Nickel-catalyzed Intramolecular Desymmetrization Addition of Aryl Halides to 1,3-Diketones

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Content

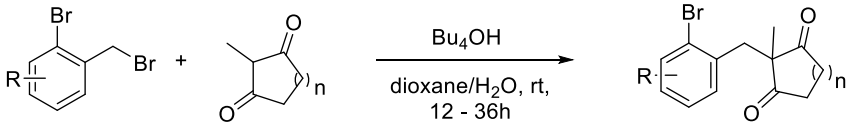
Supporting Information

1. General Considerations.

All commercially available compounds were used as received. ^{1}H and ^{13}C spectra were recorded on a Bruker Avance 400, 600 spectrometer, and $CDCl_3$ was purchased from Aldrich. The chemical shifts (δ) are given in parts per million relative to internal standard TMS (0 ppm for ^{1}H), $CDCl_3$ (77.0 ppm for ^{13}C). Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. Solvents were dried and purified according to the procedure from 'Purification of Laboratory Chemicals book'. Chiral HPLC analyses were performed on UltiMate 3000 liquid chromatography. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

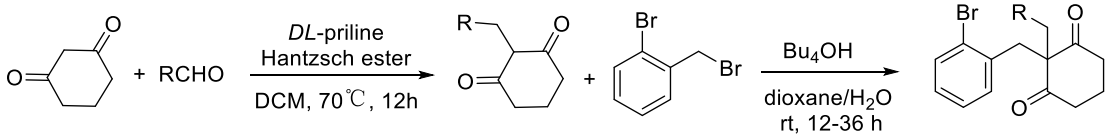
2. General Procedure for Preparation of Starting Materials

2.1 General Procedure for synthesis of 1a、1c-1i、4a



According to the literature[S1], to a stirred solution of 2-methylcyclohexane-1,3-dione (5 mmol, 1.0 equiv.) in dioxane (5 mL) was added aqueous $^{n}Bu_4NOH$ (40 % in H_2O, 3.3 mL). The mixture was stirred for 20 min at room temperature. Then a solution of substituted 1-bromo-2-(bromomethyl)benzene (6.0 mmol, 1.2 equiv) in dioxane (5 mL) was added and the reaction mixture was stirred for another 12-36 h. Upon completion, the reaction was quenched with aqueous NH_4Cl and extracted with ethyl acetate three times. The organics were combined, dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate to affording the final product.

2.2 General Procedure for synthesis of 1b、1j–1o、4b



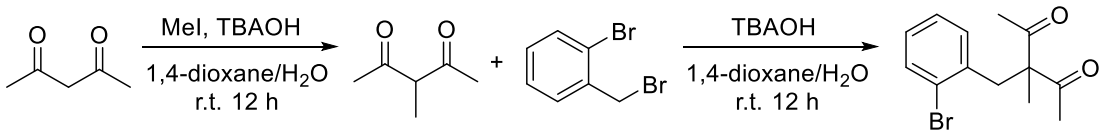
According to the literature[S1], an oven-dried 250 mL round bottom flask equipped with magnetic stir bar was charged with 1,3-cyclohexanedione (30 mmol), Hantzsh

[S1] C. Zhu, D. Wang, Y. Zhao, W. Y. Sun, Z. Shi, *J. Am. Chem. Soc.* **2017**, *139*, 16486.

ester (33 mmol, 1.1 equiv.), DL-Proline (6 mmol, 20 mol%) and DCM (50 mL). A solution of aldehyde (33 mmol, 1.1 equiv.) in DCM (5 mL) was added and the reaction mixture was refluxed at 70 ºC overnight. Upon completion, the reaction was allowed to cool to room temperature and the solvent was removed. The residue was purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate to afford the 2-substituent-cyclohexane-1,3-dione.

To a stirred solution of 2-substituent-cyclohexane-1,3-dione (5 mmol) in dioxane (5 mL) was added aqueous $^{n}Bu_4NOH$ (40% in H_2O, 3.3 mL). The mixture was stirred for 20 min at room temperature. Then a solution of 1-bromo-2-(bromomethyl)benzene (6.0 mmol, 1.2 equiv) in dioxane (5 mL) was added and the reaction mixture was stirred for another 12-36 h. Upon completion, the reaction was quenched with aqueous NH_4Cl and extracted with ethyl acetate three times. The organic layers were combined, dried over anhydrous Na_2SO_4, concentrated under vacuo. The residue was purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate to afford the final product.

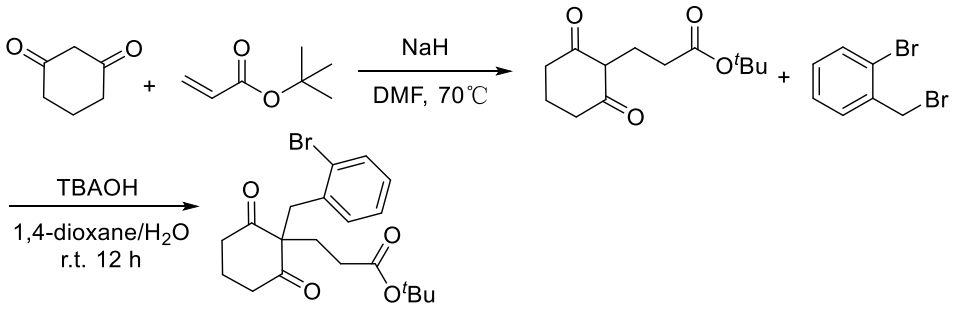
2.3 General Procedure for synthesis of 4c



To a solution of pentane-2,4-dione (20.0 mmol, 1.0 equiv) and aqueous Bu_4NOH (40% in H_2O, 13.2 mL) was added a solution of MeI (40 mmol, 2 equiv) in dioxane (40 mL). The solution was stirred for 12 h. The solution was neutralized with 10% aqueous HCl. The two liquid layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried with Na_2SO_4, and the solvent was evaporated. The residue was purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate to afford the 3-methylpentane-2,4-dione.

To a stirred solution of 3-methylpentane-2,4-dione (10 mmol) in dioxane (10 mL) was added aqueous $^{n}Bu_4NOH$ (40% in H_2O, 6.6 mL). The mixture was stirred for 20 min at room temperature. Then a solution of 1-bromo-2-(bromomethyl)benzene (12.0 mmol, 1.2 equiv) in dioxane (10 mL) was added and the reaction mixture was stirred for another 12-36 h. Upon completion, the reaction was quenched with aqueous NH_4Cl and extracted with ethyl acetate three times. The organic layers were combined, dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate to afford the final product.

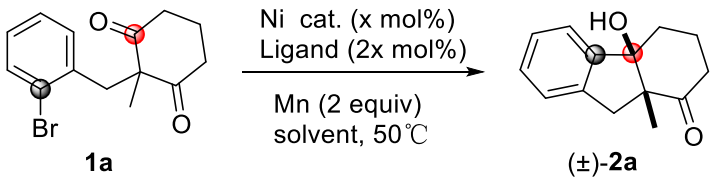
2.4 General Procedure for synthesis of 1q



According to the literatures[S2], an oven-dried 100 mL round bottom flask equipped with magnetic stir bar was added with 60% NaH (24 mmol, 1.2 equiv.) and DMF (40 mL) under nitrogen atmosphere at 0 °C. A solution of cyclohexane-1,3-dione (20 mmol) in DMF (10 mL) was added slowly and the reaction was stirred for 30 min. Then *t*-butyl acrylate (1.5 equiv.) was added and the reaction was heated at 70 °C for 4 h. Upon completion, the reaction mixture was allowed to cool to room temperature and acidified by 10% aqueous HCl. The suspension was extracted with ethyl acetate three times. The organics was combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate to afford *t*-butyl 3-(2,6-dioxocyclohexyl) propanoate.

To a stirred solution of *t*-butyl 3-(2,6-dioxocyclohexyl) propanoate (10 mmol) in dioxane (10 mL) was added aqueous $^nBu_4NOH$ (40% in H_2O, 6.6 mL). The mixture was stirred for 20 min at room temperature. Then a solution of 1-bromo-2-(bromomethyl)benzene (12.0 mmol, 1.2 equiv) in dioxane (10 mL) was added and the reaction mixture was stirred for another 12-36 h. Upon completion, the reaction was quenched with aqueous NH_4Cl and extracted with ethyl acetate three times. The organics were combined, dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate to afford the final product.

3. Screening Results.



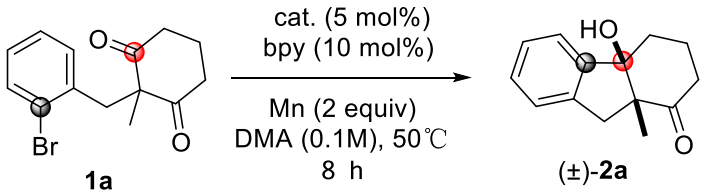
The Standard condition was listed below and the screening experiments were tested by changing the relevant parameters based on this procedure:

In the nitrogen filled glovebox, a 10 mL oven-dried Schlenk tube with a magnetic bar was charged with nickel catalyst (0.005 mmol, 5 mol %), ligand (0.01 mmol, 10 mol %) and Manganese powder (11.0 mg, 0.2 mmol, 2 equiv). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, solvent (1 mL) was added and the reaction mixture was stirred at room temperature for 30 min. **1a**

[S2] M. Konno, T. Nakae, N. Hamanaaka, *SynLett.* **1997**,1472.

(29.4 mg, 0.1 mmol) were added and the resulting solution was stirred overnight at 50 ℃. Upon completion, the reaction mixture was quenched by saturated aq. NH_4Cl (2 mL) and extracted with ethyl acetate (2 mL ×3). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuo. CH_2Br_2 (17.4 mg, 0.1 mmol) as internal standard and $CDCl_3$ were added to the residue. The yield and *dr* value of **2a** was determined via ^1H NMR analysis. The *ee* value of **2a** was determined via HPLC analysis after purification of the crude reaction mixture.

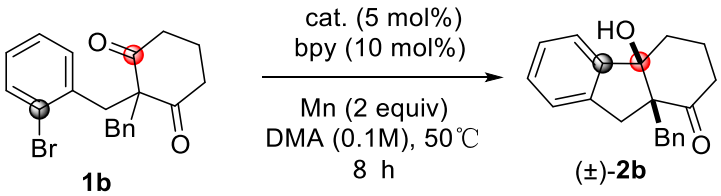
Table S1 screening results on catalyst.



1a (±)-**2a**

cat.	**2a** (%)	d:r
$NiBr_2$	86	>20:1
$NiBr_2$(dme)	78	>20:1
$Ni(PPh_3)_2Br_2$	84	>20:1
$Ni(PCy_3)_2Cl_2$	94	>20:1
$Ni(cod)_2$	>99	>20:1
Ni(dppe)Cl_2	87	>20:1
$Ni(PPh_3)_2(CO)_2$	n.r.	---
$FeBr_3$	n.r.	---
$CoBr_2$	n.r.	---
$Cu(OTf)_2$	n.r.	---
$Pd(OAc)_2$	27	>20:1
[a] $Ni(cod)_2$	96	>20:1

[a] At room temperature



1b (±)-**2b**

cat.	additive	**2b** (%)	d:r
$Ni(cod)_2$	---	46	>20:1
$Ni(cod)_2$	NaI	84	>20:1
$Ni(cod)_2$	$MgCl_2$	>99	>20:1

Table S2 screening results on ligand.

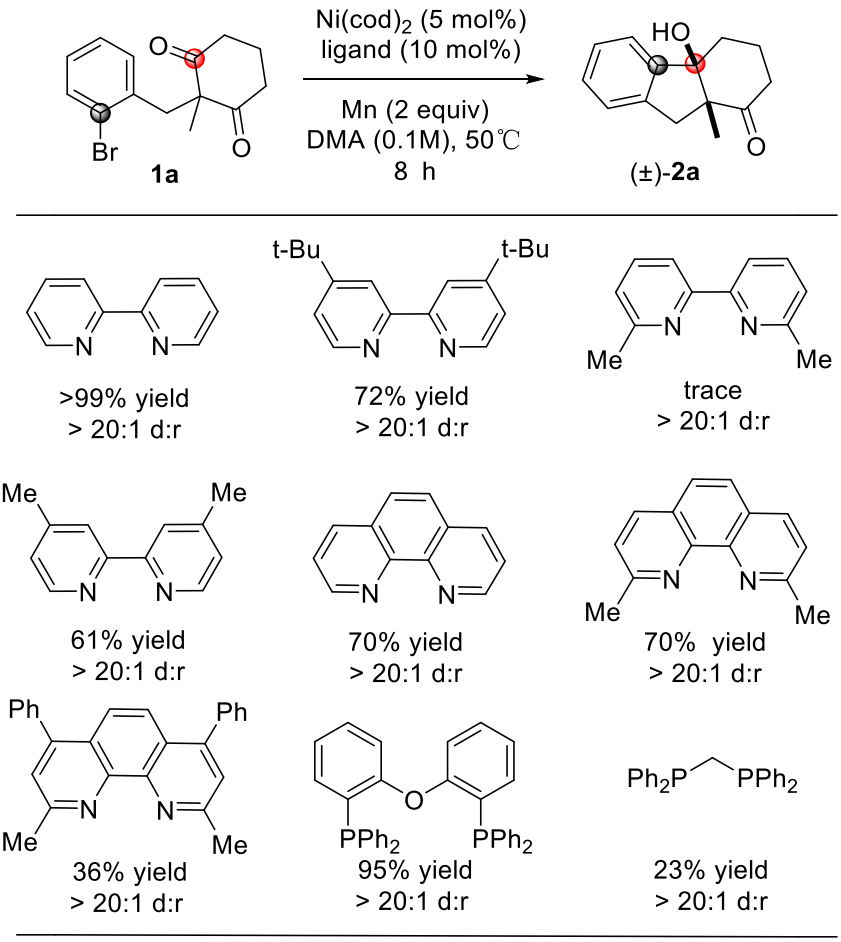
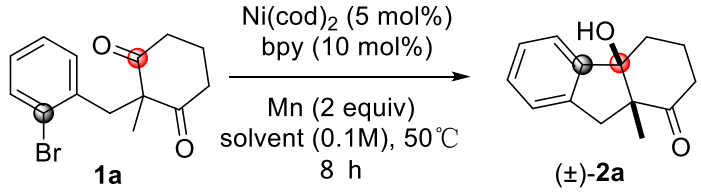
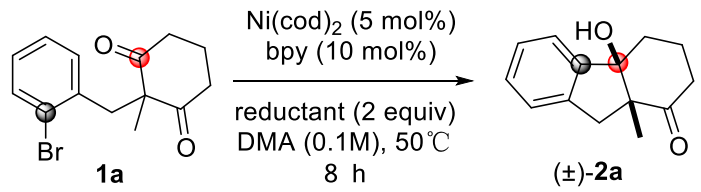


Table S3 screening results on solvent.



cat.	**2a** (%)	d:r
DMA	>99	>20:1
DMF	84	>20:1
DMSO	26	>20:1
THF	trace	>20:1
ACN	34	>20:1

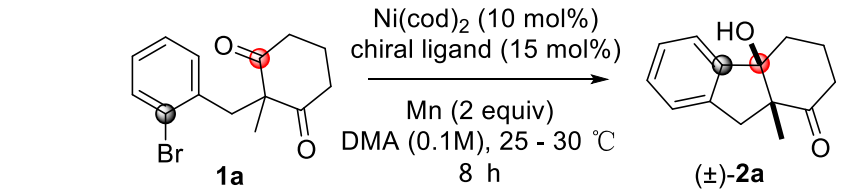
Table S4 screening results on reductant.

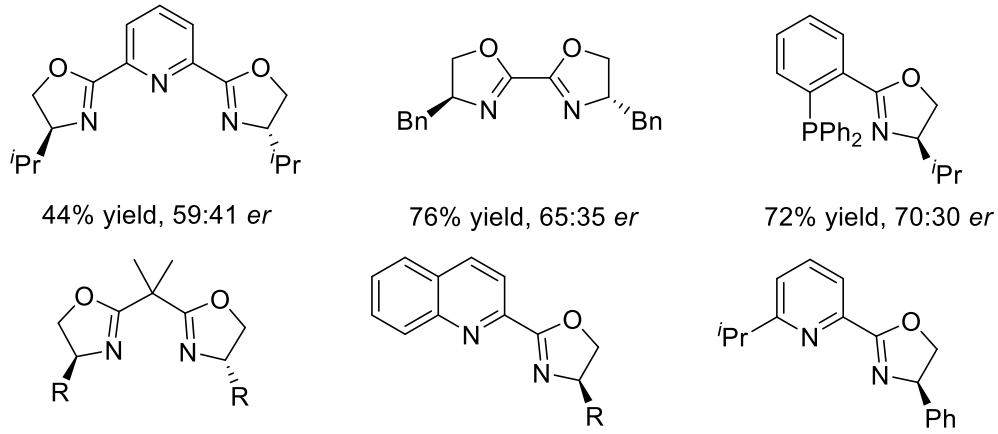


reductant	**2a** (%)	d:r
Mn	>99	. >20:1

Zn	90	>20:1
In	18	>20:1

Table S5 preliminary screening results on chiral ligand.





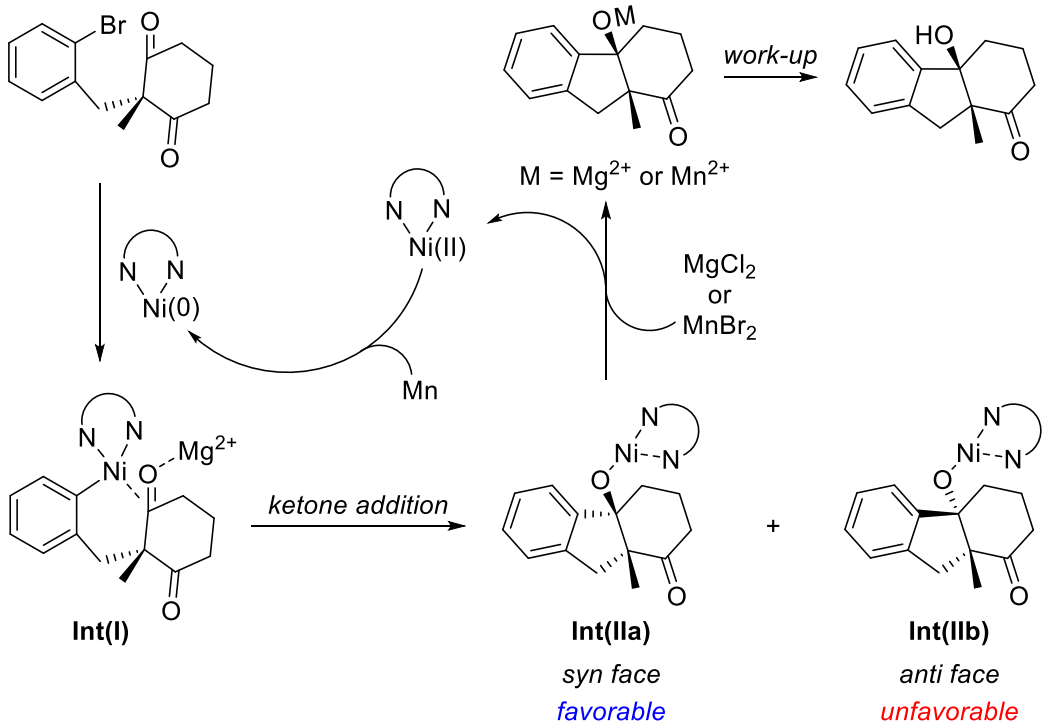
[a] DMA/1,4-dioxone (v/v = 4/1) was used as solvent. [b] $MgCl_2$ (0.2 mmol) was added as additive.

4. Mechanism discussion.

Based on the experiments and literatures[S3], a proposed catalytic cycle was listed below. An aryl-Ni species **Int(I)** was obtained after the oxidative addition of Ar-Br and Ni(0) catalyst. The carbonyl was further activated by coordination to Mg^{2+} ion, following by reacting with the C-Ni bond. It had two way to proceed the ketone addition step. The *syn* addition to give the *syn* intermediate **Int(IIa)** is favorable according to

[S3] (a) K. J. Garcia, M. M. Gilbert, D. J. Weix, *J. Am. Chem. Soc.* **2019**, *141*, 1823. (b) K. K. Majumdar, C.-H. Cheng, *Org. Lett.* **2000**, *2*, 2295.

the configuration. The nickel(II) was released by $MnBr_2$ or $MgCl_2$, which gave Ni(0) regeneration by reduction of Mn powder.



5. Nickel-catalyzed intramolecular desymmetrization addition of aryl halides to 1,3-diketones.

5.1 General procedure for synthesis of 2.

In the nitrogen filled glovebox, a 10 mL oven-dried Schlenk tube with a magnetic bar was charged with $Ni(cod)_2$ (2.7 mg, 0.01 mmol, 5 mol %), 1,1-bipyridine (bpy, 3.1 mg, 0.02 mmol, 10 mol %), Manganese powder (22.0 mg, 0.4 mmol, 2 equiv.), and $MgCl_2$ (38.0 mg, 0.4 mmol, 2 equiv.). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, DMA (2 mL) was added and the reaction mixture was stirred at room temperature for 30 min. **1** (0.2 mmol) were added and the resulting solution was stirred for 8 h at 50 ℃. Upon completion, the reaction mixture was quenched by saturated aq. NH_4Cl (2 mL) and extracted with ethyl acetate (2 mL ×3). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuo. The residue was purified by silica gel column chromatography with a gradient eluent of petroleum ether/ethyl acetate affording the product. The *dr* value of **2** was determined via ^1H NMR analysis.

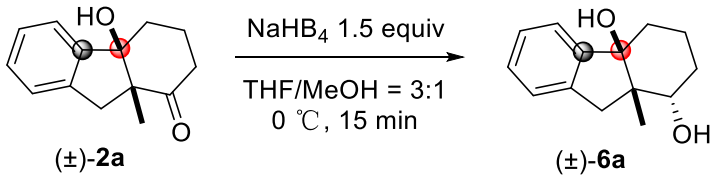
5.2 General procedure for synthesis of chiral 2.

In the nitrogen filled glovebox, a 10 mL oven-dried Schlenk tube with a magnetic bar was charged with $Ni(cod)_2$ (2.7 mg, 0.02 mmol, 10 mol %), S-^{i}Pr-Pyrox (2.7 mg, 0.03 mmol, 15 mol %) and Manganese powder (11.0 mg, 0.4 mmol, 2 equiv.). The tube was capped with a septum and took out of the glove box. Under N_2 atmosphere, DMA (0.8 mL) and 1,4-dioxane (0.2 mL) was added and the reaction mixture was stirred at

room temperature for 30 min. **1** (0.1 mmol) were added and the resulting solution was stirred for 8 h at 25-30 ºC. Upon completion, the reaction mixture was quenched by saturated aq. NH_4Cl (2 mL) and extracted with ethyl acetate (2 mL ×3). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuo. The residue was purified by silica gel column chromatography with a gradient eluent of petroleum ether/ethyl acetate affording the product. The *dr* value of **2** was determined via ^{1}H NMR analysis and *ee* value of **2** was determined via HPLC analysis.

6. General procedures for the transformations of bicyclic products.

6.1 General procedure for synthesis of 6a

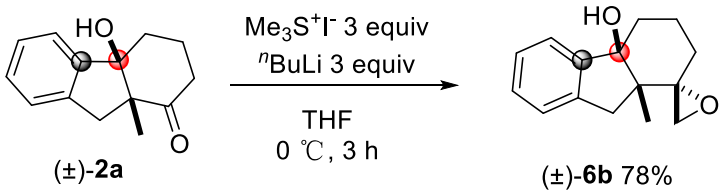


(±)-**2a** (±)-**6a**

91% yield, d:r > 20:1

To a stirred solution of **2a** (21.6 mg, 0.1 mmol) in THF (1.5 mL) and MeOH (0.5 mL) was added $NaHB_4$ (57 mg, 1.5 equiv.) and the reaction mixture was stirred for 15 min at 0 ℃. The reaction was diluted with water and extracted with ethyl acetate three times. The combined organics were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient eluent of petroleum ether/ethyl acetate affording **6a** (19.8 mg) in 91% yield. The *dr* value of **6a** was determined via ^{1}H NMR analysis.

6.2 General procedure for synthesis of 6b[S4]



(±)-**2a** (±)-**6b** 78%

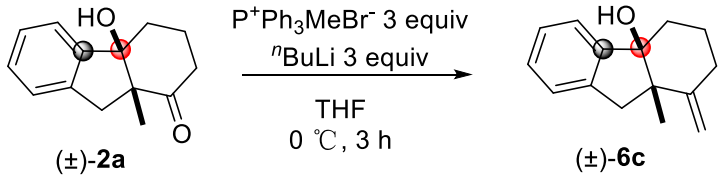
78% yield, d:r > 20:1

To a round bottom flask equipped with magnetic stirring bar, rubber septum, and N_2 inlet was added trimethyl sulfonium iodide ($Me_3S^+I^-$) (61 mg, 0.3 mmol, 3 equiv) in anhydrous tetrahydrofuran (THF, 1 mL) was stirred for 10 min at 0℃. At this point, a solution of ^{n}BuLi (0.3 mmol, 3 equiv, 1.6M solution in hexanes) was added and the resulting solution was stirred for 10 min at 0℃. Compound **2a** (21.6 mg, 0.1 mmol) in anhydrous tetrahydrofuran (THF, 1 mL) was added, and the mixture was stirred in the ice bath for 3 h. The ice bath was then removed, and the reaction was allowed to warm

[S4] C. F. D. Amigo, I. G. Collado, J. R. Hanson, R. Hernandez-Galan, P. B. Hitchcock, A. J. Macias-Sanchez, D. J. Mobbs, *J. Org. Chem.* **2001**, *66,* 4327.

to room temperature. The solution was carefully poured into ice/water (10 mL) and extracted with ethyl acetate three times. The combined organics were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a gradient eluent of petroleum ether/ethyl acetate affording **6b** (18.0 mg) in 78% yield. The *dr* value of **6b** was determined *via* ^{1}H NMR analysis.

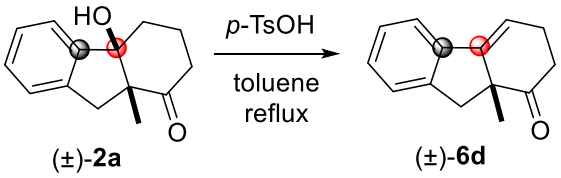
6.3 General procedure for synthesis of 6c[S5]



78% yield, d:r > 20:1

To a round bottom flask equipped with magnetic stirring bar, rubber septum, and N_2 inlet was added methyl-triphenylphosphonium bromide (P^+Ph_3MeBr, 107.5 mg, 0.3 mmol) and anhydrous tetrahydrofuran (THF) (1 mL). To the flask was added dropwise ^{n}BuLi (0.3 mmol, 3 equiv, 1.6M solution in hexanes) at 0℃. After 20 min of stirring at same temperature, a solution of ketone **2a** (21.6 mg, 0.1 mmol) in anhydrous tetrahydrofuran (THF) (1 mL) was added dropwise to the phosphonium ylide through a cannula. After the ketone **2a** was completely added the mixture was stirred in the ice bath for another 3 h. Upon completion, the reaction mixture was quenched by saturated aq. NH_4Cl (2 mL) and extracted with ethyl acetate (2 mL ×3). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuo. The residue was purified by silica gel column chromatography with a gradient eluent of petroleum ether/ethyl acetate affording **6c** (16.7 mg) in 78% yield. The *dr* value of **6c** was determined *via* ^{1}H NMR analysis.

6.4 General procedure for synthesis of 6d[S6]



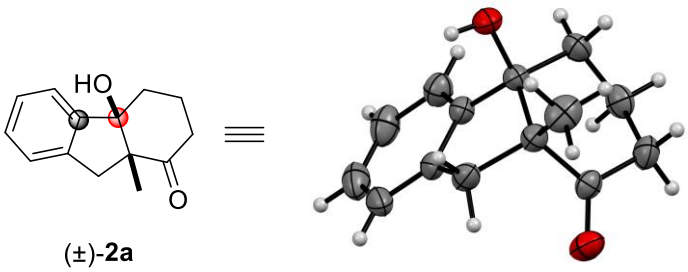
58% yield

To a stirred solution of **2a** (21.6 mg, 0.1 mmol) in anhydrous toluene (2 mL) was added *p*-toluenesulfonic acid (1 mg, 10 mmol%) and the reaction mixture was stirred for 1 h at 120 ℃. The reaction was diluted with water and extracted with ethyl acetate three times. The combined organics were dried over Na_2SO_4 and concentrated *in* vacuo. The residue was purified by silica gel column chromatography with a gradient eluent of petroleum ether/ethyl acetate affording **6d** (11.5 mg) in 58% yield.

[S5] E. M. Phillips, J. M. Roberts, K. A. Scheidt, *Org. Lett.* **2010**, *12*, 2830.

[S6] G. Mehta, D. Subrahmanyam, *J. Chem. Soc. Chem. Commun.* **1989**, 1365.

7. X-Ray Data for 2a



(±)-**2a**

Table 1. Crystal data and structure refinement for ga_90423a_a.

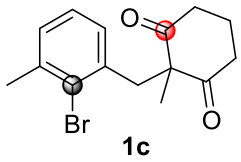
Identification code	ga_90423a_a	
Empirical formula	C14 H16 O2	
Formula weight	216.27	
Temperature	298(2) K	
Wavelength	1.34138 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.4235(5) Å	= 90°.
	b = 10.6627(7) Å	= 90°.
	c = 12.6898(8) Å	= 90°.
Volume	1139.76(12) $Å^3$	
Z	4	
Density (calculated)	1.260 Mg/m^3	
Absorption coefficient	0.420 mm^{-1}	
F(000)	464	
Crystal size	0.080 x 0.050 x 0.040 mm^3	
Theta range for data collection	5.484 to 58.095°.	
Index ranges	-10<=h<=10, -13<=k<=13, -16<=l<=16	
Reflections collected	19374	
Independent reflections	2419 [R(int) = 0.0302]	
Completeness to theta = 53.594°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.836	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2419 / 0 / 150	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0274, wR2 = 0.0704	
R indices (all data)	R1 = 0.0287, wR2 = 0.0721	
Absolute structure parameter	0.5	

Extinction coefficient	n/a
Largest diff. peak and hole	0.153 and -0.134 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ga_90423a_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

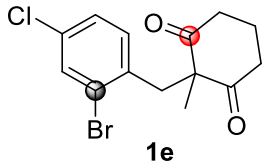
	x	y	z	U(eq)
O(1)	6501(1)	3983(1)	3546(1)	40(1)
O(2)	4452(2)	8210(1)	3530(1)	45(1)
C(1)	5608(2)	4988(1)	4008(1)	30(1)
C(2)	6367(2)	5195(2)	5084(1)	38(1)
C(3)	5717(2)	6340(2)	5644(1)	41(1)
C(4)	5977(2)	7506(2)	4974(1)	44(1)
C(5)	5248(2)	7369(1)	3899(1)	32(1)
C(6)	5601(2)	6175(1)	3269(1)	31(1)
C(7)	4218(2)	5907(1)	2502(1)	37(1)
C(8)	3083(2)	5154(1)	3159(1)	34(1)
C(9)	1481(2)	4910(2)	2998(1)	44(1)
C(10)	671(2)	4164(2)	3709(2)	51(1)
C(11)	1441(2)	3661(2)	4574(2)	49(1)
C(12)	3045(2)	3897(2)	4741(1)	40(1)
C(13)	3854(2)	4648(1)	4031(1)	31(1)
C(14)	7197(2)	6401(2)	2713(2)	48(1)

8. The characterization of the new products



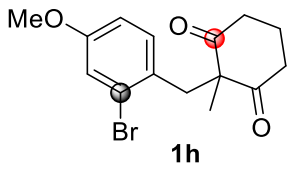
1c

The title compound **1c** was synthesized according to General Procedure (SI 2.1), and it was purified by column chromatography on silica gel.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37-7.36 (m, 1H), 7.00 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.26 (s, 2H), 2.71-2.61 (m, 4H), 2.28 (s, 3H), 1.97-1.81 (m, 2H), 1.27 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.1, 138.8, 133.6, 132.6, 131.2, 128.1, 125.4, 65.3, 41.9, 38.9, 20.6, 19.6, 17.4; HRMS: m/z (ESI) calculated $[M+H]^{+}$:309.0485, found: 309.0485.



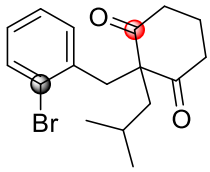
1e

The title compound **1e** was synthesized according to General Procedure (SI 2.1), and it was purified by column chromatography on silica gel.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 2.2 Hz, 1H), 7.18 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 3.28 (s, 2H), 2.73-2.61 (m, 4H), 2.00-1.85 (m, 2H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.7, 134.8, 133.4, 132.8, 131.9, 127.5, 126.0, 65.0, 40.5, 38.6, 20.6, 17.3; HRMS: m/z (ESI) calculated $[M+H]^{+}$:350.9758, found: 350.9755.



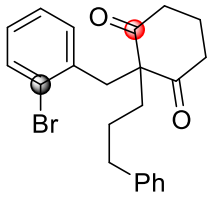
1h

The title compound **1h** was synthesized according to General Procedure (SI 2.1), and it was purified by column chromatography on silica gel.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.8 Hz, 1H), 6.65 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.57 (d, *J* = 3.0 Hz, 1H), 3.74 (s, 3H), 3.27 (s, 2H), 2.68-2.62 (m, 4H), 1.98-1.83 (m, 2H), 1.30 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.0, 158.6, 136.9, 133.7, 117.2, 116.0, 114.3, 65.1, 55.4, 41.9, 38.8, 20.3, 17.3; HRMS: m/z (ESI) calculated $[M+H]^{+}$:325.0433, found: 325.0434.



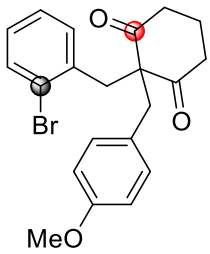
1j

The title compound **1j** was synthesized according to General Procedure (SI 2.2), and it was purified by column chromatography on silica gel.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.22-7.18 (m, 1H), 7.09-7.05 (m, 1H), 7.01 (dd, *J* = 7.7, 1.7 Hz, 1H), 3.23 (s, 2H), 2.63-2.56 (m, 2H), 2.41-2.33 (m, 2H), 1.98 (d, *J* = 6.5 Hz, 2H), 1.87- 1.82(m, 1H), 1.74-1.68 (m, 1H), 1.52-1.45 (m, 1H), 0.80 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.0, 136.1, 133.3, 131.9, 128.6, 127.3, 125.5, 67.9, 45.8, 44.3, 40.4, 25.4, 24.1, 16.6; HRMS: m/z (ESI) calculated [M+H]$^{+}$:337.0794, found: 337.0798.



1l

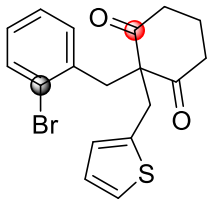
The title compound **1l** was synthesized according to General Procedure (SI 2.2), and it was purified by column chromatography on silica gel.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.28-7.24 (m, 2H), 7.13-7.11 (m, 2H), 7.09-7.05 (m, 1H), 7.00 (dd, *J* = 7.7, 1.7 Hz, 1H), 3.24 (s, 2H), 2.57-2.52 (m, 2H), 2.50-2.46 (m, 2H), 2.43-2.36 (m, 2H), 2.02-1.98 (m, 2H), 1.77-1.69 (m, 2H), 1.37-1.29 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.8, 141.6, 136.0, 133.3, 131.7, 128.7, 128.3, 127.3, 125.9, 125.5, 68.6, 42.9, 40.4, 36.6, 36.3, 27.2, 16.4; HRMS: m/z (ESI) calculated [M+H]$^{+}$:399.0953, found: 399.0954.



1m

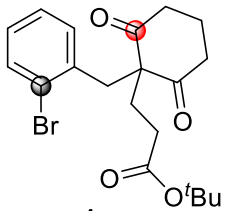
The title compound **1m** was synthesized according to General Procedure (SI 2.2), and it was purified by column chromatography on silica gel.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.22-7.18 (m, 1H), 7.11-7.04 (m, 2H), 6.96-6.92 (m, 2H), 6.75-6.72 (m, 2H), 3.75 (s, 3H), 3.41 (s, 2H), 3.24 (s, 2H), 2.19-2.01 (m, 4H), 1.39-1.30 (m, 1H), 1.13-1.04 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.6, 158.5, 136.1 , 133.5, 131.8, 131.4, 128.7, 128.3, 127.3,

125.4, 113.8, 69.7, 55.2, 43.1, 41.2, 15.3; HRMS: m/z (ESI) calculated $[M+Na]^+$:423.0570, found: 423.0566.



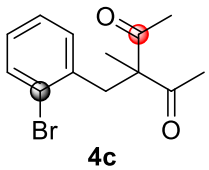
1o

The title compound **1o** was synthesized according to General Procedure (SI 2.2), and it was purified by column chromatography on silica gel.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.25-7.21 (m, 1H), 7.13-7.10 (m, 2H), 7.08-7.05 (m, 1H), 6.83 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.70 (dd, *J* = 3.5, 1.1 Hz, 1H), 3.51 (s, 2H), 3.36 (s, 2H), 2.26-2.22 (m, 4H), 1.54-1.44 (m, 1H), 1.28-1.18 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.0, 138.1, 135.4, 133.5, 132.2, 129.0, 127.9, 127.4, 126.7, 125.4, 124.6, 69.7, 43.6, 40.9, 36.6, 15.6; HRMS: m/z (ESI) calculated $[M+Na]^+$: 377.0206, found: 377.0205.



1q

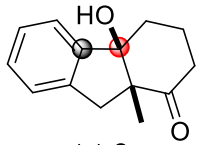
The title compound **1q** was synthesized according to General Procedure (SI 2.4), and it was purified by column chromatography on silica gel.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.22-7.18 (m, 1H), 7.10-7.05 (m, 1H), 7.02 (dd, *J* = 7.7, 1.7 Hz, 1H), 3.25 (s, 2H), 2.64-2.45 (m, 4H), 2.24-2.20 (m, 2H), 2.04-2.00 (m, 2H), 1.89-1.78 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.0, 171.8, 133.3, 131.8, 128.8, 127.3, 125.6, 80.6, 67.7, 42.9, 40.0, 30.9, 30.3, 28.1, 16.6; HRMS: m/z (ESI) calculated $[M+Na]^+$: 431.0829, found: 431.0828.



4c

The title compound **4c** was synthesized according to General Procedure (SI 2.3), and it was purified by column chromatography on silica gel.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.21-7.17 (m, 1H), 7.10-7.05 (m, 2H), 3.46 (s, 2H), 2.17 (s, 3H), 2.16 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (101

MHz, Chloroform-*d*) δ 206.9, 136.6, 133.2, 131.4, 128.4, 127.8, 126.2, 67.5, 37.8, 27.1, 17.5; HRMS: m/z (ESI) calculated $[M+Na]^+$: 305.0144, found: 305.0148.



(±)-**2a**

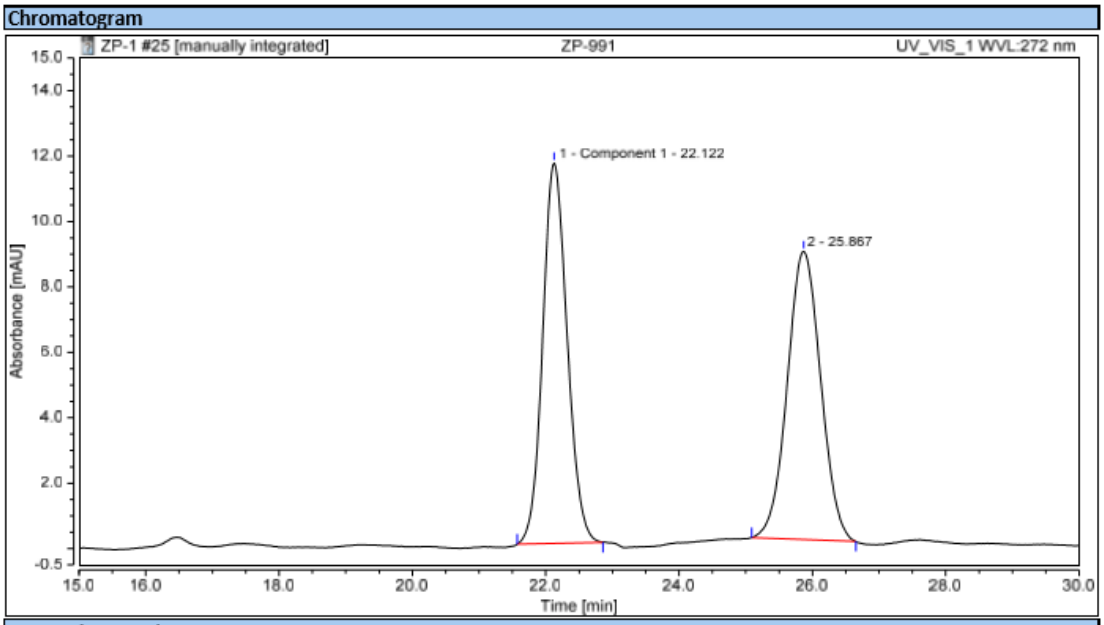
The title compound **(±)-2a** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (96% yield, 41.5 mg, white solid).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 4.2 Hz, 4H), 3.60 (d, *J* = 15.6 Hz, 1H), 2.70 (d, *J* = 15.7 Hz, 1H), 2.56-2.48 (m, 1H), 2.38-2.23 (m, 2H), 2.21-2.13 (m, 1H), 1.98-1.91 (m, 1H), 1.72 (s, 1H), 1.47-1.37 (m, 1H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.3, 144.8, 142.8, 129.0, 127.1, 125.5, 122.1, 84.8, 62.1, 38.7, 37.6, 31.9, 20.0, 17.9; HRMS: m/z (ESI) calculated $[M+Na]^+$:339.1041, found:239.1043.

The title compound **2a** was synthesized according to General Procedure (SI 5.2), and it was purified by column chromatography on silica gel (76% yield, 60% *ee*, 16.4 mg, white solid).

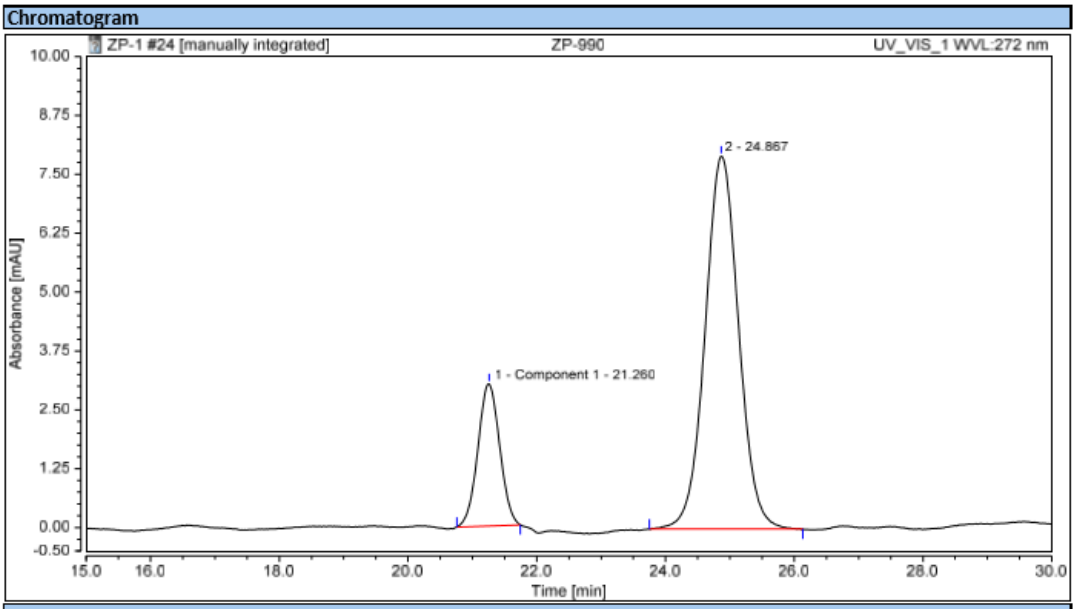
The enantiomeric excess of **2a** was determined by chiral HPLC analysis compared to the corresponding racemate.

Conditions: ChiralPark IA column; hexane/^{i}PrOH = 95:5; flow rate = 0.8 mL/min; λ= 272 nm; t_{R1}(minor)= 21.2 min; t_{R2}(major)=24.9 min.



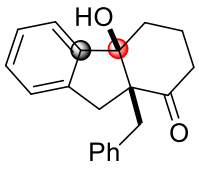
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1	Component 1	22.122	4.937	11.641	49.17	56.90	n.a.
2		25.867	5.105	8.817	50.83	43.10	n.a.
Total:			**10.042**	**20.458**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1	Component 1	21.260	1.181	3.021	19.80	27.59	n.a.
2		24.867	4.784	7.927	80.20	72.41	n.a.
Total:			**5.965**	**10.948**	**100.00**	**100.00**	



(±)-**2b**

The title compound **(±)-2b** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (89% yield, 52.0 mg, white solid).

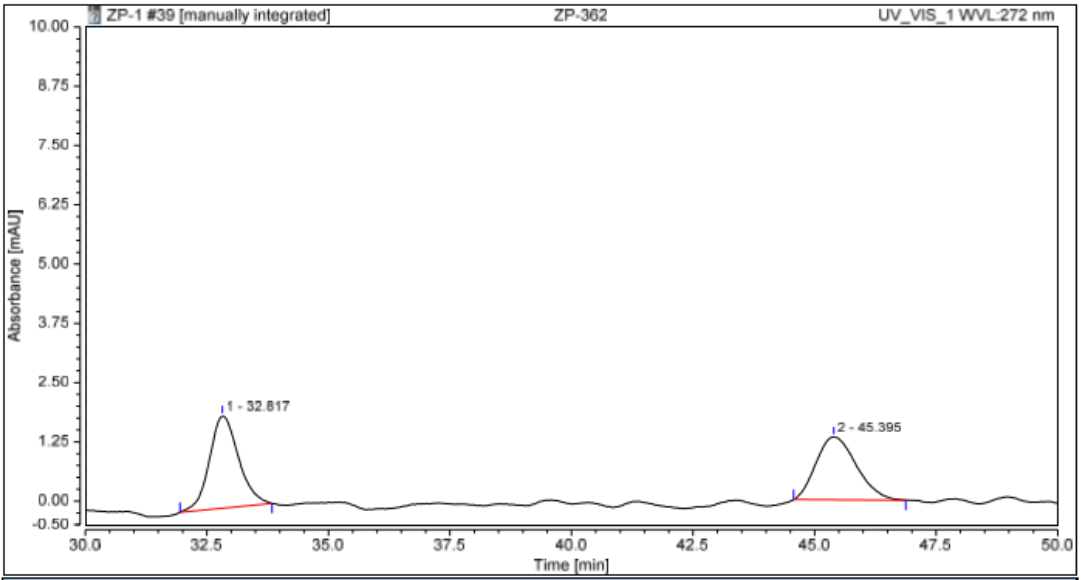
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29-7.27 (m, 2H), 7.25-7.19 (m, 4H), 7.12 (d, *J* = 8.0 Hz,, 2H), 3.45 (d, *J* = 15.4 Hz, 1H), 3.30 (dd, *J* = 36, 12 Hz, 2H), 2.83 (d, *J* = 15.4 Hz, 1H), 2.50-2.59 (m, 2H), 2.34-2.26 (m, 1H), 2.23-2.17(m, 1H), 1.93-1.87 (m, 2H), 1.33-1.25 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.0, 143.9, 143.8, 137.5, 129.7, 129.3, 128.3, 127.0, 126.7, 125.6, 121.8, 85.0, 68.1, 38.7, 38.3, 36.3, 30.6, 20.4; HRMS: m/z (ESI) calculated $[M+H]^+$: 293.1526, found: 293.1536.

The title compound **2b** was synthesized according to General Procedure (SI 5.2), and it was purified by column chromatography on silica gel (32% yield, 80% *ee*, 9.5 mg, white solid).

The enantiomeric excess of **2b** was determined by chiral HPLC analysis compared to the corresponding racemate.

Conditions: ChiralPark IA column; hexane/^{i}PrOH = 95:5; flow rate = 0.8 mL/min; λ= 272 nm; t_{R1}(minor)= 33.3 min; t_{R2}(major)=46.1 min.

