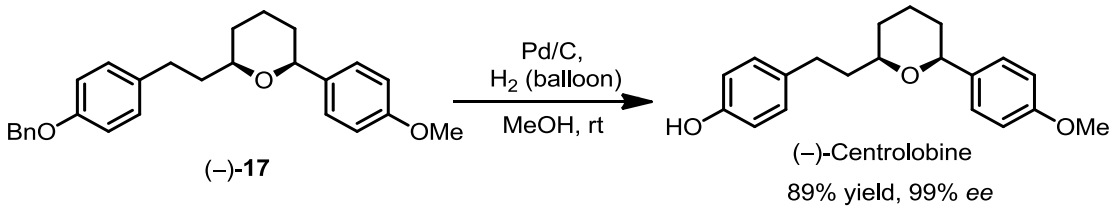
$[\alpha]^{26}_D$ = -74.9 (*c* = 0.63, in CH_2Cl_2), wavelength: 589 nm.



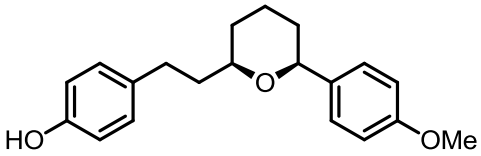
	Retention Time	Area	% Area
1	7.568	6141819	49.74
2	9.397	6207219	50.26

	Retention Time	Area	% Area
1	7.569	2804370	99.93
2	9.383	1884	0.07

A suspension of (-)-**17** (25 mg) and Pd/C (10%) (10 mg) in MeOH (1.0 mL) was stirred under H_2 atmosphere (1 atm) at room temperature for 8 hours. Then, the residue was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 3 : 1) to afford the desired product (−)-centrolobine in 89% yield.



(-)-Centrolobine

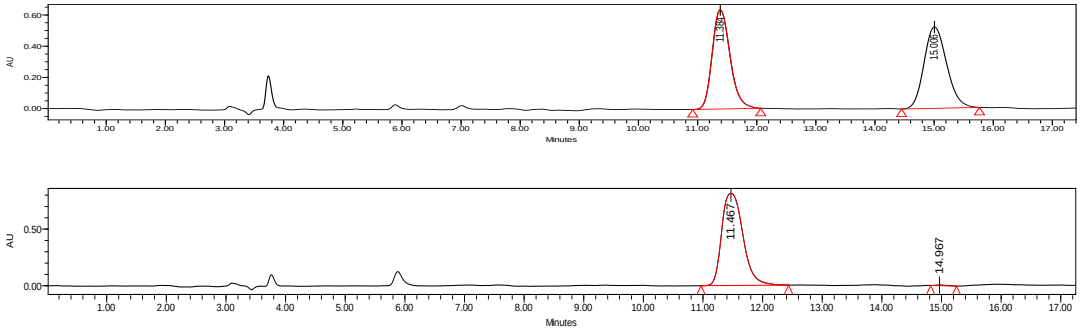


($C_{20}H_{24}O_3$) White solid, 89% yield. HPLC (Chiralcel IA, hexane/ *i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), t_r (major) = 11.47 min, t_r (minor) = 14.97 min, 99% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.94 – 6.85 (m, 2H), 6.77 – 6.66 (m, 2H), 5.26 (s, 1H), 4.31 (dd, *J* = 11.2, 4.0 Hz 1H), 3.81 (s, 3H), 3.53 – 3.41 (m, 1H), 2.79 – 2.59 (m, 2H), 2.00 – 1.69 (m, 5H), 1.68 – 1.59 (m, 2H), 1.58 – 1.47 (m, 1H), 1.42 – 1.30 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.72, 153.59, 135.79, 134.49, 129.54, 127.20, 115.14, 113.66, 79.20, 77.31, 55.33, 55.32, 38.29, 33.22, 31.25, 30.77, 24.06.

HRMS (ESI-TOF) calcd for $C_{20}H_{24}O_3$ ([M]+Na^+) = 335.1618, Found 335.1624.

$[\alpha]^{26}_D$ = -67.5 (*c* = 0.34 g/100 mL, 99% *ee*, in CH_2Cl_2), wavelength: 589 nm. (Lit[10], $[\alpha]_D$ = –50.8 (c = 3.6 g/100mL, 84% *ee*, in CH_2Cl_2), wavelength:).

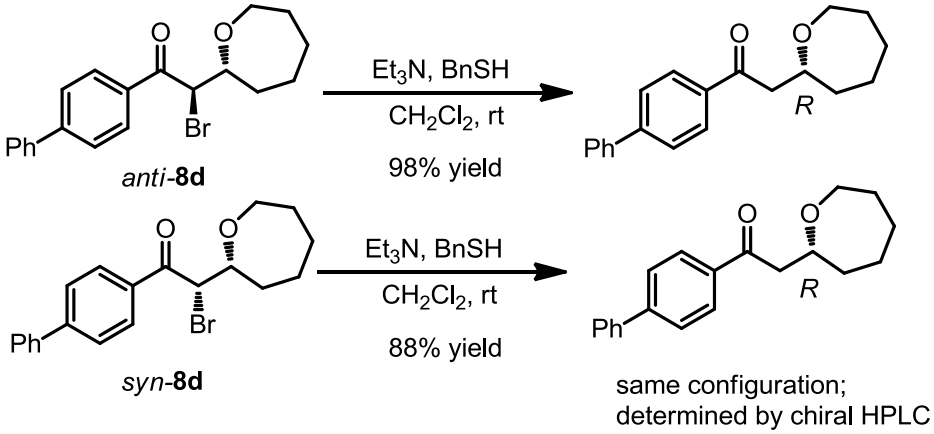


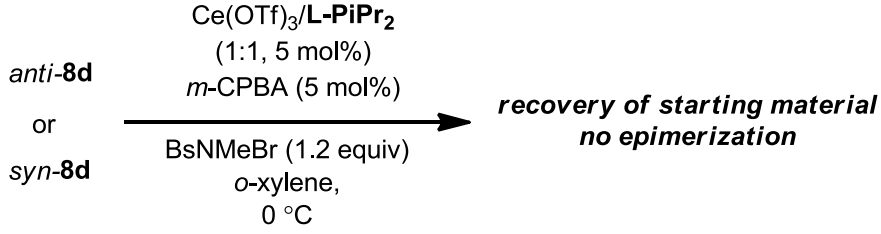
	Retention Time	Area	% Area
1	11.384	13320349	49.03
2	15.006	13847886	50.97

	Retention Time	Area	% Area
1	11.467	20097856	99.60
2	14.967	81093	0.40

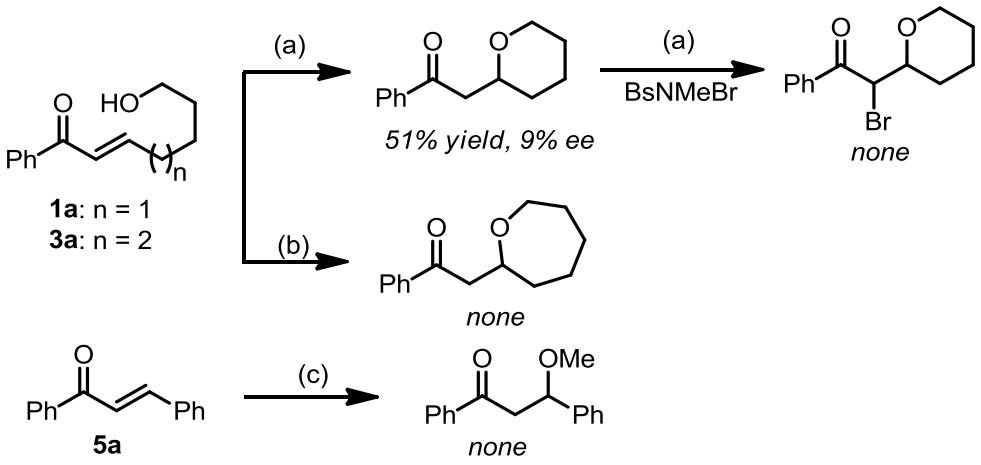
10. Mechanism study

Determine the absolute configuration of *syn*-**8d** and epimerization reaction experiment.





Control experiment:



(a) $Fe(acac)_3$/**L-PiPr$_2$** (1:1, 5 mol %), *o*-xylene, 0 °C, 4 h

(b) $Ce(OTf)_3$/**L-PiPr$_2$** (1:1, 5 mol %), *m*-CPBA (5 mol %), *o*-xylene, 0 °C, 12 h

(c) $Sc(OTf)_3$/**L-RaPr$_2$** (1:1, 10 mol %), MeOH, toluene, 35 °C, 12 h

11. Reference

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[6] P. A. Allegretti, E. M. Ferreira, *J. Am. Chem. Soc.* **2013**, 135, 17266–17269.

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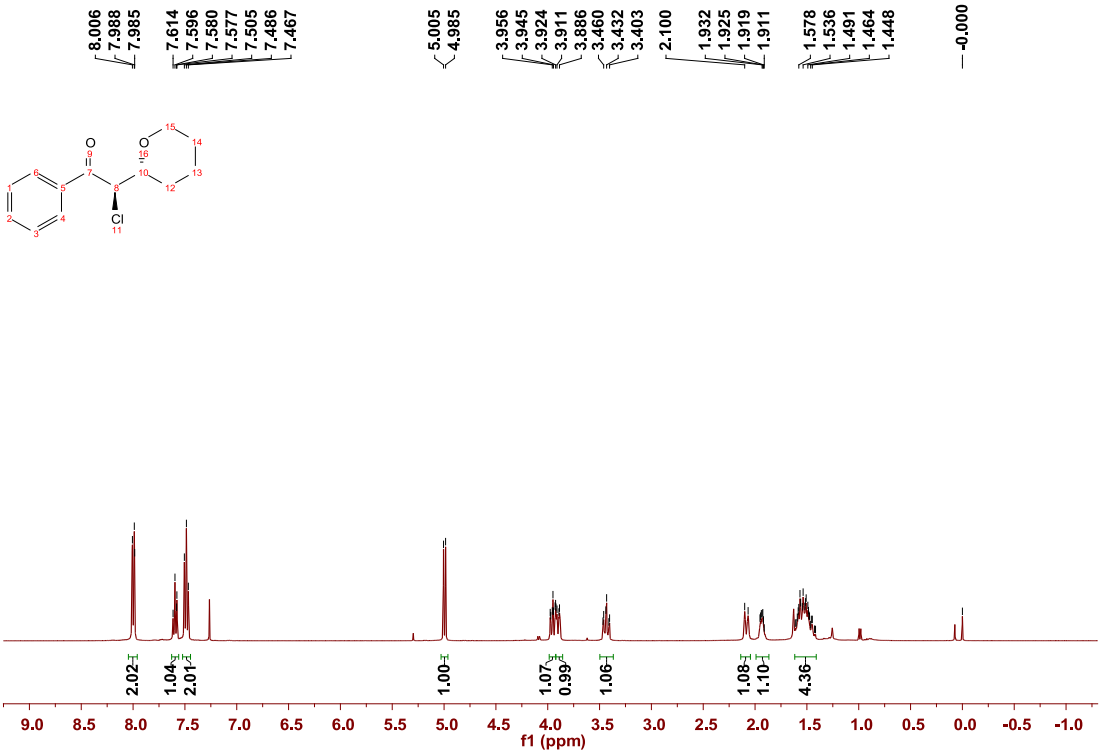
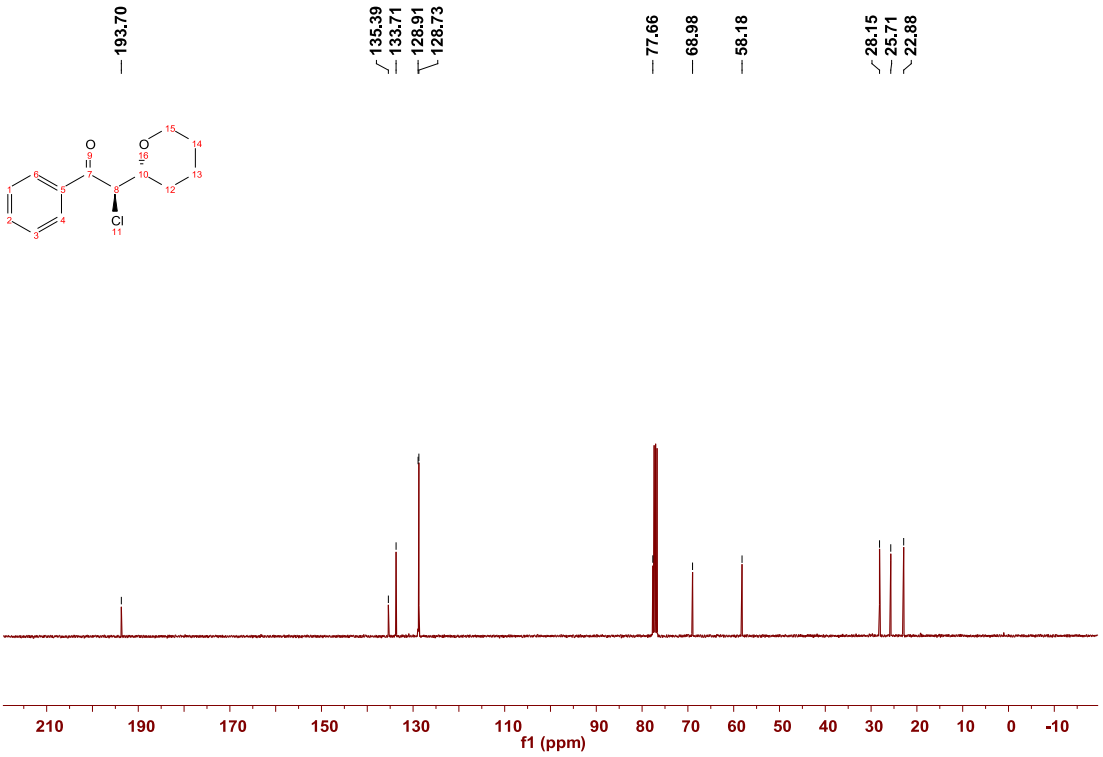
[8] Y. Lu, G. Zou, G. Zhao, *ACS Catal.* **2013**, 3, 1356–1359.

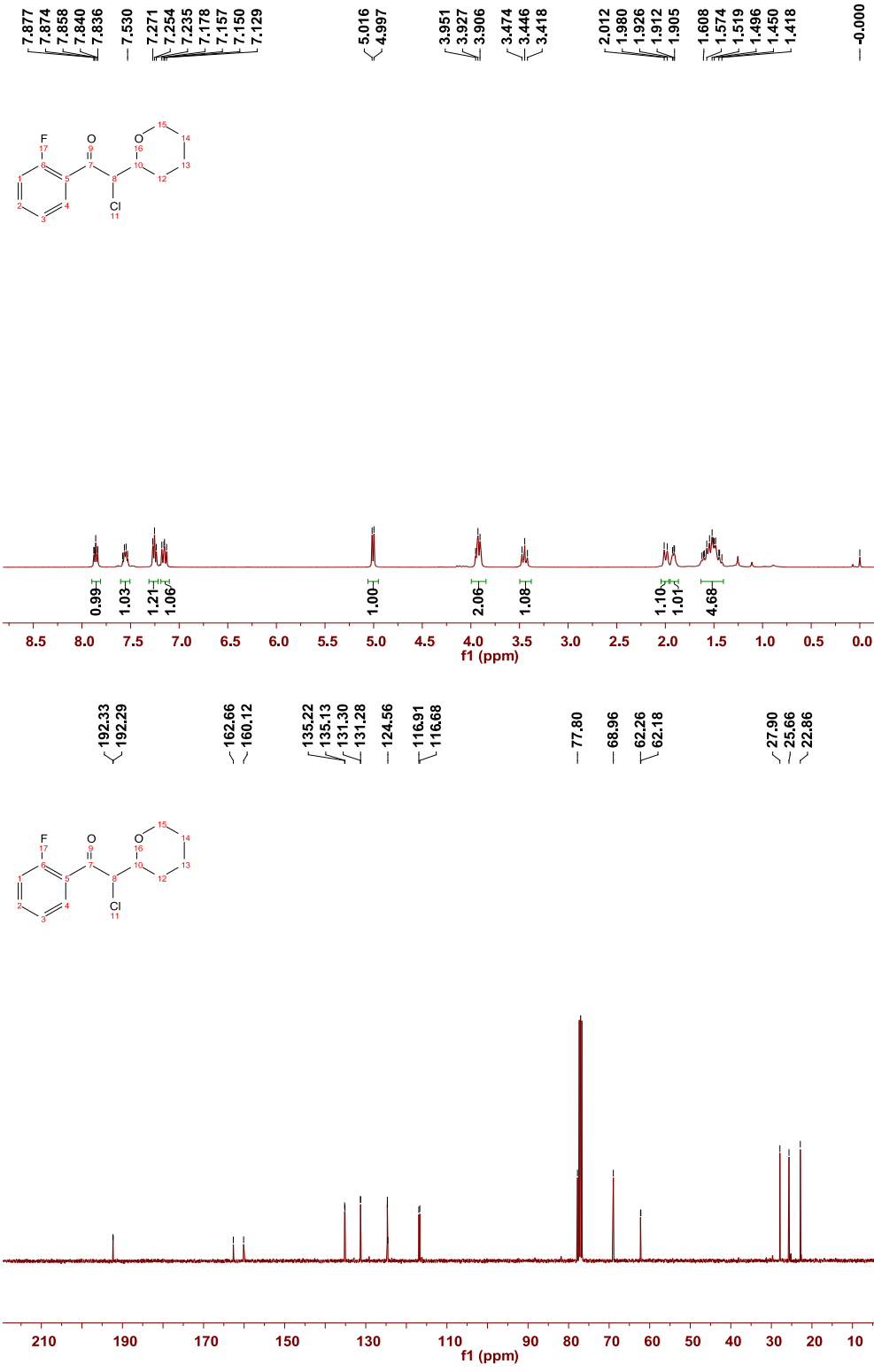
[9] H. Fujioka, K. Yahata, O. Kubo, Y. Sawama, T. Hamada, T. Maegawa, *Angew. Chem. Int. Ed.* **2011**, 50, 12232.

[10] K.-P. Chan, T.-P. Loh, *Org. Lett.* **2005**, 7, 4491–4494.

12. Copy of ^{1}H NMR and ^{13}C NMR spectra



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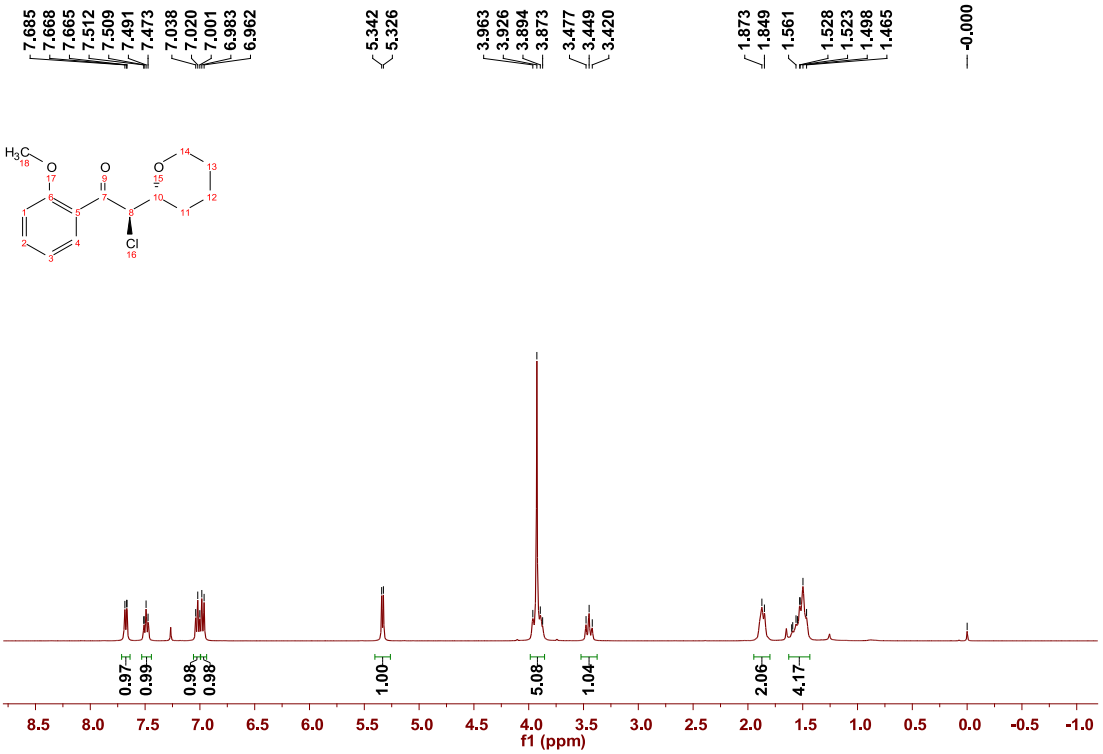
7.840
7.836
7.530
7.271
7.254
7.235
7.178
7.157
7.150
7.129
5.016
4.997
3.951
3.927
3.906
3.474
3.446
3.418
2.012
1.980
1.926
1.912
1.905
1.608
1.574
1.519
1.496
1.450
1.418
-0.000
F
O
O
Cl
0.99
1.03
1.21
1.06
1.00
2.06
1.08
1.10
1.01
4.68
f1 (ppm)
192.33
192.29
162.66
160.12
135.22
135.13
131.30
131.28
124.56
116.91
116.68
77.80
68.96
62.26
62.18
27.90
25.66
22.86
f1 (ppm)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7.509
7.491
7.473
7.038
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7.001
6.983
6.962
5.342
5.326
3.963
3.926
3.894
3.873
3.477
3.449
3.420
1.873
1.849
1.561
1.528
1.523
1.498
1.465
-0.000
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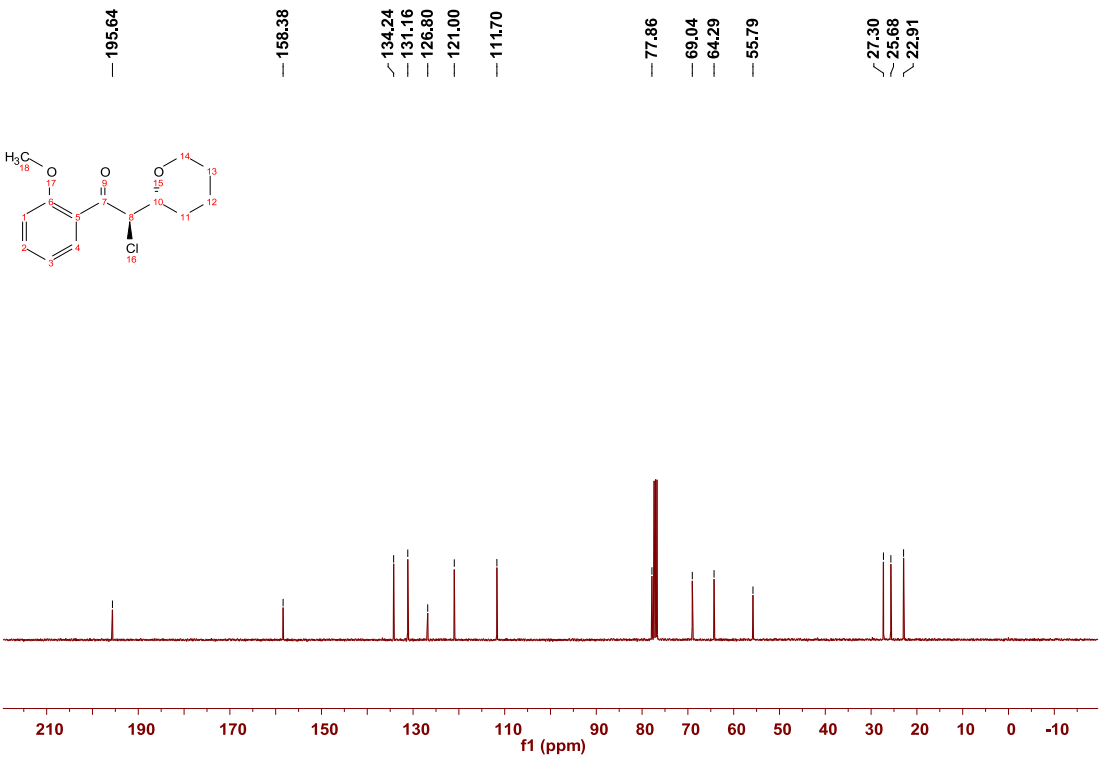
0.99
0.98
0.98
1.00
5.08
1.04
2.06
4.17
f1 (ppm)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158.38
134.24
131.16
126.80
121.00
111.70
77.86
69.04
64.29
55.79
27.30
25.68
22.91
f1 (ppm)


