Supporting Information

Carbene-organocatalyzed enantioselective [5+5] annulation of dienols and dienals towards tetrahydroisochromen-1-ones

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‡These authors contributed equally to this work.

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I. General information

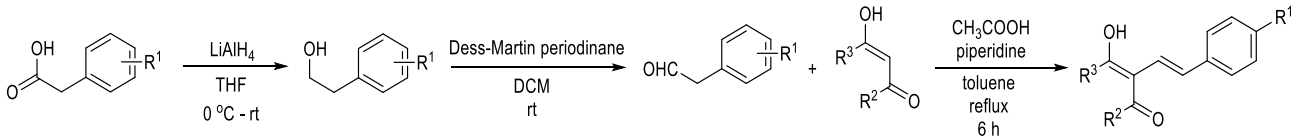
Commercial reagents were purchased from TCI, J&K, 3A Chemicals, Accela, Macklin, Bidepharm or Adamas and used without further purification. The solvents used in the experiments were all purchased anhydrous solvents and used directly. All reactions were carried out with oven-dried glassware. Analytical thin layer chromatography was performed on 0.20 mm silica gel HSGF-254 plates (Huanghai, China), and visualized under 254 nm UV light. Column chromatography was performed on 200-300 mesh silica gel (General-Reagent, China).

^{1}H, ^{19}F, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker Ascend 400MHz spectrometer and Bruker Ultrashield 300MHz at ambient temperature. Chemical shifts were recorded in parts per million (ppm, δ) relative to chloroform (for ^{1}H NMR, δ = 7.26 ppm, singlet; for ^{13}C NMR, δ = 77.16 ppm, triplet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets). All first-order splitting patterns were assigned based on the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br).

High resolution mass spectra of new compounds were recorded on Thermo scientific QExactive MS (ESI). Infrared (IR) spectra were recorded on PerkinElmer Frontier spectrometer and reported in wave numbers (cm^{-1}). The determination of enantiomeric excesses was performed via chiral stationary phases analysis using Supercritical Fluid Chromatography (SFC) by Waters Acquity UltraPerformance Convergence Chromatography (UPCC) (Chiral stationary phases column: Chiralpak OX-3, OD-3 column from Daicel Chiral Technologies and Trefoil CEL-1, CEL-2, AMY-1 column from Waters). Optical rotations were recorded on an Anton Paar MCP-500 polarimeter. Its X-ray diffraction data was collected on Rigakuoxford diffraction SuperNova using the CuKα radiation at 150 K or 100 K. Electronic circular dichroism (ECD) spectra were recorded on a Circular Dichroism Spectrometer J1700.

II. General procedure for the preparation of substrates

(1) enol substrates **1**.[1]

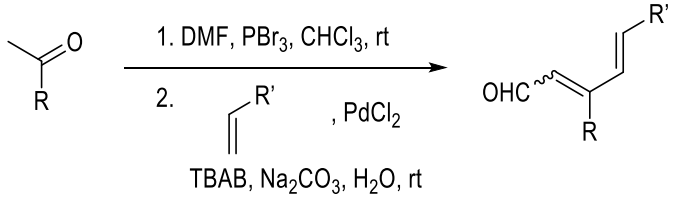


In a 50 mL Schlenk flask were placed substituted phenylacetic acid (5 mmol) and anhydrous THF (20 ml) under N_2 atmosphere. The solution was cooled down to 0 °C. $LiAlH_4$ (7.5 mmol) was added by portion and the mixture was stirred at 0 °C for 1.5 h. The mixture was quenched saturated aq. NH_4Cl, and the suspension was filtered through a celite pad. Then the filtrate was extracted with EtOAc (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Crude corresponding phenethyl alcohol was used to the next step without further purification.

To a solution of phenethyl alcohol in 20 ml CH_2Cl_2, Dess-Martin periodinane (5 mmol) was added. The mixture was stirred for 2 h at room temperature. After the reaction, the solution was diluted by H_2O and extracted with CH_2Cl_2 (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography with PE/ethyl acetate to give the corresponding substituted phenylacetaldehyde.

Acetic acid (190 μl, 3.3 mmol) and piperidine (54 μl, 0.55 mmol) were added to solution of ethyl acetoacetate (704 ml, 5.5 mmol) or other substituted diketones in toluene (20 ml) in two-neck round bottom flask. Equipped with DeaneStark apparatus and reflux condenser, corresponding phenylacetaldehyde (5 mmol) was added and the mixture was refluxed for 6 h until no more aldehyde was observed by TLC analysis. After completion of the reaction, the reaction mixture was diluted with by H_2O and extracted with ethyl acetate (30 ml×3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography with PE/ethyl acetate to give the corresponding product **1** as yellow oil or solids.

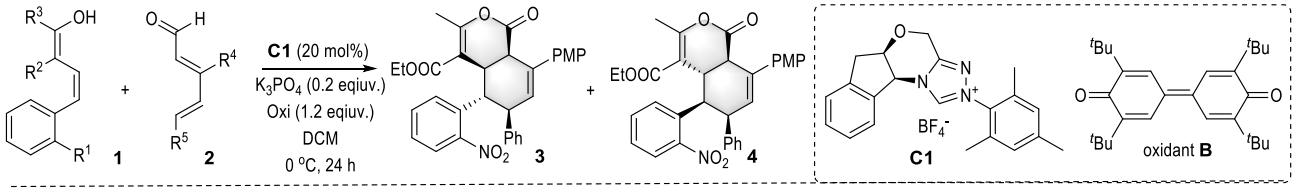
(2) unsaturated enals **2**.[2]



DMF (2 ml, 26 mmol) in 25 mL dry $CHCl_3$ was added PBr_3 (2.2 ml, 23 mmol) dropwise at 0 °C, and a white solid precipitated during the addition process. The suspension was stirred at rt for a further 30 min, and acetophenone (10 mmol) in 5 mL dry $CHCl_3$ was added dropwise at 0 °C. The mixture was allowed to warm to rt and stirred for about 8 h. After complete consumption of acetophenone determined by TLC, the mixture was poured into ice water, and $NaHCO_3$ was added to neutralize to pH ≈ 6. After extraction with CH_2Cl_2, the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced

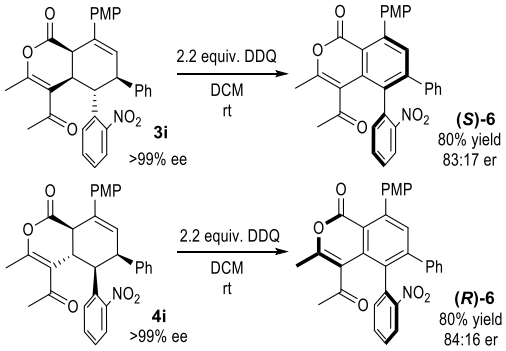
pressure and afford the crude product of β-bromo-enal. To the β-bromo-enal was added alkene (40 mmol), $PdCl_2$ (177 mg, 1 mmol), $^nBu_4NBr$ (3.2 g, 10 mmol), Na_2CO_3 (4.2 g, 40 mmol) and H_2O (50 ml). The mixture was stirred for 3 h, and then quenched with saturated NH_4Cl (aq.), extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by silica gel column chromatography to afford the corresponding α, β, γ, δ-diunsaturated enal **2**.

III. General procedure for the cycloaddition reactions of penta-substituted cyclohexene

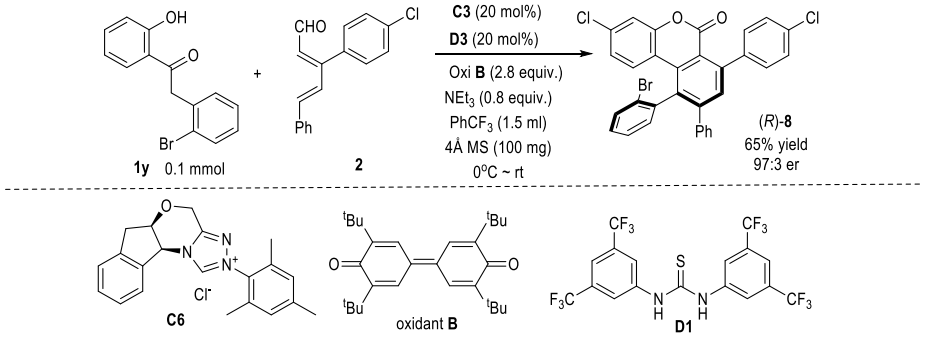


A solution of enol **1** (0.24 mmol), enal **2** (0.2 mmol), **C1** (16.4 mg, 20 mol%), K_3PO_4 (8.4 mg, 20 mol%) and oxidant **B** (82 mg, 0.24 mmol) in 6 mL DCM was stirred at 0 °C for 24 hours. The mixture was concentrated under reduced pressure and purified by silica gel column chromatography to afford the corresponding product **3** and **4**.

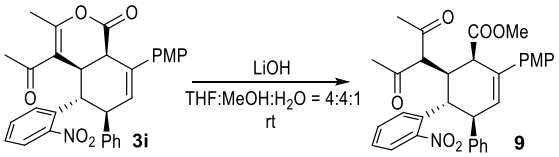
IV. Experimental details for product transformations



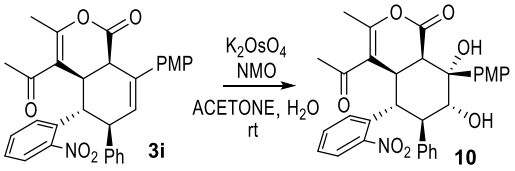
To a solution of **3i**/**4i** (50.9 mg, 0.1 mmol) in dichloromethane (2 ml) was added 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 50 mg, 0.22 mmol). The mixture was stirred at rt for 2 h before being quenched with aqueous saturated $NaHCO_3$. Products were extracted with EtOAc (10 ml×3), and extracts were dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate, by increasing the gradient from 10:1 to 3:1 v/v) to afford 38 mg (80% yield) of **6** as a yellow solid.[3]



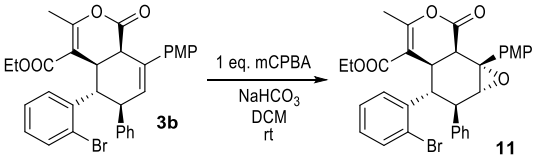
A solution of enol **1y** (0.1 mmol), enal **2** (0.2 mmol), **C3** (7.3 mg, 0.02mmol), additive **D1** (10 mg, 0.02 mmol), NEt_3 (11 μl, 0.08 mmol), oxidant B (123 mg, 0.3 mmol) and 100 mg 4Å MS in 1.5 mL $PhCF_3$ was stirred at 0 °C and slowly warm (about 3 h) to rt for 24-72 hours. The mixture was concentrated under reduced pressure and purified by silica gel column chromatography to afford the corresponding product (*R*)-**8.**



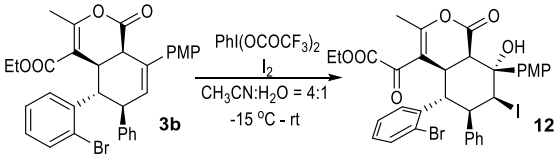
The lactone compound **3i** (0.1 mmol, 50.9mg) and LiOH monohydrate (24 mg, 10 equiv.) were charged to a 25 ml flask. To this mixture was then added MeOH (4 ml), THF (2 mL), and H_2O (1 ml). The reaction was then stirred for 2 h at room temperature and followed the course of the reaction by TLC until completion. The MeOH and THF were then removed in vacuo, and the resulting residue was diluted with H_2O (15 ml), ice, and EtOAc (20 ml). After acidification with 1M HCl, the solution was extracted with EtOAc for three times. The combined organic extract was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography to afford **9** as a white solid (32 mg, 60% yield).[4]



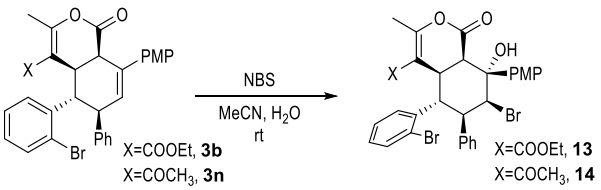
A suspension of **3i** (50.9 mg, 0.1 mmol), potassium osmate(VI) dihydrate (6 mg, 20 mmol) and N-methylmorpholine N-oxide (23 mg, 0.2 mmol) in acetone (0.8 ml) and water (0.2 ml) was vigorously stirred for 24 h at room temperature. The reaction mixture was quenched by the dropwise addition of sat. sodium sulfite (0.5 ml) and stirring continued for 5 mins before the black suspension was extracted with EtOAc (5 ml×3). The combined organic extracts were washed with H_2O and brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography to afford **10** as a white solid (42 mg, 78% yield). [5]



A solution of **3b** (57.2 mg, 0.1 mmol) in DCM (2 ml) was stirred at room temperature and Na_2CO_3 (10% w/v aq., 0.9 mL, 0.1 mmol) added in one portion. mCPBA (77% w/w, 23 mg, 0.1 mmol) was then added cautiously. Vigorous stirring was continued for 24 h and the reaction mixture subsequently diluted with DCM (10 ml). The aqueous and organic phases were separated and the organic layer washed with 2 ml sat. sodium thiosulfate, H_2O and brine before being dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by **11** as a white solid (35 mg, 60% yield).[5]



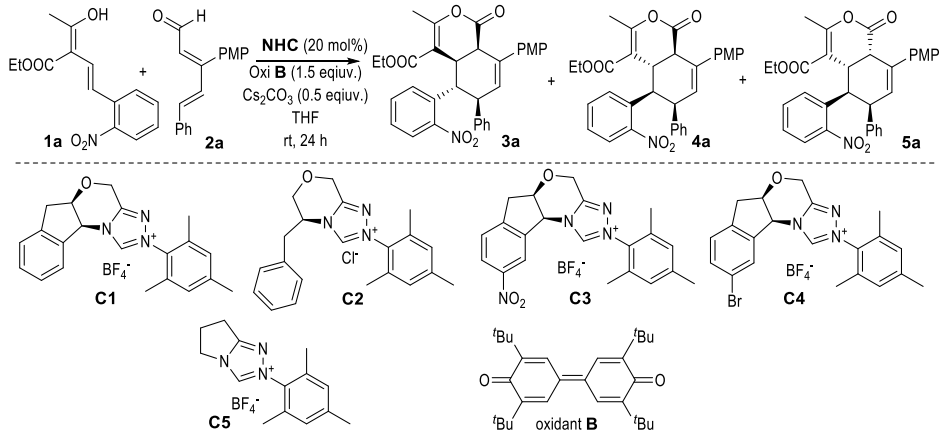
BTI (1.0 equiv.) was added at −15°C to a solution of **3b** (57.2 mg, 0.1 mmol) and I_2 (0.6 equiv.) in a 4:1 mixture of CH_3CN and H_2O and the vessel was allowed to reach room temperature. The red–brown colour of the solution disappears in a few minutes, and continually stirred for 2 h at room temperature. The reaction mixture was quenched by the dropwise addition of sat. sodium sulfite (0.5 ml) and stirring continued for 5 mins and then extracted with EtOAc (5 ml×3). The combined organic extracts were washed with H_2O and brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography to afford **12** as a white solid (65 mg, 88% yield). [6]



A solution of **3b**/**3n** (0.1 mmol), N-bromosuccinimide (0.1 mmol, 1 equiv), H_2O (5 mmol, 50 equiv) in MeCN (2 ml) was stirred at room temperature for 12 h and then extracted with EtOAc (5 ml×3). The combined organic extracts were washed with H_2O and brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified silica gel column chromatography to afford **13** as a yellow solid (38 mg, 57% yield) or **14** as a yellow solid (54 mg, 86% yield). [7]

V. Details of the Optimization of Reaction Conditions

Table S1. Screening of catalysts. [a][b][c]

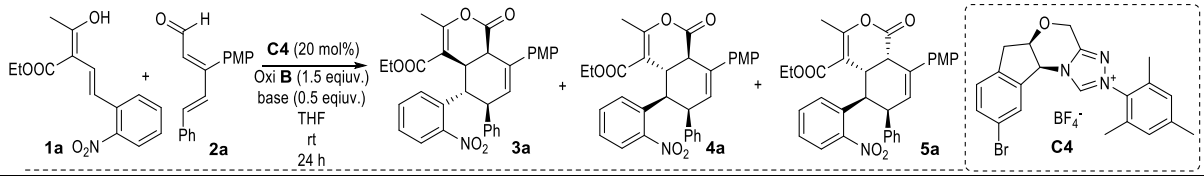


entry	NHC catalyst	yield **3a**/%[b]	ee **3a**[c]	yield **4a**/%[b]	ee **4a**[c]	yield **5a**/%[b]	ee **5a**[c]
1	**C5**	74	-	n.d.	-	15	-
2	**C1**	54	17	n.d.	-	27	78
3	**C2**	46	-3	n.d.	-	31	50
4	**C3**	57	5	n.d.	-	29	80
5	**C4**	**54**	**26**	**n.d.**	**-**	**29**	**80**

[a] All reactions were performed by using **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (20 mol%), base (50 mol%), oxidant **B** (0.15 mmol) and solvent (2 mL) at rt for 24 h. [b] Isolated yield. [c] Determined by chiral-phase stationary supercritical fluid chromatography (SFC).

Preliminary screening gave product **5a** with high enantioselectivity and product **3a** with near racemic.

Table S2. Screening of solvents.

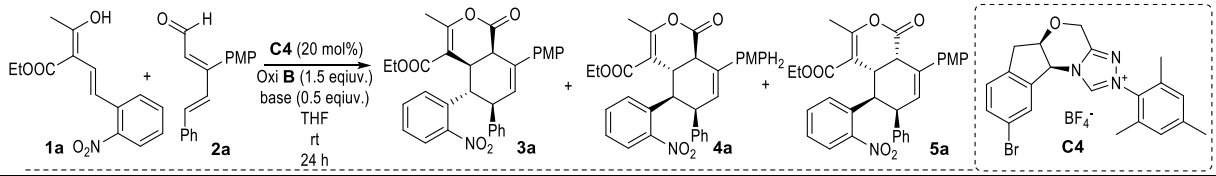


entry	base	yield **3a**/%[b]	ee **3a**[c]	yield **4a**/%[b]	ee **4a**[c]	yield **5a**/%[b]	ee **5a**[c]
1	**Cs_2CO_3**	**54**	**26**	**n.d.**	**-**	**29**	**80**
2	CsF	<5	-	n.d.	-	<5	
3	CH_3COOCs	64	-13	n.d.	-	23	79
4	DBU	55	7	n.d.	-	17	79
5	DIPEA	<5	-	n.d.	-	<5	
6	NEt_3	<5	-	n.d.	-	<5	
7	DMAP	36	2	n.d.	-	18	76
8	DABCO	47	-9	n.d.	-	15	71
9	LiOH	<5	-	n.d.	-	<5	
10	$NaHCO_3$	<5	-	n.d.	-	<5	
11	K_2CO_3	55	-10	n.d.	-	16	77
12	K_3PO_4	50	-11	n.d.	-	25	78
13	^{t}BuOK	60	-7	n.d.	-	21	77

[a] All reactions were performed by using **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (20 mol%), base (50 mol%), oxidant **B** (0.15 mmol) and solvent (2 mL) at rt for 24 h. [b] Isolated yield. [c] Determined by chiral-phase stationary supercritical fluid chromatography (SFC).

Base screening shows that inorganic strong bases are better than organic bases in yields and have similar stereoselectivity.

Table S3. Screening of solvent.

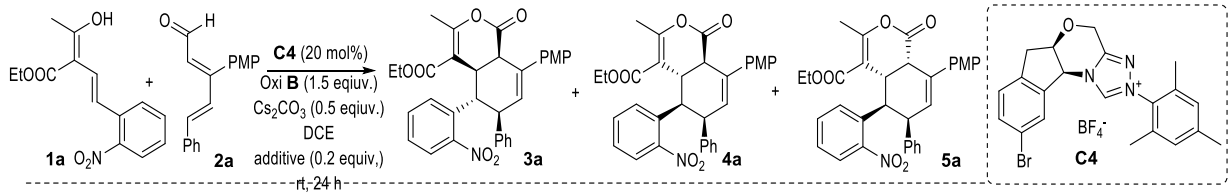


entry	solvent	yield **3a**/%[b]	ee **3a**[c]	yield **4a**/%[b]	ee **4a**[c]	yield **5a**/%[b]	ee **5a**[c]
1	THF	54	26	n.d.	-	29	80
2	Dioxane	42	16	n.d.	-	18	80
3	Et_2O	30	-30	n.d.	-	24	80
4	CH_3CN	46	42	n.d.	-	17	69
5	EA	59	6	n.d.	-	30	80
6	Toluene	35	-4	n.d.	-	15	72
7	$PhCF_3$	35	45	n.d.	-	16	82
8	DMF	33	16	n.d.	-	14	59
9	^{t}BuOH	30	-25	n.d.	-	21	72
10	Acetone	59	26	n.d.	-	15	79
11	**DCM**	**64**	**56**	**n.d.**	**-**	**28**	**81**
12	**DCE**	**62**	**57**	**n.d.**	**-**	**28**	**80**
13	$CHCl_3$	46	26	n.d.	-	26	71

[a] All reactions were performed by using **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (20 mol%), base (80 mol%), oxidant **B** (0.15 mmol) and solvent (2 mL) at rt for 24 h. [b] Isolated yield. [c] Determined by chiral-phase stationary supercritical fluid chromatography (SFC).

Solvent screening shows that chlorinated solvent (DCM/DCE) could improve the enantioselectivity of product **3a**.

Table S4. Screening of additives.

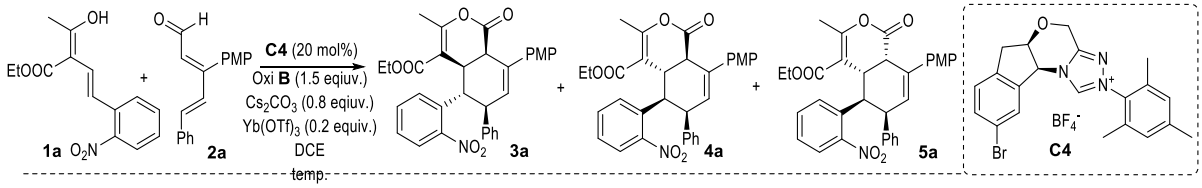


entry	additive	yield **3a**/%[b]	ee **3a**[c]	yield **4a**/%[b]	ee **4a**[c]	yield **5a**/%[b]	ee **5a**[c]
1	None	62	57	n.d.	-	26	71
2[d]	$Sc(OTf)_3$	50	78	<10	98	<10	37
3	^{t}BuOH	50	40	n.d.	-	29	80
4	1,3-bis(3,5-bis(trifluoromethyl)phenyl)thiourea	50	74	n.d.	-	11	77
5[d]	**$Yb(OTf)_3$**	**51**	**79**	**12**	**99**	**n.d.**	**-**
6	LiCl	45	66	n.d.	-	19	82

[a] All reactions were performed by using **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (20 mol%), base (50 mol%), additive (20 mol%), oxidant **B** (0.15 mmol) and solvent (2 mL) at rt for 24 h. [b] Isolated yield. [c] Determined by chiral-phase stationary supercritical fluid chromatography (SFC). [d] 0.8 equiv. base.

Additive screening shows that Lewis acid could give another product **4a** instead of **5a** and improve the enantioselectivity of **3a**. When use Lewis acid as additive, the use of 0.5 equiv. of base prevents the reaction from proceeding. It is necessary to increase the amount of base to 0.8 equiv. to react normally.

Table S5. Screening of temperature and time.

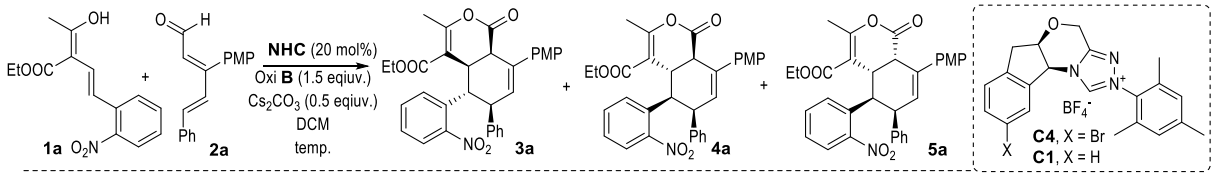


entry	temperature/°C	time/h	yield **3a**/%[b]	ee **3a**[c]	yield **4a**/%[b]	ee **4a**[c]	yield **5a**/%[b]	ee **5a**[c]
1	rt	16	19	91	<10	99	n.d.	-
2	0	8	59	94	9	30	20	99
3	45	4	65	61	<10	66	<10	99
4	60	4	61	54	n.d.	-	<10	70
5	80	4	61	56	n.d.	-	<10	63
6[d]	0	9	65	90	20	99	n.d.	-
7[e]	**0**	**6**	**52**	**93**	**17**	**99**	**n.d.**	**-**
8[f]	0	3	39	92	<10	99	n.d.	-

[a] All reactions were performed by using **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (20 mol%), base (80 mol%), additive (20 mol%), oxidant **B** (0.15 mmol) and DCE (2 mL). [b] Isolated yield. [c] Determined by chiral-phase stationary supercritical fluid chromatography (SFC). [d] 3 ml DCE. [e] 5 ml DCE. [f] 10 ml DCE.

Lower the temperature of reduce the reaction time could obtain product **4a** instead of **5a** and improve the enantioselectivity of **3a**, which means **4a** is an intermediate product.

Table S6. Screening of the amount of base.

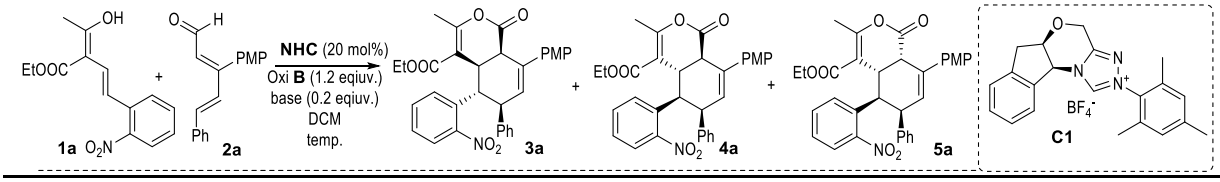


entry	**NHC**	temperature/°C	time/h	yield **3a**/%[b]	ee **3a**[c]	yield **4a**/%[b]	ee **4a**[c]	yield **5a**/%[b]	ee **5a**[c]
1	**C4**	rt	5	21	76	<10	99	<5	40
2	**C4**	0	9	21	91	<10	99	<5	20
3	**C4**	0	12	28	90	11	99	<5	26
4	**C4**	-10	10	24	91	8	99	<5	30
5	**C1**	-10	10	49	96	12	99	<5	51
6[d]	**C1**	**-20**	**24**	**49**	**99**	**15**	**99**	**<5**	**14**
7	**C1**	-20	24	51	96	9	99	<5	-14
8[e]	**C1**	-20	24	59	95	11	99	<5	8
9[f]	**C1**	-20	24	53	96	10	99	10	76
10[g]	**C1**	-20	24	36	90	n.d.	-	7	80

[a] All reactions were performed by using **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (20 mol%), base (50 mol%), oxidant **B** (0.15 mmol) and DCM (3 mL). [b] Isolated yield. [c] Determined by chiral-phase stationary supercritical fluid chromatography (SFC). [d] 0.2 equiv. base. [e] 0.8 equiv. base. [f] 1 equiv. base. [g] 2 equiv. base.

Under low temperature conditions, catalyst **C1** could give higher yields than **C4** with similar stereoselectivity control. Even though under -20 °C, the increase of the amount of base reduced the stereoselectivity of product **3a** and transforms **4a** to **5a**.

Table S7. Adjust the dosage ratio of substrates. [a][b][c]



entry	base	temperature/°C	time/h	yield **3a**/%[b]	ee **3a**[c]	yield **4a**/%[b]	ee **4a**[c]	yield **5a**/%[b]	ee **5a**[c]
1	Cs_2CO_3	-20	48	41	99	11	99	n.d.	-
2	Cs_2CO_3	-5	24	45	98	15	98	n.d.	-
3	Cs_2CO_3	0	24	48	96	17	99	n.d.	-
4	**K_3PO_4**	**0**	**24**	**51**	**96**	**19**	**99**	**n.d.**	**-**

[a] All reactions were performed by using **1a** (0.12 mmol), **2a** (0.1 mmol), catalyst (20 mol%), base (20 mol%), oxidant **B** (0.12 mmol) and DCM (3 mL). [b] Isolated yield. [c] Determined by chiral-phase stationary supercritical fluid chromatography (SFC).

Since **1a** would disappear completely and **2a** wound remain a little after most reactions, we changed the proportion of substrates to **2a** with 0.1 mmol and **1a** with 1.2 equivalent. After reduce the amount of base to 0.2 equiv., the reaction enantioselectivity could remain while increasing the reaction temperature to 0 °C. Replace the base from Cs_2CO_3 to K_3PO_4 slightly increases the product yields.

VI. Some ineffective results

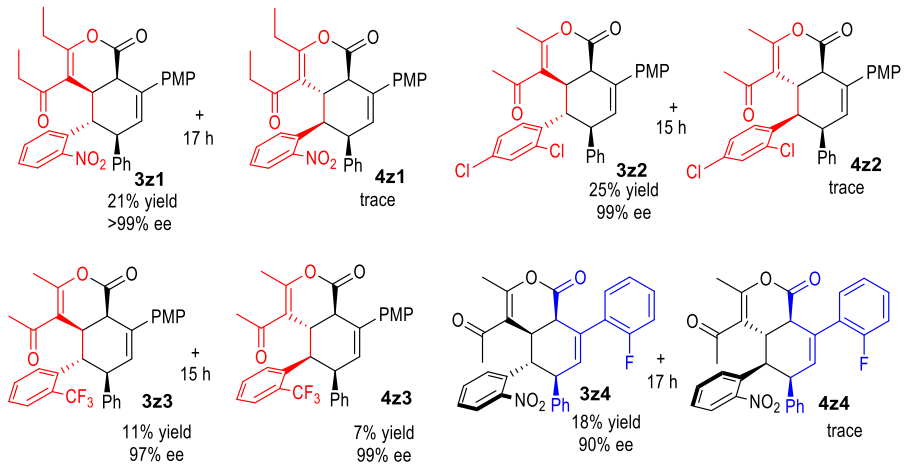


Figure S1. The ineffective results under standard reaction conditions

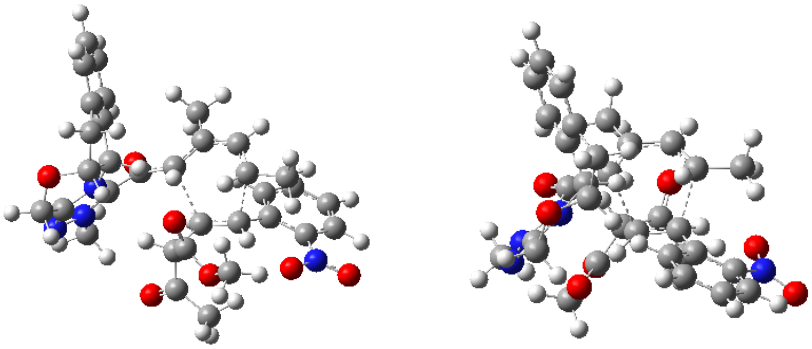
Some ineffective results were also presented in **Figure S1**. Replacing the methyl to a more steric-hindered ethyl resulted in a low yield (**3z1**). Changing ortho-NO2 to ortho-CF3 phenyl ring (**3z3**),or 2,4-Cl(**3z2**), also gave ineffective results. These might due to The weaker electron-withdrawing effect than -NO_2. Introducing ortho-F(**3z4**) led to the addition being blocked so that undesirable yield.

VII. Calculation details

I. Electrophilicity indexes,equilibrium geometries and transition states calculations

All data in this study were calculated with the Gaussian 16 Revision A.03 software package [8] and were optimized at the B3LYP-D3 level of density functional theory (DFT) [9]. The basis set 3-21G was selected for all atoms. Vibrational frequency analysis was computed to ensure the saddle points have only one corresponding imaginary frequency. VMD and Multiwfn were used for drawing the transition state model. [10,11] To take the solvent and temperature effects into account, solvation-corrected single-point energy calculations were computed with M062x/def2TZVPP based on the previous optimized geometries at 273 K. In order to reduce computational complexity, the ethyl group was replaced with methyl, and aromatic groups in diene substrate were simplified with methyl.[12] The relative free Gibbs energies (273 K, in kcal/mol) are used for the following discussion.

II. Cartesian coordinates of optimized structures and transition state



TS-endo **TS-exo**

TS-endo： -2023.8092338 Hartree

Number of imaginary freguencies: 1

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H	-2.91020858	-0.59635206	-1.02358919
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O	0.36496076	-1.69921797	-1.56297625
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C	0.25478372	1.05440096	0.40617439
C	-0.34531783	2.32428946	0.16390965
C	-1.27467492	2.42057893	-0.85943801

C	-1.73984408	1.30705494	-1.60856005
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H	2.31915952	0.09652574	-1.22080489
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H	6.61935523	2.31059325	-2.54133418
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TS-exo： -2023.8088667 Hartree

Number of imaginary freguencies: 1

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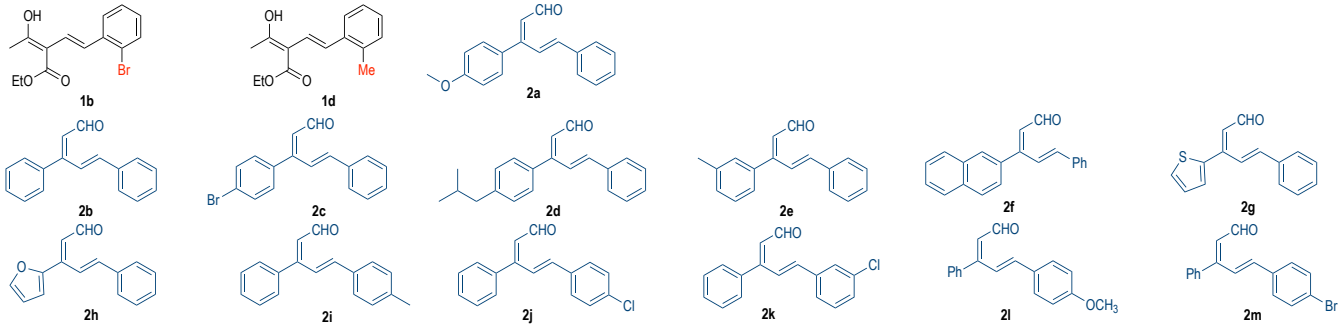
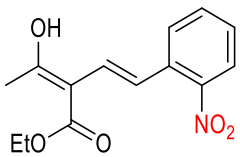
H	0.06311623	-2.46425740	3.57669544
H	-2.26636989	-2.07356311	1.24478753

VIII. Characterization of the substrates

References for the known compounds:

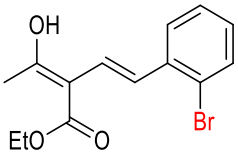
1. Guo, Y., Wu, L., Qiu, F. G., *Org. Lett.* 2022, **24**, 8370-8374. (**1b, 1d**);
2. Singha, R., Dhara, S., Ray, J. K., *Tetrahedron Lett.* 2013, **54**, 4841-4843. (**2a**, **2f**);
3. Chatterjee, I., Bastida, D., Melchiorre, P., *Adv. Synth. Catal.* 2013, **355**, 3124-3130. (**2c, 2k**);
4. Zhu, T., Mou, C., Li, B., Smetankova, M., Song, B.-A., Chi, Y. R., *J. Am. Chem. Soc.* 2015, **137**, 5658-5661. (**2b, 2d, 2g, 2h, 2l, 2m**);
5. Xu, K., Li, W., Zhu, S., Zhu, T., *Angew. Chem. Int. Ed.* 2019, **58**, 17625-17630. (**2e, 2i);**
6. Li, Y., Luo, H., Tang, Z., Li, Y., Du, L., Xin, X., Li, S., Li, B., *Org. Lett.* 2021, **23**, 6450-6454. (**2j**).





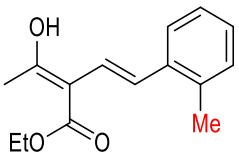
ethyl (*E*)-3-hydroxy-2-((*E*)-2-nitrostyryl) but-2-enoate (1a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.60 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 16.1 Hz, 1H), 6.76 (d, *J* = 16.1 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).



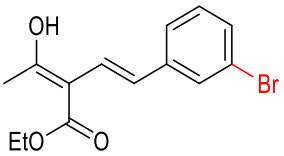
ethyl (*E*)-2-((*E*)-2-bromostyryl) -3-hydroxybut-2-enoate (1b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.55 (s, 1H), 7.57 (m, *J* = 7.8, 3.5, 1.5 Hz, 2H), 7.32 (m, *J* = 7.5, 1.3 Hz, 1H), 7.11 (m, *J* = 7.5, 1.6 Hz, 1H), 7.05 (d, 1H), 6.71 (d, *J* = 16.2 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).



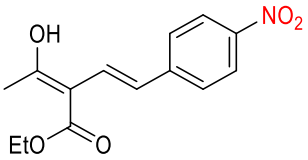
ethyl (*E*)-3-hydroxy-2-((*E*)-2-methylstyryl) but-2-enoate (1d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.39 (s, 1H), 7.52 – 7.46 (m, 1H), 7.24 – 7.14 (m, 3H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.62 (d, *J* = 16.1 Hz, 1H), 4.38 – 4.28 (m, 2H), 2.37 (s, *J* = 2.2 Hz, 3H), 2.25 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).



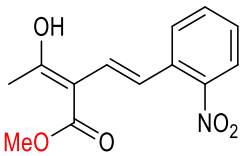
ethyl (*E*)-2-((*E*)-3-bromostyryl) -3-hydroxybut-2-enoate(1e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.44 (s, 1H), 7.53 (t, *J* = 1.8 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 16.2 Hz, 1H), 6.55 (d, *J* = 16.3 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.23 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).



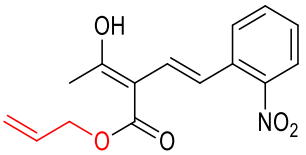
ethyl (*E*)-3-hydroxy-2-((*E*)-4-nitrostyryl) but-2-enoate (1f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.69 (s, 1H), 8.21 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 16.3 Hz, 1H), 6.78 (d, *J* = 16.2 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).



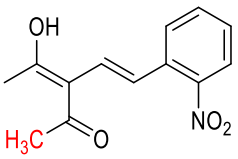
methyl (*E*)-3-hydroxy-2-((*E*)-2-nitrostyryl) but-2-enoate (1g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.54 (s, 1H), 7.58 (dd, *J* = 6.7, 4.3 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.71 (d, *J* = 16.2 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).



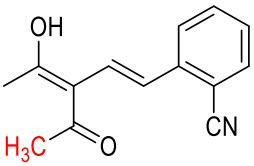
allyl (*E*)-3-hydroxy-2-((*E*)-2-nitrostyryl) but-2-enoate (1h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.43 (s, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 16.1 Hz, 1H), 6.76 (d, *J* = 16.1 Hz, 1H), 6.08 – 5.87 (m, 1H), 5.37 (d, *J* = 16.7 Hz, 1H), 5.29 (m, *J* = 10.4, 1.3 Hz, 1H), 4.77 (d, *J* = 5.7 Hz, 2H), 2.29 (s, 3H).

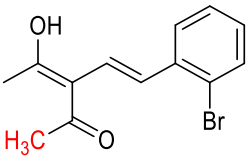


(*E*)-4-hydroxy-3-((*E*)-2-nitrostyryl) pent-3-en-2-one (1i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.57 (m, 2H), 7.43 (td, *J* = 8.4, 6.9, 1.9 Hz, 1H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.73 (d, *J* = 16.0 Hz, 1H), 2.28 (s, 6H).

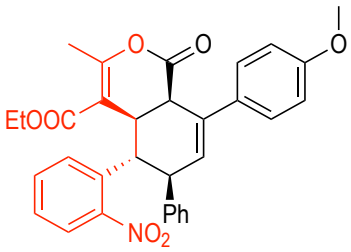


2-((1*E*,3*E*) -3-acetyl-4-hydroxypenta-1,3-dien-1-yl) benzonitrile (1j)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.8, 2.5 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.77 (d, *J* = 16.1 Hz, 1H), 2.29 (s, 6H).

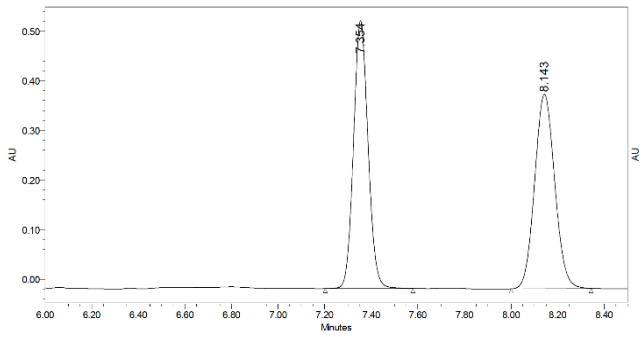


(*E*)-3-((*E*)-2-bromostyryl) -4-hydroxypent-3-en-2-one (1k)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 8.2 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.15 (td, *J* = 7.7, 1.7 Hz, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.69 (d, *J* = 16.0 Hz, 1H), 2.29 (s, 6H).

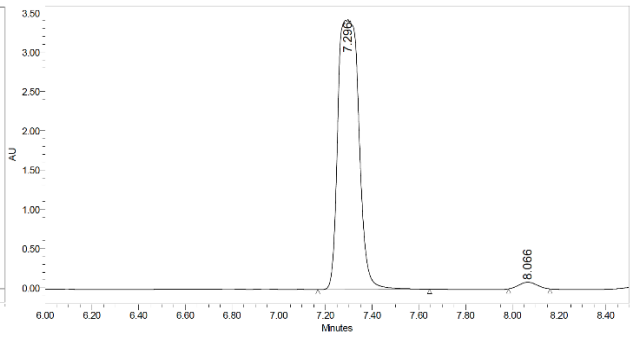
IX. Characterization and SFC Chromatograms of Products



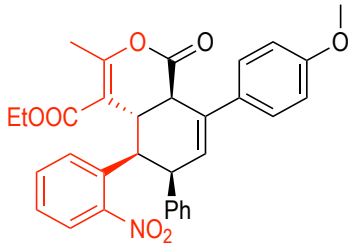
ethyl (4a*R*,5*S*,6*R*,8a*R*)-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (3a)
24h, light yellow solid; 51% yield, 96% ee;
HRMS (ESI+): calcd. for $C_{32}H_{29}NO_7$ +Na^+ [M+Na^+] 562.1836, found 562.1832;
IR: ν_{max} (film, cm^{-1}): 3480, 2931, 1780, 1708, 1515, 1247, 699;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.54 (td, *J* = 7.6, 1.4 Hz, 1H), 7.45 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.30 – 7.26 (m, 1H), 7.17 – 7.10 (m, 3H), 6.92 – 6.83 (m, 4H), 6.21 (d, *J* = 2.9 Hz, 1H), 3.92 – 3.73 (m, 8H), 3.64 (dd, *J* = 12.0, 10.4 Hz, 1H), 2.24 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (150 MHz, $CDCl_3$): δ 167.6, 166.1, 160.9, 159.4, 151.8, 141.3, 134.0, 133.4, 132.6, 131.3, 129.9, 128.8, 128.6, 128.1, 127.8, 127.2, 127.1, 123.8, 114.1, 109.6, 60.8, 55.5, 51.4, 44.1, 43.6, 38.5, 18.8, 14.2;
$[\alpha]^{25}_D$ = -262.3 (*c* = 0.7 in acetone, λ = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 50:50 in the first 5 mins and maintaining in 50:50 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 7.3 min, t_R (minor) = 8.1 min.



	RT	Area	% Area	Height	% Height
1	7.354	2342391	49.95	540083	57.95
2	8.143	2347126	50.05	391955	42.05



	RT	Area	% Area	Height	% Height
1	7.296	21426142	97.94	3433064	97.57
2	8.066	451120	2.06	85377	2.43



ethyl (4a*S*,5*R*,6*R*,8a*R*)-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (4a)

light yellow solid; 19% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{32}H_{29}NO_7$ +Na^+ [M+Na^+] 562.1836, found 562.1829;

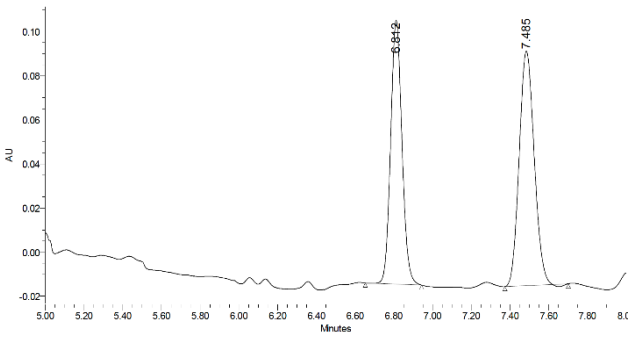
IR: ν_{max} (film, cm^{-1}): 3480, 2930, 1774, 1712, 1514, 1076, 780;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 7.18 – 7.03 (m, 4H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.77 – 6.63 (m, 2H), 6.31 (dd, *J* = 5.6, 2.0 Hz, 1H), 6.10 (dd, *J* = 8.0, 1.4 Hz, 1H), 4.38 – 4.33 (m, 2H), 4.01 – 3.93 (m, 1H), 3.83 (s, 3H), 3.60 – 3.45 (m, 3H), 1.98 (d, *J* = 1.9 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H);

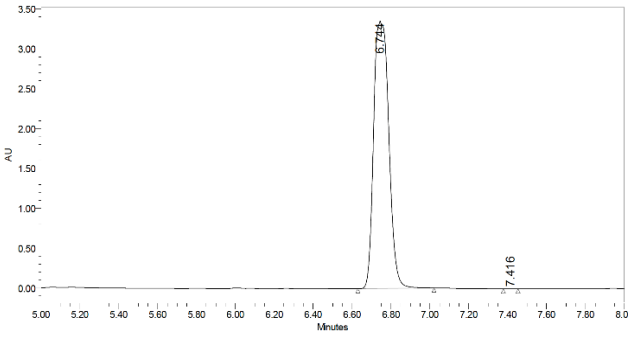
^{13}C NMR (150 MHz, $CDCl_3$): δ 167.7, 166.0, 159.1, 154.4, 150.8 138.0, 134.7, 133.4, 132.56, 131.62 130.5, 129.78, 129.5, 128.1, 127.4, 127.4, 126.4, 124.6, 114.9, 114.0, 61.1, 55.4, 46.2, 45.1, 39.7, 32.2, 17.2, 13.9;

$[\alpha]^{25}_D$ = -28.0 (*c* = 0.5 in acetone, λ = 589 nm);

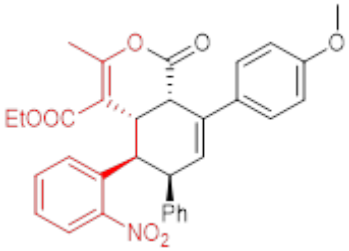
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 50:50 in the first 5 mins and maintaining in 50:50 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 6.7 min, t_R (minor) = 7.4 min.



	RT	Area	% Area	Height	% Height
1	6.812	485947	45.75	119676	52.94
2	7.485	576188	54.25	106380	47.06



	RT	Area	% Area	Height	% Height
1	6.744	18211708	99.99	3355247	99.98
2	7.416	1603	0.01	569	0.02



ethyl (4a*S*,5*R*,6*R*,8a*S*)-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (5a)

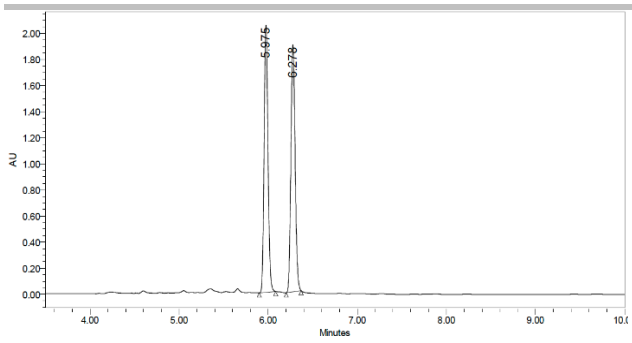
light yellow solid; 78% ee;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.21 – 7.11 (m, 4H), 6.95 – 6.90 (m, 2H), 6.89 – 6.84 (m, 3H), 6.31 (d, *J* = 4.4 Hz, 1H), 6.10 (dd, *J* = 8.1, 1.3 Hz, 1H), 4.18 (dd, *J* = 6.3, 4.4 Hz, 1H), 3.99 (d, *J* = 5.2 Hz, 1H), 3.95 – 3.85 (m, 2H), 3.83 (s, 3H), 3.83 – 3.74 (m, 2H), 2.12 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

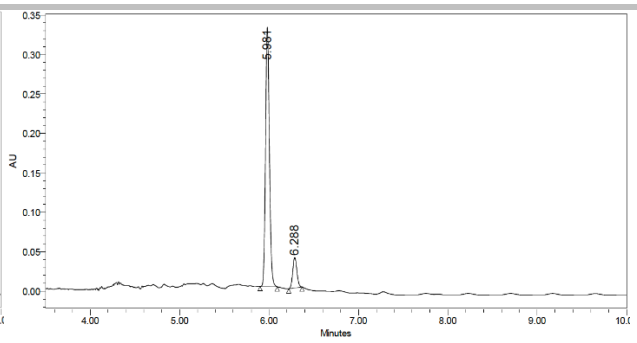
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.8, 159.5, 159.1, 151.6, 139.5, 133.3, 133.0, 132.8, 131.6, 130.4, 129.9, 128.2, 127.7, 127.5, 127.4, 127.1, 123.6, 114.2, 110.5, 61.0, 55.5, 46.9, 44.0, 41.9, 32.7, 18.6, 14.1;

$[\alpha]^{25}_D$ = -80.0 (*c* = 0.5 in acetone, λ = 589 nm);

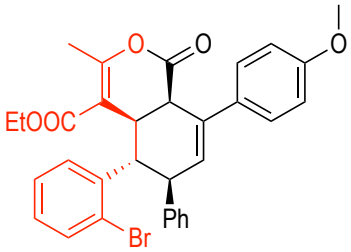
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 50:50 in the first 5 mins and maintaining in 50:50 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 6.0 min, t_R (minor) = 6.3 min.



	RT	Area	% Area	Height	% Height
1	5.975	6196731	49.98	2048287	51.96
2	6.278	6200887	50.02	1893533	48.04



	RT	Area	% Area	Height	% Height
1	5.981	990872	88.94	328463	89.52
2	6.288	123203	11.06	38435	10.48



ethyl (4a*R*,5*S*,6*R*,8a*R*)-5-(2-bromophenyl)-8-(4-methoxyphenyl)-3-methyl-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (3b)

23 h, light yellow solid; 42% yield, 96% ee;

HRMS (ESI+): calcd. for $C_{32}H_{29}BrO_5$ +Na^+ [M+Na^+] 595.1091, found 595.1082;

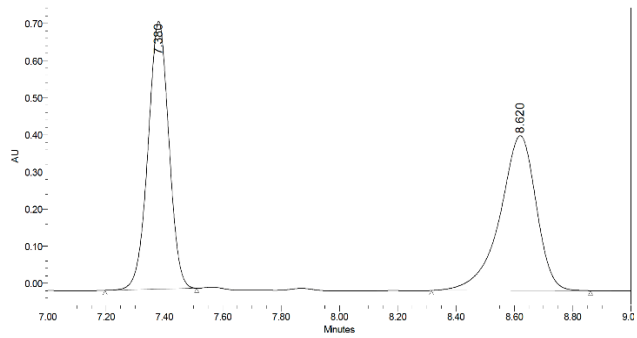
IR: ν_{max} (film, cm^{-1}): 2932, 1777, 1703, 1514, 1249, 1067, 700;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.32 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.18 – 7.10 (m, 3H), 7.02 – 6.95 (m, 3H), 6.93 – 6.87 (m, 2H), 6.25 (d, *J* = 2.8 Hz, 1H), 3.93 – 3.87 (m, 2H), 3.82 (s, 3H), 3.80 – 3.75 (m, 1H), 3.73 – 3.63 (m, 3H), 2.24 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H);

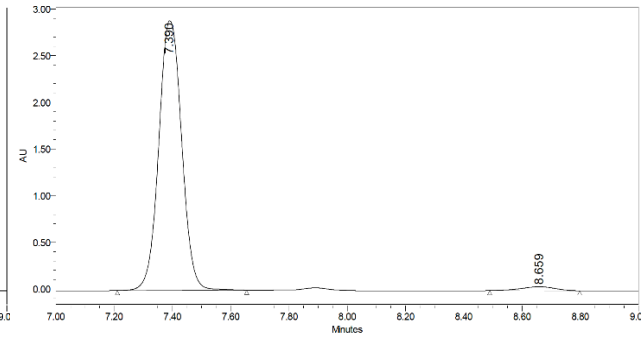
^{13}C NMR (150 MHz, $CDCl_3$): δ 168.3, 165.9, 156.0, 159.4, 141.8, 139.0, 133.1, 132.8, 132.7, 129.4, 129.3, 128.5, 128.4, 128.3, 127.6, 127.1, 126.9, 126.7, 114.1, 110.0, 60.6, 55.5, 50.7, 48.3, 43.6, 39.1, 18.6, 14.2;

$[\alpha]^{25}_D$ = -110.4 (*c* = 0.5 in acetone, *λ* = 589 nm);

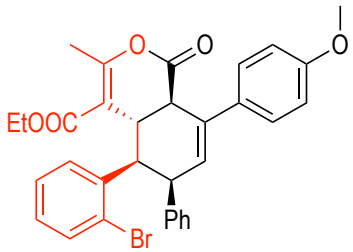
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 50:50 in the first 5 mins and maintaining in 50:50 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 7.4 min, t_R (minor) = 8.6 min.



	RT	Area	% Area	Height	% Height
1	7.380	3581893	49.87	721426	63.34
2	8.620	3601271	50.13	417471	36.66



	RT	Area	% Area	Height	% Height
1	7.390	15794290	97.93	2889200	98.56
2	8.659	334537	2.07	42314	1.44



ethyl (4a*S*,5*R*,6*R*,8a*R*)-5-(2-bromophenyl)-8-(4-methoxyphenyl)-3-methyl-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (4b)

light yellow solid; 10% yield, 99% ee;

HRMS (ESI+): calcd. for $C_{32}H_{29}BrO_5$ +Na^+ [M+Na^+] 595.1091, found 595.1085;

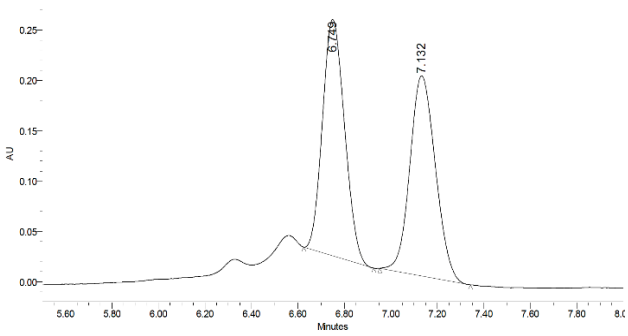
IR: ν_{max} (film, cm^{-1}): 2931, 1781, 1709, 1514, 1244, 1089, 699;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.32 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.16 – 7.11 (m, 3H), 7.01 – 6.95 (m, 3H), 6.92 – 6.87 (m, 2H), 6.25 (d, *J* = 2.8 Hz, 1H), 3.93 – 3.87 (m, 2H), 3.82 (s, 3H), 3.80 – 3.75 (m, 1H), 3.72 – 3.62 (m, 3H), 2.24 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H).

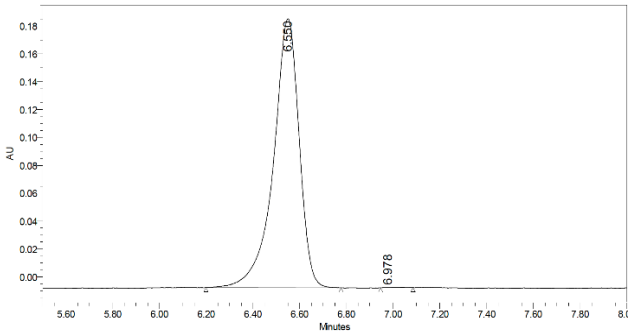
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 166.0, 160.0, 159.4, 141.8, 139.0, 133.1, 132.8, 132.7, 129.5, 129.3, 128.5, 128.4, 128.4, 127.6, 127.1, 126.9, 126.7, 114.1, 110.0, 60.6, 55.5, 50.7, 48.3, 43.6, 39.1, 18.7, 14.2.

$[\alpha]^{25}_D$ = -132.0 (*c* = 0.5 in acetone, λ = 589 nm);

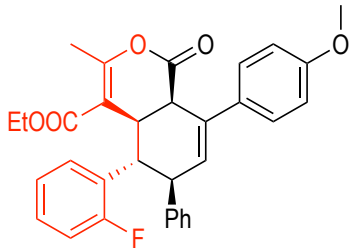
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 80:20 in the first 5 mins and maintaining in 80:20 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 6.5 min, t_R (minor) = 7.0 min.



	RT	Area	% Area	Height	% Height
1	6.749	1551817	50.52	234938	54.15
2	7.132	1519946	49.48	198937	45.85



	RT	Area	% Area	Height	% Height
1	6.550	1477231	99.88	193043	99.75
2	6.978	1812	0.12	483	0.25



ethyl (4a*R*,5*S*,6*R*,8a*R*)-5-(2-fluorophenyl)-8-(4-methoxyphenyl)-3-methyl-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (3c)

23 h, light yellow solid; 41% yield,1.2:1 dr ,97% ee;

HRMS (ESI+): calcd. for $C_{32}H_{29}FO_5$ +Na^+ [M+Na^+] 535.1891, found 535.1886;

IR: ν_{max} (film, cm^{-1}): 2989, 1777, 1704, 1516, 1261, 1066, 706;

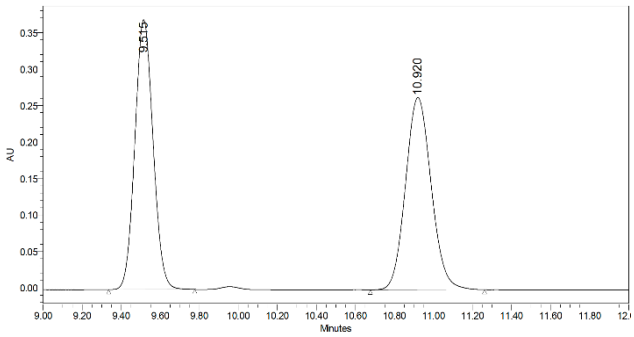
^{1}H NMR (400 MHz, $CDCl_3$):δ 7.47 (d, *J* = 6.6 Hz, 1H), 7.44 – 7.38 (m, 5H), 7.13 (dq, *J* = 10.5, 5.9, 4.5 Hz, 10H), 6.97 (s, 5H), 6.93 – 6.88 (m, 5H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 21.1 Hz, 1H), 6.25 (d, *J* = 3.0 Hz, 2H), 4.24 (d, *J* = 10.4 Hz, 1H), 4.10 – 3.99 (m, 1H), 3.90 (dd, *J* = 5.5, 1.2 Hz, 4H), 3.82 (s, 8H), 3.67 (q, *J* = 9.9, 8.1 Hz, 4H), 3.35 (t, *J* = 11.5 Hz, 1H), 2.59 (t, *J* = 11.4 Hz, 1H), 2.23 (s, 7H), 1.13 (dt, *J* = 22.9, 7.3 Hz, 7H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4(d, J_{CF} = 262.6 Hz), 167.1(d, J_{CF} = 262.6 Hz), 160.5, 159.7, 159.7 159.2,133.3, 132.9(d, J_{CF} = 7.07 Hz), 132.7(d, J_{CF} = 7.07 Hz),129.1, 128.8, 128.4, 128.2, 126.9, 126.8, 124.0, 123.3, 115.5(d, J_{CF} = 29.3 Hz),115.3(d, J_{CF} = 31.3 Hz),114.0, 111.2, 110.4, 60.6, 55.4, 51.7,49.9, 47.6, 43.3, 41.3, 38.6, 36.7, 18.4, 14.0, 13.8.

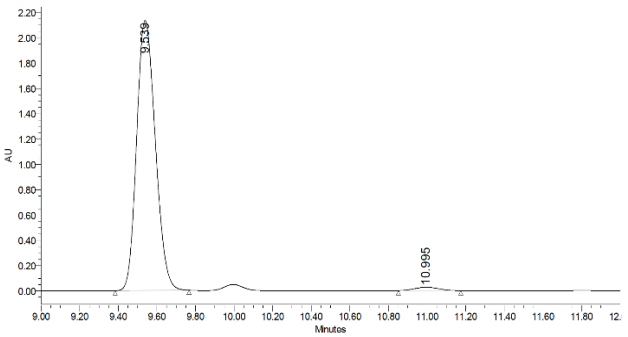
^{19}F NMR (377 MHz, $CDCl_3$) δ-111.4, -118.3.

$[\alpha]^{25}_D$ = -208.0 (*c* = 0.5 in acetone, λ = 589 nm);

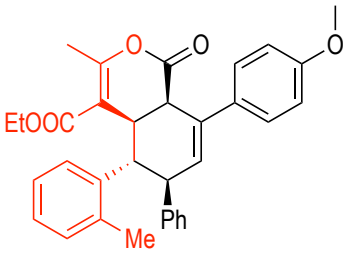
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 80:20 in the first 5 mins and maintaining in 80:20 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 9.5 min, t_R (minor) = 10.9 min.



	RT	Area	% Area	Height	% Height
1	9.515	2402166	49.93	369916	58.39
2	10.920	2409116	50.07	263573	41.61



	RT	Area	% Area	Height	% Height
1	9.539	14349885	98.42	2133343	98.76
2	10.995	230462	1.58	26786	1.24



ethyl (4a*R*,5*S*,6*R*,8a*R*)-8-(4-methoxyphenyl)-3-methyl-1-oxo-6-phenyl-5-(*o*-tolyl)-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (3d)

18 h, light yellow solid; 32% yield, 94:6 dr, 96% ee;

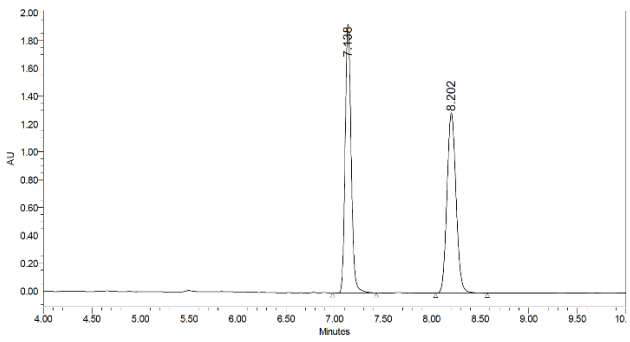
HRMS (ESI+): calcd. for $C_{33}H_{32}O_5$ +Na^+ [M+Na^+] 531.2142, found 531.2136;

IR: ν_{max} (film, cm^{-1}): 2986, 1775, 1704, 1514, 1253, 1067, 706;

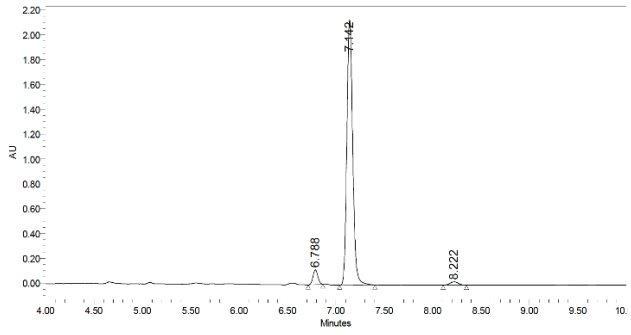
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 2H), 7.39 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.16 (td, *J* = 7.5, 1.4 Hz, 1H), 7.13 – 7.10 (m, 3H), 7.02 (td, *J* = 7.4, 1.3 Hz, 1H), 6.94 – 6.86 (m, 5H), 6.29 (d, *J* = 3.0 Hz, 1H), 3.91 (dd, *J* = 5.3, 1.2 Hz, 1H), 3.87 (dd, *J* = 10.3, 2.9 Hz, 1H), 3.83 (s, 3H), 3.81 – 3.65 (m, 3H), 3.09 (dd, *J* = 12.4, 10.2 Hz, 1H), 2.17 (s, 3H), 1.60 (s, 3H),1.12 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 166.0, 159.3, 158.0, 142.6, 138.1, 137.8, 133.2, 132.8, 129.9, 129.3, 128.4, 128.3, 127.5, 127.0, 126.7, 126.6, 125.4, 114.1, 111.8, 60.7, 55.5, 51.5, 45.7, 43.6, 39.0, 19.6, 18.2, 14.1;

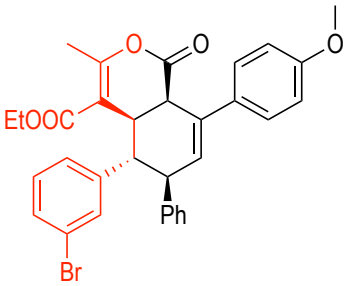
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 7.1 min, t_R (minor) = 8.2 min.



	RT	Area	% Area	Height	% Height
1	7.138	8214114	49.67	1930071	59.89
2	8.202	8322131	50.33	1292640	40.11



	RT	Area	% Area	Height	% Height
1	6.788	411729	4.34	118469	5.19
2	7.142	8921565	93.98	2138801	93.64
3	8.222	159553	1.68	26679	1.17



ethyl (4a*R*,5*S*,6*R*,8a*R*)-5-(3-bromophenyl)-8-(4-methoxyphenyl)-3-methyl-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (3e)

23 h, light yellow solid; 38% yield, 96% ee;

HRMS (ESI+): calcd. for $C_{32}H_{29}BrO_5$ +Na^+ [M+Na^+] 595.1091, found 595.1086;

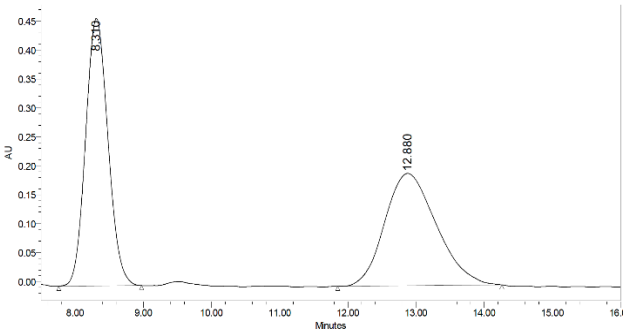
IR: ν_{max} (film, cm^{-1}): 2990, 1783, 1706, 1515, 1255, 1062, 706;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 2H), 7.31 – 7.27 (m, 1H), 7.20 – 7.08 (m, 4H), 7.03 – 6.96 (m, 1H), 6.96 – 6.85 (m, 5H), 6.23 (d, *J* = 3.0 Hz, 1H), 3.92 – 3.84 (m, 3H), 3.82 (s, 3H), 3.80 – 3.71 (m, 2H), 2.65 (dd, *J* = 12.3, 10.3 Hz, 1H), 2.23 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H);

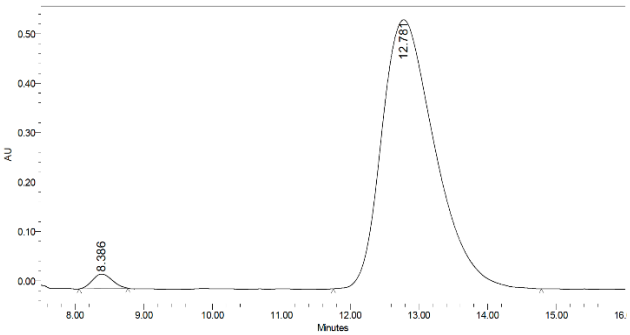
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 165.8, 159.4, 159.0, 142.2, 142.2, 133.0, 132.6, 130.3, 129.6, 128.9, 128.6, 128.4, 127.0, 127.0, 122.0, 114.1, 111.3, 61.1, 55.5, 51.9, 50.8, 43.4, 38.8, 18.5, 14.2; (two aromatic carbon signals overlap with others in the 120-135 ppm region)

$[\alpha]^{25}_D$ = -80.8 (*c* = 0.5 in acetone, *λ* = 589 nm);

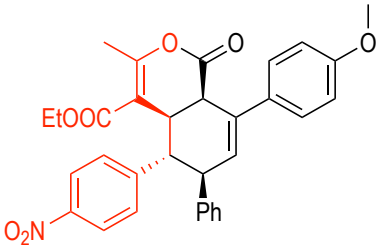
the enantioselectivity was determined by SFC (Chiralpak AD-3, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 12.8 min, t_R (minor) = 8.3 min.



	RT	Area	% Area	Height	% Height
1	8.310	10503337	50.84	462085	70.45
2	12.880	10157816	49.16	193824	29.55



	RT	Area	% Area	Height	% Height
1	8.386	585911	1.97	29415	5.13
2	12.781	29195050	98.03	544529	94.87



ethyl (4a*R*,5*S*,6*R*,8a*R*)-8-(4-methoxyphenyl)-3-methyl-5-(4-nitrophenyl)-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (3f)

27 h, light yellow solid; 46% yield, 97:3 dr, 94% ee;

HRMS (ESI+): calcd. for $C_{32}H_{29}NO_7$ +Na^+ [M+Na^+] 562.1836, found 562.1834;

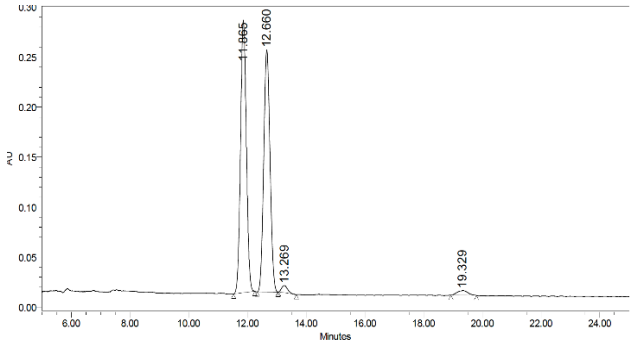
IR: ν_{max} (film, cm^{-1}): 2935, 1777, 1702, 1513, 1344, 1064, 701;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (br, 2H), 7.41 – 7.38 (m, 2H), 7.16 – 7.11 (m, 4H), 6.91 – 6.88 (m, 5H), 6.23 (d, *J* = 2.9 Hz, 1H), 3.92 – 3.88 (m, 2H), 3.84 – 3.82 (m, 1H), 3.82 (s, 3H), 3.82 – 3.80 (m, 1H), 3.78 – 3.72 (m, 1H), 2.83 (dd, *J* = 12.3, 10.2 Hz, 1H), 2.23 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H);

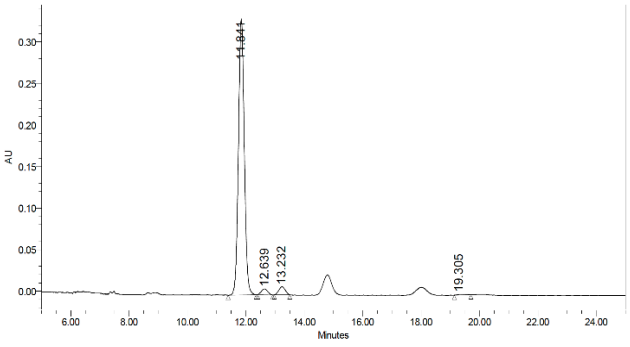
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 165.8, 159.7, 159.6, 147.8, 147.2, 141.7, 133.2, 132.4, 128.8, 128.6, 128.3, 127.2, 127.1, 123.1, 114.2, 110.9, 61.1, 55.5, 52.3, 51.0, 43.4, 38.6, 18.7, 14.2; (one aromatic carbon signal overlaps with others in the 120-135 ppm region)

$[\alpha]^{25}_D$ = -41.6 (*c* = 0.5 in acetone, *λ* = 589 nm);

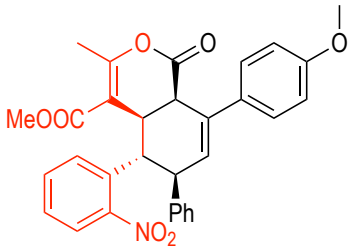
the enantioselectivity was determined by SFC (Trefoil CEL-2, gradient 100% CO_2 to CO_2/MeOH = 80:20 in the first 5 mins and maintaining in 80:20 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 11.8 min, t_R (minor) = 12.6 min.



	RT	Area	% Area	Height	% Height
1	11.865	3683470	48.98	272597	51.74
2	12.660	3613938	48.06	242265	45.99
3	13.269	102898	1.37	7252	1.38
4	19.329	119475	1.59	4695	0.89



	RT	Area	% Area	Height	% Height
1	11.841	4532122	94.51	332547	94.99
2	12.639	100712	2.10	7110	2.03
3	13.232	148148	3.09	9623	2.75
4	19.305	14633	0.31	795	0.23



methyl (4a*R*,5*S*,6*R*,8a*R*)-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (3g)

17 h, light yellow solid; 43% yield, 98% ee;

HRMS (ESI+): calcd. for $C_{31}H_{27}NO_7$ +Na^+ [M+Na^+] 548.1680, found 548.1671;

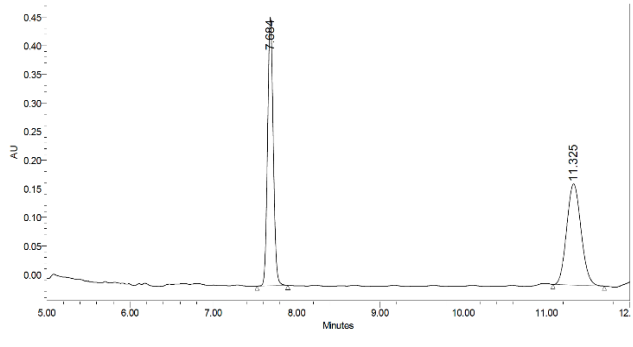
IR: ν_{max} (film, cm^{-1}): 2953, 1782, 1710, 1515, 1247, 1071, 700;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.55 (td, *J* = 7.6, 1.4 Hz, 1H), 7.45 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.31 – 7.26 (m, 1H), 7.18 – 7.11 (m, 3H), 6.93 – 6.84 (m, 4H), 6.20 (d, *J* = 2.9 Hz, 1H), 3.91 (dd, *J* = 5.1, 1.3 Hz, 1H), 3.89 – 3.84 (m, 1H), 3.82 (s, 3H), 3.79 (d, *J* = 5.3 Hz, 1H), 3.63 (dd, *J* = 12.0, 10.4 Hz, 1H), 3.37 (s, 3H), 2.24 (s, 3H);

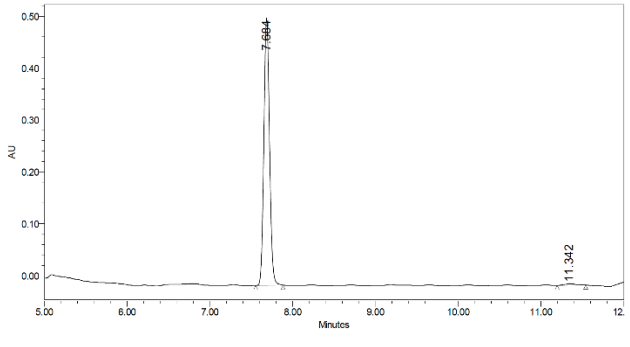
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 166.4, 161.4, 159.4, 151.7, 141.3, 133.9, 133.3, 132.6, 131.2, 129.9, 128.8, 128.7, 128.1, 127.9, 127.3, 127.1, 123.9, 114.1, 109.2, 55.5, 51.5, 51.3, 44.1, 43.5, 38.6, 18.7;

$[\alpha]^{25}_D$ = -69.6 (*c* = 0.5 in acetone, λ = 589 nm);

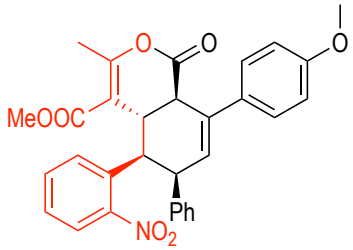
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 50:50 in the first 5 mins and maintaining in 50:50 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 7.7 min, t_R (minor) = 11.3 min.



	RT	Area	% Area	Height	% Height
1	7.684	2230064	51.29	469251	72.62
2	11.325	2118175	48.71	176963	27.38



	RT	Area	% Area	Height	% Height
1	7.684	2447943	98.86	515338	99.47
2	11.342	28212	1.14	2743	0.53



methyl (4a*S*,5*R*,6*R*,8a*R*)-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (4g)

light yellow solid; 17% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{31}H_{27}NO_7$ +Na$^+$ [M+Na$^+$] 548.1680, found 548.1669;

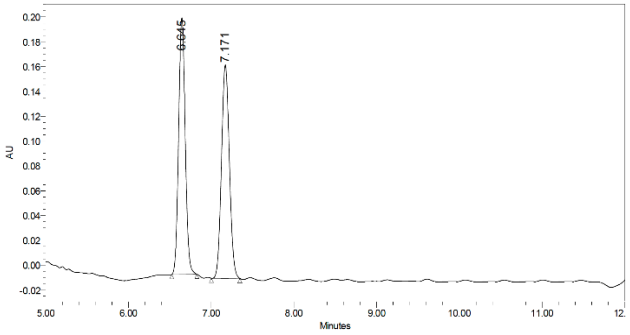
IR: ν_{max} (film, cm^{-1}): 2948, 1770, 1712, 1515, 1244, 1091, 706;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.19 – 7.13 (m, 1H), 7.12 – 7.05 (m, 3H), 6.95 – 6.86 (m, 2H), 6.70 (br, 2H), 6.32 (dd, *J* = 6.3, 1.9 Hz, 1H), 6.08 (dd, *J* = 8.1, 1.3 Hz, 1H), 4.35 (t, *J* = 5.8 Hz, 1H), 4.27 (dd, *J* = 12.7, 5.2 Hz, 1H), 3.95 (dt, *J* = 13.1, 1.7 Hz, 1H), 3.83 (s, 3H), 3.54 (td, *J* = 12.8, 2.1 Hz, 1H), 3.11 (s, 3H), 1.99 (d, *J* = 1.9 Hz, 3H);

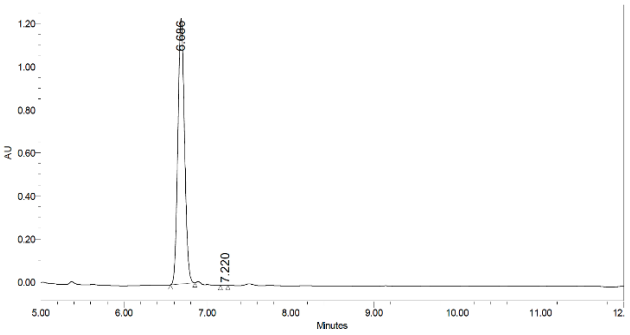
^{13}C NMR (100 MHz, CDCl$_3$) δ 167.6, 166.4, 159.1, 155.3, 150.7, 141.0, 137.8, 134.4, 133.3, 132.6, 131.8, 130.5, 129.7, 129.3, 128.1, 127.5, 126.4, 124.5, 114.4, 114.0, 55.4, 51.8, 46.2, 45.0, 39.9, 32.1, 17.3;

$[\alpha]^{25}_D$ = -20.8 (*c* = 0.5 in acetone, *λ* = 589 nm);

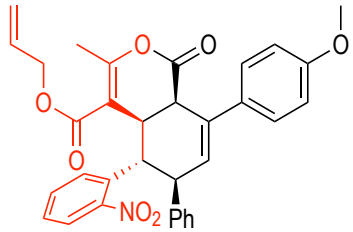
the enantioselectivity was determined by SFC (Trefoil CEL-2, gradient 100% CO_2 to CO_2/MeOH = 50:50 in the first 5 mins and maintaining in 50:50 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 6.7 min, t_R (minor) = 7.2 min.



