Supporting Information

CuH-Catalyzed Asymmetric Intramolecular Reductive Coupling of Allenes to Enones

Yun-Xuan Tan, Xiao-Qi Tang, Ping Liu, De-Shen Kong, Ya-Li Chen, Ping Tian, and Guo-Qiang Lin

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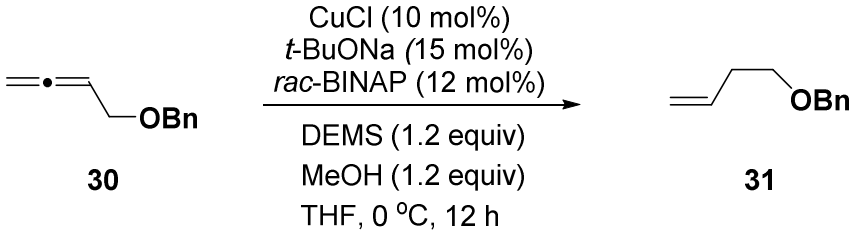
1. General Information

All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 MHz in the indicated solvents. Chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^{1}H NMR and $CDCl_3$ (δ = 77.10 ppm) for ^{13}C NMR. Coupling constants (*J*) are quoted in Hz. Optical rotations were measured on a JASCO P-1030 polarimeter. IR spectra were recorded on Nicolet iN 10 MX. ESI mass spectra were recorded on Agilent1200/G6100A.

2. Preliminary Reaction Investigation

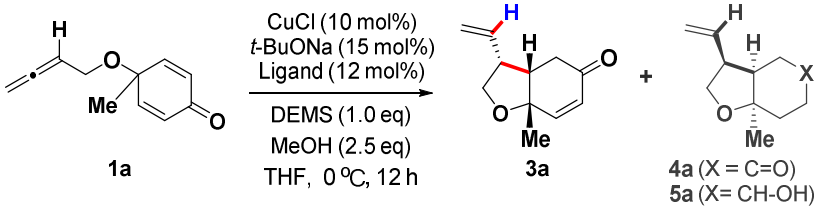
2.1 Control Experiment: CuH-Catalyzed Semireduction of α-benzyloxymethyl Allene



A dried Schlenk flask was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), *rac*-Binap (15.0 mg, 0.024 mmol, 12 mol%), *t*-BuONa (3.0 mg, 0.030 mmol, 15 mol%) and anhydrous THF (2 mL) under argon atmosphere. After the mixture was stirred at 0 °C for 10 min, DEMS was added (38 μL, 0.24 mmol, 1.2 equiv), and then stirred at 0 °C for another 10 min. A solution of substrate α-benzyloxymethyl allene **30** (0.20 mmol) in anhydrous THF (2 mL) was added, followed by anhydrous MeOH (10 μL, 0.24 mmol, 1.2 equiv). The resulting mixture was stirred at 0 °C for 12 hours. Then the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel (300–400 mesh) chromatography to afford the semireduction products **31**. 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 7.30 – 7.27 (m, 3H), 7.26 – 7.17 (m, 2H), 5.83 – 5.71 (m, 1H), 5.07 – 4.94 (m, 2H), 4.45 (s, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 2.31 (qt, *J* = 6.7, 1.3 Hz, 2H).

2.2 Initial Evaluation of Various Ligands

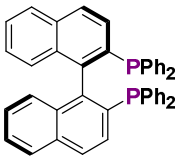
Table S1. Evaluation of Various Ligands for CuH-Catalyzed Asymmetric Intramolecular Reductive Coupling of Allenes to Enones Using **1a**.



