Supplementary Information

Facile Access to Diverse All-Carbon Quaternary Center Containing Spirobicycles by Exploring Tandem Castro-Stephens Coupling/ Acyloxy Shift/ Cyclization/ Semipinacol Rearrangement Sequence

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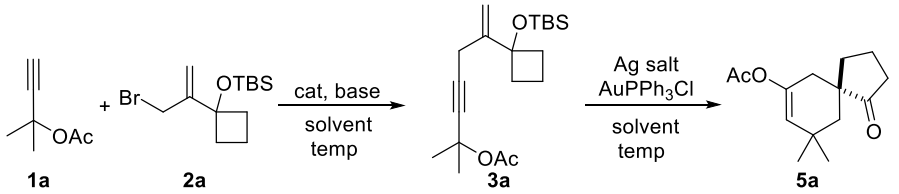
1 General information

All reactions under standard conditions were carried out in anhydrous solvent under argon atmosphere and monitored by TLC on gel F_{254} plates. Solvents were dried by standard methods and distilled. **^{1}H NMR** and **^{13}C NMR** spectra were obtained on Bruker AM-400, Varian Mercury-600 and JEOL JNM-ECS-400 instruments, both in $CDCl_3$ solution. High-resolution mass spectral analysis (**HRMS**) data were measured on the ESI Bruker Apex II with ESI resource. **IR** spectra data were recorded on a Nicolet FT-170SX spectrometer. **X-ray** diffraction data were collected on Agilent Super Nova Eos diffractometer.

2 Optimization of tandem reaction conditions

Table 1. Optimization of tandem reaction conditions[a]



1a **2a** **3a** **5a**

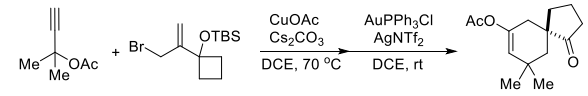
entry	for **3a**		solvent	for **5a**	temp	product	yield
	Cu cat.	base		Ag salt			
1	CuI	K_2CO_3	DCE	/	rt	**3a**	10%[b]
2	CuBr	K_2CO_3	DCE	/	rt	**3a**	52%[b]
3	CuCl	K_2CO_3	DCE	/	rt	**3a**	35%[b]
4	CuOAc	K_2CO_3	DCE	/	rt	**3a**	68%[b]
5	$Cu(OAc)_2$	K_2CO_3	DCE	/	rt	**3a**	62%[b]
6	CuOAc	Na_2CO_3	DCE	/	rt	**3a**	40%[b]
7	CuOAc	Cs_2CO_3	DCE	/	rt	**3a**	79%[b]
8	CuOAc	Et_3N	DCE	/	rt	**3a**	45%[b]
9	CuOAc	K_3PO_4	DCE	/	rt	**3a**	trace
10	**CuOAc**	**Cs_2CO_3**	**DCE**	**/**	**70 °C**	**3a**	**82%[b]**
11	CuOAc	Cs_2CO_3	benzene	/	rt	**3a**	40%[b]
12	CuOAc	Cs_2CO_3	THF	/	rt	**3a**	47%[b]
13	CuOAc	Cs_2CO_3	EtOH	/	rt	**3a**	55%[b]
14	CuOAc	Cs_2CO_3	CH_3CN	/	rt	**3a**	55%[b]
15	CuOAc	Cs_2CO_3	DMF	/	rt	**3a**	54%[b]
16	CuOAc	Cs_2CO_3	DMSO	/	rt	**3a**	33%[b]
17	CuOAc	Cs_2CO_3	DCE	/	rt[c]	**5a**	55%[d,f]
18	CuOAc	Cs_2CO_3	DCE	AgOTf	rt[c]	**5a**	57%[d]
19	CuOAc	Cs_2CO_3	DCE	$AgNTf_2$	rt[c]	**5a**	66%[d]
20	CuOAc	Cs_2CO_3	DCE	$AgSbF_6$	rt[c]	**5a**	53%[d]
21	CuOAc	Cs_2CO_3	DCE	$AgBF_4$	rt[c]	**5a**	49%[d]
22	CuOAc	Cs_2CO_3	DCE	$AgNO_2$	rt[c]	**5a**	nr
23	CuOAc	Cs_2CO_3	DCE	CF_3COOAg	rt[c]	**5a**	trace[d]
24[e]	CuOAc	Cs_2CO_3	benzene	$AgNTf_2$	rt[c]	**5a**	11[d]
25[e]	CuOAc	Cs_2CO_3	THF	$AgNTf_2$	rt[c]	**5a**	17[d]
26[e]	CuOAc	Cs_2CO_3	EtOH	$AgNTf_2$	rt[c]	**5a**	nd
27[e]	CuOAc	Cs_2CO_3	CH_3CN	$AgNTf_2$	rt[c]	**5a**	25%[d]
28[e]	CuOAc	Cs_2CO_3	DMF	$AgNTf_2$	rt[c]	**5a**	nd
29[e]	CuOAc	Cs_2CO_3	DMSO	$AgNTf_2$	rt[c]	**5a**	nd
30[e]	CuOAc	Cs_2CO_3	$CHCl_3$	$AgNTf_2$	rt[c]	**5a**	60%[d]
31[e]	CuOAc	Cs_2CO_3	acetone	$AgNTf_2$	rt[c]	**5a**	57%[d]
32	CuOAc	Cs_2CO_3	DCE	$AgNTf_2$	rt[c]	**5a**	51%[d,g]
33	CuOAc	Cs_2CO_3	DCE	$AgNTf_2$	rt[c]	**5a**	55%[d,h]
34	CuOAc	Cs_2CO_3	DCE	$AgNTf_2$	rt[c]	**5a**	nr[i]

[a]Unless specified, all reactions were carried out using **1a** (0.5 mmol, 2.5 eq.), **2a** (0.2 mmol, 1.0 eq.) and Cu cat. (30 mol%), base (50 mol%), $AuPPh_3Cl$ (10 mol%), Ag salt (10 mol%) in a reaction tube in DCE (2 mL) at indicated

temperature. [b]Isolated yield of **3a**. [c]The first coupling step was carried out at 70 ºC. [d]Isolated yield of **5a** in purification free manner. [e]After filtration, the filtrate was concentrated and diluted with the indicated solvent (4 mL) for the following operation. [f]$AuCl_3$ (10 mol%) was used instead of $AuPPh_3Cl$. [g]$AuPPh_3Cl$ and $AgNTf_2$ were both 5 mol%. [h]H_2O (10 mol%) was added. [i]4 Å MS (10 mg/ mmol) was added.

3 Scaled-up transformation of the tandem reaction

3.1 Scaled-up transformation of the tandem reaction (under standard conditions)



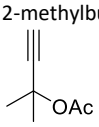
1a 10 mmol, 1.26 g | **2a** 4 mmol, 1.22 g | **5a** 43% yield

To a solution of **1a** (1.262 g, 10 mmol, 2.5 eq.) and **2a** (1.221 g, 4 mmol, 1.0 eq.) in dry DCE (20 mL) was added CuOAc (147.2 mg, 1.2 mmol, 30 mol%), Cs_2CO_3 (488.7 mg, 1.5 mmol, 50 mol%). The resulting mixture was stirred overnight at 70 °C. After a quick filtration of the reaction mixture through a celite pad to remove the residue, the reaction mixture was diluted to a volume of 20 mL with DCE, then a combination solution of $AuPPh_3Cl$ (98.9 mg, 0.2 mmol, 5 mol%) and $AgNTf_2$ (77.6 mg, 0.2 mmol, 5 mol%) which was prestirred in DCE (5 mL) for 30 mins, was added dropwise. After being stirred for another 12 hours at rt, another combination solution of $AuPPh_3Cl$ (98.9 mg, 0.2 mmol, 5 mol%) and $AgNTf_2$ (77.6 mg, 0.2 mmol, 5 mol%) which was prestirred in DCE (5 mL) was added dropwise, the solution was stirred until **2a** disappeared completely monitored by TLC. The mixture was concentrated under vacuum. The crude mixture was purified by flash chromatography on silica gel (petroleum ether: EtOAc = 6: 1) to give the desired product **5a** (406.4 mg, 1.72 mmol, 43% yield) as a colorless oil.

4 Experimental Details for 1

All propargylic esters (**1**) are known compounds and were prepared according to literature procedures. For details, **1a**[1], **1b** - **1d**[2], **1e**[3], **1f**[4], **1g**[5], **1h** – **1i**[6].

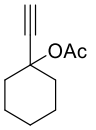
2-methylbut-3-yn-2-yl acetate (**1a**):



1a

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (s, 1H), 3.97 (s, 3H), 3.62 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 84.6, 72.1, 71.4, 28.7, 217.

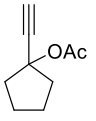
1-ethynylcyclohexyl acetate (**1b**):



1b

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 1H), 2.08 (dd, *J* = 11.6, 5.4 Hz, 2H), 2.00 (s, 3H), 1.87 – 1.77 (m, 2H), 1.59 (dt, *J* = 11.4, 5.7 Hz, 4H), 1.53 – 1.44 (m, 1H), 1.36 – 1.24 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 83.5, 74.9, 74.1, 36.8, 25.0, 22.3, 21.8.

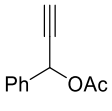
1-ethynylcyclopentyl acetate (**1c**):



1c

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 1H), 2.20 – 2.08 (m, 4H), 1.99 (s, 3H), 1.75 – 1.65 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 84.1, 80.0, 72.7, 40.2, 23.1, 21.6.

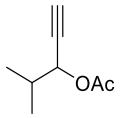
1-phenylprop-2-yn-1-yl acetate (**1d**):



1d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 3H), 6.49 (d, *J* = 2.2 Hz, 1H), 2.69 (d, *J* = 2.3 Hz, 1H), 2.12 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 136.4, 129.0, 128.6, 127.6, 80.2, 75.3, 65.2, 20.9.

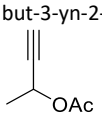
4-methylpent-1-yn-3-yl acetate (**1e**):



1e

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 – 5.12 (dd, 1H), 2.43 (d, *J* = 2.2 Hz, 1H), 2.10 (s, 3H), 2.06 – 1.96 (m, 1H), 1.02 (dd, *J* = 11.9, 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 79.9, 73.9, 68.7, 32.1, 20.9, 18.0, 17.4.

but-3-yn-2-yl acetate (**1f**):



1f

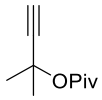
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (qd, *J* = 6.7, 2.1 Hz, 1H), 2.42 (d, *J* = 2.1 Hz, 1H), 2.02 (s, 3H), 1.44 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 82.0, 72.7, 59.8, 21.0, 20.8.

prop-2-yn-1-yl acetate (**1g**):

1g

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (d, *J* = 2.5 Hz, 2H), 2.46 (t, *J* = 2.5 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 77.6, 74.7, 51.8, 20.5.

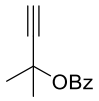
2-methylbut-3-yn-2-yl pivalate (**1h**):



1h

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 1H), 1.63 (s, 6H), 1.16 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.6, 84.8, 71.8, 71.1, 38.9, 28.7, 26.9.

2-methylbut-3-yn-2-yl benzoate (**1i**):

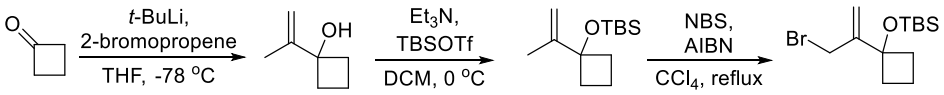


1i

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.57 – 7.48 (m, 1H), 7.45 – 7.38 (m, 2H), 2.59 (s, 1H), 1.82 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 132.7, 130.7, 129.4, 128.1, 84.5, 72.5, 72.0, 28.9.

5 Experimental Details for 2 and 6

5.1 Method A: Typical Procedure for the Synthesis of **2a**



s1 **s2** **s3** **2a**

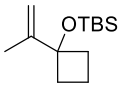
1-(prop-1-en-2-yl)cyclobutan-1-ol (**s2**):

s2

To a stirred solution of 2-bromopropene (2.66 mL, 30 mmol, 1 eq.) in THF (60 mL), *t*-BuLi (1.6 M, 33.75 mL, 54 mmol, 1.8 eq.) was added slowly at -78 °C. The reaction mixture was stirred at -78 °C for 20 mins, and then a THF (20mL) solution of **s1** (2.02 mL, 27 mmol, 0.9 eq.) was added dropwise at -78 °C. After stirring for 10 mins, the reaction was quenched by saturated NH_4Cl aqueous solution, the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum in a cold water bath (< 15 °C). The residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 8: 1) to give compound **s2** as a colorless oil (2.322 g, 20.709 mmol, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (s, 1H), 4.86 (m, 1H), 2.37 – 2.30 (m, 2H), 2.10 – 2.03 (m, 2H), 1.94 – 1.84 (m, 1H), 1.82 – 1.79 (m, 3H), 1.79 – 1.76 (m, 1H), 1.63 – 1.51 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.9, 109.5, 77.9, 34.4, 17.4, 12.8. **HRMS ESI** Calcd for $C_7H_{12}O$ [M+Na]$^+$: 135.0780, Found: 135.0782. **IR** *v* (cm^{-1}): 3351, 2987, 2949, 1648, 1441, 1248, 896.

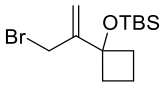
tert-butyldimethyl(1-(prop-1-en-2-yl)cyclobutoxy)silane (**s3**):



s3

An ice-cooled solution of **s2** (1.407 g, 12.54 mmol, 1 eq.) in dry DCM (50 mL) was added Et_3N (6.973 mL, 50.17 mmol, 4 eq.), and then TBSOTf (5.762 mL, 25.09 mmol, 2 eq.) was added slowly at 0 °C. The reaction system was monitored by TLC until **s2** disappeared completely. The reaction was quenched by saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether as elution solvent) to give compound **s3** as a colorless oil (2.80 g, 12.37 mmol, 99% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (s, 1H), 4.87 – 4.83 (m, 1H), 2.25 (ddt, *J* = 11.4, 8.8, 3.1 Hz, 2H), 2.16 – 2.08 (m, 2H), 1.76 (t, *J* = 1.9 Hz, 3H), 1.74 – 1.67 (m, 1H), 1.51 – 1.39 (m, 1H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.0, 108.9, 78.7, 35.3, 25.8, 18.0, 17.6, 13.1, -3.2. **HRMS ESI** Calcd for $C_{13}H_{26}OSi$ [M+Na]$^+$: 249.1645, Found: 249.1665. **IR** *v* (cm^{-1}): 2955, 2931, 1647, 1251, 836, 775.

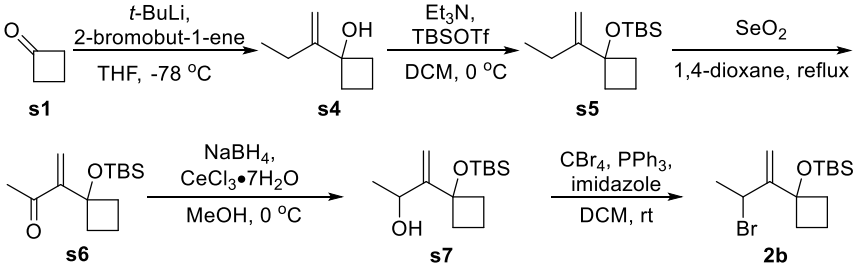
(1-(3-bromoprop-1-en-2-yl)cyclobutoxy)(*tert*-butyl)dimethylsilane (**2a**)[7]:



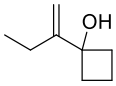
2a

s3 (1.6354 g, 7.223 mmol, 1 eq.) was dissolved in dry CCl_4 (30 mL), NBS (1.928 g, 10.834 mmol, 1.5 eq.) and AIBN (0.119 g, 0.722 mmol, 0.1 eq.) were added. The reaction mixture was refluxed overnight. Until **s3** disappeared completely by TLC monitored, the reaction was treated with saturated Na_2SO_3 aqueous solution, and the organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether as elution solvent) to give compound **2a** as a colorless oil (1.7297 g, 5.665 mmol, 78% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (s, 1H), 5.37 (s, 1H), 4.10 (d, *J* = 0.9 Hz, 2H), 2.46 – 2.40 (m, 2H), 2.25 – 2.17 (m, 2H), 1.79-1.77 (m, 1H), 1.58 – 1.53 (m, 1H), 0.91 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 114.5, 78.2, 36.0, 31.4, 25.8, 18.0, 13.2, -3.1. **HRMS ESI** Calcd for $C_{13}H_{25}BrOSi$ [M+Na]$^+$: 327.0750, Found: 327.0750; [M+Na]$^+$: 329.0730, Found: 329.0729. **IR** *v* (cm^{-1}): 2956, 2932, 2886, 2857, 1471, 776, 593.

5.2 Method B: Typical Procedure for the Synthesis of **2b**



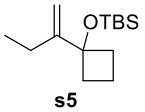
1-(but-1-en-2-yl)cyclobutan-1-ol (**s4**):



s4

To a stirred solution of 2-bromobut-1-ene (506 μL, 4.906 mmol, 1 eq.) in THF (30 mL), *t*-BuLi (1.6 M, 5.52 mL, 8.831 mmol, 1.8 eq.) was added slowly at -78 °C. The reaction mixture was stirred at -78 °C for 20 mins, and then **s1** (323 μL, 4.415 mmol, 0.9 eq.) was dissolved in THF (10 mL) was added dropwise at -78 °C. After stirring for 10 mins, the reaction was poured into saturated NH_4Cl aqueous solution, the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum in a cold water bath (< 15 °C). The residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 8: 1) to give compound **s4** as a colorless oil (434.9 mg, 3.435 mmol, 78% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (s, 1H), 4.84 (s, 1H), 2.32 – 2.26 (m, 3H), 2.11 (q, *J* = 7.4 Hz, 2H), 2.08 – 1.98 (m, 2H), 1.88 – 1.86 (m, 1H), 1.55 – 1.52 (m, 1H), 1.06 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 106.9, 78.3, 34.5, 22.6, 13.0, 12.4. **HRMS ESI** Calcd for $C_8H_{14}O$ [M+Na]$^+$: 149.0937, Found: 149.0926. **IR** *v* (cm^{-1}): 3350, 2966, 2878, 1645, 1375, 898.

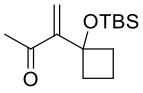
(1-(but-1-en-2-yl)cyclobutoxy)(tert-butyl)dimethylsilane (**s5**):



s5

To an ice-cooled solution of **s4** (1.362 g, 10.79 mmol, 1 eq.) in dry DCM (30 mL) was added Et_3N (2.25 mL, 16.185 mmol, 1.5 eq.), and then TBSOTf (2.97 mL, 12.948 mmol, 1.2 eq.) was added slowly at 0 °C. The reaction system was monitored by TLC until **s2** disappeared completely. The reaction was quenched by saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether as elution solvent) to give compound **s5** as a colorless oil (2.534 g, 10.54 mmol, 98% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (d, *J* = 1.0 Hz, 1H), 4.87 (dd, *J* = 2.6, 1.6 Hz, 1H), 2.30 – 2.22 (m, 2H), 2.16 – 2.07 (m, 4H), 1.78 – 1.68 (m, 1H), 1.44 (dp, *J* = 10.7, 8.6 Hz, 1H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.88 (s, 9H), 0.02 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.6, 106.1, 79.2, 35.6, 25.8, 22.1, 18.0, 13.2, 12.1, -3.2. **HRMS ESI** Calcd for $C_{14}H_{28}OSi$ [M+Na]$^+$: 263.1802, Found: 263.1801. **IR** *v* (cm^{-1}): 2957, 2930, 2857, 1645, 1251, 991, 775.

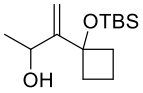
3-(1-((tert-butyldimethylsilyl)oxy)cyclobutyl)but-3-en-2-one (**s6**)[8]:



s6

In a reaction tube, to a 1,4-dioxane (20 mL) solution of **s5** (1.207 g, 5.02 mmol, 1eq.) was added SeO_2 (1.114 g, 10.04 mmol, 2 eq.), and then the reaction mixture was refluxed for 3.5 hours. The reaction system was monitored by TLC until **s5** disappeared completely. The reaction was quenched by saturated Na_2SO_3 aqueous solution, the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 20: 1) to give compound **S6** (685.8 mg, 2.696 mmol, 54% yield) as a light yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 – 5.96 (m, 1H), 5.63 (s, 1H), 2.45 – 2.34 (m, 3H), 2.34 (s, 3H), 2.30 (dd, *J* = 9.6, 2.7 Hz, 1H), 1.83 (dtt, *J* = 11.0, 9.3, 3.9 Hz, 1H), 1.55 – 1.46 (m, 1H), 0.86 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.5, 152.1, 120.1, 77.0, 36.7, 28.8, 25.7, 17.9, 13.3, -3.1. **HRMS ESI** Calcd for $C_{14}H_{26}O_2Si$ [M+Na]$^+$: 277.1594, Found: 277.1694. **IR** *v* (cm^{-1}): 3101, 2930, 2857, 1693, 1252, 1139, 1105, 776.

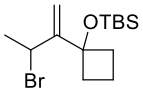
3-(1-((*tert*-butyldimethylsilyl)oxy)cyclobutyl)but-3-en-2-ol (**s7**)[9]:



s7

To a solution of **s6** (685.8 mg, 2.696 mmol, 1eq.) in MeOH (20 mL) were added $CeCl_3$•$7H_2O$ (1.506 g, 4.044 mmol, 1.5 eq.) and $NaBH_4$ (122.9 mg, 3.235 mmol, 1.2 eq.) at 0 °C, the resulting suspension was monitored by TLC until **s6** disappeared completely. The reaction was quenched by saturated NH_4Cl aqueous solution, the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 10: 1) to give compound **s7** as a colorless oil (546.9 mg, 2.132 mmol, 79% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 – 5.15 (m, 2H), 4.56 (dd, *J* = 6.4, 1.7 Hz, 1H), 2.94 (d, *J* = 2.6 Hz, 1H), 2.45 (ddd, *J* = 15.7, 8.1, 3.9 Hz, 1H), 2.30 – 2.25 (m, 3H), 1.81 – 1.73 (m, 1H), 1.55 – 1.45 (m, 1H), 1.38 (d, *J* = 6.4 Hz, 3H), 0.90 (s, 9H), 0.13 (d, *J* = 1.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 107.7, 79.5, 67.3, 36.1, 36.1, 25.8, 22.8, 18.0, 13.0, -2.6, -2.8. **HRMS ESI** Calcd for $C_{14}H_{28}O_2Si$ [M+Na]$^+$: 279.1751, Found: 279.1750. **IR** *v* (cm^{-1}): 3452, 2954, 2877, 1655, 1379, 1459, 1100.

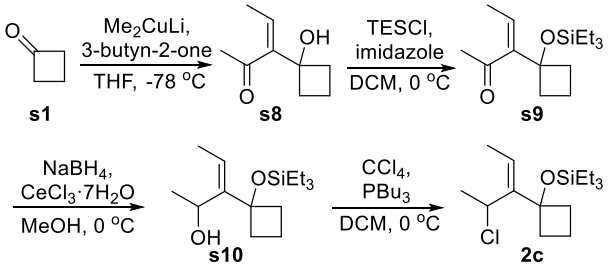
(1-(3-bromobut-1-en-2-yl)cyclobutoxy)(*tert*-butyl)dimethylsilane (**2b**)[10]:



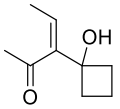
2b

s7 (688.8 mg, 2.686 mmol, 1 eq.) was dissolved in DCM (20 mL), imidazole (219.4 mg, 3.22 mmol, 1.2 eq.) PPh_3 (845.4mg, 3.22 mmol, 1.2 eq.) and CBr_4 (623.5 mg, 1.88 mmol, 0.7 eq.) were added at rt, the reaction mixture was stirred overnight. The reaction system was monitored by TLC. The reaction was quenched by saturated NH_4Cl aqueous solution, the organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether as elution solvent) to give compound **2b** as a colorless oil (428.6 mg, 1.346 mmol, 50% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (s, 1H), 5.37 (d, *J* = 0.8 Hz, 1H), 4.87 (q, *J* = 6.8 Hz, 1H), 2.56 (ddd, *J* = 15.9, 8.2, 4.1 Hz, 1H), 2.40 (ddt, *J* = 12.2, 8.1, 4.1 Hz, 1H), 2.25 – 2.16 (m, 2H), 1.87 (d, *J* = 6.9 Hz, 3H), 1.78 (dddd, *J* = 10.9, 9.2, 5.6, 3.8 Hz, 1H), 1.57 – 1.46 (m, 1H), 0.89 (s, 9H), 0.13 (s, 3H), 0.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.3, 112.2, 78.6, 44.9, 36.7, 34.8, 27.3, 25.8, 25.7, 18.1, 13.2, -2.6, -2.8. **HRMS ESI** Calcd for $C_{14}H_{27}BrOSi$ [M+Na]$^+$: 341.0907, Found: 341.0906; [M+Na]$^+$: 343.0886, Found: 343.0886. **IR** *v* (cm^{-1}): 3097, 2955, 2929, 2896, 2857, 1646, 775, 681.

5.3 Method C: Typical Procedure for the Synthesis of **2c**



(*Z*)-3-(1-hydroxycyclobutyl)pent-3-en-2-one (**s8**)[11]:

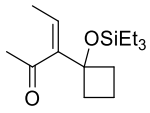


s8

MeLi (1.6 M, 16.7 mL, 26.76 mmol, 2.1 eq.) was added slowly to a mixture of CuI (3.185 g, 16.7 mmol, 1.3 eq.) in 20 mL of dry diethyl ether at 0 °C, after which the mixture was stirred vigorously for 30 mins. Then the system was moved to -78 °C and added slowly to a solution of but-3-yn-2-one (1.0 mL, 12.7 mmol, 1 eq.) in THF (10 mL). After stirring at -78 °C for 20 mins, and then was added slowly to the solution of **s1** (0.9 mL, 12.1 mmol, 0.95 eq.) in 10 mL of THF at -78 °C. The mixture was allowed to warm to rt. The reaction was quenched by saturated NH_4Cl aqueous

solution at 0 °C, the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum in a cold water bath (< 15 °C). The residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 4: 1) to give compound **s8** as a colorless oil (1.176 g, 7.623 mmol, 63% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (q, *J* = 7.2 Hz, 1H), 3.05 (d, *J* = 58.9 Hz, 1H), 2.34 (s, 3H), 2.27 (dddd, *J* = 12.0, 8.9, 6.1, 2.9 Hz, 2H), 2.15 – 2.08 (m, 2H), 2.01 – 1.91 (m, 1H), 1.86 (d, *J* = 7.2 Hz, 3H), 1.66 – 1.51 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.2, 145.9, 128.1, 77.1, 34.8, 32.2, 15.2, 13.4. **HRMS ESI** Calcd for $C_9H_{14}O_2$ [M+Na]$^+$: 177.0886, Found: 177.0886. **IR** *v* (cm^{-1}): 3424, 2984, 2947, 1689, 1165, 844.

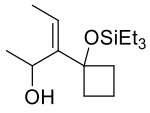
(*Z*)-3-(1-((triethylsilyl)oxy)cyclobutyl)pent-3-en-2-one (**s9**):



s9

To a stirred solution of **s8** (232.5 mg, 1.51 mmol, 1 eq.) in dry DCM (8 mL) was added imidazole (154.2 mg, 2.265 mmol, 1.5 eq.), and then TESCl (337 µL, 1.812 mmol, 1.2 eq.) was added slowly at 0 °C. The reaction system was monitored by TLC until **s8** disappeared completely. The reaction was quenched by saturated NH_4Cl aqueous solution, the organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 20: 1) to give compound **s9** as a colorless oil (360.1 mg, 1.34 mmol, 89% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (q, *J* = 7.1 Hz, 1H), 2.44 – 2.35 (m, 2H), 2.31 – 2.27 (m, 1H), 2.26 (d, *J* = 3.2 Hz, 3H), 2.25 – 2.22 (m, 1H), 1.84 – 1.78 (m, 1H), 1.78 – 1.76 (m, 3H), 1.56 – 1.45 (m, 1H), 0.92 (td, *J* = 7.9, 3.9 Hz, 9H), 0.60 – 0.52 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.7, 147.2, 124.1, 77.4, 36.8, 31.7, 14.9, 12.9, 6.9, 6.2. **HRMS ESI** Calcd for $C_{15}H_{28}O_2Si$ [M+Na]$^+$: 291.1751, Found: 291.1750. **IR** *v* (cm^{-1}): 2955, 2914, 2877, 1697, 1005, 1357, 743.

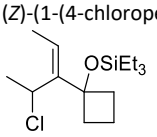
(*E*)-3-(1-((triethylsilyl)oxy)cyclobutyl)pent-3-en-2-ol (**s10**):



s10

To a solution of **s9** (360.1 mg, 1.34 mmol, 1 eq.) in MeOH (10 mL) were added $CeCl_3$•$7H_2O$ (748.9 mg, 2.01 mmol, 1.5 eq.) and $NaBH_4$ (61.2 mg, 1.61 mmol, 1.2 eq.) at 0 °C, and the resulting suspension was monitored by TLC until **s9** disappeared completely. The reaction was quenched by saturated NH_4Cl aqueous solution, the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 10: 1) to give compound **s10** as a colorless oil (293.9 mg, 1.09 mmol, 81% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 – 5.42 (m, 1H), 4.75 (p, *J* = 6.4 Hz, 1H), 3.61 (d, *J* = 5.6 Hz, 1H), 2.50 – 2.32 (m, 2H), 2.28 – 2.04 (m, 2H), 1.78 – 1.70 (m, 1H), 1.66 (d, *J* = 7.0 Hz, 3H), 1.53 – 1.42 (m, 1H), 1.36 (d, *J* = 6.7 Hz, 3H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 7.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.2, 117.3, 80.7, 67.7, 36.2, 36.1, 24.1, 13.3, 13.3, 6.9, 6.2. **HRMS ESI** Calcd for $C_{15}H_{30}O_2Si$ [M+Na]$^+$: 293.1907, Found: 293.1906. **IR** *v* (cm^{-1}): 3499, 3049, 2956, 2877, 1730, 1151, 1003, 741.

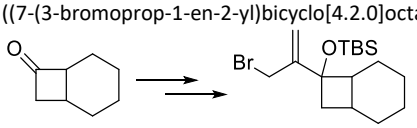
(*Z*)-(1-(4-chloropent-2-en-3-yl)cyclobutoxy)triethylsilane (**2c**)[12]:



2c

To a stirred solution of **s10** (97.0 mg, 0.359 mmol, 1 eq.) in DCM (3 mL) was added PBu_3 (266 µL, 1.076 mmol, 3 eq.), and then CCl_4 (208 µL, 2.154 mmol, 6 eq.) was added dropwise at 0 °C. The reaction mixture was stirred overnight. The reaction system was monitored by TLC until **s10** disappeared completely. The reaction was quenched by saturated NH_4Cl aqueous solution. The organic layer was separated, and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether as elution solvent) to give compound **2c** as a colorless oil (62.4 mg, 0.216 mmol, 60% yield).
^{1}H NMR (400 MHz,) δ 5.72 (q, *J* = 7.2 Hz, 1H), 4.84 – 4.79 (m, 1H), 2.40 – 2.34 (m, 2H), 2.16 – 2.11 (m, 2H), 1.95 (dd, *J* = 7.2, 2.9 Hz, 3H), 1.77 – 1.74 (m, 3H), 1.74 – 1.66 (m, 1H), 1.50 – 1.37 (m, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.59 (q, *J* = 7.9 Hz, 6H). **^{13}C NMR** (100 MHz,) δ 142.4, 123.5, 79.6, 54.6, 35.8, 34.5, 24.9, 14.4, 12.9, 7.0, 6.4. **HRMS ESI** Calcd for $C_{15}H_{29}ClOSi$ [M+Na]$^+$: 311.1568, Found: 311.1668; [M+Na]+: 313.1539, Found: 313.1539. **IR** *v* (cm^{-1}): 3046, 2955, 2876, 1459, 769, 743, 699.

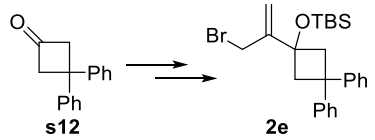
((7-(3-bromoprop-1-en-2-yl)bicyclo[4.2.0]octan-7-yl)oxy)(*tert*-butyl)dimethylsilane (**2d**):



s11 **2d**

Preparation according to the **Method A** from **s11** (73.3 mg, 0.590 mmol) afforded **2d** as a colorless oil (109.1 mg, 0.304 mmol, 51% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (d, *J* = 21.3 Hz, 2H), 4.12 – 4.05 (m, 2H), 2.46 (dt, *J* = 17.6, 8.8 Hz, 1H), 2.34 – 2.30 (m, 1H), 2.17 (t, *J* = 11.2 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.83 – 1.61 (m, 3H), 1.60 – 1.23 (m, 4H), 1.05 (tt, *J* = 16.4, 8.3 Hz, 1H), 0.88 (s, 9H), 0.07 (s, 3H), -0.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 114.6, 76.3, 42.6, 35.4, 31.7, 25.8, 25.7, 24.1, 22.8, 22.3, 21.8, 18.3, -2.9, -3.5. **HRMS ESI** Calcd for $C_{17}H_{31}BrOSi$ [M+Na]$^+$: 381.1220, Found: 381.1219; [M+Na]$^+$: 383.1199, Found: 383.1199. **IR** *v* (cm^{-1}): 3094, 2929, 2856, 1648, 836, 775, 578.

(1-(3-bromoprop-1-en-2-yl)-3,3-diphenylcyclobutoxy)(*tert*-butyl)dimethylsilane (**2e**)[a]:

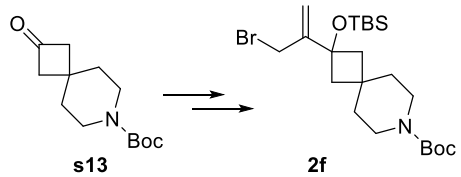


s12 **2e**

Preparation according to the **Method A** from **s12** (266.7 mg, 1.2 mmol) afforded **2e** as a colorless oil (367.9 mg, 0.804 mmol, 67% yield over five steps). [a]2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 5H), 7.25 (m, 3H), 7.11 (m, 2H), 5.26 (s, 1H), 5.09 (s, 1H), 4.05 (s, 2H), 3.50 (d, *J* = 13.2 Hz, 2H), 3.10 (d, *J* = 13.2 Hz,2H), 0.75 (s, 9H), -0.05 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.4, 148.5, 147.5, 128.3, 128.2, 126.4, 126.0, 125.4, 125.4, 116.6, 74.2, 48.1, 43.3, 31.1, 25.6, 17.9, -3.2. **HRMS ESI** Calcd for $C_{25}H_{33}BrOSi$ [M+Na]$^+$: 479.1376, Found: 479.1376; [M+Na]$^+$: 481.1356, Found: 481.1356. **IR** *v* (cm^{-1}): 3084, 3059, 2954, 2929, 2886, 2856, 1650, 1599, 775, 585, 545.

tert-butyl 2-(3-bromoprop-1-en-2-yl)-2-((tert-butyldimethylsilyl)oxy)-7-azaspiro[3.5]nonane-7-carboxylate (**2f**)[a]:

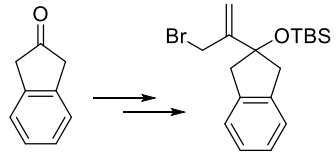


s13 **2f**

Preparation according to the **Method B** from **s13** (5.00 g, 20.9 mmol) afforded **2f** as a colorless oil (1.9083 g, 4.021 mmol, 19% yield over five steps). [a]2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (d, *J* = 0.6 Hz, 1H), 5.33 (s, 1H), 4.03 (s, 2H), 3.33 – 3.26 (m, 4H), 2.47 (d, *J* = 13.0 Hz, 2H), 2.01 (d, *J* = 12.8 Hz, 2H), 1.63 – 1.60 (m, 2H), 1.46 (d, *J* = 6.1 Hz, 2H), 1.43 (d, *J* = 0.8 Hz, 9H), 0.85 (s , 9H), -0.00 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 149.3, 116.0, 79.2, 73.9, 44.6, 39.0, 36.8, 30.8, 29.6, 28.4, 25.7, 17.9, -3.2. **HRMS ESI** Calcd for $C_{22}H_{40}BrNO_3Si$ [M+Na]$^+$: 496.1853, Found: 496.1853. [M+Na]$^+$: 498.1833, Found: 498.1833. **IR** *v* (cm^{-1}): 3095, 3052, 2956, 2929, 2857, 1693, 1246, 530.

((2-(3-bromoprop-1-en-2-yl)-2,3-dihydro-1*H*-inden-2-yl)oxy)(*tert*-butyl)dimethylsilane (**2g**)[a]:

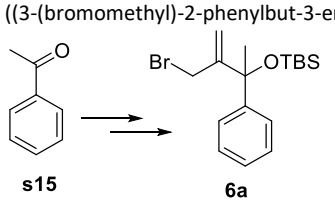


s14 **2g**

Preparation according to the **Method B** from **s14** (1.19 g, 9.0 mmol) afforded **2g** as a colorless oil (264.5 mg, 0.72 mmol, 8% yield over five steps). [a]2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 4H), 5.39 (d, J = 7.1 Hz, 2H), 4.20 (d, J = 0.5 Hz, 2H), 3.40 (d, J = 16.2 Hz, 2H), 3.16 (d, J = 16.1 Hz, 2H), 0.78 (s, 9H), -0.11 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.6, 141.1, 126.5, 124.6, 116.3, 85.9,47.0, 32.1, 25.7, 18.2, -3.1. **HRMS ESI** Calcd for $C_{18}H_{27}BrOSi$ [M+Na]$^+$: 389.0907, Found: 389.0907; [M+Na]$^+$: 391.0886, Found: 391.0886. **IR** *v* (cm^{-1}): 3072, 2955, 2928, 2896, 2856, 1638, 836, 775, 542.

((3-(bromomethyl)-2-phenylbut-3-en-2-yl)oxy)(*tert*-butyl)dimethylsilane (**6a**)[a]:

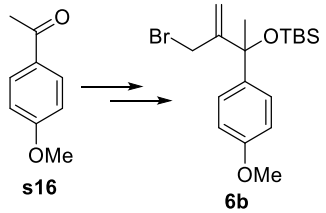


s15 **6a**

Preparation according to the **Method B** from **s15** (3.15 mL, 27.0 mmol) afforded **6a** as a colorless oil (1.9095 g, 5.373 mmol, 20% yield over five steps). [a]2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 5.54 (d, *J* = 8.4 Hz, 2H), 3.98 (d, *J* = 12.2 Hz, 1H), 3.66 (d, *J* = 12.2 Hz, 1H), 1.79 (s, 3H), 0.95 (s, 9H), 0.06 (s, 3H), -0.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.9, 146.2, 128.0, 127.0, 125.7, 115.9, 78.8, 31.8, 29.6, 29.5, 26.1, 26.0, 18.6, -2.4, -2.8. **HRMS ESI** Calcd for $C_{17}H_{27}BrOSi$ [M+Na]$^+$: 377.0907, Found: 377.0906; [M+Na]$^+$: 379.0886, Found: 379.0886. **IR** *v* (cm^{-1}): 3060, 2956, 2930, 2857, 2856, 1648, 776, 701, 556.

((3-(bromomethyl)-2-(4-methoxyphenyl)but-3-en-2-yl)oxy)(*tert*-butyl)dimethylsilane (**6b**)[a]:



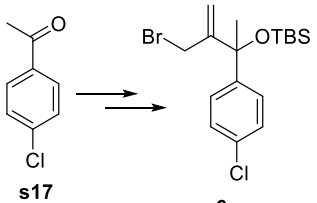
s16 **6b**

Preparation according to the **Method B** from **s16** (5.2563 g, 35 mmol) afforded **6b** as a colorless oil (2.1189 g, 5.498 mmol, 16% yield over five steps). [a]2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 6.85 – 6.83 (m, 2H), 5.54 – 5.50 (m, 2H), 3.98 (dd, *J* = 12.0, 0.8 Hz, 1H), 3.81 (s, 3H), 3.69 (dd, *J* = 12.0, 1.0 Hz, 1H), 1.79 (s, 3H), 0.95 (s, 9H), 0.05 (s, 3H), -0.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.6, 151.3, 138.3, 127.1, 126.8, 115.7, 113.3,

113.2, 78.5, 55.2, 31.8, 29.4, 26.0, 18.5, -2.5, -2.8. **HRMS ESI** Calcd for $C_{18}H_{29}BrO_2Si$ [M+Na]$^+$: 407.1012, Found: 407.1012. [M+Na]$^+$: 409.0992, Found: 409.0992. **IR** *v* (cm^{-1}): 3100, 2956, 2929, 2899, 1609, 835, 815, 563.

((3-(bromomethyl)-2-(4-chlorophenyl)but-3-en-2-yl)oxy)(*tert*-butyl)dimethylsilane (**6c**)^a:

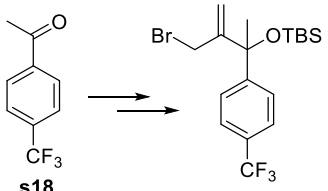


s17 **6c**

Preparation according to the **Method B** from **s17** (3.50 mL, 27 mmol) afforded **6c** as a colorless oil (2.4205 g, 6.21 mmol, 23% yield over five steps). ^{a}2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.32 – 7.29 (m, 2H), 5.56 (d, *J* = 4.4 Hz, 2H), 4.00 (d, *J* = 12.1 Hz, 1H), 3.69 (dd, *J* = 12.1, 0.9 Hz, 1H), 1.80 (s, 3H), 0.98 (s, 9H), 0.10 (s, 3H), -0.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 144.9, 132.8, 128.1, 127.2, 116.3, 78.4, 31.3, 29.5, 29.5, 26.0, 26.0, 18.5, -2.3, -2.8, -2.8. **HRMS ESI** Calcd for $C_{17}H_{26}BrClOSi$ [M+Na]$^+$: 411.0517, Found: 411.0517; [M+Na]$^+$: 413.0497, Found: 413.0497. **IR** *v* (cm^{-1}): 3086, 2956, 2930, 2857, 2886, 1648, 1594, 836, 776, 553.

((3-(bromomethyl)-2-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)oxy)(*tert*-butyl)dimethylsilane (**6d**)^a:

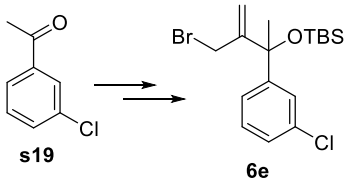


s18 **6d**

Preparation according to the **Method B** from **s18** (2.54 g, 13.5 mmol) afforded **6d** as a colorless oil (1.6905 g, 3.99 mmol, 30% yield over five steps). ^{a}2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (q, *J* = 8.6 Hz, 4H), 5.59 (d, *J* = 11.9 Hz, 2H), 4.00 (d, *J* = 12.3 Hz, 1H), 3.66 (d, *J* = 12.3 Hz, 1H), 1.81 (s, 3H), 0.98 (s, 9H), 0.11 (s, 3H), 0.02 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 150.0, 129.2 (q, $^2J_{FC}$ = 32 Hz), 125.9, 125.0 (q, $^3J_{FC}$ = 4 Hz), 124.2 (q, $^1J_{FC}$ = 272 Hz), 116.7, 78.6, 31.2, 29.7, 26.0, 18.6, -2.2, -2.9. **HRMS ESI** Calcd for $C_{18}H_{26}BrF_3OSi$ [M+Na]$^+$: 445.0781, Found: 445.0781; [M+Na]$^+$: 447.0760, Found: 447.0760. **IR** *v* (cm^{-1}): 3057, 2957, 2931, 2895, 2858, 1618, 836, 770, 609, 542.

((3-(bromomethyl)-2-(3-chlorophenyl)but-3-en-2-yl)oxy)(*tert*-butyl)dimethylsilane (**6e**)^a:

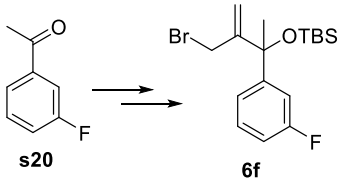


s19 **6e**

Preparation according to the **Method B** from **s19** (1.75 mL, 13.5 mmol) afforded **6e** as a colorless oil (1.8159 g, 4.657 mmol, 35% yield over five steps). ^{a}2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.24 (ddd, *J* = 17.2, 9.7, 4.1 Hz, 3H), 5.52 (d, *J* = 5.3 Hz, 2H), 3.95 (d, *J* = 12.2 Hz, 1H), 3.64 (dd, *J* = 12.2, 0.7 Hz, 1H), 1.75 (s, 3H), 0.93 (s, 9H), 0.05 (s, 3H), -0.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.3, 148.6, 134.0, 129.3, 127.2, 126.1, 123.9, 116.5, 78.5, 31.3, 29.5, 26.0, 18.6, -2.3, -2.8. **HRMS ESI** Calcd for $C_{17}H_{26}BrClOSi$ [M+Na]$^+$: 411.0517, Found: 411.0517; [M+Na]$^+$: 413.0497, Found: 413.0498. **IR** *v* (cm^{-1}): 3058, 2956, 2930, 2886, 2857, 1594, 1573, 700, 586, 542.

((3-(bromomethyl)-2-(3-fluorophenyl)but-3-en-2-yl)oxy)(*tert*-butyl)dimethylsilane (**6f**)^a:

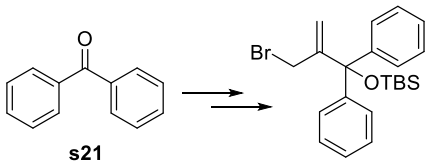


s20 **6f**

Preparation according to the **Method B** from **s20** (3.38 mL, 27 mmol) afforded **6f** as a colorless oil (2.0404 g, 5.464 mmol, 20% yield over five steps). ^{a}2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 14.1, 7.7 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.07 (ddd, *J* = 8.1, 5.4, 1.4 Hz, 1H), 5.71 (s, 2H), 4.14 (d, *J* = 12.2 Hz, 1H), 3.82 (dd, *J* = 12.2, 0.9 Hz, 1H), 1.94 (s, 3H), 1.12 (s, 9H), 0.24 (s, 3H), 0.15 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ, 162.7 (d, $^1J_{FC}$ = 245 Hz), 150.4, 149.3 (d, $^3J_{FC}$ = 6 Hz), 129.5 (d, $^3J_{FC}$ = 4 Hz), 121.2, 116.4, 116.3, 113.9 (d, $^2J_{FC}$ = 21 Hz), 113.1 (d, $^4J_{FC}$ = 6 Hz), 112.9 (d, $^2J_{FC}$ = 22 Hz), 78.5, 31.4, 31.3, 31.2, 29.6, 29.5, 26.0, 26.0, 18.5, -2.3, -2.9, -2.9. **HRMS ESI** Calcd for $C_{17}H_{26}BrFOSi$ [M+Na]$^+$: 395.0813, Found: 395.0812. [M+Na]$^+$: 397.0792, Found: 397.0792. **IR** *v* (cm^{-1}): 3077, 2956, 2930, 2886, 2857, 1614, 1591, 703, 578, 542.

((2-(bromomethyl)-1,1-diphenylallyl)oxy)(*tert*-butyl)dimethylsilane (**6g**)^a:

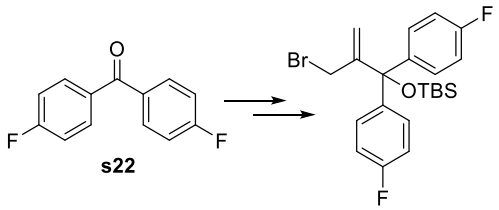


s21 **6g**

Preparation according to the **Method B** from **s21** (6.370 g, 35 mmol) afforded **6g** as a colorless oil (3.6542 g, 8.755 mmol, 25% yield over five steps). [a]2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.8, 1.8 Hz, 4H), 7.37 – 7.32 (m, 6H), 5.74 (d, *J* = 13.4 Hz, 2H), 3.93 (s, 2H), 0.99 (s, 9H), -0.39 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7, 143.4, 129.1, 127.8, 127.7, 118.4, 84.9, 32.3, 26.4, 19.2, -3.2. **HRMS ESI** Calcd for $C_{22}H_{29}BrOSi$ [M+Na]$^+$: 439.1063, Found: 439.1063; [M+Na]$^+$: 441.1043, Found: 441.1043. **IR** *v* (cm^{-1}): 3060, 2956, 2929, 2856, 2893, 1644, 1599, 703, 576.

((2-(bromomethyl)-1,1-bis(4-fluorophenyl)allyl)oxy)(*tert*-butyl)dimethylsilane (**6h**)[a]:

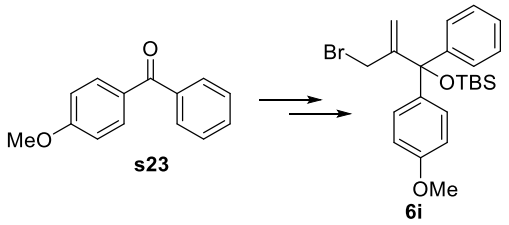


s22 **6h**

Preparation according to the **Method B** from **s22** (2.946 g, 13.5 mmol) afforded **6h** as a colorless oil (1.9221g, 4.239 mmol, 31% yield over five steps). [a]2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 4H), 7.05 (t, *J* = 8.7 Hz, 4H), 5.74 (d, *J* = 5.6 Hz, 2H), 3.91 (s, 2H), 1.00 (s, 9H), -0.35 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2 (d, $^1J_{FC}$ = 248 Hz), 149.6, 139.1, 139.0, 133.7 (d, $^2J_{FC}$ = 19 Hz), 130.7, 130.7, 128.7, 128.4 (d, $^3J_{FC}$ = 9 Hz), 118.8, 114.8, 114.6, 83.9, 31.7, 26.3, 19.1, -3.1. **HRMS ESI** Calcd for $C_{22}H_{27}BrF_2OSi$ [M+Na]$^+$: 475.0875, Found: 475.0875; [M+Na]$^+$: 477.0854, Found: 477.0855. **IR** *v* (cm^{-1}): 3049, 2957, 2930, 2896, 2857, 1602, 836, 777, 574.

((2-(bromomethyl)-1-(4-methoxyphenyl)-1-phenylallyl)oxy)(*tert*-butyl)dimethylsilane (**6i**)[a]



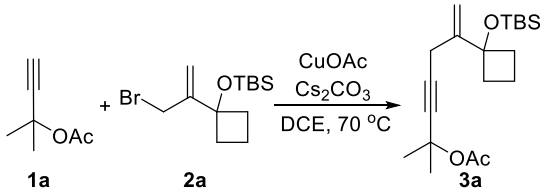
s23 **6i**

Preparation according to the **Method B** from **s23** (2.865 g, 13.5 mmol) afforded **6i** as a colorless oil (1.994 g, 4.46 mmol, 33% yield over five steps). [a]2,6-lutidine as base in step 2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.34 – 7.30 (m, 5H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.70 (d, *J* = 15.8 Hz, 2H), 3.90 (s, 2H), 3.82 (s, 3H), 0.96 (s, 9H), -0.41 (d, *J* = 8.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 150.0, 143.7, 135.3, 130.6, 128.8, 127.7, 127.5, 118.1, 113.0, 84.5, 55.3, 32.4, 26.4, 19.1, -3.2, -3.2. **HRMS ESI** Calcd for $C_{23}H_{31}BrO_2Si$ [M+Na]$^+$: 469.1169, Found: 469.1169; [M+Na]$^+$: 471.1148, Found: 471.1149. **IR** *v* (cm^{-1}): 3057, 2955, 2926, 2855, 1701, 1608, 835, 742, 581.

6 Experimental Details for 3a, 5 and 7

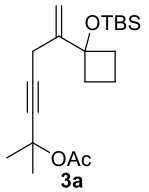
6.1 Typical Procedure for the Synthesis of **3a**



1a **2a** **3a**

Preparation according to the optimized coupling reaction conditions (Section 2, Table 1, entry 10). To a stirred solution of **1a** (63 mg, 0.5 mmol, 2.5 eq.) and **2a** (61 mg, 0.2 mmol, 1.0 eq.) in dry DCE (2 mL) were added CuOAc (7.4 mg, 0.06 mmol, 30 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 50 mol%). After stirring overnight at 70 °C, the reaction mixture was concentrated under vacuum, and then purified by flash chromomatography on silica gel (petroleum ether: EtOAc = 50: 1) to give the coupling product **3a** (54.5 mg, 0.164 mmol, 82% yield) as a colorless oil.

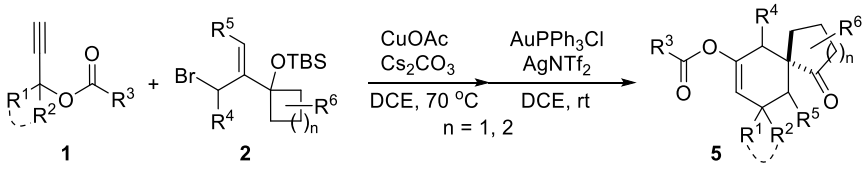
6-(1-((*tert*-butyldimethylsilyl)oxy)cyclobutyl)-2-methylhept-6-en-3-yn-2-yl acetate(**3a**):



3a

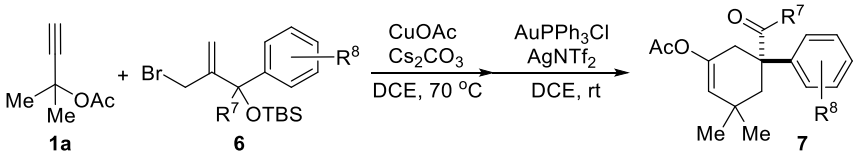
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (s, 1H), 5.17 (s, 1H), 3.03 (s, 2H), 2.26 (ddd, *J* = 8.4, 5.9, 3.0 Hz, 2H), 2.18 – 2.09 (m, 2H), 2.02 (s, 3H), 1.74 – 1.64 (m, 7H), 1.54 – 1.40 (m, 1H), 0.87 (s, 9H), 0.03 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 146.8, 109.5, 84.4, 82.3, 78.2, 72.5, 35.5, 29.3, 25.8, 22.1, 20.4, 18.0, 13.0, -3.2. **HRMS ESI** Calcd for $C_{20}H_{34}O_3Si$ [M+Na]$^+$: 373.2169, Found: 373.2160. **IR** *v* (cm^{-1}): 2955, 1743, 1250, 1137, 837, 738.

6.2 Typical Procedure for the Synthesis of **5**



1 **2** **5**

6.3 Typical Procedure for the Synthesis of **7**

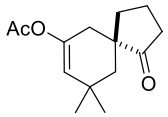


1a **6** **7**

General procedure:

To a solution of **1** (0.5 mmol, 2.5 eq.) and **2** or **6** (0.2 mmol, 1.0 eq.) in dry DCE (2 mL) was added CuOAc (0.06 mmol, 30 mol%), Cs_2CO_3 (0.1 mmol, 50 mol%). The resulting mixture was stirred overnight at 70 °C. After a quick filtration of the reaction mixture through a celite pad to remove the residue, the reaction mixture was diluted to a volume of 4 mL with DCE, then a combination solution of $AuPPh_3Cl$ (0.02 mmol, 10 mol%) and $AgNTf_2$ (0.02 mmol, 10 mol%) which was prestirred in DCE (0.5 mL) for 30 mins, was added dropwise. After being stirred for another 9 hours at rt, the mixture was concentrated under vacuum. The crude mixture was purified by flash chromatography on silica gel (petroleum ether: EtOAc = 6: 1) to give the desired product **5** or **7**.