	RT	Area	% Area	Height	% Height
1	6.645	1142200	50.03	206805	54.60
2	7.171	1140658	49.97	171950	45.40



	RT	Area	% Area	Height	% Height
1	6.686	6836728	99.99	1233010	99.98
2	7.220	505	0.01	186	0.02



allyl (4a*R*,5*S*,6*R*,8a*R*)-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (3h)

24 h, light yellow solid; 49% yield, 94:6 dr, 97% ee;

HRMS (ESI+): calcd. for $C_{33}H_{29}NO_7$ +Na$^+$ [M+Na$^+$] 574.1836, found 574.1827

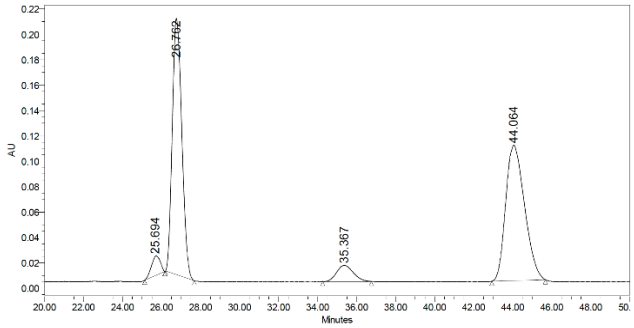
IR: ν_{max} (film, cm^{-1}): 3027, 1778, 1709, 1515, 1240, 1057, 700;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.46 – 7.37 (m, 3H), 7.31 – 7.27 (m, 1H), 7.17 – 7.12 (m, 3H), 6.92 – 6.85 (m, 4H), 6.21 (d, *J* = 2.9 Hz, 1H), 5.76 (ddt, *J* = 16.6, 10.4, 5.8 Hz, 1H), 5.27 – 5.18 (m, 2H), 4.30 (ddt, *J* = 13.2, 5.6, 1.4 Hz, 1H), 4.20 – 4.12 (m, 1H), 3.92 (dd, *J* = 5.2, 1.3 Hz, 1H), 3.88 – 3.84 (m, 1H), 3.82 (s, 3H), 3.83 – 3.79 (m, 1H), 3.64 (dd, *J* = 12.1, 10.4 Hz, 1H), 2.26 (s, 3H);

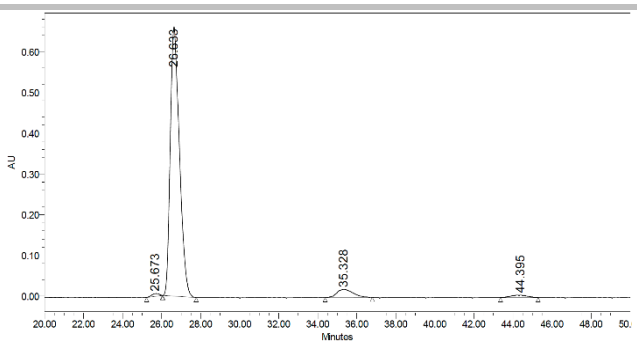
^{13}C NMR (100 MHz, CDCl$_3$) δ 167.5, 165.7, 161.4, 159.4, 151.7, 141.2, 133.8, 133.2, 132.5, 131.8, 131.4, 129.9, 128.8, 128.6, 128.1, 127.8, 127.2, 127.1, 123.8, 118.8, 114.1, 109.2, 65.5, 55.4, 51.3, 44.1, 43.5, 38.4, 18.8;

$[\alpha]^{25}_D$ = -80.8 (*c* = 0.5 in acetone, *λ* = 589 nm);

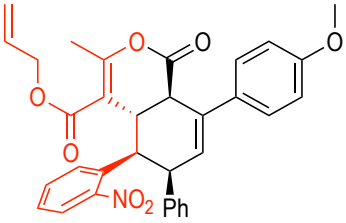
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 90:10 in the first 5 mins and maintaining in 90:10 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 26.6 min, t_R (minor) = 44.4 min.



	RT	Area	% Area	Height	% Height
1	25.694	475579	3.11	15268	4.54
2	26.762	6879119	44.97	201646	59.96
3	35.367	760499	4.97	12765	3.80
4	44.064	7180310	46.94	106600	31.70



	RT	Area	% Area	Height	% Height
1	25.673	182441	0.79	6922	1.00
2	26.633	21563901	93.02	660906	95.32
3	35.328	1127590	4.86	19842	2.86
4	44.395	308874	1.33	5674	0.82



allyl (4a*S*,5*R*,6*R*,8a*R*)-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromene-4-carboxylate (4h)

light yellow solid; 12% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{33}H_{29}NO_7$ +Na$^+$ [M+Na$^+$] 574.1836, found 574.1829

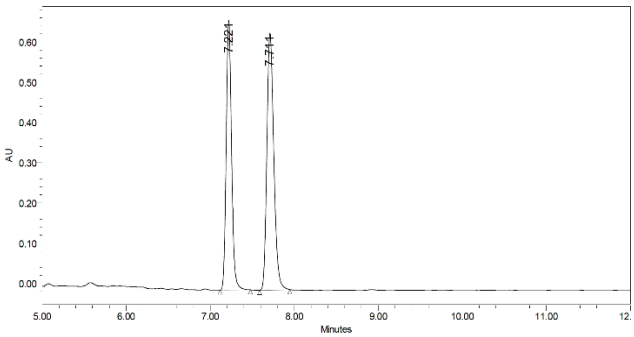
IR: ν_{max} (film, cm^{-1}): 2924, 1774, 1713, 1515, 1244, 1090, 703;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.18 – 7.02 (m, 4H), 6.95 – 6.86 (m, 2H), 6.71 (s, 2H), 6.31 (dd, *J* = 5.9, 2.1 Hz, 1H), 6.10 (dd, *J* = 8.0, 1.3 Hz, 1H), 5.57 (ddt, *J* = 17.4, 10.1, 6.0 Hz, 1H), 5.17 – 5.08 (m, 2H), 4.41 – 4.31 (m, 2H), 4.01 – 3.93 (m, 2H), 3.91 – 3.85 (m, 1H), 3.83 (s, 3H), 3.54 (td, *J* = 12.6, 2.1 Hz, 1H), 1.99 (d, *J* = 1.9 Hz, 3H);

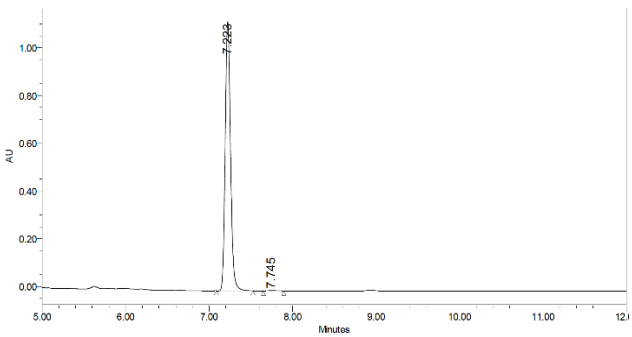
^{13}C NMR (100 MHz, CDCl$_3$) δ 167.6, 165.7, 159.1, 154.8, 150.6, 137.9, 134.6, 133.3, 132.5, 131.8, 131.3, 130.5, 129.8, 129.4, 128.1, 127.4, 126.4, 124.6, 119.4, 114.5, 114.0, 65.8, 55.4, 46.1, 45.0, 39.7, 32.2, 17.3;

$[\alpha]^{25}_D$ = -8.8 (*c* = 0.5 in acetone, *λ* = 589 nm);

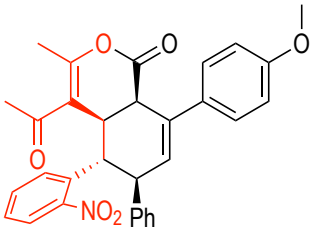
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 7.2 min, t_R (minor) = 7.7 min.



	RT	Area	% Area	Height	% Height
1	7.221	2968002	44.81	670477	51.24
2	7.711	3655337	55.19	638083	48.76



	RT	Area	% Area	Height	% Height
1	7.223	5002224	99.71	1128801	99.82
2	7.745	14555	0.29	2021	0.18



(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3i)

13 h, light yellow solid; 72% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{31}H_{27}NO_6$ +Na$^+$ [M+Na$^+$] 532.1731, found 532.1727;

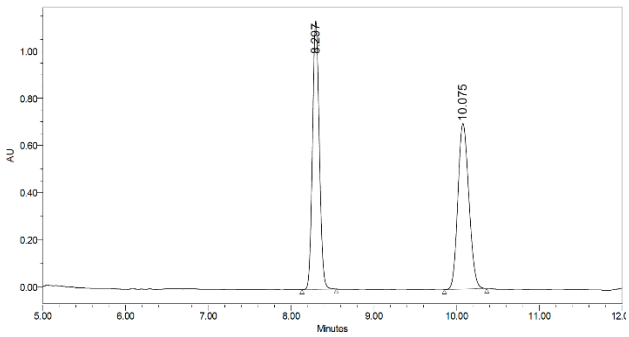
IR: ν_{max} (film, cm^{-1}): 2956, 1775, 1510, 1356, 1242, 1100, 702;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.42 – 7.35 (m, 3H), 7.32 – 7.26 (m, 1H), 7.19 – 7.12 (m, 3H), 6.94 – 6.83 (m, 4H), 6.19 (d, *J* = 2.8 Hz, 1H), 3.93 – 3.83 (m, 3H), 3.81 (s, 3H), 3.47 (t, *J* = 11.3 Hz, 1H), 2.18 (s, 3H), 1.73 (s, 3H);

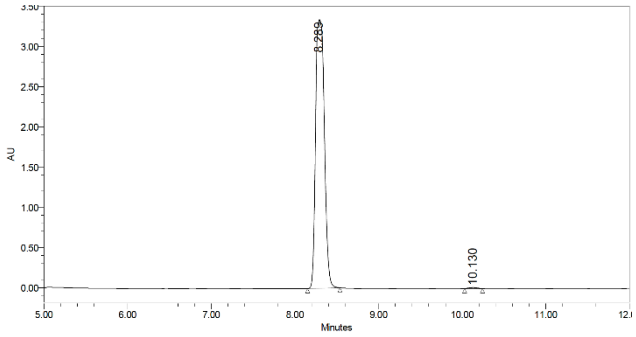
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 167.6, 159.4, 157.5, 151.8, 141.3, 134.1, 133.3, 132.6, 131.8, 130.1, 128.8, 128.6, 128.1, 128.0, 127.3, 127.1, 123.4, 119.9, 114.1, 55.5, 51.1, 44.2, 43.4, 39.2, 30.2, 19.3;

$[\alpha]^{25}_D$ = -66.4 (*c* = 0.5 in acetone, *λ* = 589 nm);

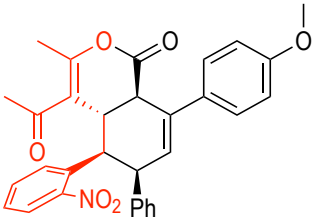
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 50:50 in the first 5 mins and maintaining in 50:50 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.3 min, t_R (minor) = 10.1 min.



	RT	Area	% Area	Height	% Height
1	8.297	6564032	50.15	1139588	61.83
2	10.075	6525983	49.85	703405	38.17



	RT	Area	% Area	Height	% Height
1	8.289	24489796	99.64	3340226	99.63
2	10.130	88881	0.36	12435	0.37



(4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (4i)

light yellow solid; 14% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{31}H_{27}NO_6$ +Na$^+$ [M+Na$^+$] 532.1731, found 532.1724;

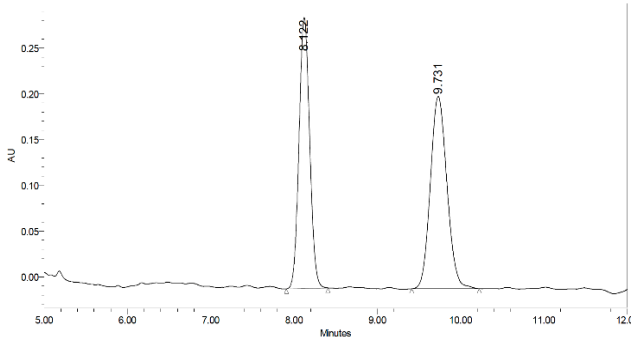
IR: ν_{max} (film, cm^{-1}): 2930, 1770, 1522, 1357, 1243, 1085, 702;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.33 – 7.27 (m,, 3H), 7.20 – 7.08 (m, 3H), 7.04 (td, *J* = 7.6, 1.4 Hz, 1H), 6.94 – 6.87 (m, 2H), 6.75 (br, 2H), 6.30 (dd, *J* = 6.2, 2.0 Hz, 1H), 6.04 (dd, *J* = 7.9, 1.3 Hz, 1H), 4.38 – 4.32 (m, 1H), 4.26 (dd, *J* = 12.7, 5.4 Hz, 1H), 3.93 (dt, *J* = 12.9, 1.7 Hz, 1H), 3.83 (s, 3H), 3.52 (td, *J* = 12.8, 2.0 Hz, 1H), 1.94 (d, *J* = 1.8 Hz, 3H), 1.54 (s, 3H);

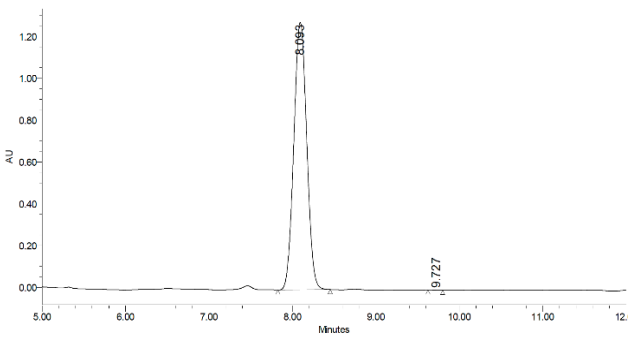
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 167.8, 159.1, 151.3, 150.9, 138.1, 135.1, 133.4, 132.6, 131.3, 130.6, 129.7, 129.6, 128.1, 127.7, 127.5, 126.5, 124.7, 123.6, 114.0, 55.4, 46.1, 45.3, 39.1, 33.8, 31.6, 17.4;

$[\alpha]^{25}_D$ = +45.6 (*c* = 0.5 in acetone, *λ* = 589 nm);

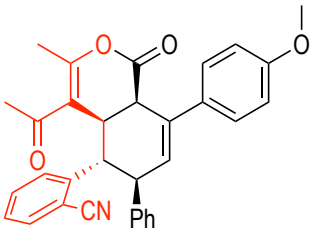
the enantioselectivity was determined by SFC (Trefoil CEL-2, gradient 100% CO_2 to CO_2/MeOH = 50:50 in the first 5 mins and maintaining in 50:50 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.1 min, t_R (minor) = 9.7 min.



	RT	Area	% Area	Height	% Height
1	8.122	2609487	47.30	296125	58.50
2	9.731	2907752	52.70	210095	41.50



	RT	Area	% Area	Height	% Height
1	8.093	13707668	99.98	1279724	99.96
2	9.727	2896	0.02	-528	0.04



2-((4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-8-(4-methoxyphenyl)-3-methyl-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-5-yl)benzonitrile (3j)

13 h, light yellow solid; 67% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{32}H_{27}NO_4$ +Na^+ [M+Na^+] 512.1832, found 512.1835

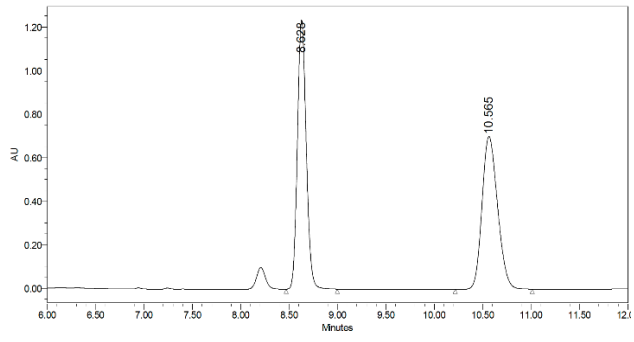
IR: ν_{max} (film, cm^{-1}): 2955, 2224, 1776, 1510, 1240, 1104, 702;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.41 – 7.37 (m, 3H), 7.30 – 7.26 (m, 1H), 7.19 – 7.13 (m, 3H), 6.96 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.91 – 6.87 (m, 2H), 6.22 (d, *J* = 2.9 Hz, 1H), 3.95 – 3.90 (m, 1H), 3.88 – 3.85 (m, 1H), 3.83 – 3.82 (m, 1H), 3.81 (s, 3H), 3.34 (dd, *J* = 11.8, 10.4 Hz, 1H), 2.22 (s, 3H), 1.71 (s, 3H);

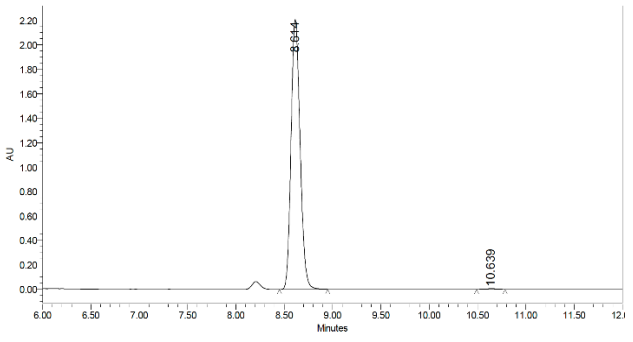
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 167.4, 159.4, 157.6, 144.0, 141.4, 133.2, 132.6, 132.6, 132.5, 128.8, 128.7, 128.6, 128.2, 127.8, 127.2, 127.1, 119.7, 116.8, 114.9, 114.1, 114.0, 55.4, 50.4, 48.9, 43.3, 39.7, 30.1, 19.2;

$[\alpha]^{25}_D$ = -114.4 (*c* = 0.5 in acetone, *λ* = 589 nm);

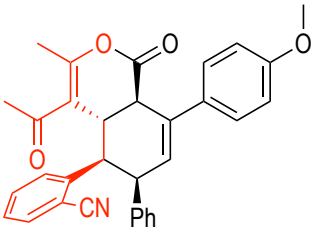
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.6 min, t_R (minor) = 10.6 min.



	RT	Area	% Area	Height	% Height
1	8.628	7778769	49.98	1235448	63.79
2	10.565	7784145	50.02	701277	36.21



	RT	Area	% Area	Height	% Height
1	8.614	14291097	99.63	2210634	99.73
2	10.639	53045	0.37	5932	0.27



2-((4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-8-(4-methoxyphenyl)-3-methyl-1-oxo-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-5-yl)benzonitrile (4j)

light yellow solid; 13% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{32}H_{27}NO_4$ +Na^+ [M+Na^+] 512.1832, found 512.1829

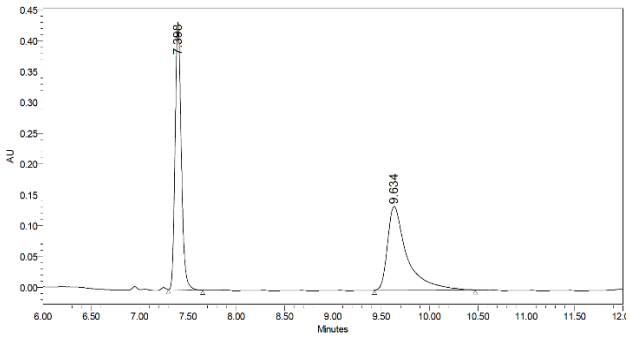
IR: ν_{max} (film, cm^{-1}): 2906, 2222, 1778, 1674, 1514, 1242, 1080, 706;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.23 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.18 – 7.12 (m, 1H), 7.11 – 7.04 (m, 3H), 6.94 – 6.87 (m, 2H), 6.62 (br, 2H), 6.28 (dd, *J* = 6.3, 2.1 Hz, 1H), 6.05 (d, *J* = 7.9 Hz, 1H), 4.31 (dd, *J* = 12.9, 5.4 Hz, 1H), 4.06 – 3.98 (m, 2H), 3.83 (s, 3H), 3.53 (td, *J* = 13.0, 2.0 Hz, 1H), 1.97 (d, *J* = 1.9 Hz, 3H), 1.64 (s, 3H);

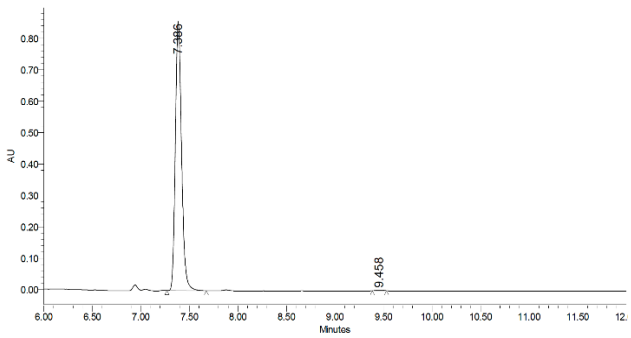
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 167.8, 159.1, 151.0, 144.2, 137.5, 133.4, 133.3, 132.9, 131.7, 130.3, 129.3, 128.1, 127.5, 127.4, 126.5, 123.5, 117.6, 114.1, 114.0, 55.4, 46.7, 45.2, 42.3, 33.1, 31.8, 17.4;

$[\alpha]^{25}_D$ = -132.0 (*c* = 0.5 in acetone, *λ* = 589 nm);

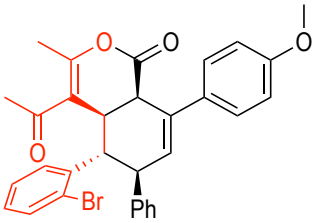
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 7.4 min, t_R (minor) = 9.4 min.



	RT	Area	% Area	Height	% Height
1	7.398	1924974	50.58	434259	76.16
2	9.634	1881149	49.42	135915	23.84



	RT	Area	% Area	Height	% Height
1	7.386	3807639	99.73	857308	99.74
2	9.458	10500	0.27	2192	0.26



(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-5-(2-bromophenyl)-8-(4-methoxyphenyl)-3-methyl-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3k)

15 h, light yellow solid; 58% yield, 99% ee;

HRMS (ESI+): calcd. for $C_{31}H_{27}BrO_4$ +Na^+ [M+Na^+] 565.0985, found 565.0981;

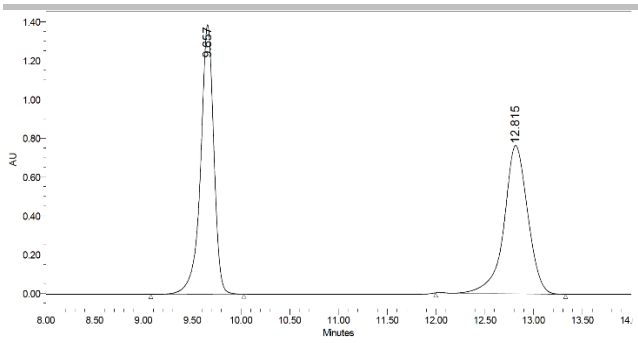
IR: ν_{max} (film, cm^{-1}): 2956, 1772, 1510, 1240, 1100, 1026, 765;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.36 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.17 – 7.10 (m, 3H), 7.02 (td, *J* = 7.6, 1.6 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.23 (d, *J* = 2.8 Hz, 1H), 3.88 – 3.83 (m, 2H), 3.82 (s, 3H), 3.76 (dd, *J* = 12.3, 5.3 Hz, 1H), 3.61 (dd, *J* = 12.2, 10.4 Hz, 1H), 2.15 (s, 3H), 1.64 (s, 3H);

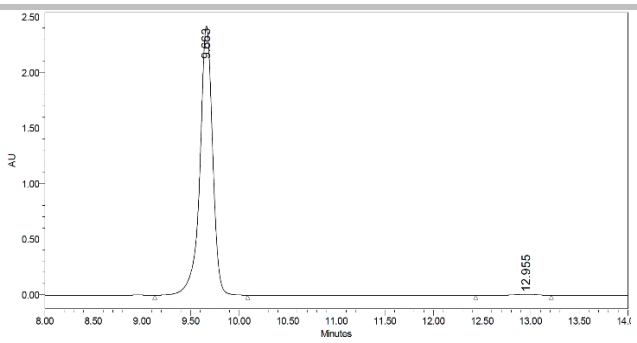
^{13}C NMR (150 MHz, $CDCl_3$) δ 199.0, 168.3, 159.4, 155.9, 141.8, 139.6, 133.1, 132.8, 132.7, 129.7, 129.2, 128.6, 128.5, 128.5, 128.4, 127.5, 127.5, 127.1, 126.9, 120.1, 114.1, 55.5, 50.6, 48.3, 43.5, 40.4, 29.9, 19.0;

$[\alpha]^{25}_D$ = -151.2 (*c* = 0.5 in acetone, *λ* = 589 nm);

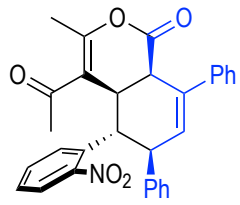
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 9.7 min, t_R (minor) = 12.9 min.



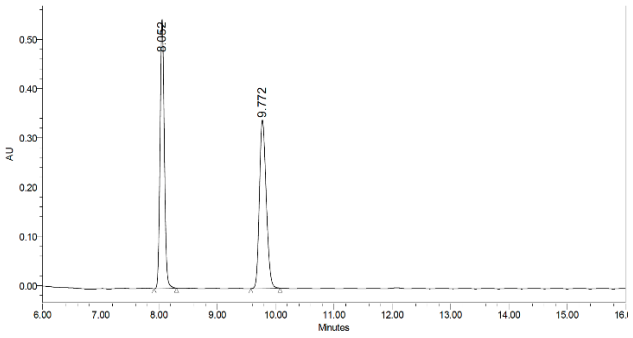
	RT	Area	% Area	Height	% Height
1	9.657	13111515	50.41	1389525	64.53
2	12.815	12899137	49.59	763931	35.47



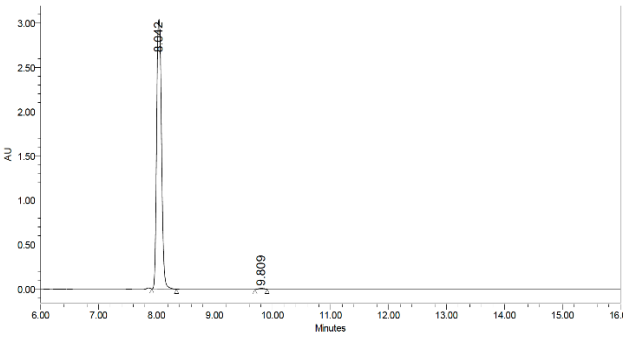
	RT	Area	% Area	Height	% Height
1	9.663	22145256	99.39	2425011	99.63
2	12.955	135517	0.61	9038	0.37



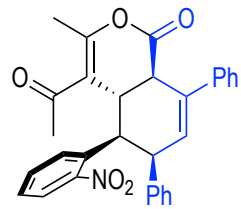
(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-3-methyl-5-(2-nitrophenyl)-6,8-diphenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3l)
13 h, light yellow solid; 45% yield, 99% ee;
HRMS (ESI+): calcd. for $C_{30}H_{25}NO_5$ +Na$^+$ [M+Na$^+$] 502.1625, found 502.1620;
IR: ν_{max} (film, cm^{-1}): 3028, 1768, 1651, 1520, 1102, 750, 698;
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62 – 7.53 (m, 2H), 7.48 – 7.43 (m, 2H), 7.42 – 7.27 (m, 5H), 7.21 – 7.13 (m, 3H), 6.92 – 6.85 (m, 2H), 6.29 (d, *J* = 2.8 Hz, 1H), 3.96 – 3.84 (m, 3H), 3.49 (dd, *J* = 11.8, 10.4 Hz, 1H), 2.19 (s, 3H), 1.74 (s, 3H);
^{13}C NMR (100 MHz, CDCl$_3$) δ 198.6, 167.6, 157.5, 151.8, 141.1, 140.0, 134.0, 134.0, 131.9, 130.2, 130.1, 128.8, 128.7, 128.1, 128.0, 127.9, 127.3, 126.0, 123.4, 119.9, 51.1, 44.2, 43.4, 39.2, 30.2, 19.3;
$[\alpha]^{25}_D$ = -83.2 (*c* = 0.5 in acetone, *λ* = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.0 min, t_R (minor) = 9.8 min.



	RT	Area	% Area	Height	% Height
1	8.052	2782529	49.93	546717	61.52
2	9.772	2790187	50.07	342009	38.48

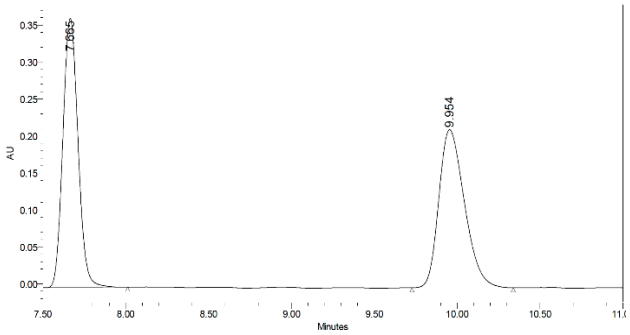


	RT	Area	% Area	Height	% Height
1	8.042	17794065	99.58	3041145	99.63
2	9.809	75102	0.42	11279	0.37

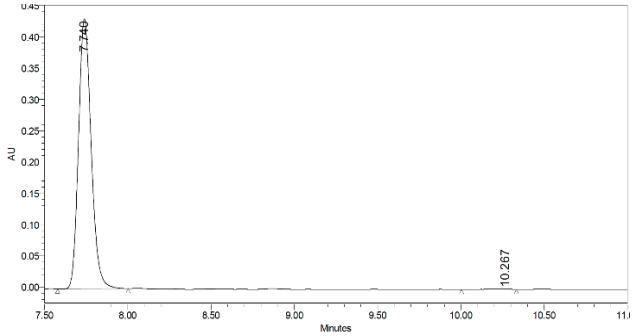


(4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-3-methyl-5-(2-nitrophenyl)-6,8-diphenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (4l)
light yellow solid; 10% yield, >99% ee;
HRMS (ESI+): calcd. for $C_{30}H_{25}NO_5$ +Na$^+$ [M+Na$^+$] 502.1625, found 502.1625;
IR: ν_{max} (film, cm^{-1}): 3031, 1772, 1522, 1359, 1085, 976, 705;

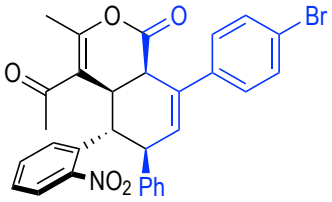
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.21 – 7.09 (m, 3H), 7.04 (td, *J* = 7.6, 1.4 Hz, 1H), 6.76 (br, 2H), 6.37 (dd, *J* = 6.2, 2.0 Hz, 1H), 6.05 (dd, *J* = 8.1, 1.4 Hz, 1H), 4.40 – 4.34 (m, 1H), 4.27 (dd, *J* = 12.8, 5.4 Hz, 1H), 3.98 (dt, *J* = 12.9, 1.7 Hz, 1H), 3.53 (td, *J* = 12.9, 2.0 Hz, 1H), 1.95 (d, *J* = 1.9 Hz, 3H), 1.54 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 167.7, 151.3, 151.0, 140.9, 138.0, 135.1, 133.2, 131.3, 131.1, 130.6, 129.6, 128.6, 128.2, 127.8, 127.5, 127.5, 125.4, 124.7, 123.5, 46.0, 45.3, 39.1, 33.8, 31.6, 17.4;
$[\alpha]^{25}_D$ = -2.4 (*c* = 0.5 in acetone, *λ* = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 7.7 min, t_R (minor) = 10.3 min.



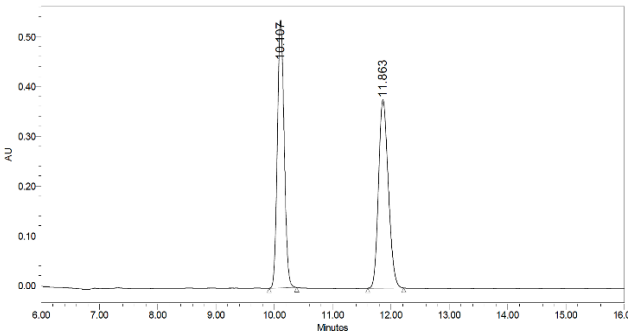
	RT	Area	% Area	Height	% Height
1	7.665	2305615	50.15	363494	62.98
2	9.954	2291546	49.85	213629	37.02



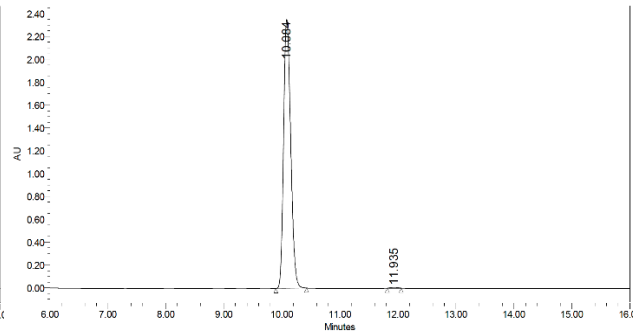
	RT	Area	% Area	Height	% Height
1	7.740	2281447	99.73	431791	99.85
2	10.267	6214	0.27	637	0.15



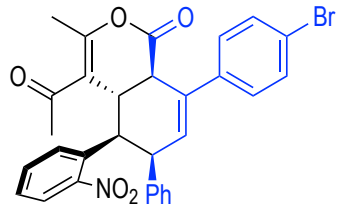
(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-8-(4-bromophenyl)-3-methyl-5-(2-nitrophenyl)-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3m)
13 h, light yellow solid; 48% yield, >99% ee;
HRMS (ESI+): calcd. for $C_{30}H_{24}BrNO_5$ +Na^+ [M+Na^+] 580.0730, found 580.0724;
IR: ν_{max} (film, cm^{-1}): 3025, 1770, 1655, 1526, 1354, 1097, 700;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 7.35 – 7.28 (m, 3H), 7.19 – 7.12 (m, 3H), 6.88 – 6.82 (m, 2H), 6.26 (d, *J* = 2.8 Hz, 1H), 3.91 (dd, *J* = 12.1, 5.3 Hz, 1H), 3.87 – 3.81 (m, 2H), 3.49 (dd, *J* = 12.0, 10.4 Hz, 1H), 2.18 (s, 3H), 1.73 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 167.4, 157.5, 151.8, 140.8, 139.0, 133.8, 133.2, 131.9, 131.8, 130.9, 123.0, 128.9, 128.1, 128.1, 127.7, 127.4, 123.5, 121.9, 119.8, 51.0, 44.0, 43.3, 39.1, 30.2, 19.3;
$[\alpha]^{25}_D$ = -71.2 (*c* = 0.5 in acetone, *λ* = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 10.1 min, t_R (minor) = 11.9 min.



	RT	Area	% Area	Height	% Height
1	10.107	4358728	49.69	538731	58.70
2	11.863	4413544	50.31	378987	41.30



	RT	Area	% Area	Height	% Height
1	10.084	20035795	99.72	2354427	99.71
2	11.935	57132	0.28	6853	0.29



(4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-8-(4-bromophenyl)-3-methyl-5-(2-nitrophenyl)-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (4m)

light yellow solid; 9% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{30}H_{24}BrNO_5$ +Na^+ [M+Na^+] 580.0730, found 580.0726;

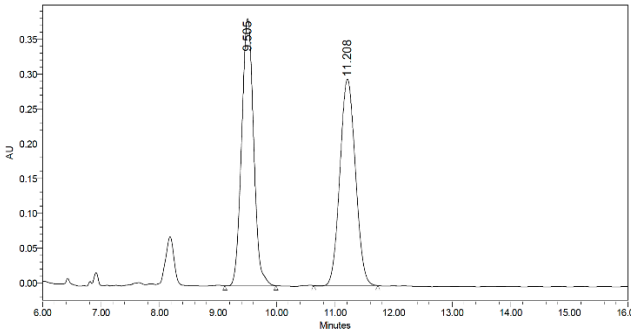
IR: ν_{max} (film, cm^{-1}): 3030, 1770, 1523, 1350, 1073, 975, 705;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.9 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.12 (br, 2H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.74 (br, 2H), 6.34 (d, *J* = 6.1 Hz, 1H), 6.05 (d, *J* = 7.9 Hz, 1H), 4.36 (t, *J* = 5.9 Hz, 1H), 4.26 (dd, *J* = 12.9, 5.4 Hz, 1H), 3.91 (d, *J* = 12.9 Hz, 1H), 3.52 (t, *J* = 12.9 Hz, 1H), 1.94 (s, 3H), 1.53 (s, 3H);

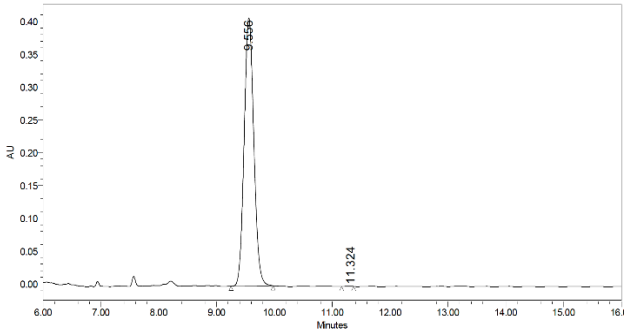
^{13}C NMR (150 MHz, $CDCl_3$) δ 201.1, 167.6, 151.3, 151.0, 140.0, 137.8, 135.0, 132.4, 131.7, 131.7, 131.4, 129.6, 128.3, 127.8, 127.6, 127.2, 124.7, 123.5, 121.4, 46.0, 45.3, 39.1, 33.8, 31.5, 17.4;

$[\alpha]^{25}_D$ = +17.6 (*c* = 0.5 in acetone, *λ* = 589 nm);

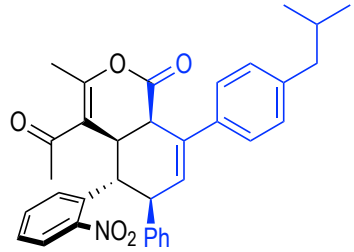
the enantioselectivity was determined by SFC (Trefoil CEL-2, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 9.5 min, t_R (minor) = 11.3 min;



	RT	Area	% Area	Height	% Height
1	9.505	5418639	49.94	383874	56.40
2	11.208	5431871	50.06	296696	43.60



	RT	Area	% Area	Height	% Height
1	9.556	4700518	99.96	408599	99.93
2	11.324	1726	0.04	285	0.07



(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-8-(4-isobutylphenyl)-3-methyl-5-(2-nitrophenyl)-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3n)

15 h, light yellow solid; 46% yield, 99% ee;

HRMS (ESI+): calcd. for $C_{34}H_{33}NO_5$ +Na^+ [M+Na^+] 558.2251, found 558.2242;

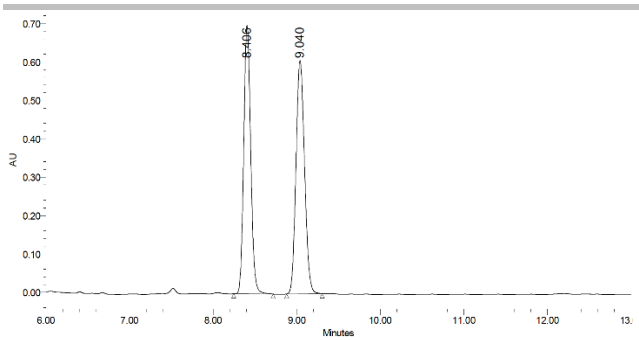
IR: ν_{max} (film, cm^{-1}): 2956, 1772, 1660, 1524, 1353, 1106, 701;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.42 – 7.34 (m, 3H), 7.30 (ddd, *J* = 8.3, 6.7, 1.9 Hz, 1H), 7.20 – 7.09 (m, 5H), 6.89 – 6.86 (m, 2H), 6.27 (d, *J* = 2.8 Hz, 1H), 3.94 – 3.84 (m, 3H), 3.49 (t, *J* = 11.1 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.18 (s, 3H), 1.86 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.74 (s, 3H), 0.90 (d, *J* = 6.6 Hz, 6H);

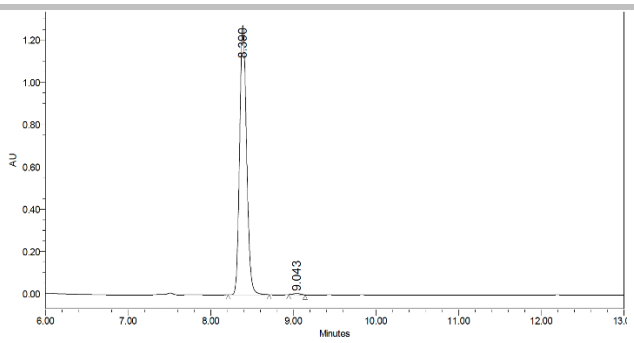
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 167.7, 157.5, 151.8, 141.6, 141.2, 137.3, 134.1, 133.8, 131.8, 130.1, 129.5, 129.3, 128.8, 128.1, 128.0, 127.3, 125.6, 123.4, 119.9, 51.1, 45.2, 44.2, 43.3, 39.2, 31.1, 30.3, 30.2, 22.5, 19.3;

$[\alpha]^{25}_D$ = -115.2 (*c* = 0.5 in acetone, *λ* = 589 nm);

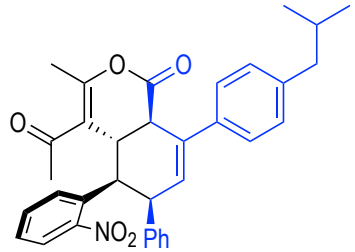
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.4 min, t_R (minor) = 9.0 min.



	RT	Area	% Area	Height	% Height
1	8.406	4007679	48.41	699314	53.50
2	9.040	4271442	51.59	607925	46.50



	RT	Area	% Area	Height	% Height
1	8.390	7429054	99.51	1273724	99.54
2	9.043	36769	0.49	5854	0.46



(4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-8-(4-isobutylphenyl)-3-methyl-5-(2-nitrophenyl)-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (4n)

light yellow solid; 8% yield, 84:16 dr, >99% ee;

HRMS (ESI+): calcd. for $C_{34}H_{33}NO_5$ +Na$^+$ [M+Na$^+$] 558.2251, found 558.2243;

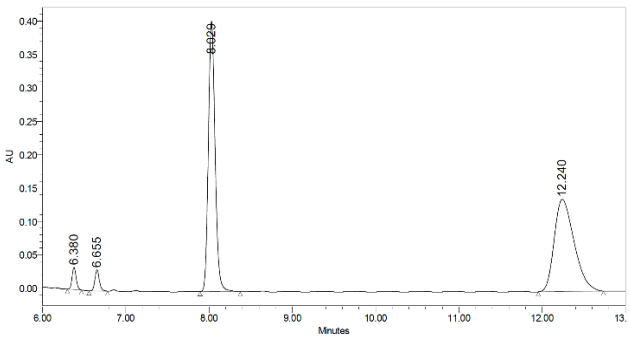
IR: ν_{max} (film, cm^{-1}): 2954, 1777, 1671, 1520, 1352, 1080, 969, 709;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.21 – 7.07 (m, 5H), 7.04 (td, *J* = 7.6, 1.4 Hz, 1H), 6.76 (br, 2H), 6.36 (dd, *J* = 6.2, 2.0 Hz, 1H), 6.04 (dd, *J* = 8.0, 1.3 Hz, 1H), 4.38 – 4.31 (m, 1H), 4.26 (dd, *J* = 12.8, 5.4 Hz, 1H), 3.97 (dt, *J* = 13.0, 1.8 Hz, 1H), 3.52 (td, *J* = 12.8, 1.9 Hz, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.94 (d, *J* = 1.9 Hz, 3H), 1.88 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.54 (s, 3H), 0.91 (d, *J* = 6.6 Hz, 6H);

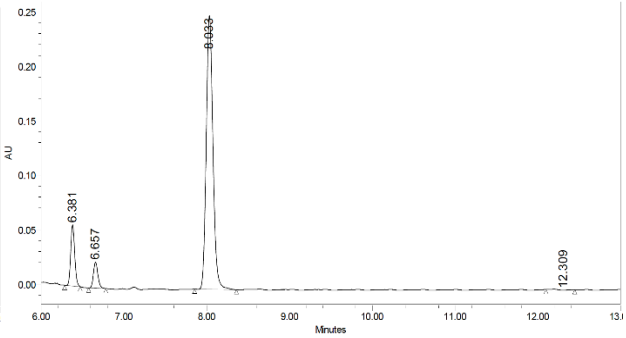
^{13}C NMR (150 MHz, CDCl$_3$) δ 201.3, 167.8, 151.3, 151.0, 141.0, 138.1, 138.1, 135.1, 133.0, 131.3, 130.6, 130.3, 129.6, 129.3, 128.1, 127.7, 127.5, 125.0, 124.7, 123.6, 46.1, 45.3, 45.3, 39.1, 33.8, 31.6, 30.3, 22.6, 17.4;

$[\alpha]^{25}_D$ = -26.4 (*c* = 0.5 in acetone, *λ* = 589 nm);

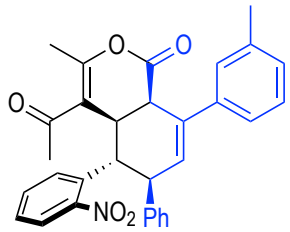
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.0 min, t_R (minor) = 12.3 min.



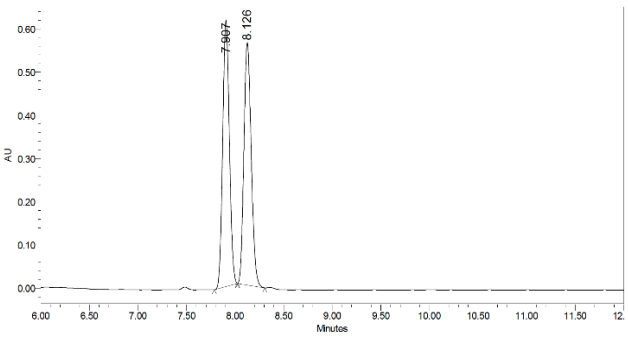
	RT	Area	% Area	Height	% Height
1	6.380	112290	2.33	33220	5.46
2	6.655	115553	2.40	31561	5.19
3	8.029	2286501	47.54	405211	66.64
4	12.240	2294886	47.72	138098	22.71



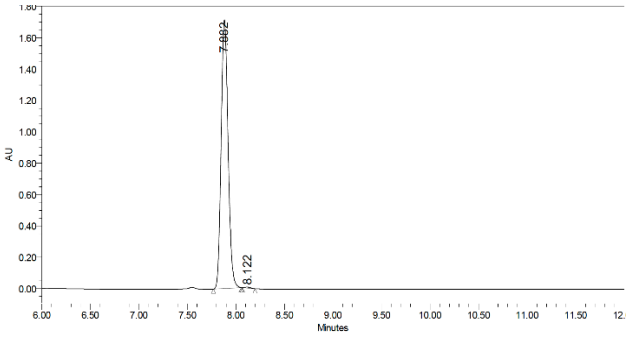
	RT	Area	% Area	Height	% Height
1	6.381	189295	11.12	56000	16.87
2	6.657	89526	5.26	24130	7.27
3	8.033	1417447	83.28	251258	75.68
4	12.309	5830	0.34	-631	0.19



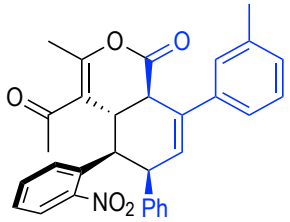
(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-3-methyl-5-(2-nitrophenyl)-6-phenyl-8-(*m*-tolyl)-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3o)
15 h, light yellow solid; 63% yield, >99% ee;
HRMS (ESI+): calcd. for $C_{31}H_{27}NO_5$ +Na$^+$ [M+Na$^+$] 516.1781, found 516.1777;
IR: ν_{max} (film, cm^{-1}): 3027, 1779, 1646, 1526, 1359, 1110, 702;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.42 – 7.38 (m, 1H), 7.30 (ddd, *J* = 8.3, 6.5, 2.1 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.26 – 7.23 (m, 2H), 7.19 – 7.14 (m, 3H), 7.13 – 7.09 (m, 1H), 6.91 – 6.85 (m, 2H), 6.27 (d, *J* = 2.9 Hz, 1H), 3.95 – 3.81 (m, 3H), 3.49 (t, *J* = 11.0 Hz, 1H), 2.36 (s, 3H), 2.19 (s, 3H), 1.74 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 167.6, 157.5, 151.8, 141.2, 139.9, 138.3, 134.0, 131.8, 130.1, 130.0, 128.8, 128.7, 128.6, 128.2, 128.0, 127.3, 126.7, 123.4, 123.1, 119.9, 51.1, 44.2, 43.3, 39.2, 30.2, 21.7, 19.3;
$[\alpha]^{25}_D$ = -85.6 (*c* = 0.5 in acetone, *λ* = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 7.9 min, t_R (minor) = 8.1 min.



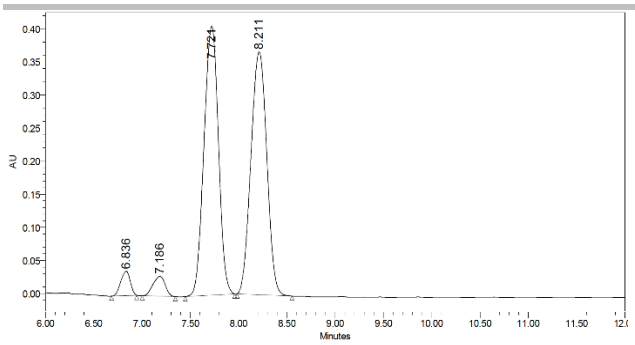
	RT	Area	% Area	Height	% Height
1	7.907	2940506	50.14	615920	52.32
2	8.126	2923667	49.86	561378	47.68



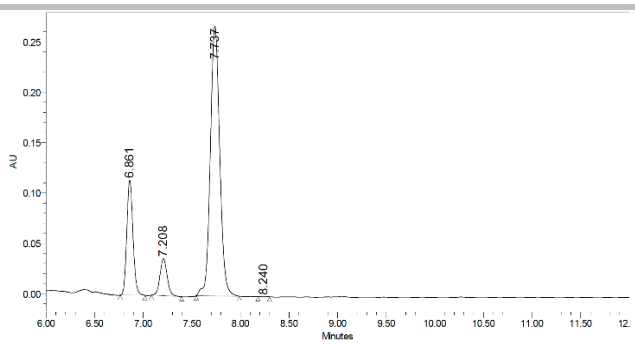
	RT	Area	% Area	Height	% Height
1	7.882	8513513	99.72	1714287	99.64
2	8.122	23865	0.28	6146	0.36



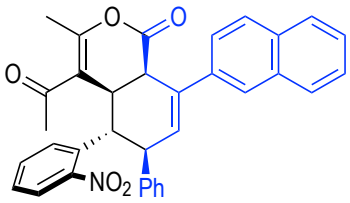
(4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-3-methyl-5-(2-nitrophenyl)-6-phenyl-8-(*m*-tolyl)-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (4o)
light yellow solid; 11% yield, 72:28 dr, >99% ee;
HRMS (ESI+): calcd. for $C_{31}H_{27}NO_5$ +Na$^+$ [M+Na$^+$] 516.1781, found 516.1780;
IR: ν_{max} (film, cm^{-1}): 2921, 1774, 1663, 1523, 1354, 1109, 699;
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.21 – 7.09 (m, 5H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.76 (br, 2H), 6.35 (dd, *J* = 6.2, 2.0 Hz, 1H), 6.05 (d, *J* = 7.9 Hz, 1H), 4.35 (t, *J* = 5.8 Hz, 1H), 4.26 (dd, *J* = 12.9, 5.4 Hz, 1H), 3.97 (dd, *J* = 12.4, 2.3 Hz, 1H), 3.56 – 3.49 (m, 1H), 2.37 (s, 3H), 1.95 (s, 3H), 1.54 (s, 3H);
^{13}C NMR (150 MHz, $CDCl_3$) δ 201.3, 167.8, 151.3, 150.9, 140.9, 138.1, 138.0, 135.1, 133.2, 131.3, 130.9, 129.6, 128.4, 128.3, 128.2, 127.7, 127.5, 126.2, 124.7, 123.5, 122.5, 46.0, 45.3, 39.1, 33.8, 31.6, 21.7, 17.4;
$[\alpha]^{25}_D$ = -2.4 (*c* = 0.5 in acetone, *λ* = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-2, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 7.7 min, t_R (minor) = 8.2 min.



	RT	Area	% Area	Height	% Height
1	6.836	252499	2.82	36982	4.40
2	7.186	263404	2.94	30129	3.58
3	7.721	4240117	47.40	406745	48.35
4	8.211	4189423	46.83	367433	43.68



	RT	Area	% Area	Height	% Height
1	6.861	503327	20.16	114272	27.28
2	7.208	190275	7.62	36692	8.76
3	7.737	1802731	72.20	267773	63.91
4	8.240	534	0.02	-215	0.05



(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-3-methyl-8-(naphthalen-2-yl)-5-(2-nitrophenyl)-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3p)

13 h, light yellow solid; 61% yield, 99% ee;

HRMS (ESI+): calcd. for $C_{34}H_{27}NO_5$ +Na$^+$ [M+Na$^+$] 552.1781, found 552.1779;

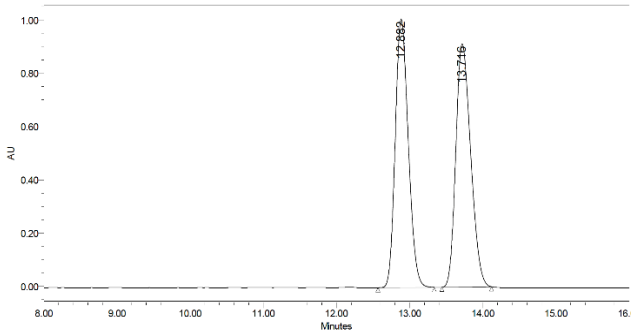
IR: ν_{max} (film, cm^{-1}): 3030, 1770, 1652, 1519, 1354, 1106, 704;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 – 7.78 (m, 4H), 7.63 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.50 – 7.44 (m, 2H), 7.41 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.31 (ddd, *J* = 8.3, 6.8, 1.7 Hz, 1H), 7.22 – 7.15 (m, 3H), 6.95 – 6.88 (m, 2H), 6.43 (d, *J* = 2.9 Hz, 1H), 4.05 (dd, *J* = 5.4, 1.3 Hz, 1H), 3.98 (dd, *J* = 12.1, 5.3 Hz, 1H), 3.94 – 3.89 (m, 1H), 3.55 (dd, *J* = 12.1, 10.5 Hz, 1H), 2.21 (s, 3H), 1.76 (s, 3H);

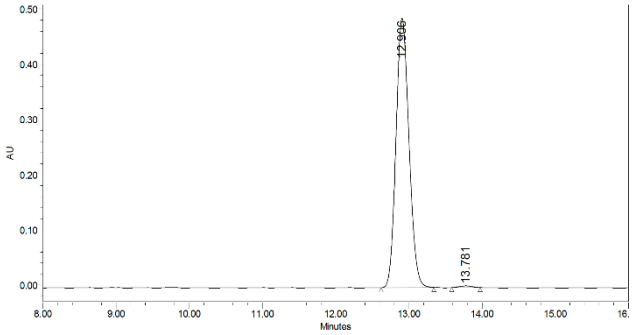
^{13}C NMR (100 MHz, CDCl$_3$) δ 198.6, 167.6, 157.6, 151.8, 141.1, 137.2, 134.0, 133.9, 133.5, 133.0, 131.9, 130.8, 130.0, 128.9, 128.4, 128.2, 128.1, 127.7, 127.4, 126.4, 126.2, 124.8, 124.2, 123.5, 119.9, 51.2, 44.2, 43.4, 39.3, 30.2, 19.3;

$[\alpha]^{25}_D$ = -74.4 (*c* = 0.5 in acetone, *λ* = 589 nm);

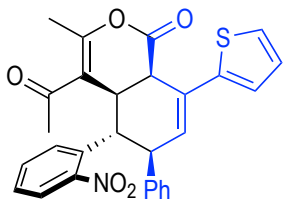
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 12.9 min, t_R (minor) = 13.7 min.



	RT	Area	% Area	Height	% Height
1	12.882	12386261	48.97	1007692	52.45
2	13.716	12905373	51.03	913410	47.55



	RT	Area	% Area	Height	% Height
1	12.906	5971995	99.42	487896	99.37
2	13.781	34899	0.58	3102	0.63



(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-3-methyl-5-(2-nitrophenyl)-6-phenyl-8-(thiophen-2-yl)-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3q)

15 h, light yellow solid; 36% yield, 98% ee;

HRMS (ESI+): calcd. for $C_{28}H_{23}NSO_5$ +Na^+ [M+Na^+] 508.1189, found 508.1196;

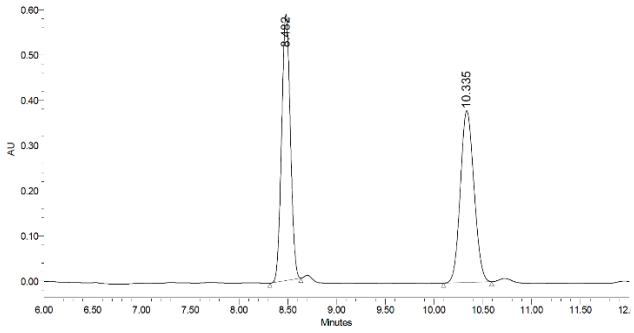
IR: ν_{max} (film, cm^{-1}): 3028, 1776, 1655, 1526, 1353, 1105, 701;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.42 – 7.38 (m, 1H), 7.33 – 7.28 (m, 1H), 7.20 (dd, *J* = 4.4, 1.8 Hz, 1H), 7.17 – 7.13 (m, 3H), 7.02 – 6.98 (m, 2H), 6.87 – 6.82 (m, 2H), 6.34 (d, *J* = 2.9 Hz, 1H), 3.91 (dd, *J* = 12.1, 5.4 Hz, 1H), 3.88 – 3.82 (m, 2H), 3.48 (dd, *J* = 12.1, 10.4 Hz, 1H), 2.20 (s, 3H), 1.74 (s, 3H);

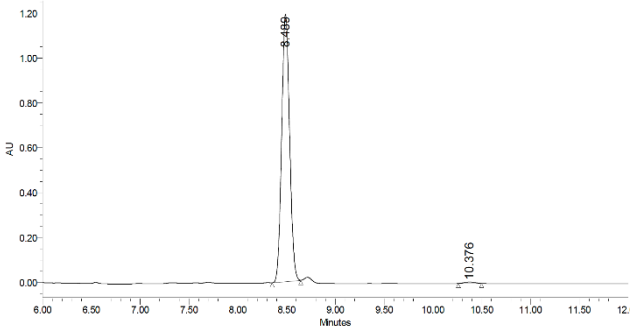
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 167.1, 157.5, 151.8, 144.1, 140.7, 133.7, 131.9, 130.0, 128.8, 128.6, 128.2, 128.1, 127.7, 127.4, 124.6, 123.7, 123.5, 119.7, 50.9, 44.2, 43.9, 38.9, 30.2, 19.3;

$[\alpha]^{25}_D$ = -180.0 (*c* = 0.5 in acetone, *λ* = 589 nm);

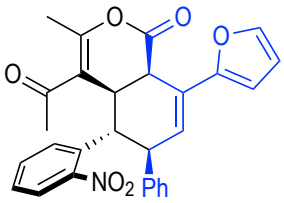
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.5 min, t_R (minor) = 10.4 min.



	RT	Area	% Area	Height	% Height
1	8.482	3660726	49.70	588582	60.79
2	10.335	3705633	50.30	379687	39.21



	RT	Area	% Area	Height	% Height
1	8.489	6710350	99.28	1191539	99.47
2	10.376	48742	0.72	6372	0.53



(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-8-(furan-2-yl)-3-methyl-5-(2-nitrophenyl)-6-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3r)

15 h, light yellow solid; 34% yield, 98% ee;

HRMS (ESI+): calcd. for $C_{28}H_{23}NO_6$ +Na^+ [M+Na^+] 492.1418, found 492.1422;

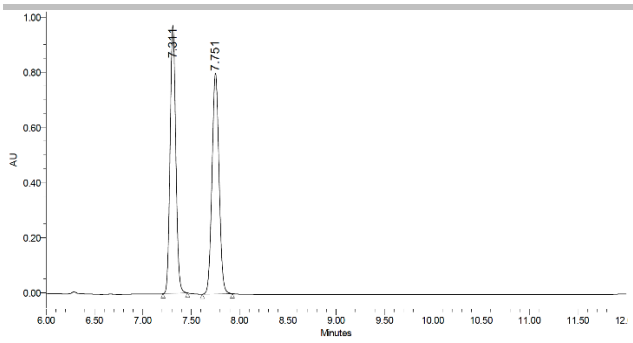
IR: ν_{max} (film, cm^{-1}): 3140, 1774, 1663, 1524, 1109, 759, 700;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 4.1 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.32 – 7.27 (m, 1H), 7.16 – 7.11 (m, 3H), 6.87 – 6.82 (m, 2H), 6.44 (d, *J* = 3.0 Hz, 1H), 6.42 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.31 (d, *J* = 3.4 Hz, 1H), 3.90 – 3.84 (m, 2H), 3.81 (dd, *J* = 5.5, 1.4 Hz, 1H), 3.48 (dd, *J* = 12.0, 10.3 Hz, 1H), 2.19 (s, 3H), 1.73 (s, 3H);

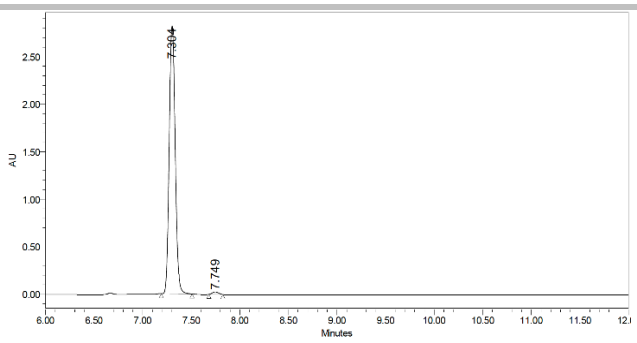
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 167.0, 157.4, 153.2, 151.7, 142.1, 140.8, 133.8, 131.9, 130.0, 128.8, 128.1, 127.3, 126.8, 124.4, 123.5, 119.6, 111.6, 106.1, 50.6, 44.2, 41.4, 38.6, 30.2, 19.3;

$[\alpha]^{25}_D$ = -146.4 (*c* = 0.5 in acetone, *λ* = 589 nm);

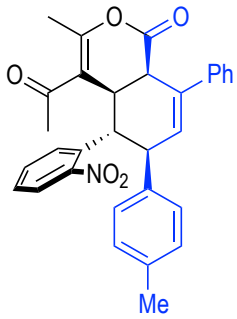
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 7.3 min, t_R (minor) = 7.7 min.



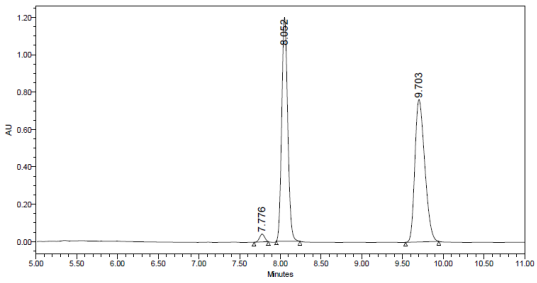
	RT	Area	% Area	Height	% Height
1	7.311	3998822	49.64	972949	54.84
2	7.751	4056809	50.36	801134	45.16



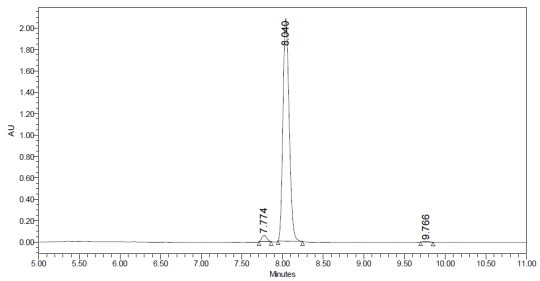
	RT	Area	% Area	Height	% Height
1	7.304	12134720	99.03	2819427	99.05
2	7.749	119267	0.97	27079	0.95



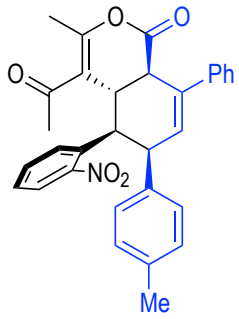
(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-3-methyl-5-(2-nitrophenyl)-8-phenyl-6-(*p*-tolyl)-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3s)
15 h, light yellow solid; 44% yield, 97:3 dr, 99% ee;
HRMS (ESI+): calcd. for $C_{31}H_{27}NO_5$ +Na$^+$ [M+Na$^+$] 516.1781, found 516.1778;
IR: ν_{max} (film, cm^{-1}): 3025, 1763, 1626, 1520, 1355, 1097, 742;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.47 – 7.40 (m, 3H), 7.38 – 7.27 (m, 4H), 6.99 – 6.94 (m, 2H), 6.81 – 6.75 (m, 2H), 6.26 (d, *J* = 2.8 Hz, 1H), 3.94 – 3.80 (m, 3H), 3.55 – 3.46 (m, 1H), 2.24 (s, 3H), 2.18 (s, 3H), 1.74 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 167.6, 157.5, 151.8, 140.0, 138.0, 136.9, 134.2, 133.7, 131.9, 130.6, 130.0, 129.5, 128.7, 128.0, 127.8, 126.0, 123.5, 119.9, 50.6, 44.0, 43.4, 39.3, 30.2, 21.2, 19.3; (one aromatic carbon signal overlaps with others in the 120-135 ppm region)
[α]$^{25}_D$ = -112.0 (*c* = 0.5 in acetone, *λ* = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.0 min, t_R (minor) = 9.7 min.



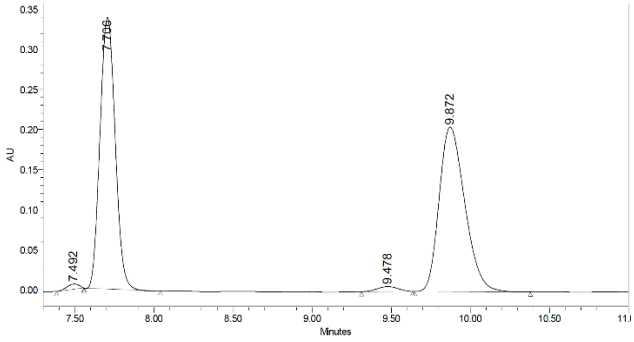
	RT	Area	% Area	Height	% Height
1	7.776	182820	1.44	41313	2.07
2	8.052	6111922	48.13	1196928	59.85
3	9.703	6404242	50.43	761690	38.09



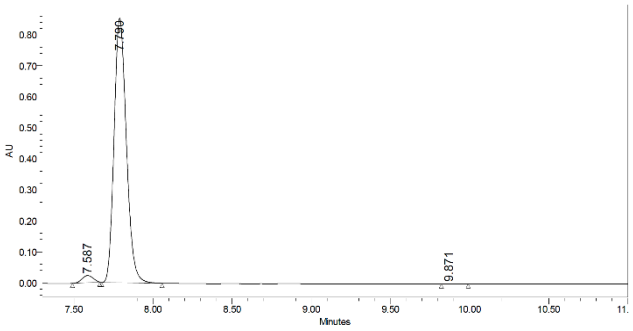
	RT	Area	% Area	Height	% Height
1	7.774	249744	2.21	59025	2.76
2	8.040	11038495	97.57	2077789	97.02
3	9.766	25049	0.22	4696	0.22



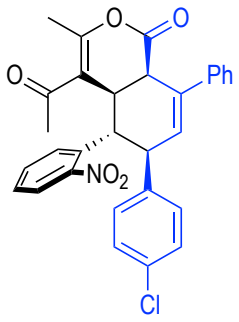
(4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-3-methyl-5-(2-nitrophenyl)-8-phenyl-6-(*p*-tolyl)-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (4s)
light yellow solid; 7% yield, >99% ee;
HRMS (ESI+): calcd. for $C_{31}H_{27}NO_5$ +Na$^+$ [M+Na$^+$] 516.1781, found 516.1779;
IR: ν_{max} (film, cm^{-1}): 2924, 1765, 1676, 1521, 1364, 1088, 726;
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.40 – 7.27 (m, 6H), 7.07 (td, *J* = 7.7, 1.4 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.64 (br, 2H), 6.35 (dd, *J* = 6.2, 2.0 Hz, 1H), 6.09 (d, *J* = 7.9 Hz, 1H), 4.31 (t, *J* = 5.5 Hz, 1H), 4.24 (dd, *J* = 12.7, 5.4 Hz, 1H), 3.97 (dt, *J* = 13.0, 1.7 Hz, 1H), 3.53 (td, *J* = 12.8, 2.0 Hz, 1H), 2.28 (s, 3H), 1.94 (d, *J* = 1.8 Hz, 3H), 1.54 (s, 3H);
^{13}C NMR (150 MHz, CDCl$_3$) δ 201.3, 167.8, 151.3, 150.9, 141.0, 137.2, 135.2, 134.7, 132.9, 131.4, 129.8, 128.9, 128.6, 127.7, 127.4, 125.4, 124.6, 123.6, 45.7, 45.4, 39.2, 33.8, 31.6, 21.1, 17.4; (one aromatic carbon signal is overlap among 120-135 ppm)
$[\alpha]^{25}_D$ = -7.2 (*c* = 0.5 in acetone, *λ* = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 7.7 min, t_R (minor) = 9.9 min.



	RT	Area	% Area	Height	% Height
1	7.492	34734	0.74	6505	1.17
2	7.706	2269195	48.55	338724	60.83
3	9.478	57127	1.22	6260	1.12
4	9.872	2312656	49.48	205384	36.88

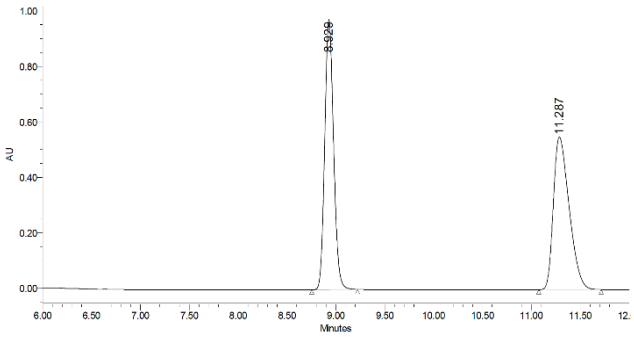


	RT	Area	% Area	Height	% Height
1	7.587	111044	2.36	23011	2.63
2	7.790	4599026	97.62	852902	97.34
3	9.871	1055	0.02	266	0.03

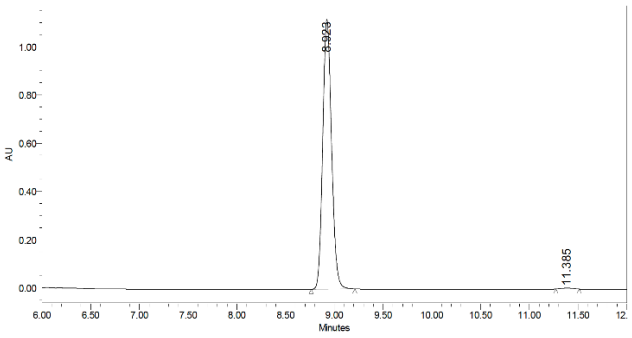


(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-6-(4-chlorophenyl)-3-methyl-5-(2-nitrophenyl)-8-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3t)
15 h, light yellow solid; 49% yield, 99% ee;
HRMS (ESI+): calcd. for $C_{30}H_{24}ClNO_5$ +Na$^+$ [M+Na$^+$] 536.1235, found 536.1238;
IR: ν_{max} (film, cm^{-1}): 3026, 1764, 1627, 1519, 1356, 1092, 743;
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56 (d, *J* = 3.9 Hz, 2H), 7.46 – 7.44 (m, 1H), 7.44 – 7.41 (m, 2H), 7.39 – 7.28 (m, 4H), 7.16 – 7.11 (m, 2H), 6.85 – 6.80 (m, 2H), 6.22 (d, *J* = 2.7 Hz, 1H), 3.91 (t, *J* = 6.1 Hz, 1H), 3.89 – 3.85 (m, 2H), 3.44 (dd, *J* = 11.7, 10.5 Hz, 1H), 2.19 (s, 3H), 1.74 (s, 3H);
^{13}C NMR (100 MHz, CDCl$_3$) δ 198.4, 167.5, 157.8, 151.8, 139.8, 139.6, 134.5, 133.6, 133.2, 131.9, 129.9, 129.6, 129.5, 129.0, 128.8, 128.2, 128.0, 126.0, 123.6, 119.8, 50.3, 44.0, 43.4, 39.2, 30.2, 19.3;

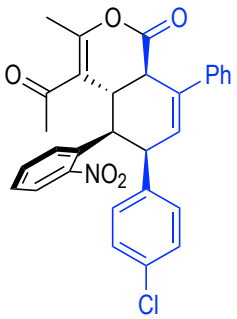
$[\alpha]^{25}_D$ = -113.6 (*c* = 0.5 in acetone, λ = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 8.9 min, t_R (minor) = 11.3 min.



	RT	Area	% Area	Height	% Height
1	8.929	6140063	49.98	974316	63.89
2	11.287	6144707	50.02	550572	36.11

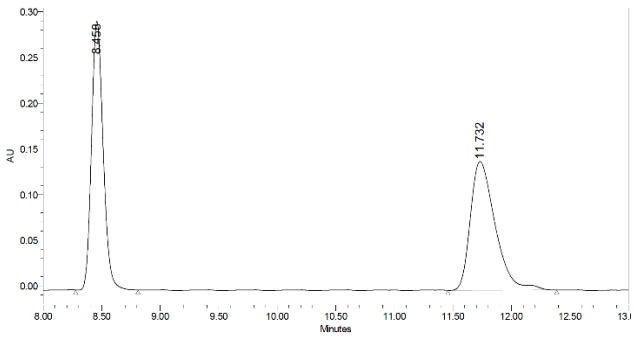


	RT	Area	% Area	Height	% Height
1	8.923	7057476	99.57	1118115	99.64
2	11.385	30398	0.43	3997	0.36

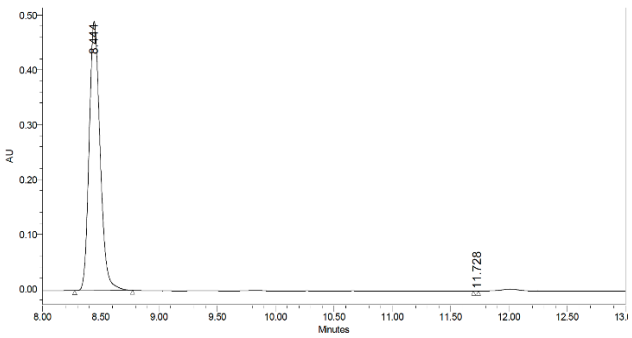


(4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-6-(4-chlorophenyl)-3-methyl-5-(2-nitrophenyl)-8-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (4t)

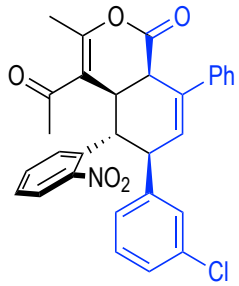
light yellow solid; 7% yield, >99% ee;
HRMS (ESI+): calcd. for $C_{30}H_{24}ClNO_5$ +Na^+ [M+Na^+] 536.1235, found 536.1233;
IR: ν_{max} (film, cm^{-1}): 3060, 1768, 1672, 1522, 1088, 728, 699;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.39 – 7.28 (m, 6H), 7.16 – 7.07 (m, 3H), 6.69 (br, 2H), 6.32 (dd, *J* = 6.2, 2.0 Hz, 1H), 6.12 (dd, *J* = 8.0, 1.3 Hz, 1H), 4.36 (td, *J* = 5.9, 1.5 Hz, 1H), 4.27 (dd, *J* = 12.8, 5.4 Hz, 1H), 3.97 (dt, *J* = 13.0, 1.8 Hz, 1H), 3.50 – 3.41 (m, 1H), 1.96 (d, *J* = 1.8 Hz, 3H), 1.55 (s, 3H);
^{13}C NMR (150 MHz, $CDCl_3$) δ 201.2, 167.6, 151.2, 140.6, 136.6, 134.8, 133.7, 133.6, 131.6, 130.5, 129.5, 128.6, 128.3, 128.0, 127.7, 125.4, 124.9, 123.3, 45.4, 45.3, 39.0, 33.7, 31.6, 17.4;
$[\alpha]^{25}_D$ = -13.6 (*c* = 0.5 in acetone, λ = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 8.4 min, t_R (minor) = 11.7 min.



	RT	Area	% Area	Height	% Height
1	8.458	2023483	49.36	294046	67.62
2	11.732	2076187	50.64	140816	32.38



	RT	Area	% Area	Height	% Height
1	8.444	3182034	100.00	491135	100.00
2	11.728	14	0.00	18	0.00



(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-6-(3-chlorophenyl)-3-methyl-5-(2-nitrophenyl)-8-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3u)

15 h, light yellow solid; 46% yield, 99% ee;

HRMS (ESI+): calcd. for $C_{30}H_{24}ClNO_5$ +Na^+ [M+Na^+] 536.1235, found 536.1232;

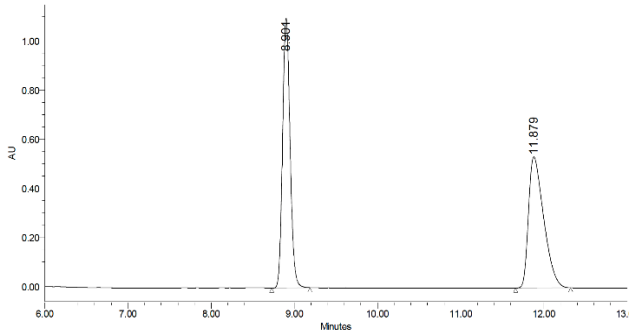
IR: ν_{max} (film, cm^{-1}): 3024, 1778, 1649, 1525, 1115, 763, 698;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.46 – 7.42 (m, 3H), 7.39 – 7.28 (m, 4H), 7.17 – 7.09 (m, 2H), 6.86 (td, *J* = 4.2, 1.7 Hz, 1H), 6.80 (d, *J* = 1.2 Hz, 1H), 6.23 (d, *J* = 2.7 Hz, 1H), 3.95 – 3.83 (m, 3H), 3.46 (t, *J* = 11.1 Hz, 1H), 2.19 (s, 3H), 1.75 (s, 3H);

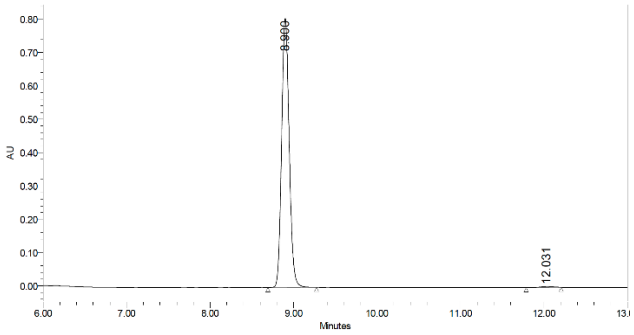
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 167.4, 157.8, 151.82 143.1, 139.8, 134.6, 134.4, 133.4, 132.0, 130.3, 129.9, 129.3, 128.8, 128.3, 128.1, 127.6, 126.2, 126.0, 123.6, 119.7, 50.6, 43.8, 43.4, 39.2, 30.2, 19.3;

$[\alpha]^{25}_D$ = -131.2 (*c* = 0.5 in acetone, *λ* = 589 nm);

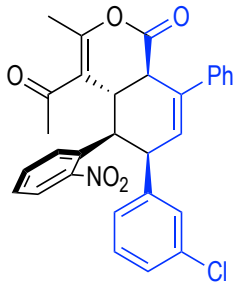
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.9 min, t_R (minor) = 12.0 min.



