Supporting Information for

Controlled Oxygenation of Multiple Contiguous C–H Bonds via Electrophotocatalysis

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1.General Information

1.1 Analytic methods

^{1}H NMR, ^{13}C NMR data were obtained on AVANCE III Bruker 400 MHz or JEOL 500 MHz nuclear resonance spectrometers unless otherwise noted. ^{1}H NMR chemical shifts (in ppm) were referenced to $CHCl_3$ (δ = 7.26 ppm) in $CDCl_3$, DMSO (δ = 2.50 ppm) in DMSO-d_6, MeOH (δ = 3.31 ppm) in CD_3OD, or as an internal standard. The data of ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. ^{13}C-NMR spectra were obtained by the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.16 ppm), DMSO-d_6 (δ = 39.52 ppm), CD_3OD (49.00 ppm). Flash chromatography was performed using 300-400 mesh silica gel with the indicated eluent according to standard techniques. Thin-layer chromatography (TLC) was conducted with silica gel 60 F_{254} pre-coated plates (0.25 mm) and visualized with UV and phosphomolybdic acid unless otherwise noted. Analysis of crude reaction mixtures was performed on a SHIMADZU GC-MS-QP2010 SE system.

The mass spectral (MS) data were obtained on a Thermo Fisher Scientific ™ Exactive ™ Plus (EMR) Orbitrap LCMS.

1.2 Reagents

All commercially available compounds were purchased from Energy Chemical, Innochem, TCI, Adamas, Alfa-Aesar. All the solvents and all the other reagents were directly used from purchased without any further purification unless otherwise specified.

2. Experimental Section

2.1 Graphical depiction of the electrophotocatalytic oxygenation of multiple contiguous C–H bonds

Materials used for set-up:

Woods clamp lamp light with aluminum reflector (12 inch). Compact fluorescent light bulb (5000K daylight, 23W).

Anode set-up: A carbon cloth (CeTech WOS1002, 15 mm × 15 mm × 0.3 mm) connected with PT-3 electrode clamp purchased from Gaoss Union.

Cathode set-up: A platinum plate (99.99%, 15 mm × 15 mm × 0.3 mm) was connected with PT-1 electrode clamp purchased from Gaoss Union.

Fig. S1 Step 1: Materials used for undivided cell set-up.

Fig. S2 Step 2: Set-up for the undivided cell.

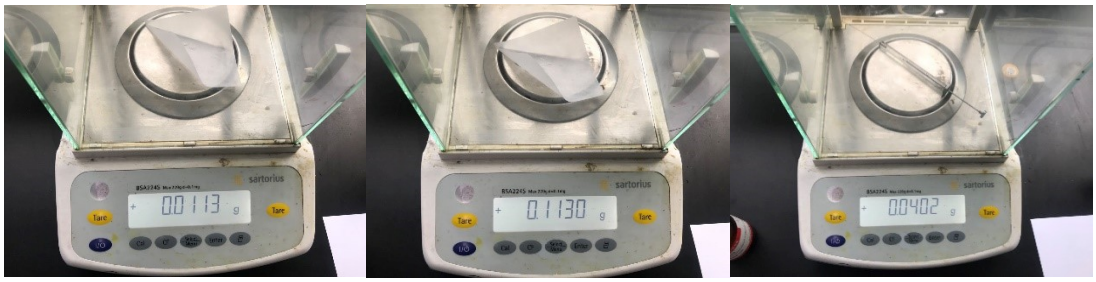


Fig. S3 Step 3: TAC$^+$ (11.3 mg, 0.024 mmol), Et_4NBF_4 (113.0 mg, 0.52 mmol, 0.1 M), *n*-butylbenzene (40.2 mg, 0.3 mmol), added to the cell.

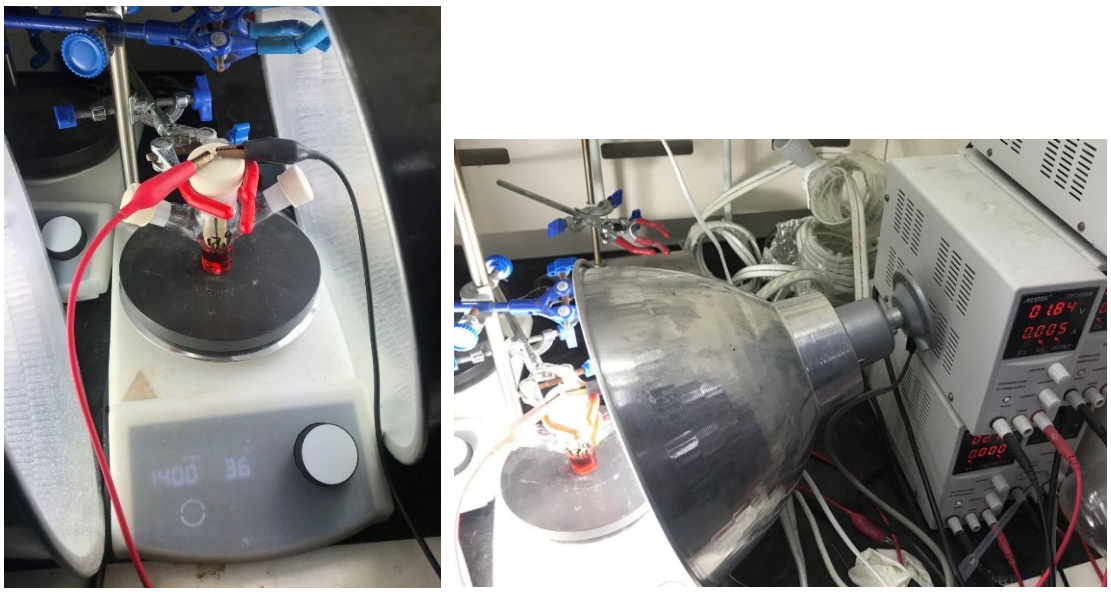


Fig. S4 Step 4: Electrolysis experiments were performed using MESTEK DC power supply. Set up the cell with constant current of 5 mA for 10 hours.

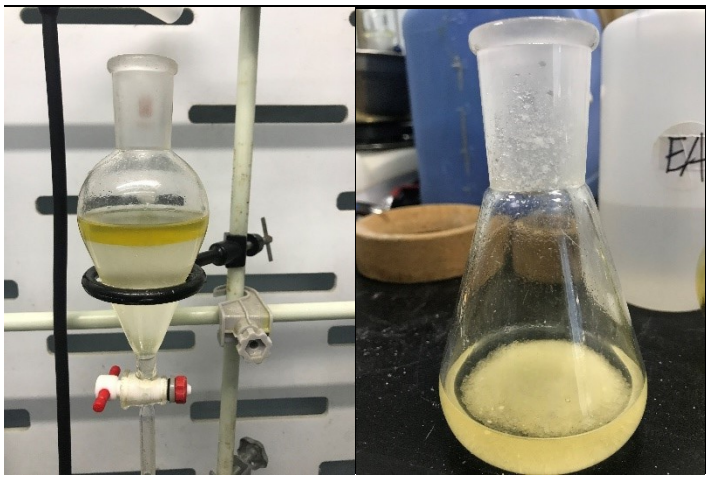


Fig. S5 Step 5: Left: dilute with EtOAc (20 mL) and washed with sat. Na_2CO_3 (aq). Right: dried over Na_2SO_4 and filtered.

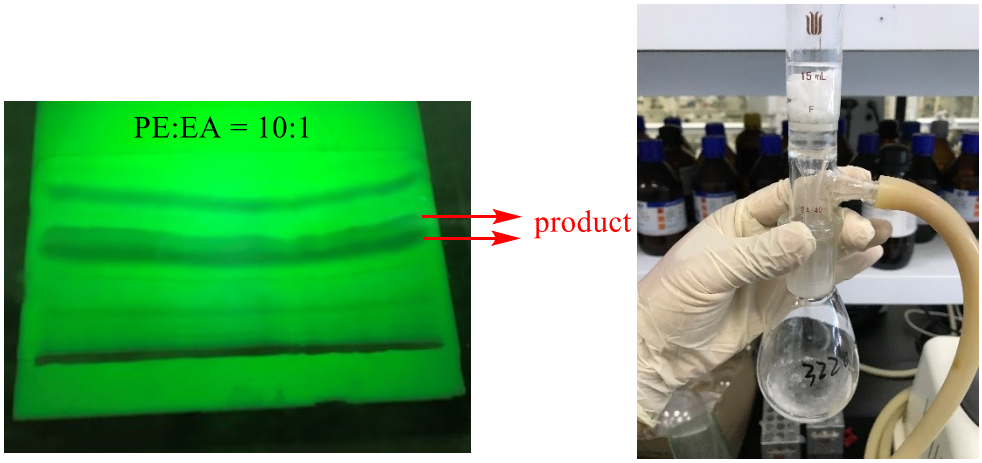
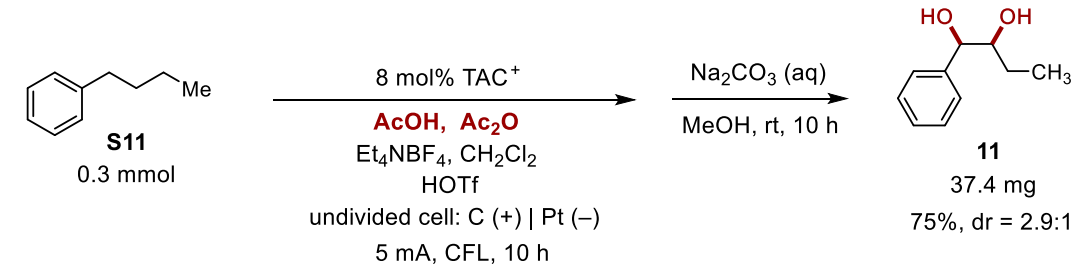


Fig. S6 Step 6: Purified by preparative thin-layer chromatography (PTLC) (eluent: petroleum ether:ethyl acetate = 10:1), note that both bands should be collected.

Fig. S7 Weight of product (55.5 mg, 74% yield). Pure product is a colorless oil.

Direct synthesis of vicinal diols after hydrolysis:

Diols were obtained followed by hydrolysis of crude mixture using saturated Na_2CO_3 (aq.) (10 mL) and MeOH (10 mL) at RT for 10 h.



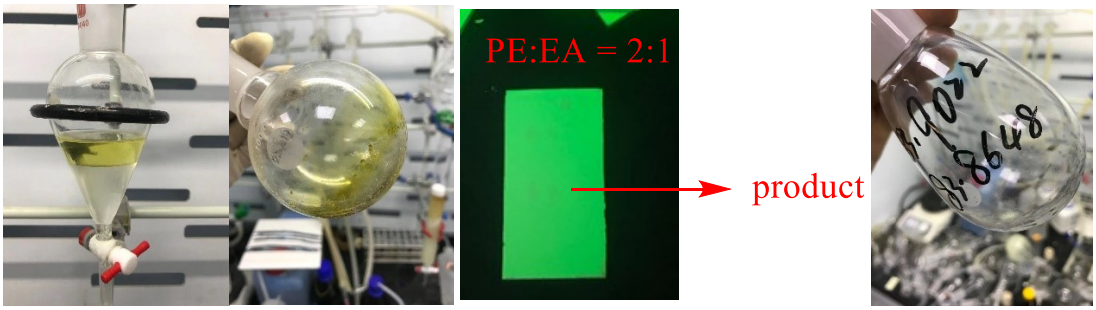
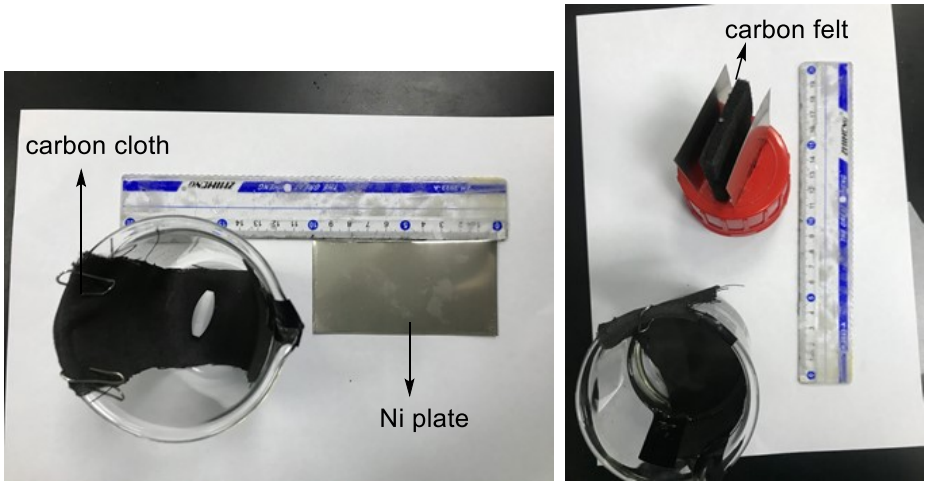


Fig. S8 Hydrolysis after *EPC* reaction with Na_2CO_3 (aq.)/MeOH

For gram scale reaction (e.g. 10 mmol for Celestolide):



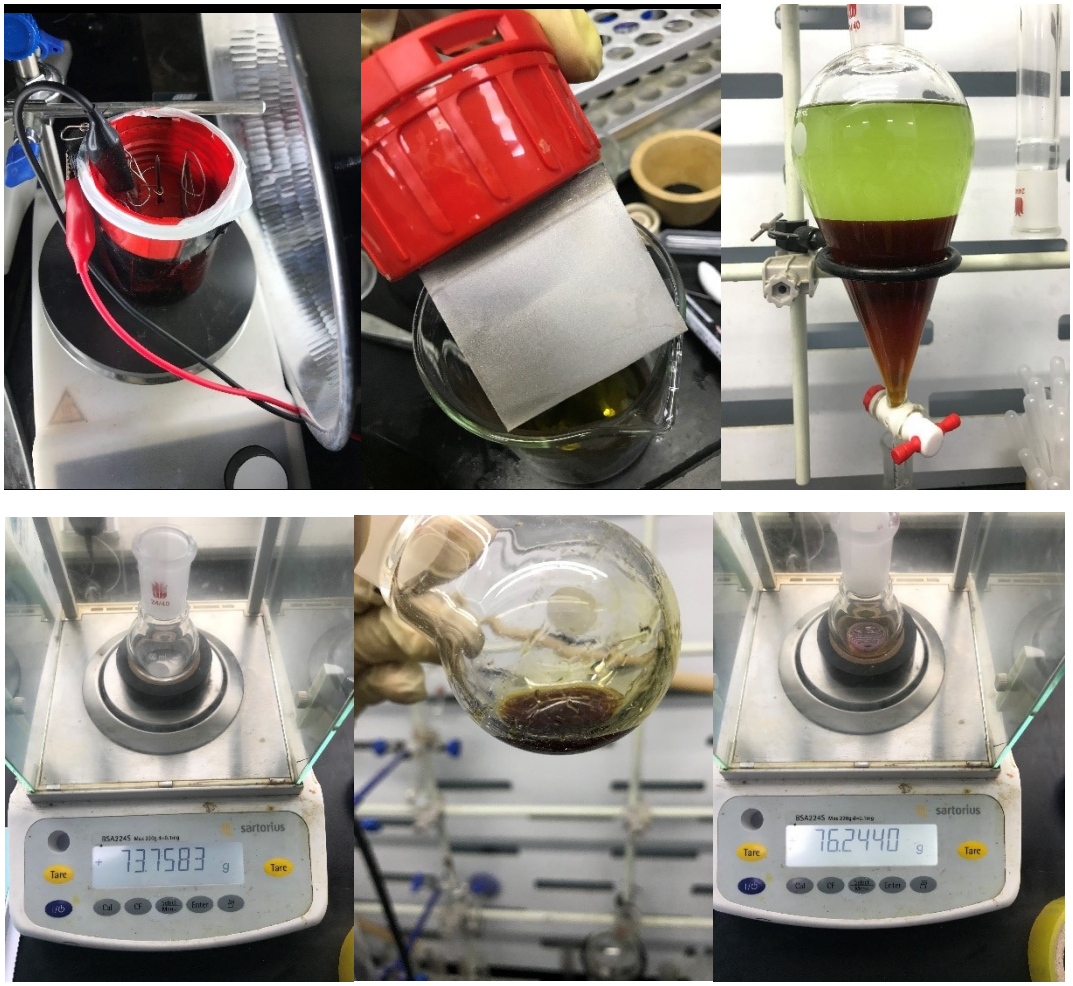


Fig. S9 Gram scale reaction set up

Experimental procedures

Typical procedure for dioxygenation products:

Condition A: For primary alkylbenzenes, an oven-dried undivided cell as described above was equipped with a stir bar. To the cell was added **TAC**$^+$ (11.3 mg, 0.024 mmol), Et_4NBF_4 (113.0 mg, 0.52 mmol, 0.1 M), HOAc (3.5 mL), Ac_2O (0.5 mL), *n*-butylbenzene **S11** (40.2 mg, 0.3 mmol), and DCM (1.0 mL). The mixture was stirred for 1 min, and then HOTf (200 μL) was carefully added. The cell was sealed using a rubber septum and parafilm and was backfilled with N_2 atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for the specified amount of time. The system was cooled by a fan throughout the duration of the reaction. After completion of the reaction as monitored by GC-MS (usually 10-15 h), the reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3×5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3×15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by preparative thin-layer chromatography (PTLC) (eluent: petroleum ether:ethyl acetate = 10:1) to afford 55.5 mg (74% yield) of **11'** as a colorless oil. In some cases, diols were obtained by subjecting the crude residue to a mixture of

saturated Na_2CO_3 (aq.) (10 mL) and MeOH (10 mL) at RT for 10 h.

Condition B: For secondary alkylbenzenes, an oven-dried undivided cell as described above was equipped with a stir bar. To the cell was added **TAC**$^+$ (11.3 mg, 0.024 mmol), Et_4NBF_4 (115 mg, 0.53 mmol, 0.1 M), HOAc (3.5 mL), Ac_2O (0.5 mL), cumene **S34** (36.0 mg, 0.3 mmol), DCM (1.0 mL), and TFA (300 μL). The cell was sealed using a rubber septum and parafilm and was backfilled with N_2 atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for 36 h. The system was cooled by a fan throughout the duration of the reaction. After completion of the reaction as monitored by GC-MS (usually 36 h), the reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3×5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3×15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by preparative thin-layer chromatography (PTLC) (eluent: petroleum ether:ethyl acetate = 10:1) to afford 51.0 mg (72% yield) of **34** as a colorless oil. In some cases, diols were obtained by subjecting the crude residue to a mixture of saturated Na_2CO_3 (aq.) (10 mL) and MeOH (10 mL) at RT for 10 h.

Typical procedure for trioxygenation products:

Condition A: An oven-dried undivided cell as described above was equipped with a stir bar. To the cell was added **TAC**$^+$ (11.3 mg, 0.024 mmol), Et_4NBF_4 (113.0 mg, 0.52 mmol, 0.1 M), HOAc (3.5 mL), Ac_2O (0.5 mL), cumene **S34** (40.2 mg, 0.3 mmol), and DCM (1.0 mL). The mixture was stirred for 1 min, and then HOTf (200 μL) was carefully added. The cell was sealed using a rubber septum and parafilm and was backfilled with N_2 atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for the specified amount of time. The system was cooled by a fan throughout the duration of the reaction. After completion of the reaction as monitored by GC-MS (usually 12-15 h), the reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3×5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3×15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by preparative thin-layer chromatography (PTLC) (eluent: petroleum ether:ethyl acetate = 5:1) to afford 53.8 mg (61% yield) of **47** as a colorless oil. In some case, triols were obtained followed by subjecting the crude residue to a mixture of saturated Na_2CO_3 (aq.) (10 mL) and MeOH (10 mL) at RT for 10 h.

Typical procedure for gram-scale reaction

Condition C: An oven-dried 250 mL baker as described above (see **Fig. S9**) was equipped with a stir bar. To the beaker was added Celestolide (2.44 g, 10 mmol), **TAC**$^+$ (235 mg, 0.5 mmol), Et_4NBF_4 (3.8 g, 0.1 M), HOAc (120 mL), Ac_2O (12 mL), and DCM (40 mL). The mixture was stirred for 1 min, and then HOTf (6 mL) was carefully added. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 50 mA for 48 h. The system was cooled by a fan throughout the duration of the reaction. The reaction mixture was poured into 300 mL water, the carbon cloth anode was washed with DCM (3×10 mL). The aqueous

layer was separated and extracted with DCM (3×100 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by flash chromatography (eluent: petroleum ether:ethyl acetate = 5:1) to afford 2.5 g (69% yield) of **65** as a yellow-brown oil.

2.2 Troubleshooting: Frequently Asked Questions

Question 1:

Are there any precautions that need to be taken for performing this reaction?

Answer: All reagents were used without any special handling. The reactions were performed under an atmosphere of N_2. Usually, the final E_{cell} was approximately 2.5-2.7 V. After the reaction, care should be taken when removing the septum in case of pressure build up from H_2 gas generation. *Carbon felt did not work well in this reaction*. Finally, the reaction was kept cool using a fan.

Question 2:

Is this reaction sensitive to water?

Answer: This reaction has been found to be not very sensitive to water. Usually, commercial acetic acid and acetic anhydride were used directly without any purification. Anhydrous electrolyte was used. However, we found that HOTf was very hygroscopic, and thus it is necessary to keep it dry. If the yield is low, using HOTf, Et_4NBF_4, acetic acid and acetic anhydride from a newly opened container might be helpful.

Question 3:

Is this reaction sensitive to air?

Answer: This reaction has been found to not be sensitive to air, and thus no rigorous degassing is required. We tested the model reaction without degassing, and the yield was only slightly decreased. However, leaving the reaction open to air results in solvent evaporation, and in some cases the air may be too wet, which may reduce the yield. Thus, we recommend performing this reaction under an inert atmosphere.

Question 4:

Is stirring crucial for this reaction?

Answer: Yes, the dioxygenation reaction is heterogeneous, and thus stirring is critical. The preferred stirring rate is from 1000 to 1400 rpm.

Question 5:

What are the common byproducts of this reaction?

Answer: When monitored by GC-MS, substrates, ketone, benzylic ester, or α-ketal ester products could be observed in small amount as byproducts. In cases where the yield of product is low, degradation of substrates to unidentified materials may be involved.

Question 6:

How do I monitor the reaction?

Answer: In general, 12-15 h is enough for high conversion (>90%) for dioxygenation of primary

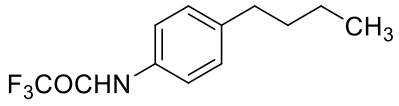
benzenes on a 0.3 mmol scale. Reaction monitoring can be done by GC-MS or by TLC analysis with UV visualization (254 nm) of disappearance of the starting material for most substrates. *Note that the complete disappearance of substrates does not mean that the reaction has necessarily finished. In most case the full conversion of the substates into a monobenzylic ester intermediate was completed quickly (4-6 h); however, at that time the dioxygenation product is typically present in significantly lower quantities. Stopping the reaction when most of the monobenzylic ester intermediate has disappeared (as determined by GC-MS) is usually optimal.*

Question 7:

How can the electrodes be cleaned after the reaction?

Answer: The carbon cloth anode should be replaced for each reaction. The Pt cathode was washed with water, immersed in concentrated sulfuric acid for 1 h (particularly if it has turned black), washed again with deionized water, and dried in the oven.

2.3 Preparation and characterization of newly reported starting materials



S16

***N*-(4-butylphenyl)-2,2,2-trifluoroacetamide:** To a 100 mL round-bottom flask charged with DCM (50 mL) and cooled to 0 °C was added 4-butylaniline (1.49 g, 10.0 mmol, 1.0 equiv.) and Et_3N (2.02 g, 20 mmol, 2.0 equiv.). Trifluoroacetic anhydride (2.52 g, 12 mmol, 1.2 equiv.) was then added dropwise. The mixture was stirred at room temperature for 4 h, partitioned between water (50 mL) and CH_2Cl_2 (50 mL), and then quenched with a saturated solution of sodium carbonate (10 mL). The organic layer was isolated, and the aqueous layer was extracted with CH_2Cl_2 (3x50 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated via rotary evaporation. The crude material was purified by flash chromatography (10% EtOAc/Hex) to afford the product **S16** as a light yellow solid (2.20 g, 9.0 mmol, 90% yield).

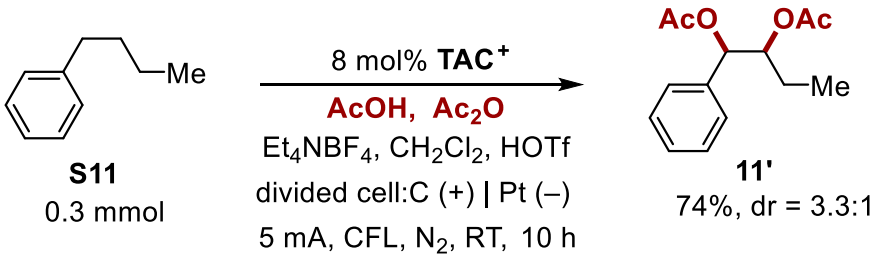
^{1}H NMR ($CDCl_3$, 500 MHz): 7.97 (brs, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 2.60 (t, J = 8.0 Hz, 2H), 1.61-1.55 (m, 2H), 1.36-1.32 (m, 2H), 0.92 (t, J = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 155.0 (q, J = 36.8 Hz), 141.5, 132.8, 129.3, 120.7, 115.9 (q, J = 286.8 Hz), 35.2, 33.6, 22.4, 14.0.

HRMS: calc. for $C_{12}H_{14}F_3NNaO^+$ $(M+Na)^+$, 268.0920, found, 268.0923.

2.4 Optimization of the reaction conditions

Table S1. Optimization of reaction conditions with *n*-butylbenzene.[a]



S11
0.3 mmol

11'
74%, dr = 3.3:1

conditions	yield of **11'**
none	78% (74%)[b]
TFA instead of HOTf	0% (87%)[c]
$MeSO_3H$ instead of HOTf	11% (73%)[c]
without HOTf	0%
without Ac_2O	49%
$LiClO_4$ instead of Et_4NBF_4	54%
$TBAPF_6$ instead of Et_4NBF_4	58%
C felt as anode	33%
C cloth as cathode	46%
Fe as cathode	<5%
Ni as cathode	44%
Ni as cathode for 18 h	66%
under air	68%
without TAC	33%
without light	38%
without electricity	0%

[a]Reaction conditions: **S11** (0.3 mmol), TAC^+ (0.024 mmol), Et_4NBF_4 (0.1 M), (HOAc:Ac_2O:DCM:HOTf = 3.5 mL:0.5 mL:1.0 mL:0.2 mL), carbon cloth anode, Pt cathode, under N_2, at RT, in an undivided cell with constant current of 5 mA for 10 h. Yields determined on NMR yield using CH_2Br_2 as internal standard. [b]Isolated yield. [c] Yield of benzylic monoester. TFA = trifluoroacetic acid, HOTf = trifluoromethanesulfonic acid.

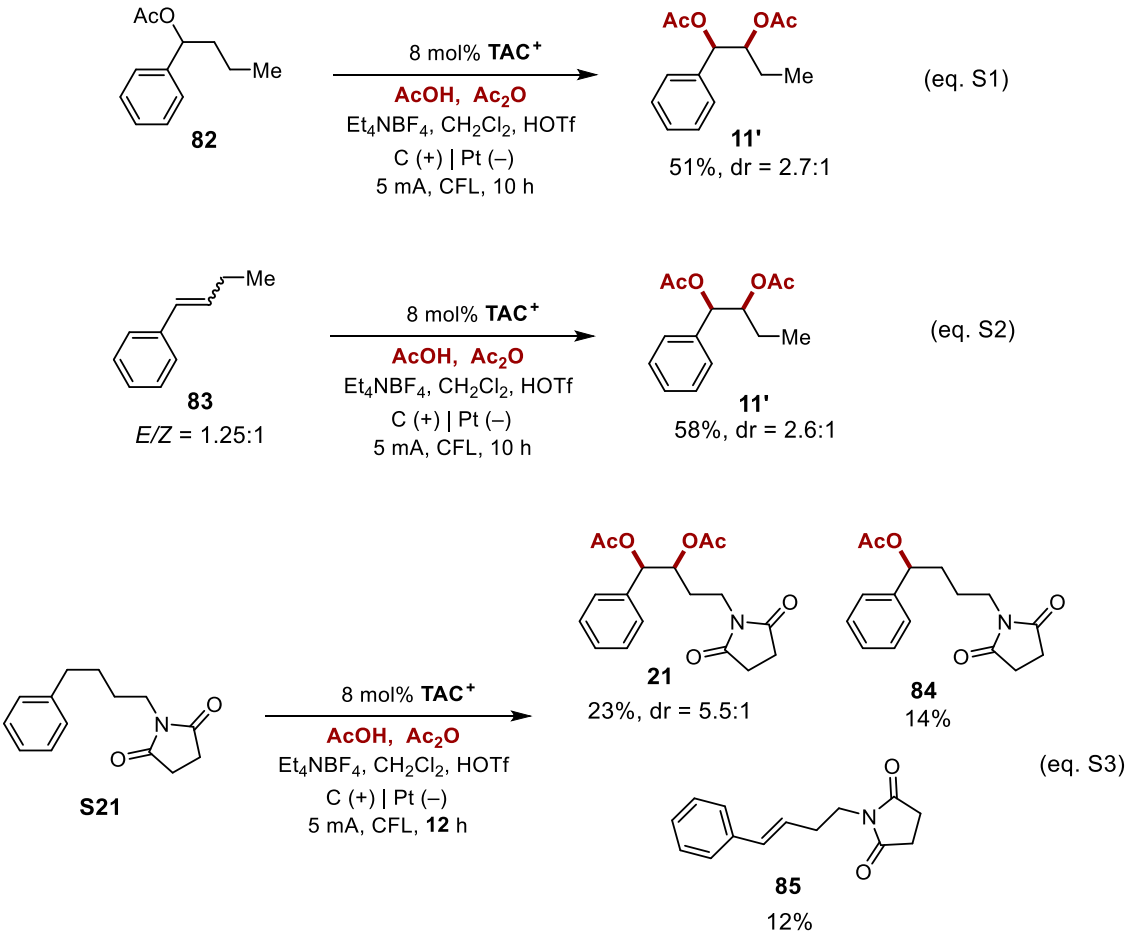
Typical reaction procedure as **Condition A**: an oven-dried undivided cell as described above was equipped with a stir bar. To the cell was added **TAC**$^+$ (11.3 mg, 0.024 mmol), Et_4NBF_4 (113.0 mg, 0.52 mmol, 0.1 M), HOAc (3.5 mL), Ac_2O (0.5 mL), *n*-butylbenzene **S11** (40.2 mg, 0.3 mmol), and DCM (1.0 mL). The mixture

was stirred for 1 min, and then HOTf (200 μL) was carefully added. The cell was sealed using a rubber septum and parafilm and was backfilled with N_2 atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for 10 h. The system was cooled by a fan throughout the duration of the reaction. The reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3×5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3×15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was mixed with CH_2Br_2 (52.2 mg, 21.0 μL) as an internal standard and $CDCl_3$ (1 mL) for the ^1H NMR experiment.

2.5 Mechanistic studies

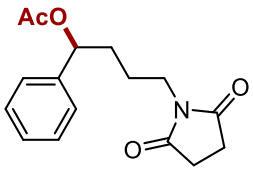
2.5.1 Verification of possible intermediates for dioxygenation of primary alkylbenene.

Some possible intermediates were tested under the standard conditions.



Eq. S3: An oven-dried H-type cell was prepared as described above and equipped with a stir bar. To the anodic chamber were added 1-(4-phenylbutyl)pyrrolidine-2,5-dione (69.3 mg, 0.3 mmol), **TAC**$^+$ (11.3 mg, 0.024 mmol), Et_4NBF_4 (113.0 mg, 0.52 mmol, 0.1 M), HOAc (3.5 mL), Ac_2O (0.5 mL), DCM (1.0 mL), and HOTf (200 μL). The cell was sealed using a rubber septum and parafilm and was backfilled with N_2

atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for 12 h. The system was cooled by a fan throughout the duration of the reaction. Then the reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3×5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3×10 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by PTLC (eluent: petroleum ether:ethyl acetate = 3:1) to afford 23.9 mg (23% yield) of **21** and 12.1 mg (14% yield) of 4-(2,5-dioxopyrrolidin-1-yl)-1-phenylbutyl acetate **84** and 8.2 mg (12% yield) of (*E*)-1-(4-phenylbut-3-en-1-yl)pyrrolidine-2,5-dione **85**.



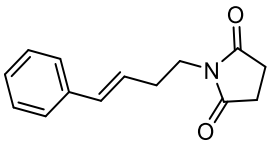
84

84: yellow oil;

^{1}H NMR ($CDCl_3$, 500 MHz): 7.35-7.28 (m, 5H), 5.73 (dd, *J* = 8.0 Hz, *J* = 6.0 Hz, 1H), 4.56-4.47 (m, 2H), 2.68 (s, 4H), 2.07 (s, 3H), 1.94-1.86 (m, 1H), 1.80-1.73 (m, 1H), 1.64-1.51 (m, 2H).

^{13}C NMR ($CDCl_3$, 500 MHz): 177.4, 170.5, 140.3, 128.6, 128.2, 126.5, 75.4, 38.5, 33.7, 28.3, 23.9, 21.4.

HRMS: calc. for $C_{16}H_{20}NO_4^+$ $(M+H)^+$, 290.1387, found, 290.1390.



85

85: white solid;

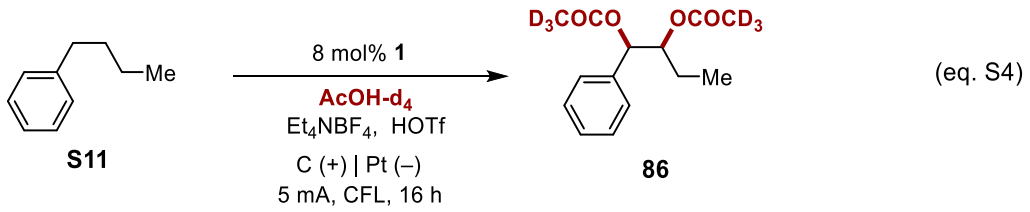
^{1}H NMR ($CDCl_3$, 500 MHz): 7.33-7.19 (m, 5H), 6.40 (d, *J* = 15.5 Hz, 1H), 6.13-6.07 (m, 1H), 3.69-3.66 (m, 2H), 2.67 (s, 4H), 2.52-2.49 (m, 2H).

^{13}C NMR ($CDCl_3$, 500 MHz): 177.4, 137.3, 132.7, 128.7, 127.5, 126.3, 126.1, 38.4, 31.4, 28.2.

HRMS: calc. for $C_{14}H_{16}NO_2^+$ $(M+H)^+$, 230.1176, found, 230.1176.

2.5.2 In situ NMR analysis for dioxygenation of primary alkylbenene

This reaction proceeded without Ac_2O, albeit in lower yield (49%, see Table S1). In situ NMR analysis was performed using HOAc-d_4 as solvent.



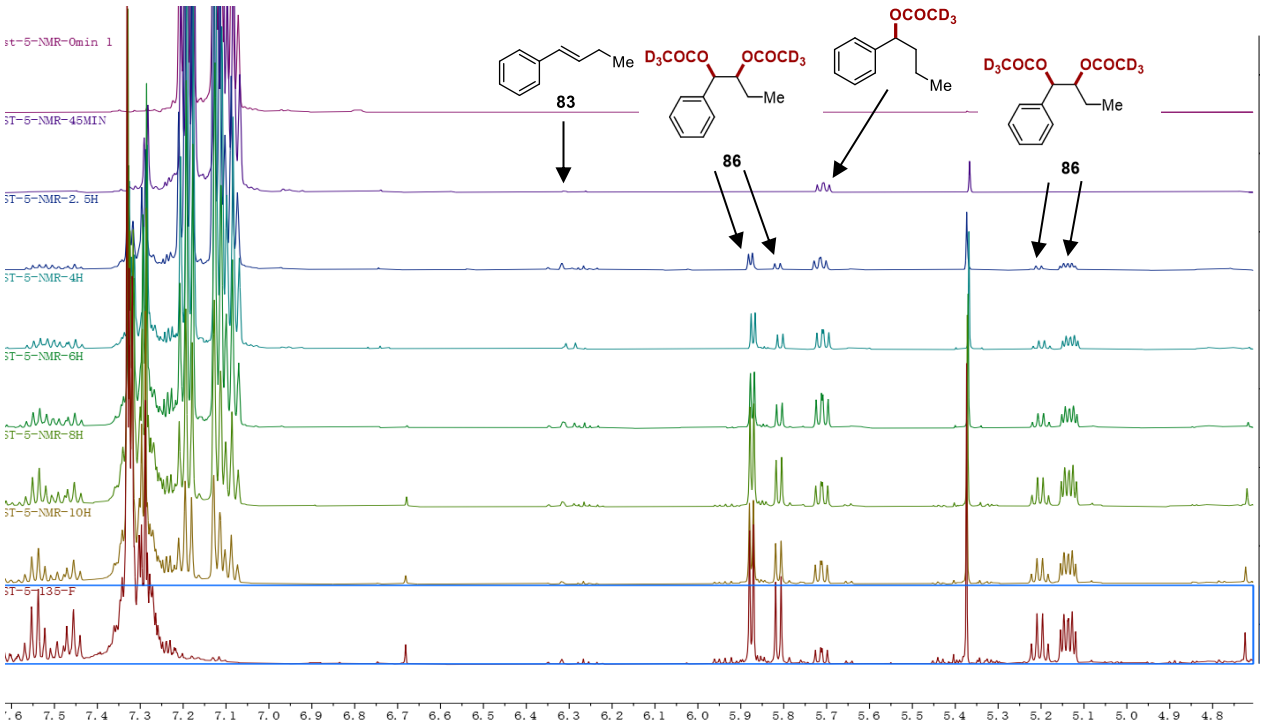


Fig. S10 In situ NMR analysis for eq. S4

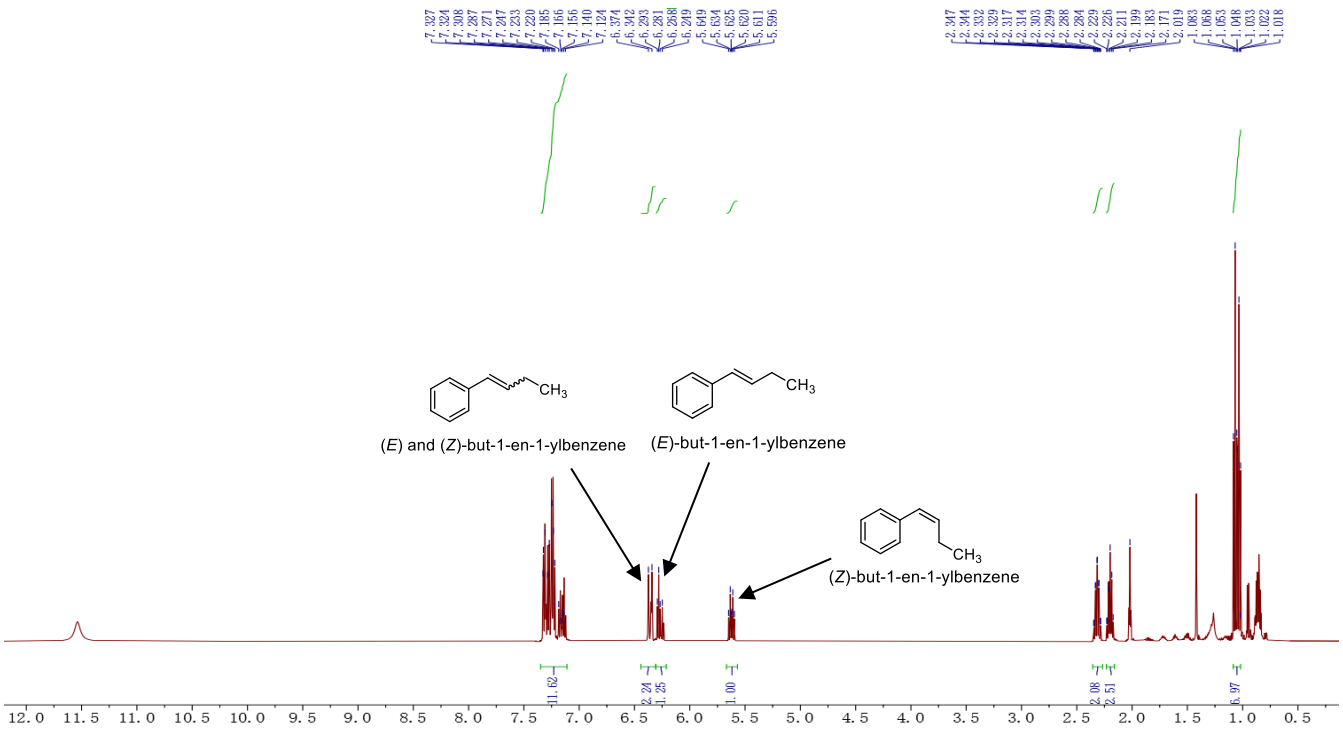


Fig. S11 ^{1}H NMR of but-1-en-1-ylbenzene **83** (*E*:*Z*=1.25:1, mixture) in HOAc-d$_4$

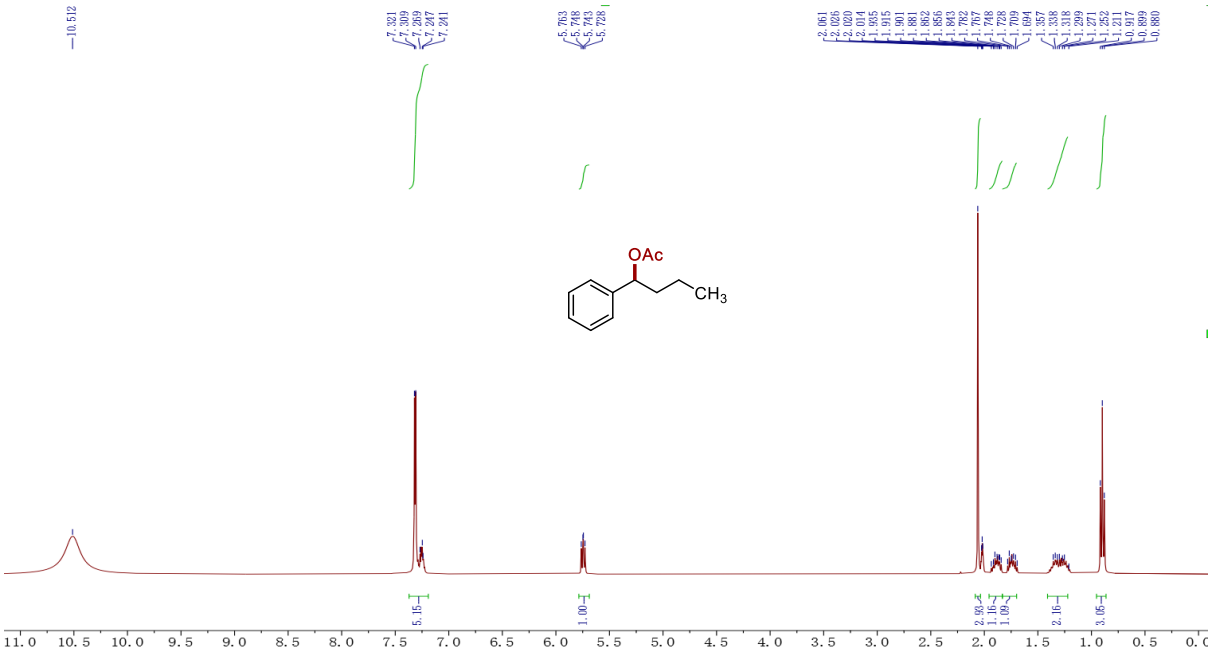


Fig. S12 ^{1}H NMR of 1-phenylbutyl acetate **82** in HOAc-d$_4$ (400 MHz)

*In addition, (E)-but-1-en-1-ylbenzene **83** and 1-phenylbutyl acetate **82** were detected under the standard conditions by GC-MS, albeit in only trace amounts. See "**2.5.4 Side products studies**"*

2.5.3 Mechanistic studies for dioxygenation and trioxygenation of secondary alkylbenene.

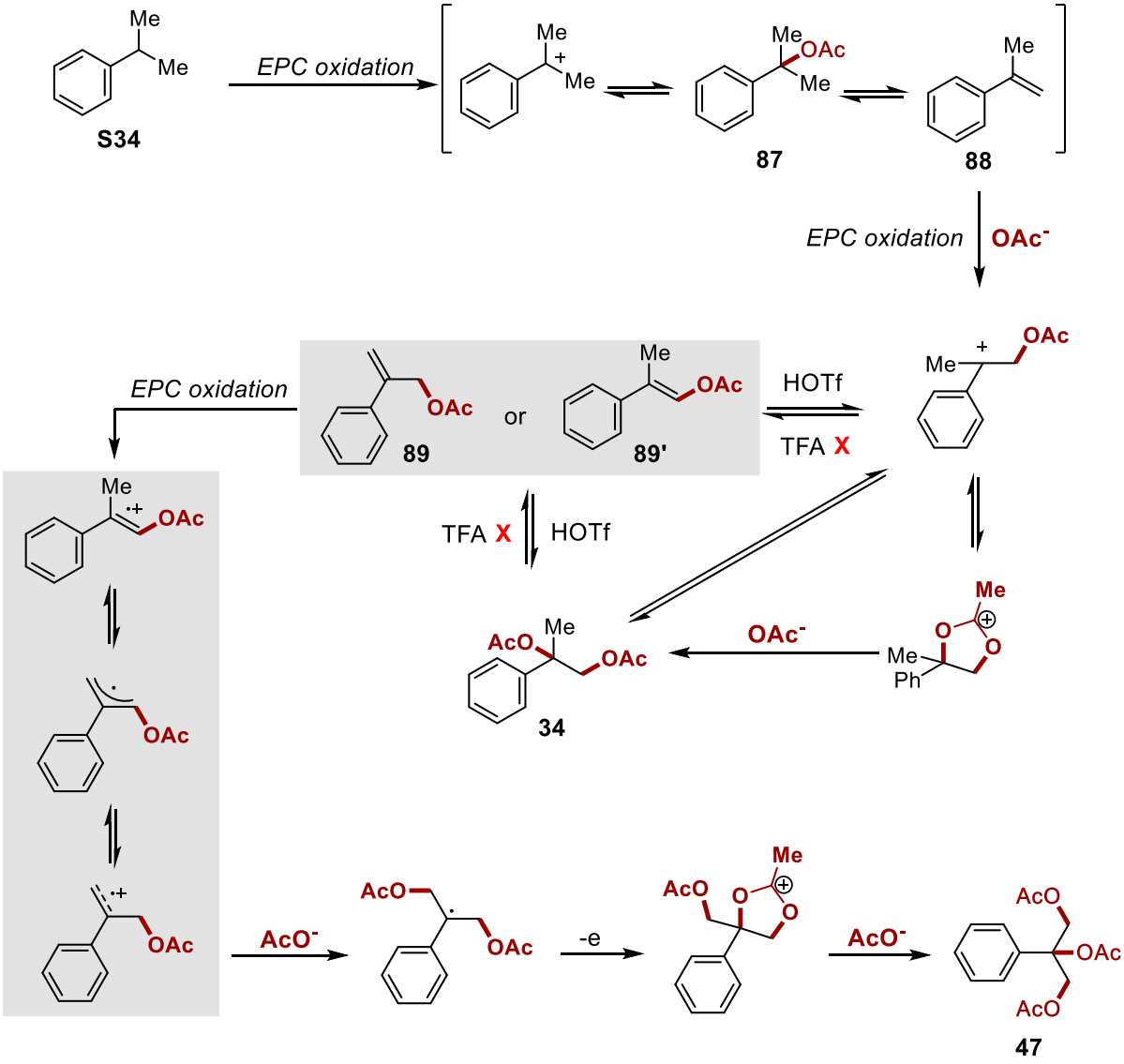


Fig. S13 Possible mechanism, red "X" means could not enable the transformation.

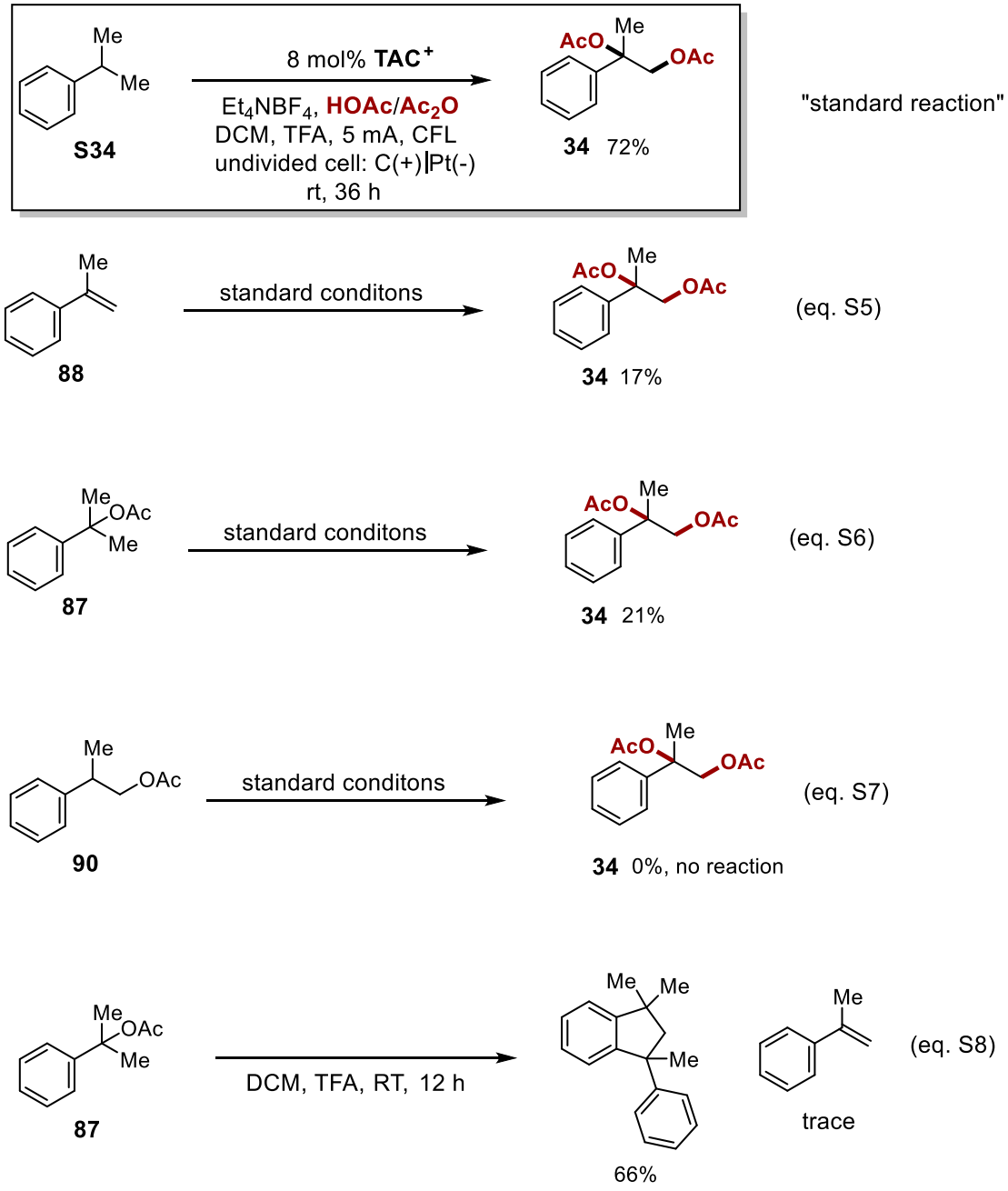


Fig. S14 Verification of possible intermediates for dioxygenation of cumene.

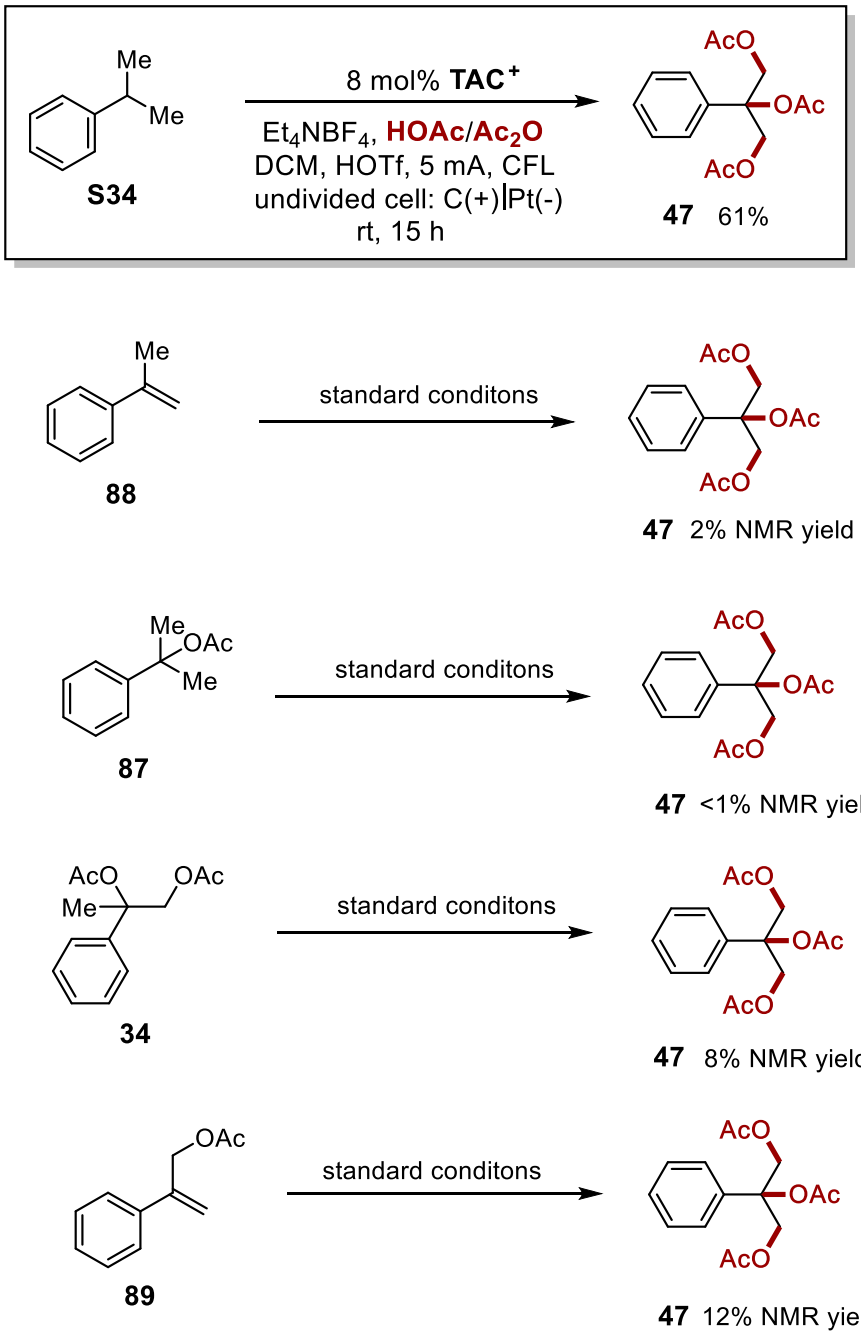
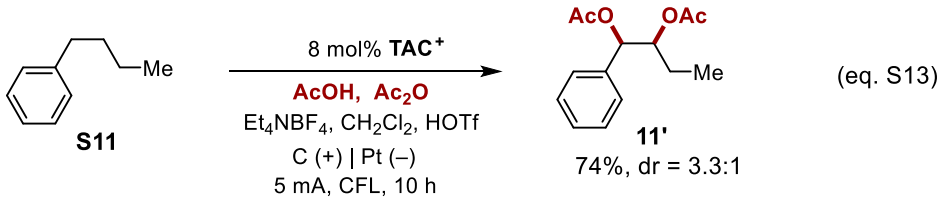


Fig. S15 Verification of possible intermediates for trioxygenation of cumene.

2.5.4 Side products studies

We have studied the dioxygenation reaction of *n*-butylbenzene to determine the mass balance for a representative reaction. The reaction was run under the standard conditions, and after 10 h the reaction mixture was analyzed by GC-MS. The peak time of each compound was referenced with standard samples.



(eq. S13)

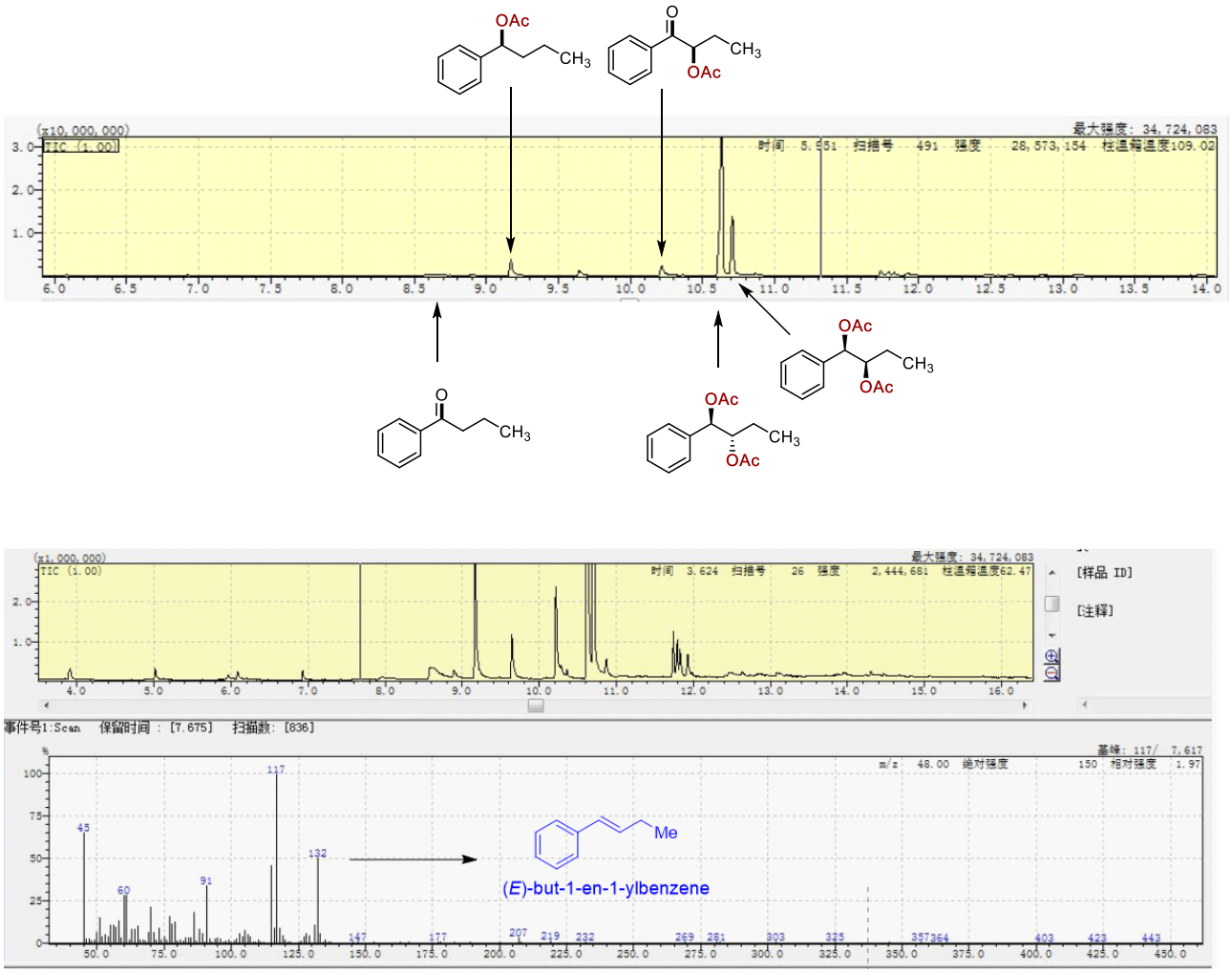


Fig. S16 GC-MS for dioxygenation reaction of *n*-butylbenzene.

In addition, (*E*)-but-1-en-1-ylbenzene **83** was detected under the standard conditions by GC-MS, albeit in only trace amounts.

The conversion of substrates is usually 100%. In cases where yields are moderate, the following factors may contribute to the diminished efficiency:

1) In some cases, ketones were detected as side products in less than 5% yield.

2) Benzylic ester (monooxygenation) products could sometimes be detected (~5%), but in some case with electron-deficient substrates, benzylic monooxygenation products are much more or even the main products, see "*2.6. Unsuccessful and Challenging Substrates*".

3) α-Ketal ester products could sometimes be detected (~5%). Although present in only small amounts, they tend to have similar R_f values as the dioxygenation products, rendering isolation by chromatography difficult. In such cases, the reaction mixture was treated with Na_2CO_3 (aq.)/MeOH to obtain the pure diols instead of the diacetate ester products.

4) In some cases, especially for some very electron-rich substrates, substrate decomposition was competitive.

2.6. Unsuccessful and Challenging Substrates

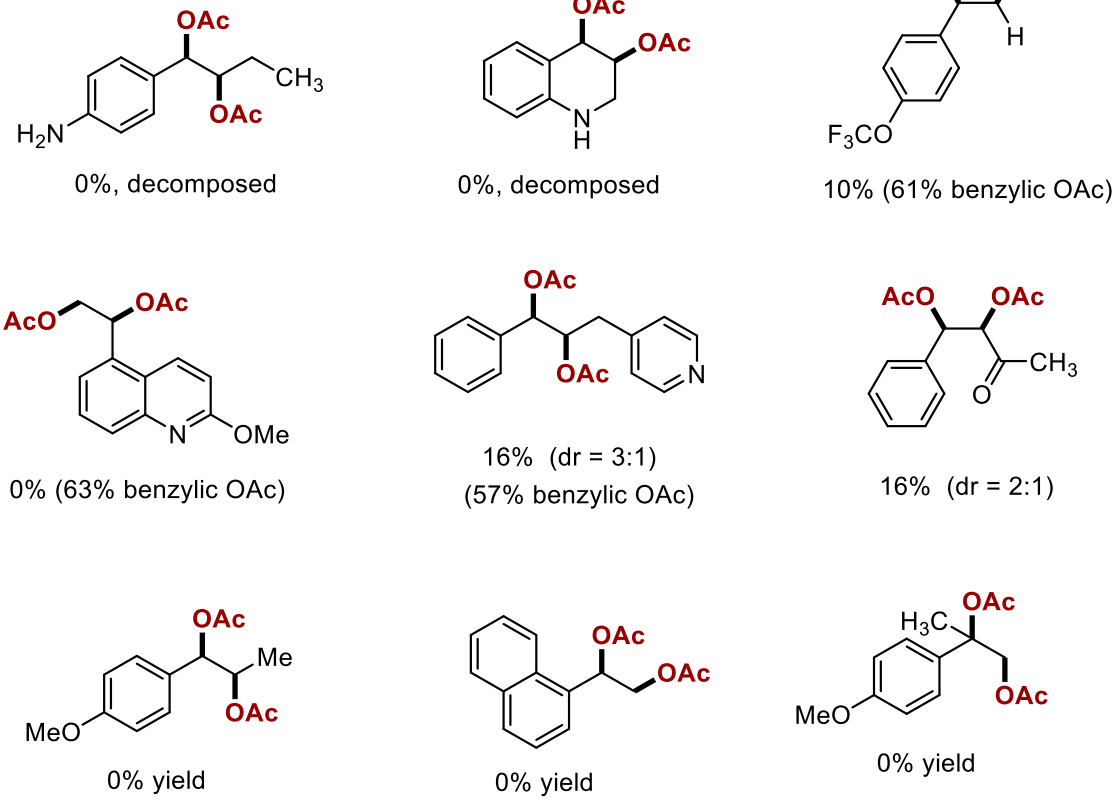
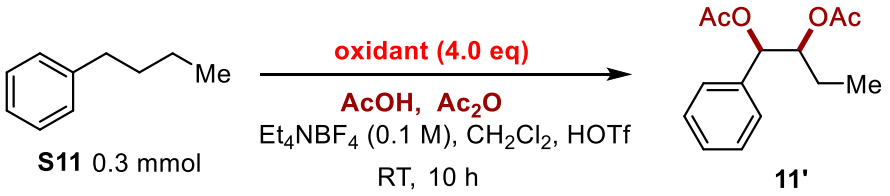


Fig. S17 Unsuccessful and challenging substrates for vicinal C-H dioxygenation.

2.7 Comparison with other chemical oxidants

2.7.1 Table. S2 Comparison with common chemical oxidants for synthesis of dioxygenation product 11'

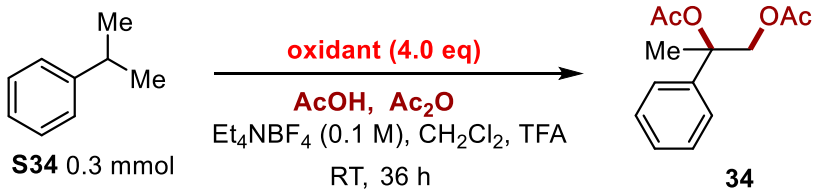


S11 0.3 mmol

11'

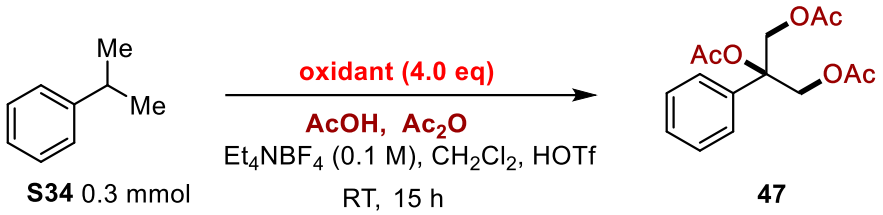
Entry	oxidant	**11'** (%)
1	$Pb(OAc)_4$	0
2	oxone	0
3	TBHP	0
4	TEMPO	0
5	MnO_2	0
6	DDQ	0
7	PIDA	0
8	NFSI	0
9	$NaIO_4$	0
10	O_2 (balloon)	0

2.7.2 Table. S3 Comparison with common chemical oxidants for synthesis of dioxygenation product 34.



Entry	oxidant	**34** (%)
1	$Pb(OAc)_4$	0
2	oxone	0
3	TBHP	0
4	TEMPO	0
5	MnO_2	0
6	DDQ	2%
7	PIDA	0
8	NFSI	0
9	$NaIO_4$	0
10	O_2 (balloon)	0

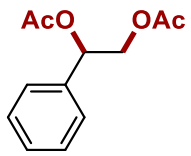
2.7.1 Table. S4 Comparison with common chemical oxidants for synthesis of trioxygenation product 47



S34 0.3 mmol **47**

Entry	oxidant	**47** (%)
1	$Pb(OAc)_4$	0
2	oxone	0
3	TBHP	0
4	TEMPO	0
5	MnO_2	0
6	DDQ	0
7	PIDA	0
8	NFSI	0
9	$NaIO_4$	0
10	O_2 (balloon)	0

2.8 Characterization of products



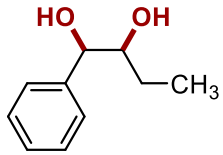
10

1-phenylethane-1,2-diyl diacetate (10)[1]

Following **Condition A** with a reaction time of 15 h, the reaction of ethylbenzene (31.8 mg, 0.3 mmol) afforded 38.6 mg (58% yield) of **10** as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.37-7.33 (m, 5H), 6.01 (dd, J = 8.0 Hz, J = 4.0 Hz, 1H), 4.35-4.27 (m, 2H), 2.12 (s, 3H), 2.06 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.8, 170.2, 136.6, 128.8, 128.7, 126.8, 73.5, 66.2, 21.2, 20.9.



11

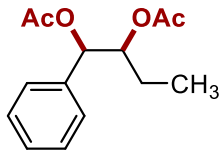
1-phenylbutane-1,2-diol (11) [2]

Following **Condition A** with a reaction time of 10 h, then hydrolysis with Na_2CO_3 (aq.)/MeOH, the reaction of *n*-butylbenzene (40.2 mg, 0.3 mmol) afforded 37.4 mg (75% yield, *anti*:*syn* = 2.9:1) of **11** as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.34-7.28 (m, 7H), 4.66 (d, J = 4.5 Hz, 1H), 4.40 (d, J = 7.0 Hz, 0.35H), 3.73-3.69 (m, 1H), 3.60-3.56 (m, 0.4H), 2.89 (brs, 2H), 2. 34 (brs, 1H), 1.44-1.26 (m, 2.8H), 0.94-0.90 (m, 4.3H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 141.4, 140.5, 128.6, 128.4, 128.1, 127.9, 127.0, 126.9, 77.8, 77.4, 76.9, 76.8, 25.7, 24.6, 10.4, 10.1.

HRMS: calc. for $C_{10}H_{15}O_2^+$ $(M+H)^+$, 167.1067, found, 167.1067.



11'

1-phenylbutane-1,2-diyl diacetate (11')

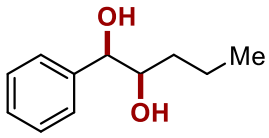
Following **Condition A** with a reaction time of 10 h, the reaction of *n*-butylbenzene (40.2 mg, 0.3 mmol) afforded 55.5 mg (74% yield, *anti*:*syn* = 3.3:1) of **11'** as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.35-7.29 (m, 6.8H), 5.91 (d, J = 4.5 Hz, 1H), 5.81 (d, J = 7.0 Hz, 0.3H), 5.23-5.19 (m, 0.3H), 5.16-5.12 (m, 1H), 2.11 (s, 3H), 2.07 (s, 1H), 2.04 (s, 1H), 2.01 (s, 3H), 1.62-1.44 (m, 2.67H), 0.87 (t, J = 7.5 Hz, 4.15H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 170.7, 170.6, 170.1, 170.0, 137.1, 136.6,

128.6, 128.4, 128.3, 127.4, 127.2, 76.4, 76.1, 75.9, 75.6, 23.7, 22.4, 21.15, 21.10, 20.98, 20.95, 9.91, 9.53.

HRMS: calc. for $C_{14}H_{18}NaO_4^+$ $(M+Na)^+$, 273.1097, found, 273.1094.



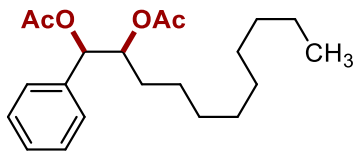
12

1-phenylpentane-1,2-diol (12) [3]

Following **Condition A** with HOAc (9.0 mL), Ac_2O (1.0 mL), DCM (2.0 mL), HOTf (0.5 mL), with a reaction time of 18 h, the reaction of pentylbenzene (148.0 mg, 1.0 mmol) afforded a mixture, which was hydrolyzed with saturated Na_2CO_3 (aq.) (20 mL) and MeOH (20 mL) at RT for 10 h to afford **12** 122.4 mg (68%, *anti*:*syn* = 2.3:1) as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.33-7.25 (m, 7.5H), 4.61 (d, J = 4.0 Hz, 1H), 4.33 (d, J = 7.0 Hz, 0.43H), 3.78-3.75 (m, 1H), 3.63-3.60 (m, 0.5H), 3.48-3.28 (m, 1.3H), 2.68-2.64 (m, 1.7H), 1.50-1.41 (m, 1.4H), 1.30-1.91 (m, 4.8H), 0.85-0.79 (m, 4.4H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 141.4, 140.5, 128.5, 128.3, 128.0, 127.7, 127.0, 126.9, 78.1, 77.0, 75.8, 75.0, 34.8, 33.4, 19.1, 18.9, 14.0, 13.9.



13

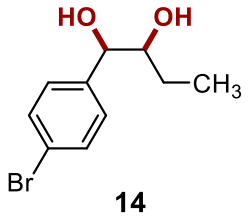
1-phenyldodecane-1,2-diyl diacetate (13)

Following **Condition A** with a reaction time of 10 h, the reaction of *n*-dodecylbenzene (73.8 mg, 0.3 mmol) afforded 84.9 mg (78% yield, *anti*:*syn* = 4:1) of **13** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.35-7.29 (m, 6.6H), 5.91 (d, J = 4.0 Hz, 1H), 5.78 (d, J = 7.0 Hz, 0.26H), 5.29-5.25 (m, 0.24H), 5.22-5.18 (m, 1H), 2.11 (s, 3H), 2.07 (s, 0.83H), 2.02 (s, 0.88H), 2.01 (s, 3H), 1.52-1.48 (m, 2H), 1.32-1.21 (m, 21H), 0.89-0.86 (m, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 170.6, 170.5, 170.0, 137.2, 136.6, 128.6, 128.4, 128.3, 127.4, 127.2, 76.6, 75.8, 74.9, 74.7, 32.0, 30.6, 29.63, 29.59, 29.56, 29.51, 29.44, 29.39, 29.35, 29.2, 25.5, 25.1, 22.8, 21.2, 21.1, 21.0, 20.9, 14.2.

HRMS: calc. for $C_{22}H_{34}NaO_4^+$ $(M+Na)^+$, 385.2349, found, 385.2348.



14

1-(4-bromophenyl)butane-1,2-diol (14)

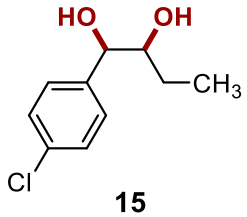
Following **Condition A** with a reaction time of 12 h, followed by hydrolysis with Na_2CO_3

(aq.)/MeOH, the reaction of 1-bromo-4-butylbenzene (63.9 mg, 0.3 mmol) afforded 56.6 mg (77% yield, *anti*:*syn* = 3.7:1) of **14** as a light yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.48-7.45 (m, 2.56H), 7.24-7.21 (m, 2.60H), 4.65 (d, J = 4.5 Hz, 1H), 4.41 (d, J = 7.0 Hz, 0.27H), 3.74-3.70 (m, 1H), 3.56-3.52 (m, 0.27H), 2.92 (brs, 0.2H), 2.65 (brs, 0.9H), 2.46 (brs, 0.29H), 2.02 (brs, 1H), 1.43-0.94 (m, 2.66H), 0.95-0.92 (m, 3.8H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 140.4, 139.5, 131.7, 131.5, 128.7, 122.0, 121.8, 77.0, 76.6, 76.3, 25.7, 24.5, 10.4, 10.1.

HRMS: calc. for $C_{10}H_{13}BrNaO_2^+$ $(M+Na)^+$, 266.9991, found, 266.9993.



15

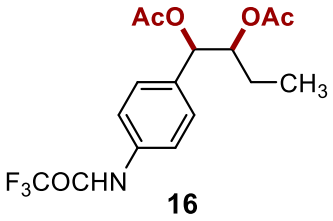
1-(4-chlorophenyl)butane-1,2-diol (15)

Following **Condition A** with a reaction time of 12 h, followed by hydrolysis with Na_2CO_3 (aq.)/MeOH, the reaction of 1-butyl-4-chlorobenzene (50.4 mg, 0.3 mmol) afforded 34.4 mg (57% yield, *anti*:*syn* = 8.3:1) of **15** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.34-7.29 (m, 5.7H), 4.69 (d, J = 4.5 Hz, 1H), 4.44 (d, J = 6.5 Hz, 0.12H), 3.76-3.72 (m, 1H), 3.58-3.54 (m, 0.12H), 2.47 (brs, 1H), 1.99 (brs, 1.1H), 1.42-1.27 (m, 2.6H), 0.96-0.93 (m, 3.5H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 138.9, 133.7, 128.6, 128.3, 76.6, 76.3, 24.6, 10.4.

HRMS: calc. for $C_{10}H_{13}ClNaO_2^+$ $(M+Na)^+$, 223.0496, found, 223.0500.



16

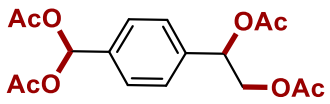
1-(4-(2,2,2-trifluoroacetamido)phenyl)butane-1,2-diyl diacetate (16)

Following **Condition A** with HOTf (100 μL) with a reaction time of 12 h, the reaction of *N*-(4-butylphenyl)-2,2,2-trifluoroacetamide (73.5 mg, 0.3 mmol) afforded 69.3 mg (64% yield, *anti*:*syn* = 1:1.2) of **16** as a yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 8.60-8.58 (m, 2H), 7.58-7.56 (m, 4.4H), 7.34-7.32 (m, 4.4H), 5.86 (d, J = 5.0 Hz, 1H), 5.76 (d, J = 7.0 Hz, 1.2H), 5.20-5.16 (m, 1.1H), 5.12-5.09 (m, 1H), 2.13 (s, 3H), 2.09 (s, 3.3H), 2.05 (s, 3.3H), 2.02 (s, 3H), 1.59-1.53 (m, 2H), 1.51-1.44 (m, 2.5H), 0.89-0.85 (m, 6.8H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.0, 170.8, 170.4, 170.2, 155.1 (q, J = 29.6 Hz), 135.8, 135.5, 135.0, 134.6, 128.2, 128.1, 120.7, 120.5, 115.8 (q, J = 285.0 Hz), 76.1, 75.9, 75.7, 75.2, 23.7, 22.5, 21.1, 21.0, 20.98, 20.95, 9.84, 9.53.

HRMS: calc. for $C_{16}H_{19}F_3NO_5^+$ $(M+H)^+$, 362.1210, found, 362.1211.



17

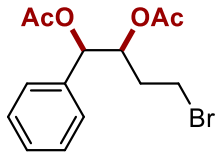
(4-(1,2-diacetoxyethyl)phenyl)methylene diacetate (17)

Following **Condition A** with a reaction time of 12 h, the reaction of 1-ethyl-4-methylbenzene (36.0 mg, 0.3 mmol) afforded 46.5 mg (44% yield) of **17** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.63 (s, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 6.01 (dd, J = 8.0 Hz, J = 3.5 Hz, 1H), 4.34-4.25 (m, 2H), 2.13-2.12 (m, 9H), 2.07 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.5, 170.1, 168.9, 138.3, 135.9, 127.2, 127.1, 89.4, 73.1, 66.0, 21.2. 21.0, 20.9.

HRMS: calc. for $C_{17}H_{20}O_8Na^+$ $(M+Na)^+$, 375.1050, found, 375.1049.



18

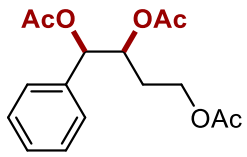
4-bromo-1-phenylbutane-1,2-diyl diacetate (18)

Following **Condition A** with a reaction time of 15 h, the reaction of (4-bromobutyl)benzene (64.0 mg, 0.3 mmol) afforded 57.2 mg (58% yield, *anti*:*syn* = 5.6:1) of **18** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.38-7.29 (m, 6H), 6.04 (d, J = 4.0 Hz, 1H), 5.82 (d, J = 6.5 Hz, 0.18H), 5.44-5.40 (m, 0.18H), 5.32-5.28 (m, 1H), 3.37-3.23 (m, 2.43H), 2.20-2.15 (m, 4.18H), 2.09-2.02 (m, 5.9H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 170.4, 170.2, 169.9, 136.3, 136.0, 128.8, 128.6, 128.5, 128.4, 127.3, 126.7, 76.0, 75.1, 73.6, 73.0, 34.1, 32.0, 28.5, 28.0, 21.2, 21.1, 20.95, 20.88.

HRMS: calc. for $C_{14}H_{17}BrNaO_4^+$ $(M+Na)^+$, 351.0202, found, 351.0207.



19

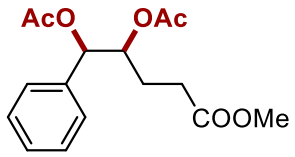
1-phenylbutane-1,2,4-triyl triacetate (19)

Following **Condition A** with a reaction time of 12 h, the reaction of 4-phenylbutyl acetate (57.6 mg, 0.3 mmol) afforded 61.0 mg (66% yield, *anti*:*syn* = 1.8:1) of **19** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.37-7.31 (m, 8H), 5.99 (d, J = 4.5 Hz, 1H), 5.83 (d, J = 7.0 Hz, 0.55H), 5.41-5.37 (m, 0.55H), 5.31-5.27 (m, 1H), 4.10-4.00 (m, 3.4H), 2.14 (s, 3H), 2.09-2.08 (m, 3H), 2.02-2.01 (m, 5H), 1.99 (s, 3H), 1.91-1.86 (m, 2.2H), 1.81-1.77 (m, 1.1H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.0, 170.9, 136.6, 136.2, 128.8, 128.7, 128.6, 128.5, 127.4, 127.0, 76.4, 75.4, 71.9, 71.6, 60.5, 60.4, 29.8, 28.1, 21.14, 21.09, 20.96, 20.91, 20.9.

HRMS: calc. for $C_{16}H_{20}NaO_6^+$ $(M+Na)^+$, 331.1152, found, 331.1153.



20

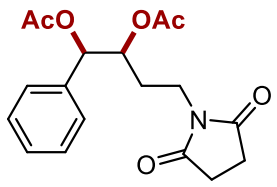
5-methoxy-5-oxo-1-phenylpentane-1,2-diyl diacetate (20)

Following **Condition A** with a reaction time of 15 h, the reaction of methyl 5-phenylpentanoate (57.6 mg, 0.3 mmol) afforded 50.8 mg (55% yield, *anti*:*syn* = 1:3.5) of **20** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.34-7.29 (m, 6.8H), 5.95 (d, J = 4.5 Hz, 0.3H), 5.78 (d, J = 7.0 Hz, 1H), 5.32-5.28 (m, 1H), 5.20-5.16 (m, 0.25H), 3.69 (s, 0.84H), 3.63 (s, 3H), 2.32-2.27 (m, 2.7H), 2.13 (s, 1H), 2.07 (s, 3H), 2.02 (s, 3H), 1.99 (s, 1H), 1.93-1.79 (m, 0.56H), 1.76-1.73 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 173.3, 173.1, 170.5, 170.4, 170.0, 136.6, 136.3, 128.85, 128.76, 128.5, 128.4, 127.4, 127.0, 76.4, 75.4, 74.2, 73.7, 51.8, 30.2, 29.9, 24.2, 21.2, 21.1, 20.93, 20.88.

HRMS: calc. for $C_{16}H_{20}NaO_6^+$ $(M+Na)^+$, 331.1152, found, 331.1151.



21

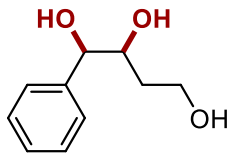
4-(2,5-dioxopyrrolidin-1-yl)-1-phenylbutane-1,2-diyl diacetate (21)

Following **Condition A** with a reaction time of 18 h, the reaction of 1-(4-phenylbutyl)pyrrolidine-2,5-dione (69.3 mg, 0.3 mmol) afforded 38.7 mg (89% purity, contains 4.3 mg, 4.8% yield of 4-(2,5-dioxopyrrolidin-1-yl)-1-oxo-1-phenylbutan-2-yl acetate that could not be further separated, *anti:syn* = 5.6:1), 33% yield of **21** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.36-7.30 (m, 6.5H), 5.92 (d, J = 4.5 Hz, 1H), 5.80 (d, J = 6.0 Hz, 0.18H), 5.18-5.14 (m, 0.17H), 5.12-5.08 (m, 1H), 3.59-3.44 (m, 2.4H), 2.69-2.67 (m, 0.78H), 2.65 (s, 4H), 2.12 (s, 3H), 2.07 (s, 0.57H), 2.04 (s, 3H), 2.02 (s, 0.57H), 1.95-1.78 (m, 2.4H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 177.2, 170.6, 169.9, 136.1, 128.62, 128.55, 128.52, 128.1, 127.3, 127.0, 75.8, 75.4, 72.3, 72.1, 35.2, 35.1, 28.24, 28.2, 26.9, 21.1, 21.0.

HRMS: calc. for $C_{18}H_{21}NNaO_6$ $(M+Na)^+$, 370.1261, found, 370.1257.



22

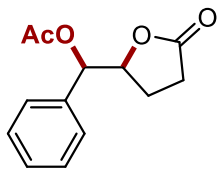
1-phenylbutane-1,2,4-triol (22)

Following **Condition A** with a reaction time of 12 h, then hydrolysis with Na_2CO_3 (aq.)/MeOH, the reaction of 4-phenylbutan-1-ol (45.0 mg, 0.3 mmol) afforded 27.3 mg (50% yield, *anti:syn* = 3.5:1) of **22** as a colorless oil after hydrolysis.

^{1}H NMR (DMSO-d_6, 500 MHz, mixture of regioisomers): 7.33-7.27 (m, 4H), 7.22-7.18 (m, 1H), 5.17 (d, *J* = 4.5 Hz, 1H), 4.53-4.25 (m, 3H), 3.65-3.61 (m, 1H), 3.52-3.42 (m, 2H), 1.62-1.56 (m, 1H), 1.42-1.37 (m, 1H).

^{13}C NMR (DMSO-d_6, 125 MHz, mixture of regioisomers): 143.5, 143.2, 127.7, 127.6, 127.2, 127.1, 126.9, 126.6, 76.6, 76.5, 72.1, 58.4, 58.3, 35.7, 34.9. (one carbon overlapped).

HRMS: calc. for $C_{10}H_{14}NaO_3^+$ $(M+Na)^+$, 205.0835, found, 205.0836.



23

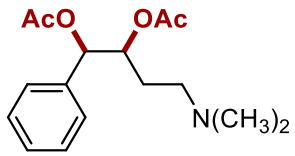
5-oxotetrahydrofuran-2-yl)(phenyl)methyl acetate (23)[4]

Following **Condition A** with a reaction time of 15 h, the reaction of 5-phenylpentanoic acid (53.4 mg, 0.3 mmol) afforded 30.9 mg (44% yield, *anti*:*syn* = 1:1) of **23** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.39-7.34 (m, 10H), 5.97 (d, *J* = 4.0 Hz, 1H), 5.80 (d, *J* = 6.5 Hz, 1H), 4.82-4.76 (m, 2H), 2.46-2.27 (m, 4H), 2.20-2.17 (m, 2H), 2.15 (s, 3H), 2.12 (s, 3H), 2.09-1.96 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 176.8, 176.6, 169.9, 169.8, 135.6, 135.0, 129.1, 129.0, 128.9, 128.6, 127.5, 127.1, 80.73, 80.7, 76.7, 75.8, 28.2, 27.9, 24.3, 22.5, 21.2, 21.1.

HRMS: calc. for $C_{13}H_{14}NaO_4^+$ $(M+Na)^+$, 257.0784, found, 257.0783.



24

4-(dimethylamino)-1-phenylbutane-1,2-diyl diacetate (24)

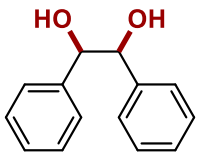
Following **Condition A** with a reaction time of 15 h, the reaction of *N,N*-dimethyl-4-phenylbutan-1-amine (53.1 mg, 0.3 mmol) afforded 25.1 mg (77% purity, contains 5.8 mg, 7.7% yield of 4-(dimethylamino)-1-oxo-1-phenylbutan-2-yl acetate that could not be further separated, *anti:syn* = 6:1), 22% yield of **24** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.35-7.27 (m, 6H), 5.95 (d, *J* = 4.5 Hz, 1H),

5.82 (d, J = 6.5 Hz, 0.16H), 5.33-5.29 (m, 0.16H), 5.23-5.20 (m, 1H), 2.61 (t, J = 8.0 Hz, 0.7H), 2.40 (t, J = 8.0 Hz, 2H), 2.28 (s, 6H), 2.16 (s, 0.5H), 2.14 (s, 3H), 2.02-2.01 (m, 3.7H), 1.81-1.76 (m, 2.33H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 170.6, 170.4, 170.2, 170.0, 136.5, 136.2, 128.8, 128.6, 128.5, 127.3, 127.0, 121.6, 76.2, 75.4, 74.3, 73.3, 58.2, 55.4, 44.7, 44.2, 26.4, 21.2, 21.1, 21.0.

HRMS: calc. for $C_{16}H_{24}NO_4^+$ $(M+H)^+$, 294.1700, found, 294.1697.



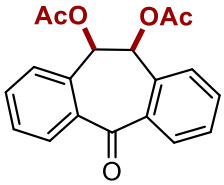
25

1,2-diphenylethane-1,2-diol (25)[5]

Following **Condition A** with HOTf (100 µL) and a reaction time of 24 h, followed by hydrolysis with Na_2CO_3 (aq.)/MeOH, the reaction of 1,2-diphenylethane (54.6 mg, 0.3 mmol) afforded 23.1 mg (36% yield, *anti:syn* = 1:3) of **25** as a white solid.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.34-7.23 (m, 10H), 7.13-7.11 (m, 4H), 4.83 (s, 0.65H), 4.71 (s, 2H), 2.89 (s, 2H), 2.24 (s, 0.63H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 139.9, 139.8, 128.4, 128.3, 128.1, 127.2, 127.1, 79.2, 78.2.



26

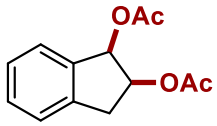
5-oxo-10,11-dihydro-5H-dibenzo[a,d][7]annulene-10,11-diyl diacetate (26)

Following **Condition A** with a reaction time of 18 h, the reaction of 10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (62.4 mg, 0.3 mmol) afforded 36.9 mg (38% yield, *anti:syn* = 1:4.2) of **26** as a light yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.99 (d, J = 9.5 Hz, 2H), 7.94 (d, J = 9.0 Hz, 0.5H), 7.56-7.44 (m, 6.8H), 7.38 (d, J = 6.0 Hz, 2H), 6.39 (s, 0.5H), 6.30 (s, 2H), 2.08 (s, 1.73H), 1.88 (s, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 194.5, 170.3, 169.7, 138.6, 134.1, 133.9, 132.7, 131.3, 130.4, 130.1, 129.5, 129.1, 74.8, 73.4, 21.1, 20.9.