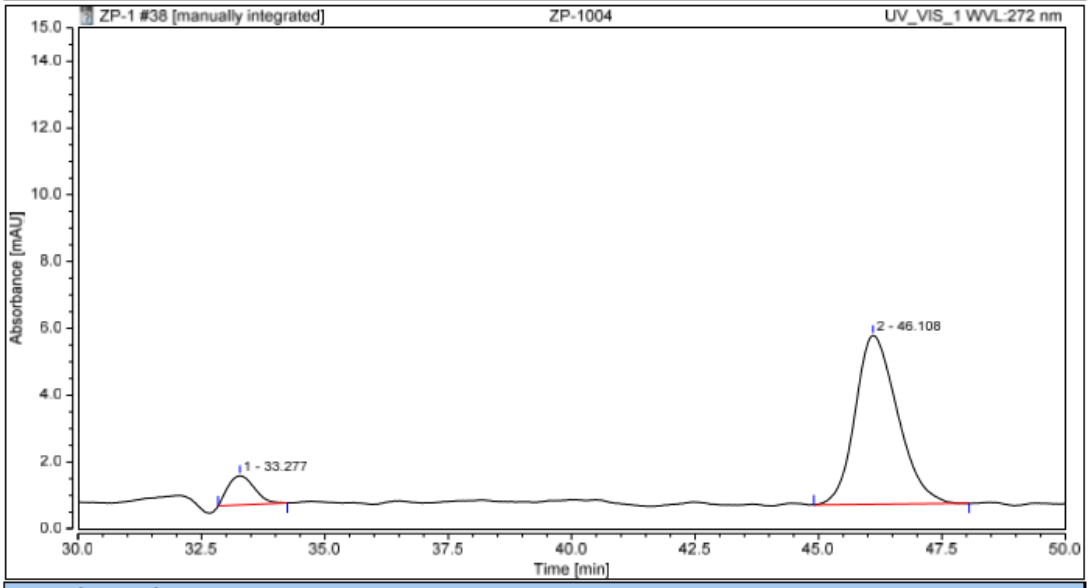
Chromatogram



Integration Results

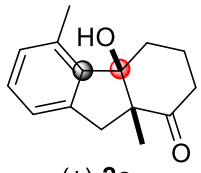
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
n.a.	Component 1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		32.817	1.356	1.955	51.52	59.46	n.a.
2		45.395	1.276	1.332	48.48	40.54	n.a.
Total:			**2.632**	**3.287**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
n.a.	Component 1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		33.277	0.543	0.881	9.74	14.83	n.a.
2		46.108	5.031	5.058	90.26	85.17	n.a.
Total:			**5.575**	**5.939**	**100.00**	**100.00**	



(±)-**2c**

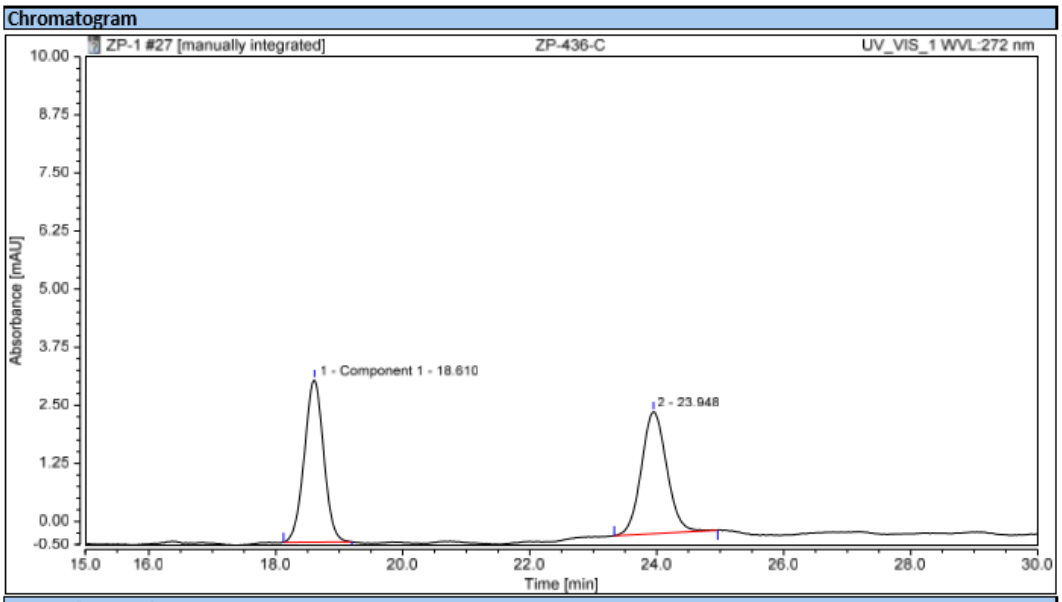
The title compound **(±)-2c** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (86% yield, 39.6 mg, colorless liquid).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.05 (t, *J* = 7.4 Hz, 1H), 6.93 (dd, *J* = 16.4, 7.4 Hz, 2H), 3.22 (d, *J* = 15.6 Hz, 1H), 2.57 (d, *J* = 15.7 Hz, 1H), 2.49-2.33 (m, 5H), 2.22-2.17 (m, 1H), 2.05-1.92 (m, 3H), 1.64-1.56 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.2, 143.0, 140.5, 134.5, 129.9, 128.3, 123.0, 87.9, 60.7, 40.5, 37.6, 33.3, 19.8, 18.2, 17.7; HRMS: m/z (ESI) calculated $[M+Na]^+$: 253.1191, found:253.1199.

The title compound **2c** was synthesized according to General Procedure (SI 5.2), and it was purified by column chromatography on silica gel (65% yield, 62% *ee*, 15.0 mg, colorless liquid).

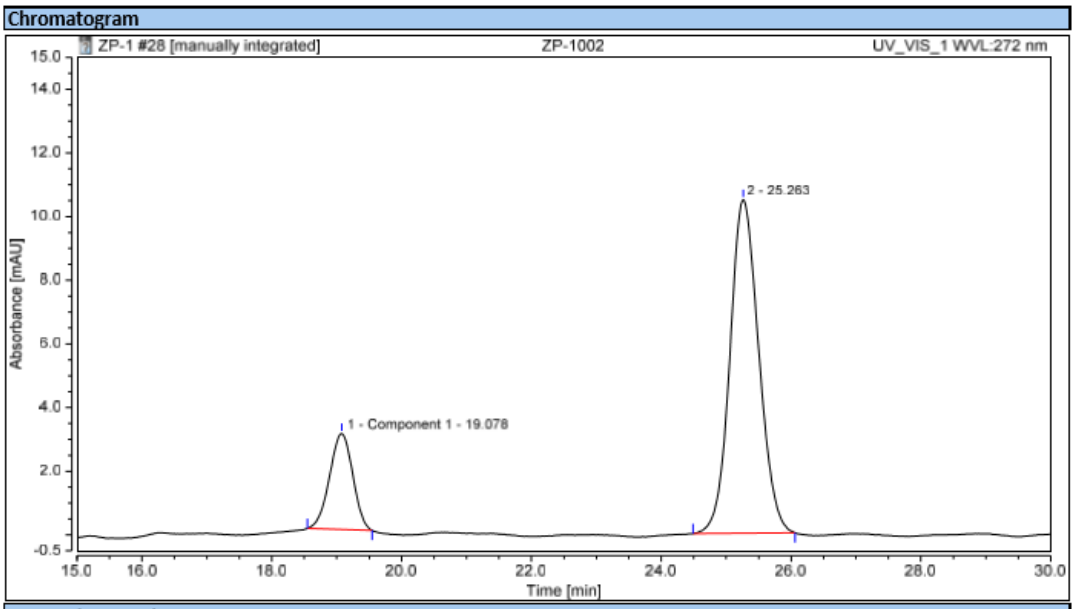
The enantiomeric excess of **2c** was determined by chiral HPLC analysis compared to the corresponding racemate.

Conditions: ChiralPark IA column; hexane/^{i}PrOH = 95:5; flow rate = 0.8 mL/min; λ= 272 nm; t_{R1}(major)= 25.3 min; t_{R2}(minor)=19.1 min.



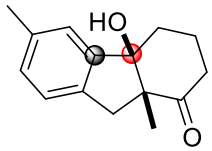
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1	Component 1	18.610	1.233	3.496	50.38	57.10	n.a.
2		23.948	1.214	2.626	49.62	42.90	n.a.
Total:			**2.447**	**6.121**	**100.00**	**100.00**	



Integration Results

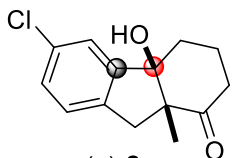
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1	Component 1	19.078	1.244	3.014	18.75	22.33	n.a.
2		25.263	5.391	10.484	81.25	77.67	n.a.
Total:			**6.636**	**13.499**	**100.00**	**100.00**	



(±)-**2d**

The title compound **(±)-2d** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (70% yield, 32.2 mg, white solid).

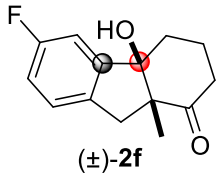
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 6.2 Hz, 2H), 3.55 (d, *J* = 15.4 Hz, 1H), 2.65 (d, *J* = 15.4 Hz, 1H), 2.56-2.48 (m, 1H), 2.35 (s, 3H), 2.33-2.24 (m, 2H), 2.19-2.11 (m, 1H), 1.98-1.88 (m, 2H), 1.49-1.37 (m, 1H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.5, 145.0, 139.70, 136.7, 129.8, 125.2, 122.6, 84.8, 62.3, 38.3, 37.6, 31.9, 21.4, 20.0, 17.9; HRMS: m/z (ESI) calculated $[M+Na]^{+}$: 253.1192, found:253.1199.



(±)-**2e**

The title compound **(±)-2e** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (77% yield, 38.5 mg, white solid).

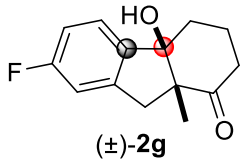
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26-7.17 (m, 3H), 3.55 (d, *J* = 15.8 Hz, 1H), 2.66 (d, *J* = 15.7 Hz, 1H), 2.56-2.48 (m, 1H), 2.31-2.26 (m, 2H), 2.20-2.12 (m, 1H), 2.00-1.92 (m, 1H), 1.84 (s, 1H), 1.47-1.37 (m, 1H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.8, 146.8, 141.1, 132.8, 129.1, 126.7, 122.5, 84.7, 62.4, 38.2, 37.4, 31.9, 19.9, 17.8; HRMS: m/z (ESI) calculated $[M+H]^+$: 283.1115, found:283.1095.



(±)-**2f**

The title compound **(±)-2f** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (79% yield, 37.9 mg, colorless liquid).

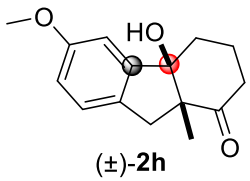
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20-7.17 (m, 1H), 6.92-6.96 (m, 2H), 3.54 (d, *J* = 15.4 Hz, 1H), 2.64 (d, *J* = 15.4 Hz, 1H), 2.48-2.56 (m, 1H), 2.31-2.24 (m, 2H), 2.19-2.12 (m, 1H), 1.99-1.91 (m, 1H), 1.89 (s, 1H), 1.47-1.36 (m, 1H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.9, 162.3 (d, *J* = 245.4 Hz), 147.0 (d, *J* = 7.1 Hz), 137.9 (d, *J* = 3.0 Hz), 126.6 (d, *J* = 8.1 Hz), 125.9 (d, *J* = 22.2 Hz) , 109.3 (d, *J* = 22.2 Hz) , 84.7 (d, *J* = 2.0 Hz), , 62.6, 38.0, 37.5, 32.0, 19.9, 17.8; HRMS: m/z (ESI) calculated $[M+Na]^+$: 267.1366, found:267.1391.



(±)-**2g**

The title compound **(±)-2g** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (81% yield, 37.9 mg, colorless liquid).

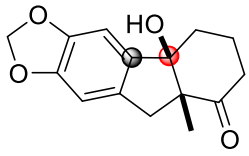
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (dd, *J* = 8.3, 5.1 Hz, 1H), 6.96-6.88 (m, 2H), 3.60 (d, *J* = 15.7 Hz, 1H), 2.68 (d, *J* = 15.7 Hz, 1H), 2.56-2.48 (m, 1H), 2.38-2.32 (m, 1H), 2.28-2.22 (m, 1H), 2.22-2.13 (m, 1H), 1.97-1.89 (m, 1H), 1.72 (s, 1H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.8, 164.4 (d, *J* = 248.5 Hz), 145.6 (d, *J* = 8.1 Hz), 140.3, 123.5 (d, *J* = 9.1 Hz), 114.1 (d, *J* = 22.2 Hz), 112.6 (d, *J* = 22.2 Hz), 84.0, 62.6, 38.2, 37.4, 31.7, 20.0, 17.9; HRMS: m/z (ESI) calculated $[M+Na]^+$: 235.1125, found:235.1129.



(±)-**2h**

The title compound **(±)-2h** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (76% yield, 37.4 mg, white solid).

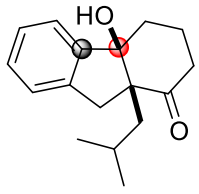
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.78-6.75 (m, 1H), 3.80 (s, 3H), 3.61 (d, *J* = 15.6 Hz, 1H), 2.68 (d, *J* = 15.6 Hz, 1H), 2.56-2.48 (m, 1H), 2.40-2.35 (m, 1H), 2.27-2.13 (m, 2H), 1.98-1.89 (m, 1H), 1.73 (s, 1H), 1.42-1.33 (m, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.3, 160.6, 145.1, 136.7, 123.0, 113.3, 110.4, 84.1, 62.7, 55.4, 38.4, 37.5, 31.5, 20.0, 18.1; HRMS: m/z (ESI) calculated $[M+H]^{+}$: 247.1329, found:247.1333.



(±)-**2i**

The title compound **(±)-2i** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (58% yield, 30.2 mg, white solid).

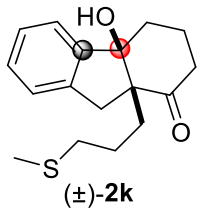
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.70 (d, *J* = 3.2 Hz, 2H), 5.93 (s, 2H), 3.51 (d, *J* = 15.3 Hz, 1H), 2.58 (d, *J* = 15.3 Hz, 1H), 2.53-2.45 (m, 1H), 2.31-2.21 (m, 2H), 2.16-2.08 (m, 1H), 1.94-1.86 (m, 1H), 1.78 (s, 1H), 1.43-1.36 (m, 1H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.2, 148.5, 147.1, 137.5, 136.8, 105.9, 102.7, 101.2, 84.4, 62.8, 38.1, 37.5, 31.5, 19.9, 18.0; HRMS: m/z (ESI) calculated $[M+Na]^{+}$: 283.0940, found:283.0941.



(±)-**2j**

The title compound **(±)-2j** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (76% yield, 39.2 mg, colorless liquid).

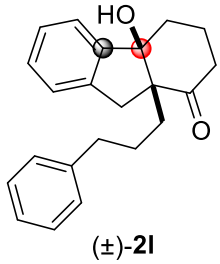
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30-7.21 (m, 2H), 7.18 (d, *J* = 3.0 Hz, 2H), 3.83 (d, *J* = 15.3 Hz, 1H), 2.66 (d, *J* = 15.3 Hz, 1H), 2.55-2.41 (m, 2H), 2.27-2.12 (m, 2H), 2.01-1.82 (m, 3H), 1.73 (s, 1H), 1.51 (m, 1H), 1.30-1.21 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.1, 144.8, 143.1, 129.2, 126.8, 125.6, 121.8, 86.1, 67.2, 41.1, 38.4, 36.4, 30.1, 25.3, 24.7, 23.6, 20.6; HRMS: m/z (ESI) calculated $[M+H]^{+}$: 259.1692, found:259.1693.



(±)-**2k**

The title compound **(±)-2k** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (48% yield, 27.8 mg, colorless liquid).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.30-7.20 (m, 4H), 3.72 (d, *J* = 15.3 Hz, 1H), 2.66 (d, *J* = 15.3 Hz, 1H), 2.56-2.47 (m, 4H), 2.29-2.10 (m, 3H), 2.08 (s, 3H), 2.03-1.90 (m, 2H), 1.66 (s, 1H), 1.42-1.25 (m, 3H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 211.8, 144.0, 143.7, 129.3, 127.0, 125.6, 121.8, 85.1, 66.8, 38.0, 35.5, 34.6, 30.6, 30.5, 24.5, 20.2, 15.4; HRMS: m/z (ESI) calculated $[M+Na]^+$: 313.1254, found:313.1233.



(±)-**2l**

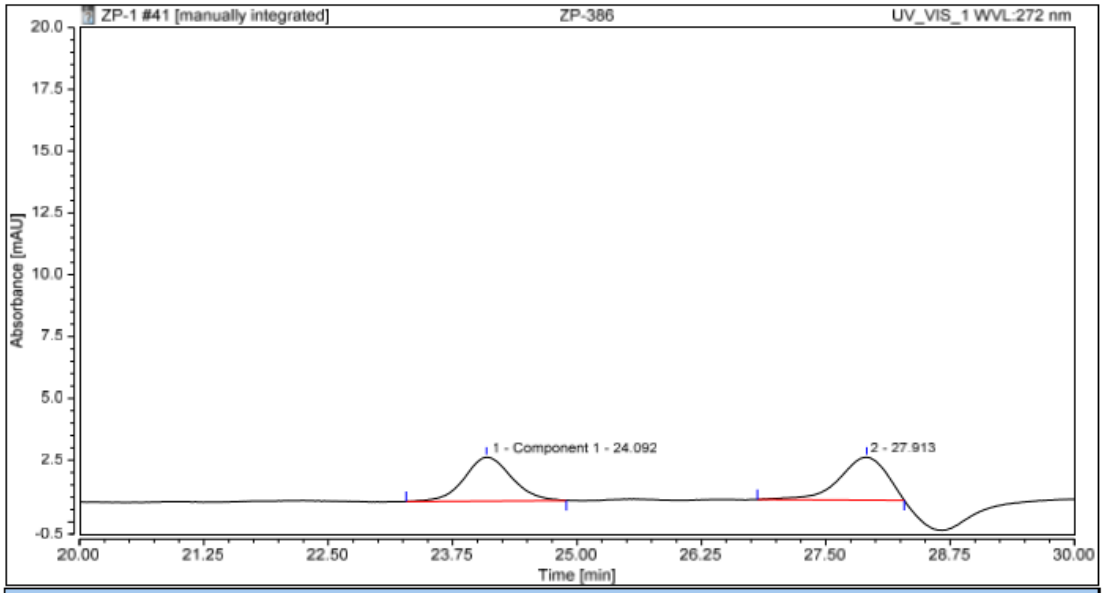
The title compound **(±)-2l** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (54% yield, 35.8 mg, white solid).

^{1}H NMR (400 MHz, Chloroform-*d*) δ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27-7.25 (m, 4H), 7.19-7.15 (m, 5H), 3.71 (d, *J* = 15.3 Hz, 1H), 2.71-2.58 (m, 3H), 2.46-2.32 (m, 2H), 2.21-2.03 (m, 3H), 1.91-1.83 (m, 2H), 1.63-1.54 (m, 1H), 1.45-1.33 (m, 1H), 1.30-1.18 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.9, 144.2, 143.7, 141.9, 129.2, 128.4, 128.4, 128.4, 128.4, 126.9, 125.9, 125.6, 121.8, 85.1, 67.1, 38.0, 36.3, 35.4, 31.2, 30.4, 26.7, 20.2; HRMS: m/z (ESI) calculated $[M+Na]^+$: 343.1674, found:343.1669.

The title compound **2l** was synthesized according to General Procedure (SI 5.2), and it was purified by column chromatography on silica gel (67% yield, 21.4 mg, white solid). The enantiomeric excess of **2l** was determined by chiral HPLC analysis compared to the corresponding racemate.

Conditions: ChiralPark IA column; hexane/^{i}PrOH = 95:5; flow rate = 0.8 mL/min; λ= 272 nm; t_{R1}(major)= 27.7 min; t_{R2}(minor)=23.9 min.

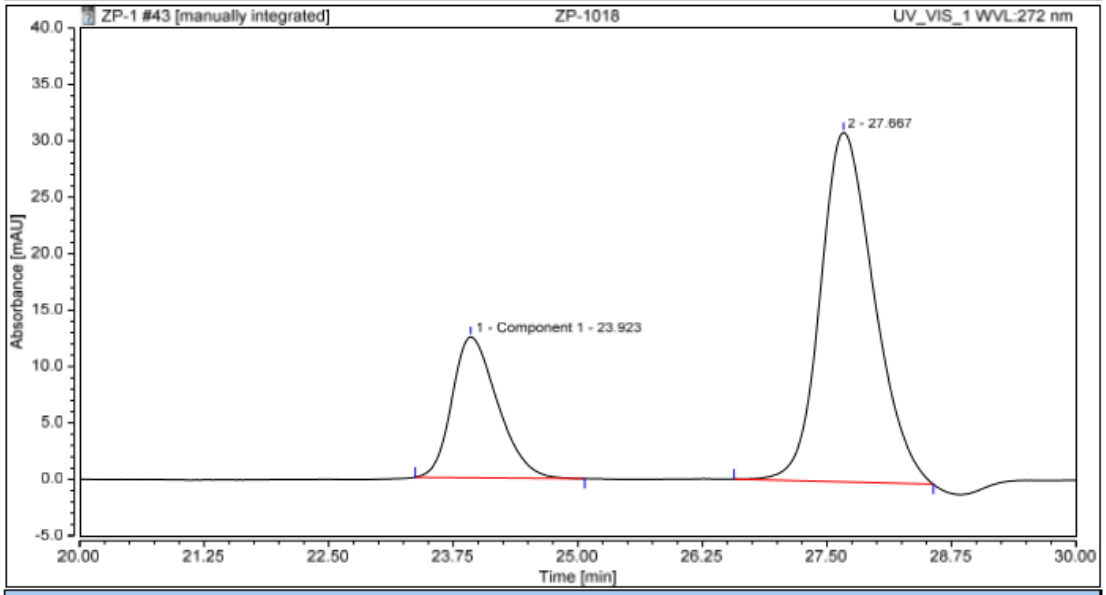
Chromatogram



Integration Results

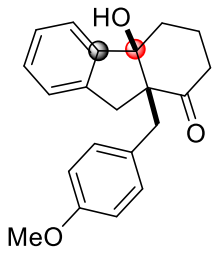
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1	Component 1	24.092	0.974	1.772	50.92	50.59	n.a.
2		27.913	0.939	1.731	49.08	49.41	n.a.
Total:			**1.913**	**3.503**	**100.00**	**100.00**	

Chromatogram



Integration Results

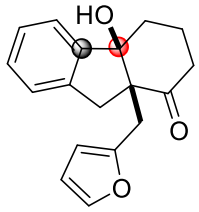
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1	Component 1	23.923	6.601	12.483	25.45	28.72	n.a.
2		27.667	19.334	30.977	74.55	71.28	n.a.
Total:			**25.934**	**43.461**	**100.00**	**100.00**	



(±)-**2m**

The title compound **(±)-2m** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (93% yield, 59.9 mg, white solid).

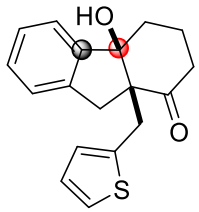
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26-7.20 (m, 4H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 3.46 (d, *J* = 15.4 Hz, 1H), 3.24 (q, *J* = 14.0 Hz, 2H), 2.82 (d, *J* = 15.4 Hz, 1H), 2.55-2.47 (m, 2H), 2.32-2.18 (m, 1H), 2.20 (d, *J* = 14.1 Hz, 1H), 1.93-1.86 (m, 1H), 1.34-1.22 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.3, 158.3, 143.9, 143.8, 130.6, 129.4, 129.3, 127.0, 125.6, 121.8, 113.7, 85.0, 68.2, 55.2, 38.9, 37.5, 36.4, 30.6, 20.3; HRMS: m/z (ESI) calculated $[M+H]^+$: 323.1643, found:323.1642.



(±)-**2n**

The title compound **(±)-2n** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (62% yield, 35.0 mg, colorless liquid).

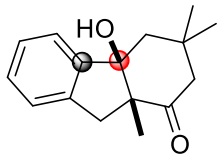
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 1.9 Hz, 1H), 7.24-7.20 (m, 4H), 6.25 (t, *J* = 2.5 Hz, 1H), 6.05 (d, *J* = 3.1 Hz, 1H), 3.58 (d, *J* = 15.7 Hz, 1H), 3.30 (d, *J* = 2.1 Hz, 2H), 2.85 (d, *J* = 15.8 Hz, 1H), 2.52-2.40 (m, 2H), 2.27-2.14 (m, 3H), 1.93-1.87 (m, 1H), 1.36-1.26 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.4, 151.7, 144.0, 143.2, 141.6, 129.2, 127.0, 125.4, 121.9, 110.4, 107.7, 85.0, 66.3, 38.4, 37.1, 31.5, 31.2, 20.0; HRMS: m/z (ESI) calculated $[M+H]^+$: 283.1326, found:283.1329.



(±)-**2o**

The title compound **(±)-2o** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (57% yield, 34.0 mg, colorless liquid).

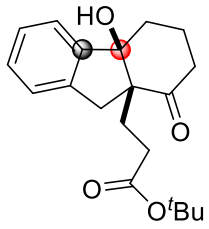
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28-7.23 (m, 4H), 7.17 (d, *J* = 5.1 Hz, 1H), 6.95-6.93 (m, 3.4 Hz, 1H), 6.80 (d, *J* = 3.4 Hz, 1H), 3.68 (d, *J* = 15.5 Hz, 1H), 3.55 (q, *J* = 15.1 Hz, 2H), 2.88 (d, *J* = 15.4 Hz, 1H), 2.62-2.51 (m, 2H), 2.37-2.23 (m, 2H), 1.98-1.93 (m, 1H), 1.86 (s, 1H), 1.40-1.34 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.6, 143.8, 143.6, 139.2, 129.4, 127.1, 126.9, 126.5, 125.7, 124.2, 121.8, 85.2, 67.6, 38.6, 36.6, 32.5, 30.9, 20.3; HRMS: m/z (ESI) calculated $[M+H]^{+}$: 299.1098, found:299.1100.



(±)-**2p**

The title compound **(±)-2p** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (63% yield, 30.7 mg, white solid).

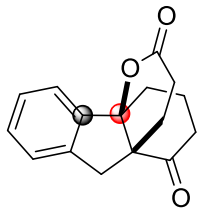
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31-7.29 (m, 1H), 7.24 (s, 3H), 3.53 (d, *J* = 15.9 Hz, 1H), 2.67 (d, *J* = 15.9 Hz, 1H), 2.52 (d, *J* = 13.4 Hz, 1H), 2.19 (d, *J* = 13.3 Hz, 1H), 2.13-2.05 (m, 2H), 1.78 (s, 1H), 1.29 (s, 3H), 1.14 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.7, 146.7, 140.4, 128.7, 127.0, 125.4, 122.8, 85.9, 60.0, 50.4, 46.1, 39.6, 33.2, 30.7, 29.5, 18.4; HRMS: m/z (ESI) calculated $[M+H]^{+}$: 277.1796, found:277.1798.



(±)-**2q**

The title compound **(±)-2q** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (17% yield, 11.2 mg, colorless liquid).

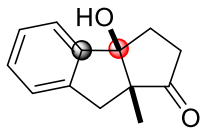
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28-7.19 (m, 5H), 3.64 (d, *J* = 15.2 Hz, 1H), 2.66 (d, *J* = 15.2 Hz, 1H), 2.60-2.54 (m, 1H), 2.47 (d, *J* = 14.1 Hz, 1H), 2.38-2.33 (m, 1H), 2.28-2.13 (m, 4H), 2.11-2.06 (m, 1H), 1.94-1.90 (m, 1H), 1.84 (s, 1H), 1.44 (s, 9H), 1.32-1.29 (m, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 212.0, 172.7, 143.9, 143.5, 129.2, 127.1, 125.6, 121.9, 84.9, 80.6, 66.1, 38.0, 35.3, 31.2, 30.7, 28.1, 26.5, 20.1; HRMS: m/z (ESI) calculated $[M+H]^{+}$: 348.2170, found:348.2169.



(±)-**3**

The title compound **(±)-3** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (69% yield, 35.3 mg, colorless liquid).

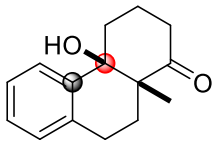
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45-7.43 (m, 1H), 7.33-7.31 (m, 2H), 7.27-7.24 (m, 1H), 3.36 (d, *J* = 16.1 Hz, 1H), 2.90 (d, *J* = 16.2 Hz, 1H), 2.60-2.57 (m, 2H), 2.48-2.43 (m, 1H), 2.41-2.27 (m, 3H), 2.01-1.95 (m, 2H), 1.85-1.81 (m, 1H), 1.78-1.73 (m, 1H) 1.66 (s, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 211.1, 170.9, 144.4, 137.6, 129.4, 128.1, 125.1, 123.2, 94.9, 56.0, 41.2, 37.7, 36.5, 27.9, 26.3, 19.0; HRMS: m/z (ESI) calculated $[M+H]^+$: 257.1168, found:257.1172.



(±)-**5a**

The title compound **(±)-5a** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (79% yield, 32.0 mg, colorless liquid).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47-7.45 (m, 1H), 7.29-7.26 (m, 2H), 7.18-7.16 (m, 1H), 3.21 (d, *J* = 16.5 Hz, 1H), 2.86 (d, *J* = 16.5 Hz, 1H), 2.61-2.45 (m, 2H), 2.33-2.24 (m, 1H), 1.96-1.86 (m, 2H), 1.20 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 221.5, 144.8, 142.3, 129.5, 127.7, 125.0, 123.3, 88.4, 58.8, 41.1, 36.9, 31.7, 15.6; HRMS: m/z (ESI) calculated $[M+Na]^+$: 225.0890, found:225.0886.

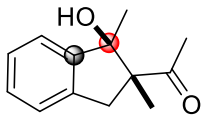


(±)-**5b**

The title compound **(±)-5b** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (67% yield, 30.8 mg, colorless liquid).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58-7.56 (m, 1H), 7.26-7.16 (m, 2H), 7.10-7.08 (m, 1H), 2.92-2.89 (m, 2H), 2.64-2.56 (m, 2H), 2.46-2.37 (m, 2H), 2.29-2.18 (m, 1H), 2.18-2.08 (m, 1H), 2.03-1.98 (m, 1H), 1.84-1.76 (m, 1H), 1.67-1.65 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.8, 142.3, 134.5, 128.7, 127.3, 126.6,

125.6, 78.0, 52.7, 37.21, 37.16, 30.8, 25.2, 21.0, 15.9; HRMS: m/z (ESI) calculated $[M+H]^+$: 231.1376, found:231.1380.

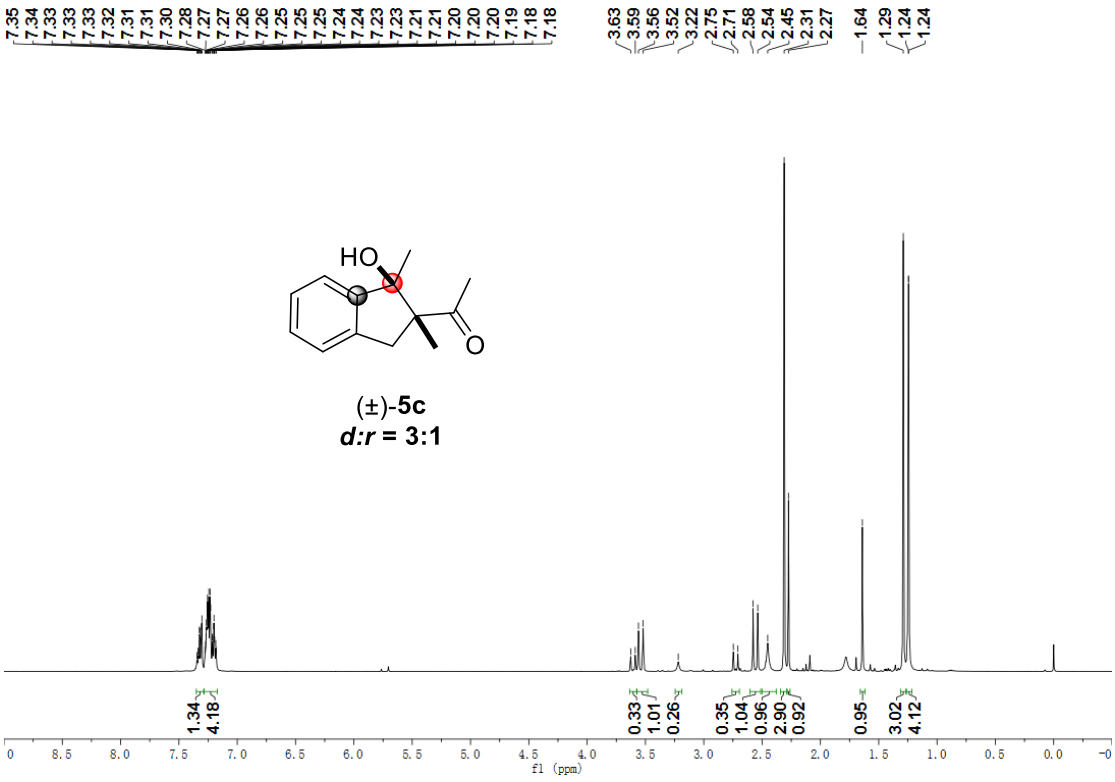


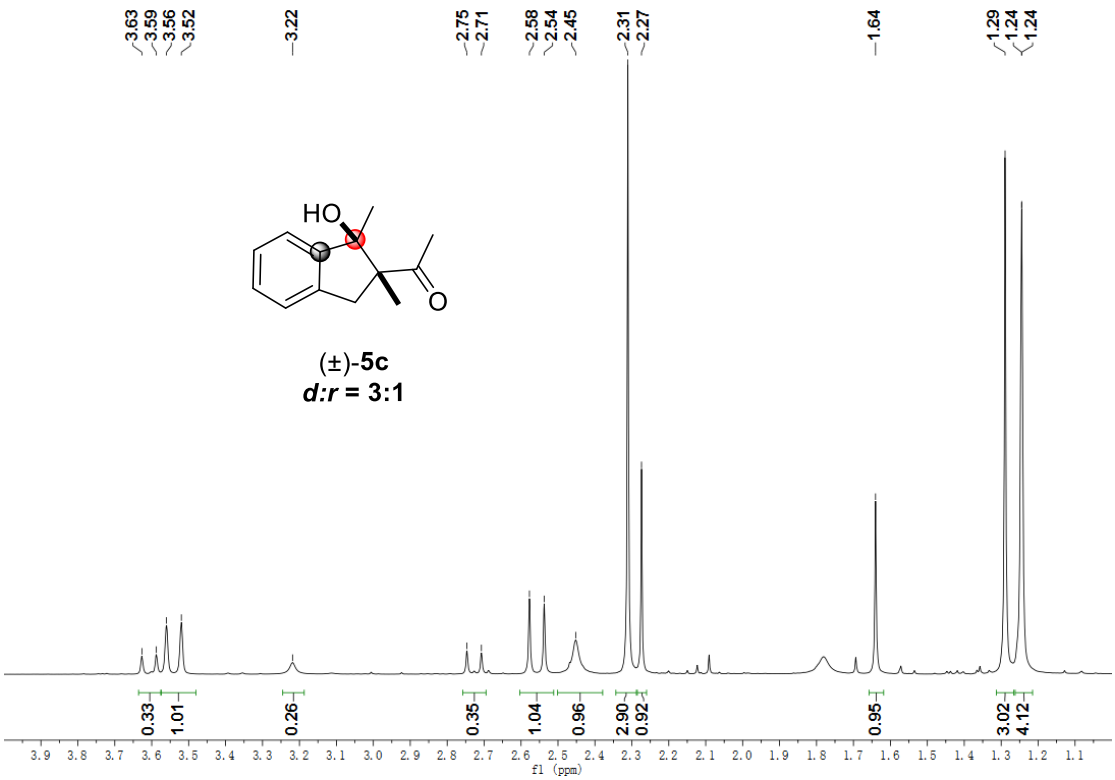
(±)-**5c**

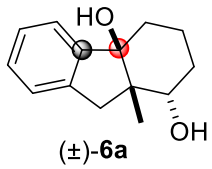
The title compound **(±)-5c** was synthesized according to General Procedure (SI 5.1), and it was purified by column chromatography on silica gel (83% yield, *dr* = 3:1, 33.9 mg, colorless liquid).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.18 (m, 4H), 3.54 (d, *J* = 16.0 Hz, 1H), 2.56 (d, *J* = 16.0 Hz, 1H), 2.45 (s, 1H), 2.31 (s, 3H), 1.29 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.7, 146.7, 138.4, 128.2, 127.3, 125.3, 122.4, 82.8, 64.5, 38.5, 27.7, 25.8, 19.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.18 (m, 1.32H), 3.61 (d, *J* = 16.0 Hz, 0.33H), 3.22 (s, 0.29H), 2.73 (d, *J* = 16.0 Hz, 0.32H), 2.27 (s, 0.98H), 1.64 (s, 0.97H), 1.24 (s, 0.98H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.4, 146.2, 139.8, 128.6, 127.3, 125.0, 122.8, 83.3, 62.4, 40.7, 27.8, 22.7, 20.9; HRMS: m/z (ESI) calculated $[M+Na]^+$: 227.1043, found:227.1043.



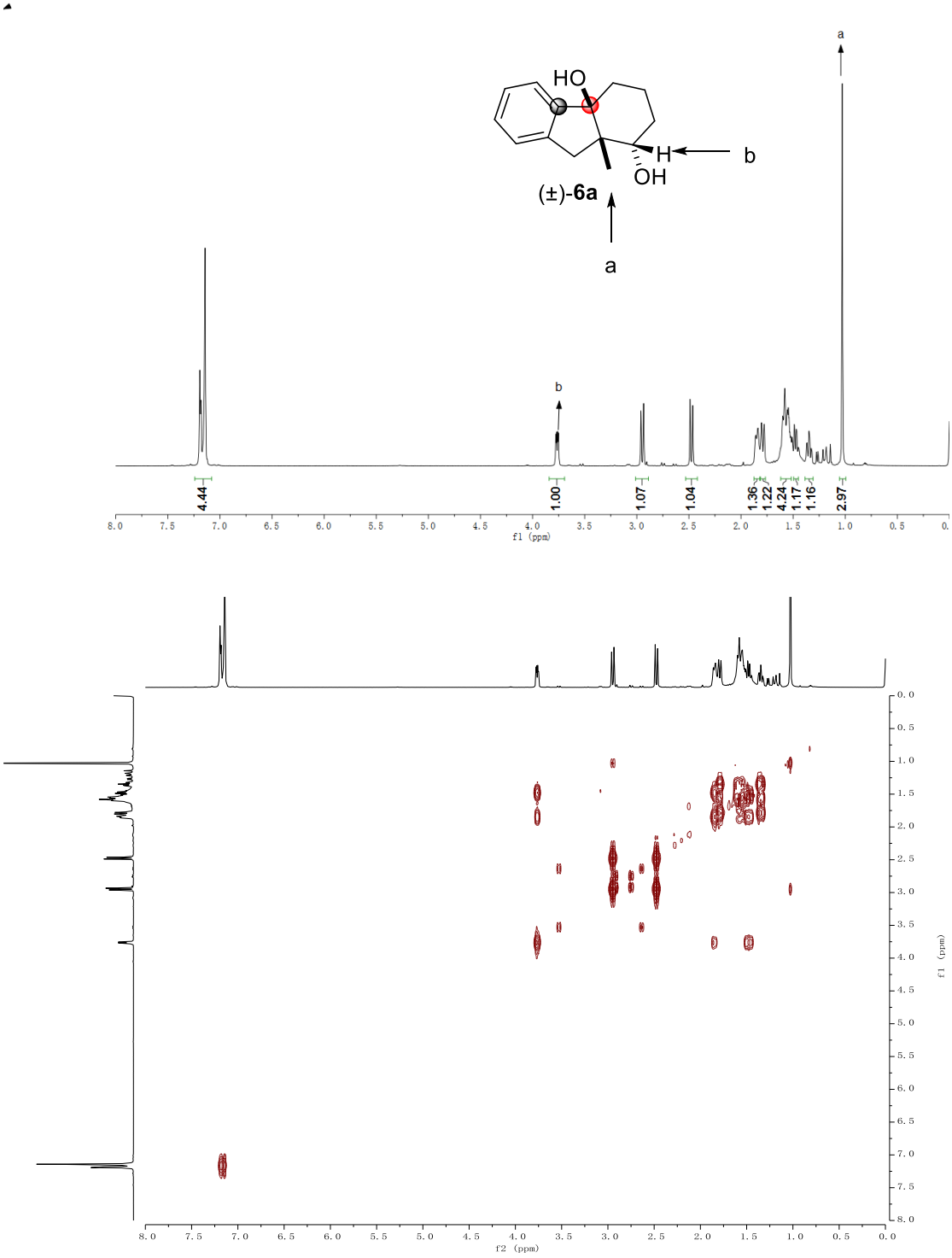




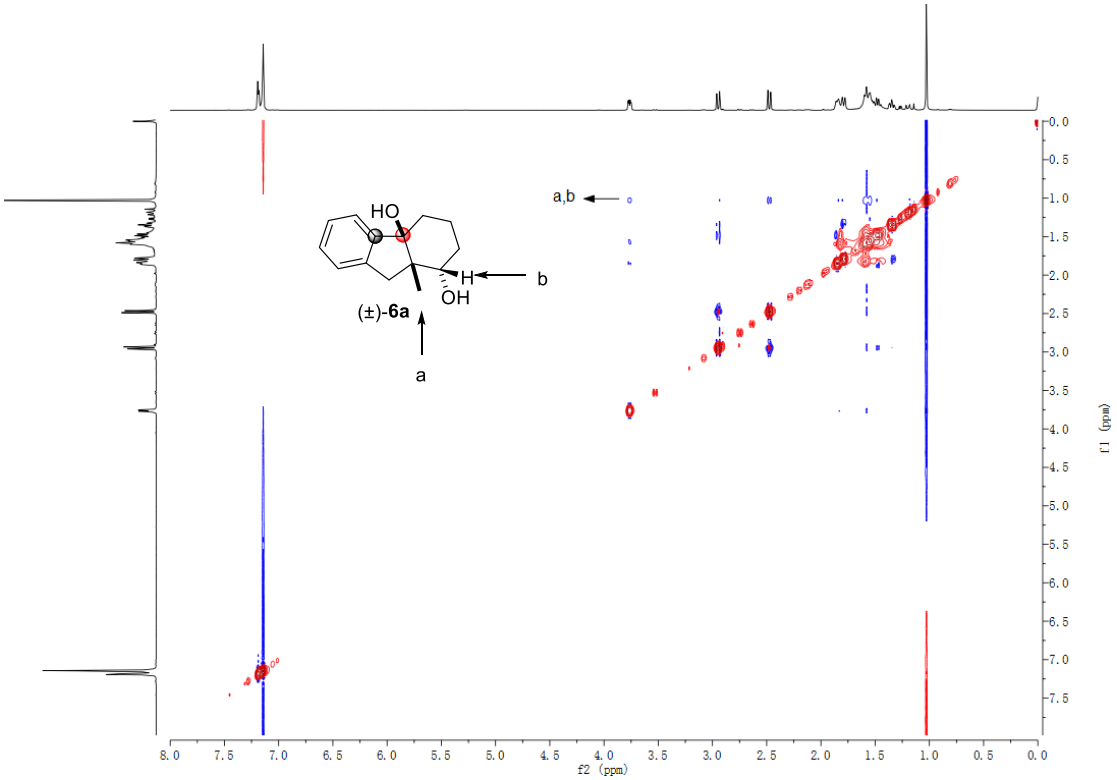
The title compound **(±)-6a** was synthesized according to General Procedure (SI 6.1), and it was purified by column chromatography on silica gel (91% yield, 19.8 mg, white solid).

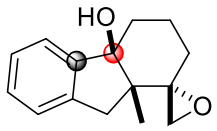
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26-7.21 (m, 4H), 3.83 (dd, *J* = 10.9, 4.8 Hz, 1H), 3.02 (d, *J* = 15.4 Hz, 1H), 2.55 (d, *J* = 15.5 Hz, 1H), 1.94-1.83 (m, 2H), 1.69-1.50 (m, 5H), 1.46-1.38 (m, 1H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.9, 139.2, 127.6, 126.7, 125.7, 121.5, 84.1, 74.8, 52.5, 37.4, 36.6, 31.2 , 20.5, 20.0; HRMS: m/z (ESI) calculated $[M+Na]^{+}$: 241.1198, found:241.1199.

2D COSY analysis of **(±)-6a**



2D NOESY analysis of **(±)-6a**



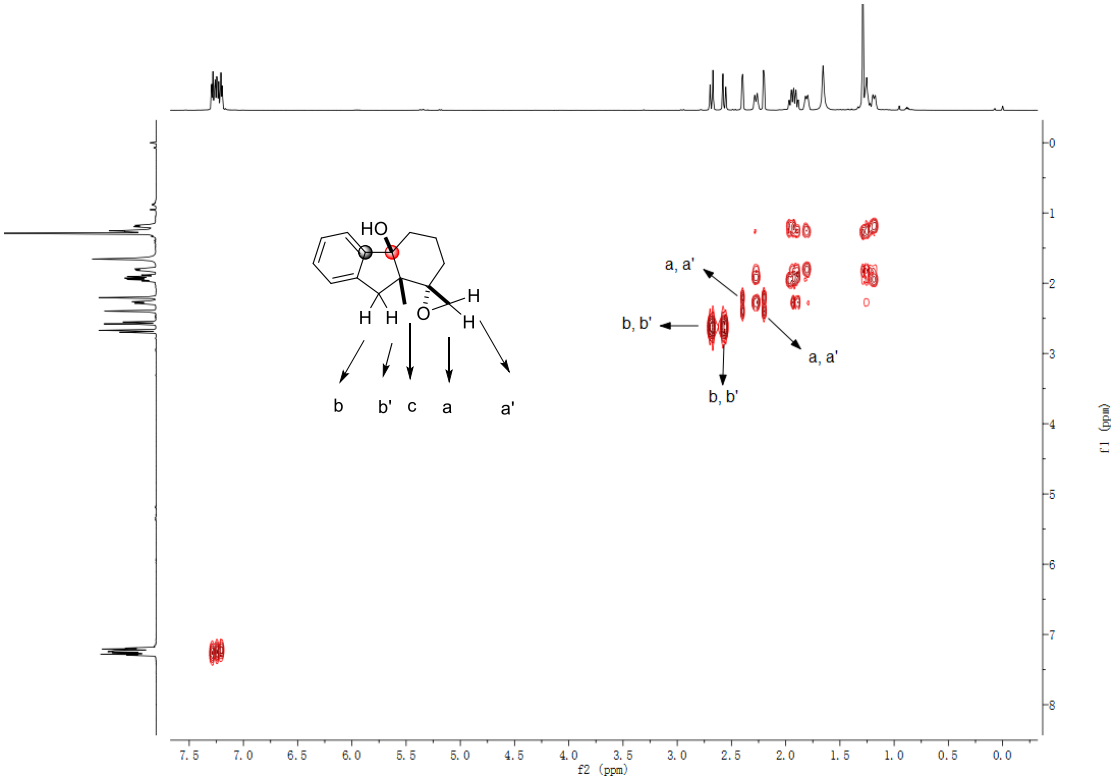


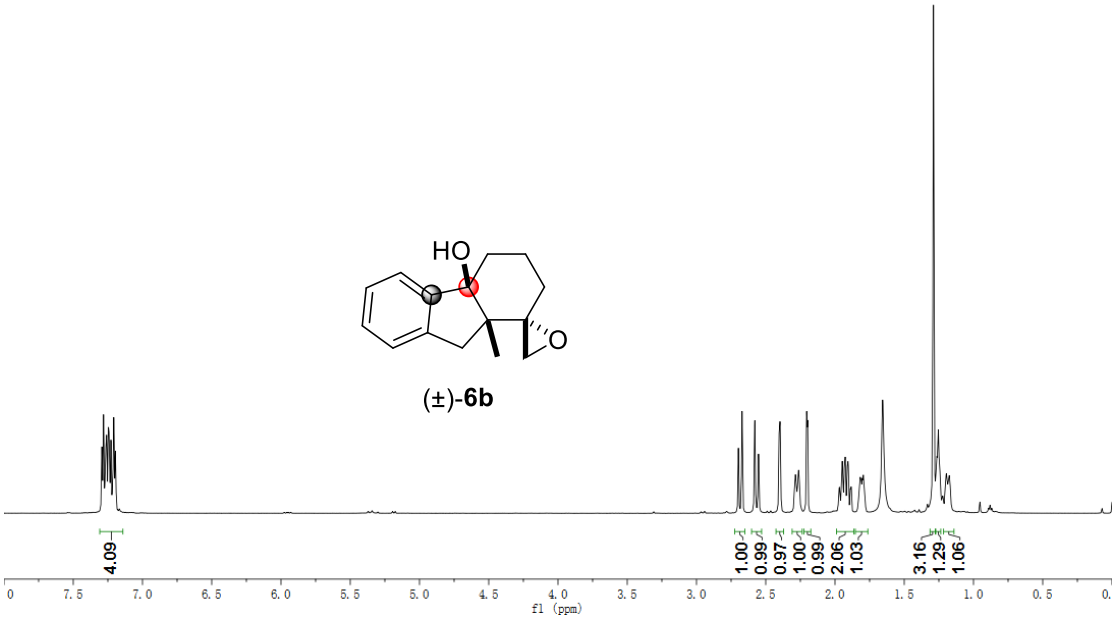
(±)-**6b**

The title compound **(±)-6b** was synthesized according to General Procedure (SI 6.2), and it was purified by column chromatography on silica gel (78% yield, 17.9 mg, colorless liquid).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30-7.19 (m, 4H), 2.69 (d, *J* = 16.0 Hz, 1H), 2.57 (d, *J* = 16.0 Hz, 1H), 2.40 (dd, *J* = 4.3, 1.8 Hz, 1H), 2.30-2.24 (m, 1H), 2.20 (d, *J* = 4.3 Hz, 1H), 1.98-1.87 (m, 2H), 1.85-1.78 (m, 1H), 1.29 (s, 3H), 1.29-1.23 (m, 1H), 1.21-1.17 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.2, 128.8, 126.8, 125.0, 122.2, 83.5, 61.2, 54.1, 51.2, 38.3, 31.9, 31.2, 20.3, 15.8. HRMS: m/z (ESI) calculated $[M+Na]^{+}$: 253.1183, found:253.1199.