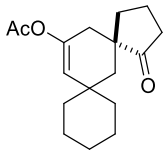
9,9-dimethyl-1-oxospiro[4.5]dec-7-en-7-yl acetate (**5a**):



5a

Colorless oil, (31.2 mg, 0.132 mmol, 66% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.21 (d, *J* = 1.9 Hz, 1H), 2.34 – 2.29 (m, 1H), 2.29 – 2.14 (m, 3H), 2.10 (s, 3H), 2.02 (ddd, *J* = 12.2, 6.0, 3.1 Hz, 1H), 1.90 (dd, *J* = 16.3, 2.0 Hz, 1H), 1.88 – 1.80 (m, 1H), 1.80 – 1.77 (m, 2H), 1.29 (d, *J* = 13.9 Hz, 1H), 1.09 (d, *J* = 9.6 Hz, 6H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ 222.3, 169.4, 144.3, 123.3, 49.6, 42.4, 37.2, 35.5, 32.9, 32.4, 32.4, 29.5, 21.0, 19.5. **HRMS ESI** Calcd for $C_{14}H_{20}O_3$ [M+Na]$^+$: 259.1305, Found: 259.1294. **IR** *v* (cm^{-1}): 2958, 2924, 1736, 1220, 1104, 734.

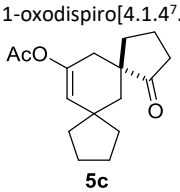
1-oxodispiro[4.1.5^7.3^5]pentadec-13-en-14-yl acetate (**5b**):



5b

Colorless oil, (29.3 mg, 0.106 mmol, 53% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.41 (s, 1H), 2.30 – 2.23 (m, 2H), 2.18 (dd, *J* = 19.8, 10.9 Hz, 2H), 2.11 (s, 3H), 2.01 (dd, *J* = 6.1, 3.2 Hz, 1H), 1.92 (d, *J* = 16.2 Hz, 1H), 1.83 – 1.76 (m, 2H), 1.53 – 1.48 (m, 8H), 1.43 – 1.36 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 222.6, 169.4, 144.7, 121.7, 49.4, 40.8, 37.3, 35.7, 35.3, 33.5, 25.9, 21.8, 21.7, 21.1, 19.5. **HRMS ESI** Calcd for $C_{17}H_{24}O_3$ [M+Na]$^+$: 299.1618, Found: 299.1605. **IR** *v* (cm^{-1}): 2926, 2853, 1736, 1223, 1184, 738.

1-oxodispiro[4.1.4^7.3^5]tetradec-12-en-13-yl acetate (**5c**):

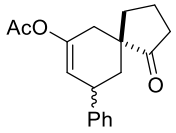


5c

Colorless oil, (28.9 mg, 0.11 mmol, 55% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.31 (s, 1H), 2.29 (dd, *J* = 10.2, 5.8 Hz, 1H), 2.25 (d, *J* = 5.1 Hz, 1H), 2.21 (t, *J* = 4.2 Hz, 1H), 2.19 – 2.15 (m, 1H), 2.12 (d, *J* = 10.5 Hz, 3H), 2.03 – 1.95 (m, 1H), 1.95 – 1.91 (m, 1H), 1.89 (d, *J* = 4.0 Hz, 1H), 1.86 (s, 1H), 1.82 (t, *J* = 5.8 Hz, 1H), 1.74 – 1.65 (m, 3H), 1.65 – 1.60 (m, 3H), 1.58 (s, 1H), 1.53 – 1.46 (m, 1H), 1.36 (d, *J* = 13.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

222.2, 169.4, 144.2, 121.7, 49.8, 43.3, 42.1, 40.5, 39.4, 37.4, 34.8, 33.4, 24.5, 23.1, 21.1, 19.2. **HRMS ESI** Calcd for $C_{16}H_{22}O_3$ [M+Na]$^+$: 285.1461, Found: 285.1449. **IR** *v* (cm^{-1}): 2956, 2923, 1755, 1370, 1219, 738.

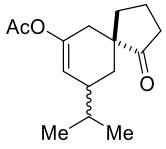
1-oxo-9-phenylspiro[4.5]dec-7-en-7-yl acetate (**5d**):



5d

Colorless oil, (21.7 mg, 0.074 mmol, 37% yield), inseparable, dr = 1: 1.1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 4H), 7.23 (t, *J* = 6.4 Hz, 6H), 5.56 (s, 1H), 5.44 (s, 1H), 3.70 (d, *J* = 2.8 Hz, 1H), 3.54 (s, 1H), 2.54 (d, *J* = 16.7 Hz, 1H), 2.31 (dd, *J* = 14.5, 7.9 Hz, 4H), 2.17 (s, 1H), 2.15 (s, 3H), 2.14 (s, 3H), 2.11 – 2.04 (m, 2H), 2.02 – 1.96 (m, 2H), 1.92-1.86 (m, 4H), 1.66-1.53 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 221.1, 220.7, 169.4, 169.3, 147.3, 146.7, 144.7, 144.2, 128.6, 128.5, 127.7, 127.5, 126.7, 126.5, 117.3, 117.1, 49.7, 48.2, 39.2, 38.4, 37.9, 37.7, 37.6, 37.1, 33.7, 33.6, 33.1, 21.1, 21.0, 19.0, 18.5. **HRMS ESI** Calcd for $C_{18}H_{20}O_3$ [M+Na]$^+$: 307.1305, Found: 307.1292. **IR** *v* (cm^{-1}): 2956, 2924, 1736, 1369, 1219, 702.

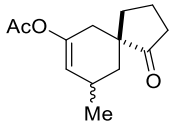
9-isopropyl-1-oxospiro[4.5]dec-7-en-7-yl acetate (**5e**):



5e

Colorless oil, (**5e-1**: 11.4 mg, 0.045 mmol, 23% yield; **5e-2**: 13.7 mg, 0.054 mmol, 27% yield), **5e-1**: **5e-2** = 1: 1.2;
5e-1: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.26 (s, 1H), 2.33 – 2.22 (m, 3H), 2.18 – 2.09 (m, 1H), 2.04 (d, *J* = 8.3 Hz, 3H), 2.02 – 1.96 (m, 1H), 1.94 – 1.79 (m, 3H), 1.78 – 1.72 (m, 1H), 1.60 (tt, *J* = 13.3, 6.7 Hz, 1H), 1.34 (dd, *J* = 20.2, 9.2 Hz, 2H), 0.85 (dd, *J* = 7.0, 1.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 221.8, 169.1, 146.7, 116.1, 49.1, 38.3, 37.5, 33.7, 33.5, 31.6, 31.0, 20.9, 19.2, 19.2, 18.8. **HRMS ESI** Calcd for $C_{15}H_{22}O_3$ [M+Na]$^+$: 273.1461, Found: 273.1450. **IR** *v* (cm^{-1}): 2960, 2935, 1756, 1736, 1323, 1217, 1126, 890.
5e-2: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.37 (s, 1H), 2.32-2.26 (m, 1H), 2.26 – 2.20 (m, 2H), 2.20 – 2.16 (m, 1H), 2.06 (s, 3H), 1.95 (ddd, *J* = 16.1, 14.8, 8.5 Hz, 2H), 1.90 – 1.85 (m, 1H), 1.85 – 1.81 (m, 2H), 1.72 (dd, *J* = 13.2, 5.1 Hz, 1H), 1.63 – 1.54 (m, 1H), 1.25 (dd, *J* = 13.5, 10.3 Hz, 1H), 0.86 (dd, *J* = 6.8, 4.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.1, 169.1, 145.6, 116.7, 47.5, 38.4, 37.8, 36.8, 33.1, 31.5, 31.2, 20.9, 19.5, 19.2, 18.1. **HRMS ESI** Calcd for $C_{15}H_{22}O_3$ [M+Na]$^+$: 273.1461, Found: 273.1451. **IR** *v* (cm^{-1}): 2958, 2872, 1753, 1737, 1693, 1219, 611.

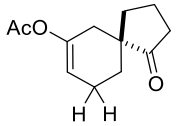
9-methyl-1-oxospiro[4.5]dec-7-en-7-yl acetate (**5f**):



5f

Colorless oil, (**5f**^{a}: 10 mg, 0.045 mmol, 22% yield; **5f**^{b}: 14.3 mg, 0.064 mmol, 32% yield), **5f**^{a}: **5f**^{b} = 1: 1.4;
5f^a: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.25 (s, 1H), 2.40 – 2.35 (m, 2H), 2.33-2.29 (m, 2H), 2.11 (s, 3H), 2.03 (dd, *J* = 9.5, 5.7 Hz, 1H), 1.98 – 1.91 (m, 2H), 1.90 – 1.85 (m, 1H), 1.80 (d, *J* = 16.6 Hz, 1H), 1.51 – 1.42 (m, 1H), 1.32 – 1.23 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 221.8, 169.4, 146.1, 119.1, 49.4, 37.6, 36.6, 33.7, 33.6, 27.2, 21.1, 21.0, 19.0. **HRMS ESI** Calcd for $C_{13}H_{18}O_3$ [M+Na]$^+$: 245.1148, Found: 245.1137. **IR** *v* (cm^{-1}): 2958, 2923, 1736, 1219, 738.
5f^b: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.33 (s, 1H), 2.56 – 2.45 (m, 1H), 2.32 – 2.26 (m, 2H), 2.22-2.17(m, 2H), 2.11 (s, 3H), 2.08 – 2.00 (m, 2H), 1.89 (dt, *J* = 12.7, 7.5 Hz, 4H), 1.19 (dd, *J* = 13.7, 8.5 Hz, 1H), 1.04 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.7, 169.4, 145.2, 119.5, 48.0, 37.9, 37.0, 36.4, 32.9, 27.0, 21.2, 21.0, 18.5. **HRMS ESI** Calcd for $C_{13}H_{18}O_3$ [M+Na]$^+$: 245.1148, Found: 245.1139. **IR** *v* (cm^{-1}): 2957, 2923, 1755, 1737, 1220, 736.

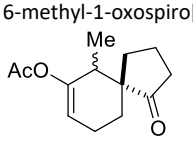
1-oxospiro[4.5]dec-7-en-7-yl acetate (**5g**):



5g

Colorless oil, (20 mg, 0.096 mmol, 48% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.42 – 5.36 (m, 1H), 2.37 (d, *J* = 16.7 Hz, 1H), 2.34 – 2.27 (m, 2H), 2.22 (s, 1H), 2.11 (s, 3H), 1.95 (m, 4H), 1.85 (t, *J* = 11.7 Hz, 2H), 1.69 – 1.61 (m, 1H), 1.45 – 1.39 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 221.7, 169.4, 146.4, 113.0, 48.5, 37.5, 33.6, 27.3, 21.0, 20.8, 18.8. **HRMS ESI** Calcd for $C_{12}H_{16}O_3$ [M+Na]$^+$: 231.0992, Found: 231.0982. **IR** *v* (cm^{-1}): 2923, 1752, 1737, 1219, 737.

6-methyl-1-oxospiro[4.5]dec-7-en-7-yl acetate (**5h**):



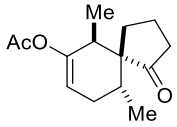
5h

Colorless oil, (**5h**^{a}: 5.7 mg, 0.026 mmol, 13% yield; **5h**^{b}: 10.3 mg, 0.046 mmol, 23% yield), **5h**^{a}: **5h**^{b} = 1: 1.8; $CHCl_3$ was used as the solvent instead of DCE after Castro-Stephens coupling.

5h^{a}: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.35 – 5.33 (m, 1H), 2.38 – 2.31 (m, 2H), 2.31 – 2.27 (m, 1H), 2.25 – 2.20 (m, 1H), 2.19 – 2.14 (m, 1H), 2.13 (s, 3H), 2.11 – 2.06 (m, 1H), 2.00 – 1.96 (m, 1H), 1.96 – 1.89 (m, 2H), 1.72 – 1.64 (m, 1H), 1.25-1.20 (m, 1H), 0.96 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.9, 169.8, 150.2, 113.3, 51.6, 37.8, 35.7, 34.4, 24.2, 21.1, 20.8, 18.0, 14.7. **HRMS ESI** Calcd for $C_{13}H_{18}O_3$ [M+Na]$^{+}$: 245.1148, Found: 245.1146. **IR** *v* (cm-1): 2965, 2939, 1752, 1734, 1219, 1092, 917, 733.

5h^{b}: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.31 (dd, *J* = 6.2, 3.7 Hz, 1H), 2.91 – 2.84 (m, 1H), 2.45 – 2.35 (m, 1H), 2.19 (ddd, *J* = 6.9, 6.2, 2.9 Hz, 3H), 2.12 (s, 3H), 2.00 – 1.93 (m, 1H), 1.92 – 1.83 (m, 2H), 1.82 – 1.74 (m, 1H), 1.58 – 1.53 (m, 2H), 0.80 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 221.7, 169.4, 149.6, 113.0, 52.3, 37.9, 35.9, 28.3, 27.9, 20.9, 20.7, 18.8, 12.3. **HRMS ESI** Calcd for $C_{13}H_{18}O_3$ [M+Na]$^{+}$: 245.1148, Found: 245.1140. **IR** *v* (cm^{-1}): 2964, 1752, 1734, 1219, 1007, 804.

(5*S*,6*R*,10*S*)-6,10-dimethyl-1-oxospiro[4.5]dec-7-en-7-yl acetate (**5i**):

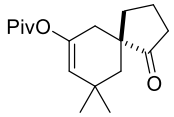


5i

Colorless oil, (26.5 mg, 0.11 mmol, 56% yield), dr = 1: 1.2: 4; $AuCl_3$ (10 mol%) in 2 mL HFB (hexafluorobenzene) was used instead of the combination of $AuPPh_3Cl$ and $AgNTf_2$ after Castro-Stephens coupling

Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.24 (dt, J = 4.9, 2.4 Hz, 1H), 2.95 – 2.91 (m, 1H), 2.52 – 2.46 (m, 1H), 2.41 – 2.34 (m, 1H), 2.19 – 2.17 (m, 1H), 2.13 (s, 3H), 2.04 – 1.98 (m, 1H), 1.97 – 1.91 (m, 2H), 1.90 – 1.86 (m, 1H), 1.86 – 1.84 (m, 1H), 1.84 – 1.81 (m, 1H), 0.99 (d, J = 7.0 Hz, 3H), 0.81 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 219.9, 169.4, 148.9, 111.5, 54.9, 38.0, 31.4, 30.6, 29.2, 28.9, 20.7, 18.3, 14.8, 11.9. **HRMS ESI** Calcd for $C_{14}H_{20}O_3$ [M+Na]$^{+}$: 259.1305, Found: 259.1301. **IR** *v* (cm^{-1}): 2919, 1736, 1656, 1100, 785.

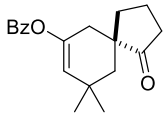
9,9-dimethyl-1-oxospiro[4.5]dec-7-en-7-yl pivalate (**5j**):



5j

Colorless oil, (29.5 mg, 0.11 mmol, 53% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.17 (d, *J* = 1.8 Hz, 1H), 2.35 – 2.29 (m, 2H), 2.26 – 2.16 (m, 1H), 2.08 (dd, *J* = 16.3, 1.6 Hz, 1H), 2.01 (ddd, *J* = 11.4, 7.5, 4.4 Hz, 1H), 1.89 – 1.83 (m, 2H), 1.80 (dd, *J* = 15.7, 9.6 Hz, 2H), 1.30 (d, *J* = 13.9 Hz, 1H), 1.23 (s, 9H), 1.09 (d, *J* = 10.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 222.4, 177.3, 144.5, 123.0, 49.7, 42.4, 38.8, 37.3, 35.5, 32.7, 32.5, 32.5, 29.5, 27.0, 19.5. **HRMS ESI** Calcd for $C_{17}H_{26}O_3$ [M+Na]$^{+}$: 301.1774, Found: 301.1759. **IR** *v* (cm^{-1}): 2959, 2924, 1739, 1131, 856, 547.

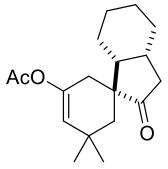
9,9-dimethyl-1-oxospiro[4.5]dec-7-en-7-yl benzoate (**5k**):



5k

Colorless oil, (30.3 mg, 0.10 mmol, 50% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 8.06 (m, 2H), 7.61 – 7.58 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.35 (d, *J* = 1.8 Hz, 1H), 2.41 (ddd, *J* = 7.0, 5.1, 3.3 Hz, 1H), 2.38 – 2.29 (m, 1H), 2.27 (d, *J* = 9.8 Hz, 1H), 2.22 (dd, *J* = 10.1, 8.6 Hz, 1H), 2.10 – 2.06 (m, 1H), 2.03 (td, *J* = 5.9, 2.4 Hz, 1H), 1.90 (dd, *J* = 10.9, 9.5 Hz, 2H), 1.86 – 1.81 (m, 1H), 1.35 (d, *J* = 13.9 Hz, 1H), 1.14 (d, *J* = 10.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 222.3, 165.2, 144.5, 133.3, 129.9, 129.8, 128.4, 123.6, 49.7, 42.5, 37.3, 35.6, 33.0, 32.6, 32.4, 29.6, 19.5. **HRMS ESI** Calcd for $C_{19}H_{22}O_3$ [M+Na]$^{+}$: 321.1461, Found: 321.1448. **IR** *v* (cm^{-1}): 2958, 2924, 1734, 1272, 115, 734, 710.

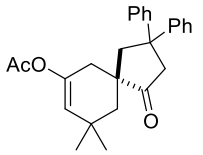
5,5-dimethyl-2'-oxo-2',3',3a',4',5',6',7',7a'-octahydrospiro[cyclohexane-1,1'-inden]-3-en-3-yl acetate (**5l**):



5l

Colorless oil, (27.5 mg, 0.094 mmol, 47% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.20 (d, *J* = 2.0 Hz, 1H), 2.66 (s, 1H), 2.23 – 2.19 (m, 3H), 2.10 (s, 3H), 1.96 (dd, *J* = 16.5, 2.5 Hz, 1H), 1.79 (d, *J* = 12.6 Hz, 2H), 1.75 – 1.59 (m, 4H), 1.54 (d, *J* = 13.2 Hz, 1H), 1.46 (d, *J* = 14.7 Hz, 1H), 1.24 (dddd, *J* = 15.8, 13.0, 7.8, 4.5 Hz, 2H), 1.13 – 1.04 (m, 6H), 0.75 (qd, *J* = 13.1, 3.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 221.5, 169.4, 143.5, 123.6, 56.7, 42.6, 36.9, 35.4, 32.5, 32.4, 32.0, 31.0, 30.7, 26.8, 25.1, 25.0, 21.0, 19.9. **HRMS ESI** Calcd for $C_{18}H_{26}O_3$ [M+Na]$^{+}$: 313.1774, Found: 313.1764. **IR** *v* (cm^{-1}): 2956, 2923, 1737, 1218, 740, 704.

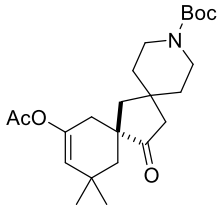
9,9-dimethyl-1-oxo-3,3-diphenylspiro[4.5]dec-7-en-7-yl acetate (**5m**):



5m

Colorless oil, (42.7 mg, 0.11 mmol, 55% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (s, 4H), 7.27 – 7.11 (m, 6H), 5.17 (s, 1H), 3.44 (d, *J* = 17.1 Hz, 1H), 3.17 (d, *J* = 12.9 Hz, 1H), 2.87 (dd, *J* = 32.0, 15.1 Hz, 2H), 2.12 (d, *J* = 16.7 Hz, 1H), 1.96 (s, 3H), 1.65 (d, *J* = 13.7 Hz, 1H), 1.43 – 1.28 (m, 2H), 1.16 (s, 3H), 1.03 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.0, 168.9, 148.3, 145.6, 144.3, 128.6, 127.0, 126.5, 126.4, 126.3, 123.3, 50.1, 49.6, 49.5, 47.8, 45.2, 35.1, 32.8, 32.5, 29.8, 20.8. **HRMS ESI** Calcd for $C_{26}H_{28}O_3$ $[M+Na]^+$: 411.1931, Found: 411.1930. **IR** *v* (cm^{-1}): 2957, 1738, 1220, 1209, 1110, 702.

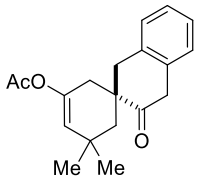
tert-butyl 12-acetoxy-10,10-dimethyl-14-oxo-3-azadispiro[5.1.5^8.2^6]pentadec-11-ene-3-carboxylate (**5n**):



5n

Colorless oil, (40 mg, 0.098 mmol, 49% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.24 (s, 1H), 3.63 (s, 2H), 3.21 – 3.16 (m, 2H), 2.42 – 2.18 (m, 4H), 2.15 – 2.04 (m, 3H), 1.89 (t, *J* = 14.1 Hz, 2H), 1.63 (dd, *J* = 48.2, 14.8 Hz, 6H), 1.46 (s, 9H), 1.10 (d, *J* = 32.2 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 221.2, 169.5, 154.7, 144.2, 123.5, 79.5, 49.5, 48.6, 46.9, 45.3, 36.3, 36.0, 32.8, 32.4, 28.4, 21.1. **HRMS ESI** Calcd for $C_{23}H_{35}NO_5$ $[M+Na]^+$: 428.2407, Found: 428.2390. **IR** *v* (cm^{-1}): 2927, 1685, 1265, 740, 705.

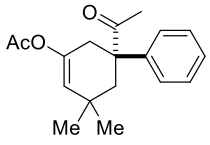
5,5-dimethyl-3'-oxo-3',4'-dihydro-1'*H*-spiro[cyclohexane-1,2'-naphthalen]-3-en-3-yl acetate (**5o**):



5o

Colorless oil, (31.6 mg, 0.106 mmol, 53% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (dt, *J* = 9.2, 4.0 Hz, 3H), 7.13 – 7.11 (m, 1H), 5.20 (s, 1H), 3.68 (dd, *J* = 80.0, 19.5 Hz, 2H), 3.11 (dd, *J* = 77.4, 15.7 Hz, 2H), 2.62 (dd, *J* = 16.7, 1.5 Hz, 1H), 2.12 (s, 3H), 1.92 (d, *J* = 16.7 Hz, 1H), 1.76 (d, *J* = 14.1 Hz, 1H), 1.53 (d, *J* = 14.1 Hz, 1H), 1.08 (s, 3H), 0.99 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 211.8, 169.3, 144.6, 134.8, 133.0, 128.8, 127.7, 126.9, 126.8, 122.1, 48.2, 43.5, 42.3, 41.0, 33.4, 32.5, 31.4, 30.7, 21.0. **HRMS ESI** Calcd for $C_{19}H_{22}O_3$ $[M+Na]^+$: 321.1461, Found: 321.1461. **IR** *v* (cm^{-1}): 2958, 1751, 1713, 1364, 1214, 1112, 749.

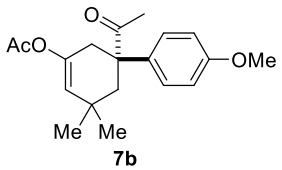
1-acetyl-5,5-dimethyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl acetate (**7a**):



7a

Colorless oil, (28.7 mg, 0.10 mmol, 50% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.27 – 7.24 (m, 1H), 5.18 (s, 1H), 2.71 (dt, *J* = 37.3, 8.9 Hz, 2H), 2.22 (d, *J* = 14.1 Hz, 1H), 2.18 (s, 3H), 2.13 (d, *J* = 14.2 Hz, 1H), 1.88 (s, 3H), 1.02 (s, 3H), 0.64 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.6, 169.5, 143.7, 141.4, 128.9, 127.2, 126.5, 123.3, 55.8, 42.8, 33.2, 32.3, 31.1, 29.7, 25.4, 21.1. **HRMS ESI** Calcd for $C_{18}H_{22}O_3$ $[M+Na]^+$: 309.1461, Found: 309.1447. **IR** *v* (cm^{-1}): 2924, 2853, 1682, 1219, 736, 701.

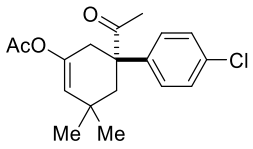
1-acetyl-4'-methoxy-5,5-dimethyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl acetate (**7b**):



7b

Colorless oil, (33 mg, 0.104 mmol, 52% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 10.2, 5.8 Hz, 1H), 6.94-6.94 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.80 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.18 (s, 1H), 3.81 (s, 3H), 2.67 (s, 2H), 2.18 (s, 3H), 2.20 – 2.10 (m, 2H), 1.89 (s, 3H), 1.01 (s, 3H), 0.65 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.4, 169.5, 160.1, 143.7, 143.0, 129.8, 123.3, 119.0, 112.8, 112.2, 55.8, 55.3, 42.7, 33.1, 32.3, 31.2, 29.6, 25.4, 21.1. **HRMS ESI** Calcd for $C_{19}H_{24}O_4$ $[M+Na]^+$: 339.1567, Found: 339.1553. **IR** *v* (cm^{-1}): 2925, 1752, 1706, 1513, 1254, 739.

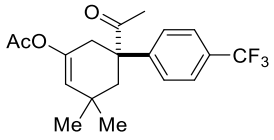
1-acetyl-4'-chloro-5,5-dimethyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl acetate (**7c**):



7c

Colorless oil, (39.8 mg, 0.124 mmol, 62% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 5.19 (s, 1H), 2.67 (p, *J* = 16.9 Hz, 2H), 2.19 (s, 3H), 2.13 (d, *J* = 19.6 Hz, 2H), 1.88 (s, 3H), 1.01 (s, 3H), 0.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.0, 169.5, 143.3, 139.9, 133.2, 129.0, 128.1, 123.6, 55.5, 42.8, 33.0, 32.3, 31.3, 29.6, 25.4, 21.1. **HRMS ESI** Calcd for $C_{18}H_{21}ClO_3$ [M+Na]$^+$: 343.1071, Found: 343.1060. **IR** *v* (cm^{-1}): 2923, 1710, 1467, 1219, 1097, 738.

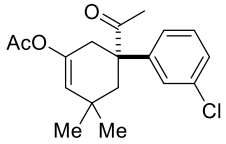
1-acetyl-5,5-dimethyl-4'-(trifluoromethyl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl acetate (**7d**):



7d

Colorless oil, (34.7 mg, 0.098 mmol, 49% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 5.21 (s, 1H), 2.76 – 2.67 (m, 2H), 2.23 (d, *J* = 14.2 Hz, 1H), 2.20 (s, 3H), 2.14 (d, *J* = 14.2 Hz, 1H), 1.89 (s, 3H), 1.03 (s, 3H), 0.60 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.6, 169.5, 145.5, 143.2, 129.5 (q, $^2J_{FC}$ = 33 Hz), 127.2, 125.9, 125.8, 124.0 (q, $^1J_{FC}$ = 271 Hz), 123.8, 56.0, 43.0, 32.9, 32.3, 31.3, 29.5, 25.5, 21.1. **HRMS ESI** Calcd for $C_{19}H_{21}F_3O_3$ [M+Na]$^+$: 377.1335, Found: 377.1336. **IR** *v* (cm^{-1}): 2924, 1871, 1752, 1710, 1328, 1126, 608.

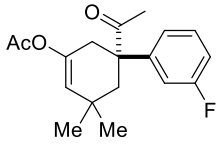
1-acetyl-3'-chloro-5,5-dimethyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl acetate (**7e**):



7e

Colorless oil, (32.7 mg, 0.102 mmol, 51% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.23 (dd, *J* = 12.9, 4.5 Hz, 2H), 5.20 (s, 1H), 2.68 (q, *J* = 16.9 Hz, 2H), 2.22 (s, 1H), 2.19 (s, 3H), 2.10 (d, J = 14.1 Hz, 1H), 1.91 (s, 3H), 1.02 (s, 3H), 0.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.9, 169.6, 143.5, 143.3, 134.9, 130.1, 127.5, 126.8, 124.8, 123.5, 55.7, 42.7, 33.0, 32.3, 31.0, 29.7, 25.5, 21.1. **HRMS ESI** Calcd for $C_{18}H_{21}ClO_3$ [M+Na]$^+$: 343.1071, Found: 343.1071. **IR** *v* (cm-1): 2957, 1754, 1710, 1219, 1207, 1100, 699.

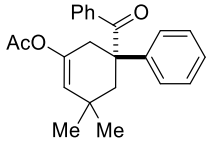
1-acetyl-3'-fluoro-5,5-dimethyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl acetate (**7f**):



7f

Colorless oil, (29.2 mg, 0.096 mmol, 48% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 14.4, 8.1 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.97 (t, *J* = 8.1 Hz, 1H), 5.19 (s, 1H), 2.68 (q, *J* = 17.0 Hz, 2H), 2.18 (s, 3H), 2.17 (s, 1H), 2.10 (d, *J* = 14.1 Hz, 1H), 1.89 (s, 3H), 1.02 (s, 3H), 0.64 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.8, 169.5, 162.3 (d, $^1J_{FC}$ = 246 Hz), 144.1 (d, $^3J_{FC}$ = 7 Hz), 143.4, 130.5 (d, $^3J_{FC}$ = 8 Hz), 123.5, 122.4 (d, $^4J_{FC}$ = 3 Hz), 114.3 (d, $^2J_{FC}$ = 21 Hz), 113.9 (d, $^2J_{FC}$ = 22 Hz) 55.8, 42.8, 33.1, 32.3, 31.2, 29.6, 25.4, 21.1. **HRMS ESI** Calcd for $C_{18}H_{21}FO_3$ [M+Na]$^+$: 327.1367, Found: 327.1360. **IR** *v* (cm^{-1}): 2923, 2852, 1754, 1710, 1220, 735.

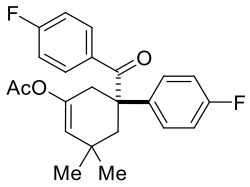
1-benzoyl-5,5-dimethyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl acetate (**7g**):



7g

Colorless oil, (34.8 mg, 0.10 mmol, 50% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.4 Hz, 4H), 7.36 (dd, *J* = 8.2, 7.0 Hz, 3H), 7.29 (s, 1H), 7.23 (t, *J* = 7.7 Hz, 2H), 5.21 (s, 1H), 2.80 – 2.68 (m, 2H), 2.37 (dd, *J* = 34.1, 14.0 Hz, 2H), 2.15 (s, 3H), 0.90 (s, 3H), 0.61 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.4, 169.5, 144.0, 142.0, 136.7, 131.7, 129.6, 129.1, 128.1, 127.2, 126.7, 123.3, 54.7, 44.8, 35.9, 32.4, 31.5, 29.3, 21.1. **HRMS ESI** Calcd for $C_{23}H_{24}O_3$ [M+Na]$^+$: 371.1618, Found: 371.1617. **IR** *v* (cm^{-1}): 2922, 1632, 1467, 1219, 735.

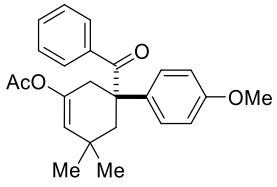
4'-fluoro-1-(4-fluorobenzoyl)-5,5-dimethyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl acetate (**7h**):



7h

Colorless oil, (26.9 mg, 0.07 mmol, 35% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.46 – 7.43 (m, 2H), 7.09 – 7.05 (m, 2H), 6.94 – 6.90 (m, 2H), 5.22 (s, 1H), 2.77 – 2.64 (m, 2H), 2.37 – 2.30 (m, 2H), 2.16 (s, 3H), 0.89 (s, 3H), 0.61 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.5, 169.6, 164.6 (d, $^1J_{FC}$ = 254 Hz), 161.9 (d, $^1J_{FC}$ = 247 Hz), 143.6, 137.8 (d, $^4J_{FC}$ = 3 Hz), 132.5 (d, $^4J_{FC}$ = 3 Hz), 132.2 (d, $^3J_{FC}$ = 9 Hz), 128.3 (d, $^3J_{FC}$ = 8 Hz), 123.4, 116.2 (d, $^2J_{FC}$ = 21 Hz), 115.3 (d, $^2J_{FC}$ = 22 Hz), 54.1, 44.9, 36.0, 32.3, 31.5, 29.3, 21.1. **HRMS ESI** Calcd for $C_{23}H_{22}F_2O_3$ [M+Na]$^+$: 407.1429, Found: 407.1424. **IR** *v* (cm^{-1}): 2957, 1751, 1678, 1235, 837, 739.

1-benzoyl-4'-methoxy-5,5-dimethyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl acetate (**7i**):

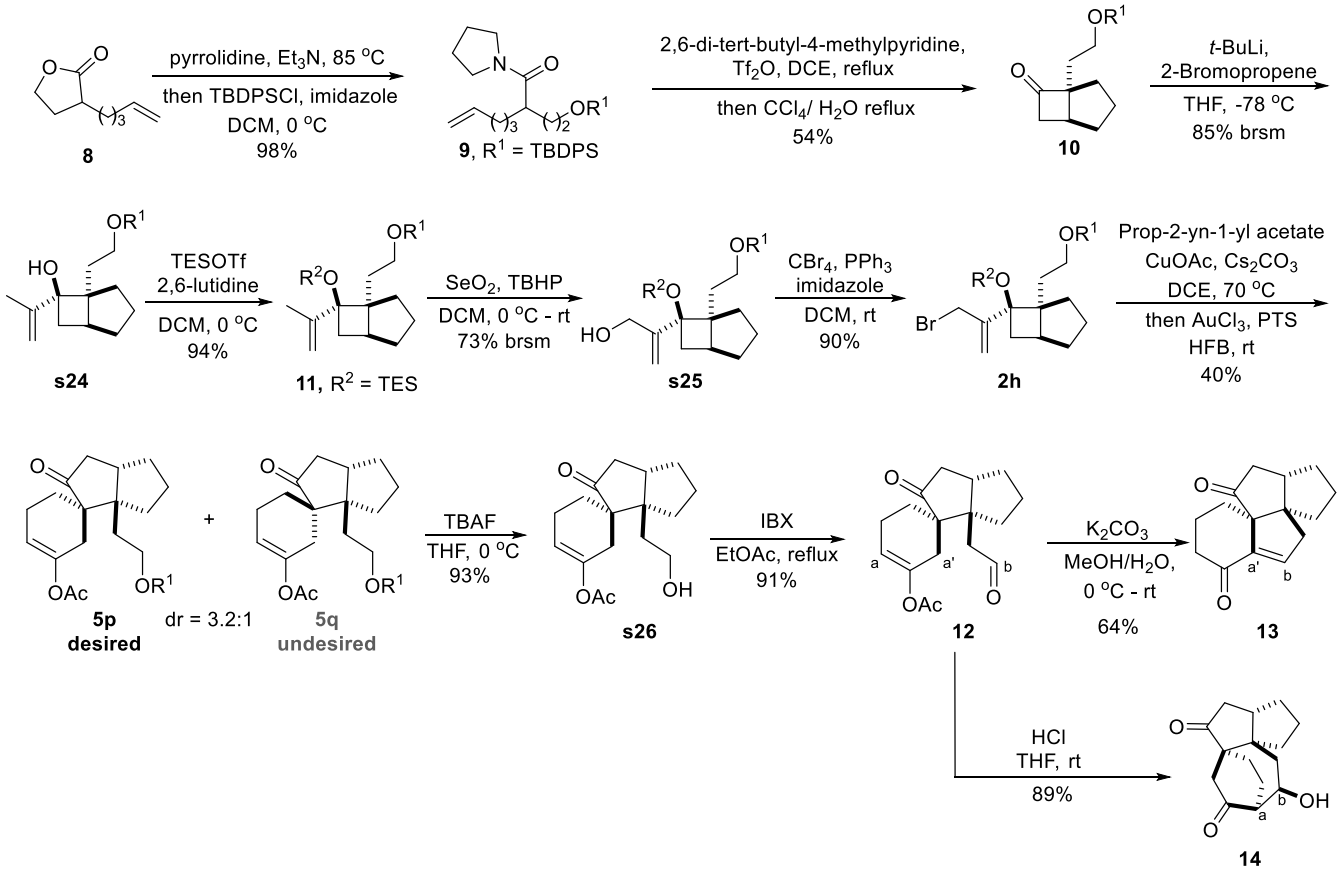


7i

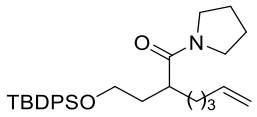
Colorless oil, (22.7 mg, 0.06 mmol, 30% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.40 – 7.35 (m, 3H), 7.23 (t, *J* = 7.7 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 5.20 (s, 1H), 3.81 (s, 3H), 2.70 (q, *J* = 17.2 Hz, 2H), 2.32 (dd, *J* = 40.5, 14.0 Hz, 2H), 2.15 (s, 3H), 0.90 (s, 3H), 0.61 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.7, 169.5, 158.7, 148.6, 143.9, 136.9, 133.7, 131.6, 129.6, 128.1, 127.9, 123.4, 114.7, 114.4, 58.5, 55.2, 55.1, 54.0, 46.5, 44.8, 44.4, 35.9, 34.8, 32.4, 32.1, 31.7, 30.5, 29.2, 21.7, 21.1. **HRMS ESI** Calcd for $C_{24}H_{26}O_4$ [M+Na]$^+$: 401.1723, Found: 401.1731. **IR** *v* (cm^{-1}): 2956, 2925, 1752, 1675, 1253, 710.

7 Synthetic utility to the tetracyclic skeleton of waihoensene

7.1 The synthesis of the tetracyclic skeleton **13** of waihoensene



2-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-1-(pyrrolidin-1-yl)hept-6-en-1-one (**9**):

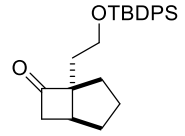


9

A solution of **8**[13] (444 mg, 2.88 mmol, 1 eq.), pyrrolidine (473 μL, 5.76 mmol, 2 eq.) and Et_3N (2.0 mL, 14.39 mmol, 5 eq.) were heated to 85 °C for 3.5 hours. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* to remove the solvent. Then the residue was dissolved in DCM (10 mL), imidazole (68.1 mg, 4.32 mmol, 1.5 eq.) and TBDPSCl (823 μL, 3.17 mmol, 1.1 eq.) were added. The reaction mixture was stirred at 0 °C for 10 mins, and then quenched by saturated NH_4Cl aqueous solution, extracted with DCM. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography (petroleum ether: EtOAc = 4: 1) to give **9** (1.32 g, 98% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 4H), 7.48 – 7.34 (m, 6H), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07 – 4.90 (m, 2H), 3.71 (dt, *J* = 10.5, 5.3 Hz, 1H), 3.63 (ddd, *J* = 16.7, 10.2, 5.7 Hz, 2H), 3.45 (ddd, *J* = 14.1, 11.8, 6.9 Hz, 3H), 2.92 – 2.81 (m, 1H), 2.04 (t, *J* = 6.3 Hz, 2H), 1.96 – 1.76 (m, 5H), 1.74 – 1.60 (m, 2H), 1.52 – 1.30 (m, 3H), 1.07 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.4, 138.6, 135.4, 135.4, 133.7, 133.6, 129.6, 129.5, 127.6, 114.5, 61.7, 46.5, 45.4, 39.7, 35.4, 33.8, 32.0, 26.9, 26.8, 26.0, 24.3, 19.1. **HRMS ESI** Calcd for $C_{29}H_{41}NO_2Si$ $[M+Na]^+$: 486.2799, Found: 486.2780. **IR** *v* (cm^{-1}): 2954, 1640, 1429, 1111, 703, 506.

(1*S*,5*R*)-5-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)bicyclo[3.2.0]heptan-6-one (**10**):

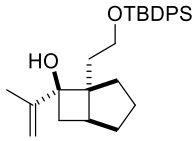


10

To a stirred solution of **9** (662.8 mg, 1.43 mmol, 1 eq.) in DCE (25 mL) were added 2,6-di-*tert*-butyl-4-methylpyridine (440.3 mg, 2.14 mmol, 1.5 eq.) and Tf_2O (288.5 μL, 1.72 mmol, 1.2 eq.) via an addition funnel (dissolved in 5 mL DCE) about 30 mins. The reaction solution was refluxed overnight and concentrated under vacuum, then to the mixture were added the mixed solvent of CCl_4 (20 mL) and H_2O (20 mL). The reaction mixture was refluxed overnight. Extract with DCM, the combined organic layers was washed with brine, and dried over Na_2SO_4, concentrated under vacuum. The crude product was purified by flash chromatography (petroleum ether: EtOAc = 20: 1) to give **10** (304.9 mg, 54% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 4H), 7.46 – 7.27 (m, 6H), 3.83 – 3.72 (m, 2H), 3.20 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.73 (m, 1H), 2.42 (dd, *J* = 18.4, 4.4 Hz, 1H), 2.09 – 1.93 (m, 2H), 1.90 – 1.75 (m, 4H), 1.75 – 1.58 (m, 1H), 1.49 – 1.33 (m, 1H), 1.06 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 217.2, 135.5, 135.5, 133.7, 133.5, 129.6, 127.6, 73.7, 61.2, 49.4, 35.8, 35.6, 34.0, 32.7, 26.8, 24.7, 19.1. **HRMS ESI** Calcd for $C_{25}H_{32}O_2Si$ $[M+Na]^+$: 415.2064, Found: 415.2050. **IR** *v* (cm-1): 2931, 1771, 1111, 738, 703, 505.

(1*S*,5*R*,6*S*)-5-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-6-(prop-1-en-2-yl)bicyclo[3.2.0]heptan-6-ol (**s24**):

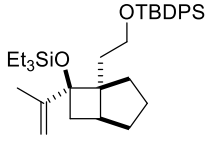


s24

Under argon atmosphere, to a round-bottom flask were charged with 2-bromopropene (148 μL, 1.67 mmol, 1.2 eq.) and anhydrous THF (10 mL). The reaction was cooled to -78 °C, *t*-BuLi (1.3 M, 2.44 mL, 3.17 mmol, 2.3 eq.) was then added dropwise, allowing the reaction mixture to stir for 15 mins. A solution of **10** (546.1 mg, 1.39 mmol, 1 eq.) in THF (5 mL) was added. The reaction was stirred for 3 hours at -78 °C. The reaction was quenched by saturated NH_4Cl aqueous solution, extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (petroleum ether: EtOAc = 20: 1) to give **s24** (444.9 mg, 74% yield, 89% brsm) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 4H), 7.48 – 7.40 (m, 6H), 5.00 (s, 1H), 4.98 (s, 1H), 3.72 – 3.54 (m, 2H), 2.58 (dd, *J* = 13.3, 9.1 Hz, 1H), 2.09 (ddd, *J* = 21.6, 10.8, 4.6 Hz, 2H), 1.98 – 1.83 (m, 2H), 1.82 (s, 3H), 1.80 – 1.71 (m, 2H), 1.65 (s, 1H), 1.52 – 1.44 (m, 2H), 1.40 (dd, *J* = 13.2, 7.0 Hz, 2H), 1.08 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 135.5, 134.0, 129.5, 127.5, 111.4, 77.3, 61.3, 56.0, 38.1, 36.4, 36.0, 32.2, 30.8, 26.8, 26.0, 20.4, 19.1. **HRMS ESI** Calcd for $C_{28}H_{38}O_2Si$ $[M+Na]^+$: 457.2533, Found: 457.2544. **IR** *v* (cm^{-1}): 2931, 1428, 1111, 1084, 703, 506.

tert-butyldiphenyl(2-((1*R*,5*S*,7*S*)-7-(prop-1-en-2-yl)-7-((triethylsilyl)oxy)bicyclo[3.2.0]heptan-1-yl)ethoxy)silane (**11**):



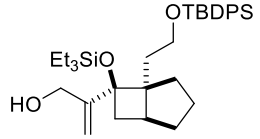
11

To a stirred solution of **s24** (527.6 mg, 1.21 mmol, 1 eq.) in anhydrous DCM (10 mL) was added TESOTf (329.3 μL, 1.46 mmol, 1.2 eq.) and 2,6-lutidine (212.1 μL, 1.82 mmol, 1.5 eq.) at 0 °C. The reaction was stirred for 5 mins, and then quenched by saturated NH_4Cl aqueous solution, extracted with DCM. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (petroleum ether as elution solvent) to give **11** (624.1 mg, 94% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.7, 1.4 Hz, 4H), 7.46 – 7.38 (m, 6H), 4.94 (s, 2H), 3.68 – 3.55 (m, 2H), 2.51 (dd, *J* = 12.8, 8.7 Hz, 1H), 2.26 (ddd, *J* = 13.4, 8.3, 1.5 Hz, 1H), 1.95 (dd, *J* = 13.5, 7.8 Hz, 1H), 1.90 – 1.75 (m, 2H), 1.74 (s, 3H), 1.73 – 1.67 (m, 2H), 1.49 (dd, *J* = 12.9, 7.6 Hz, 1H), 1.45 – 1.27 (m, 3H), 1.06 (s, 9H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.3, 135.6, 134.1, 129.5, 127.5,

110.8, 79.0, 61.6, 57.6, 38.2, 36.6, 35.4, 32.3, 30.1, 26.9, 25.8, 20.8, 19.1, 7.1, 6.2. **HRMS ESI** Calcd for $C_{34}H_{52}O_2Si_2$ [M+Na]$^+$: 571.3398, Found: 571.3388. **IR** *v* (cm^{-1}): 2954, 1428, 1112, 1084, 702.

2-((1*S*,5*R*,6*R*)-5-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-6-((triethylsilyl)oxy)bicyclo[3.2.0]heptan-6-yl)prop-2-en-1-ol (**s25**):

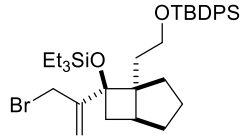


s25

A stirred solution of **11** (77.4 mg, 0.14 mmol, 1 eq.), TBHP (5.5 M, 102.5 μL, 0.56 mmol, 4 eq.) and SeO_2 (7.8 mg, 0.07 mmol, 0.5 eq.) in anhydrous DCM (1.5 mL) was stirred for 2 days at rt, and then quenched by saturated $Na_2S_2O_3$ aqueous solution, extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (petroleum ether: EtOAc = 20: 1) to give **s25** (32.7 mg, 41% yield, 73% brsm) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 4H), 7.47 – 7.39 (m, 6H), 5.27 (s, 1H), 5.07 (s, 1H), 4.15 (q, *J* = 15.2 Hz, 2H), 3.68 – 3.58 (m, 2H), 2.52 (dd, *J* = 12.9, 8.8 Hz, 1H), 2.24 (dd, *J* = 12.2, 8.6 Hz, 1H), 1.97 (dd, *J* = 12.3, 7.2 Hz, 1H), 1.82 – 1.67 (m, 4H), 1.57 (dd, *J* = 12.9, 7.6 Hz, 1H), 1.51 – 1.27 (m, 4H), 1.06 (s, 9H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 7.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 135.6, 135.6, 134.0, 133.9, 129.5, 129.5, 127.6, 108.7, 78.8, 64.0, 61.5, 58.0, 38.2, 36.7, 35.9, 32.3, 29.7, 26.8, 25.7, 19.0, 7.0, 6.2. **HRMS ESI** Calcd for $C_{34}H_{52}O_3Si_2$ [M+Na]$^+$: 587.3347, Found: 587.3339. **IR** *v* (cm^{-1}): 2954, 1471, 1112, 738, 702.

(((1*S*,5*R*,6*R*)-6-(3-bromoprop-1-en-2-yl)-5-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)bicyclo[3.2.0]heptan-6-yl)oxy)triethylsilane (**2h**):

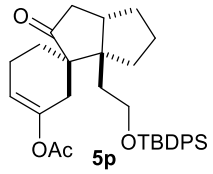


2h

In a reaction tube, **s25** (442.7 mg, 0.78 mmol, 1 eq.) was added. A solution of CBr_4 (181.9 mg, 0.55 mmol, 0.7 eq.), PPh_3 (246.6 mg, 0.94 mmol, 1.2 eq.), imidazole (64.0 mg, 0.94 mmol, 1.2 eq.) in anhydrous DCM (5 mL) was added. The reaction was stirred overnight at rt. CBr_4 (91 mg, 0.28 mmol, 0.35 eq.), PPh_3 (123.3 mg, 0.47 mmol, 0.6 eq.), imidazole (32.0 mg, 0.47 mmol, 0.6 eq.) were added. Until **s25** disappeared completely, the reaction was quenched by saturated $NaHCO_3$ aqueous solution, extracted with DCM. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (petroleum ether as elution solvent) to give **2h** (445.1 mg, 90% yield) as a colorless oil.

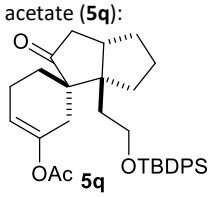
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 4H), 7.46 – 7.38 (m, 6H), 5.53 (s, 1H), 5.33 (s, 1H), 4.08 (d, *J* = 12.3 Hz, 1H), 3.88 (d, *J* = 12.3 Hz, 1H), 3.69 – 3.45 (m, 2H), 2.61 (dd, *J* = 13.1, 8.7 Hz, 1H), 2.29 – 2.14 (m, 1H), 1.96 (dd, *J* = 12.7, 7.4 Hz, 1H), 1.89 – 1.68 (m, 2H), 1.62 (tdd, *J* = 17.4, 7.9, 5.4 Hz, 3H), 1.51 – 1.23 (m, 3H), 1.04 (s, 9H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.9, 135.6, 134.0, 134.0, 129.5, 127.6, 116.4, 79.0, 61.2, 57.9, 38.7, 36.9, 35.6, 33.1, 32.3, 30.0, 26.8, 25.6, 19.1, 7.0, 6.2. **HRMS ESI** Calcd for $C_{34}H_{51}BrO_2Si_2$ [M+Na]$^+$: 649.2503, Found: 649.2498; [M+Na]$^+$: 651.2483, Found: 651.2477. **IR** *v* (cm^{-1}): 2954, 1428, 1227, 1110, 739, 702.

(1*R*,3a'*S*,6a'*R*)-6a'-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-2'-oxo-3',3a',4',5',6',6a'-hexahydro-2'H-spiro[cyclohexane-1,1'-pentalen]-3-en-3-yl acetate (**5p**):



5p

(1*S*,3a'*S*,6a'*R*)-6a'-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-2'-oxo-3',3a',4',5',6',6a'-hexahydro-2'*H*-spiro[cyclohexane-1,1'-pentalen]-3-en-3-yl acetate (**5q**):



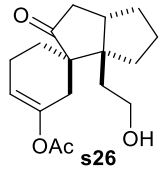
5q

To a stirred solution of **2h** (220.7 mg, 0.35 mmol, 1 eq.) in DCE (4 mL) were added **1g** (86 mg, 0.88 mmol, 2.5 eq.) and CuOAc (12.9 mg, 0.11 mmol, 0.3 eq.) and Cs_2CO_3 (57.3 mg, 0.18 mmol, 0.5 eq.) at rt. The reaction was moved to 70 °C for 9 hours until **2h** disappeared. After a quick filtration of the reaction mixture through a celite pad, the filtrate was concentrated under vacuum, hexafluorobenzene (4 mL), $AuCl_3$ (10.7 mg, 0.04 mmol, 0.1 eq.) and PTS (3 mg, 0.02 mmol, 0.05 eq.) were added at rt. The reaction mixture was stirred for 15 hours, and then concentrated. The crude product was purified by flash chromatography (petroleum ether: EtOAc = 6: 1) to give **5p** (17.7 mg, 9% yield) and **5q** (56.7 mg, 30.5% yield) as a colorless oil.

5p: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.67 (m, 4H), 7.46 – 7.39 (m, 6H), 5.41 (s, 1H), 3.73 (dtd, *J* = 17.8, 10.1, 7.7 Hz, 2H), 2.78 – 2.63 (m, 2H), 2.42 (dd, *J* = 16.9, 1.9 Hz, 1H), 2.31 – 2.20 (m, 1H), 2.12 (d, *J* = 9.1 Hz, 3H), 2.03 (d, *J* = 19.3 Hz, 1H), 1.95 – 1.84 (m, 2H), 1.80 – 1.57 (m, 6H), 1.53 – 1.38 (m, 3H), 1.25 (ddd, *J* = 12.9, 11.7, 8.0 Hz, 1H), 1.07 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.2, 169.3, 144.4, 135.5, 133.7, 133.6, 129.7, 127.7, 127.6, 114.2, 60.9, 55.8, 55.3, 42.4, 41.8, 36.8, 31.8, 31.0, 30.5, 26.8, 24.8, 22.9, 21.1, 21.0, 19.0. **HRMS ESI** Calcd for $C_{33}H_{42}O_4Si$ [M+Na]$^+$: 553.2745, Found: 553.2732. **IR** *v* (cm^{-1}): 2929, 1737, 1219, 1112, 740, 703.

5q: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (ddd, *J* = 6.2, 4.1, 1.7 Hz, 4H), 7.49 – 7.33 (m, 6H), 5.41 – 5.34 (m, 1H), 3.91 – 3.80 (m, 1H), 3.80 – 3.68 (m, 1H), 2.72 (dd, *J* = 19.4, 11.1 Hz, 1H), 2.31 (dt, *J* = 16.2, 5.4 Hz, 1H), 2.12 (d, *J* = 6.0 Hz, 3H), 2.10 – 2.06 (m, 1H), 2.01 (d, *J* = 16.3 Hz, 1H), 1.94 – 1.86 (m, 2H), 1.86 – 1.79 (m, 1H), 1.78 – 1.69 (m, 3H), 1.69 – 1.64 (m, 1H), 1.59 (ddt, *J* = 18.1, 13.5, 4.0 Hz, 2H), 1.53 – 1.39 (m, 4H), 1.07 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.1, 169.05, 146.6, 135.6, 135.6, 133.7, 133.7, 129.6, 129.6, 127.7, 127.6, 112.7, 60.8, 56.3, 55.9, 42.1, 42.0, 36.7, 31.4, 31.1, 29.5, 26.9, 25.7, 22.9, 21.1, 20.8, 19.1. **HRMS ESI** Calcd for $C_{33}H_{42}O_4Si$ $[M+Na]^+$: 553.2745, Found: 553.2732. **IR** *v* (cm^{-1}): 2931, 1752, 1737, 1220, 1114, 704.

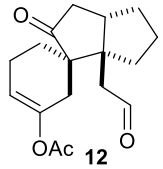
(1*R*,3a'*S*,6a'*R*)-6a'-(2-hydroxyethyl)-2'-oxo-3',3a',4',5',6',6a'-hexahydro-2'*H*-spiro[cyclohexane-1,1'-pentalen]-3-en-3-yl acetate (**s26**):



s26

5p (61.4 mg, 0.12 mmol, 1 eq.) was dissolved in anhydrous THF (1.5 mL), and a THF solution of TBAF (1.19 M, 102 μL, 0.12 mmol, 1.1 eq.) was added at 0 °C. After 2.5 hours, the reaction was quenched by water, and then extracted with EtOAc, the combined organic layers were washed with saturated NH_4Cl aqueous solution and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (petroleum ether: EtOAc = 2: 3) to give **s26** (31.7 mg, 94% yield) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (s, 1H), 3.78 (dd, *J* = 15.9, 9.4 Hz, 1H), 3.72 – 3.68 (m, 1H), 2.79 – 2.69 (m, 1H), 2.69 – 2.61 (m, 1H), 2.51 (dd, *J* = 17.2, 2.4 Hz, 1H), 2.38 (dd, *J* = 16.4, 7.9 Hz, 1H), 2.19 – 2.12 (m, 1H), 2.11 (s, 3H), 2.07 – 1.98 (m, 1H), 1.95 (d, *J* = 17.8 Hz, 1H), 1.91 – 1.82 (m, 2H), 1.77 (ddd, *J* = 16.4, 11.1, 4.9 Hz, 4H), 1.71 – 1.62 (m, 2H), 1.61 – 1.51 (m, 2H), 1.37 (dt, *J* = 13.4, 9.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.6, 169.7, 144.6, 114.6, 59.9, 56.1, 55.4, 42.7, 41.8, 37.3, 32.3, 31.1, 30.8, 25.0, 23.0, 21.2, 21.0. **HRMS ESI** Calcd for $C_{17}H_{24}O_4$ $[M+Na]^+$: 315.1567, Found: 315.1561. **IR** *v* (cm^{-1}): 2928, 1735, 1219, 1120, 1040, 790.