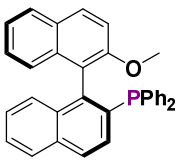
Entry	Ligand	Conv./ (%)[a]	Yield/(%)[b]	Ee/ (%)[c]
1	(*R*)-Binap, **L1**	97	78	39
2	(*S*)-MOP, **L2**	18	11	-16

3	(*R*)-Synphos, **L3**	88	54	13
4	(*R*)-Segphos, **L4**	80	63	10
5	(*R*)-H_8-Binap, **L5**	70	61	41
6	(*R*)-Difluorphos, **L6**	98	65	29
7	(*R*)-XylBinap, **L7**	93	64	26
8	(*R*)-DTBM-Segphos, **L8**	90	30	7
9	(R,S_p)-Josiphos, **L9**	85	51	-5
10	(R,S_p)-PPF-P(*t*-Bu)$_2$, **L10**	0	/	/
11	(S,S_p)-*i*-Pr-FOXAP, **L11**	60	0	/
12	(R,S_p)-Xyl-Josiphos, **L12**	83	46	-5
13	(*R*)-MeO-BIPHEP, **L13**	98	81	33
14	(*R*)-**L14**	45	40	5
15	(*R*)-MeO-F_{12}-BIPHEP, **L15**	72	60	11
16	(*S*)-P-Phos, **L16**	100	81	-35
17	(*R*)-BTFM-Garphos, **L17**	78	41	-14
18	(*Ra,R,R*)-**L18**	0	/	/
19	(*Sa,R,R*)-Siphos-PE, **L19**	0	/	/
20	(*R*)-**L20**	0	/	/
21	(*R,R*)-*i*-Pr-Duphos, **L21**	88	60	52
22	(*S,S*)-Me-Duphos, **L22**	87	47	-5
23	(*S,S*)-DIPAMP, **L23**	0	/	/
24	(*R,R*)-QuinoxP, **L24**	85	56	23
25	(*R,R,S,S*)-DUANPHOS, **L25**	68	33	-2
26	(*S,S,R,R*)-TANGPHOS, **L26**	0	/	/
27	(*R*)-SDP, **L27**	52	22	34
28	(1*S*,4*R*)-**L28**	90	0	/
29	(*R,R*)-Ph-BPE, **L29**	75	31	-50
30	**L30**	44	0	/
31	(*R*)-*i*-Pr-Phox, **L31**	50	17	-29
32	**L32**	82	0	/
33	**L33**	19	19	29

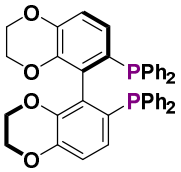
[a] Determined by ^{1}H-NMR of unpurified mixtures using CH_2Br_2 as an internal standard. [b] Determined by ^{1}H-NMR of isolated and purified product **3a**. [c] Determined by HPLC analysis using a chiral stationary phase.



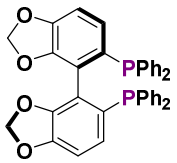
(*R*)-Binap, **L1**
97% conv., 78% yield
39% *ee*



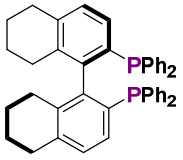
(*S*)-MOP, **L2**
18% conv., 11% yield
-16% *ee*



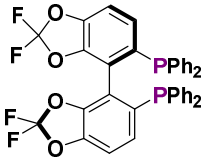
(*R*)-Synphos, **L3**
88% conv., 54% yield
13% *ee*



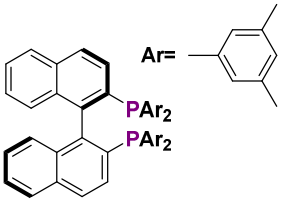
(*R*)-Segphos, **L4**
80% conv., 63% yield
10% *ee*



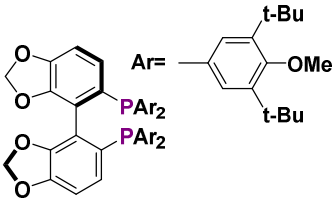
(*R*)-H_8-Binap, **L5**
70% conv., 61% yield
41% *ee*



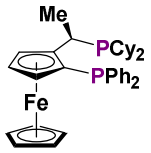
(*R*)-Difluorphos, **L6**
98% conv., 65% yield
29% *ee*



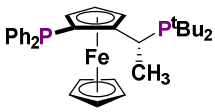
(*R*)-XylBinap, **L7**
93% conv., 64% yield
26% *ee*



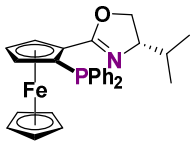
(*R*)-DTBM-Segphos, **L8**
90% conv., 30% yield
7% *ee*



