A Catalytic Asymmetric One-Pot [3+2] Cyclization/Semipinacol Rearrangement Sequence: An Efficient Construction of Multi-Substituted 3*H*-Spiro[benzofuran-2,1'-cyclopentane] Skeleton

Lin Liu,[a] Lin-Sheng Lei,[a] Zong-Song Zhan,[a] Si-Zhan Liu,[a] Yu-Xiao Wang,[a] Yong-Qiang Tu,*[a] Fu-Min Zhang,[a] Xiao-Ming Zhang,[a] Ai-Jun Ma,[b] Shao-Hua Wang*[ab]

[a]State Key Laboratory of Applied Organic Chemistry & School of Pharmacy, Lanzhou University, Lanzhou 730000 (P. R. China)

[b]School of Biotechnology and Health Science, Wuyi University, Jiangmen 529020 (P. R. China)

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1. General Information:

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on silica gel F254 plates. Column chromatography was performed on silica gel (200-300 meshes) or neutral alumina (200-300 meshes). Solvents for reaction were distilled prior to use, and all air- or moisture-sensitive reactions were conducted under an argon atmosphere. The melting points were measured using micro melting point apparatus. **^{1}H NMR** and **^{13}C NMR** spectra were recorded in $CDCl_3$ solution, C_6D_6 solution or Actone-d_6 solution on instruments (400 MHz for **^{1}H NMR** and 100 MHz for **^{13}C NMR**) and spectra data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. High-resolution mass analysis (HRMS) data were measured by means of the ESI technique on Fourier transform ion cyclotron resonance mass analyzer. Ee values were determined by high performance liquid chromatography (HPLC) analysis employing Darcel Chiracel IF-3 columns. Optical rotation was measured using a 0.1-mL cell with a 1-cm path length by the Perkin Elmer 341 polarimeter.

2. Optimization of Reaction Conditions

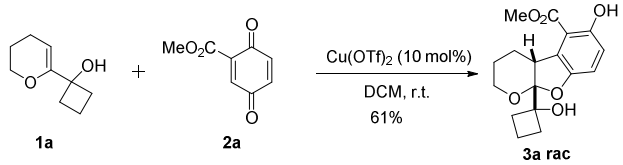
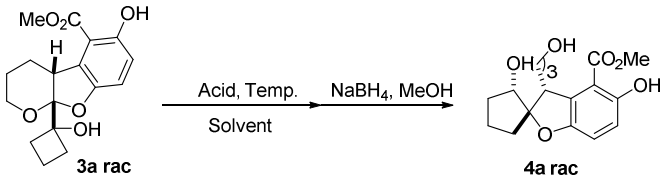


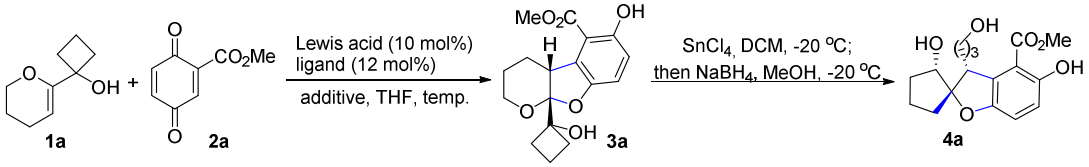
Table 1. Optimization of Semipinacol Rearrangement Reaction Conditions[a]

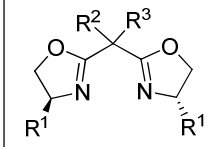


Acid	Temp.	solvent	yield[b]	dr[c]
$Cu(OTf)_2$	r.t.	DCM	NR	---
PTS	r.t.	DCM	NR	---
TfOH	0 °C	DCM	51%	4.0:1
$SnCl_4$	0 °C	DCM	66%	5.5:1
TMSOTf	0 °C	DCM	68%	4.5:1
$BF_3{\cdot}OEt_2$	0 °C	DCM	68%	2.2:1
$SnCl_4$	**-20 °C**	**DCM**	**81%**	**7.2:1**
$SnCl_4$	-40 °C	DCM	76%	7.2:1

[a]Unless specified, reaction was conducted in DCM (4 mL) using **3a-rac** (0.1 mmol, 1.0 equiv), Lewis acid (2.0 equiv.) at the indicated temperature; [b]Isolated yields; [c]dr was determined by ^{1}H NMR.

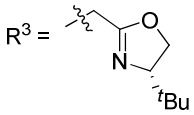
Table 2. Optimization of the One-Pot Asymmetric Reaction Conditions[a]





L1: R^1 = ^{i}Pr, R^2 = R^3 = Bn
L2: R^1 = Ph, R^2 = R^3 = Bn
L3: R^1 = ^{t}Bu, R^2 = R^3 = Bn
L4: R^1 = ^{t}Bu, R^2 = Me, R^3 = Bn
L5: R^1 = ^{t}Bu, R^2 = R^3 = Me
L6: R^1 = ^{i}Bu, R^2 = R^3 = Me
L7: R^1 = Cy, R^2 = R^3 = Me
L8: R^1 = ^{t}Bu, R^2 = Me, R^3 = H

L9 : R^1 = ^{t}Bu, R^2 = R^3 = Et
L10: R^1 = ^{t}Bu, R^2, R^3 = -$(CH_2)_5$-
L11: R^1 = ^{t}Bu, R^2 = Me,



Entry	Lewis acid	Ligand	Additive	Product	Temp.	Yield[b] (%)	ee[c] (%)
1	$Cu(OTf)_2$	-	-	**3a**	r.t.	61	-
2	$Cu(OTf)_2$	**L1**	-	**3a**	-20 °C	57	3
3	$Cu(OTf)_2$	**L2**	-	**3a**	-20 °C	67	38
4	$Cu(OTf)_2$	**L3**	-	**3a**	-20 °C	47	41
5	$Cu(OTf)_2$	**L3**	-	**3a**	-78 °C	41	57
6	$Cu(OTf)_2$	**L4**	-	**3a**	-78 °C	45	61
7	$Cu(OTf)_2$	**L5**	-	**3a**	-78 °C	37	81
8	$Cu(BF_4)\cdot 6H_2O$	**L5**	-	**3a**	-78 °C	61	67
9	$Cu(SbF_6)_2$	**L5**	-	**3a**	-78 °C	78	7
10	$Cu(PF_6)_2$	**L5**	-	**3a**	-78 °C	51	12
11	$Sc(OTf)_3$	**L5**	-	**3a**	-78 °C	91	2
12	$Zn(OTf)_2$	**L5**	-	**3a**	-78 °C	60	20
13	$Ni(ClO_4)_2\cdot 6H_2O$	**L5**	-	**3a**	-78 °C	20	1
14	$Cu(ClO_4)_2\cdot 6H_2O$	**L5**	-	**3a**	-78 °C	41	87
15	$Cu(ClO_4)_2\cdot 6H_2O$	**L6**	-	**3a**	-78 °C	41	60
16	$Cu(ClO_4)_2\cdot 6H_2O$	**L7**	-	**3a**	-78 °C	67	77
17	$Cu(ClO_4)_2\cdot 6H_2O$	**L8**	-	**3a**	-78 °C	35	9
18	$Cu(ClO_4)_2\cdot 6H_2O$	**L9**	-	**3a**	-78 °C	51	54
19	$Cu(ClO_4)_2\cdot 6H_2O$	**L10**	-	**3a**	-78 °C	61	76
20	$Cu(ClO_4)_2\cdot 6H_2O$	**L11**	-	**3a**	-78 °C	31	11
21[d]	$Cu(ClO_4)_2\cdot 6H_2O$	**L5**	3Å MS	**3a**	-78 °C	60	86
22[e]	$Cu(ClO_4)_2\cdot 6H_2O$	**L5**	4Å MS	**3a**	-78 °C	55	87
23[f]	$Cu(ClO_4)_2\cdot 6H_2O$	**L5**	5Å MS	**3a**	-78 °C	87	91
24[fg]	$Cu(ClO_4)_2\cdot 6H_2O$	**L5**	5Å MS	**3a**	-78 °C	85	89
25[fh]	$Cu(ClO_4)_2\cdot 6H_2O$	**L5**	5Å MS	**4a**	-78 °C	61	91

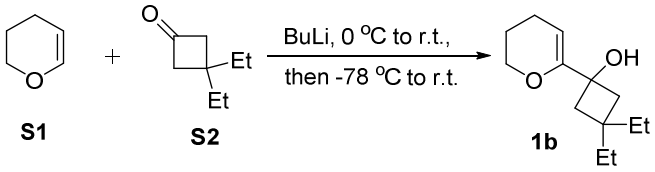
[a]Unless specified, reaction was conducted (also see supporting information) in THF (1.5 mL) using **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), Lewis acid (10 mol%), ligand (12 mol%) at the indicated temperature; [b]Isolated yields; [c]Determined by chiral HPLC; [d]3Å MS (50 mg) was added; [e]4Å MS (50 mg) was added; [f]5Å MS (50 mg) was added; [g]Lewis acid (5 mol%), ligand (6 mol%) was used; [h]dr = 7.2:1 (determined by ^{1}H NMR).

3. Syntheses of the Substrates 1 and Spectroscopic Data of Substrates

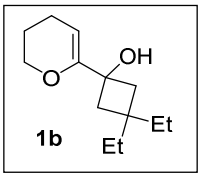
1a was synthesized according to a known procedure.[1]

General procedure A: Allylic tertiary alcohol from enol-ethers (**1b** as an example):

3.1 Synthesis of the Substrate 1b



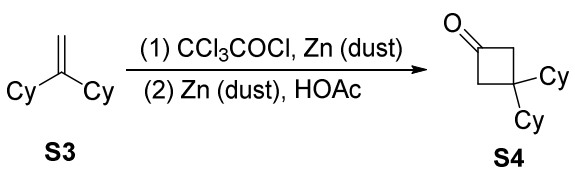
To a solution of 3,4-dihydro-2*H*-pyran **S1** (1 mL, 10.9 mmol, 1.5 equiv.) in anhydrous THF (15 mL) at 0 °C was added n-butyllithium (5.6 mL, 1.6 M in hexane, 9.1mmol, 1.25 equiv.) over 10 minutes. The mixture was allowed to warm up to room temperature and stirred for a further 3 h, before it was cooled down to -78 °C. The substituted cyclobutanone **S2** (0.91 g, 7.2 mmol, 1 equiv.) was then added dropwise into the solution over 15 minutes. The reaction was then allowed to warm slowly to room temperature and then stirred for a further 2 h before quenched with saturated $NaHCO_3$ solution and extracted with EtOAc, the combined organic layer was washed with brine and dried over $MgSO_4$ before concentrated in vacuo. The product was purified by flash chromatography using neutral alumina to afford the desired product **1b** as a colorless oil (0.622 g, 2.95 mmol, 41%).

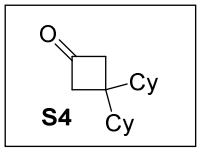


^{1}H NMR (400 MHz, Actone-d_6) δ 4.81 (t, *J* = 3.6 Hz, 1H), 3.97 (t, *J* = 5.2 Hz, 2H), 3.75 (s, 1H), 2.82 (s, 2H), 2.13-2.10 (m, 2H), 1.78-1.60 (m, 6H), 1.41 (q, *J* = 7.2 Hz, 2H), 0.75 (t, *J* = 7.6 Hz, 3H), 0.70 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, Actone-d_6) δ 158.8, 93.7, 70.5, 66.6, 43.6, 34.8, 30.3, 23.1, 20.6, 8.2, 8.1;

3.2 Synthesis of the Substrates S4 and 1c

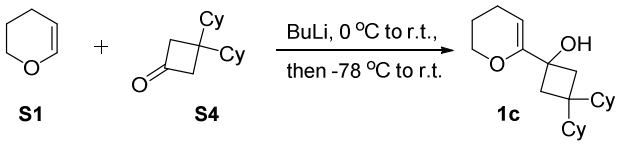


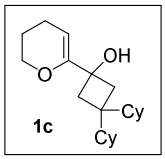


To a 100 mL three-neck round bottomed flask were added 1,1-dicyclohexylethene **S3** (4.0 g, 20.8 mmol, 1 equiv.), Zn dust (1.76 g, 27.1 mmol, 1.3 equiv) and Et_2O (40 mL). Next, a solution of trichloroacetic chloride (3.04 mL, 27.1 mmol, 1.3 equiv) in Et_2O (10 mL) was added dropwise to the above suspension. This mixture was sonicated at room temperature for 3 h, and the solid was removed by filtration and the ether solution was washed with NH_4Cl, saturated $NaHCO_3$ and brine. Evaporation of the resulting solution dried over $MgSO_4$ gave a pale yellow liquid, which was directly used for the next step. A solution of the crude intermediate mentioned above in HOAc (25 mL) was added dropwise to a vigorously stirred suspension of zinc dust (5.41 g, 83.2 mmol, 4 equiv) in HOAc (25 ml) at 0 °C. After the addition, the reaction mixture was heated at 70 °C for 24 h, and cooled down to room temperature. The acetic acid was then removed by rotavapor. The residue was dissolved in Et_2O (50 mL) and then poured into a separation funnel containing H_2O (50 mL) and Et_2O (200 mL). The organic layer was washed with H_2O, saturated $NaHCO_3$ and brine, and dried over $MgSO_4$. Then the solution was concentrated followed by purification with flash chromatography giving the substituted cyclobutanone **S4** as a colorless oil (1.460 g, 6.24 mmol, 30%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.72 (s, 4H), 1.72 (t, *J* = 12.8 Hz, 8H), 1.65-1.57 (m, 4H), 1.23-1.04 (m, 6H), 0.95-0.85 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 49.2, 41.5, 38.2, 27.9, 26.7, 26.3.





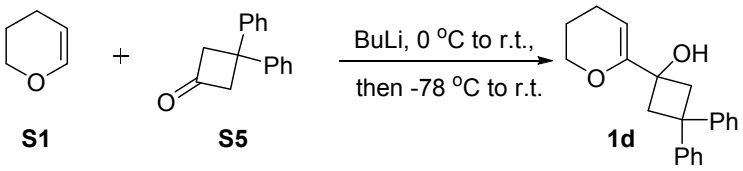
Preparation according to the general procedure A from **S4** (0.780 g, 3.33 mmol) afforded **1c** as an amorphous solid (0.413 g, 1.30 mmol, 39% yield).

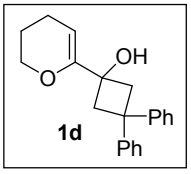
^{1}H NMR (400 MHz, Actone-d_6) δ 4.79 (t, *J* = 5.2 Hz, 1H), 3.97 (t, *J* = 5.2 Hz, 2H), 3.61 (s, 1H), 2.67-2.61 (m, 1H), 2.44-2.43 (m, 1H), 2.29-2.26 (dd, *J* = 2.8 Hz, 10.8 Hz, 2H), 2.00 (dt, *J* = 4.0 Hz, 6.4 Hz, 2H), 1.90-1.87 (m, 1H), 1.86-1.84 (m, 1H), 1.78-1.72 (m, 8H), 1.68-1.56 (m, 6H), 1.24-1.01 (m, 8H);

^{13}C NMR (100 MHz, Actone-d_6) δ 159.0, 94.3, 70.3, 66.6, 39.8, 39.1, 30.3, 29.7, 29.6, 29.1, 28.2, 28.1, 27.5, 27.4, 23.1, 20.7;

HRMS ESI Calcd for $C_{21}H_{34}O_2Na$ $[M+Na]^+$: 341.2451, Found: 341.2451.

3.3 Synthesis of the Substrate 1d





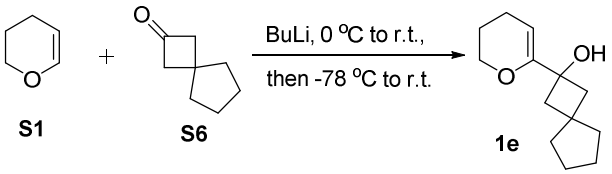
Preparation according to the general procedure A from **S5** (0.570 g, 2.57 mmol) afforded **1d** as an amorphous solid (0.401 g, 1.31 mmol, 51% yield).

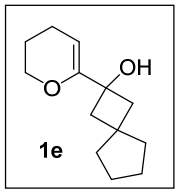
^{1}H NMR (400 MHz, Actone-d_6) δ 7.41 (dd, *J* = 0.8 Hz, 8.4 Hz, 2H), 7.35 (dd, *J* = 0.8 Hz, 8.4 Hz, 2H), 7.26-7.21 (m, 4H), 7.09-7.04 (m, 2H), 4.75 (t, *J* = 3.6 Hz, 1H), 3.96 (s, 1H), 3.84 (t, *J* = 5.2 Hz, 2H), 3.34 (d, *J* = 12.8 Hz, 2H), 2.88 (d, *J* = 12.8 Hz, 2H), 1.86 (dt, *J* = 3.6 Hz, 6.4 Hz, 2H), 1.66-1.60 (m, 2H);

^{13}C NMR (100 MHz, Actone-d_6) δ 156.1, 150.8, 149.9, 127.7, 127.6, 126.0, 125.9, 124.7, 97.4, 70.2, 65.5, 46.2, 43.2, 21.8, 19.5;

HRMS ESI Calcd for $C_{21}H_{22}O_2Na$ $[M+Na]^+$: 329.1512, Found: 329.1502.

3.4 Synthesis of the Substrate 1e





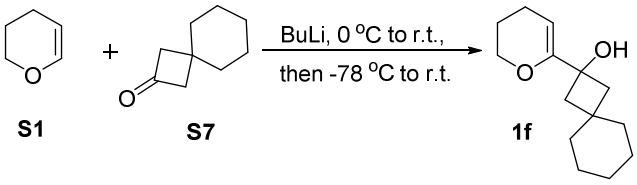
Preparation according to the general procedure A from **S6** (0.901 g, 7.25 mmol) afforded **1e** as an amorphous solid (0.628 g, 3.02 mmol, 42% yield).

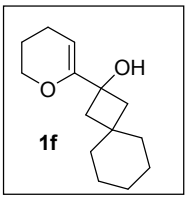
^{1}H NMR (400 MHz, C_6D_6) δ 4.81 (t, *J* = 4.0 Hz, 1H), 3.70 (t, *J* = 5.2 Hz, 2H), 2.48 (dd, *J* = 2.8 Hz, 10.0 Hz, 2H), 2.10 (dd, *J* = 2.8 Hz, 10.0 Hz, 2H), 2.03 (s, 1H), 1.81-1.76 (m, 4H), 1.60 (t, *J* = 6.4 Hz, 2H), 1.54-1.49 (m, 4H), 1.43-1.37 (m, 2H);

^{13}C NMR (100 MHz, Actone-d_6) δ 158.5, 94.1, 71.0, 66.7, 45.7, 41.6, 40.2, 38.8, 24.3, 23.1, 20.7;

HRMS ESI Calcd for $C_{13}H_{20}O_2Na$ $[M+Na]^+$: 231.1356, Found: 231.1345.

3.5 Synthesis of the Substrate 1f





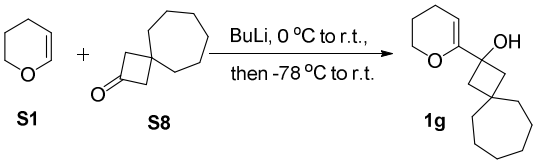
Preparation according to the general procedure A from **S7** (0.99 g, 7.2 mmol) afforded **1f** as an amorphous solid (0.590 g, 2.66 mmol, 37% yield).

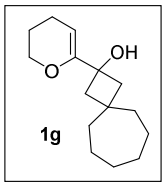
^{1}H NMR (400 MHz, Actone-d_6) δ 4.83 (t, *J* = 3.6 Hz, 1H), 3.98 (t, *J* = 4.8 Hz, 2H), 3.79 (s, 1H), 2.84 (s, 1H), 2.16 (d, *J* = 12.8 Hz, 2H), 2.07 (s, 1H), 1.80-1.70 (m, 4H), 1.68-1.53 (m, 2H), 1.42-1.25 (m, 8H);

^{13}C NMR (100 MHz, Actone-d_6) δ 158.7, 93.7, 70.7, 66.6, 44.9, 39.9, 38.9, 31.8, 26.5, 23.6, 23.3, 23.1, 20.6;

HRMS ESI Calcd for $C_{14}H_{22}O_2Na$ $[M+Na]^+$: 245.1512, Found: 245.1500.

3.6 Synthesis of the Substrate 1g





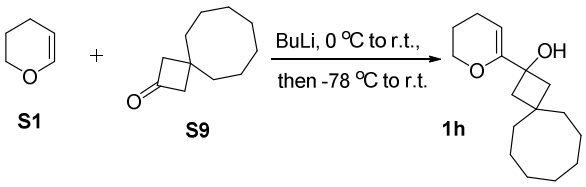
Preparation according to the general procedure A from **S8** (0.77 g, 5.1 mmol) afforded **1g** as an amorphous solid (0.550 g, 2.32 mmol, 46% yield).

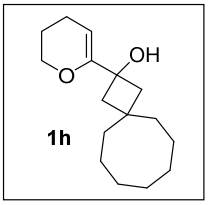
^{1}H NMR (400 MHz, Actone-d_6) δ 4.81 (t, *J* = 3.6 Hz, 1H), 3.97 (t, *J* = 5.2 Hz, 2H), 3.77 (s, 1H), 2.18 (dd, *J* = 2.8 Hz, 10.0 Hz, 2H), 2.00 (dt, *J* = 3.6 Hz, 6.4 Hz, 2H), 1.82-1.77 (m, 2H), 1.76-1.74 (m, 2H), 1.73-1.71 (m, 2H), 1.60-1.56 (m, 2H), 1.52-1.47 (m, 6H), 1.47-1.41 (m, 2H);

^{13}C NMR (100 MHz, Actone-d_6) δ 158.7, 93.7, 70.5, 66.6, 45.8, 43.3, 42.1, 34.6, 23.5, 23.4, 23.1, 20.6;

HRMS ESI Calcd for $C_{15}H_{24}O_2Na$ $[M+Na]^+$: 259.1669, Found: 259.1658.

3.7 Synthesis of the Substrate 1h





Preparation according to the general procedure A from **S9** (1.12 g, 7.2 mmol) afforded **1h** as an amorphous solid (0.648 g, 2.58 mmol, 36% yield).

^{1}H NMR (400 MHz, Actone-d_6) δ 4.82 (t, *J* = 3.6 Hz, 1H), 3.98 (t, *J* = 1.2 Hz, 2H), 3.77 (s, 1H), 2.83 (s, 2H), 2.15 (d, *J* = 13.2 Hz, 2H), 2.04-1.99 (m, 2H), 1.88-1.77 (m, 2H), 1.77-1.72 (m, 1H), 1.69 (d, *J* = 15.6 Hz, 1H), 1.64-1.62 (m, 2H), 1.60-1.30 (m, 10H);

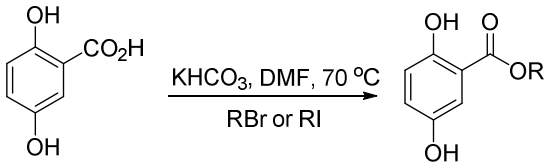
^{13}C NMR (100 MHz, Actone-d_6) δ 158.8, 93.7, 70.5, 66.6, 45.8, 38.1, 37.2, 34.2, 24.7, 23.2, 23.08, 22.99, 20.6;

HRMS ESI Calcd for $C_{16}H_{26}O_2Na$ $[M+Na]^+$: 273.1825, Found: 273.1816.

4. Syntheses of 1,4-dihydroxybenzene-2-carboxylates and the substrates 2 and spectroscopic data of substrates

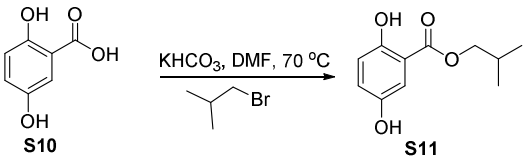
Substrates **2a, 2k, 2l and 2q** were synthesized according to known literatures.[2]

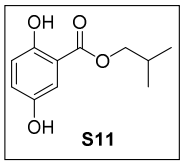
General procedure B: Synthesis of 1,4-dihydroxybenzene-2-carboxylate from 2,5-dihydroxybenzoic acid.



Solid $KHCO_3$ (2.619 g, 26.2 mmol, 2.7 equiv.) was added to a stirred mixture of 2,5-dihydroxybenzoic acid (1.50 g, 9.7 mmol, 1 equiv.) and RBr or RI (38.8 mmol, 4.0 equiv.) in DMF (30 mL). The mixture was heated to 70 °C and stirred for 5-24 h. The reaction mixture was cooled down to room temperature, diluted with 1 M HCl and extracted with EtOAc. The organic phases were washed with water and dried over $MgSO_4$. Then the solution was filtered, and concentrated followed by purification with flash chromatography giving the desired 1,4-dihydroxybenzene-2-carboxylate.

4.1 Synthesis of the Substrate S11





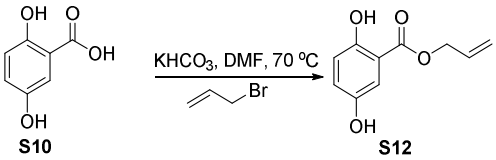
Preparation according to the general procedure B from **S10** (1.50 g, 9.7 mmol, 1 equiv.) and isobutyl bromide (4.2 mL, 38.8 mmol, 4 equiv.) afforded **S11** as a colorless oil (1.772 g, 8.43 mmol, 87% yield).

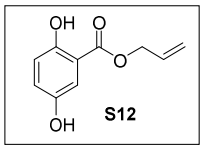
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.32 (d, *J* = 3.2 Hz, 1H), 7.03 (dd, *J* = 3.2 Hz, 8.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.57 (s, 1H), 4.10 (d, *J* = 6.8 Hz, 2H), 2.93 (d, *J* = 28 Hz, 3H), 2.11-2.02 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 155.4, 148.3, 124.0, 118.2, 114.7, 112.4, 71.3, 36.8, 27.7, 27.7, 19.0.

HRMS ESI Calcd for $C_{11}H_{14}O_4Na$ $[M+Na]^+$: 233.0784, Found: 233.0778.

4.2 Synthesis of the Substrate S12



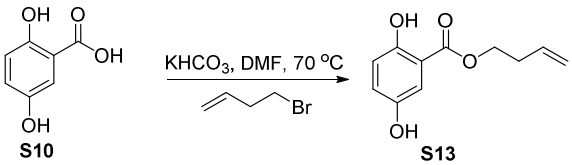


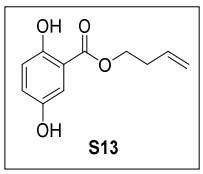
Preparation according to the general procedure B from **S10** (1.50 g, 9.7 mmol, 1 equiv.) and allyl bromide (2.85 mL, 38.8 mmol, 4 equiv.) afforded **S12** as an amorphous solid (1.787 g, 9.21 mmol, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.32 (d, *J* = 3.2 Hz, 1H), 7.02 (dd, *J* = 3.2 Hz, 8.8 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.02-5.95 (m, 1H), 5.41 (dd, *J* = 1.2 Hz, 17.2 Hz, 1H), 5.30 (dd, *J* = 0.8 Hz, 10.4 Hz, 1H), 4.81 (d, *J* = 5.6 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 155.6, 147.8, 131.3, 124.2, 119.0, 118.5, 114.9, 112.2, 66.0.

4.3 Synthesis of the Substrate S13



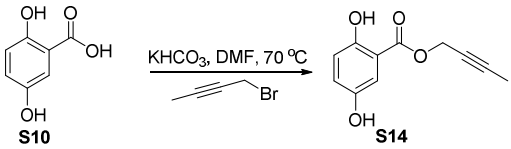


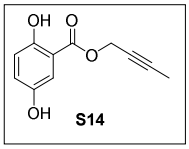
Preparation according to the general procedure B from **S10** (1.5 g, 9.7 mmol, 1 equiv.) and 4-bromo-1-butene (3.9 mL, 38.8 mmol, 4equiv.) afforded **S13** as an amorphous solid (1.836 g, 8.83 mmol, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.29 (d, *J* = 3.2Hz, 1H), 7.05 (s, 1H), 6.84 (d, *J* = 1.2 Hz, 2H), 5.82-5.89 (m, 1H), 5.17-5.11 (m, 2H), 4.38-4.34 (m, 2H), 2.52-2.49 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 155.4, 147.9, 133.4, 124.1, 118.3, 117.7, 114.8, 112.3, 64.4, 32.8.

4.4 Synthesis of the Substrate S14





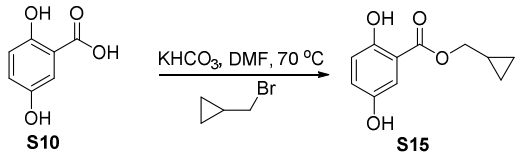
Preparation according to the general procedure B from **S10** (1.5 g, 9.7 mmol, 1 equiv.) and 1-bromo-2-butyne (3.34 mL, 38.8 mmol, 4 equiv.) afforded **S14** as an amorphous solid (1.758 g, 8.53 mmol, 88% yield).

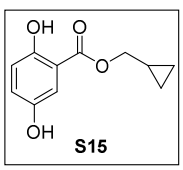
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.32 (d, *J* = 3.2 Hz, 1H), 7.03 (dd, *J* = 3.2 Hz, 5.2 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 4.91-4.86 (m, 3H), 1.88 (t, *J* = 2.4 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 155.9, 147.8, 124.4, 118.6, 114.9, 111.9, 84.1, 72.6, 53.7, 3.6;

HRMS ESI Calcd for $C_{11}H_{10}O_4Na$ $[M+Na]^+$: 229.0471, Found: 229.0463.

4.5 Synthesis of the Substrate S15





Preparation according to the general procedure B from **S10** (1.5 g, 9.7 mmol, 1 equiv.) and

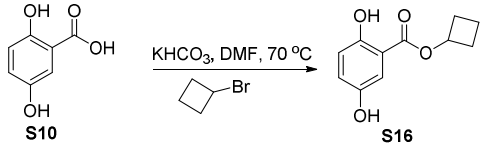
(bromomethyl) cyclopropane (3.76 mL, 38.8 mmol, 4 equiv.) afforded **S15** as a colorless oil (1.896 g, 9.11 mmol, 94% yield).

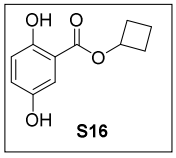
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (d, *J* = 2.8 Hz, 1H), 7.35 (d, *J* = 3.2 Hz, 1H), 7.02 (dd, *J* = 3.2 Hz, 8.8 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 5.90-5.20 (m, 1H), 4.16 (d, *J* = 7.2 Hz, 2H), 1.28-1.22 (m, 1H), 0.65-0.61 (m, 2H), 0.38-0.35 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 155.7, 147.9, 124.0, 118.4, 114.9, 112.5, 70.2, 9.7, 3.4;

HRMS ESI Calcd for $C_{11}H_{12}O_4Na$ $[M+Na]^+$: 231.0628, Found: 231.0626.

4.6 Synthesis of the Substrate S16





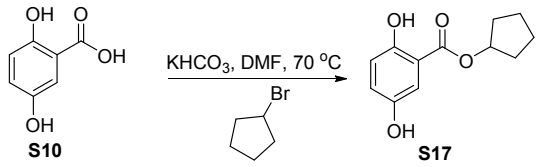
Preparation according to the general procedure B from **S10** (1.5 g, 9.7 mmol, 1 equiv.) and cyclobutyl bromide (3.65 mL, 38.8 mmol, 4 equiv.) afforded **S16** as a colorless oil (1.532 g, 7.37 mmol, 76% yield).

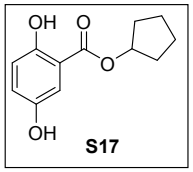
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.31 (d, *J* = 3.2 Hz, 1H), 7.01 (dd, *J* = 3.2 Hz, 4.8 Hz, 1H), 6.86 (d, *J* = 8.8Hz, 1H), 5.20 (t, *J* = 7.6 Hz, 1H), 2.48-2.41 (m, 2H), 2.38-2.18 (m, 2H), 1.92-1.84 (m, 1H), 1.74-1.67 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 155.7, 147.8, 124.0, 118.4, 114.8, 112.3, 69.9, 30.2, 13.5.

HRMS ESI Calcd for $C_{11}H_{12}O_4Na$ $[M+Na]^+$: 231.0628, Found: 231.0630.

4.7 Synthesis of the Substrate S17





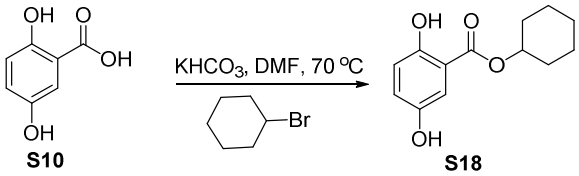
Preparation according to the general procedure B from **S10** (1.5 g, 9.7 mmol, 1 equiv.) and cyclopentyl bromide (4.20 mL, 38.8 mmol, 4 equiv.) afforded **S17** as a colorless oil (1.486 g, 6.69 mmol, 69% yield).

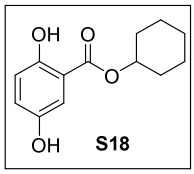
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.27 (s, 1H), 7.01-6.98 (m, 1H), 6.88-6.86 (m, 1H), 5.42 (t, *J* = 2.8 Hz, 1H), 1.98-1.95 (m, 2H), 1.86-1.79 (m, 4H), 1.73-1.10 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 155.6, 147.7, 123.8, 118.3, 114.80, 114.78, 112.8, 78.6, 32.7, 23.7;

HRMS ESI Calcd for $C_{12}H_{14}O_4Na$ $[M+Na]^+$: 245.0784, Found: 245.0788.

4.8 Synthesis of the Substrate S18





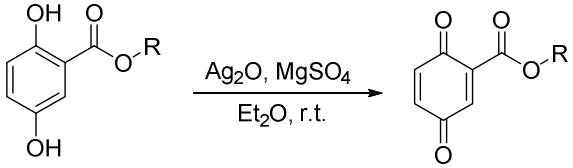
Preparation according to the general procedure B from **S10** (1.5 g, 9.7 mmol, 1 equiv.) and cyclohexyl bromide (4.77 mL, 38.8 mmol, 4 equiv.) afforded **S18** as a colorless oil (1.488 g, 6.30 mmol, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.31 (d, *J* = 3.2 Hz, 1H), 7.00 (dd, *J* = 3.2 Hz, 9.2 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 5.08-5.02 (m, 1H), 1.92-1.78 (m, 2H), 1.77-1.64 (m, 2H), 1.61-1.49 (m, 2H), 1.46-1.24 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 155.9, 147.6, 123.7, 118.4, 114.8, 112.9, 73.9, 31.5, 25.3, 23.5;

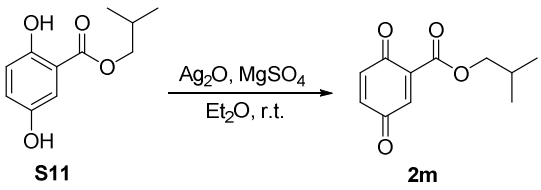
HRMS ESI Calcd for $C_{13}H_{16}O_4Na$ $[M+Na]^+$: 259.0941, Found: 259.0941.

General procedure C: Synthesis of 2-alkoxycarbonyl-1,4-benzoquinone from 1,4-dihydroxybenzene-2-carboxylate.

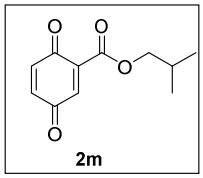


Silver oxide (1.392 g, 6.0 mmol, 3.0 equiv.) and magnesium sulfate (0.72 g, 6.0 mmol, 3.0 equiv.) were added to a solution of 1,4-dihydroxybenzene-2-carboxylate (2.0 mmol, 1 equiv.) in diethyl ether (20 mL). The reaction mixture was stirred at 25 °C for 1.5 h. After filtration, the filtrate was evaporated in vacuo to furnish the desired quinone **2**.

4.9 Synthesis of the Substrate 2m



S11 **2m**



2m

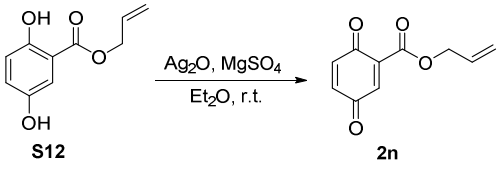
Preparation according to the general procedure C from **S11** (0.42 g, 2 mmol) afforded **2m** as a red oil (0.391 g, 1.88 mmol, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 1H), 6.79 (s, 2H), 4.05 (d, *J* = 6.8 Hz, 2H), 2.03-1.97 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 6H);

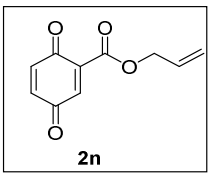
^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 182.9, 162.6, 137.4, 136.8, 136.00, 135.96, 72.2, 27.6, 18.9;

HRMS ESI Calcd for $C_{11}H_{12}O_4Na$ $[M+Na]^+$: 231.0628, Found: 231.0626.

4.10 Synthesis of the Substrate 2n



S12 **2n**



2n

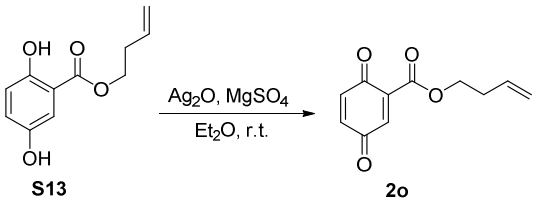
Preparation according to the general procedure C from **S12** (0.388 g, 2 mmol) afforded **2n** as a red oil (0.365 g, 1.9 mmol, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 0.8 Hz, 1.6 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 2H), 5.99-5.91 (m, 1H), 5.43 (d, *J* = 1.6 Hz, 1H), 5.31 (dd, *J* = 0.8 Hz, 10.4 Hz, 1H), 4.79 (td, *J* = 1.2 Hz, 6.0 Hz, 2H);

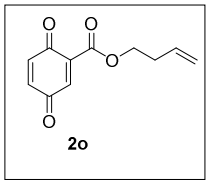
^{13}C NMR (100 MHz, $CDCl_3$) δ 186.8, 182.9, 162.3, 137.1, 136.9, 136.4, 136.1, 130.9, 119.5, 66.7;

HRMS ESI Calcd for $C_{10}H_8O_4Na$ $[M+Na]^+$: 215.0315, Found: 215.0312.

4.11 Synthesis of the Substrate 2o



S13 **2o**



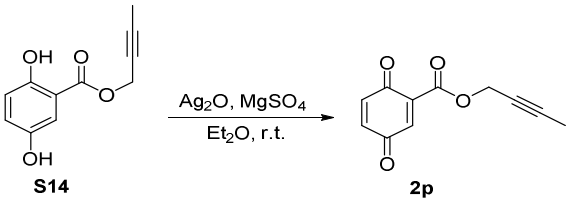
Preparation according to the general procedure C from **S13** (0.42 g, 2 mmol) afforded **2o** as a red oil (0.383 g, 1.86 mmol, 93% yield).

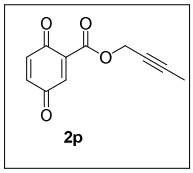
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 1H), 6.85 (dd, *J* = 1.2 Hz, 8.8 Hz, 1H), 5.85-5.78 (m, 2H), 5.18-5.08 (m, 2H), 4.37 (dt, *J* = 2.0 Hz, 6.8 Hz, 2H), 2.52-2.47 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 182.9, 162.5, 137.2, 136.86, 136.85, 136.1, 133.3, 117.8, 65.2, 32.8;

HRMS ESI Calcd for $C_{11}H_{10}O_4Na$ $[M+Na]^+$: 229.0471, Found: 229.0471.

4.12 Synthesis of the Substrate 2p





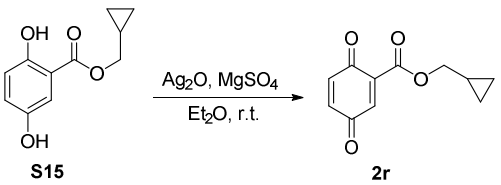
Preparation according to the general procedure C from **S14** (0.412 g, 2 mmol) afforded **2p** as a red oil (0.347 g, 1.70 mmol, 85% yield).

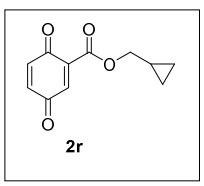
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 2.0 Hz, 2H), 4.82 (q, *J* = 2.4 Hz, 2H), 1.83 (t, *J* = 2.4 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.7, 182.7, 161.8, 136.8, 136.7, 136.4, 136.1, 84.5, 71.9, 54.4, 3.6;

HRMS ESI Calcd for $C_{11}H_8O_4Na$ $[M+Na]^+$: 227.0315, Found: 227.0304.

4.13 Synthesis of the Substrate 2r





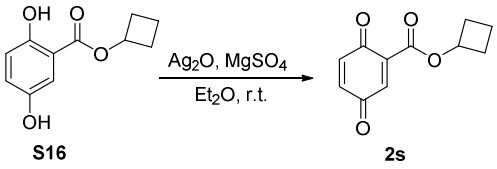
Preparation according to the general procedure C from **S15** (0.415 g, 2 mmol) afforded **2r** as a red oil (0.376 g, 1.83 mmol, 92% yield).

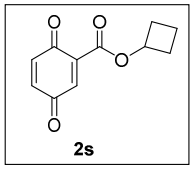
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 6.80 (s, 2H), 4.11 (d, *J* = 7.2 Hz, 2H), 1.22-1.15 (m, 1H), 0.61 (dd, *J* = 5.6 Hz, 13.2 Hz, 2H), 0.32 (dd, *J* = 5.6 Hz, 10.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 183.0, 162.6, 137.3, 136.8, 136.02, 135.99, 71.1, 9.5, 3.4;

HRMS ESI Calcd for $C_{11}H_{10}O_4Na$ $[M+Na]^+$: 229.0471, Found: 229.0461.

4.14 Synthesis of the Substrate 2s





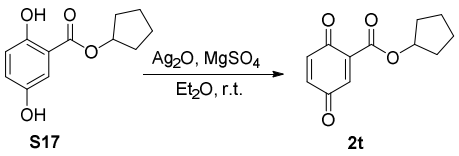
Preparation according to the general procedure C from **S16** (0.417 g, 2 mmol) afforded **2s** as a red oil (0.391 g, 1.88 mmol, 94% yield).

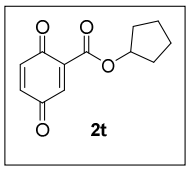
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 1.6 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 2H), 5.20-5.13 (m, 1H), 2.46-2.38 (m, 2H), 2.22-2.11 (m, 2H), 1.90-1.81 (m, 1H), 1.73-1.61 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 183.0, 161.9, 137.2, 136.9, 136.04, 136.02, 70.7, 30.2, 13.5;

HRMS ESI Calcd for $C_{11}H_{10}O_4Na$ $[M+Na]^+$: 229.0471, Found: 229.0463.

4.15 Synthesis of the Substrate 2t





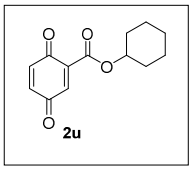
Preparation according to the general procedure C from **S17** (0.444 g, 2 mmol) afforded **2t** as a red oil (0.42 g, 1.90 mmol, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 2.0 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 2H), 5.38 (dt, *J* = 2.8 Hz, 5.6 Hz, 1H), 1.95-1.90 (m, 2H), 1.81-1.73 (m, 4H), 1.64-1.61 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 183.1, 162.4, 137.7, 136.8, 136.0, 135.6, 79.6, 32.6, 23.6;

HRMS ESI Calcd for $C_{12}H_{12}O_4Na$ $[M+Na]^+$: 243.0628, Found: 243.0624.

4.16 Synthesis of the Substrate 2u



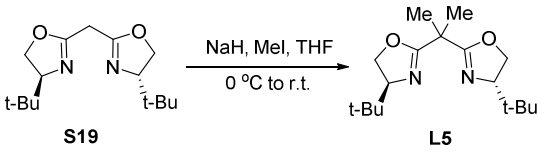
Preparation according to the general procedure C from **S18** (0.471 g, 2 mmol) afforded **2u** as a red oil (0.441 g, 1.88 mmol, 94% yield).

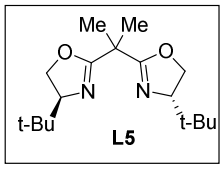
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 0.4 Hz, 2.0 Hz, 1H), 6.81 (d, *J* = 2.0 Hz, 2H), 5.04-4.98 (m, 1H), 1.94-1.89 (m, 2H), 1.80-1.74 (m, 2H), 1.60-1.51 (m, 3H), 1.47-1.25 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 183.1, 162.1, 137.8, 136.9, 136.0, 135.6, 75.1, 31.3, 25.2, 23.4;

HRMS ESI Calcd for $C_{13}H_{114}O_4Na$ $[M+Na]^+$: 257.0784, Found: 257.0784.

5. Synthesis of the Ligand L5



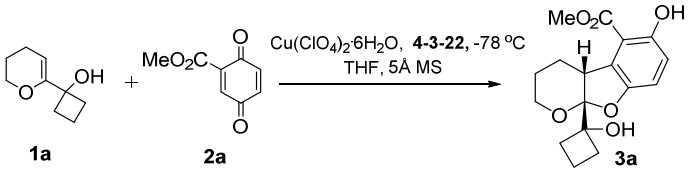


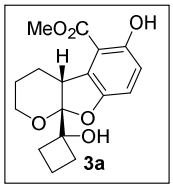
To a solution of **S19** (750 mg 2.82 mmol) in THF (50 mL) in a flame-dried round-bottom flask was added NaH (338 mg, 60 % dispersion in mineral oil, 8.46 mmol, 3 equiv.) at 0 °C. The mixture was stirred at the same temperature for 30 min, and iodomethane (526 µL, 8.46 mmol, 3.0 equiv) was added via syringe. After the addition, the cold bath was removed and the mixture was allowed to stir at room temperature for an additional 6 h. Next, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography to give **L5** as a colorless solid (581 mg, 1.97 mmol, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14-4.03 (m, 4H), 3.83 (dt, *J* = 2.8 Hz, 10.0 Hz, 2H), 1.484 (s, 3H), 1.478 (s, 3H), 0.843 (s, 9H), 0.838 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 75.2, 68.9, 38.5, 33.9, 25.6, 24.4.

6. Experimental Procedures of the [3+2] Cyclization and Spectroscopic Data of Products (3a as an example)





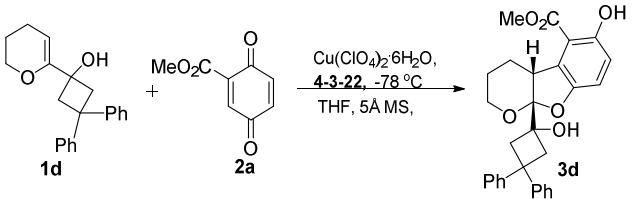
A mixture of $Cu(ClO_4)_2{\cdot}6H_2O$ (3.7 mg, 0.01 mmol, 0.1 equiv.) and ligand **L5** (3.5 mg, 0.012 mmol, 0.12 equiv.) in THF (1.0 mL) with activated 5Å MS (50 mg) was stirred at room temperature for 2 h under an argon atmosphere. Then the mixture was cooled down to -78 °C for 30 minutes, and substituted benzoquinone **2a** (24.9 mg, 0.15 mmol, 1.5 equiv.) was added followed by allylic alcohol **1a** (15.4 mg, 0.1 mmol, 1 equiv.) in THF (0.5 mL). The resulting solution was stirred until **1a** was completely consumed (monitored by TLC, PE/EtOAc = 2/1). Then the mixture was passed through a short silica gel column and eluted with EtOAc (20 mL). The combined elution was concentrated under reduced pressure, which was further purified by flash chromatography on silica gel (PE/EtOAc = 15/1) to give compound **3a** as a colorless oil (28.2 mg, 0.088 mmol, 88%).

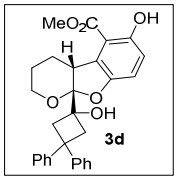
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 3.94 (s, 3H), 3.90-3.77 (m, 3H), 2.55-2.50 (m, 1H), 2.37 (d, *J* = 8.8 Hz, 1H), 2.08-2.00 (m, 1H), 1.98-1.87 (m, 3H), 1.86-1.76 (m, 2H), 1.71-1.53 (m, 2H), 1.38-1.23 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 156.5, 151.4, 130.5, 117.1, 116.2, 112.4, 109.2, 78.6, 60.2, 52.2, 40.1, 30.4, 29.2, 23.4, 18.3, 12.9;

HRMS ESI Calcd for $C_{17}H_{20}O_6Na$ $[M+Na]^+$: 343.1152, Found: 343.1144;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 8.409 min, t_{minor} =10.195 min, 91% ee; $[\alpha]_D^{26.1}$ = 28.0 (c = 5.0, $CHCl_3$).





Preparation according to the general procedure of **3a** from **1d** (30.6 mg, 0.1 mmol) and **2a** (24.9 mg, 0.15 mmol) afforded **3d** as a colorless solid (42.2 mg, 0.090 mmol, 90%).

Mp 69.3-72.1 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.31-7.21 (m, 5H), 7.19-7.06 (m, 5H), 6.66 (d, *J* = 8.8 Hz, 1H), 6.28 (d, *J* = 8.8 Hz, 1H), 3.91 (s, 3H), 3.86-3.71 (m, 2H), 3.53-3.50 (m, 1H), 1.94-1.90 (m, 1H), 1.75-1.70(m, 1H), 1.56-1.51(m, 2H), 1.33-1.26 (m, 3H), 0.9-0.83 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 156.6, 151.0, 150.6, 149.0, 130.2, 128.2, 128.1, 126.4, 126.3, 125.4, 125.2, 117.0, 116.8, 111.7, 108.9, 74.4, 60.5, 52.2, 44.3, 42.9, 42.8, 40.1, 26.9, 23.6, 18.4;

HRMS ESI Calcd for $C_{29}H_{28}O_6Na$ $[M+Na]^+$: 495.1778, Found: 495.1757;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 27.313 min, t_{minor} = 30.269 min, 87% ee; $[\alpha]_D^{26.0}$ = 30.0 (c = 2.0, $CHCl_3$).

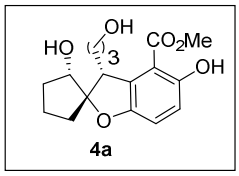
7. Experimental Procedures of the One-Pot [3+2] Cyclization/Semipinacol Rearrangement Cascade and Spectroscopic Data of Products

General procedure D: Experimental Procedures of the One-Pot [3+2] Cyclization/Semipinacol Rearrangement Cascade (using **4a** as an example)

A mixture of $Cu(ClO_6)_2{\cdot}6H_2O$ (3.7 mg, 0.01 mmol, 0.1 equiv.) and ligand **L5** (3.5 mg, 0.012 mmol, 0.12 equiv.) in THF (1.0 mL) with activated 5Å MS (50 mg) was stirred at room temperature for 2 h under an argon atmosphere. Then the mixture was cooled down to -78 °C for 30 minutes, and substituted benzoquinone **2a** (24.9 mg, 0.15 mmol, 1.5 equiv.) was added followed by allylic alcohol **1a** (15.4 mg, 0.1 mmol, 1 equiv.) in THF (0.5 mL). The resulting solution was stirred until **1a** was completely consumed (monitored by TLC, PE/EtOAc = 2/1). Then the mixture was passed through a short silica gel column and eluted with EtOAc (20 mL). The combined elution was concentrated under reduced pressure, and then was added dry DCM (4.0 mL) and cooled down to -20 °C for 10 minutes, $SnCl_4$ (0.20 mL, 0.2 mmol, 1 mol/L in DCM, 2.0 equiv.) was added and stirred at this temperature until **3a** was completely consumed (monitored by TLC, PE/EtOAc = 2/1). And then MeOH (2.0 mL) and $NaBH_4$ (15.4 mg，0.4 mmol, 4.0 equiv.) was added and stirred at this temperature for 2 h before it was quenched with the saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum, which was further purified by flash chromatography on silica gel (PE/EtOAc = 2/1) to give compound **4a** as a colorless oil (19.5

mg, 0.0609 mmol, 61%, dr = 7.2:1).

Preparation according to the general procedure D from **1a** (154.1 mg, 1 mmol) and **2a** (249.0 mg, 1.5 mmol) afforded **4a** as a colorless oil (174.1 mg, 0.54 mmol, 54% yield, dr = 7.2:1).



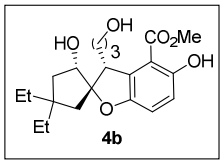
4a

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 4.36 (t, *J* = 7.2 Hz, 1H), 3.96 (s, 3H), 3.54 (t, *J* = 5.6 Hz, 2H), 3.45 (dd, *J* = 2.4 Hz, 7.6 Hz, 1H), 2.65 (br, 1H), 2.18-2.16 (m, 1H), 2.04-1.98 (m, 2H), 1.97-1.80 (m, 3H), 1.63-1.54 (m, 4H), 1.46-1.32 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 156.6, 150.1, 132.4, 118.0, 117.0, 109.3, 97.0, 73.4, 62.5, 52.2, 50.2, 37.6, 33.0, 30.5, 27.2, 18.6;

HRMS ESI Calcd for $C_{17}H_{22}O_6Na$ $[M+Na]^+$: 345.1309, Found: 345.1324;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 15.416 min, t_{minor} = 23.265 min, 91% ee; $[\alpha]_D^{17.4}$ = 4.8 (c = 6.2, $CHCl_3$).



4b

Preparation according to the general procedure D from **1b** (20.9 mg, 0.1 mmol) and **2a** (24.9 mg, 0.15 mmol) afforded **4b** as a colorless oil (15.3 mg, 0.041 mmol, 41% yield, dr = 10:1).

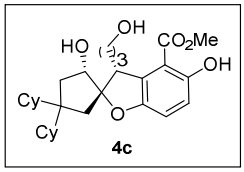
Preparation according to the general procedure D from **1b** (208.8 mg, 1 mmol) and **2a** (249.0 mg, 1.5 mmol) afforded **4b** as a colorless oil (124.2 mg, 0.33 mmol, 33% yield, dr = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.38 (br, 1H), 3.93 (s, 3H), 3.52-3.46 (m, 2H), 3.37 (d, *J* = 1.6 Hz, 1H), 2.75-2.25 (m, 1H), 2.10-1.96 (m, 3H), 1.84 (d, *J* = 14.8 Hz, 1H), 1.72 (dd, *J* = 10.8 Hz, 12.4 Hz, 1H), 1.58-1.49 (m, 2H), 1.47-1.40 (m, 2H), 1.39-1.26 (m, 3H), 1.22 (t, *J* = 11.2 Hz, 1H), 0.76 (t, *J* = 7.2 Hz, 3H), 0.72 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 156.5, 149.7, 132.8, 118.0, 116.9, 109.1, 97.6, 72.7, 62.3, 52.2, 50.7, 49.4, 45.0, 39.3, 32.4, 32.0, 30.8, 27.2, 8.7, 8.6;

HRMS ESI Calcd for $C_{21}H_{30}O_6Na$ $[M+Na]^+$: 401.1935, Found: 401.1942;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 13.494 min, t_{minor} = 20.138 min, 91% ee; $[\alpha]_D^{19.8}$ = -10.0 (c = 1.0, $CHCl_3$).



4c

Preparation according to the general procedure D from **1c** (31.8 mg, 0.1 mmol) and **2a** (24.9 mg, 0.15 mmol) afforded **4c** as a colorless oil (19.4 mg, 0.040 mmol, 40% yield, dr > 20:1).

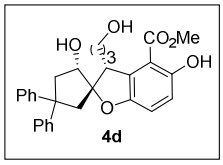
Preparation according to the general procedure D from **1c** (319.4 mg, 1 mmol) and **2a** (249.0 mg, 1.5 mmol) afforded **4c** as a colorless oil (180.1 mg, 0.37 mmol, 37% yield, dr > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 4.37 (t, *J* = 9.2 Hz, 1H), 3.98 (s, 3H), 3.97-3.91 (m, 1H), 3.56 (t, *J* = 8 Hz, 2H), 3.41 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 2.47 (br, 1H), 3.13-2.01 (m, 1H), 1.85-1.76 (m, 10H), 1.69-1.57 (m, 10H), 1.55-1.45 (m, 2H), 1.89-1.06 (m, 4H), 0.91-0.81 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 156.6, 149.4, 133.4, 118.1, 117.0, 109.2, 94.4, 77.2, 73.4, 62.5, 52.3, 51.1, 45.1, 44.0, 43.3, 43.1, 39.9, 30.9, 29.7, 28.1, 27.9, 27.8, 27.4, 27.3, 27.1, 27.0, 26.8, 26.7;

HRMS ESI Calcd for $C_{29}H_{42}O_6Na$ $[M+Na]^+$: 509.2874, Found: 509.2862;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 13.962 min, t_{minor} = 25.945 min, 89% ee; $[\alpha]_D^{20.2}$ = -16.7 (c = 1.2, $CHCl_3$).



4d

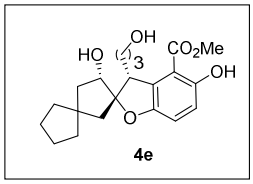
Preparation according to the general procedure D from **1d** (30.0 mg, 0.1 mmol) and **2a** (24.9 mg, 0.15 mmol) afforded **4d** as a colorless oil (30.9 mg, 0.067 mmol, 67% yield, dr = 15.5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.32-7.24 (m, 5H), 7.22-7.16 (m, 2H), 7.14-7.12 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 4.52-4.48 (m, 1H), 3.94 (s, 3H), 3.51-3.46 (m, 2H), 3.16 (dd, *J* = 6.0 Hz, 12.4 Hz, 1H), 2.90 (d, *J* = 14.8 Hz, 1H), 2.89 (br, 1H), 2.75 (d, *J* = 14.8 Hz, 1H), 2.55 (dd, *J* = 2.8 Hz, 8.4 Hz, 1H), 2.32-2.26 (m, 1H), 2.04 (s, 1H), 1.97-1.87 (m, 1H), 1.68 (br, 1H), 1.57-1.42 (m, 1H), 1.32-1.23 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 156.8, 149.8, 149.6, 148.3, 132.3, 128.5, 128.1, 126.7, 126.5, 126.0, 125.7, 118.1, 117.2, 109.3, 96.4, 72.1, 62.4, 60.4, 52.9, 52.2, 51.6, 49.3, 46.7, 30.3, 27.2, 14.1;

HRMS ESI Calcd for $C_{29}H_{30}O_6Na$ $[M+Na]^+$: 497.1935, Found: 497.1938;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 23.816 min, t_{minor} = 30.598 min, 92% ee; $[\alpha]_D^{20.3}$ = -72.7 (c = 1.1, $CHCl_3$).



4e

Preparation according to the general procedure D from **1e** (20.9 mg, 0.1 mmol) and **2a** (24.9 mg, 0.15 mmol) afforded **4e** as a colorless oil (17.3 mg, 0.047 mmol, 47% yield, dr > 20:1).

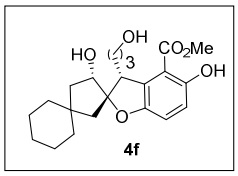
Preparation according to the general procedure D from **1e** (208.8 mg, 1 mmol) and **2a** (249.0 mg, 1.5 mmol) afforded **4e** as a colorless oil (165.0 mg, 0.44 mmol, 44% yield, dr > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 4.46-4.41 (m, 1H), 3.97 (s, 3H), 3.57-3.52 (m, 2H), 3.45 (dd, *J* = 2.4 Hz, 8.0 Hz, 1H), 2.46 (d, *J* = 9.6 Hz, 1H), 2.10-1.98 (m, 3H), 1.89-1.78 (m, 2H), 1.67-1.44 (m, 10H), 1.28-1.24 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 156.7, 150.0, 132.6, 118.1, 117.1, 109.3, 97.5, 73.2, 62.6, 52.2, 51.5, 50.9, 46.8, 44.3, 41.8, 41.7, 30.8, 27.2, 23.8, 23.6;

HRMS ESI Calcd for $C_{21}H_{28}O_6Na$ $[M+Na]^+$: 399.1778, Found: 399.1771;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 16.083 min, t_{minor} = 23.715 min, 86% ee; $[\alpha]_D^{20.0}$ = -22.2 (c = 0.9, $CHCl_3$).



4f

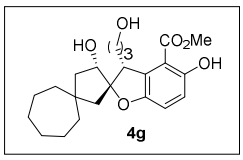
Preparation according to the general procedure D from **1f** (22.1 mg, 0.1 mmol) and **2a** (24.9 mg, 0.15 mmol) afforded **4f** as a colorless oil (19.6 mg, 0.051 mmol, 51% yield, dr > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 4.45-4.43 (m, 1H), 3.97 (s, 3H), 3.57 (t, *J* = 5.6 Hz, 2H), 3.45 (dd, *J* = 2.4 Hz, 5.6 Hz, 1H), 2.40 (br, 1H), 2.18-2.09 (m, 1H), 2.05 (d, *J* = 14.0 Hz, 1H), 1.96 (d, *J* = 14.8 Hz, 1H), 1.88-1.78 (m, 1H), 1.75-1.65 (m, 1H), 1.63-1.47 (m, 6H), 1.47-1.25 (m, 8H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 156.6, 149.8, 132.7, 118.1, 117.0, 109.2, 97.4, 72.6, 62.5, 52.2, 50.8, 40.5, 40.4, 36.9, 30.9, 27.2, 25.7, 23.3, 23.2;

HRMS ESI Calcd for $C_{22}H_{30}O_6Na$ $[M+Na]^+$: 413.1935, Found: 413.1917;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 15.517 min, t_{minor} = 22.968 min, 88% ee; $[\alpha]_D^{20.1}$ = -12.5 (c = 1.6, $CHCl_3$).



4g

Preparation according to the general procedure D from **1g** (23.7 mg, 0.1 mmol) and **2a** (24.9 mg, 0.15 mmol) afforded **4g** as a colorless oil (22.4 mg, 0.056 mmol, 56% yield, dr > 20:1).

