Supporting Information

Catalytic Asymmetric Acyloin Rearrangements of α-Ketols, α-Hydroxy aldehydes and α-Iminols by *N*,*N*′-Dioxide−Metal Complexes

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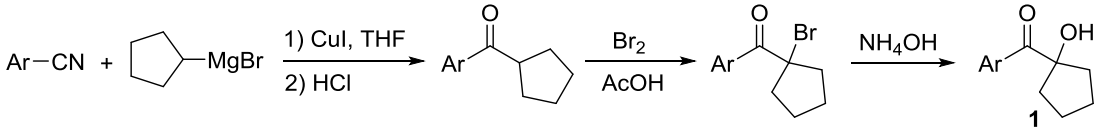
2. General Remarks

^{1}H NMR (400 MHz) spectra were recorded on bruker ASCEND^{TM} 400M. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. $^{13}C\{^{1}H\}$ NMR spectra were collected on bruker ASCEND^{TM} 400M (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). $^{19}F\{^{1}H\}$ NMR spectra were collected on bruker ASCEND^{TM} 400M (376 MHz) with complete proton decoupling. Chemical shifts are reported in ppm with the $PhCF_3$ as internal standard (δ = –63.2). Enantiomeric excesses (ee) were determined by chiral HPLC analysis on Daicel Chiralcel IG, IA and ODH at 23 °C with UV detector at 220 or 254 nm in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]D^{T}$ (λ = 589 nm, *c* = g/100 mL, in solvent). HRMS was recorded on Thermo Q-Exactive Focus (FTMS+c ESI). IR was detected by Bruker Tensor II spectrometer with Plantium ATR accessory. All the solvents were purified by usual methods before use. Silica gel for thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd. Unless otherwise indicated, reagents obtained from commercial sources were used without further purification. For reaction temperature below 40 °C, it was controlled in a water bath by using heidolph MR Hei-Tec, otherwise a oil bath was used by the same instrument. The chiral *N*,*N*'-dioxide ligands were synthesized by the same procedure in the literature.[1] Unless otherwise noticed, starting materials of α-ketol or α-iminol were prepared according to reported procedure.[2]

3. Experimental Procedures

1. Typical experimental procedure for the synthesis of the starting materials of 1

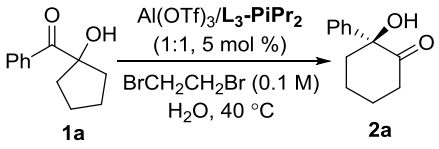


Step 1: To a 100 mL dry round flask, CuI (0.05 mmol) and nitrile (20 mmol) was added. Under the atmosphere of nitrogen, 20 mL of dry THF was injected via a syringe. The flask was then placed in an ice bath and Grignard reagent (20 mL, 1.0 M in THF) was added dropwise. The resulting mixture was stirred overnight at room temperature. After adding HCl (1N) to quench the reaction, the mixture would be stirred for another 4 hours at room temperature. The two layers were separated and the aqueous layer was extracted with ethyl acetate (3x10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The crude residue was directly used in next step without purification.

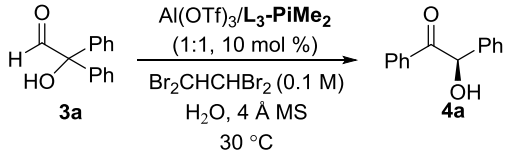
Step 2: The crude ketone product was transfered to a 100 mL dry round flask. After diluted with 20 mL DCM, the flask was cooled to 0 °C, followed by the addition of one drop of AcOH, and then a solution of Br_2 (1.13 mL, 20 mmol) in DCM (5 mL) was added dropwise. The resulting mixture was stirred overnight at room temperature. The mixture was poured into $Na_2S_2O_3$ (aq) to quench the reaction. The two layers were separated and the aqueous layer was extracted with DCM (3x10 mL). The combined organic layer was washed by brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude residue was directly used in next step without purification.

Step 3: The crude α-bromide ketone was transfered to a 100 mL round flask. Then $NH_3 \bullet H_2O$ (50 mL) was added into the flask. After stirred for 2 days at room temperature, the mixture was extracted with DCM (3x10 mL), and the combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The crude residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1, v/v) to afford the corresponding product.

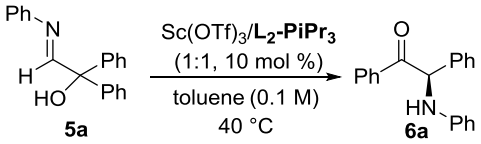
2. Typical experimental procedure for the catalytic asymmetric rearrangement reactions



Procedure A: An oven-dried test tube was charged with *N*,*N*'-dioxide **L_3-PiPr$_2$** (3.3 mg, 0.005 mmol), $Al(OTf)_3$ (2.4 mg, 0.005 mmol) under N_2 atmosphere, then dry $BrCH_2CH_2Br$ (1.0 mL) and H_2O (3 μL) were added, the resulting mixture was stirred at 35 °C in a water bath for 30 minutes. After the addition of cyclic α-ketol **1a** (0.1 mmol), the system was stirred at 40 °C in a water bath for 24 hours. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1, v/v) to afford the corresponding ring-expansion product **2a** as a white solid.



Procedure B: An oven-dried test tube was charged with *N*,*N*'-dioxide **L_3-PiMe$_2$** (5.4 mg, 0.010 mmol), $Al(OTf)_3$ (4.7 mg, 0.010 mmol), 4 Å MS (10 mg) and acyclic α-hydroxy aldehyde **3a**. After adding the solvent and water, the system was stirred at 30 °C in a water bath for 24 hours. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1, v/v) to afford the corresponding α-hydroxy ketone **4a** as a white solid.

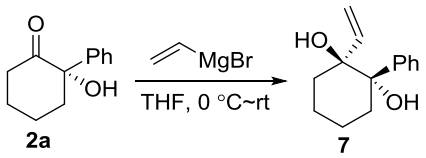


Procedure C: An oven-dried test tube was charged with *N*,*N*'-dioxide **L_2-PiPr$_3$** (7.2 mg, 0.010 mmol), $Sc(OTf)_3$ (4.9 mg, 0.010 mmol) or $In(OTf)_3$ (5.6 mg, 0.010 mmol) and acyclic α-hydroxy aldimine **5a**. After adding the solvent, the system was stirred at 40 °C in a water bath for 24 hours. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1, v/v) to afford the corresponding acyclic α-amino ketone product **6a** as a yellow solid.

3. Typical experimental procedure for gram-scale synthesis of 2-hydroxy-2-phenylcyclohexanone 1a

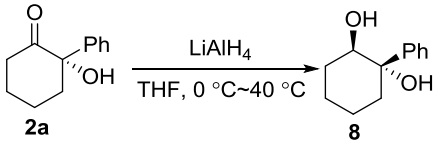
Steps: An oven-dried round-bottom flask was charged with *N*,*N*'-dioxide **L_3-PiPr$_2$** (162.0 mg, 0.25 mmol), $Al(OTf)_3$ (118.5 mg, 0.25 mmol) under N_2 atmosphere, after the addition of dry $BrCH_2CH_2Br$ (40.0 mL) with H_2O (150 μL), the mixture was stirred at 35 °C in a water bath for 30 minutes. Then cyclic α-ketol **1a** (5.0 mmol) was added and the system was stirred at 40 °C in a water bath. After the substrate was consumed as judged by TLC, the reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1, v/v) to afford the corresponding ring-expansion product **2a** as a white solid (0.95 g, 99% yield, 92% ee).

4. Typical experimental procedure for synthesis of the diol compound 7 by treating with vinylmagnesium bromide



Steps: An oven-dried test tube was charged with 2-hydroxy-2-phenylcyclohexanone **2a** (0.1 mmol) under N_2 atmosphere, dry THF (1.0 mL) was added through a syringe. After adding commercially available vinylmagnesium bromide (1.0 M in THF, 2.0 equiv) under 0 °C, the reaction was carried out at room temperature overnight. The reaction would be quenched by NH_4Cl (aq), dried by $MgSO_4$, filtered and concentrated in vacuo, and the reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1, v/v) to afford the diol compound **7**.

5. Typical experimental procedure for the synthesis of diol compound 8

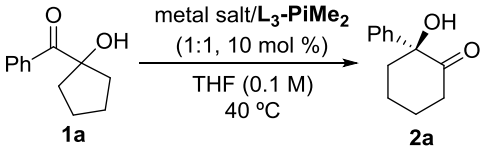


Steps: An oven-dried test tube was charged with 2-hydroxy-2-phenylcyclohexanone **2a** (0.1 mmol) and $LiAlH_4$ (1.5 equiv) under N_2 atmosphere, after THF (1.0 mL) was added under 0 °C, the reaction was carried out at 40 °C in a water bath overnight. Then the reaction would be quenched by H_2O, dried over $MgSO_4$, and then directly filtrated through a Celite pad which was washed with DCM (3x10 mL), and then concentrated in vacuo to afford diol compound **8**.

4. Results and Discussion

1. Optimization of the reaction conditions

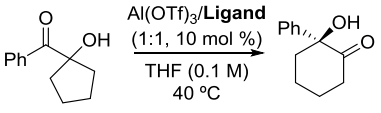
Table S1. Screening of metal salts in the asymmetric rearrangement of cyclic α-ketol **1a**.

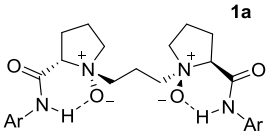


entry[a]	metal salt	yield (%)[b]	ee (%)[c]
1[d]	$Al(OTf)_3$	37	0
2[e]	$Al(OTf)_3$	34	0
3	$Al(OTf)_3$	47	55
4	$In(OTf)_3$	49	27
5	$Fe(OTf)_3$	48	53

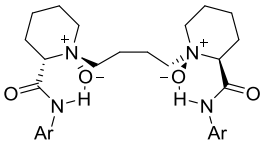
[a]Unless otherwise noted, the reactions were performed with metal salt/**L_3-PiMe$_2$** (1:1, 10 mol %), **1a** (0.1 mmol), in THF (1.0 mL) at 40 °C for 24 h. [b]Yield of isolated product. [c]Determined by HPLC analysis using a chiral stationary phase. [d]The reaction was performed without ligand. [e]*rac*-**L_3-PiMe$_2$** was used.

Table S2. Screening of chiral ligands in the asymmetric rearrangement of cyclic α-ketol **1a**.

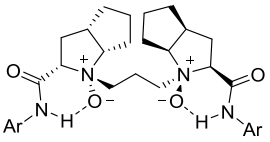




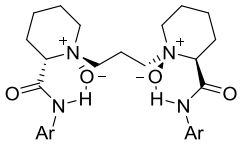
L_3-PrMe$_2$: Ar = 2,6-$Me_2C_6H_3$
L_3-PrPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$



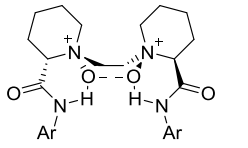
L_4-PiPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$



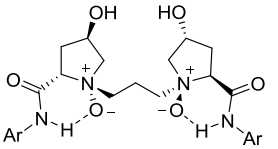
L_3-RaMe$_2$: Ar = 2,6-$Me_2C_6H_3$
L_3-RaPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$



L_3-PiPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$
L_3-PiPh: Ar = C_6H_5
L_3-PiMe$_2$: Ar = 2,6-$Me_2C_6H_3$
L_3-Pi(MeO)$_2$: Ar = 2,6-$(MeO)_2C_6H_3$
L_3-PiPr$_3$: Ar = 2,4,6-*i*$Pr_3C_6H_2$
L_3-PiPr$_2$Br: Ar = 2,6-*i*Pr_2-4-Br-C_6H_2
L_3-PiPr$_2$*t*Bu: Ar = 2,6-*i*Pr_2-4-*t*Bu-C_6H_2



L_2-PiPr$_3$: Ar = 2,4,6-*i*$Pr_3C_6H_2$
L_2-PiPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$



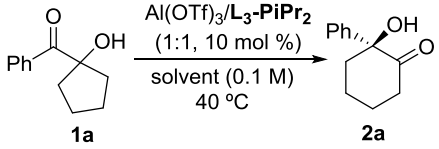
L_3-$_{OH}$PrPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$

entry[a]	ligand	yield (%)[b]	ee (%)[c]
1	**L_3-PrMe$_2$**	62	55
2	**L_3-RaMe$_2$**	55	27
3	**L_3-$_{OH}$PrPr$_2$**	41	80
4	**L_3-PrPr$_2$**	39	85
5	**L_3-PiPr$_2$**	50	87
6	**L_3-RaPr$_2$**	28	69
7	**L_3-PiPh**	22	23
8	**L_3-PiPr$_3$**	62	69

9	**L_2-PiPr$_3$**	20	61
10	**L_2-PiPr$_2$**	30	68
11	**L_3-PiPr$_2$Br**	54	79
12	**L_3-PiPr$_2$^{t}Bu**	34	81

[a]Unless otherwise noted, the reactions were performed with Al(OTf)$_3$/**Ligand** (1:1, 10 mol %), **1a** (0.1 mmol), in THF (1.0 mL) at 40 °C for 24 h. [b]Yield of isolated product. [c]Determined by HPLC analysis using a chiral stationary phase.

Table S3. Screening of solvents in the asymmetric rearrangement of cyclic α-ketol **1a**.

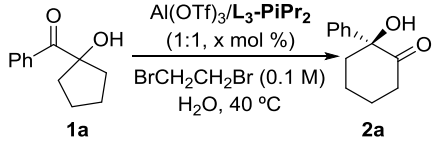


1a **2a**

entry[a]	solvent	yield (%)[b]	ee (%)[c]
1	toluene	66	80
2	ethyl acetate	45	65
3	$CHCl_3$	61	82
4	MeOH	66	22
5	CH_3CN	40	40
6	*n*-hexane	54	53
7	bromobenzene	63	85
8	$ClCH_2CH_2Cl$	57	73
9	$Cl_2CH_2CH_2Cl$	40	88
10	$Cl_2CH_2CH_2Cl_2$	57	88
11	$BrCH_2CH_2Br$	69	87
12[d]	$BrCH_2CH_2Br$	99	91

[a]Unless otherwise noted, the reactions were performed with Al(OTf)$_3$/**L_3-PiPr$_2$** (1:1, 10 mol %), **1a** (0.1 mmol), in 1.0 mL solvent at 40 °C for 24 h. [b]Yield of isolated product. [c]Determined by HPLC analysis using a chiral stationary phase. [d]H_2O (3 μL) was added.

Table S4. Screening of catalyst loading in the asymmetric rearrangement of cyclic α-ketol **1a**.

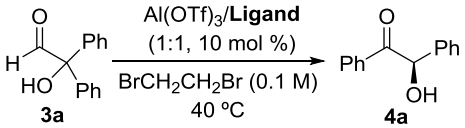


1a **2a**

entry[a]	x mol %	yield (%)[b]	ee (%)[c]
1	10	99	91
2	5	98	91
3	2.5	59	91

[a]Unless otherwise noted, the reactions were performed with Al(OTf)$_3$/**L_3-PiPr$_2$** (1:1, x mol %), **1a** (0.1 mmol) with H_2O (3 μL) in $BrCH_2CH_2Br$ (1.0 mL) at 40 °C for 24 h. [b]Yield of isolated product. [c]Determined by HPLC analysis using a chiral stationary phase

Table S5. Screening of ligands in the asymmetric rearrangement of acyclic α-hydroxyl aldehyde **3a**.



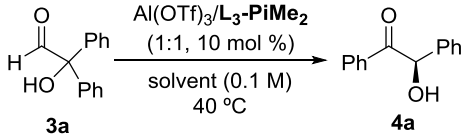
3a **4a**

entry[a]	ligand	yield (%)[b]	ee (%)[c]
1	**L_3-PrPr$_2$**	7	–24
2	**L_3-RaPr$_2$**	15	–18

3	**$L_{3\text{-}OH}PrPr_2$**	10	–12
4	**L_3-$PiPr_2$**	3	11
5[d]	**L_3-$PiPr_2$**	75	race
6	**L_3-$PiMe_2$**	16	74
7	**L_4-$PiPr_2$**	NR	---
8	**L_3-$PrMe_2$**	4	55
9	**L_3-$RaMe_2$**	57	47
10	**L_3-PiPh**	4	–11
11	**L_3-Pi^{t}Bu**	22	–2
12	**L_3-Pi(MeO)$_2$**	trace	---

[a]Unless otherwise noted, the reactions were performed with Al(OTf)$_3$/**Ligand** (1:1, 10 mol %), **3a** (0.1 mmol) with H_2O (3 μL) in $BrCH_2CH_2Br$ (1.0 mL) at 40 °C for 20 h. [b]Yield of isolated product. [c]Determined by HPLC analysis using a chiral stationary phase. [d]80 °C in toluene.

Table S6. Screening of solvents in the asymmetric rearrangement of acyclic α-hydroxyl aldehyde **3a**.

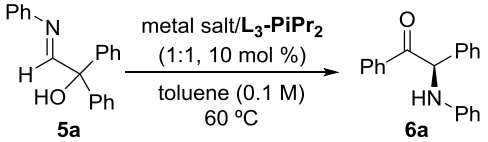


3a **4a**

entry[a]	solvent	yield (%)[b]	ee (%)[c]
1	toluene	27	72
2	TCE	55	70
3	THF	66	54
4	EtOAc	75	44
5	$CHCl_3$	40	69
6	bromobenzene	40	72
7	*p*-xylene	trace	60
8	mesitylene	trace	65
9[d]	$Br_2CHCHBr_2$	54	82
10[d,e]	$Br_2CHCHBr_2$	23	39

[a]Unless otherwise noted, the reactions were performed with Al(OTf)$_3$/**L_3-$PiMe_2$** (1:1, 10 mol %), **3a** (0.1 mmol) in 1.0 mL solvent at 40 °C for 20 h. [b]Yield of isolated product. [c]Determined by HPLC analysis using a chiral stationary phase. [d]H_2O (3 μL) and 4 Å MS (10 mg) were added at 30 °C. [e]In(OTf)$_3$ was used.

Table S7. Screening of metal salts in the asymmetric rearrangement of acyclic α-hydroxyl aldimine **5a**.

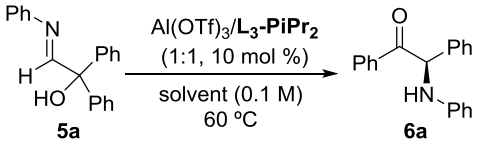


5a **6a**

entry[a]	metal salt	yield (%)[b]	ee (%)[c]
1	Al(OTf)$_3$	33	4
2	Sc(OTf)$_3$	91	48
3	Y(OTf)$_3$	99	9
4	Gd(OTf)$_3$	97	–2
5	Mg(OTf)$_2$	25	–29
6	Ni(acac)$_2$	trace	---
7	Yb(OTf)$_3$	98	24

[a]Unless otherwise noted, the reactions were performed with metal salt/**L_3-$PiPr_2$** (1:1, 10 mol %), **5a** (0.1 mmol) in toluene (1.0 mL) at 60 °C for 20 h. [b]Yield of isolated product. [c]Determined by HPLC analysis using a chiral stationary phase.

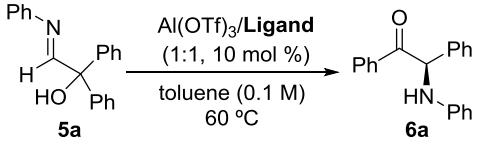
Table S8. Screening of solvents in the asymmetric rearrangement of acyclic α-hydroxyl aldimine **5a**.



entry[a]	solvent	yield (%)[b]	ee (%)[c]
1	TCE	99	34
2	DCE	99	45
3	bromobenzene	99	42
4	mesitylene	96	48
5	$CHCl_3$	99	40
6	hexane	77	17

[a]Unless otherwise noted, the reactions were performed with Al(OTf)$_3$/**L$_3$-PiPr$_2$** (1:1, 10 mol %), **5a** (0.1 mmol) in 1.0 mL solvent at 60 °C for 20 h. [b]Yield of isolated product. [c]Determined by HPLC analysis using a chiral stationary phase.

Table S9. Screening of ligands in the asymmetric rearrangement of acyclic α-hydroxyl aldimine **5a**.

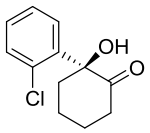


entry[a]	ligand	yield (%)[b]	ee (%)[c]
1	**L$_3$-PrPr$_2$**	99	35
2	**L$_3$-RaPr$_2$**	94	18
3	**L$_{3\text{-}OH}$PrPr$_2$**	99	40
4	**L$_4$-PiPr$_2$**	99	43
5	**L$_2$-PiPr$_2$**	99	55
6	**L$_2$-PiPr$_3$**	99	55
7	**L-PiMe$_2$**	95	race
8[d]	**L$_2$-PiPr$_3$**	99	68
9[d,e]	**L$_2$-PiPr$_3$**	41	93

[a]Unless otherwise noted, the reactions were performed with Al(OTf)$_3$/**Ligand** (1:1, 10 mol %), **5a** (0.1 mmol) in toluene (1.0 mL) at 60 °C for 20 h. [b]Yield of isolated product. [c]Determined by HPLC analysis using a chiral stationary phase. [d]The reaction was performed at 40 °C. [e]In(OTf)$_3$ was used.

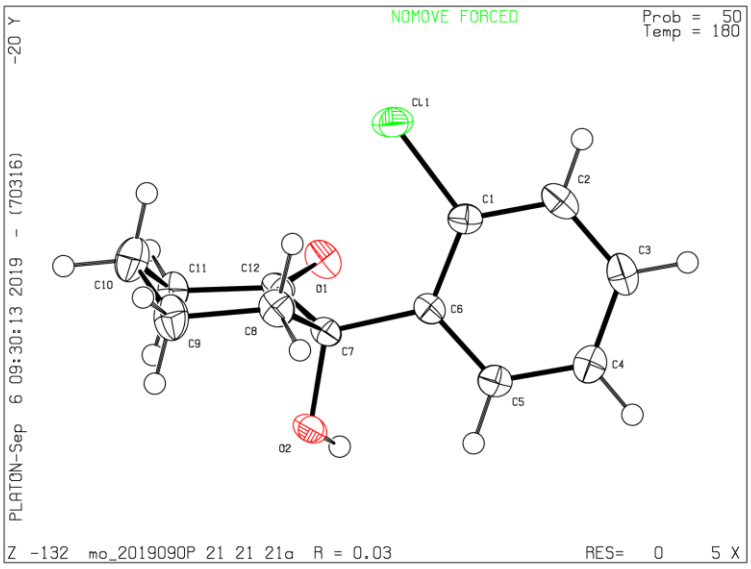
2. Crystallographic data for products.

Figure S1. ORTEP diagram of product **2i**.



2i

The configuration of **2i** was determined to be (*S*) by single-crystal X-ray crystallographic analysis. Crystals of **2i** [$C_{12}H_{13}ClO_2$] were obtained from the mixture of DCM and petroleum ether. CCDC 1951895 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The colourless crystals in block shape are picked up and mounted for the single-crystal X-ray diffraction. The measurements were taken in a Bruker D8 Venture diffractometer equipped with Photon II CMOS detector by omega and phi scan methods. The data were integrated by *APEX3* provided by Bruker Inc with multi-scan absorption corrections. The structure solution and refinement were processed by *SHELXTL* (version 6.14) and OLEX 2.3 program package.[3] The ellipsoid contour was in 50% probability.



Crystallographic data for **2i**.

Formula	$C_{12}H_{13}ClO_2$
Formula mass (amu)	224.67
Space group	P 21 21 21
a (Å)	7.173 (5)
b (Å)	8.114 (7)
c (Å)	18.608 (16)
α (deg)	90

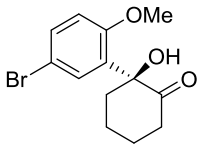
β (deg)	90
γ (deg)	90
V (Å^3)	1083.1 (15)
Z	4
λ (Å)	0.71073
T (K)	180
ρ_{calcd} (g cm^{-3})	1.378
μ (mm^{-1})	0.328
Transmission factors	0.666, 0.746
$2\theta_{max}$ (deg)	28.281
No. of unique data, including $F_o^2 <$ 0	2578
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	2390
No. of variables	138
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0312
$R_w(F_o^2)$ [b]	0.0975
Goodness of fit	1.001

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

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

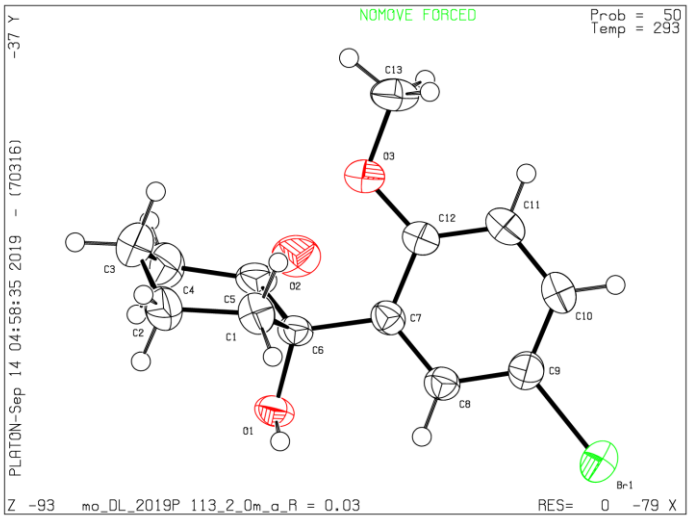
where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

Figure S2. ORTEP diagram of product **2l**.



2l

The configuration of **2l** was determined to be (*S*) by single-crystal X-ray crystallographic analysis. Crystals of **2l** [$C_{13}H_{15}BrO_3$] were obtained from the mixture of DCM, ethyl acetate and petroleum ether. CCDC 1954319 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambrige Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The colourless crystals in block shape are picked up and mounted for the single-crystal X-ray diffraction. The measurements were taken in a Bruker D8 Venture diffractometer equipped with Photon II CMOS detector by omega and phi scan methods. The data were integrated by *APEX3* provided by Bruker Inc with multi-scan absorption corrections. The structure solution and refinement were processed by *SHELXTL* (version 6.14) and OLEX 2.3 program package.[3] The ellipsoid contour was in 50% probability.



Crystallographic data for **2l**.

Formula	C_{13} H_{15} Br O_3
Formula mass (amu)	299.16
Space group	P 1
a (Å)	5.7794 (18)
b (Å)	6.058 (3)
c (Å)	9.329 (4)
α (deg)	84.597 (12)
β (deg)	79.775 (10)
γ (deg)	77.363 (10)
V (Å^3)	313.2 (2)
Z	1
λ (Å)	0.71073
T (K)	293
ρ_{calcd} (g cm^{-3})	1.586
μ (mm^{-1})	3.275
Transmission factors	0.544, 0.746
$2\theta_{max}$ (deg)	32.550
No. of unique data, including F_o^2 <	4217

0	
No. of unique data, with F_o^2 > $2\sigma(F_o^2)$	3479
No. of variables	159
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0253
$R_w(F_o^2)$ [b]	0.0653
Goodness of fit	0.999

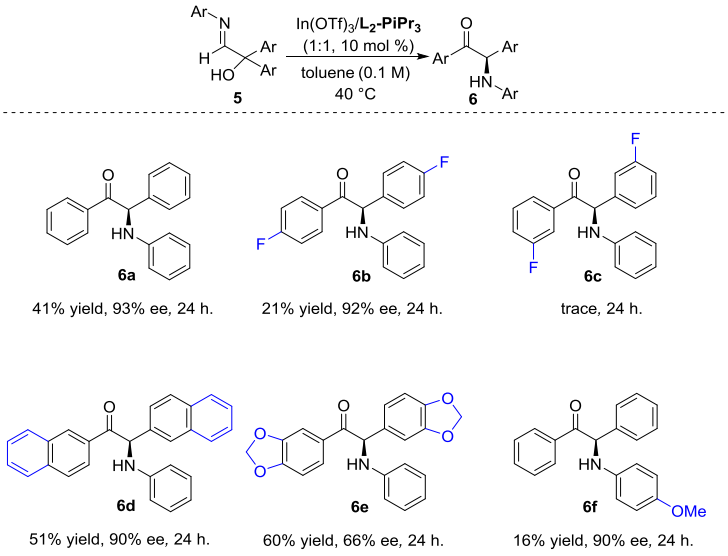
[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

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

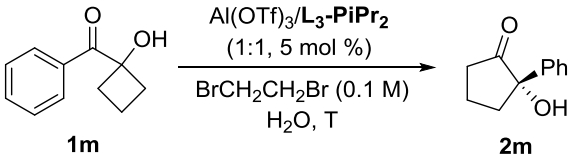
where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

3. Substrate scope of acyclic aldmines 5 under the conditions of In(OTf)$_3$

Scheme S1. Substrate scope of acyclic aldimines **5** under the conditions of In(OTf)$_3$

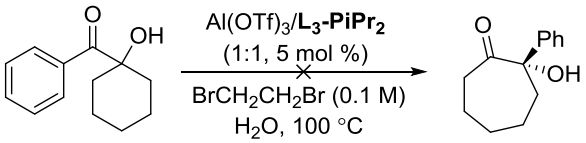


4. Other examples



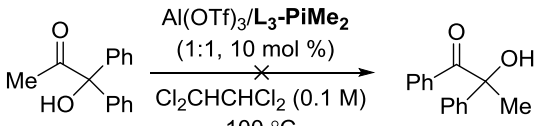
1m **2m**

40 °C: 99% yield, 25% ee;
rt: 99% yield, 25% ee;



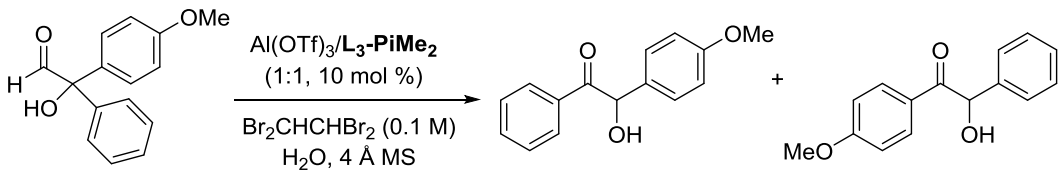
1n **2n**

NR



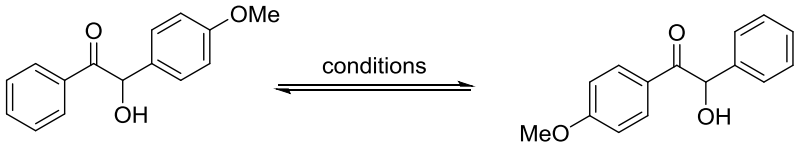
3j **4j**

NR



3k **4k** **4k'**

Changes	Ratio	ee %
none	1.73:1	77%/78%
rac-**PiMe$_2$** instead of **L$_3$-PiMe$_2$** at 80 °C	1.53:1	0/0
80 °C instead of 30 °C	1:1.55	49%/20%



4k **4k'**

Conditions	Ratio	ee
standard	1.73:1	77%/78%
with catalyst at 80 °C	1:4.80	14%/-14%
without catalyst at 80 °C	1.72:1	80%/86%

Results of substrates **1m**, **1n** and **3j** indicated that the stability of starting materials determined the reactivity of the migration process. On the other hands, the substrate **3k** with two different aryl group showed interesting results. Under the standard conditions (30 °C), **4k** and **4k'** were afforded in a ratio of 1.73:1 with 77% ee and 78% ee, respectively. While performing the reaction at 80 °C, the ratio turned to 1:1.55 with only 49% ee and 20 % ee, respectively. Subjecting the enantioenriched product **4k**/**4k'** into the standard conditions at 80 °C, the ratio turned into 1:4.80 with 14% ee for each. In contrast, When the same reaction was carried out without the catalyst, there is no reaction.

5. Proposed working modes.

Figure S3. Proposed working modes for cyclic α-ketols.

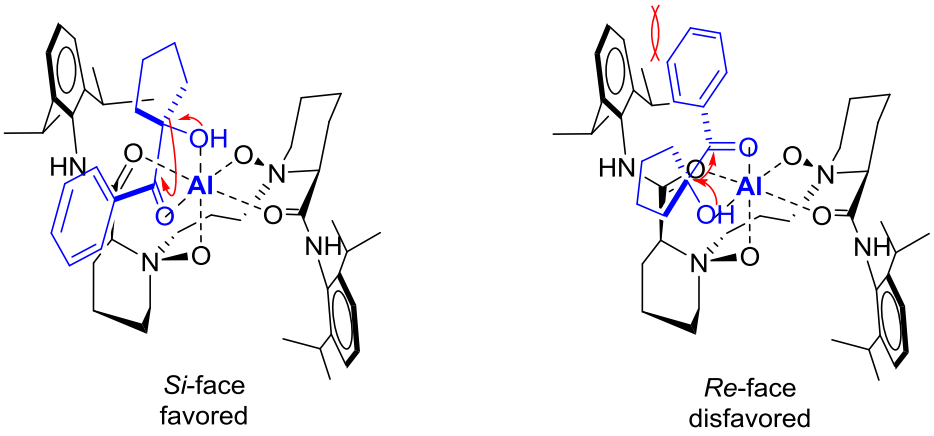


Figure S4. Proposed working modes for acyclic α-hydroxy aldehydes.

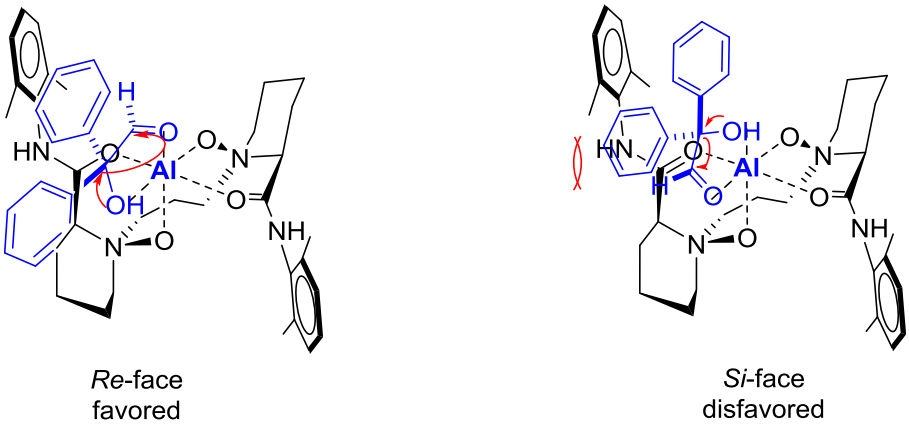
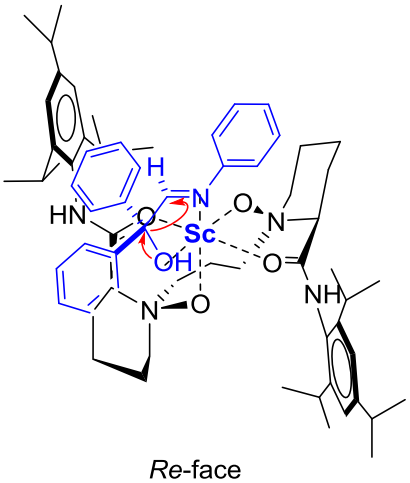
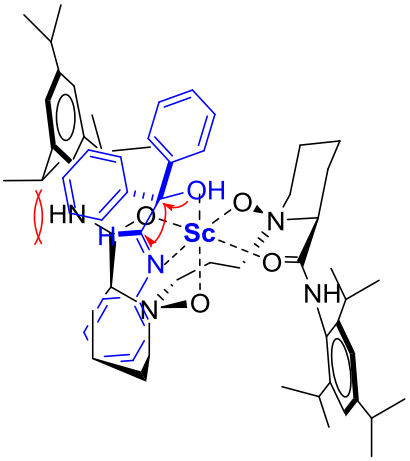


Figure S5. Proposed working modes for acyclic α-hydroxy aldimines.



Re-face
favored



Si-face
disfavored

5. References

(1) (a) Wen, Y. H.; Huang, X.; Huang, J. L.; Xiong, Y.; Qin, B.; Feng, X. M. Asymmetric Cyanosilylation of Aldehydes Catalyzed by Novel Organocatalysts. *Synlett* **2005**, 2445. (b) Yu, Z. P.; Liu, X. H.; Dong, Z. H.; Xie, M. S.; Feng, X. M. An *N*,*N*′-dioxide/In(OTf)$_3$ Catalyst for the Asymmetric Hetero–Diels–Alder Reaction Between Danishefsky's Dienes and Aldehydes: Application in the Total Synthesis of Triketide. *Angew. Chem., Int. Ed.* **2008**, *47*, 1308. (c) Zhou, X.; Shang, D. J.; Zhang, Q.; Lin, L. L.; Liu, X. H.; Feng, X. M. Enantioselective Three-Component Kabachnik−Fields Reaction Catalyzed by Chiral Scandium(III)−*N*,*N*′-dioxide Complexes *Org. Lett*. **2009**, *11*, 1401 and references therein.

(2) Zhang, X.; Staples, R. J.; Rheingold, A. L.; Wulff, W. D. Catalytic Asymmetric α-Iminol Rearrangement: New Chiral Platforms. *J. Am. Chem. Soc*. **2014**, *136*, 13971.

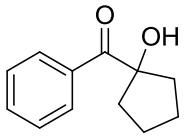
(3) (a) Sheldrick, G. M. *Acta Cryst*. **2008**, *A*64, 112. (b) Sheldrick, G. M. *Acta Cryst.* **2015**, *A*71, 3. (c) Sheldrick, G. M. *Acta Cryst.* **2015**, *C*71, 3. (d) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339.

(4) Shevchenko, G. A.; Pupo, G.; List, B. Direct Asymmetric α-Hydroxylation of Cyclic α-Branched Ketones through Enol Catalysis. *Synlett* **2019**, *30*, 49.

(5) (a) Soeta, T.; Tabatake, Y.; Inomata, K.; Ukaji, Y. Asymmetric Benzoin Condensation Promoted by Chiral Triazolium Precatalyst Bearing a Pyridine Moiety. *Tetrahedron* **2012**, *68*, 894. (b) Dhayalan, V.; Gadekar, S. C.; Alassad, Z.; Milo, A. Unravelling Mechanistic Features of Organocatalysis with *in situ* Modifications at the Secondary Sphere. *Nat. Chem*. **2019**, *11*, 543 and references therein.

6. Characterization of Starting Materials

(1-Hydroxycyclopentyl)(phenyl) methanone (1a)



1a

Colorless oil;

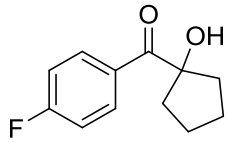
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.55 – 7.51 (m, 1H), 7.44 – 7.40 (m, 2H), 3.93 (s, 1H), 2.37 – 2.30 (m, 2H), 2.03 – 1.82 (m, 6H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.6, 133.9, 132.7, 129.5, 128.2, 87.1, 40.6, 25.3.

IR: 3440, 2957, 2872, 1668, 1597, 1446, 1375, 1177, 1061, 1012, 914, 852, 787, 707, 666 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{15}O_2^+$ 191.1067; Found 191.1067.

(4-Fluorophenyl)(1-hydroxycyclopentyl) methanone (1b)



1b

Colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 2H), 7.08 – 7.04 (m, 2H), 4.04 (s, 1H), 2.23 – 2.21 (m, 2H), 1.99 – 1.71 (m, 6H);

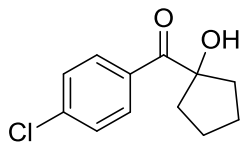
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 201.6, 165.1 (d, $J_{C\text{-}F}$ = 253.0 Hz), 132.5 (d, $J_{C\text{-}F}$ = 9.0 Hz), 130.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 115.0 (d, $J_{C\text{-}F}$ = 22.0 Hz), 87.1, 39.9, 24.9;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −105.3 (s, 1F).

IR: 3449, 2961, 2874, 2362, 1671, 1597, 1504, 1447, 1409, 1264, 1236, 1194, 1157, 1012, 915, 848, 757, 688, 614, 506 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}FO_2^+$ 209.0972; Found 209.0972.

(4-Chlorophenyl)(1-hydroxycyclopentyl) methanone (1c)



1c

White solid; mp: 58−60 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.42 – 7.38 (m, 2H), 3.64 (s, 1H), 2.35 – 2.24 (m, 2H), 2.05 – 1.74 (m, 6H);

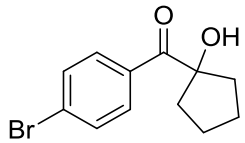
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.2, 139.2, 132.3, 131.2, 128.5, 87.2, 40.4, 25.3.

IR: 3487, 2970, 2872, 2335, 2157, 2093, 2024, 1962, 1658, 1587, 1485, 1449, 1399, 1372, 1270, 1198, 1175, 1092, 1060, 1013, 947, 917, 832, 752, 682, 624, 582, 528, 482, 440 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{34.9689}ClO_2^+$ 225.0677; Found 225.0675;

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{36.9659}ClO_2^+$ 227.0647; Found 227.0644.

(4-Bromophenyl)(1-hydroxycyclopentyl) methanone (1d)



1d

White solid; mp: 61−64 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 2H), 7.59 – 7.56 (m, 2H), 3.61 (s, 1H), 2.34 – 2.26 (m, 2H), 2.03 – 1.80 (m, 6H);

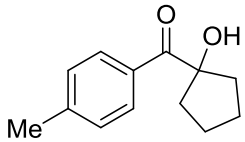
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.5, 132.7, 131.5, 131.2, 128.0, 87.2, 40.5, 25.3.

IR: 3444, 2960, 2872, 2363, 1672, 1583, 1481, 1445, 1395, 1175, 1072, 1009, 914, 837, 750, 682, 583, 469 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{78.9183}BrO_2^+$ 269.0172; Found 269.0165;

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{80.9163}BrO_2^+$ 271.0151; Found 271.0143.

(1-Hydroxycyclopentyl)(*p*-tolyl) methanone (1e)



1e

Colorless oil;

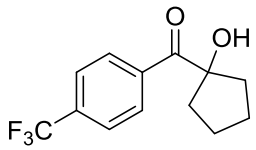
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 2H), 7.22 – 7.20 (m, 2H), 4.14 (s, 1H), 2.38 (s, 3H), 2.35 – 2.27 (m, 2H), 2.02 – 1.96 (m, 2H), 1.91 – 1.80 (m, 4H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.0, 143.4, 131.0, 129.7, 128.8, 86.9, 40.6, 25.3, 21.4.

IR: 3433, 2954, 2871, 1663, 1605, 1569, 1445, 1408, 1376, 1264, 1175, 1114, 1011, 949, 915, 828, 787, 746, 690, 617, 481 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}O_2^+$ 205.1223; Found 205.1222.

(1-Hydroxycyclopentyl)[4-(trifluoromethyl)phenyl] methanone (1f)



1f

White solid; mp: 46−49 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.10 (m, 2H), 7.71 – 7.69 (m, 2H), 3.35 (s, 1H), 2.36 – 2.28 (m, 2H), 2.05 – 1.96 (m, 2H), 1.95 – 1.82 (m. 4H);

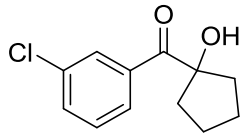
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.8, 137.4, 133.9 (q, $J_{C\text{-}F}$ = 33.0, 65.0 Hz), 129.9, 125.2 (q, $J_{C\text{-}F}$ = 3.0, 7.0 Hz), 123.5 (q, $J_{C\text{-}F}$ = 271.0, 542.0 Hz), 87.5, 40.3, 25.2;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −63.2 (s, 3F).

IR: 3472, 3359, 2970, 2879, 1681, 1509, 1408, 1327, 1170, 1121, 1067, 1011, 909, 853, 770, 704, 594, 467 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}F_3O_2^+$ 259.0940; Found 259.0938.

(3-Chlorophenyl)(1-hydroxycyclopentyl) methanone (1g)



1g

Colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.97 (m, 1H), 7.88 – 7.85 (m, 1H), 7.49 – 7.46 (m, 1H), 7.36 – 7.32 (t, 1H, *J* = 8.0 Hz), 3.81 (s, 1H), 2.30 – 2.21 (m, 2H), 1.96 – 1.77 (m, 6H);

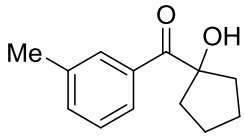
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.2, 135.8, 134.2, 132.4, 129.6, 129.3, 127.6, 87.3, 40.0, 25.0.

IR: 3447, 3070, 2962, 2874, 2049, 2021, 1676, 1568, 1416, 1252, 1190, 1075, 1013, 902, 799, 744, 677, 500, 420 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{34.9689}ClO_2^+$ 225.0677; Found 225.0680;

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{36.9659}ClO_2^+$ 227.0647; Found 227.0644.

(1-Hydroxycyclopentyl)(*m*-tolyl) methanone (1h)



1h

Colorless oil;

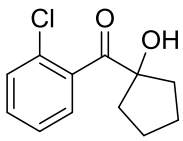
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.32 – 7.25 (m, 2H), 4.12 (s, 1H), 2.36 (s, 3H), 2.33 – 2.27 (m, 2H), 1.97 – 1.90 (m, 2H), 1.89 – 1.77 (m, 4H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.7, 137.7, 133.9, 133.2, 129.9, 127.7, 126.5, 87.0, 40.2, 25.1, 21.1.

IR: 3440, 2955, 2871, 1666, 1600, 1446, 1377, 1268, 1165, 1012, 934, 804, 738, 685, 438 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}O_2^+$ 205.1223; Found 205.1223.

(2-Chlorophenyl)(1-hydroxycyclopentyl) methanone (1i)



1i

Orange oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 4H), 3.46 (s, 1H), 2.17 – 2.07 (m, 2H), 1.92 – 1.83 (m, 4H), 1.76 – 1.68 (m, 2H);

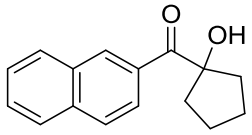
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.2, 138.1, 130.4, 130.0, 129.6, 127.0, 126.1, 88.1, 39.0, 24.1.

IR: 3473, 2959, 2874, 2361, 1693, 1591, 1468, 1434, 1369, 1278, 1238, 1200, 1033, 903, 762, 743, 702, 645, 454 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{34.9689}ClO_2^+$ 225.0677; Found 225.0677;

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{36.9659}ClO_2^+$ 227.0647; Found 227.0645.

(1-Hydroxycyclopentyl)(naphthalen-2-yl) methanone (1j)



1j

White solid; mp: 56–60 °C;

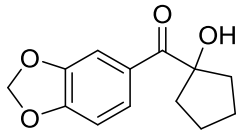
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.99 – 7.96 (m, 1H), 7.87 (d, 1H, *J* = 8.0 Hz), 7.79 – 7.76 (m, 2H), 7.55 – 7.45 (m, 2H), 4.03 (s, 1H), 2.43 – 2.36 (m, 2H), 2.03– 1.84 (m, 6H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.4, 135.0, 132.0, 131.4, 131.1, 129.6, 128.4, 127.8, 127.5, 126.5, 125.2, 87.3, 40.6, 25.3.

IR: 3428, 3058, 2955, 2871, 1664, 1625, 1595, 1505, 1462, 1354, 1273, 1228, 1172, 1126, 1102, 1060, 1012, 955, 918, 865, 819, 758, 594, 475 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}O_2^+$ 241.1223; Found 241.1223.

Benzo[d][1,3]dioxol-5-yl(1-hydroxycyclopentyl) methanone (1k)



1k

Orange solid; mp: 33–34 °C;

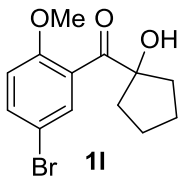
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 1H), 7.48 – 7.47 (m, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.00 (s, 2H), 4.14 (s, 1H), 2.30 – 2.22 (m, 2H), 1.99 – 1.75 (m, 6H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 201.0, 151.4, 147.2, 128.0, 126.0, 109.5, 107.2, 101.5, 86.8, 40.2, 24.9.

IR: 3440, 2955, 1659, 1605, 1484, 1436, 1349, 1252, 1190, 1094, 1036, 930, 883, 806, 752, 720, 650, 576, 424 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}O_4^+$ 235.0965; Found 235.0967.