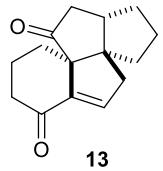
(1*R*,3a'*S*,6a'*R*)-2'-oxo-6a'-(2-oxoethyl)-3',3a',4',5',6',6a'-hexahydro-2'*H*-spiro[cyclohexane-1,1'-pentalen]-3-en-3-yl acetate (**12**):



12

To a mixture of **s26** (21.3 mg, 0.073 mmol, 1 eq.) in a solution of EtOAc (1 mL) was added IBX (24.5 mg, 0.087 mmol, 1.2 eq.). The resulting mixture was refluxed for 3 hours, until TLC indicated **8** disappeared completely. The reaction mixture was concentrated under vacuum to give a crude product, which was purified by column chromatography (petroleum ether: EtOAc = 1: 1) to give **12** (19.3 mg, 91% yield) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (t, *J* = 3.0 Hz, 1H), 5.46 (t, *J* = 3.8 Hz, 1H), 2.77 (dd, *J* = 19.4, 10.6 Hz, 1H), 2.65 – 2.53 (m, 4H), 2.38 (dd, *J* = 17.0, 1.7 Hz, 1H), 2.20 – 2.12 (m, 1H), 2.11 (s, 3H), 2.05 (d, *J* = 17.1 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.93 – 1.71 (m, 5H), 1.69 – 1.61 (m, 1H), 1.59 – 1.44 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 218.3, 202.1, 169.4, 144.6, 114.5, 57.0, 55.4, 48.0, 42.3, 41.8, 32.6, 31.5, 30.6, 24.9, 22.8, 21.1, 21.0. **HRMS ESI** Calcd for $C_{17}H_{22}O_4$ $[M+Na]^+$: 313.1410, Found: 313.1403. **IR** *v* (cm^{-1}): 2927, 1736, 1716, 1218, 1120, 603.

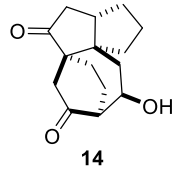
(3a*R*,9a*S*,11a*S*)-2,3,8,9,11,11a-hexahydro-4H-pentaleno[6a,1-*c*]indene-6,10(1*H*,7*H*)-dione (**13**):



13

To a stirred solution of **12** (6 mg, 0.02 mmol, 1 eq.) in a mixed solvent of MeOH/H_2O (0.5 mL, v/v = 100:1) at 0 °C was added K_2CO_3 (7.1 mg, 0.05 mmol, 2.5 eq.). The reaction mixture was allowed to stir at the same temperature for 3 hours, and then warmed to rt. After stirring for 3 hours, to the resulting mixture was added K_2CO_3 (7.1 mg, 0.05 mmol, 2.5 eq.). After stirred for 6 hours, it was poured into saturated NH_4Cl, and then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (petroleum ether: EtOAc = 3: 1) to give **13** (4.1 mg, 64% yield) as a colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.41 (t, *J* = 2.5 Hz, 1H), 2.70 (dd, *J* = 19.4, 2.2 Hz, 1H), 2.63 (dt, *J* = 17.1, 5.0 Hz, 1H), 2.56 (ddd, *J* = 14.3, 9.5, 5.6 Hz, 2H), 2.45 – 2.36 (m, 1H), 2.30 (ddd, *J* = 14.8, 8.2, 6.6 Hz, 1H), 2.24 (ddd, *J* = 16.5, 10.1, 6.2 Hz, 1H), 2.18 (dd, *J* = 17.7, 6.3 Hz, 1H), 2.15 – 2.07 (m, 1H), 2.03 (dt, *J* = 13.6, 7.0 Hz, 1H), 1.90 (dt, *J* = 13.2, 4.7 Hz, 1H), 1.85 – 1.67 (m, 4H), 1.63 – 1.59 (m, 1H), 1.37 (td, *J* = 14.1, 7.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 219.5, 200.2, 142.2, 136.6, 66.4, 61.6, 48.3, 45.8, 43.5, 39.5, 35.9, 33.5, 28.4, 25.9, 19.9. **HRMS ESI** Calcd for $C_{15}H_{18}O_2$ $[M+Na]^+$: 253.1199, Found: 253.1195. **IR** *v* (cm^{-1}): 2933, 1727, 1688, 1458, 1173, 789

(3a*S*,5a*R*,8*S*,9*R*,10a*R*)-9-hydroxyhexahydro-6*H*-5a,8-ethanocyclopenta[c]azulene-5,7(1*H*,8*H*)-dione(**14**)



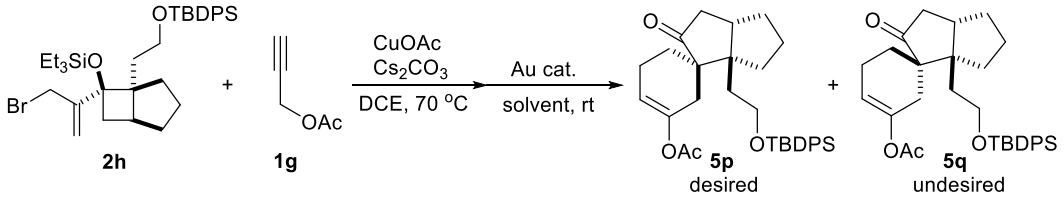
14

To a solution of **12** (4.5 mg, 0.015 mmol, 1 eq.) dissolved in THF (0.4 mL) was added 2M HCl (39 μL, 0.078 mmol, 5 eq.). The reaction mixture was stirred for 5 hours, and then quenched by saturated $NaHCO_3$ aqueous solution, extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (petroleum ether: EtOAc = 1: 1) to give **14** (3.5 mg, 89% yield) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (dd, J = 11.9, 5.1 Hz, 1H), 2.69 (dd, J = 19.8, 9.8 Hz, 1H), 2.63 (d, J = 6.4 Hz, 1H), 2.40 (dd, J = 18.8, 3.3 Hz, 1H), 2.30 (dd, J = 17.2, 9.0 Hz, 1H), 2.20 (dd, J = 14.1, 4.4 Hz, 1H), 2.14 – 1.84 (m, 9H), 1.75 (ddd, J = 13.1, 7.5, 2.9 Hz, 1H), 1.71 – 1.59 (m, 3H), 1.45 (dtd, J = 11.6, 9.7, 1.8 Hz, 1H), 1.35 (ddd, J = 14.0, 12.0, 1.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 219.0, 211.2, 74.2, 56.4, 55.6, 54.7, 44.6, 44.4, 43.1, 40.5, 32.0, 29.2, 23.4, 22.5, 21.7. **HRMS ESI** Calcd for $C_{15}H_{20}O_3$ $[M+Na]^+$: 271.1305, Found: 271.1300. **IR** *v* (cm^{-1}): 2955, 1933, 1094, 1029, 799

7.2 Optimization of the tandem reaction conditions of the synthetic utility toward the skeleton of waihoensene

Table 2. Optimization of tandem reaction conditions between **1g** and **2h**[a]



entry	catalyst	solvent	dr ratio (**5p** : **5q**)	Yield[b]
1	$AuPPh_3Cl$	DCE	1:3	41%[d]
2[c]	$AuCl_3$	DCM	1:1.9	35%
3	$AuCl_3$	DCE	1:2	32%
4[c]	$AuCl_3$	$CHCl_3$	1:1.8	31%
5[c]	$AuCl_3$	benzene	1:1.2	45%
6[c]	$AuCl_3$	toluene	1:2.4	39%
7[c]	$AuCl_3$	HFB	1.2:1	70%
8[c]	$AuCl_3$	Pentafluorobenzene	/	nr
9[c]	$AuCl_3$	Chlorobenzene	1:2.3	17%
10[c]	$AuCl_3$	Benzotrifluoride	1:1.2	26%
11[c]	$AuCl_3$	Octafluorotoluene	1:1.2	trace
12[c]	$AuCl_3$	Bromopentafluorobenzene	1:1.1	37%
13[c]	$AuBr_3$	HFB	1:1.2	12%
14[c]	$HAuCl_4{\cdot}4H_2O$	HFB	1.3:1	63%
15[c]	$AuPPh_3Cl$	HFB	1:20	55%[d]
16[c]	$AuCl_3$	HFB	/	nd[e]
17[c]	$AuCl_3$	HFB	1.2:1	64%[f]
18[c]	$AuCl_3$	HFB	/	nr[g]
19[c]	**$AuCl_3$**	**HFB**	**3.2:1**	**40%[h]**
20[c]	$AuCl_3$	HFB	2.8:1	19%[i]
21[c]	$AuCl_3$	HFB	2.1:1	32%[j]

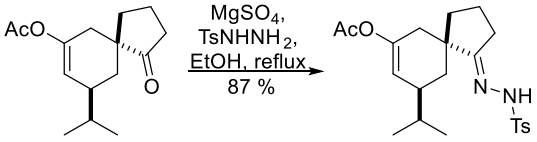
[a]Unless specified, all reactions were carried out using **1g** (0.5 mmol, 2.5 eq.), **2h** (0.2 mmol, 1.0 eq.) and Au cat. (10 mol%) in a reaction tube in DCE (2 mL) at indicated temperature. [b]Isolated yield. [c]After filtration, the filtrate was concentrated and diluted with the indicated solvent (4 mL) for the following operation. [d]$AgNTf_2$ (10 mol%) was added. [e]$AgNTf_2$ (30 mol%) was added. [f]H_2O (5 mol%) was added. [g]4 Å MS (10 mg/ mmol) was added. [h]PTS (5 mol%) was added. [i]K_2CO_3 (5 mol%) was added. [j]Benzoic acid (5 mol%) was added.

The key tandem reactions between **1g** and **2h** under standard conditions after Castro-Stephens coupling using the combination of 10 mol% $AuPPh_3Cl$ and $AgNTf_2$ in DCE at rt could promote the desired reaction to give the product **5p** and **5q** with a dr ratio of 1:3 in 41% yield (Table 2, entry 1). Thus a further detailed optimization of tandem reactions conditions after Castro-Stephens coupling between **1g** and **2h** were investigated. After the screening of solvent, gold catalysts, the use of $AuCl_3$ in HFB with PTS as additive was selected as the optimal conditions (Table 2, entry 19).

8 The determination of the relative configuration of 5e-1, 5p, 5q, 5i, 7a and 11

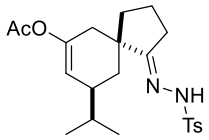
8.1 The relative configuration of **5e-1**, **5p**, **5q**, **7a** and **11** was determinated by the X-ray structure of their derivatives **15**, **16a**, **17**, **18** and **19**, respectively.

8.1.1 The determination of the relative configuration of **5e-1**.
(a) The synthesis of compound **15**.



5e-1 **15**
X-ray

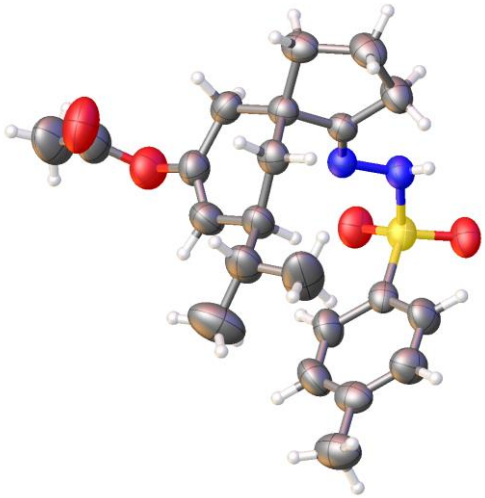
(*E*)-9-isopropyl-1-(2-tosylhydrazono)spiro[4.5]dec-7-en-7-yl acetate (**15**):



15

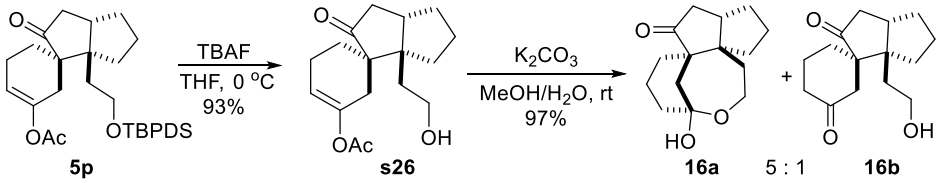
5e-1 (23 mg, 0.092 mmol, 1 eq.), p-toluenesulfonyl hydrazide (17.1 mg, 0.092 mmol, 1 eq.) and anhydrous $MgSO_4$ (110.6 mg, 0.92 mmol, 10 eq.) were suspended in 1 mL EtOH in a reaction tube containing a stirring bar. The reaction was refluxed for 9 hours and then concentrated under vacuum. The resulting mixture was purified by column chromatography (petroleum ether: EtOAc = 3: 1) to give **15** (33.4 mg, 87% yield) as a colorless solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.21 (s, 1H), 2.41 (s, 3H), 2.35 – 2.28 (m, 1H), 2.24 (dd, *J* = 15.4, 7.2 Hz, 2H), 2.13 (s, 3H), 1.96 (d, *J* = 16.9 Hz, 1H), 1.83 – 1.71 (m, 3H), 1.69 – 1.61 (m, 2H), 1.49 (td, *J* = 13.6, 6.1 Hz, 2H), 1.17 (dd, *J* = 13.2, 10.9 Hz, 1H), 0.93 – 0.85 (m, 1H), 0.78 (dd, *J* = 6.8, 4.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 168.7, 146.2, 143.6, 135.2, 129.2, 128.4, 116.4, 45.8, 40.1, 37.8, 35.4, 32.6, 31.4, 26.8, 21.6, 21.2, 19.9, 19.6, 19.2. **m.p.**: 88-90 °C. **HRMS ESI** Calcd for $C_{22}H_{30}N_2O_4S$ [M+Na]$^+$: 441.1824, Found: 441.1820. **IR** *v* (cm^{-1}): 2946, 2856, 1734, 1450, 1078, 604, 592.

(b) X-ray ellipsoid plots of compound **15**.



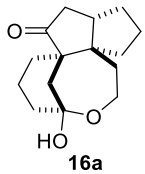
X-Ray ellipsoid plots of compound **15** (CCDC 1962296)

8.1.2 The determination of the relative configuration of **5p**.
(a) The synthesis of compound **16a**.



5p **s26** **16a** 5 : 1 **16b**
X-ray

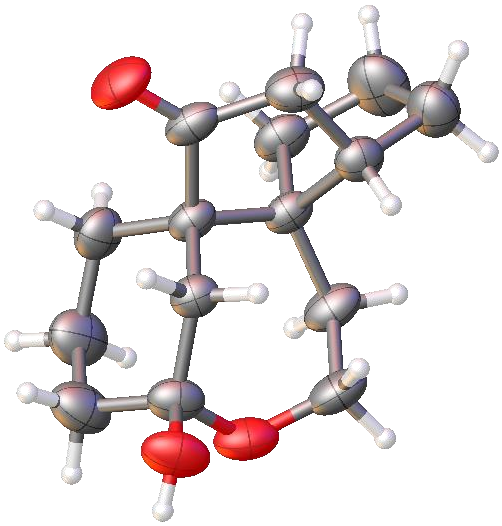
(4*R*,7a*R*,9a*S*,12a*R*)-4-hydroxydecahydro-4,7a-methanopentaleno[6a,1-*d*]oxonin-8(9*H*)-one (**16a**):



16a

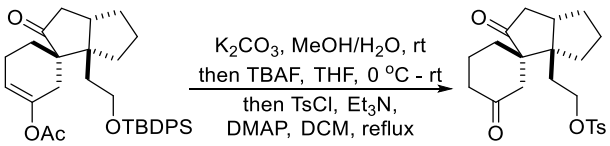
5p (61.4 mg, 0.12 mmol, 1 eq.) was dissolved in anhydrous THF (1.5 mL), and a THF solution of TBAF (1.19 M, 102 μL, 0.12 mmol, 1.1 eq.) was added at 0 °C. After 2.5 hours, the reaction was quenched by water, and then extracted with EtOAc, the combined organic layers were washed with saturated NH_4Cl aqueous solution and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (petroleum ether: EtOAc = 2: 3) to give **s26** (31.7 mg, 94% yield) as a colorless oil. Then to a stirred solution of **s26** (31.7 mg, 0.11 mmol, 1 eq.) in a mixed solvent of MeOH/H_2O (1 mL, v/v = 10: 1) was added K_2CO_3 (18 mg, 0.13 mmol, 1.2 eq.) at rt. The reaction was stirred for 20 mins, and then was quenched by saturated NH_4Cl aqueous solution, extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (petroleum ether: EtOAc = 2: 3) to give inseparable compound **16a** and **16b** (26.4 mg, 90% yield over 2 steps) as a colorless solid, the ratio of compound **16a** and **16b** was determined by ^{1}H NMR.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (ddd, *J* = 12.9, 8.7, 3.8 Hz, 1H), 3.69 (dt, *J* = 13.5, 3.4 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.63 (dd, *J* = 9.1, 5.9 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.31 – 2.24 (m, 1H), 2.00 (tdd, *J* = 13.4, 8.8, 4.5 Hz, 1H), 1.83 – 1.70 (m, 9H), 1.66 – 1.55 (m, 1H), 1.54 – 1.40 (m, 3H), 1.35 – 1.21 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.2, 99.0, 59.5, 57.5, 55.8, 41.6, 39.3, 38.6, 38.6, 37.3, 36.3, 28.9, 26.7, 22.1, 20.5. **m.p.**: 96-98 °C. **HRMS ESI** Calcd for $C_{15}H_{22}O_3$ [M+Na]$^+$: 273.1461, Found: 273.1457. **IR** *v* (cm^{-1}): 2946, 2877, 1734, 1450, 1078, 604.

(b) X-ray ellipsoid plots of compound **16a**.

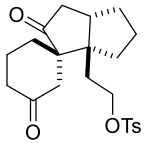


X-Ray ellipsoid plots of compound **16a** (CCDC 1962275)

8.1.3 The determination of the relative configuration of **5q**.
(a) The synthesis of compound **17**.



2-((1*S*,3a'*S*,6a'*R*)-2',3-dioxohexahydro-6a'*H*-spiro[cyclohexane-1,1'-pentalen]-6a'-yl)ethyl 4-methylbenzenesulfonate (**17**):

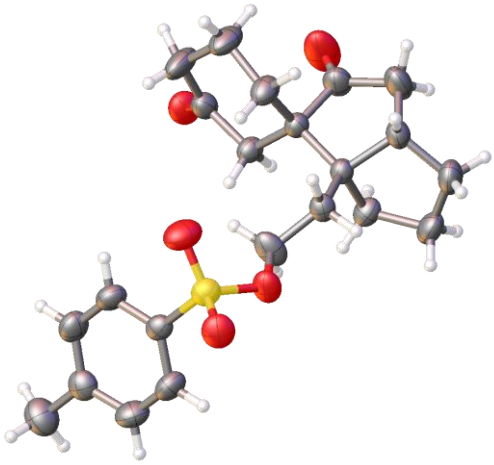


17

To a stirred solution of **5q** (98 mg, 0.18 mmol, 1 eq.) in a mixed solvent of MeOH/H_2O (2 mL, v/v = 10: 1) was added K_2CO_3 (30.6 mg, 0.22 mmol, 1.2 eq.) at rt. The reaction was stirred for 20 mins, and then treated with saturated NH_4Cl aqueous solution, extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was then dissolved in anhydrous THF (2 mL), added a THF solution of TBAF (1.19 M, 171 μL, 0.20 mmol, 1.1 eq.) at 0 °C. The reaction was stirred warm to rt for 4 hours. The reaction was poured into saturated NH_4Cl aqueous solution, extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4

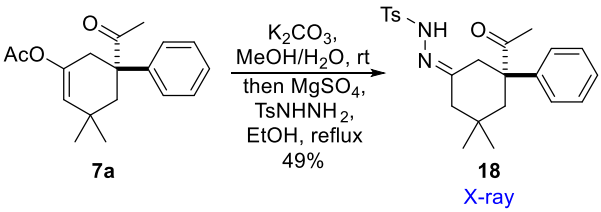
and concentrated. Then the crude product was dissolved in anhydrous DCM (2 mL), and added Et_3N (77 μL, 0.55 mmol, 3 eq.), DMAP (4.5 mg, 0.04 mmol, 0.2 eq.), TsCl (70.4 mg, 0.37 mmol, 2 eq.), refluxed for 3 hours. The reaction was quenched by saturated NH_4Cl aqueous solution, extracted with DCM. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude was purified by flash chromatography (petroleum ether: EtOAc = 1: 3) to give **17** (56.5 mg, 76% yield) as a colorless solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.13 (t, *J* = 7.1 Hz, 2H), 2.70 (dd, *J* = 19.9, 10.8 Hz, 1H), 2.46 (s, 3H), 2.40 (dd, *J* = 10.4, 6.3 Hz, 2H), 2.23 (dd, *J* = 9.5, 7.6 Hz, 1H), 2.12 – 1.90 (m, 4H), 1.90 – 1.69 (m, 6H), 1.69 – 1.64 (m, 1H), 1.61 – 1.45 (m, 3H), 1.15 (dt, *J* = 13.5, 9.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.1, 208.7, 145.3, 132.7, 130.0, 127.8, 66.9, 59.7, 56.1, 44.1, 42.8, 41.9, 39.8, 32.0, 31.1, 30.0, 28.1, 22.4, 21.7, 20.2. **m.p.**: 90-92 °C. **HRMS ESI** Calcd for $C_{22}H_{28}O_5S$ [M+Na]$^+$: 427.1550, Found: 427.1541. **IR** *v* (cm^{-1}): 2923, 1735, 1097, 782, 662.

(b) X-ray ellipsoid plots of compound **17**.

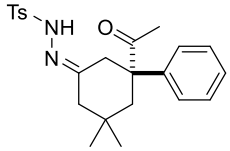


X-Ray ellipsoid plots of compound **17** (CCDC 1962272)

8.1.4 The determination of the relative configuration of **7a**.
(a) The synthesis of compound **18**.



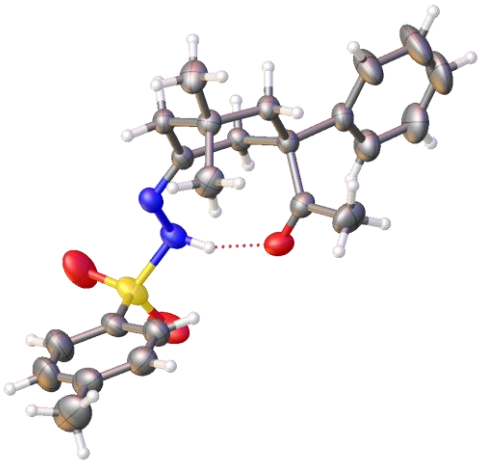
(*Z*)-N'-(3-acetyl-5,5-dimethyl-3-phenylcyclohexylidene)-4-methylbenzenesulfonohydrazide (**18**):



18

To a stirred solution of **7a** (32.2 mg, 0.112 mmol, 1 eq.) in MeOH/H_2O (1.5 mL, v/v = 10: 1) was added K_2CO_3 (18.6 mg, 0.135 mmol, 1.2 eq.) at rt for 30 mins. The reaction was diluted with EtOAc, and water was added to quench the reaction. Extract with EtOAc, the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Then to a solution of the resulting mixture in EtOH (1.5 mL) was added $TsNHNH_2$ (62.6 mg, 0.336 mmol, 3 eq.) and $MgSO_4$ (135.2 mg, 1.12 mmol, 10 eq.). The reaction was refluxed for 5 hours, and then concentrated. The crude product was purified by flash chromatography (petroleum ether: EtOAc = 2: 1) to give **18** (22.8 mg, 49% yield) as a colorless solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.32 – 7.29 (m, 1H), 7.29 – 7.27 (m, 2H), 7.25 (d, *J* = 1.0 Hz, 2H), 3.45 (dt, *J* = 13.7, 2.0 Hz, 1H), 2.39 (d, *J* = 4.6 Hz, 3H), 2.36 (s, 1H), 2.16 (d, *J* = 14.2 Hz, 1H), 2.10 – 1.95 (m, 2H), 1.79 (s, 3H), 1.69 (d, *J* = 13.8 Hz, 1H), 1.10 (s, 3H), 0.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.2, 157.8, 143.3, 140.8, 135.3, 129.3, 128.9, 128.4, 128.0, 125.5, 59.4, 48.2, 44.6, 35.3, 35.0, 33.0, 25.3, 23.9, 21.5. **m.p.**: 96-98 °C. **HRMS ESI** Calcd for $C_{23}H_{28}N_2O_{3S}$ [M+Na]$^+$: 435.1718, Found: 435.1716. **IR** *v* (cm^{-1}): 2946, 2877, 1734, 1450, 1078, 604.

(b) X-ray ellipsoid plots of compound **18**.

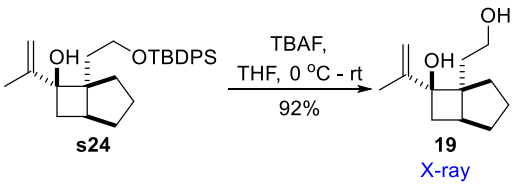


X-Ray ellipsoid plots of compound **18 (**CCDC 1962295**)**

8.1.5 The determination of the relative configuration of **11**.

The relative configuration of **11** was determinated by the X-ray structure of the diol derivative **19** from its tertiary alcohols precursor **s24**. (1*S*,5*R*,6*S*)-5-(2-hydroxyethyl)-6-(prop-1-en-2-yl)bicyclo[3.2.0]heptan-6-ol (**19**):

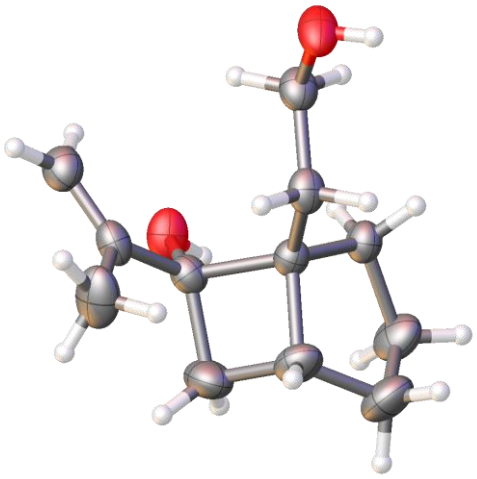
(a) The synthesis of compound **19**.



An ice-cooled solution of **s24** (1.52 g, 3.50 mmol, 1 eq.) in anhydrous THF (20 mL) was treated with a THF solution of TBAF (1.19 M, 3.09 mL, 3.68mmol, 1.05 eq.) dropwise, then the reaction was warmed to rt. After stirring for 17 hours, the reaction was treated with saturated NH_4Cl aqueous solution, extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (petroleum ether: EtOAc = 1: 2) to give **19** (0.63 g, 92% yield) as a colorless solid.

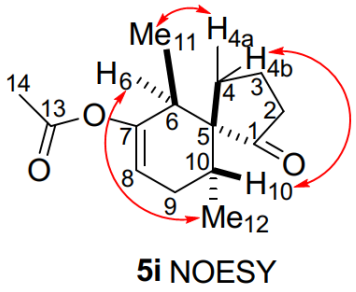
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (s, 2H), 3.63 – 3.51 (m, 2H), 2.57 (dd, *J* = 13.2, 9.0 Hz, 1H), 2.23 – 2.14 (m, 1H), 2.10 (dd, *J* = 14.6, 7.1 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.87 (d, *J* = 0.5 Hz, 3H), 1.86 – 1.74 (m, 3H), 1.70 – 1.60 (m, 1H), 1.58 – 1.34 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.6, 111.6, 77.2, 60.1, 55.9, 38.4, 36.8, 35.9, 32.2, 31.0, 25.9, 20.6. **m.p.**: 74-76 °C. **HRMS ESI** Calcd for $C_{12}H_{20}O_2$ $[M+Na]^+$: 219.1356, Found: 219.1353. **IR** *v* (cm^{-1}): 3369, 2950, 1449, 1228, 1027, 894, 739.

(b) X-ray ellipsoid plots of compound **19.**



X-Ray ellipsoid plots of compound **19** (CCDC 1962417)

8.2 The relative configuration of **5i** was elucidated by the 2D NOESY spectrum.



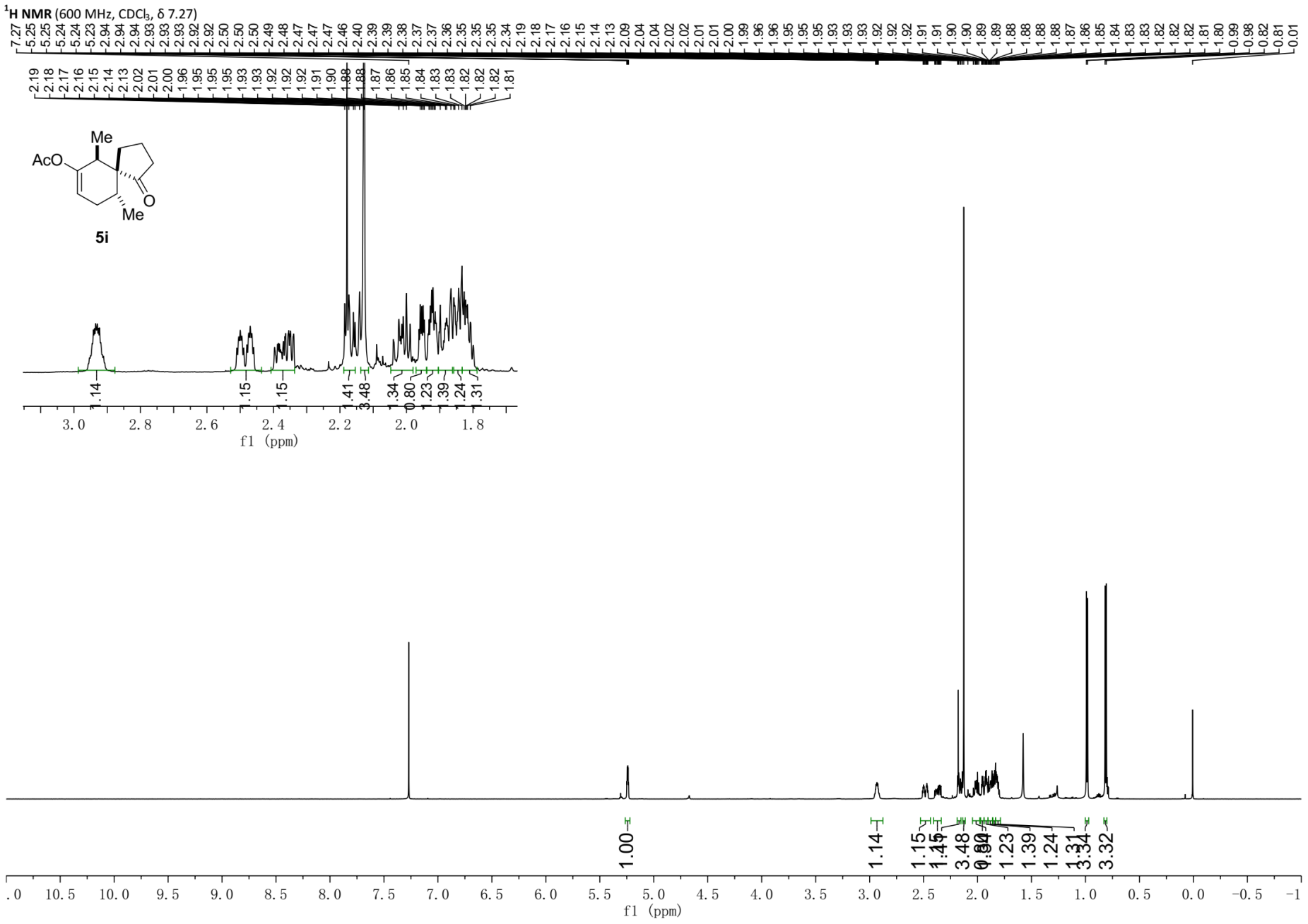
5i NOESY

The ^{1}H NMR, ^{13}C NMR, HSQC spectrum displayed signals for two C-H bearing vicinal CH_3 group [δ_H (0.82, d, 7.2 Hz, C*H*$_3$-11) and δ_H (0.99, d, 7 Hz, C*H*$_3$-12)], an acetyl group [δ_C 169.4 (C-13) and 20.7 (C-14); δ_H 2.13 (3H, s, C*H*$_3$-14)], a carbonyl group [δ_C 219.9 (C-1)] and a trisubstituted double bond [δ_C 148.9 (C-7) and 111.5 (C-8); δ_H 5.24 (1H, dt, 4.9, 2.4, 1 Hz, H-8)]. The quaternary carbon was then connected by detail HMBC - no HSQC analysis. The HMBC cross-peaks of H-8 with C-7 and C-9, C*H*$_3$-11 with C-5, C-6 and C-7, C*H*$_3$-12 with C-5, C-9 and C-10 revealed that C-6 and C-10 are connected a quaternary carbon to form the spirobicycle. In addition, the attachment of CH_2 group at C-4 was achieved by the key HMBC correlations of H-4a and H-4b with C-5, C-6 and C-10, respectively.

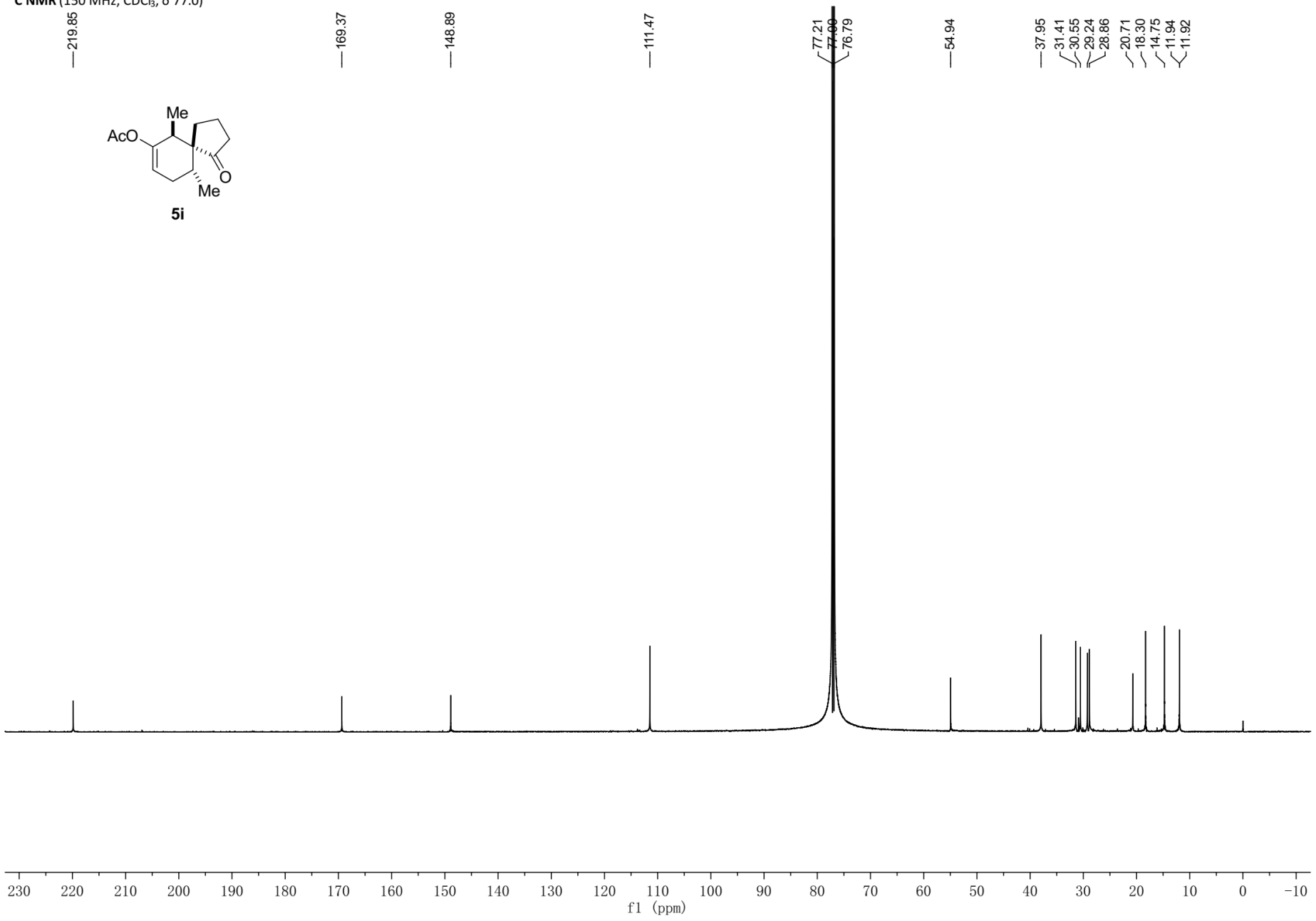
The relative configurations at C-5, C-6, and C-10 were resolved using 2D NOESY experiments. The cross-peak observed between the protons H-6/C*H*$_3$-12, indicated that H-6 and CH_3-12 were on the same side and were arbitrarily assigned α-orientations. The NOESY correlation pairs of H-4a/C*H*$_3$-11 and H-4b/H-10 suggested that CH_2-4 group were β-oriented.

Table 3. ^{1}H and ^{13}C NMR data for compound **5i**.

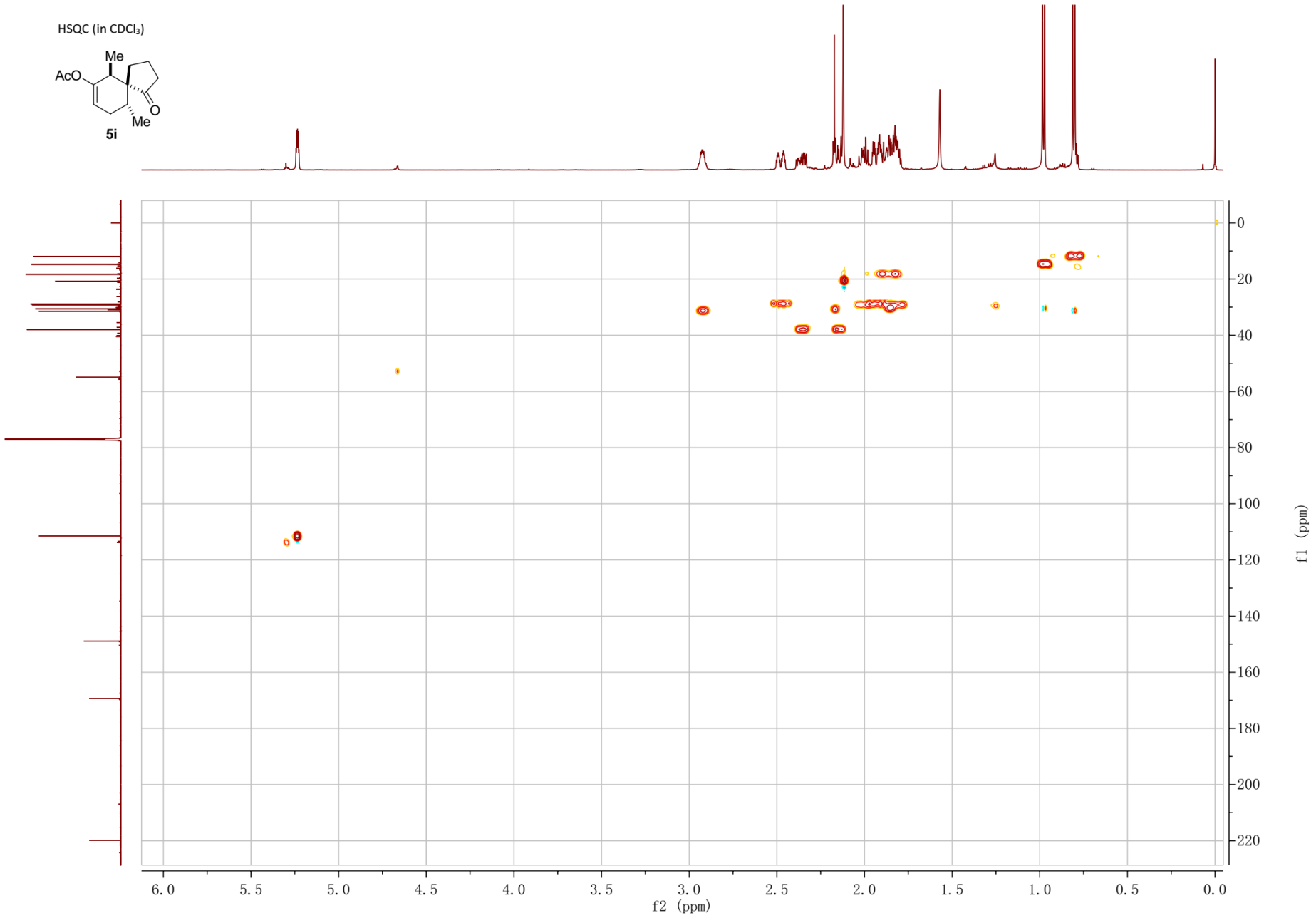
no.	δ_H (mult, J, Hz)	δ_C
1		219.9
2	2.38 m	38.0
	2.18 m	
3	1.92 m	18.3
	1.82 m	
4	2.03 m	29.2
	1.85 m	
5		54.9
6	2.93 m	31.4
7		148.9
8	5.24 dt (4.9, 2.4, 1)	111.5
9	2.48 m	28.9
	1.95 m	
10	1.87 m	30.6
11	0.82 d (7.2)	11.9
12	0.99 d (7)	14.8
13		169.4
14	2.13 s	20.7


1H NMR (600 MHz, CDCl3, δ 7.27)
Me
AcO
O
Me
5i
f1 (ppm)

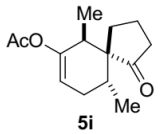
^{13}C NMR (150 MHz, $CDCl_3$, δ 77.0)



5i

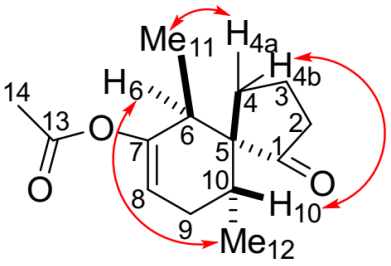

HSQC (in CDCl3)
Me
AcO
O
Me
5i
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)

HMBC – no HSQC (in $CDCl_3$)

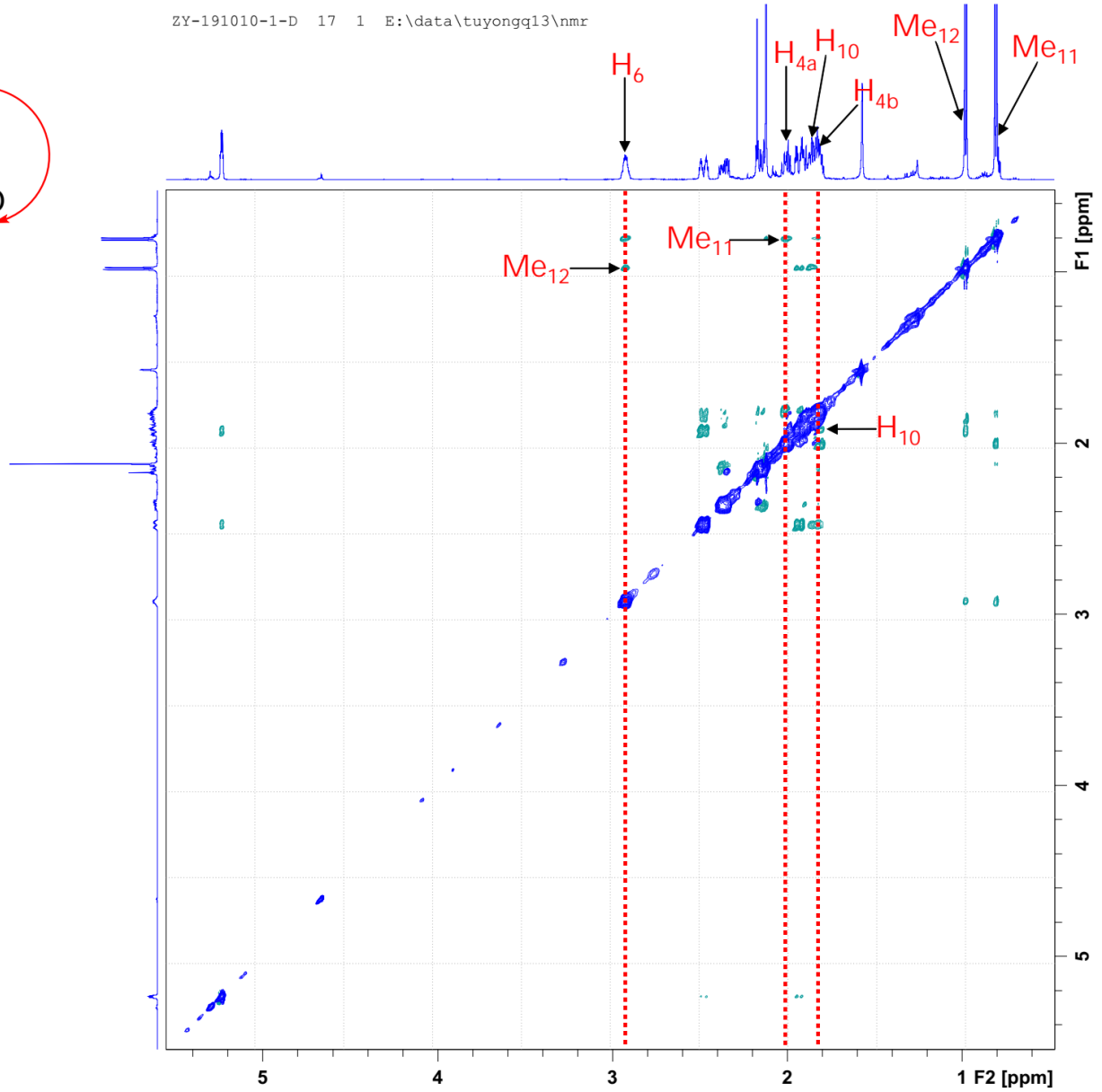


5i

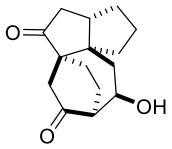
(600 MHz, in $CDCl_3$)



5i NOESY

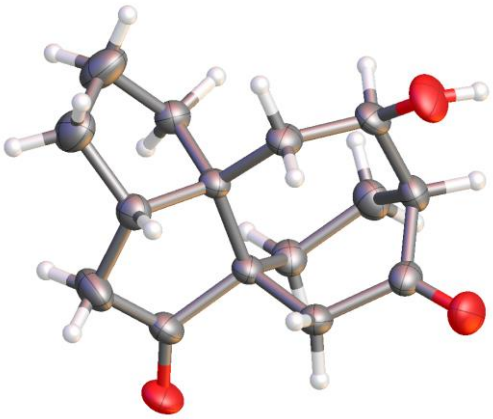


9 The X-ray ellipsoid plots of compound 14



14

X-ray



X-Ray ellipsoid plots of compound **14** (CCDC 1962276)

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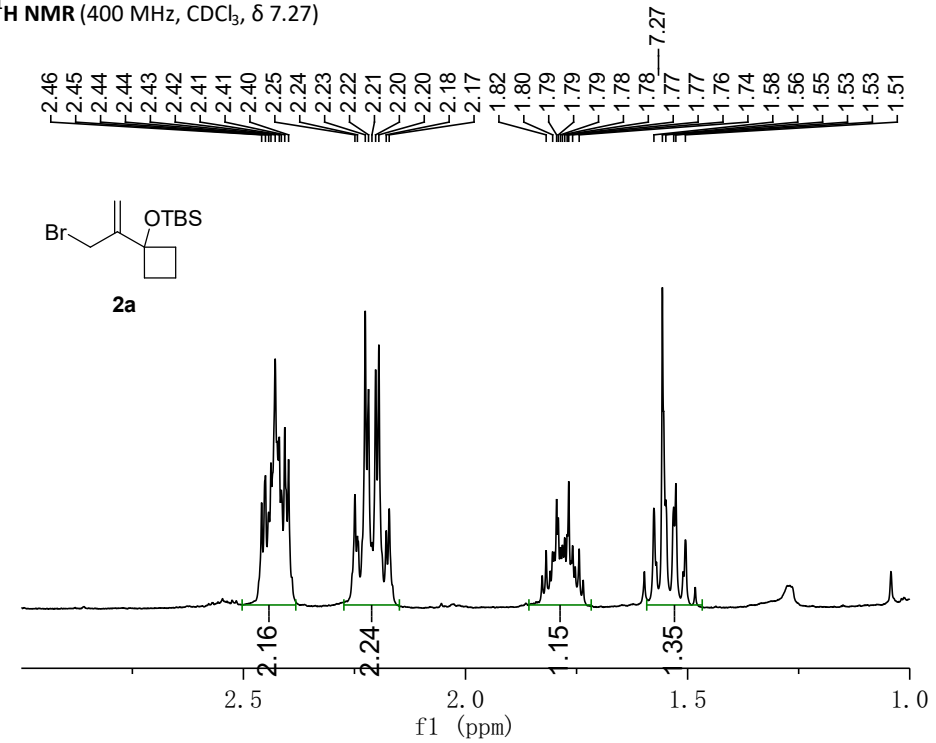
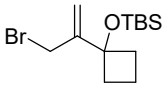
11 Copies of the ^{1}H and ^{13}C NMR of new compounds

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

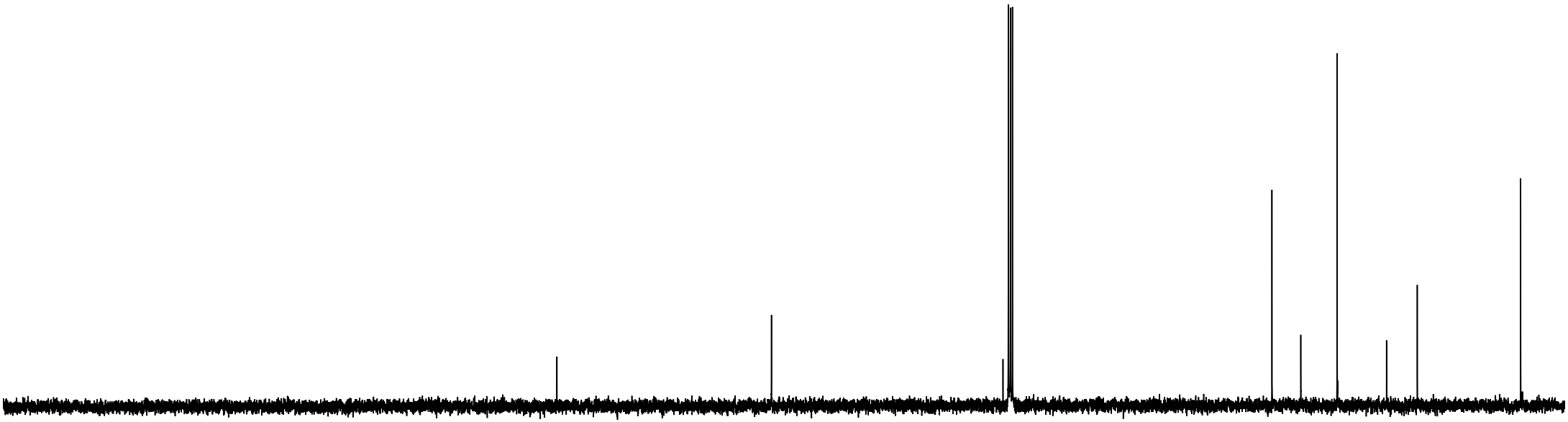


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



2a

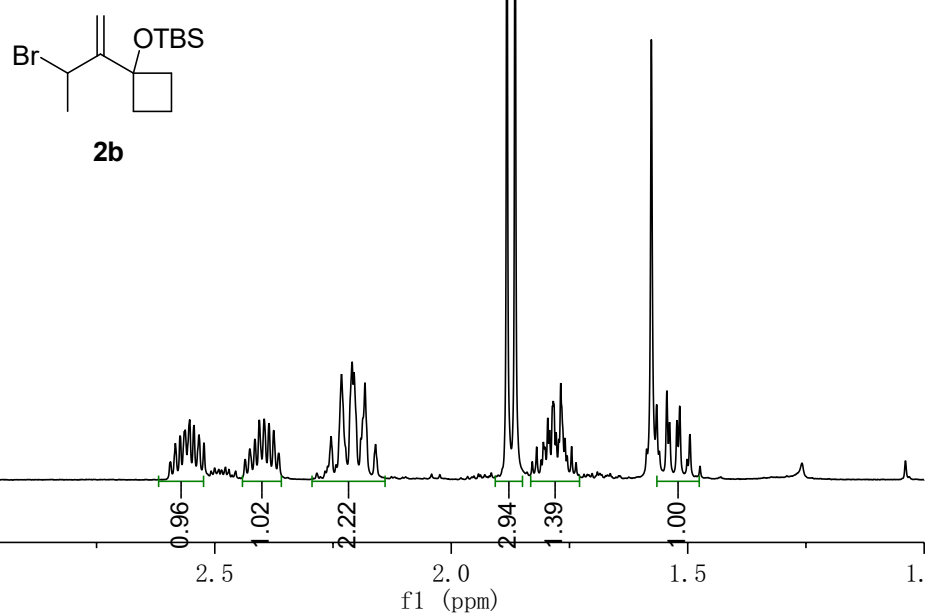
148.15
114.49
78.16
77.32
77.00
76.68
35.97
31.44
25.75
17.99
13.17
-3.05



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



2b

f1 (ppm)

f1 (ppm)

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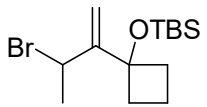