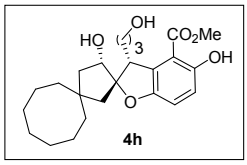
Preparation according to the general procedure D from **1g** (235.7 mg, 1 mmol) and **2a** (249.0 mg, 1.5 mmol) afforded **4g** as a colorless oil (190.0 mg, 0.47 mmol, 47% yield, dr > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6,79 (d, *J* = 8.8 Hz, 1H), 4.41 (dd, *J* = 7.6 Hz, 10.4 Hz, 1H), 3.97-3.94 (m, 1H), 3.96 (s, 3H), 3.57 (t, *J* = 5.6 Hz, 2H), 3.43 (dd, *J* = 2.4 Hz, 8.0 Hz, 1H), 2.17-2.05 (m, 2H), 2.00 (d, *J* = 14.4 Hz, 1H), 1.74 (dd, *J* = 10.8 Hz, 12.4 Hz, 2H), 1.66-1.52 (m, 8H), 1.51-1.37 (m, 8H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 156.6, 149.8, 132.7, 118.1, 117.0, 109.2, 97.6, 72.6, 62.5, 52.6, 52.2, 50.9, 47.9, 44.0, 43.5, 40.0, 30.9, 29.0, 28.9, 27.2, 23.6, 23.4;

HRMS ESI Calcd for $C_{23}H_{32}O_6Na$ $[M+Na]^+$: 427.2091, Found: 427.2072;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 16.898 min, t_{minor} = 25.782 min, 92% ee; $[\alpha]_D^{20.2}$ = -18.2 (c = 1.1, $CHCl_3$).



4h

Preparation according to the general procedure D from **1h** (24.9 mg, 0.1 mmol) and **2a** (24.9 mg, 0.15 mmol) afforded **4h** as a colorless oil (22.8 mg, 0.055 mmol, 55% yield, dr > 20:1).

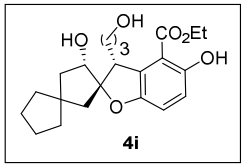
Preparation according to the general procedure D from **1h** (249.4 mg, 1 mmol) and **2a** (249.0 mg, 1.5 mmol) afforded **4h** as a colorless oil (199.7 mg, 0.48 mmol, 48% yield, dr > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.43 (br, 1H), 3.96 (s, 3H), 3.56 (t, *J* = 5.6 Hz, 2H), 3.42 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H), 2.48 (br, 1H), 2.18-2.01 (m, 3H), 1.97 (d, *J* = 10.8 Hz, 1H), 1.70 (dd, *J* = 10.8 Hz, 12.8 Hz, 3H), 1.61-1.60 (m, 3H), 1.60-1.56 (m, 1H), 1.56-1.45 (m, 9H), 1.44-1.35 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 156.6, 149.8, 132.8, 118.0, 117.0, 109.2, 97.7, 72.6, 62.4, 52.2, 52.1, 50.9, 47.3, 39.9, 38.5, 38.1, 30.9, 28.6, 28.3, 27.3, 24.7, 23.2, 23.1;

HRMS ESI Calcd for $C_{24}H_{34}O_6Na$ $[M+Na]^+$: 441.2248, Found: 441.2235;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 19.329 min, t_{minor} = 25.994 min, 92% ee; $[\alpha]_D^{20.3}$ = -14.3 (c = 1.4, $CHCl_3$).



4i

Preparation according to the general procedure D from **1e** (20.7 mg, 0.1 mmol) and **2b** (27.0 mg, 0.15 mmol) afforded **4i** as a colorless oil (19.7 mg, 0.051 mmol, 51% yield, dr > 20:1).

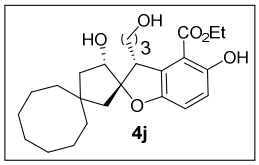
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 4.48-4.41 (m, 3H), 3.56 (t, *J* = 5.6 Hz, 2H), 3.46 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 2.09-2.02 (m, 2H), 2.00 (d, *J* = 14.4 Hz, 1H), 1.91-1.88 (m, 1H), 1.67-1.46 (m, 12H), 1.46 (t, *J* = 7.2 Hz, 5H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 156.8, 149.9, 132.5, 117.9, 117.1, 109.5, 97.4, 73.2, 62.6, 61.6,

51.3, 50.8, 46.7, 41.8, 30.5, 27.1, 23.8, 23.6, 14.3;

HRMS ESI Calcd for $C_{22}H_{30}O_6Na$ $[M+Na]^+$: 413.1935, Found: 413.1944;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 13.789 min, t_{minor} = 23.829 min, 75% ee; $[\alpha]_D^{20.1}$ = -15.4 (c = 1.3, $CHCl_3$).



4j

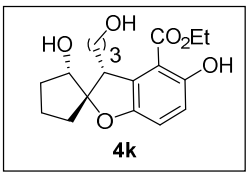
Preparation according to the general procedure D from **1h** (25.0 mg, 0.1 mmol) and **2b** (27.0 mg, 0.15 mmol) afforded **4j** as a colorless oil (22.5 mg, 0.051 mmol, 53% yield, dr > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 4.48-4.40 (m, 3H), 3.56 (t, *J* = 5.6 Hz, 2H), 3.44 (dd, *J* = 2.0 Hz, 8.8 Hz, 1H), 2.53-2.32 (m, 1H), 2.16-2.047 (m, 1H), 2.02-1.96 (m, 2H), 1.92-1.79 (m, 1H), 1.73-1.56 (m, 8H), 1.56-1.52 (m, 2H), 1.46-1.41 (m, 8H), 1.37-1.33 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 156.7, 149.7, 132.7, 118.0, 117.0, 109.4, 97.7, 72.7, 62.6, 61.6, 51.9, 50.9, 47.3, 40.0, 38.5, 38.2, 30.7, 28.6, 28.3, 27.2, 24.7, 23.24, 23.15, 14.3;

HRMS ESI Calcd for $C_{25}H_{36}O_6Na$ $[M+Na]^+$: 455.2404, Found: 455.2403;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 16.813 min, t_{minor} = 27.576 min, 86% ee; $[\alpha]_D^{20.2}$ = -13.3 (c = 1.5, $CHCl_3$).



4k

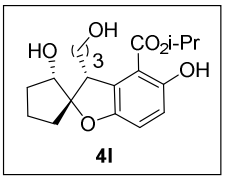
Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2b** (27.0 mg, 0.15 mmol) afforded **4k** as a colorless oil (20.2 mg, 0.06 mmol, 60% yield, dr = 12.6:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 4.49-4.37 (m, 3H), 3.54 (t, *J* = 6.0 Hz, 2H), 3.47 (dd, *J* = 2.4 Hz, 8.0 Hz, 1H), 2.57 (br, 1H), 2.20-2.12 (m, 1H), 2.04-1.86 (m, 3H), 1.84-1.64 (m, 2H), 1.63-1.50 (m, 4H), 1.43 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 156.8, 150.1, 132.4, 117.9, 117.1, 109.5, 97.0, 73.4, 62.6, 61.7, 50.2, 37.6, 33.0, 30.3, 27.1, 18.5, 14.3;

HRMS ESI Calcd for $C_{18}H_{24}O_6Na$ $[M+Na]^+$: 359.1465, Found: 359.1454;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 14.317 min, t_{minor} = 23.956 min, 88% ee; $[\alpha]_D^{17.9}$ = -8.3 (c = 1.0, $CHCl_3$).



4l

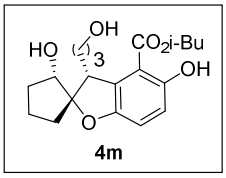
Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2c** (29.2 mg, 0.15 mmol) afforded **4l** as a colorless oil (19.7 mg, 0.057 mmol, 57% yield, dr = 9.4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 5.37-5.31 (m, 1H), 4.40 (t, *J* = 7.2 Hz, 1H), 3.54 (t, *J* = 6.0 Hz, 2H), 3.47 (dd, *J* = 2.0 Hz, 8.0 Hz, 1H), 2.47 (br, 1H), 2.20-2.16 (m, 1H), 2.05-2.00 (m, 2H), 1.85-1.77 (m, 2H), 1.66-1.56 (m, 5H), 1.42 (d, *J* = 4.8 Hz, 3H), 1.41 (d, *J* = 5.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 156.9, 150.0, 132.3, 117.8, 117.1, 109.9, 96.9, 73.5, 67.9, 62.6, 50.1, 37.5, 33.0, 30.2, 27.1, 22.0, 21.8, 18.5;

HRMS ESI Calcd for $C_{19}H_{26}O_6Na$ $[M+Na]^+$: 373.1622, Found: 373.1617;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 13.468 min, t_{minor} = 20.366 min, 80% ee; $[\alpha]_D^{18.2}$ = -14.3 (c = 0.7, $CHCl_3$).



4m

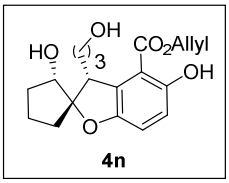
Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2m** (31.4 mg, 0.15 mmol) afforded **4m** as a colorless oil (19.4 mg, 0.054 mmol, 54% yield, dr = 4.7:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 4.37 (t, *J* = 7.2 Hz, 1H), 4.78 (dd, *J* = 3.2 Hz, 10.8 Hz, 1H), 4.08 (d, *J* = 6.4 Hz, 1H), 3.51 (t, *J* = 6.4 Hz, 3H), 2.75 (br, 1H), 2.17-2.08 (m, 2H), 2.03-1.84 (m, 2H), 1.83-1.62 (m, 3H), 1.61-1.53 (m, 4H), 1.30-1.25 (m, 1H), 1.03 (d, *J* = 2.8 Hz, 3H), 1.01 (d, *J* = 3.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 156.7, 150.2, 132.2, 117.8, 117.1, 109.6, 97.0, 73.3, 71.8, 62.5, 50.1, 37.4, 32.9, 29.8, 27.8, 27.1, 19.4, 19.2, 18.5;

HRMS ESI Calcd for $C_{20}H_{28}O_6Na$ $[M+Na]^+$: 387.1778, Found: 387.1769;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 11.103 min, t_{minor} = 18.840 min, 80% ee; $[\alpha]_D^{19.1}$ = 7.1 (c = 1.4, $CHCl_3$).



4n

Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2n** (28.7 mg,

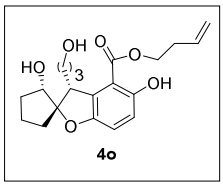
0.15 mmol) afforded **4n** as a colorless oil (17.7 mg, 0.051 mmol, 51% yield, dr = 4.7:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.11-6.04 (m, 1H), 5.37 (dt, *J* = 1.2 Hz, 7.6 Hz, 2H), 4.92-4.89 (m, 1H), 4.39 (d, *J* = 7.2 Hz, 2H), 3.55-3.51 (m, 2H), 3.47 (dd, *J* = 2.0 Hz, 8.0 Hz, 1H), 2.20-2.14 (m, 1H), 2.05-1.90 (m, 2H), 1.86-1.77 (m, 4H), 1.66-1.54 (m, 4H), 1.43-1.26 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 156.9, 150.1, 132.5, 131.4, 120.1, 118.1, 117.1, 109.3, 97.0, 66.4, 62.6, 50.2, 37.6, 33.0, 30.4, 27.1, 18.6;

HRMS ESI Calcd for $C_{19}H_{24}O_6Na$ $[M+Na]^+$: 371.1465, Found: 371.1459;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 13.772 min, t_{minor} = 22.585 min, 84% ee; $[\alpha]_D^{19.4}$ -14.3 (c = 1.4, $CHCl_3$).



4o

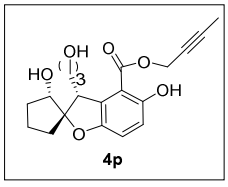
Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2o** (31.2 mg, 0.15 mmol) afforded **4o** as a colorless oil (19.8 mg, 0.055 mmol, 55% yield, dr = 4.6:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 5.87-5.79 (m, 1H), 5.20 (m, 2H), 4.52-4.42 (m, 1H), 4.41-4.35 (m, 2H), 3.55-3.48 (m, 2H), 2.57-2.52 (m, 2H), 2.23-2.12 (m, 1H), 2.04-1.88 (m, 2H), 1.87-1.63 (m, 4H), 1.63-1.53 (m, 4H), 1.42-1.40 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 156.7, 150.2, 132.3, 117.94, 117.87, 117.1, 109.5, 97.1, 77.3, 73.4, 64.6, 62.5, 50.0, 37.3, 33.0, 32.9, 29.9, 27.0, 18.5;

HRMS ESI Calcd for $C_{20}H_{26}O_6K$ $[M+K]^+$: 401.1361, Found: 401.1382;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 13.119 min, t_{minor} = 21.234 min, 83% ee; $[\alpha]_D^{20.6}$ = -10.0 (c = 2.0, $CHCl_3$).



4p

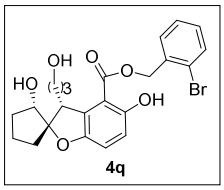
Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2p** (30.5 mg, 0.15 mmol) afforded **4p** as a colorless oil (18.8 mg, 0.057 mmol, 52% yield, dr = 3.9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.05-4.95 (m, 1H), 4.88-4.80 (m, 1H), 4.39 (t, *J* = 7.2 Hz, 1H), 3.58-3.45 (m, 3H), 2.76 (br, 1H), 2.21-2.05 (m, 2H), 2.03-1.93 (m, 1H), 1.88-1.80 (m, 3H), 1.87 (s, 3H), 1.74-1.44 (m, 5H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.4, 156.8, 156.4, 150.5, 150.1, 133.2, 132.7, 118.2, 118.1, 117.0, 116.8, 109.2, 109.0, 101.1, 97.0, 84.3, 84.1, 73.4, 72.5, 63.0, 62.6, 53.6, 53.4, 50.3, 47.8, 37.6, 35.2, 33.7, 32.9, 30.7, 29.2, 27.7, 27.3, 19.5, 18.5, 3.61, 3.58;

HRMS ESI Calcd for $C_{20}H_{25}O_6$ $[M+H]^+$: 361.1646, Found: 361.1633;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 14.961 min, t_{minor} = 25.074 min, 86% ee; $[\alpha]_D^{19.2}$ = -9.1 (c = 2.2, $CHCl_3$).



4q

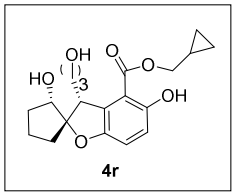
Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2q** (48.1 mg, 0.15 mmol) afforded **4q** as a colorless oil (22.2 mg, 0.047 mmol, 47% yield, dr = 11.4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.65-7.60 (m, 1H), 7.52-7.46 (m, 1H), 7.37 (dt, *J* = 0.8 Hz, 7.6 Hz, 1H), 7.28 (dd, *J* = 0.8 Hz, 2 Hz, 1H), 6.95 (d, *J* = 9.6 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 5.48 (d, *J* = 3.2 Hz, 2H), 4.30 (t, *J* = 7.2 Hz, 1H), 3.41 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 3.33 (t, *J* = 6.0 Hz, 2H), 2.17-2.08 (m, 1H), 2.02-1.90 (m, 2H), 1.86-1.68 (m, 4H), 1.60-1.52 (m, 2H), 1.45-1.36 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 156.9, 150.1, 134.3, 133.3, 132.8, 131.7, 130.8, 127.8, 124.8, 118.2, 117.0, 109.0, 97.0, 73.2, 67.0, 62.5, 50.0, 37.1, 32.8, 30.0, 27.0, 18.4;

HRMS ESI Calcd for $C_{23}H_{25}BrO_6Na$ $[M+Na]^+$: 499.0727, Found: 499.0717;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 18.563 min, t_{minor} = 37.175 min, 74% ee; $[\alpha]_D^{20.8}$ = -3.8 (c = 2.6, $CHCl_3$).



4r

Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2r** (30.6 mg, 0.15 mmol) afforded **4r** as a colorless oil (18.6 mg, 0.052 mmol, 52% yield, dr = 4.7:1).

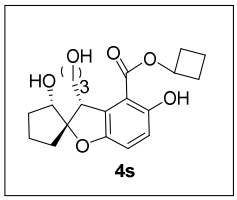
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 4.37 (t, *J* = 6.8 Hz, 1H), 4.25-4.11 (m, 2H), 3.50 (m, 3H), 2.88 (br, 1H), 2.61 (br, 1H), 2.20-1.82 (m, 3H), 1.81-1.75 (m, 3H), 1.70-1.42 (m, 3H), 1.28-1.25 (m, 1H), 1.24-1.22 (m, 1H), 0.67-0.61 (m, 2H), 0.36 (dd, *J* = 4.8 Hz, 9.6 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 156.7, 150.1, 132.4, 117.8, 116.9, 109.5, 100.8, 97.0, 73.3, 70.6, 62.5, 50.2, 37.5, 32.8, 30.1, 27.1, 18.5, 9.7, 3.7;

HRMS ESI Calcd for $C_{20}H_{26}O_6Na$ $[M+Na]^+$: 385.1622, Found: 385.1627;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm,

retention time: t_{major} = 13.792 min, t_{minor} = 23.171 min, 78% ee; $[\alpha]_D^{19.5}$ = -5.0 (c = 2.0, $CHCl_3$).



4s

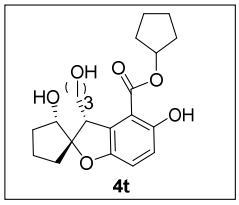
Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2s** (30.6 mg, 0.15 mmol) afforded **4s** as a colorless oil (20.9 mg, 0.057 mmol, 57% yield, dr = 7.8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 5.24 (t, *J* = 7.6 Hz, 1H), 4.39 (t, *J* = 7.6 Hz, 1H), 3.54 (t, *J* = 5.6 Hz, 2H), 3.50 (dd, *J* = 2.4 Hz, 8.0 Hz, 1H), 2.52-2.44 (m, 2H), 2.27-2.12 (m, 3H), 2.11-1.98 (m, 2H), 1.95-1.79 (m, 3H), 1.78-1.69 (m, 1H), 1.68-1.54 (m, 4H), 1.48-1.37 (m, 1H), 1.29-1.23 (m, 1H), 0.93-0.84 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 156.8, 150.0, 132.3, 117.9, 117.0, 109.4, 96.9, 73.4, 70.1, 62.6, 50.2, 37.6, 33.0, 30.5, 30.31, 30.29, 27.2, 18.5, 13.7;

HRMS ESI Calcd for $C_{20}H_{26}O_6Na$ $[M+Na]^+$: 385.1622, Found: 385.1634;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 14.345 min, t_{minor} = 24.116 min, 77% ee; $[\alpha]_D^{20.4}$ = -9.5 (c = 2.1, $CHCl_3$).



4t

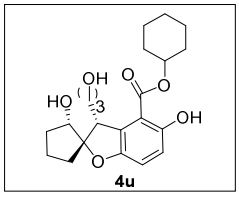
Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2t** (32.8 mg, 0.15 mmol) afforded **4t** as a colorless oil (20.2 mg, 0.054 mmol, 54% yield, dr = 6.7:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.49-5.43 (m, 1H), 4.38 (t, *J* = 7.2 Hz, 1H), 3.54-3.48 (m, 2H), 3.46 (dd, *J* = 2.8 Hz, 8 Hz, 1H), 2.21-2.14 (m, 1H), 2.03-1.93 (m, 4H), 1.89-1.78 (m, 6H), 1.76-1.61 (m, 6H), 1.59-1.50 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 156.7, 150.1, 132.0, 117.7, 117.1, 109.8, 96.9, 79.0, 73.3, 62.5, 50.1, 37.4, 32.9, 32.8, 32.5, 29.6, 27.0, 23.9, 23.7, 18.5;

HRMS ESI Calcd for $C_{21}H_{28}O_6Na$ $[M+Na]^+$: 399.1778, Found: 399.1791;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 13.156 min, t_{minor} = 21.162 min, 81% ee; $[\alpha]_D^{20.5}$ = -21.4 (c = 1.4, $CHCl_3$).



4u

Preparation according to the general procedure D from **1a** (15.4 mg, 0.1 mmol) and **2u** (35.2 mg,

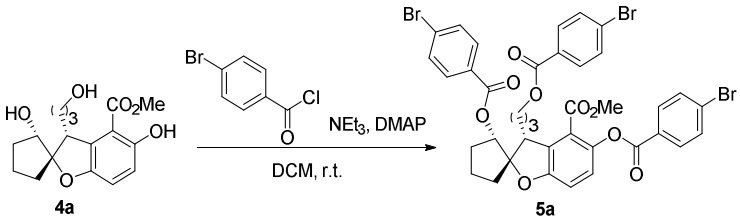
0.15 mmol) afforded **4u** as a colorless oil (22.3 mg, 0.057 mmol, 57% yield, dr = 5.4:1).

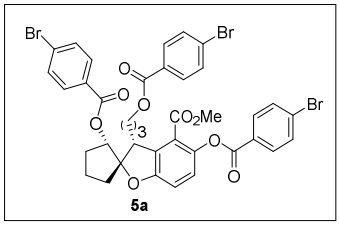
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 5.09-5.02 (m, 1H), 4.37 (t, *J* = 7.2 Hz, 1H), 3.52-3.47 (m, 3H), 2.85 (br, 1H), 2.12-2.06 (m, 1H), 2.11-1.98 (m, 5H), 1.83-1.75 (m, 5H), 1.64-1.54 (m, 6H), 1.54-1.24 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 156.7, 150.1, 132.2, 117.7, 117.0, 109.8, 96.9, 74.9, 73.3, 62.5, 50.1, 37.4, 32.9, 31.8, 31.7, 29.8, 27.1, 25.2, 24.1, 24.0, 18.5;

HRMS ESI Calcd for $C_{22}H_{30}O_6Na$ $[M+Na]^+$: 413.1935, Found: 413.1942;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 11.736 min, t_{minor} = 20.430 min, 78% ee; $[\alpha]_D^{19.7}$ = -3.7 (c = 2.7, $CHCl_3$).





To a stirred solution of **4a** (30.1 mg, 0.093 mmol, 1 equiv.) in dry DCM (2 mL) was added DMAP (11.4 mg, 1.0 equiv.), Et_3N (52.0 µL, 4.0 equiv.) and bromobenzoyl chloride (82.1 mg, 4.0 equiv.) successively at r.t. and stirred overnight before it was quenched with the saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified via column chromatography on silica gel to give product compound **5a** as a colorless solid (58.3 mg, 0.067 mmol, 72% yield).

Mp 159.9-162.3 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.02 (m, 2H), 7.76 (dd, *J* = 0.2 Hz, 8.0 Hz, 4H), 7.67-7.65 (m, 2H), 7.56-7.50 (m, 4H), 7.03 (d, *J* = 8.4 Hz, 11.6Hz, 2H), 5.50 (t, *J* = 6.8Hz, 1H), 4.13-4.08 (m, 2H), 3.74 (q, *J* = 3.6 Hz, 1H), 3.62 (s, 3H), 2.51-2.27 (m, 2H), 2.14-1.90 (m, 4H), 1.86-1.64 (m, 4H);

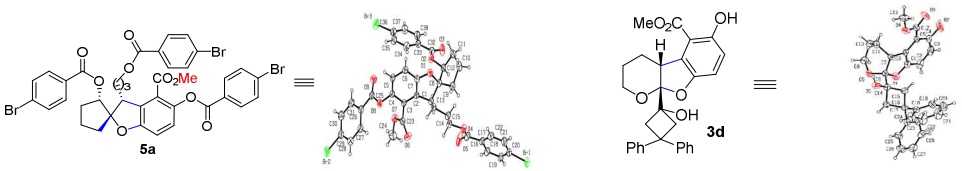
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.2, 165.0, 156.4, 143.2, 133.1, 132.0, 131.8, 131.6, 131.1, 131.0, 128.9, 128.8, 128.7, 128.2, 123.5, 113.6, 97.6, 75.3, 64.9, 52.1, 47.9, 36.5, 29.7, 29.1, 27.2, 26.2, 18.6;

HRMS ESI Calcd for $C_{38}H_{31}Br_3O_9Na$ $[M+Na]^+$: 890.9410, Found: 890.9399;

HPLC: Chiralpak IF-3 column, n-hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm,

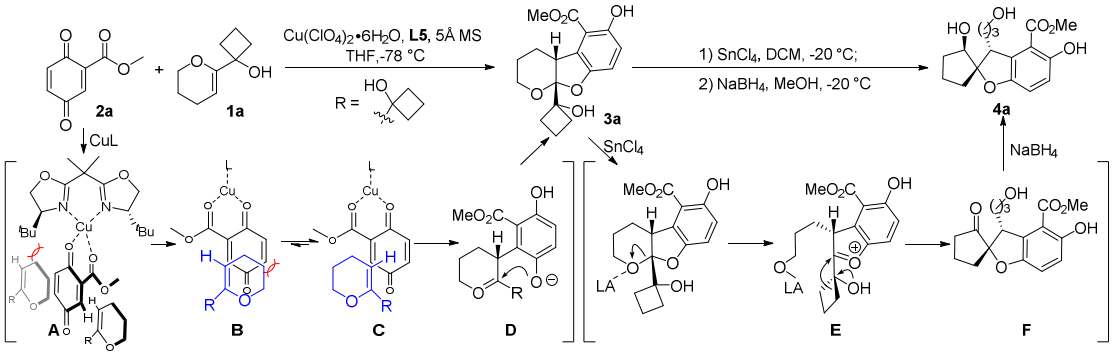
retention time: t_{major} = 30.810 min, t_{minor} = 36.724 min, 94% ee; $[\alpha]_D^{20.7}$ = 42.9 (c = 1.4, $CHCl_3$).

8. X-Ray Ellipsoid Plots of 3d and 5a



The crystal structure of **3d** and **5a** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers (CCDC number): 1883807 and 1883805.

9. Proposed Reaction Mechanism



10. References

[1] Q.-W. Zhang, C.-A. Fan, H.-J. Zhang, Y.-Q. Tu, Y.-M. Zhao, P. Gu, and Z.-M. Chen, *Angew. Chem. Int. Ed*. 2009, **48,** 8572-8574.

[2] Y.-H. Chen, D.-J. Cheng, J. Zhang, Y. Wang, X.-Y. Liu, B. Tan, *J. Am. Chem. Soc.*, 2015, **137,** 15062–15065.

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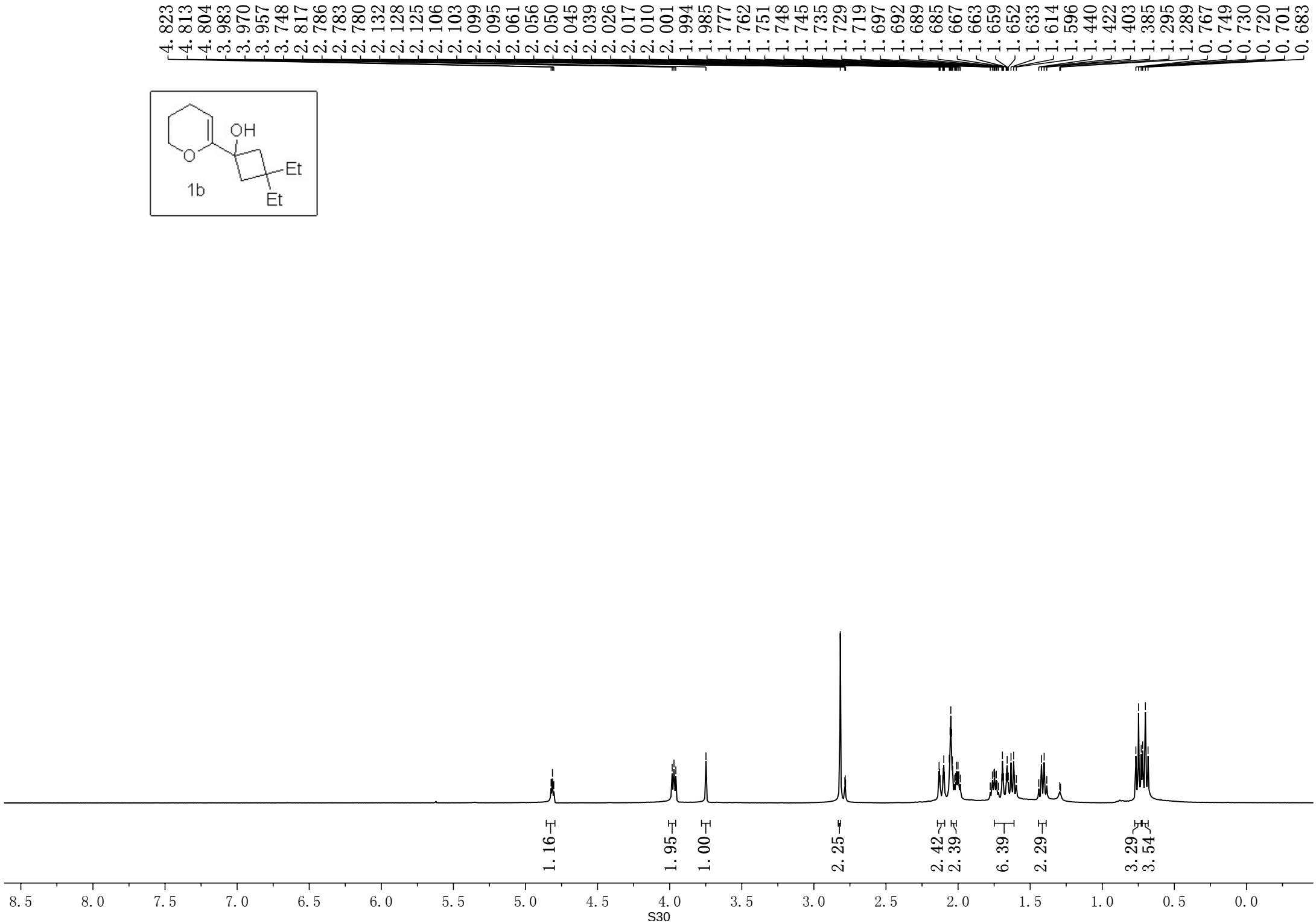
Et
1b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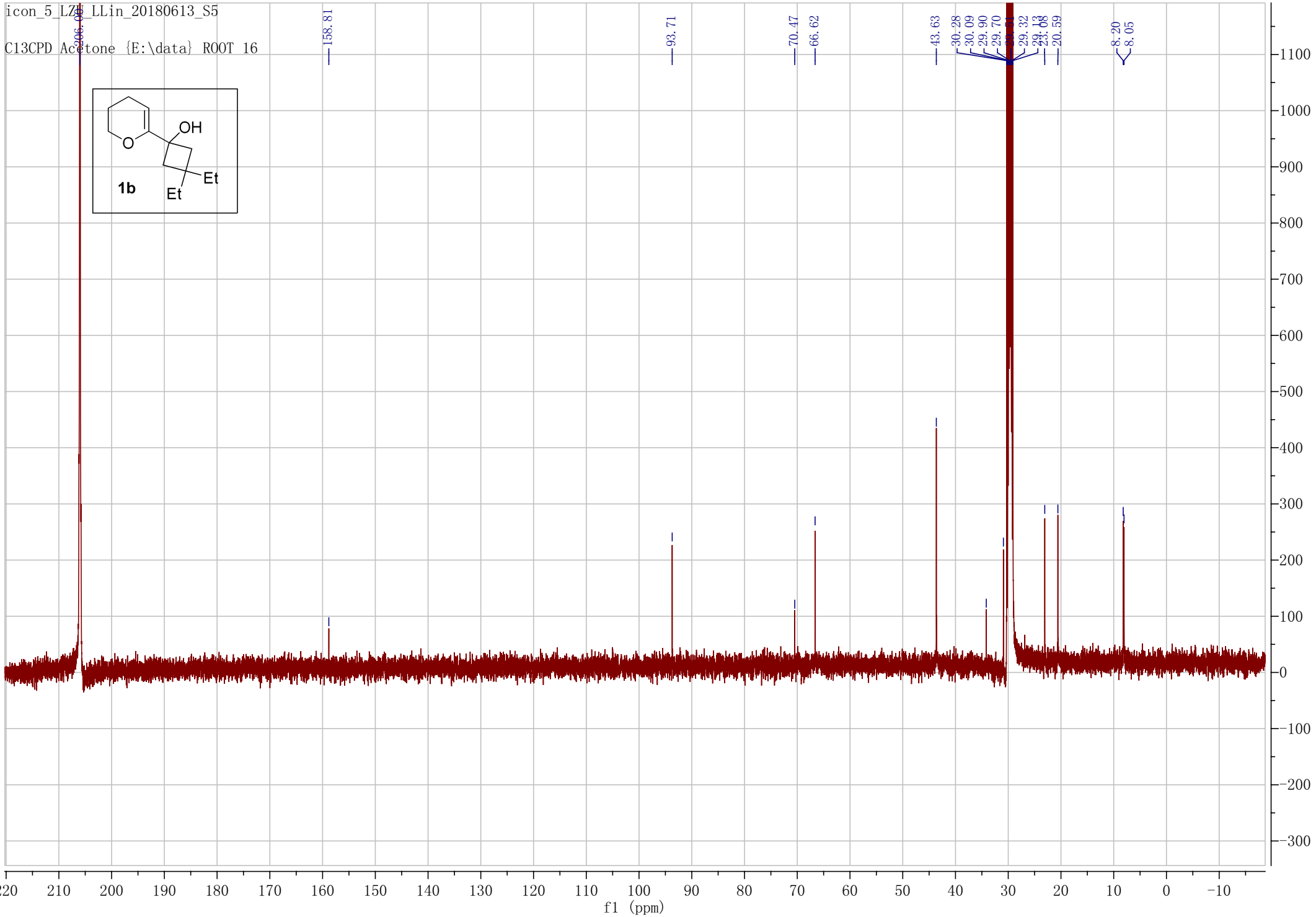
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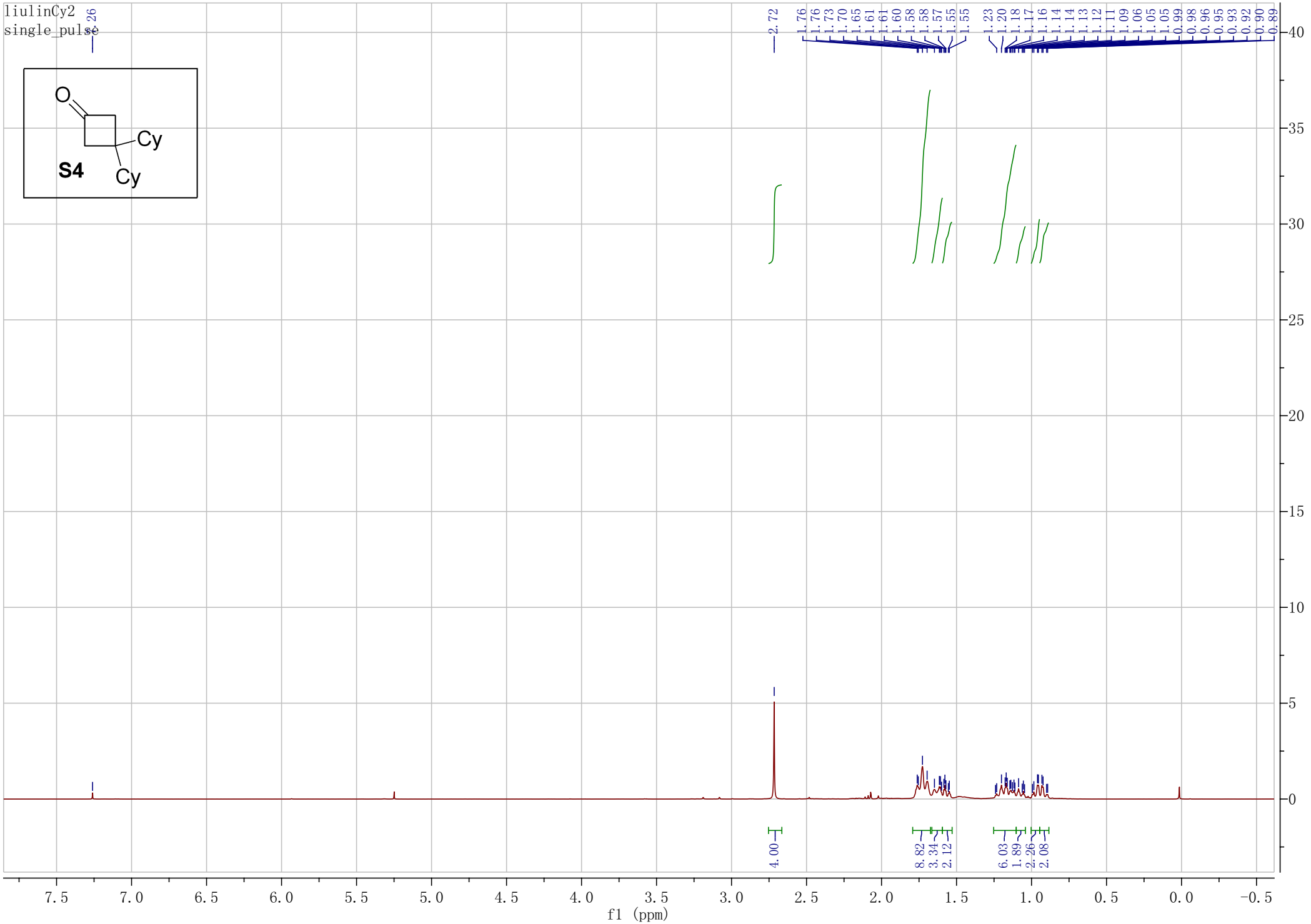
Et
Et
1b
f1 (ppm)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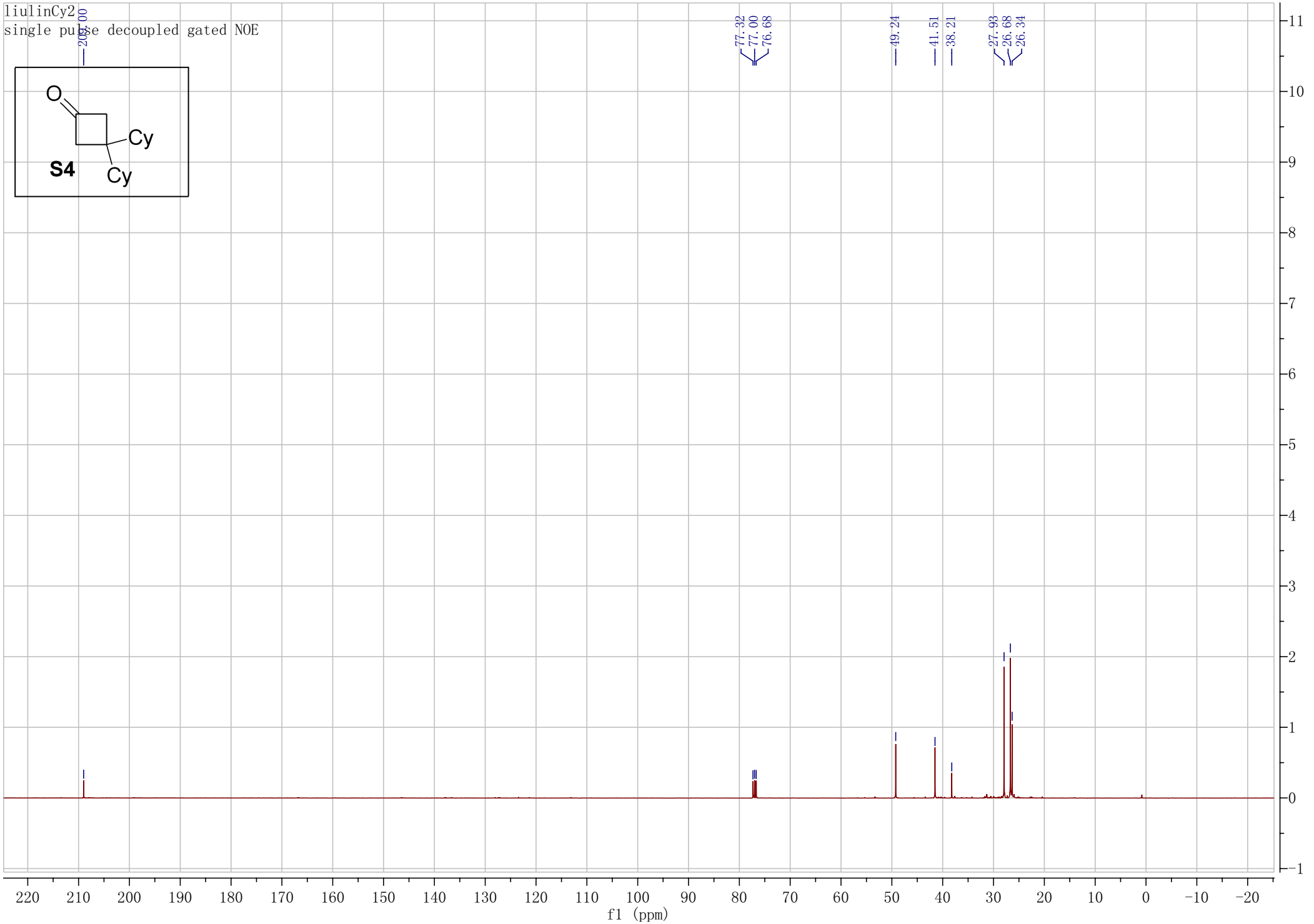
Cy
f1 (ppm)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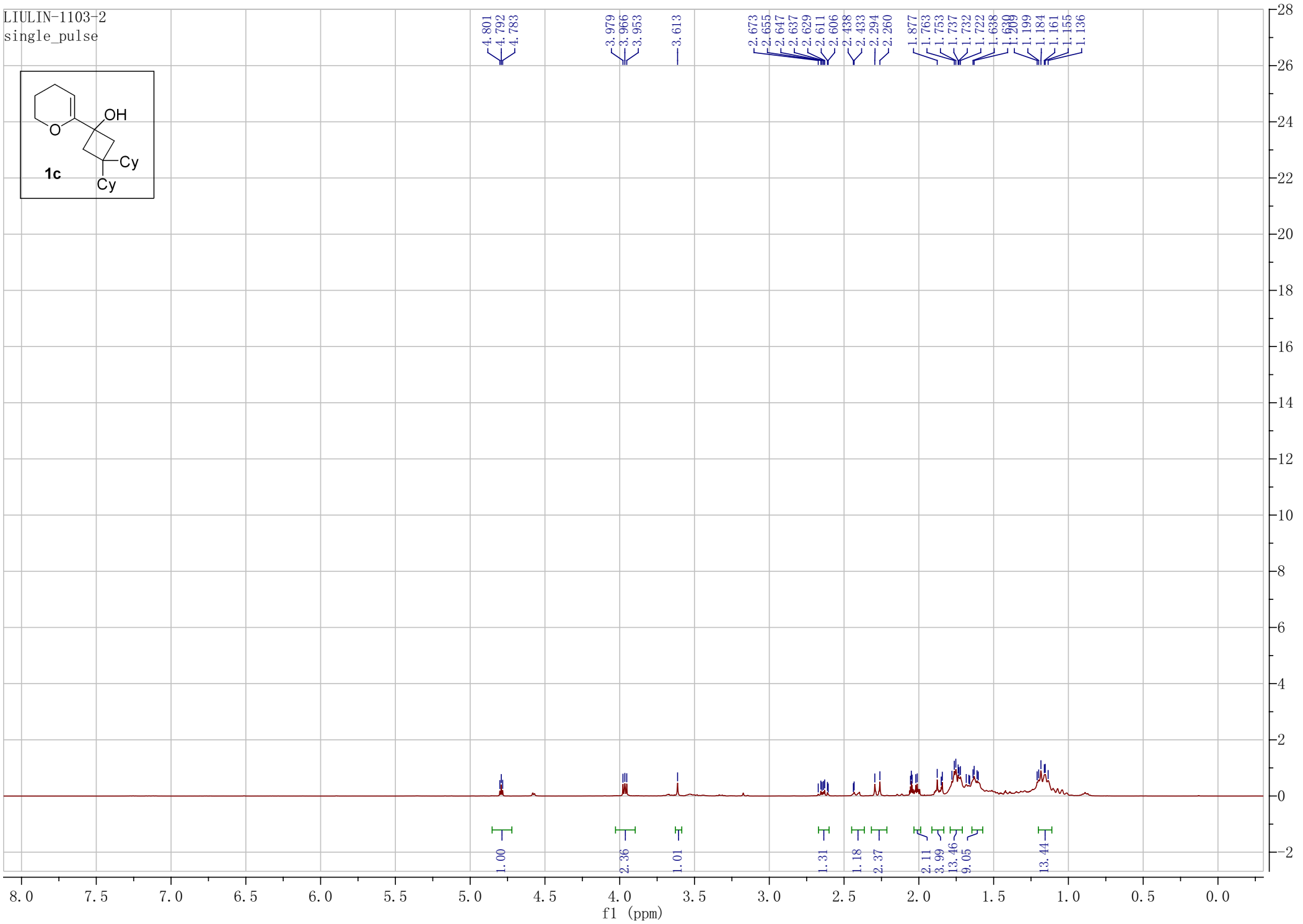
Cy
Cy
S4
f1 (ppm)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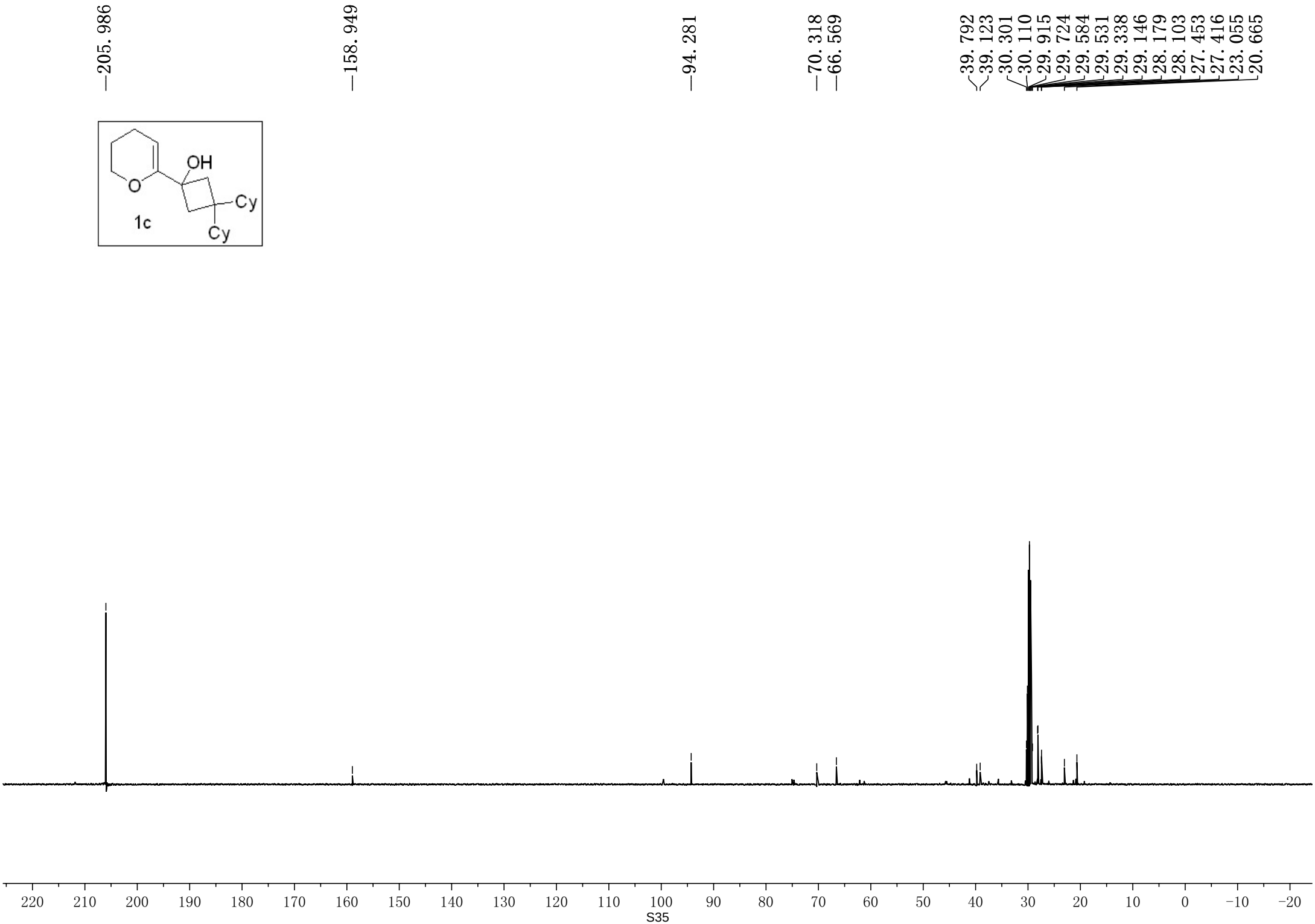
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23.055
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O
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Cy
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200
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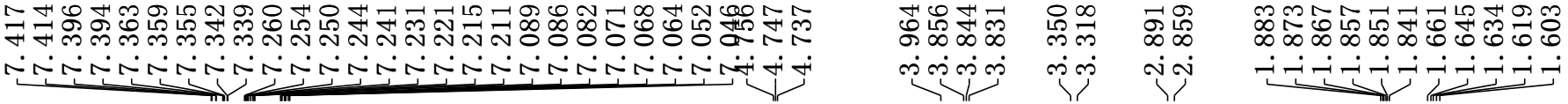
−20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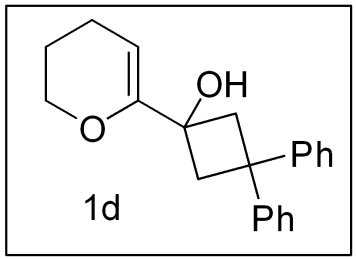
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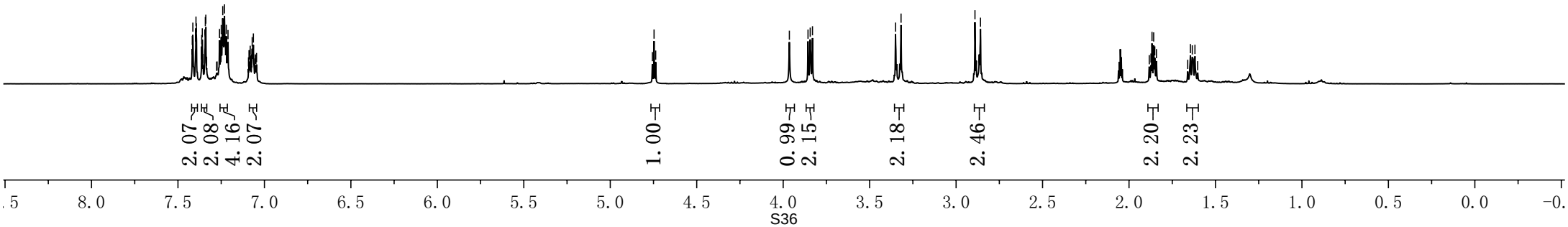
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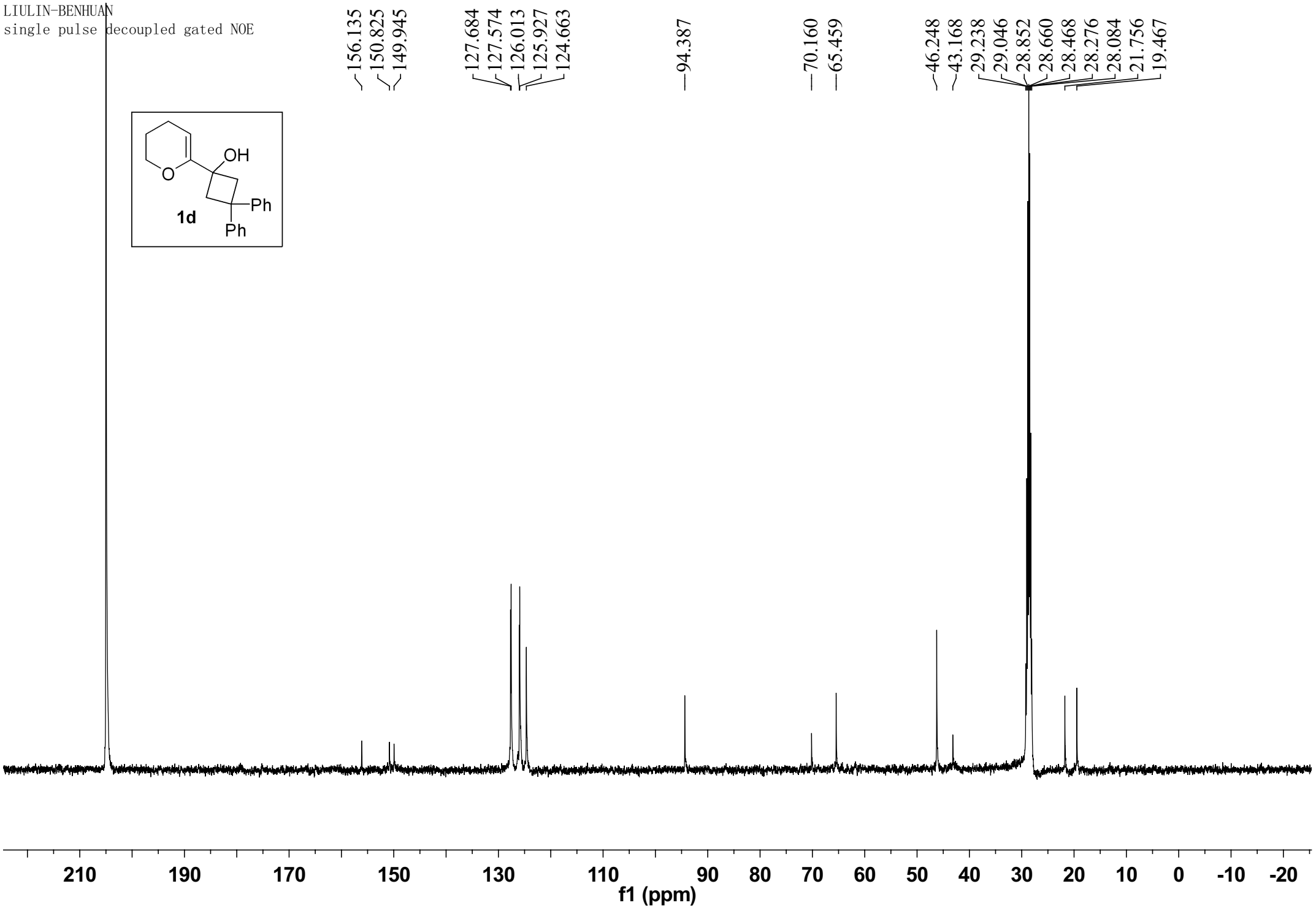
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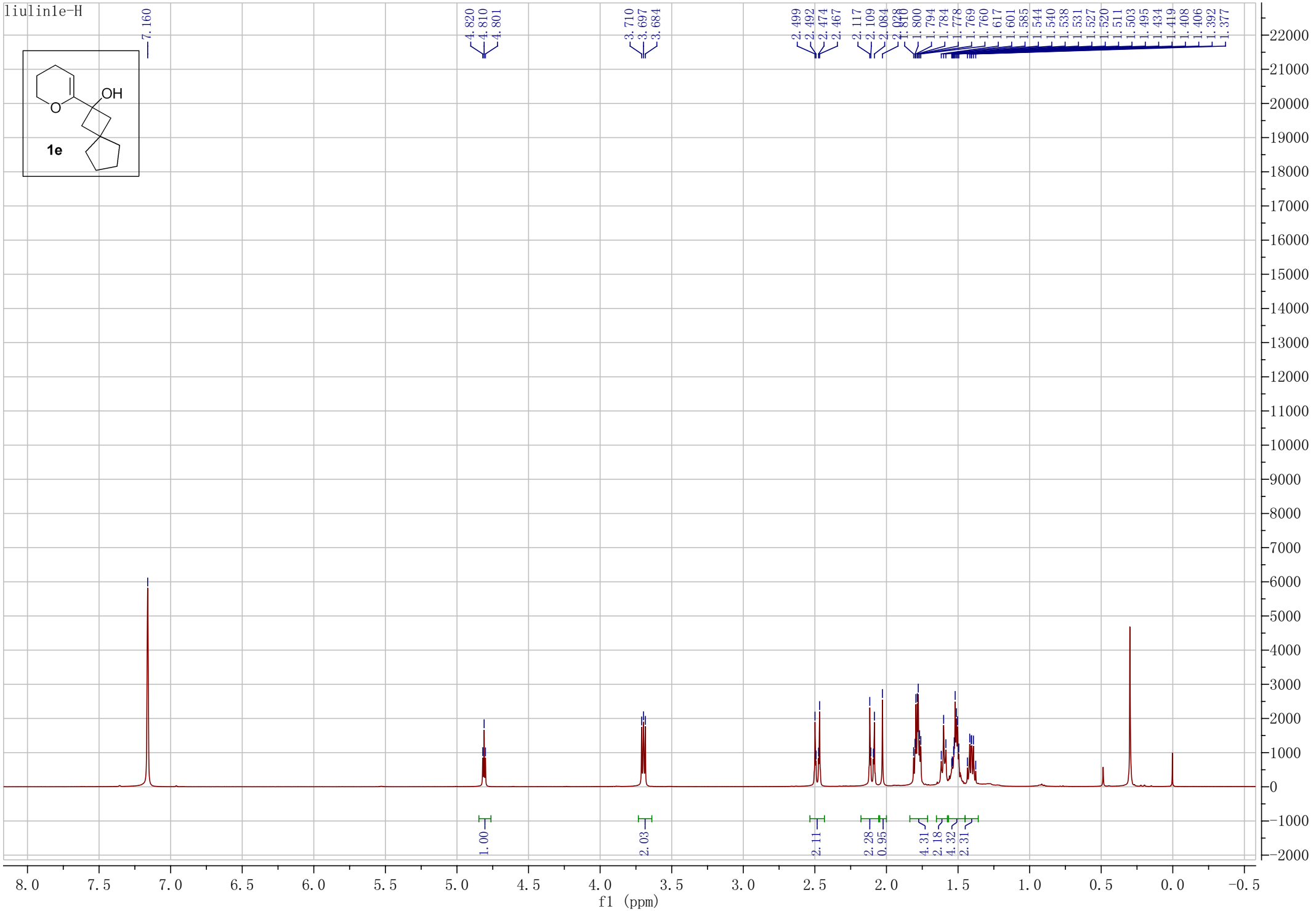
f1 (ppm)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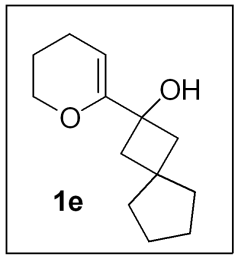

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f1 (ppm)

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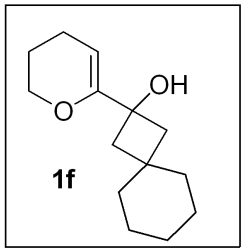