(5-Bromo-2-methoxyphenyl)(1-hydroxycyclopentyl) methanone (1l)



1l

White solid; mp: 97–101 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 1H), 7.38 – 7.37 (m, 1H), 6.82 (d, 1H, *J* = 9.2 Hz), 3.85 (s, 3H), 3.62 (s, 1H), 2.15 – 2.08 (m, 2H), 1.96 – 1.70 (m, 6H);

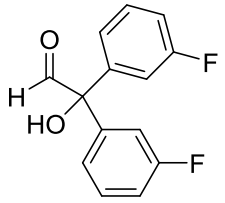
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.5, 154.8, 134.1, 131.2, 130.9, 113.3, 112.8, 88.4, 55.9, 39.7, 24.6.

IR: 3522, 2944, 2870, 1681, 1590, 1481, 1390, 1254, 1185, 1140, 1090, 1018, 942, 880, 817, 760, 659, 621, 532, 434cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}{}^{78.9183}BrO_3^+$ 299.0277; Found 299.0267;

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}{}^{80.9163}BrO_3^+$ 301.0257; Found 301.0266.

2,2-Bis(3-fluorophenyl)-2-hydroxyacetaldehyde (3c)



3c

Colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (d, 1H, J = 1.6 Hz), 7.32 – 7.27 (m, 2H), 7.06 – 6.96 (m, 6H), 4.39 (d, 1H, J = 1.2 Hz);

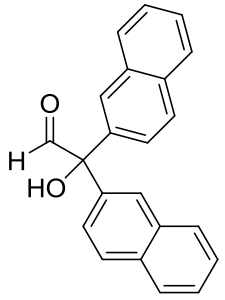
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.8, 163.0 (d, $J_{C\text{-}F}$ = 240.0 Hz), 141.3 (d, $J_{C\text{-}F}$ = 6.0 Hz), 130.5 (d, $J_{C\text{-}F}$ = 9.0 Hz), 122.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.5 (d, $J_{C\text{-}F}$ = 23.0 Hz), 82.5 (t, $J_{C\text{-}F}$ = 2.0);

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −110.9 (s, 2F).

IR: 3465, 3077, 2362, 1724, 1588, 1484, 1440, 1332, 1234, 1146, 1071, 984, 937, 876, 770, 693, 524, 484, 456 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}F_2O_2^+$ 249.0722; Found 249.0727.

2-Hydroxy-2,2-di(naphthalen-2-yl)acetaldehyde (3g)



3g

White solid; mp: 134−138 °C;

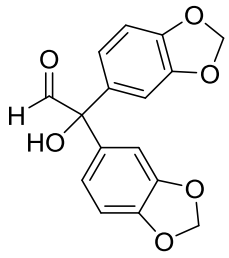
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (d, 1H, J = 1.2), 7.92 – 7.81 (m, 8H), 7.56 – 7.49 (m, 4H), 7.48 – 7.45 (m, 2H), 4.55 (d, 1H, J = 1.6 Hz);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.1, 136.7, 133.1, 133.1, 128.9, 128.3, 127.7, 126.8, 126.8, 126.6, 125.0, 83.8.

IR: 3477, 3055, 2834, 2362, 1721, 1598, 1505, 1355, 1270, 1161, 1126, 974, 898, 858, 819, 750, 657, 624, 588, 477 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}O_2^+$ 313.1223; Found 313.1220.

2,2-Bis{benzo[d][1,3]dioxol-5-yl}-2-hydroxyacetaldehyde (3h)



3h

Sticky oil;

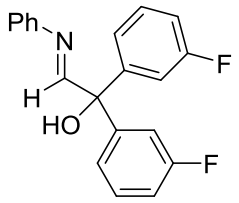
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.84 (m, 1H), 6.84 – 6.81 (m, 6H), 5.98 – 5.97 (m, 4H), 4.31 – 4.31 (m, 1H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.2, 148.2, 147.8, 133.2, 121.0, 108.3, 108.0, 101.3, 82.9.

IR: 3469, 2898, 2362, 1720, 1609, 1483, 1438, 1350, 1241, 1102, 1036, 976, 930, 888, 814, 780, 676, 647, 554, 430 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}O_6^+$ 301.0707; Found 301.0713.

(*E*)-1,1-Bis(3-fluorophenyl)-2-(phenylimino)ethan-1-ol (5c)



5c

White solid; mp: 59─62 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.41 (m, 1H), 7.40 – 7.26 (m, 5H), 7.20 – 7.16 (m, 6H), 7.05 – 7.00 (m, 2H), 5.80 – 5.79 (m, 1H);

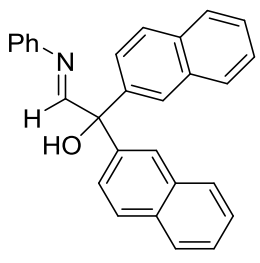
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.2, 163.3, 161.7, 148.1, 145.4, 145.3, 130.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.3, 127.2, 122.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 121.2, 115.0 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.3 (d, $J_{C\text{-}F}$ = 23.0 Hz), 78.0;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −111.7 (s, 2F).

IR: 3387, 3074, 2927, 2362, 1650, 1589, 1484, 1442, 1378, 1328, 1239, 1145, 1074, 994, 944, 882, 784, 751, 694, 525, 446 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}F_2NO_2^+$ 324.1194; Found 324.1199.

(*E*)-1,1-Bi(naphthalen-2-yl)-2-(phenylimino)ethan-1-ol (5d)



5d

White solid; mp: 135─139 °C;

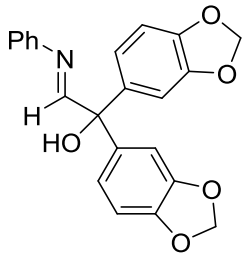
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 – 8.68 (m, 1H), 7.97 – 7.97 (m, 2H), 7.86 – 7.82 (m, 6H), 7.55 – 7.55 (m, 1H), 7.53 – 7.52 (m, 1H), 7.51– 7.47 (m, 4H), 7.41– 7.37 (m, 2H), 7.29– 7.27 (m, 1H), 7.22– 7.20 (m, 2H), 5.91– 5.90 (m, 1H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.6, 140.5, 133.1, 132.8, 129.3, 128.4, 128.3, 127.6, 126.9, 126.4, 126.3, 126.1, 125.3, 121.2, 79.2.

IR: 3388, 3055, 2362, 1647, 1595, 1486, 1382, 1324, 1269, 1209, 1158, 1125, 1074, 989, 948, 902, 860, 820, 789, 750, 694, 661, 627, 555, 477 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{22}NO^+$ 388.1696; Found 388.1698.

(*E*)-1,1-Bis{benzo[d][1,3]dioxol-5-yl}-2-(phenylimino)ethan-1-ol (5e)



5e

White solid; mp: 111−117 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.39 – 7.35 (m, 2H), 7.27 – 7.23 (m, 1H), 7.17 – 7.14 (m, 2H), 6.92 – 6.92 (m, 2H), 6.89 – 6.86 (m, 2H), 6.80 – 6.75 (m, 2H), 5.96 (s, 4H), 5.65 (s, 1H);

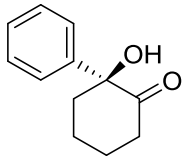
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.5, 148.5, 147.9, 147.2, 137.3, 129.3, 129.2, 126.8, 121.1, 120.6, 115.1, 108.0, 108.0, 101.2.

IR: 3383, 2893, 2779, 2362, 1647, 1598, 1481, 1463, 1323, 1237, 1095, 1036, 987, 932, 864, 805, 756, 694, 560, 526, 427 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NO_5^+$ 376.1179; Found 376.1181.

7. Characterization of the Products

(*S*)-2-Hydroxy-2-phenylcyclohexan-1-one (2a)



2a

White solid; mp: 88–93 °C; 18.6 mg, 98% yield, 91% ee. $[\alpha]_D^{26}$ = +169.5 (*c* 0.30 in $CHCl_3$). lit: $[\alpha]_D^{25}$ = +166.0 (*c* 0.20 in $CHCl_3$) for (*S*), 96% ee.[4]

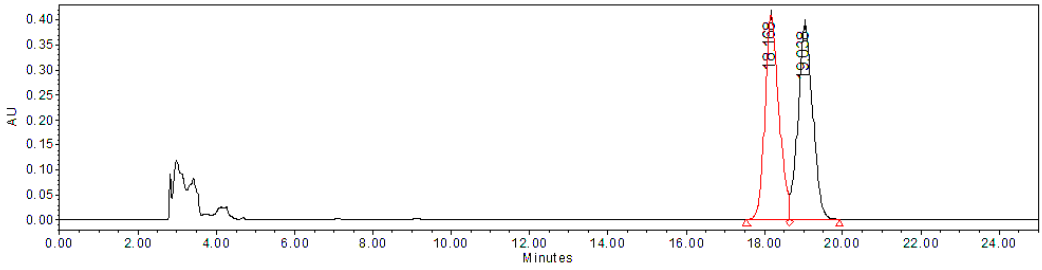
HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (minor) = 18.46 min, t_R (major) = 19.17 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.28 (m, 3H), 4.50 (s, 1H), 3.04 – 2.97 (m, 1H), 2.56 – 2.51 (m, 1H), 2.47 – 2.38 (m, 1H), 2.09 – 2.01 (m, 1H), 1.90 – 1.82 (m, 2H), 1.80 – 1.68 (m, 2H);

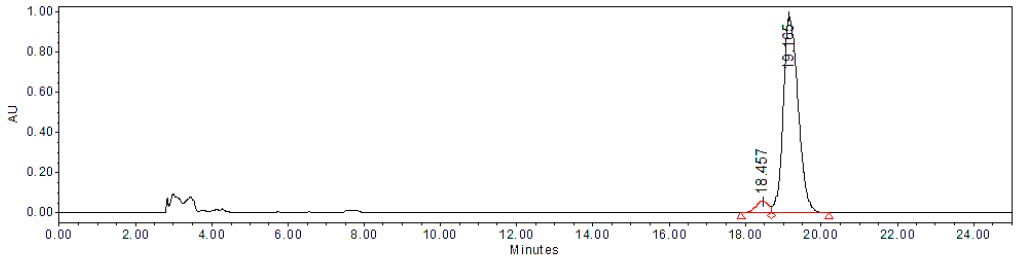
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.7, 139.9, 129.1, 128.3, 126.3, 80.0, 38.8, 38.8, 28.3, 23.0.

IR: 3467, 2943, 1867, 1712, 1495, 1450, 1366, 1311, 1255, 1196, 1101, 1068, 952, 906, 852, 796, 760, 701, 608, 564 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{15}O_2^+$ 191.1067; Found 191.1065.

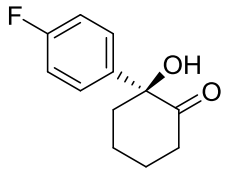


	Retention Time	Area	% Area
1	18.168	10068462	49.79
2	19.038	10153783	50.21



	Retention Time	Area	% Area
1	18.457	1259520	4.56
2	19.165	26337649	95.44

(*S*)-2-(4-Fluorophenyl)-2-hydroxycyclohexan-1-one (2b)



2b

Colorless oil; 20.8 mg, 99% yield, 89% ee. $[\alpha]_D^{19}$ = +142.2 (*c* 0.60 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (minor) = 14.65 min, t_R (major) = 15.89 min.

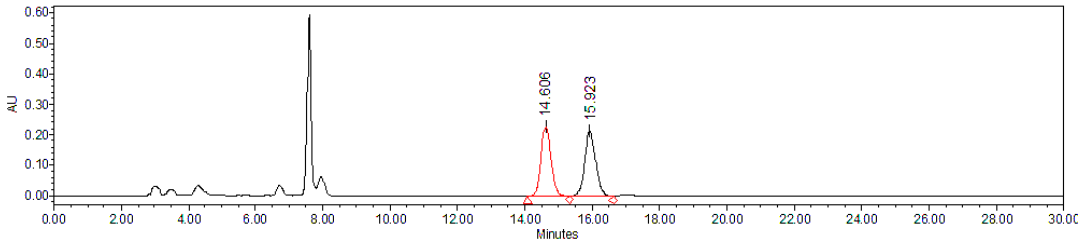
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.11 – 7.06 (m, 2H), 4.51 (s, 1H), 2.98 – 2.92 (m, 1H), 2.57 – 2.51 (m, 1H), 2.44 – 2.36 (m, 1H), 2.11 – 2.03 (m, 1H), 1.91 – 1.83 (m, 2H), 1.78 – 1.69 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.4, 162.4 (d, $J_{C\text{-}F}$ = 247.0 Hz), 135.8 (d, $J_{C\text{-}F}$ = 4.0 Hz), 128.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.0 Hz), 79.4, 39.1, 28.7, 28.3, 23.0;

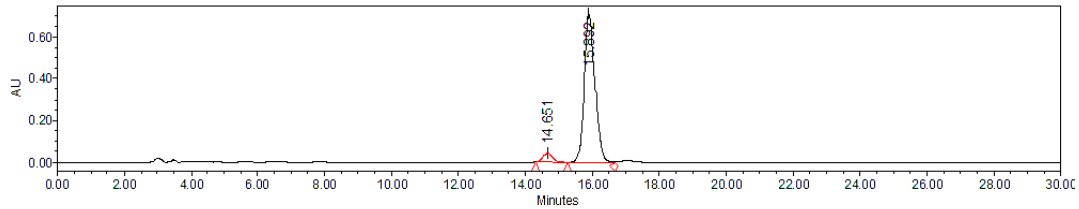
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −113.5 (s, 1F).

IR: 3461, 2942, 2868, 1711, 1602, 1508, 1453, 1425, 1364, 1309, 1228, 1164, 1095, 1066, 1046, 1011, 952, 929, 905, 836, 725, 693, 640, 559, 474 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}FO_2^+$ 209.0972; Found 209.0969.

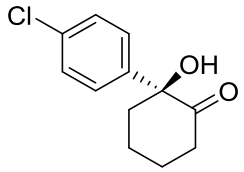


	Retention Time	Area	% Area
1	14.606	4607520	49.30
2	15.923	4737484	50.70



	Retention Time	Area	% Area
1	14.651	888277	5.27
2	15.892	15977651	94.73

(*S*)-2-(4-Chlorophenyl)-2-hydroxycyclohexan-1-one (2c)



2c

White solid; mp: 53–57 °C, 21.8 mg, 97% yield, 91% ee. $[\alpha]_D^{18}$ = +134.5 (*c* 0.73 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (minor) = 15.78 min, t_R (major) = 16.96 min.

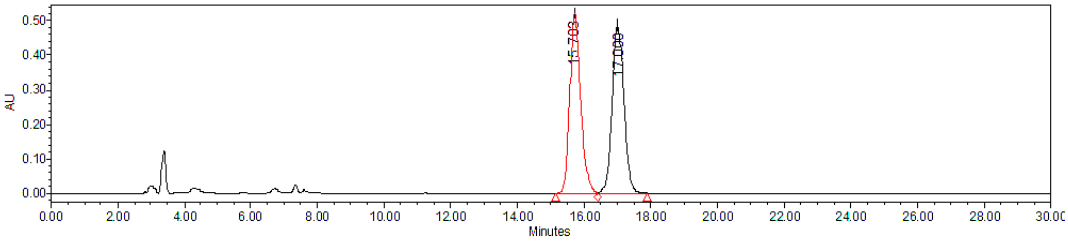
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.27 – 7.22 (m, 2H), 4.51 (s, 1H), 2.96 – 2.91 (m, 1H), 2.57 – 2.52 (m, 1H), 2.43 – 2.34 (m, 1H), 2.10 – 2.04 (m, 1H), 1.91 – 1.83 (m, 2H), 1.78 – 1.68 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.2, 138.5, 134.3, 129.3, 127.9, 79.5, 38.9, 38.8, 28.3, 23.0.

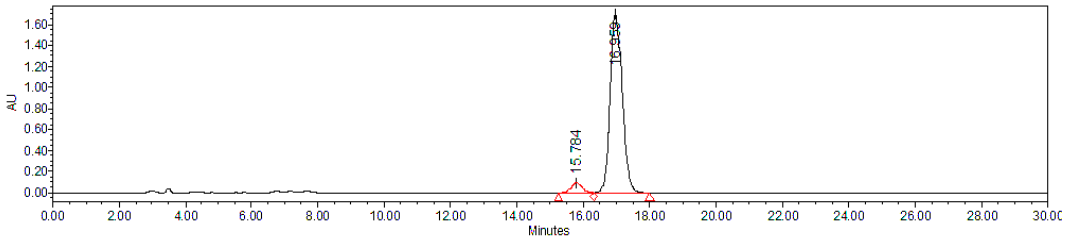
IR: 3457, 2941, 2866, 1712, 1594, 1490, 1452, 1363, 1309, 1254, 1195, 1094, 1068, 1046, 1011, 952, 928, 905, 830, 720, 621, 563, 531, 446 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{34.9689}ClO_2^+$ 225.0677; Found 225.0665;

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{36.9659}ClO_2^+$ 227.0647; Found 227.0645.

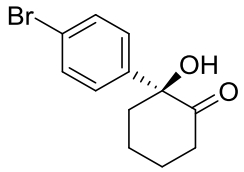


	Retention Time	Area	% Area
1	15.703	11814401	49.96
2	17.000	11833079	50.04



	Retention Time	Area	% Area
1	15.784	2007610	4.46
2	16.959	42955694	95.54

(*S*)-2-(4-Bromophenyl)-2-hydroxycyclohexan-1-one (2d)



2d

White solid; mp: 49–53 °C, 22.7 mg, 85% yield, 90% ee. $[\alpha]_D^{17}$ = +19.8 (*c* 1.29 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IA 2-propanol/*n*-hexane = 05/95, flow rate = 1.0 mL/min, λ = 220 nm, t_R (major) = 14.51 min, t_R (minor) = 15.95 min.

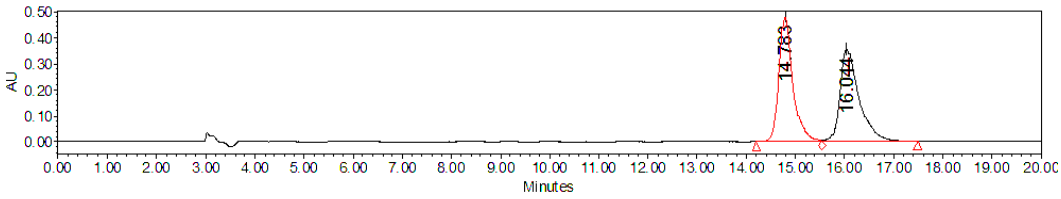
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.20 – 7.16 (m, 2H), 4.50 (s, 1H), 2.96 – 2.90 (m, 1H), 2.57 – 2.52 (m, 1H), 2.42 – 2.34 (m, 1H), 2.10 – 2.04 (m, 1H), 1.90 – 1.82 (m, 2H), 1.77 – 1.68 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.1, 139.0, 132.2, 128.2, 122.4, 79.5, 38.9, 38.8, 28.2, 23.0.

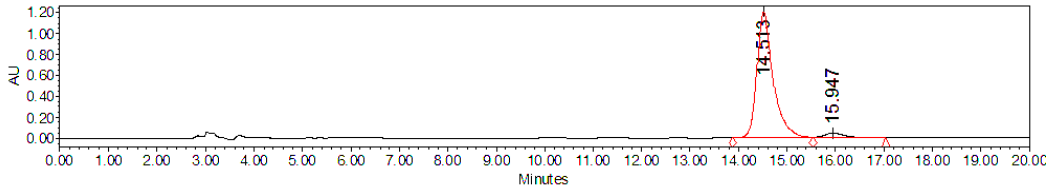
IR: 3433, 2950, 2870, 1714, 1671, 1582, 1483, 1446, 1394, 1260, 1174, 1071, 1007, 949, 910, 832, 749, 682, 562, 467 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{78.9183}BrO_2^+$ 269.0172; Found 269.0170;

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{80.9163}BrO_2^+$ 271.0151; Found 271.0146.

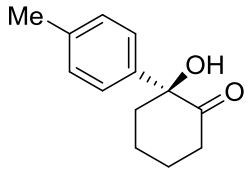


	Retention Time	Area	% Area
1	14.783	9398092	49.62
2	16.044	9541190	50.38



	Retention Time	Area	% Area
1	14.513	28426667	95.00
2	15.947	1496339	5.00

(*S*)-2-Hydroxy-2-(*p*-tolyl)cyclohexan-1-one (2e)



2e

Colorless oil; 20.4 mg, 99% yield, 89% ee. $[\alpha]_D^{27}$ = +140.6 (*c* 0.29 in $CHCl_3$). lit: $[\alpha]_D^{25}$ = +127.3 (*c* 0.11 in $CHCl_3$) for (*S*), 95% ee.[4]

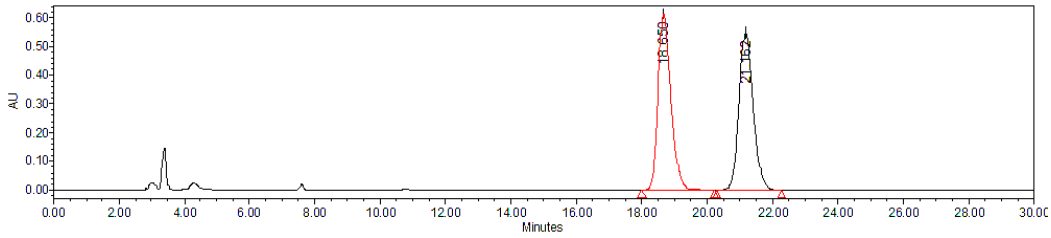
HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 05/95, flow rate = 1.0 mL/min, λ = 220 nm, t_R (minor) = 18.78 min, t_R (major) = 21.11 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.17 (m, 4H), 4.44 (s, 1H), 3.01 – 2.95 (m, 1H), 2.55 – 2.49 (m, 1H), 2.48 – 2.40 (m, 1H), 2.34 (s, 3H), 2.08 – 2.01 (m, 1H), 1.90 – 1.80 (m, 2H), 1.78 – 1.66 (m, 2H);

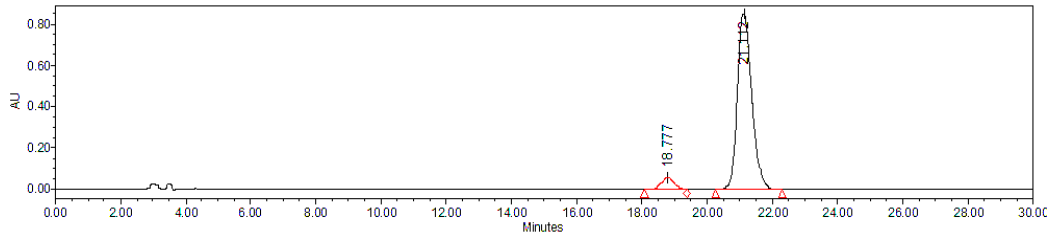
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.9, 138.1, 129.8, 126.2, 79.8, 38.8, 38.8, 28.3, 23.1, 21.0.

IR: 3471, 2941, 2866, 1711, 1513, 1451, 1367, 1311, 1255, 1192, 1098, 1046, 952, 929, 906, 851, 821, 723, 694, 641, 561 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}O_2^+$ 205.1223; Found 205.1220.

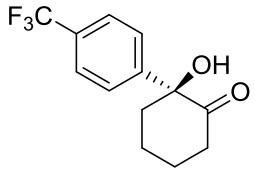


	Retention Time	Area	% Area
1	18.650	16569736	50.19
2	21.162	16442427	49.81



	Retention Time	Area	% Area
1	18.777	1534861	5.63
2	21.112	25729098	94.37

(*S*)-2-Hydroxy-2-[4-(trifluoromethyl)phenyl]cyclohexan-1-one (2f)



2f

Colorless oil; 15.2 mg, 59% yield, 92% ee. $[\alpha]_D^{27}$ = +112.8 (*c* 0.38 in $CHCl_3$). lit: $[\alpha]_D^{25}$ = +166.0 (*c* 0.20 in $CHCl_3$) for (*S*), 96% ee.[4]

HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (major) = 8.61 min, t_R (minor) = 9.46 min.

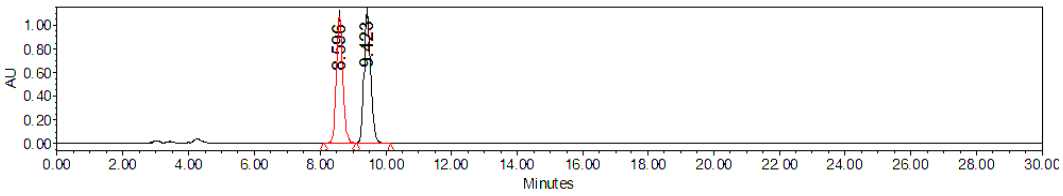
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 2H), 7.45 – 7.43 (m, 2H), 4.57 (s, 1H), 3.02 – 2.95 (m, 1H), 2.62 – 2.56 (m, 1H), 2.41 – 2.33 (m, 1H), 2.12 – 2.06 (m, 1H), 1.95 – 1.87 (m, 2H), 1.81 – 1.69 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 211.8, 143.9, 130.5 (q, $J_{C\text{-}F}$ = 41.0 , 74.0 Hz), 126.9, 126.1 (q, $J_{C\text{-}F}$ = 3.0, 7.0 Hz), 123.8 (q, $J_{C\text{-}F}$ = 271.0, 541.0 Hz), 79.6, 38.9, 38.9, 28.7, 28.2, 22.9;

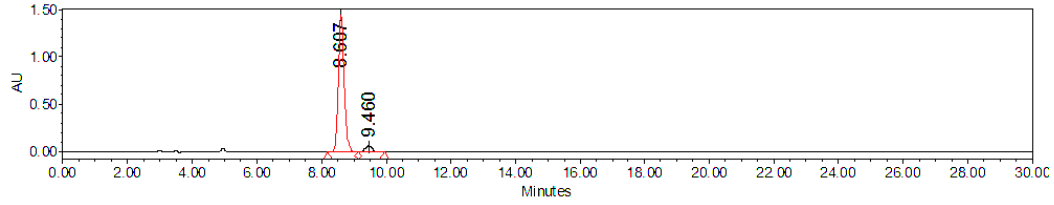
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −62.8 (s, 3F).

IR: 3455, 2946, 2870, 1716, 1619, 1412, 1327, 1167, 1121, 1070, 1016, 906, 843, 695, 607 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}F_3O_2^+$ 259.0940; Found 259.0948.

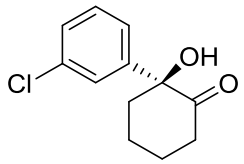


	Retention Time	% Area
1	8.596	50.03
2	9.423	49.97



	Retention Time	Area	% Area
1	8.607	18944070	95.86
2	9.460	819074	4.14

(*S*)-2-(3-Chlorophenyl)-2-hydroxycyclohexan-1-one (2g)



2g

Colorless oil; 19.7 mg, 88% yield, 88% ee. $[\alpha]_D^{15}$ = +150.0 (*c* 0.56 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (minor) = 13.21 min, t_R (major) = 15.33 min.

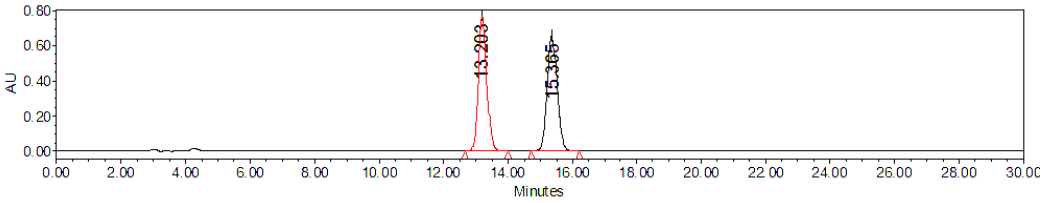
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 3H), 7.19 – 7.16 (m, 1H), 4.53 (s, 1H), 2.97 – 2.91 (m, 1H), 2.59 – 2.54 (m, 1H), 2.44 – 2.36 (m, 1H), 2.11 – 2.05 (m, 1H), 1.92 – 1.83 (m, 2H), 1.79 – 1.70 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 211.9, 142.0, 135.0, 130.4, 128.5, 126.7, 124.6, 79.6, 38.8, 28.2, 23.0.

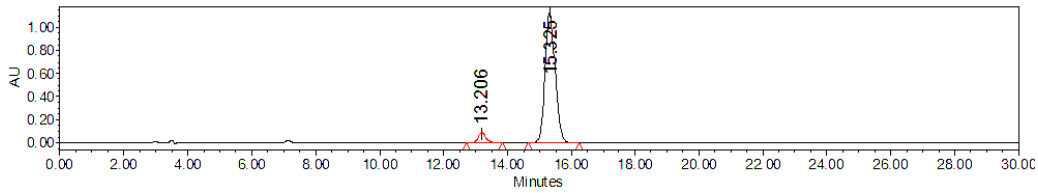
IR: 3454, 2941, 2866, 1711, 1594, 1571, 1454, 1423, 1360, 1310, 1234, 1196, 1102, 1046, 999, 952, 904, 878, 786, 739, 696, 662, 614, 588, 487, 443 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{34.9689}ClO_2^+$ 225.0677; Found 225.0676;

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{36.9659}ClO_2^+$ 227.0647; Found 227.0643.

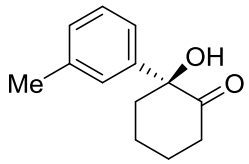


	Retention Time	Area	% Area
1	13.203	14170830	49.90
2	15.365	14228098	50.10



	Retention Time	Area	% Area
1	13.206	1534582	5.83
2	15.325	24801564	94.17

(*S*)-2-Hydroxy-2-(m-tolyl)cyclohexan-1-one (2h)



2h

Colorless oil; 13.6 mg, 67% yield, 84% ee. $[\alpha]_D^{15}$ = +125.7 (*c* 0.30 in CH_2Cl_2).

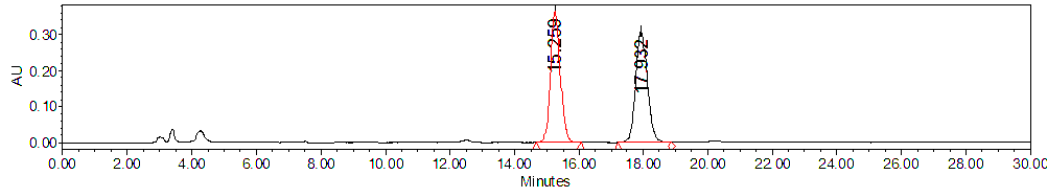
HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (minor) = 15.30 min, t_R (major) = 17.94 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 1H), 7.15 – 7.08 (m, 3H), 4.47 (s, 1H), 3.03 – 2.97 (m, 1H), 2.56 – 2.50 (m, 1H), 2.48 – 2.39 (m, 1H), 2.35 (s, 3H), 2.08 – 2.02 (m, 1H), 1.89 – 1.81 (m, 2H), 1.74 – 1.67 (m, 2H);

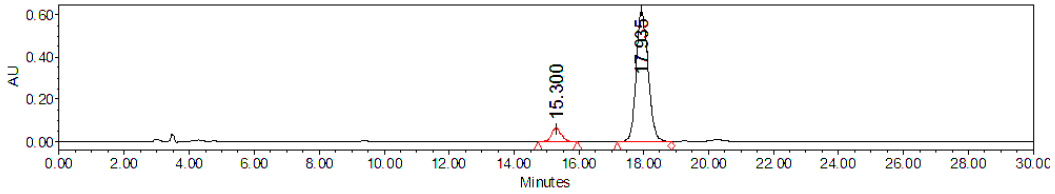
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.8, 139.9, 138.9, 129.0 (d, *J* = 8.0 Hz), 127.0, 123.3, 80.0, 38.9, 38.8, 29.7, 28.3, 23.1, 21.5.

IR: 3470, 2940, 2865, 1712, 1606, 1454, 1361, 1246, 1173, 1101, 952, 907, 829, 795, 706, 587, 445 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}O_2^+$ 205.1223; Found 205.1225.

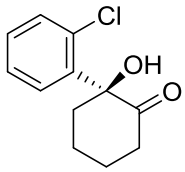


	Retention Time	Area	% Area
1	15.259	7722977	49.81
2	17.932	7783032	50.19



	Retention Time	Area	% Area
1	15.300	1334765	7.84
2	17.935	15696599	92.16

(*S*)-2-(2-Chlorophenyl)-2-hydroxycyclohexan-1-one (2i)



2i

White solid; mp: 120−127 °C; 21.1 mg, 94% yield, 87% ee. $[\alpha]_D^{16}$ = +40.5 (*c* 0.44 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (major) = 11.28 min, t_R (minor) = 12.76 min.

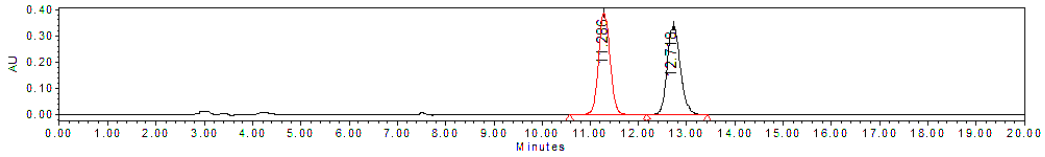
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.67 (m, 1H), 7.40 – 7.27 (m, 3H), 4.51 (s, 1H), 3.02 – 2.93 (m, 1H), 2.65 – 2.59 (m, 1H), 2.50 – 2.42 (m, 1H), 2.11 – 2.02 (m, 1H), 1.85 – 1.71 (m, 4H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.6, 137.4, 133.9, 131.3, 129.7, 128.6, 127.0, 80.5, 41.8, 38.7, 29.5, 22.8.

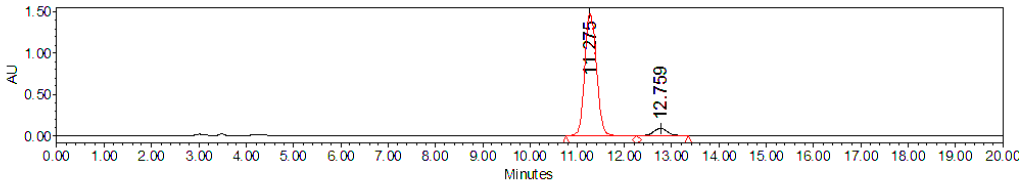
IR: 3397, 2929, 2859, 2361, 1705, 1594, 1437, 1366, 1328, 1260, 1195, 1126, 1099, 1046, 997, 951, 901, 806, 761, 721, 640, 564, 528, 493, 460, 428 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{34.9689}ClO_2^+$ 225.0677; Found 225.0673;

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}{}^{36.9659}ClO_2^+$ 227.0647; Found 227.0641.

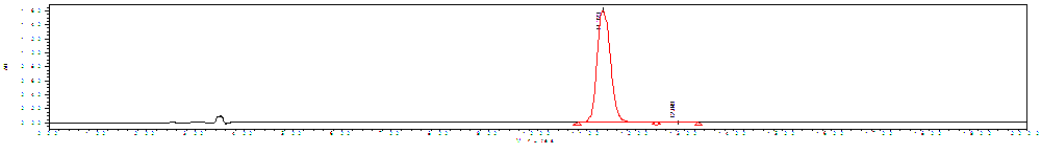


	Retention Time	Area	% Area
1	11.286	6304811	50.03
2	12.718	6296987	49.97



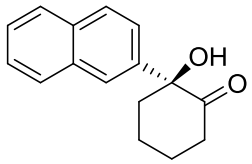
	Retention Time	Area	% Area
1	11.275	25566824	93.53
2	12.759	1768592	6.47

HPLC data of the crystal **2i**



	Retention Time	Area	% Area
1	11.323	30605345	99.71
2	12.849	88519	0.29

(*S*)-2-Hydroxy-2-(naphthalen-2-yl)cyclohexan-1-one (2j)



2j

White solid; mp: 81–85 °C; 15.2 mg, 63% yield, 87% ee. $[\alpha]_D^{26}$ = +168.2 (*c* 0.52 in $CHCl_3$). lit: $[\alpha]_D^{25}$ = +161.8 (*c* 0.11 in $CHCl_3$) for (*S*), 95% ee.[4]

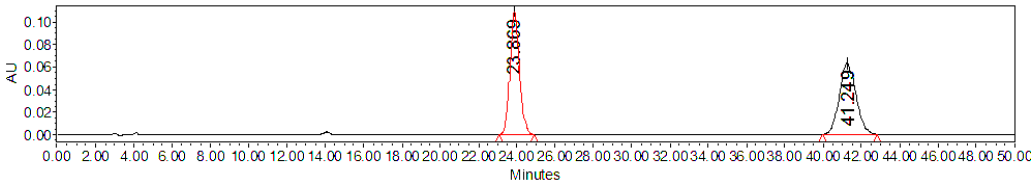
HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 24.02 min, t_R (major) = 41.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 4H), 7.53 – 7.49 (m, 2H), 7.37 – 7.34 (m, 1H), 4.59 (s, 1H), 3.17 – 3.12 (m, 1H), 2.60 – 2.55 (m, 1H), 2.50 – 2.42 (m, 1H), 2.10 – 2.04 (m, 1H), 1.99 – 1.90 (m, 2H), 1.89 – 1.71 (m, 2H);

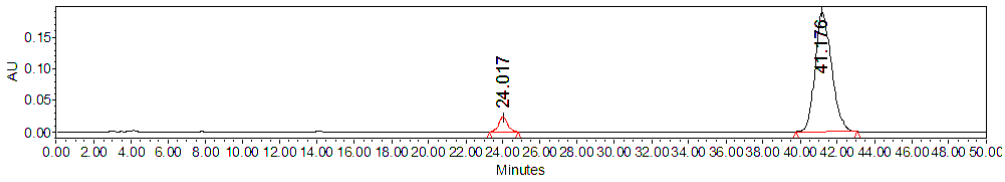
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.8, 137.2, 133.3, 133.0, 129.1, 128.2, 127.6, 126.6, 126.4, 125.6, 124.0, 80.2, 39.0, 39.0, 28.4, 23.2.

IR: 3462, 3056, 2934, 2862, 1709, 1599, 1505, 1451, 1336, 1254, 1180, 1098, 1046, 955, 901, 859, 821, 743, 699, 641, 618, 554, 478 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}O_2^+$ 241.1223; Found 241.1219.

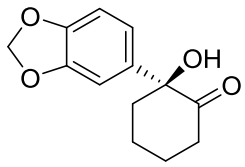


	Retention Time	Area	% Area
1	23.869	3786646	49.85
2	41.249	3809278	50.15



	Retention Time	Area	% Area
1	24.017	792747	6.34
2	41.176	11717797	93.66

(*S*)-2-{Benzo[*d*][1,3]dioxol-5-yl}-2-hydroxycyclohexan-1-one (2k)



2k

White solid; mp: 77−81 °C, 20.9 mg, 89% yield, 88% ee. $[\alpha]_D^{26}$ = +136.2 (*c* 0.46 in $CHCl_3$). lit: $[\alpha]_D^{25}$ = +154.7 (*c* 0.15 in $CHCl_3$) for (*S*), 94% ee.[4]

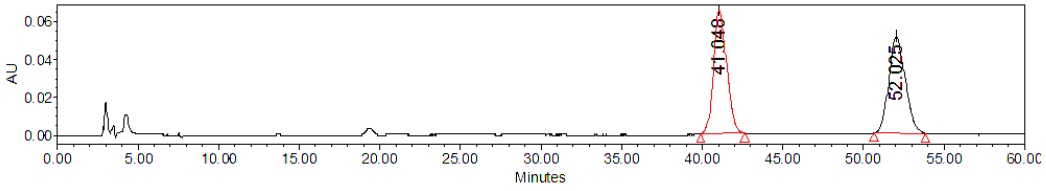
HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (minor) = 41.27 min, t_R (major) = 51.55 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 – 6.75 (m, 3H), 5.97 – 5.96 (m, 2H), 4.44 (s, 1H), 2.93 – 2.87 (m, 1H), 2.54 – 2.41 (m, 2H), 2.09 – 2.03 (m, 1H), 1.88 – 1.68 (m, 4H);

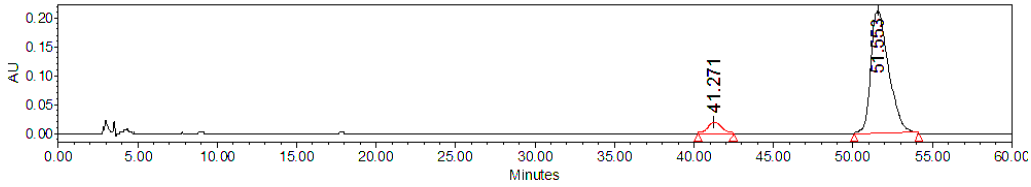
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.5, 148.3, 147.5, 133.8, 120.0, 108.6, 106.9, 101.3, 101.3, 79.7, 39.0, 38.7, 28.2, 23.0.

IR: 3466, 2930, 2865, 1709, 1488, 1437, 1371, 1238, 1095, 1037, 932, 890, 868, 814, 728, 696, 642, 612, 576, 487 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}O_4^+$ 235.0965; Found 235.0968.

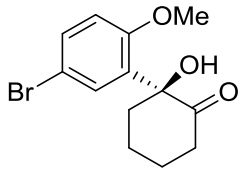


	Retention Time	Area	% Area
1	41.048	3720823	50.31
2	52.025	3675520	49.69



	Retention Time	Area	% Area
1	41.271	1050280	6.05
2	51.553	16313311	93.95

(*S*)-2-(5-Bromo-2-methoxyphenyl)-2-hydroxycyclohexan-1-one (2l)



2l

White solid; mp: 80–87 °C, 29.1 mg, 97% yield, 91% ee. $[\alpha]_D^{13}$ = +61.2 (*c* 0.74 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (minor) = 21.05 min, t_R (major) = 34.92 min.

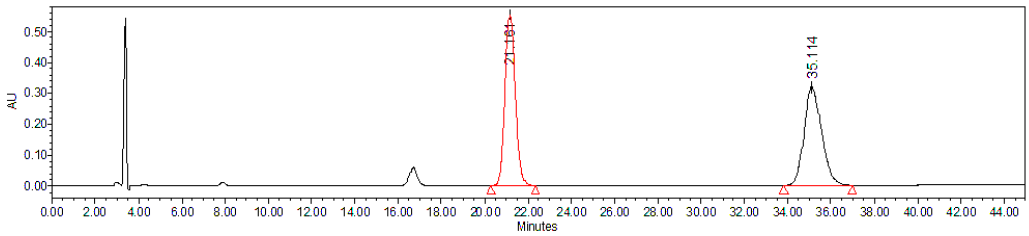
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, 1H, *J* = 2.4 Hz), 7.45 – 7.42 (m, 1H), 6.78 (d, 1H, *J* = 8.8 Hz), 4.54 (s, 1H), 3.71 (s, 3H), 2.88 – 2.80 (m, 1H), 2.56 – 2.51 (m, 1H), 2.38 – 2.30 (m, 1H), 2.05 – 1.96 (m, 1H), 1.87 – 1.65 (m, 4H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 211.7, 156.0, 132.4, 130.9, 130.5, 113.7, 113.6, 78.1, 55.7, 40.5, 38.1, 29.1, 22.7.

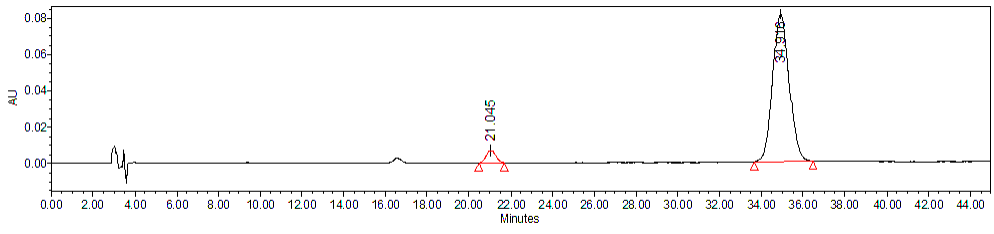
IR: 3437, 2939, 2865, 1715, 1592, 1485, 1461, 1360, 1288, 1247, 1183, 1095, 1025, 954, 902, 812, 683, 618, 523 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}{}^{78.9183}BrO_3^+$ 299.0277; Found 299.0281;

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}{}^{80.9163}BrO_3^+$ 301.0257; Found 301.0262.

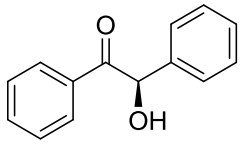


	Retention Time	Area	% Area
1	21.161	18206510	50.02
2	35.114	18191892	49.98



	Retention Time	Area	% Area
1	21.045	220502	4.66
2	34.916	4513960	95.34

(*R*)-2-Hydroxy-1,2-diphenylethan-1-one (4a)



4a

White solid; mp: 133−135 °C; 11.5 mg, 54% yield, 82% ee. $[\alpha]_D^{26}$ = −129.8 (*c* 0.25 in MeOH). lit: $[\alpha]_D^{25}$ = −150.1 (*c* 0.56 in MeOH) for (*R*), 99% ee.[5]

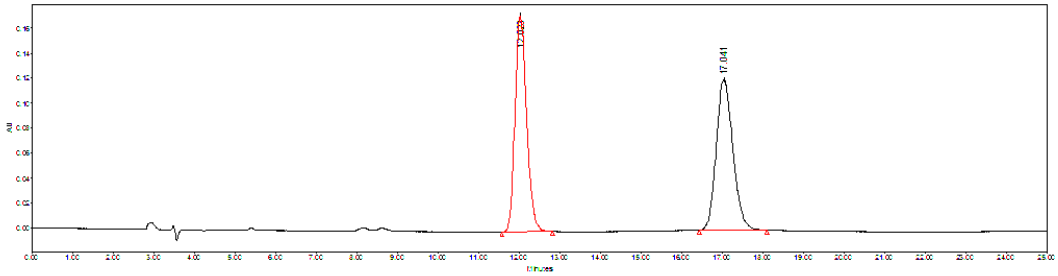
HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 11.73 min, t_R (major) = 16.95 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.54 – 7.50 (m, 1H), 7.42 – 7.27 (m, 7H), 5.96 (d, 1H, *J* = 6.0 Hz), 4.56 (d, 1H, *J* = 6.0 Hz);

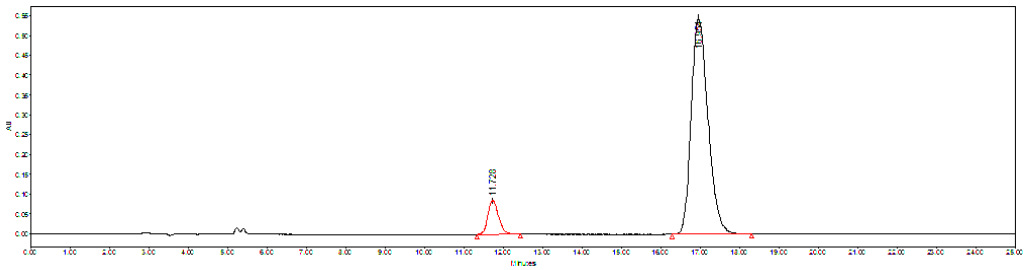
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.9, 139.0, 133.9, 133.4, 129.1, 129.1, 128.7, 128.6, 127.7, 78.2.

IR: 3413, 3061, 2925, 2854, 1676, 1596, 1490, 1449, 1390, 1335, 1258, 1207, 1180, 1094, 1067, 1029, 1002, 975, 926, 854, 833, 753, 697, 601, 511 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}O_2^+$ 213.0910; Found 213.0906.

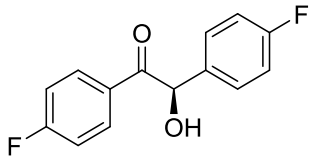


	Retention Time	Area	% Area
1	12.023	3429799	49.88
2	17.041	3446166	50.12



	Retention Time	Area	% Area
1	11.728	1620017	9.09
2	16.954	16203285	90.91

(*R*)-1,2-Bis(4-fluorophenyl)-2-hydroxyethan-1-one (4b)



4b

White solid; mp: 64−68 °C; 12.1 mg, 49% yield, 80% ee. $[\alpha]_D^{26}$ = −111.2 (*c* 0.26 in $CHCl_3$). lit: $[\alpha]_D^{25}$ = −128.2 (*c* 0.24 in $CHCl_3$) for (*R*), 99% ee.[5]

HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 9.63 min, t_R (major) = 10.14 min.