7.961
7.877
7.857
7.574
7.554
7.450
7.430
7.410
4.893
4.872
3.924
3.901
3.875
3.447
3.419
3.397
3.391
2.114
2.084
1.946
1.935
1.539
1.481
1.451
1.430
1.422
-0.000
1.00
0.98
0.98
1.01
1.02
2.08
1.08
1.07
1.08
4.41
f1 (ppm)
192.74
137.00
135.06
133.58
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128.94
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57.95
28.28
25.67
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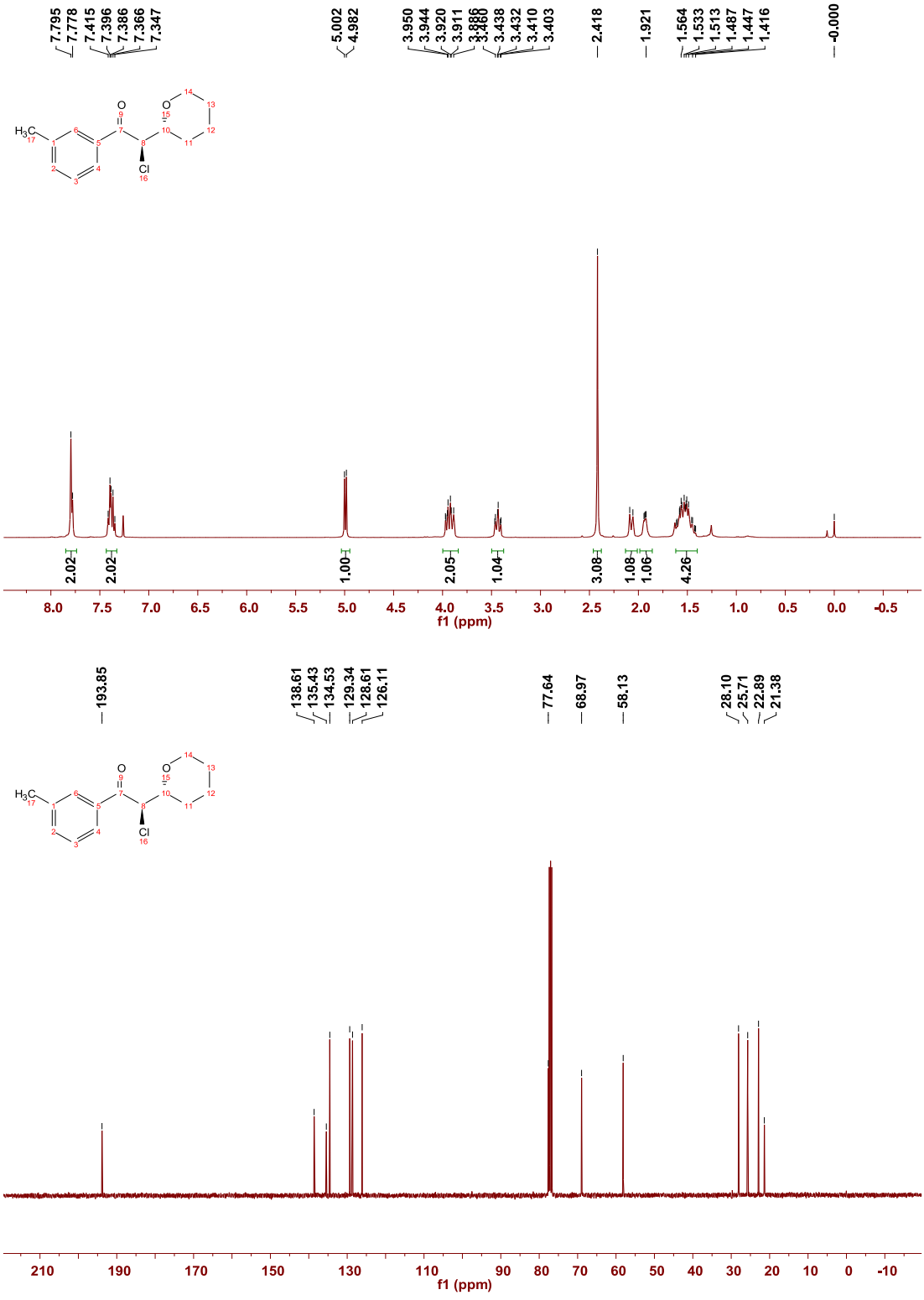
f1 (ppm)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3.911
3.438
3.432
3.410
3.403
2.418
1.921
1.564
1.533
1.513
1.487
1.447
1.416
-0.000
2.02
2.02
1.00
2.05
1.04
3.08
1.08
1.06
4.26
f1 (ppm)
193.85
138.61
135.43
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58.13
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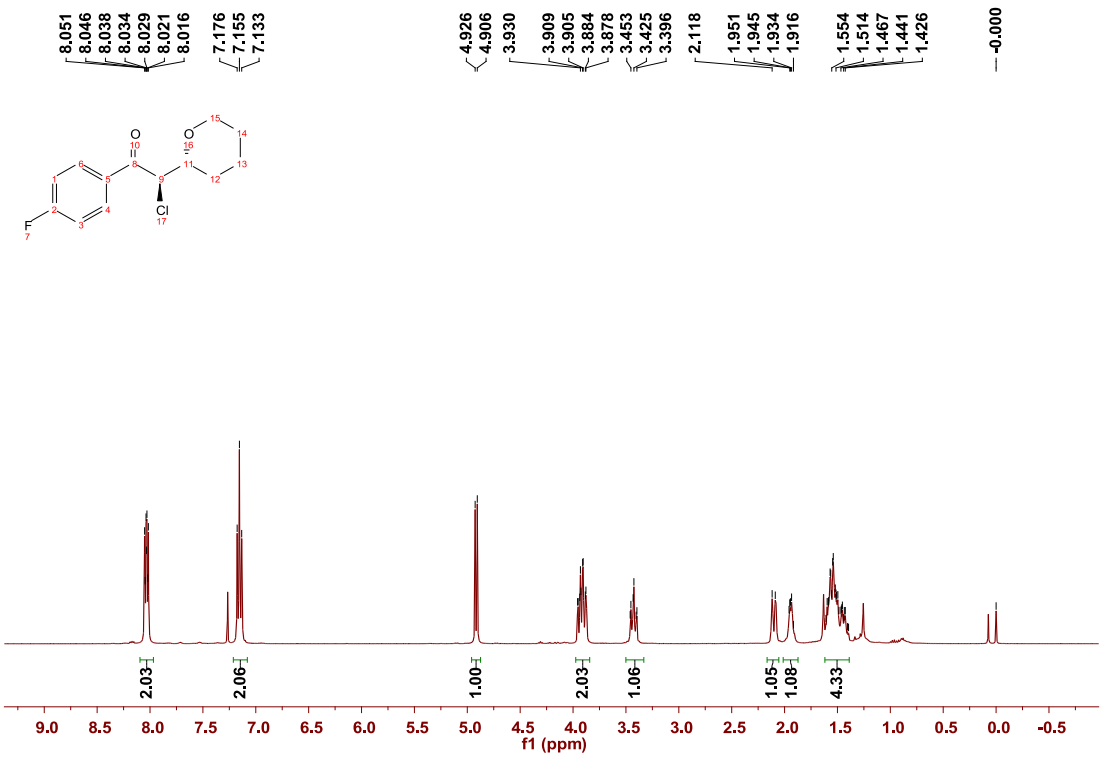
21.38
f1 (ppm)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7.133
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3.930
3.909
3.905
3.884
3.878
3.453
3.425
3.396
2.118
1.951
1.945
1.934
1.916
1.554
1.514
1.467
1.441
1.426
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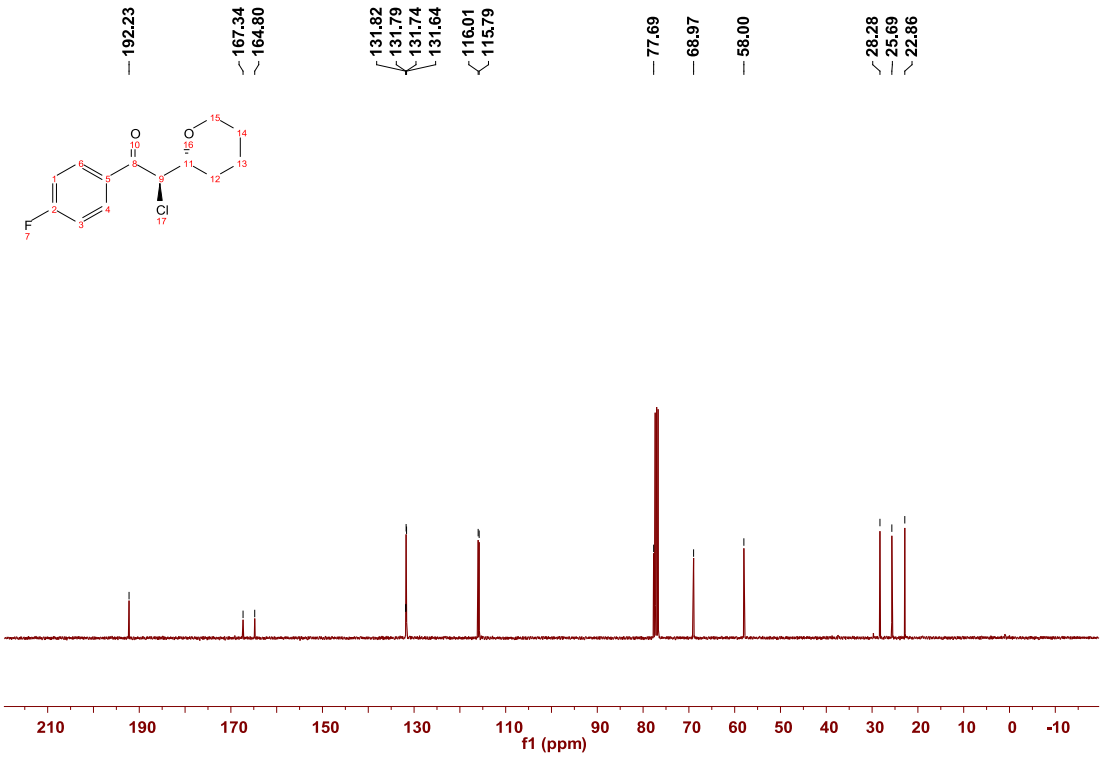
2.06
1.00
2.03
1.06
1.05
1.08
4.33
f1 (ppm)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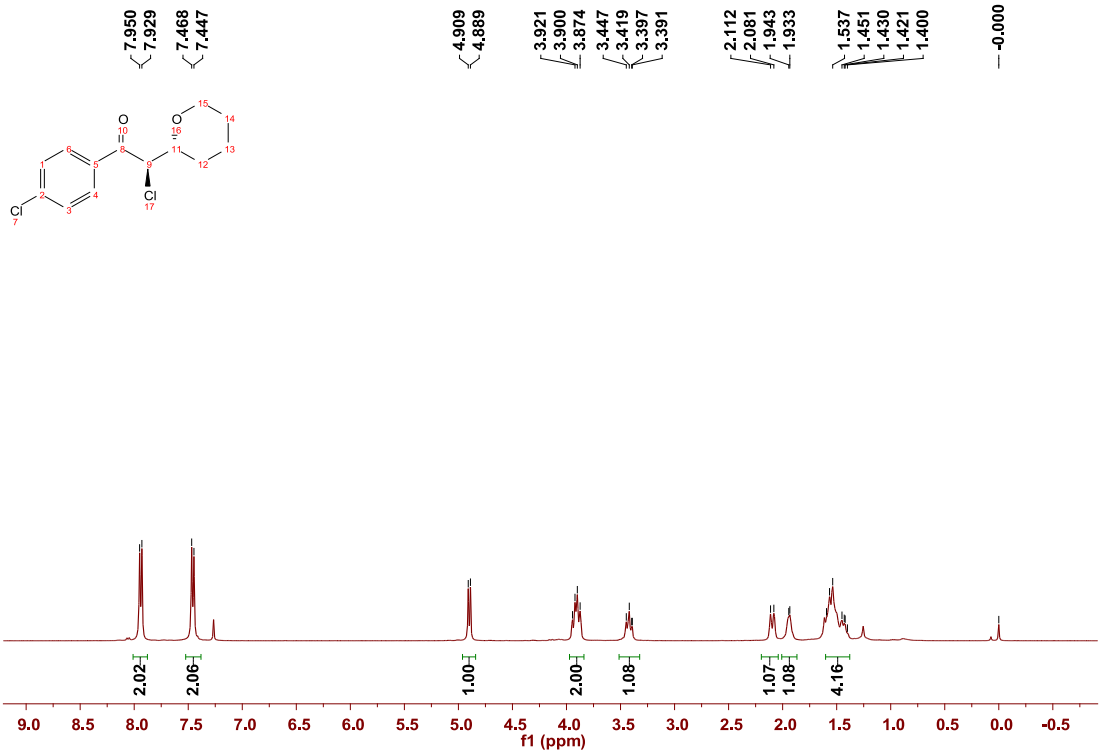
25.69
22.86
f1 (ppm)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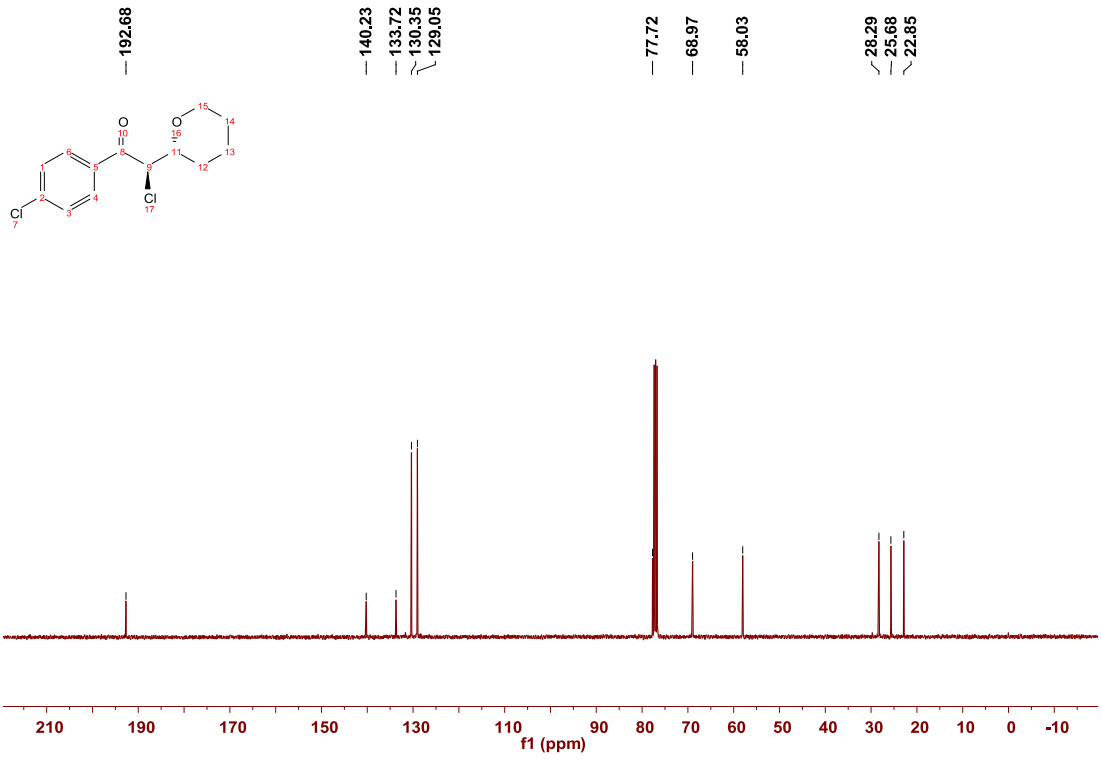
3.874
3.447
3.419
3.397
3.391
2.112
2.081
1.943
1.933
1.537
1.451
1.430
1.421
1.400
-0.000
2.02
2.06
1.00
2.00
1.08
1.07
1.08
4.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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25.68
22.85
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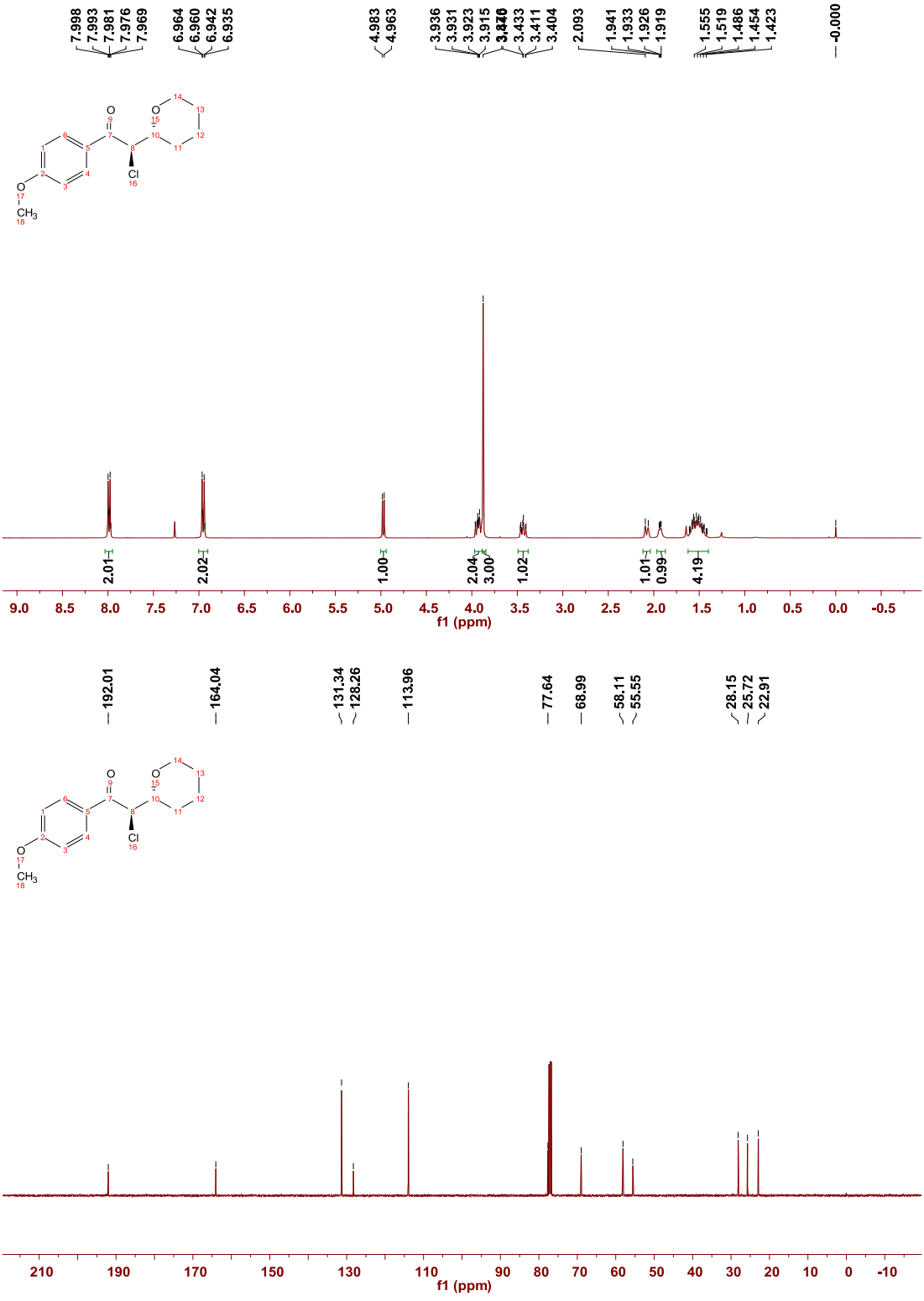
f1 (ppm)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6.935
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4.963
3.936
3.931
3.923
3.915
3.433
3.411
3.404
2.093
1.941
1.933
1.926
1.919
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1.519
1.486
1.454
1.423
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2.01
2.02
1.00
2.04
3.00
1.02
1.01
0.99
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f1 (ppm)
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113.96
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55.55
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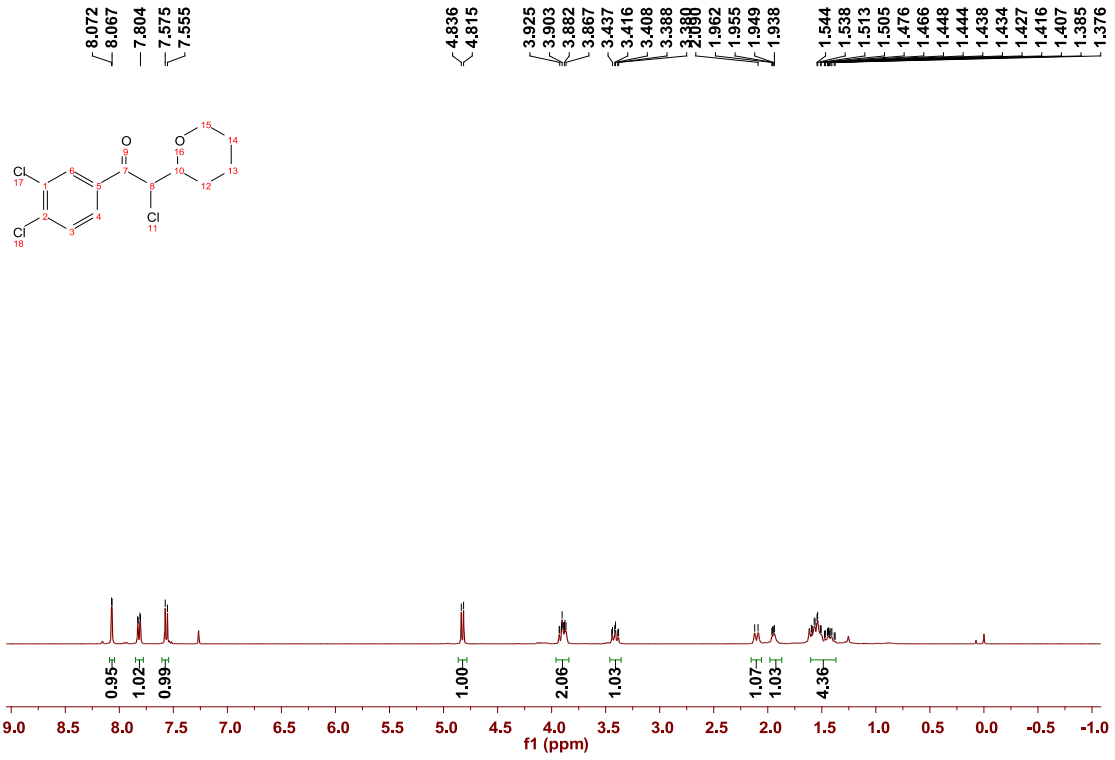
22.91
f1 (ppm)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3.416
3.408
3.388
2.090
1.962
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1.438
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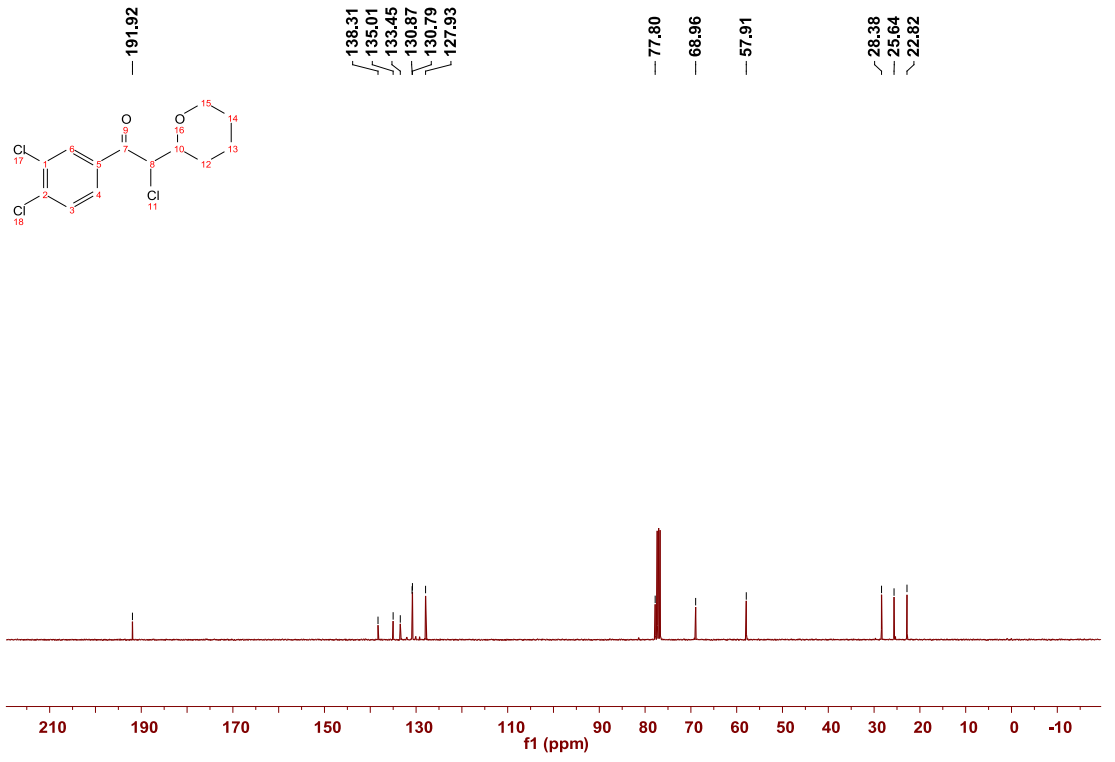
f1 (ppm)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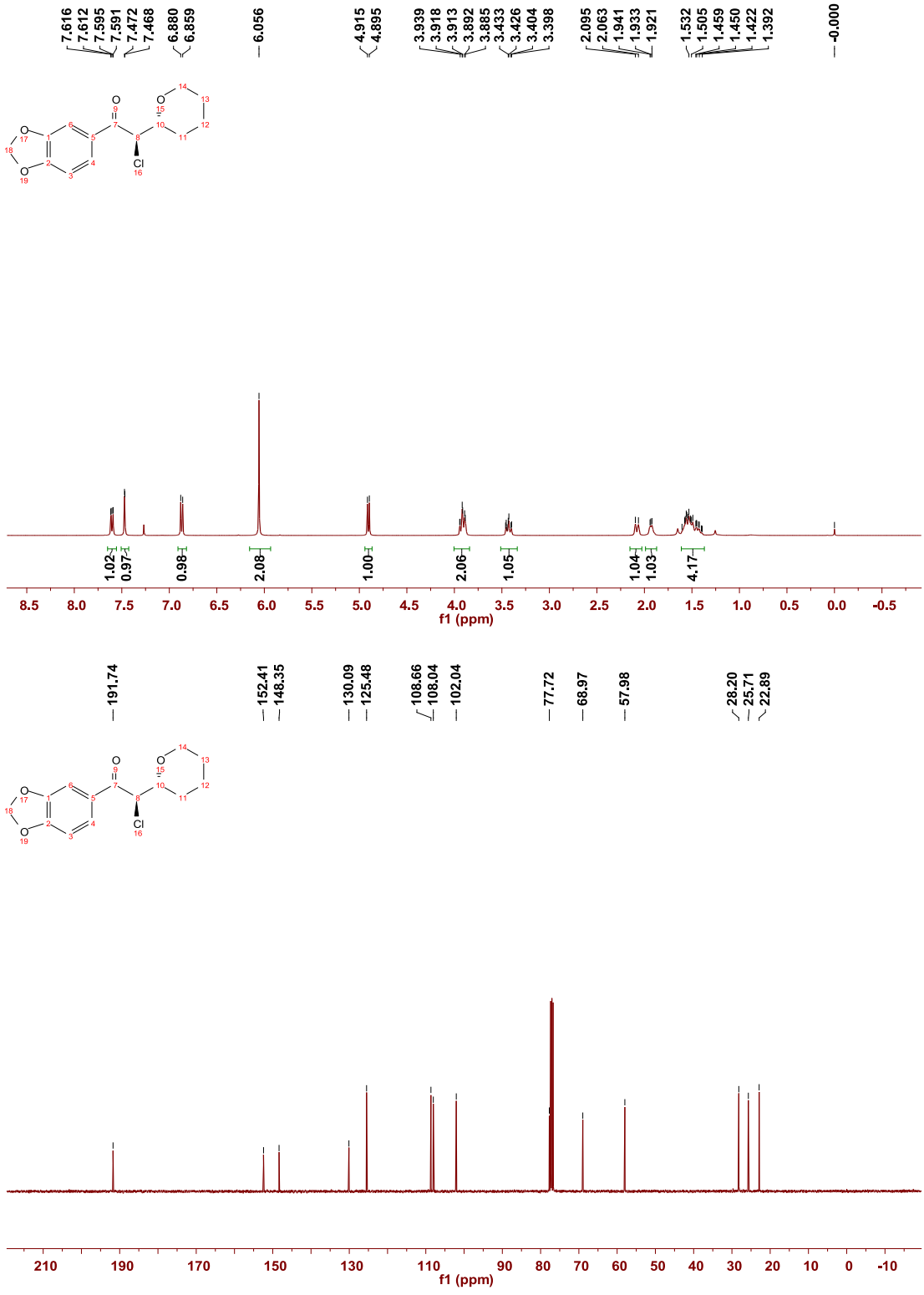
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3.918
3.913
3.892
3.885
3.433
3.426
3.404
3.398
2.095
2.063
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1.933
1.921
1.532
1.505
1.459
1.450
1.422
1.392
-0.000
1.02
0.97
0.98
2.08
1.00
2.06
1.05
1.04
1.03
4.17
f1 (ppm)
191.74
152.41
148.35
130.09
125.48
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108.04
102.04
77.72
68.97
57.98
28.20
25.71
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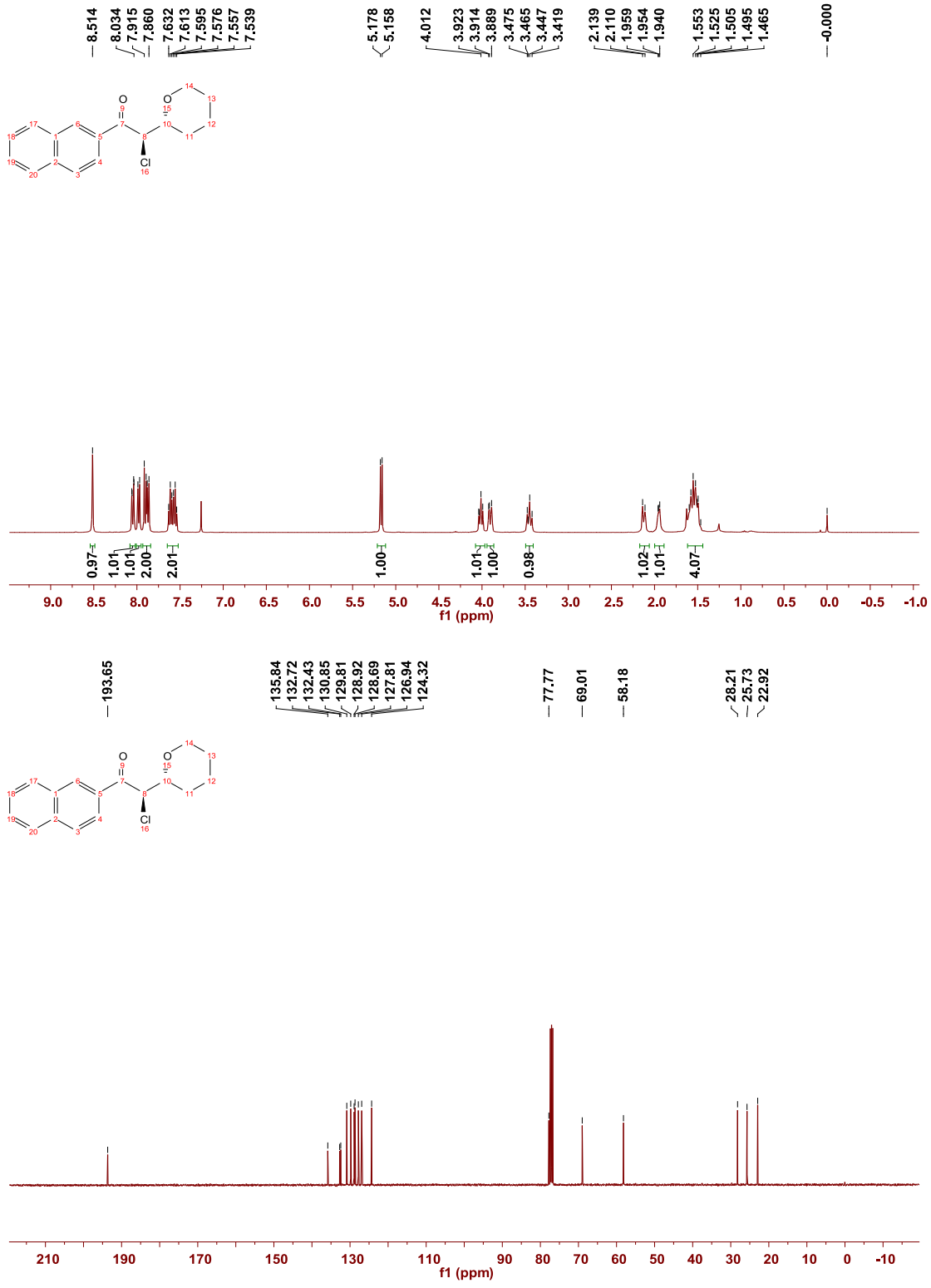
f1 (ppm)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5.158
4.012
3.923
3.914
3.889
3.475
3.465
3.447
3.419
2.139
2.110
1.959
1.954
1.940
1.553
1.525
1.505
1.495
1.465
-0.000
0.97
1.01
1.01
2.00
2.01
1.00
1.01
1.00
0.98
1.02
1.01
4.07
f1 (ppm)
193.65
135.84
132.72
132.43
130.85
129.81
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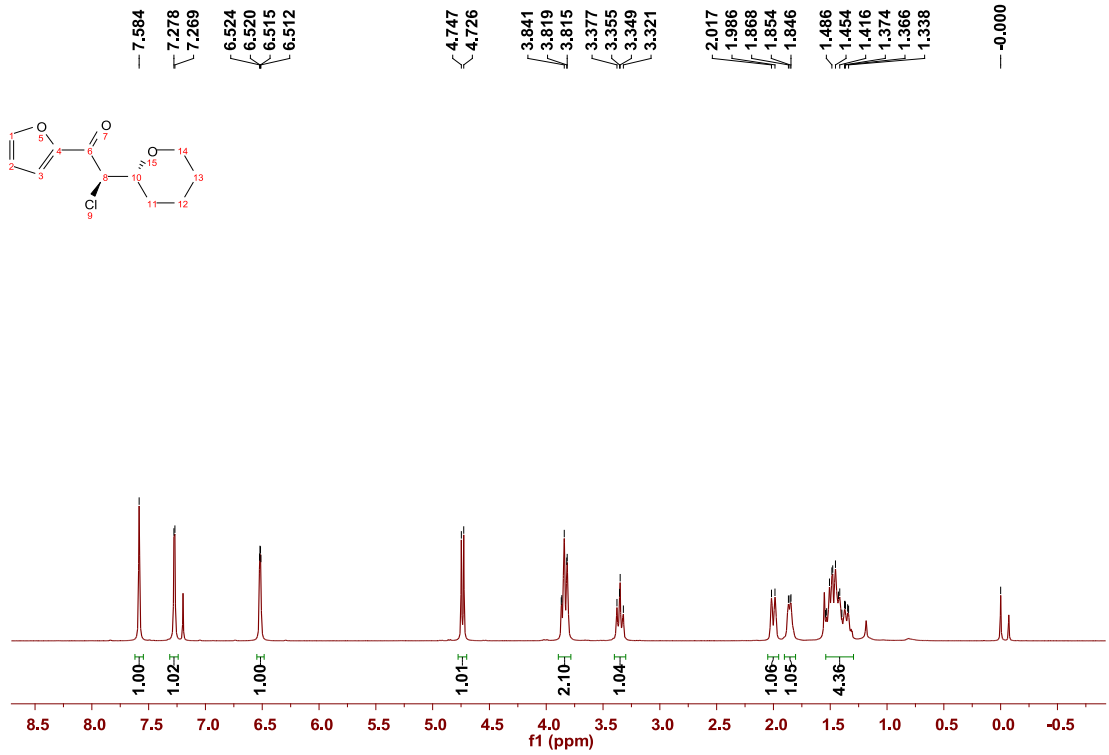
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3.349
3.321
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1.374
1.366
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1.01
2.10
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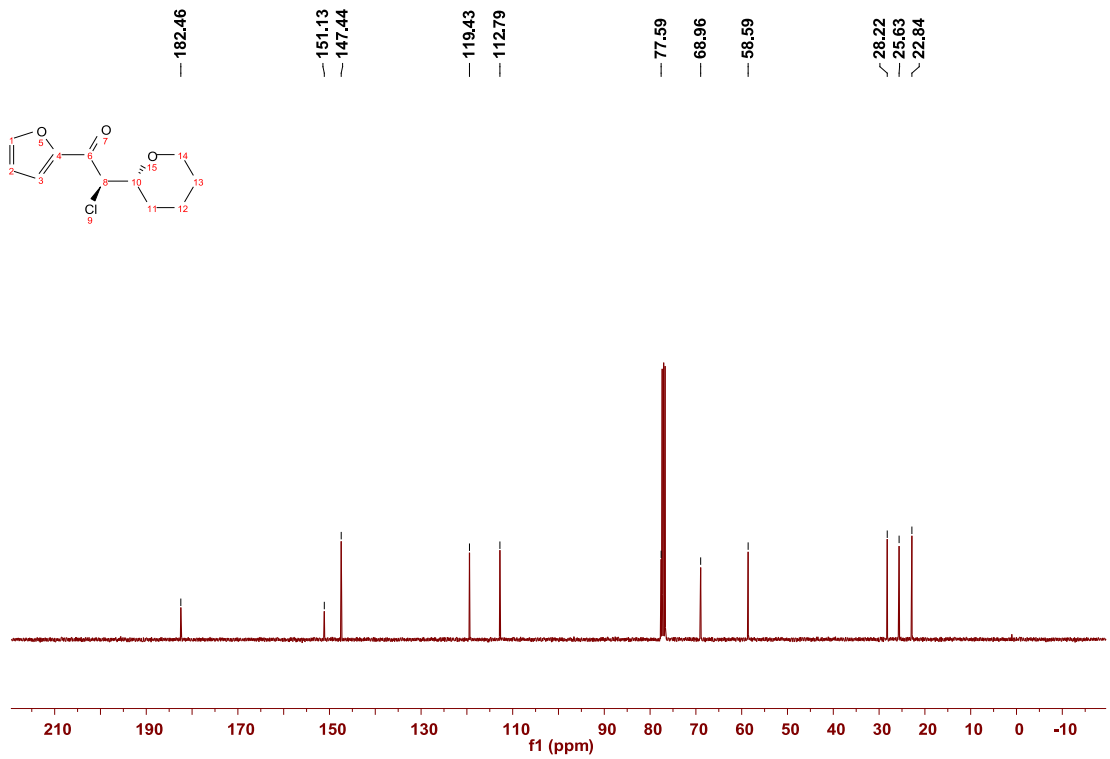
1.06
1.05
4.36
f1 (ppm)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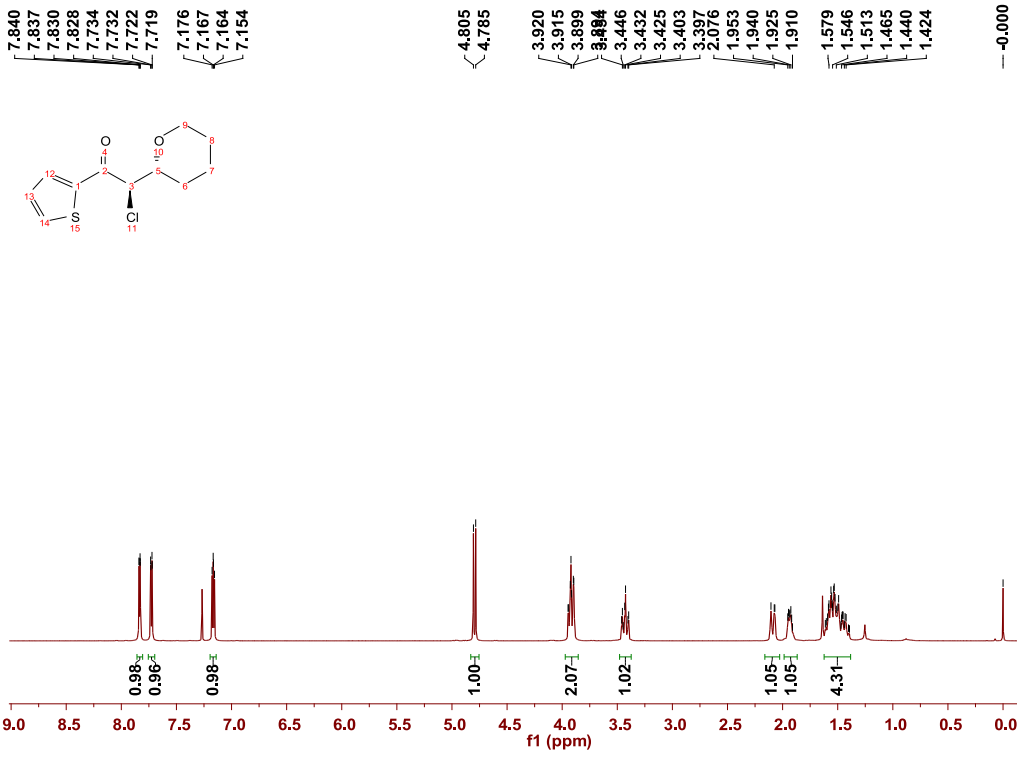
22.84
f1 (ppm)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7.154
4.805
4.785
3.920
3.915
3.899
3.446
3.432
3.425
3.403
3.397
2.076
1.953
1.940
1.925
1.910
1.579
1.546
1.513
1.465
1.440
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0.96
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1.00
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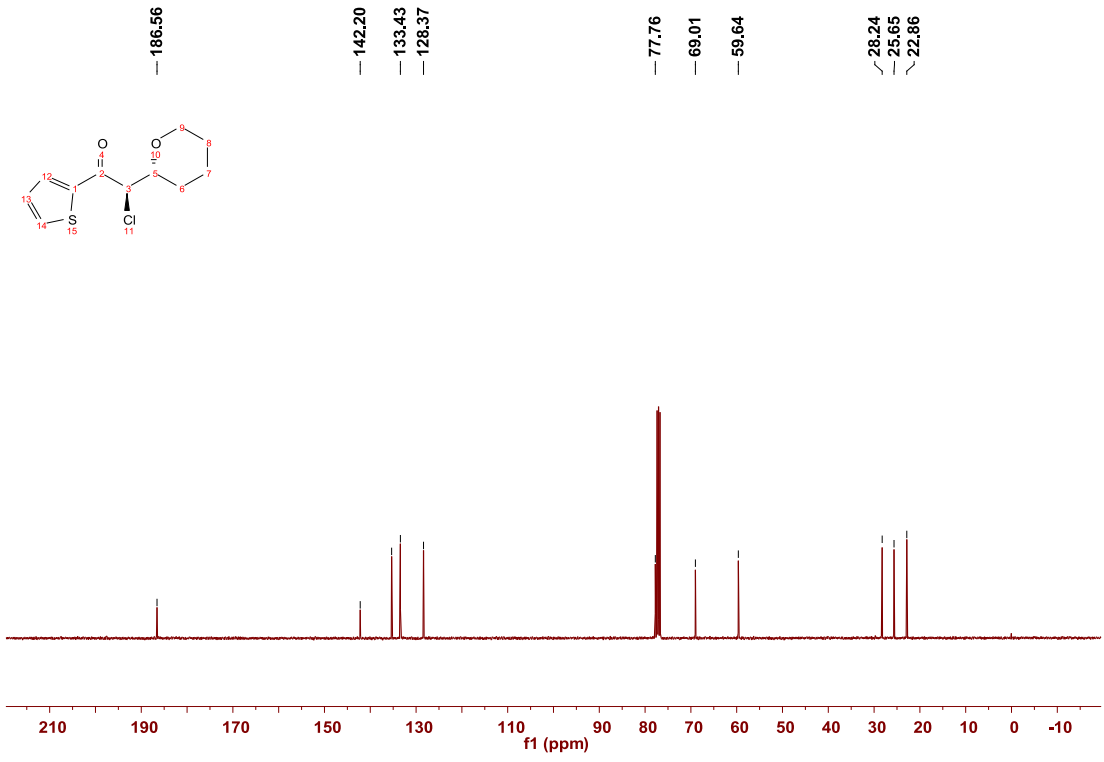
f1 (ppm)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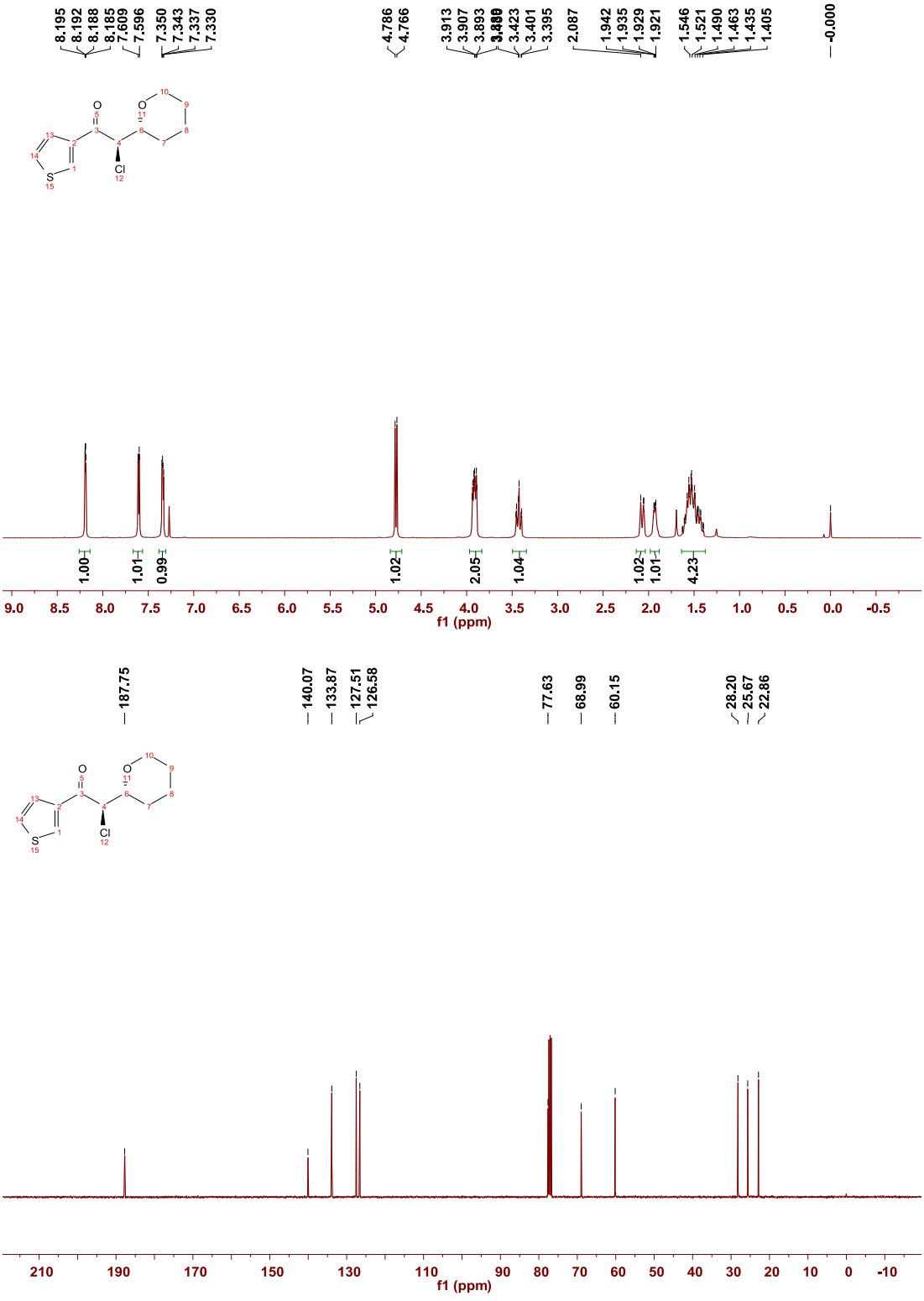
25.65
22.86
f1 (ppm)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3.907
3.893
3.423
3.401
3.395
2.087
1.942
1.935
1.929
1.921
1.546
1.521
1.490
1.463
1.435
1.405
0.000
1.00
1.01
0.99
1.02
2.05
1.04
1.02
1.01
4.23
f1 (ppm)
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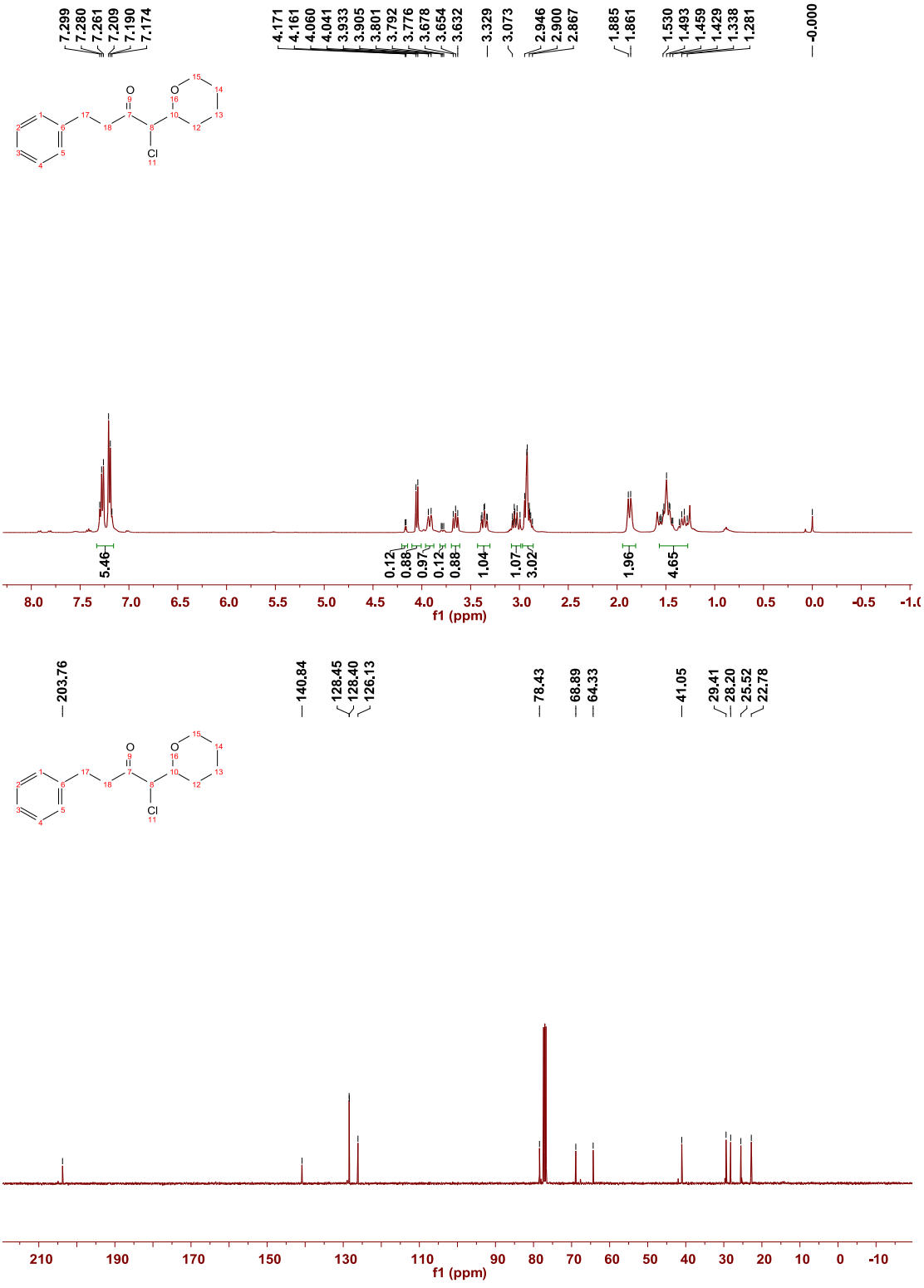
140.07
133.87
127.51
126.58
77.63
68.99
60.15
28.20
25.67
22.86
f1 (ppm)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7.280
7.261
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7.190
7.174
4.171
4.161
4.060
4.041
3.933
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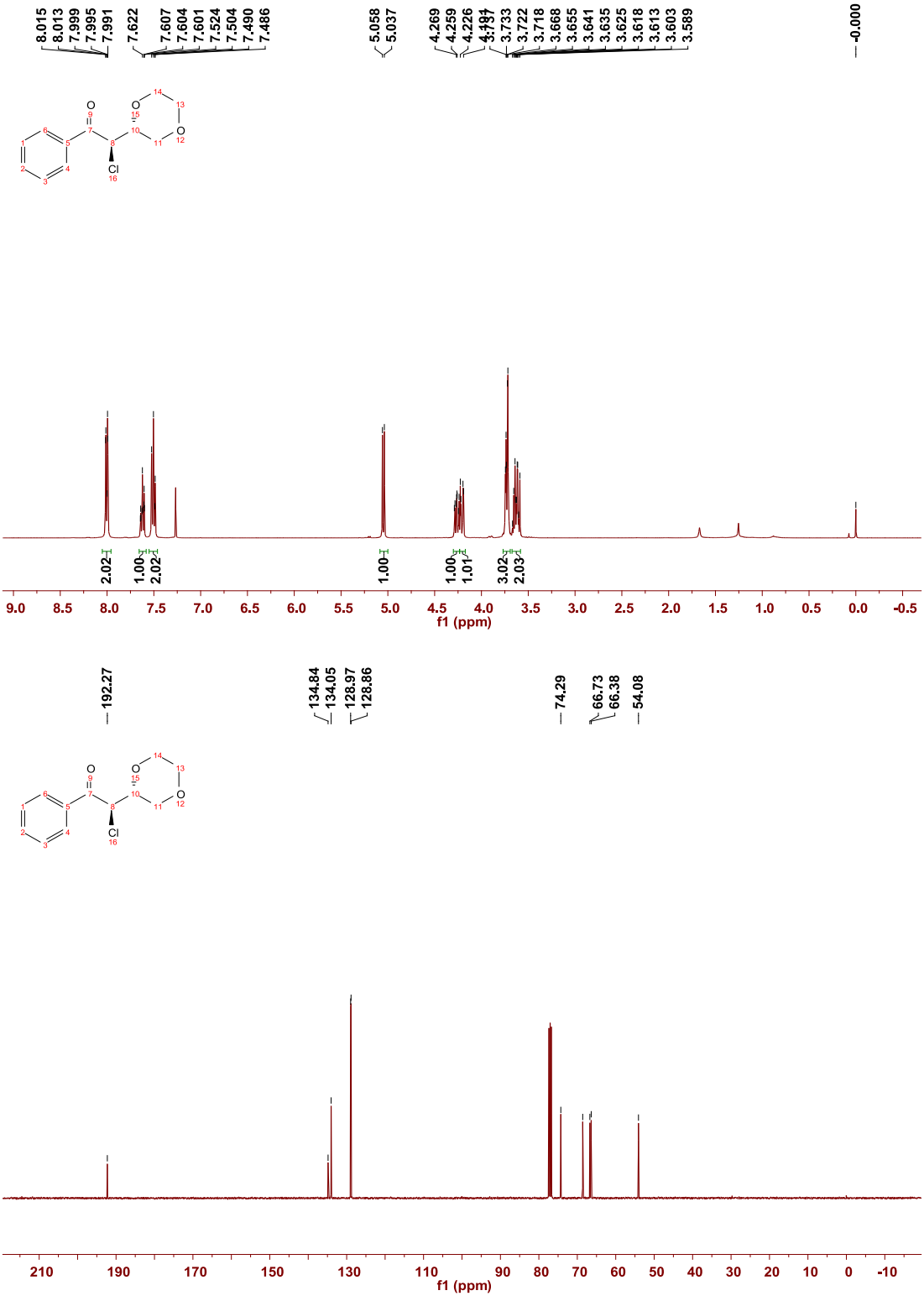
3.801
3.792
3.776
3.678
3.654
3.632
3.329
3.073
2.946
2.900
2.867
1.885
1.861
1.530
1.493
1.459
1.429
1.338
1.281
0.000
5.46
0.12
0.88
0.97
0.12
0.88
1.04
1.07
3.02
1.96
4.65
f1 (ppm)
203.76
140.84
128.45
128.40
126.13
78.43
68.89
64.33
41.05
29.41
28.20
25.52
22.78
f1 (ppm)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7.607
7.604
7.601
7.524
7.504
7.490
7.486
5.058
5.037
4.269
4.259
4.226
3.733
3.722
3.718
3.668
3.655
3.641
3.635
3.625
3.618
3.613
3.603
3.589
-0.000
2.02
1.00
2.02
1.00
1.00
1.01
3.02
2.03
f1 (ppm)
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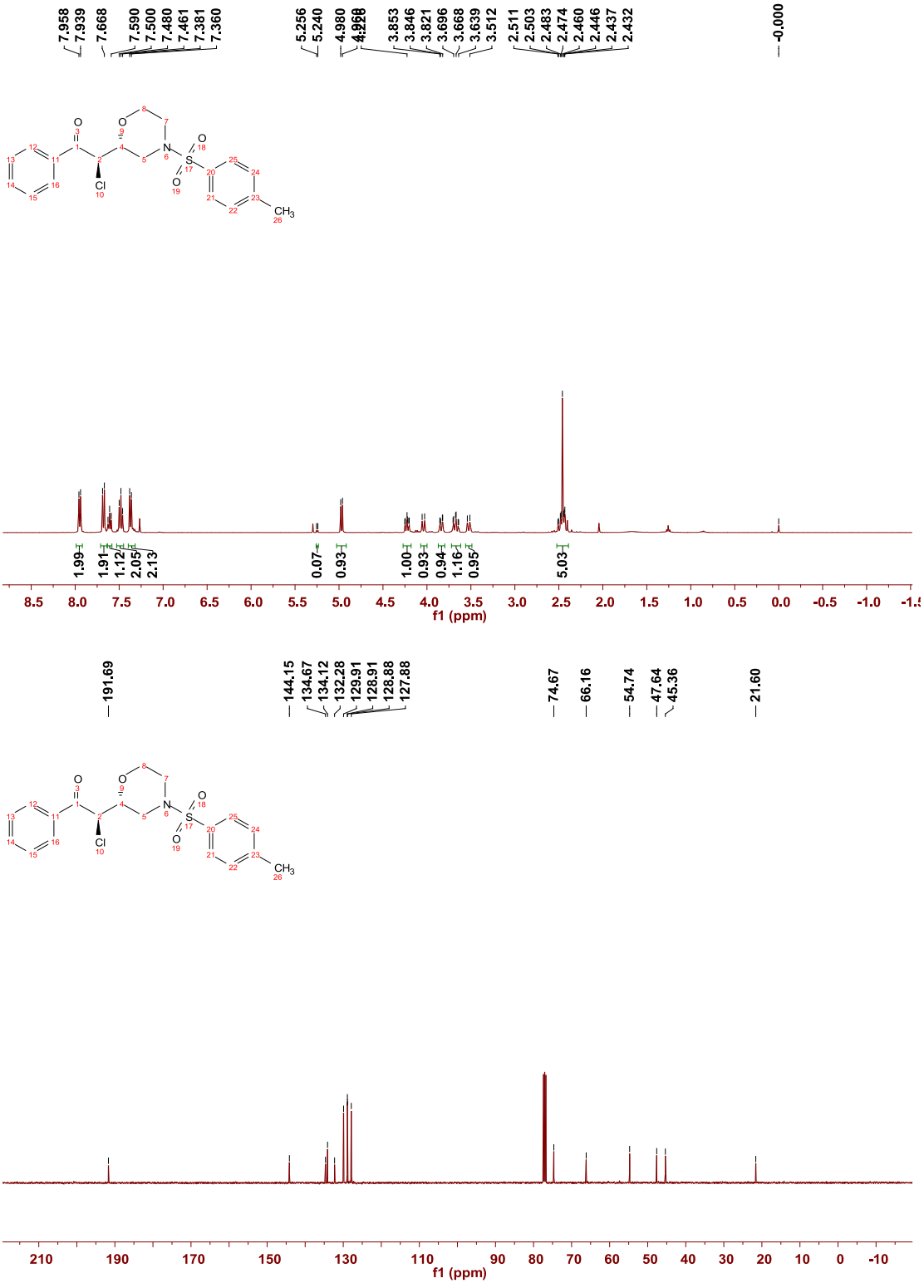
134.84
134.05
128.97
128.86
74.29
66.73
66.38
54.08
f1 (ppm)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7.939
7.668
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7.480
7.461
7.381
7.360
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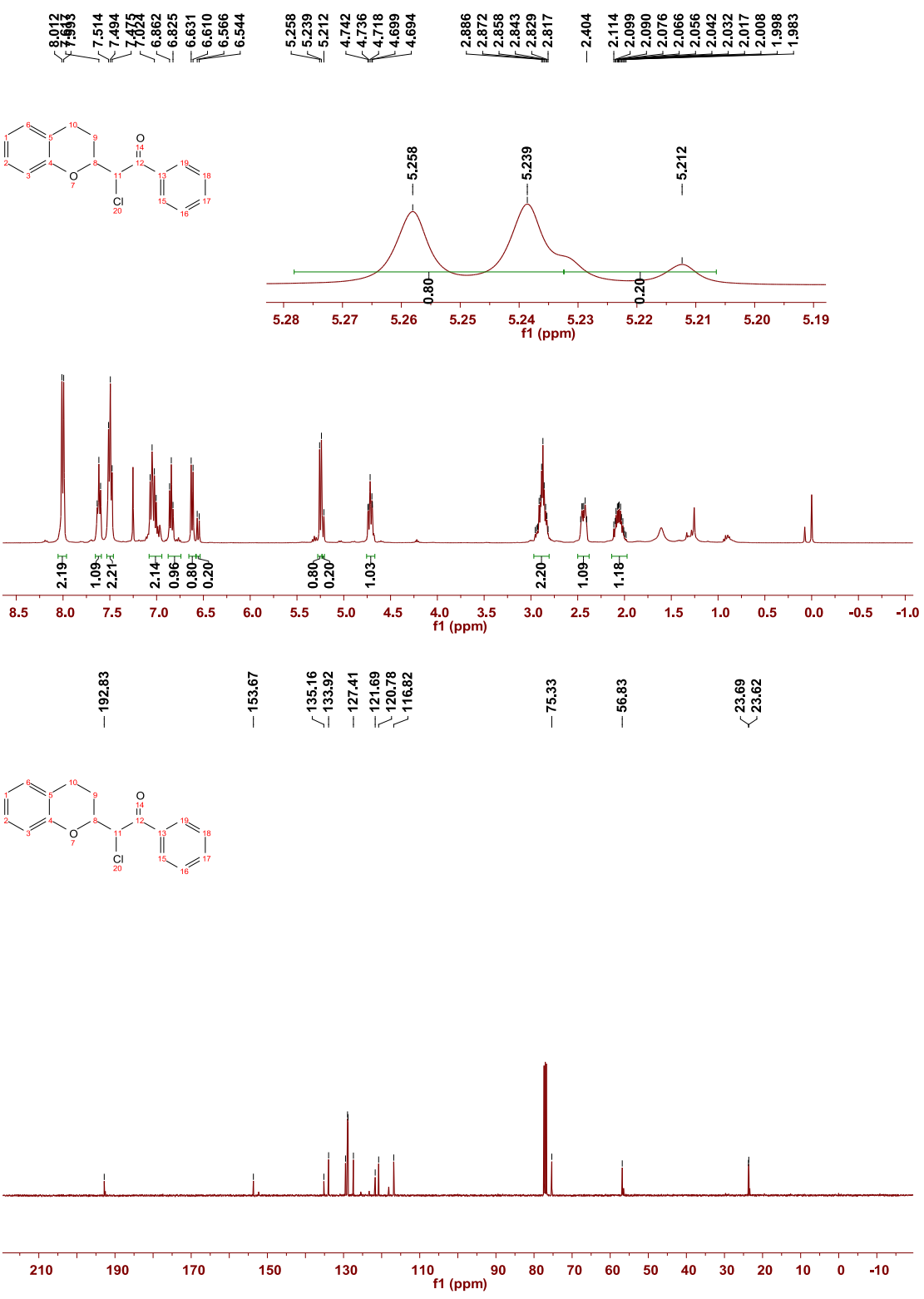
5.240
4.980
3.853
3.846
3.821
3.696
3.668
3.639
3.512
2.511
2.503
2.483
2.474
2.460
2.446
2.437
2.432
-0.000
1.99
1.91
1.12
2.05
2.13
0.07
0.93
1.00
0.93
0.94
1.16
0.95
5.03
f1 (ppm)
191.69
144.15
134.67
134.12
132.28
129.91
128.91
128.88
127.88
74.67
66.16
54.74
47.64
45.36
21.60
f1 (ppm)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6.825
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6.610
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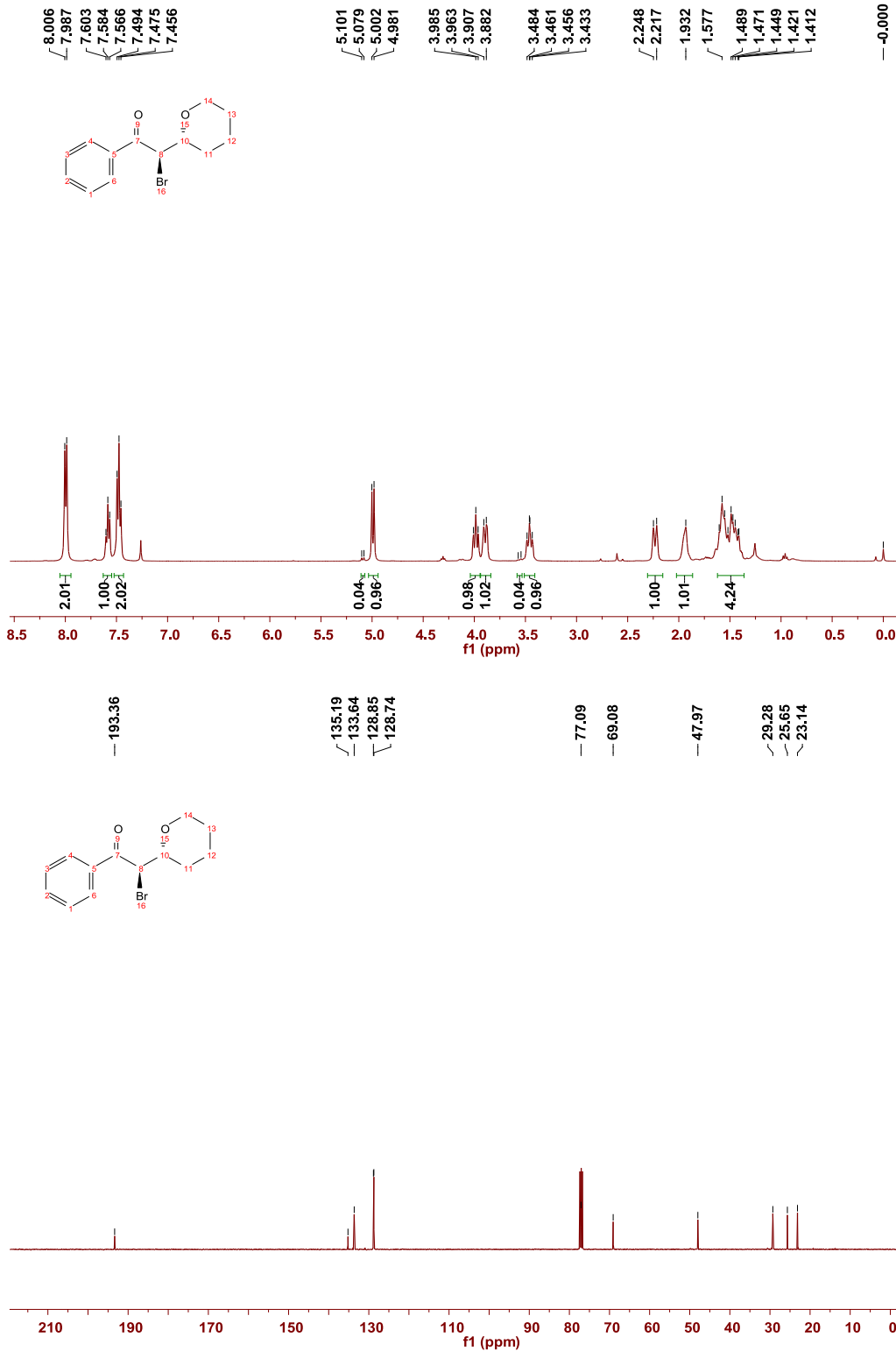
6.544
5.258
5.239
5.212
4.742
4.736
4.718
4.699
4.694
2.886
2.872
2.858
2.843
2.829
2.817
2.404
2.114
2.099
2.090
2.076
2.066
2.056
2.042
2.032
2.017
2.008
1.998
1.983
O
Cl
5.258
5.239
5.212
0.80
0.20
5.28
5.27
5.26
5.25
5.24
5.23
5.22
5.21
5.20
5.19
f1 (ppm)
2.19
1.09
2.21
2.14
0.96
0.80
0.20
0.80
0.20
1.03
2.20
1.09
1.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
192.83
153.67
135.16
133.92
127.41
121.69
120.78
116.82
75.33
56.83
23.69
23.62
O
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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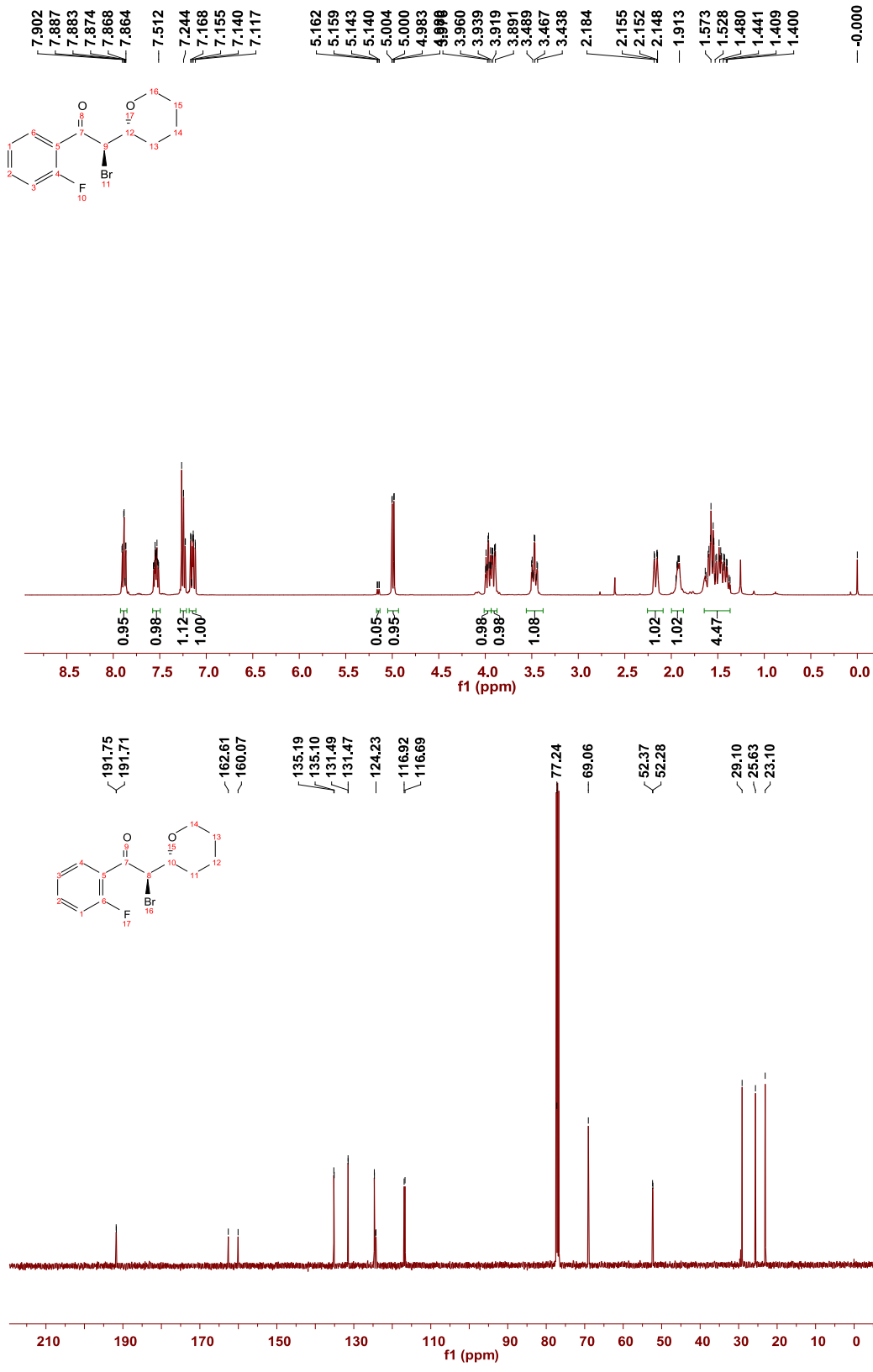
7.566
7.494
7.475
7.456
5.101
5.079
5.002
4.981
3.985
3.963
3.907
3.882
3.484
3.461
3.456
3.433
2.248
2.217
1.932
1.577
1.489
1.471
1.449
1.421
1.412
0.000
O
O
Br
2.01
1.00
2.02
0.04
0.96
0.98
1.02
0.04
0.96
1.00
1.01
4.24
f1 (ppm)
193.36
135.19
133.64
128.85
128.74
77.09
69.08
47.97
29.28
25.65
23.14
f1 (ppm)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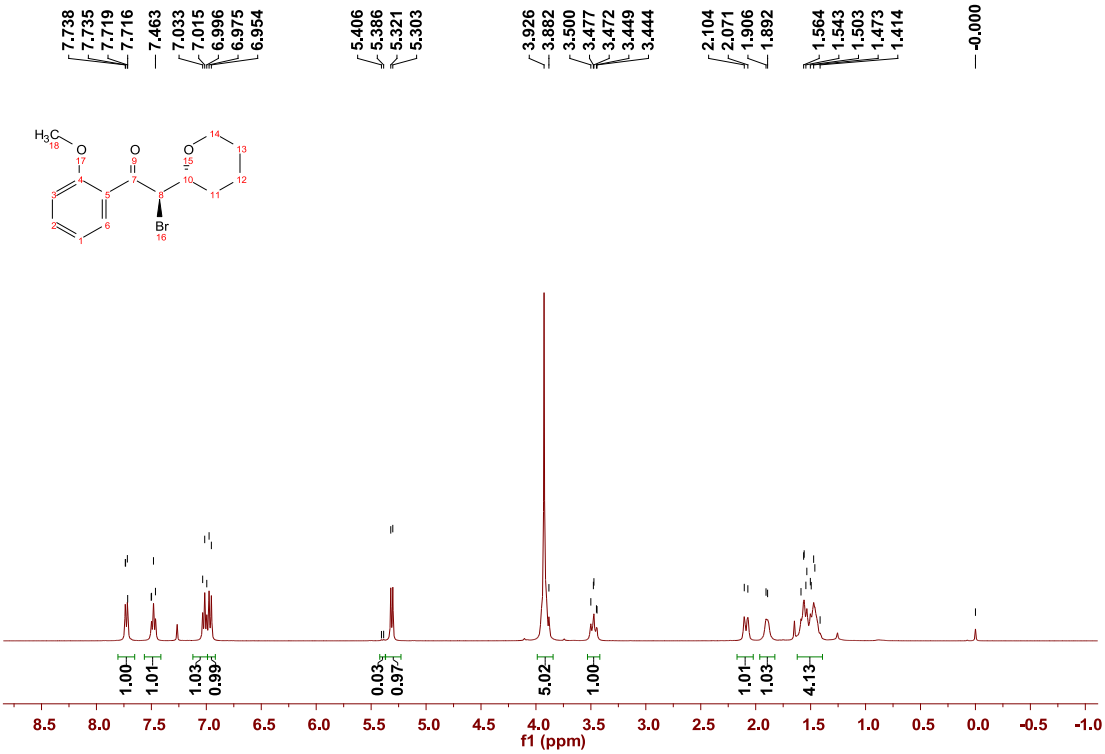
7.887
7.883
7.874
7.868
7.864
7.512
7.244
7.168
7.155
7.140
7.117
5.162
5.159
5.143
5.140
5.004
5.000
4.983
3.960
3.939
3.919
3.891
3.489
3.467
3.438
2.184
2.155
2.152
2.148
1.913
1.573
1.528
1.480
1.441
1.409
1.400
-0.000
O
O
Br
F
0.95
0.98
1.12
1.00
0.05
0.95
0.98
0.98
1.08
1.02
1.02
4.47
f1 (ppm)
191.75
191.71
162.61
160.07
135.19
135.10
131.49
131.47
124.23
116.92
116.69
77.24
69.06
52.37
52.28
29.10
25.63
23.10
f1 (ppm)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7.719
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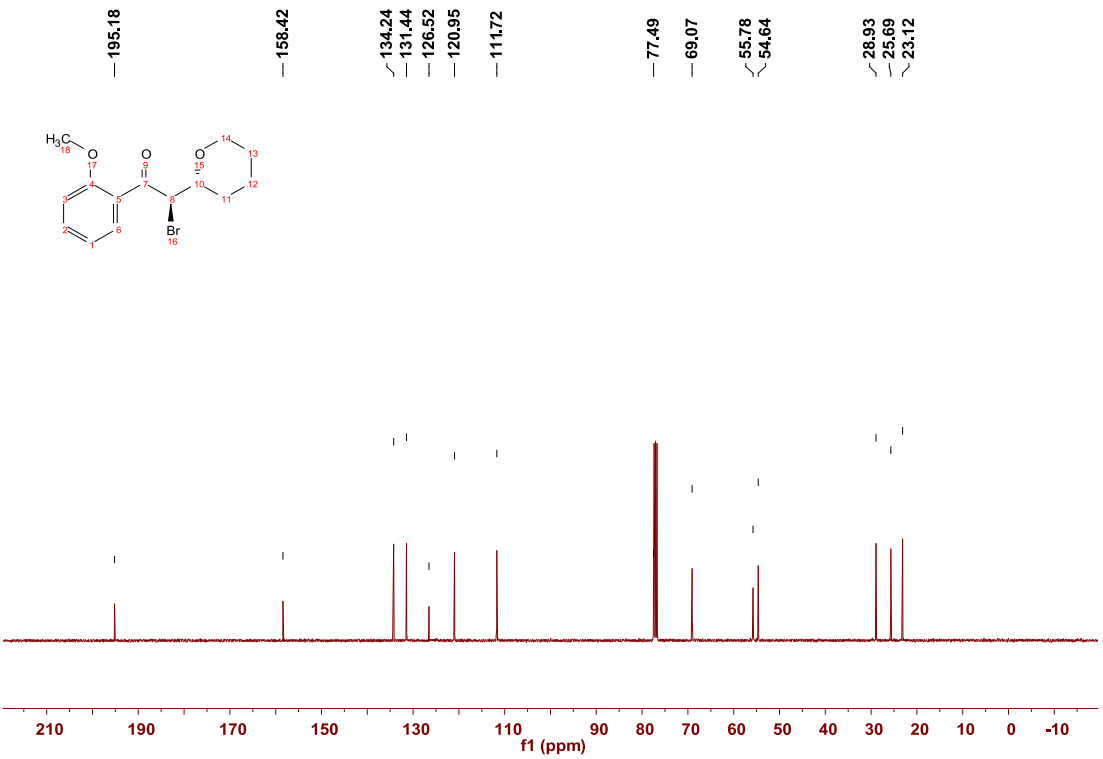
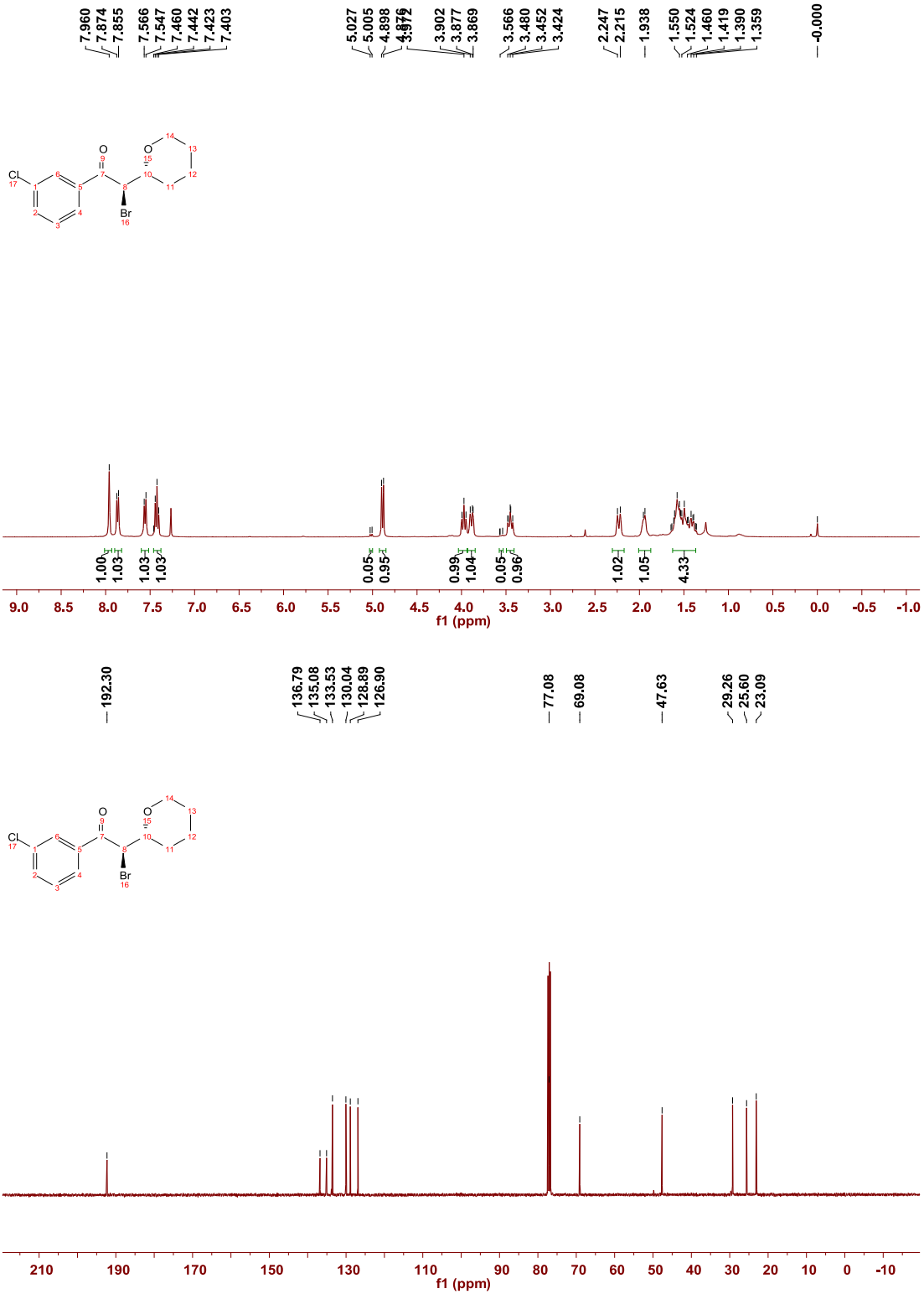
7.033
7.015
6.996
6.975
6.954
5.406
5.386
5.321
5.303
3.926
3.882
3.500
3.477
3.472
3.449
3.444
2.104
2.071
1.906
1.892
1.564
1.543
1.503
1.473
1.414
-0.000
1.00
1.01
1.03
0.99
0.03
0.97
5.02
1.00
1.01
1.03
4.13
f1 (ppm)