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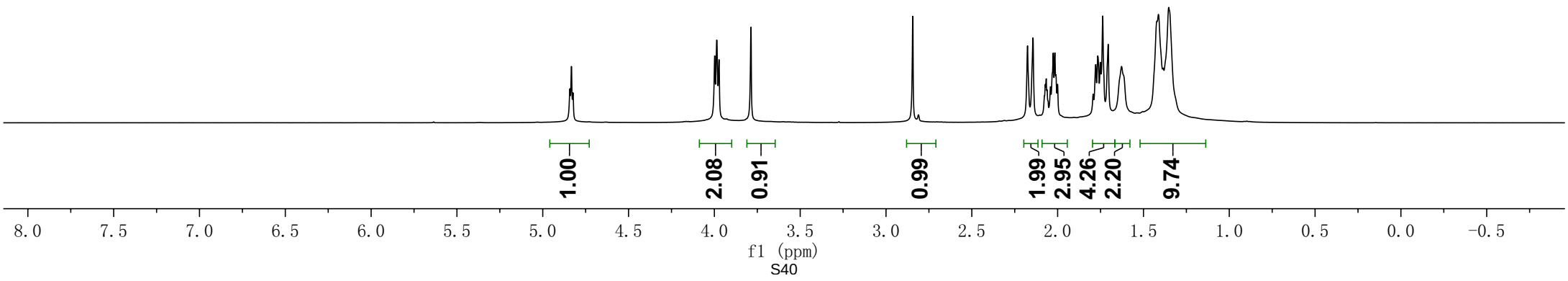
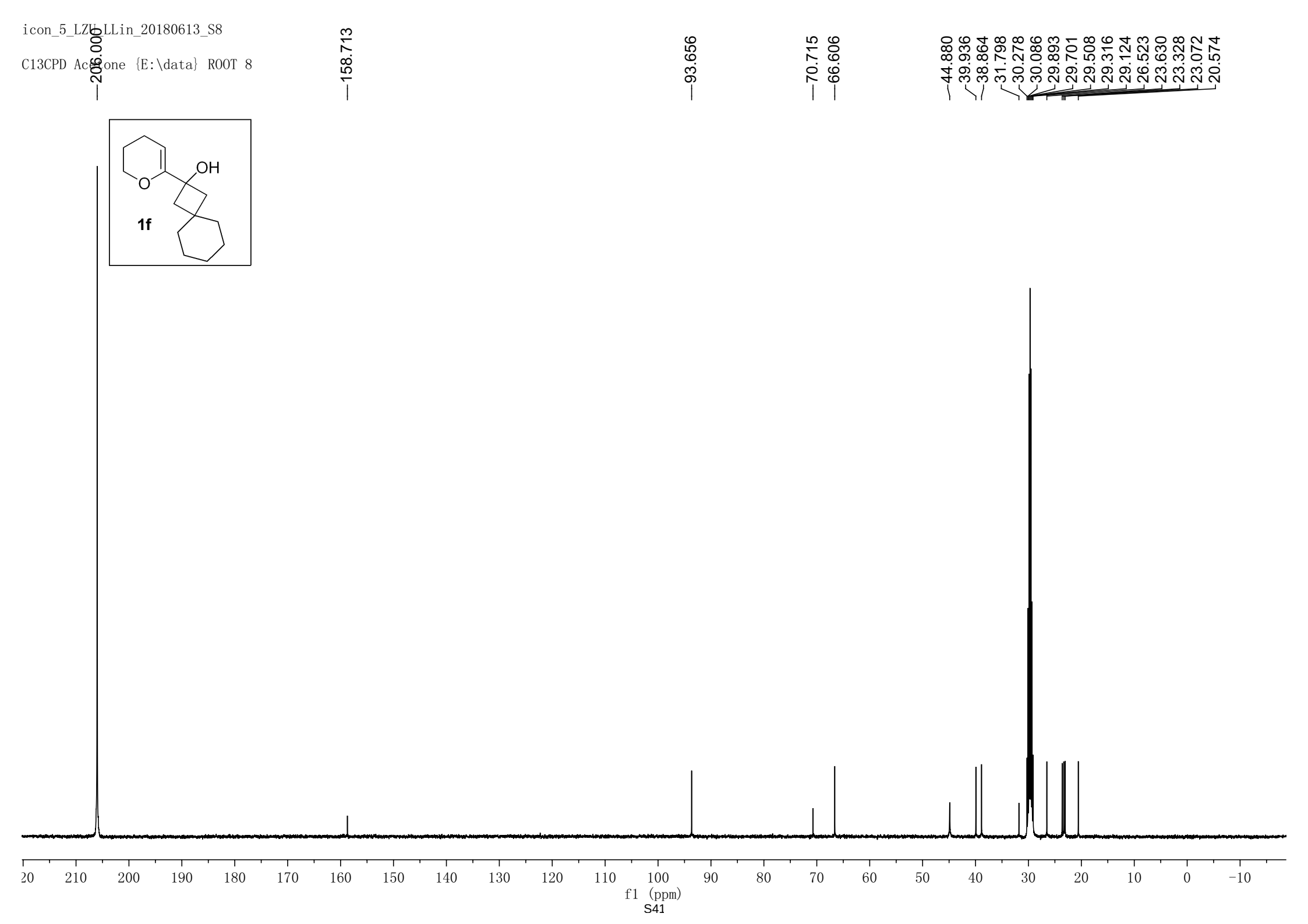
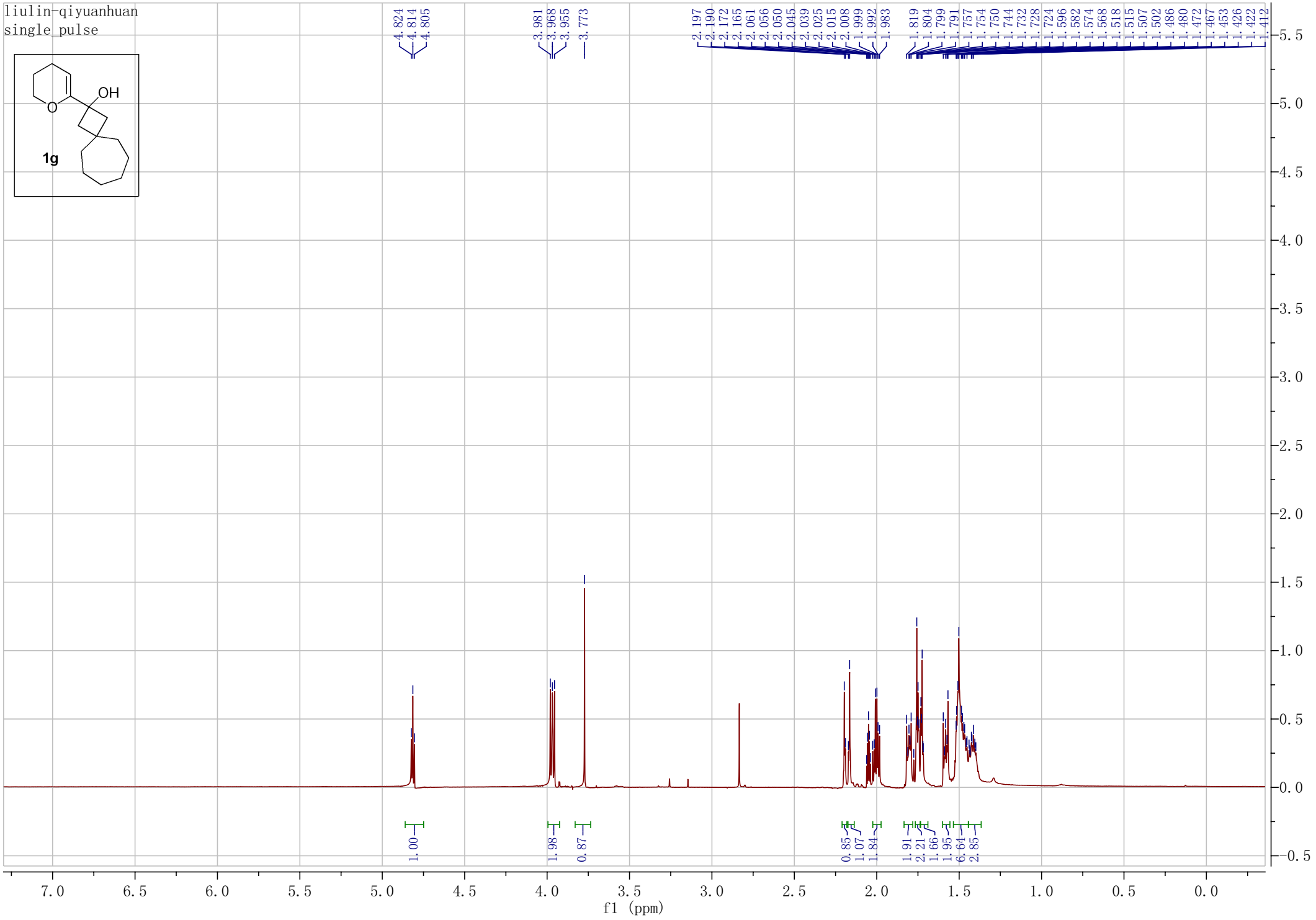
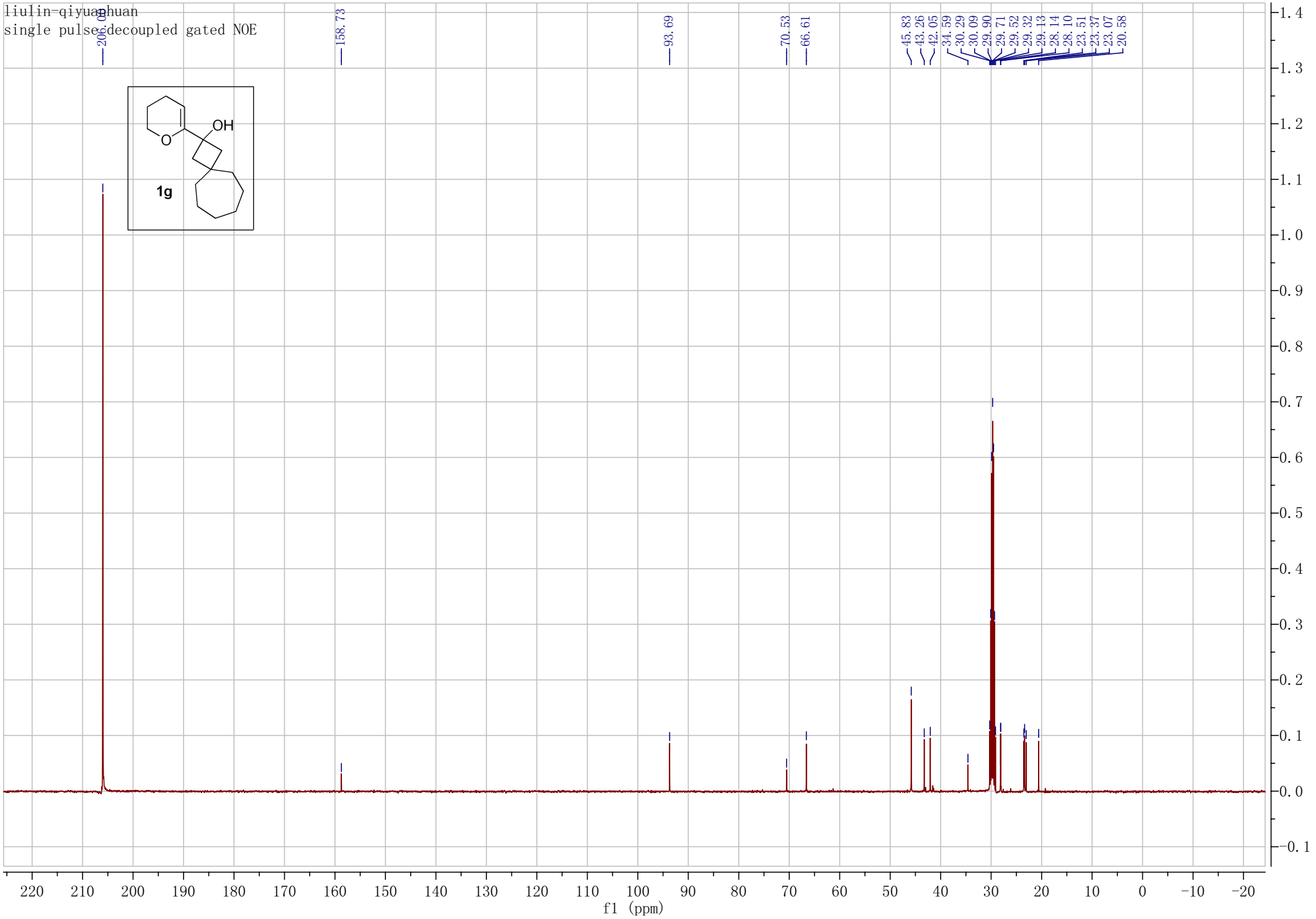
1.385
1.353



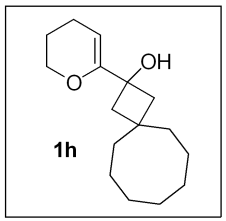

icon_5_LZH_LLin_20180613_S8
C13CPD Acetone {E:\data} ROOT 8
206.000
158.713
93.656
70.715
66.606
44.880
39.936
38.864
31.798
30.278
30.086
29.893
29.701
29.508
29.316
29.124
26.523
23.630
23.328
23.072
20.574
OH
O
1f
f1 (ppm)


liulin-qiyuanhuan
single_pulse
OH
O
1g
4.824
4.814
4.805
3.981
3.968
3.955
3.773
2.197
2.190
2.172
2.165
2.061
2.056
2.050
2.045
2.039
2.025
2.015
2.008
1.999
1.992
1.983
1.819
1.804
1.799
1.791
1.757
1.754
1.750
1.744
1.732
1.728
1.724
1.596
1.582
1.574
1.568
1.518
1.515
1.507
1.502
1.486
1.480
1.472
1.467
1.453
1.426
1.422
1.412
1.00
1.98
0.87
0.85
1.07
1.84
1.91
2.21
1.66
1.95
6.64
2.85
f1 (ppm)


liulin-qiyuanhuan
single pulse decoupled gated NOE
206.88
158.73
93.69
70.53
66.61
45.83
43.26
42.05
34.59
30.29
30.09
29.90
29.71
29.52
29.32
29.13
28.14
28.10
23.51
23.37
23.07
20.58
OH
O
1g
f1 (ppm)

icon_5_LZU_LLin_20180613_S10

PROTON Acetone {E:\data} ROOT 6

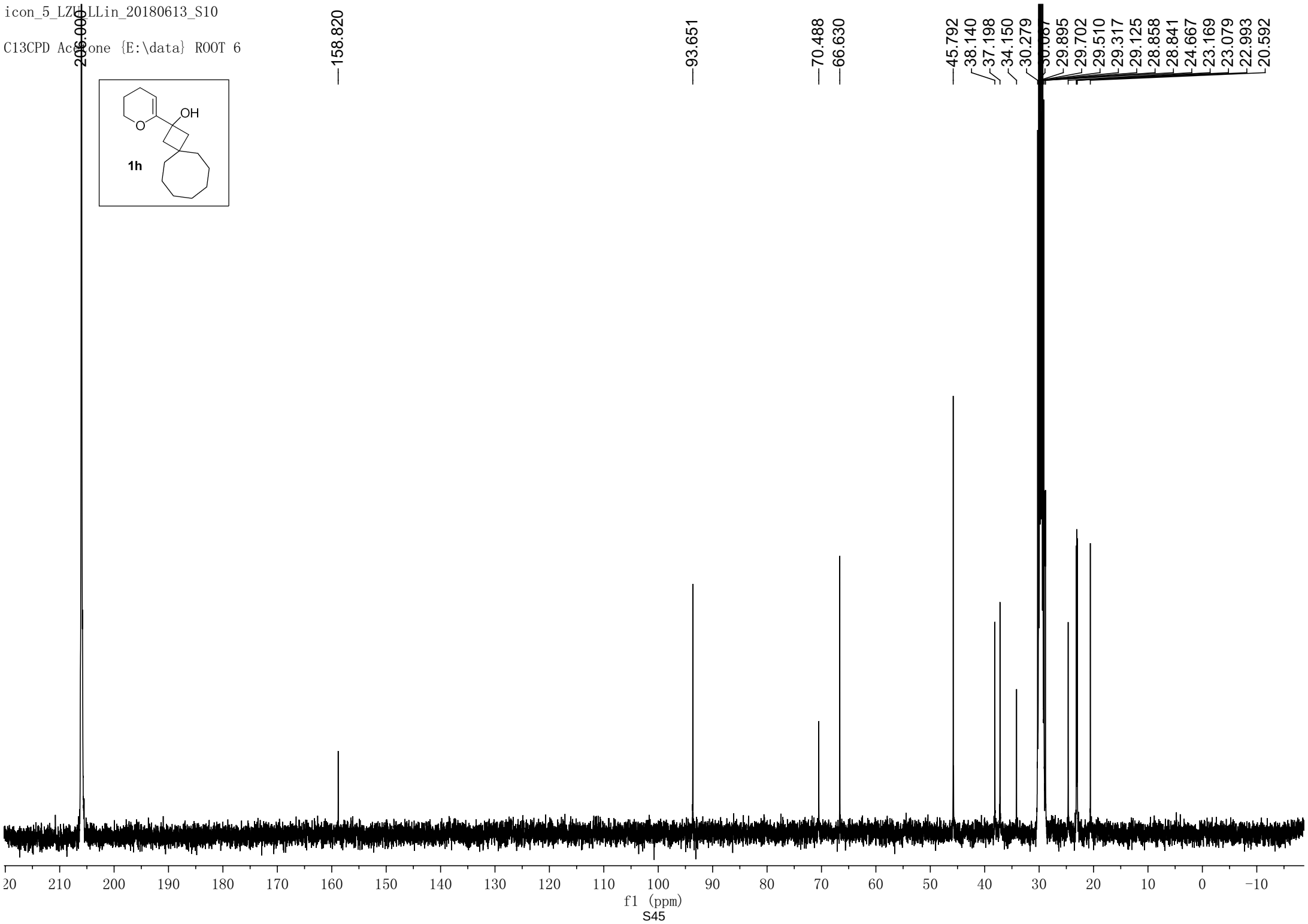


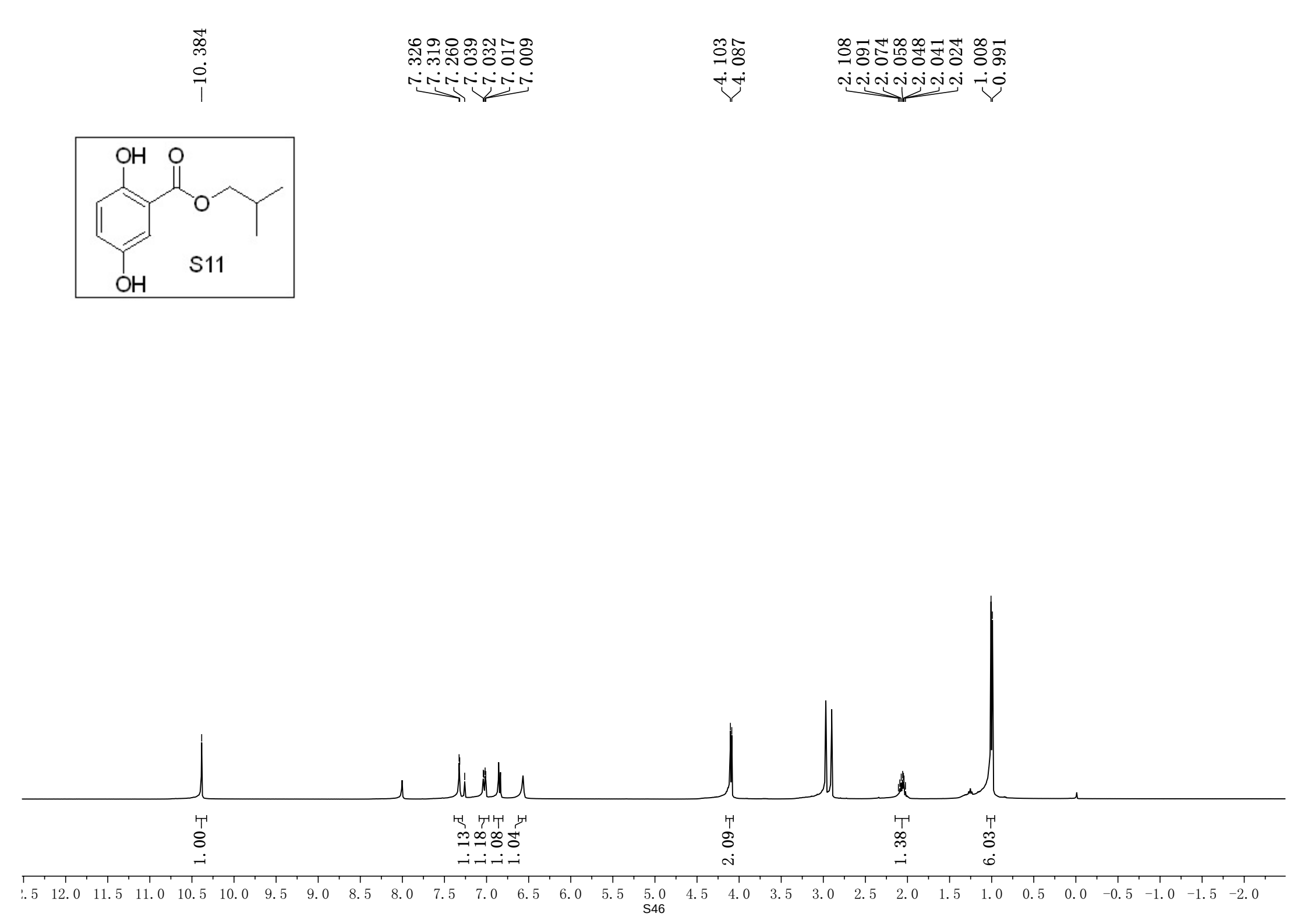
4.827 4.818 4.809 3.991 3.978 3.965 3.767 2.832 2.155 2.122 2.071 2.066 2.060 2.055 2.050 2.034 2.024 2.018 2.008 2.002 1.993 1.881 1.866 1.769 1.756 1.743 1.725 1.692 1.653 1.639 1.626 1.522 1.459

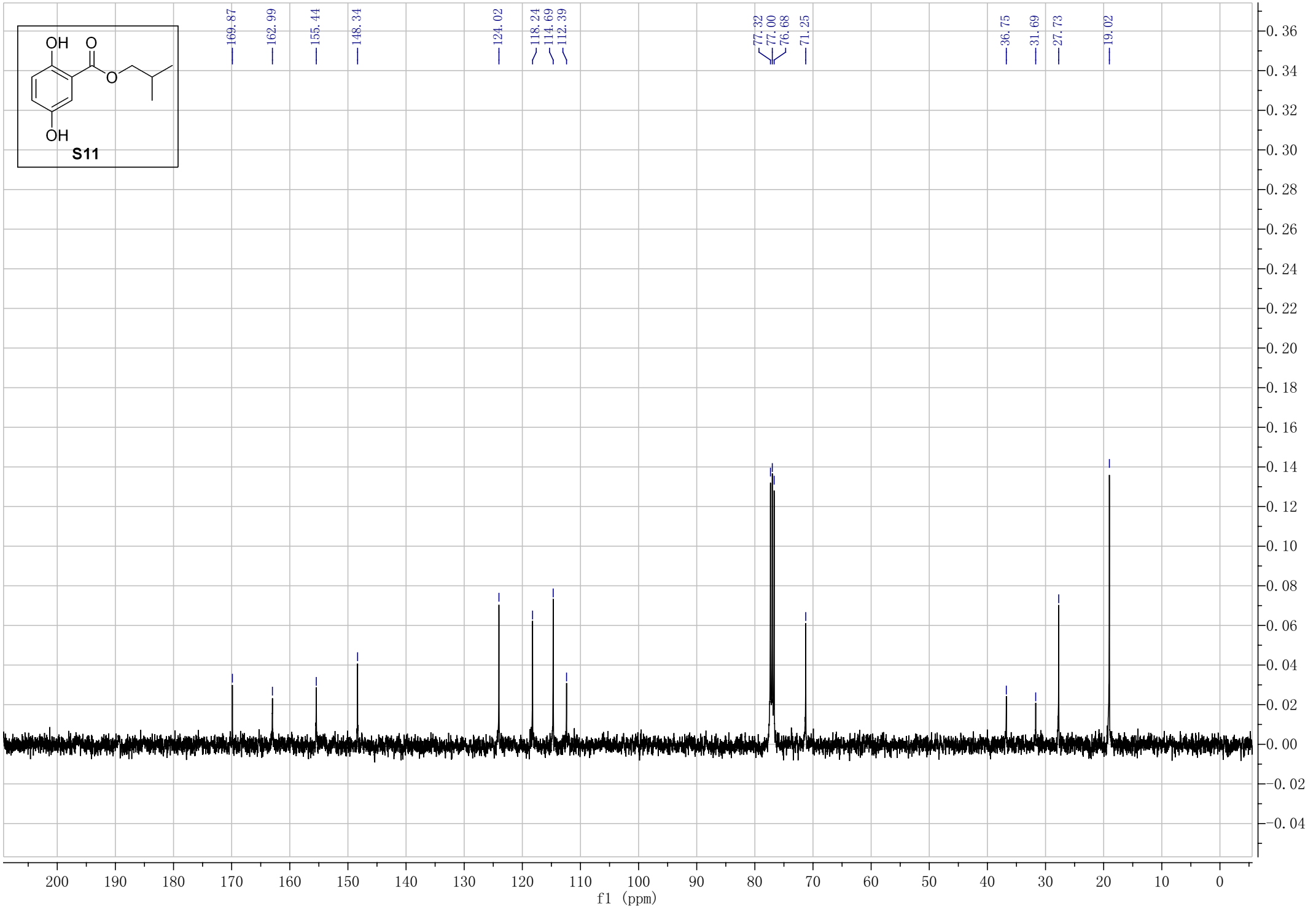
1.00 2.09 0.90 1.93 2.25 2.22 2.63 2.92 1.17 1.06 2.36 12.28

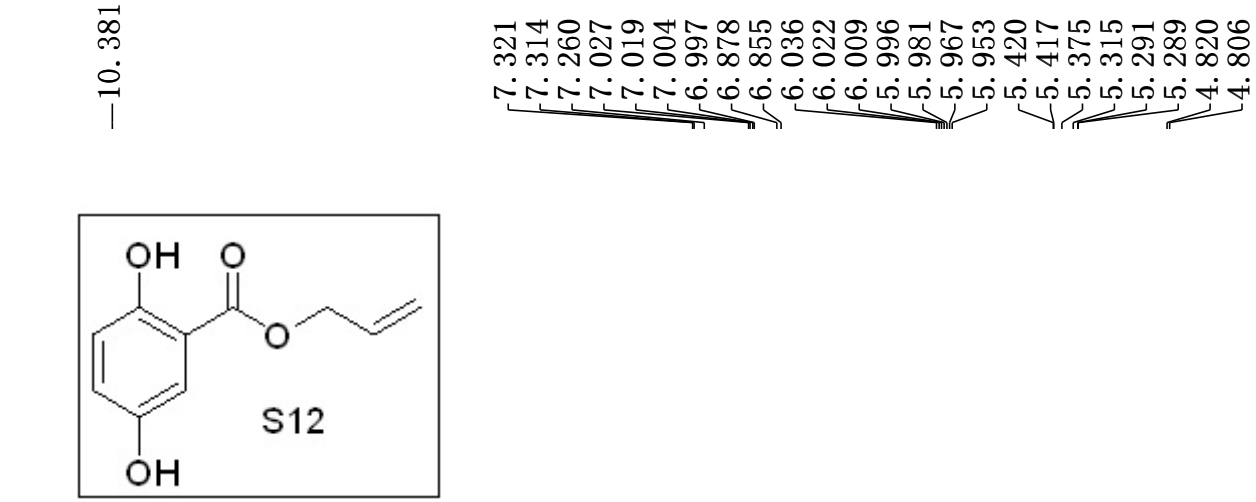
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

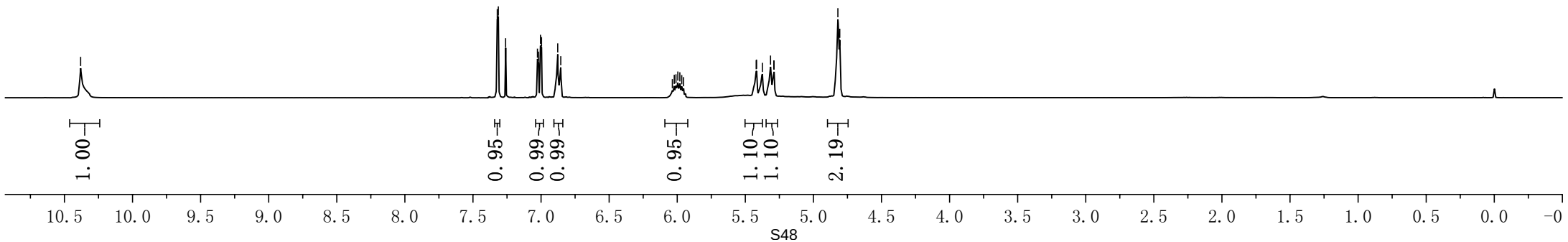
f1 (ppm)

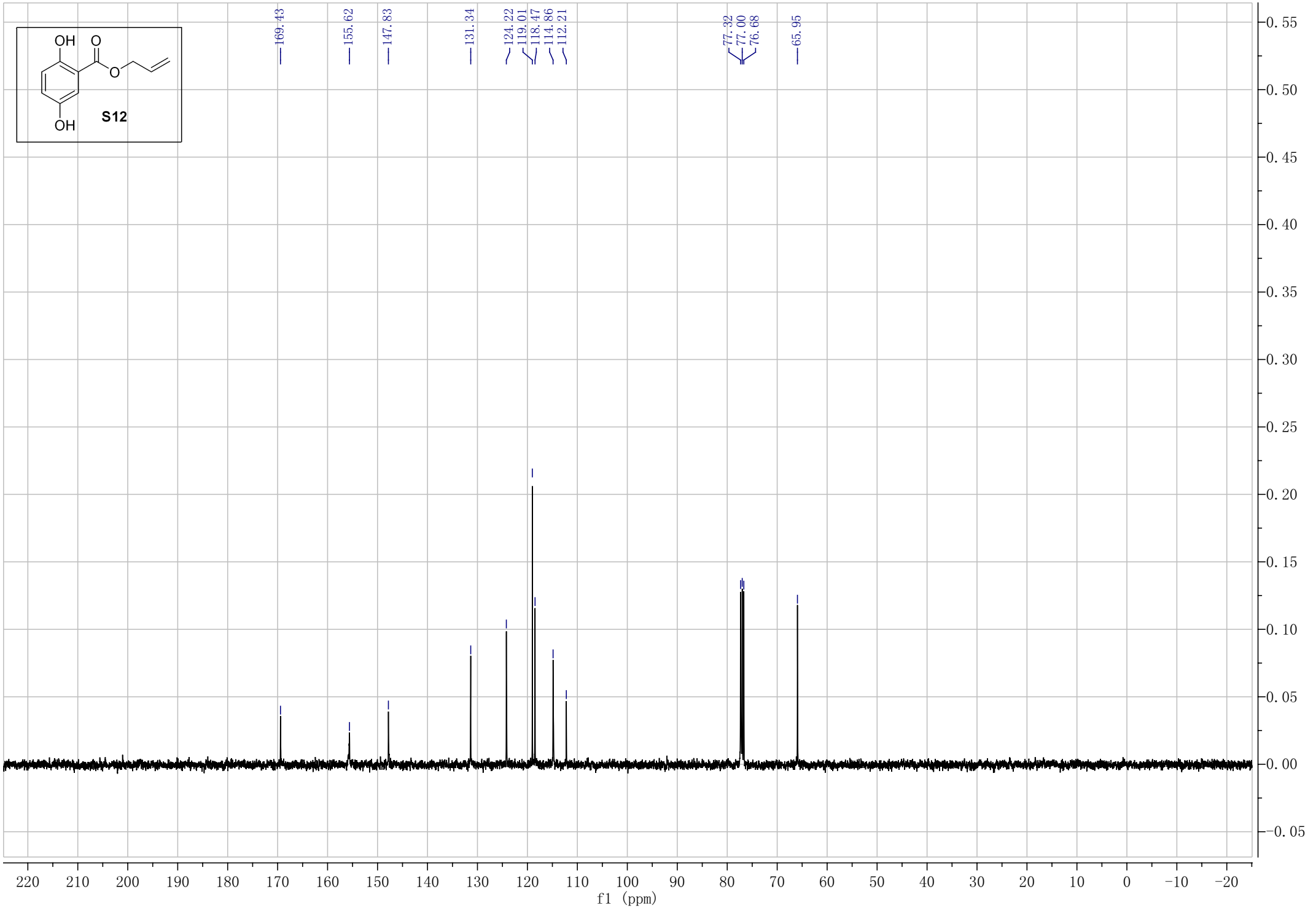

icon_5_LZG_LLin_20180613_S10
C13CPD Acetone {E:\data} ROOT 6
206.000
158.820
93.651
70.488
66.630
45.792
38.140
37.198
34.150
30.279
30.067
29.895
29.702
29.510
29.317
29.125
28.858
28.841
24.667
23.169
23.079
22.993
20.592
OH
O
1h
f1 (ppm)

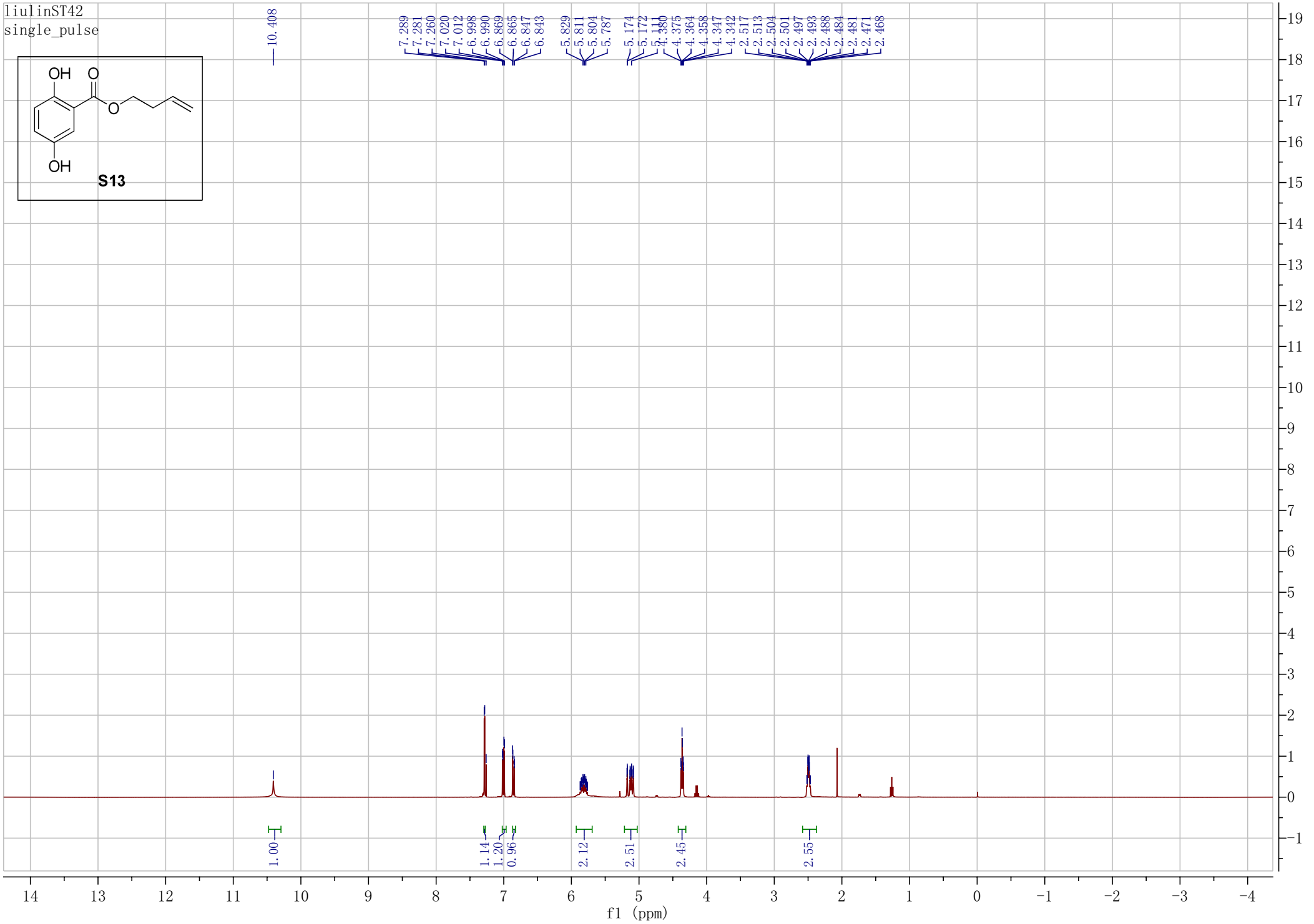

10.384
7.326
7.319
7.260
7.039
7.032
7.017
7.009
4.103
4.087
2.108
2.091
2.074
2.058
2.048
2.041
2.024
1.008
0.991
OH
O
O
OH
S11
1.00
1.13
1.18
1.08
1.04
2.09
1.38
6.03
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0

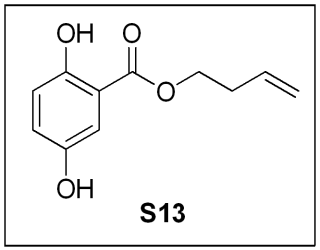

OH
O
O
OH
S11
169.87
162.99
155.44
148.34
124.02
118.24
114.69
112.39
77.32
77.00
76.68
71.25
36.75
31.69
27.73
19.02
f1 (ppm)


10.381
7.321
7.314
7.260
7.027
7.019
7.004
6.997
6.878
6.855
6.036
6.022
6.009
5.996
5.981
5.967
5.953
5.420
5.417
5.375
5.315
5.291
5.289
4.820
4.806
OH
O
O
S12
OH


1.00
0.95
0.99
0.99
0.95
1.10
1.10
2.19
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

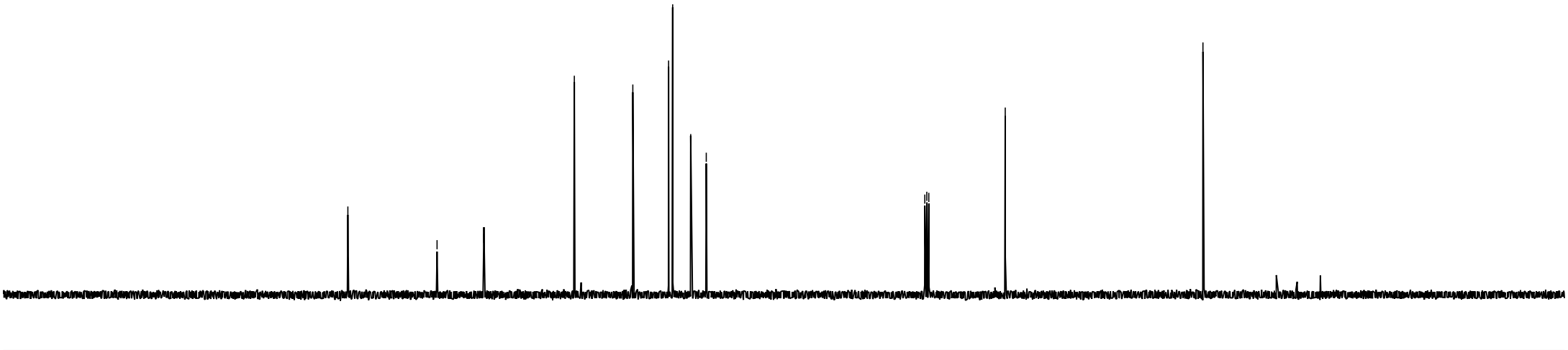

OH
O
O
OH
S12
169.43
155.62
147.83
131.34
124.22
119.01
118.47
114.86
112.21
77.32
77.00
76.68
65.95
f1 (ppm)


liulinST42
single_pulse
OH
O
O
OH
S13
10.408
7.289
7.281
7.260
7.020
7.012
6.998
6.990
6.869
6.865
6.847
6.843
5.829
5.811
5.804
5.787
5.174
5.172
4.375
4.364
4.358
4.347
4.342
2.517
2.513
2.504
2.501
2.497
2.493
2.488
2.484
2.481
2.471
2.468
1.00
1.14
1.20
0.96
2.12
2.51
2.45
2.55
f1 (ppm)

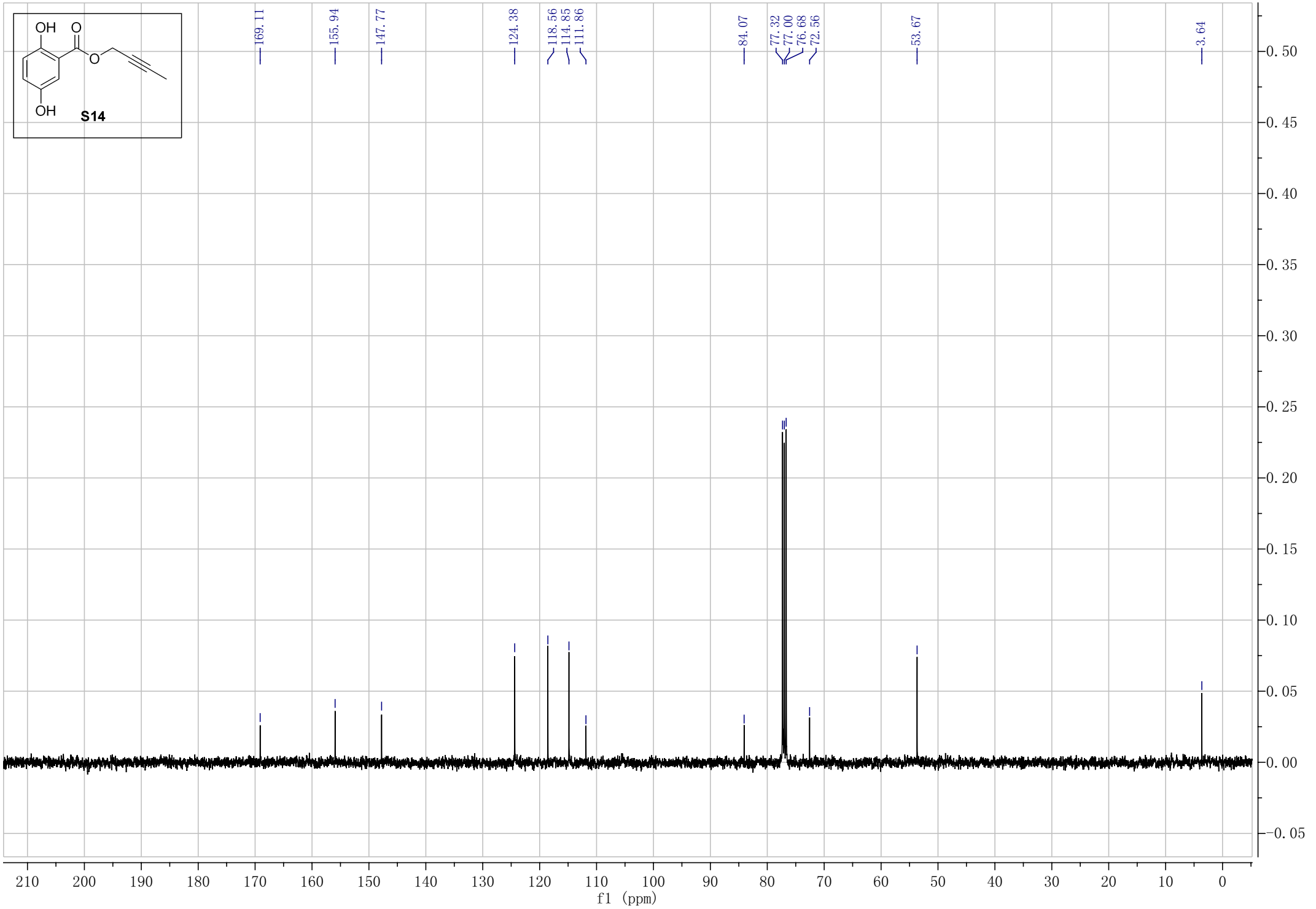


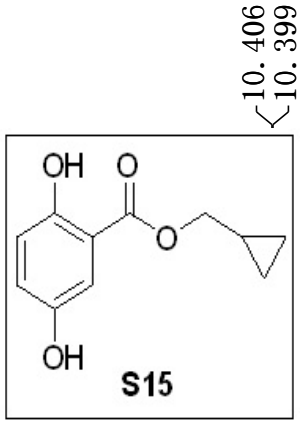
S13

169.665
155.391
147.912
133.420
124.056
118.331
117.678
114.791
112.301
77.320
77.001
76.682
64.447
32.803

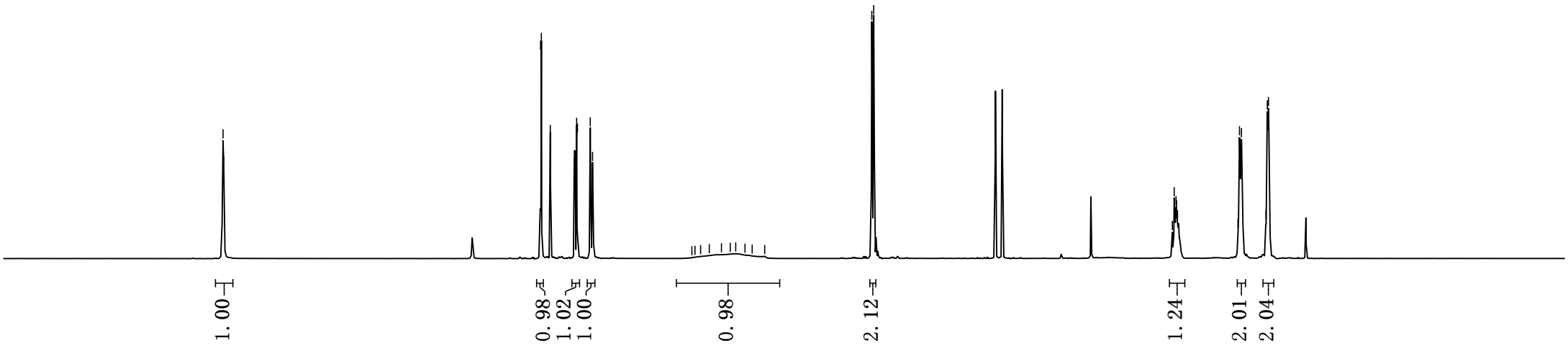


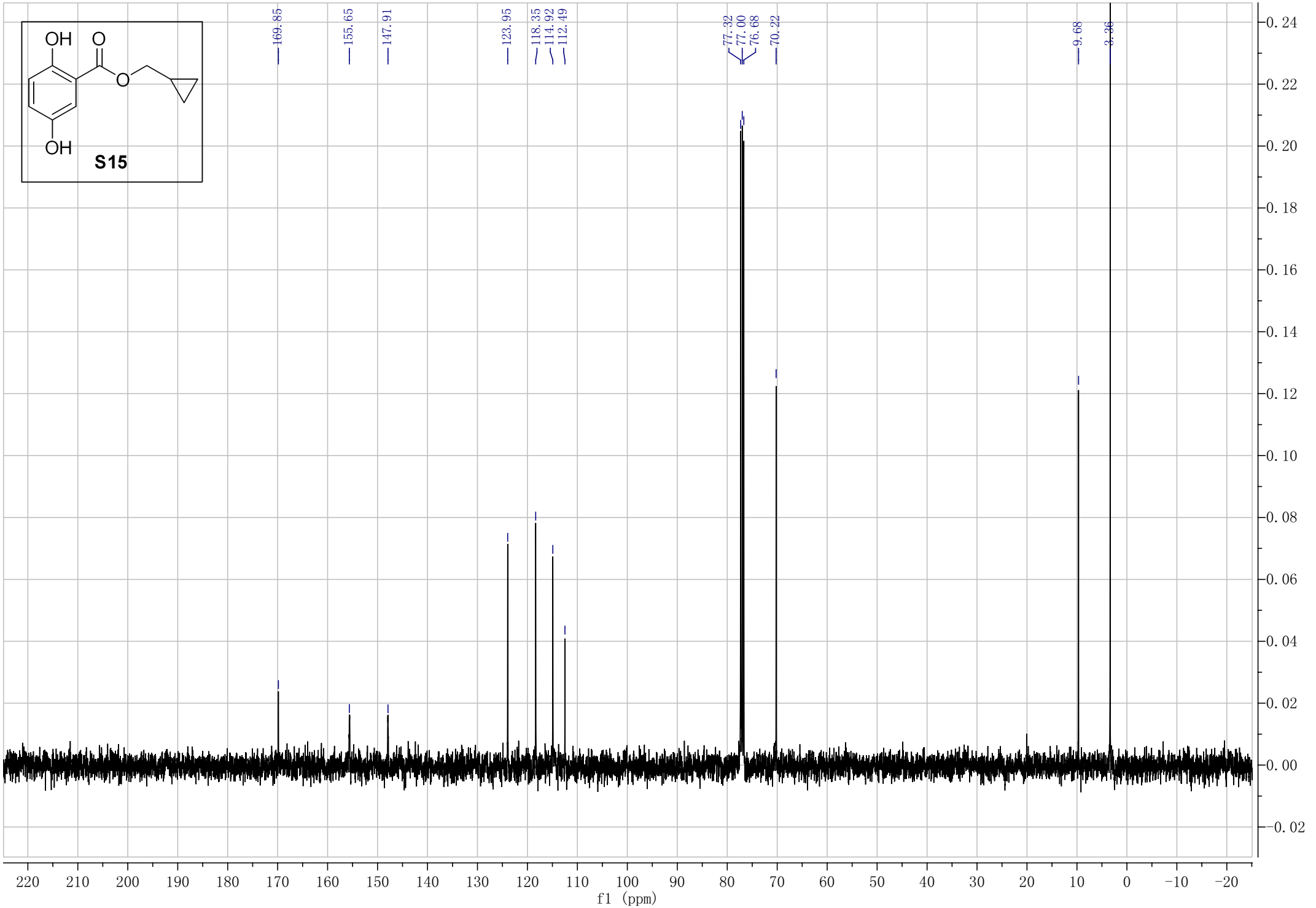

liulin22333-2
single_pulse
10.183
7.328
7.320
7.260
7.039
7.032
7.017
7.009
6.891
6.869
4.903
4.897
4.891
4.885
4.868
1.885
1.879
1.873
OH
O
O
OH
S14
1.00
1.17
1.20
1.09
3.42
3.09
f1 (ppm)

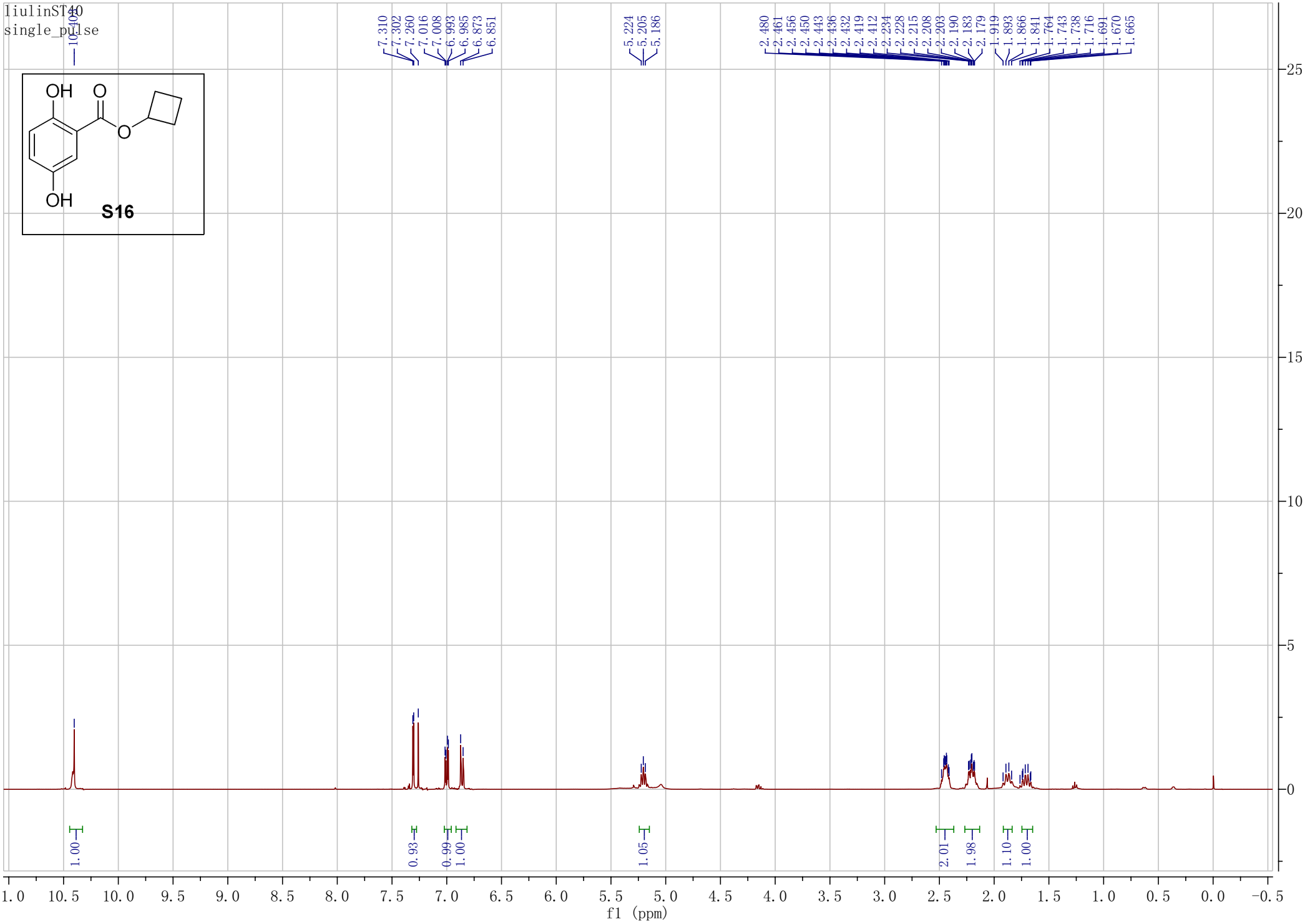

OH
O
O
OH
S14
169.11
155.94
147.77
124.38
118.56
114.85
111.86
84.07
77.32
77.00
76.68
72.56
53.67
3.64
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
−0.05
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

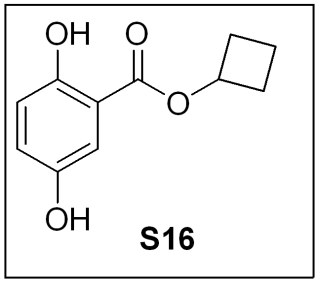


10.406
10.399
7.354
7.346
7.260
7.029
7.022
7.007
6.999
6.876
6.854
5.899
5.869
5.815
5.732
5.615
5.530
5.478
5.388
5.319
5.199
4.170
4.151
1.280
1.262
1.244
1.240
1.231
0.650
0.635
0.616
0.381
0.367
0.356

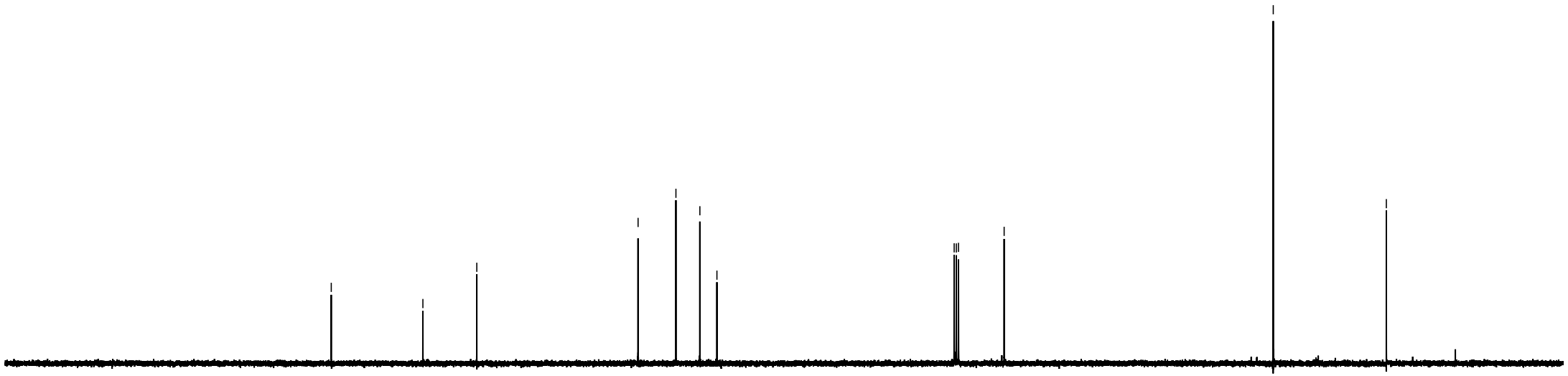


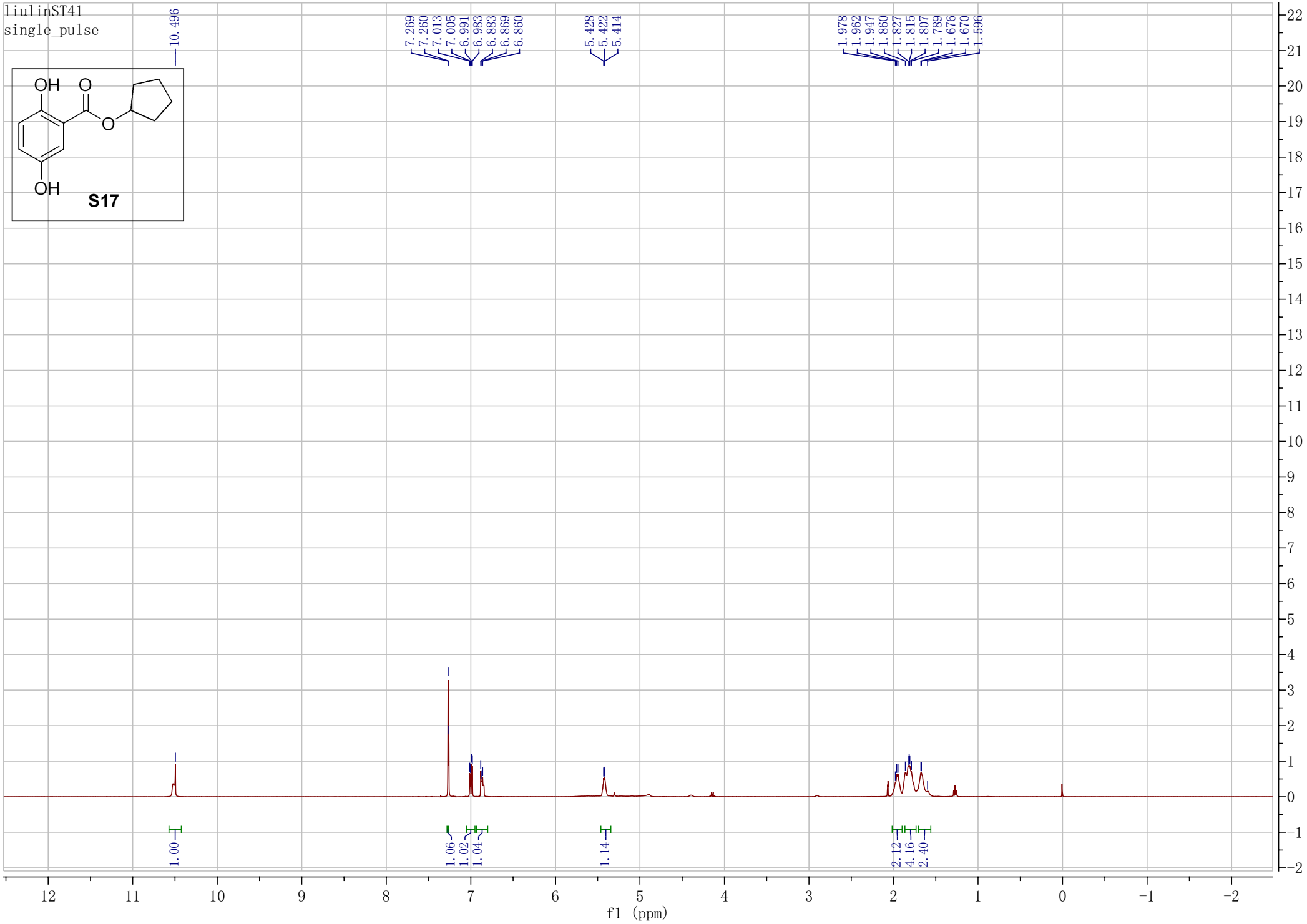

OH
O
O
OH
S15
169.85
155.65
147.91
123.95
118.35
114.92
112.49
77.32
77.00
76.68
70.22
9.68
3.36
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

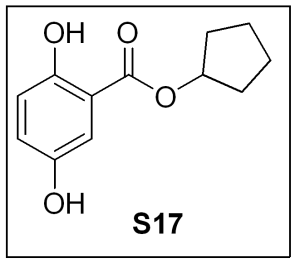

liulinST40
single_pulse
10.446
7.310
7.302
7.260
7.016
7.008
6.993
6.985
6.873
6.851
5.224
5.205
5.186
2.480
2.461
2.456
2.450
2.443
2.436
2.432
2.419
2.412
2.234
2.228
2.215
2.208
2.203
2.190
2.183
2.179
1.919
1.893
1.866
1.841
1.764
1.743
1.738
1.716
1.691
1.670
1.665
OH
O
O
OH
S16
1.00
0.93
0.99
1.00
1.05
2.01
1.98
1.10
1.00
f1 (ppm)



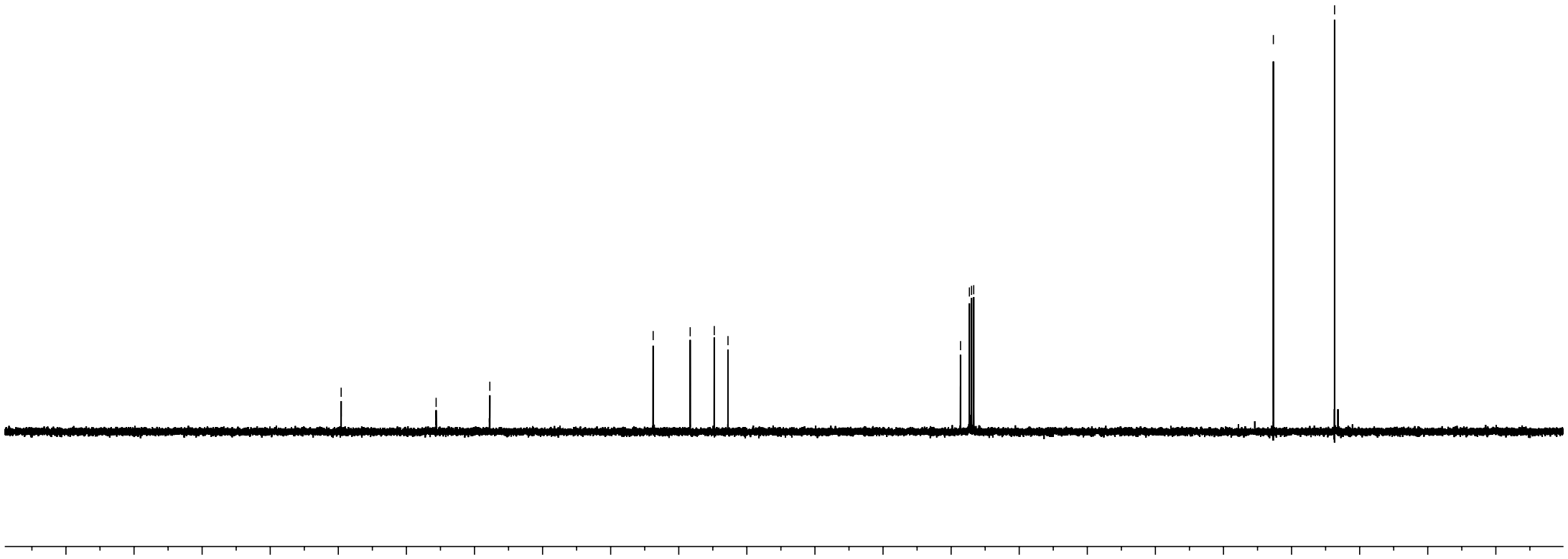
169.242
155.720
147.765
123.965
118.379
114.846
112.329
77.318
77.000
76.682
69.944
30.231
13.542