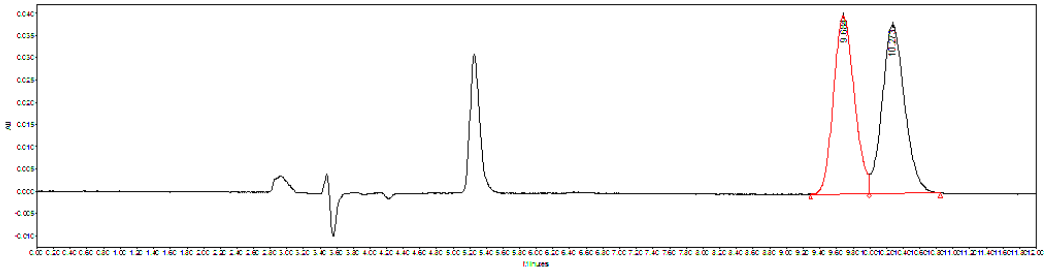
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.32 – 7.27 (m, 2H), 7.11 – 7.07 (m, 2H), 7.04 – 7.01 (m, 2H), 5.90 (d, 1H, *J* = 6.0 Hz), 4.50 (d, 1H, *J* = 6.0 Hz);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.2, 166.1 (d, $J_{C\text{-}F}$ = 256.0 Hz), 162.8 (d, $J_{C\text{-}F}$ = 246.0 Hz), 134.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 131.9 (d, $J_{C\text{-}F}$ = 9.0 Hz), 129.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 116.3 (d, $J_{C\text{-}F}$ = 16.0 Hz), 116.0 (d, $J_{C\text{-}F}$ = 16.0 Hz), 75.3;

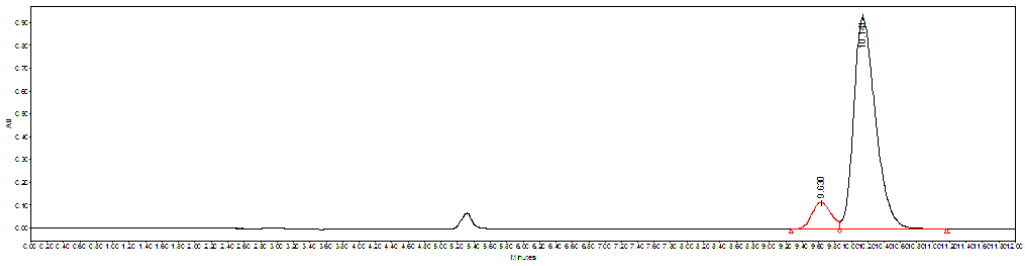
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −102.6 (s, 1F), −112.6 (s, 1F).

IR: 3442, 2924, 1680, 1597, 1507, 1411, 1230, 1184, 1157, 1077, 1014, 976, 834, 800, 657, 605, 566, 515 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}F_2O_2^+$ 249.0722; Found 249.0724.

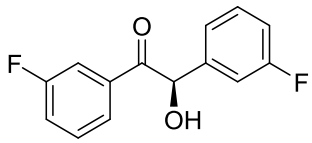


	Retention Time	Area	% Area
1	9.684	699161	49.49
2	10.273	713564	50.51



	Retention Time	Area	% Area
1	9.630	1900061	9.99
2	10.141	17125147	90.01

(*R*)-1,2-Bis(3-fluorophenyl)-2-hydroxyethan-1-one (4c)



4c

White solid; mp: 49─55 °C; 6.5 mg, 26% yield, 74% ee. $[\alpha]_D^{26}$ = –70.8 (*c* 0.18 in $CHCl_3$). lit: $[\alpha]_D^{20}$ = –38.2 (*c* 2.5 in $CHCl_3$) for (*R*), 97% ee.[5]

HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 9.41 min, t_R (major) = 11.69 min.

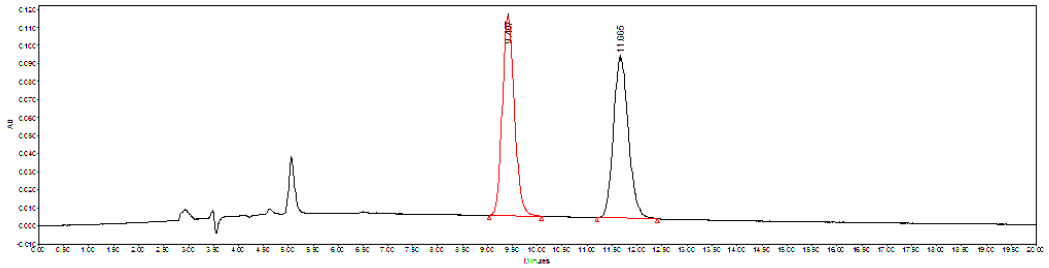
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 1H), 7.62 – 7.58 (m, 1H), 7.43 – 7.38 (m, 1H), 7.34 – 7.23 (m, 2H), 7.13 – 7.11 (m, 1H), 7.04 – 6.97 (m, 2H), 5.90 (d, 1H, *J* = 6.0 Hz), 4.45 (d, 1H, *J* = 6.0 Hz);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.4, 164.1 (d, $J_{C\text{-}F}$ = 38.0 Hz), 161.6 (d, $J_{C\text{-}F}$ = 40.0), 140.8 (d, $J_{C\text{-}F}$ = 7.0 Hz), 135.3 (d, $J_{C\text{-}F}$ = 6.0 Hz), 130.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 130.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 124.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 123.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 121.2 (d, $J_{C\text{-}F}$ = 21.0 Hz), 75.8;

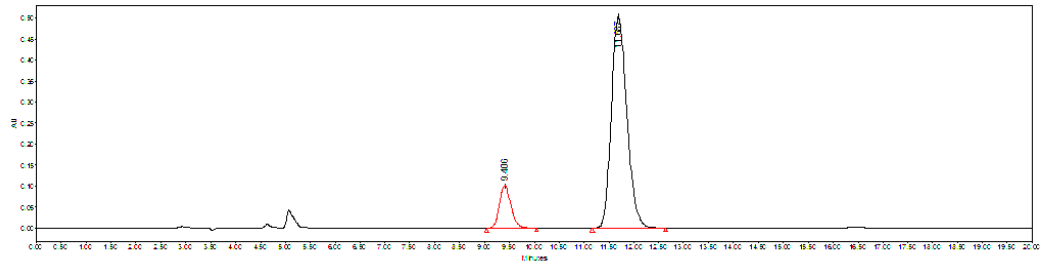
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –110.7 (s, 1F), –111.3 (s, 1F).

IR: 3445, 3076, 2925, 2362, 1688, 1589, 1486, 1265, 1172, 1136, 1083, 1015, 952, 885, 824, 785, 701, 521 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}F_2O_2^+$ 249.0722; Found 249.0719.

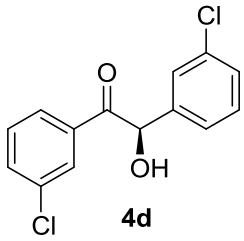


	Retention Time	Area	% Area
1	9.407	1862049	50.06
2	11.665	1857813	49.94



	Retention Time	Area	% Area
1	9.406	1636624	13.03
2	11.687	10919557	86.97

(*R*)-1,2-Bis(3-chlorophenyl)-2-hydroxyethan-1-one (4d)



4d

White solid; mp: 83–87 °C; 3.1 mg, 11% yield, 81% ee. $[\alpha]_D^{26}$ = –17.2 (*c* 0.37 in $CHCl_3$). lit: $[\alpha]_D^{20}$ = –31.0 (*c* 1.2 in $CHCl_3$) for (*R*), >99% ee.[5]

HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 10.02 min, t_R (major) = 13.18 min.

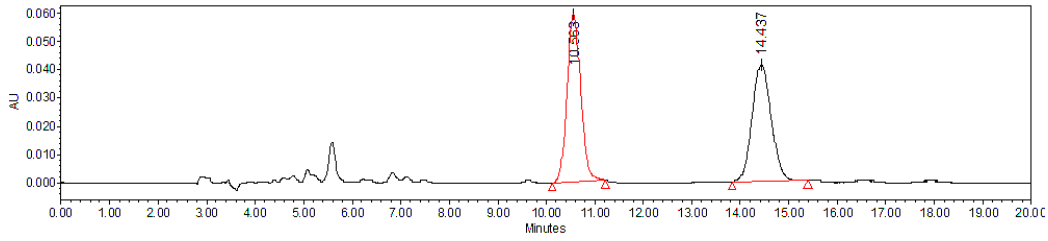
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.90 (m, 1H), 7.75 – 7.72 (m, 1H), 7.54 – 7.51 (m, 1H), 7.39 – 7.35 (m, 3H), 7.28 – 7.27 (m, 2H), 5.87 (d, 1H, *J* = 6.0 Hz), 4.43 (d, 1H, *J* = 6.4 Hz);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.8, 140.8, 135.2, 134.1, 130.5, 130.1, 129.1, 129.0, 127.8, 127.5, 127.1, 125.9, 125.4, 75.7.

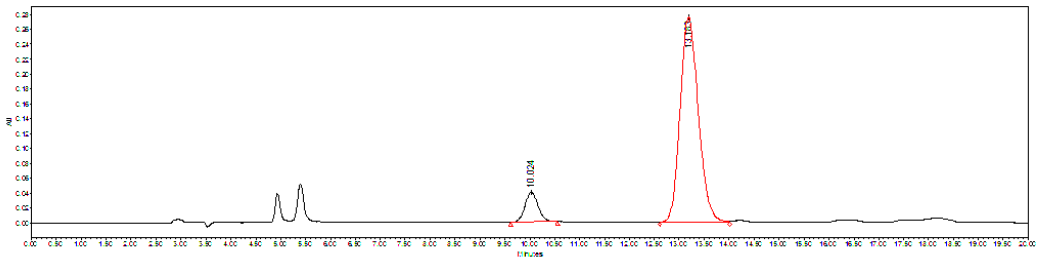
IR: 3445, 3069, 2925, 2855, 2361, 1726, 1688, 1571, 1474, 1423, 1257, 1183, 1079, 1002, 978, 893, 789, 745, 698, 479, 439 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{10}{}^{34.9689}Cl_2NaO_2^+$ 302.9950; Found 302.9953;

HRMS (FTMS+c ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{10}{}^{36.9659}Cl_2NaO_2^+$ 304.9921; Found 304.9927.

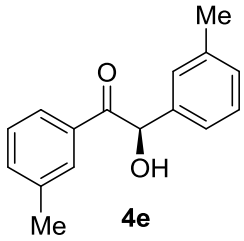


	Retention Time	Area	% Area
1	10.563	1158088	50.80
2	14.437	1121547	49.20



	Retention Time	Area	% Area
1	10.024	722363	9.35
2	13.183	7006025	90.65

(*R*)-2-Hydroxy-1,2-di-*m*-tolylethan-1-one (4e)



4e

White solid; mp: 62–67 °C; 5.7 mg, 24% yield, 86% ee. $[\alpha]_D^{26}$ = –48.4 (*c* 0.26 in MeOH). lit: $[\alpha]_D^{25}$ = –127.8 (*c* 1.0 in MeOH) for (*R*), 95% ee.[5]

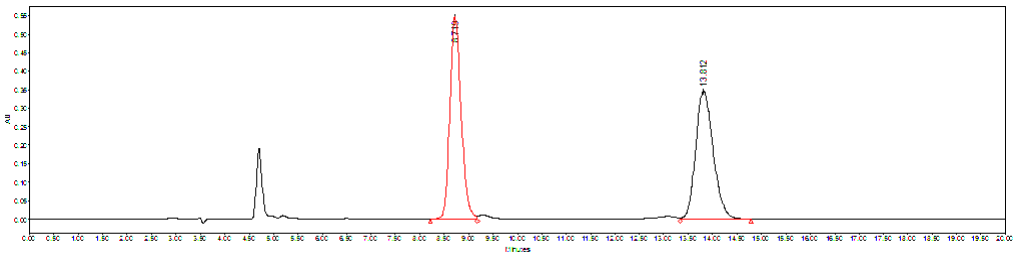
HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 8.76 min, t_R (major) = 13.80 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.70 – 7.68 (m, 1H), 7.34 – 7.32 (m, 1H), 7.29 – 7.25 (m, 1H), 7.22 – 7.18 (m, 1H), 7.14 – 7.12 (m, 2H), 7.08 – 7.06 (m, 1H), 5.90 (d, 1H, *J* = 6.0 Hz), 4.52 (d, 1H, *J* = 6.0 Hz), 2.35 (s, 3H), 2.30 (s, 3H);

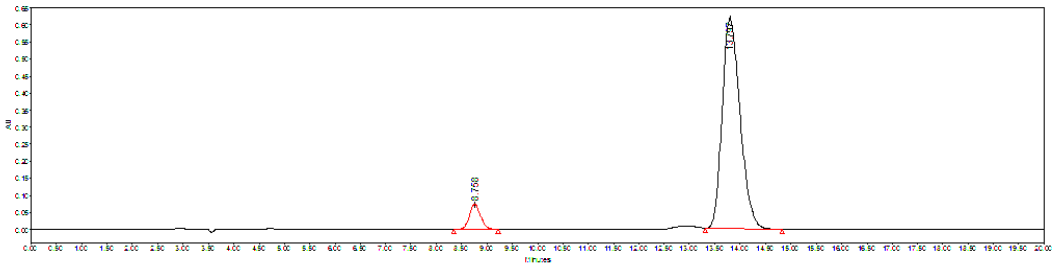
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.1, 139.0, 138.9, 138.6, 134.7, 133.5, 129.6, 129.3, 128.9, 128.5, 128.2, 126.4, 124.9, 76.2, 21.4, 21.3.

IR: 3454, 2923, 2856, 2361, 1675, 1603, 1454, 1277, 1250, 1155, 1080, 1028, 981, 942, 746, 705, 649, 616, 444 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}O_2^+$ 241.1223; Found 241.1221.

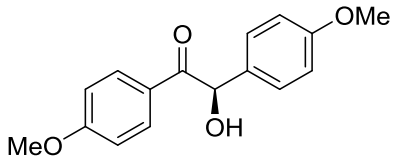


	Retention Time	Area	% Area
1	8.719	8698871	50.20
2	13.812	8628045	49.80



	Retention Time	Area	% Area
1	8.758	1138197	6.95
2	13.797	15234917	93.05

(*R*)-2-Hydroxy-1,2-bis(4-methoxyphenyl)ethan-1-one (4f)



4f

White solid; mp: 106–112 °C; 10.7 mg, 39% yield, 85% ee. $[\alpha]_D^{25}$ = –95.2 (*c* 0.19 in $CHCl_3$). lit: $[\alpha]_D^{25}$ = –43.8 (*c* 0.05 in $CHCl_3$) for (*R*), 99% ee.[5]

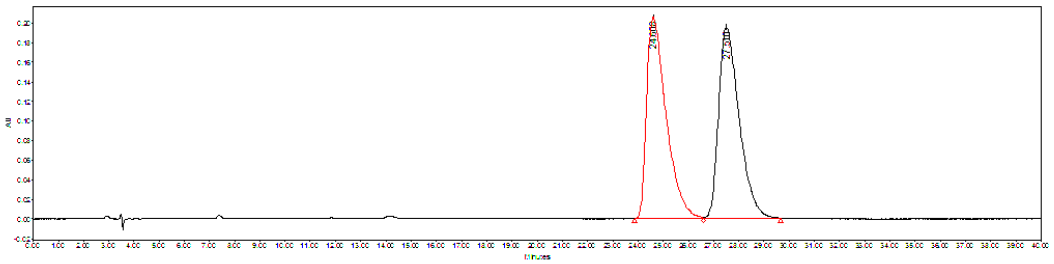
HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 24.96 min, t_R (major) = 27.28 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 2H), 7.26 – 7.23 (m, 2H), 6.88 – 6.82 (m, 4H), 5.84 (d, 1H, *J* = 6.0 Hz), 4.57 (d, 1H, *J* = 6.0 Hz), 3.82 (s, 3H), 3.75 (s, 3H);

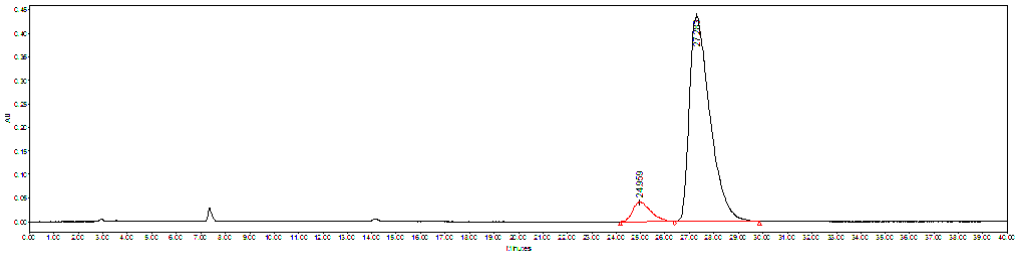
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.3, 164.0, 159.6, 131.8, 131.5, 129.0, 126.3, 114.5, 113.9, 75.2, 55.5, 55.2.

IR: 3447, 3007, 2956, 2935, 2839, 1669, 1600, 1511, 1462, 1442, 1422, 1308, 1256, 1172, 1114, 1076, 1030, 975, 867, 831, 793, 576, 533 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}O_4^+$ 273.1121; Found 273.1115.

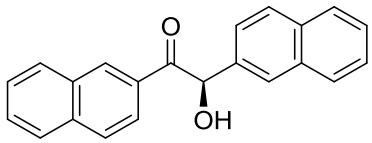


	Retention Time	Area	% Area
1	24.608	11092825	49.98
2	27.510	11100742	50.02



	Retention Time	Area	% Area
1	24.959	2077812	7.55
2	27.283	25459197	92.45

(*R*)-2-Hydroxy-1,2-di(naphthalen-2-yl)ethan-1-one (4g)



4g

White solid; mp: 122−125 °C; 13.1 mg, 42% yield, 88% ee. $[\alpha]_D^{26}$ = +39.4 (*c* 0.35 in MeOH). lit: $[\alpha]_D^{25}$ = +52.4 (*c* 0.37 in MeOH) for (*R*), 93% ee.[5]

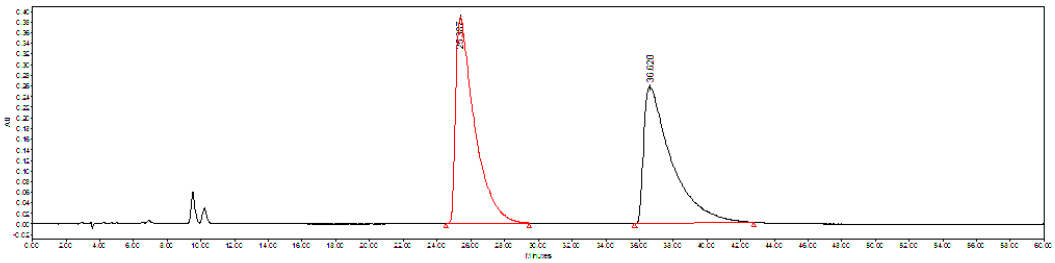
HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 26.12 min, t_R (major) = 35.32 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (m, 1H), 8.00 – 7.98 (m, 1H), 7.91(m, 1H),7.87 – 7.85 (m, 1H), 7.81 – 7.73 (m, 5H), 7.57 – 7.42 (m, 5H), 6.27 (d, 1H, *J* = 6.0 Hz), 4.72 (d, 1H, *J* = 6.4 Hz);

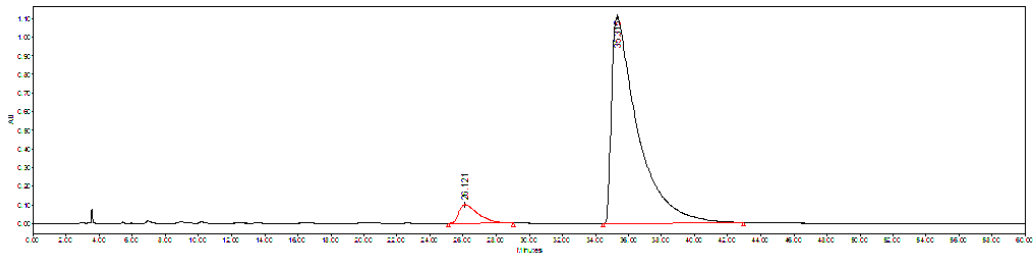
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.9, 136.6, 135.8, 133.4, 133.2, 132.2, 131.4, 130.8, 129.7, 129.1, 129.0, 128.6, 128.0, 127.7, 127.7, 127.5, 127.0, 126.5, 126.4, 124.8, 124.2, 76.4.

IR: 3443, 3056, 2923, 2854, 2361, 1673, 1626, 1597, 1465, 1354, 1275, 1230, 1184, 1124, 1074, 1015, 981, 942, 899, 861, 808, 742, 687, 590, 558, 476 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}O_2^+$ 313.1223; Found 313.1220.

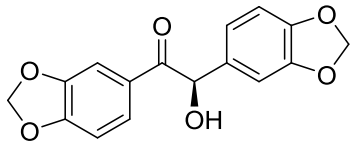


	Retention Time	Area	% Area
1	25.387	30258460	50.53
2	36.620	29624305	49.47



	Retention Time	Area	% Area
1	26.121	7942245	6.14
2	35.315	121427116	93.86

(*R*)-1,2-Bis{benzo[d][1,3]dioxol-5-yl}-2-hydroxyethan-1-one (4h)



4h

White solid; mp: 117−121 °C; 15.8 mg, 53% yield, 85% ee. $[\alpha]_D^{12}$ = −77.1 (*c* 0.62 in CH_2Cl_2).

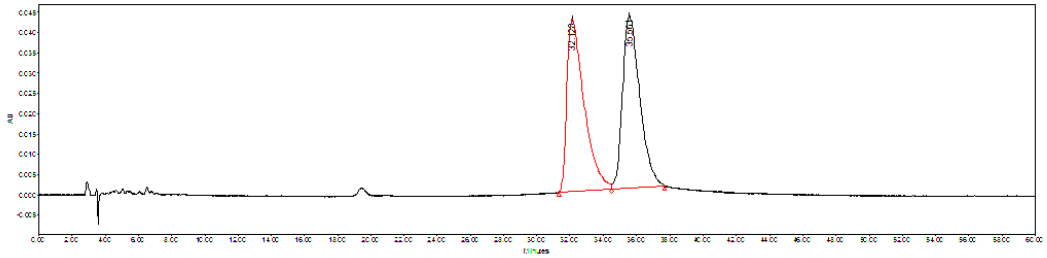
HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 32.42 min, t_R (major) = 35.04 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 1H), 7.39 – 7.39 (m, 1H), 6.84 – 6.73 (m, 4H), 6.01 (s, 2H), 5.93 – 5.91 (m, 2H), 5.76 (d, 1H, *J* = 6.0 Hz), 4.51 (d, 1H, *J* = 6.4 Hz);

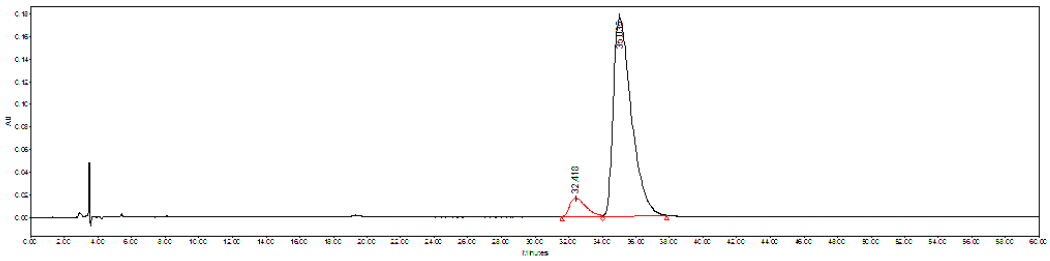
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.7, 152.4, 148.2, 148.2, 147.8, 133.3, 127.9, 125.9, 121.7, 108.7, 108.7, 108.1, 107.7, 102.0, 101.2, 75.5.

IR: 3445, 2918, 2361, 1669, 1605, 1487, 1442, 1354, 1251, 1100, 1035, 987, 928, 895, 801, 733, 699, 646, 577, 525 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}O_6^+$ 301.0707; Found 301.0703.

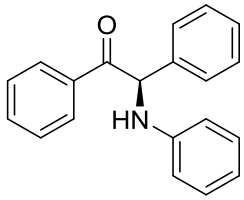


	Retention Time	Area	% Area
1	32.128	3066626	49.94
2	35.561	3074541	50.06



	Retention Time	Area	% Area
1	32.418	1086516	7.64
2	35.035	13137259	92.36

(*R*)-1,2-Diphenyl-2-(phenylamino)ethan-1-one (6a)



6a

Yellow solid; mp: 90−96 °C; 28.7 mg, 99% yield, 68% ee. $[\alpha]_D^{11}$ = –34.4 (*c* 0.57 in CH_2Cl_2). lit: $[\alpha]_D^{20}$ = +132.1 (*c* 1.0 in CH_2Cl_2) for (*S*), 97% ee.[2]

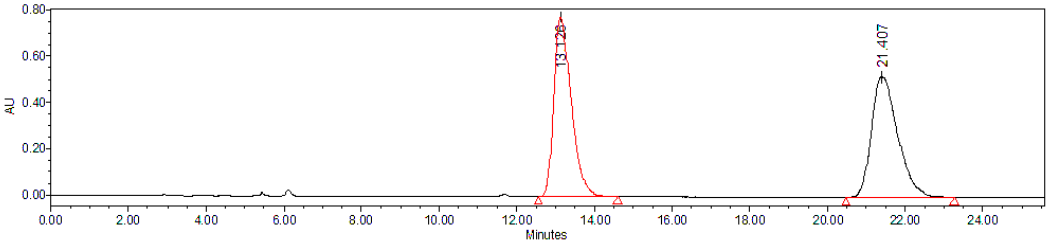
HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 13.12 min, t_R (minor) = 21.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 2H), 7.54 – 7.50 (m, 1H), 7.45 – 7.40 (m, 4H), 7.29 – 7.24 (m, 2H), 7.21 – 7.17 (m, 1H), 7.15 – 7.10 (m, 2H), 6.70 – 6.66 (m, 3H), 6.02 (s, 1H), 5.41 (s, 1H);

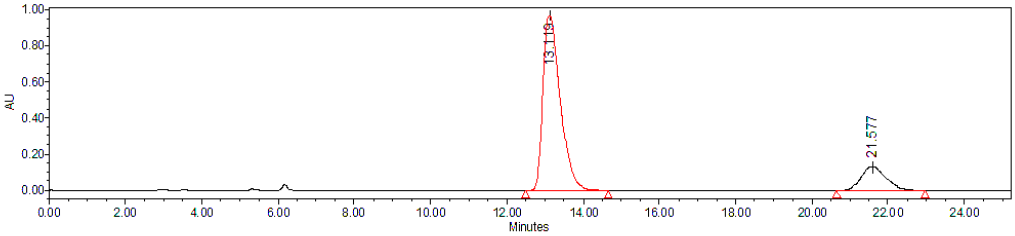
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.0, 146.1, 137.7, 135.0, 133.5, 129.2, 129.0, 128.8, 128.7, 128.1, 128.1, 117.8, 113.5, 62.7.

IR: 3396, 3057, 1676, 1597, 1499, 1447, 1316, 1249, 1174, 1073, 1025, 993, 918, 748, 691, 640, 533, 510 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{18}NO^+$ 288.1383; Found 288.1386.

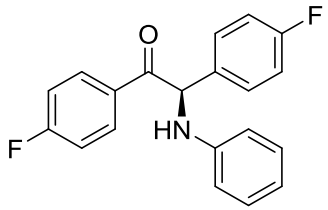


	Retention Time	Area	% Area
1	13.126	24141916	49.88
2	21.407	24255918	50.12



	Retention Time	Area	% Area
1	13.119	30347821	83.96
2	21.577	5797261	16.04

(*R*)-1,2-Bis(4-fluorophenyl)-2-(phenylamino)ethan-1-one (6b)



6b

Yellow solid; mp: 84−92 °C; 32.0 mg, 99% yield, 76% ee. $[\alpha]_D^{11}$ = −75.3 (*c* 0.55 in CH_2Cl_2). lit: $[\alpha]_D^{20}$ = −85.1 (*c* 1.0 in CH_2Cl_2) for (*R*), >99% ee.[2]

HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 15.12 min, t_R (minor) = 42.25 min.

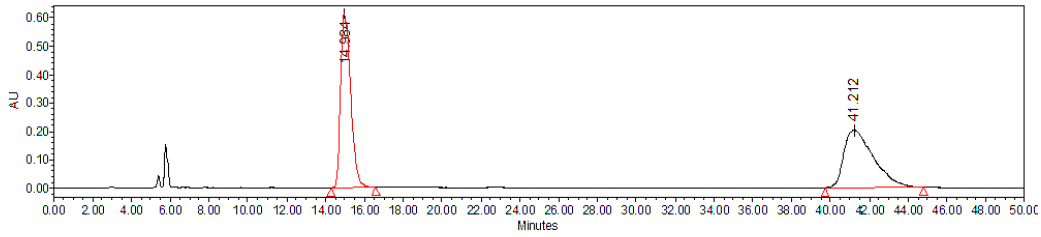
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.42 – 7.37 (m, 2H), 7.16 – 7.08 (m, 4H), 7.00 – 6.94 (m, 2H), 6.72 – 6.68 (m, 1H), 6.65 – 6.62 (m, 2H), 5.96 – 5.95 (m, 1H), 5.36 – 5.35 (m, 1H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.3, 167.2, 164.6, 163.6, 161.2, 145.8, 133.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 131.5 (d, $J_{C\text{-}F}$ = 10.0 Hz), 131.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.3, 118.1, 116.1 (q, $J_{C\text{-}F}$ = 14.0, 22.0 Hz), 113.5, 61.9;

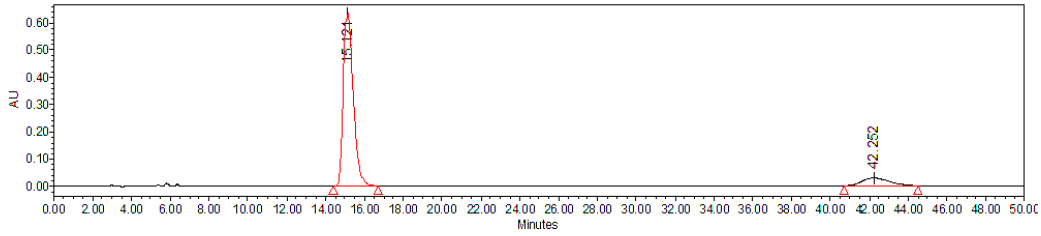
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −103.6 (s, 1F), −113.4 (s, 1F).

IR: 3397, 3052, 2923, 1682, 1596, 1502, 1411, 1310, 1228, 1181, 1155, 1098, 994, 899, 864, 834, 797, 748, 693, 661, 607, 566, 510, 443 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}F_2NO^+$ 324.1194; Found 324.1187.

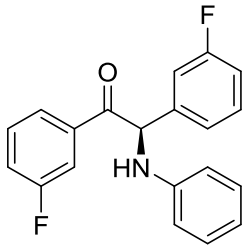


	Retention Time	Area	% Area
1	14.984	21856077	50.17
2	41.212	21704905	49.83



	Retention Time	Area	% Area
1	15.121	22412101	87.97
2	42.252	3064936	12.03

(*R*)-1,2-Bis(3-fluorophenyl)-2-(phenylamino)ethan-1-one (6c)



6c

Oil; 23.5 mg, 73% yield, 66% ee. $[\alpha]_D^{14}$ = +11.3 (*c* 0.49 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 12.68 min, t_R (minor) = 45.97 min.

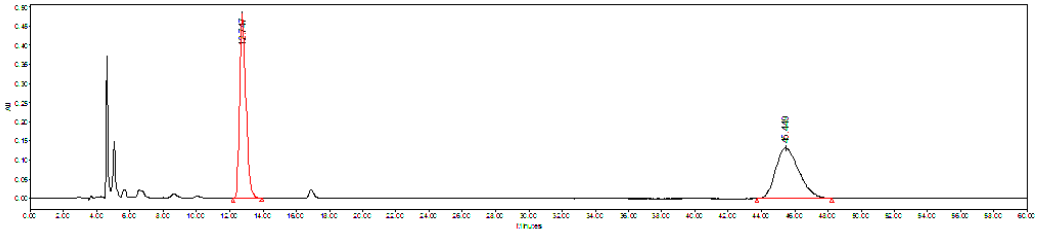
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 1H), 7.66 – 7.62 (m, 1H), 7.46 – 7.41 (m, 1H), 7.29 – 7.21 (m, 3H), 7.17 – 7.11 (m, 3H), 6.94 – 6.89 (m, 1H), 6.74 – 6.69 (m, 1H), 6.68 – 6.64 (m, 2H), 5.96 – 5.95 (m, 1H), 5.37 – 5.36 (m, 1H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.4, 164.2 (d, $J_{C\text{-}F}$ = 35.0 Hz), 161.7 (d, $J_{C\text{-}F}$ = 37.0 Hz), 145.6, 139.9 (d, $J_{C\text{-}F}$ = 6.0 Hz), 136.9 (d, $J_{C\text{-}F}$ = 6.0 Hz), 130.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 130.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.3, 124.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 123.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 120.8 (d, $J_{C\text{-}F}$ = 22.0 Hz), 118.3, 115.7 (d, $J_{C\text{-}F}$ = 23.0 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.9 (d, $J_{C\text{-}F}$ = 230.0 Hz), 113.5, 62.5;

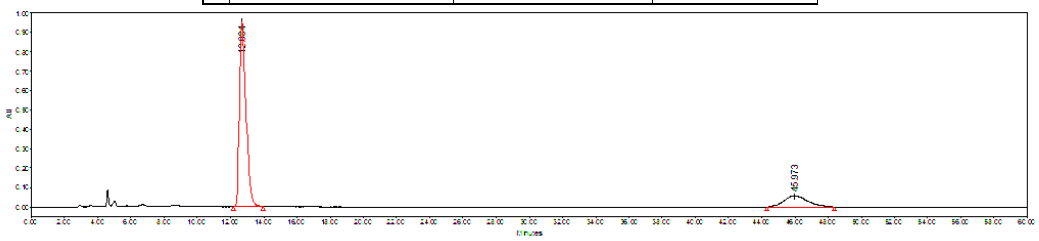
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −110.9 (s, 1F), −113.3 (s, 1F).

IR: 3302, 3070, 2923, 1674, 1585, 1538, 1485, 1441, 1383, 1251, 1202, 1138, 1074, 1003, 889, 831, 788, 753, 691, 648, 519 cm^{-}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}F_2NO^+$ 324.1194; Found 324.1186.

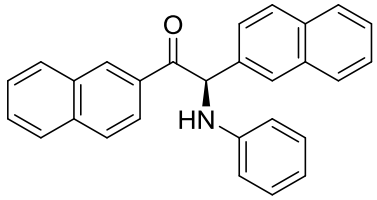


	Retention Time	Area	% Area
1	12.747	12779853	49.91
2	45.449	12824394	50.09



	Retention Time	Area	% Area
1	12.684	26096001	82.99
2	45.973	5350425	17.01

(*R*)-1,2-Di(naphthalen-2-yl)-2-(phenylamino)ethan-1-one (6d)



6d

Yellow solid; mp: 186–190 °C; 30.3 mg, 78% yield, 98% ee. $[\alpha]_D^{16}$ = +55.9 (*c* 0.72 in CH_2Cl_2).

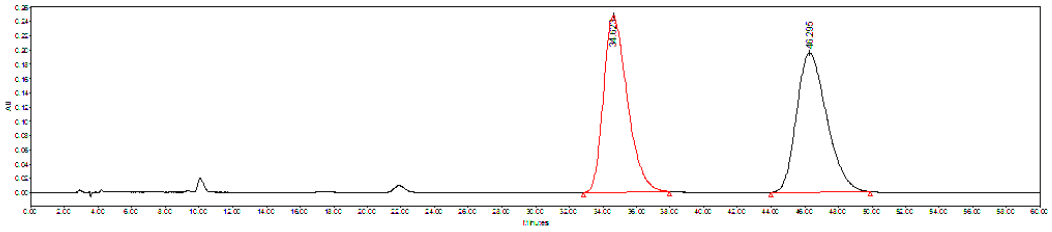
HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 34.25 min, t_R (minor) = 47.36 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (m, 1H), 8.05 – 8.02 (m, 1H), 7.98 (m, 1H), 7.93 – 7.91 (m, 1H), 7.83 – 7.68 (m, 5H), 7.61 – 7.58 (m, 1H), 7.57 – 7.48 (m, 2H), 7.42 – 7.36 (m, 2H), 7.15 – 7.11 (m, 2H), 6.77 – 6.74 (m, 2H), 6.70 – 6.66 (m, 1H), 6.35 – 6.34 (m, 1H), 5.58 – 5.57 (m, 1H);

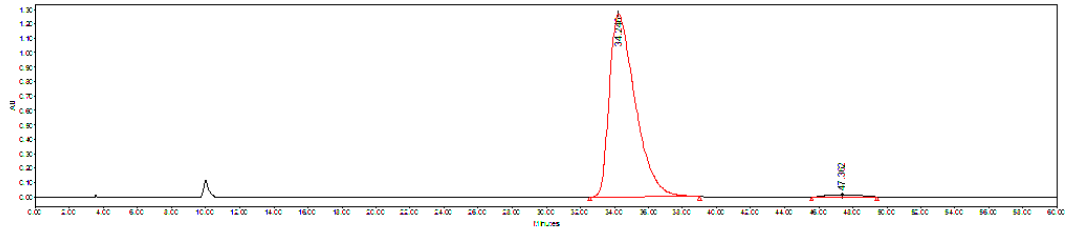
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.9, 146.1, 135.7, 135.3, 133.4, 133.0, 132.4, 132.3, 130.7, 129.6, 129.2, 129.0, 128.8, 128.6, 127.9, 127.7, 127.6, 126.9, 126.3, 125.4, 124.3, 117.9, 113.6, 62.9.

IR: 3395, 3053, 2923, 2361, 1676, 1625, 1600, 1504, 1468, 1429, 1358, 1123, 1027, 991, 951, 897, 862, 797, 745, 692, 657, 564, 510, 477 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{22}NO^+$ 388.1690; Found 388.1697.

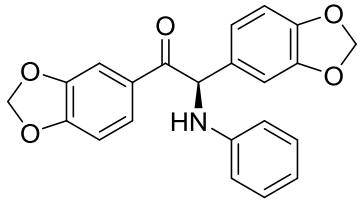


	Retention Time	Area	% Area
1	34.623	24474198	49.96
2	46.295	24512088	50.04



	Retention Time	Area	% Area
1	34.246	133140816	98.89
2	47.362	1490506	1.11

(*R*)-1,2-Bis{benzo[d][1,3]dioxol-5-yl}-2-(phenylamino)ethan-1-one (6e)



6e

Yellow solid; mp: 131−133 °C; 37.5 mg, 99% yield, 53% ee. $[\alpha]_D^{13}$ = –35.7 (*c* 0.92 in CH_2Cl_2).

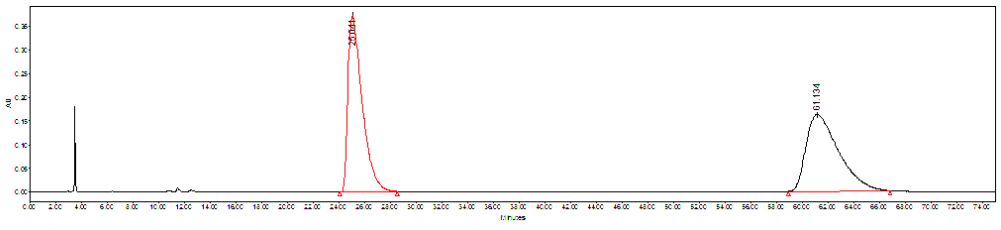
HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 25.46 min, t_R (minor) = 63.34 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 1H), 7.45 – 7.44 (m, 1H), 7.25 – 7.11 (m, 2H), 6.94 – 6.92 (m, 1H), 6.88 – 6.87 (m, 1H), 6.72 – 6.64 (m, 4H), 6.02 – 6.01 (m, 2H), 5.88 (s, 2H), 5.84 – 5.83 (m, 2H), 5.34 – 5.33 (m, 1H);

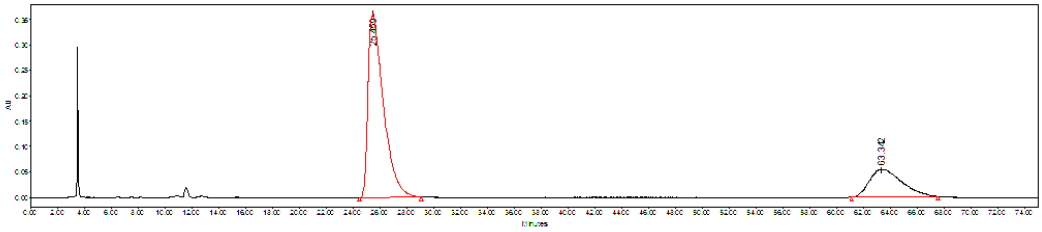
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.8, 152.2, 148.3, 148.2, 147.4, 146.0, 131.8, 129.5, 129.2, 125.2, 121.8, 117.8, 113.5, 108.7, 108.6, 108.0, 107.9, 102.0, 101.2, 61.8.

IR: 3396, 2903, 2362, 1674, 1603, 1500, 1439, 1357, 1318, 1249, 1101, 1037, 998, 929, 869, 813, 749, 696, 505 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NO_5^+$ 376.1179; Found 376.1171.

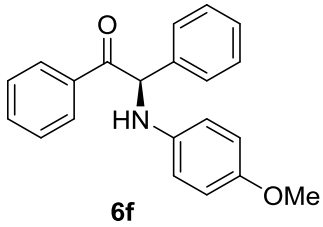


	Retention Time	Area	% Area
1	25.041	28775813	50.28
2	61.134	28451213	49.72



	Retention Time	Area	% Area
1	25.459	28695043	76.25
2	63.342	8937978	23.75

(*R*)-2-[(4-Methoxyphenyl)amino]-1,2-diphenylethan-1-one (6f)



6f

Yellow solid; mp: 83−91 °C; 30.7 mg, 97% yield, 77% ee. $[\alpha]_D^{13}$ = –41.5 (*c* 0.68 in CH_2Cl_2). lit: $[\alpha]_D^{20}$ = –130.7 (*c* 1.0 in CH_2Cl_2) for (*R*), 98% ee.[2]

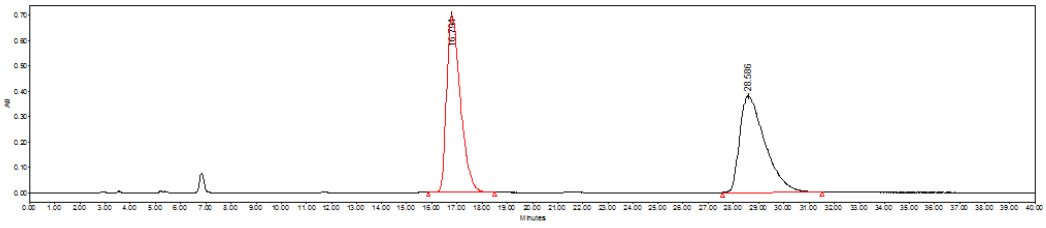
HPLC DAICEL CHIRALCEL ODH 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 17.08 min, t_R (major) = 28.34 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.54 – 7.49 (m, 1H), 7.44 – 7.39 (m, 4H), 7.29 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 6.74 – 6.70 (m, 2H), 6.65 – 6.61 (m, 2H), 5.96 (s, 1H), 5.09 (s, 1H), 3.69 (s, 3H);

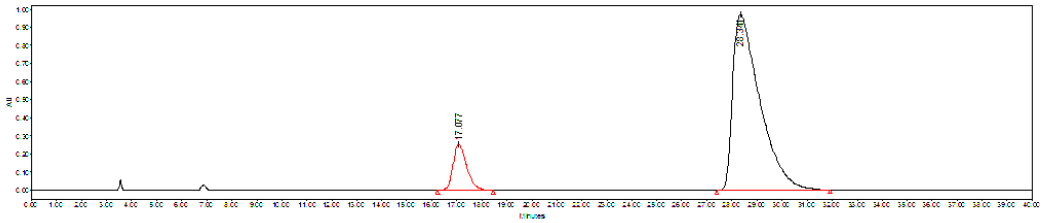
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.4, 152.3, 140.4, 137.9, 135.2, 133.4, 129.0, 128.8, 128.6, 128.1, 128.0, 115.0, 114.8, 63.8, 55.7.

IR: 3390, 3060, 2925, 1677, 1599, 1508, 1448, 1290, 1238, 1175, 1109, 1072, 1031, 932, 899, 823, 759, 695, 646, 612, 534 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}NO_2^+$ 318.1489; Found 318.1482.

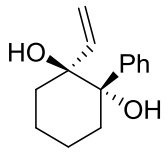


	Retention Time	Area	% Area
1	16.794	26656435	50.02
2	28.586	26640301	49.98



	Retention Time	Area	% Area
1	17.077	9444389	11.46
2	28.341	72949343	88.54

(1*S*,2*S*)-1-Phenyl-2-vinylcyclohexane-1,2-diol (7)



7

Colorless oil; 16.0 mg, 73% yield, >19:1 dr, 90% ee. $[\alpha]_D^{12}$ = –37.6 (*c* 0.76 in CH_2Cl_2).

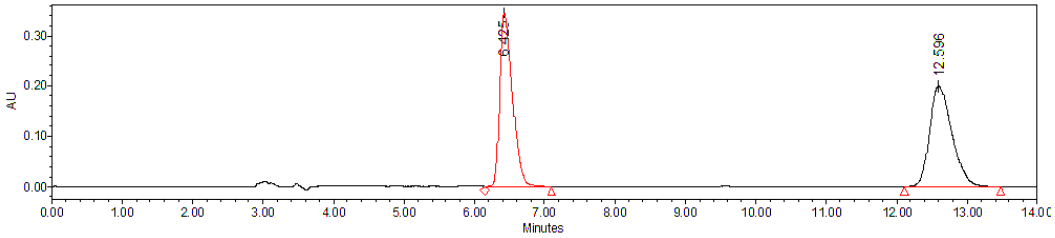
HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (minor) = 6.48 min, t_R (major) = 12.47 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.41 – 7.23 (m, 3H), 6. 18– 6.11 (m, 1H), 4.95 – 4.88 (m, 2H), 2.68 – 2.58 (m, 1H), 2.14 – 2.04 (m, 1H), 1.89 – 1.52 (m, 7H), 1.33 – 1.32 (m, 1H);

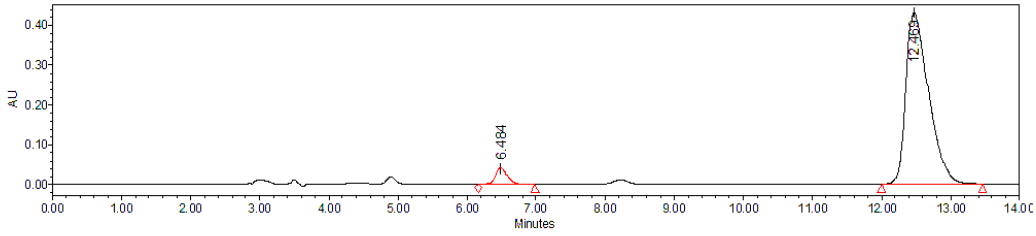
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.3, 142.7, 127.6, 127.2, 126.7, 113.1, 76.6, 75.3, 34.1, 33.6, 20.7, 20.6.

IR: 3453, 3059, 2926, 2861, 2361, 1712, 1638, 1492, 1443, 1354, 1188, 1158, 1091, 1067, 999, 918, 893, 858, 799, 752, 700, 661, 588, 455 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{19}O_2^+$ 219.1380; Found 219.1378.