HRMS: calc. for $C_{19}H_{17}O_5^+$ $(M+H)^+$, 325.1071, found, 325.1068.



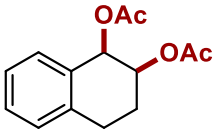
27

2,3-dihydro-1H-indene-1,2-diyl diacetate (27)[1]

Following **Condition A** with a reaction time of 18 h, the reaction of 2,3-dihydro-1H-indene (35.4 mg, 0.3 mmol) afforded 34.4 mg (49% yield, *anti:syn* = 4:1) of **27** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.40-7.24 (m, 5.5H), 6.25 (d, J = 3.5 Hz, 1H), 6.22 (d, J = 5.5 Hz, 0.25H), 5.56-5.53 (m, 0.25H), 5.47-5.44 (m, 1H), 3.52 (dd, J = 17.0 Hz, J = 7.0 Hz, 1H), 3.24 (dd, J = 16.0 Hz, J = 6.5 Hz, 0.25H), 3.13 (dd, J = 16.0 Hz, J = 6.0 Hz, 0.25H), 2.90 (dd, J = 17.0 Hz, J = 4.5 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 0.8H), 2.08 (s, 3H), 2.07 (s, 0.8H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 170.80, 170.76, 170.6, 140.7, 140.3, 138.4, 138.2, 129.8, 129.7, 127.58, 127.57, 125.9, 125.8, 125.14, 125.08, 80.9, 78.9, 75.2, 73.4, 37.0, 36.0, 21.23, 21.20, 21.0, 20.9.



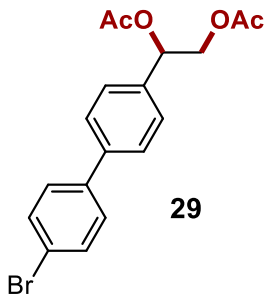
28

1,2,3,4-tetrahydronaphthalene-1,2-diyl diacetate (28)[1]

Following **Condition A** with a reaction time of 18 h, the reaction of 1,2,3,4-tetrahydronaphthalene (39.6 mg, 0.3 mmol) afforded 53.6 mg (72% yield, *anti:syn* = 1:1) of **28** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz, mixture of regioisomers): 7.28-7.14 (m, 8H), 6.18 (d, J = 3.6 Hz, 1H), 6.06 (d, J = 5.6 Hz, 1H), 5.27-5.22 (m, 1H), 5.20-5.16 (m, 1H), 3.08-2.87 (m, 4H), 2.29-2.16 (m, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.05-2.04 (m, 6H), 2.02-1.95 (m, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 170.7, 170.5, 170.4, 136.7, 136.5, 132.79, 132.77, 130.1, 129.2, 128.9,128.8, 128.7, 128.4, 126.6, 126.5, 71.5, 71.0, 70.2, 69.4, 27.2, 25.8, 25.0, 23.4, 21.3, 21.23, 21.18.



29

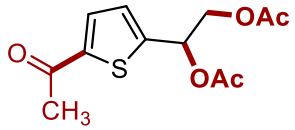
1-(4'-bromo-[1,1'-biphenyl]-4-yl)ethane-1,2-diyl diacetate (29)

Following **Condition A** with a reaction time of 15 h, the reaction of 4-bromo-4'-ethyl-1,1'-biphenyl (78.6 mg, 0.3 mmol) afforded 41.8 mg (37% yield) of **29** as a yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.55 (dd, J = 8.0 Hz, J = 6.0 Hz, 4H), 7.44 (dd, J = 8.5 Hz, J = 3.5 Hz, 4H), 6.04 (dd, J = 8.0 Hz, J = 4.0 Hz, 1H), 4.39-4.30 (m, 2H), 2.14 (s, 3H), 2.08 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.8, 170.2, 140.5, 139.5, 136.0, 132.1, 128.8, 127.4, 127.3, 122.0, 73.2, 66.1, 21.2, 21.0.

HRMS: calc. for $C_{18}H_{17}BrNaO_4^+$ $(M+Na)^+$, 399.0202, found, 399.0202.



30

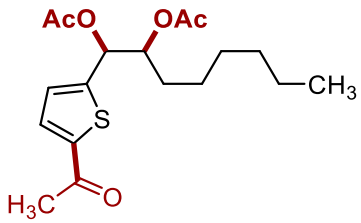
1-(5-acetylthiophen-2-yl)ethane-1,2-diyl diacetate (30)

Following **Condition A** with a reaction time of 18 h, the reaction of 2-ethylthiophene (33.6 mg, 0.3 mmol) afforded 41.3 mg (51% yield) of **30** as a yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.56 (d, J = 3.5 Hz, 1H), 7.08 (d, J = 4.5 Hz, 1H), 6.22 (dd, J = 7.0 Hz, J = 4.0 Hz, 1H), 4.22 (dd, J = 12.0 Hz, J = 4.0 Hz, 1H), 4.30 (dd, J = 12.0 Hz, J = 7.0 Hz, 1H), 2.52 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 190.7, 170.5, 169.8, 147.7, 144.6, 132.2, 127.1, 69.6, 65.4, 26.7, 21.0, 20.8.

HRMS: calc. for $C_{12}H_{15}O_5S^+$ $(M+H)^+$, 271.0635, found, 271.0634.



31

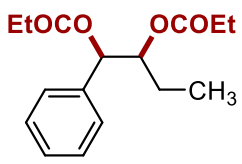
1-(5-acetylthiophen-2-yl)octane-1,2-diyl diacetate (31)

Following **Condition A** with a reaction time of 12 h, the reaction of 2-octylthiophene (58.8 mg, 0.3 mmol) afforded 68.0 mg (64% yield, *anti:syn* = 1.4:1) of **31** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.56-7.54 (m, 1.8H), 7.06-7.04 (m, 1.8H), 6.09 (d, J = 3.5 Hz, 1H), 6.06 (d, J = 5.0 Hz, 0.72H), 5.26-5.18 (m, 1.76H), 2.53 (s, 3H), 2.51 (s, 2.3H), 2.09 (s, 5.6H), 2.07 (s, 3H), 2.05 (s, 2.3H), 1.52-1.46 (m, 3.6H), 1.26-1.20 (m, 14H), 0.85-0.82 (m, 5.6H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 190.8, 190.7, 170.5, 170.3, 169.8, 169.7, 148.4, 147.2, 144.8, 144.5, 132.2, 131.9, 127.8, 127.2, 74.1, 73.7, 72.2, 71.8, 31.7, 30.5, 29.9, 29.03, 29.0, 26.7, 25.3, 25.1, 22.6, 21.1, 21.0, 20.9, 20.88, 14.1.

HRMS: calc. for $C_{18}H_{27}O_5S^+$ $(M+H)^+$, 355.1574, found, 355.1574.



32

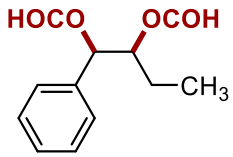
1-phenylbutane-1,2-diyl dipropionate (32)

Following **Condition A** with a reaction time of 12 h, the reaction of *n*-butylbenzene (40.2 mg, 0.3 mmol) with propionic acid and propionic anhydride afforded 55.0 mg (66% yield, *anti:syn* =4.6:1) of **32** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.37-7.27 (m, 6.4H), 5.92 (d, J = 5.0 Hz, 1H), 5.81 (d, J = 7.0 Hz, 0.22H), 5.26-5.22 (m, 0.22H), 5.18-5.15 (m, 1H), 2.44-2.23 (m, 5H), 1.63-1.42 (m, 2.63H), 1.17-1.06 (m, 7.5H), 0.89-0.83 (m, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 174.1, 174.0, 173.5, 173.3, 137.3, 136.9, 128.63, 128.58, 128.4, 128.2, 127.4, 127.3, 76.3, 75.9, 75.6, 75.5, 27.84, 27.82, 27.8, 28.7, 23.8, 22.6, 9.9, 9.5, 9.4, 9.22, 9.16.

HRMS: calc. for $C_{16}H_{23}O_4^+$ $(M+H)^+$, 279.1591, found, 279.1590.



33

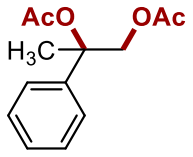
((1-phenylbutane-1,2-diyl)bis(oxy))bis((λ^2-methanol) (33)

Following **Condition A** with a reaction time of 16 h, the reaction of *n*-butylbenzene (40.2 mg, 0.3 mmol) with formic acid afforded 34.0 mg (51% yield, *anti:syn* = 1:2.3) of **33** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 8.13-8.07 (m, 2.7H), 7.40-7.32 (m, 7.6H), 6.05 (d, J = 4.5 Hz, 0.43H), 5.93 (d, J = 6.5 Hz, 1H), 5.39-5.35 (m, 1H), 5.32-5.28 (m, 0.45H), 1.64-1.58 (m, 0.84H), 1.52-1.46 (m, 2H), 0.88 (t, J = 7.5 Hz, 4.5H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 160.6, 160.5, 160.0, 159.9, 136.1, 135.5, 129.1, 128.9, 128.8, 128.6, 127.5, 127.4, 75.9, 75.7, 75.4, 75.1, 23.7, 22.4, 9.8, 9.4.

HRMS: calc. for $C_{12}H_{14}NaO_4^+$ $(M+Na)^+$, 245.0784, found, 245.0783.



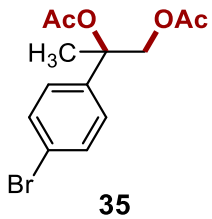
34

2-phenylpropane-1,2-diyl diacetate (34)[6]

Following **Condition B**, the reaction of cumene (36.0 mg, 0.3 mmol) afforded 51.0 mg (72% yield) of **34** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.37-7.29 (m, 5H), 4.38 (d, J = 11.5 Hz, 1H), 4.29 (d, J = 11.5 Hz, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 1.89 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.7, 169.6, 141.3, 128.5, 127.9, 125.0, 81.7, 70.1, 22.2, 21.9, 21.0.



35

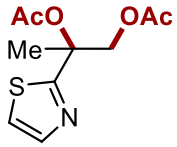
2-(4-bromophenyl)propane-1,2-diyl diacetate (35)

Following **Condition B**, the reaction of 1-bromo-4-isopropylbenzene (59.7 mg, 0.3 mmol) afforded 86.9 mg (92% yield) of **35** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.47 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 4.33 (d, J = 11.5 Hz, 1H), 4.28 (d, J = 11.5 Hz, 1H), 2.07 (s, 3H), 2.04 (s, 3H), 1.86 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.5, 169.5, 140.5, 131.7, 126.9, 121.9, 81.2, 69.6, 22.1, 21.9, 20.9.

HRMS: calc. for $C_{13}H_{15}BrNaO_4^+$ $(M+Na)^+$, 337.0046, found, 337.0044.



36

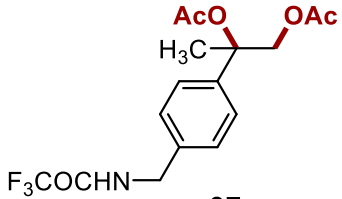
2-(thiazol-2-yl)propane-1,2-diyl diacetate (36)

Following **Condition C** for 24 h, the reaction of 2-isopropylthiazole (38.1 mg, 0.3 mmol) afforded 32.1 mg (44% yield) of **36** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.75 (d, J = 3.0 Hz, 1H), 7.33 (d, J = 3.0 Hz, 1H), 4.67 (d, J = 11.5 Hz, 1H), 4.57 (d, J = 11.5 Hz, 1H), 2.11 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 171.0, 170.4, 169.5, 142.5, 119.7, 81.5, 68.3, 22.6, 22.0, 20.8.

HRMS: calc. for $C_{10}H_{13}NNaO_4S^+$ $(M+Na)^+$, 266.0457, found, 266.0460.



37

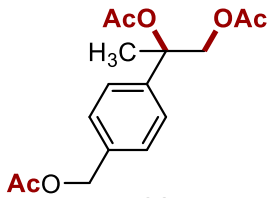
2-(4-((2,2,2-trifluoroacetamido)methyl)phenyl)propane-1,2-diyl diacetate (37)

Following **Condition B**, the reaction of 2,2,2-trifluoro-*N*-(4-isopropylbenzyl)acetamide (73.5 mg, 0.3 mmol) afforded 81.2 mg (75% yield) of **37** as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.32 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 6.95 (brs, 1H), 4.47 (d, J = 6.0 Hz, 2H), 4.35 (d, J = 11.5 Hz, 1H), 4.26 (d, J = 11.5 Hz, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 1.87 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.7, 169.7, 157.4 (q, J = 37.2 Hz), 141.5, 135.5, 128.2, 125.7, 116.0 (q, J = 286.1 Hz), 81.4, 69.9, 43.5, 22.1, 21.9, 20.9.

HRMS: calc. for $C_{16}H_{18}F_3NNaO_5^+$ $(M+Na)^+$, 384.1029, found, 384.1028.



38

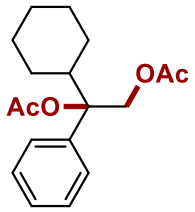
2-(4-(acetoxymethyl)phenyl)propane-1,2-diyl diacetate (38)

(4-Isopropylphenyl)methanol (45.0 mg, 0.3 mmol) was stirred with Ac_2O (0.5 mL) for 1 h in the undivided cell, then followed **Condition B** to afford 61.0 mg (66% yield) of **38** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.35-7.30 (m, 4H), 5.07 (s, 2H), 4.35 (d, J = 11.5 Hz, 1H), 4.27 (d, J = 11.5 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.87 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.9, 170.5, 169.5, 141.4, 135.4, 128.4, 125.2, 81.4, 69.8, 65.8, 22.1, 21.9, 21.0, 20.8.

HRMS: calc. for $C_{16}H_{20}NaO_6^+$ $(M+Na)^+$, 331.1152, found, 331.1152.



39

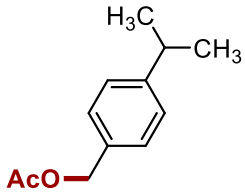
1-cyclohexyl-1-phenylethane-1,2-diyl diacetate (39)

Following **Condition B**, the reaction of (1-cyclohexylethyl)benzene (56.4 mg, 0.3 mmol) afforded 54.7 mg (60% yield) of **39** as a light yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.32 (t, J = 7.5 Hz, 2H), 7.28-7.25 (m, 1H), 7.19 (t, J = 7.0 Hz, 2H), 5.05 (d, J = 12.0 Hz, 1H), 4.97 (d, J = 12.0 Hz, 1H), 2.14 (s, 3H), 2.06 (s, 3H), 1.79-1.57 (m, 6H), 1.22-1.13 (m, 2H), 0.99-0.74 (m, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.8, 169.8, 138.9, 127.9, 127.4, 125.6, 86.5, 63.9, 44.6, 27.7, 26.8, 26.6, 26.4, 26.3, 22.1, 21.0.

HRMS: calc. for $C_{18}H_{24}NaO_4^+$ $(M+Na)^+$, 327.1567, found, 327.1567.



40

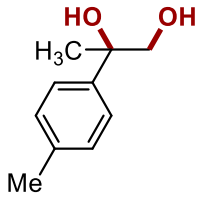
4-isopropylbenzyl acetate (40)

Following **Condition B** without Ac_2O, the reaction of *p*-cymene (40.2 mg, 0.3 mmol) afforded 12.7 mg (22% yield) of **40** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.28 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 5.07 (s, 2H), 2.94-2.88 (m, 1H), 2.08 (s, 3H), 1.24 (d, J = 7.5 Hz, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): 171.1, 149.2, 133.4, 128.6, 126.8, 66.4, 34.0, 24.0, 21.1.

HRMS: calc. for $C_{12}H_{17}O_2^+$ $(M+H)^+$, 193.1223, found, 193.1223.



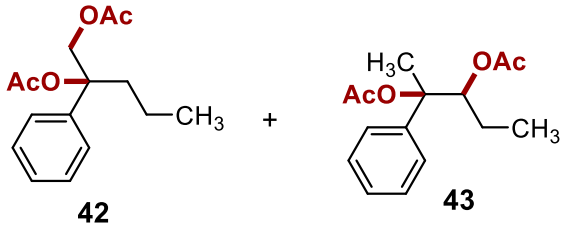
41

2-hydroxy-2-(p-tolyl)propyl acetate (41)[7]

Following **Condition B** without Ac_2O, the reaction of *p*-cymene (40.2 mg, 0.3 mmol) afforded 13.9 mg (28% yield) of **41** as a light yellow solid after hydrolysis.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.34 (d, J = 7.5 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 3.78 (d, J = 11.0 Hz, 1H), 3.62 (d, J = 11.0 Hz, 1H), 2.55 (brs, 1H), 2.34 (s, 3H), 1.82 (brs, 1H), 1.52 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 142.1, 137.0, 129.3, 125.1, 74.9, 71.3, 26.2, 21.1.



42 **43**

1.2:1

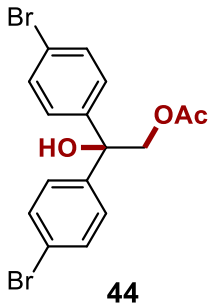
2-phenylpentane-1,2-diyl diacetate (42)

Following **Condition B** for 48 h, the reaction of pentan-2-ylbenzene (44.4 mg, 0.3 mmol) afforded 42.0 mg mixture of **42** (29% yield) and **43** (24% yield, *anti:syn* = 3.6:1) as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.36-7.27 (m, 10.5H), 5.14 (dd, J = 10.5 Hz, J = 2.5 Hz, 0.65H), 5.03 (dd, J = 10.5 Hz, J = 2.5 Hz, 0.18H), 4.76 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 2.30-2.24 (m, 1H), 2.12 (s, 3H), 2.08 (s, 2.6H), 1.98 (s, 2.2H), 1.92 (s, 3H), 1.74-1.70 (m, 0.23H), 1.52-1.36 (m, 1H), 1.30-1.10 (m, 3.6H), 0.87 (t, J = 7.5 Hz, 3H), 0.76 (t, J = 7.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 170.7, 170.6, 169.7, 169.3, 141.3, 141.1, 128.4, 128.1, 127.7, 127.5, 125.7, 125.6, 125.1, 84.7, 84.4, 83.9, 80.1, 80.0, 66.6, 38.2, 22.3, 22.2, 22.1, 22.0, 21.1, 20.9, 20.8, 20.2, 18.3, 16.5, 14.3, 10.6, 10.5.

HRMS: calc. for $C_{15}H_{20}NaO_4^+$ $(M+Na)^+$, 287.1254, found, 287.1253.

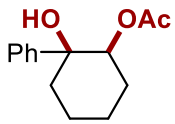


44

2,2-bis(4-bromophenyl)-2-hydroxyethyl acetate (44)

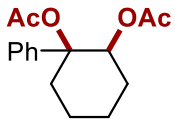
Following **Condition B** without Ac_2O, the reaction of 4,4'-(ethane-1,1-diyl)bis(bromobenzene) (102.0 mg, 0.3 mmol) afforded 83.2 mg (67% yield) of **44** as a light yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.41-7.25 (m, 8H), 4.68 (s, 2H), 3.02 (brs, 1H), 2.02 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): 171.0, 143.6, 128.5, 127.7, 126.4, 77.6, 70.0, 21.0.
HRMS: calc. for $C_{16}H_{14}Br_2NaO_3^+$ $(M+Na)^+$, 434.9202, found, 434.9205.



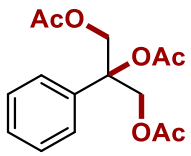
cis-**45**

2-hydroxy-2-phenylcyclohexyl acetate (45)[1]
Following **Condition B**, the reaction of cyclohexylbenzene (48.0 mg, 0.3 mmol) afforded 7.7 mg (11% yield) of **45** as a white solid. This product was isolated as a single diastereomer (*cis*).
^{1}H NMR ($CDCl_3$, 500 MHz): 7.46-7.44 (m, 2H), 7.33 (t, J = 8.0 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 5.29 (dd, J = 10.8 Hz, J = 5.2 Hz, 1H), 2.26 (brs, 1H), 2.25-1.84 (m, 4H), 1.81 (s, 3H), 1.77-1.63 (m, 3H), 1.48-1.40 (m, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz): 169.9, 146.1, 128.4, 127.1, 124.8, 76.4, 75.4, 39.8, 27.3, 24.3, 21.2, 21.0.



cis-**46**

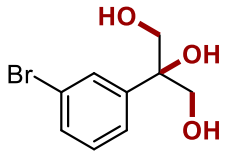
1-phenylcyclohexane-1,2-diyl diacetate (46) [1]
Following **Condition B**, the reaction of cyclohexylbenzene (48.0 mg, 0.3 mmol) afforded 20.7 mg (25% yield) of **46** as a white solid. This product was isolated as a single diastereomer (*cis*).
^{1}H NMR ($CDCl_3$, 500 MHz): 7.31-7.23 (m, 5H), 4.75 (dd, J = 11.5 Hz, J = 4.0 Hz, 1H), 3.02-2.99 (m, 1H), 2.19 (s, 3H), 2.13-2.08 (m, 1H), 1.98-1.90 (m, 1H), 1.88-1.79 (m, 2H), 1.85 (s, 3H), 1.72-1.68 (m, 1H), 1.53-1.38 (m, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz): 169.9, 169.5, 140.6, 128.1, 127.5, 125.5, 83.9, 77.4, 31.3, 27.7, 24.1, 22.1, 21.0, 20.9.
HRMS: calc. for $C_{12}H_{15}O_4^+$ $(M+H)^+$, 223.0965, found, 223.0965.



47

2-phenylpropane-1,2,3-triyl triacetate (47)
Following **Condition A** with a reaction time of 15 h, the reaction of cumene (36.0 mg, 0.3 mmol) afforded 53.8 mg (61% yield) of **47** as a light yellow oil.
^{1}H NMR ($CDCl_3$, 500 MHz): 7.38-7.31 (m, 5H), 4.68 (dd, J = 18.0 Hz, J = 12.0 Hz, 4H), 2.11 (s, 3H), 2.04 (s, 6H).
^{13}C NMR ($CDCl_3$, 125 MHz): 170.3, 169.2, 138.1, 128.7, 128.4, 125.1, 81.6, 64.8, 21.8, 20.8.

HRMS: calc. for $C_{15}H_{18}NaO_6^+$ $(M+Na)^+$, 317.0996, found, 317.0998.



48

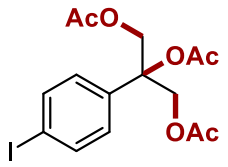
2-(3-bromophenyl)propane-1,2,3-triol (48)

Following **Condition A** with a reaction time of 18 h, the reaction of 1-bromo-3-isopropylbenzene (59.7 mg, 0.3 mmol) afforded 56.3 mg (76% yield) of **48** as a light yellow oil after hydrolysis.

^{1}H NMR (DMSO-d_6, 500 MHz): 7.65 (s, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H), 4.93 (s, 1H), 4.65 (t, J = 6.0 Hz, 2H), 3.59-3.50 (m, 4H).

^{13}C NMR (DMSO-d_6, 125 MHz): 147.6, 129.6, 129.2, 129.0, 125.4, 121.1, 76.2, 66.1.

HRMS: calc. for $C_9H_{11}BrNaO_3^+$ $(M+Na)^+$, 268.9784, found, 268.9785.



49

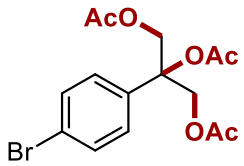
2-(4-iodophenyl)propane-1,2,3-triyl triacetate (49)

Following **Condition A** with a reaction time of 15 h, the reaction of 1-iodo-4-isopropylbenzene (73.8 mg, 0.3 mmol) afforded 40.3 mg (32% yield) of **49** as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.69 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 4.64 (s, 4H), 2.10 (s, 3H), 2.04 (s, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz): 170.2, 169.2, 138.0, 137.8, 127.1, 94.3, 81.3, 64.4, 21.8, 20.8.

HRMS: calc. for $C_{15}H_{17}INaO_6^+$ $(M+Na)^+$, 442.9962, found, 442.9963.



50

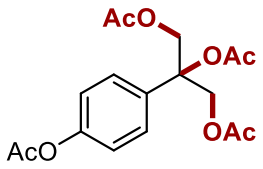
2-(4-bromophenyl)propane-1,2,3-triyl triacetate (50)

Following **Condition A** with a reaction time of 15 h, the reaction of 1-bromo-4-isopropylbenzene (59.7 mg, 0.3 mmol) afforded 70.5 mg (63% yield) of **50** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.49 (d, J = 9.0 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H), 4.65 (dd, J = 13.5 Hz, J = 12.0 Hz, 4H), 2.10 (s, 3H), 2.04 (s, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.2, 169.1, 137.3, 131.8, 126.9, 122.6, 81.2, 64.4, 21.7, 20.8.

HRMS: calc. for $C_{15}H_{17}BrNaO_6^+$ $(M+Na)^+$, 395.0101, found, 395.0103.



51

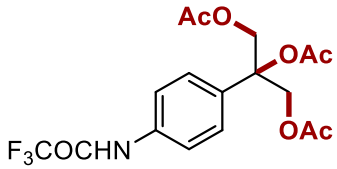
2-(4-acetoxyphenyl)propane-1,2,3-triyl triacetate (51)

Following **Condition A** with a reaction time of 12 h, the reaction of 4-isopropylphenyl acetate (53.4 mg, 0.3 mmol) afforded 38.0 mg (36% yield) of **51** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.36 (d, J = 9.0 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 4.67 (dd, J = 15.0 Hz, J = 11.5 Hz, 4H), 2.30 (s, 3H), 2.10 (s, 3H), 2.05 (s, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.3, 169.3, 169.2, 150.6, 135.6, 126.4, 121.8, 81.4, 64.7, 21.8, 21.3, 20.8.

HRMS: calc. for $C_{17}H_{20}NaO_8^+$ $(M+Na)^+$, 375.1050, found, 375.1048.



52

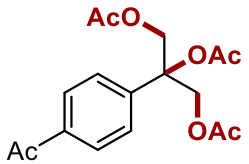
2-(4-(2,2,2-trifluoroacetamido)phenyl)propane-1,1,2,3-tetrayl tetraacetate (52)

Following **Condition A** with a reaction time of 12 h, the reaction of 2,2,2-trifluoro-*N*-(4-isopropylphenyl)acetamide (69.3 mg, 0.3 mmol) afforded 55.9 mg (46% yield) of **52** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 8.84 (brs, 1H), 7.59 (d, J = 9.0 Hz, 2H), 7.31 (d, J = 9.0 Hz, 2H), 4.70-4.64 (m, 4H), 2.12 (s, 3H), 2.05 (s, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.4, 169.6, 155.1 (q, J = 37.8 Hz), 135.7, 135.6, 126.0, 120.6, 115.8 (q, J = 286.8 Hz), 81.2, 64.5, 21.7, 20.7.

HRMS: calc. for $C_{17}H_{18}F_3NNaO_7^+$ $(M+Na)^+$, 428.0928, found, 428.0927.



53

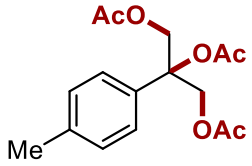
2-(4-acetylphenyl)propane-1,2,3-triyl triacetate (53)

Following **Condition A** with a reaction time of 18 h, the reaction of 1-(4-isopropylphenyl)ethan-1-one (48.6 mg, 0.3 mmol) afforded 39.3 mg (39% yield, 95% pure, containing2 mg, 2% yield of 2-(4-acetylphenyl)-2-hydroxypropane-1,3-diyl diacetate), 37% yield of **53** as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.96 (d, J = 9.0 Hz, 2H), 7.44 (d, J = 9.0 Hz, 2H), 4.69 (dd, J = 14.5 Hz, J = 11.5 Hz, 4H), 2.60 (s, 3H), 2.13 (s, 3H), 2.05 (s, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): 197.5, 170.2, 169.2, 143.3, 136.9, 128.7, 125.5, 81.2, 64.4, 26.7, 21.8, 20.8.

HRMS: calc. for $C_{17}H_{20}NaO_7^+$ $(M+Na)^+$, 359.1101, found, 359.1101



54

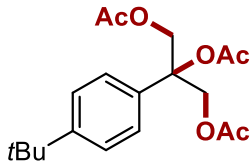
2-(p-tolyl)propane-1,2,3-triyl triacetate (51)

Following **Condition A** with a reaction time of 12 h, the reaction of *p*-cymene (40.2 mg, 0.3 mmol) afforded 47.1 mg (51% yield) of **54** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.22 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 4.67 (dd, J = 15.0 Hz, J = 11.5 Hz, 4H), 2.33 (s, 3H), 2.10 (s, 3H), 2.04 (s, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.4, 169.3, 138.2, 135.1, 129.4, 125.0, 81.5, 64.9, 21.9, 21.2, 20.9.

HRMS: calc. for $C_{16}H_{20}NaO_6^+$ $(M+Na)^+$, 331.1152, found, 331.1153.



55

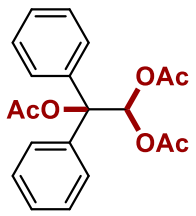
2-(4-(tert-butyl)phenyl)propane-1,2,3-triyl triacetate (55)

Following **Condition A** with a reaction time of 12 h, the reaction of 1-(*tert*-butyl)-4-isopropylbenzene (52.8 mg, 0.3 mmol) afforded 38.9 mg (37% yield) of **55** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.37 (d, J = 9.0 Hz, 2H), 7.25 (d, J = 9.0 Hz, 2H), 4.67 (dd, J = 20.0 Hz, J = 11.5 Hz, 4H), 2.10 (s, 3H), 2.05 (s, 6H), 1.30 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.4, 169.3, 151.3, 134.9, 125.6, 124.8, 81.6, 65.0, 34.6, 31.4, 21.9, 20.9.

HRMS: calc. for $C_{19}H_{26}NaO_6^+$ $(M+Na)^+$, 373.1622, found, 373.1620.



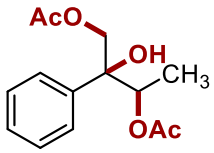
56

2,2-diphenylethane-1,1,2-triyl triacetate (56)

Following **Condition A** with a reaction time of 12 h, the reaction of ethane-1,1-diyldibenzen (54.6 mg, 0.3 mmol) afforded 38.4 mg (36% yield) of **56** as a light yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz): 8.13 (s, 1H), 7.53-7.31 (m, 10H), 2.04 (s, 3H), 2.02 (s, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): 168.4, 168.3, 139.1, 128.7, 128.2, 127.6, 87.3, 85.4, 22.0, 20.9.
HRMS: calc. for $C_{20}H_{20}NaO_6^+$ $(M+Na)^+$, 379.1152, found, 379.1161.



57

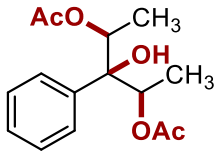
2-hydroxy-2-phenylbutane-1,3-diyl diacetate (57)

Following **Condition A** with a reaction time of 18 h, the reaction of *sec*-butylbenzene (40.2 mg, 0.3 mmol) afforded 47.9 mg (60% yield, *anti:syn* = 1:1) of **57** as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, mixture of regioisomers): 7.52-7.45 (m, 4H), 7.39-7.27 (m, 6H), 5.32 (q, J = 6.4 Hz, 1H), 5.25 (q, J = 6.4 Hz, 1H), 4.55-4.31 (m, 4H), 2.86-2.85 (m, 2H), 2.11 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.11 (d, J = 6.4 Hz, 3H), 1.03 (d, J = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.3, 170.4, 170.1, 140.1, 139.6, 128.5, 128.3, 127.9, 127.8, 126.3, 125.6, 77.0, 76.9, 73.9, 72.9, 69.1, 67.9, 21.4, 21.3, 20.93, 20.91, 14.7, 14.2. (one carbon overlapped).

HRMS: calc. for $C_{14}H_{18}NaO_5^+$ $(M+Na)^+$, 289.1046, found, 289.1047.



58

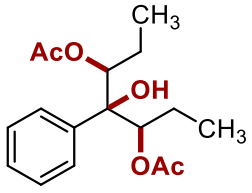
3-hydroxy-3-phenylpentane-2,4-diyl diacetate (58)

Following **Condition A** with a reaction time of 12 h, the reaction of pentan-3-ylbenzene (44.4 mg, 0.3 mmol) afforded 44.5 mg (53% yield, *anti:syn* = 14:1) of **58** as a light yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.42-7.29 (m, 5.4H), 5.45 (q, J = 6.5 Hz, 2H), 5.37 (q, J = 6.0 Hz, 0.14H), 2.86 (s, 1H), 2.49 (s, 0.06H), 2.10 (s, 6H), 1.91 (s, 0.44H), 1.14 (d, J = 6.5 Hz, 0.45H), 1.03 (d, J = 6.5 Hz, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 170.8, 138.6, 128.1, 127.6, 126.5, 79.3, 74.1, 21.4, 15.4.

HRMS: calc. for $C_{15}H_{21}O_5^+$ $(M+H)^+$, 281.1384, found, 281.1385.



59

4-hydroxy-4-phenylheptane-3,5-diyl diacetate (59)

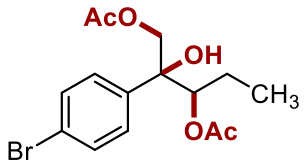
Following **Condition A** with a reaction time of 20 h, the reaction of heptan-4-ylbenzene (52.8 mg, 0.3 mmol) afforded 35.1 mg (38% yield, *anti:syn* = 10:1) of **59** as a light yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.41-7.29 (m, 5.9H), 5.31 (dd, J = 11.0 Hz,

J = 2.0 Hz, 2H), 5.03 (dd, J = 10.0 Hz, J = 2.5 Hz, 0.2H), 2.75 (brs, 1H), 2.15-2.13 (m, 6.9H), 1.55-1.48 (m, 2.3H), 1.43-1.37 (m, 2.2H), 0.76 (t, J = 7.5 Hz, 6H), 0.70 (t, J = 7.5 Hz, 0.65H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.8, 138.6, 128.0, 127.6, 126.7, 80.1, 78.6, 22.9, 21.1, 10.6.

HRMS: calc. for $C_{17}H_{24}NaO_5^+$ $(M+Na)^+$, 331.1516, found, 331.1520.



60

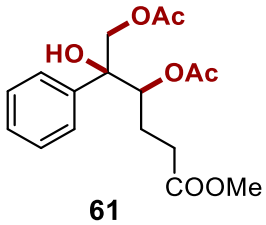
2-(4-bromophenyl)pentane-1,2,3-triol (60)

Following **Condition A** with a reaction time of 18 h, the reaction of 1-bromo-4-(pentan-2-yl)benzene (68.1 mg, 0.3 mmol) afforded 53.8 mg (50% yield, *anti:syn* = 1.8:1) of **60** as a light yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.51-7.35 (m, 6.6H), 5.22 (dd, J = 11.0 Hz, J = 3.0 Hz, 1H), 5.17 (dd, J = 11.0 Hz, J = 3.0 Hz, 0.56H), 4.49 (d, J = 11.5 Hz, 0.54H), 4.38 (d, J = 11.5 Hz, 1H), 4.26 (d, J = 12.0 Hz, 1H), 4.24 (d, J = 12.5 Hz, 0.54H), 3.03 (s, 0.54H), 2.97 (s, 1H), 2.14 (s, 3H), 2.06 (s, 1.7H), 2.04 (s, 0.7H), 1.98 (s, 3H), 1.66-1.62 (m, 0.57H), 1.57-1.52 (m, 1H), 1.33-1.28 (m, 1H), 1.24-1.19 (m, 0.57H), 0.81 (t, J = 7.5 Hz, 1.7H), 0.75 (t, J = 7.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.2, 170.9, 170.4, 139.5, 139.0, 131.6, 131.3, 128.1, 127.6, 122.1, 121.9, 78.1, 77.2, 77.1, 68.8, 67.9, 22.6, 21.7, 21.1, 21.0, 20.9, 20.8, 10.5, 10.2.

HRMS: calc. for $C_{15}H_{19}BrNaO_5^+$ $(M+Na)^+$, 381.0308, found, 381.0308.



61

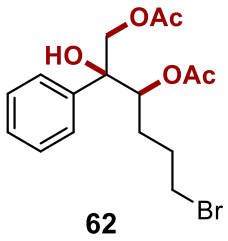
2-hydroxy-6-methoxy-6-oxo-2-phenylhexane-1,3-diyl diacetate (61)

Following **Condition A** with a reaction time of 24 h, the reaction of methyl 5-phenylhexanoate (61.8 mg, 0.3 mmol) afforded 37.5 mg (37% yield, *anti:syn* = 2.6:1) of **61** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.53 (d, J = 8.0 Hz, 0.9H), 7.47 (d, J = 8.0 Hz, 2H), 7.40-7.35 (m, 3H), 7.33-7.29 (m, 1.5H), 5.38 (dd, J = 10.0 Hz, J = 3.0 Hz, 1H), 5.27 (dd, J = 10.0 Hz, J = 2.5 Hz, 0.38H), 4.56 (d, J = 11.5 Hz, 0.4H), 4.39 (d, J = 11.5 Hz, 1H), 4.29 (d, J = 11.5 Hz, 1H), 4.22 (d, J = 11.5 Hz, 0.4H), 3.64 (s, 1.36H), 3.61 (s, 3H), 3.11 (brs, 0.35H), 2.98 (s, 1H), 2.30-2.23 (m, 1.3H), 2.22-2.16 (m, 2H), 2.14 (s, 3H), 2.045-2.041 (m, 2.6H), 1.98 (s, 3H), 1.95 (s, 3H), 1.92-1.85 (m, 1H), 1.71-1.64 (m, 1.6H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 173.6, 173.3, 171.2, 170.8, 170.4, 139.9, 139.4, 128.6, 128.3, 128.0, 127.9, 126.2, 125.6, 77.2, 77.0, 76.0, 75.0, 69.1, 68.1, 51.8, 51.7, 30.5, 30.2, 25.0, 24.0, 21.2, 21.0, 20.9, 20.8.

HRMS: calc. for $C_{17}H_{22}NaO_7^+$ $(M+Na)^+$, 361.1258, found, 361.1267.



62

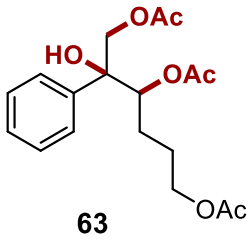
6-bromo-2-hydroxy-2-phenylhexane-1,3-diyl diacetate (62)

Following **Condition A** with a reaction time of 24 h, the reaction of (6-bromohexan-2-yl)benzene (72.0 mg, 0.3 mmol) afforded 40.3 mg (36% yield, *anti:syn* = 1:1.2) of **62** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.53-7.30 (m, 9H), 5.34 (dd, J = 10.0 Hz, J = 2.5 Hz, 0.87H), 5.25 (dd, J = 10.5 Hz, J = 2.5 Hz, 1H), 4.54 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 11.5 Hz, 0.84H), 4.30 (d, J = 11.5 Hz, 0.84H), 4.25 (d, J = 11.5 Hz, 1H), 3.34-3.24 (m, 4H), 2.92-2.90 (m, 2H), 2.15 (s, 2.6H), 2.05 (s, 6H), 1.98 (s, 2.6H), 1.83-1.69 (m, 6H), 1.49-1.46 (m, 1H), 1.40-1.35 (m, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.3, 171.2, 170.8, 170.4, 139.9, 139.4, 128.6, 128.3, 128.0, 127.9, 126.2, 125.4, 77.2, 77.0, 76.1, 74.9, 69.1, 68.0, 33.2, 32.9, 29.1, 28.9, 28.2, 27.4, 21.1, 20.9, 20.8.

HRMS: calc. for $C_{16}H_{21}BrNaO_5^+$ $(M+Na)^+$, 395.0465, found, 395.0465.



63

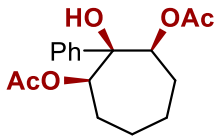
2-hydroxy-2-phenylhexane-1,3,6-triyl triacetate (63)

Following **Condition A** with a reaction time of 24 h, the reaction of 5-phenylhexan-1-ol (53.4 mg, 0.3 mmol) afforded 42.2 mg (40% yield, *anti:syn* = 1.8:1) of **63** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.52-7.30 (m, 8.5H), 5.35 (dd, J = 10.5 Hz, J = 2.5 Hz, 1H), 5.27 (dd, J = 10.5 Hz, J = 2.5 Hz, 0.5H), 4.54 (d, J = 12.0 Hz, 0.5H), 4.42 (d, J = 11.5 Hz, 1H), 4.29 (d, J = 12.0 Hz, 1H), 4.23 (d, J = 11.5 Hz, 0.5H), 4.03-3.90 (m, 3H), 3.00 (brs, 0.5H), 2.97 (brs, 1H), 2.15 (s, 3H), 2.06 (s, 1.6H), 2.04 (s, 1.6H), 2.00 (s, 1.6H), 1.97 (s, 3H), 1.95 (s, 3H), 1.70-1.63 (m, 2H), 1.58-1.52 (m, 2H), 1.46-1.24 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.3, 171.1, 170.8, 170.4, 140.1, 139.5, 128.6, 128.3, 128.0, 127.9, 126.2, 125.6, 77.3, 77.1, 76.5, 75.3, 69.1, 68.0, 64.0, 63.8, 26.0, 25.2, 25.1, 24.8, 21.1, 21.04, 20.97, 20.91, 20.8.

HRMS: calc. for $C_{18}H_{25}O_7^+$ $(M+H)^+$, 353.1595, found, 353.1594.



64

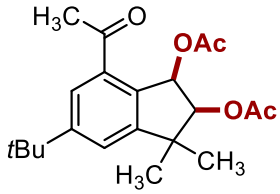
2-hydroxy-2-phenylcycloheptane-1,3-diyl diacetate (64)

Following **Condition A** with a reaction time of 12 h, the reaction of phenylcycloheptane (52.2 mg, 0.3 mmol) afforded 40.4 mg (44% yield, *cis*, dr>20:1) of **64** as a white solid.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.38 (d, J = 8.0 Hz, 2H), 7.31-7.28 (m, 2H), 7.20 (t, J = 8.5 Hz, 1H), 5.21 (dd, J = 10.5 Hz, J = 2.5 Hz, 2H), 2.78 (s, 1H), 2.33-2.25 (m, 2H), 1.84-1.75 (m, 4H), 1.70-1.66 (m, 2H), 1.65 (s, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): 169.5, 143.3, 128.1, 127.2, 125.0, 80.1, 77.7, 27.1, 21.9, 20.7.

HRMS: calc. for $C_{17}H_{22}NaO_5^+$ $(M+Na)^+$, 329.1359, found, 329.1360.



65

7-Acetyl-5-(tert-butyl)-3,3-dimethyl-2,3-dihydro-1H-indene-1,2-diyl diacetate (65)

Following **Condition A** with a reaction time of 12 h, the reaction of 1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one (73.2 mg, 0.3 mmol) afforded 88.6 mg (82% yield, *anti:syn* = 1:1.3) of **65** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.78 (d, J = 1.5 Hz, 0.74H), 7.72 (d, J = 1.5 Hz, 1H), 7.42 (d, J = 1.5 Hz, 0.75H), 7.36 (d, J = 1.5 Hz, 1H), 6.60 (d, J = 6.0 Hz, 0.73H), 6.49 (d, J = 3.5 Hz, 1H), 5.25-5.24 (m, 1.82), 2.57 (s, 2.4H), 2.56 (s, 3H), 2.08 (s, 6H), 2.05 (s, 2.4H), 2.02 (s, 3H), 1.36-1.35 (m, 18H), 1.34 (s, 2.2H), 1.26 (s, 2.4H), 1.21 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 199.2, 198.7, 170.5, 170.4, 170.1, 169.9, 154.2, 153.9, 152.8, 152.7, 135.0, 134.8, 132.9, 132.3, 126.4, 126.0, 123.7, 123.3, 85.2, 78.8, 78.6, 72.6, 45.5, 44.6, 35.2, 35.1, 31.44, 31.42, 28.5, 28.2, 28.1, 26.4, 25.9, 23.5, 21.1, 21.0, 20.82, 20.79.

HRMS: calc. for $C_{21}H_{28}NaO_5^+$ $(M+Na)^+$, 383.1829, found, 383.1833.

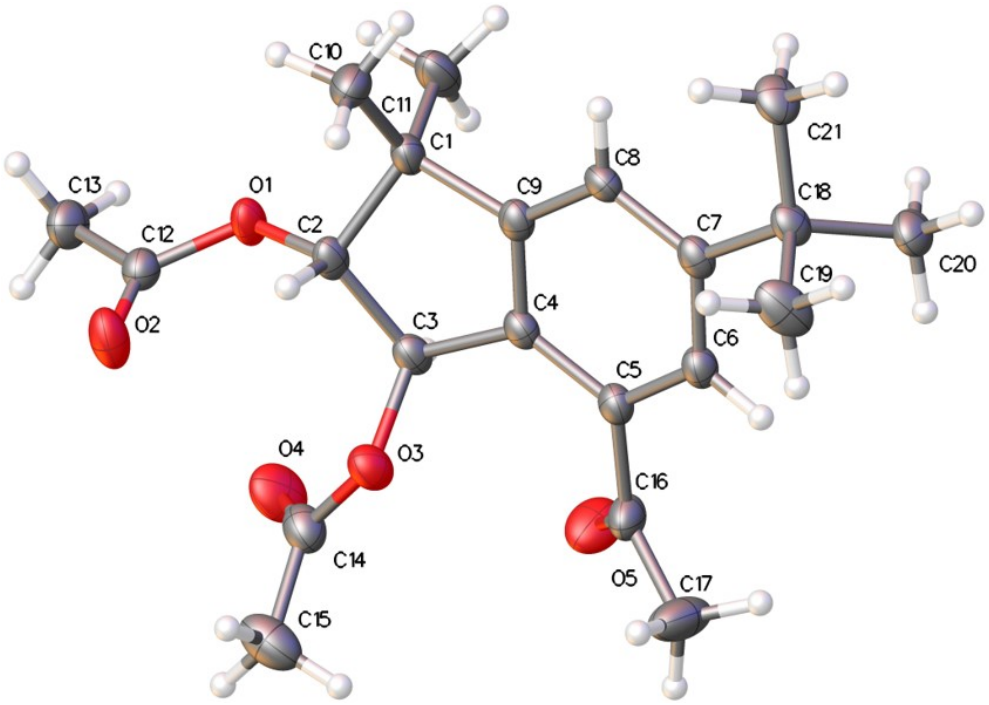
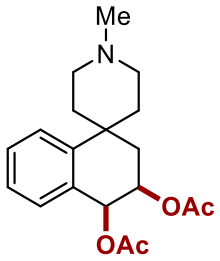


Fig. S18. ORTEP structure of **65-anti**.



66

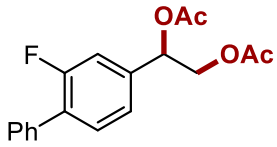
2-hydroxy-2-phenylhexane-1,3,6-triyl triacetate (66)

Following **Condition A** with a reaction time of 12 h, the reaction of 1'-methyl-3,4-dihydro-2H-spiro[naphthalene-1,4'-piperidine] (64.5 mg, 0.3 mmol) afforded 55.6 mg (56% yield, *anti:syn* =1:1) of **66** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.54-7.47 (m, 1H), 7.40-7.28 (m, 1H), 7.24-7.13 (m, 2H), 6.18-6.16 (m, 1H), 5.20-5.14 (m, 1H), 2.88-2.83 (m, 2H), 2.47-2.28 (m, 7H), 2.16-2.08 (m, 6H), 2.03-1.94 (m, 2H), 1.90-1.76 (m, 1H), 1.70-1.63 (m, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.1, 170.7, 170.6, 144.6, 144.0, 133.0, 132.3, 131.0, 129.9, 128.7, 127.3, 127.0, 126.9, 126.8, 126.4, 72.7, 70.3, 69.8, 68.3, 52.0, 51.5, 51.3, 46.7, 46.3, 46.2, 39.8, 39.1, 37.6, 37.0, 36.9, 36.6, 33.1, 29.8, 21.3, 21.27, 21.2.

HRMS: calc. for $C_{19}H_{25}NNaO_4^+$ $(M+Na)^+$, 354.1676, found, 354.1678.



67

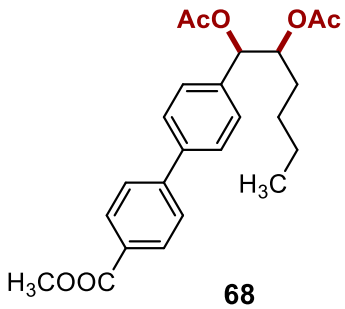
1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethane-1,2-diyl diacetate (67)

Following **Condition A** with HOTf (300 μL) and a reaction time of 12 h, the reaction of 4-ethyl-2-fluoro-1,1'-biphenyl (60.0 mg, 0.3 mmol) afforded 33.2 mg (35% yield) of **67** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.52 (d, J = 7.2 Hz, 2H), 7.46-7.37 (m, 4H), 7.26-7.16 (m, 2H), 6.02 (dd, J = 8.0 Hz, J = 4.8 Hz, 1H), 4.40-4.27 (m, 2H), 2.15 (s, 3H), 2.07 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 170.7, 170.1, 159.8 (d, J = 247.1 Hz), 138.0 (d, J = 7.1 Hz), 135.3, 131.4 (d, J = 4.2 Hz), 129.4 (d, J = 13.8 Hz), 129.1 (d, J = 3.0 Hz), 128.6, 128.0, 122.7 (d, J = 3.6 Hz), 114.6 (d, J = 24.0 Hz), 72.6, 65.9, 21.1, 20.8.

HRMS: calc. for $C_{18}H_{17}FNaO_4^+$ $(M+Na)^+$, 339.1003, found, 339.1001.



68

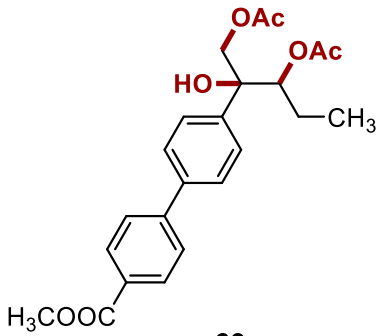
1-(4'-(Methoxycarbonyl)-[1,1'-biphenyl]-4-yl)hexane-1,2-diyl diacetate (68)

Following **Condition A** for 15 h, the reaction of methyl 4'-hexyl-[1,1'-biphenyl]-4-carboxylate (88.8 mg, 0.3 mmol) afforded 71.7 mg (58% yield, *anti:syn* = 1.8:1) of **68** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 8.11-8.09 (m, 3H), 7.66-7.60 (m, 7H), 7.46-7.44 (m, 3H), 5.95 (d, *J* = 4.5 Hz, 1H), 5.83 (d, *J* = 6.5 Hz, 0.54H), 5.33-5.29 (m, 0.54H), 5.26-5.23 (m, 1H), 3.95 (s, 1.6H), 1.94 (s, 3H), 2.14 (s, 3H), 2.10 (s, 1.6H), 2.05 (s, 1.7H), 2.04 (s, 3H), 1.57-1.25 (m, 10H), 0.87-0.83 (m, 4.7H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 170.6, 170.5, 170.1, 170.0, 167.0, 145.1, 145.0, 140.2, 139.9, 137.1, 136.6, 130.2, 129.1, 128.0, 127.9, 127.5, 127.2, 127.1, 127.0, 76.3, 75.6, 74.8, 74.5, 52.2, 30.3, 29.0, 27.6, 27.3, 22.5, 21.2, 21.1, 21.06, 21.0, 14.0, 13.9.

HRMS: calc. for $C_{24}H_{28}NaO_6^+$ $(M+Na)^+$, 435.1778, found, 435.1777.



69

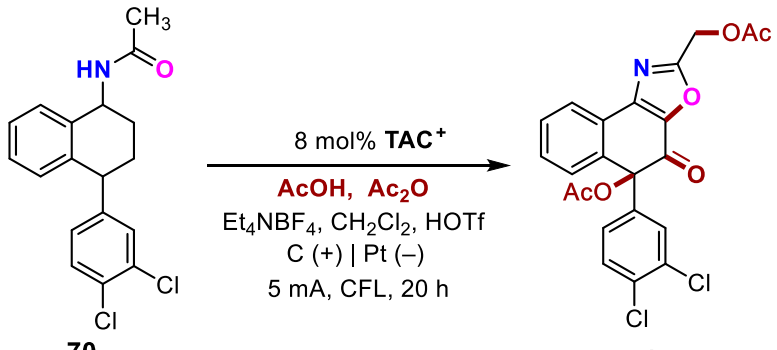
2-hydroxy-2-phenylhexane-1,3,6-triyl triacetate (69)

Following **Condition A** with a reaction time of 12 h, the reaction of methyl 4'-(pentan-2-yl)-[1,1'-biphenyl]-4-carboxylate (84.6 mg, 0.3 mmol) afforded 50.9 mg (41% yield, *anti:syn* = 1.8:1) of **69** as a light yellow oil.

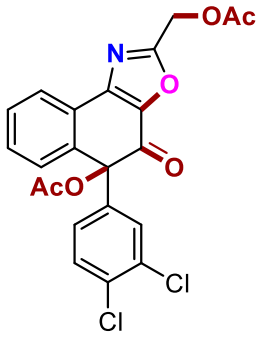
^{1}H NMR ($CDCl_3$, 400 MHz, mixture of regioisomers): 8.11 (d, *J* = 8.4 Hz, 3.5H), 7.69-7.56 (m, 9.7H), 5.32 (d, *J* = 12.8 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 0.56H), 4.57 (d, *J* = 11.6 Hz, 0.55H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.34-4.28 (m, 1.54H), 3.95 (m, 5H), 3.07 (brs, 054H), 3.01 (brs, 1H), 2.16 (s, 3H), 2.09 (s, 1.6H), 2.05 (s, 1.6H), 1.99 (s, 3H), 1.72-1.56 (m, 2H), 1.43-1.32 (m, 1H), 1.85-1.81 (m, 1.8H), 0.78 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.3, 171.2, 171.0, 170.5, 167.1, 145.0, 144.9, 140.4, 140.0, 139.4, 139.2, 130.2, 129.1, 129.0, 127.3, 127.0, 126.9, 126.3, 78.3, 77.34, 77.30, 69.1, 68.0, 52.2, 22.7, 21.8, 21.1, 21.0, 20.9, 20.8, 10.5, 10.3.

HRMS: calc. for $C_{23}H_{26}NaO_7^+$ $(M+Na)^+$, 437.1571, found, 437.1571.



70 **71**



71

(5-acetoxy-5-(3,4-dichlorophenyl)-4-oxo-4,5-dihydronaphtho[1,2-d]oxazol-2-yl)methyl acetate (71)

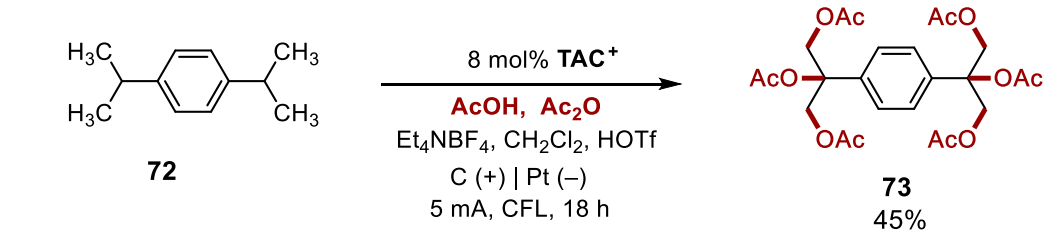
Following **Condition A** with a reaction time of 20 h: The reaction of *N*-(4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide **70** (100.2 mg, 0.3 mmol) for 18 h afforded 64.7 mg (47% yield) of **71** as a white solid.

^{1}H NMR ($CDCl_3$, 500 MHz): 8.10-8.08 (m, 1H), 7.52 (td, J = 8.0 Hz, J = 1.5 Hz, 1H), 7.46 (td, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.31-7.28 (m, 2H), 6.98 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H), 5.30 (s, 2H), 2.25 (s, 3H), 2.20 (s, 3H).

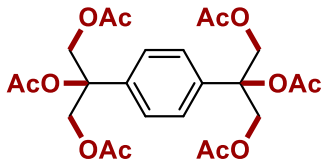
^{13}C NMR ($CDCl_3$, 125 MHz): 180.8, 170.0, 169.5, 165.3, 150.7, 141.9, 141.3, 137.1, 133.7, 133.2, 131.3, 130.7, 129.5, 128.7, 126.9, 125.9, 125.6, 124.8, 84.4, 57.9, 21.0, 20.6.

HRMS: calc. for $C_{22}H_{16}Cl_2NO_6^+$ $(M+H)^+$, 460.0349, found, 460.0342.

Hexaoxidation of 1,4-diisopropylbenzene



72 **73** 45%



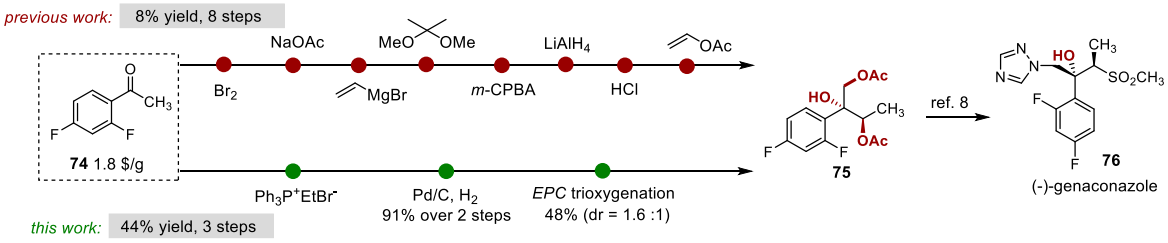
73

Following **Condition A** with a reaction time of 18 h: The reaction of 1,4-diisopropylbenzene **72** (48.6 mg, 0.3 mmol) for 15 h afforded 68.9 mg (45% yield) of **73** as a yellow oil.

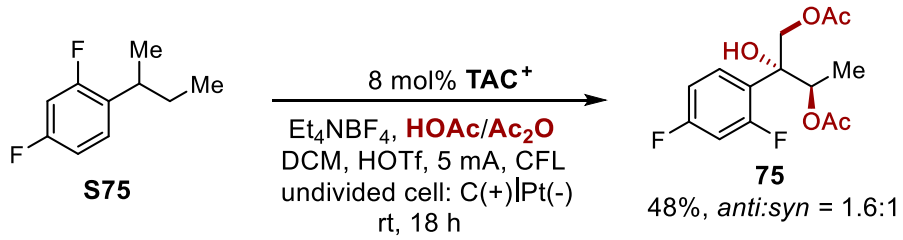
^{1}H NMR ($CDCl_3$, 500 MHz): 7.34 (s, 4H), 4.67 (dd, J = 20.0 Hz, J = 11.5 Hz, 8H), 2.11 (s, 6H), 2.04 (s, 12H).

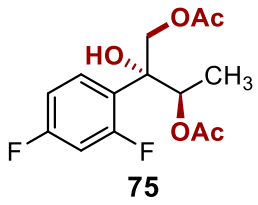
^{13}C NMR ($CDCl_3$, 125 MHz): 170.3, 169.2, 138.2, 125.5, 81.4, 64.7, 21.8, 20.8.

HRMS: calc. for $C_{24}H_{30}NaO_{12}^+$ $(M+Na)^+$, 533.1629, found, 533.1637.



1-(*sec*-butyl)-2,4-difluorobenzene was synthesized from 1-(2,4-difluorophenyl)ethan-1-one via Wittig reaction and palladium-catalyzed hydrogenation in 91% yield in two steps.





2-(2,4-difluorophenyl)-2-hydroxybutane-1,3-diyl diacetate (75)

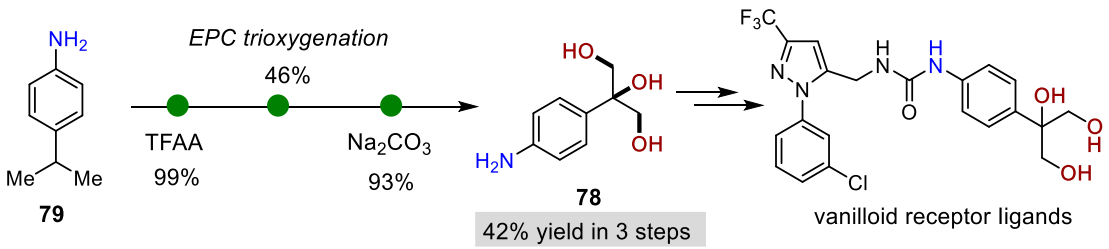
Following **Condition A** with a reaction time of 18 h: The reaction of 1-(*sec*-butyl)-2,4-difluorobenzene (51.0 mg, 0.3 mmol) for 18 h afforded 43.5 mg (48% yield, *anti:syn* = 1.6 :1) of **75** as a yellow oil.[8]

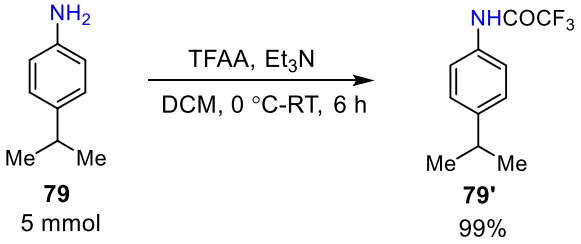
^{1}H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.68-7.58 (m, 1.6H), 6.91-6.85 (m, 1.6H), 6.80-6.74 (m, 1.6H), 5.46 (qd, J = 6.5 Hz, J = 2.0 Hz, 1H), 5.34 (q, J = 6.5 Hz, 0.64H), 4.56-4.43 (m, 3.4H), 3.61 (s, 0.6H), 3.44 (s, 1H), 2.10 (s, 3H), 1.94 (s, 2H), 1.90 (s, 3H), 1.97 (s, 2H), 1.22 (d, J = 6.5 Hz, 2H), 1.01 (d, J = 6.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.93, 171.91, 170.2, 170.0, 162.8 (dd, J = 248.0 Hz, J = 11.8 Hz), 162.5 (dd, J = 247.9 Hz, J = 11.4 Hz), 159.6 (dd, J = 247.5 Hz, J = 11.5 Hz), 159.0 (dd, J = 247.0 Hz, J = 11.9 Hz), 130.6 (dd, J = 9.4 Hz, J = 5.8 Hz), 130.3 (dd, J = 9.5 Hz, J = 5.8 Hz), 123.0 (dd, J = 12.8 Hz, J = 3.9 Hz), 122.9 (dd, J = 13.0 Hz, J = 3.8 Hz), 111.5 (dd, J = 20.6 Hz, J = 3.4 Hz), 111.0 (dd, J = 20.5 Hz, J = 3.5 Hz), 104.3 (dd, J = 28.2 Hz, J = 25.2 Hz), 104.2 (dd, J = 27.2 Hz, J = 25.1 Hz), 77.0 (d, J = 4.8 Hz), 76.8 (d, J = 4.8 Hz), 72.6 (d, J = 4.8 Hz), 72.5 (d, J = 4.8 Hz), 68.9 (d, J = 5.5 Hz), 68.0 (d, J = 5.5 Hz), 21.2, 20.9, 20.7, 14.6, 14.5.

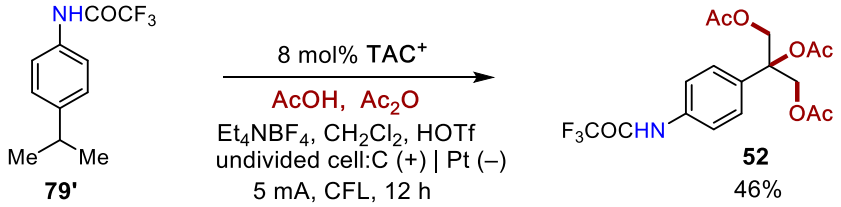
^{19}F NMR ($CDCl_3$, 471 MHz): -107.1, -107.9, -110.7, -110.9.

MS (70 eV): m/z (%): 242 (M^+-60, 2), 173.1 (100).

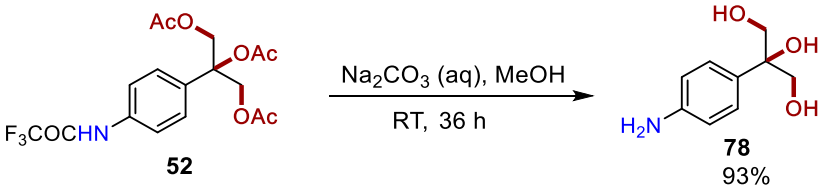




To a 100 mL round-bottom flask cooled to 0 °C were added 4-isopropylaniline **79** (675 mg, 5 mmol), Et_3N (1.01 g, 10 mmol, 2.0 equiv.) and DCM (20 mL). Trifluoroacetic anhydride (1.26 g, 6 mmol, 1.2 equiv.) was then added dropwise. The mixture was stirred at room temperature for 6 h, partitioned between water (50 mL) and CH_2Cl_2 (50 mL), and then quenched with a saturated solution of sodium carbonate (10 mL). The organic layer was isolated, and the aqueous layer was extracted with CH_2Cl_2 (3x50 mL). The organic layers were combined, washed twice with sodium carbonate (10 mL) and twice with HCl (aq) (10 mL), then dried over $MgSO_4$ and concentrated via rotary evaporation to furnish the product **79'** as a light yellow solid (1.14 g, 4.95 mmol, 99% yield), which was directly used in the next step.



Following **Condition A** , the reaction of 2,2,2-trifluoro-*N*-(4-isopropylphenyl)acetamide (69.3 mg, 0.3 mmol) for 12 h afforded 55.9 mg (46% yield) of **52** as a yellow oil.[9]



2-(4-aminophenyl)propane-1,2,3-triol (78)

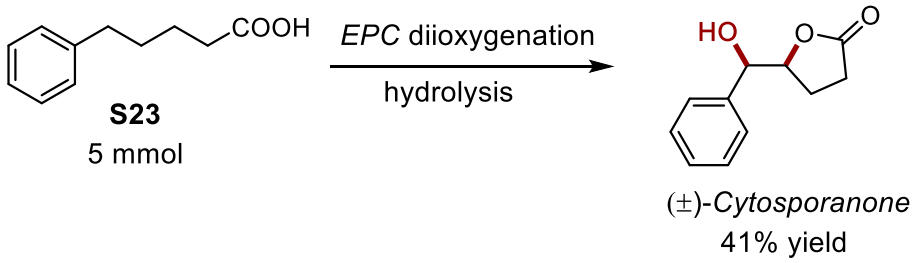
52 (55.9 mg) was added to a mixture of saturated solution of sodium carbonate (10 mL) and MeOH (10 mL), and the mixture was stirred at room temperature for 36 h. The mixture was concentrated in vacuo to remove MeOH and water, and the mixture was dissolved in MeOH (1.0 mL) and passed through a short silica gel column (5 cm) with EtOAc/MeOH=1:1 (50 mL). The eluent solution was

concentrated in vacuo to afford 23.4 mg (93% yield) of **78** as a yellow oil.

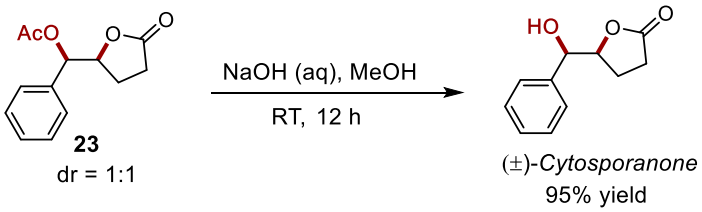
^{1}H NMR (DMSO-d_6, 500 MHz): 7.11 (d, J = 8.5 Hz, 2H), 6.47 (d, J = 8.0 Hz, 2H), 4.86 (brs, 1H), 4.44-4.39 (m, 3H), 3.58 (s, 1H), 3.53-3.80 (m, 4H).

^{13}C NMR (DMSO-d_6, 125 MHz): 147.4, 132.1, 127.1, 113.6, 76.0, 66.8.

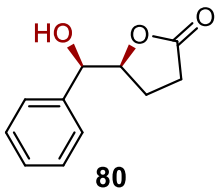
HRMS: calc. for $C_9H_{13}NNaO_3^+$ $(M+Na)^+$, 206.0788, found, 206.0788.



Following **Condition C** with Ni plate as cathode, the reaction of 5-phenylpentanoic acid **S23** (890 mg, 5 mmol) for 48 h afforded 503 mg (43% yield) of 5-oxotetrahydrofuran-2-yl)(phenyl)methyl acetate **23** (dr = 1:1) as a yellow oil.

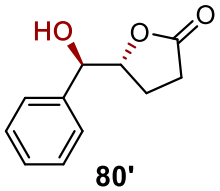


23 (503 mg) was added to a mixture of 3 M NaOH (aq) (50 mL) and MeOH (50.0 mL), and the mixture was stirred at room temperature for 12 h. The mixture was then poured into water and extracted with EtOAc (3×20 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by chromatography (eluent: petroleum ether:ethyl acetate = 2:1) to afford 202 mg of *syn* regioisomer and 192 mg *anti* regioisomer as white solid.[10]



syn: **^{1}H NMR** ($CDCl_3$, 500 MHz): 7.41-7.30 (m, 5H), 5.11 (dd, J = 15.0 Hz, J = 12.0 Hz, 1H), 4.71-4.68 (m, 1H), 3.16 (brs, 1H), 2.59-2.52 (m, 1H), 2.46-2.40 (m, 1H), 2.39-2.24 (m, 1H), 1.95-1.88 (m, 1H).

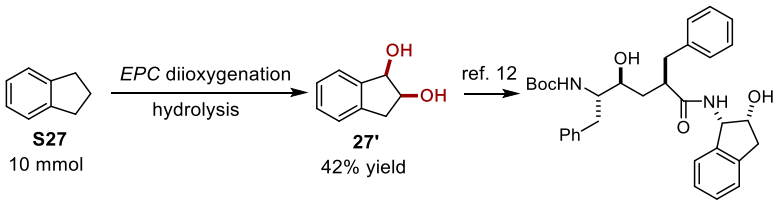
^{13}C NMR ($CDCl_3$, 125 MHz): 178.2, 138.7, 128.7, 128.1, 126.2, 83.6, 73.4, 28.7, 20.7.



anti: **^{1}H NMR** ($CDCl_3$, 500 MHz): 7.41-7.32 (m, 5H), 4.69-4.62 (m, 2H), 3.04 (brs, 1H), 2.46-2.42

(m, 2H), 2.04-1.99 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): 177.2, 138.6, 128.8, 128.7, 127.1, 83.6, 76.4, 28.6, 24.1.



S27
10 mmol

27'
42% yield

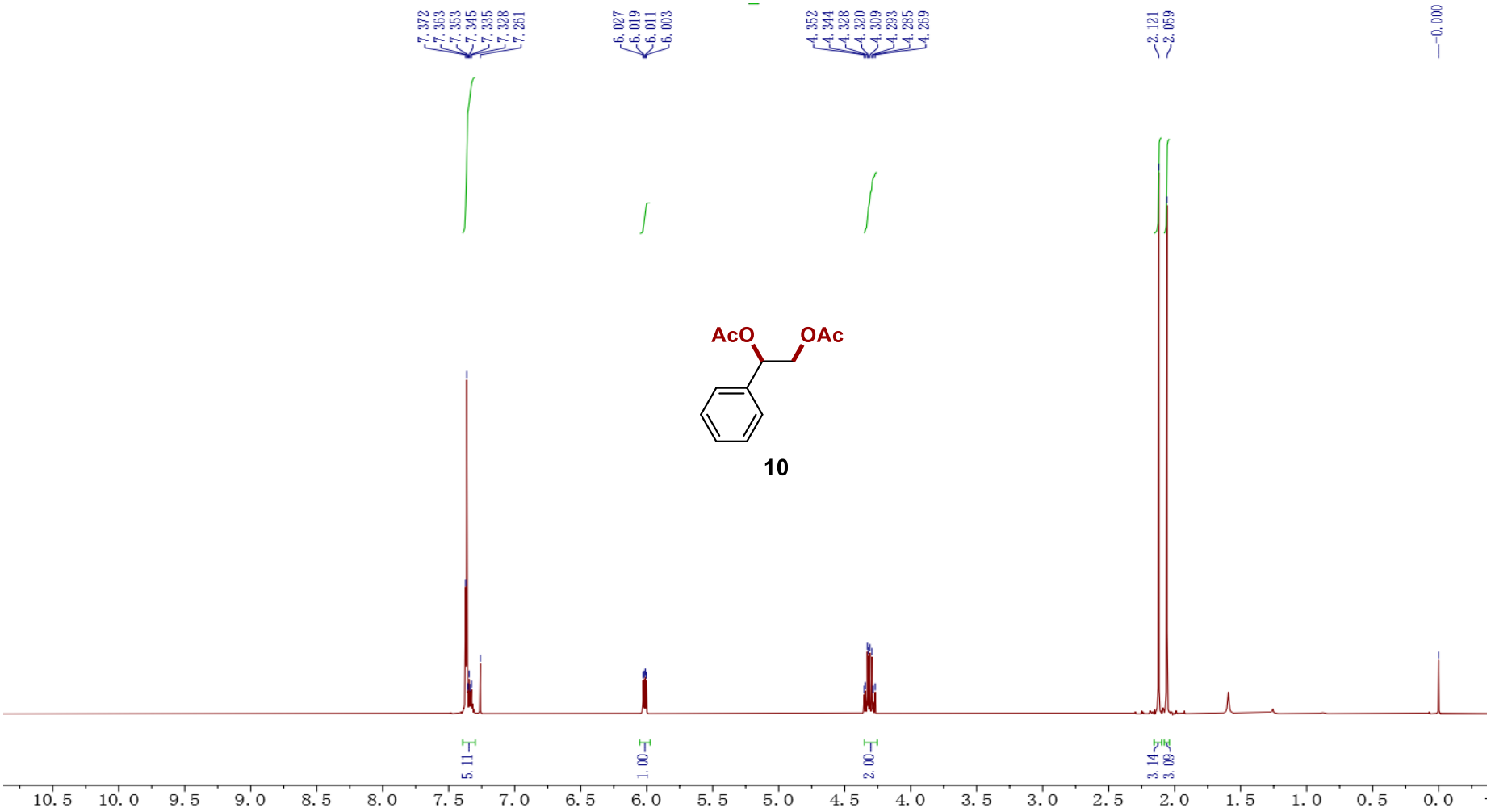
inhibitors of HIV-1 protease

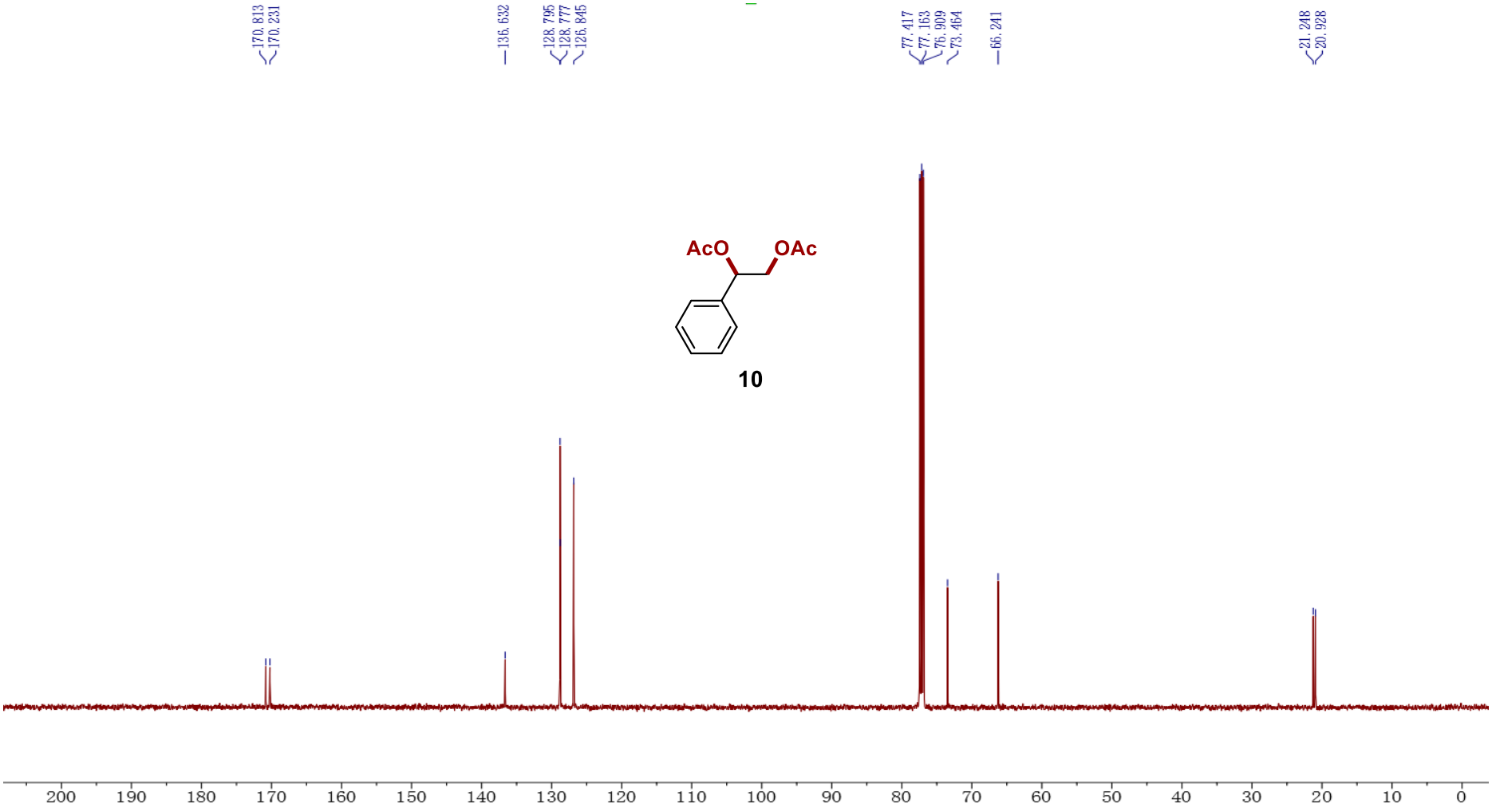
Following **Condition C** with a reaction time of 48 h and Ni plate as cathode, the reaction of 2,3-dihydro-1H-indene **S27** (1.18 g, 10.0 mmol) afforded 1.05 g (45% yield) of **27** as a light yellow oil. **27** (1.05 g) was added to a mixture of saturated solution of sodium carbonate (50 mL) and MeOH (50.0 mL), and the mixture was stirred at 60 ℃ for 12 h. The mixture was then poured into water and extracted with EtOAc (3×20 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by chromatography (eluent: petroleum ether:ethyl acetate = 2:1) to afford 631 mg **27'** (93%, *anti:syn* = 7:1) as a yellow solid.[11]

^{1}H NMR (CD_3OD, 500 MHz, mixture of regioisomers): 7.38-7.33 (m, 1.12H), 7.23-7.17 (m, 3.4H), 4.89-4.86 (m, 1.12H), 4.04-4.37 (m, 0.15H), 4.27-4.23 (m, 1H), 3.21 (dd, J = 16.0 Hz, J = 7.0 Hz, 1H), 3.04 (dd, J = 16.0 Hz, J = 6.0 Hz, 0.15H), 2.92 (dd, J = 16.0 Hz, J = 4.5 Hz, 0.15H), 2.72 (dd, J = 16.0 Hz, J = 7.0 Hz, 1H).

^{13}C NMR (CD_3OD, 125 MHz, mixture of regioisomers): 143.9, 141.6, 140.7, 129.4, 129.3, 128.0, 127.8, 126.1, 126.0, 125.8, 125.4, 82.5, 81.6, 76.8, 74.7, 39.1, 38.9. (one carbon overlapped).