	RT	Area	% Area	Height	% Height
1	8.901	6874870	50.45	1096222	67.28
2	11.879	6752117	49.55	533091	32.72



	RT	Area	% Area	Height	% Height
1	8.900	5064992	99.44	807424	99.67
2	12.031	28331	0.56	2660	0.33



(4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-6-(3-chlorophenyl)-3-methyl-5-(2-nitrophenyl)-8-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (4u)

light yellow solid; 7% yield, 63:37 dr, >99% ee;

HRMS (ESI+): calcd. for $C_{30}H_{24}ClNO_5$ +Na^+ [M+Na^+] 536.1235, found 536.1234;

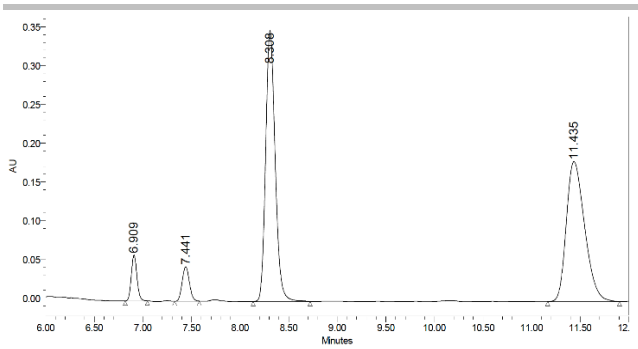
IR: ν_{max} (film, cm^{-1}): 2920, 1769, 1522, 1350, 1087, 979, 753;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.35 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.14 – 7.06 (m, 2H), 6.78 – 6.54 (m, 3H), 6.32 (d, *J* = 6.0 Hz, 1H), 6.12 (d, *J* = 7.9 Hz, 1H), 4.35 (t, *J* = 6.0 Hz, 1H), 4.29 (dd, *J* = 13.0, 5.4 Hz, 1H), 3.97 (d, *J* = 13.0 Hz, 1H), 3.46 (t, *J* = 13.1 Hz, 1H), 1.95 (s, 3H), 1.55 (s, 3H);

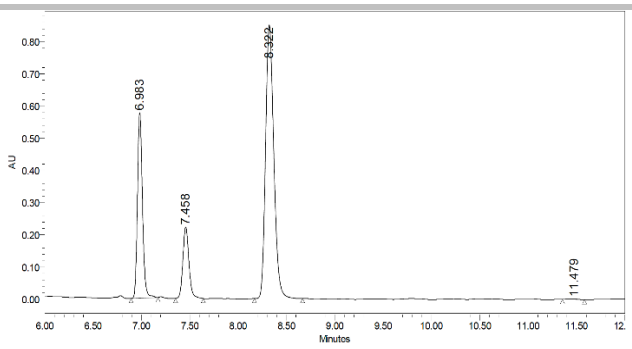
^{13}C NMR (150 MHz, $CDCl_3$) δ 201.2, 167.4, 151.3, 151.2, 140.7, 140.4, 134.8, 134.2, 134.0, 131.4, 130.2, 129.4, 129.4, 128.6, 128.1, 127.7, 127.7, 125.5, 124.9, 123.3, 45.8, 45.3, 39.1, 33.8, 31.6 17.4;

$[\alpha]^{25}_D$ = -3.2 (*c* = 0.5 in acetone, *λ* = 589 nm);

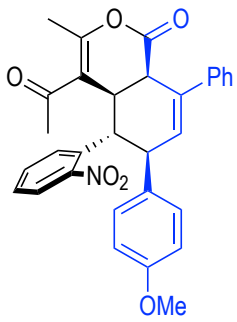
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.3 min, t_R (minor) = 11.5 min.



	RT	Area	% Area	Height	% Height
1	6.909	236803	4.54	58989	9.31
2	7.441	229460	4.40	44524	7.03
3	8.308	2379980	45.60	349591	55.16
4	11.435	2373188	45.47	180683	28.51



	RT	Area	% Area	Height	% Height
1	6.983	2052260	25.51	576120	34.94
2	7.458	954317	11.86	221514	13.44
3	8.322	5027833	62.50	849506	51.53
4	11.479	9673	0.12	1512	0.09



(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-6-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-8-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3v)

13 h, light yellow solid; 86% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{31}H_{27}NO_6$ +Na^+ [M+Na^+] 532.1731, found 532.1725;

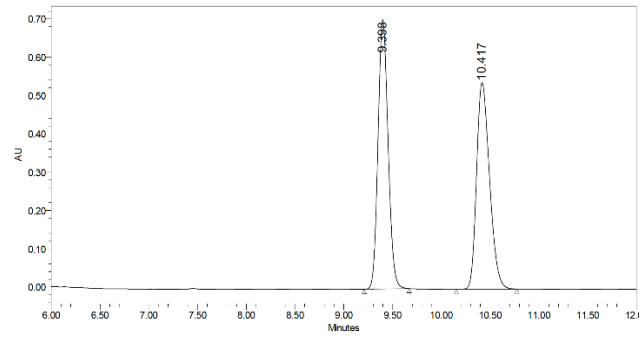
IR: ν_{max} (film, cm^{-1}): 2836, 1764, 1661, 1509, 1238, 1095, 759;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.47 – 7.40 (m, 3H), 7.38 – 7.27 (m, 4H), 6.83 – 6.77 (m, 2H), 6.72 – 6.66 (m, 2H), 6.26 (d, *J* = 2.9 Hz, 1H), 3.93 – 3.85 (m, 2H), 3.82 (dd, *J* = 10.3, 2.4 Hz, 1H), 3.72 (s, 3H), 3.48 (t, *J* = 10.8 Hz, 1H), 2.18 (s, 3H), 1.74 (s, 3H);

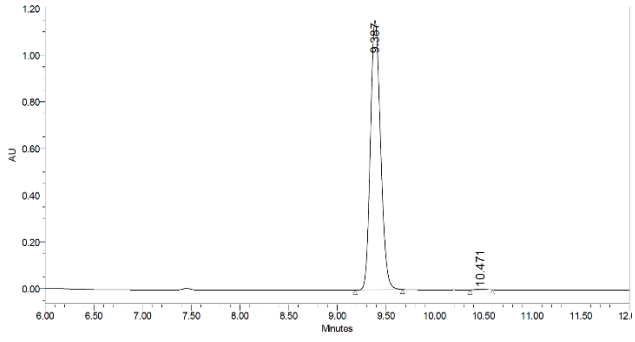
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 167.6, 158.8, 157.5, 151.8, 140.0, 134.2, 133.7, 133.1, 131.9, 130.7, 130.0, 129.1, 128.7, 128.0, 127.8, 126.0, 123.5, 119.9, 114.2, 55.3, 50.2, 44.2, 43.4, 39.3, 30.2, 19.3;

$[\alpha]^{25}_D$ = -108.0 (*c* = 0.5 in acetone, *λ* = 589 nm);

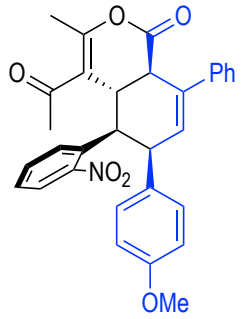
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 9.4 min, t_R (minor) = 10.5 min.



	RT	Area	% Area	Height	% Height
1	9.398	5067407	50.35	702844	56.59
2	10.417	4996239	49.65	539163	43.41



	RT	Area	% Area	Height	% Height
1	9.387	8393477	99.75	1153802	99.75
2	10.471	20913	0.25	2862	0.25



(4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-6-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-8-phenyl-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (4v)

light yellow solid; 7% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{31}H_{27}NO_6$ +Na$^+$ [M+Na$^+$] 532.1731, found 532.1725;

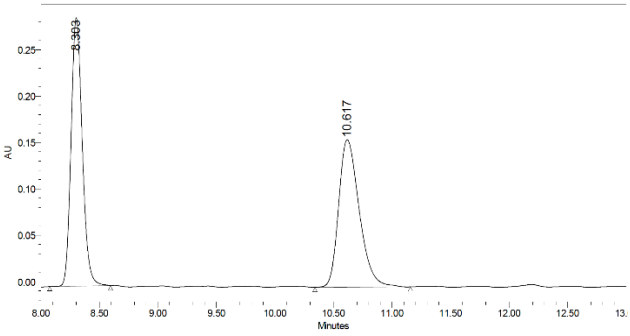
IR: ν_{max} (film, cm^{-1}): 3007, 1761, 1678, 1511, 1254, 1075, 728;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.27 (m, 7H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.67 (br, 3H), 6.35 (d, *J* = 6.1 Hz, 1H), 6.11 (d, *J* = 7.9 Hz, 1H), 4.30 (t, *J* = 5.8 Hz, 1H), 4.23 (dd, *J* = 12.7, 5.3 Hz, 1H), 4.03 – 3.90 (m, 1H), 3.76 (d, *J* = 1.2 Hz, 3H), 3.50 (t, *J* = 12.8 Hz, 1H), 1.94 (s, 3H), 1.55 (d, *J* = 1.1 Hz, 3H);

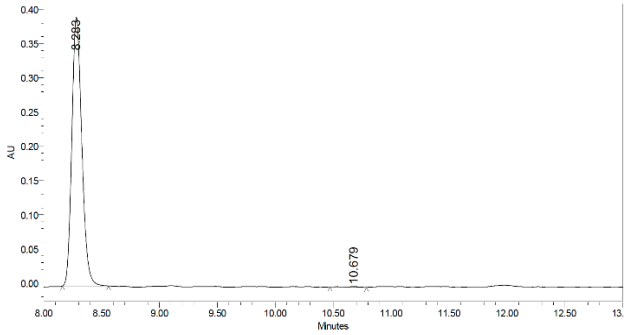
^{13}C NMR (150 MHz, CDCl$_3$) δ 201.3, 167.8, 159.1, 151.3, 150.9, 140.9, 135.2, 132.8, 131.4, 131.4, 129.8, 128.6, 127.7, 127.5, 125.4, 124.6, 123.6, 113.5, 55.4, 45.3, 45.3, 39.2, 33.8, 31.6, 17.4;

$[\alpha]^{25}_D$ = -12.8 (*c* = 0.5 in acetone, *λ* = 589 nm);

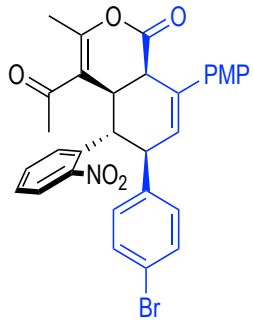
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.3 min, t_R (minor) = 10.7 min.



	RT	Area	% Area	Height	% Height
1	8.303	1912552	49.67	289146	64.53
2	10.617	1937732	50.33	158925	35.47



	RT	Area	% Area	Height	% Height
1	8.283	2351129	99.68	392545	99.77
2	10.679	7522	0.32	909	0.23



(4a*R*,5*S*,6*R*,8a*R*)-4-acetyl-6-(4-bromophenyl)-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (3w)

15 h, light yellow solid; 71% yield, 99% ee;

HRMS (ESI+): calcd. for $C_{31}H_{26}BrNO_6$ +Na$^+$ [M+Na$^+$] 610.0836, found 610.0829;

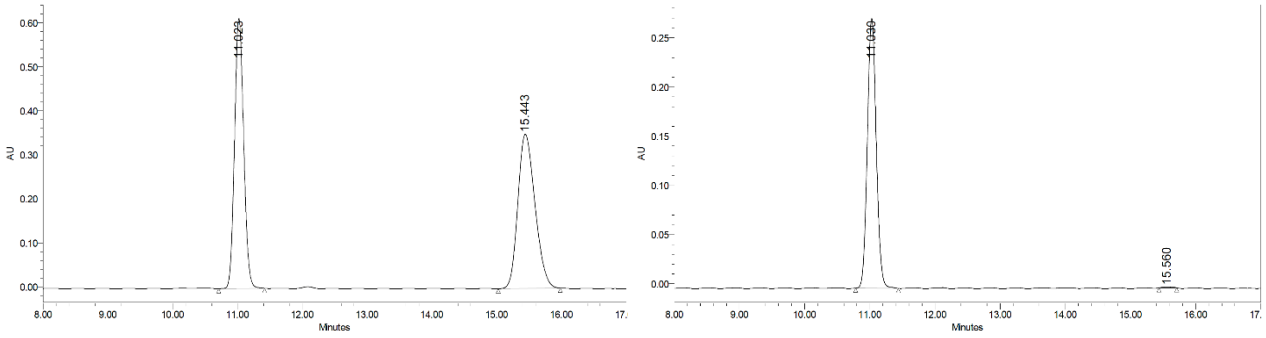
IR: ν_{max} (film, cm^{-1}): 2958, 1776, 1510, 1356, 1241, 1098, 823;

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 – 7.52 (m, 2H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.26 (m, 5H), 6.93 – 6.86 (m, 2H), 6.80 – 6.73 (m, 2H), 6.13 (d, *J* = 2.8 Hz, 1H), 3.91 – 3.82 (m, 3H), 3.81 (s, 3H), 3.41 (dd, *J* = 12.0, 10.4 Hz, 1H), 2.18 (s, 3H), 1.74 (s, 3H);

^{13}C NMR (100 MHz, CDCl$_3$) δ 198.4, 167.6, 159.5, 157.7, 151.8, 140.4, 133.8, 133.6, 132.3, 131.9, 129.9, 129.8, 128.2, 127.9, 127.1, 123.6, 121.2, 119.8, 114.1, 55.5, 50.4, 43.9, 43.4, 39.2, 30.2, 19.3;

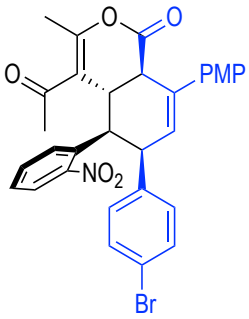
$[\alpha]^{25}_D$ = -99.2 (*c* = 0.5 in acetone, *λ* = 589 nm);

the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 11.0 min, t_R (minor) = 15.5 min.



	RT	Area	% Area	Height	% Height
1	11.023	5952782	48.02	613553	63.65
2	15.443	6443171	51.98	350367	36.35

	RT	Area	% Area	Height	% Height
1	11.030	2587525	99.63	274150	99.68
2	15.560	9667	0.37	888	0.32



(4a*S*,5*R*,6*R*,8a*R*)-4-acetyl-6-(4-bromophenyl)-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-4a,5,6,8a-tetrahydro-1*H*-isochromen-1-one (4w)

light yellow solid; 6% yield, >99% ee;

HRMS (ESI+): calcd. for $C_{31}H_{26}BrNO_6$ +Na^+ [M+Na^+] 610.0836, found 610.0831;

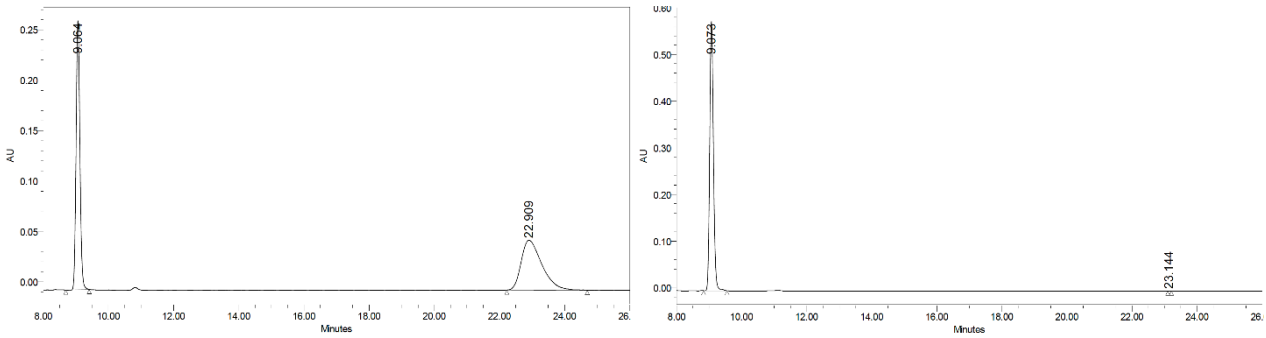
IR: ν_{max} (film, cm^{-1}): 2928, 1778, 1673, 1511, 1349, 1072, 822, 732;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.25 – 7.23 (m, 1H), 7.14 (td, *J* = 7.7, 1.4 Hz, 1H), 6.95 – 6.85 (m, 2H), 6.62 (br, 2H), 6.25 (dd, *J* = 6.1, 2.0 Hz, 1H), 6.11 (dd, *J* = 8.0, 1.3 Hz, 1H), 4.37 – 4.30 (m, 1H), 4.26 (dd, *J* = 12.7, 5.4 Hz, 1H), 3.92 (dt, *J* = 13.0, 1.7 Hz, 1H), 3.83 (s, 3H), 3.43 (ddd, *J* = 14.8, 11.9, 2.0 Hz, 1H), 1.95 (d, *J* = 1.8 Hz, 3H), 1.55 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 201.2, 167.7, 159.2, 151.3, 151.2, 137.2, 134.8, 133.1, 132.2, 131.6, 131.2, 129.5, 129.1, 128.0, 126.4, 124.8, 123.4, 121.6, 114.0, 55.4, 45.5, 45.3, 38.9, 33.8, 31.5, 17.4.

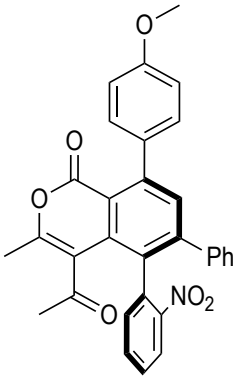
$[\alpha]^{25}_D$ = +27.2 (*c* = 0.5 in acetone, λ = 589 nm);

the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 9.1 min, t_R (minor) = 23.1 min.

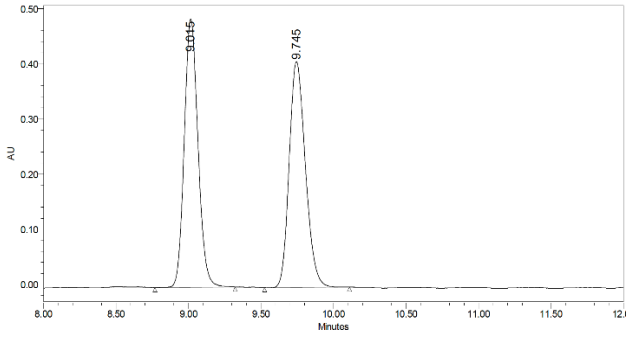


	RT	Area	% Area	Height	% Height
1	9.064	2194593	50.25	266630	84.38
2	22.909	2173031	49.75	49372	15.62

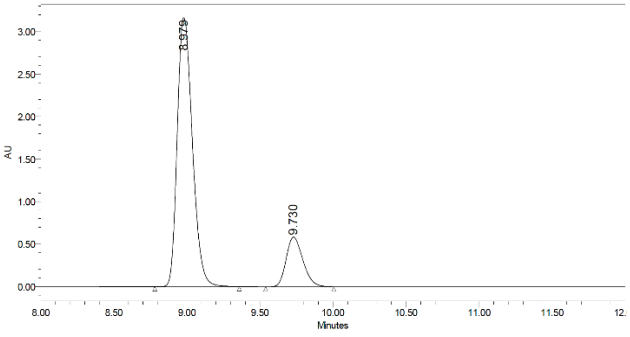
	RT	Area	% Area	Height	% Height
1	9.073	4618320	99.99	577093	99.98
2	23.144	414	0.01	135	0.02



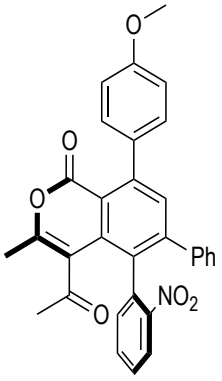
(*S*)-4-acetyl-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-6-phenyl-1*H*-isochromen-1-one (*S*-6)
light yellow solid; 80% yield, 83:17 er;
HRMS (ESI+): calcd. for $C_{31}H_{23}NO_6$ +H^+ [M+H^+] 506.1598, found 506.1598;
IR: ν_{max} (film, cm^{-1}): 2840, 1738, 1692, 1515, 1337, 1040, 700;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.57 (td, *J* = 7.5, 1.4 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.42 (s, 1H), 7.39 – 7.32 (m, 3H), 7.20 – 7.08 (m, 3H), 7.00 – 6.95 (m, 2H), 6.89 – 6.85 (m, 2H), 3.87 (s, 3H), 2.17 (s, 3H), 1.83 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 159.5, 159.5, 153.0, 149.5, 147.5, 146.3, 139.1, 137.0, 134.8, 134.1, 133.6, 133.0, 132.6, 131.6, 130.3, 129.9, 129.1, 128.1, 127.8, 125.0, 118.9, 117.7, 113.6, 55.4, 32.0, 18.2;
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 9.0 min, t_R (minor) = 9.7 min.



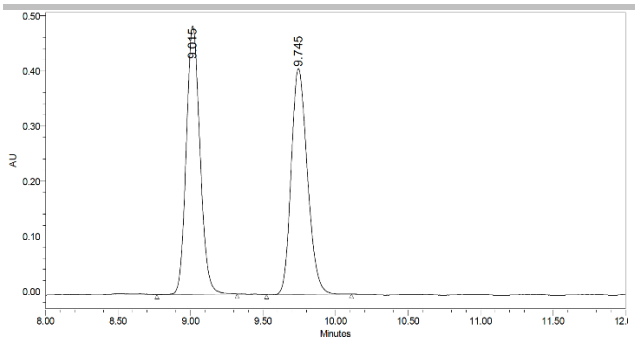
	RT	Area	% Area	Height	% Height
1	9.015	3185028	50.06	486329	54.30
2	9.745	3177250	49.94	409280	45.70



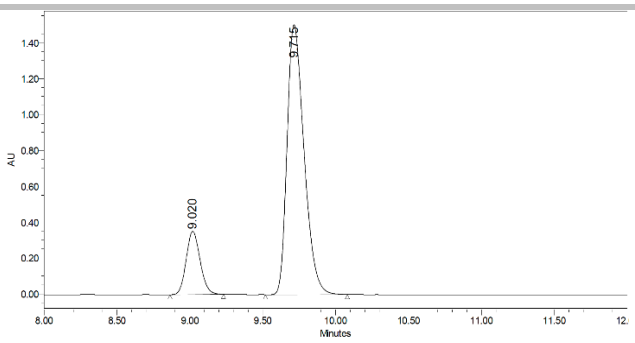
	RT	Area	% Area	Height	% Height
1	8.979	22689842	82.94	3165224	84.42
2	9.730	4668391	17.06	584259	15.58



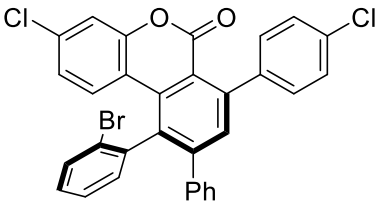
(*R*)-4-acetyl-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-6-phenyl-1*H*-isochromen-1-one (*R*-6)
light yellow solid; 80% yield, 84:16 er;
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 9.7 min, t_R (minor) = 9.0 min.



	RT	Area	% Area	Height	% Height
1	9.015	3185028	50.06	486329	54.30
2	9.745	3177250	49.94	409280	45.70



	RT	Area	% Area	Height	% Height
1	9.020	2340601	16.17	352566	18.99
2	9.715	12131830	83.83	1504112	81.01



(*R*)-10-(2-bromophenyl)-3-chloro-7-(4-chlorophenyl)-9-phenyl-6*H*-benzo[*c*]chromen-6-one (8)

yellow solid; 65% yield, 94% ee;

the enantioselectivity was determined by UPCC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 80:20 in the first 5 mins and maintaining in 80:20 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 22.0 min, t_R (minor) = 21.1 min;

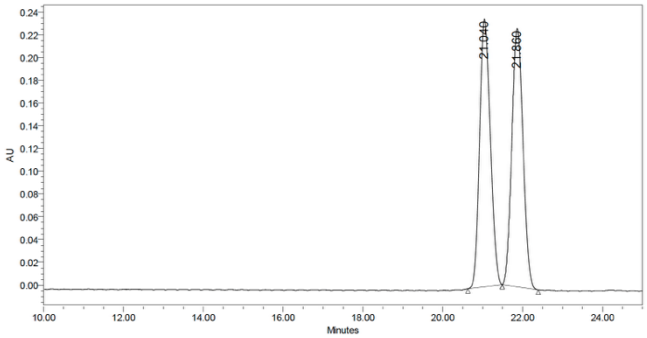
$[\alpha]_D^{20} = -0.60$ (*c* = 0.67 in acetone, λ = 589 nm);

HRMS (ESI+): calcd. for $C_{31}H_{17}BrCl_2O_2$+Na^+ [M+Na^+] 592.9681, found 592.9656;

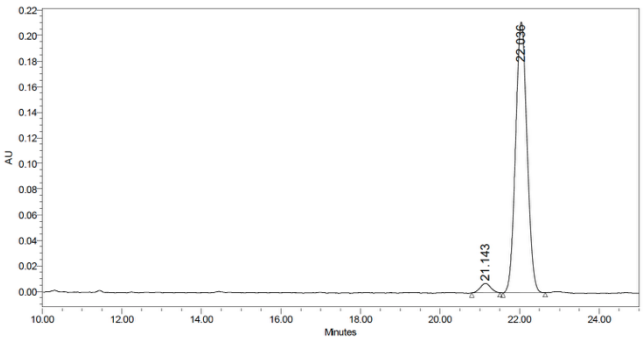
IR: ν_{max} (film, cm^{-1}): 3061, 1734, 1604, 1397, 1088, 1067, 737, 705;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.48 (s, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.34 – 7.31 (m, 1H), 7.27 (s, 1H), 7.23 – 7.13 (m, 5H), 7.11 – 7.06 (m, 2H), 6.78 (d, *J* = 1.9 Hz, 2H);

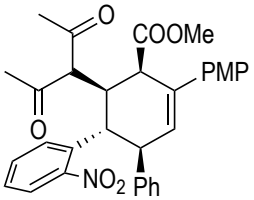
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 151.8, 148.6, 145.5, 140.5, 140.4, 139.6, 135.9, 135.7, 134.6, 134.5, 133.8, 133.5, 132.7, 130.0, 129.8, 129.1, 128.4, 128.2, 127.9, 127.6, 125.0, 124.1, 118.8, 117.7, 117.5.



	RT	Area	% Area	Height	% Height
1	21.040	4411958	50.00	235357	50.90
2	21.860	4412471	50.00	227070	49.10



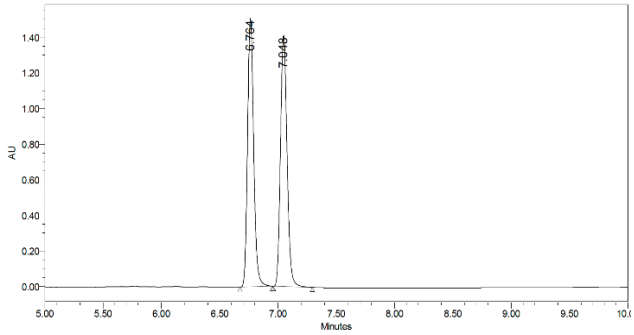
	RT	Area	% Area	Height	% Height
1	21.143	133627	3.05	7372	3.37
2	22.036	4251388	96.95	211475	96.63



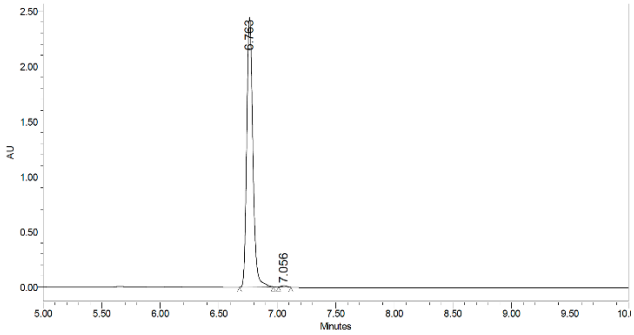
methyl (1'*R*,2'*R*,3'*S*,4'*R*)-3'-(2,4-dioxopentan-3-yl)-5'-(4-methoxyphenyl)-2''-nitro-1',2',3',4'-tetrahydro-[1,1':2',1''-terphenyl]-4'-carboxylate (9)

light yellow solid; 70% yield, 99% ee;

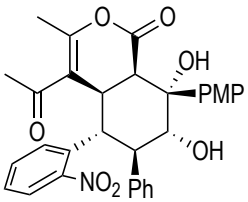
HRMS (ESI+): calcd. for $C_{32}H_{31}NO_7$ +Na^+ [M+Na^+] 564.1993, found 564.1986;
IR: ν_{max} (film, cm^{-1}): 2955, 1733, 1536, 1233, 1159, 767, 708;
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.26 (m, 3H), 7.14 – 7.07 (m, 3H), 6.86 – 6.82 (m, 4H), 6.07 (d, *J* = 2.7 Hz, 1H), 4.55 (d, *J* = 10.4 Hz, 1H), 4.23 (d, *J* = 4.4 Hz, 1H), 3.85 (t, *J* = 11.0 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.75 – 3.67 (m, 2H), 2.30 (s, 3H), 1.50 (s, 3H);
^{13}C NMR (150 MHz, $CDCl_3$) δ 202.6, 201.5, 172.8, 159.4, 152.5, 142.2, 134.7, 134.5, 132.9, 132.4, 131.7, 128.7, 128.5, 128.2, 128.0, 127.3, 127.1, 123.1, 114.0, 71.0, 55.4, 52.9, 52.4, 45.8, 43.3, 42.8, 31.7, 30.4;
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 6.8 min, t_R (minor) = 7.0 min.



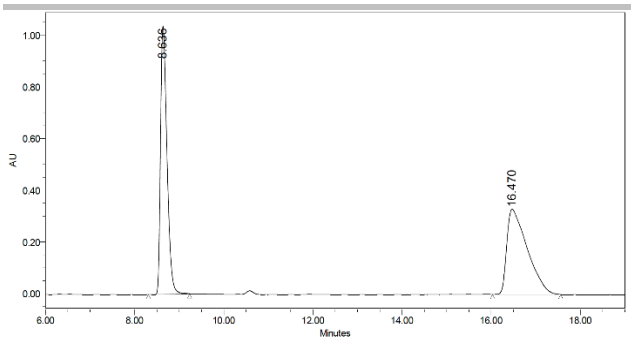
	RT	Area	% Area	Height	% Height
1	6.764	5479529	49.82	1509908	51.67
2	7.048	5518597	50.18	1412115	48.33



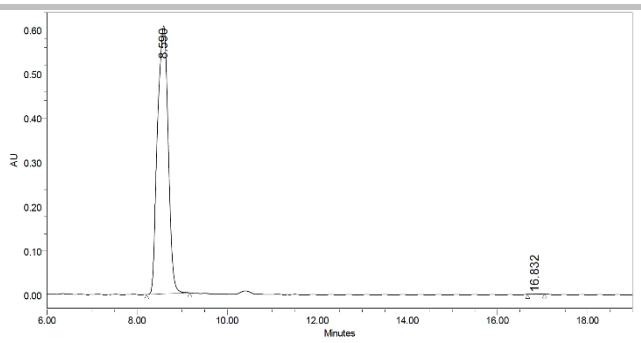
	RT	Area	% Area	Height	% Height
1	6.763	8893470	99.54	2444809	99.48
2	7.056	40670	0.46	12868	0.52



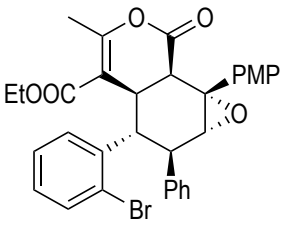
(4a*R*,5*R*,6*R*,8*R*,8a*R*)-4-acetyl-7,8-dihydroxy-8-(4-methoxyphenyl)-3-methyl-5-(2-nitrophenyl)-6-phenyl-4a,5,6,7,8,8a-hexahydro-1*H*-isochromen-1-one (10)
light yellow solid; 78% yield, >99% ee;
HRMS (ESI+): calcd. for $C_{31}H_{29}NO_8$+Na^+ [M+Na^+] 566.1785, found 566.1778;
IR: ν_{max} (film, cm^{-1}): 3460, 2932, 1783, 1649, 1524, 1357, 1250, 1036, 699;
^{1}H NMR (400 MHz, Acetone) δ 7.80 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.55 (td, *J* = 7.7, 1.4 Hz, 1H), 7.47 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.17 – 7.08 (m, 4H), 7.06 – 7.00 (m, 1H), 6.87 – 6.81 (m, 2H), 4.96 (dd, *J* = 9.6, 6.4 Hz, 1H), 4.30 (d, *J* = 1.3 Hz, 1H), 4.22 (dd, *J* = 11.8, 5.0 Hz, 1H), 3.90 (dd, *J* = 6.5, 1.7 Hz, 1H), 3.82 (d, *J* = 12.0 Hz, 1H), 3.77 (s, 3H), 3.65 (dd, *J* = 12.0, 9.6 Hz, 1H), 3.49 (d, *J* = 4.9 Hz, 1H), 2.82 (d, *J* = 1.5 Hz, 1H), 2.06 (s, 3H), 1.79 (s, 3H).
^{13}C NMR (100 MHz, Acetone) δ 197.1, 167.0, 159.5, 158.4, 151.8, 141.6, 137.5, 135.1, 133.0, 131.2, 130.2, 129.9, 128.9, 128.5, 127.2, 124.6, 120.2, 113.3, 75.5, 72.6, 55.4, 53.5, 52.9, 43.2, 38.2, 18.8.
$[\alpha]^{25}_D$ = +179.2 (*c* = 0.5 in acetone, *λ* = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.6 min, t_R (minor) = 16.8 min.



	RT	Area	% Area	Height	% Height
1	8.636	10460093	49.88	1038049	75.89
2	16.470	10512220	50.12	329769	24.11



	RT	Area	% Area	Height	% Height
1	8.590	10033520	99.95	606030	99.92
2	16.832	5518	0.05	-494	0.08



ethyl (1a*R*,2*R*,3*R*,3a*R*,7a*R*,7b*R*)-3-(2-bromophenyl)-7b-(4-methoxyphenyl)-5-methyl-7-oxo-2-phenyl-1a,3,3a,7,7a,7b-hexahydro-2*H*-oxireno[2,3-*h*]isochromene-4-carboxylate (11)

light yellow solid; 60% yield, 95% ee;

HRMS (ESI+): calcd. for $C_{32}H_{29}BrO_6$ +Na^+ [M+Na^+] 611.1040, found 611.1030;

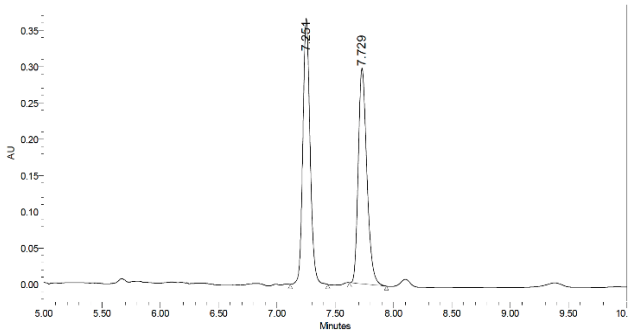
IR: ν_{max} (film, cm^{-1}): 2930, 1773, 1697, 1516, 1248, 1022, 759;

^{1}H NMR (400 MHz, Acetone) δ 7.64 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.41 (td, *J* = 7.6, 1.3 Hz, 1H), 7.30 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.27 – 7.17 (m, 3H), 7.13 – 7.05 (m, 3H), 6.96 – 6.91 (m, 2H), 4.17 (dd, *J* = 4.8, 0.8 Hz, 1H), 3.86 – 3.80 (m, 4H), 3.79 – 3.75 (m, 2H), 3.69 (d, *J* = 10.3 Hz, 1H), 3.64 – 3.56 (m, 1H), 3.43 (dd, *J* = 12.4, 10.4 Hz, 1H), 2.17 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H);

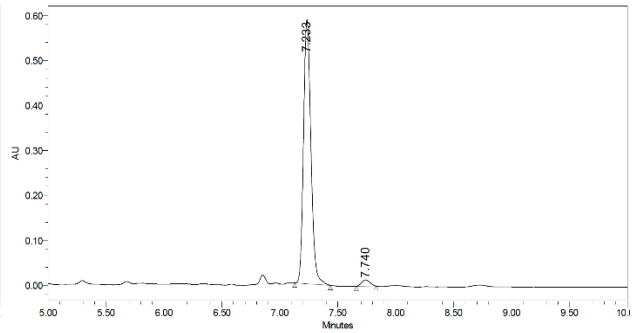
^{13}C NMR (100 MHz, Acetone) δ 168.1, 165.7, 161.3, 160.6, 141.9, 140.2, 133.0, 132.0, 131.3, 130.1, 129.5, 129.3, 129.2, 128.1, 127.8, 127.5, 114.3, 110.6, 62.3, 62.1, 61.0, 55.6, 49.8, 48.1, 45.2, 35.4, 18.4, 14.3;

$[\alpha]^{25}_D$ = -18.4 (*c* = 0.5 in acetone, *λ* = 589 nm);

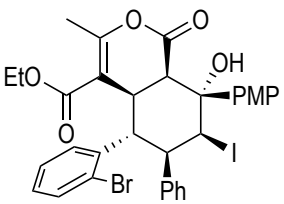
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 7.2 min, t_R (minor) = 7.7 min.



	RT	Area	% Area	Height	% Height
1	7.251	1570242	50.67	366603	55.23
2	7.729	1528818	49.33	297165	44.77



	RT	Area	% Area	Height	% Height
1	7.233	2587129	97.44	587265	97.70
2	7.740	67890	2.56	13814	2.30



ethyl 2-((4a*R*,5*R*,6*R*,7*S*,8*R*,8a*R*)-5-(2-bromophenyl)-8-hydroxy-7-iodo-8-(4-methoxyphenyl)-3-methyl-1-oxo-6-phenyl-4a,5,6,7,8,8a-hexahydro-1*H*-isochromen-4-yl)-2-oxoacetate (12)

light yellow solid; 88% yield, 85:15 dr, 93% ee;

HRMS (ESI+): calcd. for $C_{32}H_{30}IO_6Br$ +Na^+ [M+Na^+] 739.0163, found 739.0141;

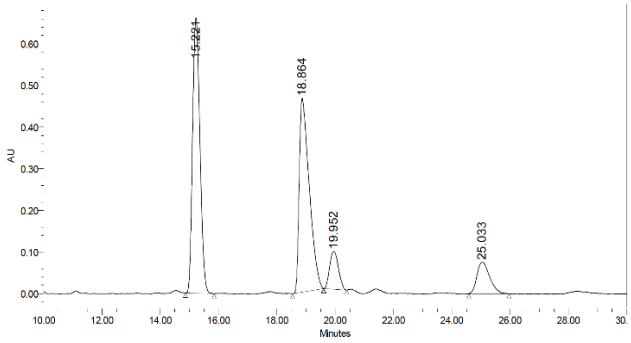
IR: ν_{max} (film, cm^{-1}): 3480, 2899, 1764, 1663, 1518, 1251, 1023, 758;

^{1}H NMR (400 MHz, Acetone) δ 7.65 – 7.59 (m, 2H), 7.45 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.33 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.17 – 7.08 (m, 5H), 7.07 – 7.02 (m, 1H), 6.98 – 6.92 (m, 1H), 6.90 – 6.84 (m, 2H), 5.19 (s, 1H), 5.10 (ddd, *J* = 9.6, 3.1, 1.4 Hz, 1H), 4.19 – 4.11 (m, 3H), 4.08 – 4.03 (m, 1H), 3.81 (s, 3H), 3.68 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.47 (dq, *J* = 10.9, 7.1 Hz, 1H), 2.24 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H).

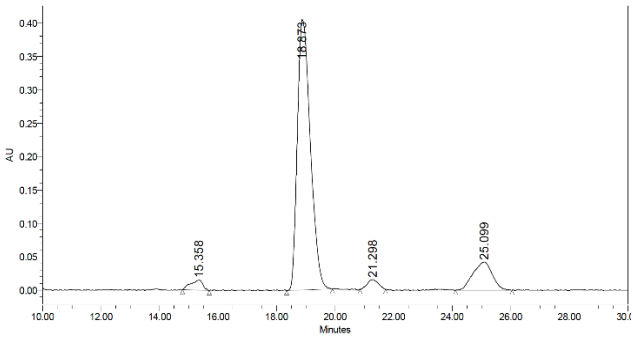
^{13}C NMR (100 MHz, Acetone) δ 166.2, 165.5, 160.7, 159.9, 143.3, 140.5, 136.9, 133.2, 131.5, 130.6, 128.8, 128.6, 128.2, 128.0, 127.1, 113.50 110.2, 75.8, 60.7, 55.5, 49.0, 47.2, 46.9, 44.9, 44.8, 39.4, 18.8, 14.3.

$[\alpha]^{25}_D$ = +226.4 (*c* = 0.5 in acetone, λ = 589 nm);

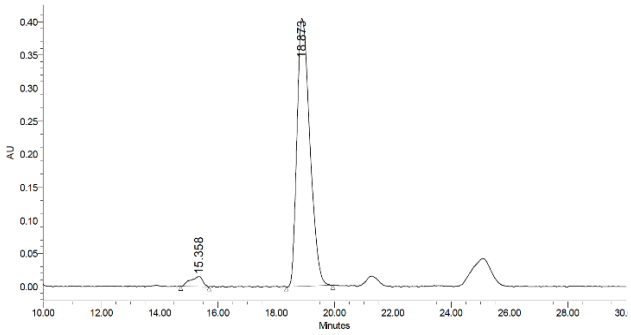
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 80:20 in the first 5 mins and maintaining in 80:20 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, λ= 254 nm), t_R (major) = 18.9 min, t_R (minor) = 15.3 min.



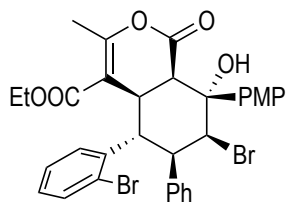
	RT	Area	% Area	Height	% Height
1	15.221	11402490	42.91	661789	51.16
2	18.864	10998687	41.39	465438	35.98
3	19.952	1894213	7.13	90971	7.03
4	25.033	2279642	8.58	75492	5.84



	RT	Area	% Area	Height	% Height
1	15.358	432013	2.85	15017	3.15
2	18.873	12424723	82.01	405056	84.99
3	21.298	371566	2.45	14420	3.03
4	25.099	1922766	12.69	42109	8.84



	RT	Area	% Area	Height	% Height
1	15.358	450897	3.50	15274	3.63
2	18.873	12414927	96.50	404992	96.37



ethyl (4a*R*,5*R*,6*R*,7*S*,8*R*,8a*R*)-7-bromo-5-(2-bromophenyl)-8-hydroxy-8-(4-methoxyphenyl)-3-methyl-1-oxo-6-phenyl-4a,5,6,7,8,8a-hexahydro-1*H*-isochromene-4-carboxylate (13)

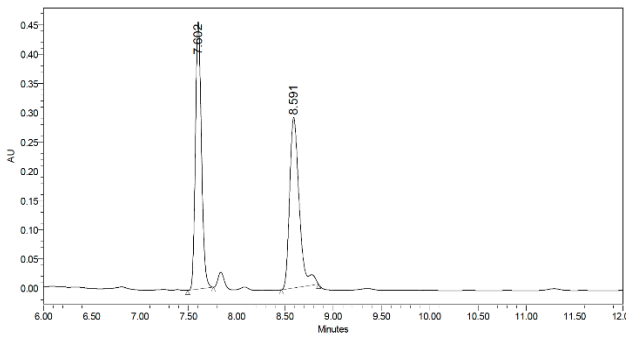
light yellow solid; 57% yield, 93% ee;

HRMS (ESI+): calcd. for $C_{32}H_{30}Br_2O_6$ +Na^+ [M+Na^+] 691.0301, found 691.0294;

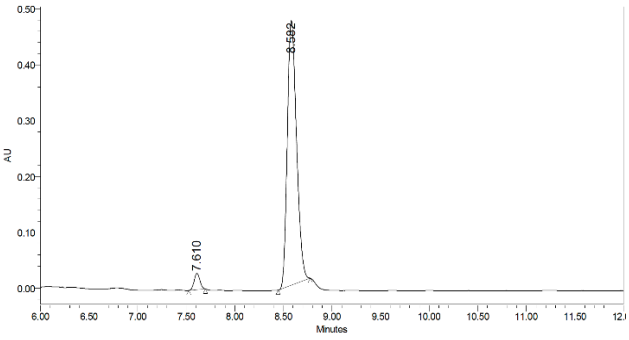
IR: ν_{max} (film, cm^{-1}): 3481, 2895, 1769, 1706, 1250, 1061, 1025, 760;

^{1}H NMR (400 MHz, Acetone) δ 7.65 – 7.60 (m, 2H), 7.43 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.35 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.15 – 7.08 (m, 3H), 7.07 – 7.01 (m, 1H), 6.95 (ddd, *J* = 8.8, 7.3, 1.7 Hz, 1H), 6.90 – 6.85 (m, 2H), 5.20 (s, 1H), 5.01 (d, *J* = 2.7 Hz,

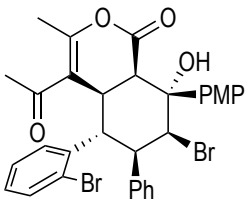
1H), 4.59 (dd, *J* = 11.7, 2.9 Hz, 1H), 4.34 – 4.25 (m, 1H), 4.15 – 4.08 (m, 2H), 3.81 (s, 3H), 3.68 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.46 (dq, *J* = 10.9, 7.1 Hz, 1H), 2.23 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (100 MHz, Acetone) δ 166.2, 165.1, 160.8, 159.9, 141.9, 140.4, 136.4, 133.2, 131.2, 130.7, 128.9, 128.5, 128.3, 128.2, 128.0, 127.1, 113.7, 110.3, 76.3, 62.8, 60.7, 55.5, 48.6, 47.3, 42.8, 39.1, 18.9, 14.3;
$[\alpha]^{25}_D$ = +179.2 (*c* = 0.5 in acetone, *λ* = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 8.6 min, t_R (minor) = 7.6 min.



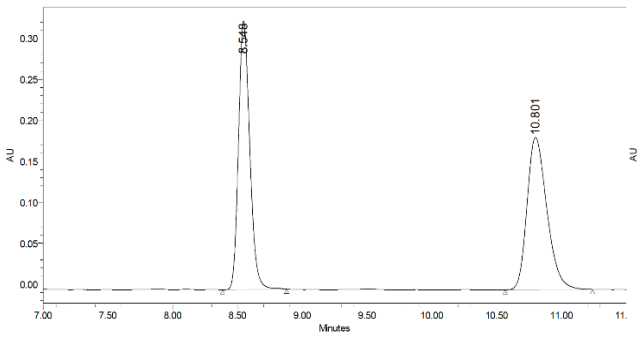
	RT	Area	% Area	Height	% Height
1	7.602	1969866	49.52	457223	61.05
2	8.591	2007887	50.48	291672	38.95



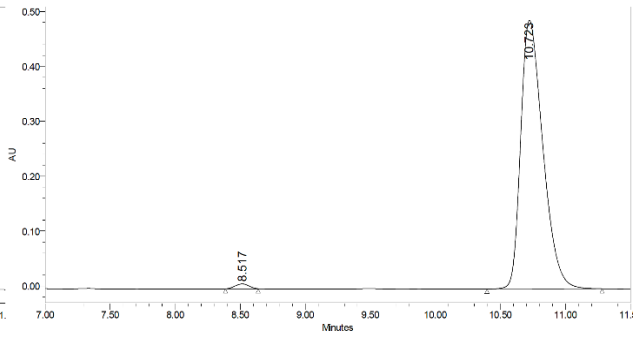
	RT	Area	% Area	Height	% Height
1	7.610	120376	3.74	29342	5.83
2	8.582	3101141	96.26	473724	94.17



(4a*R*,5*R*,6*R*,7*S*,8*R*,8a*R*)-4-acetyl-7-bromo-5-(2-bromophenyl)-8-hydroxy-8-(4-methoxyphenyl)-3-methyl-6-phenyl-4a,5,6,7,8,8a-hexahydro-1*H*-isochromen-1-one (14)
light yellow solid; 86% yield, 98% ee;
HRMS (ESI+): calcd. for $C_{31}H_{28}Br_2O_6$ +Na^+ [M+Na^+] 661.0196, found 661.0187;
IR: ν_{max} (film, cm^{-1}): 3480, 2899, 1762, 1664, 1252, 1105, 1029, 759;
^{1}H NMR (600 MHz, MeOD) δ 7.62 – 7.57 (m, 2H), 7.42 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.24 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.18 – 7.15 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 2H), 7.07 – 7.01 (m, 2H), 6.96 – 6.93 (m, 1H), 6.93 – 6.89 (m, 2H), 4.90 – 4.88 (br, 1H), 4.49 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.26 (t, *J* = 11.6 Hz, 1H), 4.08 – 4.01 (m, 2H), 3.81 (s, 3H), 2.19 (s, 3H), 1.79 (s, 3H);
^{13}C NMR (100 MHz, MeOD) δ 199.8, 166.9, 160.4, 159.0, 141.9, 141.2, 136.5, 133.9, 131.2, 130.9, 129.4, 128.8, 128.7, 128.6, 128.6 127.5, 120.1, 114.1, 76.5, 62.9, 55.7, 48.9, 47.7, 43.1, 40.6, 29.7, 19.3;
$[\alpha]^{25}_D$ = +51.2 (*c* = 0.5 in acetone, *λ* = 589 nm);
the enantioselectivity was determined by SFC (Trefoil CEL-1, gradient 100% CO_2 to CO_2/MeOH = 60:40 in the first 5 mins and maintaining in 60:40 CO_2/MeOH in the rest of time, flow rate: 0.5 mL/min, *λ*= 254 nm), t_R (major) = 10.7 min, t_R (minor) = 8.5 min.



	RT	Area	% Area	Height	% Height
1	8.548	1972727	49.97	327685	63.82
2	10.801	1975425	50.03	185794	36.18



	RT	Area	% Area	Height	% Height
1	8.517	65659	1.12	8848	1.78
2	10.723	5805836	98.88	489451	98.22

X. Absolute configuration determination

X-Ray Crystallographic Data

Absolute configurations of products **3** were assigned based on the crystal X-ray structures of **3i, 3j**. Absolute configurations of products **4, 5** were assigned based on the crystal X-ray structures of **4a, 5a**. Absolute configurations of products **8** were assigned based on the crystal X-ray structures of **8**. Absolute configurations of all-substituted cyclohexanes were assigned based on the crystal X-ray structures of *rac*-**9**, *rac*-**10**, and *rac*-**14**. A light yellow rodlike crystal of **3i, 3j** were obtained by vaporization of *n*-hexane/DCM (3:1) solution of corresponding compounds. A light yellow rodlike crystal of **8** was obtained by vaporization of *n*-hexane/DCM/CH_3CN (3:2:1) solution of compound **8**. A light yellow needle-like crystal of **4a, 5a** were obtained by vaporization of *n*-hexane/Acetone (3:1) solution of corresponding compounds. A light yellow block-shaped crystal of *rac*-**9**, *rac*-**10**, *rac*-**14** were obtained by vaporization of *n*-hexane/DCM (3:1) solution of corresponding compounds.

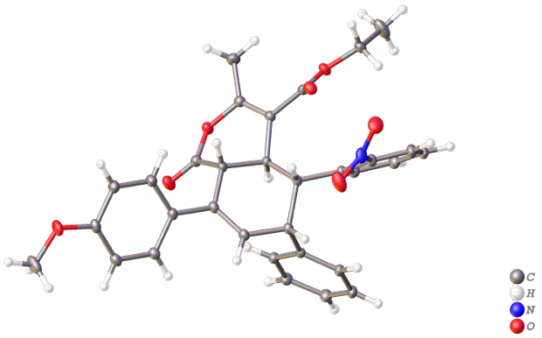


Figure S2. The crystal structure of **4a**.

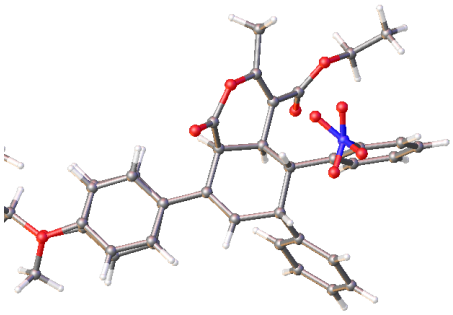


Figure S3. The crystal structure of **5a**

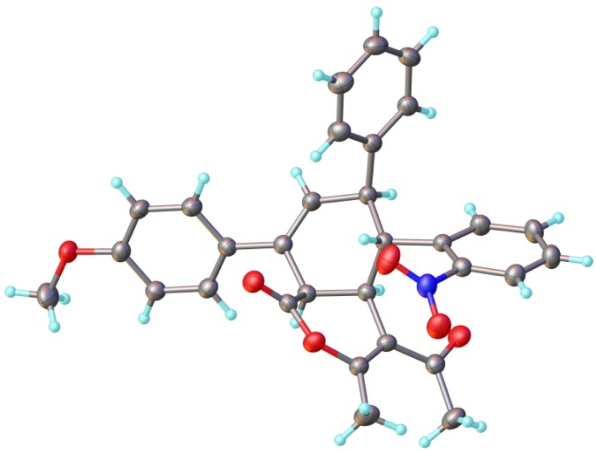


Figure S4. The crystal structure of **3i**.

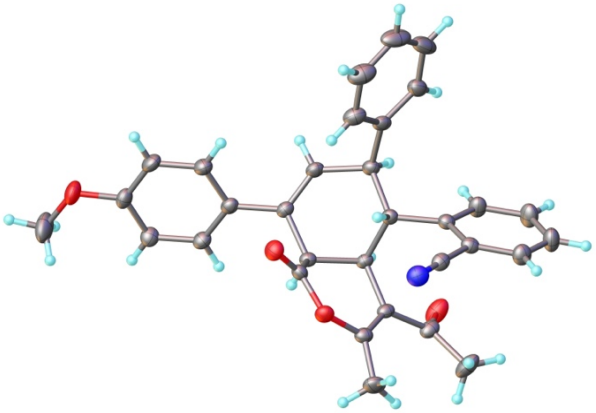


Figure S5. The crystal structure of **3j**.

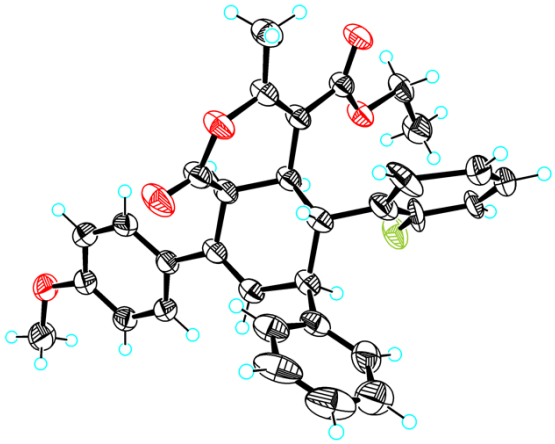


Figure S6. The crystal structure of *rac*-**3c**.

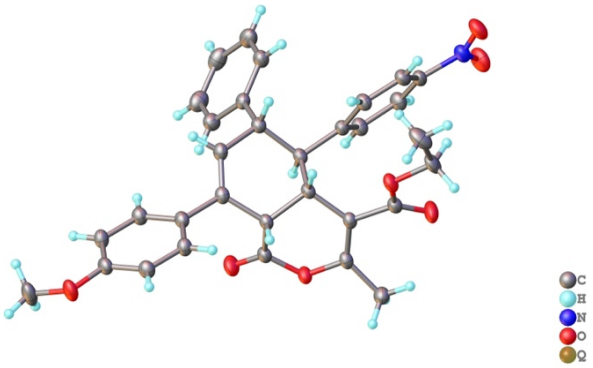


Figure S7. The crystal structure of *rac*-**3f**

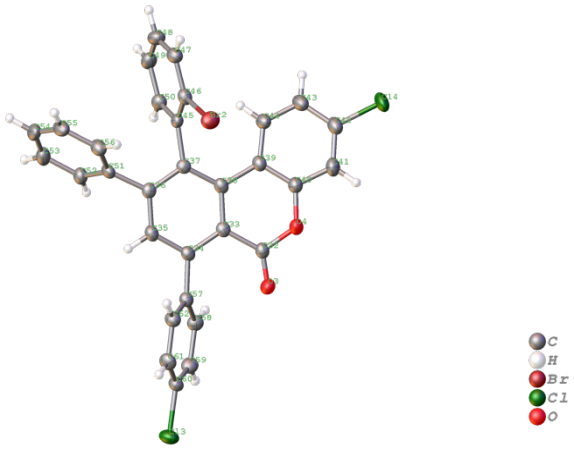


Figure S8. The crystal structure of (*R*)-**8**.

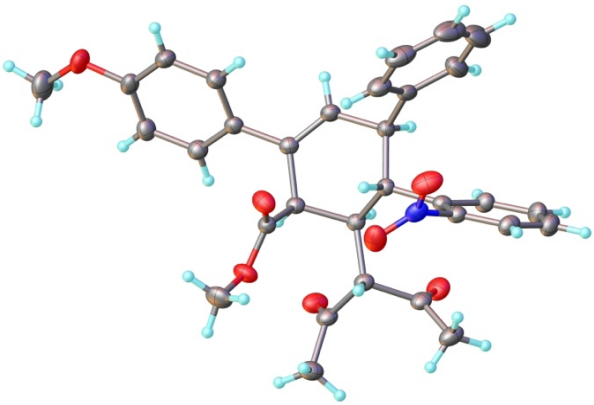


Figure S9. The crystal structure of *rac*-**9**

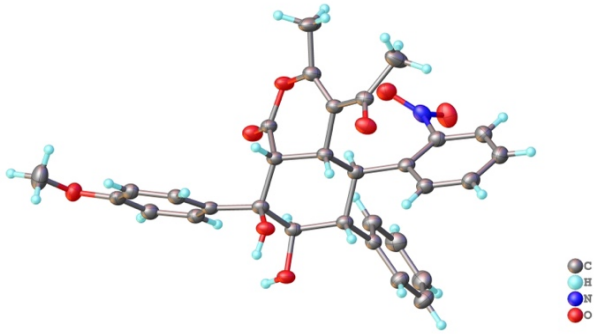


Figure S10. The crystal structure of *rac*-**10.**

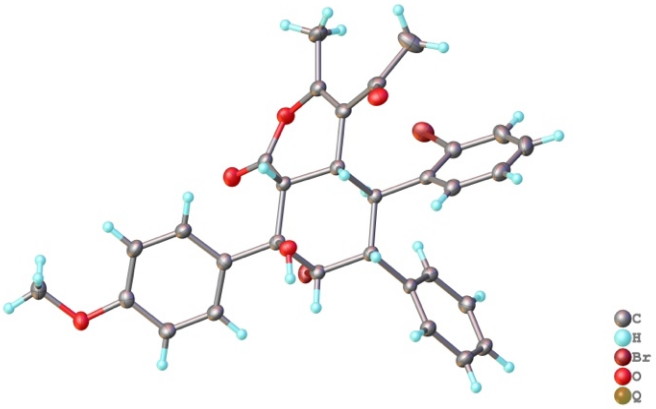


Figure S11. The crystal structure of *rac*-**14**.

Table S8. Crystal data and structure refinement of optical compounds.

Compound number	**4a**	**5a**	**3i**	**3j**	*(R)*-**8**
Deposition number	2246562	2377578	2244572	2244570	2235169
Empirical formula	$C_{32}H_{29}NO_7$	$C_{32}H_{29}NO_7$	$C_{31}H_{27}NO_6$	$C_{32}H_{27}NO_4$	$C_{31}H_{17}BrCl_2O_2$
Formula weight	539.56	539.56	509.56	489.57	572.26
Temperature/K	100(2)	149.99(10)	150.00(10)	150.00(10)	149.99(10)
Crystal system	orthorhombic	tetragonal	monoclinic	triclinic	monoclinic
Space group	$P2_12_12_1$	$P4_3$	$P2_1$	$P1$	$C2$
a/Å	10.51673(10)	16.7397(3)	7.02860(10)	7.28960(10)	43.9803(4)
b/Å	11.34590(10)	16.7397(3)	19.9167(2)	9.99900(10)	8.17570(10)
c/Å	22.2044(2)	10.5216(3)	10.57480(10)	10.3560(2)	14.36051(10)
α/°	90	90	90	90.9030(10)	90
β/°	90	90	103.5740(10)	104.2710(10)	105.4170(10)
γ/°	90	90	90	97.5320(10)	90
Volume/Å^3	2649.47(4)	2948.33(12)	1438.98(3)	724.321(19)	4977.80(9)
Z	4	4	2	1	8
ρ_{calc}g/cm^3	1.353	1.313	1.372	1.317	1.527
μ/mm^{-1}	0.096	0.742	2.415	2.327	4.450
F(000)	1136	1236	620	300	2304
Crystal size/mm^3	0.260 × 0.180 × 0.120	0.22 × 0.15 × 0.08	0.1 × 0.09 × 0.07	0.13 × 0.12 × 0.1	0.31 × 0.06 × 0.04
Radiation	Mo *K*α (λ = 0.71073)	Cu *K*α (λ = 1.54184)	Cu *K*α (*λ* = 1.54184)	Cu *K*α (*λ* = 1.54184)	Cu*Kα* (*λ* = 1.54184)
2Θ range for data collection/°	5.592 to 59.992	7.468 to 152.312	8.602 to 148.556	8.822 to 148.958	6.384 to 148.378
Index ranges	-14 ≤ h ≤ 13, -15 ≤ k ≤ 15, -31 ≤ l ≤ 31	-19 ≤ h ≤ 19, -20 ≤ k ≤ 13, -12 ≤ l ≤ 12	-8 ≤ h ≤ 8, -24 ≤ k ≤ 24, -12 ≤ l ≤ 11	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -12 ≤ l ≤ 12	-54 ≤ h ≤ 54, -10 ≤ k ≤ 9, -17 ≤ l ≤ 17
Reflections collected	48521	20352	15310	21601	37893
Independent reflections	7623 [R_{int} = 0.0247, R_{sigma} = 0.0139]	5846 [R_{int} = 0.0265, R_{sigma} = 0.0251]	5652 [R_{int} = 0.0367, R_{sigma} = 0.0419]	5516 [R_{int} = 0.0259, R_{sigma} = 0.0210]	9656 [R_{int} = 0.0611, R_{sigma} = 0.0438]
Data/restraints/parameters	7623/0/364	5846/60/539	5652/1/373	5516/3/364	9656/2/649
Goodness-of-fit on F^2	1.045	1.055	1.056	1.022	1.065
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0297, wR_2 = 0.0791	R_1 = 0.0710, wR_2 = 0.2088	R_1 = 0.0364, wR_2 = 0.0926	R_1 = 0.0295, wR_2 = 0.0766	R_1 = 0.0386, wR_2 = 0.1032
Final *R* indexes [all data]	R_1 = 0.0303, wR_2 = 0.0798	R_1 = 0.0749, wR_2 = 0.2159	R_1 = 0.0395, wR_2 = 0.0945	R_1 = 0.0302, wR_2 = 0.0774	R_1 = 0.0399, wR_2 = 0.1051
Largest diff.peak/hole/eÅ^{-3}	0.30/-0.17	0.80/-0.36	0.39/-0.37	0.20/-0.33	0.64/-0.93
Flack parameter	-0.06(12)	0.01(2)	-0.023(9)	0.005(4)	-0.016(9)

Table S9. Crystal data and structure refinement of racemic compounds.

Compound number	*rac*-**3c**	*rac*-**3f**	*rac*-**9**	*rac*-**10**	*rac*-**14**
Deposition number	2244575	2244573	2244569	2244568	2243102
Empirical formula	$C_{32}H_{29}FO_5$	$C_{32}H_{29}NO_7$	$C_{32}H_{31}NO_7$	$C_{31}H_{29}NO_8$	$C_{31}H_{28}Br_2O_5$
Formula weight	512.55	539.56	541.58	543.6	640.35
Temperature/K	100.00(10)	149.99(10)	149.99(10)	100.00(10)	99.98(10)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	10.7735(2)	10.3074(3)	8.2745(2)	22.0372(3)	14.45320(10)
b/Å	28.0445(5)	10.5620(4)	33.3961(7)	9.66930(10)	14.99130(10)
c/Å	8.8667(2)	12.7619(4)	10.3175(2)	26.7286(4)	12.68540(10)
α/°	90	102.425(3)	90	90	90
β/°	104.427(2)	99.324(3)	104.258(2)	110.983(2)	101.1850(10)
γ/°	90	101.043(3)	90	90	90
Volume/Å^3	2594.48(9)	1301.40(8)	2763.27(11)	5317.76(14)	2696.37(3)
Z	4	2	4	4	4
ρ_{calc}g/cm^3	1.312	1.377	1.302	1.358	1.577
μ/mm^{-1}	0.758	0.799	0.752	0.814	4.143
F(000)	1080	568	1144	2288	1296.0
Crystal size/mm^3	0.11 × 0.1 × 0.07	0.25 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.23 × 0.12 × 0.04	0.18×0.15×0.13
Radiation	Cu *K*α (*λ* = 1.54184)	Cu *K*α (*λ* = 1.54184)	Cu *K*α (*λ* = 1.54184)	Cu *K*α (*λ* = 1.54184)	Cu *Kα* (*λ* = 1.54184)
2Θ range for data collection/°	6.304 to 148.372	7.258 to 149.078	9.232 to 149.438	6.472 to 148.89	8.574 to 149.004
Index ranges	-13 ≤ h ≤ 12, -28 ≤ k ≤ 34, -9 ≤ l ≤ 11	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 8	-9 ≤ h ≤ 10, -35 ≤ k ≤ 41, -12 ≤ l ≤ 11	-25 ≤ h ≤ 27, -12 ≤ k ≤ 11, -33 ≤ l ≤ 31	-9 ≤ h ≤ 17, -17 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	13083	12729	15386	30744	15346
Independent reflections	5108 [R_{int} = 0.0564, R_{sigma} = 0.0521]	5112 [R_{int} = 0.0274, R_{sigma} = 0.0388]	5479 [R_{int} = 0.0340, R_{sigma} = 0.0406]	10519 [R_{int} = 0.0591, R_{sigma} = 0.0484]	5330 [R_{int} = 0.0276, R_{sigma} = 0.0252]
Data/restraints/parameters	5108/62/401	5112/0/364	5479/0/365	10519/0/731	5330/0/347
Goodness-of-fit on F^2	1.12	1.068	1.072	1.06	1.068
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0634, wR_2 = 0.1862	R_1 = 0.0436, wR_2 = 0.1115	R_1 = 0.0417, wR_2 = 0.1043	R_1 = 0.0534, wR_2 = 0.1479	R_1 = 0.0309, wR_2 = 0.0852
Final *R* indexes [all data]	R_1 = 0.0794, wR_2 = 0.1954	R_1 = 0.0522, wR_2 = 0.1160	R_1 = 0.0514, wR_2 = 0.1090	R_1 = 0.0607, wR_2 = 0.1560	R_1 = 0.0320, wR_2 = 0.0860
Largest diff.peak/hole/eÅ^{-3}	0.23/-0.23	0.24/-0.21	0.19/-0.23	0.32/-0.34	0.82/-0.81

ECD determination Data

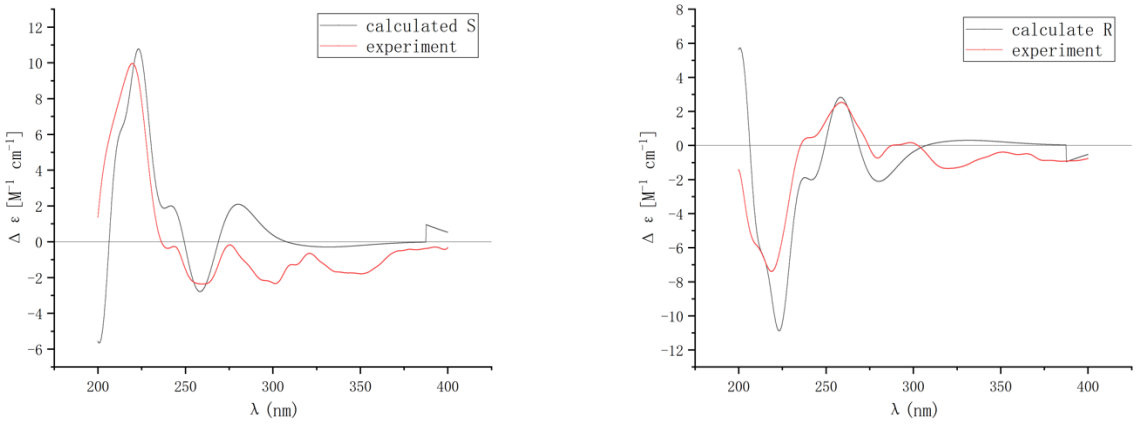
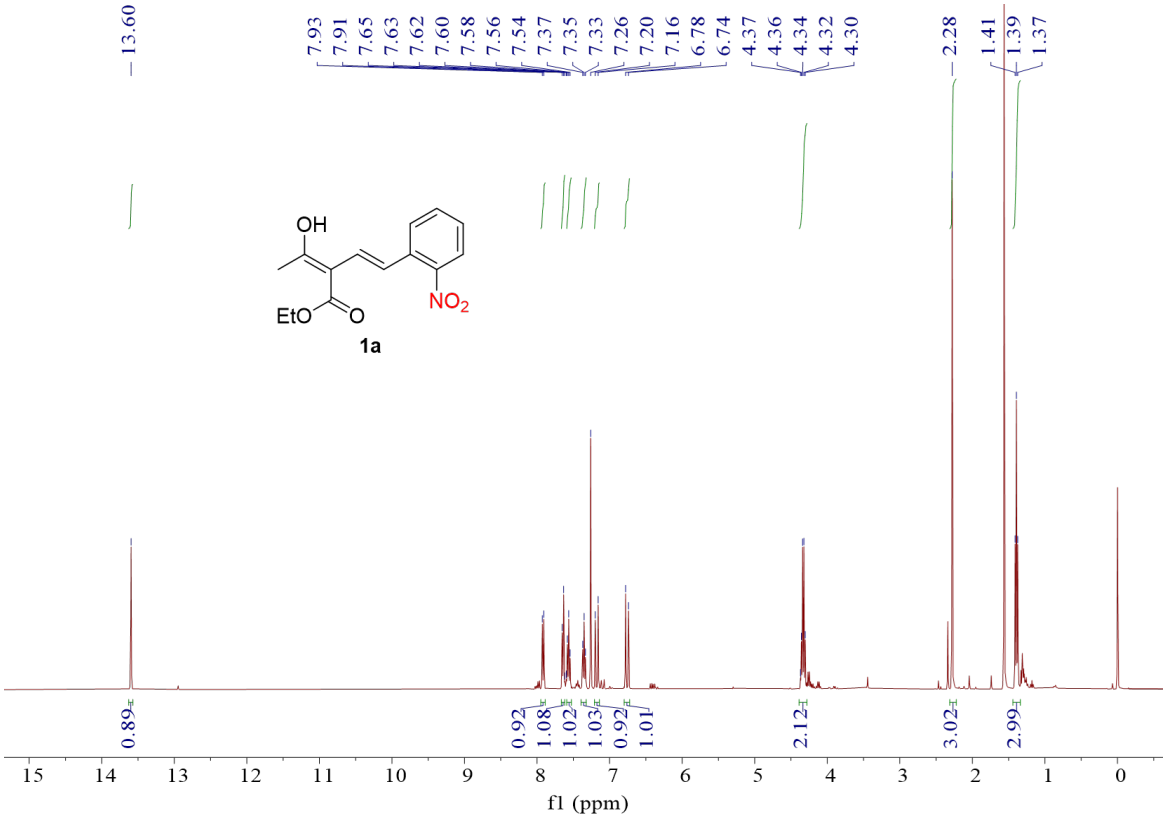


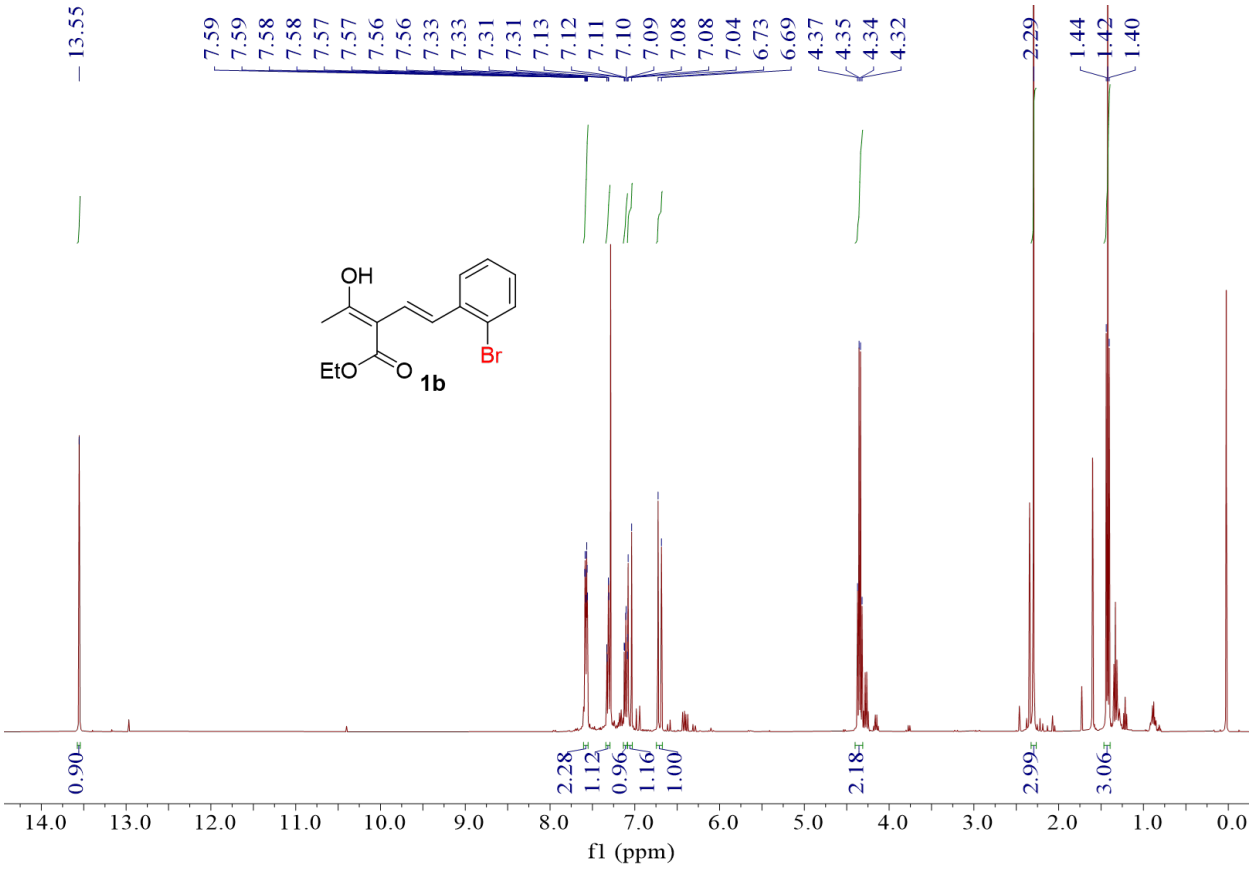
Figure S12. Comparsion of the calculated vs experimental ECD spectra in CH_3CN for compound **6** (left from **3i**, right from **4i**).

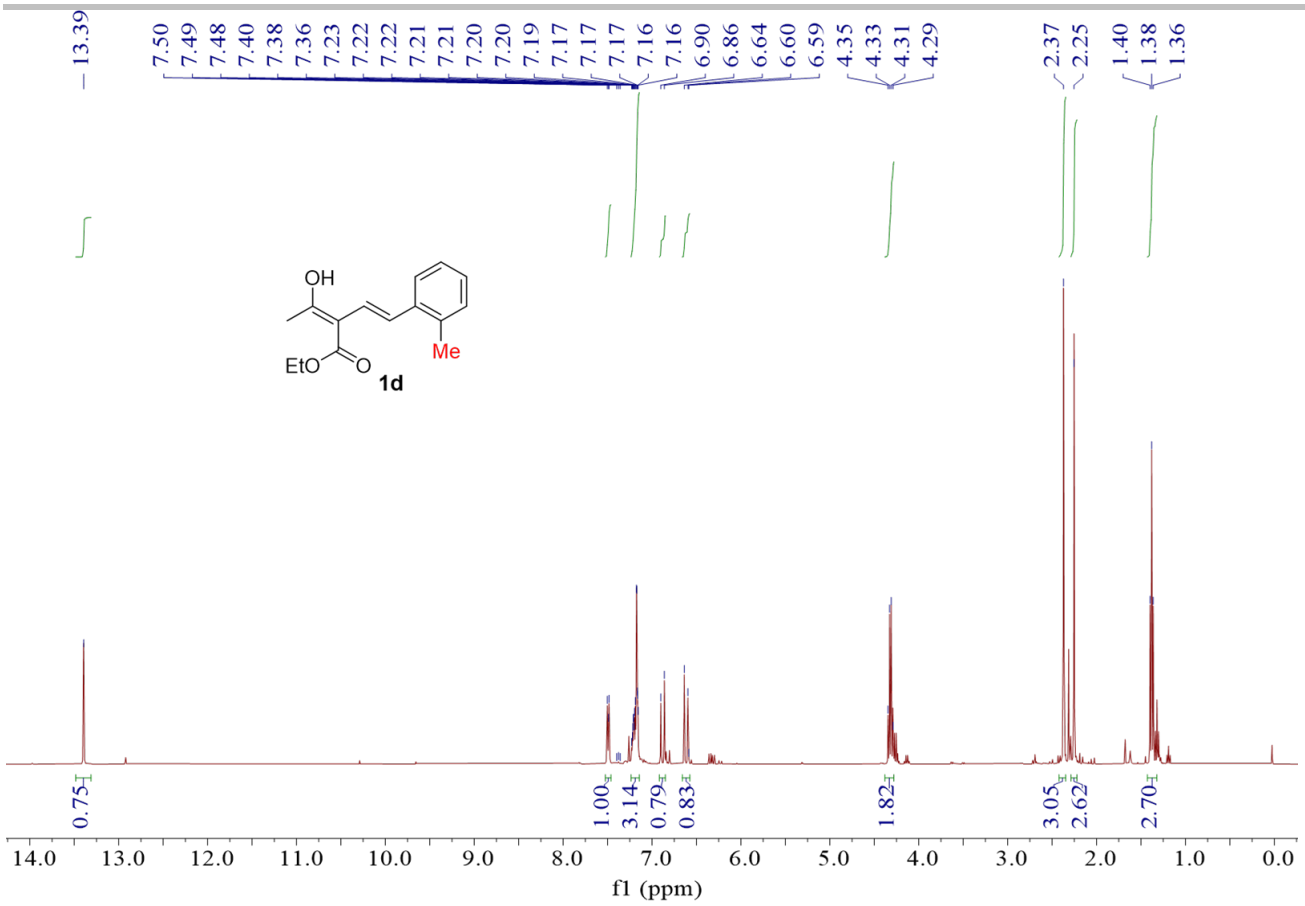
ECD calculation methods:

Monte Carlo conformational searches were carried out by means of the Spartan's 14 software using Merck Molecular Force Field (MMFF). The conformers with Boltzmann-population of over 5% were chosen for ECD calculations, and then the conformers were initially optimized at B3LYP/6-31g level in gas. The theoretical calculation of ECD was conducted in Acetonitrile using Time-dependent Density functional theory (TD-DFT) at the B3LYP/6-31+g (d, p) level for all conformers of compounds **6**. Rotatory strengths for a total of 30 excited states were calculated. ECD spectra were generated using the program SpecDis 1.6 (University of Würzburg, Würzburg, Germany) and GraphPad Prism 5 (University of California San Diego, USA) from dipole-length rotational strengths by applying Gaussian band shapes with sigma = 0.3 eV.