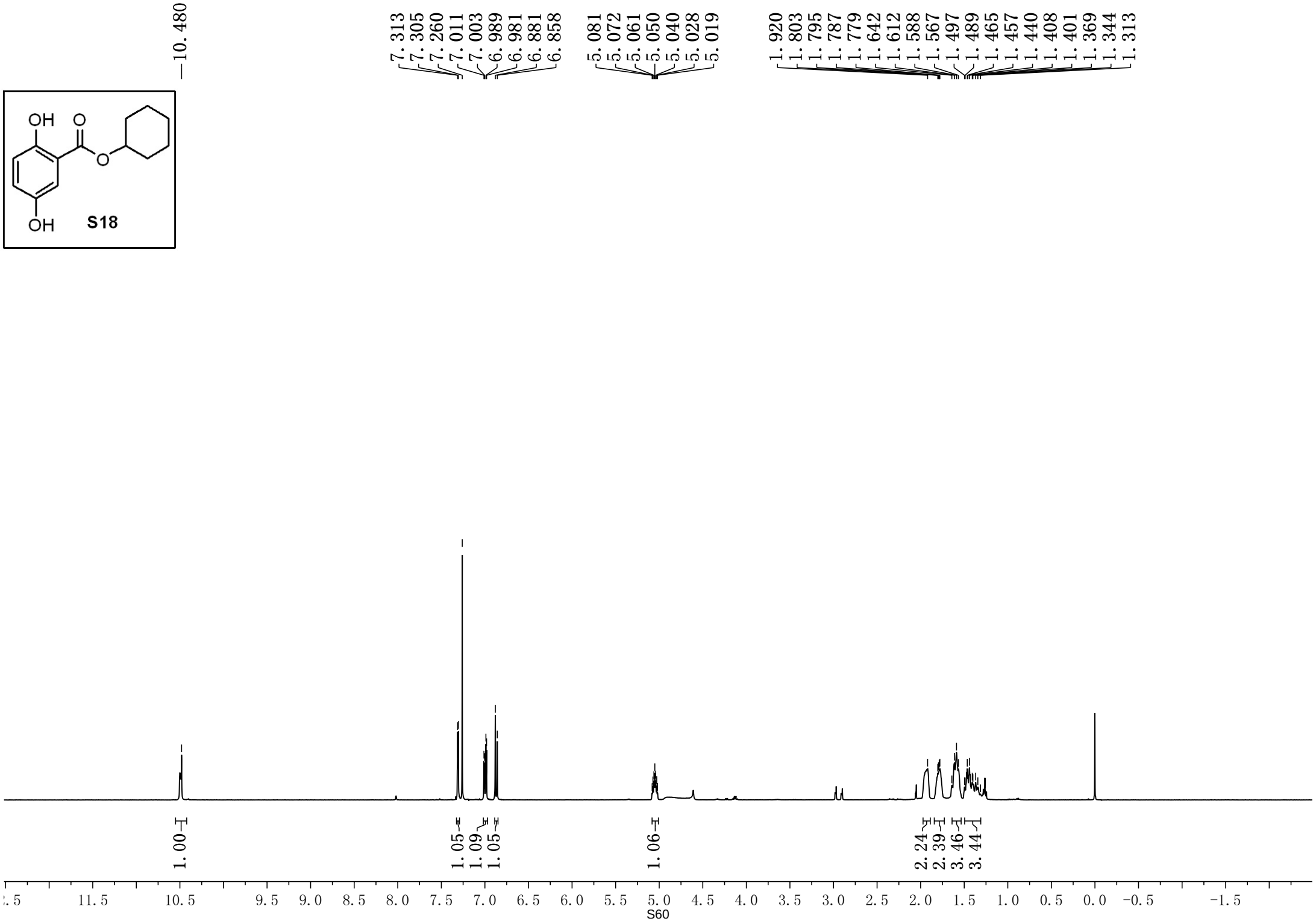

liulinST41
single_pulse
10.496
7.269
7.260
7.013
7.005
6.991
6.983
6.883
6.869
6.860
5.428
5.422
5.414
1.978
1.962
1.947
1.860
1.827
1.815
1.807
1.789
1.676
1.670
1.596
OH
O
O
OH
S17
1.00
1.06
1.02
1.04
1.14
2.12
4.16
2.40
f1 (ppm)



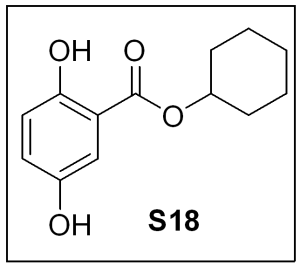
169.583
155.635
147.749
123.760
118.323
114.795
114.787
112.771
78.620
77.318
77.000
76.682
32.676
23.684



OH
O
O
OH
S18

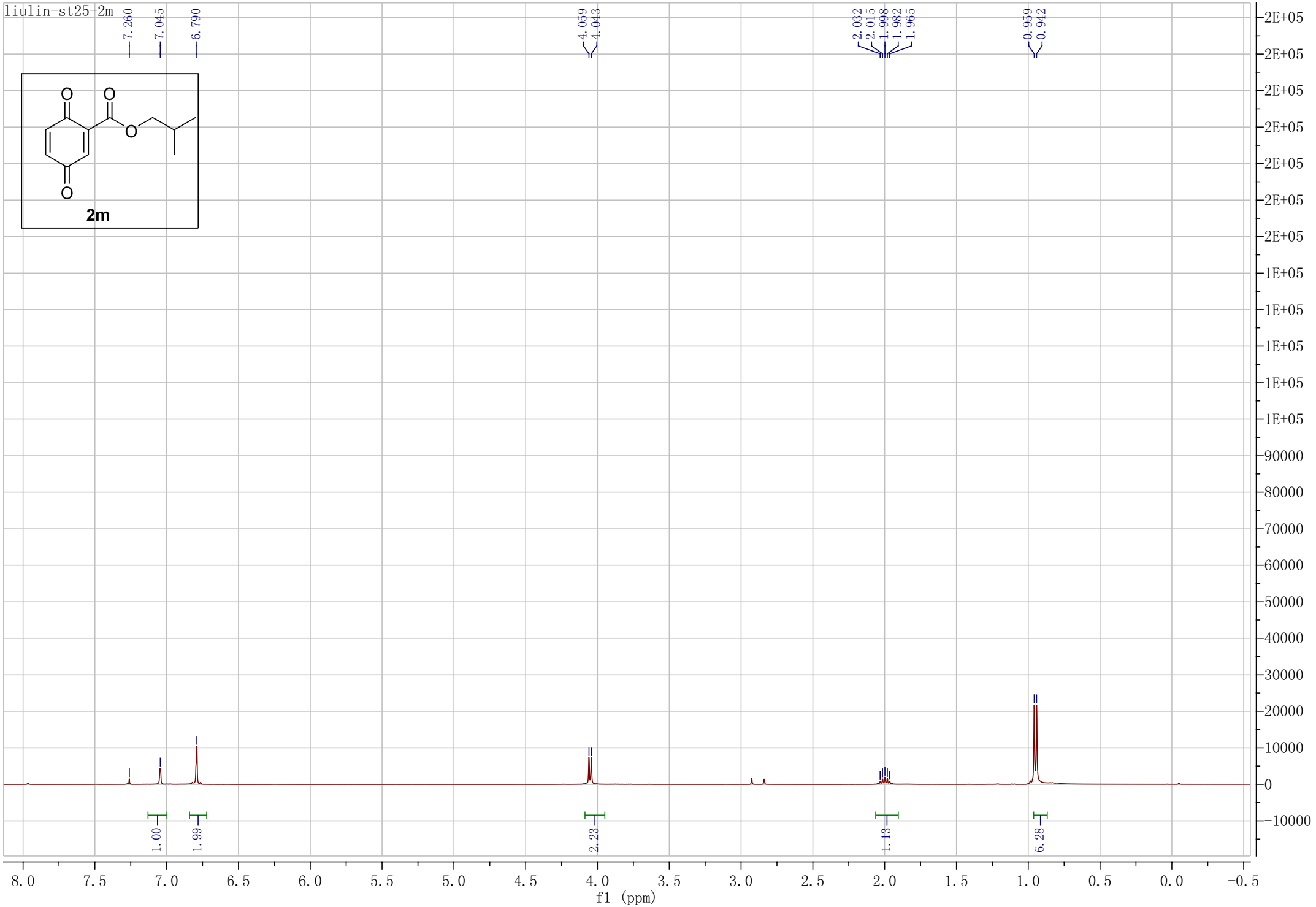

10.480
7.313
7.305
7.260
7.011
7.003
6.989
6.981
6.881
6.858
5.081
5.072
5.061
5.050
5.040
5.028
5.019
1.920
1.803
1.795
1.787
1.779
1.642
1.612
1.588
1.567
1.497
1.489
1.465
1.457
1.440
1.408
1.401
1.369
1.344
1.313
1.00
1.05
1.09
1.05
1.06
2.24
2.39
3.46
3.44
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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
-1.5

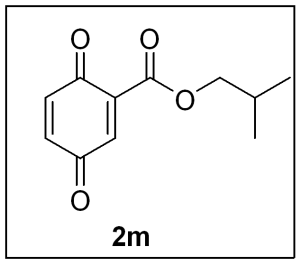
liulin2133-5/12



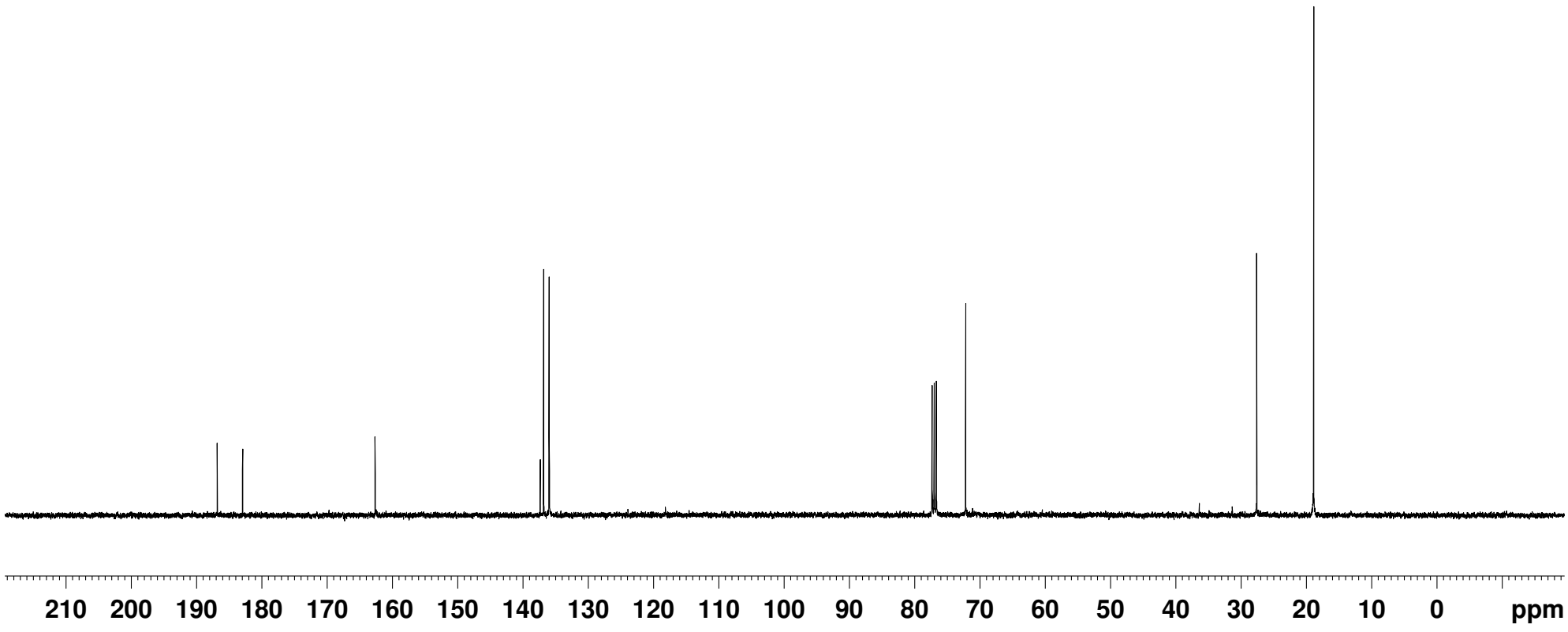
169.18
155.88
147.64
123.74
118.41
114.83
112.90
77.32
77.00
76.68
73.94
31.47
25.34
23.52

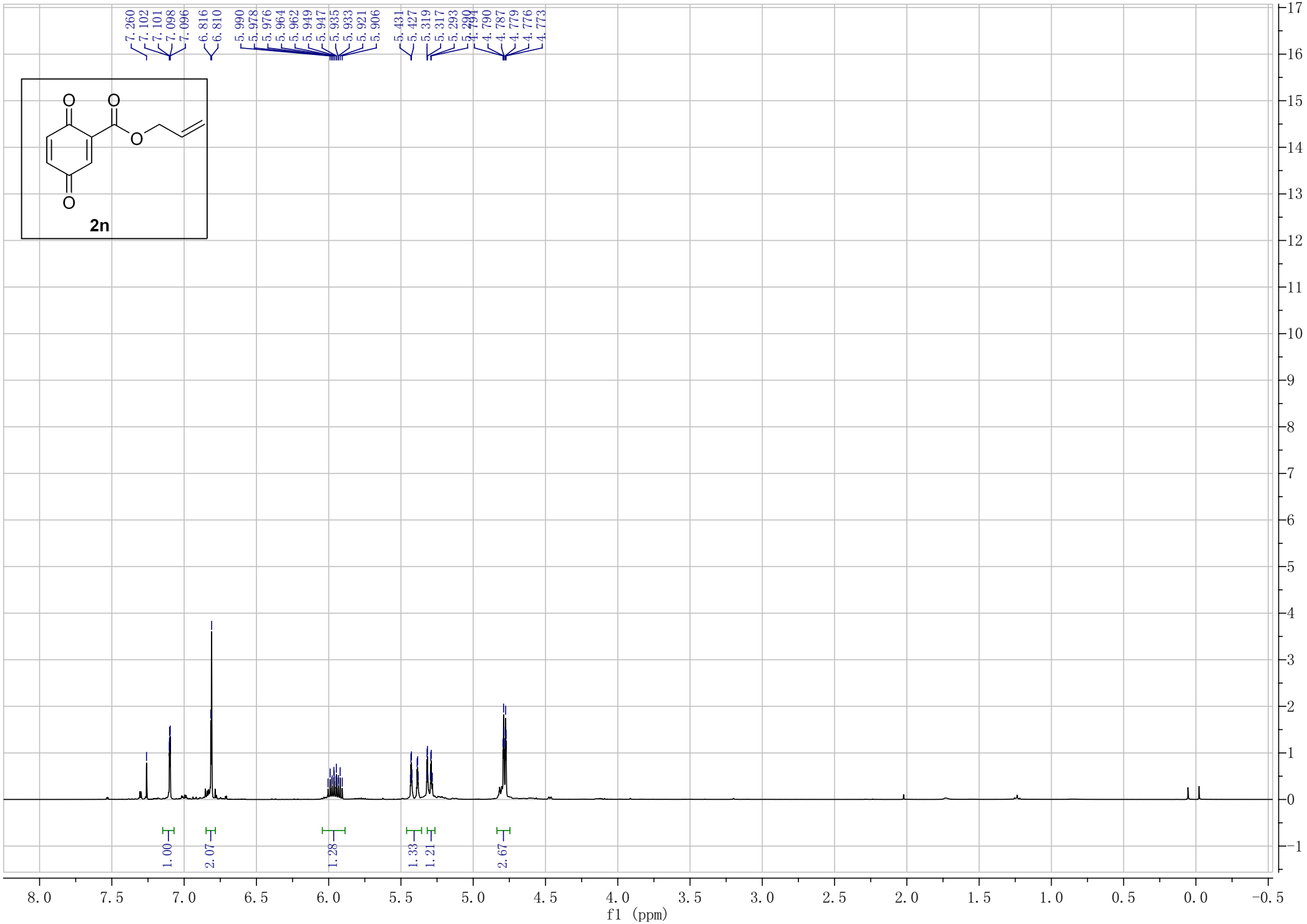
f1 (ppm)


liulin-st25-2m
7.260
7.045
6.790
4.059
4.043
2.032
2.015
1.998
1.982
1.965
0.959
0.942
2m
1.00
1.99
2.23
1.13
6.28
f1 (ppm)

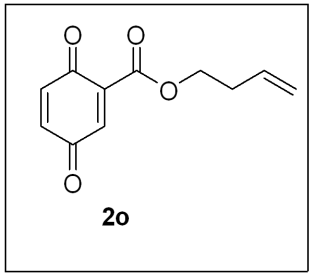


186.85
182.94
162.64
137.36
136.82
136.00
135.96
77.32
77.00
76.68
72.17
27.59
18.85




7.260
7.102
7.101
7.098
7.096
6.816
6.810
5.990
5.978
5.976
5.964
5.962
5.949
5.947
5.935
5.933
5.921
5.906
5.431
5.427
5.319
5.317
5.293
5.290
4.791
4.790
4.787
4.779
4.776
4.773
O
O
O
O
2n
1.00
2.07
1.28
1.33
1.21
2.67
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

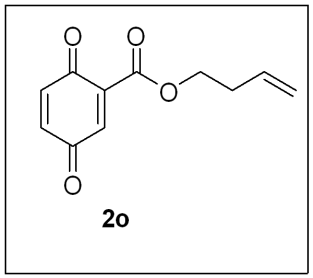

liulinst23
single pulse decoupled gated NOE
186.79
182.88
162.28
137.05
136.89
136.36
136.09
130.87
119.50
77.32
77.00
76.68
66.72
2n
f1 (ppm)



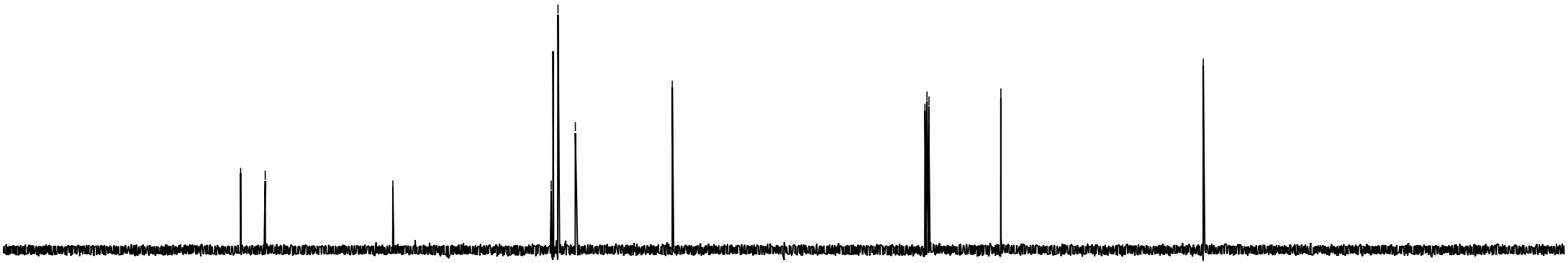
7.260
7.054
6.807
6.803
5.847
5.830
5.820
5.804
5.787
5.778
5.762
5.745
5.159
5.115
5.113
5.086
4.359
4.347
4.342
4.331
4.326
2.496
2.494
2.480
2.463
2.446

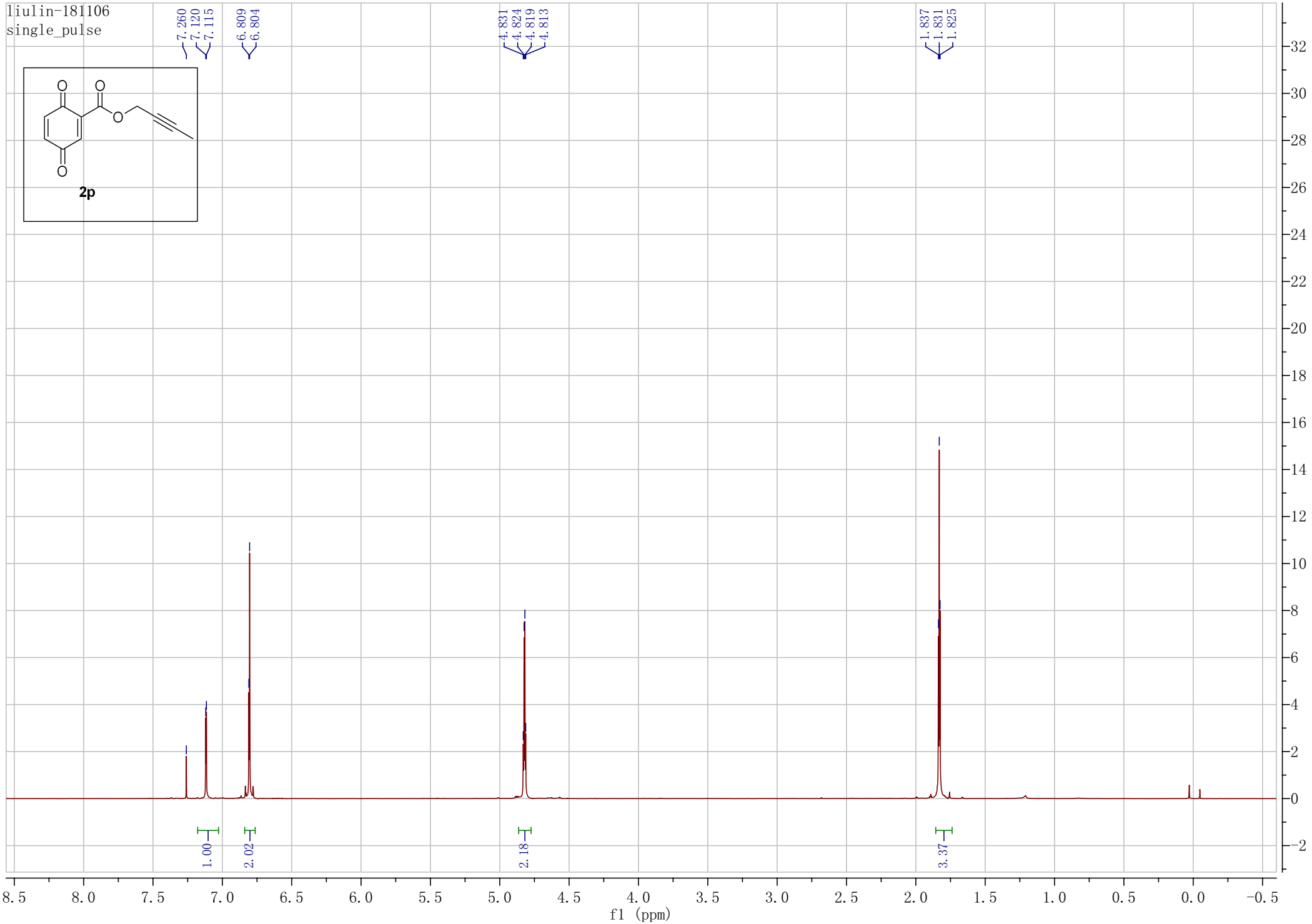
1.00
1.99
1.01
2.12
2.09
2.14

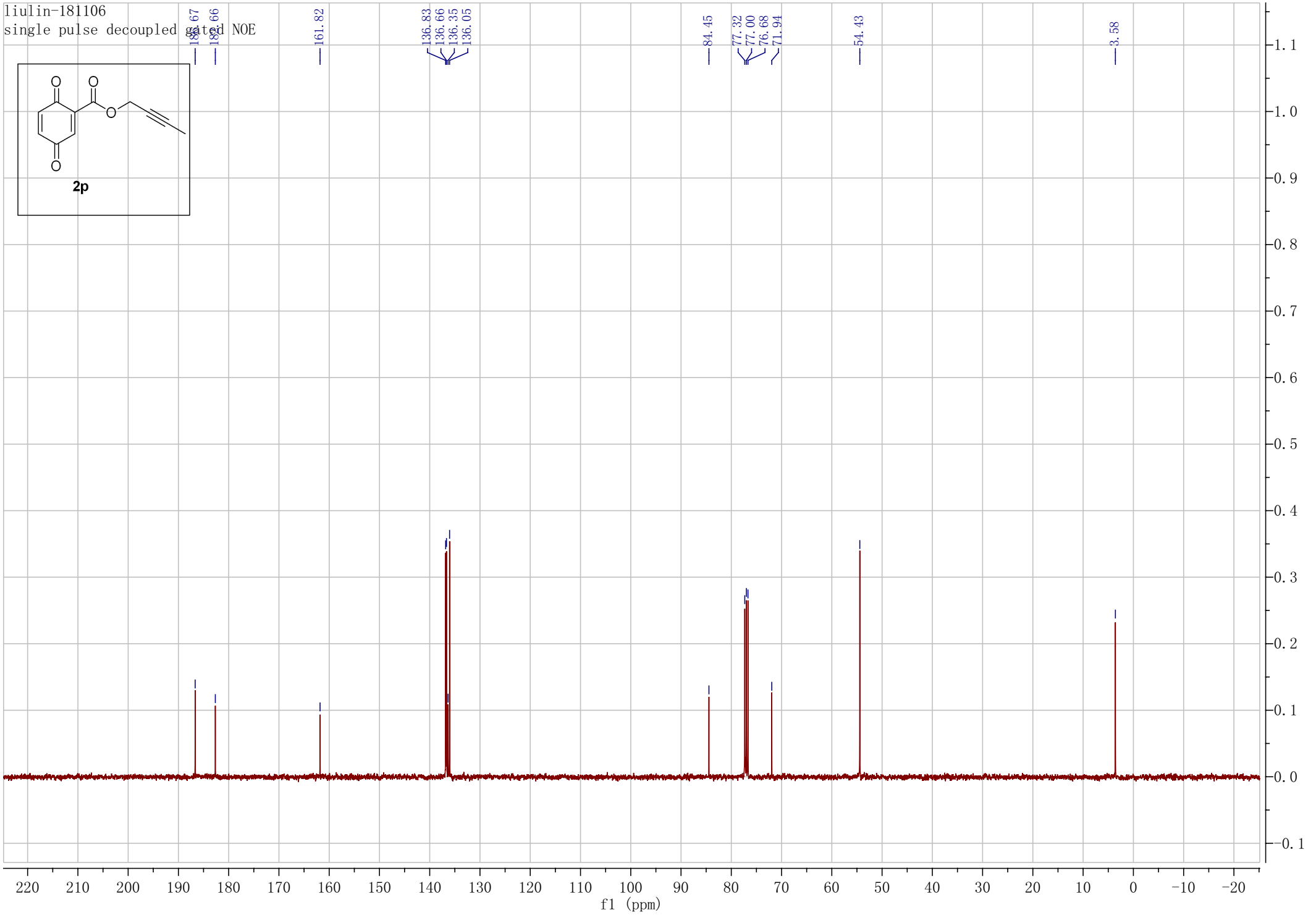
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

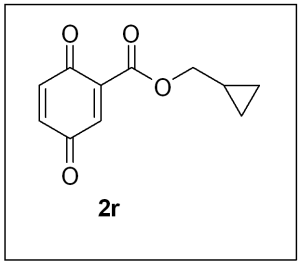


186.856
182.922
162.494
137.152
136.855
136.853
136.060
133.286
117.769
77.318
77.000
76.681
65.177
32.780




liulin-181106
single_pulse
7.260
7.120
7.115
6.809
6.804
4.831
4.824
4.819
4.813
1.837
1.831
1.825
2p
1.00
2.02
2.18
3.37
f1 (ppm)

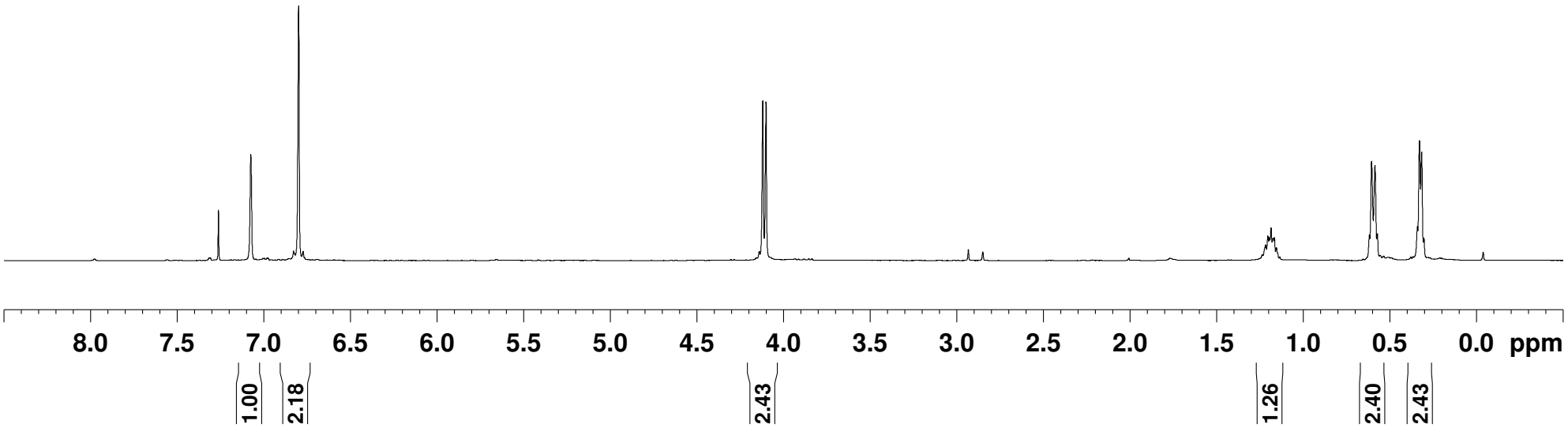

liulin-181106
single pulse decoupled gated NOE
188.67
182.66
161.82
136.83
136.66
136.35
136.05
84.45
77.32
77.00
76.68
71.94
54.43
3.58
2p
f1 (ppm)

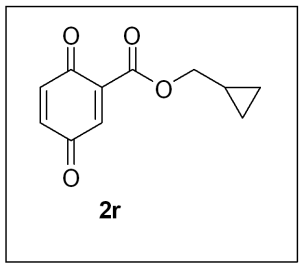


7.260
7.074
6.800

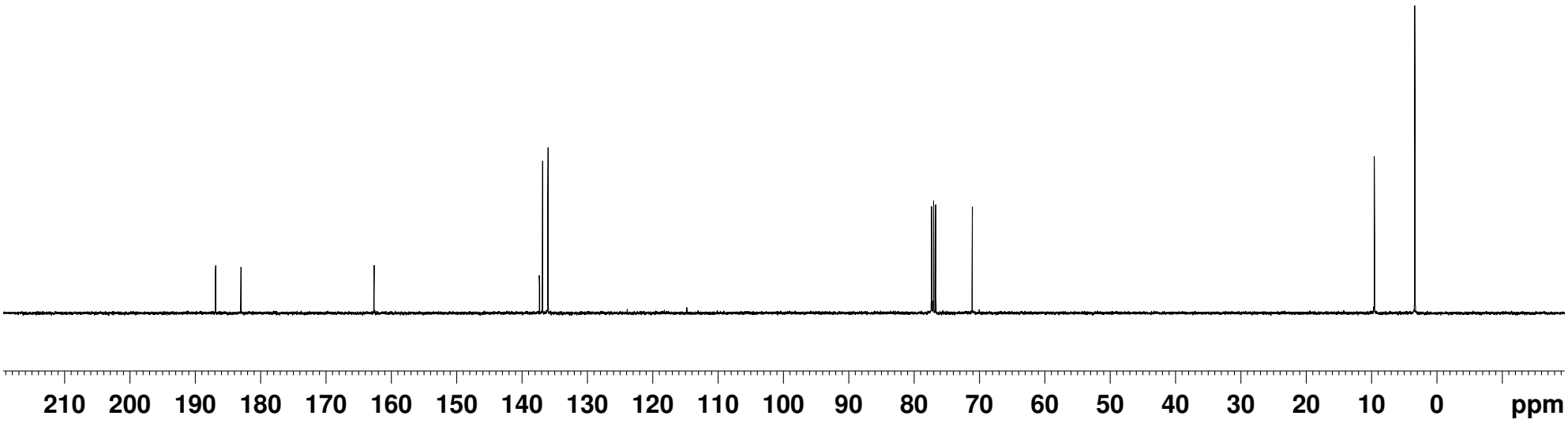
4.120
4.102

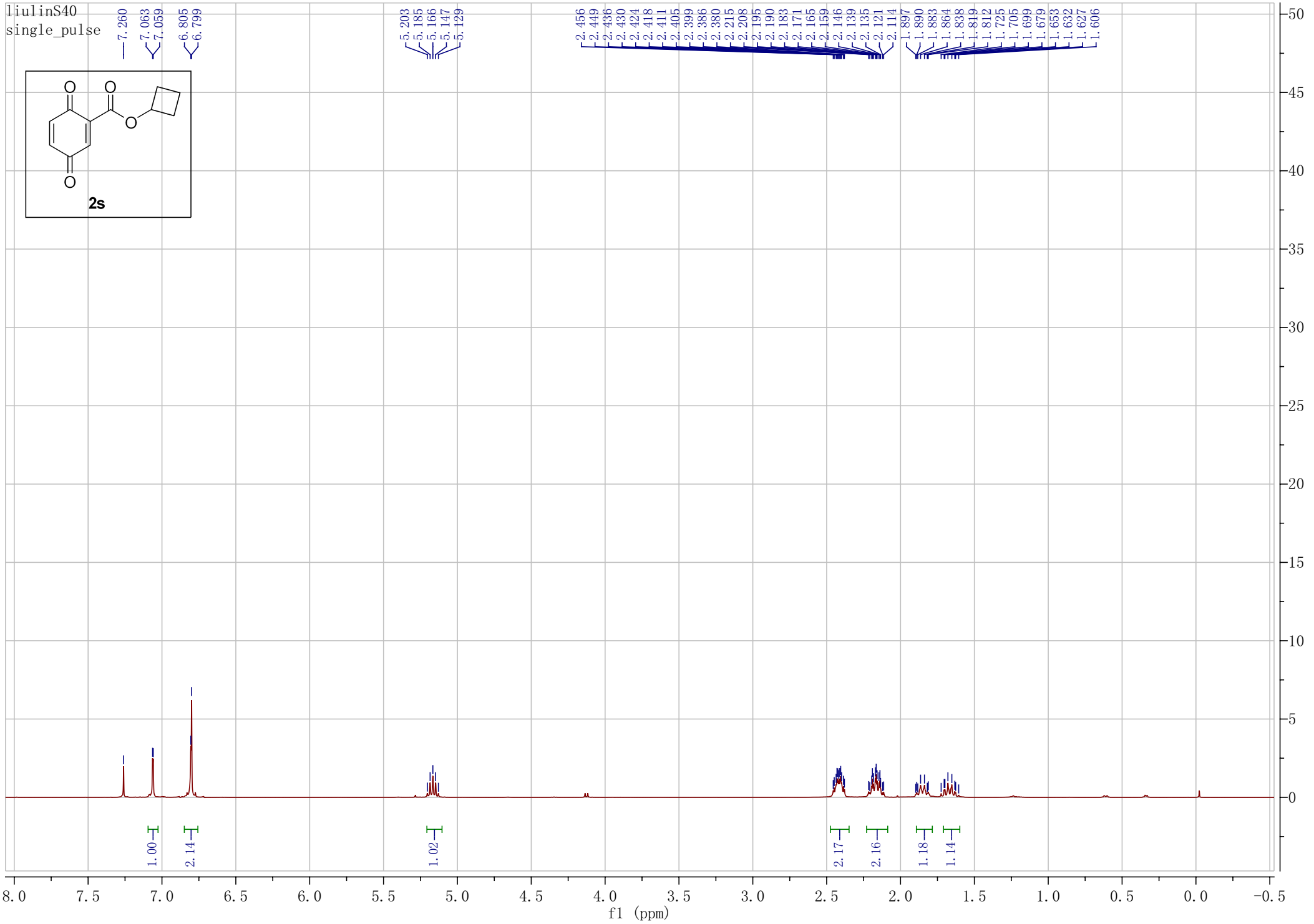
1.217
1.205
1.197
1.186
1.175
1.167
1.155
0.619
0.605
0.586
0.572
0.341
0.329
0.317
0.303

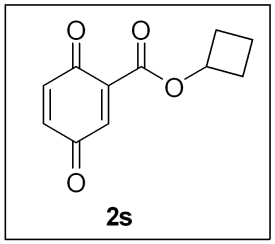




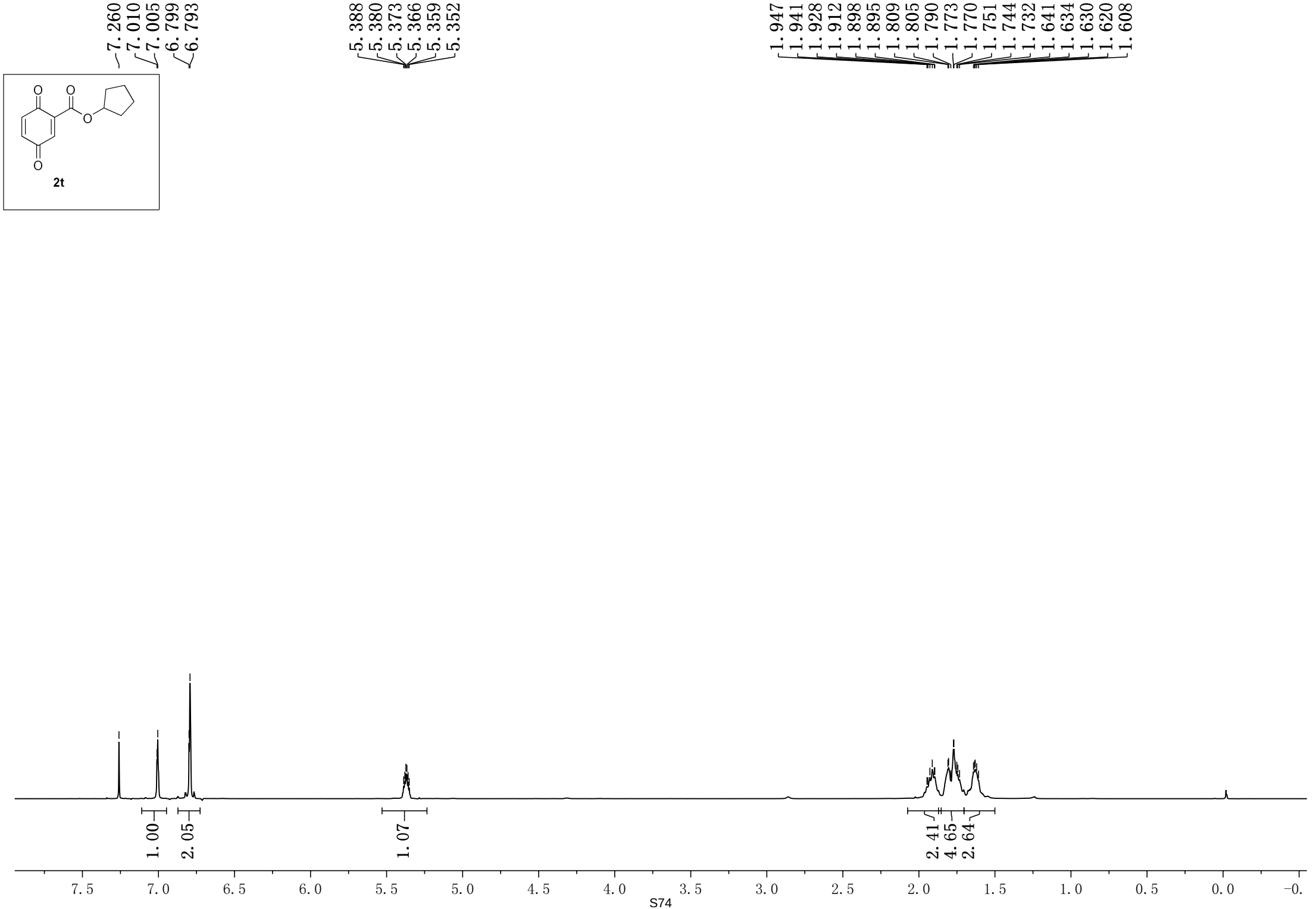
186.90
183.00
162.64
137.32
136.84
136.02
135.99
77.32
77.00
76.68
71.09
9.54
3.35

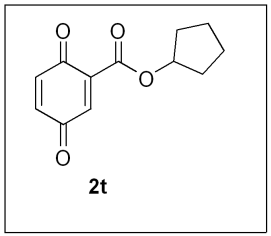



liulinS40
single_pulse
7.260
7.063
7.059
6.805
6.799
5.203
5.185
5.166
5.147
5.129
2.456
2.449
2.436
2.430
2.424
2.418
2.411
2.405
2.399
2.386
2.380
2.215
2.208
2.195
2.190
2.183
2.171
2.165
2.159
2.146
2.139
2.135
2.121
2.114
1.897
1.890
1.883
1.864
1.838
1.819
1.812
1.725
1.705
1.699
1.679
1.653
1.632
1.627
1.606
2s
1.00
2.14
1.02
2.17
2.16
1.18
1.14
f1 (ppm)

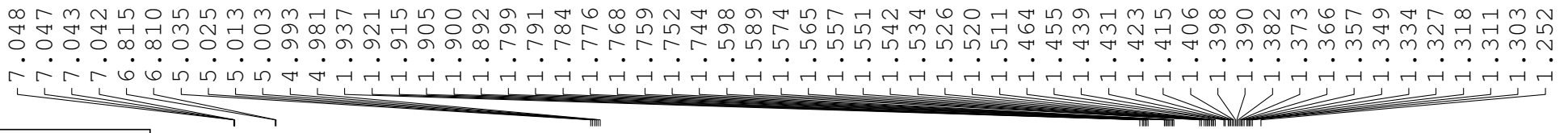


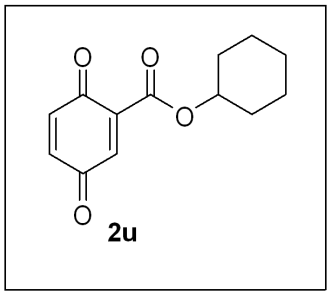
186.913
183.031
161.867
137.172
136.862
136.038
136.022
77.318
77.000
76.682
70.721
30.160
13.477

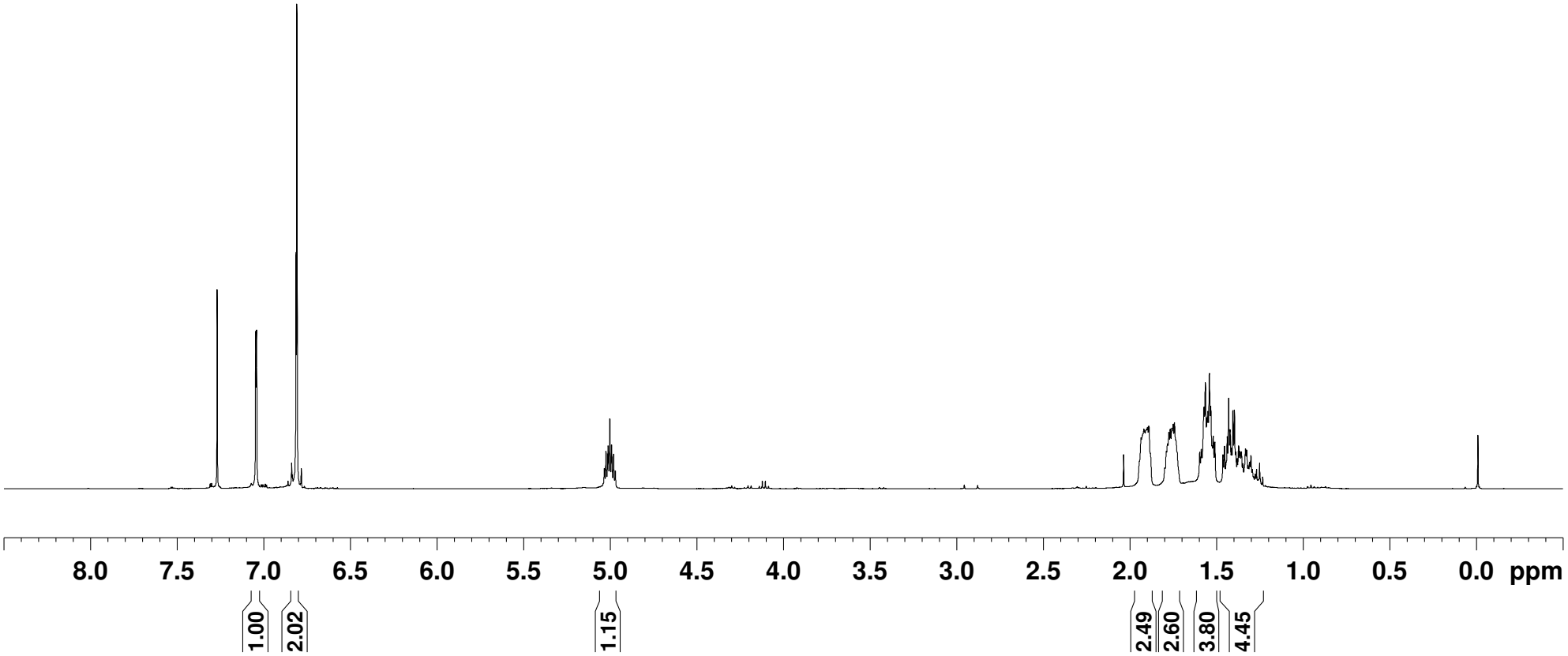

7.260
7.010
7.005
6.799
6.793
5.388
5.380
5.373
5.366
5.359
5.352
1.947
1.941
1.928
1.912
1.898
1.895
1.809
1.805
1.790
1.773
1.770
1.751
1.744
1.732
1.641
1.634
1.630
1.620
1.608
2t
1.00
2.05
1.07
2.41
4.65
2.64
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.

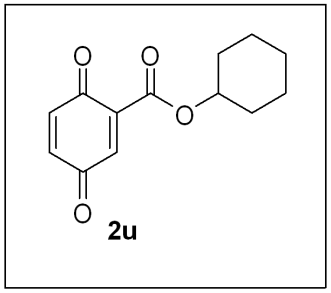


186.992
183.129
162.407
137.720
136.825
136.025
135.597
79.626
77.318
77.000
76.681
32.617
23.611

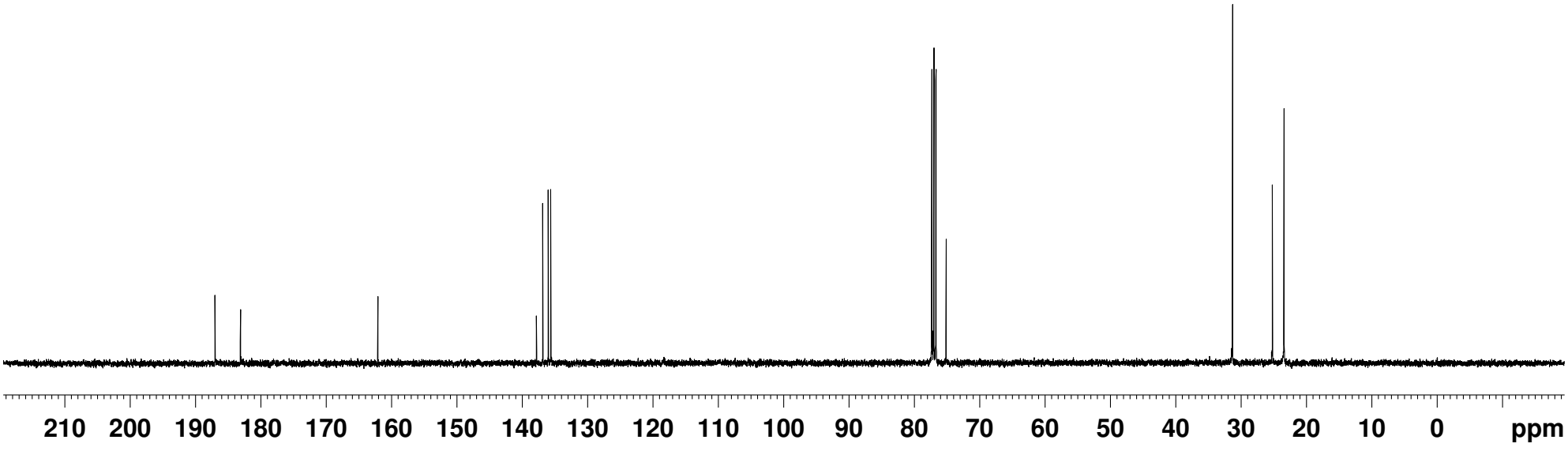

7.048
7.047
7.043
7.042
6.815
6.810
5.035
5.025
5.013
5.003
4.993
4.981
1.937
1.921
1.915
1.905
1.900
1.892
1.799
1.791
1.784
1.776
1.768
1.759
1.752
1.744
1.598
1.589
1.574
1.565
1.557
1.551
1.542
1.534
1.526
1.520
1.511
1.464
1.455
1.439
1.431
1.423
1.415
1.406
1.398
1.390
1.382
1.373
1.366
1.357
1.349
1.334
1.327
1.318
1.311
1.303
1.252

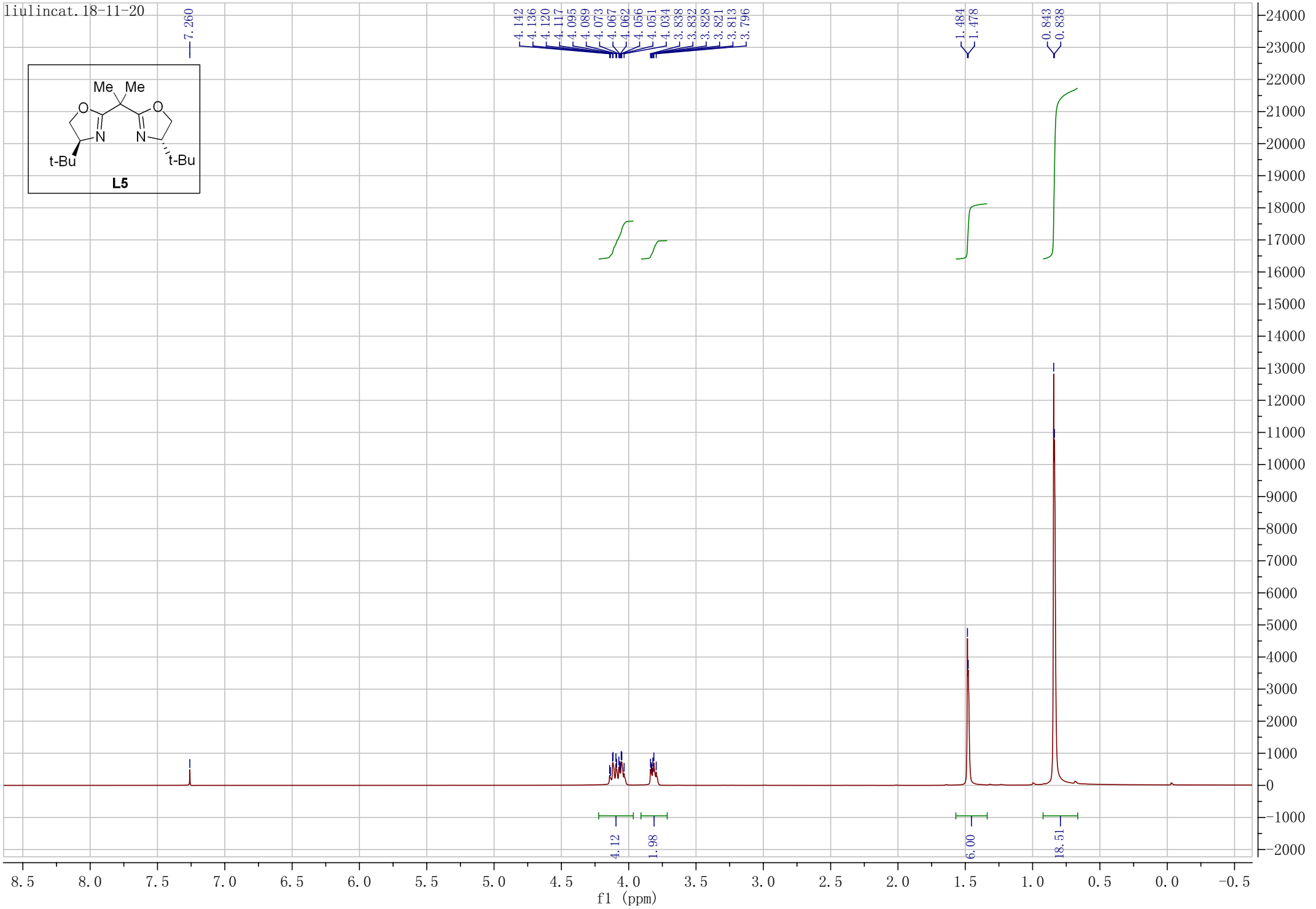

O
O
O
O
2u

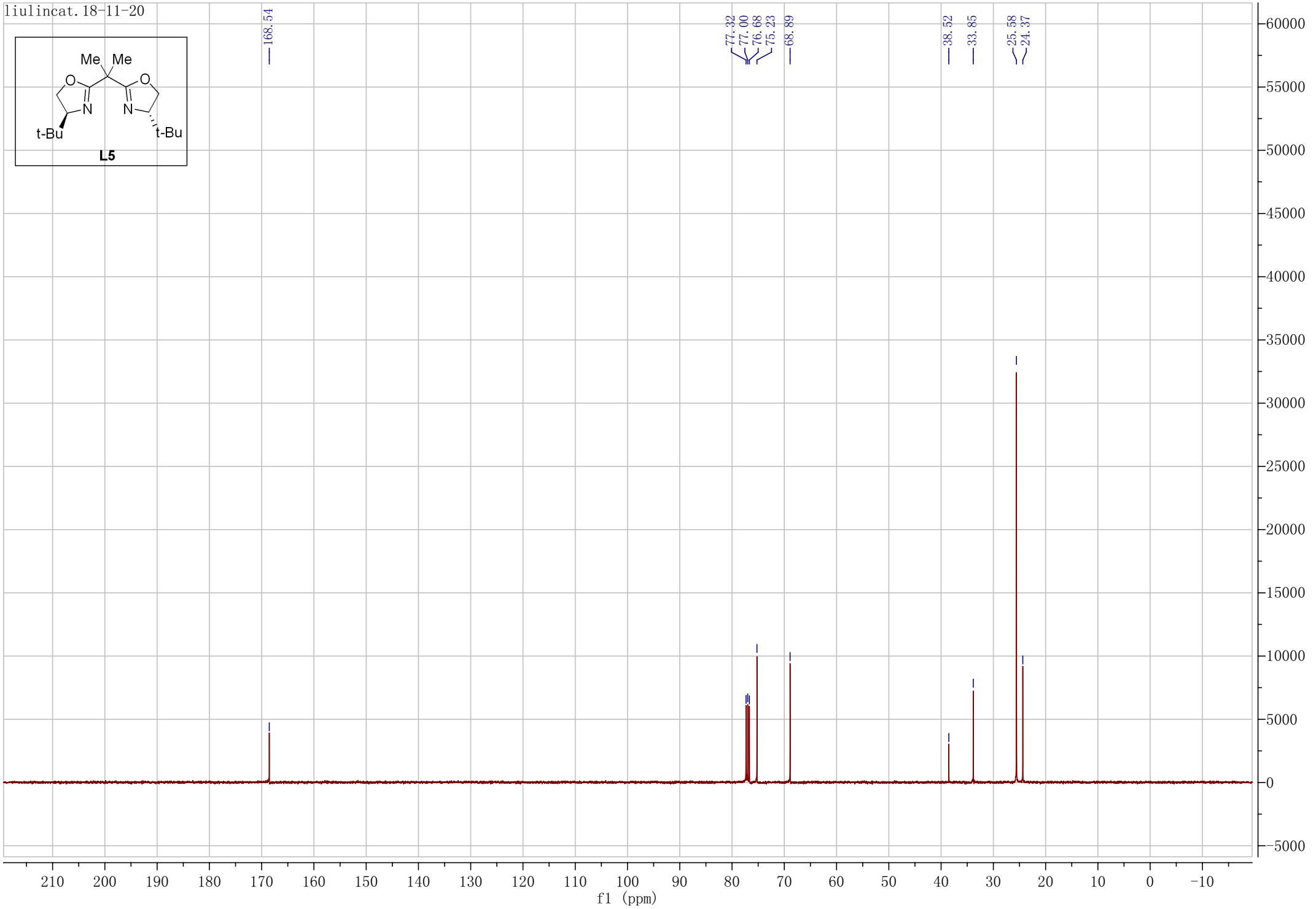

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
2.02
1.15
2.49
2.60
3.80
4.45

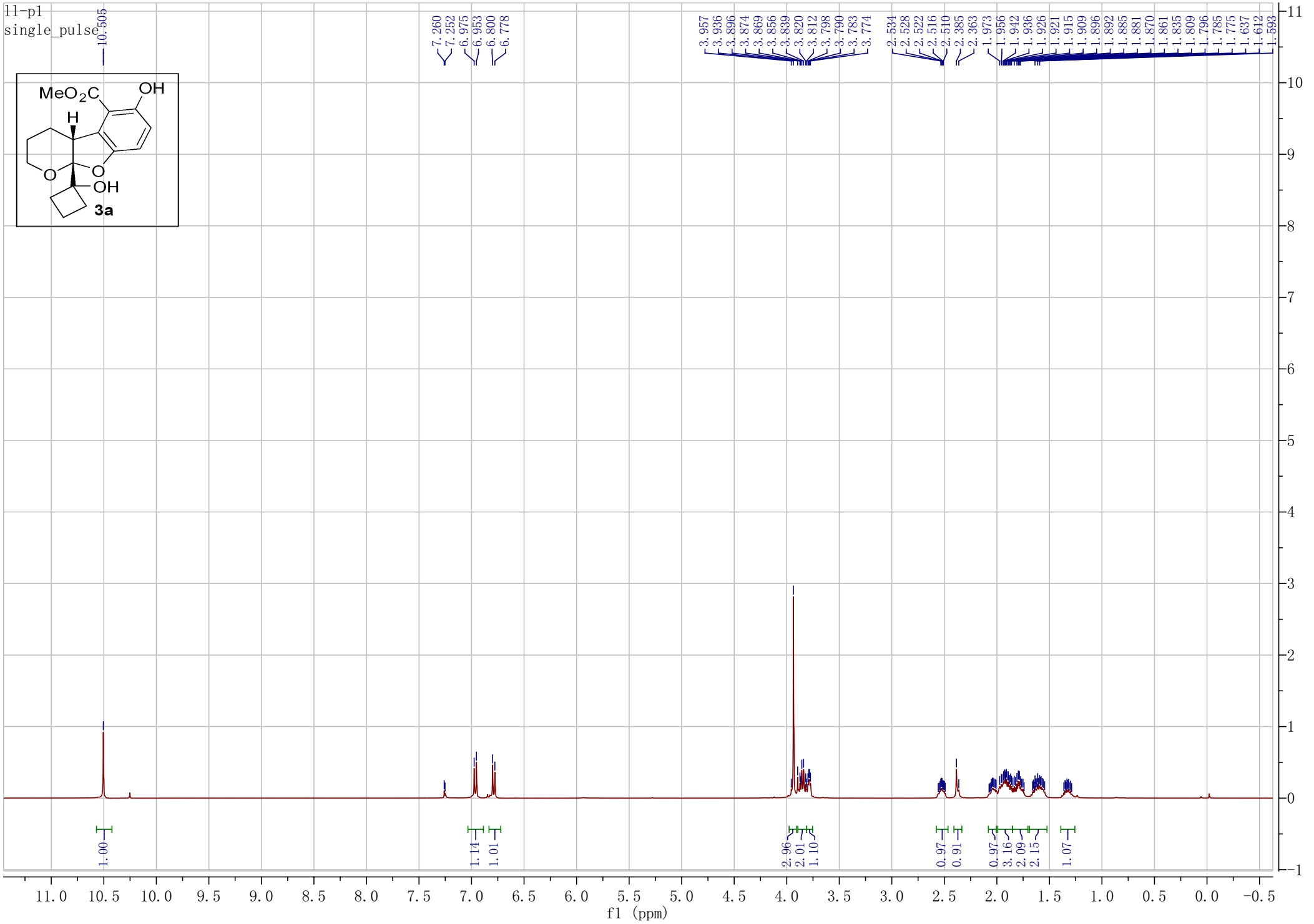


187.03
183.12
162.10
137.82
136.86
136.03
135.63
77.32
77.00
76.68
75.12
31.28
25.19
23.40



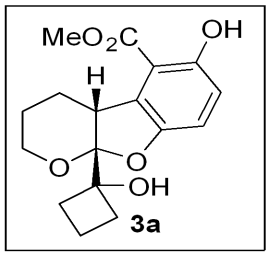

liulincat.18-11-20
7.260
4.142
4.136
4.120
4.117
4.095
4.089
4.073
4.067
4.062
4.056
4.051
4.034
3.838
3.832
3.828
3.821
3.813
3.796
1.484
1.478
0.843
0.838
Me
Me
O
O
N
N
t-Bu
t-Bu
L5
4.12
1.98
6.00
18.51
f1 (ppm)


liulincat.18-11-20
Me
Me
O
O
N
N
t-Bu
t-Bu
L5
168.54
77.32
77.00
76.68
75.23
68.89
38.52
33.85
25.58
24.37
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


11-p1
single_pulse
10.505
7.260
7.252
6.975
6.953
6.800
6.778
3.957
3.936
3.896
3.874
3.869
3.856
3.839
3.820
3.812
3.798
3.790
3.783
3.774
2.534
2.528
2.522
2.516
2.510
2.385
2.363
1.973
1.956
1.942
1.936
1.926
1.921
1.915
1.909
1.896
1.892
1.885
1.881
1.870
1.861
1.835
1.809
1.796
1.785
1.775
1.637
1.612
1.593
MeO2C
OH
H
O
O
OH
3a
1.00
1.14
1.01
2.96
2.01
1.10
0.97
0.91
0.97
3.16
2.09
2.15
1.07
f1 (ppm)