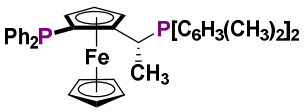
(R,S_p)-Josiphos, **L9**
85% conv., 51% yield
-5% *ee*



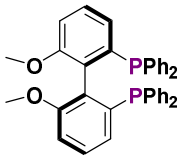
(R,S_p)-PPF-P(*t*-Bu)$_2$, **L10**
0% conv., 0% yield



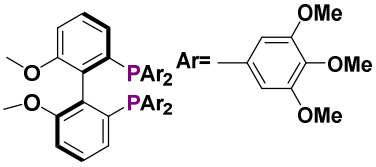
(S,S_p)-*i*-Pr-FOXAP, **L11**
60% conv., 0% yield



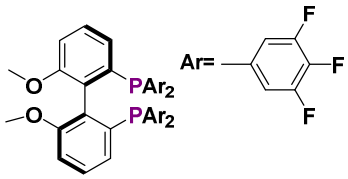
(R,S_p)-Xyl-Josiphos, **L12**
83% conv., 46% yield
-5% *ee*



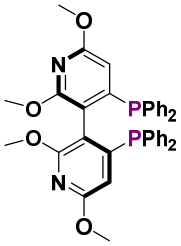
(*R*)-MeO-BIPHEP, **L13**
98% conv., 81% yield
33% *ee*



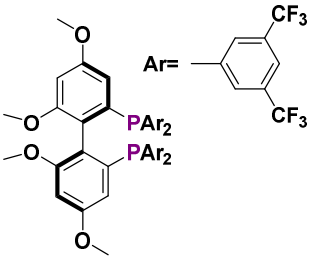
(*R*)-**L14**
45% conv., 40% yield
5% *ee*



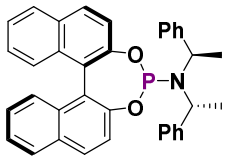
(*R*)-MeO-F_{12}-BIPHEP, **L15**
72% conv., 60% yield
11% *ee*



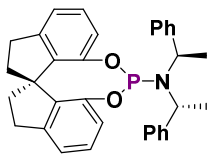
(*S*)-P-Phos, **L16**
100% conv., 81% yield
-35% *ee*



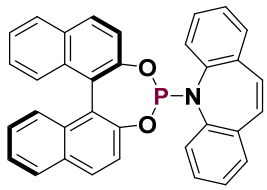
(*R*)-BTFM-Garphos, **L17**
78% conv., 41% yield
-14% *ee*



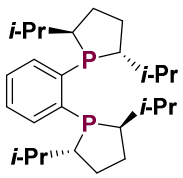
(R_a,R,R)-**L18**
yield 0 %



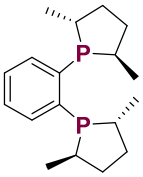
(S_a,R,R)-Siphos-PE, **L19**
yield 0 %



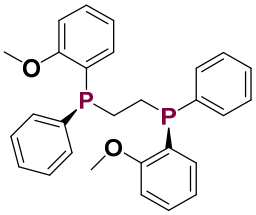
(*R*)-**L20**
0% conv., 0% yield



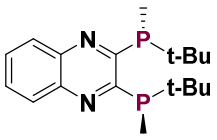
(*R*,*R*)-*i*-Pr-Duphos, **L21**
88% conv., 60% yield
52% *ee*



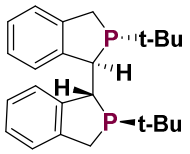
(*S*,*S*)-Me-Duphos, **L22**
87% conv., 47% yield
-5% *ee*



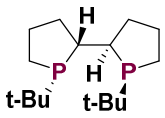
(*S*,*S*)-DIPAMP**, L23**
0% conv., 0% yield



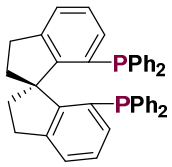
(*R*,*R*)-QuinoxP, **L24**
85% conv., 56% yield
23% *ee*



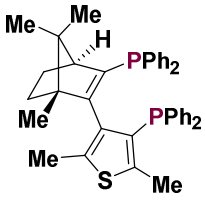
(*R*,*R*,*S*,*S*)-DUANPHOS, **L25**
68% conv., 33% yield
-2% *ee*