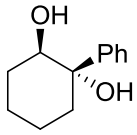


	Retention Time	Area	% Area
1	6.425	4342908	49.52
2	12.596	4426619	50.48



	Retention Time	Area	% Area
1	6.484	493712	4.76
2	12.469	9885768	95.24

(1*S*,2*R*)-1-Phenylcyclohexane-1,2-diol (8)



8

White solid; mp: 88–93 °C; 19.0 mg, 9:1 dr, 99% yield, 9:1 dr, 90% ee. $[\alpha]_D^{27}$ = –50.4 (*c* 0.26 in $CHCl_3$). lit: $[\alpha]_D^{25}$ = –27.8 (*c* 0.18 in $CHCl_3$) for (1*S*,2*R*), 96% ee.[4]

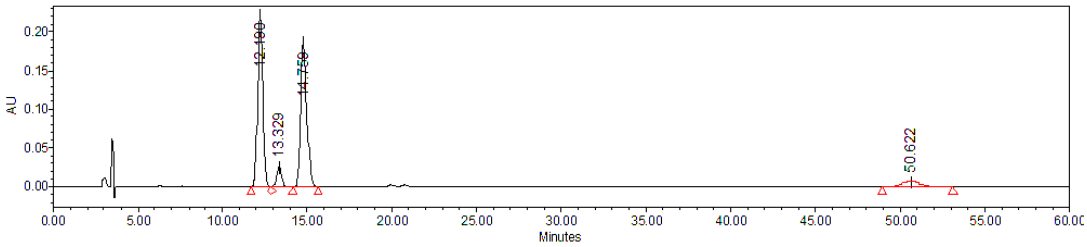
HPLC DAICEL CHIRALCEL IG 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm, t_R (minor) = 12.25 min, t_R (major)= 14.64 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H), 7.40 – 7.36 (m, 2H), 7.32 – 7.27 (m, 1H), 4.00 – 3.75 (m, 1H), 2.61 – 2.40 (m, 1H), 2.08 – 1.91 (m, 1H), 1.86 – 1.74 (m, 2H), 1.72 (s, 1H), 1.70 – 1.63 (m, 3H), 1.54 – 1.46 (m, 1H), 1.33 – 1.26 (m, 1H);

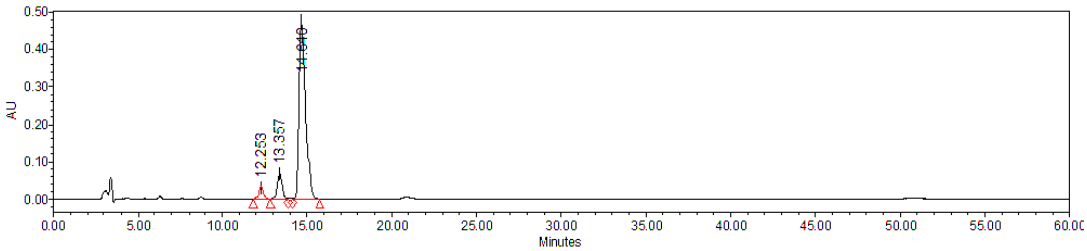
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.9, 128.5, 128.4, 127.6, 127.0, 126.0, 125.1, 74.6, 74.5, 73.2, 38.5, 31.4, 29.2, 28.4, 24.3, 21.1, 21.0, 19.2.

IR: 3395, 3059, 2926, 2860, 2361, 1602, 1493, 1444, 1355, 1238, 1211, 1152, 1116, 1040, 1001, 916, 886, 835, 760, 699, 659, 596, 563 cm^{-1}.

HRMS (FTMS+c ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{17}O_2^+$ 193.1223; Found 193.1221.



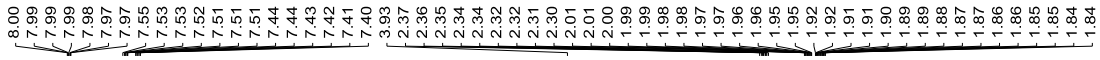
	Retention Time	Area	% Area
1	12.089	6354873	44.68
2	13.342	717967	5.05
3	14.601	6420550	45.14
4	51.015	730205	5.13

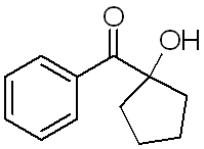


	Retention Time	Area	% Area
1	12.253	652472	4.32
2	13.357	1435768	9.51
3	14.640	13013602	86.17

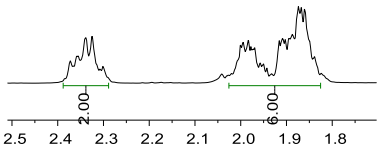
8. Copies of ^{1}H, $^{13}C\{1H\}$, $^{19}F\{1H\}$ NMR Spectra

(1-Hydroxycyclopentyl)(phenyl) methanone (1a)

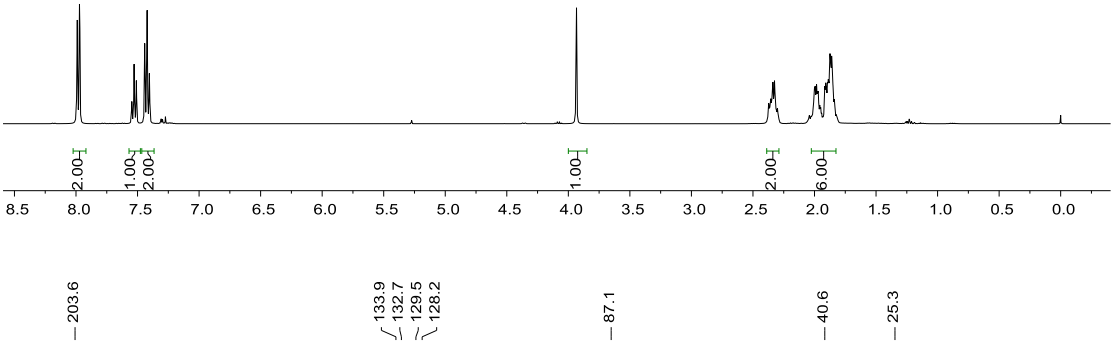




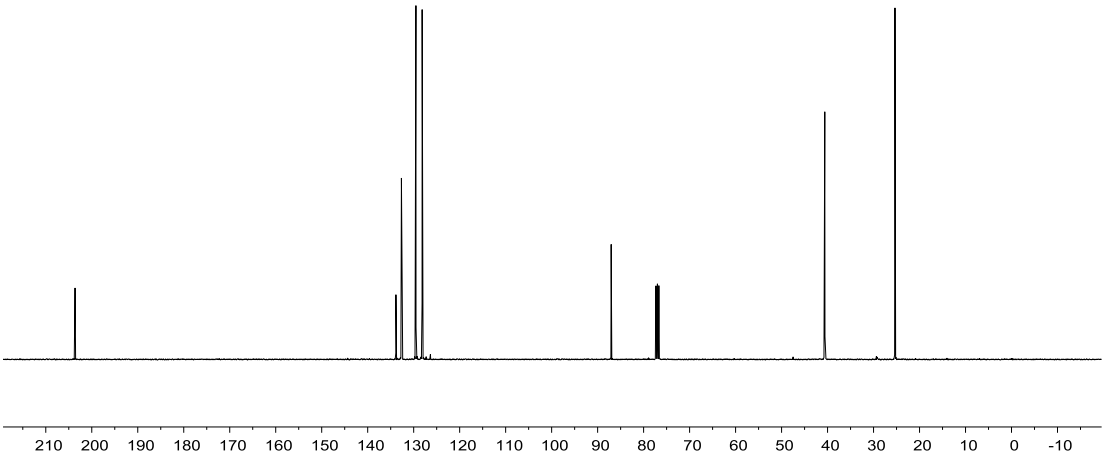
1a



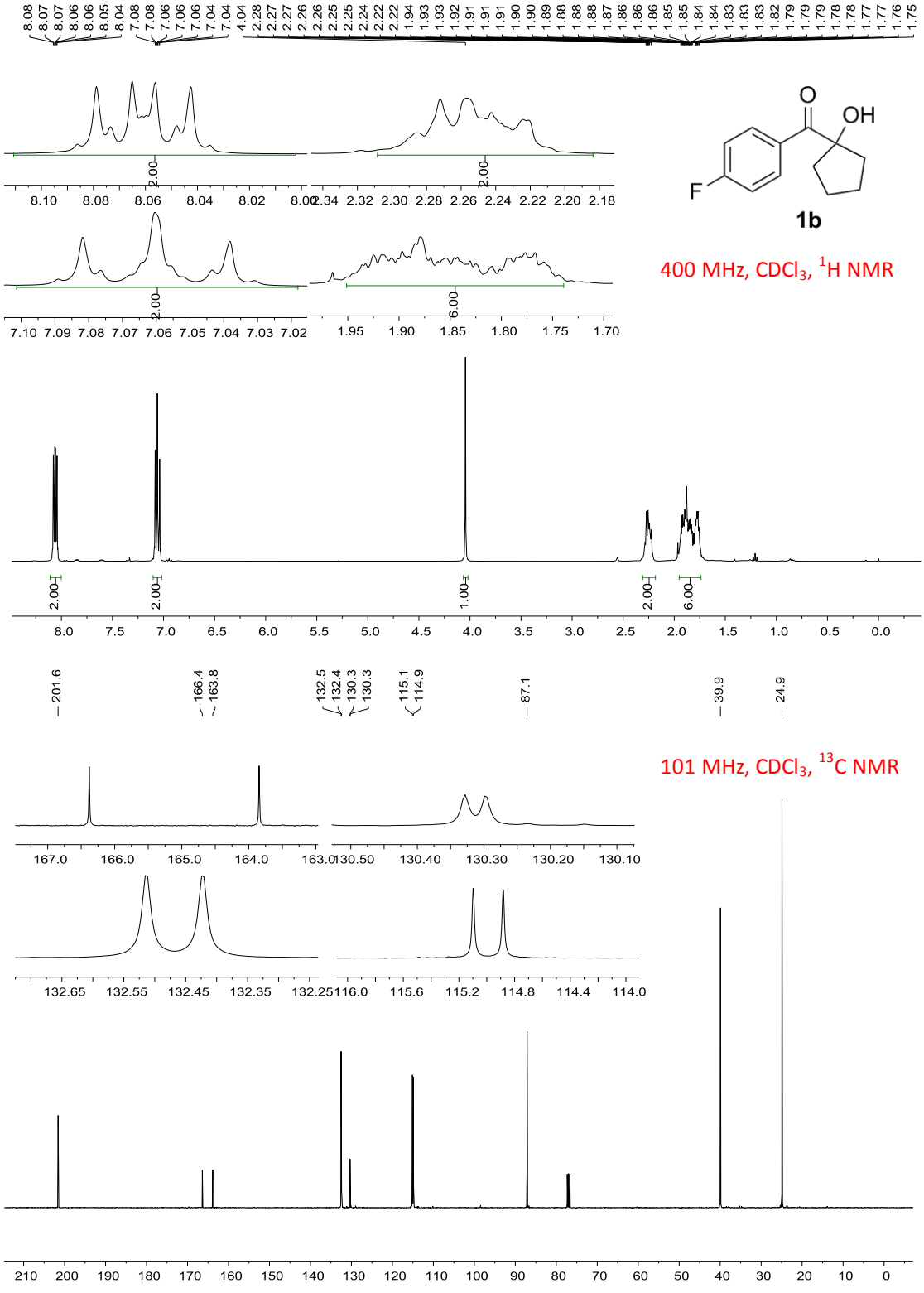
400 MHz, $CDCl_3$, ^{1}H NMR



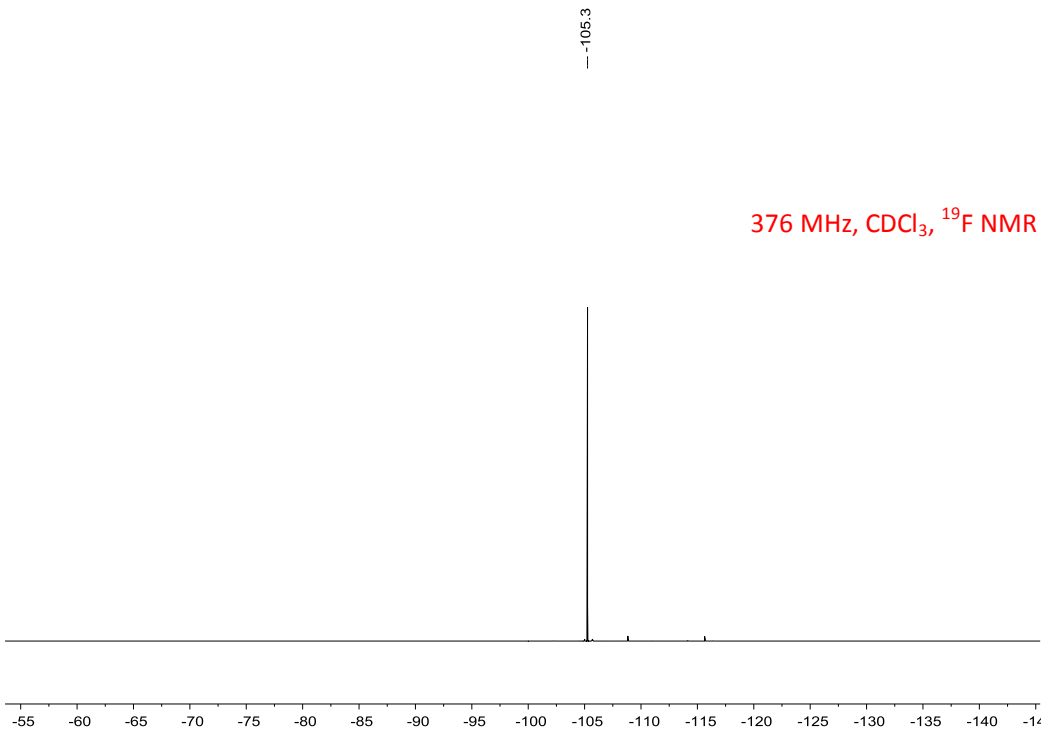
101 MHz, $CDCl_3$, ^{13}C NMR



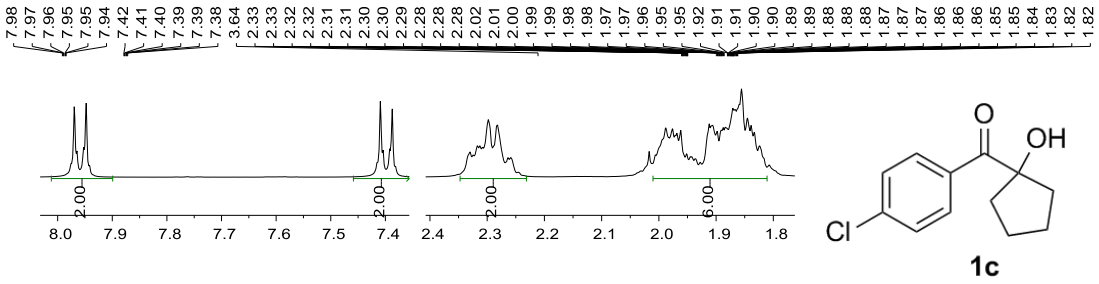
(4-Fluorophenyl)(1-hydroxycyclopentyl)methanone (1b)



376 MHz, $CDCl_3$, ^{19}F NMR

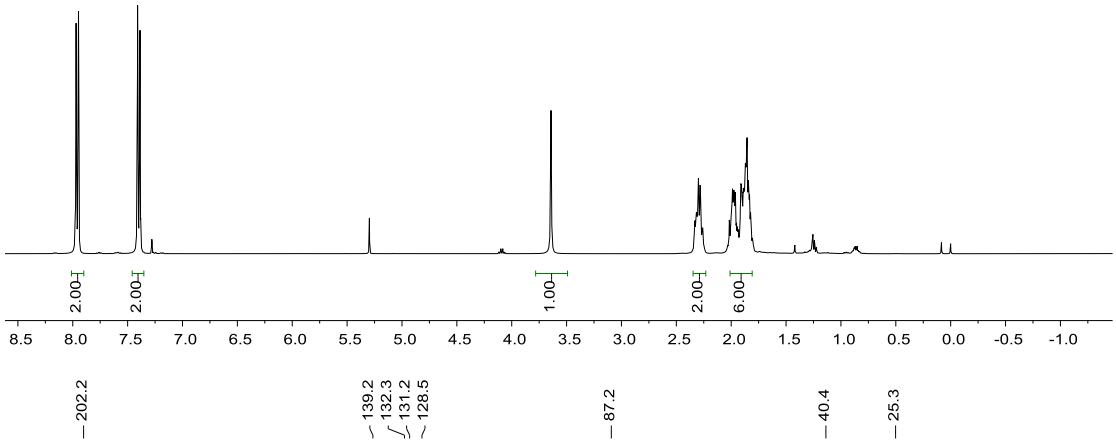


(4-Chlorophenyl)(1hydroxycyclopentyl)methanone (1c)

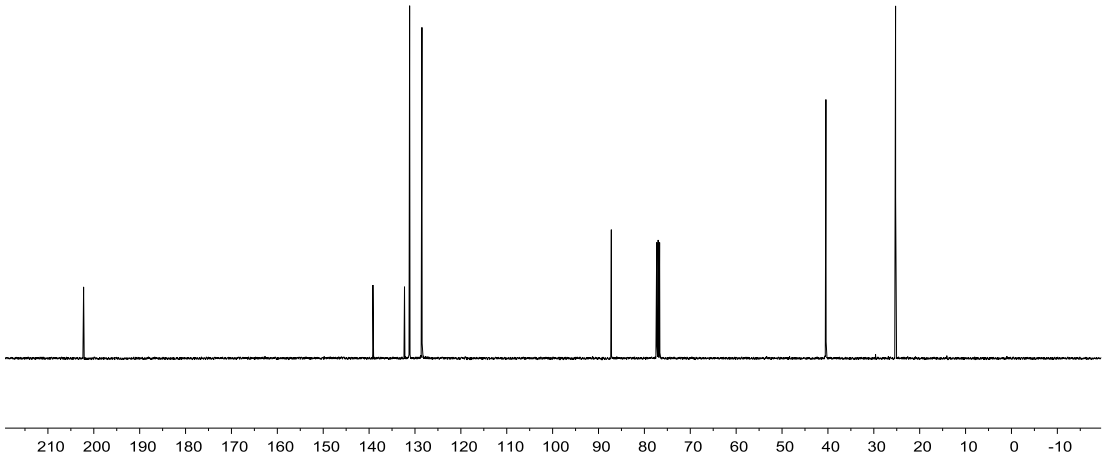


1c

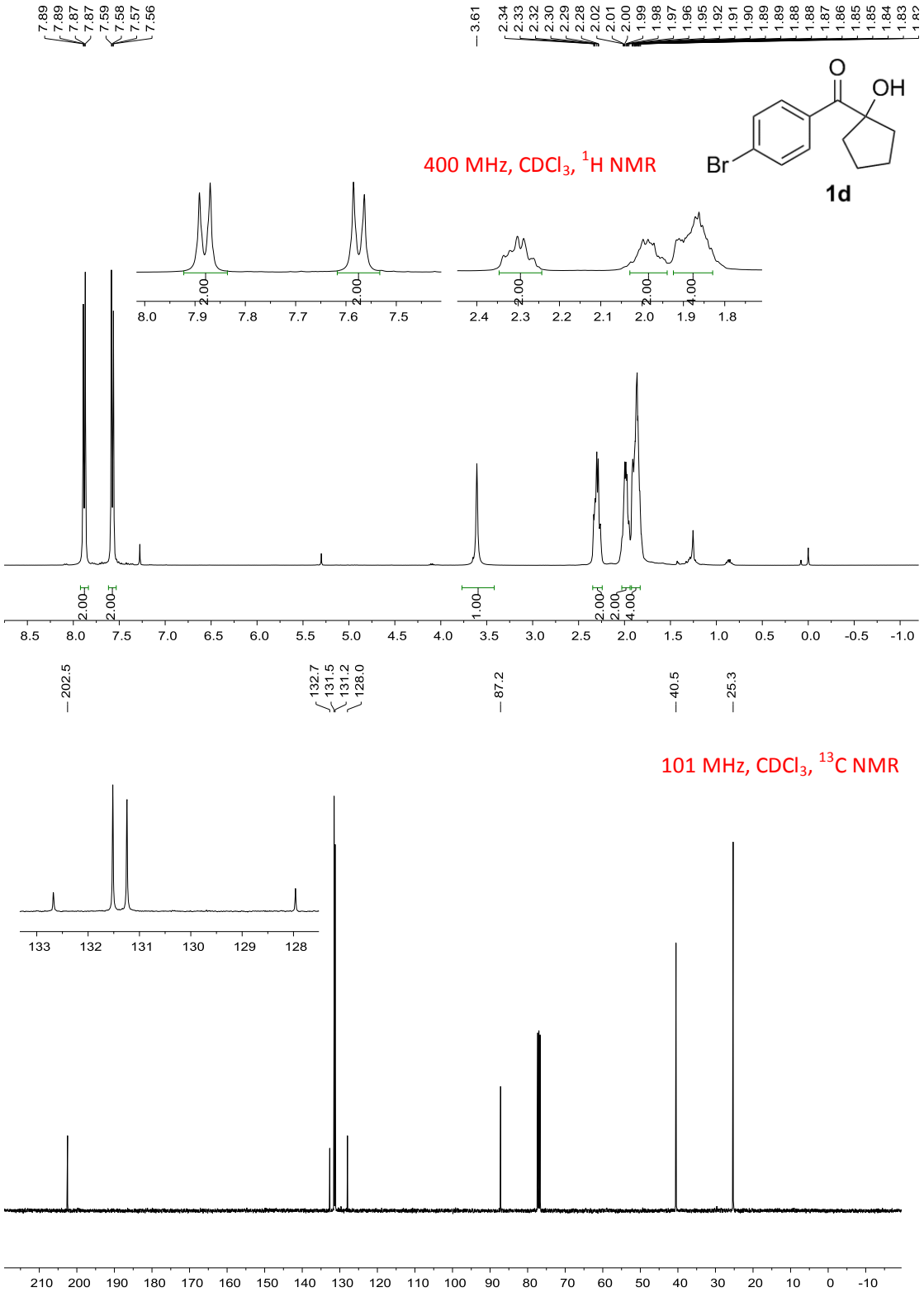
400 MHz, $CDCl_3$, ^1H NMR



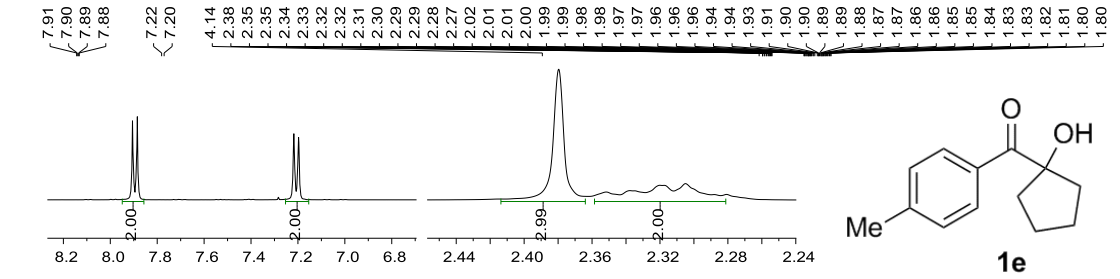
101 MHz, $CDCl_3$, ^{13}C NMR



(4-Bromophenyl)(1-hydroxycyclopentyl)methanone (1d)

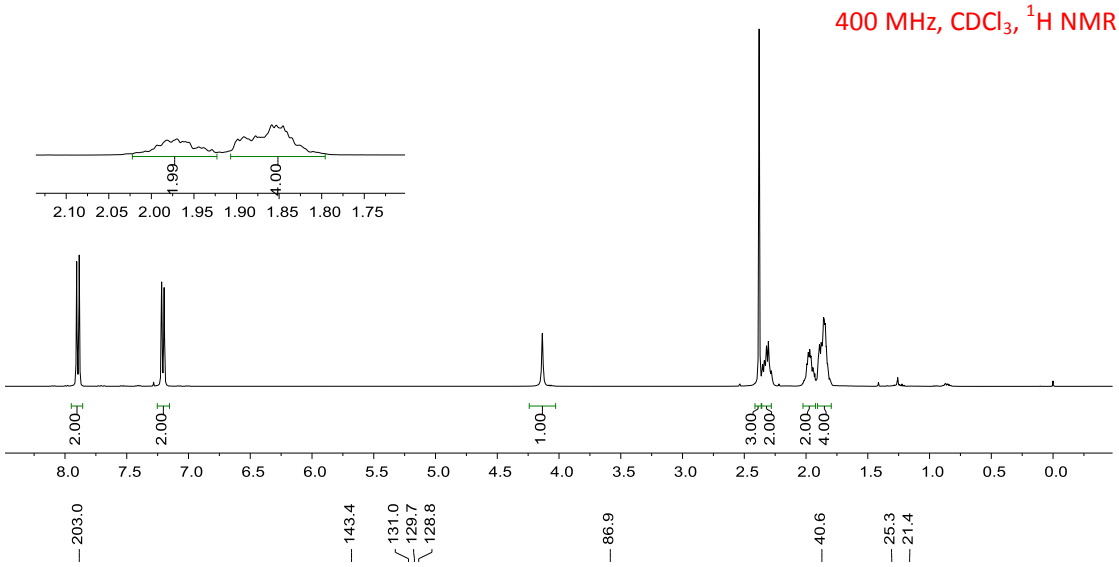


(1-Hydroxycyclopentyl)(p-tolyl)methanone (1e)

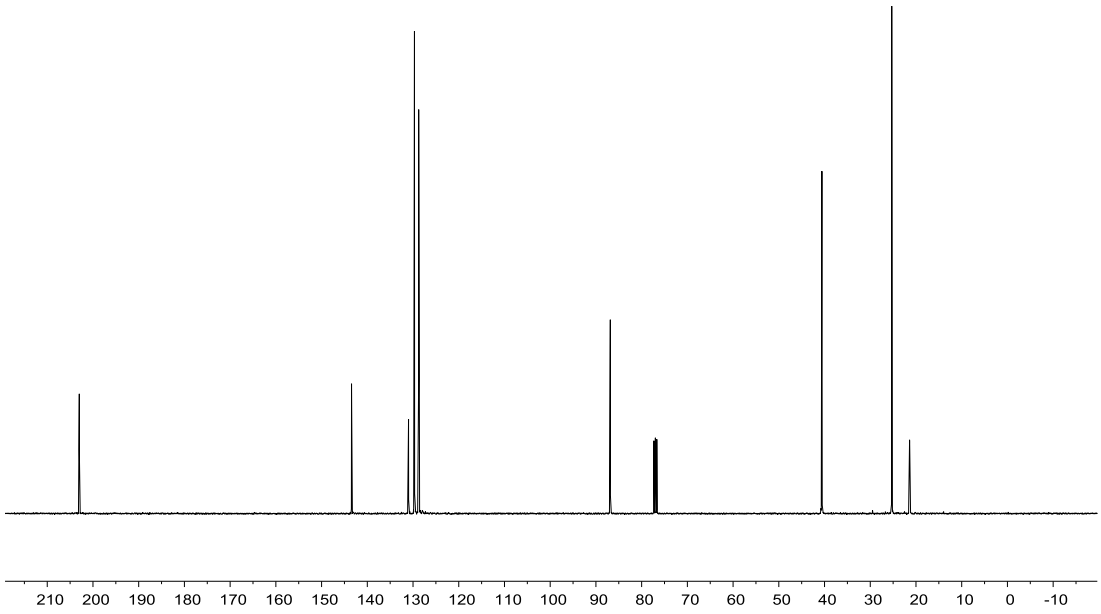


1e

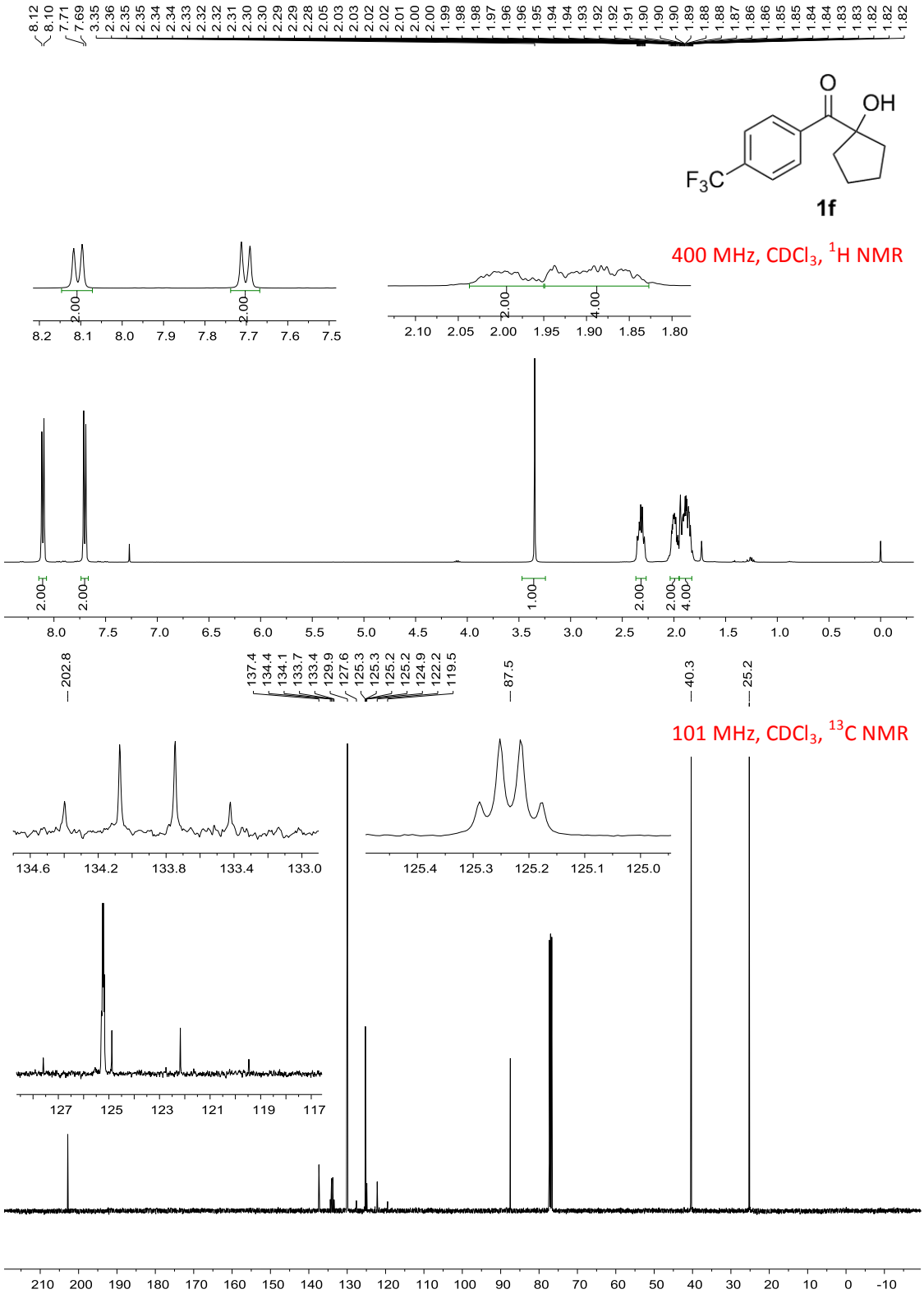
400 MHz, $CDCl_3$, ^1H NMR



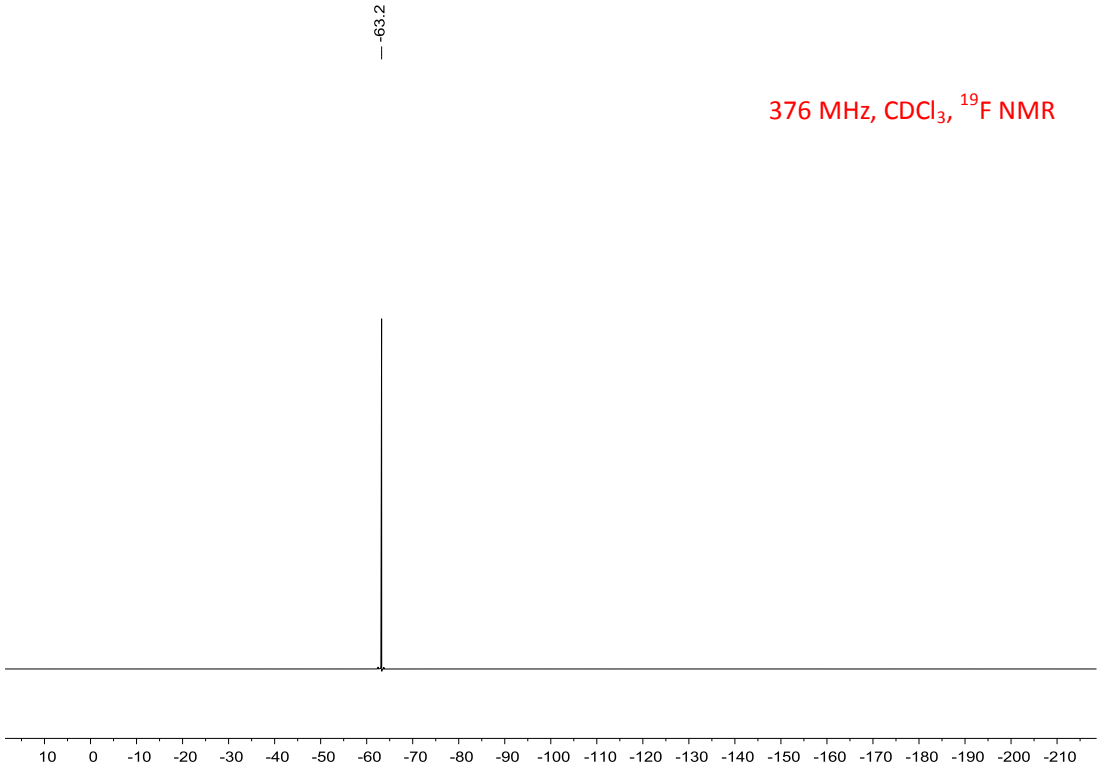
101 MHz, $CDCl_3$, ^{13}C NMR



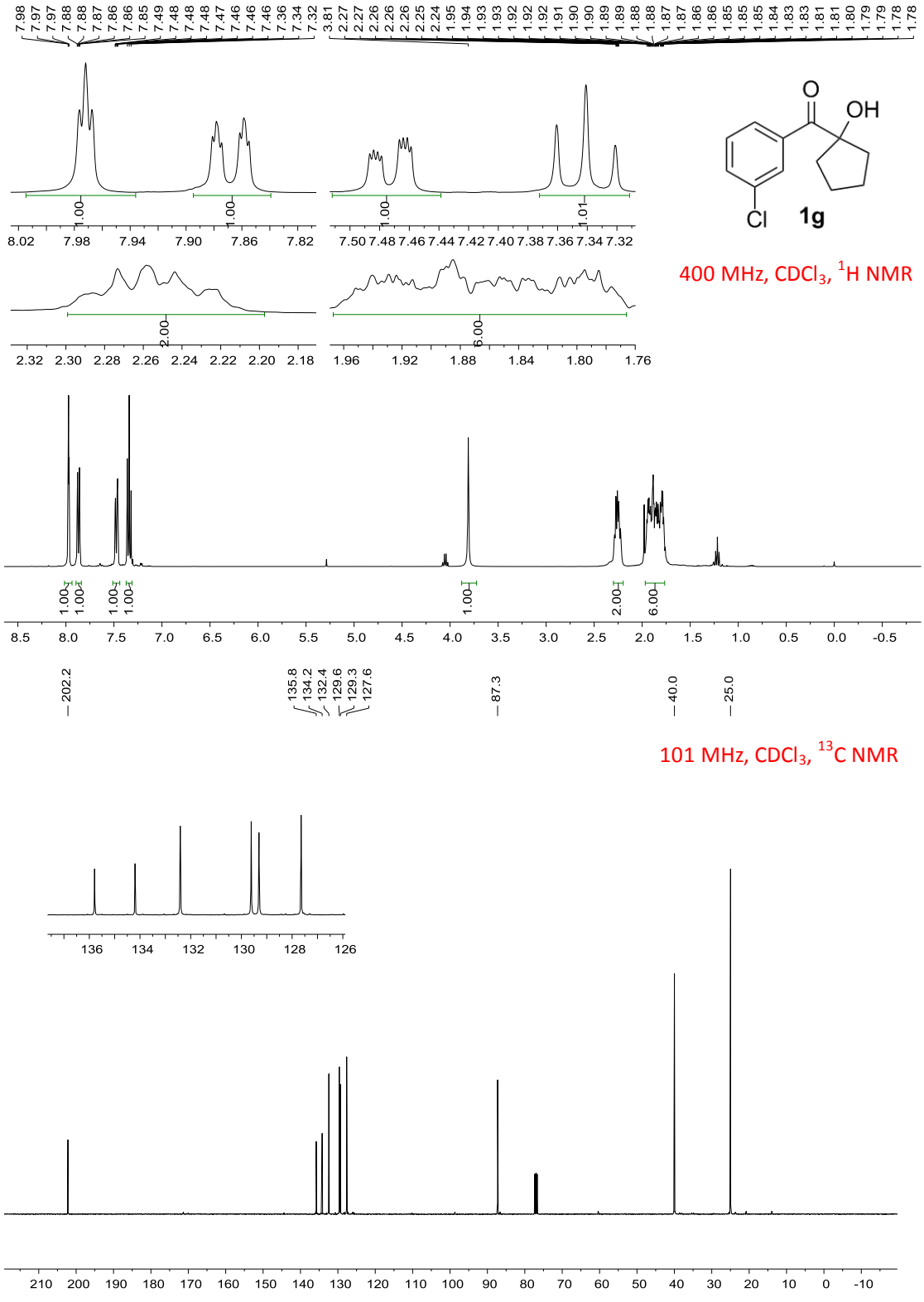
(1-Hydroxycyclopentyl)(4-(trifluoromethyl)phenyl)methanone (1f)



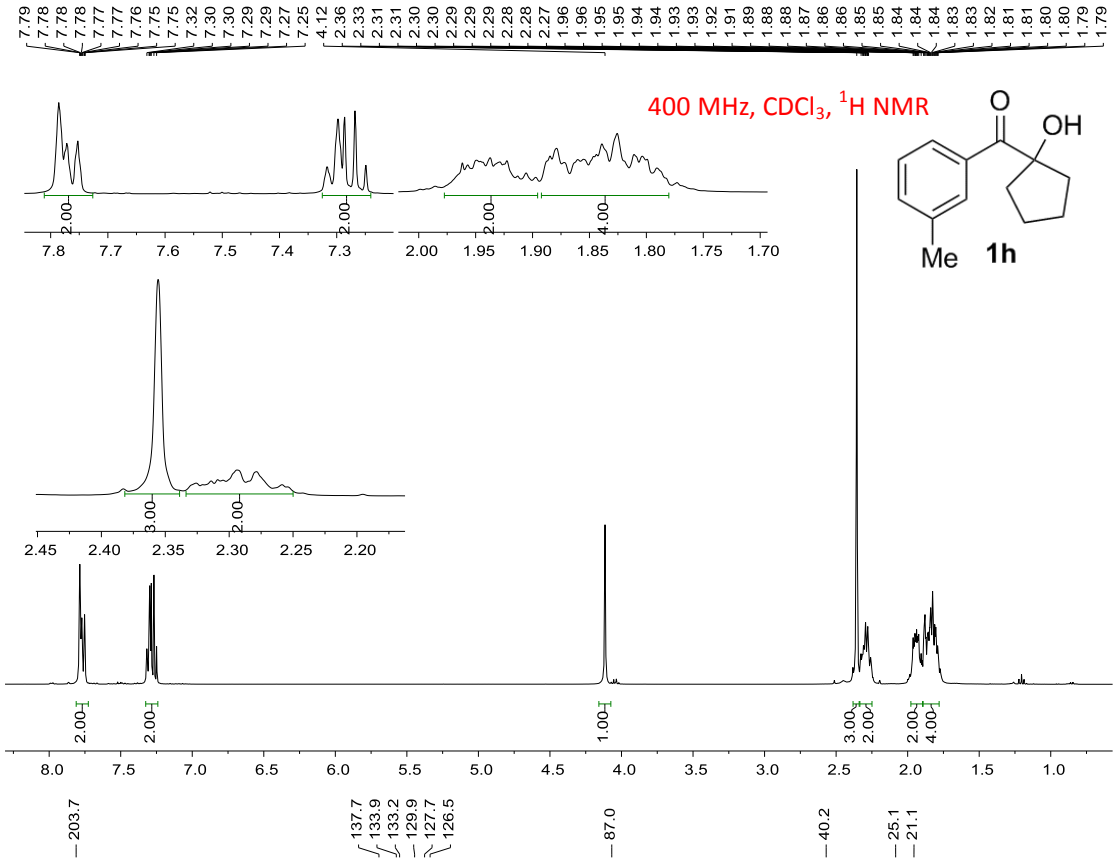
376 MHz, $CDCl_3$, ^{19}F NMR

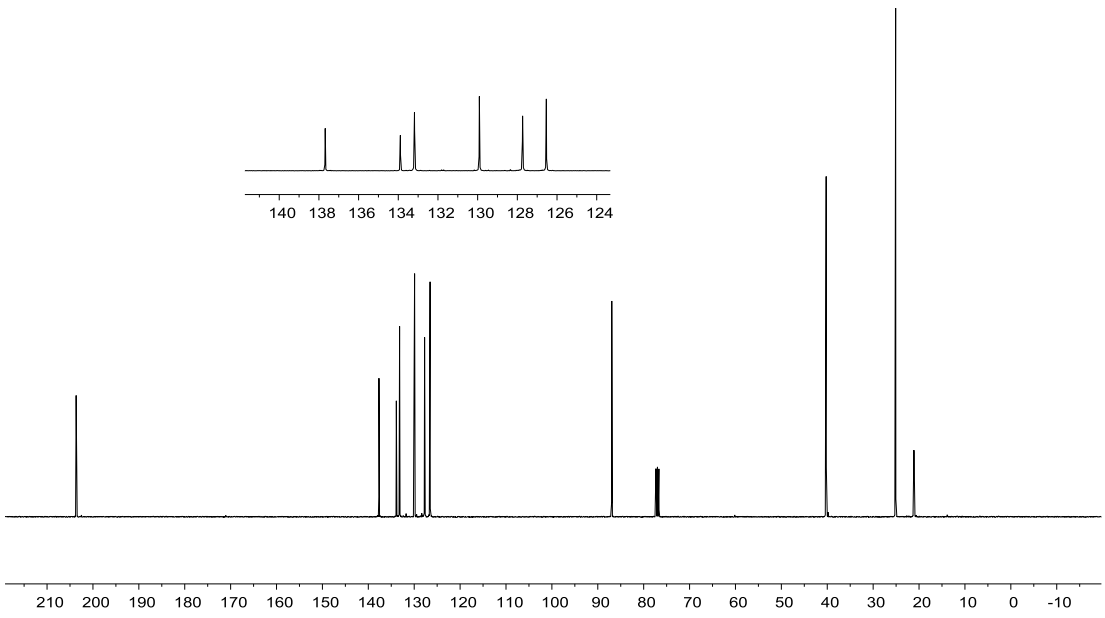


(3-Chlorophenyl)(1-hydroxycyclopentyl)methanone (1g)

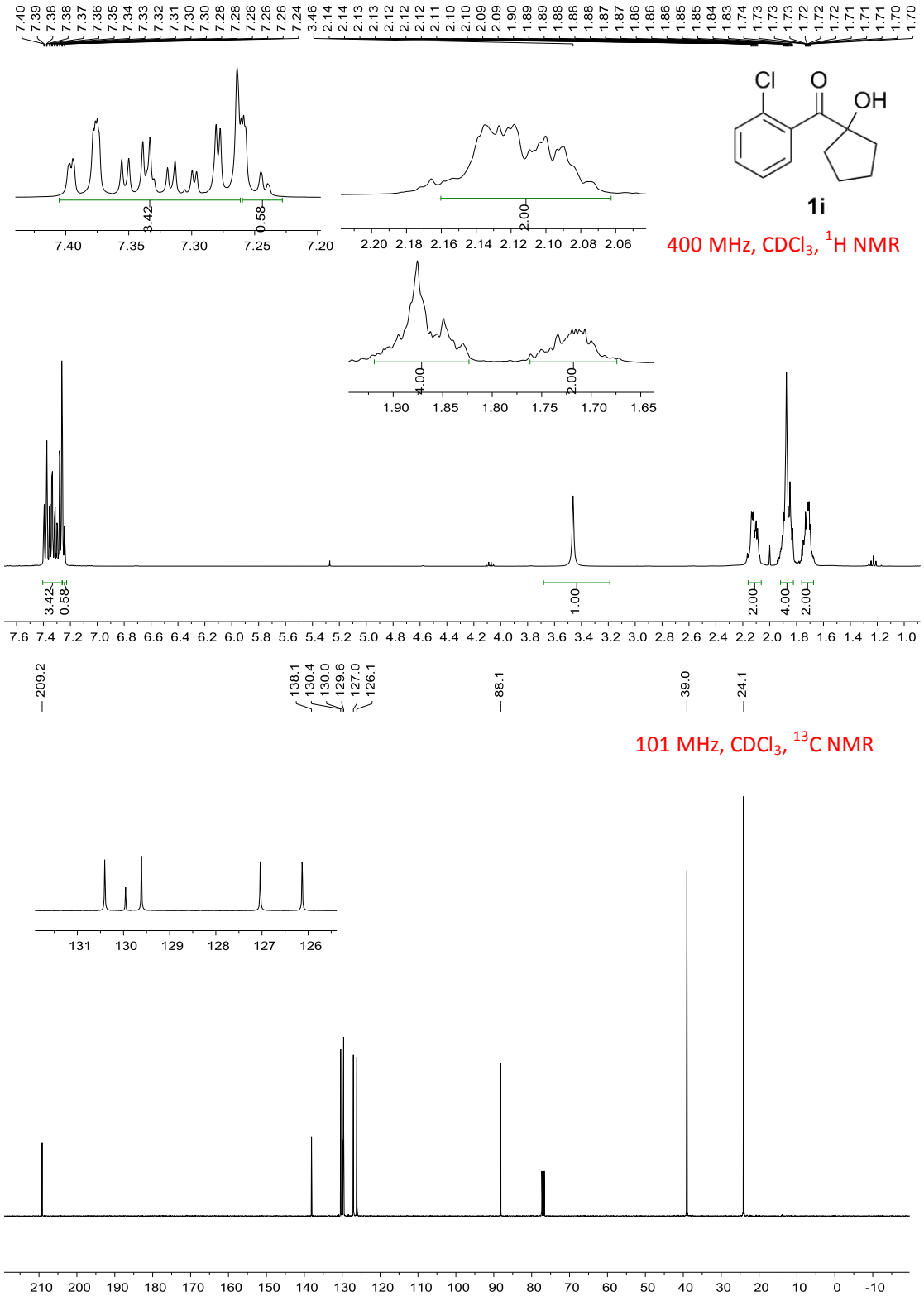


(1-Hydroxycyclopentyl)(m-tolyl)methanone (1h)