195.18
158.42
134.24
131.44
126.52
120.95
111.72
77.49
69.07
55.78
54.64
28.93
25.69
23.12
f1 (ppm)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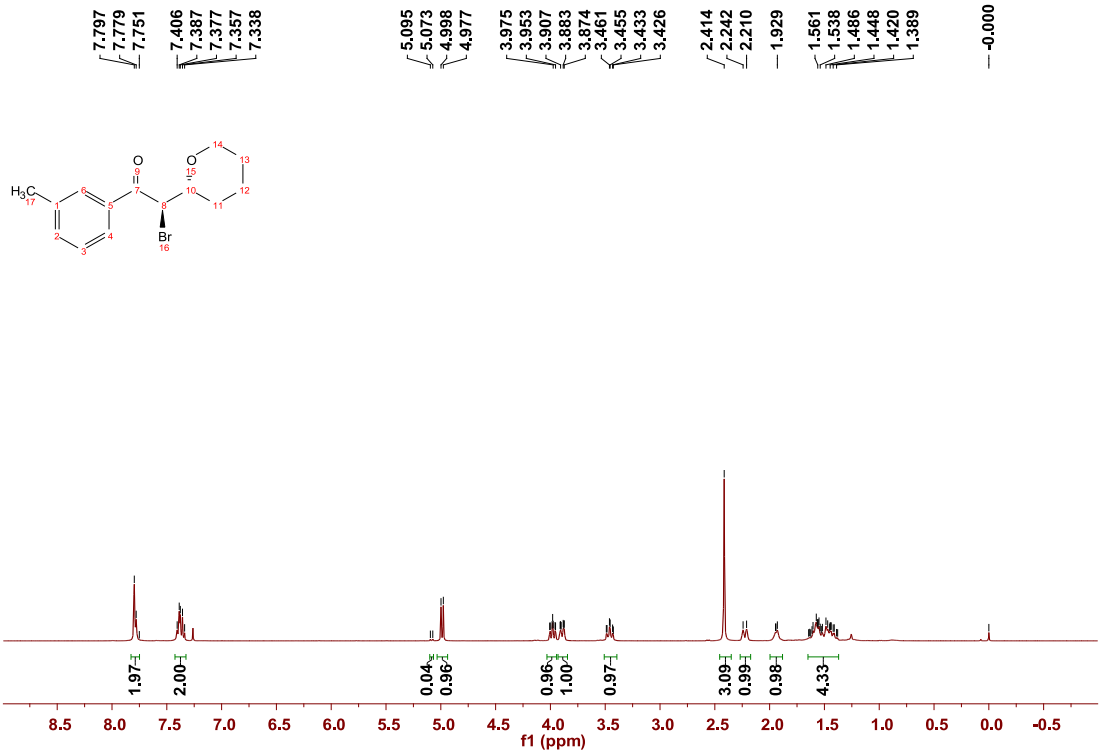
7.566
7.547
7.460
7.442
7.423
7.403
5.027
5.005
4.898
3.902
3.877
3.869
3.566
3.480
3.452
3.424
2.247
2.215
1.938
1.550
1.524
1.460
1.419
1.390
1.359
0.000
Cl
O
O
Br
1.00
1.03
1.03
1.03
0.05
0.95
0.99
1.04
0.05
0.96
1.02
1.05
4.33
f1 (ppm)
192.30
136.79
135.08
133.53
130.04
128.89
126.90
77.08
69.08
47.63
29.26
25.60
23.09
f1 (ppm)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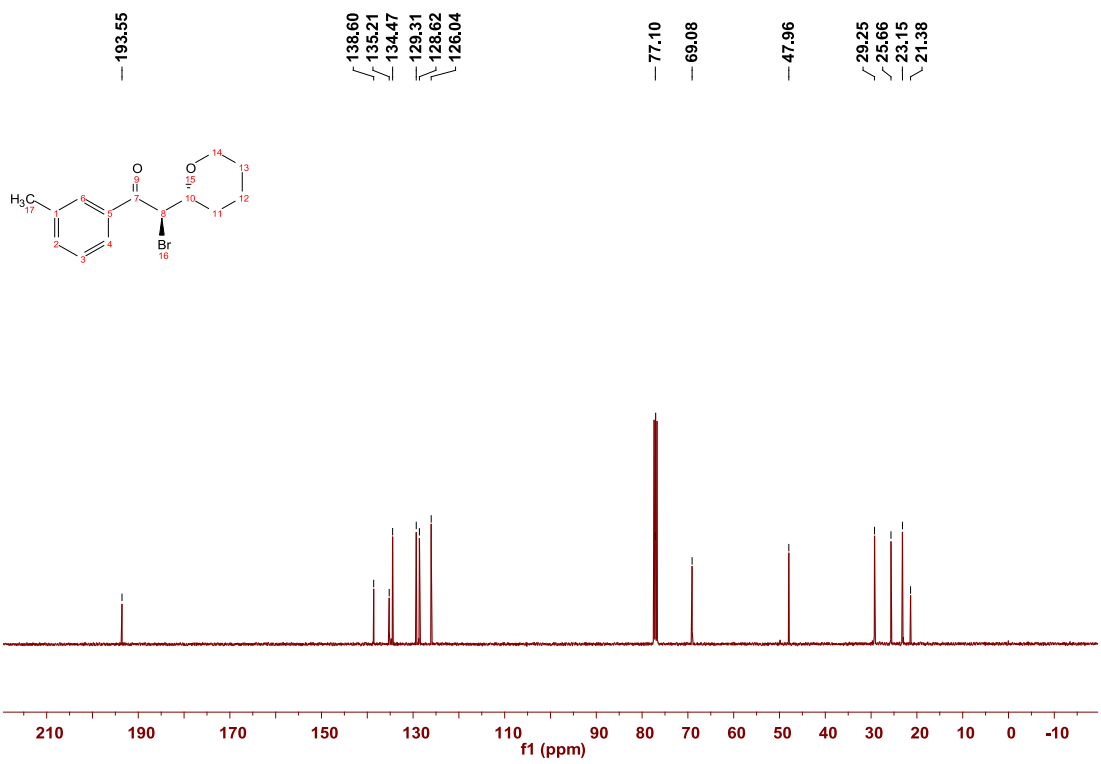
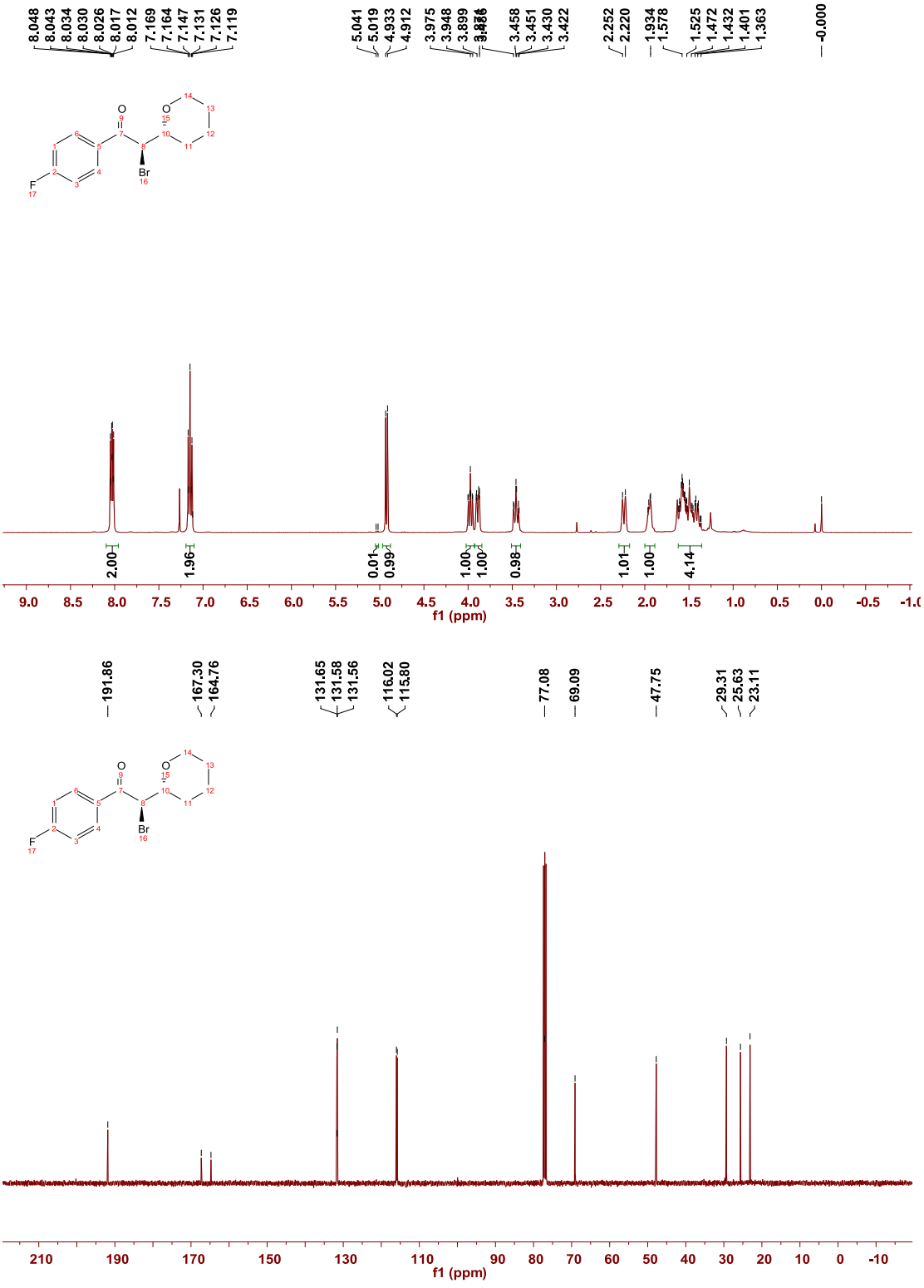
7.387
7.377
7.357
7.338
5.095
5.073
4.998
4.977
3.975
3.953
3.907
3.883
3.874
3.461
3.455
3.433
3.426
2.414
2.242
2.210
1.929
1.561
1.538
1.486
1.448
1.420
1.389
0.000
1.97
2.00
0.04
0.96
0.96
1.00
0.97
3.09
0.99
0.98
4.33
f1 (ppm)


193.55
138.60
135.21
134.47
129.31
128.62
126.04
77.10
69.08
47.96
29.25
25.66
23.15
21.38
f1 (ppm)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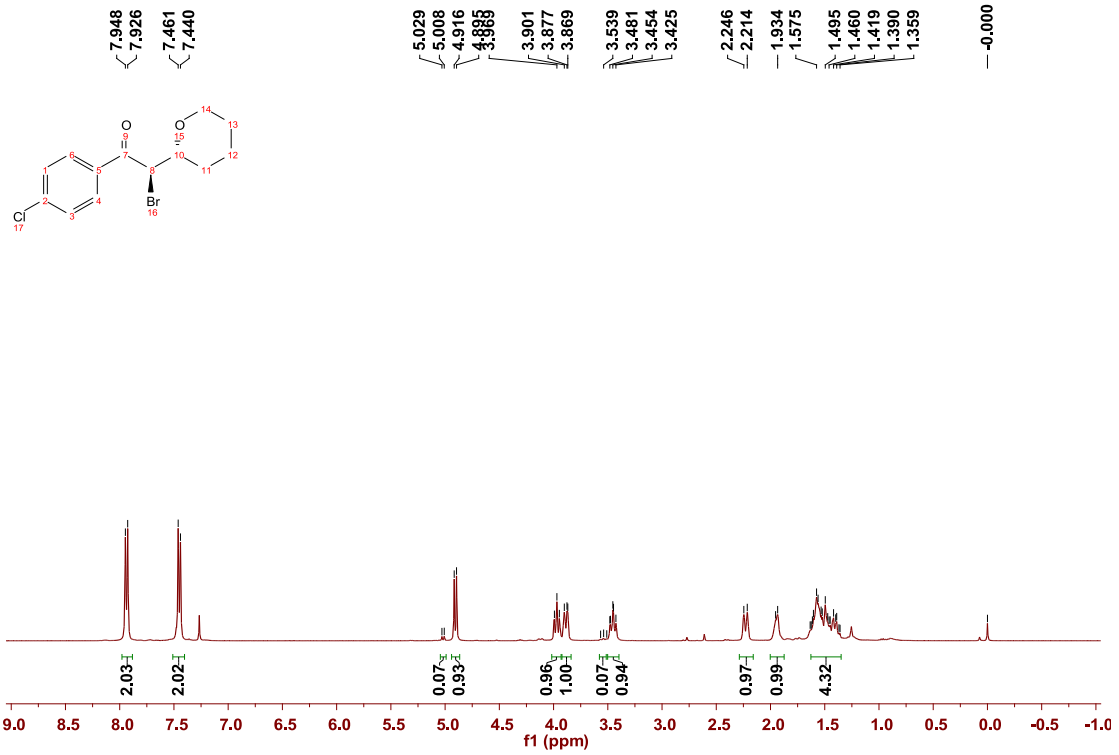
8.030
8.026
8.017
8.012
7.169
7.164
7.147
7.131
7.126
7.119
5.041
5.019
4.933
4.912
3.975
3.948
3.899
3.458
3.451
3.430
3.422
2.252
2.220
1.934
1.578
1.525
1.472
1.432
1.401
1.363
-0.000
2.00
1.96
0.01
0.99
1.00
1.00
0.98
1.01
1.00
4.14
f1 (ppm)
191.86
167.30
164.76
131.65
131.58
131.56
116.02
115.80
77.08
69.09
47.75
29.31
25.63
23.11
f1 (ppm)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7.926
7.461
7.440
5.029
5.008
4.916
3.901
3.877
3.869
3.539
3.481
3.454
3.425
2.246
2.214
1.934
1.575
1.495
1.460
1.419
1.390
1.359
-0.000
2.03
2.02
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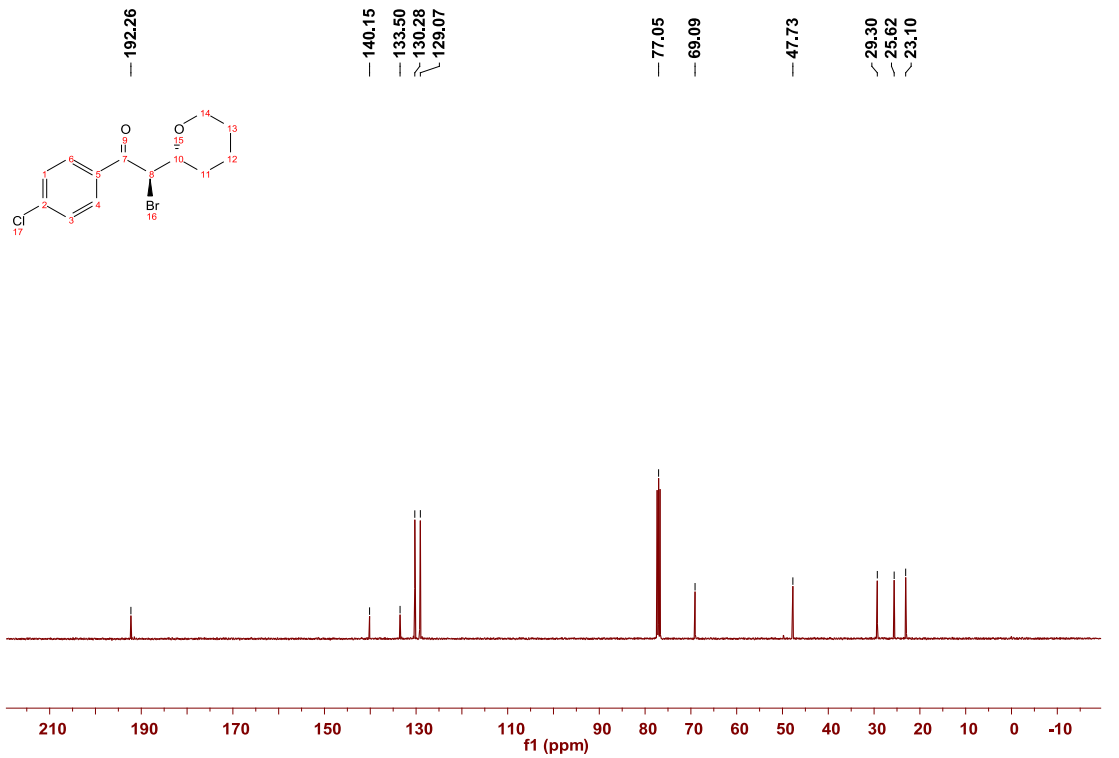
0.93
0.96
1.00
0.07
0.94
0.97
0.99
4.32
f1 (ppm)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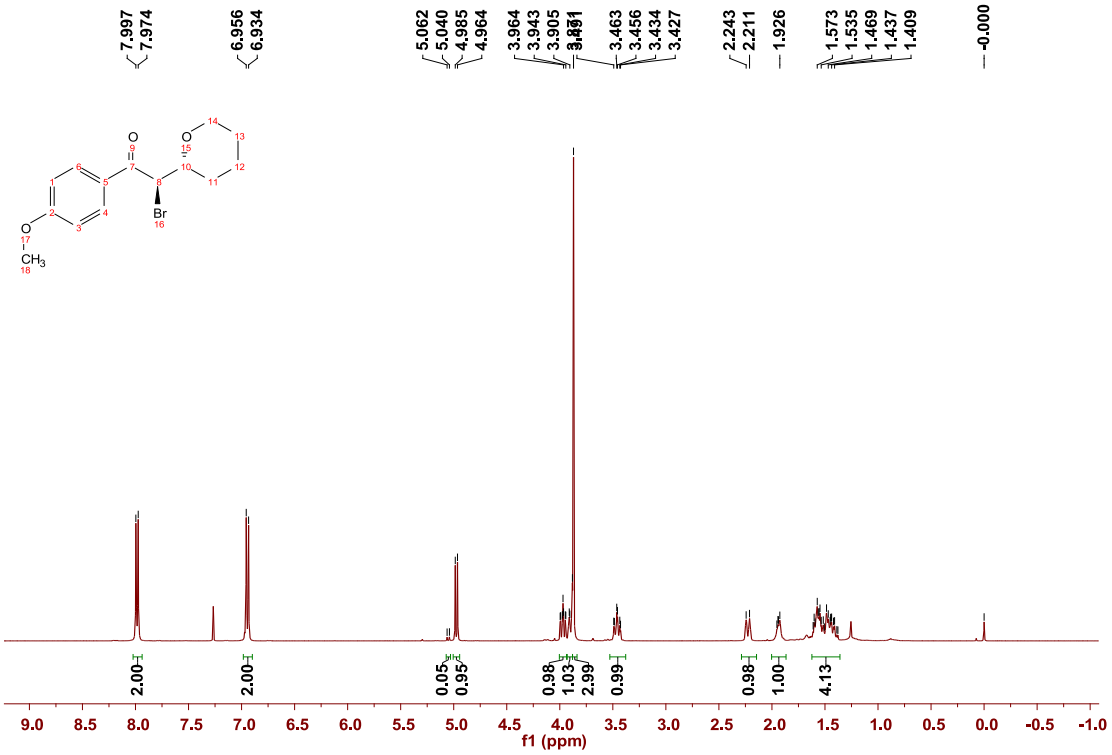
129.07
77.05
69.09
47.73
29.30
25.62
23.10
f1 (ppm)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7.974
6.956
6.934
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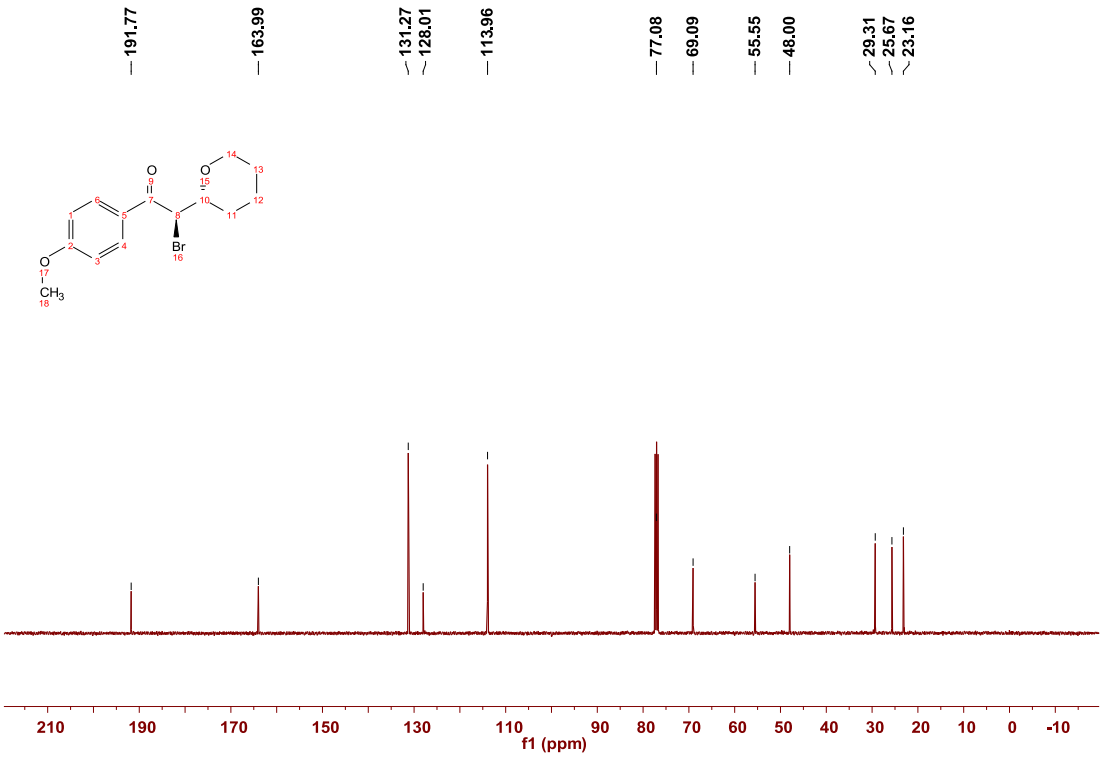
5.040
4.985
4.964
3.964
3.943
3.905
3.463
3.456
3.434
3.427
2.243
2.211
1.926
1.573
1.535
1.469
1.437
1.409
-0.000
2.00
2.00
0.05
0.95
0.98
1.03
2.99
0.99
0.98
1.00
4.13
f1 (ppm)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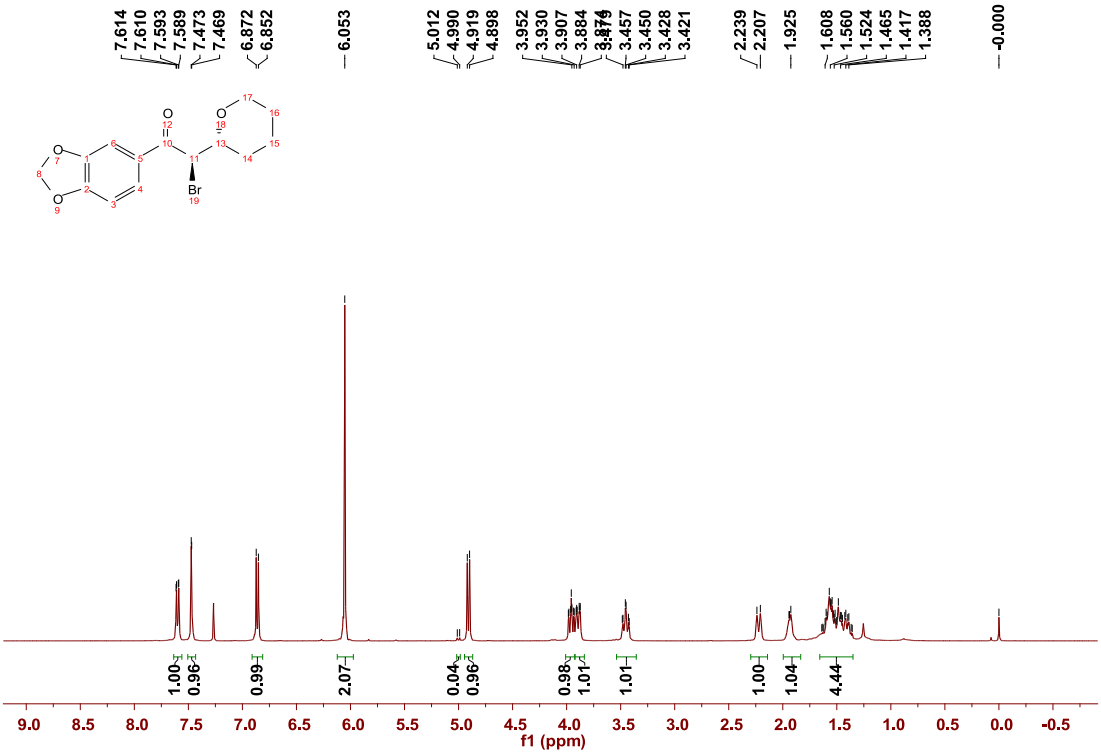
128.01
113.96
77.08
69.09
55.55
48.00
29.31
25.67
23.16
f1 (ppm)


8.068
8.063
7.799
7.569
7.548
4.983
4.962
4.847
4.826
3.954
3.895
3.445
3.438
3.416
3.409
2.243
2.211
1.939
1.613
1.575
1.535
1.475
1.407
1.379
-0.000
Cl
Cl
Br
O
O
1.00
1.03
1.04
0.05
0.95
0.99
1.00
1.01
0.97
1.03
4.42
f1 (ppm)
191.412
138.246
134.790
133.475
130.810
130.794
127.834
77.098
69.083
47.494
29.281
25.582
23.070
f1 (ppm)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7.593
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7.469
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6.852
6.053
5.012
4.990
4.919
4.898
3.952
3.930
3.907
3.884
3.457
3.450
3.428
3.421
2.239
2.207
1.925
1.608
1.560
1.524
1.465
1.417
1.388
-0.000
1.00
0.96
0.99
2.07
0.04
0.96
0.98
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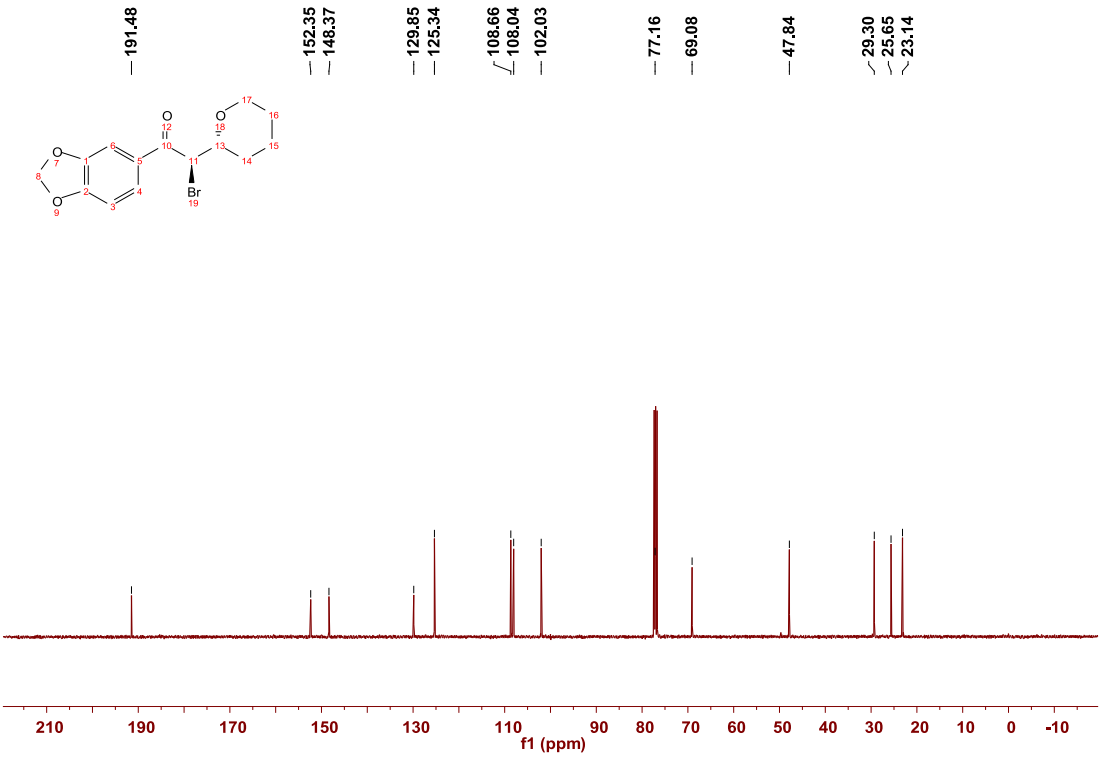
1.01
1.00
1.04
4.44
f1 (ppm)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125.34
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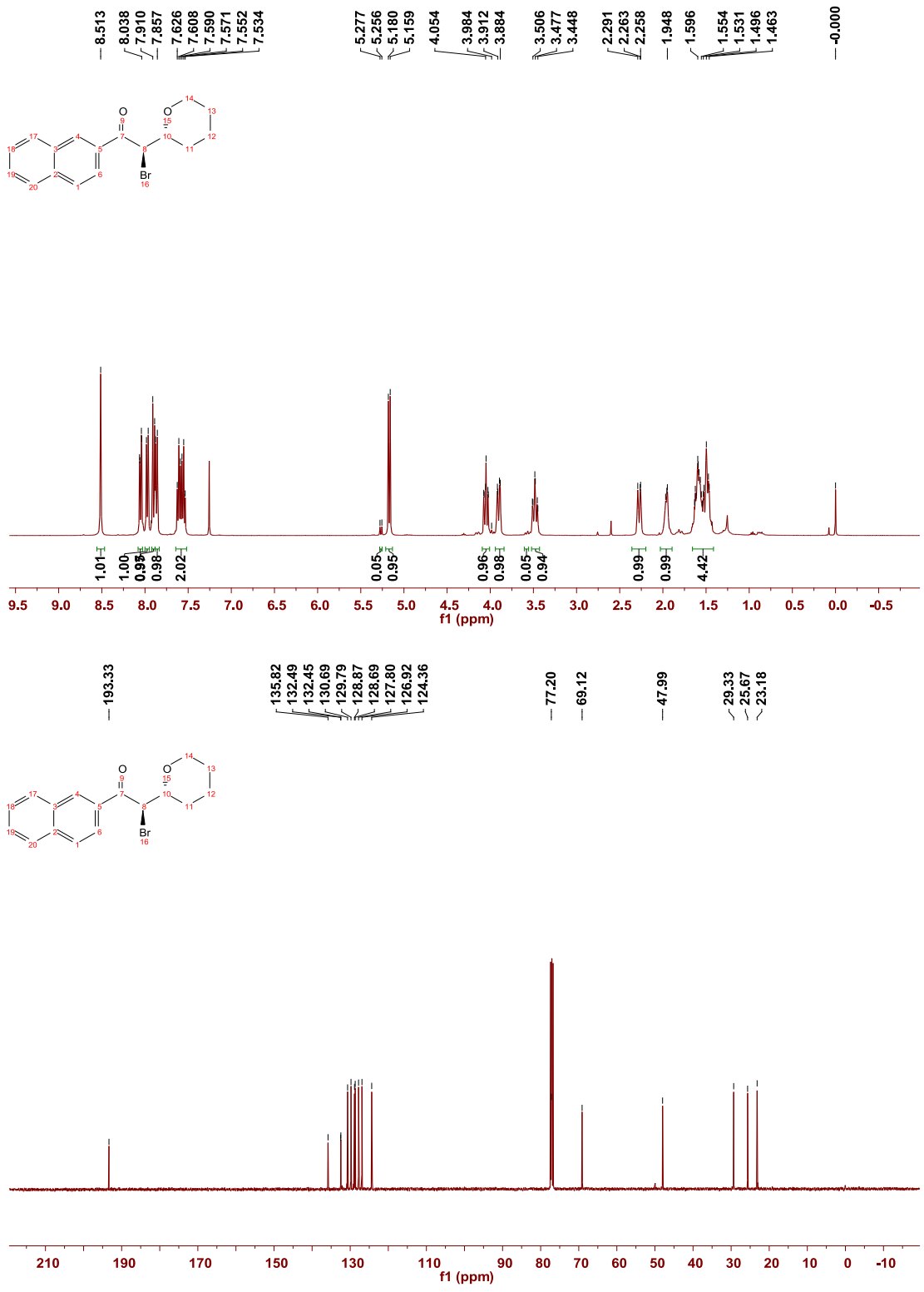
108.04
102.03
77.16
69.08
47.84
29.30
25.65
23.14
f1 (ppm)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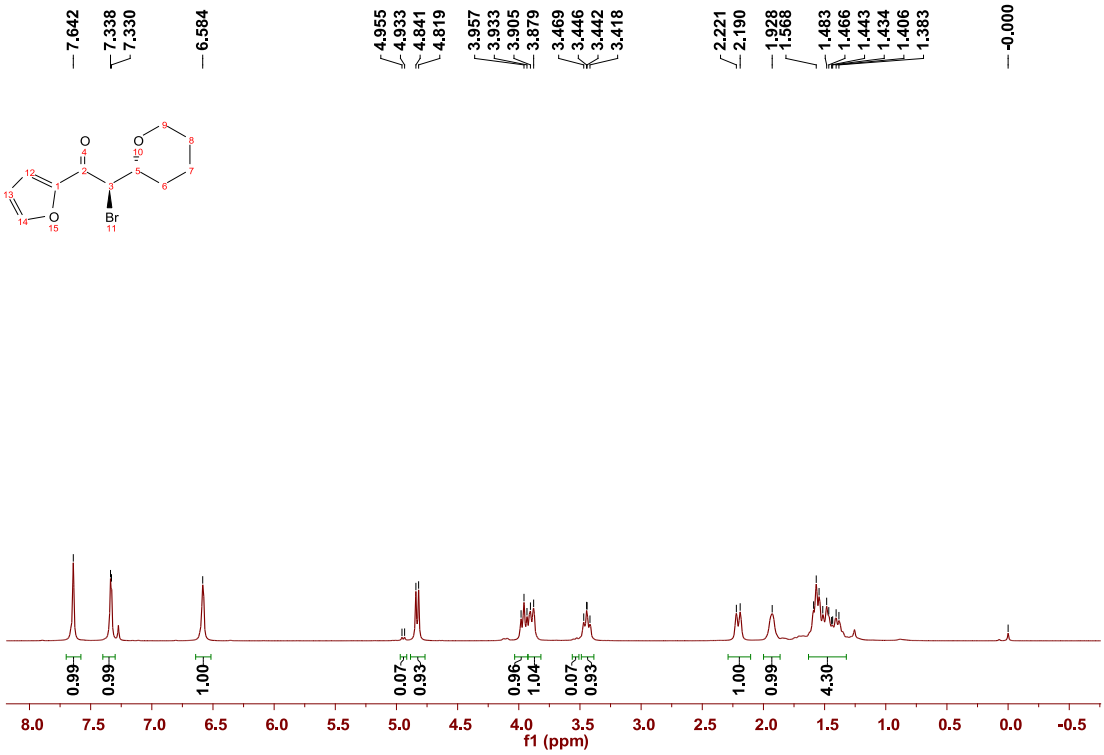
7.626
7.608
7.590
7.571
7.552
7.534
5.277
5.256
5.180
5.159
4.054
3.984
3.912
3.884
3.506
3.477
3.448
2.291
2.263
2.258
1.948
1.596
1.554
1.531
1.496
1.463
0.000
1.01
1.00
0.95
0.98
2.02
0.05
0.95
0.96
0.98
0.05
0.94
0.99
0.99
4.42
f1 (ppm)
193.33
135.82
132.49
132.45
130.69
129.79
128.87
128.69
127.80
126.92
124.36
77.20
69.12
47.99
29.33
25.67
23.18
f1 (ppm)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6.584
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4.933
4.841
4.819
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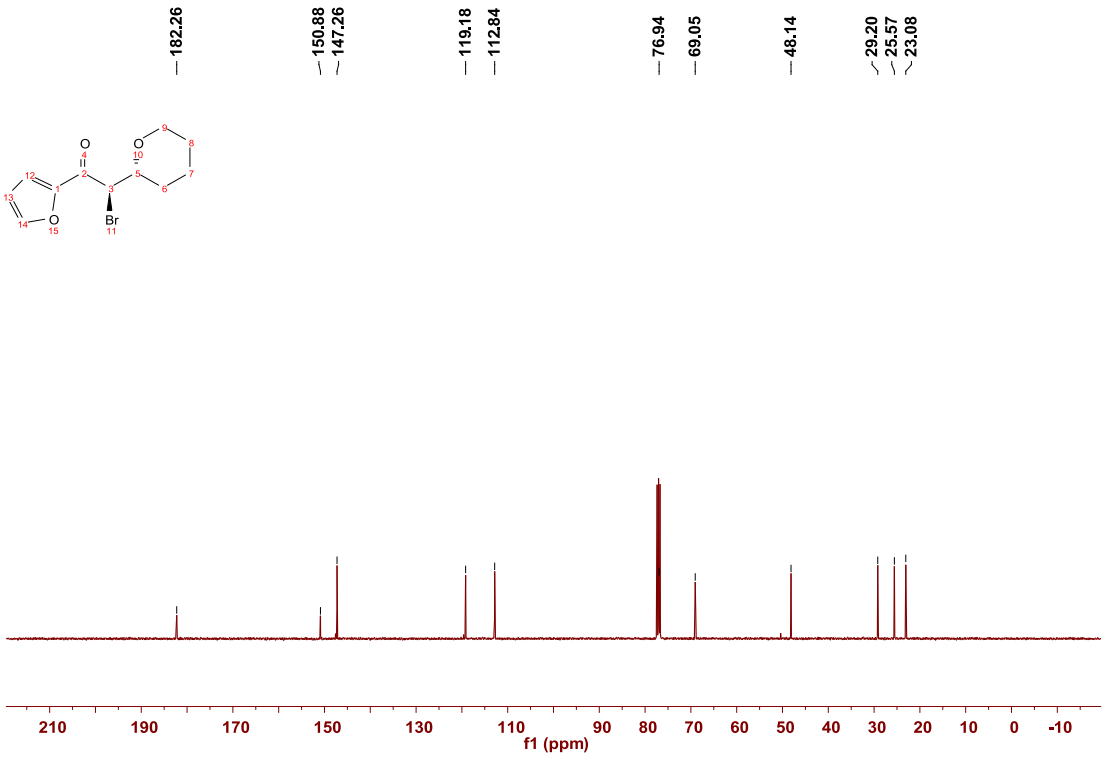
3.933
3.905
3.879
3.469
3.446
3.442
3.418
2.221
2.190
1.928
1.568
1.483
1.466
1.443
1.434
1.406
1.383
0.000
O
O
Br
0.99
0.99
1.00
0.07
0.93
0.96
1.04
0.07
0.93
1.00
0.99
4.30
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


182.26
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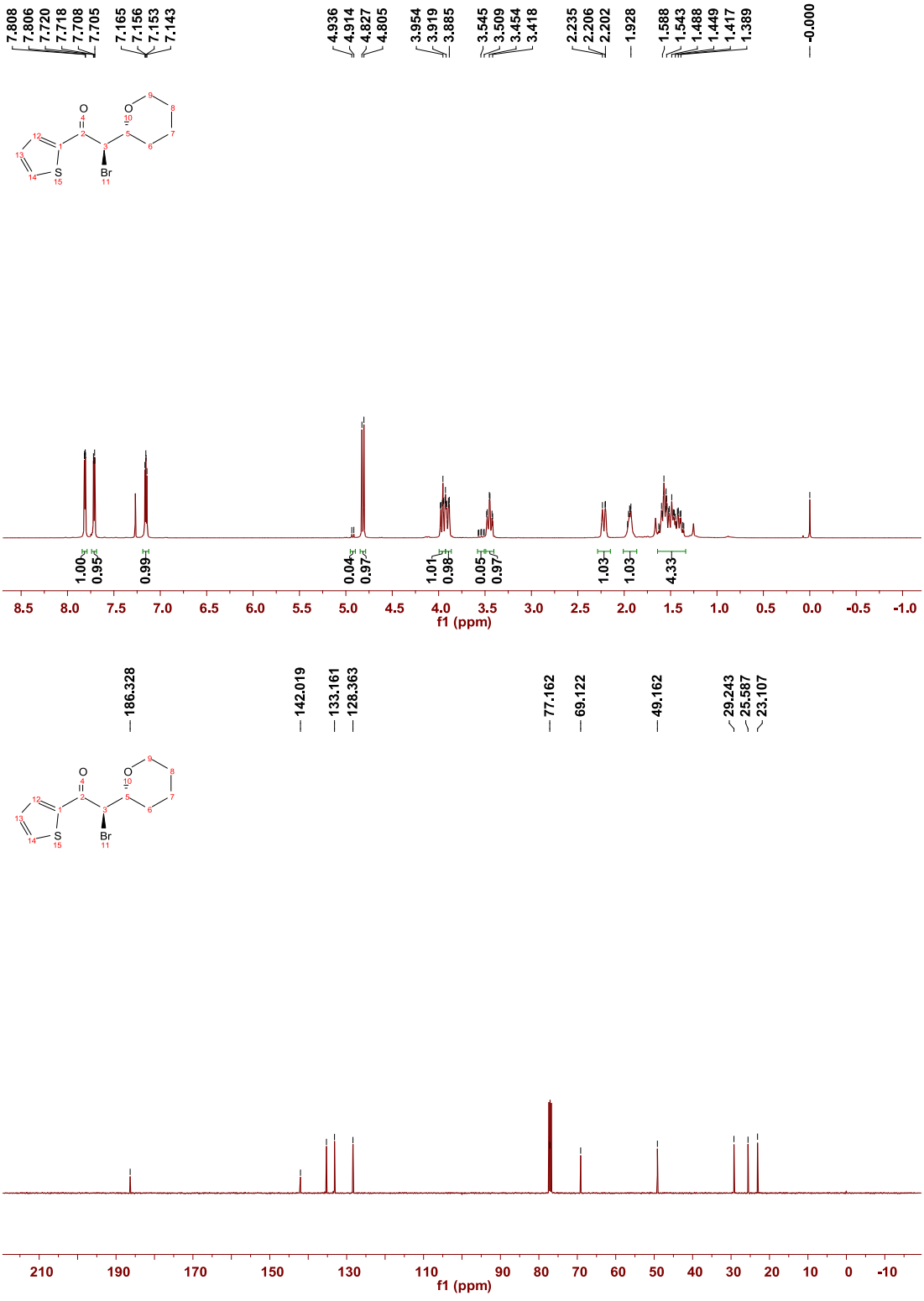
147.26
119.18
112.84
76.94
69.05
48.14
29.20
25.57
23.08
O
O
Br
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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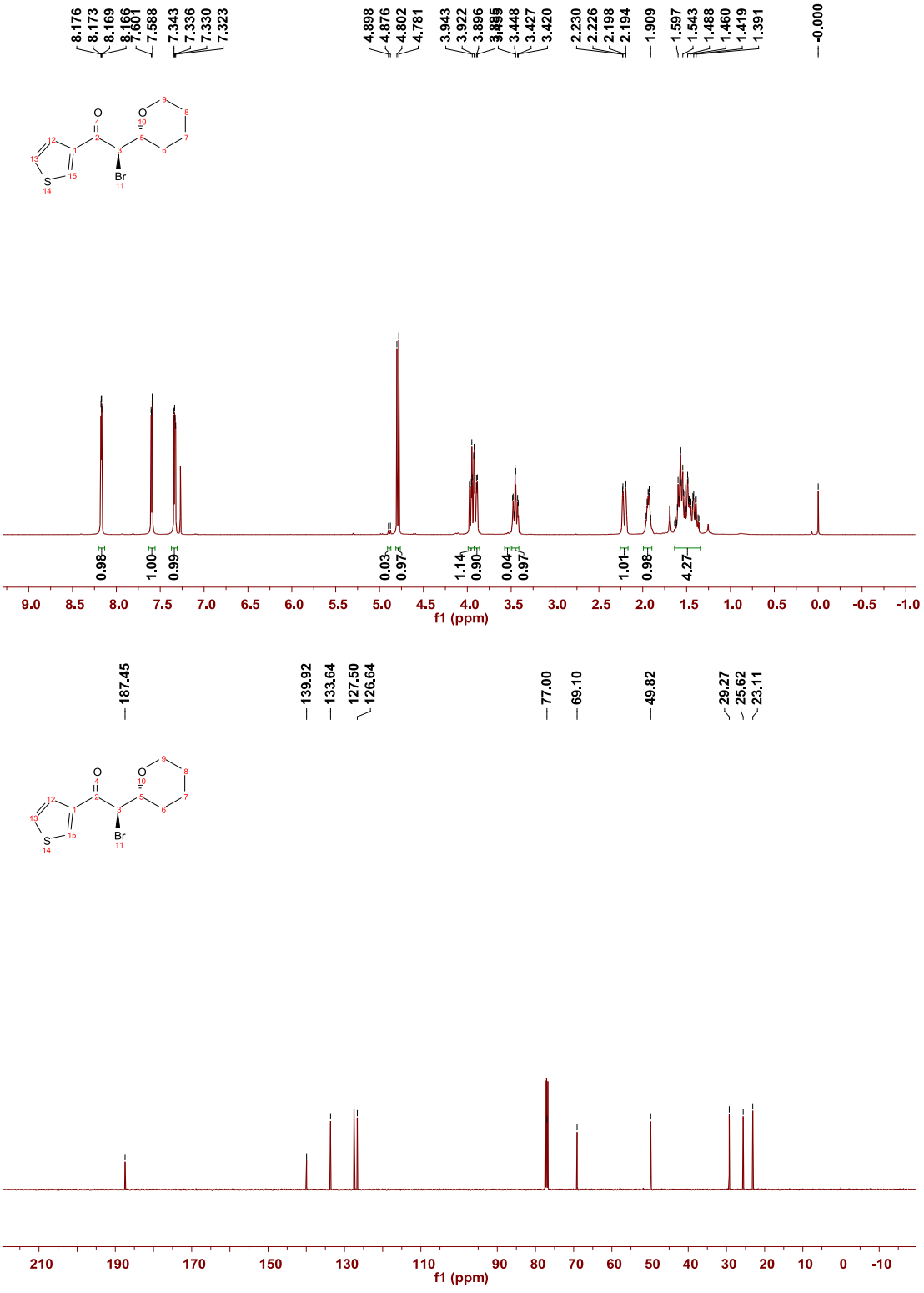
7.806
7.720
7.718
7.708
7.705
7.165
7.156
7.153
7.143
4.936
4.914
4.827
4.805
3.954
3.919
3.885
3.545
3.509
3.454
3.418
2.235
2.206
2.202
1.928
1.588
1.543
1.488
1.449
1.417
1.389
0.000
1.00
0.95
0.99
0.04
0.97
1.01
0.98
0.05
0.97
1.03
1.03
4.33
f1 (ppm)
186.328
142.019
133.161
128.363
77.162
69.122
49.162
29.243
25.587
23.107
f1 (ppm)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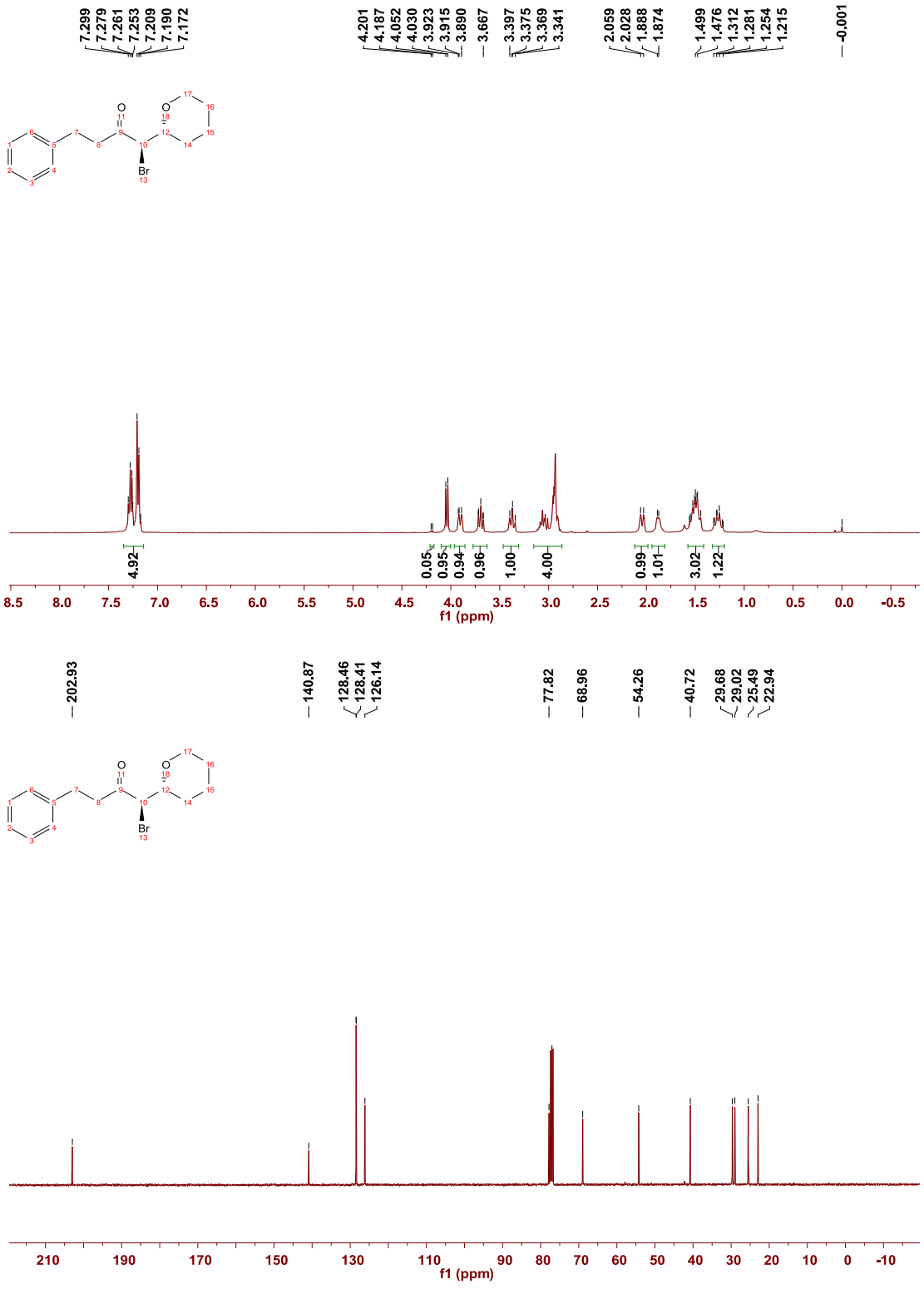
8.173
8.169
8.166
7.601
7.588
7.343
7.336
7.330
7.323
4.898
4.876
4.802
4.781
3.943
3.922
3.896
3.448
3.427
3.420
2.230
2.226
2.198
2.194
1.909
1.597
1.543
1.488
1.460
1.419
1.391
0.000
0.98
1.00
0.99
0.03
0.97
1.14
0.90
0.04
0.97
1.01
0.98
4.27
f1 (ppm)
187.45
139.92
133.64
127.50
126.64
77.00
69.10
49.82
29.27
25.62
23.11
f1 (ppm)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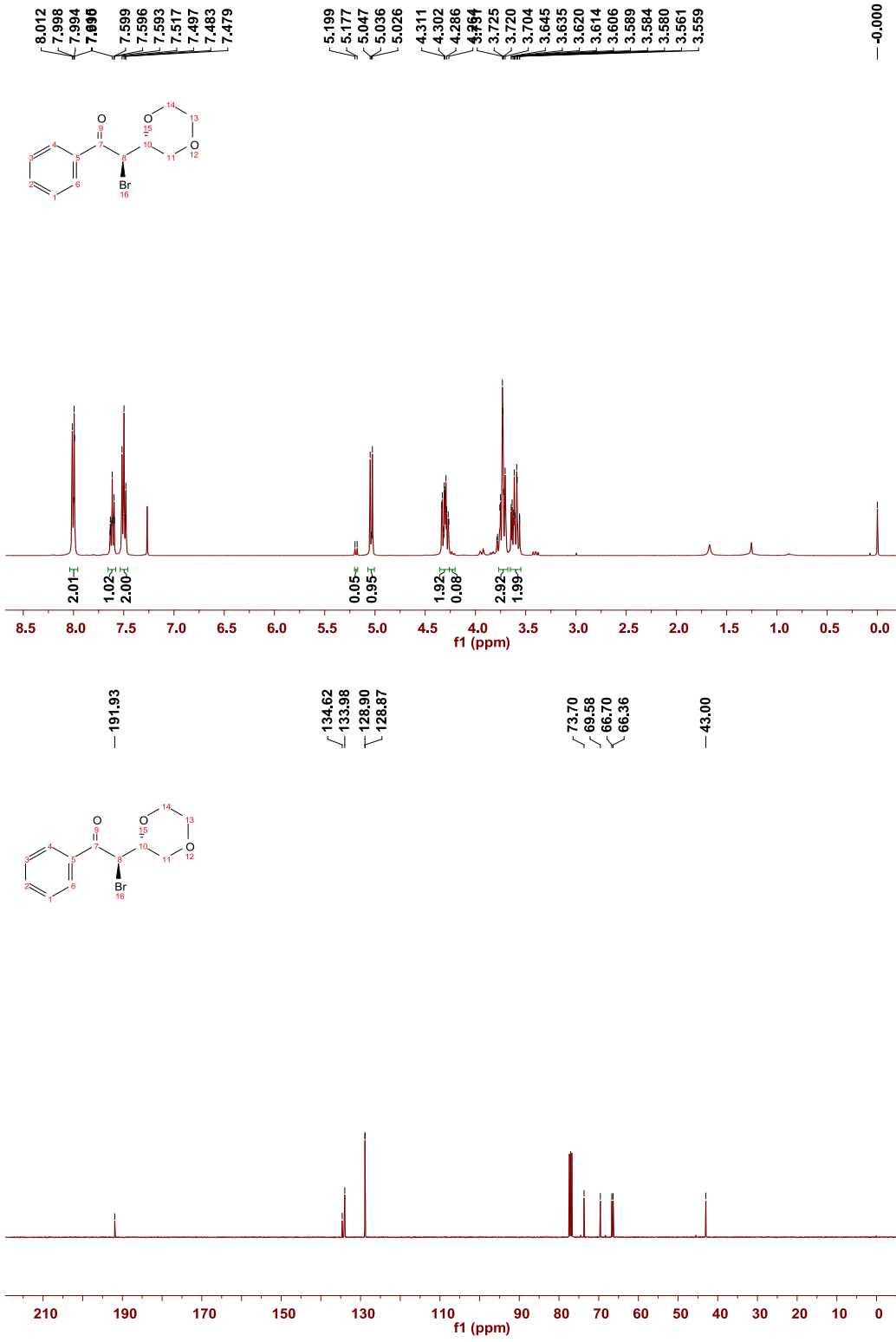
7.279
7.261
7.253
7.209
7.190
7.172
4.201
4.187
4.052
4.030
3.923
3.915
3.890
3.667
3.397
3.375
3.369
3.341
2.059
2.028
1.888
1.874
1.499
1.476
1.312
1.281
1.254
1.215
-0.001
Br
4.92
0.05
0.95
0.94
0.96
1.00
4.00
0.99
1.01
3.02
1.22
f1 (ppm)
202.93
140.87
128.46
128.41
126.14
77.82
68.96
54.26
40.72
29.68
29.02
25.49
22.94
f1 (ppm)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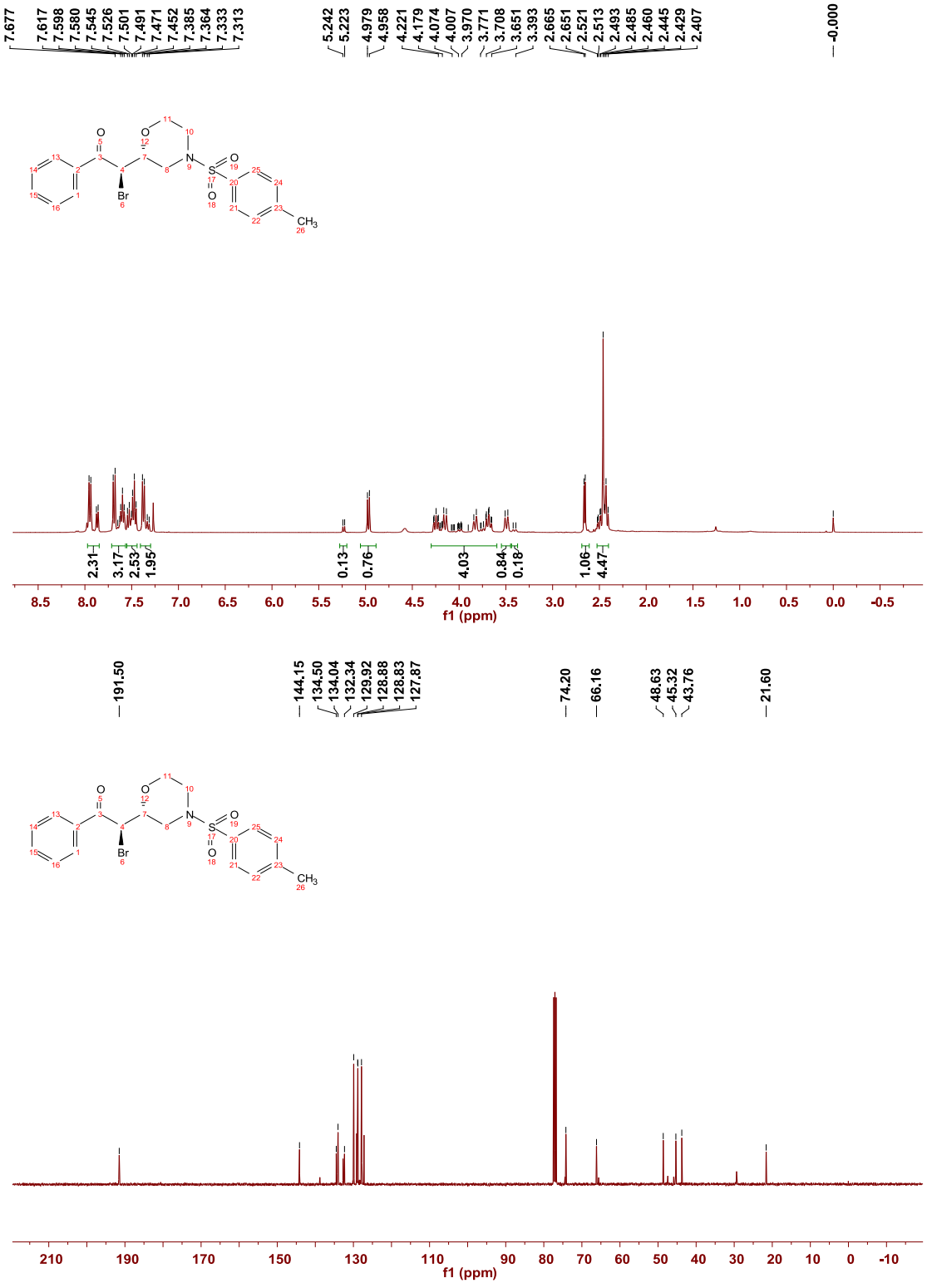
7.998
7.994
7.599
7.596
7.593
7.517
7.497
7.483
7.479
5.199
5.177
5.047
5.036
5.026
4.311
4.302
4.286
3.725
3.720
3.704
3.645
3.635
3.620
3.614
3.606
3.589
3.584
3.580
3.561
3.559
0.000
Br
2.01
1.02
2.00
0.05
0.95
1.92
0.08
2.92
1.99
f1 (ppm)
191.93
134.62
133.98
128.90
128.87
73.70
69.58
66.70
66.36
43.00
Br
f1 (ppm)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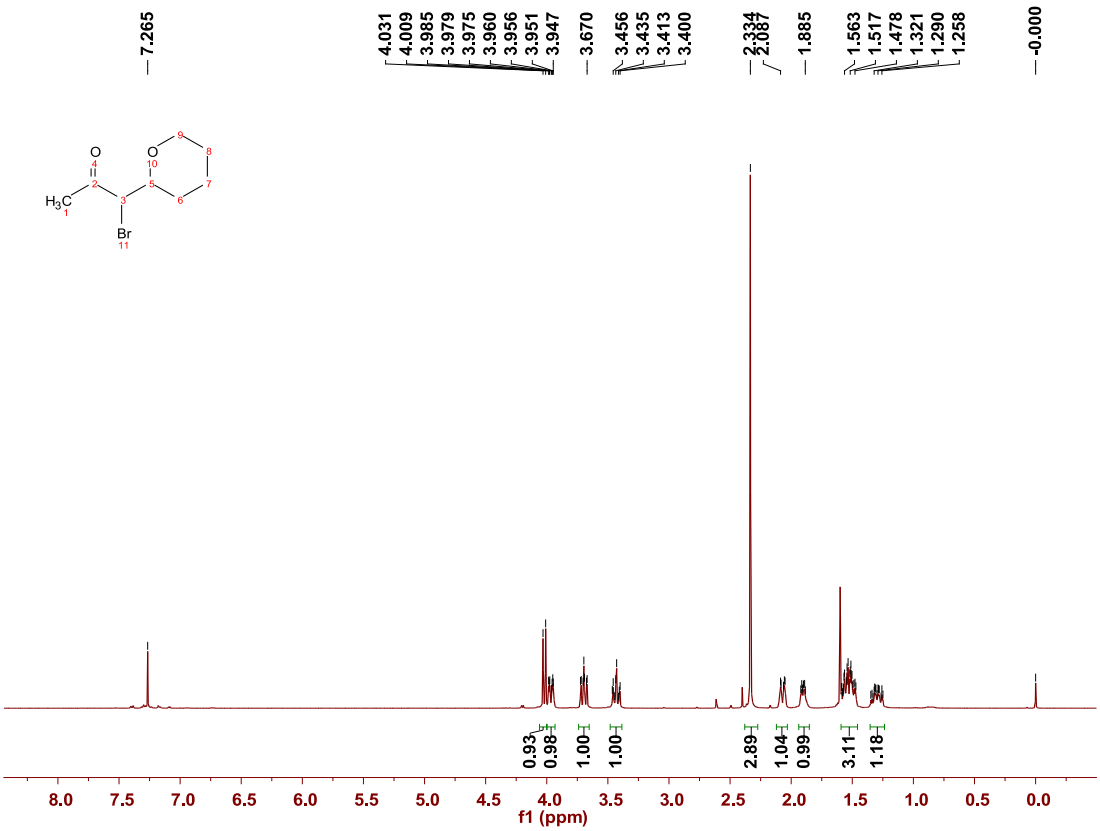
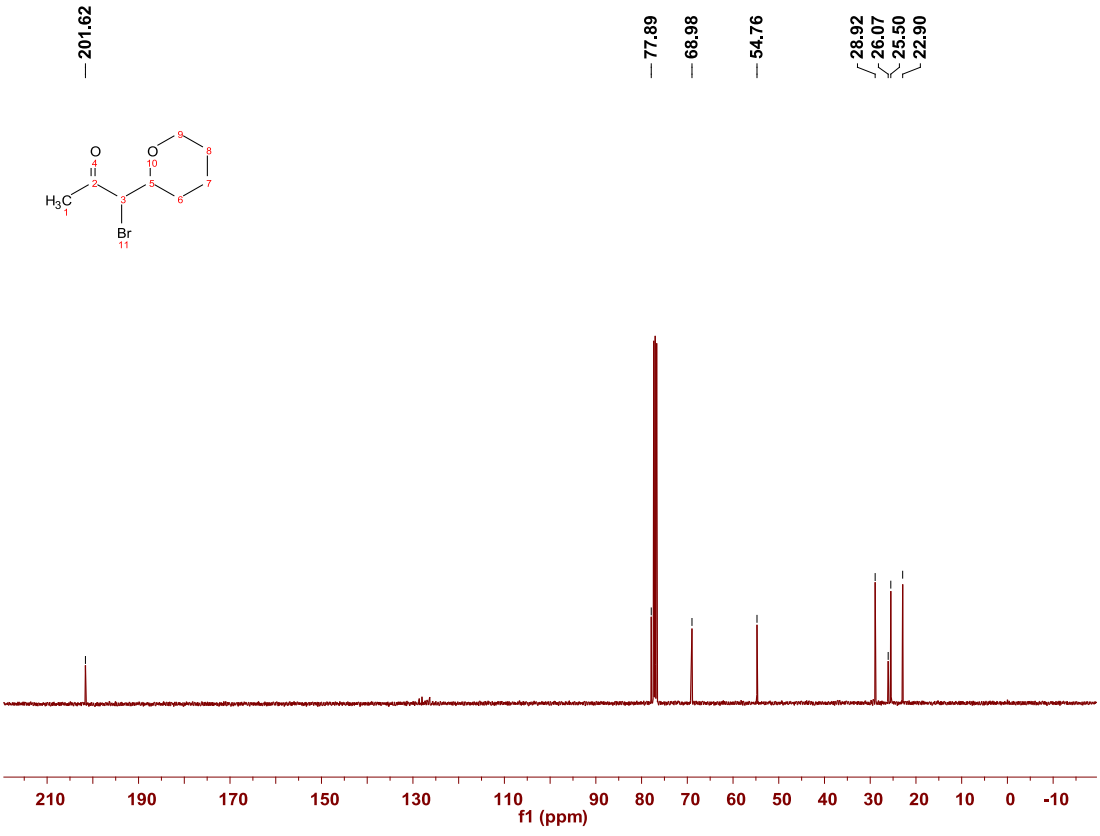
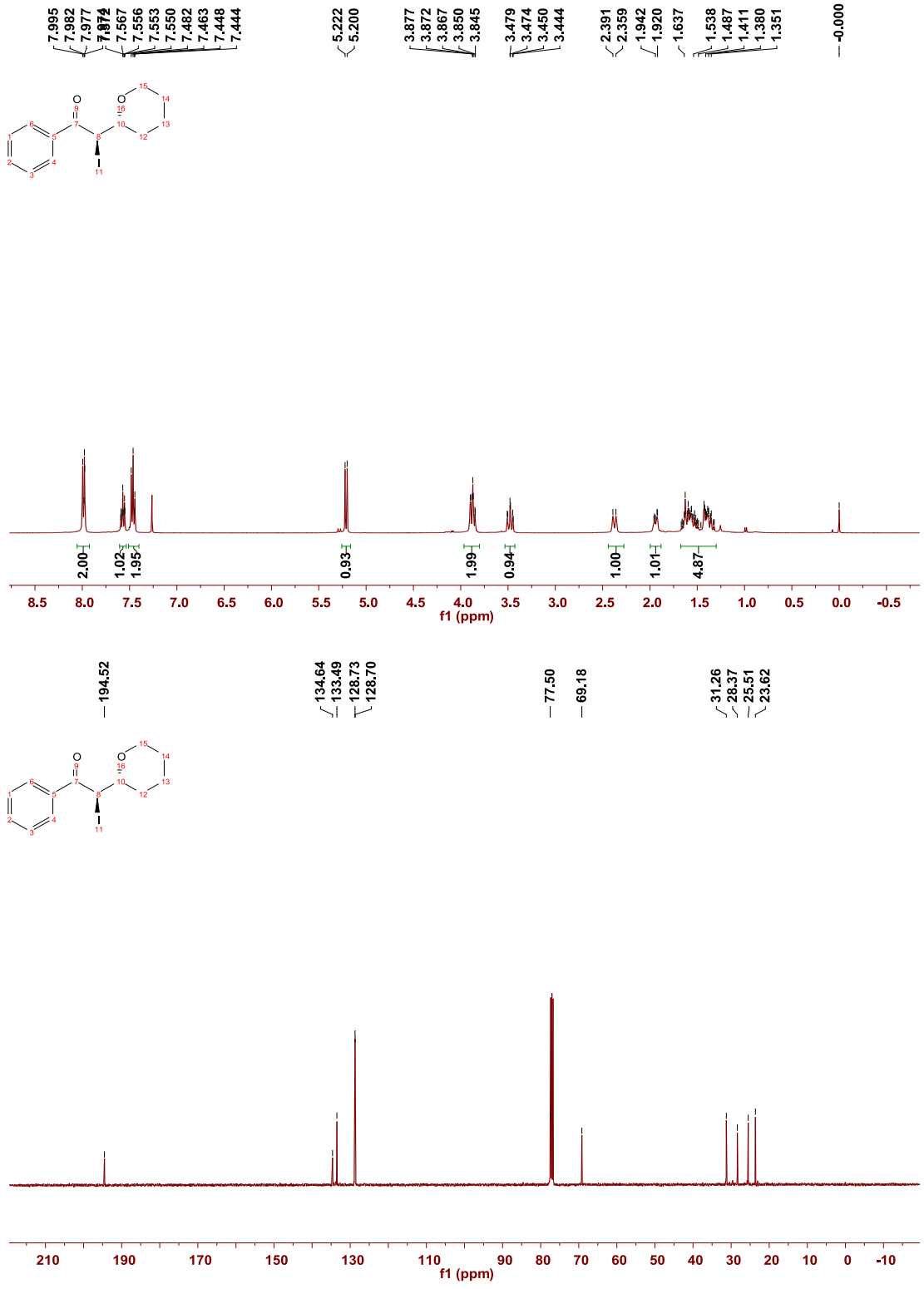
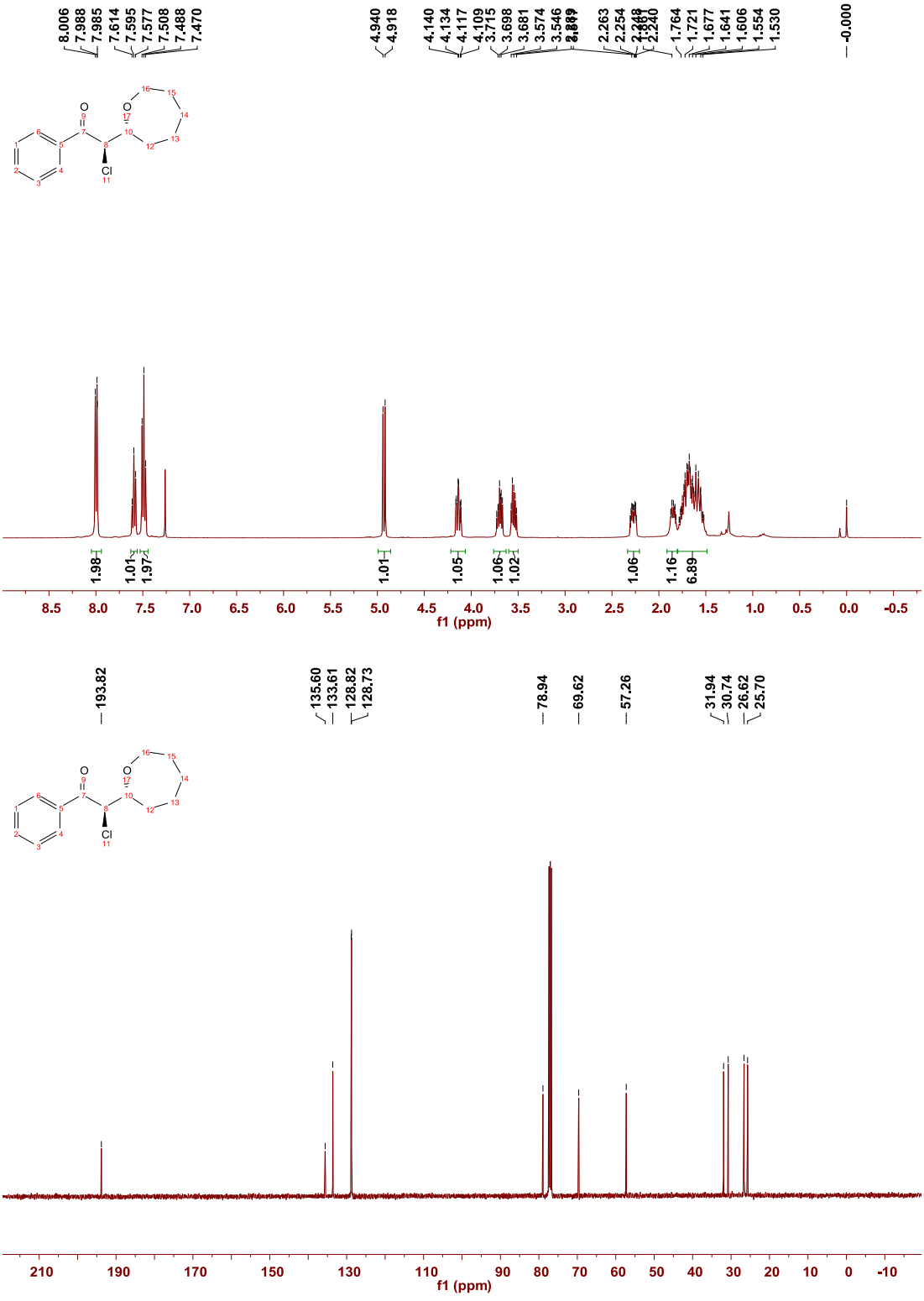
7.617
7.598
7.580
7.545
7.526
7.501
7.491
7.471
7.452
7.385
7.364
7.333
7.313
5.242
5.223
4.979
4.958
4.221
4.179
4.074
4.007
3.970
3.771
3.708
3.651
3.393
2.665
2.651
2.521
2.513
2.493
2.485
2.460
2.445
2.429
2.407
-0.000
Br
CH3
2.31
3.17
2.53
1.95
0.13
0.76
4.03
0.84
0.18
1.06
4.47
f1 (ppm)
191.50
144.15
134.50
134.04
132.34
129.92
128.88
128.83
127.87
74.20
66.16
48.63
45.32
43.76
21.60
f1 (ppm)