XI. Copies of ^{1}H NMR spectra of 1



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7.17
7.17
7.16
7.16
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6.86
6.64
6.60
6.59
4.35
4.33
4.31
4.29
2.37
2.25
1.40
1.38
1.36
OH
EtO
O
Me
1d
0.75
1.00
3.14
0.79
0.83
1.82
3.05
2.62
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14.0
13.0
12.0
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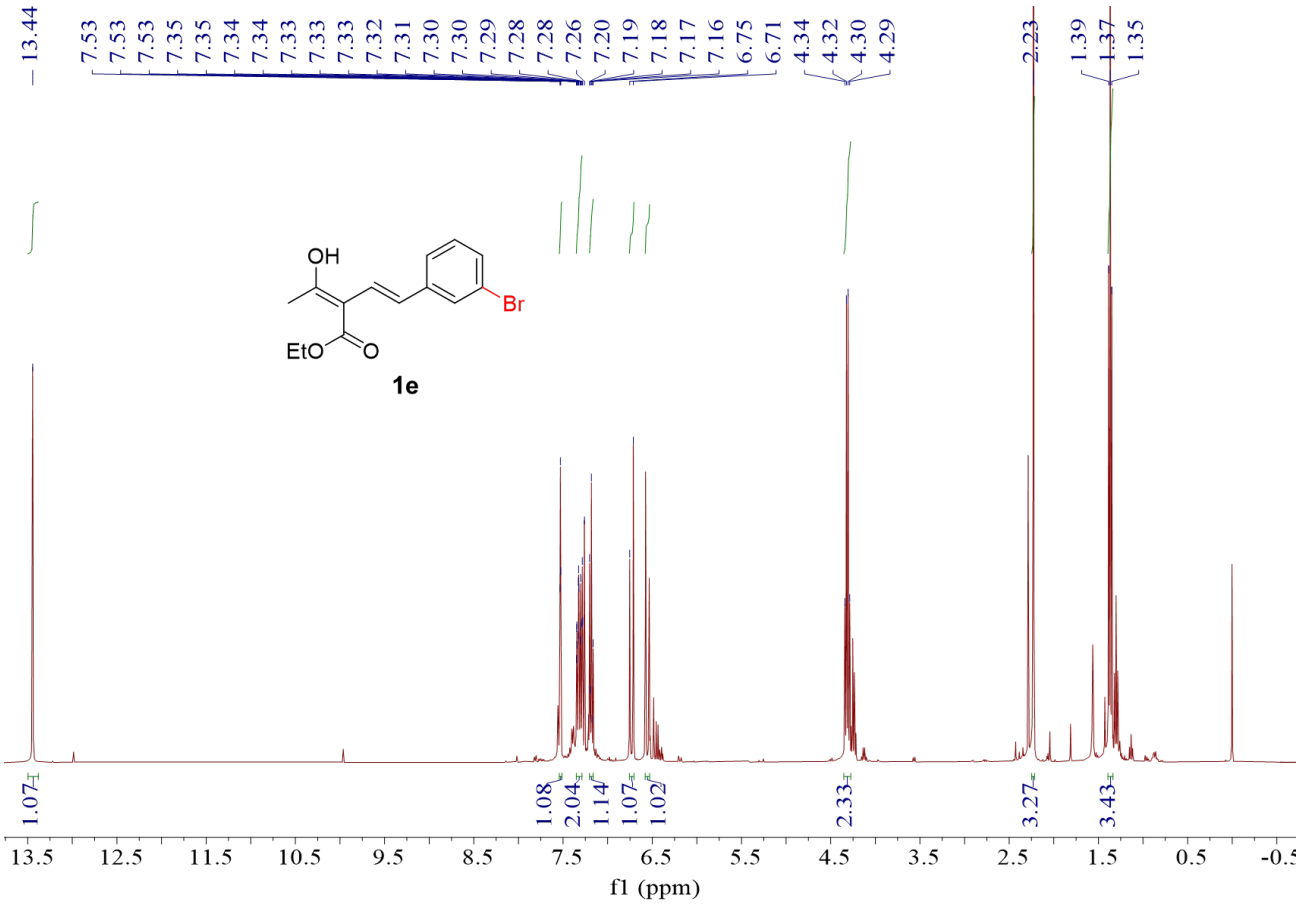
0.0
f1 (ppm)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1.37
1.35
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EtO
O
Br
1e
1.07
1.08
2.04
1.14
1.07
1.02
2.33
3.27
3.43
13.5
12.5
11.5
10.5
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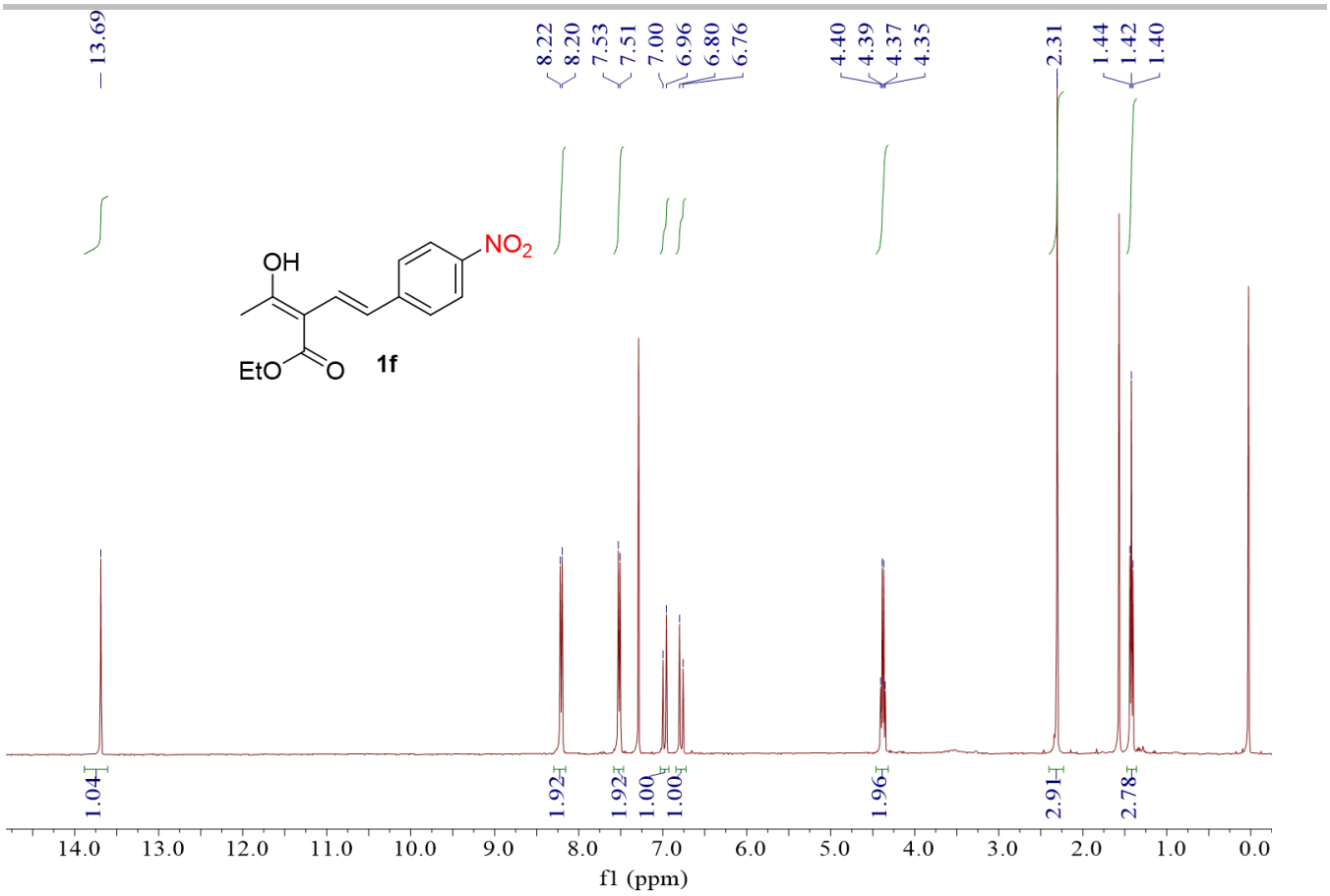
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1.92
1.00
1.00
1.96
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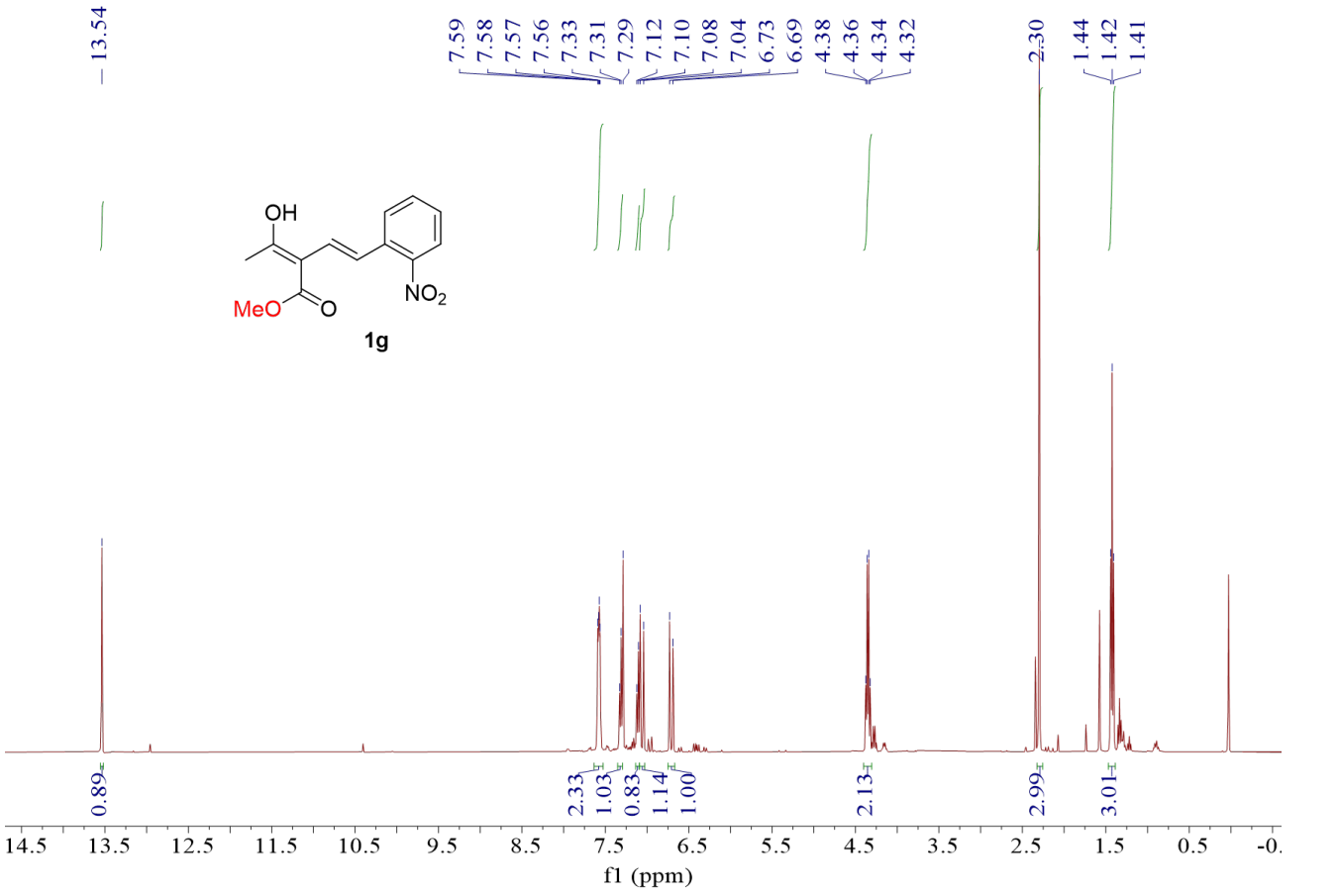
f1 (ppm)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1.41
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O
NO2
1g
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2.33
1.03
0.83
1.14
1.00
2.13
2.99
3.01
14.5
13.5
12.5
11.5
10.5
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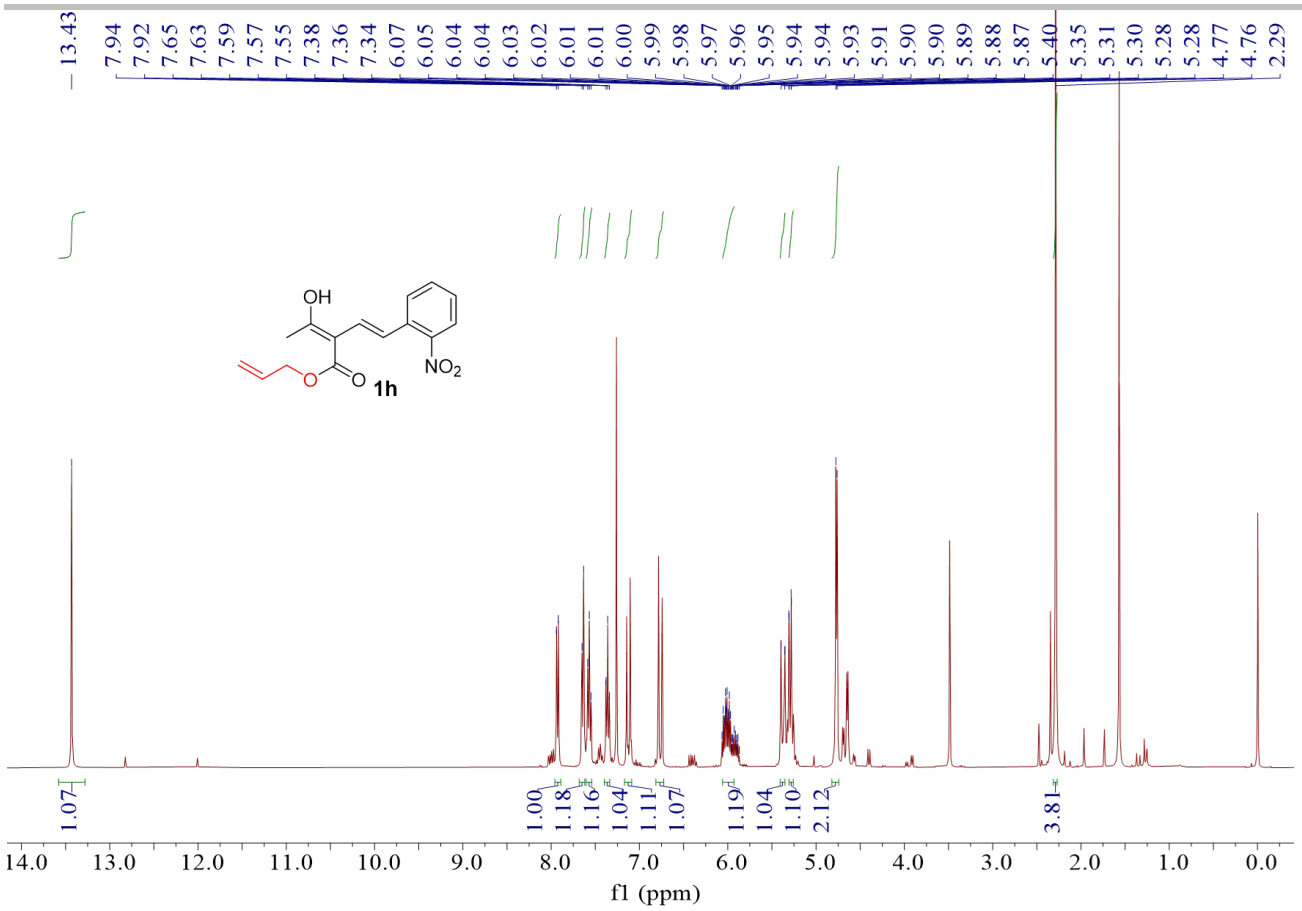
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.
f1 (ppm)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7.34
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6.05
6.04
6.04
6.03
6.02
6.01
6.01
6.00
5.99
5.98
5.97
5.96
5.95
5.94
5.94
5.93
5.91
5.90
5.90
5.89
5.88
5.87
5.40
5.35
5.31
5.30
5.28
5.28
4.77
4.76
2.29
OH
NO2
O
O
1h
1.07
1.00
1.18
1.16
1.04
1.11
1.07
1.19
1.04
1.10
2.12
3.81
14.0
13.0
12.0
11.0
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5.0
4.0
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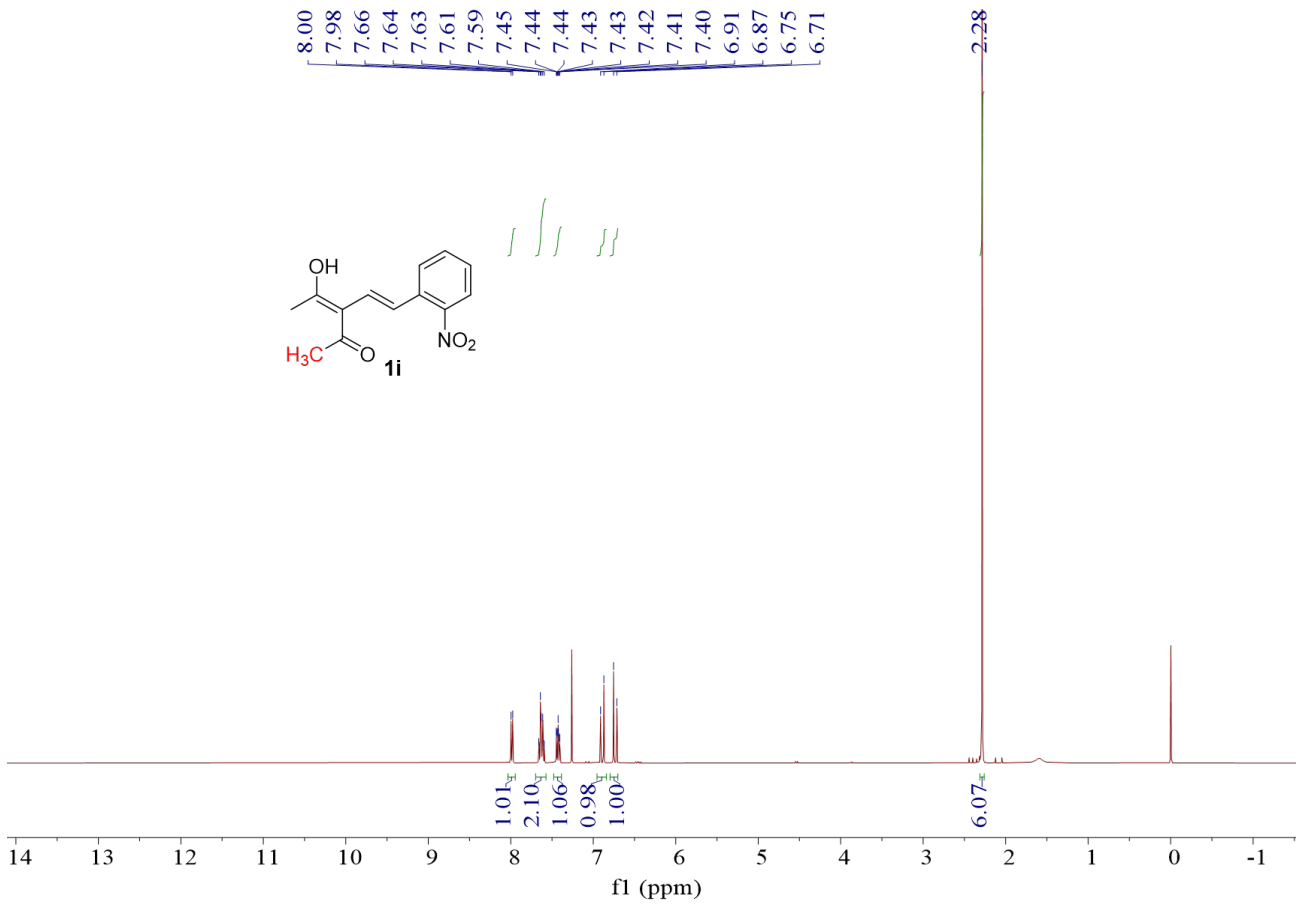
2.0
1.0
0.0
f1 (ppm)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7.59
7.45
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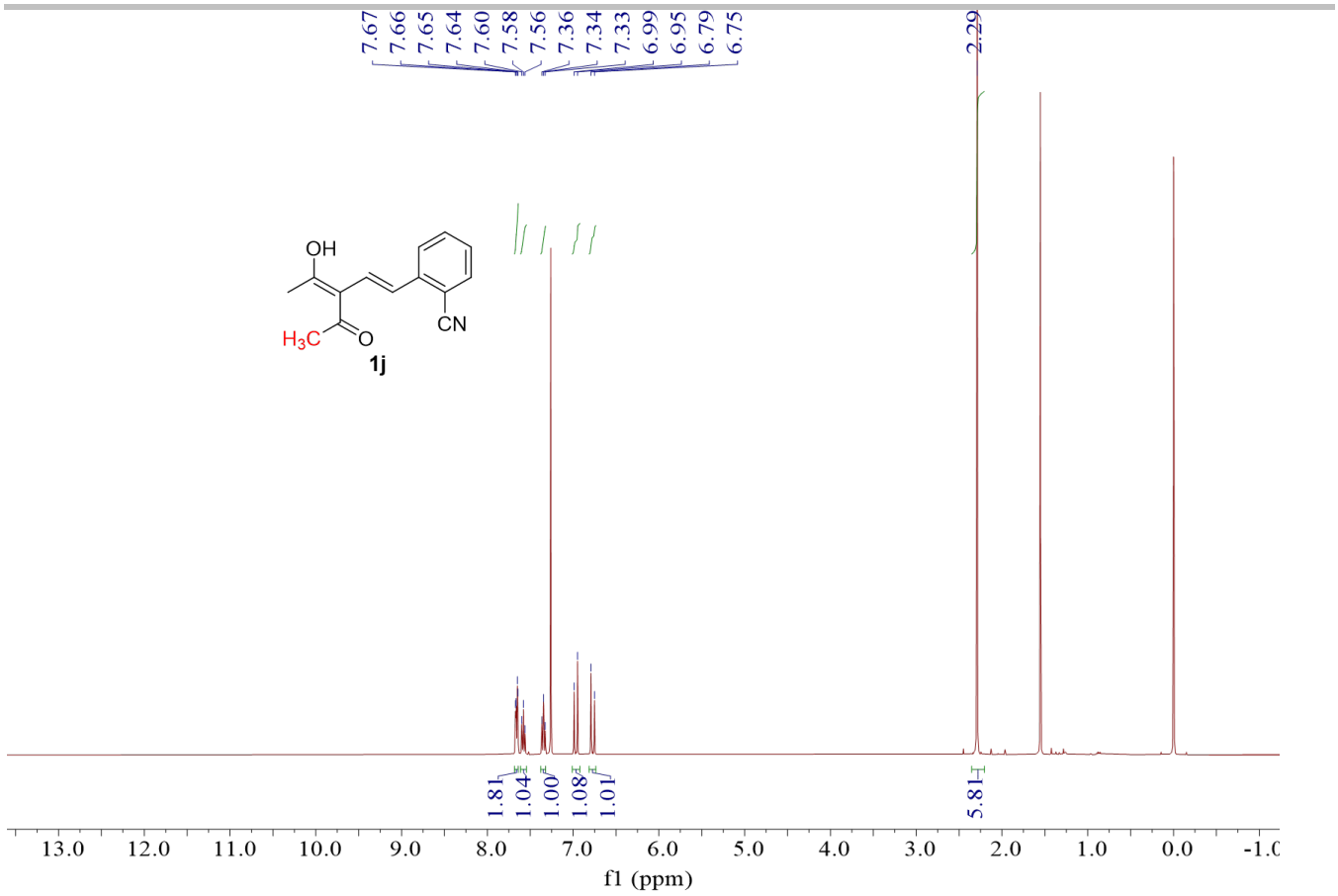
7.44
7.43
7.43
7.42
7.41
7.40
6.91
6.87
6.75
6.71
2.28
OH
NO2
H3C
O
1i
1.01
2.10
1.06
0.98
1.00
6.07
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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7.56
7.36
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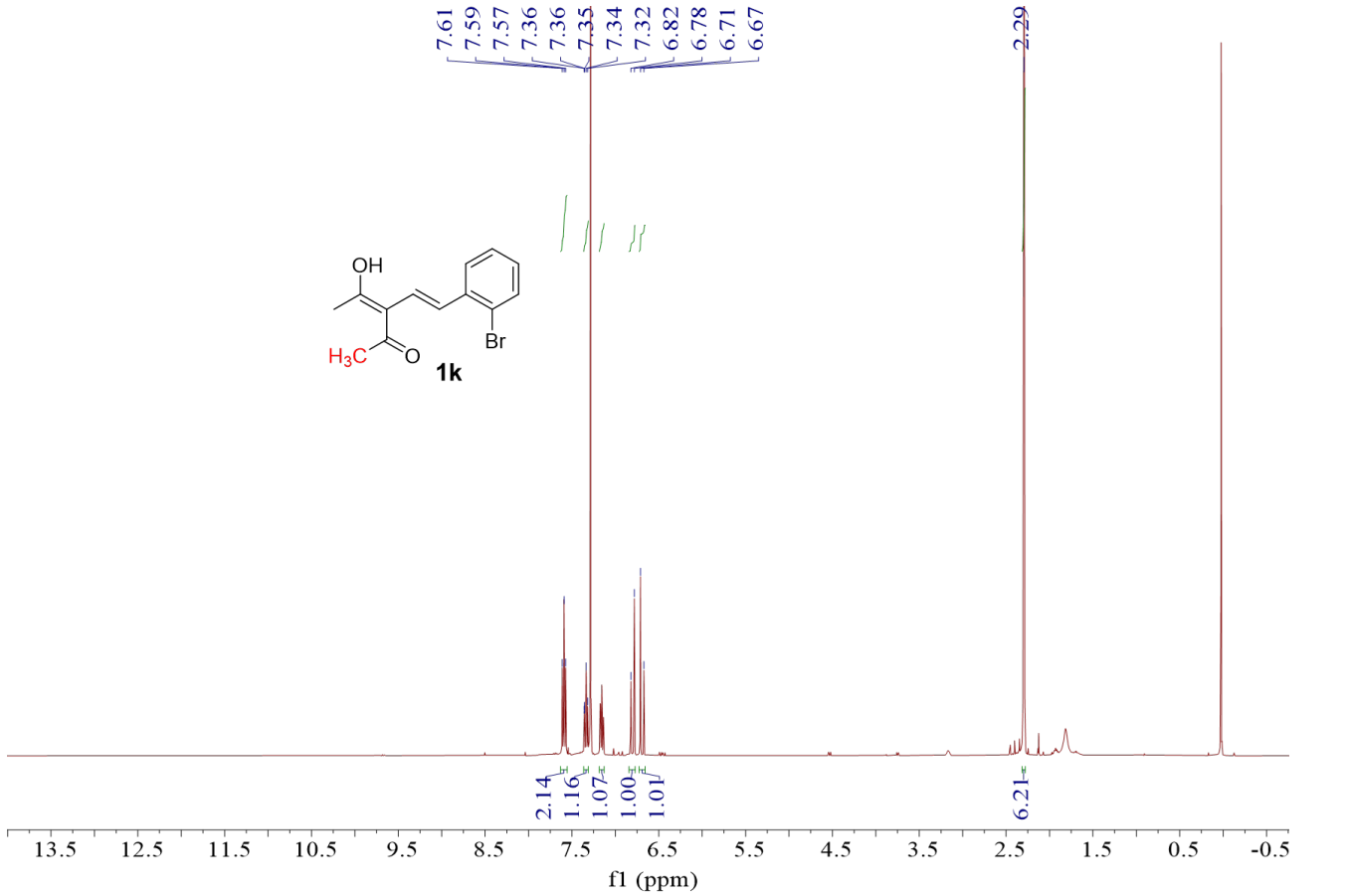
7.33
6.99
6.95
6.79
6.75
2.29
OH
CN
H3C
O
1j
1.81
1.04
1.00
1.08
1.01
5.81
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)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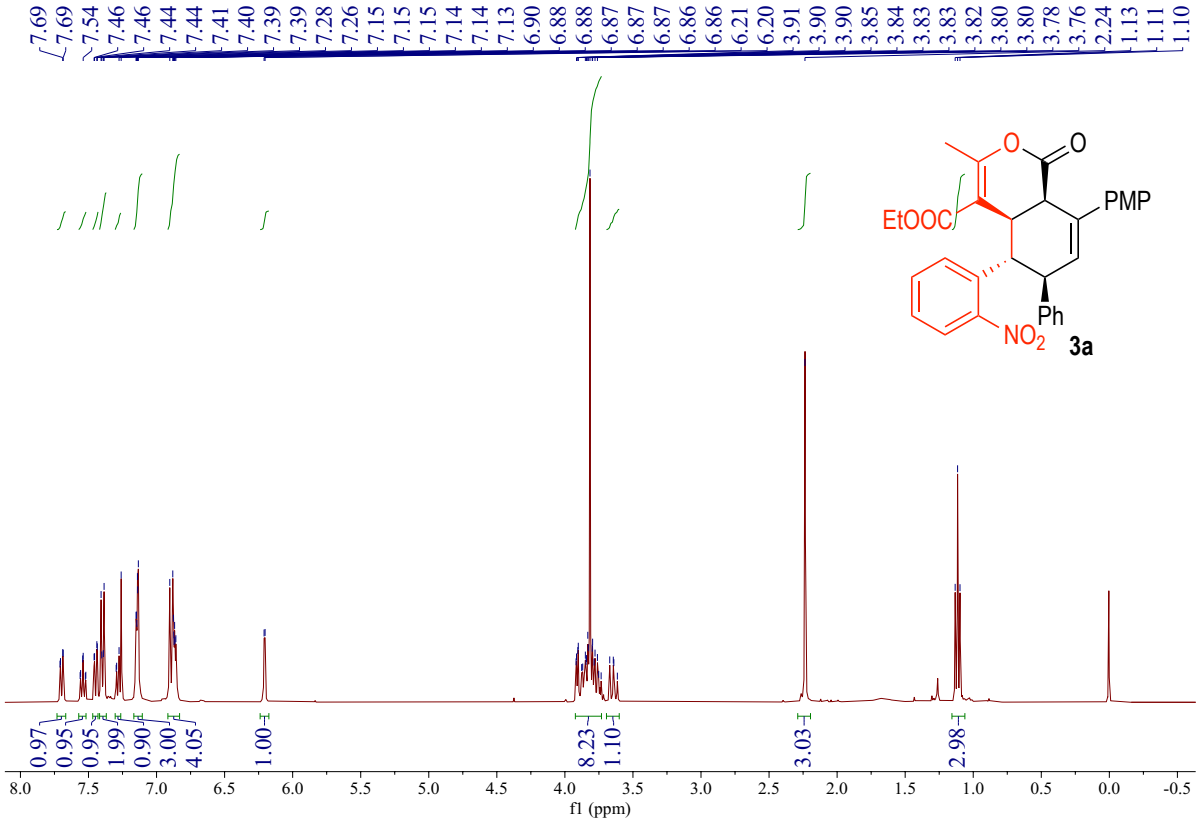
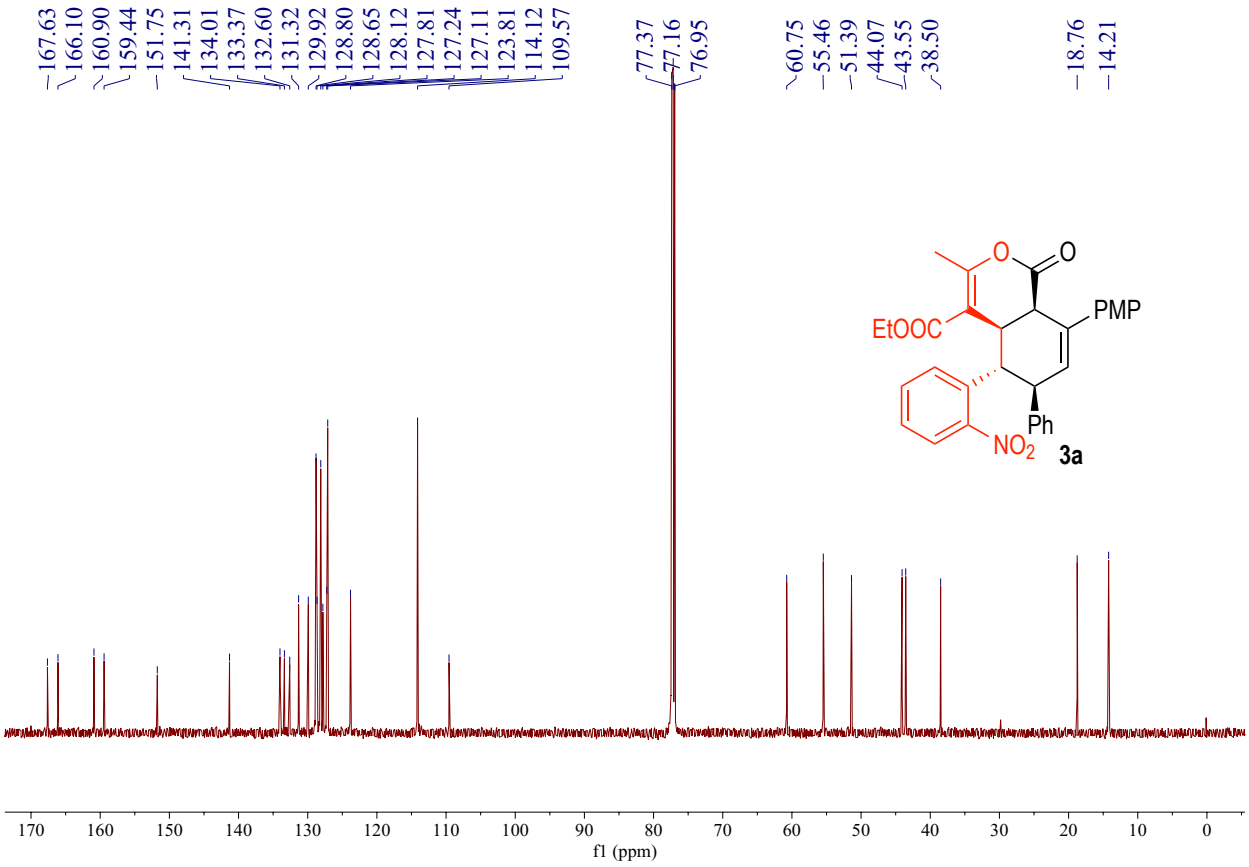
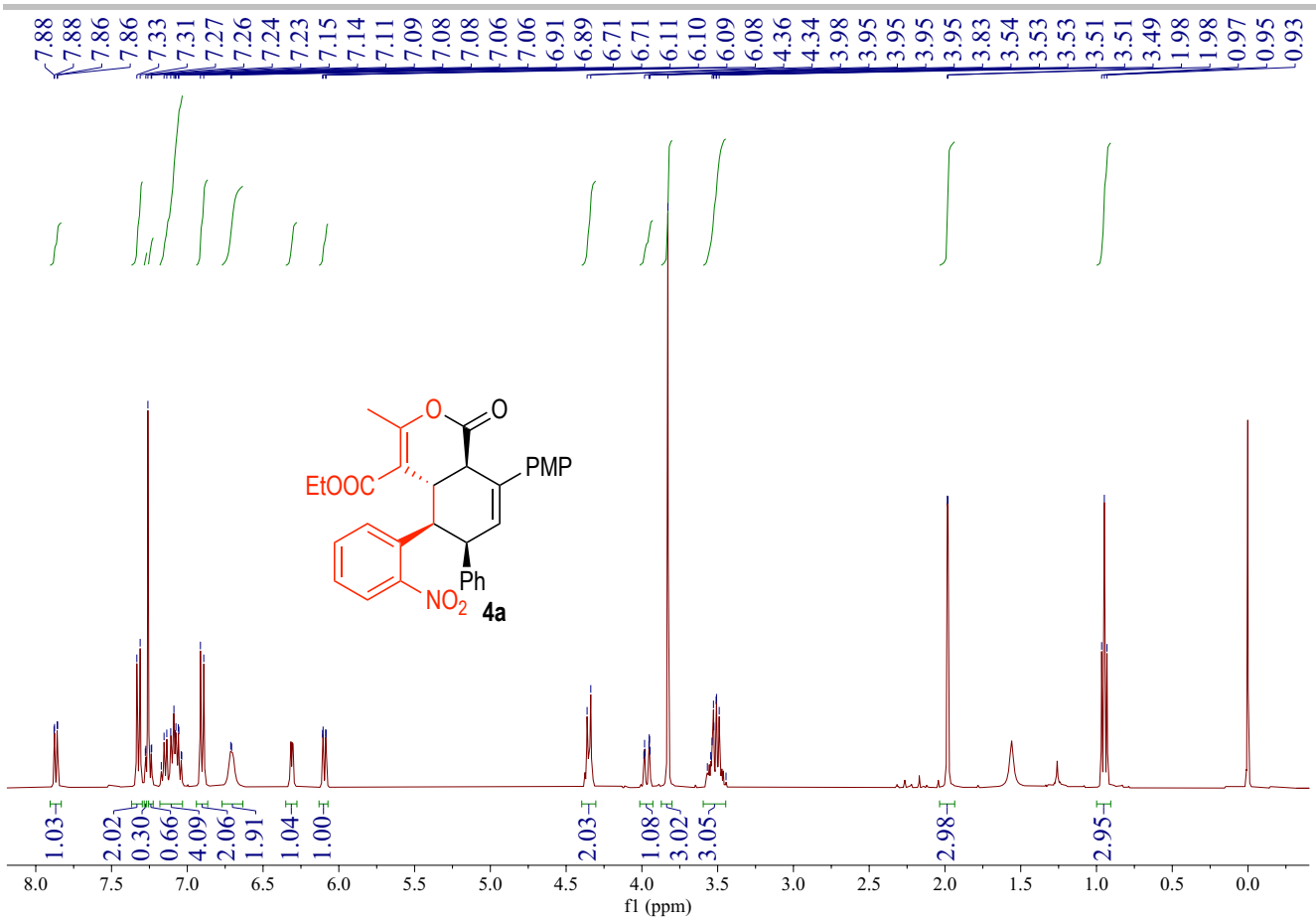
7.34
7.32
6.82
6.78
6.71
6.67
2.29
OH
Br
H3C
O
1k
2.14
1.16
1.07
1.00
1.01
6.21
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

XII. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra of products



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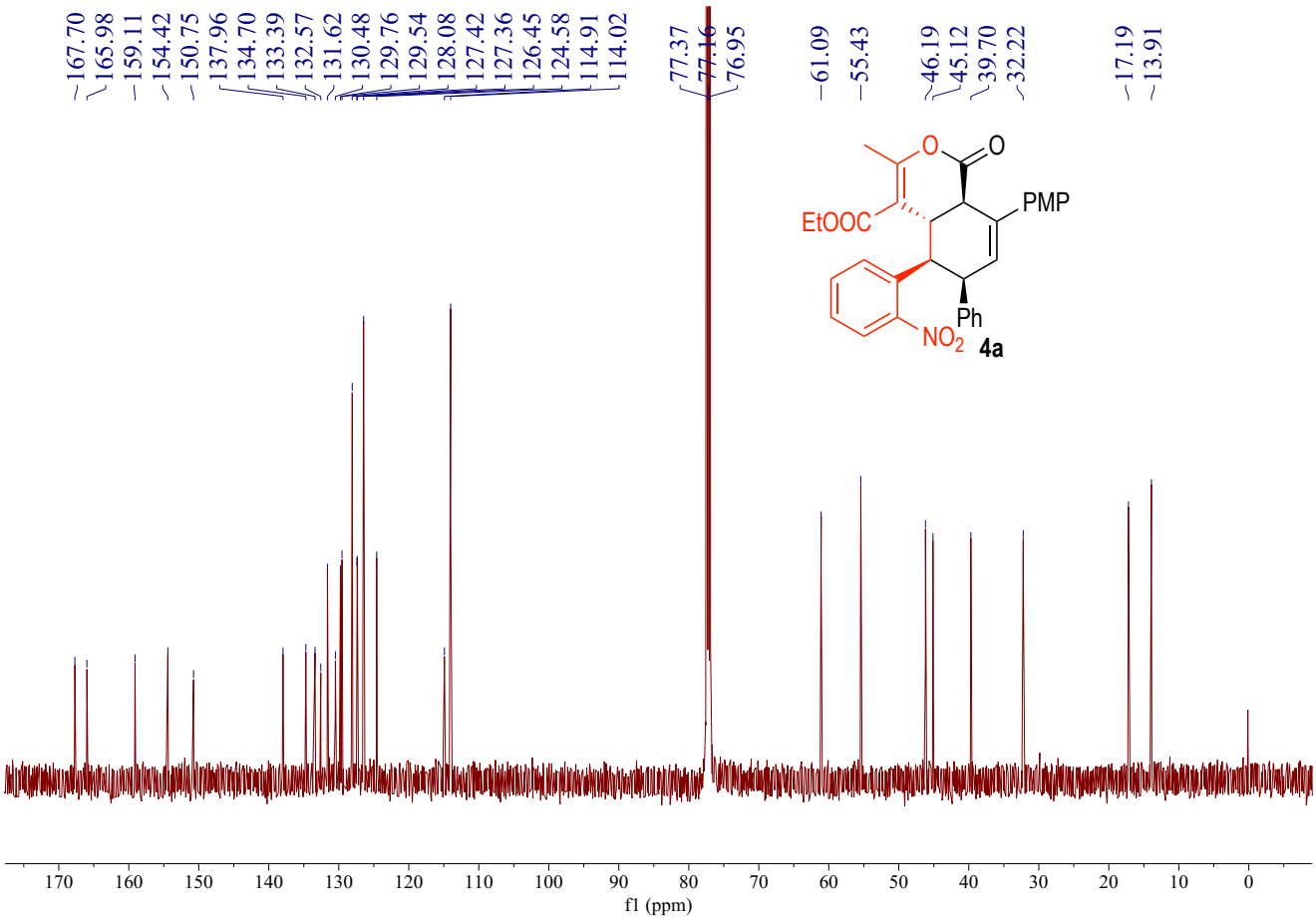
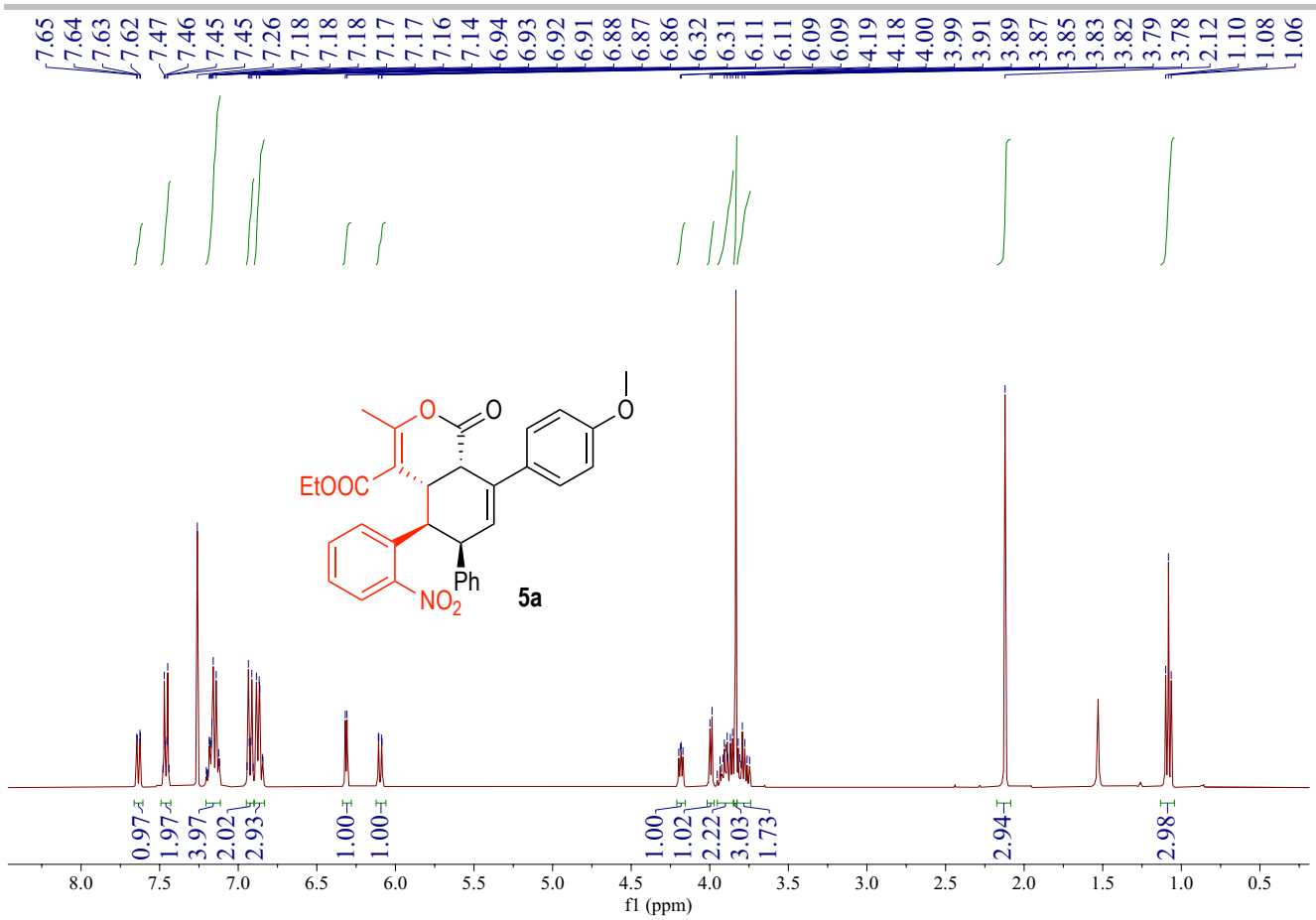
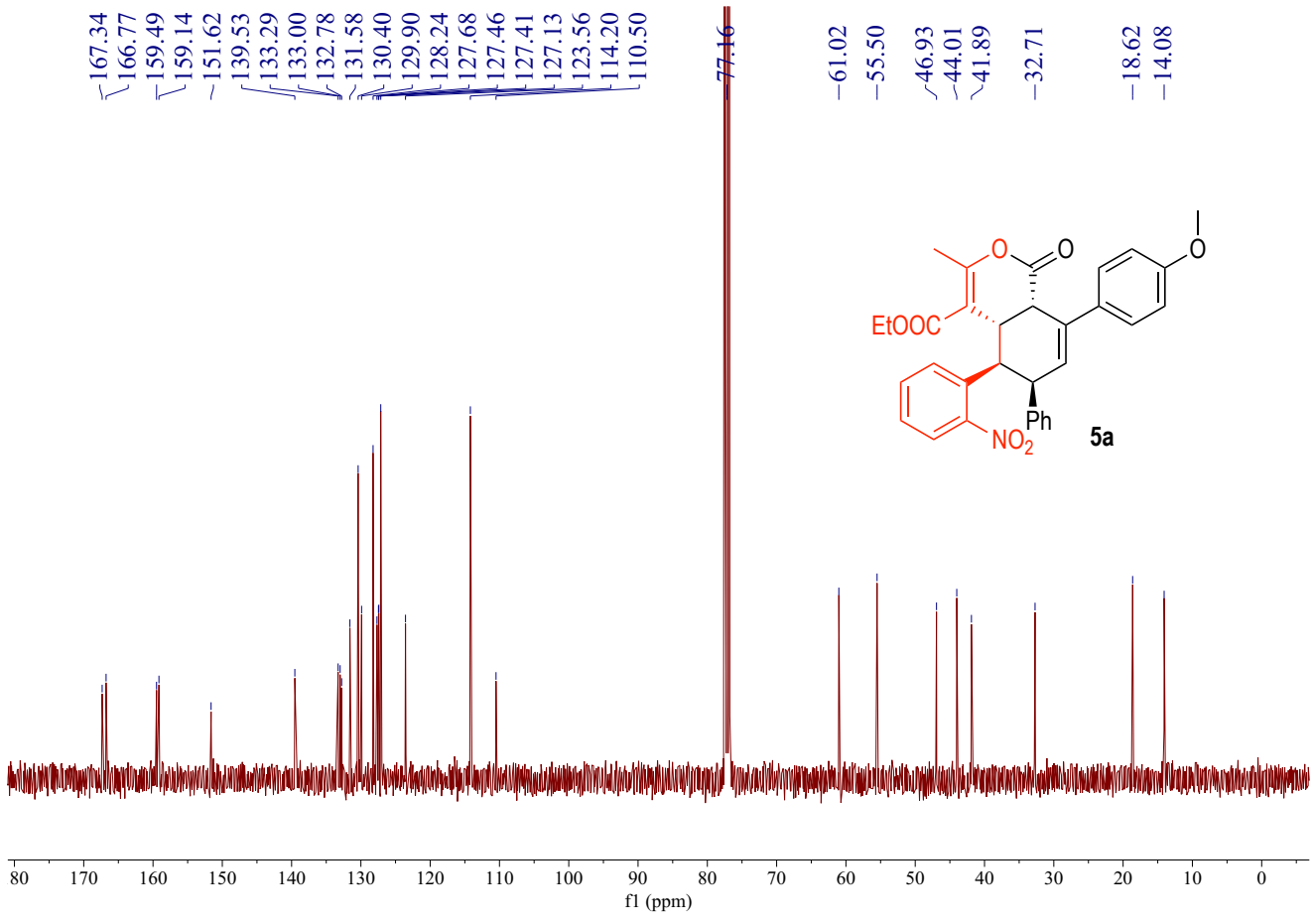
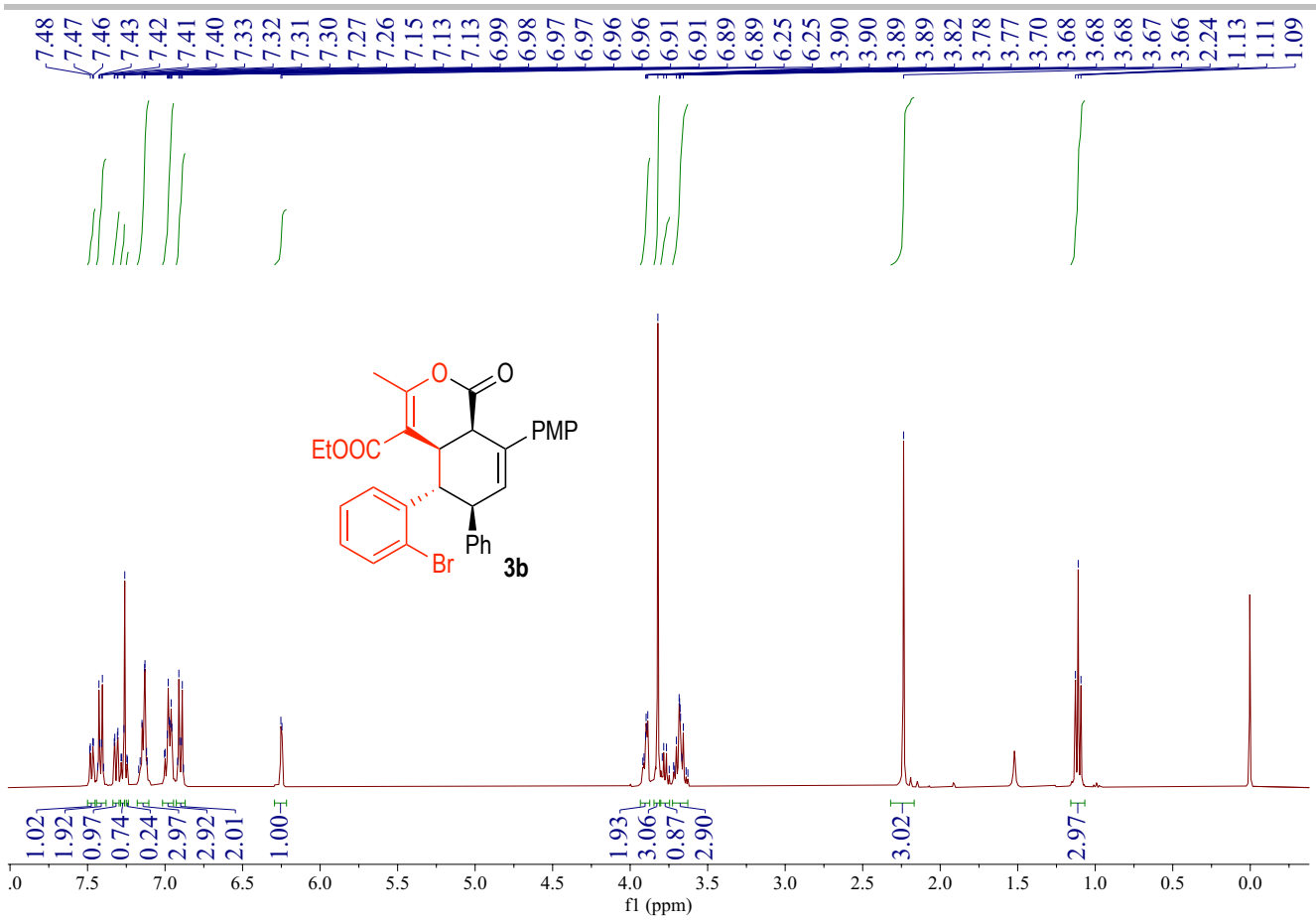
1.03 2.02 0.30 0.66 4.09 2.06 1.91 1.04 1.00 2.03 1.08 3.02 3.05 2.98 2.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
EtOOC
PMP
Ph
NO2
4a


167.70 165.98 159.11 154.42 150.75 137.96 134.70 133.39 132.57 131.62 130.48 129.76 129.54 128.08 127.42 127.36 126.45 124.58 114.91 114.02
77.37 77.16 76.95
61.09 55.43 46.19 45.12 39.70 32.22 17.19 13.91
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
EtOOC
PMP
Ph
NO2
4a


7.65 7.64 7.63 7.62 7.47 7.46 7.45 7.45 7.26 7.18 7.18 7.18 7.17 7.17 7.16 7.14 6.94 6.93 6.92 6.91 6.88 6.87 6.86 6.32 6.31 6.11 6.11 6.09 6.09 4.19 4.18 4.00 3.99 3.91 3.89 3.87 3.85 3.83 3.82 3.79 3.78 2.12 1.10 1.08 1.06
EtOOC
Ph
NO2
5a
0.97 1.97 3.97 2.02 2.93 1.00 1.00 1.00 1.02 2.22 3.03 1.73 2.94 2.98
f1 (ppm)


167.34 166.77 159.49 159.14 151.62 139.53 133.29 133.00 132.78 131.58 130.40 129.90 128.24 127.68 127.46 127.41 127.13 123.56 114.20 110.50
77.16
61.02 55.50 46.93 44.01 41.89 32.71 18.62 14.08
EtOOC
Ph
NO2
5a
f1 (ppm)


7.48 7.47 7.46 7.43 7.42 7.41 7.40 7.33 7.32 7.31 7.30 7.27 7.26 7.15 7.13 7.13 6.99 6.98 6.97 6.97 6.96 6.96 6.91 6.91 6.89 6.89 6.25 6.25 3.90 3.90 3.89 3.89 3.82 3.78 3.77 3.70 3.68 3.68 3.68 3.67 3.66 2.24 1.13 1.11 1.09
EtOOC
PMP
Ph
Br
3b
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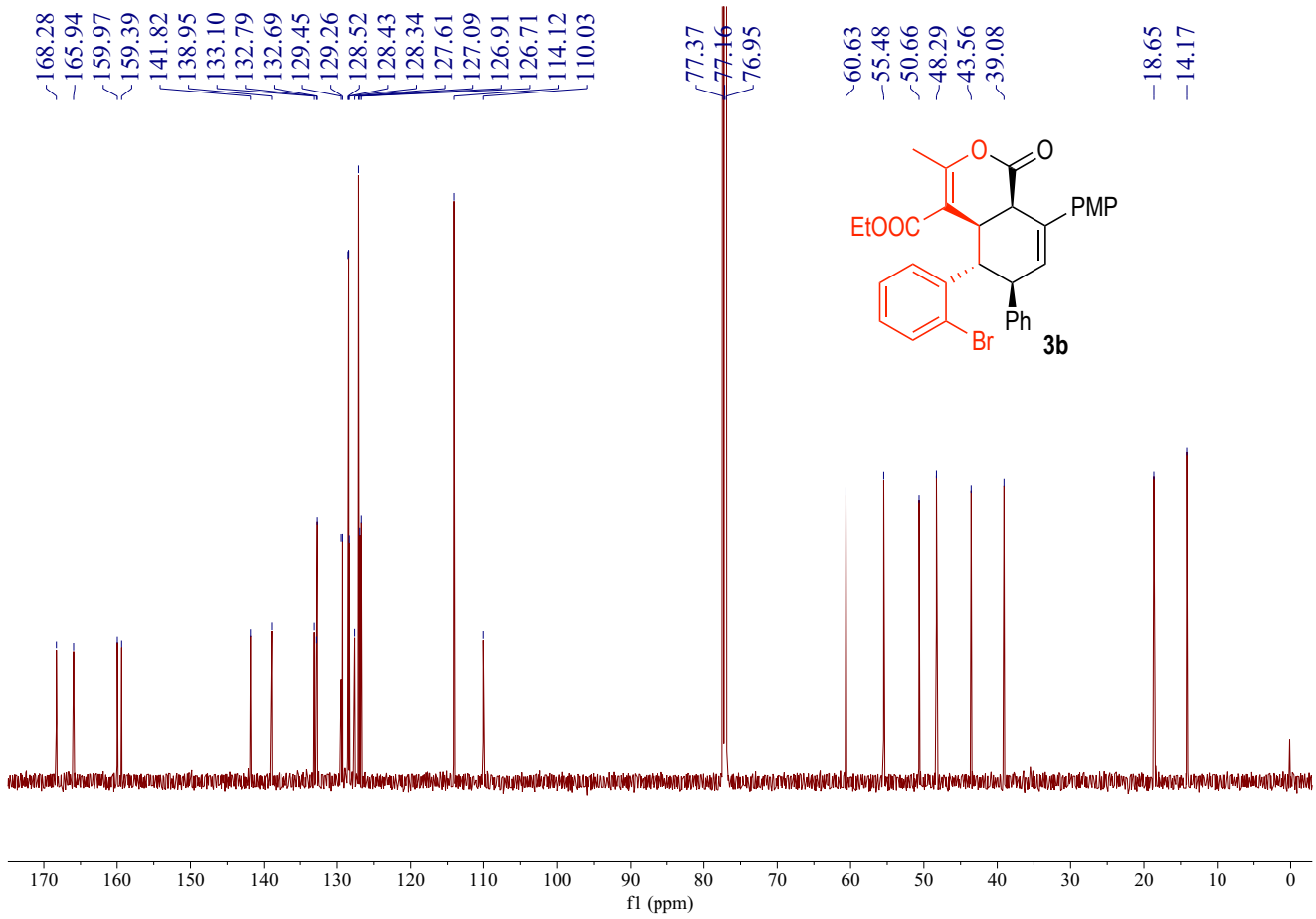
f1 (ppm)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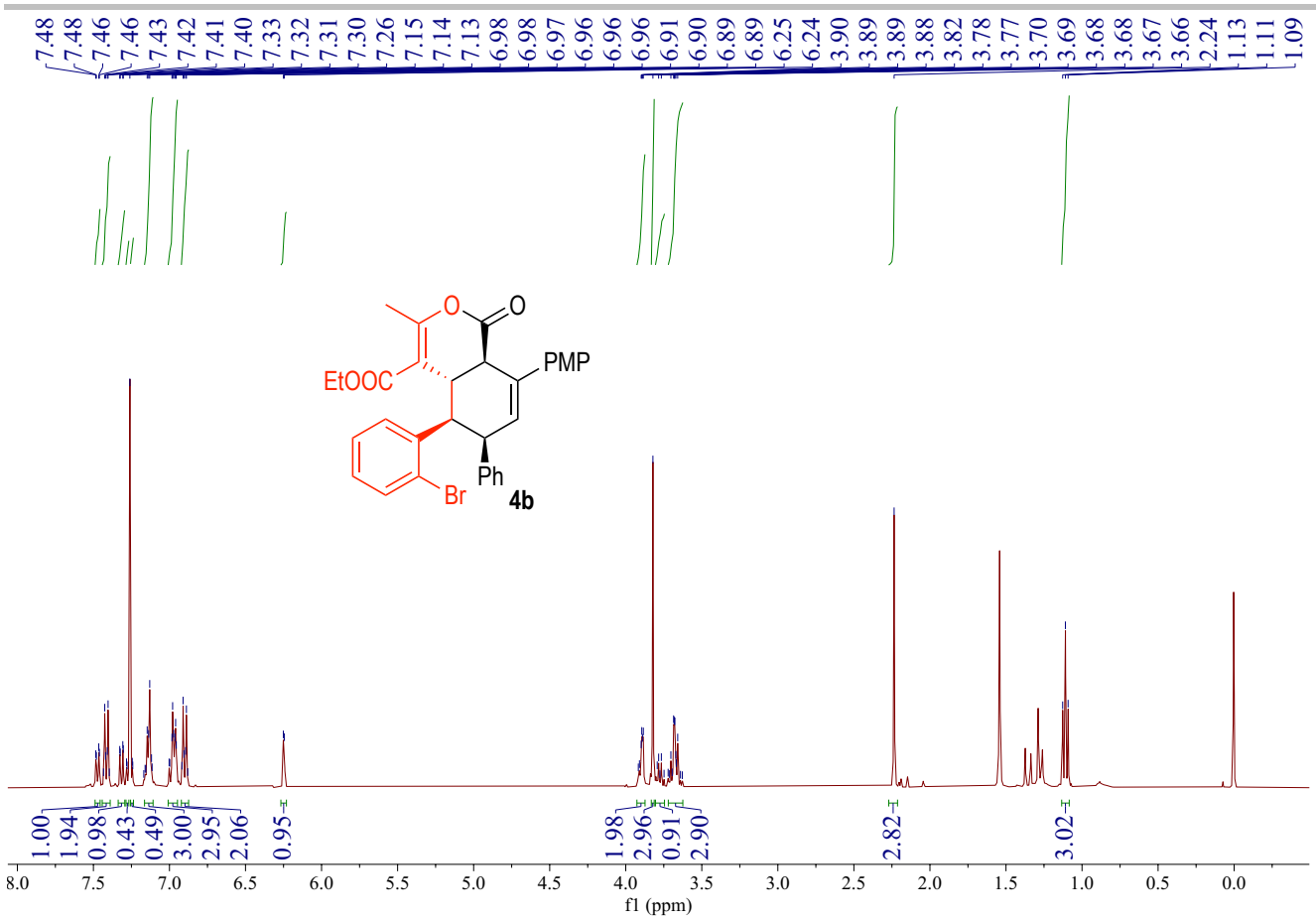
77.37 77.16 76.95
60.63 55.48 50.66 48.29 43.56 39.08
18.65 14.17
EtOOC
PMP
Ph
Br
3b
f1 (ppm)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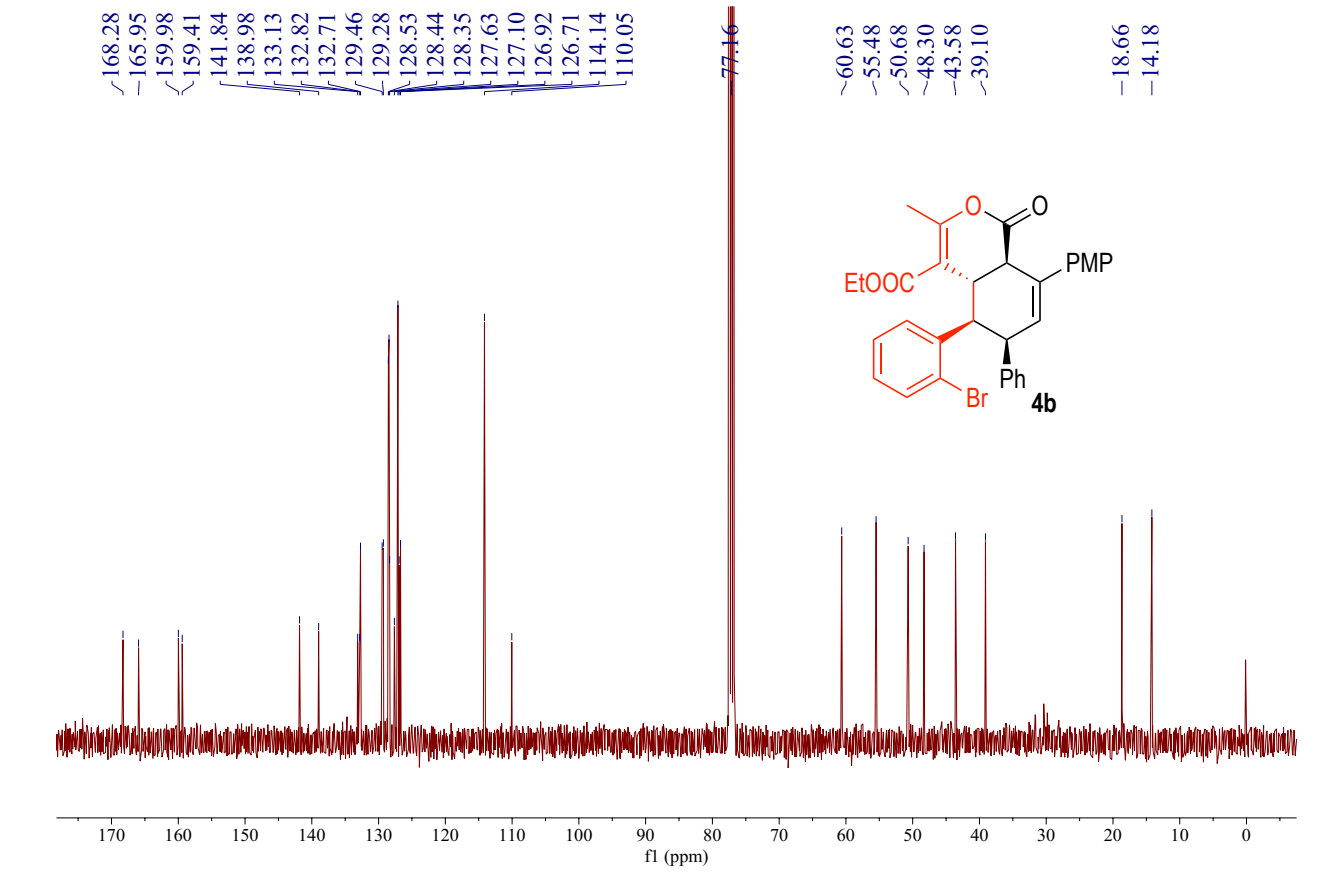
O
O
EtOOC
PMP
Ph
Br
4b
1.00 1.94 0.98 0.43 0.49 3.00 2.95 2.06 0.95 1.98 2.96 0.91 2.90 2.82 3.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.16
60.63 55.48 50.68 48.30 43.58 39.10
18.66 14.18
O
O
EtOOC
PMP
Ph
Br
4b
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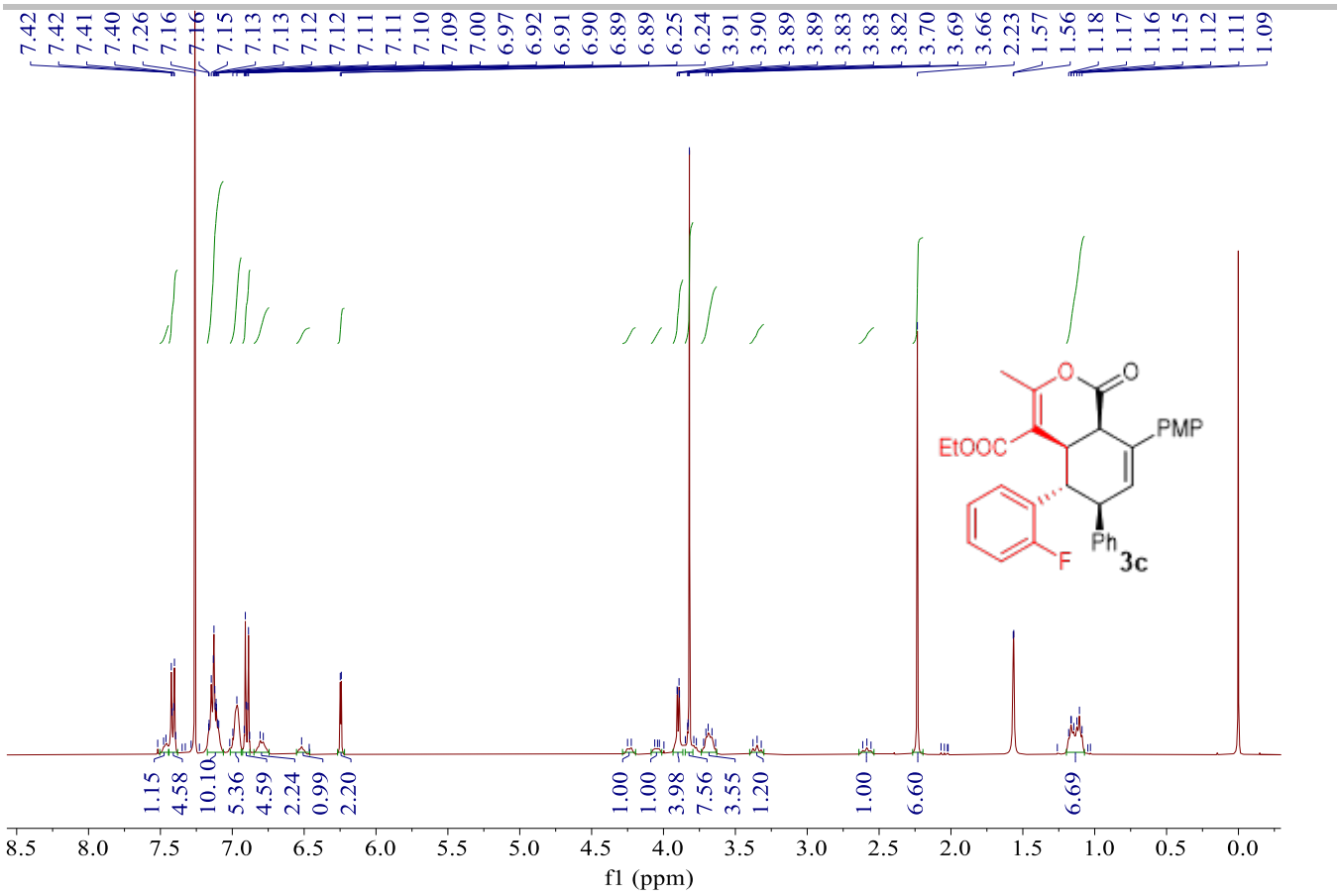
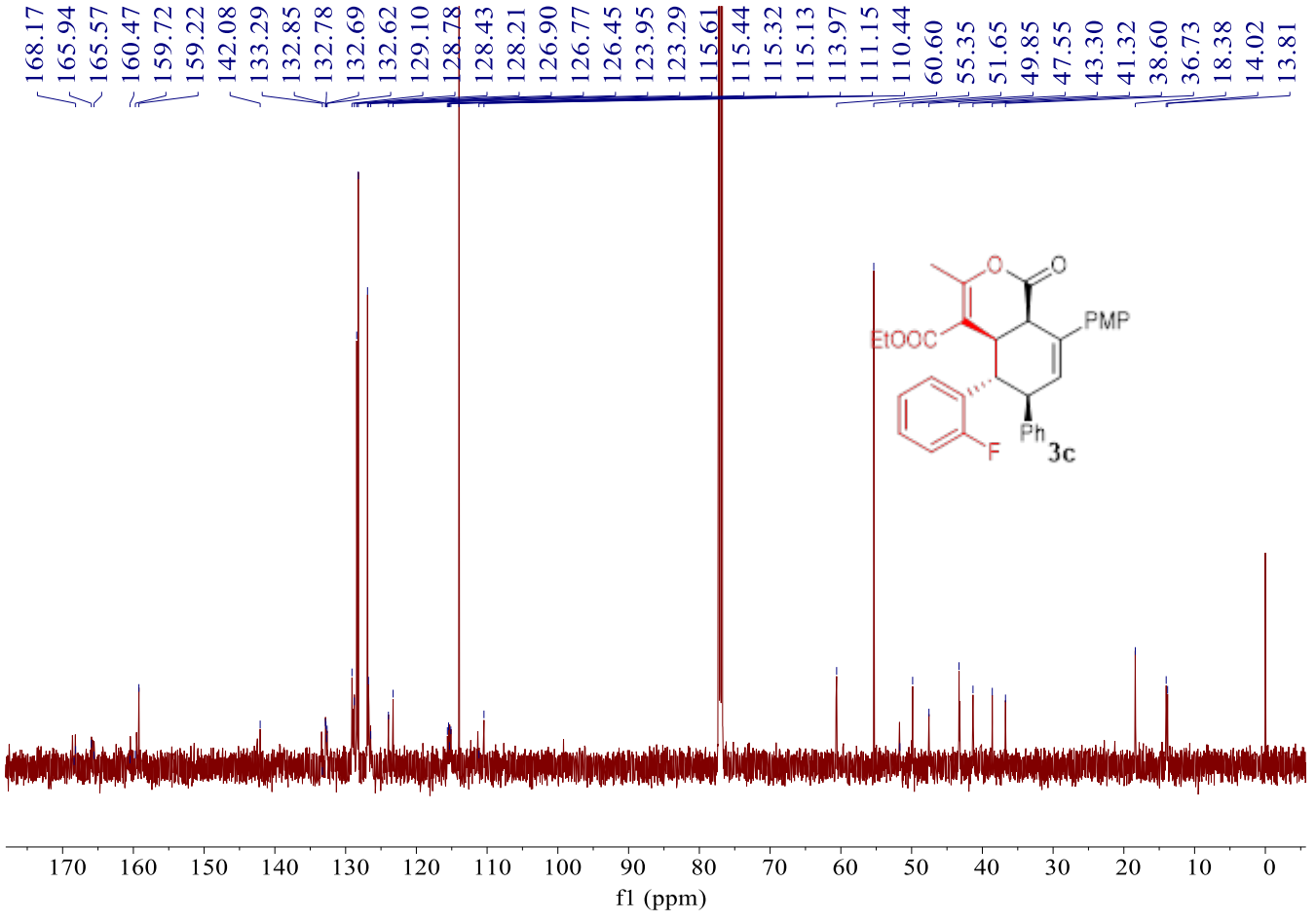
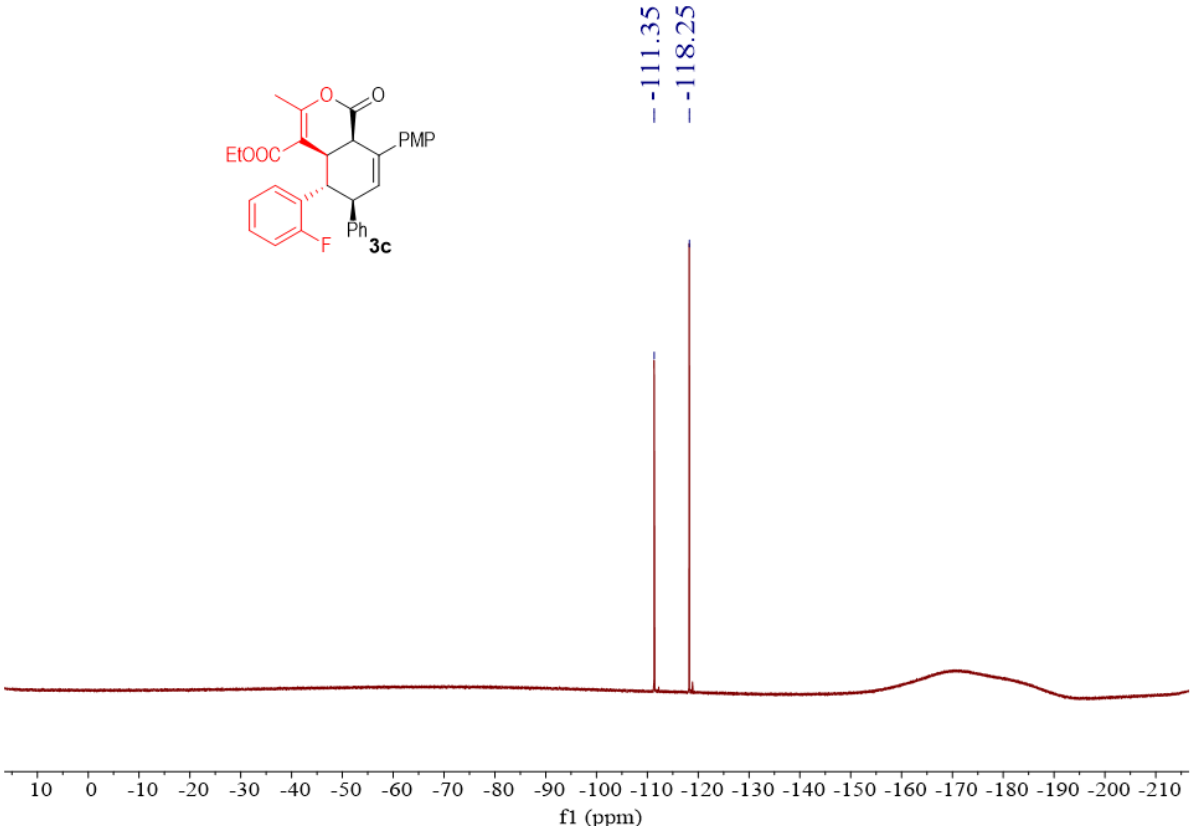
f1 (ppm)