4. NMR Spectra

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OAc
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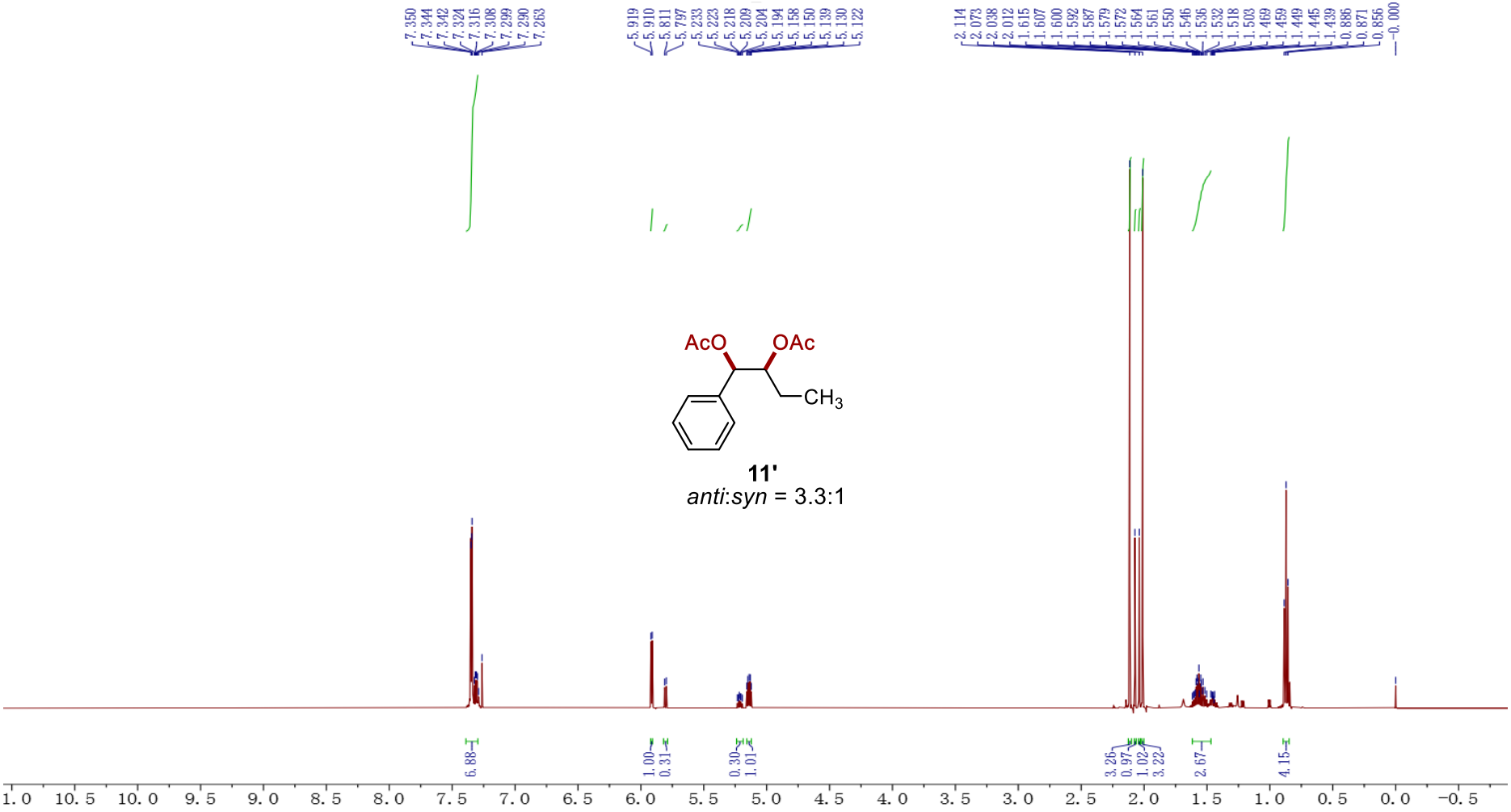
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5.233
5.223
5.218
5.209
5.204
5.194
5.158
5.150
5.139
5.130
5.122
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2.012
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1.579
1.572
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1.449
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0.886
0.871
0.856
0.000
AcO
OAc
CH3
11'
anti:syn = 3.3:1
6.88
1.00
0.31
0.30
1.01
3.26
0.97
1.02
3.22
2.67
4.15
1.0
10.5
10.0
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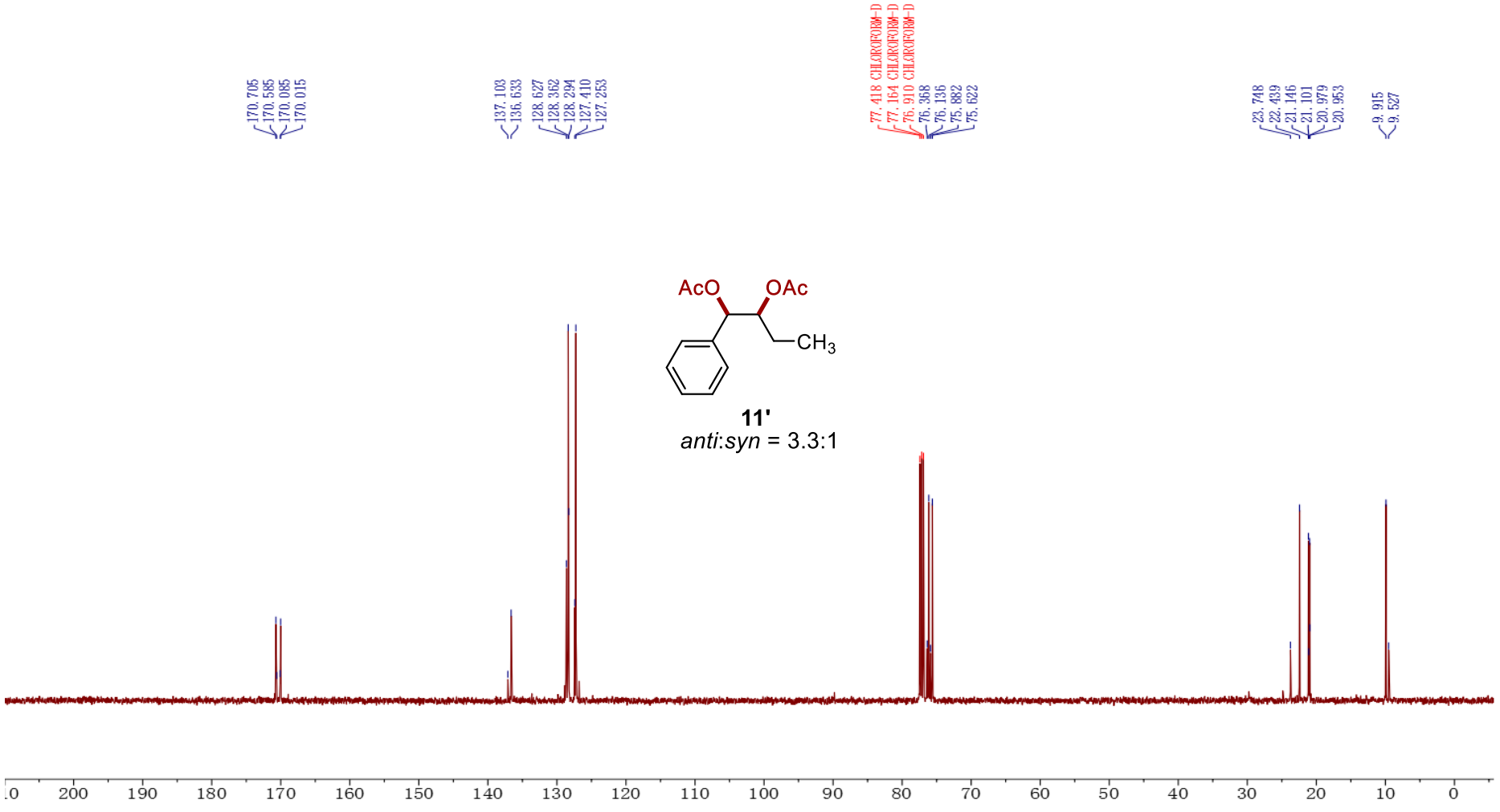
−0.5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21.146
21.101
20.979
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9.915
9.527
AcO
OAc
CH3
11'
anti:syn = 3.3:1
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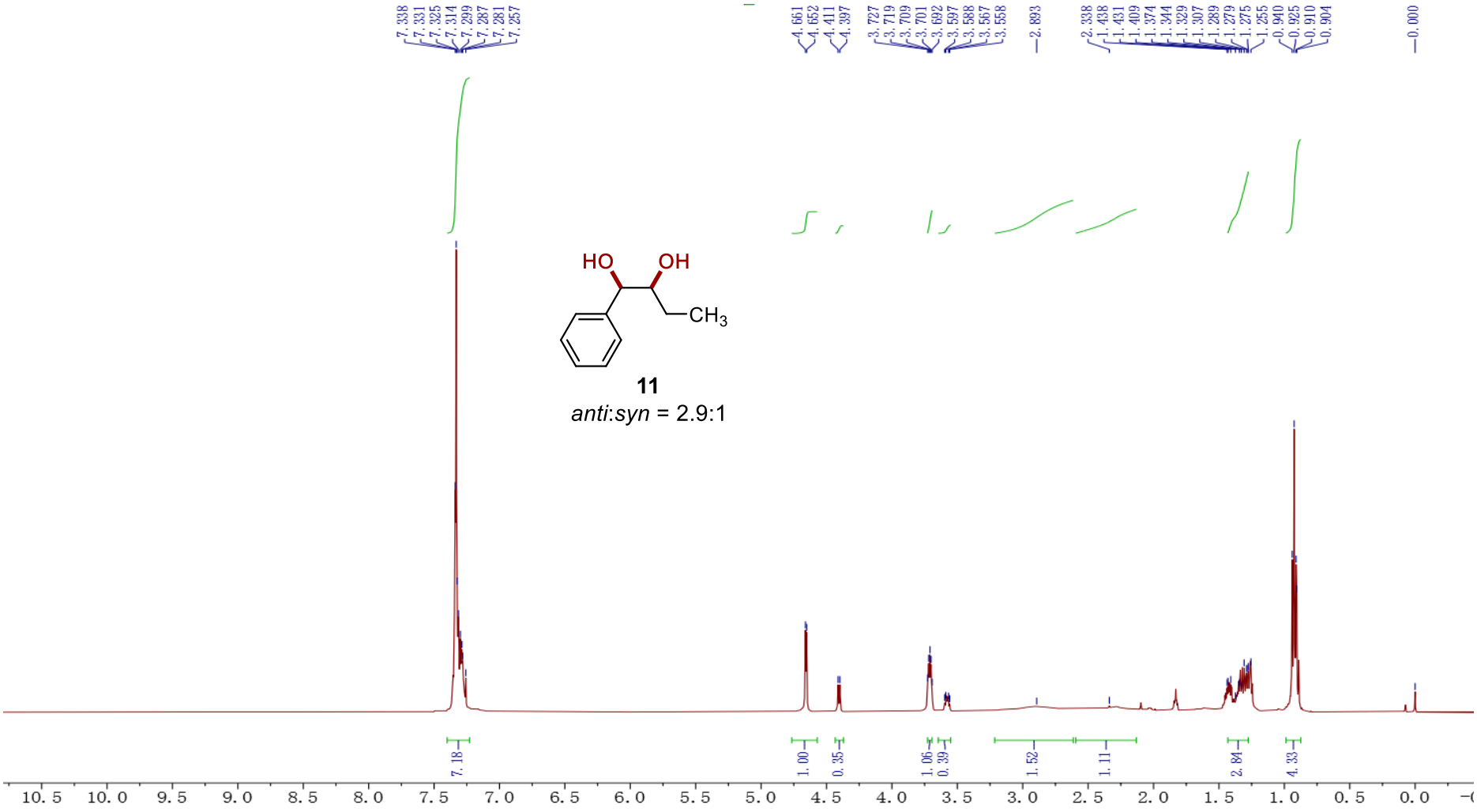
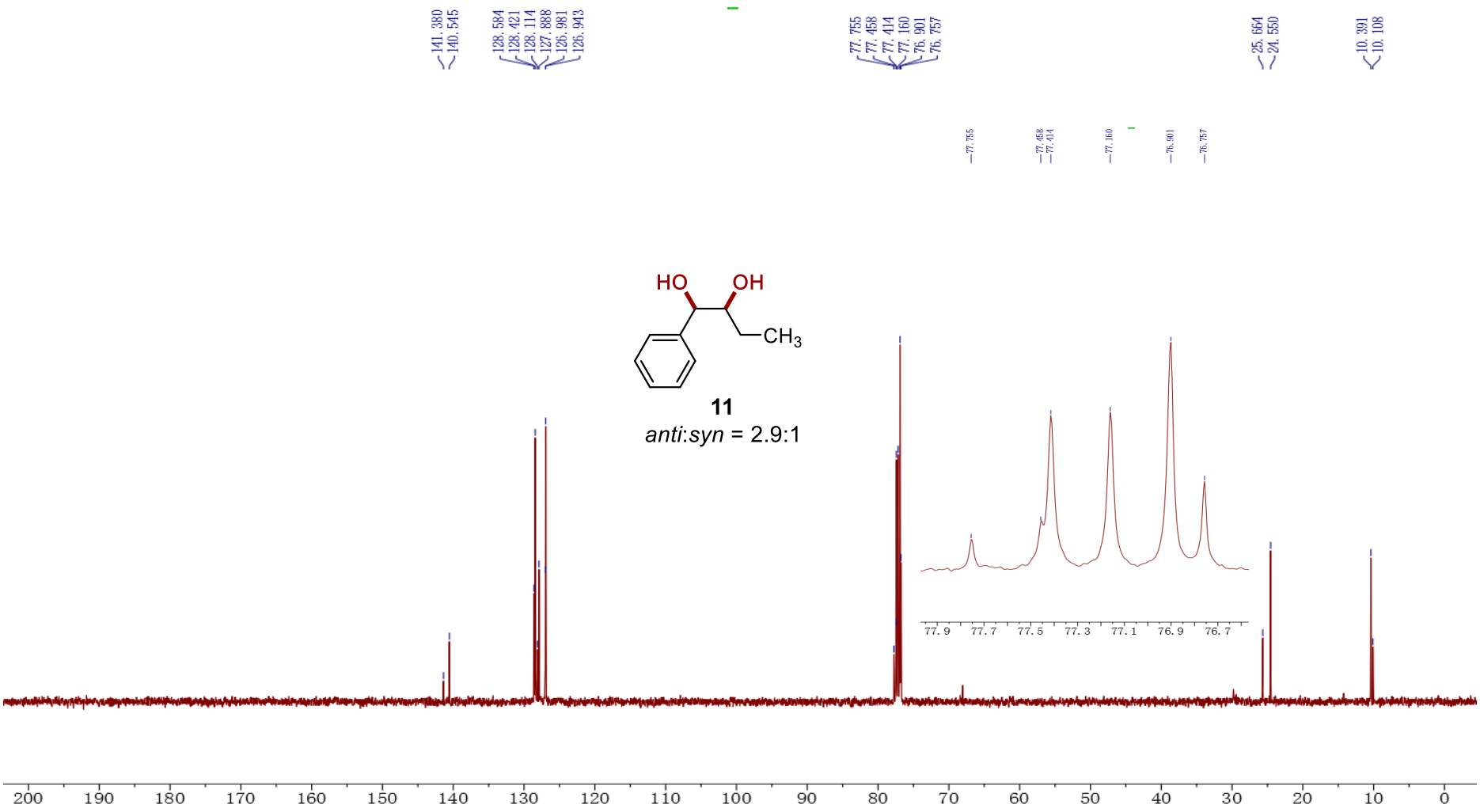
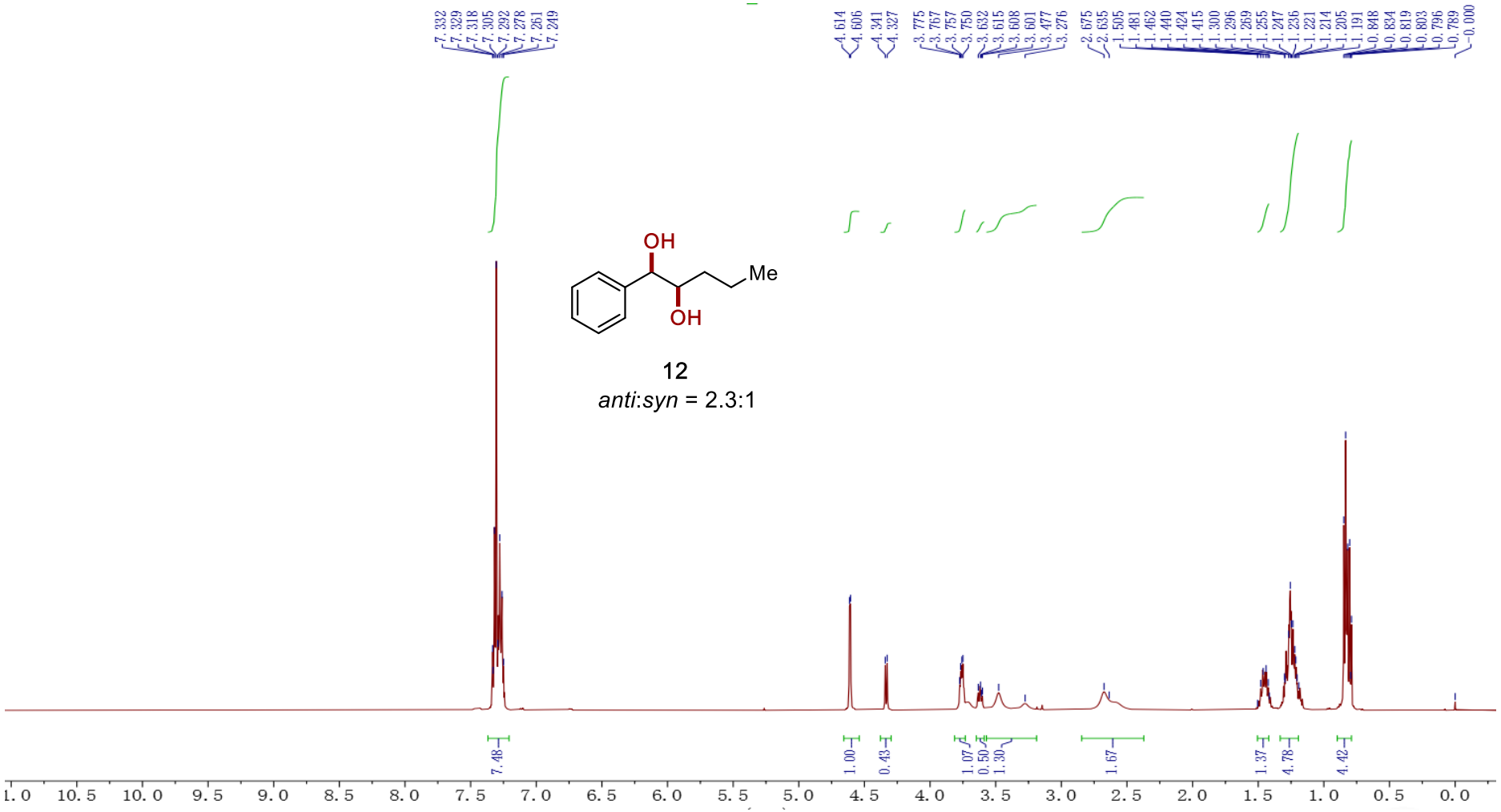


11

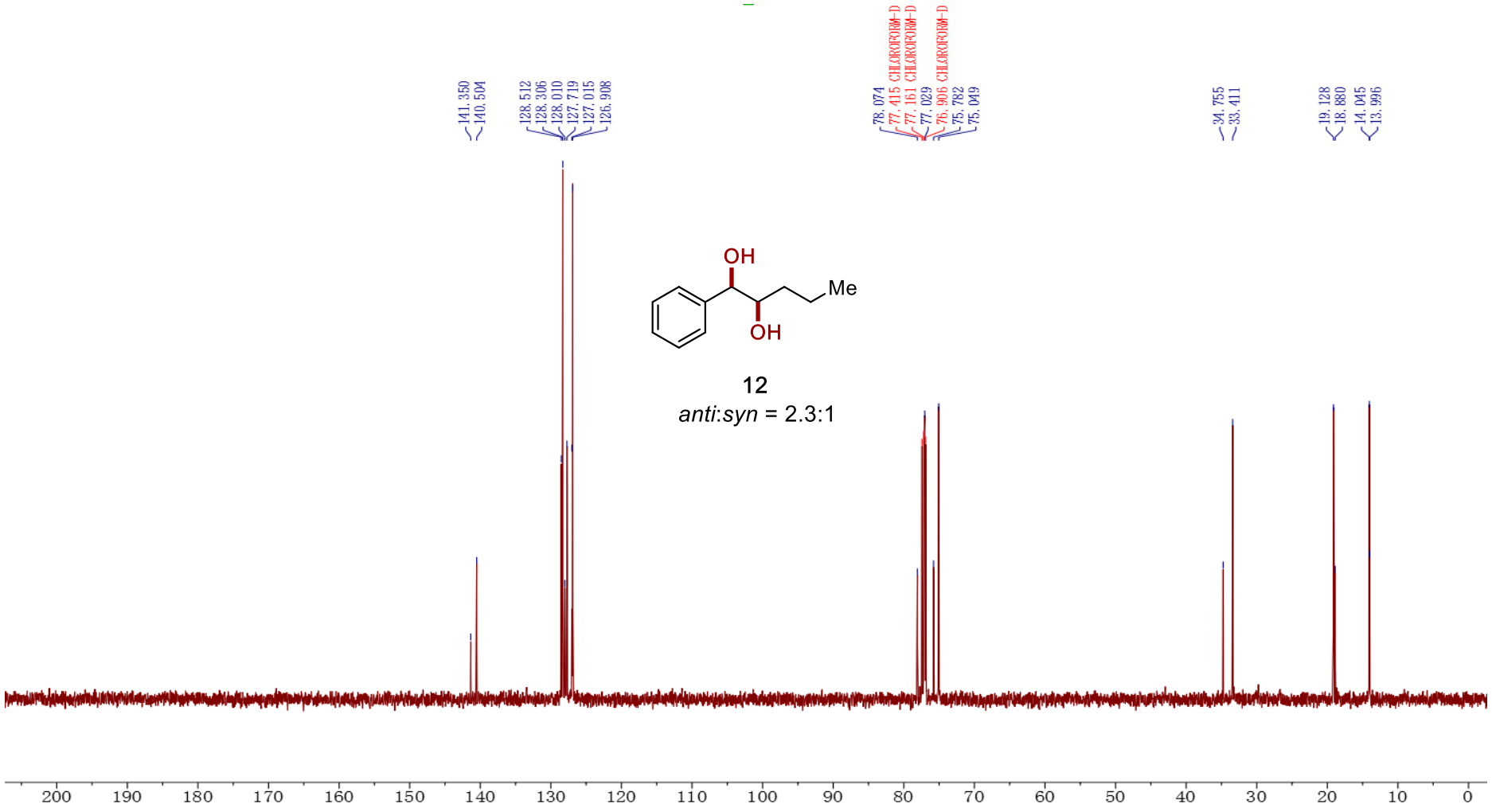
anti:*syn* = 2.9:1


141.380
140.545
128.584
128.421
128.114
127.888
126.981
126.943
77.755
77.458
77.414
77.160
76.901
76.757
25.664
24.550
10.391
10.108
HO
OH
CH3
11
anti:syn = 2.9:1
77.9
77.7
77.5
77.3
77.1
76.9
76.7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



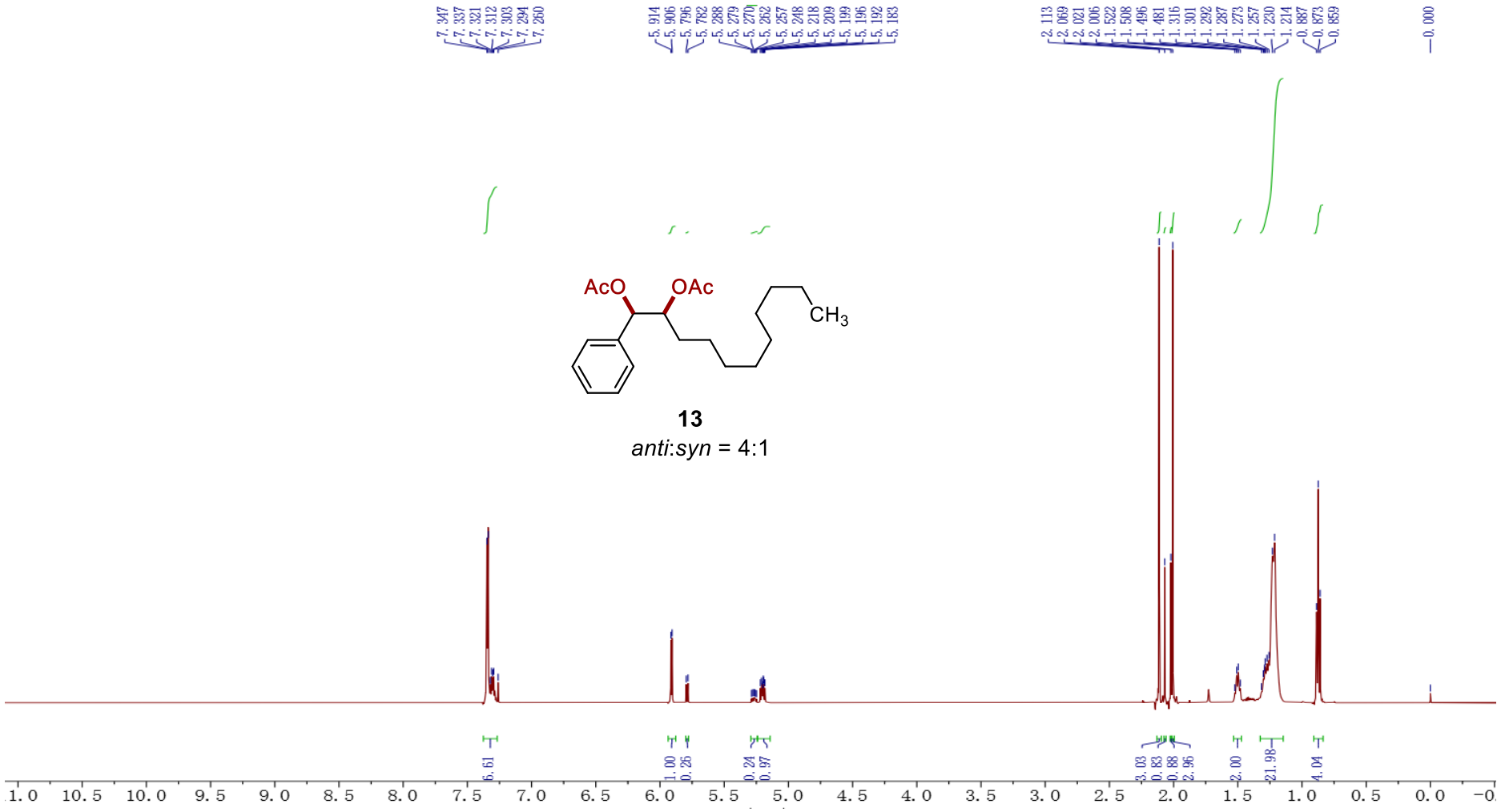
12

anti:*syn* = 2.3:1



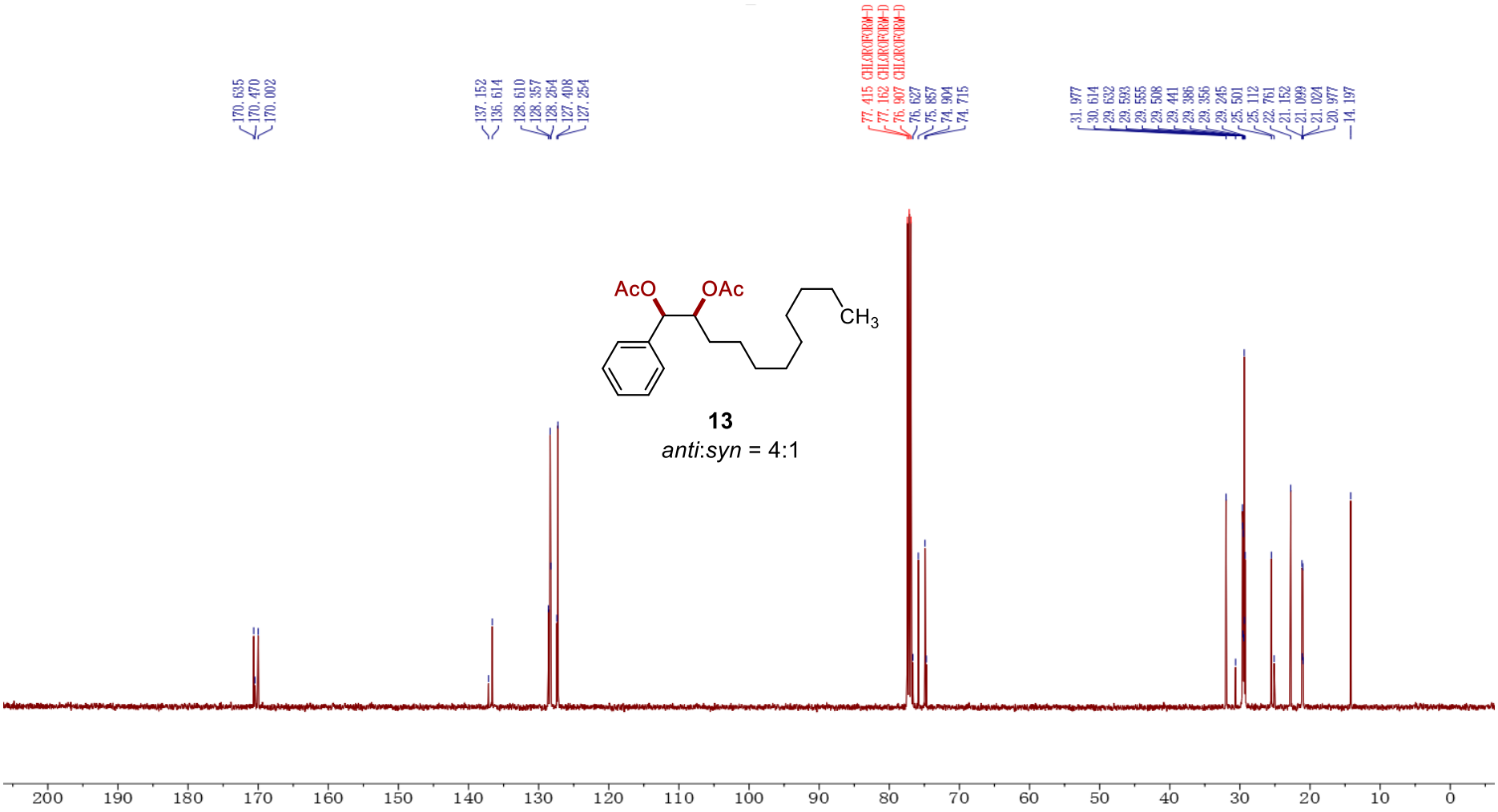
12

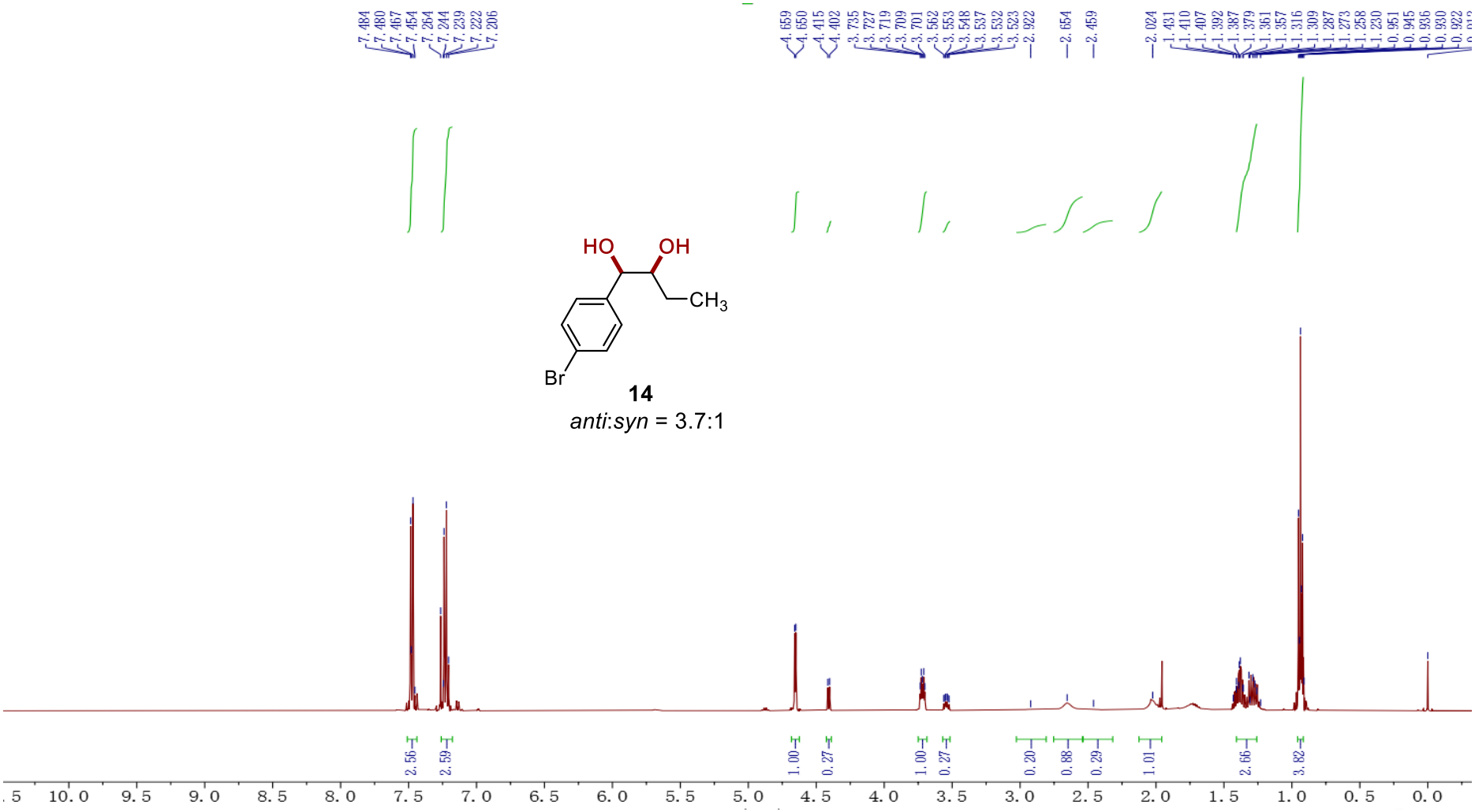
anti:*syn* = 2.3:1

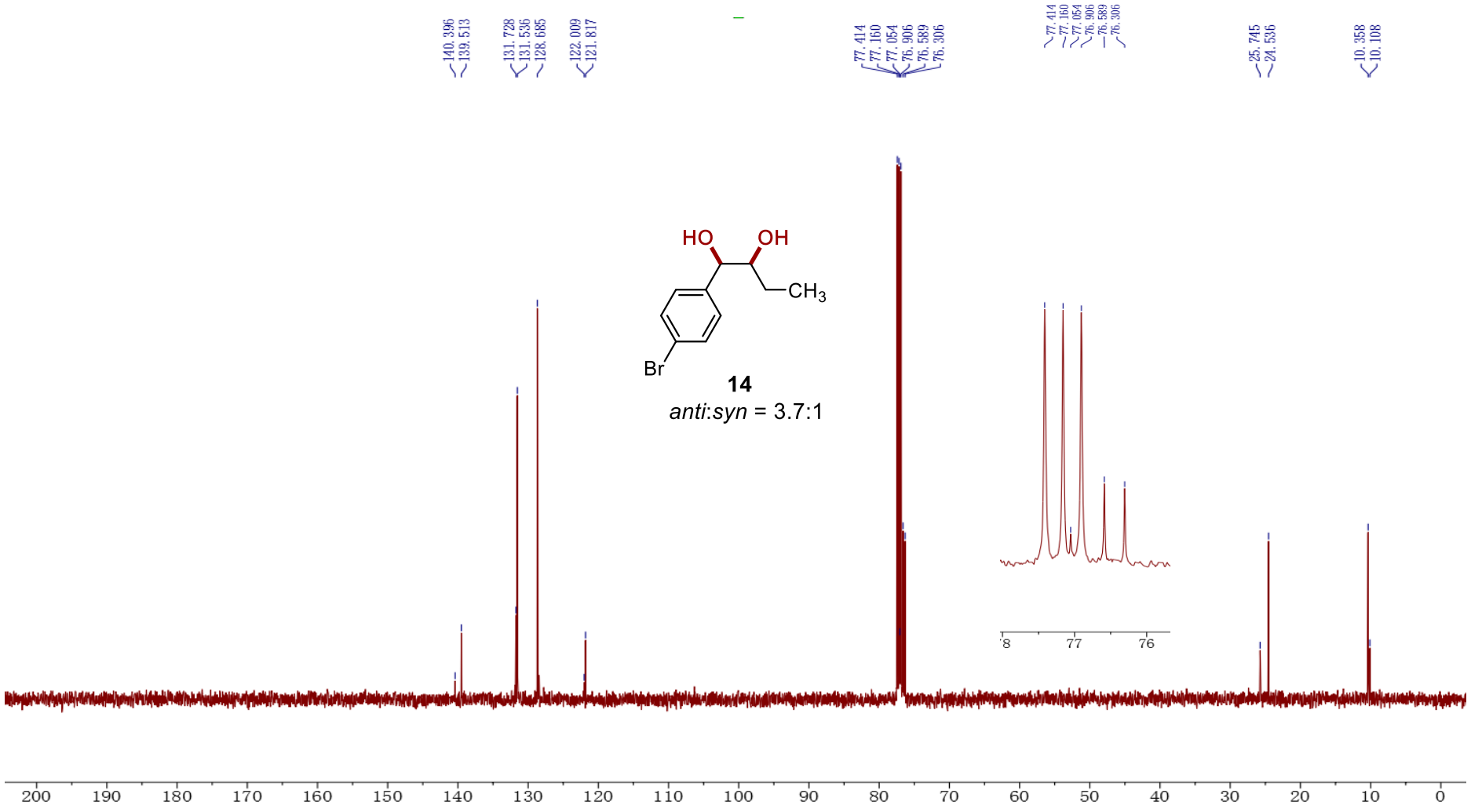


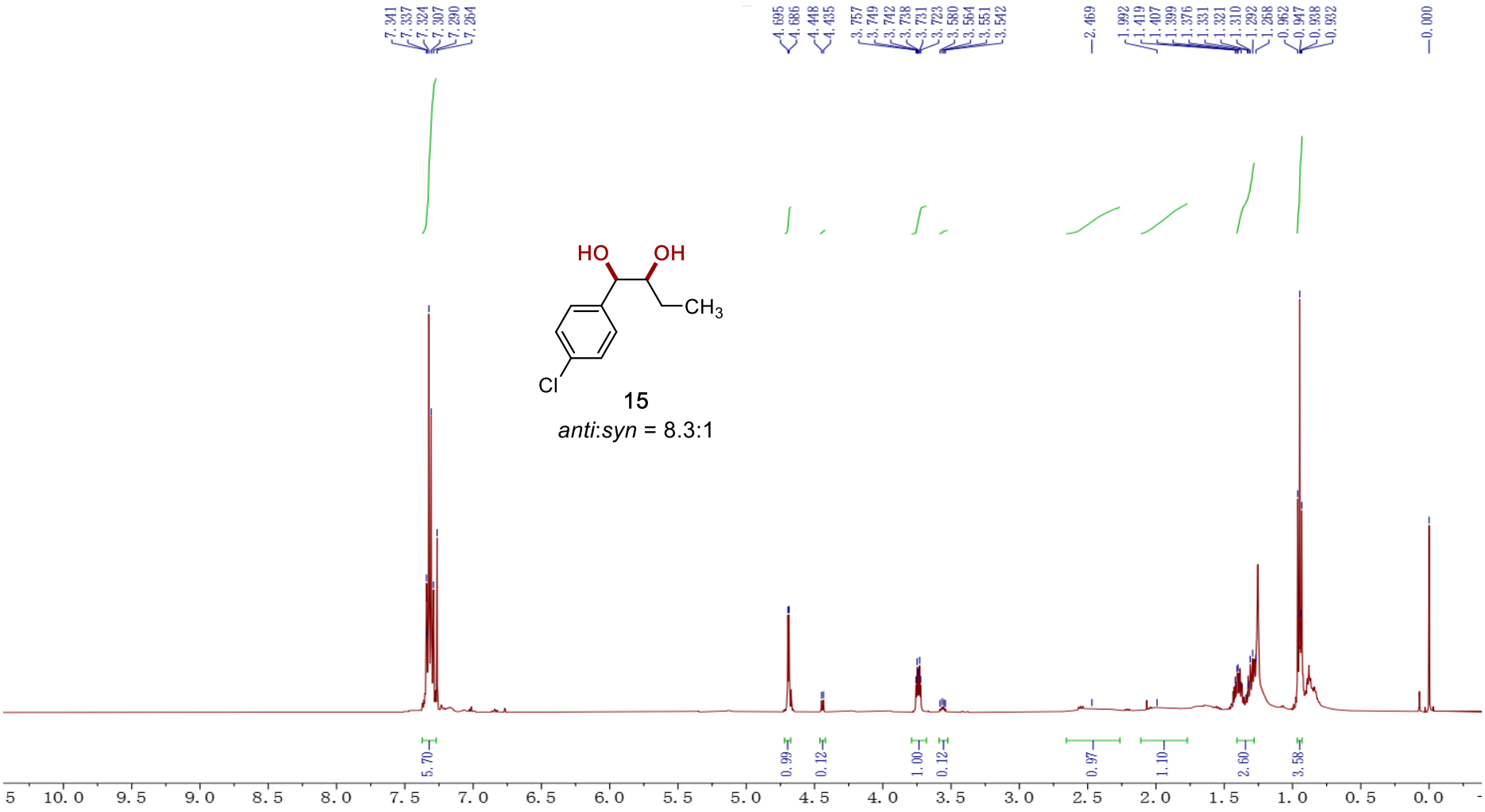
13

anti:*syn* = 4:1


170.635
170.470
170.002
137.152
136.614
128.610
128.357
128.264
127.408
127.254
77.415 CHLOROFORM-D
77.162 CHLOROFORM-D
76.907 CHLOROFORM-D
76.627
75.857
74.904
74.715
31.977
30.614
29.632
29.593
29.555
29.508
29.441
29.386
29.356
29.245
25.501
25.112
22.761
21.152
21.099
21.024
20.977
14.197
AcO
OAc
CH3
13
anti:syn = 4:1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

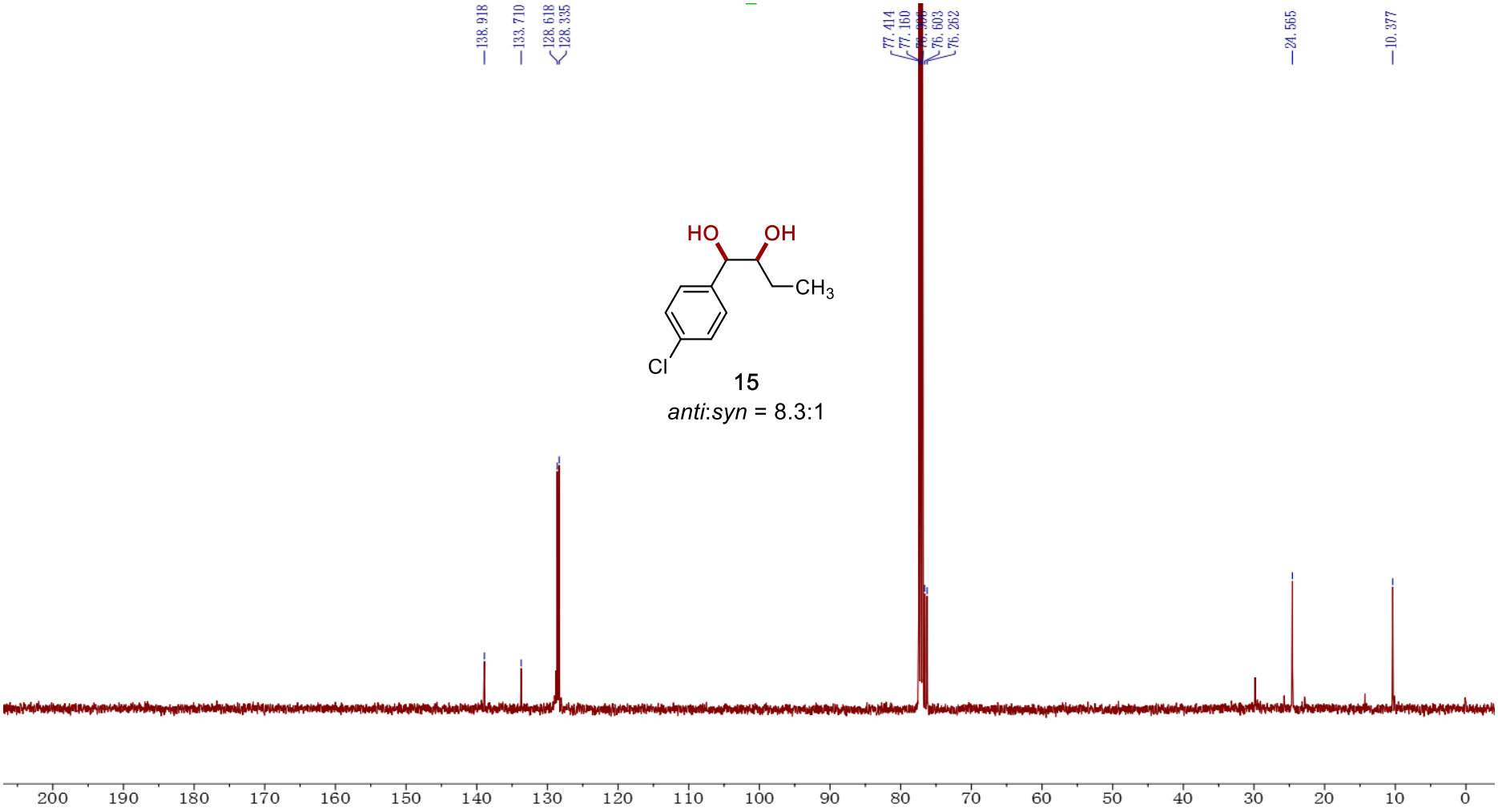

7.484
7.480
7.467
7.454
7.264
7.244
7.239
7.222
7.206
4.659
4.650
4.415
4.402
3.735
3.727
3.719
3.709
3.701
3.562
3.553
3.548
3.537
3.532
3.523
2.922
2.654
2.459
2.024
1.431
1.410
1.407
1.392
1.387
1.379
1.361
1.357
1.316
1.309
1.287
1.273
1.258
1.230
0.951
0.945
0.936
0.930
0.922
HO
OH
CH3
Br
14
anti:syn = 3.7:1
2.56
2.59
1.00
0.27
1.00
0.27
0.20
0.88
0.29
1.01
2.66
3.82
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


140.396
139.513
131.728
131.536
128.685
122.009
121.817
77.414
77.160
77.054
76.906
76.589
76.306
25.745
24.536
10.358
10.108
HO
OH
CH3
Br
14
anti:syn = 3.7:1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



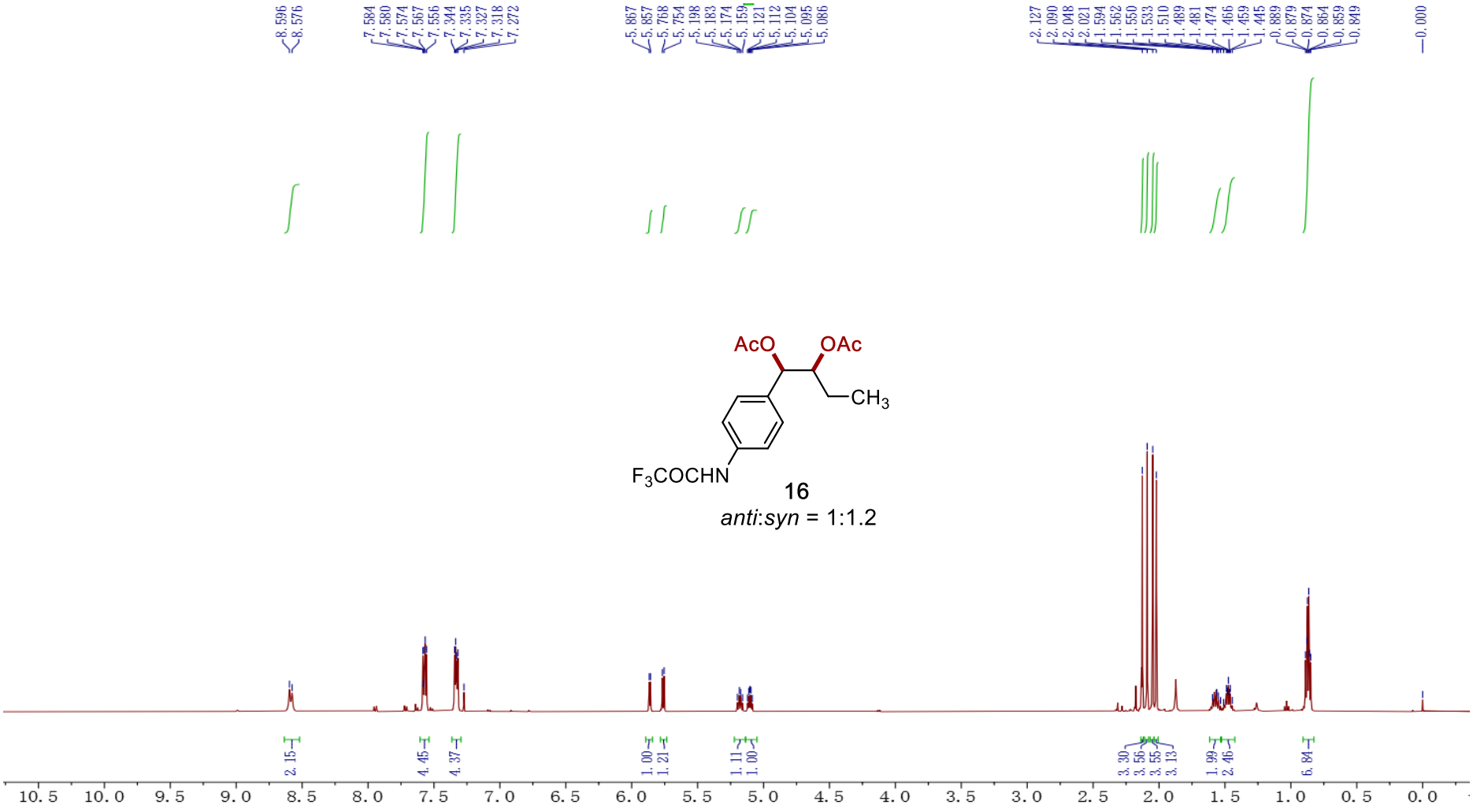
15

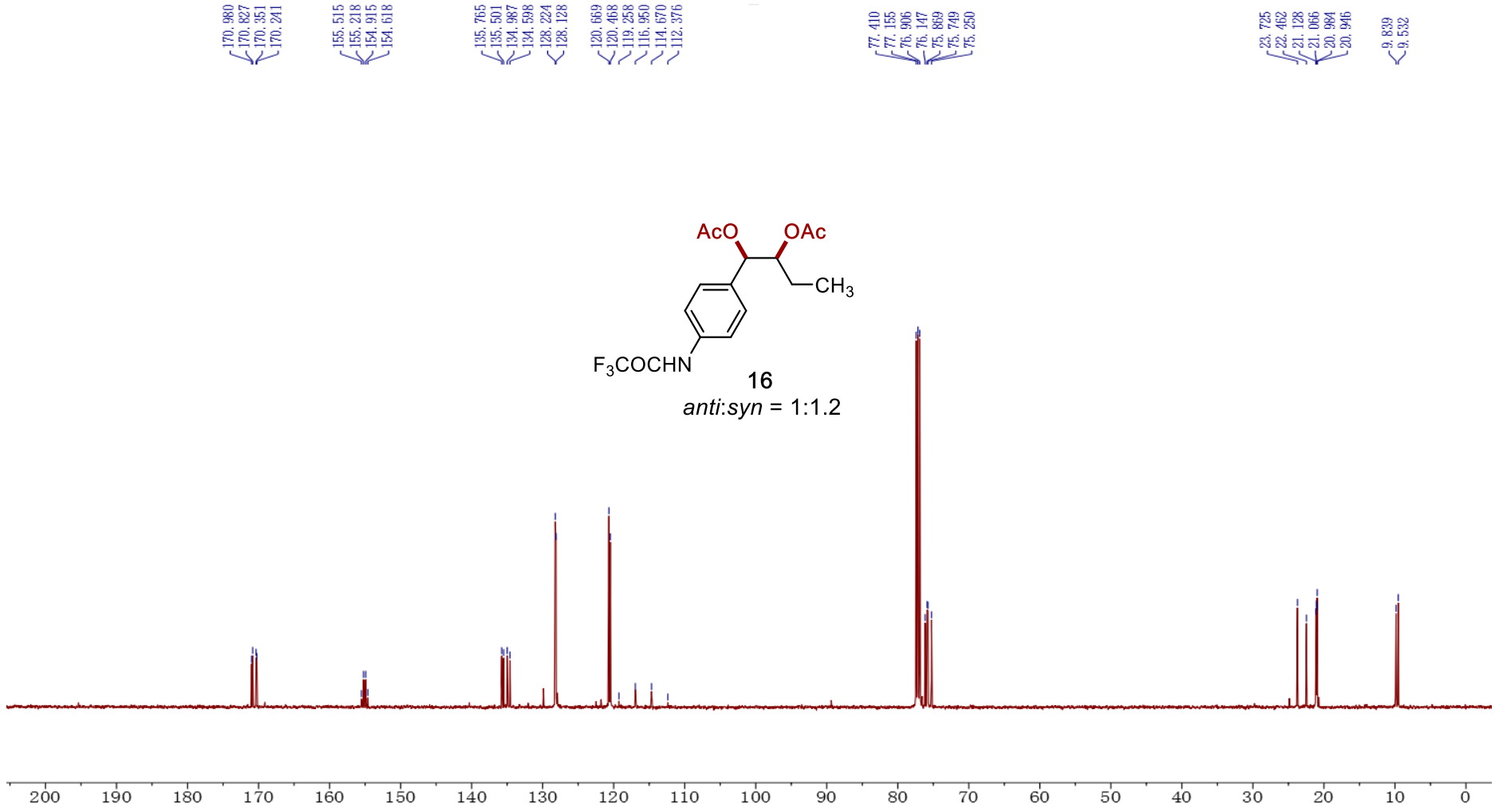
anti:*syn* = 8.3:1

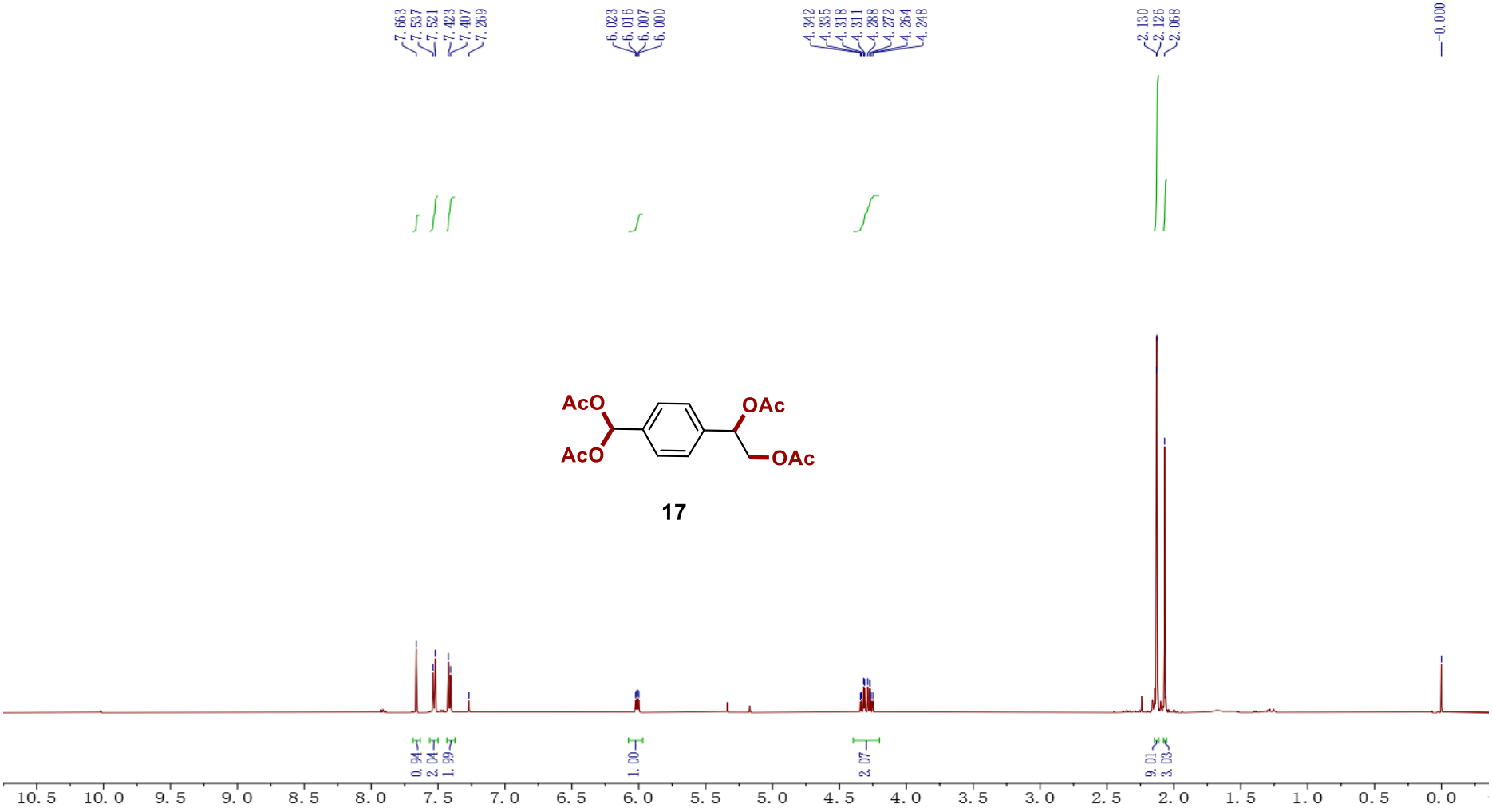


15

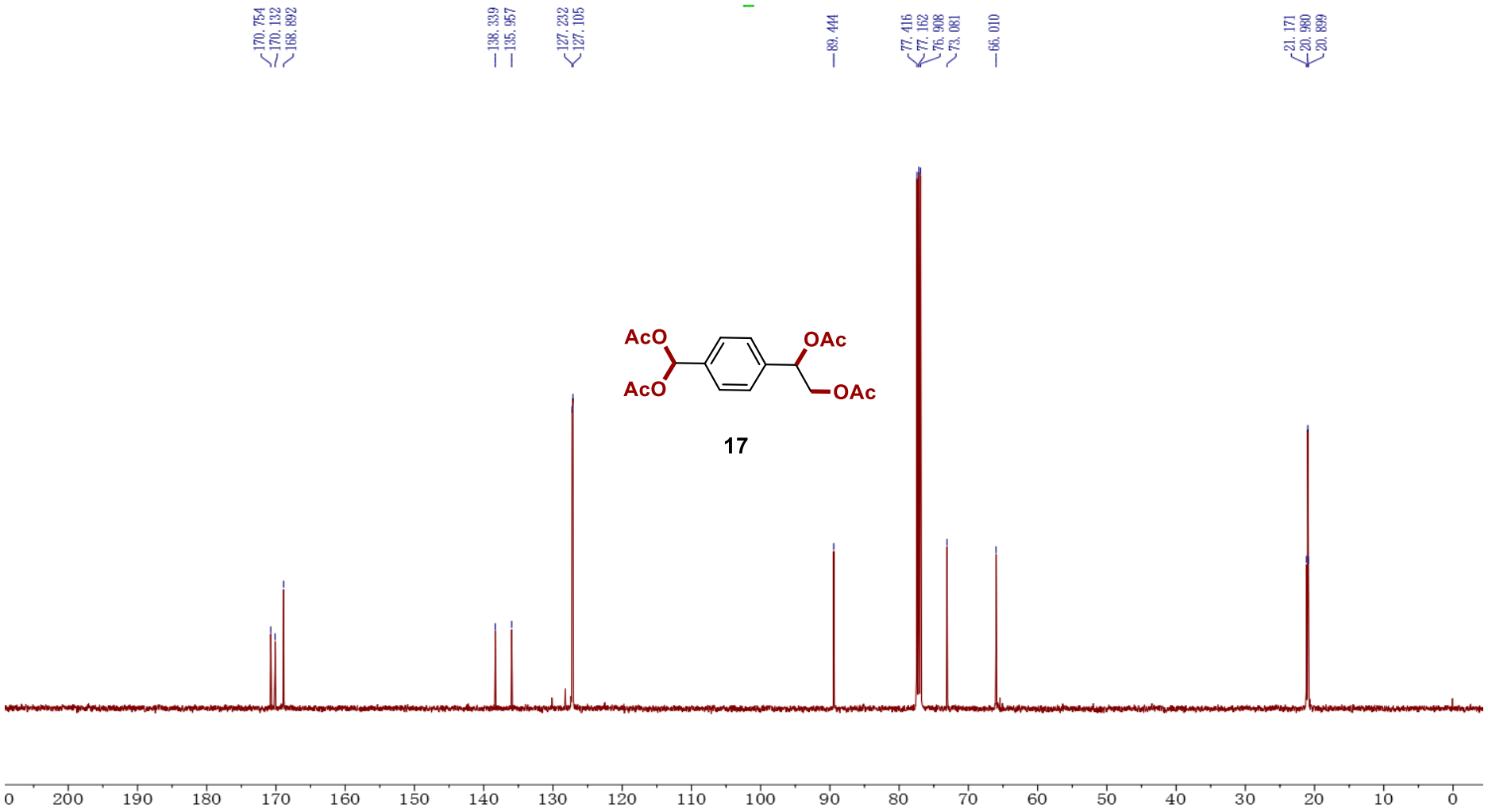
anti:*syn* = 8.3:1

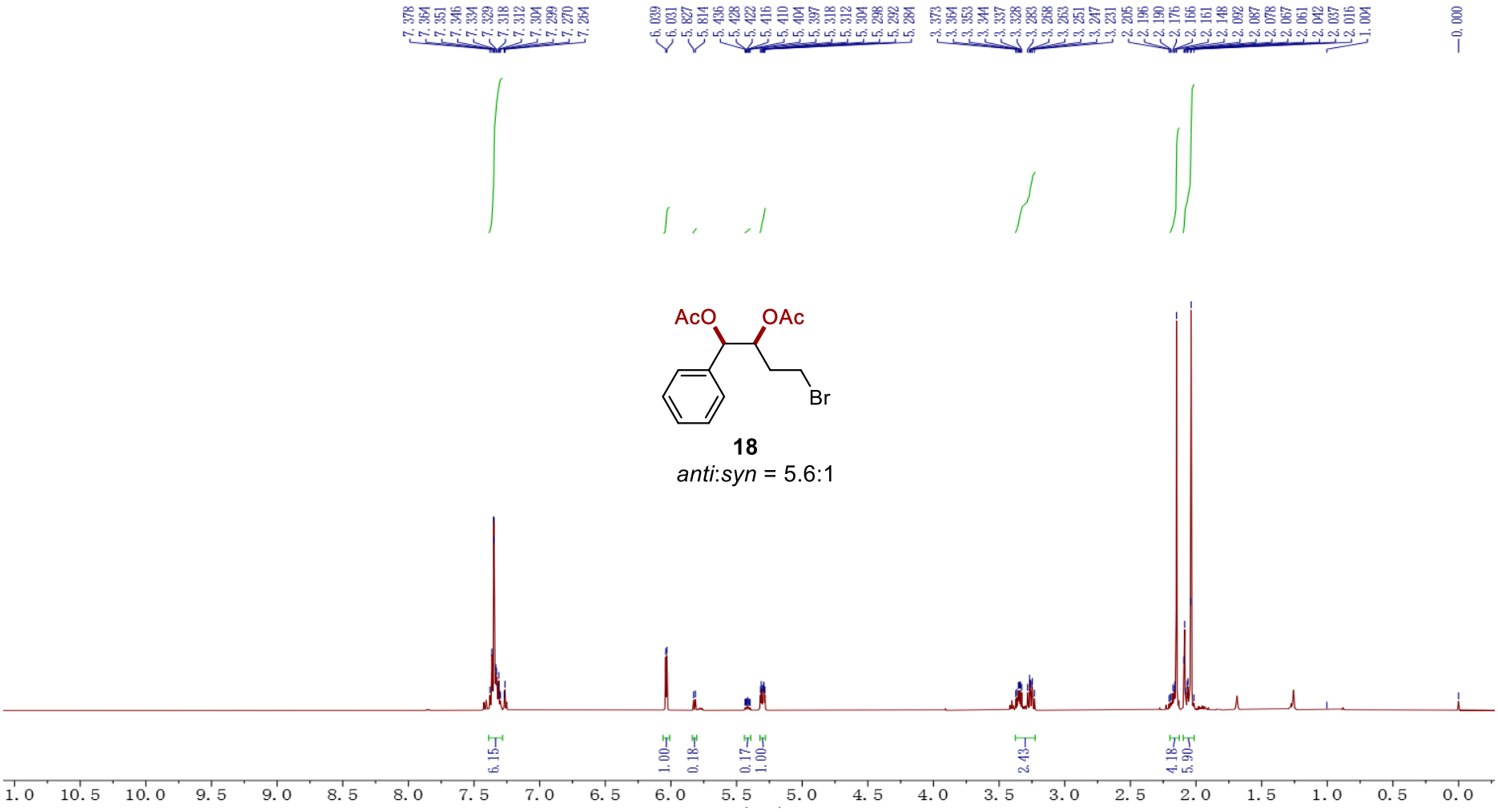

8.596
8.576
7.584
7.580
7.574
7.567
7.556
7.344
7.335
7.327
7.318
7.272
5.867
5.857
5.768
5.754
5.198
5.183
5.174
5.159
5.121
5.112
5.104
5.095
5.086
2.127
2.090
2.048
2.021
1.594
1.562
1.550
1.533
1.510
1.489
1.481
1.474
1.466
1.459
1.445
0.889
0.879
0.874
0.864
0.859
0.849
0.000
AcO
OAc
CH3
F3COCHN
16
anti:syn = 1:1.2
2.15
4.45
4.37
1.00
1.21
1.11
1.00
3.30
3.56
3.55
3.13
1.99
2.46
6.84
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


170.980
170.827
170.351
170.241
155.515
155.218
154.915
154.618
135.765
135.501
134.987
134.598
128.224
128.128
120.669
120.468
119.258
116.950
114.670
112.376
77.410
77.155
76.906
76.147
75.869
75.749
75.250
23.725
22.462
21.128
21.066
20.984
20.946
9.839
9.532
AcO
OAc
CH3
F3COCHN
16
anti:syn = 1:1.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.663
7.537
7.521
7.423
7.407
7.269
6.023
6.016
6.007
6.000
4.342
4.335
4.318
4.311
4.288
4.272
4.264
4.248
2.130
2.126
2.068
0.000
AcO
AcO
OAc
OAc
0.94
2.04
1.99
1.00
2.07
9.01
3.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

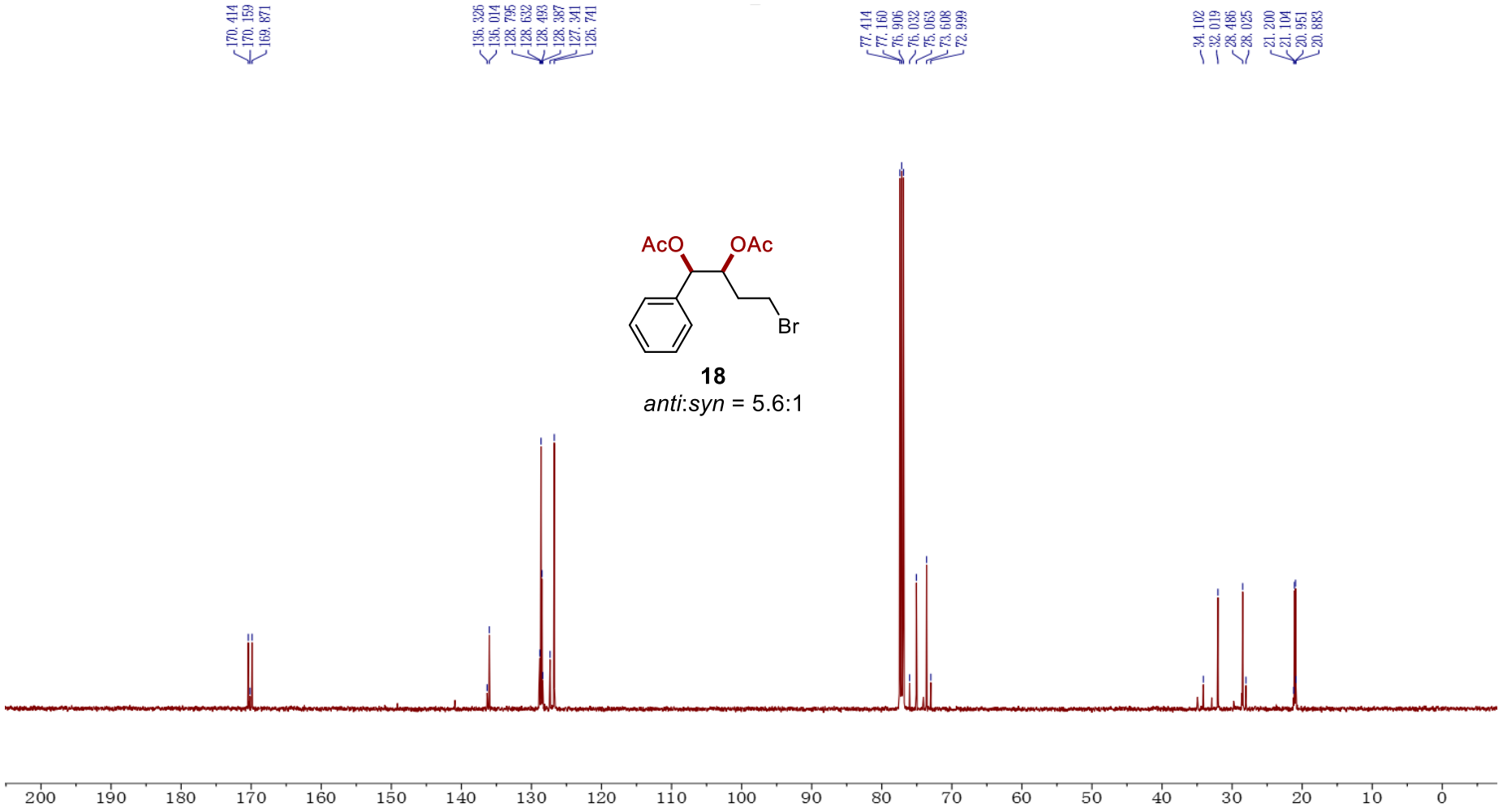
17

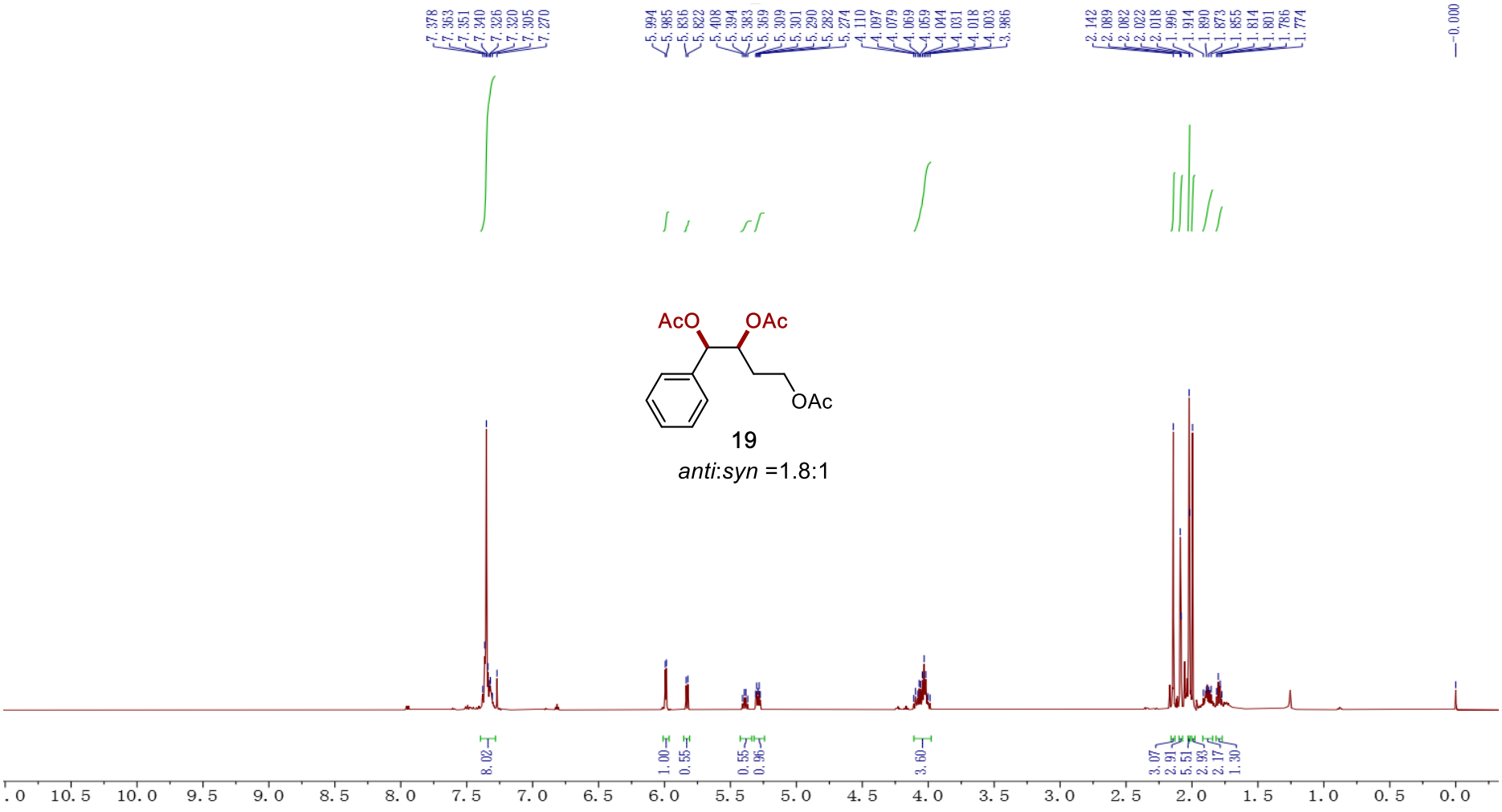

170.754
170.132
168.892
138.339
135.957
127.232
127.105
89.444
77.416
77.162
76.908
73.081
66.010
21.171
20.980
20.899
AcO
AcO
OAc
OAc
17
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

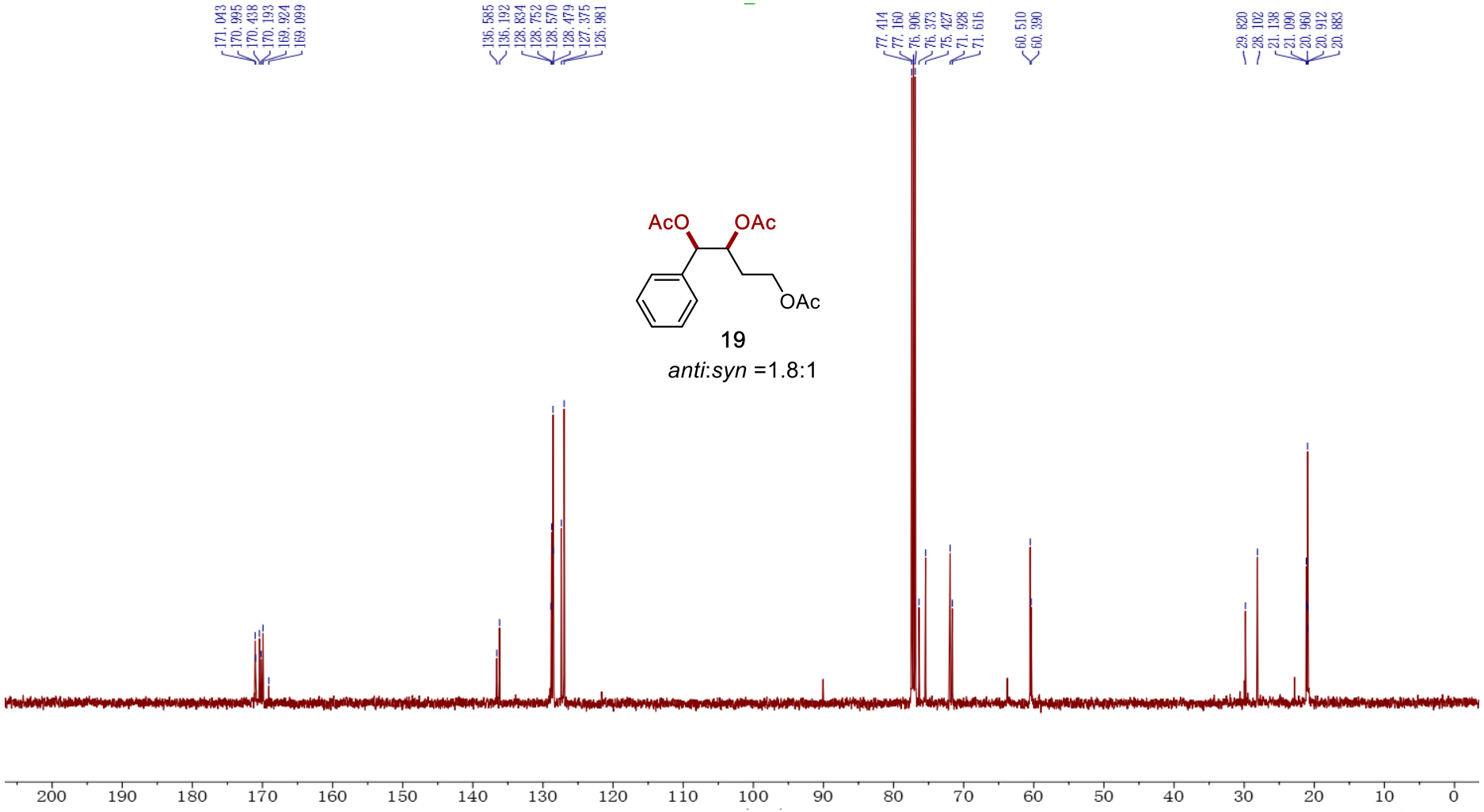


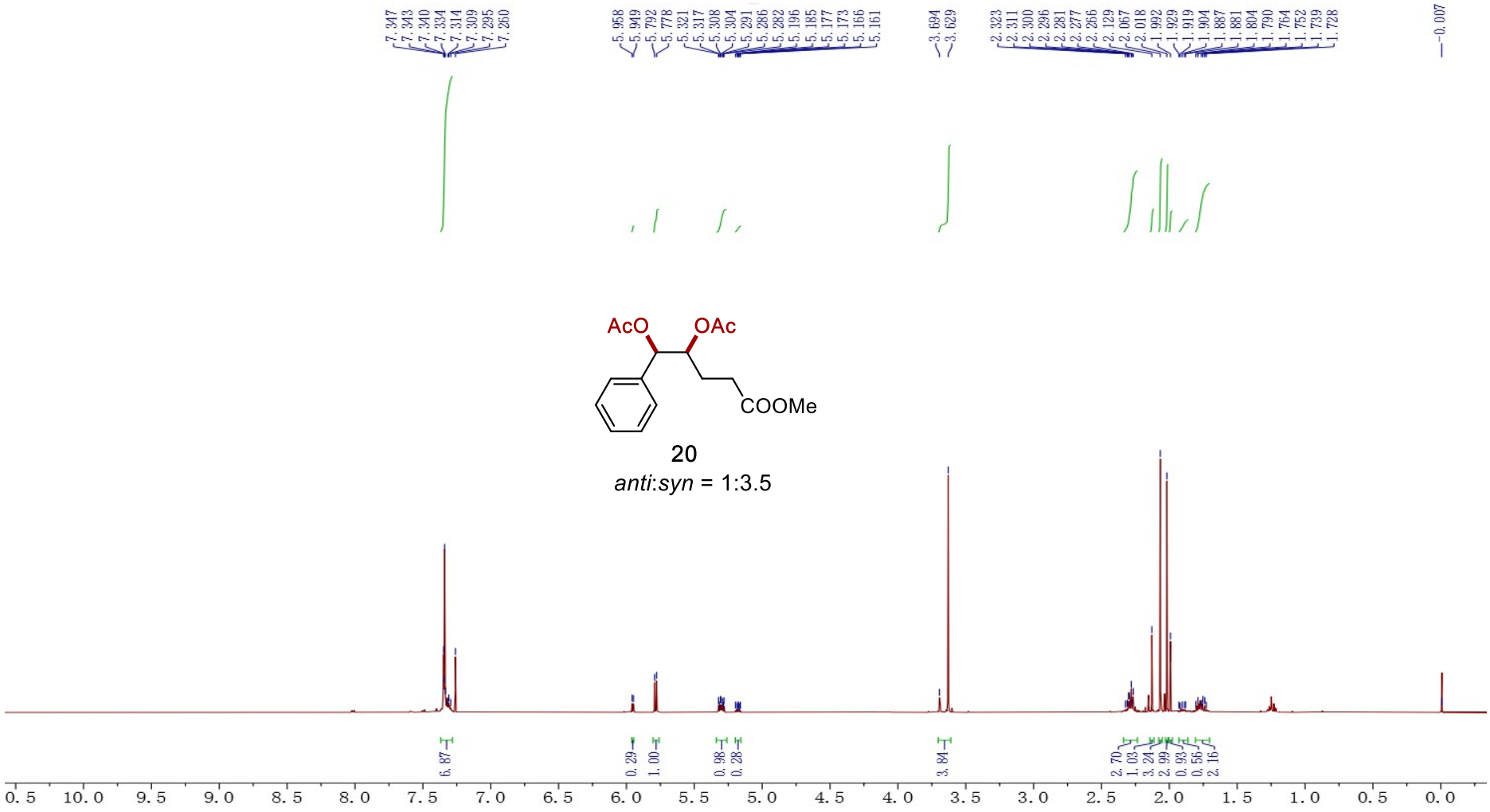
18

anti:*syn* = 5.6:1


170.414
170.159
169.871
136.326
136.014
128.795
128.632
128.493
128.387
127.941
126.741
77.414
77.160
76.906
76.032
75.063
73.608
72.999
34.102
32.019
28.486
28.025
21.200
21.104
20.951
20.883
AcO
OAc
Br
18
anti:syn = 5.6:1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

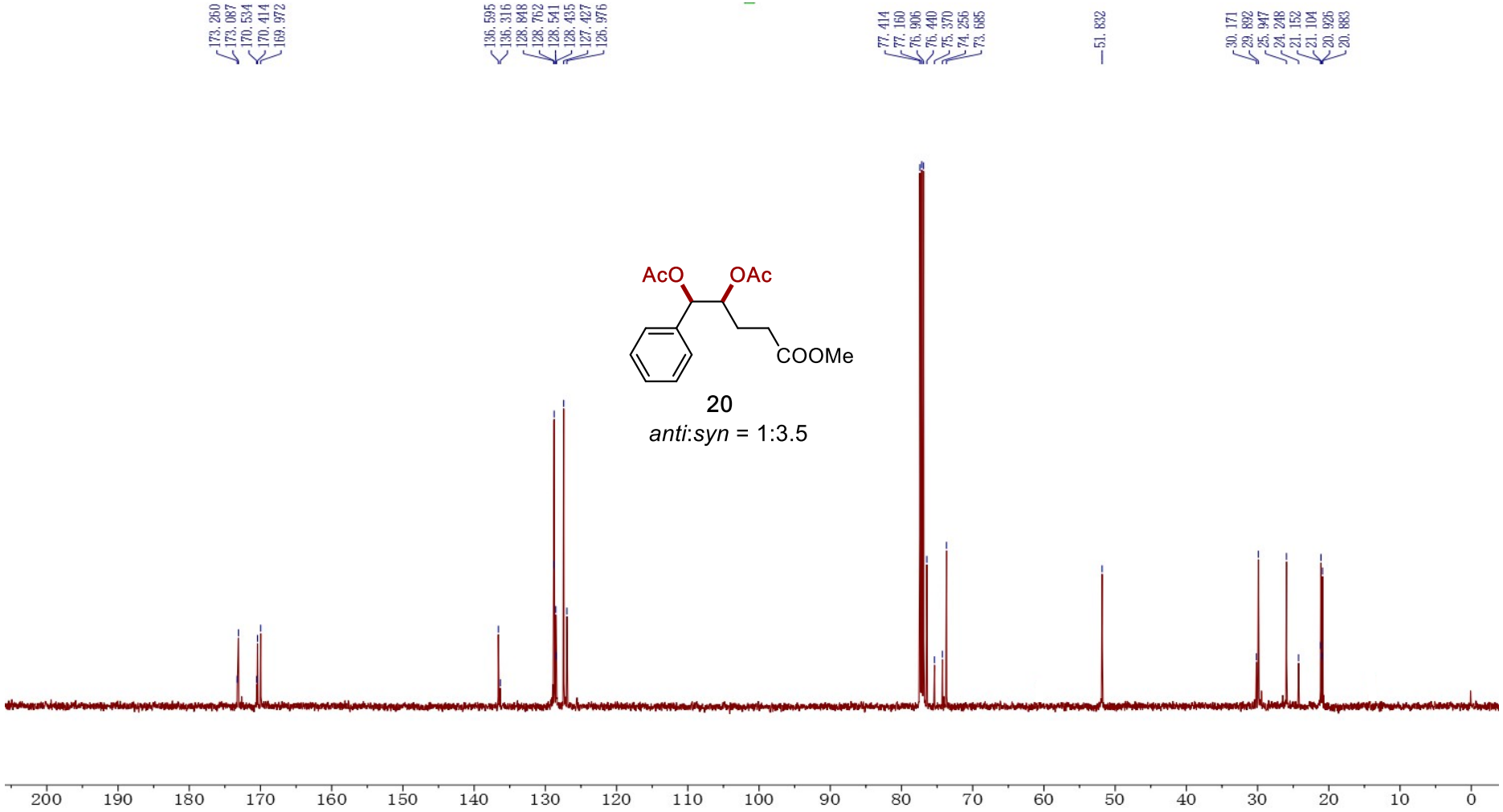

7.378
7.363
7.351
7.340
7.326
7.320
7.305
7.270
5.994
5.985
5.836
5.822
5.408
5.394
5.383
5.369
5.309
5.301
5.290
5.282
5.274
4.110
4.097
4.079
4.069
4.059
4.044
4.031
4.018
4.003
3.986
2.142
2.089
2.082
2.022
2.018
1.996
1.914
1.890
1.873
1.855
1.814
1.801
1.786
1.774
0.000
AcO
OAc
OAc
19
anti:syn =1.8:1
8.02
1.00
0.55
0.55
0.96
3.60
3.07
2.91
5.51
2.93
2.17
1.30
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

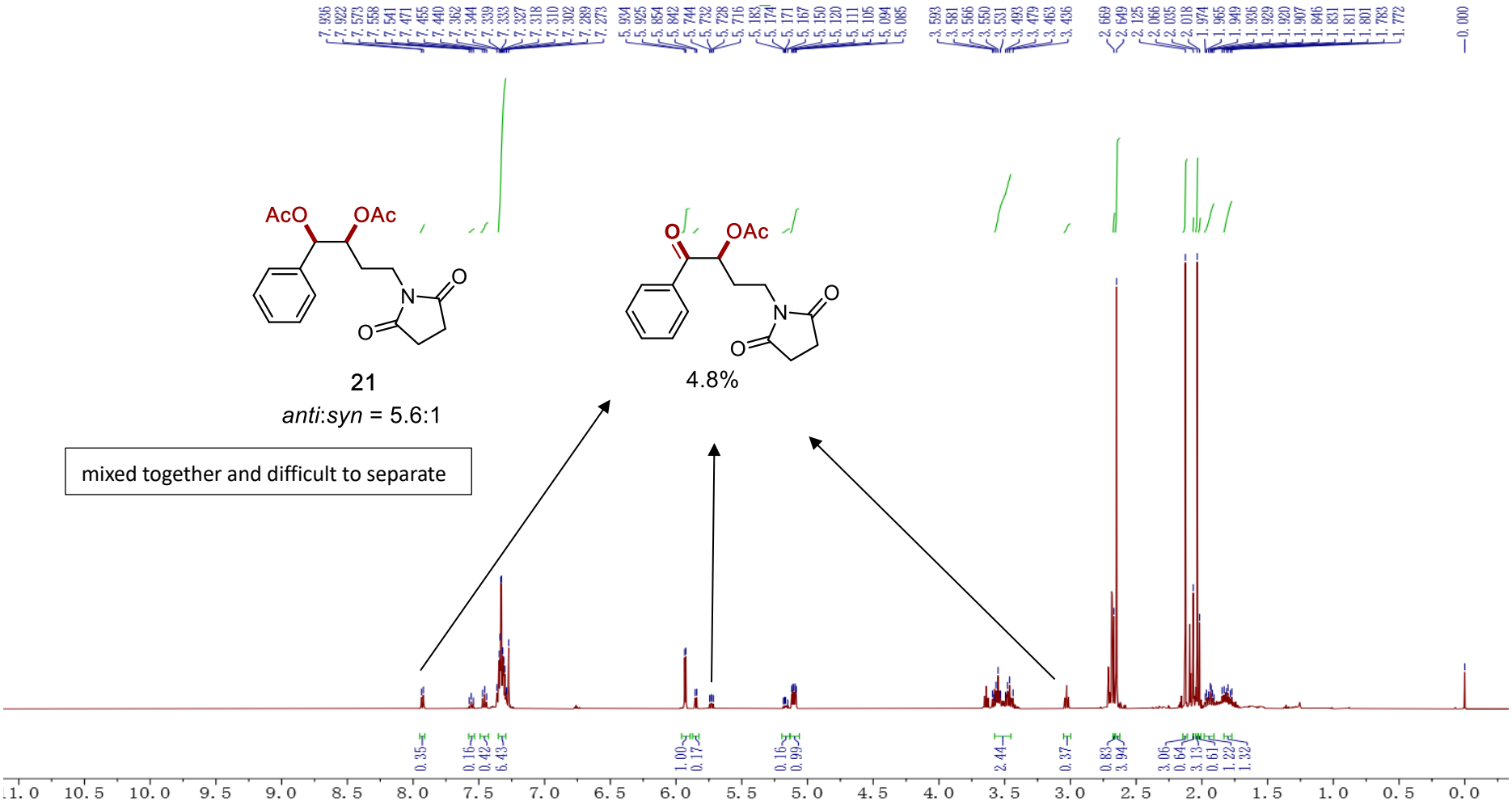

171.043
170.995
170.438
170.193
169.924
169.099
136.585
136.192
128.834
128.752
128.570
128.479
127.375
126.981
77.414
77.160
76.906
76.373
75.427
71.928
71.616
60.510
60.390
29.820
28.102
21.138
21.090
20.960
20.912
20.883
AcO
OAc
OAc
19
anti:syn =1.8:1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

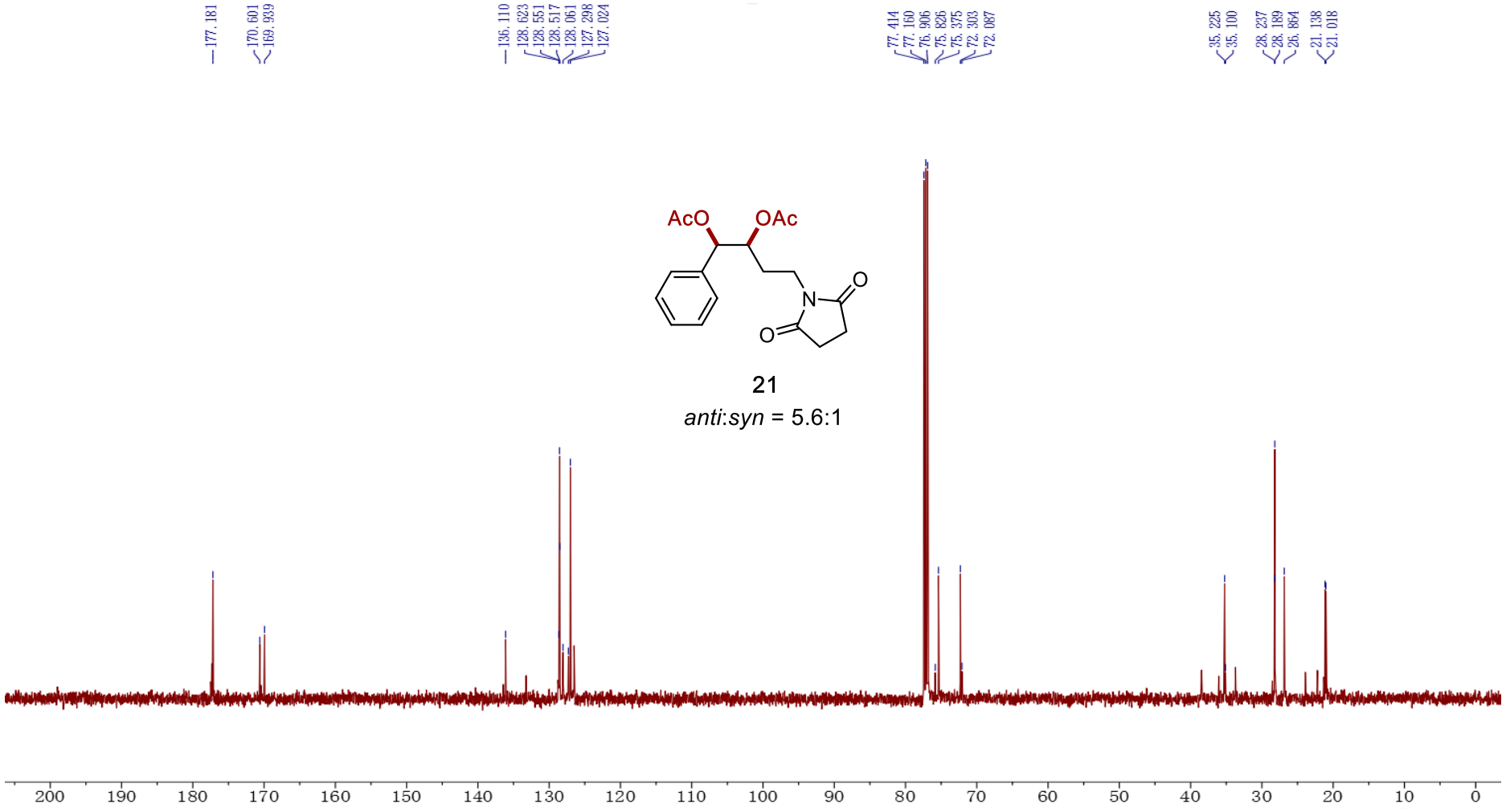


20

anti:*syn* = 1:3.5

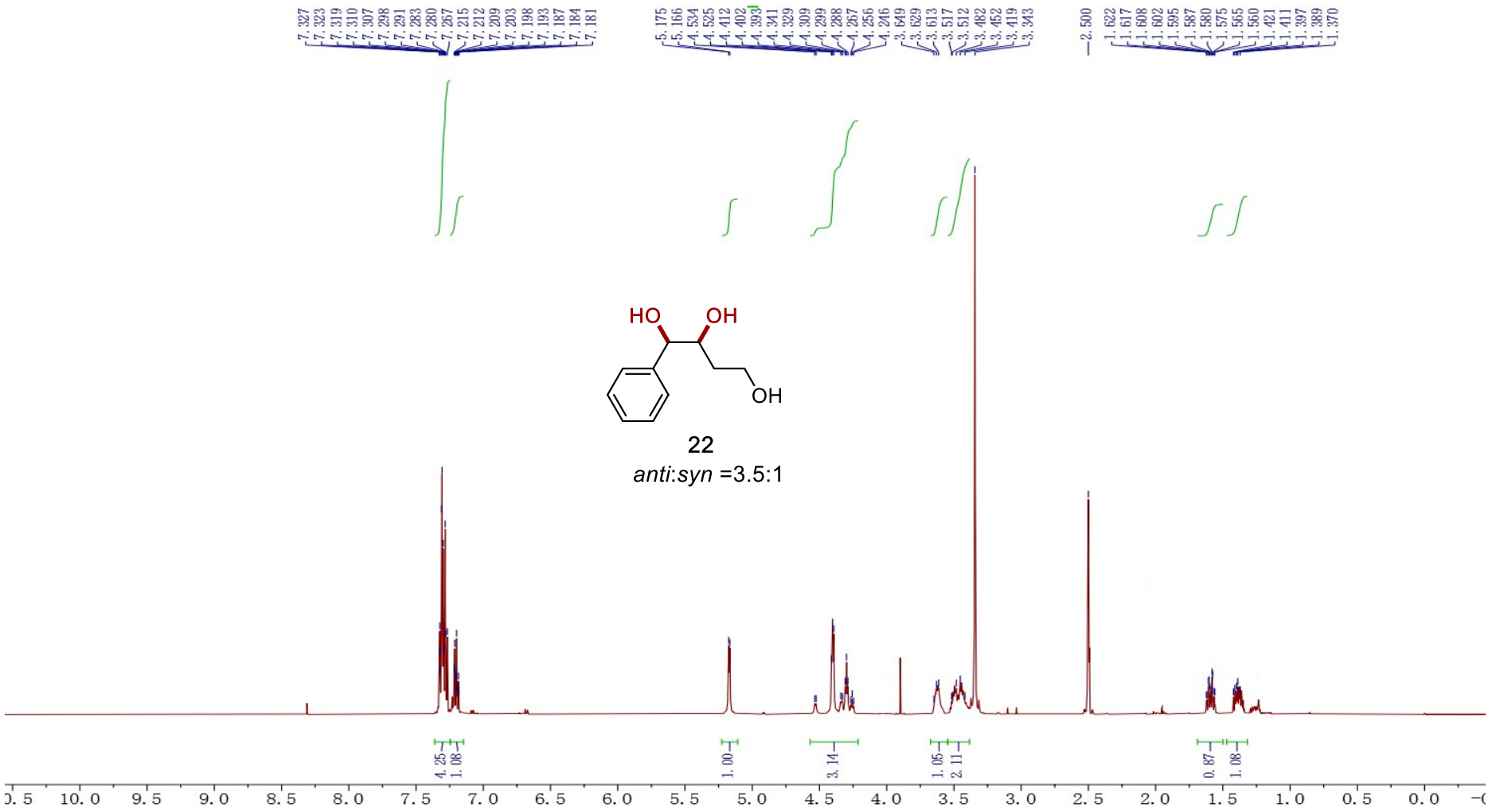

173.260
173.087
170.534
170.414
169.972
136.595
136.316
128.848
128.762
128.541
128.435
127.427
126.976
77.414
77.160
76.906
76.440
75.370
74.256
73.685
51.832
30.171
29.892
25.947
24.248
21.152
21.104
20.926
20.883
AcO
OAc
COOMe
20
anti:syn = 1:3.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


AcO
OAc
O
N
O
O
21
anti:syn = 5.6:1
mixed together and difficult to separate
O
OAc
N
O
O
4.8%