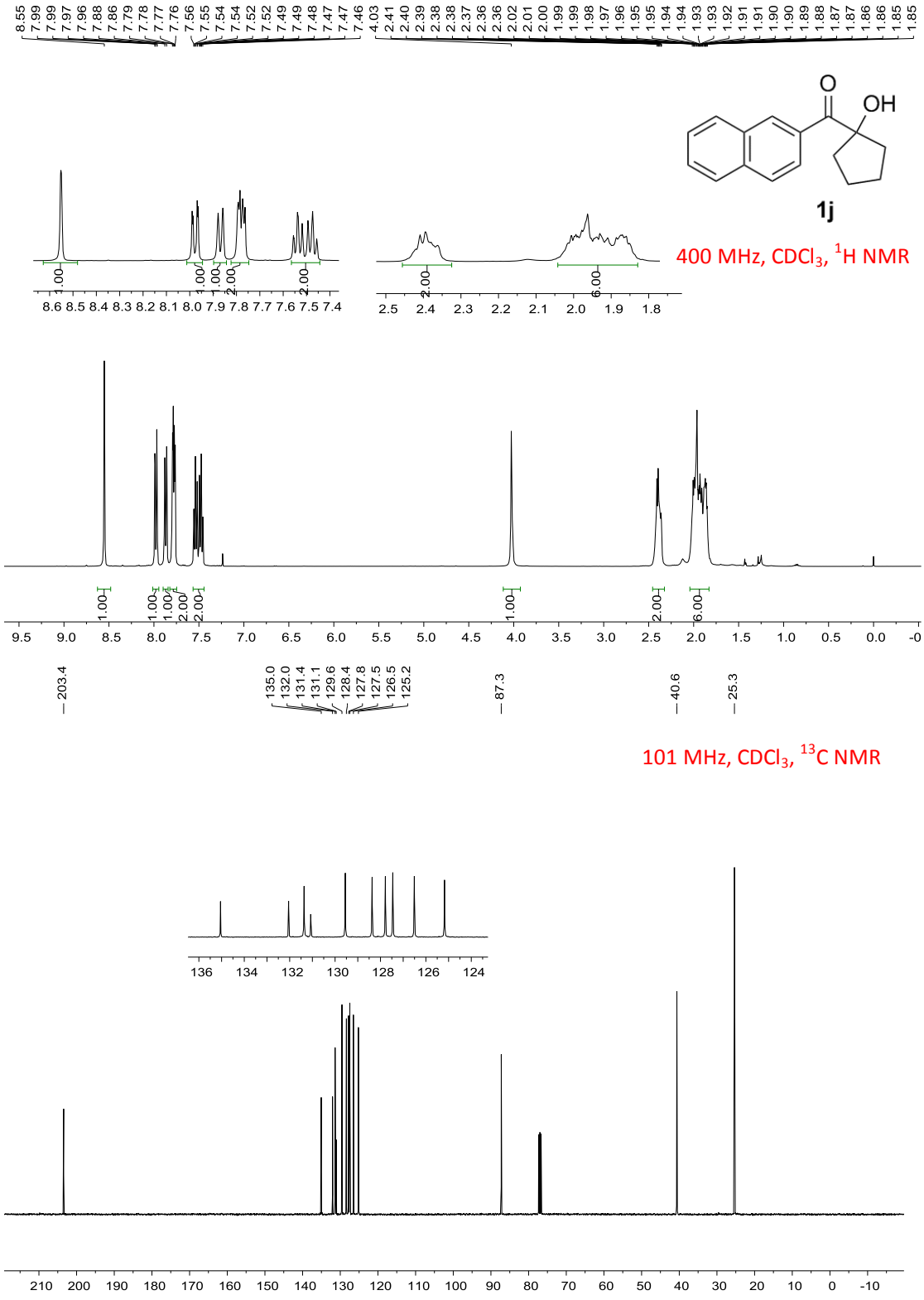




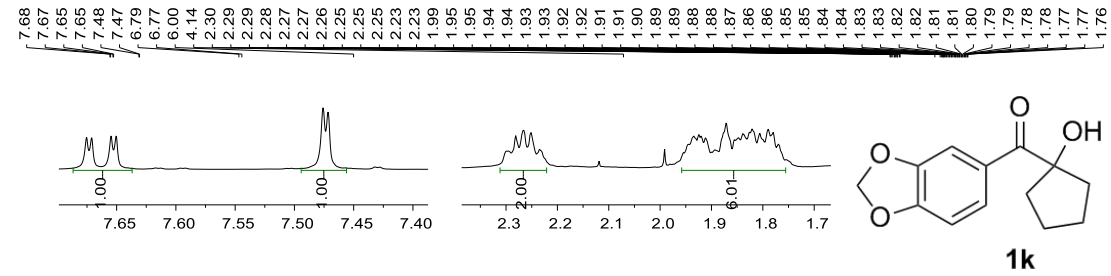
(2-Chlorophenyl)(1-hydroxycyclopentyl)methanone (1i)



(1-Hydroxycyclopentyl)(naphthalen-2-yl)methanone (1j)

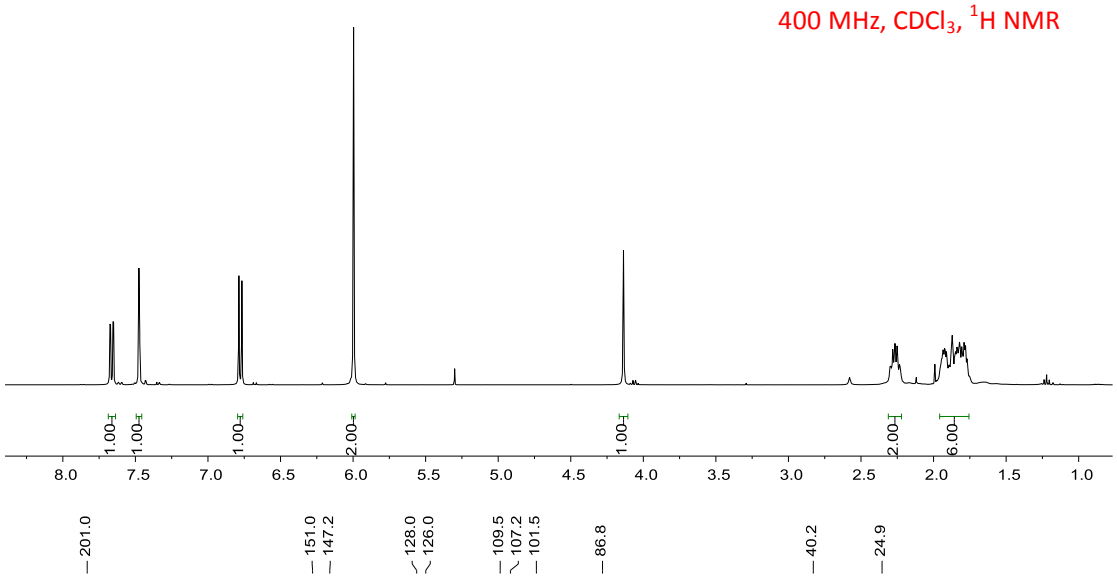


Benzo[d][1,3]dioxol-5-yl(1-hydroxycyclopentyl)methanone (1k)

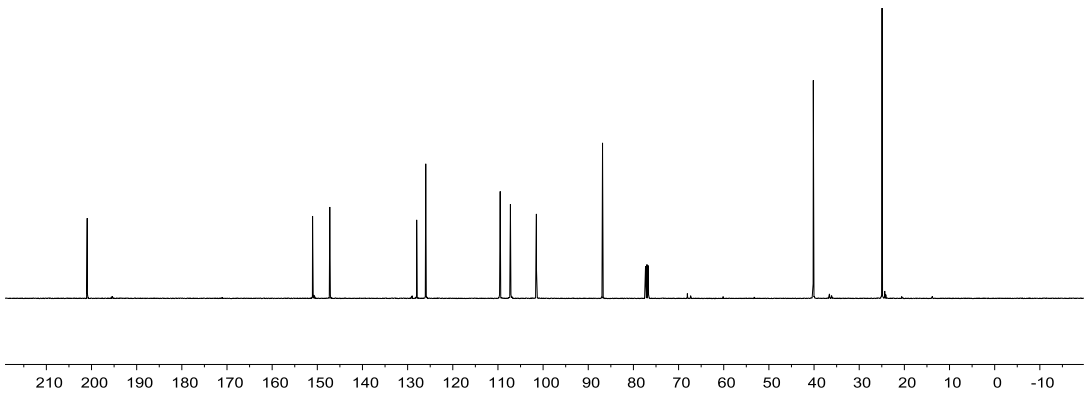


1k

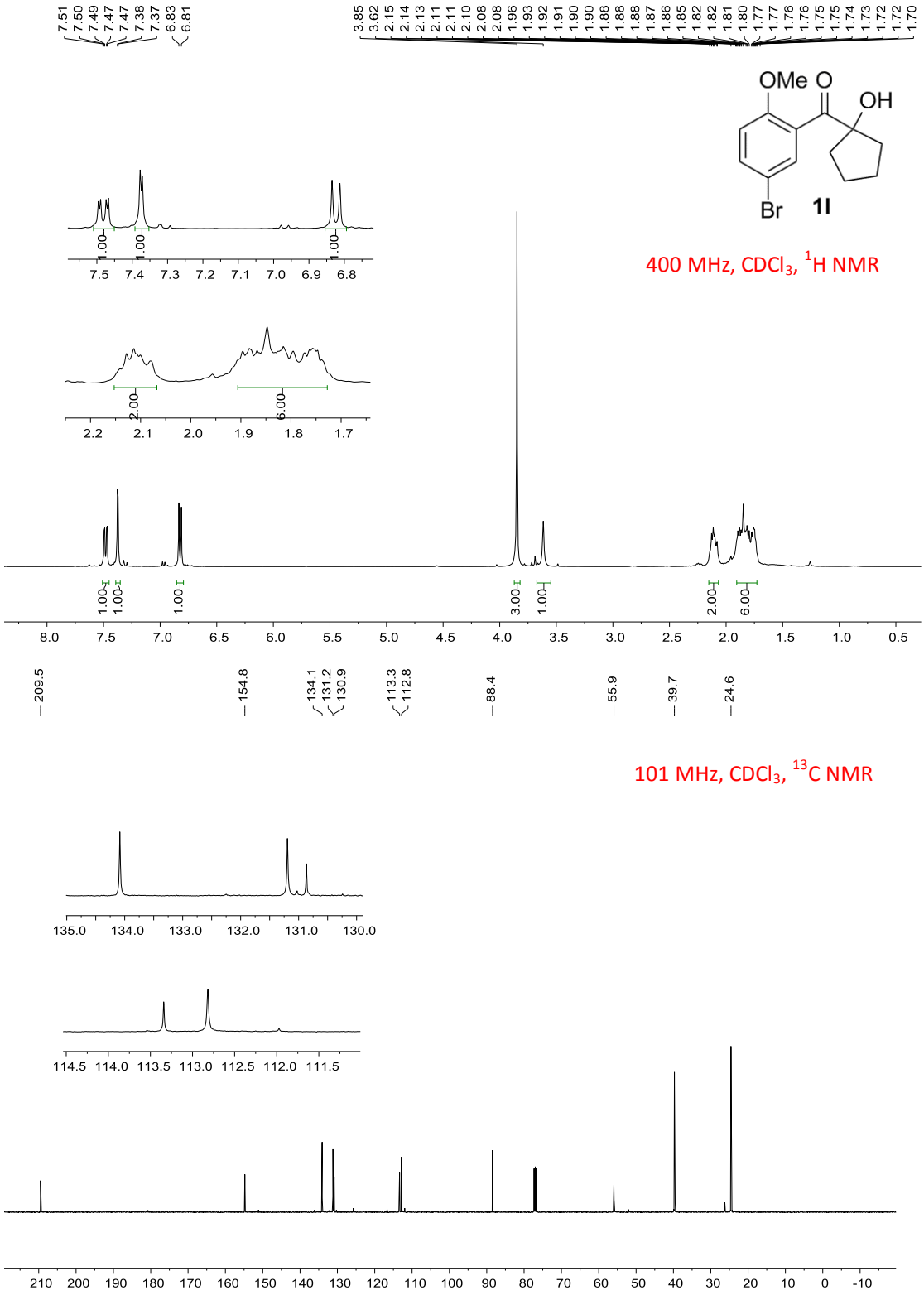
400 MHz, $CDCl_3$, ^1H NMR



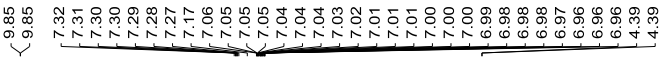
101 MHz, $CDCl_3$, ^{13}C NMR

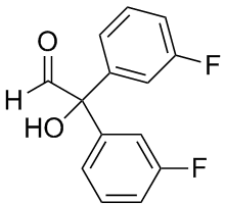


(5-Bromo-2-methoxyphenyl)(1-hydroxycyclopentyl)methanone (1l)



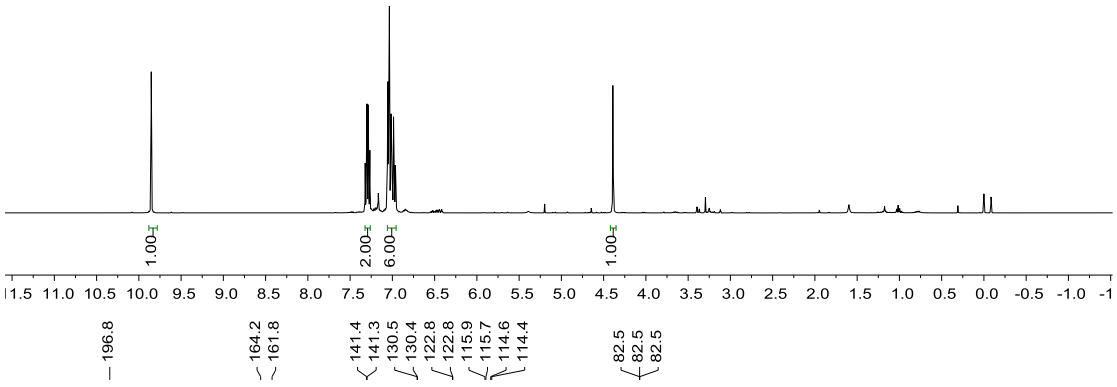
2,2-Bis(3-fluorophenyl)-2-hydroxyacetaldehyde (3c)



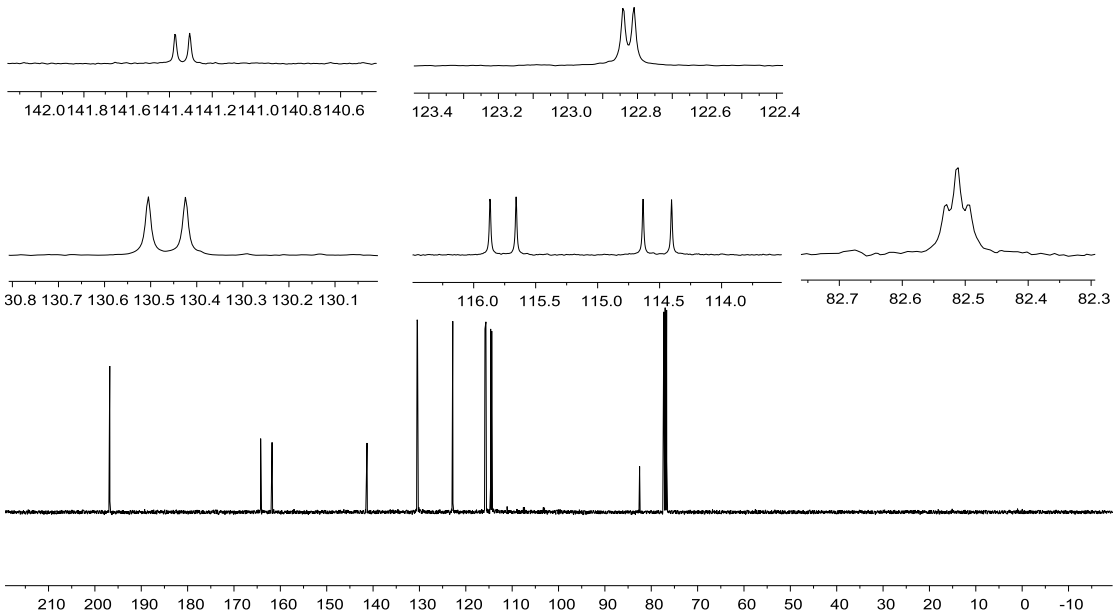


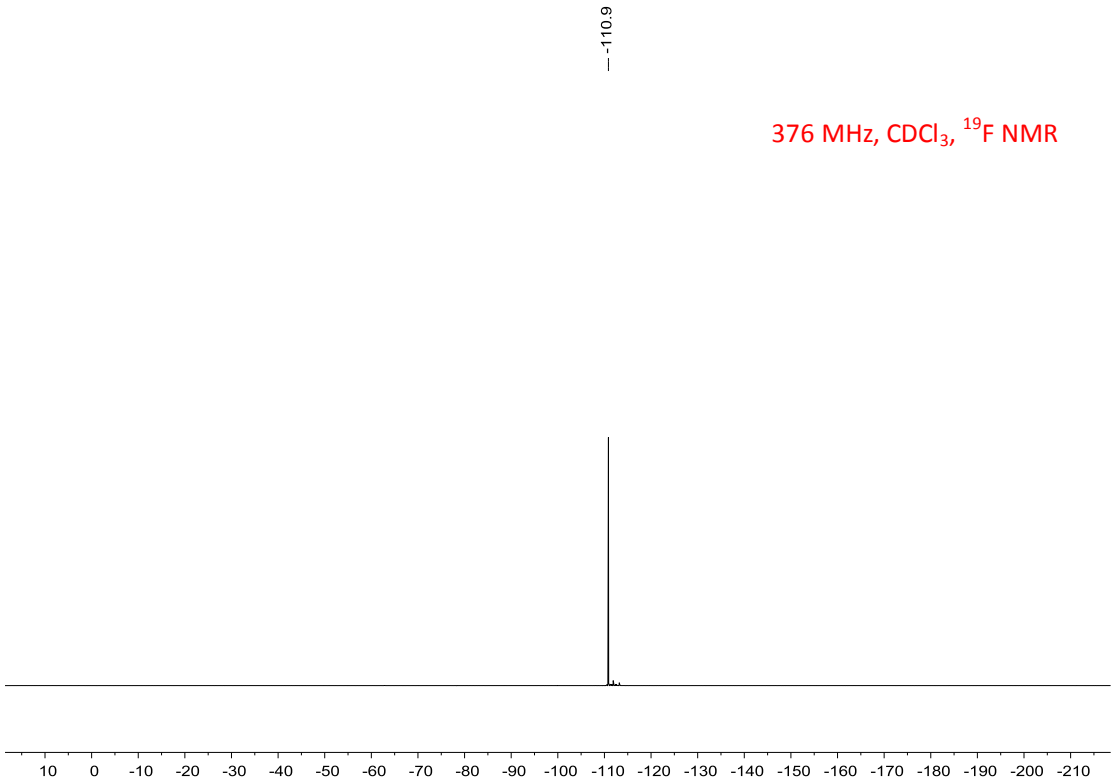
3c

400 MHz, $CDCl_3$, ^1H NMR



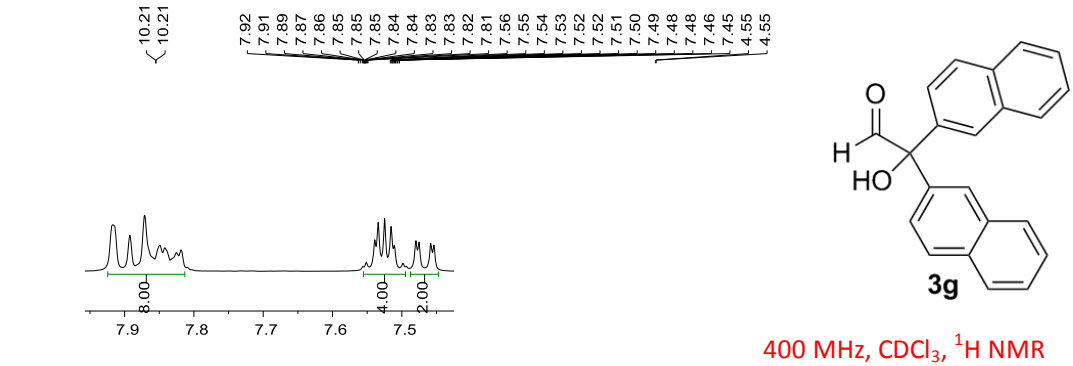
101 MHz, $CDCl_3$, ^{13}C NMR



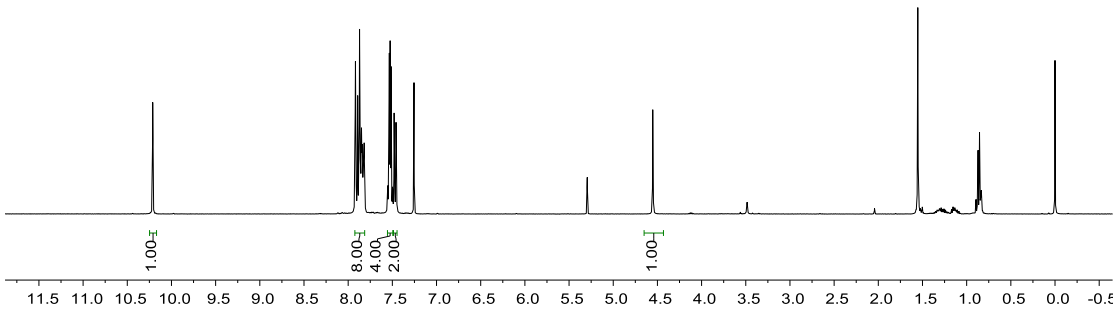


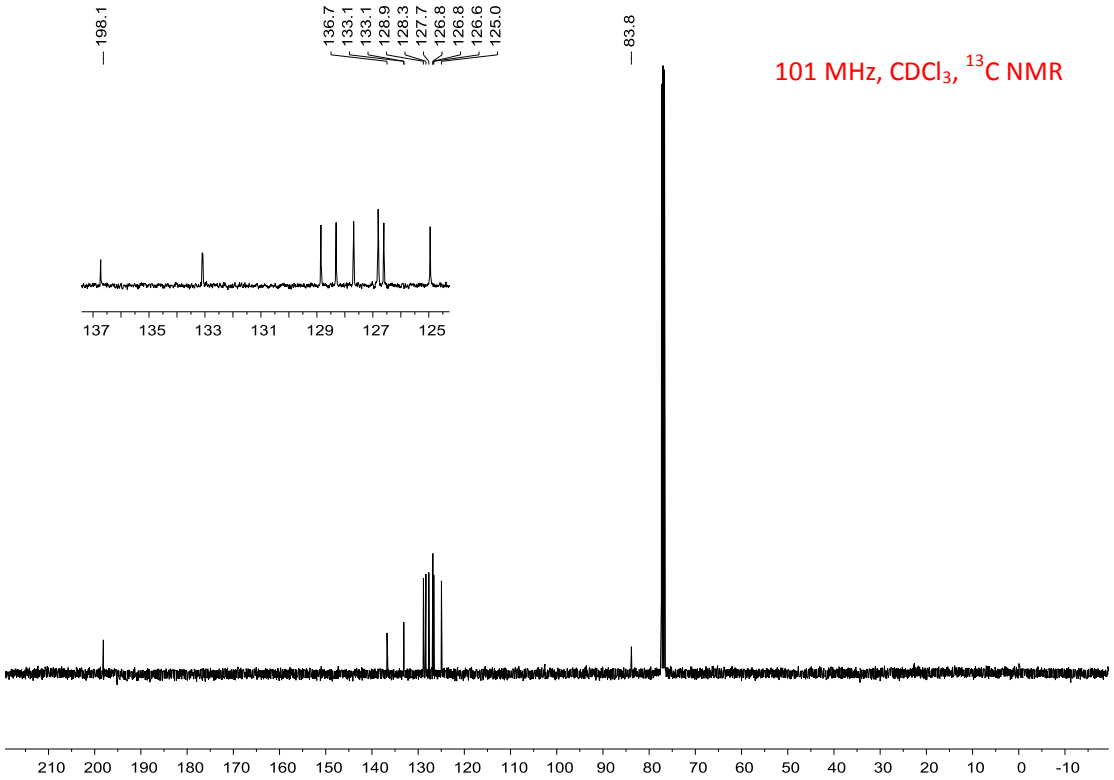
376 MHz, $CDCl_3$, ^{19}F NMR

2-Hydroxy-2,2-di(naphthalen-2-yl)acetaldehyde (3g)



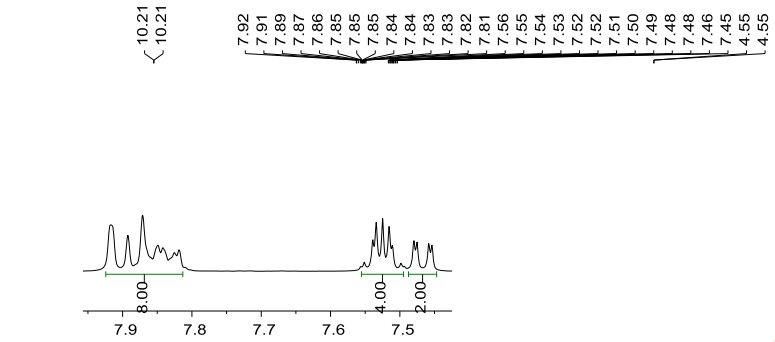
400 MHz, $CDCl_3$, ^1H NMR

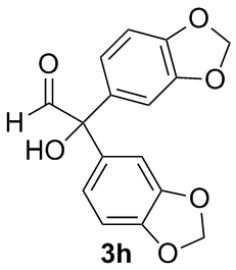




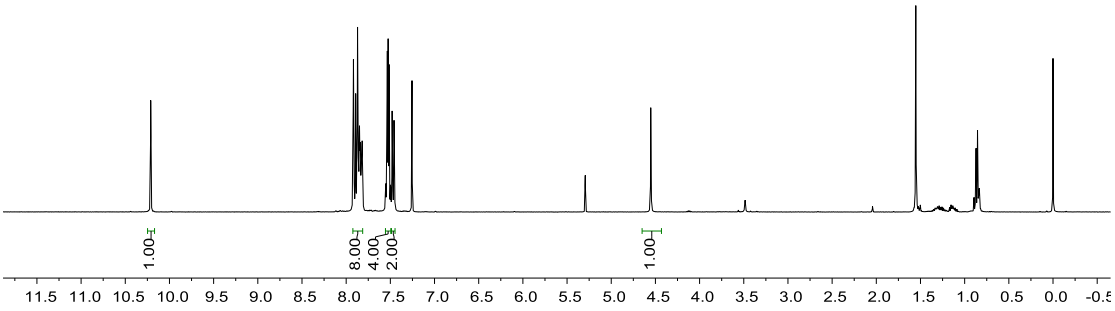
101 MHz, $CDCl_3$, ^{13}C NMR

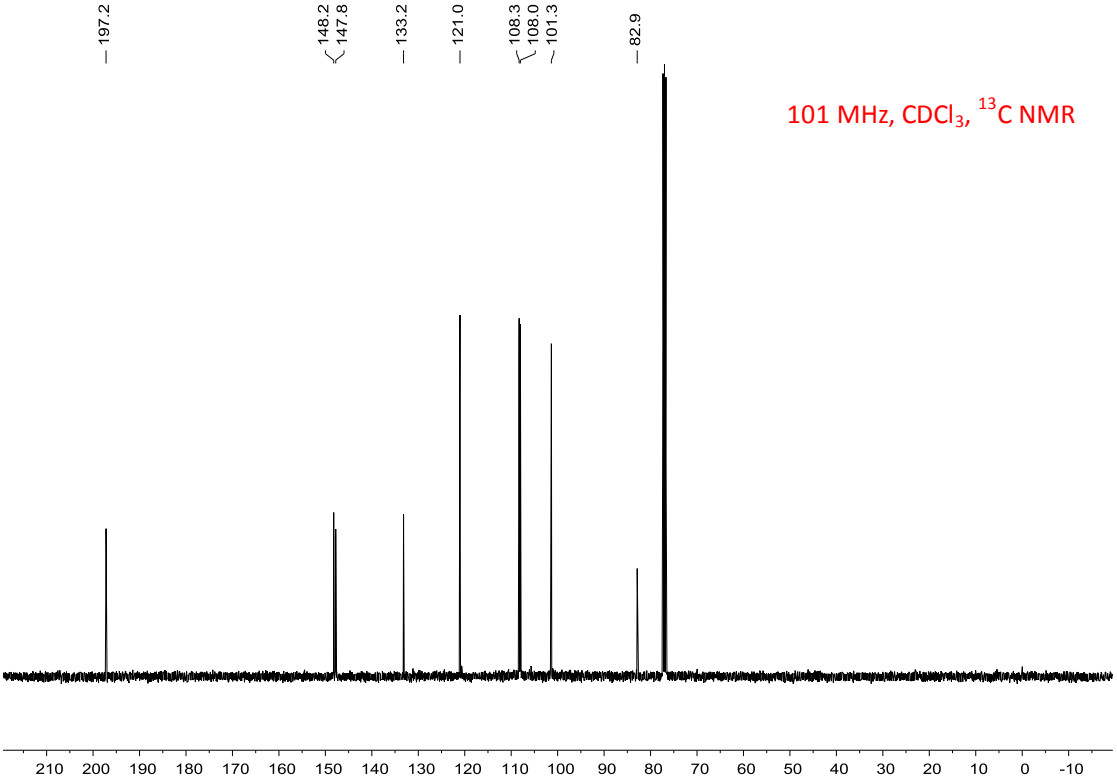
2,2-Bis(benzo[d][1,3]dioxol-5-yl)-2-hydroxyacetaldehyde (3h)





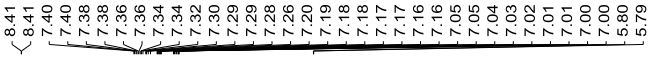
400 MHz, $CDCl_3$, ^1H NMR

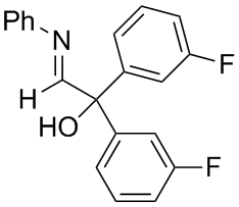




101 MHz, $CDCl_3$, ^{13}C NMR

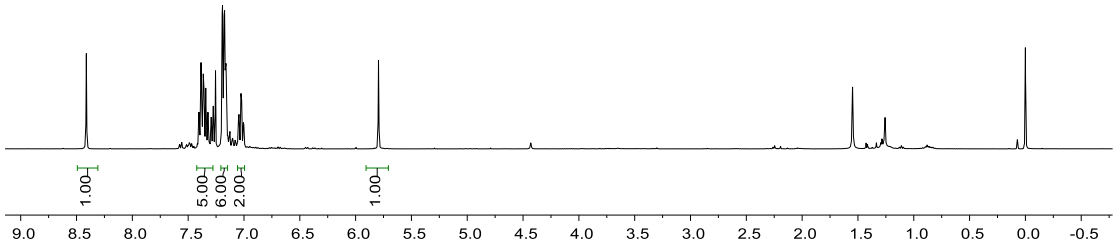
(*E*)-1,1-Bis(3-fluorophenyl)-2-(phenylimino)ethan-1-ol (5c)



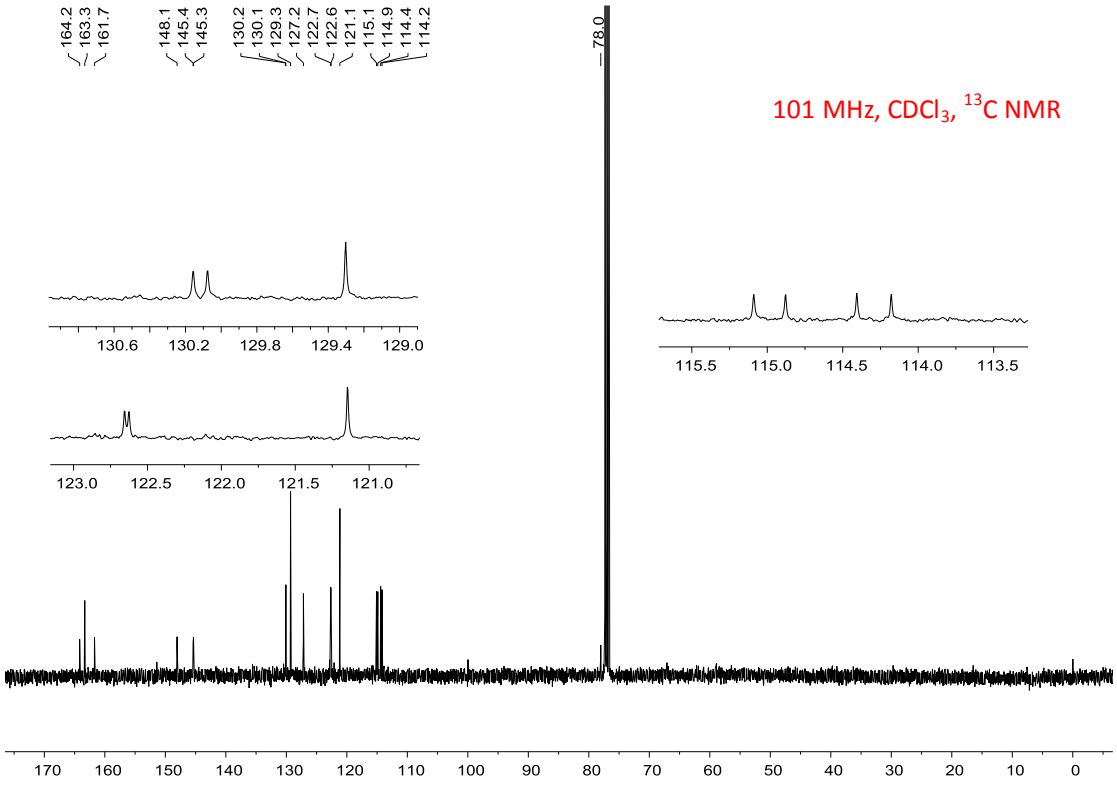


5c

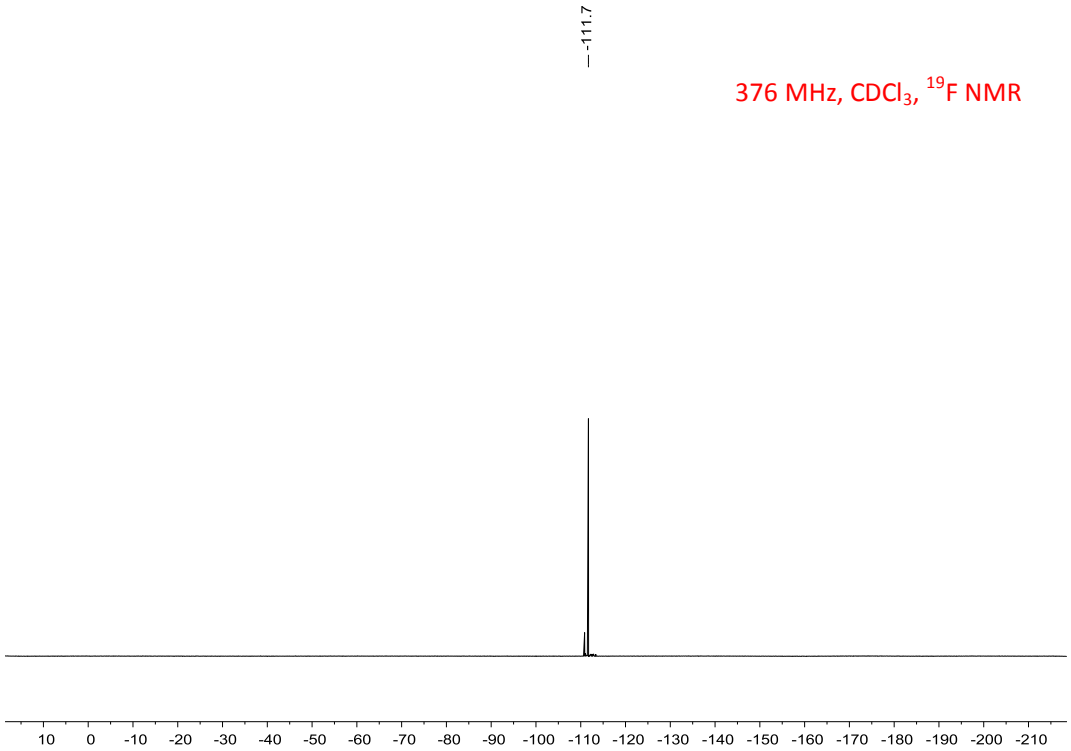
400 MHz, $CDCl_3$, ^1H NMR



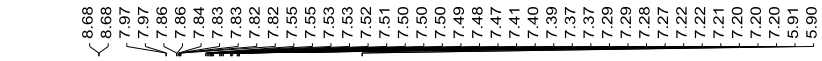
101 MHz, $CDCl_3$, ^{13}C NMR

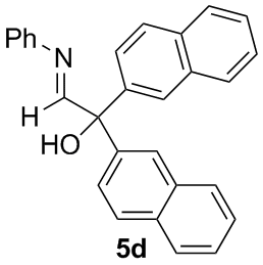


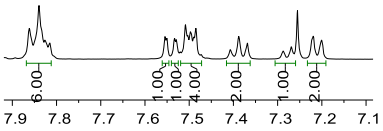
376 MHz, $CDCl_3$, ^{19}F NMR



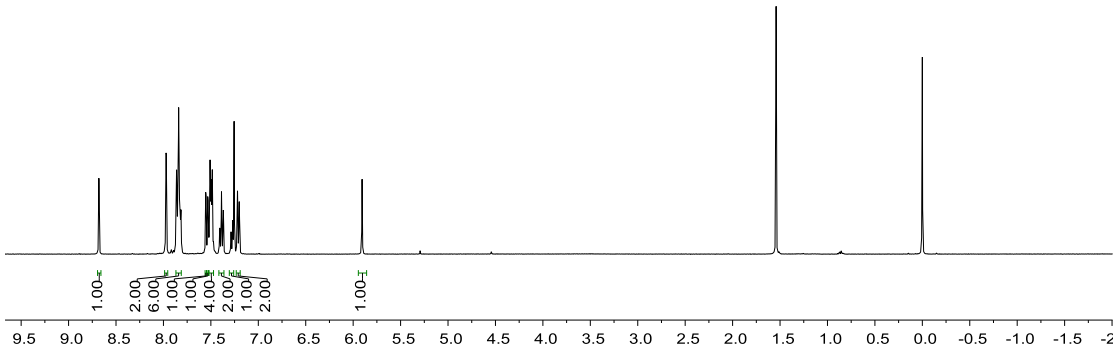
(*E*)-1,1-Di(naphthalen-2-yl)-2-(phenylimino)ethan-1-ol (5d)



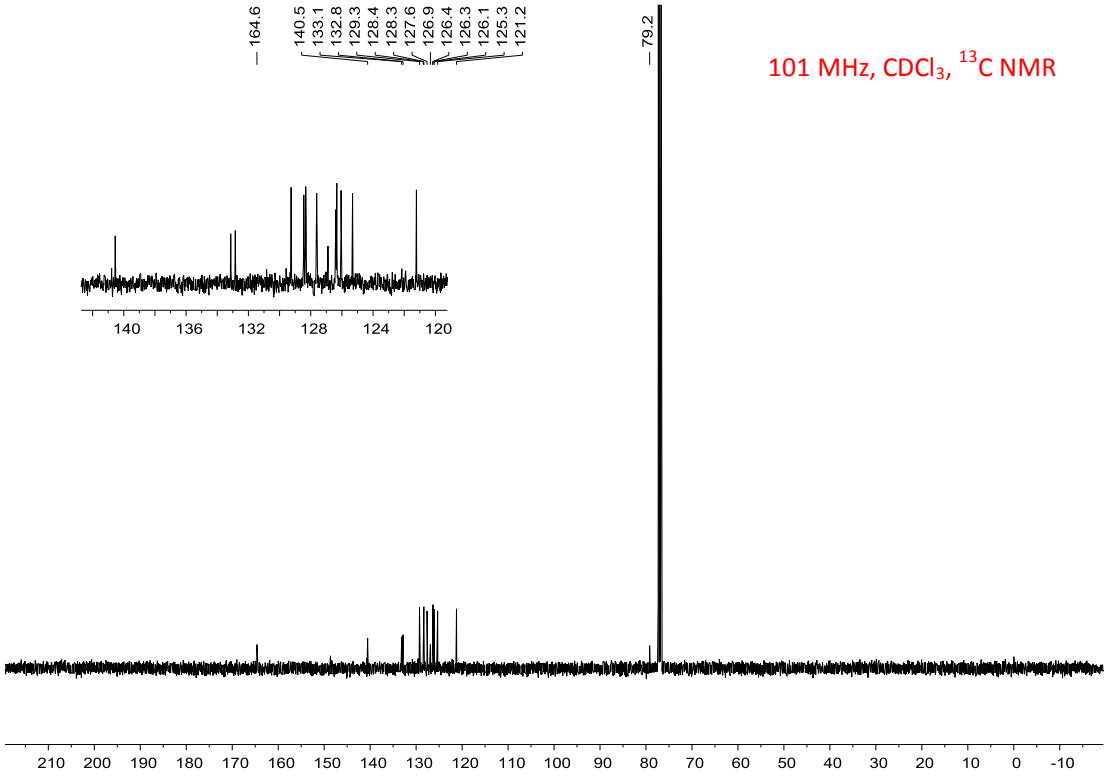




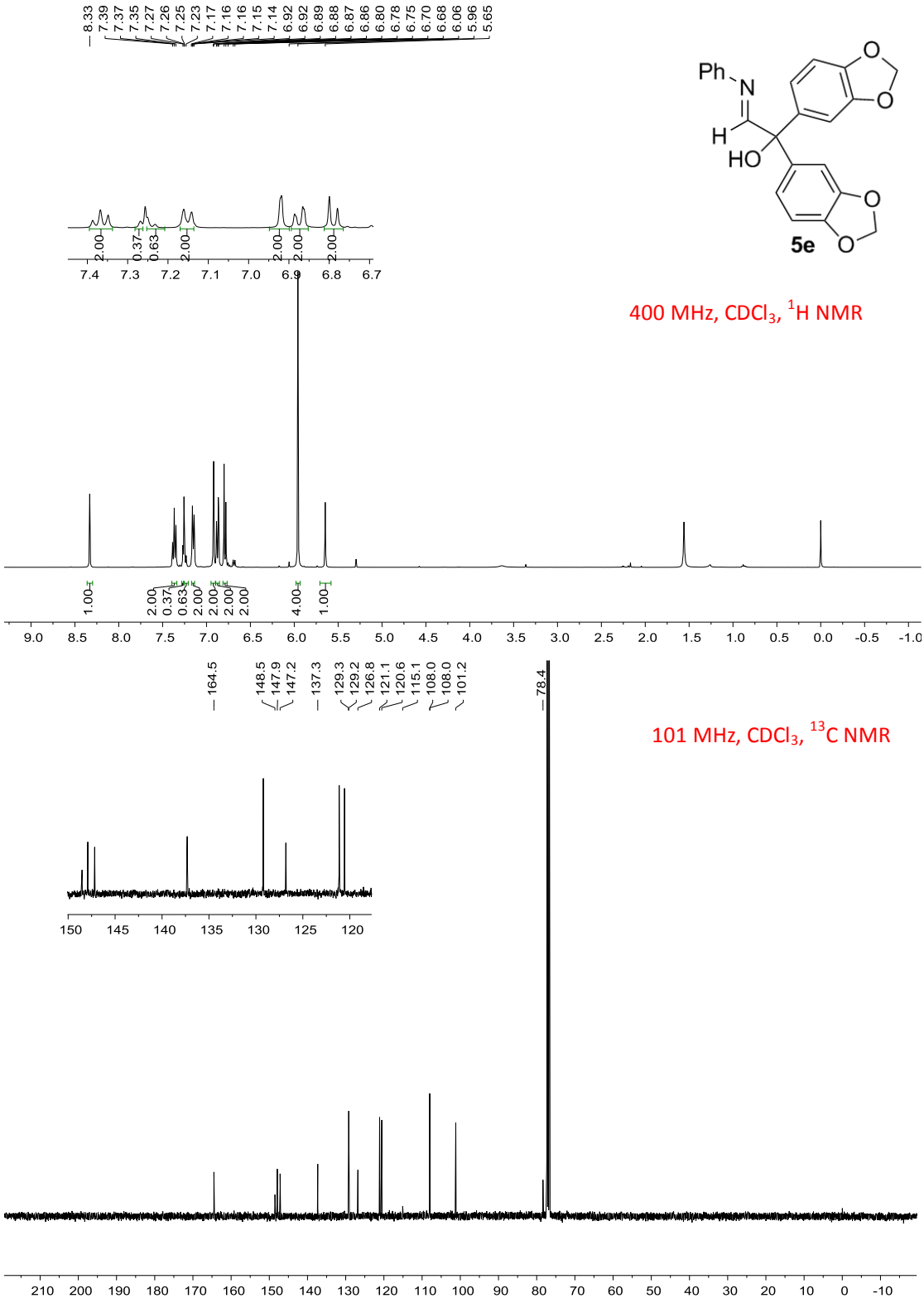
400 MHz, $CDCl_3$, ^1H NMR



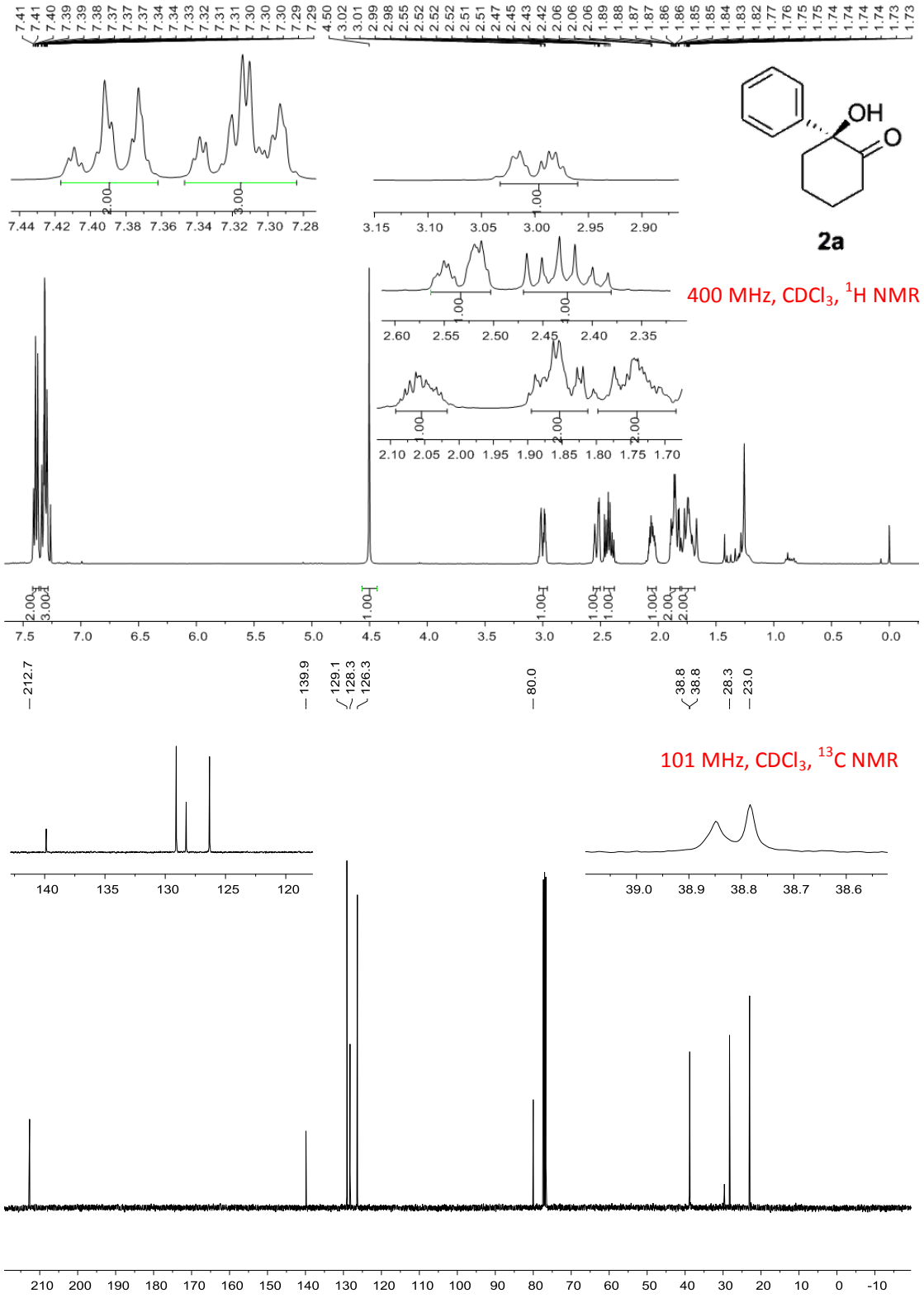
101 MHz, $CDCl_3$, ^{13}C NMR



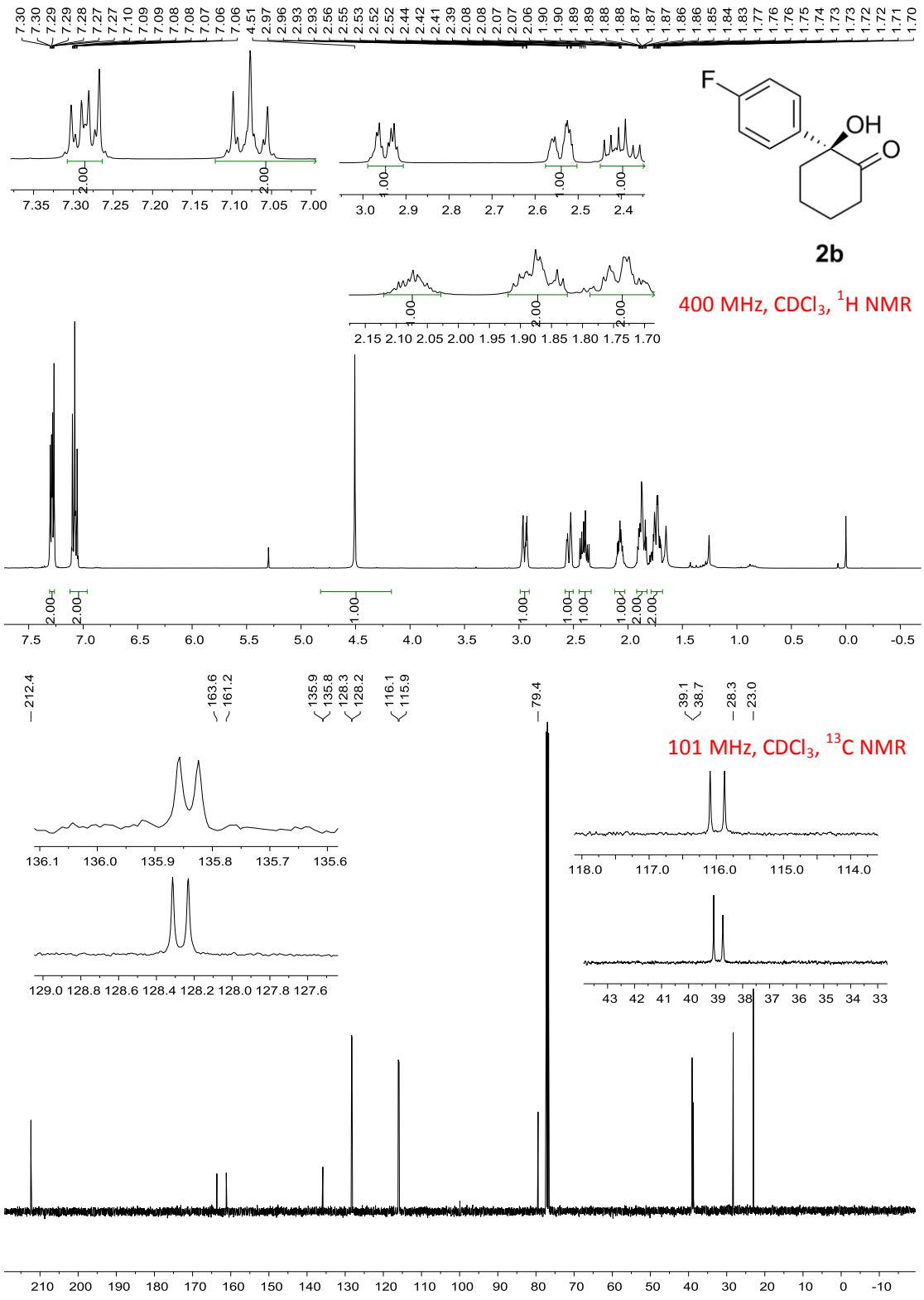
(*E*)-1,1-Bis(benzo[d][1,3]dioxol-5-yl)-2-(phenylimino)ethan-1-ol (5e)