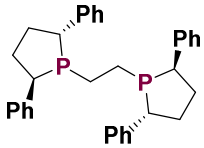
(*S*,*S*,*R*,*R*)-TANGPHOS**, L26**
0% conv., 0% yield



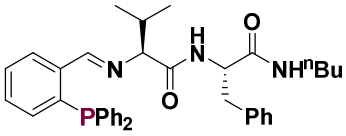
(*R*)-SDP, **L27**
52% conv., 22% yield
34% *ee*



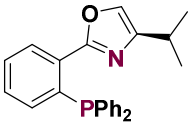
(1*S*,4*R*)-**L28**
90% conv., 0% yield



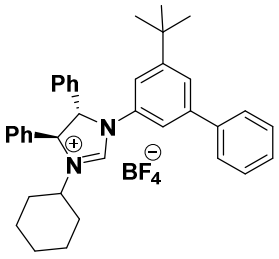
(*R*,*R*)-Ph-BPE, **L29**
75% conv., 31% yield
-50% *ee*



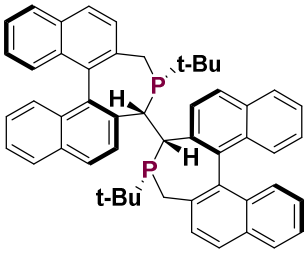
L30
44% conv., 0% yield



(*R*)-*i*-Pr-PHOX, **L31**
50% conv.,17% yield
-29% *ee*



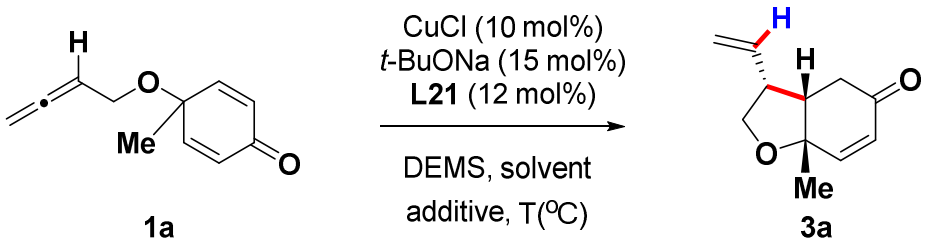
L32
82% conv., 0% yield



L33
19% conv., 19% yield
29% *ee*

2.2 Further Evaluation of Reaction Parameters

Table S2. Evaluation of Other Reaction Parameters for CuH-Catalyzed Asymmetric Intramolecular Reductive Coupling of Allenes to Enones Using **1a**.

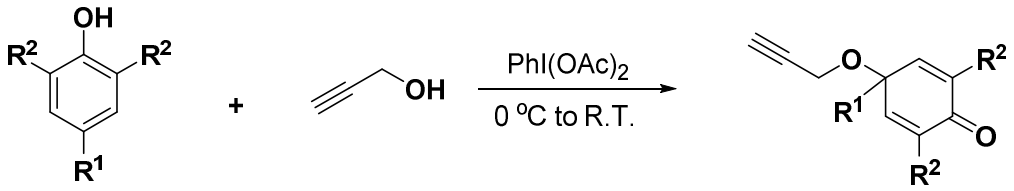


Entry	T/℃	Additive[a]	Solvent	DEMS/eq	t/h	Conv./ %[b]	Yield/%[c]	Ee/%[d]
1	-20	MeOH	THF	1.0	24	84	55	60
2	-40	---	THF	1.0	48	78	57	57
3	-40	MeOH	THF	1.0	48	81	67	57
4	-78	---	THF	2.5	48	15	13	37
5	-78	MeOH	THF	2.5	48	32	31	37
6	-40	MeOH	THF	1.5	48	98	65	68
7	-40	MeOH	Et_2O	1.5	48	100	45	74
8	-40	MeOH	1,4-dioxane	1.5	48	99	46	32
9	-40	MeOH	MTBE	1.5	48	100	52	51
10	-40	---	THF	2.0	48	100	53	82
11	-40	MeOH	THF	2.0	48	100	51	86
12	-40	MeOH	THF	2.2	48	100	43	95

[a] Additive (2.5 eq).
[b] Determined by ^{1}H-NMR of unpurified mixtures using CH_2Br_2 as an internal standard.
[c] Determined by ^{1}H-NMR of isolated and purified product **3a**.
[d] Determined by HPLC analysis using a chiral stationary phase.