7.42 7.42 7.41 7.40 7.26 7.16 7.16 7.15 7.13 7.13 7.12 7.12 7.11 7.11 7.10 7.09 7.00 6.97 6.92 6.91 6.90 6.89 6.89 6.25 6.24 3.91 3.90 3.89 3.89 3.83 3.83 3.82 3.70 3.69 3.66 2.23 1.57 1.56 1.18 1.17 1.16 1.15 1.12 1.11 1.09
EtOOC
PMP
Ph
F
3c
1.15 4.58 10.10 5.36 4.59 2.24 0.99 2.20 1.00 1.00 3.98 7.56 3.55 1.20 1.00 6.60 6.69
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.17 165.94 165.57 160.47 159.72 159.22 142.08 133.29 132.85 132.78 132.69 132.62 129.10 128.78 128.43 128.21 126.90 126.77 126.45 123.95 123.29 115.61 115.44 115.32 115.13 113.97 111.15 110.44 60.60 55.35 51.65 49.85 47.55 43.30 41.32 38.60 36.73 18.38 14.02 13.81
EtOOC
PMP
Ph
F
3c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-111.35
-118.25
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Ph
F
3c
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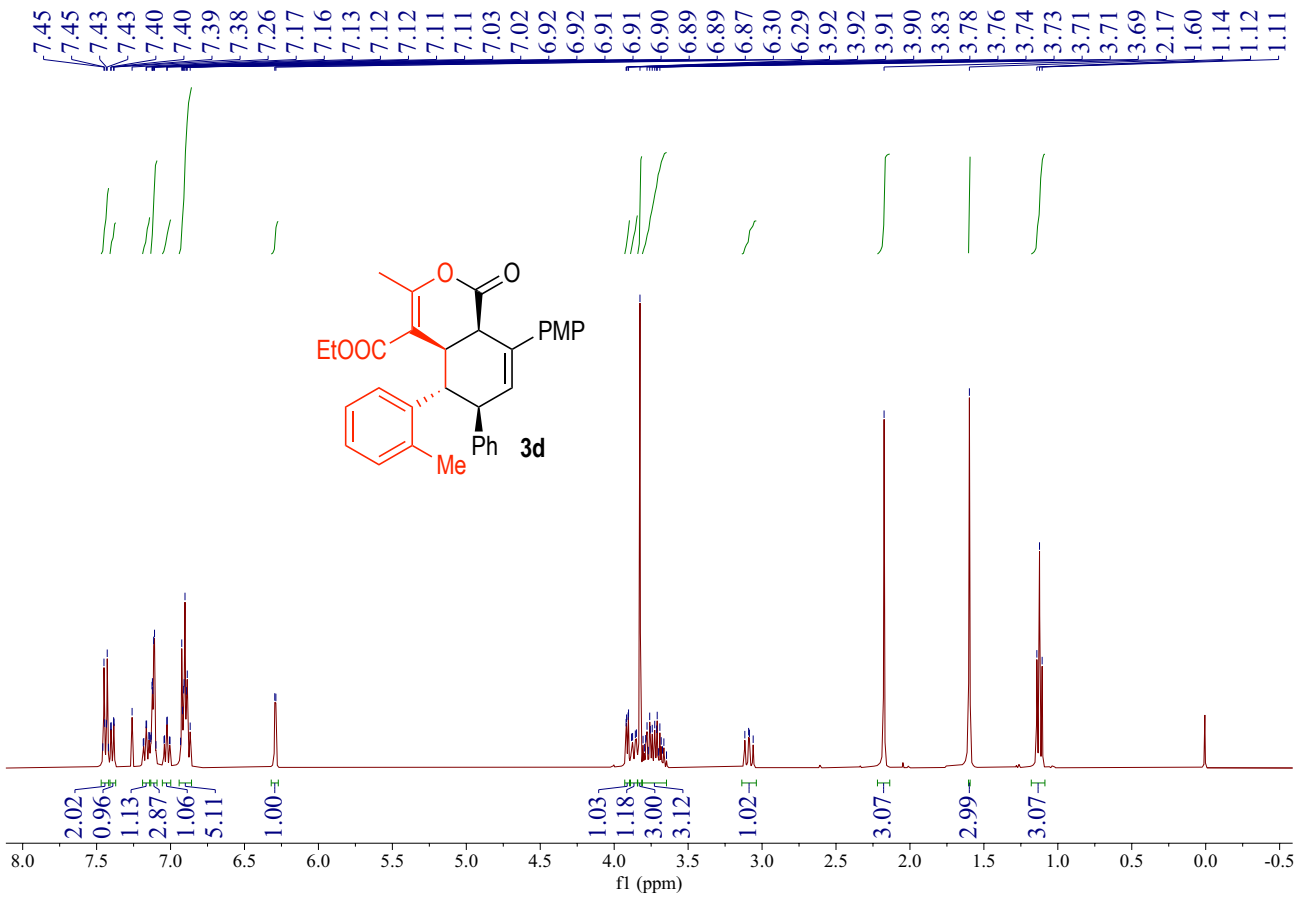
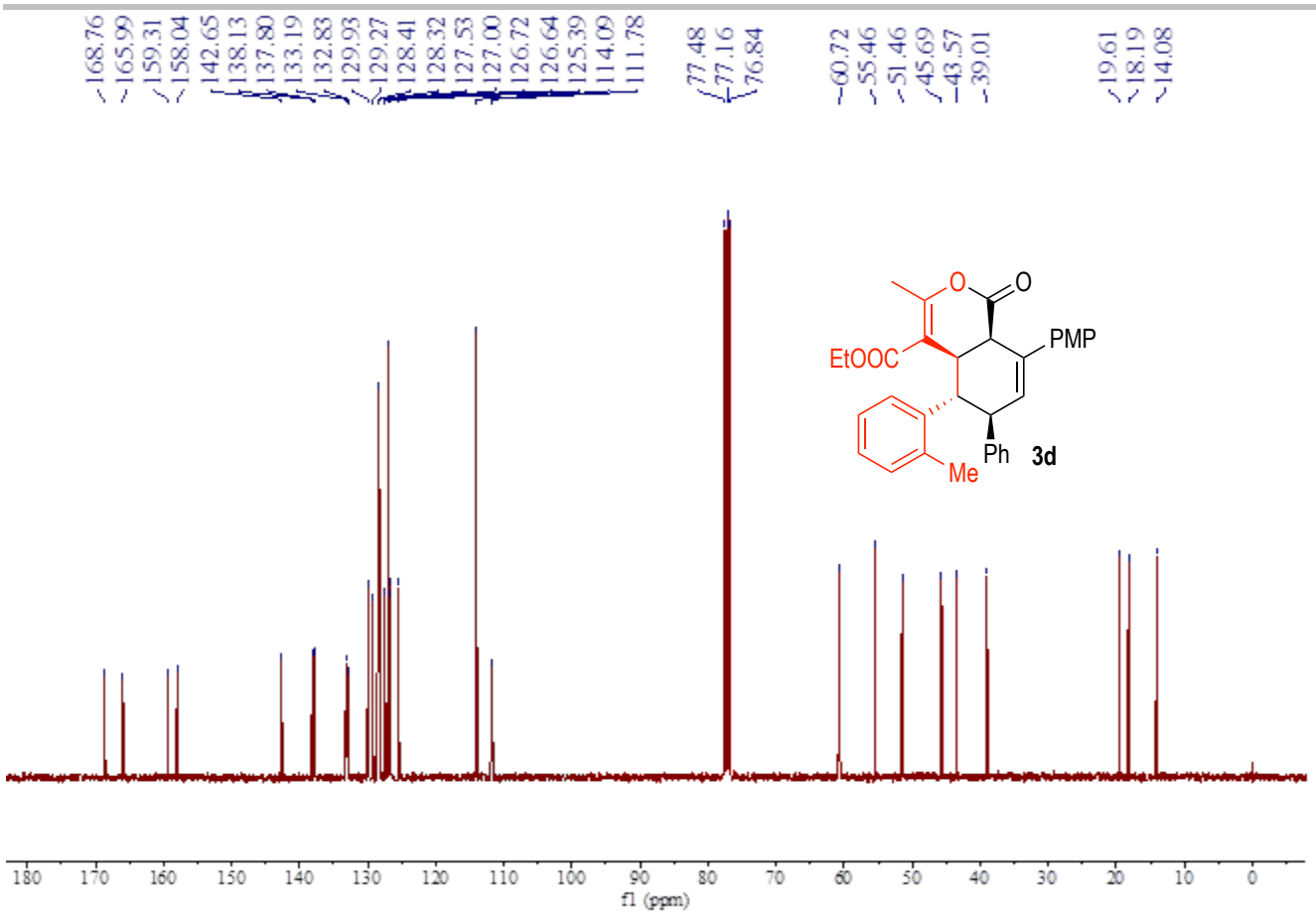
f1 (ppm)