2b

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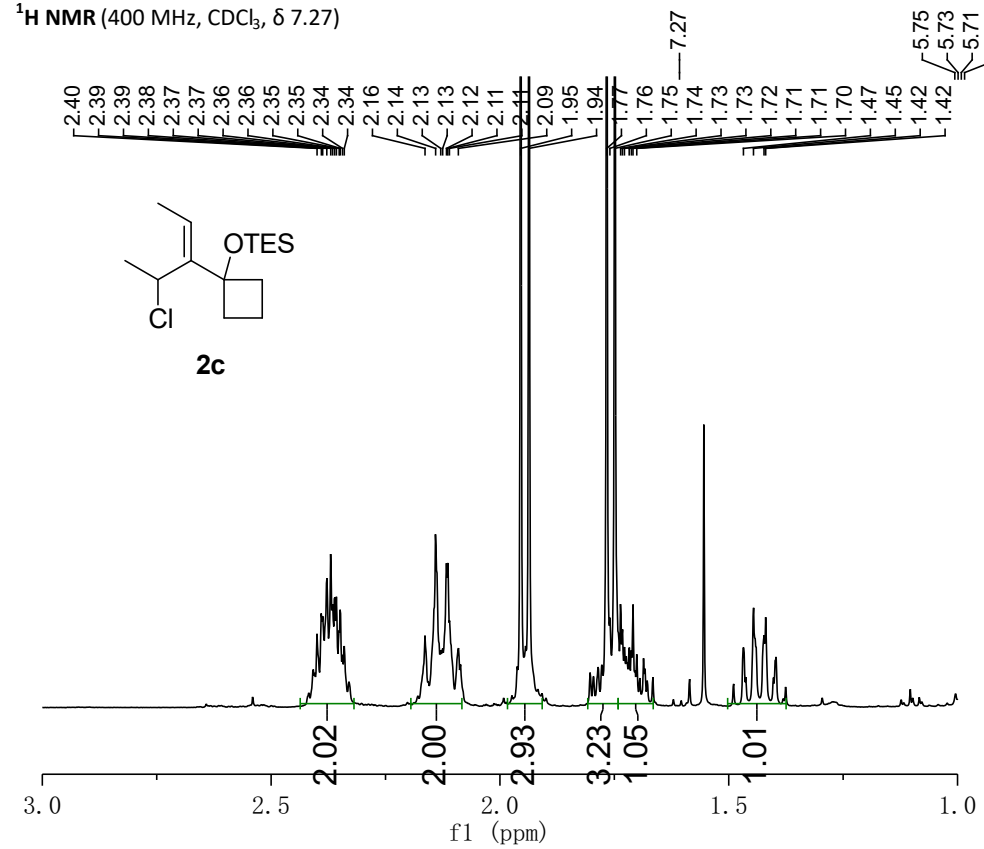
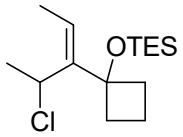
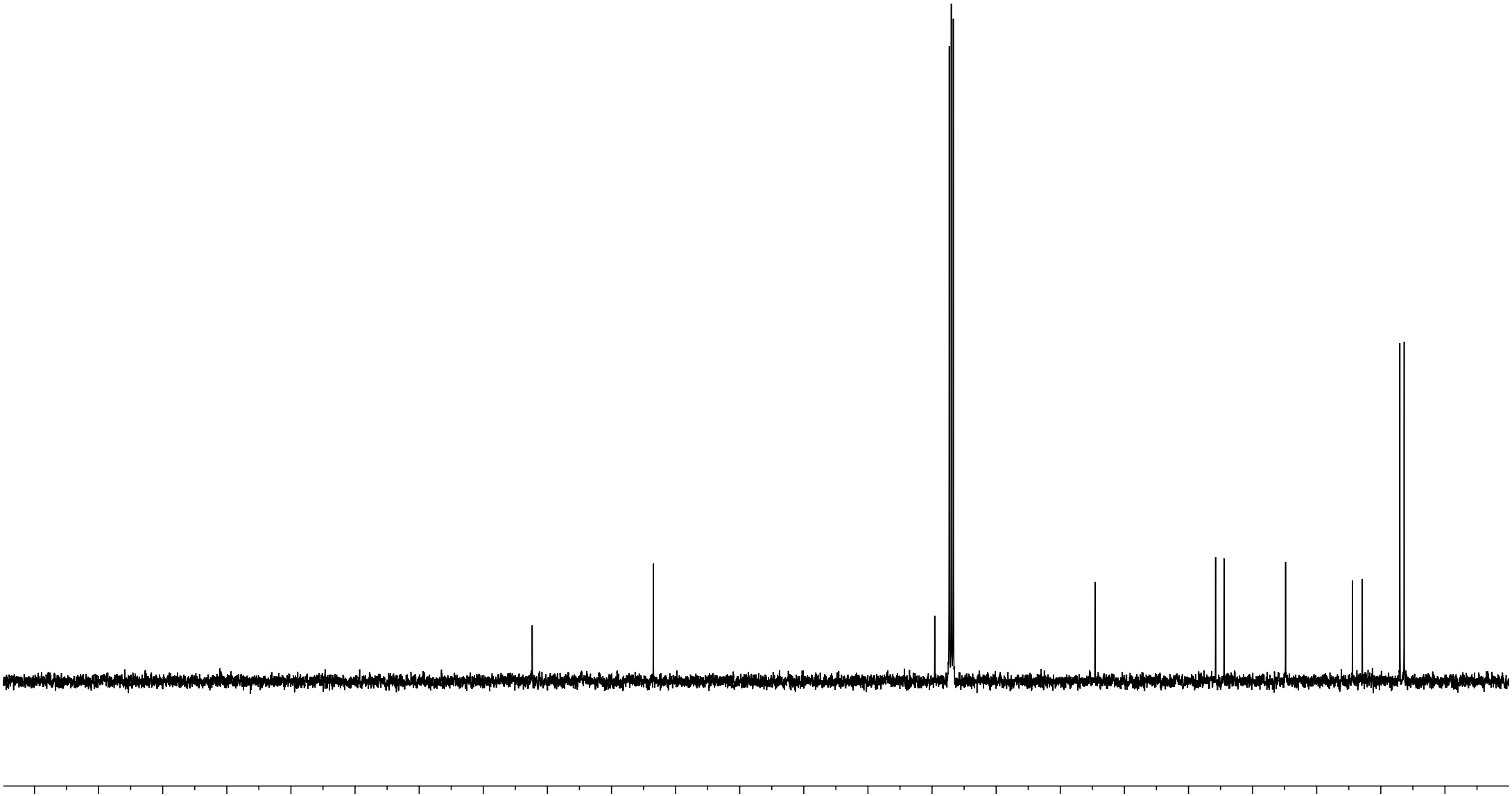


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



2c

142.37
123.48
79.58
77.32
77.00
76.68
54.58
35.77
34.46
24.86
14.42
12.89
7.03
6.36



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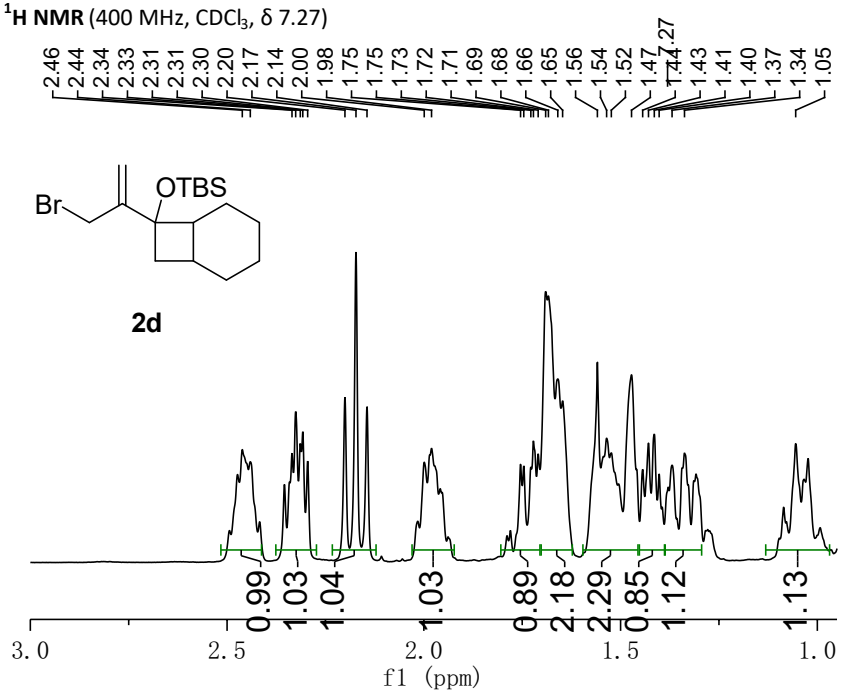

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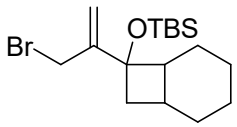
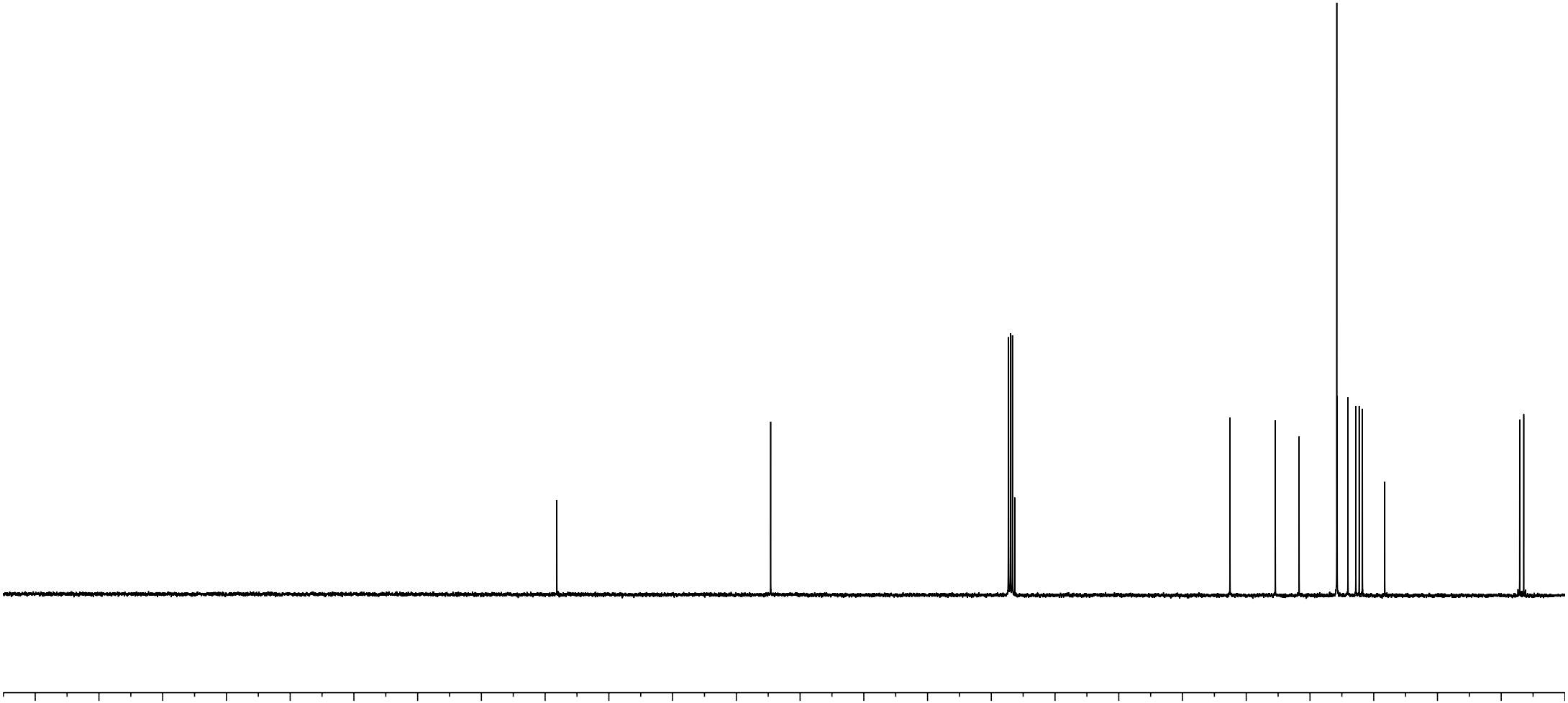


2d

148.17
114.61
77.32
77.00
76.68
76.33
42.55
35.44
31.71
25.79
25.74
24.05
22.81
22.28
21.78
18.27
-2.90
-3.54



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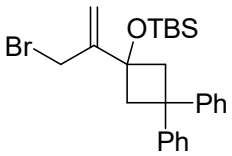
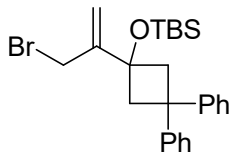


2e

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



2e

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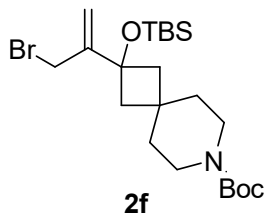
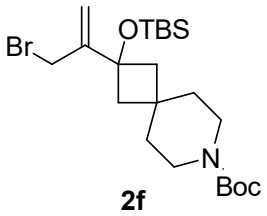


2f

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



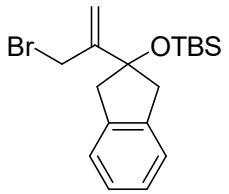
2f

154.89
149.33
116.02
79.17
77.32
77.00
76.68
73.90
44.59
38.96
36.75
30.76
29.63
28.40
25.68
17.93
-3.17

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



2g

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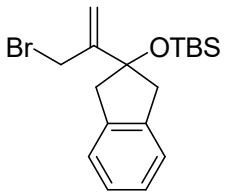

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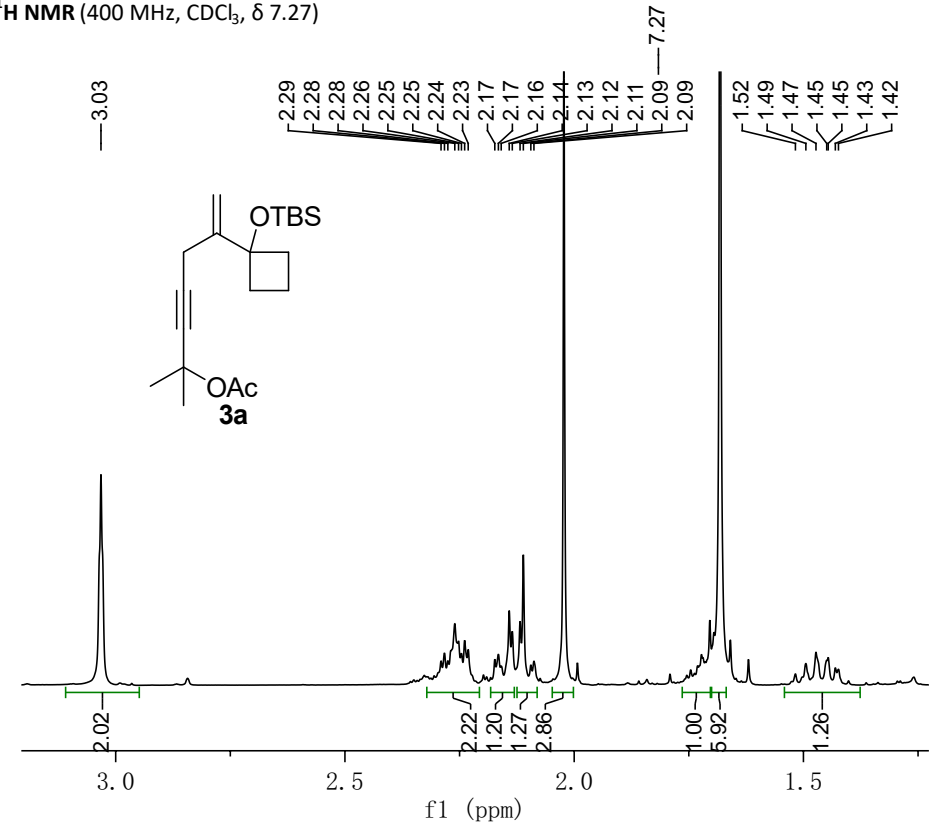

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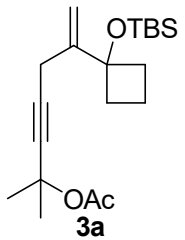
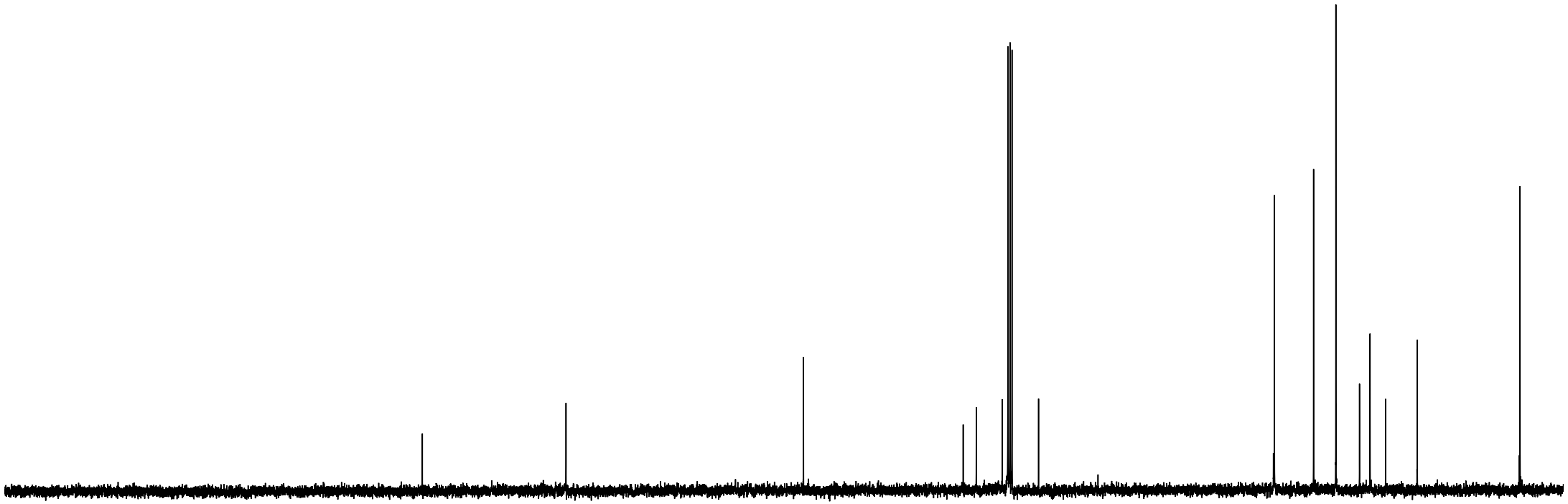


3a

169.37
146.78
109.46
84.36
82.30
78.22
77.32
77.00
76.68
72.51
35.45
29.28
25.78
22.06
20.41
17.96
12.99
-3.16



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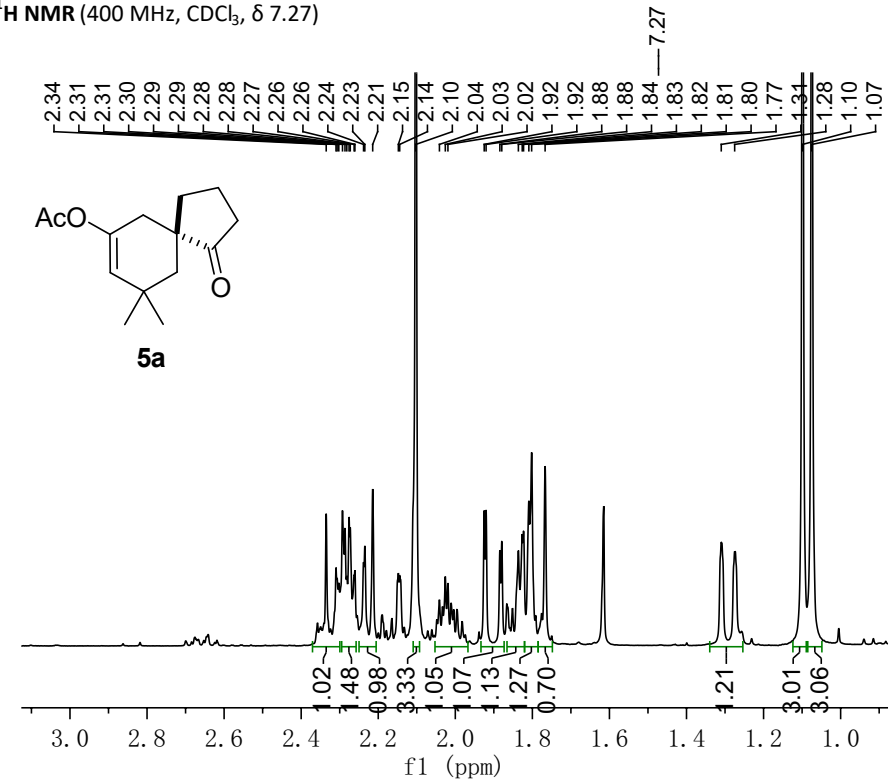
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



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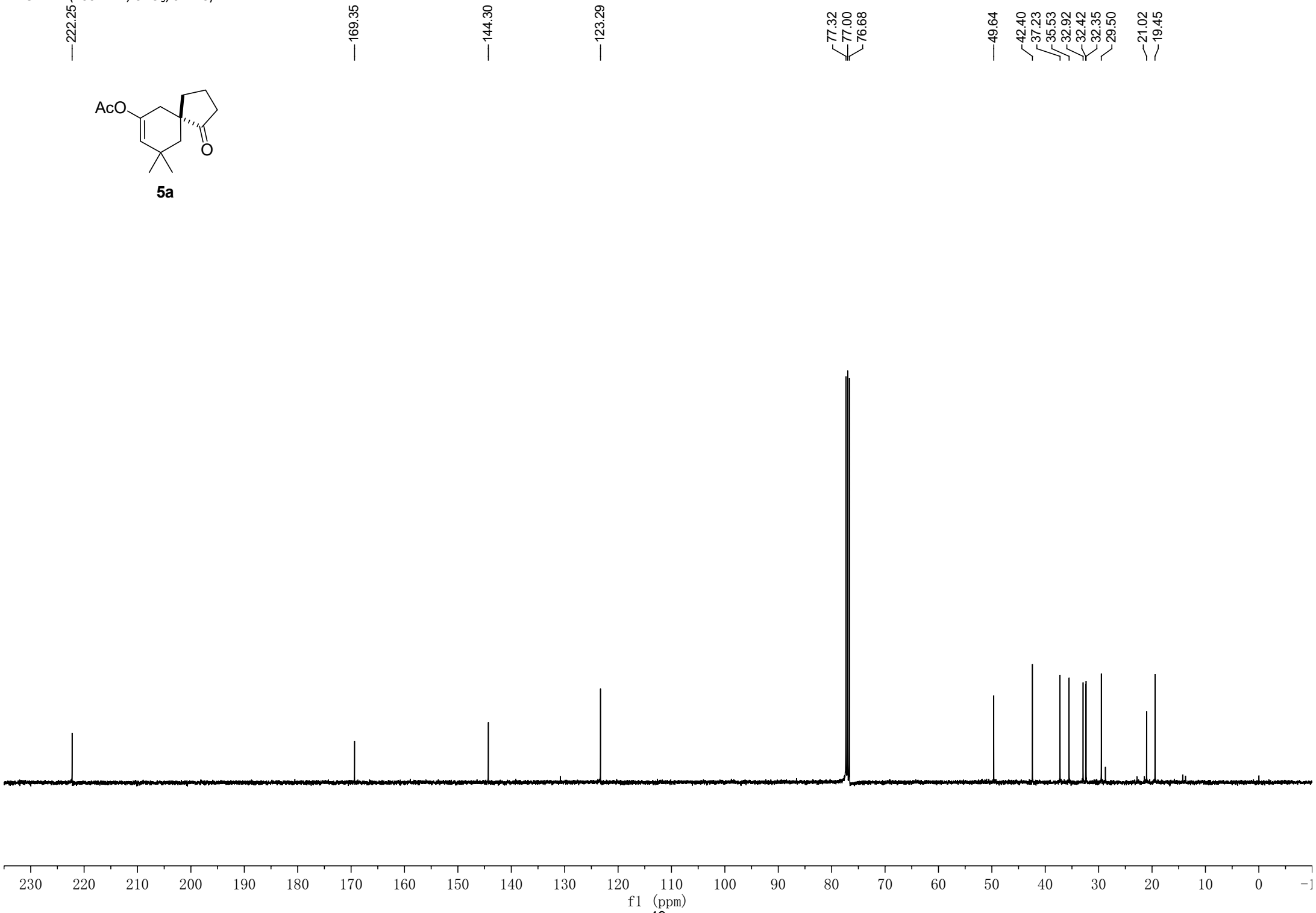

5a

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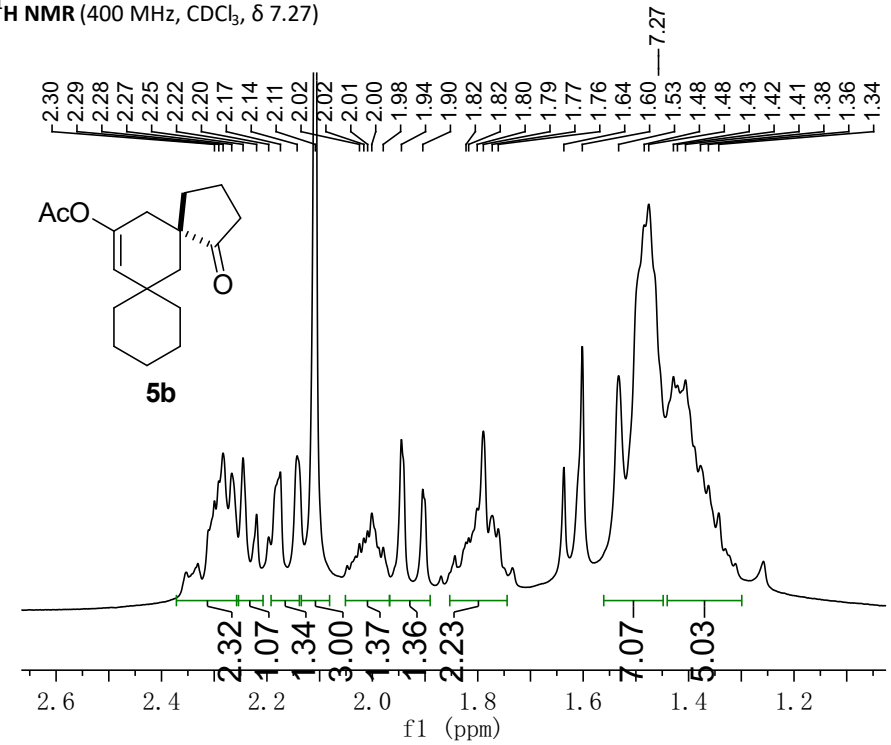

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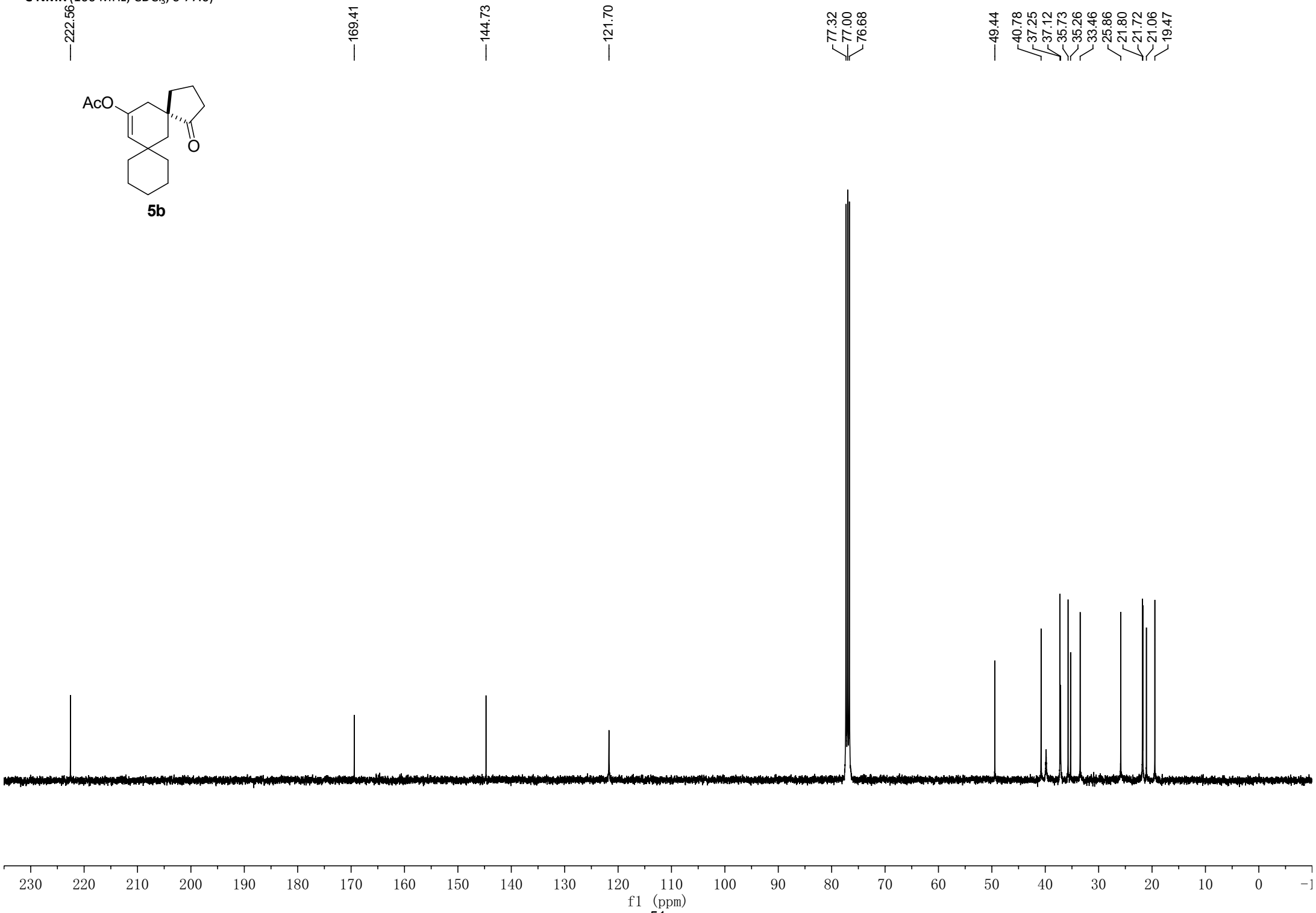

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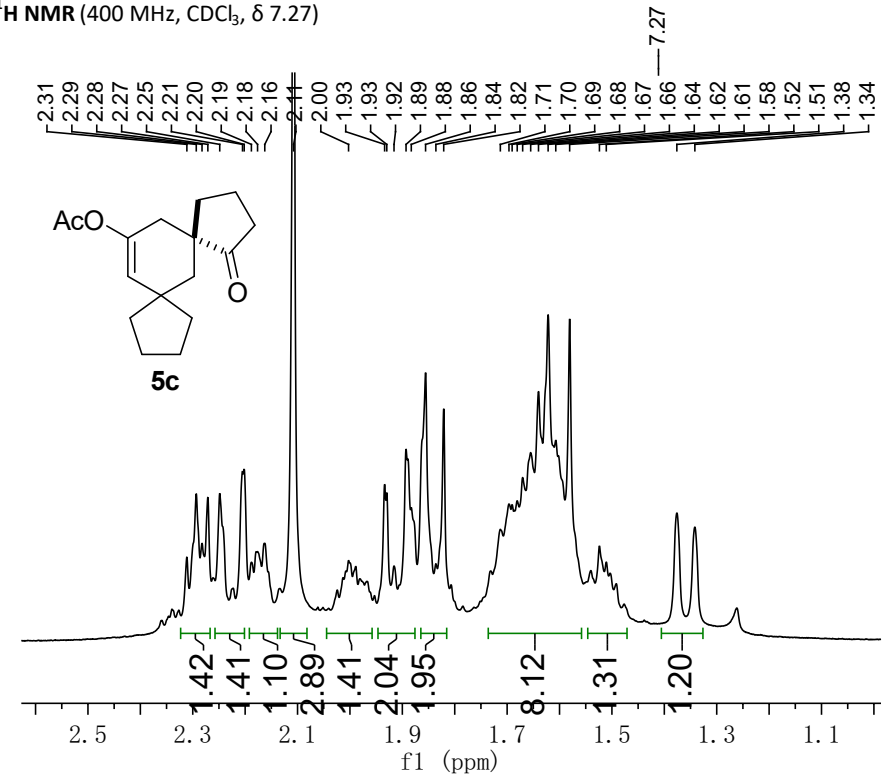

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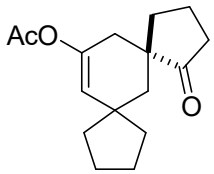

5c

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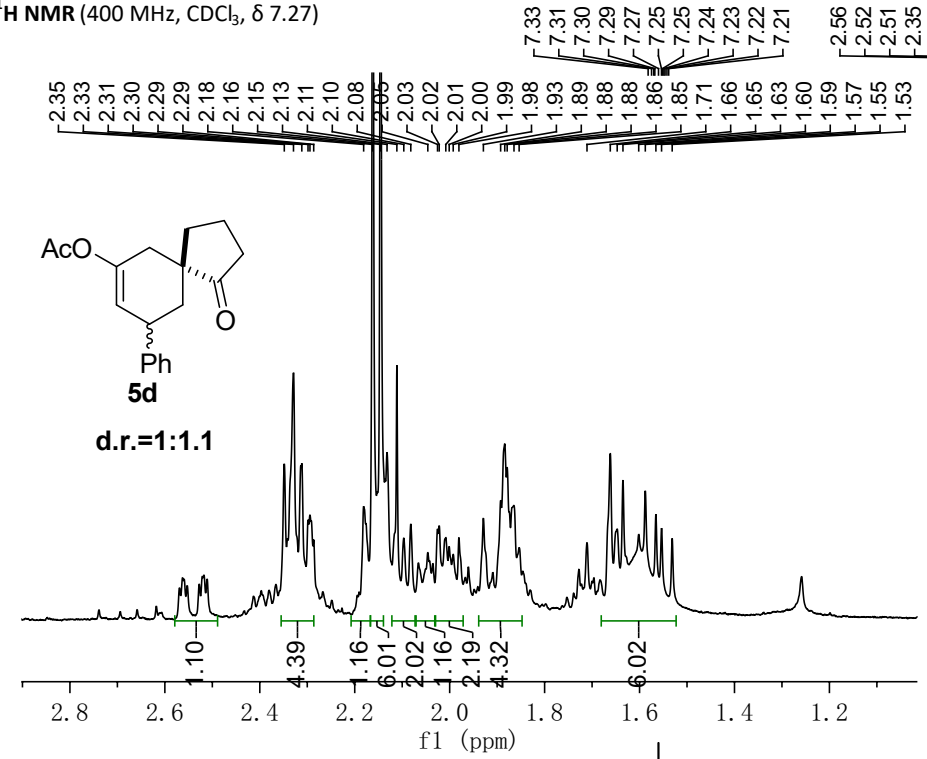

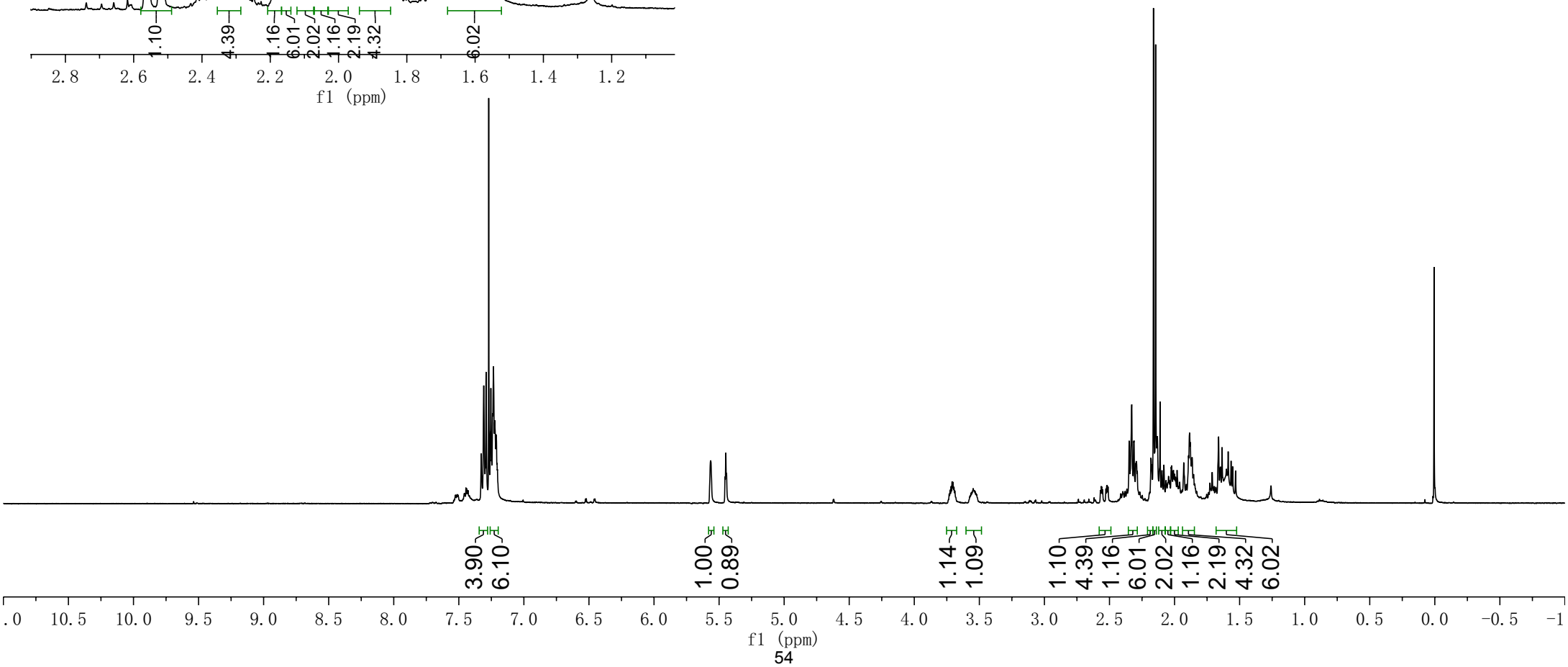

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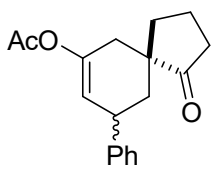

5d

d.r.=1:1.1

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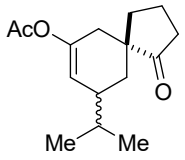
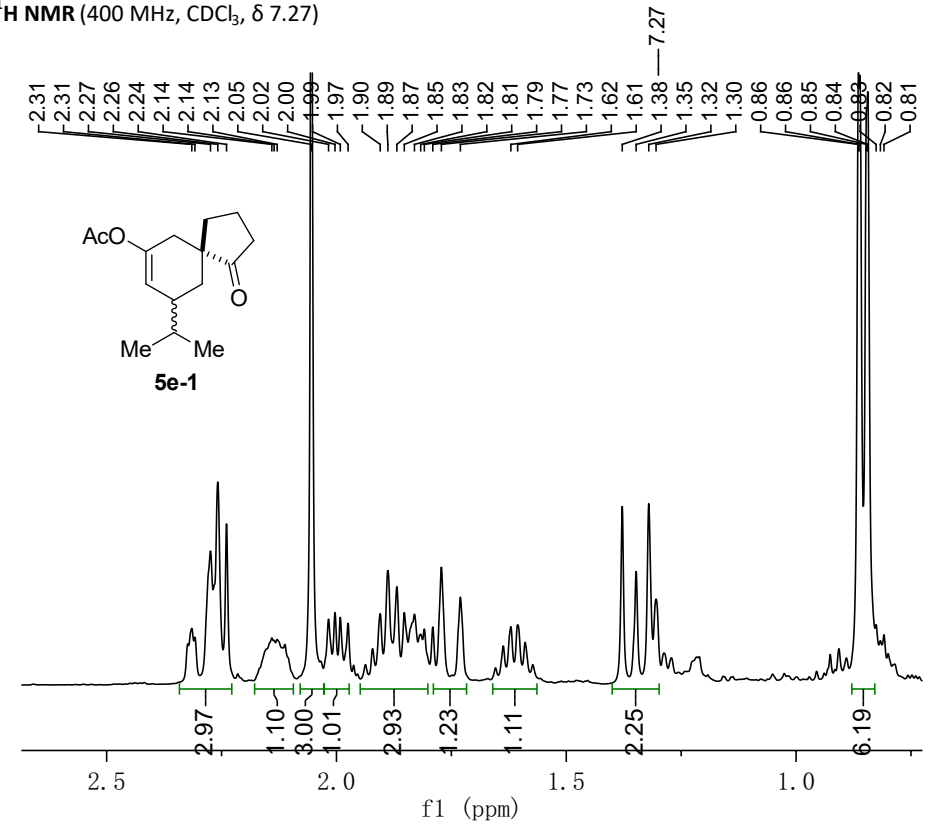
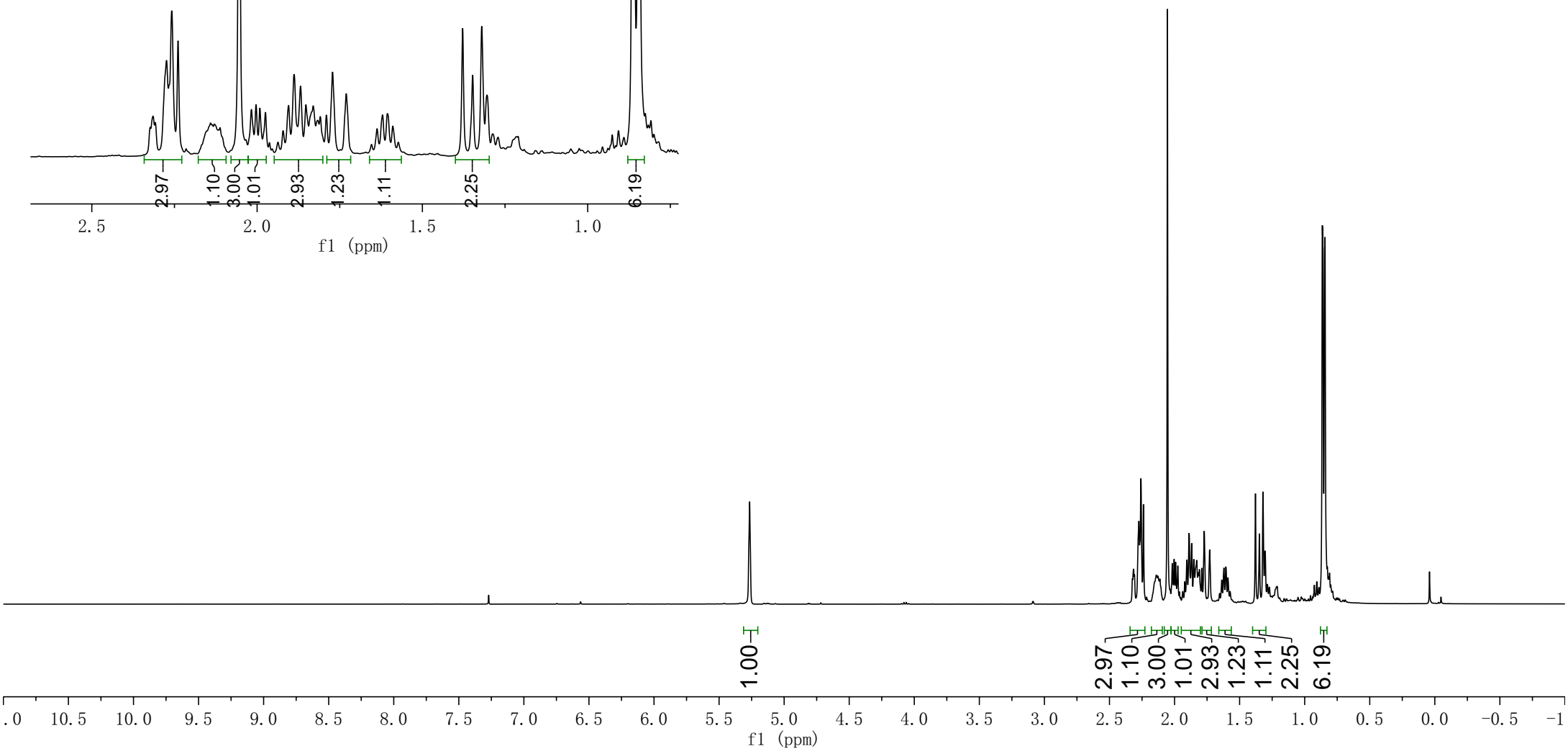


5e

5e-1:5e-2=1:1.2

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)





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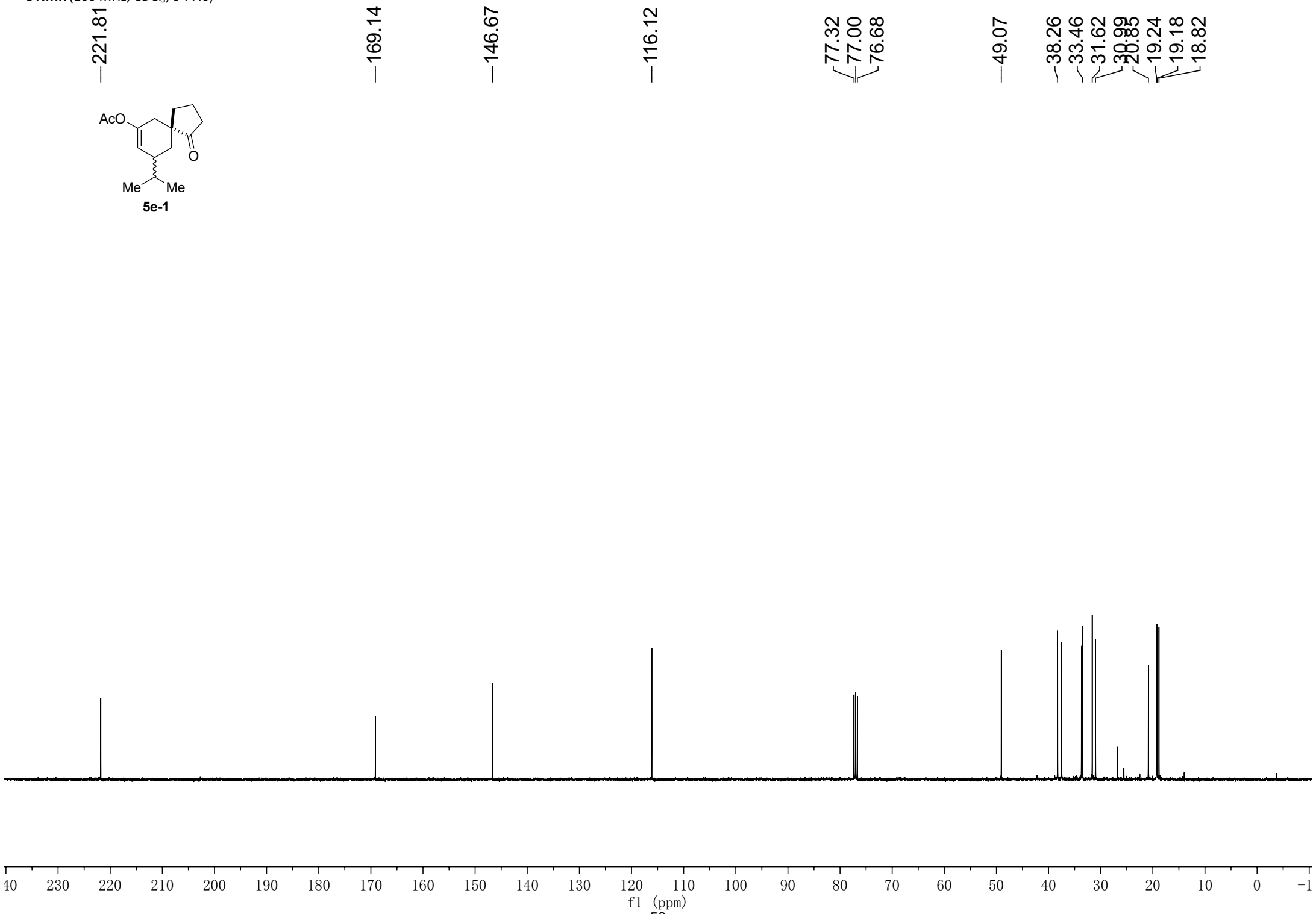

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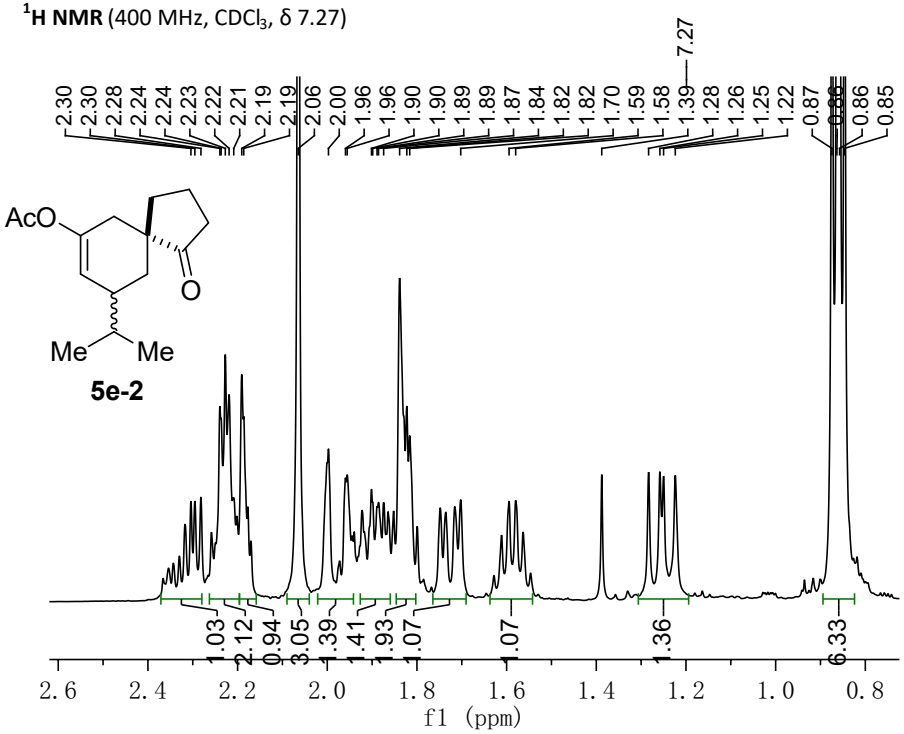

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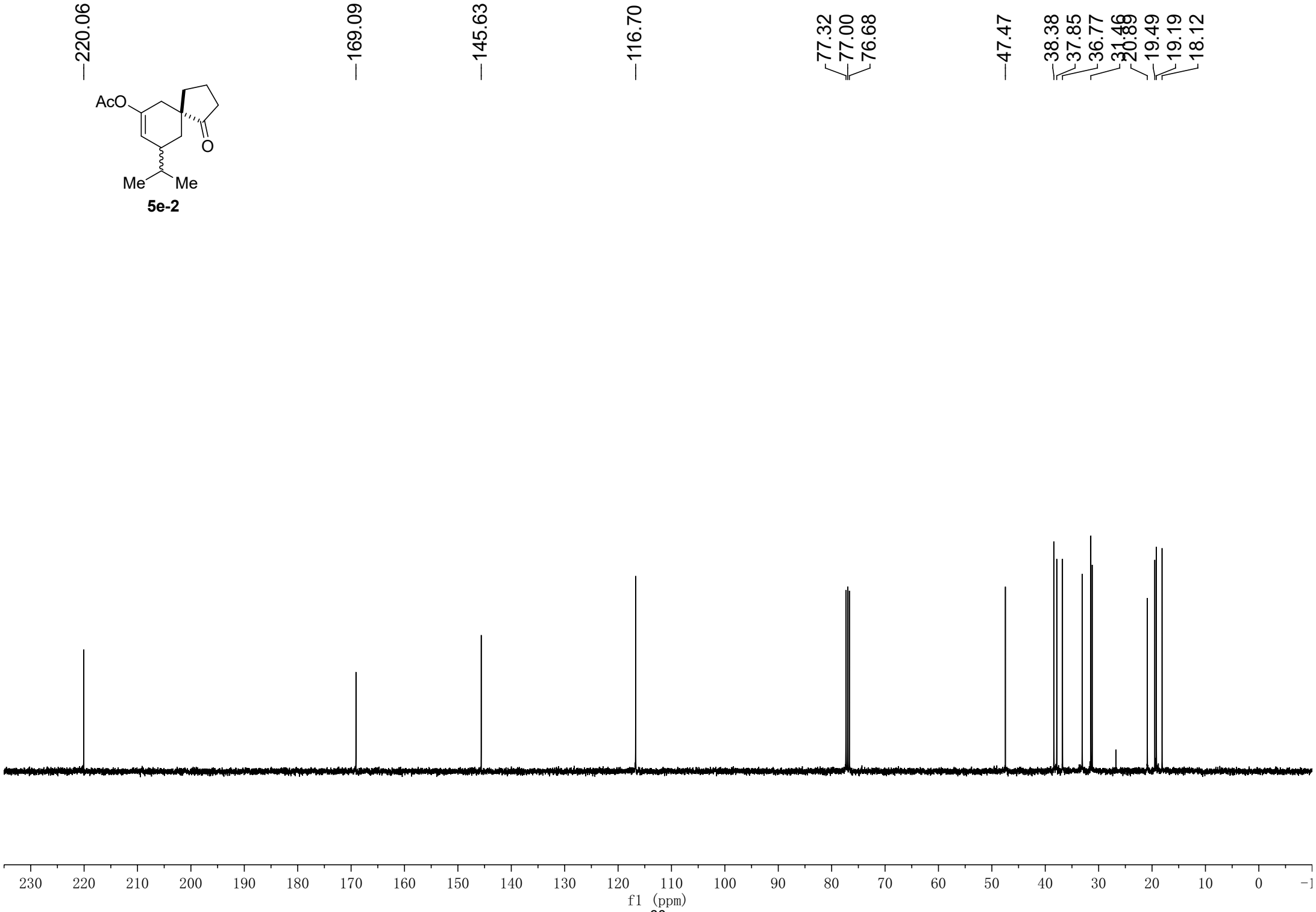

5e-2

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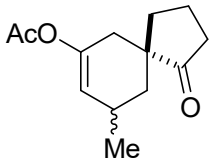