7.265
4.031
4.009
3.985
3.979
3.975
3.960
3.956
3.951
3.947
3.670
3.456
3.435
3.413
3.400
2.334
2.087
1.885
1.563
1.517
1.478
1.321
1.290
1.258
-0.000
0.93
0.98
1.00
1.00
2.89
1.04
0.99
3.11
1.18
f1 (ppm)


201.62
77.89
68.98
54.76
28.92
26.07
25.50
22.90
f1 (ppm)


7.995
7.982
7.977
7.567
7.556
7.553
7.550
7.482
7.463
7.448
7.444
5.222
5.200
3.877
3.872
3.867
3.850
3.845
3.479
3.474
3.450
3.444
2.391
2.359
1.942
1.920
1.637
1.538
1.487
1.411
1.380
1.351
0.000
2.00
1.02
1.95
0.93
1.99
0.94
1.00
1.01
4.87
f1 (ppm)
194.52
134.64
133.49
128.73
128.70
77.50
69.18
31.26
28.37
25.51
23.62
f1 (ppm)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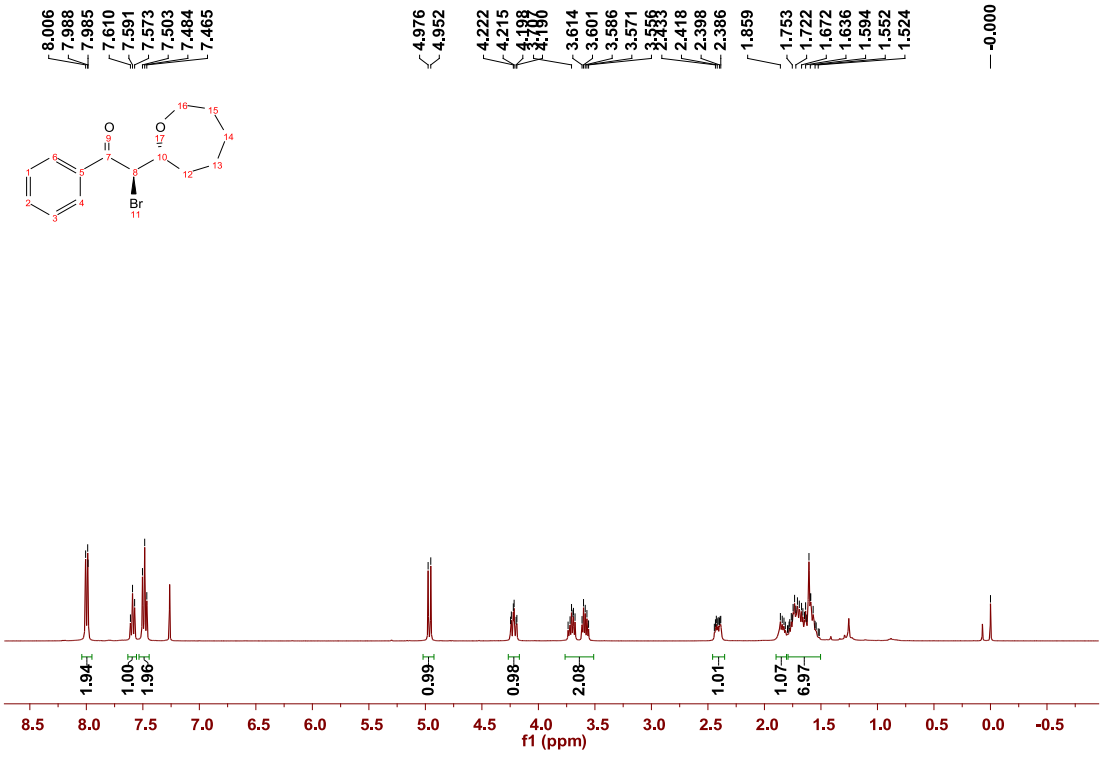
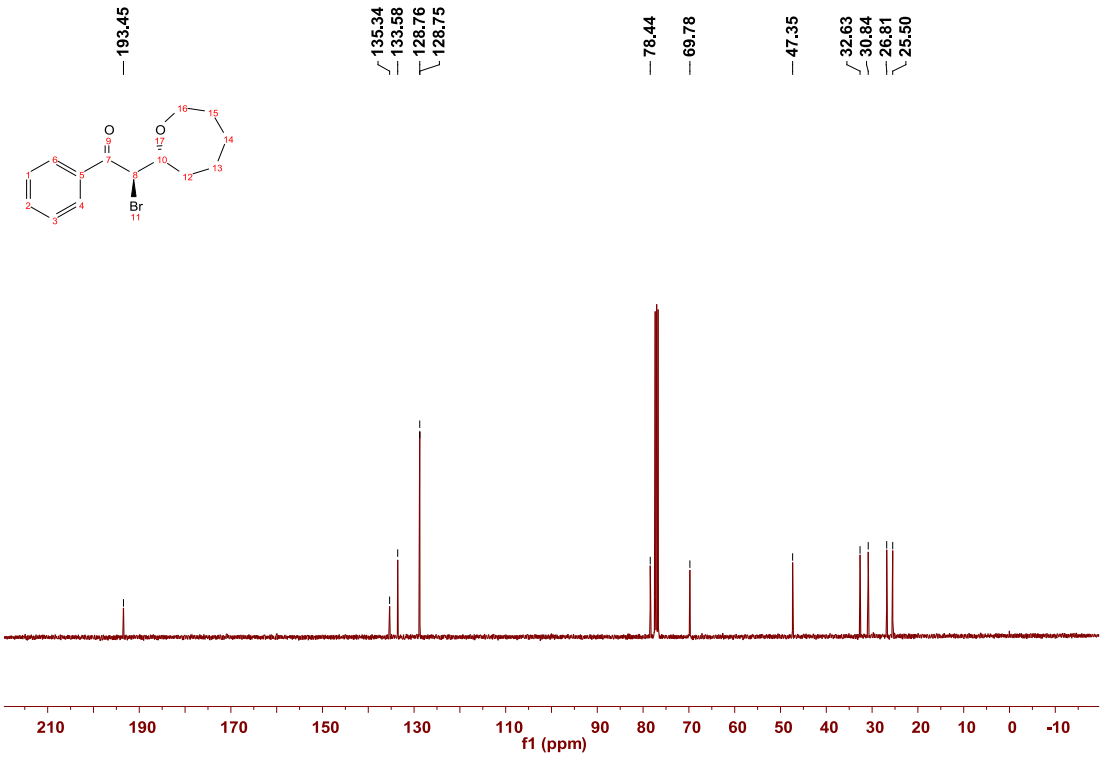
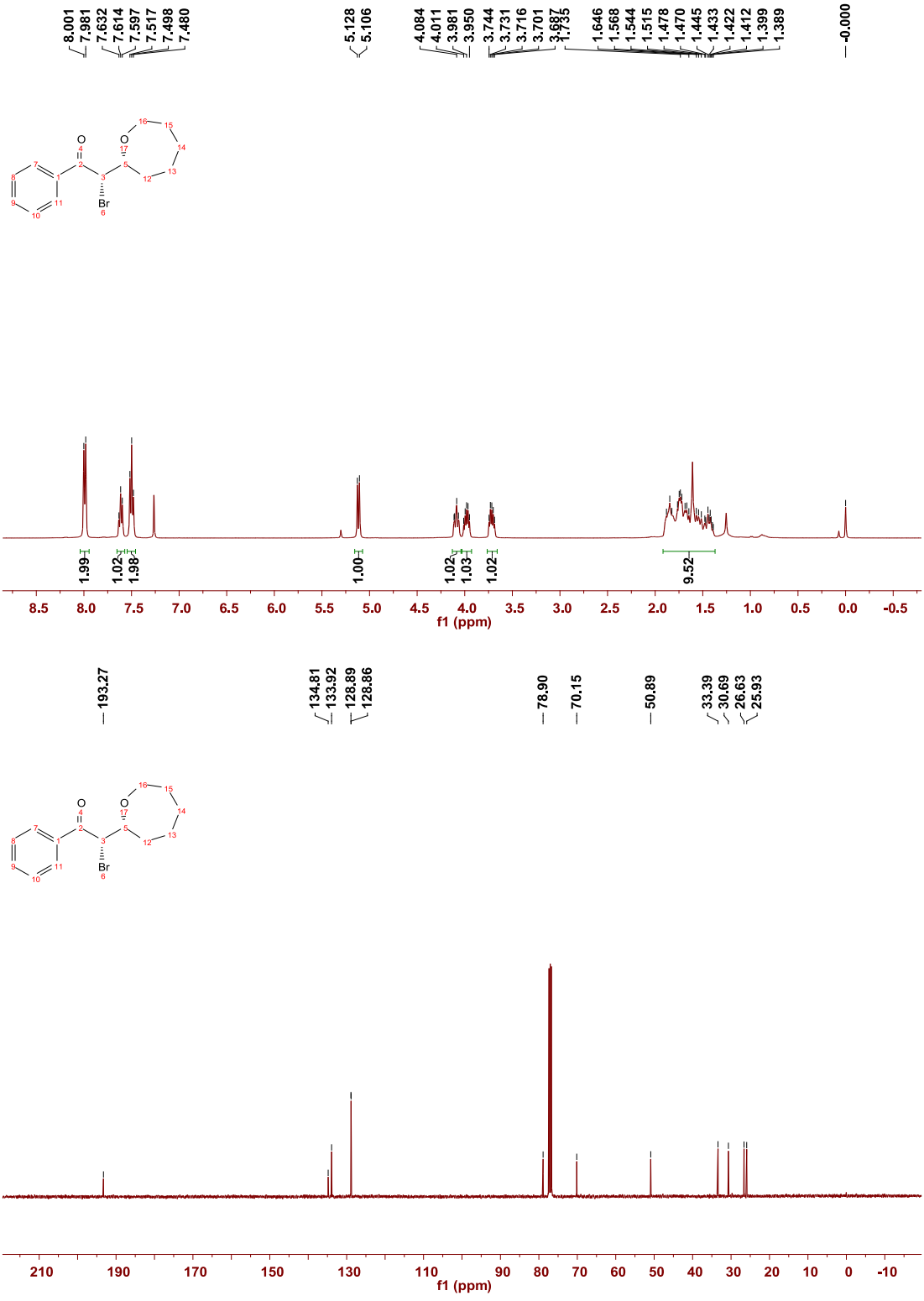
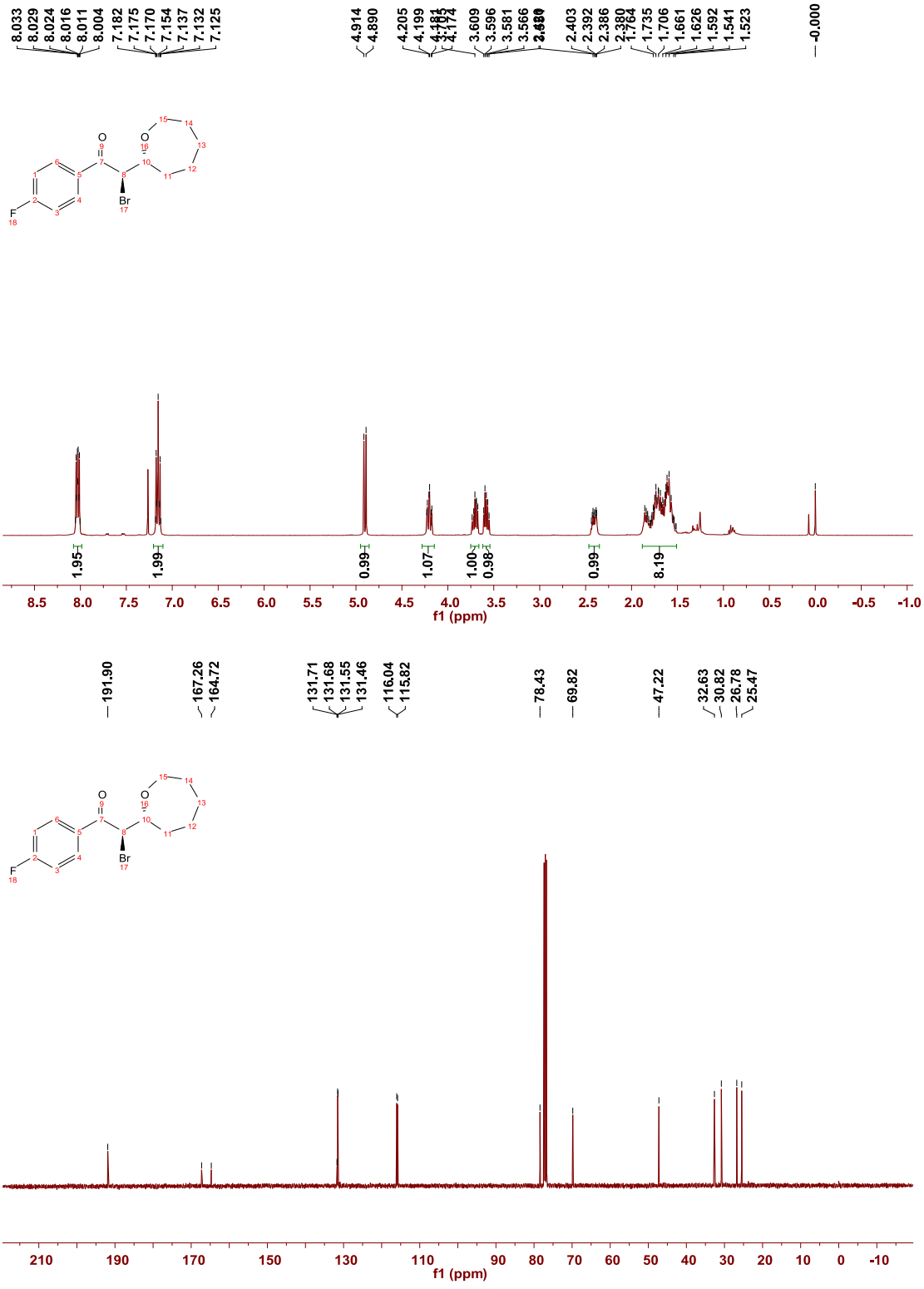
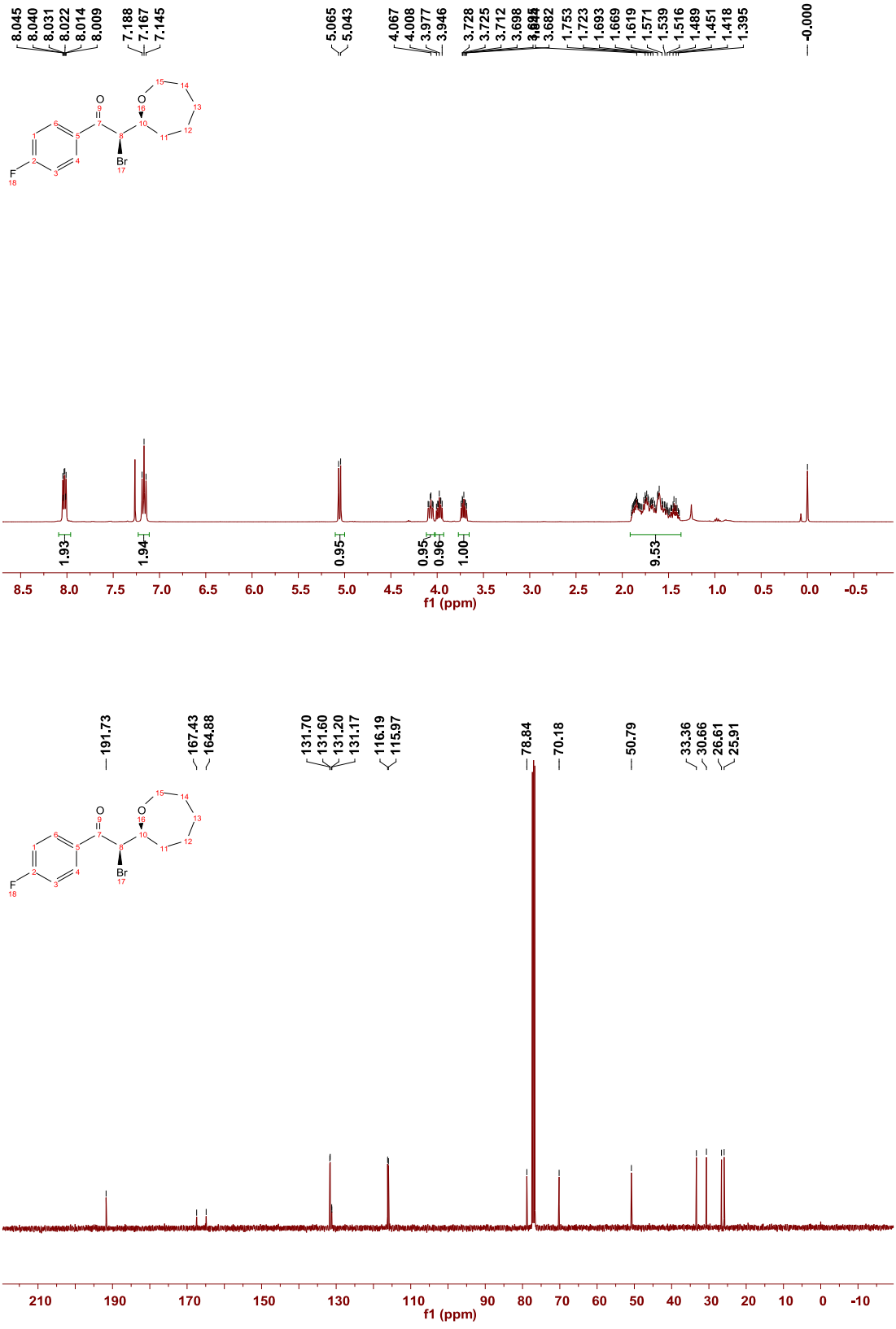
7.988
7.985
7.614
7.595
7.577
7.508
7.488
7.470
4.940
4.918
4.140
4.134
4.117
4.109
3.715
3.698
3.681
3.574
3.546
2.263
2.254
2.240
1.764
1.721
1.677
1.641
1.606
1.554
1.530
-0.000
O
O
Cl
1.98
1.01
1.97
1.01
1.05
1.06
1.02
1.06
1.16
6.89
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
193.82
135.60
133.61
128.82
128.73
78.94
69.62
57.26
31.94
30.74
26.62
25.70
O
O
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

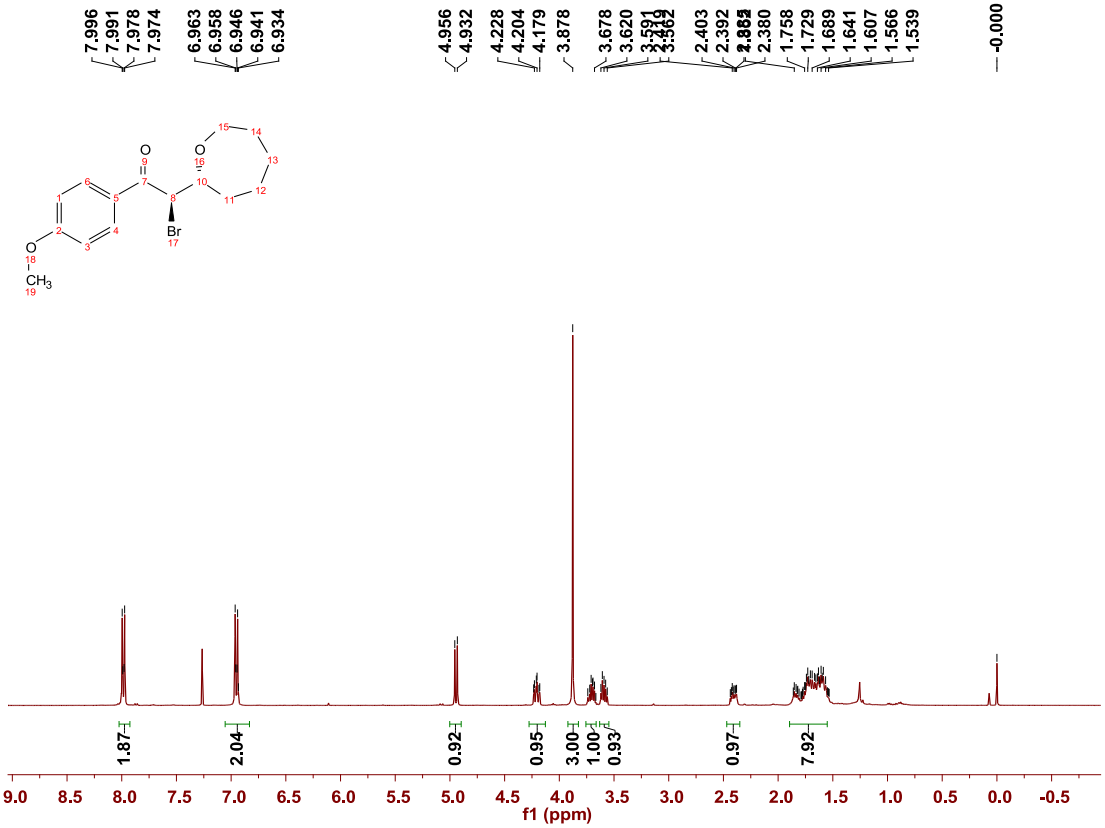

8.006
7.988
7.985
7.610
7.591
7.573
7.503
7.484
7.465
4.976
4.952
4.222
4.215
3.614
3.601
3.586
3.571
2.418
2.398
2.386
1.859
1.753
1.722
1.672
1.636
1.594
1.552
1.524
-0.000
Br
1.94
1.00
1.96
0.99
0.98
2.08
1.01
1.07
6.97
f1 (ppm)


193.45
135.34
133.58
128.76
128.75
78.44
69.78
47.35
32.63
30.84
26.81
25.50
Br
f1 (ppm)


8.001
7.981
7.632
7.614
7.597
7.517
7.498
7.480
5.128
5.106
4.084
4.011
3.981
3.950
3.744
3.731
3.716
3.701
3.687
1.646
1.568
1.544
1.515
1.478
1.470
1.445
1.433
1.422
1.412
1.399
1.389
-0.000
1.99
1.02
1.98
1.00
1.02
1.03
1.02
9.52
f1 (ppm)
193.27
134.81
133.92
128.89
128.86
78.90
70.15
50.89
33.39
30.69
26.63
25.93
f1 (ppm)


8.033
8.029
8.024
8.016
8.011
8.004
7.182
7.175
7.170
7.154
7.137
7.132
7.125
4.914
4.890
4.205
4.199
3.609
3.596
3.581
3.566
2.403
2.392
2.386
2.380
1.764
1.735
1.706
1.661
1.626
1.592
1.541
1.523
-0.000
1.95
1.99
0.99
1.07
1.00
0.98
0.99
8.19
f1 (ppm)
191.90
167.26
164.72
131.71
131.68
131.55
131.46
116.04
115.82
78.43
69.82
47.22
32.63
30.82
26.78
25.47
f1 (ppm)


8.045
8.040
8.031
8.022
8.014
8.009
7.188
7.167
7.145
5.065
5.043
4.067
4.008
3.977
3.946
3.728
3.725
3.712
3.698
3.682
1.753
1.723
1.693
1.669
1.619
1.571
1.539
1.516
1.489
1.451
1.418
1.395
0.000
1.93
1.94
0.95
0.95
0.96
1.00
9.53
f1 (ppm)
191.73
167.43
164.88
131.70
131.60
131.20
131.17
116.19
115.97
78.84
70.18
50.79
33.36
30.66
26.61
25.91
f1 (ppm)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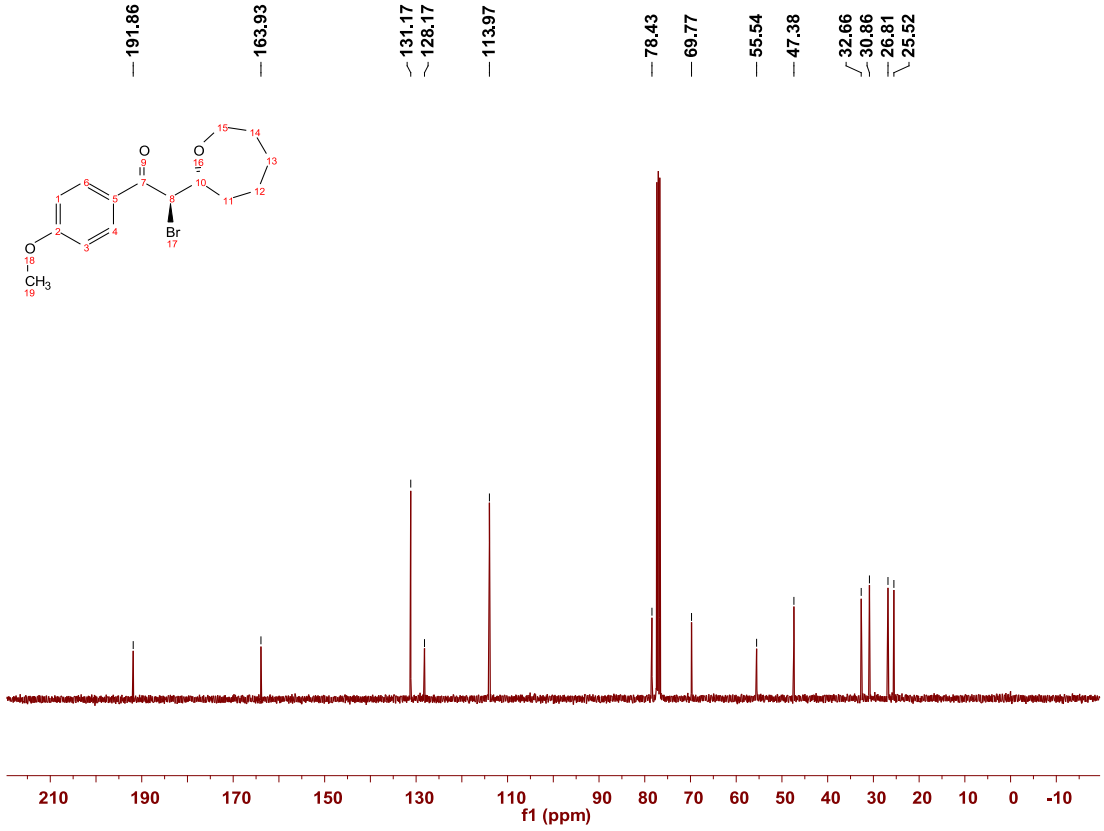
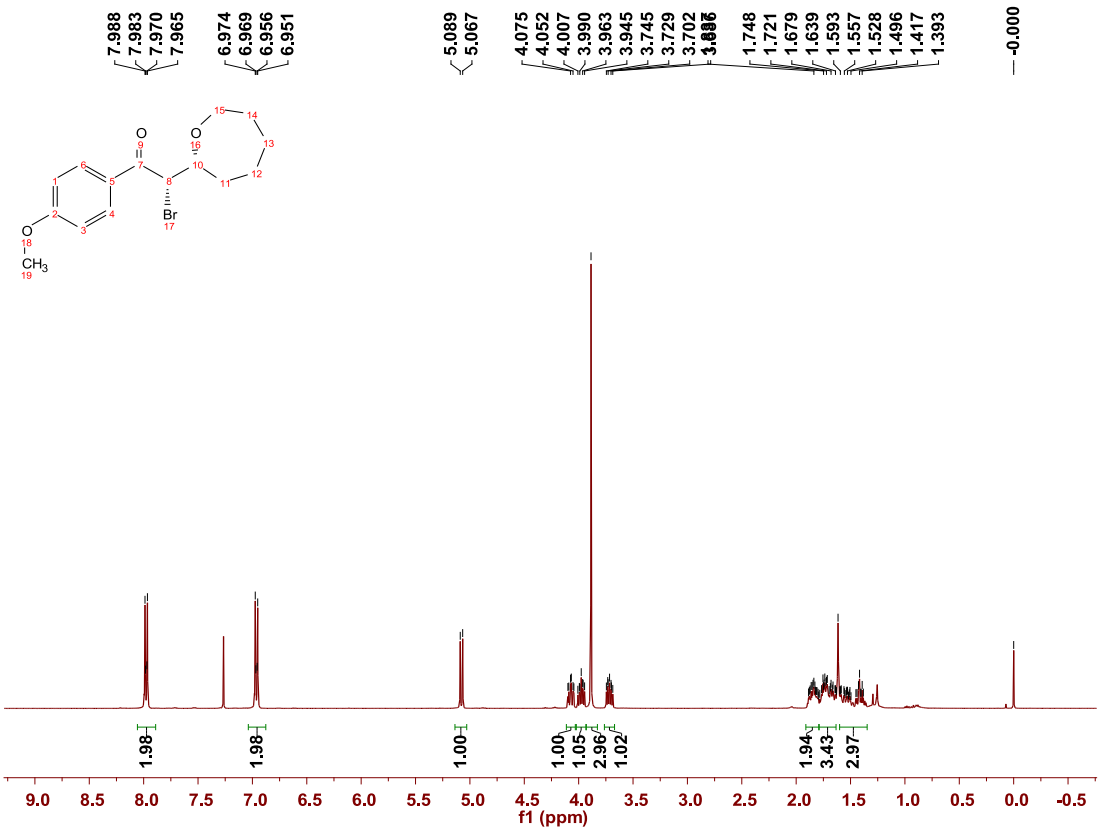
7.991
7.978
7.974
6.963
6.958
6.946
6.941
6.934
4.956
4.932
4.228
4.204
4.179
3.878
3.678
3.620
3.591
3.582
2.403
2.392
2.380
1.758
1.729
1.689
1.641
1.607
1.566
1.539
-0.000
1.87
2.04
0.92
0.95
3.00
1.00
0.93
0.97
7.92
f1 (ppm)


191.86
163.93
131.17
128.17
113.97
78.43
69.77
55.54
47.38
32.66
30.86
26.81
25.52
f1 (ppm)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7.965
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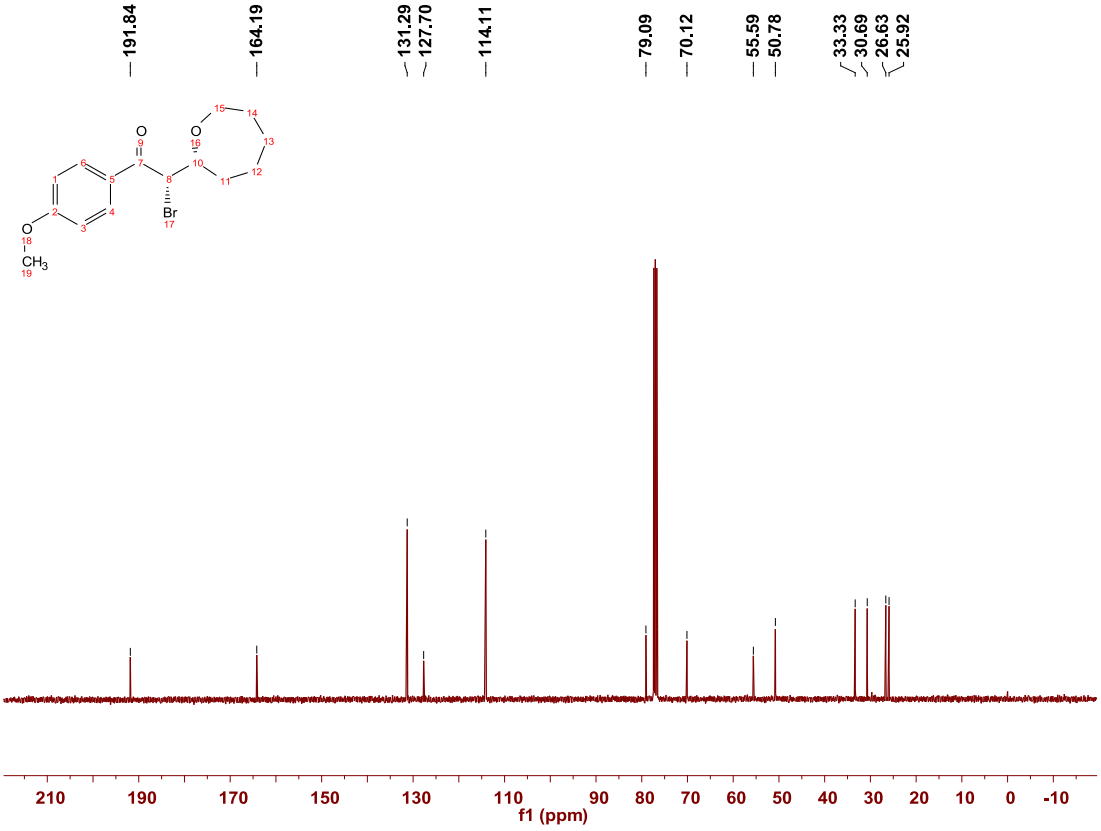
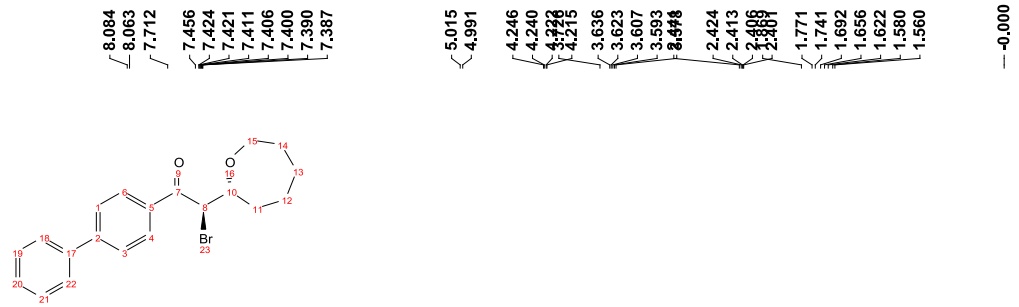
6.969
6.956
6.951
5.089
5.067
4.075
4.052
4.007
3.990
3.963
3.945
3.745
3.729
3.702
1.748
1.721
1.679
1.639
1.593
1.557
1.528
1.496
1.417
1.393
-0.000
1.98
1.98
1.00
1.00
1.05
2.96
1.02
1.94
3.43
2.97
f1 (ppm)


191.84
164.19
131.29
127.70
114.11
79.09
70.12
55.59
50.78
33.33
30.69
26.63
25.92
f1 (ppm)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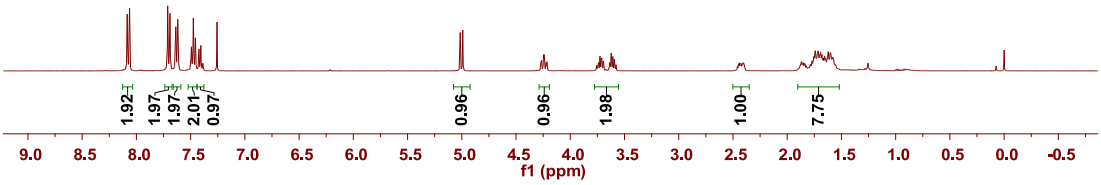
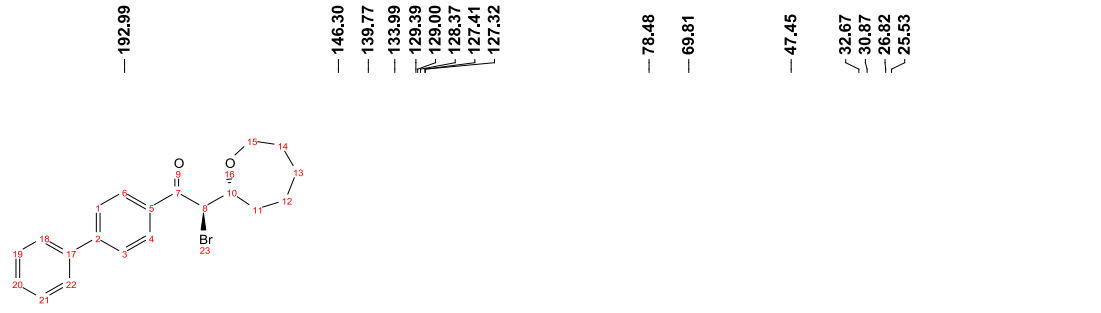
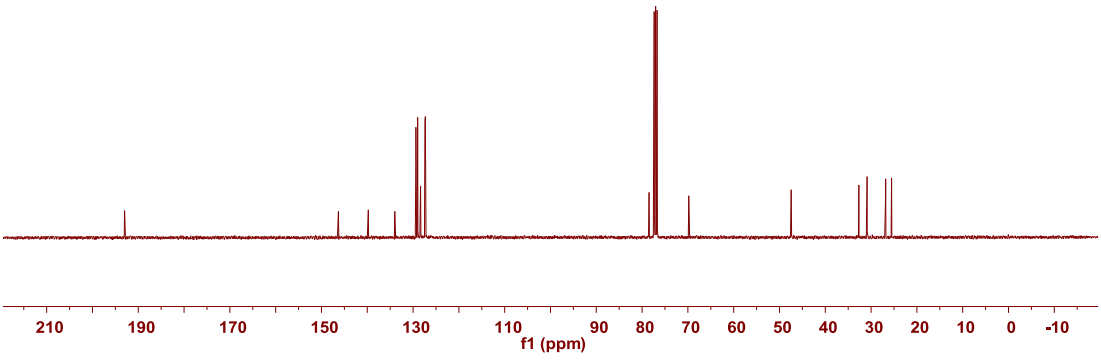
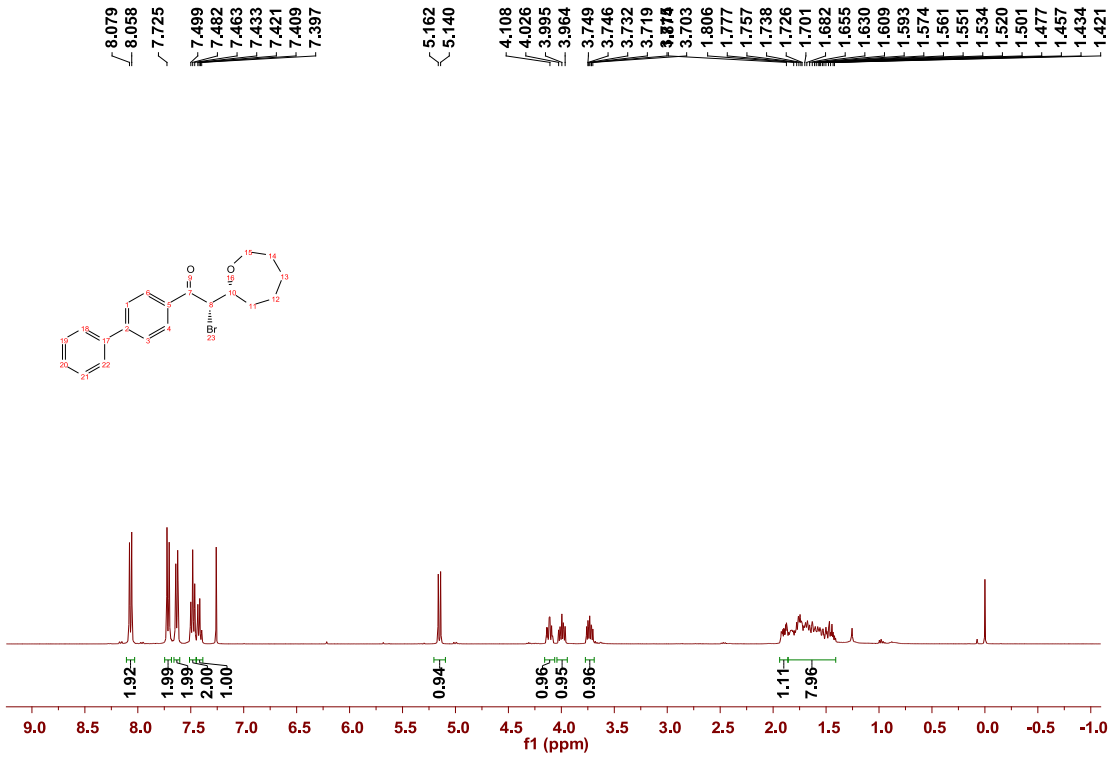
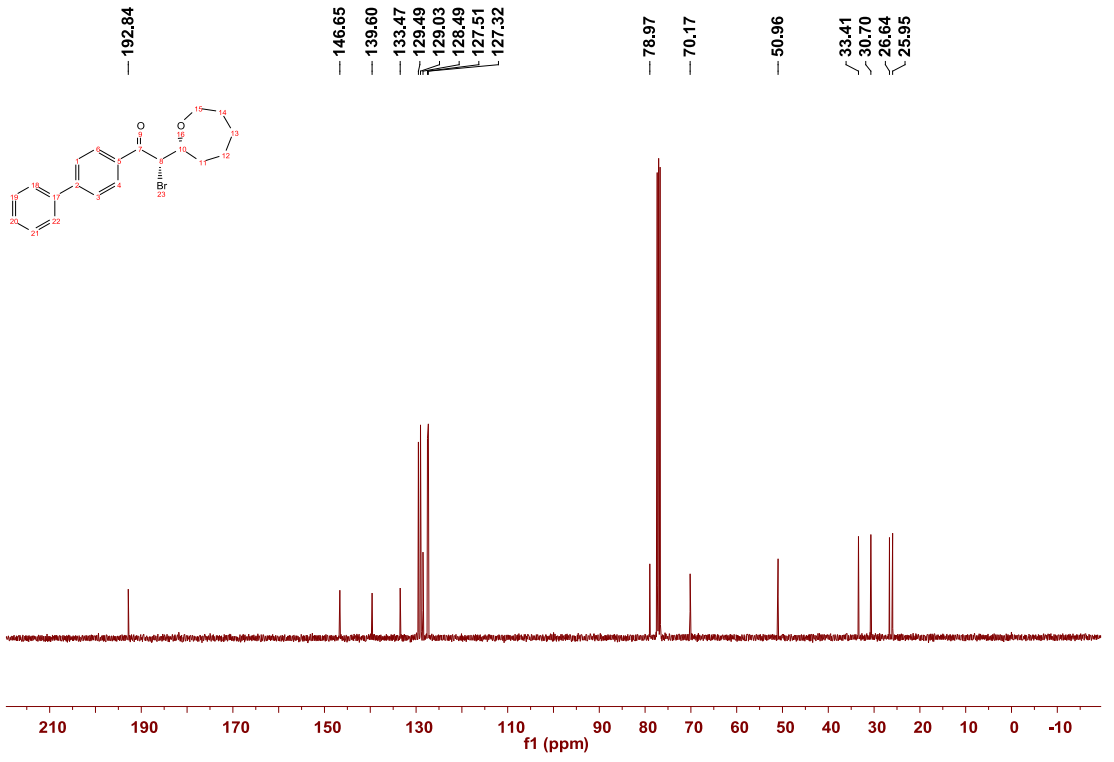
8.063
7.712
7.456
7.424
7.421
7.411
7.406
7.400
7.390
7.387
5.015
4.991
4.246
4.240
3.636
3.623
3.607
3.593
2.424
2.413
1.771
1.741
1.692
1.656
1.622
1.580
1.560
-0.000


1.92
1.97
1.97
2.01
0.97
0.96
0.96
1.98
1.00
7.75
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


192.99
146.30
139.77
133.99
129.39
129.00
128.37
127.41
127.32
78.48
69.81
47.45
32.67
30.87
26.82
25.53


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.079
8.058
7.725
7.499
7.482
7.463
7.433
7.421
7.409
7.397
5.162
5.140
4.108
4.026
3.995
3.964
3.749
3.746
3.732
3.719
3.703
1.806
1.777
1.757
1.738
1.726
1.701
1.682
1.655
1.630
1.609
1.593
1.574
1.561
1.551
1.534
1.520
1.501
1.477
1.457
1.434
1.421
O
O
Br
1.92
1.99
1.99
2.00
1.00
0.94
0.96
0.95
0.96
1.11
7.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