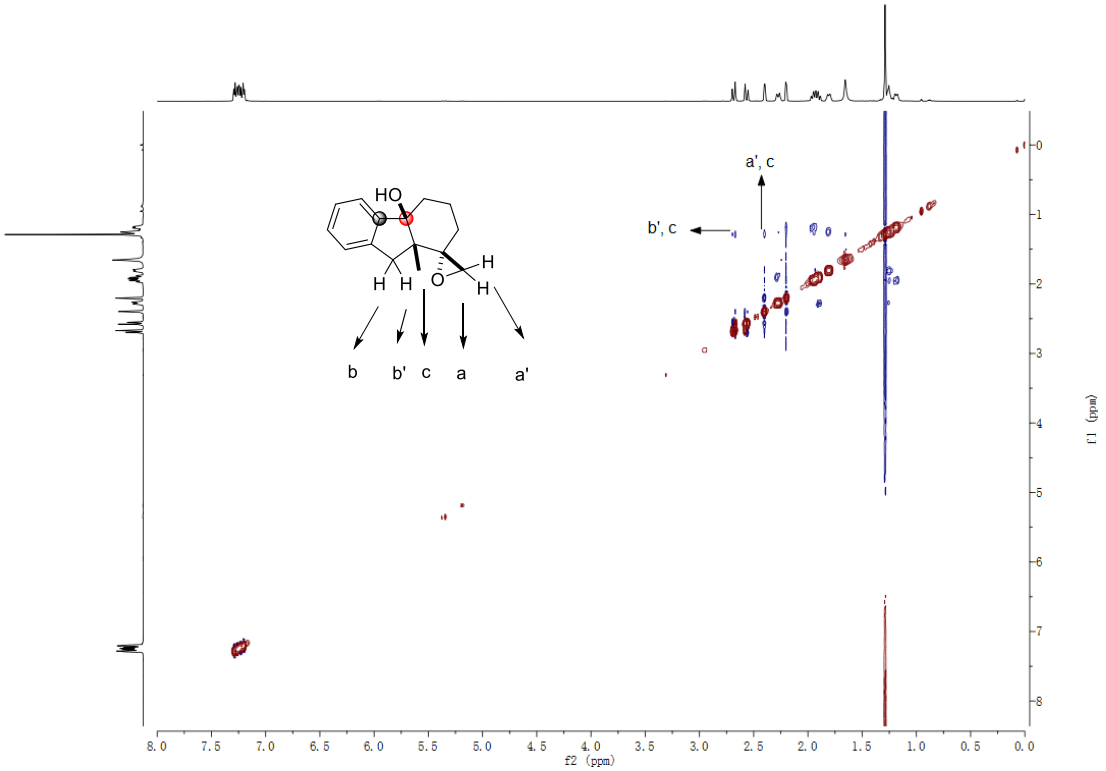
2D COSY analysis of **(±)-6b**

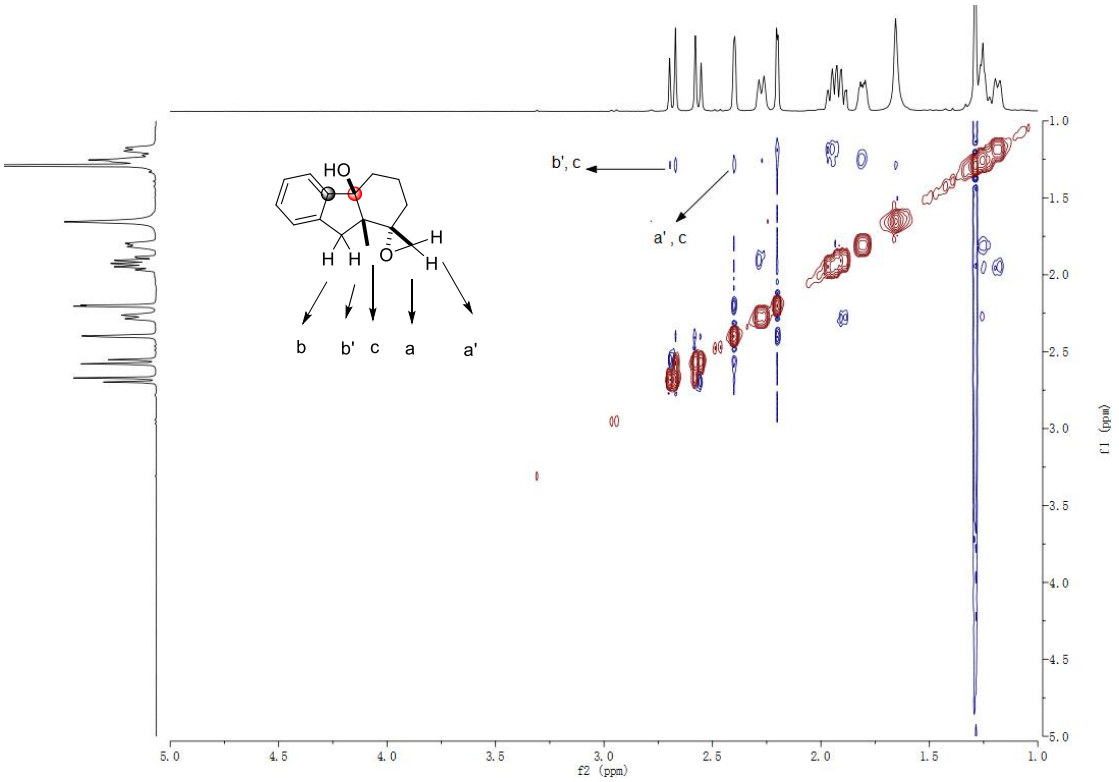


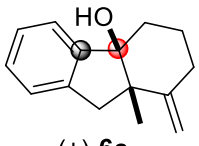


(±)-**6b**

2D NOESY analysis of **(±)-6b**


HO
H H
O
H
H
b b' c a a'
a', c
b', c
f2 (ppm)
f1 (ppm)

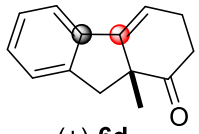

HO
H H
O
H
H
b b' c a a'
b', c
a', c
f2 (ppm)
f1 (ppm)


HO

(±)-**6c**

The title compound **(±)-6c** was synthesized according to General Procedure (SI 6.3), and it was purified by column chromatography on silica gel (78% yield, 16.7 mg, colorless liquid).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27-724 (m, 1H), 7.23-7.19 (m, 3H), 4.85 (dd, *J* = 14.6, 1.4 Hz, 2H), 3.19 (d, *J* = 15.5 Hz, 1H), 2.70 (d, *J* = 15.5 Hz, 1H), 2.39-2.20 (m, 2H), 1.97-1.85 (m, 2H), 1.78 (s, 1H), 1.72-1.64 (m, 1H), 1.47-1.40 (m, 1H), 1.22 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.0, 147.6, 141.4, 127.8, 126.6, 125.2, 122.1, 109.5, 84.4, 53.2, 41.9, 35.2, 32.6, 22.7, 20.4; HRMS: m/z (ESI) calculated $[M+Na]^{+}$: 237.1249, found:237.1250.

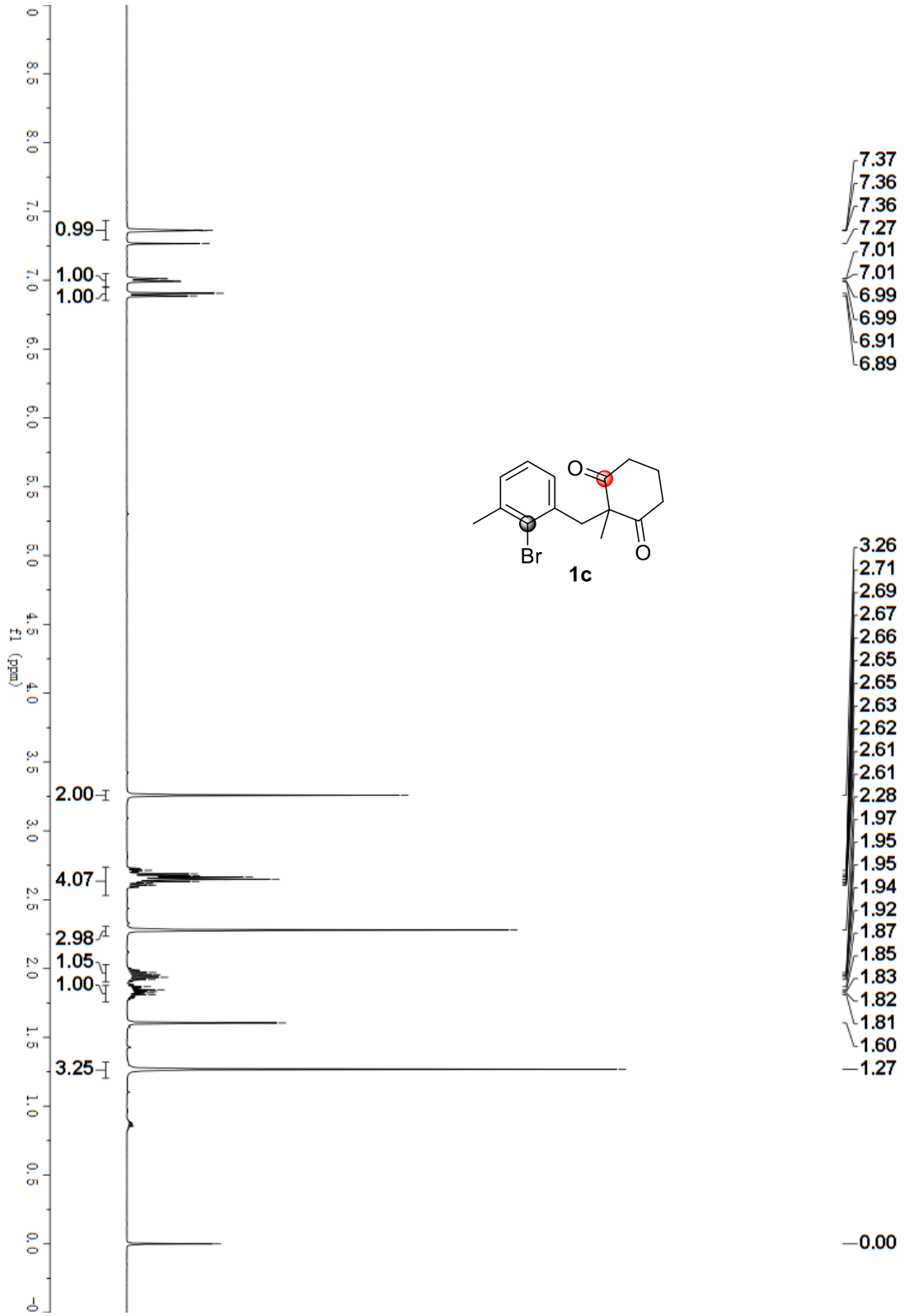


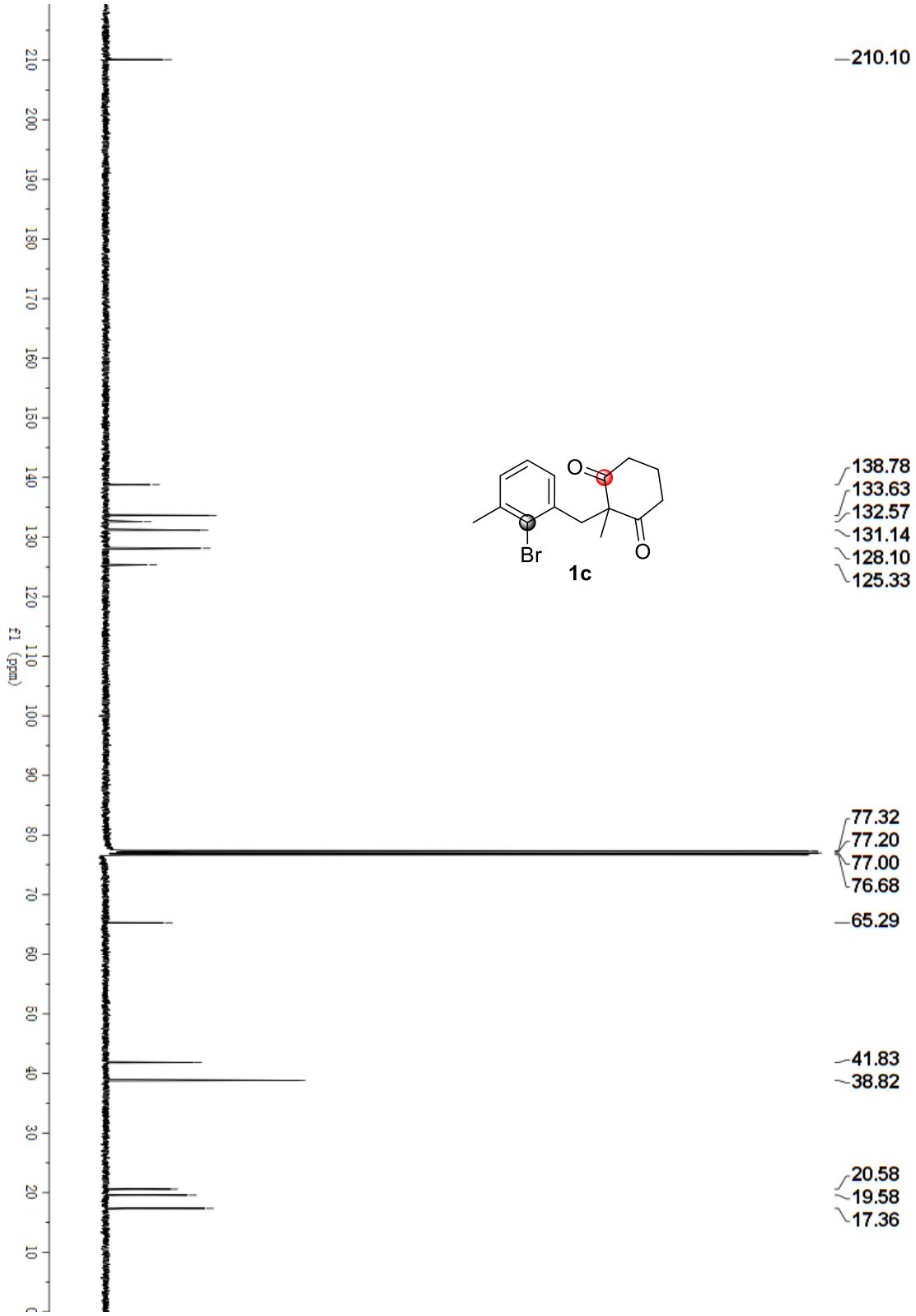
(±)-**6d**

The title compound **(±)-6d** was synthesized according to General Procedure (SI 6.4), and it was purified by column chromatography on silica gel (58% yield, 11.0 mg, white solid).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45-7.44 (m, 1H), 7.27-7.21 (m, 3H), 6.28-6.26 (m, 1H), 3.39 (d, *J* = 16.5 Hz, 1H), 2.81-2.72 (m, 3H), 2.63-2.58 (m, 1H), 2.39-2.33 (m, 1H), 1.32 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 214.9, 147.1, 142.1, 138.0, 128.5, 126.9, 125.8, 120.9, 116.1, 55.0, 40.2, 35.6, 24.1, 23.4; HRMS: m/z (ESI) calculated $[M+Na]^{+}$: 199.1125, found:199.1117.

9. Spectroscopic Data (NMR Spectrum)

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133.63
132.57
131.14
128.10
125.33
77.32
77.20
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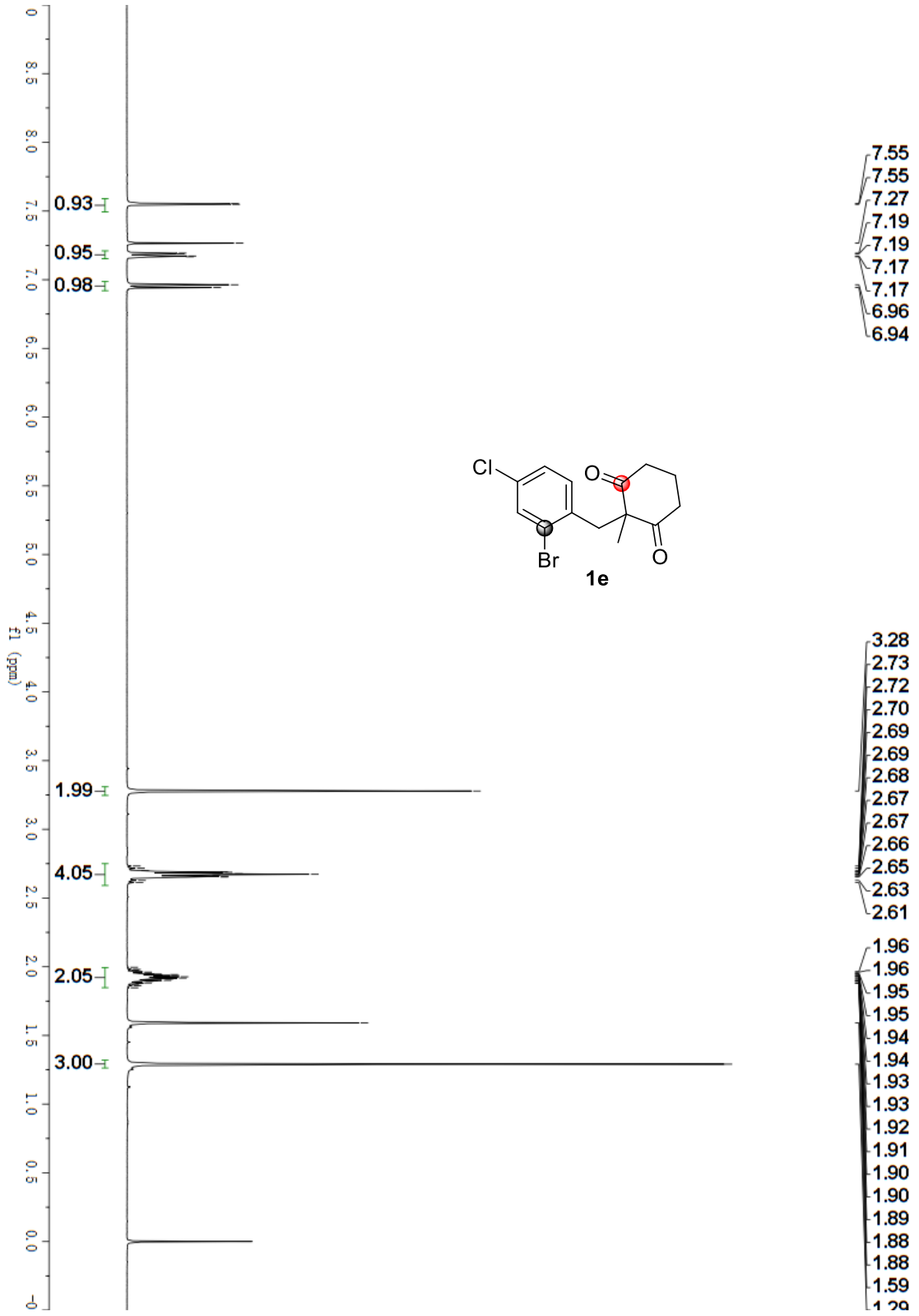
76.68
65.29
41.83
38.82
20.58
19.58
17.36
O
Br
O
1c
f1 (ppm)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0.95
0.98
1.99
4.05
2.05
3.00
f1 (ppm)
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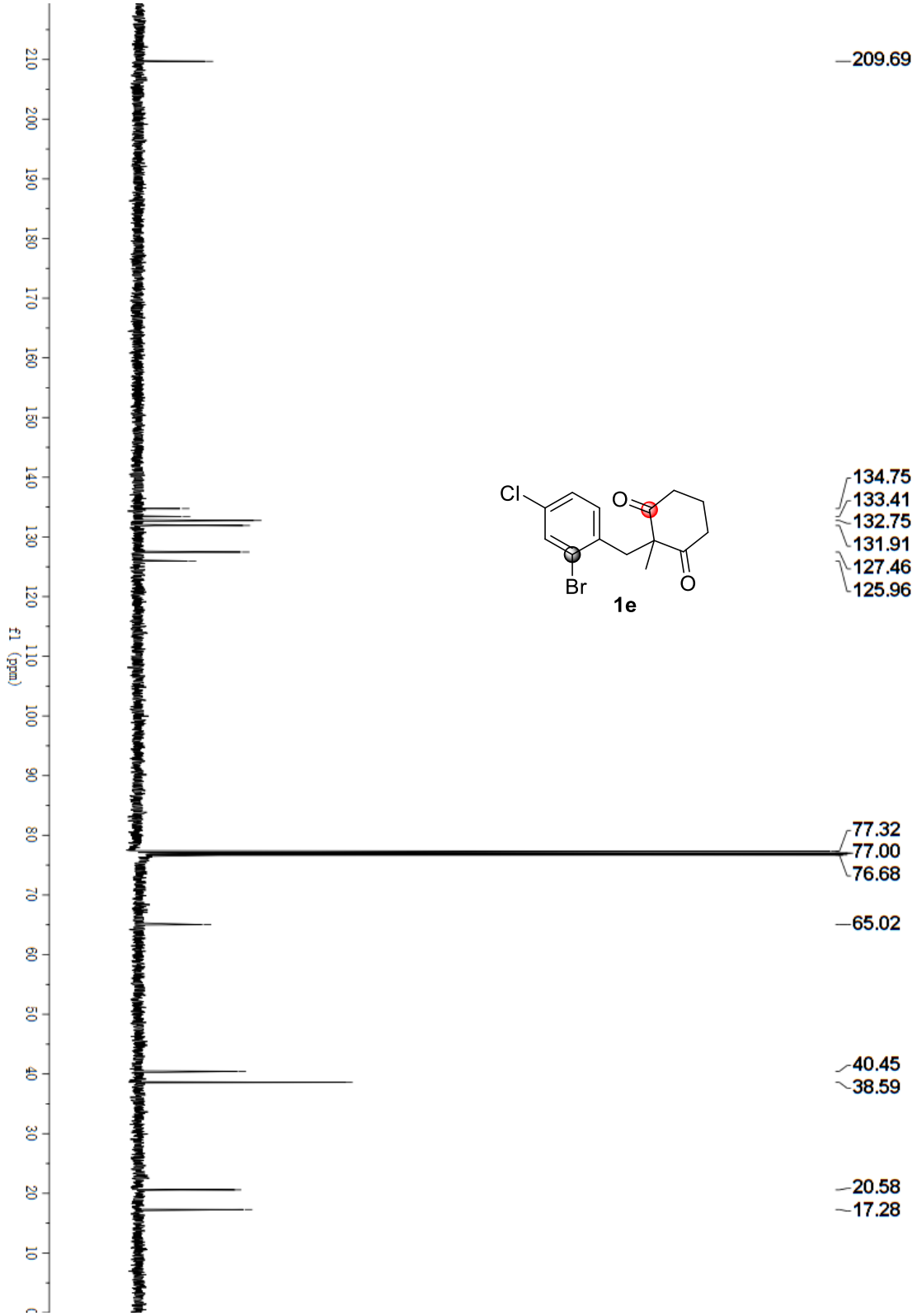
7.55
7.27
7.19
7.19
7.17
7.17
6.96
6.94
Cl
O
Br
O
1e
3.28
2.73
2.72
2.70
2.69
2.69
2.68
2.67
2.67
2.66
2.65
2.63
2.61
1.96
1.96
1.95
1.95
1.94
1.94
1.93
1.93
1.92
1.91
1.90
1.90
1.89
1.88
1.88
1.59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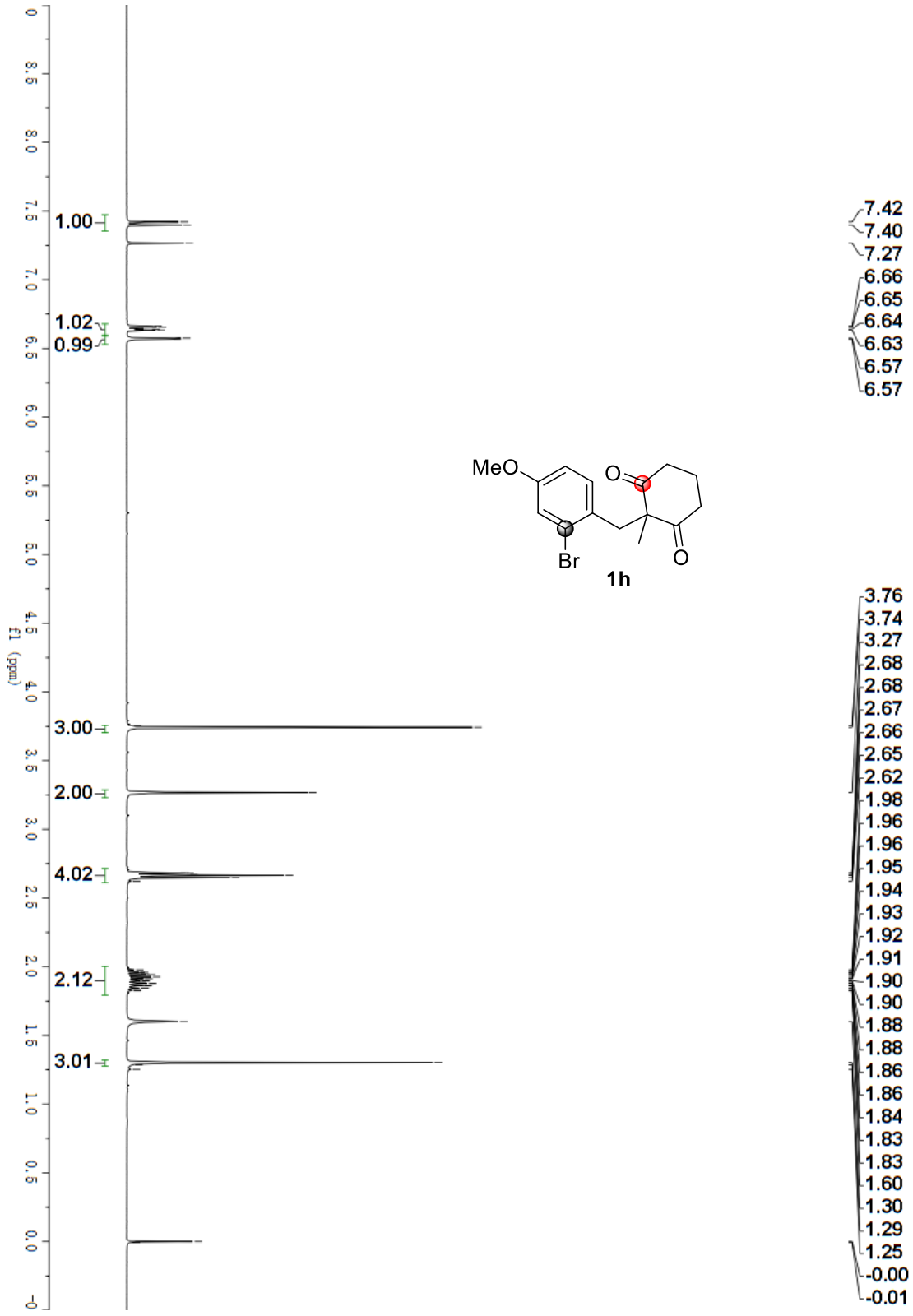
132.75
131.91
127.46
125.96
77.32
77.00
76.68
65.02
40.45
38.59
20.58
17.28
Cl
O
Br
O
1e
f1 (ppm)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3.00
2.00
4.02
2.12
3.01
f1 (ppm)
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O
Br
O
1h
7.42
7.40
7.27
6.66
6.65
6.64
6.63
6.57
6.57
3.76
3.74
3.27
2.68
2.68
2.67
2.66
2.65
2.62
1.98
1.96
1.96
1.95
1.94
1.93
1.92
1.91
1.90
1.90
1.88
1.88
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1.25
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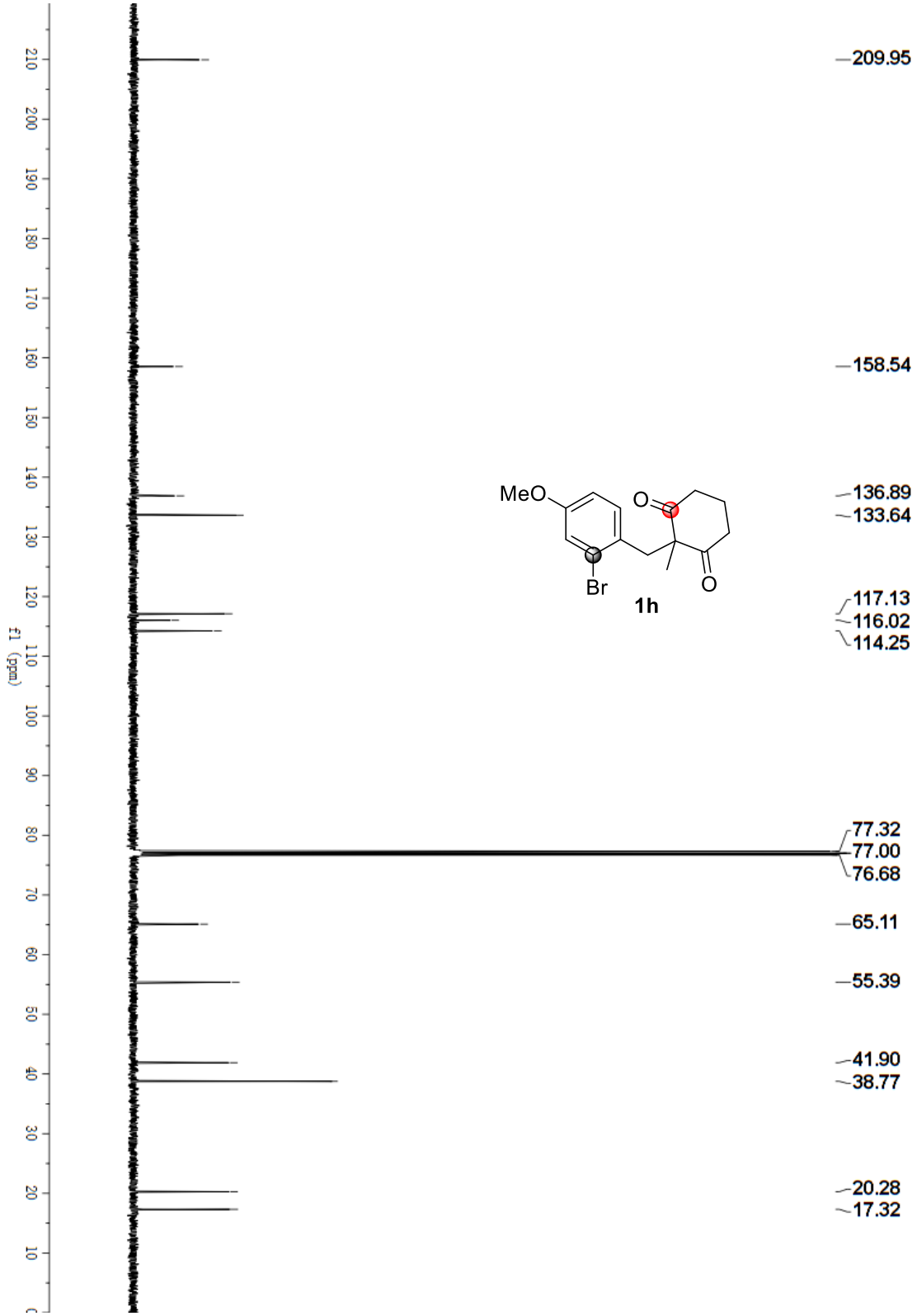
-0.01

7.427.42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114.25
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77.00
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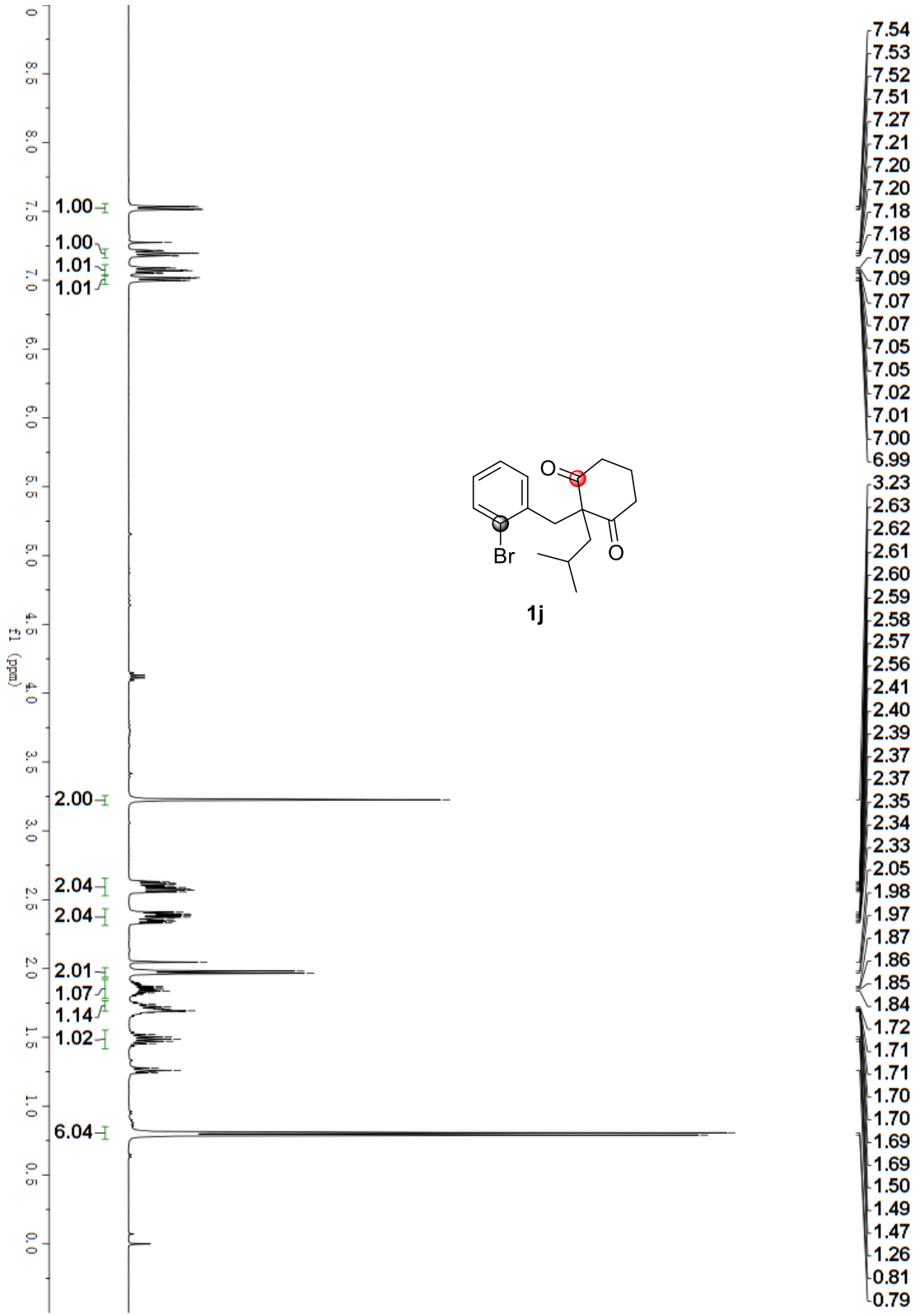
55.39
41.90
38.77
20.28
17.32
MeO
O
Br
O
1h
f1 (ppm)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1.01
1.01
2.00
2.04
2.04
2.01
1.07
1.14
1.02
6.04
f1 (ppm)
O
O
Br
1j
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7.53
7.52
7.51
7.27
7.21
7.20
7.20
7.18
7.18
7.09
7.09
7.07
7.07
7.05
7.05
7.02
7.01
7.00
6.99
3.23
2.63
2.62
2.61
2.60
2.59
2.58
2.57
2.56
2.41
2.40
2.39
2.37
2.37
2.35
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1.72
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1.70
1.69
1.69
1.50
1.49
1.47
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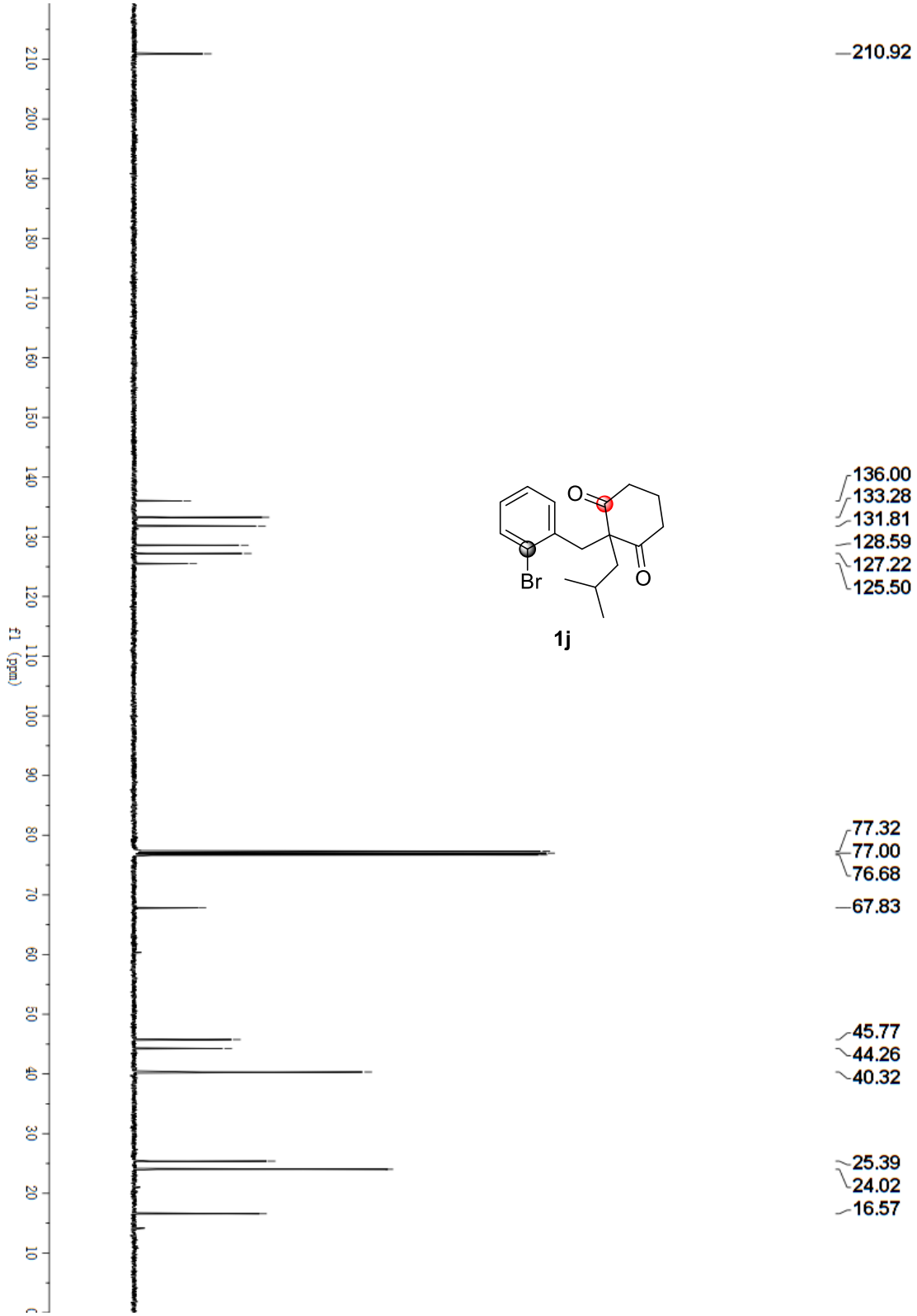
0.79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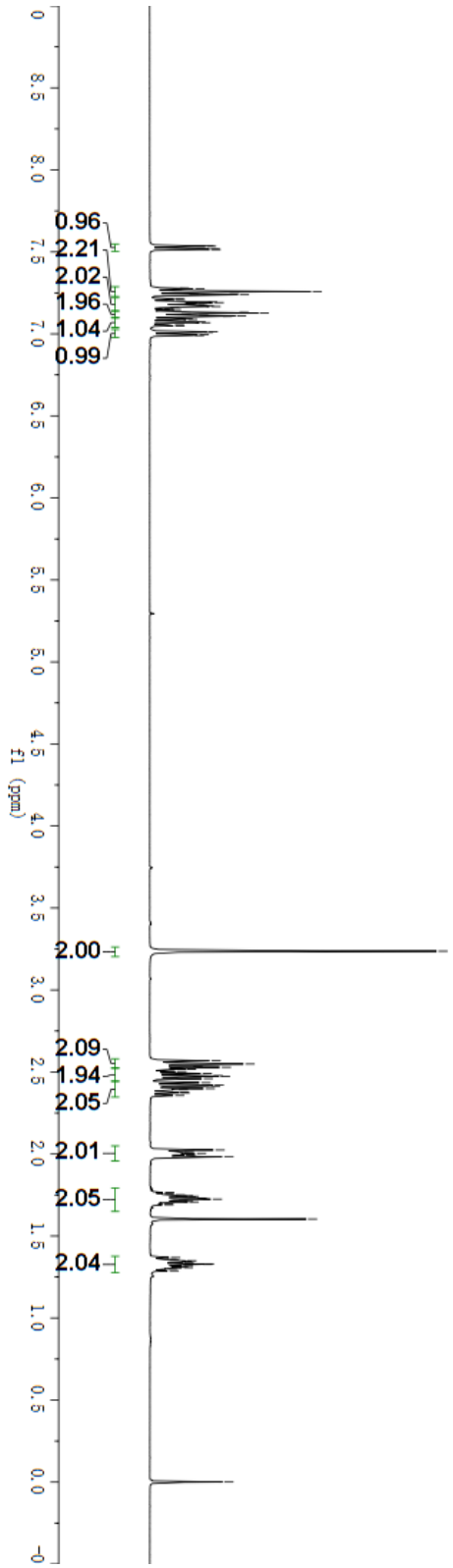
24.02
16.57
O
Br
O
1j
f1 (ppm)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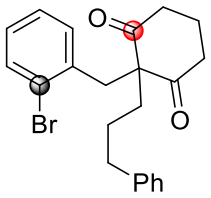
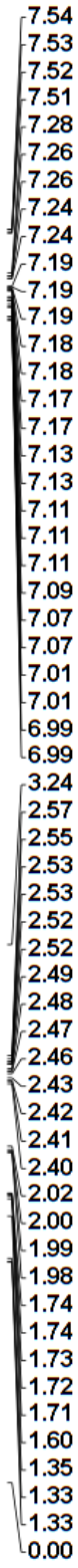
2.01
2.05
2.04
f1 (ppm)