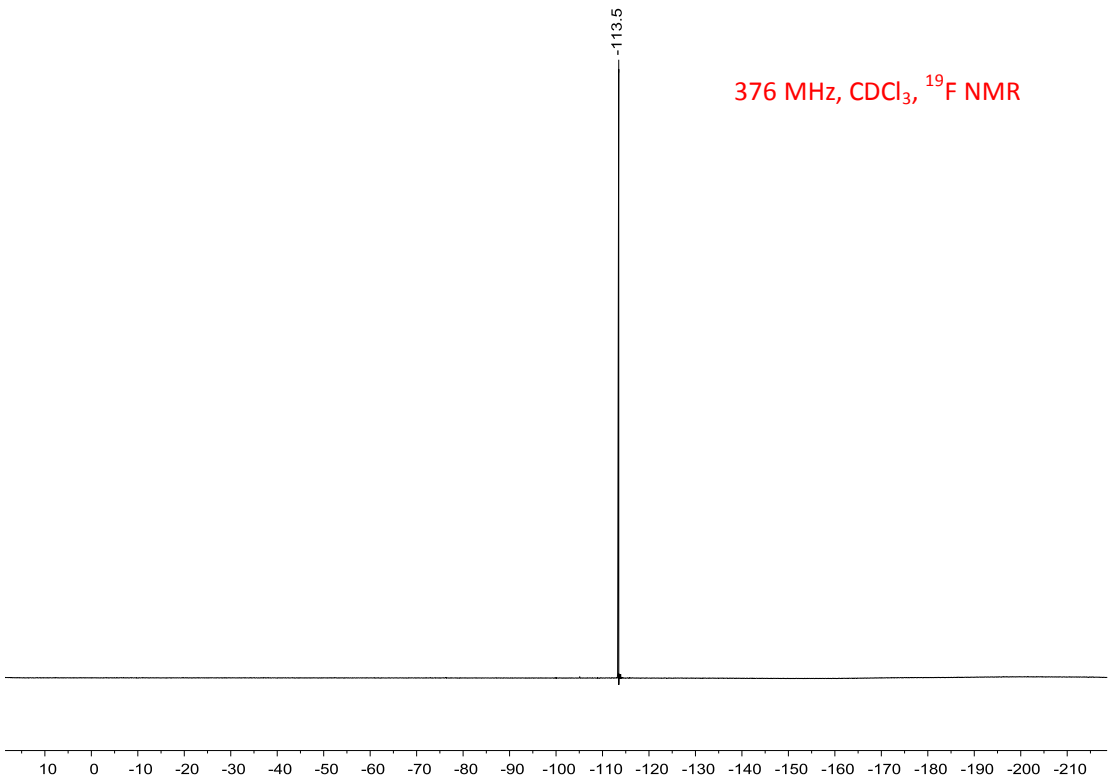


(*S*)-2-Hydroxy-2-phenylcyclohexan-1-one (2a)

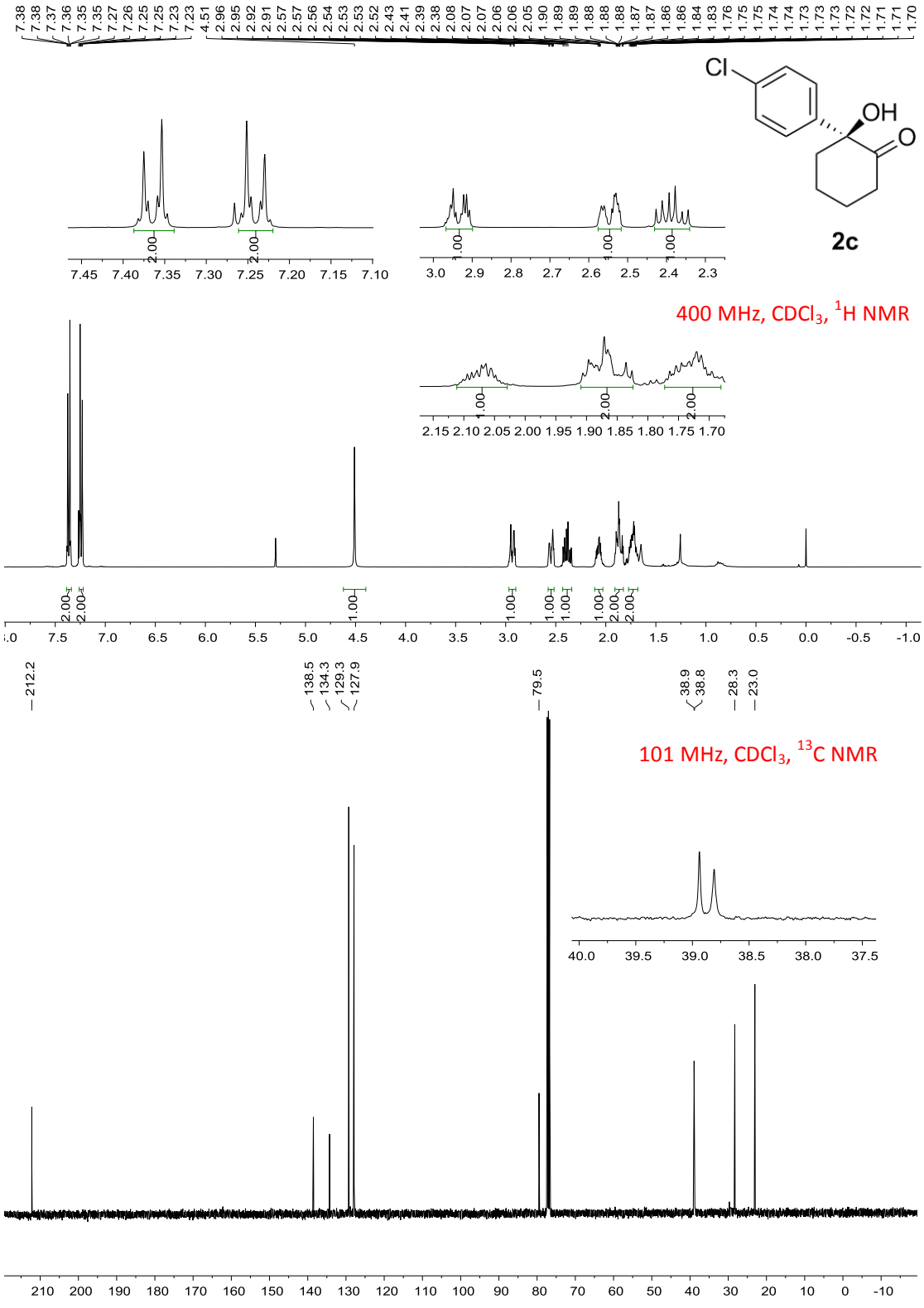


(*S*)-2-(4-Fluorophenyl)-2-hydroxycyclohexan-1-one (2b)

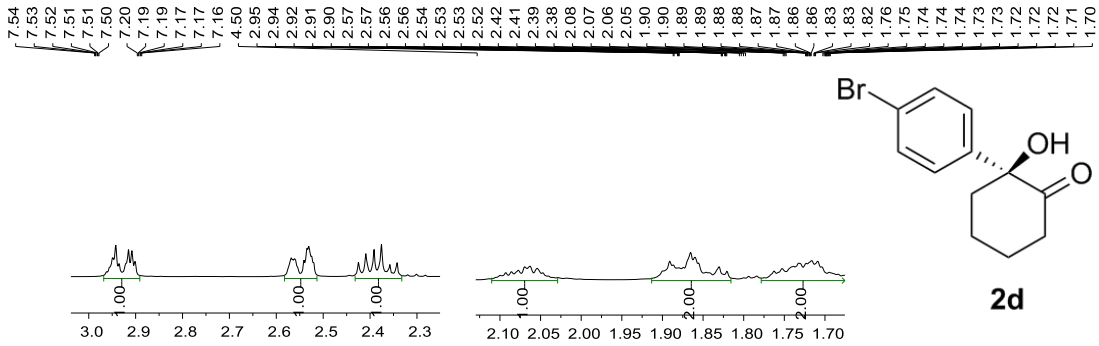



-113.5
376 MHz, CDCl3, 19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

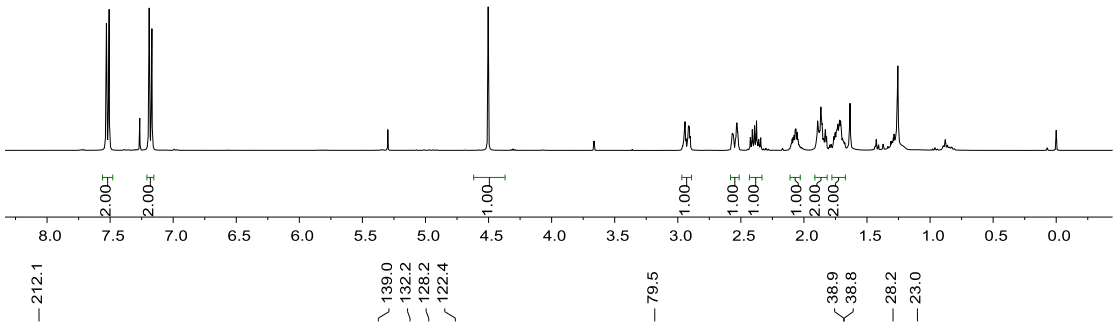
(*S*)-2-(4-Chlorophenyl)-2-hydroxycyclohexan-1-one (2c)



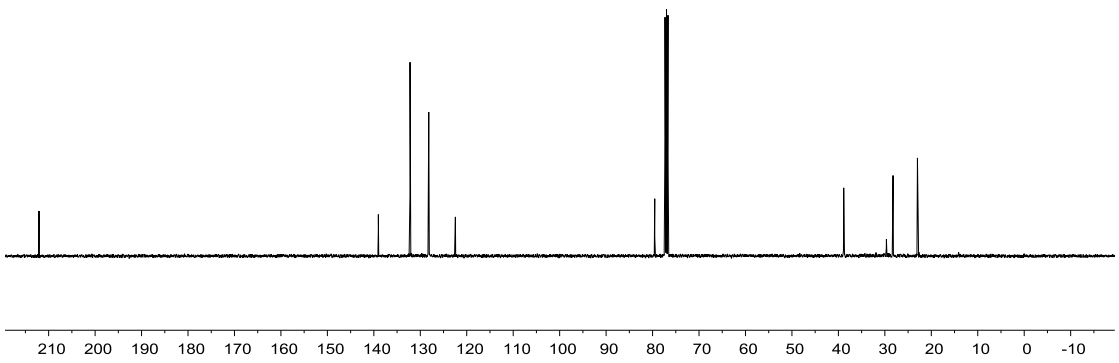
(*S*)-2-(4-Bromophenyl)-2-hydroxycyclohexan-1-one (2d)



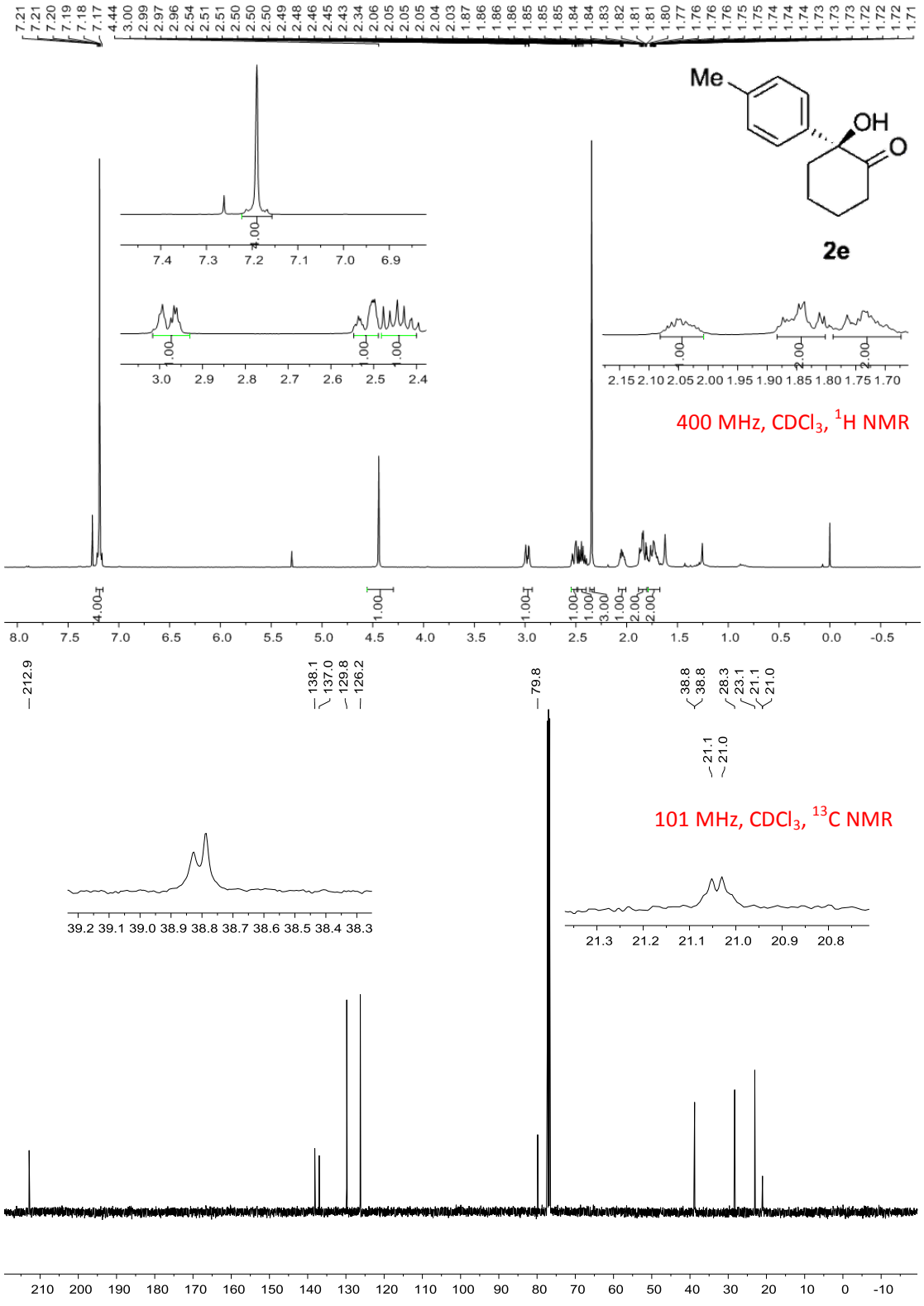
400 MHz, $CDCl_3$, ^1H NMR



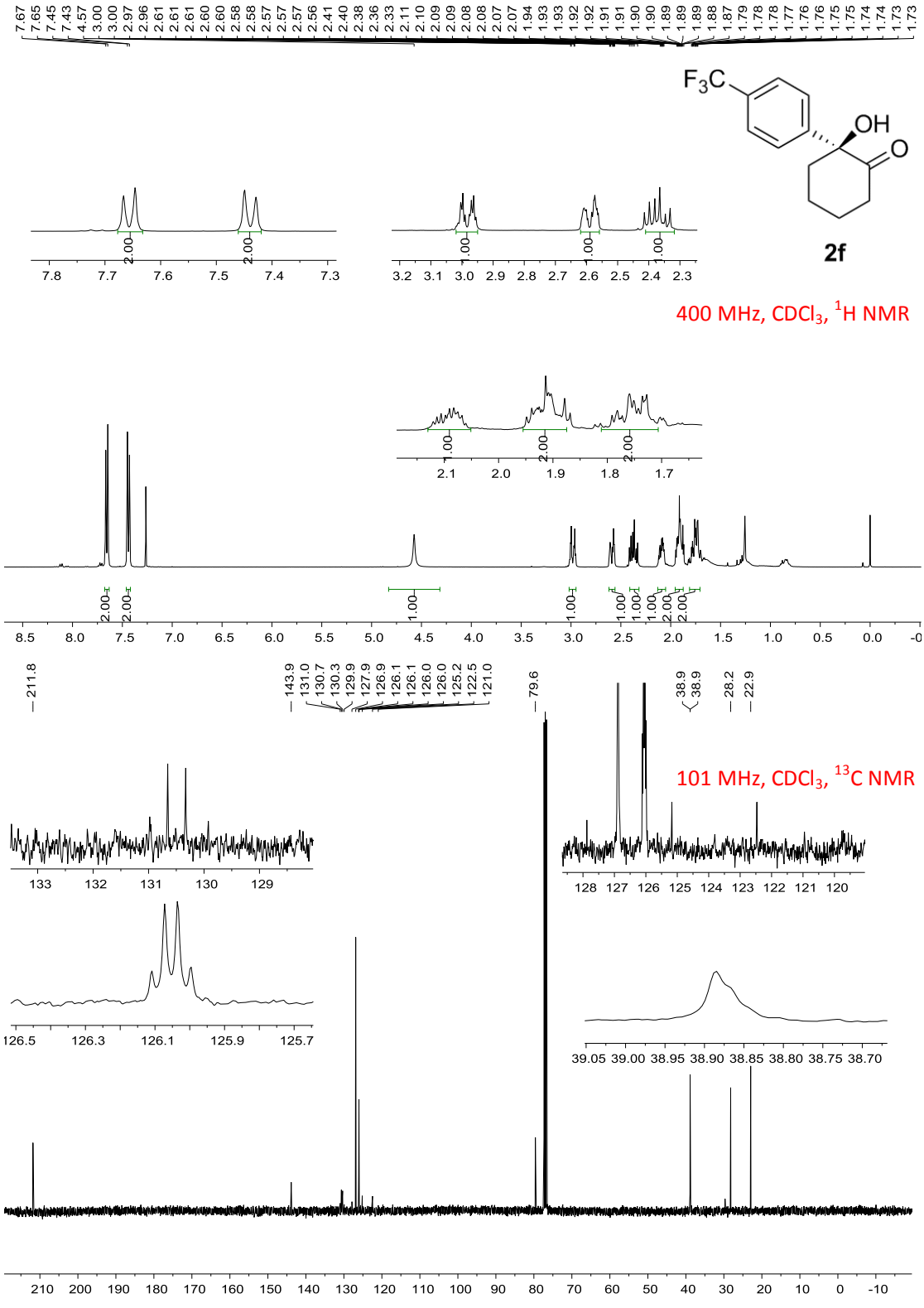
101 MHz, $CDCl_3$, ^{13}C NMR

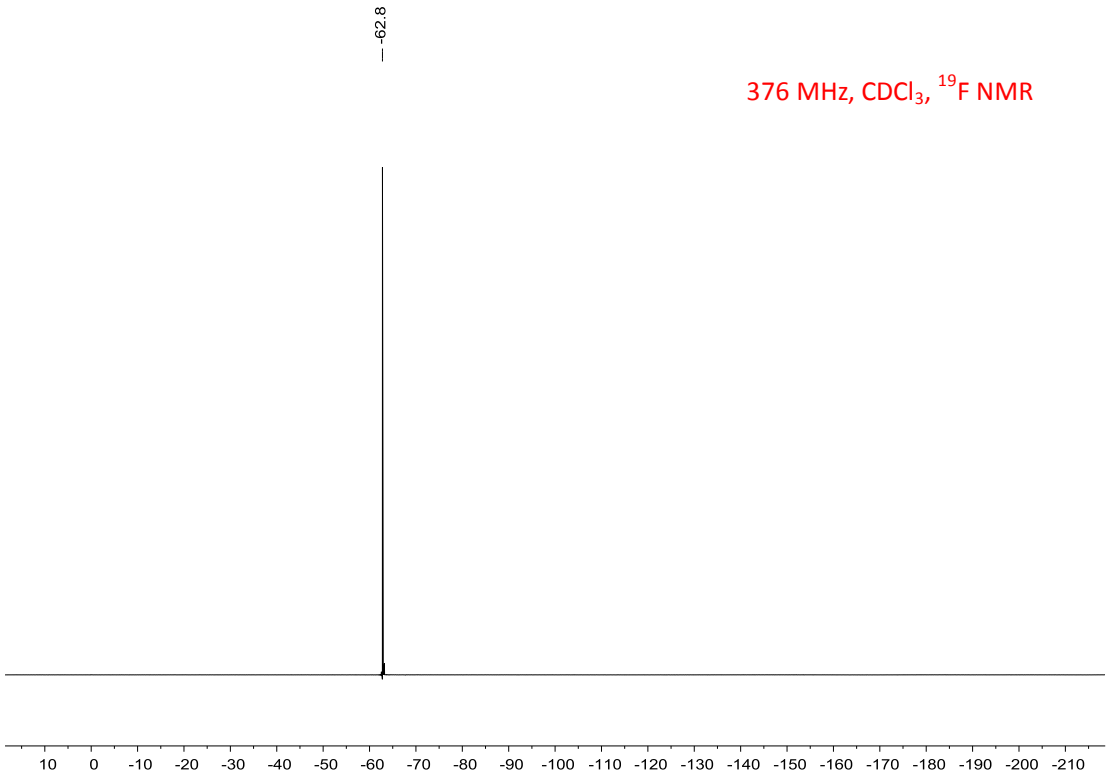


(*S*)-2-Hydroxy-2-(*p*-tolyl)cyclohexan-1-one (2e)

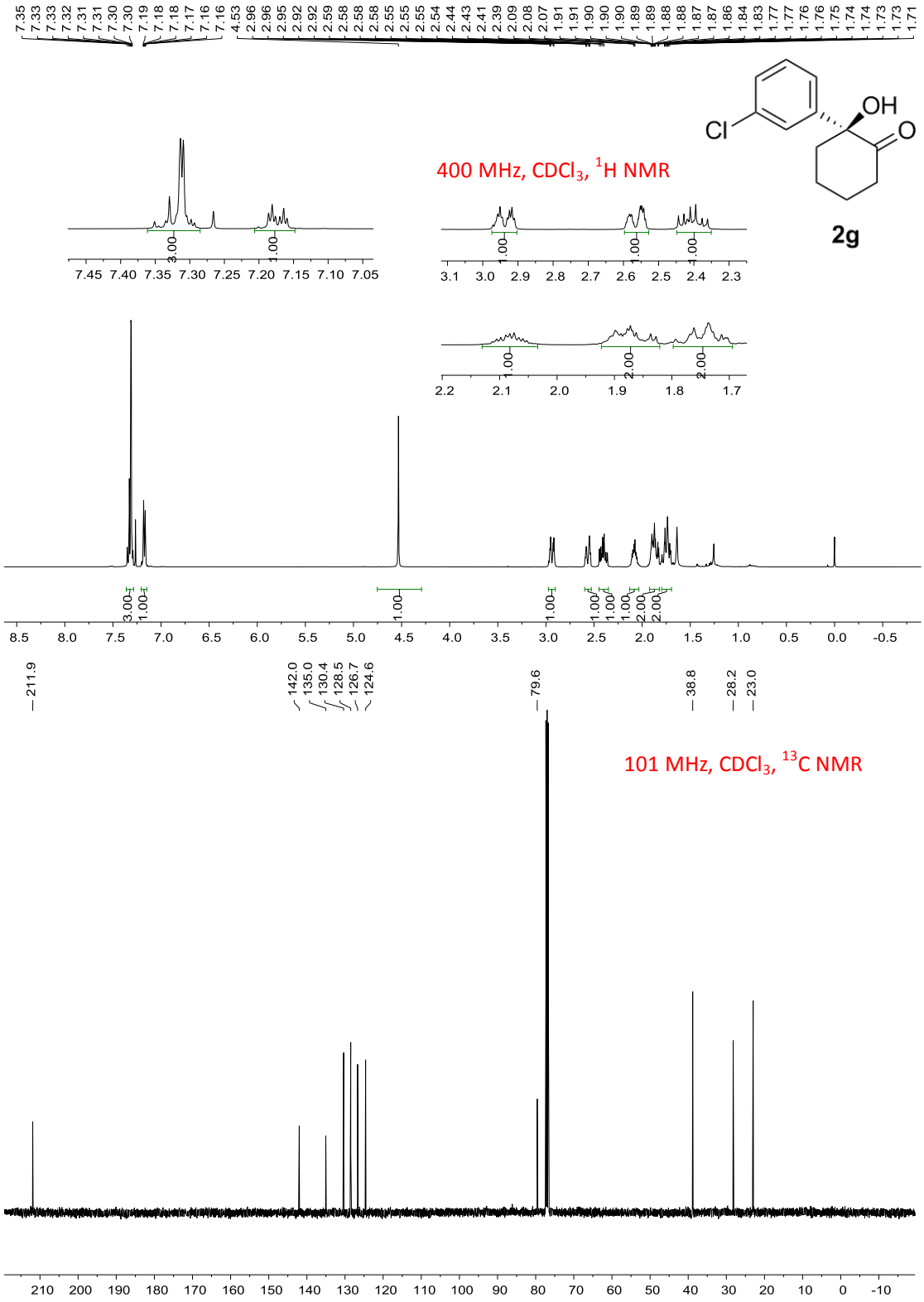


(*S*)-2-Hydroxy-2-(4-(trifluoromethyl)phenyl)cyclohexan-1-one (2f)

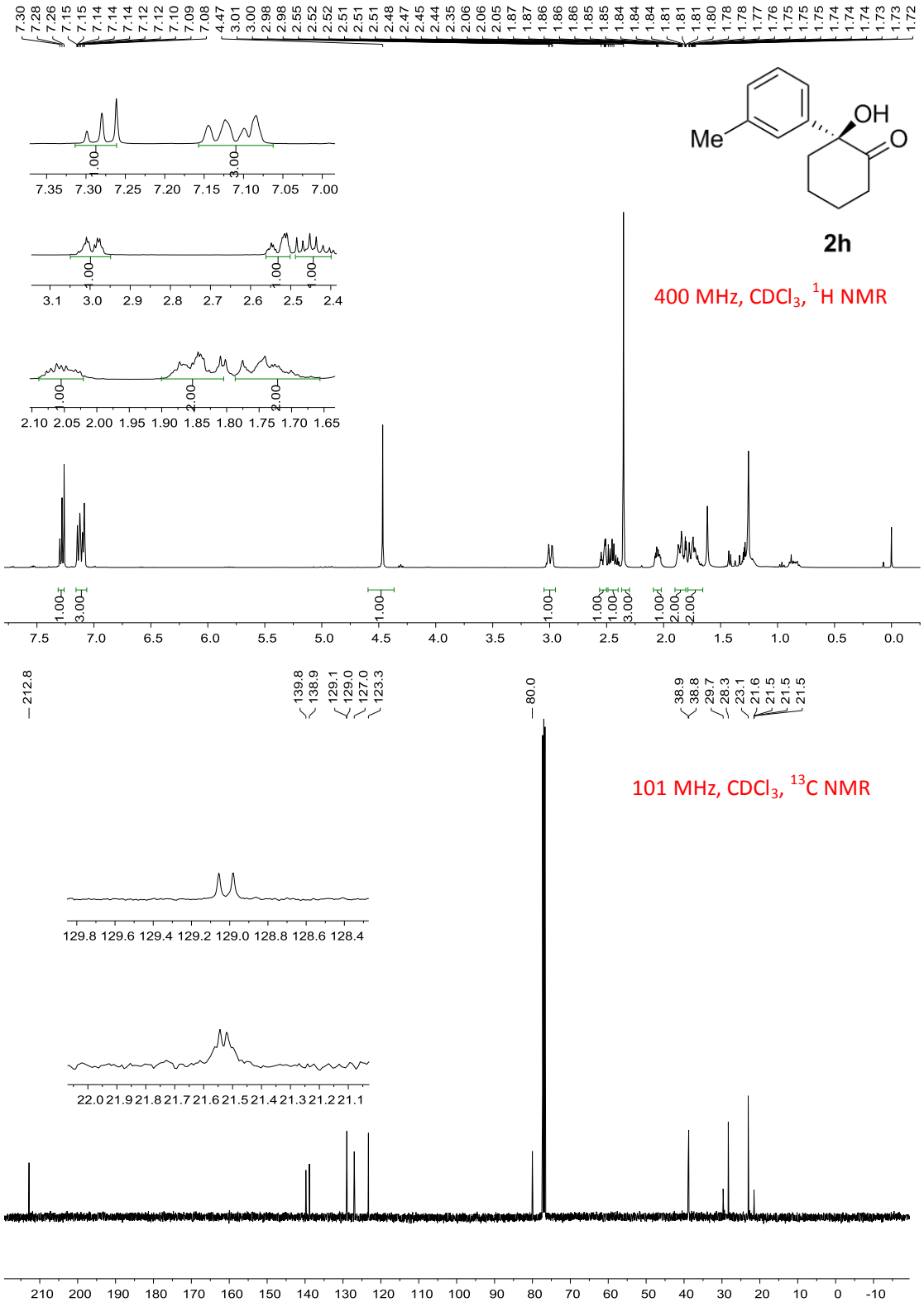



-62.8
376 MHz, CDCl3, 19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

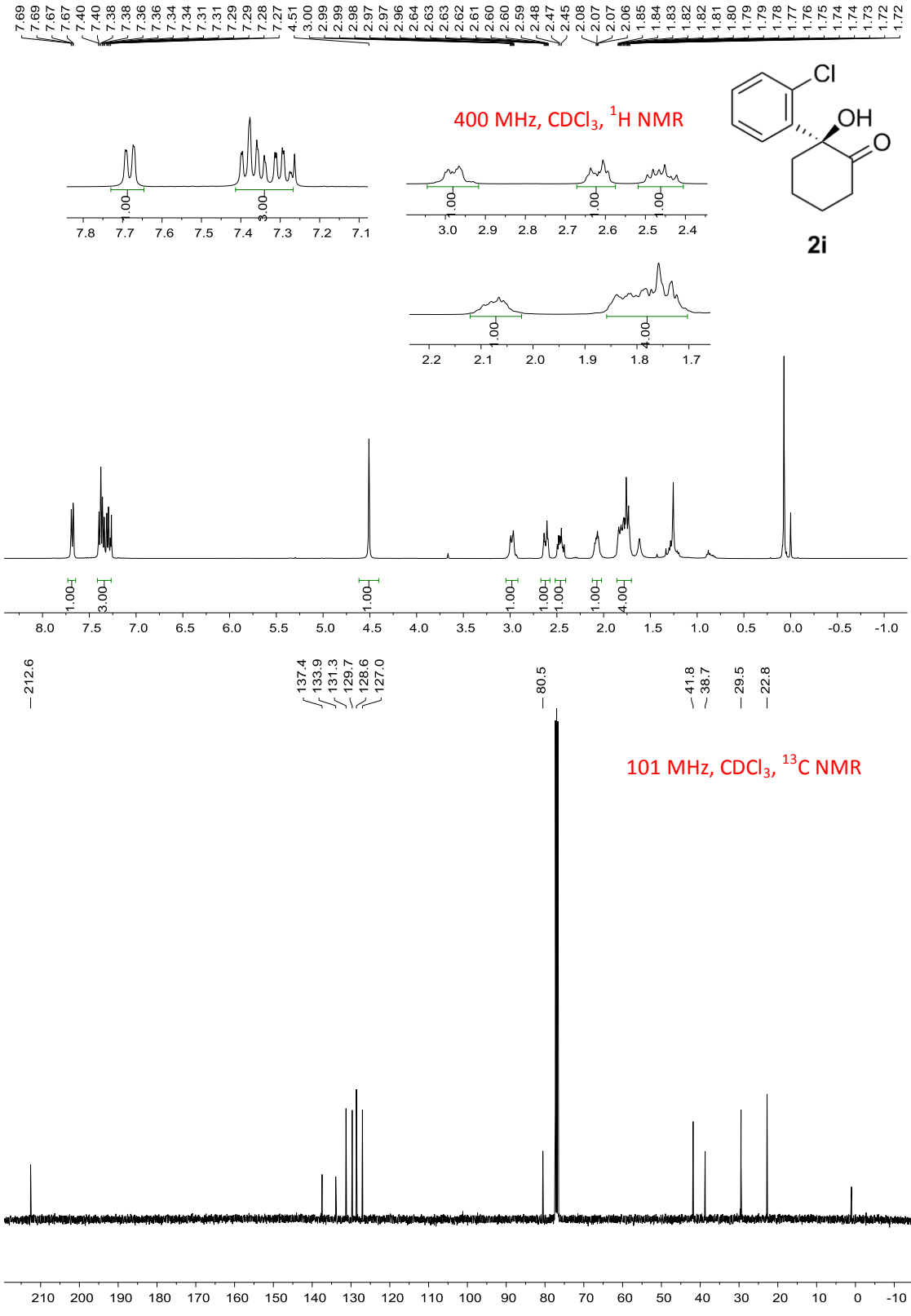
(*S*)-2-(3-Chlorophenyl)-2-hydroxycyclohexan-1-one (2g)



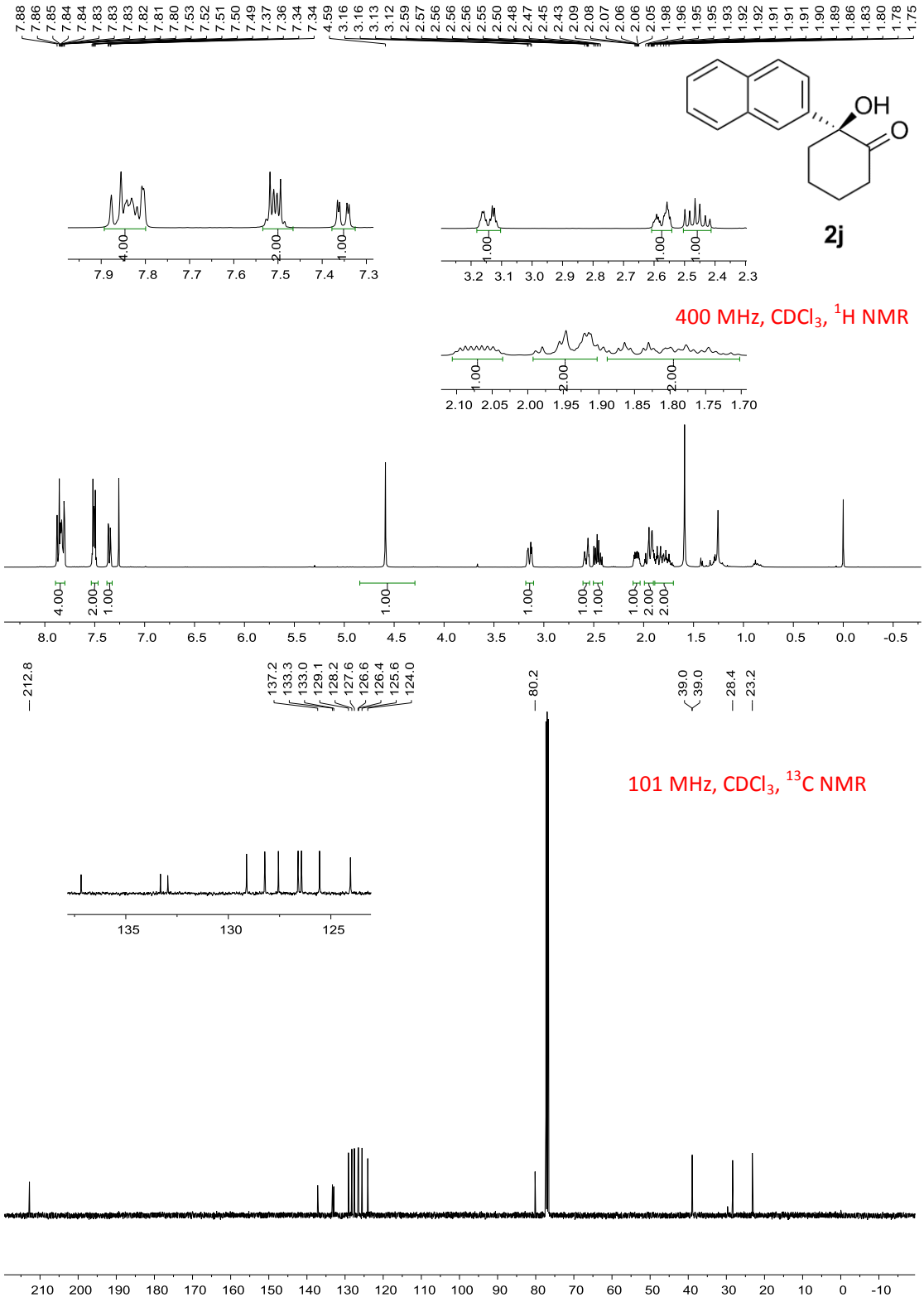
(*S*)-2-Hydroxy-2-(*m*-tolyl)cyclohexan-1-one (2h)



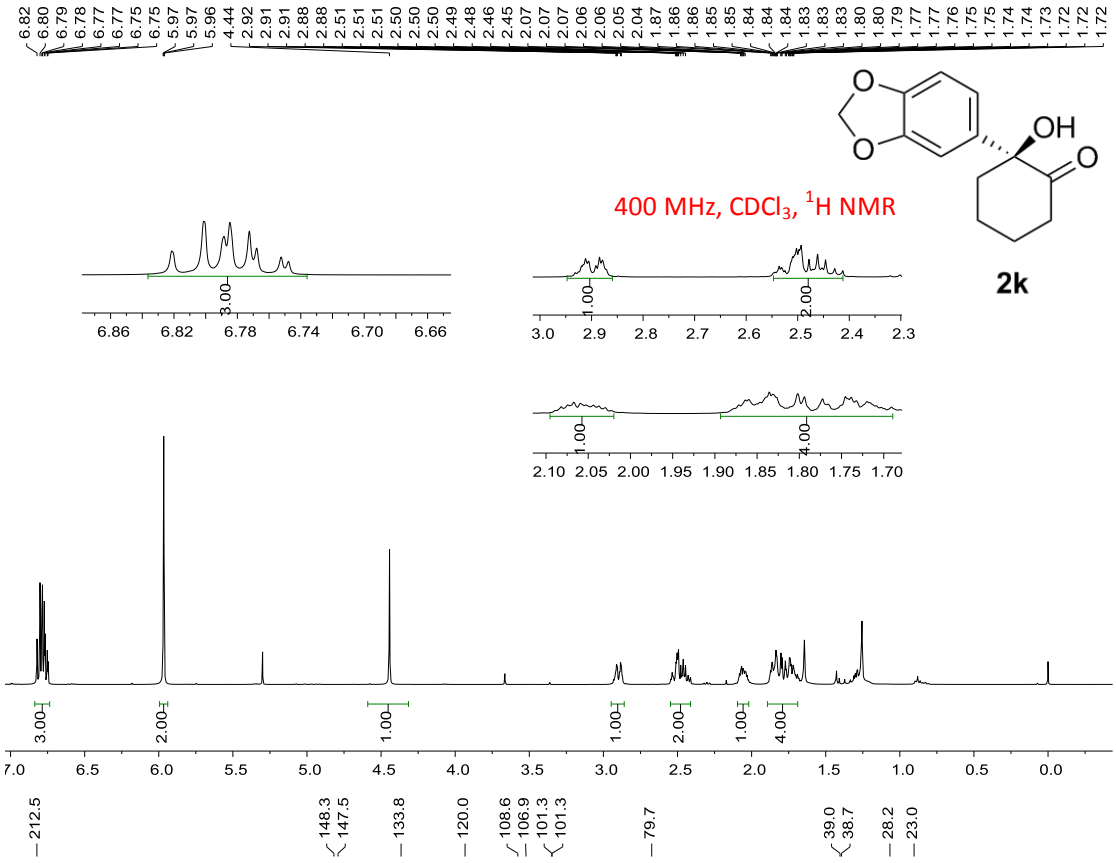
(*S*)-2-(2-Chlorophenyl)-2-hydroxycyclohexan-1-one (2i)



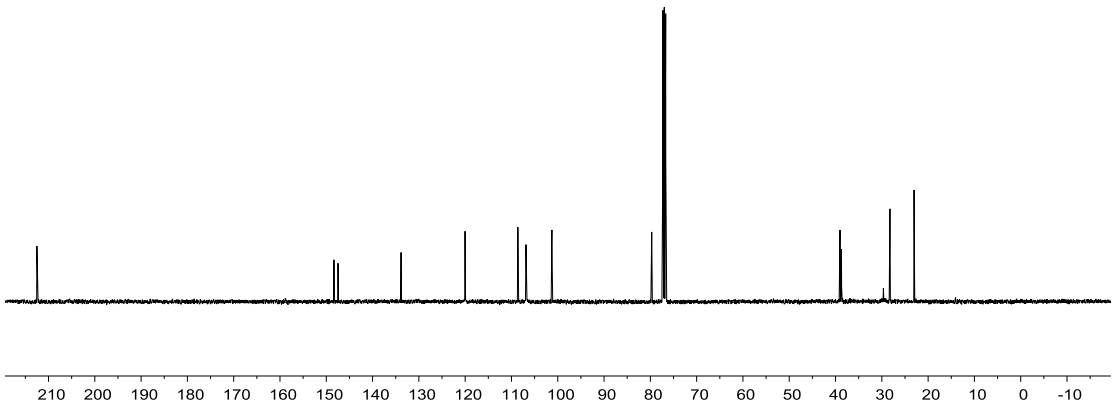
(*S*)-2-Hydroxy-2-(naphthalen-2-yl)cyclohexan-1-one (2j)



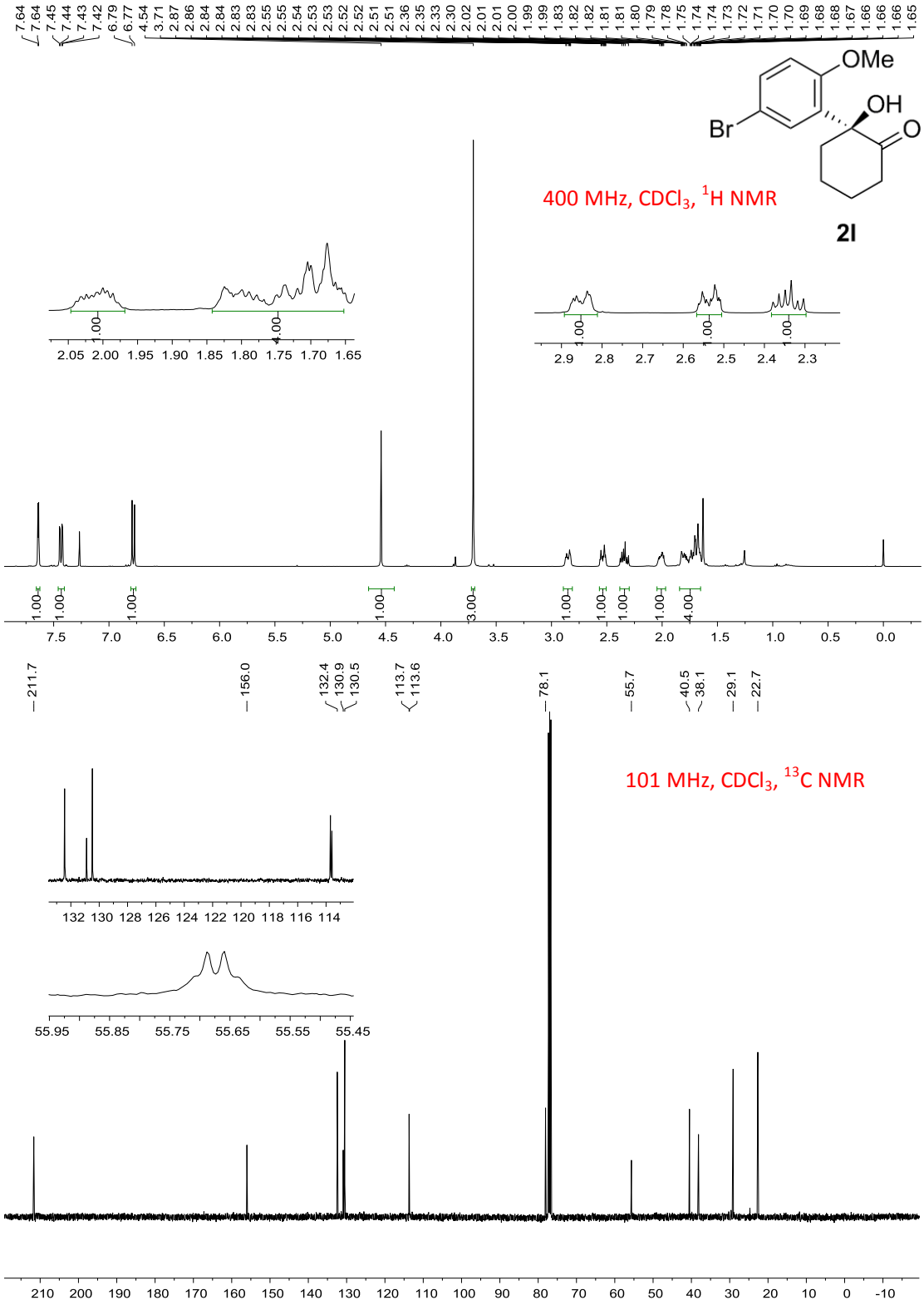
(*S*)-2-(Benzo[d][1,3]dioxol-5-yl)-2-hydroxycyclohexan-1-one (2k)