5f

$5f^a$:$5f^b$=1:1.4

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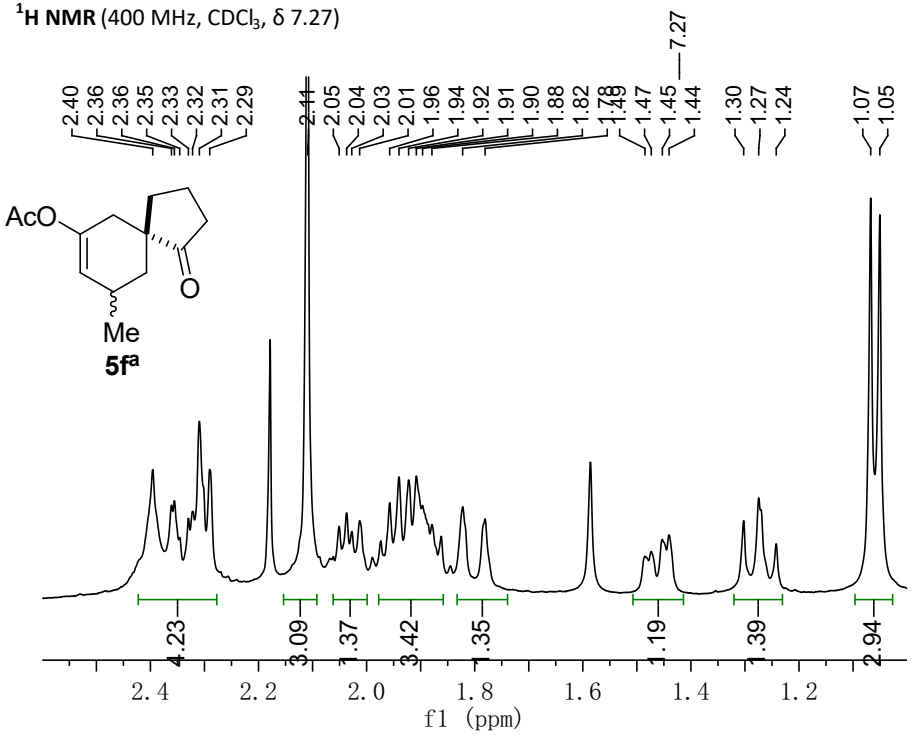
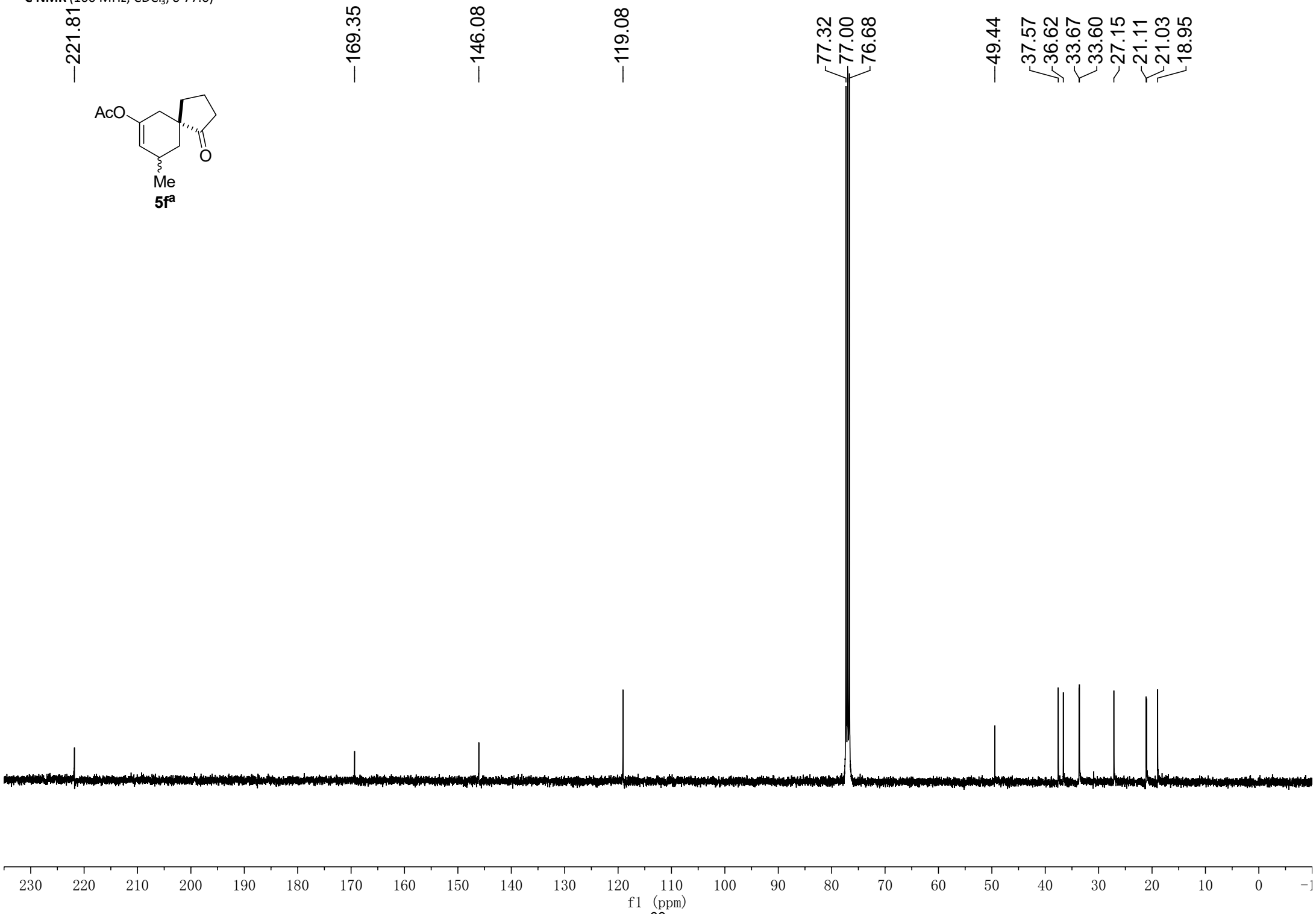


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



5f[a]

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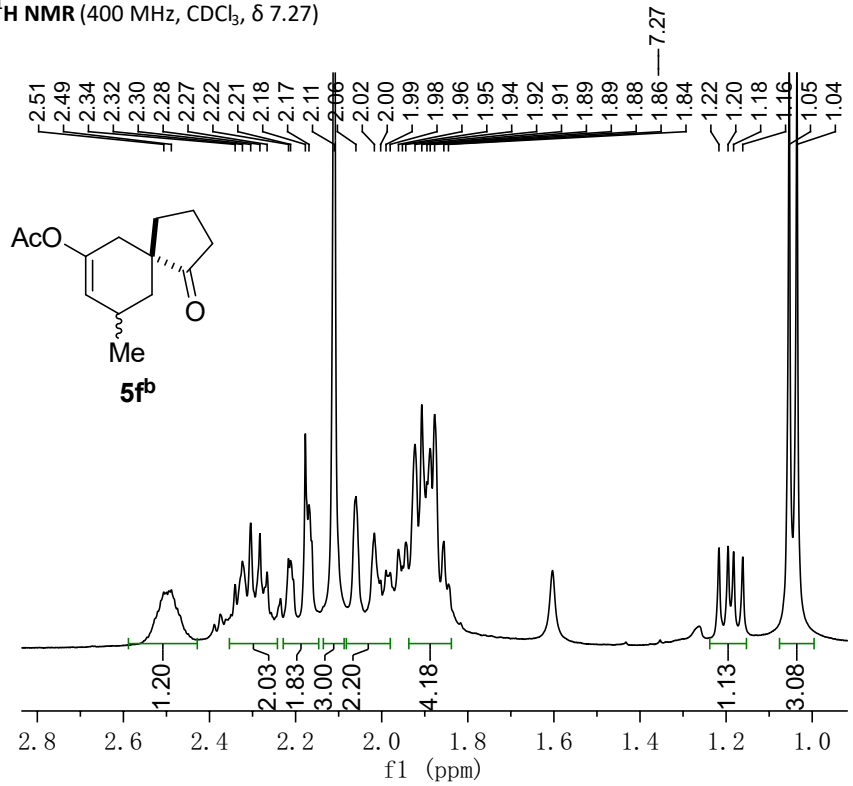

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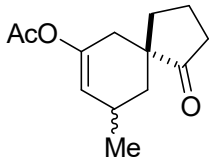
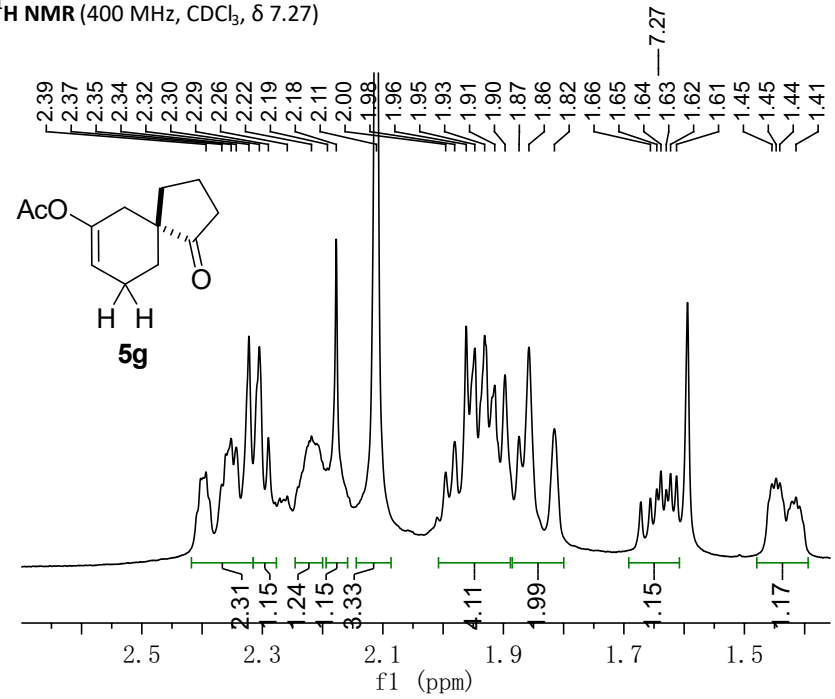
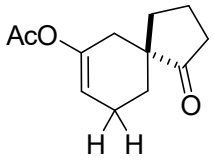


5f[b]

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

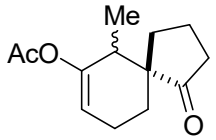


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



5g

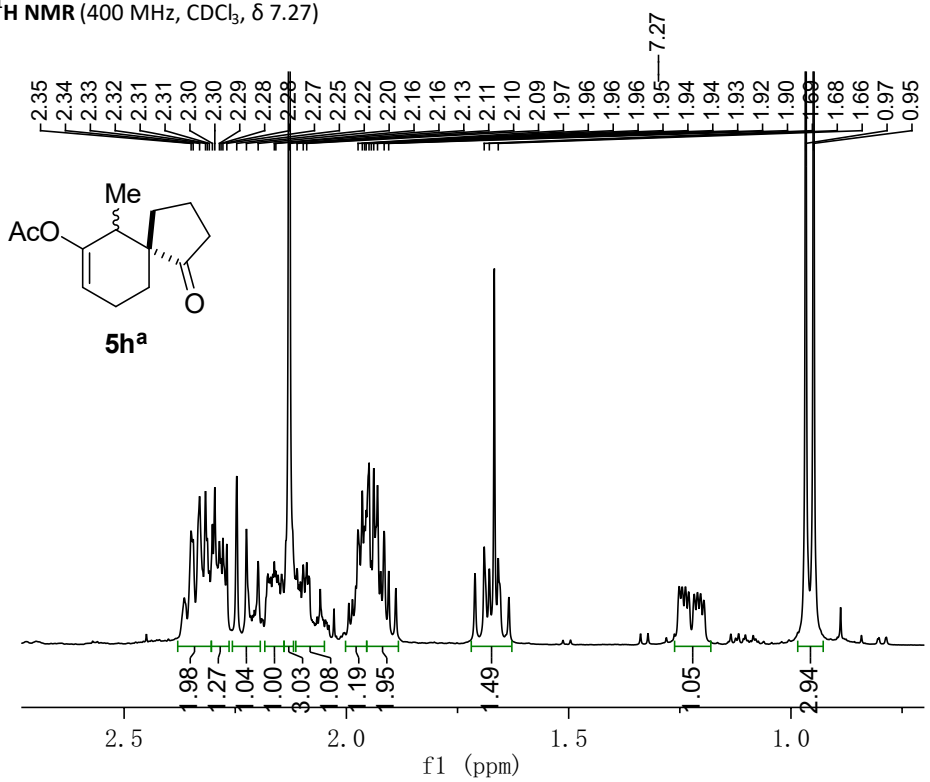
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



5h

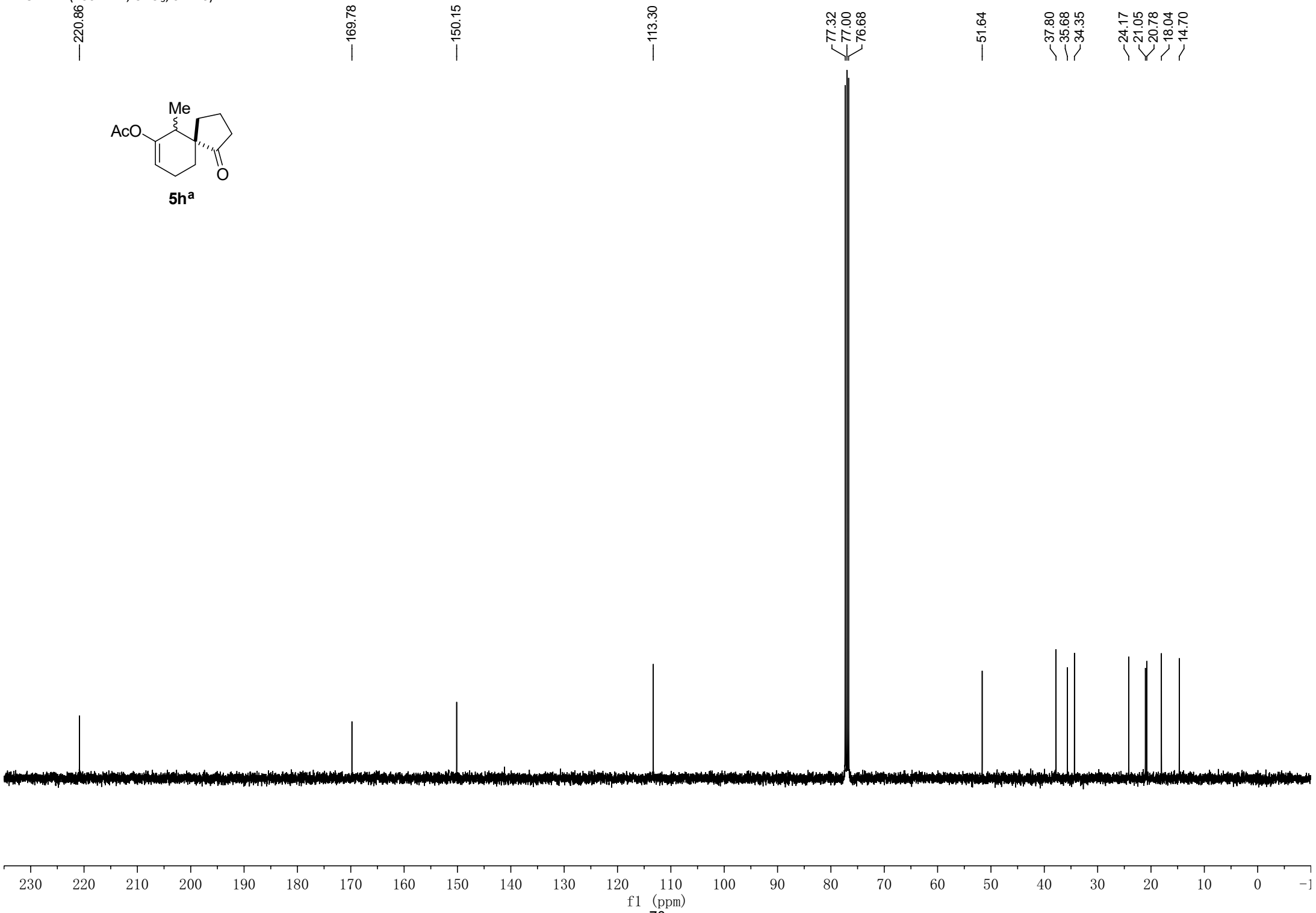
$5h^a$:$5h^b$=1:1.8

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



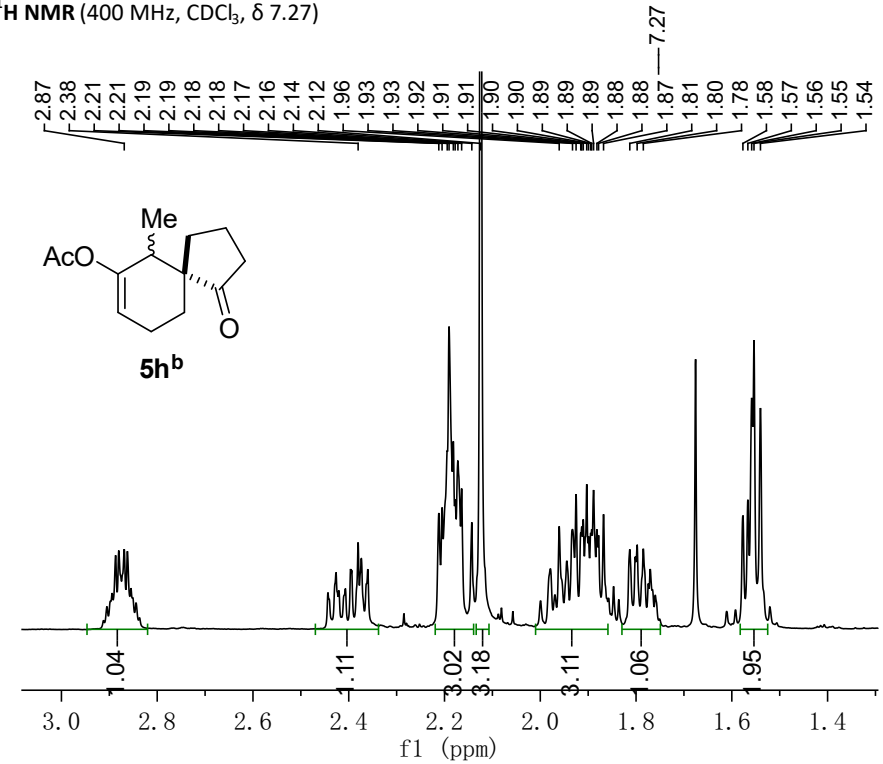
5h[a]

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

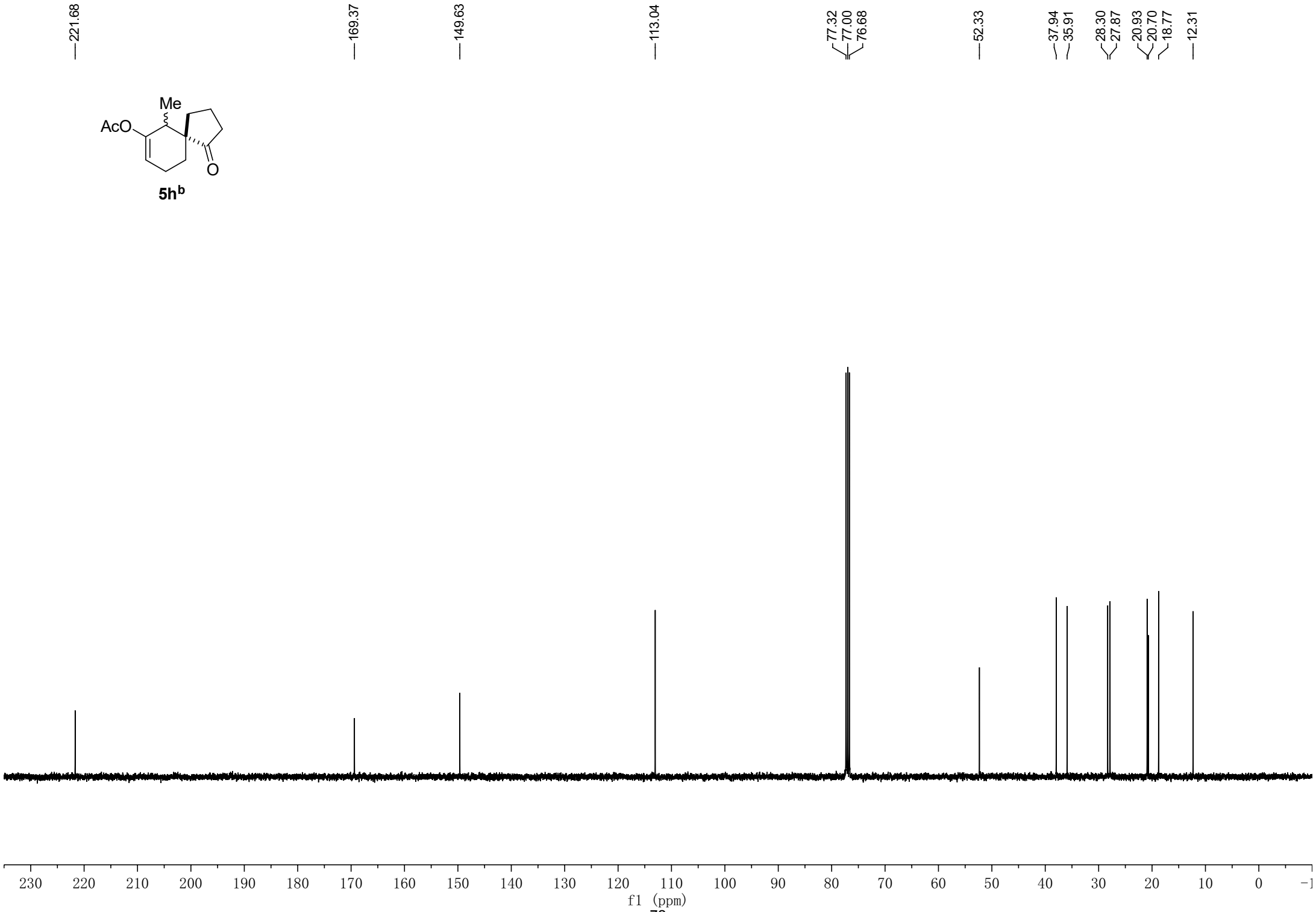


5h[a]

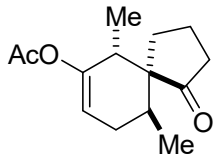
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

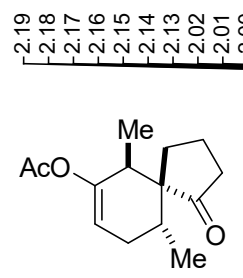


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



5i
d.r.=1:1.2:4

^{1}H NMR (600 MHz, $CDCl_3$, δ 7.27)

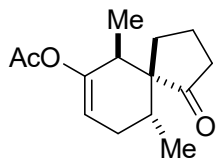


5i

f1 (ppm)

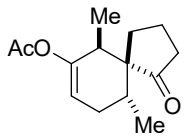
f1 (ppm)

^{13}C NMR (150 MHz, $CDCl_3$, δ 77.0)



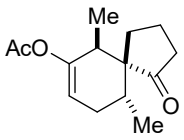
5i

HSQC (in $CDCl_3$)



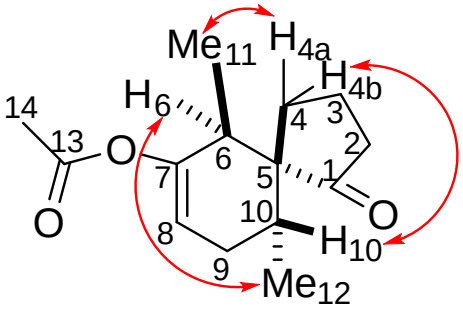
5i

HMBC – no HSQC (in $CDCl_3$)

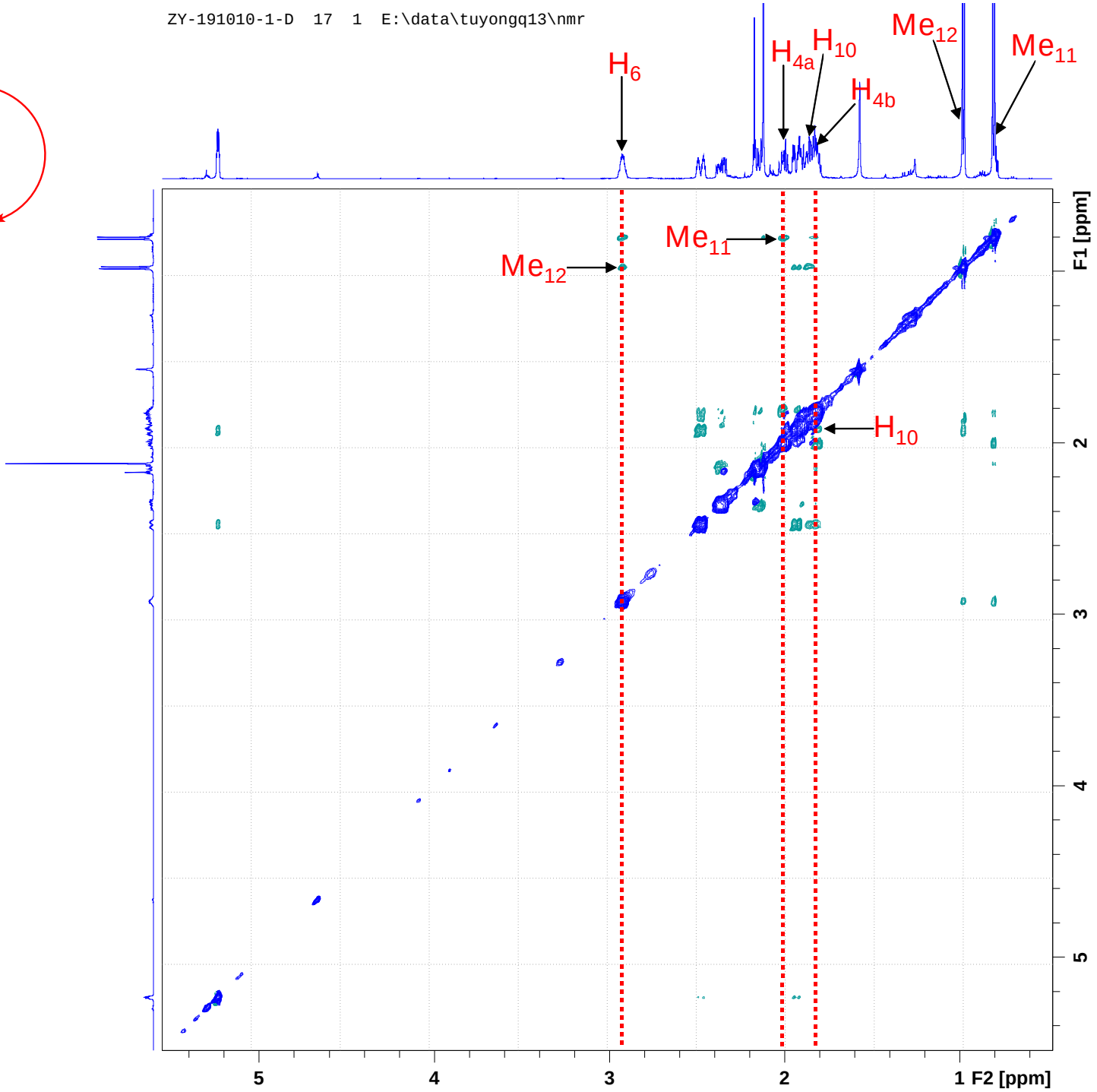


5i

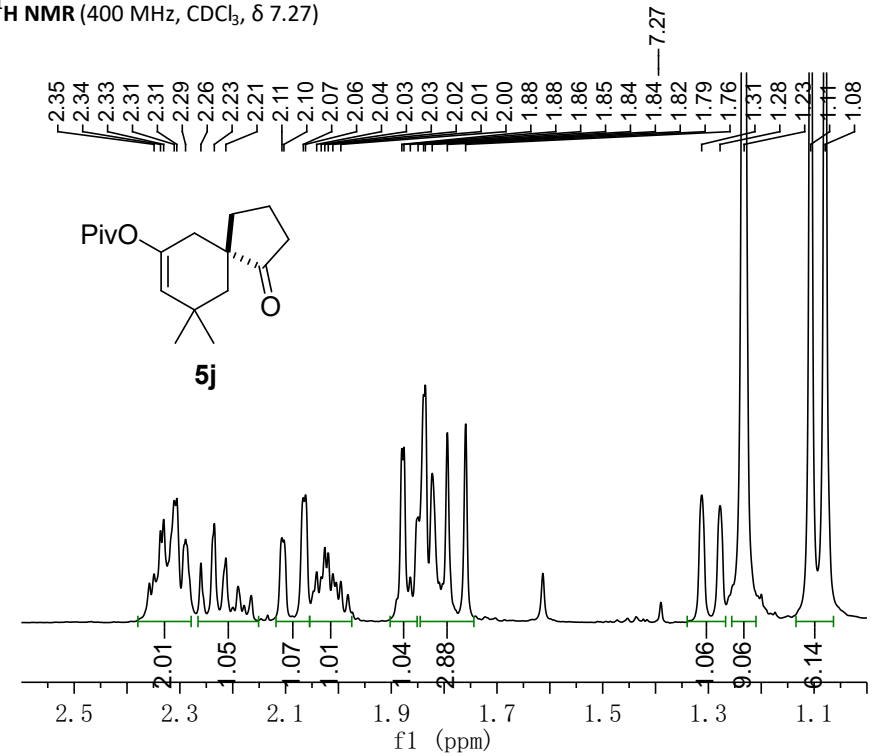
(600 MHz, in $CDCl_3$)



5i NOESY

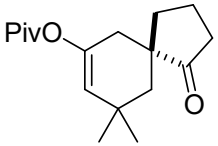


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

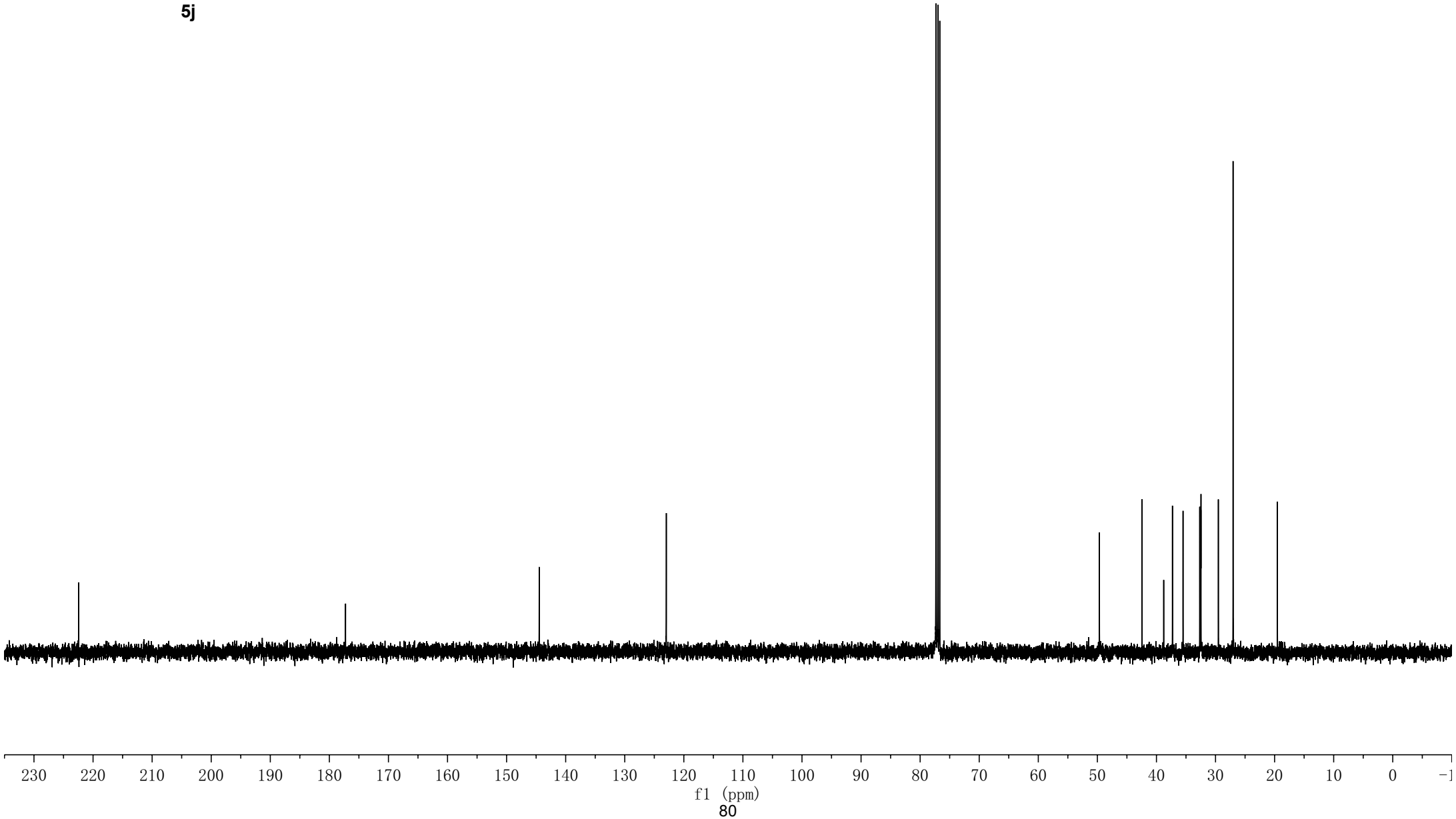


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

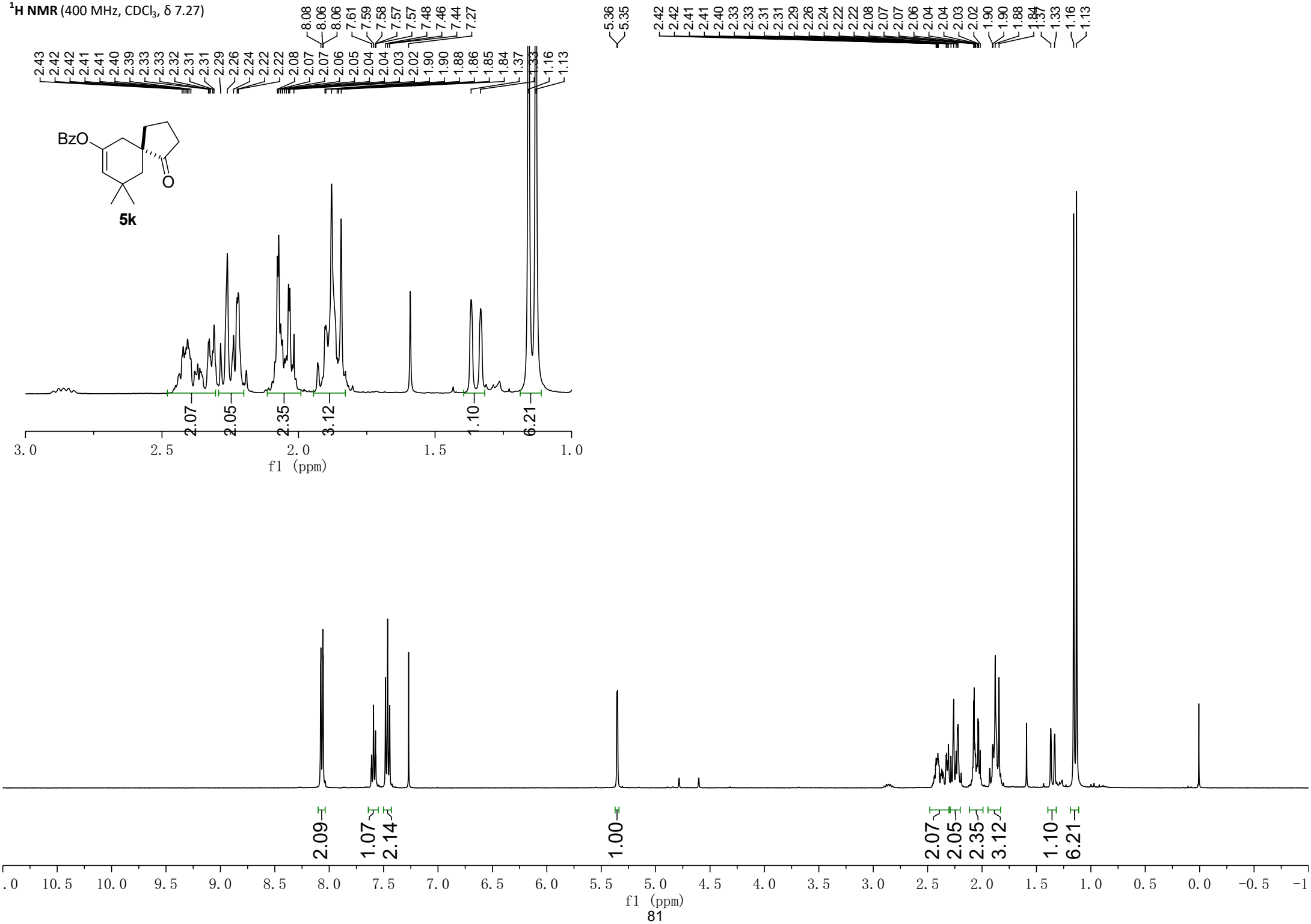
222.42 177.26 144.48 122.96 77.32 77.00 76.68 49.65 42.44 38.77 37.29 35.50 32.67 32.48 32.46 29.52 27.03 19.53



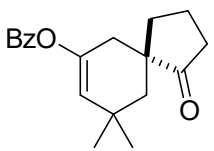
5j



^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

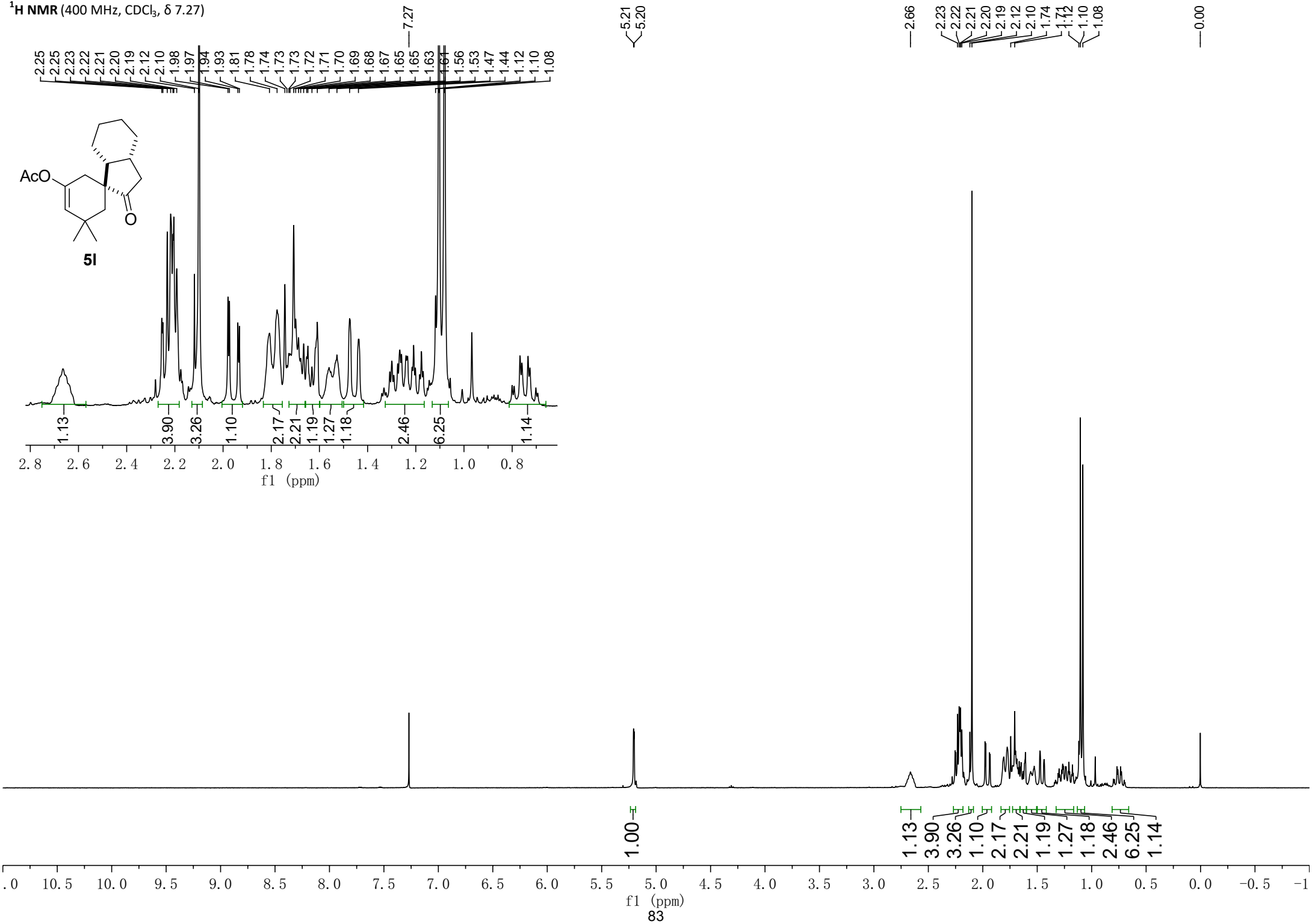


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

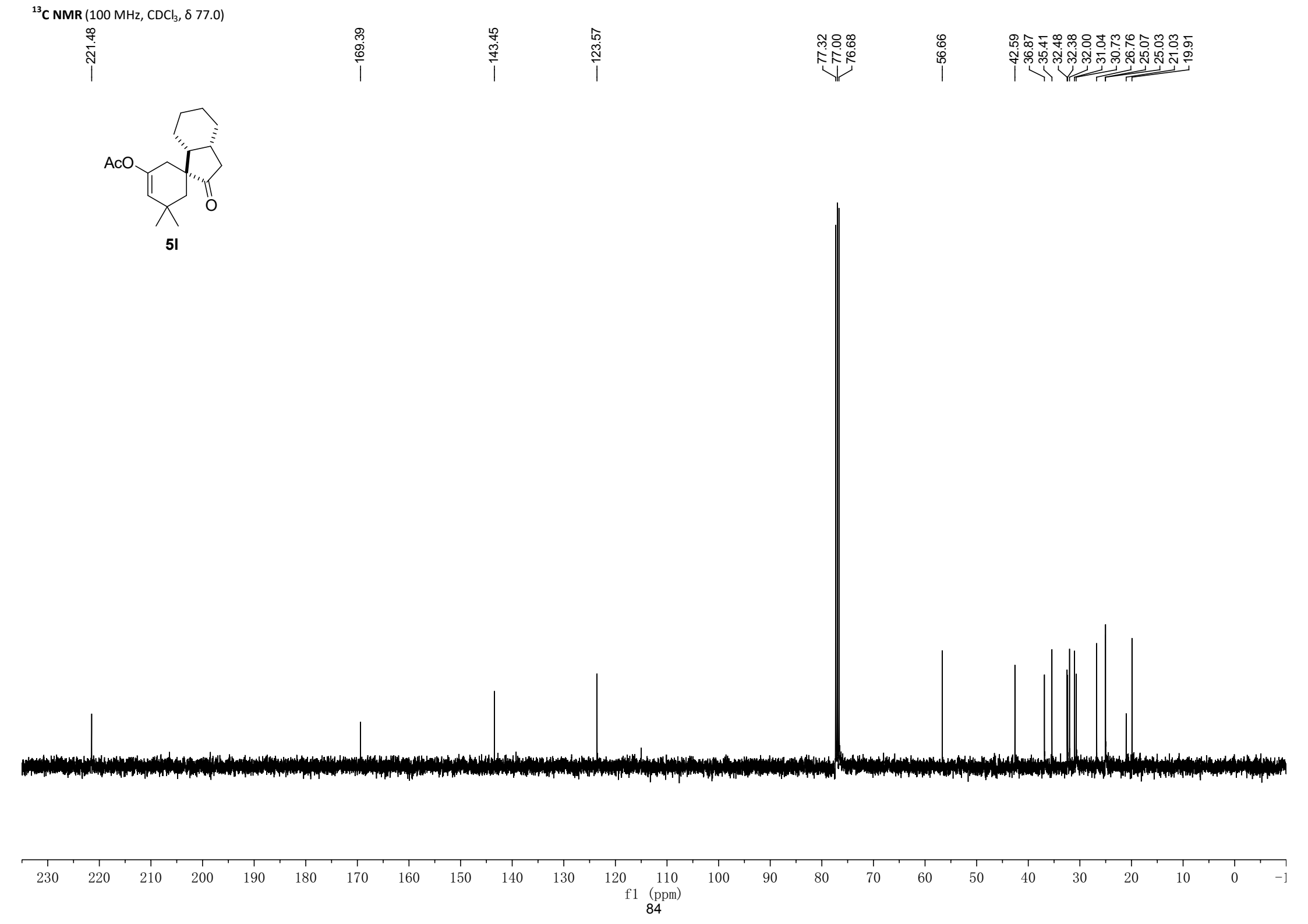


5k

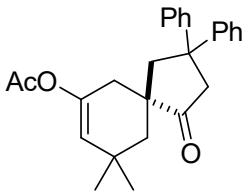
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

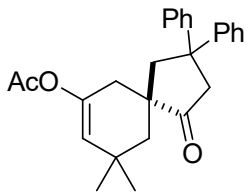


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



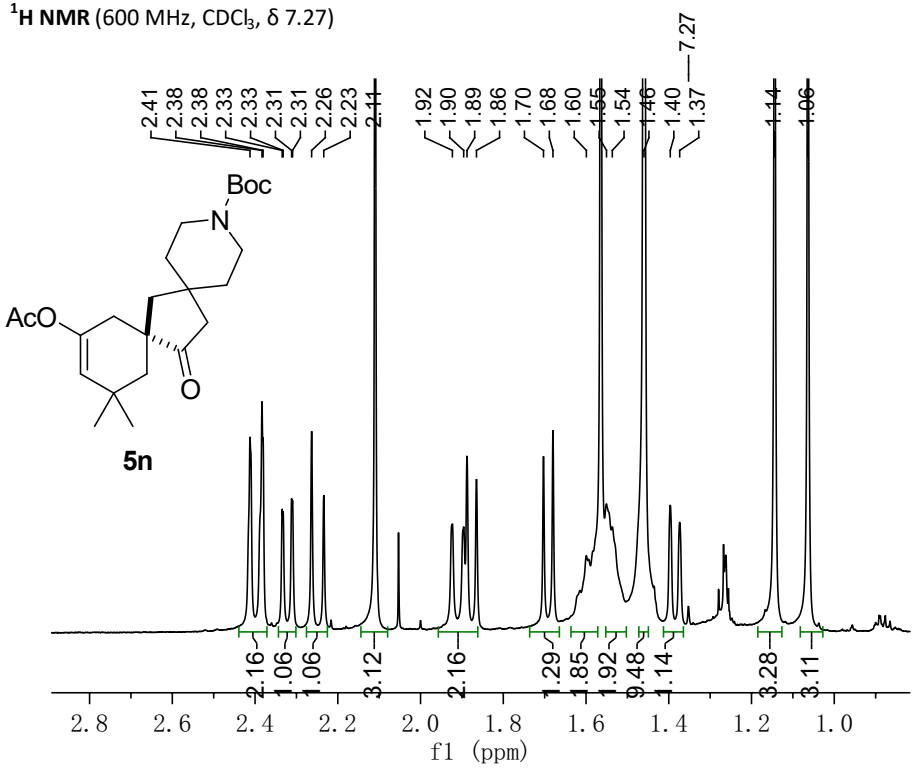
5m

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

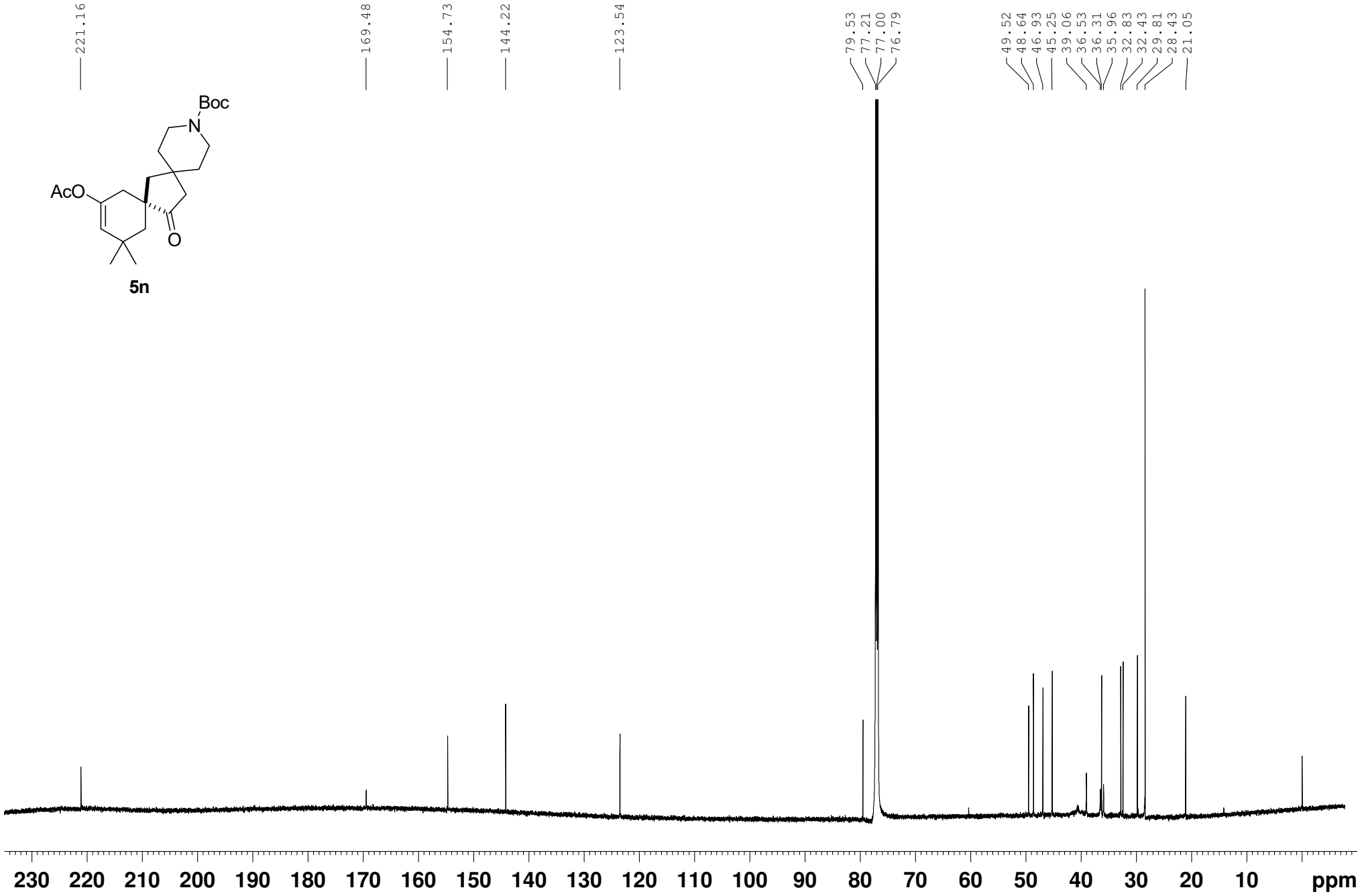


5m

^{1}H NMR (600 MHz, $CDCl_3$, δ 7.27)

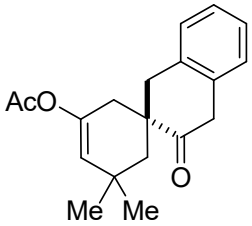


^{13}C NMR (150 MHz, $CDCl_3$, δ 77.0)

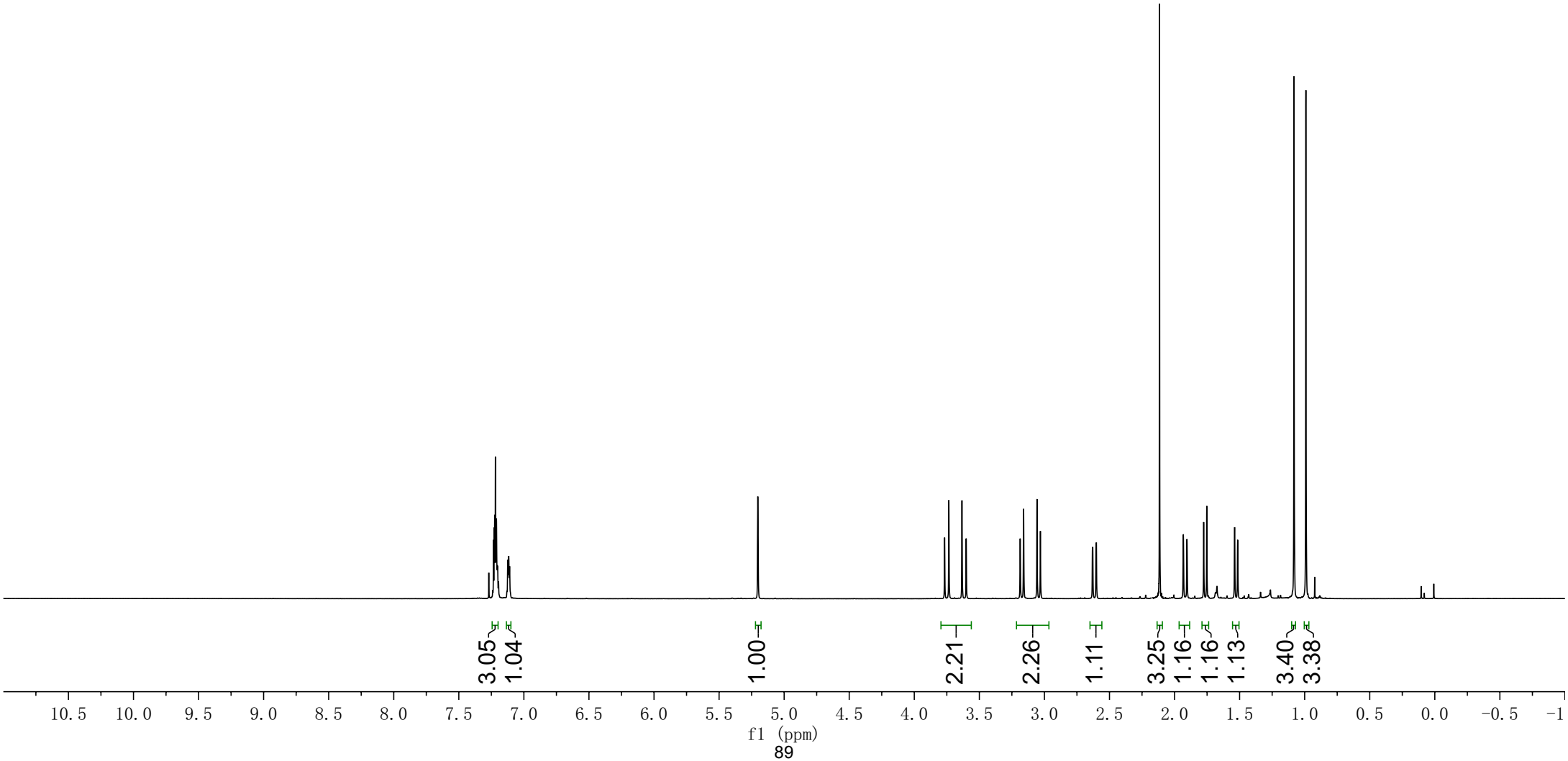


5n

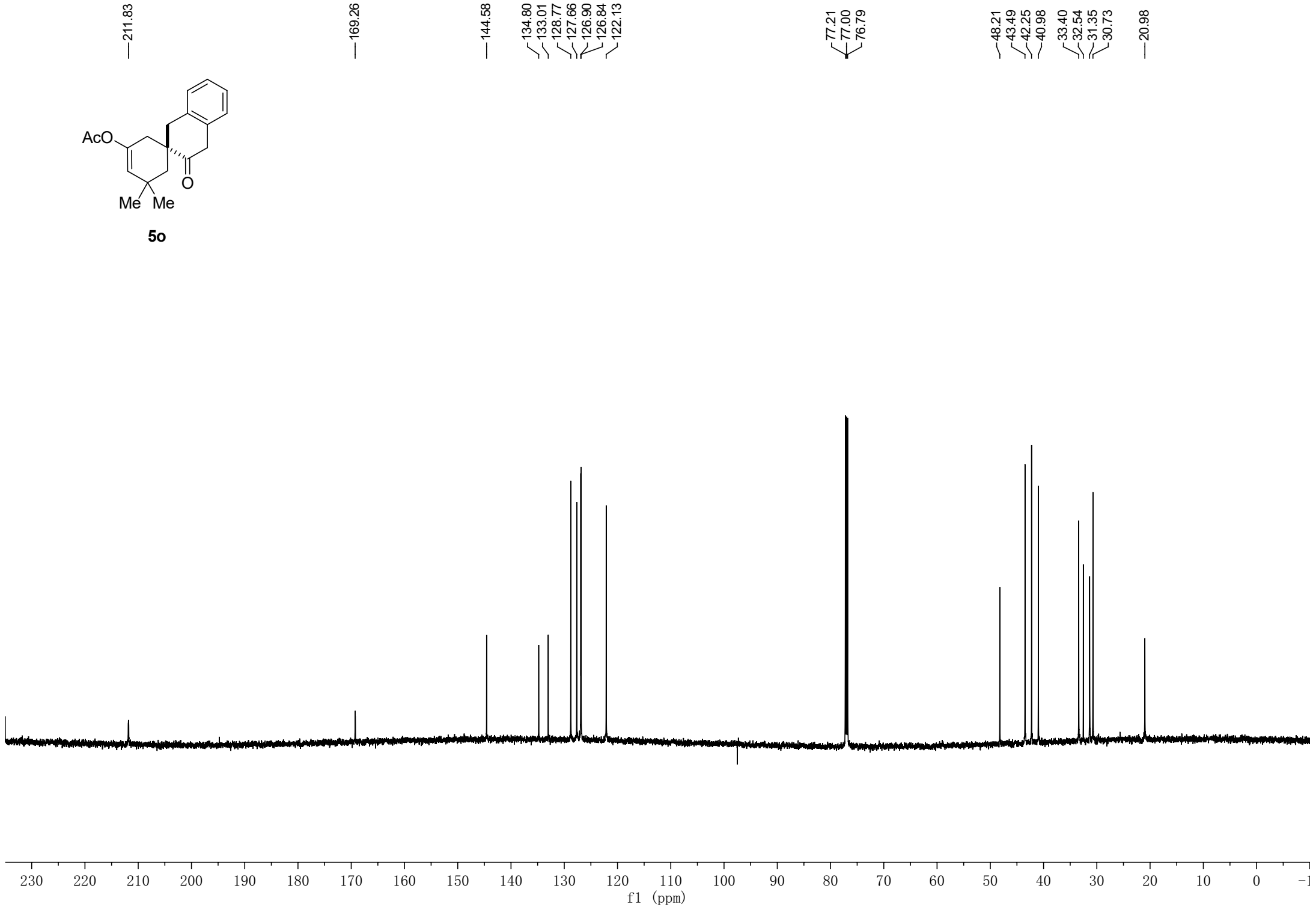
^{1}H NMR (600 MHz, $CDCl_3$, δ 7.27)