7.45 7.45 7.43 7.43 7.40 7.40 7.39 7.38 7.26 7.17 7.16 7.13 7.12 7.12 7.11 7.11 7.03 7.02 6.92 6.92 6.91 6.91 6.90 6.89 6.89 6.87 6.30 6.29 3.92 3.92 3.91 3.90 3.83 3.78 3.76 3.74 3.73 3.71 3.71 3.69 2.17 1.60 1.14 1.12 1.11
EtOOC
PMP
Ph
Me
3d
2.02 0.96 1.13 2.87 1.06 5.11 1.00 1.03 1.18 3.00 3.12 1.02 3.07 2.99 3.07
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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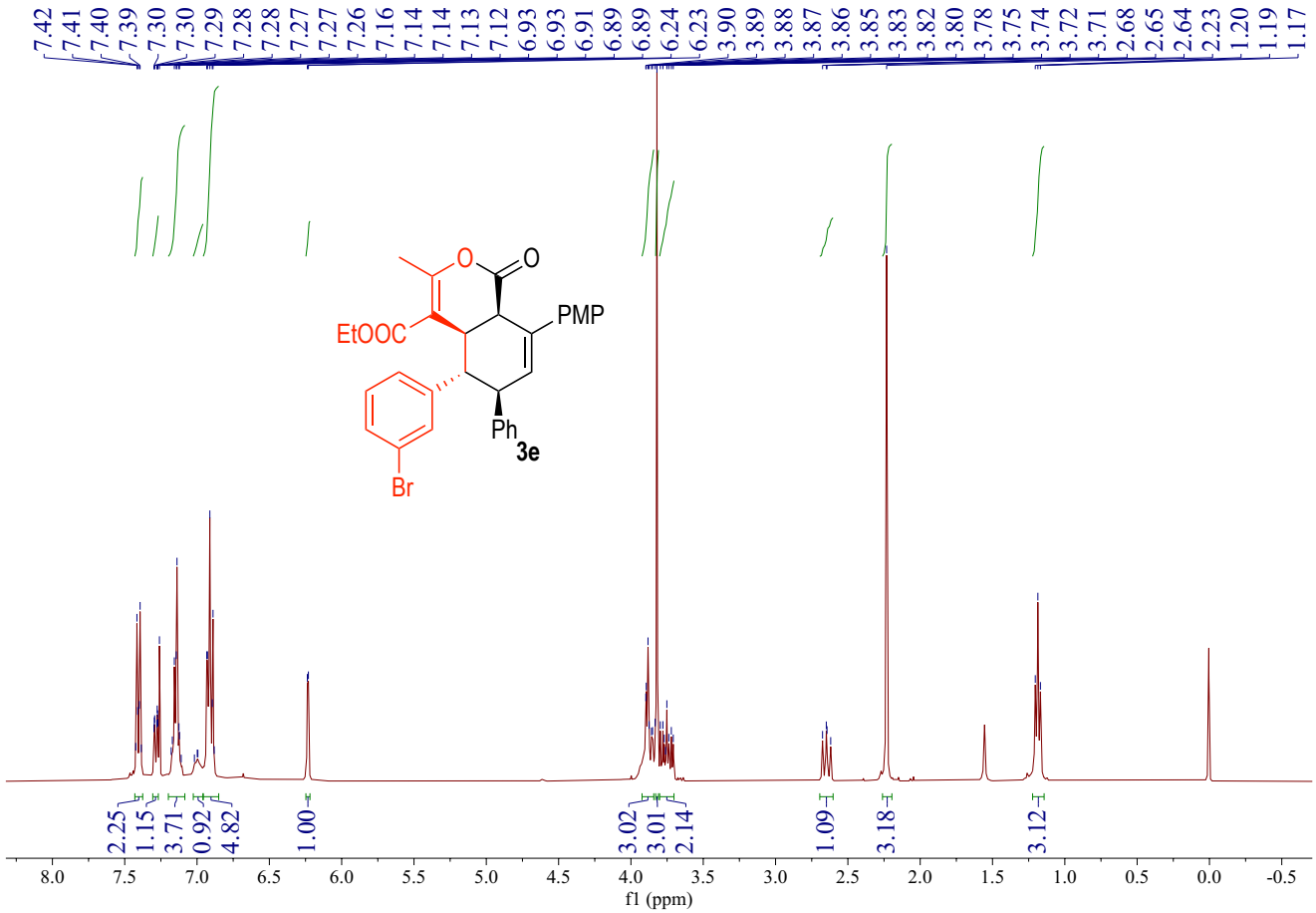
128.41
128.32
127.53
127.00
126.72
126.64
125.39
114.09
111.78
77.48
77.16
76.84
60.72
55.46
51.46
45.69
43.57
39.01
19.61
18.19
14.08
O
O
EtOOC
PMP
Ph
Me
3d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.16
7.14
7.14
7.13
7.12
6.93
6.93
6.91
6.89
6.89
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6.23
3.90
3.89
3.88
3.87
3.86
3.85
3.83
3.82
3.80
3.78
3.75
3.74
3.72
3.71
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2.23
1.20
1.19
1.17
O
O
EtOOC
PMP
Ph
3e
Br
2.25
1.15
3.71
0.92
4.82
1.00
3.02
3.01
2.14
1.09
3.18
3.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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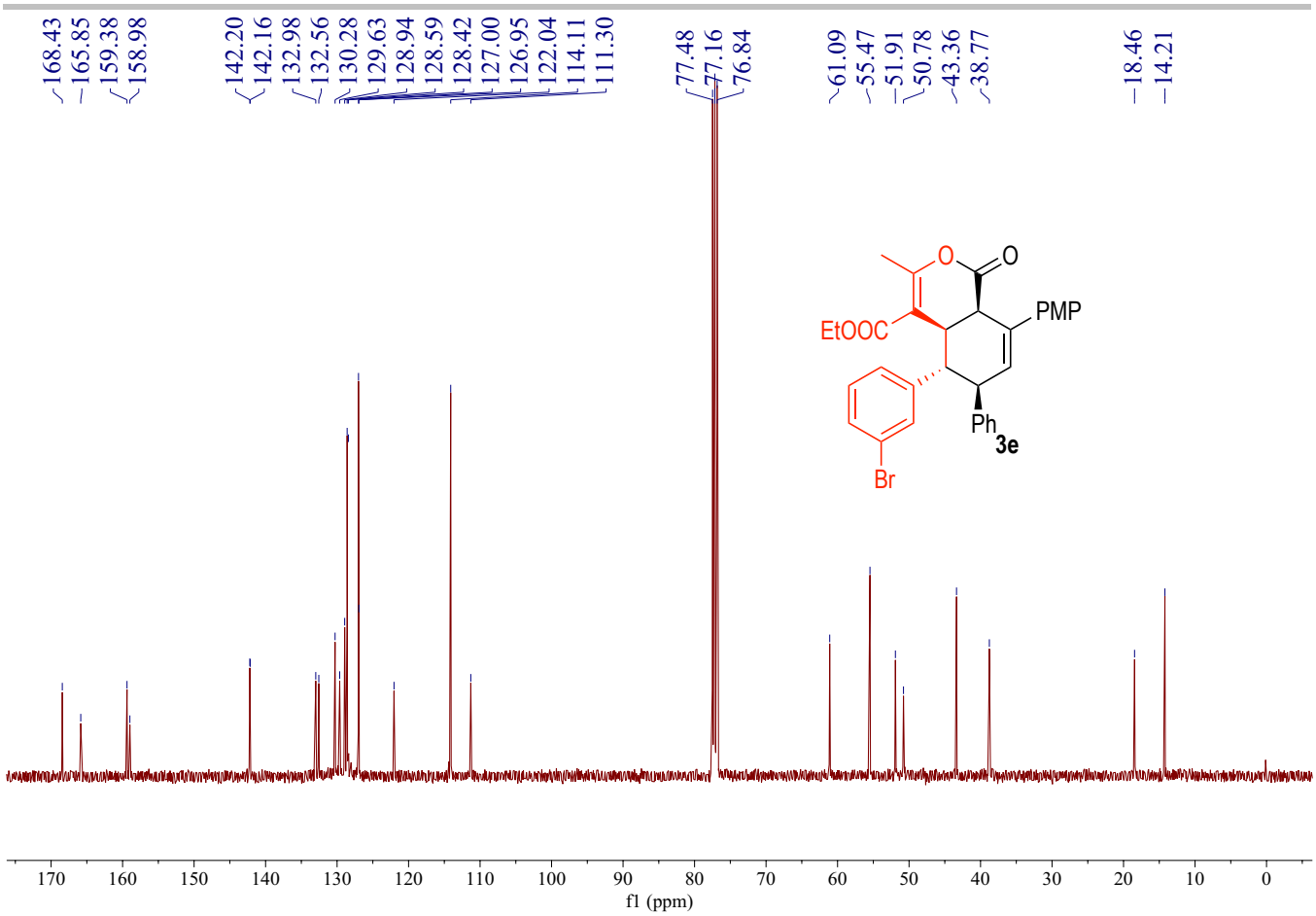
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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129.63
128.94
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126.95
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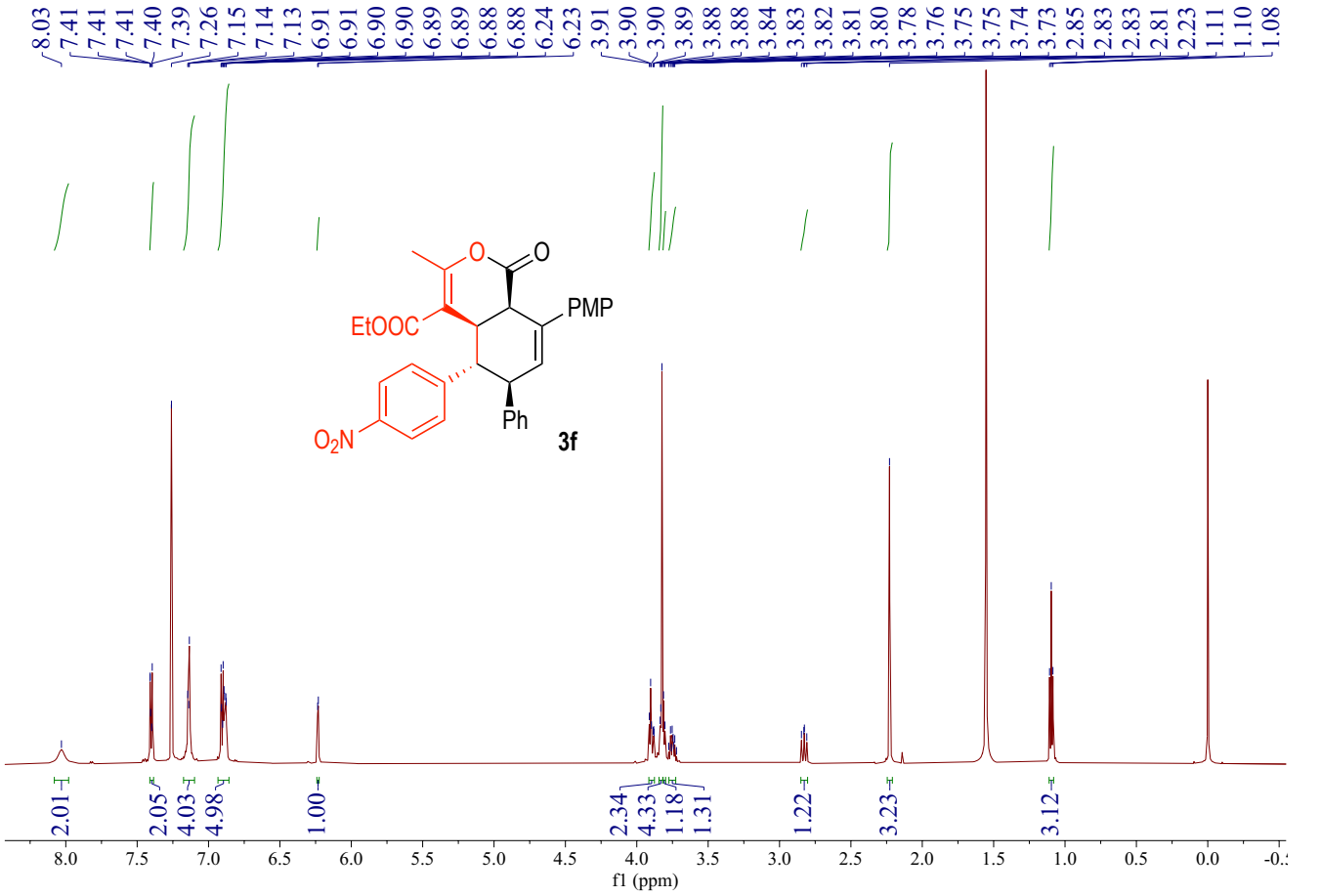
EtOOC
PMP
Ph
Br
3e
f1 (ppm)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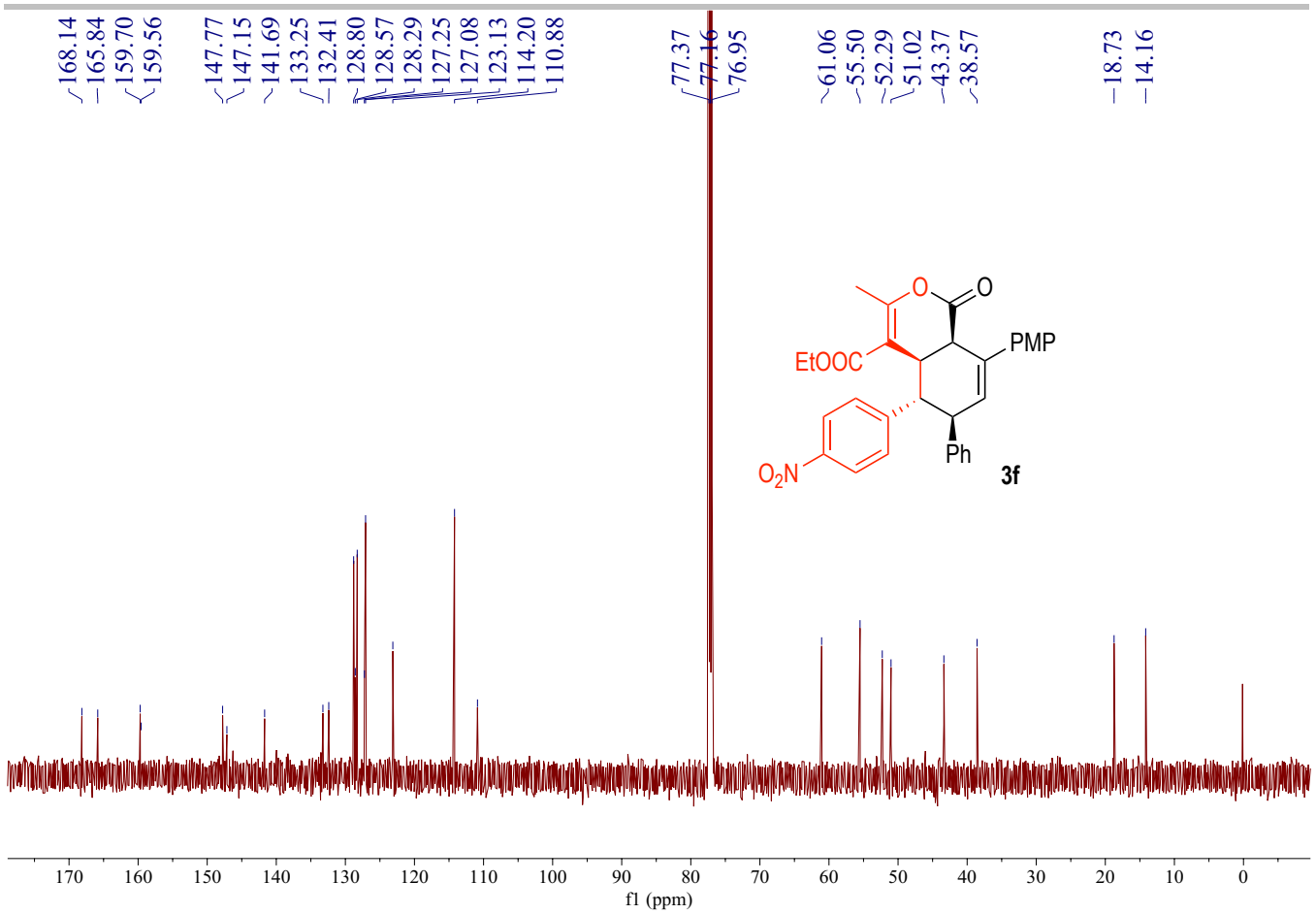
3.88
3.84
3.83
3.82
3.81
3.80
3.78
3.76
3.75
3.75
3.74
3.73
2.85
2.83
2.83
2.81
2.23
1.11
1.10
1.08
EtOOC
PMP
Ph
O2N
3f
2.01
2.05
4.03
4.98
1.00
2.34
4.33
1.18
1.31
1.22
3.23
3.12
f1 (ppm)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132.41
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128.57
128.29
127.25
127.08
123.13
114.20
110.88
77.37
77.16
76.95
61.06
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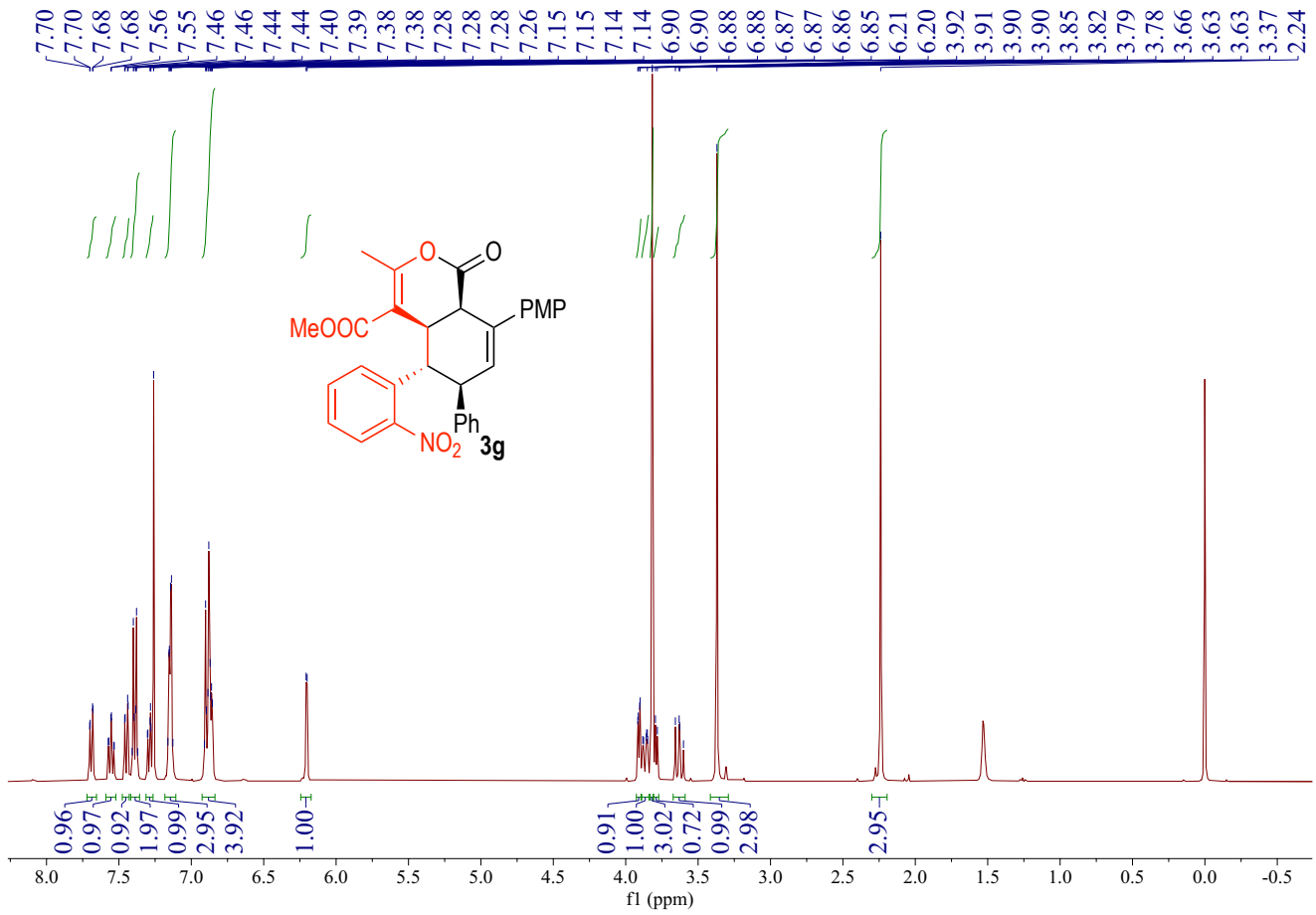
43.37
38.57
18.73
14.16
EtOOC
PMP
Ph
O2N
3f
f1 (ppm)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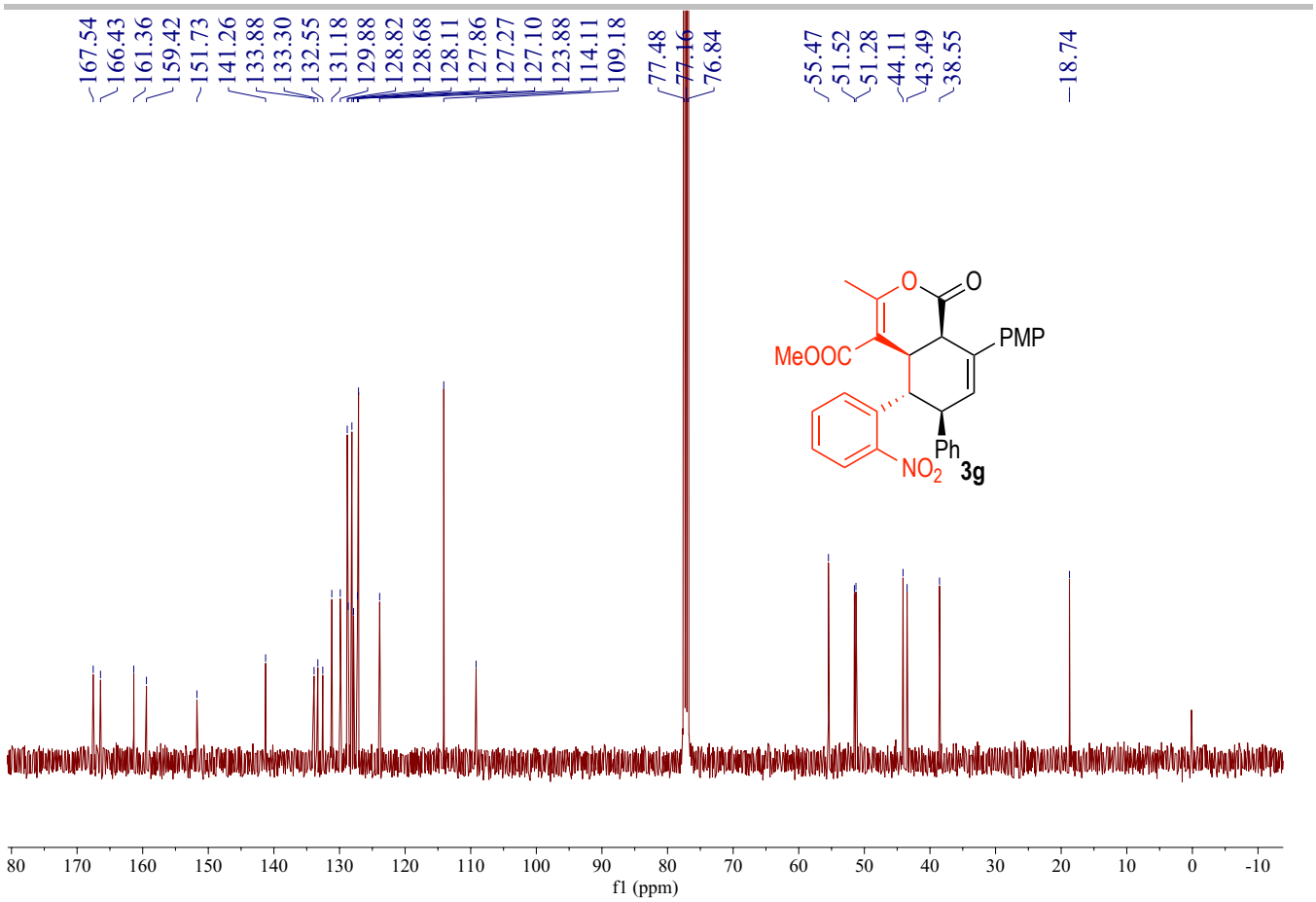
7.15
7.14
7.14
6.90
6.90
6.88
6.88
6.87
6.87
6.86
6.85
6.21
6.20
3.92
3.91
3.90
3.90
3.85
3.82
3.79
3.78
3.66
3.63
3.63
3.37
2.24
MeOOC
PMP
Ph
NO2
3g
0.96
0.97
0.92
1.97
0.99
2.95
3.92
1.00
0.91
1.00
3.02
0.72
0.99
2.98
2.95
f1 (ppm)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PMP
Ph
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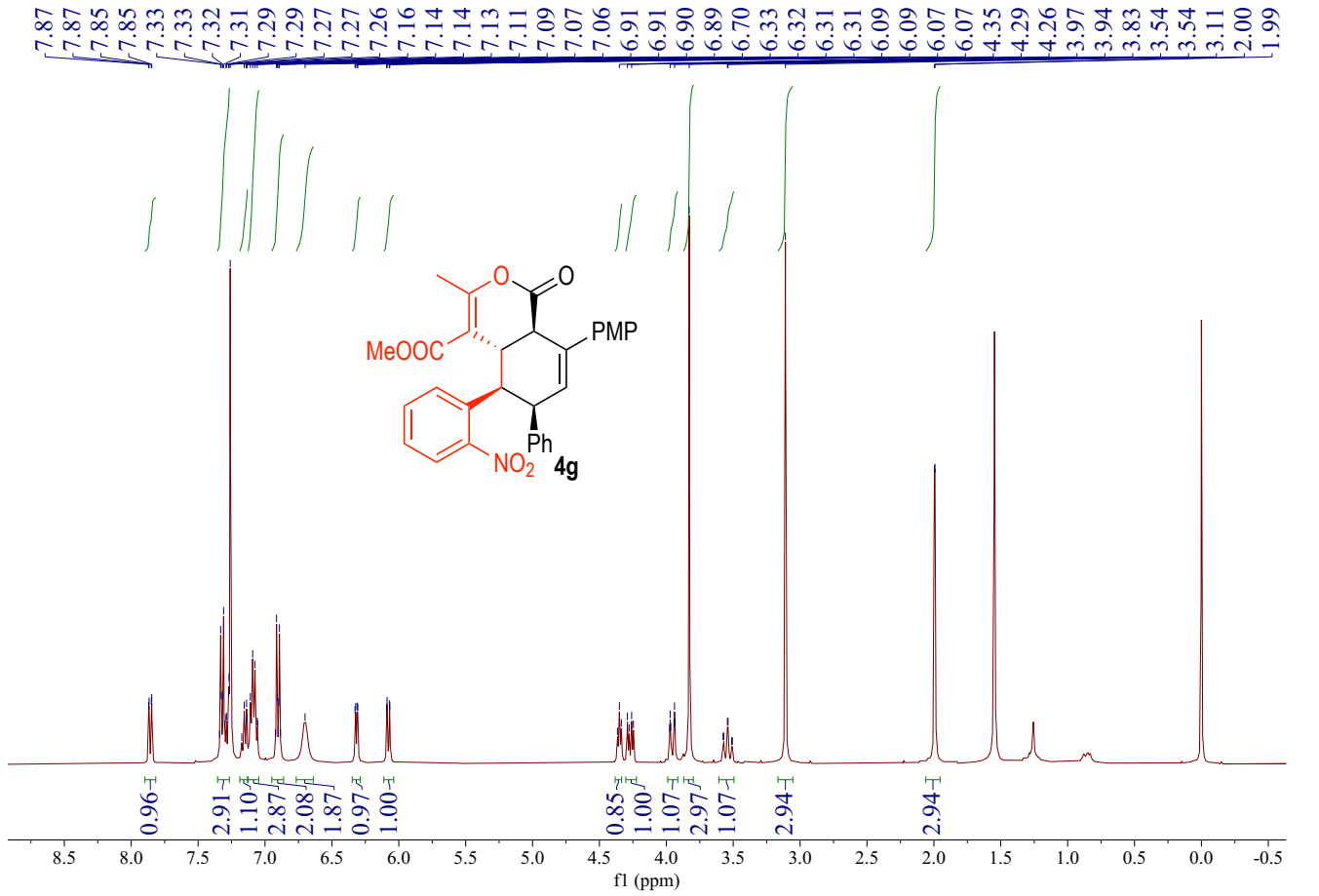
3g
f1 (ppm)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6.31
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6.09
6.07
6.07
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4.29
4.26
3.97
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3.83
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3.54
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PMP
Ph
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4g
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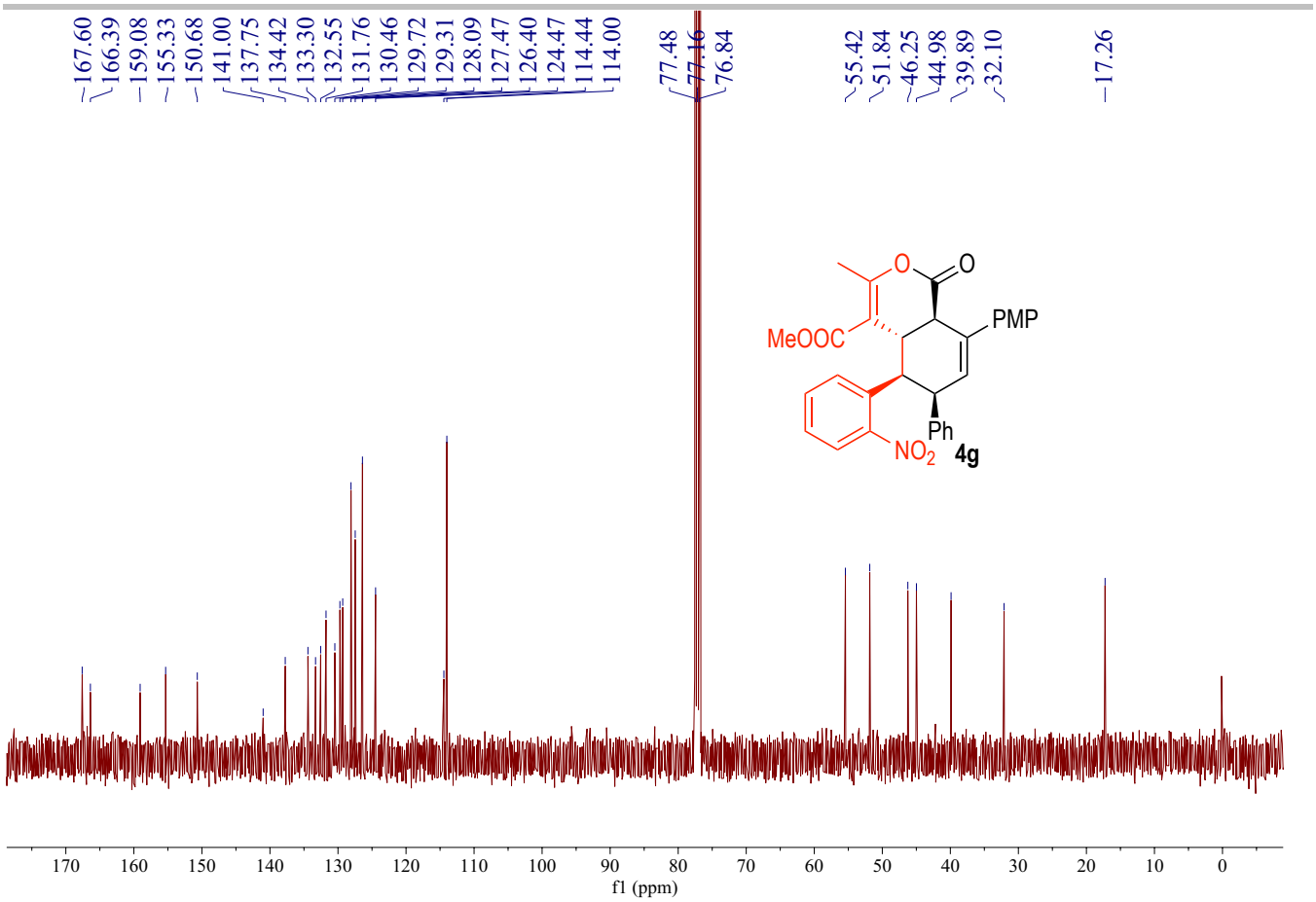
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PMP
Ph
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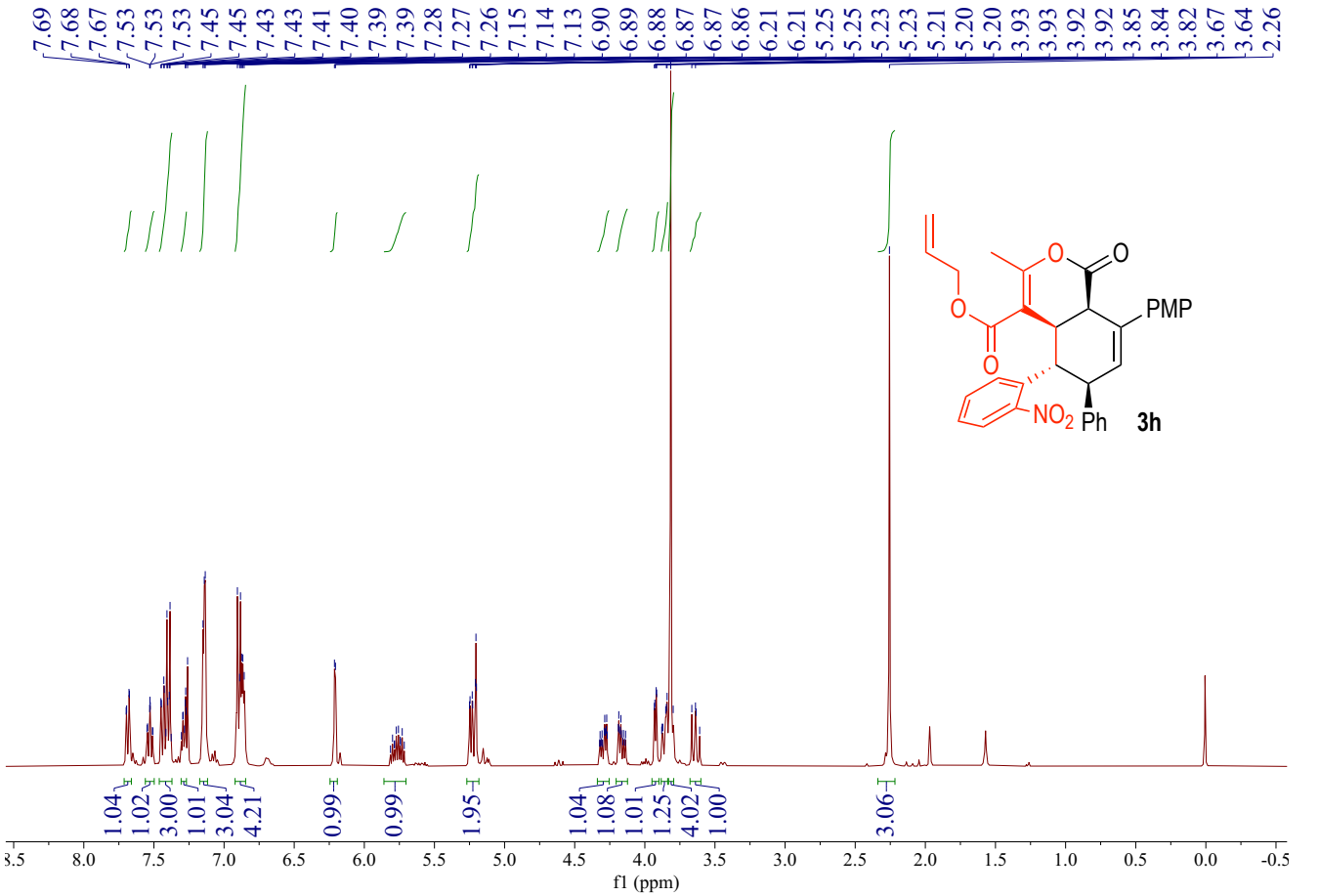
4g
f1 (ppm)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5.21
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3.93
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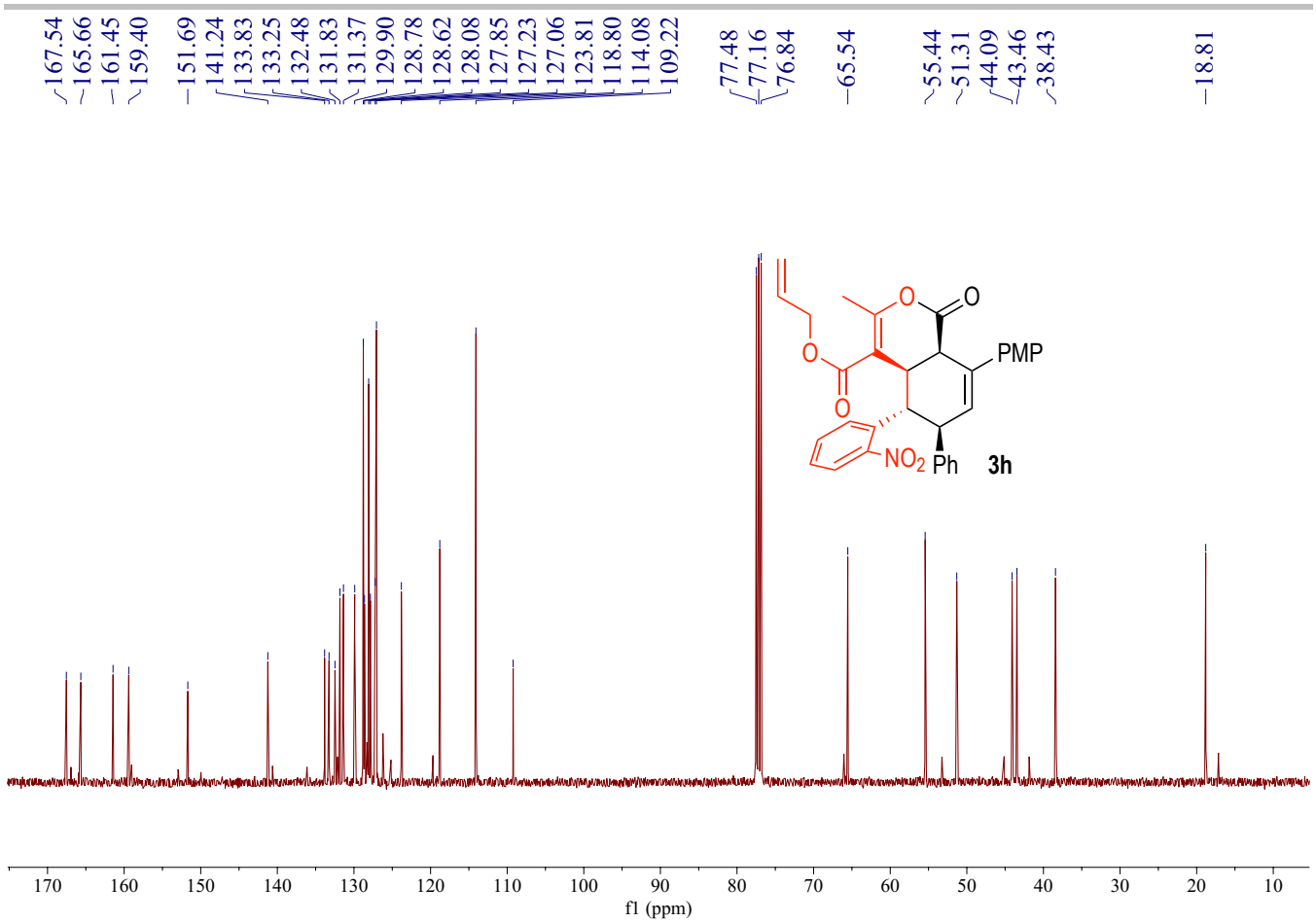
f1 (ppm)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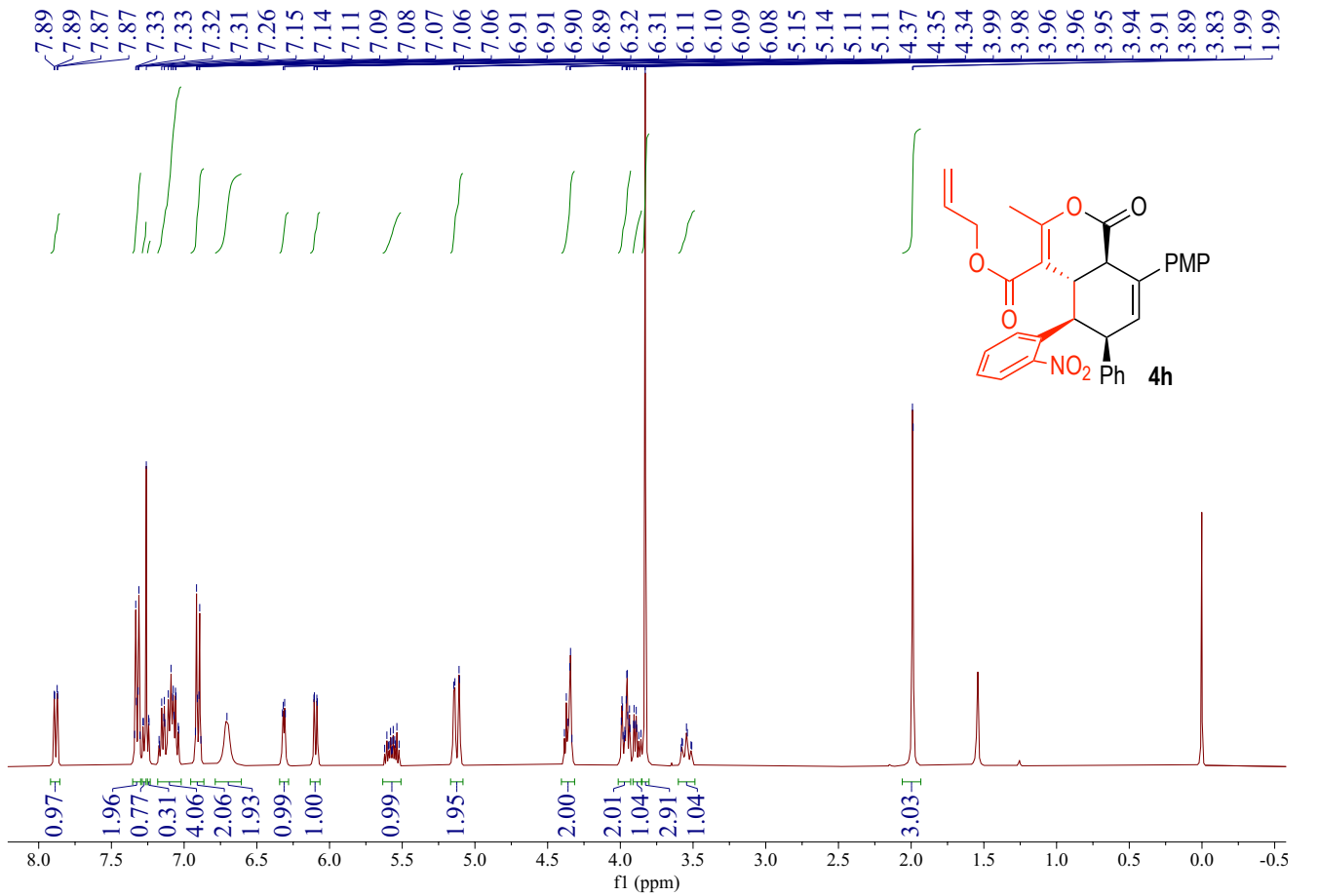
f1 (ppm)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1.99
PMP
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Ph
4h
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1.96
0.77
0.31
4.06
2.06
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2.91
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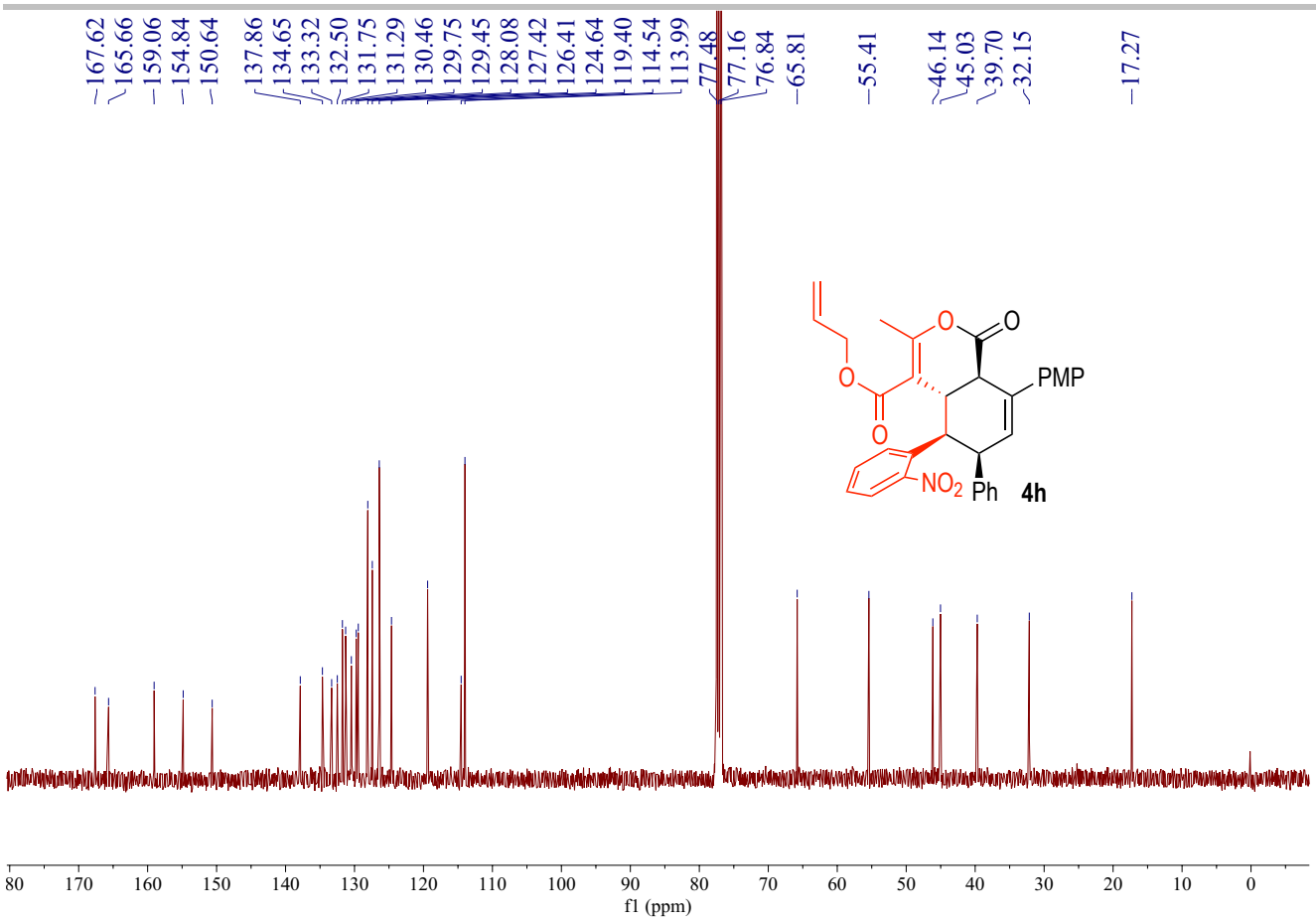
f1 (ppm)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PMP
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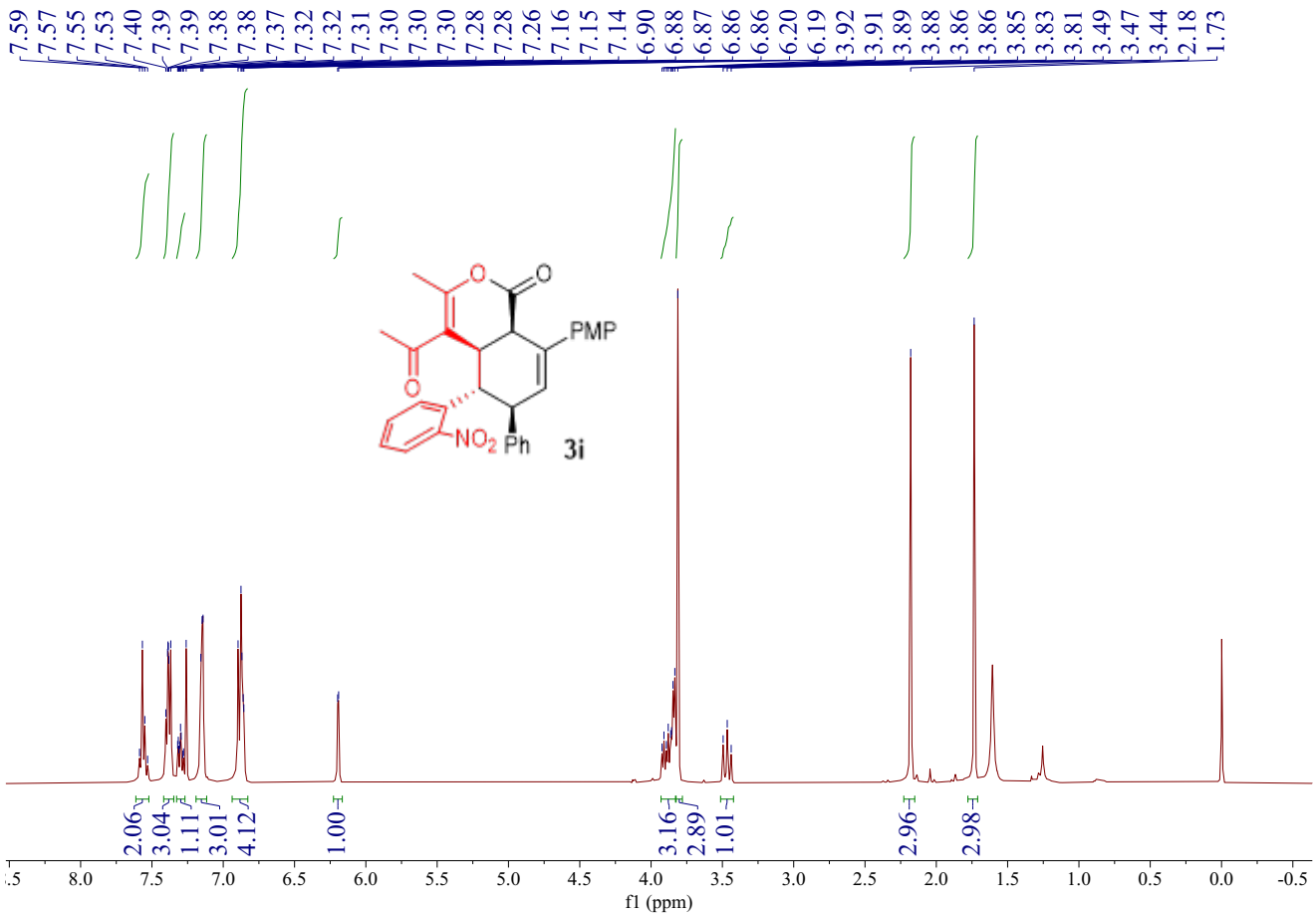
Ph
4h
f1 (ppm)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3.81
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Ph
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1.01
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2.98
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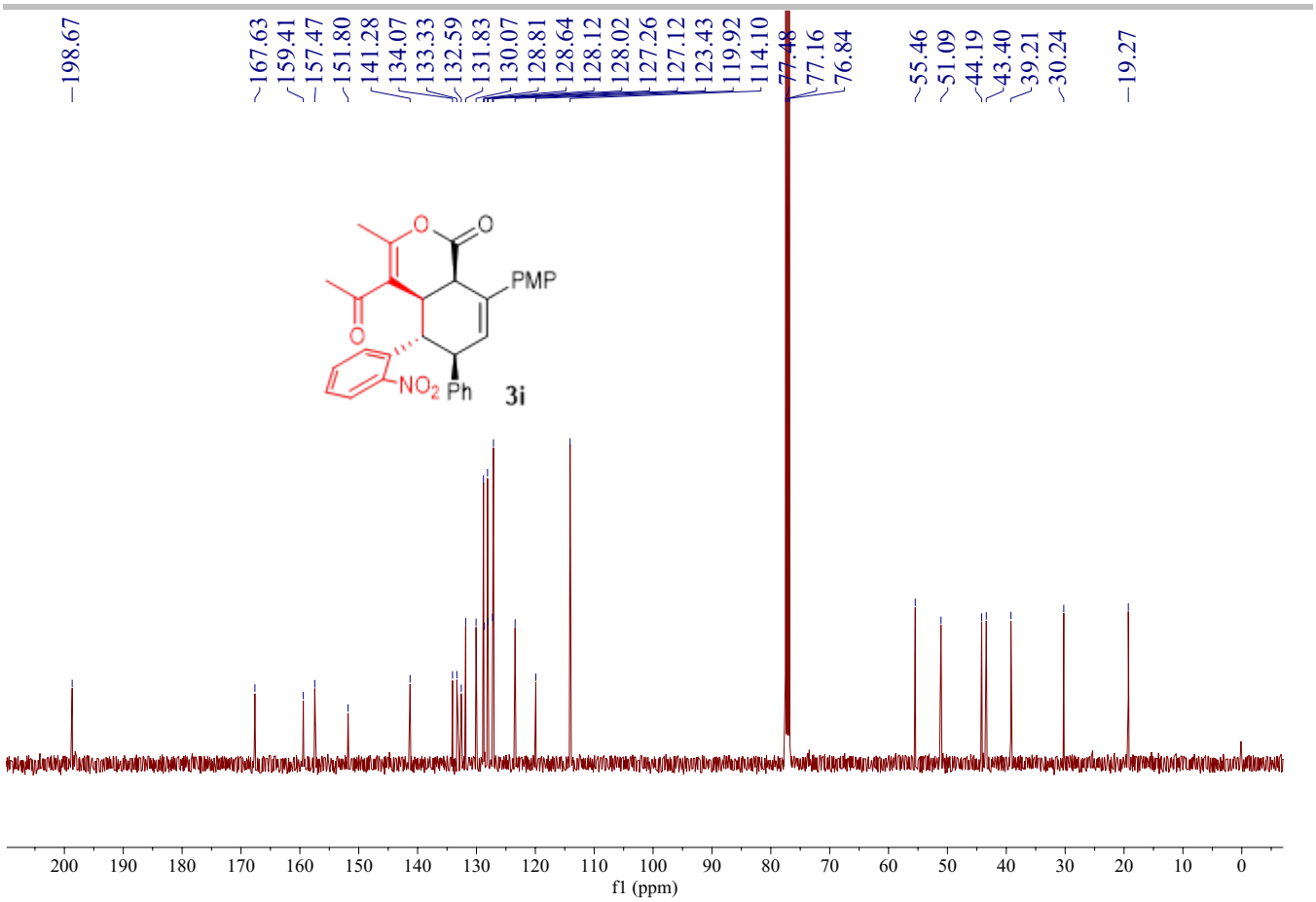
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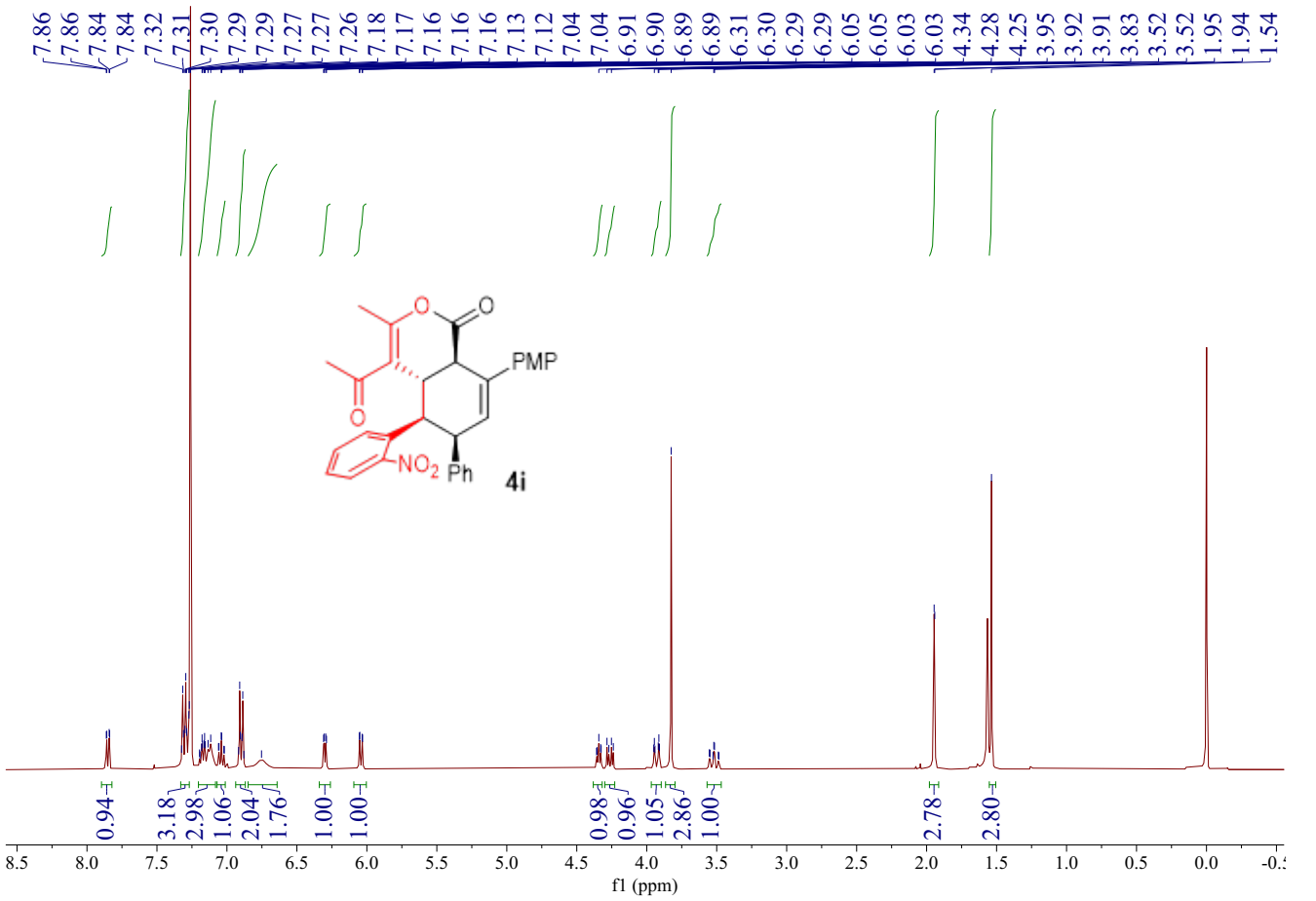
Ph
3i
f1 (ppm)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PMP
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Ph
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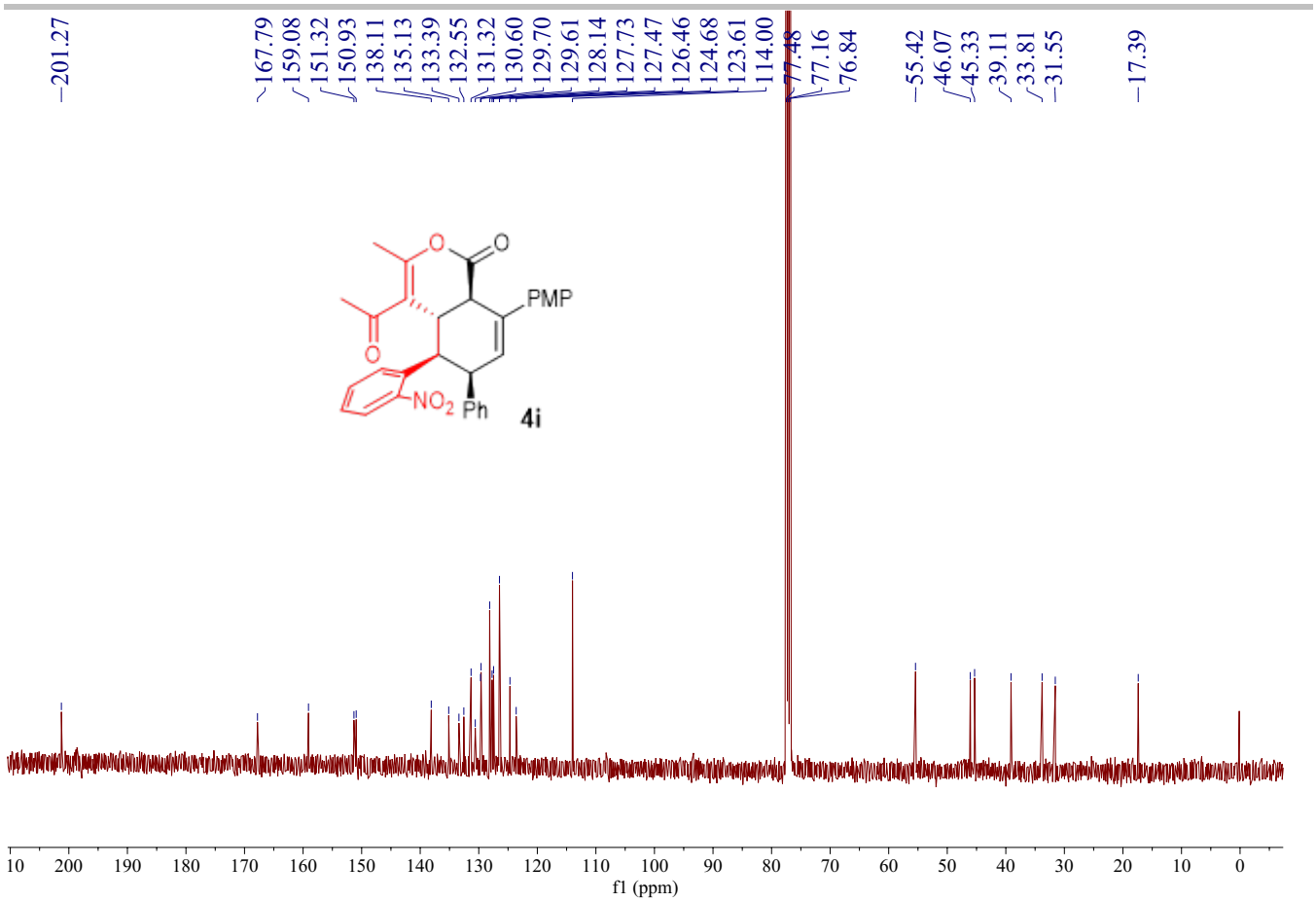
f1 (ppm)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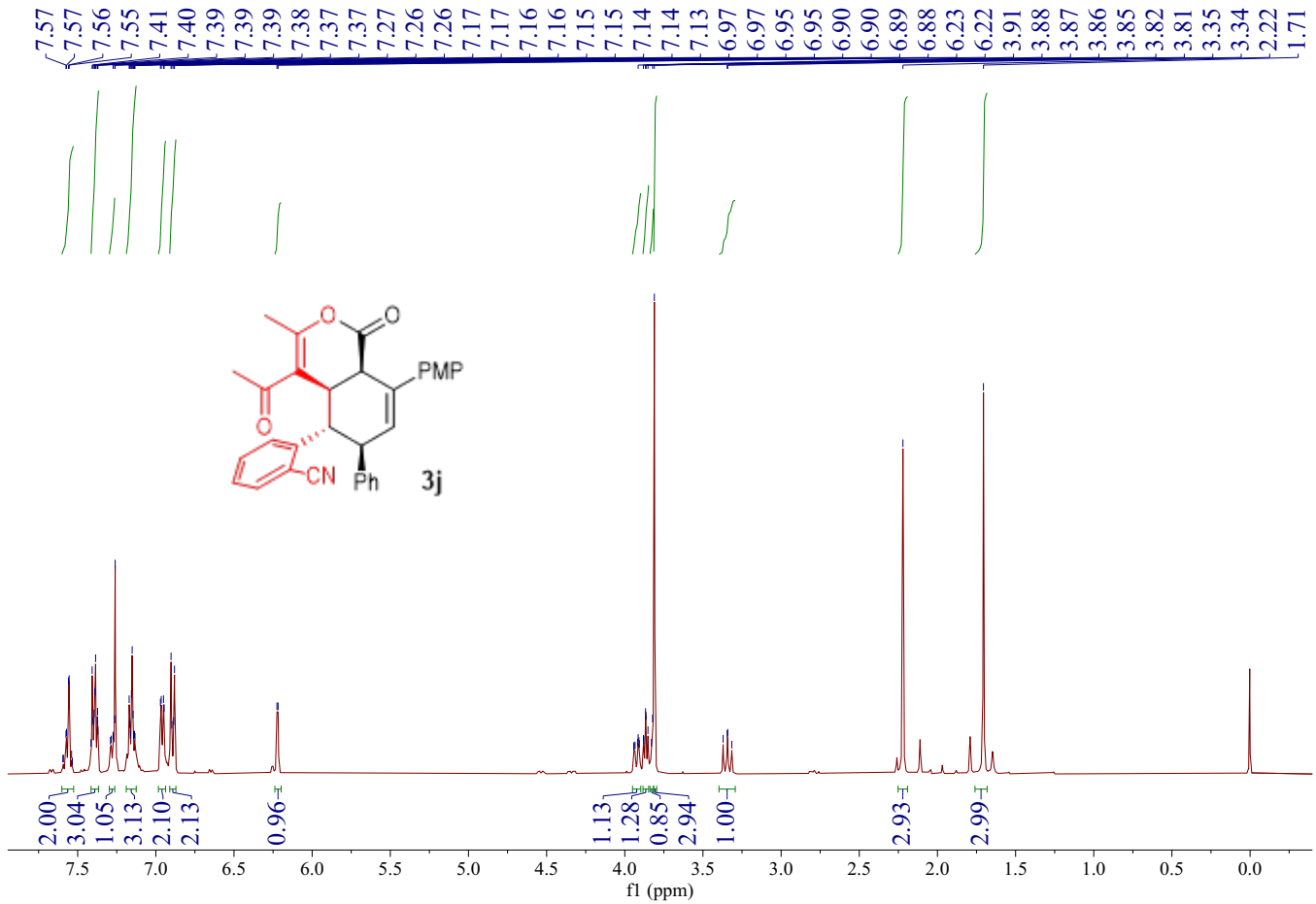
Ph
4i
f1 (ppm)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1.00
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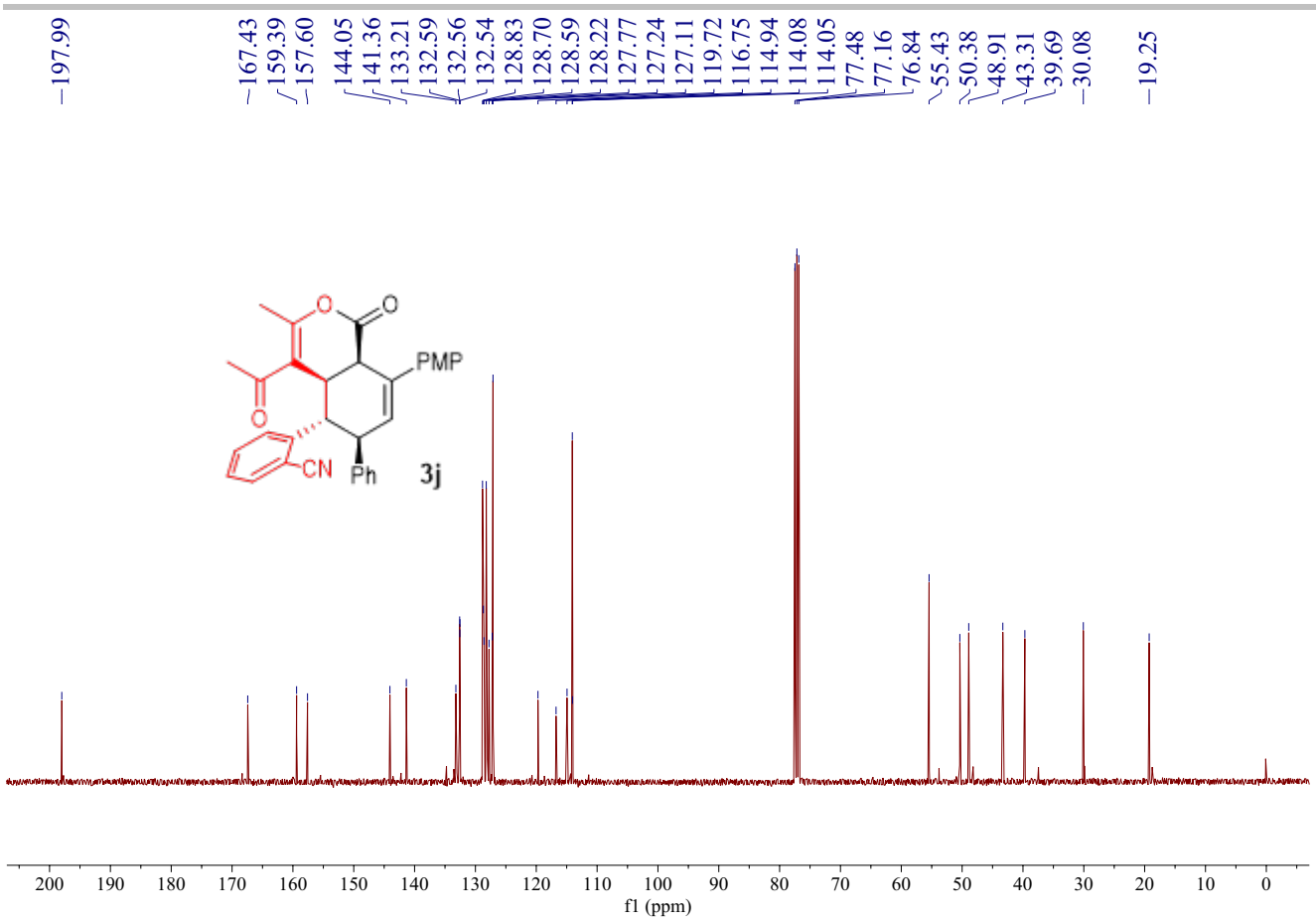
2.99
f1 (ppm)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Ph
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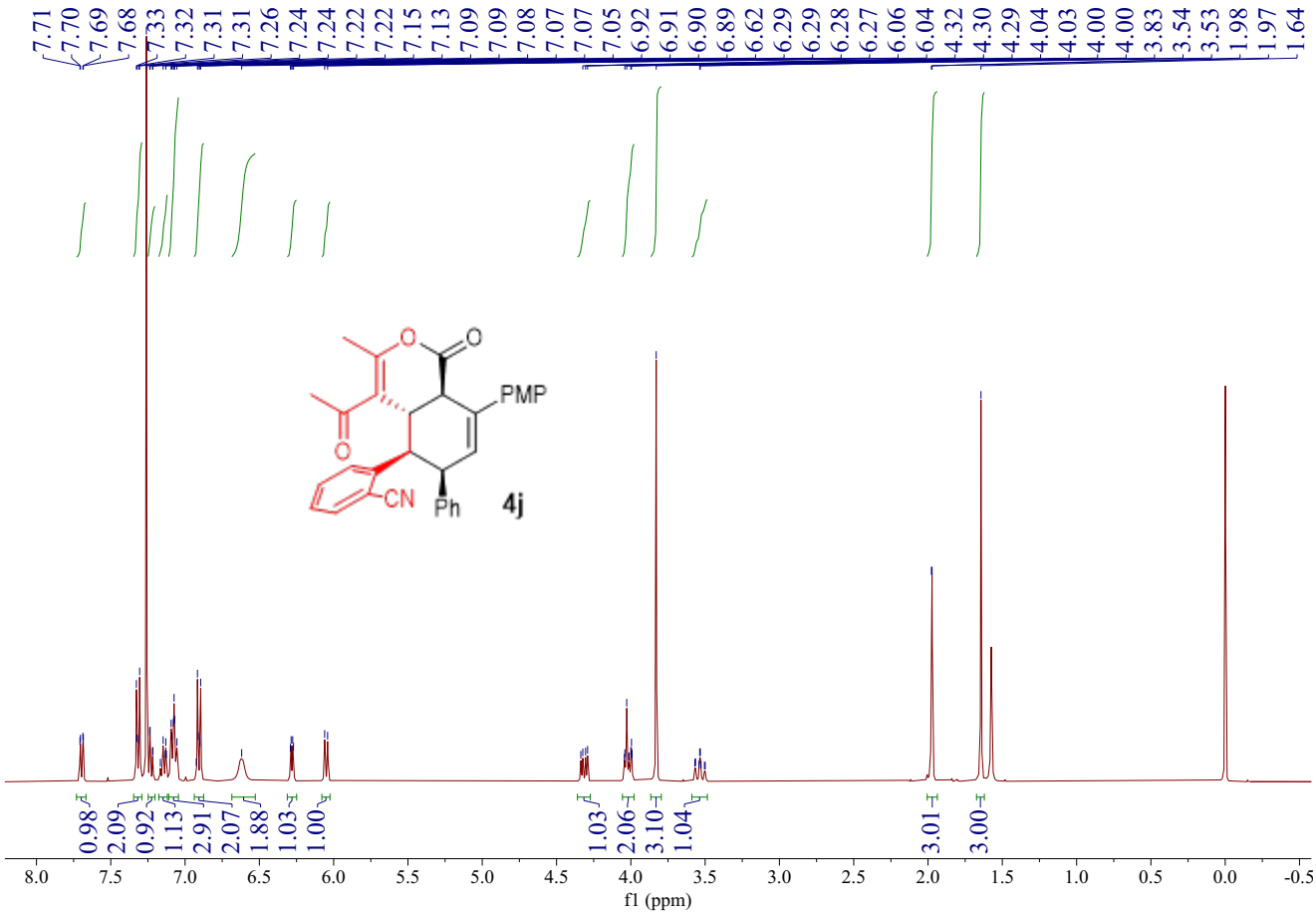
f1 (ppm)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O
O
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CN
Ph
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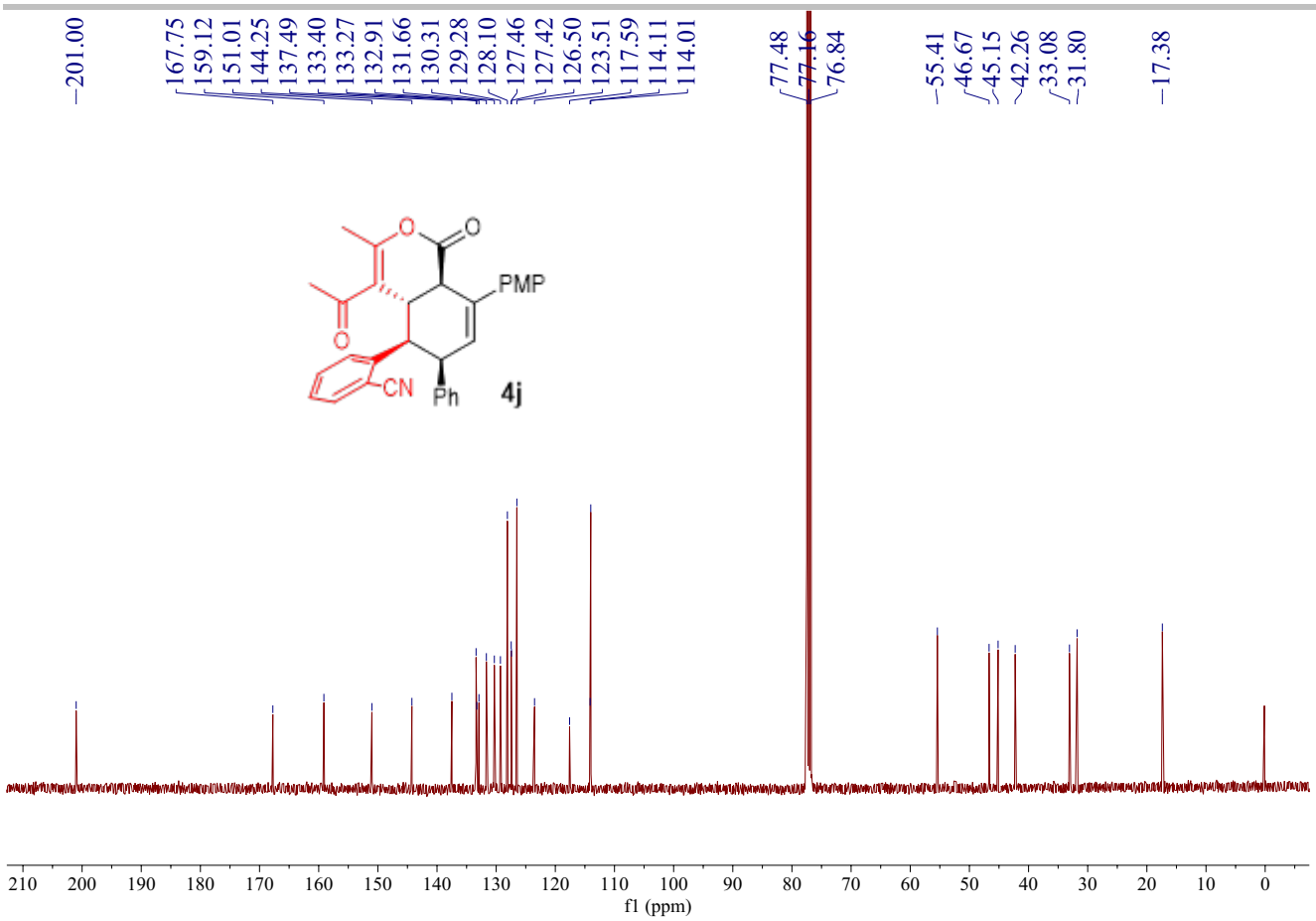
1.88
1.03
1.00
1.03
2.06
3.10
1.04
3.01
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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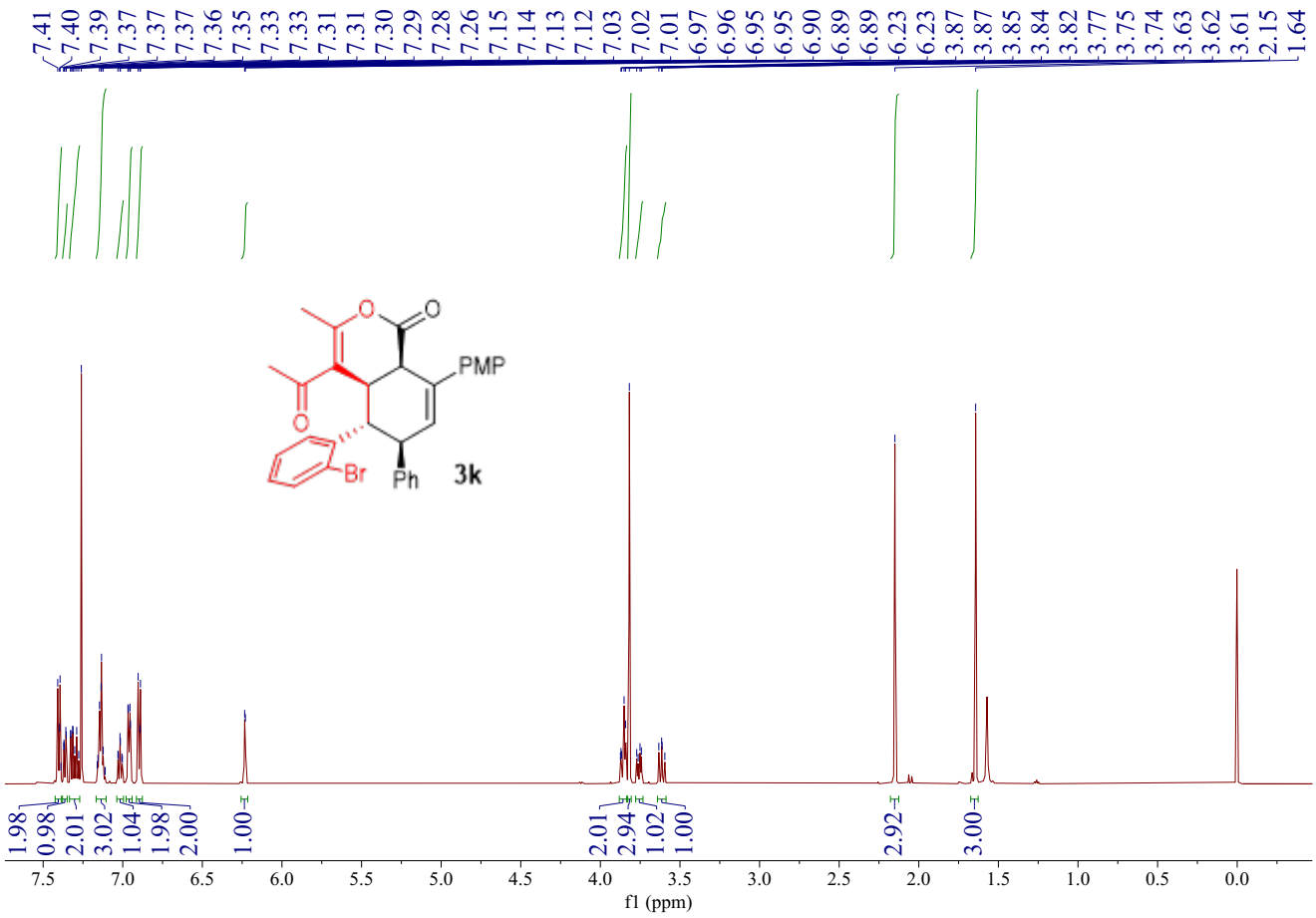
17.38
PMP
CN
Ph
4j
f1 (ppm)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Br
Ph
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1.00
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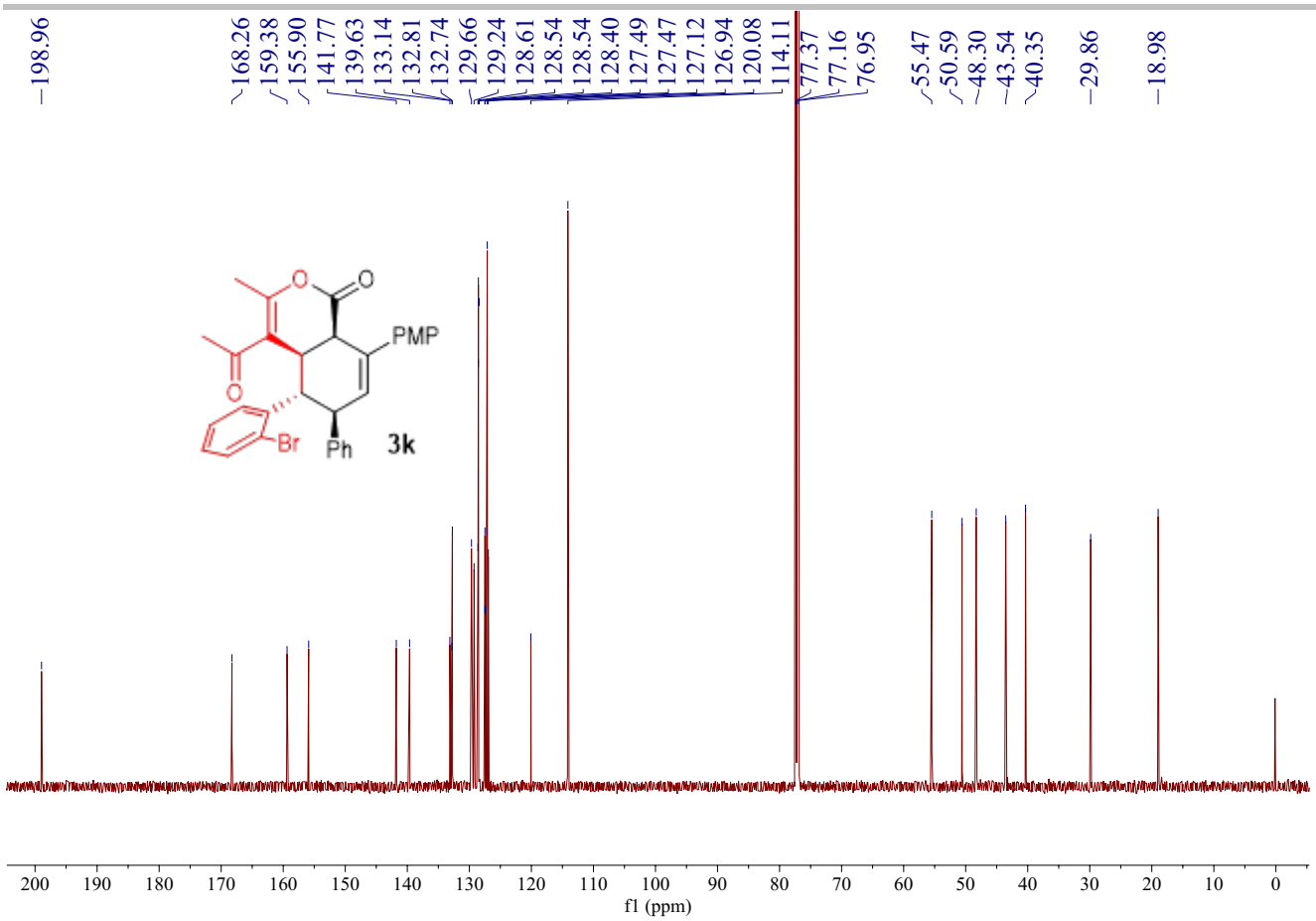
3.00
f1 (ppm)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Ph
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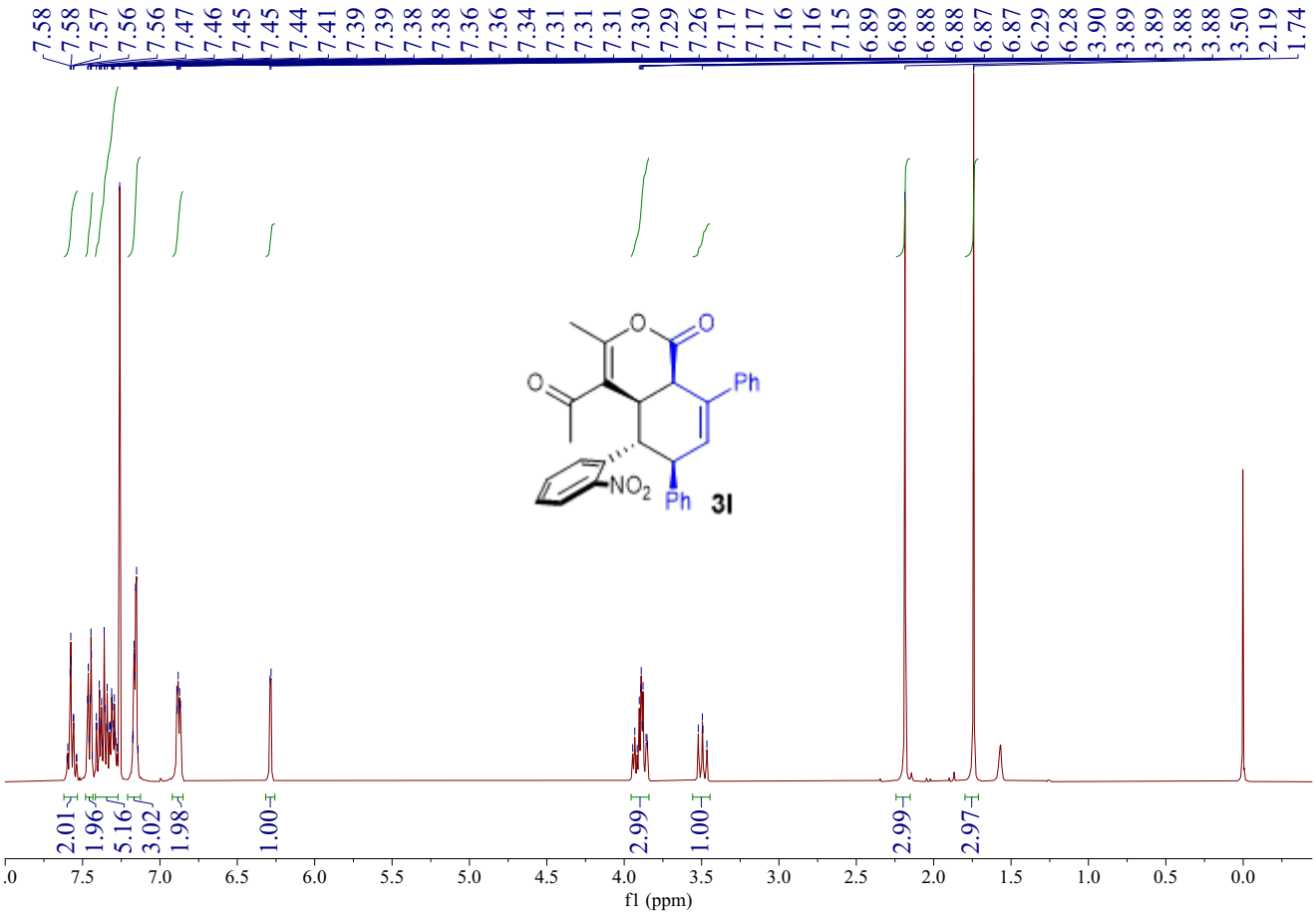
f1 (ppm)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1.00
2.99
2.97
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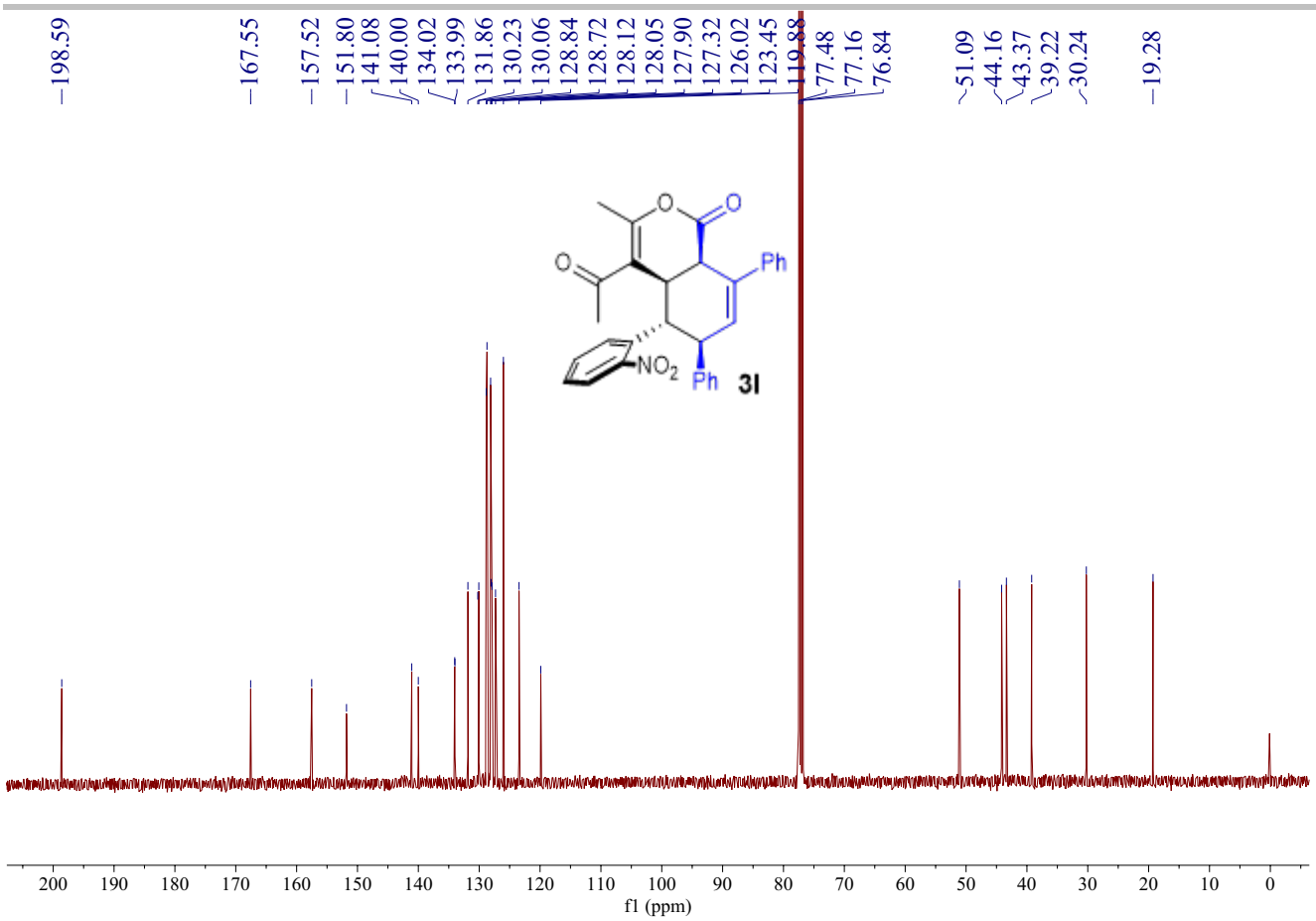
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127.32
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77.16
76.84
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39.22
30.24
19.28
O
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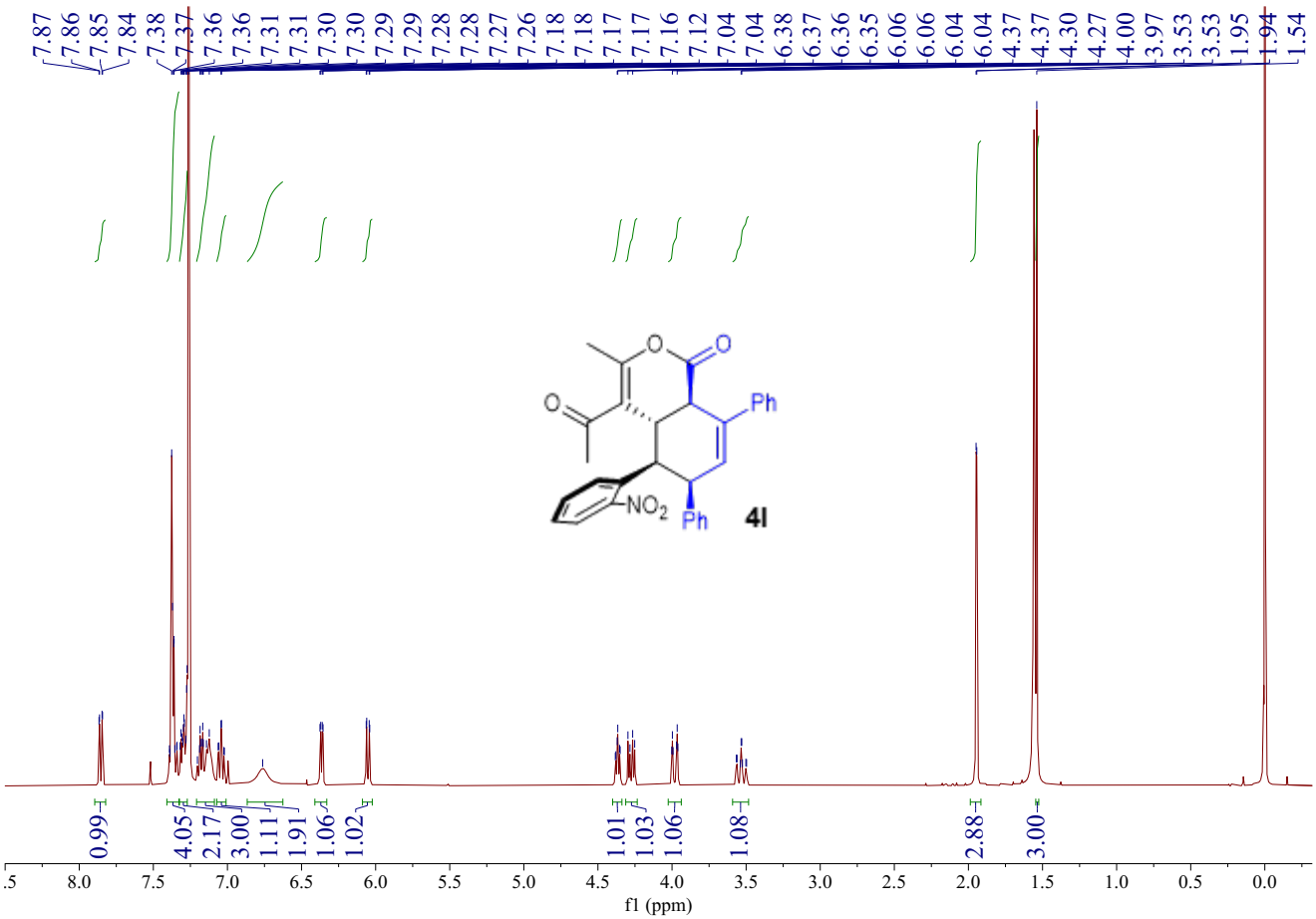
O
Ph
NO2
Ph
3l
f1 (ppm)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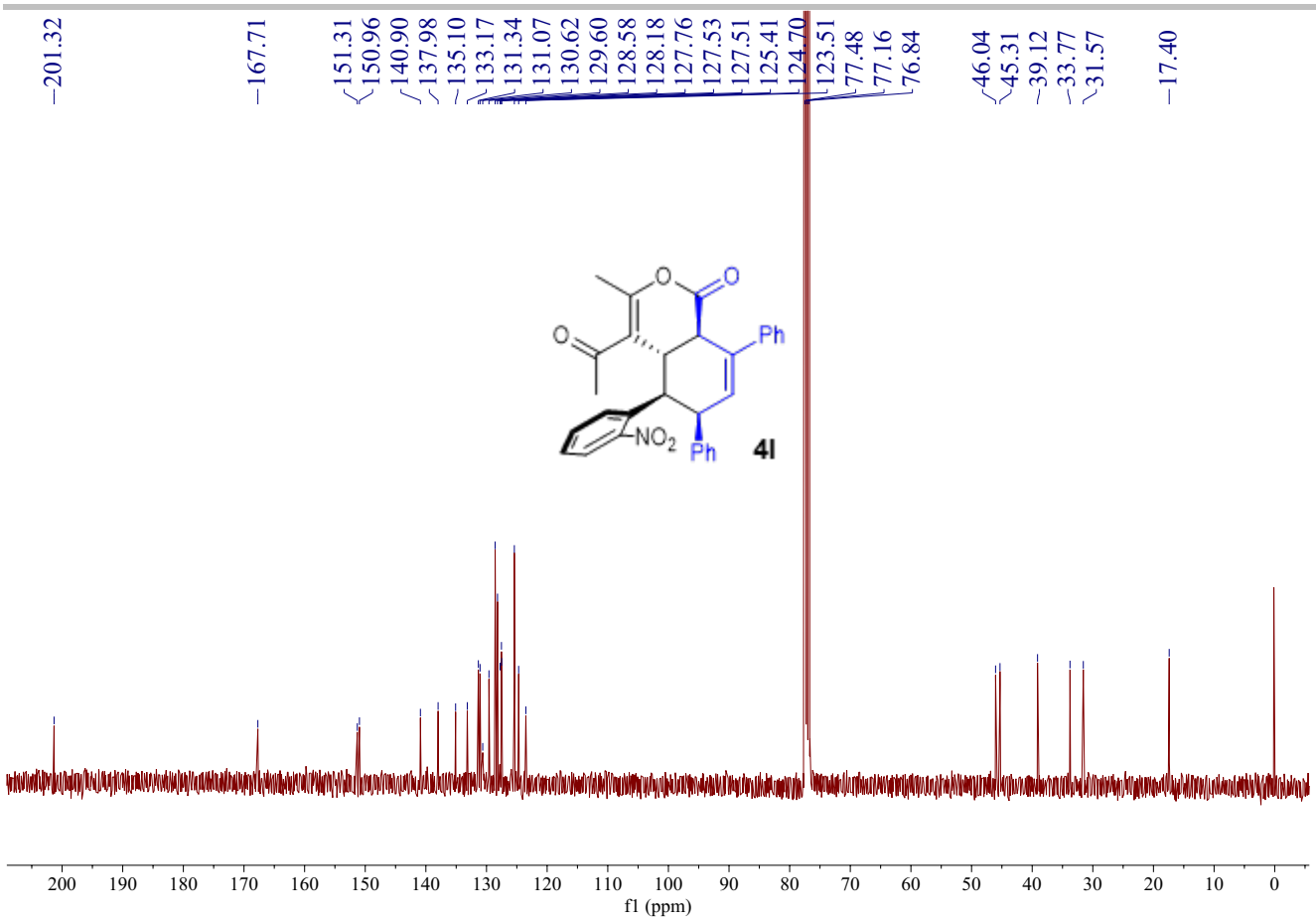
Ph
4l
f1 (ppm)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39.12
33.77
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O
Ph
NO2
Ph
4l
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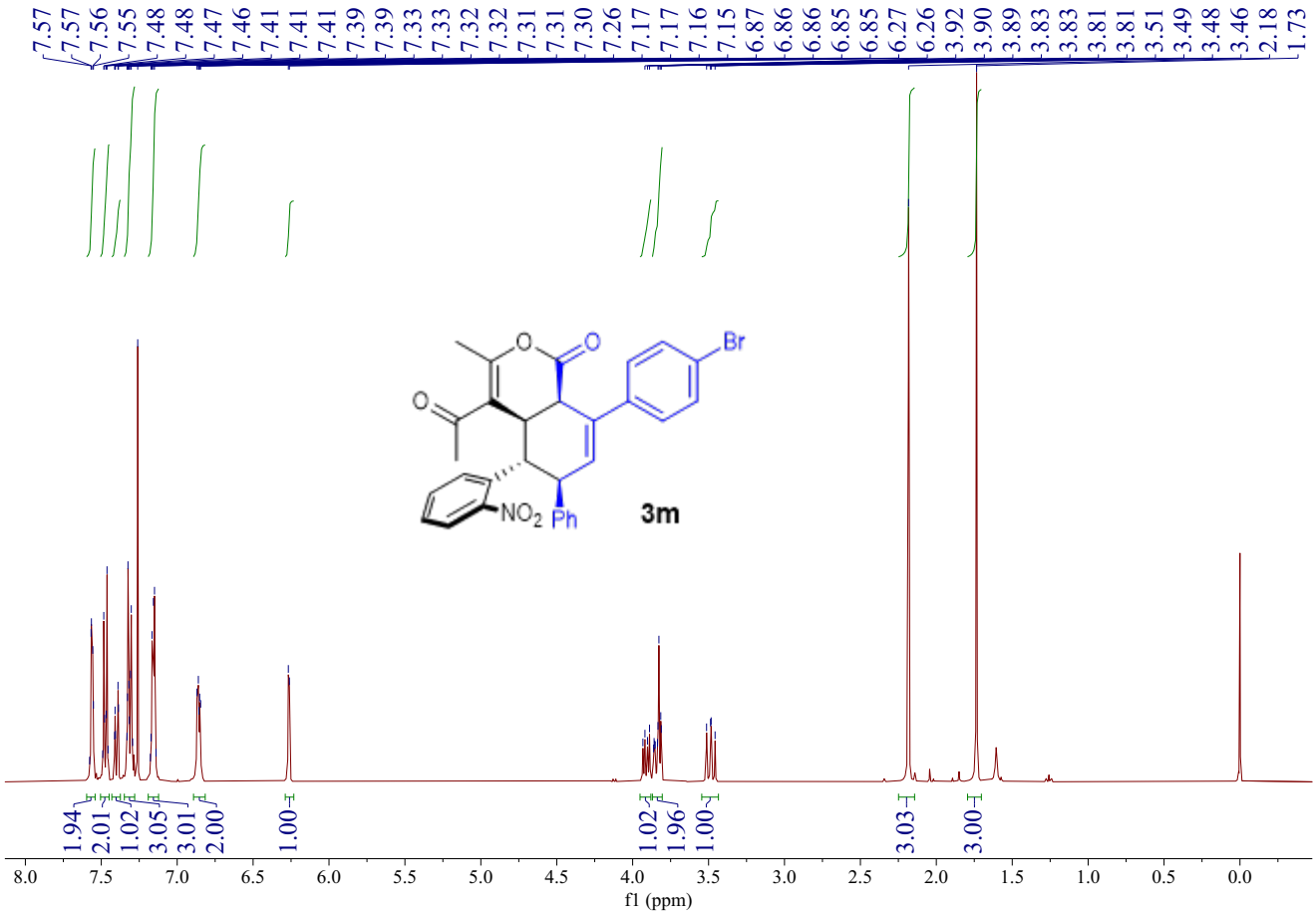
f1 (ppm)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O
O
Br
NO2
Ph
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2.01
1.02
3.05
3.01
2.00
1.00
1.02
1.96
1.00
3.03
3.00
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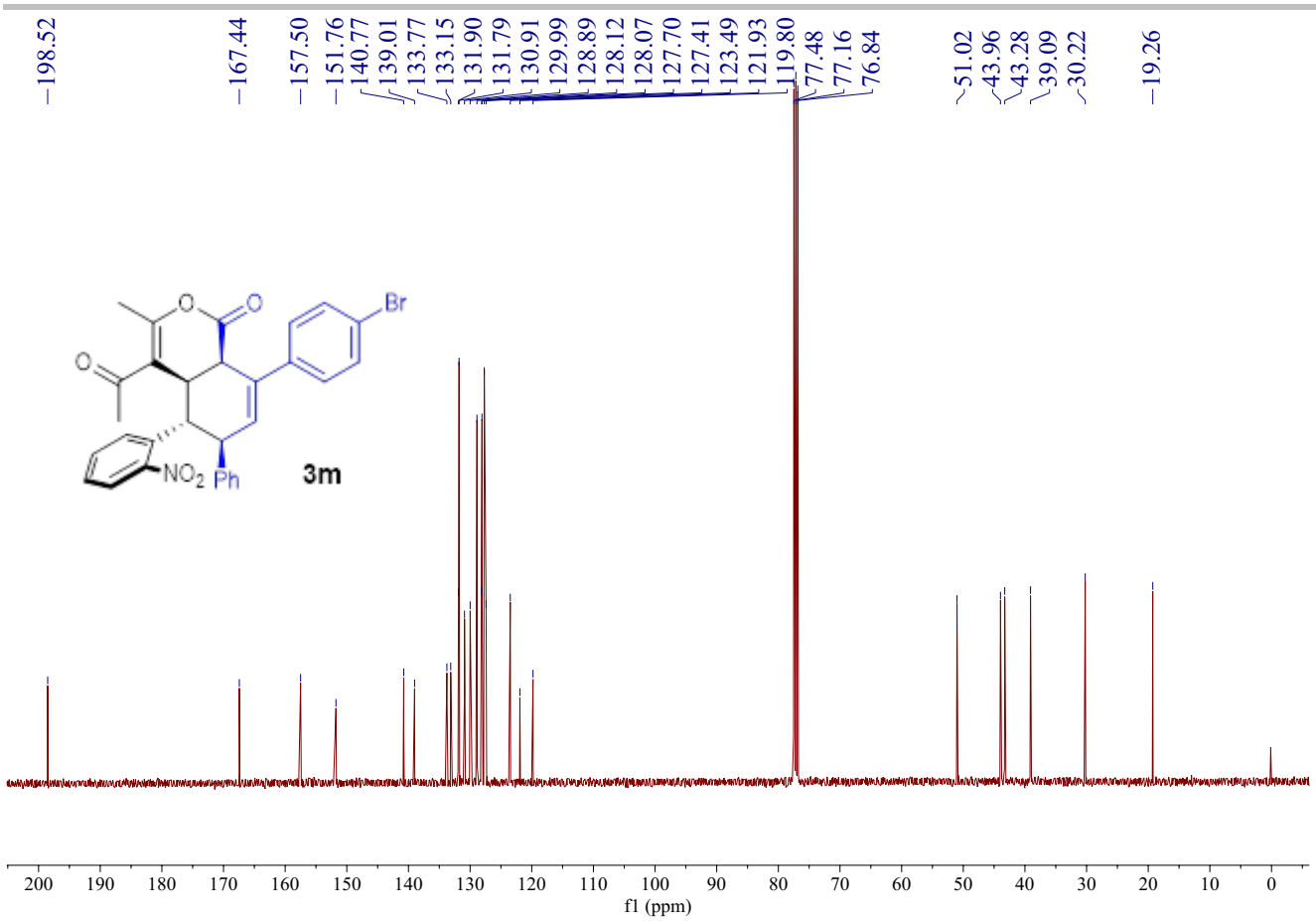
f1 (ppm)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Ph
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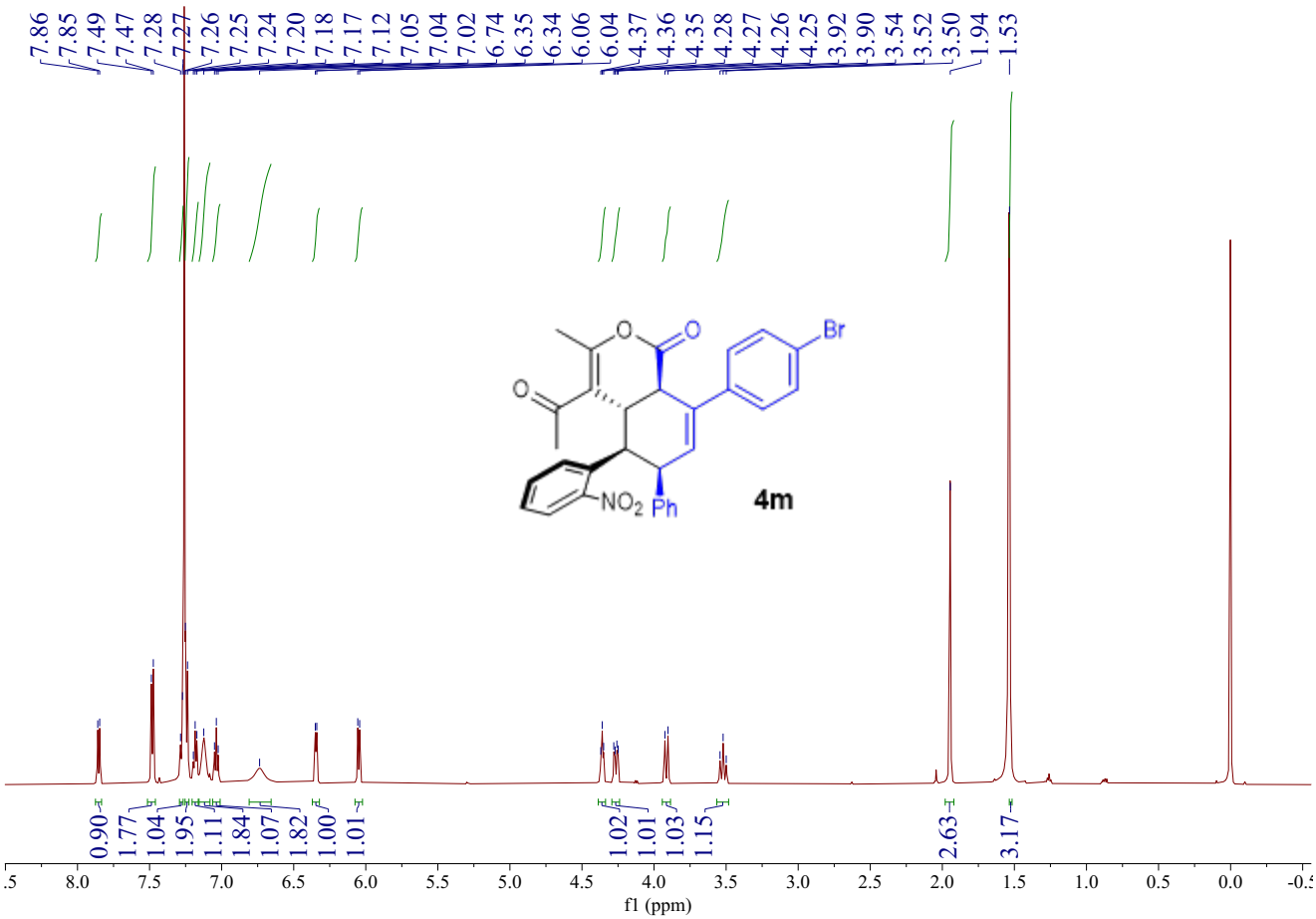
f1 (ppm)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1.53
Br
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O
NO2
Ph
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1.84
1.07
1.82
1.00
1.01
1.02
1.01
1.03
1.15
2.63
3.17
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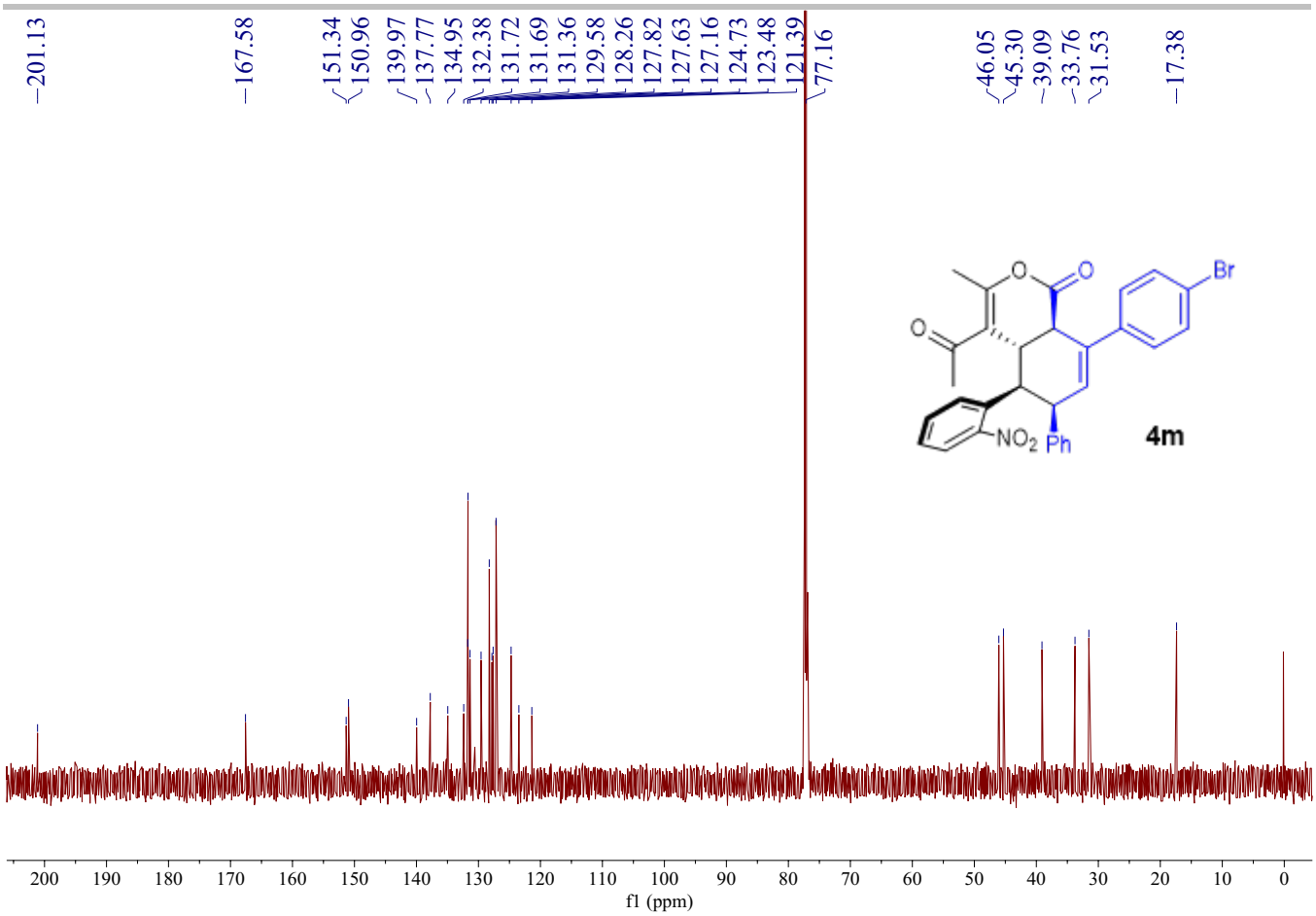
f1 (ppm)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45.30
39.09
33.76
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O
NO2 Ph
4m
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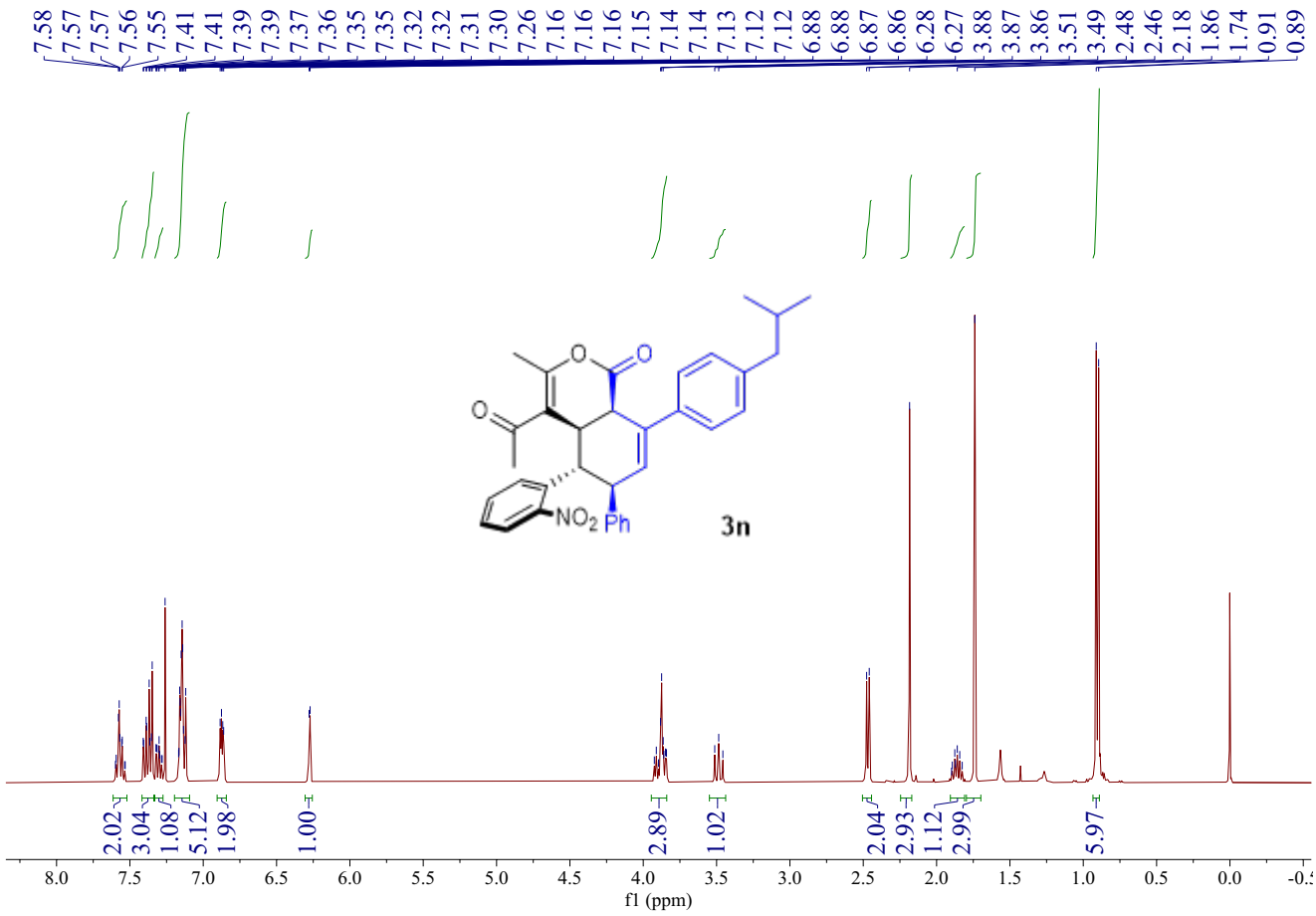
f1 (ppm)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O
O
NO2 Ph
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1.08
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1.02
2.04
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1.12
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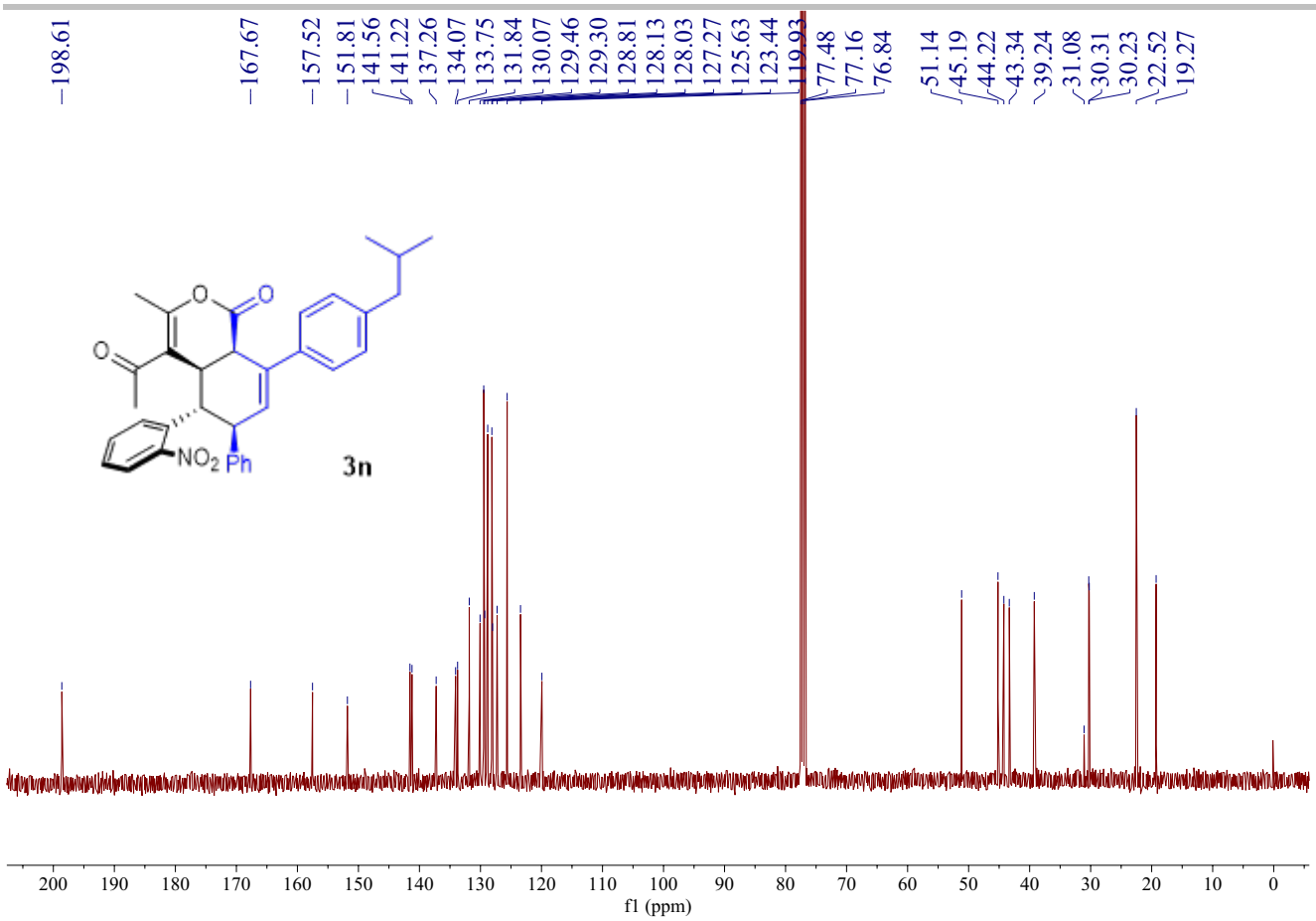