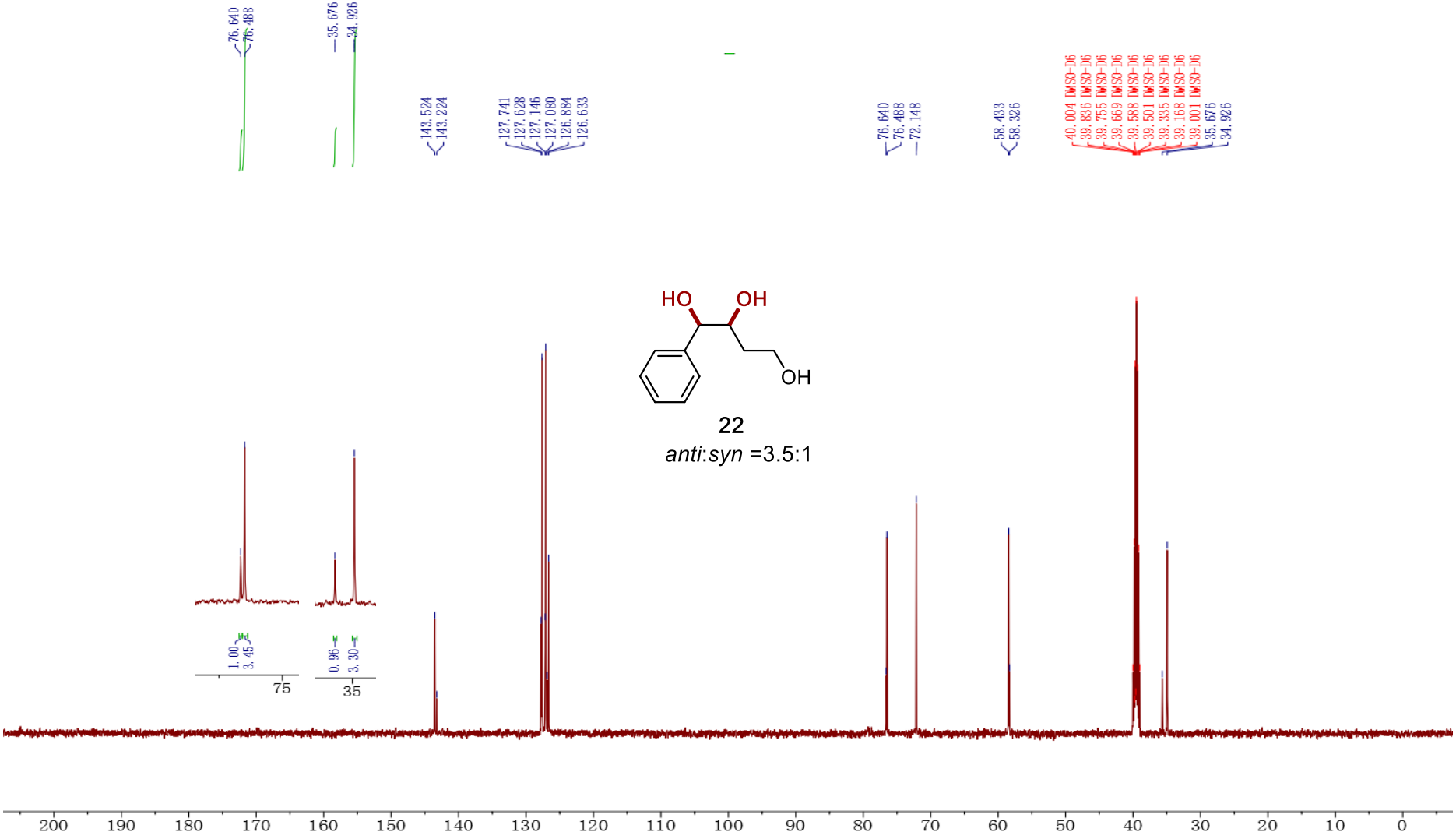
21

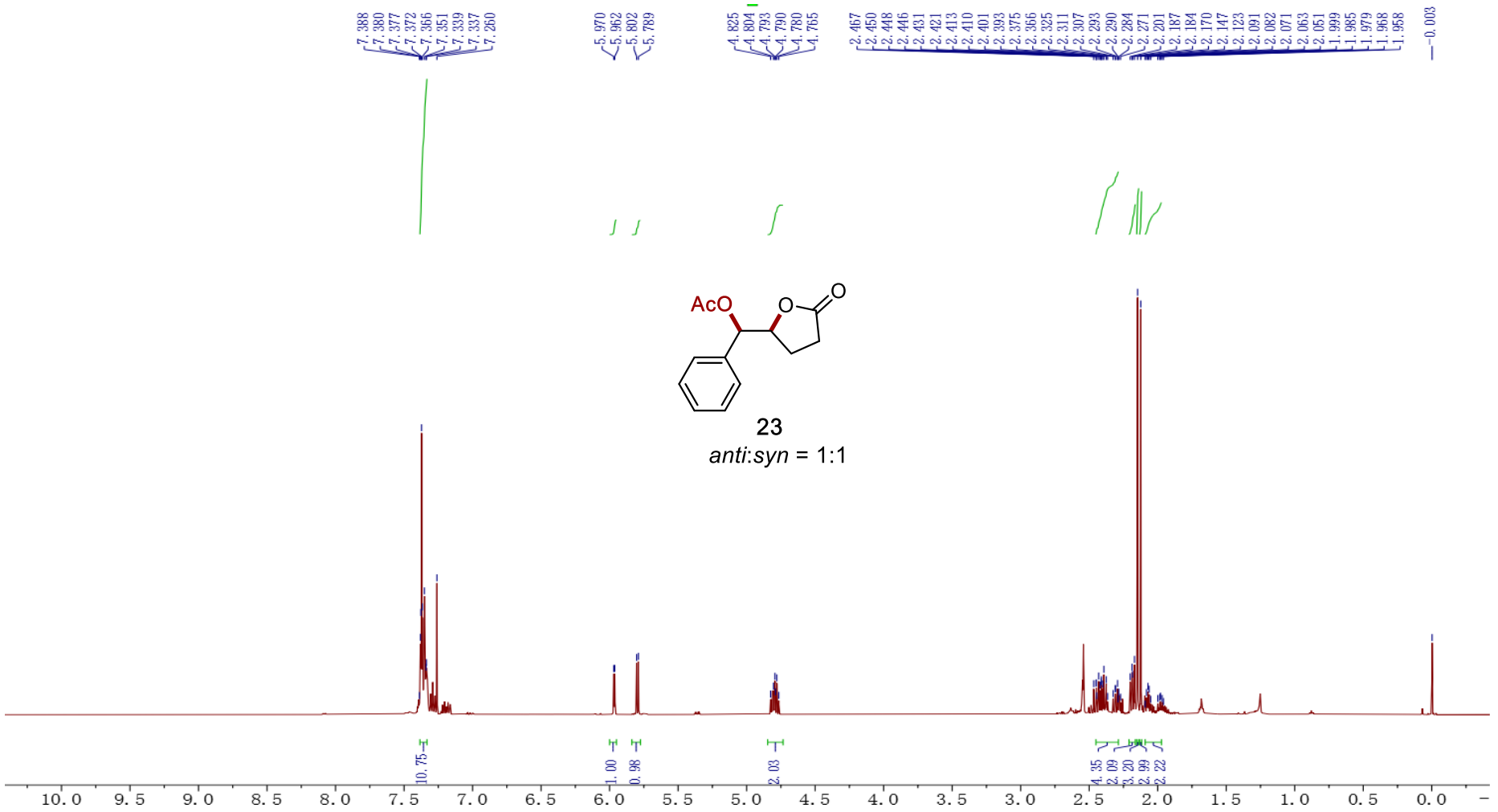
anti:*syn* = 5.6:1

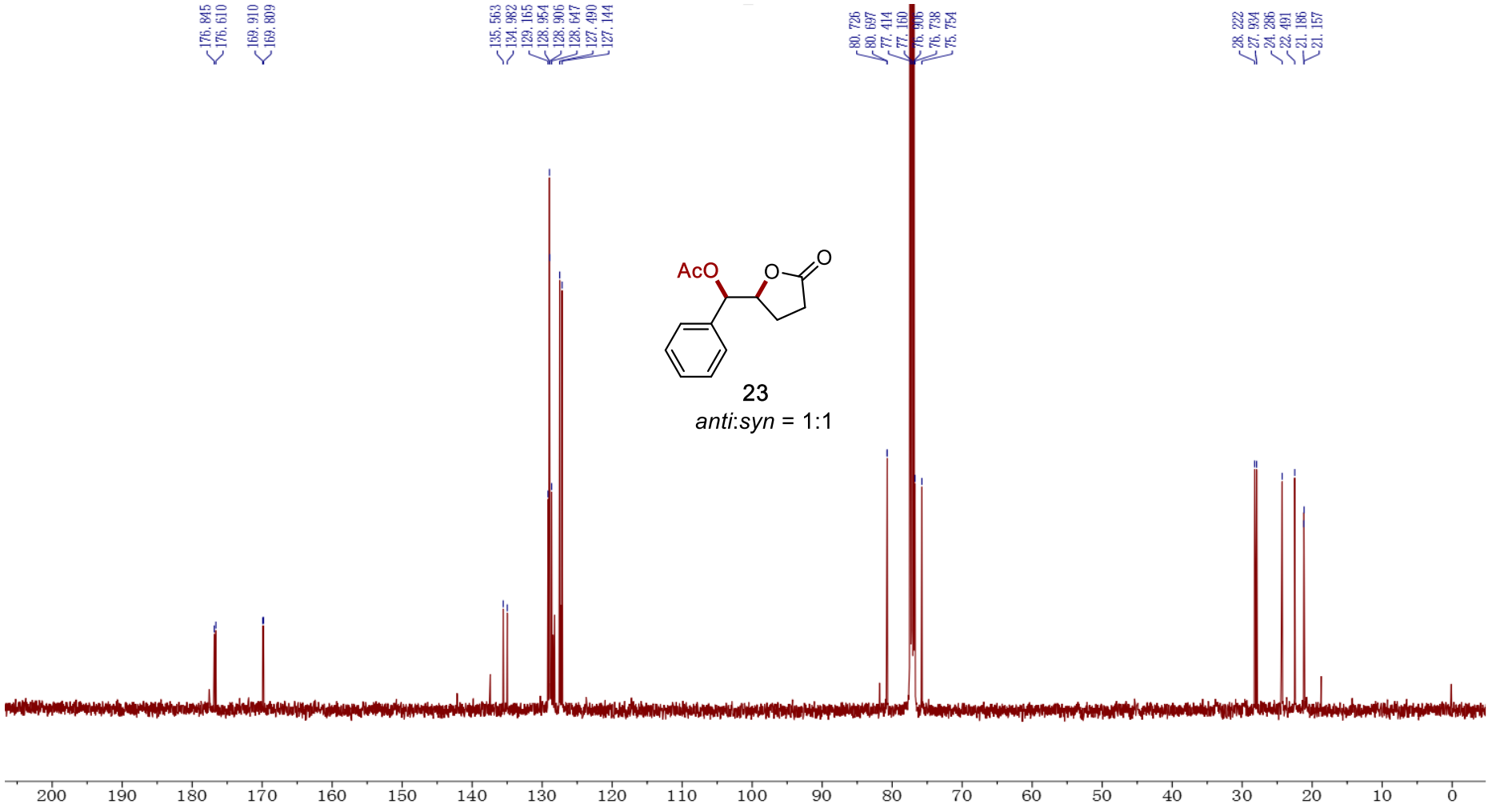


22

anti:*syn* =3.5:1

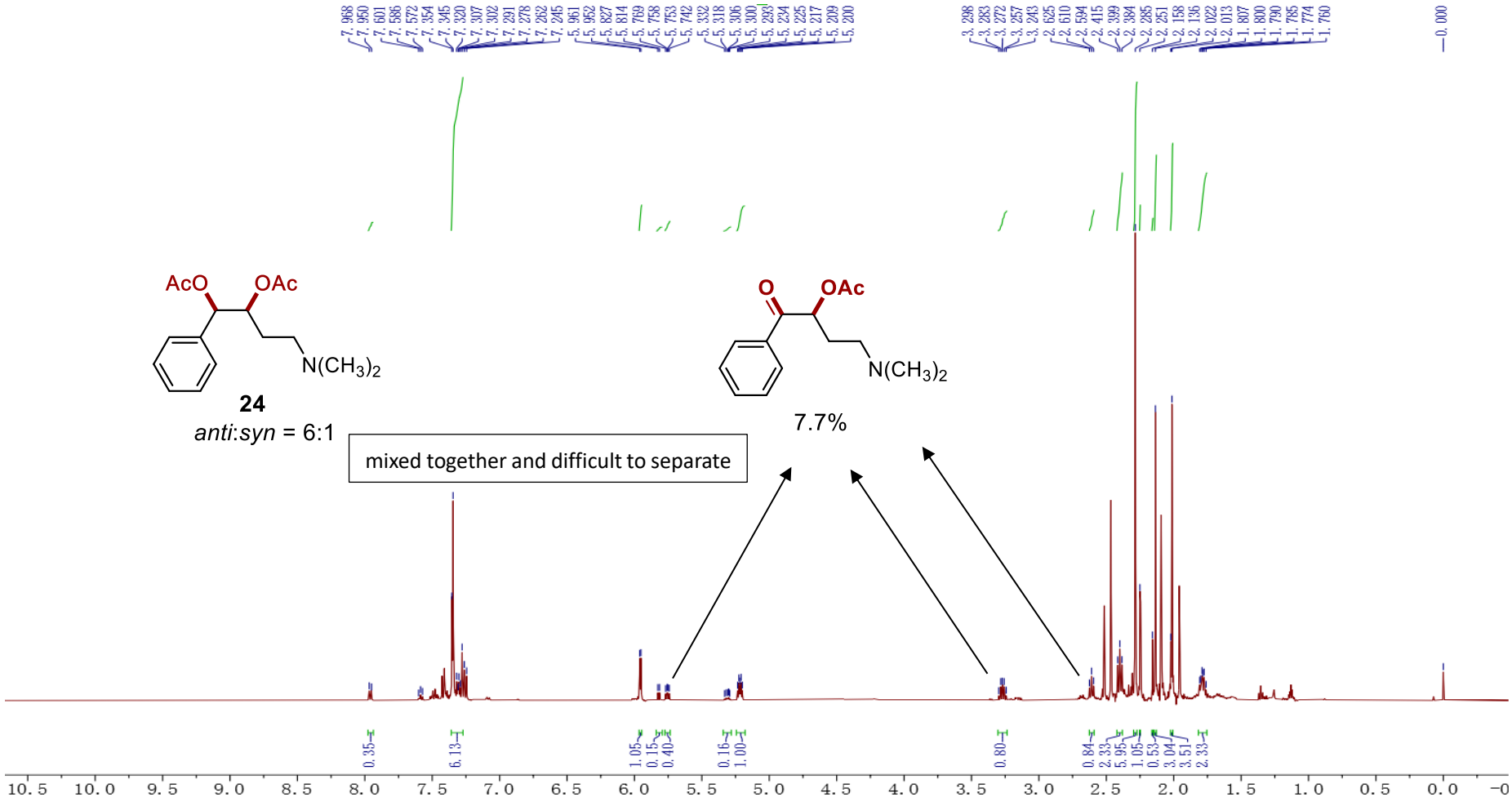

76.640
76.488
35.676
34.926
143.524
143.224
127.741
127.628
127.146
127.080
126.884
126.633
76.640
76.488
72.148
58.433
58.326
40.004 DMSO-D6
39.836 DMSO-D6
39.755 DMSO-D6
39.669 DMSO-D6
39.588 DMSO-D6
39.501 DMSO-D6
39.335 DMSO-D6
39.168 DMSO-D6
39.001 DMSO-D6
35.676
34.926
HO
OH
OH
22
anti:syn =3.5:1
1.00
3.45
0.96
3.30
75
35
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

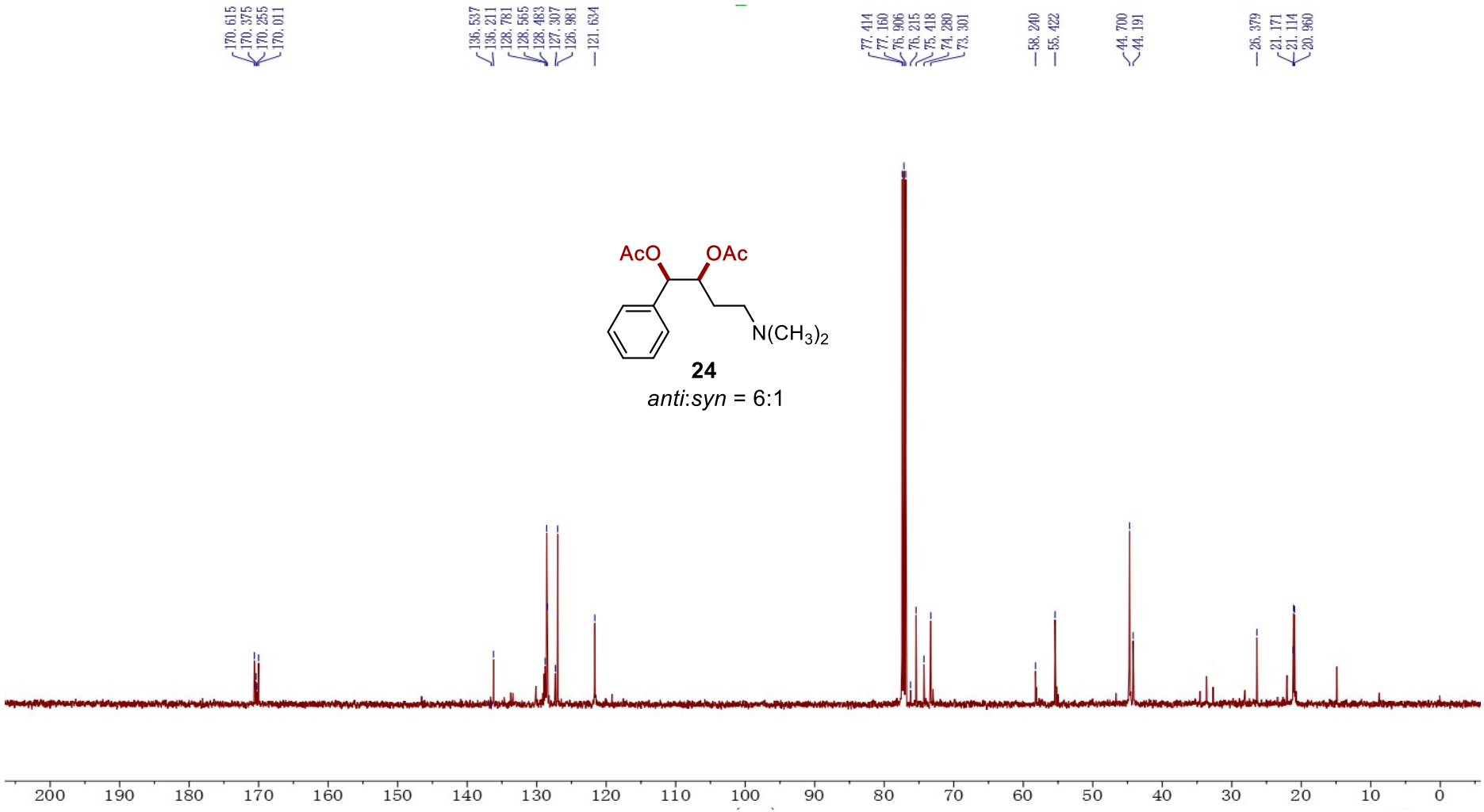

AcO
O
O
23
anti:syn = 1:1

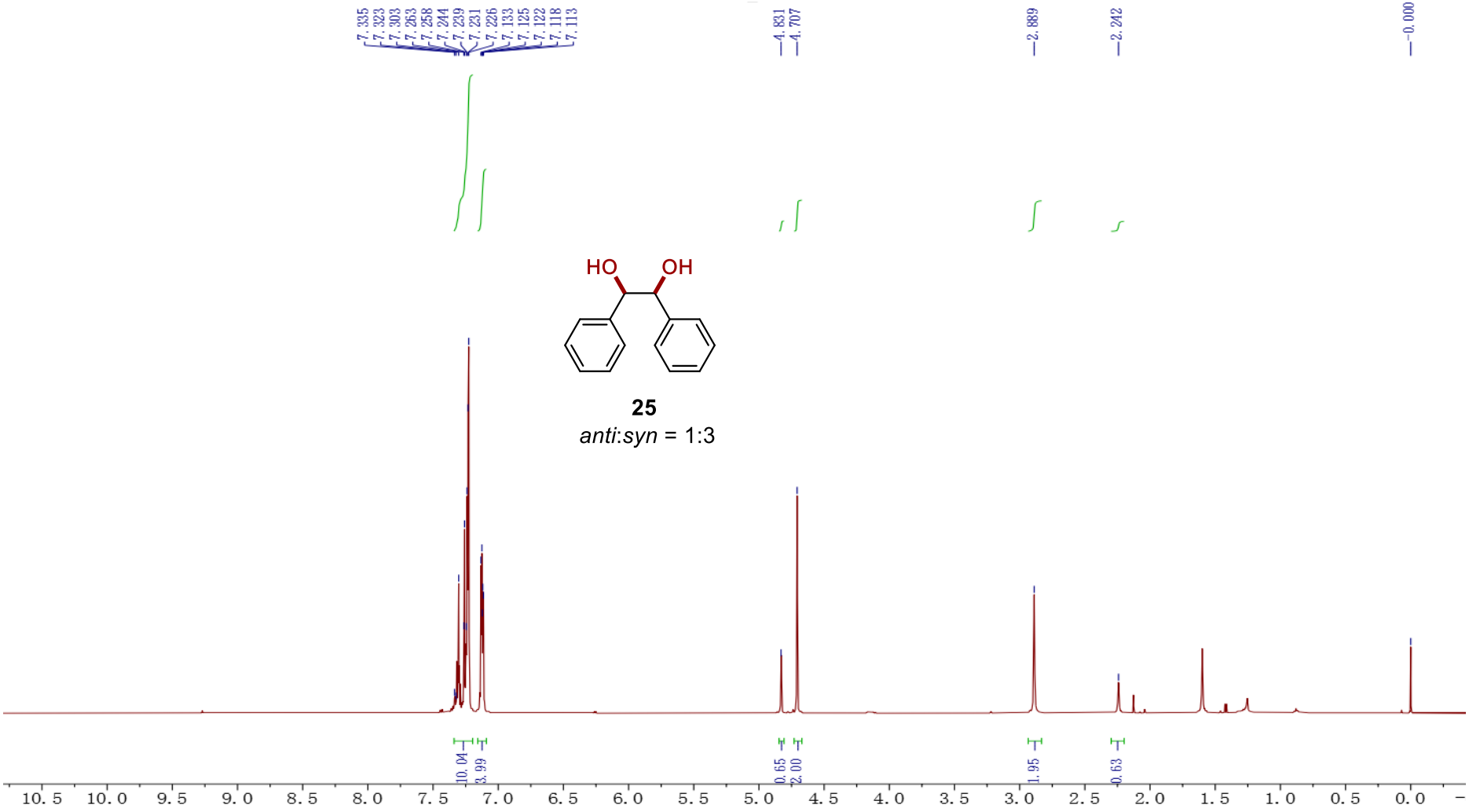


23

anti:*syn* = 1:1

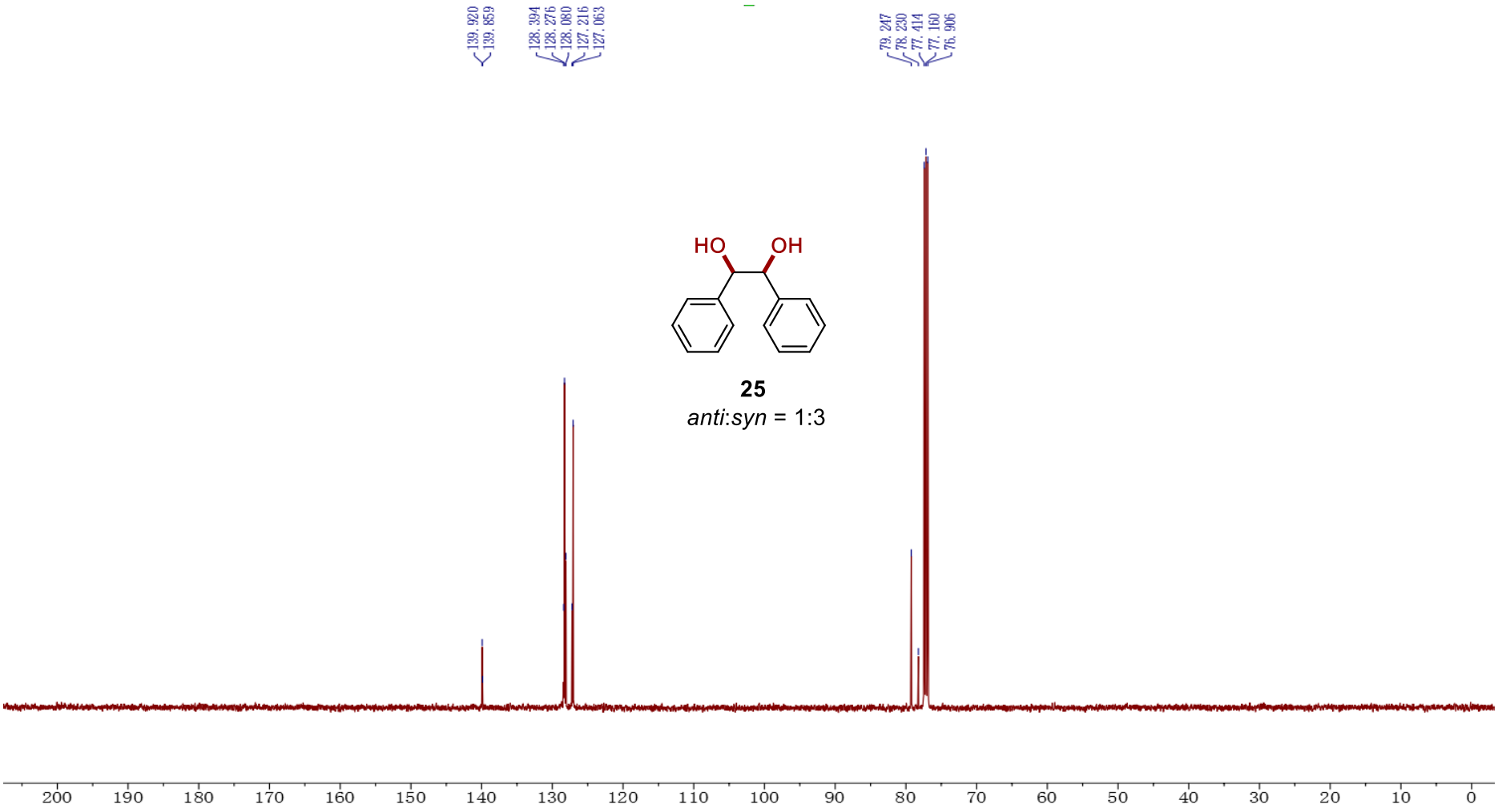

AcO
OAc
N(CH3)2
24
anti:syn = 6:1
mixed together and difficult to separate
O
OAc
N(CH3)2
7.7%


170.615
170.375
170.255
170.011
136.537
136.211
128.781
128.565
128.483
127.307
126.981
121.634
77.414
77.160
76.906
76.215
75.418
74.280
73.301
58.240
55.422
44.700
44.191
26.379
21.171
21.114
20.960
AcO
OAc
N(CH3)2
24
anti:syn = 6:1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



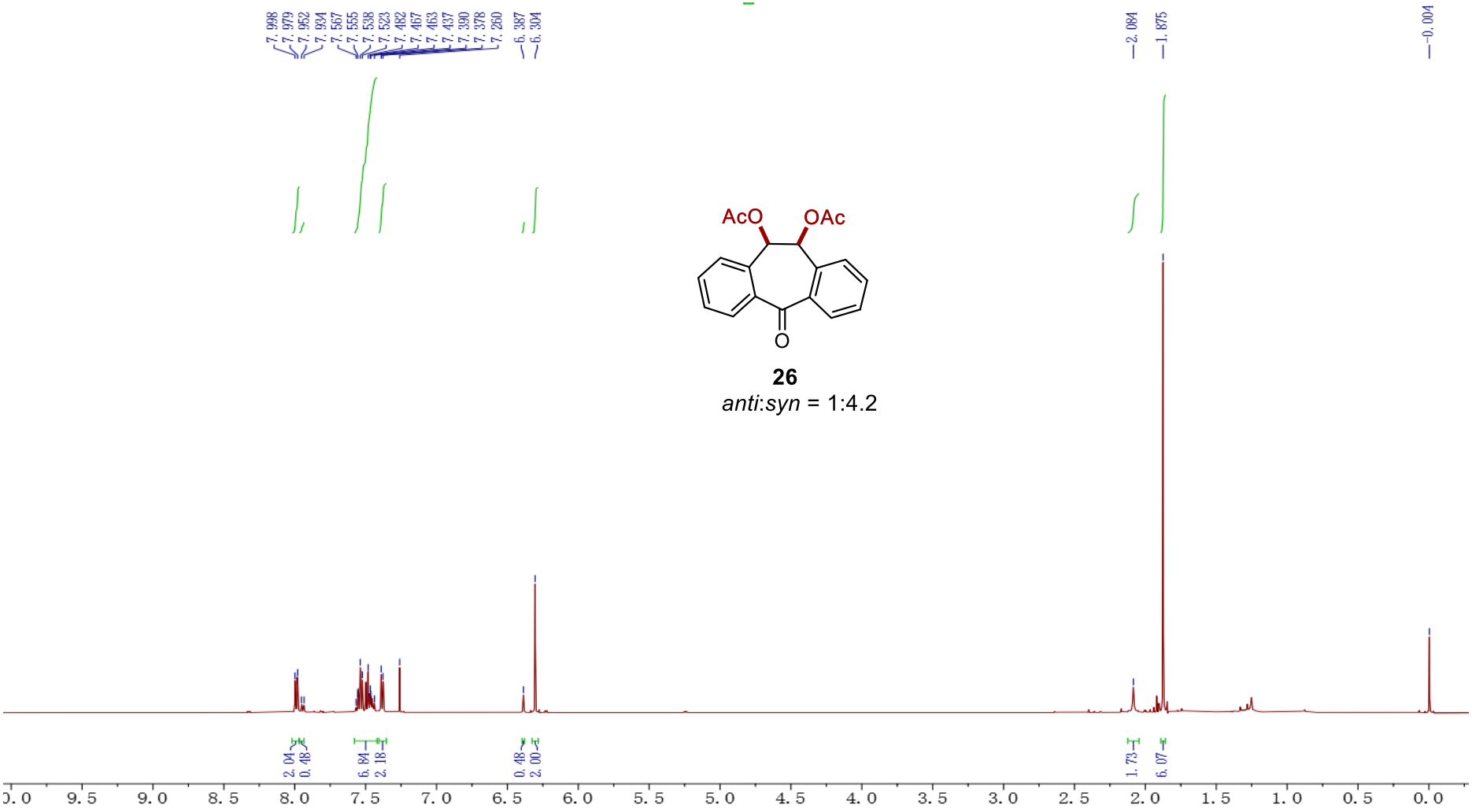
25

anti:*syn* = 1:3



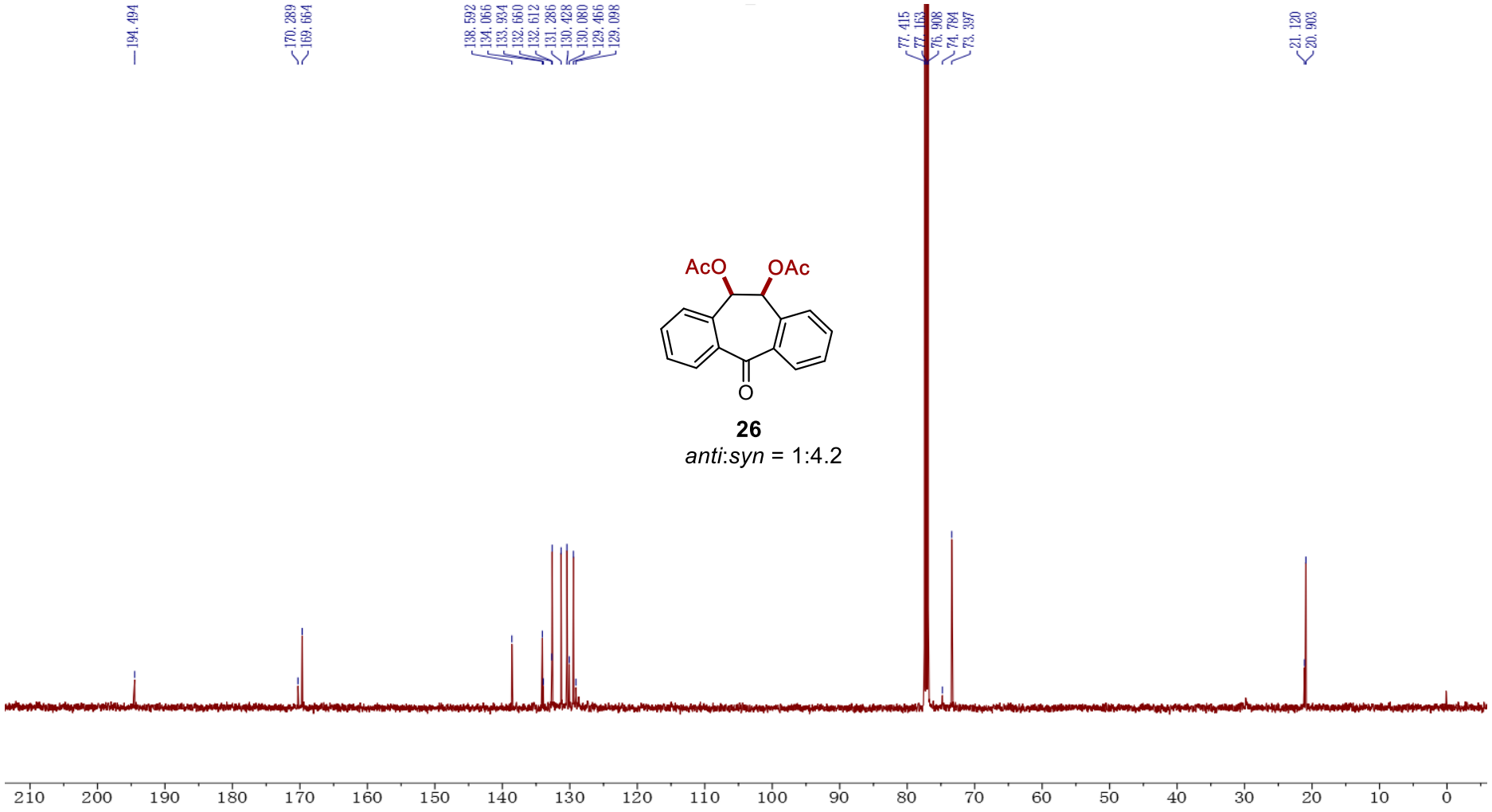
25

anti:*syn* = 1:3



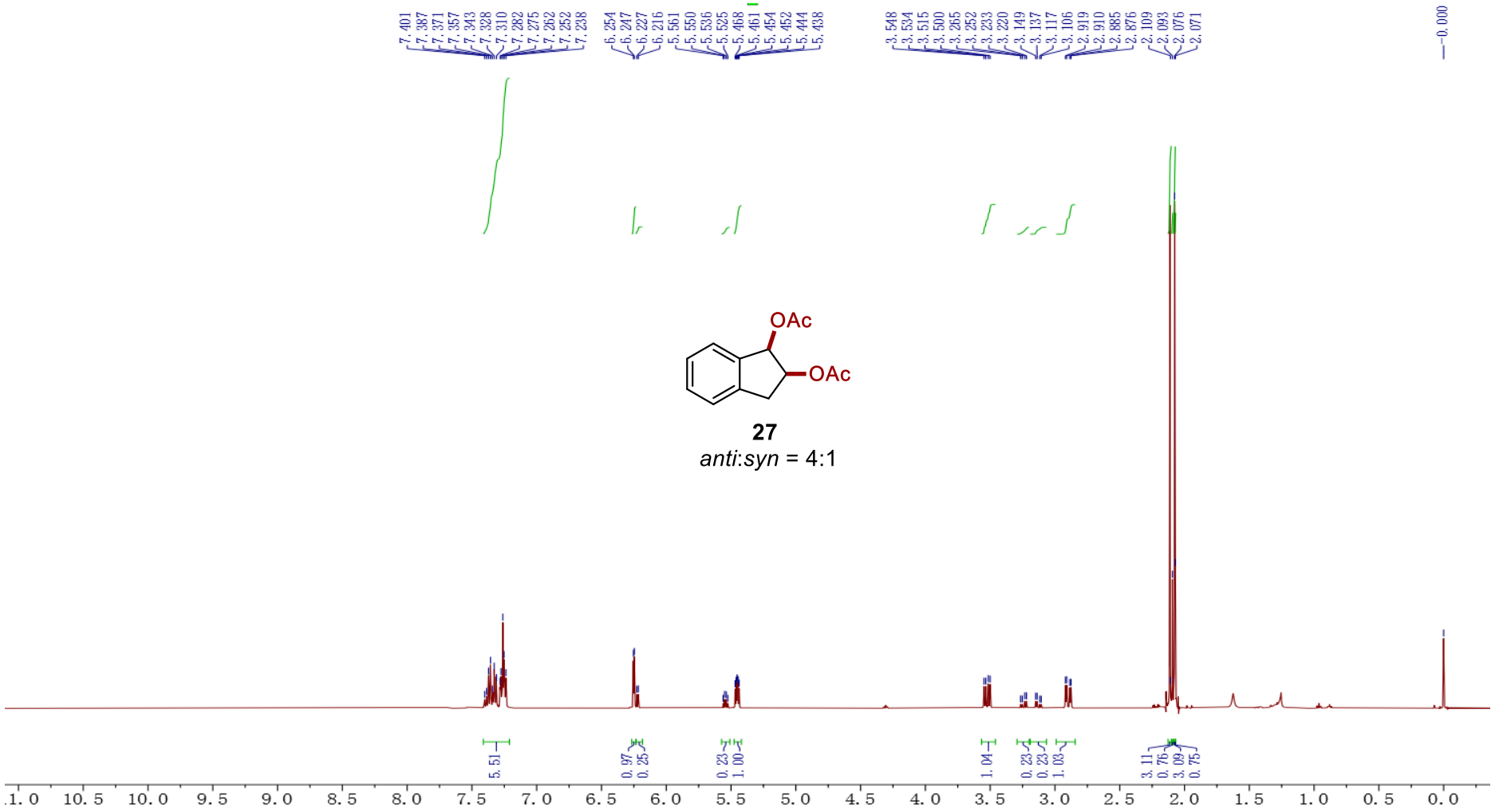
26

anti:*syn* = 1:4.2



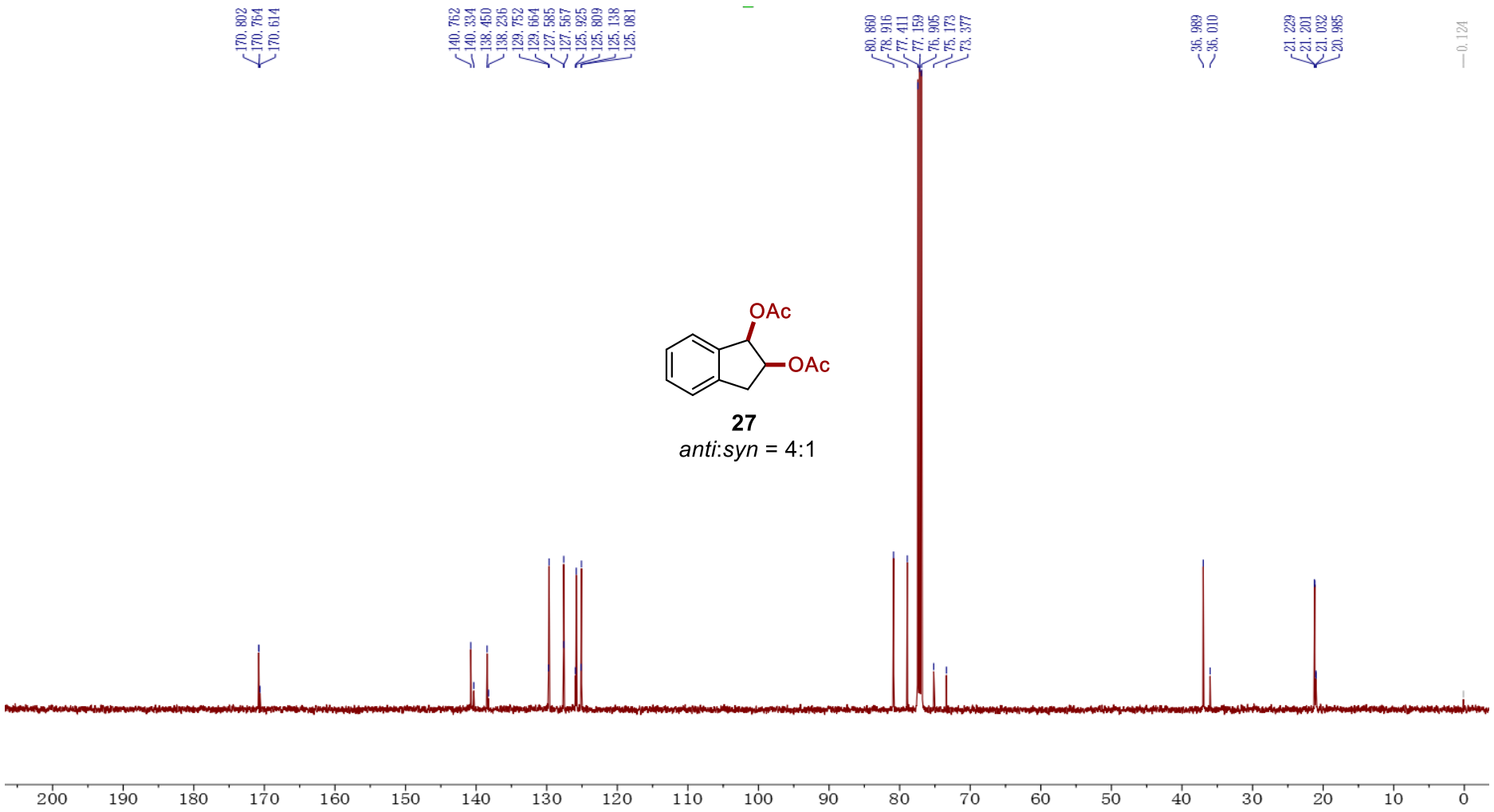
26

anti:*syn* = 1:4.2



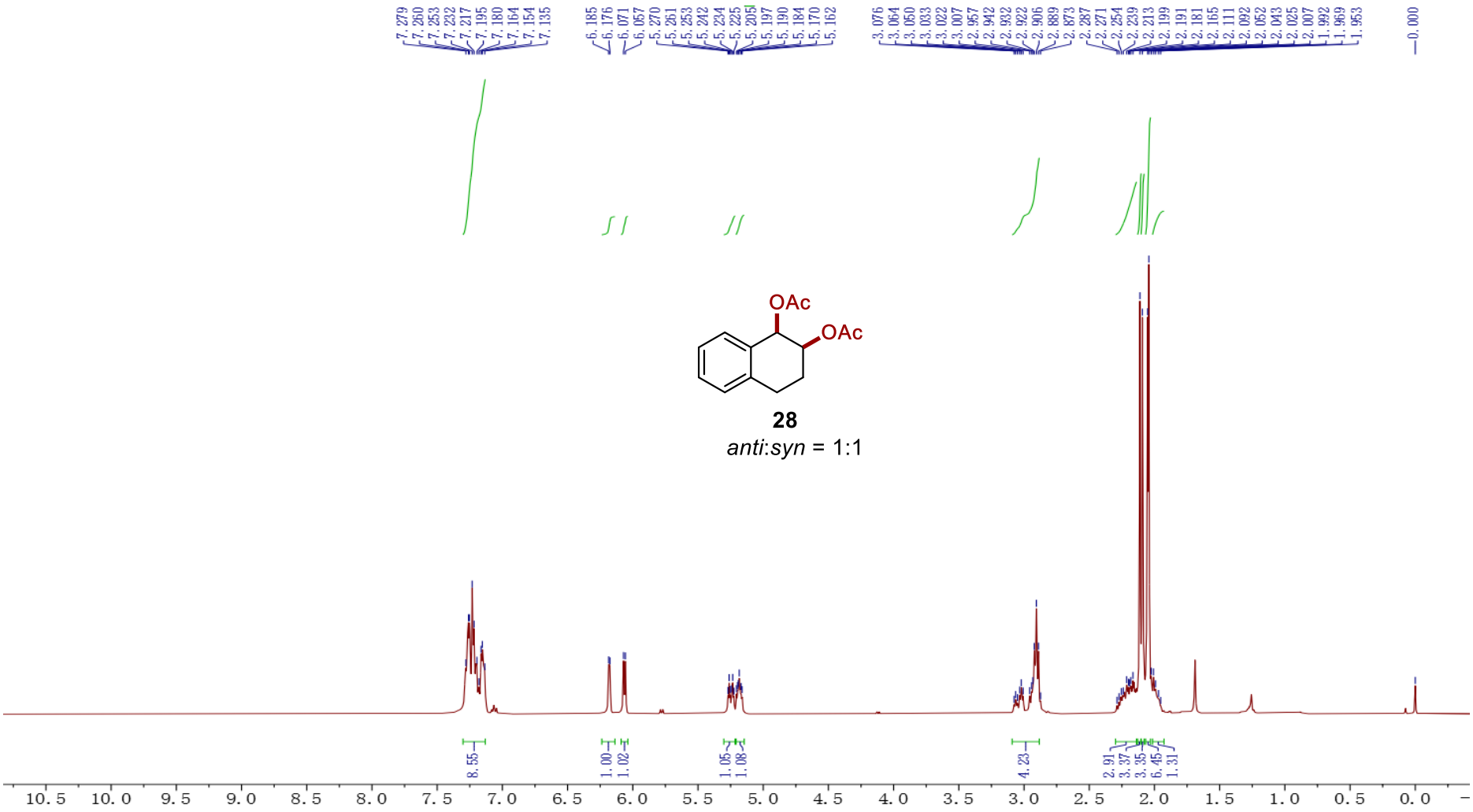
27

anti:*syn* = 4:1



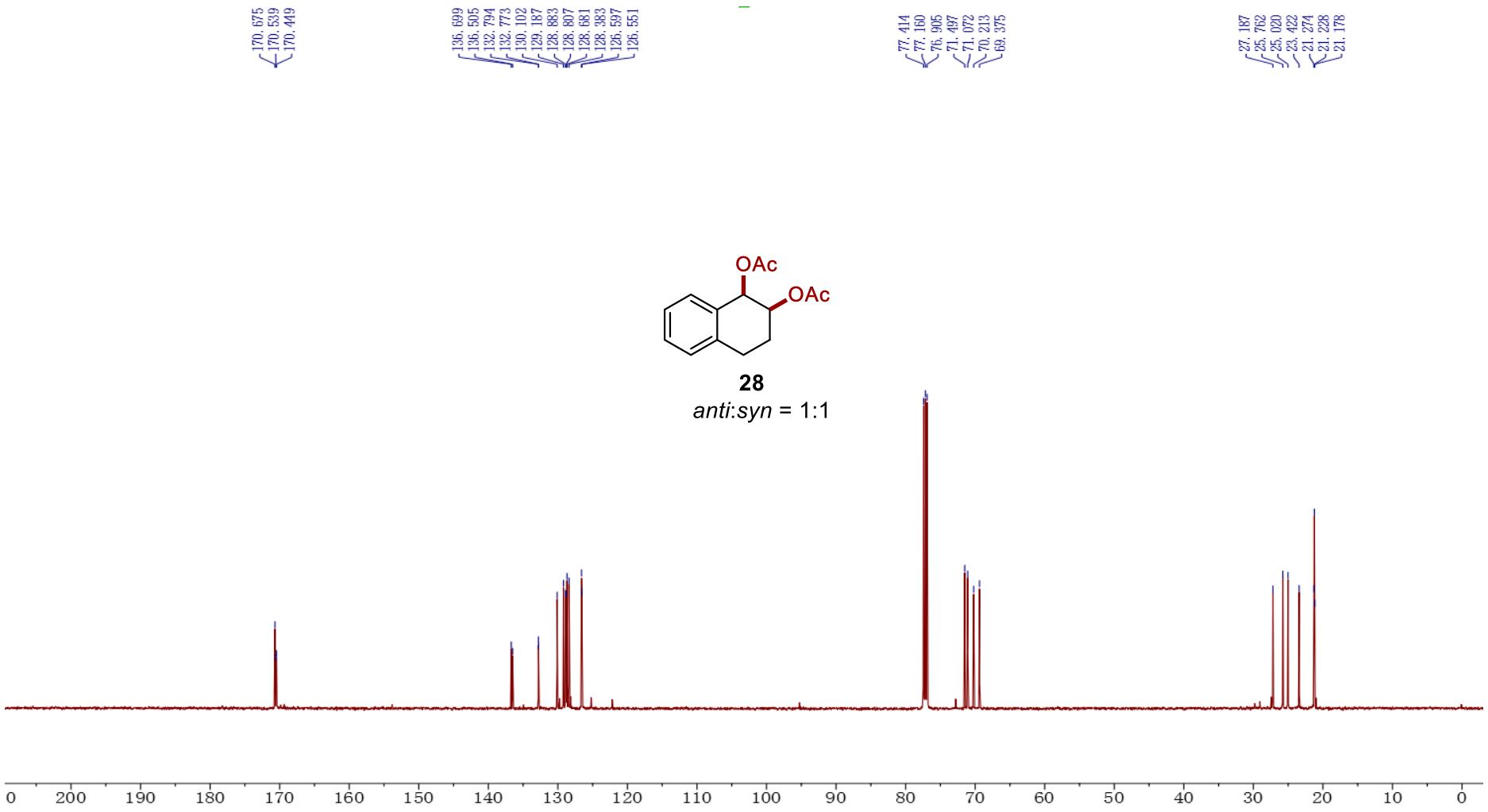
27

anti:*syn* = 4:1



28

anti:*syn* = 1:1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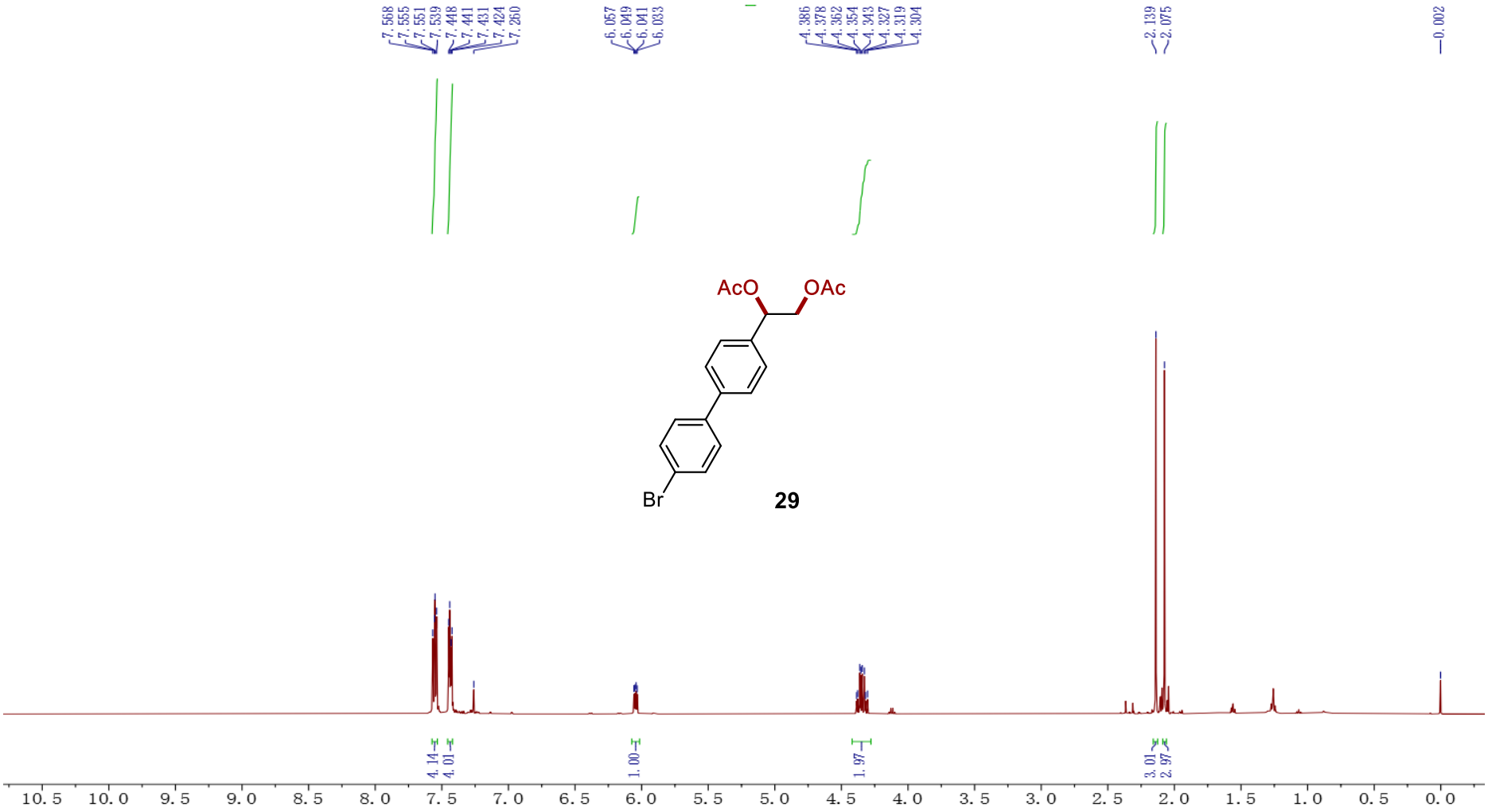
170.449
136.699
136.505
132.794
132.773
130.102
129.187
128.883
128.807
128.681
128.383
126.597
126.551
77.414
77.160
76.905
71.497
71.072
70.213
69.375
27.187
25.762
25.020
23.422
21.274
21.228
21.178
OAc
OAc
28
anti:syn = 1:1
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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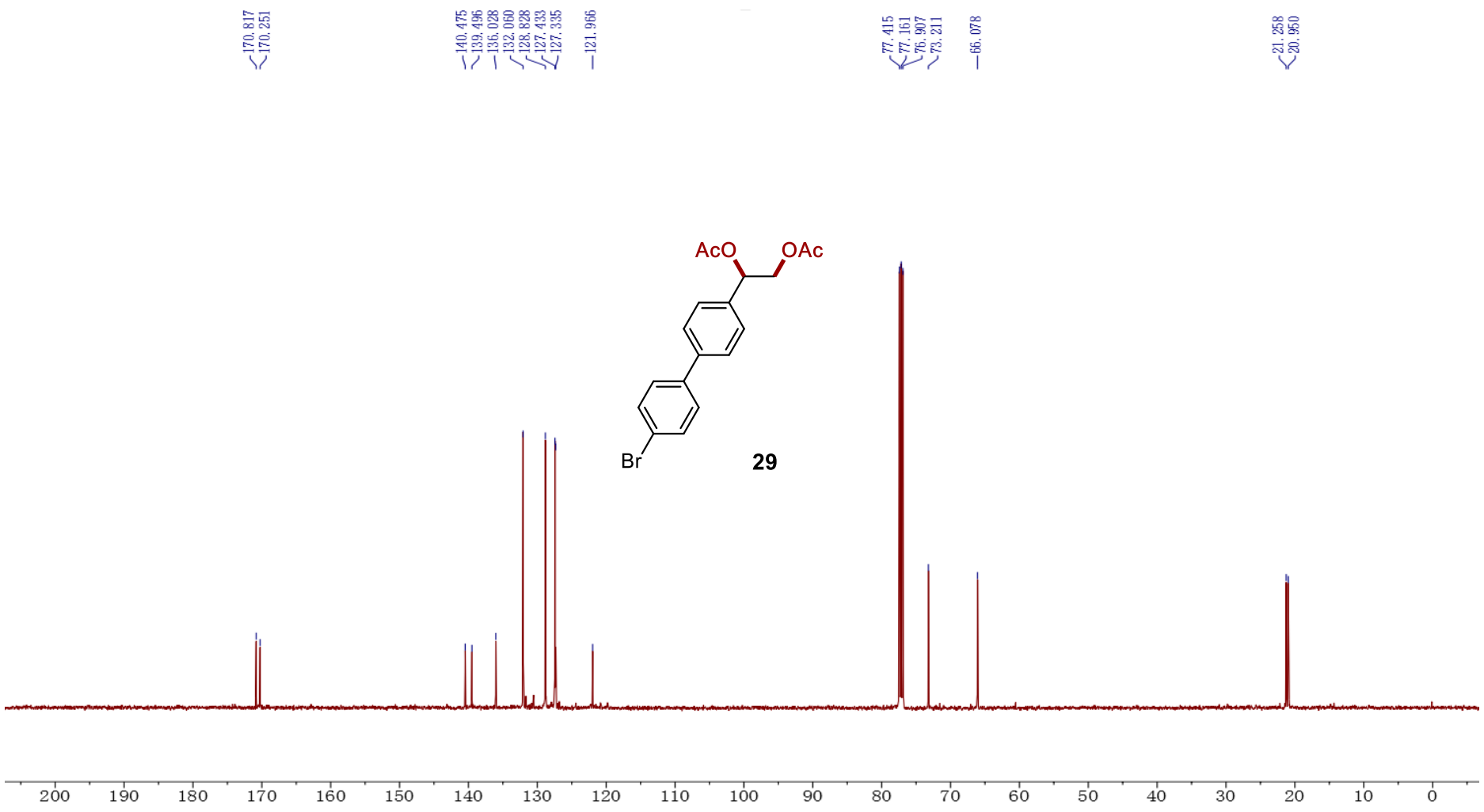
7.555
7.551
7.539
7.448
7.441
7.431
7.424
7.260
6.057
6.049
6.041
6.033
4.386
4.378
4.362
4.354
4.343
4.327
4.319
4.304
2.139
2.075
0.002
AcO
OAc
Br
29
4.14
4.01
1.00
1.97
3.01
2.97
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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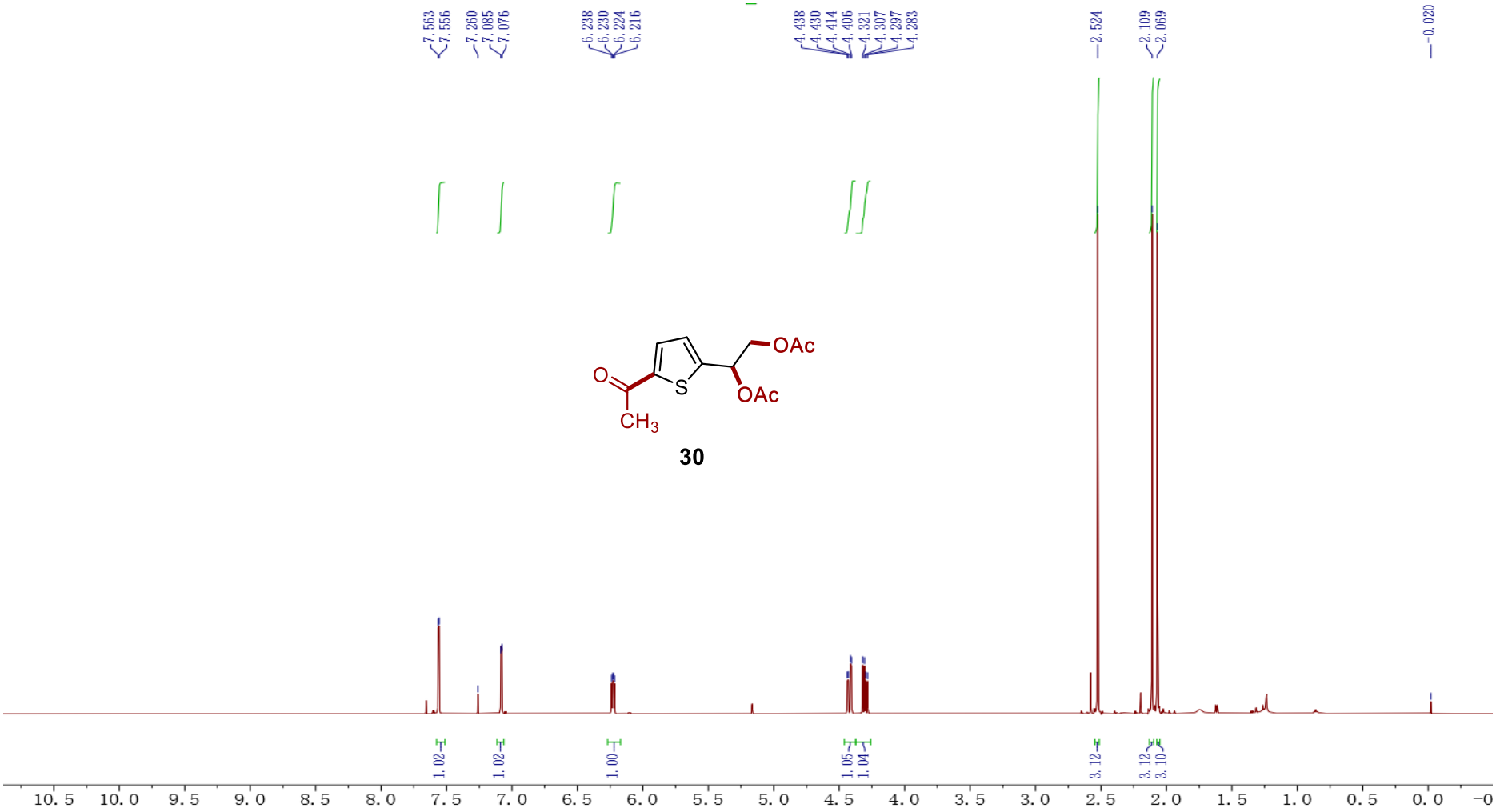
170.251
140.475
139.496
136.028
132.060
128.828
127.433
127.335
121.966
77.415
77.161
76.907
73.211
66.078
21.258
20.950
AcO
OAc
Br
29
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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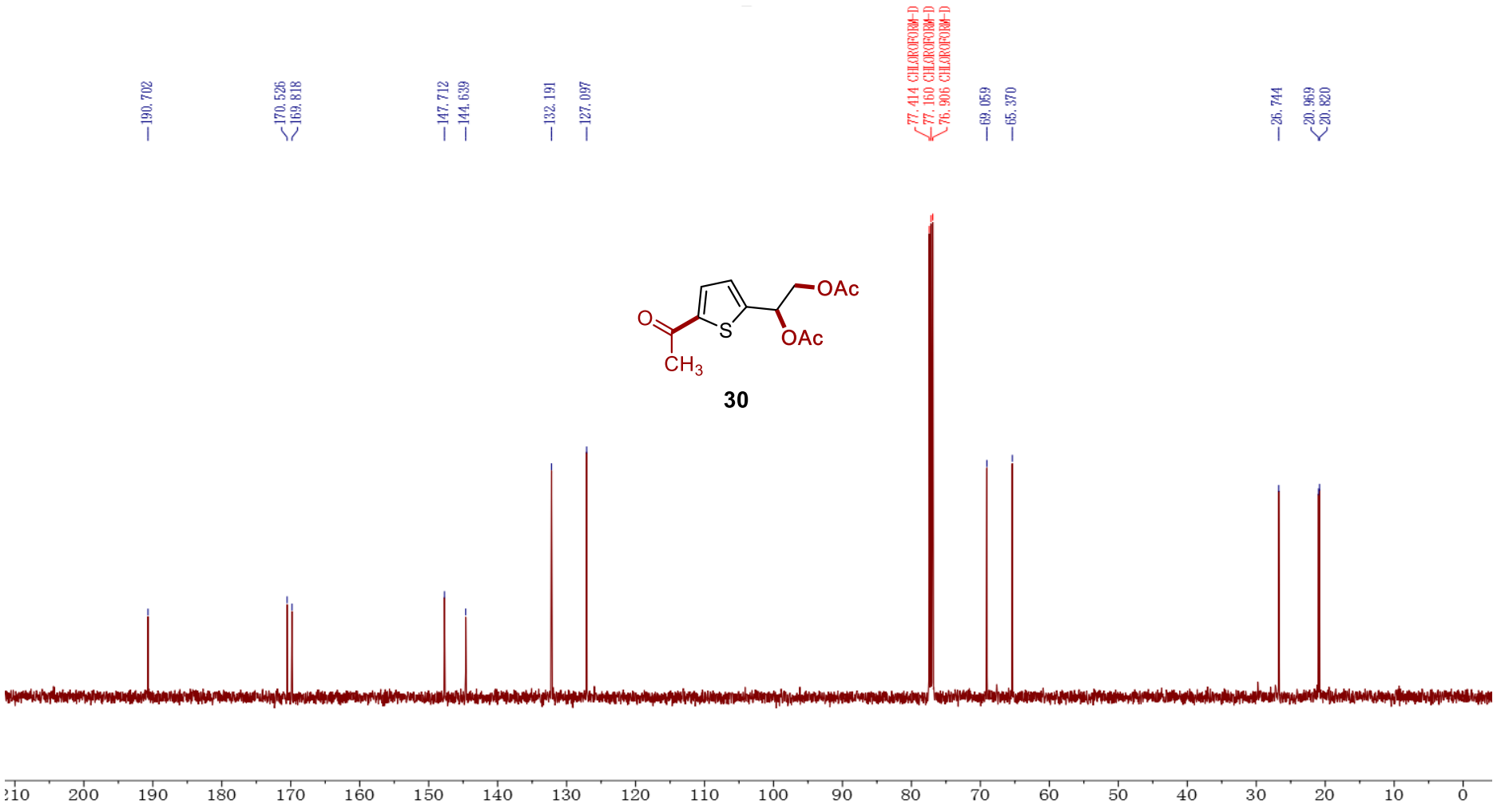
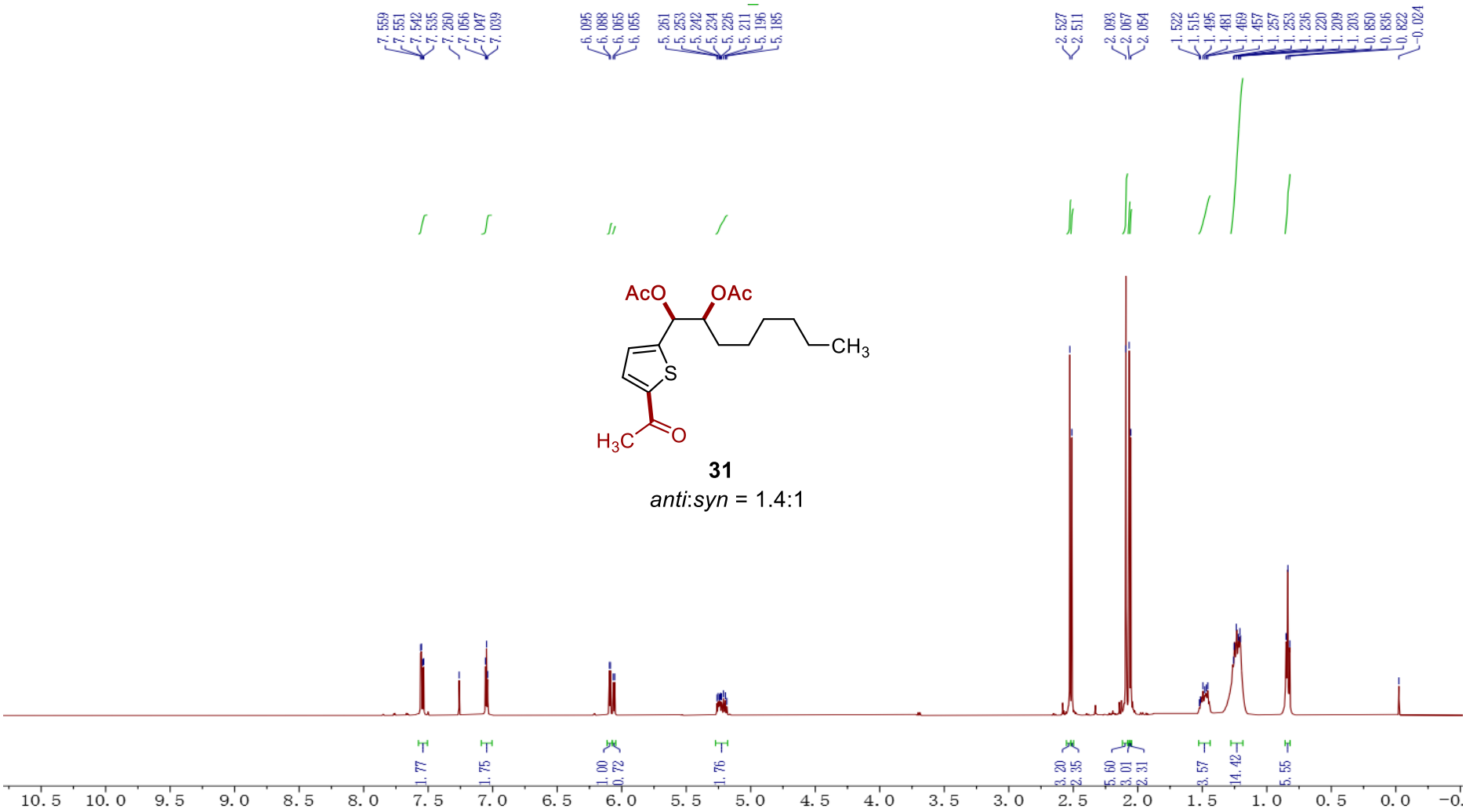
7.556
7.260
7.085
7.076
6.238
6.230
6.224
6.216
4.438
4.430
4.414
4.406
4.321
4.307
4.297
4.283
2.524
2.109
2.069
0.020
OAc
OAc
O
S
CH3
1.02
1.02
1.00
1.05
1.04
3.12
3.12
3.10
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0

30

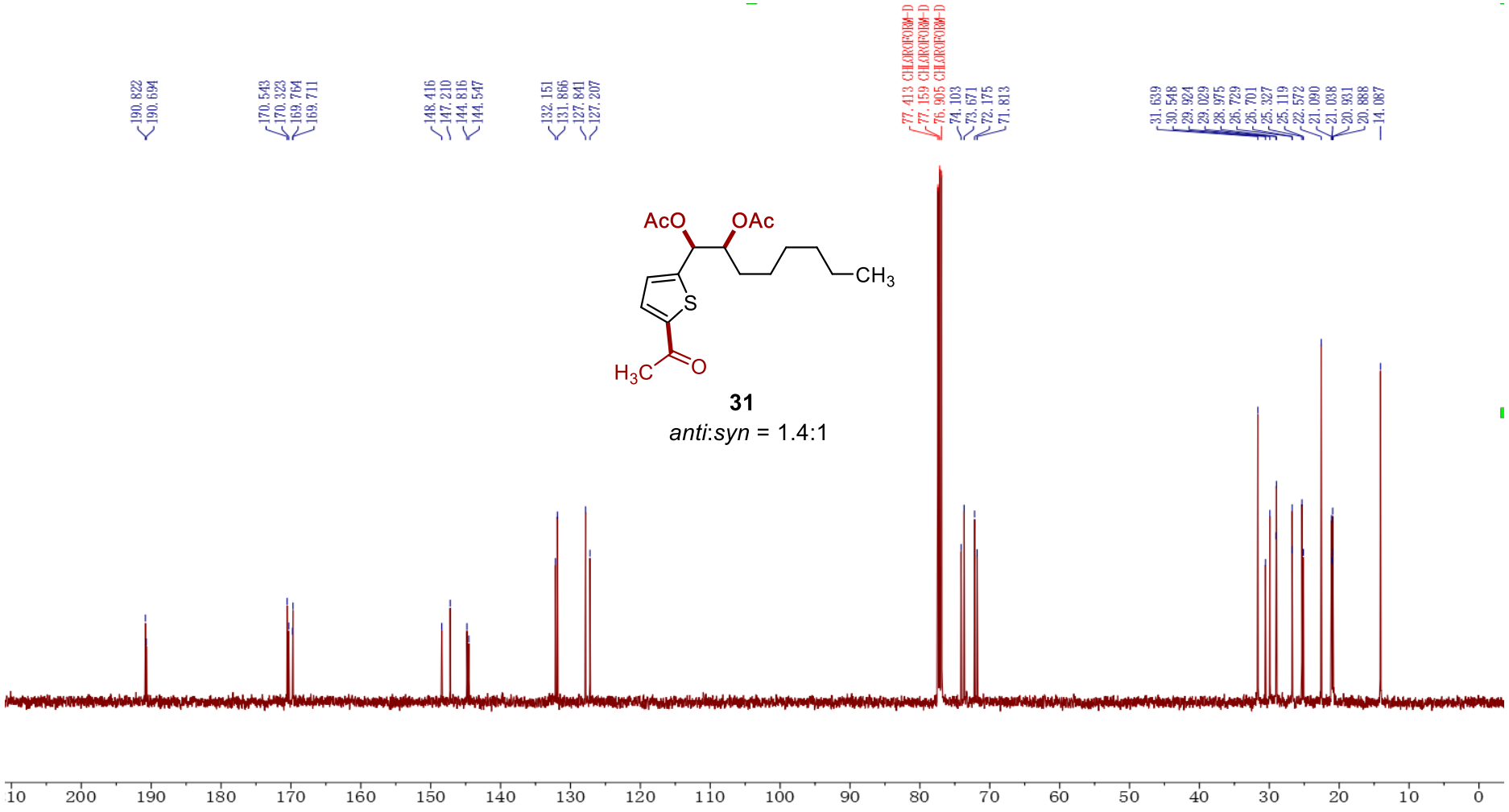

190.702
170.526
169.818
147.712
144.639
132.191
127.097
77.414 CHLOROFORM-D
77.160 CHLOROFORM-D
76.906 CHLOROFORM-D
69.059
65.370
26.744
20.969
20.820
OAc
OAc
O
S
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

30



31

anti:*syn* = 1.4:1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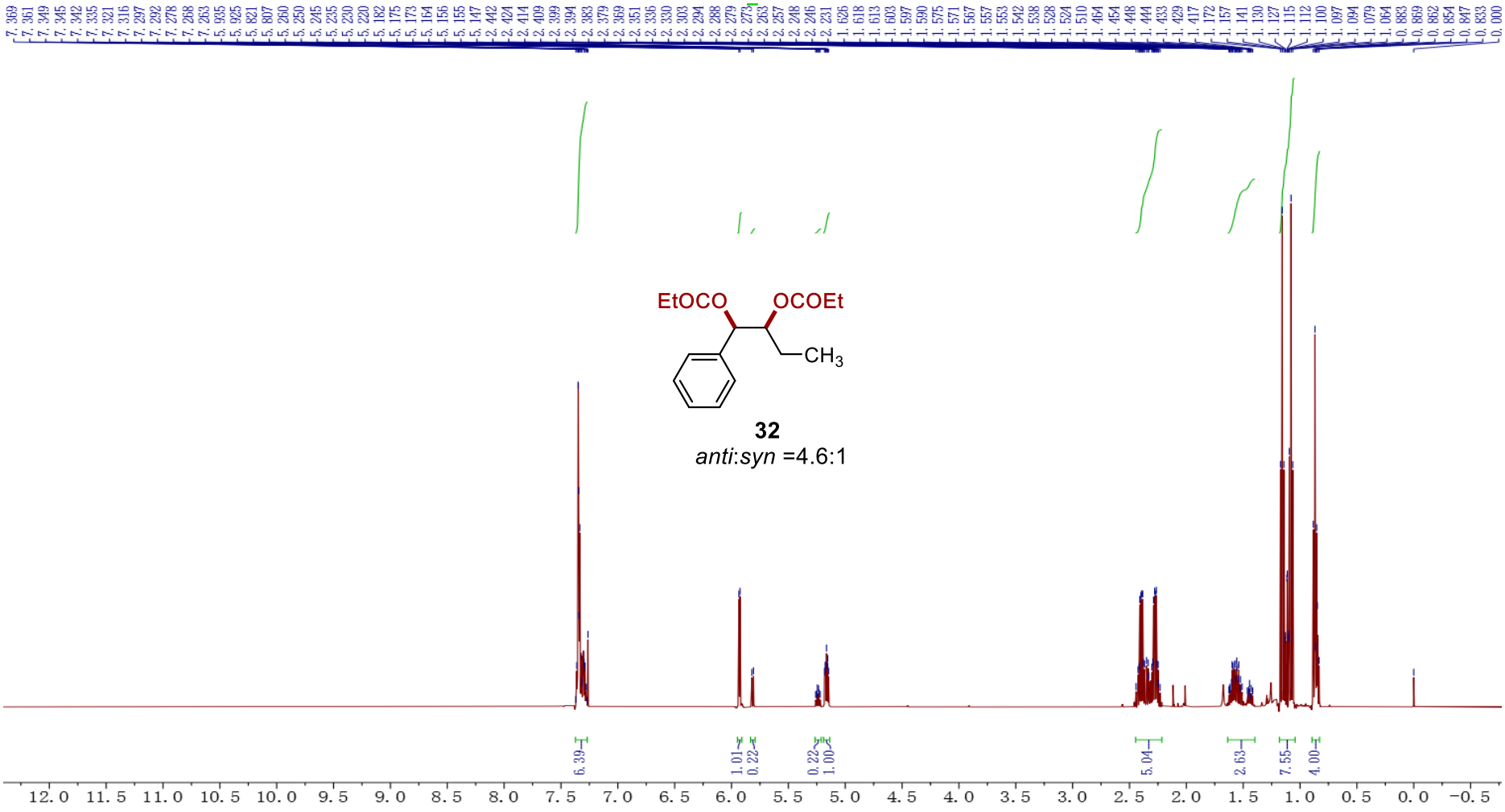
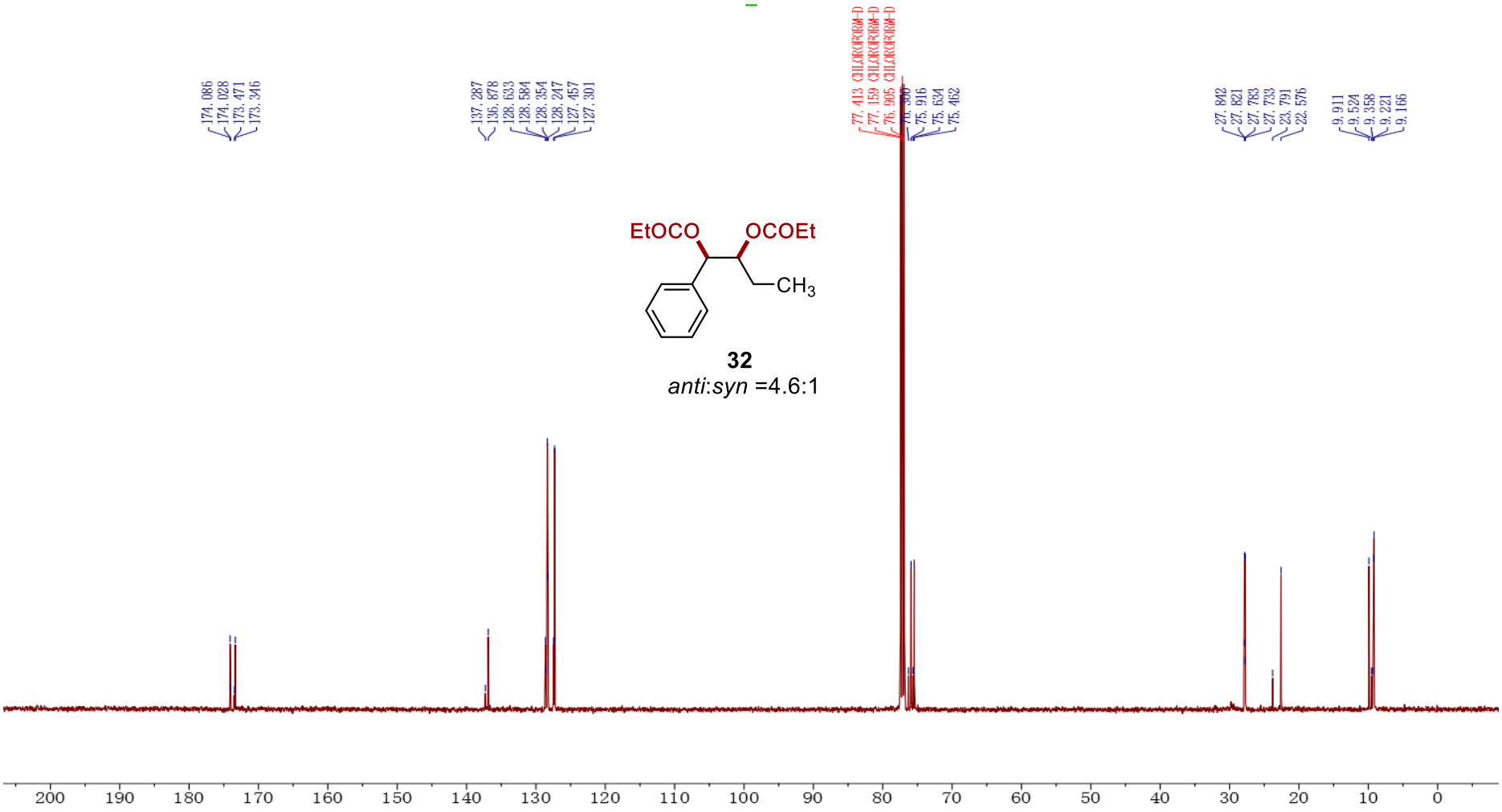
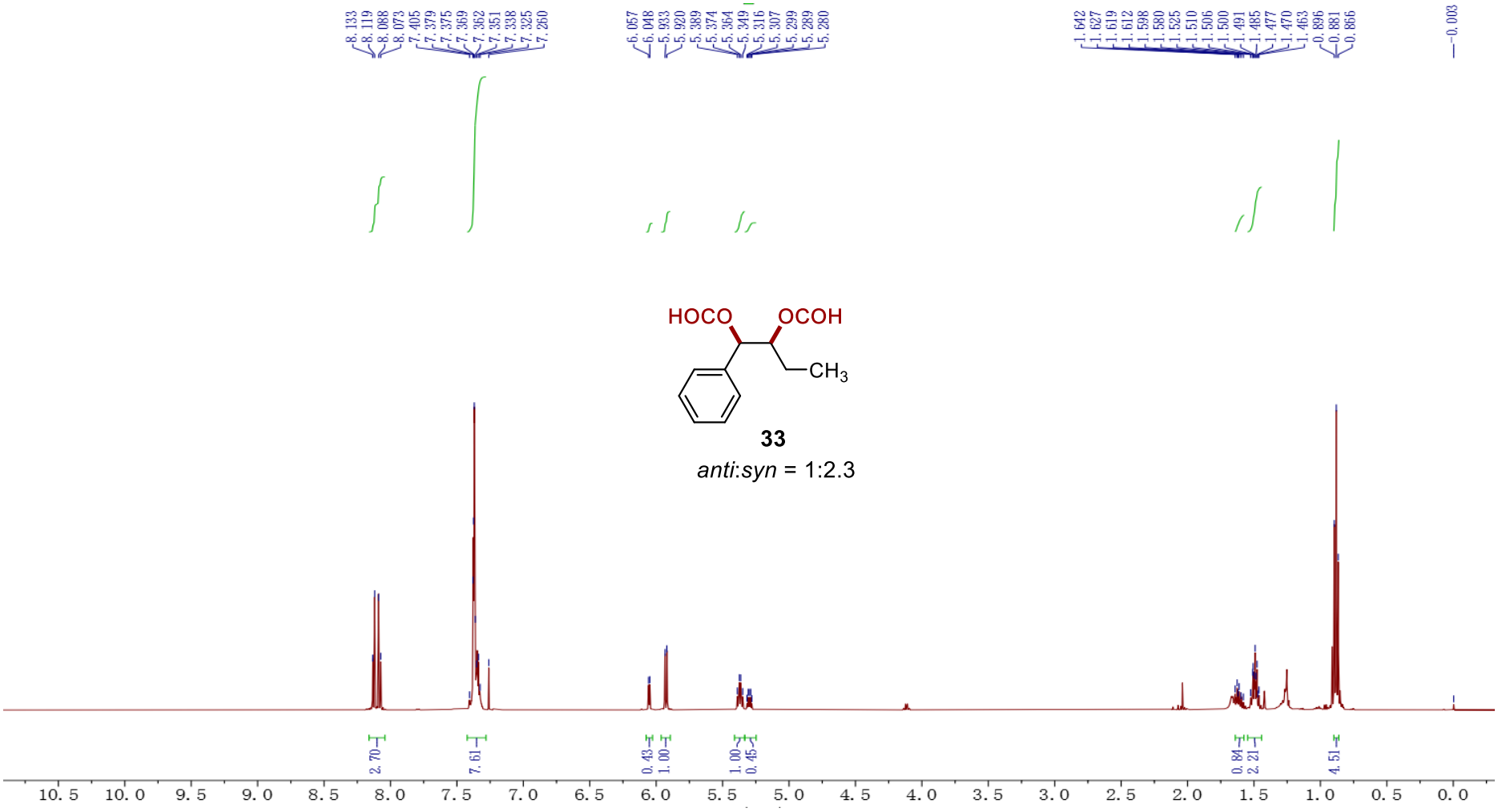
190.694
170.543
170.323
169.764
169.711
148.416
147.210
144.816
144.547
132.151
131.866
127.841
127.207
77.413 CHLOROFORM-D
77.159 CHLOROFORM-D
76.905 CHLOROFORM-D
74.103
73.671
72.175
71.813
31.639
30.548
29.924
29.029
28.975
28.729
26.701
25.327
25.119
22.572
21.090
21.038
20.931
20.888
14.087
AcO
OAc
CH3
S
H3C
O
31
anti:syn = 1.4:1
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