O
Br
O
Ph

1l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7.26
7.24
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7.19
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7.17
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7.07
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7.01
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6.99
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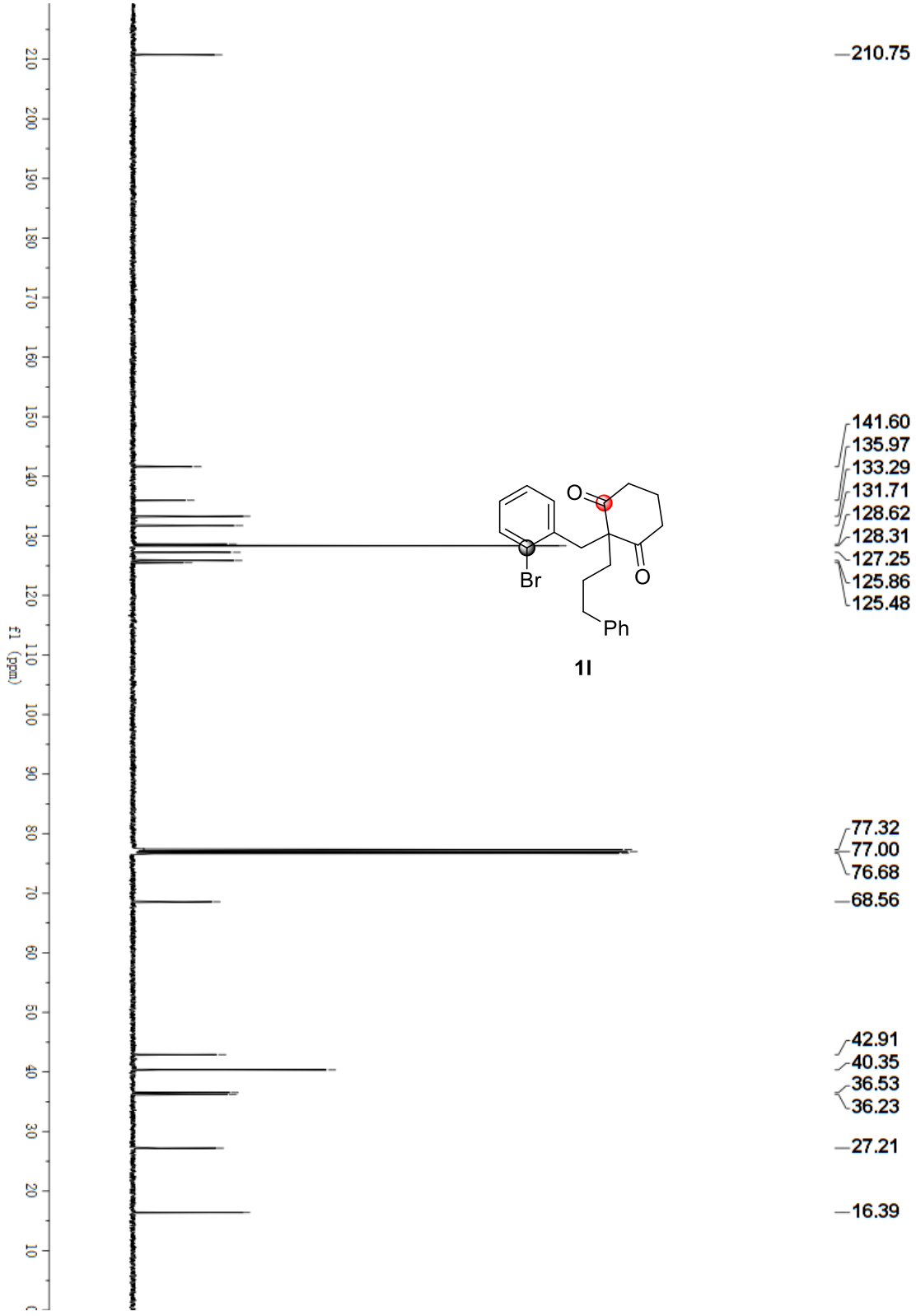
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125.48
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36.23
27.21
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O
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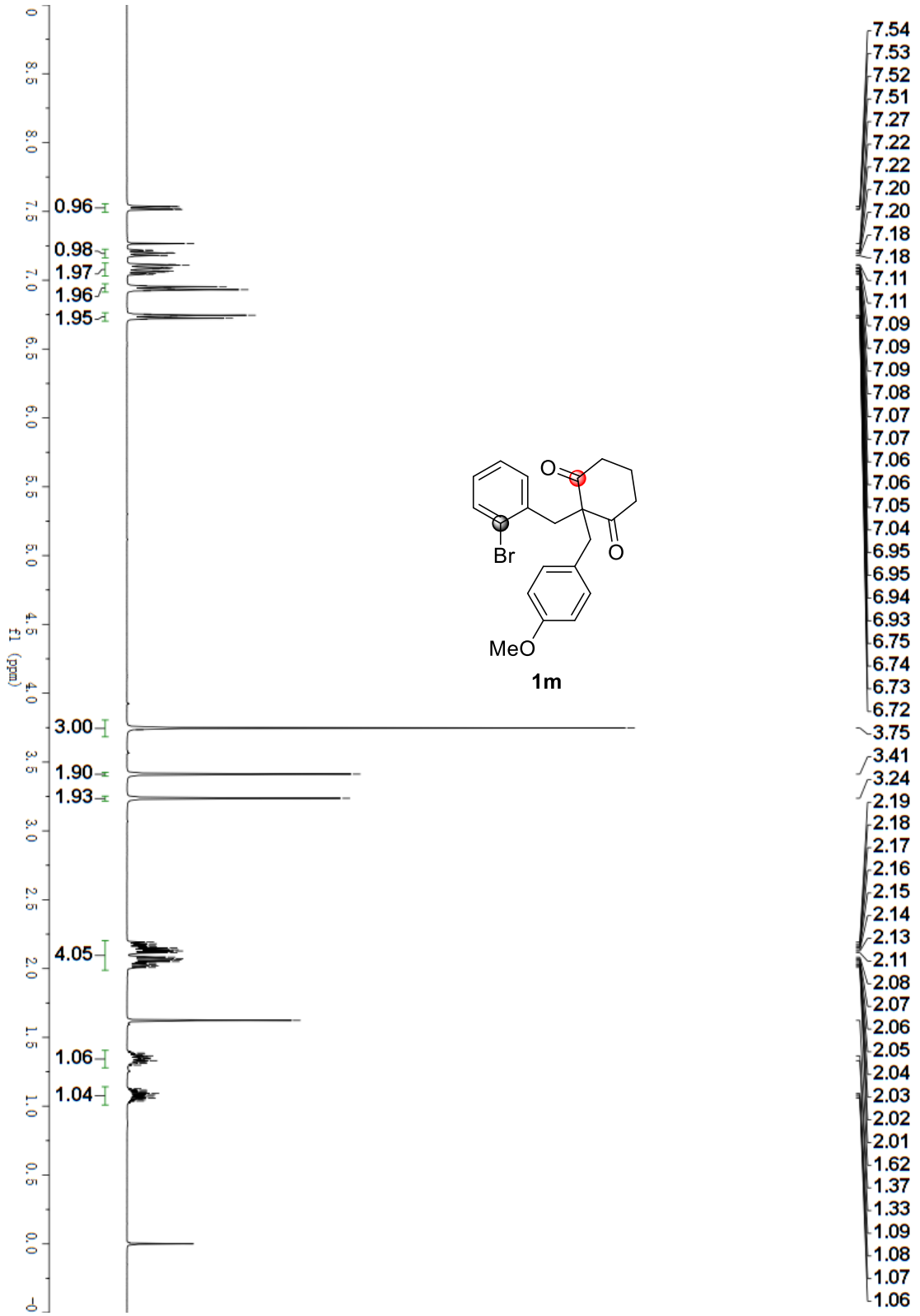
Br
Ph
1l
f1 (ppm)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1.04
f1 (ppm)
O
O
Br
MeO
1m
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7.53
7.52
7.51
7.27
7.22
7.22
7.20
7.20
7.18
7.18
7.11
7.11
7.09
7.09
7.09
7.08
7.07
7.07
7.06
7.06
7.05
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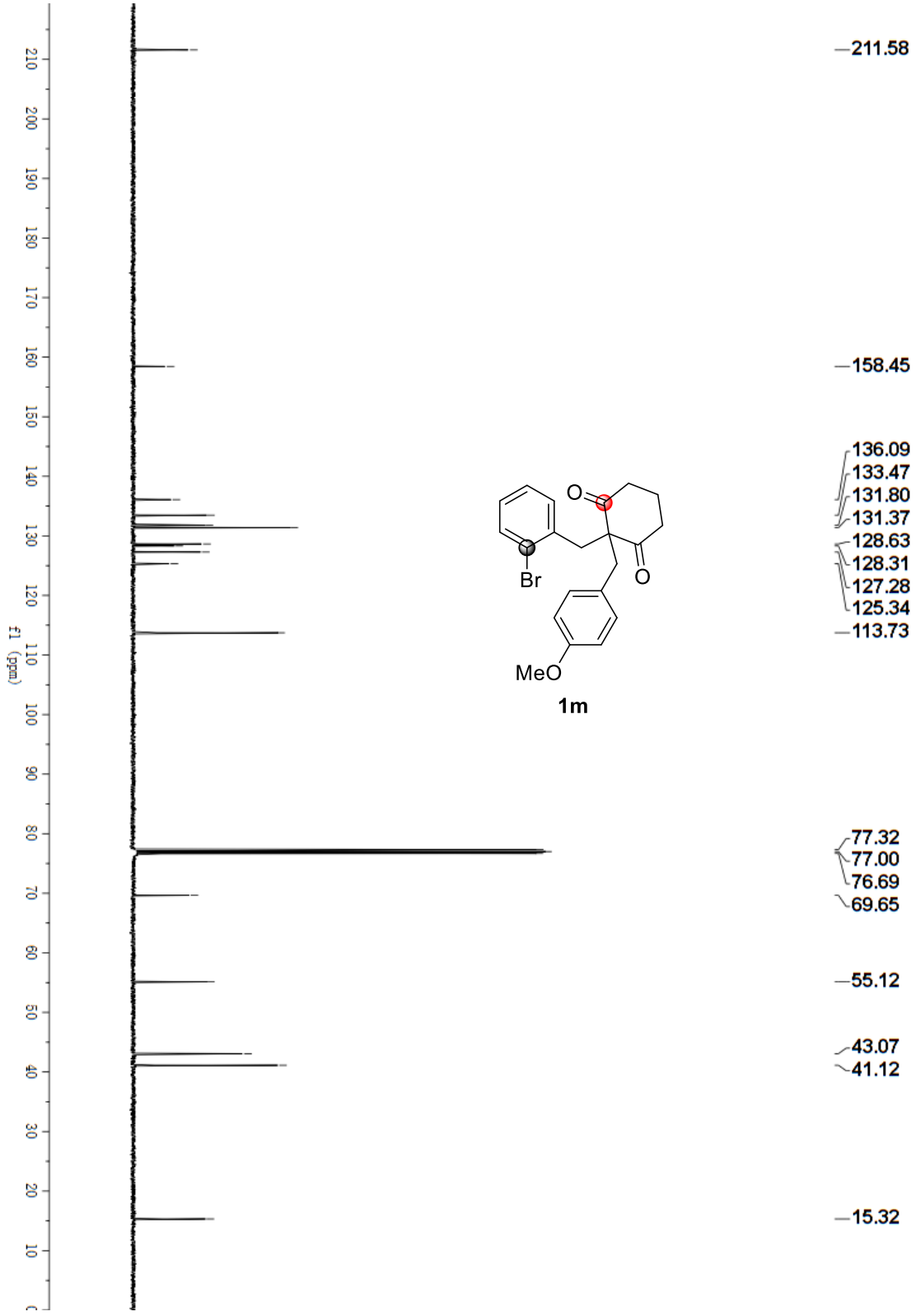
1.06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128.31
127.28
125.34
113.73
77.32
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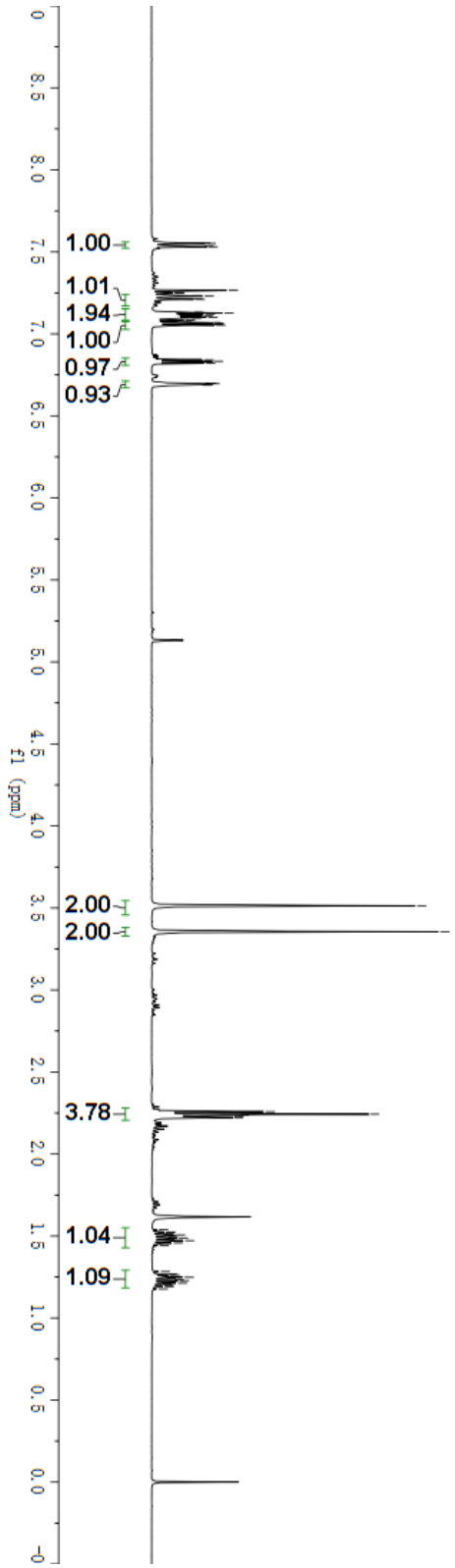
76.69
69.65
55.12
43.07
41.12
15.32
f1 (ppm)
O
O
Br
MeO
1m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1.01
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1.00
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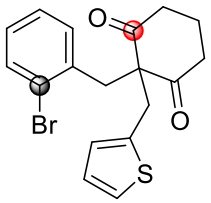
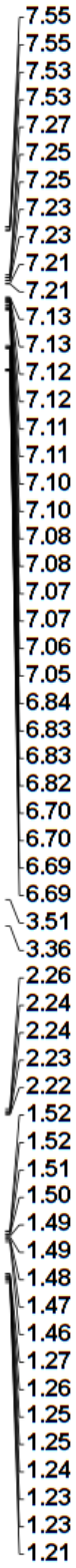
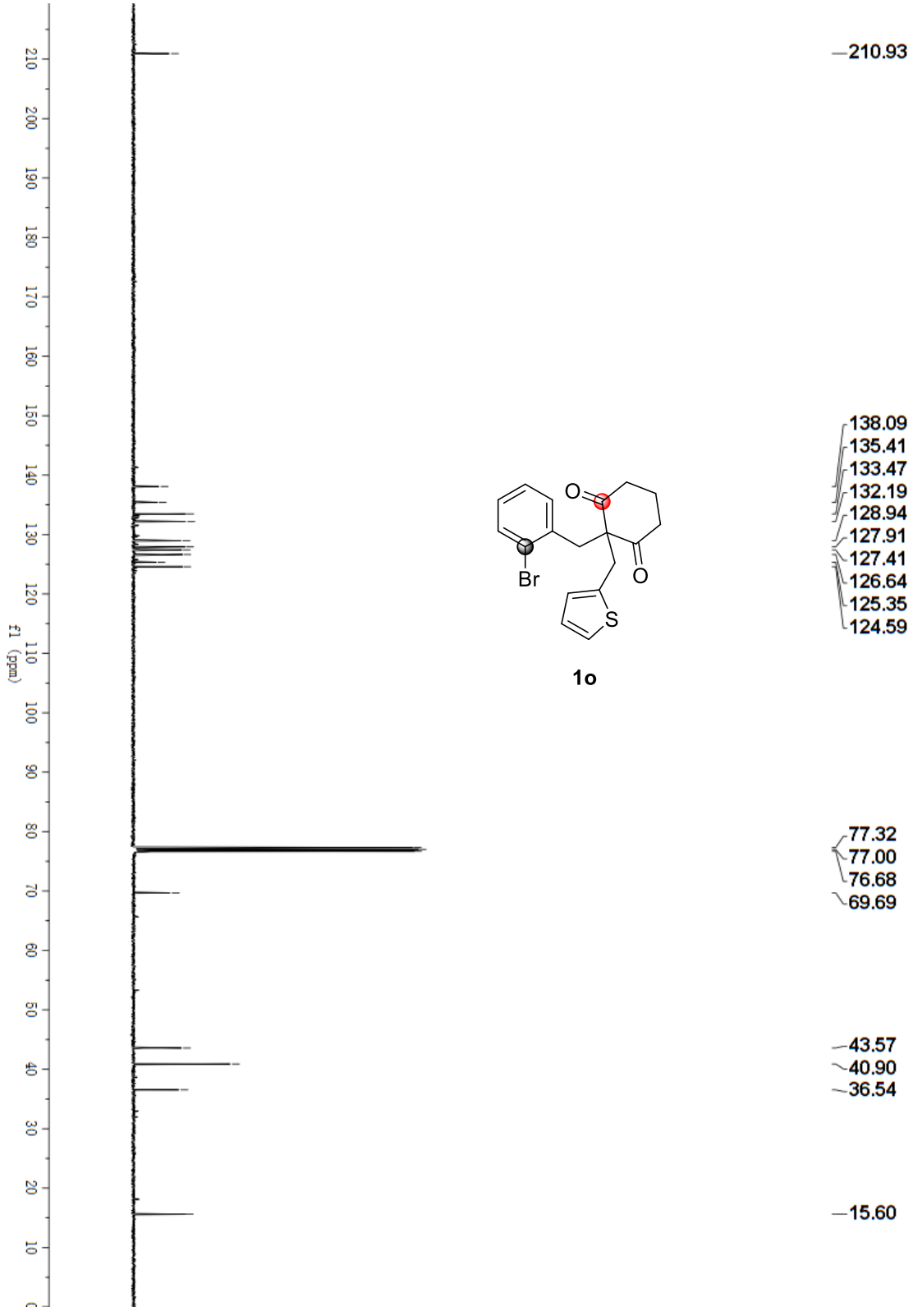
0.93
2.00
2.00
3.78
1.04
1.09
f1 (ppm)

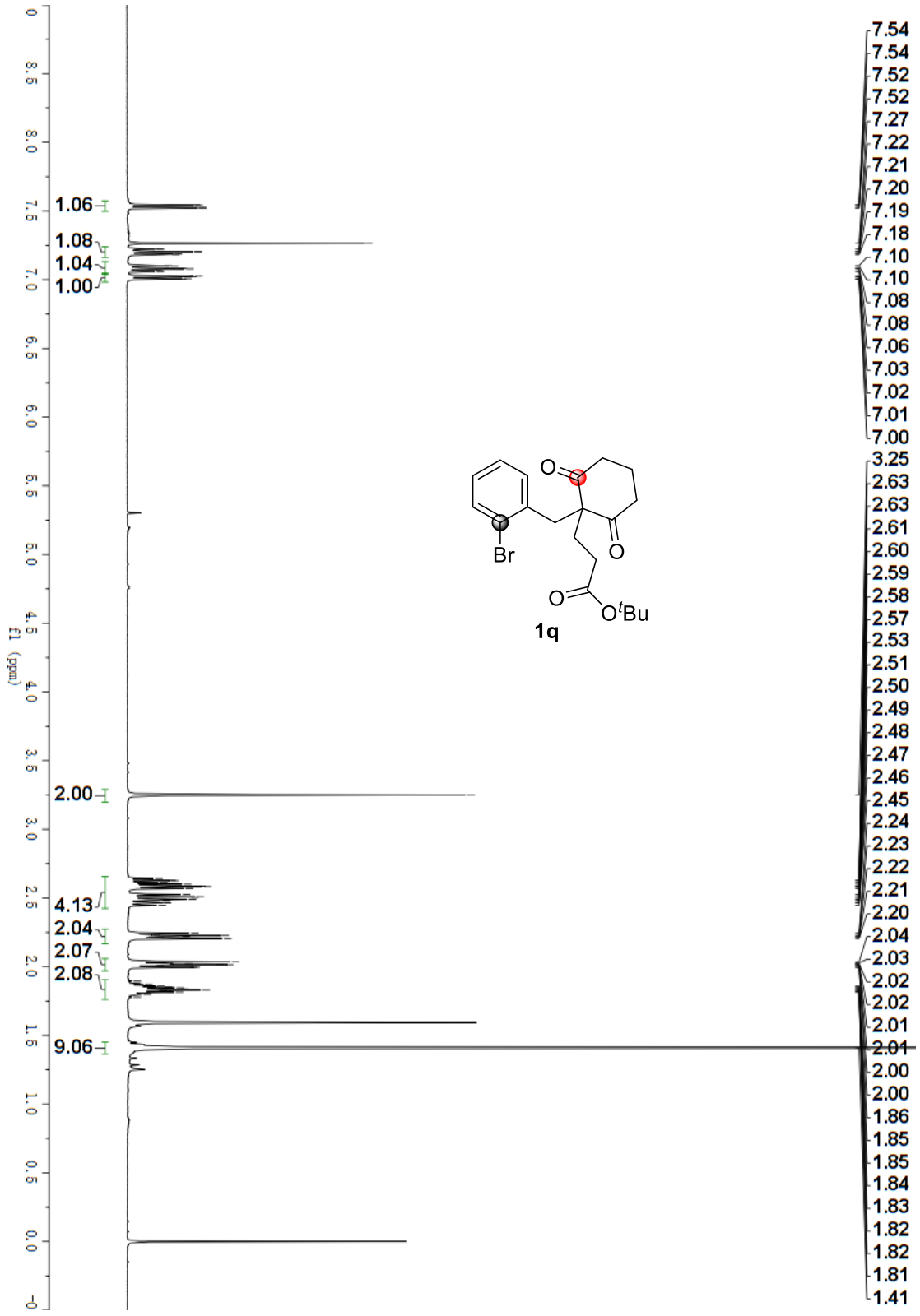

O
Br
O
S

1o

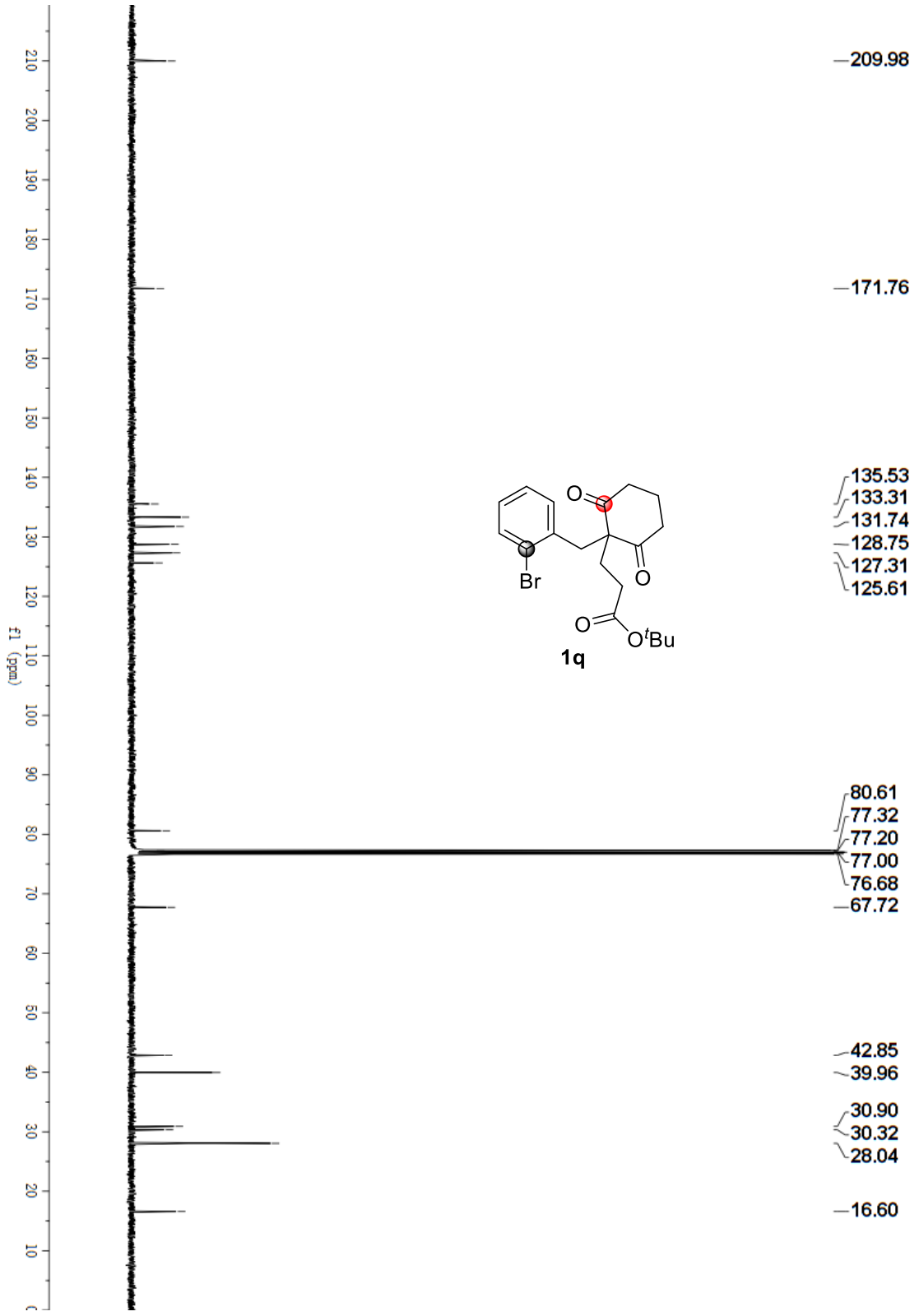

7.55
7.55
7.53
7.53
7.27
7.25
7.25
7.23
7.23
7.21
7.21
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.10
7.08
7.08
7.07
7.07
7.06
7.05
6.84
6.83
6.83
6.82
6.70
6.70
6.69
6.69
3.51
3.36
2.26
2.24
2.24
2.23
2.22
1.52
1.52
1.51
1.50
1.49
1.49
1.48
1.47
1.46
1.27
1.26
1.25
1.25
1.24
1.23
1.23
1.21

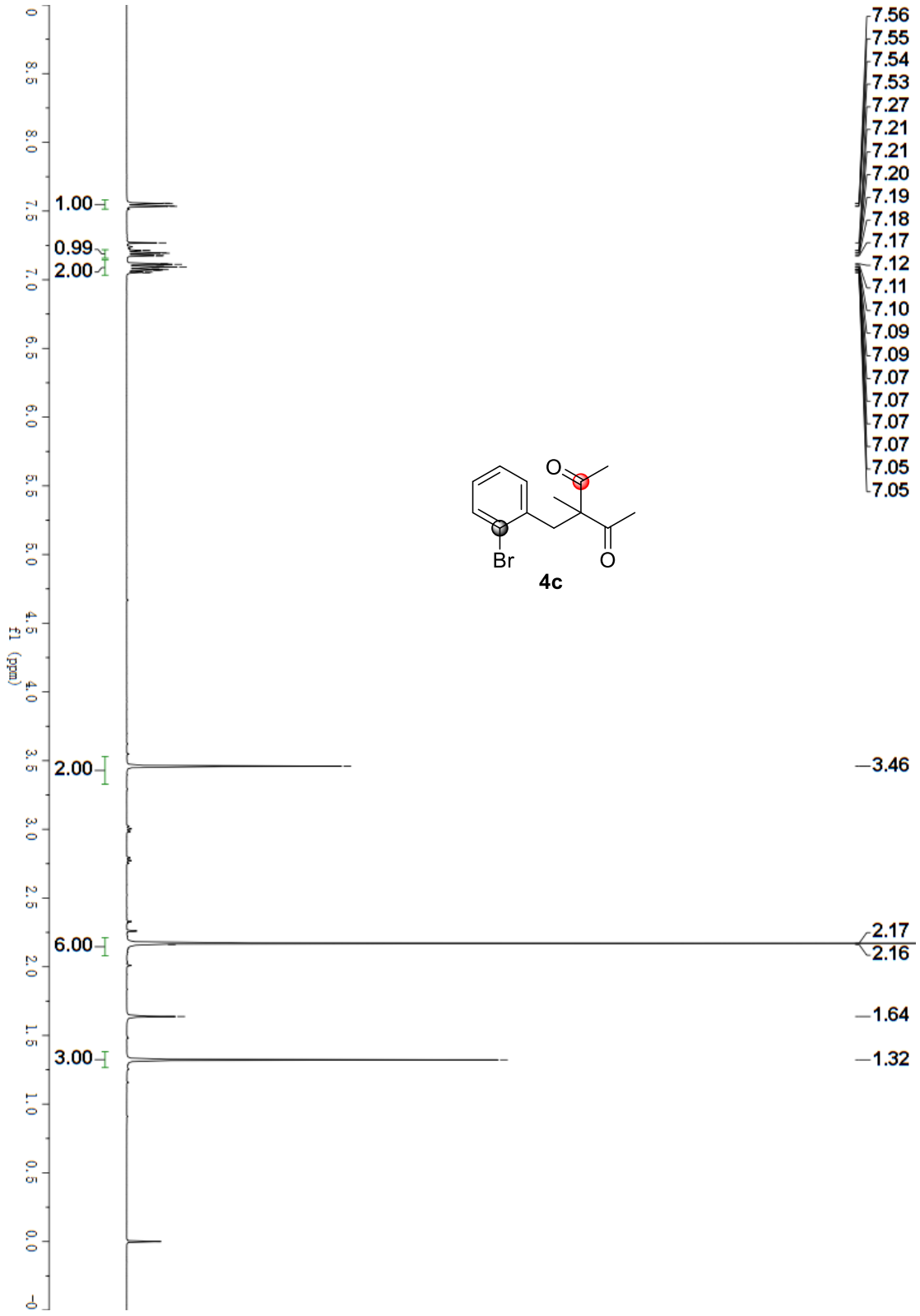

210.93
138.09
135.41
133.47
132.19
128.94
127.91
127.41
126.64
125.35
124.59
77.32
77.00
76.68
69.69
43.57
40.90
36.54
15.60
f1 (ppm)
O
O
Br
S

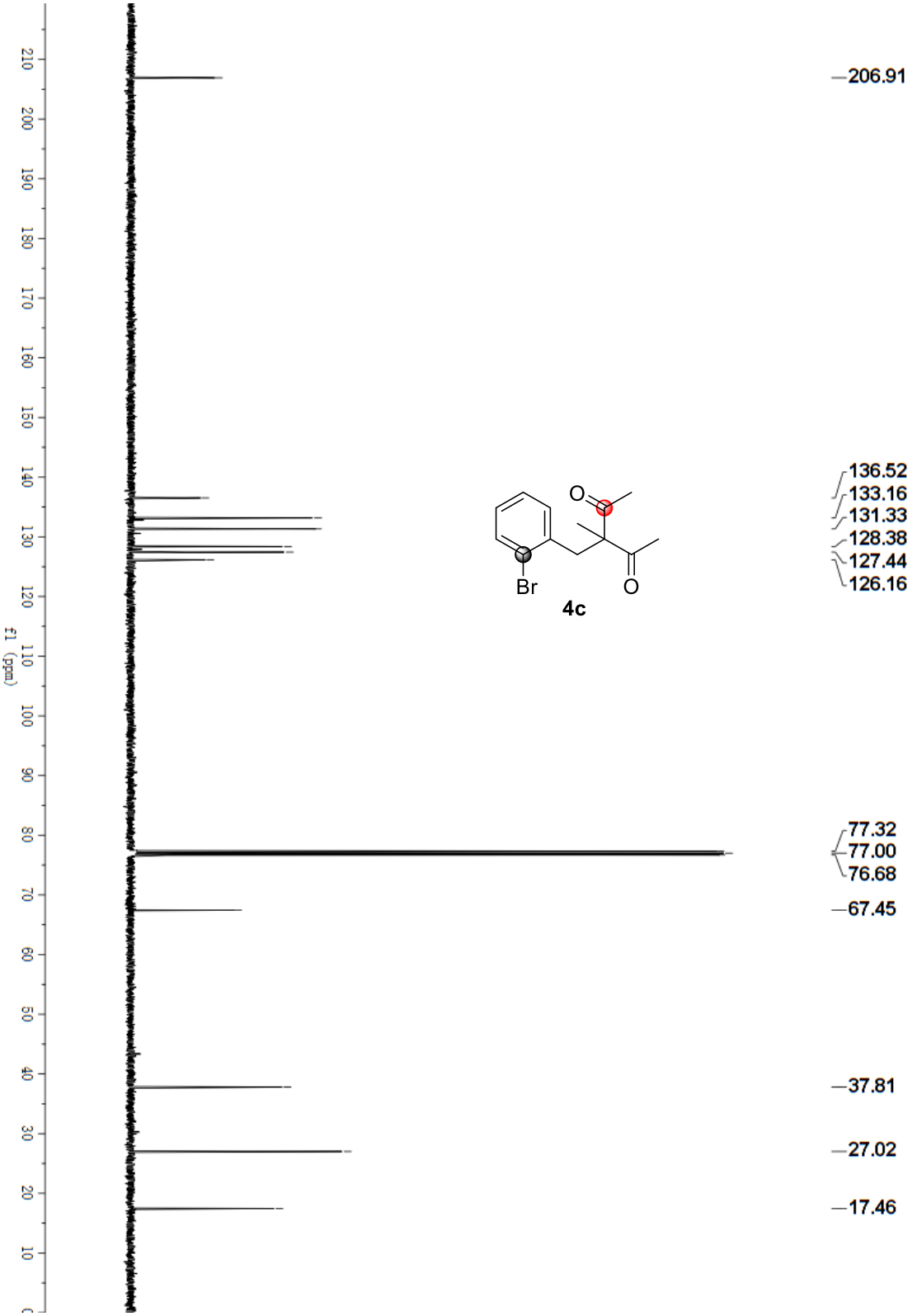
1o

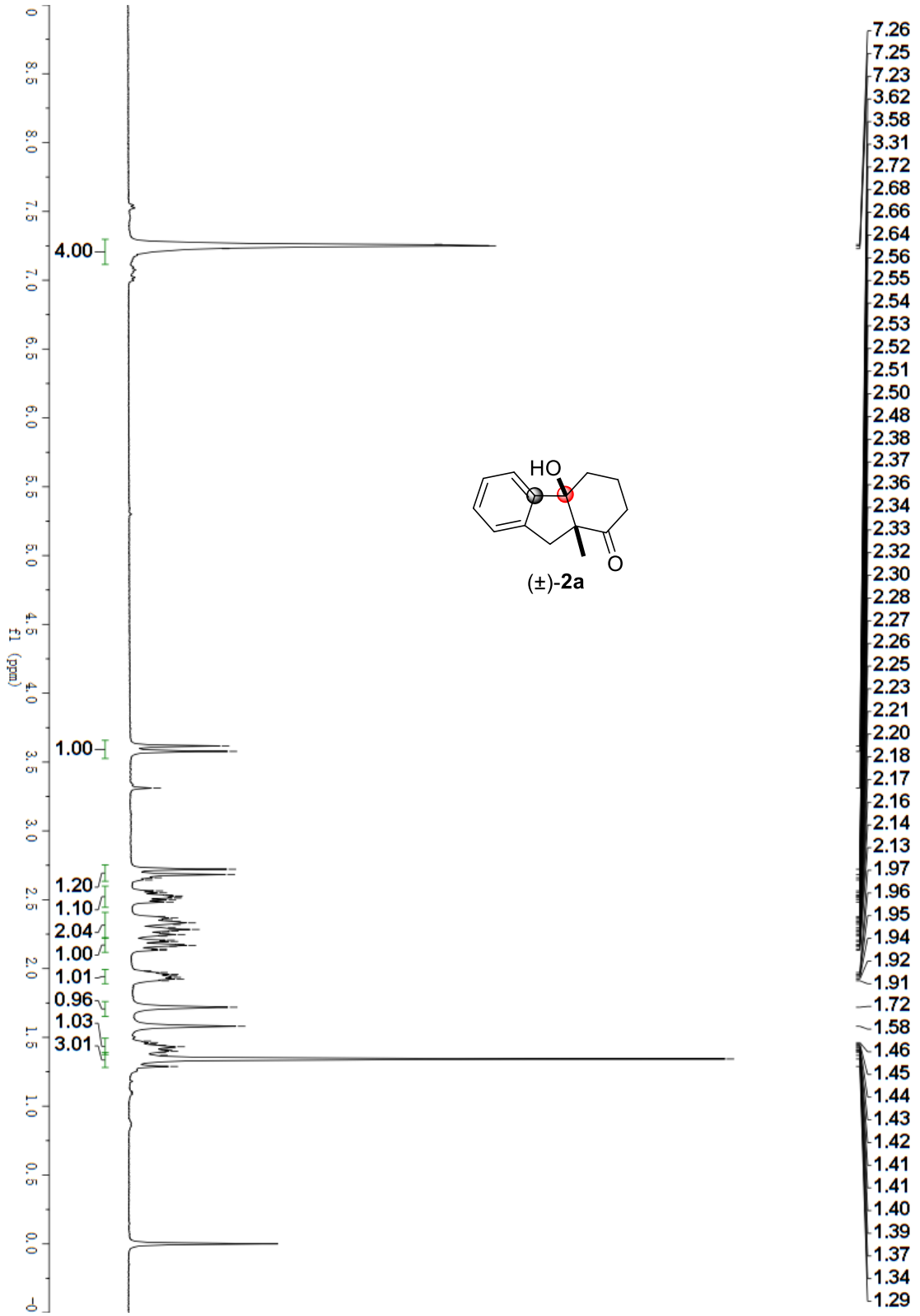

1.06
1.08
1.04
1.00
2.00
4.13
2.04
2.07
2.08
9.06
f1 (ppm)
7.54
7.54
7.52
7.52
7.27
7.22
7.21
7.20
7.19
7.18
7.10
7.10
7.08
7.08
7.06
7.03
7.02
7.01
7.00
3.25
2.63
2.63
2.61
2.60
2.59
2.58
2.57
2.53
2.51
2.50
2.49
2.48
2.47
2.46
2.45
2.24
2.23
2.22
2.21
2.20
2.04
2.03
2.02
2.02
2.01
2.01
2.00
2.00
1.86
1.85
1.85
1.84
1.83
1.82
1.82
1.81
1.41
O
Br
O
O
O
OtBu

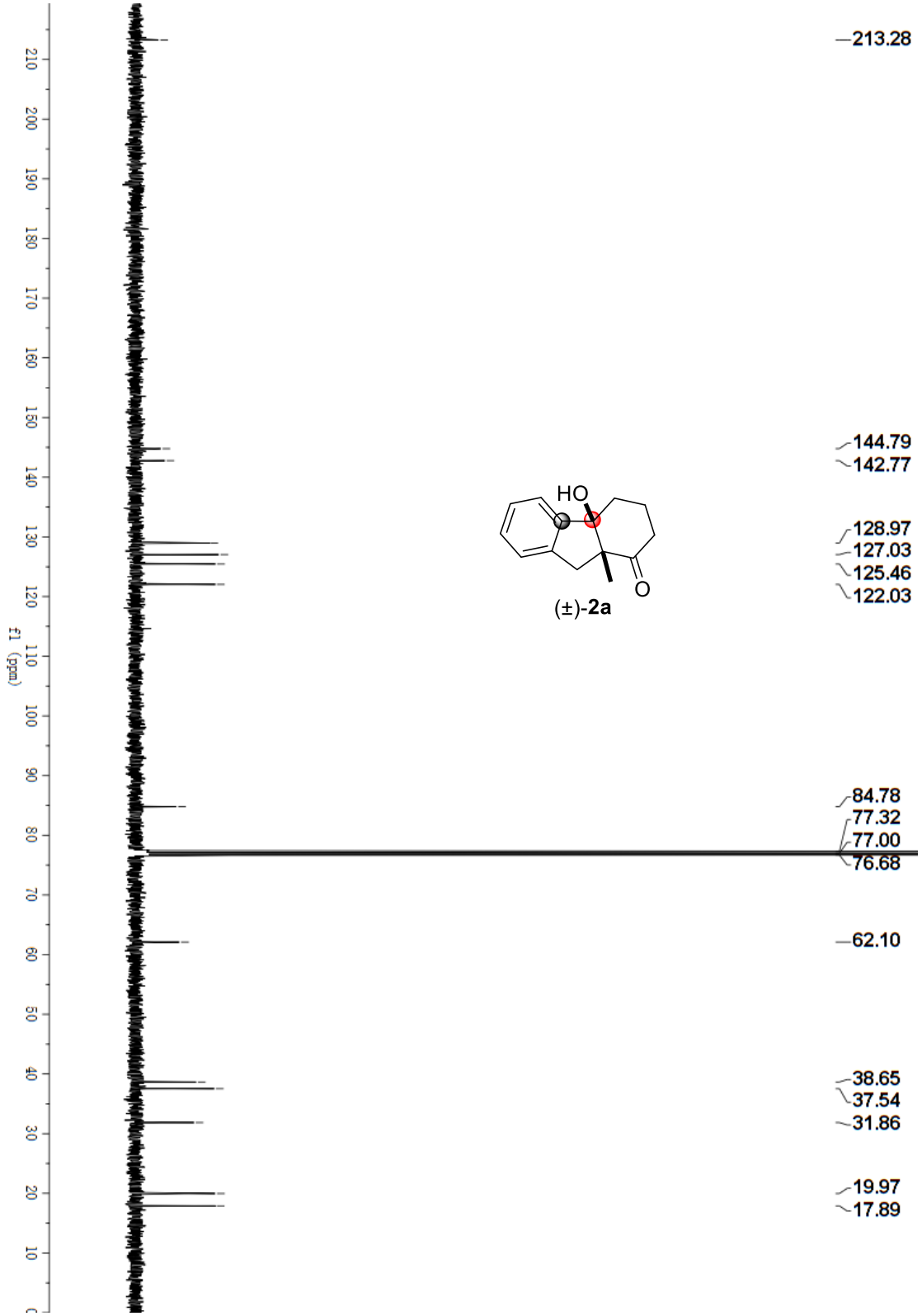
1q

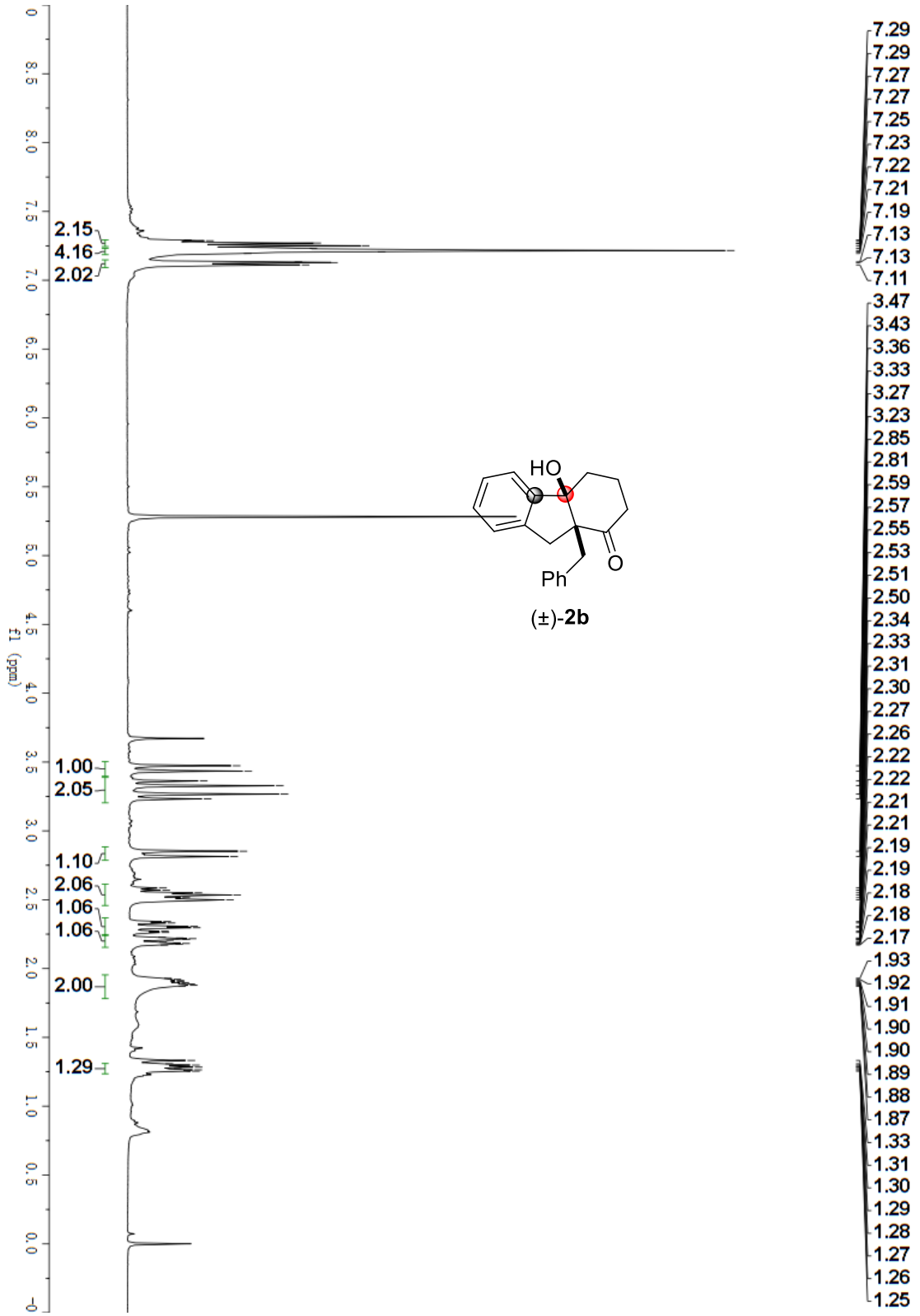

209.98
171.76
135.53
133.31
131.74
128.75
127.31
125.61
80.61
77.32
77.20
77.00
76.68
67.72
42.85
39.96
30.90
30.32
28.04
16.60
f1 (ppm)
Br
O
O
O
O
tBu
1q

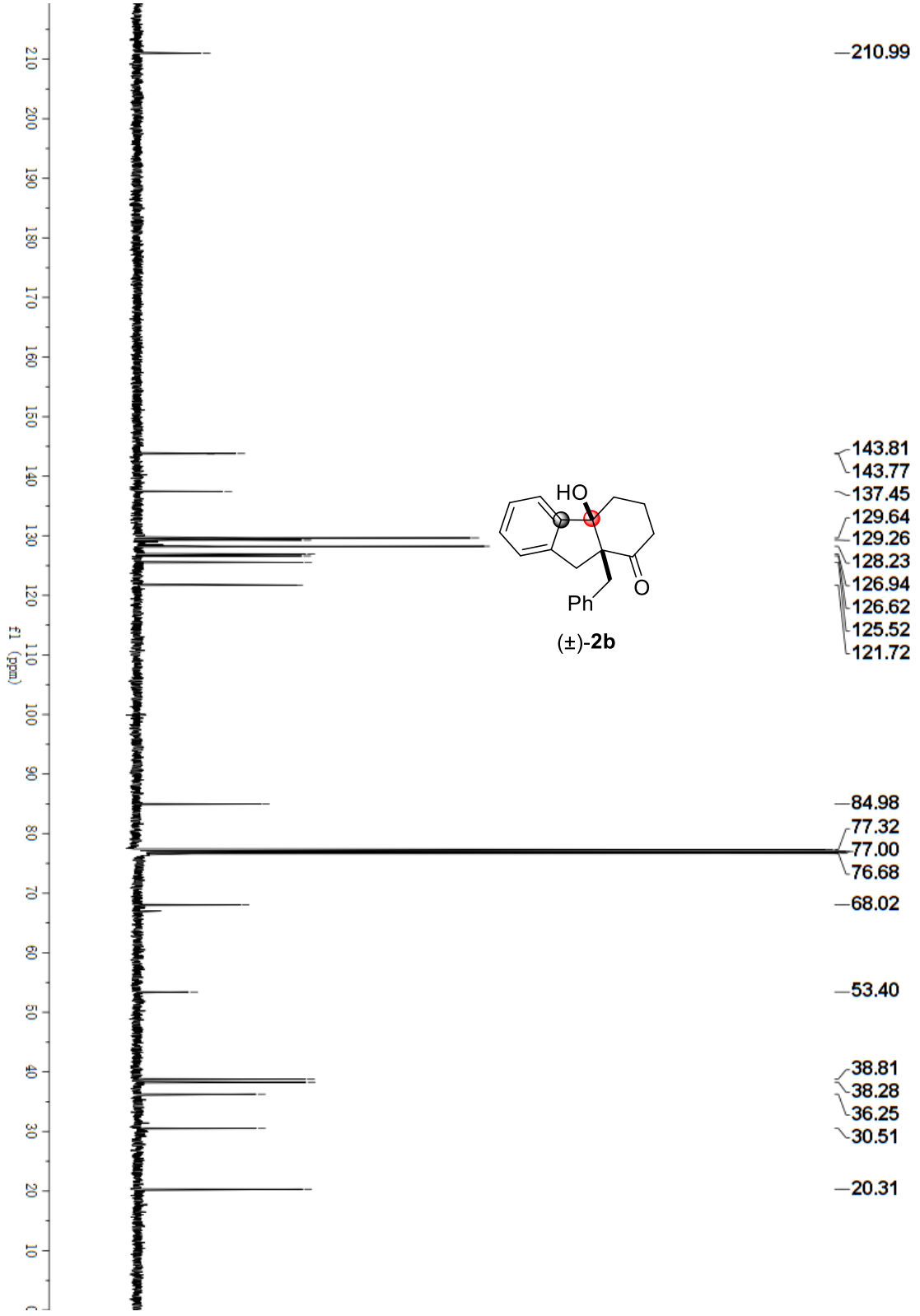

7.56
7.55
7.54
7.53
7.27
7.21
7.21
7.20
7.19
7.18
7.17
7.12
7.11
7.10
7.09
7.09
7.07
7.07
7.07
7.07
7.05
7.05
1.00
0.99
2.00
2.00
6.00
3.00
3.46
2.17
2.16
1.64
1.32
O
Br
O
4c
f1 (ppm)