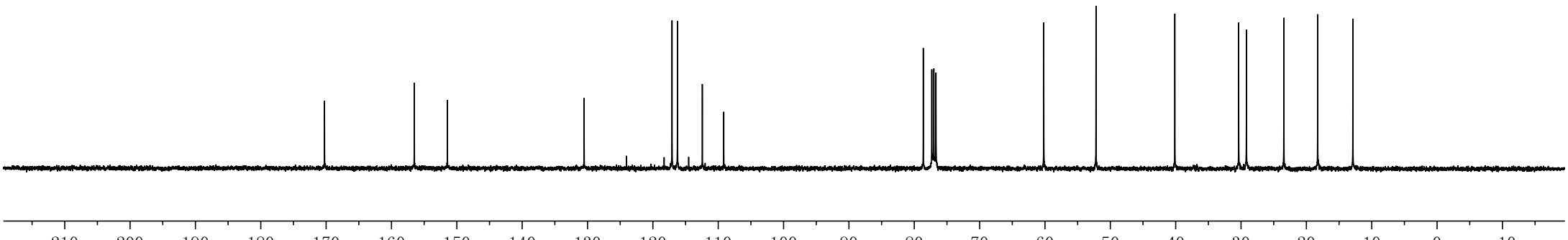
icon_5_LZU_LLin_20180612_P1

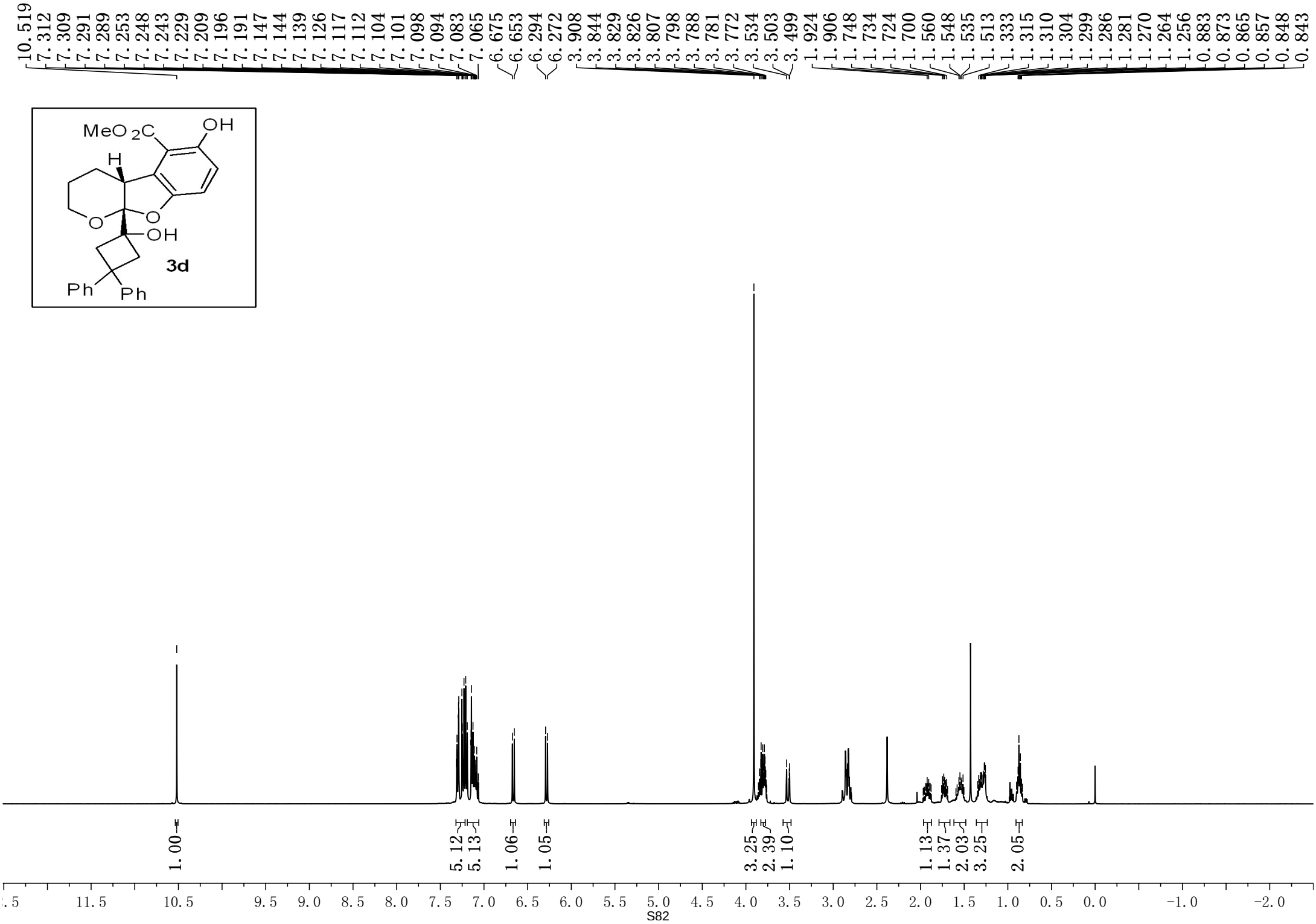
C13CPD CDCl3 {E:\data} ROOT 7



3a

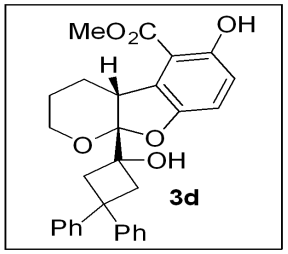
170.243
156.498
151.441
130.518
117.068
116.232
112.430
109.152
78.622
77.318
77.000
76.682
60.188
52.193
40.129
30.359
29.174
23.445
18.275
12.884



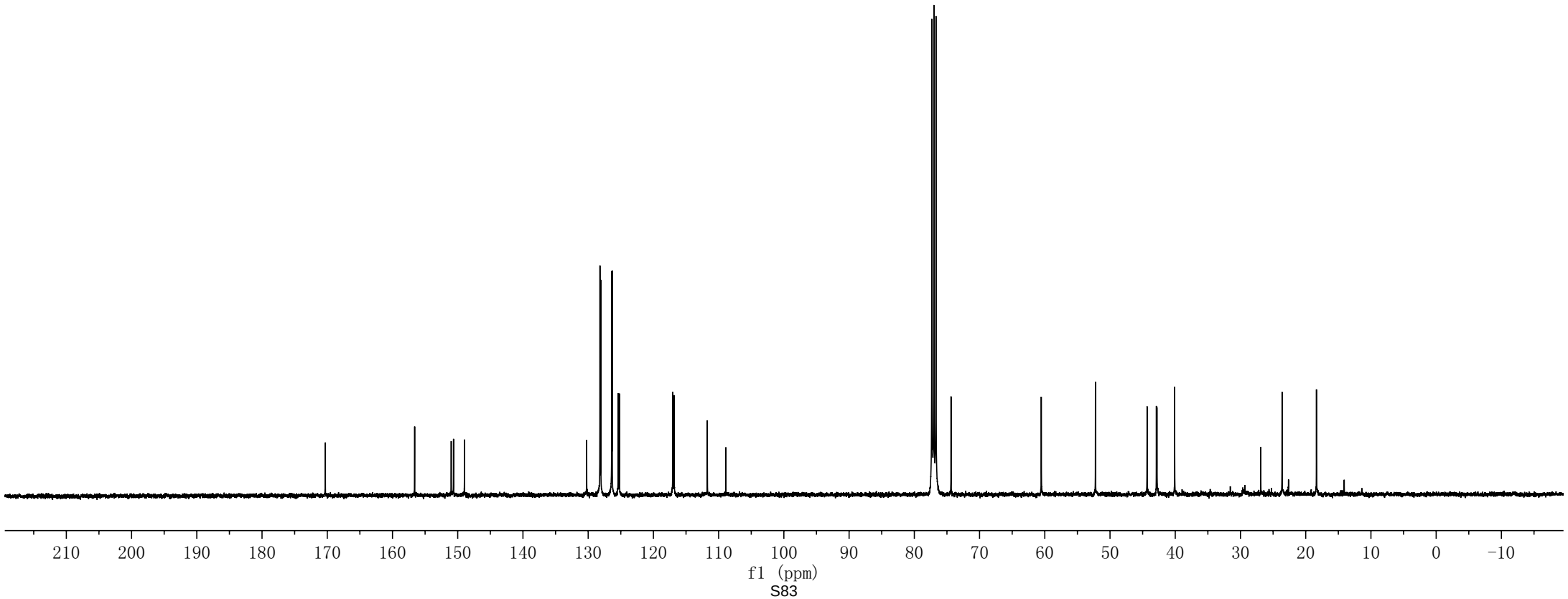

10.519
7.312
7.309
7.291
7.289
7.253
7.248
7.243
7.229
7.209
7.196
7.191
7.147
7.144
7.139
7.126
7.117
7.112
7.104
7.101
7.098
7.094
7.083
7.065
6.675
6.653
6.294
6.272
3.908
3.844
3.829
3.826
3.807
3.798
3.788
3.781
3.772
3.534
3.503
3.499
1.924
1.906
1.748
1.734
1.724
1.700
1.560
1.548
1.535
1.513
1.333
1.315
1.310
1.304
1.299
1.286
1.281
1.270
1.264
1.256
0.883
0.873
0.865
0.857
0.848
0.843
MeO2C
OH
H
O
O
OH
3d
Ph
Ph
1.00
5.12
5.13
1.06
1.05
3.25
2.39
1.10
1.13
1.37
2.03
3.25
2.05
11.5
10.5
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
-1.0
-2.0

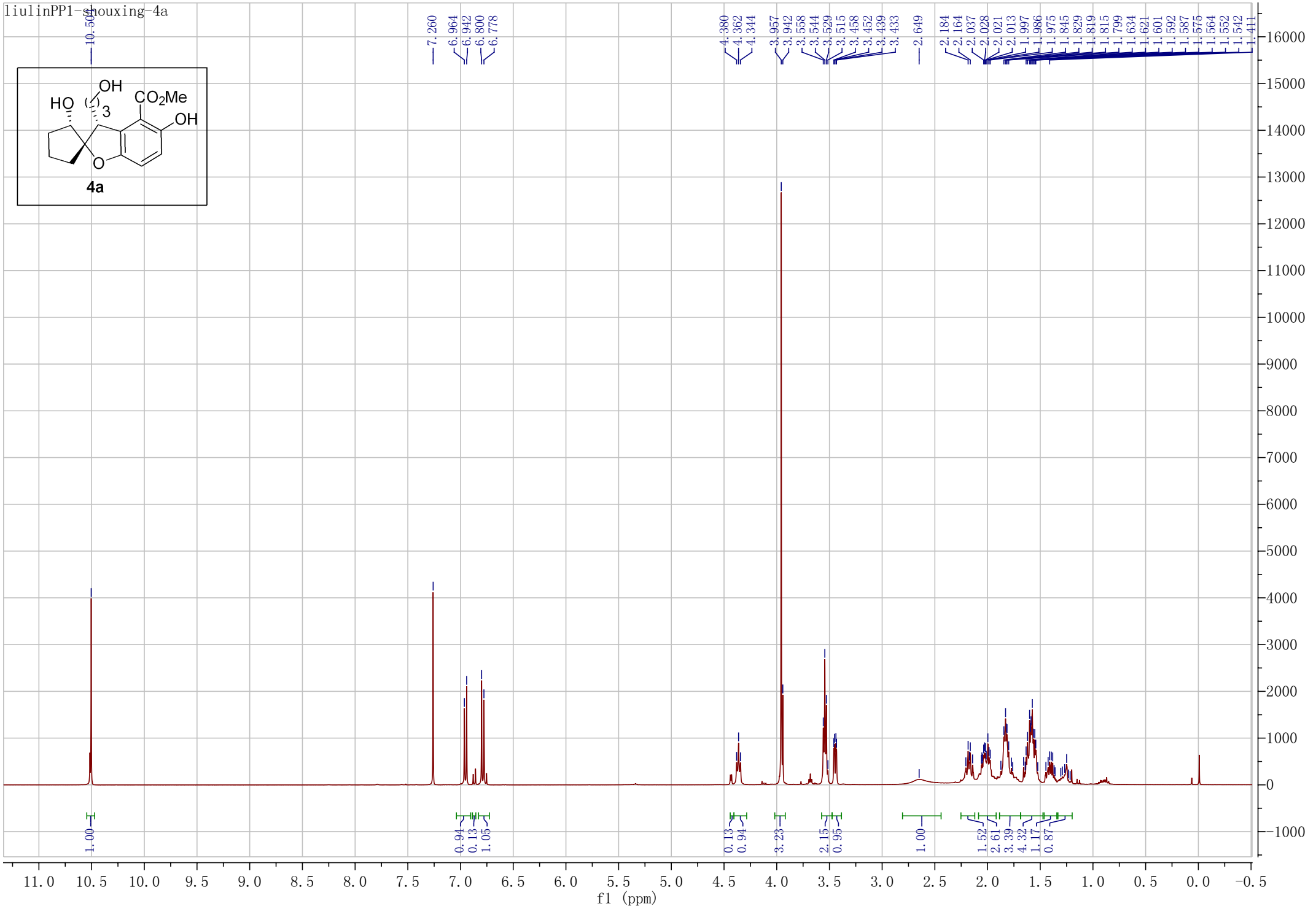
icon_5_LZU_LLin_20180612_P11

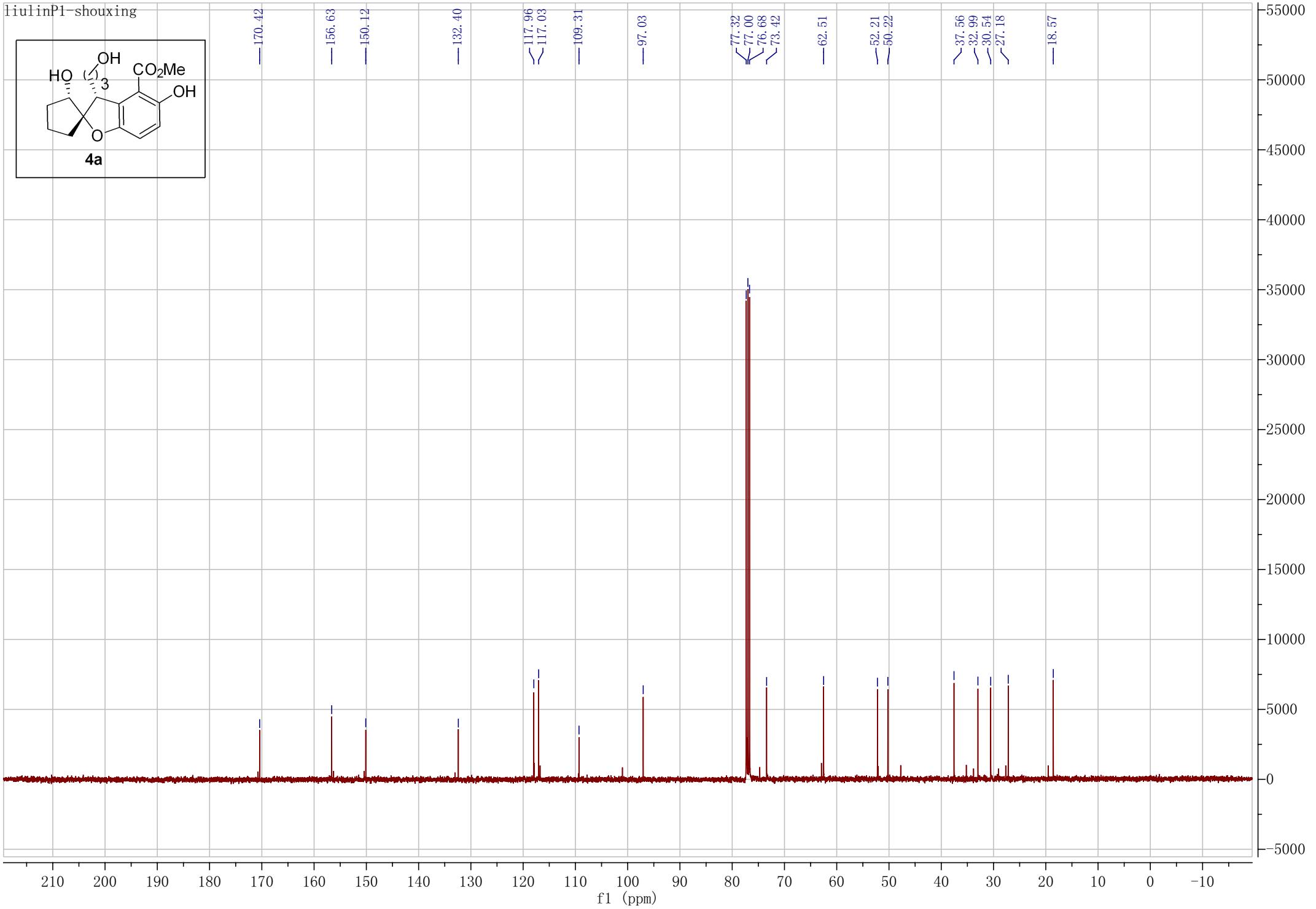
C13CPD CDCl3 {E:\data} ROOT 1

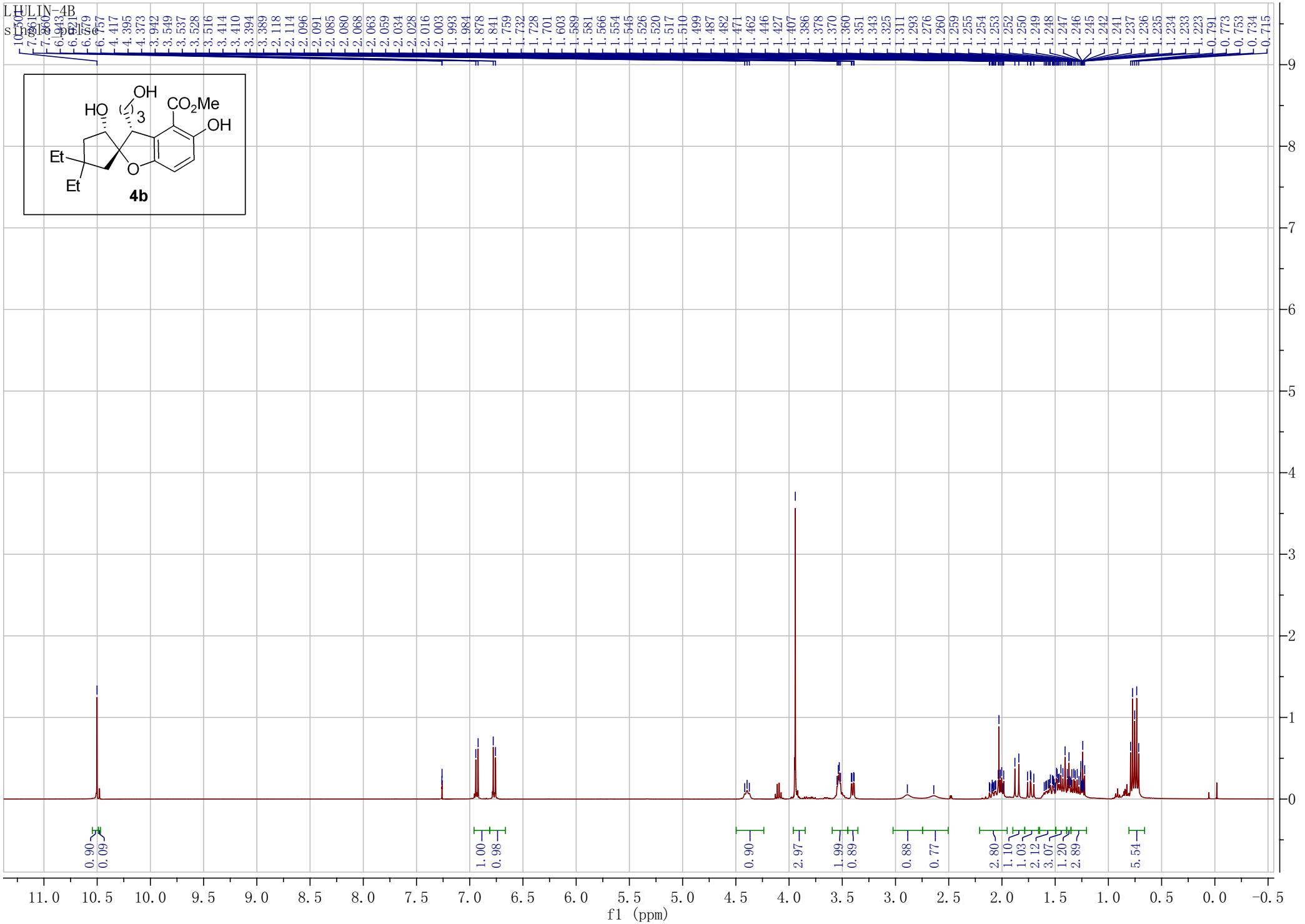


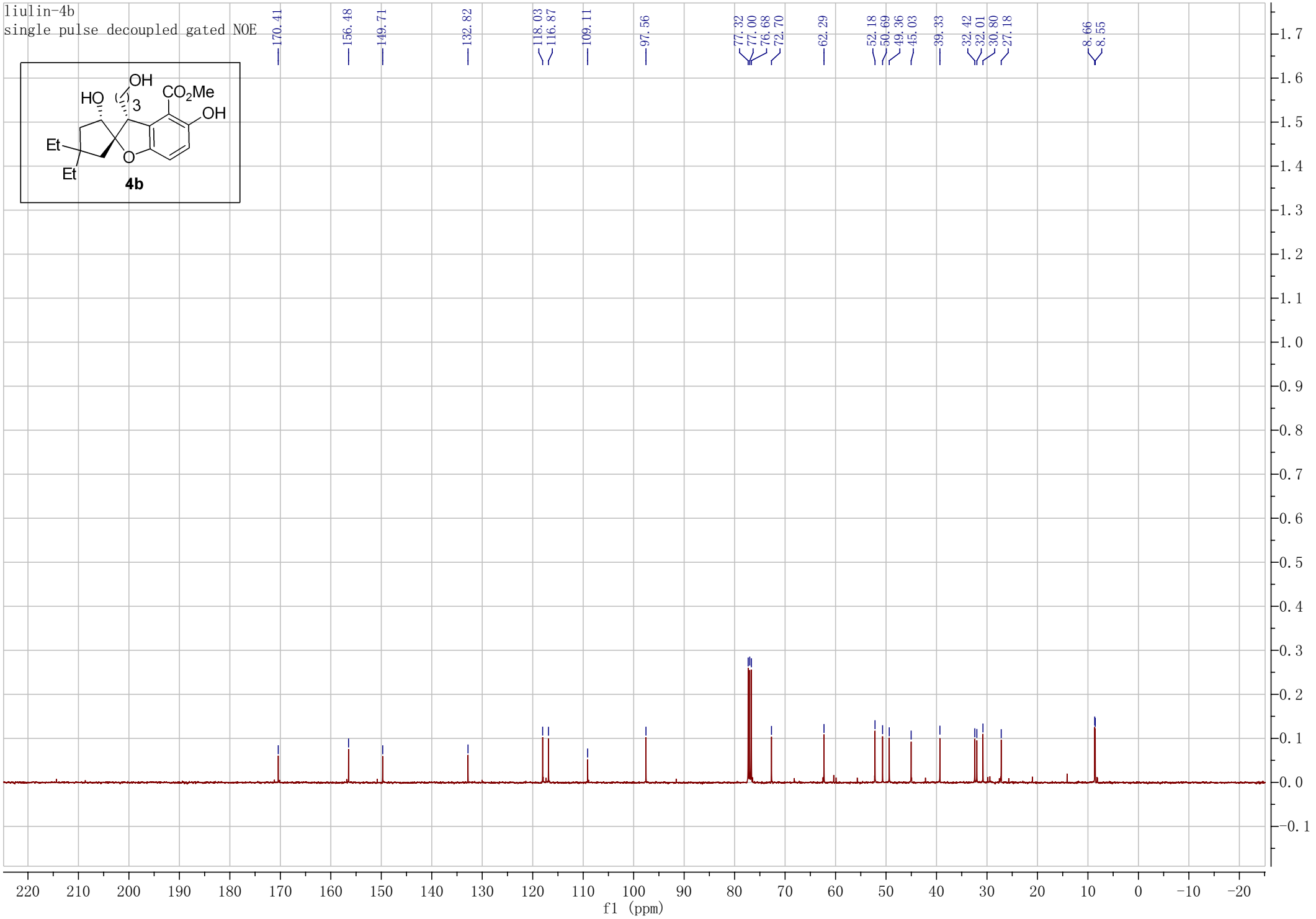
170.294
156.600
150.997
150.643
148.964
130.231
128.194
128.068
126.390
126.323
125.384
125.216
117.034
116.831
111.731
108.895
77.318
77.000
76.683
74.372
60.536
52.233
44.317
42.894
42.805
40.093
26.892
23.622
18.354

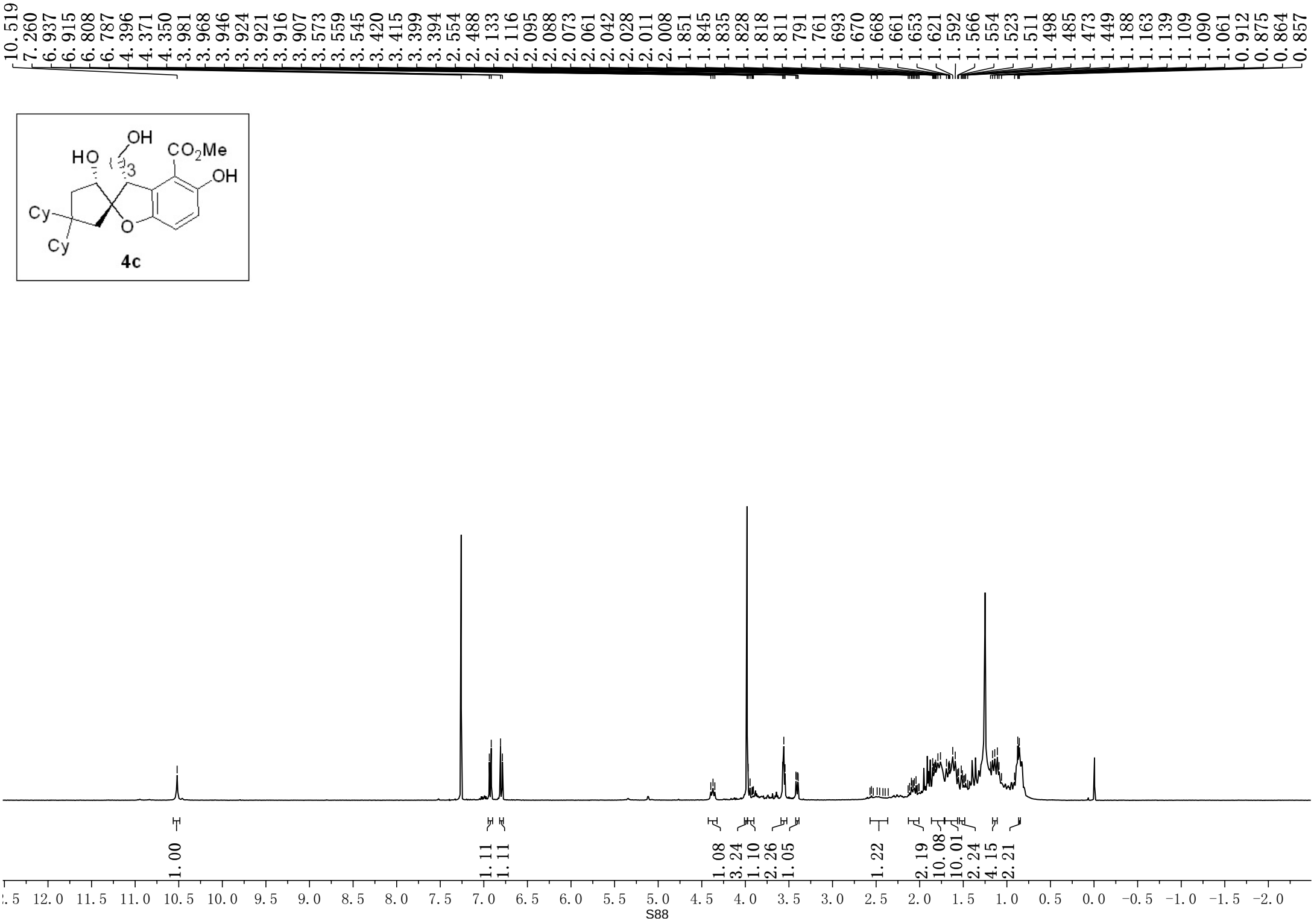



liulinPP1-shouxing-4a
10.501
7.260
6.964
6.942
6.800
6.778
4.380
4.362
4.344
3.957
3.942
3.558
3.544
3.529
3.515
3.458
3.452
3.439
3.433
2.649
2.184
2.164
2.037
2.028
2.021
2.013
1.997
1.986
1.975
1.845
1.829
1.819
1.815
1.799
1.634
1.621
1.601
1.592
1.587
1.575
1.564
1.552
1.542
1.411
OH
HO
3
CO2Me
OH
O
4a
1.00
0.94
0.13
1.05
0.13
0.94
3.23
2.15
0.95
1.00
1.52
2.61
3.39
4.32
1.17
0.87
f1 (ppm)


liulinP1-shouxing
OH
HO
3
CO2Me
OH
O
4a
170.42
156.63
150.12
132.40
117.96
117.03
109.31
97.03
77.32
77.00
76.68
73.42
62.51
52.21
50.22
37.56
32.99
30.54
27.18
18.57
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


LHJLIN-4B
single pulse
OH
HO
3
CO2Me
OH
Et
Et
O
4b
f1 (ppm)


liulin-4b
single pulse decoupled gated NOE
OH
HO
3
CO2Me
OH
Et
Et
O
4b
170.41
156.48
149.71
132.82
118.03
116.87
109.11
97.56
77.32
77.00
76.68
72.70
62.29
52.18
50.69
49.36
45.03
39.33
32.42
32.01
30.80
27.18
8.66
8.55
f1 (ppm)


10.519
7.260
6.937
6.915
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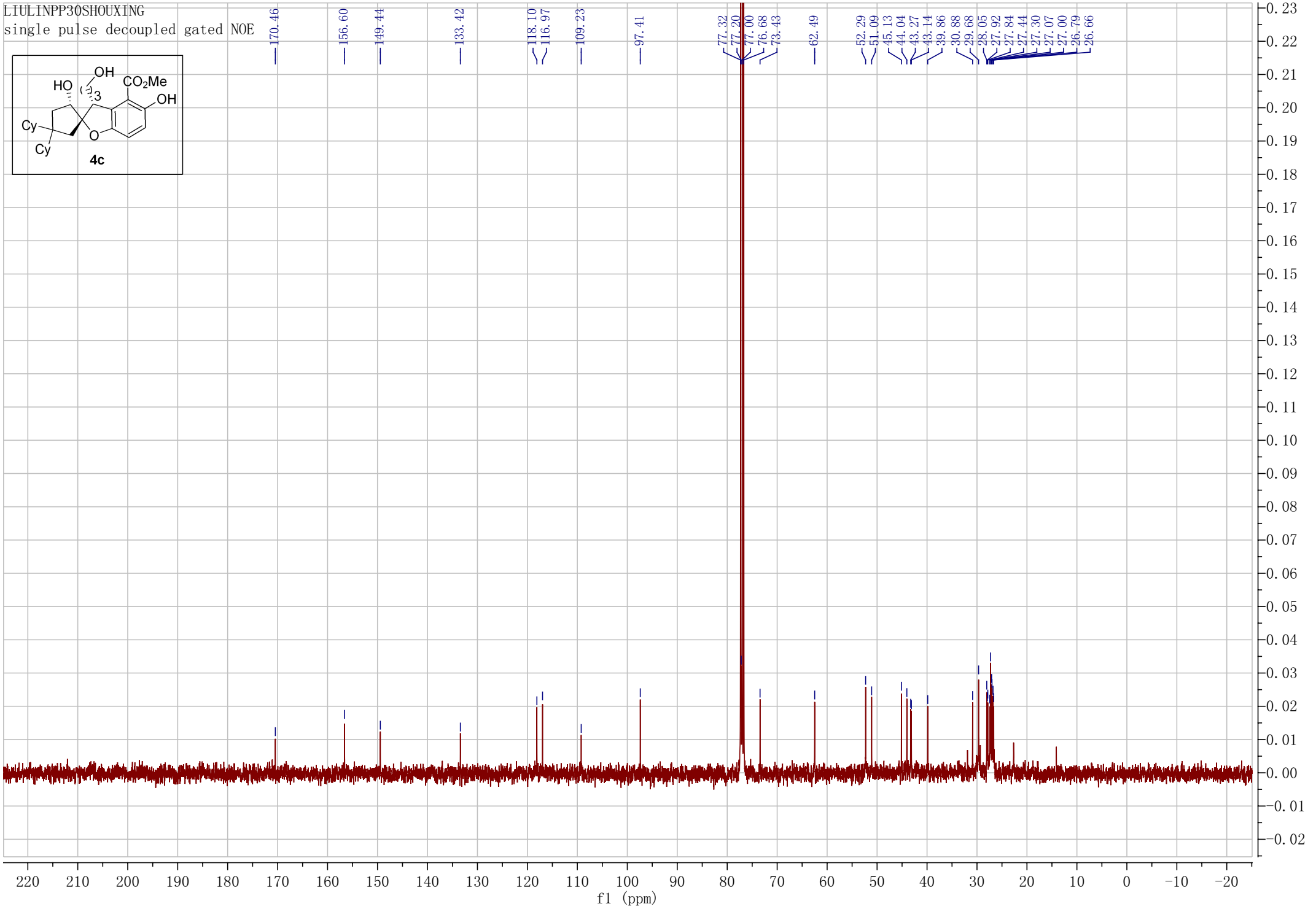
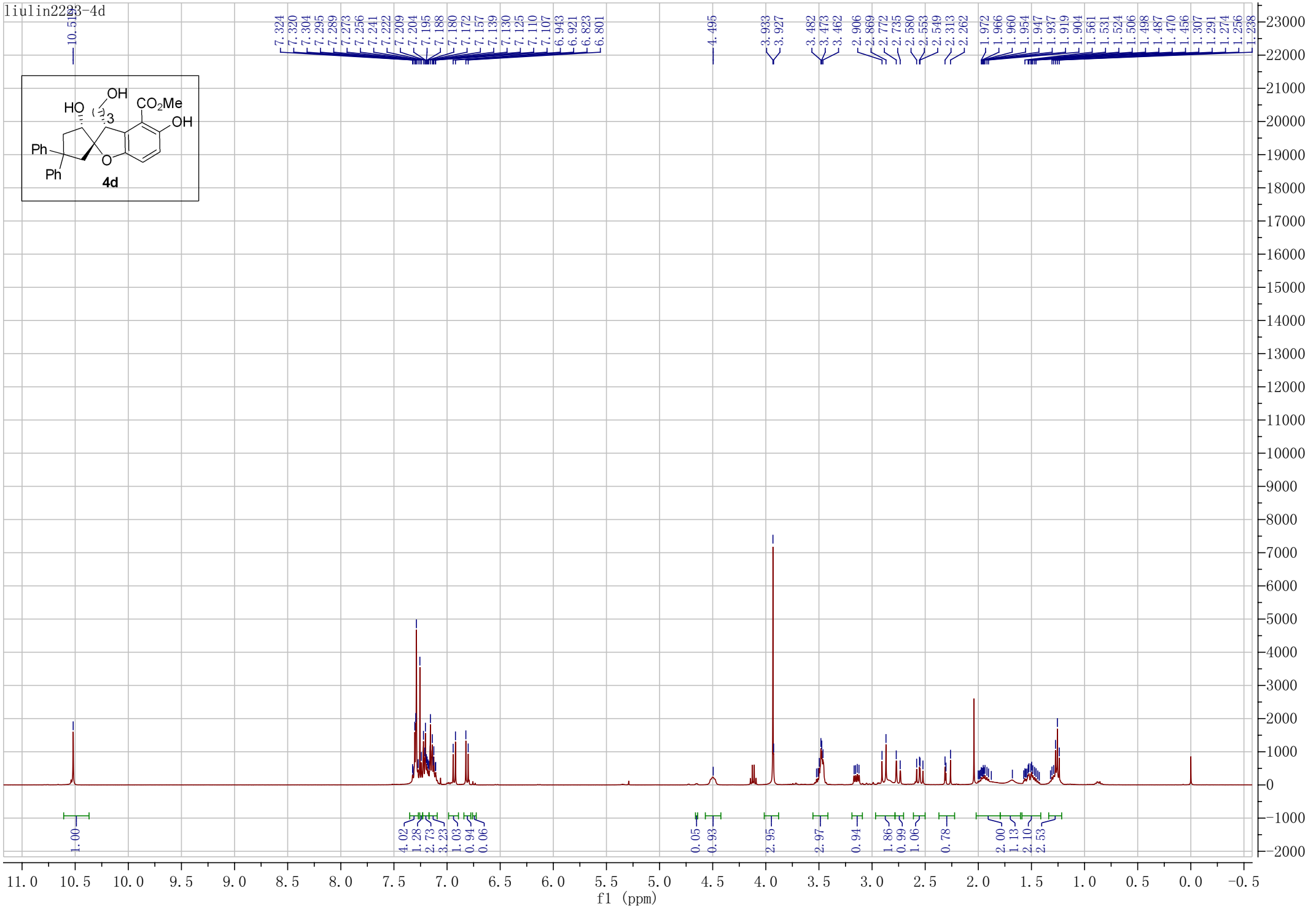
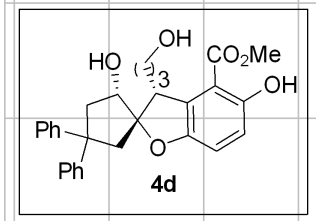
6.787
4.396
4.371
4.350
3.981
3.968
3.946
3.924
3.921
3.916
3.907
3.573
3.559
3.545
3.420
3.415
3.399
3.394
2.554
2.488
2.133
2.116
2.095
2.088
2.073
2.061
2.042
2.028
2.011
2.008
1.851
1.845
1.835
1.828
1.818
1.811
1.791
1.761
1.693
1.670
1.668
1.661
1.653
1.621
1.592
1.566
1.554
1.523
1.511
1.498
1.485
1.473
1.449
1.188
1.163
1.139
1.109
1.090
1.061
0.912
0.875
0.864
0.857
OH
HO
CO2Me
OH
Cy
Cy
O
4c
1.00
1.11
1.11
1.08
3.24
1.10
2.26
1.05
1.22
2.19
10.08
10.01
2.24
4.15
2.21
12.0
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
-0.5
-1.0
-1.5
-2.0


LIULINPP30SHOUXING
single pulse decoupled gated NOE
170.46
156.60
149.44
133.42
118.10
116.97
109.23
97.41
77.32
77.20
77.00
76.68
73.43
62.49
52.29
51.09
45.13
44.04
43.27
43.14
39.86
30.88
29.68
28.05
27.92
27.84
27.44
27.30
27.07
27.00
26.79
26.66
OH
HO
CO2Me
OH
Cy
Cy
O
4c
f1 (ppm)


liulin2223-4d
10.513
7.324
7.320
7.304
7.295
7.289
7.273
7.256
7.241
7.222
7.209
7.204
7.195
7.188
7.180
7.172
7.157
7.139
7.130
7.125
7.110
7.107
6.943
6.921
6.823
6.801
4.495
3.933
3.927
3.482
3.473
3.462
2.906
2.869
2.772
2.735
2.580
2.553
2.549
2.313
2.262
1.972
1.966
1.960
1.954
1.947
1.937
1.919
1.904
1.561
1.531
1.524
1.506
1.498
1.487
1.470
1.456
1.307
1.291
1.274
1.256
1.238
HO
OH
CO2Me
OH
Ph
Ph
O
3
4d
1.00
4.02
1.28
2.73
3.23
1.03
0.94
0.06
0.05
0.93
2.95
2.97
0.94
1.86
0.99
1.06
0.78
2.00
1.13
2.10
2.53
f1 (ppm)

本课题

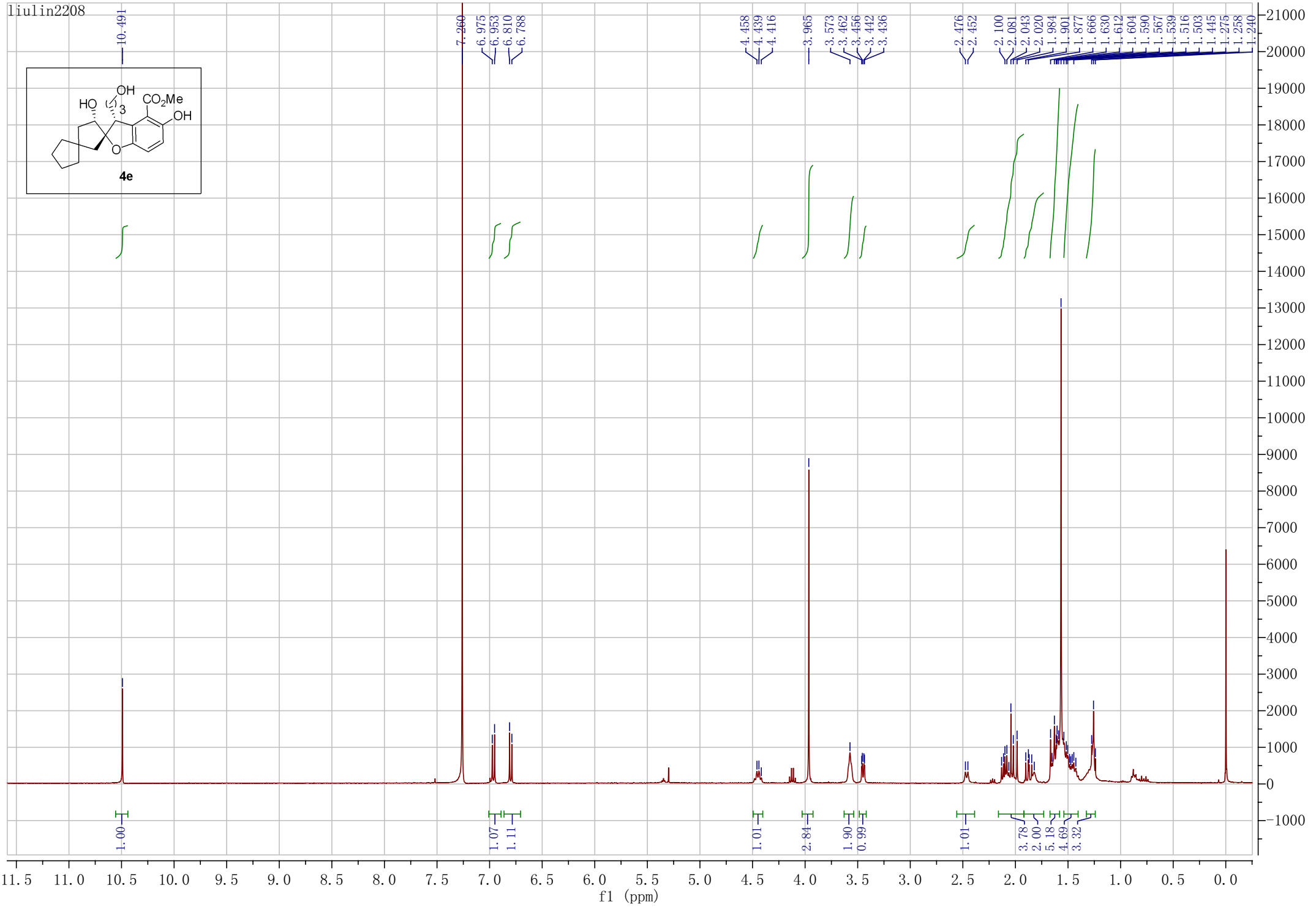


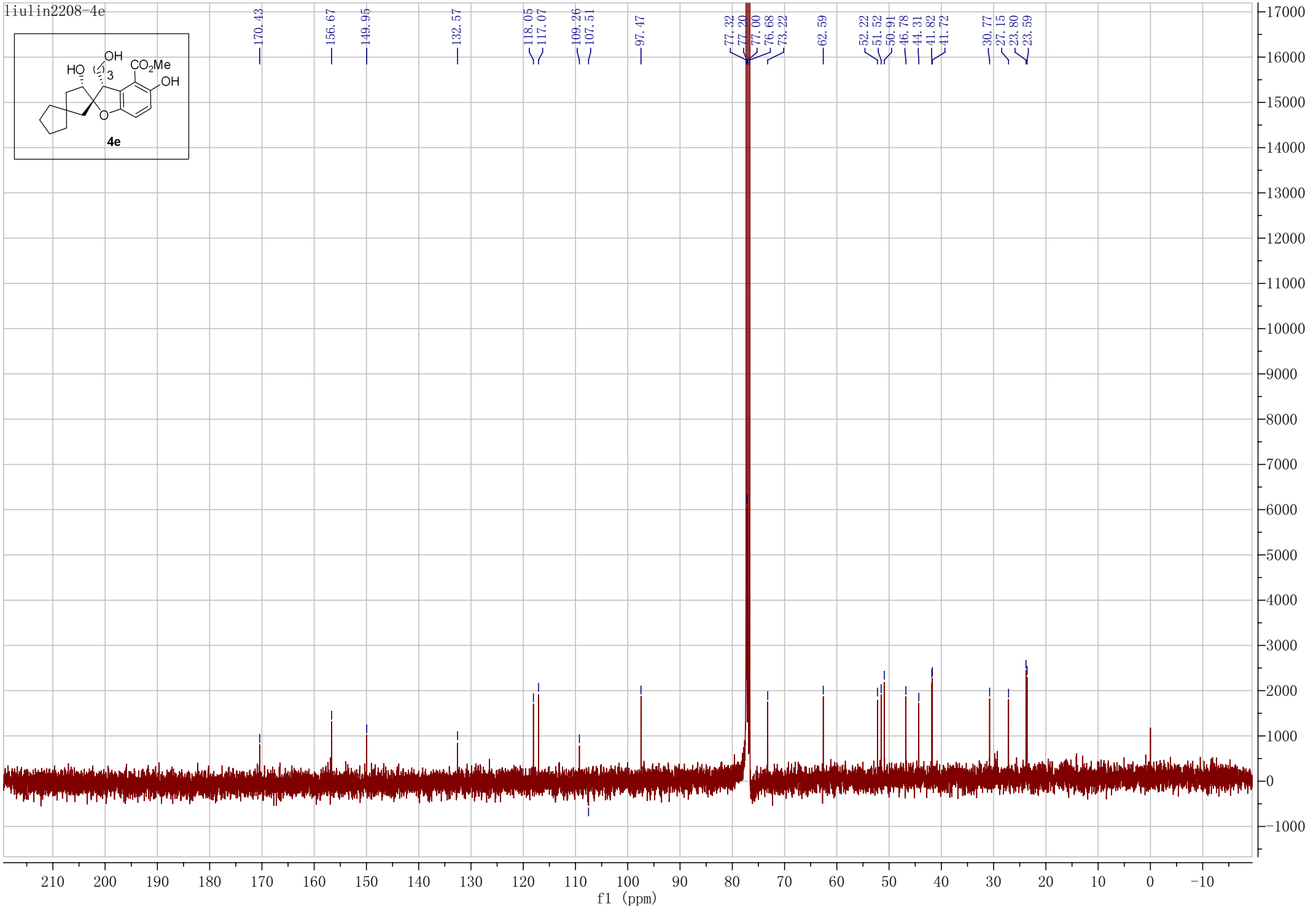
170.30
156.81
149.80
149.57
148.34
132.34
128.45
128.13
126.65
126.50
126.02
125.74
118.05
117.21
109.30
96.37
77.32
77.00
76.68
72.10
62.37
60.38
52.93
52.19
51.16
49.32
46.70
30.26
27.20
21.00
14.14

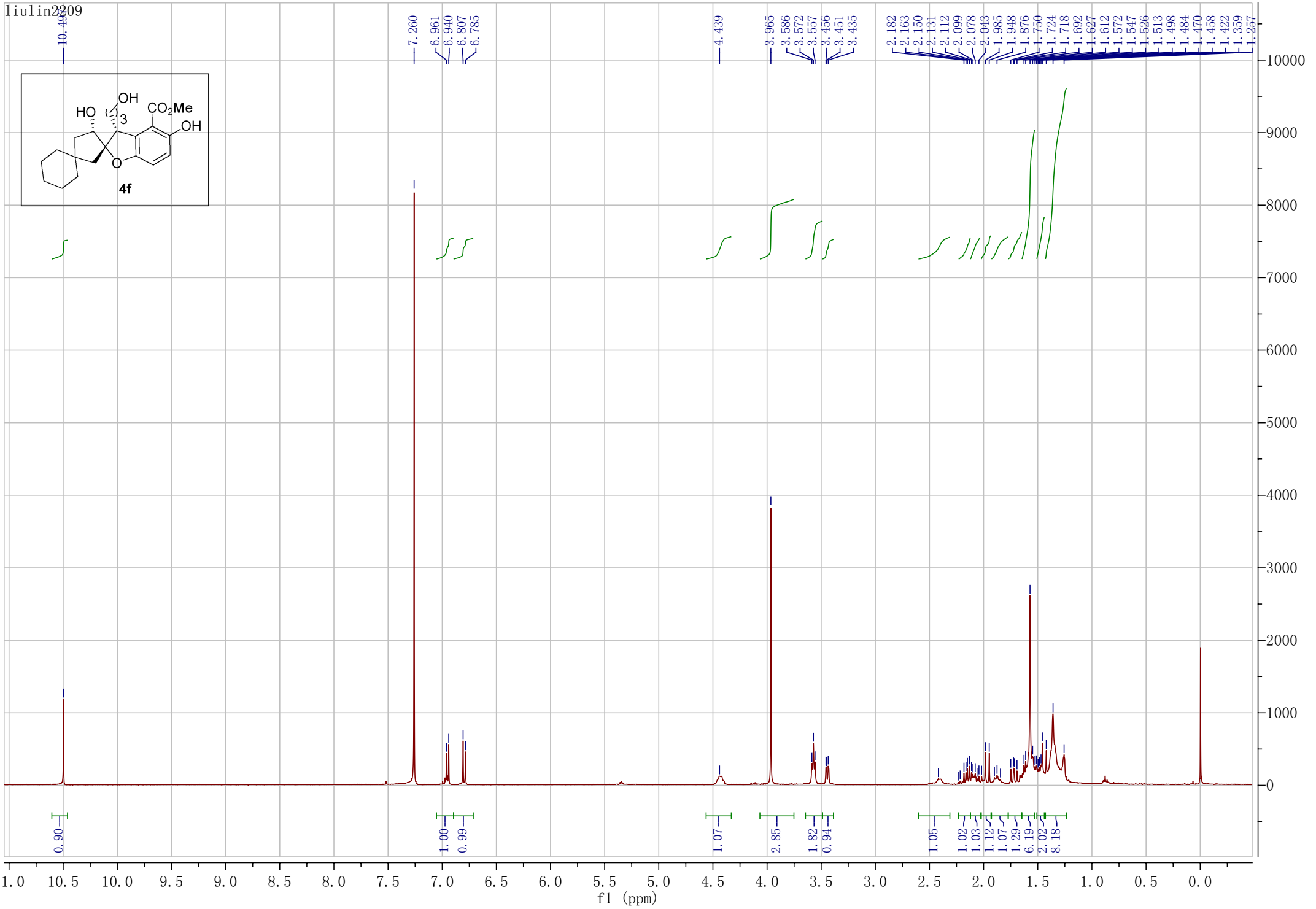
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000

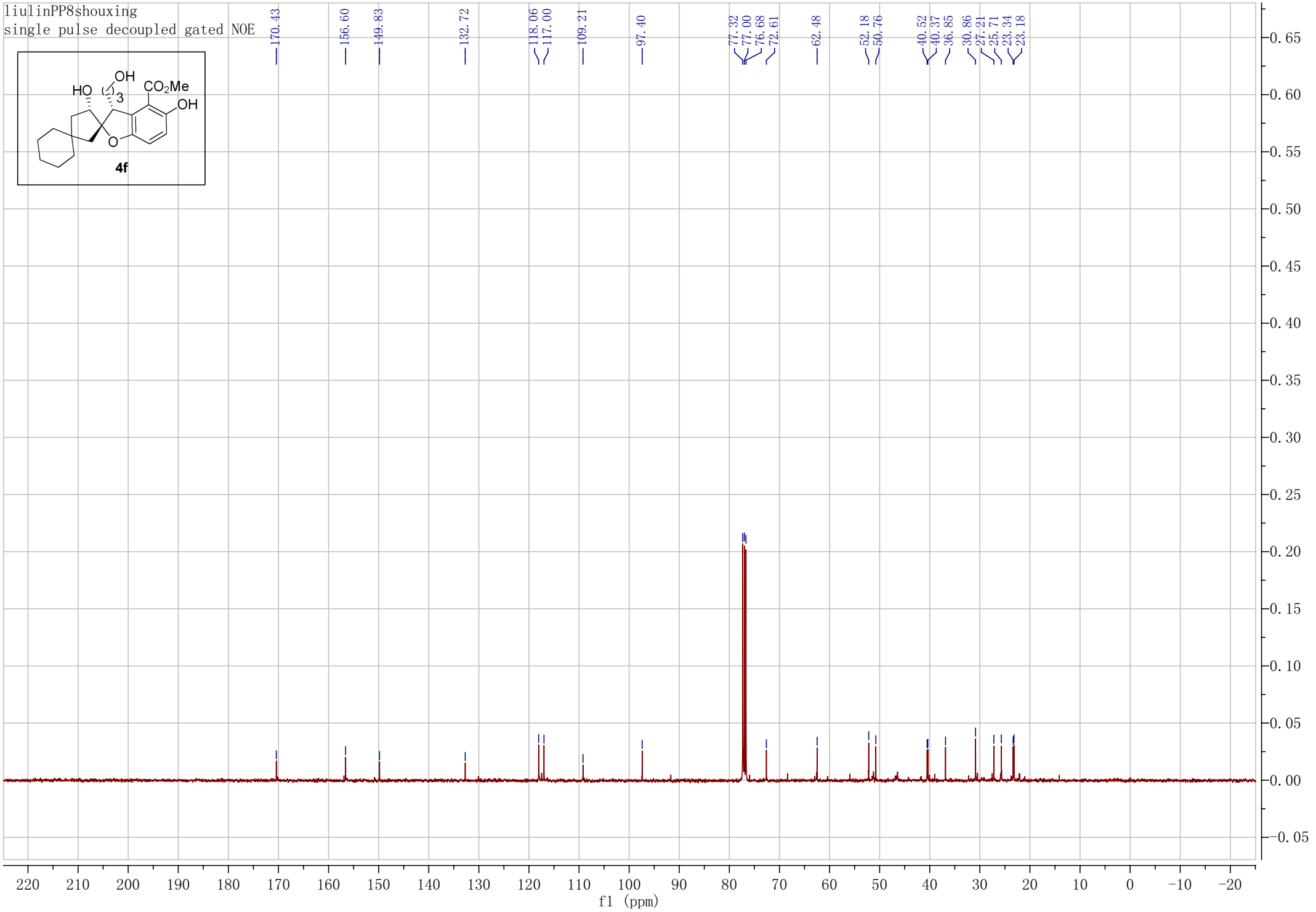
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

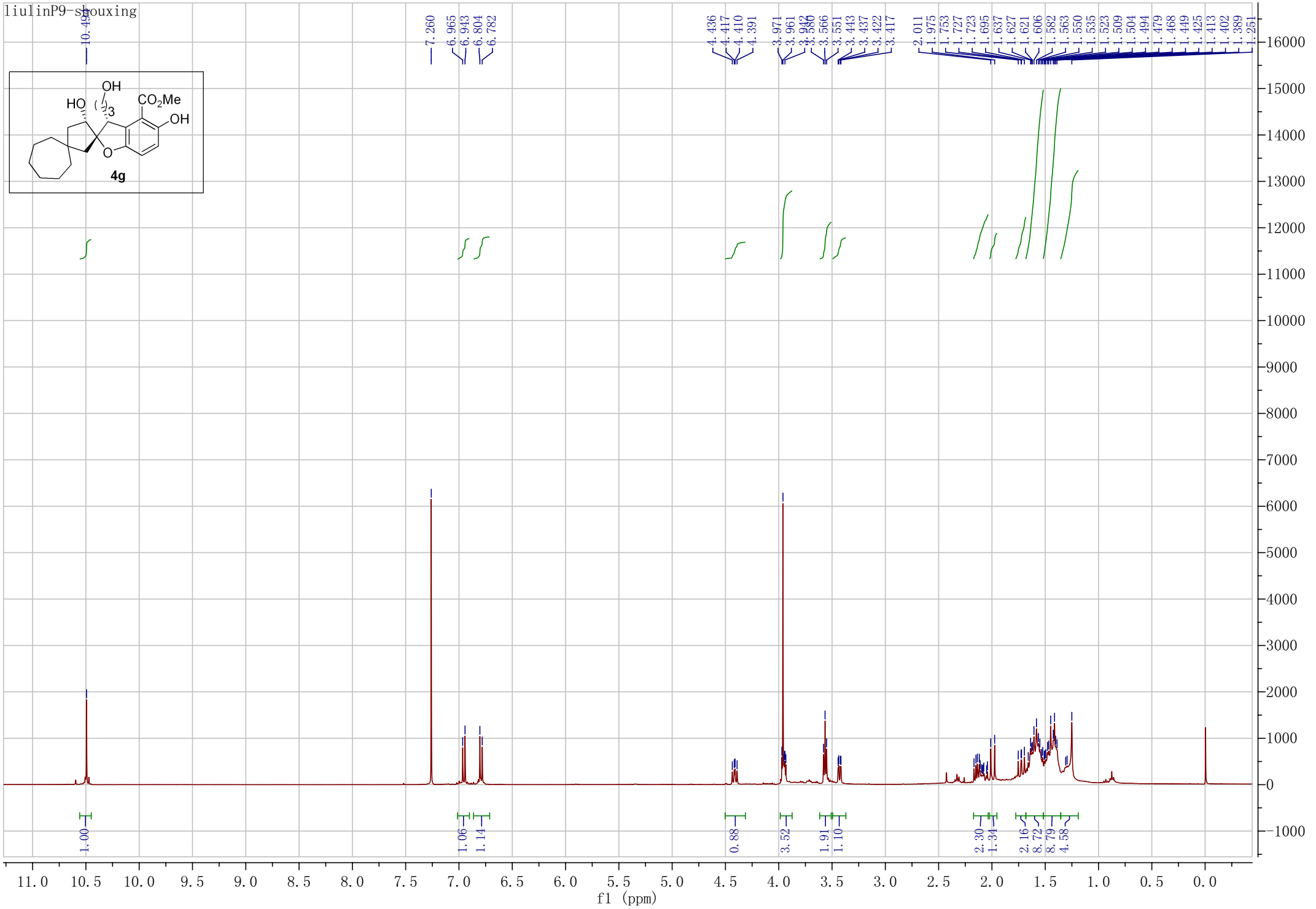
f1 (ppm)

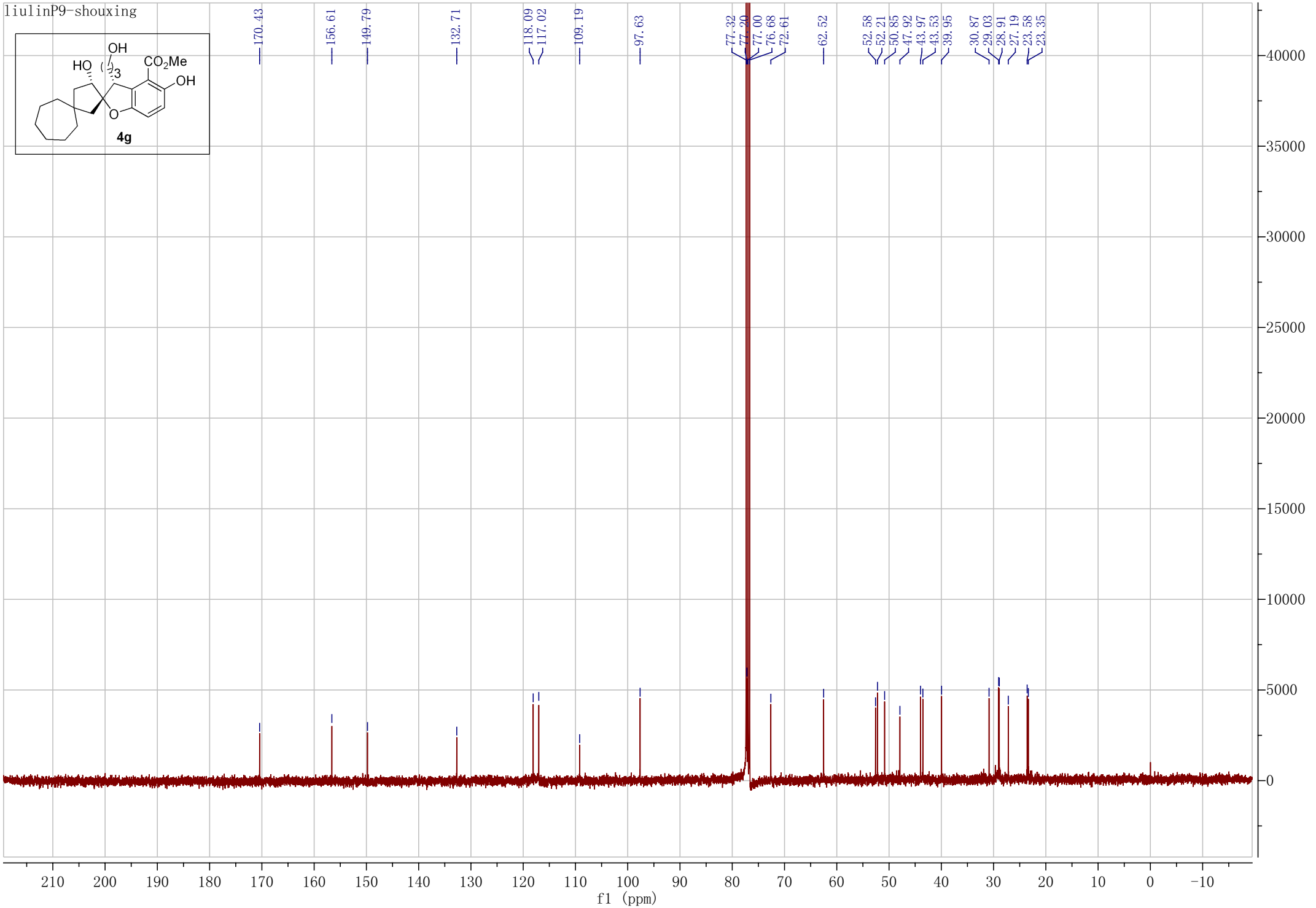

liulin2208
10.491
7.260
6.975
6.953
6.810
6.788
4.458
4.439
4.416
3.965
3.573
3.462
3.456
3.442
3.436
2.476
2.452
2.100
2.081
2.043
2.020
1.984
1.901
1.877
1.666
1.630
1.612
1.604
1.590
1.567
1.539
1.516
1.503
1.445
1.275
1.258
1.240
OH
HO
3
CO2Me
OH
O
4e
1.00
1.07
1.11
1.01
2.84
1.90
0.99
1.01
3.78
2.00
5.18
4.69
3.32
f1 (ppm)