EtOCO
OCOEt
CH3
32
anti:syn =4.6:1



32

anti:*syn* =4.6:1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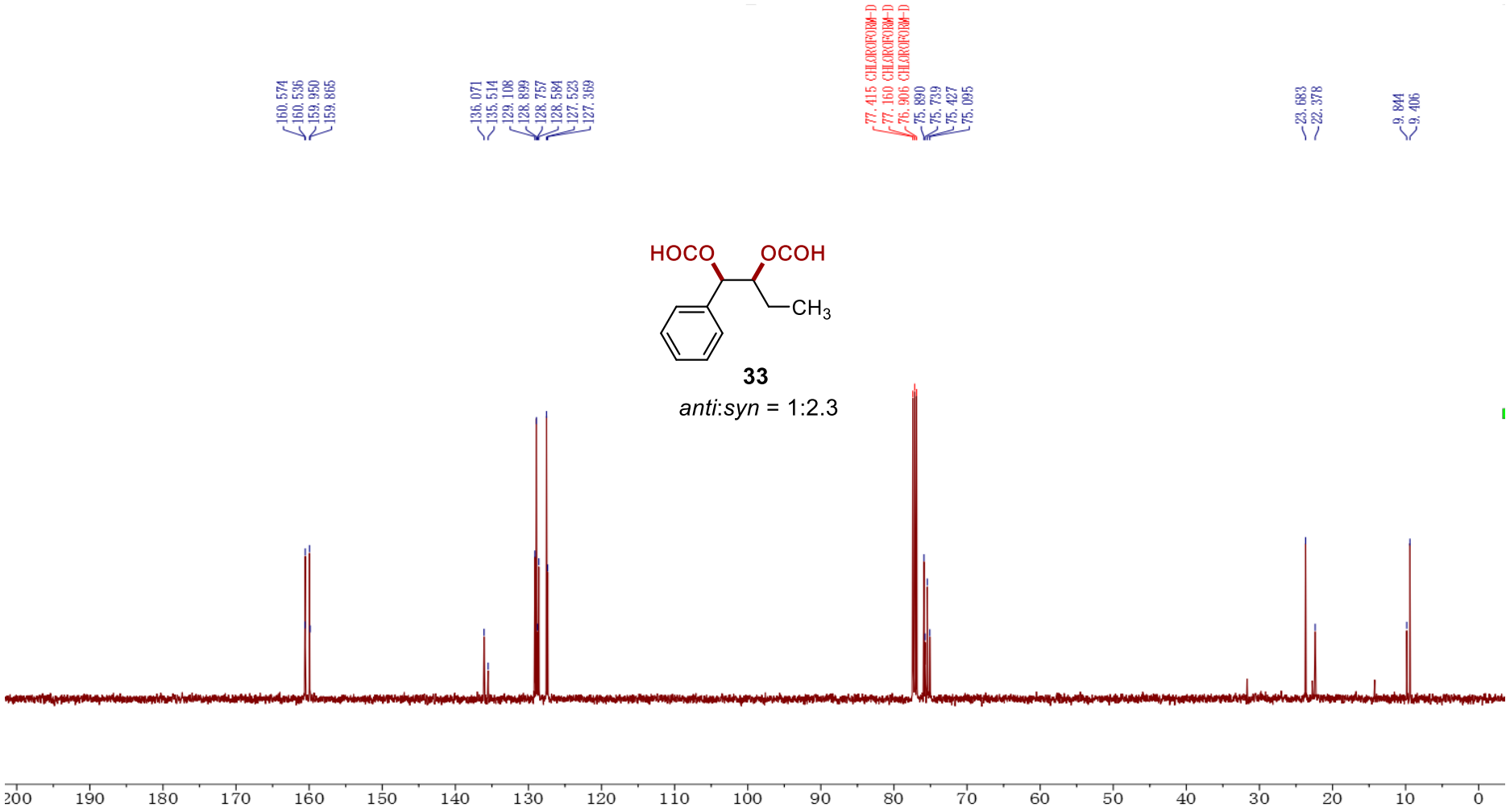
8.119
8.088
8.073
7.405
7.379
7.375
7.359
7.362
7.351
7.338
7.325
7.260
6.057
6.048
5.933
5.920
5.389
5.374
5.364
5.349
5.316
5.307
5.299
5.289
5.280
1.642
1.627
1.619
1.612
1.598
1.580
1.525
1.510
1.506
1.500
1.491
1.485
1.477
1.470
1.463
0.896
0.881
0.866
0.003
HOCO
OCOH
CH3
33
anti:syn = 1:2.3
2.70
7.61
0.43
1.00
1.00
0.45
0.84
2.21
4.51
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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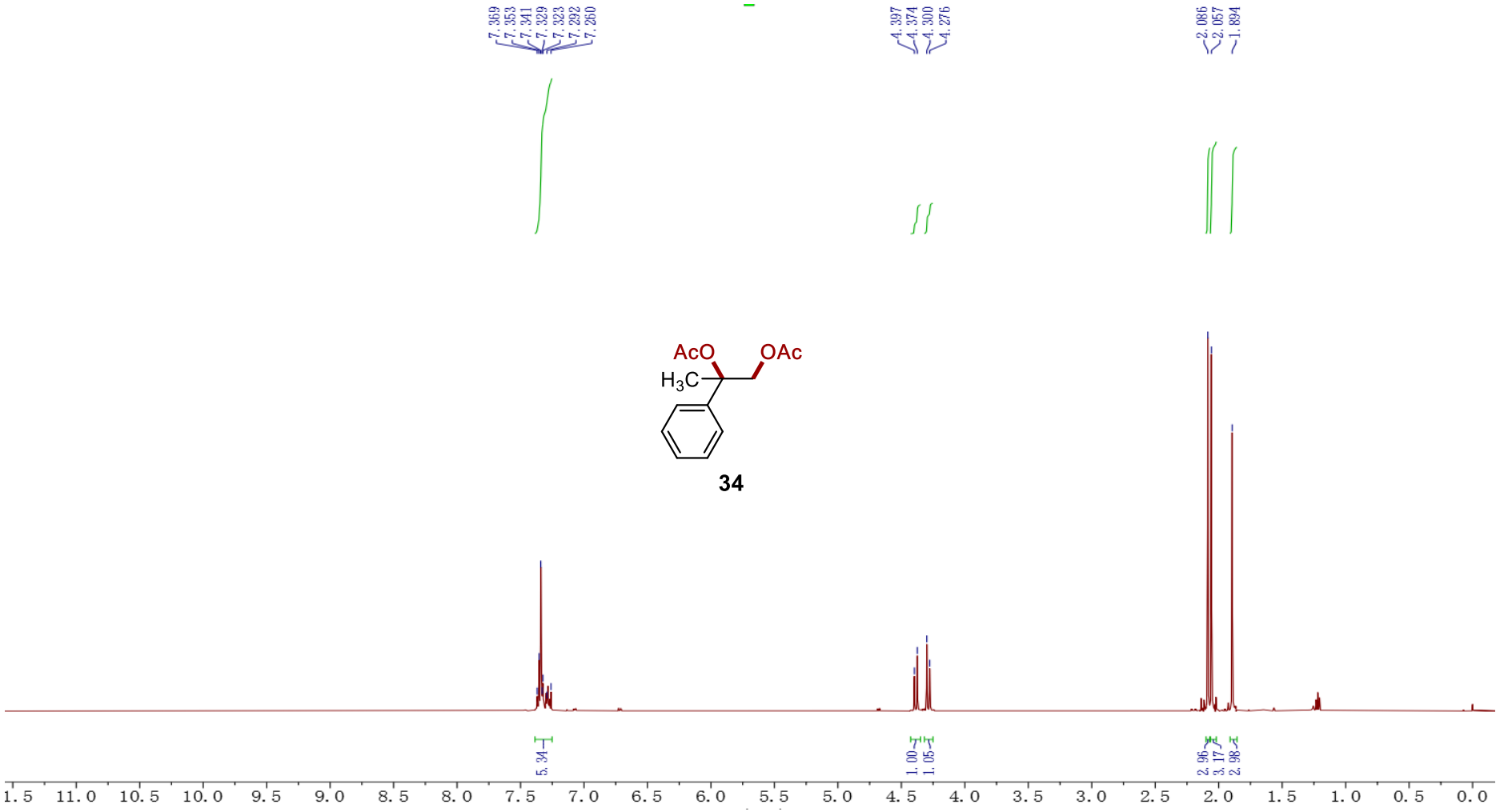
160.536
159.950
159.865
136.071
135.514
129.108
128.899
128.757
128.584
127.523
127.369
77.415 CHLOROFORM-D
77.160 CHLOROFORM-D
76.906 CHLOROFORM-D
75.890
75.739
75.427
75.095
23.683
22.378
9.844
9.406
HOCO
OCOH
CH3
33
anti:syn = 1:2.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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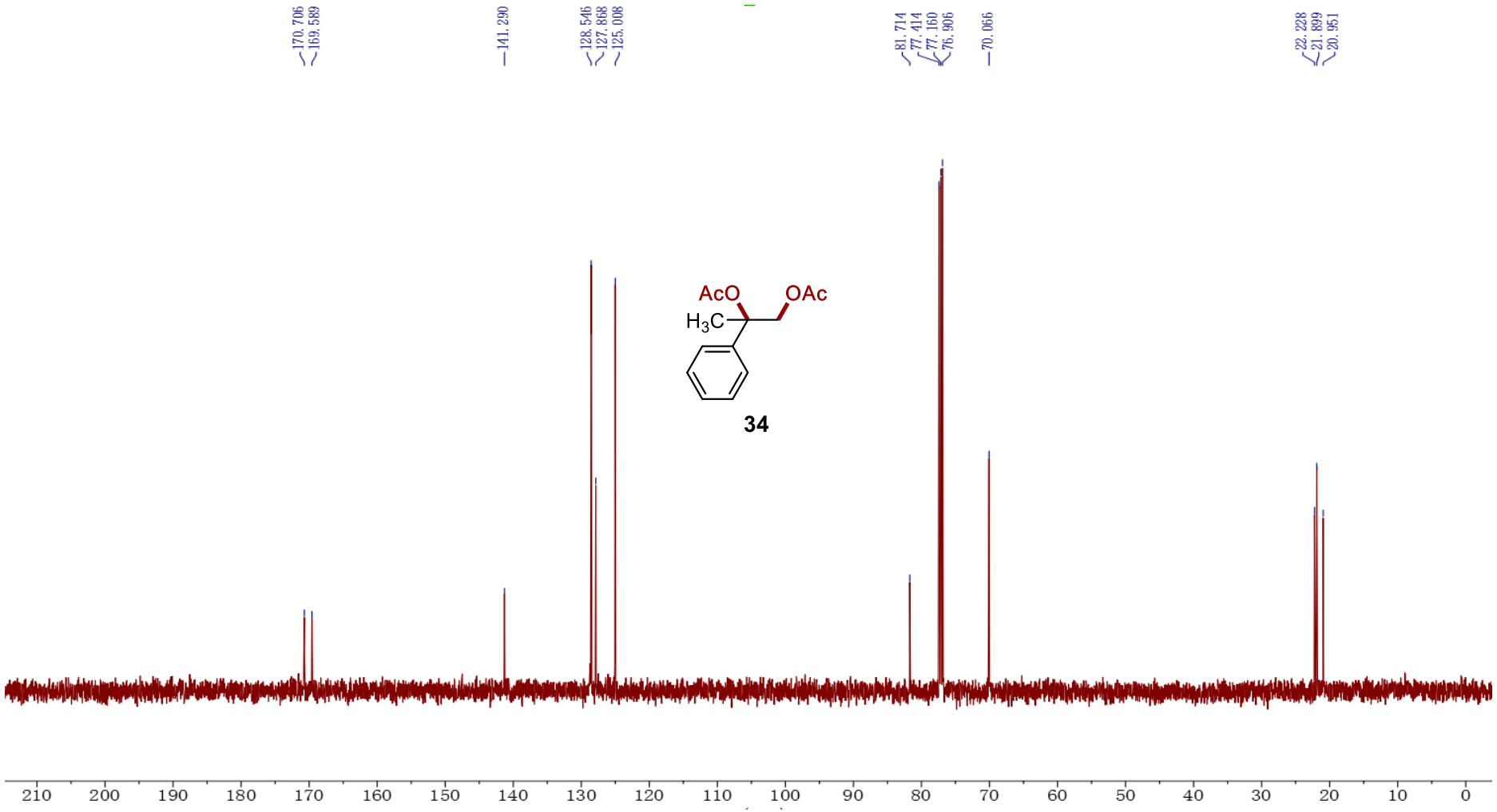
7.341
7.329
7.323
7.292
7.260
4.397
4.374
4.300
4.276
2.086
2.057
1.894
AcO
OAc
H3C
34
5.34
1.00
1.05
2.96
3.17
2.98
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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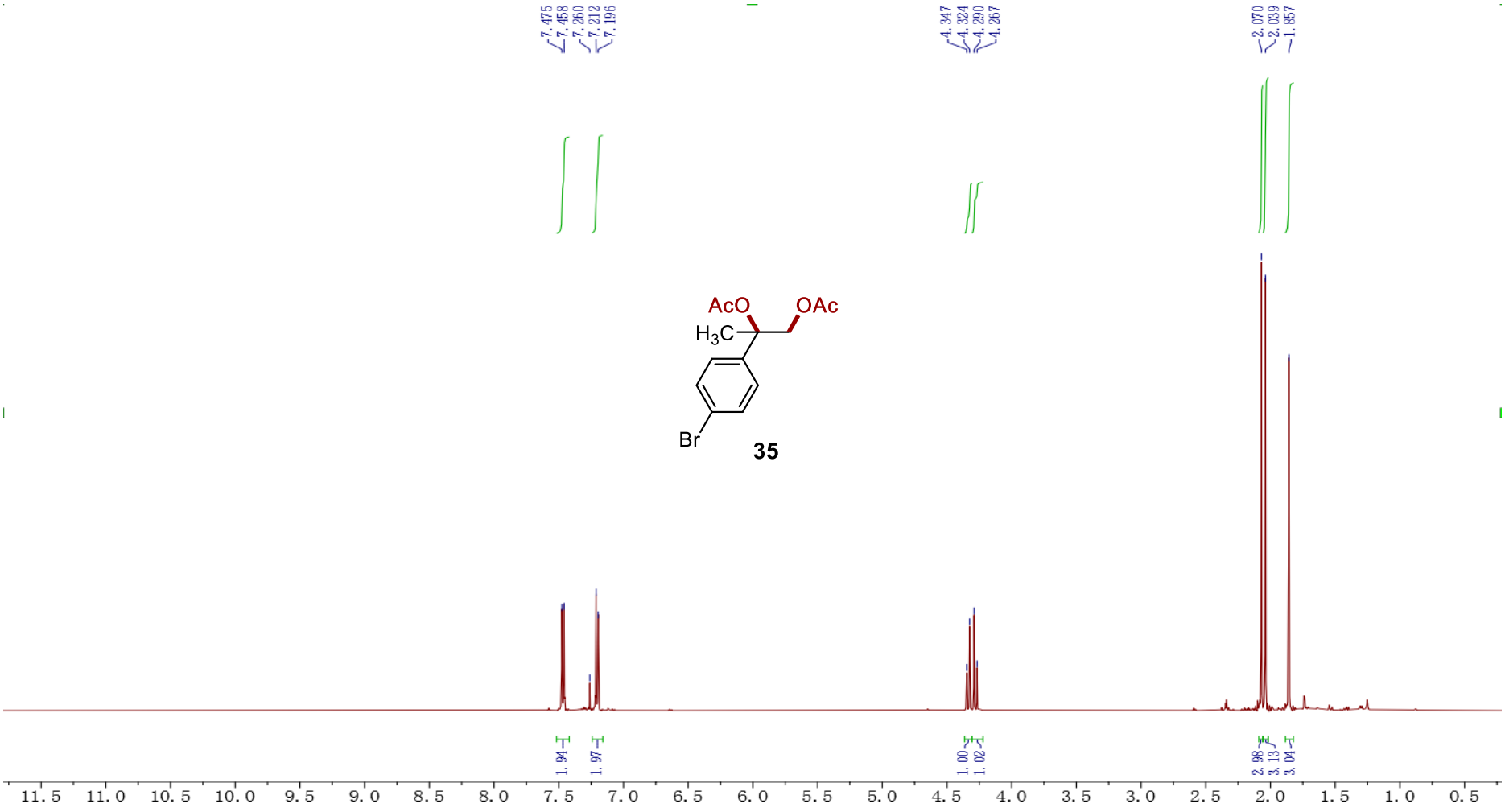
141.290
128.546
127.868
125.008
81.714
77.414
77.160
76.906
70.066
22.228
21.899
20.951
AcO
OAc
H3C
34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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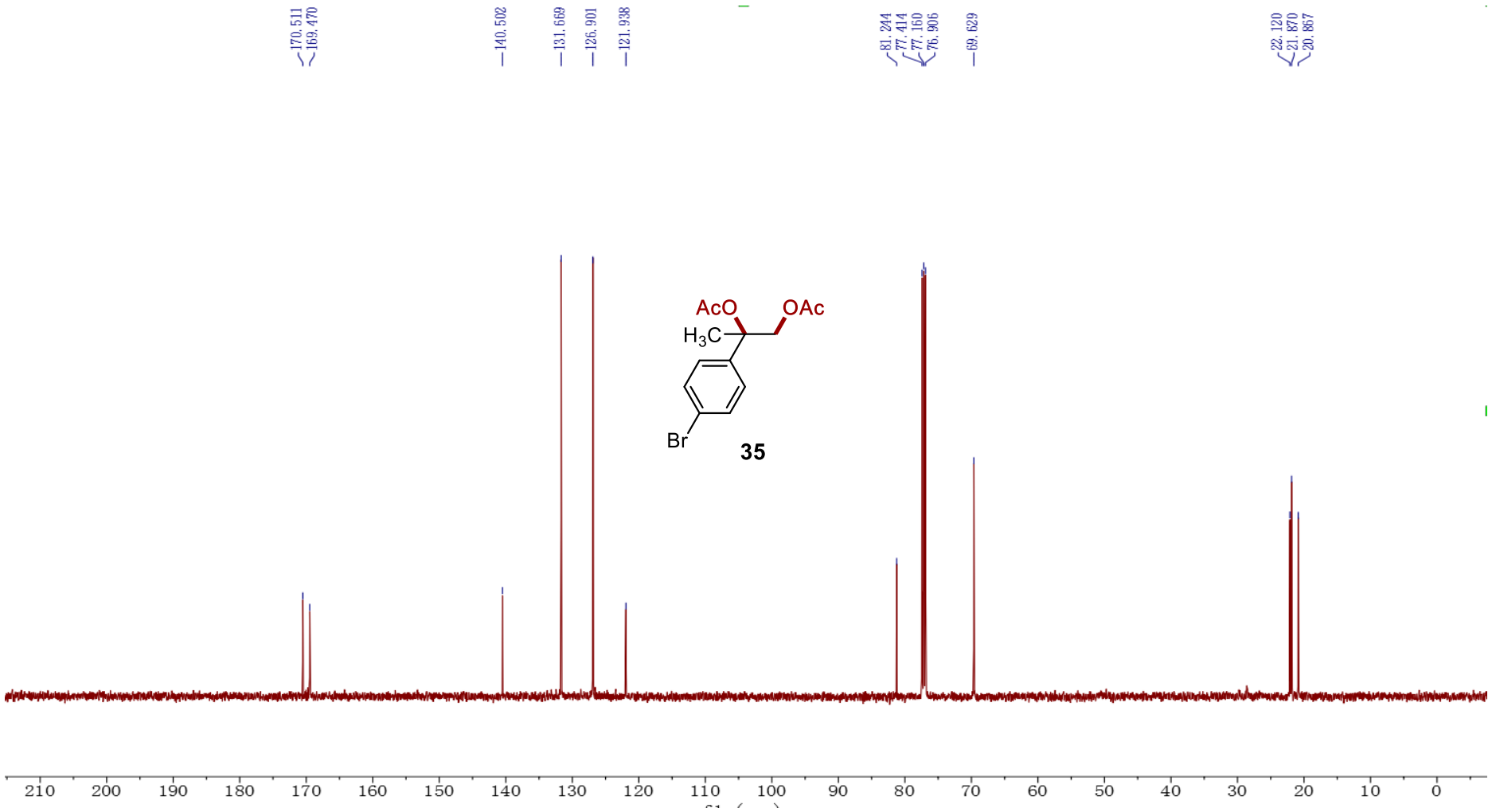
7.458
7.260
7.212
7.196
4.347
4.324
4.290
4.267
2.070
2.039
1.857
AcO
OAc
H3C
Br
35
1.94
1.97
1.00
1.02
2.98
3.13
3.04
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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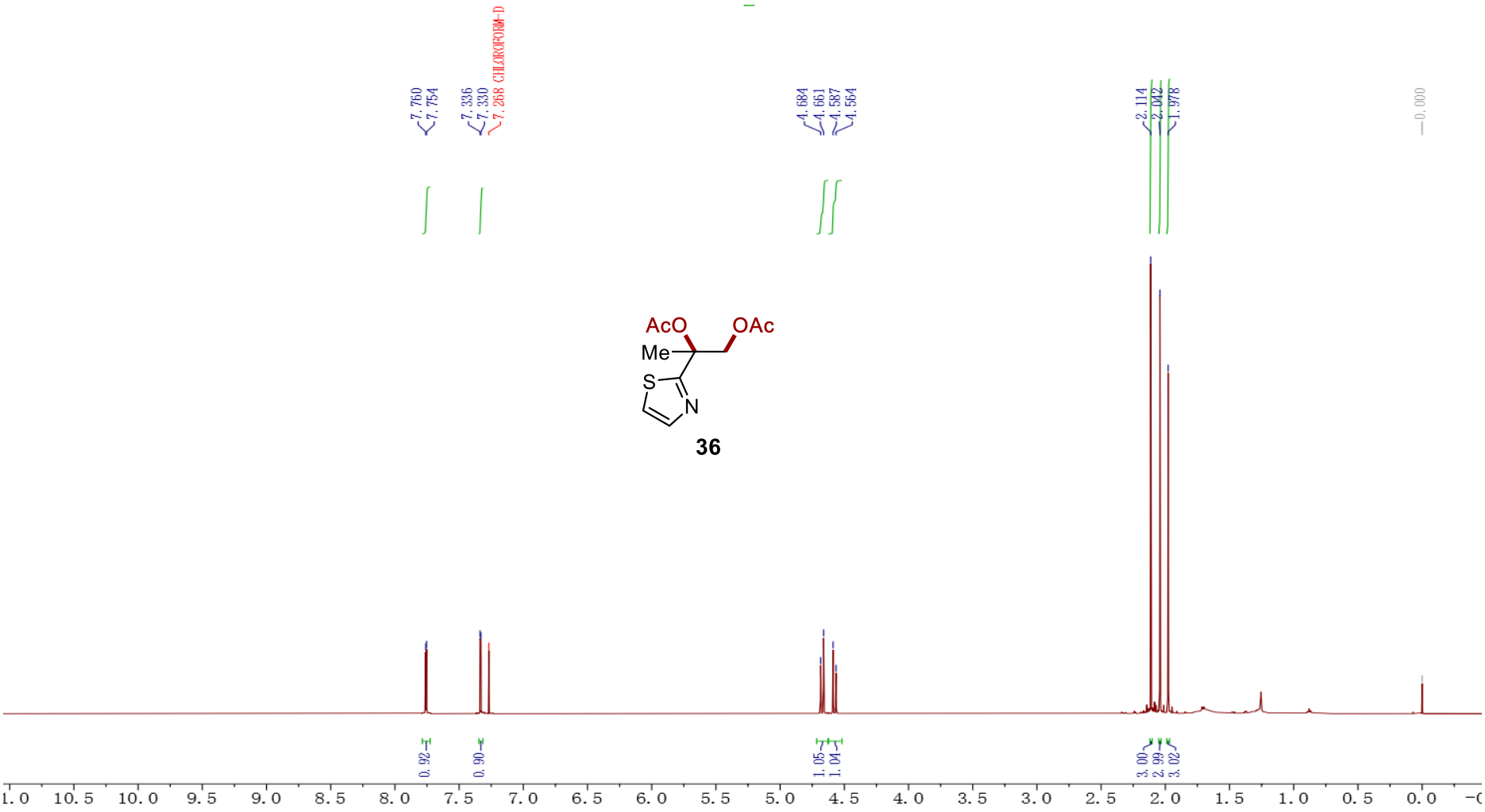
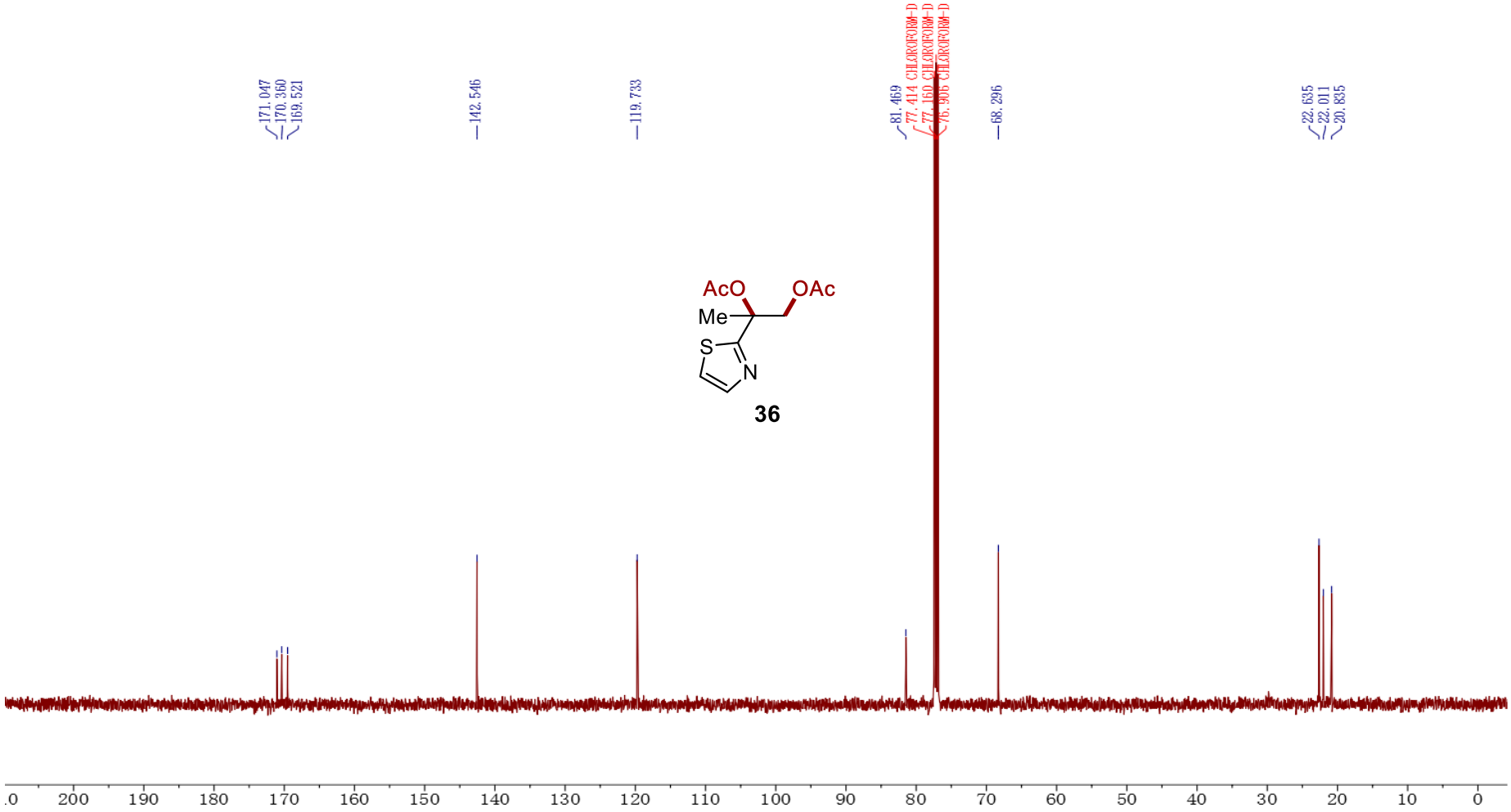
169.470
140.502
131.669
126.901
121.938
81.244
77.414
77.160
76.906
69.629
22.120
21.870
20.867
AcO
OAc
H3C
Br
35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.760
7.754
7.336
7.330
7.268
4.684
4.661
4.587
4.564
2.114
2.042
1.978
0.000
AcO
OAc
Me
S
N
36
0.92
0.90
1.05
1.04
3.00
2.99
3.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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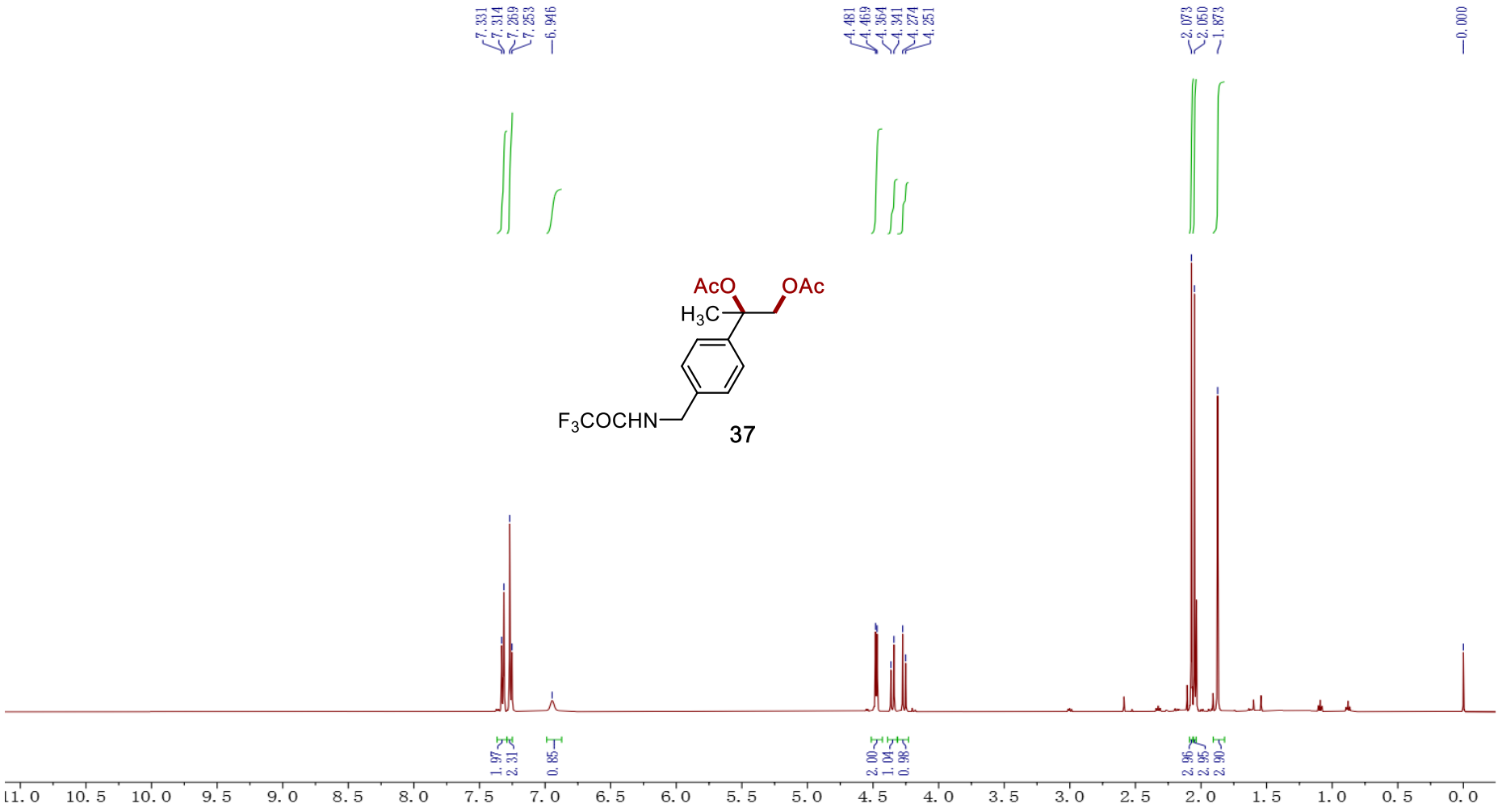
169.521
142.546
119.733
81.469
77.414 CHLOROFORM-D
77.160 CHLOROFORM-D
76.905 CHLOROFORM-D
68.296
22.635
22.011
20.835
AcO
OAc
Me
S
N
36
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.331
7.314
7.269
7.253
6.946
4.481
4.469
4.354
4.341
4.274
4.251
2.073
2.050
1.873
0.000
AcO
OAc
H3C
F3COCHN
37
1.97
2.31
0.85
2.00
1.04
0.98
2.96
2.95
2.90
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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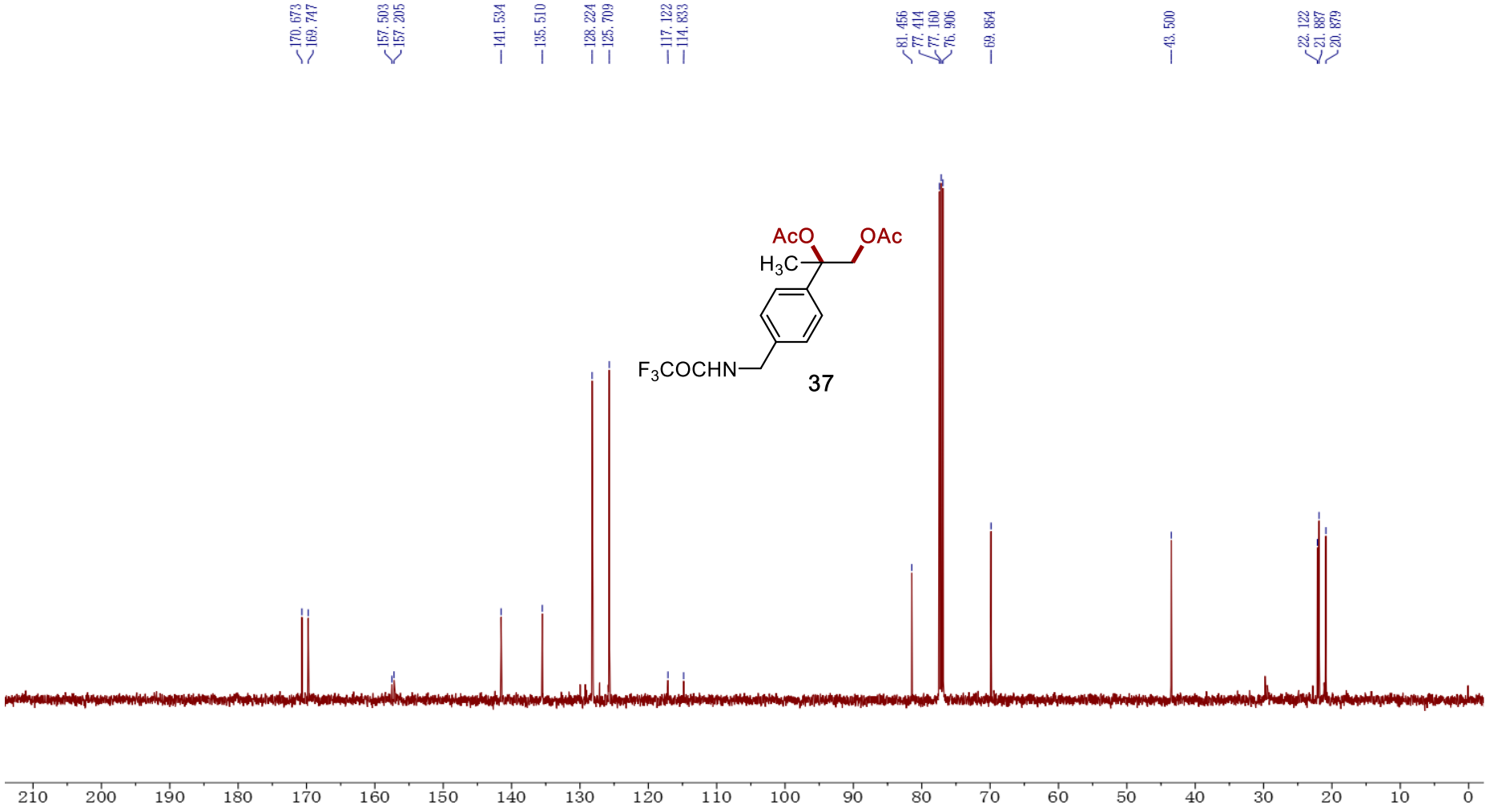
2.0
1.5
1.0
0.5
0.0


170.673
169.747
157.503
157.205
141.534
135.510
128.224
125.709
117.122
114.833
81.456
77.414
77.160
76.906
69.864
43.500
22.122
21.887
20.879
AcO
OAc
H3C
F3COCHN
37
210
200
190
180
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150
140
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120
110
100
90
80
70
60
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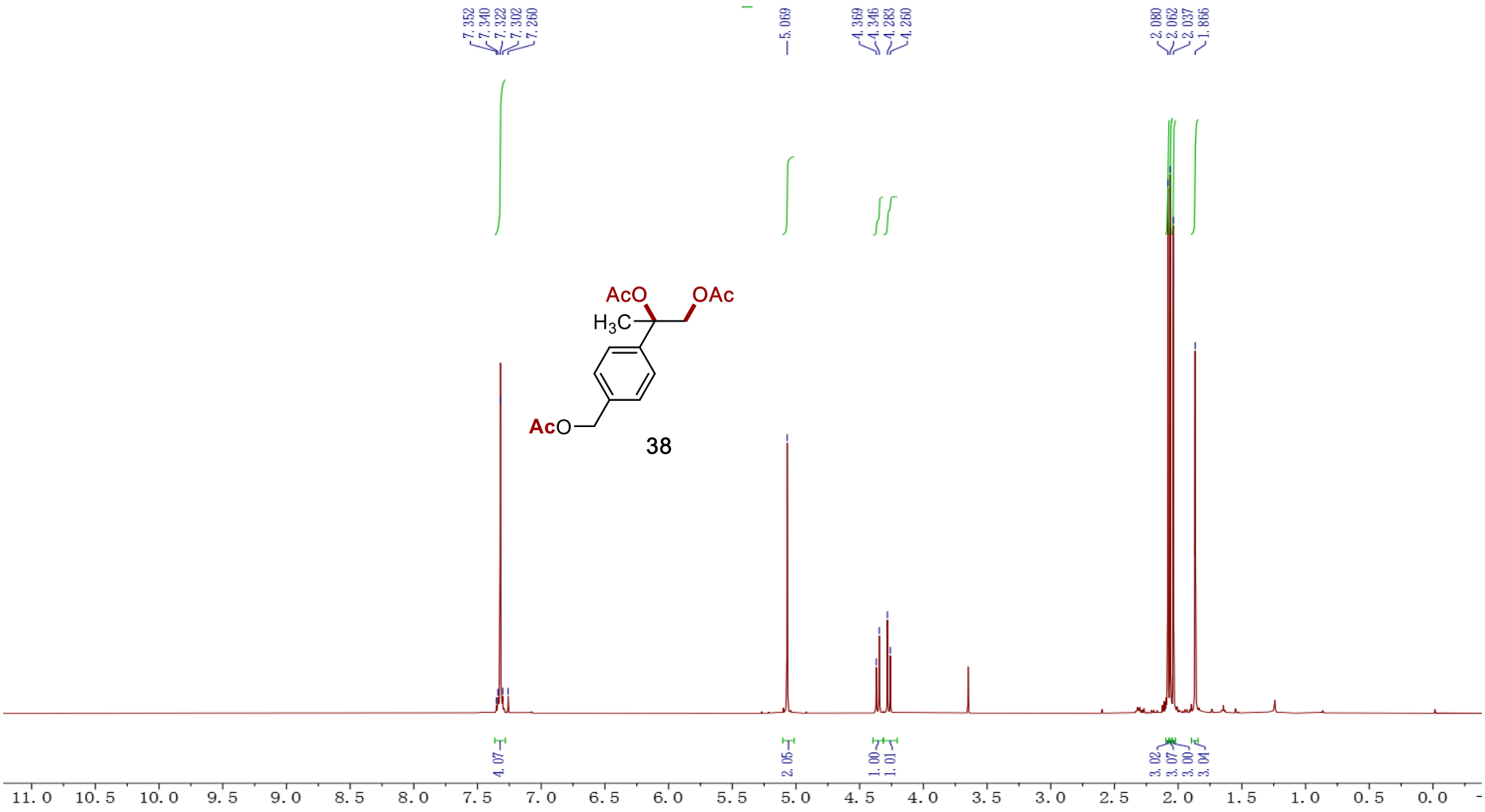
30
20
10
0


7.352
7.340
7.322
7.302
7.260
5.069
4.369
4.346
4.283
4.260
2.080
2.062
2.037
1.866
AcO
OAc
H3C
AcO
38
4.07
2.05
1.00
1.01
3.02
3.07
3.00
3.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
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2.0
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1.0
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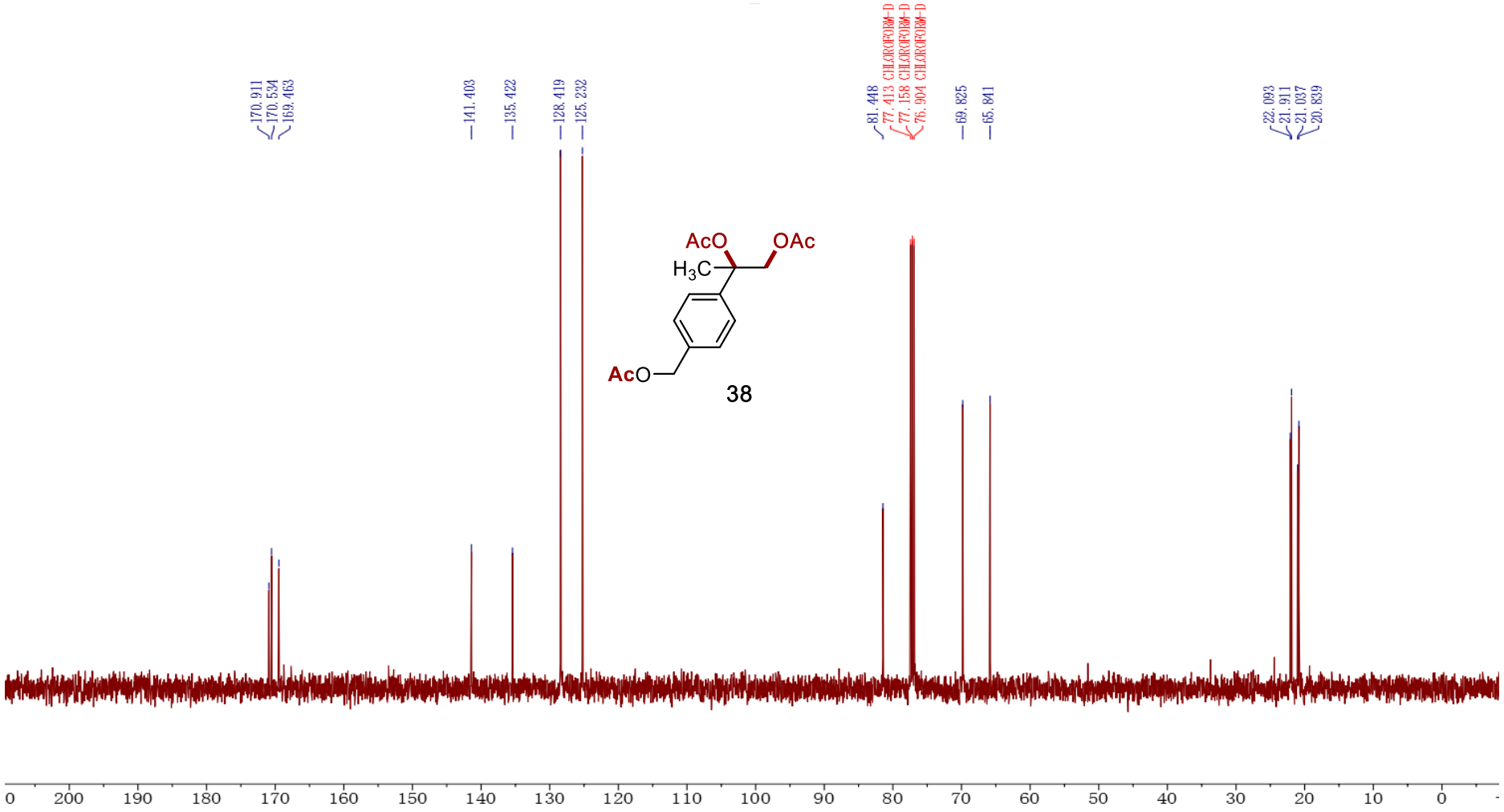
0.0


170.911
170.534
169.463
141.403
135.422
128.419
125.232
81.448
77.413 CHLOROFORM-D
77.158 CHLOROFORM-D
76.904 CHLOROFORM-D
69.825
65.841
22.093
21.911
21.037
20.839
AcO
OAc
H3C
AcO
38
0
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180
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150
140
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120
110
100
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70
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40
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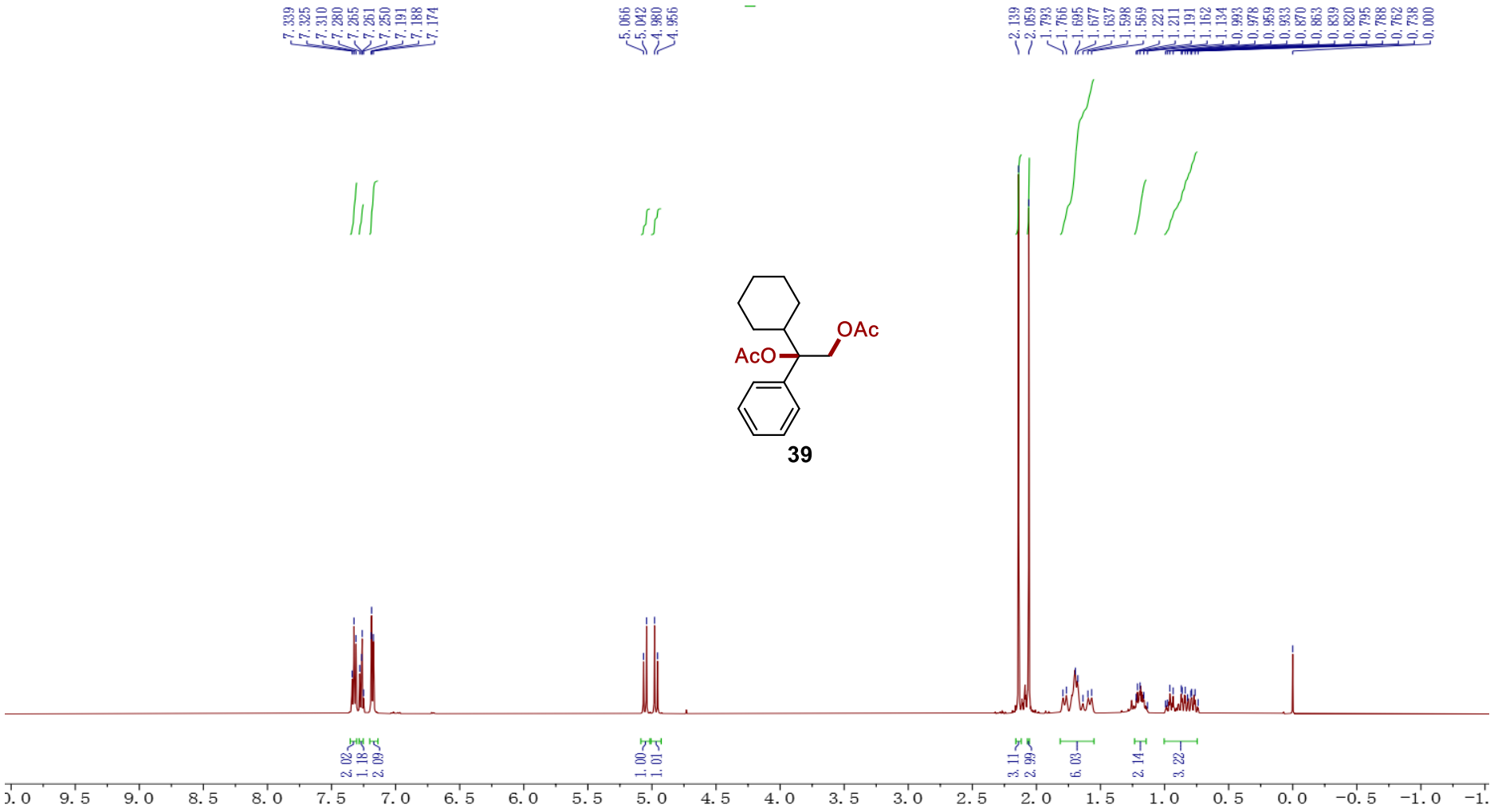
20
10
0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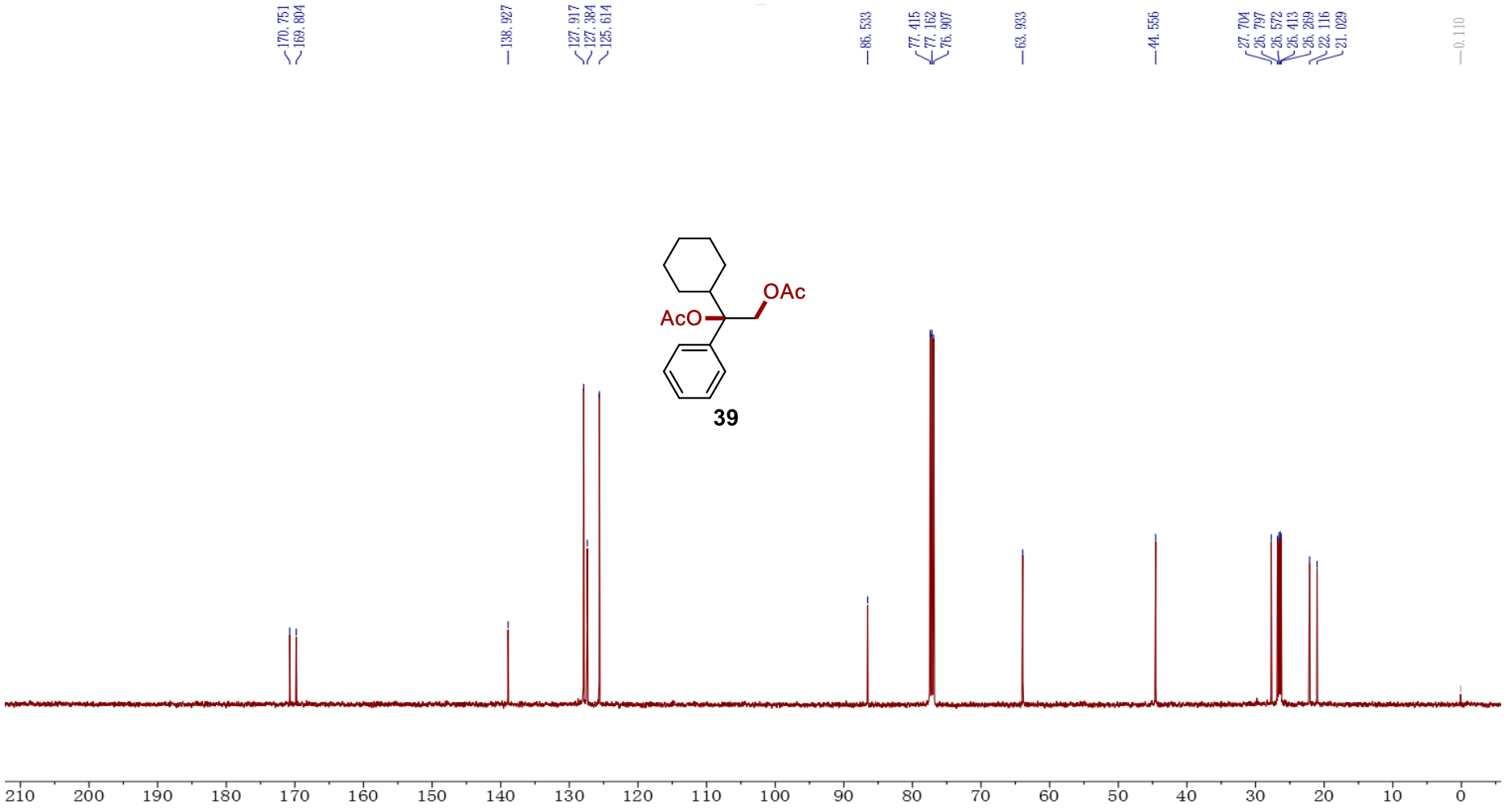
7.310
7.280
7.265
7.261
7.250
7.191
7.188
7.174
5.066
5.042
4.980
4.956
2.139
2.059
1.793
1.766
1.695
1.677
1.637
1.598
1.569
1.221
1.211
1.191
1.162
1.134
0.993
0.978
0.959
0.933
0.870
0.863
0.839
0.820
0.795
0.788
0.762
0.738
0.000
OAc
AcO
39
2.02
1.18
2.09
1.00
1.01
3.11
2.99
6.03
2.14
3.22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26.269
22.116
21.029
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AcO
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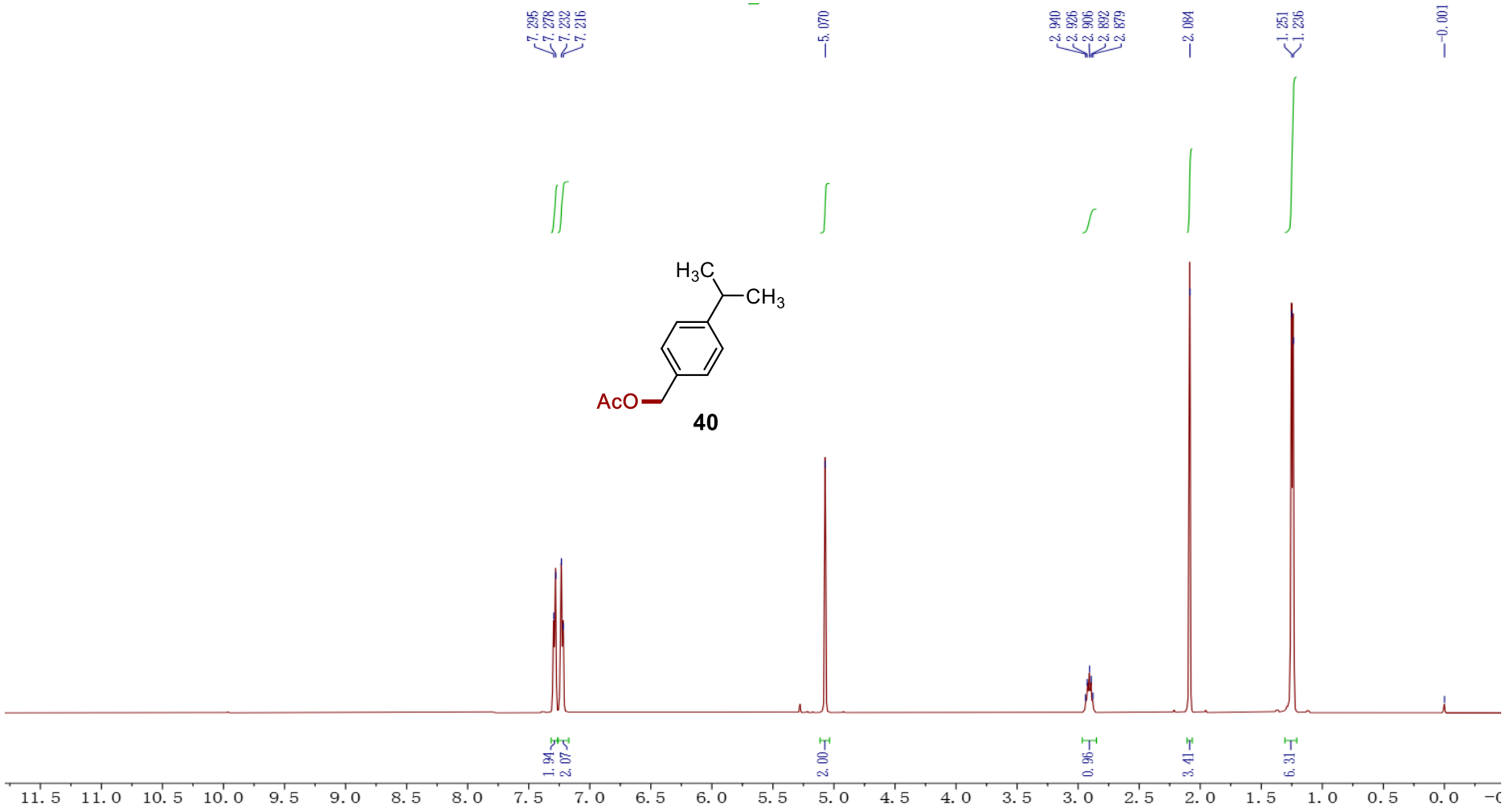
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1.236
0.001
H3C
CH3
AcO
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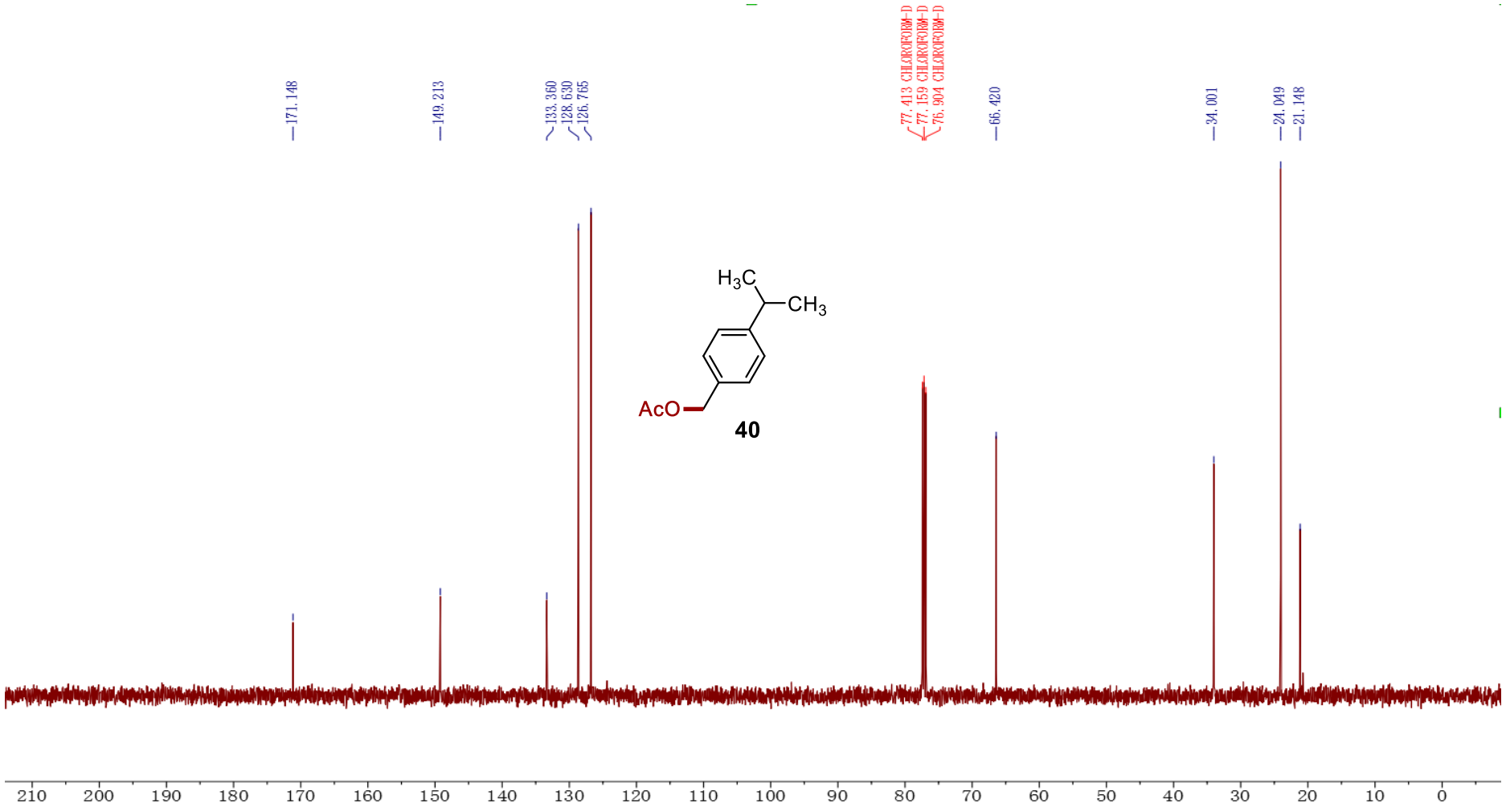
2.07
2.00
0.96
3.41
6.31
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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77.159 CHLOROFORM-D
76.904 CHLOROFORM-D
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H3C
CH3
AcO
40
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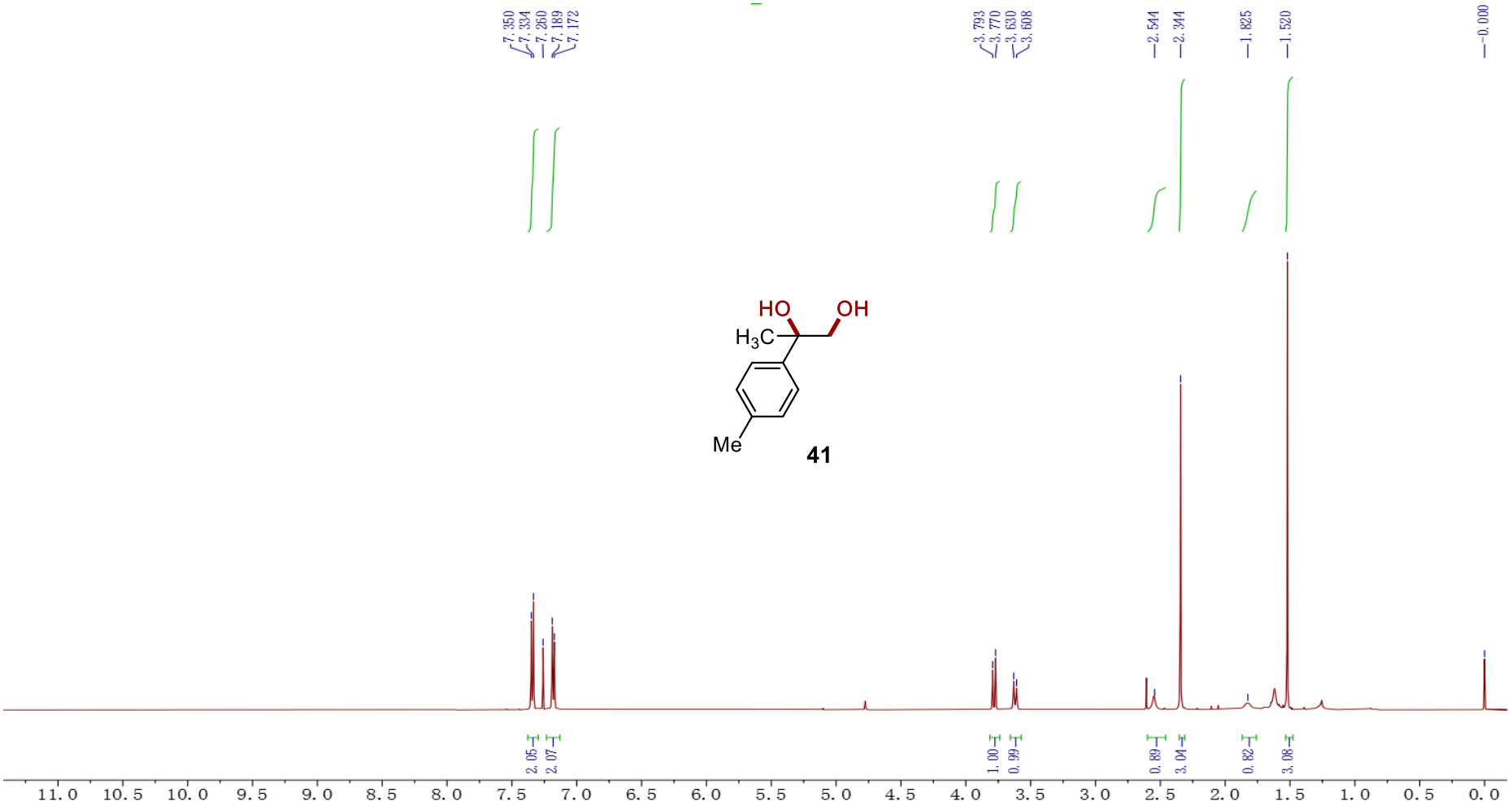
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1.520
0.000
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OH
H3C
Me
41
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0.99
0.89
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0.82
3.08
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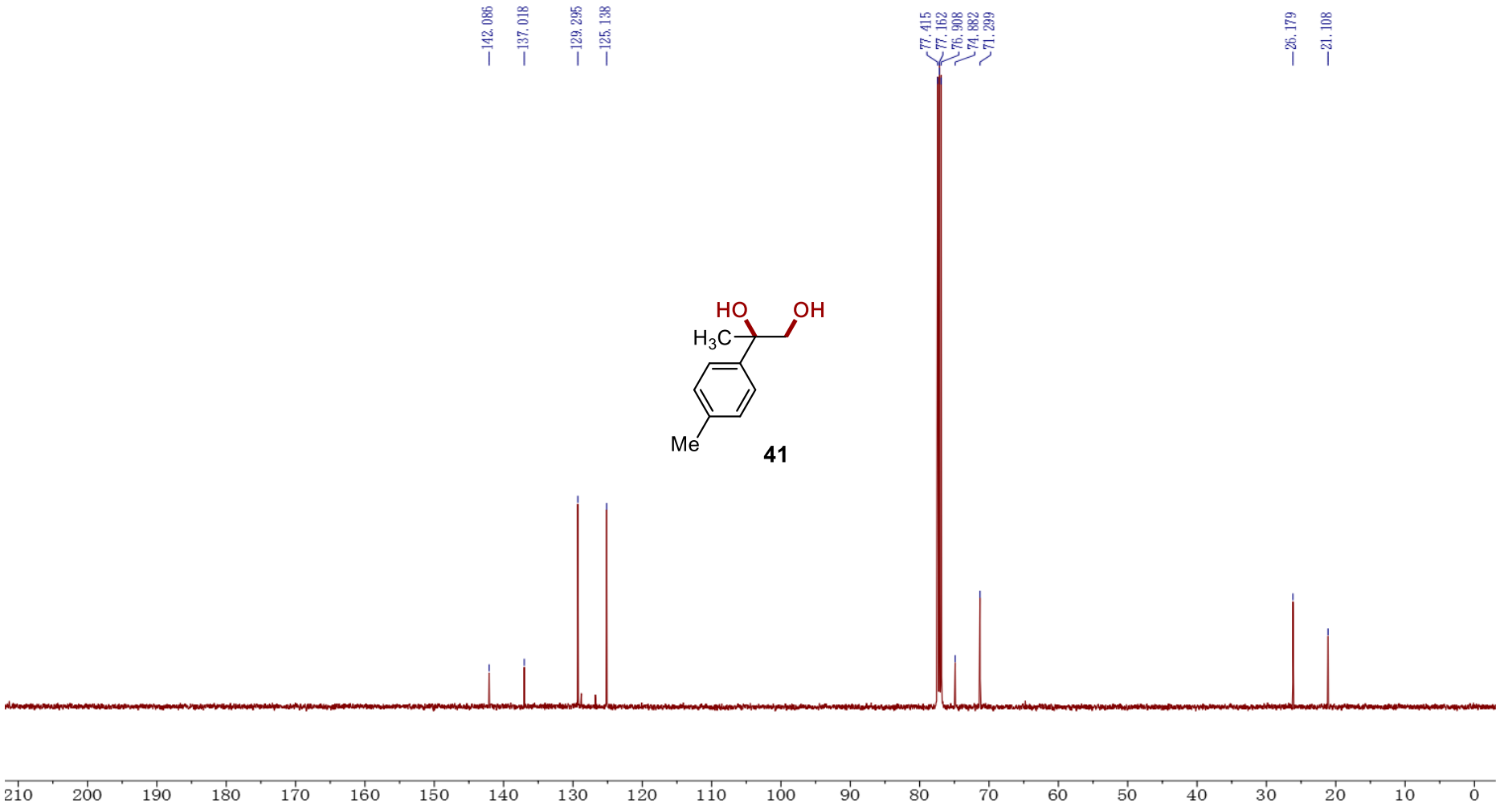
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OH
H3C
Me
41
210
200
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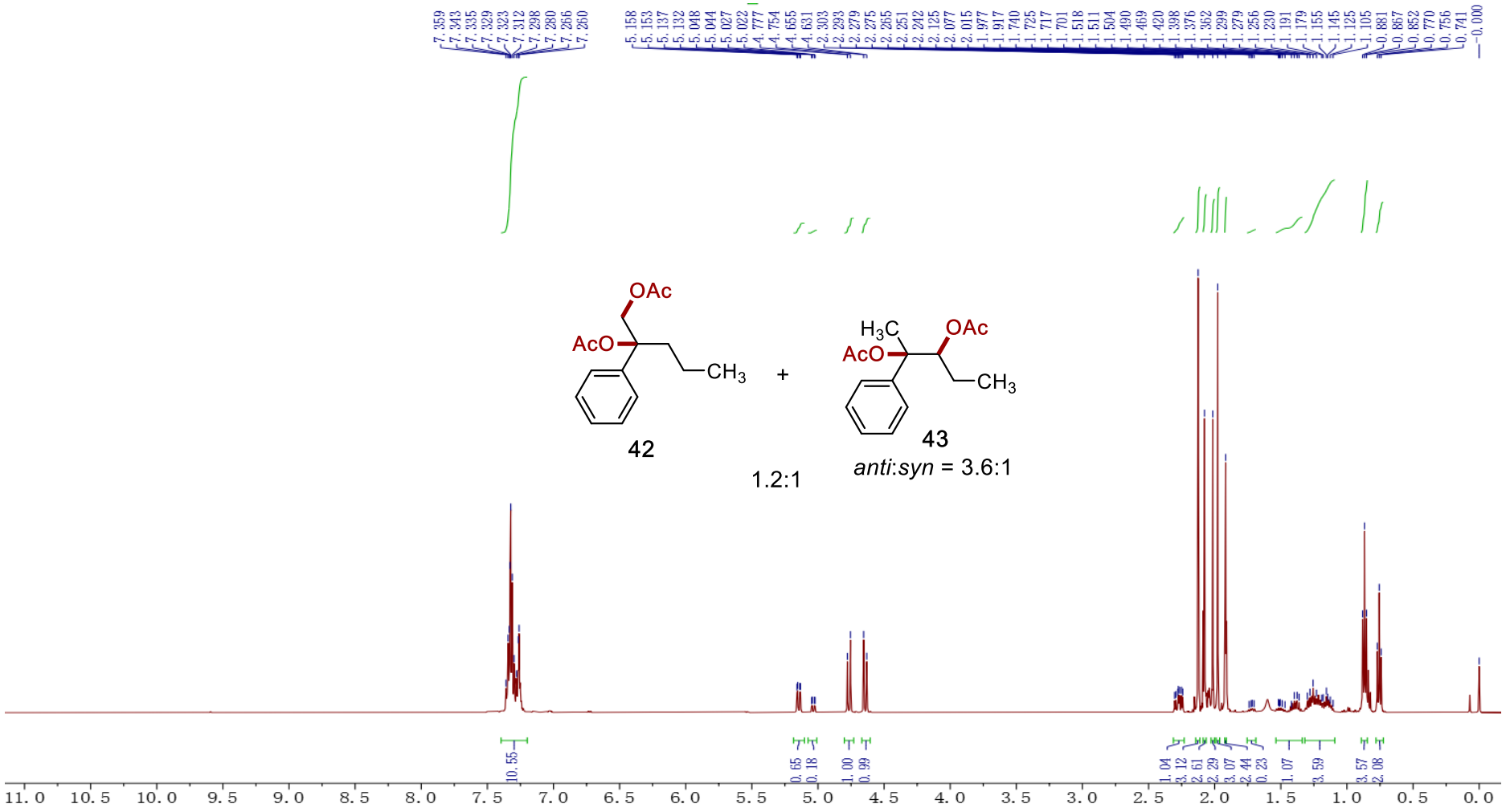
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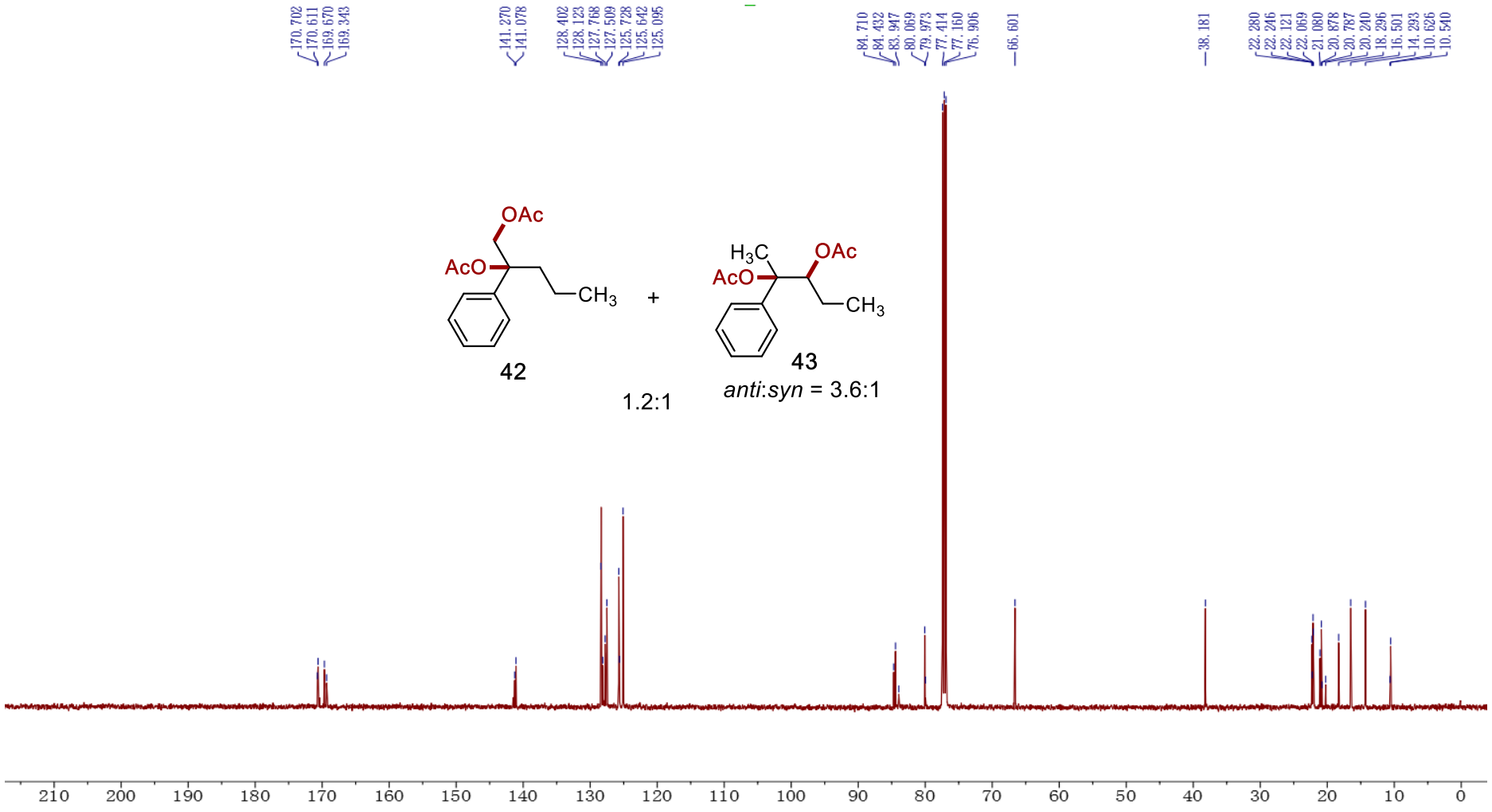
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80.069
79.973
77.414
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76.906
66.601
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22.280
22.246
22.121
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21.080
20.878
20.787
20.240
18.296
16.501
14.293
10.626
10.540
OAc
AcO
CH3
+
H3C
OAc
AcO
CH3
42
1.2:1
43
anti:syn = 3.6:1
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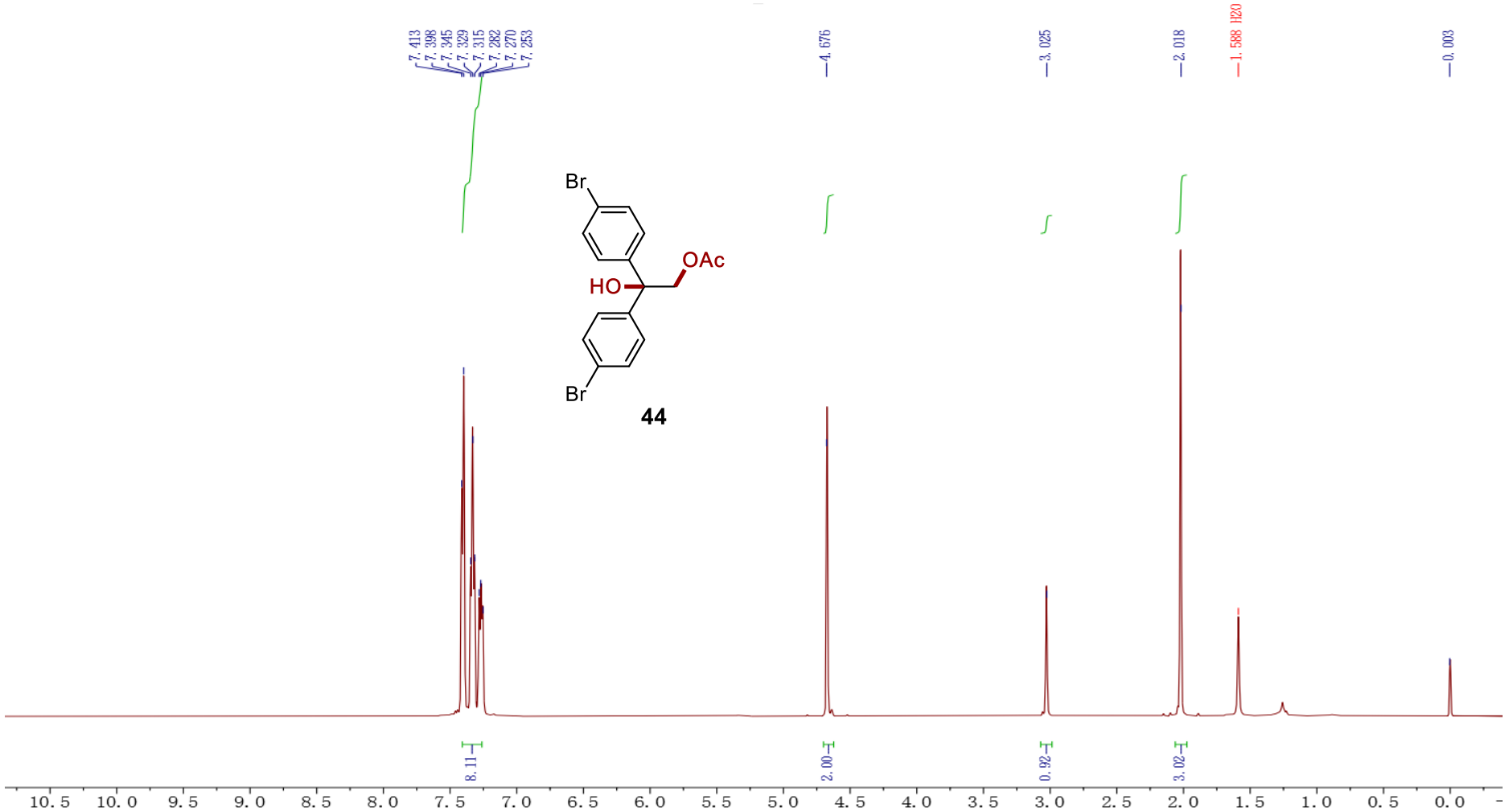
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1.120
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OAc
HO
Br
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2.00
0.92
3.02
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9.0
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8.0
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6.0
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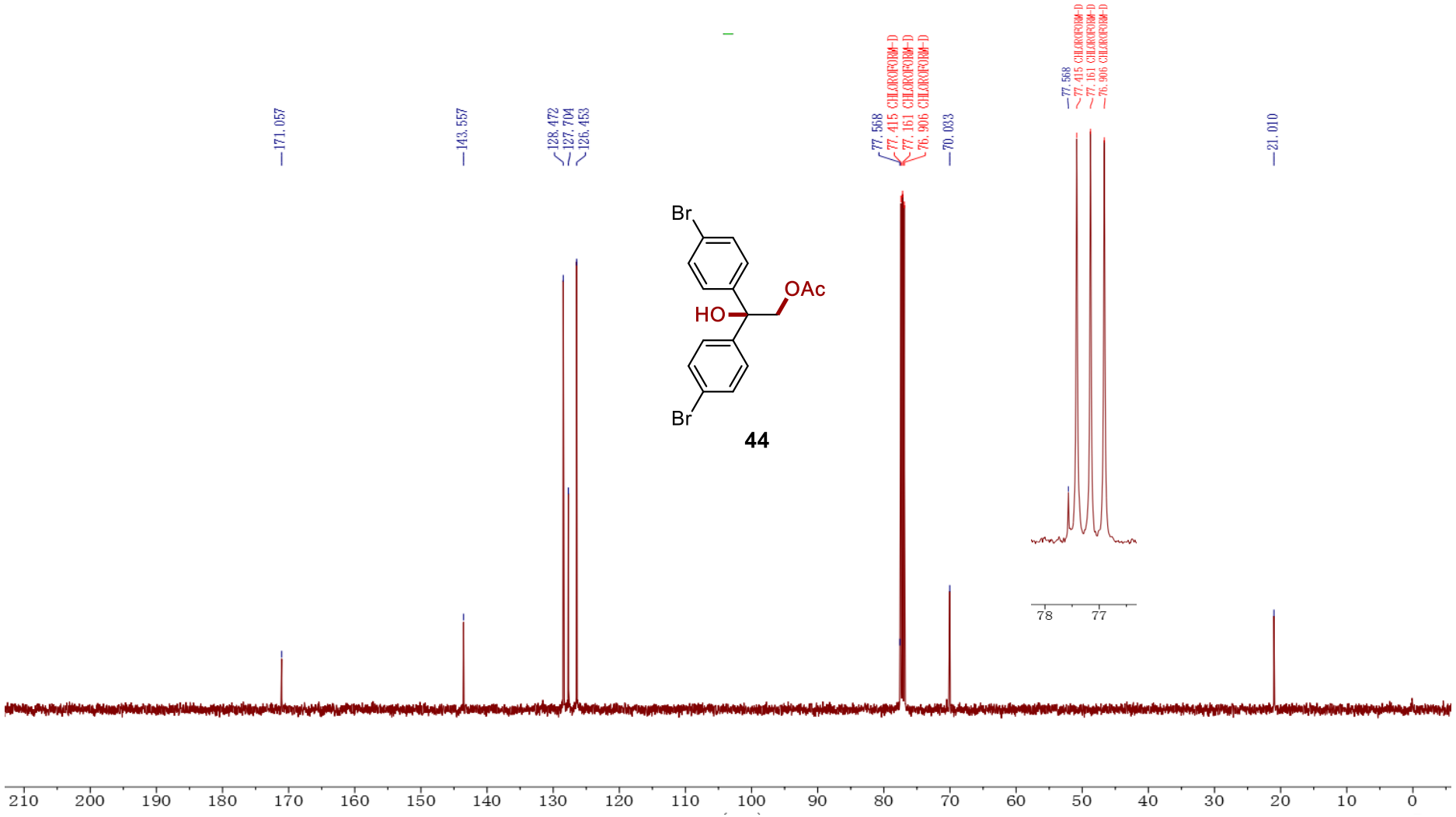
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76.906 CHLOROFORM-D
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OAc
HO
Br
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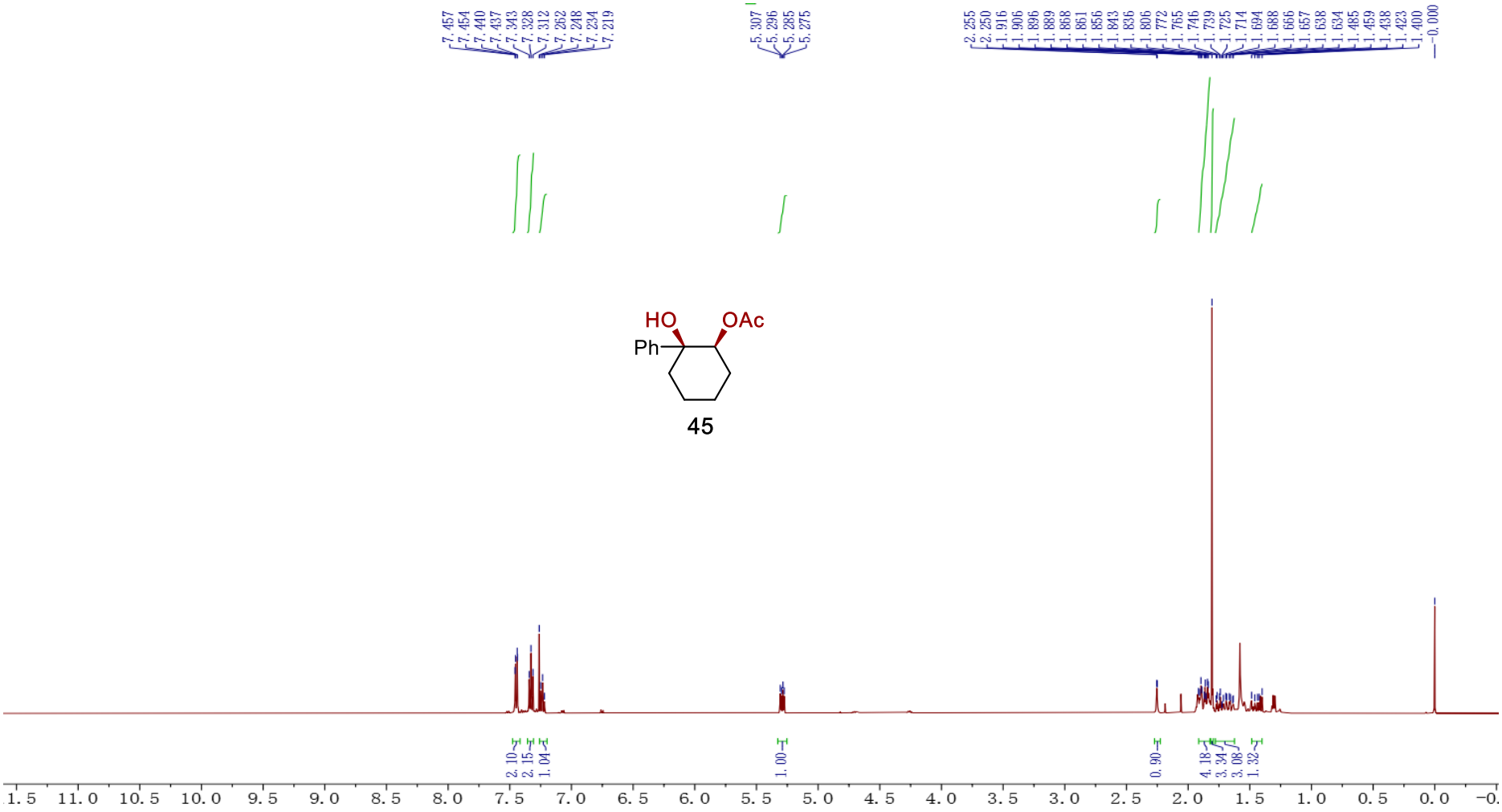
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2.250
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1.906
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1.889
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1.856
1.843
1.836
1.806
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1.765
1.746
1.739
1.725
1.714
1.694
1.688
1.666
1.657
1.638
1.634
1.485
1.459
1.438
1.423
1.400
0.000
HO
OAc
Ph
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2.15
1.04
1.00
0.90
4.18
3.34
3.08
1.32
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10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
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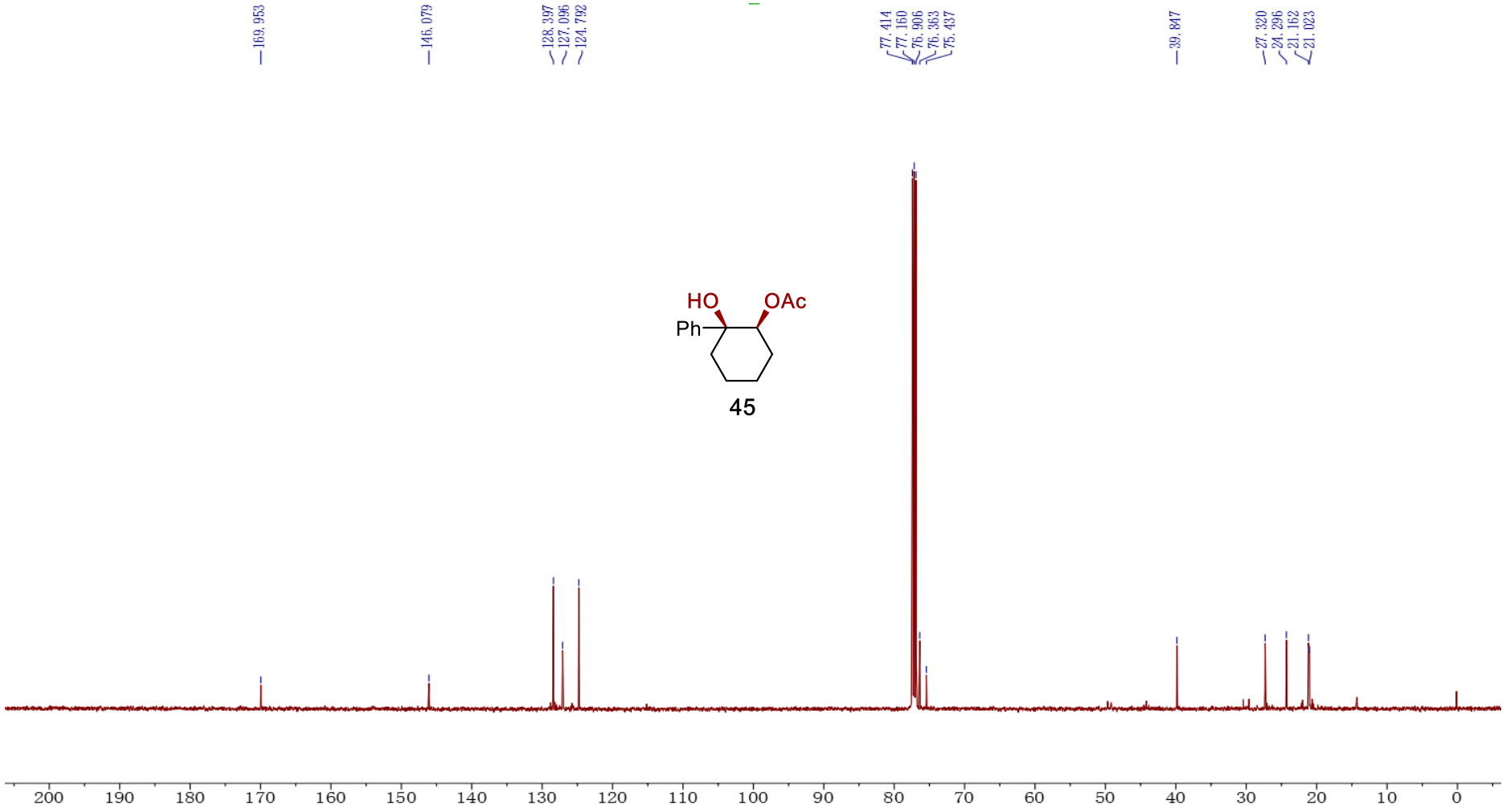
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21.023
HO
OAc
Ph
45
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120
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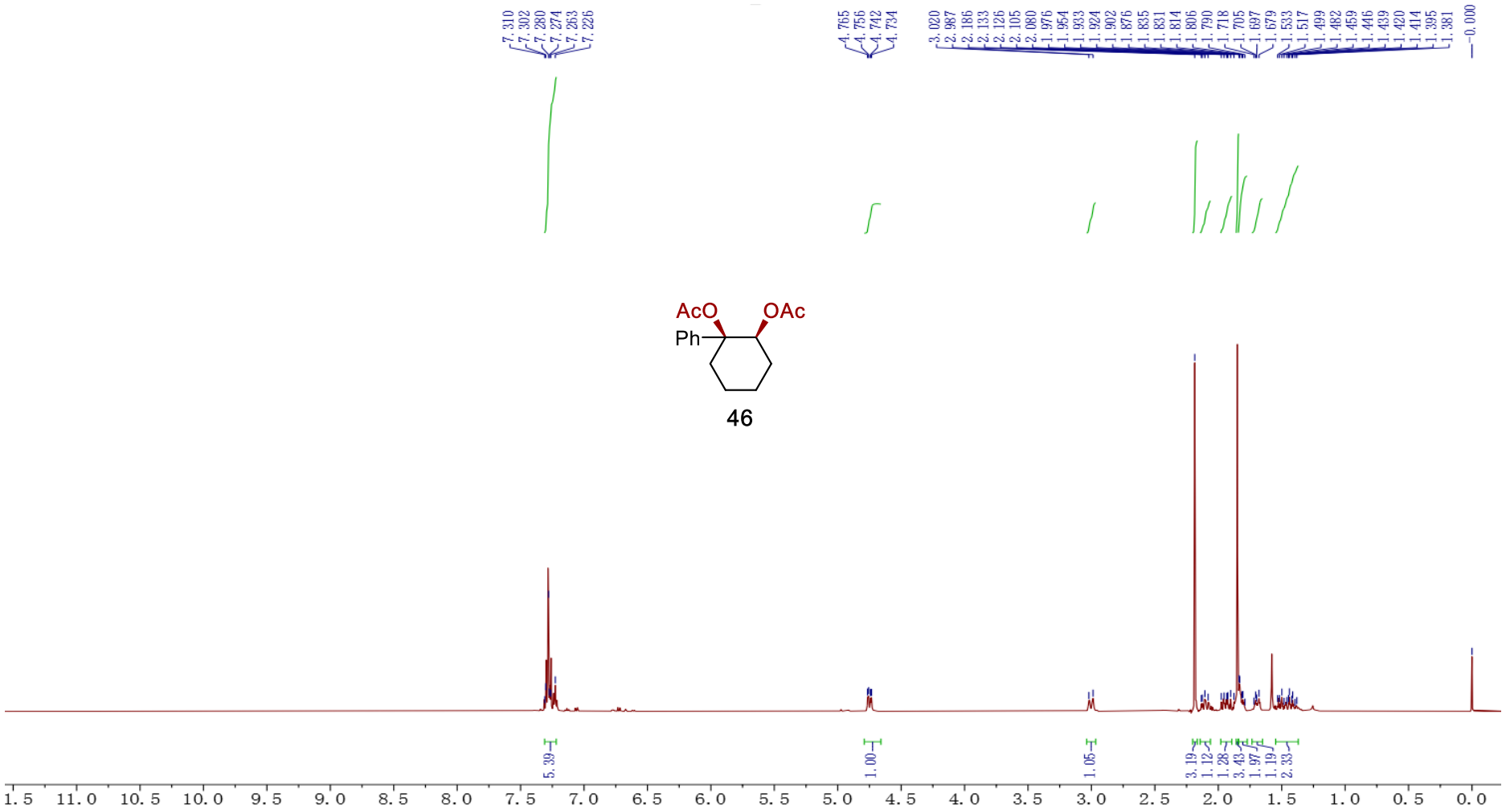
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2.105
2.080
1.976
1.954
1.933
1.924
1.902
1.876
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1.831
1.814
1.806
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1.459
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AcO
OAc
Ph
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1.12
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3.43
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2.33
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9.5
9.0
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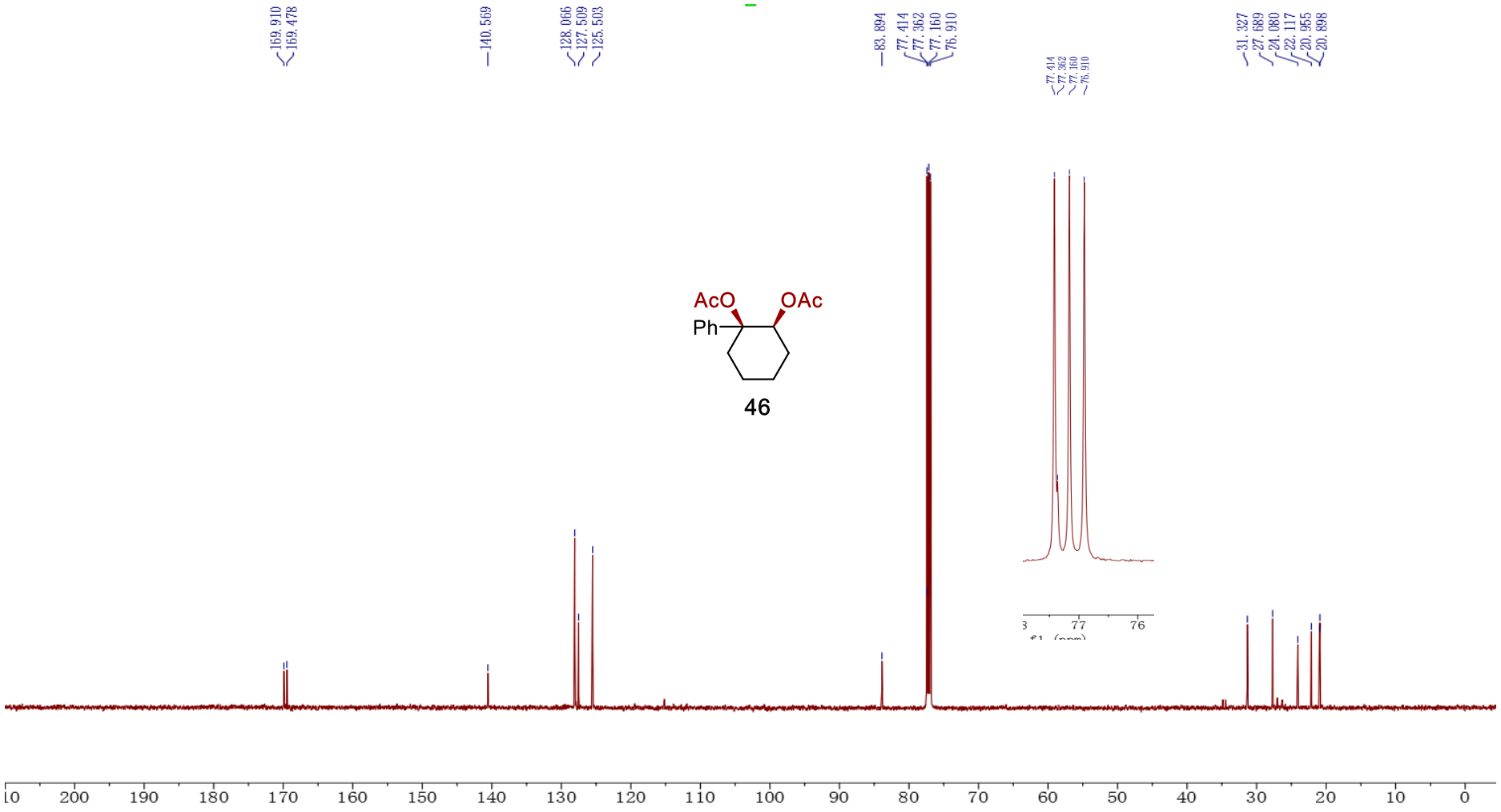
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OAc
Ph
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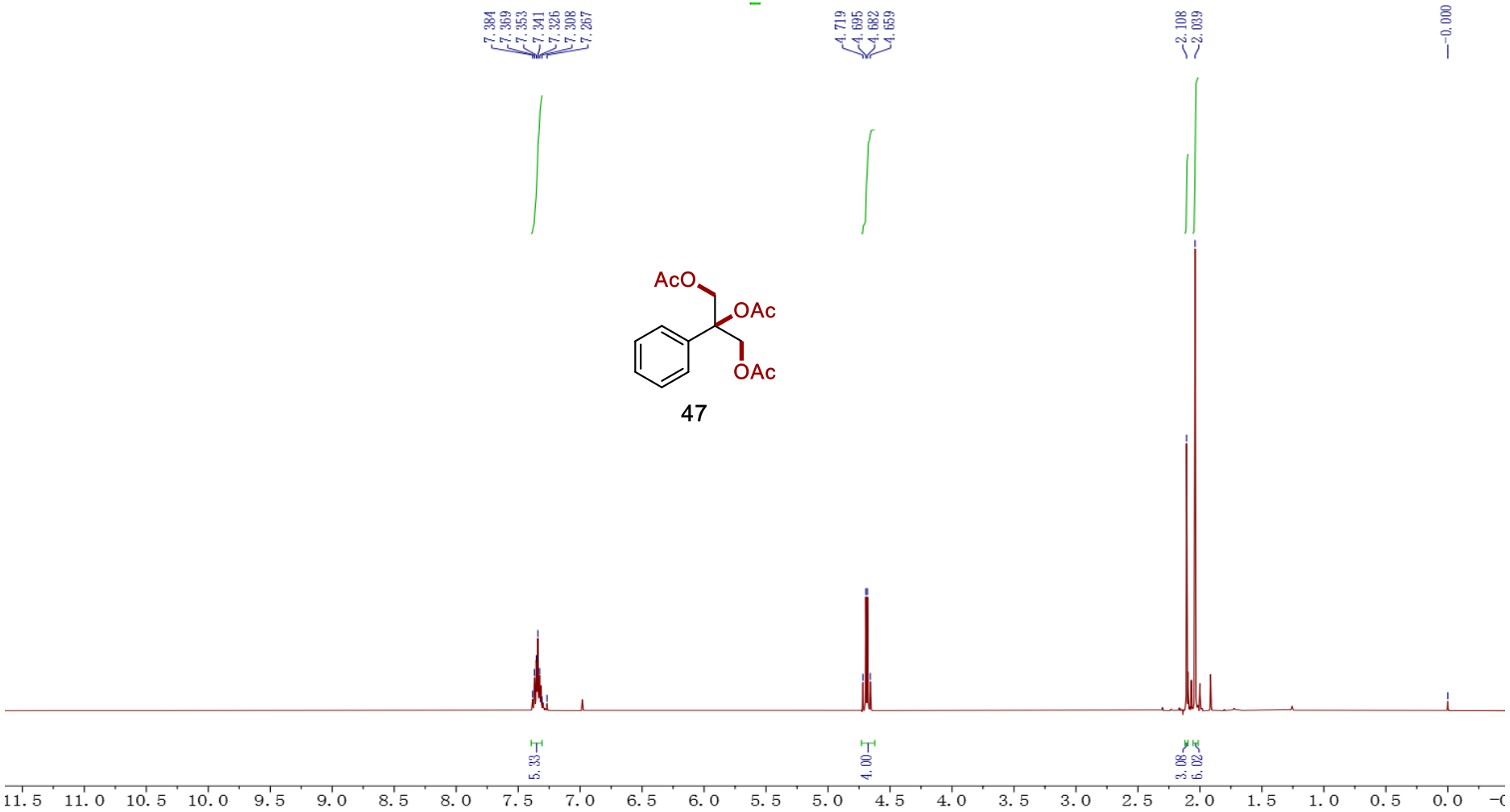
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OAc
OAc
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4.00
3.08
6.02
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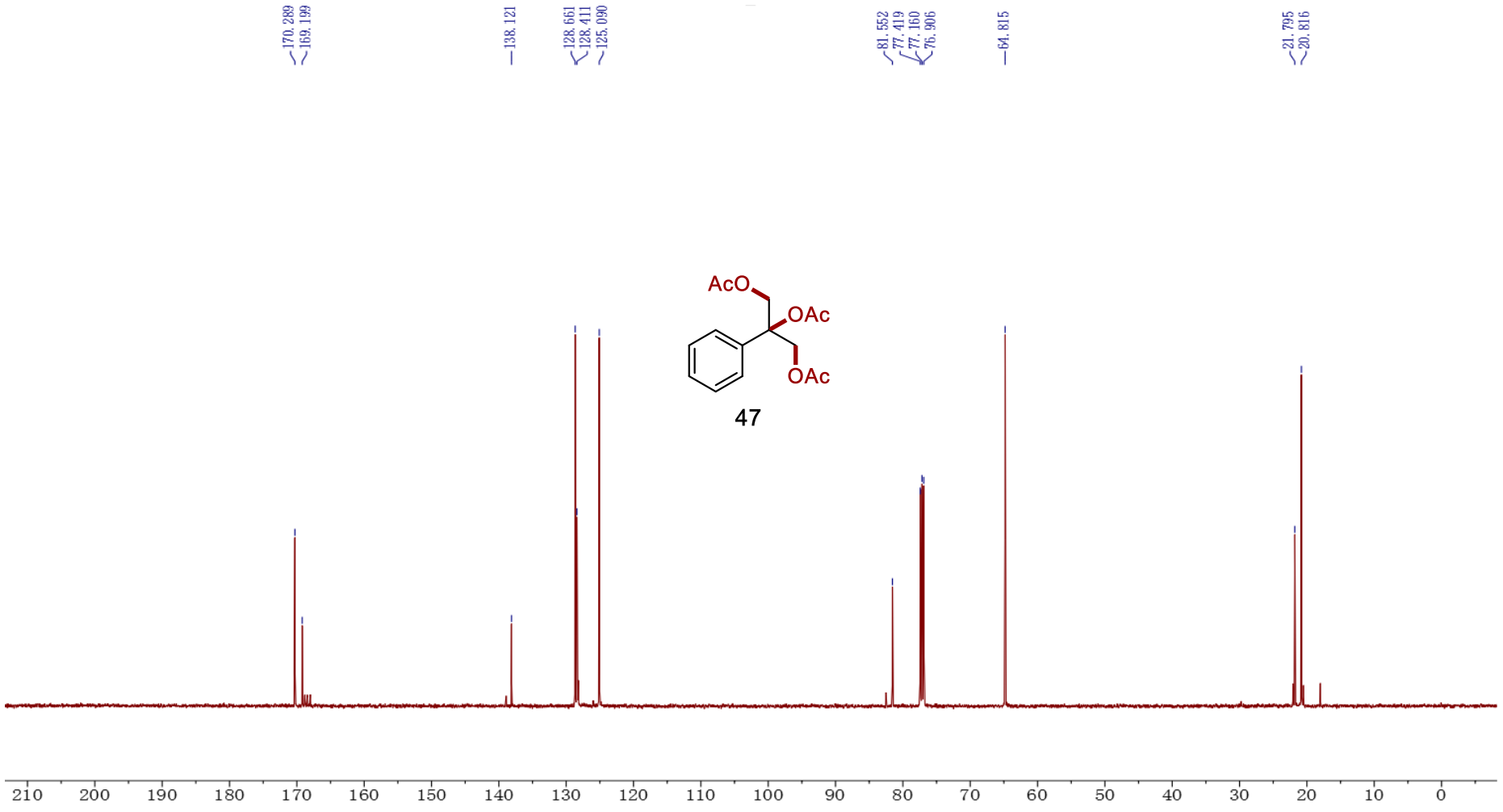
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OAc
OAc
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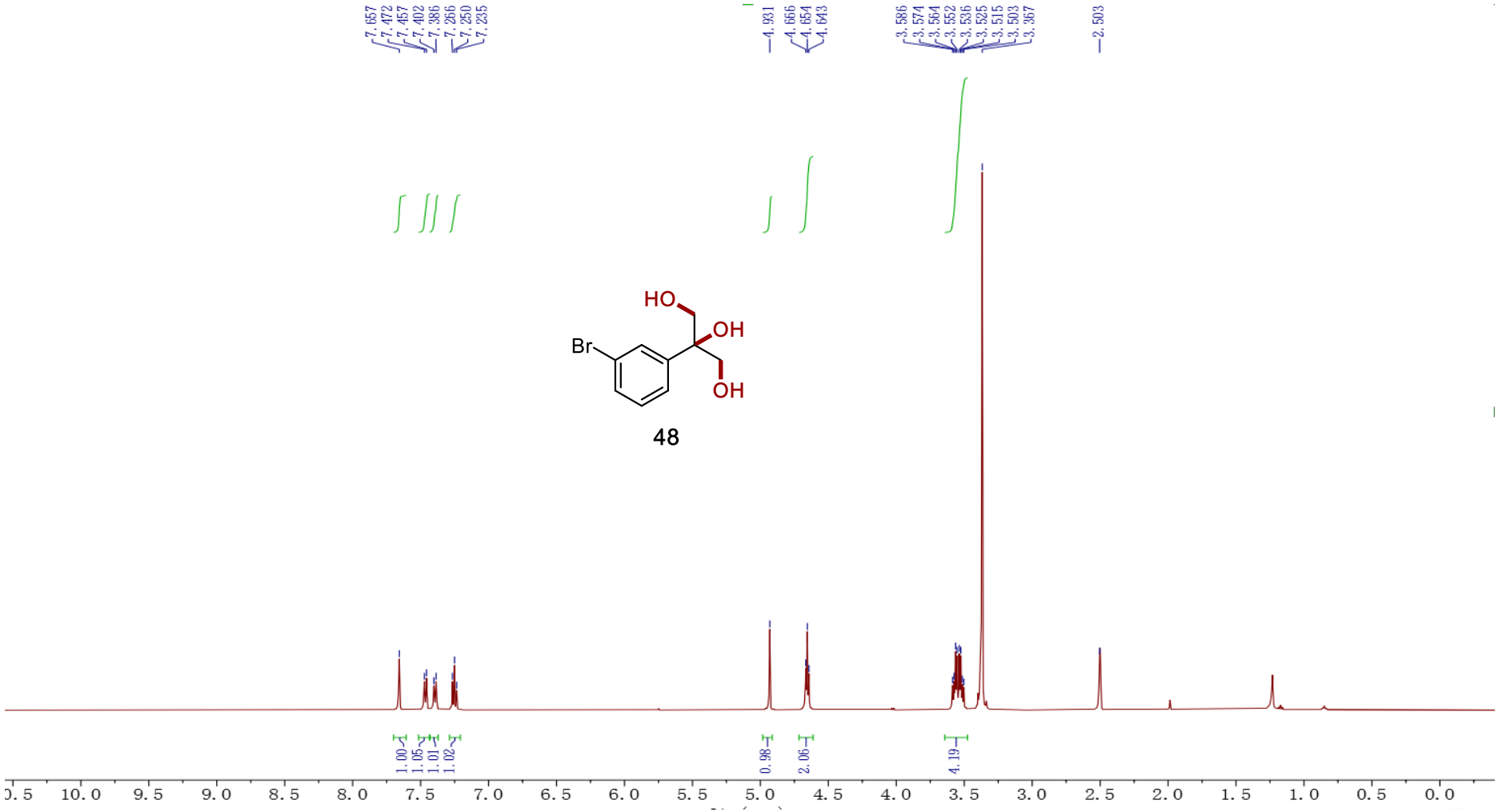
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3.564
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3.536
3.525
3.515
3.503
3.367
2.503
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OH
Br
OH
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1.05
1.01
1.02
0.98
2.06
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9.5
9.0
8.5
8.0
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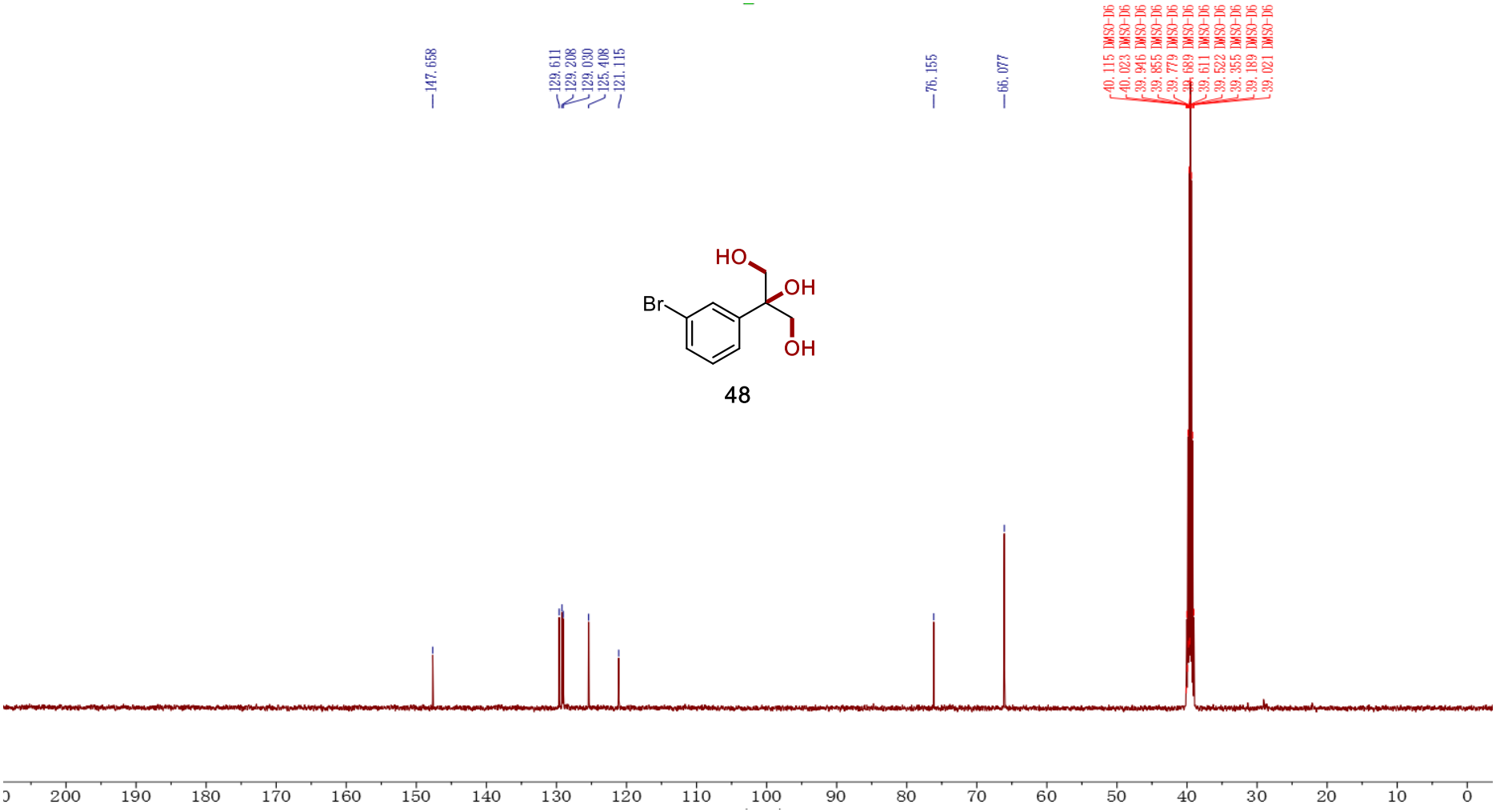
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66.077
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39.946 DMSO-D6
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39.189 DMSO-D6
39.021 DMSO-D6
HO
OH
Br
OH
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200
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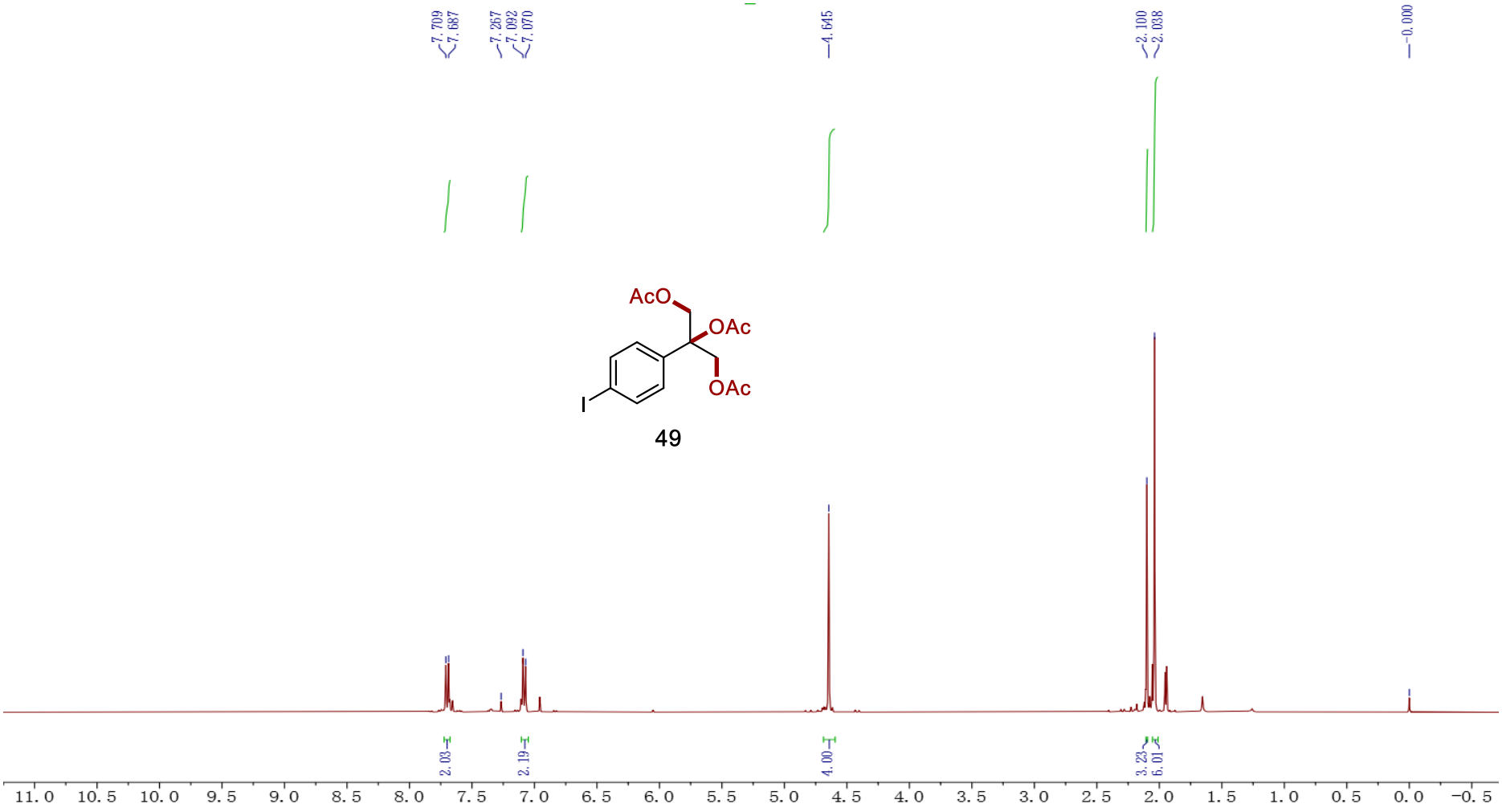
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OAc
OAc
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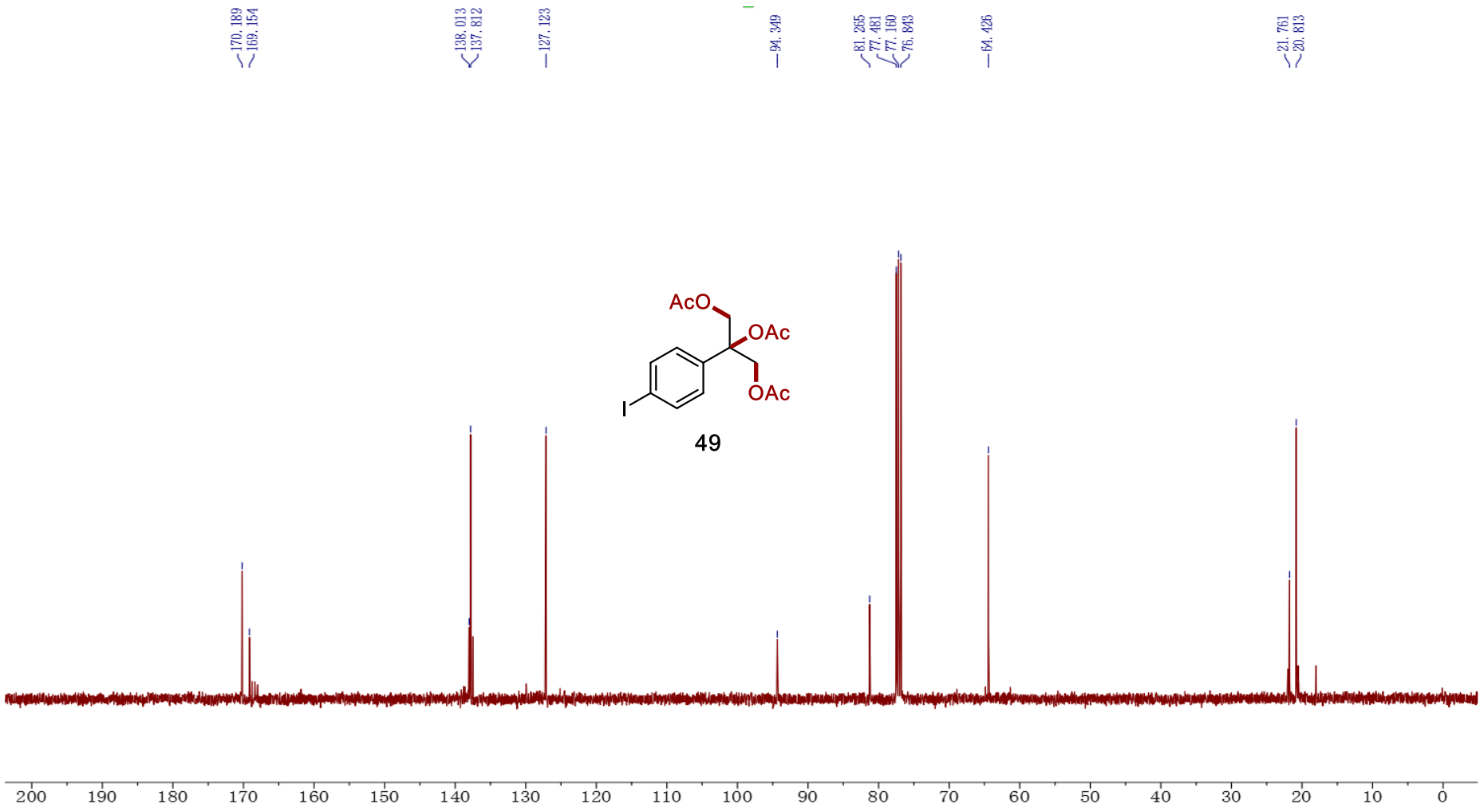
2.19
4.00
3.23
6.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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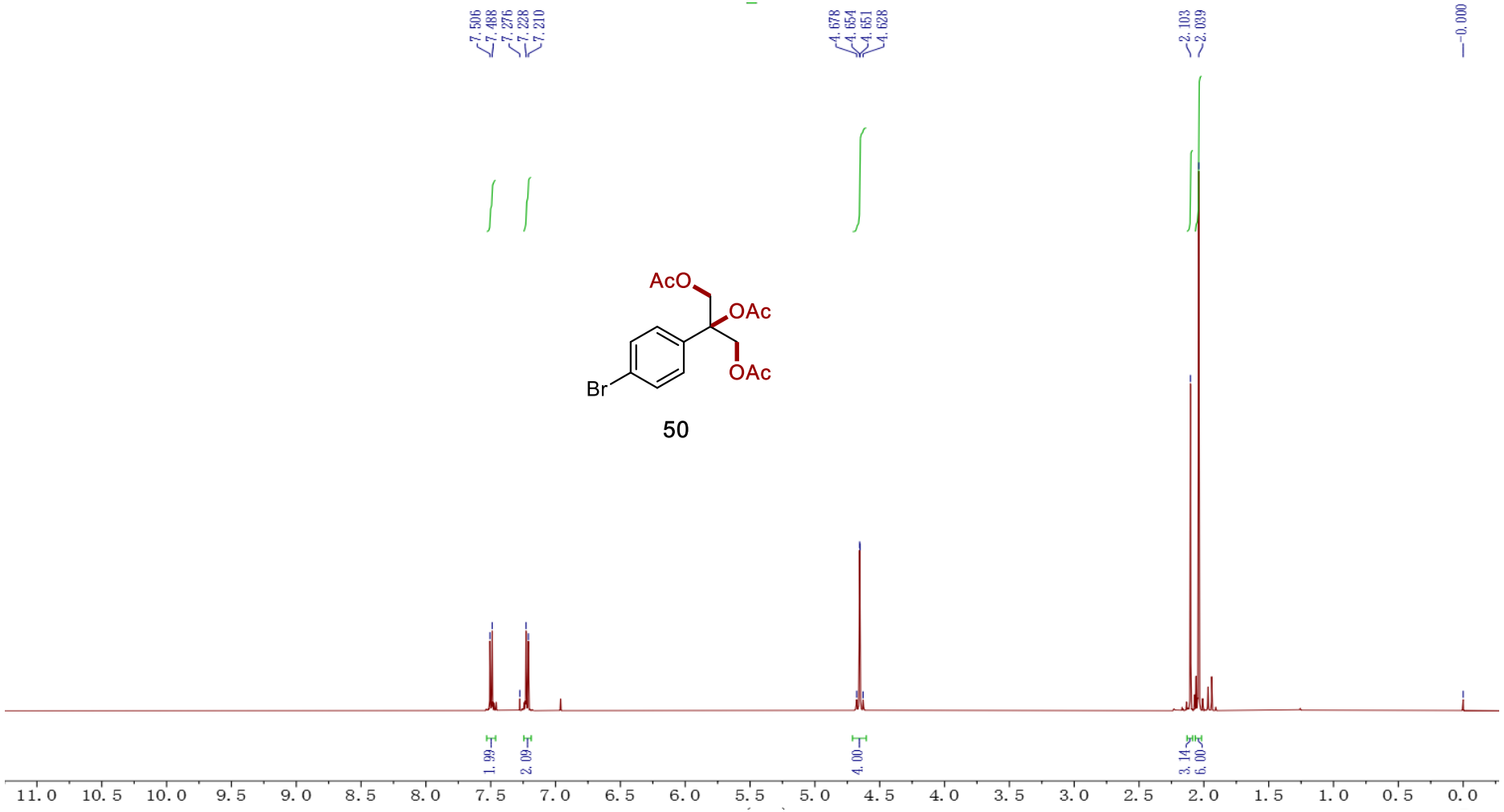
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OAc
Br
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6.00
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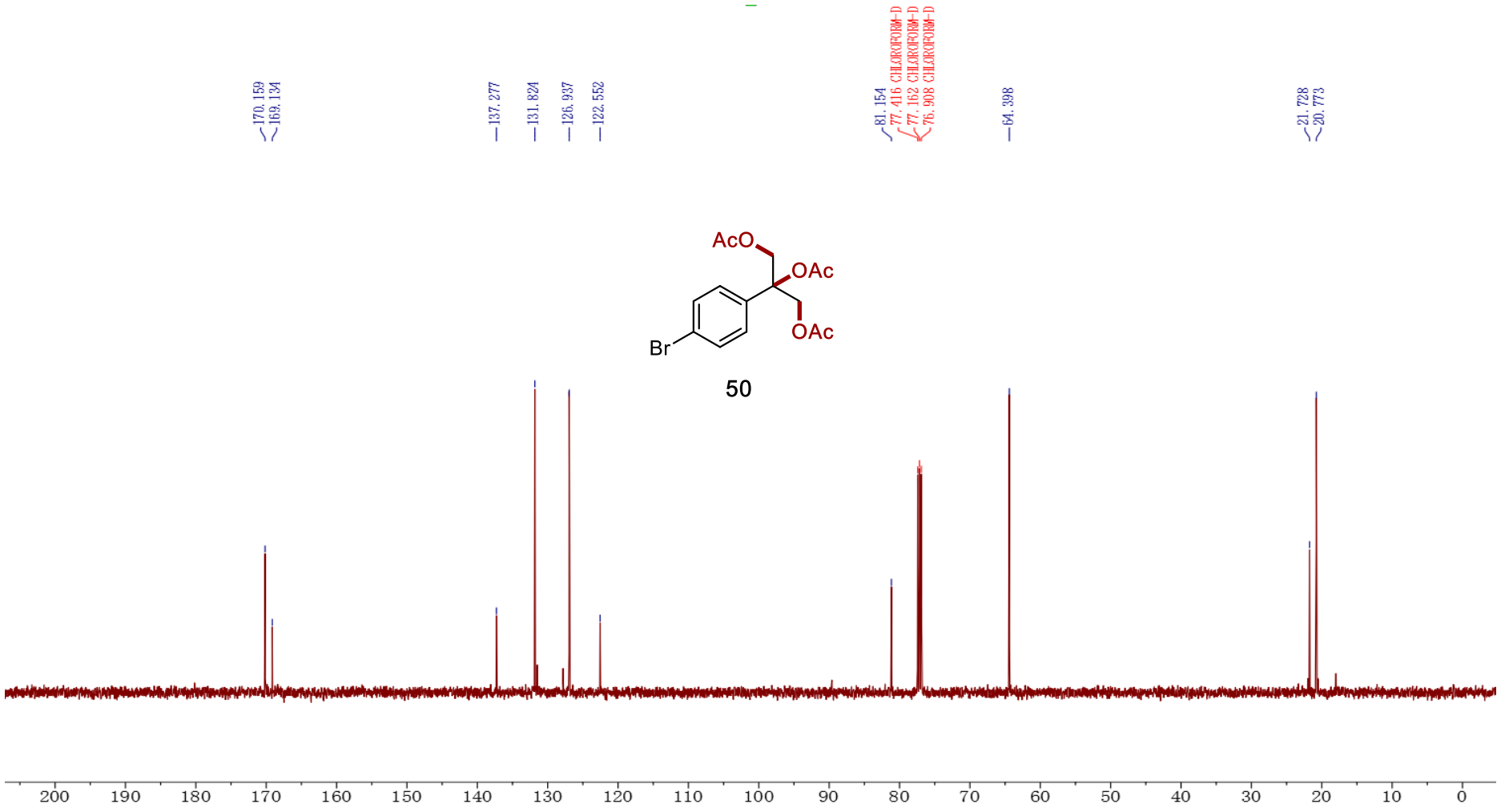
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77.162 CHLOROFORM-D
76.908 CHLOROFORM-D
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20.773
AcO
OAc
OAc
Br
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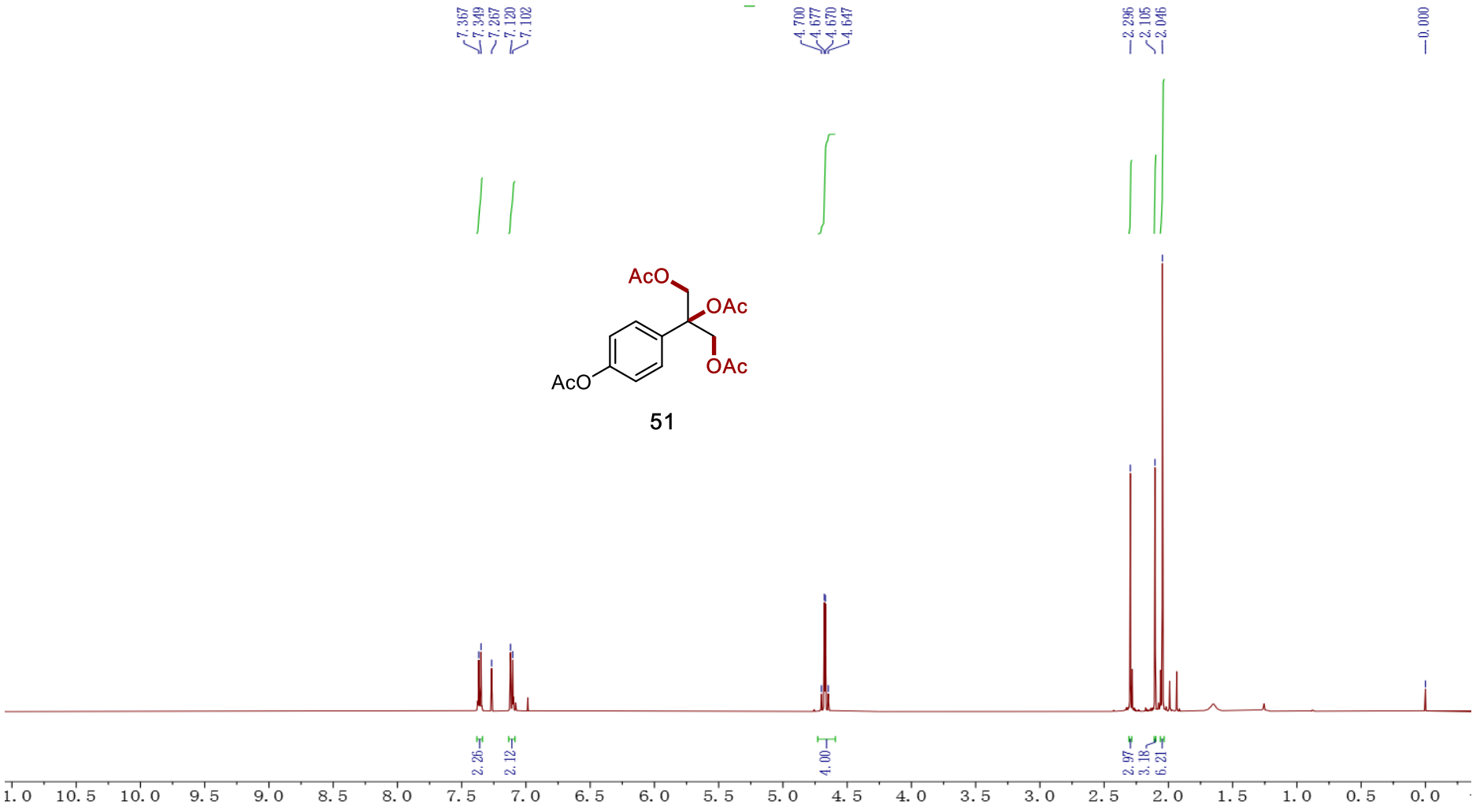
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OAc
AcO
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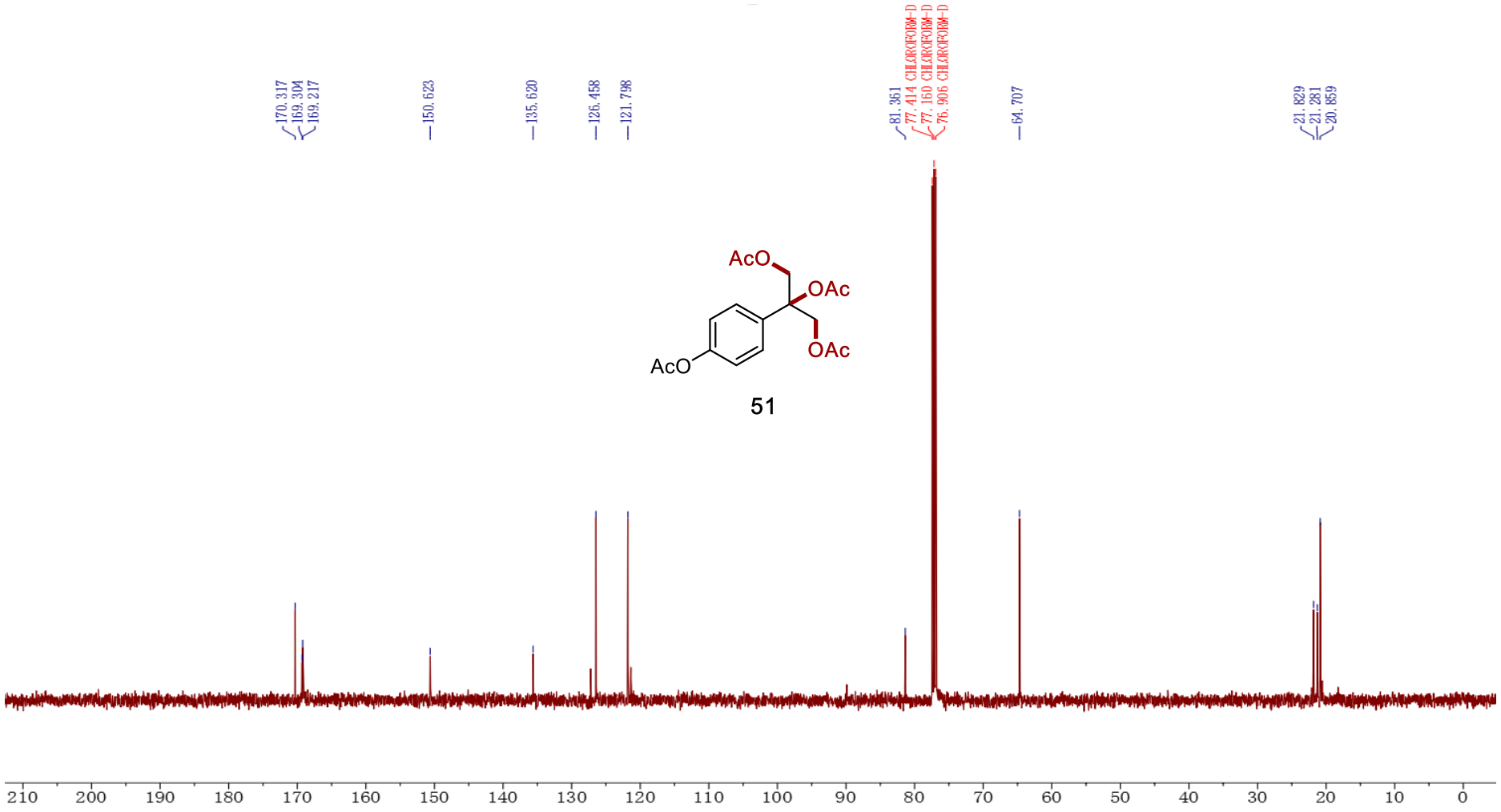
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AcO
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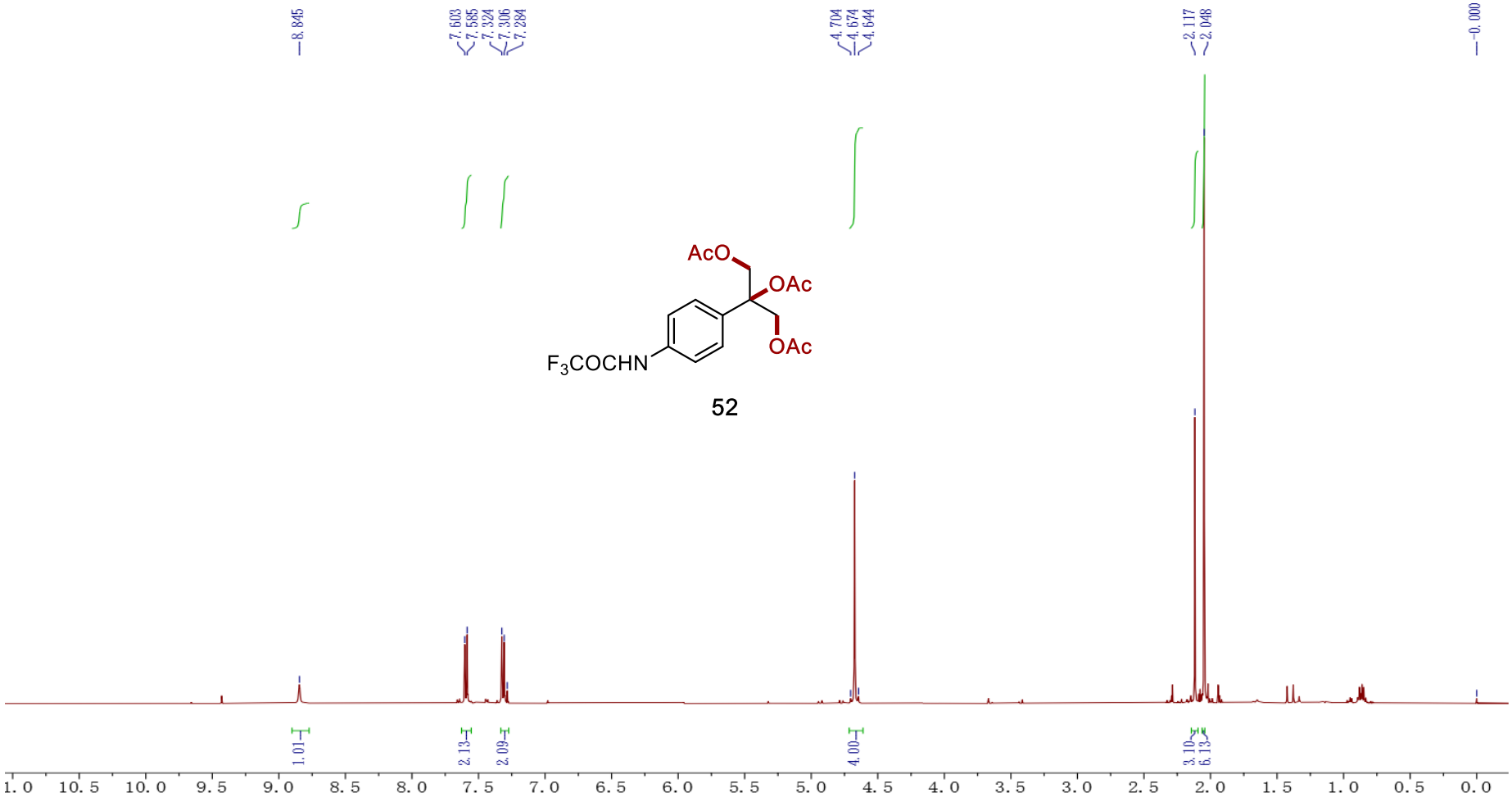
0