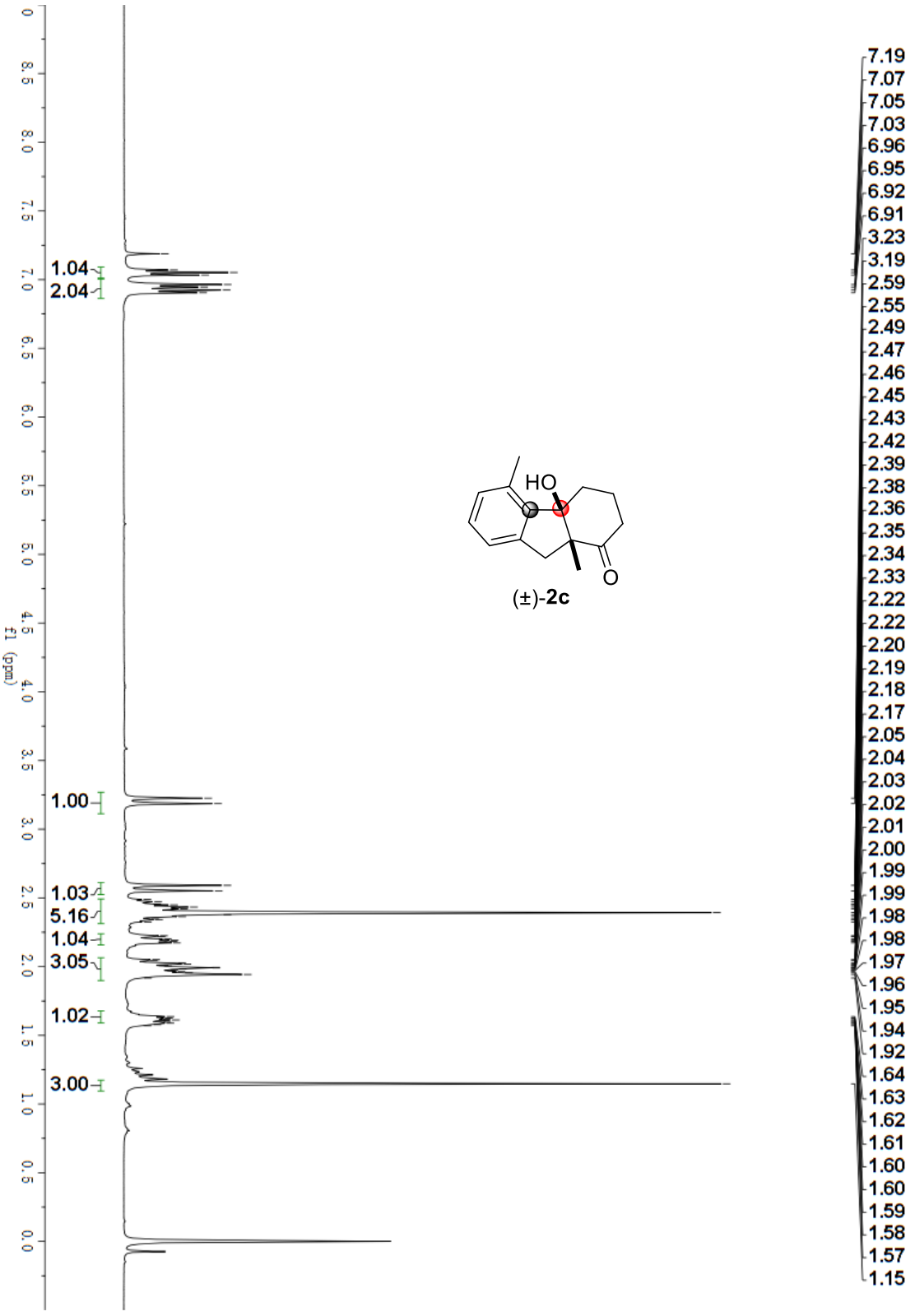

206.91
136.52
133.16
131.33
128.38
127.44
126.16
77.32
77.00
76.68
67.45
37.81
27.02
17.46
O
Br
O
4c
f1 (ppm)


HO
O
(±)-2a
4.00
1.00
1.20
1.10
2.04
1.00
1.01
0.96
1.03
3.01
f1 (ppm)
7.26
7.25
7.23
3.62
3.58
3.31
2.72
2.68
2.66
2.64
2.56
2.55
2.54
2.53
2.52
2.51
2.50
2.48
2.38
2.37
2.36
2.34
2.33
2.32
2.30
2.28
2.27
2.26
2.25
2.23
2.21
2.20
2.18
2.17
2.16
2.14
2.13
1.97
1.96
1.95
1.94
1.92
1.91
1.72
1.58
1.46
1.45
1.44
1.43
1.42
1.41
1.41
1.40
1.39
1.37
1.34
1.29


213.28
144.79
142.77
128.97
127.03
125.46
122.03
84.78
77.32
77.00
76.68
62.10
38.65
37.54
31.86
19.97
17.89
HO
O
(±)-2a
f1 (ppm)


2.15
4.16
2.02
1.00
2.05
1.10
2.06
1.06
1.06
2.00
1.29
f1 (ppm)
HO
O
Ph
(±)-2b
7.29
7.29
7.27
7.27
7.25
7.23
7.22
7.21
7.19
7.13
7.13
7.11
3.47
3.43
3.36
3.33
3.27
3.23
2.85
2.81
2.59
2.57
2.55
2.53
2.51
2.50
2.34
2.33
2.31
2.30
2.27
2.26
2.22
2.22
2.21
2.21
2.19
2.19
2.18
2.18
2.17
1.93
1.92
1.91
1.90
1.90
1.89
1.88
1.87
1.33
1.31
1.30
1.29
1.28
1.27
1.26
1.25


210.99
143.81
143.77
137.45
129.64
129.26
128.23
126.94
126.62
125.52
121.72
84.98
77.32
77.00
76.68
68.02
53.40
38.81
38.28
36.25
30.51
20.31
HO
O
Ph
(±)-2b
f1 (ppm)


HO
O
(±)-2c
1.04
2.04
1.00
1.03
5.16
1.04
3.05
1.02
3.00
f1 (ppm)
7.19
7.07
7.05
7.03
6.96
6.95
6.92
6.91
3.23
3.19
2.59
2.55
2.49
2.47
2.46
2.45
2.43
2.42
2.39
2.38
2.36
2.35
2.34
2.33
2.22
2.22
2.20
2.19
2.18
2.17
2.05
2.04
2.03
2.02
2.01
2.00
1.99
1.99
1.98
1.98
1.97
1.96
1.95
1.94
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1.63
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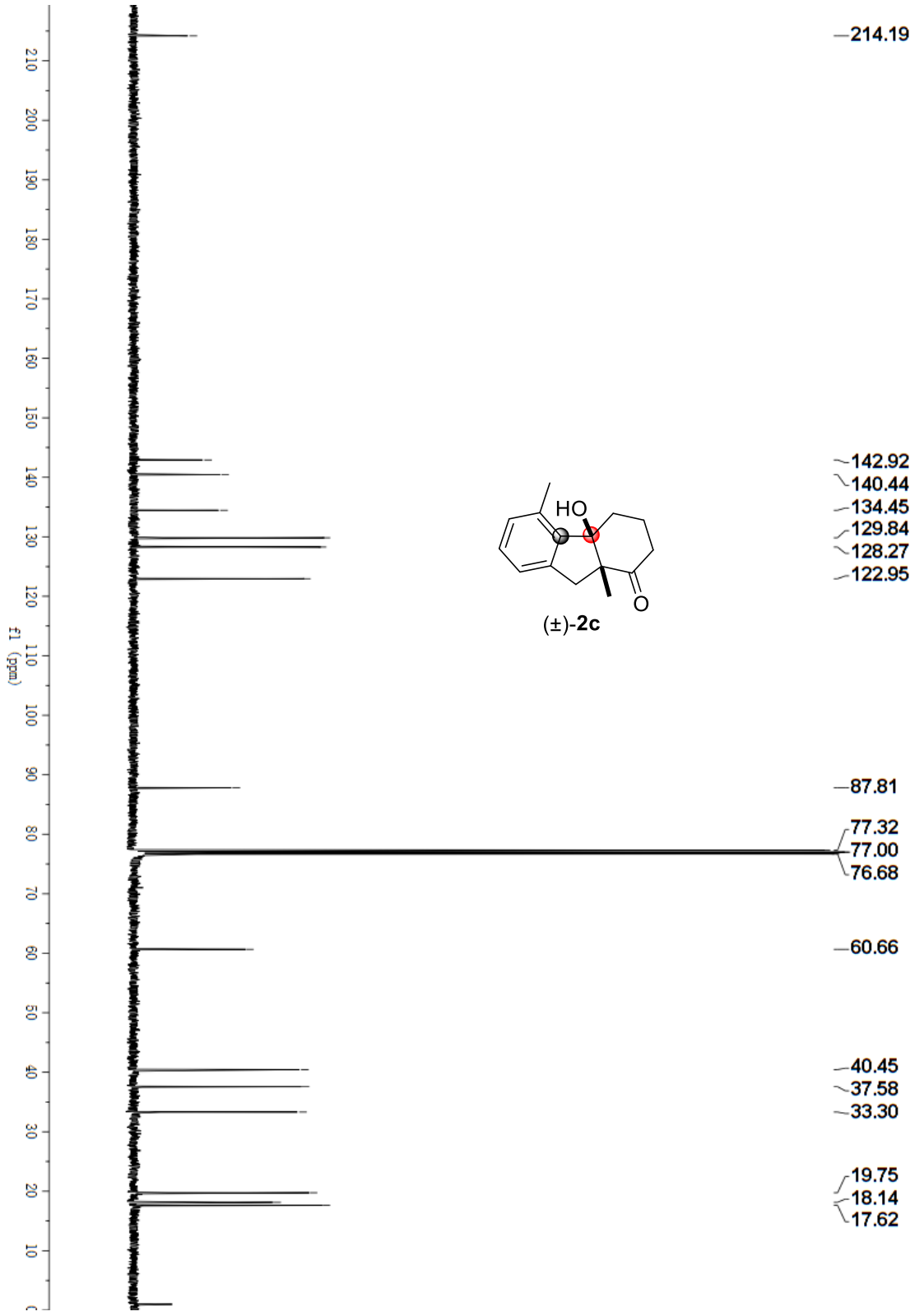
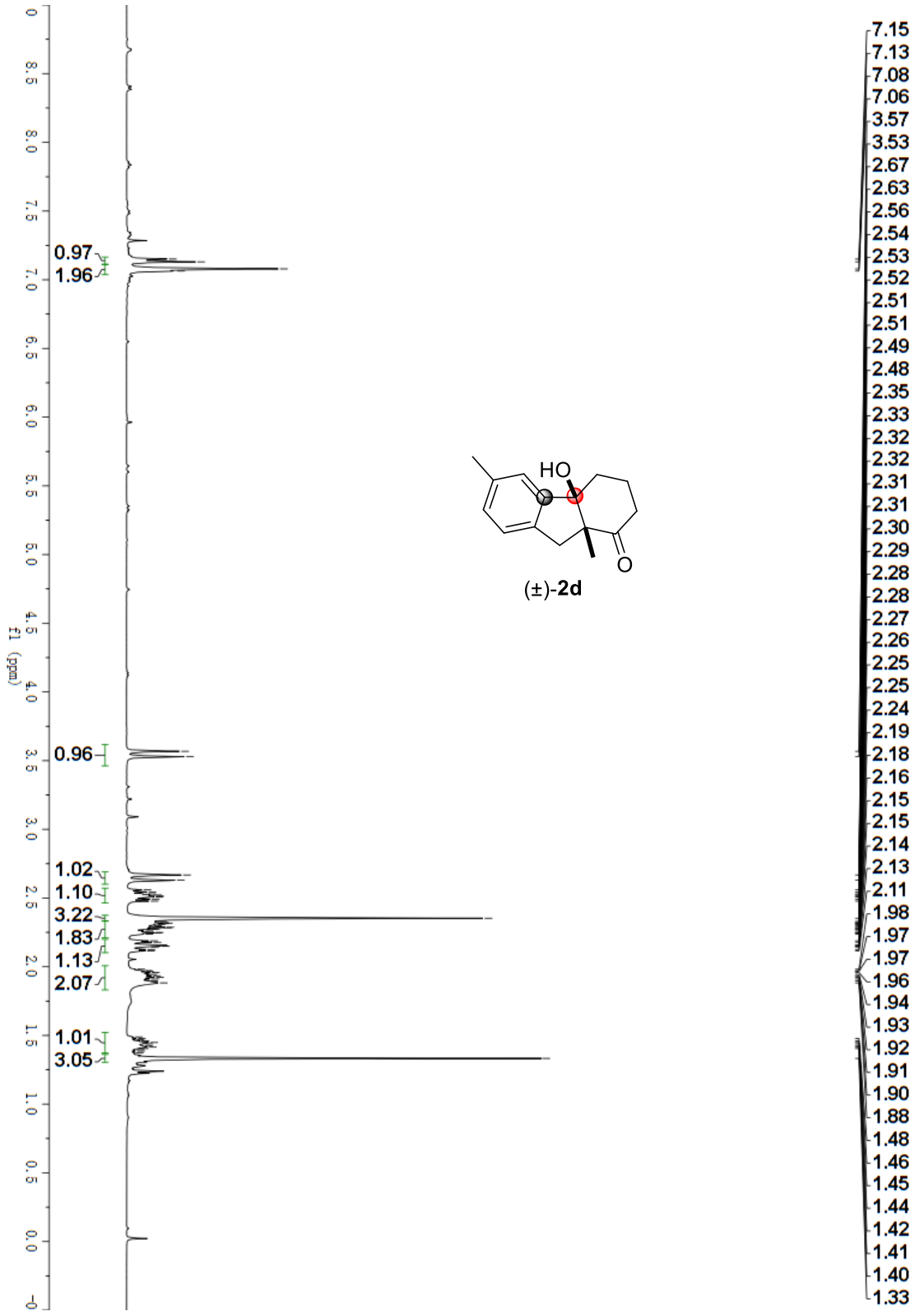
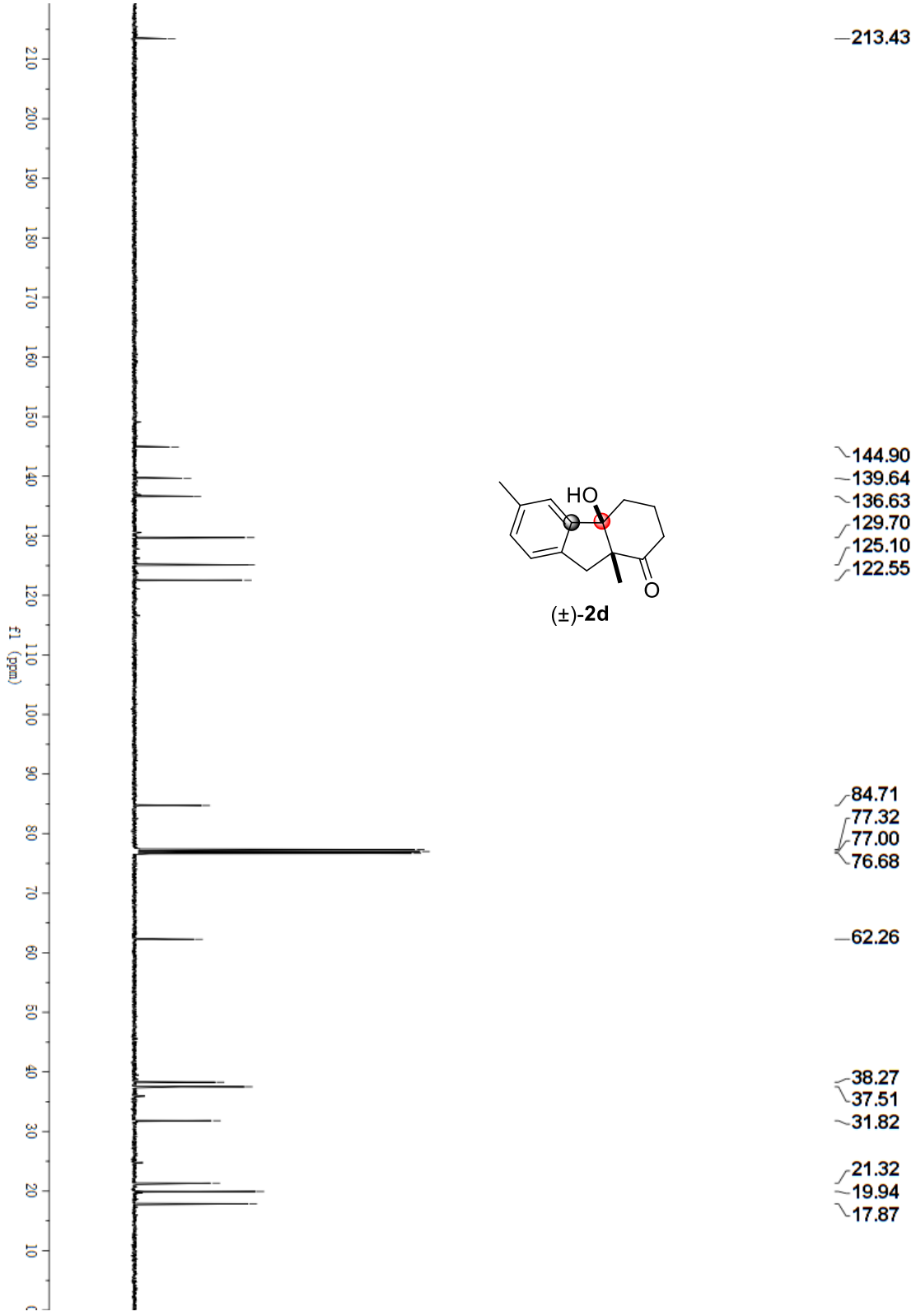
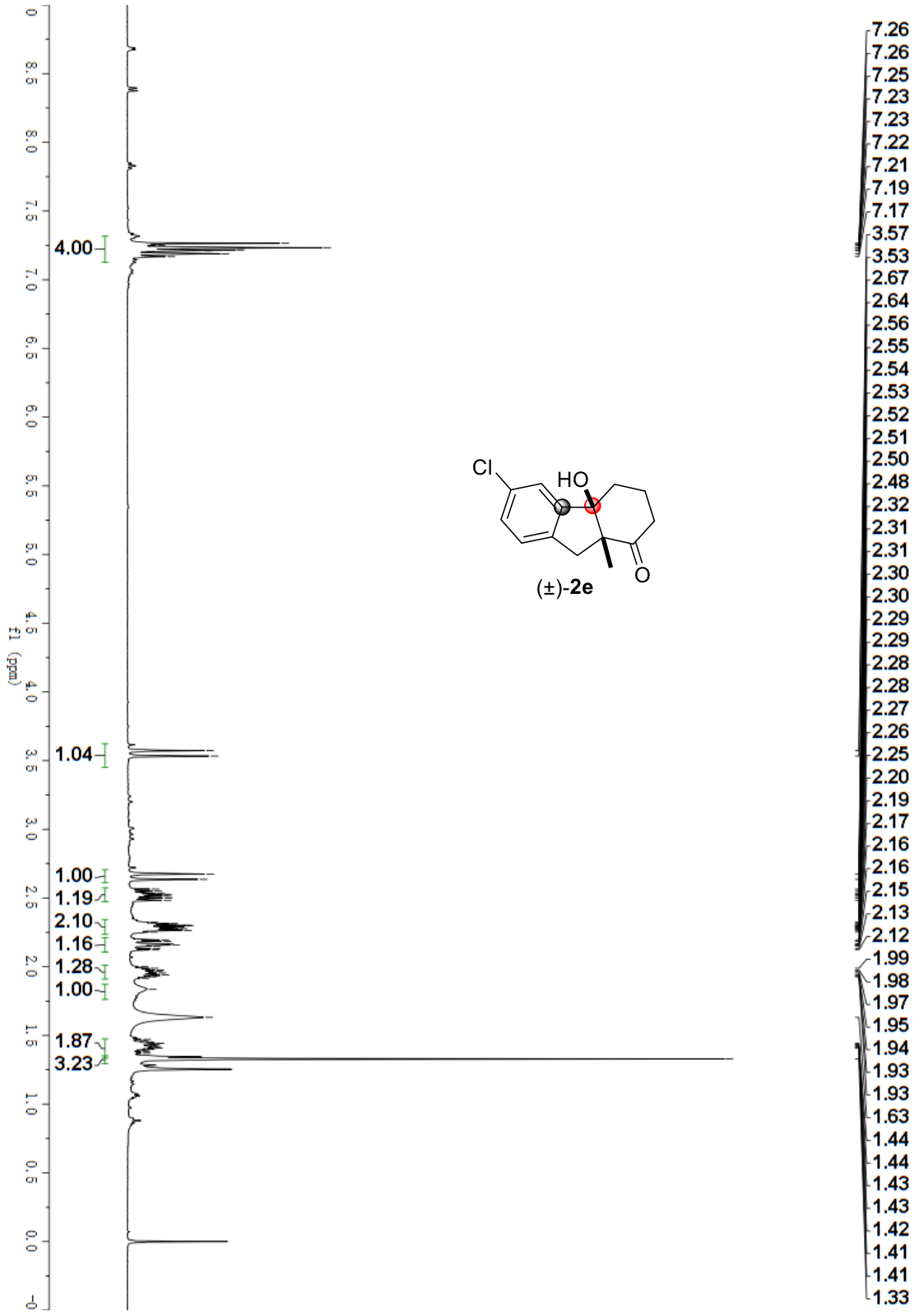
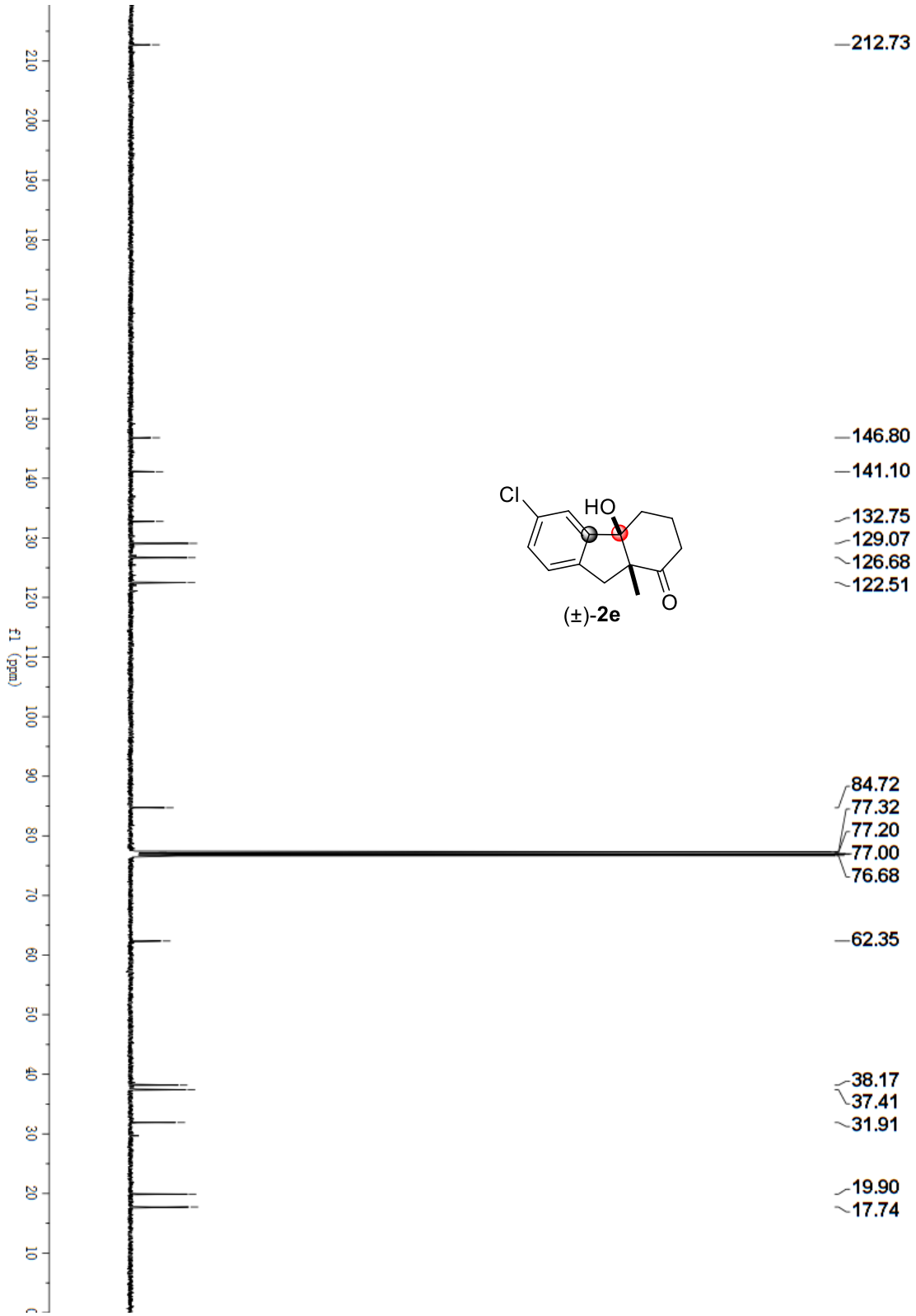
1.60
1.60
1.59
1.58
1.57
1.15

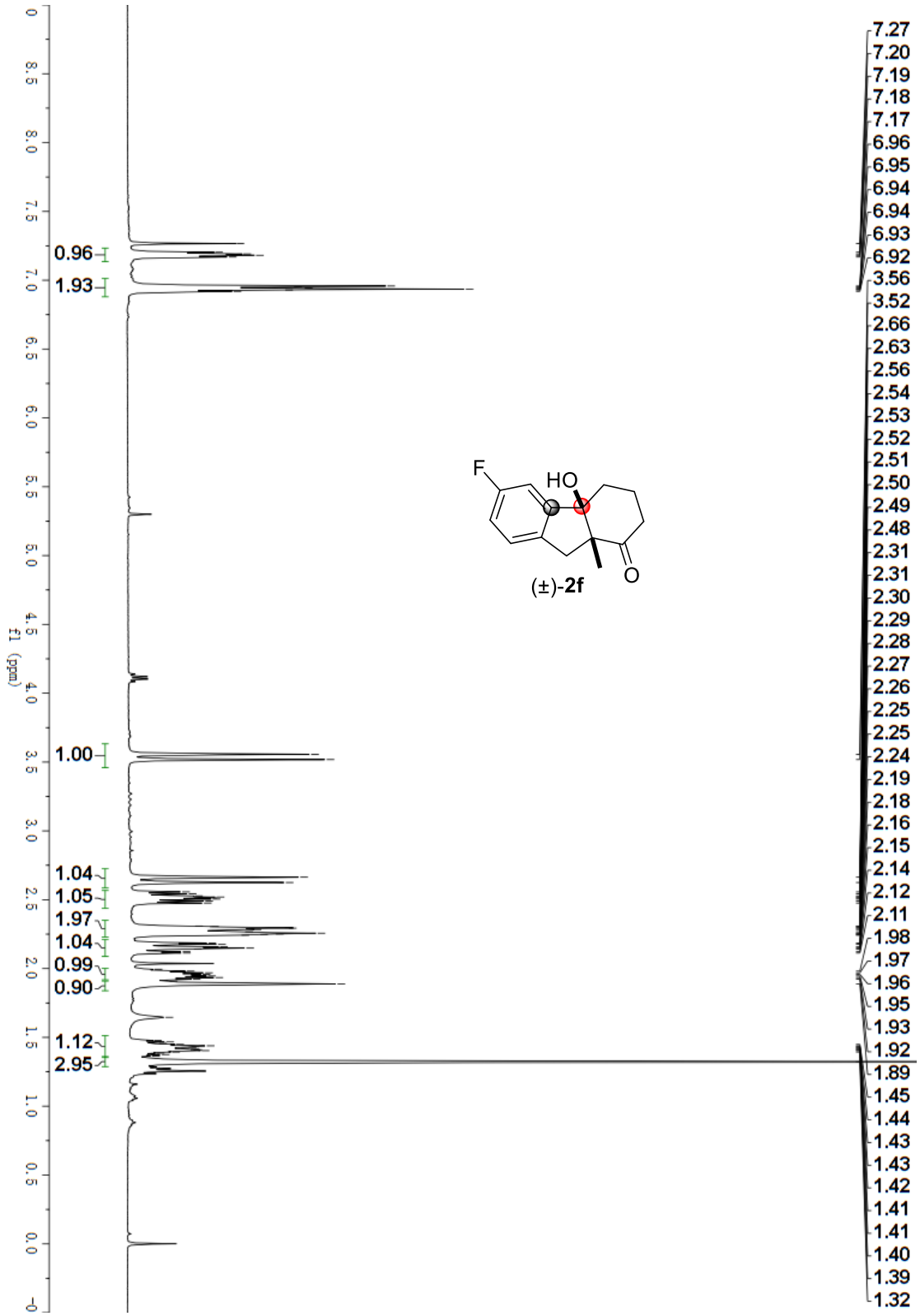

214.19
142.92
140.44
134.45
129.84
128.27
122.95
87.81
77.32
77.00
76.68
60.66
40.45
37.58
33.30
19.75
18.14
17.62
HO
O
(±)-2c
f1 (ppm)

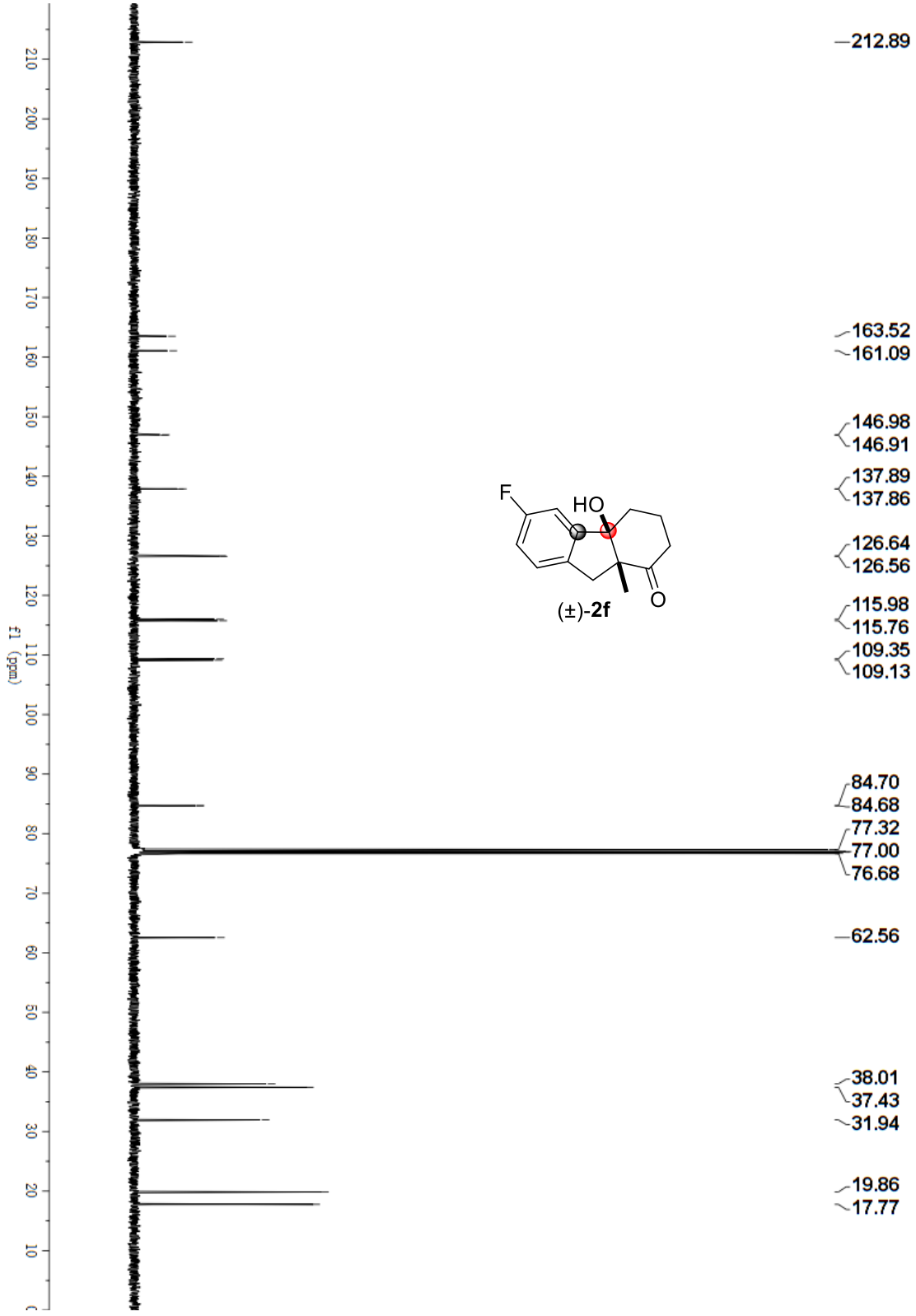

0.97
1.96
0.96
1.02
1.10
3.22
1.83
1.13
2.07
1.01
3.05
f1 (ppm)
HO
O
(±)-2d
7.15
7.13
7.08
7.06
3.57
3.53
2.67
2.63
2.56
2.54
2.53
2.52
2.51
2.51
2.49
2.48
2.35
2.33
2.32
2.32
2.31
2.31
2.30
2.29
2.28
2.28
2.27
2.26
2.25
2.25
2.24
2.19
2.18
2.16
2.15
2.15
2.14
2.13
2.11
1.98
1.97
1.97
1.96
1.94
1.93
1.92
1.91
1.90
1.88
1.48
1.46
1.45
1.44
1.42
1.41
1.40
1.33

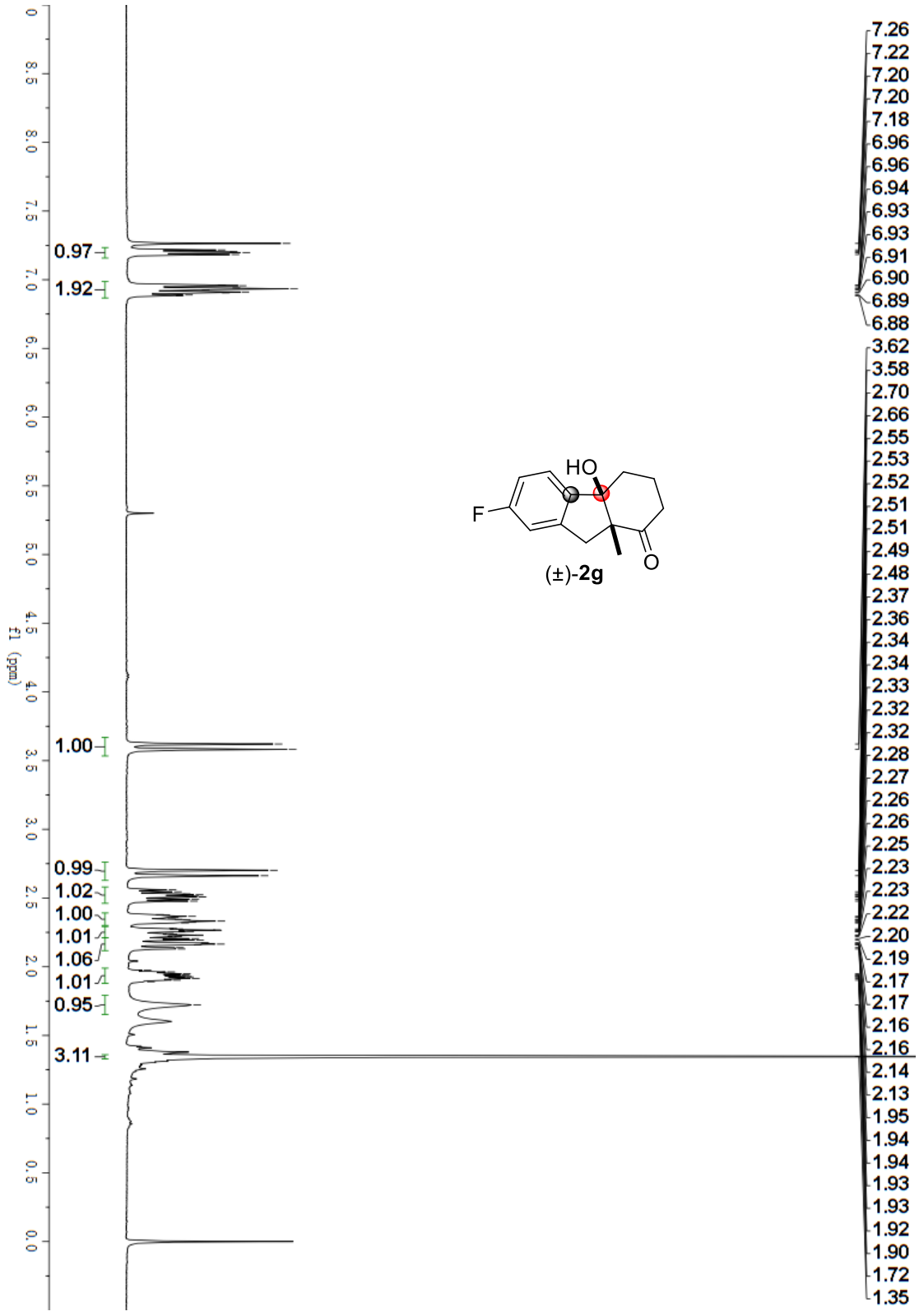

213.43
144.90
139.64
136.63
129.70
125.10
122.55
84.71
77.32
77.00
76.68
62.26
38.27
37.51
31.82
21.32
19.94
17.87
HO
O
(±)-2d
f1 (ppm)

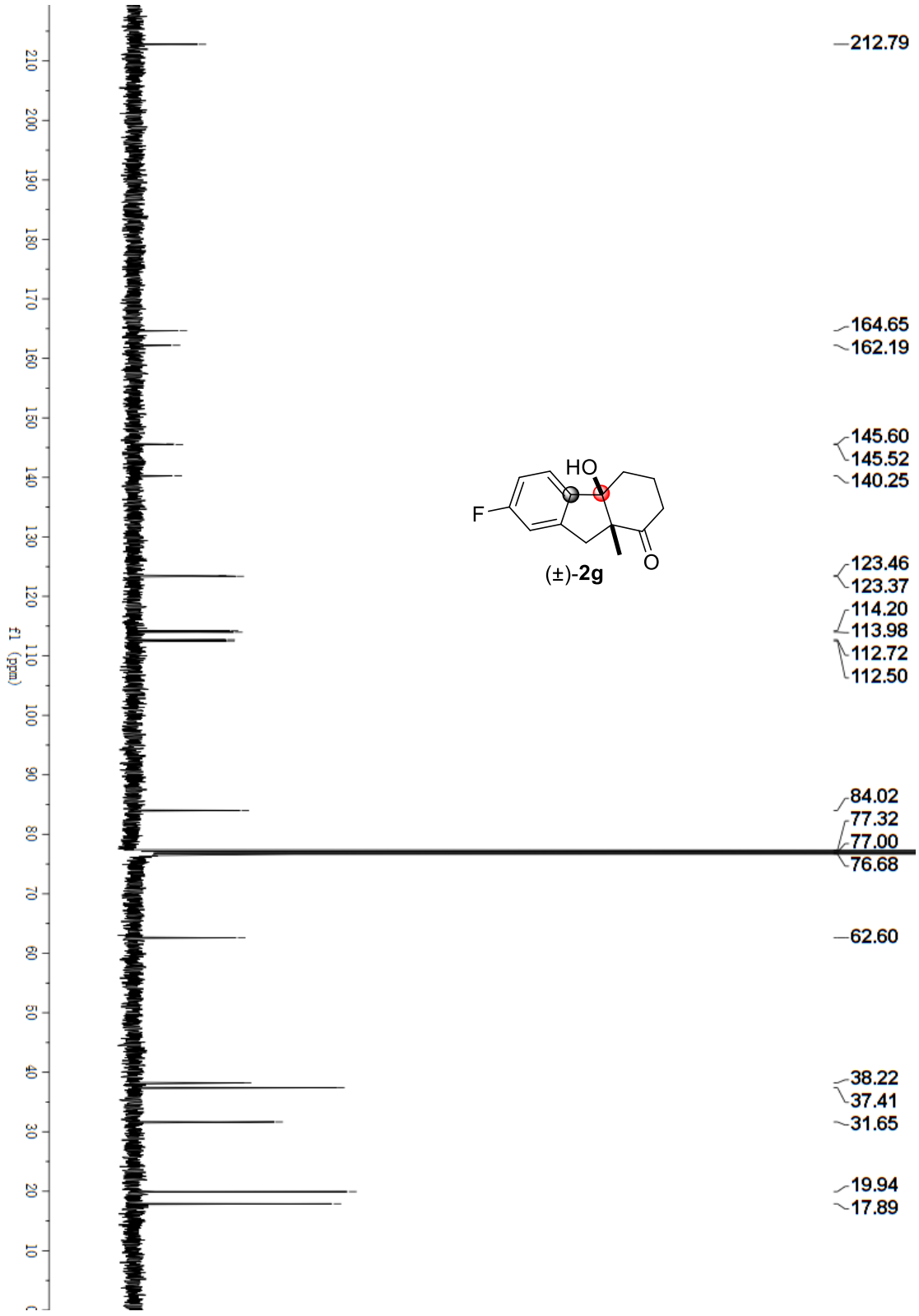

4.00
1.04
1.00
1.19
2.10
1.16
1.28
1.00
1.87
3.23
f1 (ppm)
Cl
HO
O
(±)-2e
7.26
7.26
7.25
7.23
7.23
7.22
7.21
7.19
7.17
3.57
3.53
2.67
2.64
2.56
2.55
2.54
2.53
2.52
2.51
2.50
2.48
2.32
2.31
2.31
2.30
2.30
2.29
2.29
2.28
2.28
2.27
2.26
2.25
2.20
2.19
2.17
2.16
2.16
2.15
2.13
2.12
1.99
1.98
1.97
1.95
1.94
1.93
1.93
1.63
1.44
1.44
1.43
1.43
1.42
1.41
1.41
1.33

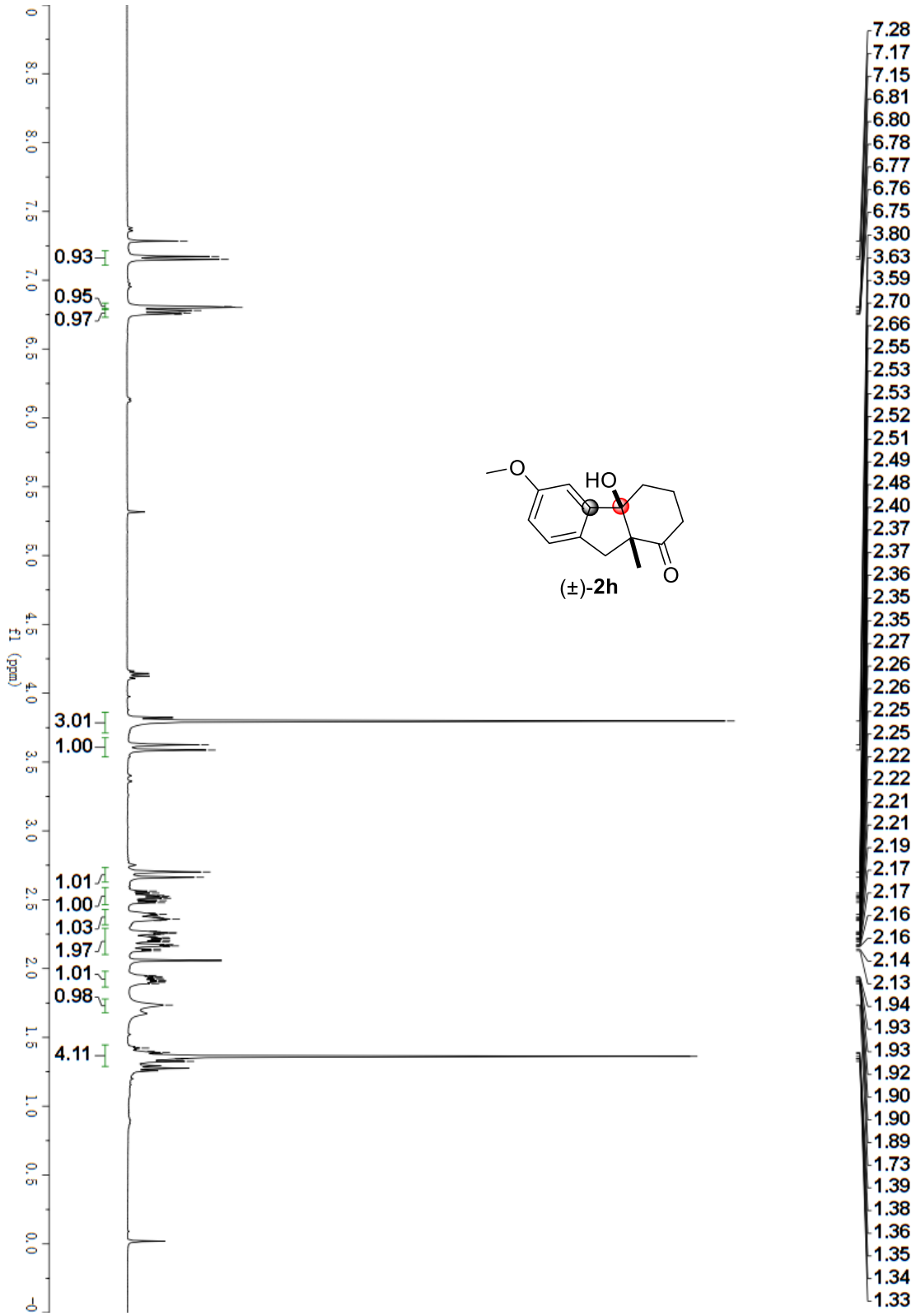

212.73
146.80
141.10
132.75
129.07
126.68
122.51
84.72
77.32
77.20
77.00
76.68
62.35
38.17
37.41
31.91
19.90
17.74
Cl
HO
O
(±)-2e
f1 (ppm)

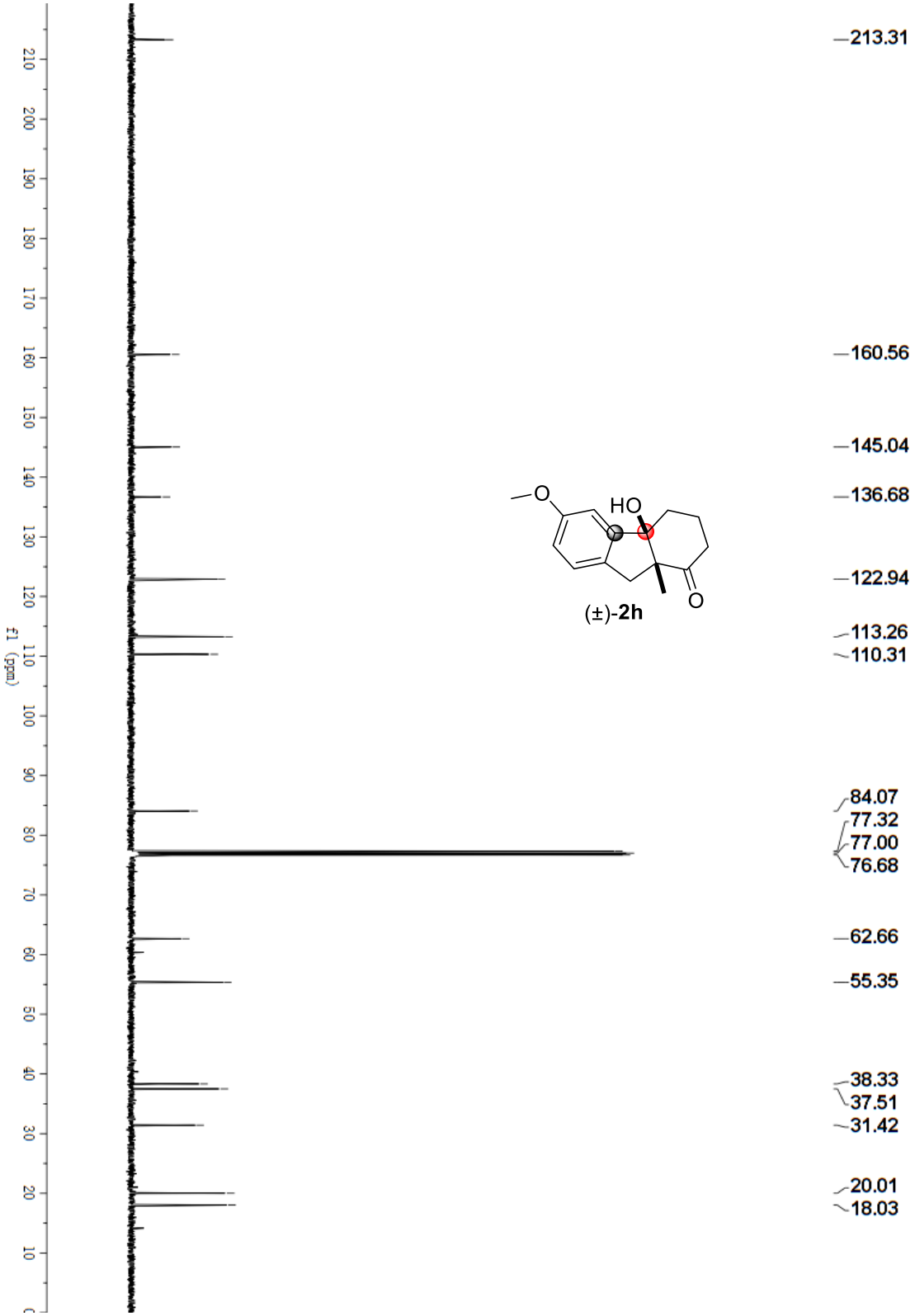

F
HO
O
(±)-2f
f1 (ppm)
0.96
1.93
1.00
1.04
1.05
1.97
1.04
0.99
0.90
1.12
2.95
7.27
7.20
7.19
7.18
7.17
6.96
6.95
6.94
6.94
6.93
6.92
3.56
3.52
2.66
2.63
2.56
2.54
2.53
2.52
2.51
2.50
2.49
2.48
2.31
2.31
2.30
2.29
2.28
2.27
2.26
2.25
2.25
2.24
2.19
2.18
2.16
2.15
2.14
2.12
2.11
1.98
1.97
1.96
1.95
1.93
1.92
1.89
1.45
1.44
1.43
1.43
1.42
1.41
1.41
1.40
1.39
1.32