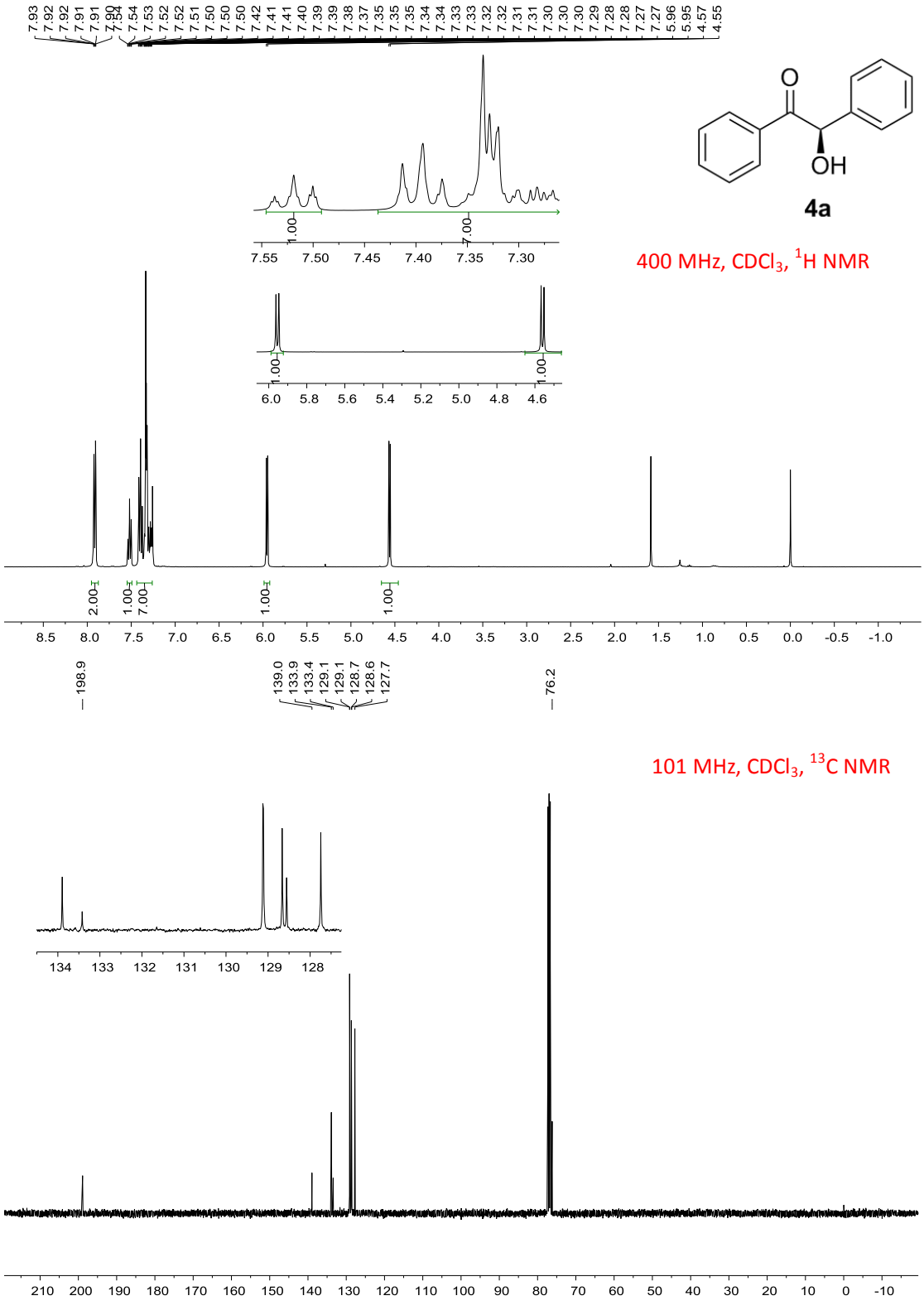
101 MHz, $CDCl_3$, ^{13}C NMR



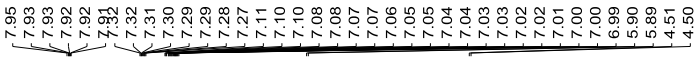
(*S*)-2-(5-Bromo-2-methoxyphenyl)-2-hydroxycyclohexan-1-one (2l)

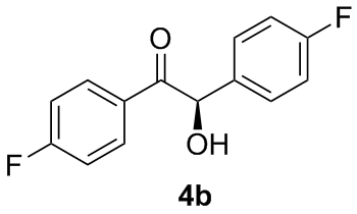


(*R*)-2-Hydroxy-1,2-diphenylethan-1-one (4a)

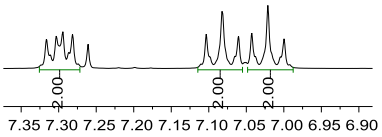


(*R*)-1,2-Bis(4-fluorophenyl)-2-hydroxyethan-1-one (4b)

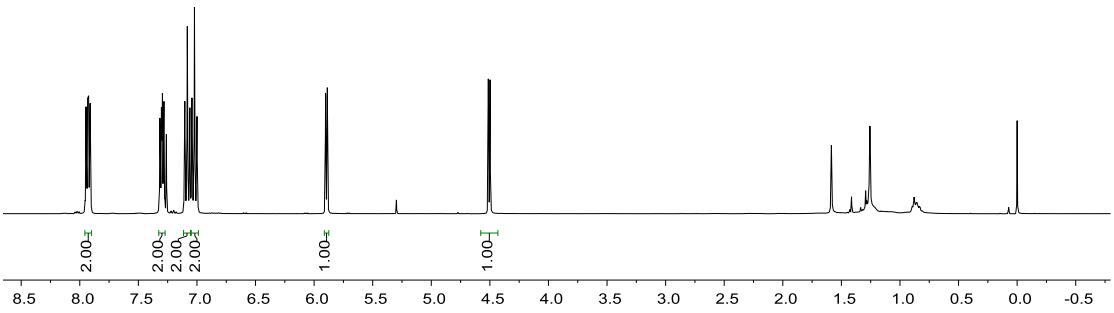




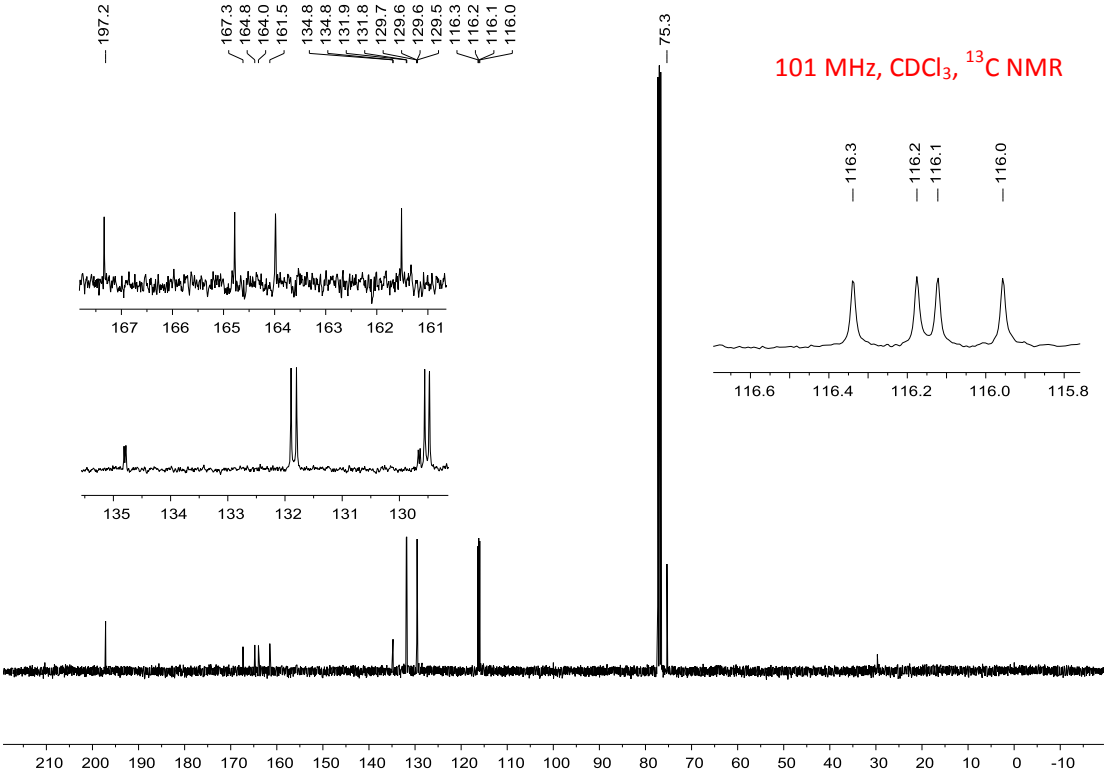
4b

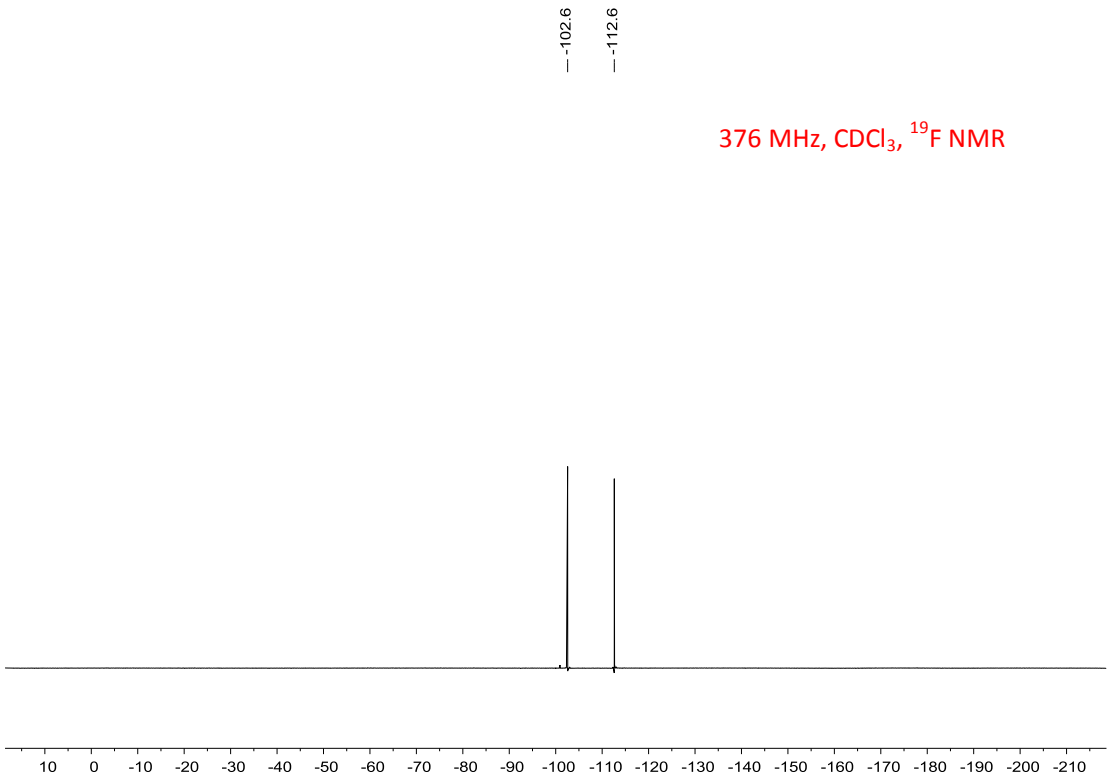


400 MHz, $CDCl_3$, ^1H NMR

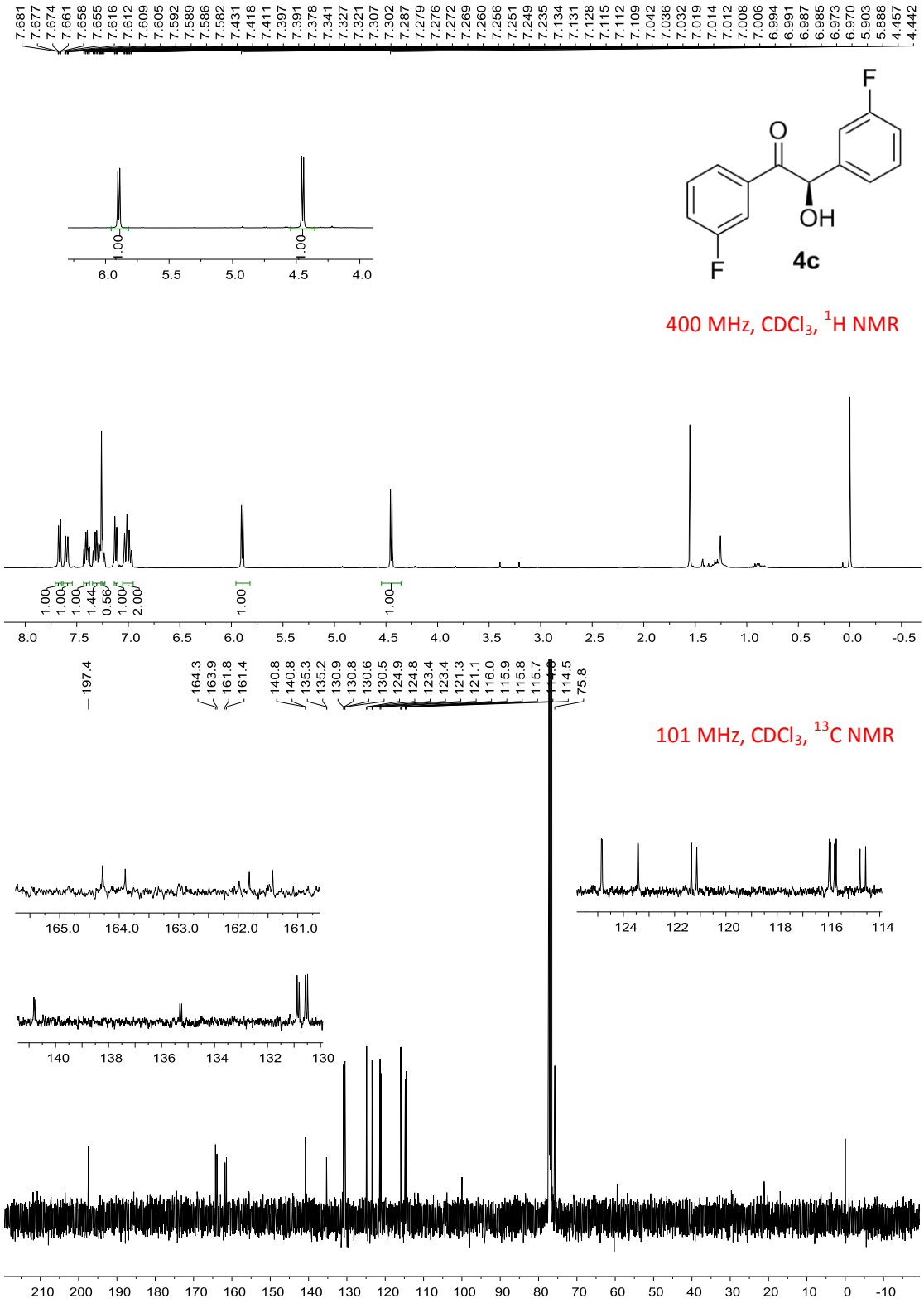


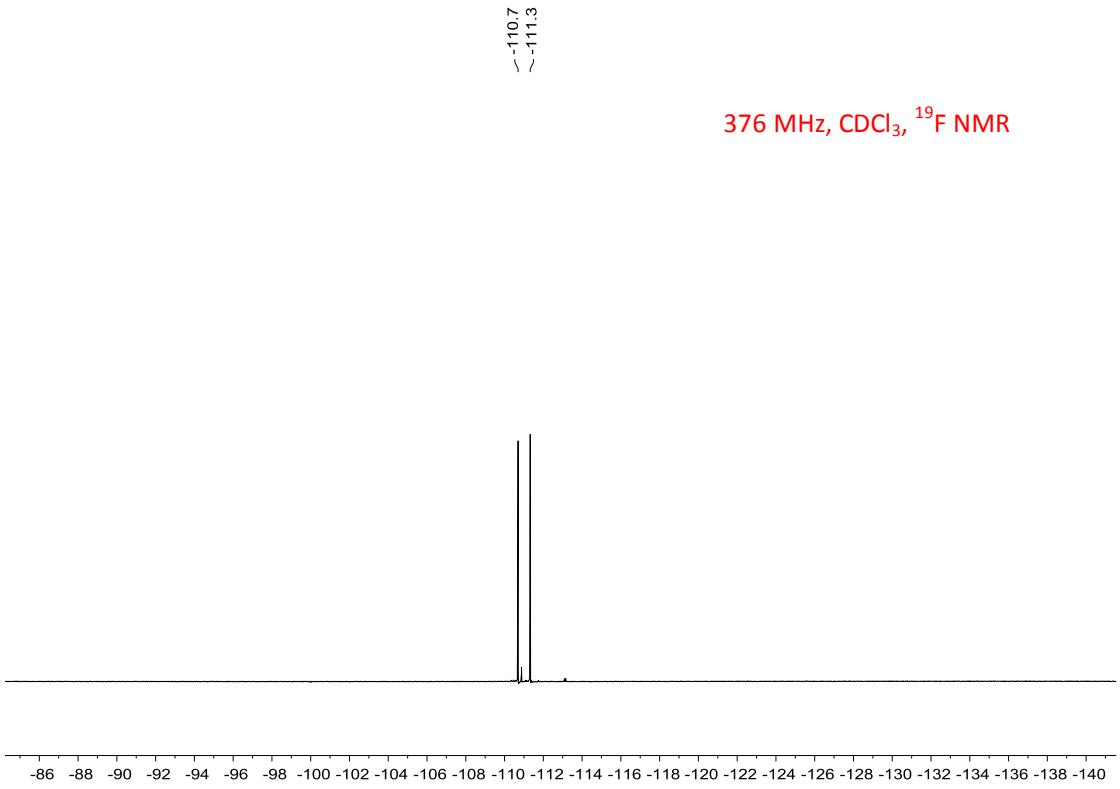
101 MHz, $CDCl_3$, ^{13}C NMR




-102.6
-112.6
376 MHz, CDCl3, 19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

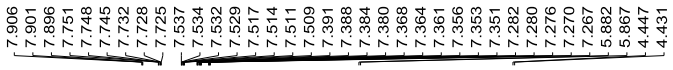
(*R*)-1,2-Bis(3-fluorophenyl)-2-hydroxyethan-1-one (4c)

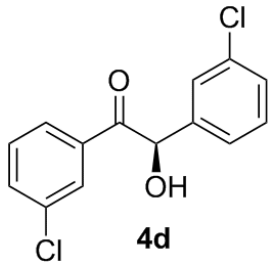




376 MHz, $CDCl_3$, ^{19}F NMR

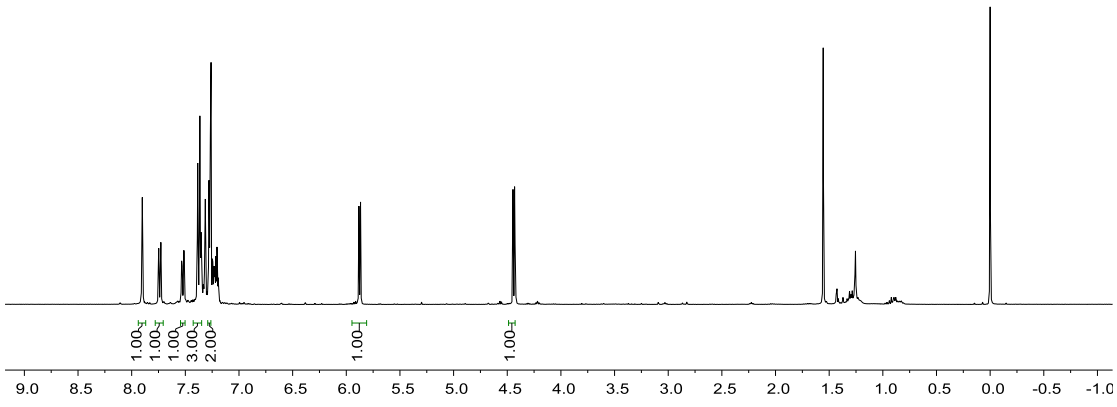
(*R*)-1,2-Bis(3-chlorophenyl)-2-hydroxyethan-1-one (4d)

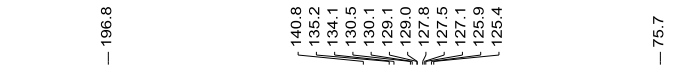




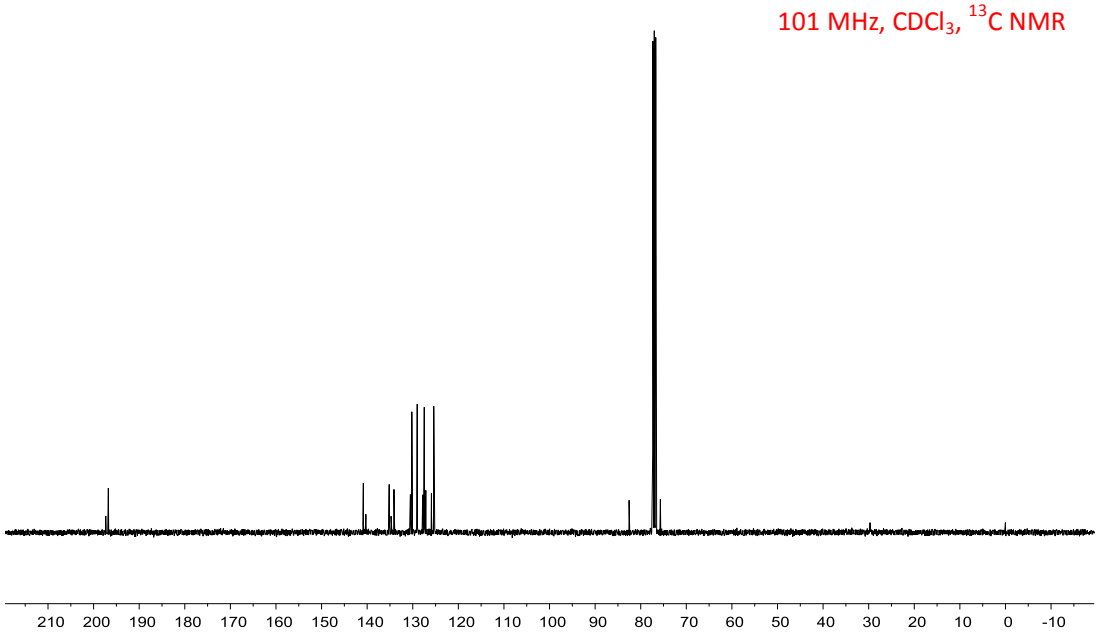
4d

400 MHz, $CDCl_3$, ^1H NMR

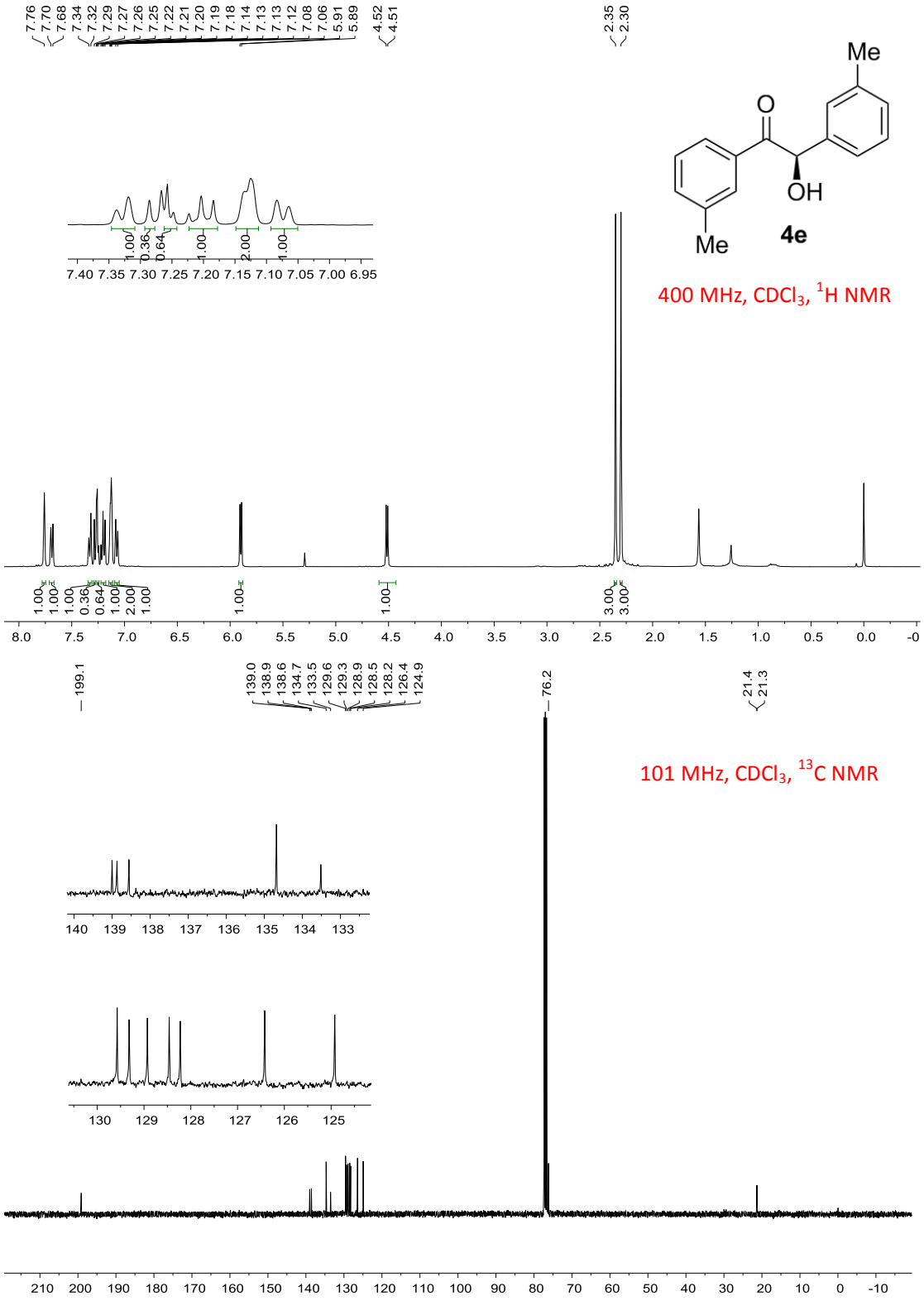




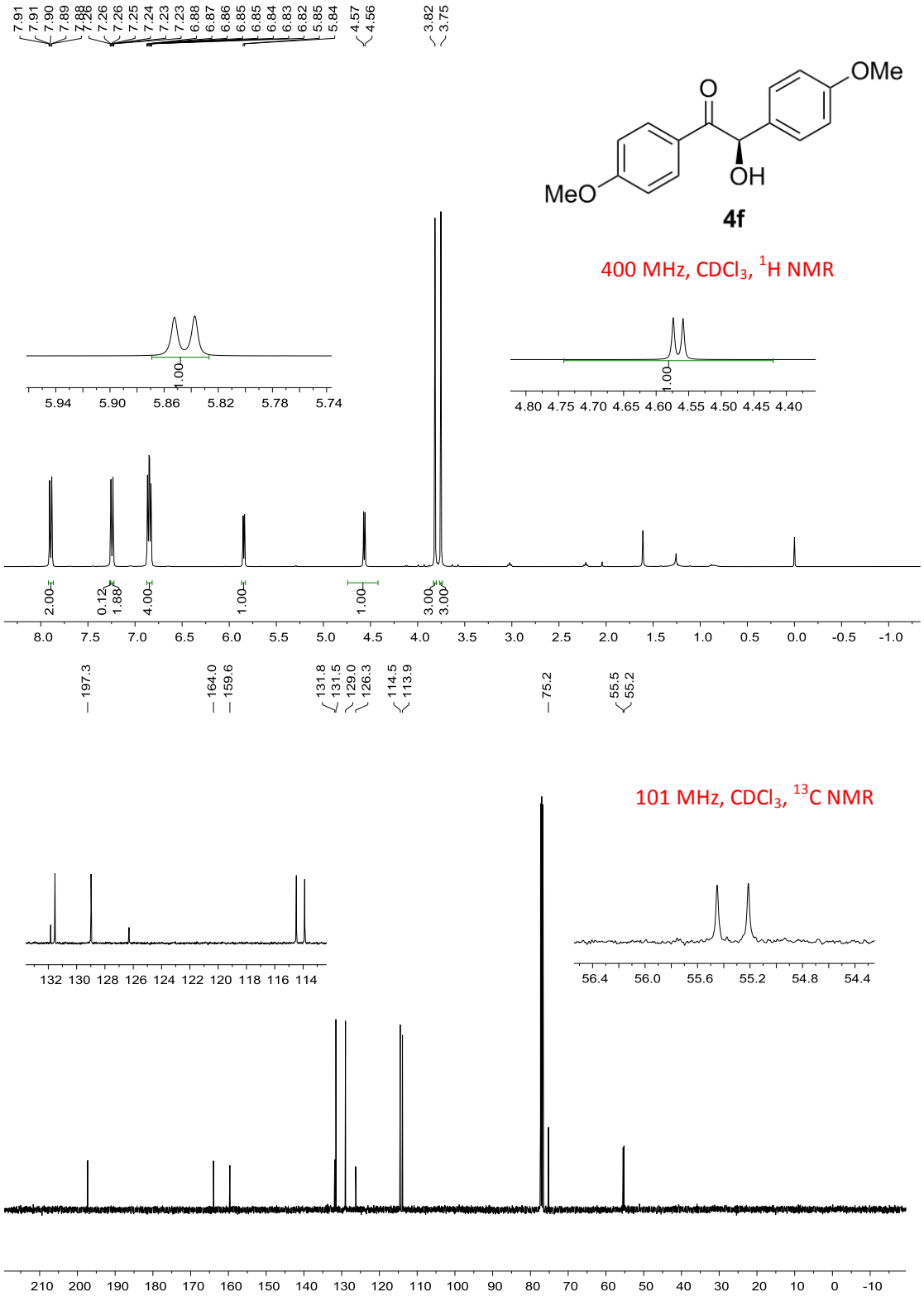
101 MHz, $CDCl_3$, ^{13}C NMR



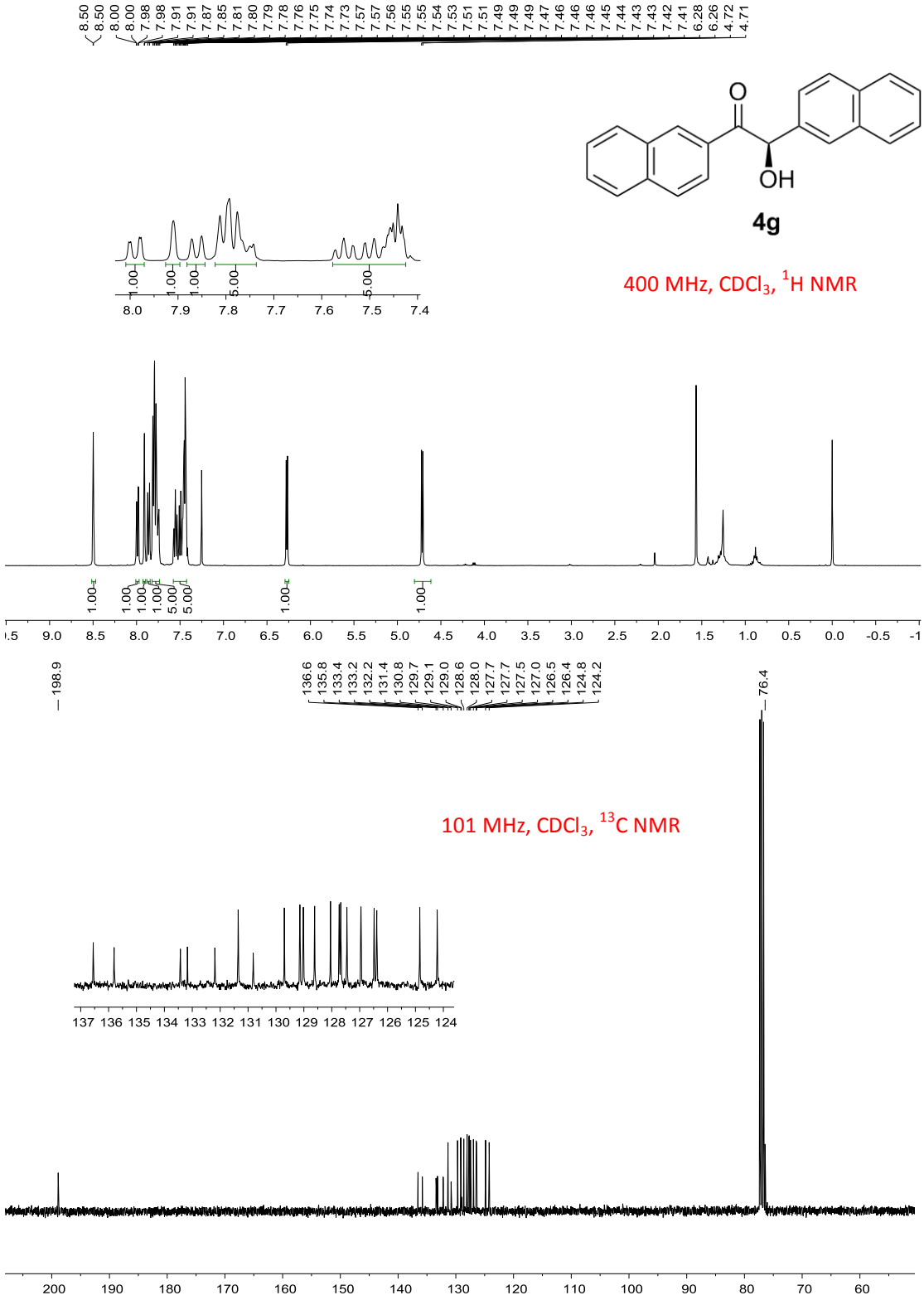
(*R*)-2-Hydroxy-1,2-di-*m*-tolylethan-1-one (4e)



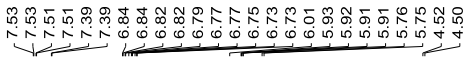
(*R*)-2-Hydroxy-1,2-bis(4-methoxyphenyl)ethan-1-one (4f)

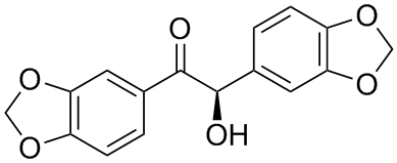


(*R*)-2-Hydroxy-1,2-di(naphthalen-2-yl)ethan-1-one (4g)



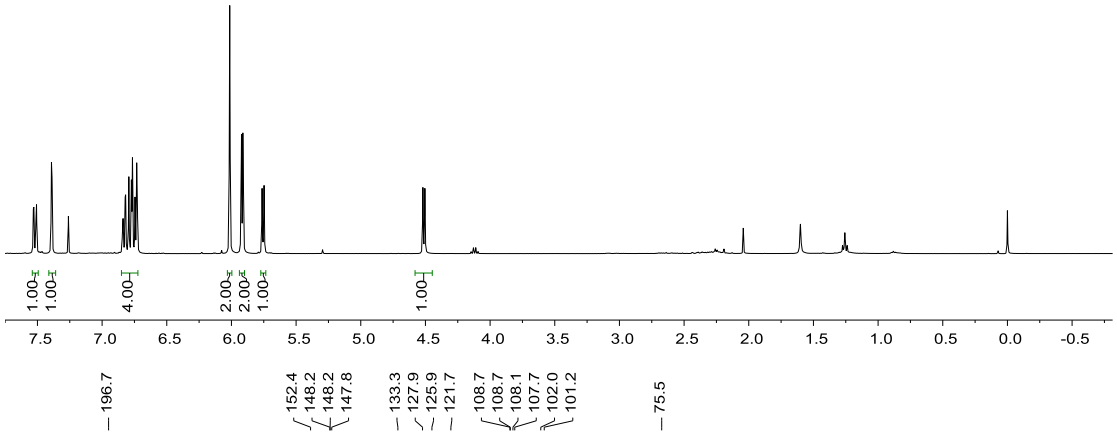
(*R*)-1,2-Bis(benzo[d][1,3]dioxol-5-yl)-2-hydroxyethan-1-one (4h)



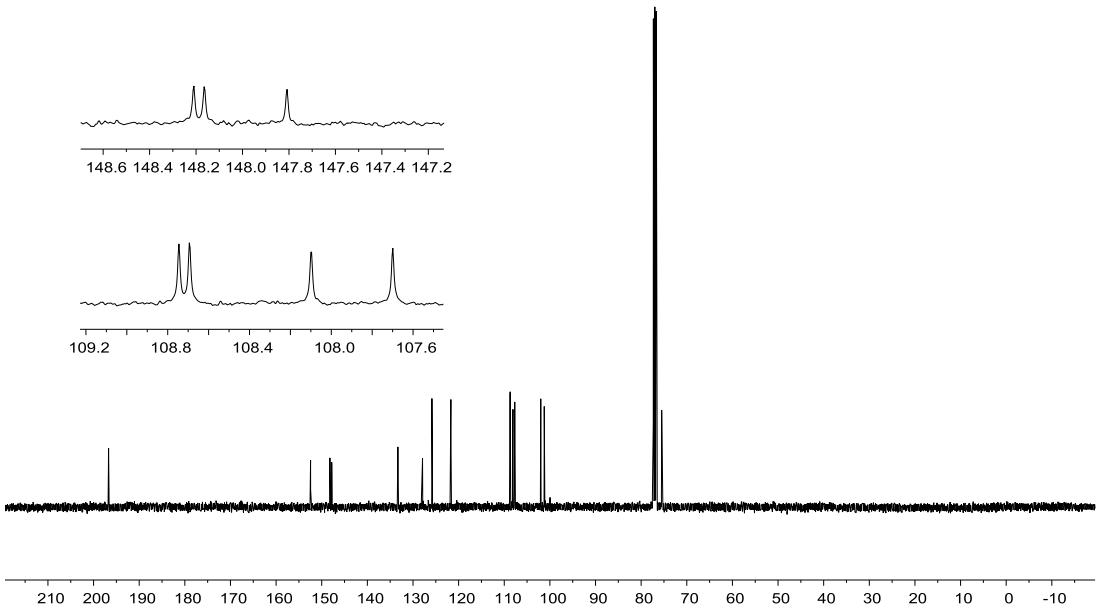


4h

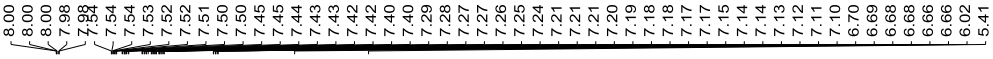
400 MHz, $CDCl_3$, ^1H NMR

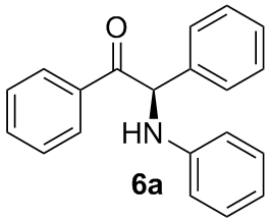


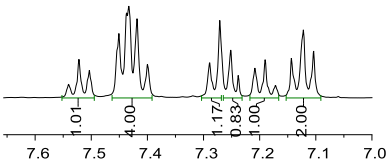
101 MHz, $CDCl_3$, ^{13}C NMR



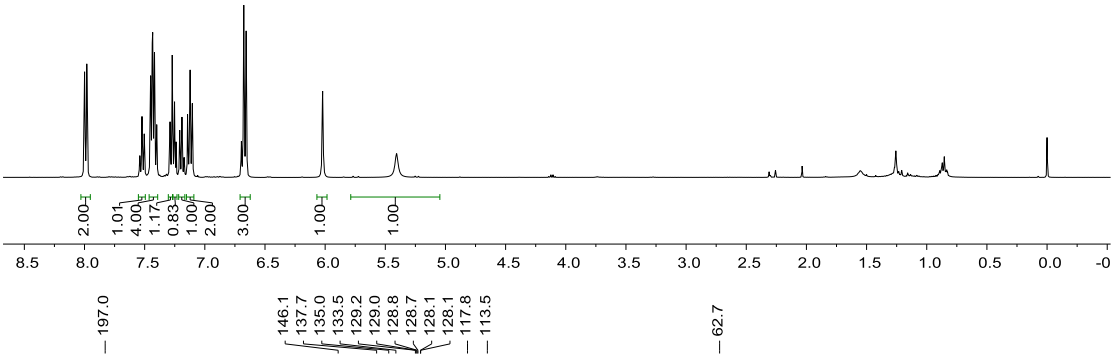
(*R*)-1,2-Diphenyl-2-(phenylamino)ethan-1-one (6a)



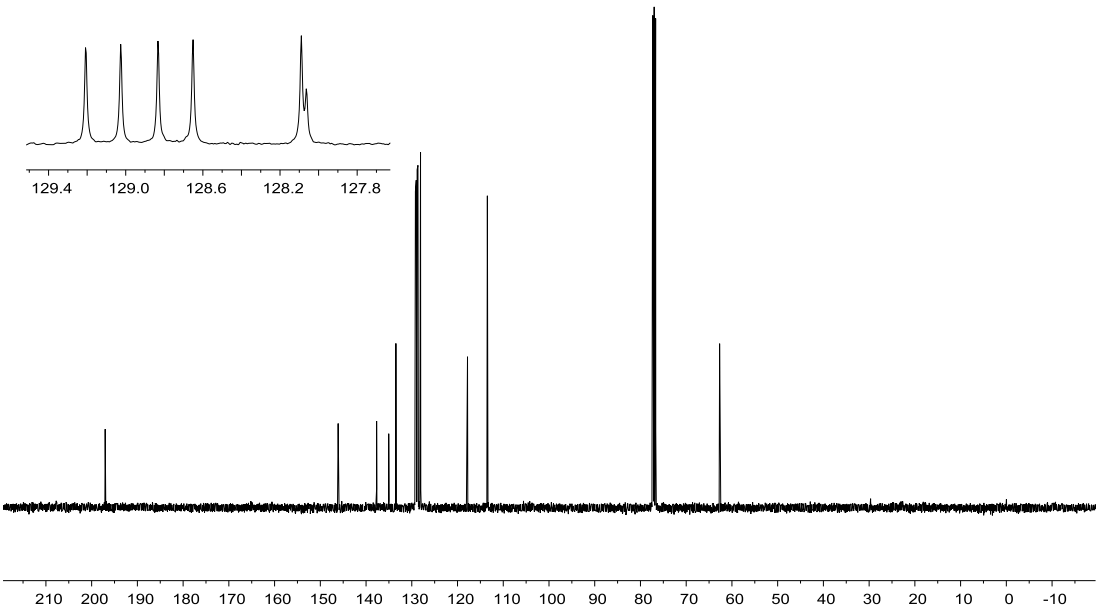




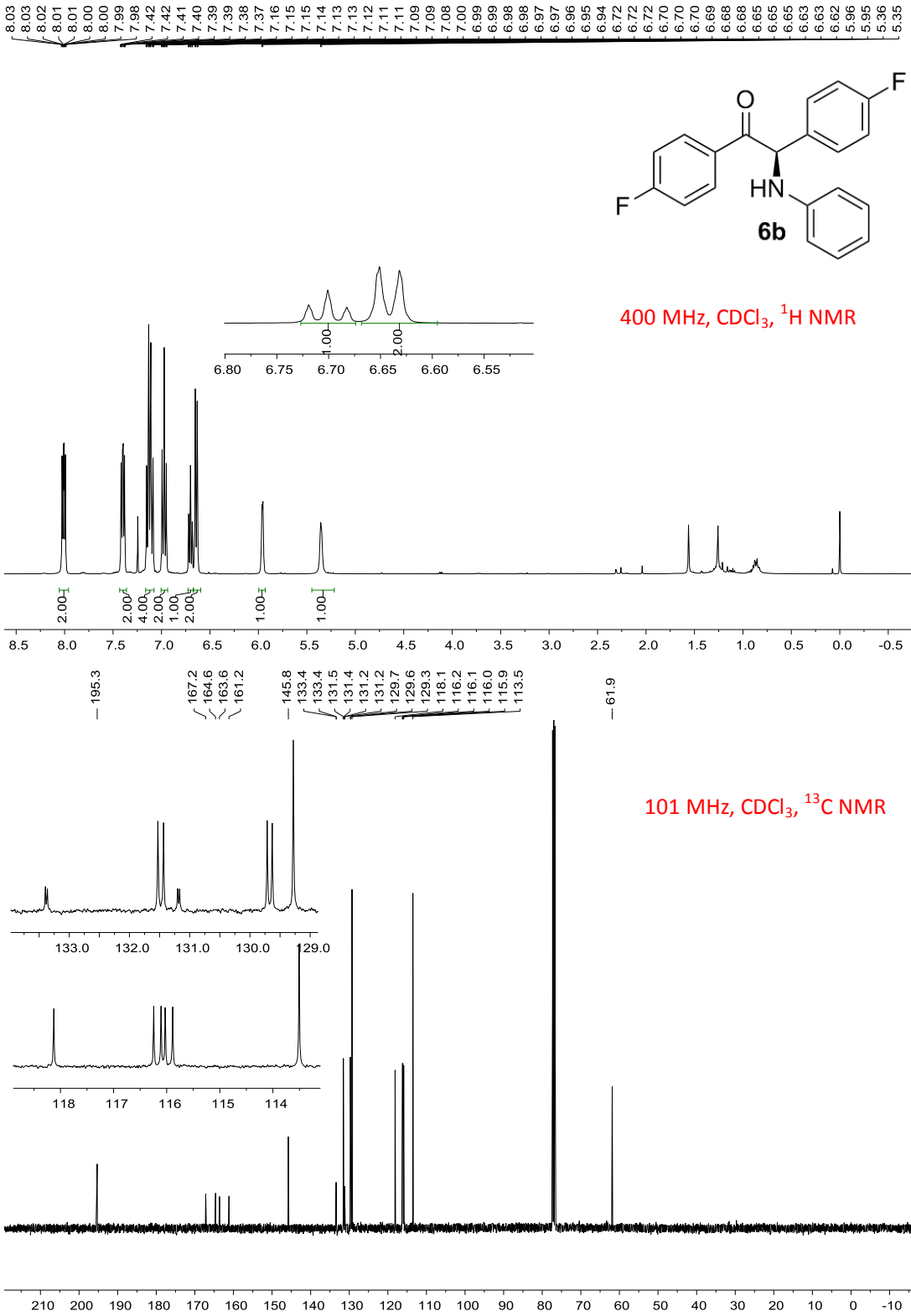
400 MHz, $CDCl_3$, ^1H NMR

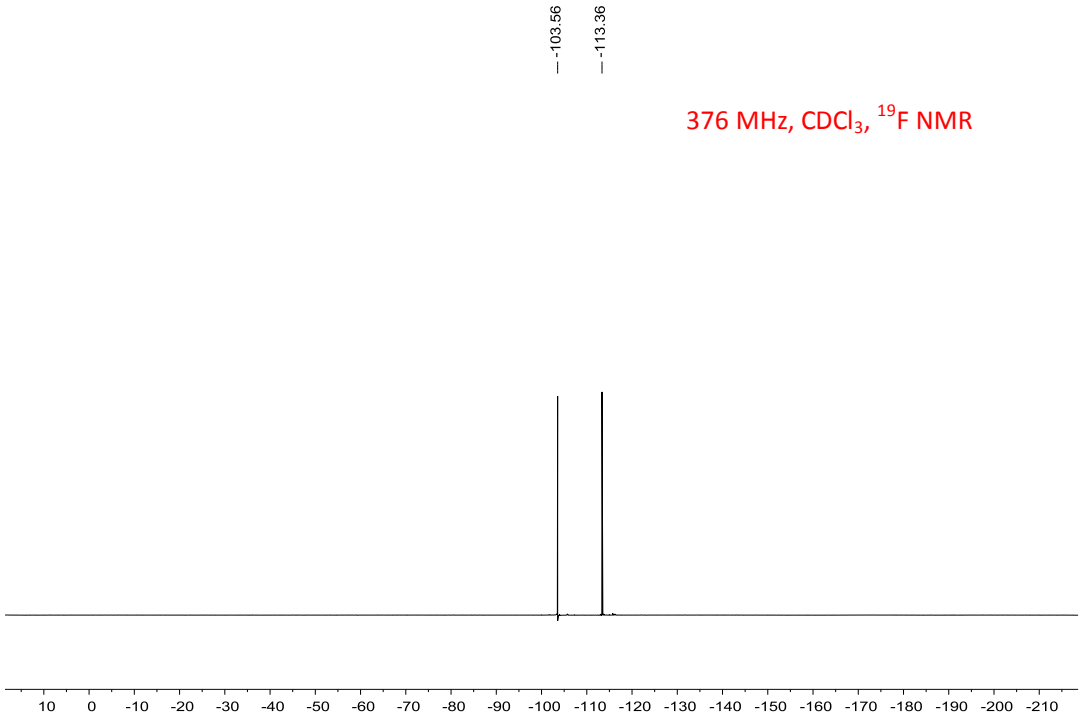


101 MHz, $CDCl_3$, ^{13}C NMR

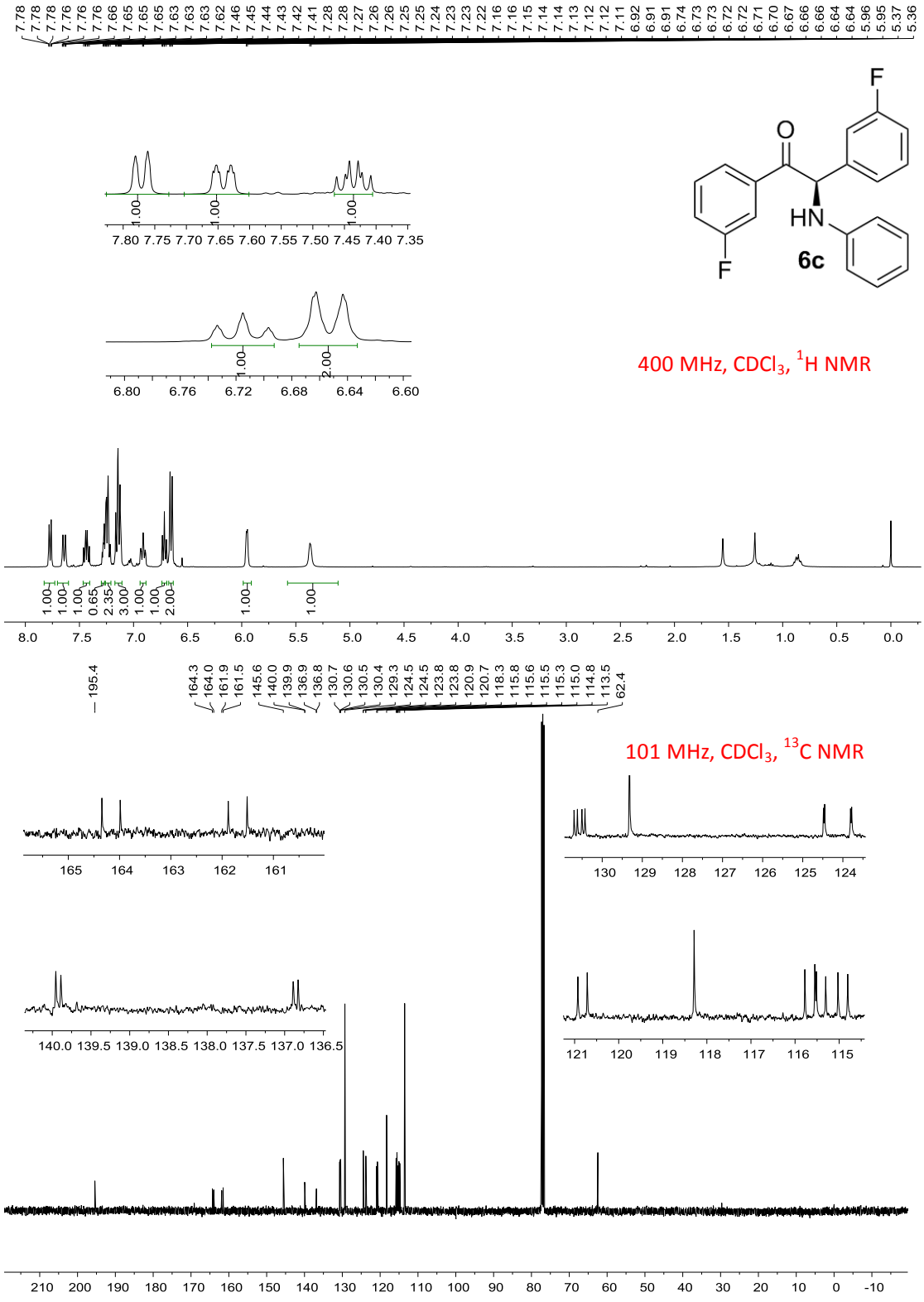


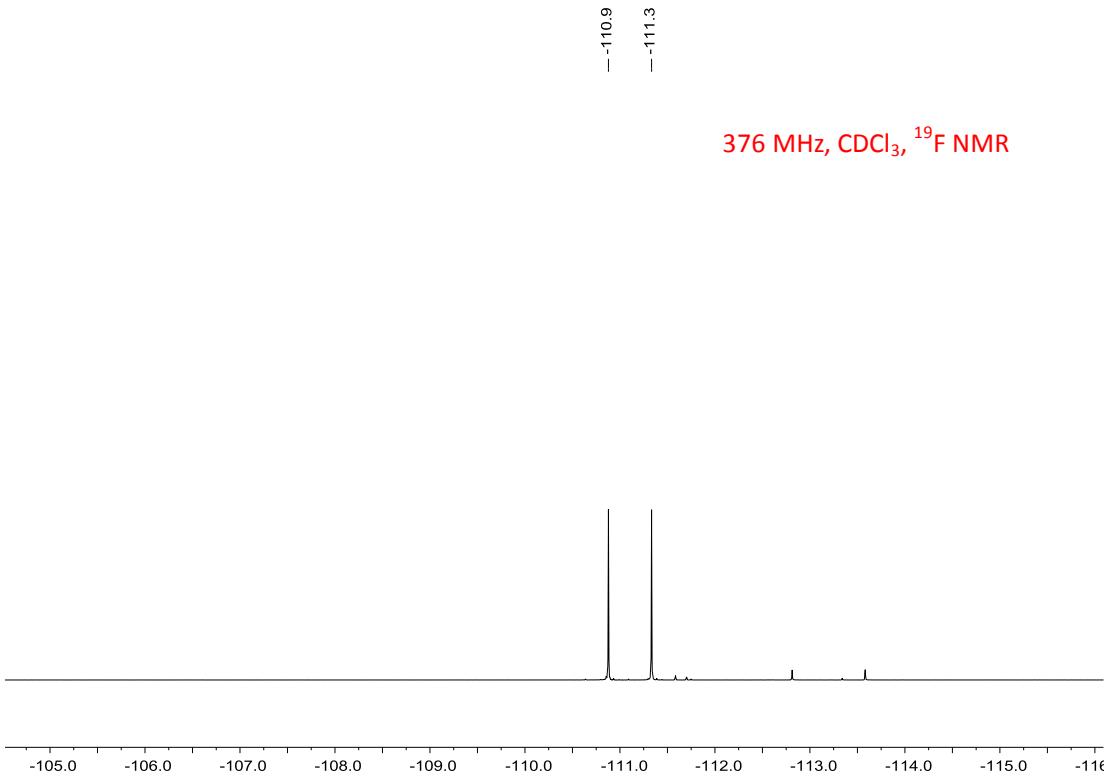
(*R*)-1,2-Bis(4-fluorophenyl)-2-(phenylamino)ethan-1-one (6b)