51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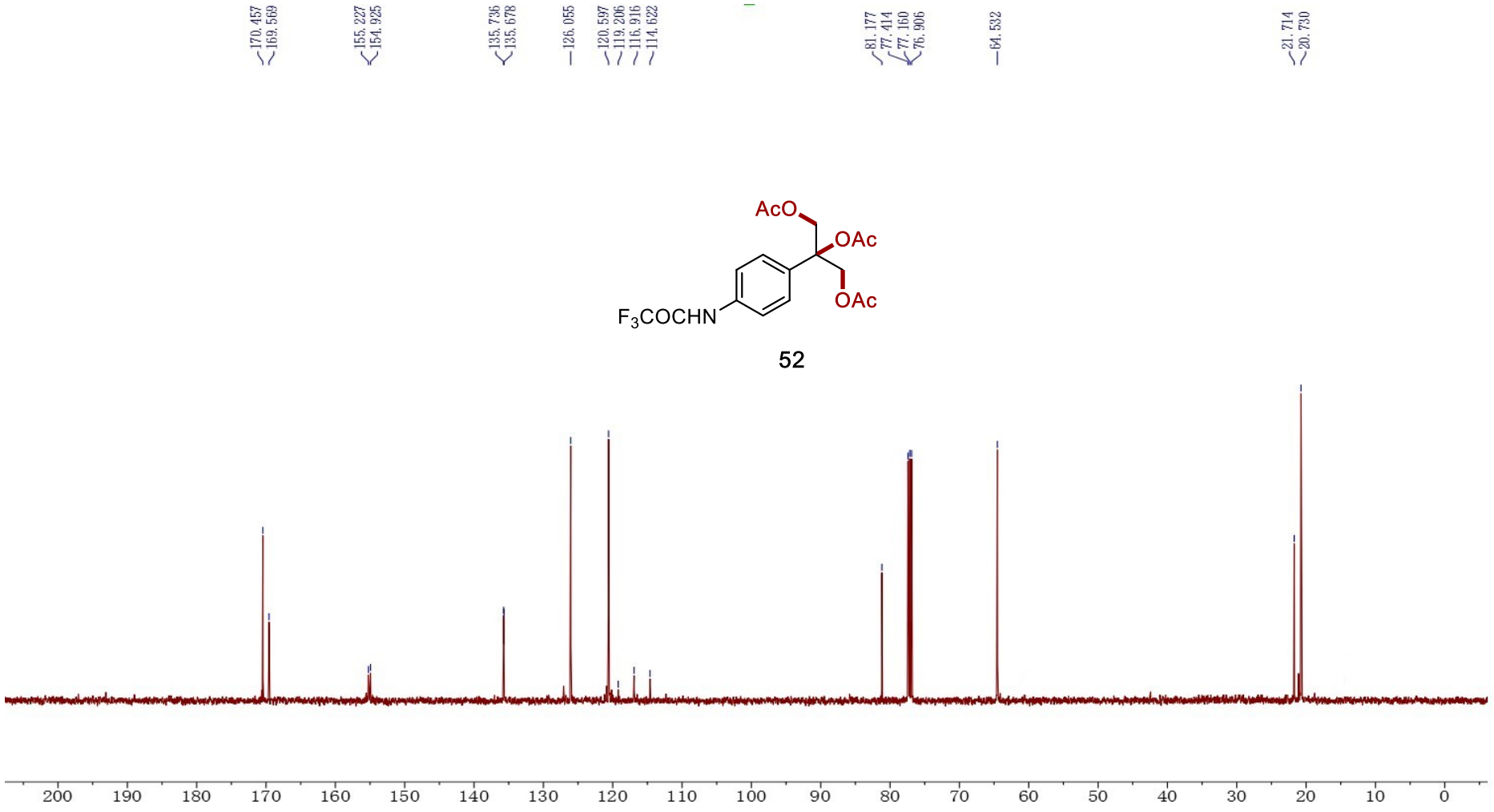
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154.925
135.736
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120.597
119.206
116.916
114.622
81.177
77.414
77.160
76.906
64.532
21.714
20.730
AcO
OAc
OAc
F3COCHN
52
200
190
180
170
160
150
140
130
120
110
100
90
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70
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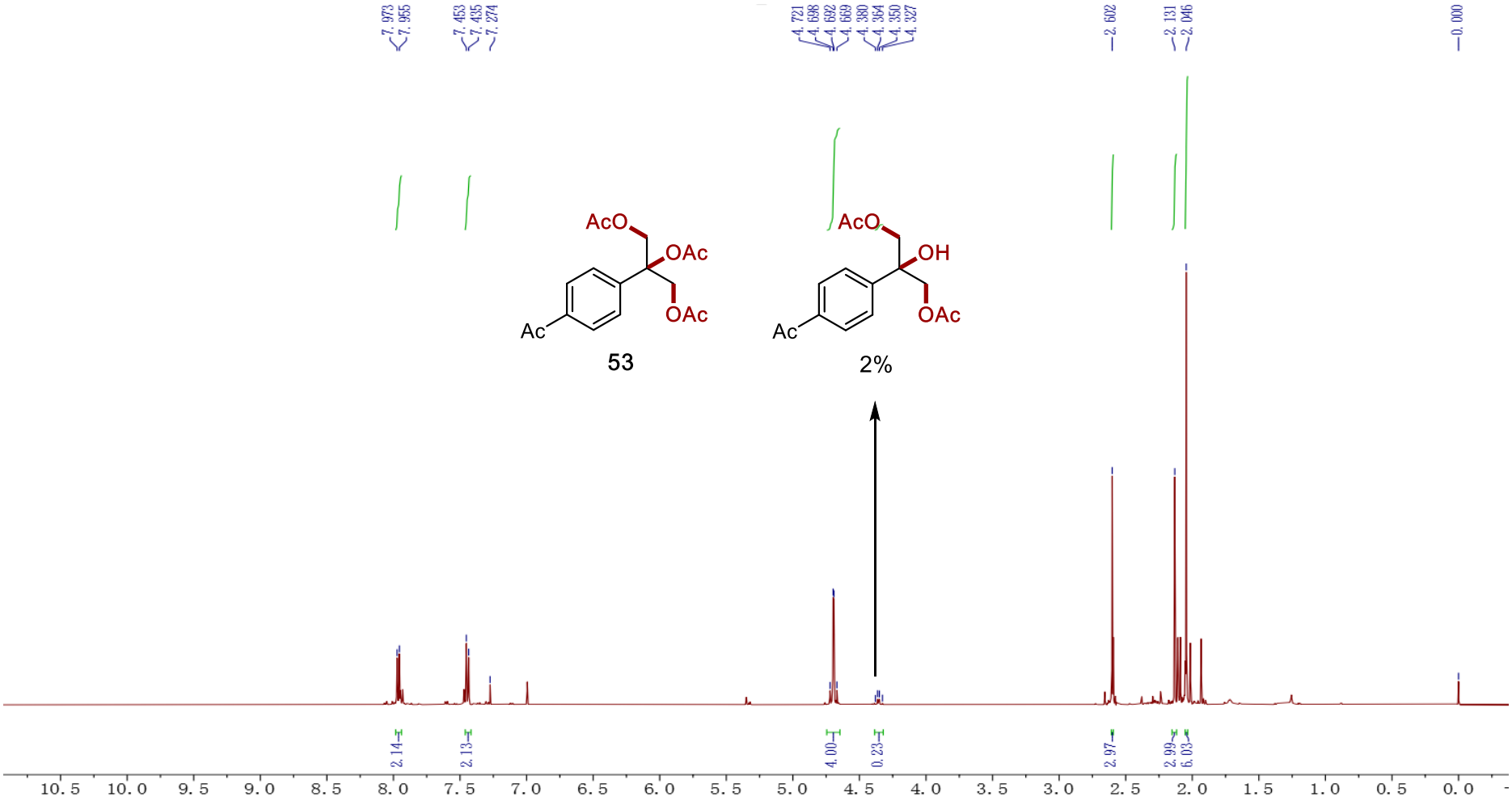
30
20
10
0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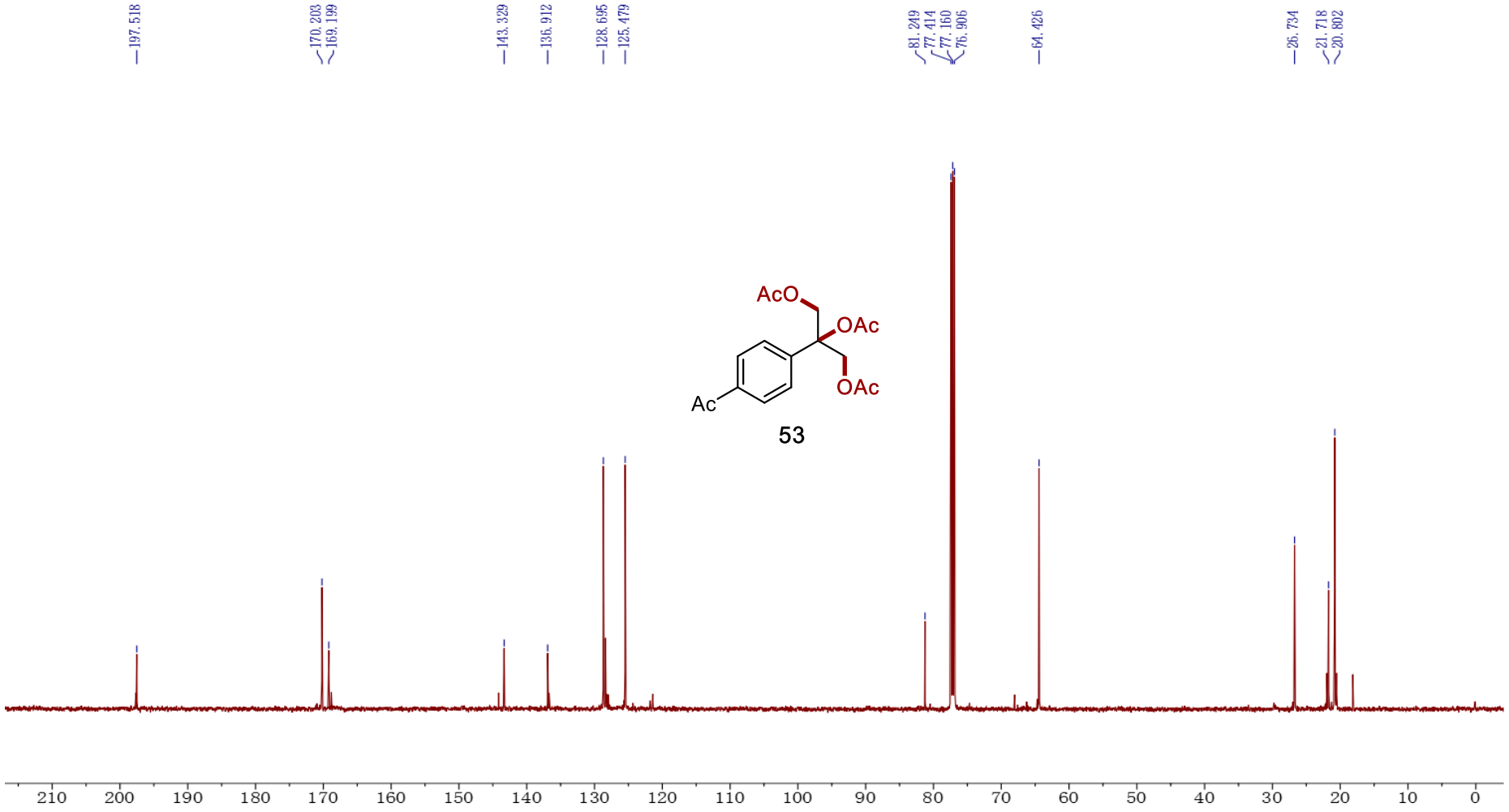
7.955
7.453
7.435
7.274
4.721
4.698
4.692
4.669
4.380
4.364
4.350
4.327
2.602
2.131
2.046
0.000
AcO
OAc
OAc
Ac
53
AcO
OH
OAc
Ac
2%
2.14
2.13
4.00
0.23
2.97
2.99
6.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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125.479
81.249
77.414
77.160
76.906
64.426
26.734
21.718
20.802
AcO
OAc
OAc
Ac
53
210
200
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150
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70
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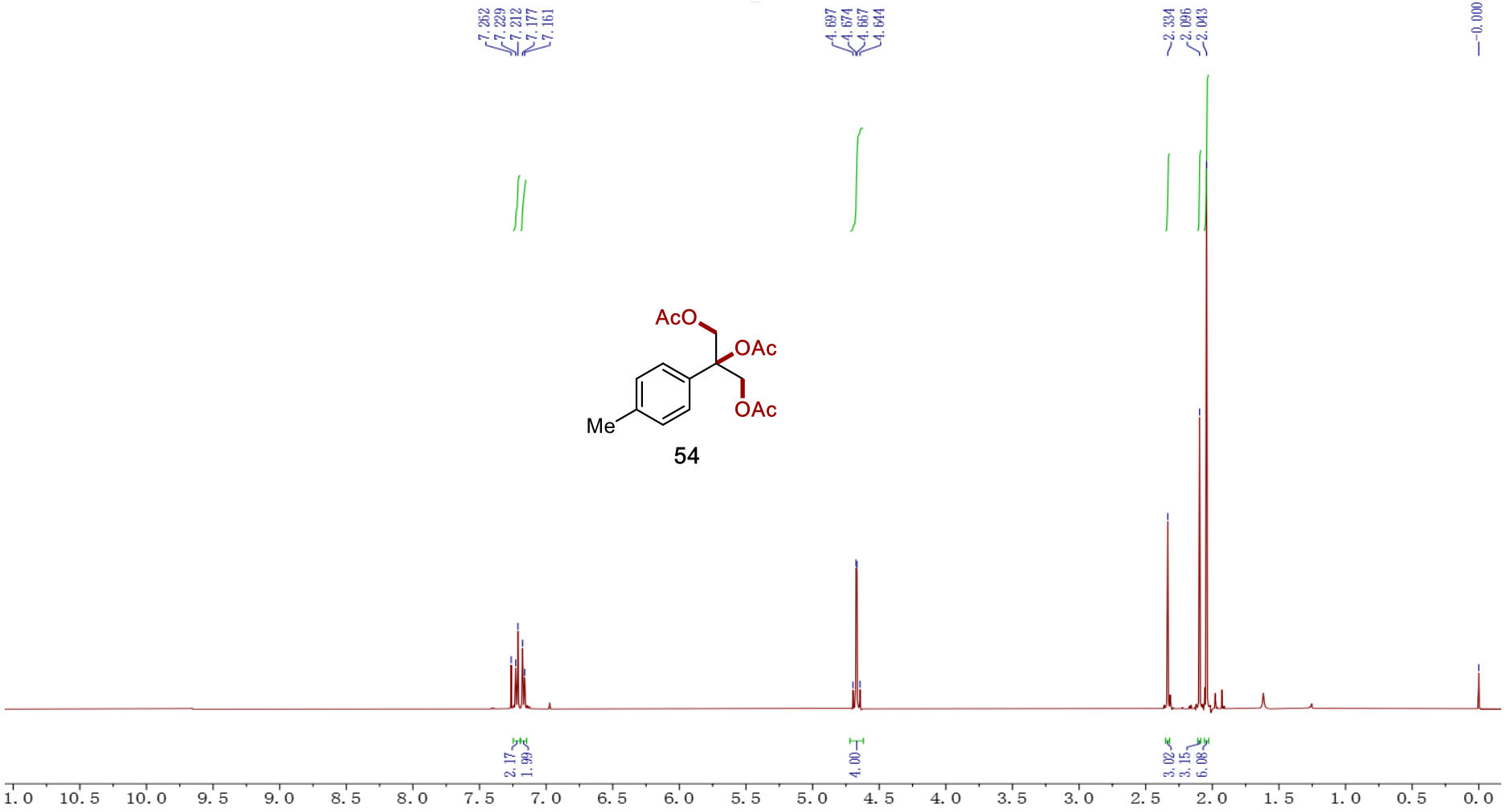
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7.229
7.212
7.177
7.161
4.697
4.674
4.667
4.644
2.334
2.096
2.043
0.000
AcO
OAc
OAc
Me
54
2.17
1.99
4.00
3.02
3.15
6.08
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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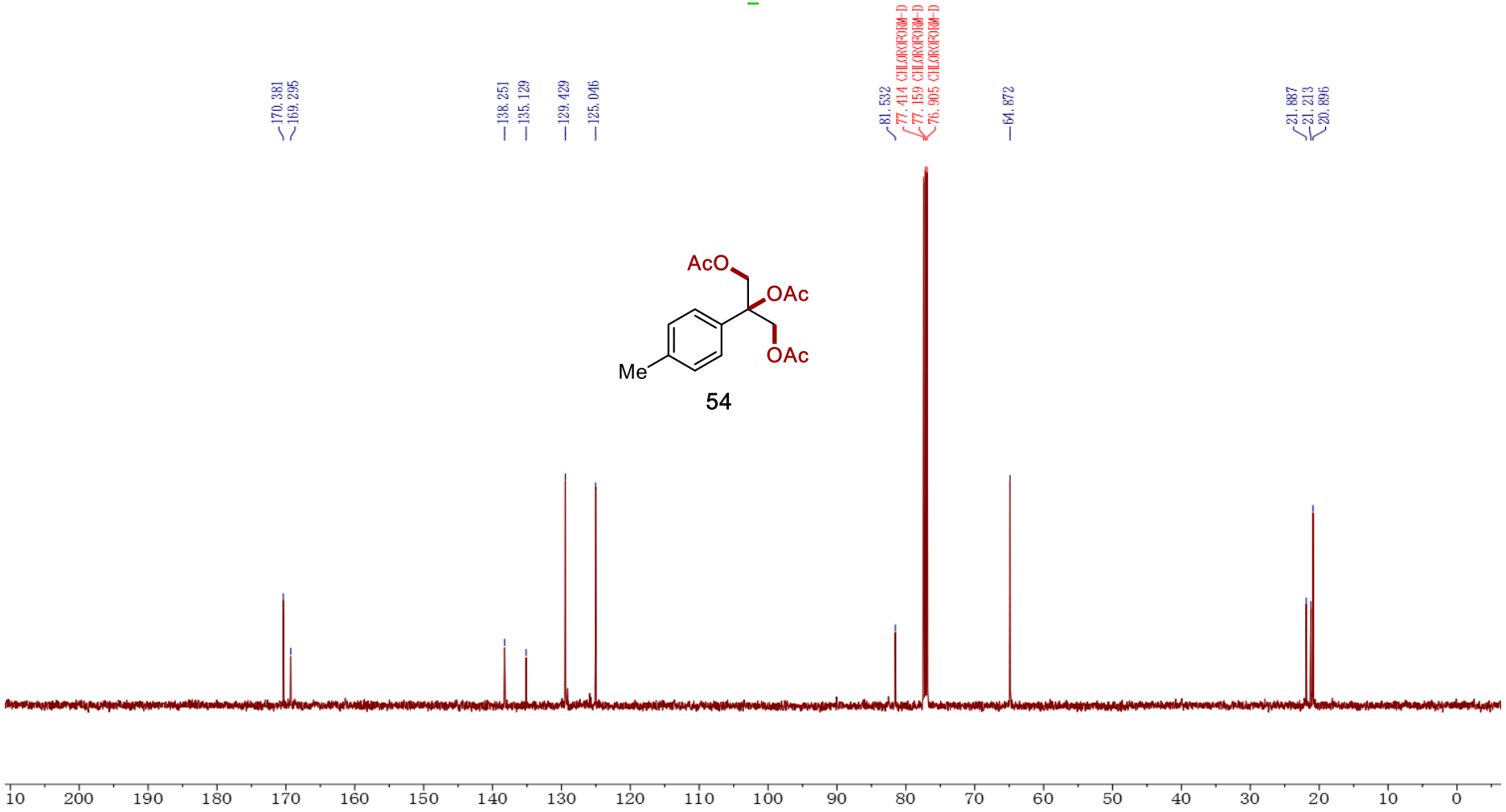
0.0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125.046
81.532
77.414 CHLOROFORM-D
77.159 CHLOROFORM-D
76.905 CHLOROFORM-D
64.872
21.887
21.213
20.896
AcO
OAc
OAc
Me
54
10
200
190
180
170
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150
140
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120
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100
90
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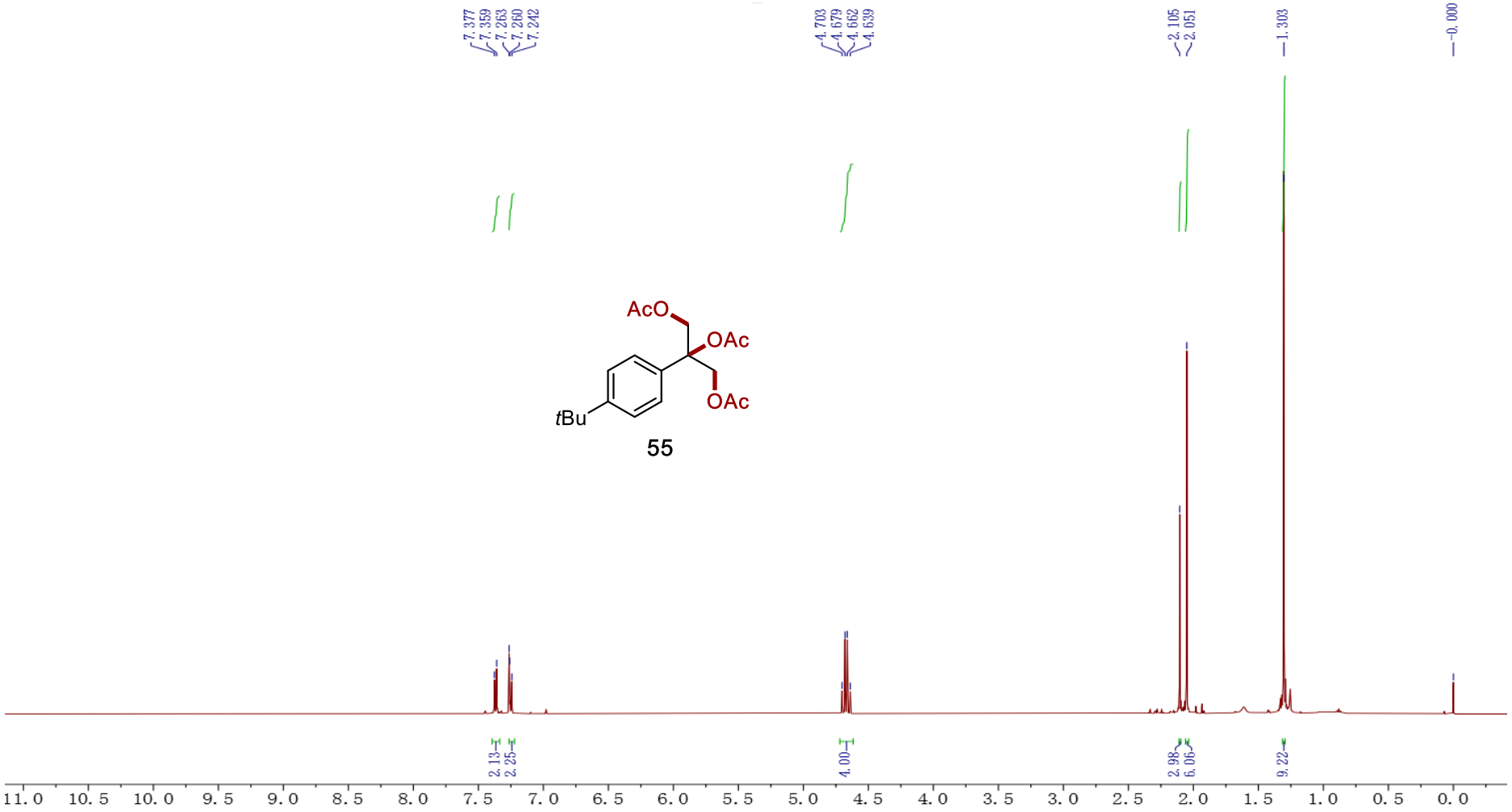
10
0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7.263
7.260
7.242
4.703
4.679
4.662
4.639
2.105
2.051
1.303
0.000
AcO
OAc
OAc
tBu
55
2.13
2.25
4.00
2.98
6.06
9.22
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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2.0
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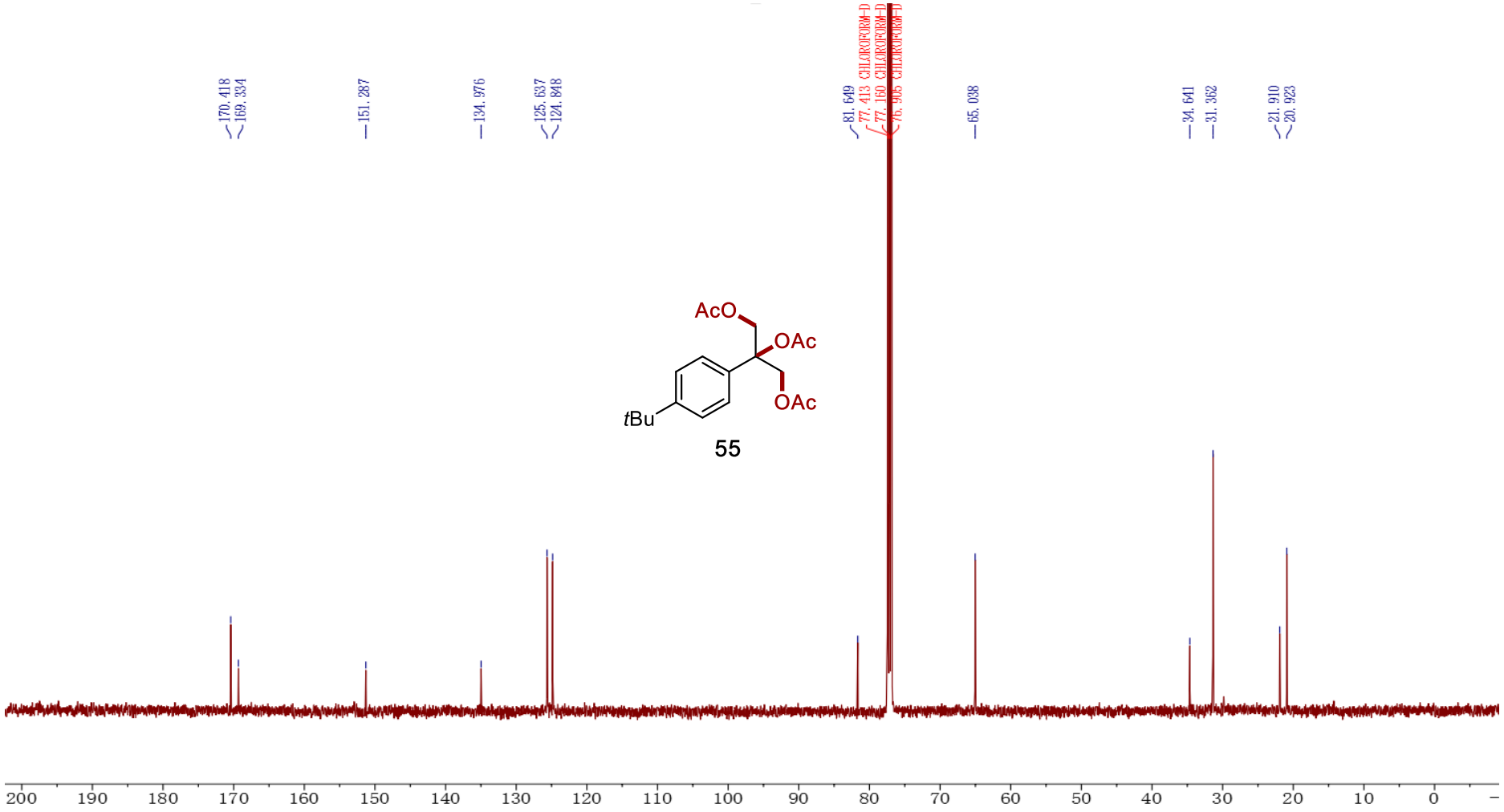
0.0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169.334
151.287
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124.848
81.649
77.413
77.160
76.905
65.038
34.641
31.362
21.910
20.923
AcO
OAc
OAc
tBu
55
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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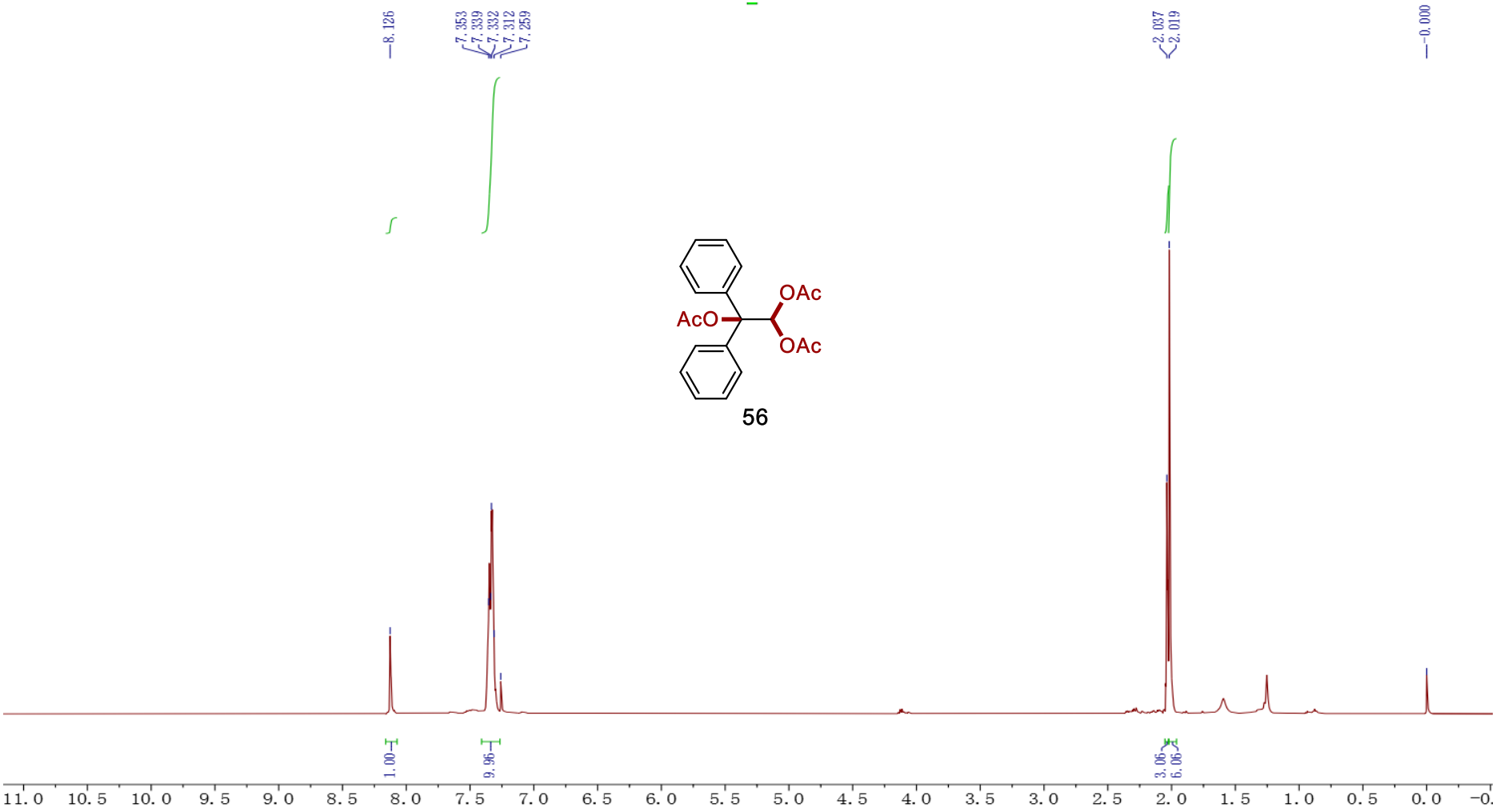
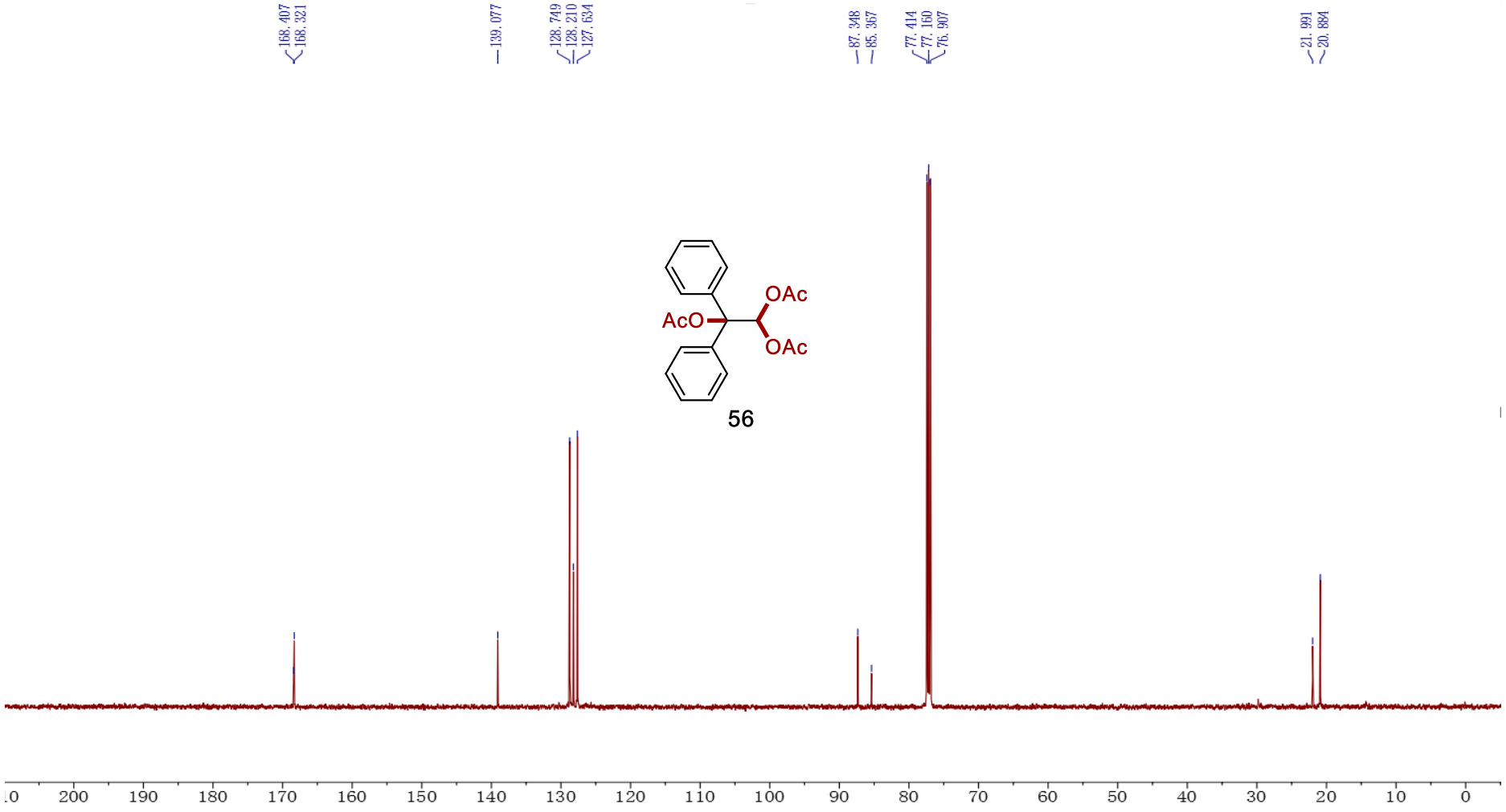
30
20
10
0


8.126
7.353
7.339
7.332
7.312
7.259
2.037
2.019
0.000
OAc
AcO
OAc
56
1.00
9.96
3.06
6.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.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168.321
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128.210
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87.348
85.357
77.414
77.160
76.907
21.991
20.884
OAc
AcO
OAc
56
200
190
180
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150
140
130
120
110
100
90
80
70
60
50
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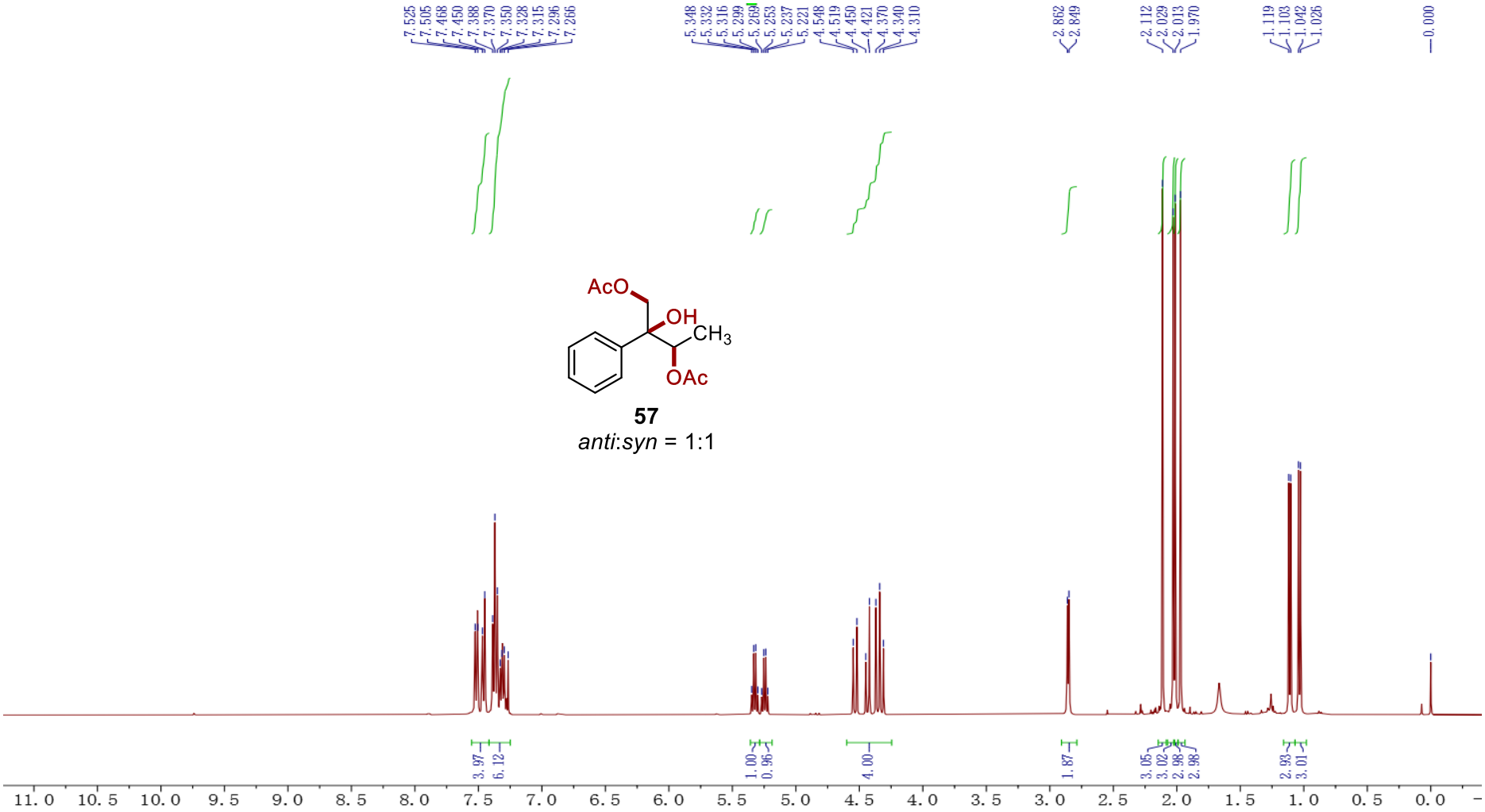
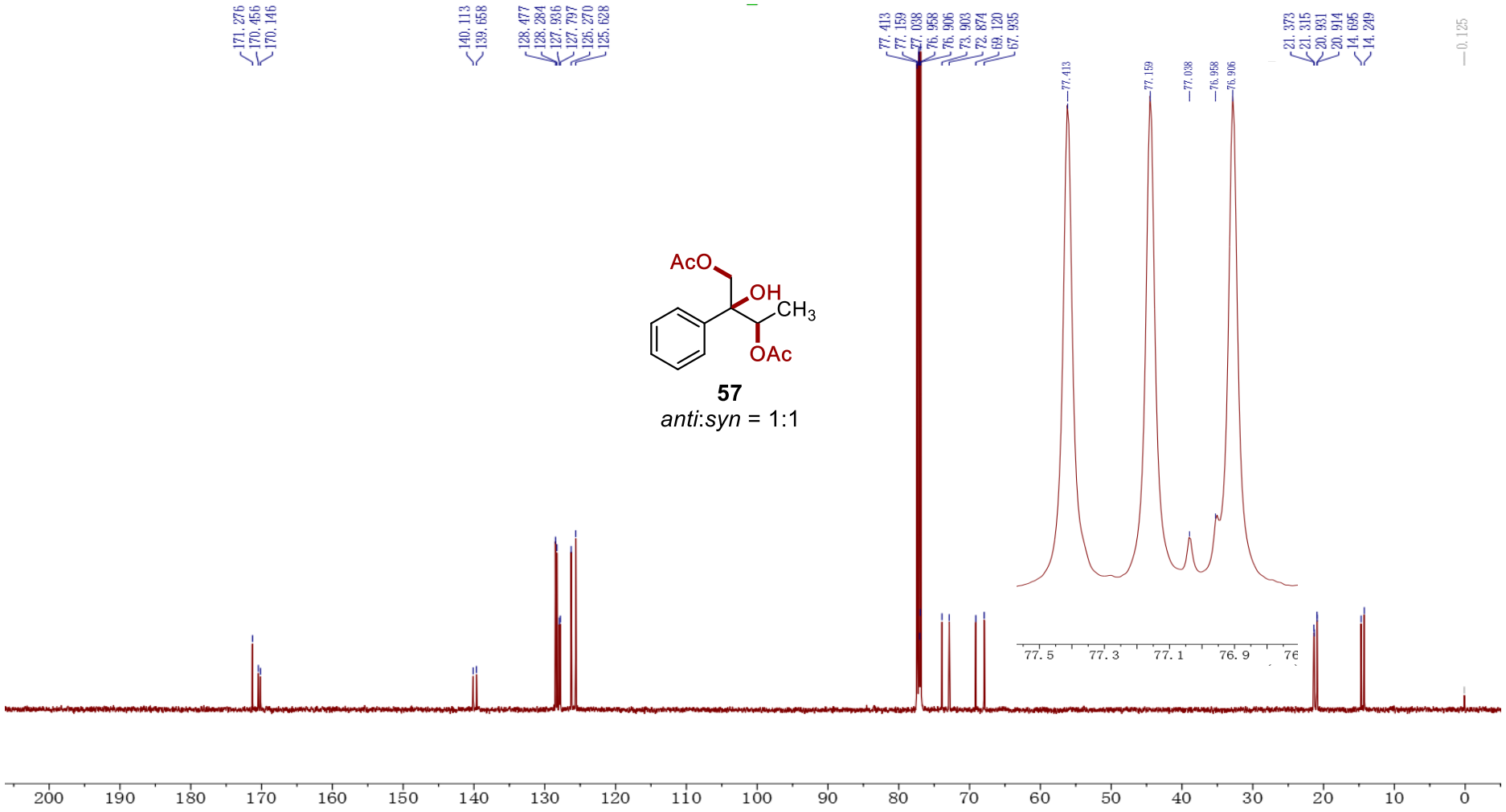
30
20
10
0