f1 (ppm)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43.34
39.24
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30.31
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O
NO2 Ph
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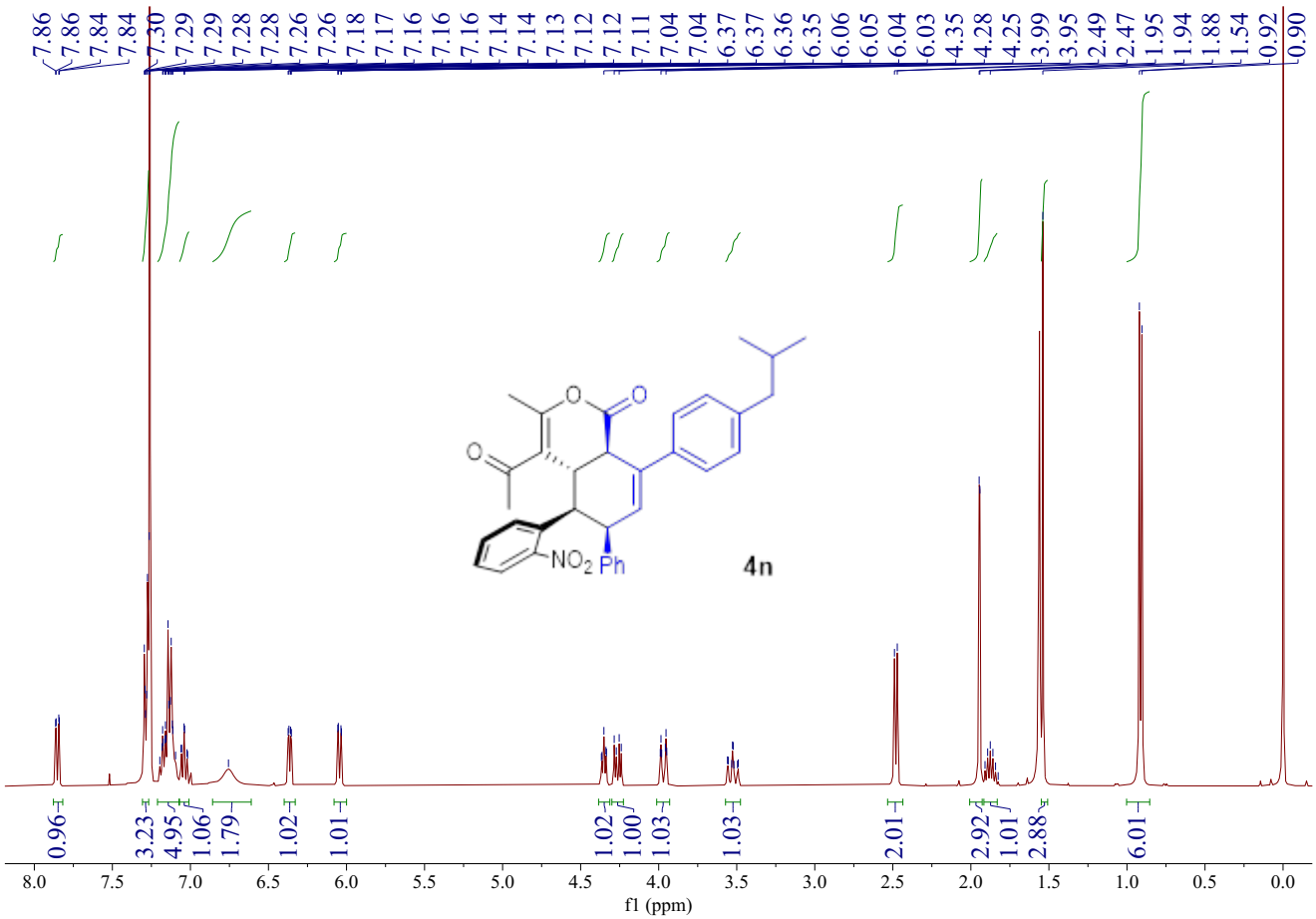
f1 (ppm)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7.12
7.11
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6.04
6.03
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4.28
4.25
3.99
3.95
2.49
2.47
1.95
1.94
1.88
1.54
0.92
0.90
O
O
O
NO2 Ph
4n
0.96
3.23
4.95
1.06
1.79
1.02
1.01
1.02
1.00
1.03
1.03
2.01
2.92
1.01
2.88
6.01
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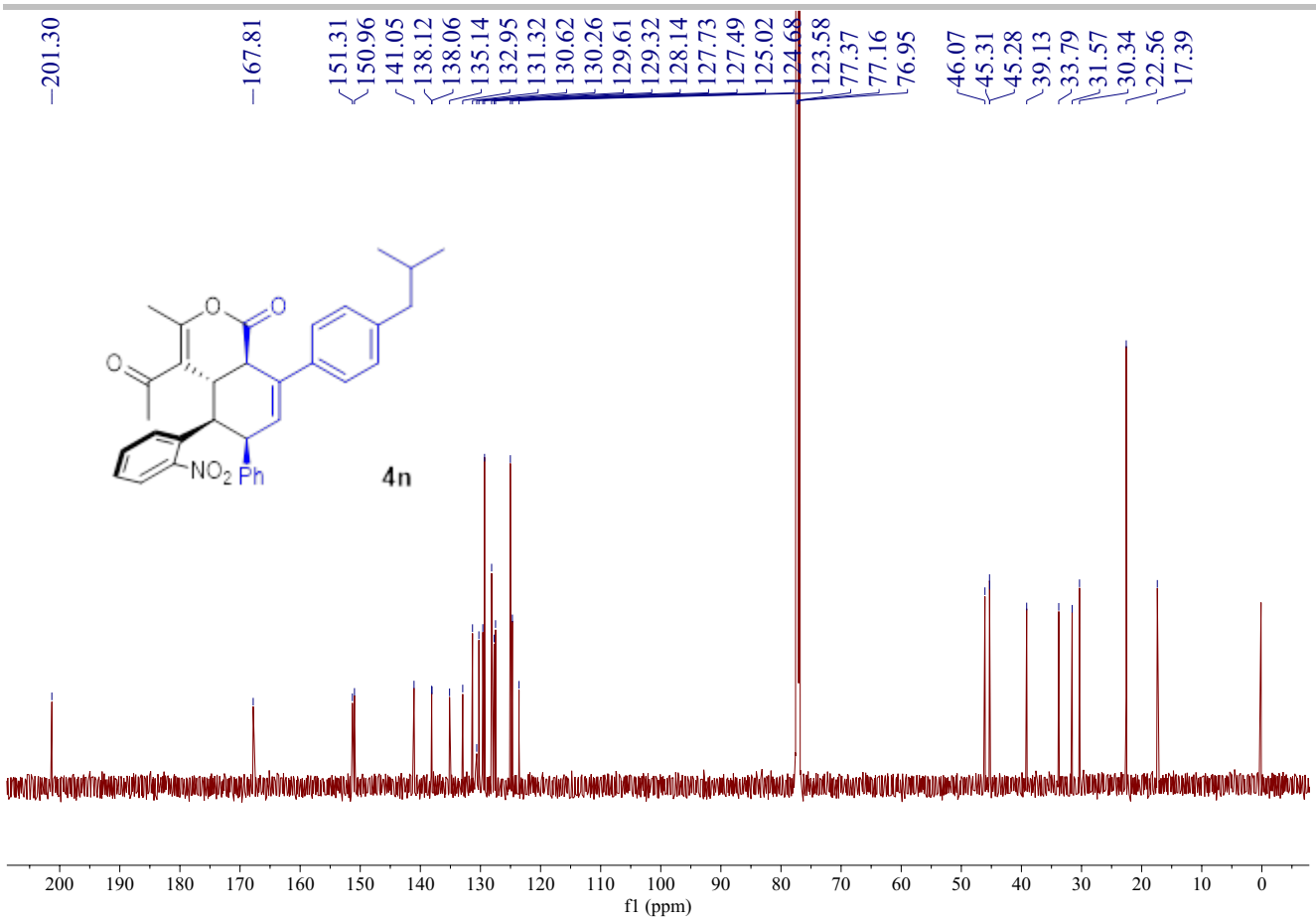
f1 (ppm)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128.14
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76.95
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45.31
45.28
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33.79
31.57
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O
O
NO2 Ph
4n
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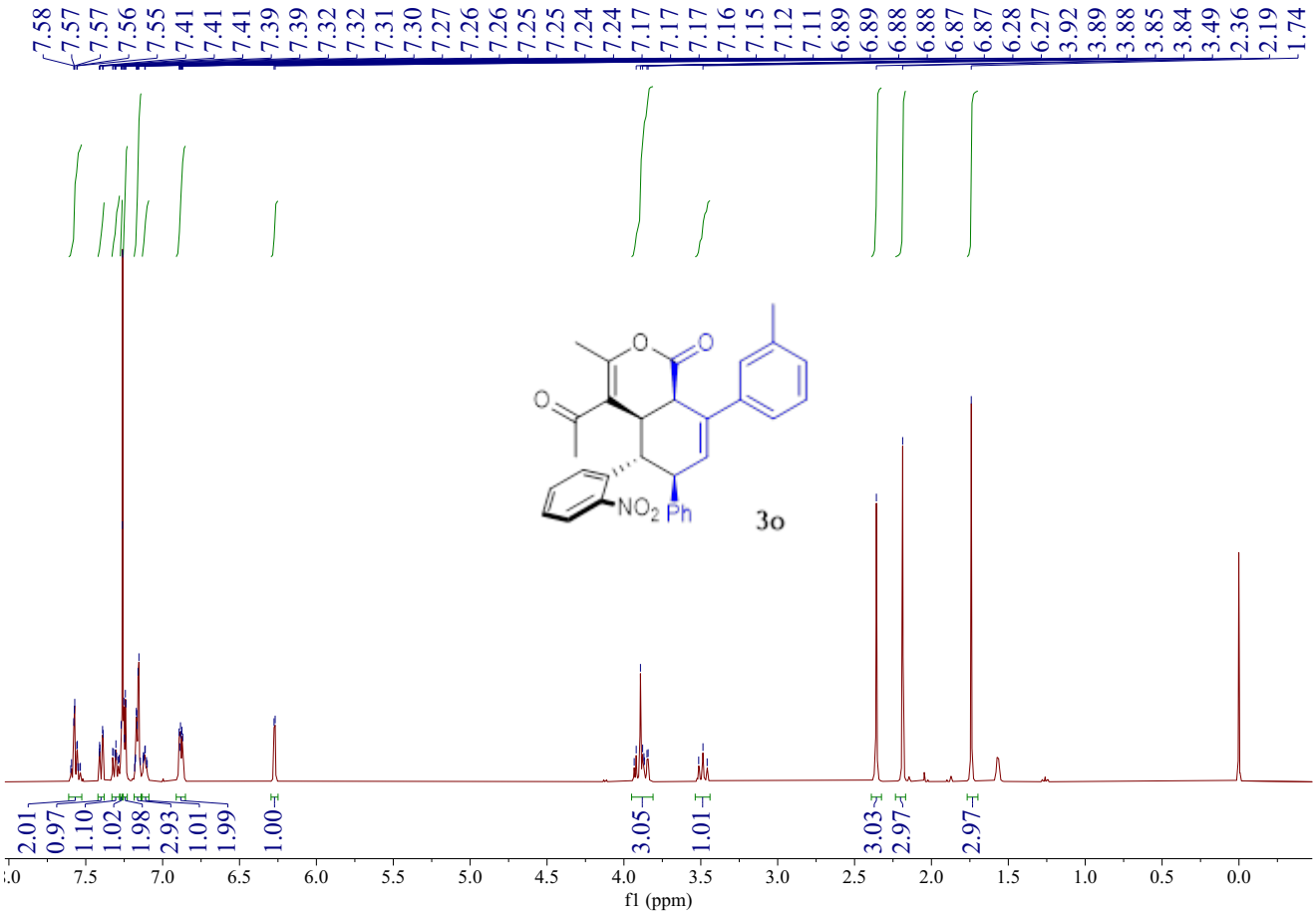
f1 (ppm)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7.12
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3.88
3.85
3.84
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2.36
2.19
1.74
O
O
O
NO2 Ph
3o
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1.01
1.99
1.00
3.05
1.01
3.03
2.97
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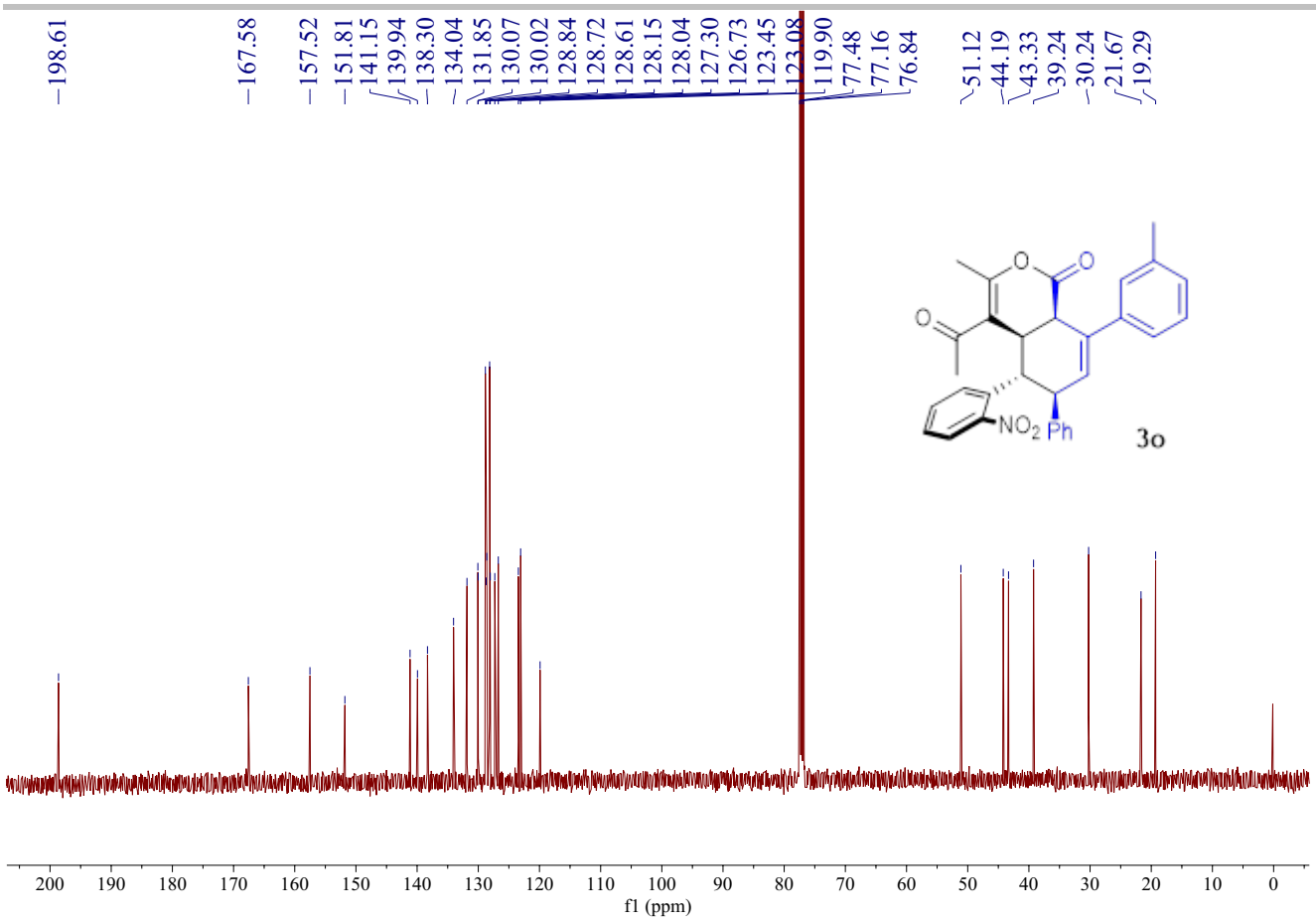
f1 (ppm)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44.19
43.33
39.24
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O
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NO2 Ph
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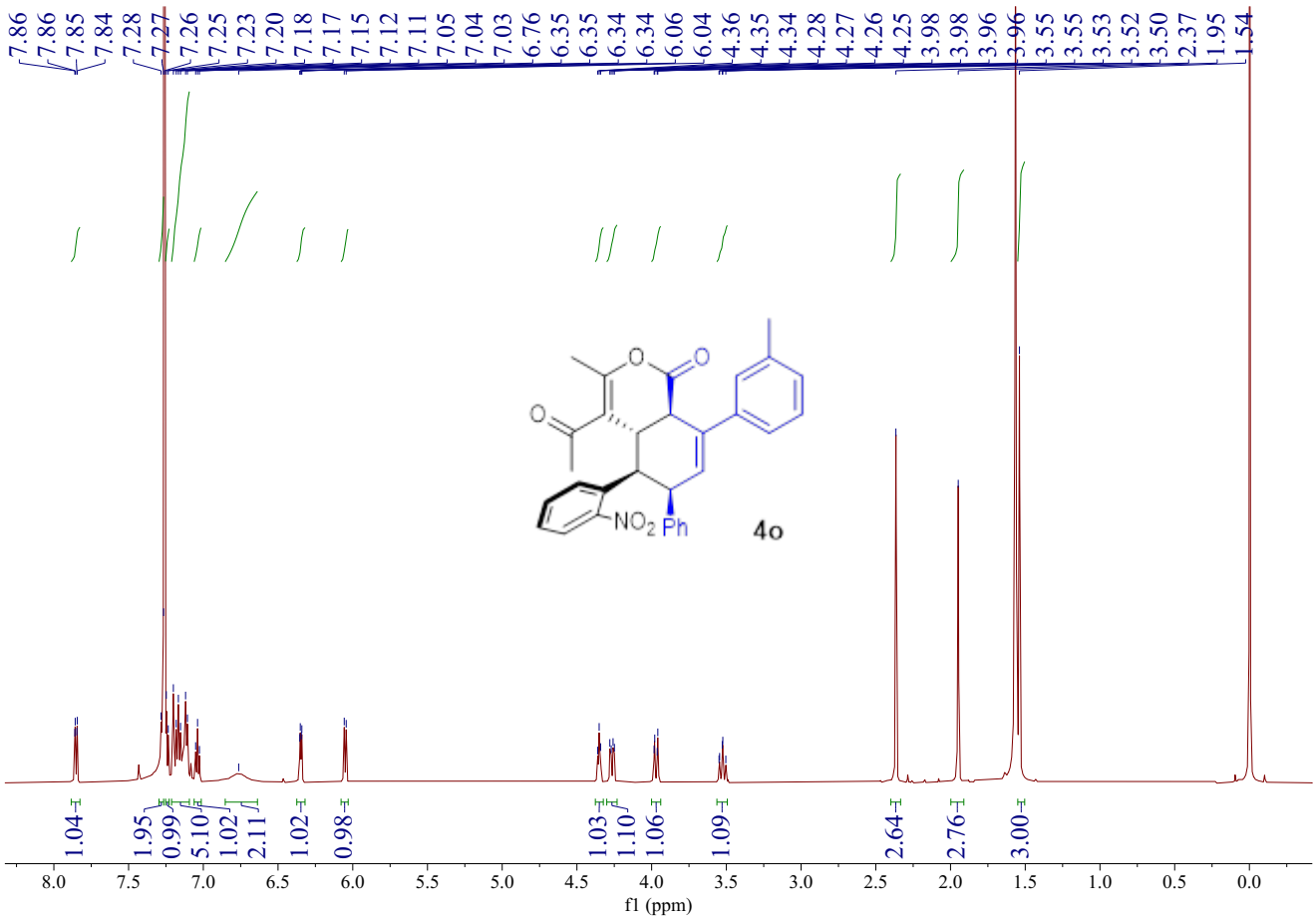
f1 (ppm)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4.25
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3.98
3.96
3.96
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3.53
3.52
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1.54
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O
O
NO2 Ph
4o
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5.10
1.02
2.11
1.02
0.98
1.03
1.10
1.06
1.09
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3.00
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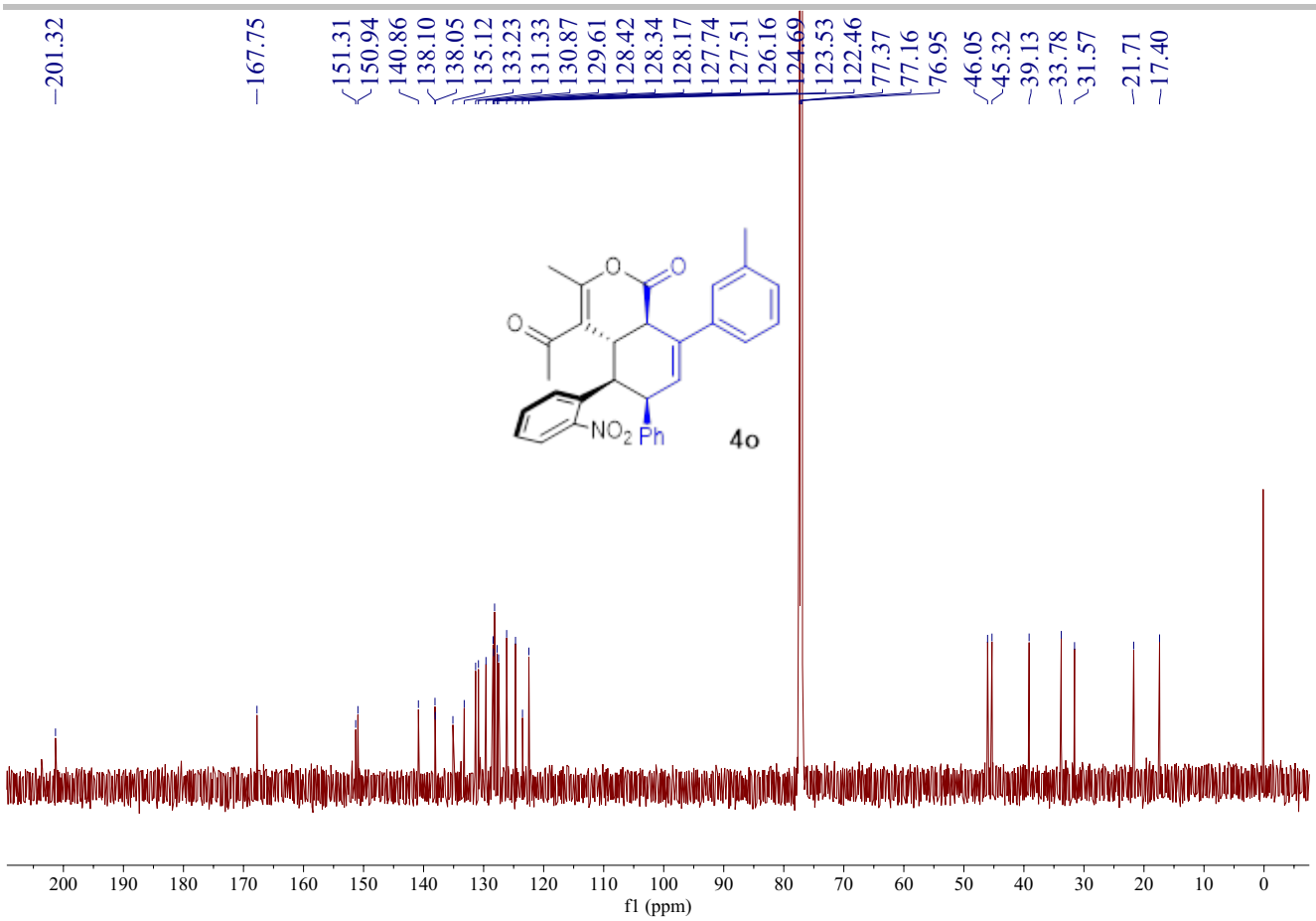
f1 (ppm)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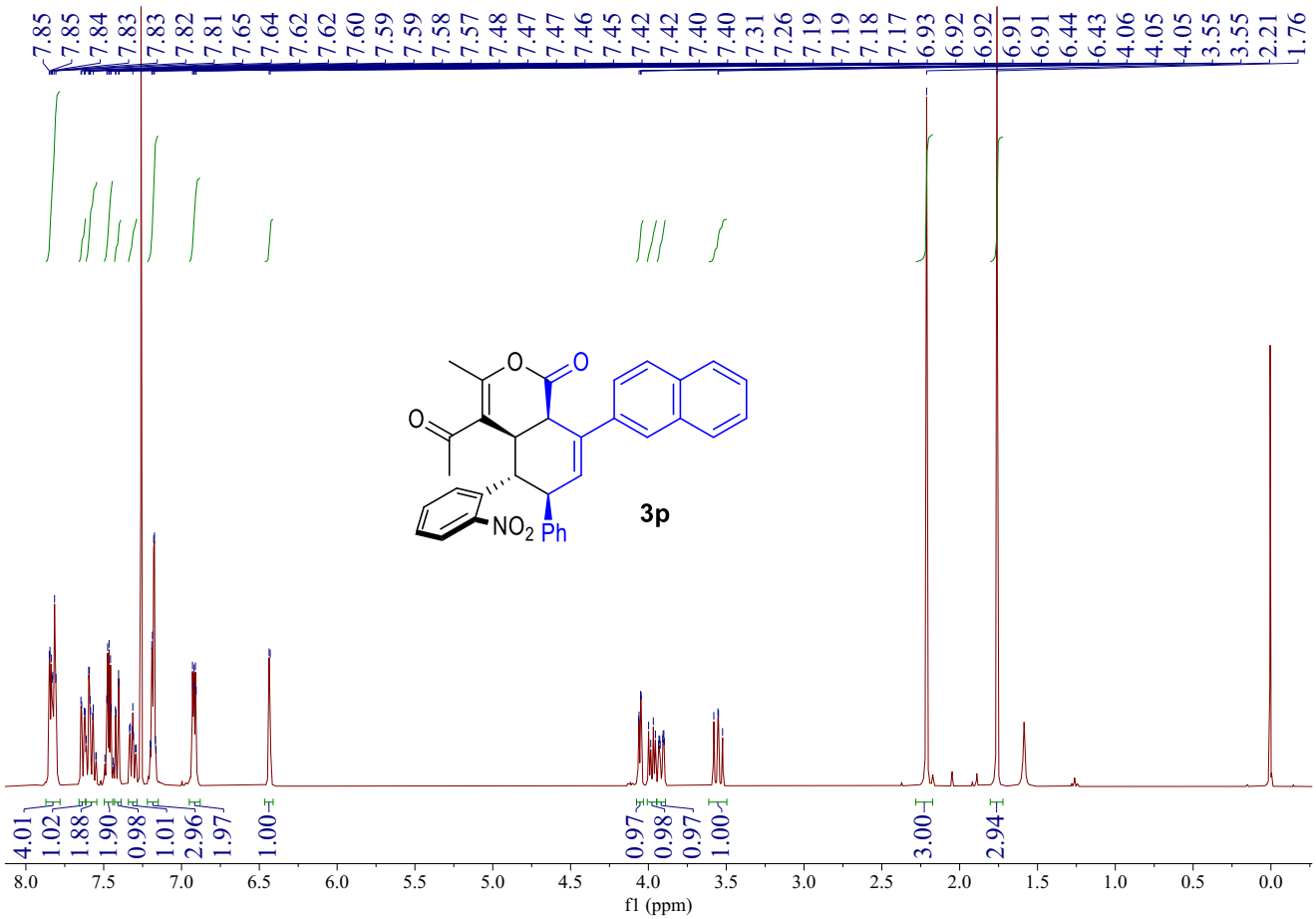
21.71
17.40
NO2 Ph
4o
f1 (ppm)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1.01
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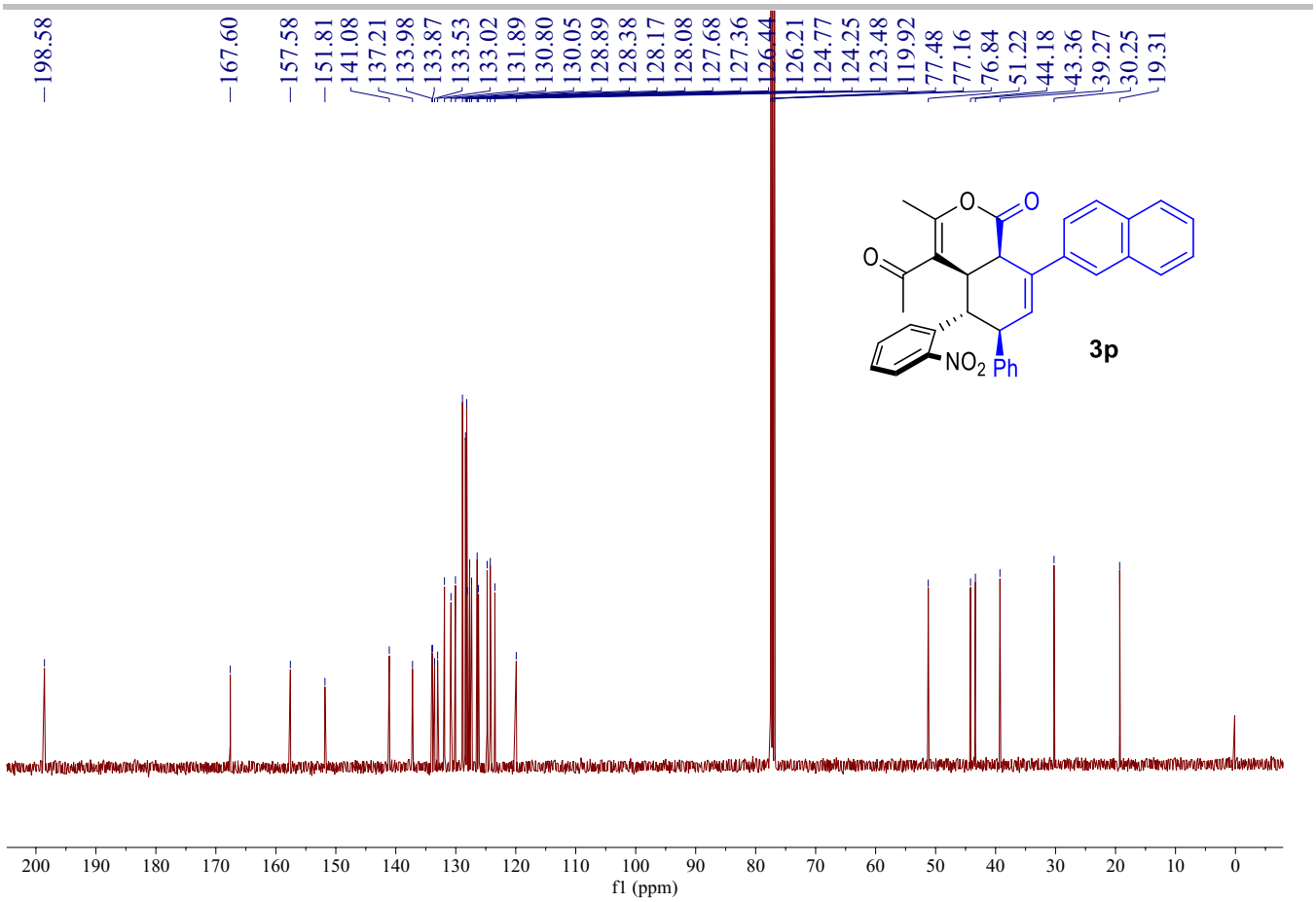
3.00
2.94
NO2 Ph
3p
f1 (ppm)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43.36
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O
O
NO2 Ph
3p
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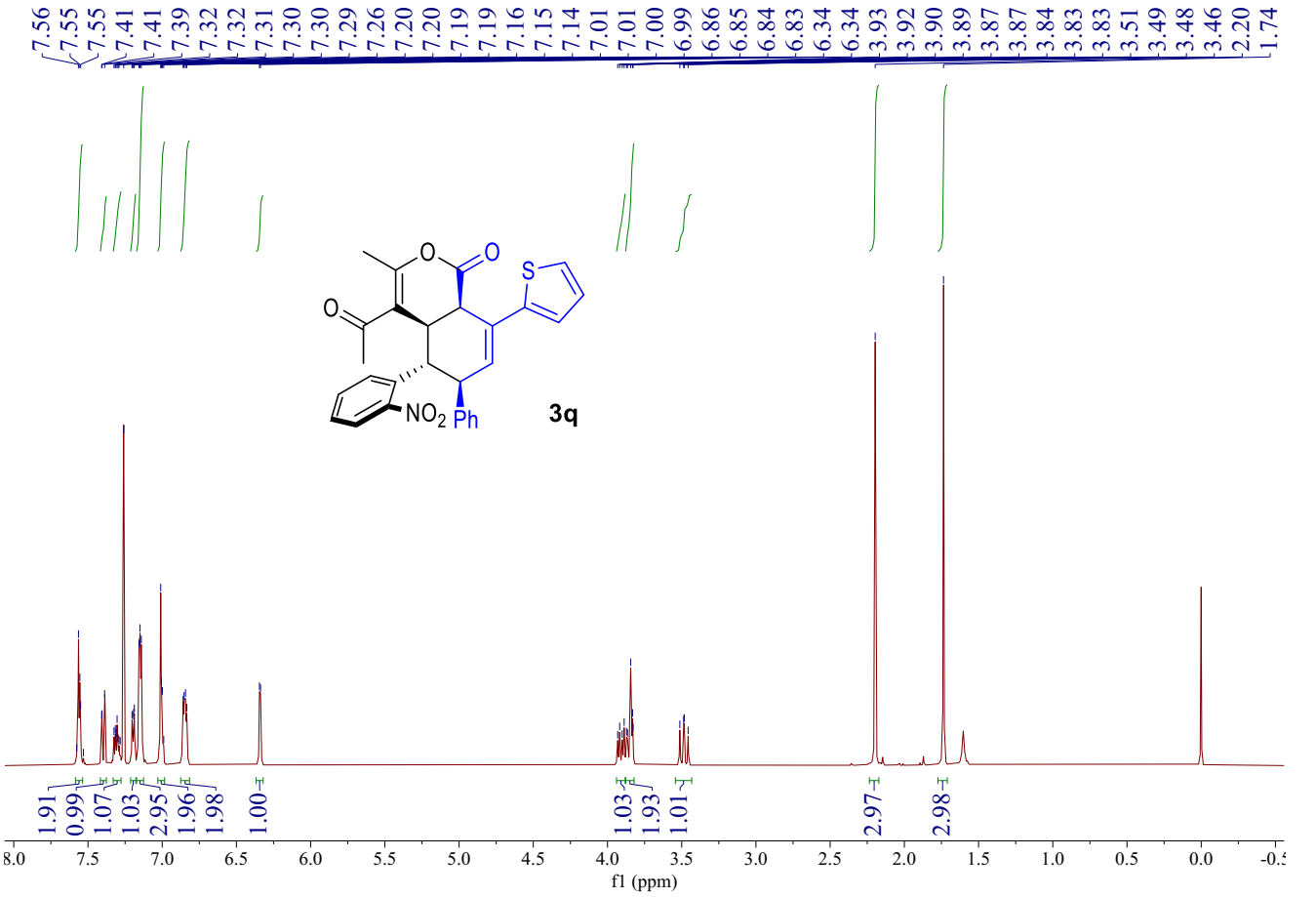
f1 (ppm)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O
O
S
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1.03
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1.98
1.00
1.03
1.93
1.01
2.97
2.98
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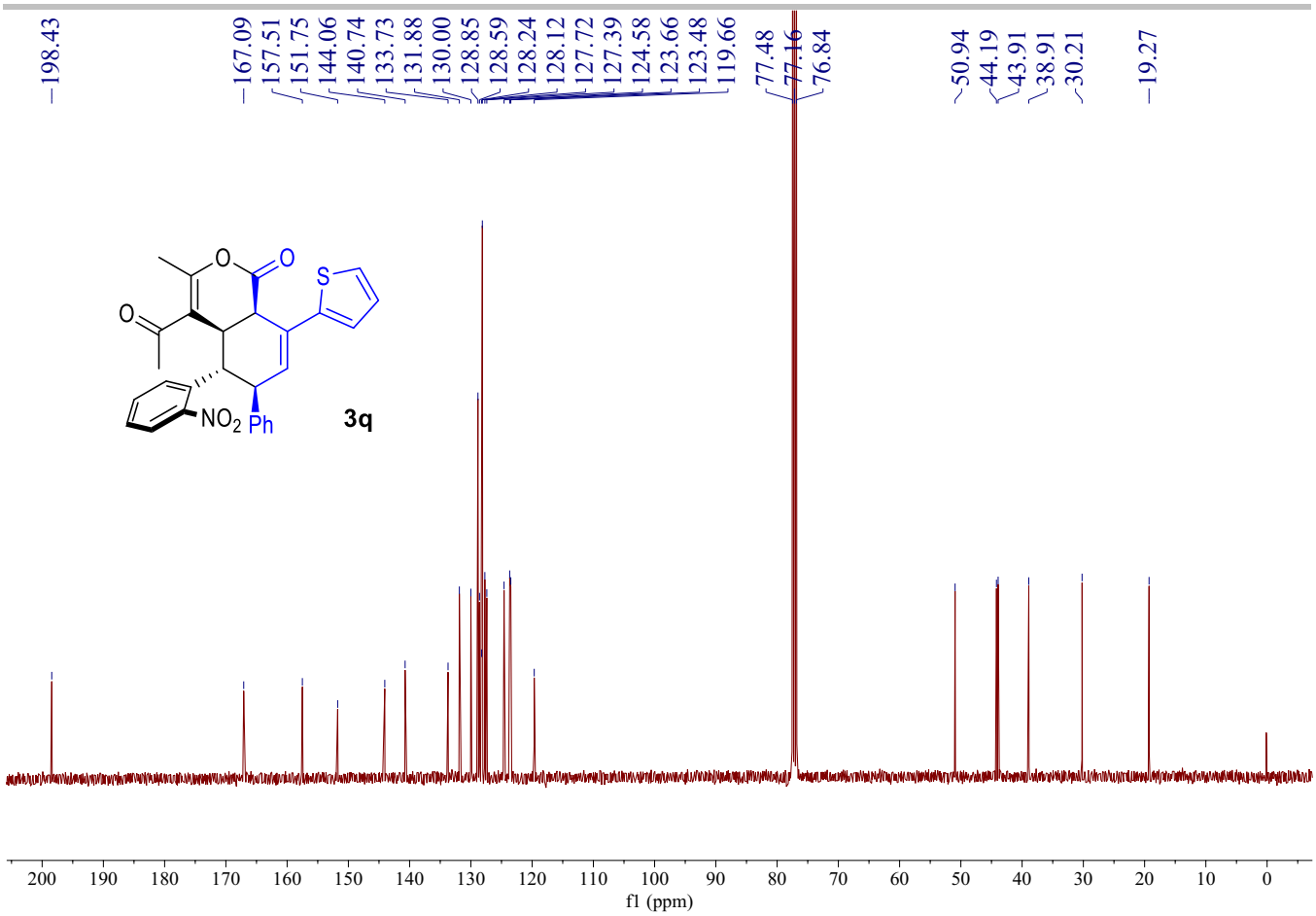
f1 (ppm)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76.84
50.94
44.19
43.91
38.91
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O
O
S
NO2
Ph
3q
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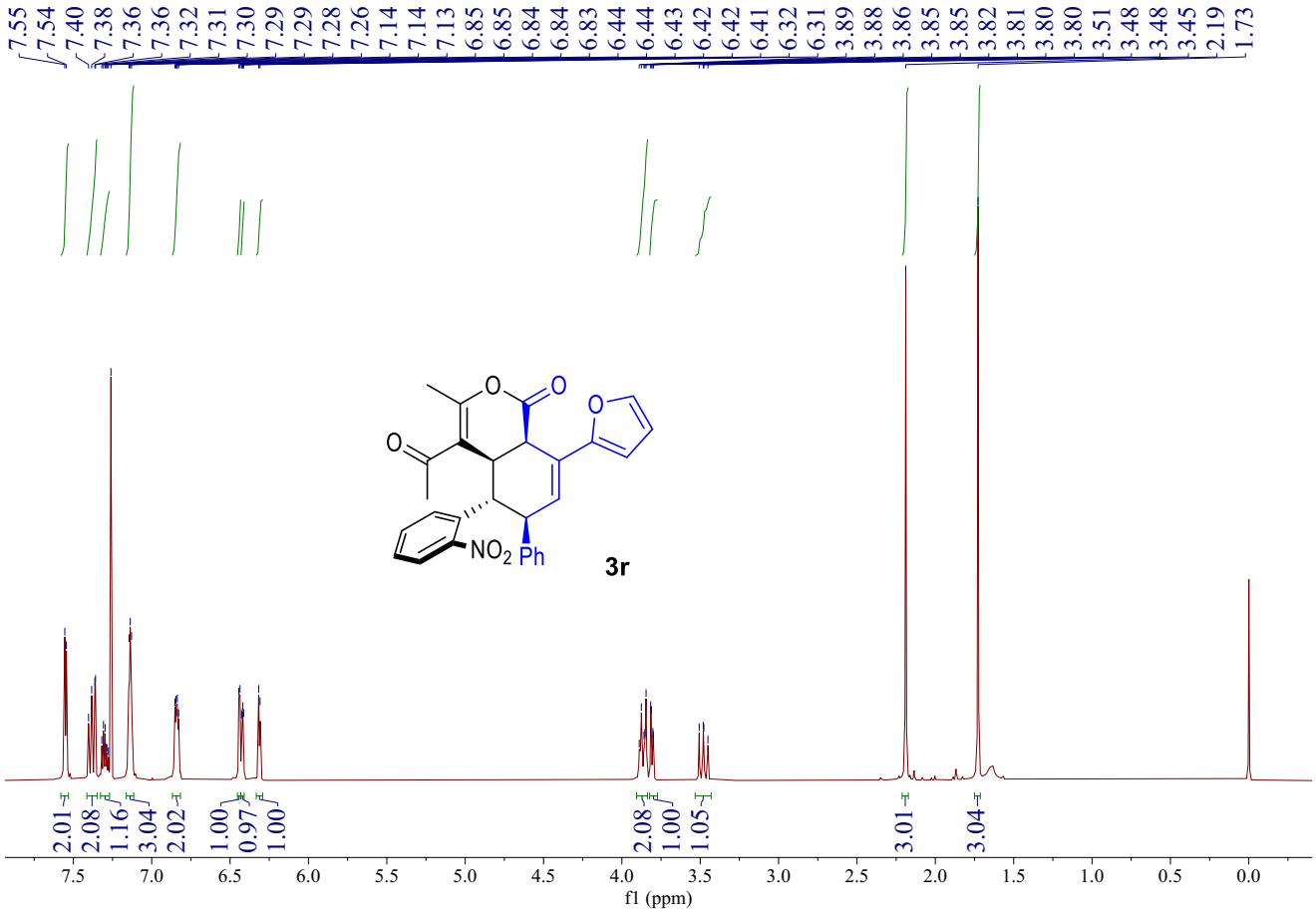
f1 (ppm)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O
O
NO2
Ph
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2.02
1.00
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1.00
2.08
1.00
1.05
3.01
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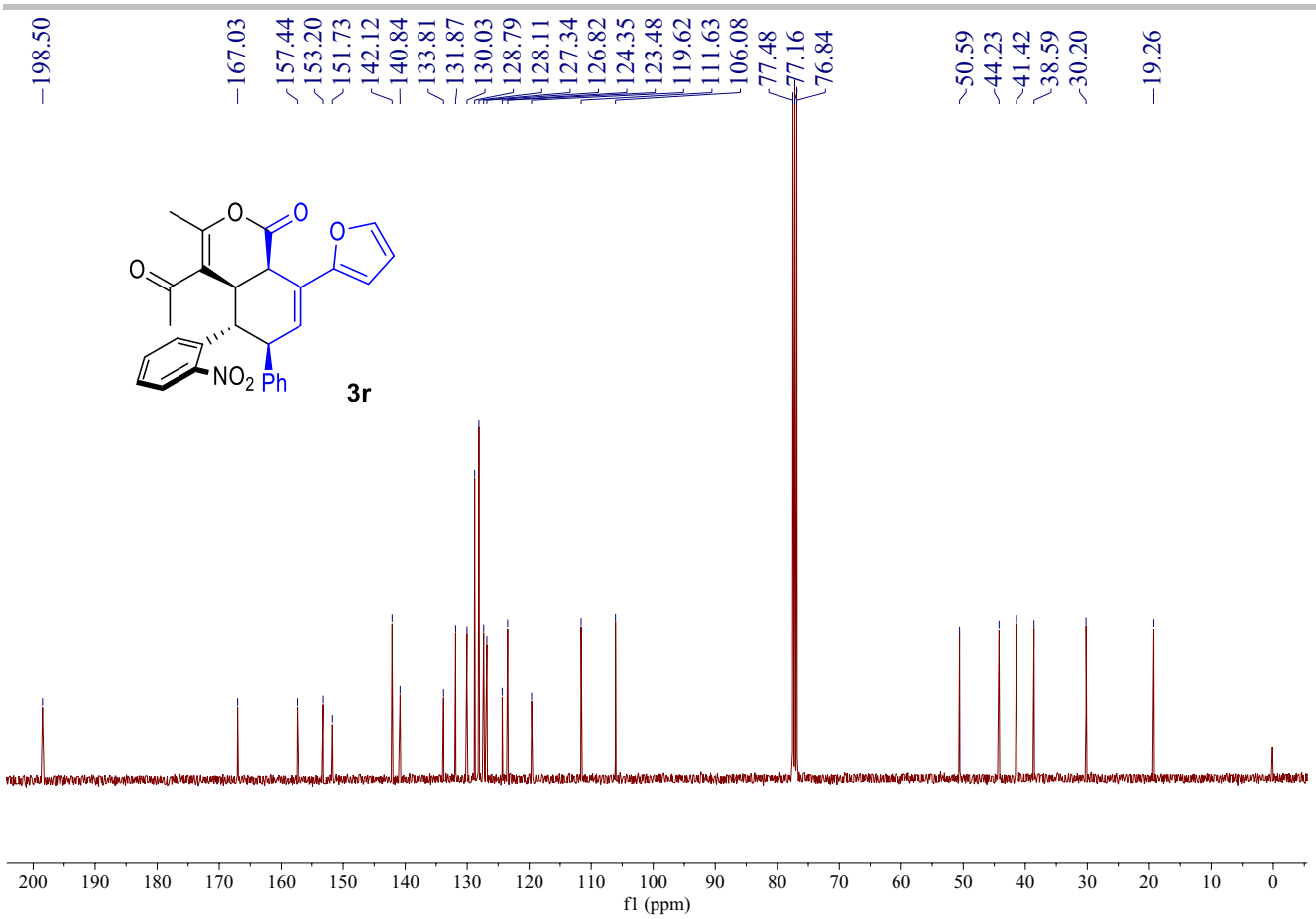
f1 (ppm)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76.84
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44.23
41.42
38.59
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O
O
NO2
Ph
3r
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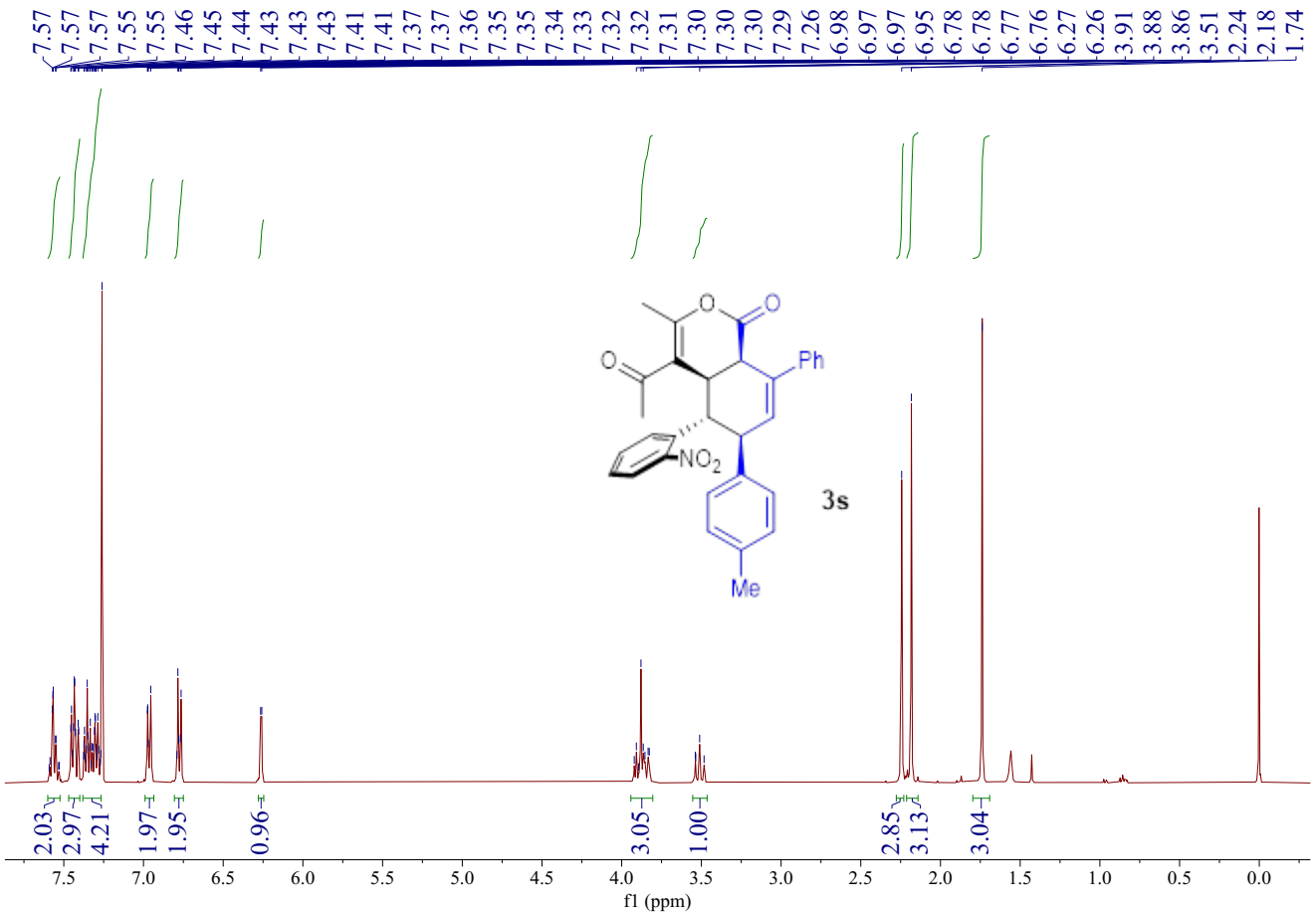
f1 (ppm)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2.24
2.18
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O
O
O
Ph
NO2
Me
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0.96
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1.00
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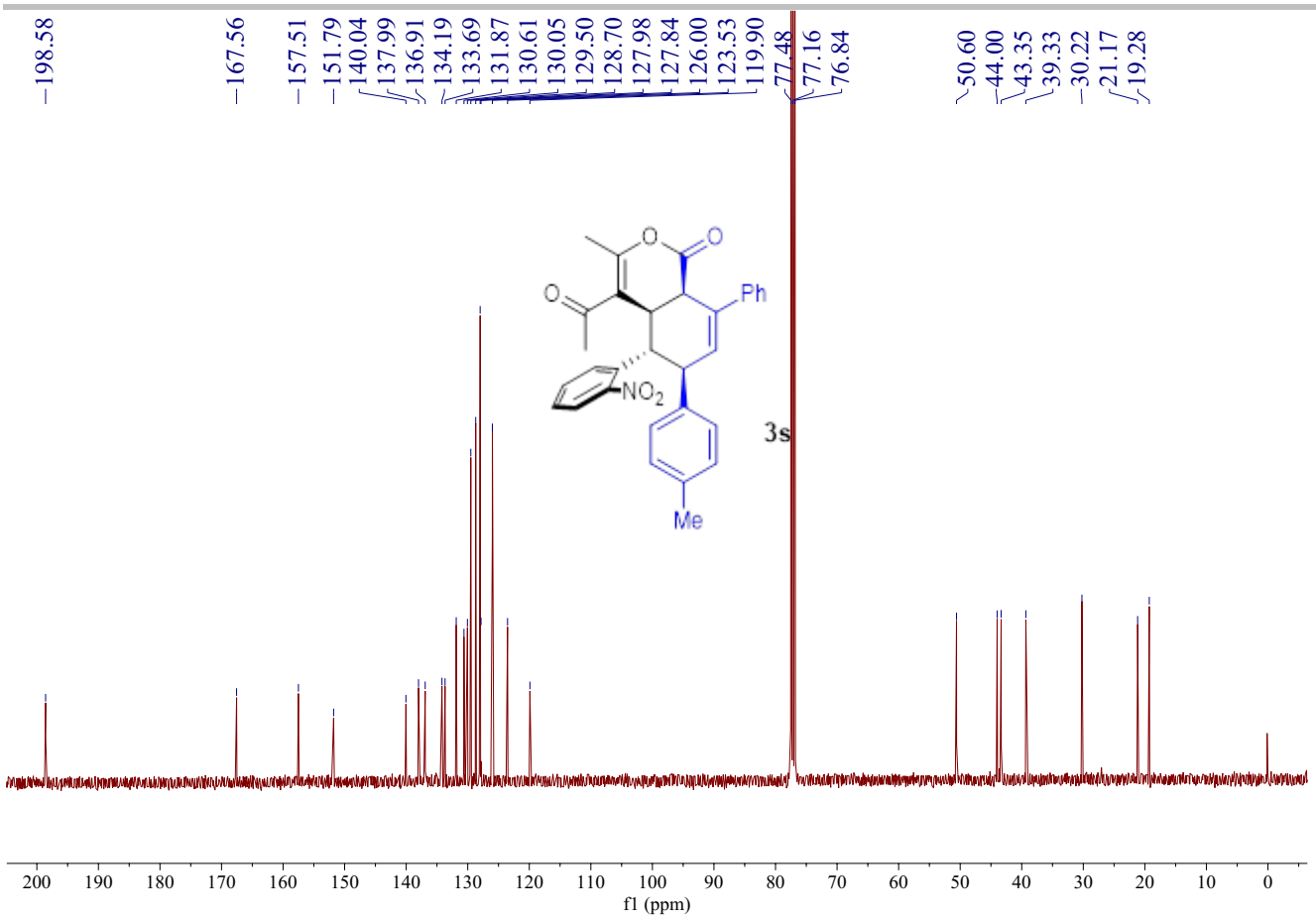
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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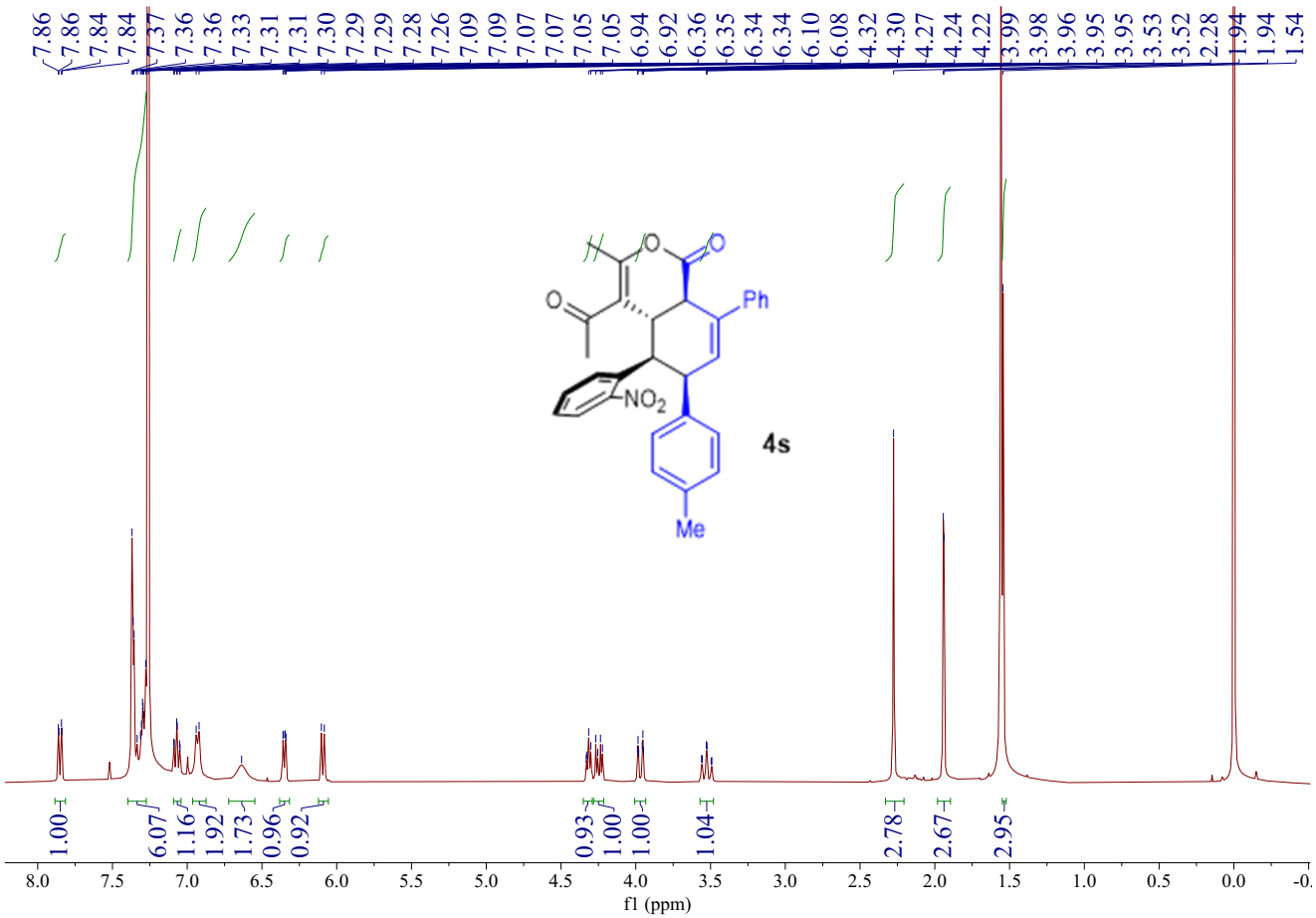
19.28
Ph
NO2
Me
3s
f1 (ppm)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7.05
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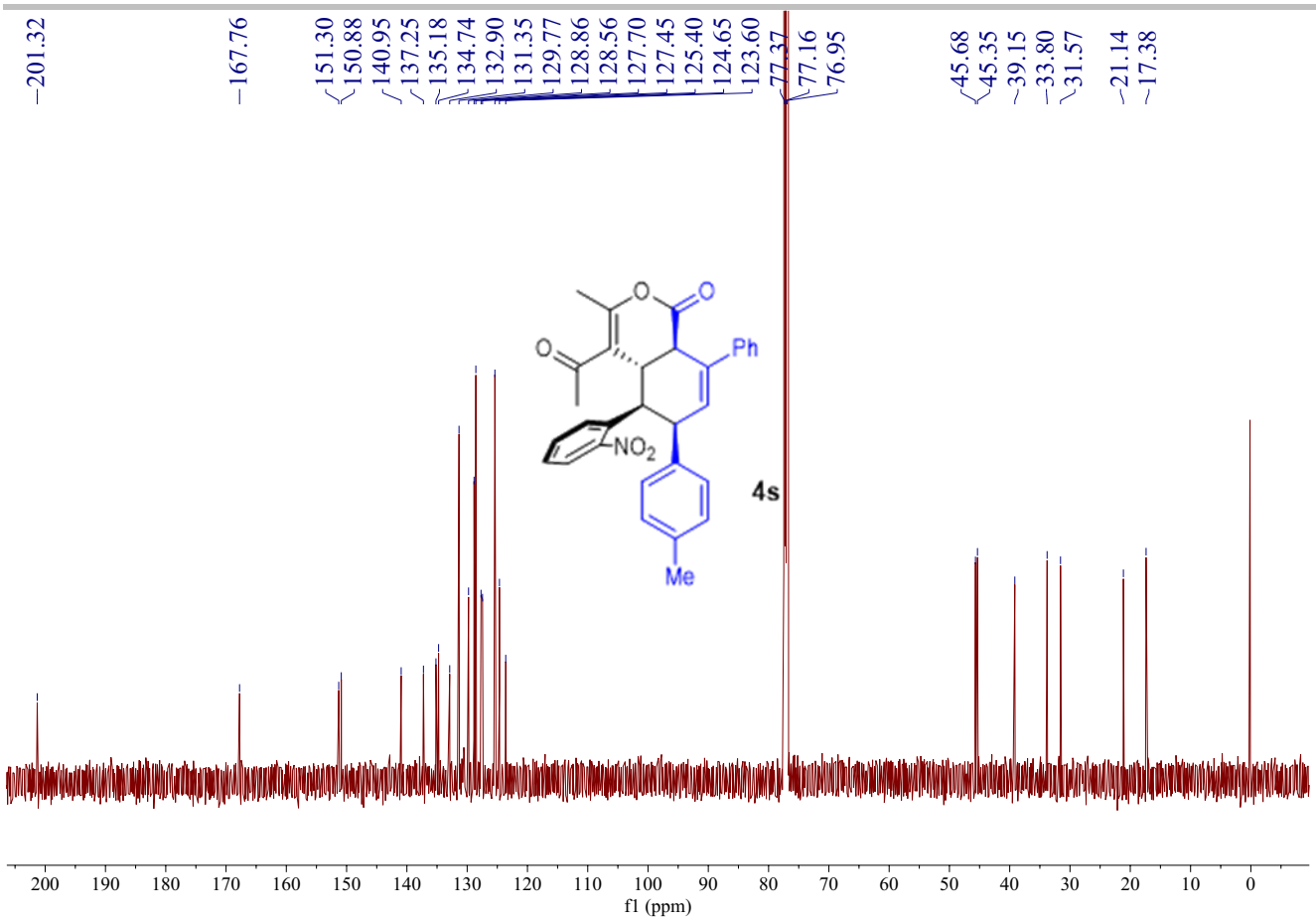
Me
4s
f1 (ppm)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Ph
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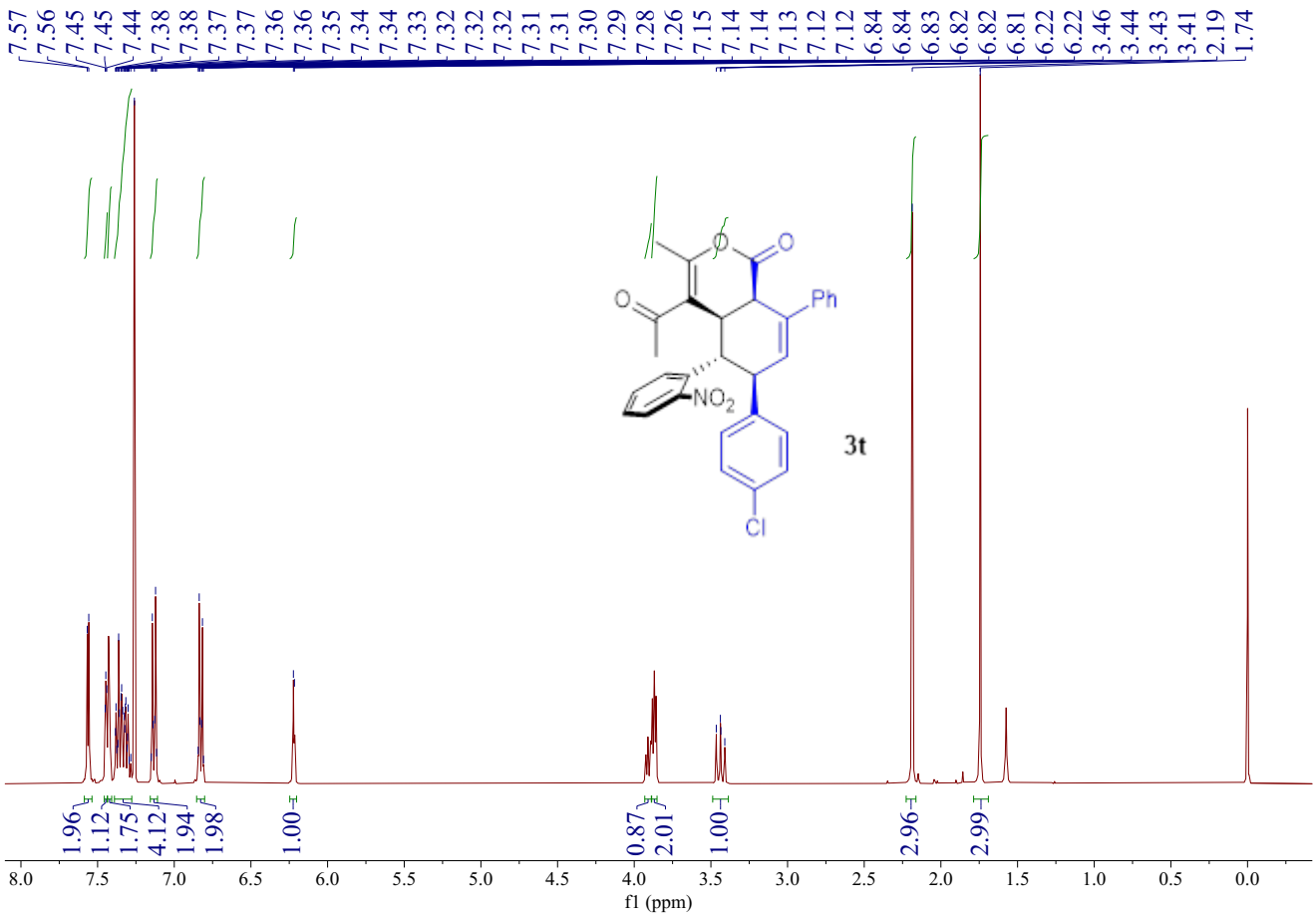
Me
4s
f1 (ppm)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2.19
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Ph
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Cl
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1.00
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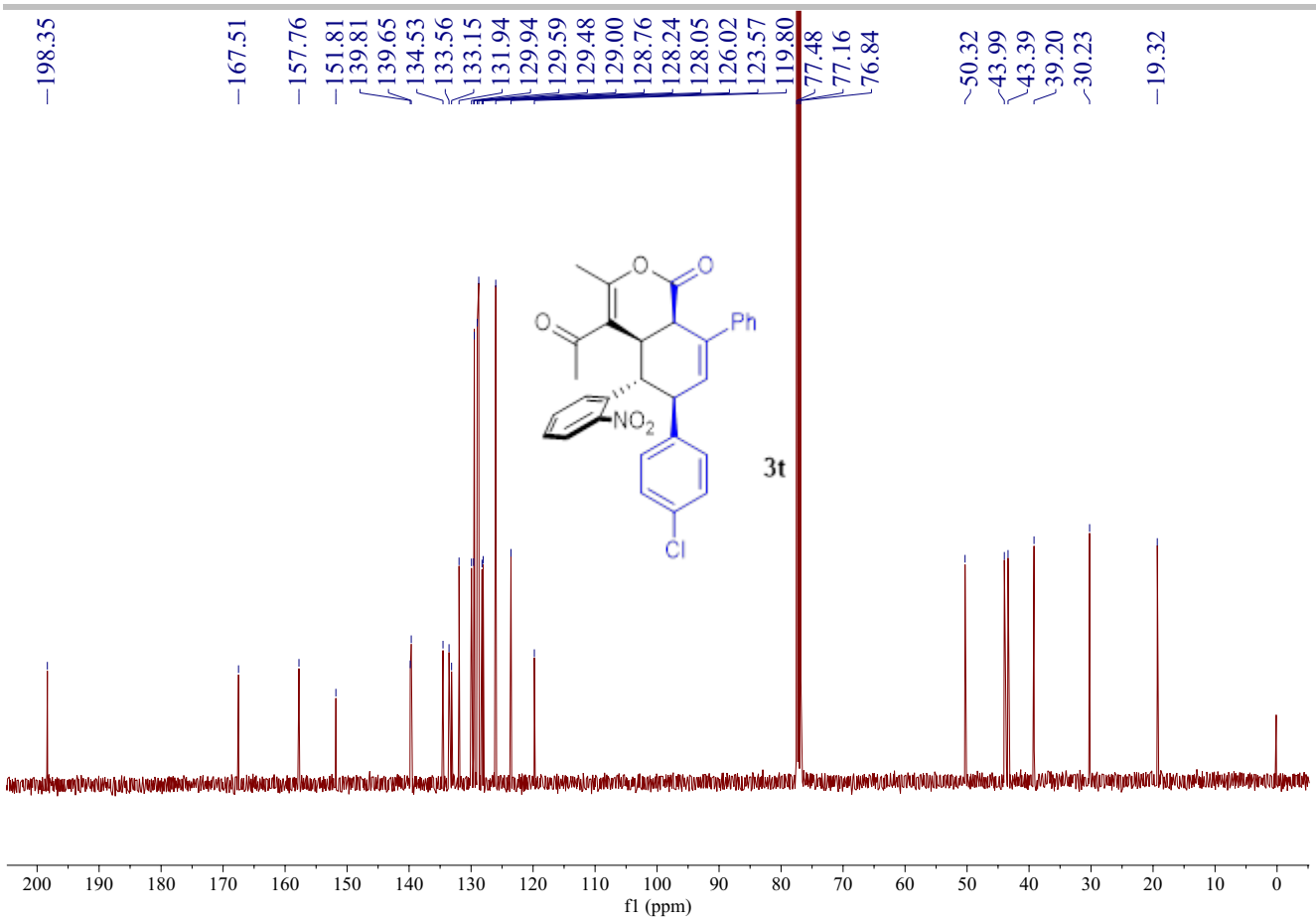
2.99
f1 (ppm)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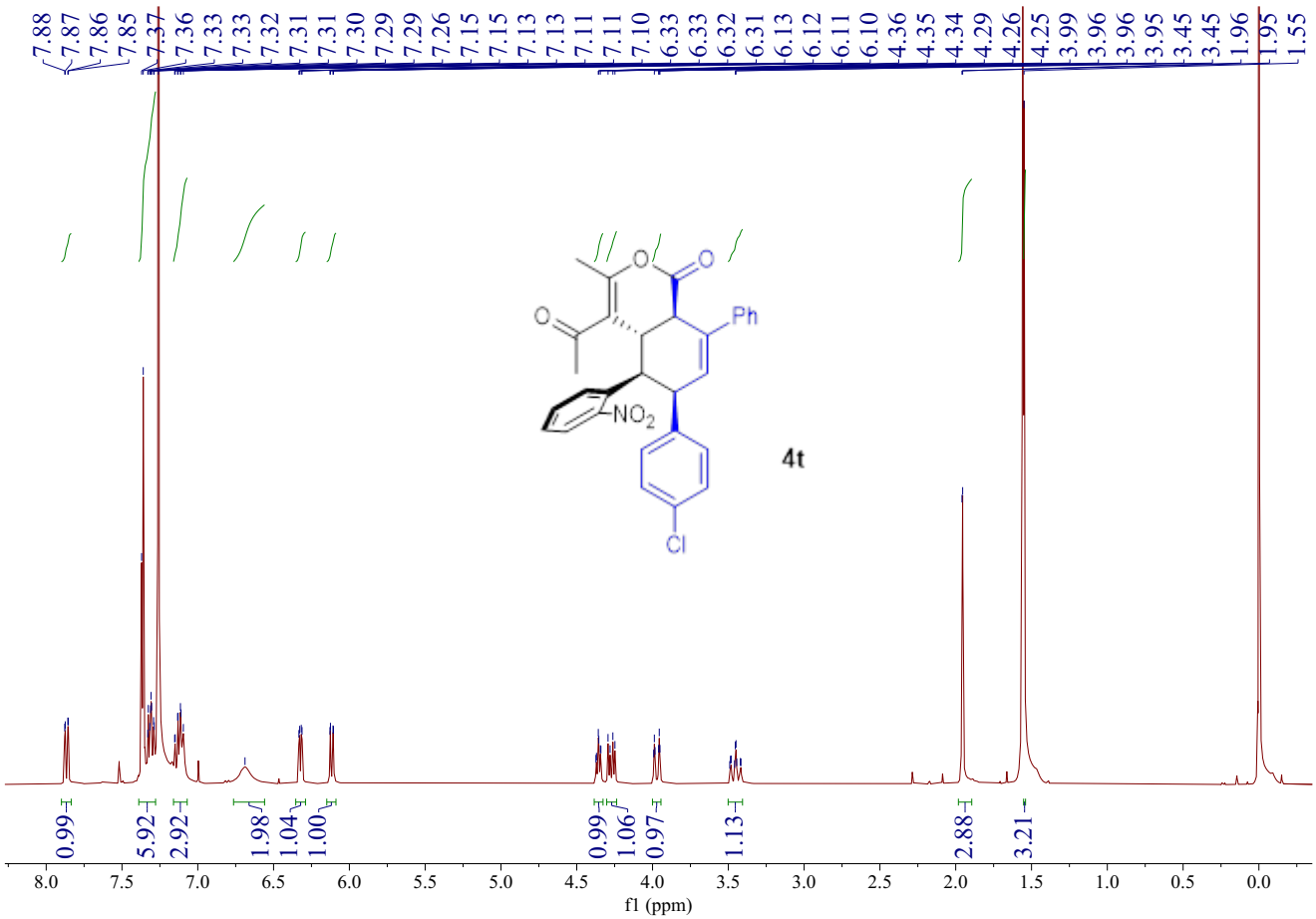
19.32
Ph
NO2
Cl
3t
f1 (ppm)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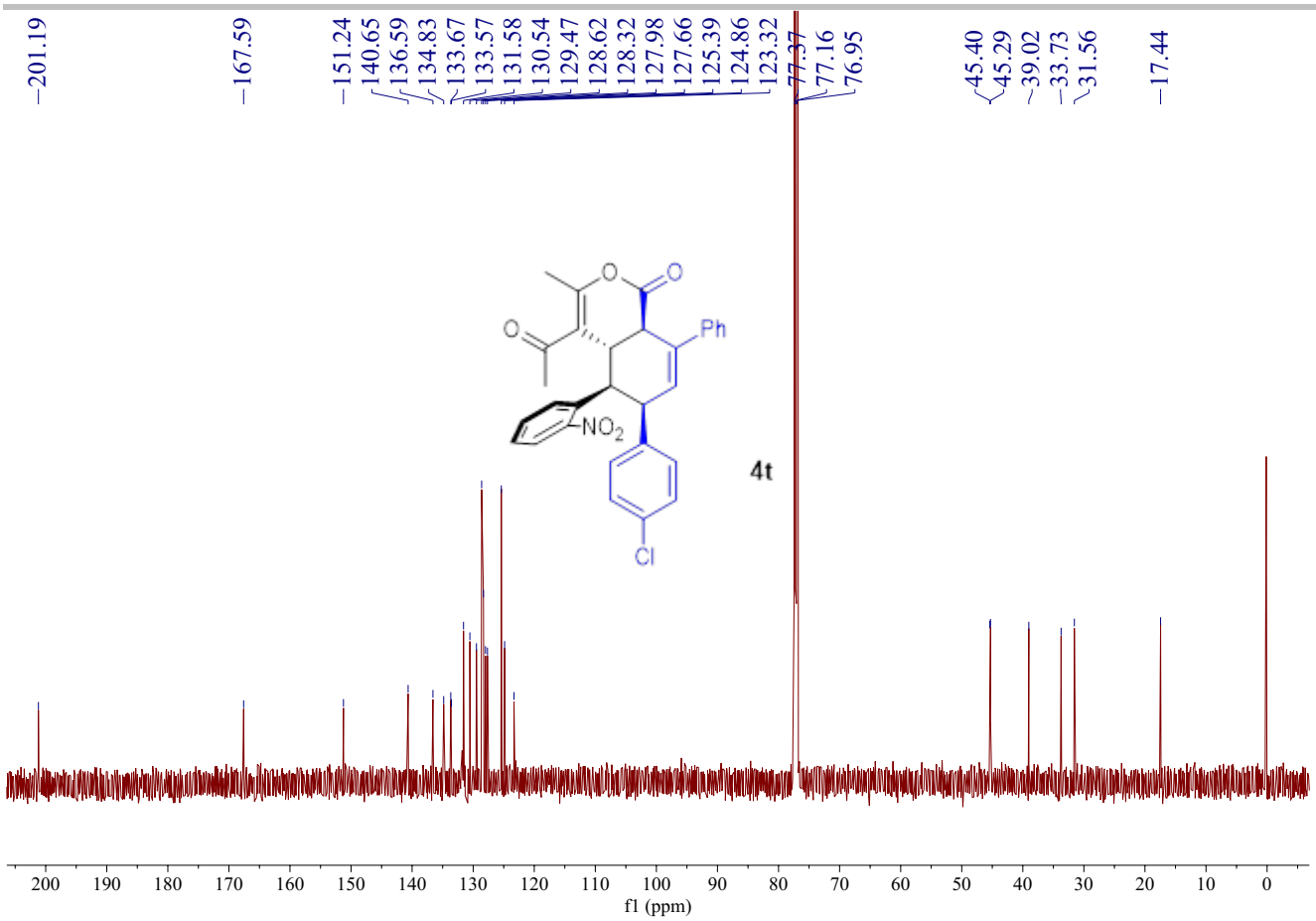
Cl
4t
f1 (ppm)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127.66
125.39
124.86
123.32
77.37
77.16
76.95
45.40
45.29
39.02
33.73
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O
O
Ph
NO2
Cl
4t
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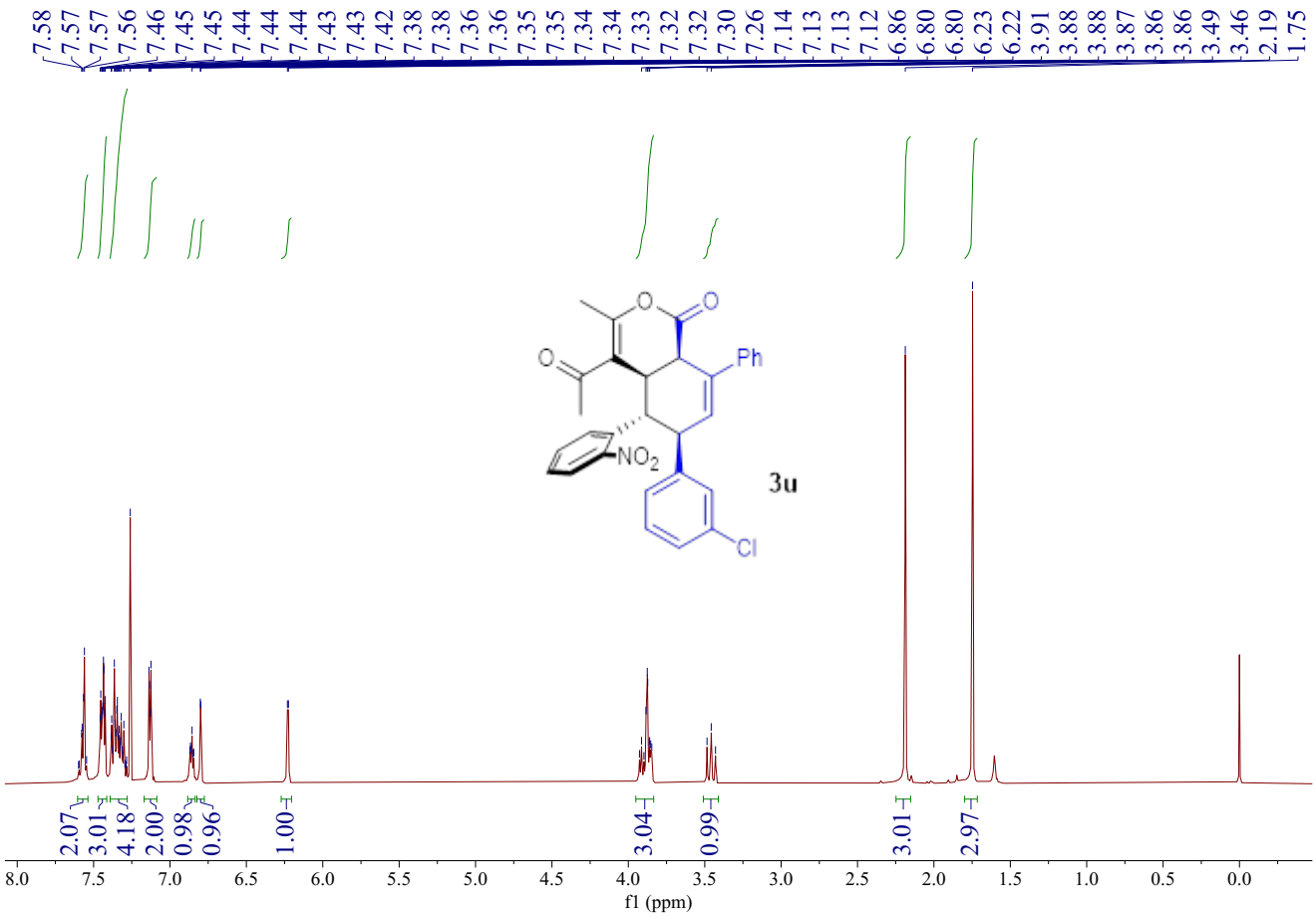
f1 (ppm)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7.12
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6.22
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3.88
3.87
3.86
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3.46
2.19
1.75
O
O
O
Ph
NO2
Cl
3u
2.07
3.01
4.18
2.00
0.98
0.96
1.00
3.04
0.99
3.01
2.97
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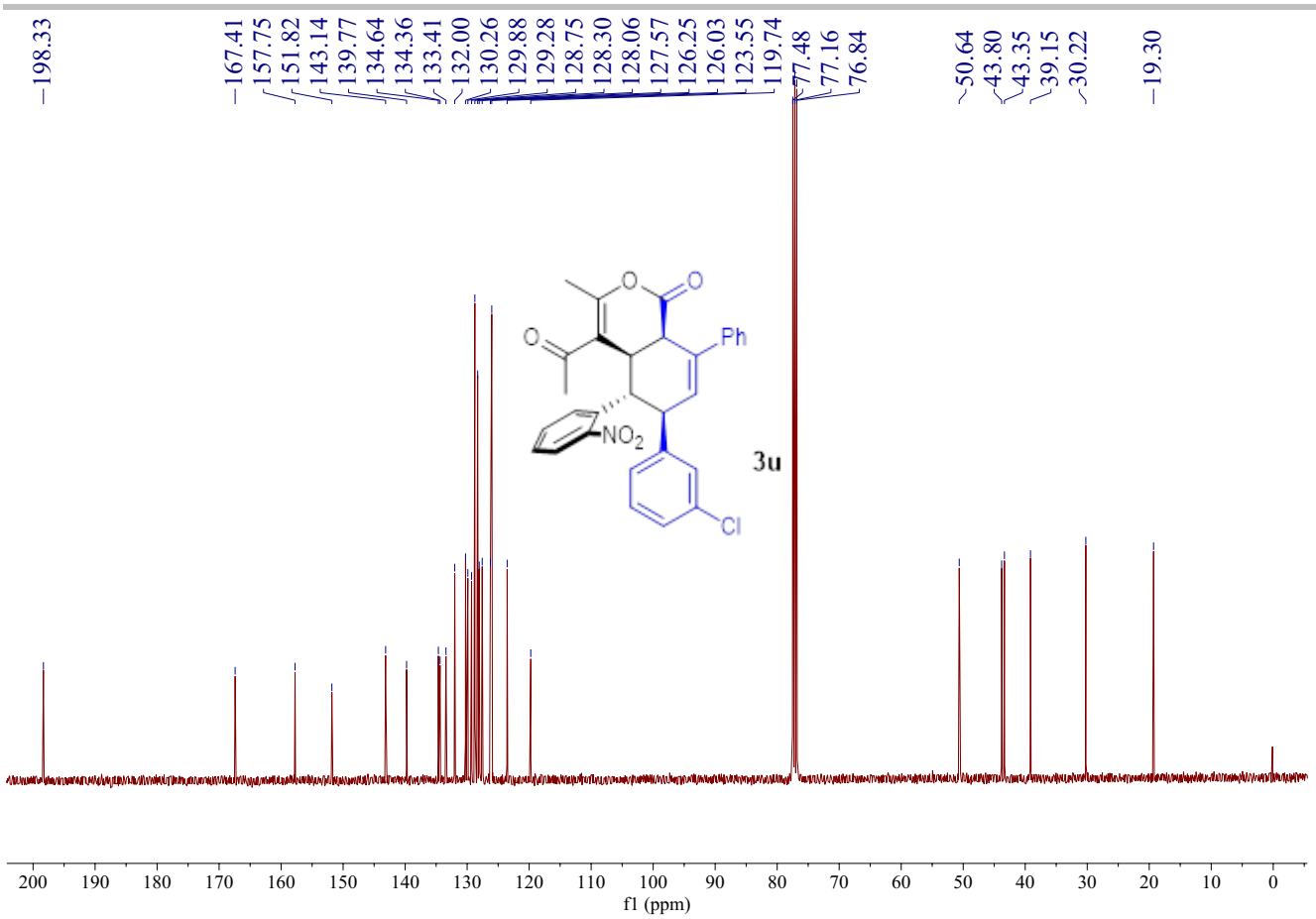
f1 (ppm)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123.55
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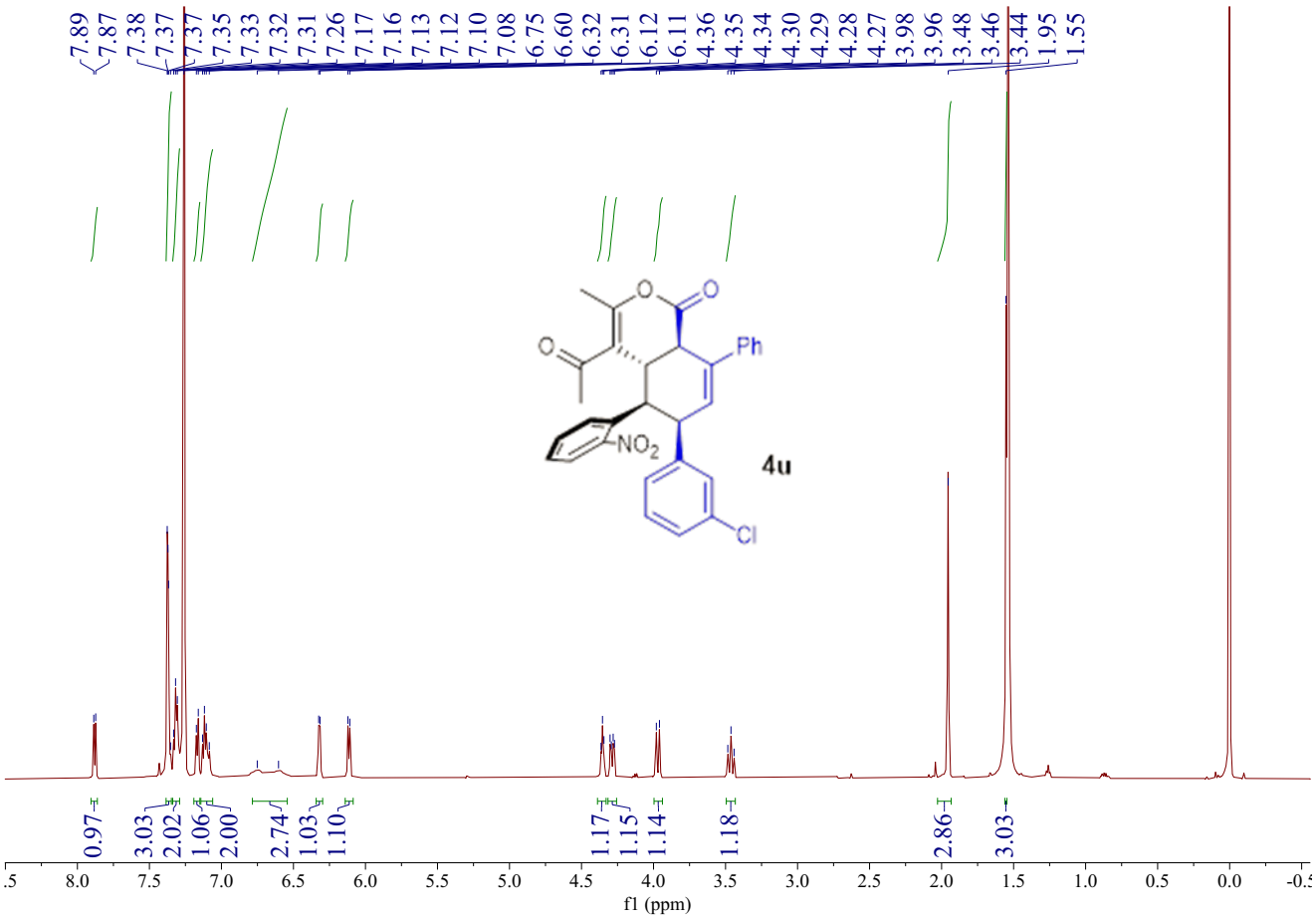
39.15
30.22
19.30
Ph
NO2
Cl
3u
f1 (ppm)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3.46
3.44
1.95
1.55
0.97
3.03
2.02
1.06
2.00
2.74
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1.15
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1.18
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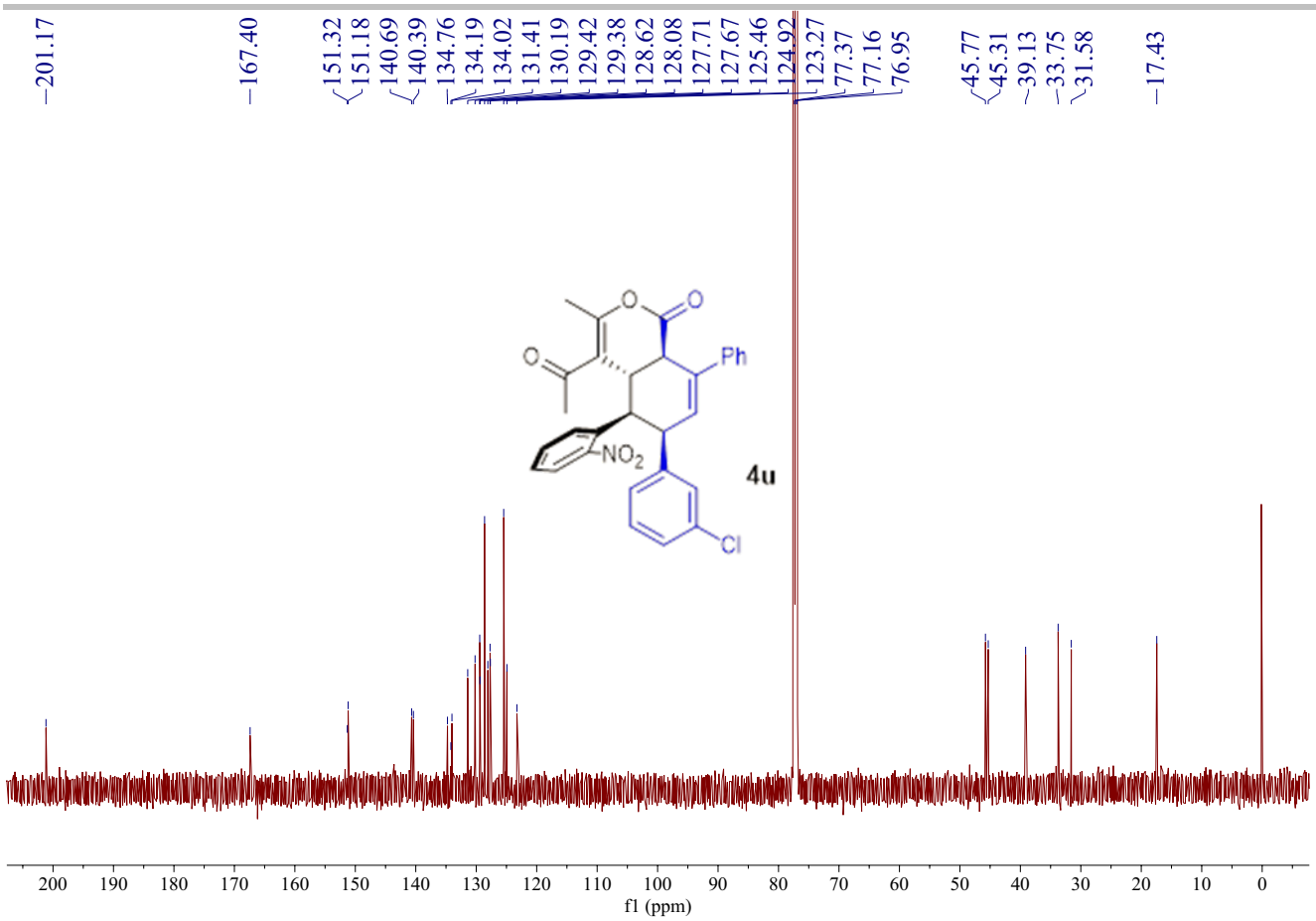
3.03
Ph
NO2
Cl
4u
f1 (ppm)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123.27
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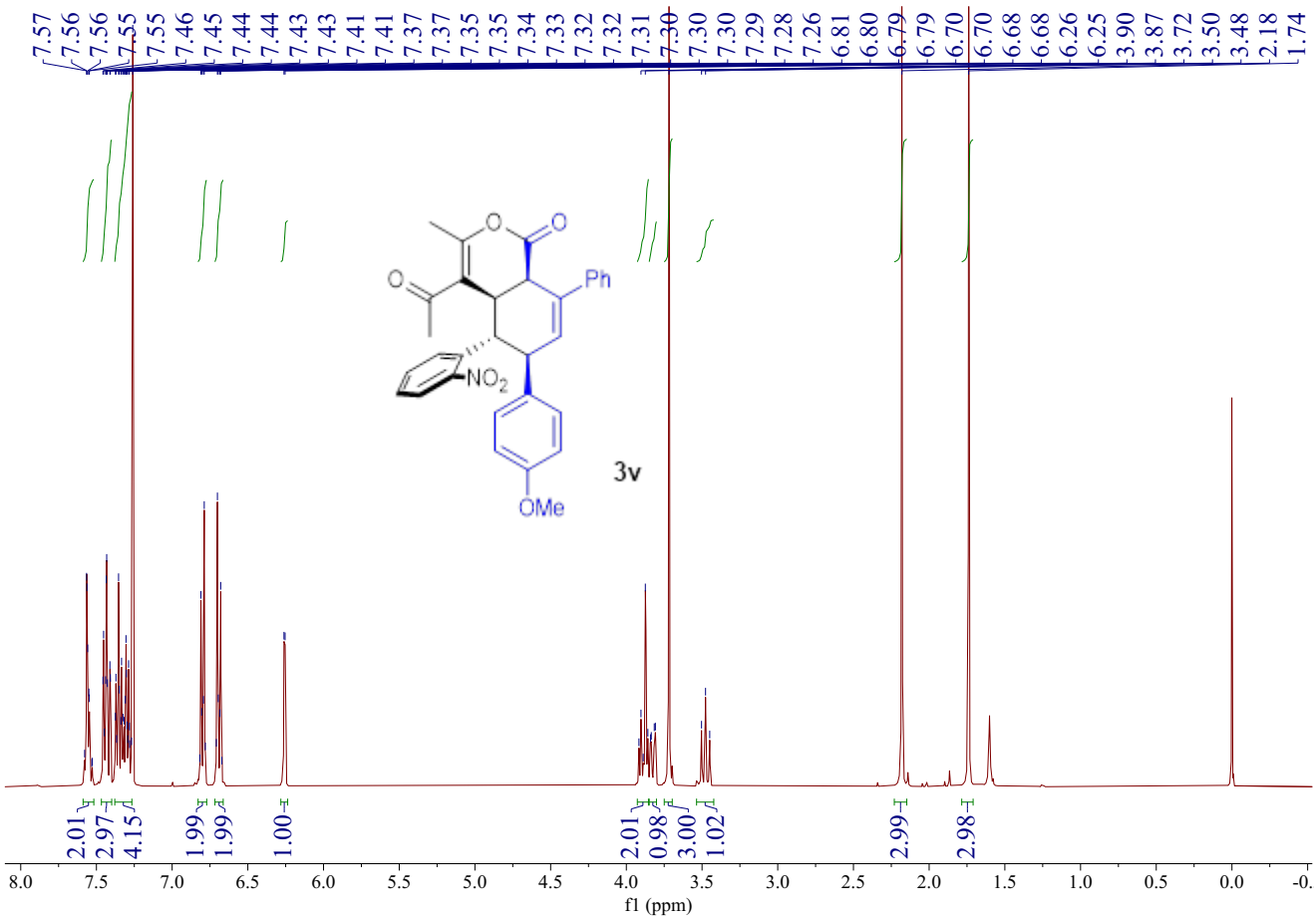
33.75
31.58
17.43
Ph
NO2
Cl
4u
f1 (ppm)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6.68
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3.72
3.50
3.48
2.18
1.74
Ph
NO2
OMe
3v
2.01
2.97
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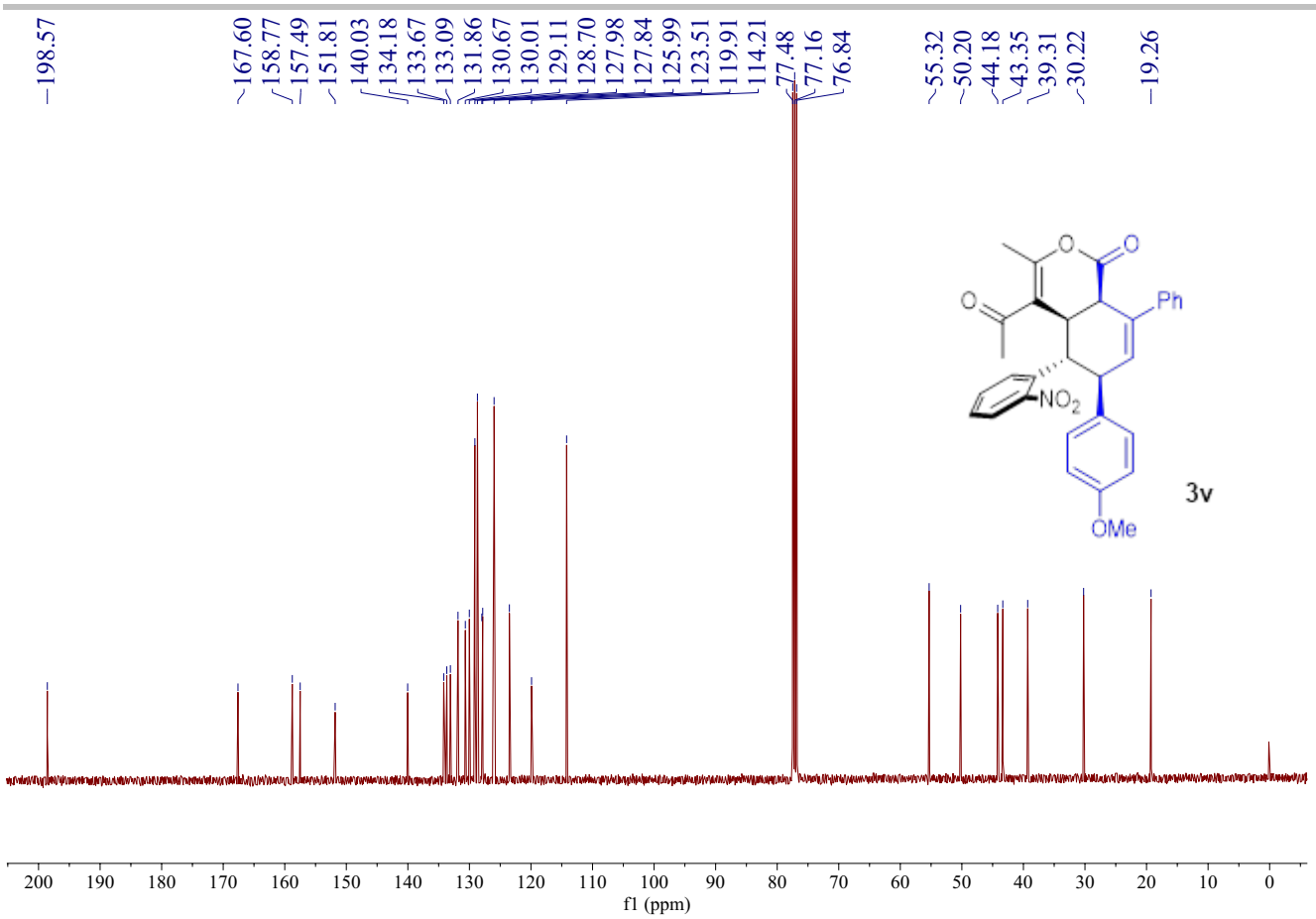
1.99
1.00
2.01
0.98
3.00
1.02
2.99
2.98
f1 (ppm)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77.48
77.16
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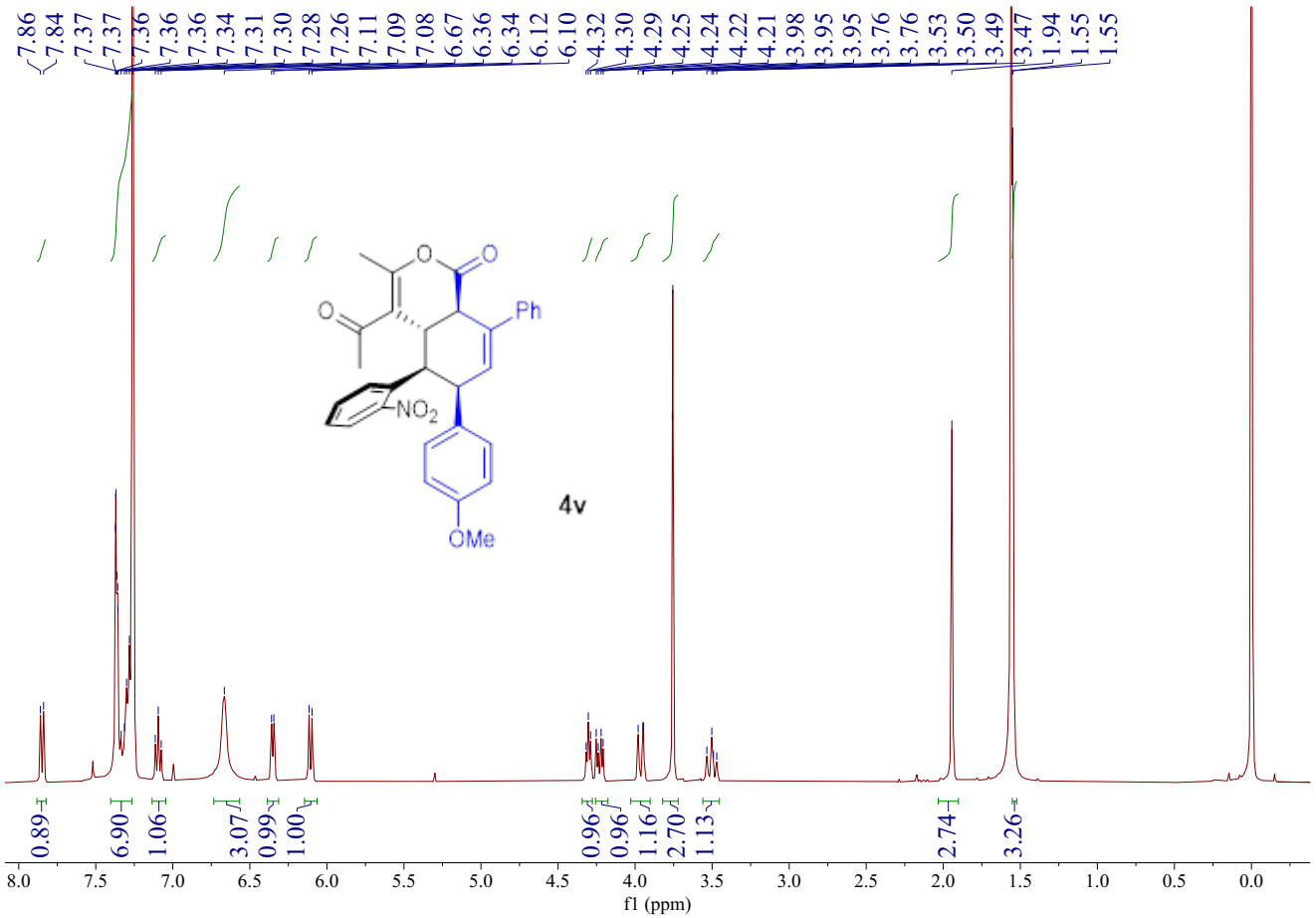
44.18
43.35
39.31
30.22
19.26
Ph
NO2
OMe
3v
f1 (ppm)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3.47
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1.55
1.55
Ph
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OMe
4v
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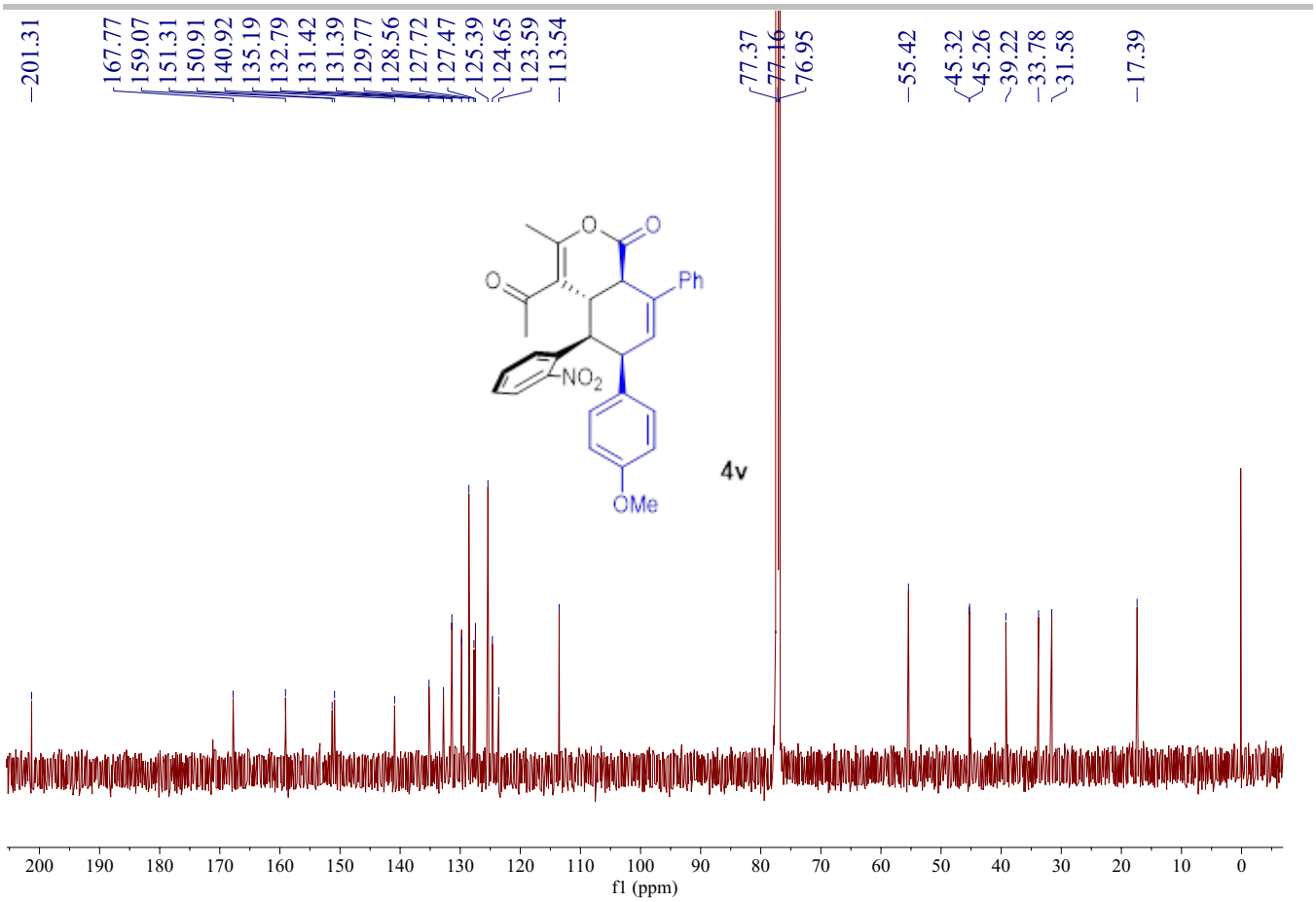
2.74
3.26
f1 (ppm)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31.58
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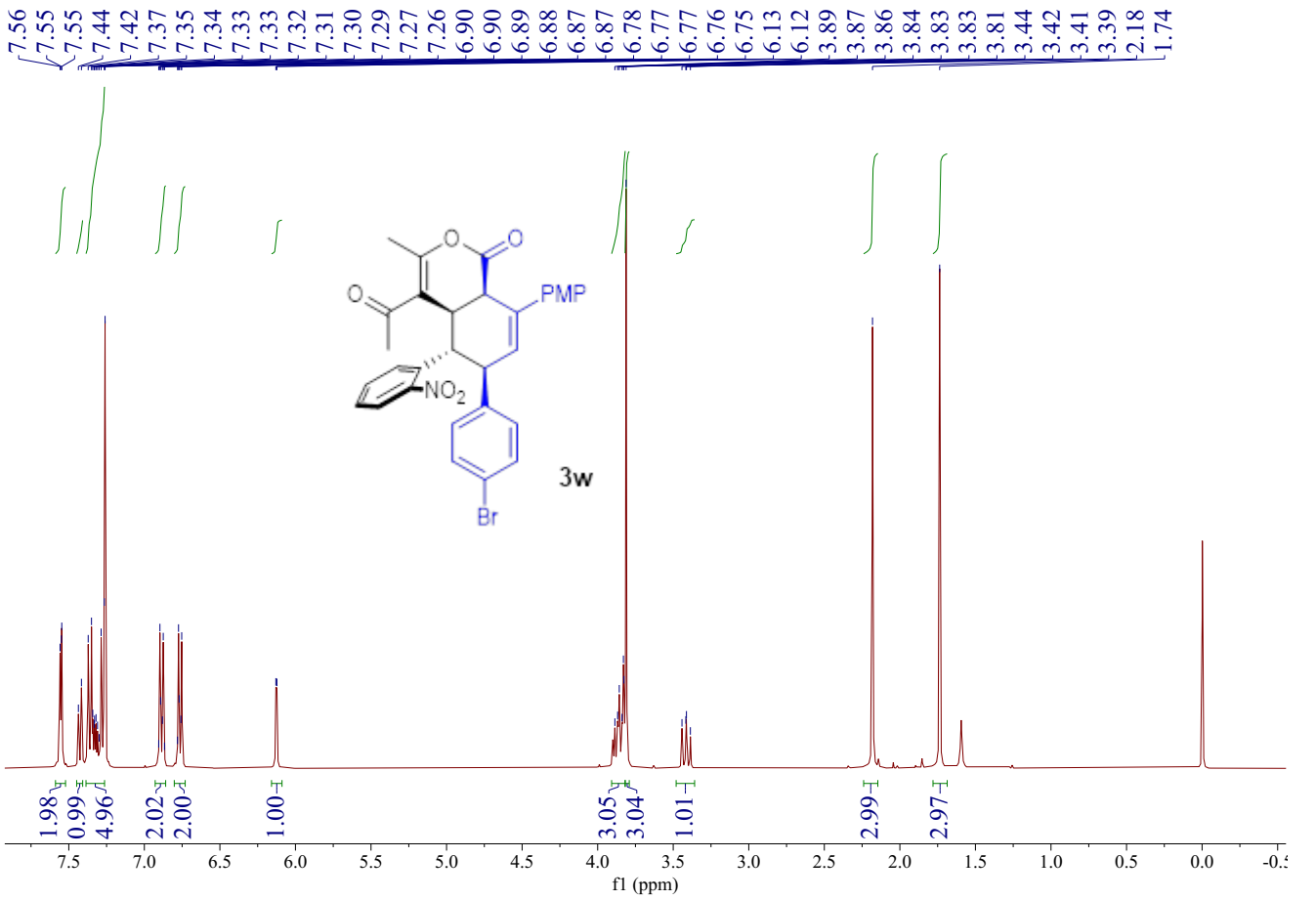
Ph
NO2
OMe
4v
f1 (ppm)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3.41
3.39
2.18
1.74
PMP
NO2
Br
3w
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2.00
1.00
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3.04