5o

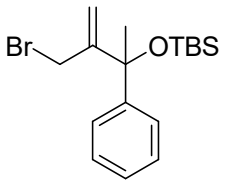


^{13}C NMR (150 MHz, $CDCl_3$, δ 77.0)



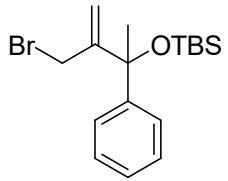
5o

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



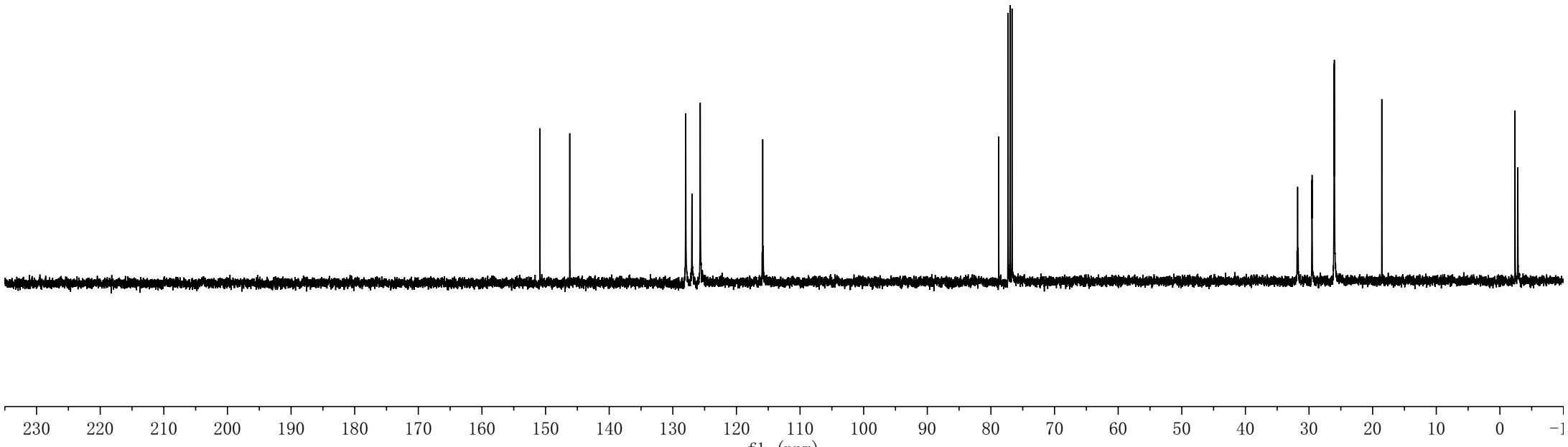
6a

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

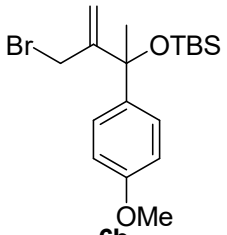


6a

150.88
146.20
127.97
126.99
125.69
115.87
78.77
77.32
77.00
76.68
31.79
29.55
29.52
26.06
26.02
18.56
-2.38
-2.82

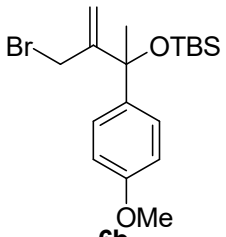


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



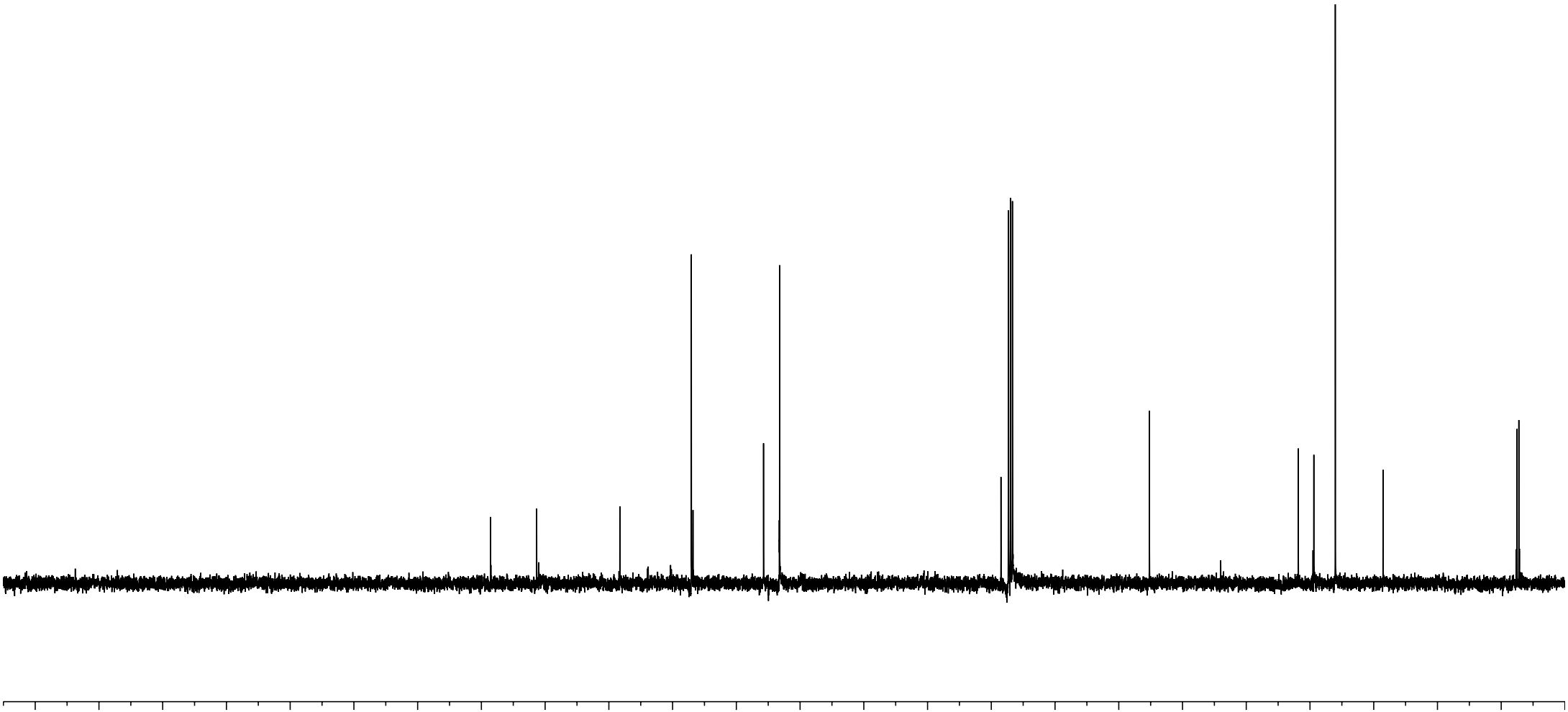
6b

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



6b

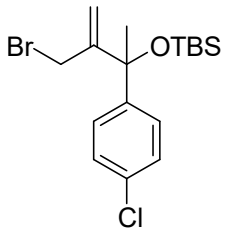
158.56
151.33
138.28
127.06
126.80
115.73
113.26
113.21
78.48
77.32
77.00
76.68
55.19
31.84
29.40
26.03
18.53
-2.48
-2.77



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

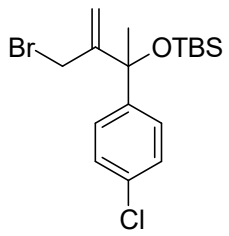
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



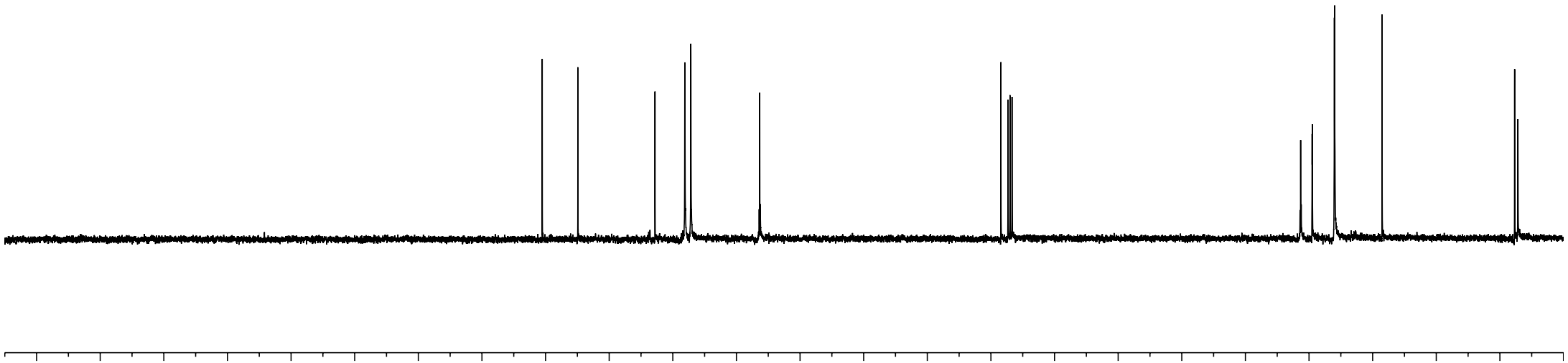
6c

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

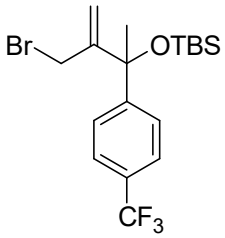


6c

150.52
144.92
132.80
128.11
127.17
116.34
78.43
77.32
77.00
76.68
31.32
29.51
29.49
26.02
25.97
18.51
-2.32
-2.82
-2.84

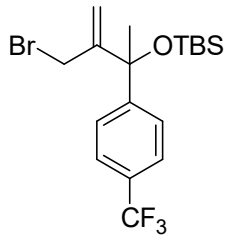


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



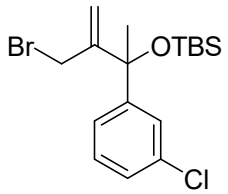
6d

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



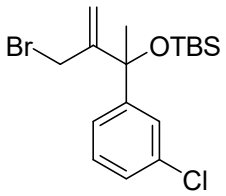
6d

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



6e

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



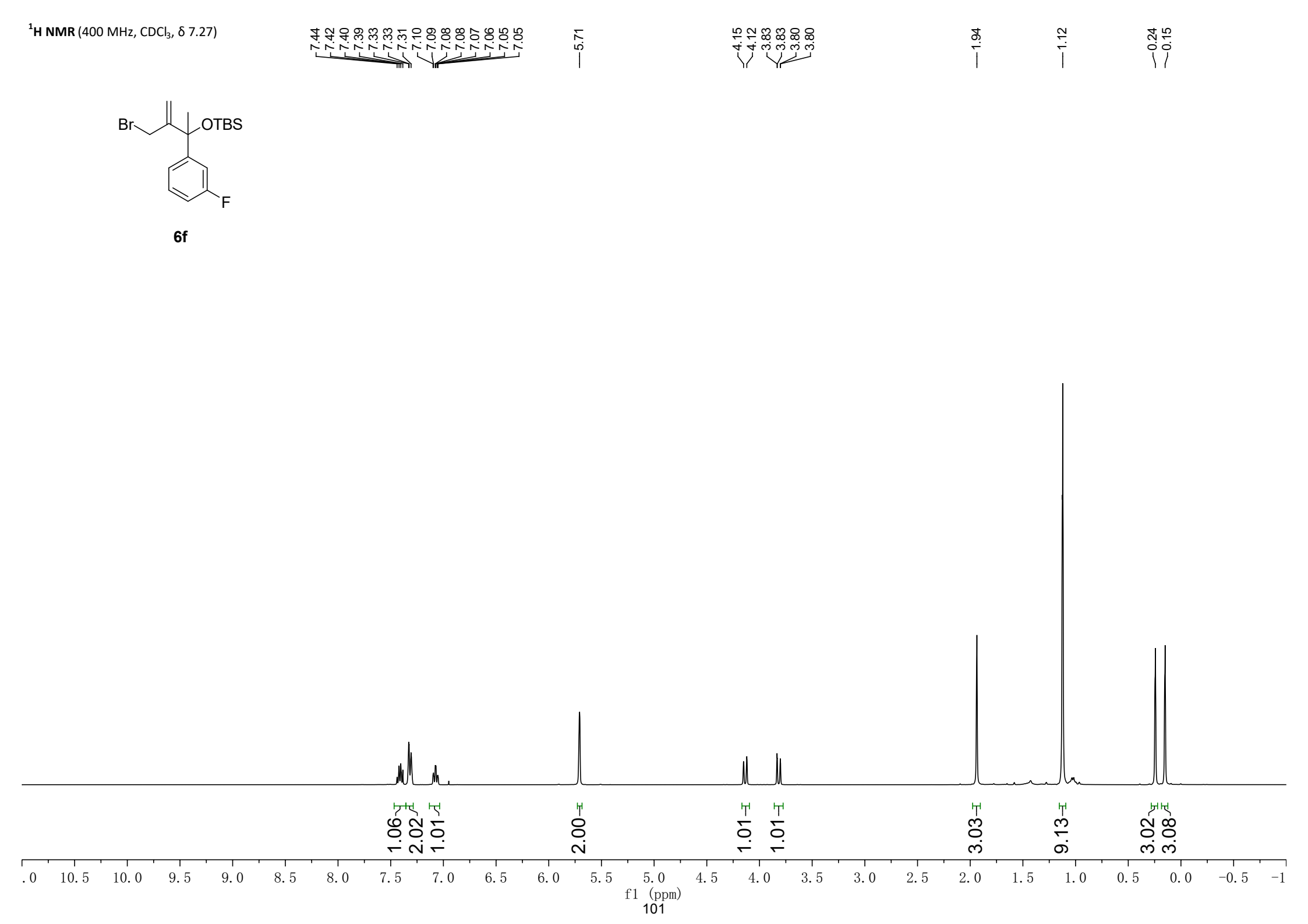
6e

150.34
148.63
134.04
129.32
127.19
126.12
123.86
116.52
78.49
77.32
77.00
76.68
31.31
29.49
26.00
18.55
-2.32
-2.84

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

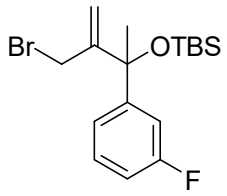
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



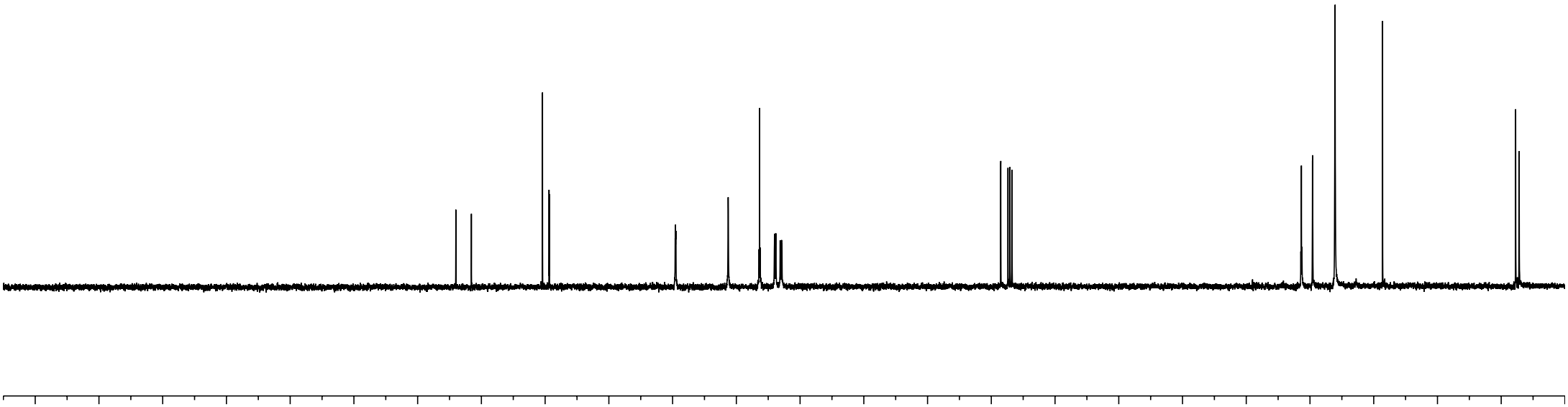
6f

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

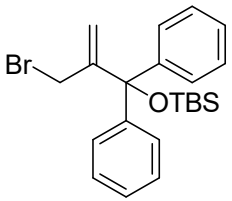


6f

164.01
161.57
150.41
149.38
149.32
129.55
129.48
121.28
116.44
116.35
116.26
114.01
113.80
113.13
113.07
112.90
112.84
78.51
77.38
77.06
76.75
31.35
29.61
29.58
26.10
26.06
18.61
-2.26
-2.80
-2.82

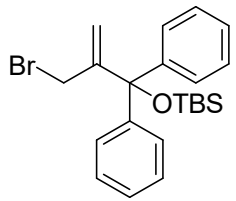


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



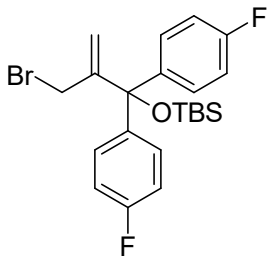
6g

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



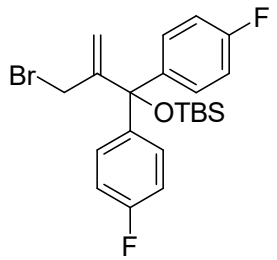
6g

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



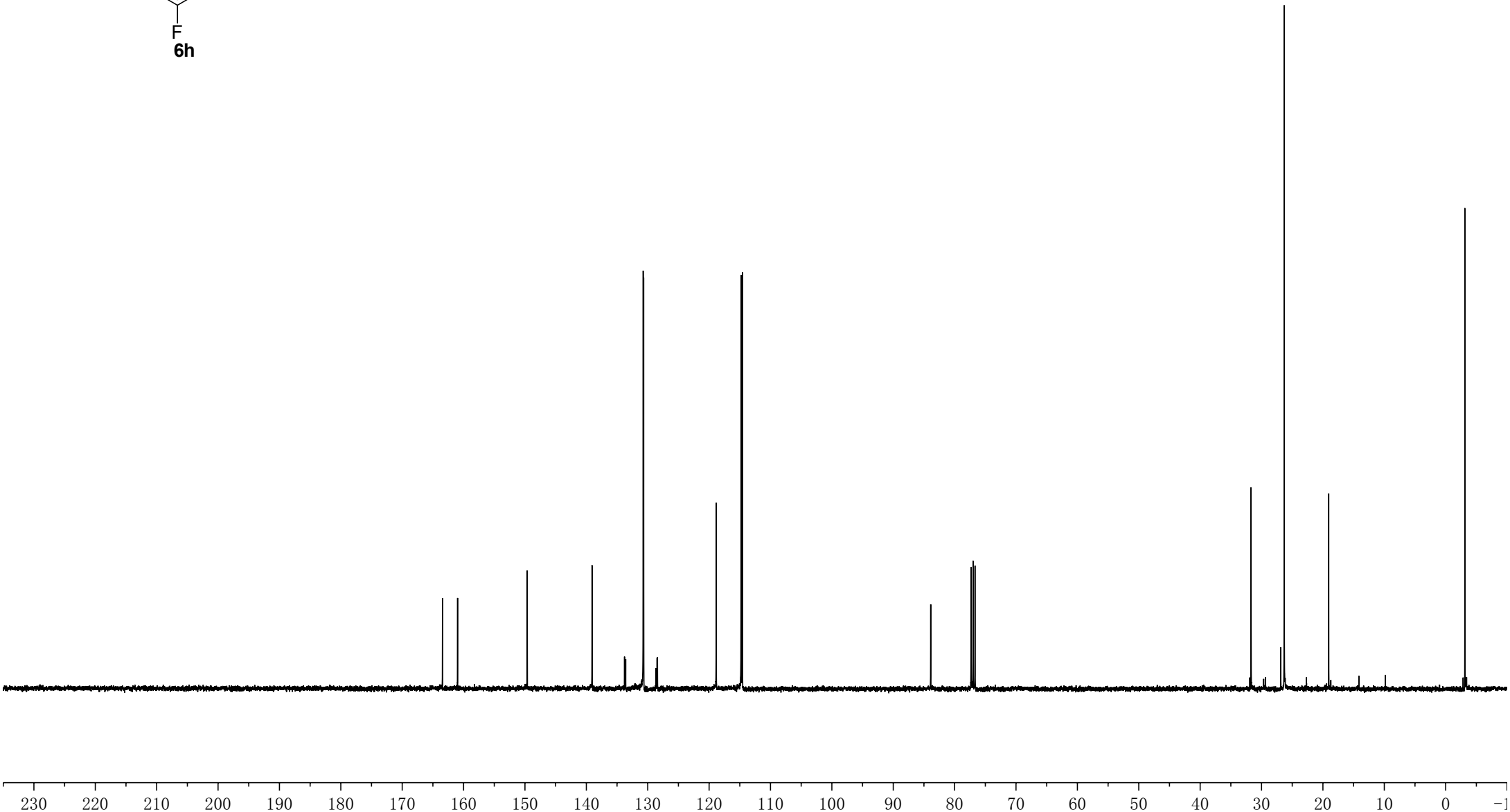
6h

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

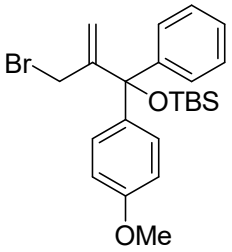


6h

163.44
160.98
149.62
139.07
139.04
133.78
133.59
130.74
130.66
128.66
128.48
128.41
118.84
114.79
114.58
83.90
77.32
77.00
76.68
31.70
26.31
19.06
-3.13

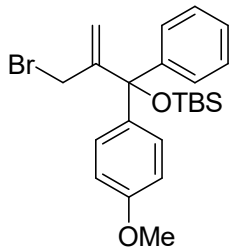


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



6i

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



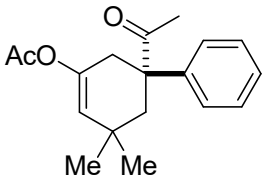
6i

159.05
149.96
143.72
135.30
130.58
128.80
128.71
127.71
127.51
118.08
112.98
84.47
77.32
77.00
76.68
55.26
32.39
26.41
19.10
-3.16
-3.18

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

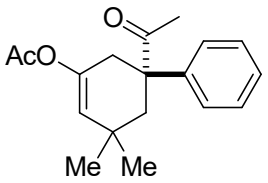
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



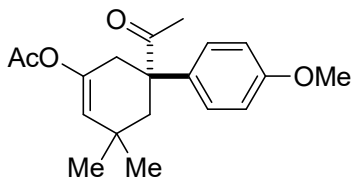
7a

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

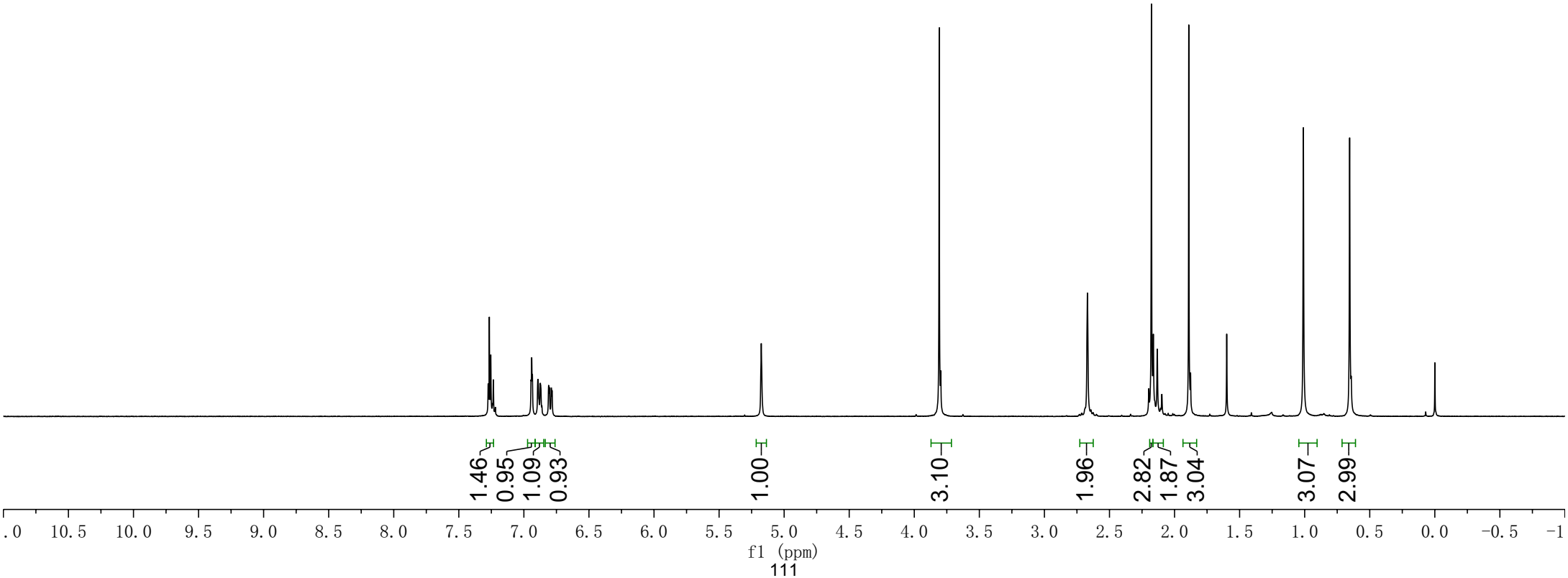


7a

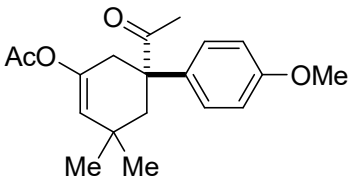
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



7b



^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



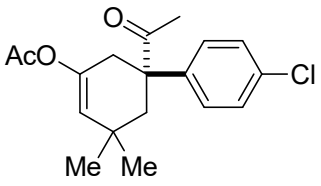
7b

208.43
169.48
160.05
143.65
143.03
129.80
123.32
118.95
112.78
112.19
77.32
77.00
76.68
55.79
55.31
42.74
33.10
32.29
31.16
29.58
25.36
21.09

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

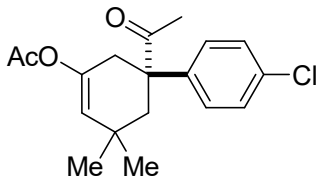
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



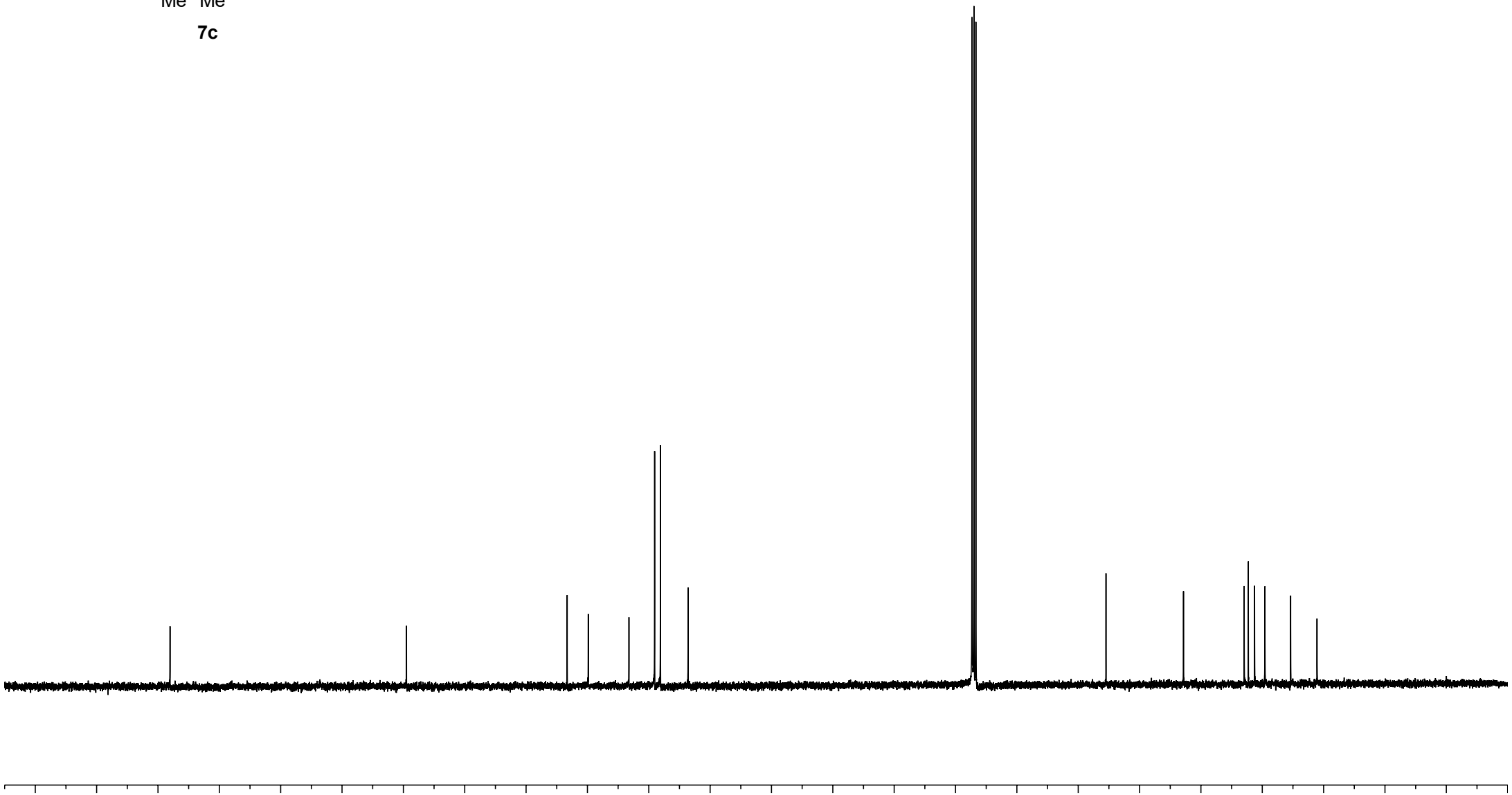
7c

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

208.03 169.50 143.30 139.87 133.23 129.04 128.10 123.59 77.32 77.00 76.68 55.47 42.84 32.95 32.27 31.25 29.57 25.38 21.08



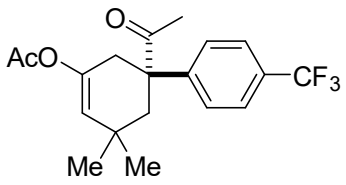
7c



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

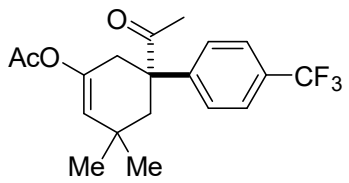
f1 (ppm)

^{1}H NMR (600 MHz, $CDCl_3$, δ 7.27)



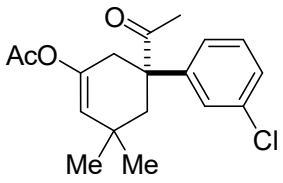
7d

^{13}C NMR (150 MHz, $CDCl_3$, δ 77.0)



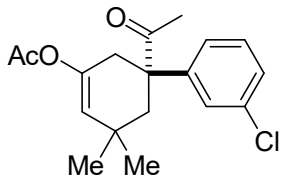
7d

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



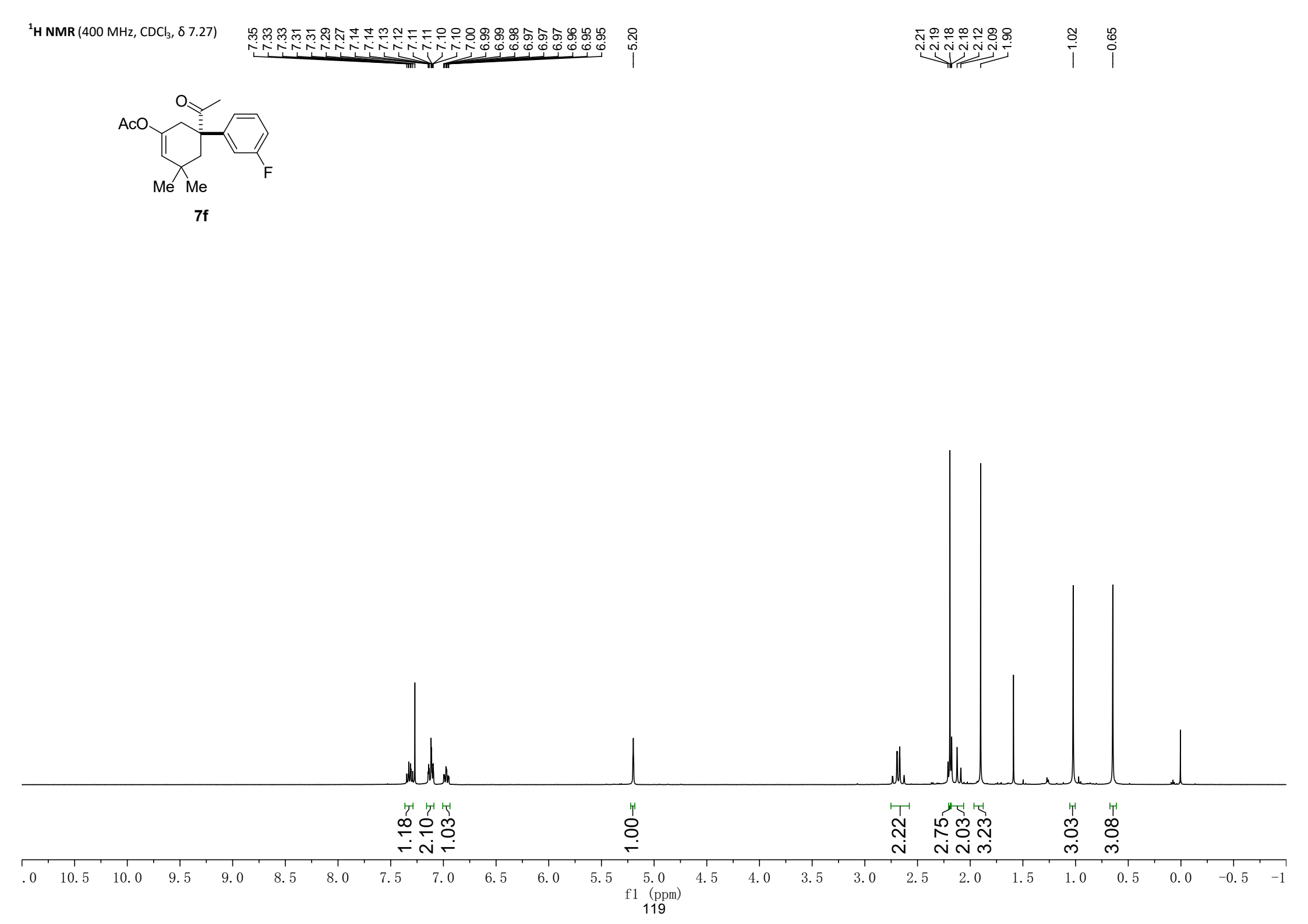
7e

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



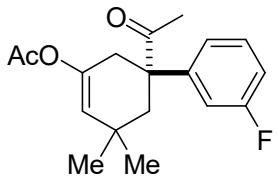
7e

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



7f

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



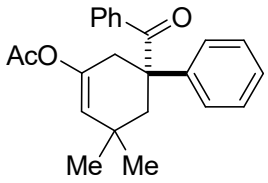
7f

207.84
169.51
164.48
162.03
144.17
143.35
130.41
130.33
123.53
122.41
122.38
114.35
114.14
114.01
113.79
77.32
77.00
76.68
55.78
42.84
33.06
32.28
31.17
29.59
25.39
21.06

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

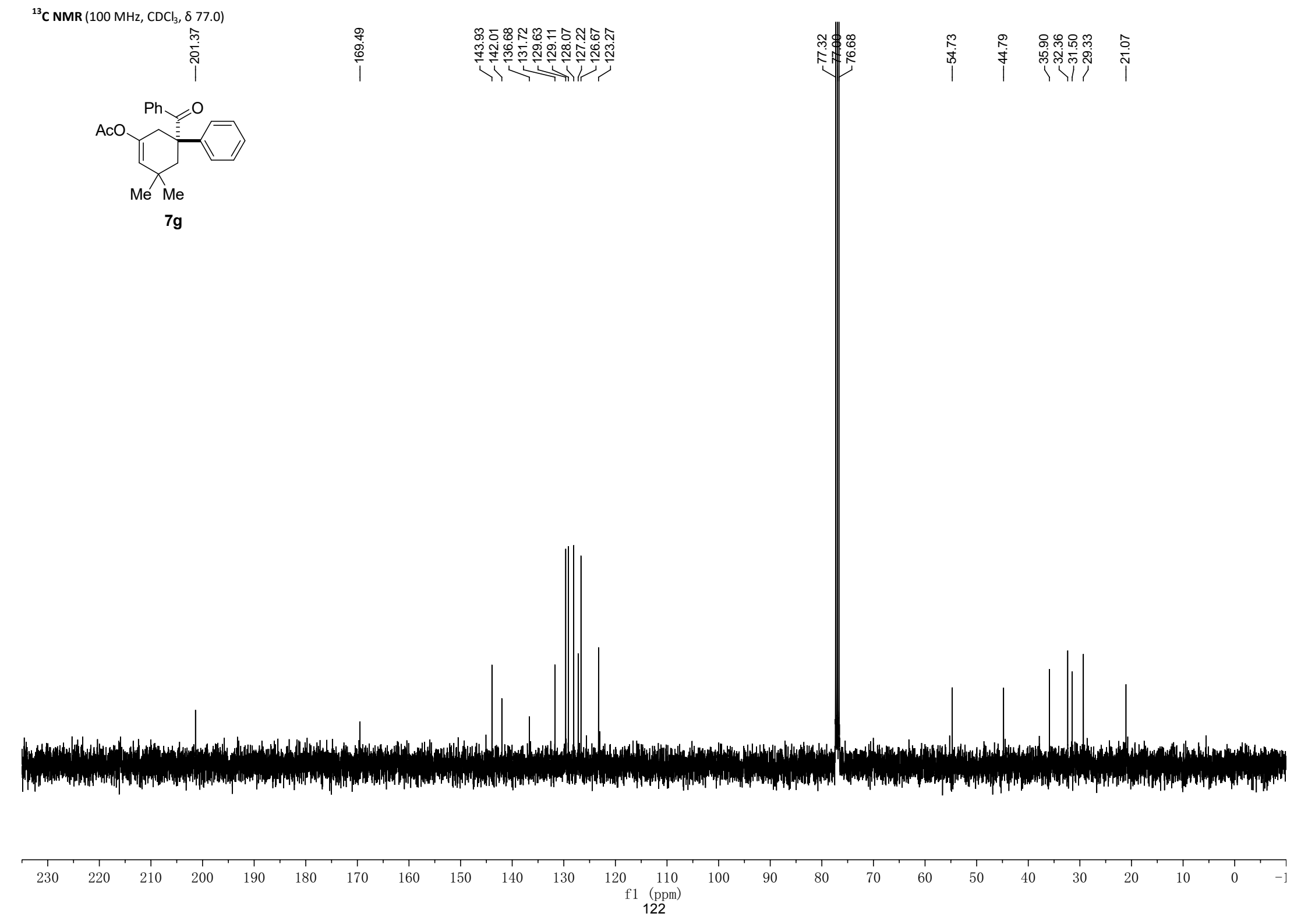
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

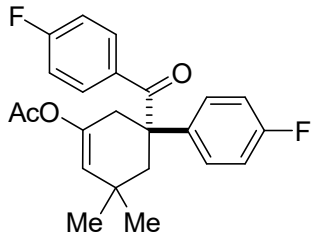


7g

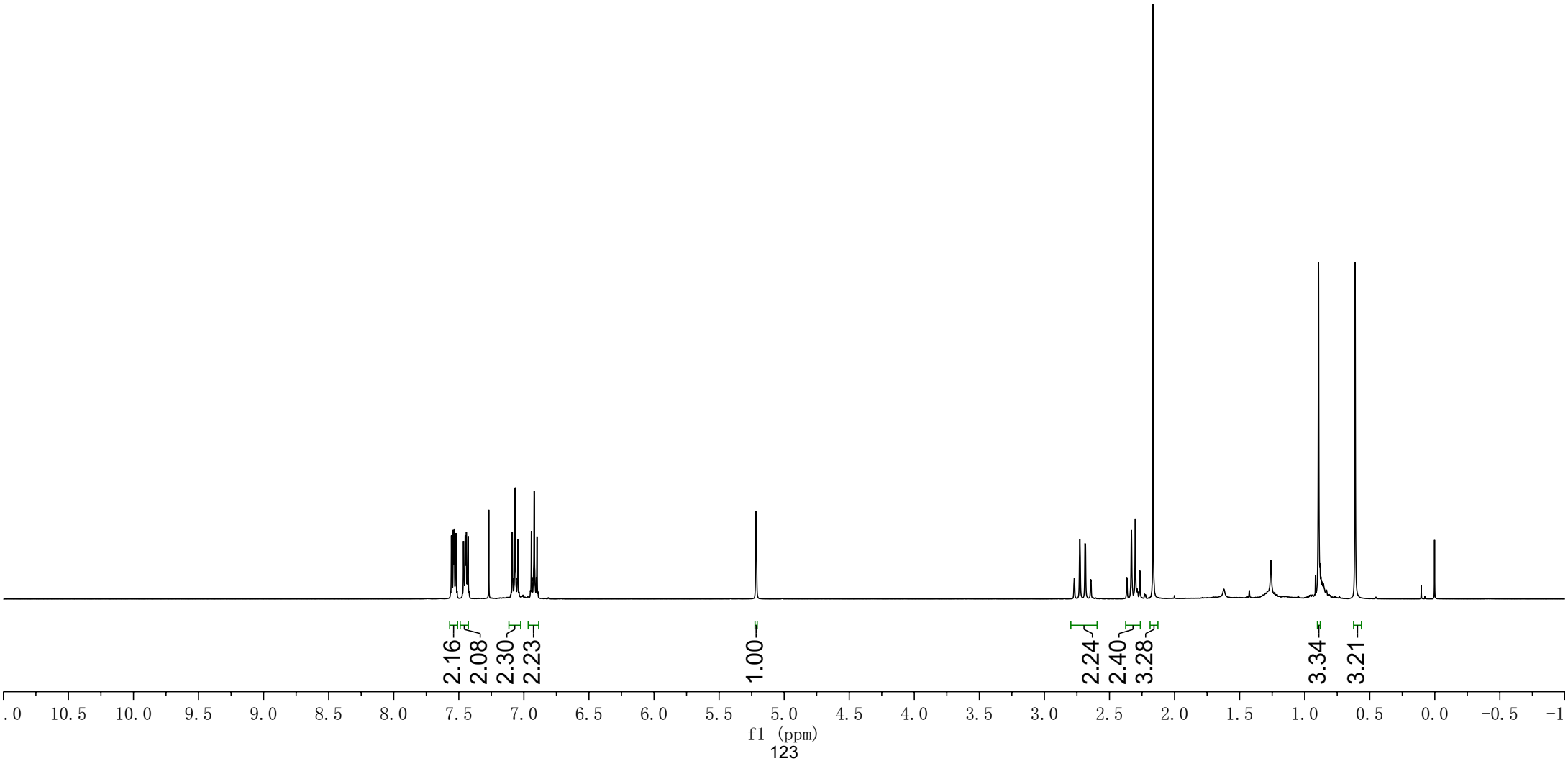
^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



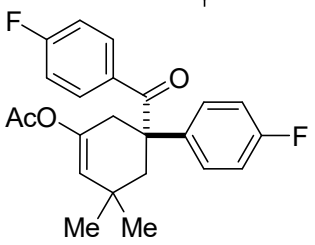
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



7h



^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



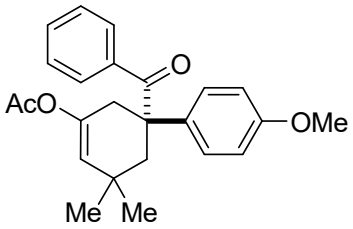
7h

199.47
169.63
165.85
163.32
163.15
160.69
143.60
137.73
132.47
132.31
132.22
128.32
128.24
116.05
115.39
115.18
77.32
77.00
76.68
54.13
44.90
35.96
32.31
31.48
29.25
21.07

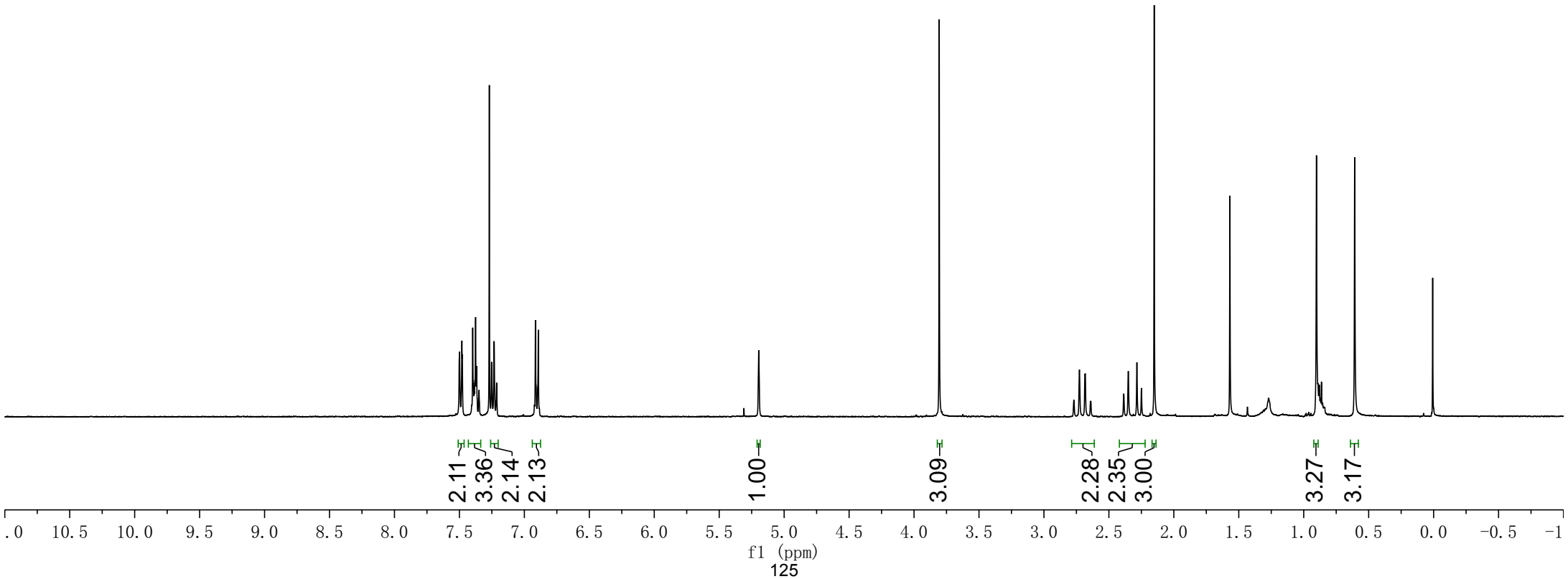
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

f1 (ppm)

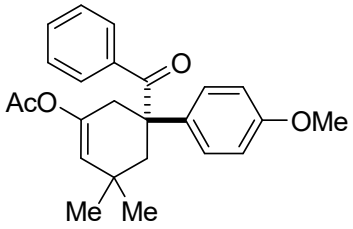
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



7i



^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

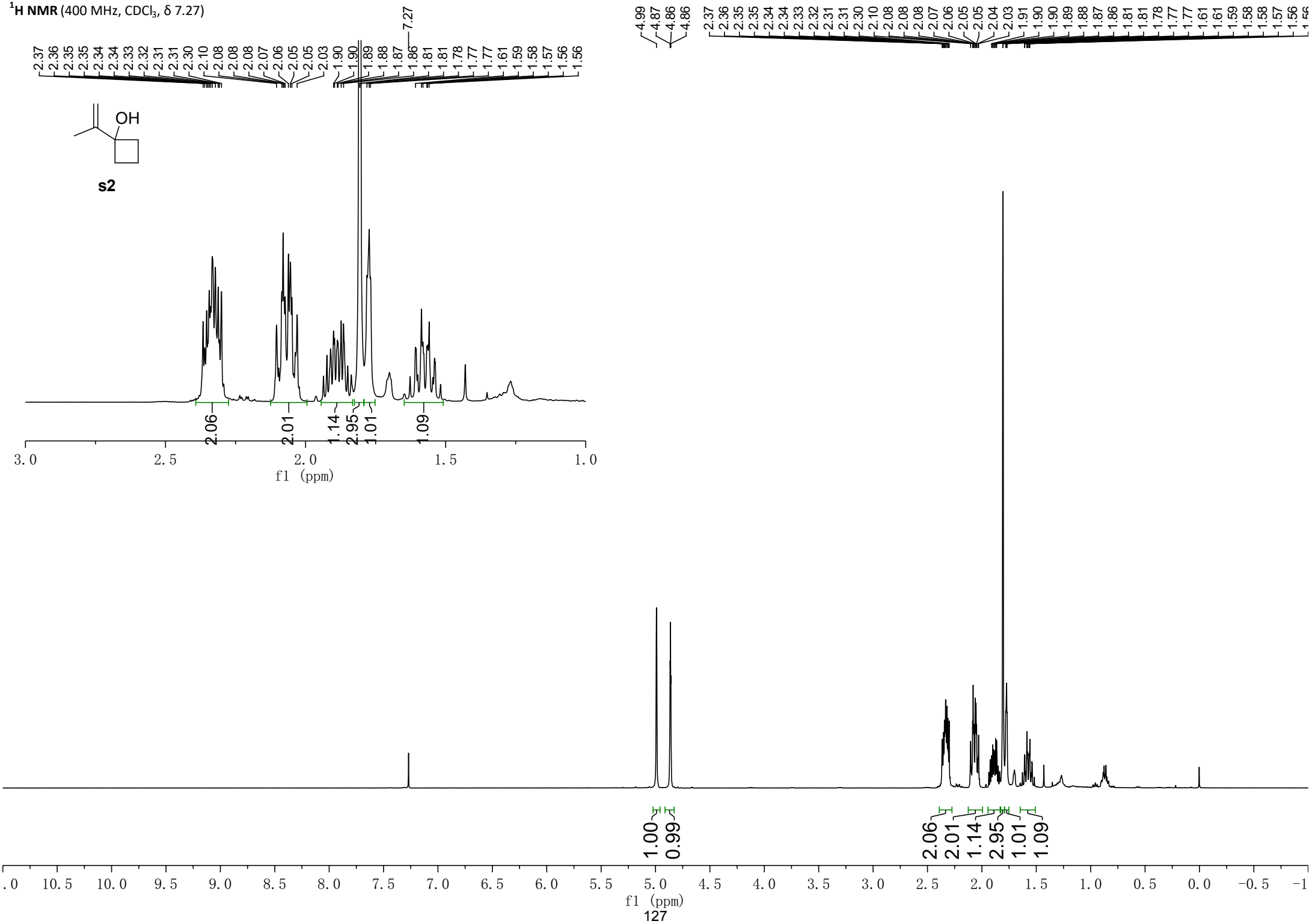


7i

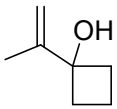
201.66
169.54
158.66
148.57
143.92
136.86
133.74
131.63
129.60
128.07
127.85
123.36
114.71
114.44
77.32
77.00
76.68
58.46
55.20
55.07
54.00
46.46
44.80
44.37
35.85
34.78
32.36
31.66
29.23
21.70
21.08

f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

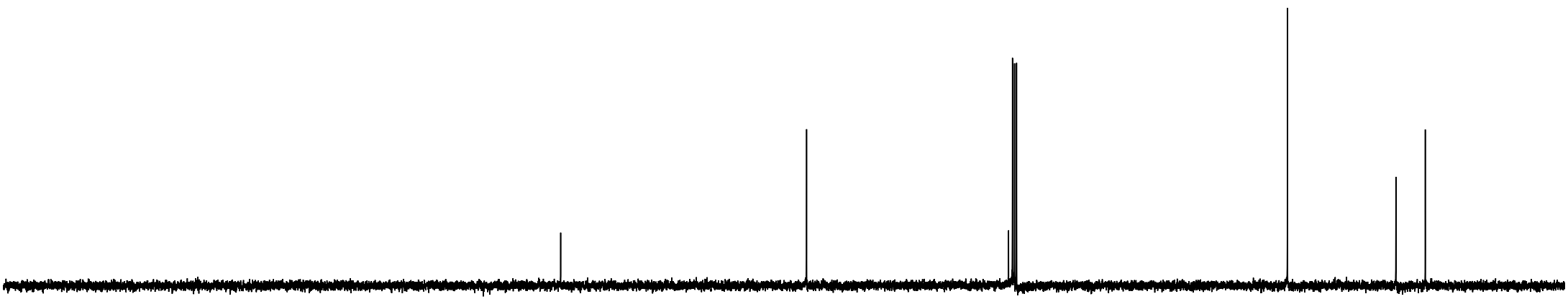


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



s2

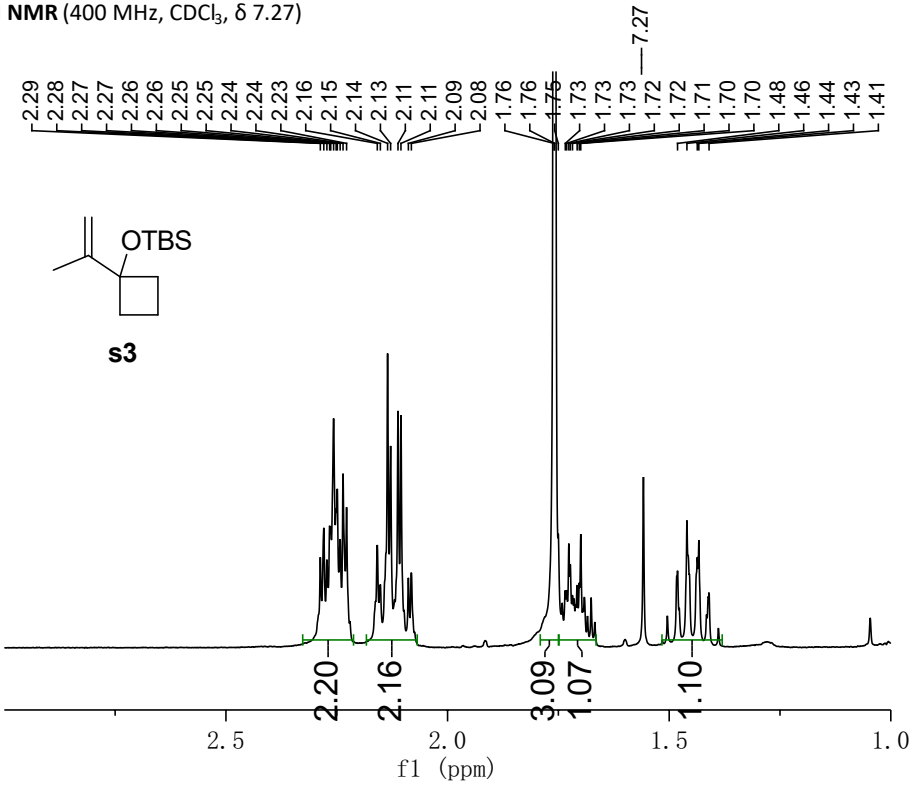
147.92
109.49
77.93
77.32
77.00
76.68
34.36
17.41
12.82