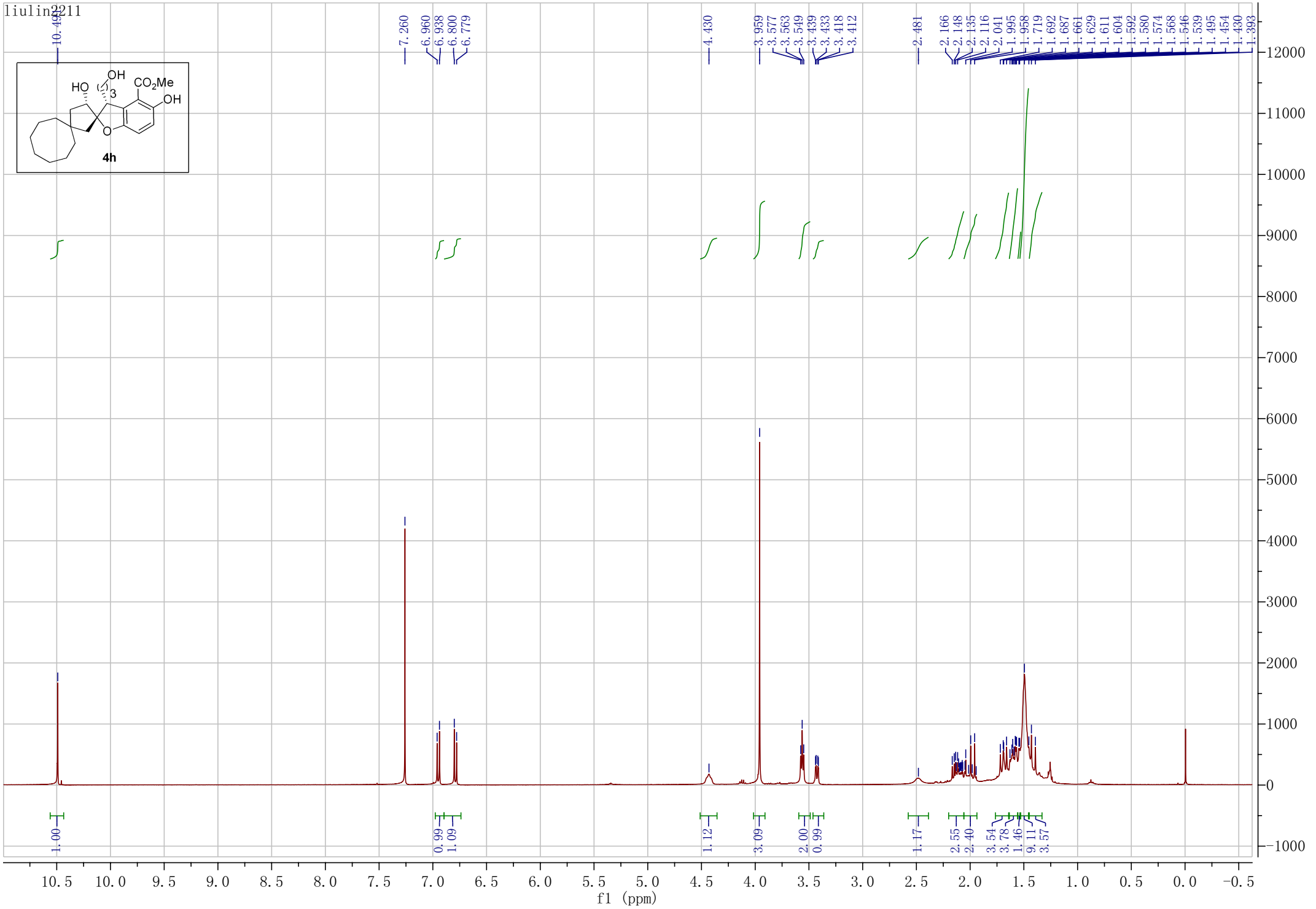

liulin2208-4e
OH
HO
3
CO2Me
OH
O
4e
170.43
156.67
149.95
132.57
118.05
117.07
109.26
107.51
97.47
77.32
77.20
77.00
76.68
73.22
62.59
52.22
51.52
50.91
46.78
44.31
41.82
41.72
30.77
27.15
23.80
23.59
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


liulin2209
10.494
7.260
6.961
6.940
6.807
6.785
4.439
3.965
3.586
3.572
3.557
3.456
3.451
3.435
2.182
2.163
2.150
2.131
2.112
2.099
2.078
2.043
1.985
1.948
1.876
1.750
1.724
1.718
1.692
1.627
1.612
1.572
1.547
1.526
1.513
1.498
1.484
1.470
1.458
1.422
1.359
1.257
OH
HO
3
CO2Me
OH
O
4f
0.90
1.00
0.99
1.07
2.85
1.82
0.94
1.05
1.02
1.03
1.12
1.07
1.29
6.19
2.02
8.18
f1 (ppm)


liulinPP8shouxing
single pulse decoupled gated NOE
170.43
156.60
149.83
132.72
118.06
117.00
109.21
97.40
77.32
77.00
76.68
72.61
62.48
52.18
50.76
40.52
40.37
36.85
30.86
27.21
25.71
23.34
23.18
HO
OH
3
CO2Me
OH
O
4f
f1 (ppm)

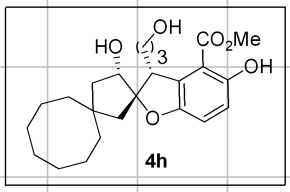

liulinP9-shouxing
10.492
7.260
6.965
6.943
6.804
6.782
4.436
4.417
4.410
4.391
3.971
3.961
3.566
3.551
3.443
3.437
3.422
3.417
2.011
1.975
1.753
1.727
1.723
1.695
1.637
1.627
1.621
1.606
1.582
1.563
1.550
1.535
1.523
1.509
1.504
1.494
1.479
1.468
1.449
1.425
1.413
1.402
1.389
1.251
OH
HO
CO2Me
OH
O
4g
1.00
1.06
1.14
0.88
3.52
1.91
1.10
2.30
1.34
2.16
8.72
8.79
4.58
f1 (ppm)


liulinP9-shouxing
OH
HO
CO2Me
OH
O
4g
170.43
156.61
149.79
132.71
118.09
117.02
109.19
97.63
77.32
77.20
77.00
76.68
72.61
62.52
52.58
52.21
50.85
47.92
43.97
43.53
39.95
30.87
29.03
28.91
27.19
23.58
23.35
40000
35000
30000
25000
20000
15000
10000
5000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


liulin2211
10.495
7.260
6.960
6.938
6.800
6.779
4.430
3.959
3.577
3.563
3.549
3.439
3.433
3.418
3.412
2.481
2.166
2.148
2.135
2.116
2.041
1.995
1.958
1.719
1.692
1.687
1.661
1.629
1.611
1.604
1.592
1.580
1.574
1.568
1.546
1.539
1.495
1.454
1.430
1.393
HO
OH
CO2Me
OH
O
3
4h
1.00
0.99
1.09
1.12
3.09
2.00
0.99
1.17
2.55
2.40
3.54
3.78
1.46
9.11
3.57
f1 (ppm)

liulinPP10shouxing

single pulse decoupled gated NOE

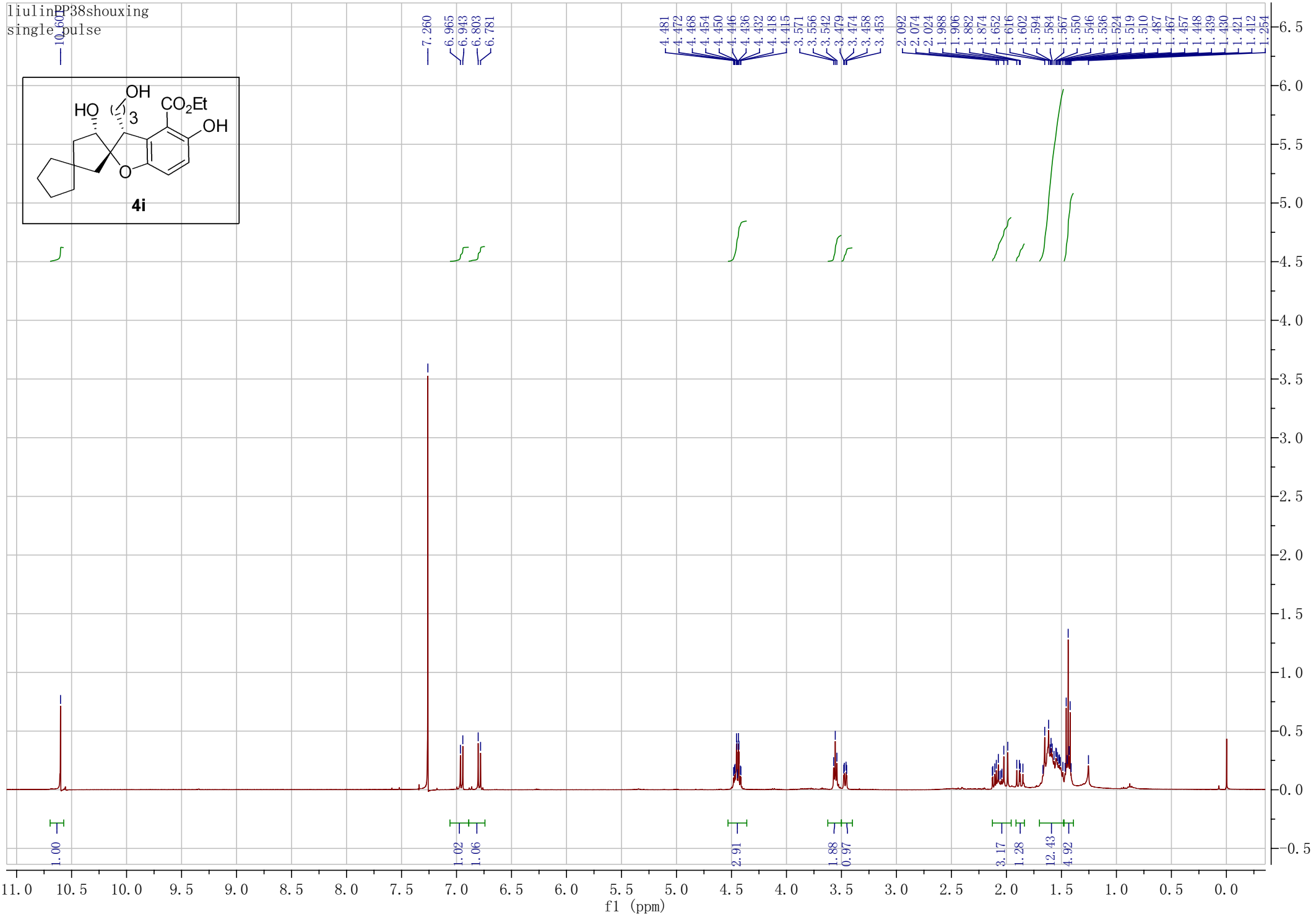


170.43
156.56
149.78
132.78
118.04
116.97
109.20
97.70
77.32
77.20
77.00
76.68
72.59
62.43
52.17
52.05
50.88
47.28
39.94
38.50
38.14
30.87
28.57
28.26
27.25
24.65
23.20
23.13

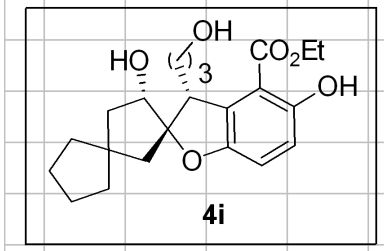
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


liulinPP38shouxing
single_pulse
OH
HO
3
CO2Et
OH
O
4i
10.601
7.260
6.965
6.943
6.803
6.781
4.481
4.472
4.468
4.454
4.450
4.446
4.436
4.432
4.418
4.415
3.571
3.556
3.542
3.479
3.474
3.458
3.453
2.092
2.074
2.024
1.988
1.906
1.882
1.874
1.652
1.616
1.602
1.594
1.584
1.567
1.550
1.546
1.536
1.524
1.519
1.510
1.487
1.467
1.457
1.448
1.439
1.430
1.421
1.412
1.254
1.00
1.02
1.06
2.91
1.88
0.97
3.17
1.28
12.43
4.92
f1 (ppm)

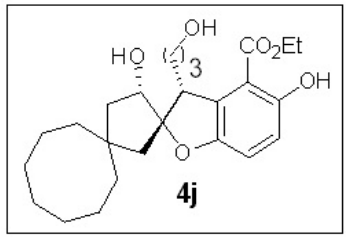
liulinPP38shouxing
single pulse decoupled gated NOE



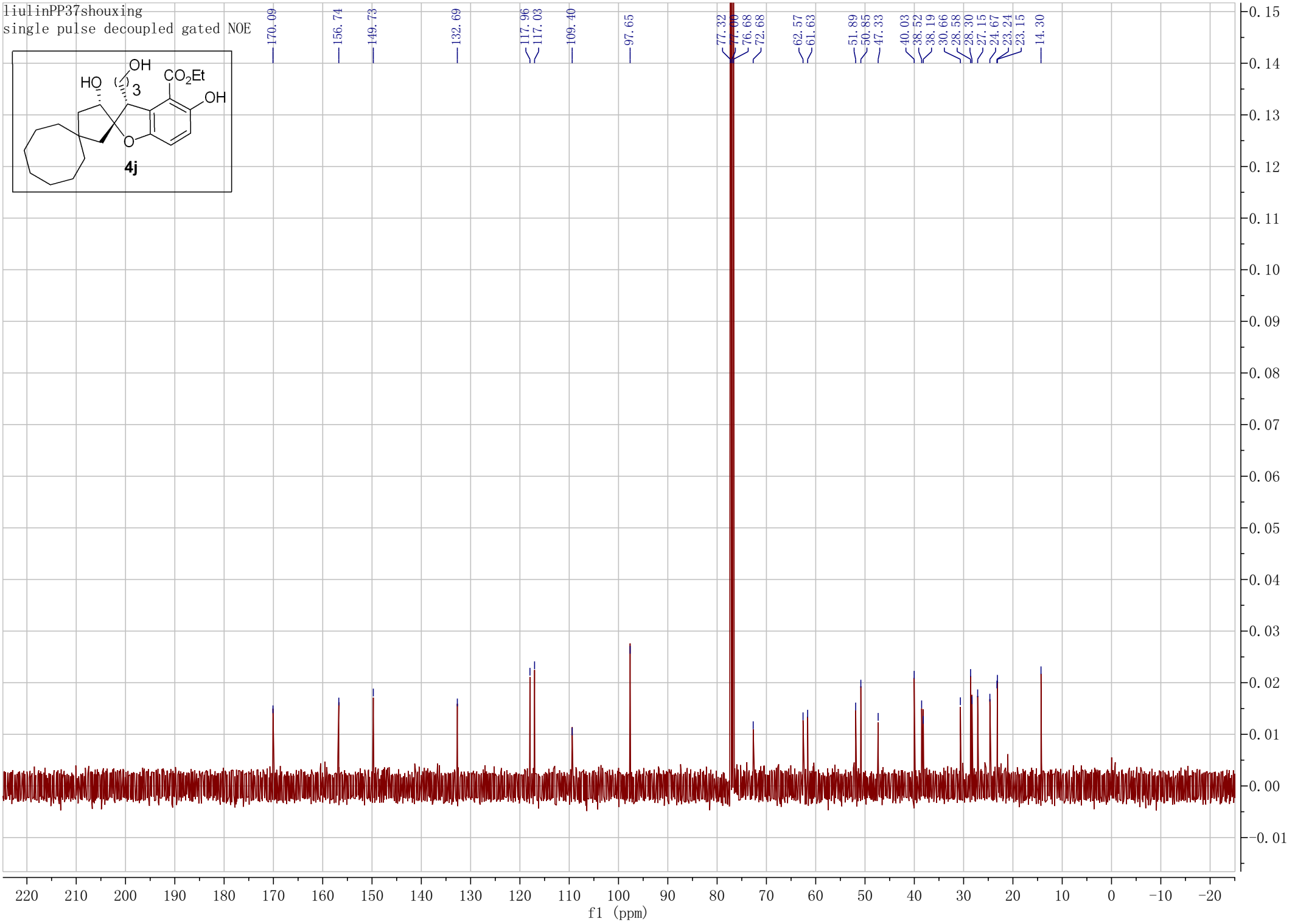
4i

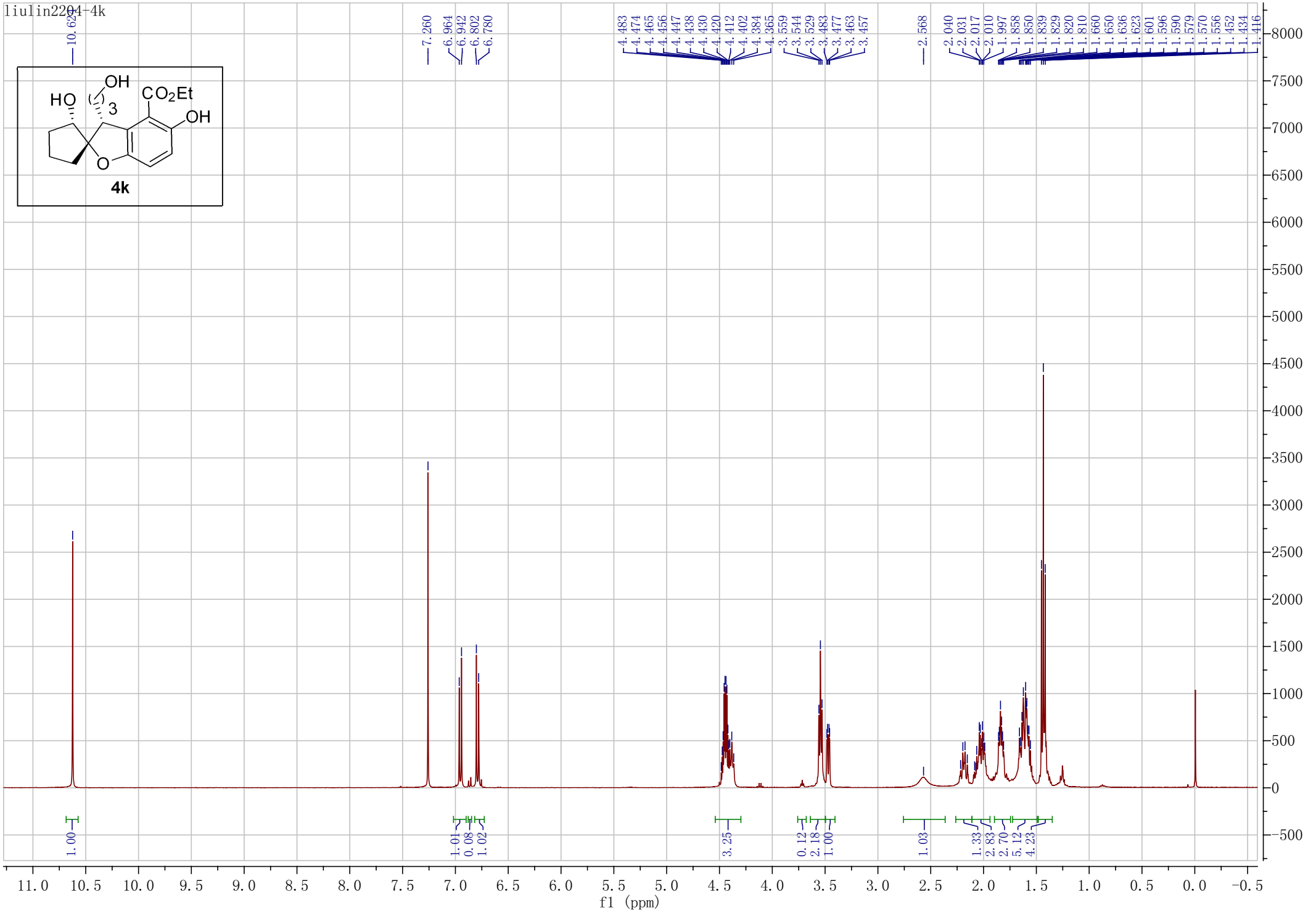
170.08
156.77
149.94
132.50
117.91
117.06
109.47
97.42
77.32
77.00
76.68
73.20
62.61
61.64
51.26
50.80
46.71
41.77
30.48
27.08
23.78
23.57
14.28

f1 (ppm)



4j


liulinPP37shouxing
single pulse decoupled gated NOE
OH
HO
3
CO2Et
OH
O
4j
170.09
156.74
149.73
132.69
117.96
117.03
109.40
97.65
77.32
76.68
72.68
62.57
61.63
51.89
50.85
47.33
40.03
38.52
38.19
30.66
28.58
28.30
27.15
24.67
23.24
23.15
14.30
f1 (ppm)


liulin2204-4k
10.623
7.260
6.964
6.942
6.802
6.780
4.483
4.474
4.465
4.456
4.447
4.438
4.430
4.420
4.412
4.402
4.384
4.365
3.559
3.544
3.529
3.483
3.477
3.463
3.457
2.568
2.040
2.031
2.017
2.010
1.997
1.858
1.850
1.839
1.829
1.820
1.810
1.660
1.650
1.636
1.623
1.601
1.596
1.590
1.579
1.570
1.556
1.452
1.434
1.416
OH
HO
3
CO2Et
OH
O
4k
1.00
1.01
0.08
1.02
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0.12
2.18
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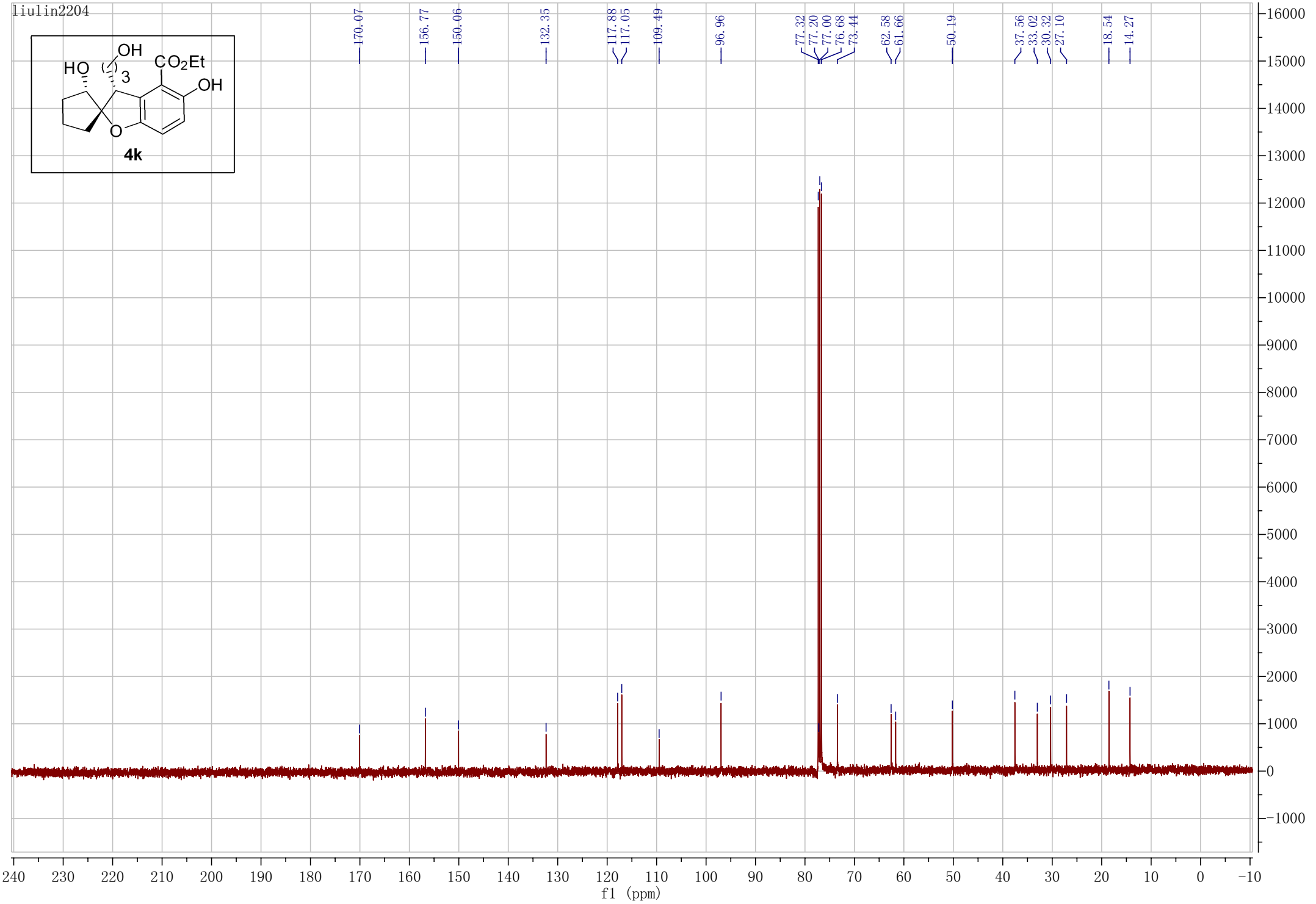
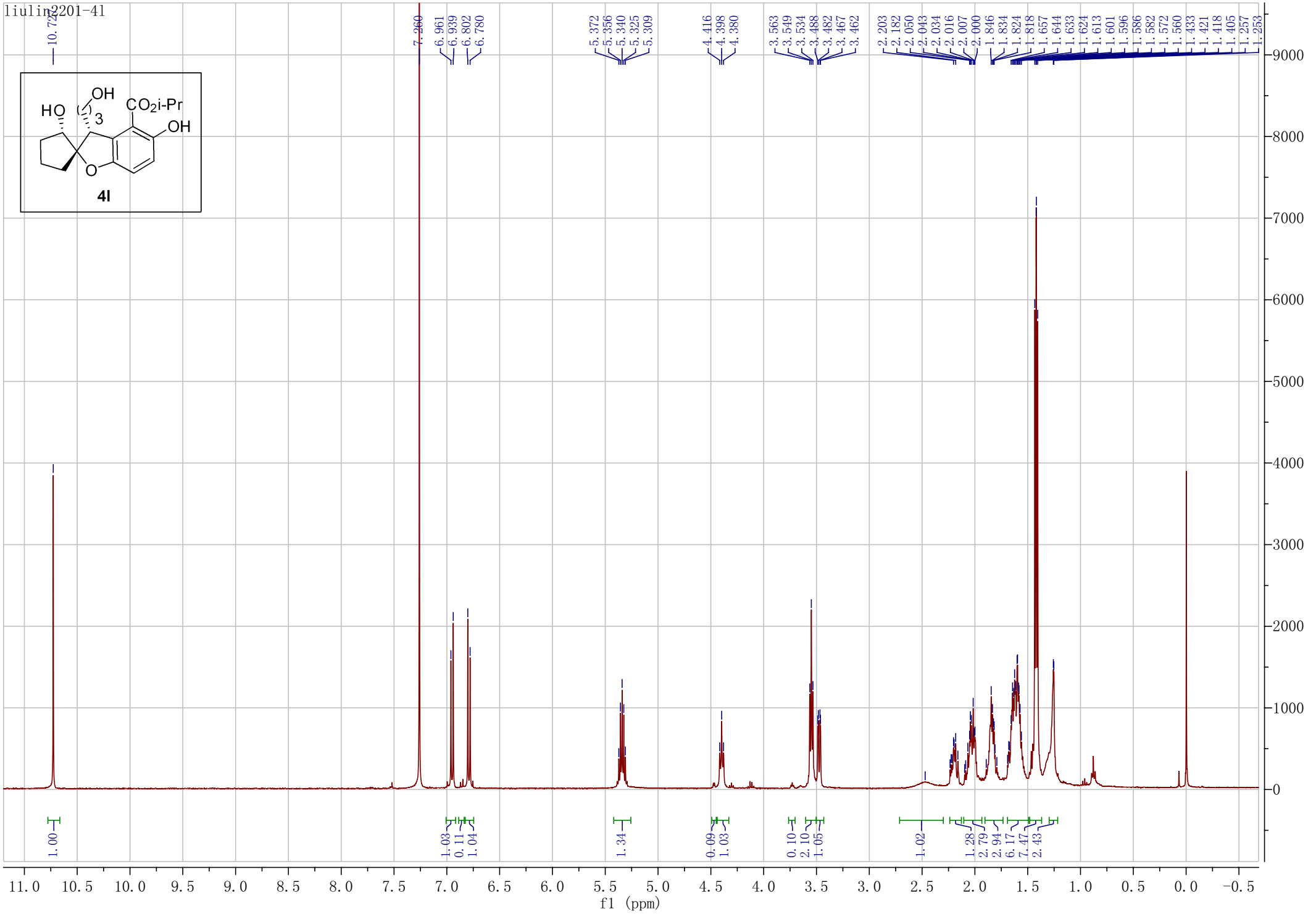
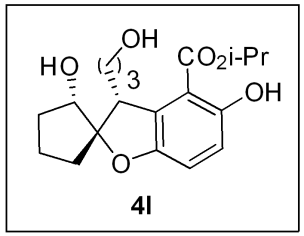
1.03
1.33
2.83
2.70
5.12
4.23
f1 (ppm)


liulin2204
OH
HO
3
CO2Et
OH
O
4k
170.07
156.77
150.06
132.35
117.88
117.05
109.49
96.96
77.32
77.20
77.00
76.68
73.44
62.58
61.66
50.19
37.56
33.02
30.32
27.10
18.54
14.27
f1 (ppm)

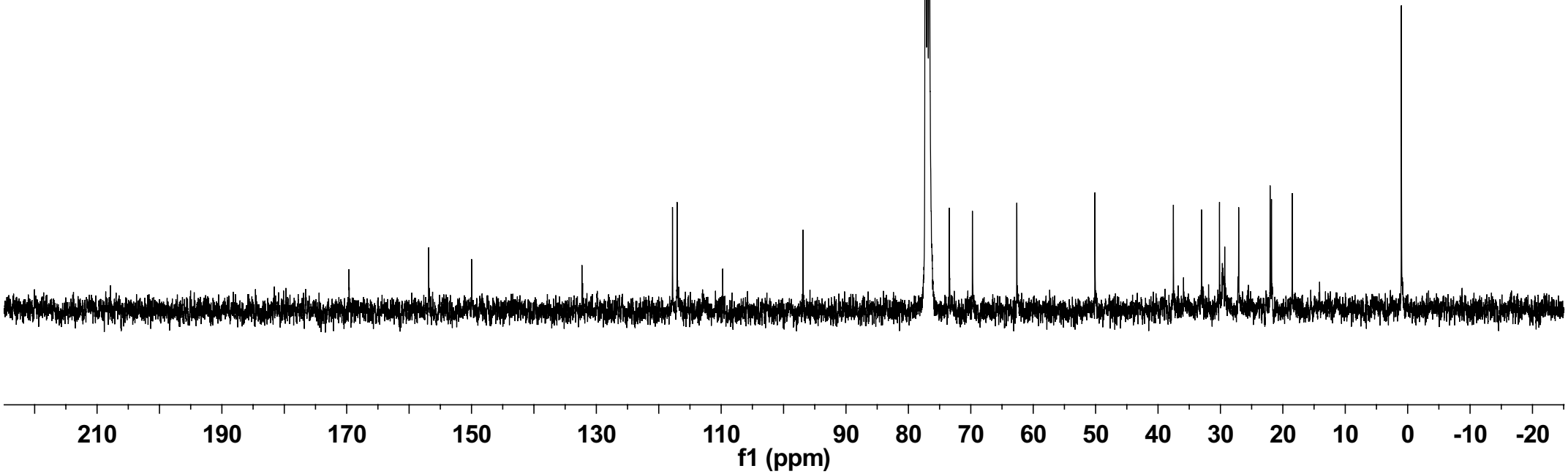

liulin2201-41
10.724
7.260
6.961
6.939
6.802
6.780
5.372
5.356
5.340
5.325
5.309
4.416
4.398
4.380
3.563
3.549
3.534
3.488
3.482
3.467
3.462
2.203
2.182
2.050
2.043
2.034
2.016
2.007
2.000
1.846
1.834
1.824
1.818
1.657
1.644
1.633
1.624
1.613
1.601
1.596
1.586
1.582
1.572
1.560
1.433
1.421
1.418
1.405
1.257
1.253
OH
HO
3
CO2i-Pr
OH
O
4l
1.00
1.03
0.11
1.04
1.34
0.09
1.03
0.10
2.10
1.05
1.02
1.28
2.79
2.94
6.17
7.47
2.43
f1 (ppm)

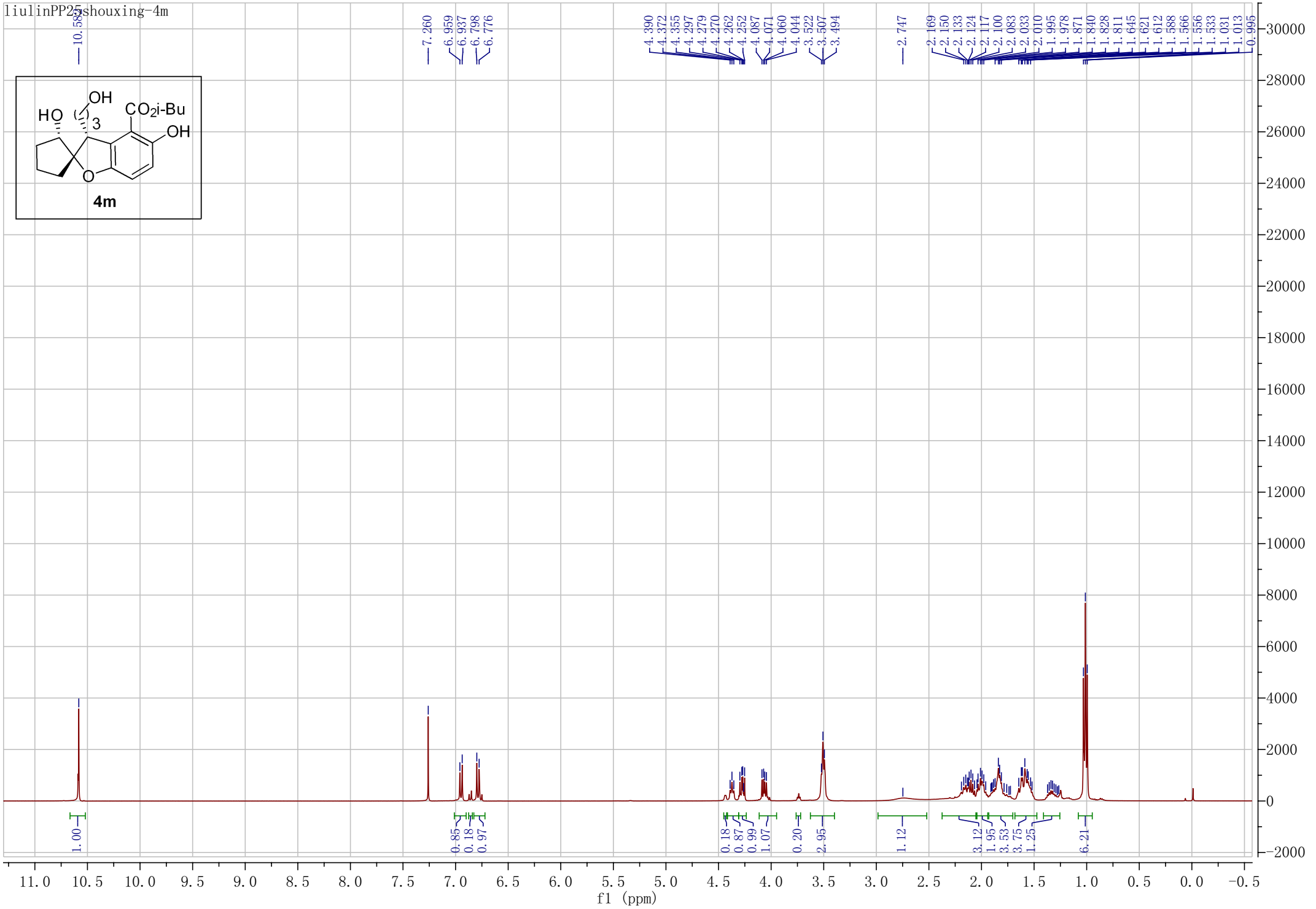
LIULINPP22XIAOXUAN
single pulse decoupled gated NOE

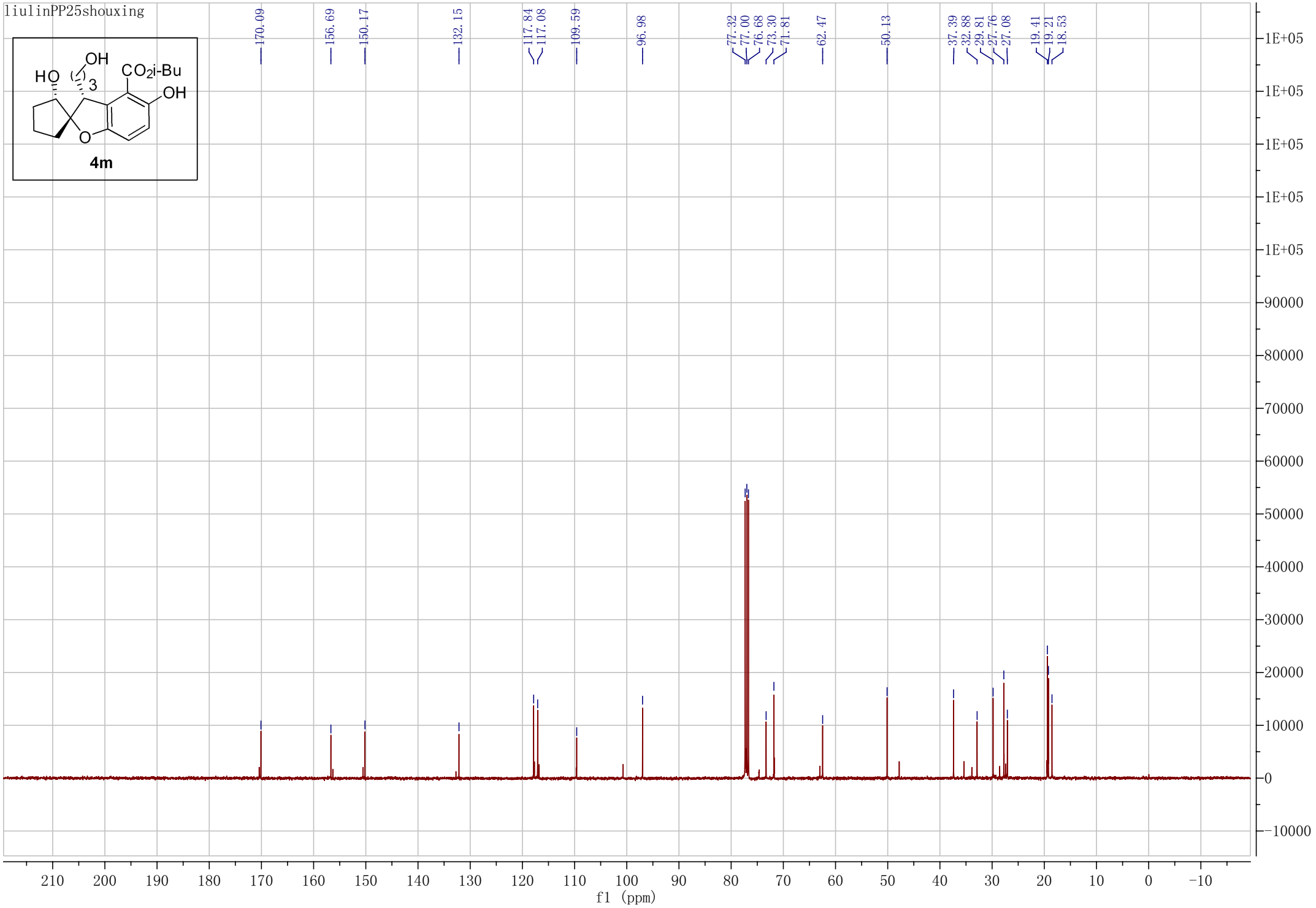


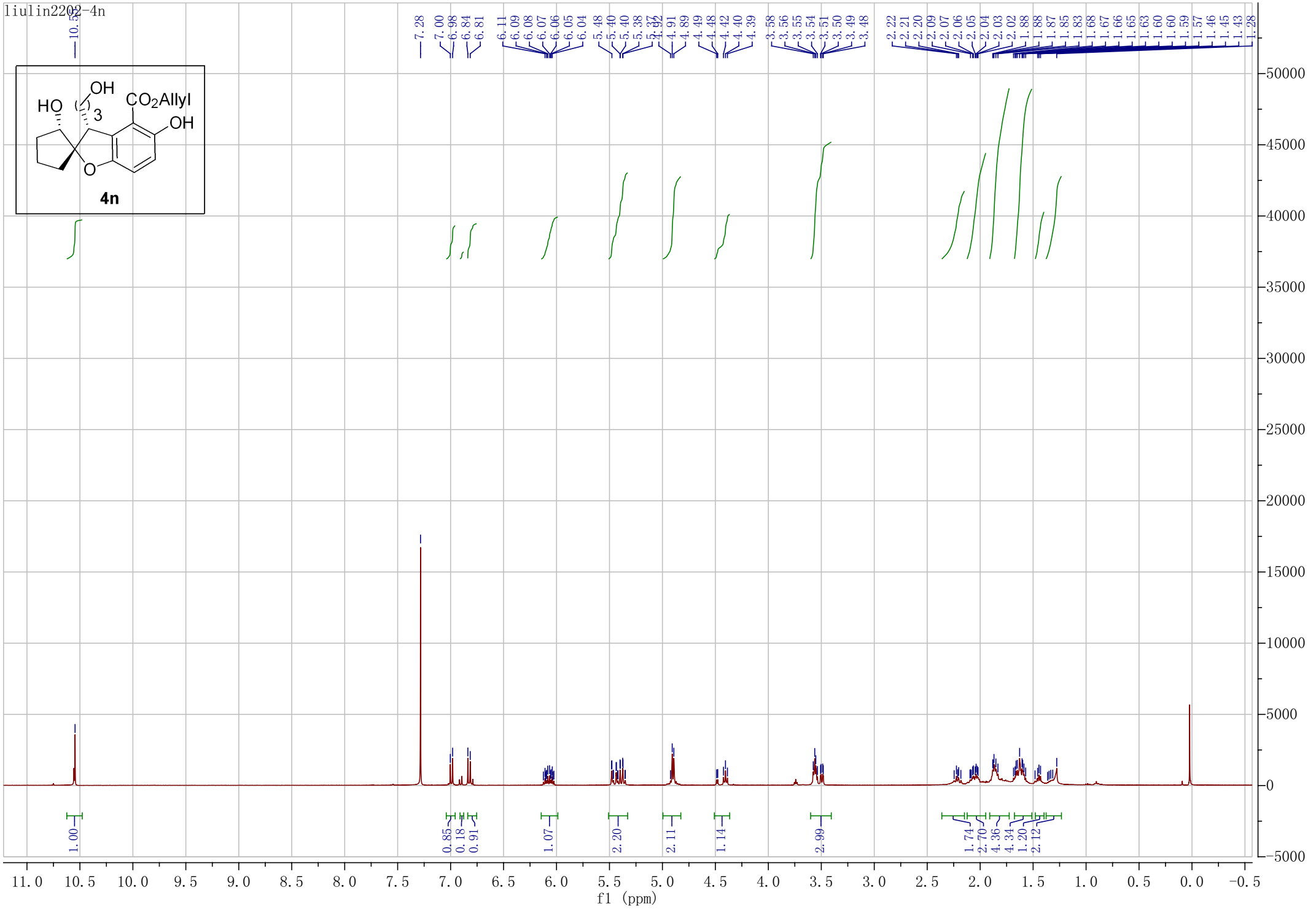
4l

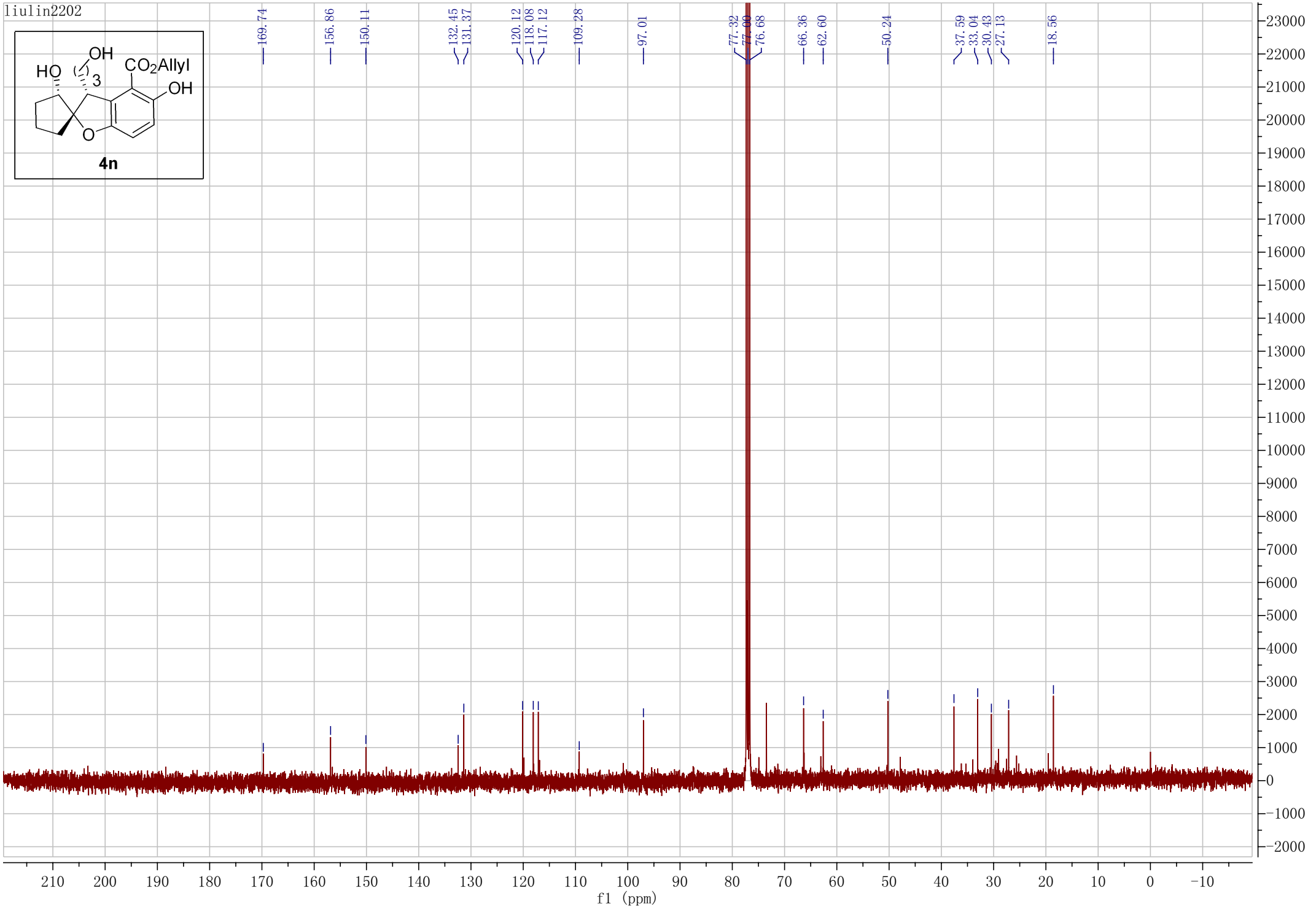
169.296
156.861
149.989
132.304
117.798
117.059
109.894
96.875
77.317
77.206
77.000
76.681
73.452
69.742
62.625
50.115
37.540
33.025
30.153
27.076
22.043
21.820
18.496
1.011




liulinPP25shouxing-4m
10.582
7.260
6.959
6.937
6.798
6.776
4.390
4.372
4.355
4.297
4.279
4.270
4.262
4.252
4.087
4.071
4.060
4.044
3.522
3.507
3.494
2.747
2.169
2.150
2.133
2.124
2.117
2.100
2.083
2.033
2.010
1.995
1.978
1.871
1.840
1.828
1.811
1.645
1.621
1.612
1.588
1.566
1.556
1.533
1.031
1.013
0.995
OH
HO
3
CO2i-Bu
OH
O
4m
1.00
0.85
0.18
0.97
0.18
0.87
0.99
1.07
0.20
2.95
1.12
3.12
1.95
3.53
3.75
1.25
6.21
f1 (ppm)

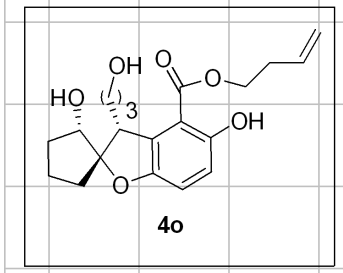

liulinPP25shouxing
OH
HO
3
CO2i-Bu
OH
O
4m
170.09
156.69
150.17
132.15
117.84
117.08
109.59
96.98
77.32
77.00
76.68
73.30
71.81
62.47
50.13
37.39
32.88
29.81
27.76
27.08
19.41
19.21
18.53
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


liulin2202-4n
HO
OH
3
CO2Allyl
OH
O
4n
f1 (ppm)


liulin2202
OH
HO
3
CO2Allyl
OH
O
4n
169.74
156.86
150.11
132.45
131.37
120.12
118.08
117.12
109.28
97.01
77.32
77.00
76.68
66.36
62.60
50.24
37.59
33.04
30.43
27.13
18.56
f1 (ppm)


lijulinPP42xiaoxuan 1
single pulse
OH
O
O
HO
3
OH
O
4o
f1 (ppm)

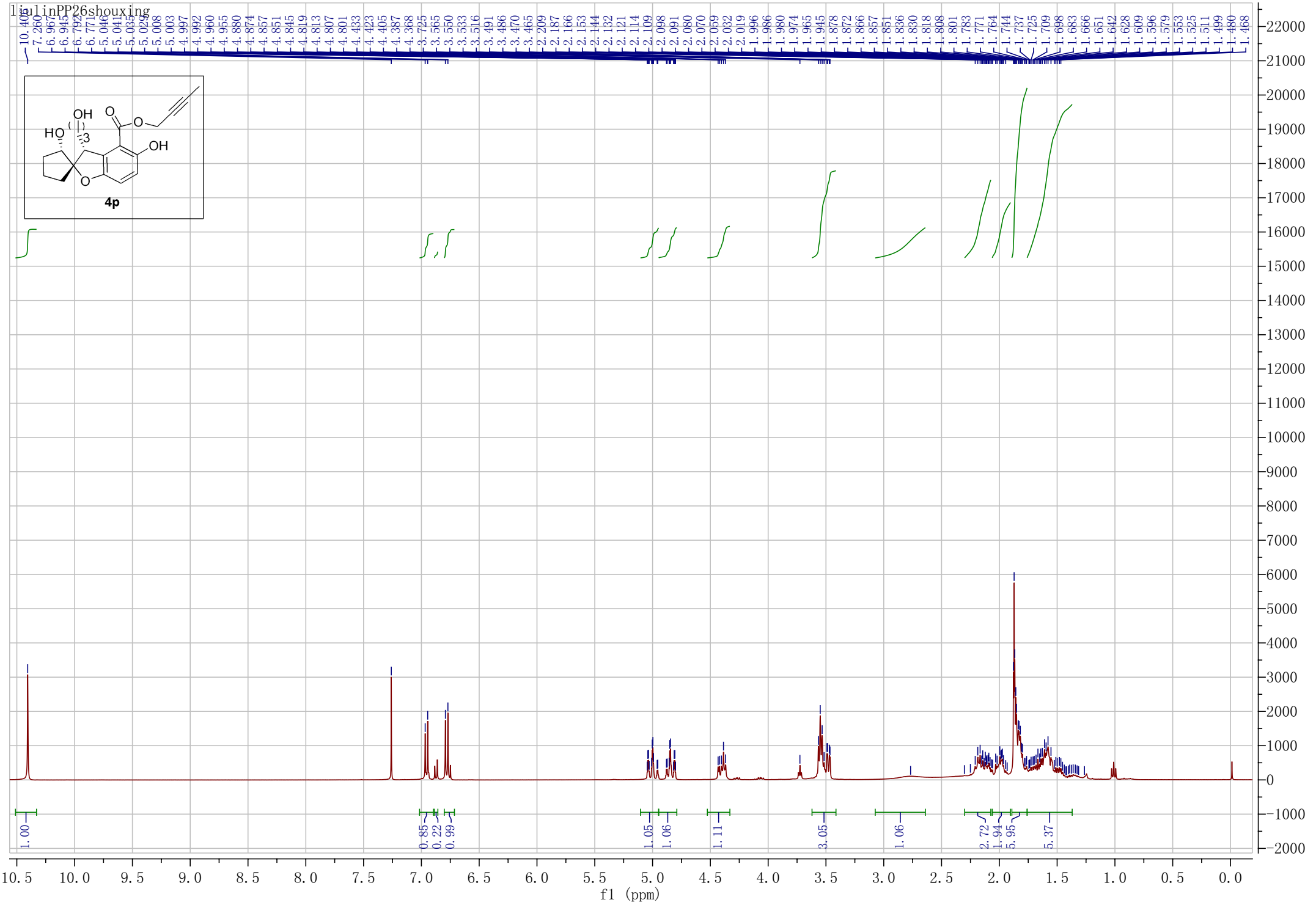
liulinPP42xiaoxuan 1
single pulse decoupled gated NOE

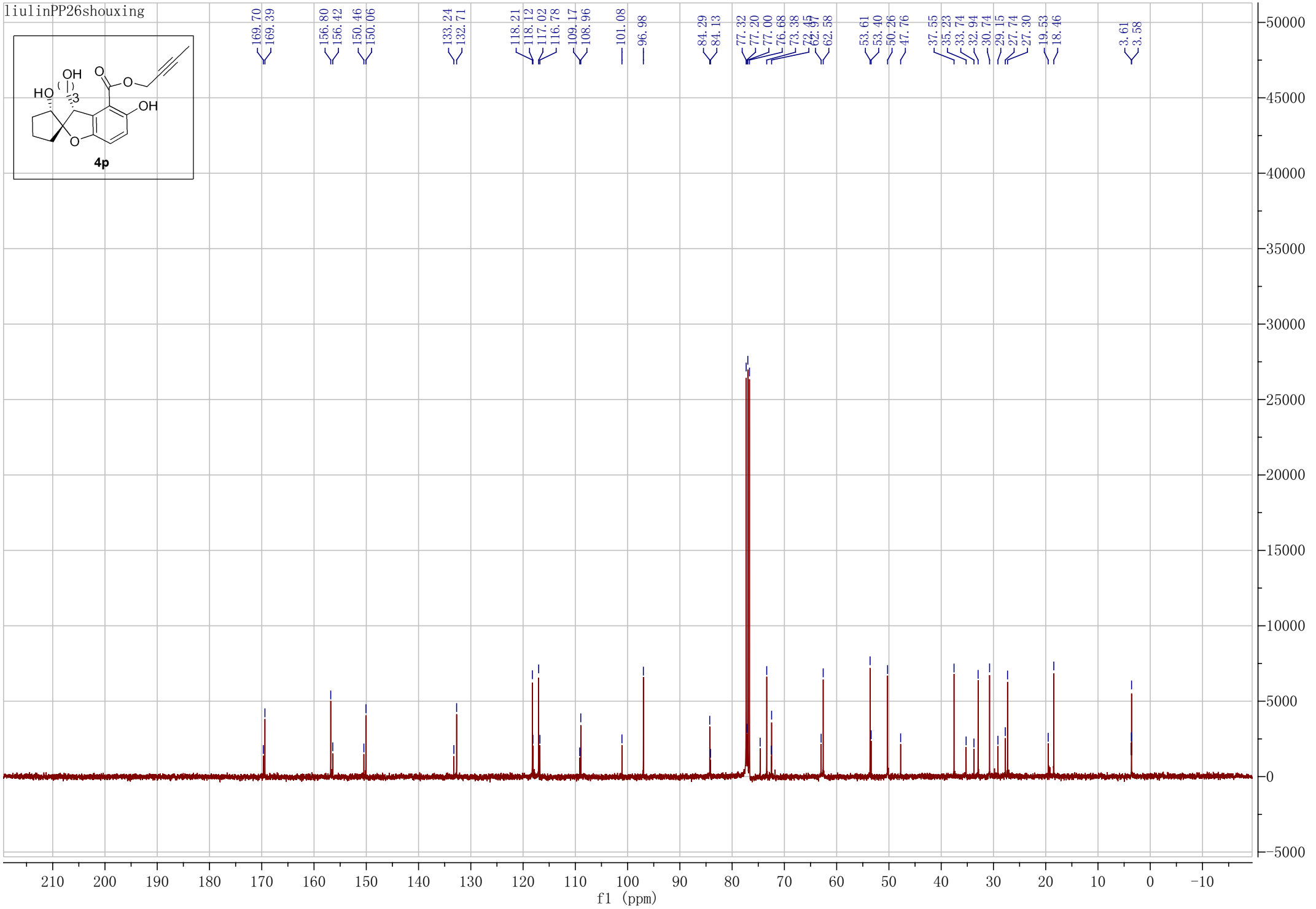


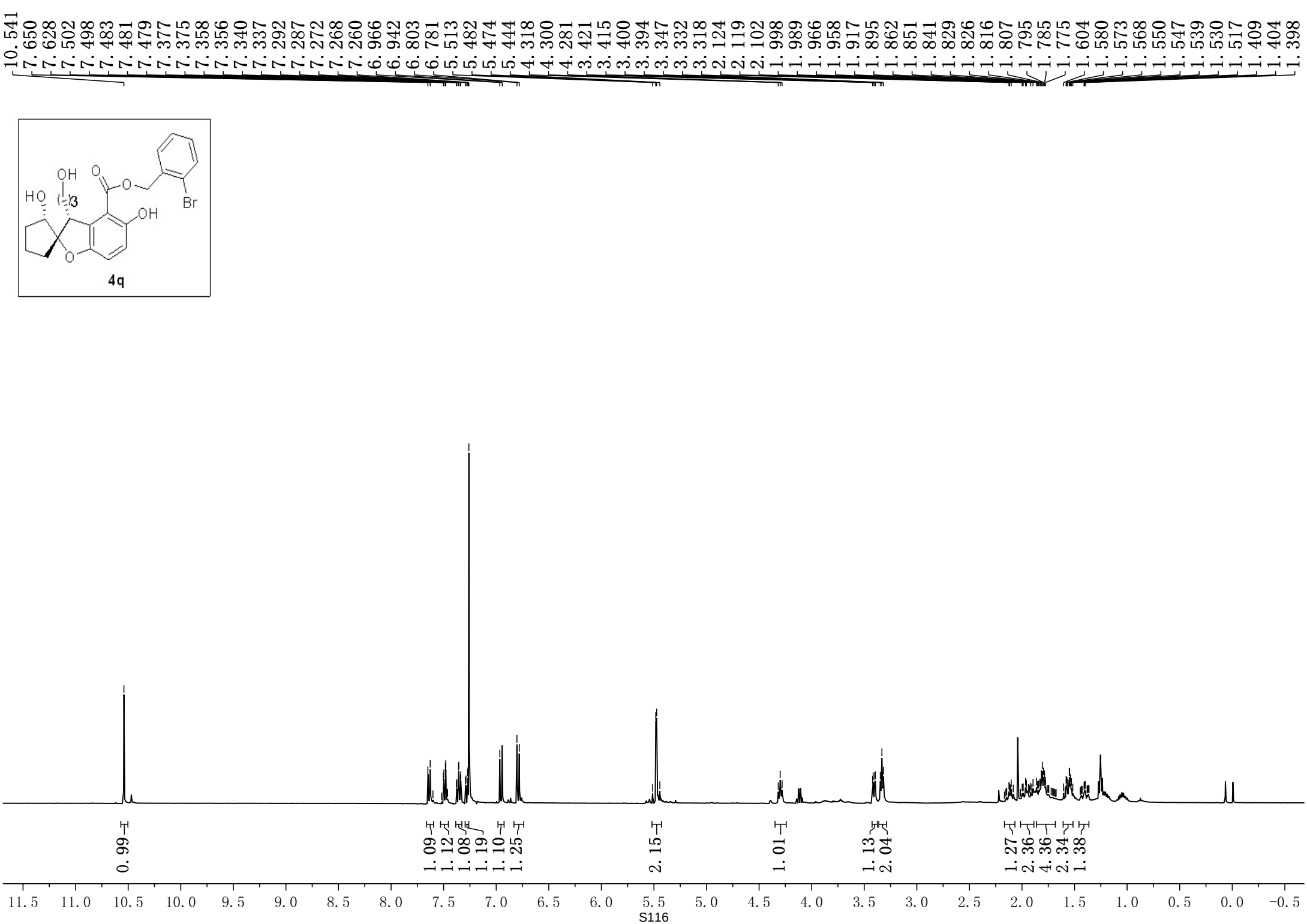
4o

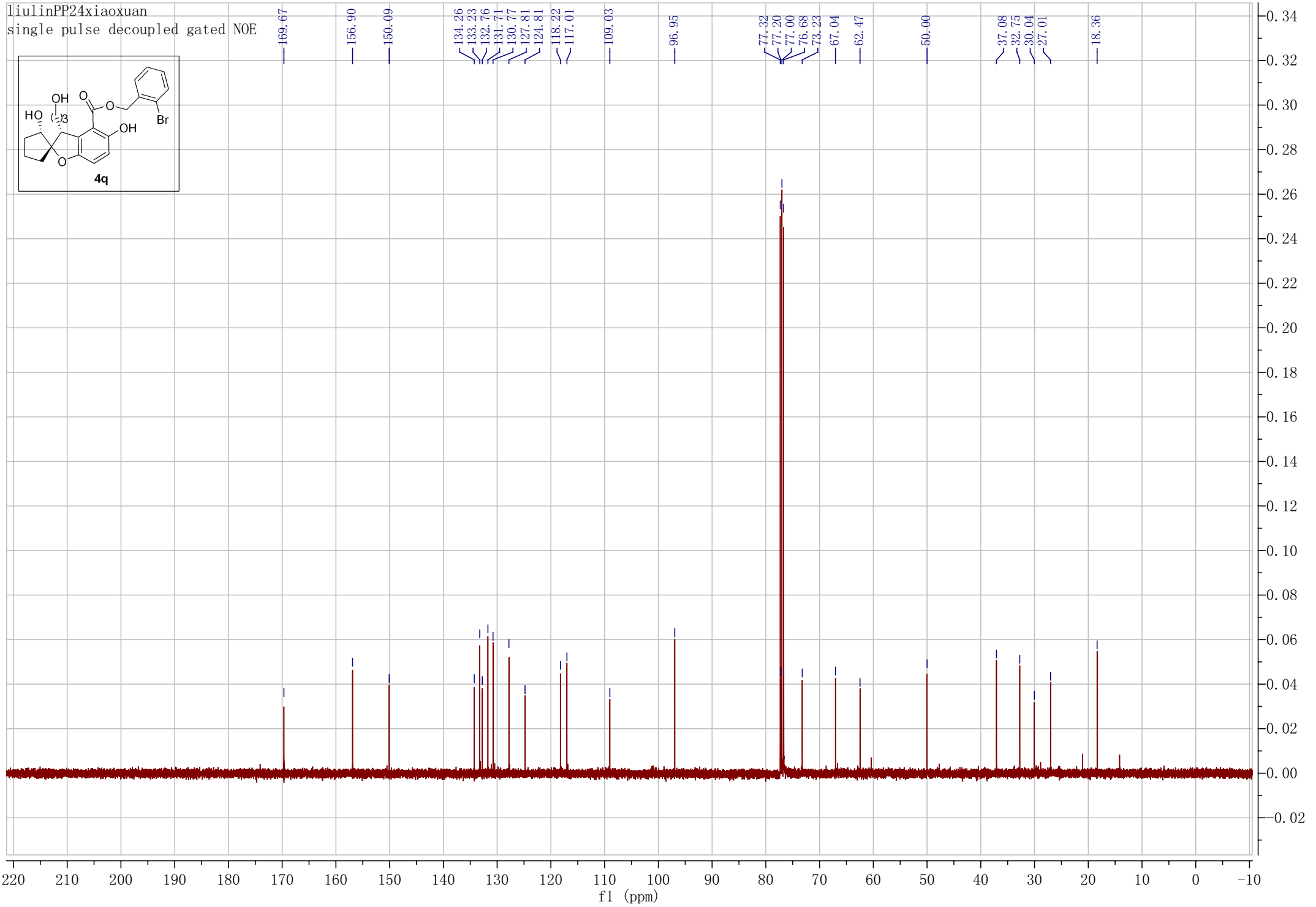
169.97
156.72
150.20
132.30
117.94
117.87
117.07
109.45
97.05
77.32
77.21
77.19
77.00
76.68
73.37
64.63
62.53
49.95
37.31
33.02
32.88
29.88
26.96
18.54

f1 (ppm)