192.84
146.65
139.60
133.47
129.49
129.03
128.49
127.51
127.32
78.97
70.17
50.96
33.41
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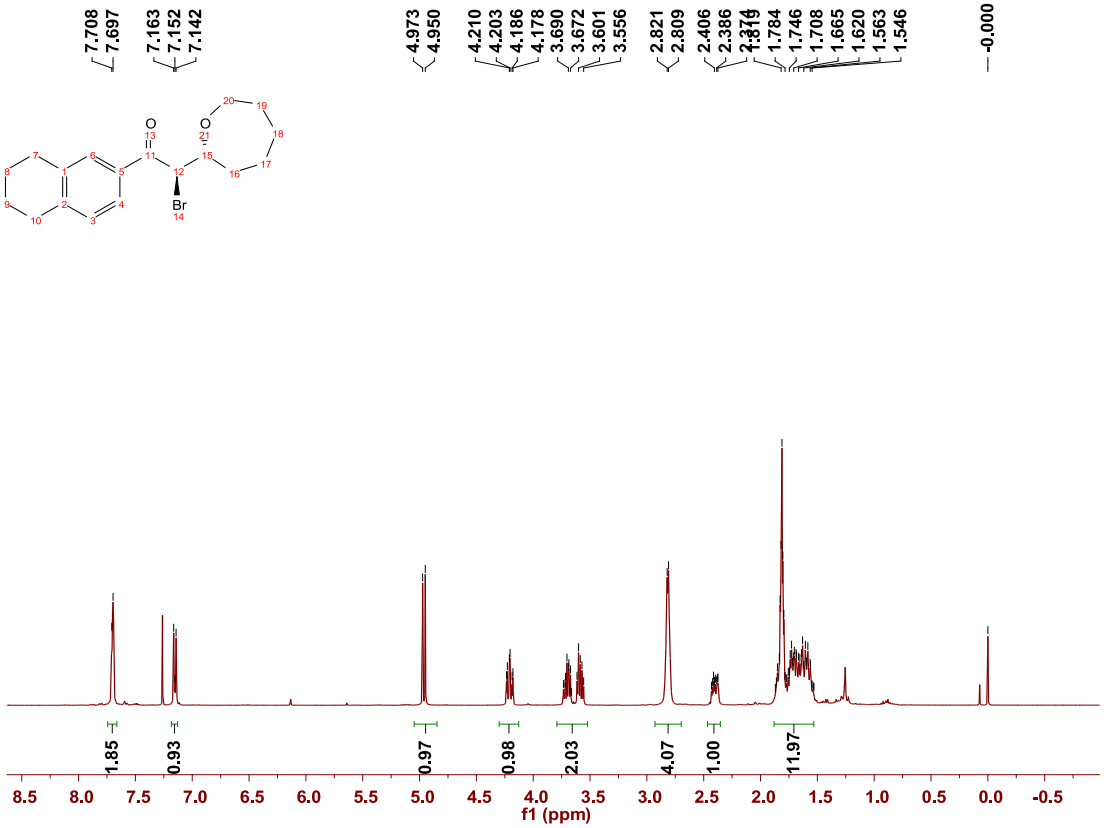
26.64
25.95
O
O
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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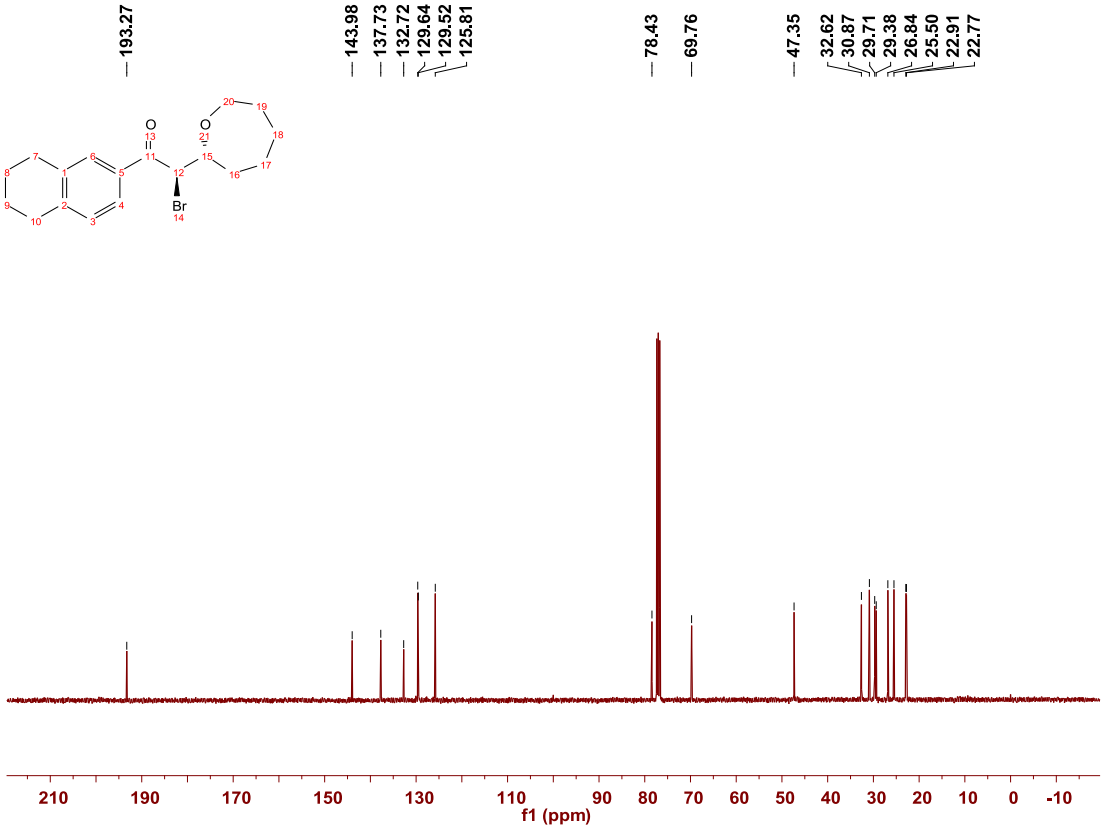
7.163
7.152
7.142
4.973
4.950
4.210
4.203
4.186
4.178
3.690
3.672
3.601
3.556
2.821
2.809
2.406
2.386
1.784
1.746
1.708
1.665
1.620
1.563
1.546
-0.000
Br
1.85
0.93
0.97
0.98
2.03
4.07
1.00
11.97
f1 (ppm)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137.73
132.72
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129.52
125.81
78.43
69.76
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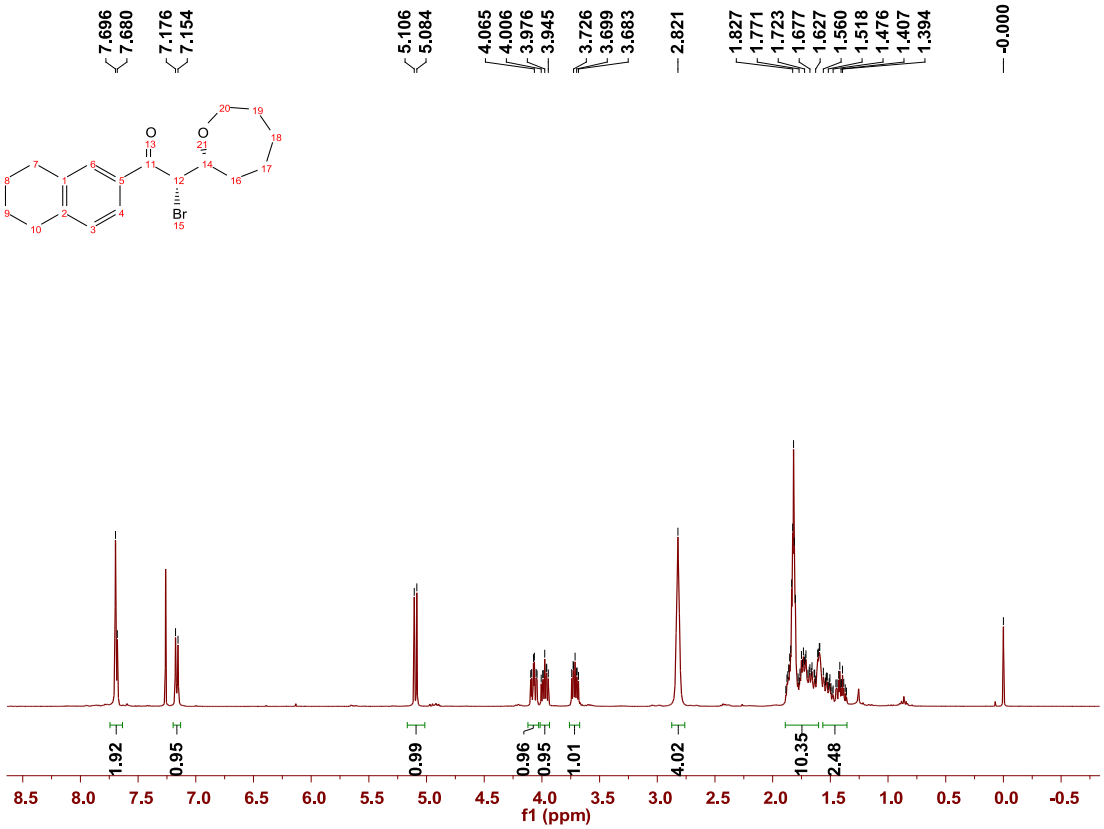
32.62
30.87
29.71
29.38
26.84
25.50
22.91
22.77
Br
f1 (ppm)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7.680
7.176
7.154
5.106
5.084
4.065
4.006
3.976
3.945
3.726
3.699
3.683
2.821
1.827
1.771
1.723
1.677
1.627
1.560
1.518
1.476
1.407
1.394
-0.000
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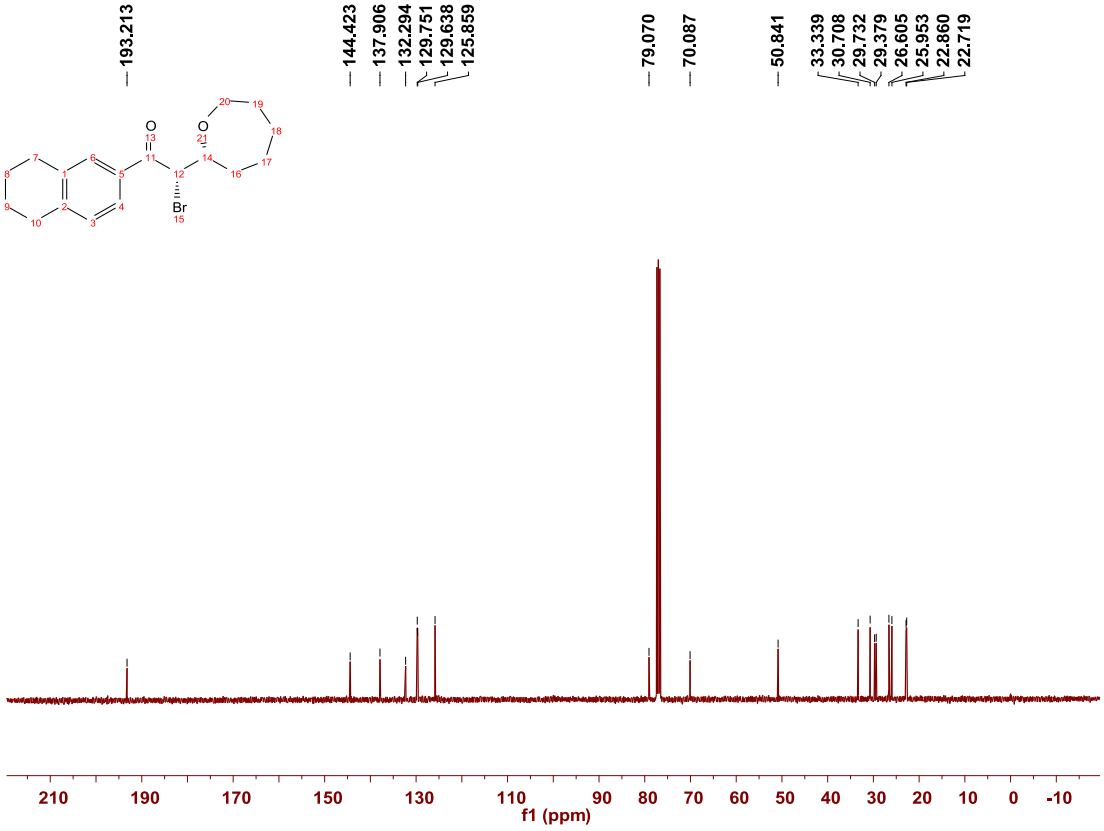
0.95
0.99
0.96
0.95
1.01
4.02
10.35
2.48
f1 (ppm)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144.423
137.906
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129.638
125.859
79.070
70.087
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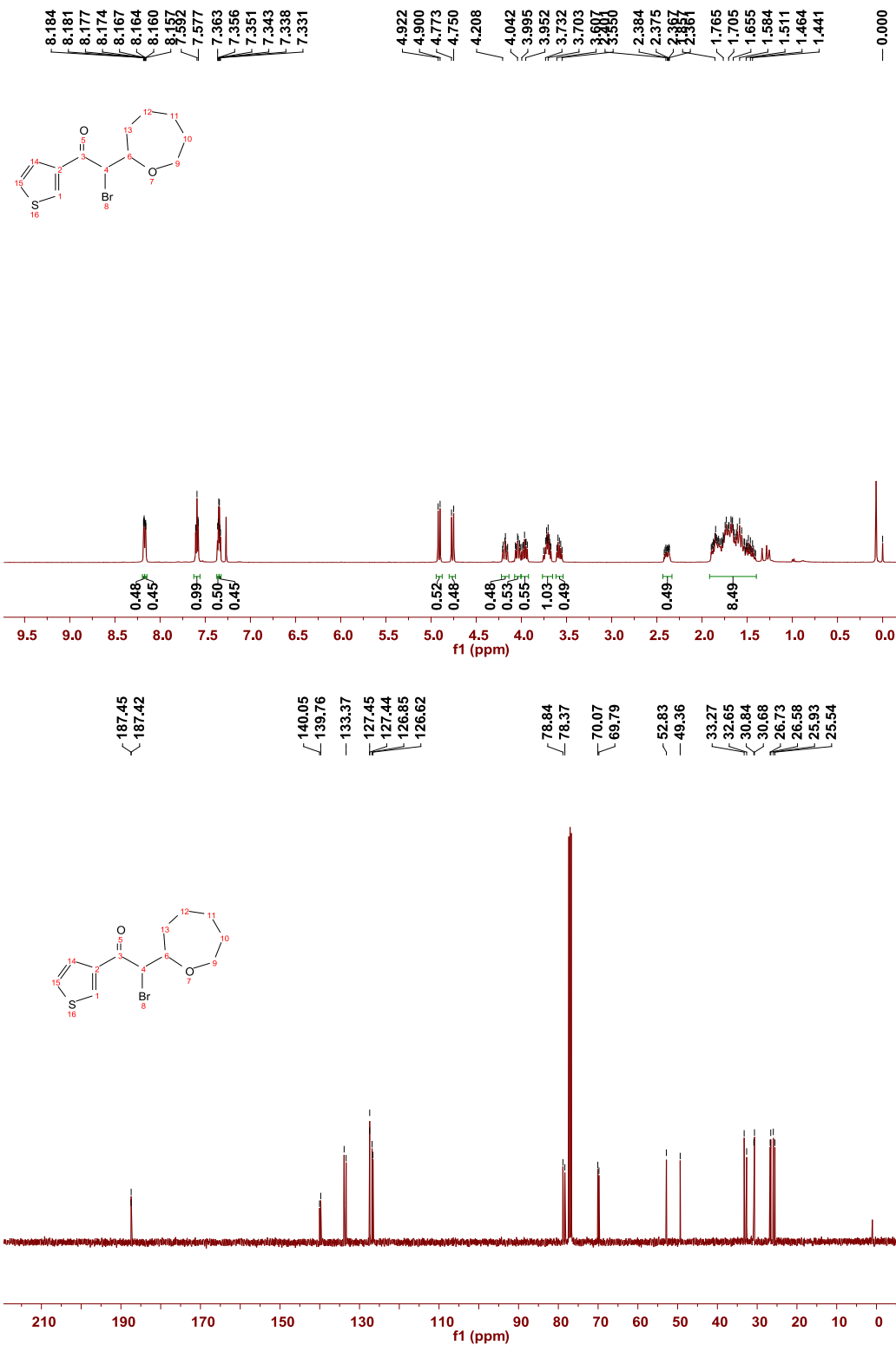
29.732
29.379
26.605
25.953
22.860
22.719
f1 (ppm)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8.181
8.177
8.174
8.167
8.164
8.160
8.157
7.592
7.577
7.363
7.356
7.351
7.343
7.338
7.331
4.922
4.900
4.773
4.750
4.208
4.042
3.995
3.952
3.732
3.703
3.607
3.550
2.384
2.375
2.367
2.361
1.765
1.705
1.655
1.584
1.511
1.464
1.441
0.000
O
O
Br
S
0.48
0.45
0.99
0.50
0.45
0.52
0.48
0.48
0.53
0.55
1.03
0.49
0.49
8.49
f1 (ppm)
187.45
187.42
140.05
139.76
133.37
127.45
127.44
126.85
126.62
78.84
78.37
70.07
69.79
52.83
49.36
33.27
32.65
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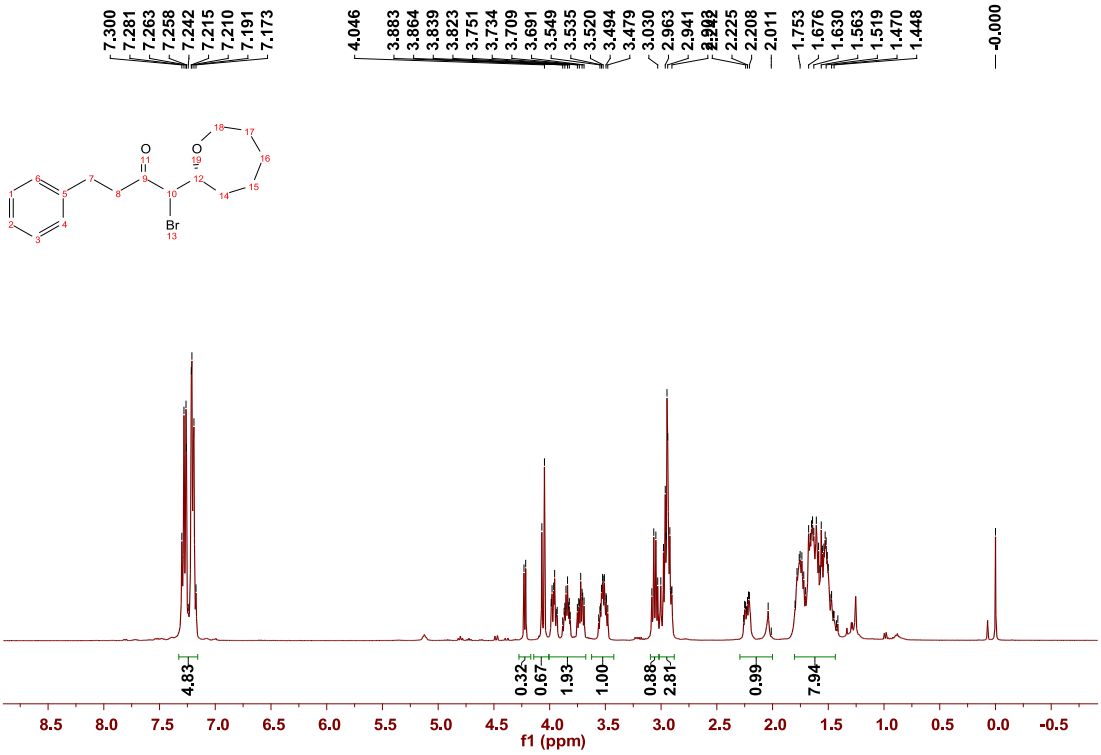
30.68
26.73
26.58
25.93
25.54
f1 (ppm)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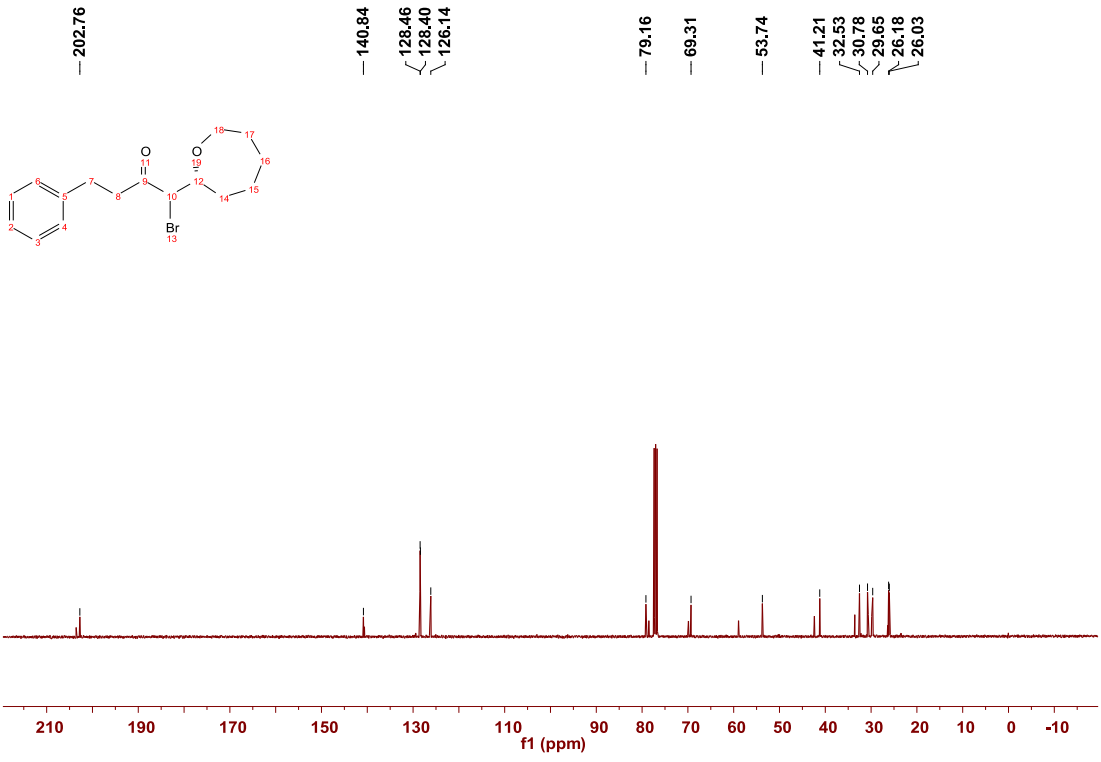
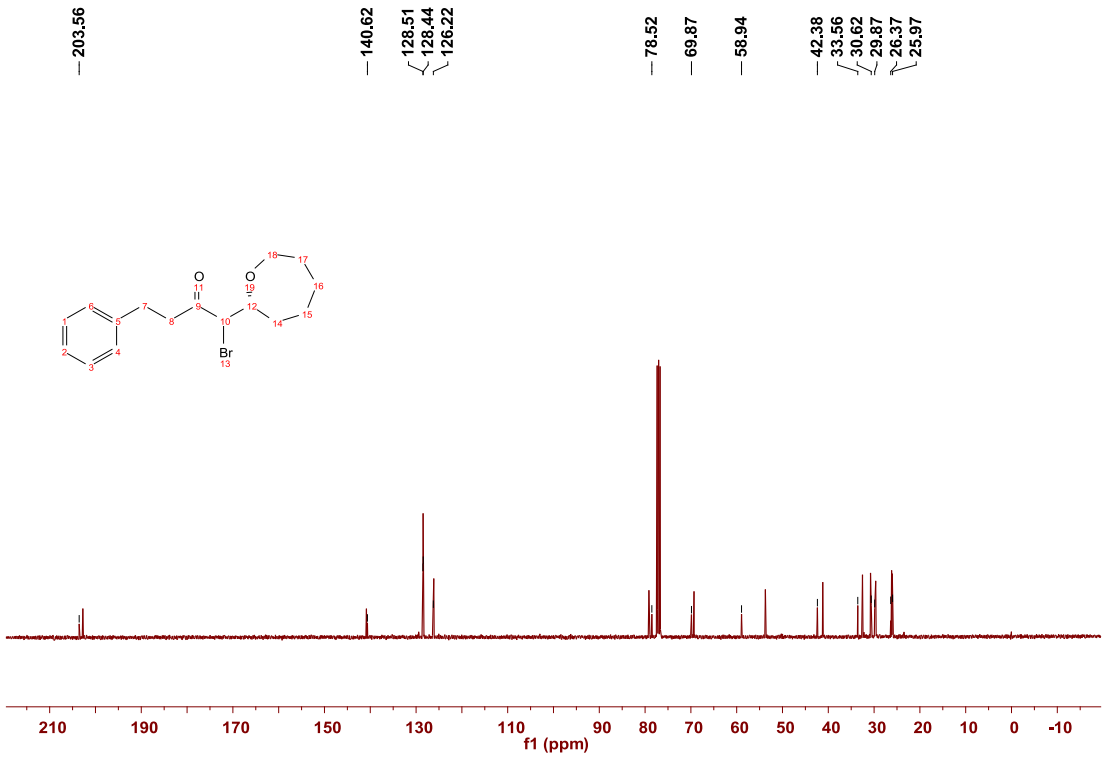
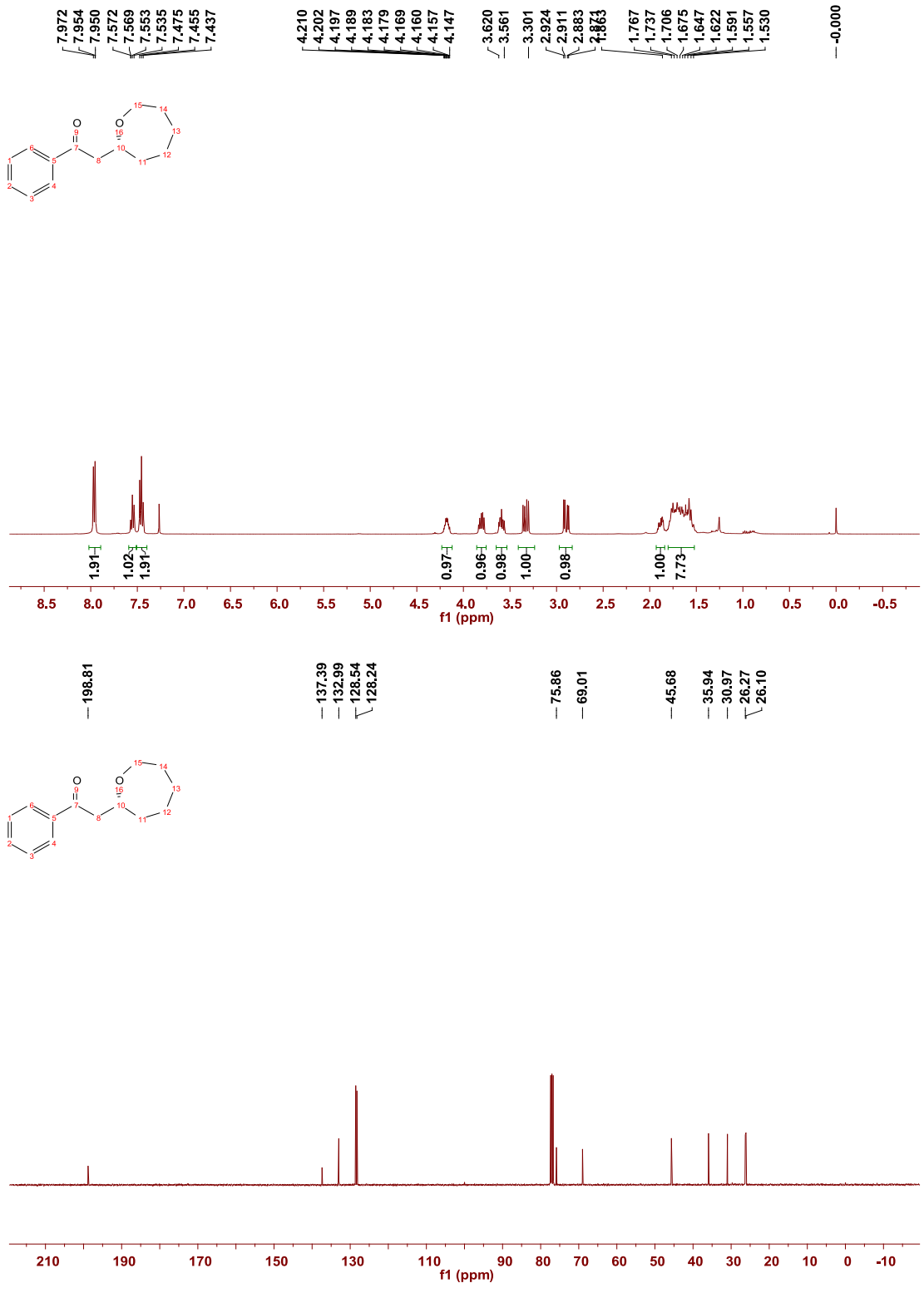
7.258
7.242
7.215
7.210
7.191
7.173
4.046
3.883
3.864
3.839
3.823
3.751
3.734
3.709
3.691
3.549
3.535
3.520
3.494
3.479
3.030
2.963
2.941
2.225
2.208
2.011
1.753
1.676
1.630
1.563
1.519
1.470
1.448
-0.000
Br
4.83
0.32
0.67
1.93
1.00
0.88
2.81
0.99
7.94
f1 (ppm)


202.76
140.84
128.46
128.40
126.14
79.16
69.31
53.74
41.21
32.53
30.78
29.65
26.18
26.03
Br
f1 (ppm)


203.56
140.62
128.51
128.44
126.22
78.52
69.87
58.94
42.38
33.56
30.62
29.87
26.37
25.97
O
O
Br
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.950
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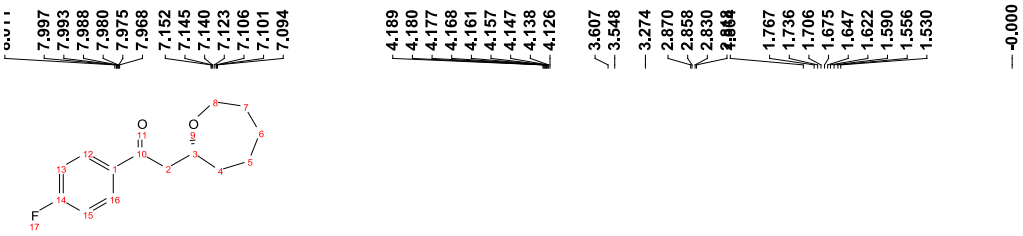
7.569
7.553
7.535
7.475
7.455
7.437
4.210
4.202
4.197
4.189
4.183
4.179
4.169
4.160
4.157
4.147
3.620
3.561
3.301
2.924
2.911
2.883
1.767
1.737
1.706
1.675
1.647
1.622
1.591
1.557
1.530
-0.000
1.91
1.02
1.91
0.97
0.96
0.98
1.00
0.98
1.00
7.73
f1 (ppm)
198.81
137.39
132.99
128.54
128.24
75.86
69.01
45.68
35.94
30.97
26.27
26.10
f1 (ppm)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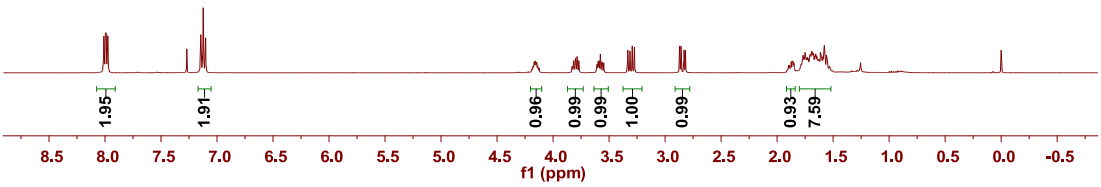
7.993
7.988
7.980
7.975
7.968
7.152
7.145
7.140
7.123
7.106
7.101
7.094
4.189
4.180
4.177
4.168
4.161
4.157
4.147
4.138
4.126
3.607
3.548
3.274
2.870
2.858
2.830
1.767
1.736
1.706
1.675
1.647
1.622
1.590
1.556
1.530
0.000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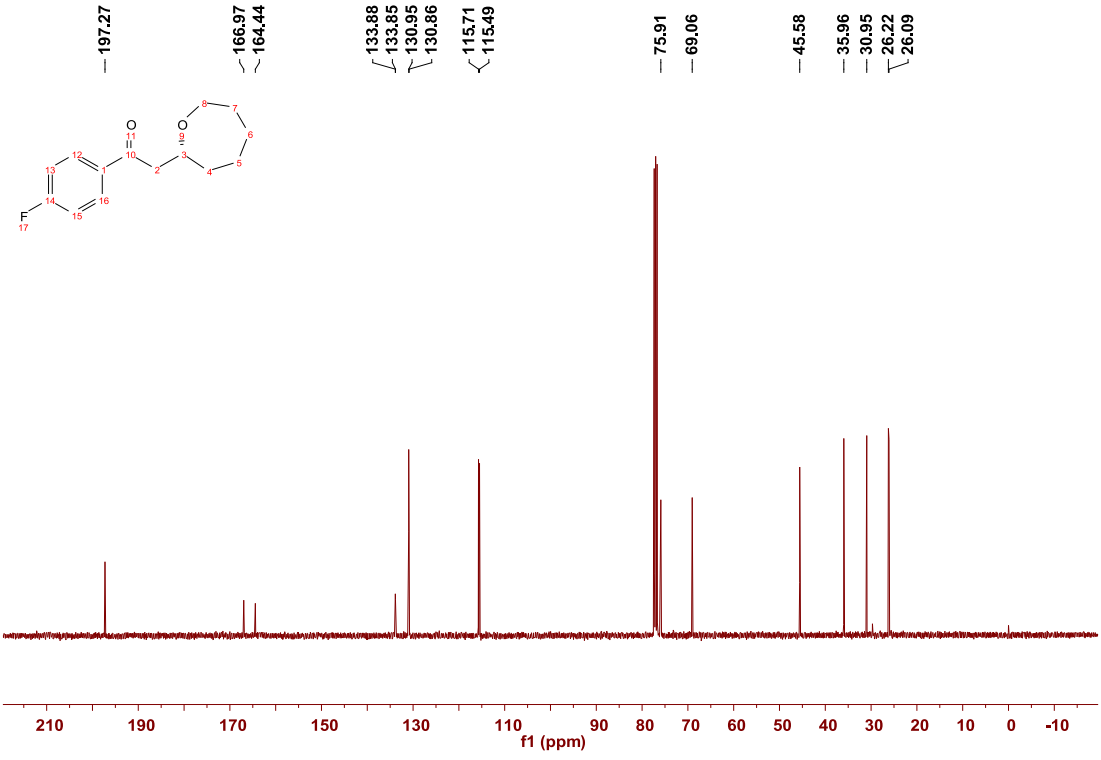
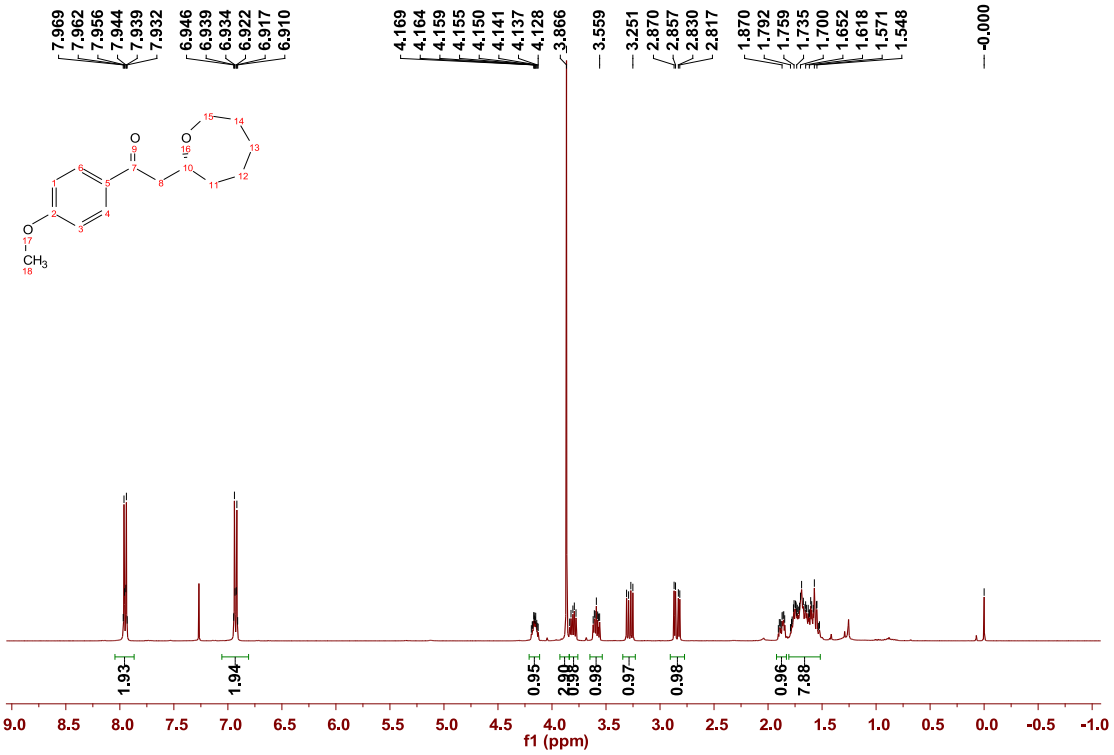
1.91
0.96
0.99
0.99
1.00
0.99
0.93
7.59
f1 (ppm)


197.27
166.97
164.44
133.88
133.85
130.95
130.86
115.71
115.49
75.91
69.06
45.58
35.96
30.95
26.22
26.09
f1 (ppm)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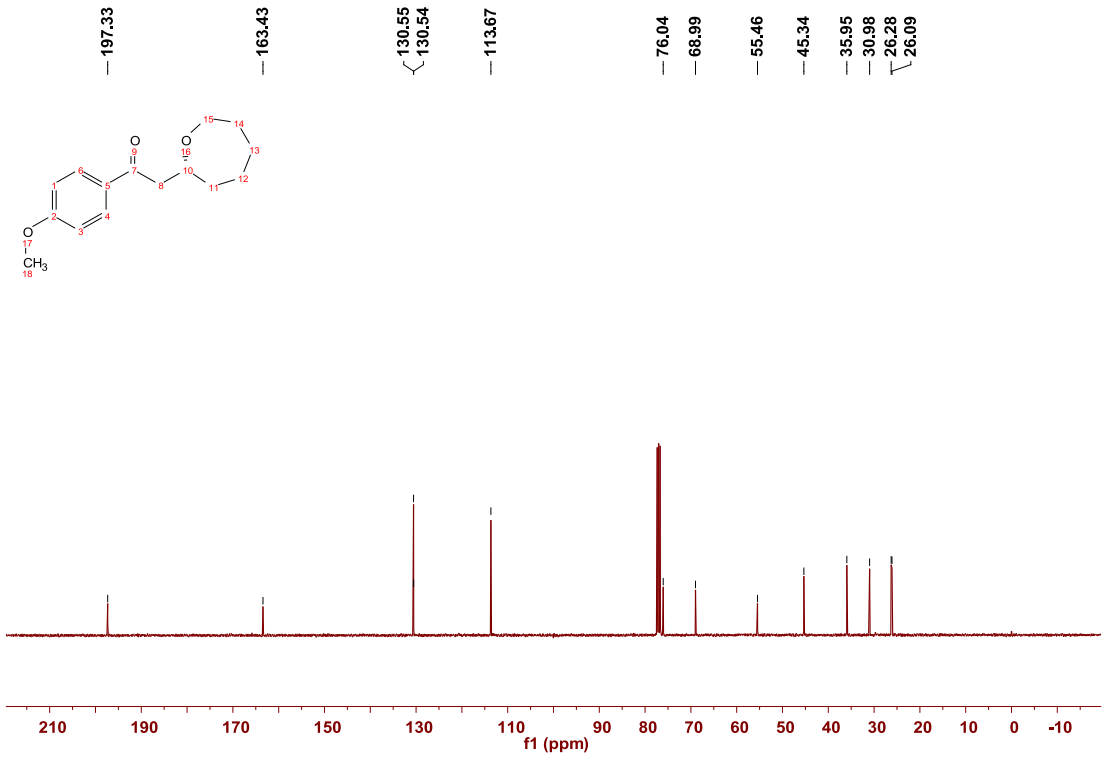
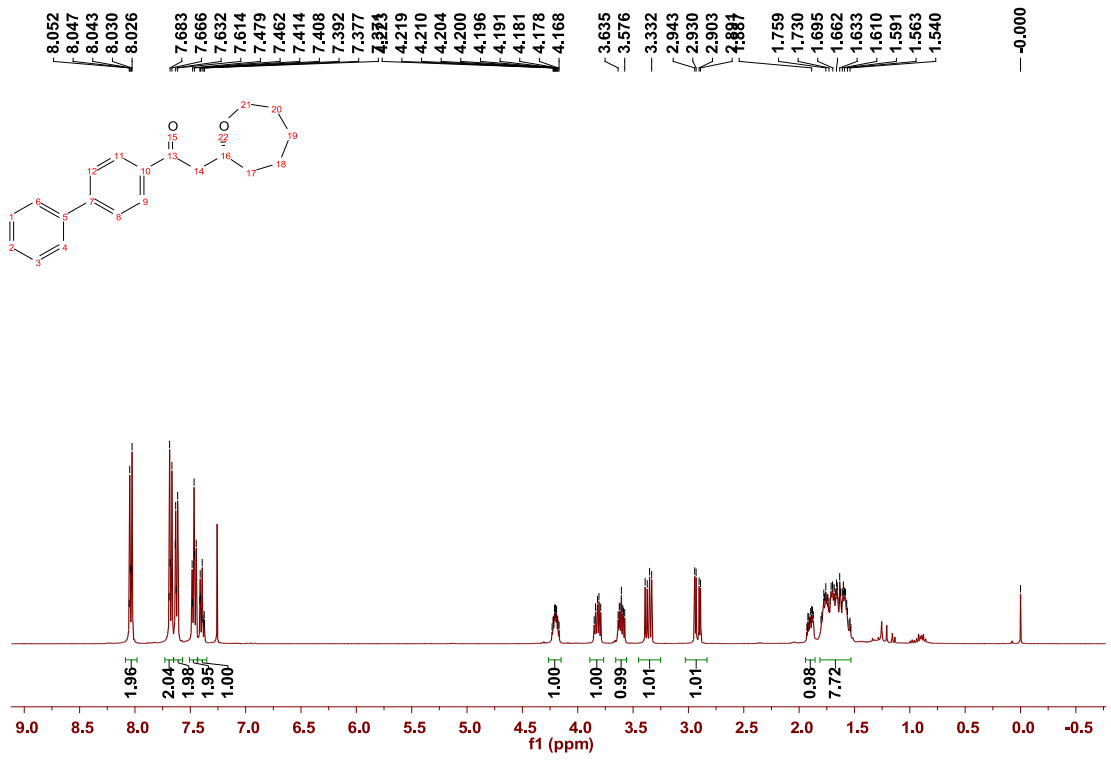
7.939
7.932
6.946
6.939
6.934
6.922
6.917
6.910
4.169
4.164
4.159
4.155
4.150
4.141
4.137
4.128
3.866
3.559
3.251
2.870
2.857
2.830
2.817
1.870
1.792
1.759
1.735
1.700
1.652
1.618
1.571
1.548
-0.000
1.93
1.94
0.95
2.90
0.98
0.98
0.97
0.98
0.96
7.88
f1 (ppm)