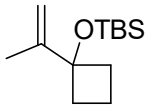
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

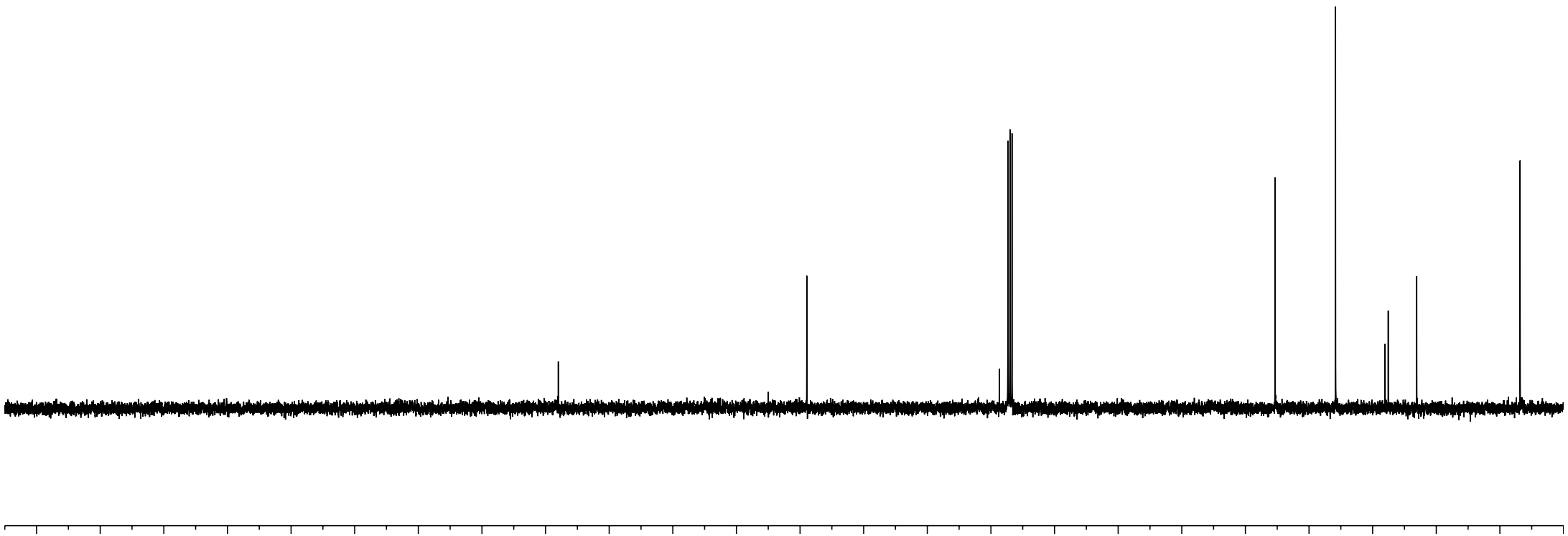


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



s3

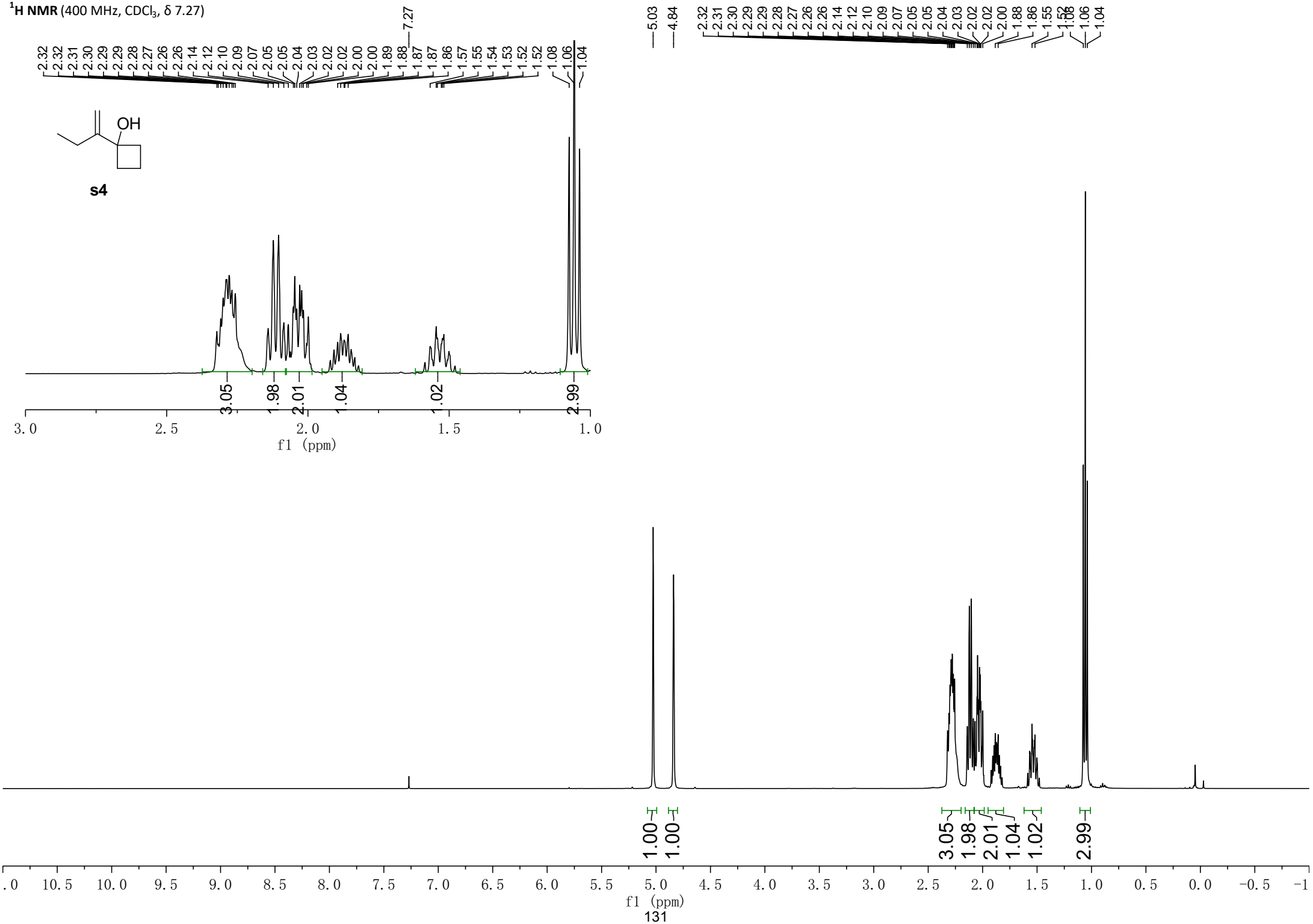
148.00
108.94
78.67
77.32
77.00
76.68
35.33
25.83
18.04
17.55
13.08
-3.18



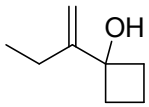
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

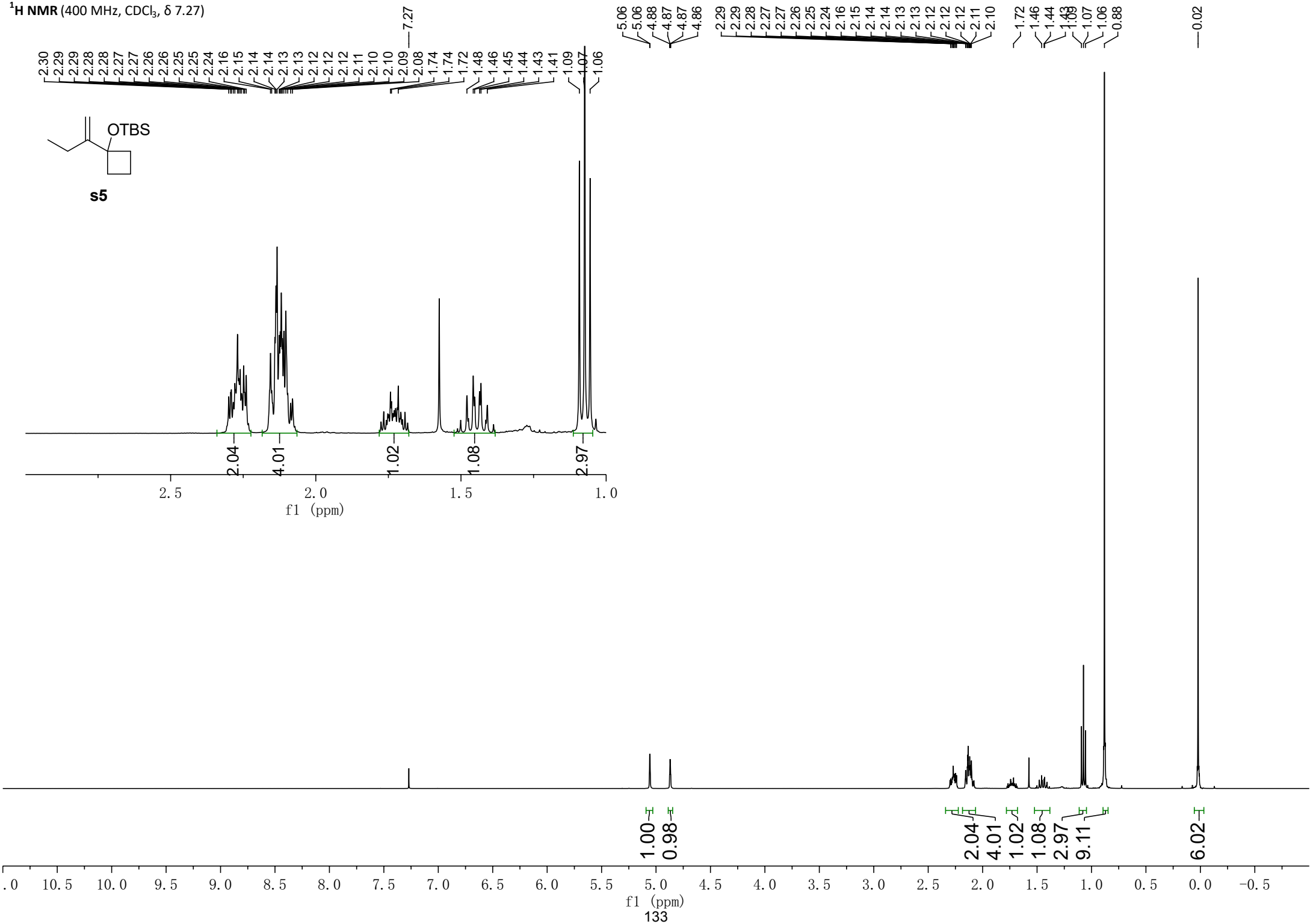


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

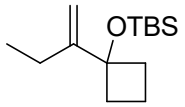


s4

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

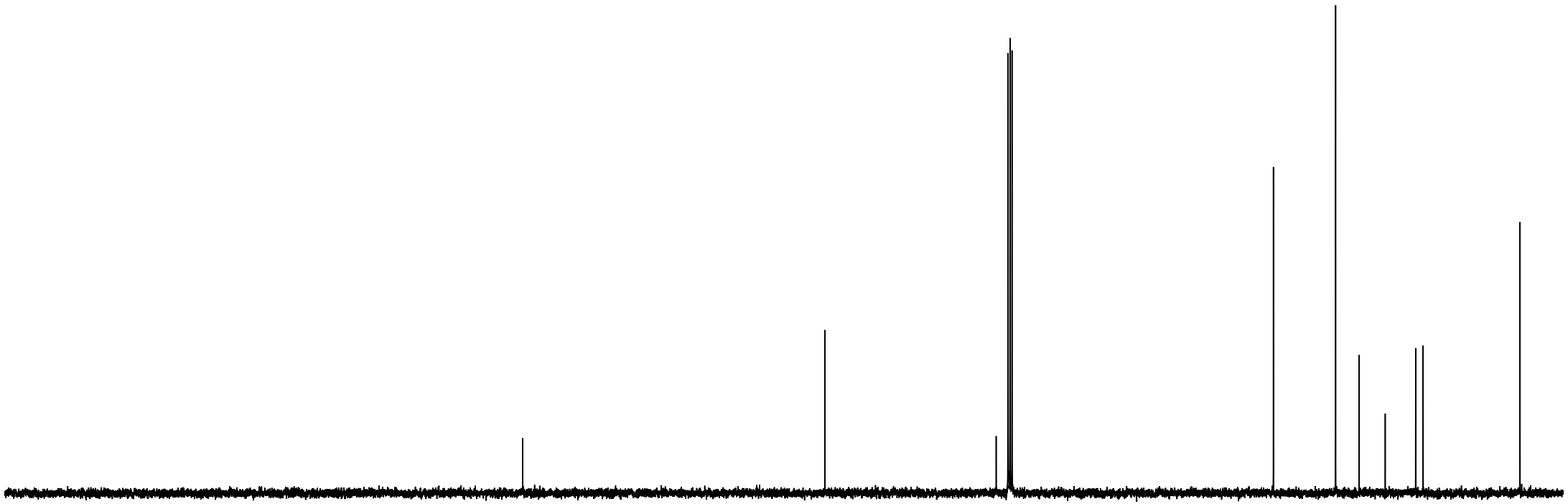


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



s5

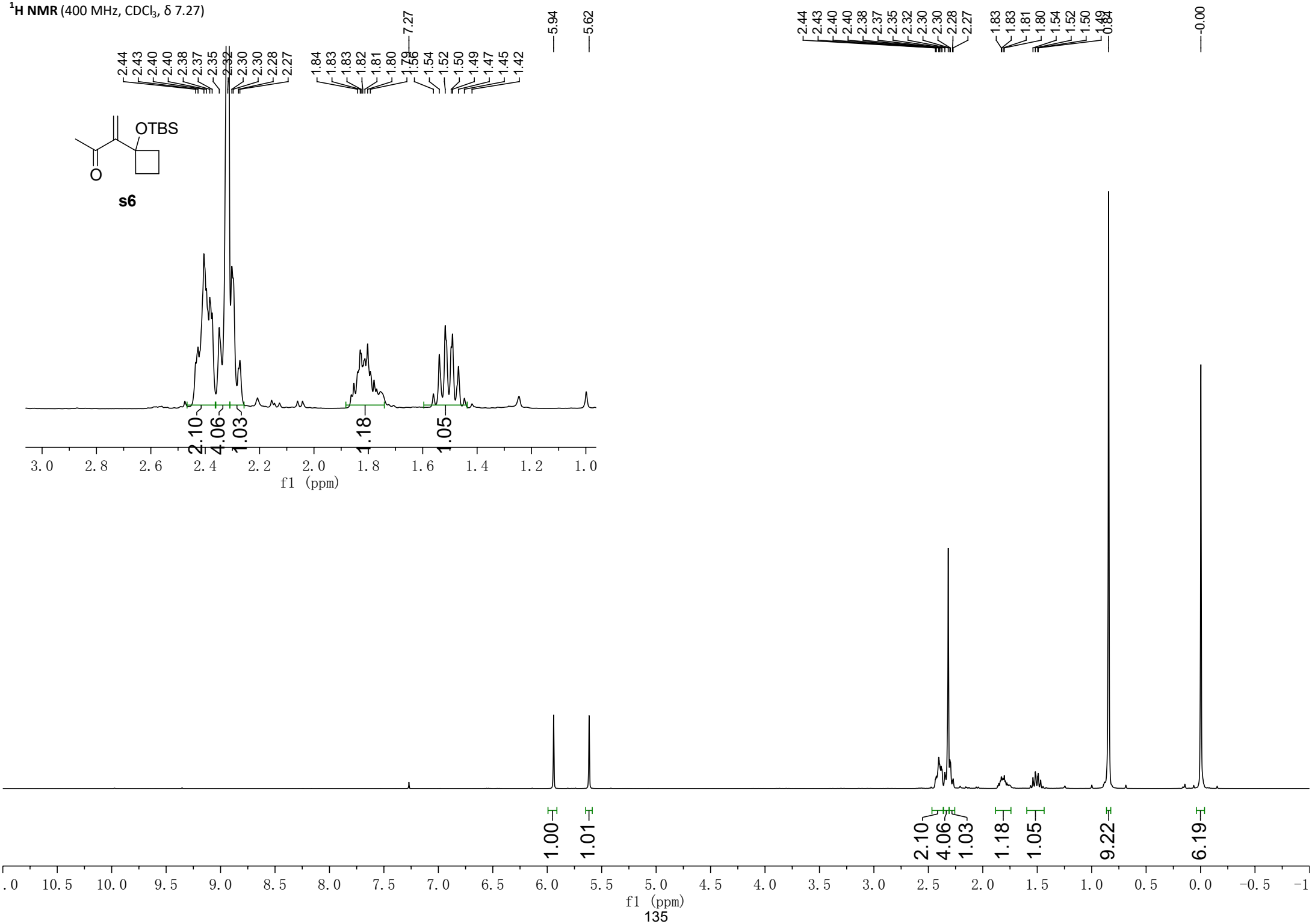
153.59
106.10
79.17
77.32
77.00
76.68
35.60
25.82
22.13
18.02
13.24
12.07
-3.15



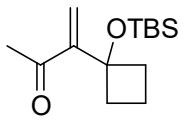
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

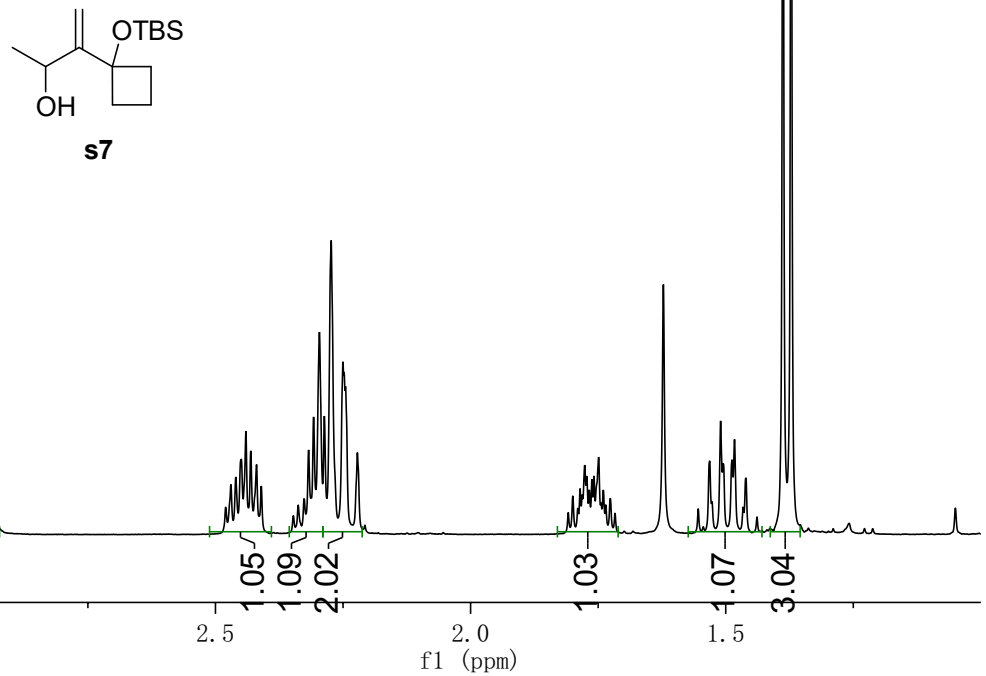


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



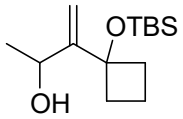
s6

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



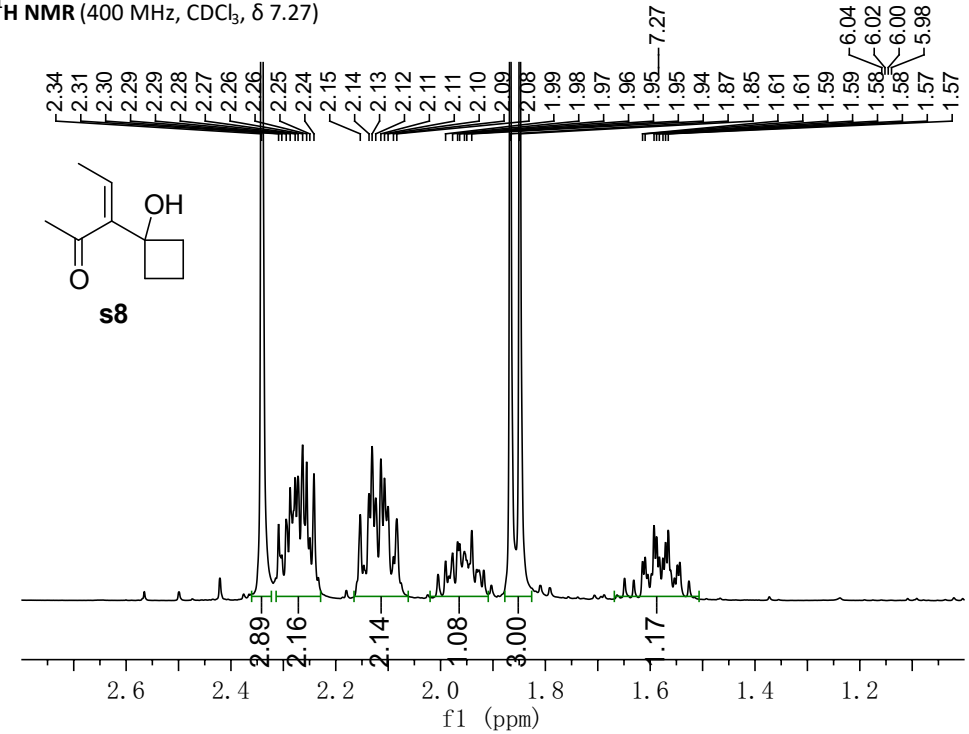
s7

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

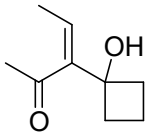


s7

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

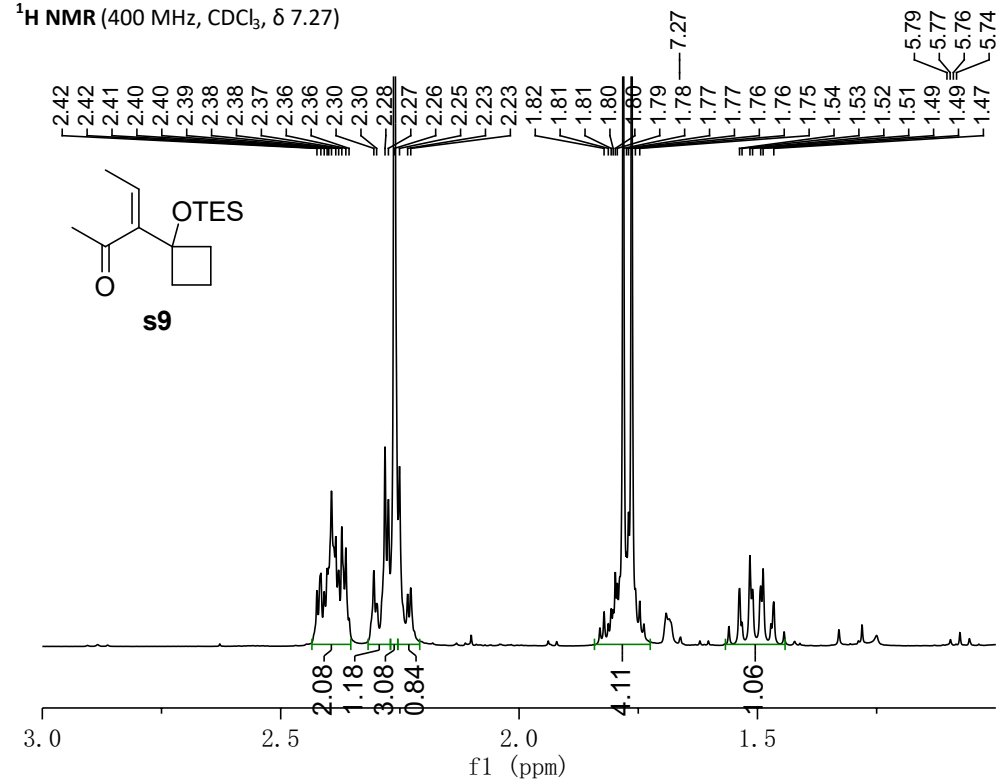


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

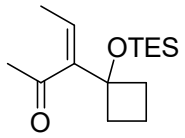


s8

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

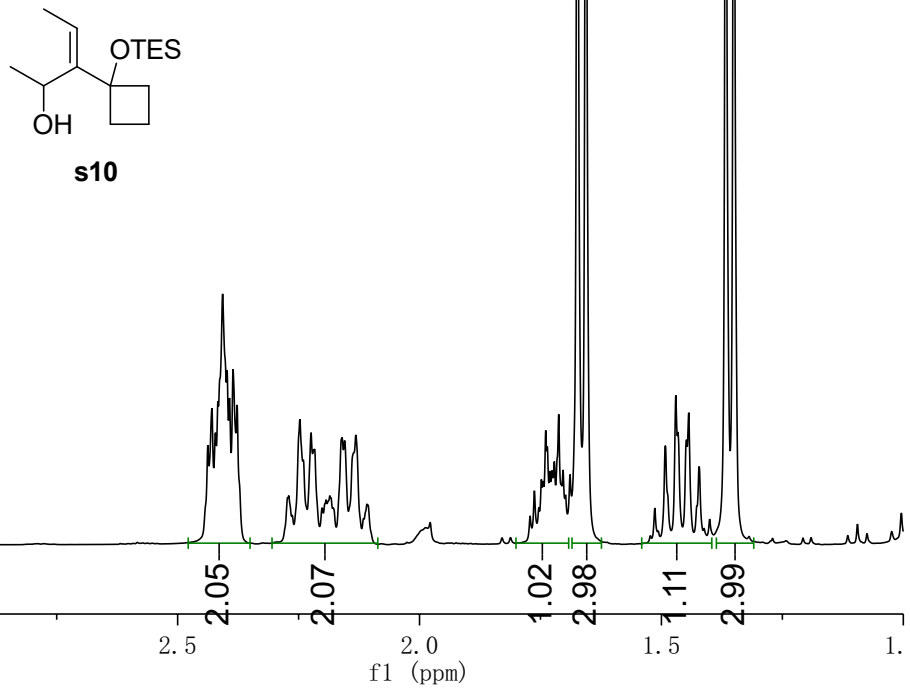


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



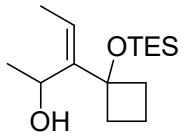
s9

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



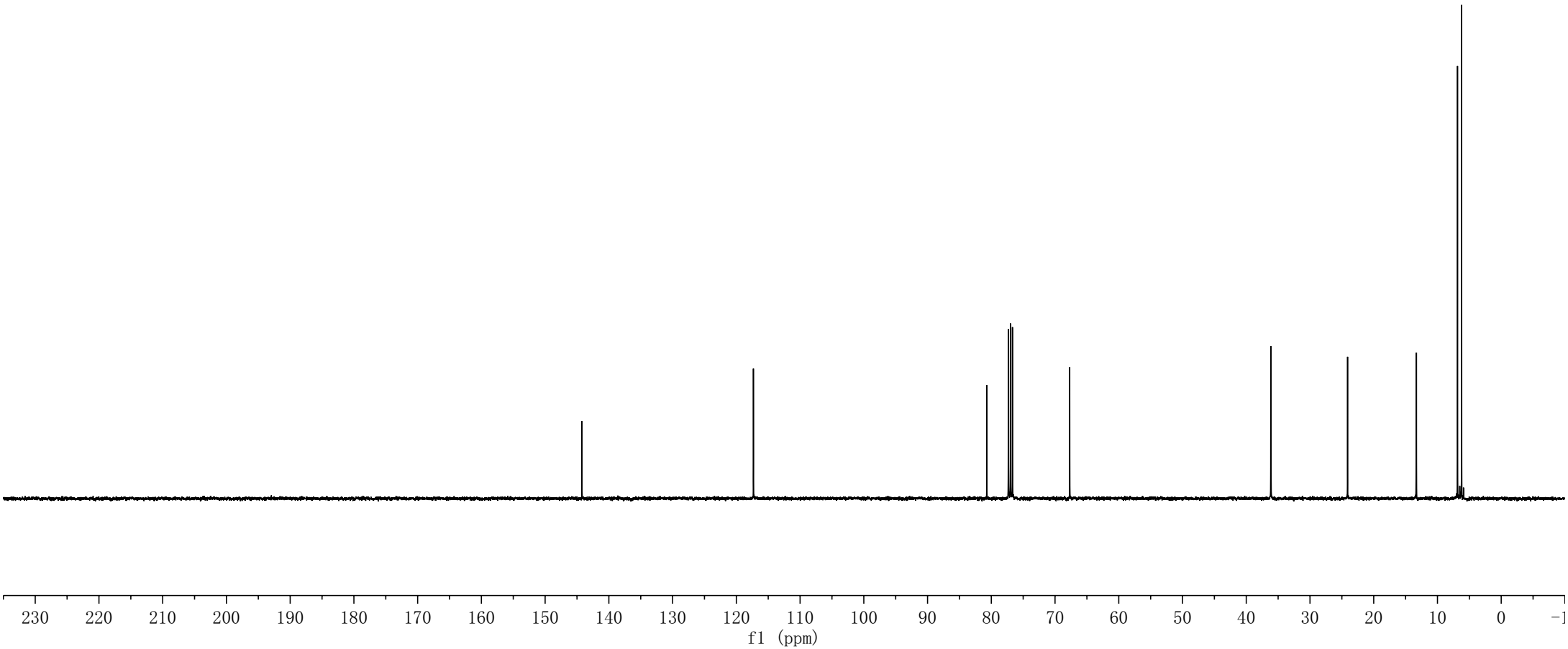
s10

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

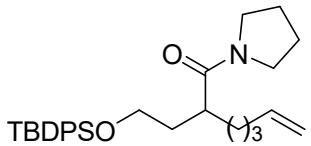


s10

144.24
117.32
80.71
77.32
77.00
76.68
67.70
36.15
36.12
24.10
13.34
13.30
6.85
6.21

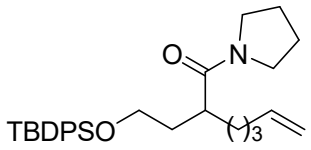


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



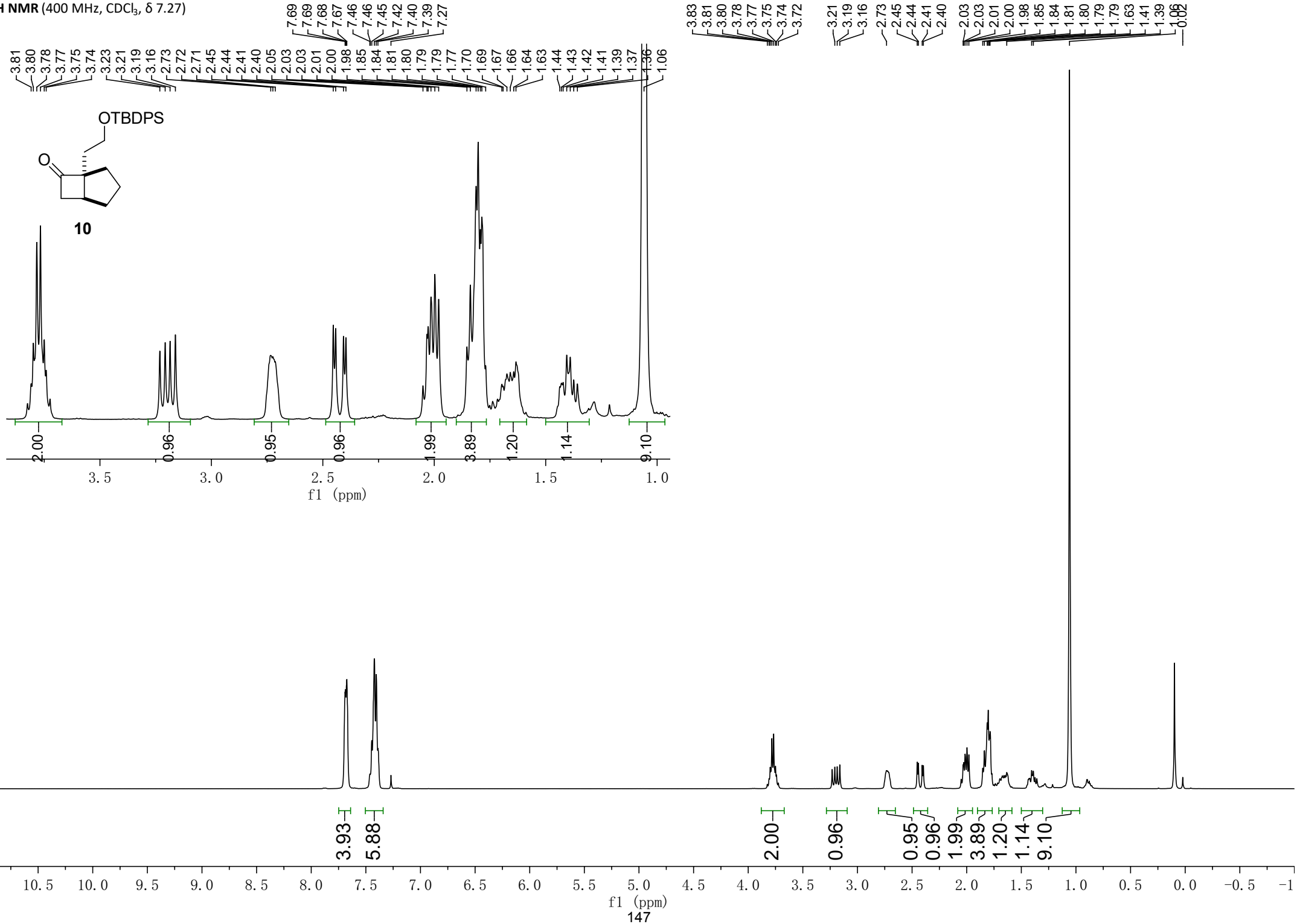
9

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

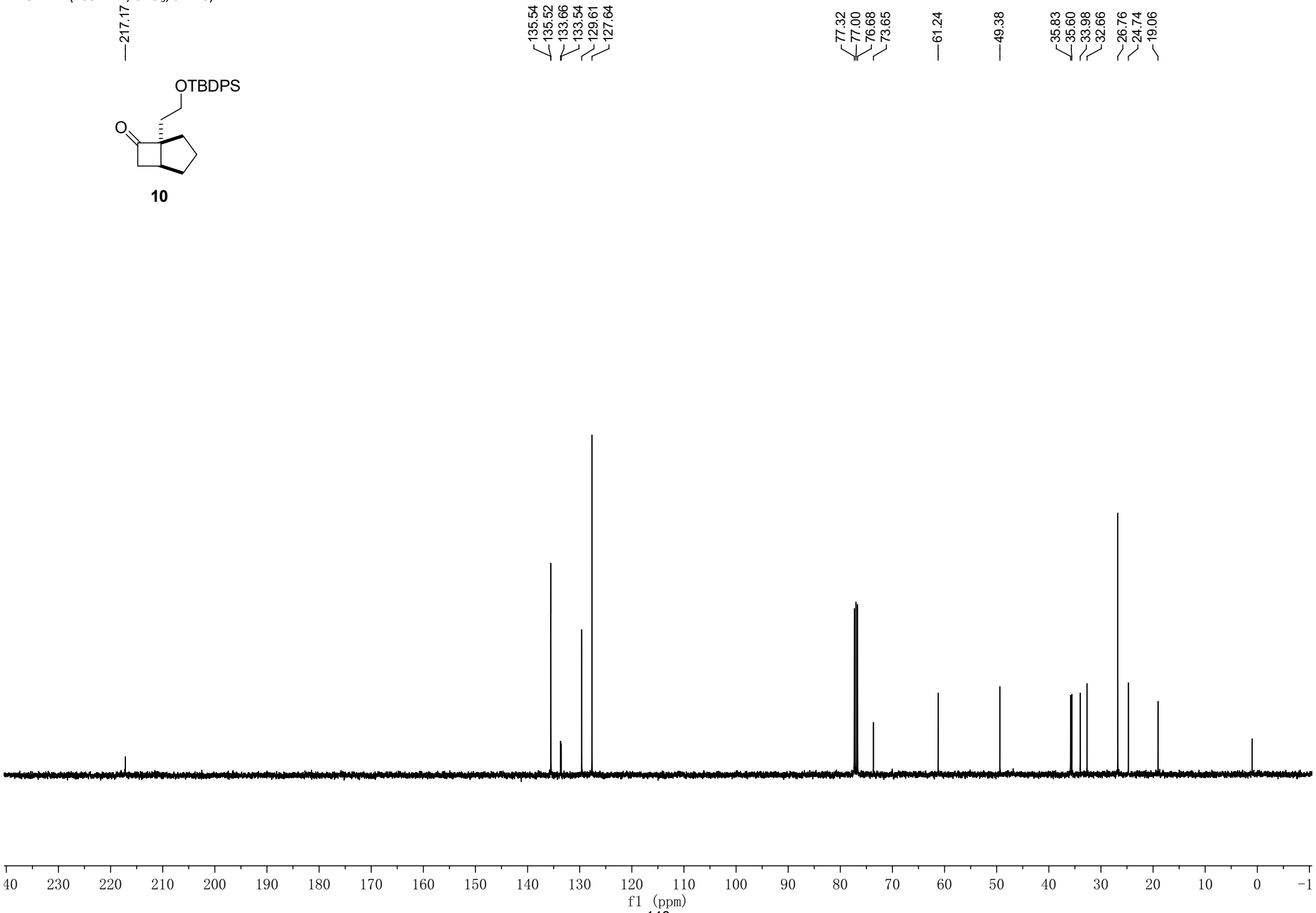


9

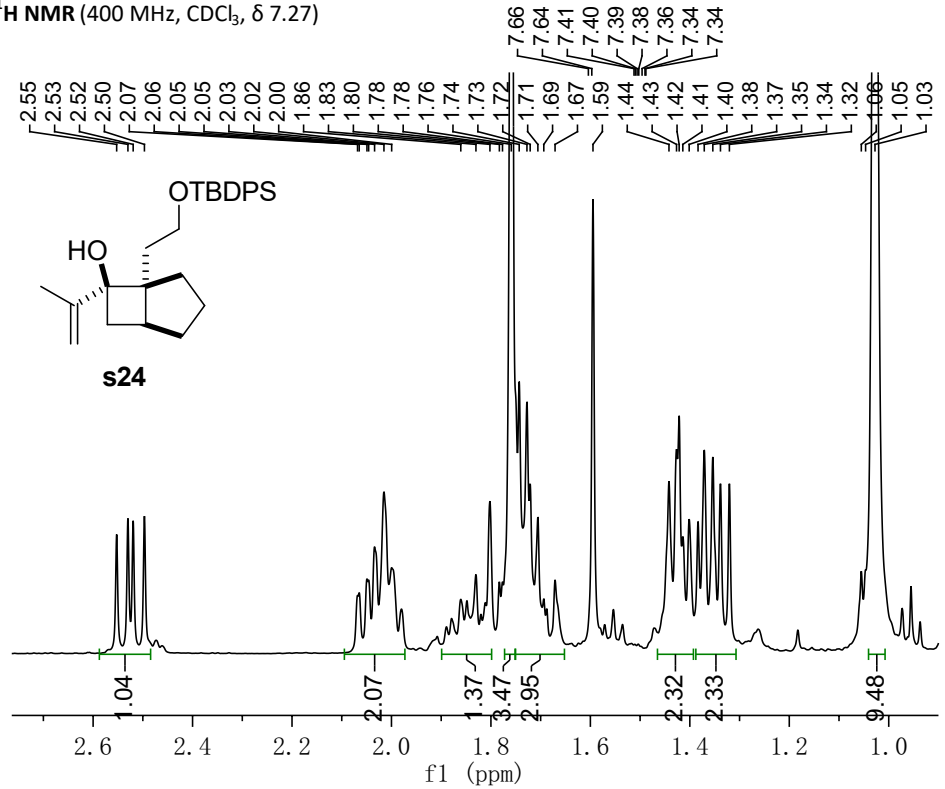
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



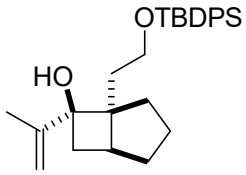
^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

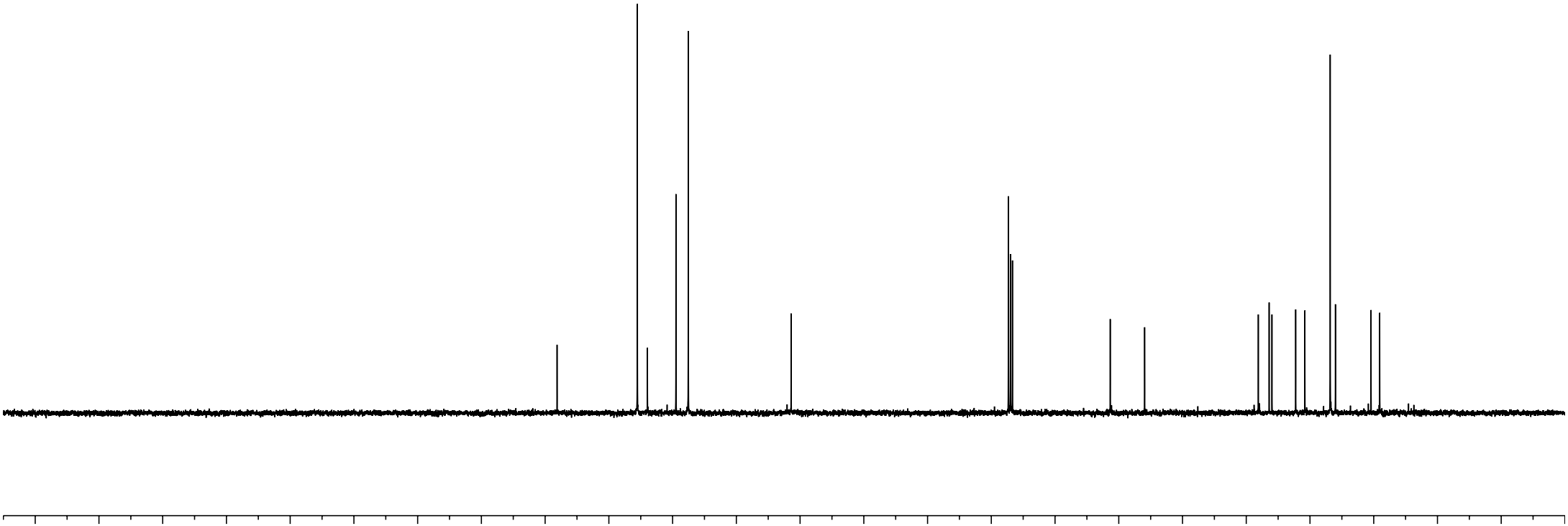


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

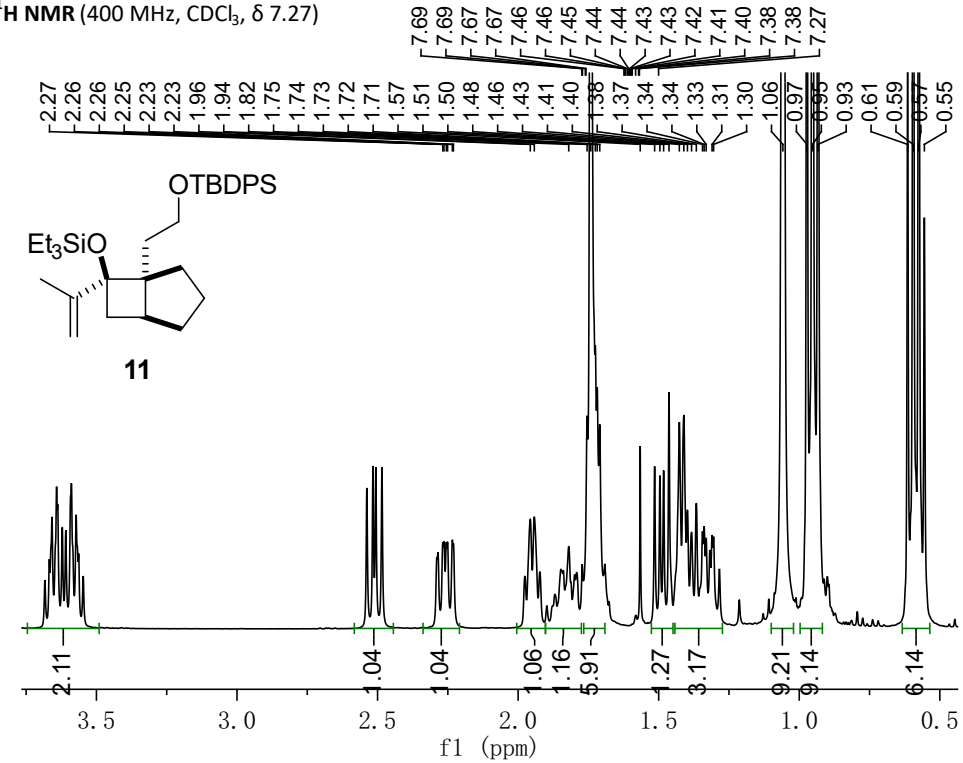


s24

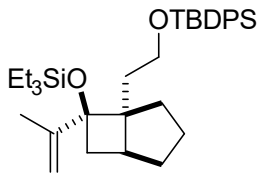
148.12
135.53
133.95
129.48
127.54
111.40
77.31
77.00
76.68
61.34
55.94
38.11
36.41
35.97
32.24
30.80
26.83
26.01
20.42
19.06



^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

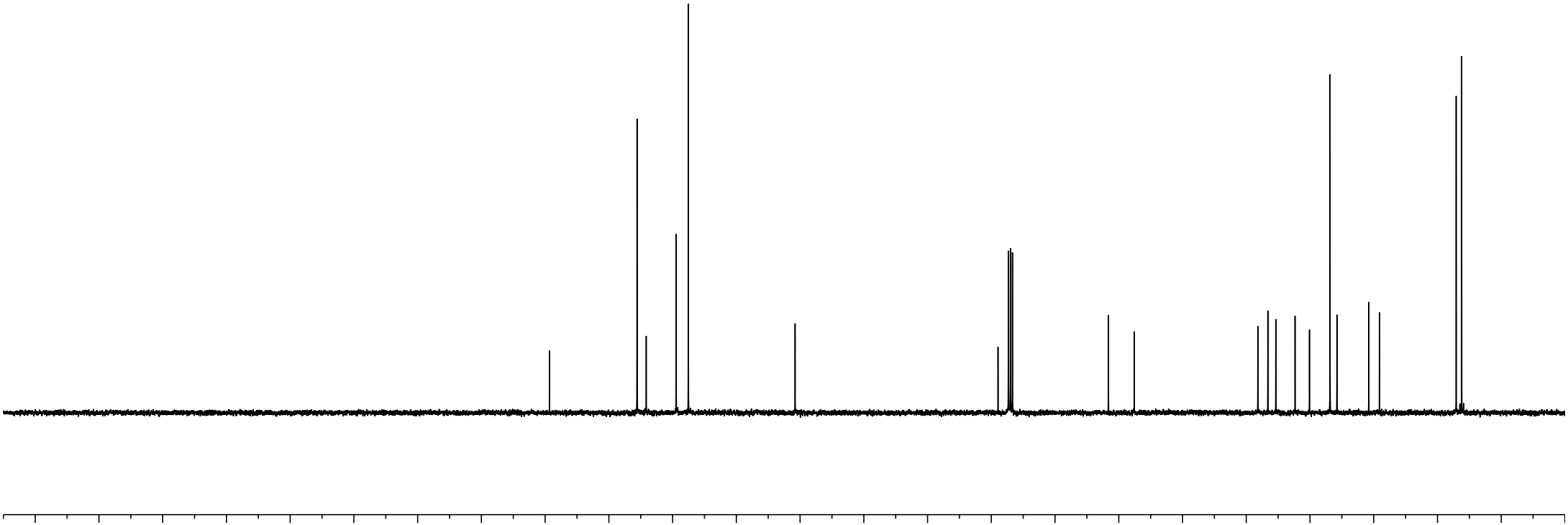


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

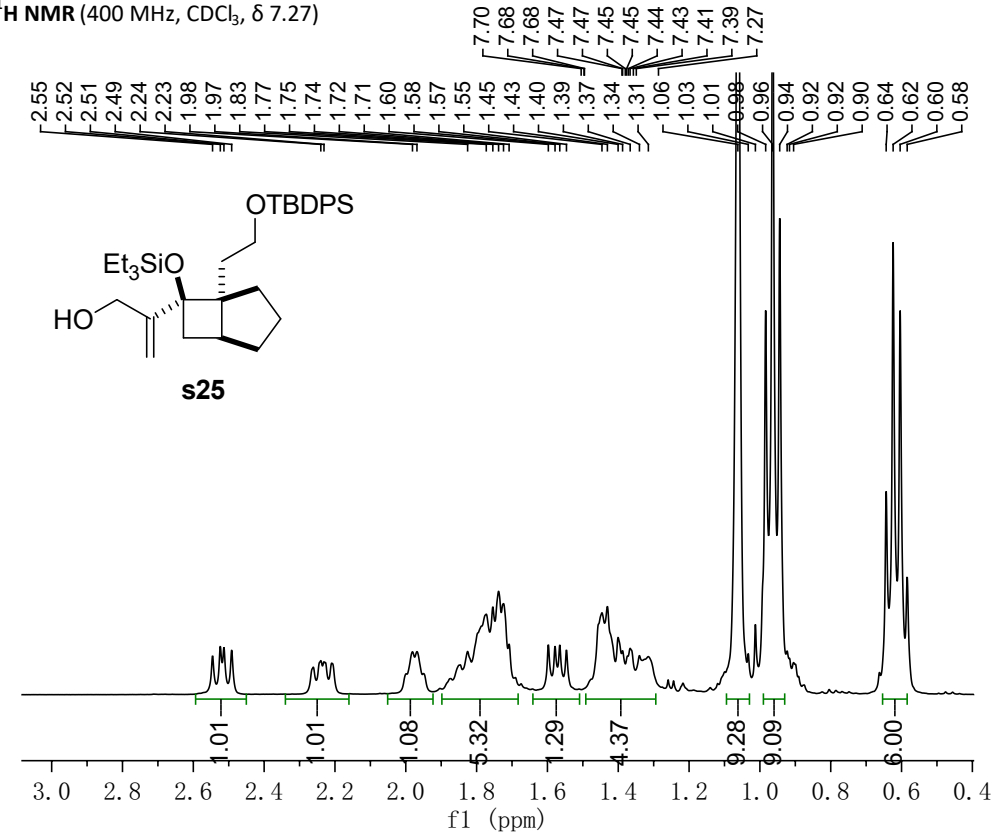


11

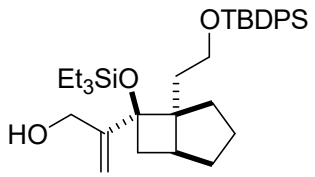
149.32
135.58
134.14
129.45
127.53
110.78
78.95
77.32
77.00
76.68
61.63
57.57
38.18
36.61
35.36
32.34
30.08
26.85
25.77
20.78
19.11
7.07
6.20



^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

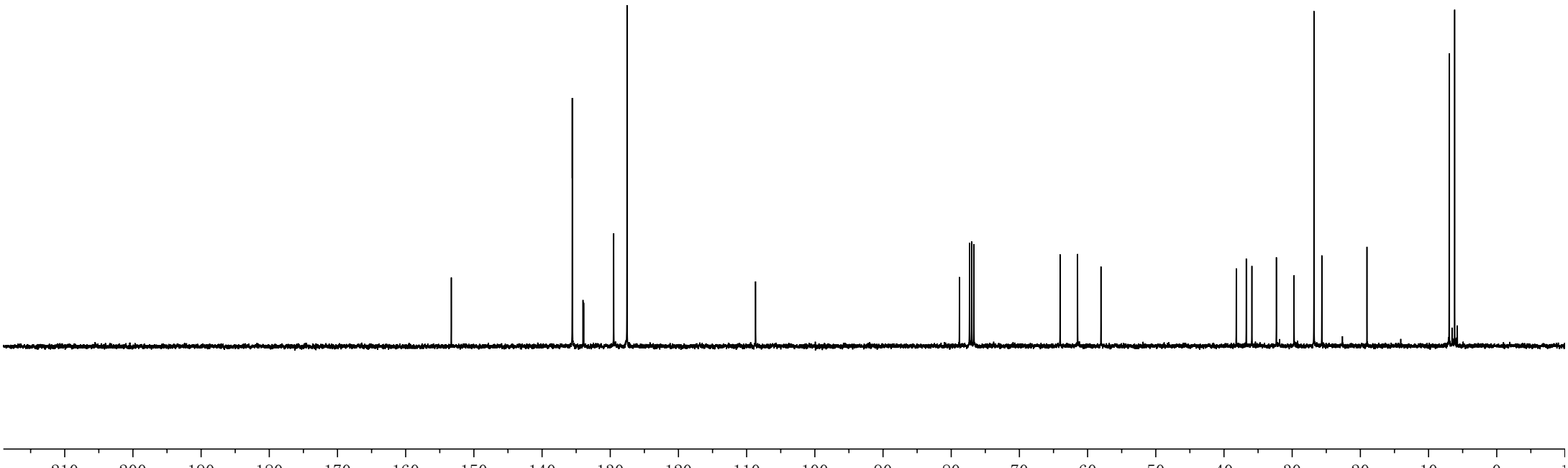


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



s25

153.31
135.58
135.55
134.00
133.89
129.51
129.49
127.55
108.70
78.80
77.32
77.00
76.68
64.03
61.47
58.04
38.20
36.73
35.91
32.31
29.73
26.81
25.65
19.03
6.98
6.17