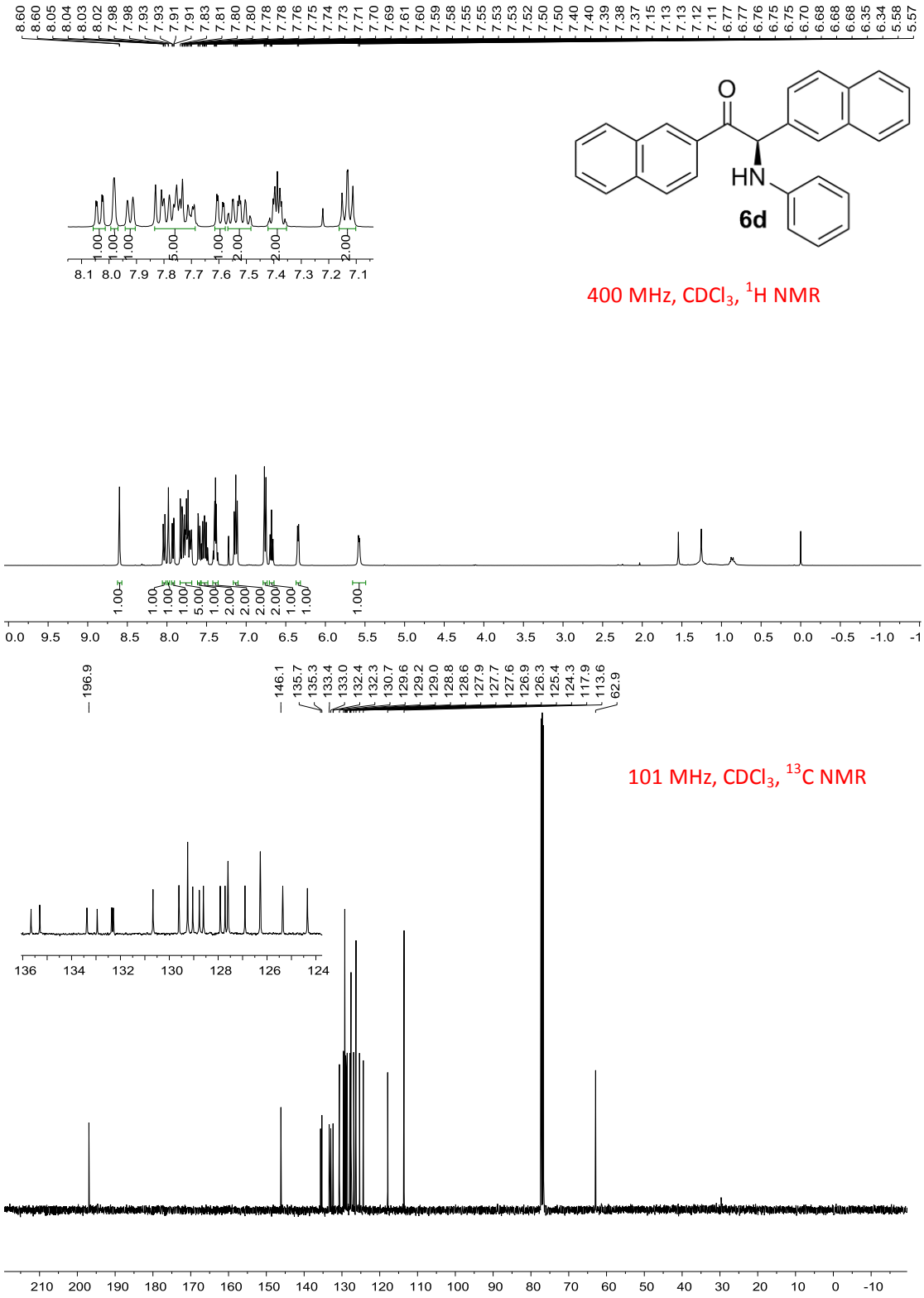

-103.56
-113.36
376 MHz, CDCl3, 19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

(*R*)-1,2-Bis(3-fluorophenyl)-2-(phenylamino)ethan-1-one (6c)

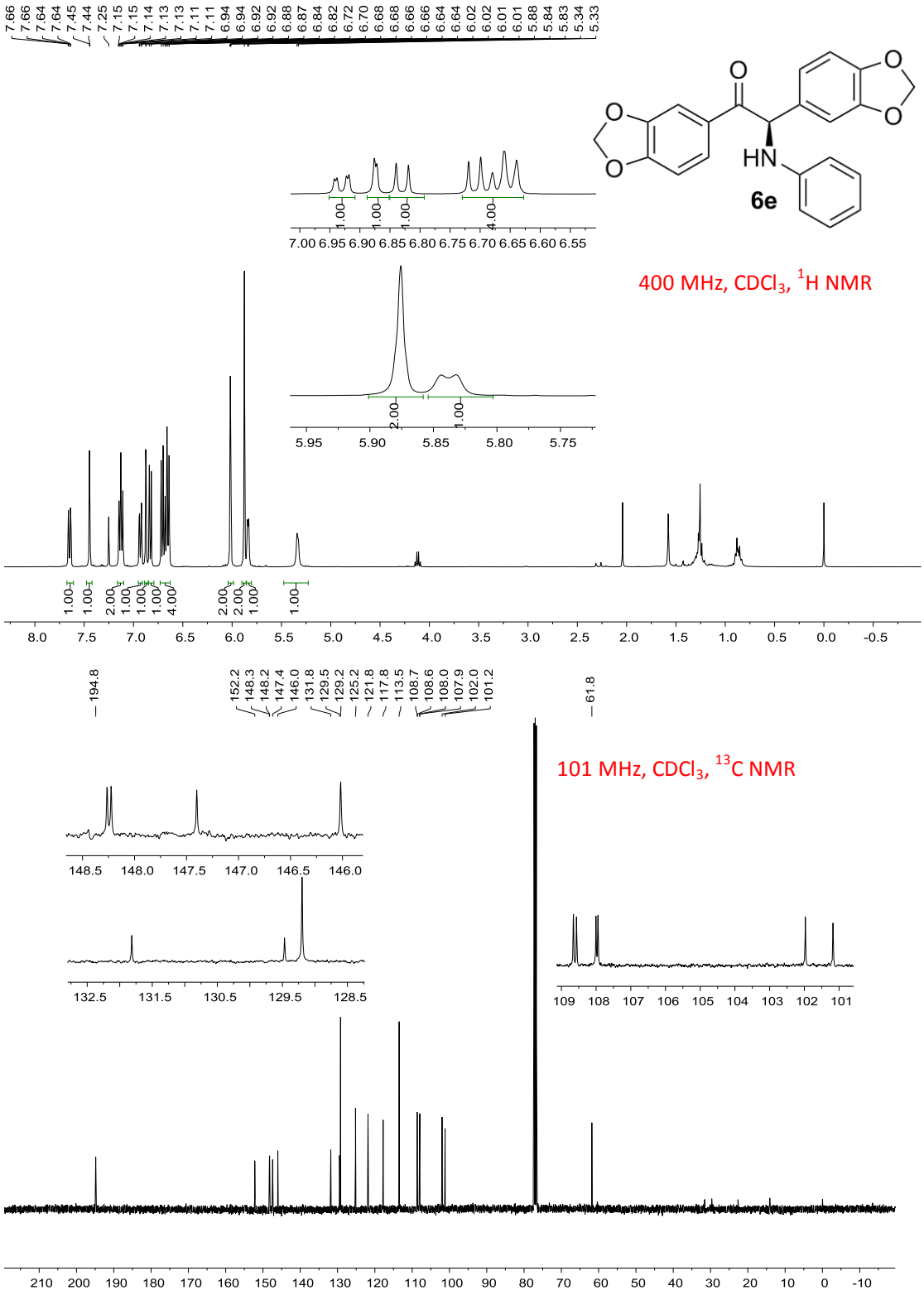



-110.9
-111.3
376 MHz, CDCl3, 19F NMR
-105.0
-106.0
-107.0
-108.0
-109.0
-110.0
-111.0
-112.0
-113.0
-114.0
-115.0

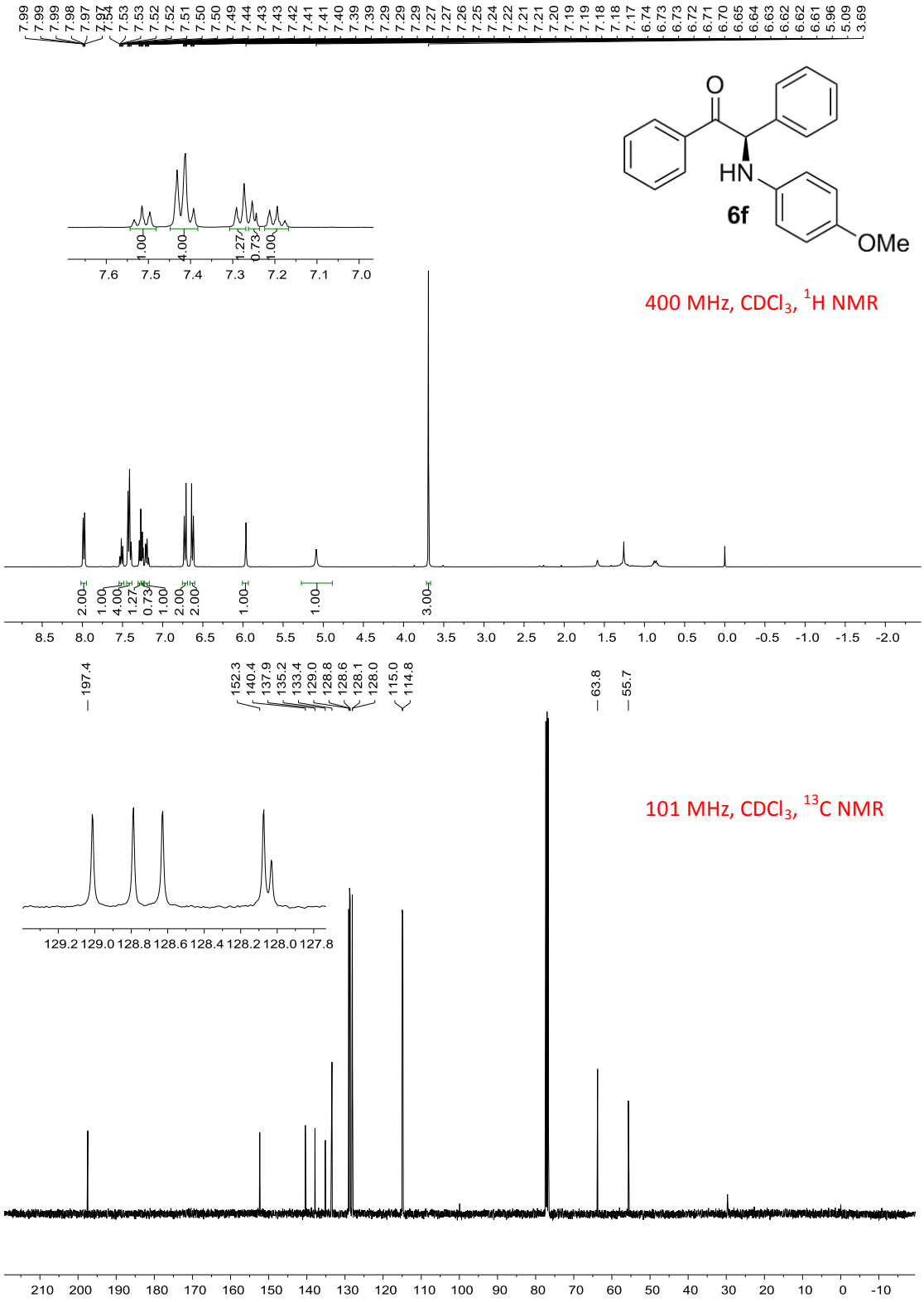
(*R*)-1,2-Di(naphthalen-2-yl)-2-(phenylamino)ethan-1-one (6d)



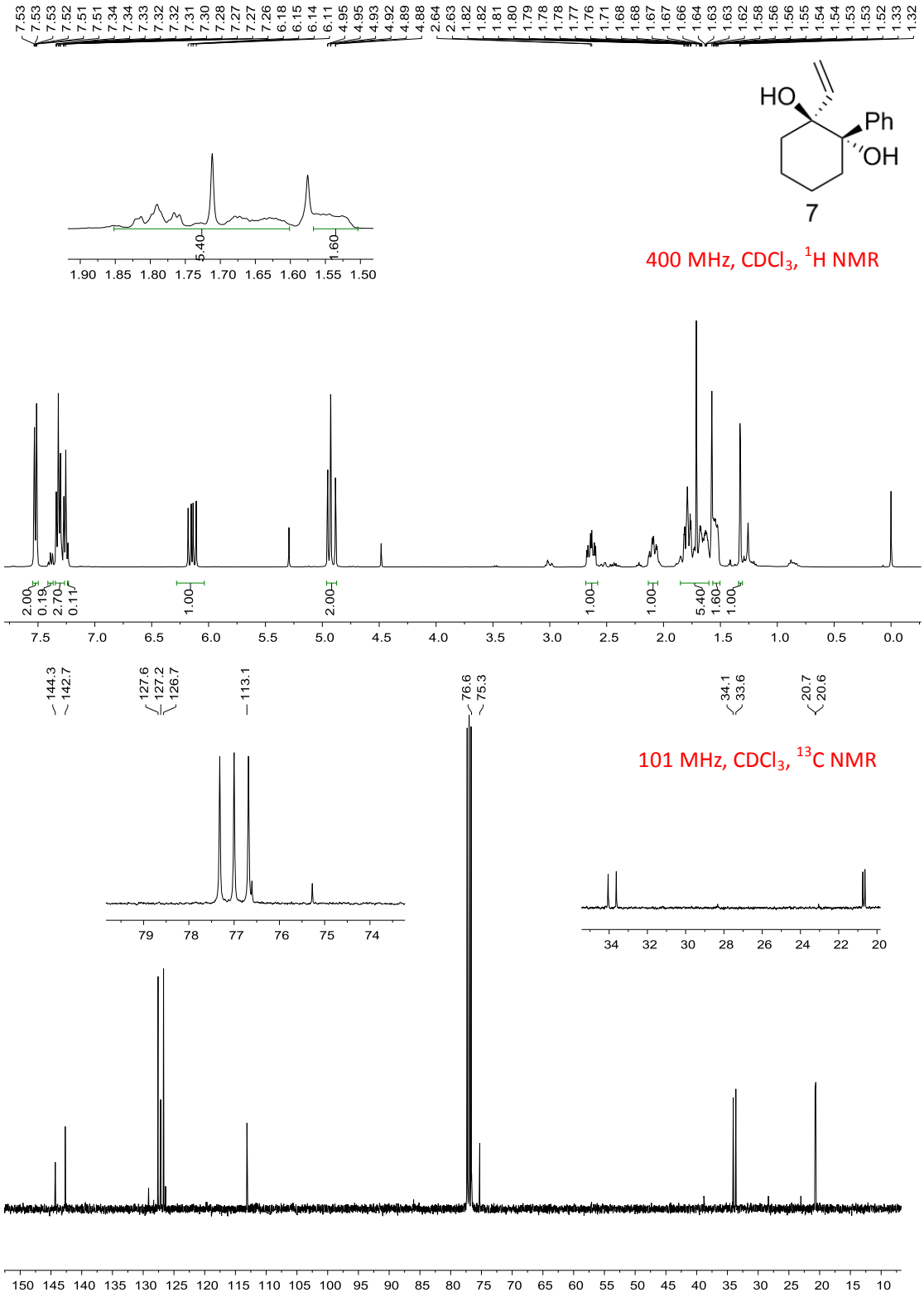
(*R*)-1,2-Bis(benzo[d][1,3]dioxol-5-yl)-2-(phenylamino)ethan-1-one (6e)



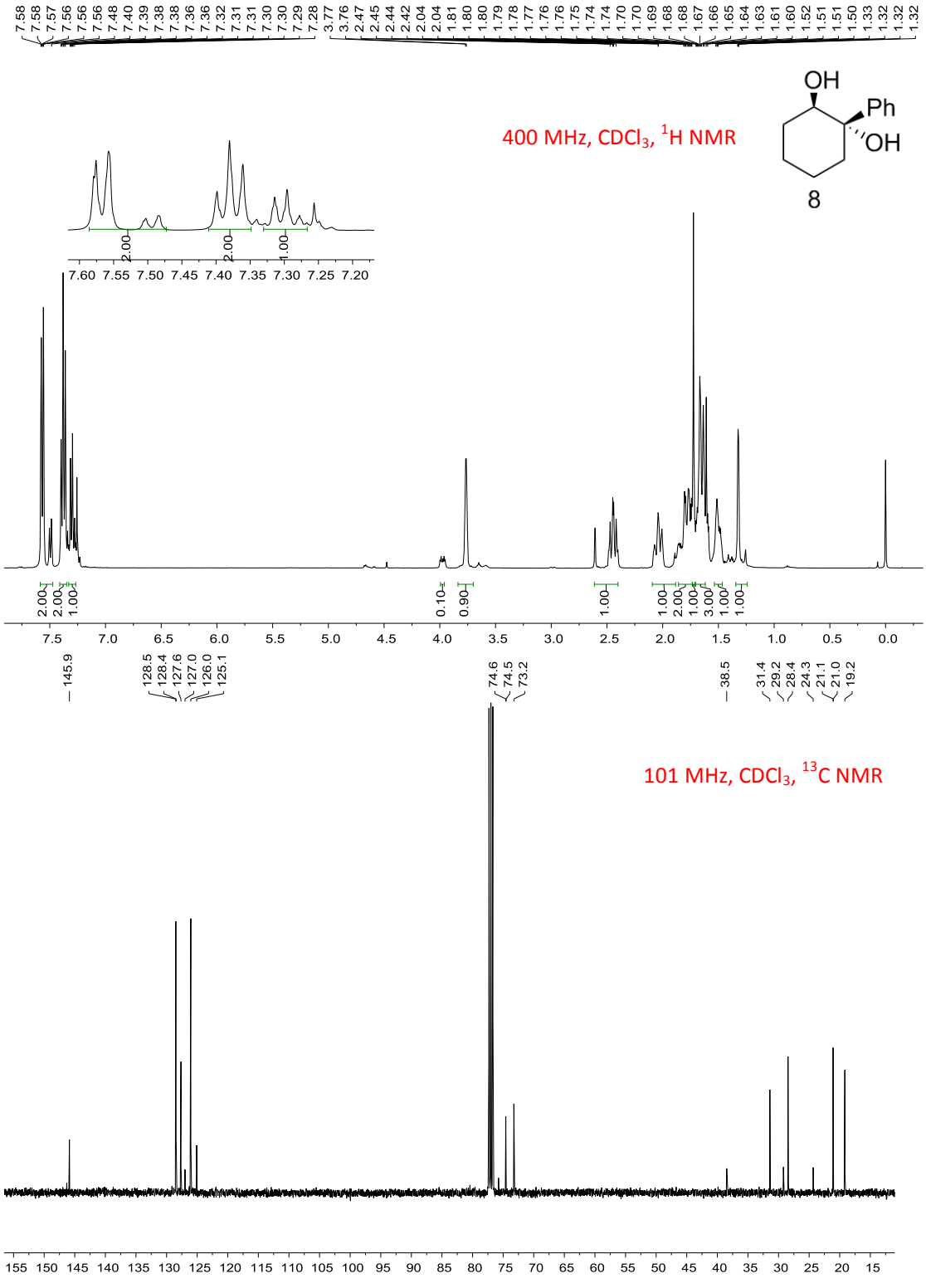
(*R*)-2-((4-Methoxyphenyl)amino)-1,2-diphenylethan-1-one (6f)



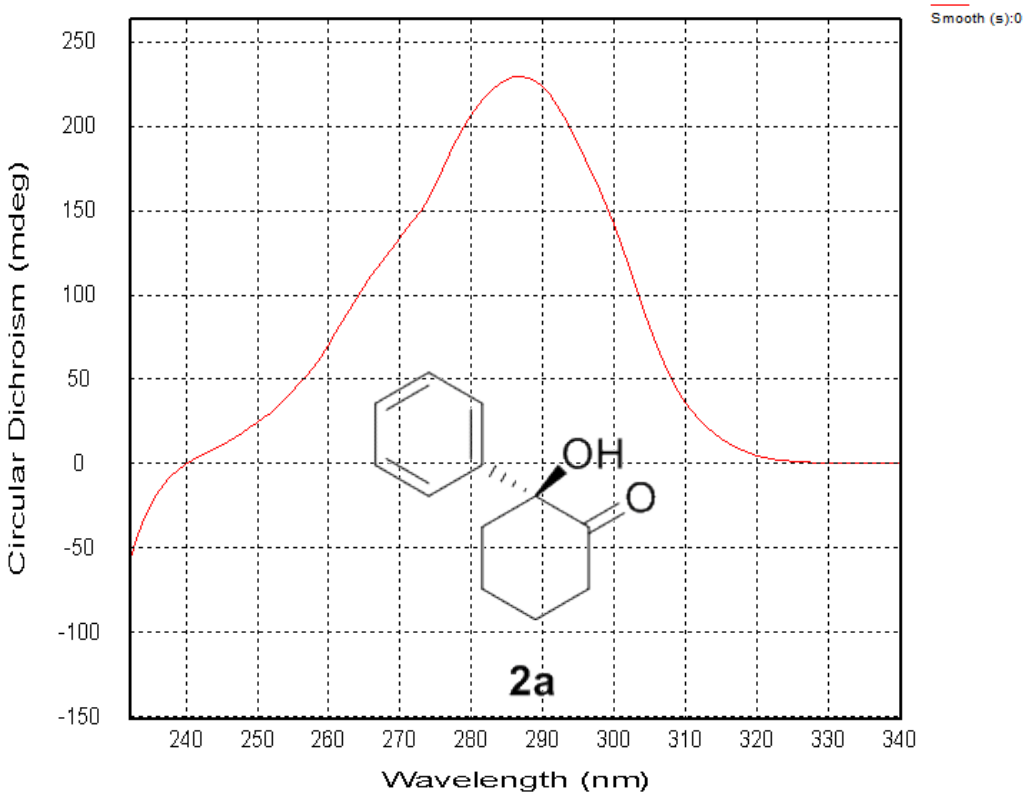
(1*S*,2*S*)-1-phenyl-2-vinylcyclohexane-1,2-diol (7)

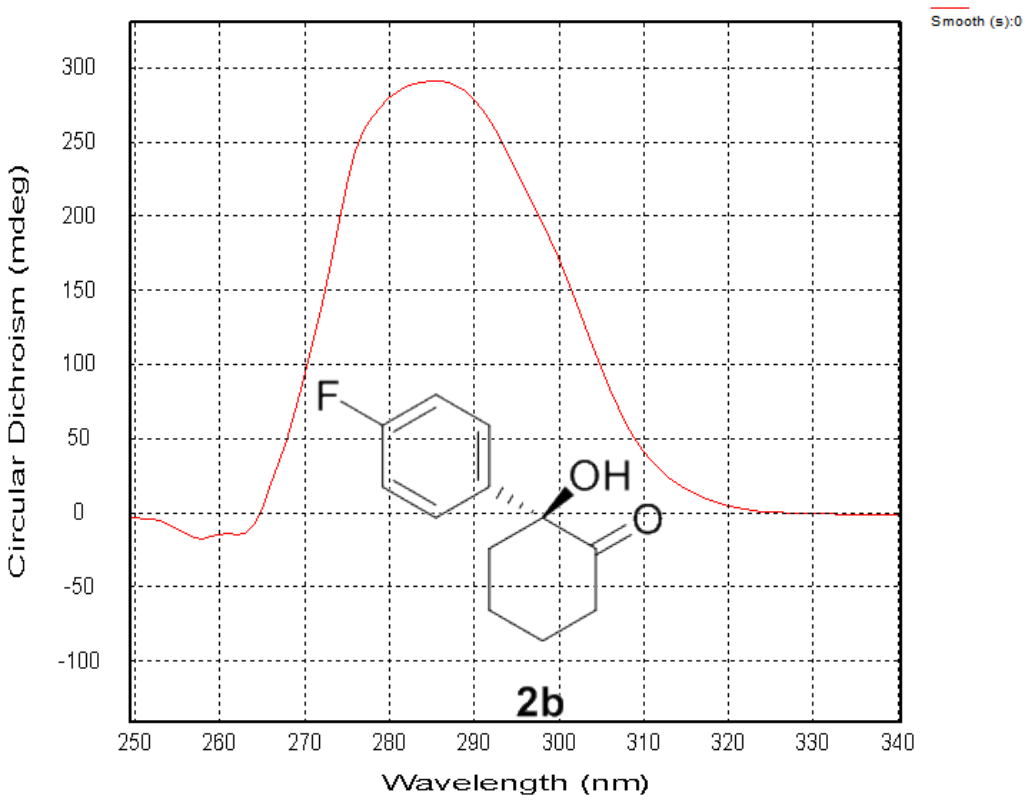


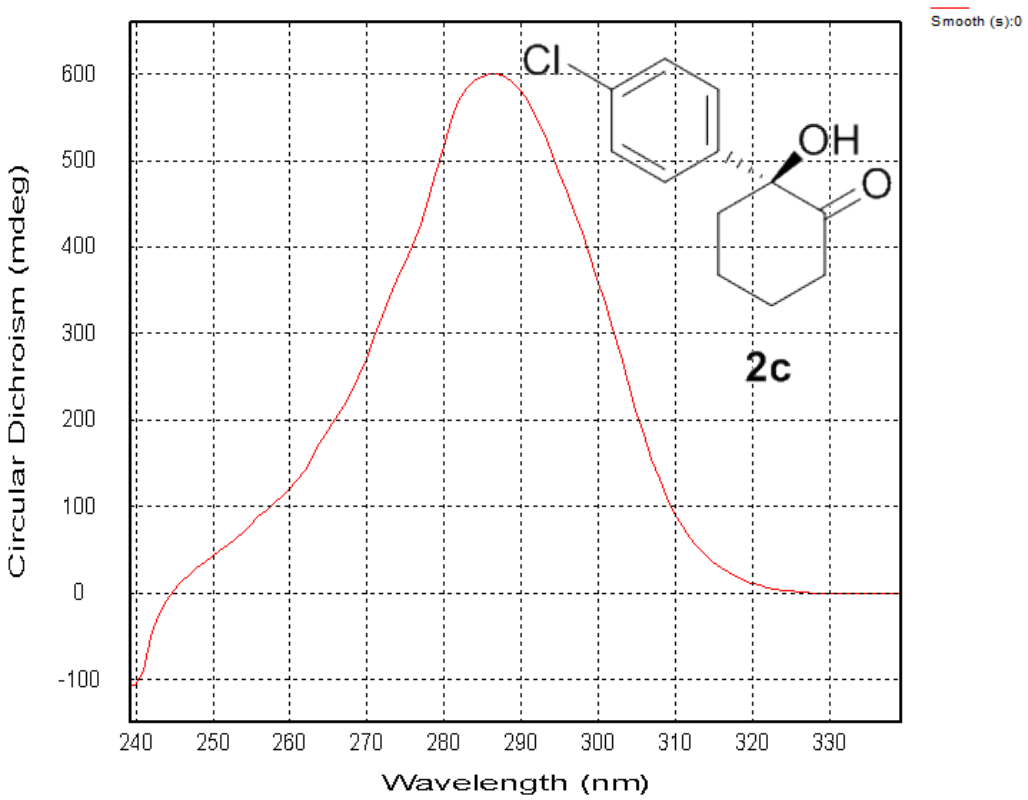
(1*S*,2*R*)-1-phenylcyclohexane-1,2-diol (8)

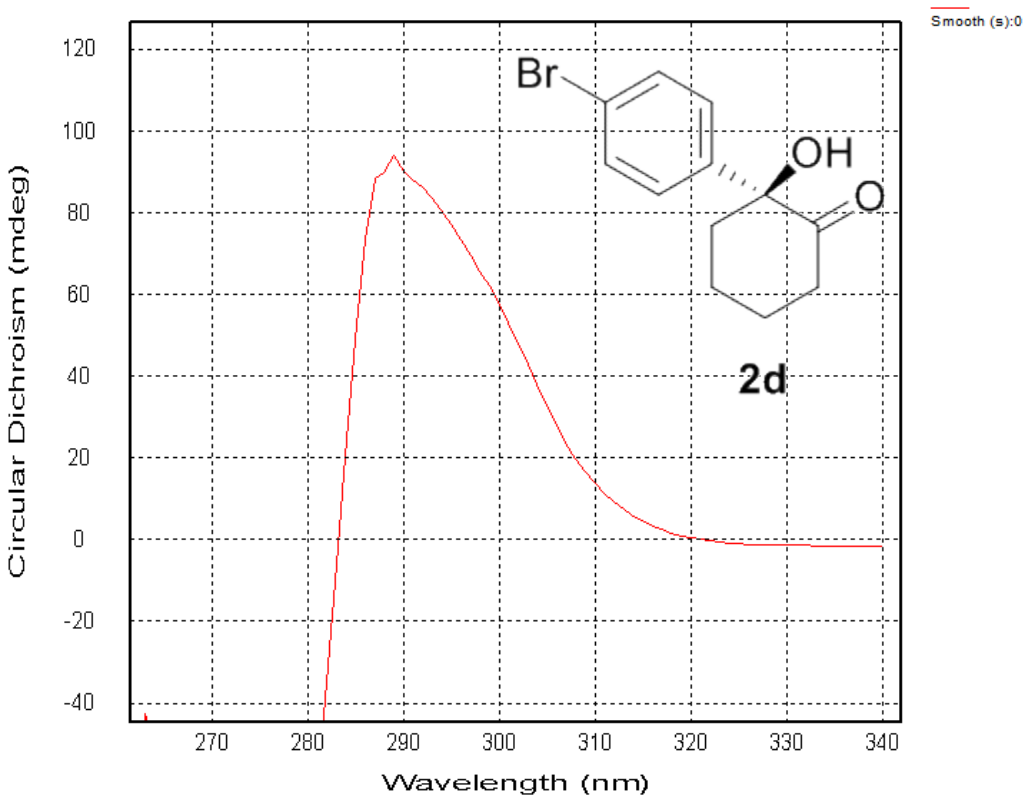


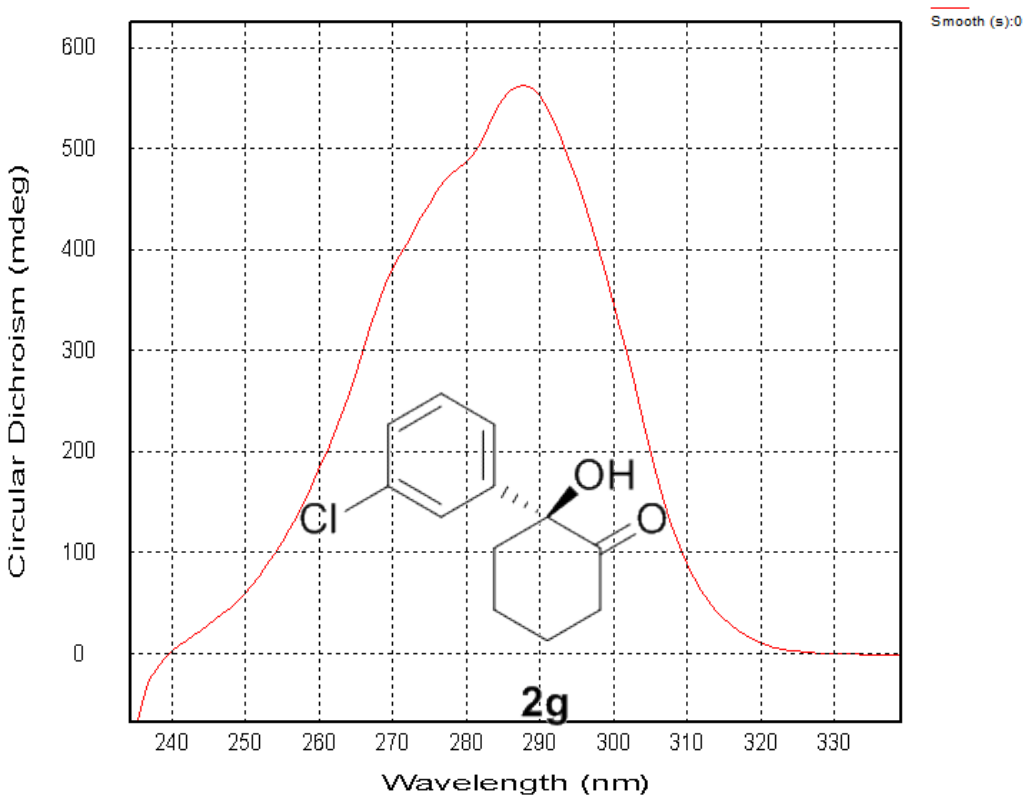
9. Copies of CD Spectra

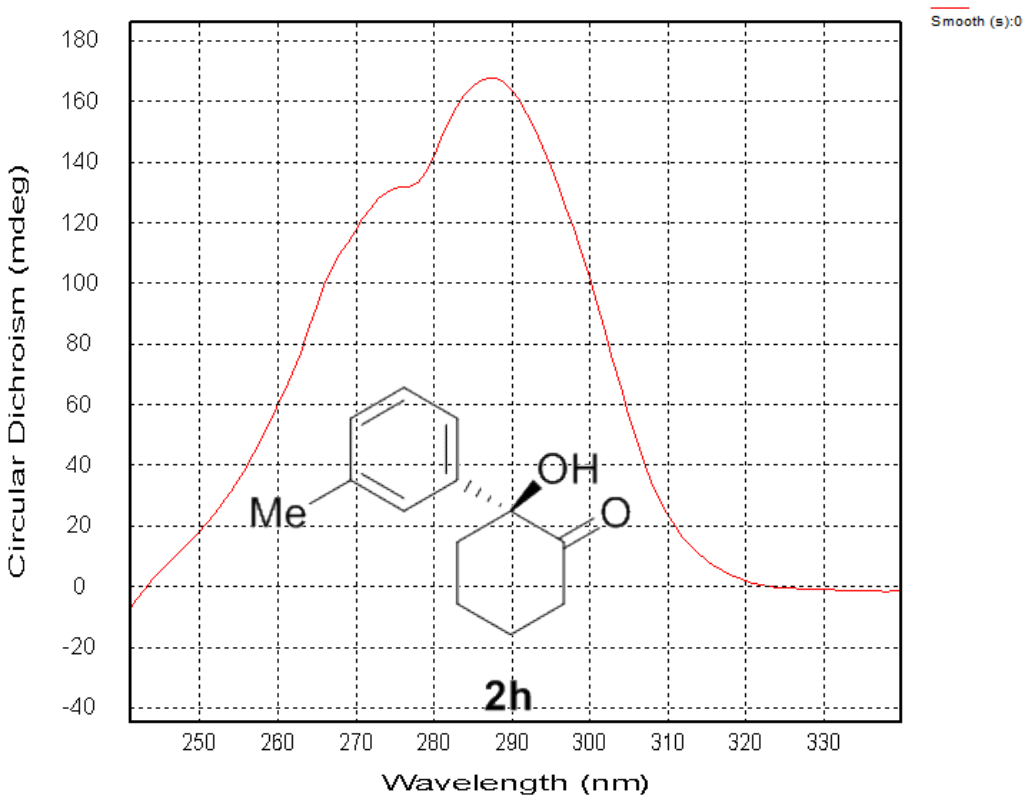


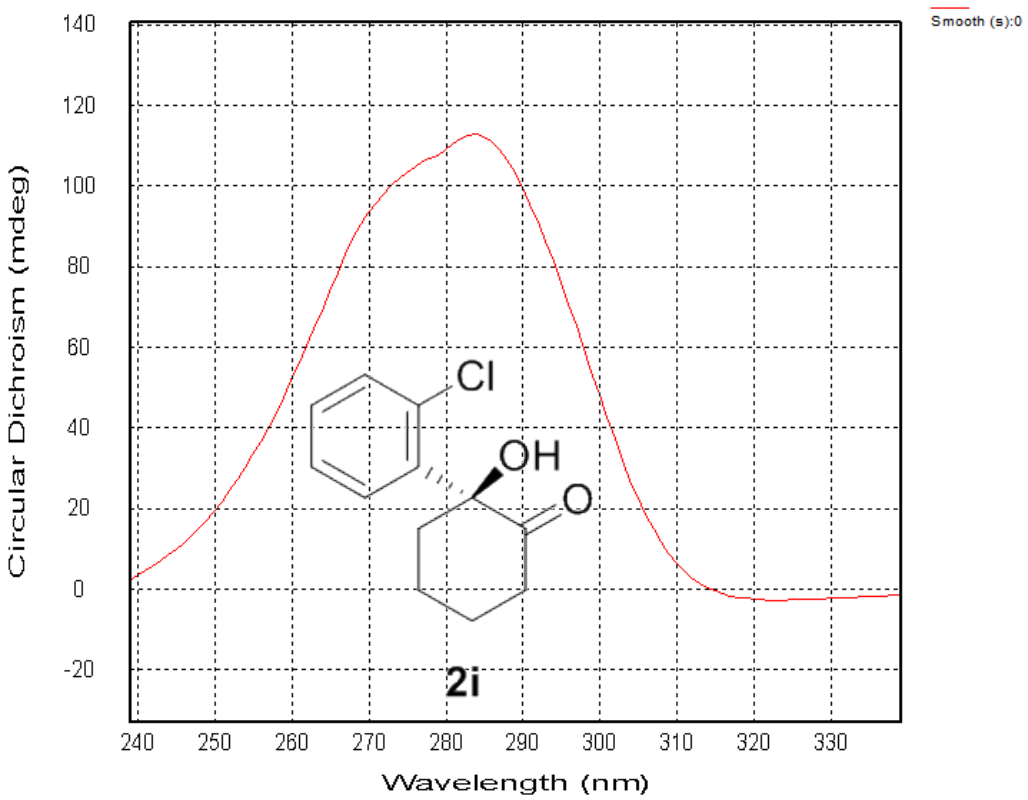

Smooth (s):0
Circular Dichroism (mdeg)
300
250
200
150
100
50
0
-50
-100
F
OH
O
2b
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)

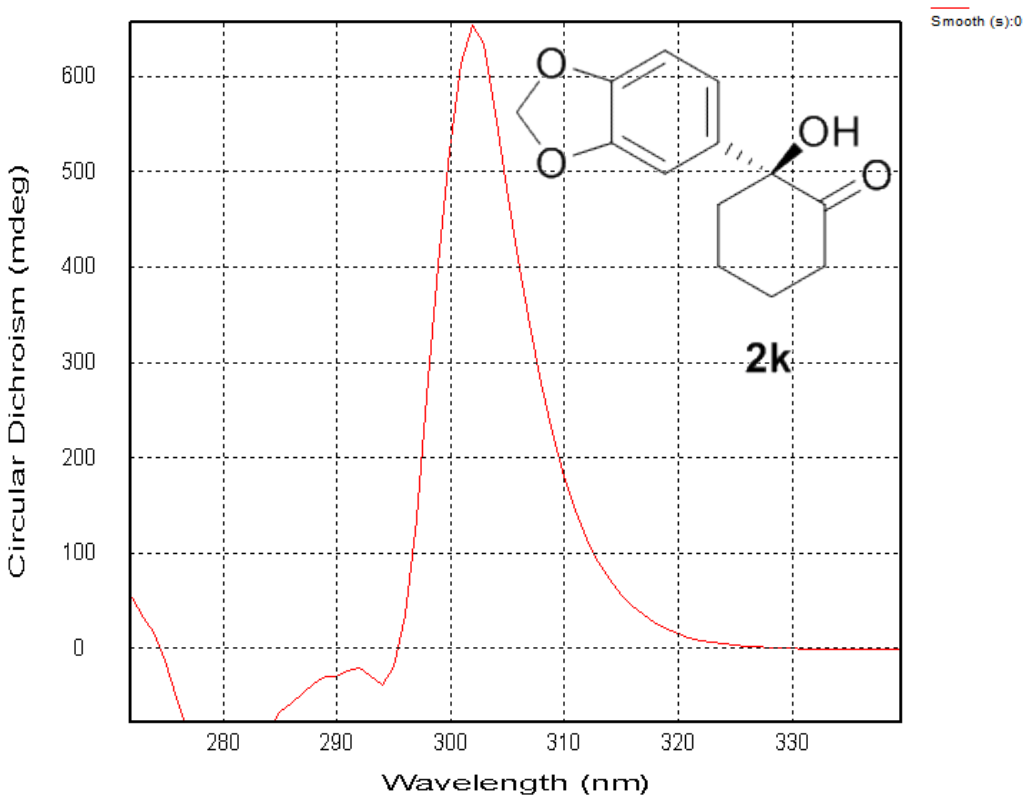

Smooth (s):0
Circular Dichroism (mdeg)
600
500
400
300
200
100
0
-100
240
250
260
270
280
290
300
310
320
330
Wavelength (nm)
Cl
OH
O
2c


Smooth (s):0
Circular Dichroism (mdeg)
120
100
80
60
40
20
0
-20
-40
270
280
290
300
310
320
330
340
Wavelength (nm)
Br
OH
O
2d


Smooth (s):0
Circular Dichroism (mdeg)
600
500
400
300
200
100
0
240
250
260
270
280
290
300
310
320
330
Wavelength (nm)
Cl
OH
O
2g


Smooth (s):0
Circular Dichroism (mdeg)
180
160
140
120
100
80
60
40
20
0
-20
-40
250
260
270
280
290
300
310
320
330
Wavelength (nm)
Me
OH
O
2h


Smooth (s):0
Circular Dichroism (mdeg)
140
120
100
80
60
40
20
0
-20
240
250
260
270
280
290
300
310
320
330
Wavelength (nm)
Cl
OH
O
2i



As for compound **4h**, **6c**, **6d**, **6e**, we attempted to confirm the absolute configuration of them by comparing the CD spectrum of compound **4a** and **6a** respectively, unfortunately, the CD response of **4a** and **6a** were both too fuzzy which made the effort a failure.