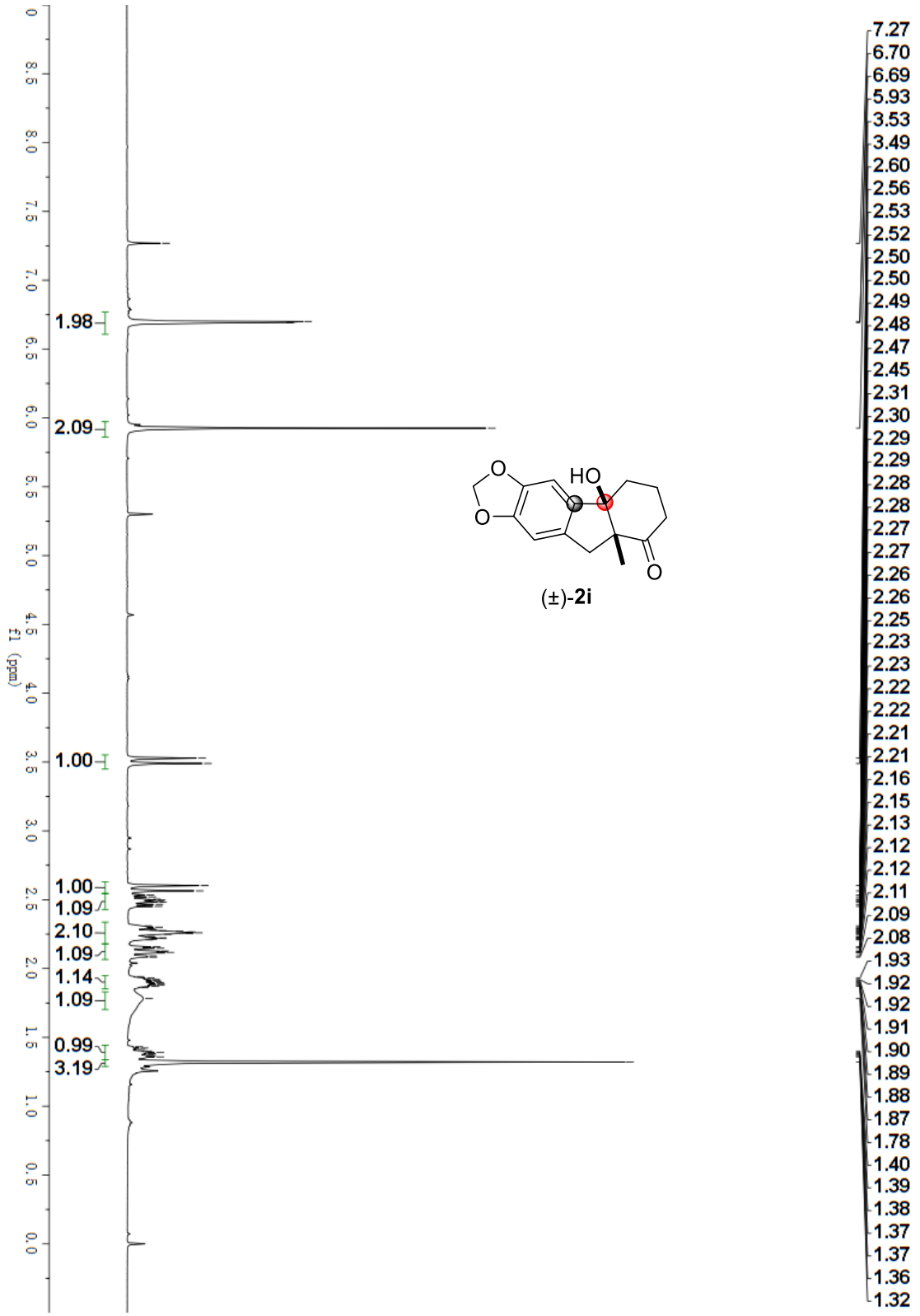

212.89
163.52
161.09
146.98
146.91
137.89
137.86
126.64
126.56
115.98
115.76
109.35
109.13
84.70
84.68
77.32
77.00
76.68
62.56
38.01
37.43
31.94
19.86
17.77
F
HO
O
(±)-2f
f1 (ppm)

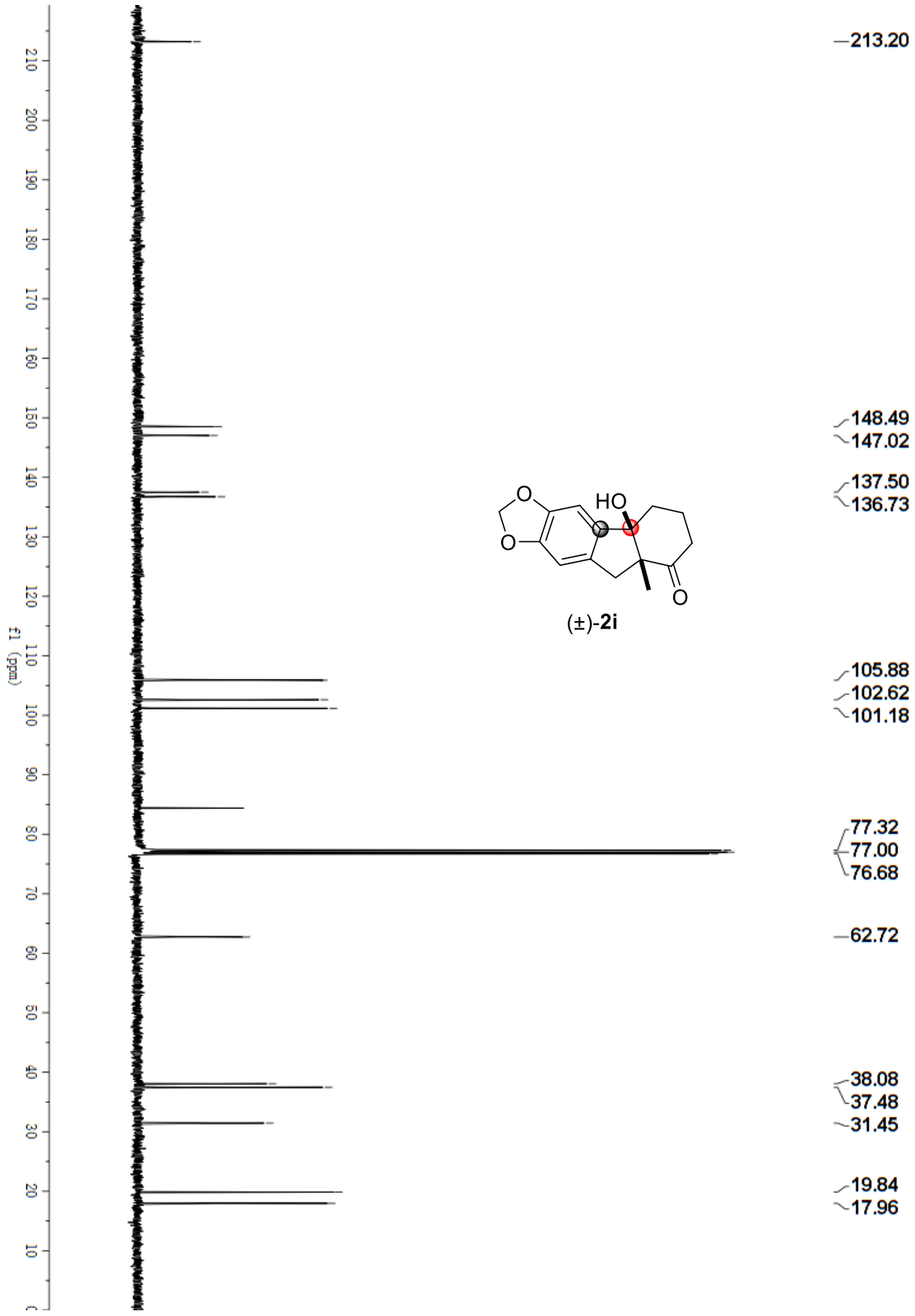

HO
F
O
(±)-2g
f1 (ppm)
0.97
1.92
1.00
0.99
1.02
1.00
1.01
1.06
1.01
0.95
3.11
7.26
7.22
7.20
7.20
7.18
6.96
6.96
6.94
6.93
6.93
6.91
6.90
6.89
6.88
3.62
3.58
2.70
2.66
2.55
2.53
2.52
2.51
2.51
2.49
2.48
2.37
2.36
2.34
2.34
2.33
2.32
2.32
2.28
2.27
2.26
2.26
2.25
2.23
2.23
2.22
2.20
2.19
2.17
2.17
2.16
2.16
2.14
2.13
1.95
1.94
1.94
1.93
1.93
1.92
1.90
1.72
1.35

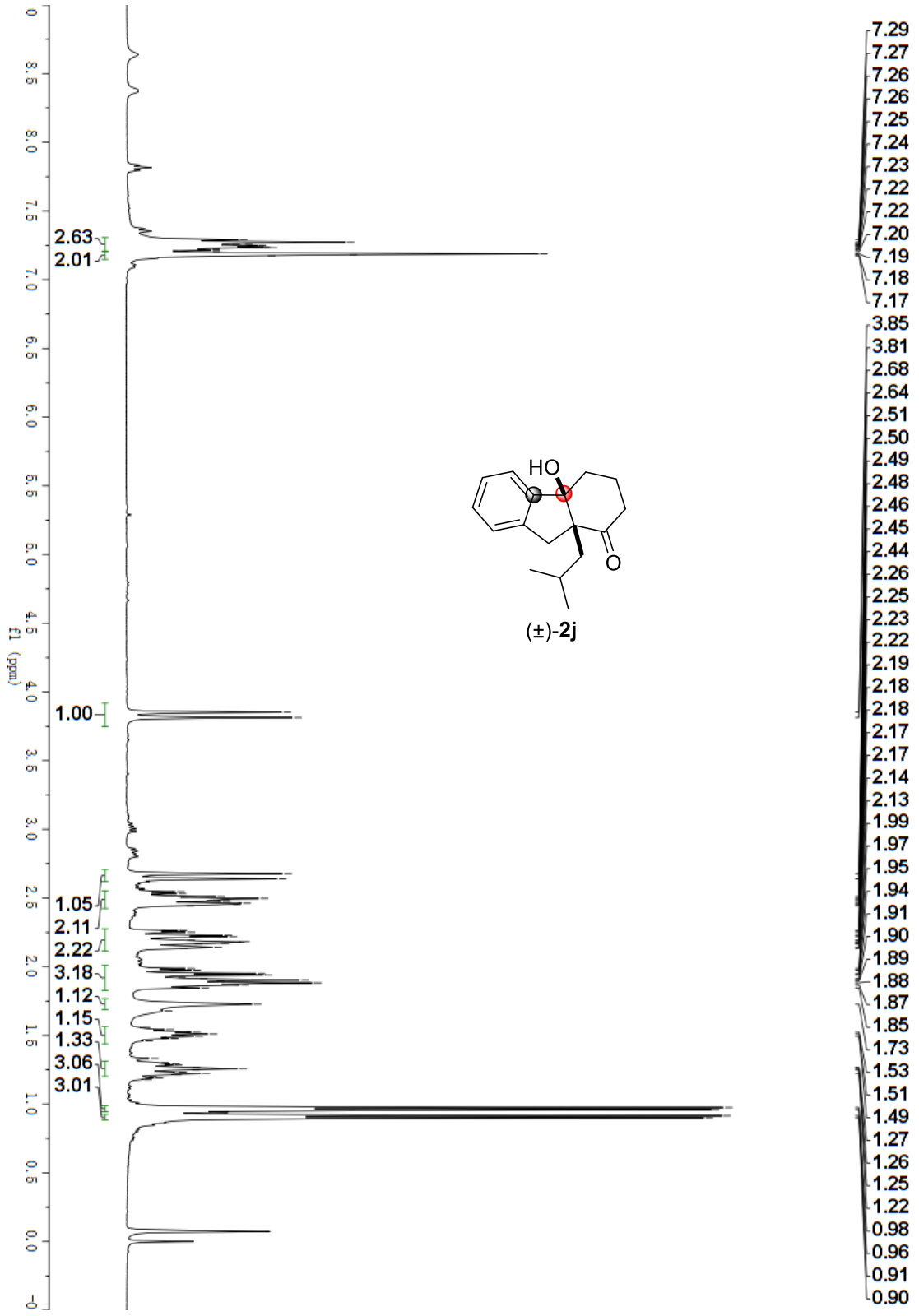

212.79
164.65
162.19
145.60
145.52
140.25
123.46
123.37
114.20
113.98
112.72
112.50
84.02
77.32
77.00
76.68
62.60
38.22
37.41
31.65
19.94
17.89
HO
F
O
(±)-2g
f1 (ppm)

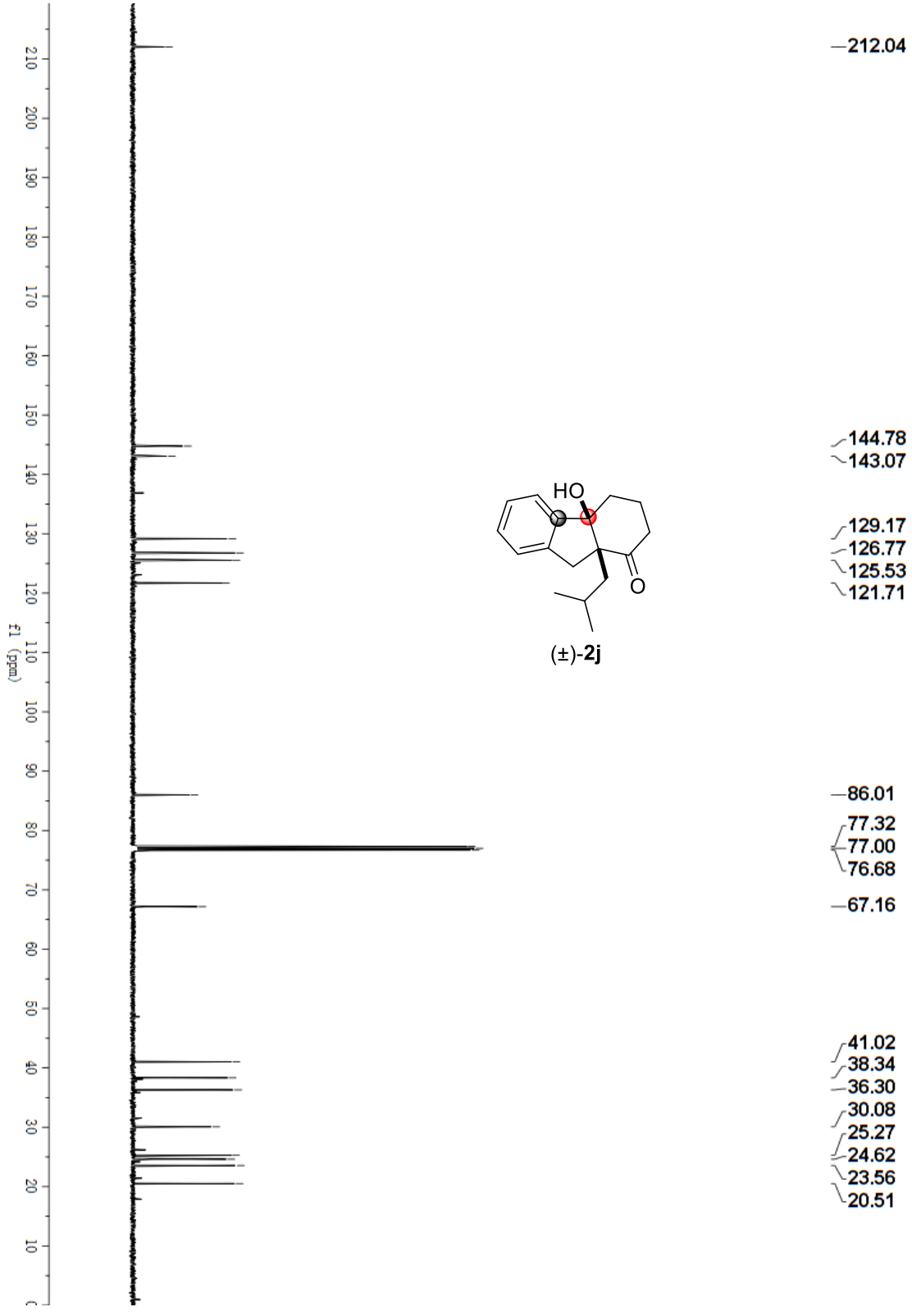

0.93
0.95
0.97
3.01
1.00
1.01
1.00
1.03
1.97
1.01
0.98
4.11
f1 (ppm)
O
HO
O
(±)-2h
7.28
7.17
7.15
6.81
6.80
6.78
6.77
6.76
6.75
3.80
3.63
3.59
2.70
2.66
2.55
2.53
2.53
2.52
2.51
2.49
2.48
2.40
2.37
2.37
2.36
2.35
2.35
2.27
2.26
2.26
2.25
2.25
2.22
2.22
2.21
2.21
2.19
2.17
2.17
2.16
2.16
2.14
2.13
1.94
1.93
1.93
1.92
1.90
1.90
1.89
1.73
1.39
1.38
1.36
1.35
1.34
1.33


213.31
160.56
145.04
136.68
122.94
113.26
110.31
84.07
77.32
77.00
76.68
62.66
55.35
38.33
37.51
31.42
20.01
18.03
HO
O
O
(±)-2h
f1 (ppm)

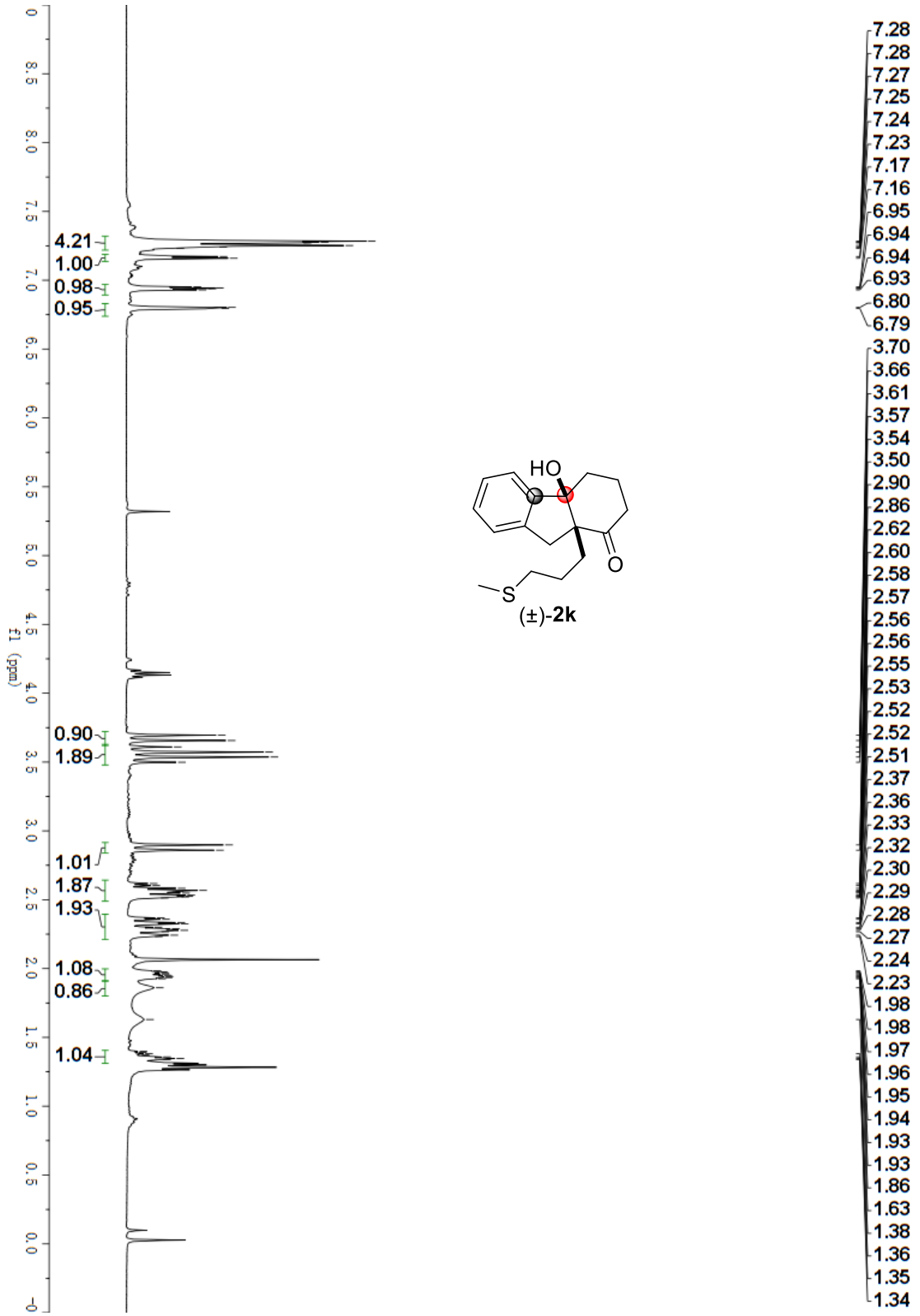

f1 (ppm)
1.98
2.09
1.00
1.00
1.09
2.10
1.09
1.14
1.09
0.99
3.19
HO
O
O
O
(±)-2i
7.27
6.70
6.69
5.93
3.53
3.49
2.60
2.56
2.53
2.52
2.50
2.50
2.49
2.48
2.47
2.45
2.31
2.30
2.29
2.29
2.28
2.28
2.27
2.27
2.26
2.26
2.25
2.23
2.23
2.22
2.22
2.21
2.21
2.16
2.15
2.13
2.12
2.12
2.11
2.09
2.08
1.93
1.92
1.92
1.91
1.90
1.89
1.88
1.87
1.78
1.40
1.39
1.38
1.37
1.37
1.36
1.32

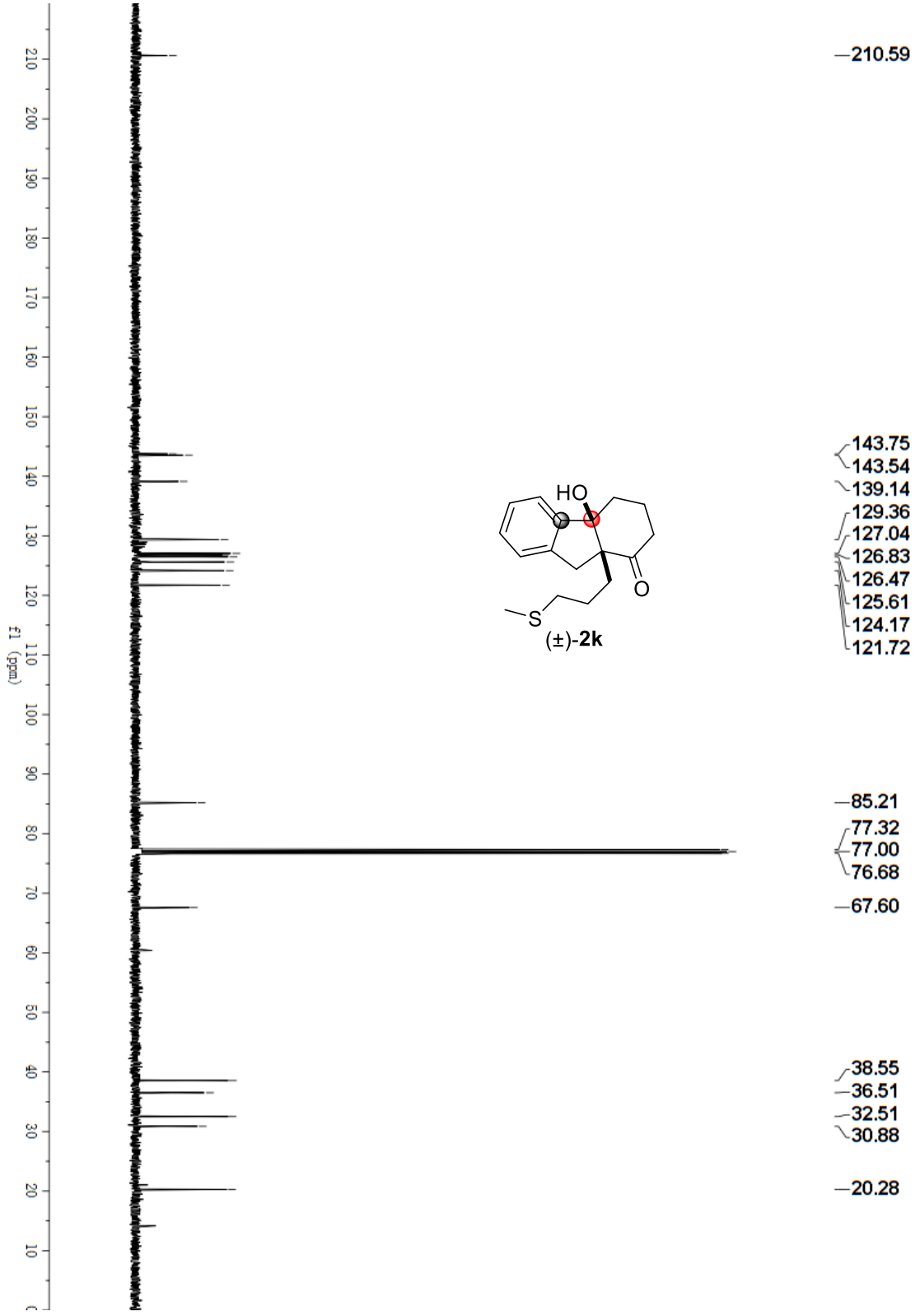

213.20
148.49
147.02
137.50
136.73
105.88
102.62
101.18
77.32
77.00
76.68
62.72
38.08
37.48
31.45
19.84
17.96
HO
O
O
O
(±)-2i
f1 (ppm)

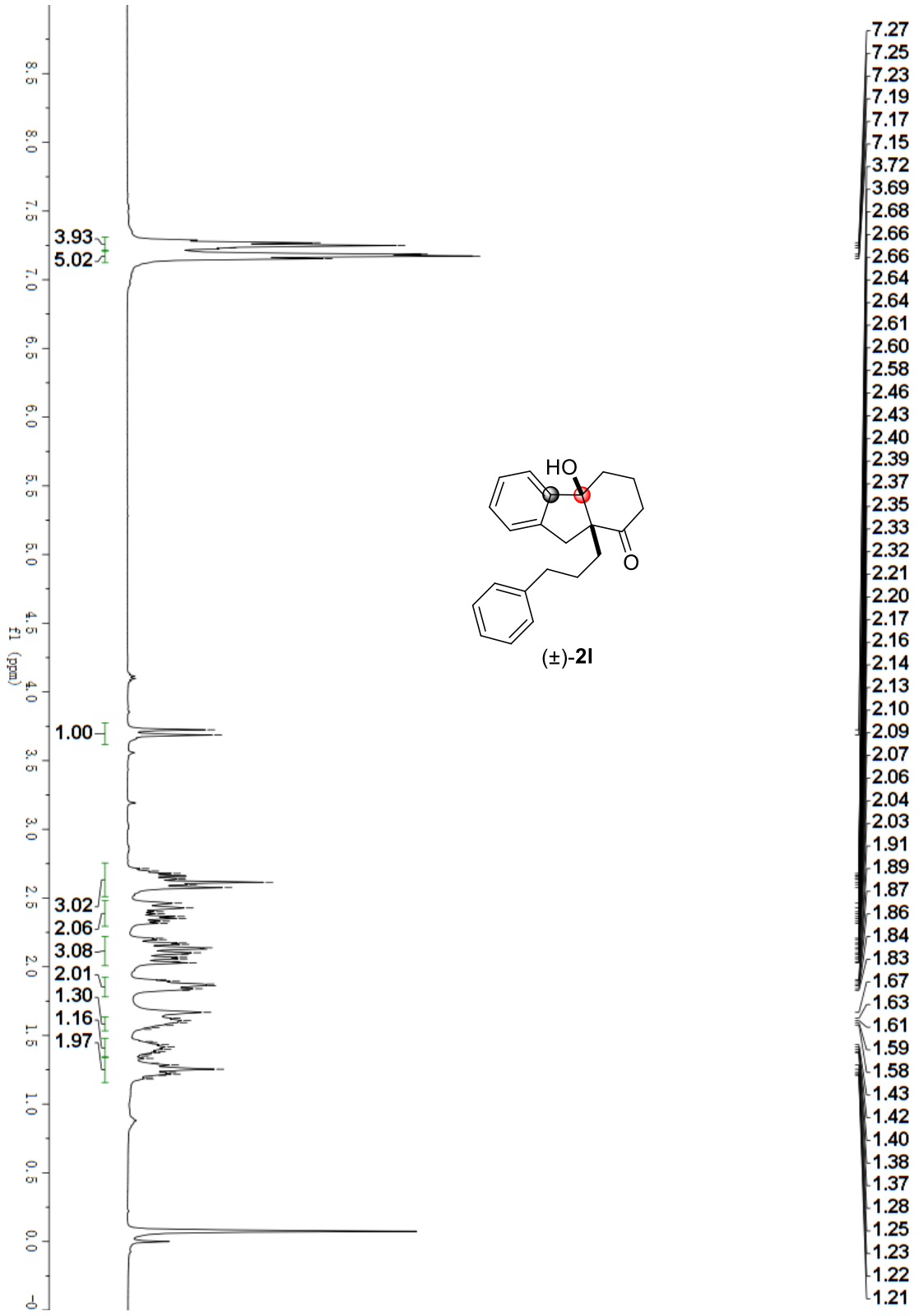

HO
O
(±)-2j
2.63
2.01
1.00
1.05
2.11
2.22
3.18
1.12
1.15
1.33
3.06
3.01
f1 (ppm)
7.29
7.27
7.26
7.26
7.25
7.24
7.23
7.22
7.22
7.20
7.19
7.18
7.17
3.85
3.81
2.68
2.64
2.51
2.50
2.49
2.48
2.46
2.45
2.44
2.26
2.25
2.23
2.22
2.19
2.18
2.18
2.17
2.17
2.14
2.13
1.99
1.97
1.95
1.94
1.91
1.90
1.89
1.88
1.87
1.85
1.73
1.53
1.51
1.49
1.27
1.26
1.25
1.22
0.98
0.96
0.91
0.90

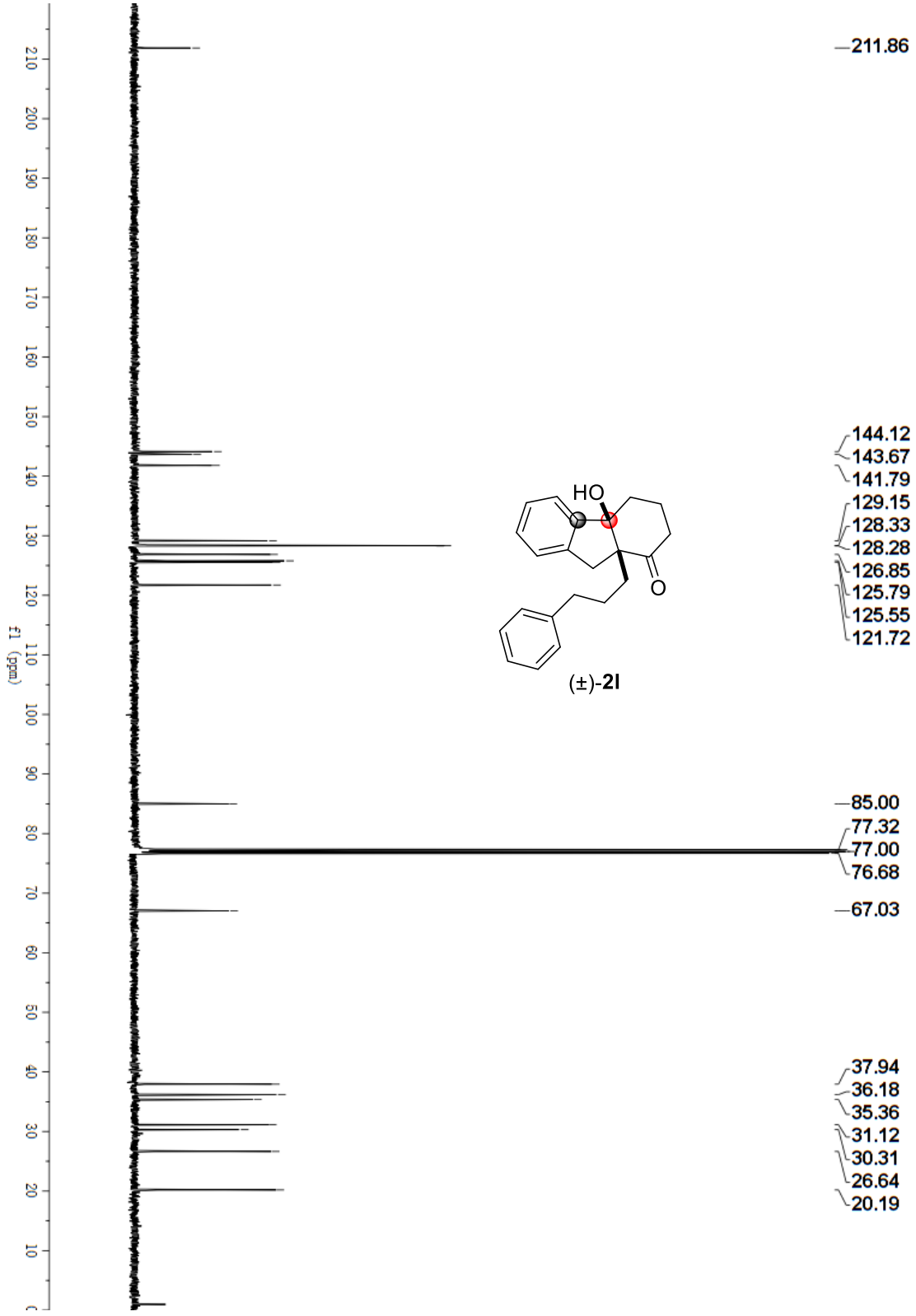

212.04
144.78
143.07
129.17
126.77
125.53
121.71
86.01
77.32
77.00
76.68
67.16
41.02
38.34
36.30
30.08
25.27
24.62
23.56
20.51
HO
O
f1 (ppm)

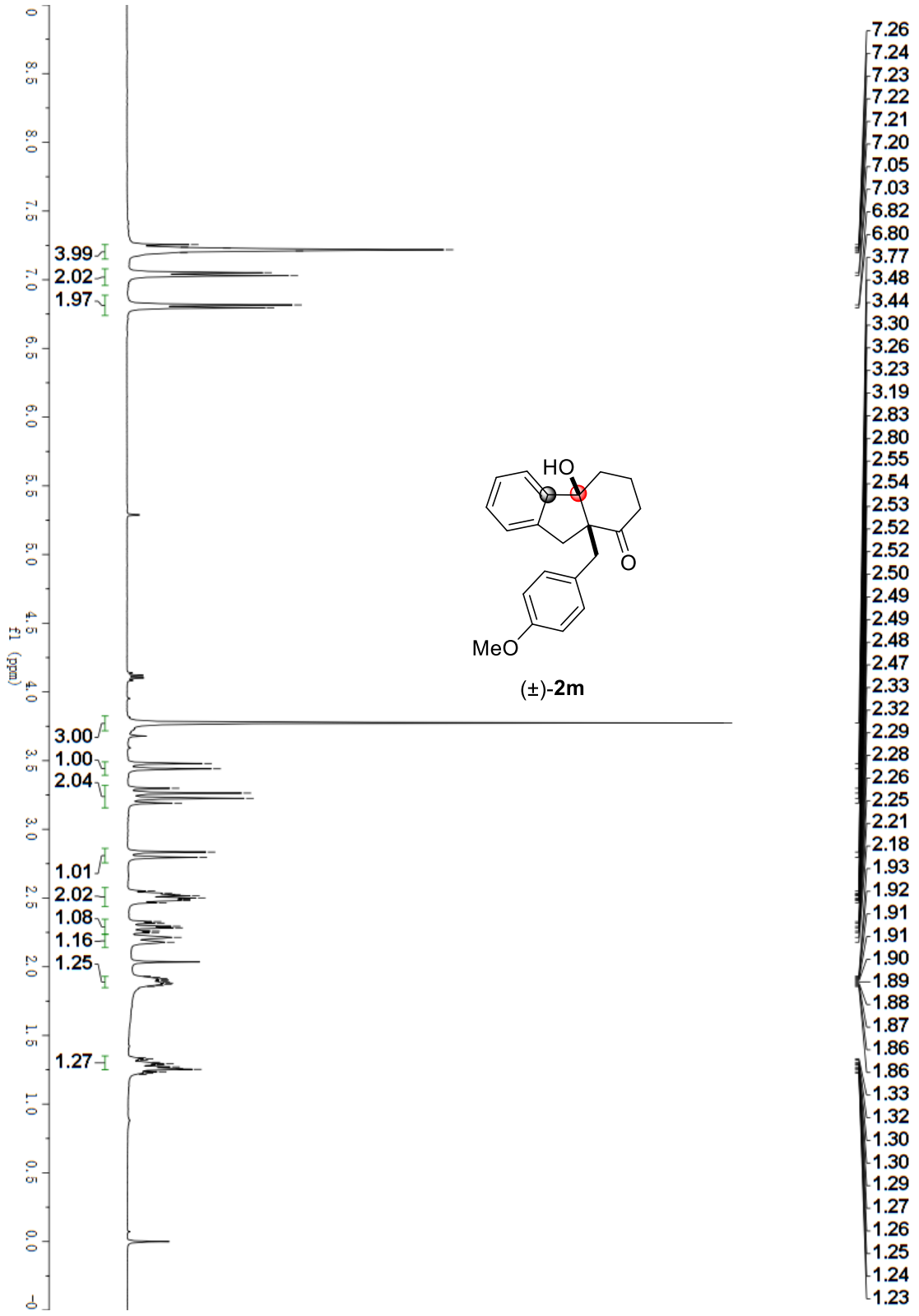
(±)-**2j**

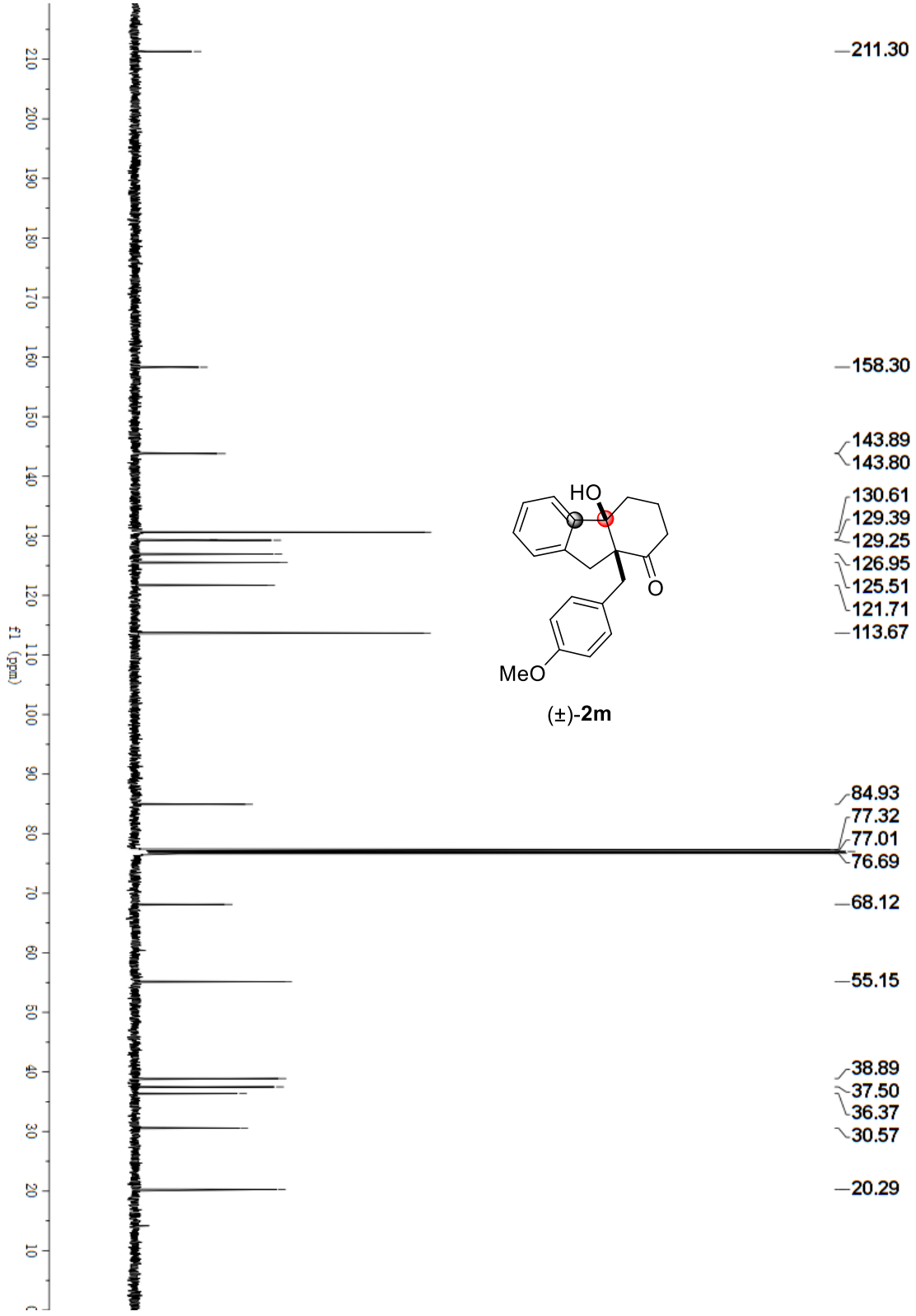

4.21
1.00
0.98
0.95
0.90
1.89
1.01
1.87
1.93
1.08
0.86
1.04
f1 (ppm)
HO
O
S
(±)-2k
7.28
7.28
7.27
7.25
7.24
7.23
7.17
7.16
6.95
6.94
6.94
6.93
6.80
6.79
3.70
3.66
3.61
3.57
3.54
3.50
2.90
2.86
2.62
2.60
2.58
2.57
2.56
2.56
2.55
2.53
2.52
2.52
2.51
2.37
2.36
2.33
2.32
2.30
2.29
2.28
2.27
2.24
2.23
1.98
1.98
1.97
1.96
1.95
1.94
1.93
1.93
1.86
1.63
1.38
1.36
1.35
1.34


210.59
143.75
143.54
139.14
129.36
127.04
126.83
126.47
125.61
124.17
121.72
85.21
77.32
77.00
76.68
67.60
38.55
36.51
32.51
30.88
20.28
HO
O
S
(±)-2k
f1 (ppm)

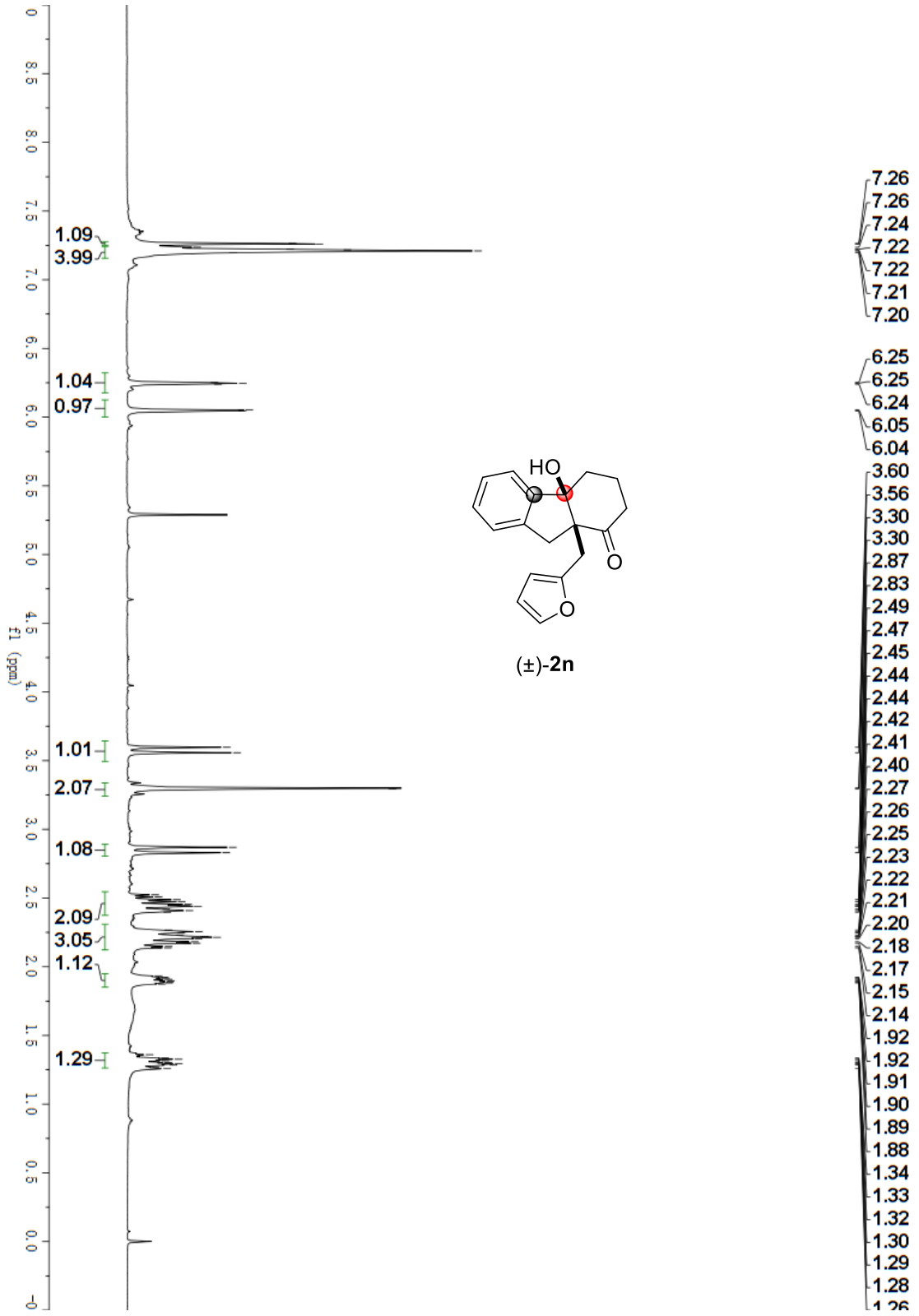

3.93
5.02
1.00
3.02
2.06
3.08
2.01
1.30
1.16
1.97
f1 (ppm)
HO
O
(±)-2l
7.27
7.25
7.23
7.19
7.17
7.15
3.72
3.69
2.68
2.66
2.66
2.64
2.64
2.61
2.60
2.58
2.46
2.43
2.40
2.39
2.37
2.35
2.33
2.32
2.21
2.20
2.17
2.16
2.14
2.13
2.10
2.09
2.07
2.06
2.04
2.03
1.91
1.89
1.87
1.86
1.84
1.83
1.67
1.63
1.61
1.59
1.58
1.43
1.42
1.40
1.38
1.37
1.28
1.25
1.23
1.22
1.21


211.86
144.12
143.67
141.79
129.15
128.33
128.28
126.85
125.79
125.55
121.72
85.00
77.32
77.00
76.68
67.03
37.94
36.18
35.36
31.12
30.31
26.64
20.19
HO
O
(±)-2l
f1 (ppm)