197.33
163.43
130.55
130.54
113.67
76.04
68.99
55.46
45.34
35.95
30.98
26.28
26.09
f1 (ppm)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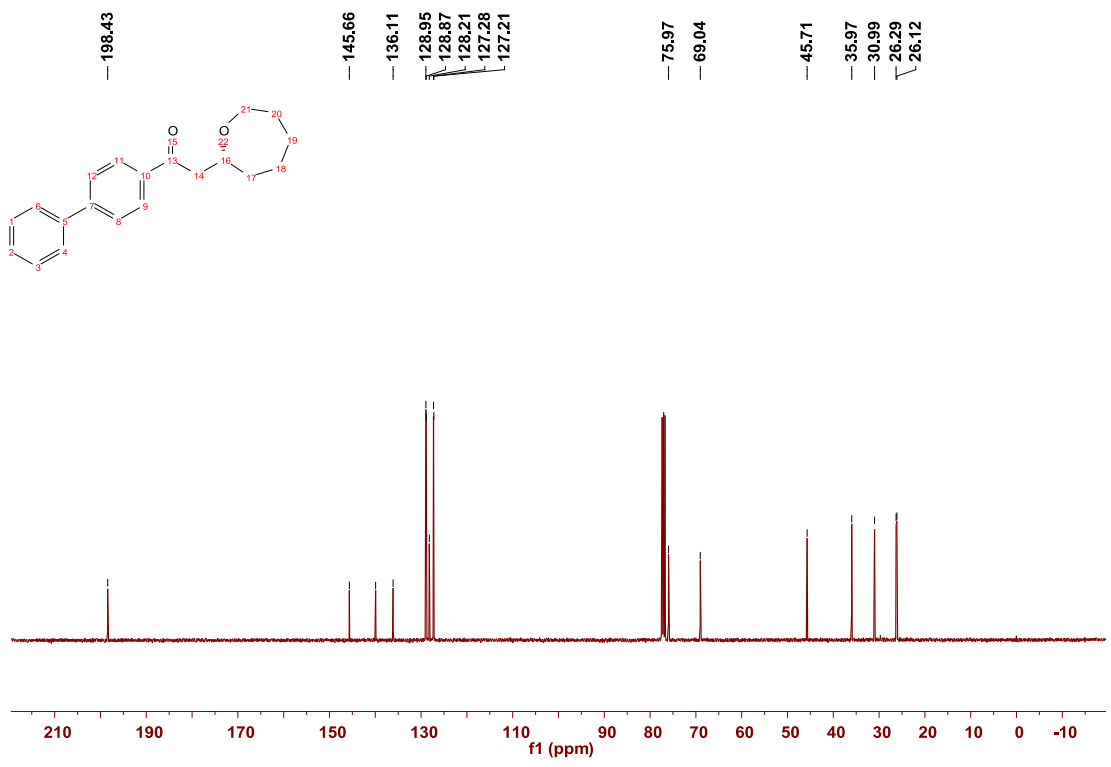
7.462
7.414
7.408
7.392
7.377
4.219
4.210
4.204
4.200
4.196
4.191
4.181
4.178
4.168
3.635
3.576
3.332
2.943
2.930
2.903
1.759
1.730
1.695
1.662
1.633
1.610
1.591
1.563
1.540
-0.000
1.96
2.04
1.98
1.95
1.00
1.00
1.00
0.99
1.01
1.01
0.98
7.72
f1 (ppm)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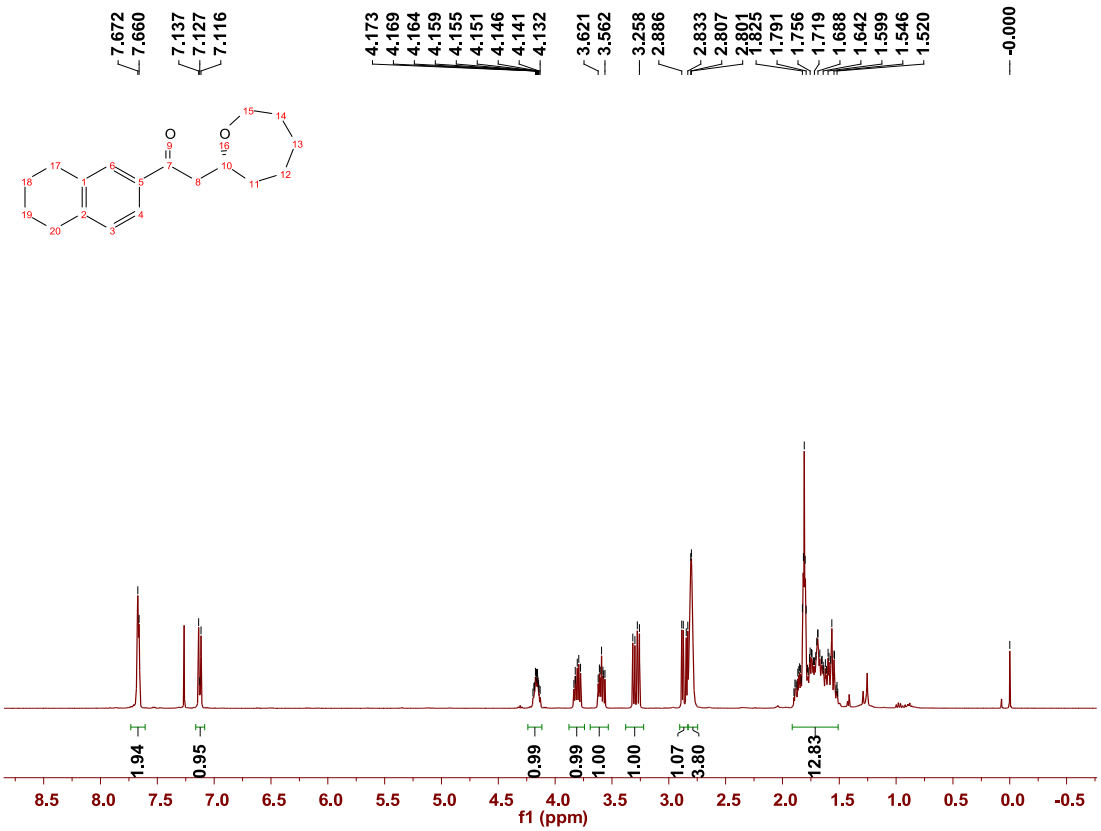
145.66
136.11
128.95
128.87
128.21
127.28
127.21
75.97
69.04
45.71
35.97
30.99
26.29
26.12
f1 (ppm)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4.169
4.164
4.159
4.155
4.151
4.146
4.141
4.132
3.621
3.562
3.258
2.886
2.833
2.807
2.801
1.825
1.791
1.756
1.719
1.688
1.642
1.599
1.546
1.520
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1.00
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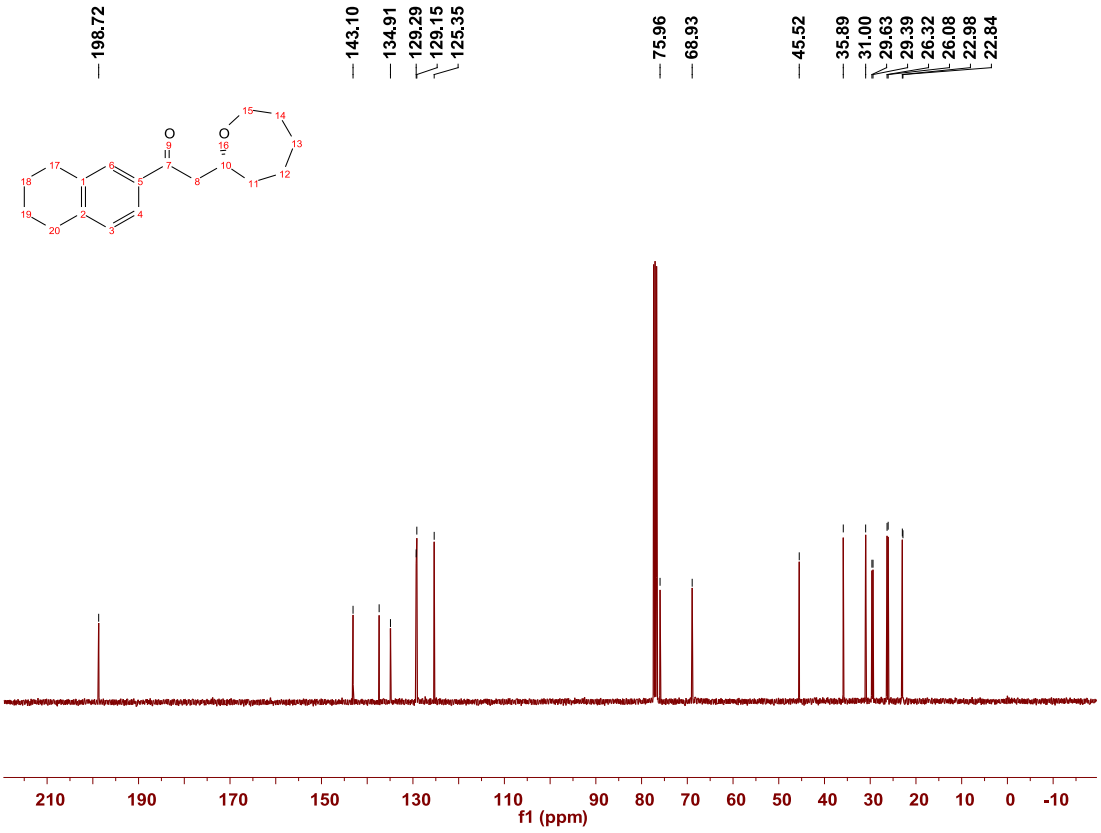
1.07
3.80
12.83
f1 (ppm)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125.35
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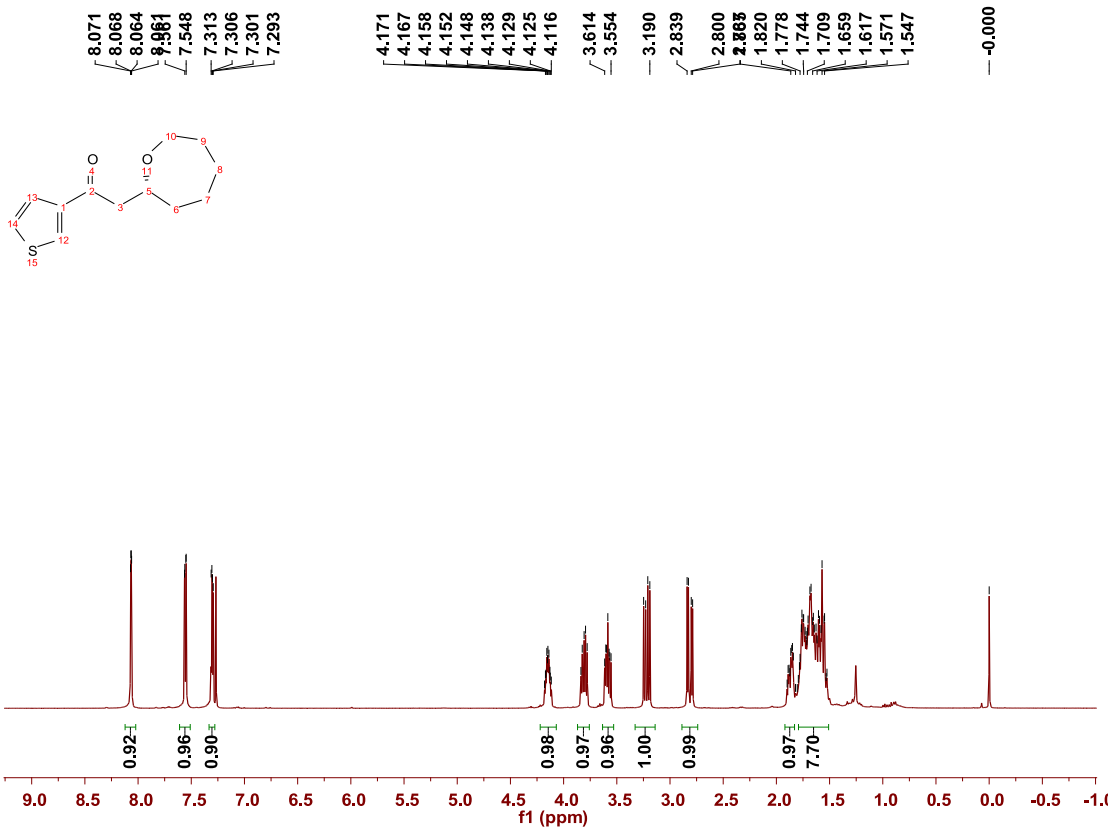
26.08
22.98
22.84
f1 (ppm)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7.301
7.293
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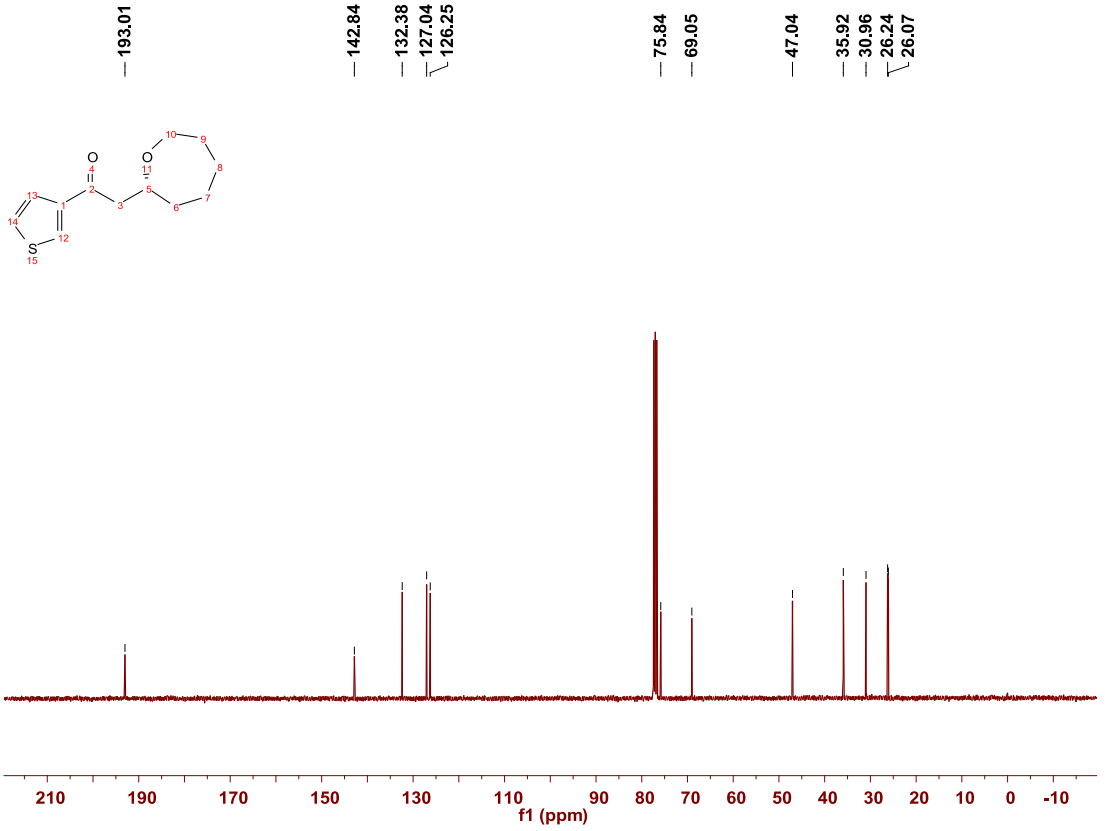
4.167
4.158
4.152
4.148
4.138
4.129
4.125
4.116
3.614
3.554
3.190
2.839
2.800
1.820
1.778
1.744
1.709
1.659
1.617
1.571
1.547
-0.000
0.92
0.96
0.90
0.98
0.97
0.96
1.00
0.99
0.97
7.70
f1 (ppm)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75.84
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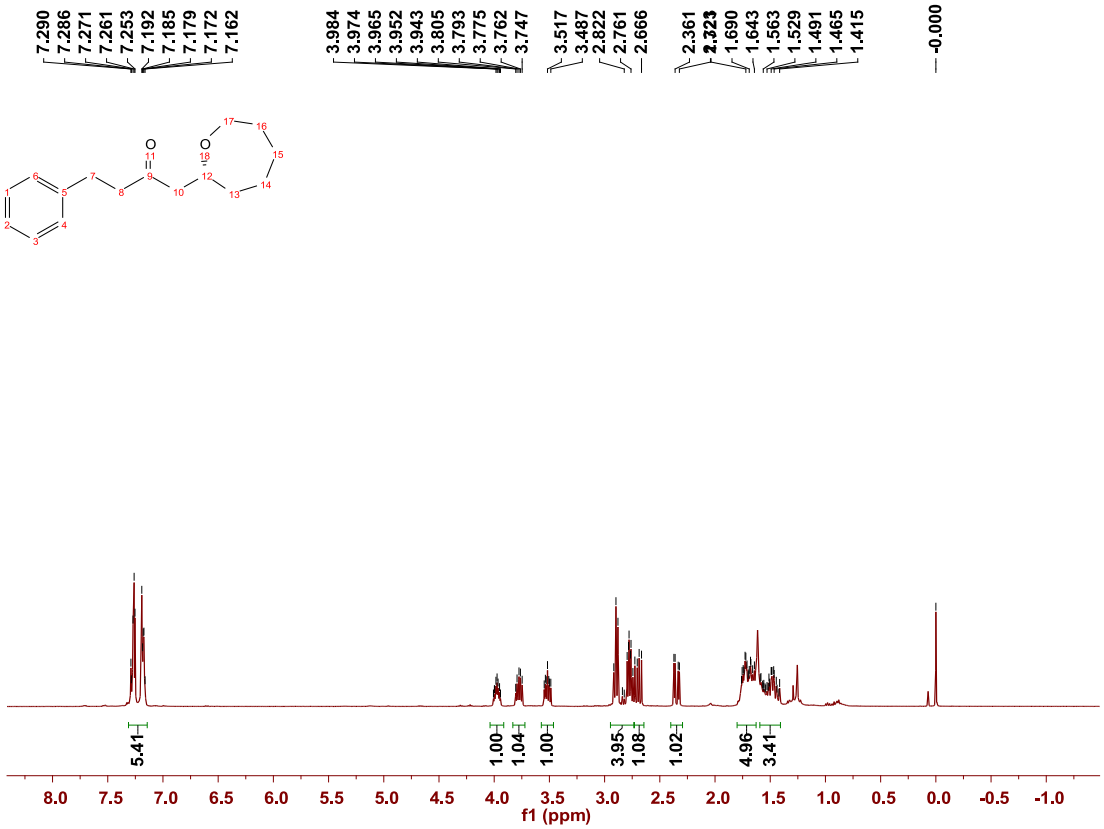
47.04
35.92
30.96
26.24
26.07
f1 (ppm)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7.179
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3.974
3.965
3.952
3.943
3.805
3.793
3.775
3.762
3.747
3.517
3.487
2.822
2.761
2.666
2.361
1.690
1.643
1.563
1.529
1.491
1.465
1.415
-0.000
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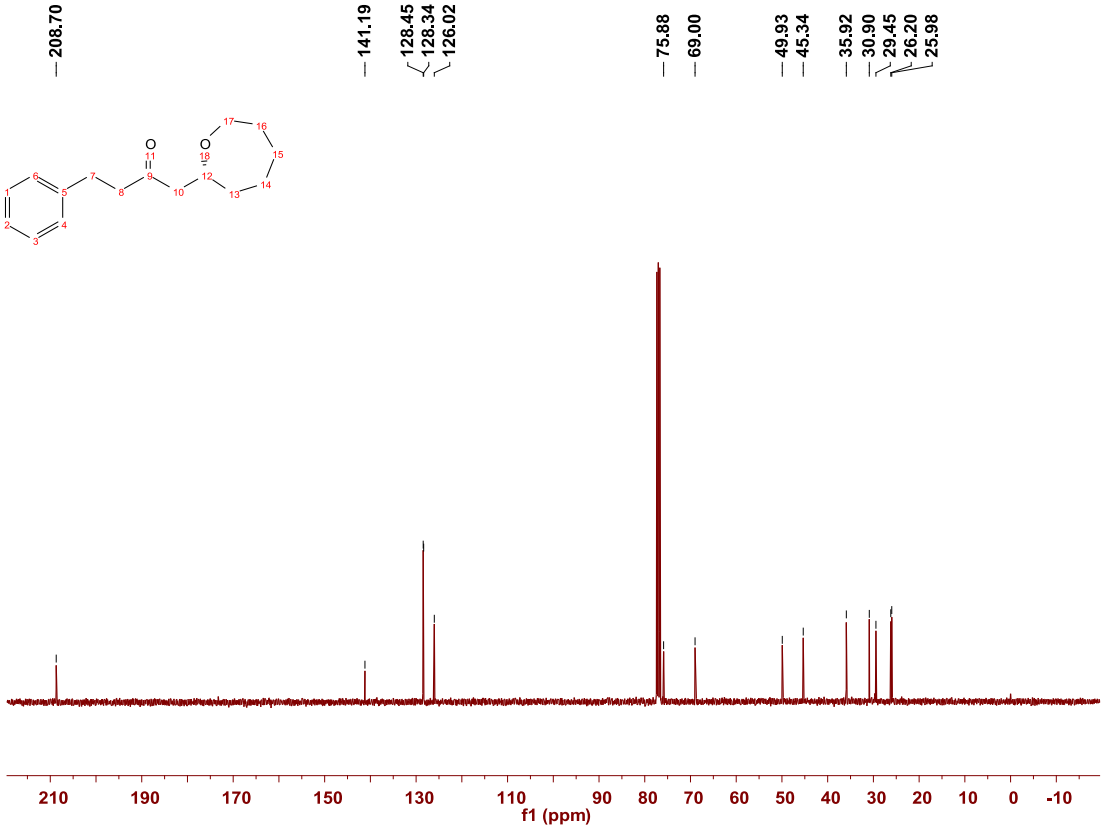
1.00
1.04
1.00
3.95
1.08
1.02
4.96
3.41
f1 (ppm)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128.45
128.34
126.02
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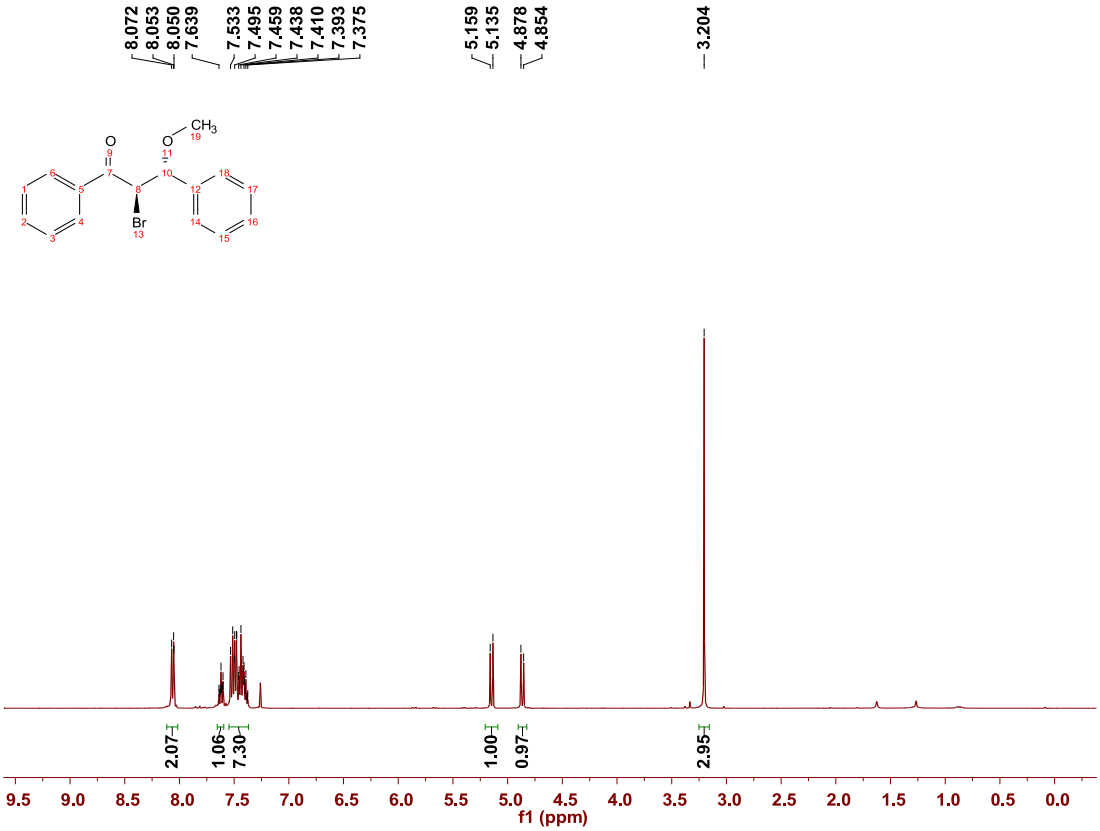
69.00
49.93
45.34
35.92
30.90
29.45
26.20
25.98
f1 (ppm)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7.459
7.438
7.410
7.393
7.375
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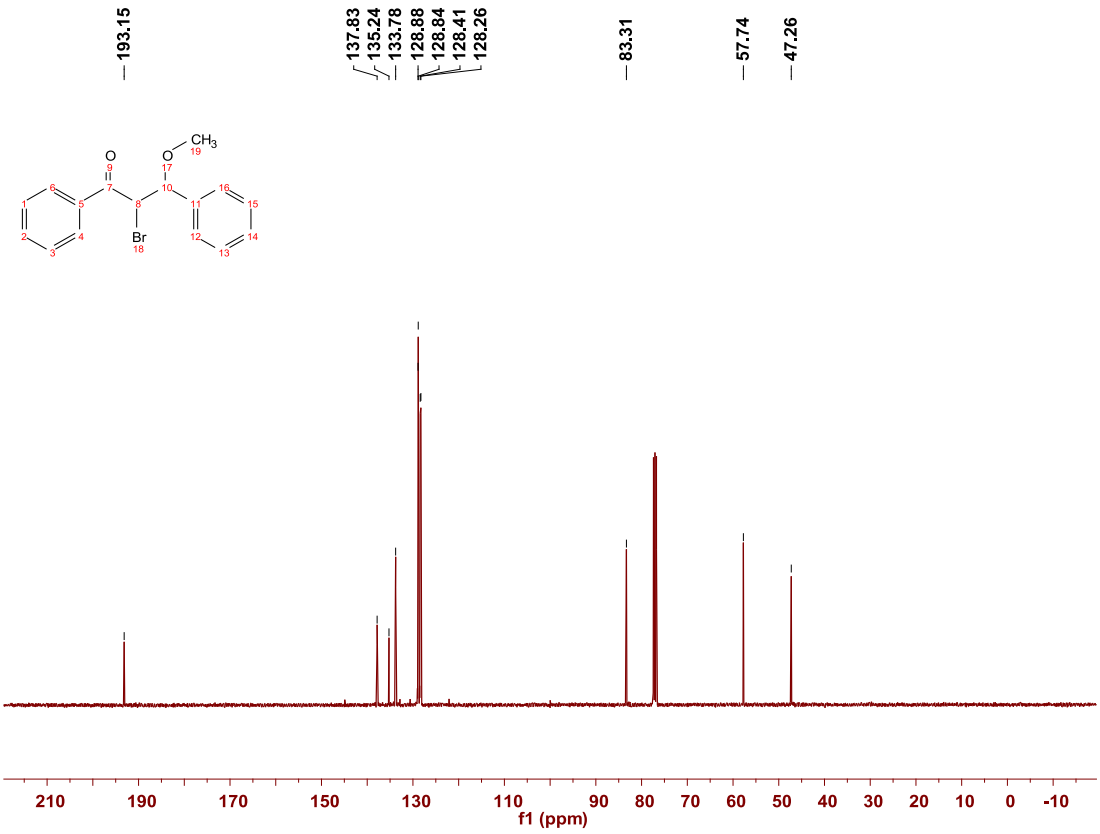
4.854
3.204
2.07
1.06
7.30
1.00
0.97
2.95
f1 (ppm)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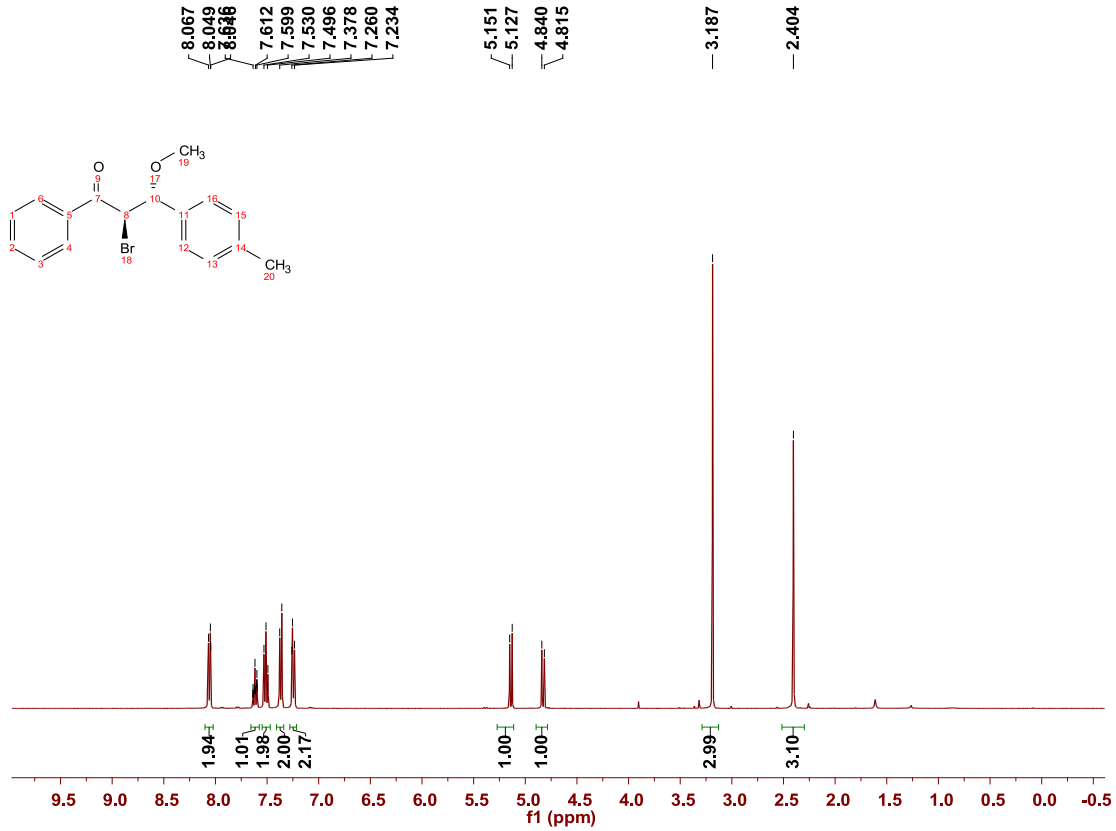
133.78
128.88
128.84
128.41
128.26
83.31
57.74
47.26
f1 (ppm)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5.127
4.840
4.815
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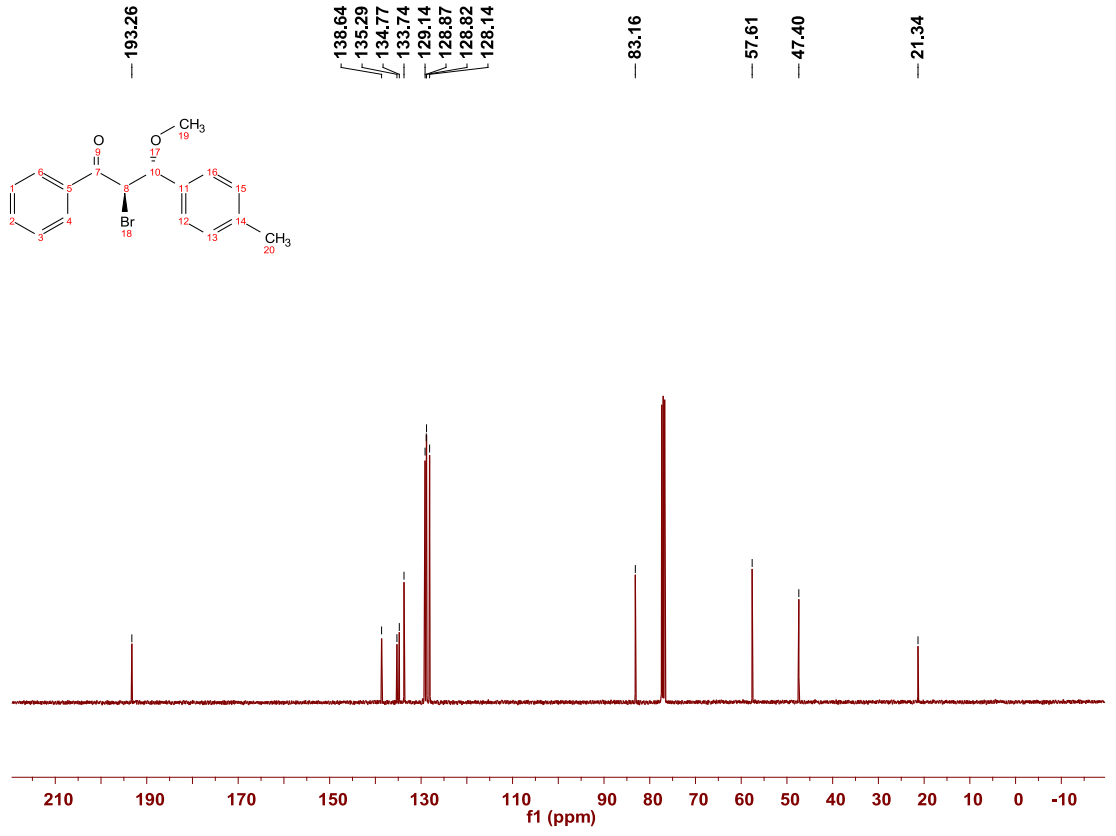
1.01
1.98
2.00
2.17
1.00
1.00
2.99
3.10
f1 (ppm)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128.82
128.14
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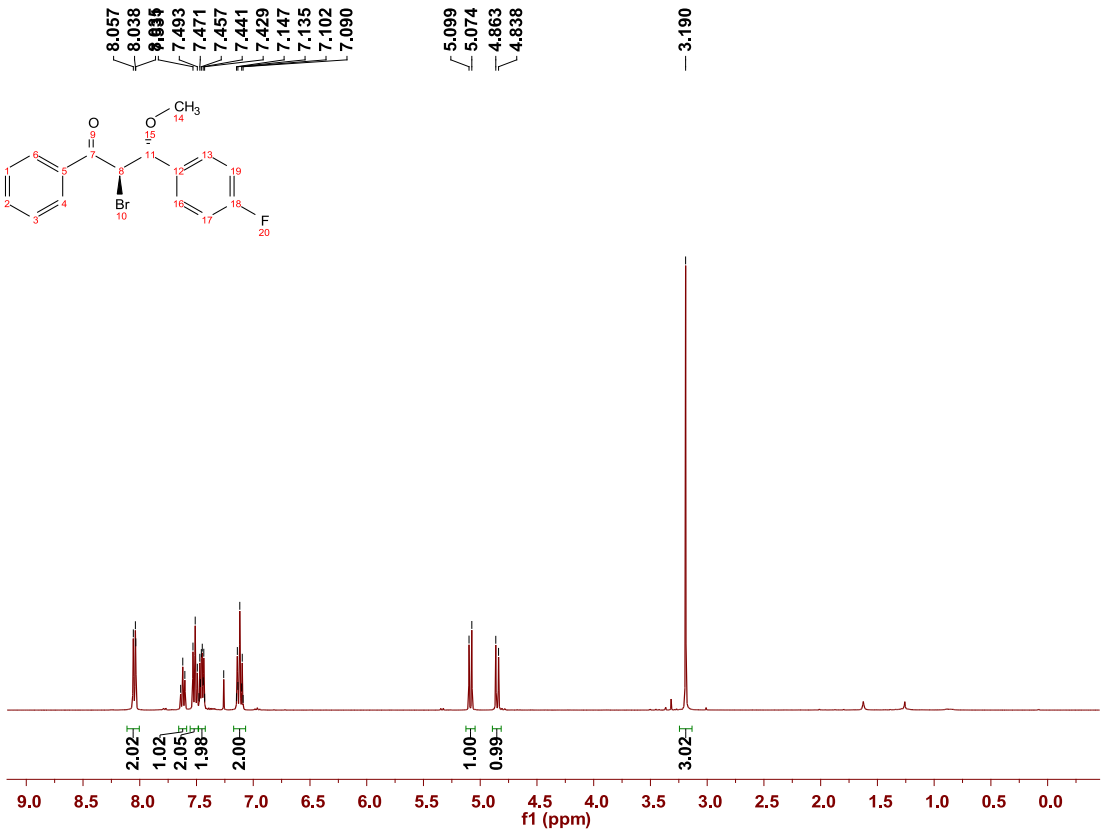
57.61
47.40
21.34
f1 (ppm)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8.038
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7.147
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7.102
7.090
5.099
5.074
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4.838
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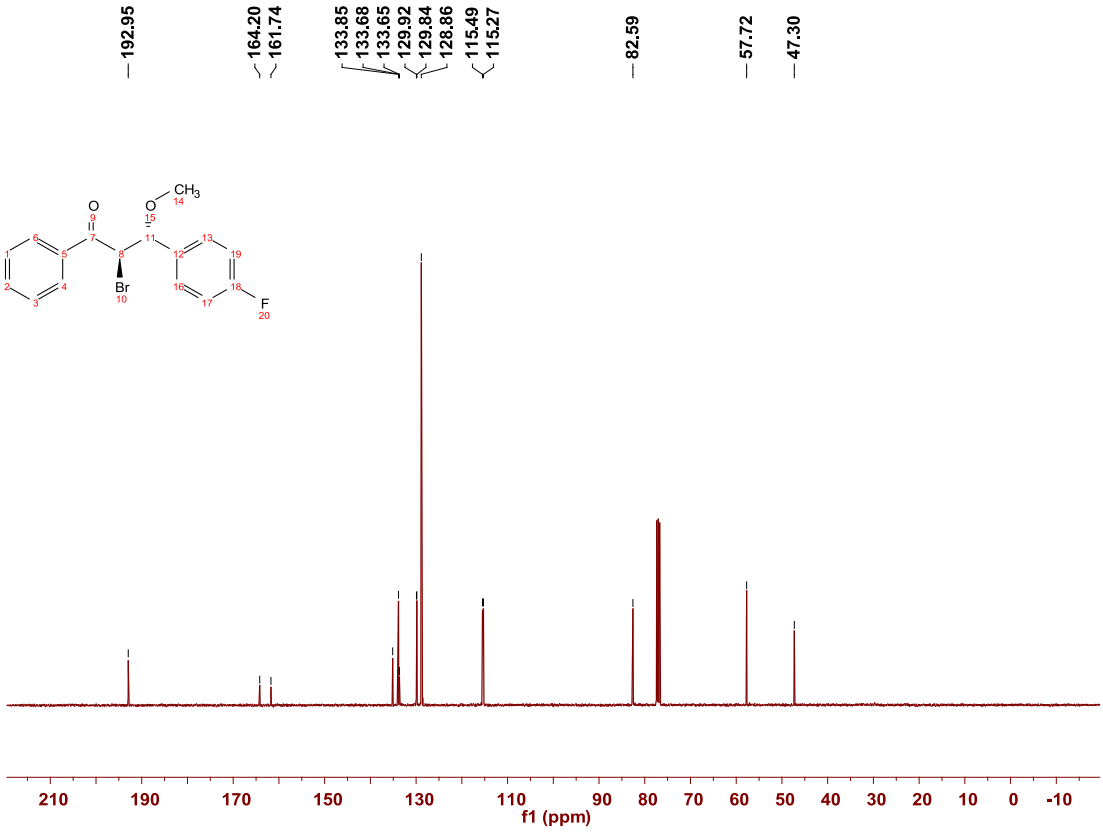
2.02
1.02
2.05
1.98
2.00
1.00
0.99
3.02
f1 (ppm)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129.84
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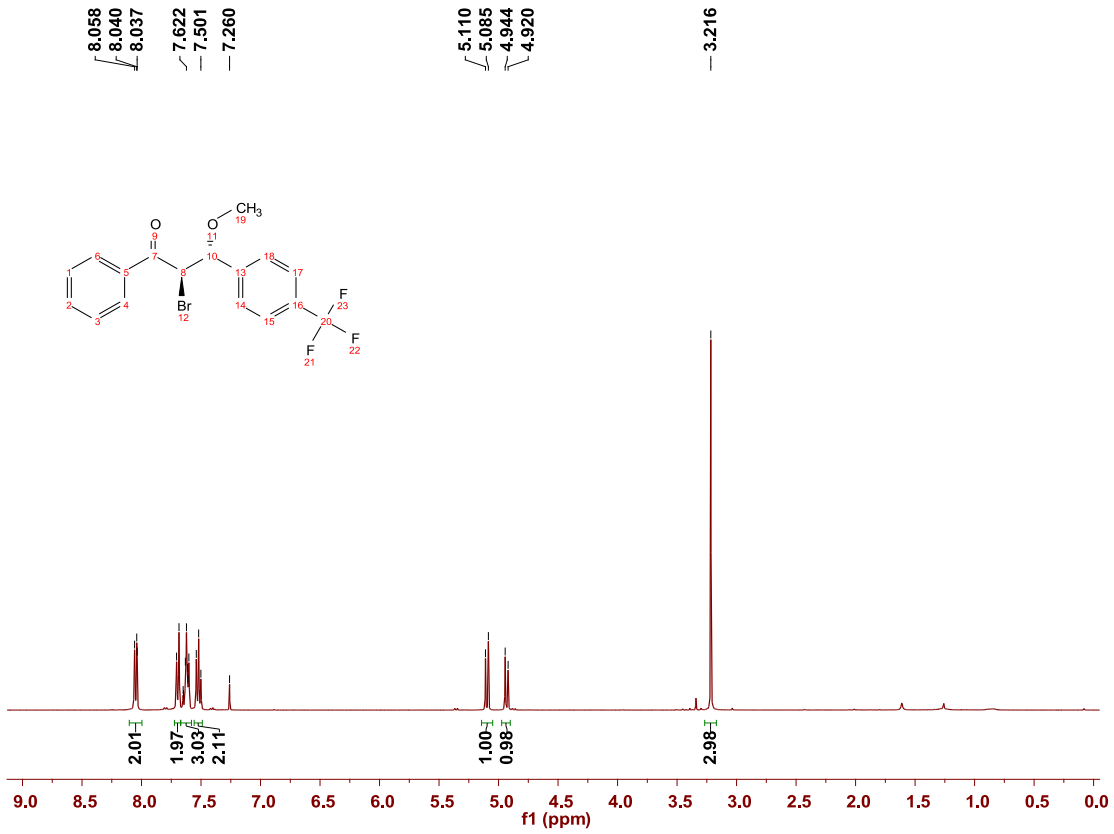
115.49
115.27
82.59
57.72
47.30
f1 (ppm)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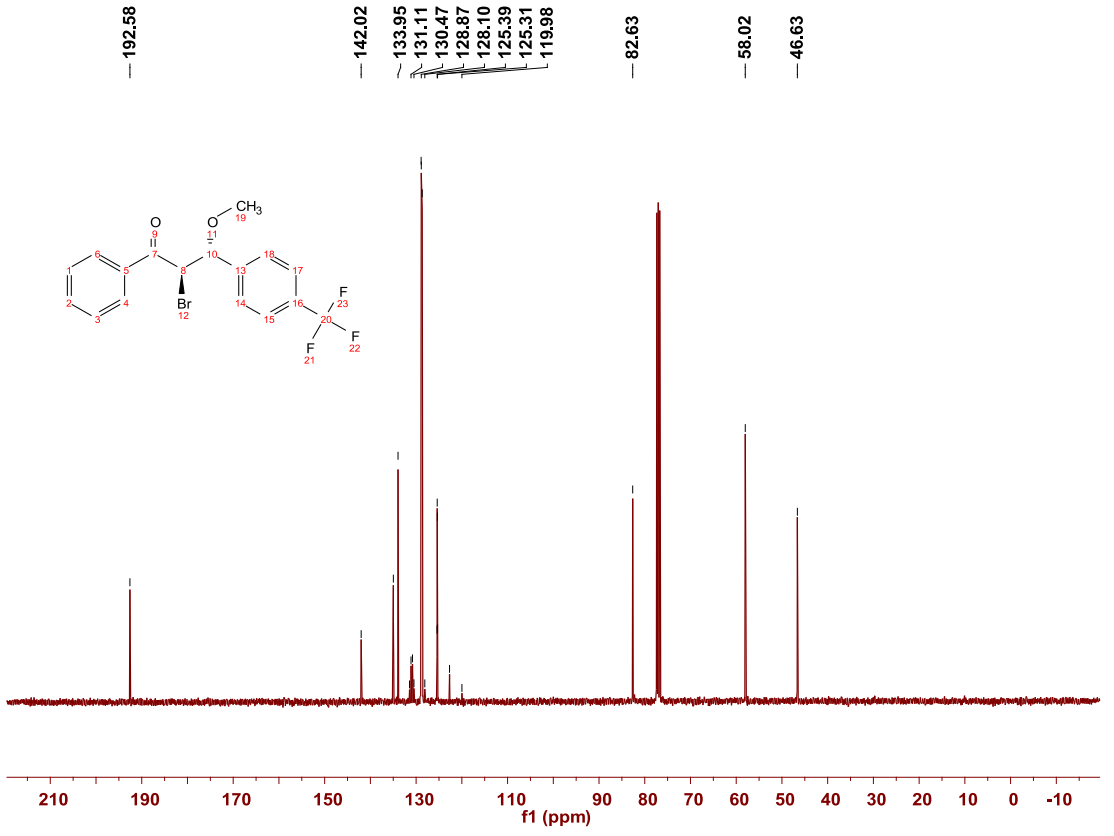
7.622
7.501
7.260
5.110
5.085
4.944
4.920
3.216
2.01
1.97
3.03
2.11
1.00
0.98
2.98
f1 (ppm)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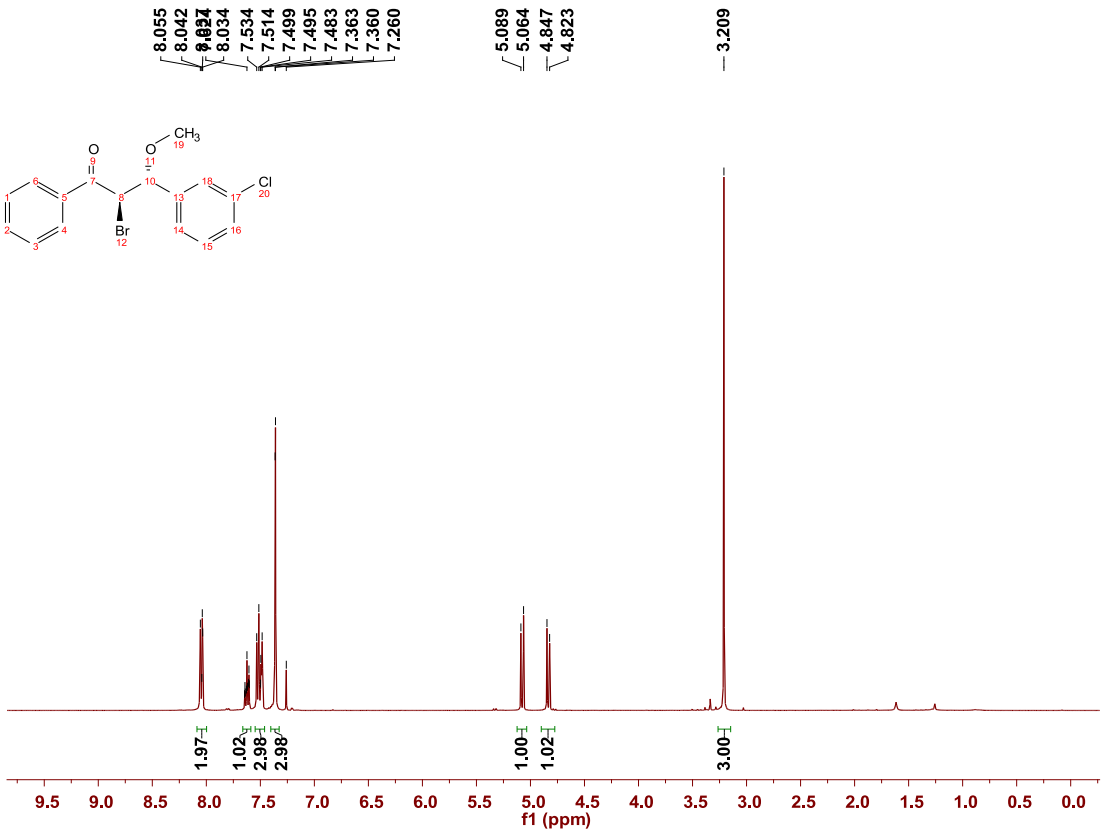
142.02
133.95
131.11
130.47
128.87
128.10
125.39
125.31
119.98
82.63
58.02
46.63
f1 (ppm)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8.042
8.034
7.534
7.514
7.499
7.495
7.483
7.363
7.360
7.260
5.089
5.064
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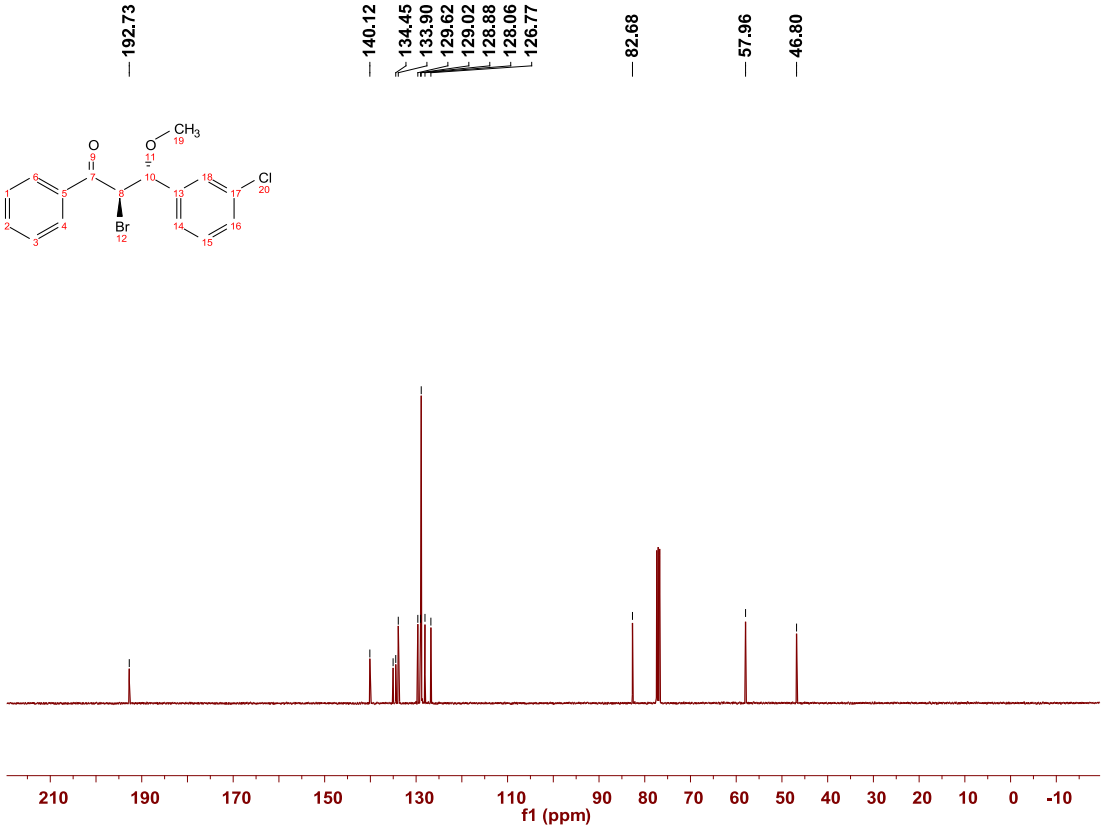
3.209
1.97
1.02
2.98
2.98
1.00
1.02
3.00
f1 (ppm)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134.45
133.90
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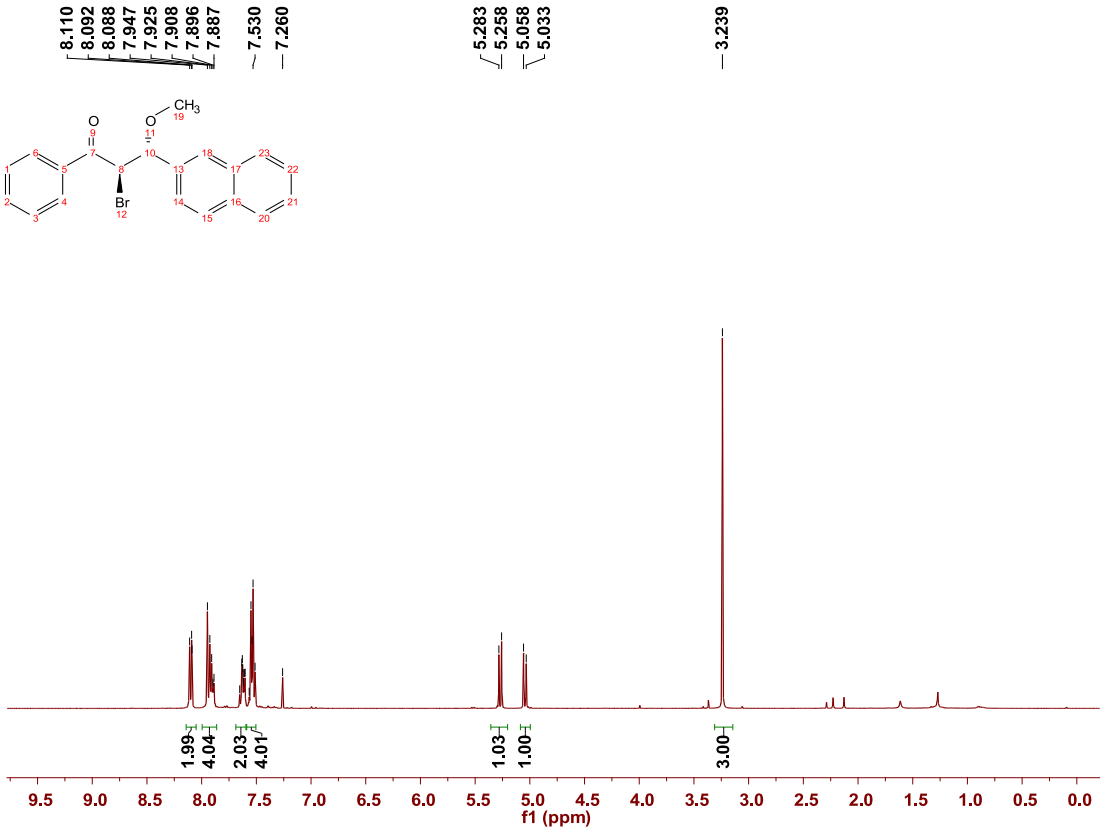
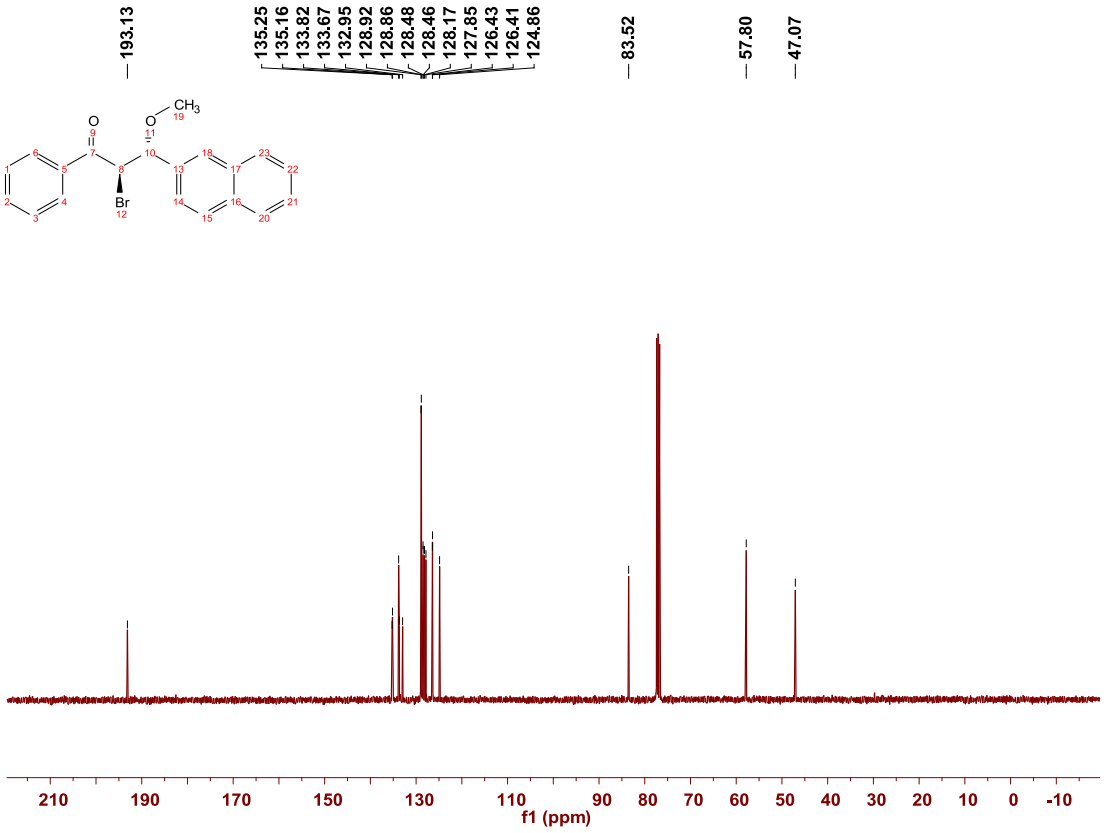
129.02
128.88
128.06
126.77
82.68
57.96
46.80
f1 (ppm)


8.110
8.092
8.088
7.947
7.925
7.908
7.896
7.887
7.530
7.260
5.283
5.258
5.058
5.033
3.239
O
O
CH3
Br
1.99
4.04
2.03
4.01
1.03
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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135.16
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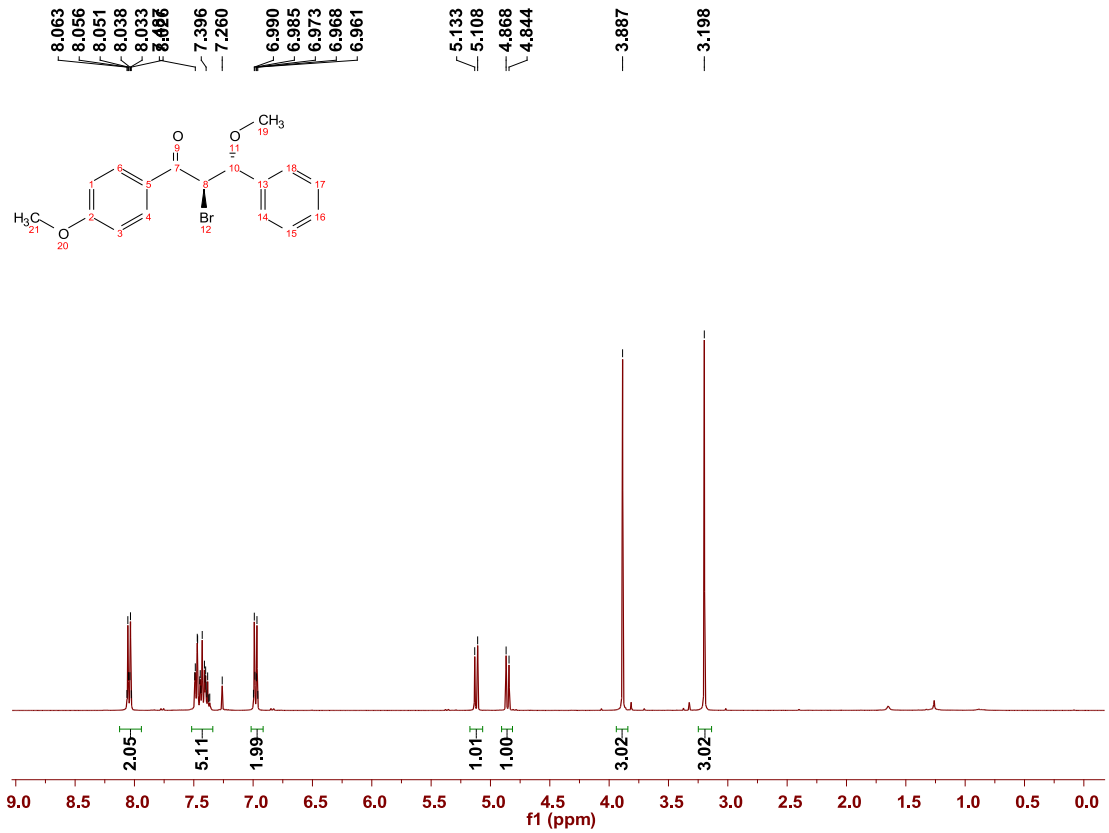
133.67
132.95
128.92
128.86
128.48
128.46
128.17
127.85
126.43
126.41
124.86
83.52
57.80
47.07
O
O
CH3
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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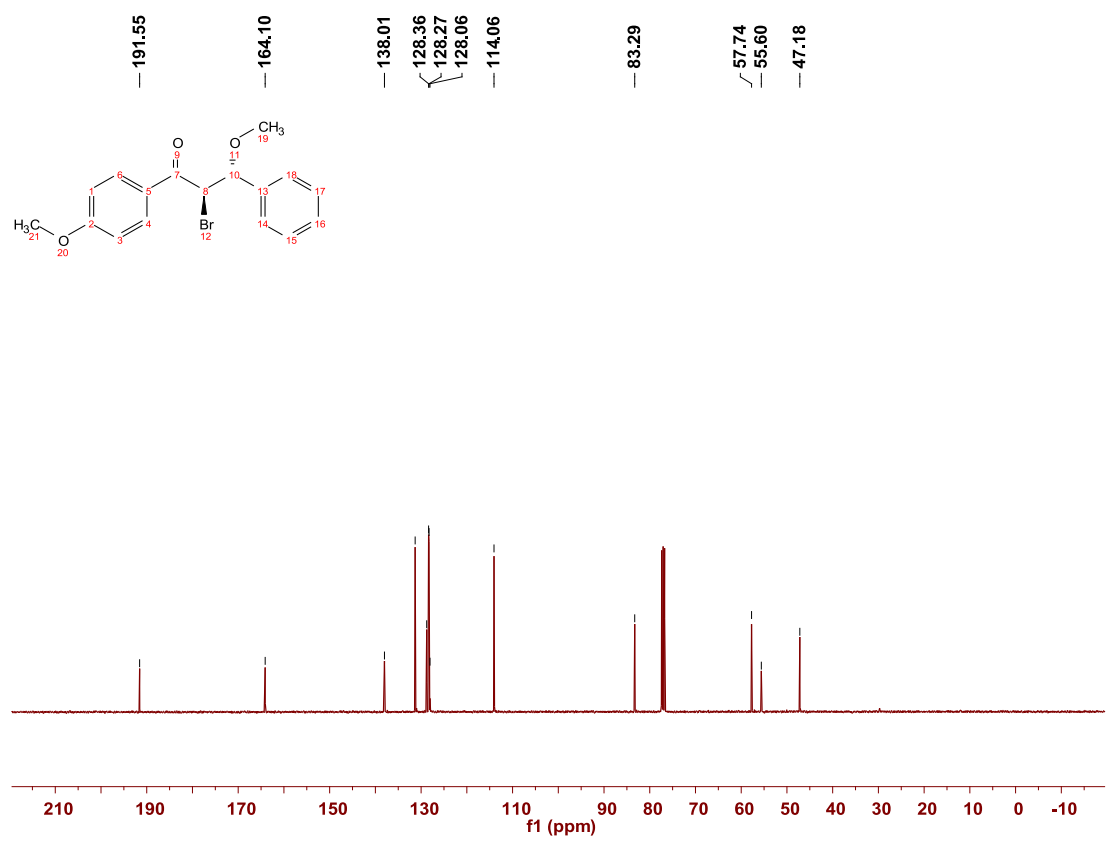
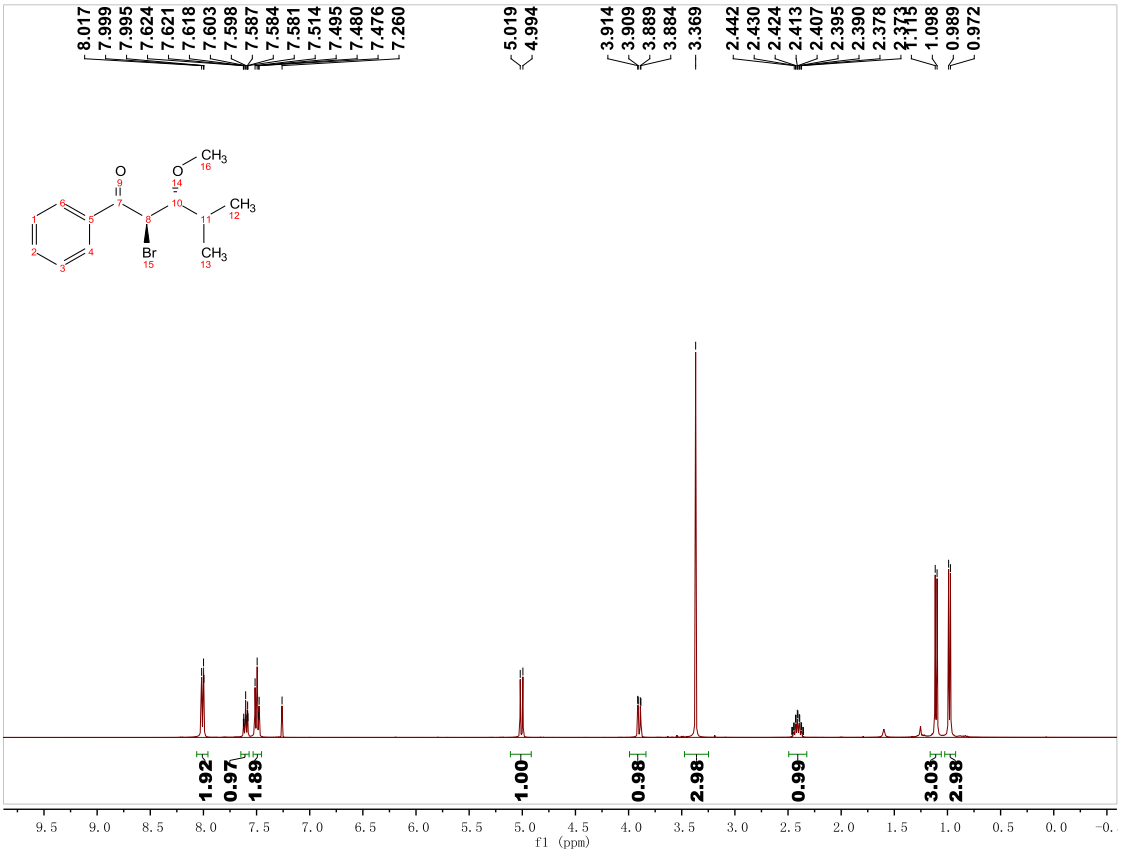
8.056
8.051
8.038
8.033
7.396
7.260
6.990
6.985
6.973
6.968
6.961
5.133
5.108
4.868
4.844
3.887
3.198
2.05
5.11
1.99
1.01
1.00
3.02
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