57

anti:*syn* = 1:1



57

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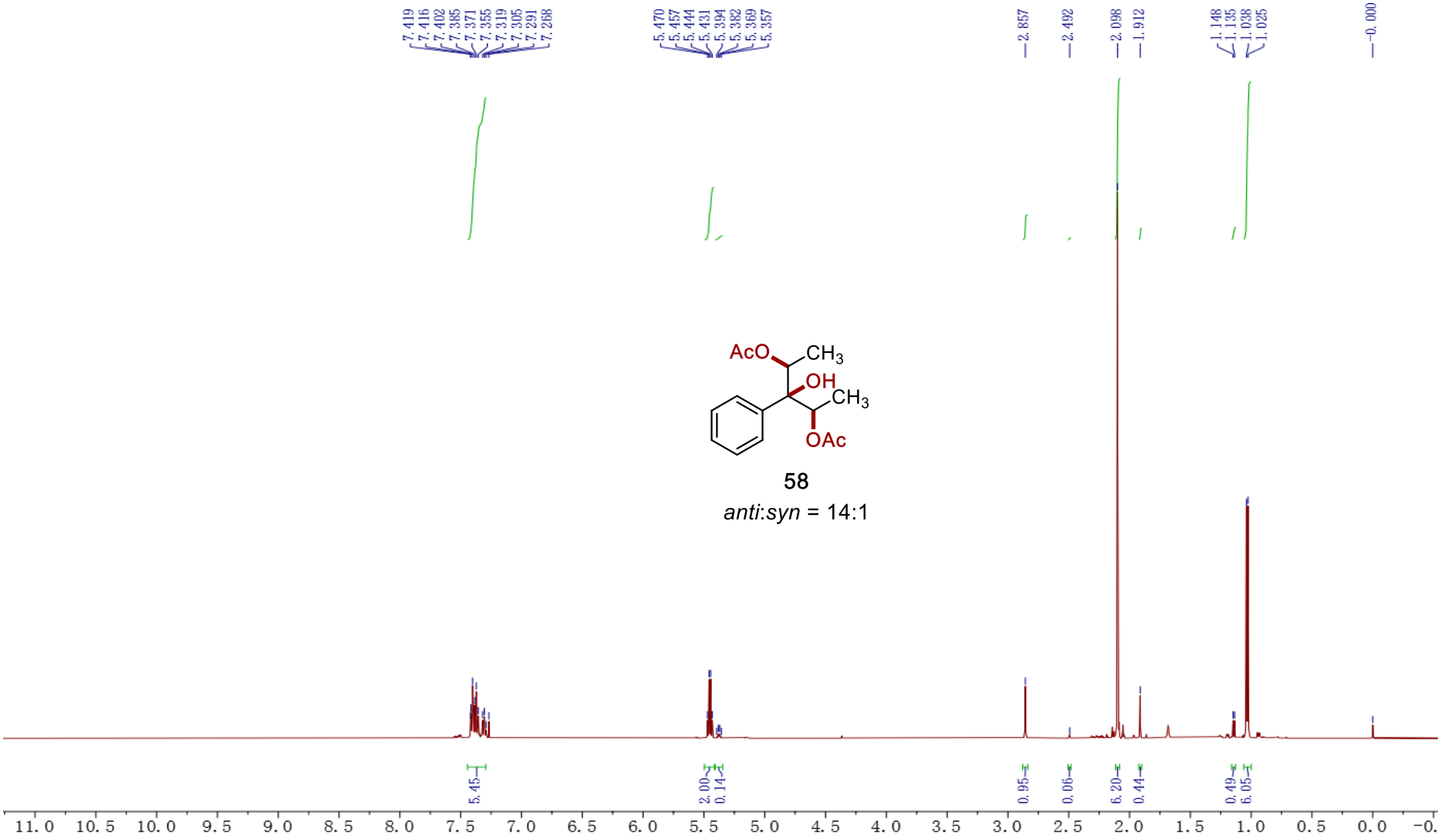
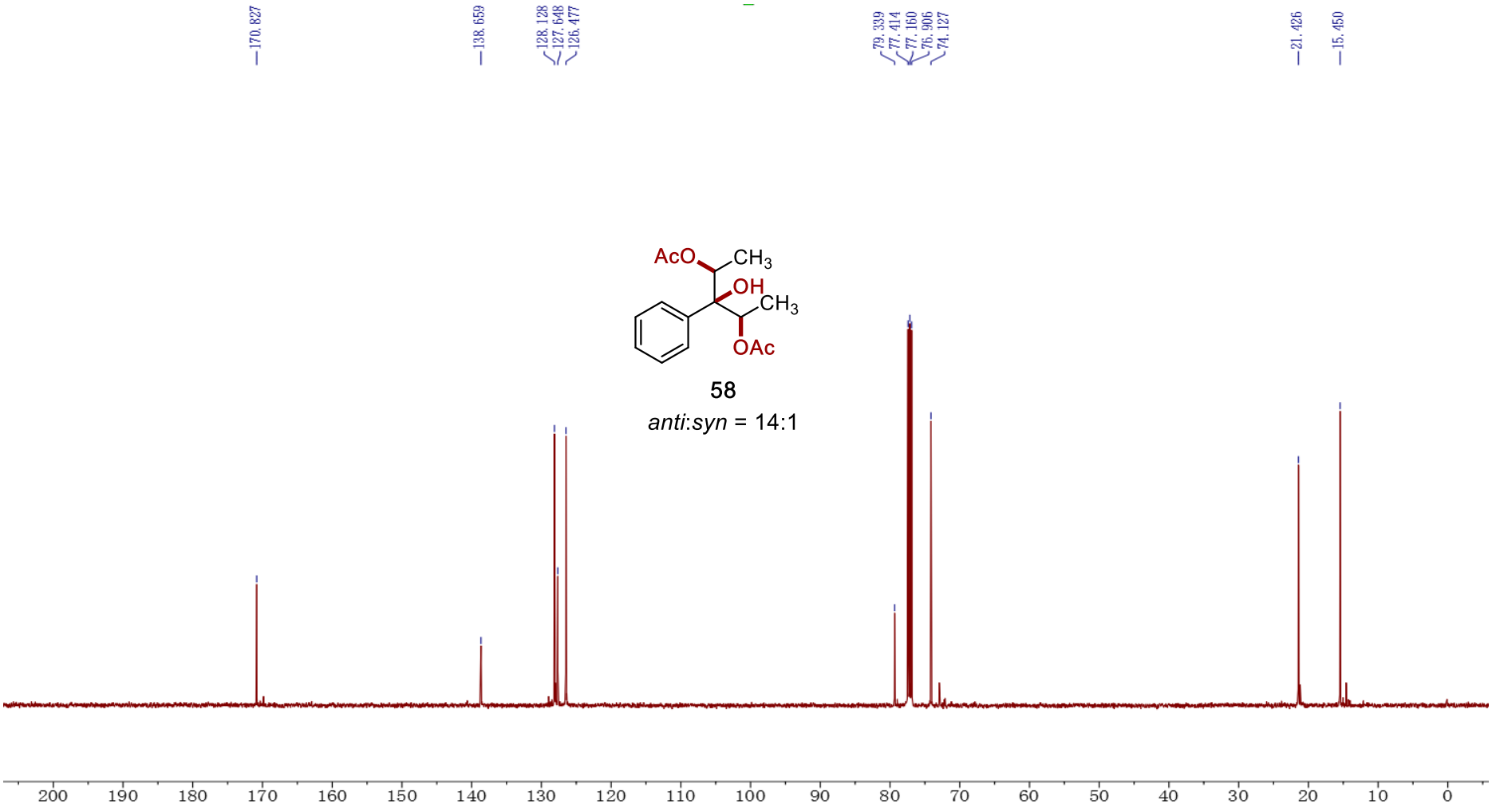


58

anti:*syn* = 14:1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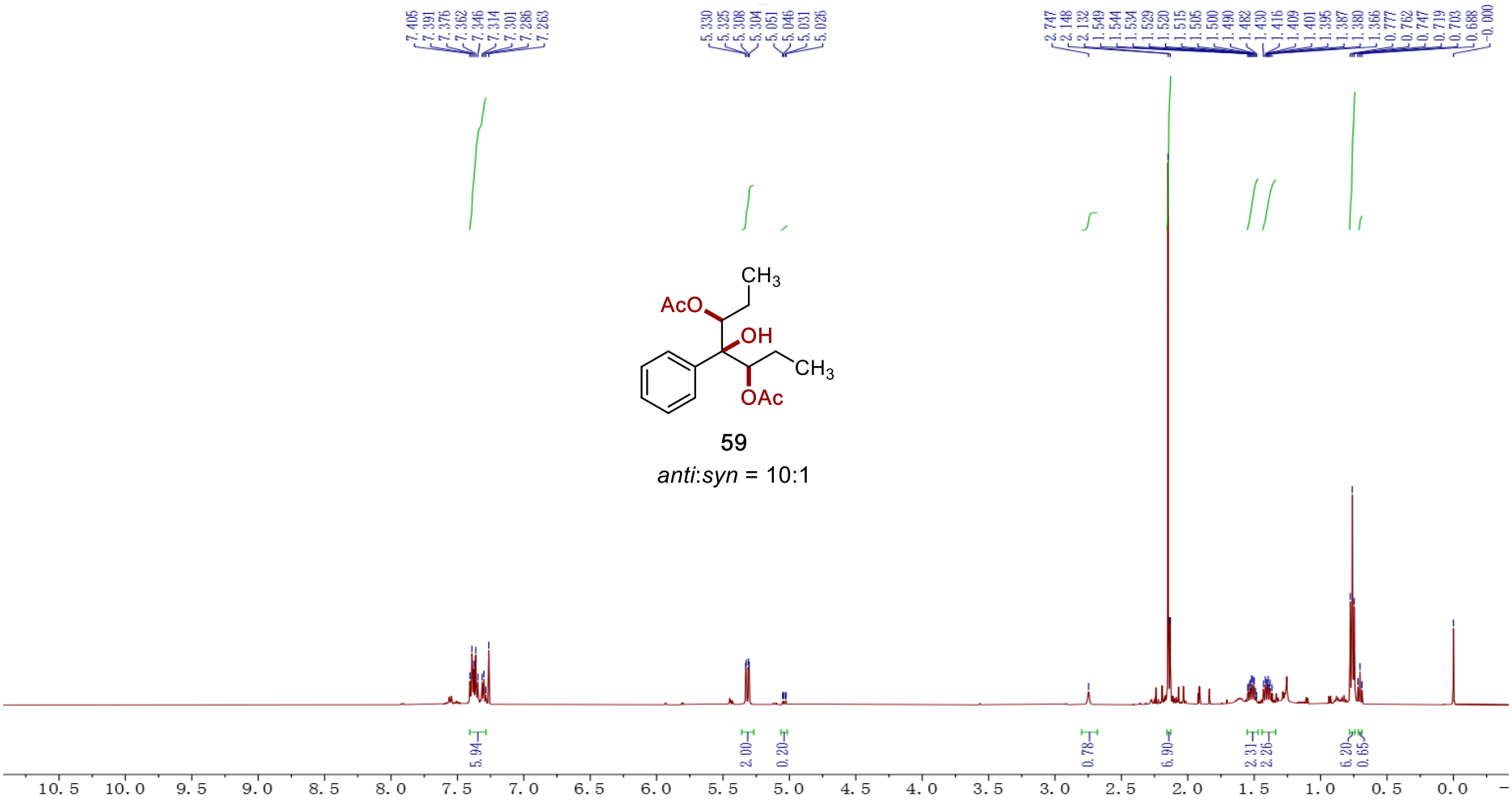
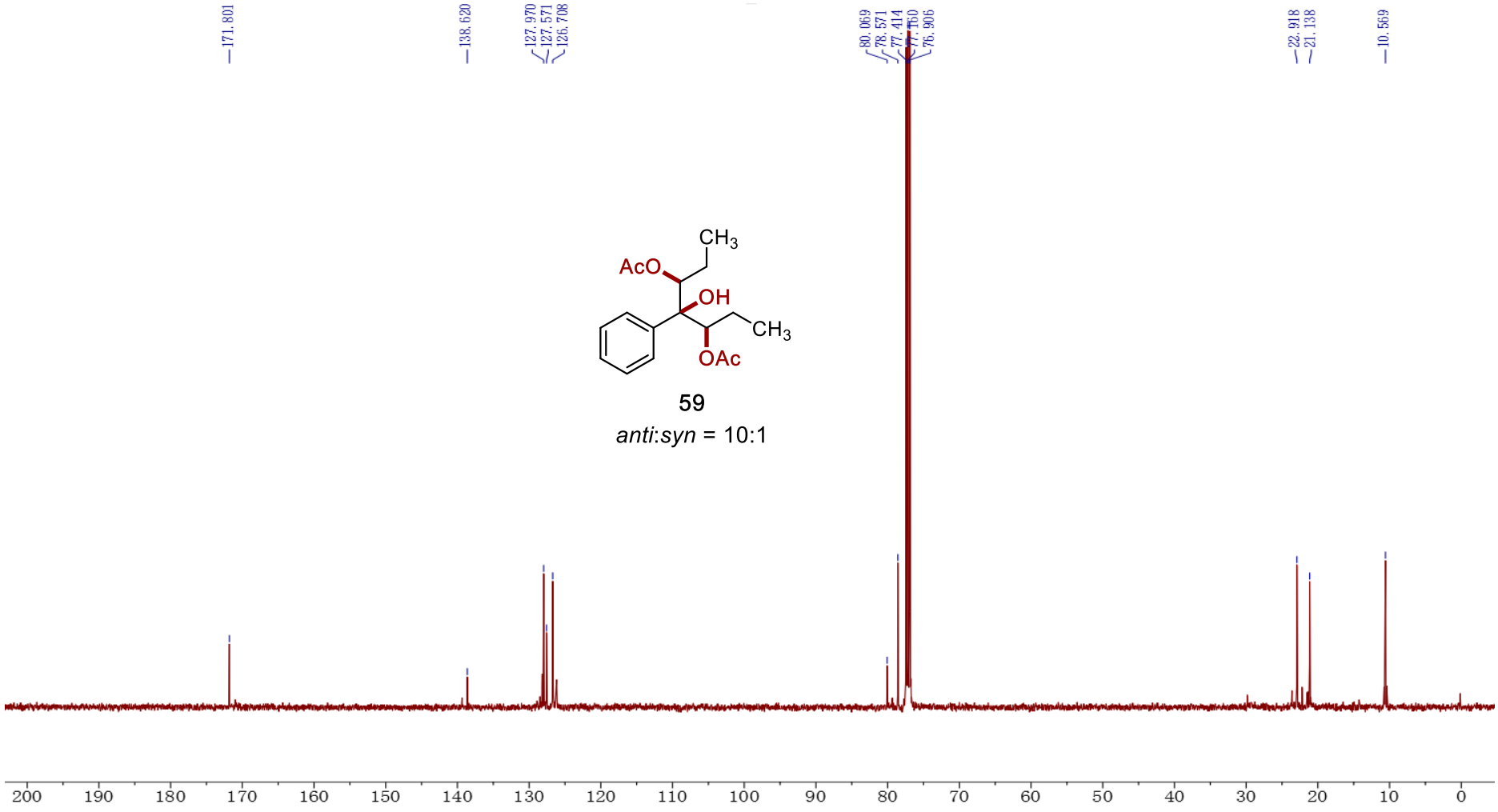
128.128
127.648
126.477
79.339
77.414
77.160
76.906
74.127
21.426
15.450
AcO
CH3
OH
CH3
OAc
58
anti:syn = 14:1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



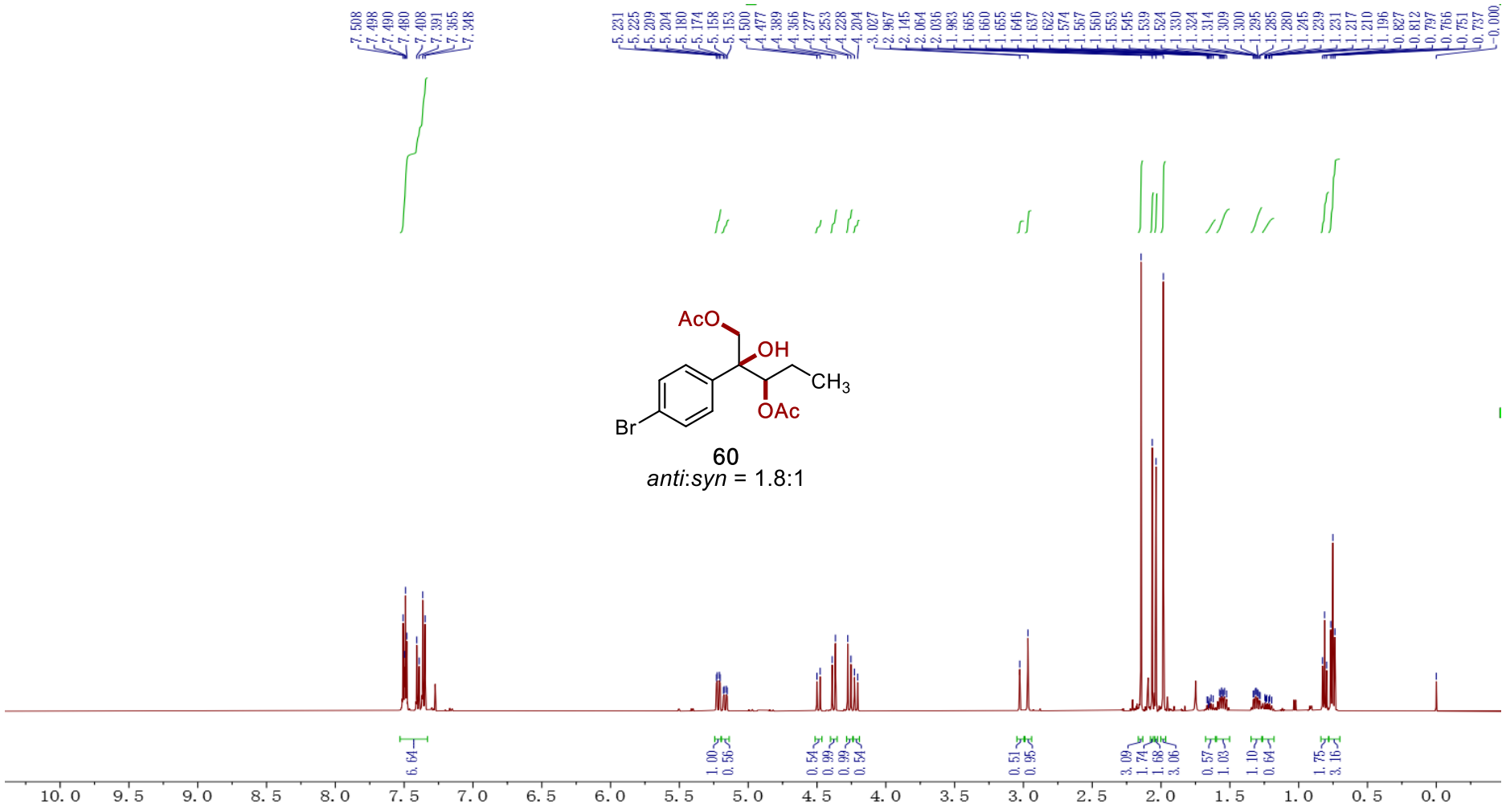
59

anti:*syn* = 10:1



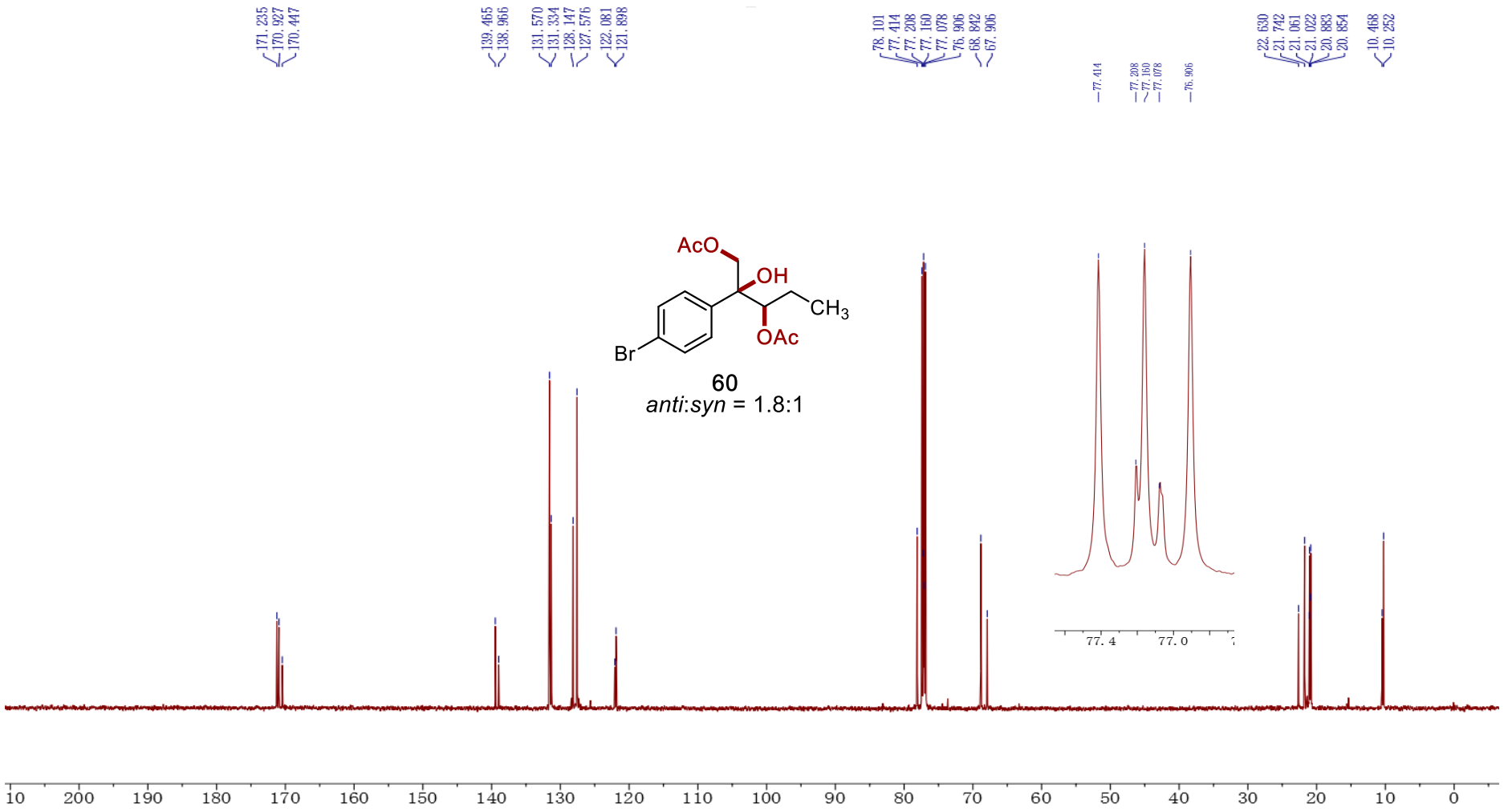
59

anti:*syn* = 10:1



60

anti:*syn* = 1.8:1



60

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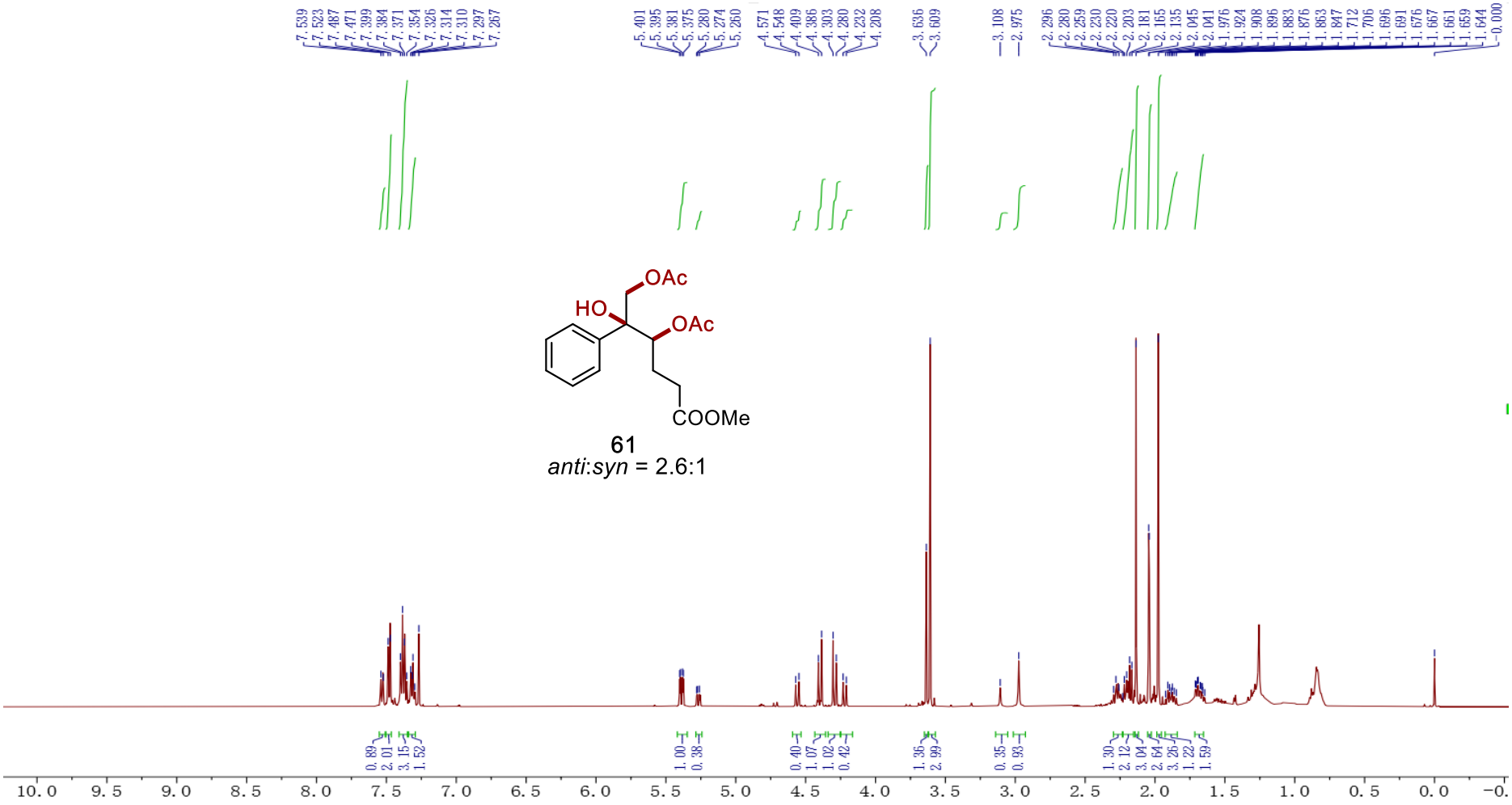
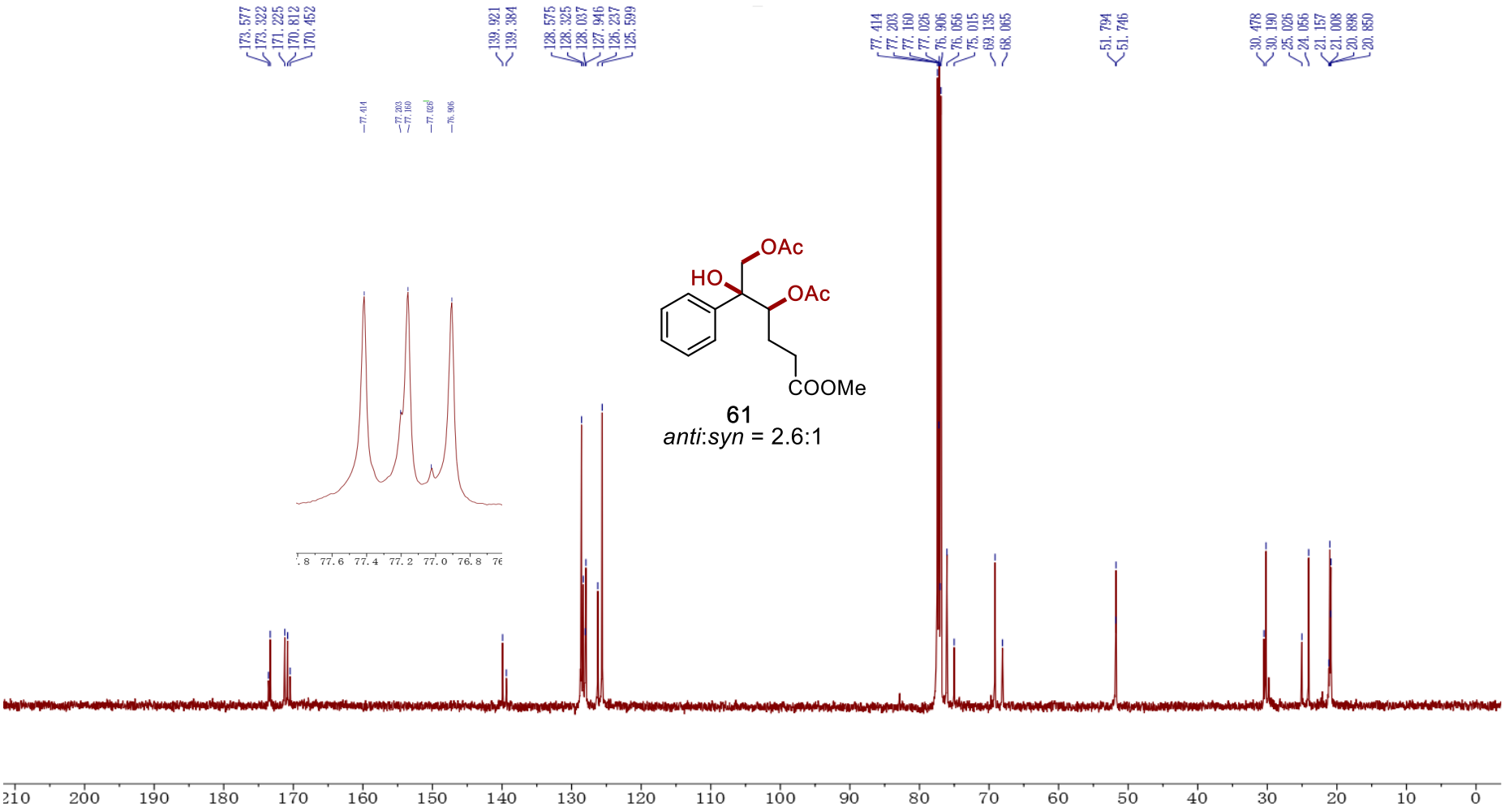


61

anti:*syn* = 2.6:1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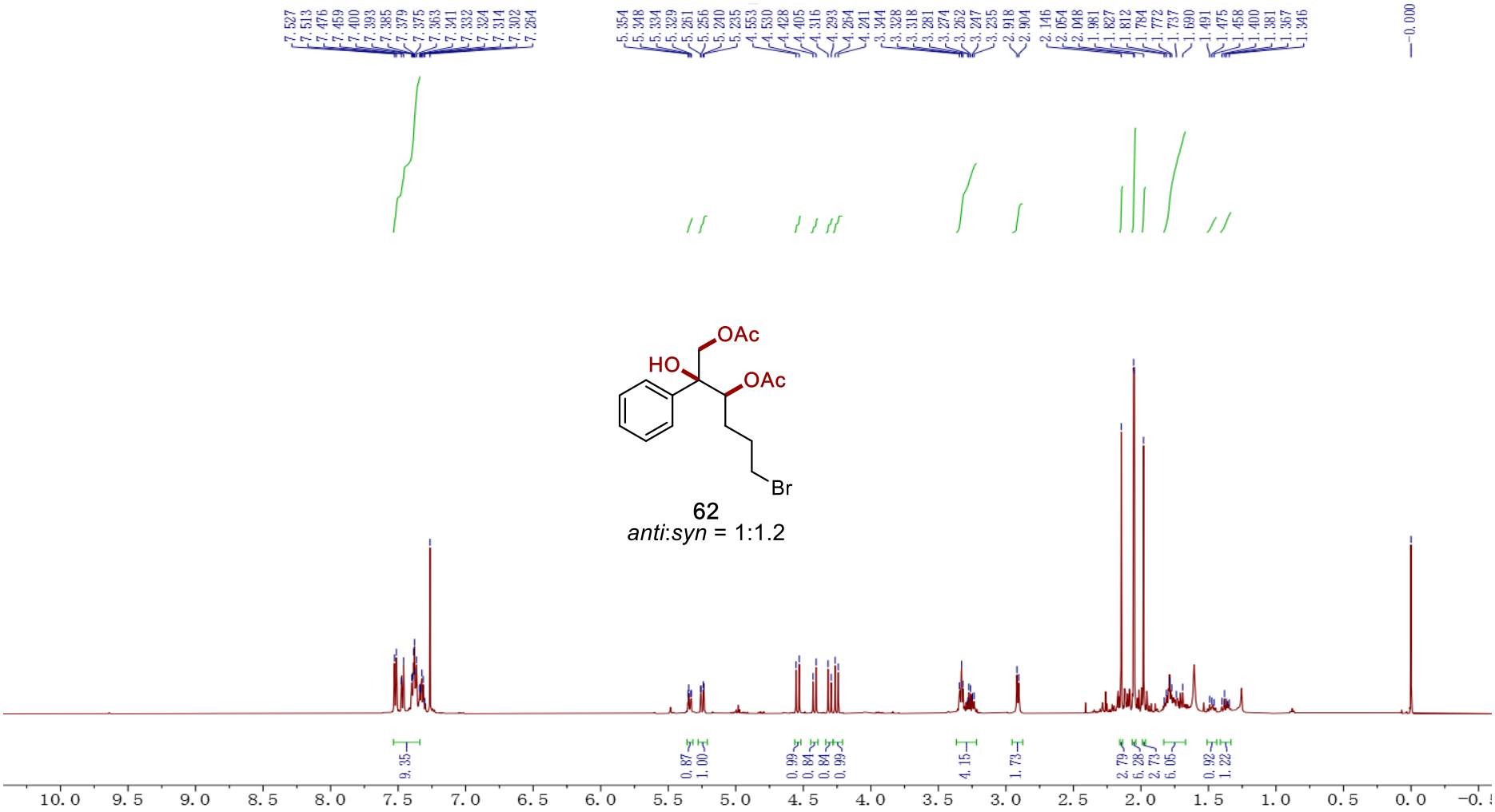
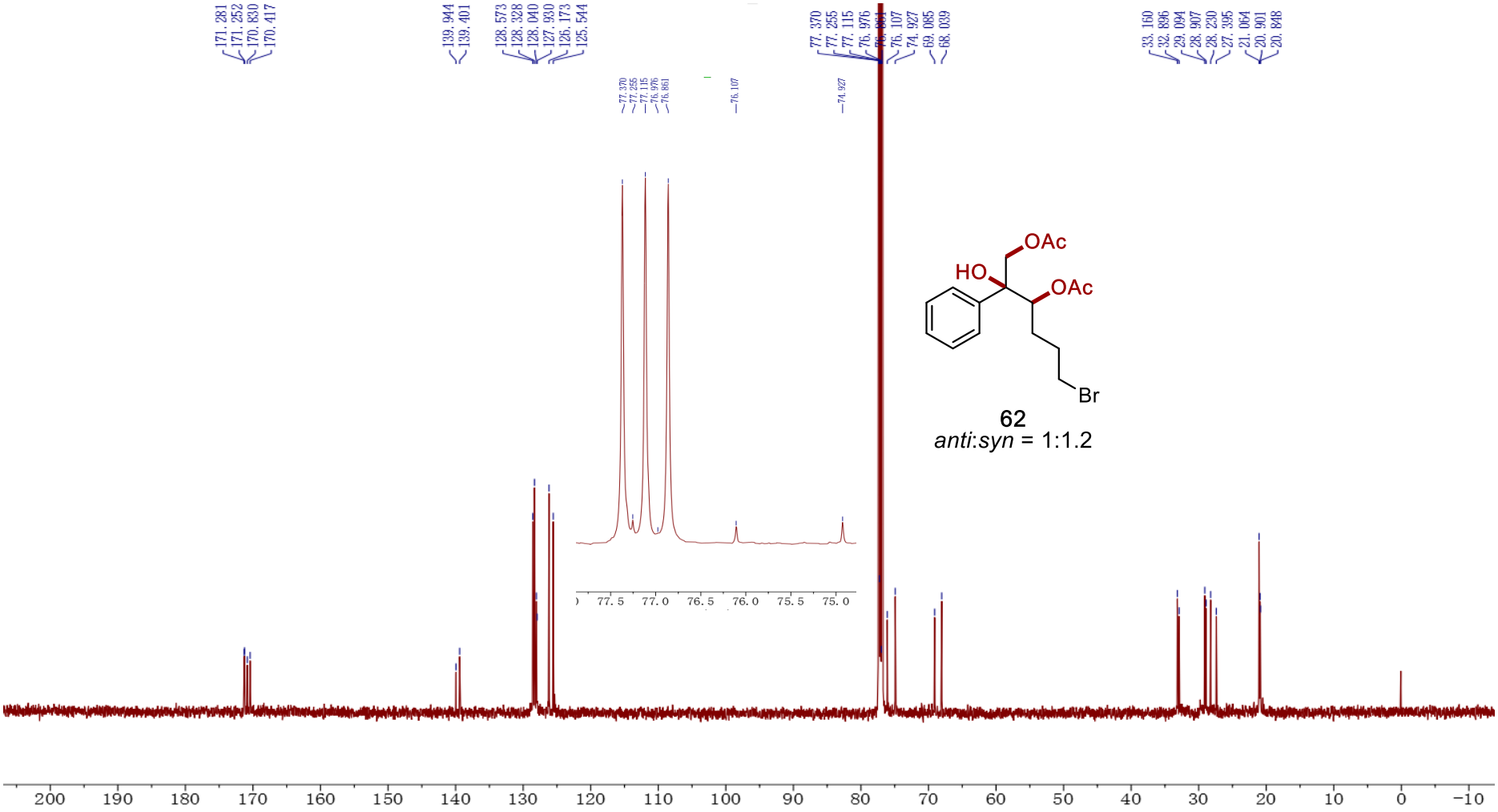
173.322
171.225
170.812
170.452
139.921
139.384
128.575
128.325
128.037
127.946
126.237
125.599
77.414
77.203
77.160
77.026
76.906
76.056
75.015
69.135
68.065
51.794
51.746
30.478
30.190
25.026
24.056
21.157
21.008
20.898
20.850
OAc
HO
OAc
COOMe
61
anti:syn = 2.6:1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



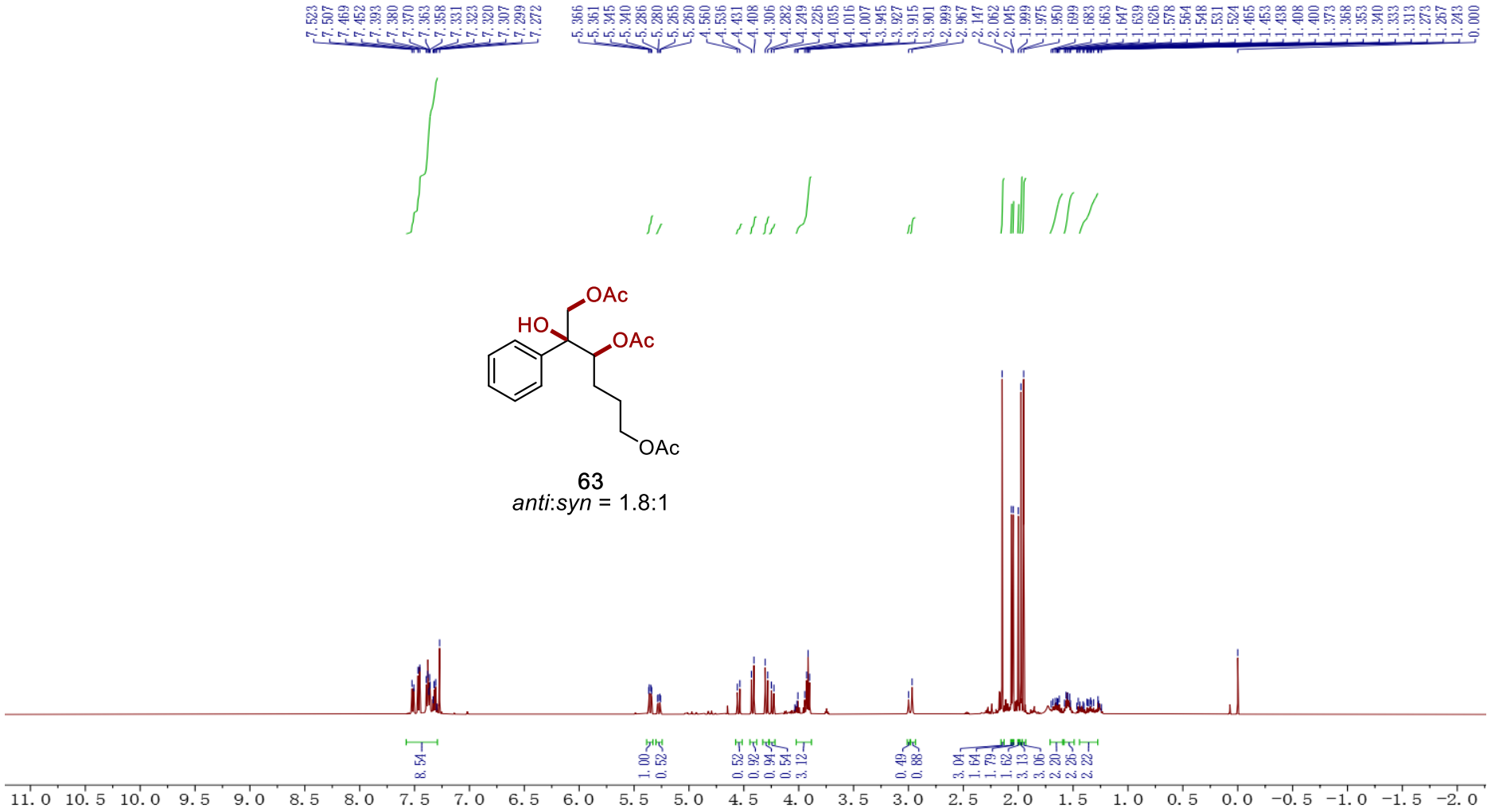
62

anti:*syn* = 1:1.2

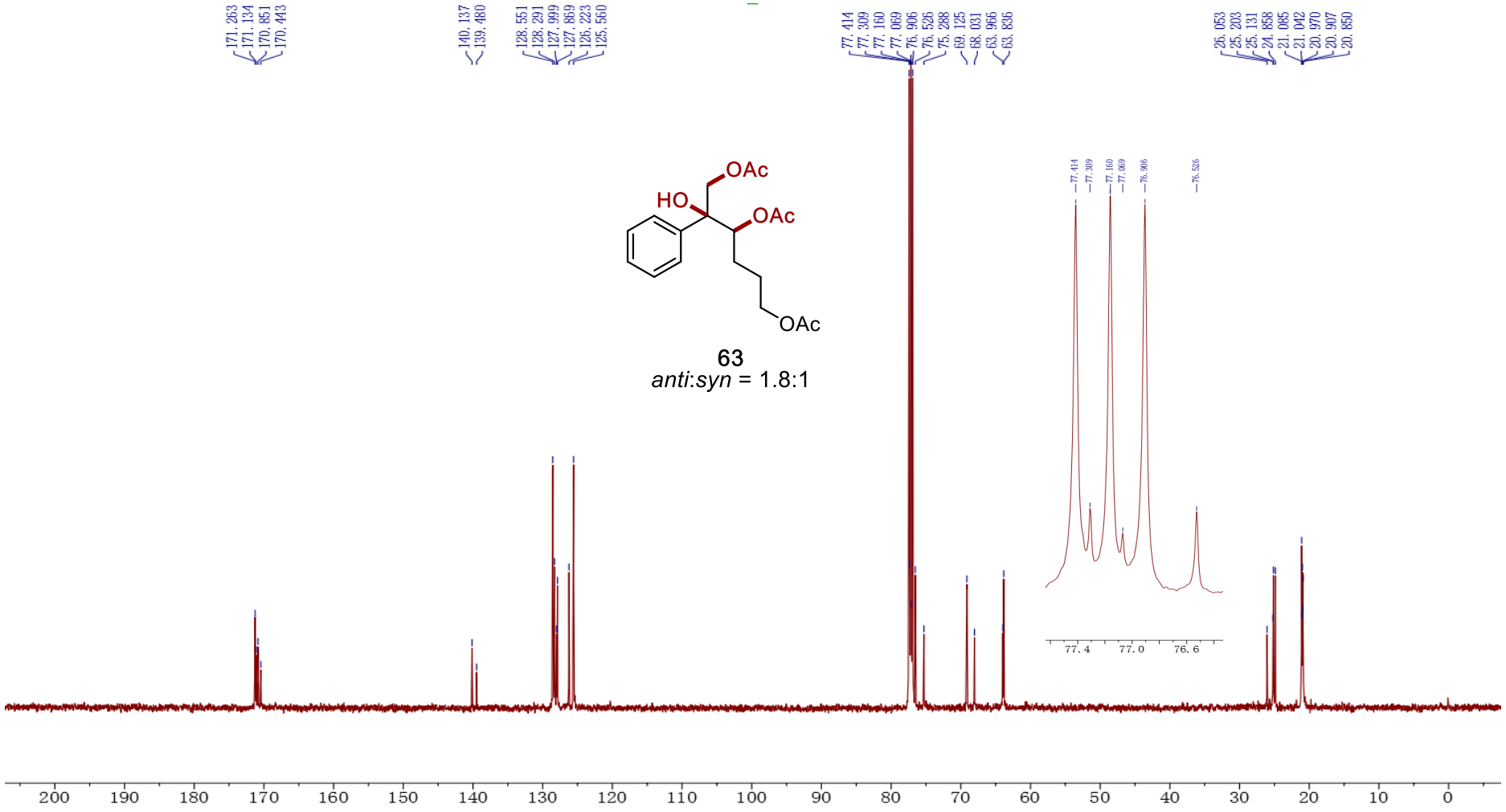


62

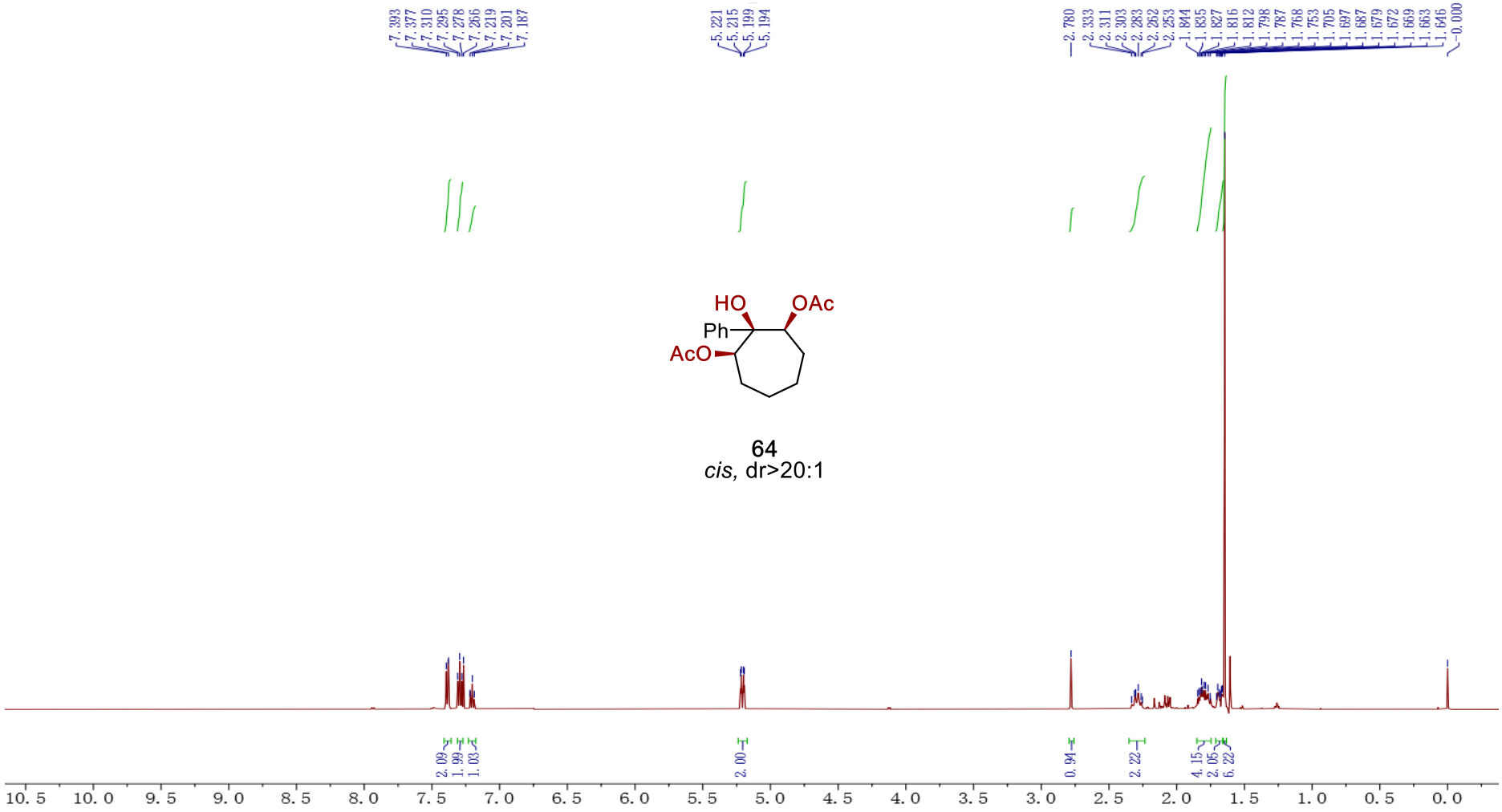
anti:*syn* = 1:1.2



63
anti:*syn* = 1.8:1



63
anti:*syn* = 1.8:1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7.266
7.219
7.201
7.187
5.221
5.215
5.199
5.194
2.780
2.333
2.311
2.303
2.283
2.262
2.253
1.844
1.835
1.827
1.816
1.812
1.798
1.787
1.768
1.753
1.705
1.697
1.687
1.679
1.672
1.669
1.663
1.646
-0.000
HO
OAc
Ph
AcO
2.09
1.99
1.03
2.00
0.94
2.22
4.15
2.05
6.22
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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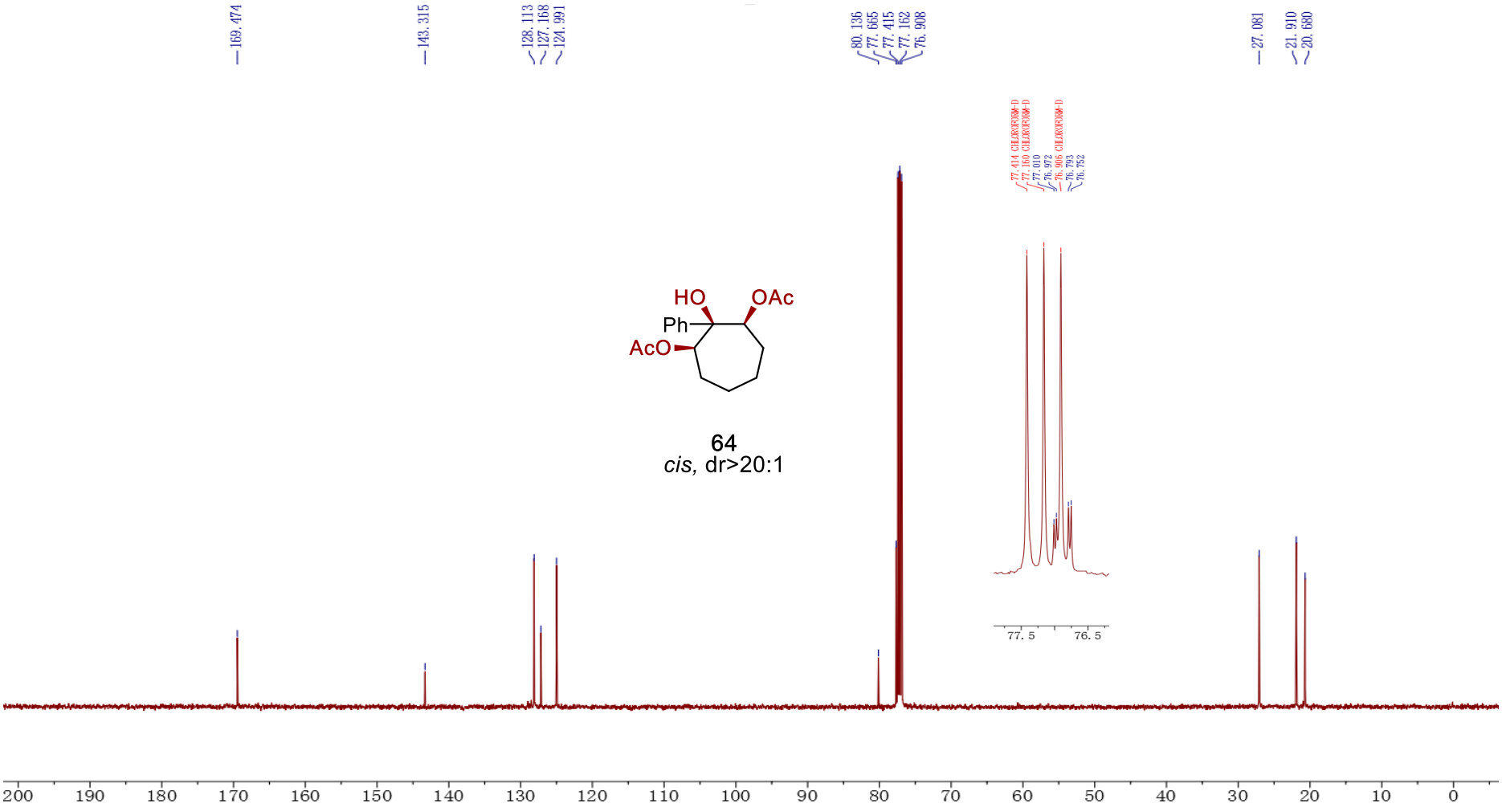
3.0
2.5
2.0
1.5
1.0
0.5
0.0

64
cis, dr>20:1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143.315
128.113
127.168
124.991
80.136
77.665
77.415
77.162
76.908
27.081
21.910
20.680
HO
OAc
Ph
AcO
64
cis, dr>20:1
77.5
76.5
200
190
180
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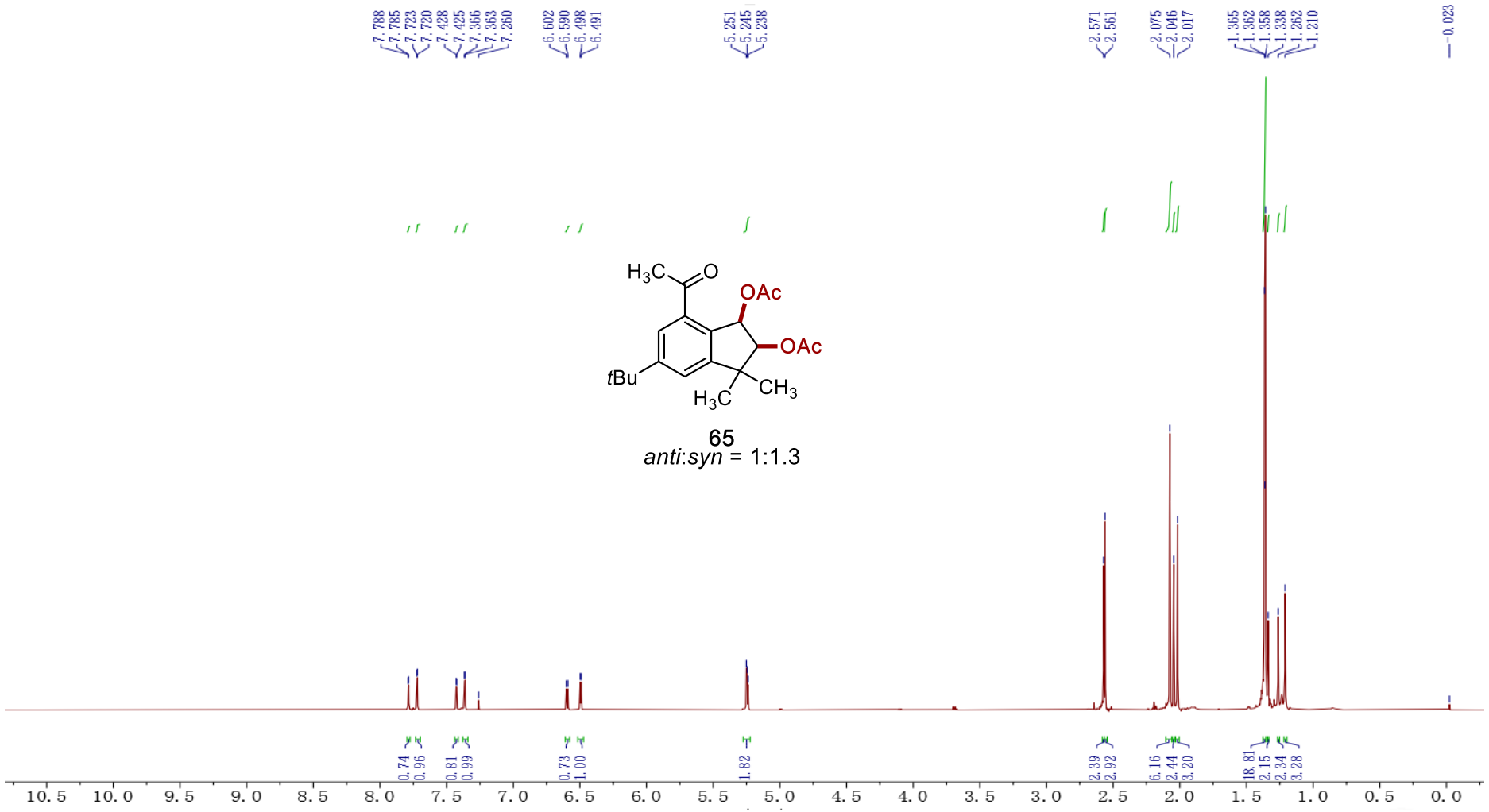
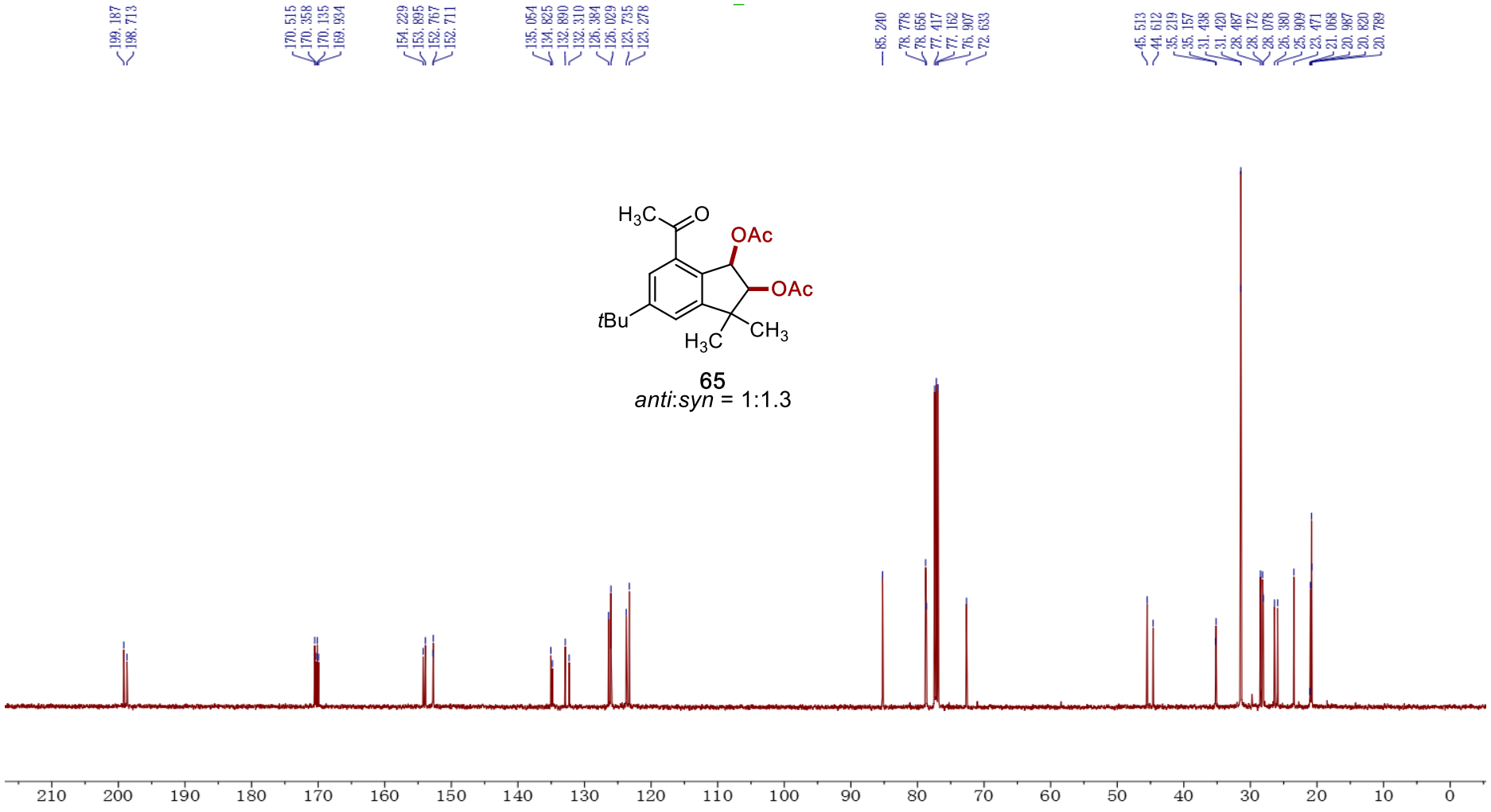
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

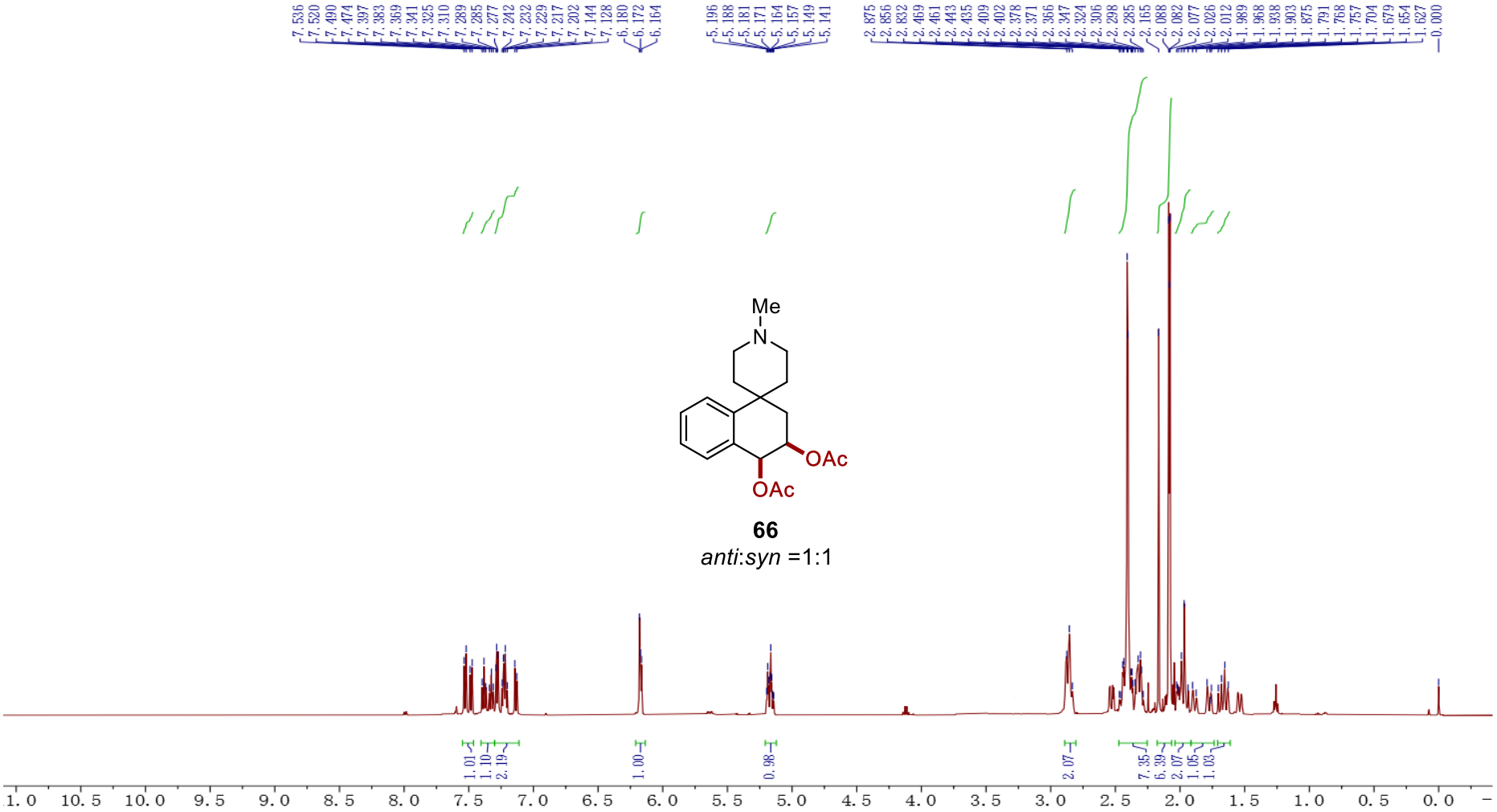


65
anti:*syn* = 1:1.3



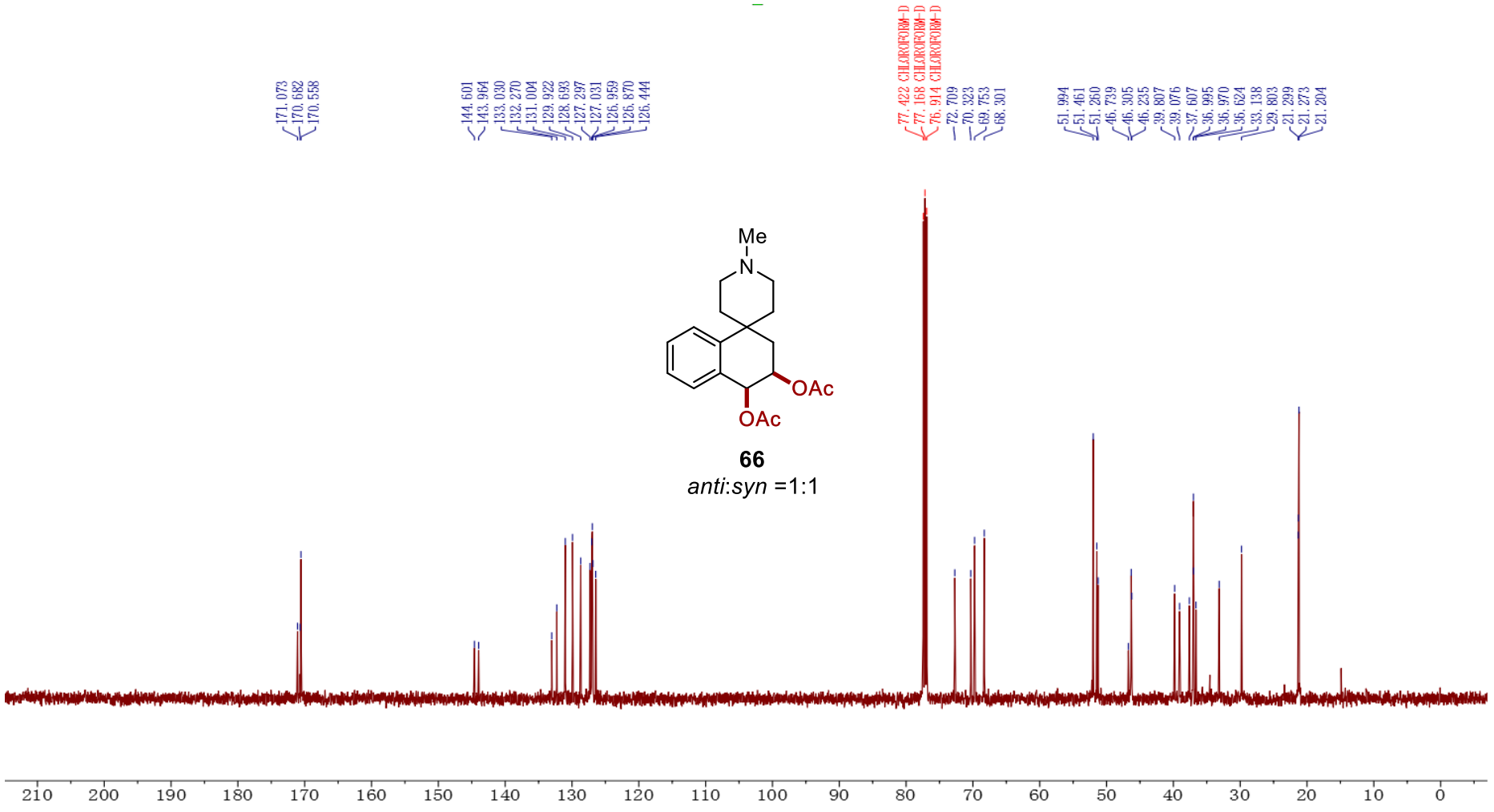
65

anti:*syn* = 1:1.3



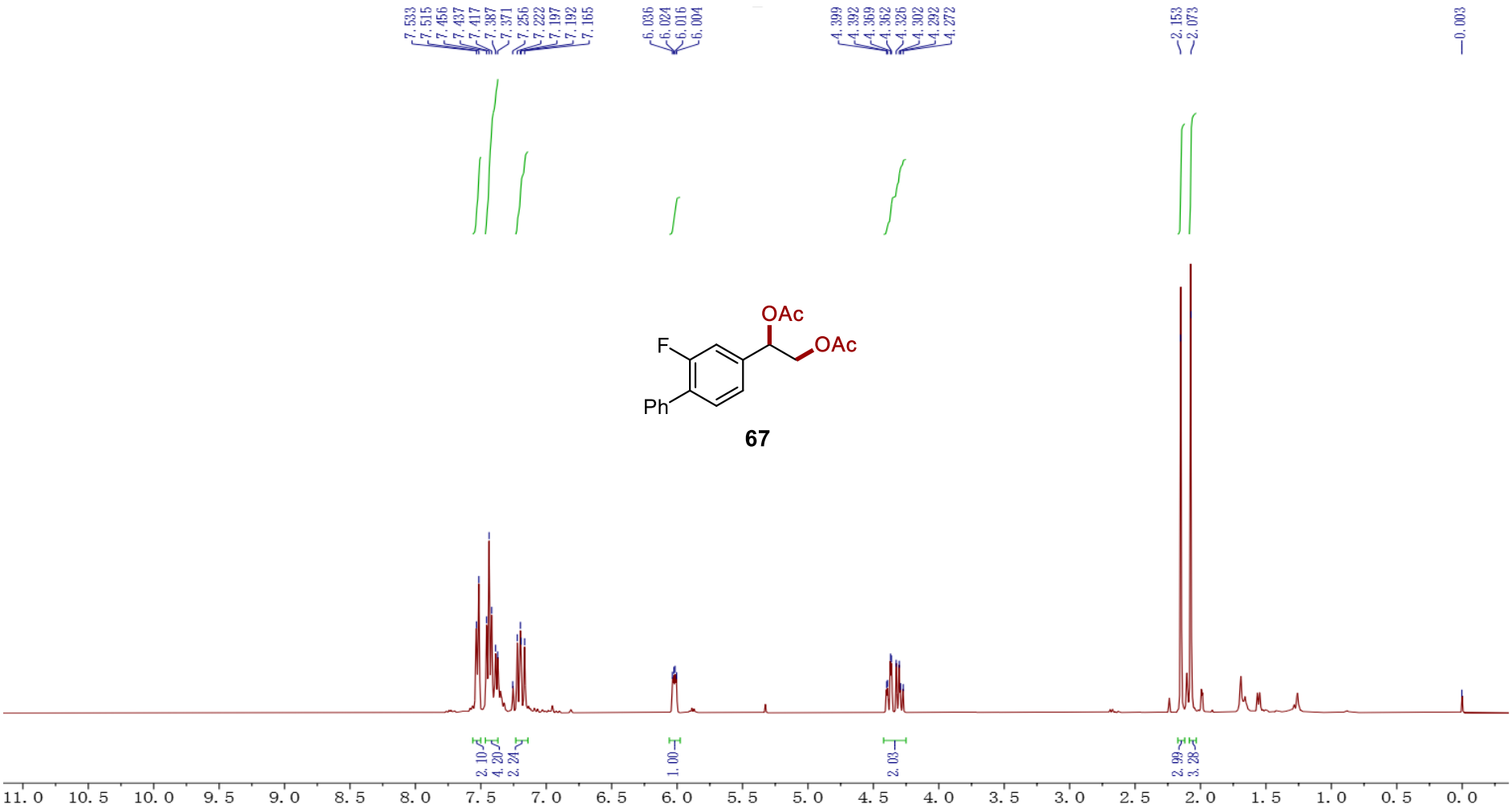
66

anti:*syn* =1:1



66

anti:*syn* =1:1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7.256
7.222
7.197
7.192
7.165
6.036
6.024
6.016
6.004
4.399
4.392
4.369
4.362
4.326
4.302
4.292
4.272
2.153
2.073
0.003
OAc
OAc
F
Ph
67
2.10
4.20
2.24
1.00
2.03
2.99
3.28
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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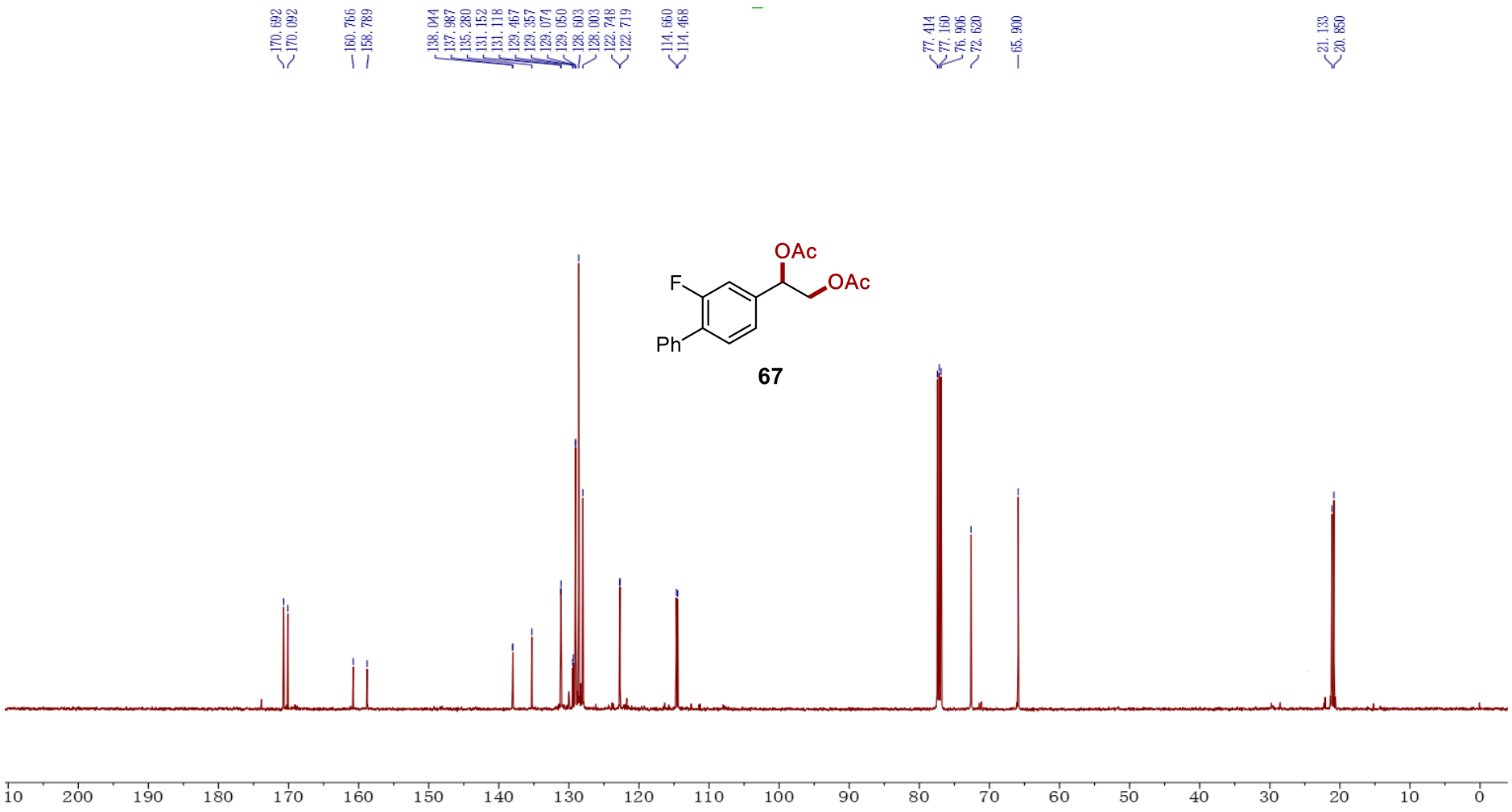
0.0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160.766
158.789
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137.987
135.280
131.152
131.118
129.467
129.357
129.074
129.050
128.603
128.003
122.748
122.719
114.660
114.468
77.414
77.160
76.906
72.620
65.900
21.133
20.850
OAc
OAc
F
Ph
67
10
200
190
180
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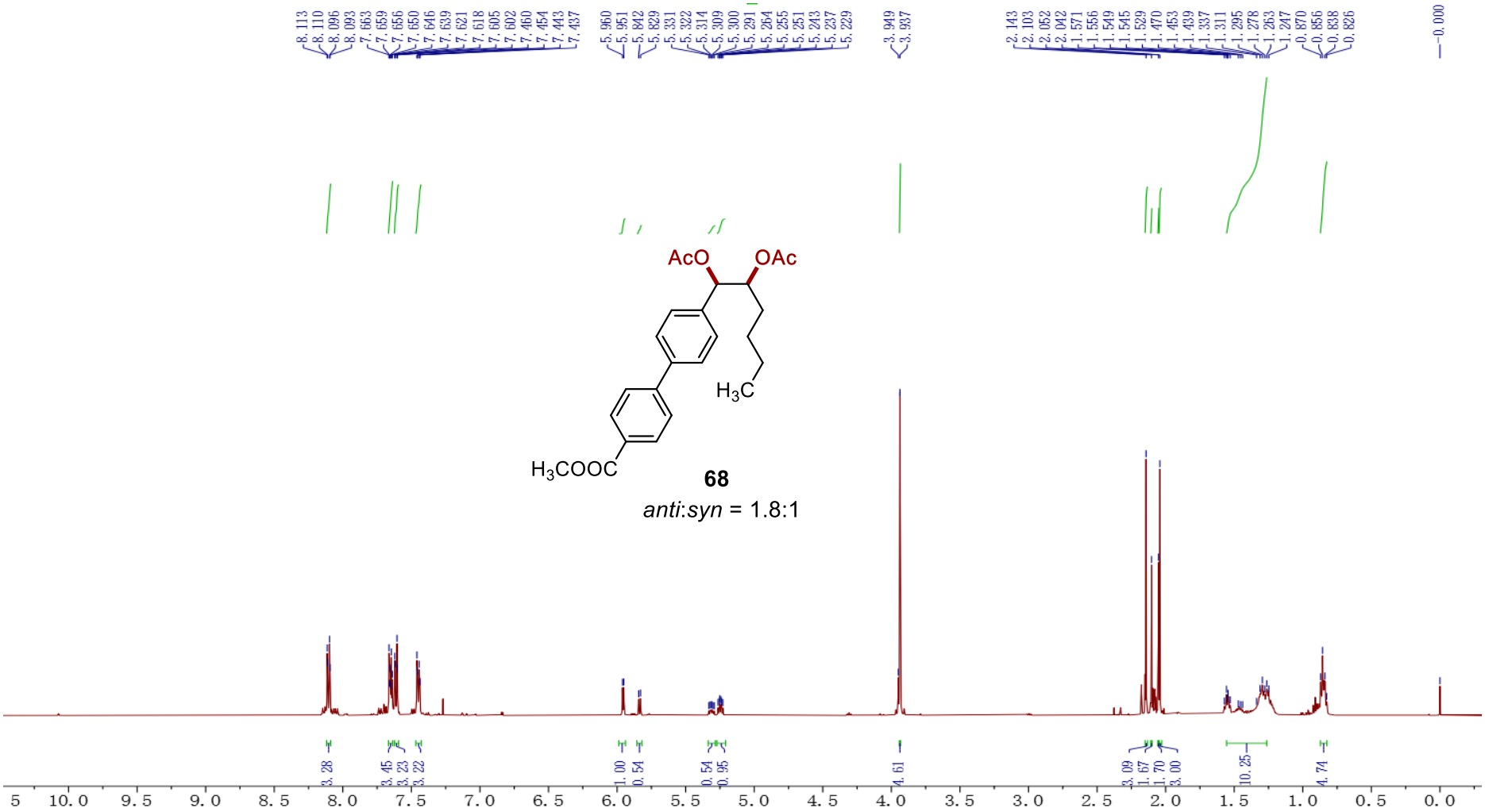
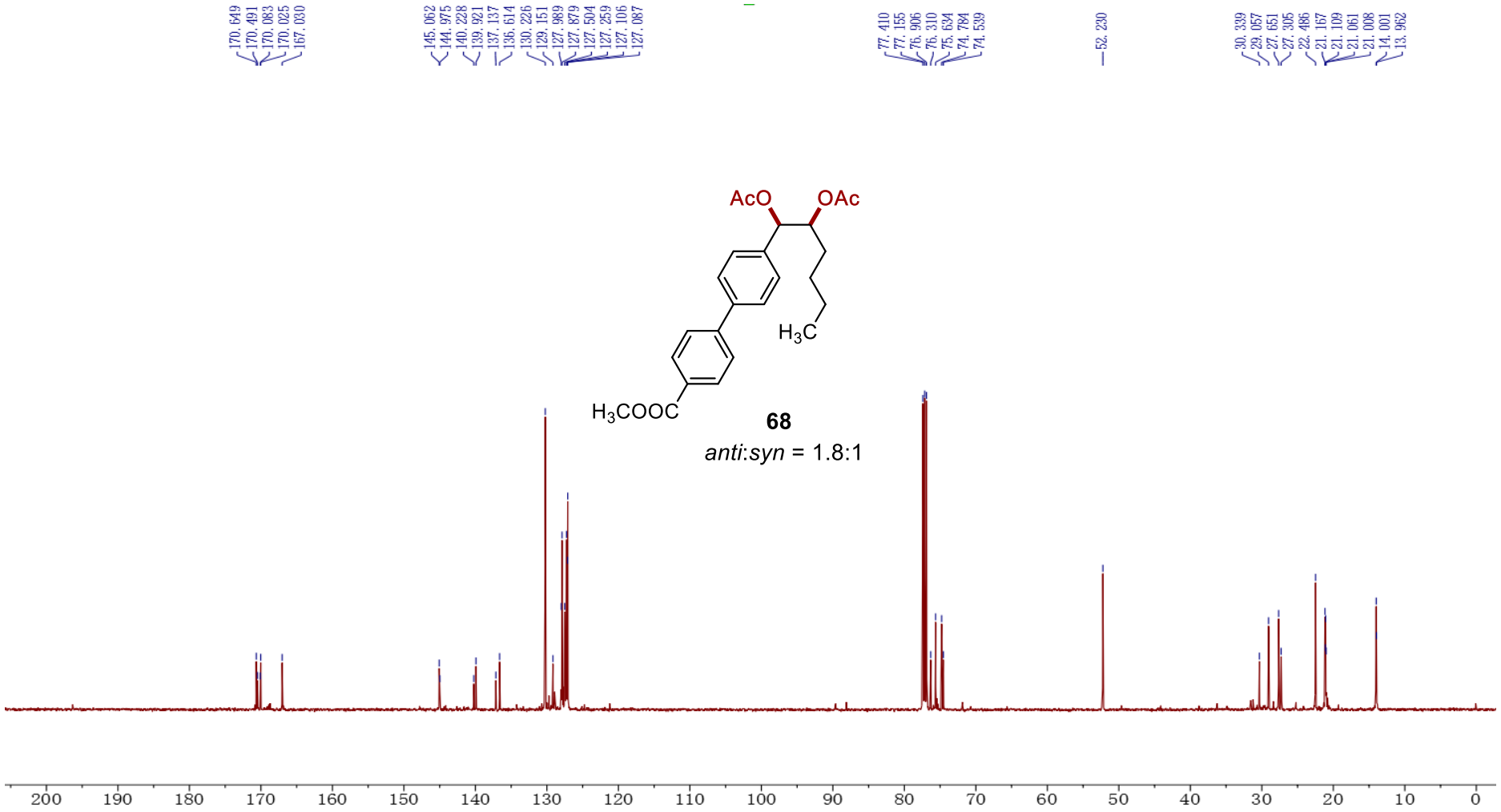
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