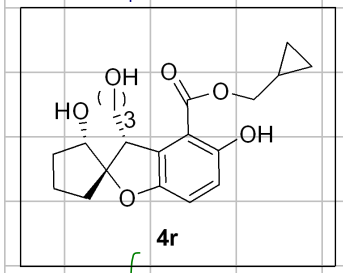

liulinPP26shouxing
OH
HO
3
O
O
O
OH
4p
f1 (ppm)


liulinPP26shouxing
169.70
169.39
156.80
156.42
150.46
150.06
133.24
132.71
118.21
118.12
117.02
116.78
109.17
108.96
101.08
96.98
84.29
84.13
77.32
77.20
77.00
76.68
73.38
72.45
62.97
62.58
53.61
53.40
50.26
47.76
37.55
35.23
33.74
32.94
30.74
29.15
27.74
27.30
19.53
18.46
3.61
3.58
OH
HO
3
O
O
OH
O
4p
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


10.541
7.650
7.628
7.502
7.498
7.483
7.481
7.479
7.377
7.375
7.358
7.356
7.340
7.337
7.292
7.287
7.272
7.268
7.260
6.966
6.942
6.803
6.781
5.513
5.482
5.474
5.444
4.318
4.300
4.281
3.421
3.415
3.400
3.394
3.347
3.332
3.318
2.124
2.119
2.102
1.998
1.989
1.966
1.958
1.917
1.895
1.862
1.851
1.841
1.829
1.826
1.816
1.807
1.795
1.785
1.775
1.604
1.580
1.573
1.568
1.550
1.547
1.539
1.530
1.517
1.409
1.404
1.398
HO
OH
O
O
Br
OH
O
4q
0.99
1.09
1.12
1.08
1.19
1.10
1.25
2.15
1.01
1.13
2.04
1.27
2.36
4.36
2.34
1.38
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
-0.5

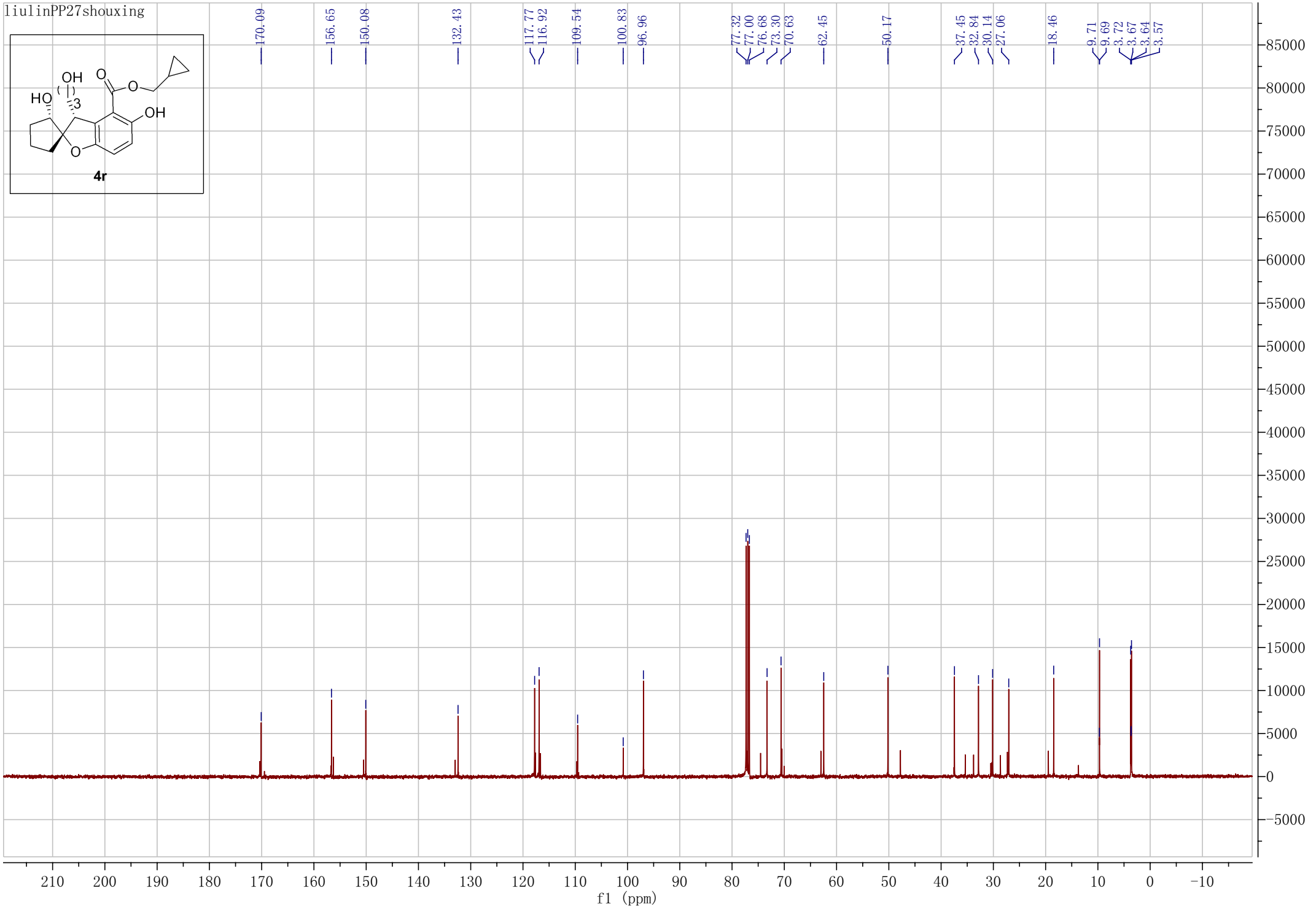

liulinPP24xiaoxuan
single pulse decoupled gated NOE
169.67
156.90
150.09
134.26
133.23
132.76
131.71
130.77
127.81
124.81
118.22
117.01
109.03
96.95
77.32
77.20
77.00
76.68
73.23
67.04
62.47
50.00
37.08
32.75
30.04
27.01
18.36
OH
HO
O
O
OH
Br
O
4q
f1 (ppm)

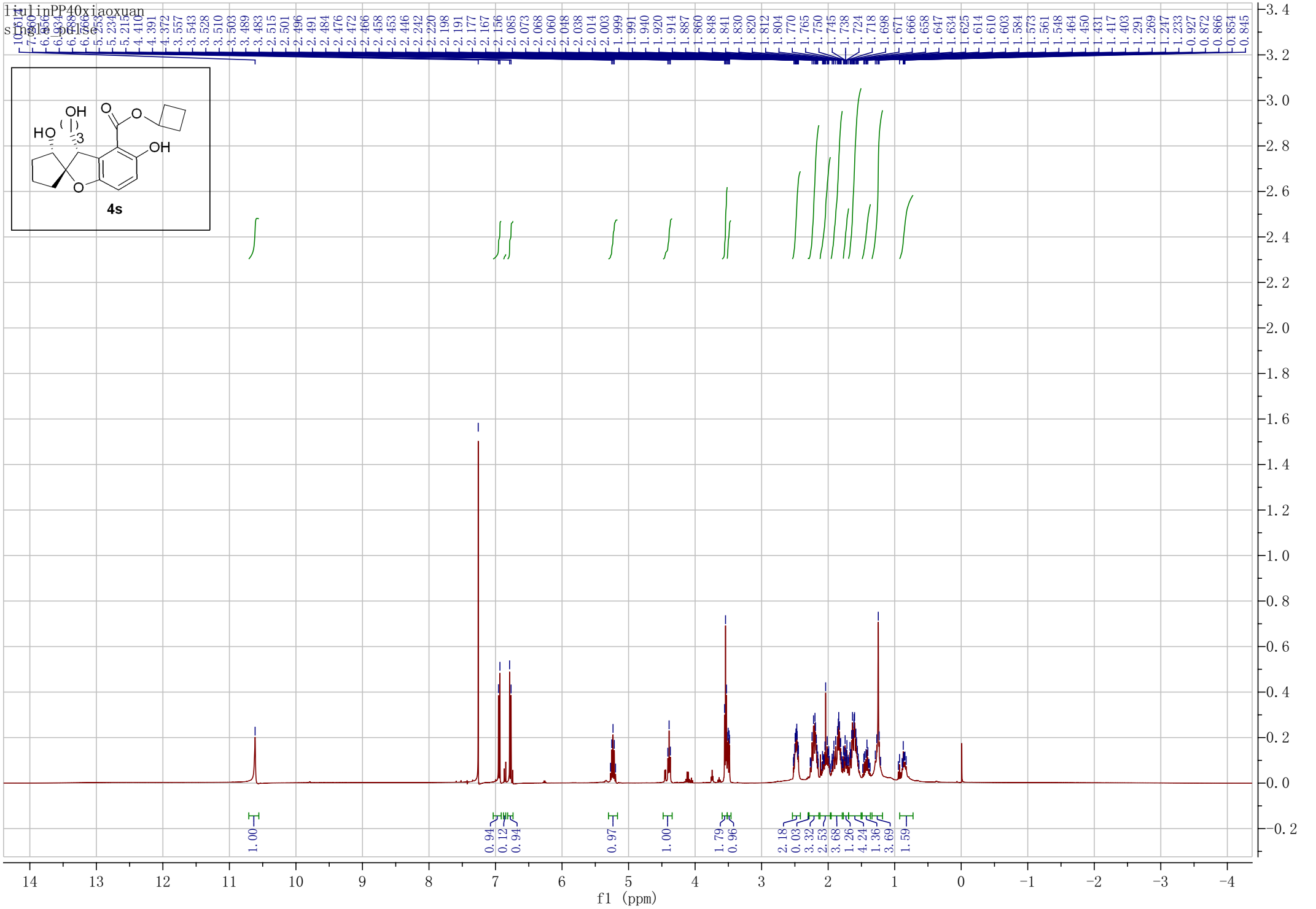
liulinPP27shouxing



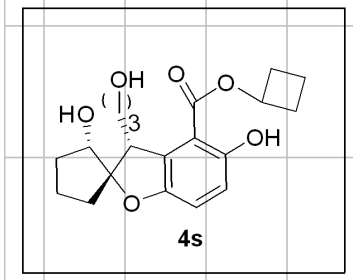
4r

f1 (ppm)


liulinPP27shouxing
OH
HO
3
O
O
OH
O
4r
170.09
156.65
150.08
132.43
117.77
116.92
109.54
100.83
96.96
77.32
77.00
76.68
73.30
70.63
62.45
50.17
37.45
32.84
30.14
27.06
18.46
9.71
9.69
3.72
3.67
3.64
3.57
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


liulinPP40xiaoxuan
single pulse
OH
HO
3
O
O
O
OH
4s
f1 (ppm)

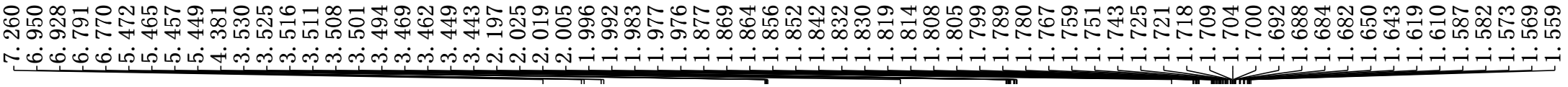
liulinPP40xiaoxuan
single pulse decoupled gated NOE

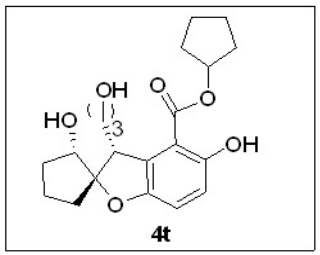


4s

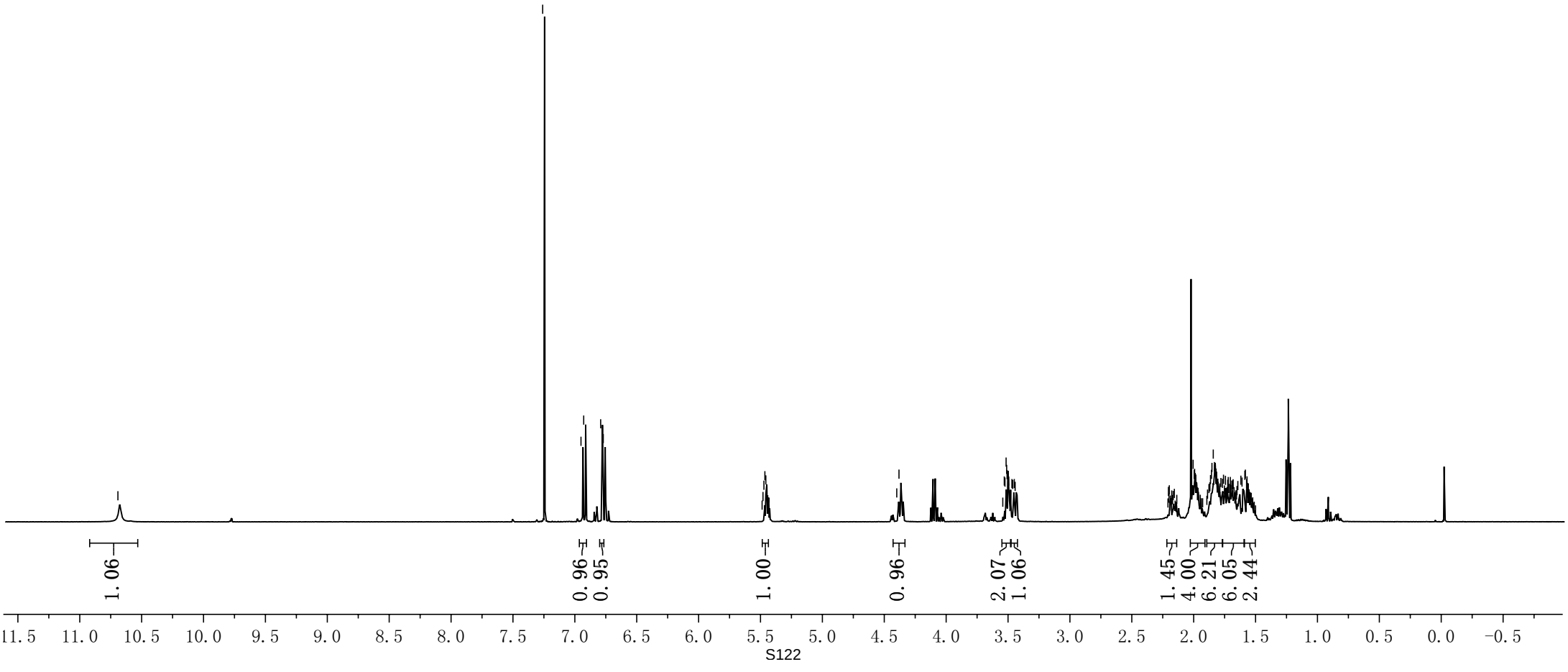
169.50
156.83
150.01
132.34
117.88
117.02
109.36
96.93
77.32
77.00
76.68
73.42
70.06
62.55
50.16
37.59
32.98
30.52
30.31
30.29
27.20
18.50
13.74

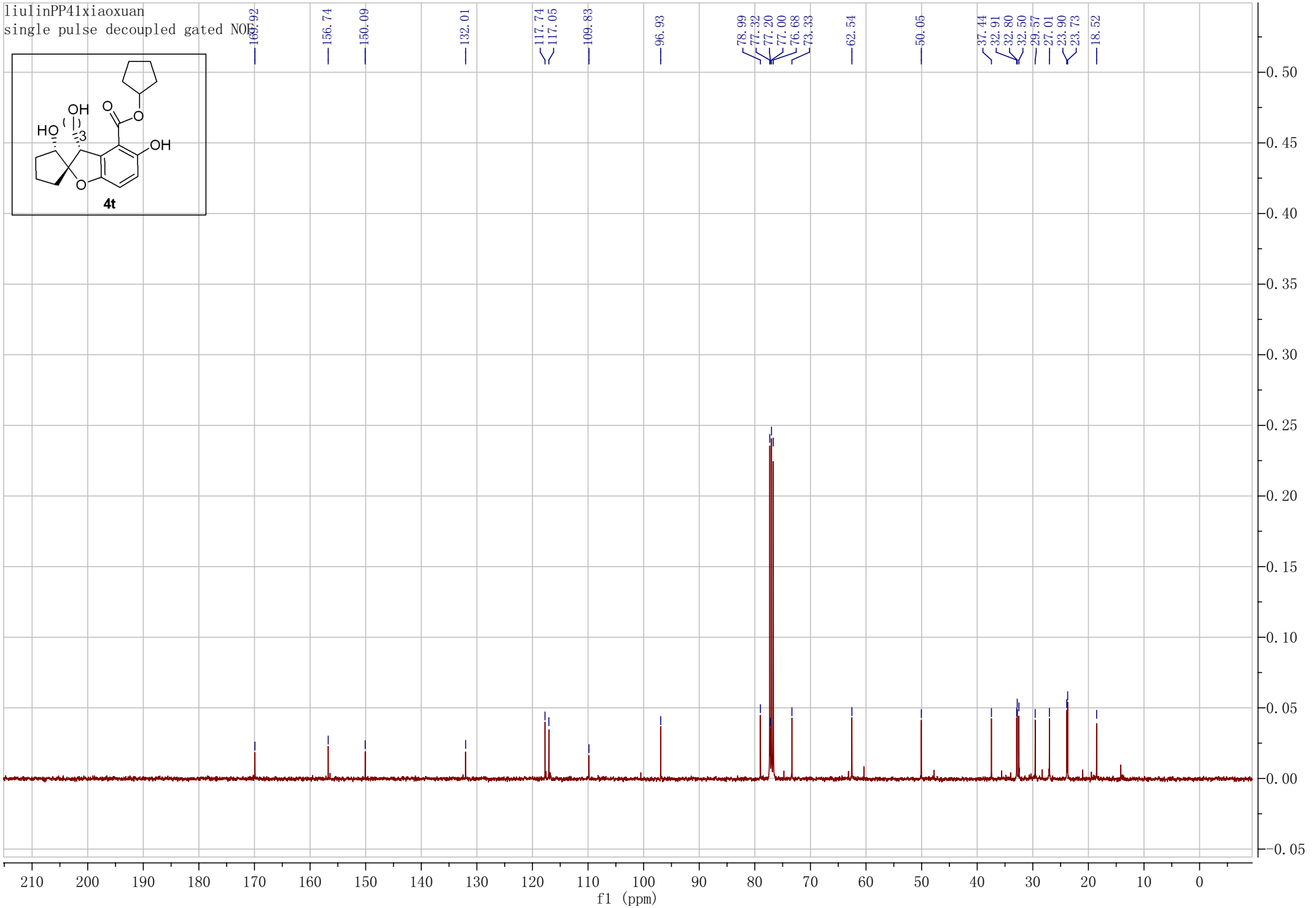
f1 (ppm)

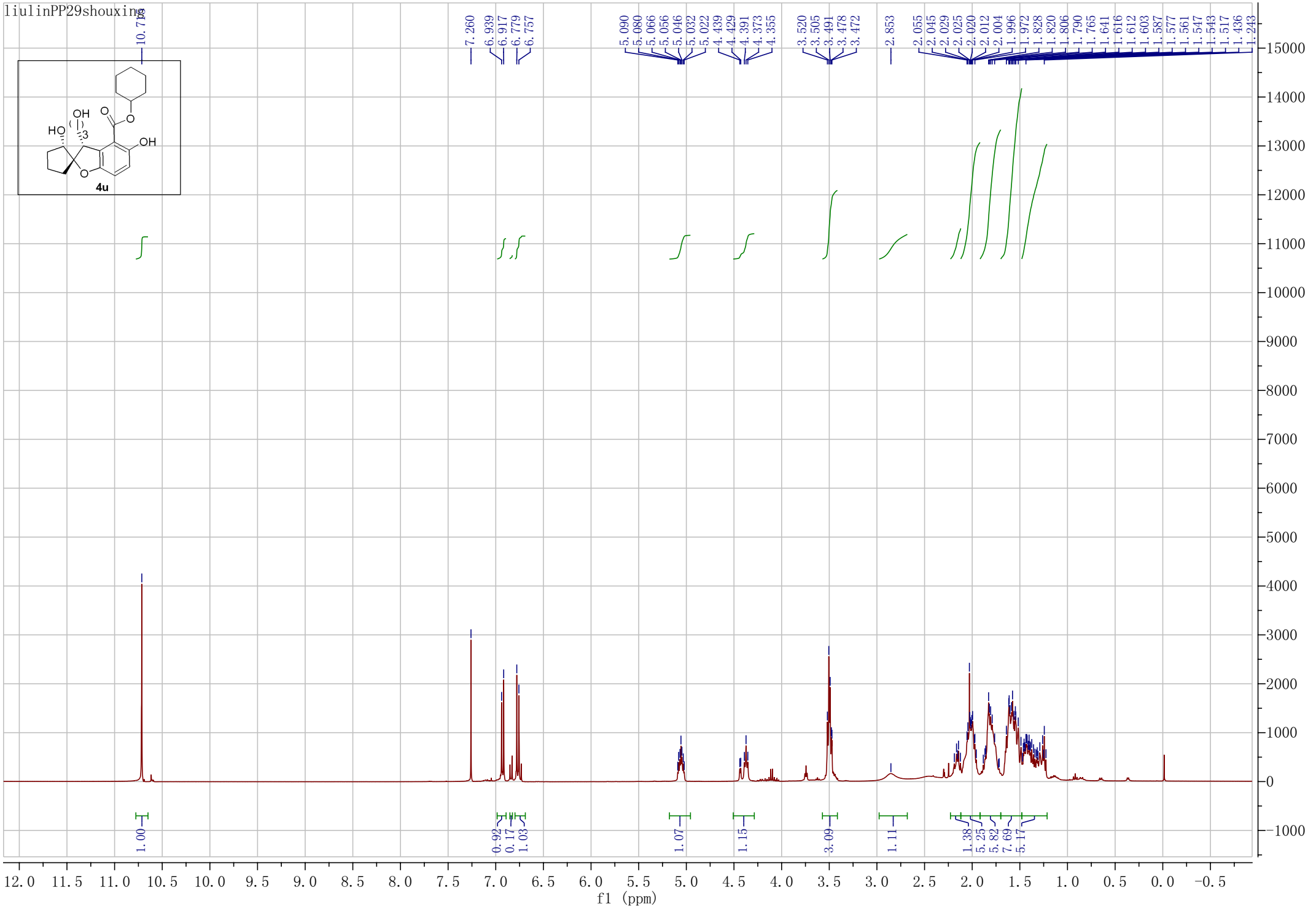

7.260
6.950
6.928
6.791
6.770
6.472
5.465
5.457
5.449
4.381
3.530
3.525
3.516
3.511
3.508
3.501
3.494
3.469
3.462
3.449
3.443
2.197
2.025
2.019
2.005
1.996
1.992
1.983
1.977
1.976
1.877
1.869
1.864
1.856
1.852
1.842
1.832
1.830
1.819
1.814
1.808
1.805
1.799
1.789
1.780
1.767
1.759
1.751
1.743
1.725
1.721
1.718
1.709
1.704
1.700
1.692
1.688
1.684
1.682
1.650
1.643
1.619
1.610
1.587
1.582
1.573
1.569
1.559

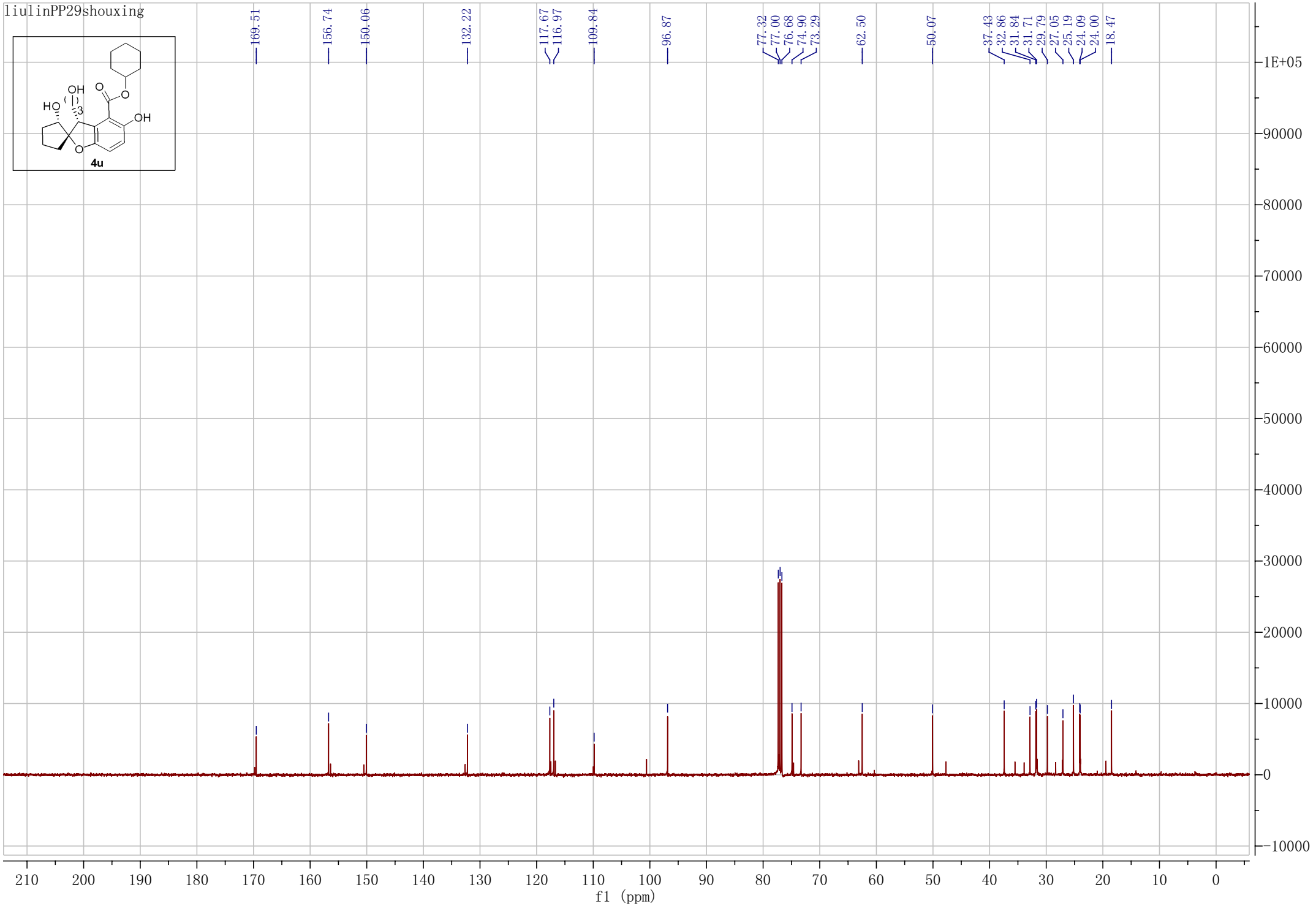

OH
HO
3
O
O
OH
O

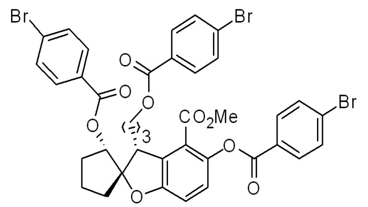
4t


1.06
0.96
0.95
1.00
0.96
2.07
1.06
1.45
4.00
6.21
6.05
2.44
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
-0.5


liulinPP41xiaoxuan
single pulse decoupled gated NOE
169.92
156.74
150.09
132.01
117.74
117.05
109.83
96.93
78.99
77.32
77.20
77.00
76.68
73.33
62.54
50.05
37.44
32.91
32.80
32.50
29.57
27.01
23.90
23.73
18.52
OH
HO
3
O
O
O
OH
4t
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

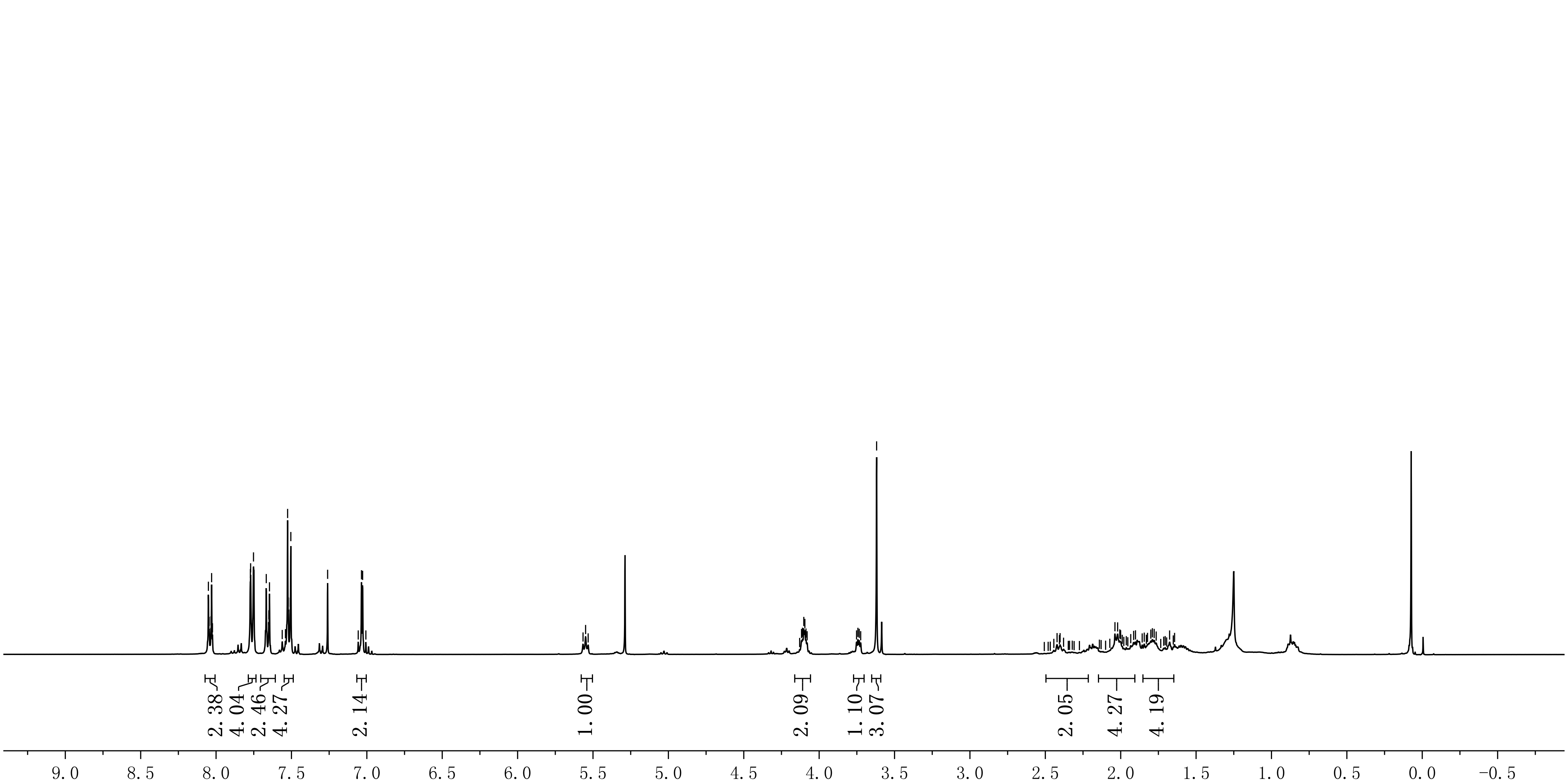

liulinPP29shouxing
10.715
7.260
6.939
6.917
6.779
6.757
5.090
5.080
5.066
5.056
5.046
5.032
5.022
4.439
4.429
4.391
4.373
4.355
3.520
3.505
3.491
3.478
3.472
2.853
2.055
2.045
2.029
2.025
2.020
2.012
2.004
1.996
1.972
1.828
1.820
1.806
1.790
1.765
1.641
1.616
1.612
1.603
1.587
1.577
1.561
1.547
1.543
1.517
1.436
1.243
OH
HO
O
O
OH
O
4u
1.00
0.92
0.17
1.03
1.07
1.15
3.09
1.11
1.38
5.25
5.82
7.69
5.17
f1 (ppm)


liulinPP29shouxing
169.51
156.74
150.06
132.22
117.67
116.97
109.84
96.87
77.32
77.00
76.68
74.90
73.29
62.50
50.07
37.43
32.86
31.84
31.71
29.79
27.05
25.19
24.09
24.00
18.47
4u
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Br
Br
Br
O
O
O
O
CO2Me
3
O
O
O
O

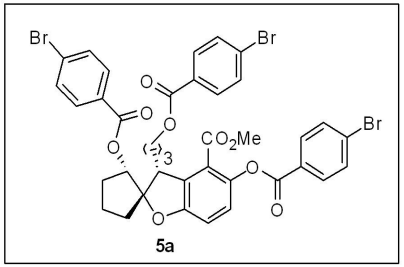
5a



8.051 8.046 8.034 8.030 8.024 7.772 7.771 7.752 7.667 7.650 7.646 7.561 7.540 7.526 7.521 7.508 7.504 7.260 7.057 7.036 7.028 7.007 5.566 5.549 5.532 4.129 4.117 4.110 4.102 4.095 4.088 4.080 3.752 3.743 3.734 3.725 3.619 2.422 2.407 2.402 2.379 2.038 2.020 2.006 2.001 1.990 1.979 1.963 1.953 1.934 1.914 1.902 1.858 1.844 1.830 1.822 1.800 1.790 1.778 1.765 1.715 1.705 1.695 1.676 1.651 1.643
2.38 4.04 2.46 4.27 2.14 1.00 2.09 1.10 3.07 2.05 4.27 4.19
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

LIULINSHANGXIU

single pulse decoupled gated NOE

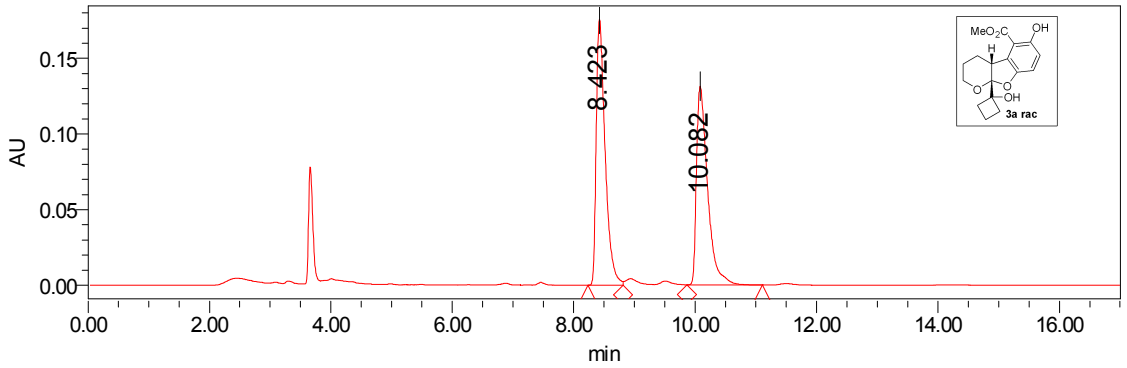


165.59
165.15
165.02
156.38
143.15
133.14
131.95
131.75
131.57
131.11
131.02
128.89
128.83
128.65
128.24
123.45
113.62
97.55
77.32
77.00
76.68
75.34
64.87
52.14
47.90
36.46
29.65
29.11
27.23
26.16
18.61

f1 (ppm)

Sample Name: 3a-rac
Column: 10.00 ul

Wave Length: PDA 254 nm



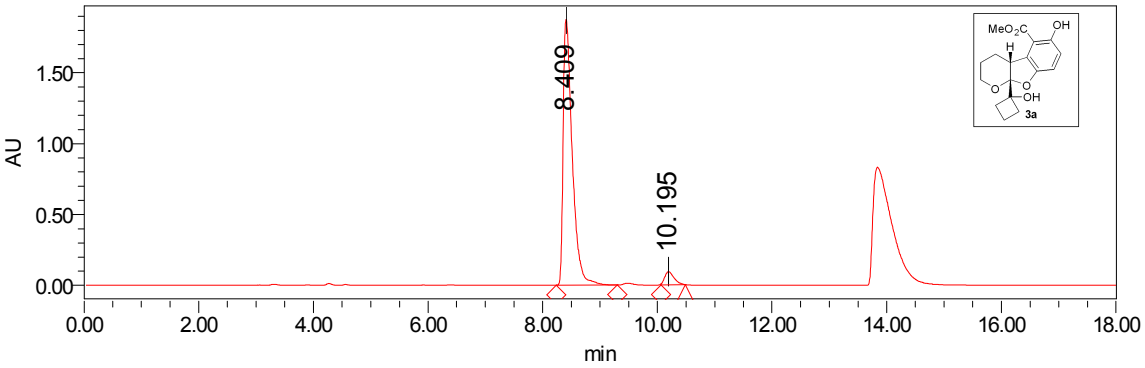
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	8.423	1792840.003	51.738	175776
2	10.082	1672395.158	48.262	131378

Sample Information

Sample Name: 3a
Column: 10.00 ul

Wave Length: PDA 254 nm



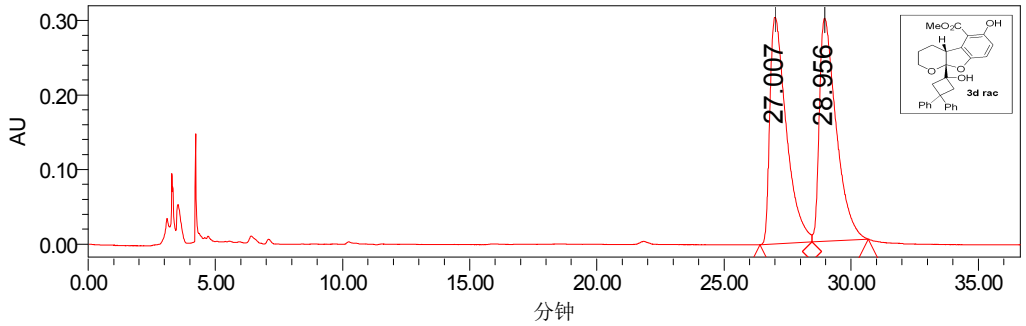
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	8.409	20647135.691	95.253	1877227
2	10.195	1029046.778	4.747	92423

Sample Information

Sample Name: 3d-rac
Column: 10.00 ul

Wave Length: PDA 254 nm



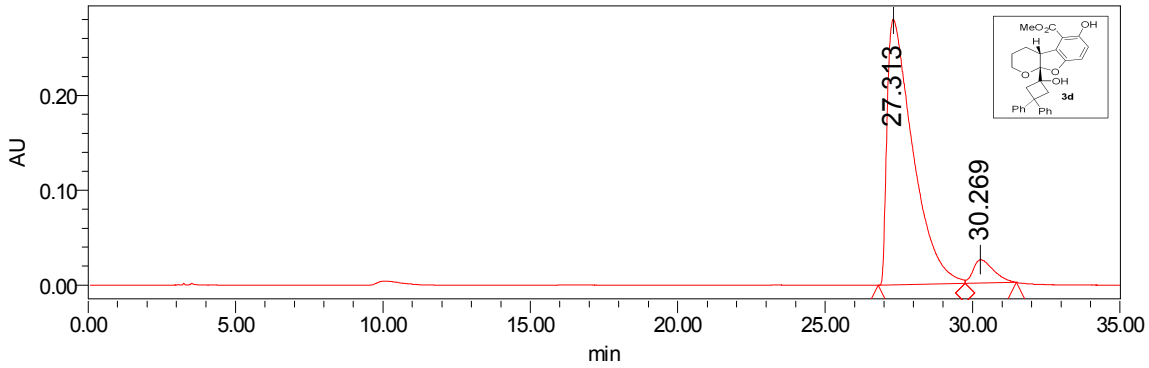
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	27.007	13780336.166	49.849	304233
2	28.956	13863744.802	50.151	299443

Sample Information

Sample Name: 3d
Column: 10.00 ul

Wave Length: PDA 254 nm



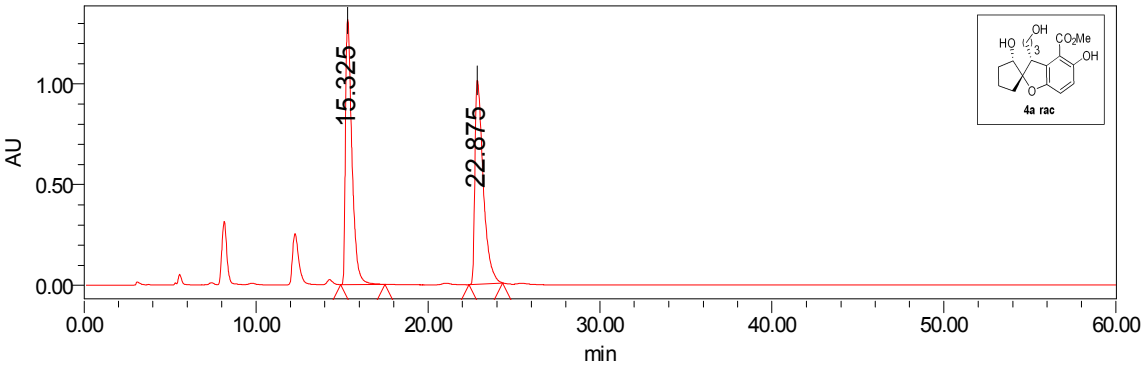
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	27.313	17021892.191	93.486	280036
2	30.269	1186013.144	6.514	24603

Sample Information

Sample Name: 4a rac
Column: 10.00 ul

Wave Length: PDA 254 nm

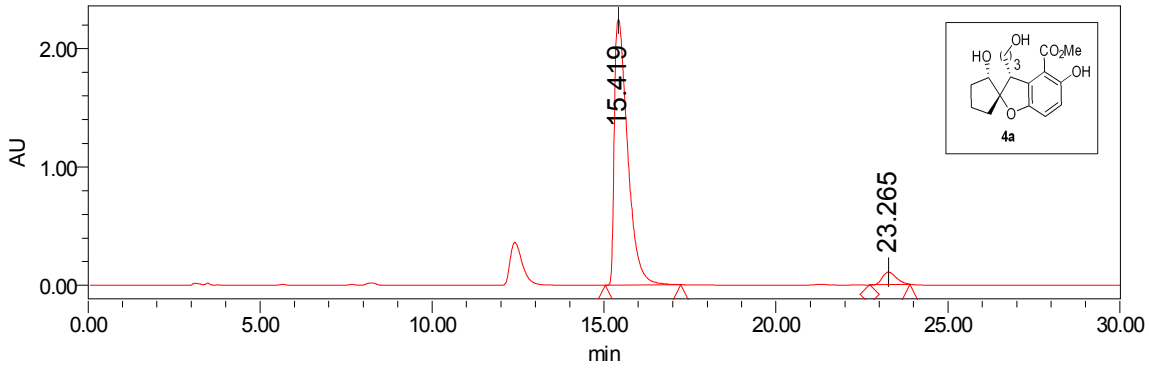


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	15.325	34076912.804	49.955	1316017
2	22.875	34138291.791	50.045	1011606

Sample Name: 4a
Column: 10.00 ul

Wave Length: PDA 254 nm

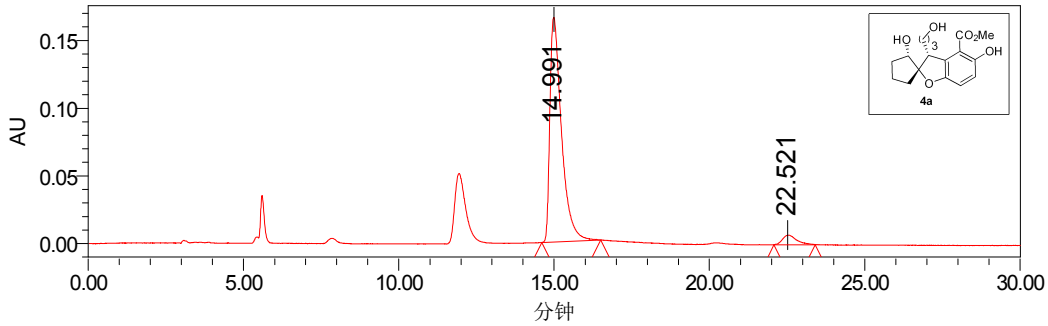


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	15.419	60225242.981	95.404	2245084
2	23.265	2901615.567	4.596	103391

2019/2/21 16:03:54 CST

Sample Name: 4a (1 mmol scale) Wave Length: PDA 254 nm
Column: 10.00 ul



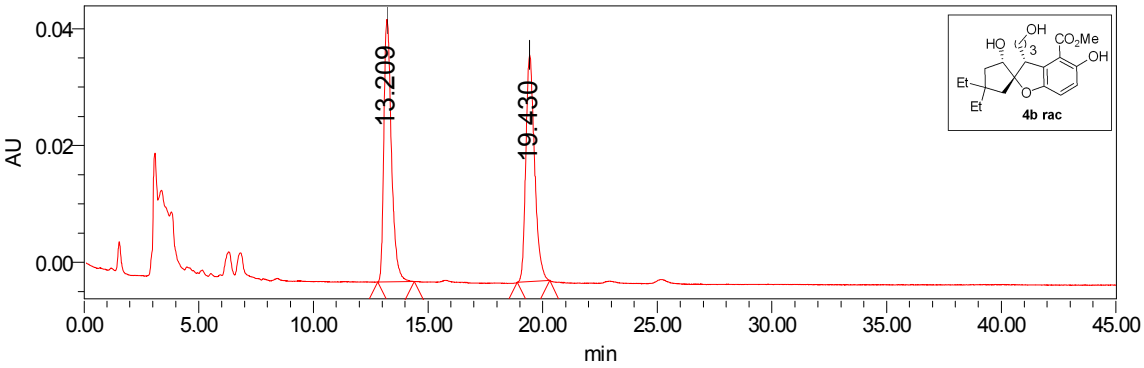
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	14.991	4312807.627	95.107	166151
2	22.521	221896.209	4.893	7162

Sample Information

Sample Name: 4b rac
Column: 10.00 ul

Wave Length: PDA 254 nm



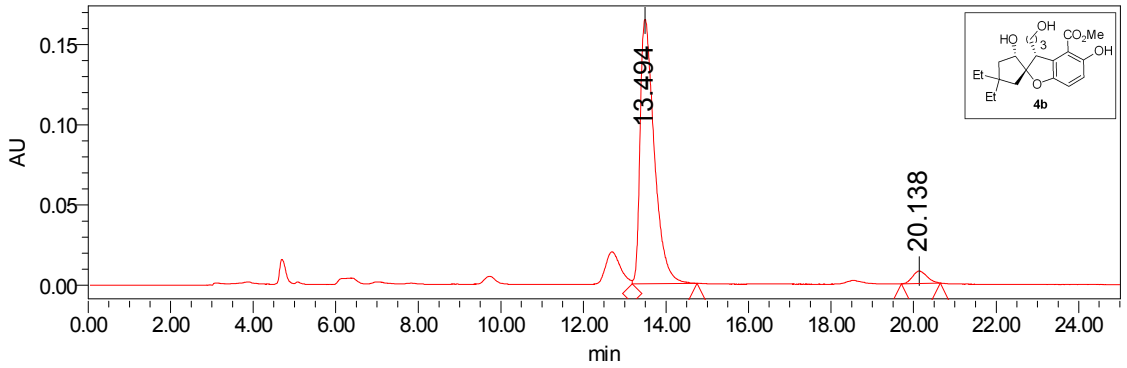
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.209	1029518.176	49.954	44988
2	19.430	1031422.731	50.046	38880

Sample Information

Sample Name: 4b
Column: 10.00 ul

Wave Length: PDA 254 nm



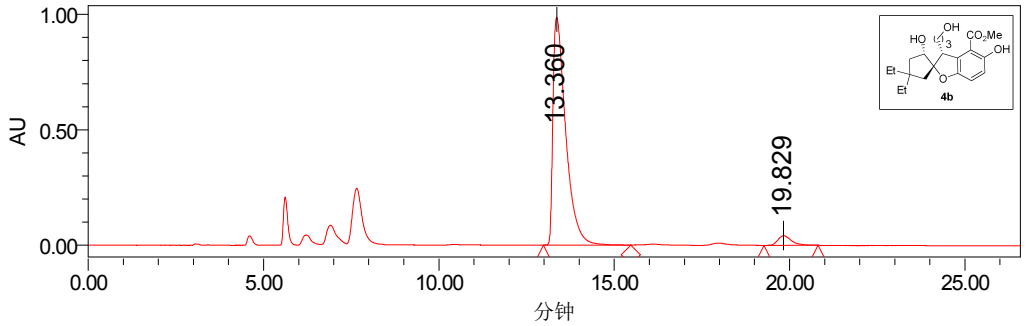
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.494	3906930.236	95.421	164704
2	20.138	187475.789	4.579	7689

2019/2/21 16:34:49 CST

Sample Name: 4b (1 mmol scale)
Column: 10.00 ul

Wave Length: PDA 254 nm

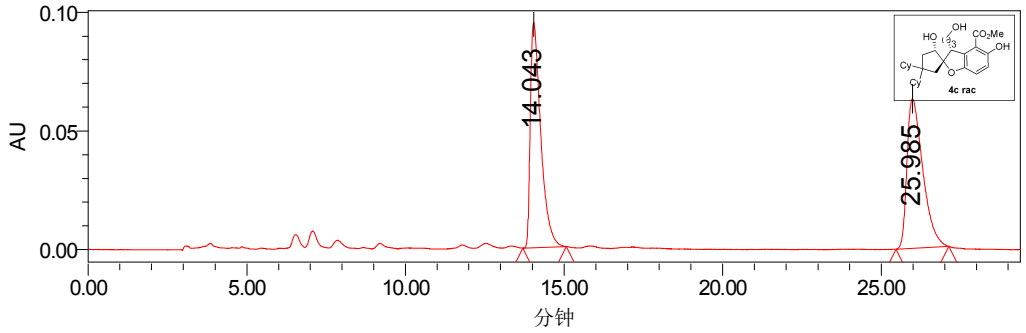


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.360	24877492.542	95.610	987389
2	19.829	1142344.137	4.390	42121

Sample Name: 4c rac
Column: 10.00 ul

Wave Length: PDA 254 nm

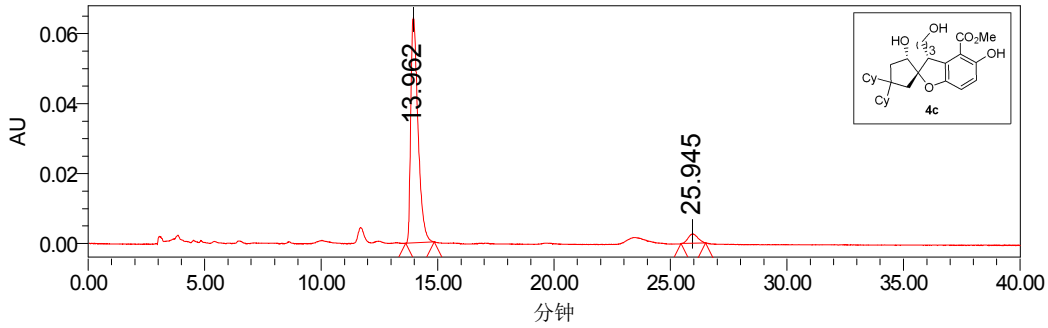


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	14.043	2179845.825	49.931	95136
2	25.985	2185858.346	50.069	63084

Sample Name: 4c
Column: 10.00 ul

Wave Length: PDA 254 nm

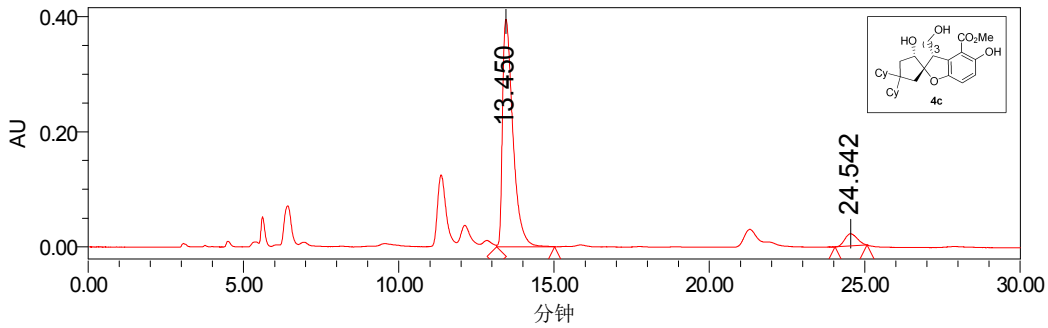


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.962	1402808.198	94.650	64603
2	25.945	79292.152	5.350	2716

2019/2/21 17:02:06 CST

Sample Name: 4c (1 mmol scale) Wave Length: PDA 254 nm
Column: 10.00 ul



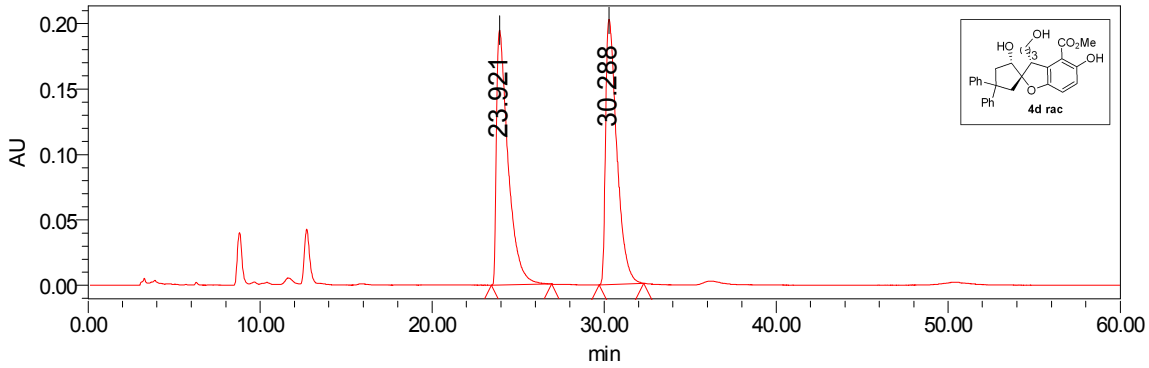
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.450	9061835.833	93.851	395104
2	24.542	593763.960	6.149	21304

Sample Information

Sample Name: 4d rac
Column: 10.00 ul

Wave Length: PDA 254 nm



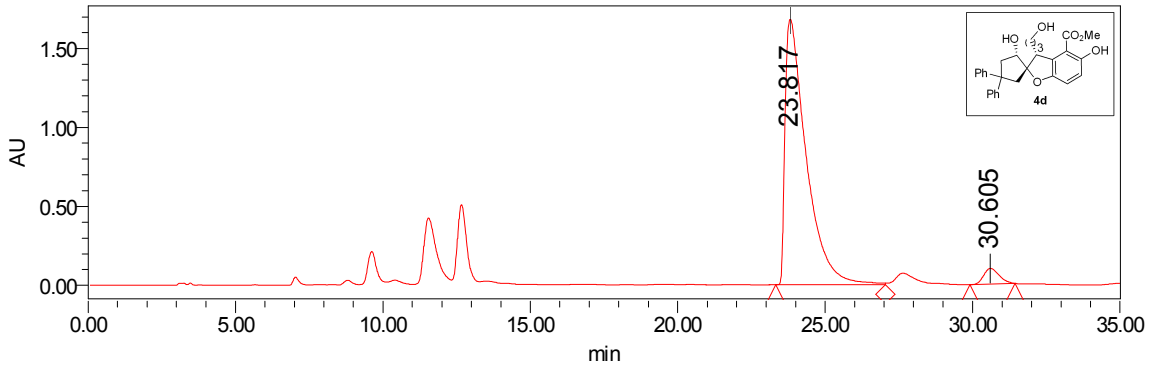
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	23.921	9125828.977	49.876	194818
2	30.288	9171253.028	50.124	202643

Sample Information

Sample Name: 4d
Column: 10.00 ul

Wave Length: PDA 254 nm



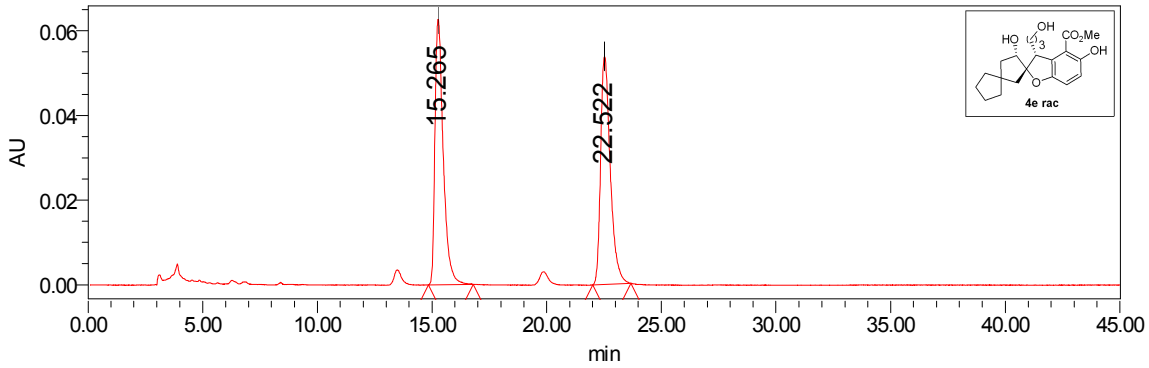
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	23.817	84027973.697	95.863	1681745
2	30.605	3626505.197	4.137	99298

Sample Information

Sample Name: 4e rac
Column: 10.00 ul

Wave Length: PDA 254 nm

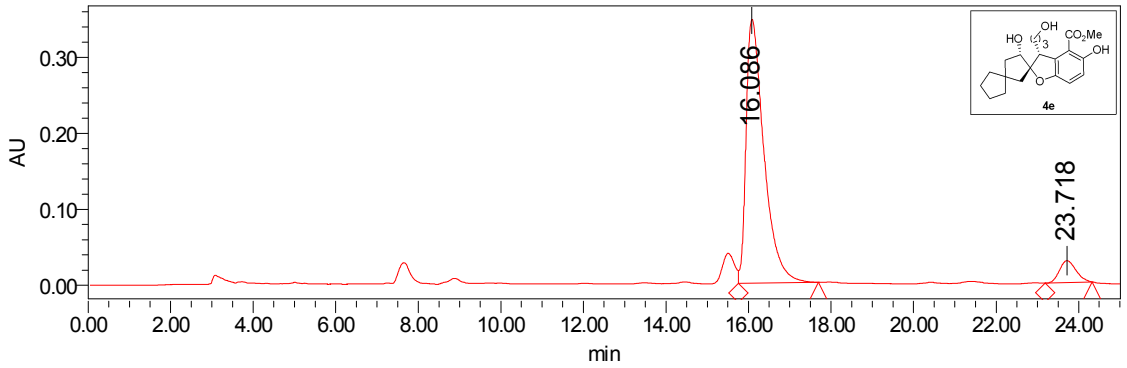


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	15.265	1571150.017	50.015	62681
2	22.522	1570222.247	49.985	53852