191.55
164.10
138.01
128.36
128.27
128.06
114.06
83.29
57.74
55.60
47.18
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.995
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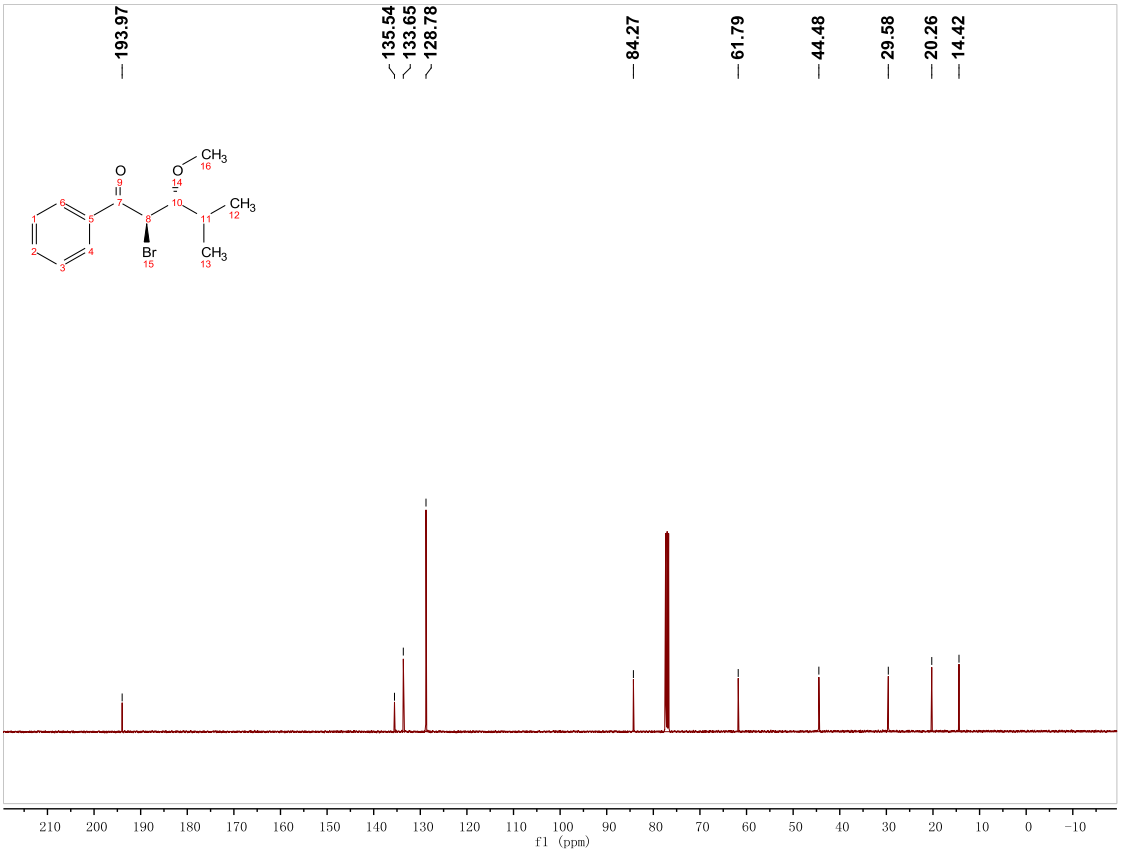
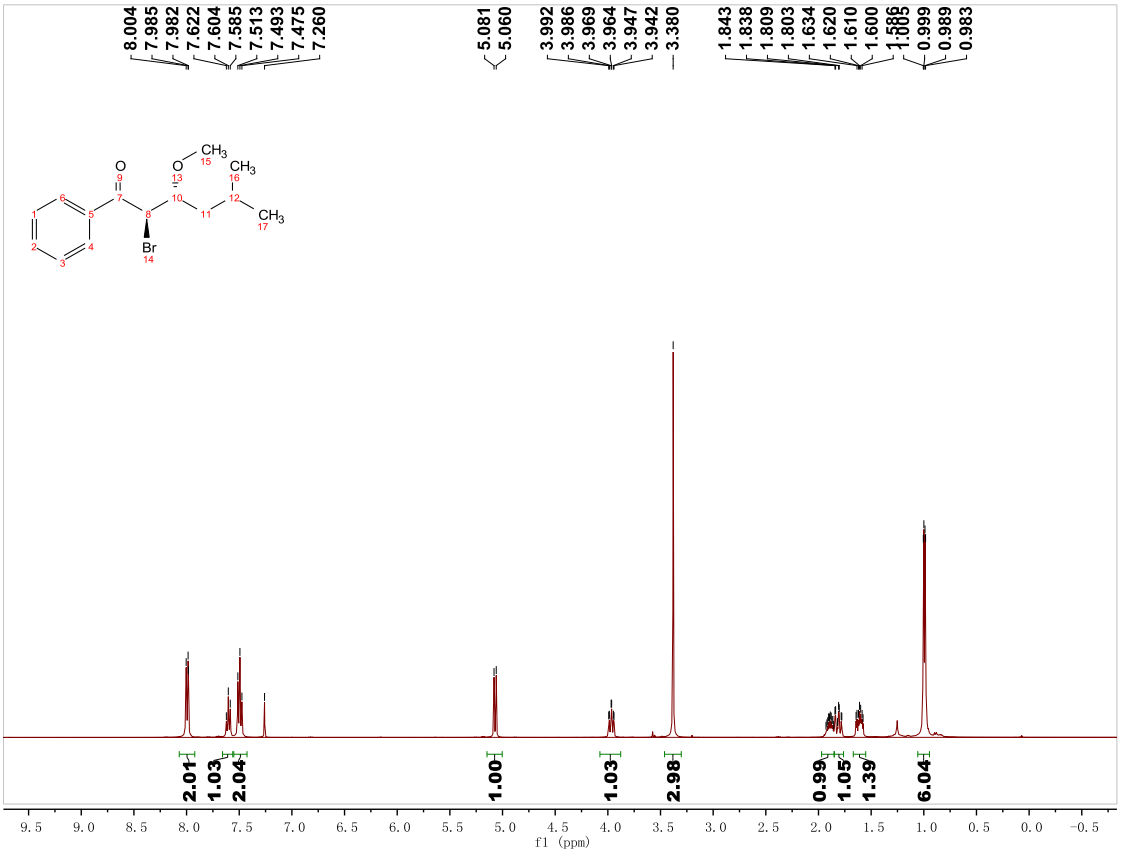
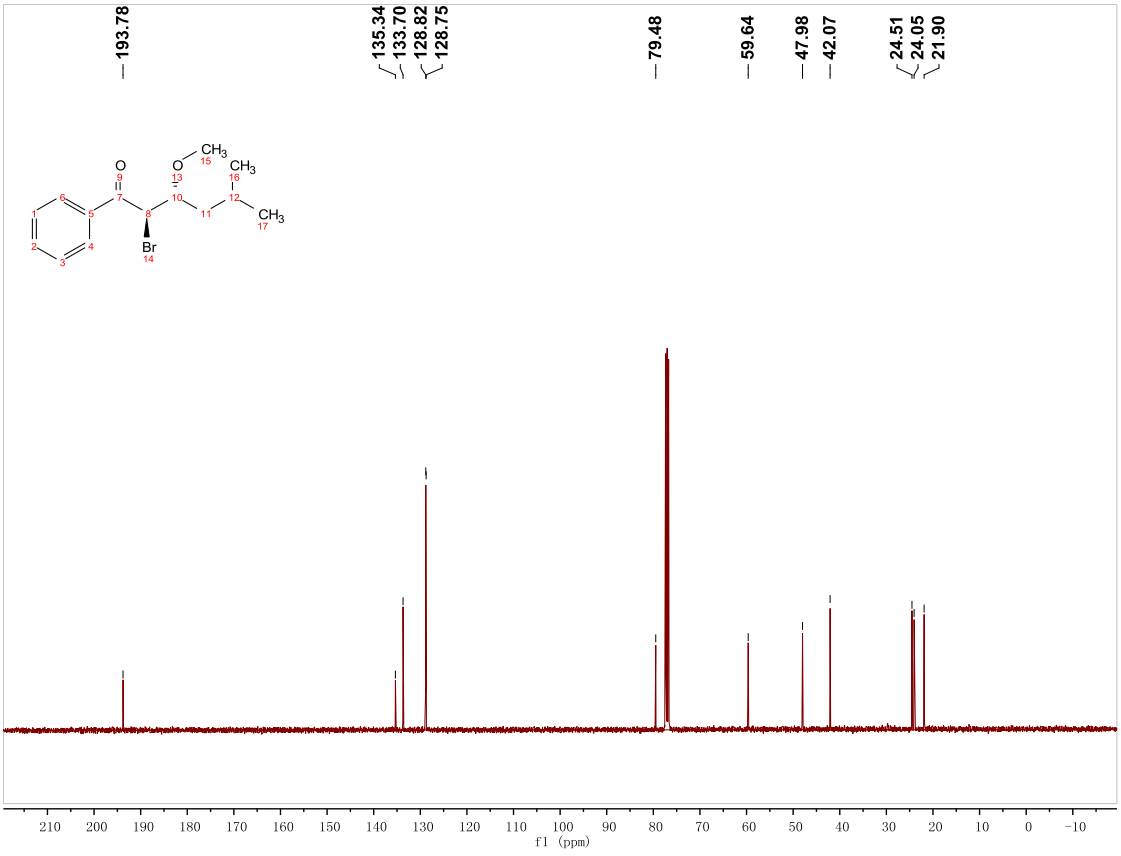
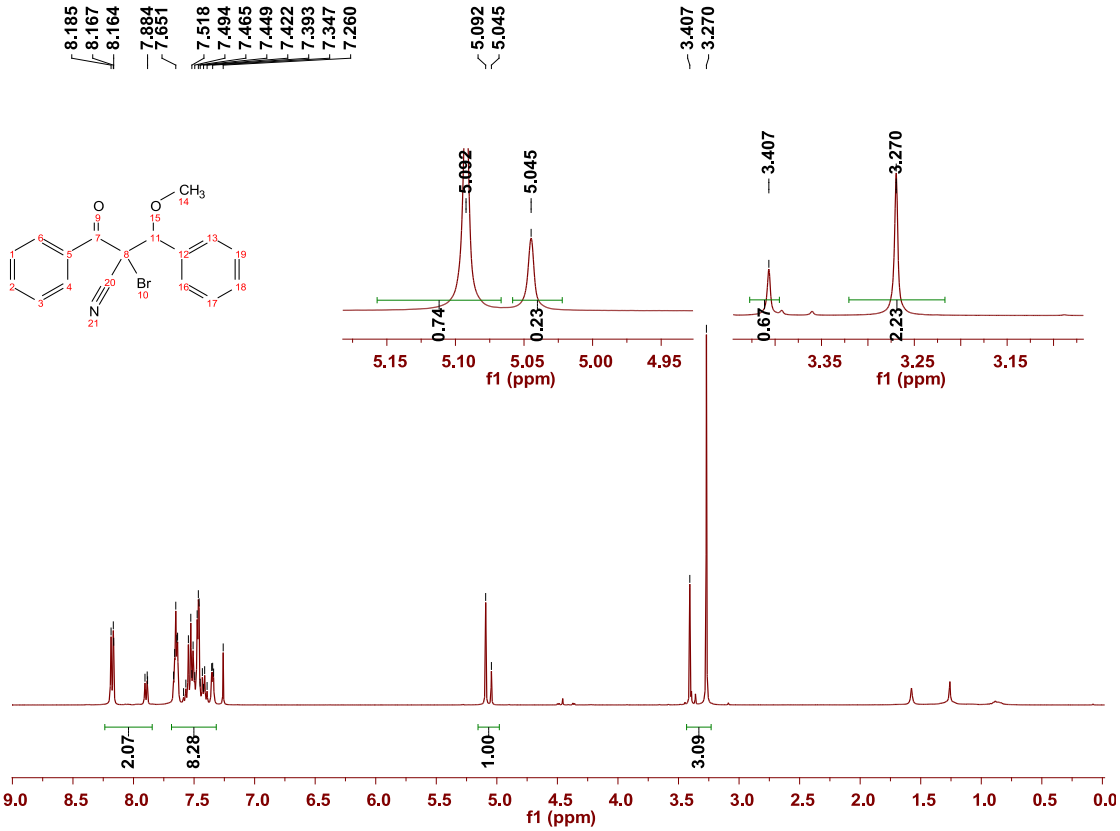
7.618
7.603
7.598
7.587
7.584
7.581
7.514
7.495
7.480
7.476
7.260
5.019
4.994
3.914
3.909
3.889
3.884
3.369
2.442
2.430
2.424
2.413
2.407
2.395
2.390
2.378
1.115
1.098
0.989
0.972
1.92
0.97
1.89
1.00
0.98
2.98
0.99
3.03
2.98
f1 (ppm)


193.97
135.54
133.65
128.78
84.27
61.79
44.48
29.58
20.26
14.42
f1 (ppm)


8.004
7.985
7.982
7.622
7.604
7.585
7.513
7.493
7.475
7.260
5.081
5.060
3.992
3.986
3.969
3.964
3.947
3.942
3.380
1.843
1.838
1.809
1.803
1.634
1.620
1.610
1.600
0.999
0.989
0.983
2.01
1.03
2.04
1.00
1.03
2.98
0.99
1.05
1.39
6.04
f1 (ppm)


193.78
135.34
133.70
128.82
128.75
79.48
59.64
47.98
42.07
24.51
24.05
21.90
f1 (ppm)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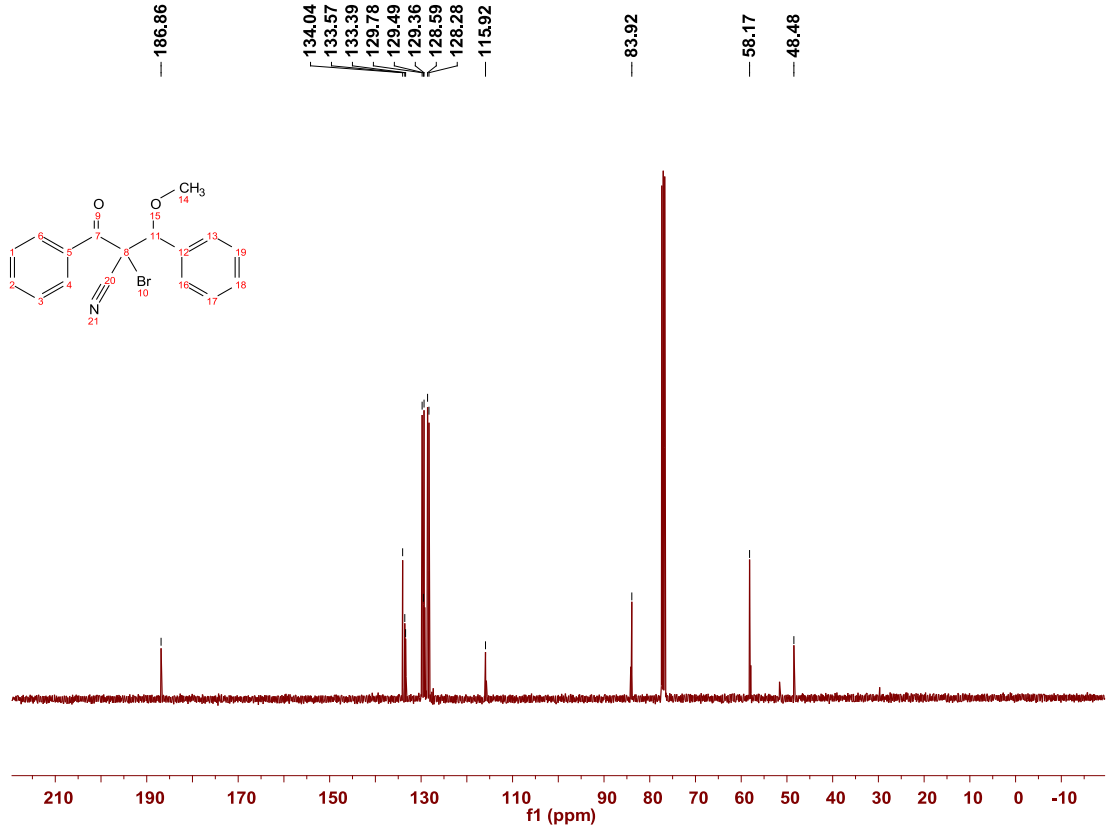
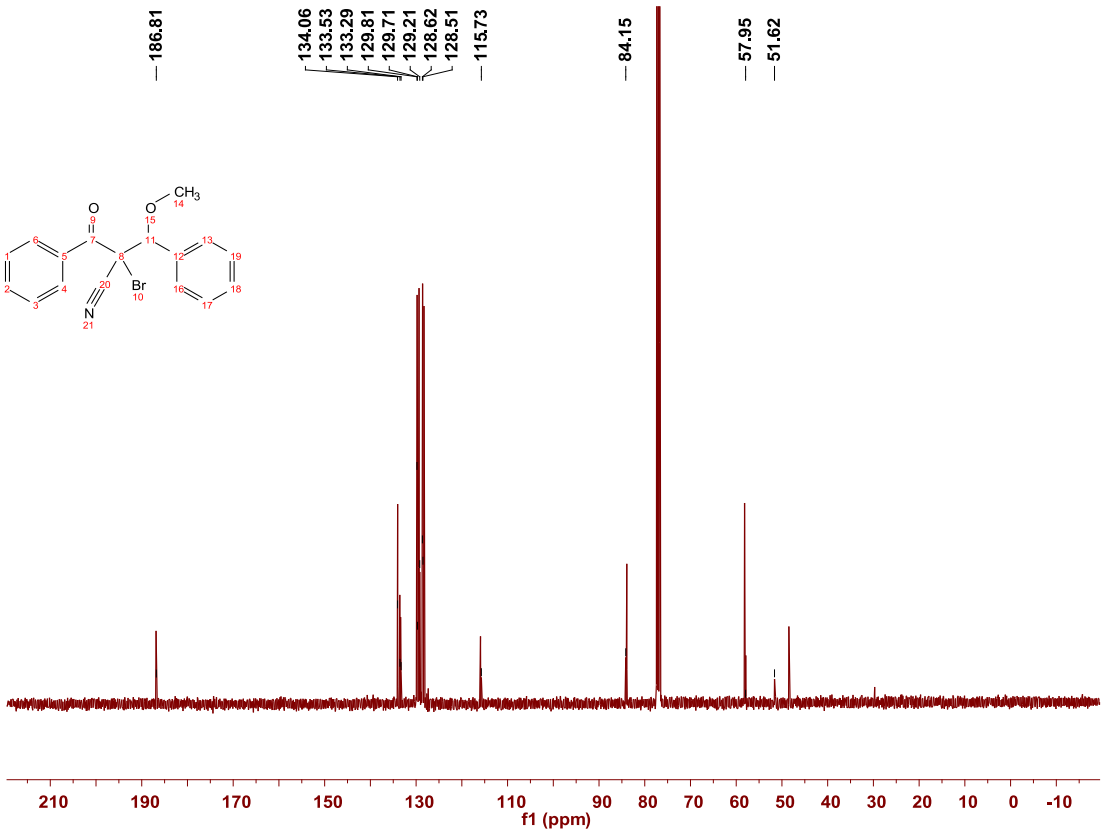
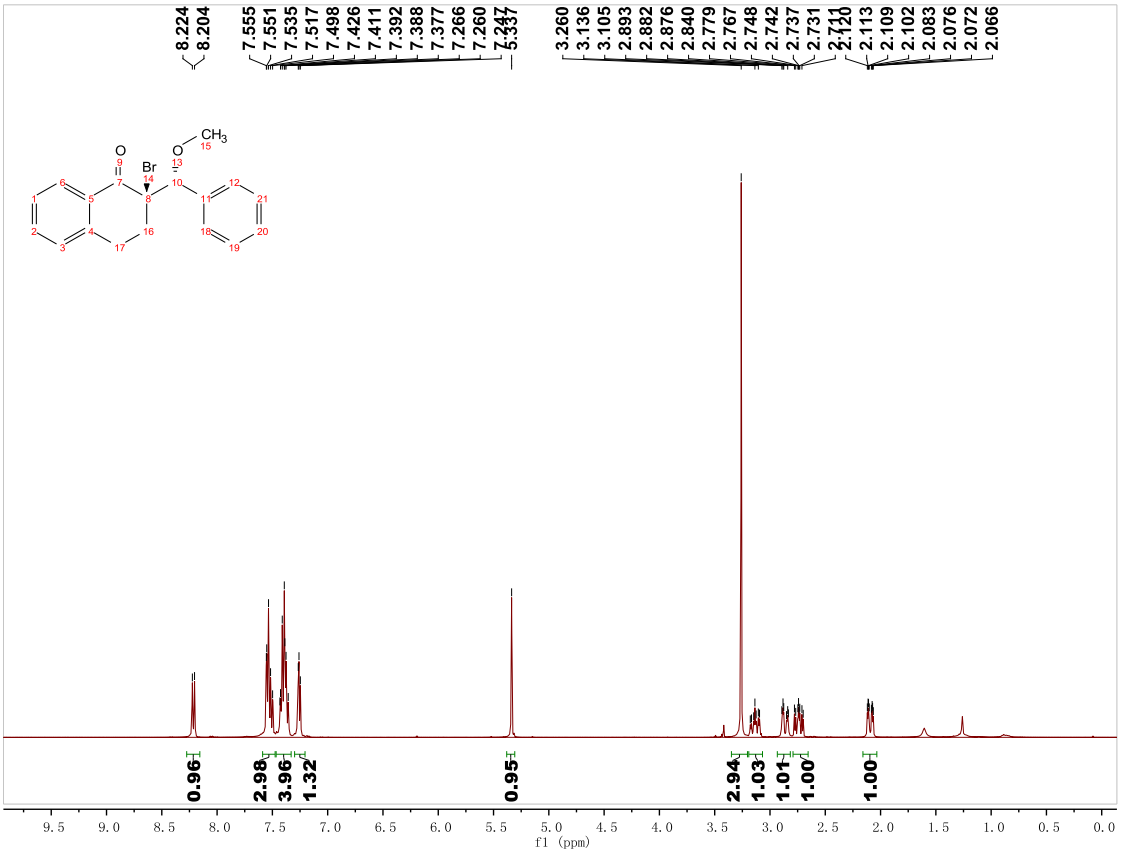
8.167
8.164
7.884
7.651
7.518
7.494
7.465
7.449
7.422
7.393
7.347
7.260
5.092
5.045
3.407
3.270
O
O
CH3
Br
N
5.092
5.045
0.74
0.23
5.15
5.10
5.05
5.00
4.95
f1 (ppm)
3.407
3.270
0.67
2.23
3.35
3.25
3.15
f1 (ppm)
2.07
8.28
1.00
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


186.86
134.04
133.57
133.39
129.78
129.49
129.36
128.59
128.28
115.92
83.92
58.17
48.48
O
O
CH3
Br
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


186.81
134.06
133.53
133.29
129.81
129.71
129.21
128.62
128.51
115.73
84.15
57.95
51.62
O
O
CH3
Br
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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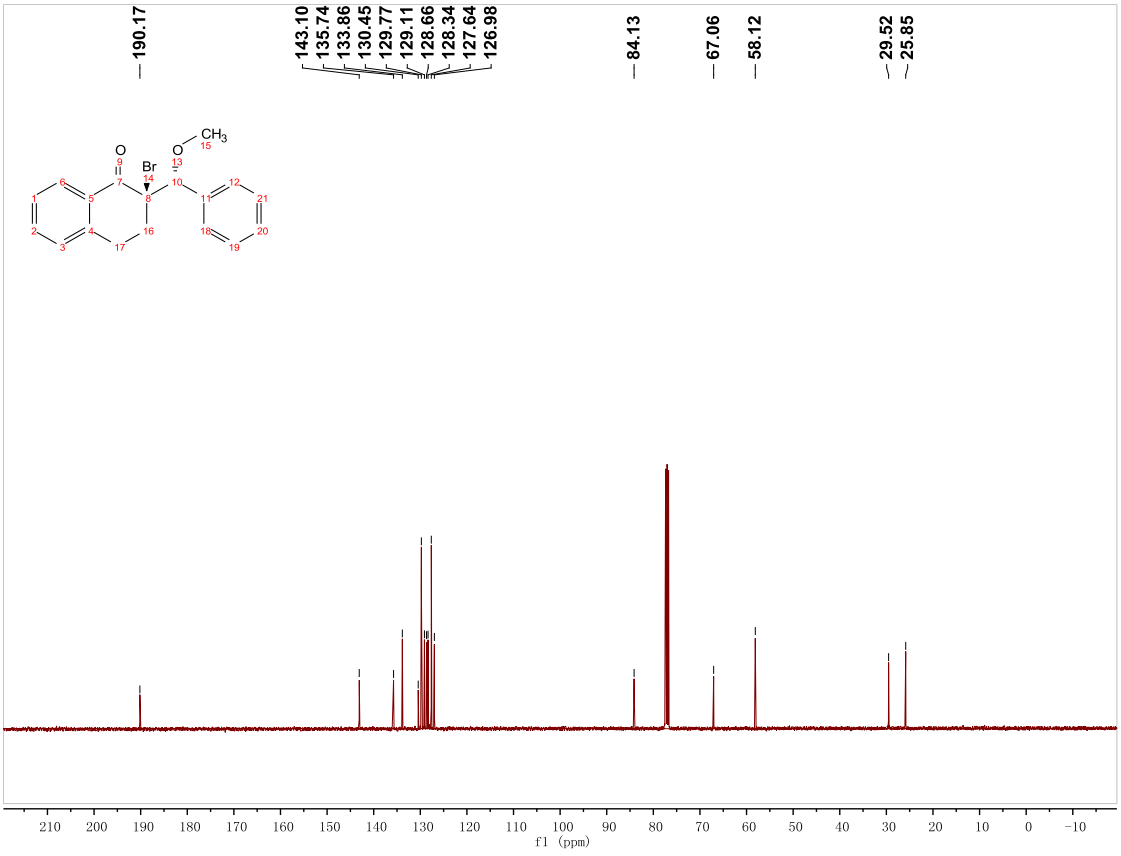
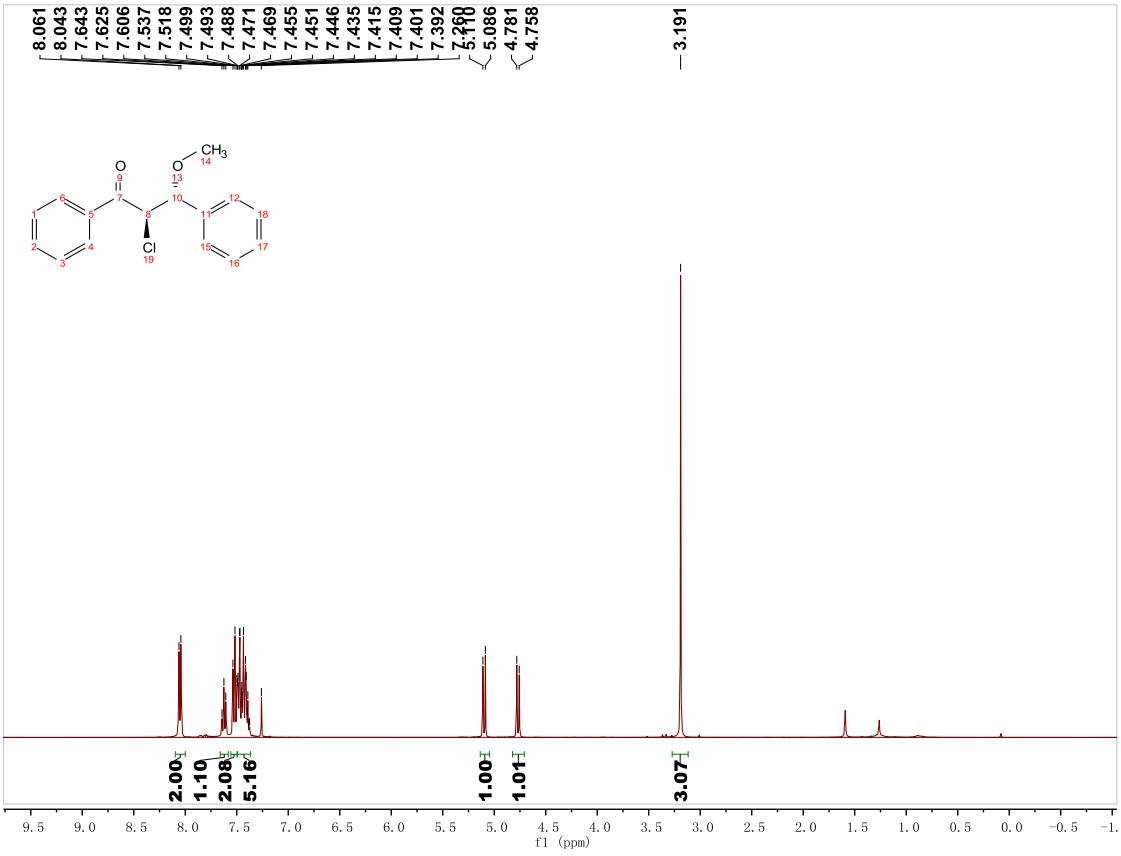
7.551
7.535
7.517
7.498
7.426
7.411
7.392
7.388
7.377
7.266
7.260
5.337
3.260
3.136
3.105
2.893
2.882
2.876
2.840
2.779
2.767
2.748
2.742
2.737
2.731
2.120
2.113
2.109
2.102
2.083
2.076
2.072
2.066
0.96
2.98
3.96
1.32
0.95
2.94
1.03
1.01
1.00
1.00
f1 (ppm)


190.17
143.10
135.74
133.86
130.45
129.77
129.11
128.66
128.34
127.64
126.98
84.13
67.06
58.12
29.52
25.85
f1 (ppm)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7.643
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7.537
7.518
7.499
7.493
7.488
7.471
7.469
7.455
7.451
7.446
7.435
7.415
7.409
7.401
7.392
7.260
5.110
5.086
4.781
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3.191
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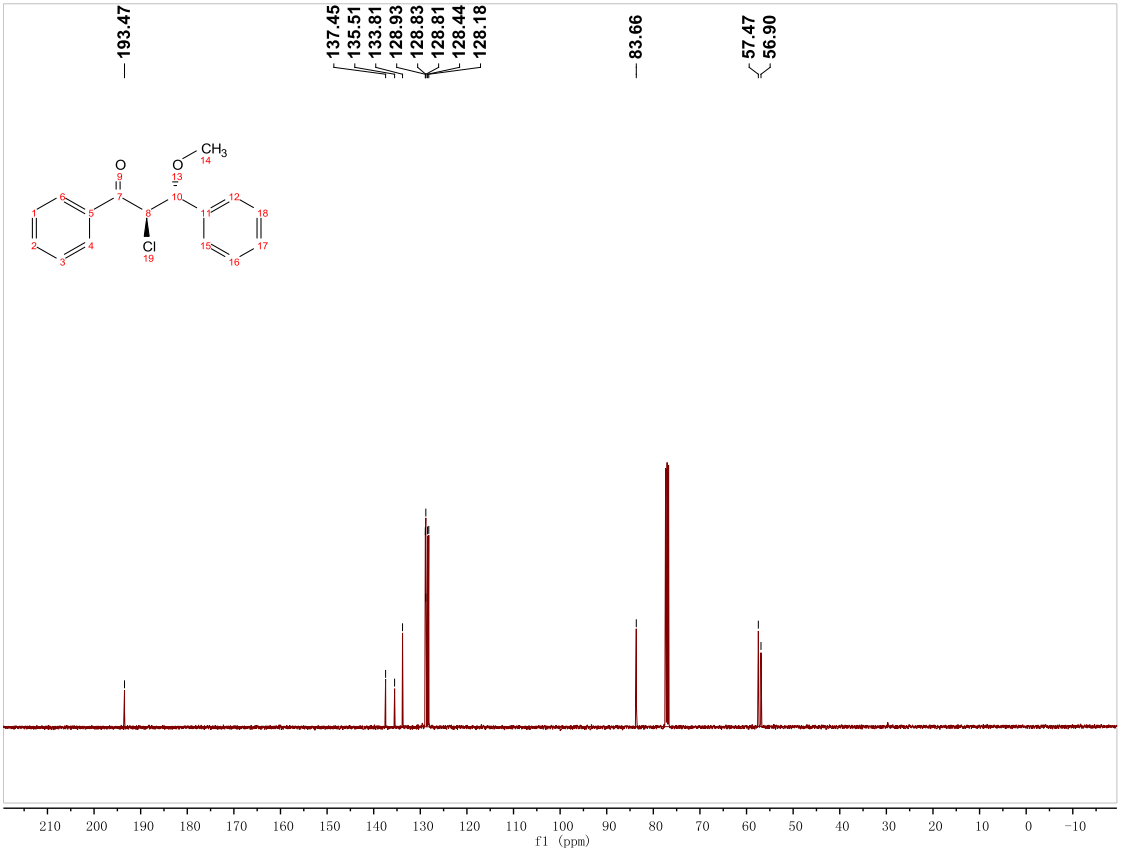
1.10
2.08
5.16
1.00
1.01
3.07
f1 (ppm)


193.47
137.45
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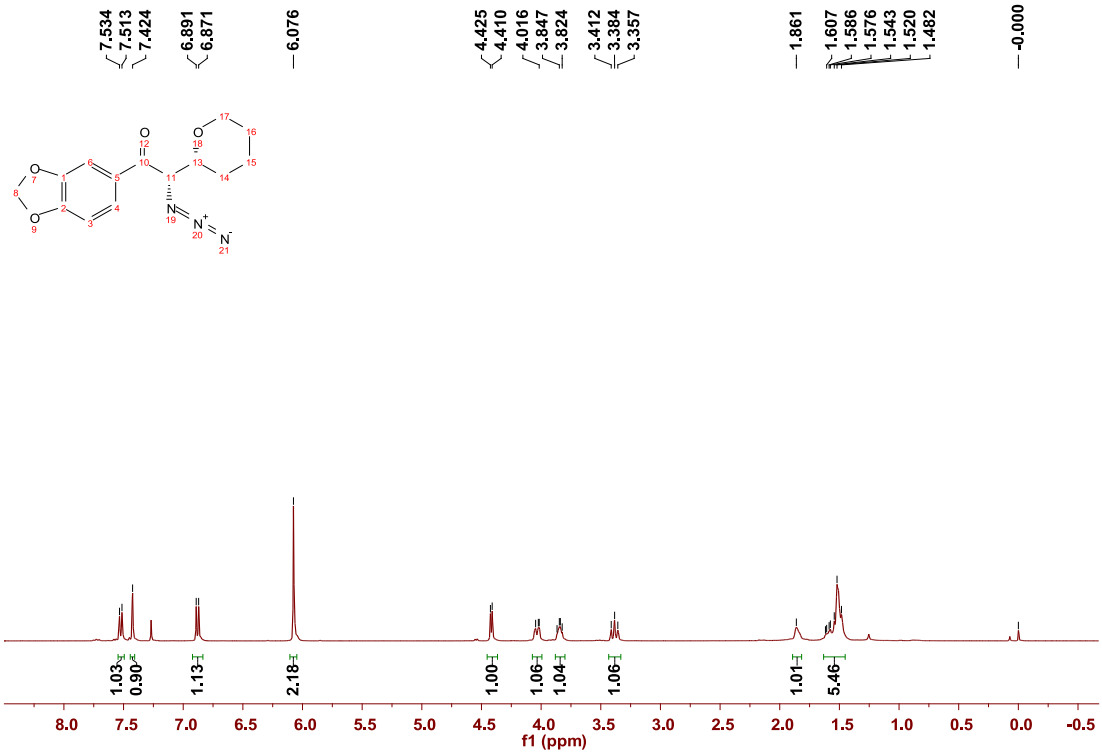
133.81
128.93
128.83
128.81
128.44
128.18
83.66
57.47
56.90
f1 (ppm)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4.410
4.016
3.847
3.824
3.412
3.384
3.357
1.861
1.607
1.586
1.576
1.543
1.520
1.482
-0.000
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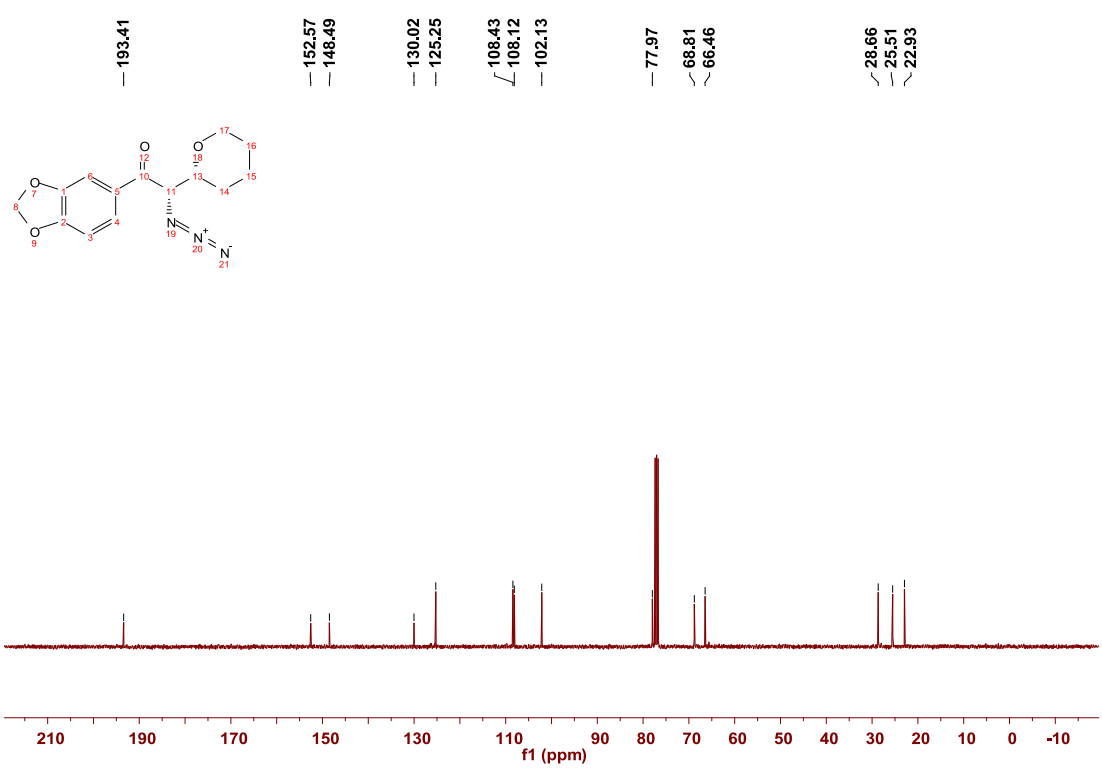
0.90
1.13
2.18
1.00
1.06
1.04
1.06
1.01
5.46
f1 (ppm)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152.57
148.49
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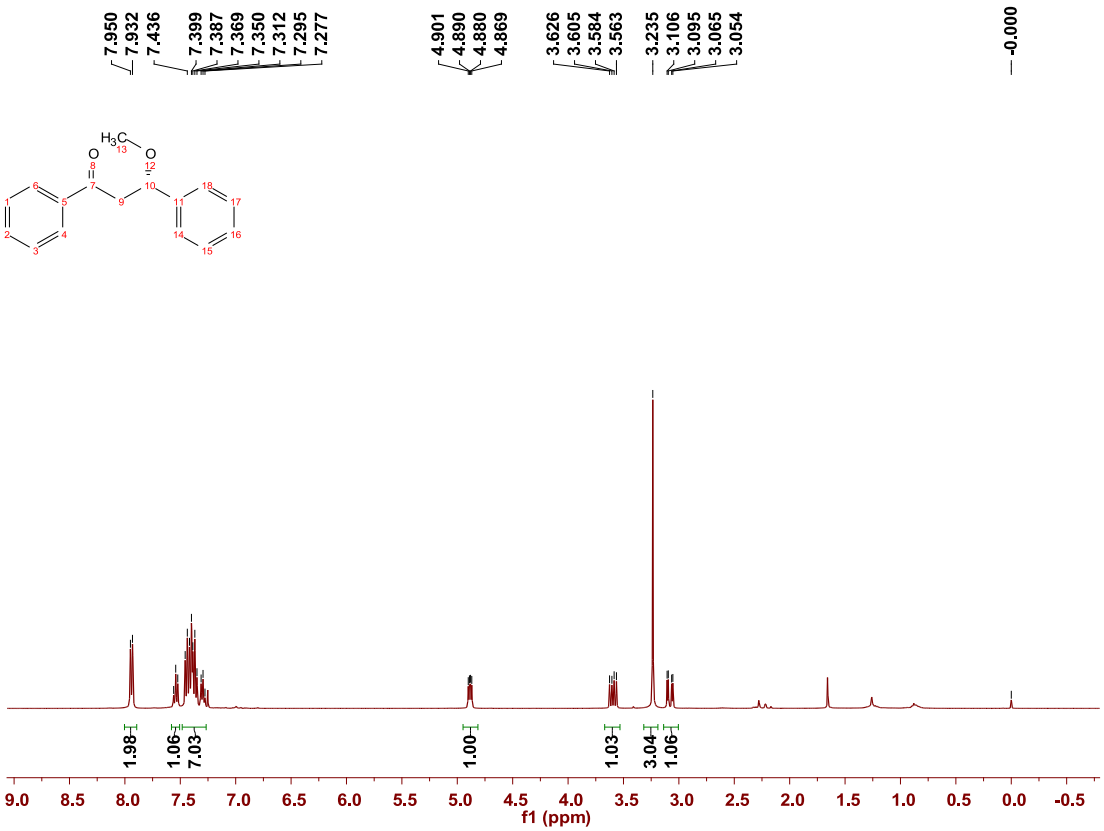
108.12
102.13
77.97
68.81
66.46
28.66
25.51
22.93
f1 (ppm)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7.312
7.295
7.277
4.901
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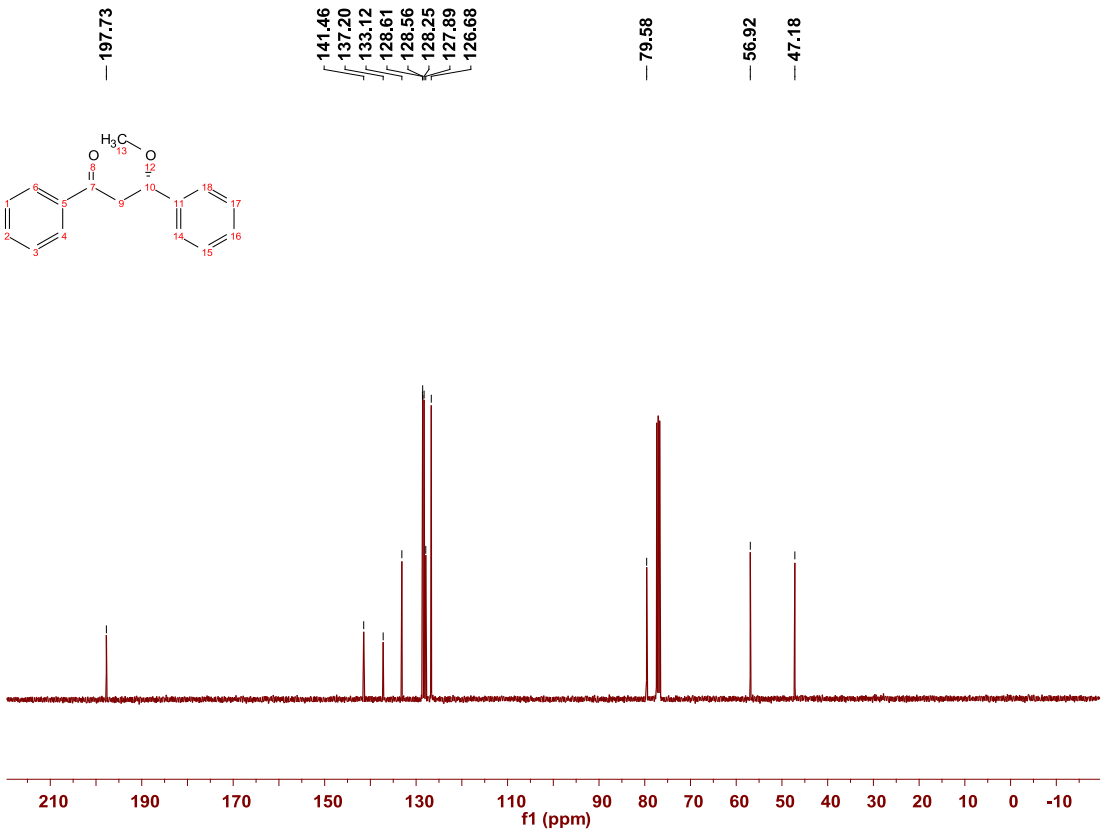
4.880
4.869
3.626
3.605
3.584
3.563
3.235
3.106
3.095
3.065
3.054
-0.000
1.98
1.06
7.03
1.00
1.03
3.04
1.06
f1 (ppm)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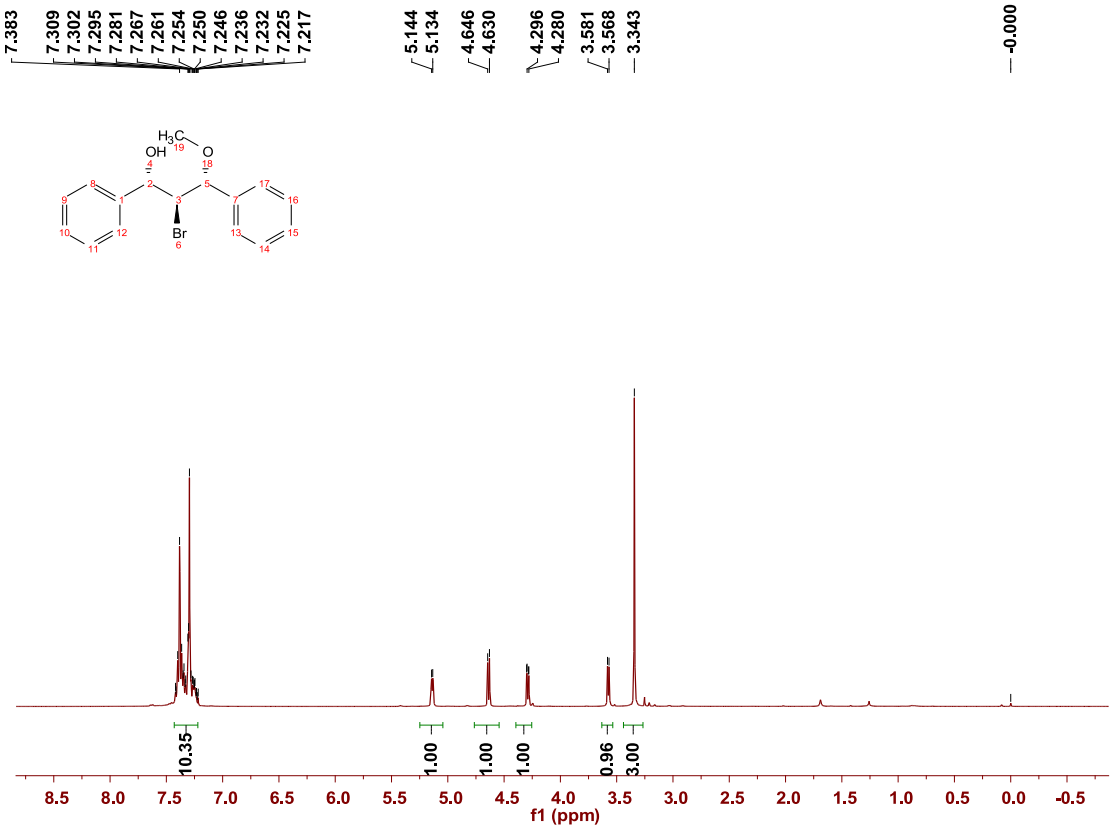
128.25
127.89
126.68
79.58
56.92
47.18
f1 (ppm)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7.246
7.236
7.232
7.225
7.217
5.144
5.134
4.646
4.630
4.296
4.280
3.581
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3.343
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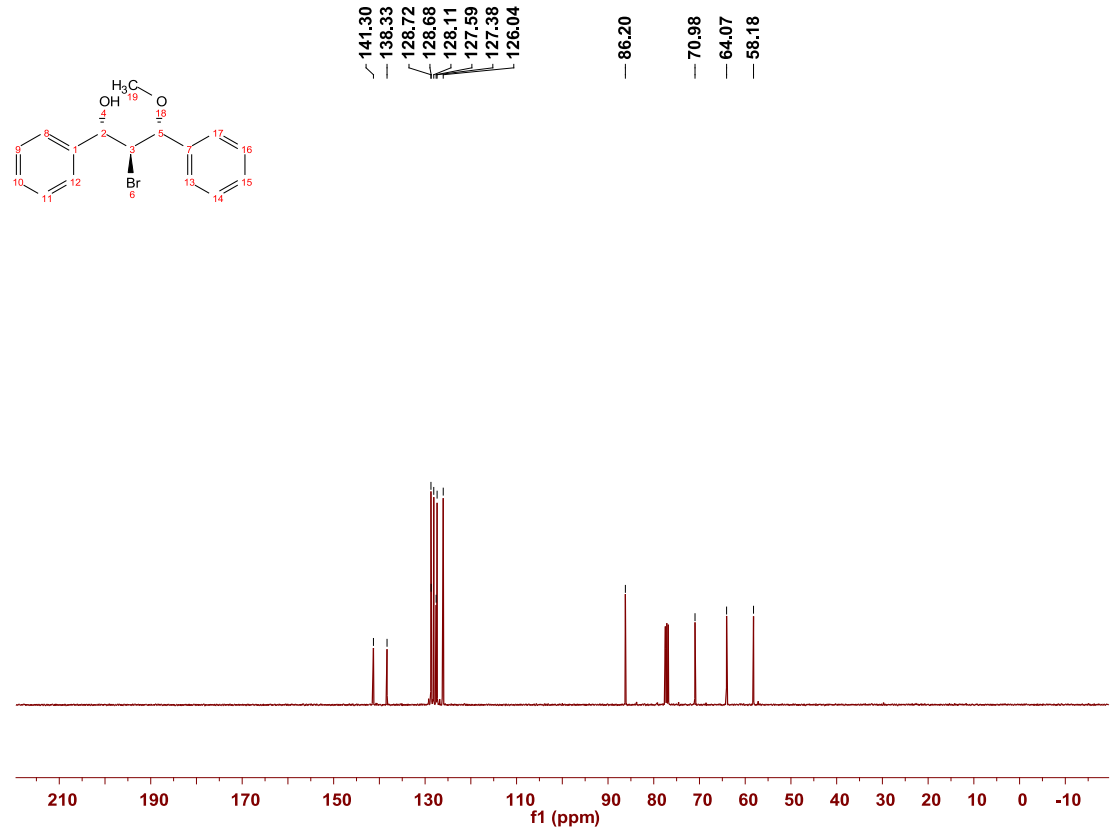
10.35
1.00
1.00
1.00
0.96
3.00
f1 (ppm)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127.59
127.38
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86.20
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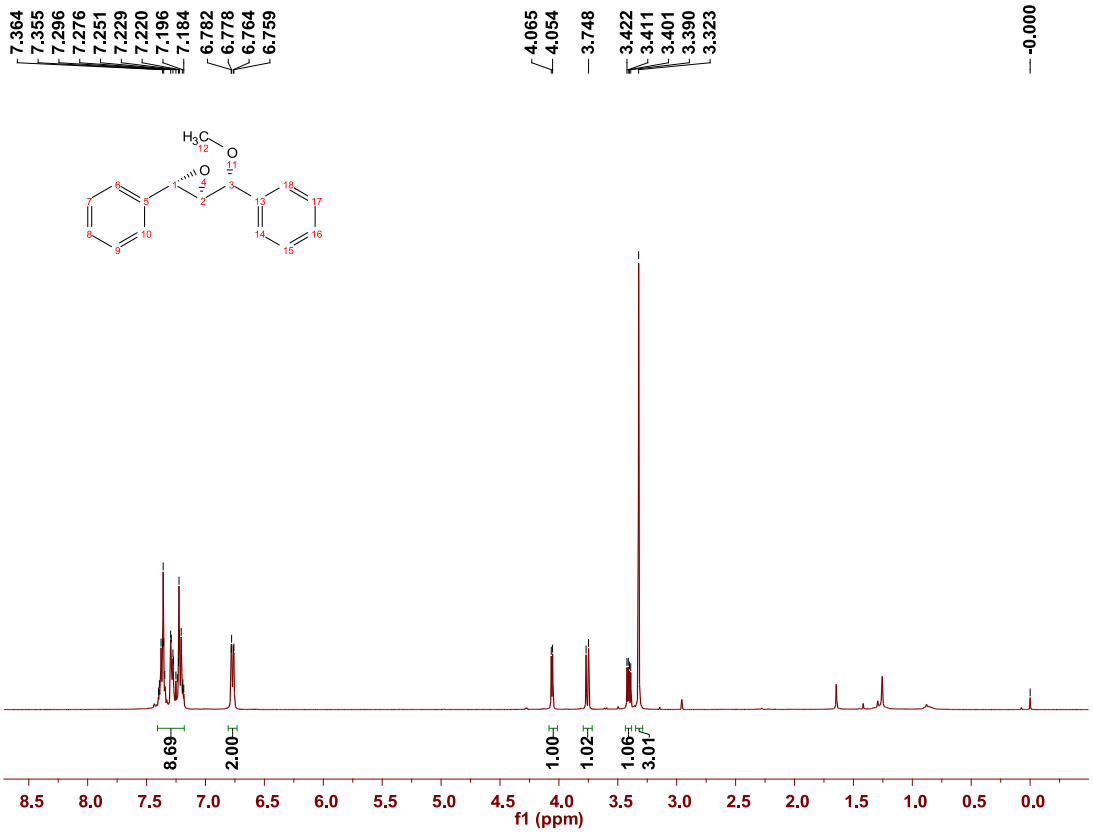
58.18
f1 (ppm)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6.778
6.764
6.759
4.065
4.054
3.748
3.422
3.411
3.401
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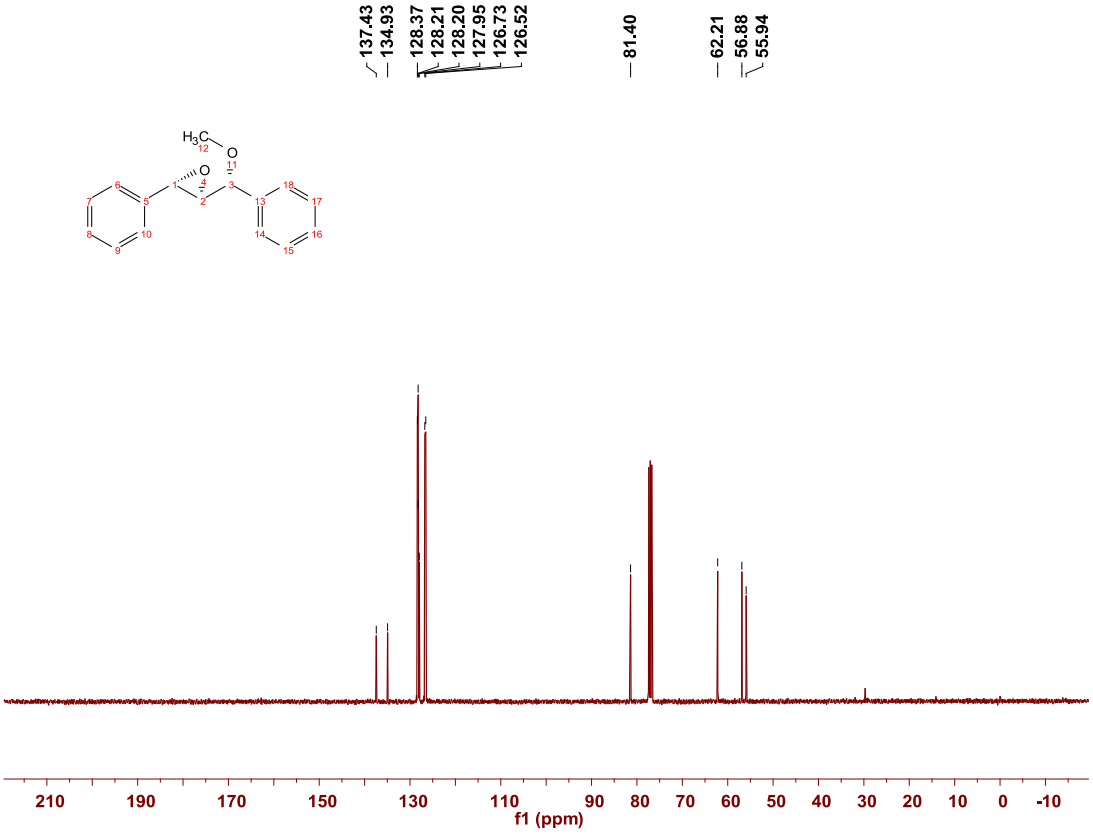
8.69
2.00
1.00
1.02
1.06
3.01
f1 (ppm)