AcO
OAc
H3C
H3COOC
68
anti:syn = 1.8:1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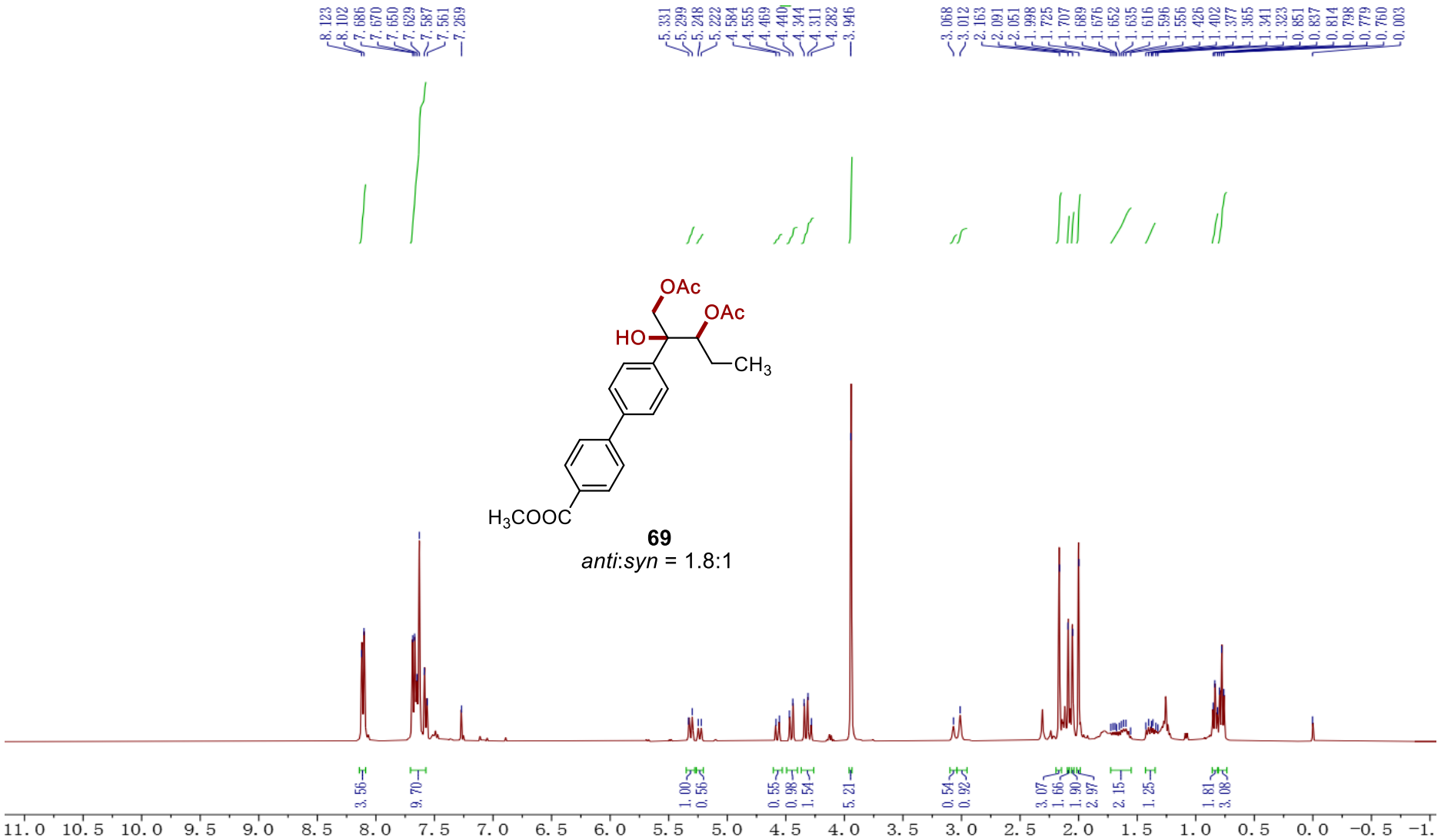
170.025
167.030
145.062
144.975
140.228
139.921
137.137
136.614
130.226
129.151
127.989
127.879
127.504
127.259
127.106
127.087
77.410
77.155
76.906
76.310
75.634
74.784
74.539
52.230
30.339
29.057
27.651
27.305
22.486
21.167
21.109
21.061
21.008
14.001
13.962
AcO
OAc
H3C
H3COOC
68
anti:syn = 1.8:1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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8.102
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9.0
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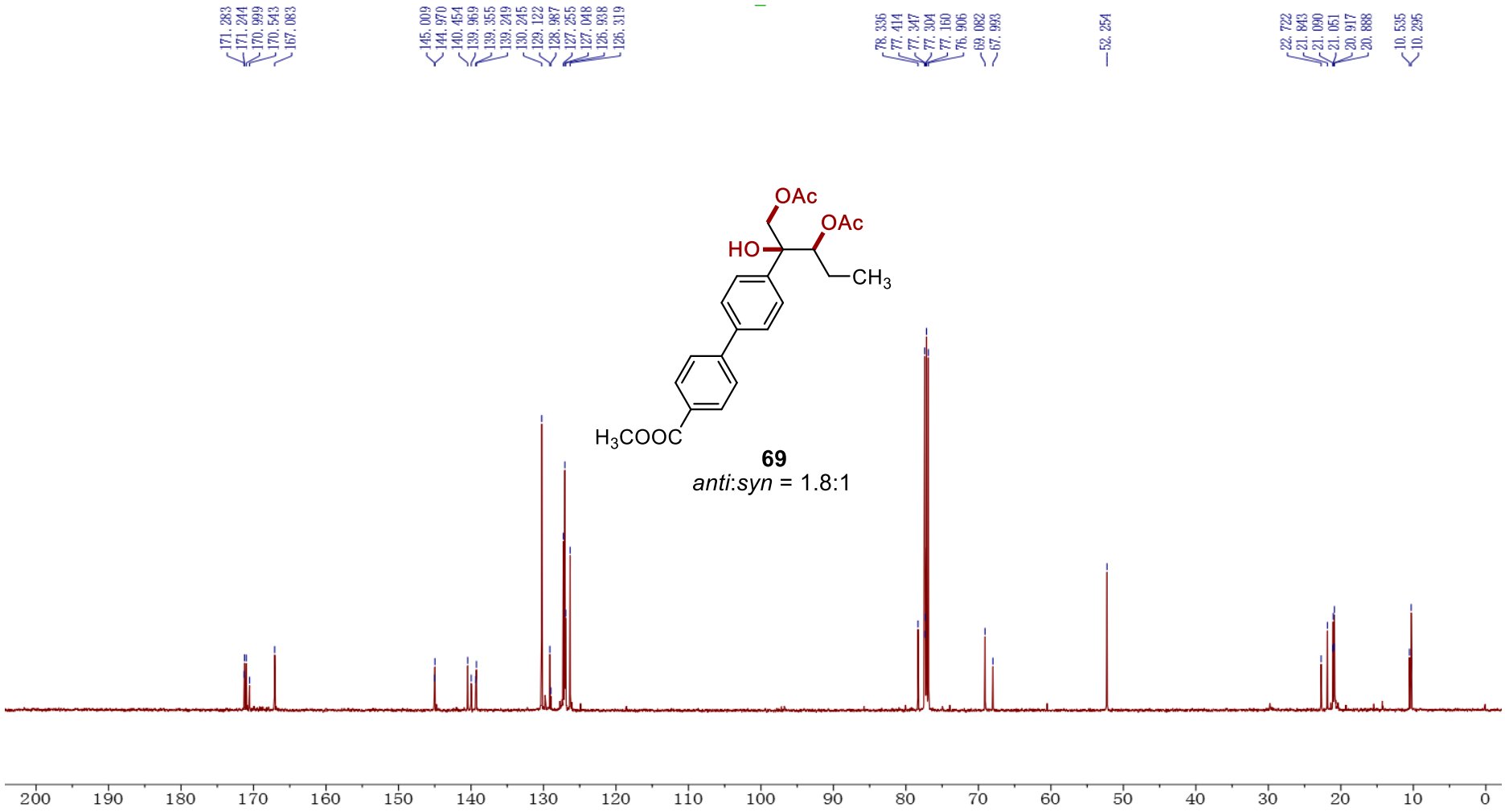
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127.255
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125.319
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77.347
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OAc
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CH3
H3COOC
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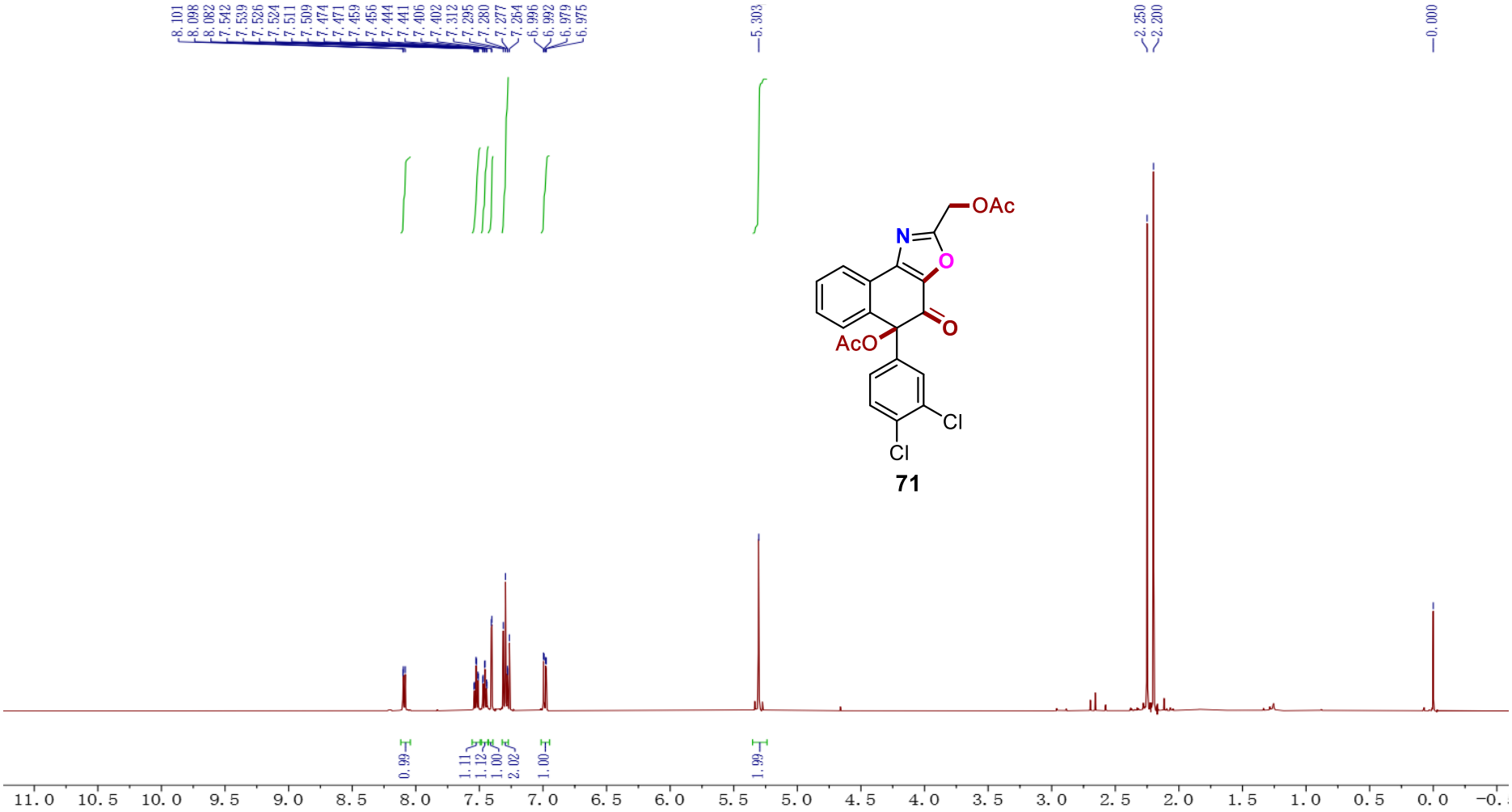
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7.456
7.444
7.441
7.406
7.402
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Cl
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1.00
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8.5
8.0
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6.5
6.0
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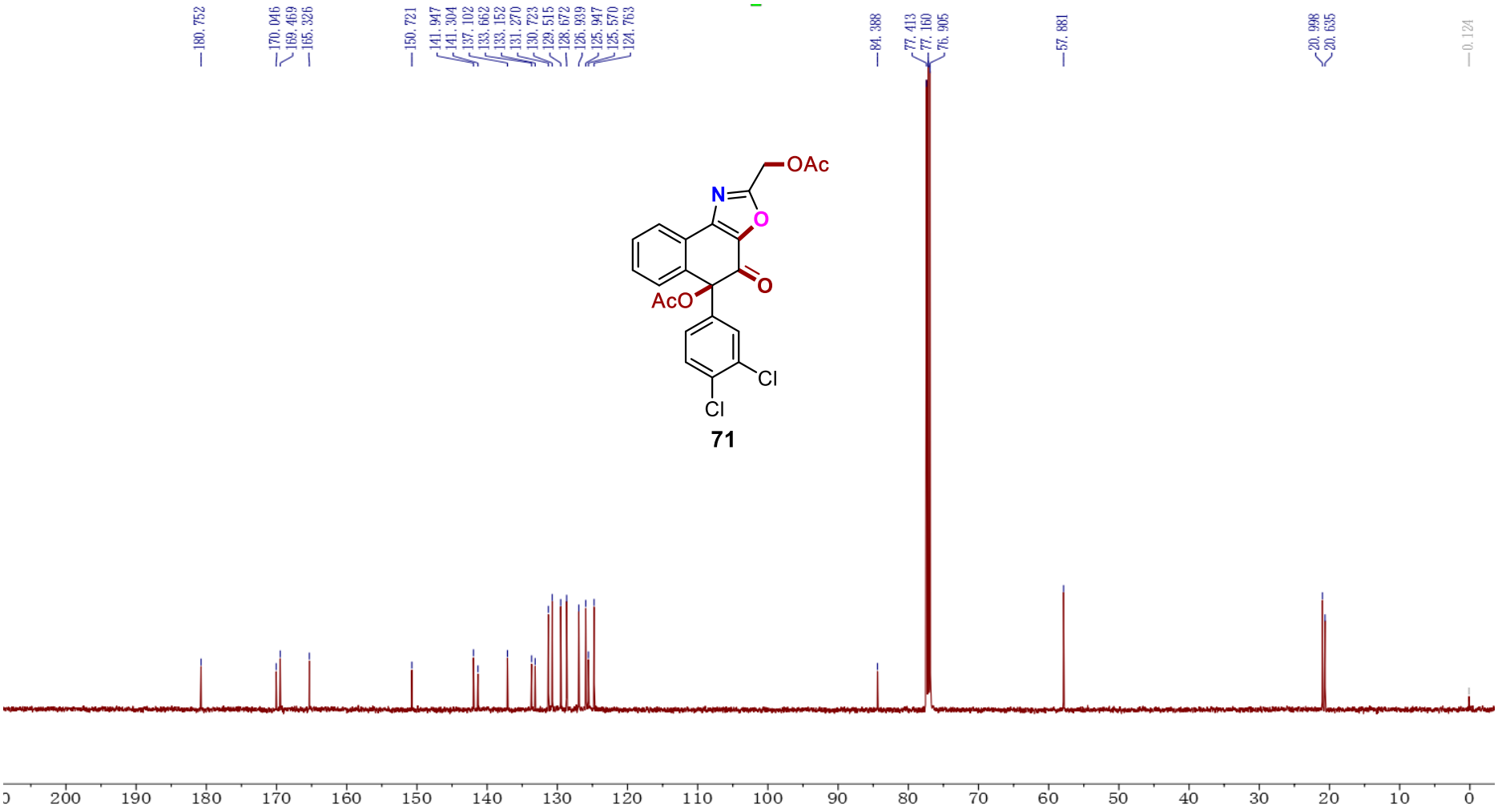
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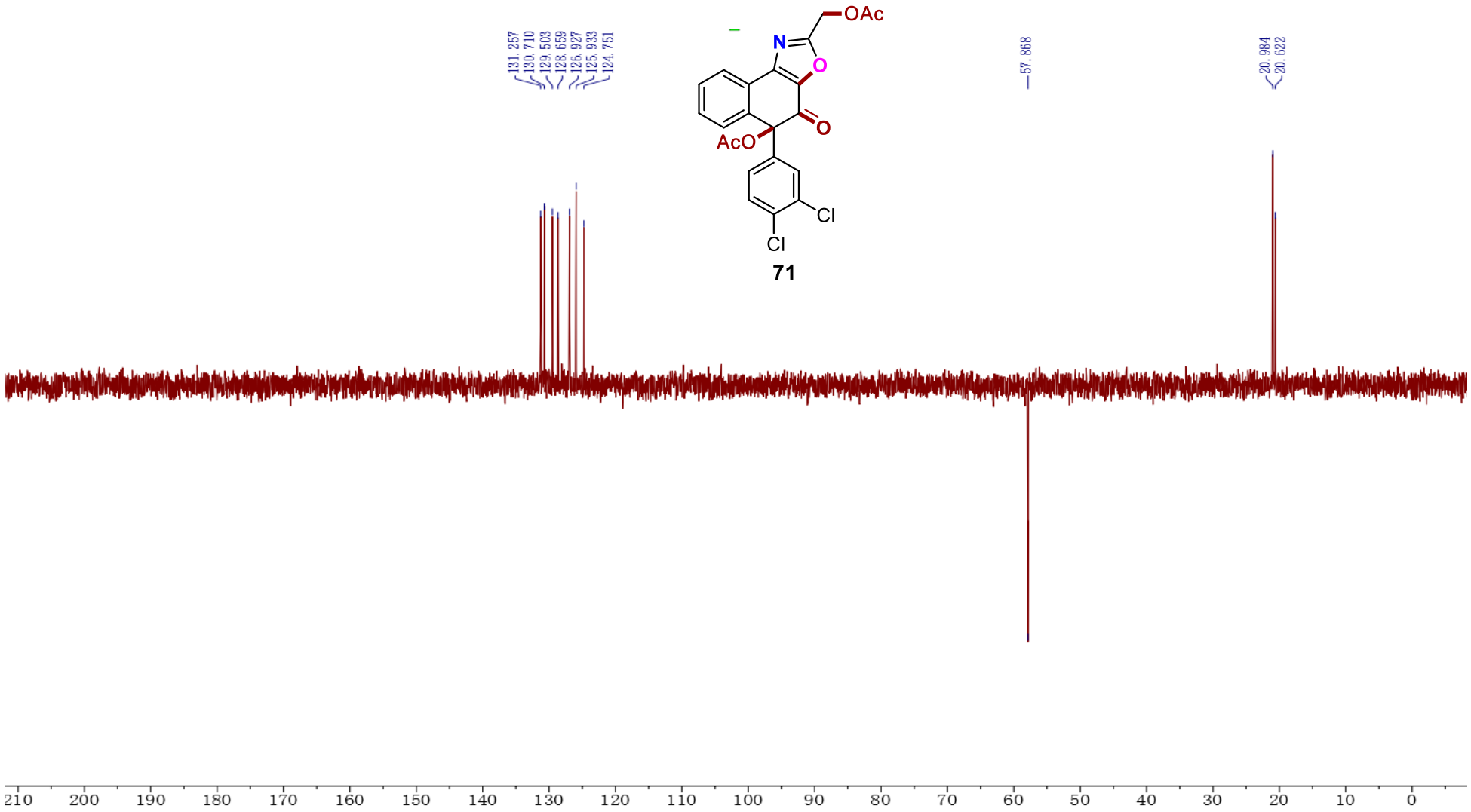

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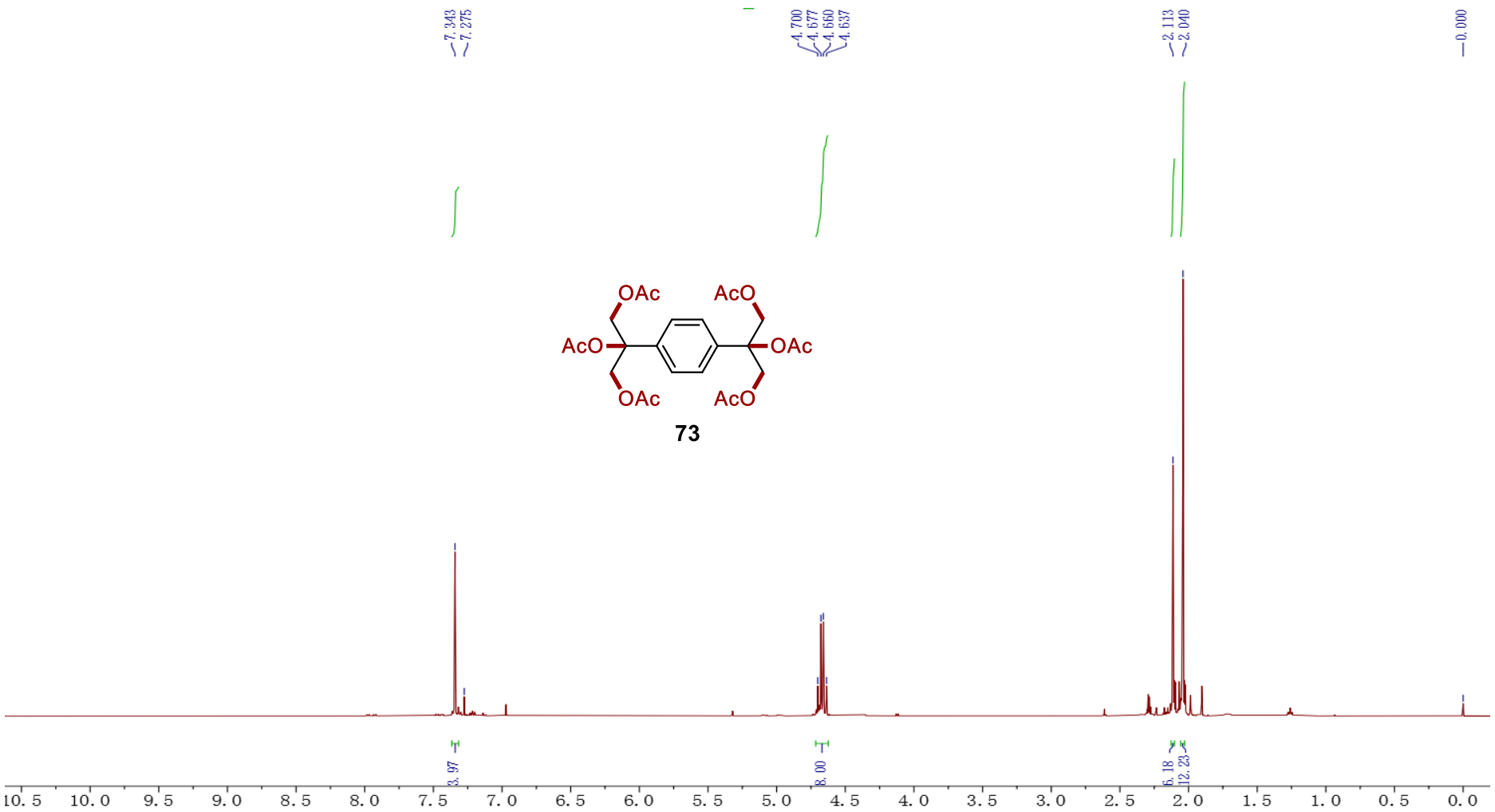
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OAc
OAc
AcO
73
3.97
8.00
6.18
12.23
10.5
10.0
9.5
9.0
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8.0
7.5
7.0
6.5
6.0
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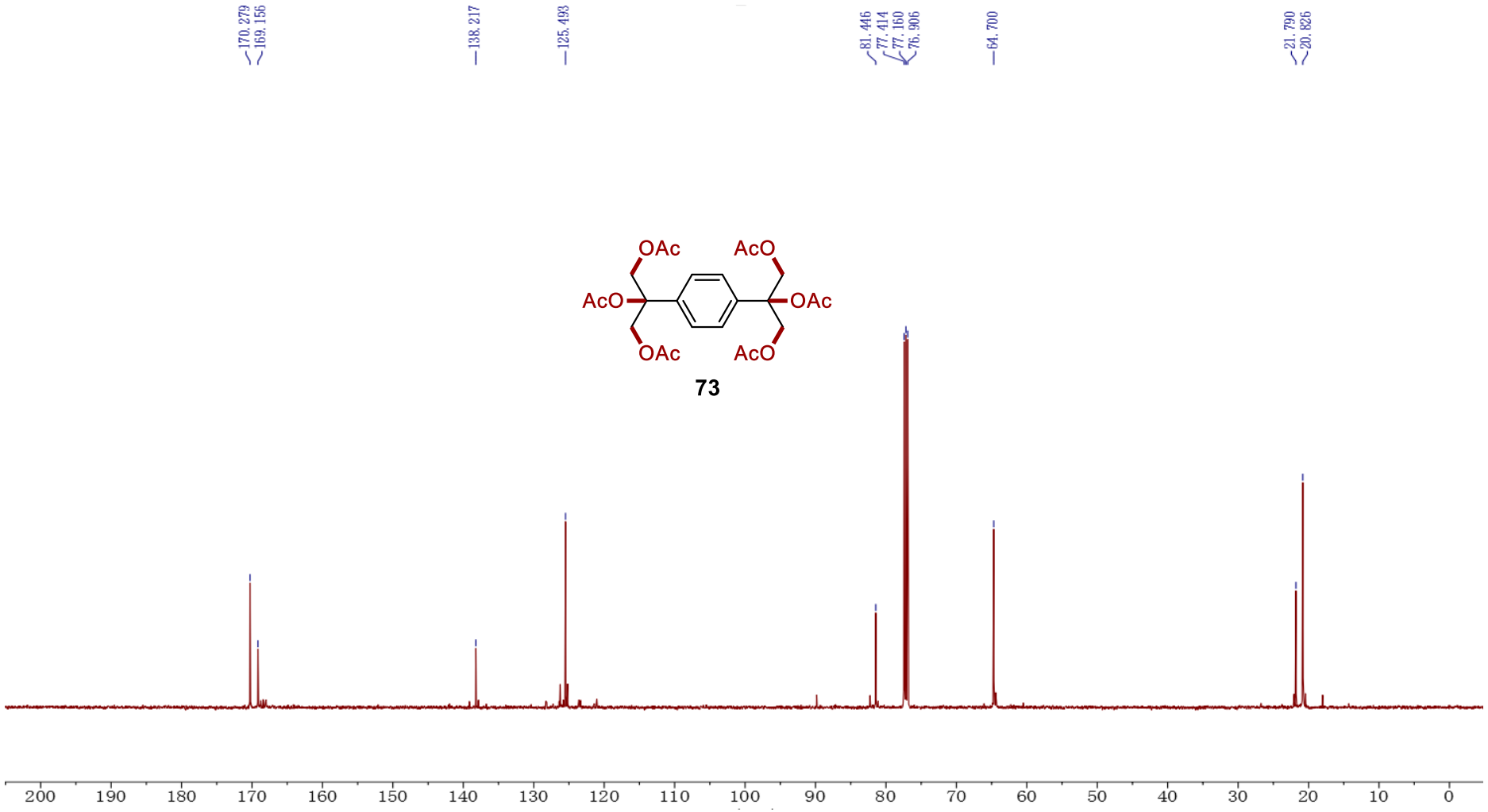
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138.217
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77.414
77.160
76.906
64.700
21.790
20.826
OAc
AcO
AcO
OAc
OAc
AcO
200
190
180
170
160
150
140
130
120
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100
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80
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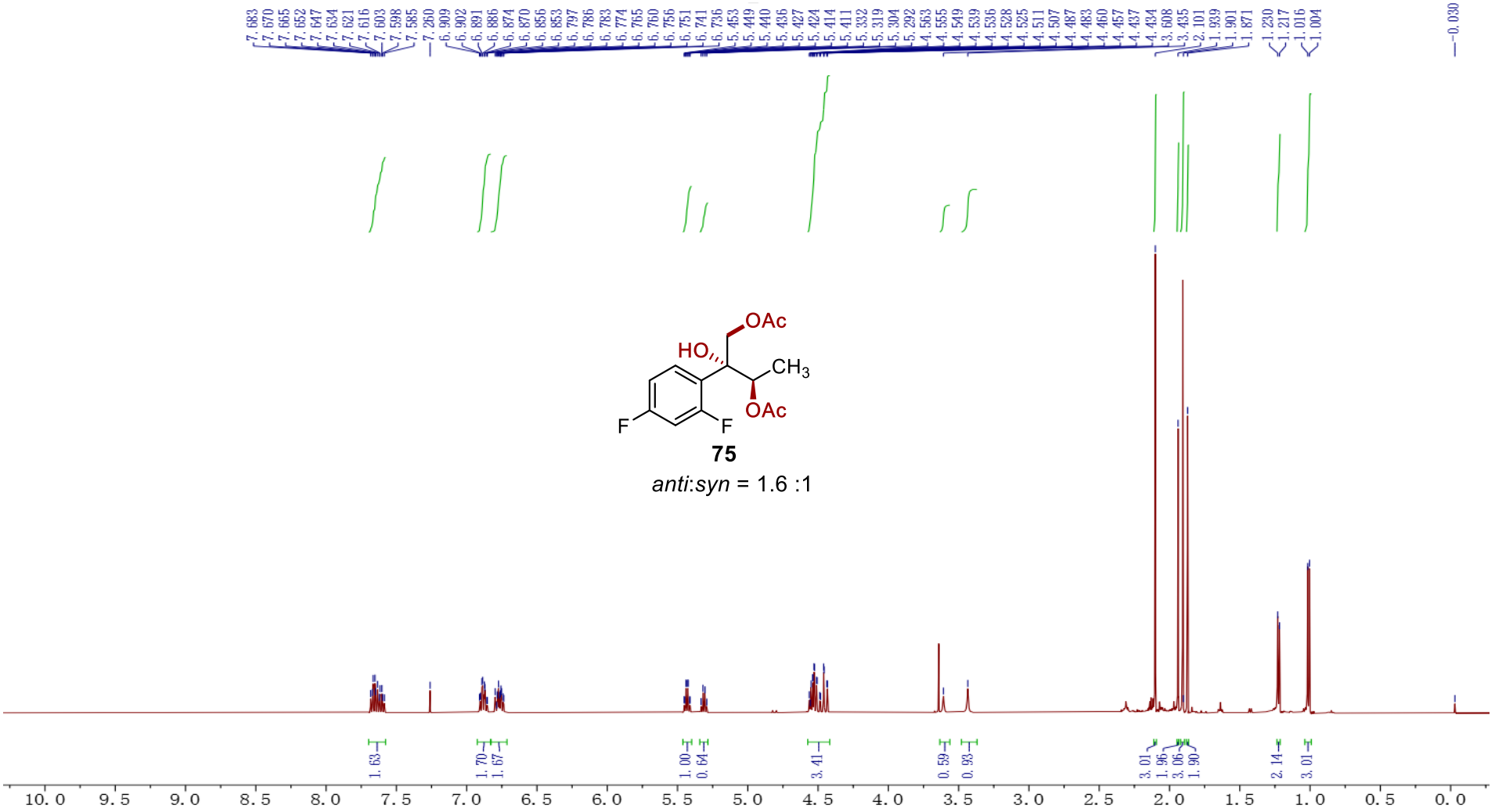
60
50
40
30
20
10
0

73



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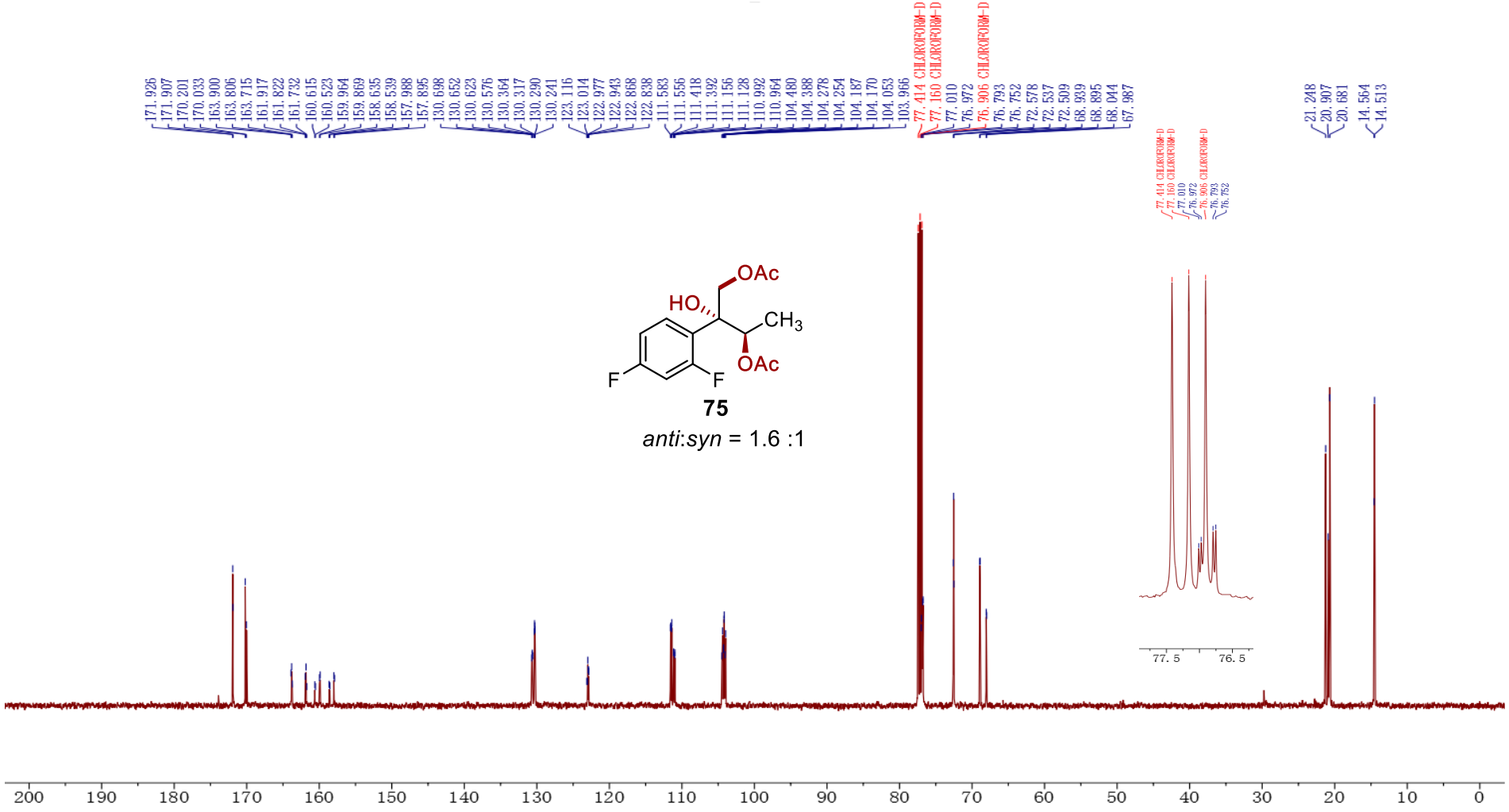
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CH3
OAc
F
F
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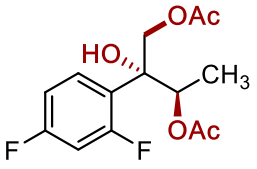
anti:syn = 1.6 :1



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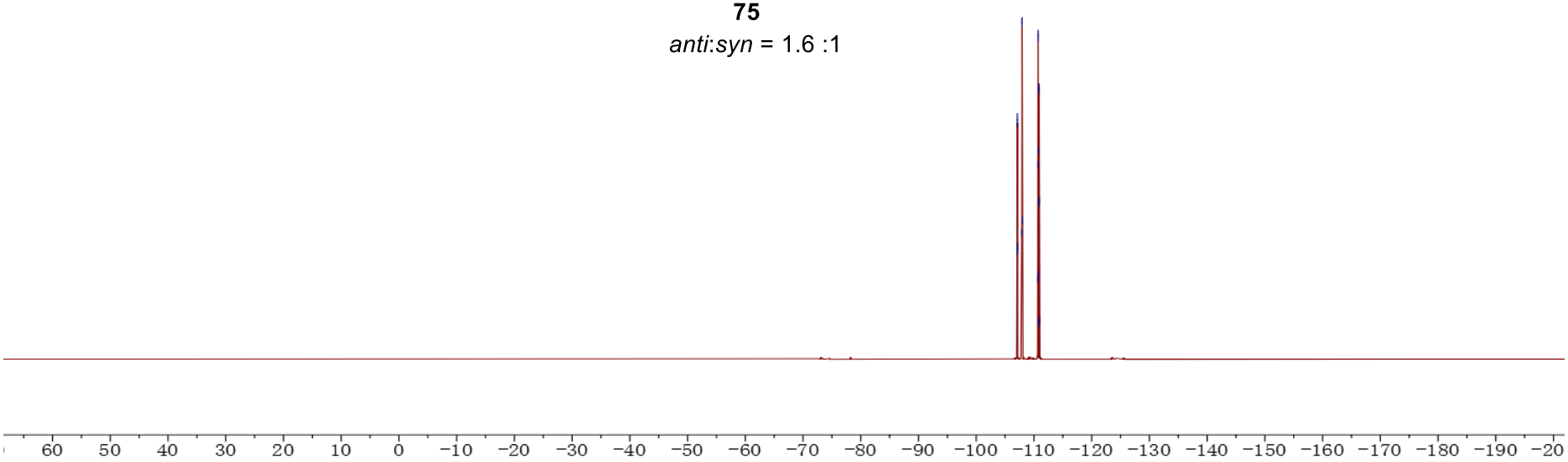

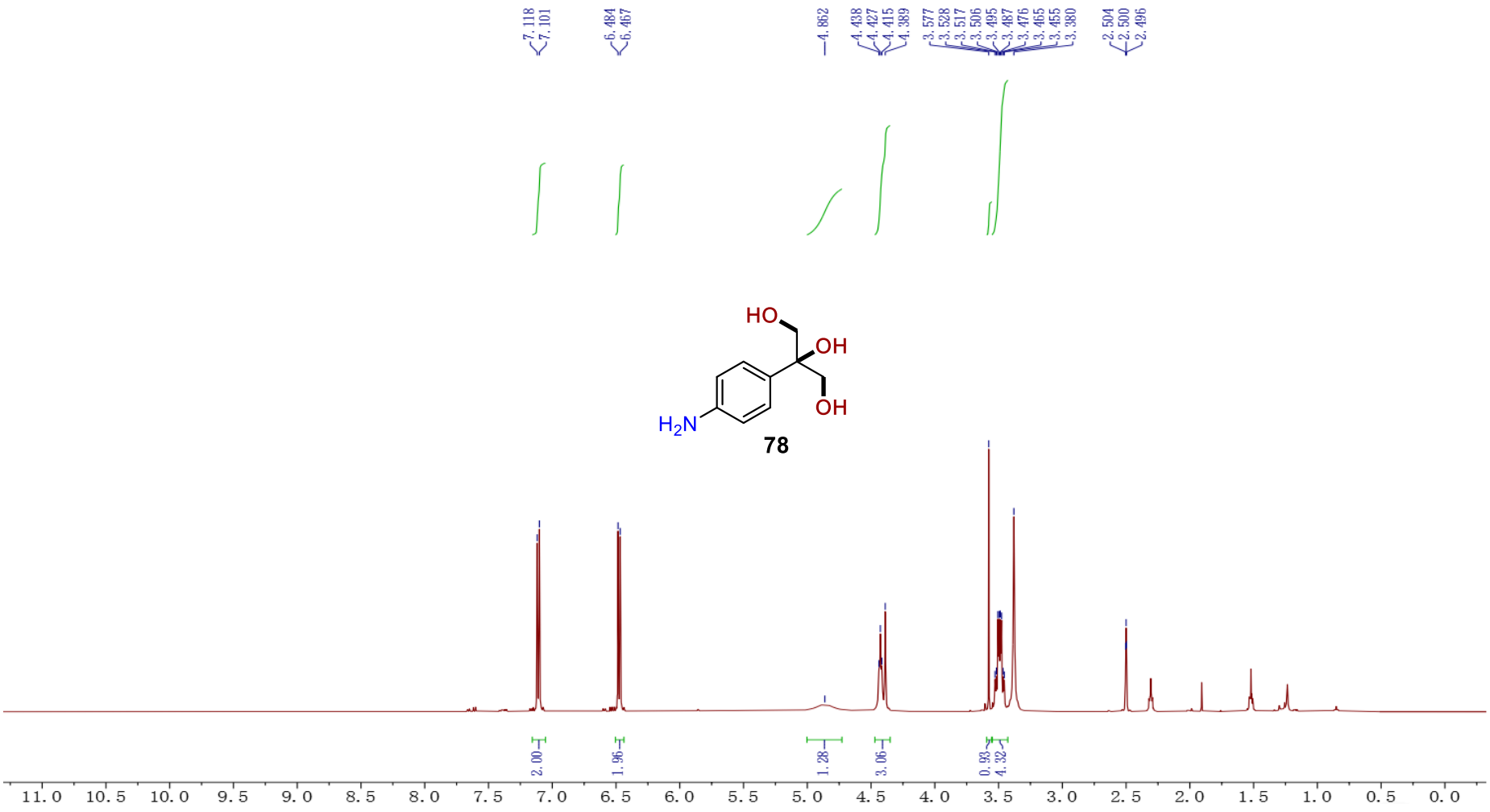
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3.506
3.495
3.487
3.476
3.465
3.455
3.380
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2.500
2.496
HO
OH
OH
H2N
78
2.00
1.96
1.28
3.06
0.93
4.32
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10.0
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8.0
7.5
7.0
6.5
6.0
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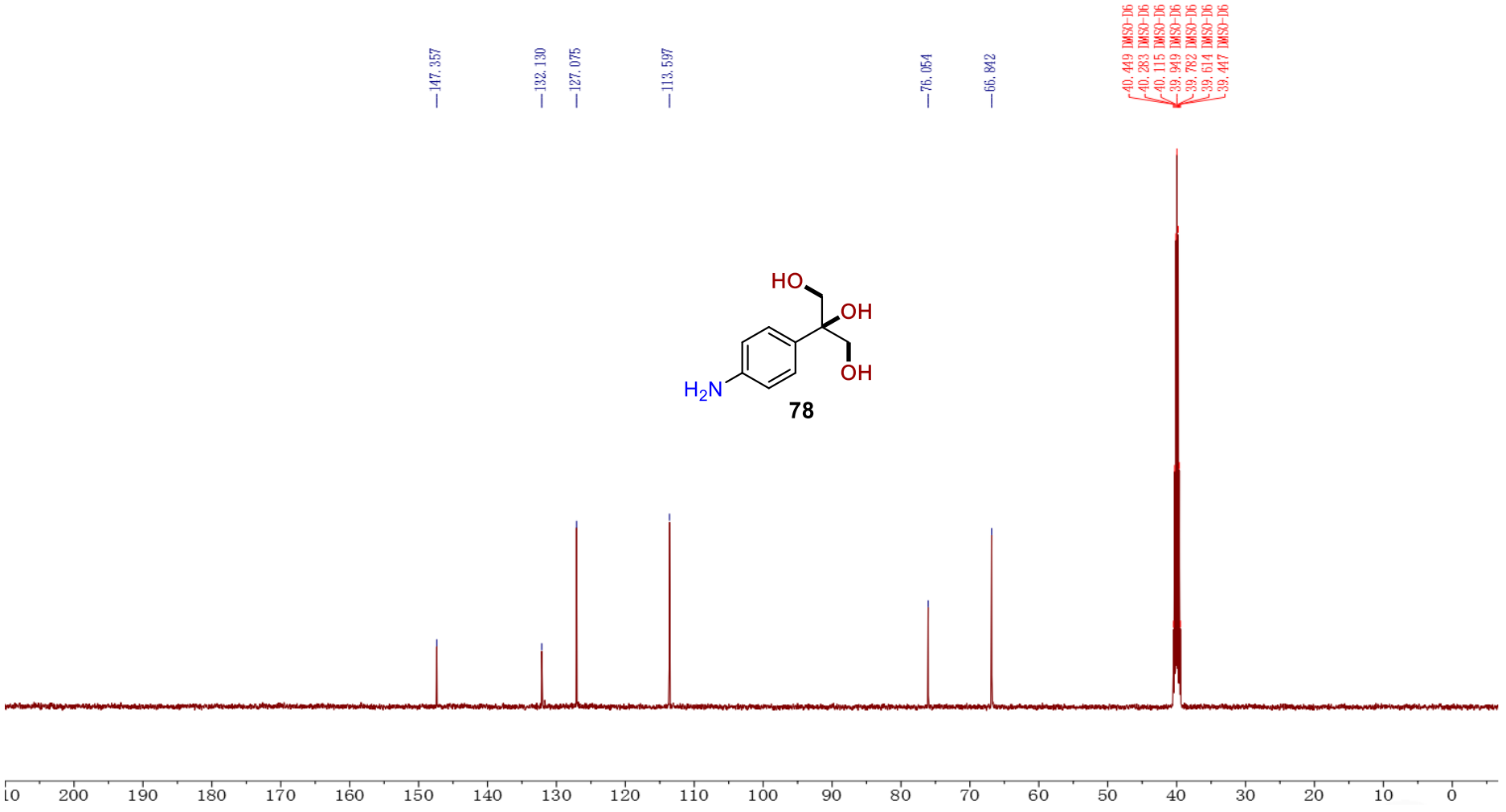
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40.115 DMSO-D6
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39.782 DMSO-D6
39.614 DMSO-D6
39.447 DMSO-D6
HO
OH
OH
H2N
78
210
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150
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90
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70
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40
30
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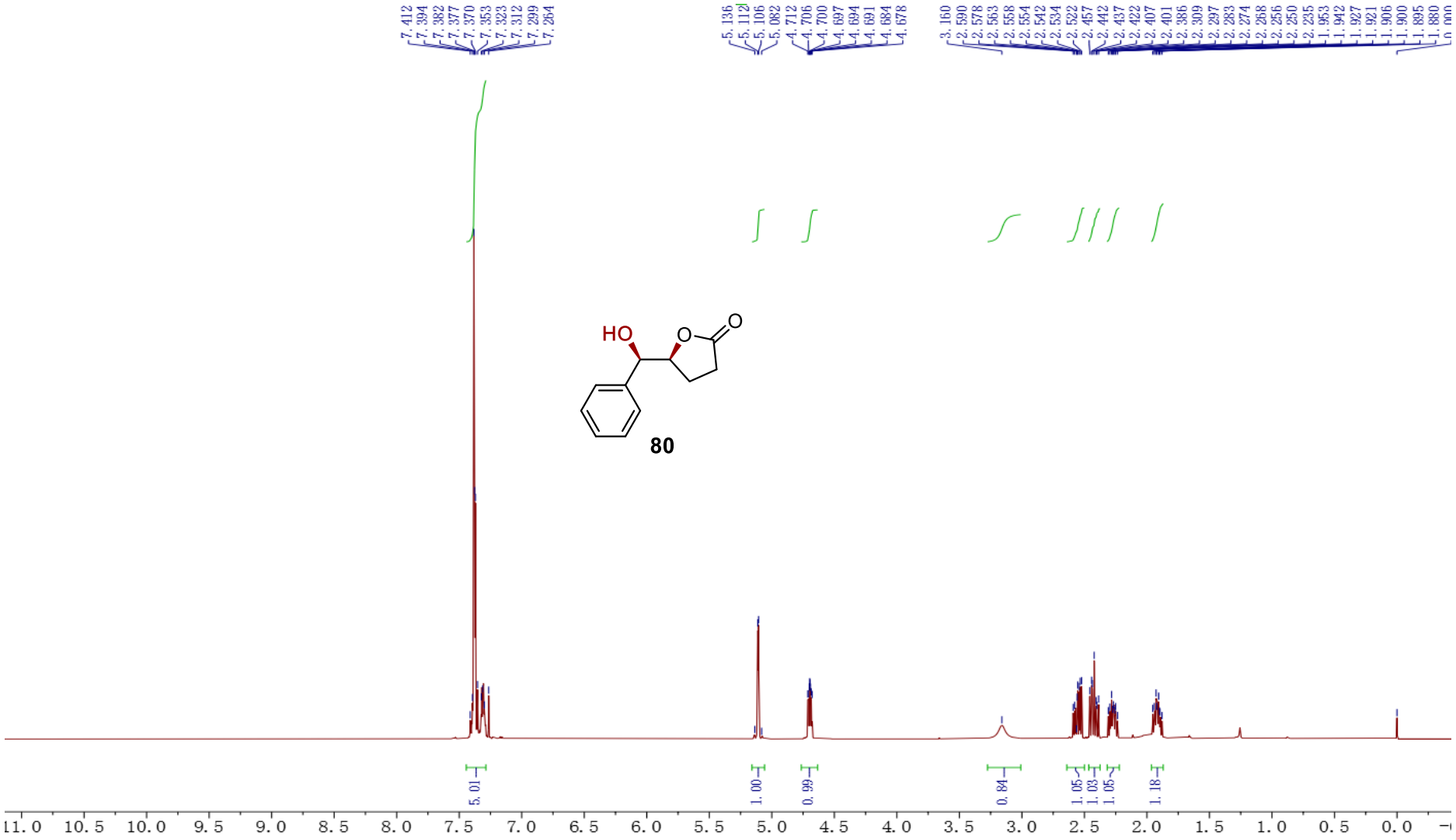
10
0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O
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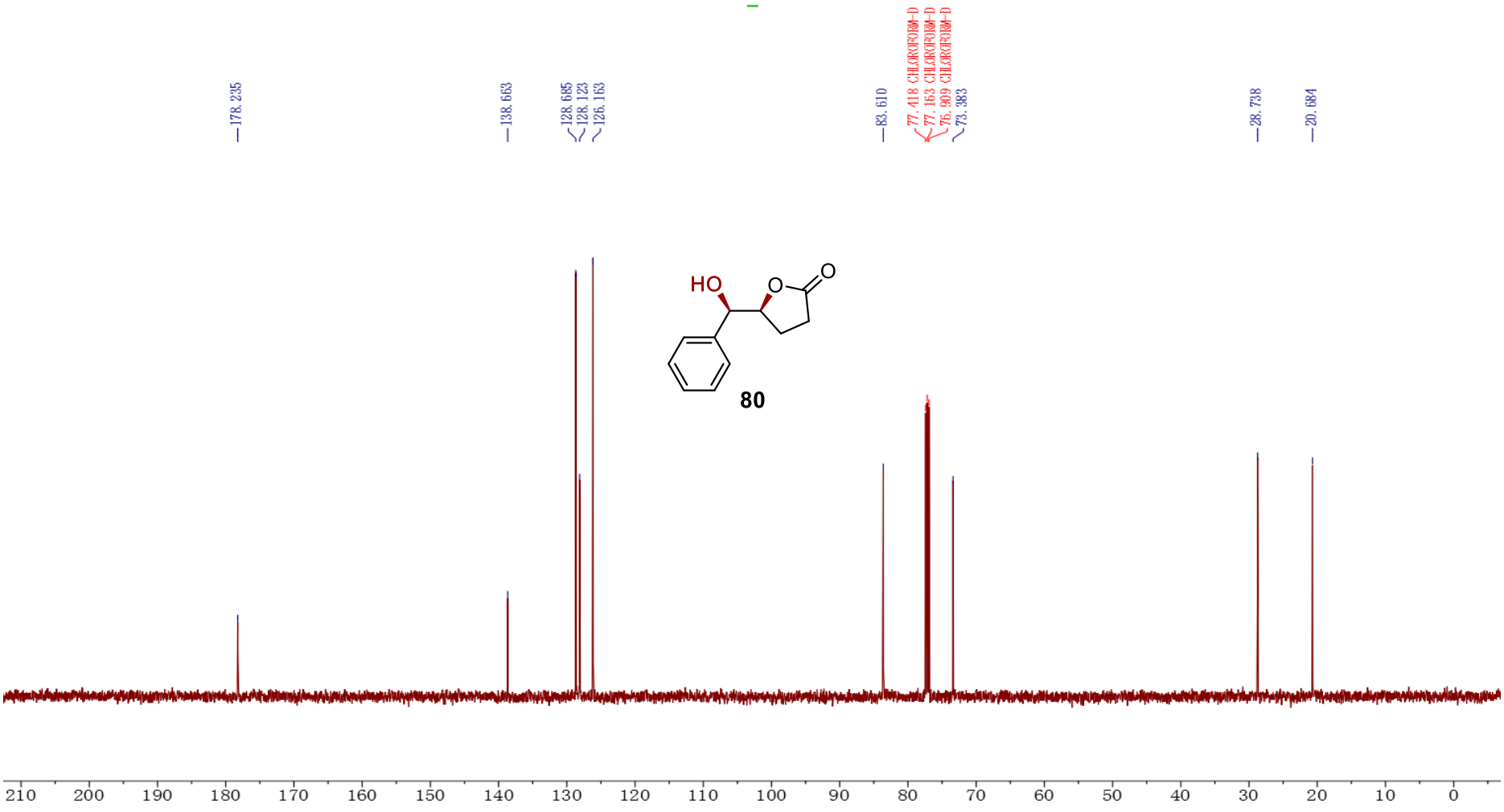
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77.163 CHLOROFORM-D
76.909 CHLOROFORM-D
73.383
28.738
20.684
HO
O
O
80
210
200
190
180
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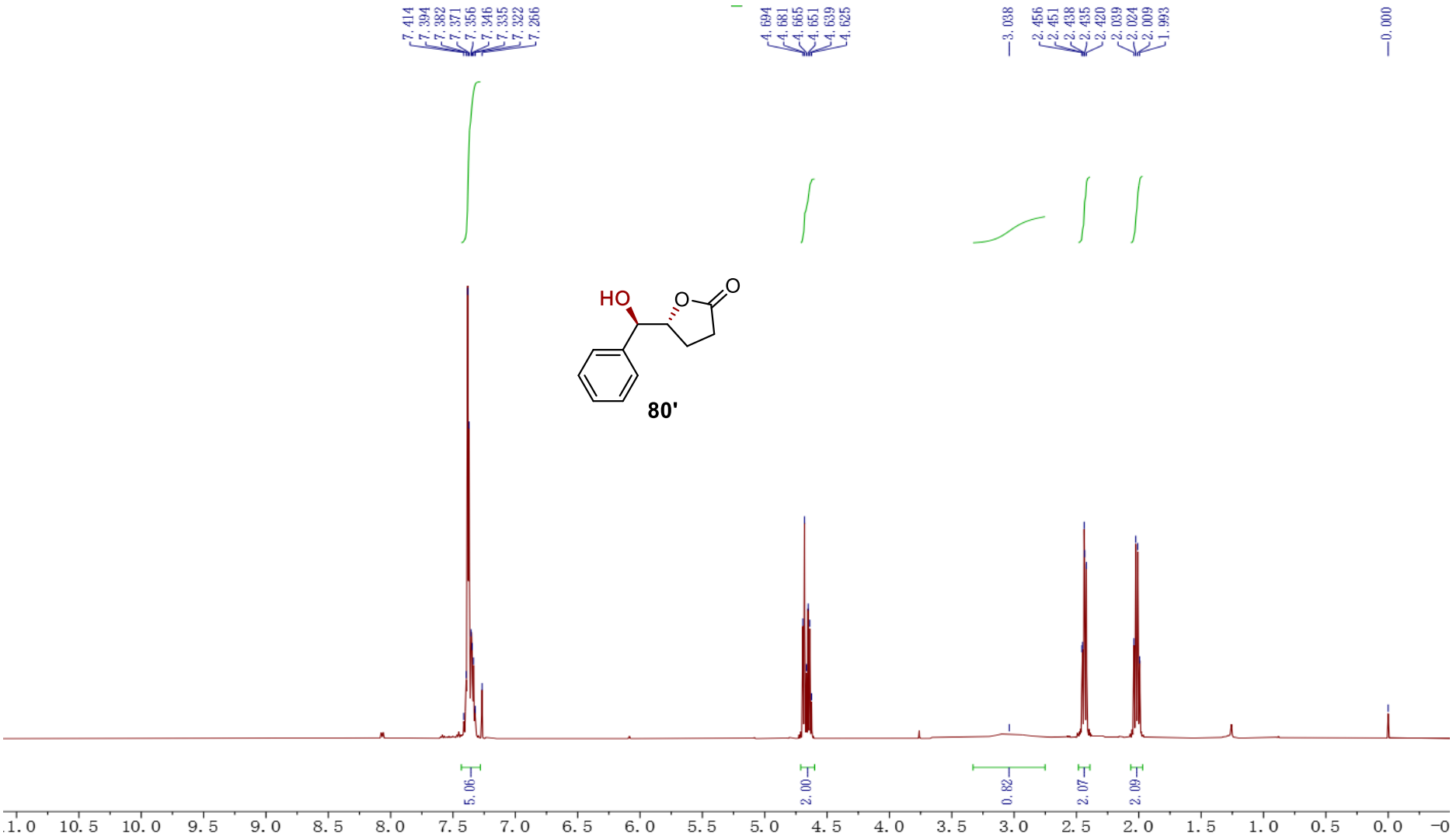
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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7.322
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2.435
2.420
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2.024
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1.993
0.000
HO
O
O
80'
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2.00
0.82
2.07
2.09
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10.0
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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2.0
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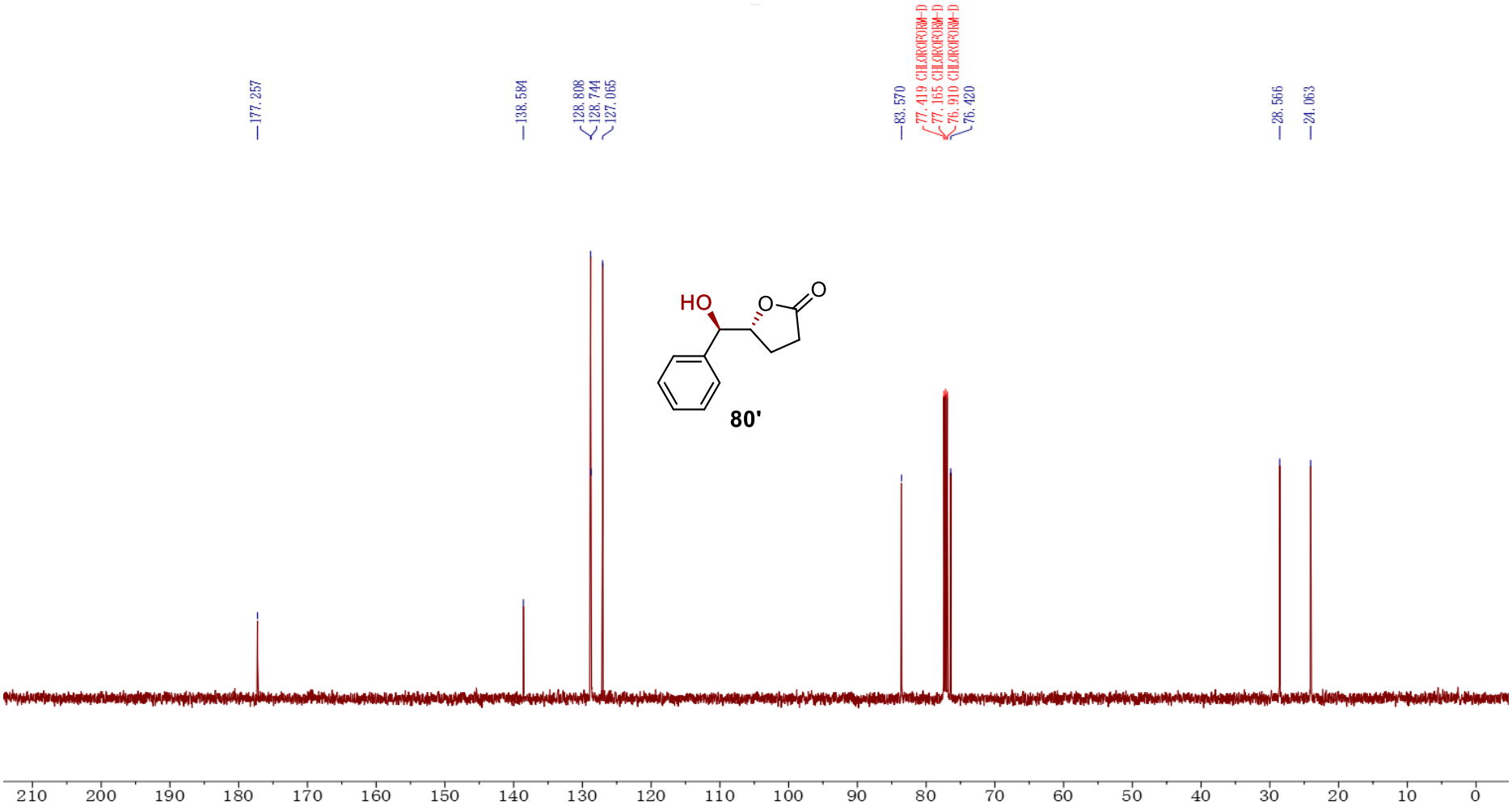
0.5
0.0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77.165 CHLOROFORM-D
76.910 CHLOROFORM-D
76.420
28.566
24.063
HO
O
O
80'
210
200
190
180
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150
140
130
120
110
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90
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10
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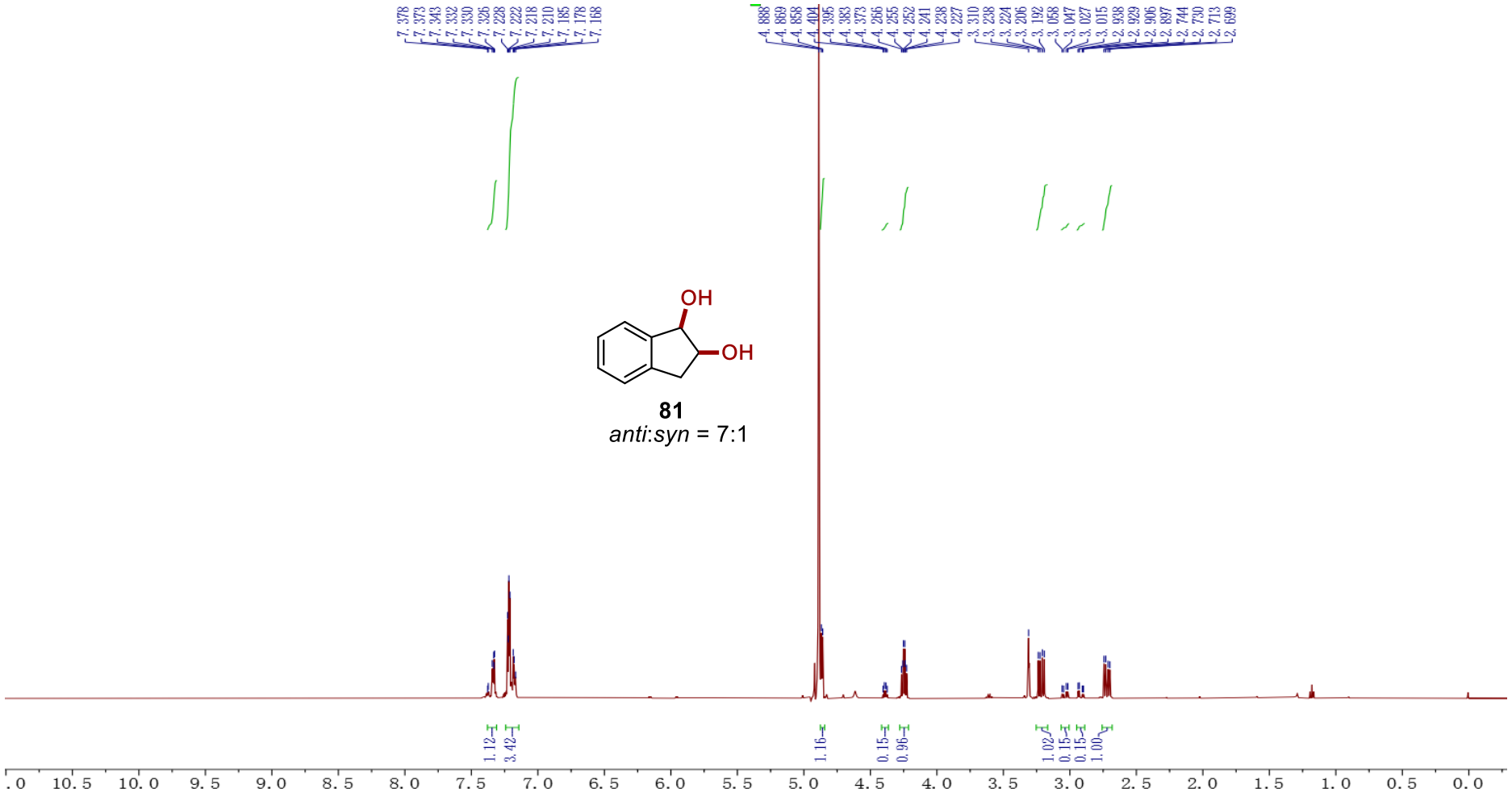

81

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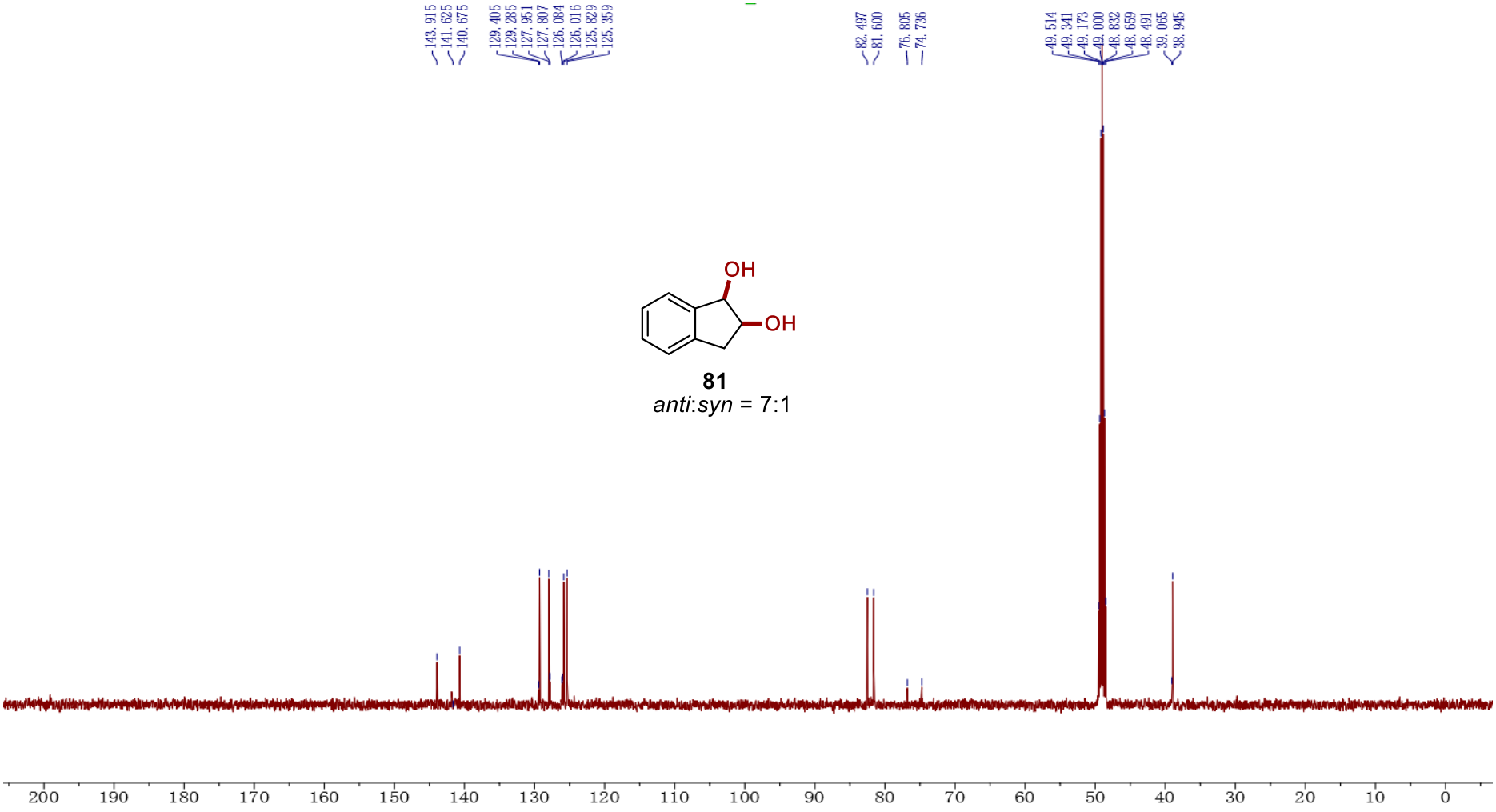

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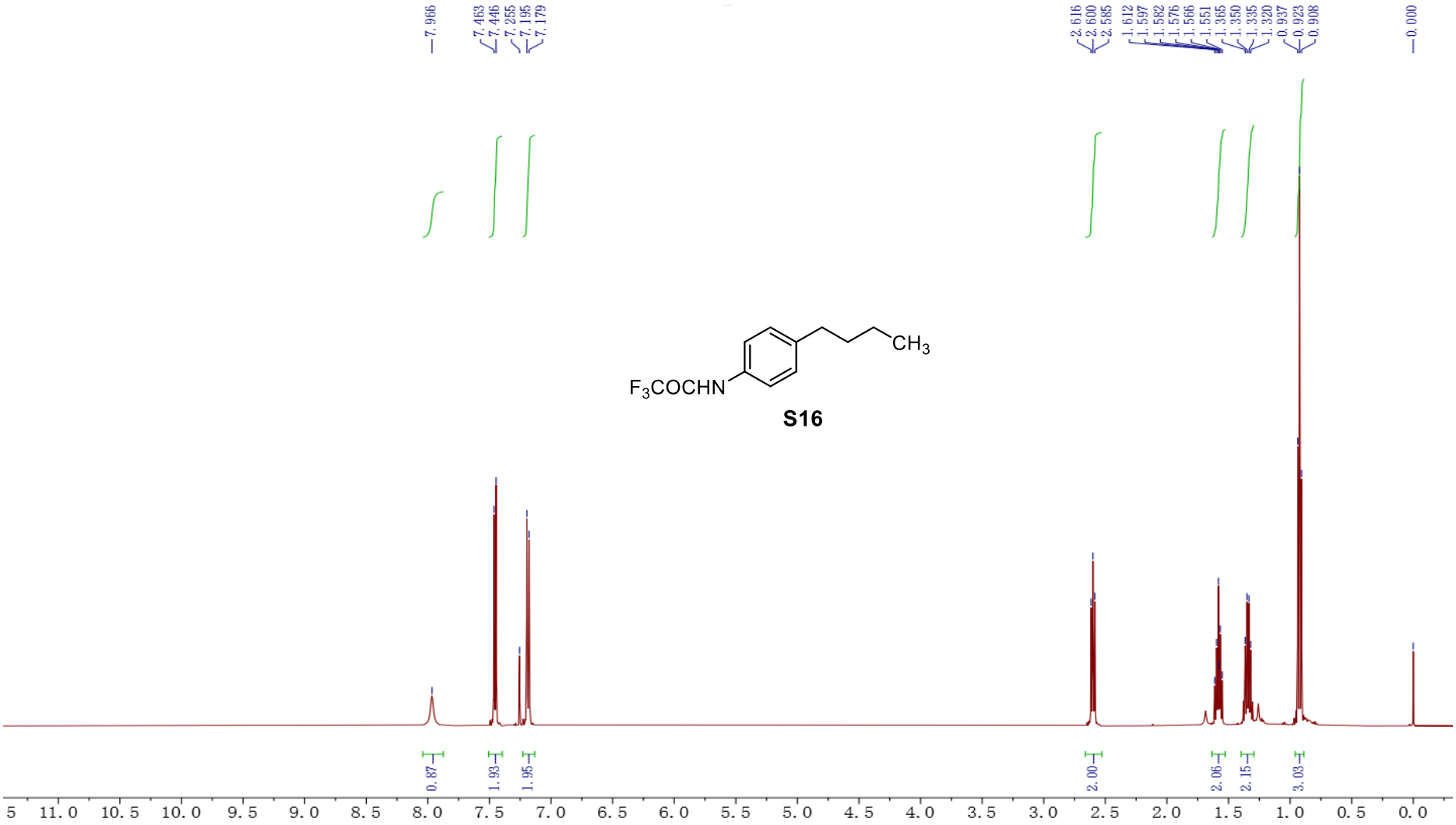
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1.576
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1.551
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1.350
1.335
1.320
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0.908
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CH3
S16
0.87
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1.95
2.00
2.06
2.15
3.03
5
11.0
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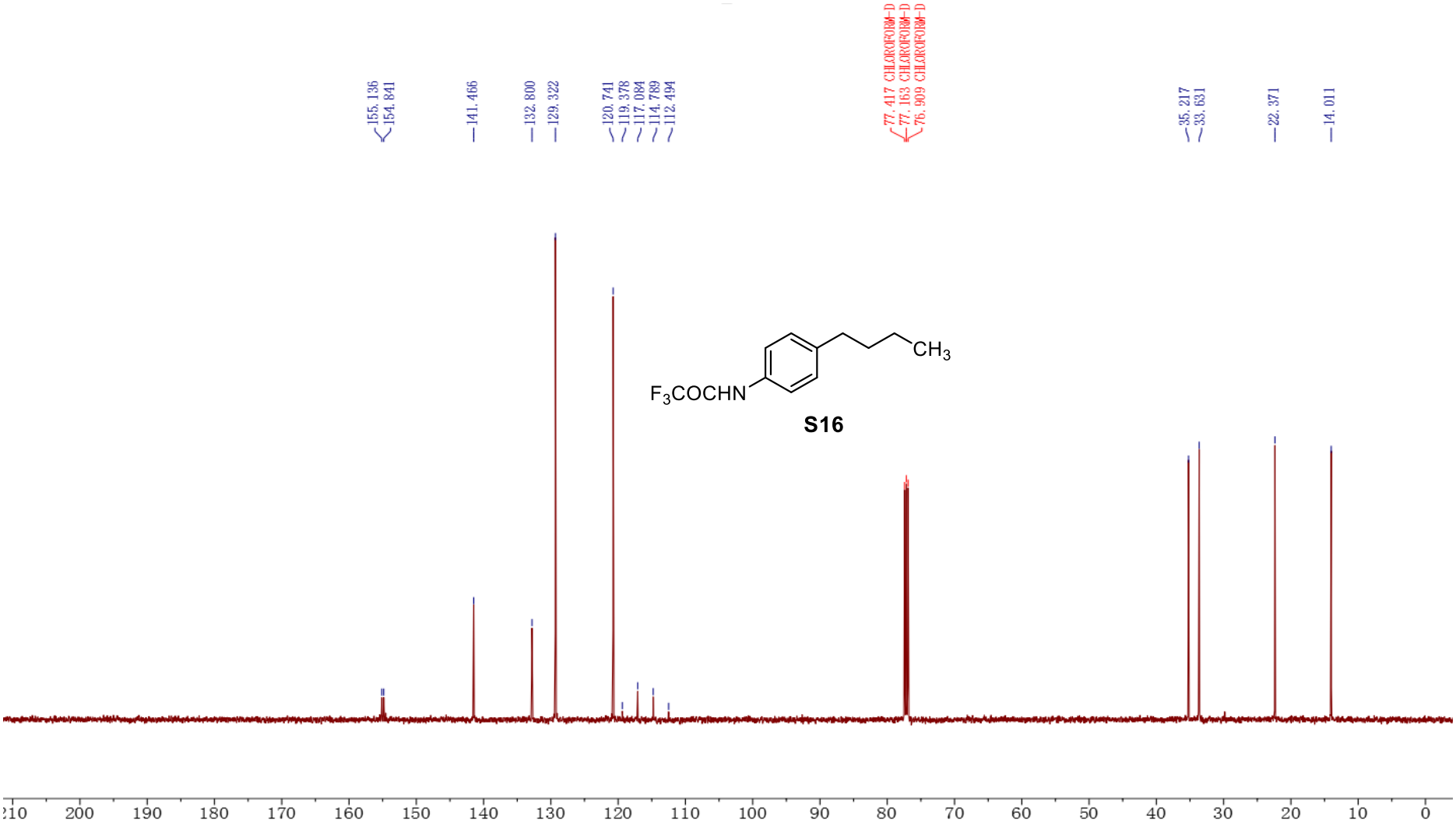
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117.084
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77.163 CHLOROFORM-D
76.909 CHLOROFORM-D
35.217
33.631
22.371
14.011
F3COCHN
CH3
S16
210
200
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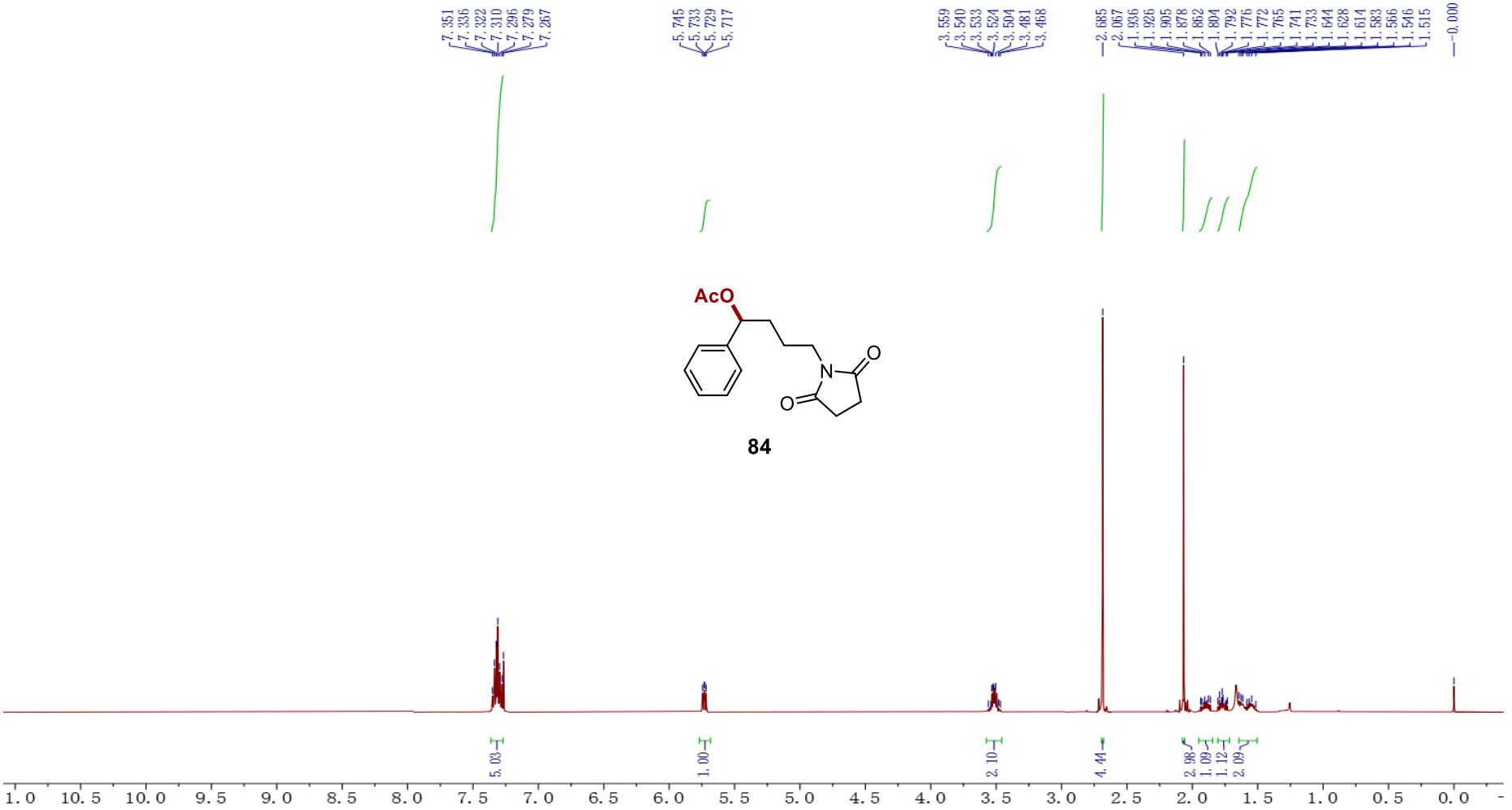
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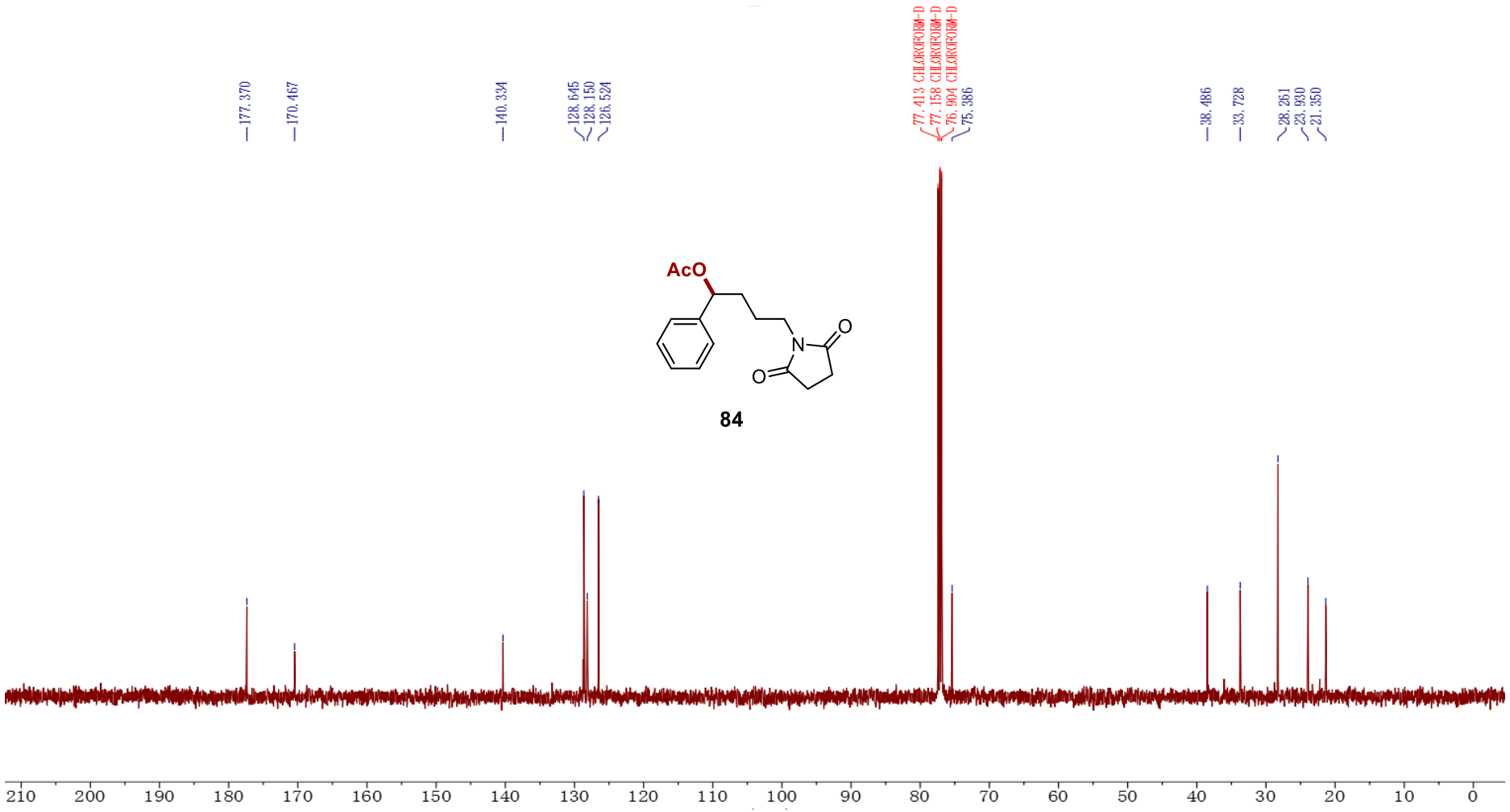
84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N
O
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200
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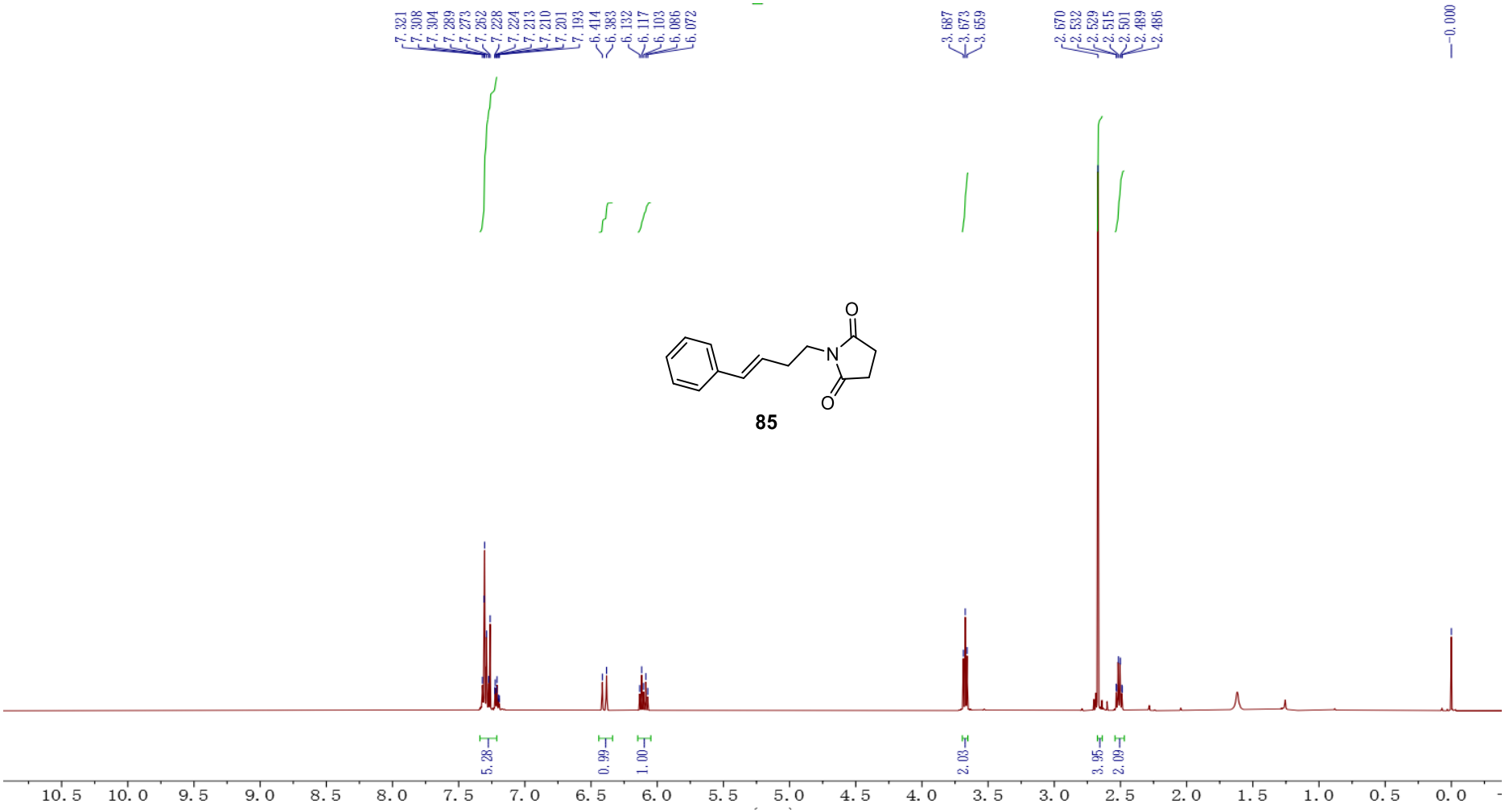
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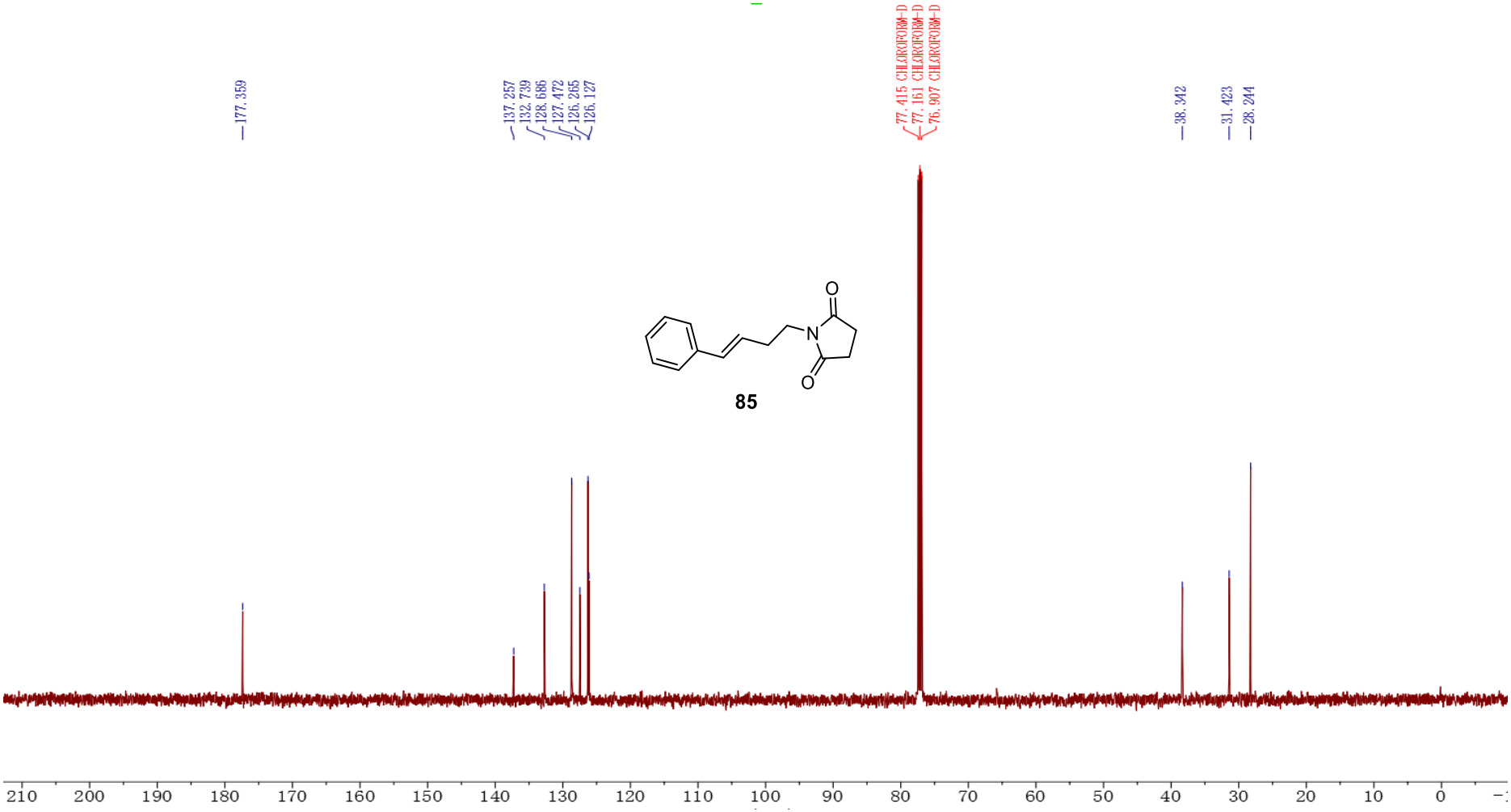
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O
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210
200
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130
120
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0

3. References

1. W. Zhong, J. Yang, X. Meng, Z., Li. *J. Org. Chem.* **2011**, *76*, 9997−10004.
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