1.01
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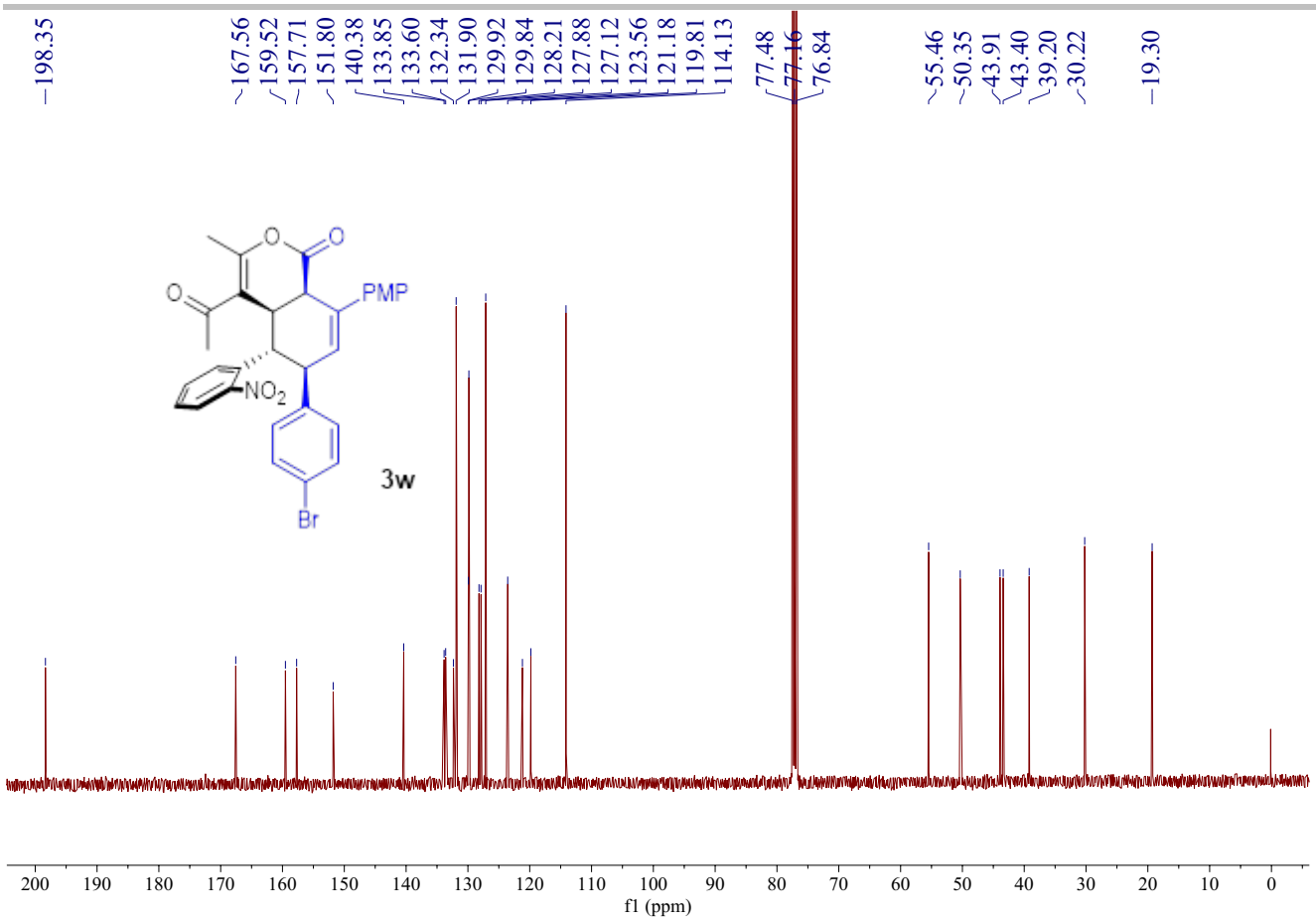
f1 (ppm)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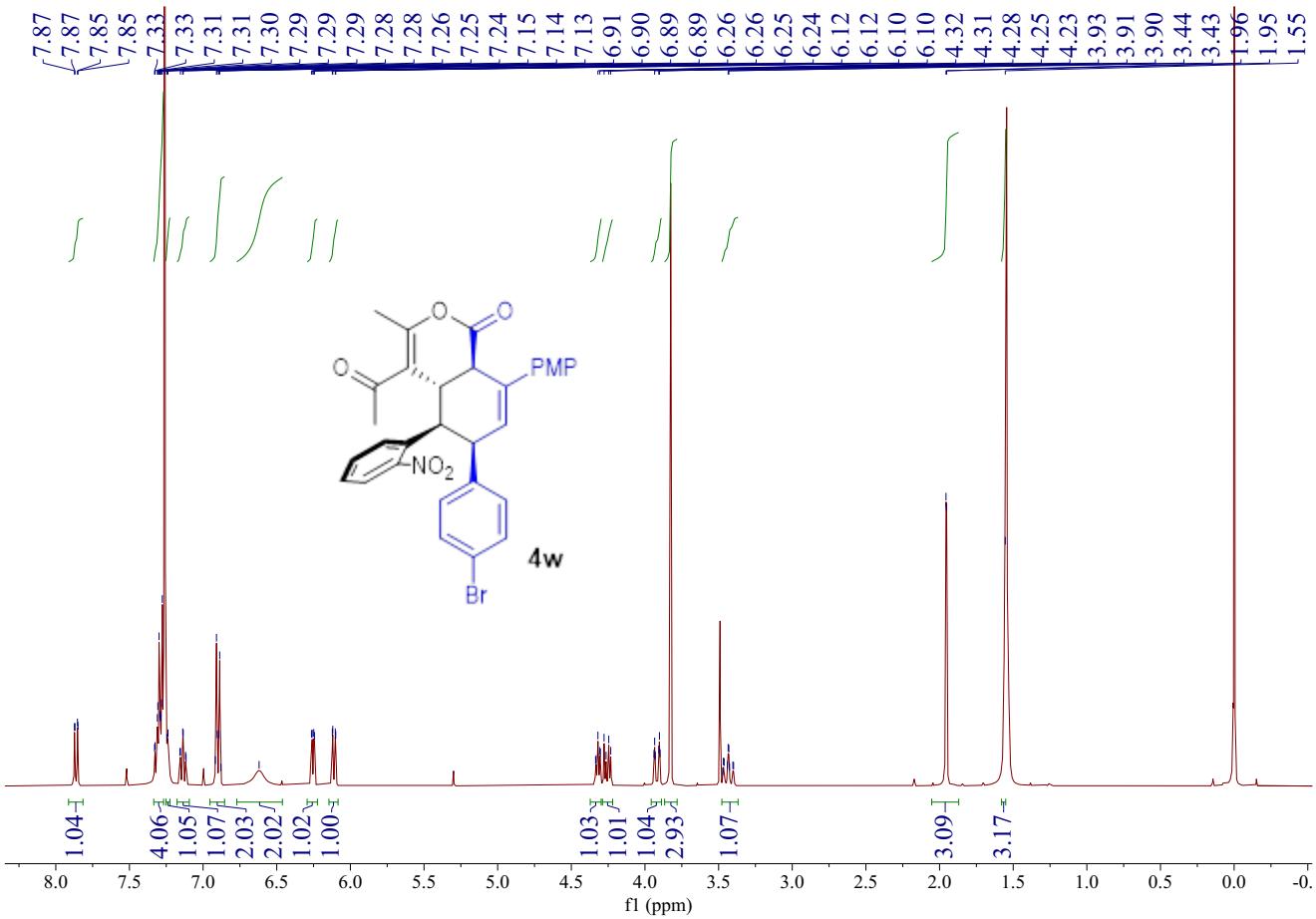
PMP
NO2
Br
3w
f1 (ppm)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1.95
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PMP
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Br
4w
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4.06
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1.07
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1.03
1.01
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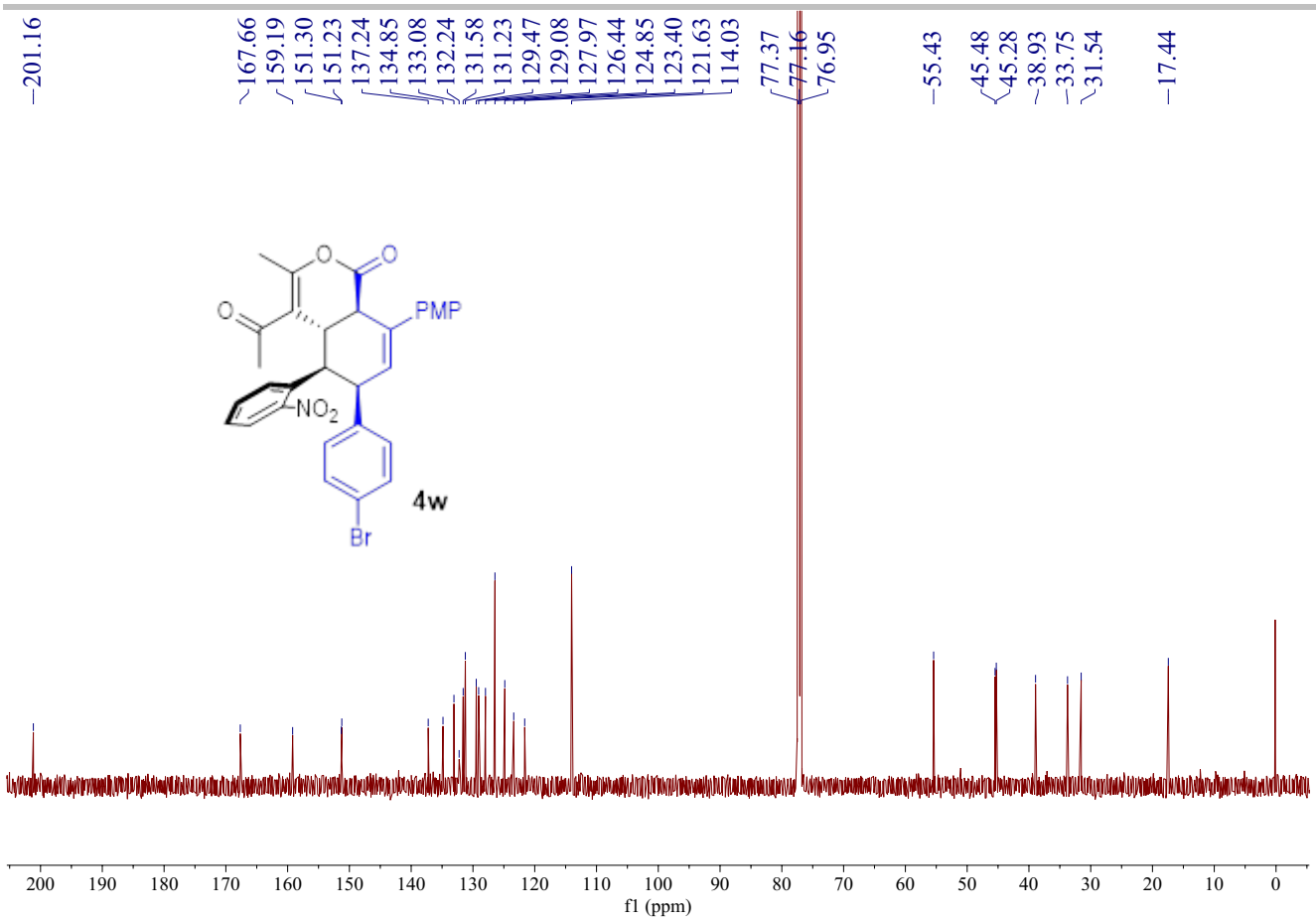
3.17
f1 (ppm)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124.85
123.40
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114.03
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77.16
76.95
55.43
45.48
45.28
38.93
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PMP
NO2
Br
4w
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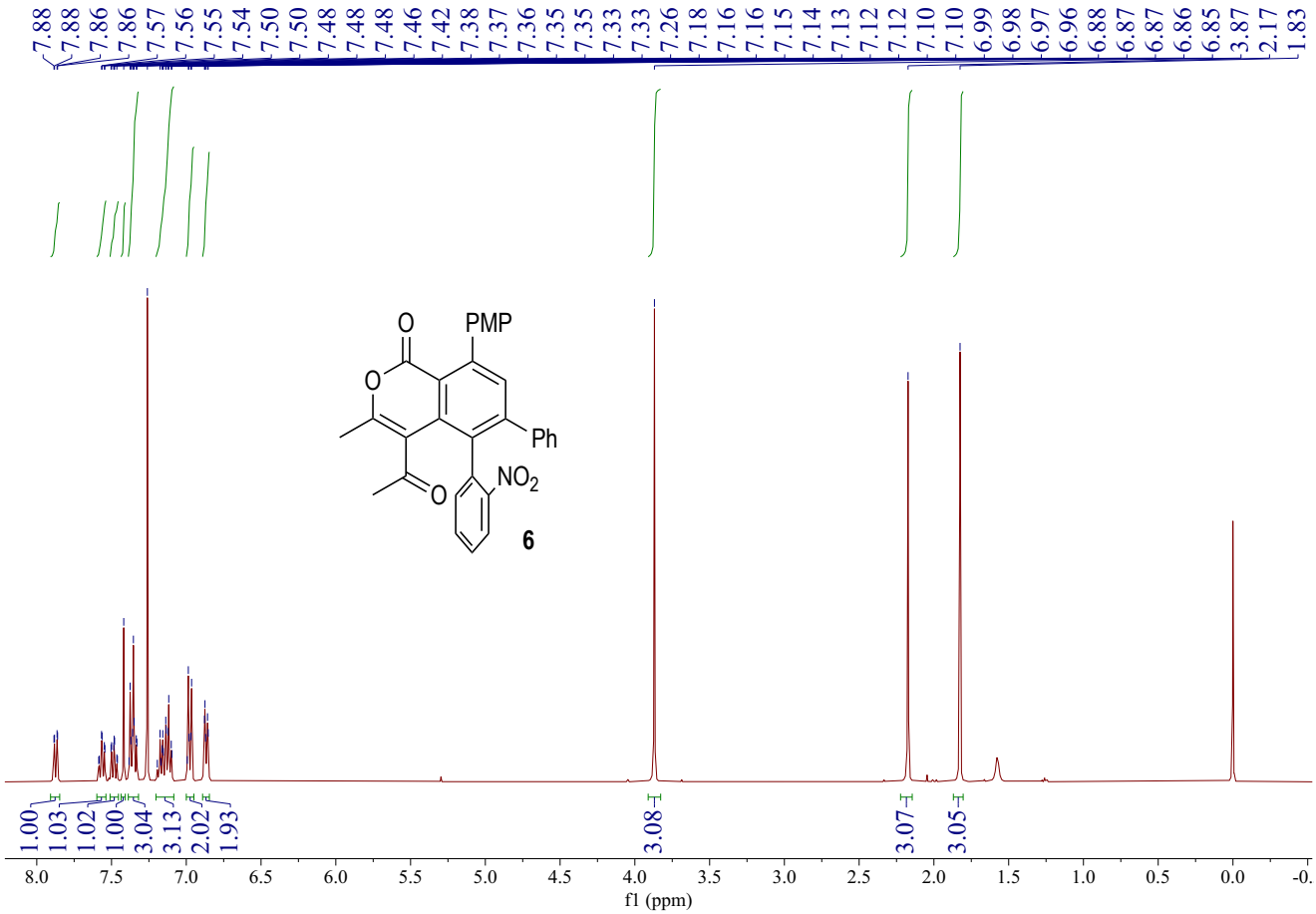
f1 (ppm)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6.98
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2.17
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O
PMP
O
Ph
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O
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1.03
1.02
1.00
3.04
3.13
2.02
1.93
3.08
3.07
3.05
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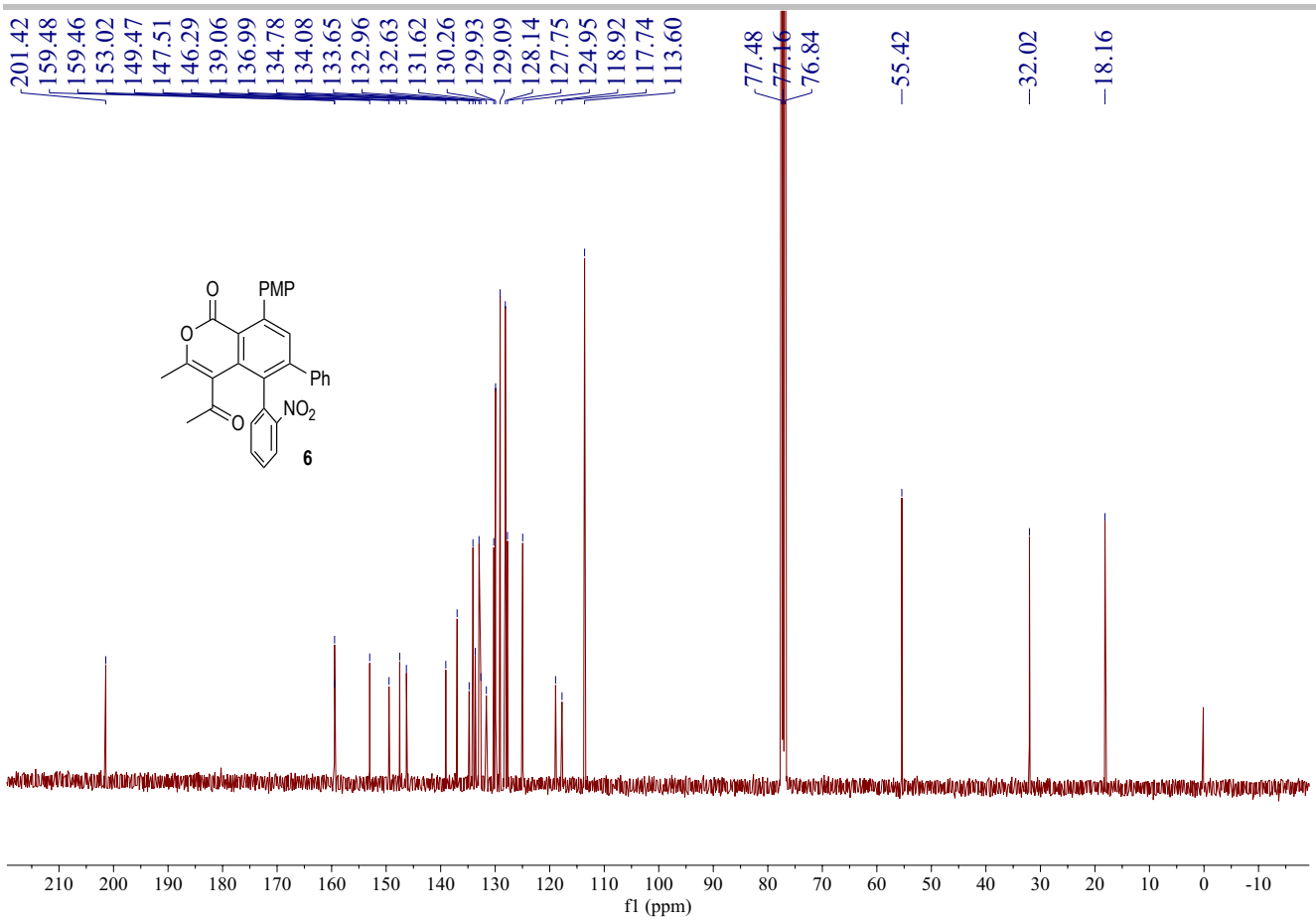
f1 (ppm)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130.26
129.93
129.09
128.14
127.75
124.95
118.92
117.74
113.60
77.48
77.16
76.84
55.42
32.02
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O
PMP
O
Ph
NO2
O
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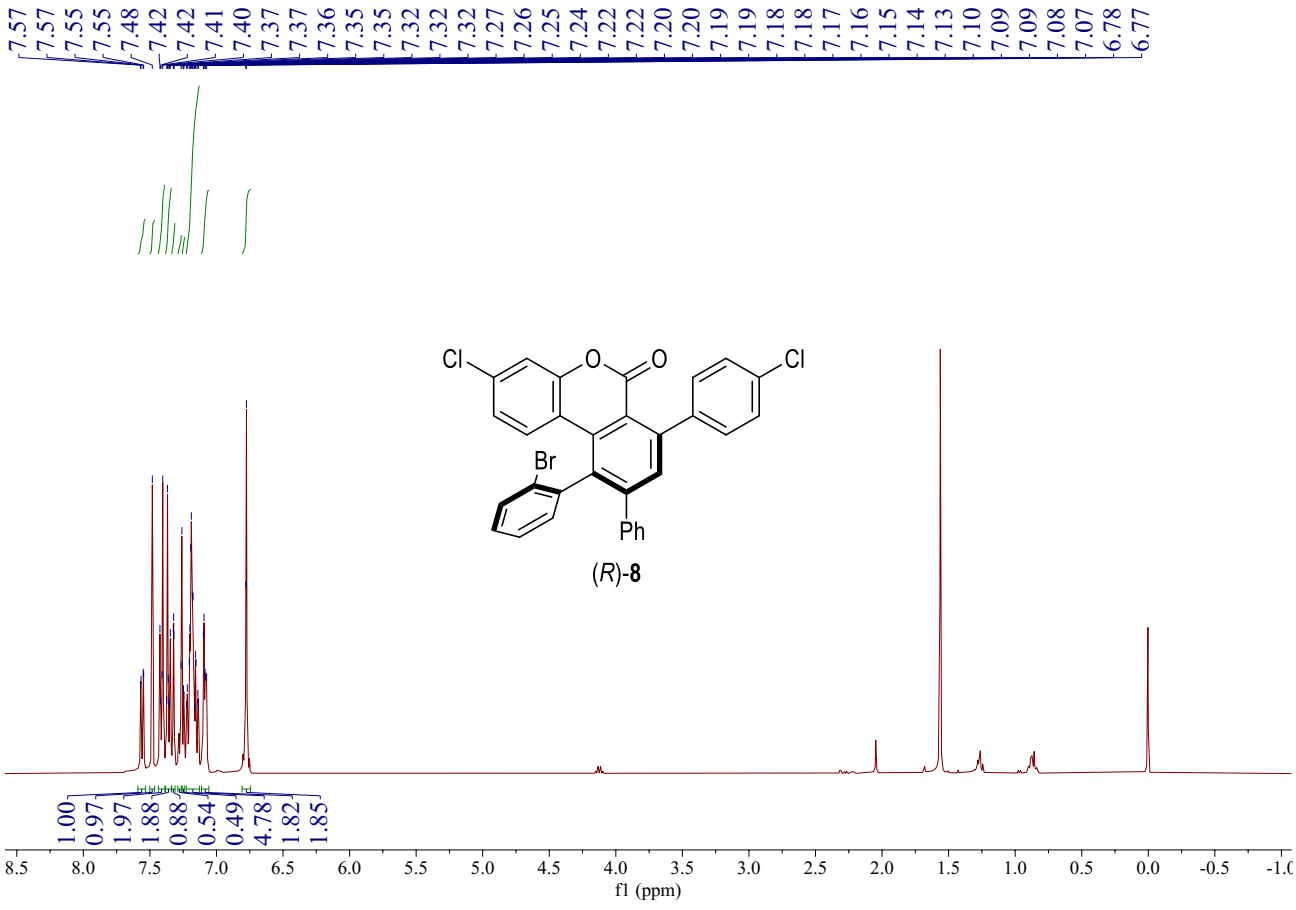
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.16
7.15
7.14
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7.10
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7.09
7.08
7.07
6.78
6.77
Cl
O
O
Cl
Br
Ph
(R)-8
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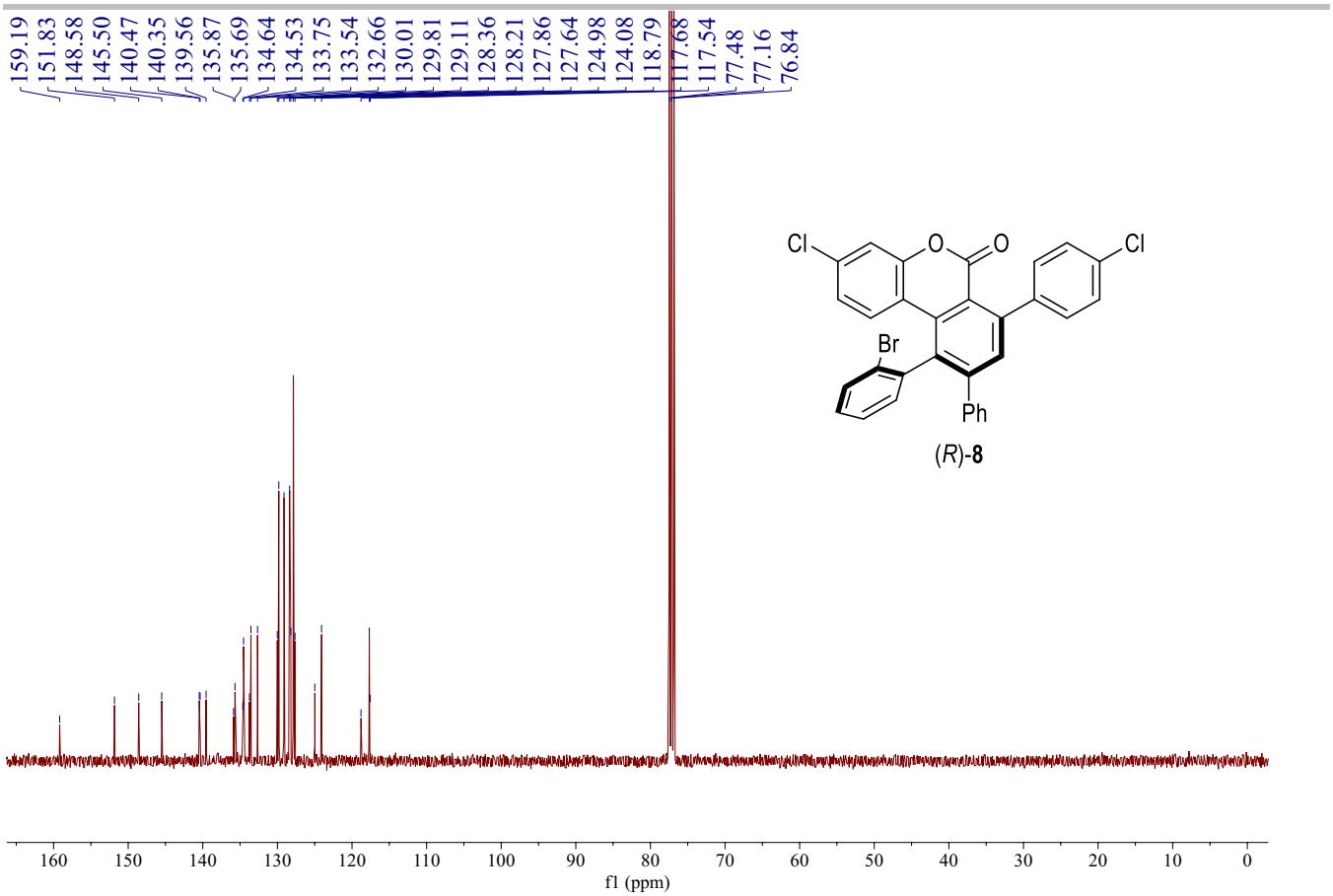
1.97
1.88
0.88
0.54
0.49
4.78
1.82
1.85
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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134.64
134.53
133.75
133.54
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129.81
129.11
128.36
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127.86
127.64
124.98
124.08
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77.48
77.16
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Cl
Br
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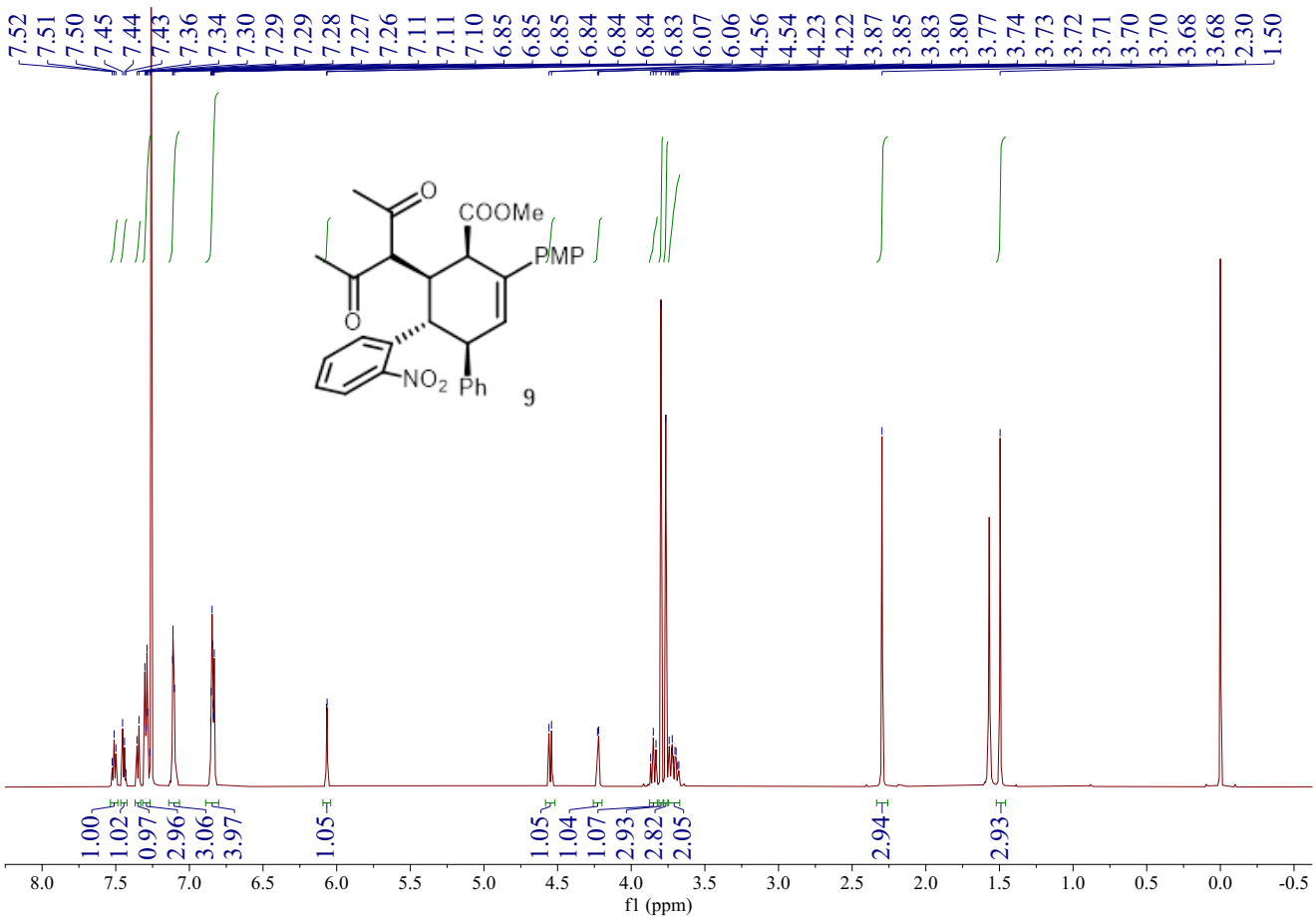
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6.84
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6.06
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3.73
3.72
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3.70
3.70
3.68
3.68
2.30
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O
COOMe
PMP
O
NO2
Ph
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1.02
0.97
2.96
3.06
3.97
1.05
1.05
1.04
1.07
2.93
2.82
2.05
2.94
2.93
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7.0
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6.0
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5.0
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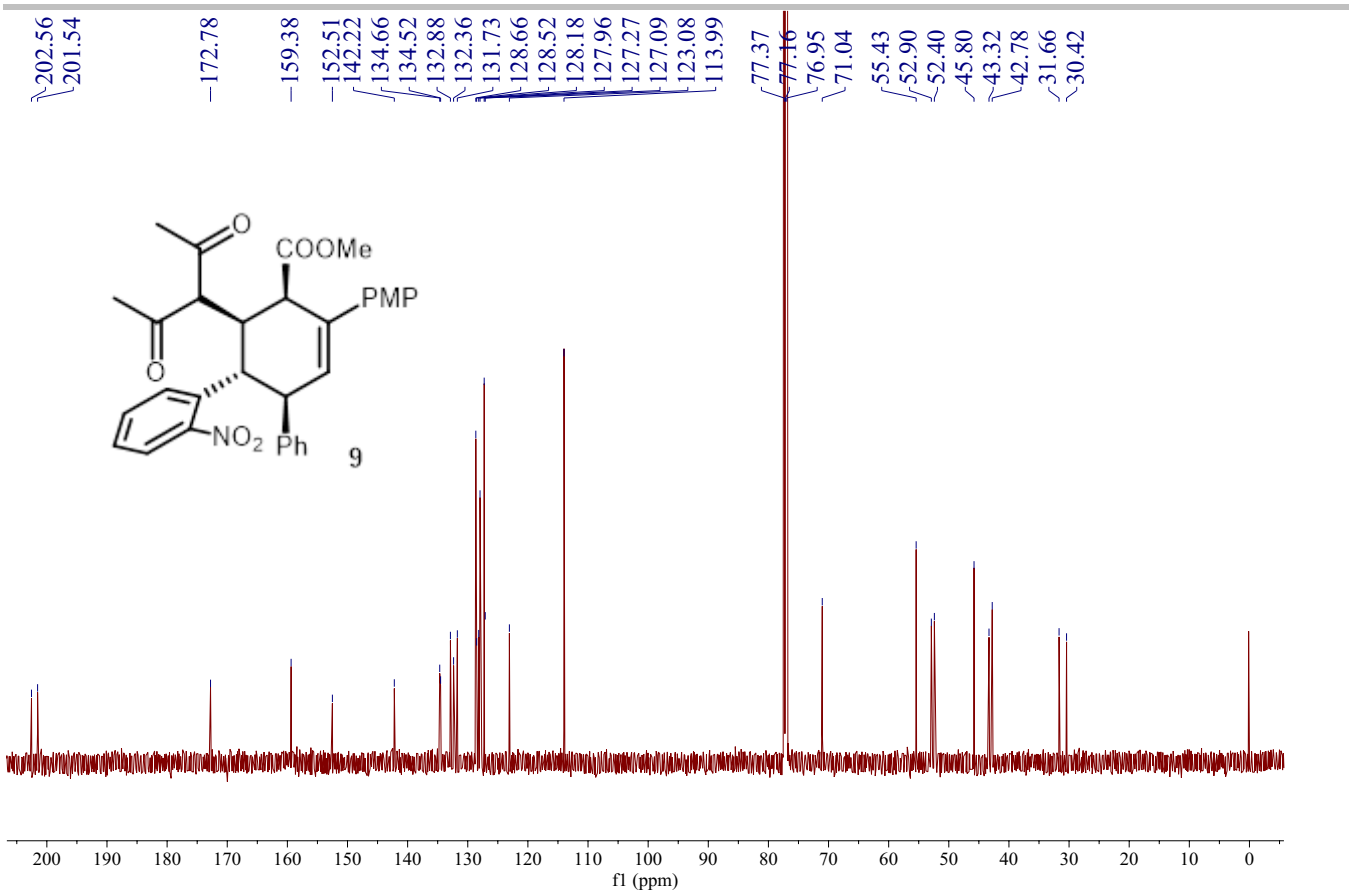
f1 (ppm)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127.96
127.27
127.09
123.08
113.99
77.37
77.16
76.95
71.04
55.43
52.90
52.40
45.80
43.32
42.78
31.66
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PMP
O
NO2
Ph
9
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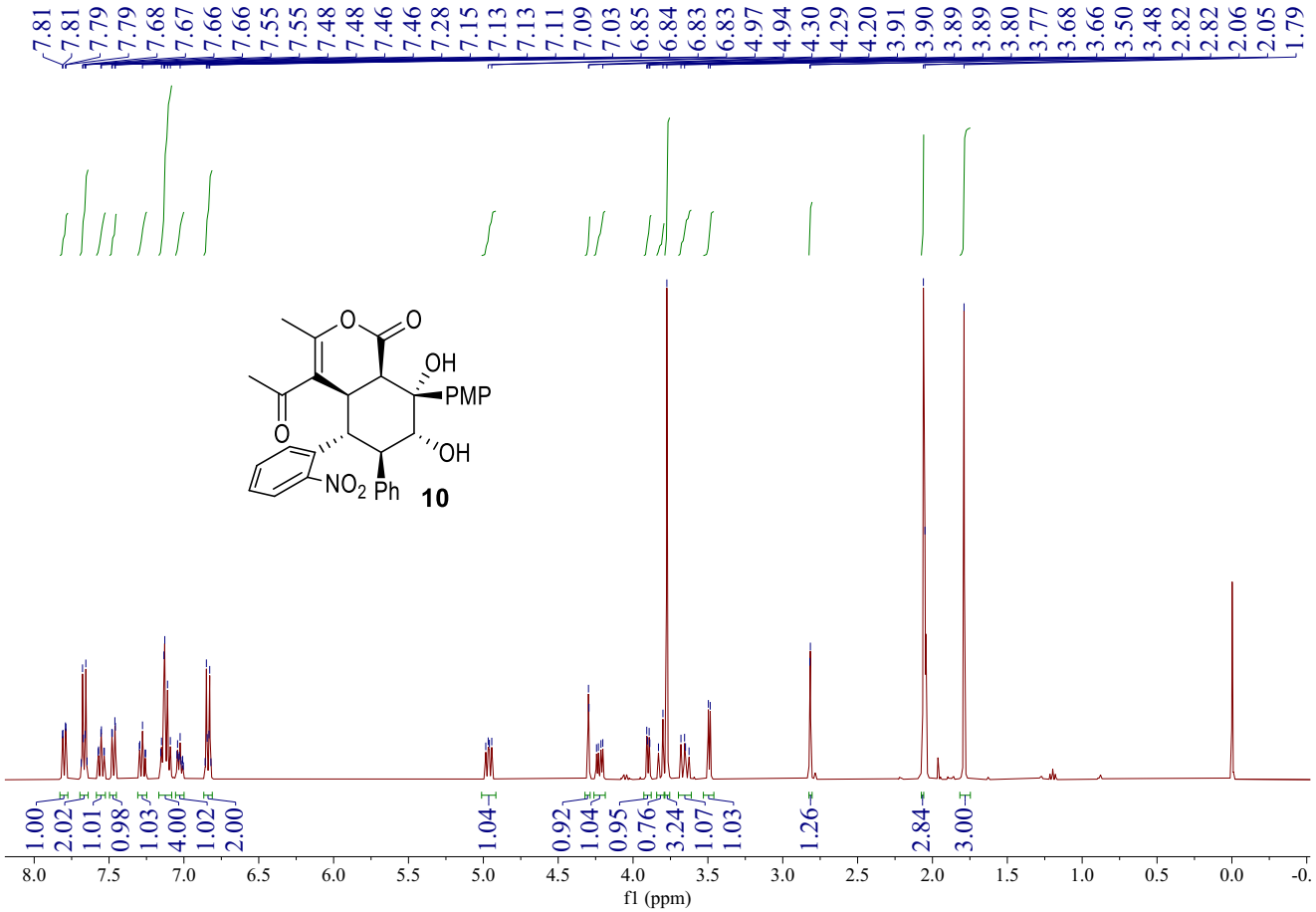
f1 (ppm)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7.13
7.11
7.09
7.03
6.85
6.84
6.83
6.83
4.97
4.94
4.30
4.29
4.20
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3.90
3.89
3.89
3.80
3.77
3.68
3.66
3.50
3.48
2.82
2.82
2.06
2.05
1.79
O
O
OH
PMP
O
OH
NO2
Ph
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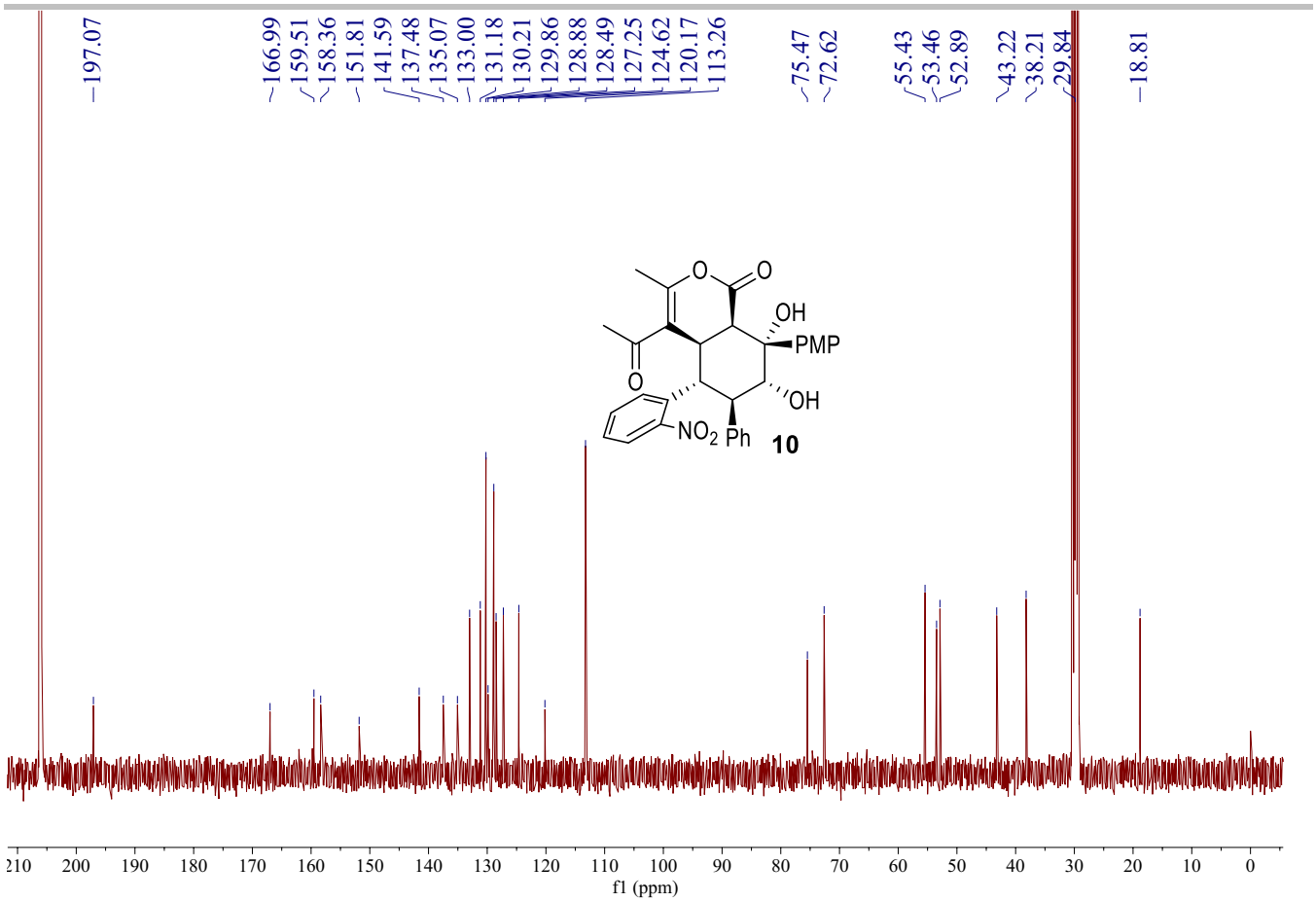
1.00
2.02
1.01
0.98
1.03
4.00
1.02
2.00
1.04
0.92
1.04
0.95
0.76
3.24
1.07
1.03
1.26
2.84
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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120.17
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53.46
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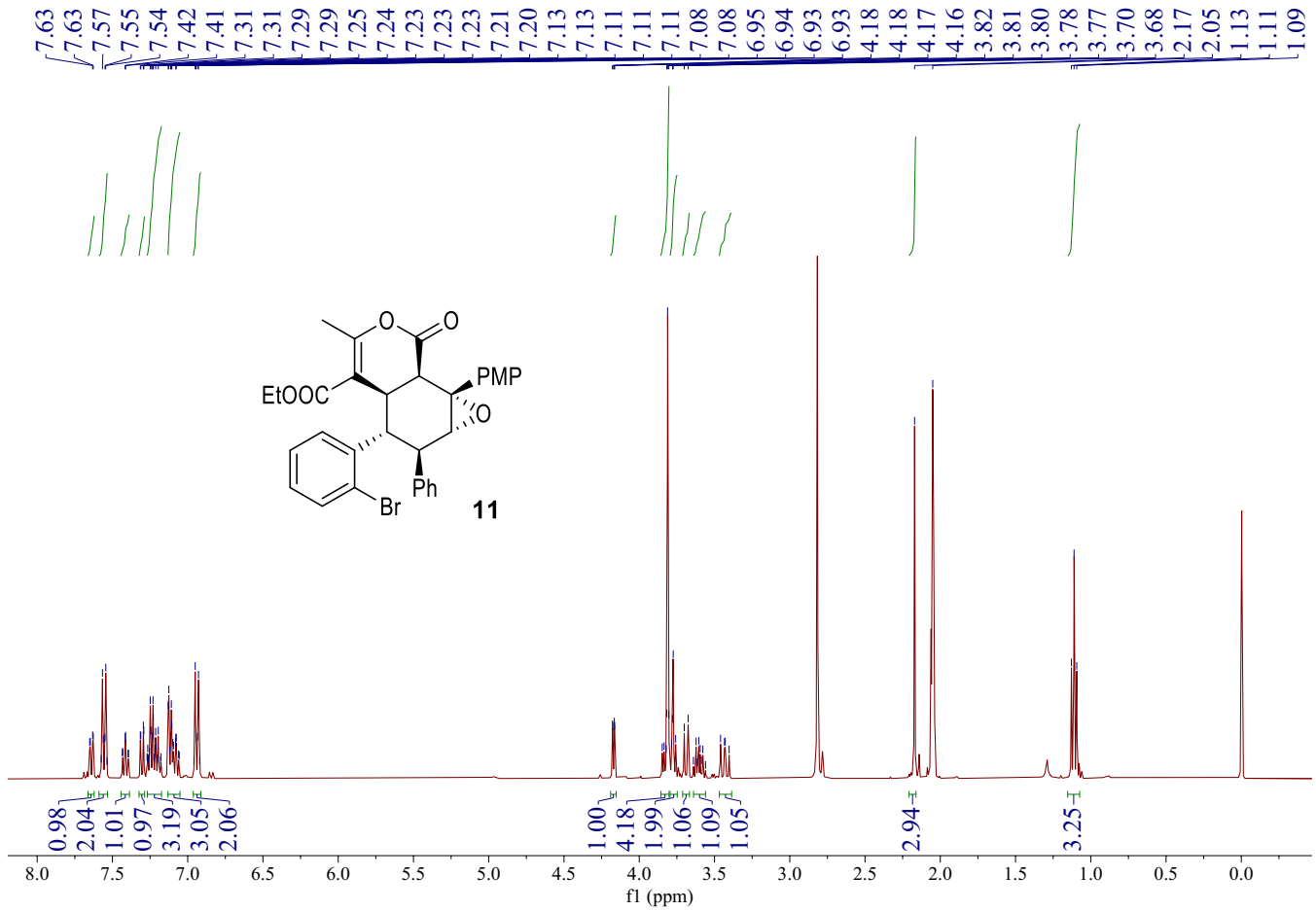
PMP
O
OH
NO2 Ph
10
f1 (ppm)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7.23
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7.13
7.11
7.11
7.11
7.08
7.08
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6.94
6.93
6.93
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4.18
4.17
4.16
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3.80
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3.77
3.70
3.68
2.17
2.05
1.13
1.11
1.09
O
O
EtOOC
PMP
O
Ph
Br
11
0.98
2.04
1.01
0.97
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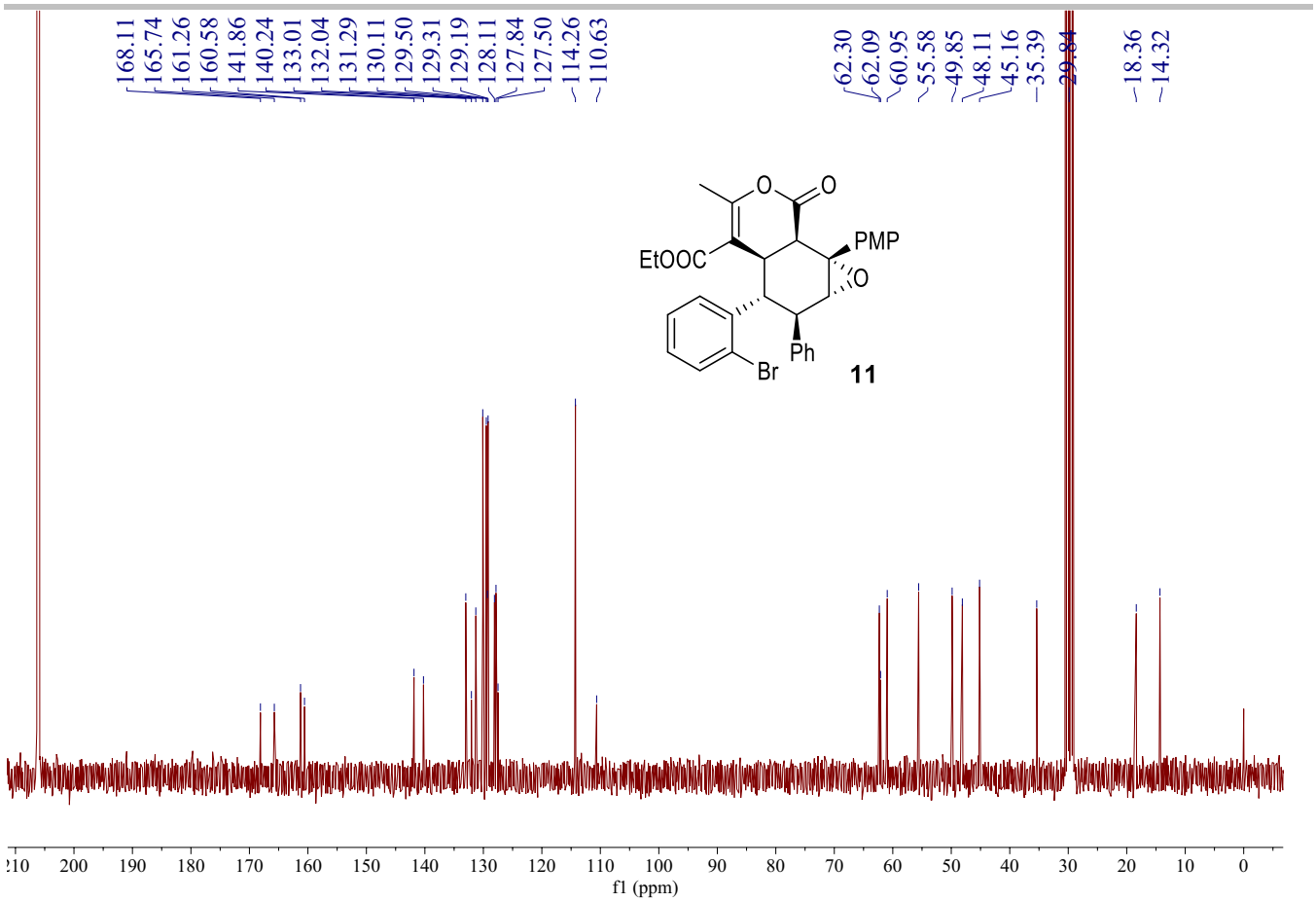
2.06
1.00
4.18
1.99
1.06
1.09
1.05
2.94
3.25
f1 (ppm)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127.50
114.26
110.63
62.30
62.09
60.95
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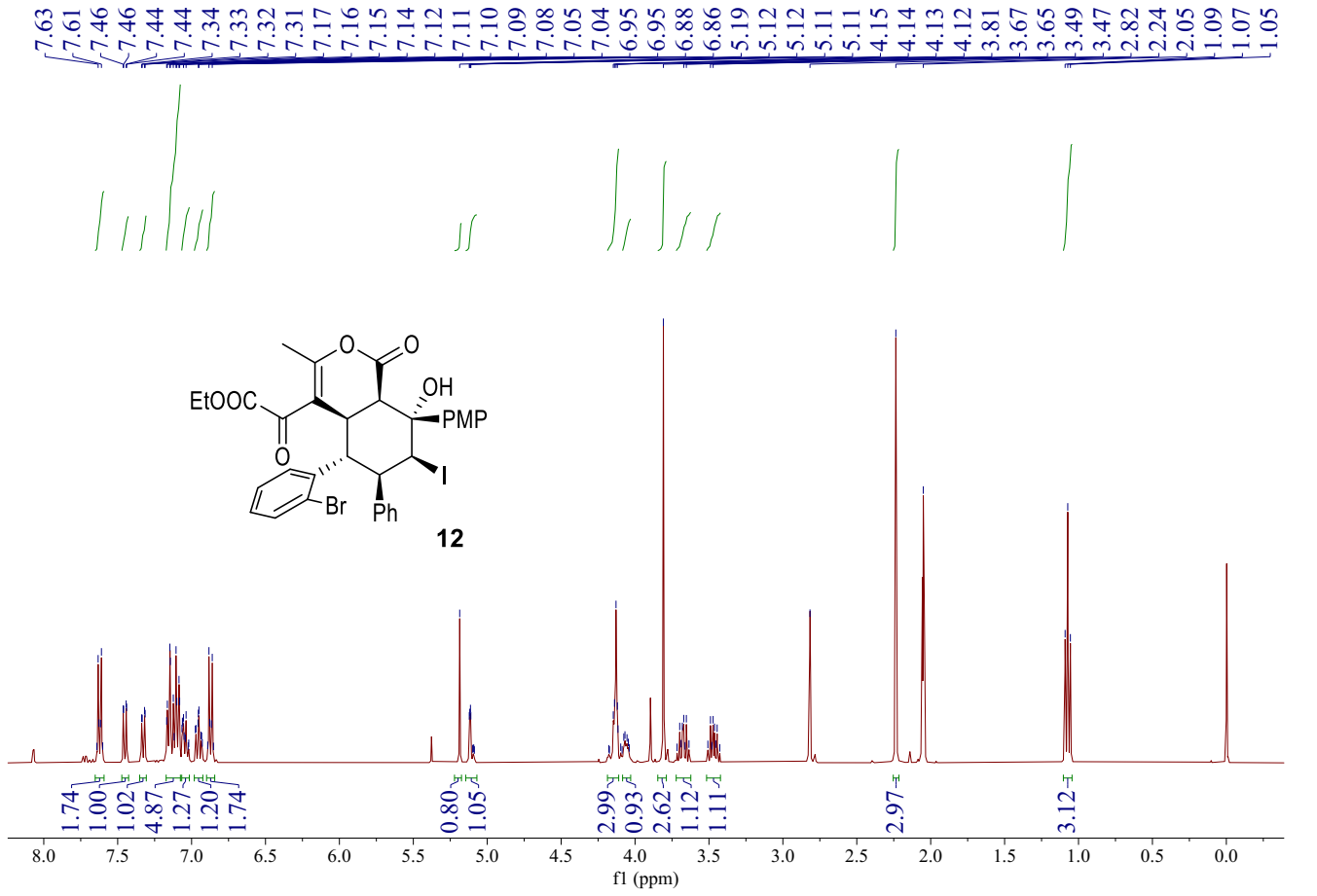
EtOOC
PMP
Br
Ph
11
f1 (ppm)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7.12
7.11
7.10
7.09
7.08
7.05
7.04
6.95
6.95
6.88
6.86
5.19
5.12
5.12
5.11
5.11
4.15
4.14
4.13
4.12
3.81
3.67
3.65
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3.47
2.82
2.24
2.05
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1.07
1.05
EtOOC
OH
PMP
I
Br
Ph
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1.02
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1.27
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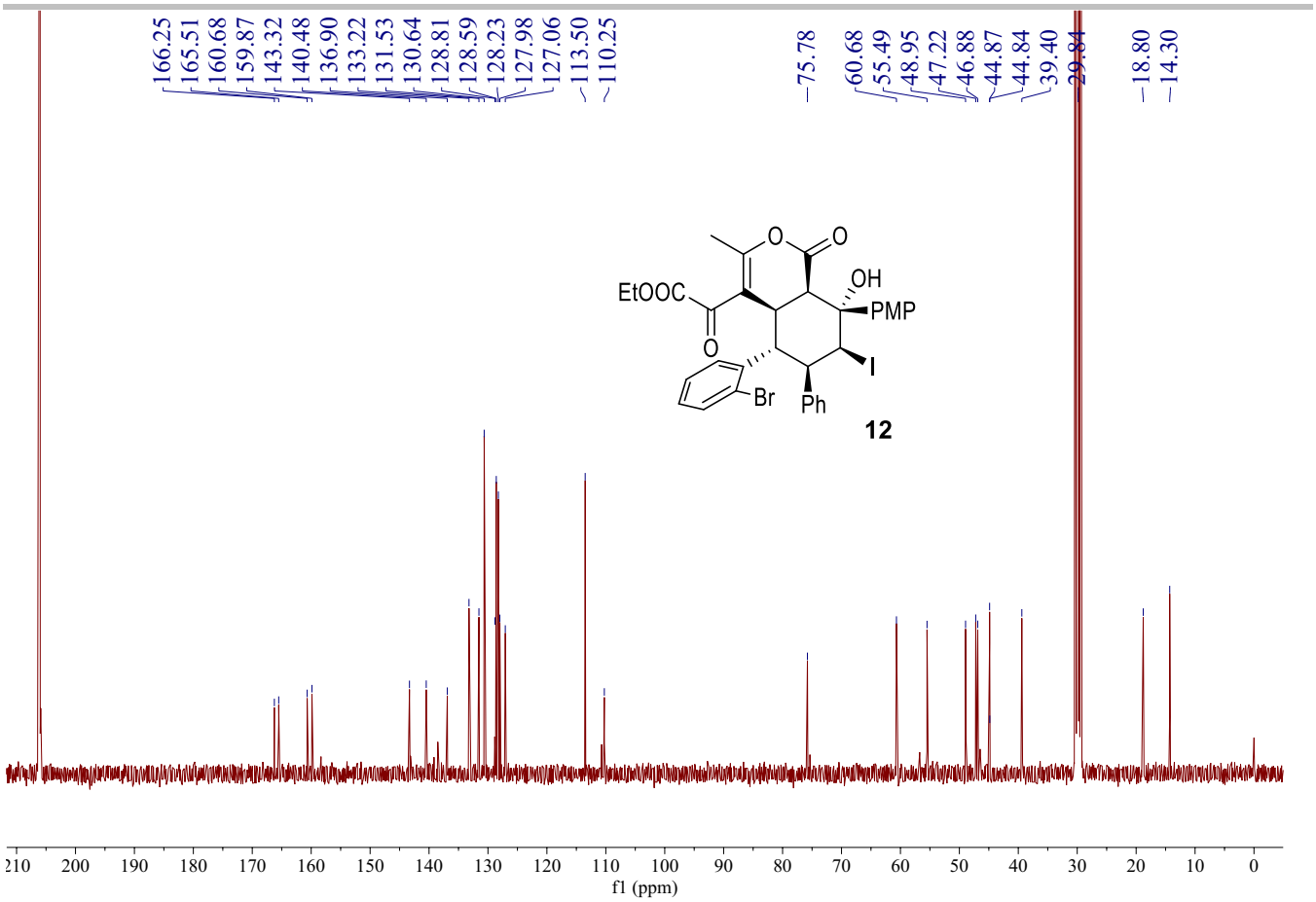
1.11
2.97
3.12
f1 (ppm)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128.23
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127.06
113.50
110.25
75.78
60.68
55.49
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47.22
46.88
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14.30
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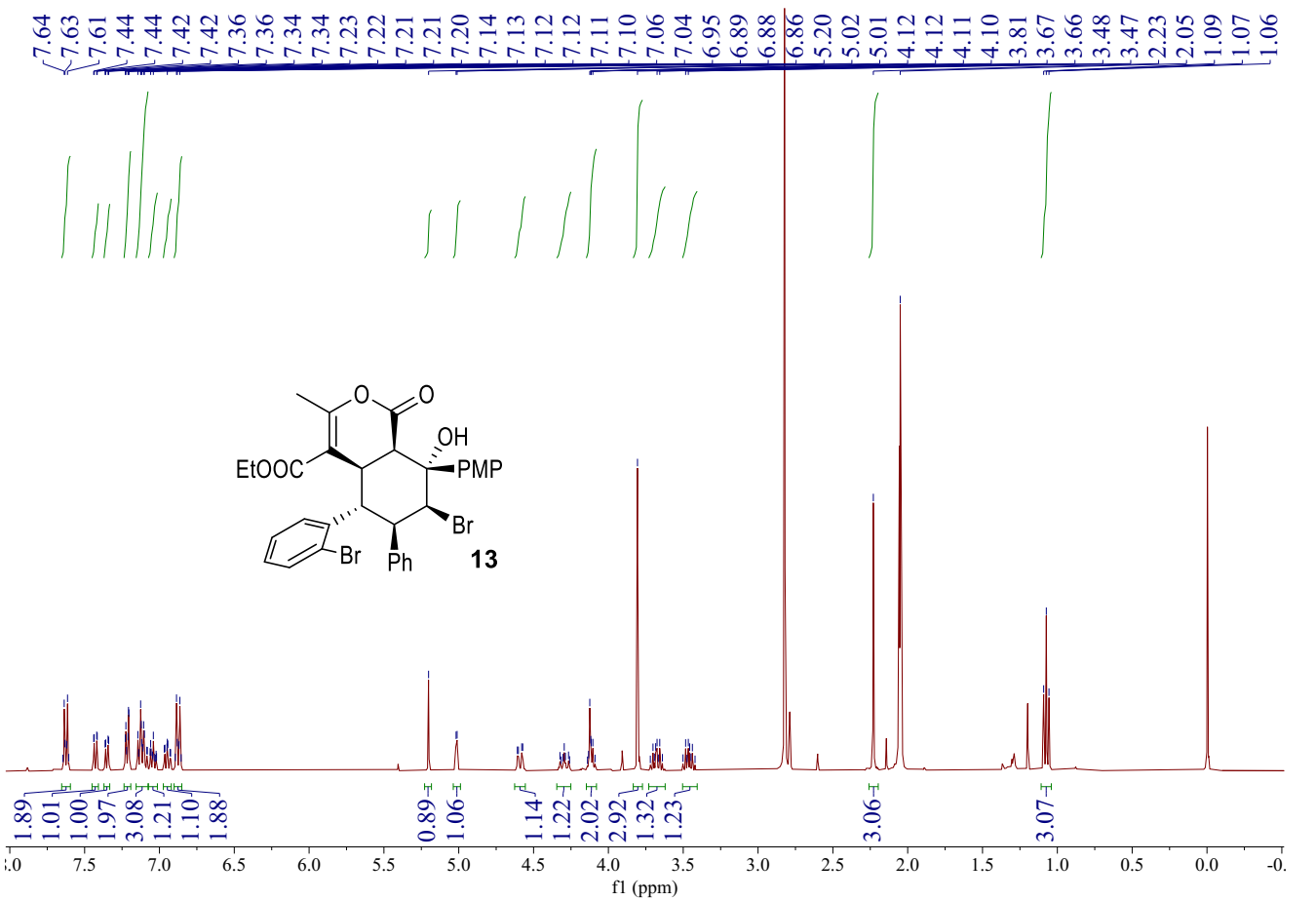
OH
PMP
I
Br
Ph
12
f1 (ppm)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7.14
7.13
7.12
7.12
7.11
7.10
7.06
7.04
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6.89
6.88
6.86
5.20
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4.11
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2.05
1.09
1.07
1.06
EtOOC
OH
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Br
Br
Ph
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1.21
1.10
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1.14
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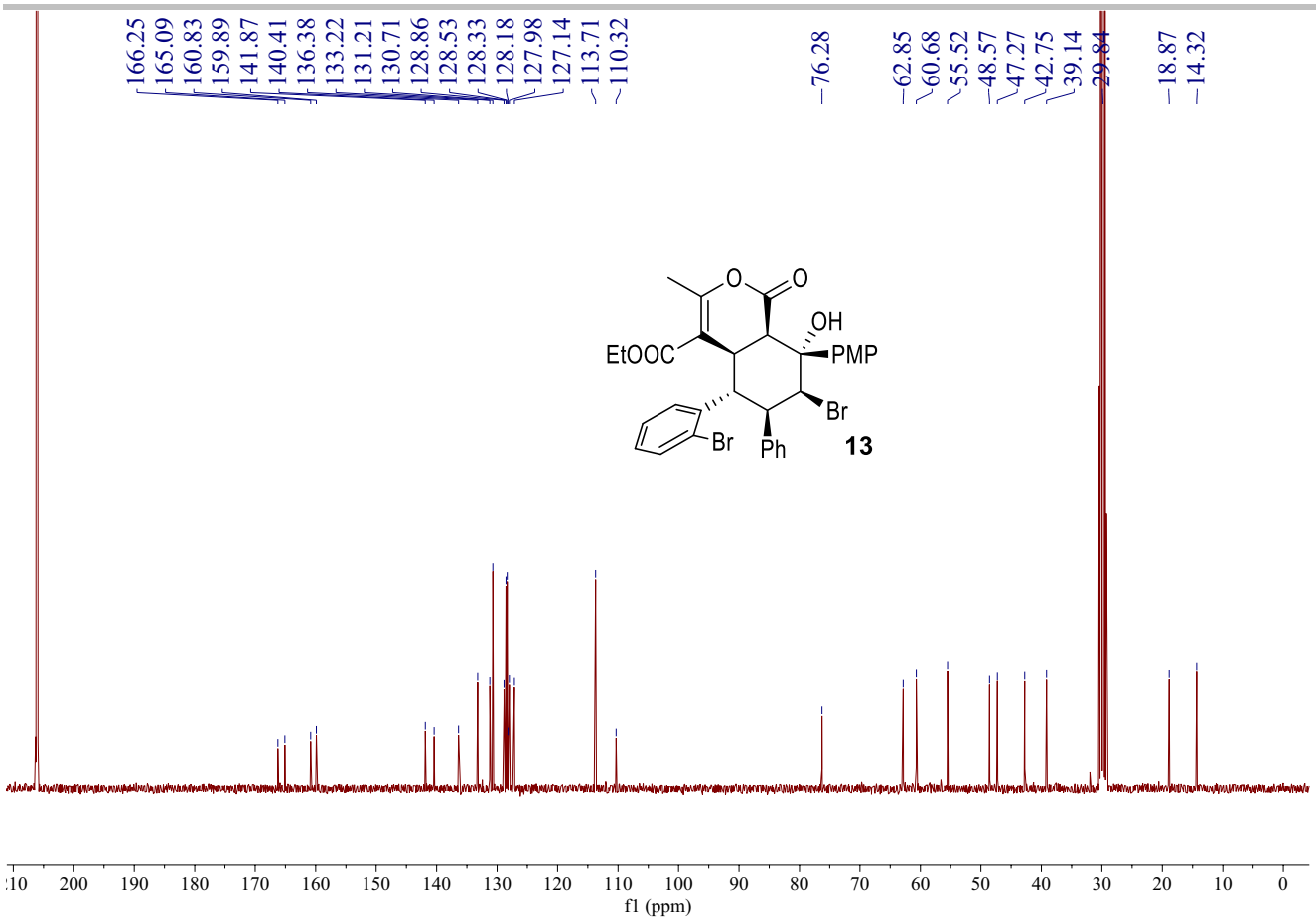
f1 (ppm)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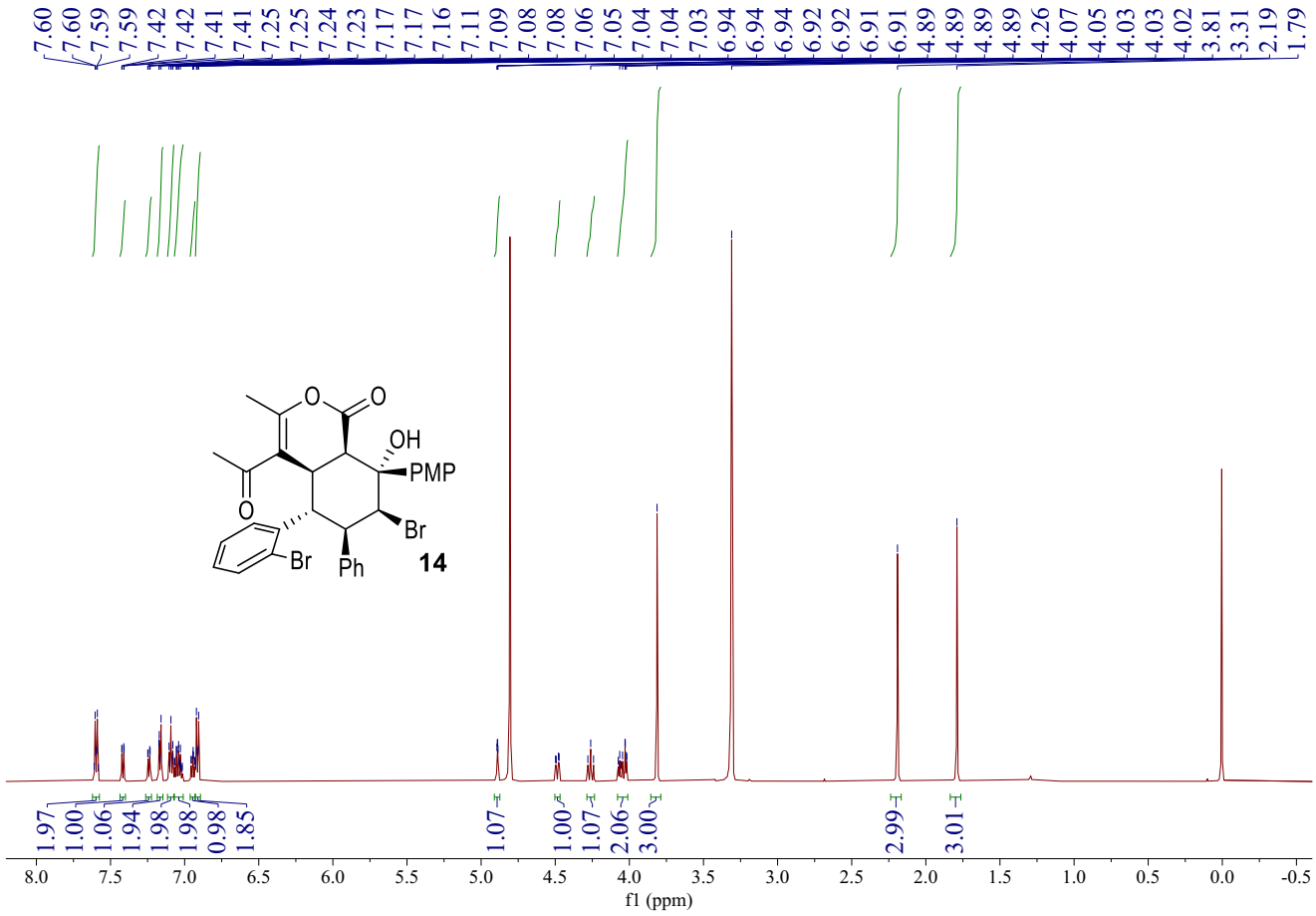
PMP
Br
Br
Ph
13
f1 (ppm)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7.08
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7.06
7.05
7.04
7.04
7.03
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2.19
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PMP
Br
Br
Ph
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1.94
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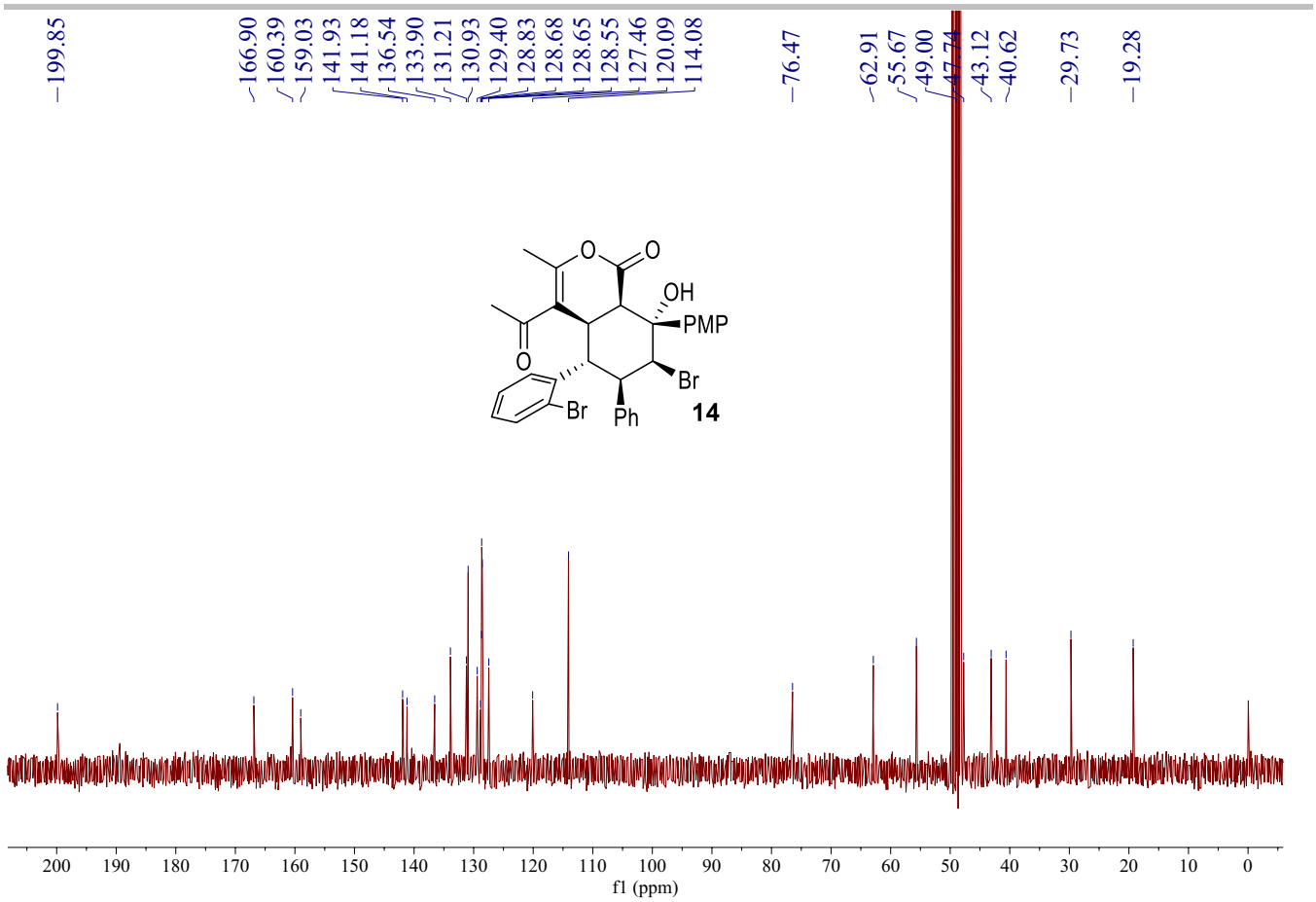
1.07
2.06
3.00
2.99
3.01
f1 (ppm)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76.47
62.91
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49.00
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43.12
40.62
29.73
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PMP
O
Br
Br
Ph
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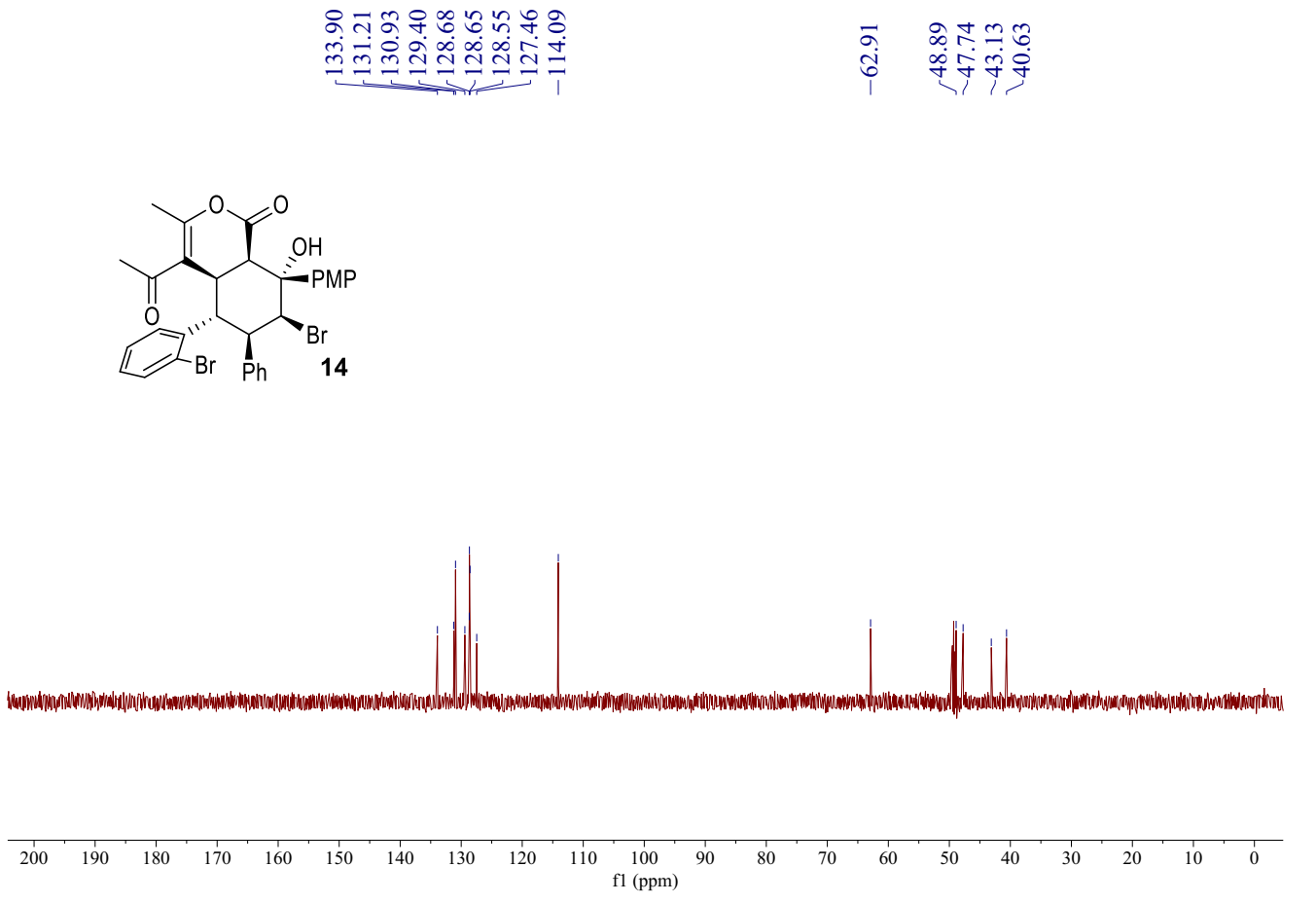
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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48.89
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43.13
40.63
O
O
OH
PMP
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Br
Ph
14
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f1 (ppm)

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