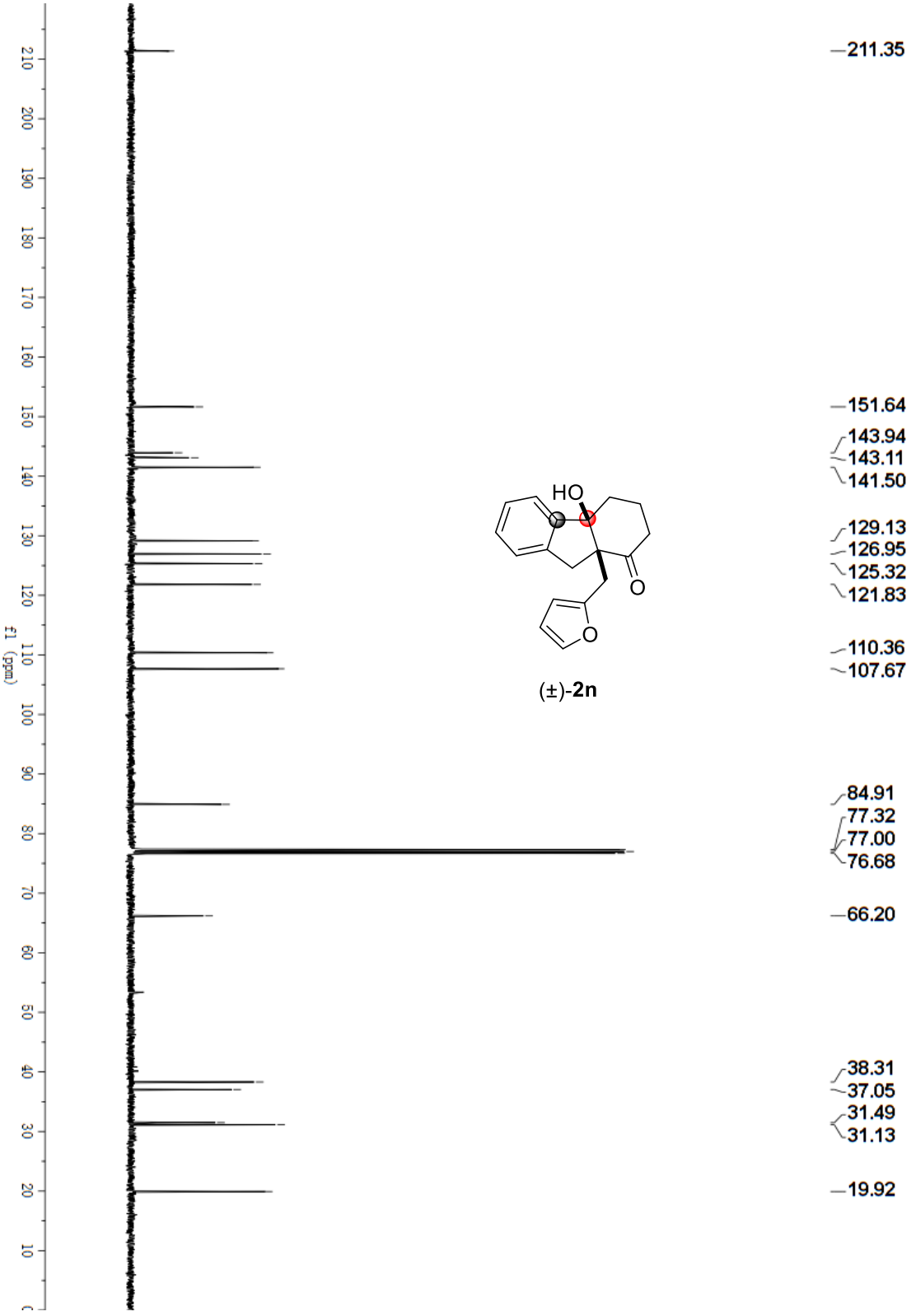

3.99
2.02
1.97
3.00
1.00
2.04
1.01
2.02
1.08
1.16
1.25
1.27
f1 (ppm)
HO
O
MeO
(±)-2m
7.26
7.24
7.23
7.22
7.21
7.20
7.05
7.03
6.82
6.80
3.77
3.48
3.44
3.30
3.26
3.23
3.19
2.83
2.80
2.55
2.54
2.53
2.52
2.52
2.50
2.49
2.49
2.48
2.47
2.33
2.32
2.29
2.28
2.26
2.25
2.21
2.18
1.93
1.92
1.91
1.91
1.90
1.89
1.88
1.87
1.86
1.86
1.33
1.32
1.30
1.30
1.29
1.27
1.26
1.25
1.24
1.23


211.30
158.30
143.89
143.80
130.61
129.39
129.25
126.95
125.51
121.71
113.67
84.93
77.32
77.01
76.69
68.12
55.15
38.89
37.50
36.37
30.57
20.29
HO
O
MeO
f1 (ppm)

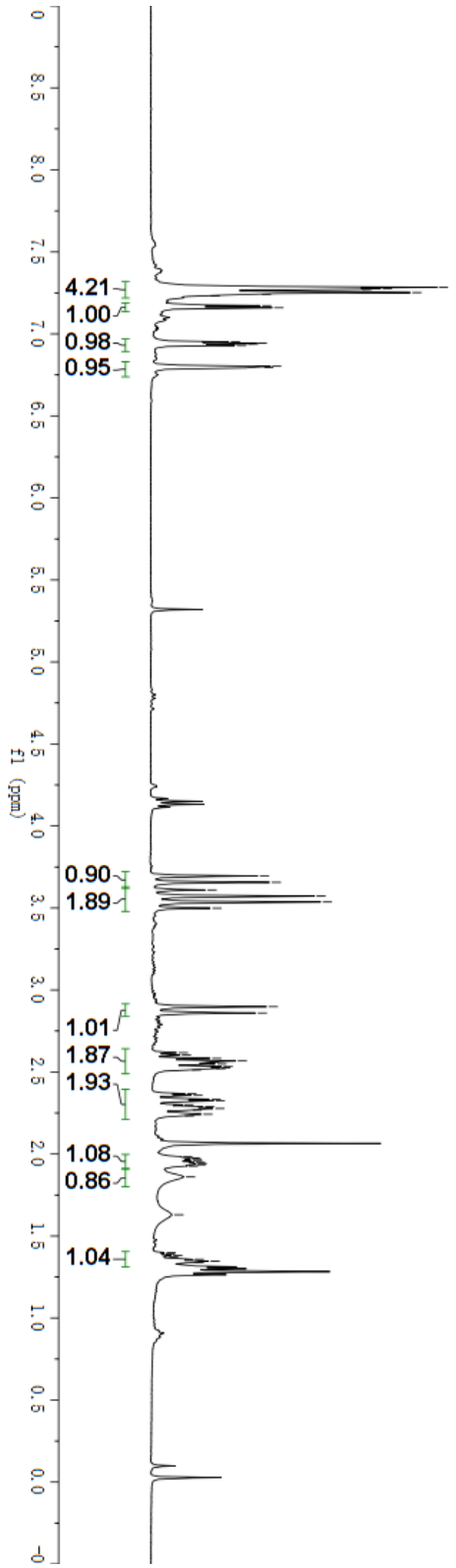
(±)-**2m**

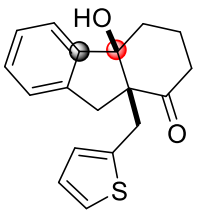

1.09
3.99
1.04
0.97
1.01
2.07
1.08
2.09
3.05
1.12
1.29
f1 (ppm)
HO
O
O
7.26
7.26
7.24
7.22
7.22
7.21
7.20
6.25
6.25
6.24
6.05
6.04
3.60
3.56
3.30
3.30
2.87
2.83
2.49
2.47
2.45
2.44
2.44
2.42
2.41
2.40
2.27
2.26
2.25
2.23
2.22
2.21
2.20
2.18
2.17
2.15
2.14
1.92
1.92
1.91
1.90
1.89
1.88
1.34
1.33
1.32
1.30
1.29
1.28

(±)-**2n**

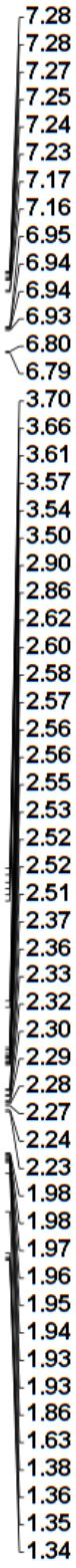

211.35
151.64
143.94
143.11
141.50
129.13
126.95
125.32
121.83
110.36
107.67
84.91
77.32
77.00
76.68
66.20
38.31
37.05
31.49
31.13
19.92
HO
O
O
f1 (ppm)

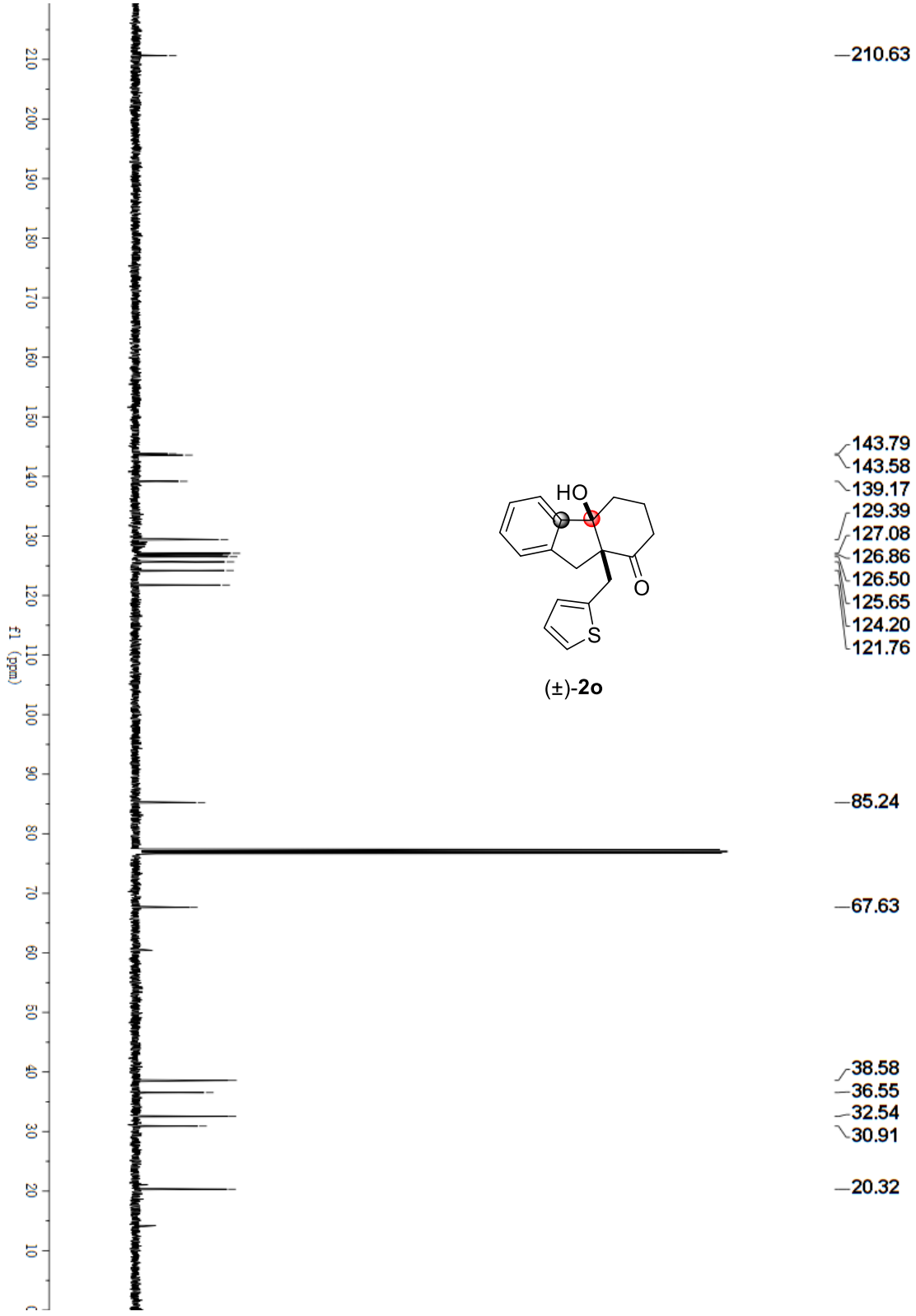
(±)-**2n**


4.21
1.00
0.98
0.95
0.90
1.89
1.01
1.87
1.93
1.08
0.86
1.04
f1 (ppm)

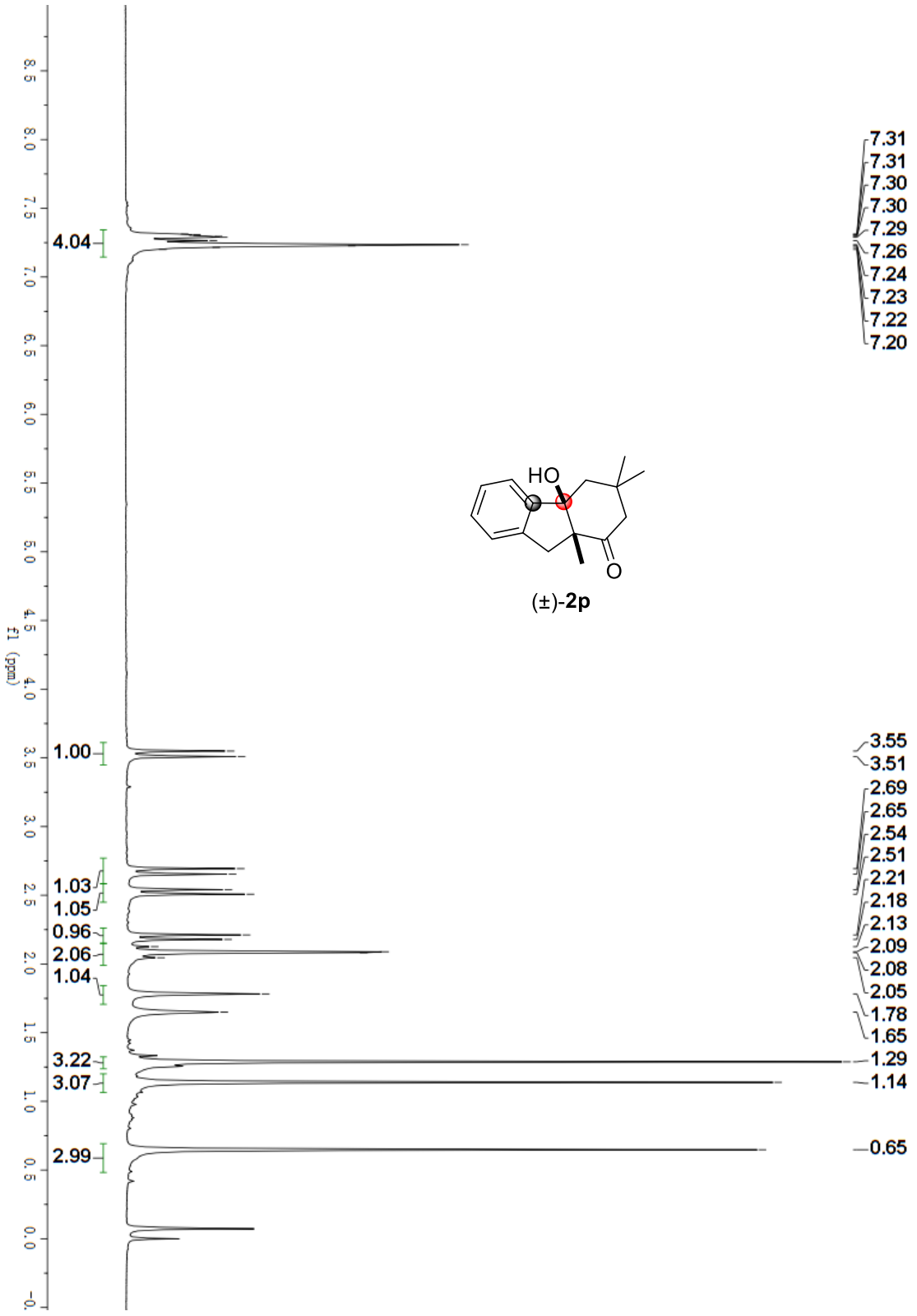

HO
O
S

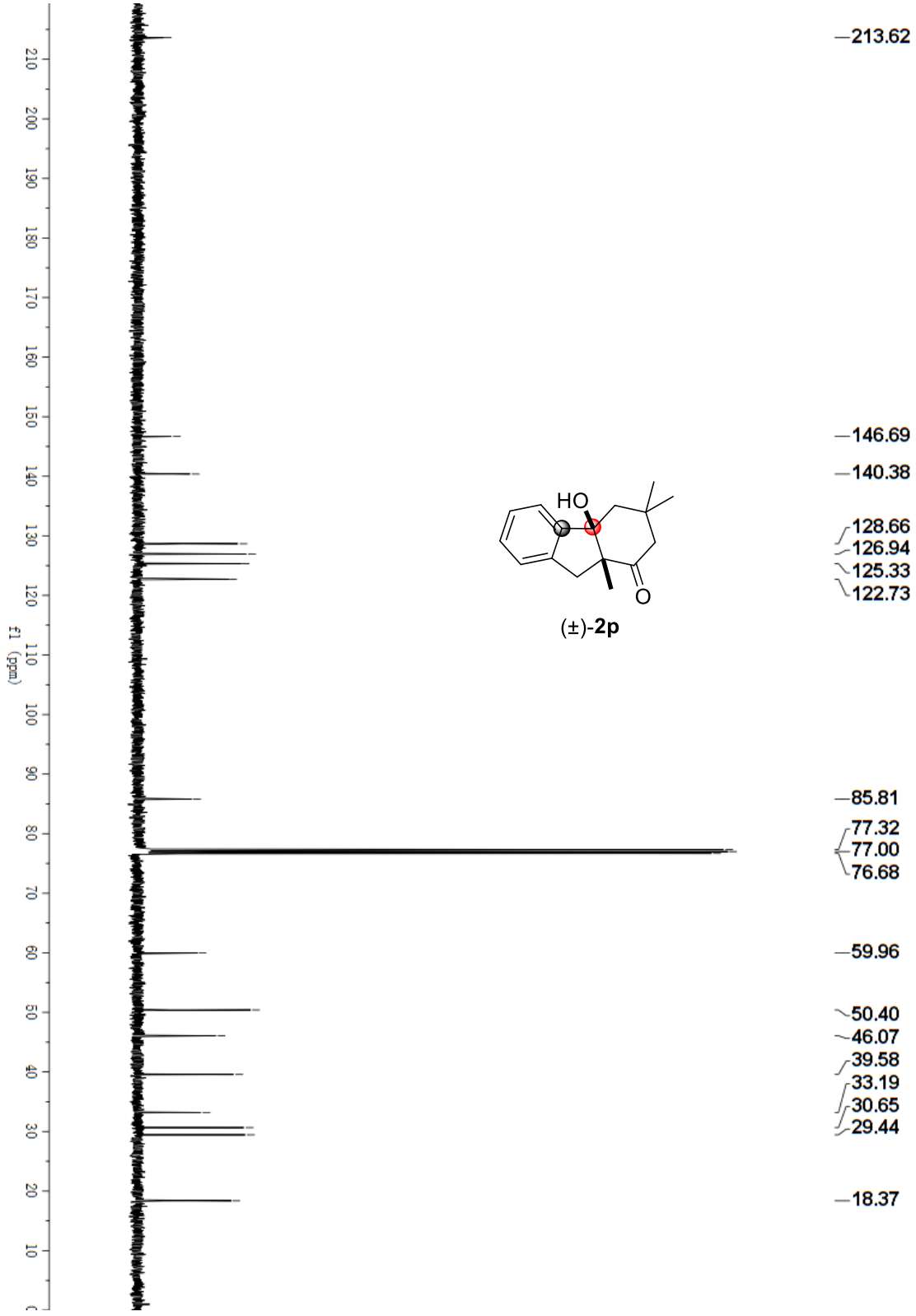
(±)-**2o**


7.28
7.28
7.27
7.25
7.24
7.23
7.17
7.16
6.95
6.94
6.94
6.93
6.80
6.79
3.70
3.66
3.61
3.57
3.54
3.50
2.90
2.86
2.62
2.60
2.58
2.57
2.56
2.56
2.55
2.53
2.52
2.52
2.51
2.37
2.36
2.33
2.32
2.30
2.29
2.28
2.27
2.24
2.23
1.98
1.98
1.97
1.96
1.95
1.94
1.93
1.93
1.86
1.63
1.38
1.36
1.35
1.34

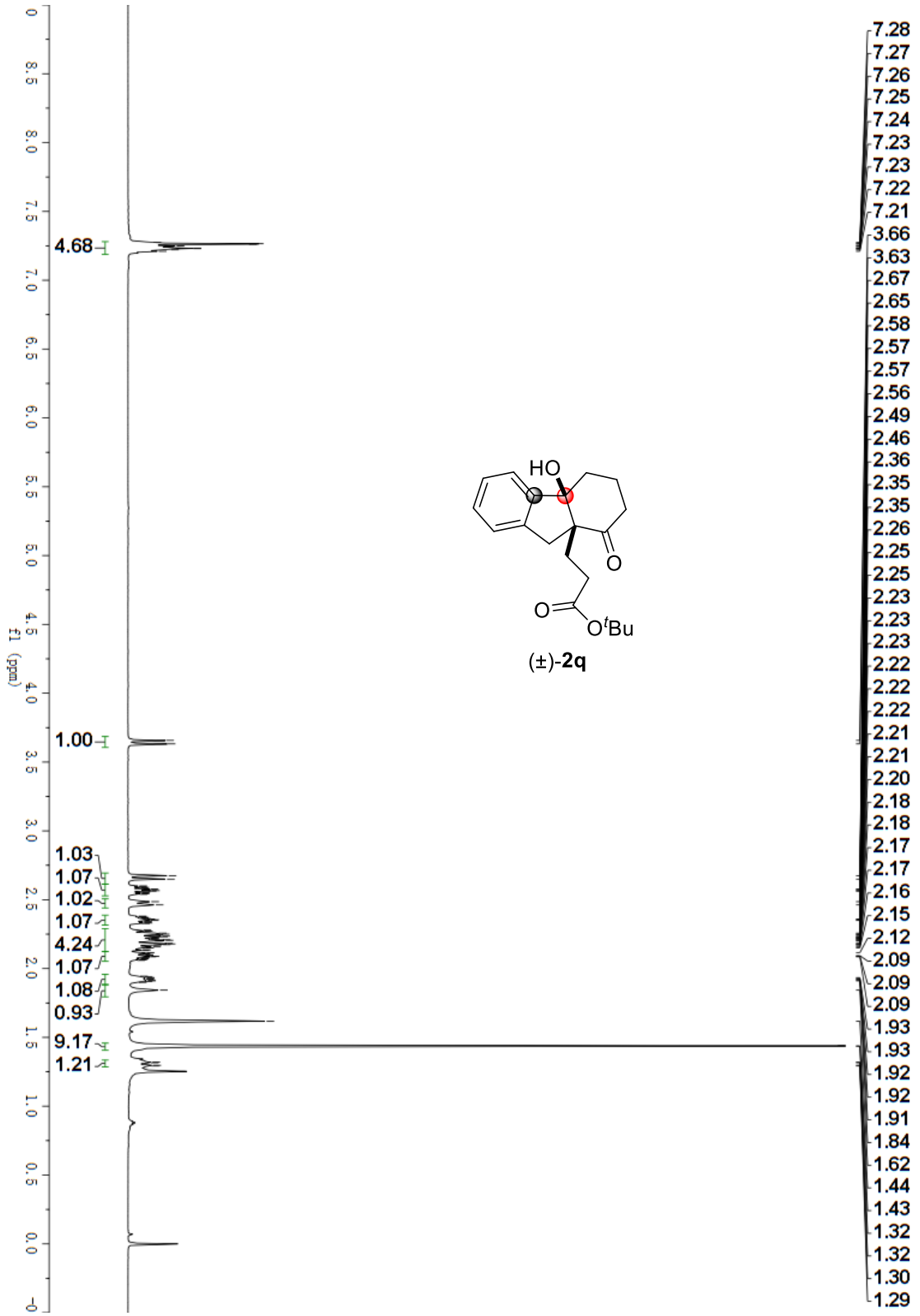

210.63
143.79
143.58
139.17
129.39
127.08
126.86
126.50
125.65
124.20
121.76
85.24
67.63
38.58
36.55
32.54
30.91
20.32
HO
O
S
f1 (ppm)

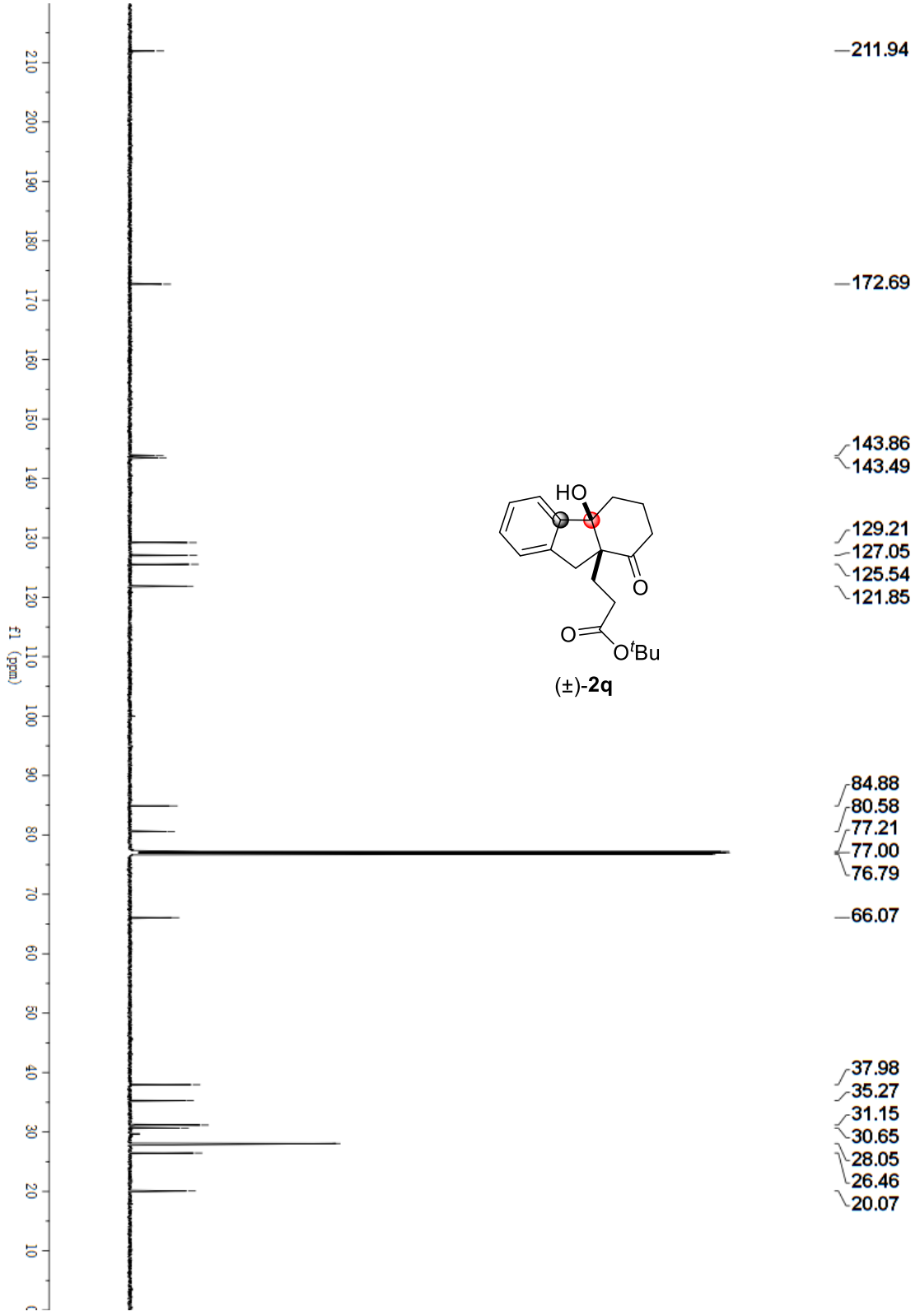
(±)-**2o**


7.31
7.31
7.30
7.30
7.29
7.26
7.24
7.23
7.22
7.20
HO
O
(±)-2p
4.04
1.00
1.03
1.05
0.96
2.06
1.04
3.22
3.07
2.99
3.55
3.51
2.69
2.65
2.54
2.51
2.21
2.18
2.13
2.09
2.08
2.05
1.78
1.65
1.29
1.14
0.65
f1 (ppm)

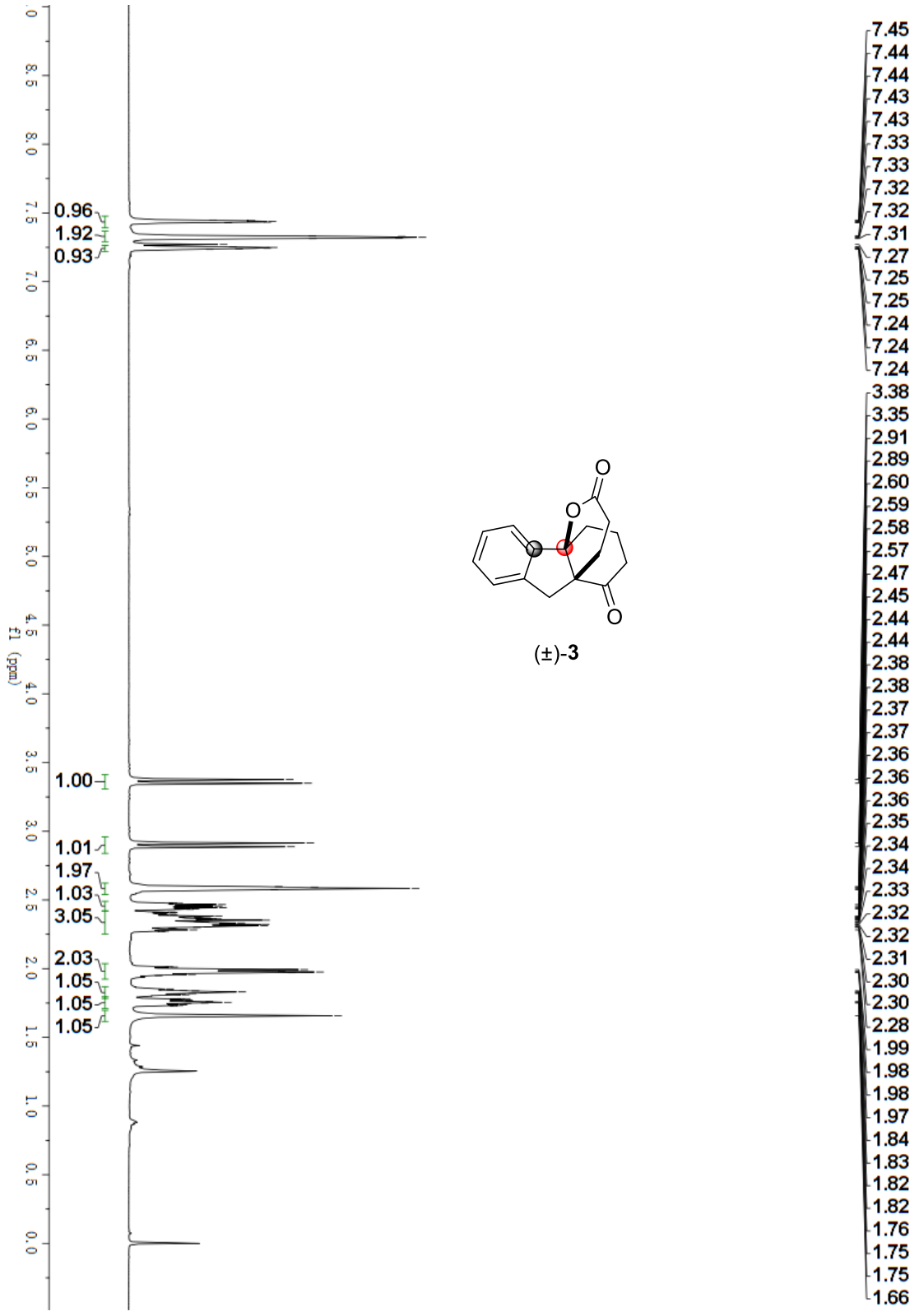

213.62
146.69
140.38
128.66
126.94
125.33
122.73
85.81
77.32
77.00
76.68
59.96
50.40
46.07
39.58
33.19
30.65
29.44
18.37
HO
O
f1 (ppm)

(±)-**2p**

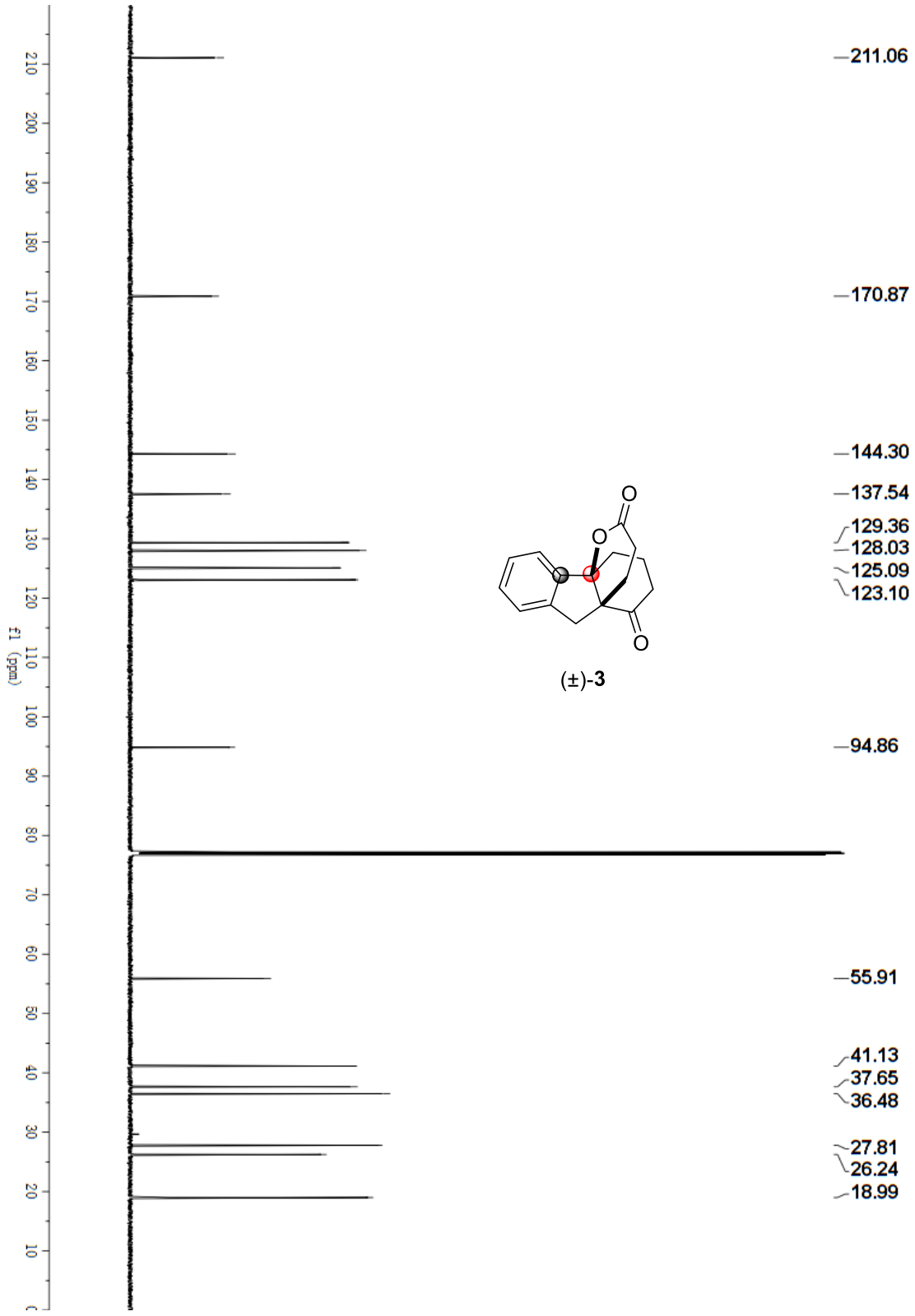

HO
O
O
O^{t}Bu
(±)-2q
4.68
1.00
1.03
1.07
1.02
1.07
4.24
1.07
1.08
0.93
9.17
1.21
7.28
7.27
7.26
7.25
7.24
7.23
7.23
7.22
7.21
3.66
3.63
2.67
2.65
2.58
2.57
2.57
2.56
2.49
2.46
2.36
2.35
2.35
2.26
2.25
2.25
2.23
2.23
2.23
2.22
2.22
2.22
2.21
2.21
2.20
2.18
2.18
2.17
2.17
2.16
2.15
2.12
2.09
2.09
2.09
1.93
1.93
1.92
1.92
1.91
1.84
1.62
1.44
1.43
1.32
1.32
1.30
1.29
f1 (ppm)


211.94
172.69
143.86
143.49
129.21
127.05
125.54
121.85
84.88
80.58
77.21
77.00
76.79
66.07
37.98
35.27
31.15
30.65
28.05
26.46
20.07
HO
O
O
O^{t}Bu
f1 (ppm)

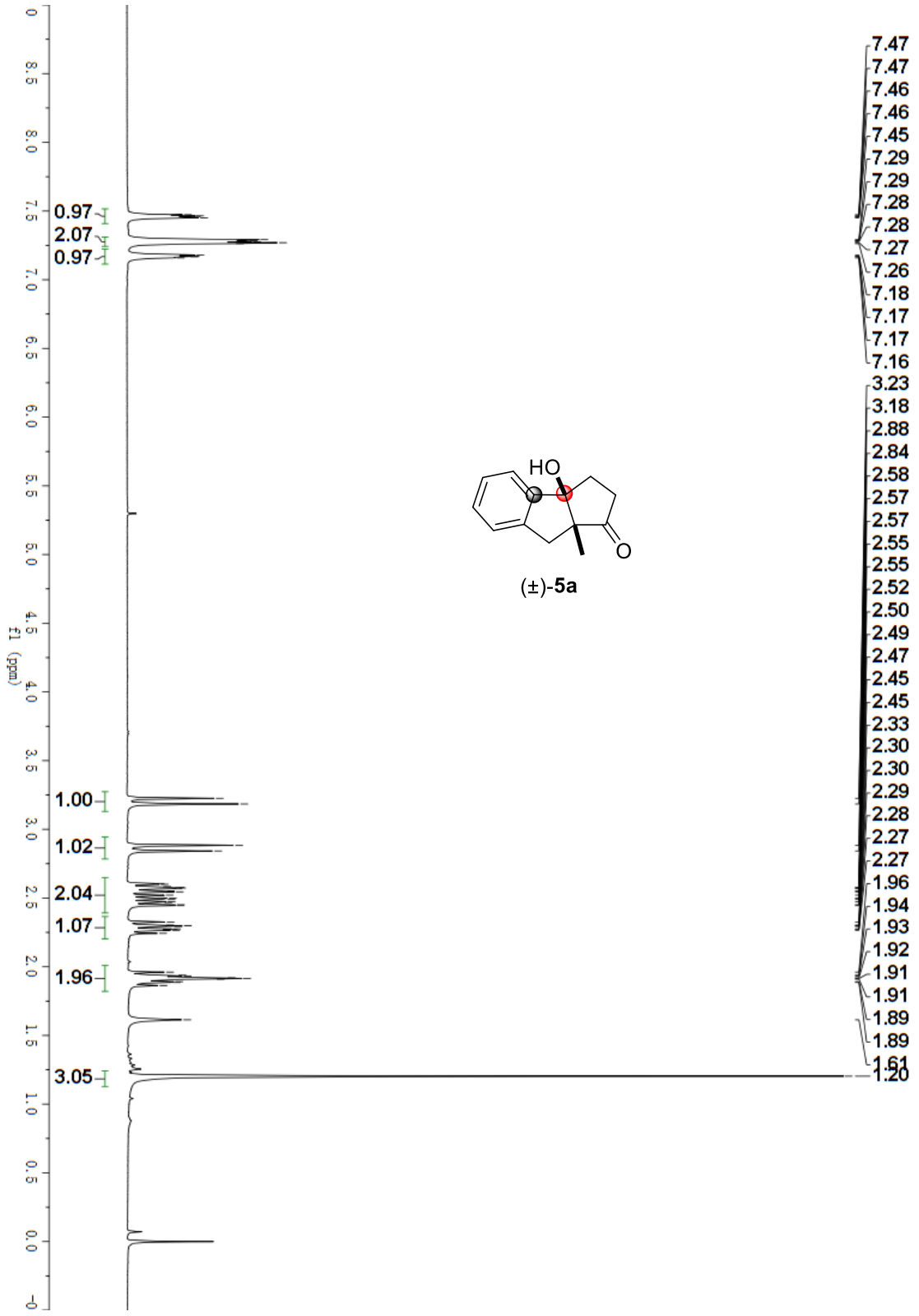
(±)-**2q**

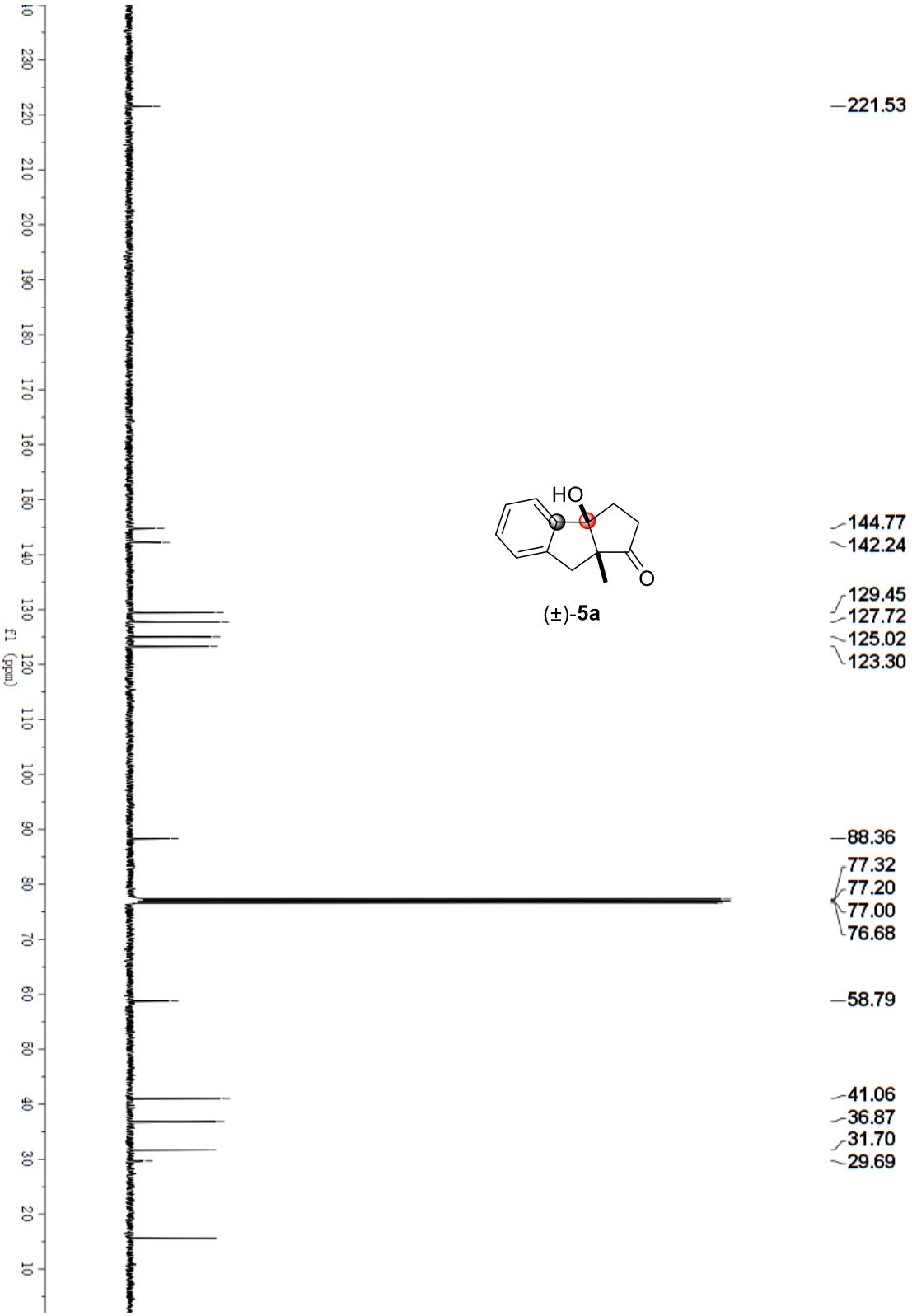

0.96
1.92
0.93
1.00
1.01
1.97
1.03
3.05
2.03
1.05
1.05
1.05
f1 (ppm)
7.45
7.44
7.44
7.43
7.43
7.33
7.33
7.32
7.32
7.31
7.27
7.25
7.25
7.24
7.24
7.24
3.38
3.35
2.91
2.89
2.60
2.59
2.58
2.57
2.47
2.45
2.44
2.44
2.38
2.38
2.37
2.37
2.36
2.36
2.36
2.35
2.34
2.34
2.33
2.32
2.32
2.31
2.30
2.30
2.28
1.99
1.98
1.98
1.97
1.84
1.83
1.82
1.82
1.76
1.75
1.75
1.66