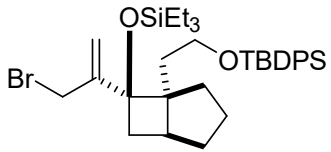


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

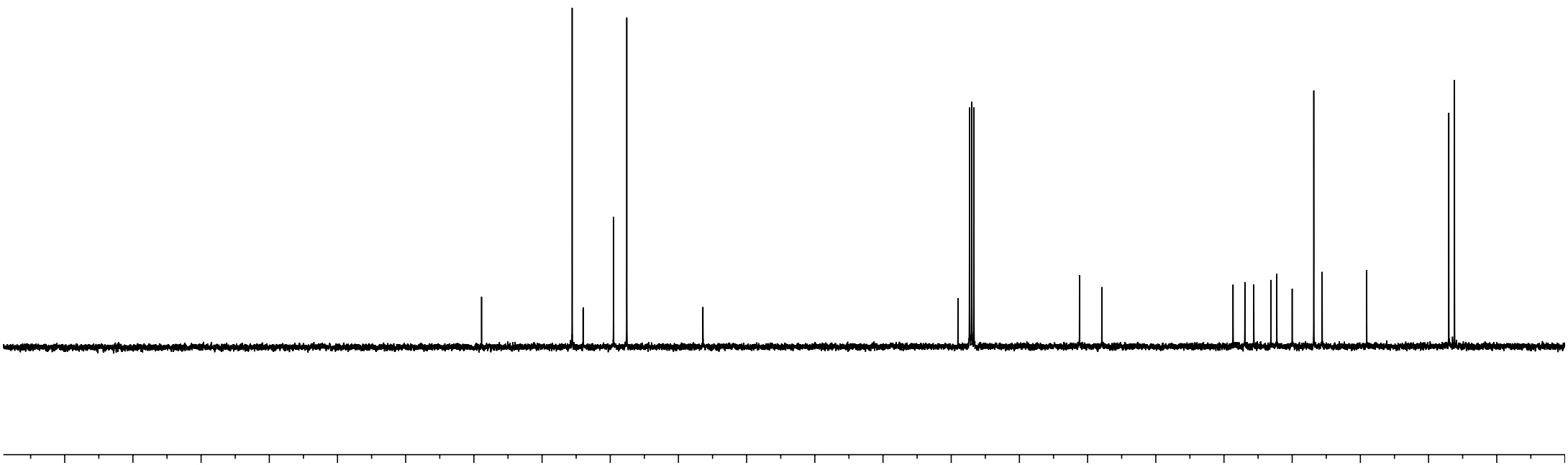
2h

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

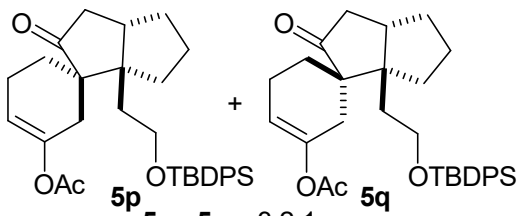
148.87
135.59
133.99
133.95
129.52
127.58
116.41
79.01
77.32
77.00
76.68
61.18
57.91
38.67
36.94
35.63
33.11
32.26
30.00
26.83
25.60
19.07
7.03
6.20



2h

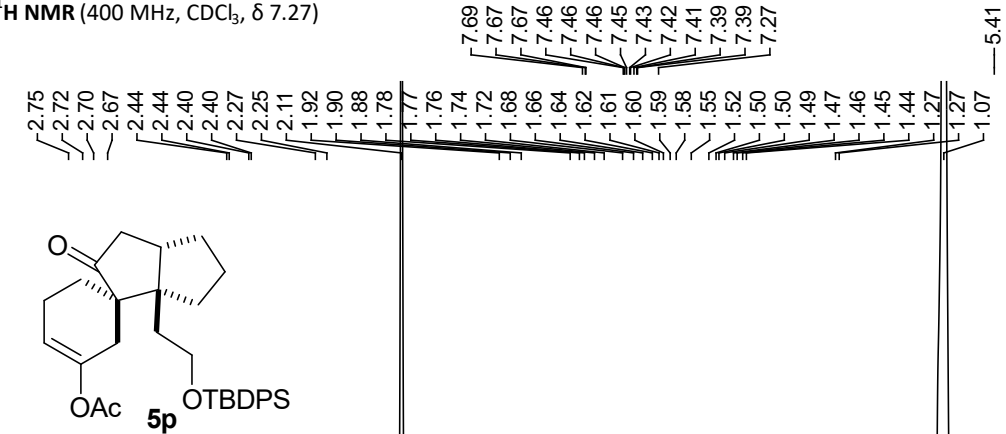


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

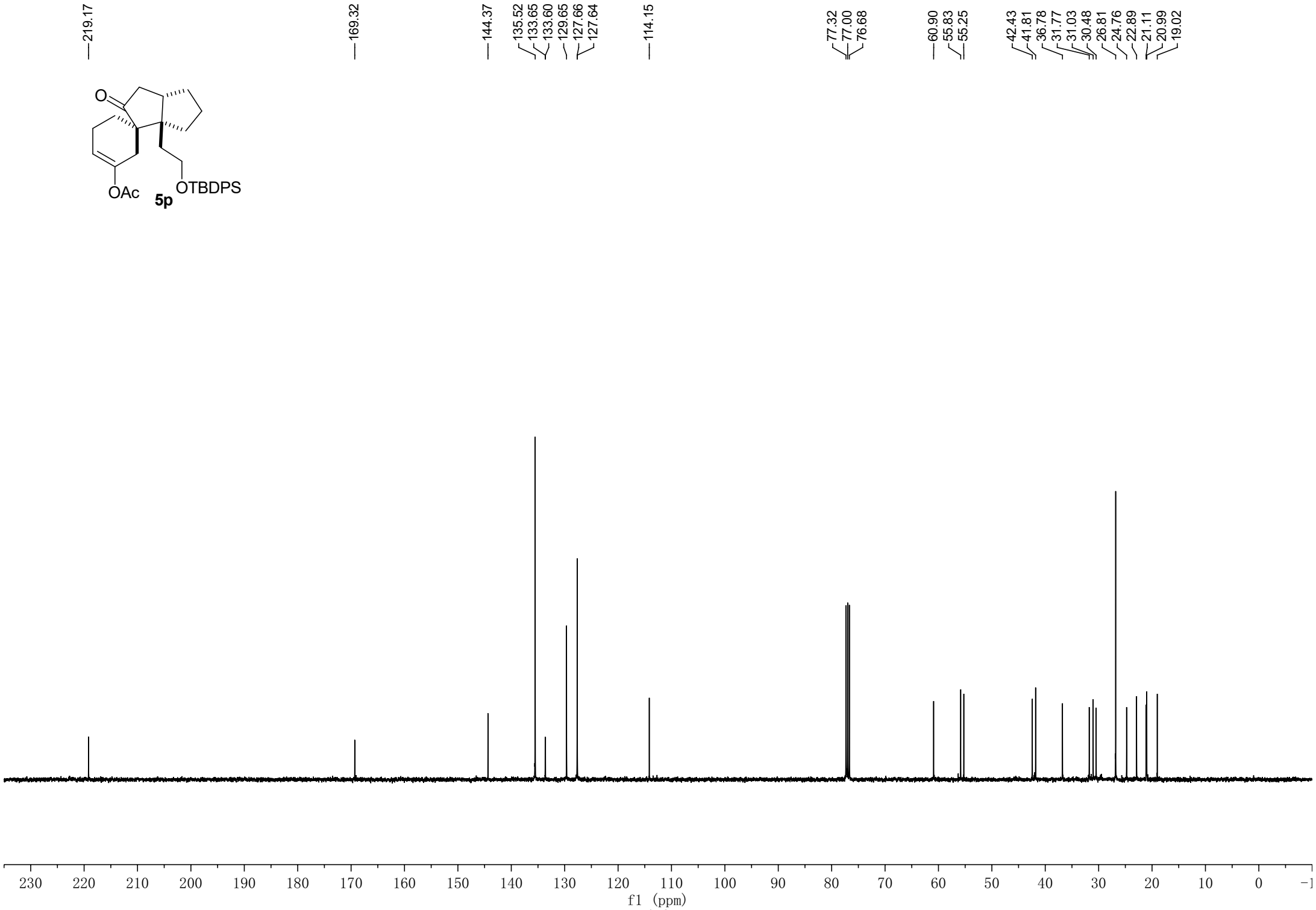


5p : **5q** = 3.2:1

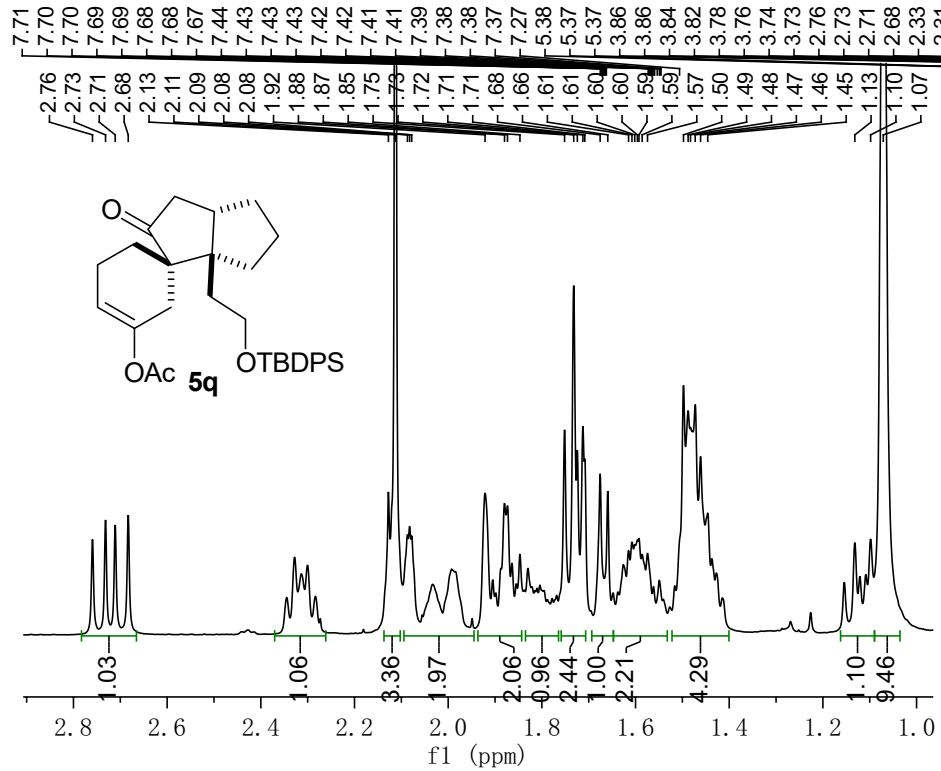
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

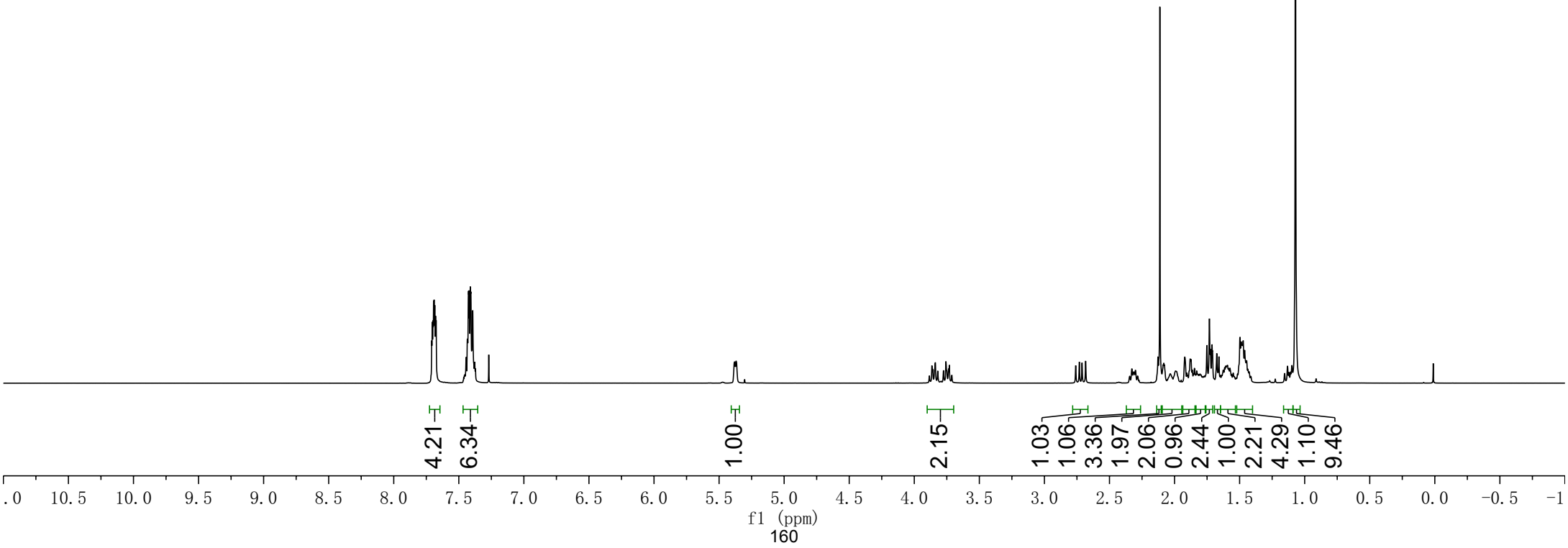


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

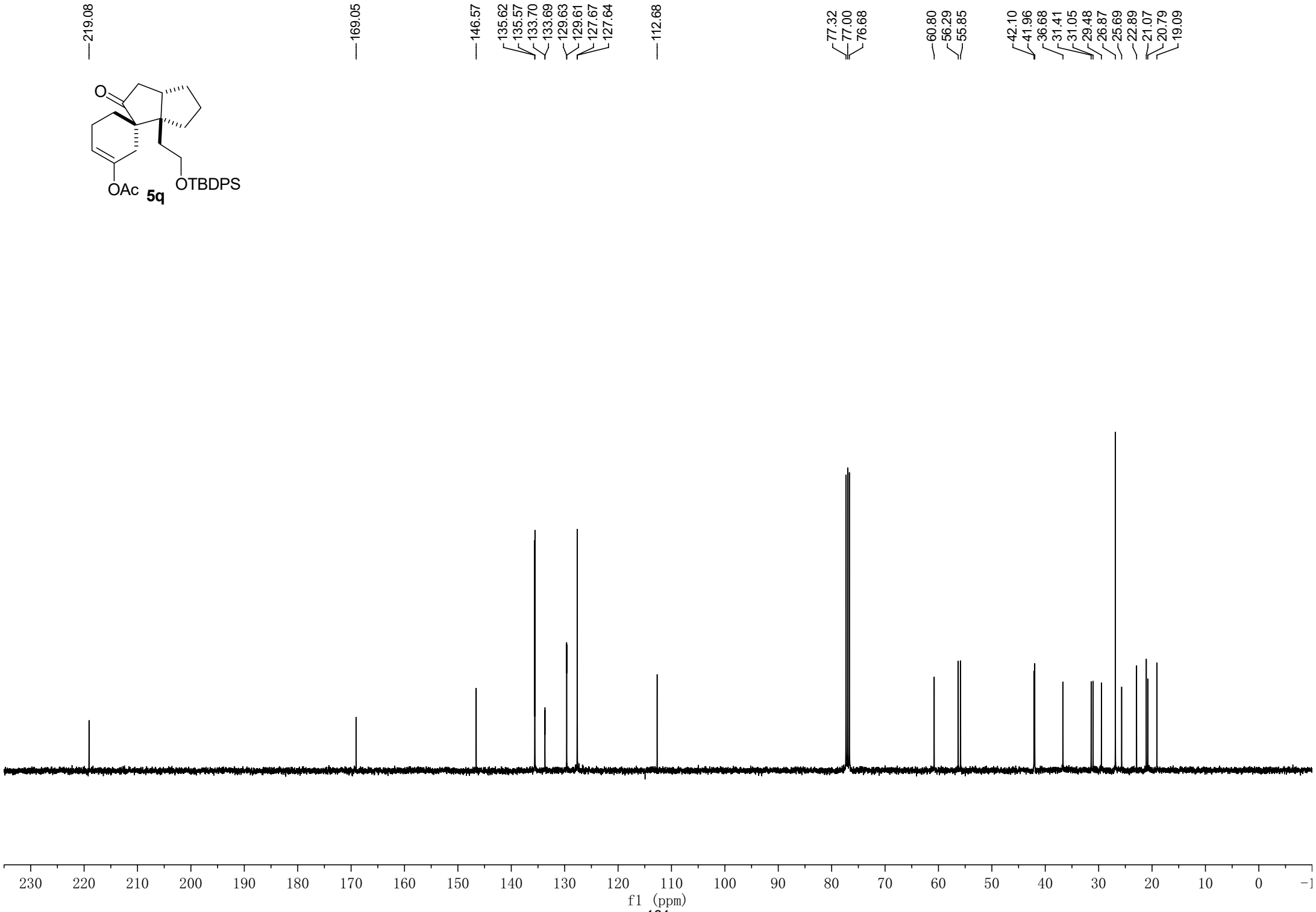


^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

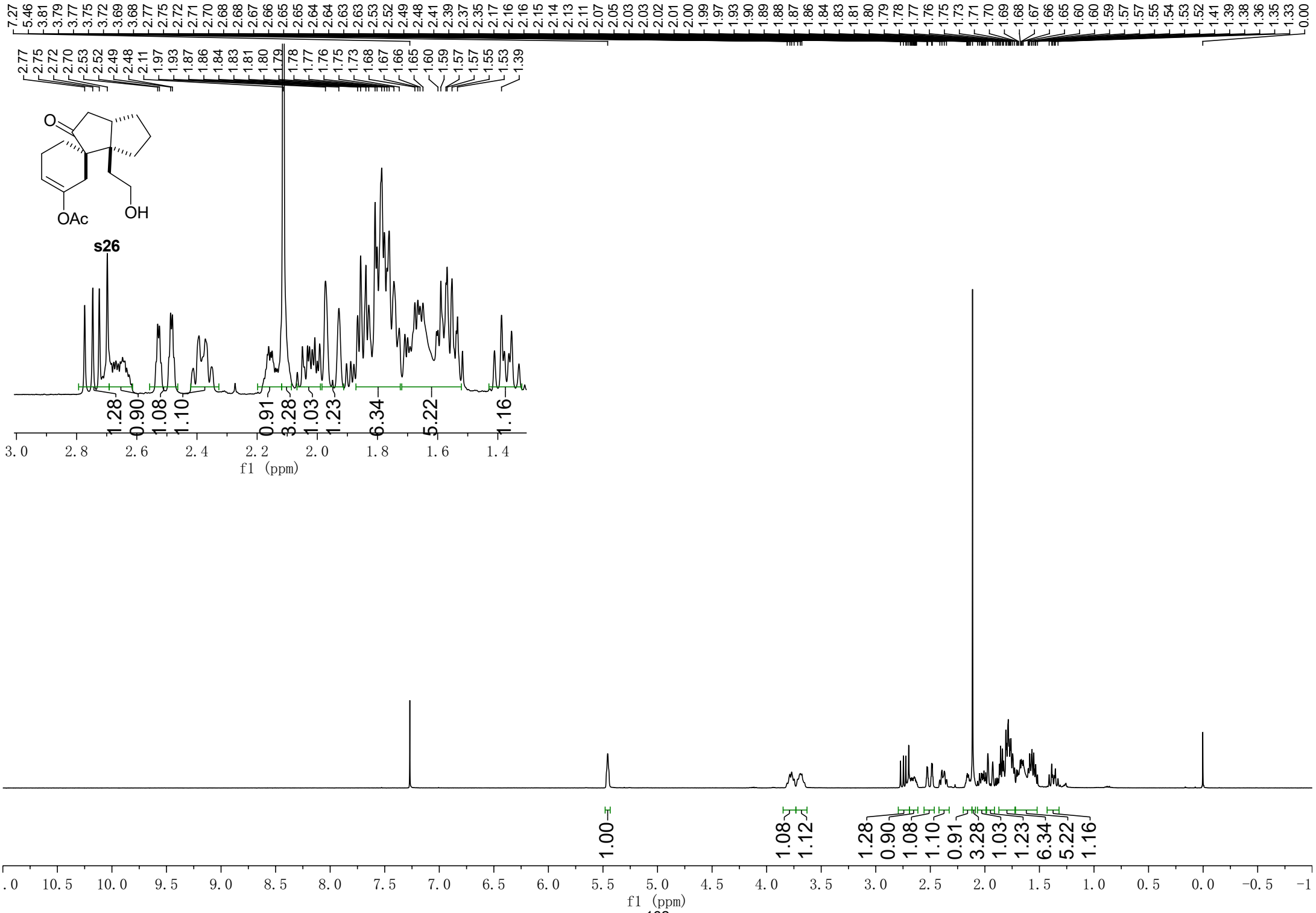




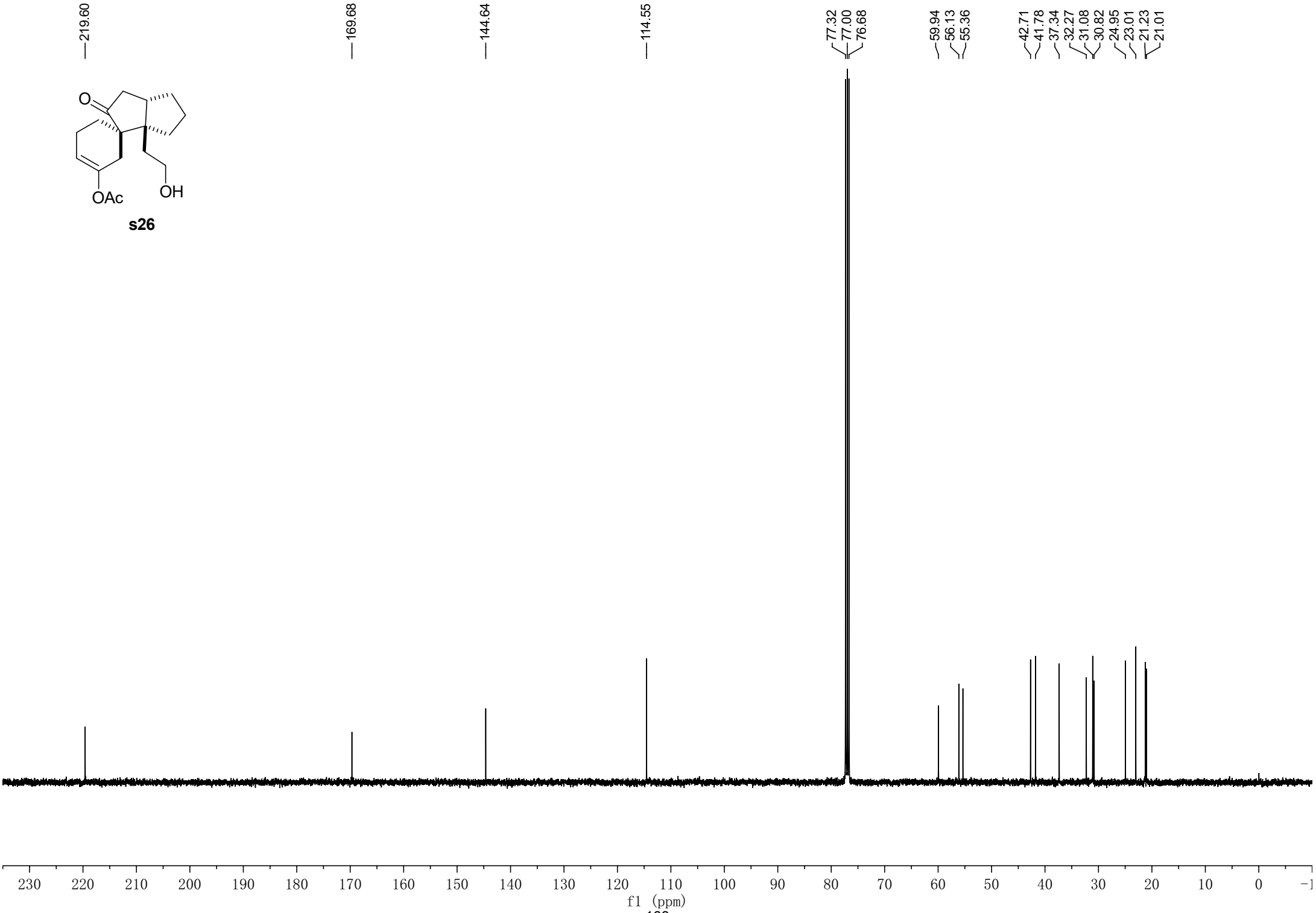
^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

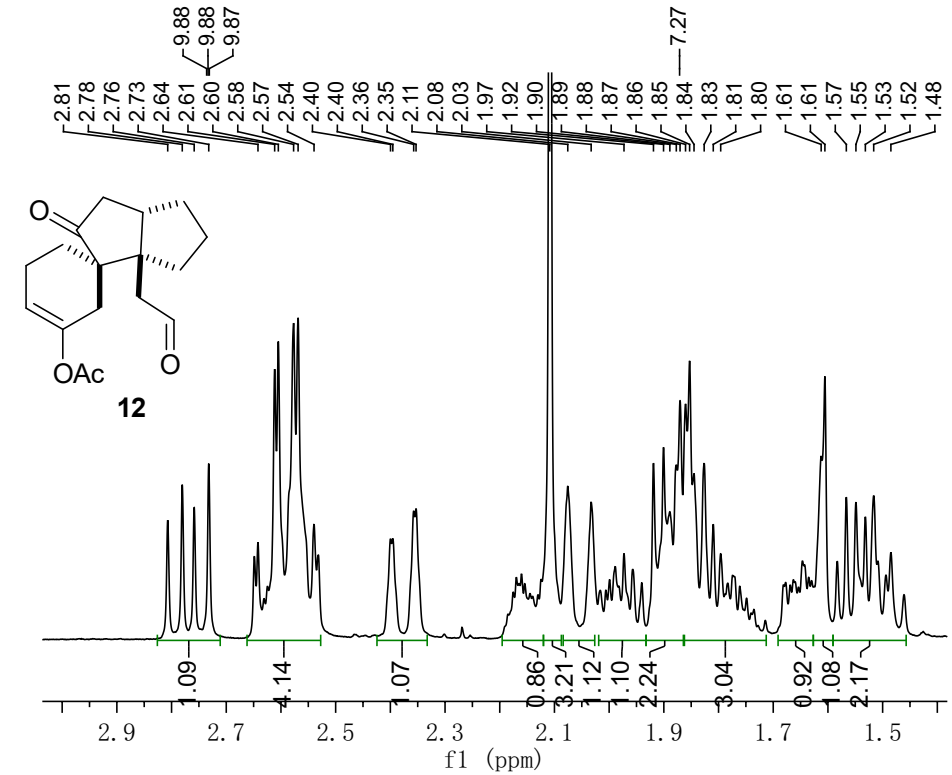


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

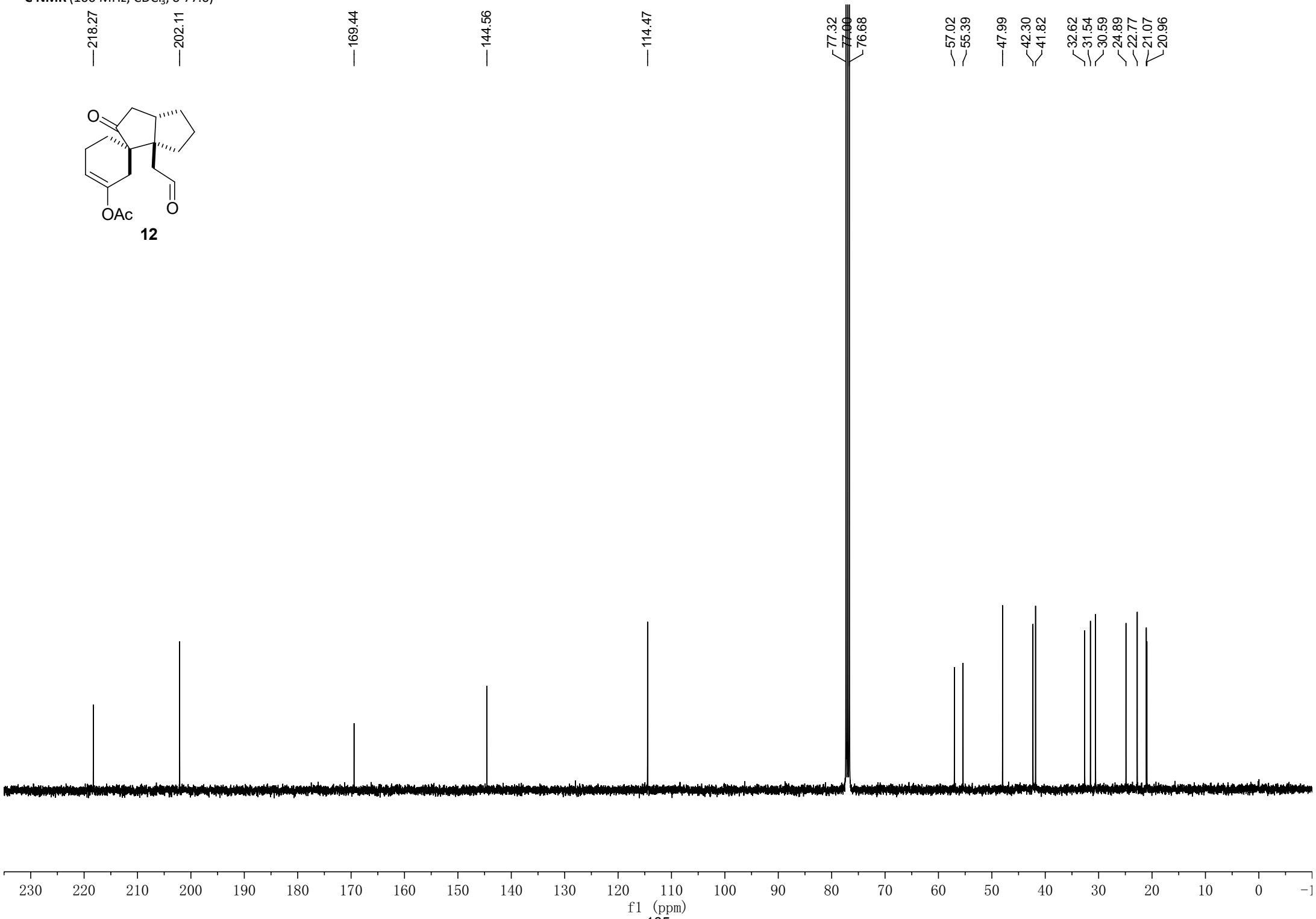


s26

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

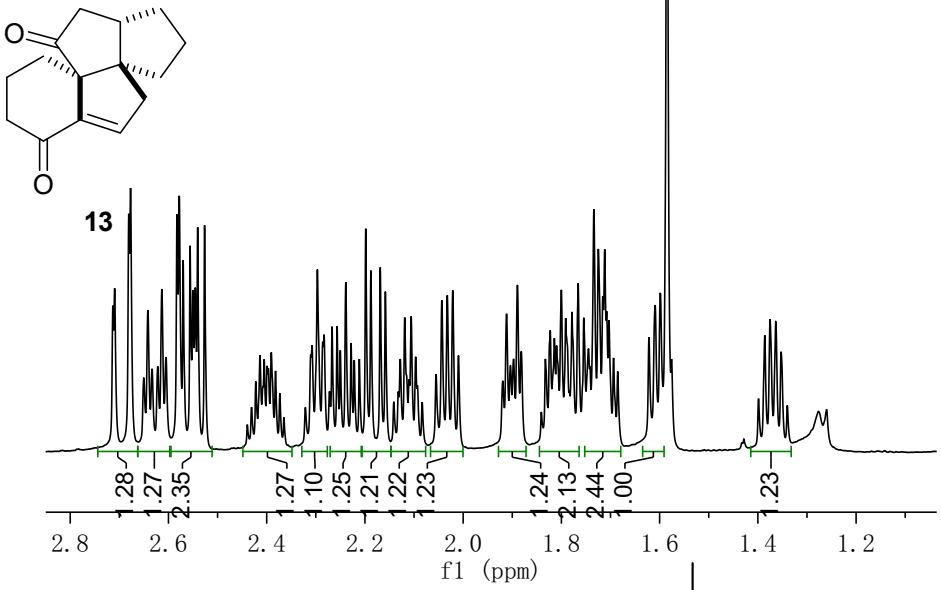


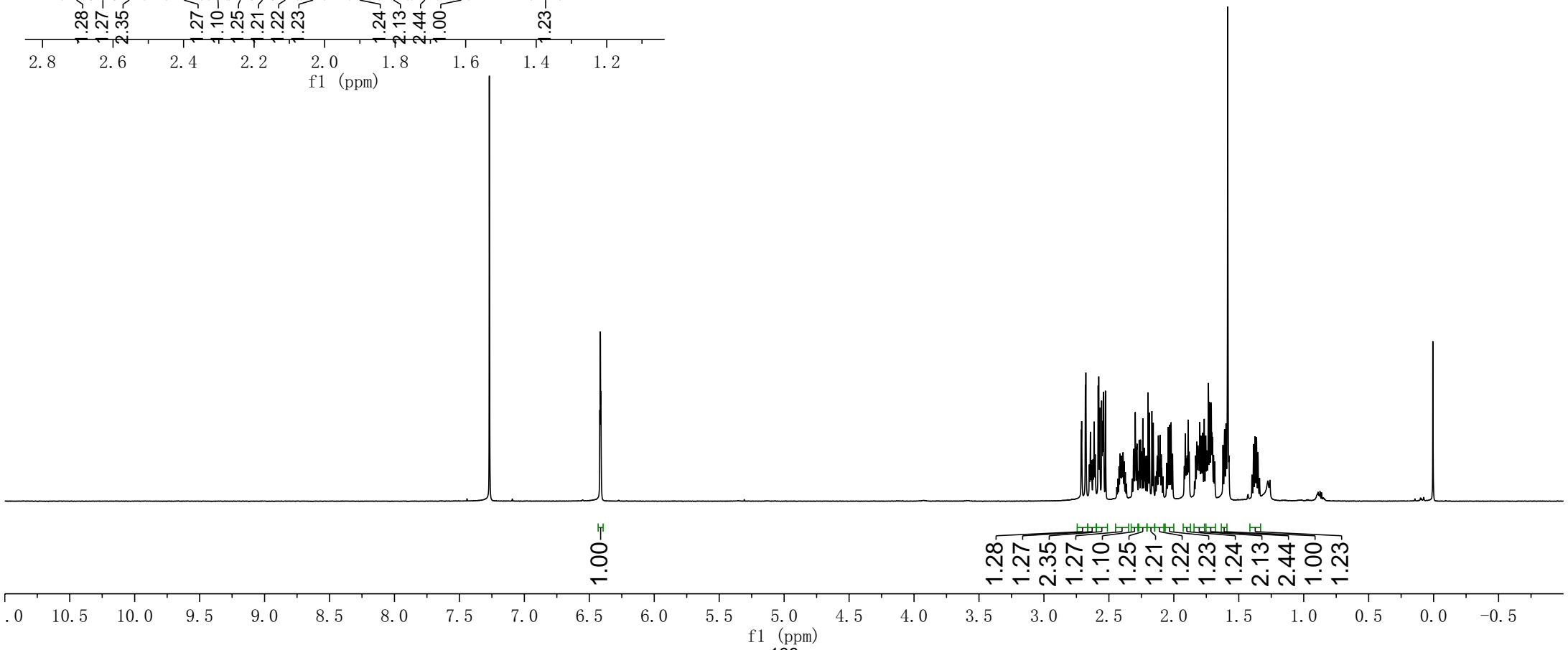
^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



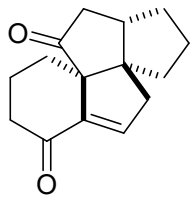
12

^{1}H NMR (600 MHz, $CDCl_3$, δ 7.27)



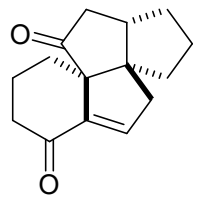


^{13}C NMR (150 MHz, $CDCl_3$, δ 77.0)



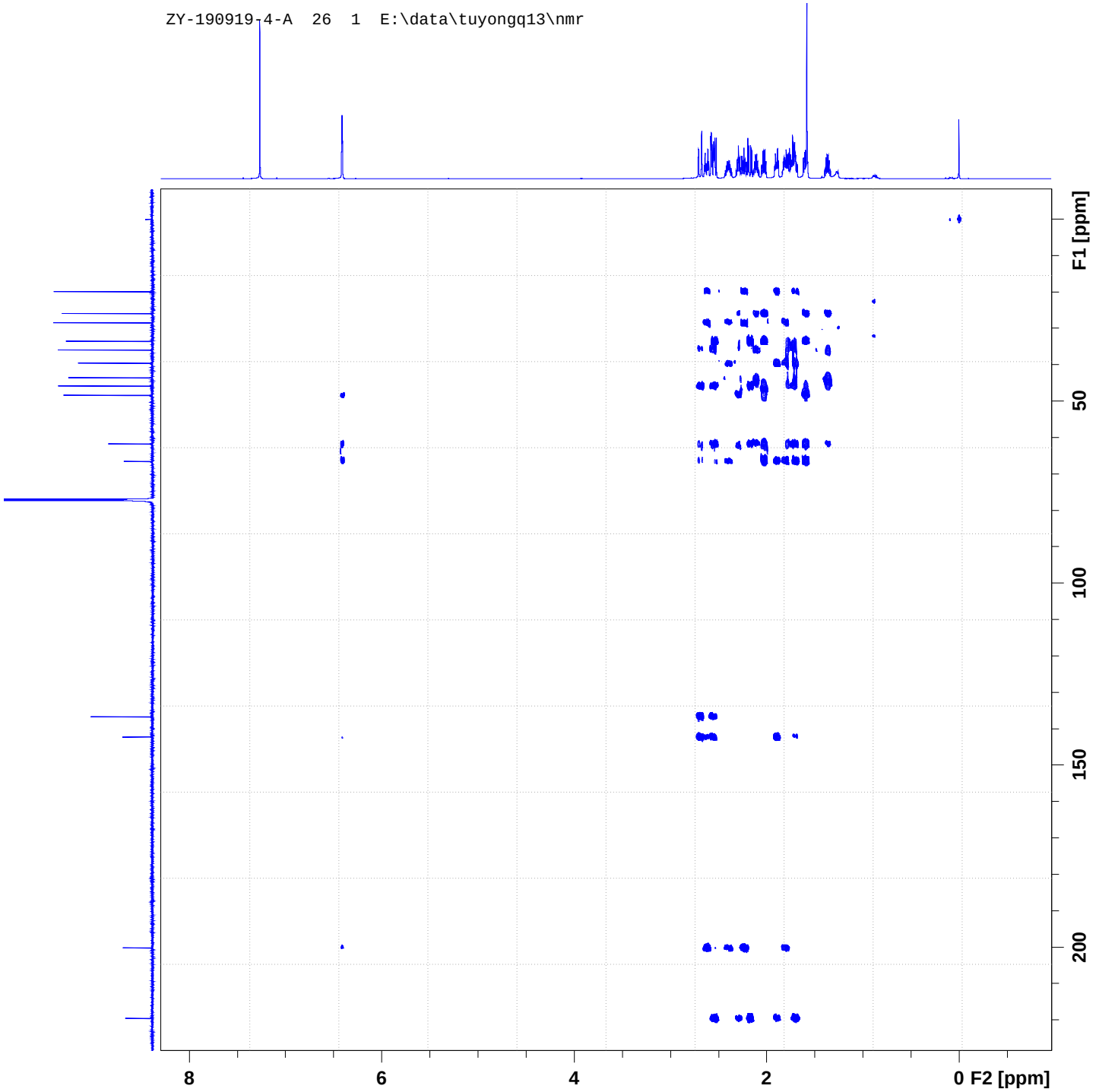
13

^{1}H NMR (600 MHz, $CDCl_3$, δ 7.27)

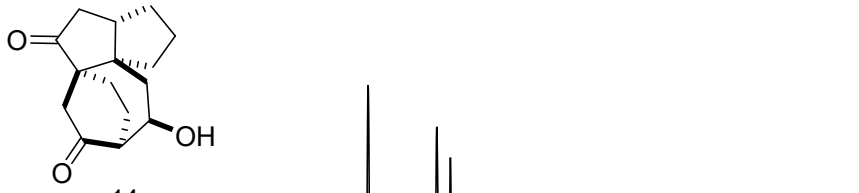


13

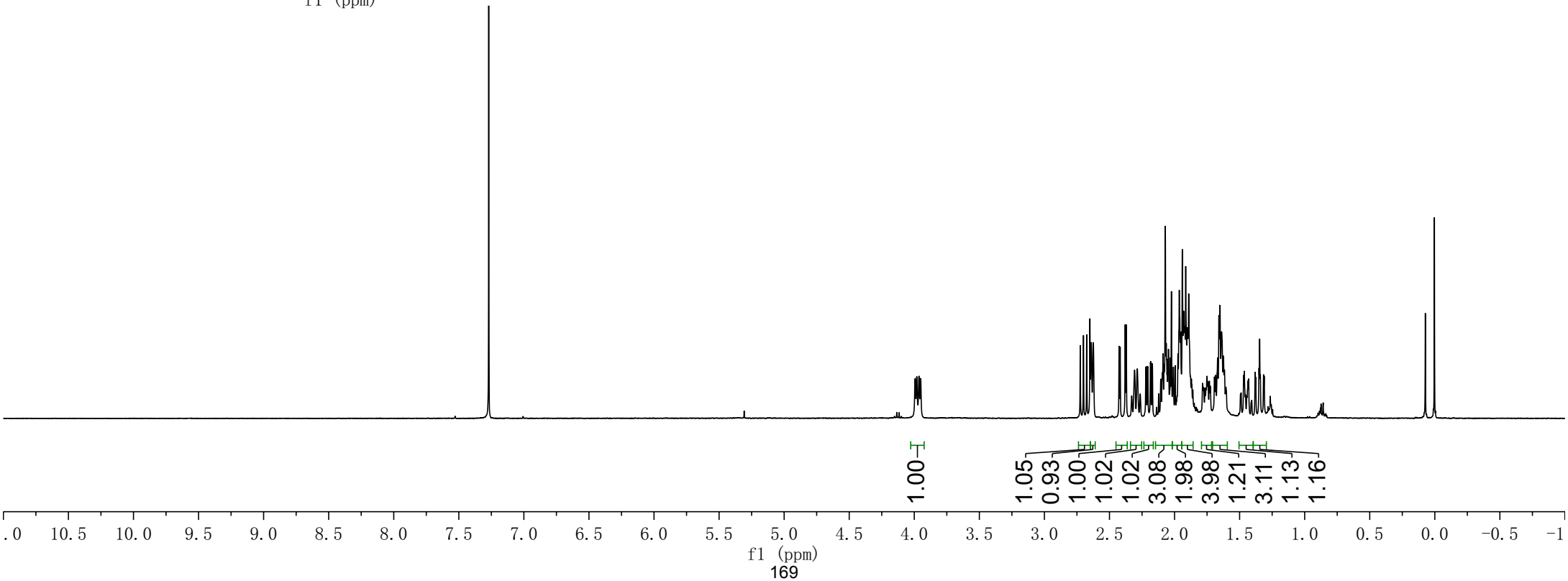
HMBC - no HSQC



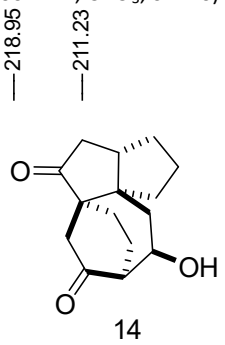
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



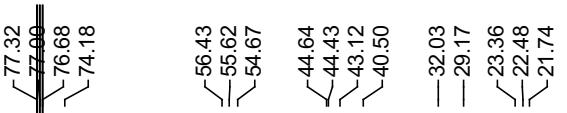
14

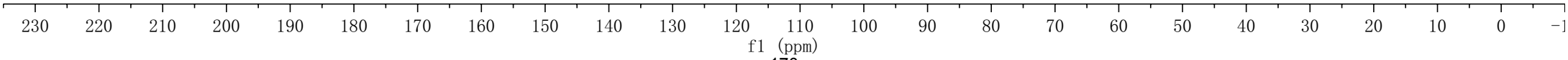


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

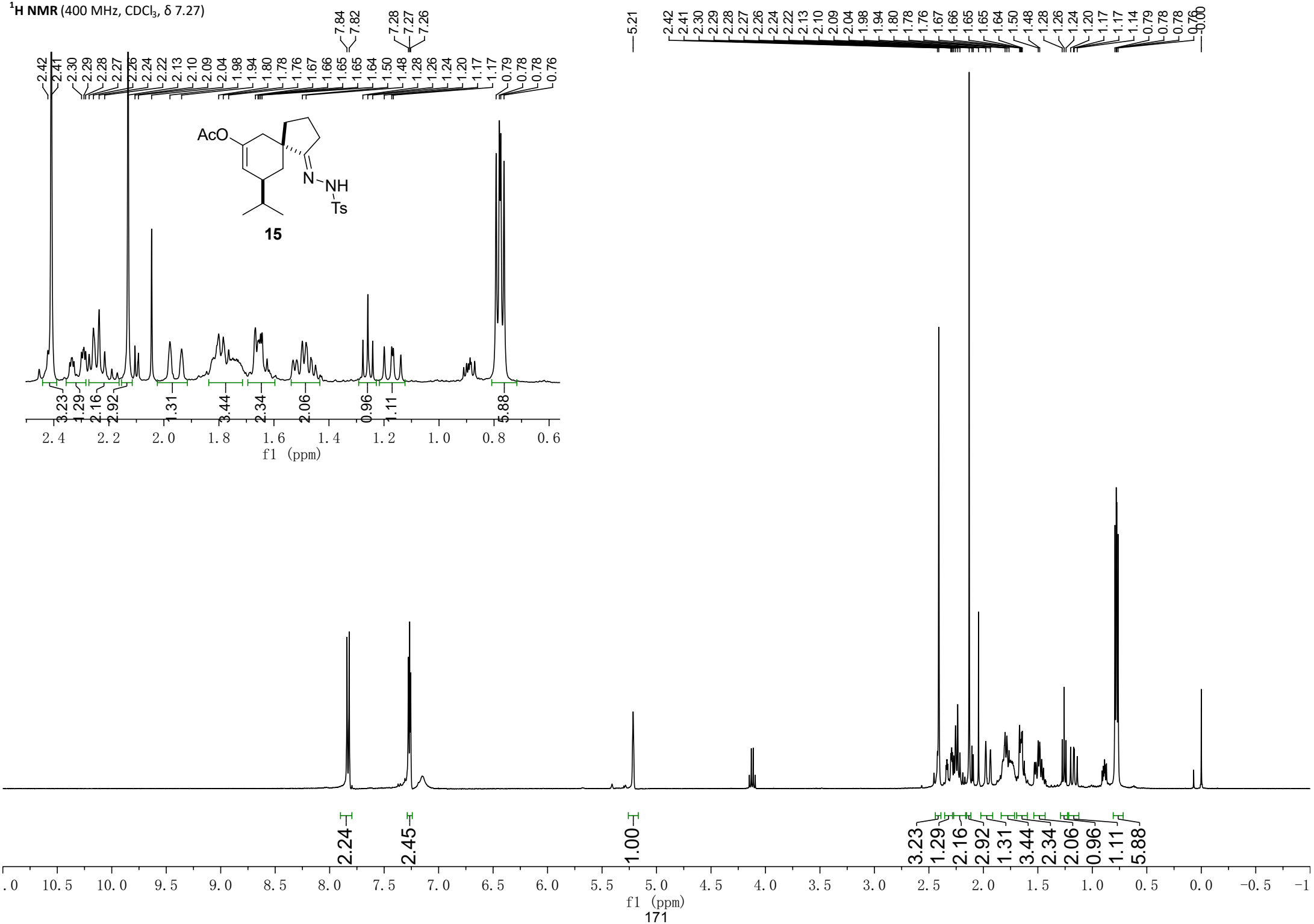


14

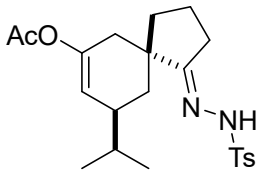




^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)

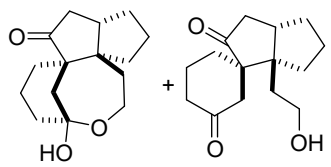


^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



15

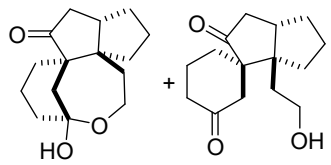
^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



16a 5 : 1 **16b**

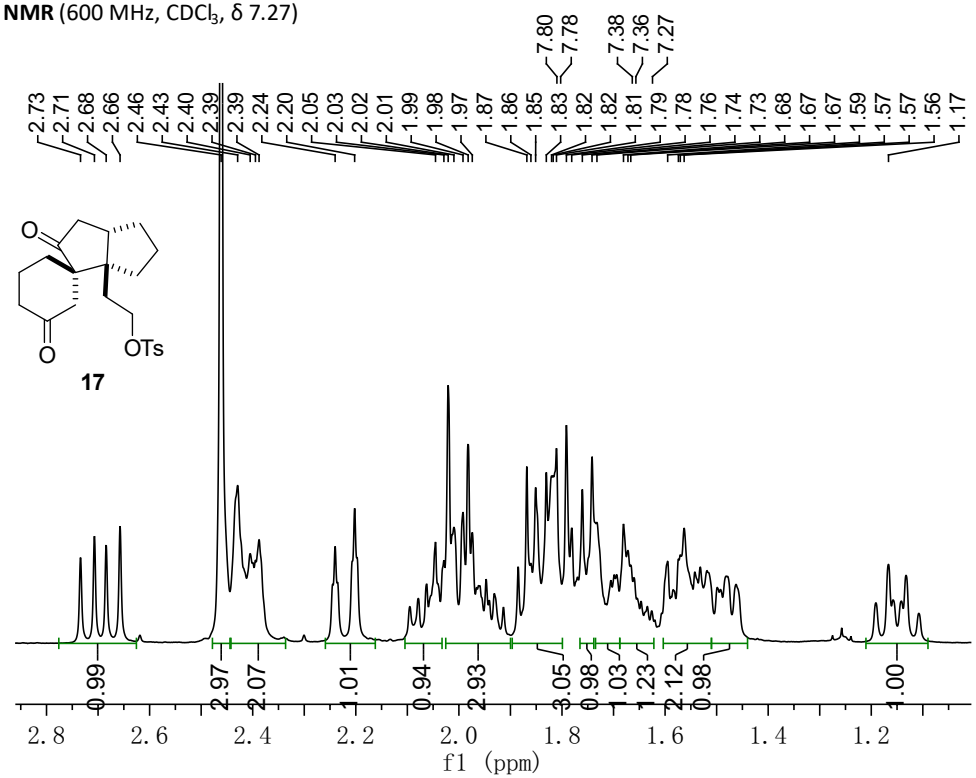
f1 (ppm)

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

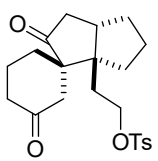


16a 5 : 1 **16b**

^{1}H NMR (600 MHz, $CDCl_3$, δ 7.27)

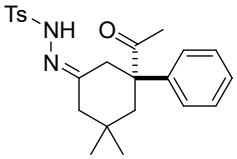


^{13}C NMR (150 MHz, $CDCl_3$, δ 77.0)



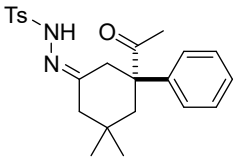
17

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



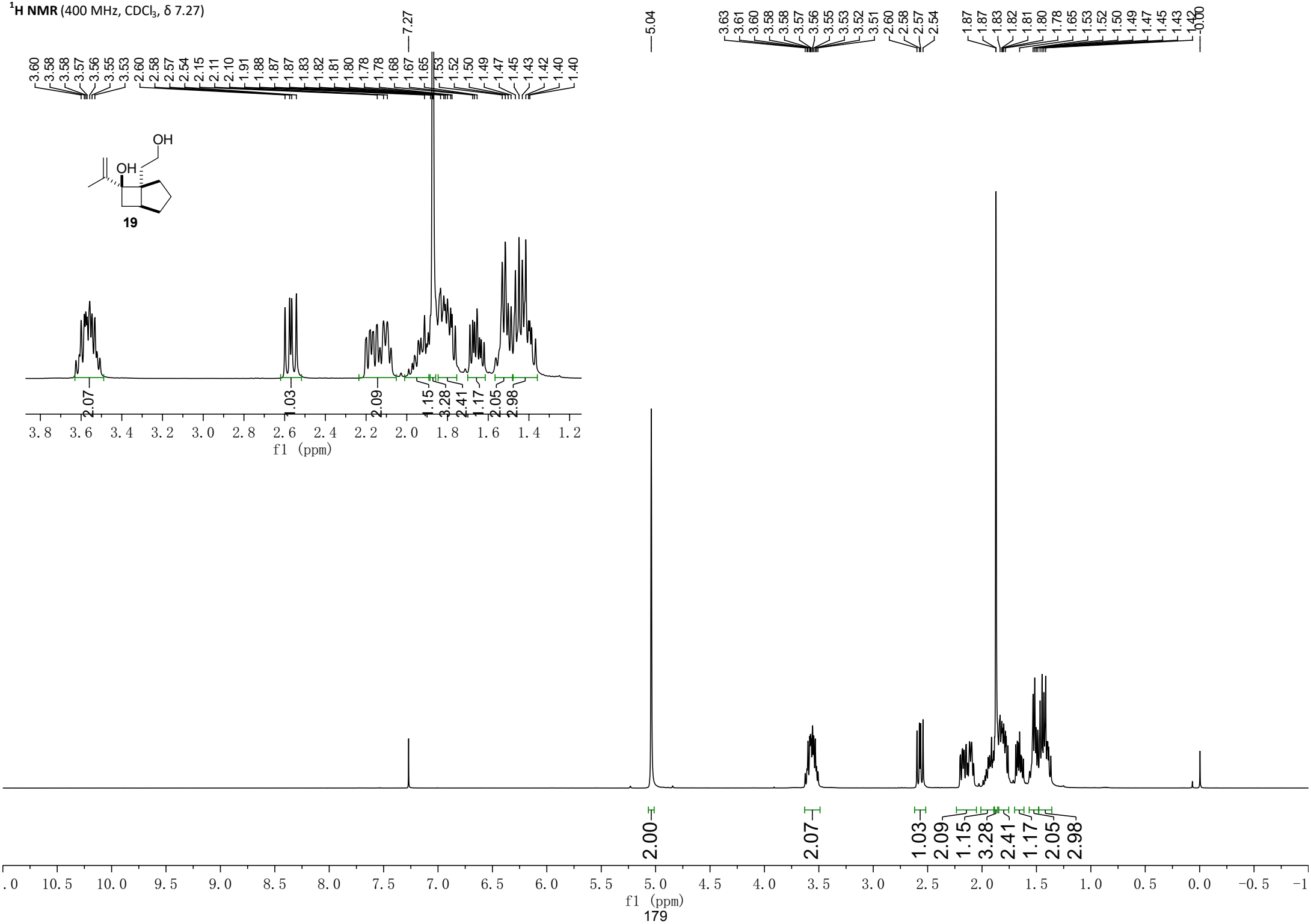
18

^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)



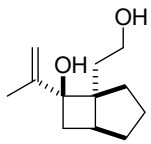
18

^{1}H NMR (400 MHz, $CDCl_3$, δ 7.27)



^{13}C NMR (100 MHz, $CDCl_3$, δ 77.0)

148.59
111.57
77.32
77.21
77.00
76.68
60.09
55.85
38.40
36.80
35.86
32.15
30.97
25.94
20.60



19