137.43
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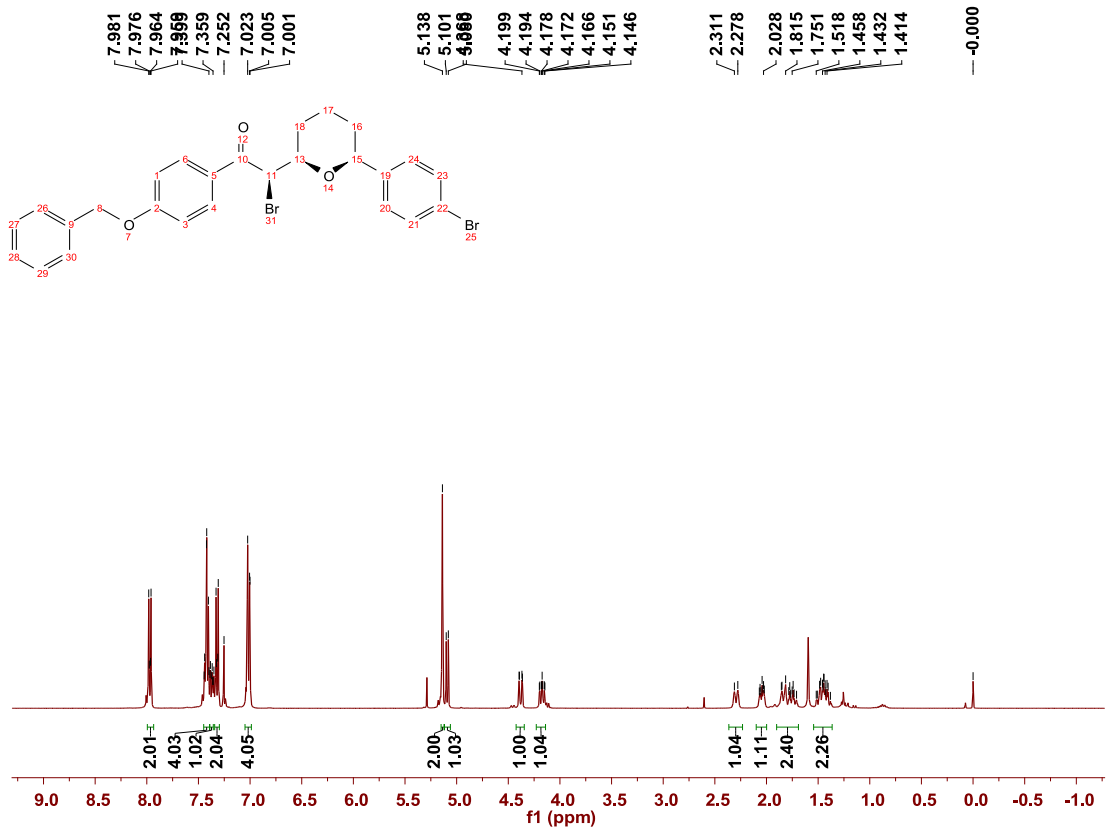
55.94
f1 (ppm)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7.001
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5.101
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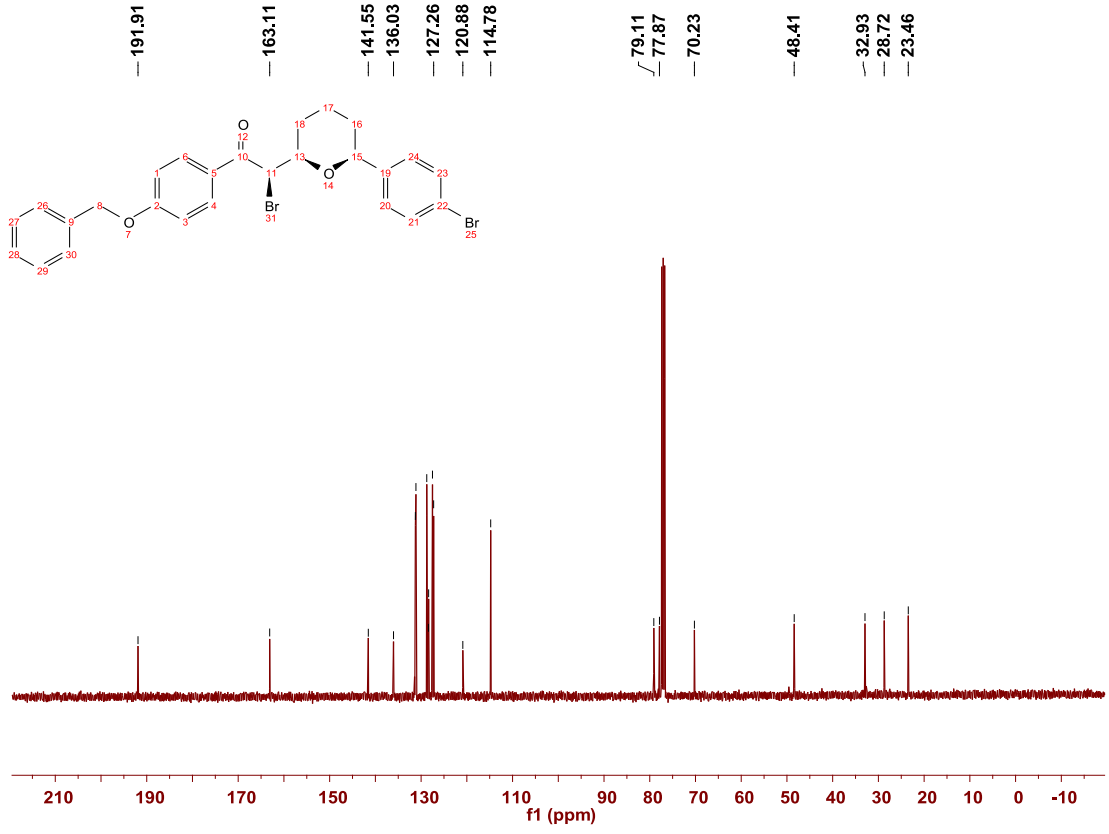
4.178
4.172
4.166
4.151
4.146
2.311
2.278
2.028
1.815
1.751
1.518
1.458
1.432
1.414
-0.000
2.01
4.03
1.02
2.04
4.05
2.00
1.03
1.00
1.04
1.04
1.11
2.40
2.26
f1 (ppm)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114.78
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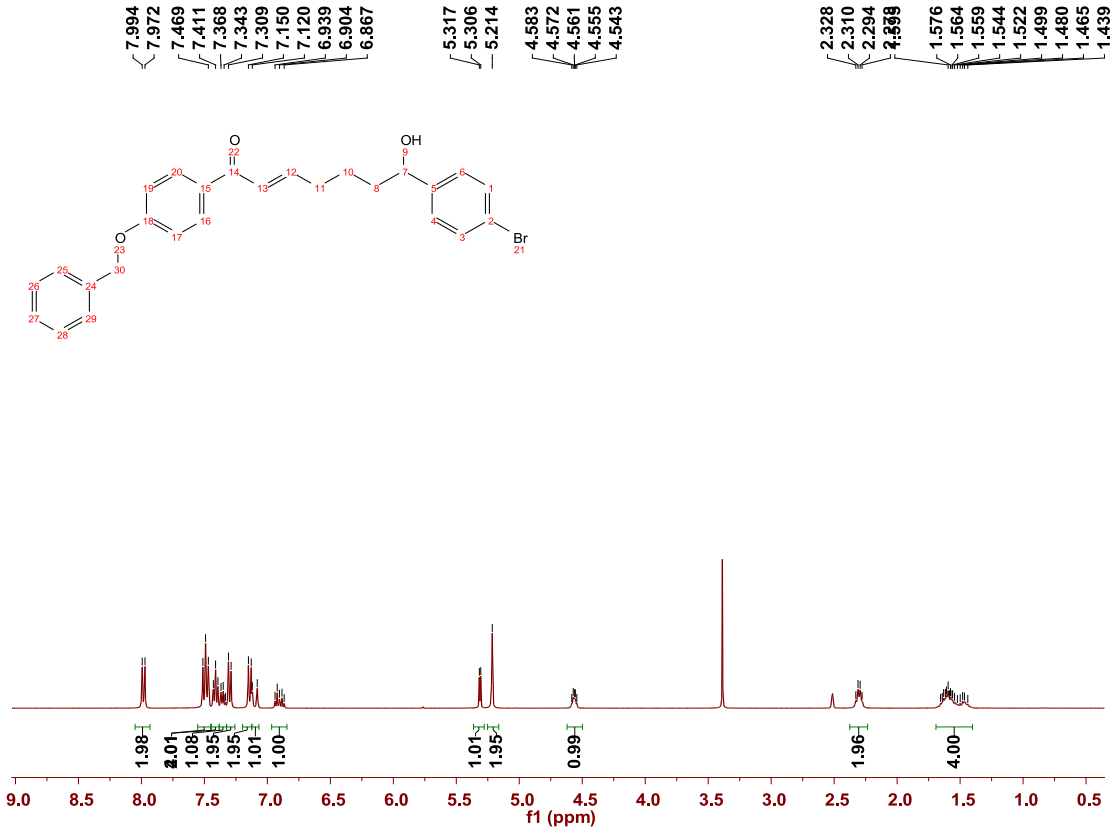
77.87
70.23
48.41
32.93
28.72
23.46
f1 (ppm)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6.867
5.317
5.306
5.214
4.583
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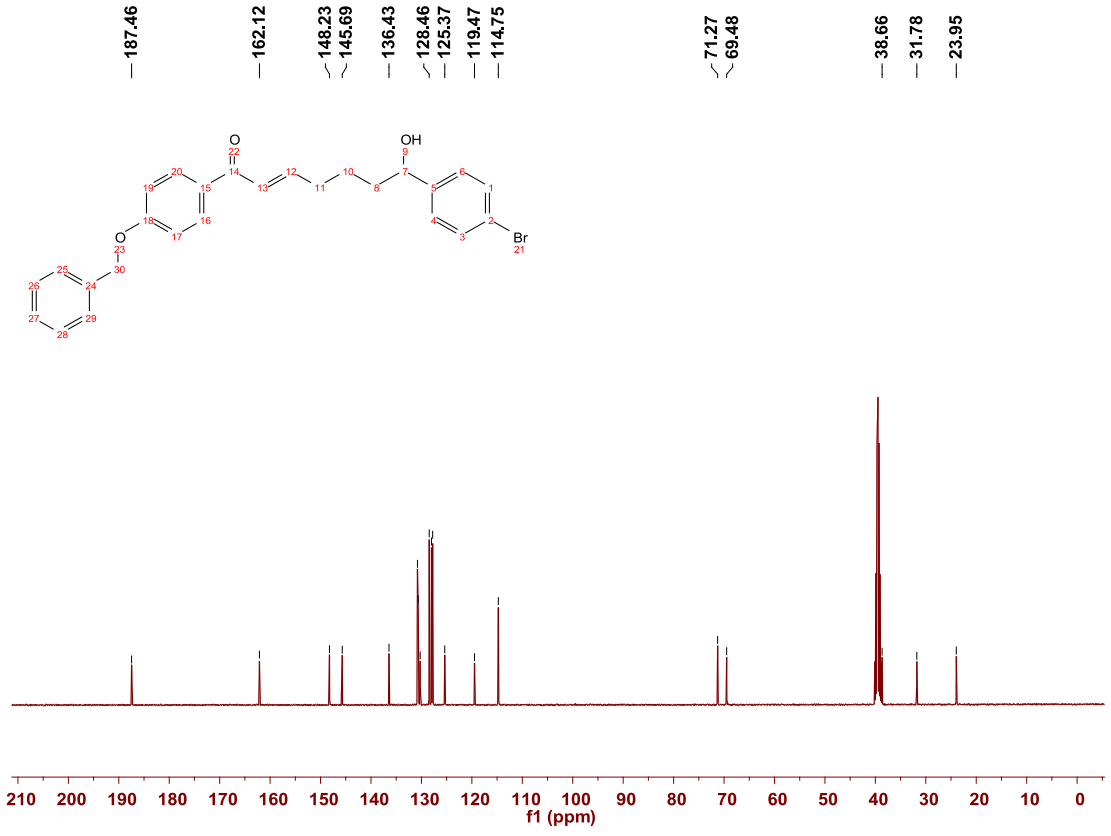
4.561
4.555
4.543
2.328
2.310
2.294
1.576
1.564
1.559
1.544
1.522
1.499
1.480
1.465
1.439
O
OH
Br
1.98
1.01
1.08
1.95
1.95
1.01
1.00
1.01
1.95
0.99
1.96
4.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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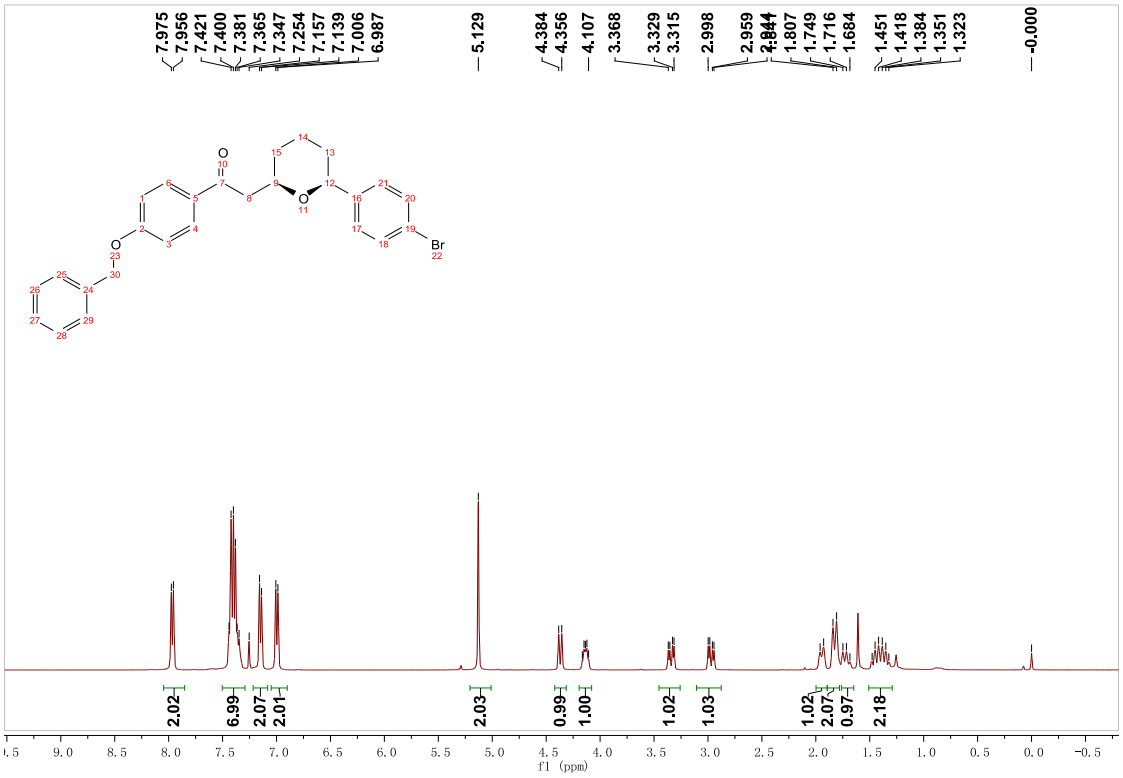
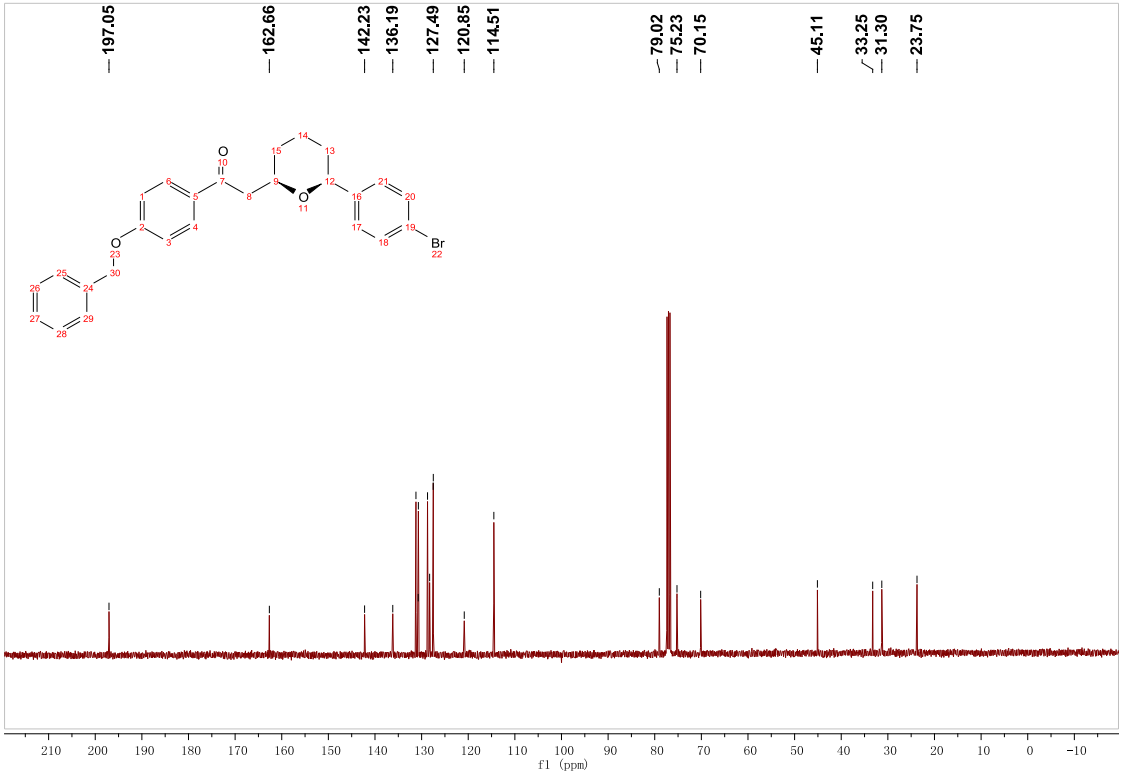
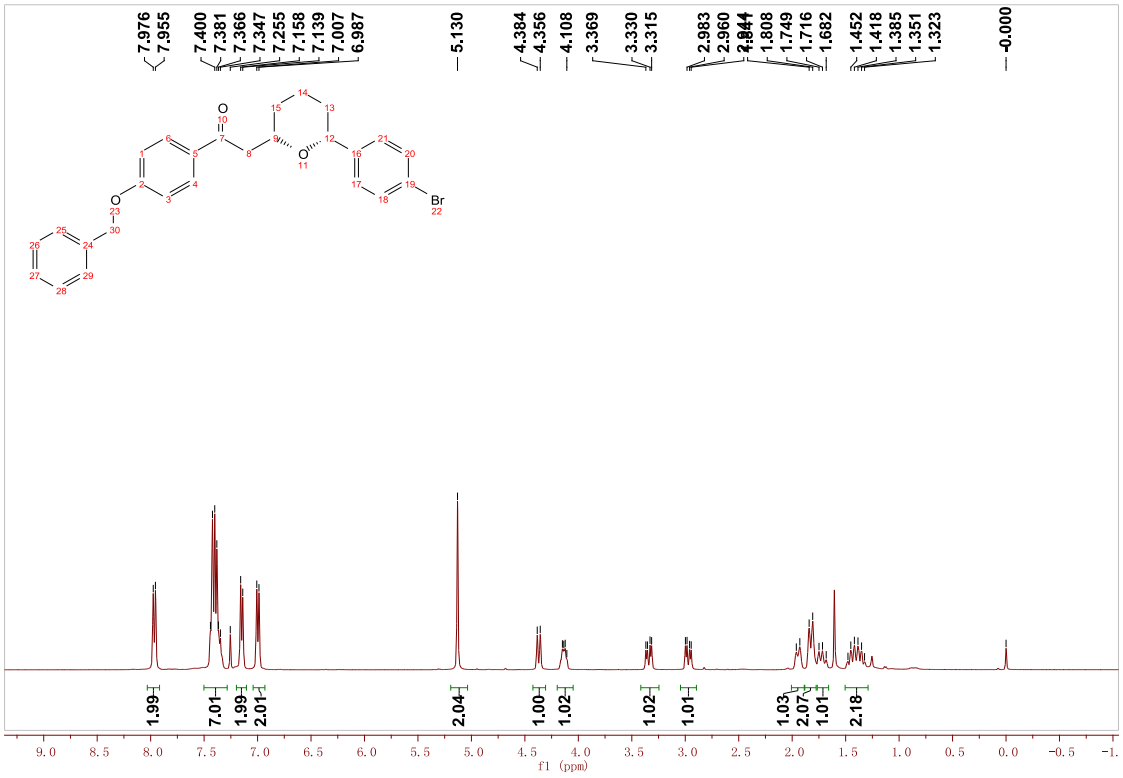
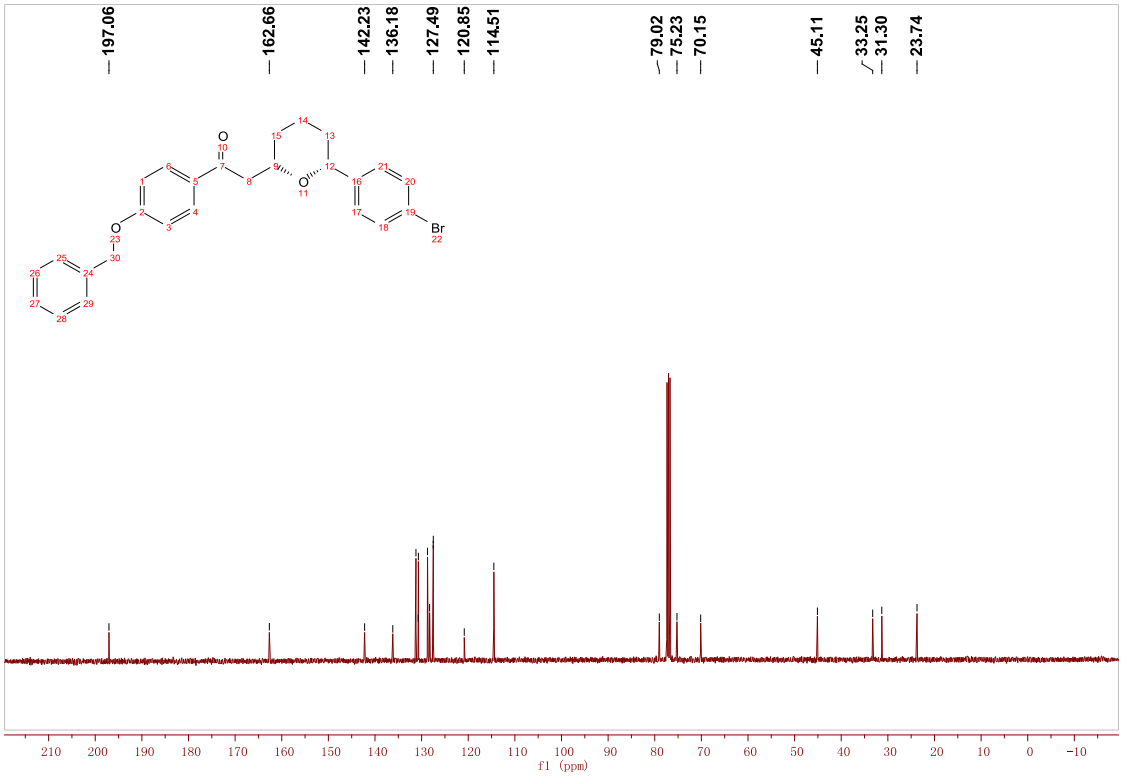
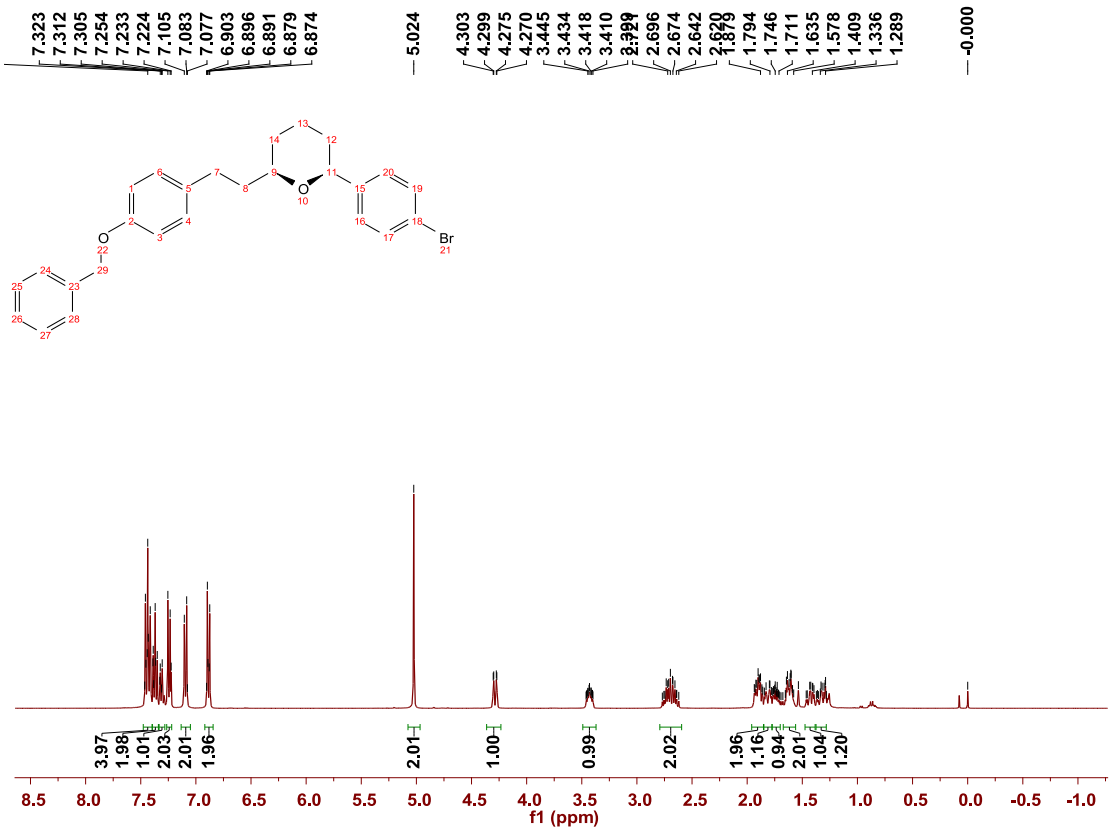
148.23
145.69
136.43
128.46
125.37
119.47
114.75
71.27
69.48
38.66
31.78
23.95
O
OH
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

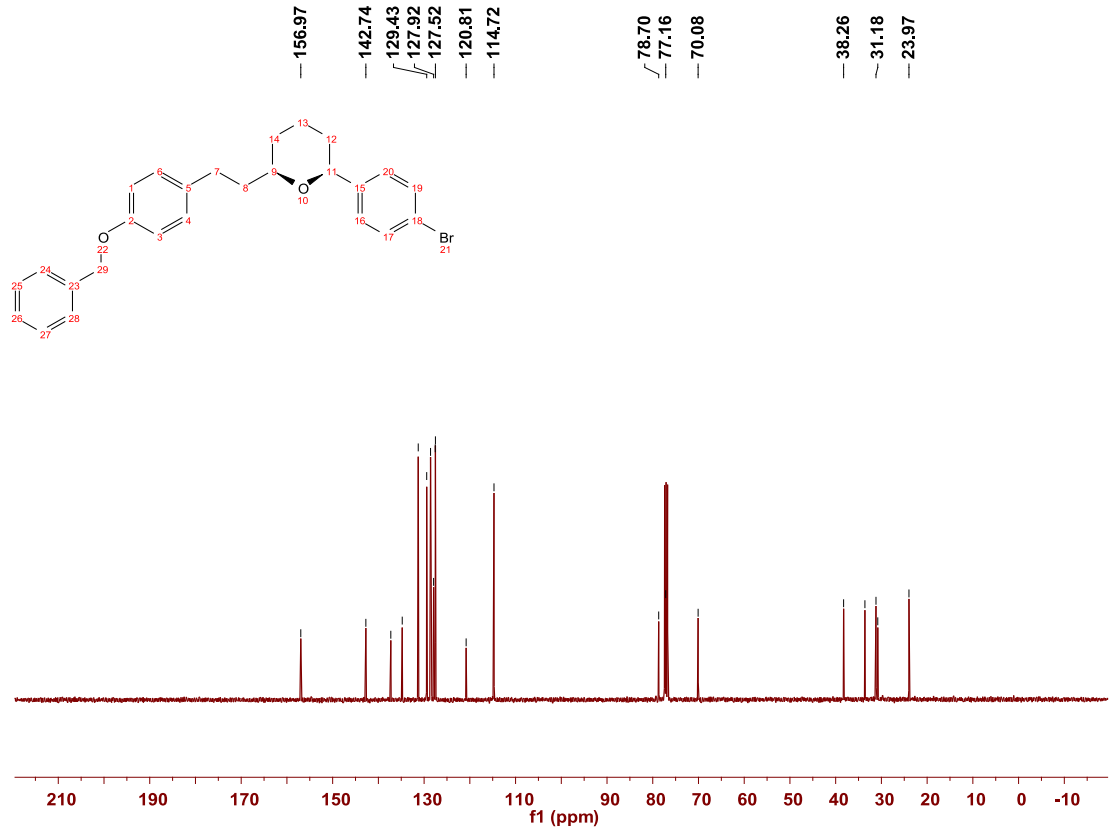

7.975
7.956
7.421
7.400
7.381
7.365
7.347
7.254
7.157
7.139
7.006
6.987
5.129
4.384
4.356
4.107
3.368
3.329
3.315
2.998
2.959
1.807
1.749
1.716
1.684
1.451
1.418
1.384
1.351
1.323
-0.000
Br
2.02
6.99
2.07
2.01
2.03
0.99
1.00
1.02
1.03
1.02
2.07
0.97
2.18
f1 (ppm)

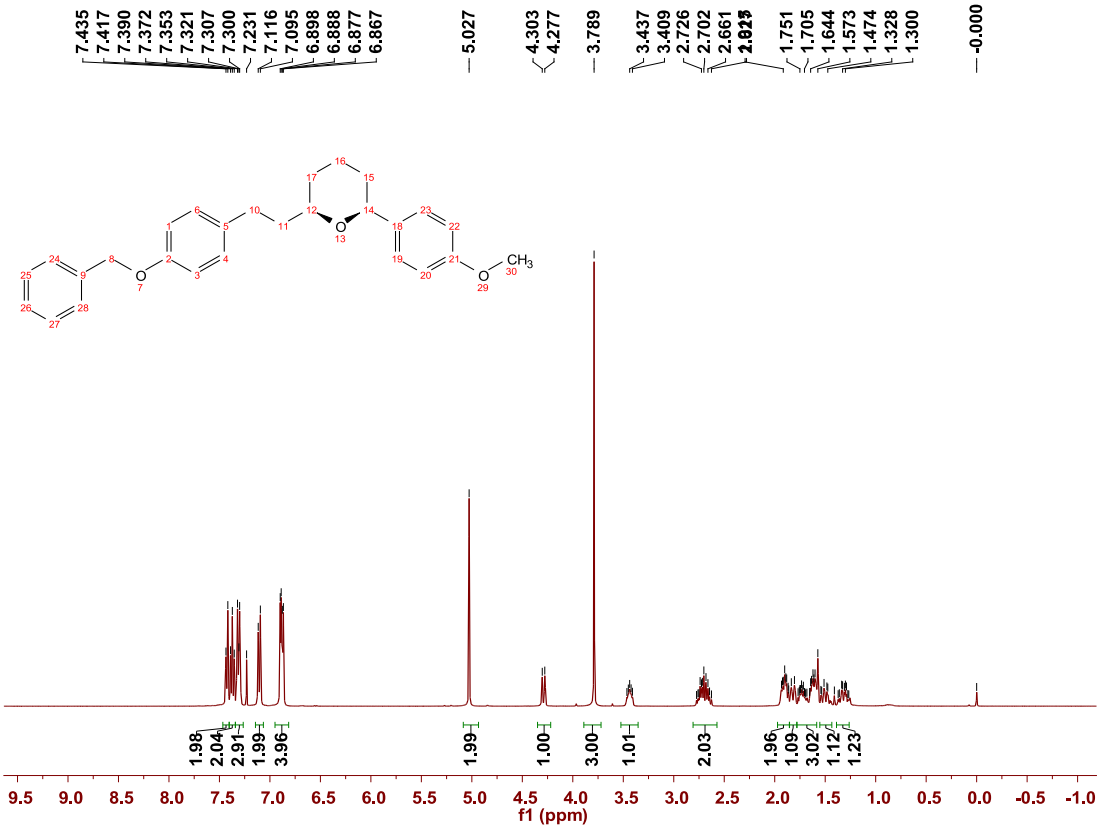

197.05
162.66
142.23
136.19
127.49
120.85
114.51
79.02
75.23
70.15
45.11
33.25
31.30
23.75
Br
f1 (ppm)

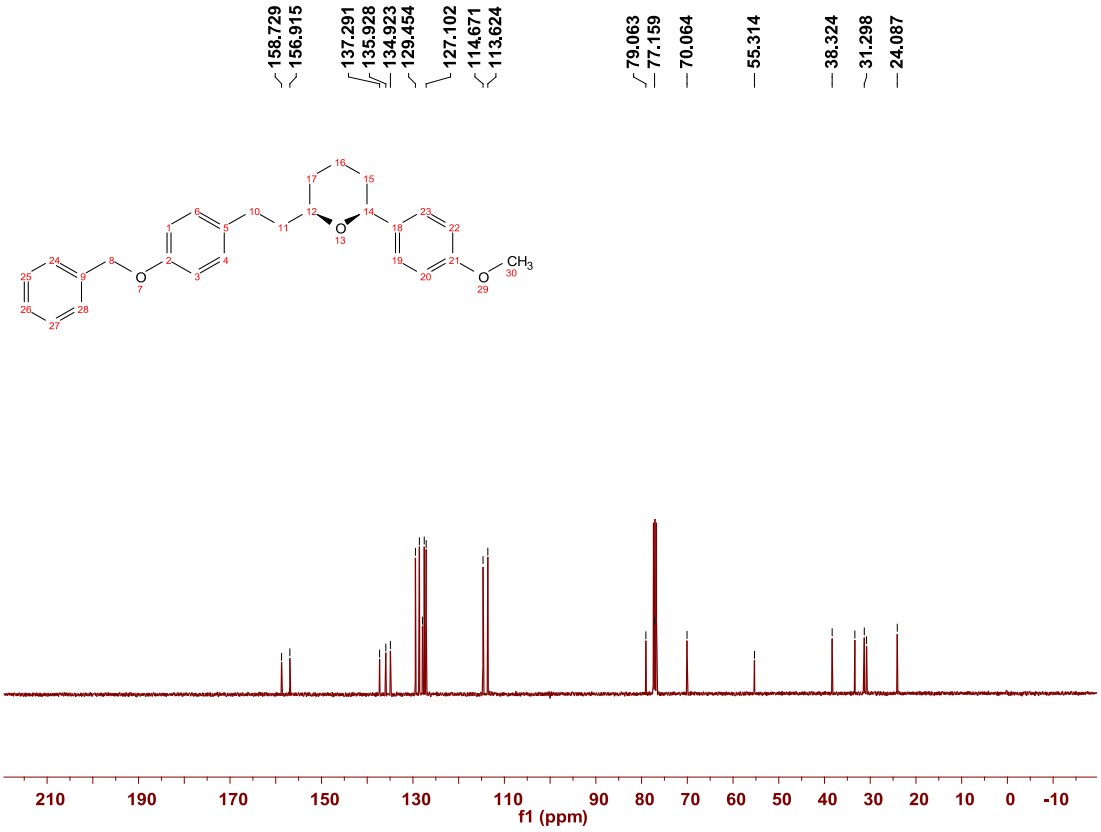

7.976
7.955
7.400
7.381
7.366
7.347
7.255
7.158
7.139
7.007
6.987
5.130
4.384
4.356
4.108
3.369
3.330
3.315
2.983
2.960
1.808
1.749
1.716
1.682
1.452
1.418
1.385
1.351
1.323
-0.000
Br
1.99
7.01
1.99
2.01
2.04
1.00
1.02
1.02
1.01
1.03
2.07
1.01
2.18
f1 (ppm)

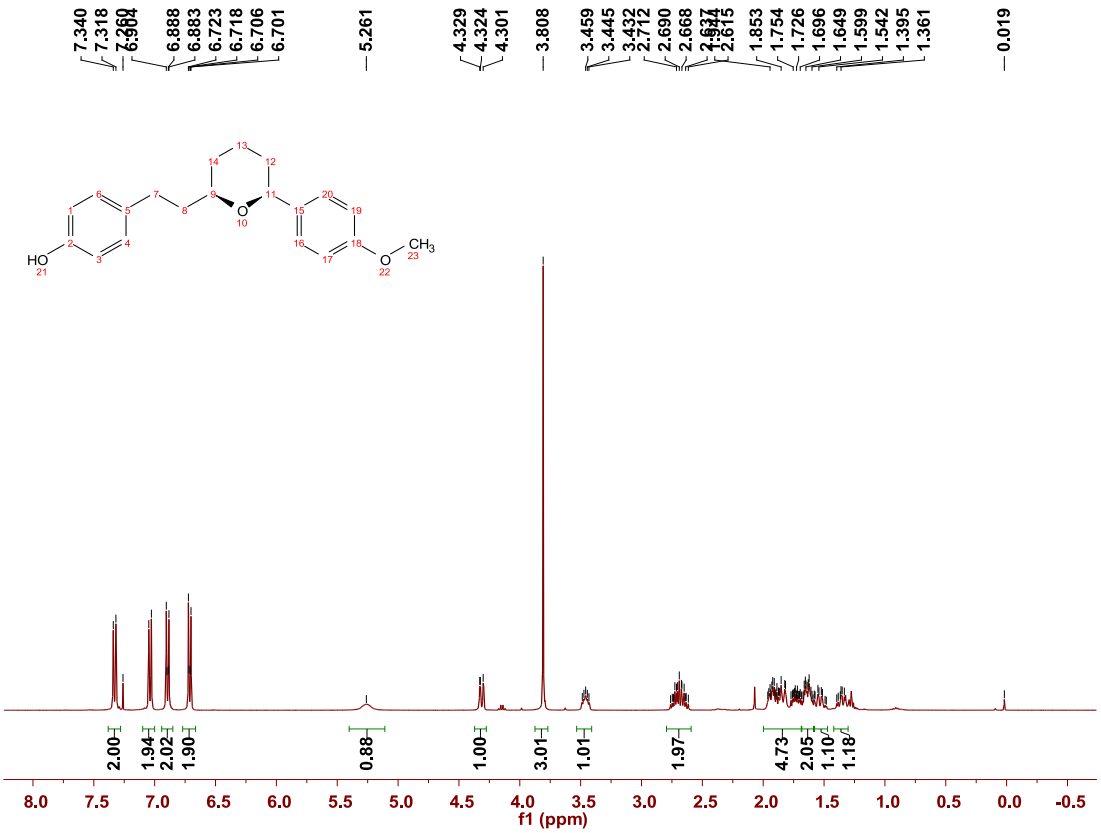

197.06
162.66
142.23
136.18
127.49
120.85
114.51
79.02
75.23
70.15
45.11
33.25
31.30
23.74
Br
f1 (ppm)

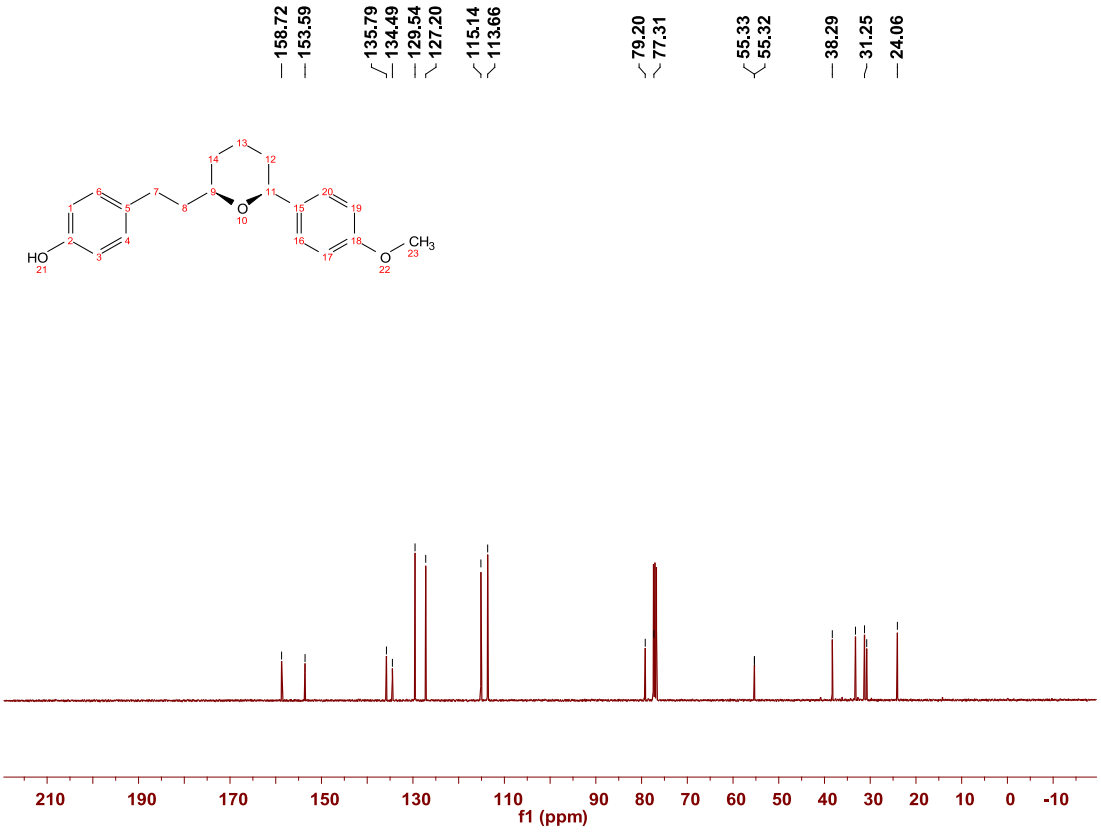

7.323
7.312
7.305
7.254
7.233
7.224
7.105
7.083
7.077
6.903
6.896
6.891
6.879
6.874
5.024
4.303
4.299
4.275
4.270
3.445
3.434
3.418
3.410
2.696
2.674
2.642
1.879
1.794
1.746
1.711
1.635
1.578
1.409
1.336
1.289
-0.000
Br
3.97
1.98
1.01
2.03
2.01
1.96
2.01
1.00
0.99
2.02
1.96
1.16
0.94
2.01
1.04
1.20
f1 (ppm)

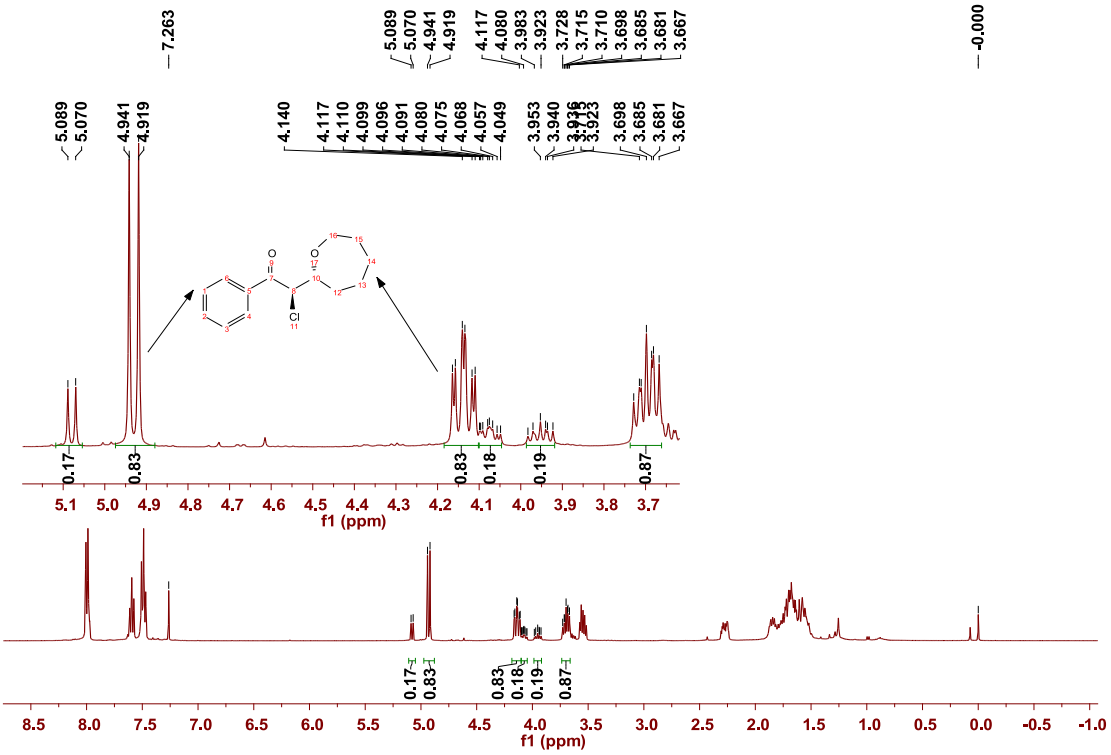

156.97
142.74
129.43
127.92
127.52
120.81
114.72
78.70
77.16
70.08
38.26
31.18
23.97
Br
f1 (ppm)

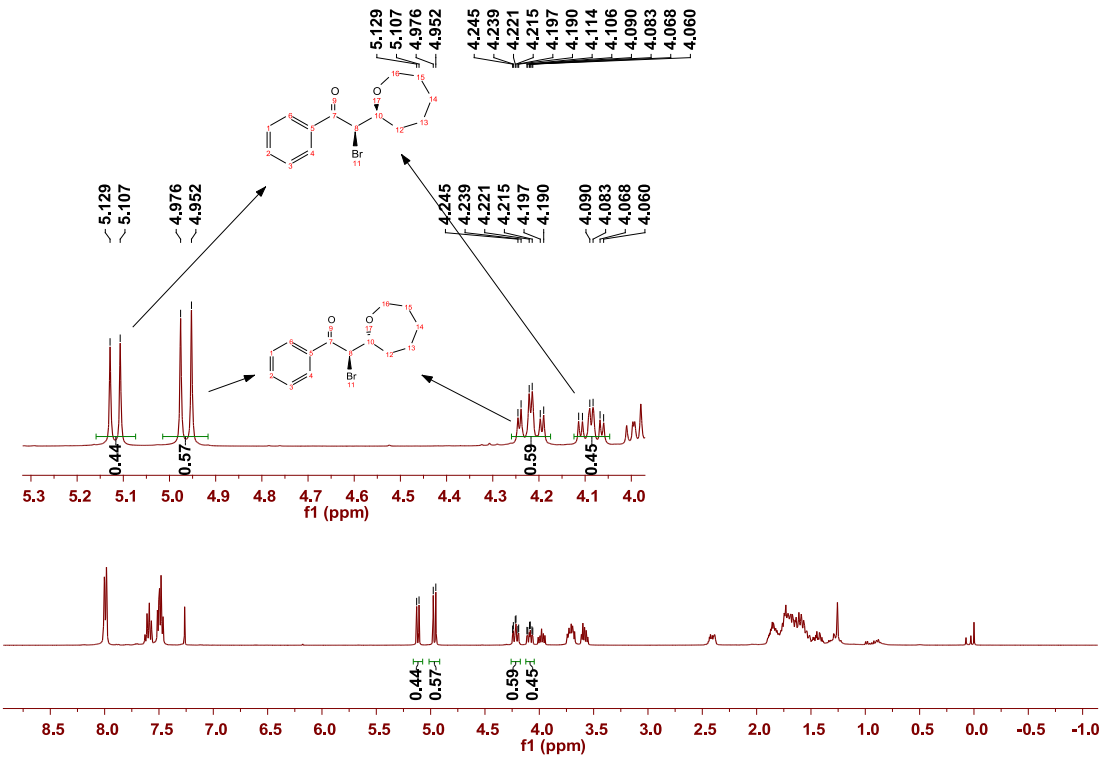

7.435
7.417
7.390
7.372
7.353
7.321
7.307
7.300
7.231
7.116
7.095
6.898
6.888
6.877
6.867
5.027
4.303
4.277
3.789
3.437
3.409
2.726
2.702
2.661
1.751
1.705
1.644
1.573
1.474
1.328
1.300
-0.000
1.98
2.04
2.91
1.99
3.96
1.99
1.00
3.00
1.01
2.03
1.96
1.09
3.02
1.12
1.23
f1 (ppm)

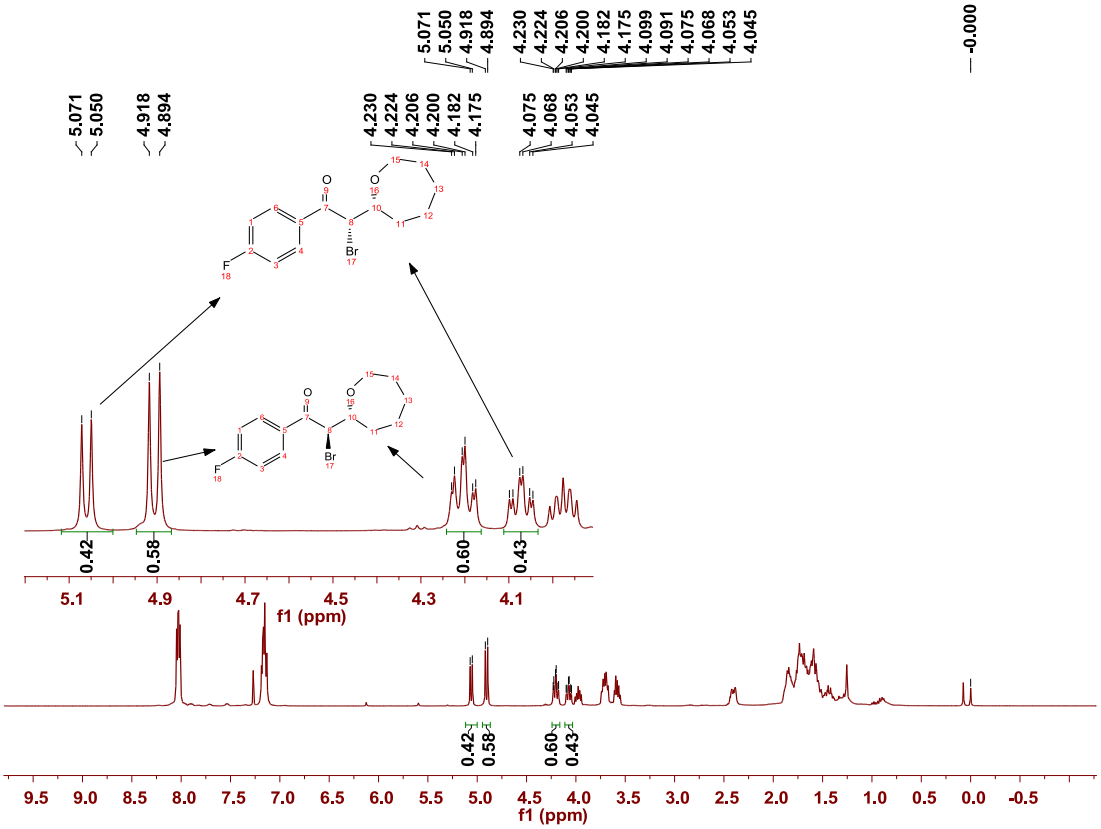

158.729
156.915
137.291
135.928
134.923
129.454
127.102
114.671
113.624
79.063
77.159
70.064
55.314
38.324
31.298
24.087
f1 (ppm)

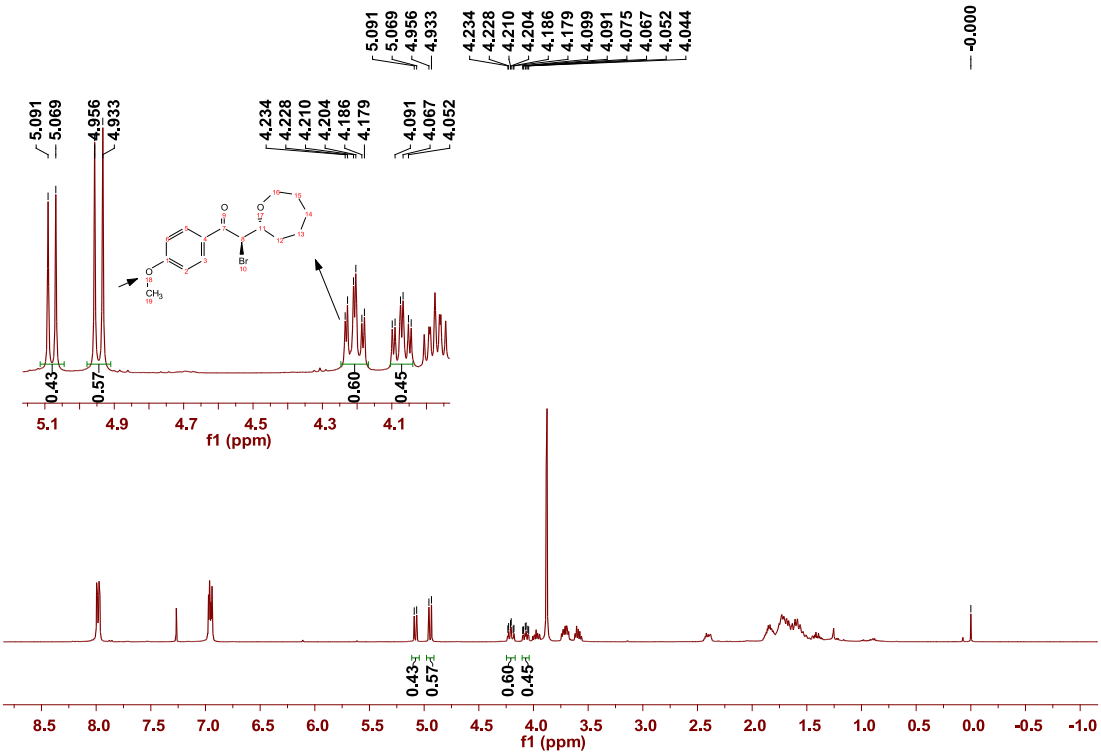

7.340
7.318
6.888
6.883
6.723
6.718
6.706
6.701
5.261
4.329
4.324
4.301
3.808
3.459
3.445
3.432
2.712
2.690
2.668
2.615
1.853
1.754
1.726
1.696
1.649
1.599
1.542
1.395
1.361
0.019
HO
CH3
2.00
1.94
2.02
1.90
0.88
1.00
3.01
1.01
1.97
4.73
2.05
1.10
1.18
f1 (ppm)

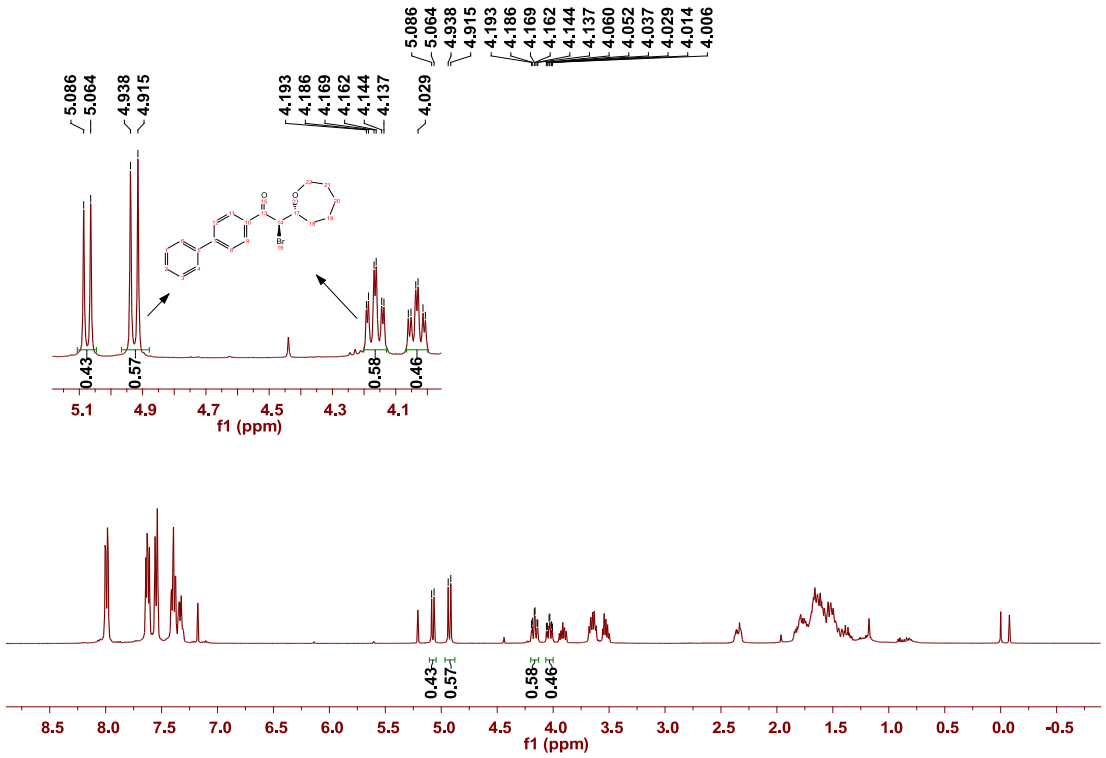

158.72
153.59
135.79
134.49
129.54
127.20
115.14
113.66
79.20
77.31
55.33
55.32
38.29
31.25
24.06
HO
CH3
f1 (ppm)

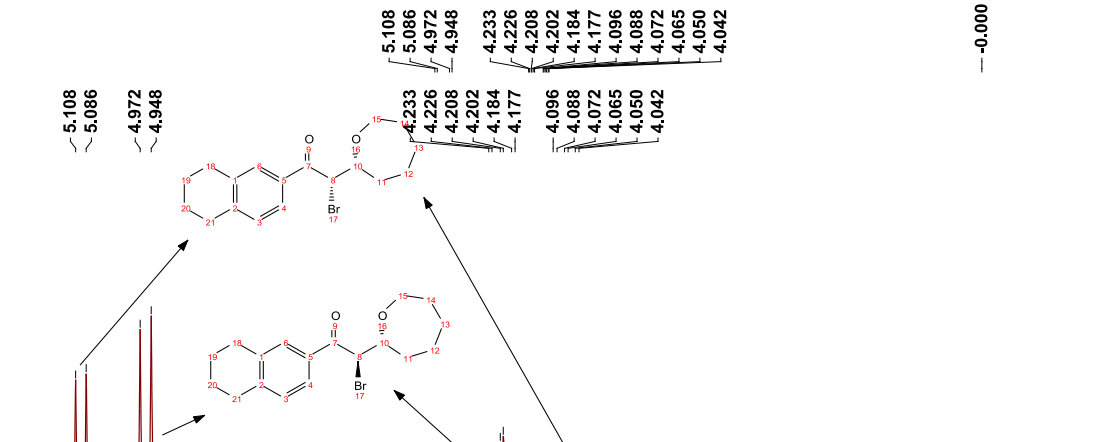

7.263
5.089
5.070
4.941
4.919
4.140
4.117
4.110
4.099
4.096
4.091
4.080
4.075
4.068
4.057
4.049
3.953
3.940
3.923
3.698
3.685
3.681
3.667
-0.000
0.17
0.83
0.83
0.18
0.19
0.87
f1 (ppm)


5.129
5.107
4.976
4.952
4.245
4.239
4.221
4.215
4.197
4.190
4.114
4.106
4.090
4.083
4.068
4.060
0.44
0.57
0.59
0.45
f1 (ppm)


5.071
5.050
4.918
4.894
4.230
4.224
4.206
4.200
4.182
4.175
4.099
4.091
4.075
4.068
4.053
4.045
-0.000
0.42
0.58
0.60
0.43
f1 (ppm)


5.091
5.069
4.956
4.933
4.234
4.228
4.210
4.204
4.186
4.179
4.099
4.091
4.075
4.067
4.052
4.044
-0.000
0.43
0.57
0.60
0.45
f1 (ppm)


5.086
5.064
4.938
4.915
4.193
4.186
4.169
4.162
4.144
4.137
4.060
4.052
4.037
4.029
4.014
4.006
4.029
0.43
0.57
0.58
0.46
f1 (ppm)


0.43
0.57
0.58
0.46
f1 (ppm)

5.108
5.086
4.972
4.948
4.233
4.226
4.208
4.202
4.184
4.177
4.096
4.088
4.072
4.065
4.050
4.042
-0.000
0.43
0.57
0.60
0.43
f1 (ppm)