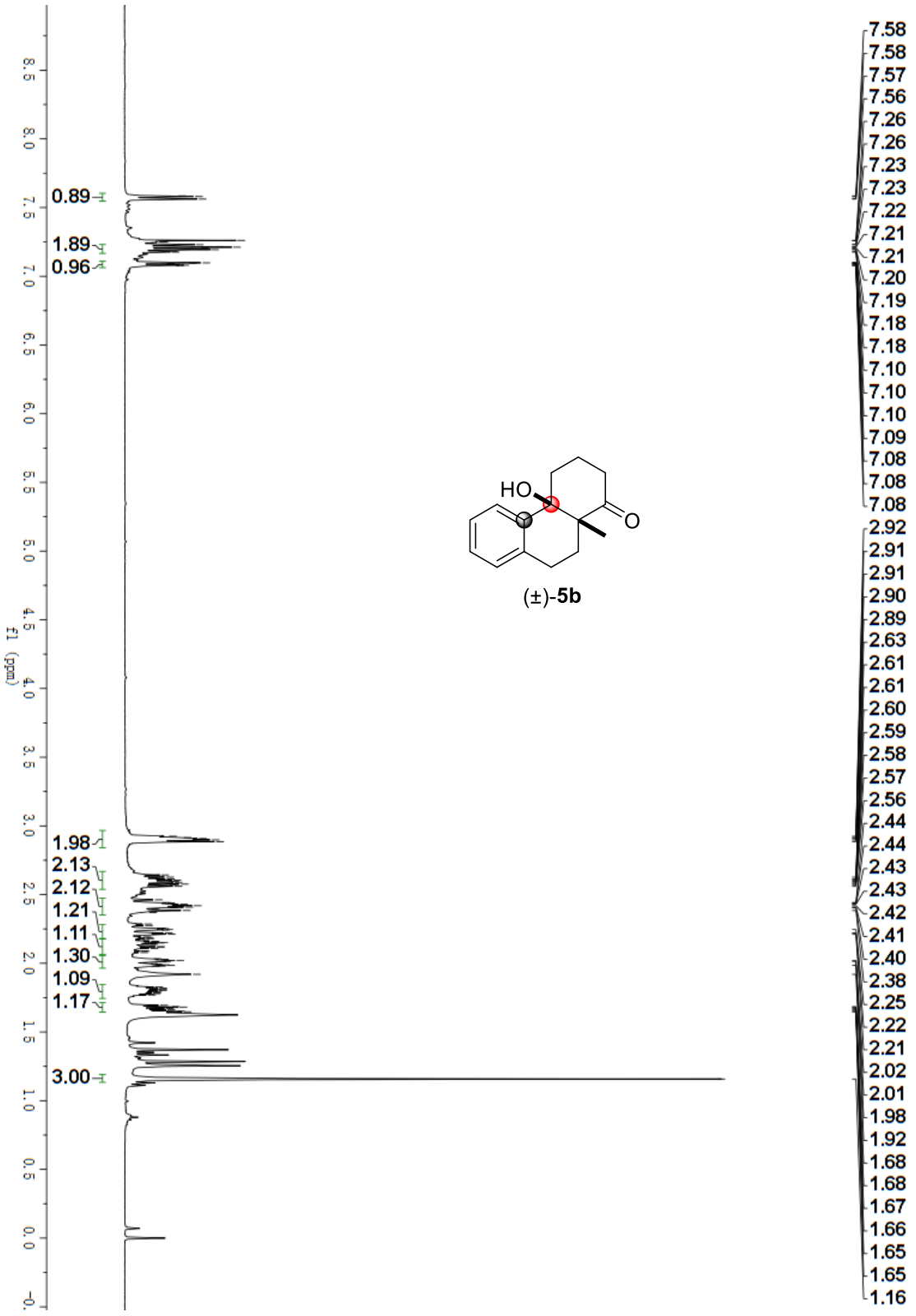
(±)-**3**

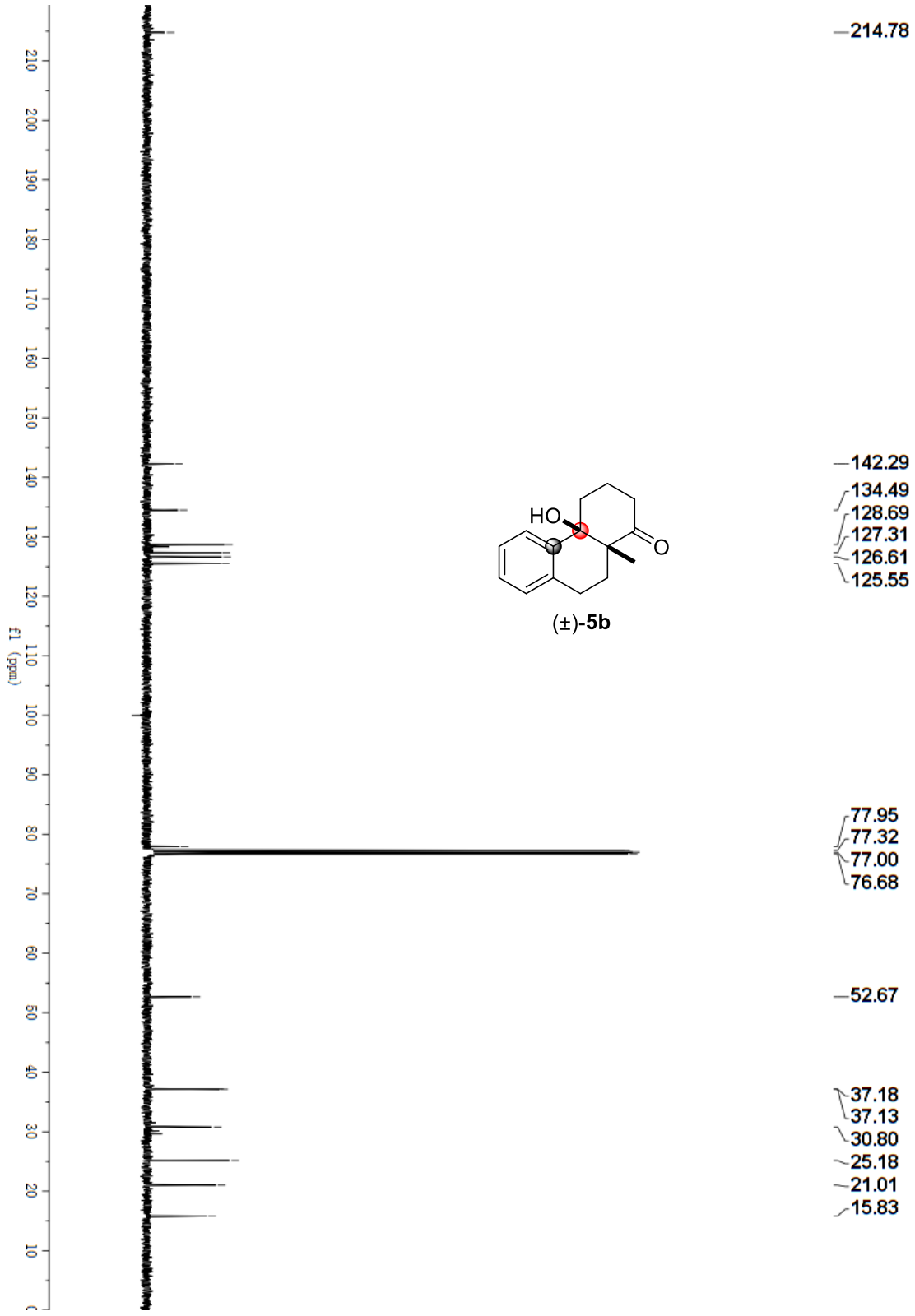

211.06
170.87
144.30
137.54
129.36
128.03
125.09
123.10
94.86
55.91
41.13
37.65
36.48
27.81
26.24
18.99
f1 (ppm)
O
O
O

(±)-3

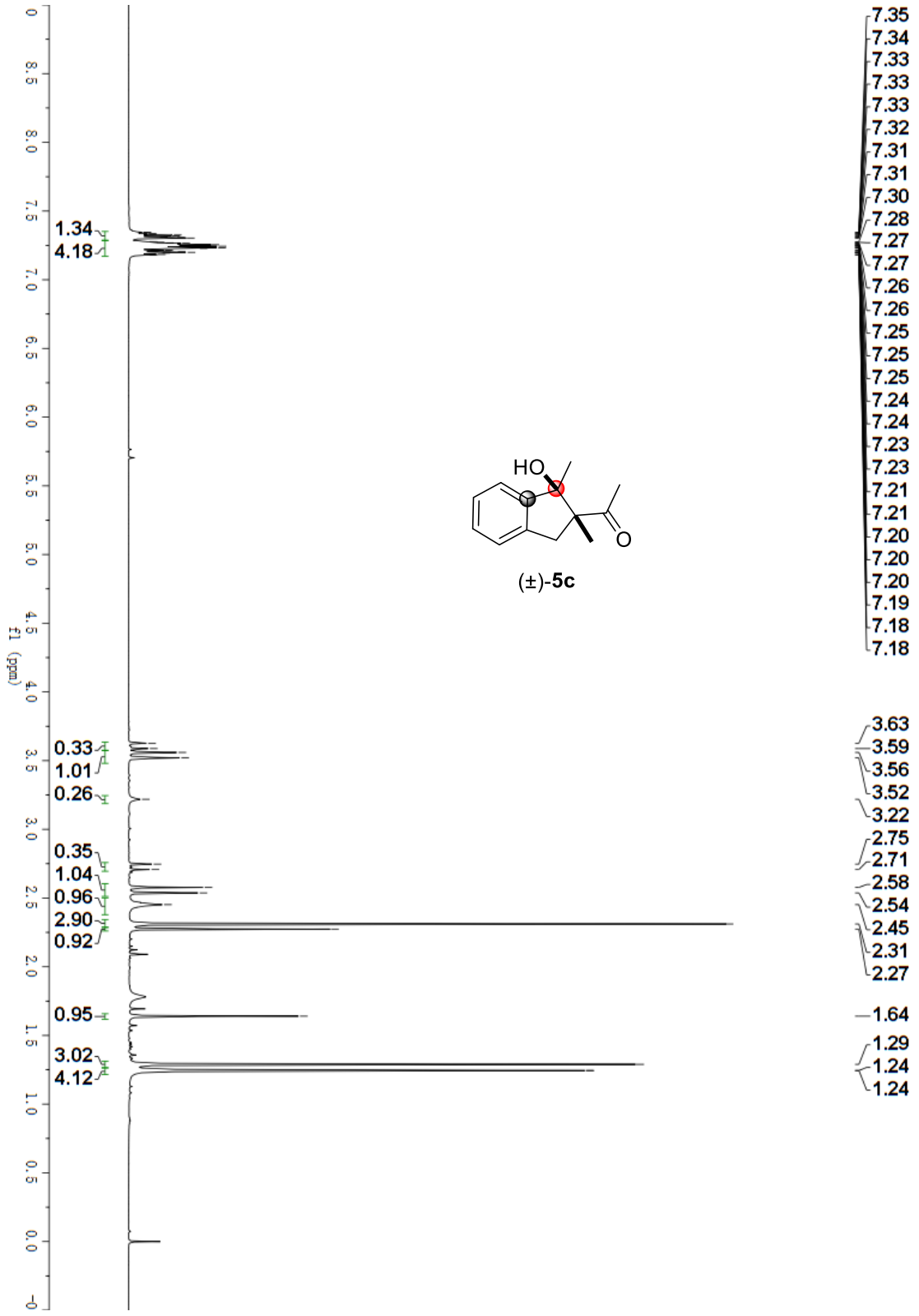

HO
O
(±)-5a
f1 (ppm)
0.97
2.07
0.97
1.00
1.02
2.04
1.07
1.96
3.05
7.47
7.47
7.46
7.46
7.45
7.29
7.29
7.28
7.28
7.27
7.26
7.18
7.17
7.17
7.16
3.23
3.18
2.88
2.84
2.58
2.57
2.57
2.55
2.55
2.52
2.50
2.49
2.47
2.45
2.45
2.33
2.30
2.30
2.29
2.28
2.27
2.27
1.96
1.94
1.93
1.92
1.91
1.91
1.89
1.89
1.61
1.20

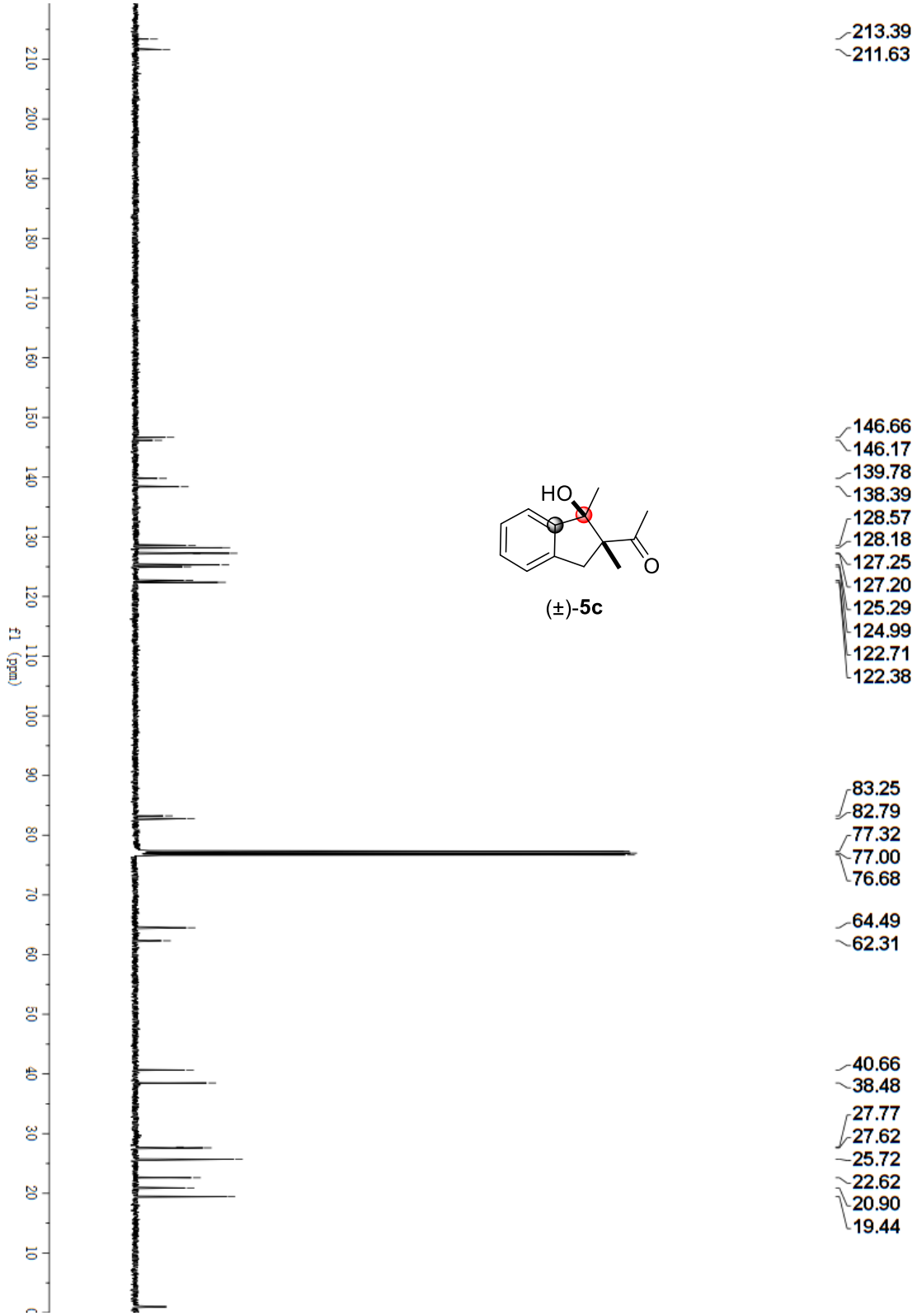

221.53
144.77
142.24
129.45
127.72
125.02
123.30
88.36
77.32
77.20
77.00
76.68
58.79
41.06
36.87
31.70
29.69
HO
O
(±)-5a
f1 (ppm)

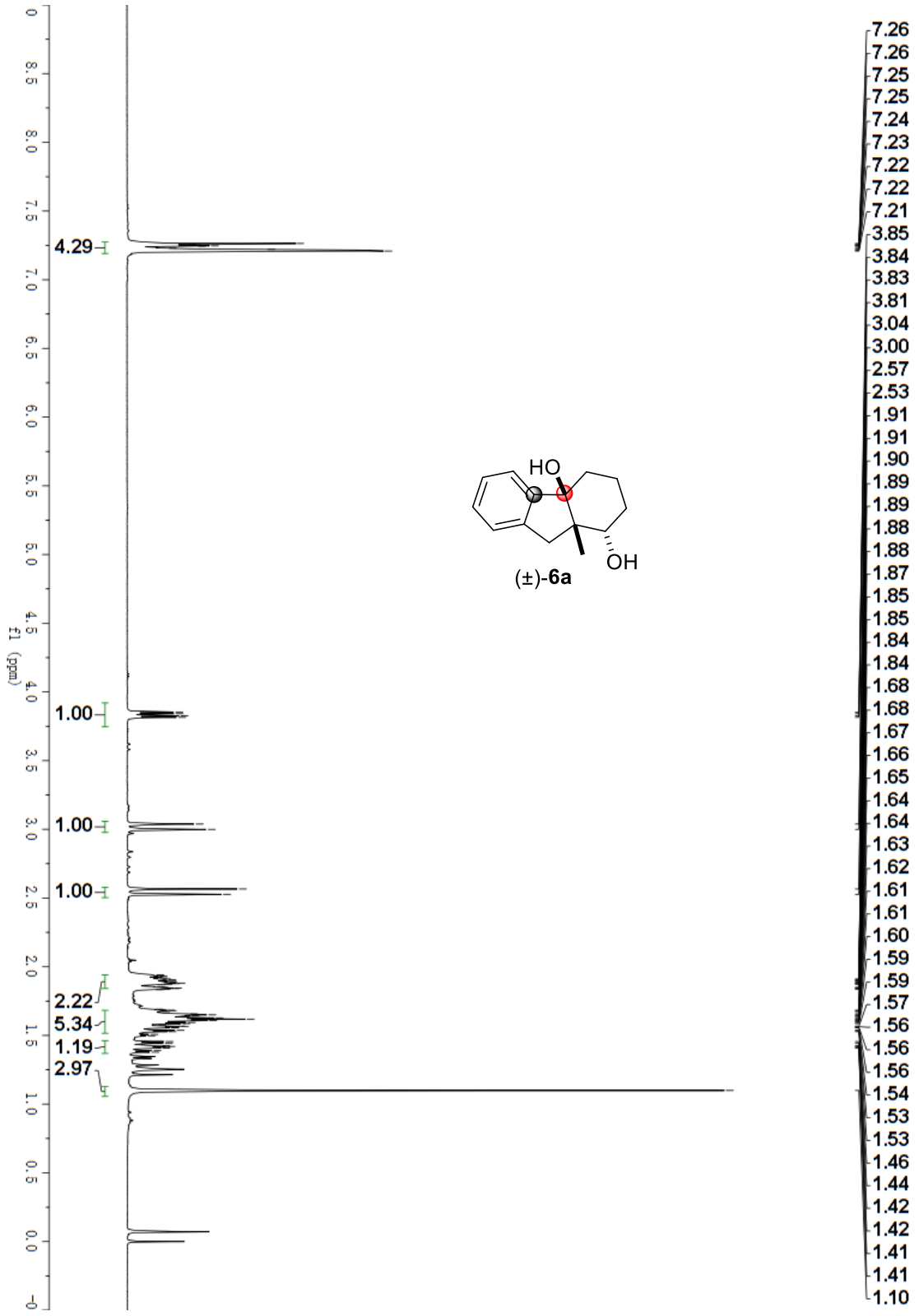

HO
O
(±)-5b
f1 (ppm)
0.89
1.89
0.96
1.98
2.13
2.12
1.21
1.11
1.30
1.09
1.17
3.00
7.58
7.58
7.57
7.56
7.26
7.26
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.18
7.10
7.10
7.10
7.09
7.08
7.08
7.08
2.92
2.91
2.91
2.90
2.89
2.63
2.61
2.61
2.60
2.59
2.58
2.57
2.56
2.44
2.44
2.43
2.43
2.42
2.41
2.40
2.38
2.25
2.22
2.21
2.02
2.01
1.98
1.92
1.68
1.68
1.67
1.66
1.65
1.65
1.16

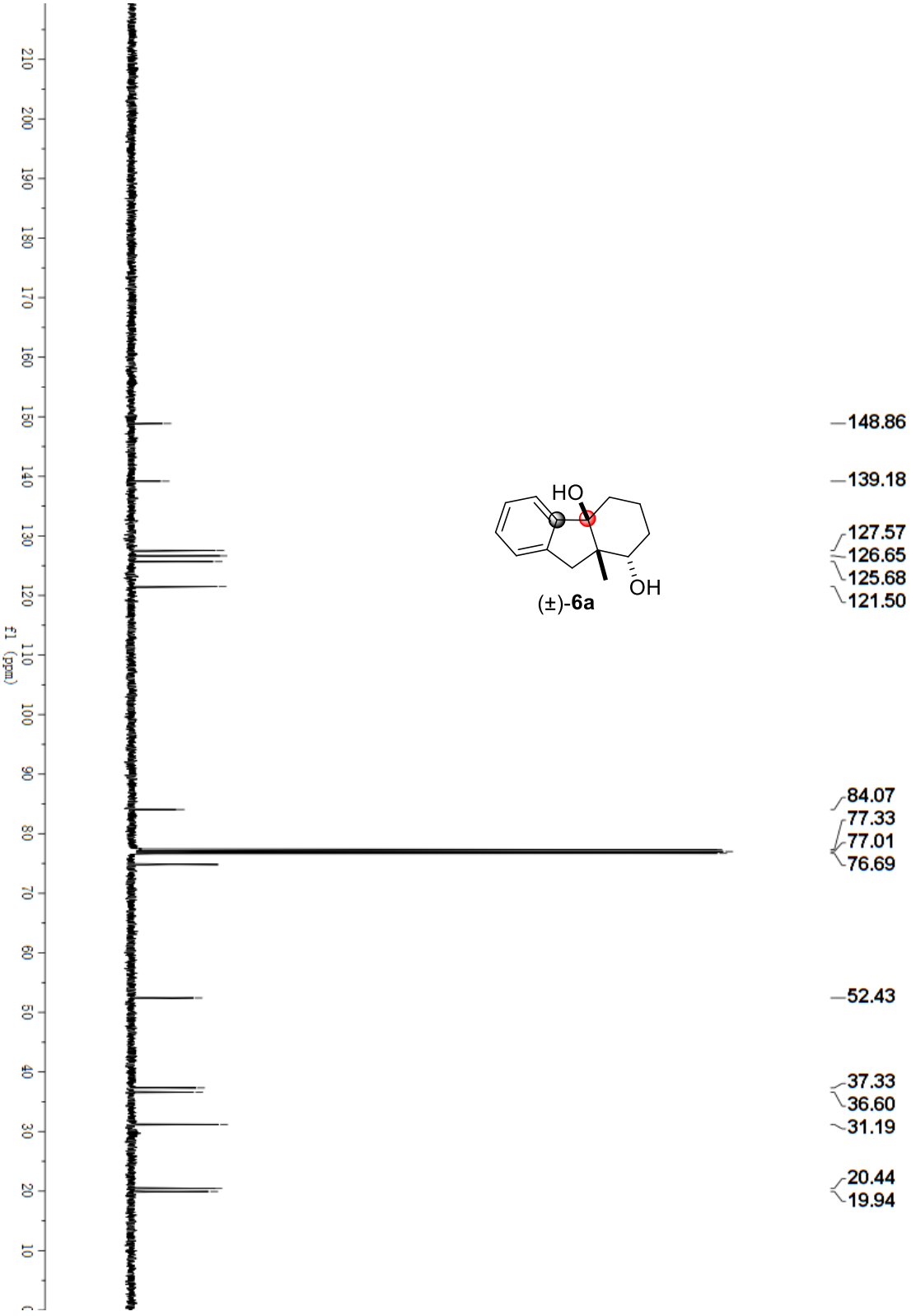

214.78
142.29
134.49
128.69
127.31
126.61
125.55
77.95
77.32
77.00
76.68
52.67
37.18
37.13
30.80
25.18
21.01
15.83
HO
O
f1 (ppm)

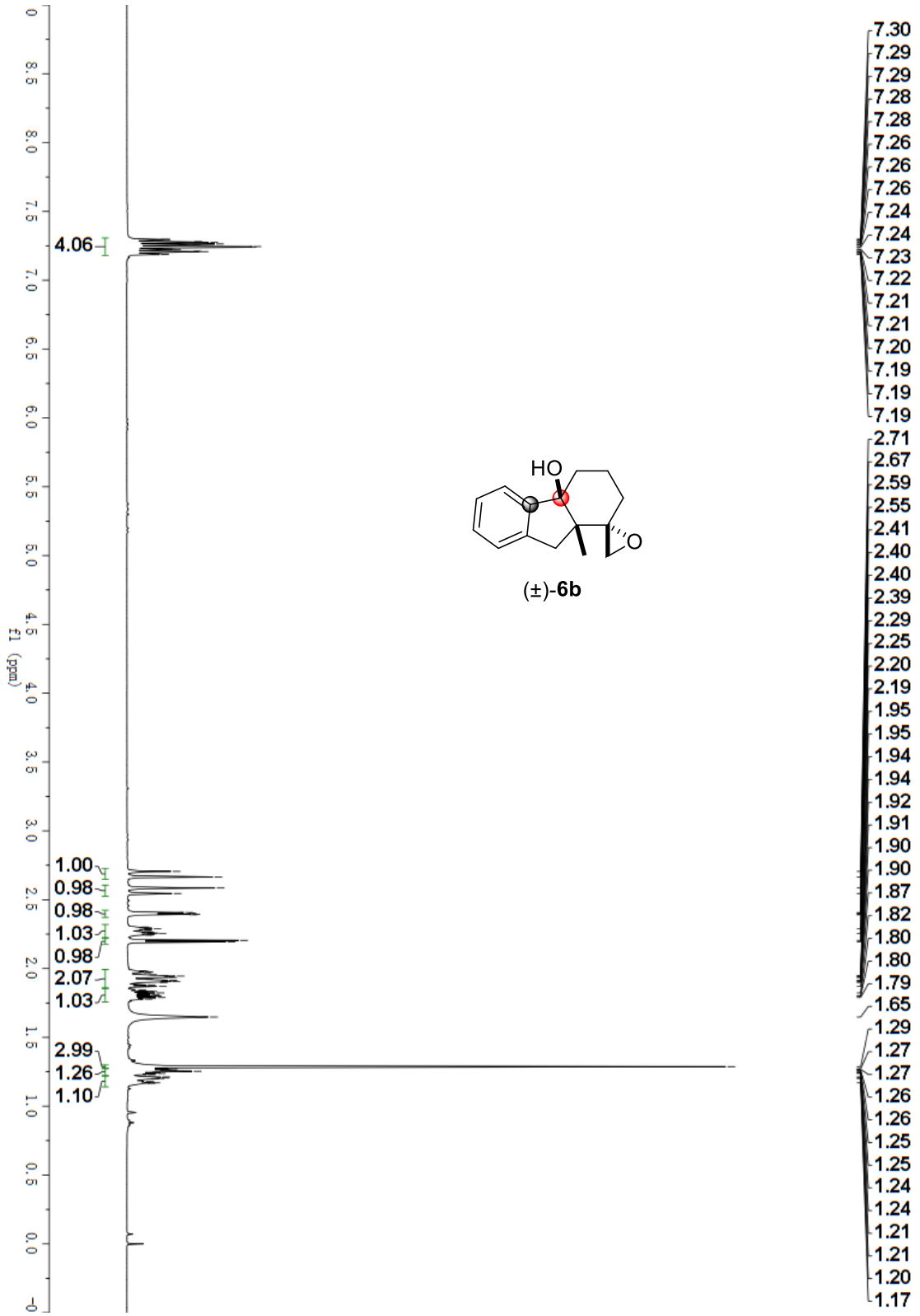
(±)-**5b**

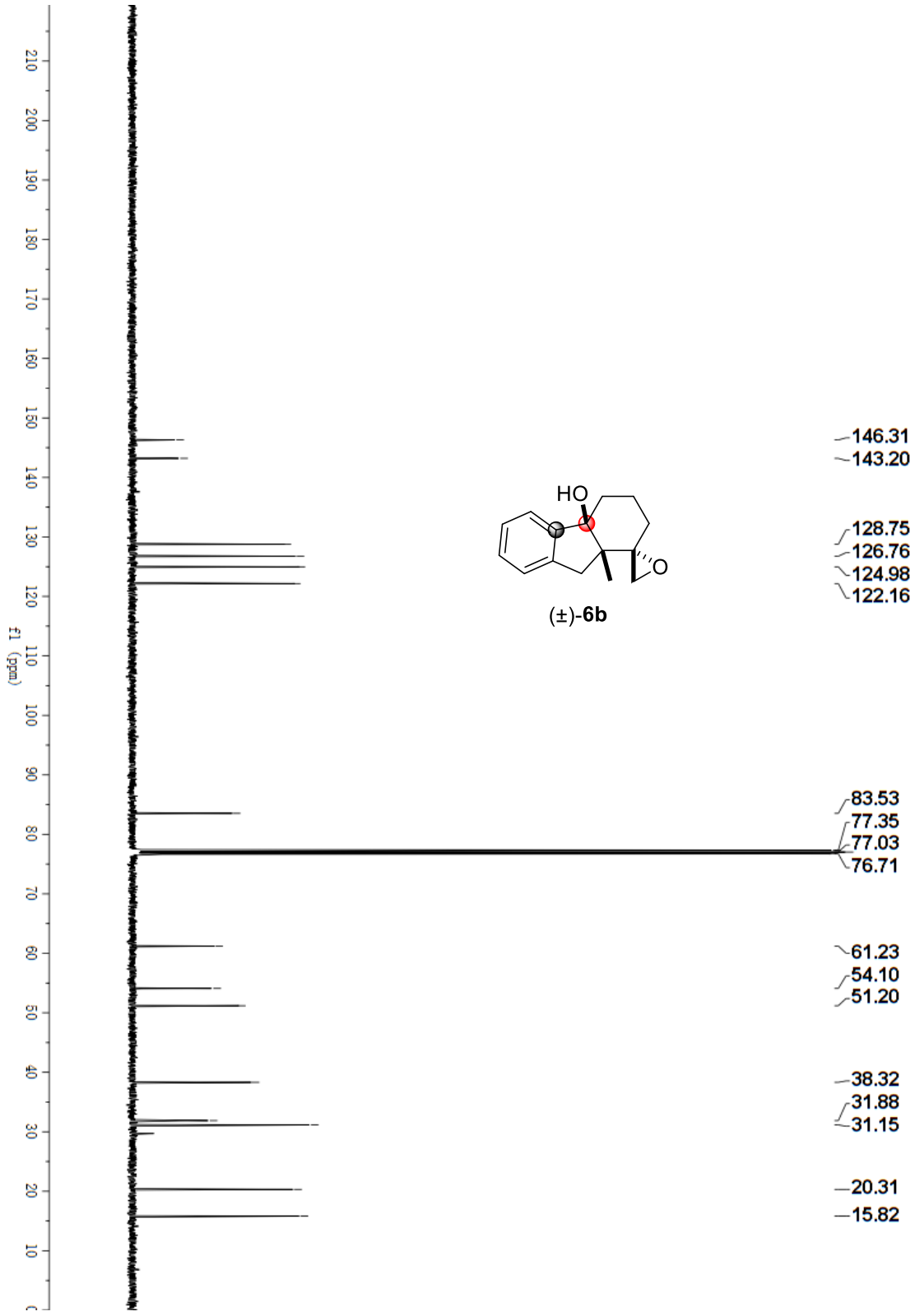

HO
O
(±)-5c
f1 (ppm)
1.34
4.18
0.33
1.01
0.26
0.35
1.04
0.96
2.90
0.92
0.95
3.02
4.12
7.35
7.34
7.33
7.33
7.33
7.32
7.31
7.31
7.30
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.23
7.23
7.21
7.21
7.20
7.20
7.20
7.19
7.18
7.18
3.63
3.59
3.56
3.52
3.22
2.75
2.71
2.58
2.54
2.45
2.31
2.27
1.64
1.29
1.24
1.24


213.39
211.63
146.66
146.17
139.78
138.39
128.57
128.18
127.25
127.20
125.29
124.99
122.71
122.38
83.25
82.79
77.32
77.00
76.68
64.49
62.31
40.66
38.48
27.77
27.62
25.72
22.62
20.90
19.44
HO
O
(±)-5c
f1 (ppm)

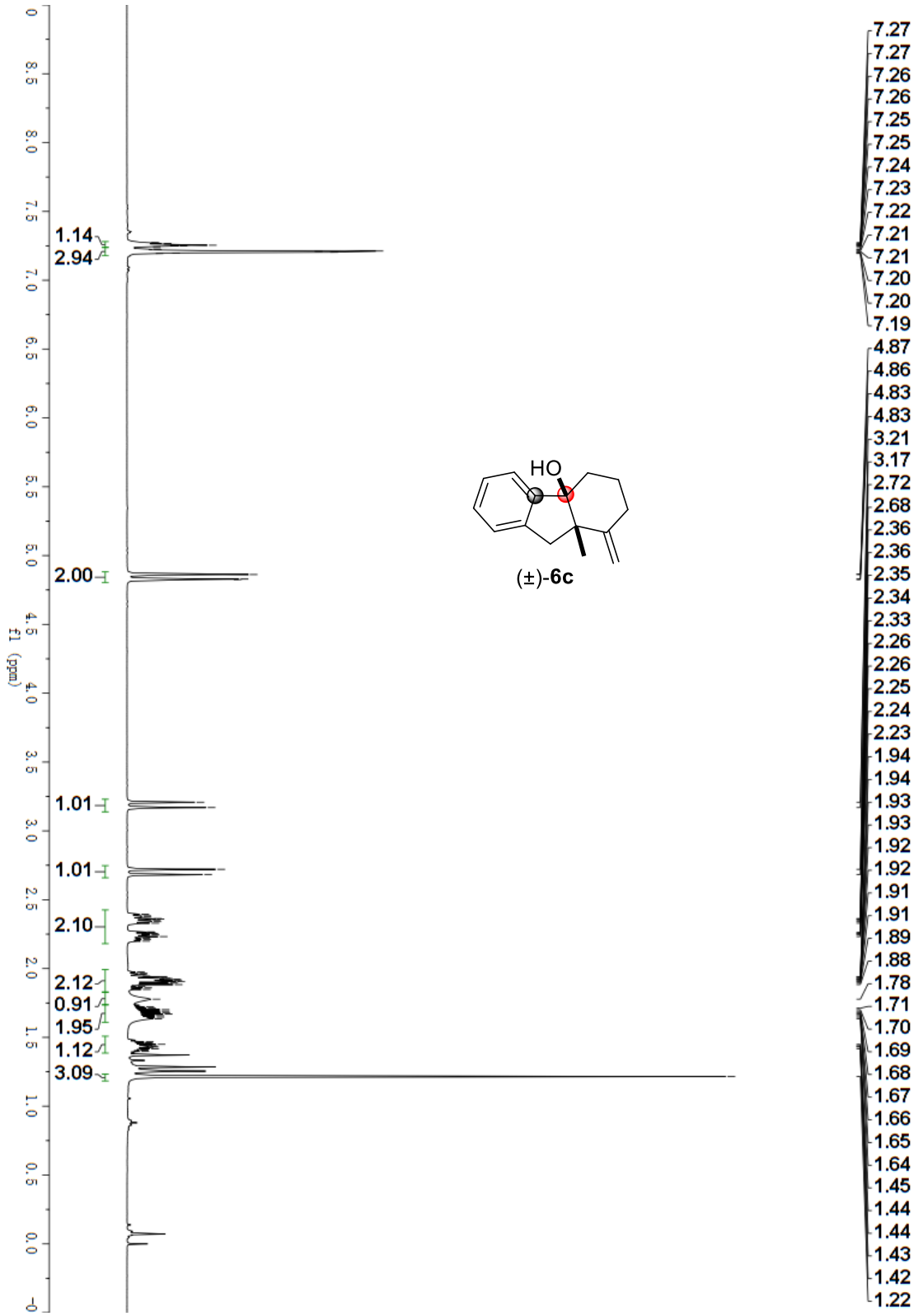

HO
OH
(±)-6a
4.29
1.00
1.00
1.00
2.22
5.34
1.19
2.97
f1 (ppm)
7.26
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.21
3.85
3.84
3.83
3.81
3.04
3.00
2.57
2.53
1.91
1.91
1.90
1.89
1.89
1.88
1.88
1.87
1.85
1.85
1.84
1.84
1.68
1.68
1.67
1.66
1.65
1.64
1.64
1.63
1.62
1.61
1.61
1.60
1.59
1.59
1.57
1.56
1.56
1.56
1.54
1.53
1.53
1.46
1.44
1.42
1.42
1.41
1.41
1.10

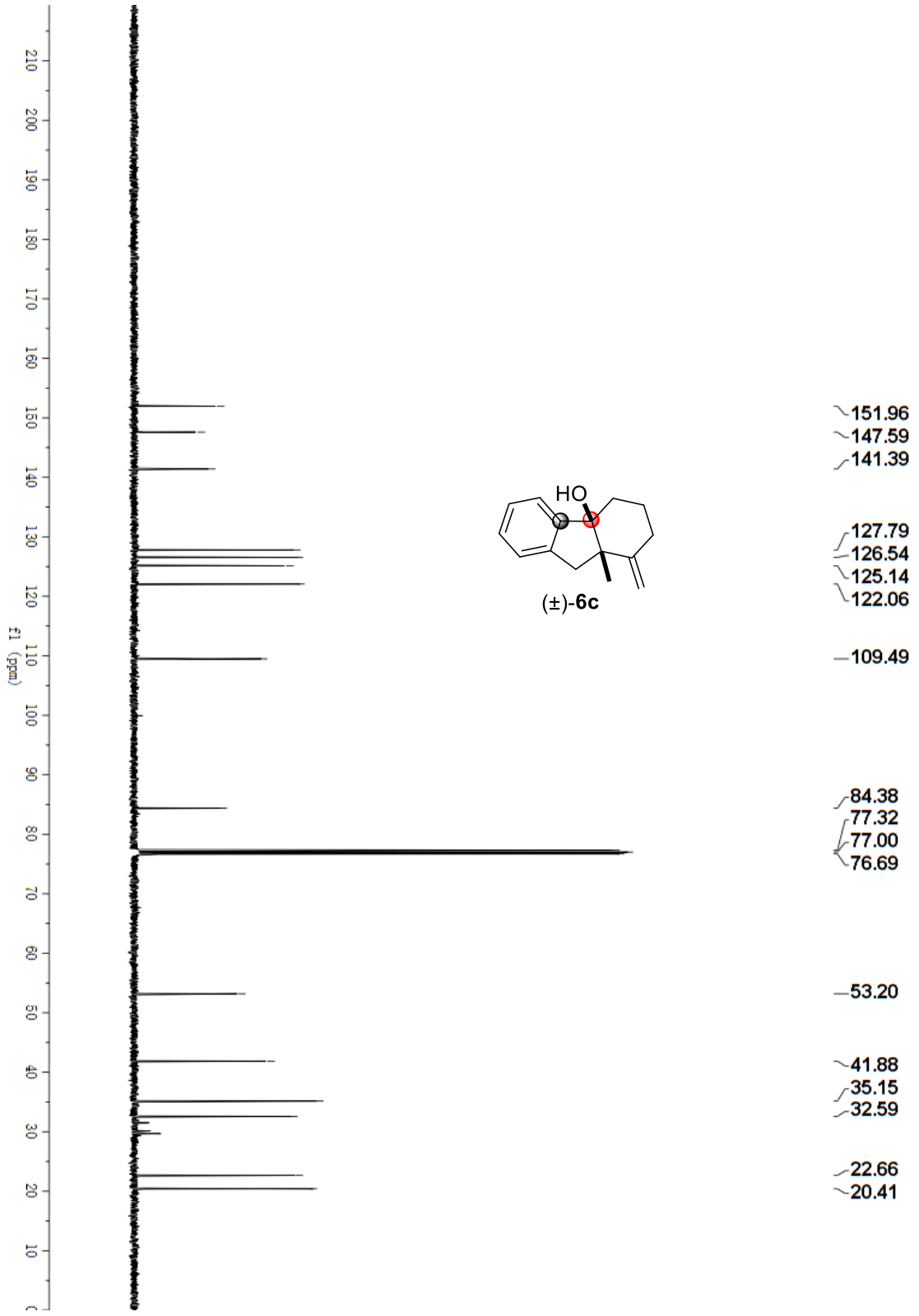

148.86
139.18
127.57
126.65
125.68
121.50
84.07
77.33
77.01
76.69
52.43
37.33
36.60
31.19
20.44
19.94
HO
OH
(±)-6a
f1 (ppm)

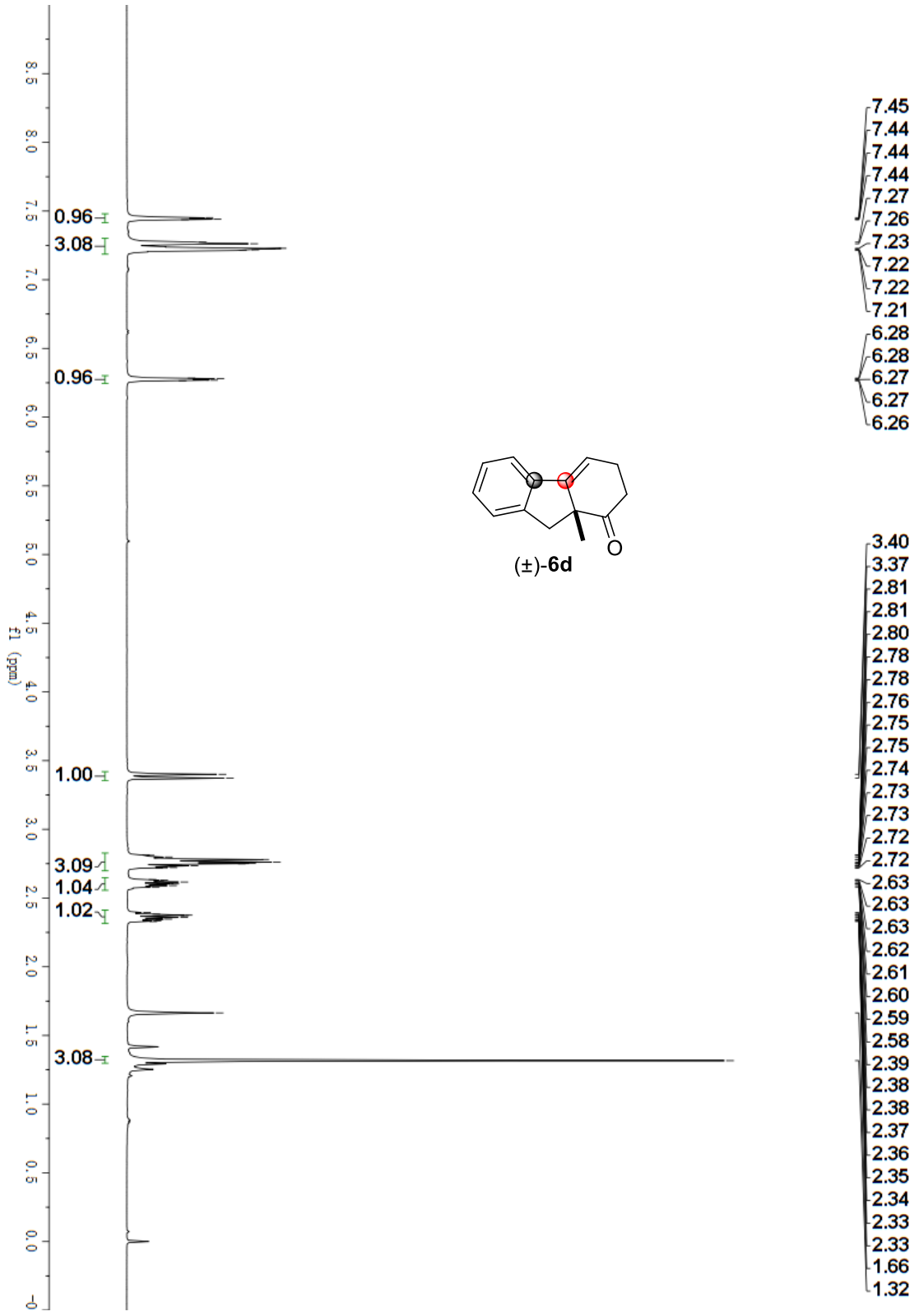

4.06
1.00
0.98
0.98
1.03
0.98
2.07
1.03
2.99
1.26
1.10
f1 (ppm)
HO
O
(±)-6b
7.30
7.29
7.29
7.28
7.28
7.26
7.26
7.26
7.24
7.24
7.23
7.22
7.21
7.21
7.20
7.19
7.19
7.19
2.71
2.67
2.59
2.55
2.41
2.40
2.40
2.39
2.29
2.25
2.20
2.19
1.95
1.95
1.94
1.94
1.92
1.91
1.90
1.90
1.87
1.82
1.80
1.80
1.79
1.65
1.29
1.27
1.27
1.26
1.26
1.25
1.25
1.24
1.24
1.21
1.21
1.20
1.17

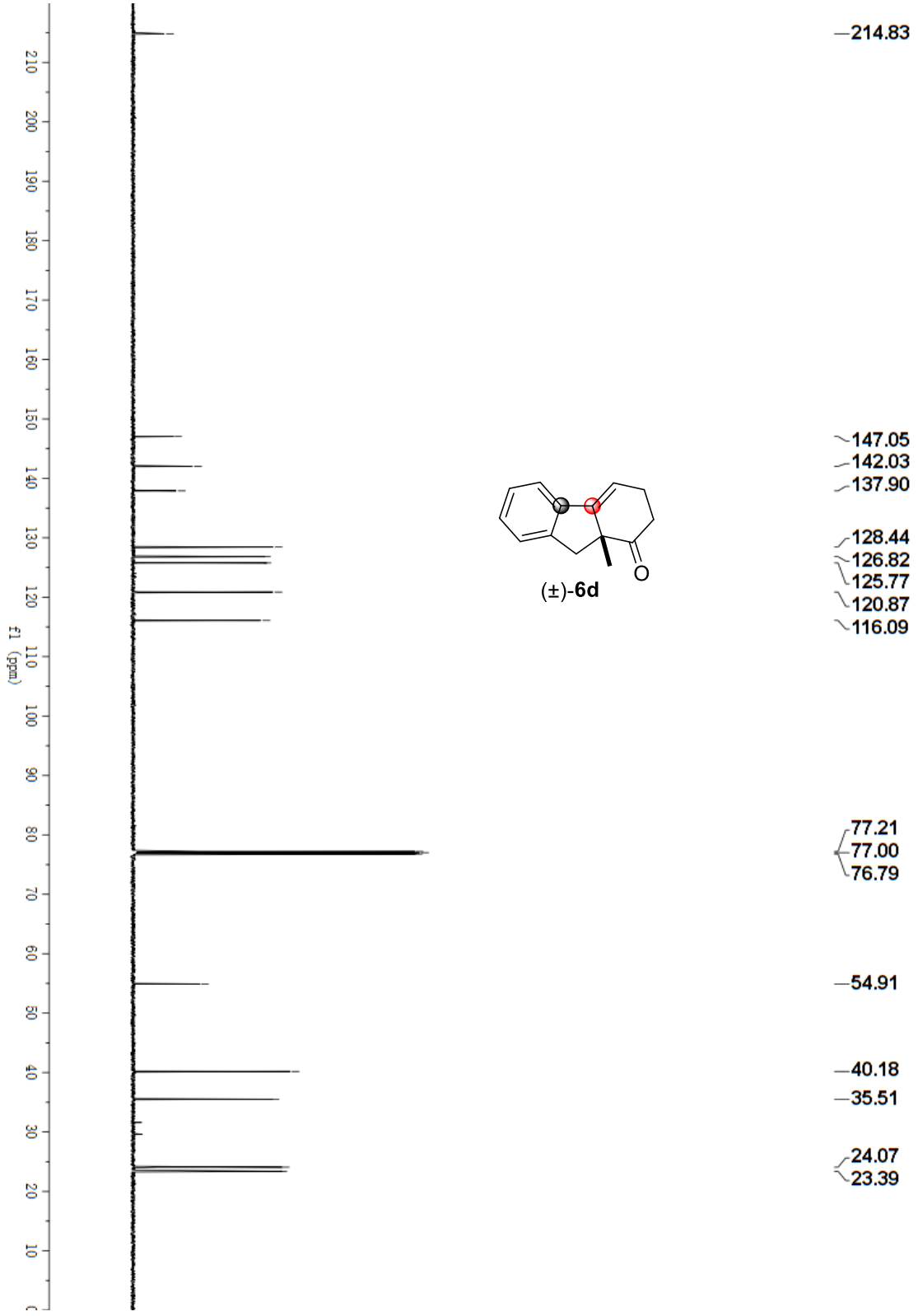

146.31
143.20
128.75
126.76
124.98
122.16
83.53
77.35
77.03
76.71
61.23
54.10
51.20
38.32
31.88
31.15
20.31
15.82
HO
O
f1 (ppm)

(±)-**6b**


HO
(±)-6c
1.14
2.94
2.00
1.01
1.01
2.10
2.12
0.91
1.95
1.12
3.09
f1 (ppm)
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.20
7.19
4.87
4.86
4.83
4.83
3.21
3.17
2.72
2.68
2.36
2.36
2.35
2.34
2.33
2.26
2.26
2.25
2.24
2.23
1.94
1.94
1.93
1.93
1.92
1.92
1.91
1.91
1.89
1.88
1.78
1.71
1.70
1.69
1.68
1.67
1.66
1.65
1.64
1.45
1.44
1.44
1.43
1.42
1.22


HO
(±)-6c
151.96
147.59
141.39
127.79
126.54
125.14
122.06
109.49
84.38
77.32
77.00
76.69
53.20
41.88
35.15
32.59
22.66
20.41
f1 (ppm)


0.96
3.08
0.96
1.00
3.09
1.04
1.02
3.08
f1 (ppm)
7.45
7.44
7.44
7.44
7.27
7.26
7.23
7.22
7.22
7.21
6.28
6.28
6.27
6.27
6.26
O
(±)-6d
3.40
3.37
2.81
2.81
2.80
2.78
2.78
2.76
2.75
2.75
2.74
2.73
2.73
2.72
2.72
2.63
2.63
2.63
2.62
2.61
2.60
2.59
2.58
2.39
2.38
2.38
2.37
2.36
2.35
2.34
2.33
2.33
1.66
1.32


214.83
147.05
142.03
137.90
128.44
126.82
125.77
120.87
116.09
77.21
77.00
76.79
54.91
40.18
35.51
24.07
23.39
O
(±)-6d
f1 (ppm)