Sample Name: 4e
Column: 10.00 ul

Wave Length: PDA 254 nm



Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	16.086	10432703.879	92.865	347459
2	23.718	801613.460	7.135	28908

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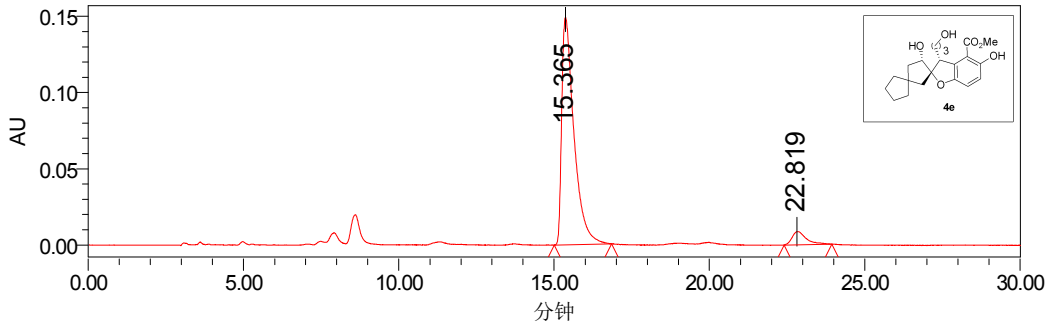
Sample Name: 4e (1 mmol scale) Wave Length: PDA 254 nm
Column:
10.00 ul



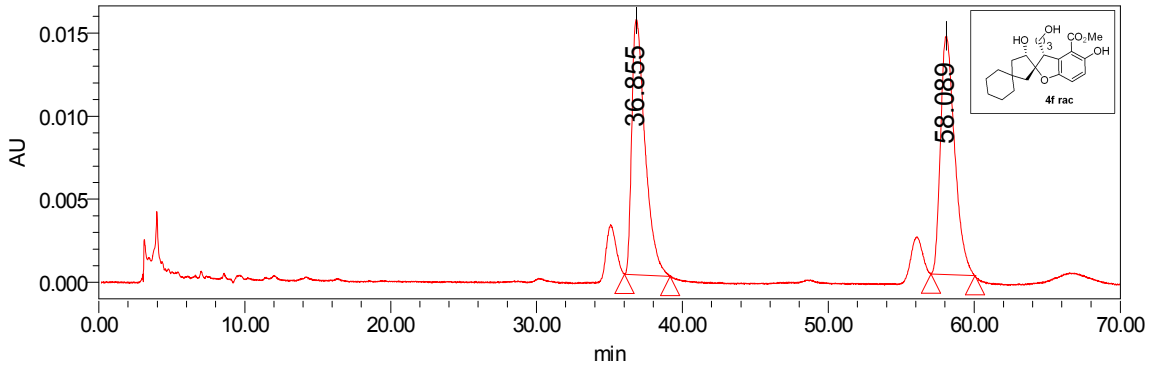
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	15.365	4109921.339	93.635	149381
2	22.819	279360.275	6.365	8731

Sample Information

Sample Name: 4f rac
Column: 10.00 ul

Wave Length: PDA 254 nm



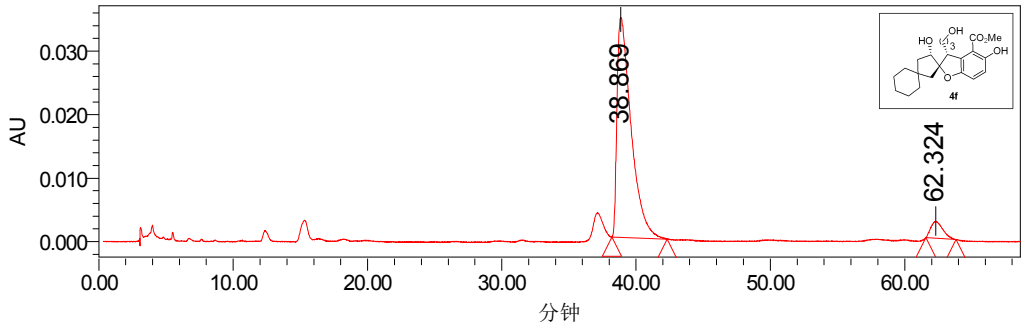
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	36.855	977696.305	50.192	15381
2	58.089	970228.898	49.808	14366

Sample Information

Sample Name: 4f
Column: 10.00 ul

Wave Length: PDA 254 nm



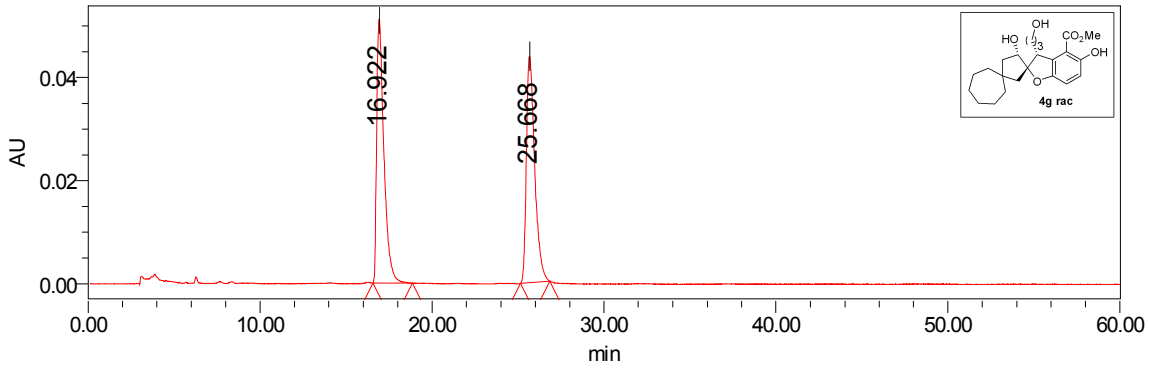
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	38.869	2540269.039	93.894	34727
2	62.324	165194.234	6.106	2681

Sample Information

Sample Name: 4g rac
Column: 10.00 ul

Wave Length: PDA 254 nm



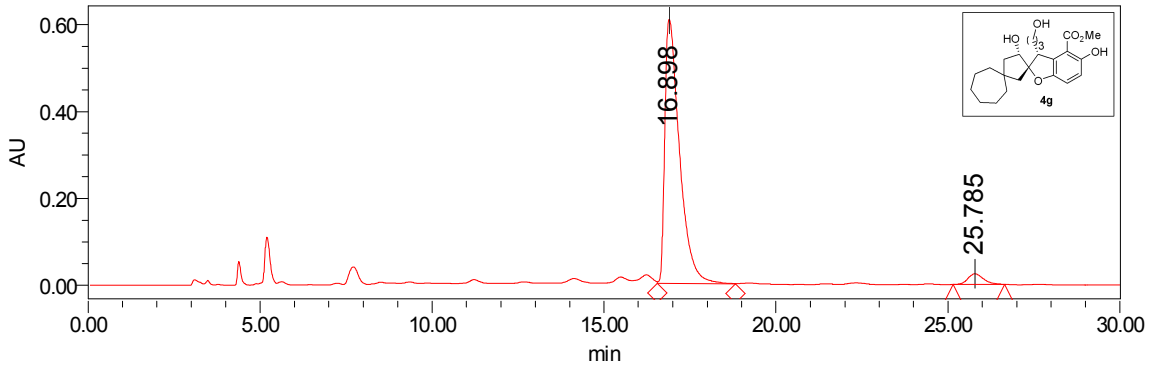
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	16.922	1479067.415	50.071	51131
2	25.668	1474864.437	49.929	43925

Sample Information

Sample Name: 4g
Column: 10.00 ul

Wave Length: PDA 254 nm

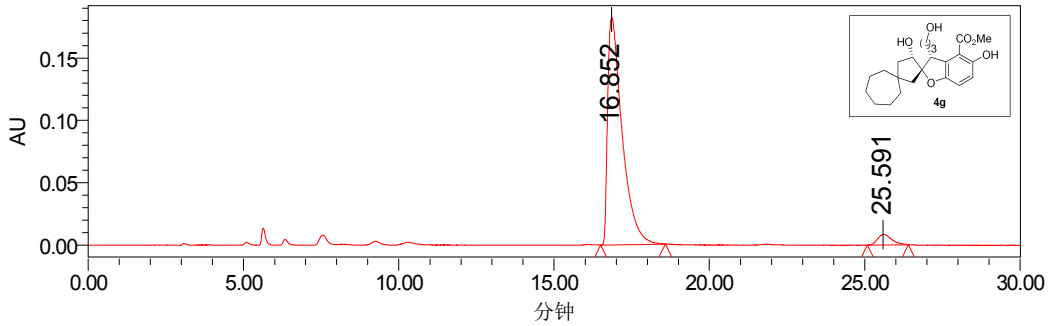


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	16.898	18014229.865	95.917	607962
2	25.785	766763.260	4.083	24253

2019/2/21 18:44:11 CST

Sample Name: 4g (1 mmol scale) Wave Length: PDA 254 nm
Column: 10.00 ul



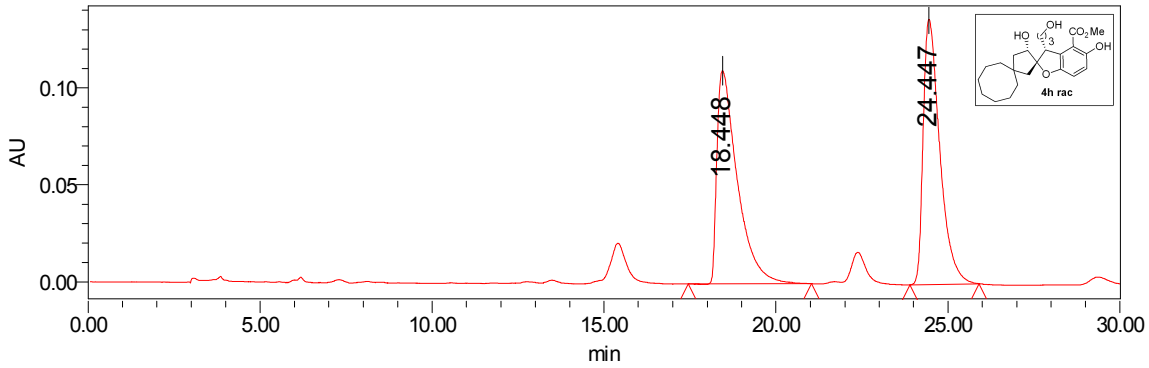
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	16.852	5889494.928	95.615	182672
2	25.591	270120.267	4.385	8463

Sample Information

Sample Name: 4h rac
Column: 10.00 ul

Wave Length: PDA 254 nm

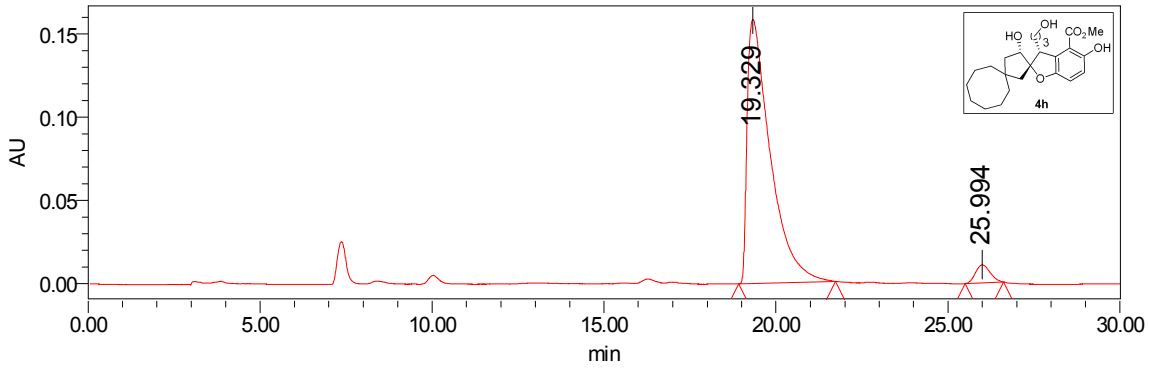


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	18.448	4539503.975	49.772	109924
2	24.447	4581045.852	50.228	136754

Sample Name: 4h
Column: 10.00 ul

Wave Length: PDA 254 nm



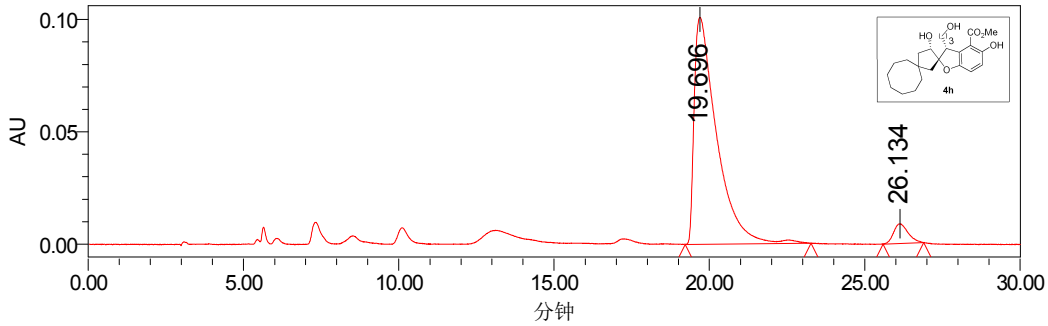
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	19.329	7395252.364	95.848	158741
2	25.994	320372.181	4.152	10845

2019/2/21 19:14:52 CST

Sample Name: 4h (1 mmol scale)
Column: 10.00 ul

Wave Length: PDA 254 nm

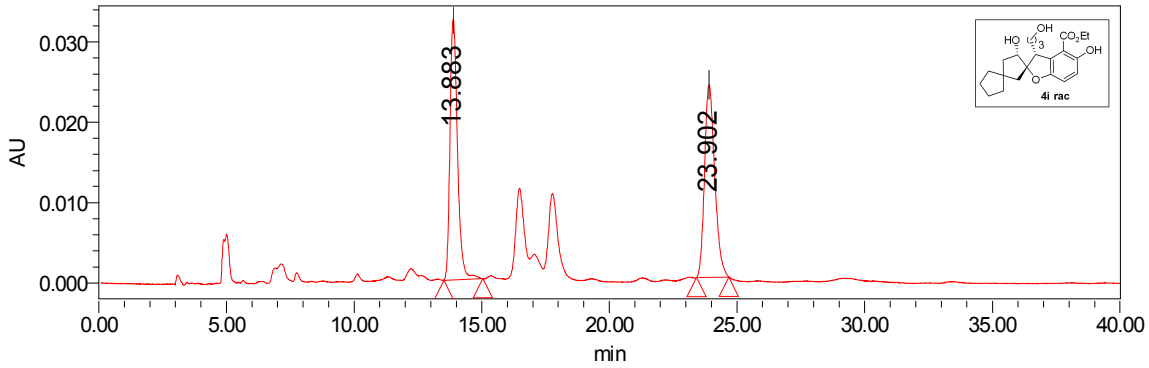


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	19.696	5102531.106	94.761	101134
2	26.134	282101.096	5.239	8738

Sample Name: 4i rac
Column: 10.00 ul

Wave Length: PDA 254 nm

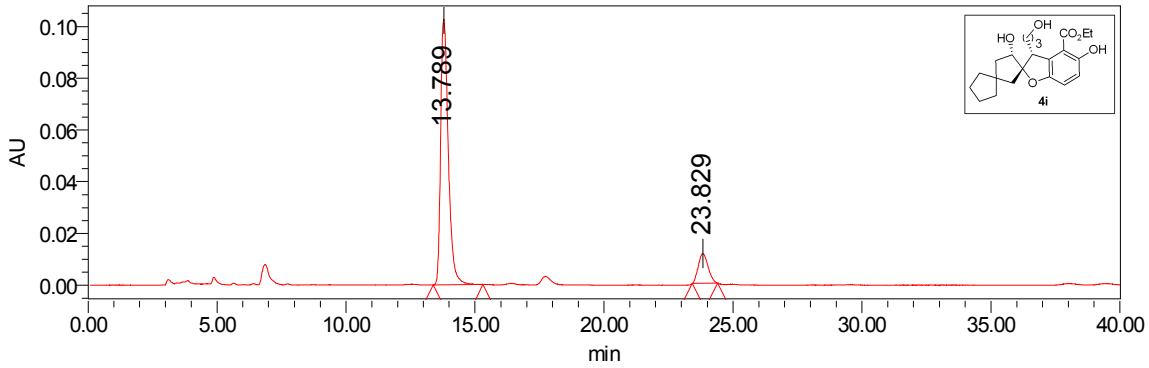


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.883	663309.241	49.830	32451
2	23.902	667828.803	50.170	23966

Sample Name: 4i
Column: 10.00 ul

Wave Length: PDA 254 nm



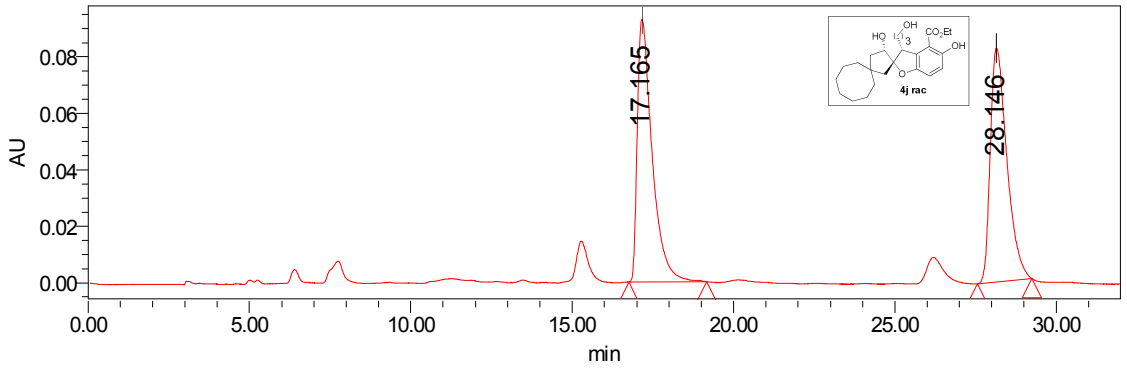
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.789	2114825.123	87.431	102605
2	23.829	304019.061	12.569	11486

Sample Information

Sample Name: 4j rac
Column: 10.00 ul

Wave Length: PDA 254 nm



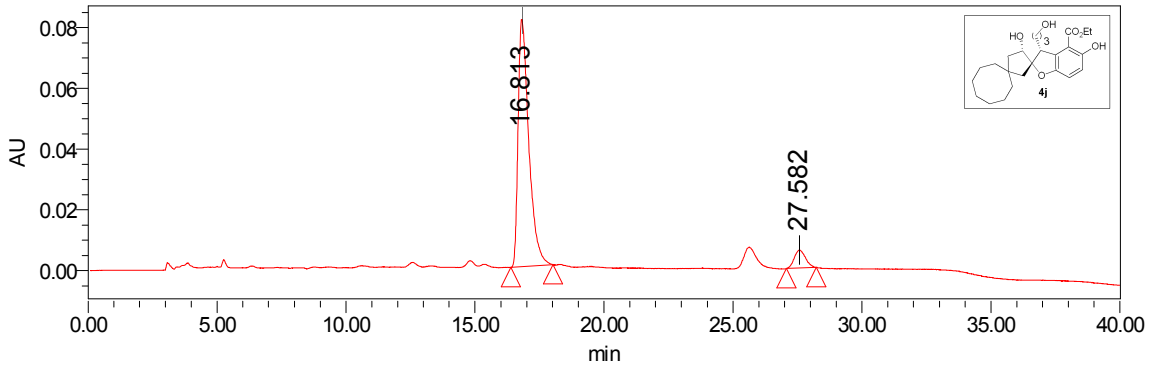
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	17.165	2967333.124	50.089	92985
2	28.146	2956799.620	49.911	82836

Sample Information

Sample Name: 4j
Column: 10.00 ul

Wave Length: PDA 254 nm



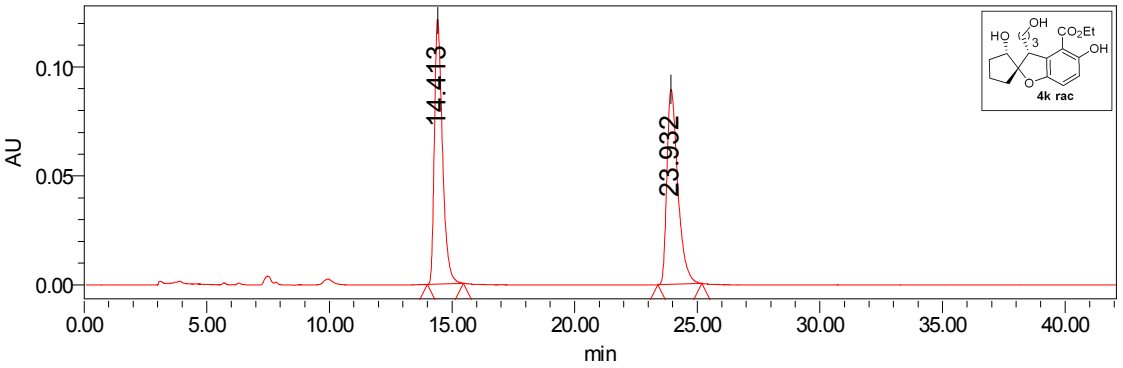
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	16.813	2349475.329	92.948	81506
2	27.582	178246.132	7.052	5926

Sample Information

Sample Name: 4k rac
Column: 10.00 ul

Wave Length: PDA 254 nm



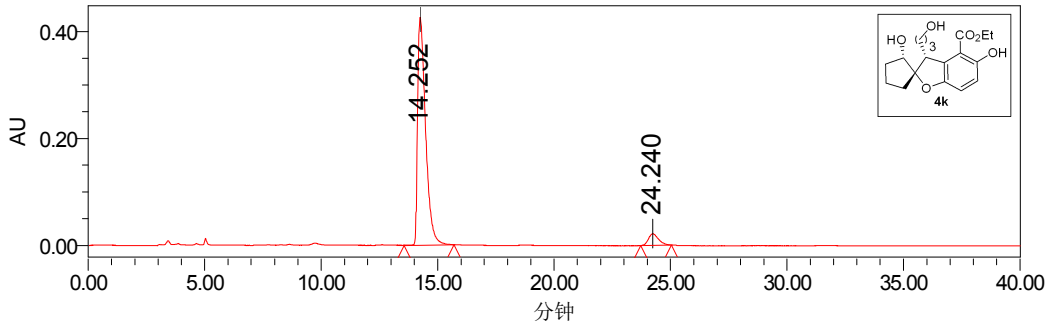
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	14.413	2776633.743	50.021	121418
2	23.932	2774288.533	49.979	89423

Sample Information

Sample Name: 4k
Column: 10.00 ul

Wave Length: PDA 254 nm

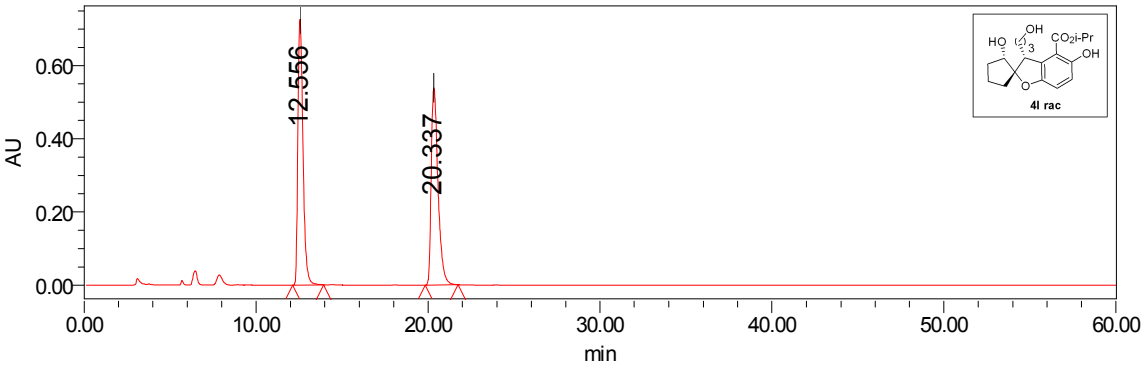


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	14.252	9984056.972	93.808	426511
2	24.240	659068.739	6.192	21783

Sample Name: 4l rac
Column: 10.00 ul

Wave Length: PDA 254 nm

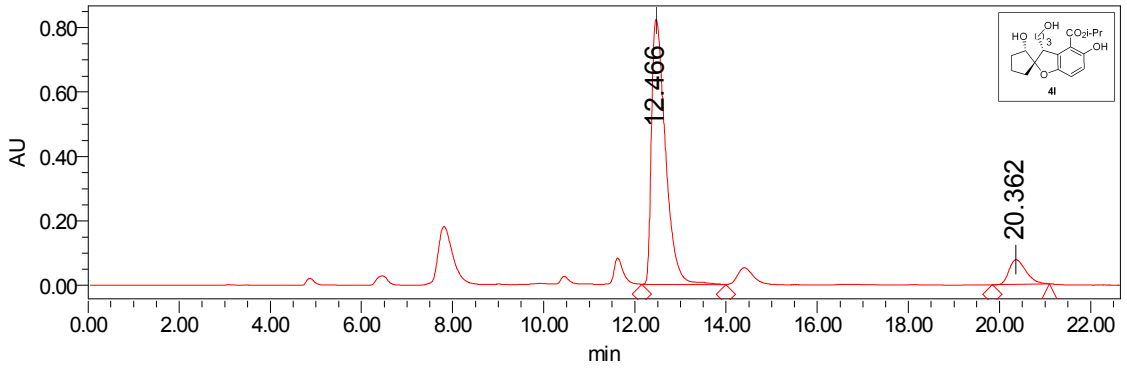


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	12.556	14834610.284	50.083	726490
2	20.337	14785611.804	49.917	538905

Sample Name: 4l
Column: 10.00 ul

Wave Length: PDA 254 nm



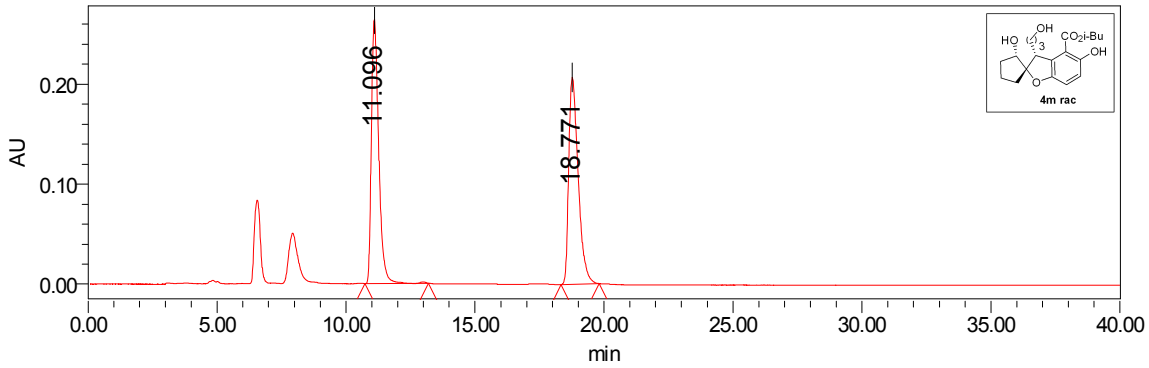
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	12.466	17455492.174	89.833	822711
2	20.362	1975451.642	10.167	76637

Sample Information

Sample Name: 4m rac
Column: 10.00 ul

Wave Length: PDA 254 nm



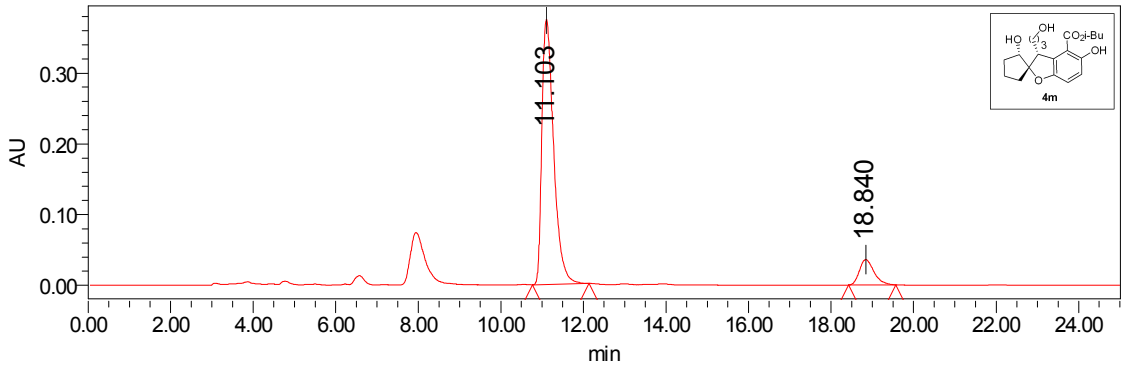
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	11.096	5227057.791	49.899	264259
2	18.771	5248209.155	50.101	206546

Sample Information

Sample Name: 4m
Column: 10.00 ul

Wave Length: PDA 254 nm



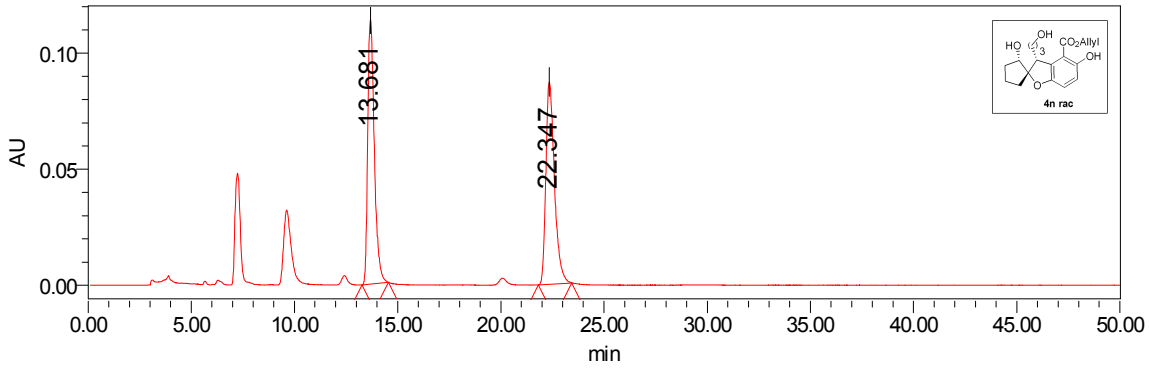
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	11.103	7403126.473	89.349	374850
2	18.840	882510.661	10.651	36001

Sample Information

Sample Name: 4n rac
Column: 10.00 ul

Wave Length: PDA 254 nm



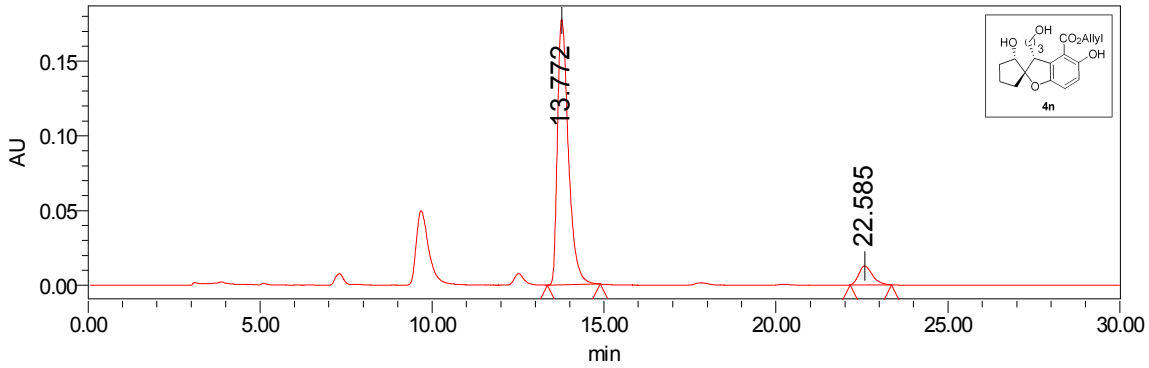
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.681	2519354.239	49.995	114075
2	22.347	2519892.671	50.005	87156

Sample Information

Sample Name: 4n
Column: 10.00 ul

Wave Length: PDA 254 nm

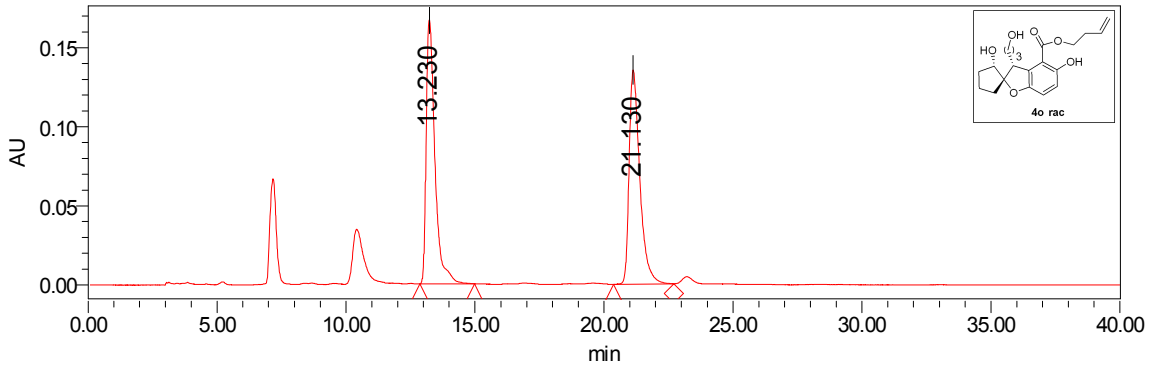


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.772	3949836.133	91.914	177759
2	22.585	347476.858	8.086	12574

Sample Name: 4o rac
Column: 10.00 ul

Wave Length: PDA 254 nm

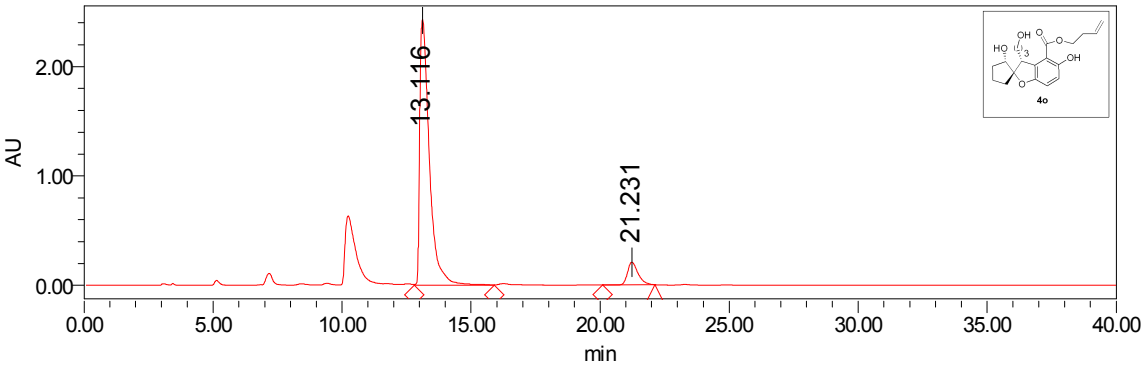


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.230	3923853.165	50.031	167386
2	21.130	3918926.863	49.969	135511

Sample Name: 4o
Column: 10.00 ul

Wave Length: PDA 254 nm



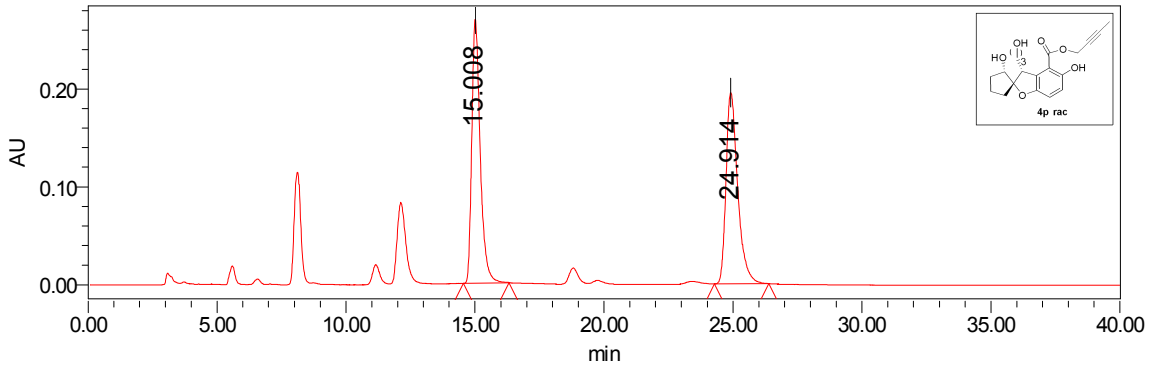
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.116	63101618.153	91.516	2430432
2	21.231	5849544.457	8.484	205636

Sample Information

Sample Name: 4p rac
Column: 10.00 ul

Wave Length: PDA 254 nm

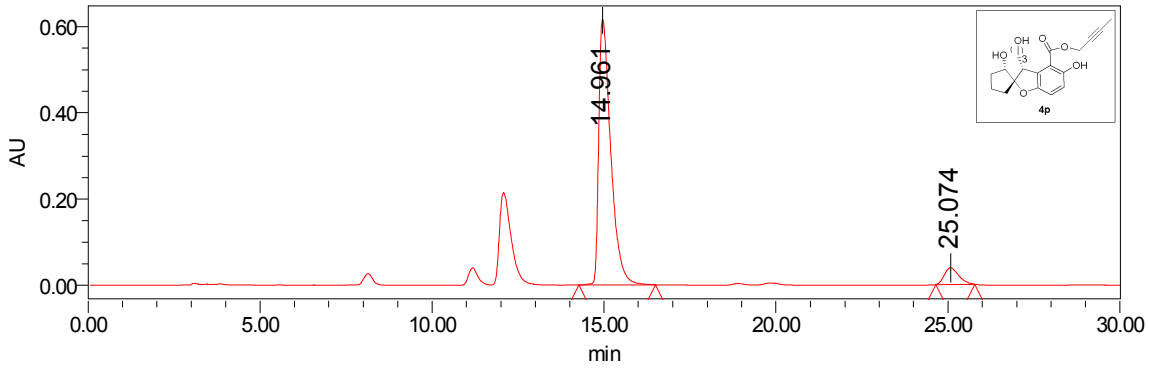


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	15.008	6179372.165	50.081	269603
2	24.914	6159451.777	49.919	195302

Sample Name: 4p
Column: 10.00 ul

Wave Length: PDA 254 nm

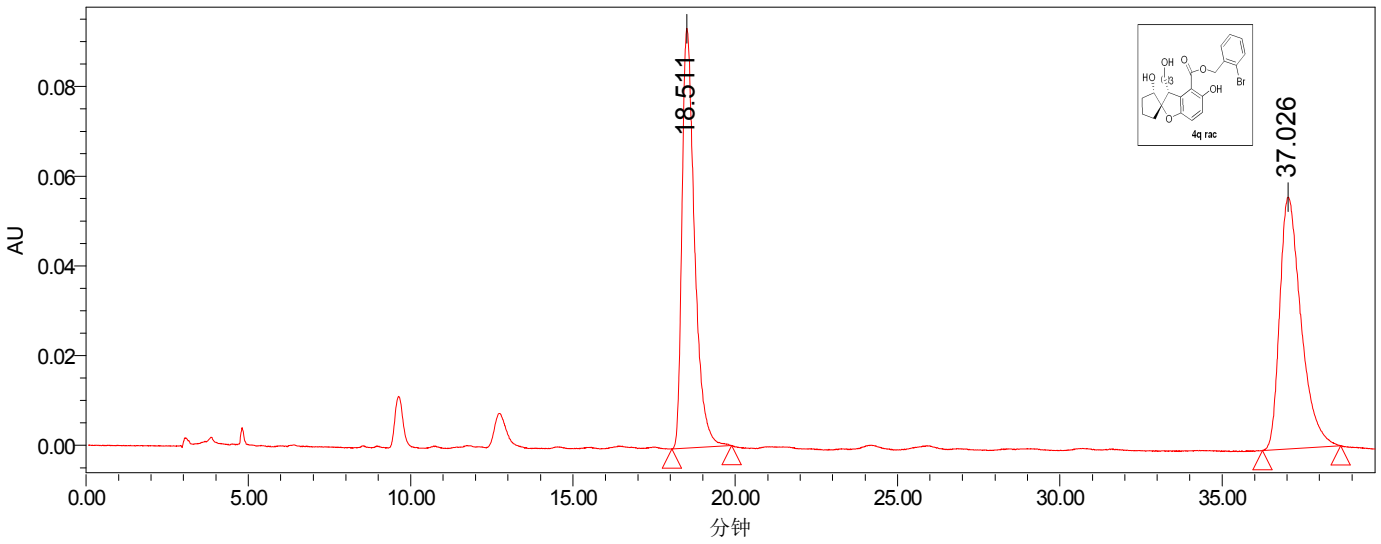


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	14.961	14945157.820	93.084	615974
2	25.074	1110454.297	6.916	38201

Sample Name: 4q rac
Column: 10.00 ul

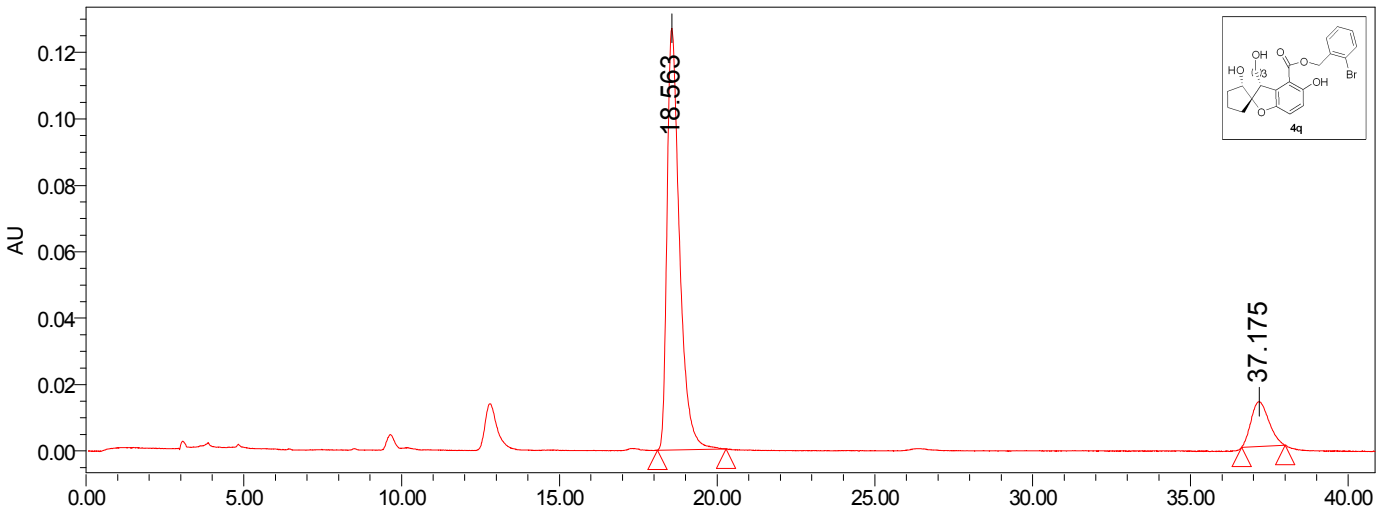
Wave Length: PDA 254 nm



Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	18.511	2510695	49.41	93528
2	37.026	2570163	50.59	56176

Sample Name: 4q Wave Length: PDA 254 nm
Column: 10.00 ul

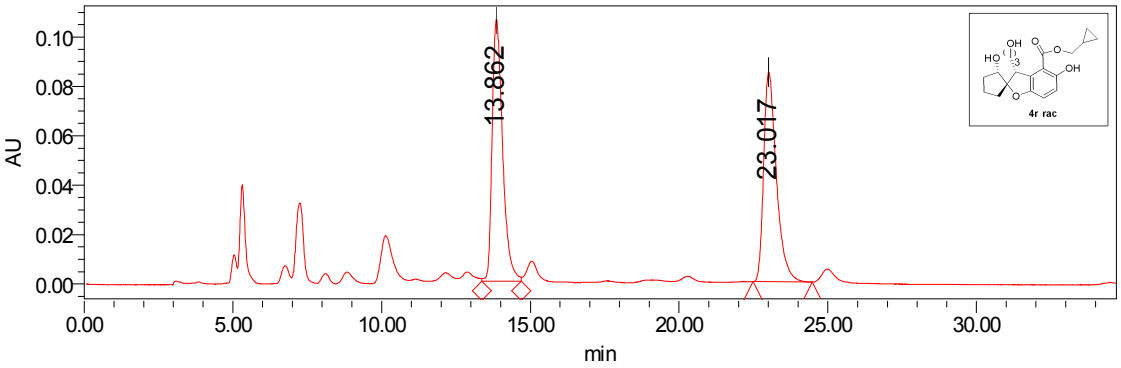


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	18.563	3502751	86.80	126891
2	37.175	532642	13.20	13529

Sample Name: 4r rac
Column: 10.00 ul

Wave Length: PDA 254 nm

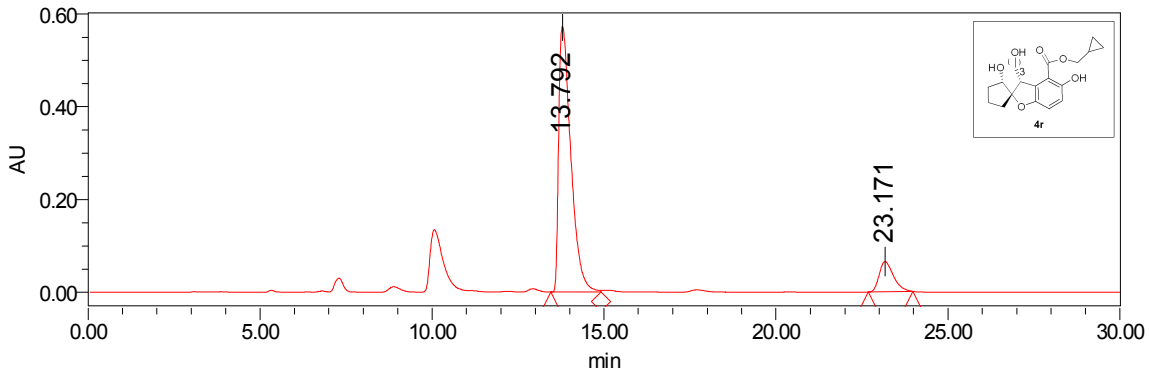


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.862	2578133.577	50.457	105991
2	23.017	2531408.469	49.543	84867

Sample Name: 4r
Column: 10.00 ul

Wave Length: PDA 254 nm

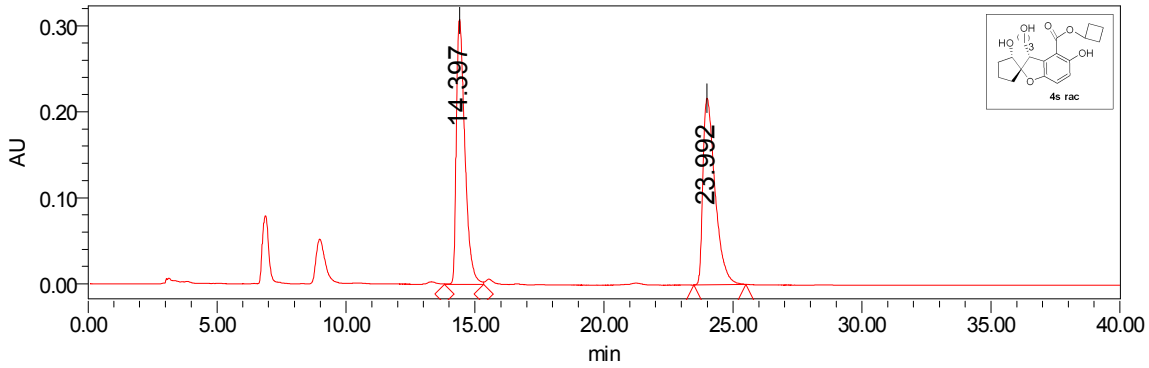


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.792	14089218.211	88.253	572798
2	23.171	1875434.940	11.747	65144

Sample Name: 4s rac
Column: 10.00 ul

Wave Length: PDA 254 nm



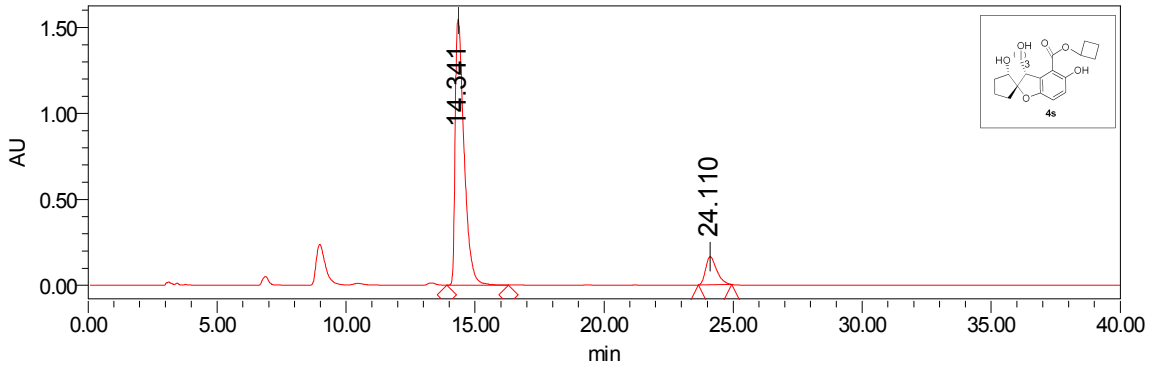
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	14.397	7080663.682	49.933	308136
2	23.992	7099623.474	50.067	217190

Sample Information

Sample Name: 4s
Column: 10.00 ul

Wave Length: PDA 254 nm



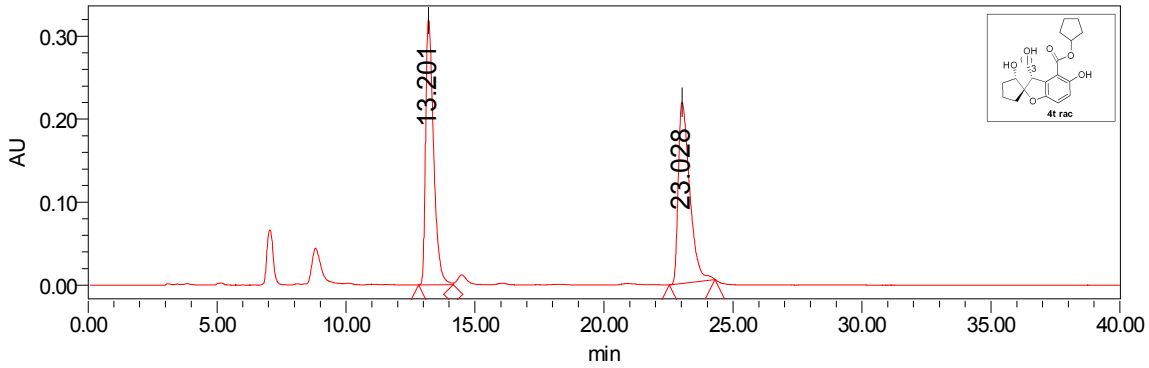
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	14.341	37110036.273	88.353	1547286
2	24.110	4891996.030	11.647	163167

Sample Information

Sample Name: 4t rac
Column: 10.00 ul

Wave Length: PDA 254 nm

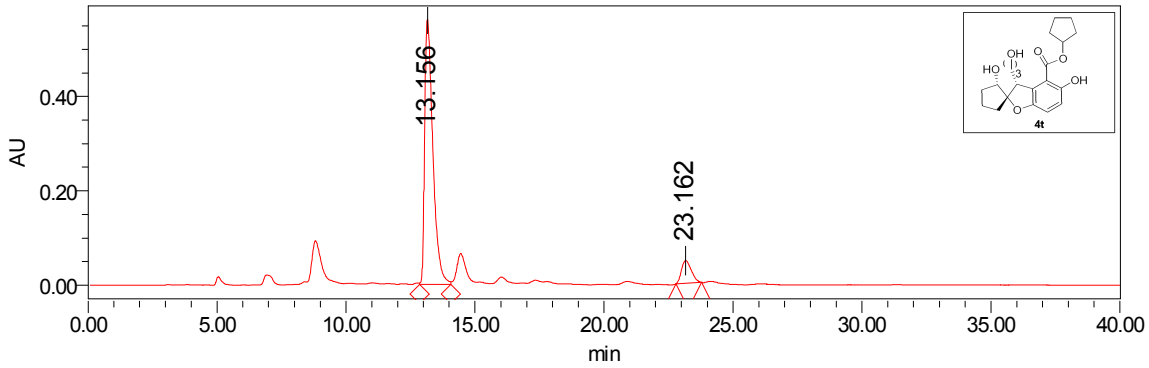


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.201	6866809.017	50.459	319985
2	23.028	6741962.430	49.541	218346

Sample Name: 4t
Column: 10.00 ul

Wave Length: PDA 254 nm

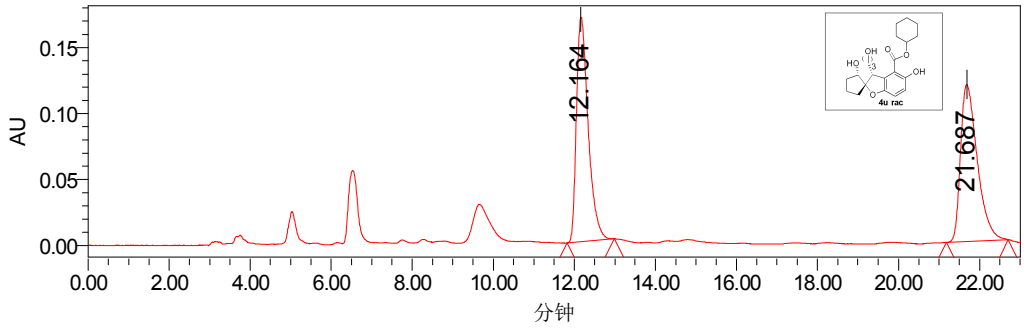


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	13.156	12347927.869	90.565	561633
2	23.162	1286419.999	9.435	48300

Sample Name: 4u rac
Column: 10.00 ul

Wave Length: PDA 254 nm



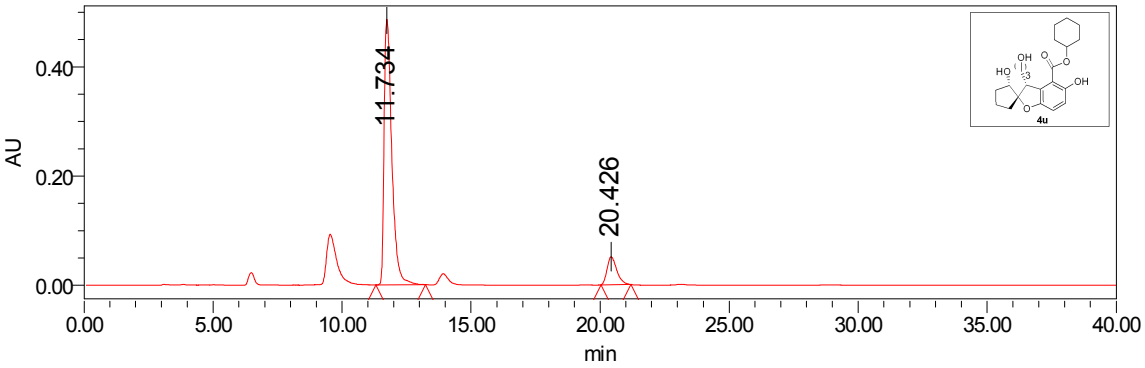
Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	12.164	3426936.987	50.159	170376
2	21.687	3405262.470	49.841	119052

Sample Information

Sample Name: 4u
Column: 10.00 ul

Wave Length: PDA 254 nm

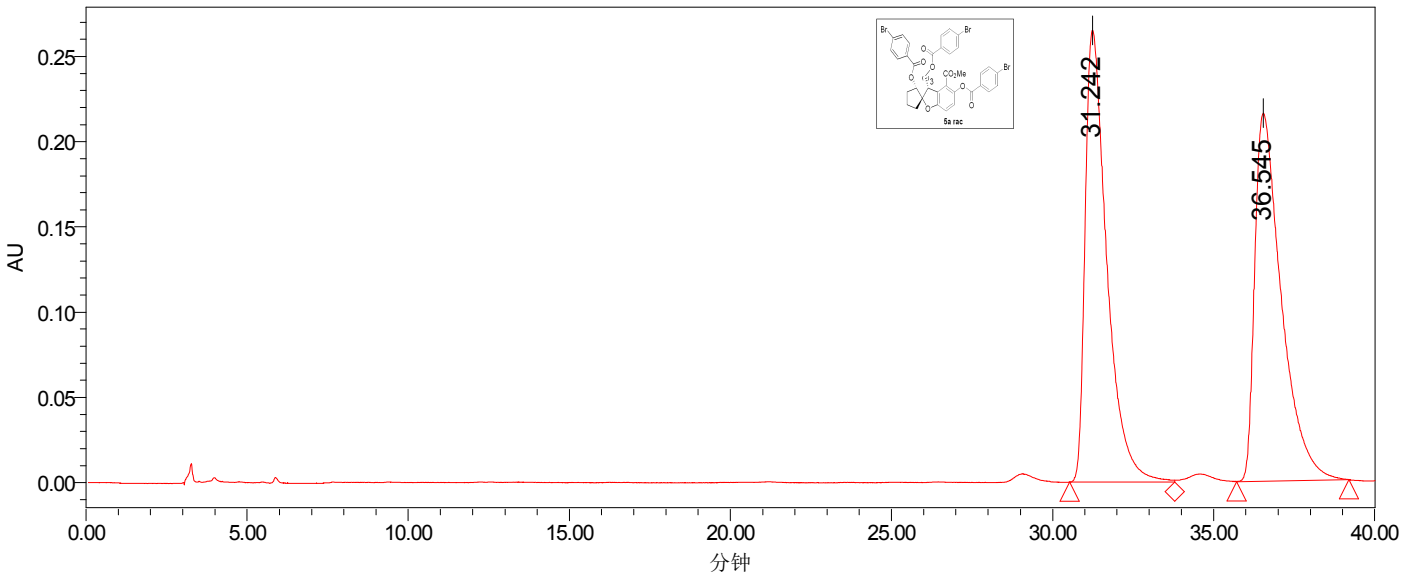


Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	11.734	10081317.903	88.362	485878
2	20.426	1327789.476	11.638	51017

Sample Name: 5a rac
Column: 10.00 ul

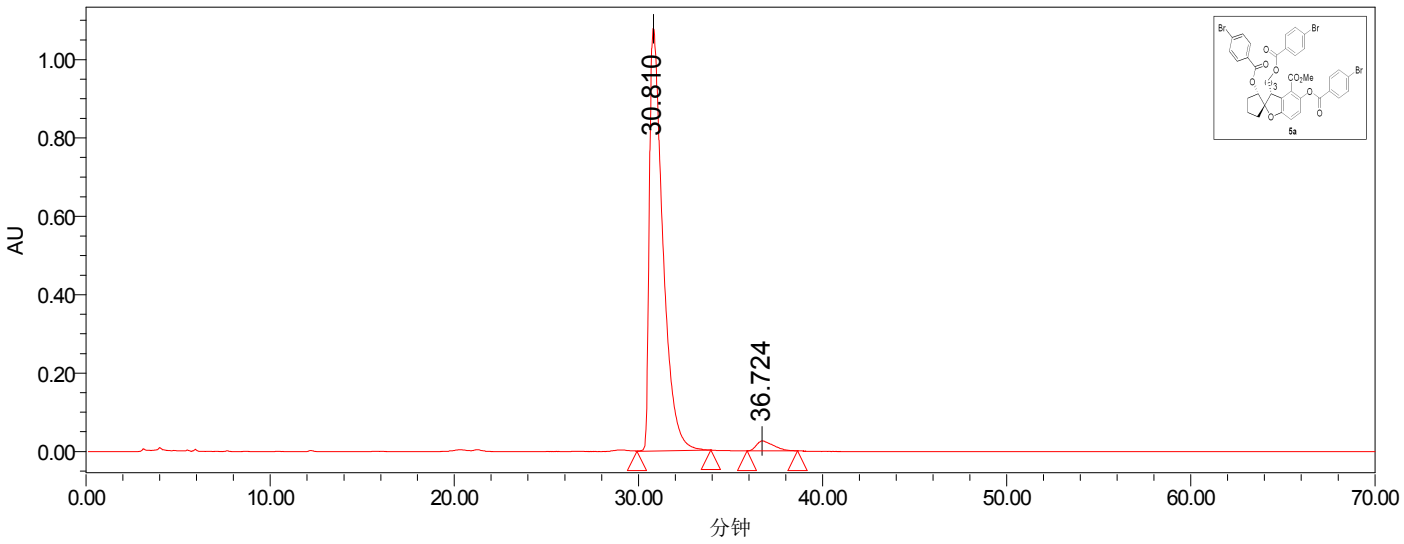
Wave Length: PDA 254 nm



Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	31.242	12379456	49.95	265110
2	36.545	12403999	50.05	215831

Sample Name: 5a
Column: 10.00 ul
Wave Length: PDA 254 nm



Peak Information:

	RetTime (min)	Area (μV*S)	Area (%)	Height (μV)
1	30.810	54542601	97.04	1077964
2	36.724	1665753	2.96	25449