3. SUBSTRATE PREPARATION

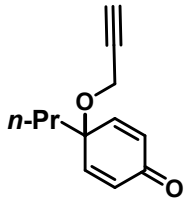
3.1 General Procedures for the Preparation of Cyclohexadienone-Tethered Alkynes



A well-stirred solution of substituted phenol **20** (1.0 mmol, 1.0 eq) in 1 mL of propargyl alcohol (**21**) was cooled to 0 °C and treated with phenyliodine (III) diacetate (PIDA, 483 mg, 1.5 mmol, 1.5 eq) in several portions. The resulting mixture was warmed to room temperature and stirred overnight. Then it was diluted with water (30 mL) and extracted with DCM (30 mL × 3). The combined organic phases were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the desired product **22**.

(Note that compounds **22a, 22b, 22e–22k, 22m, 22n, 22p-22r** were prepared according to the corresponding report.[1])

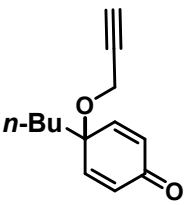
4-(prop-2-yn-1-yloxy)-4-propylcyclohexa-2,5-dienone (22c)



22c

Red oil. 72 mg, 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.80 (d, J = 10.2 Hz, 2H), 6.36 (d, J = 10.2 Hz, 2H), 4.00 (d, J = 2.4 Hz, 2H), 2.46 (t, J = 2.4 Hz, 1H), 1.80 – 1.72 (m, 2H), 1.34 – 1.22 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.34, 150.16, 131.54, 80.50, 76.56, 74.89, 53.53, 41.57, 16.93, 14.26. ESI-MS: $[M+Na]^{\oplus}$ 213.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{12}H_{15}O_2^{\oplus}$ 191.1067, found 191.1065; IR (KBr) ν (cm^{-1}) 3285, 2962, 2935, 1671, 1383, 1175, 1060, 862.

4-butyl-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dienone (22d)



22d

Yellow white solid. 70 mg, 35% yield. m.p. 63-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.79 (d, J = 10.0 Hz, 2H), 6.36 (d, J = 10.0 Hz, 2H), 4.01 (d, J = 2.0 Hz, 2H), 2.45 (s, 1H), 1.82 – 1.74 (m, 2H), 1.33 – 1.18 (m, 4H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 185.18, 150.02, 131.47, 80.43, 76.49, 74.83, 53.43, 39.07, 25.47, 22.77, 13.79. ESI-MS: $[M+Na]^{\oplus}$ 227.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{17}O_2^{\oplus}$ 205.1223, found 205.1223; IR (KBr) ν (cm^{-1}) 3279, 2975, 2947, 1672, 1461, 1382, 1067, 875, 680.

2,4,6-trimethyl-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dienone (22s)

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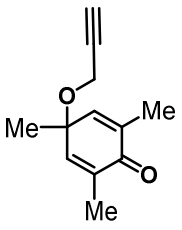
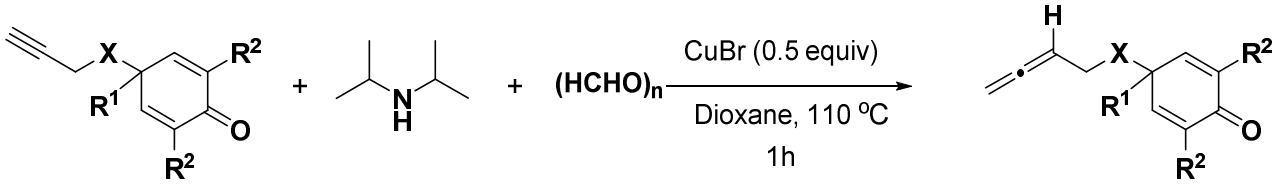
[1] He, Z.-T.; Tang, X.-Q.; Xie, L.-B.; Cheng, M.; Tian, P.; Lin, G.-Q. *Angew. Chem., Int. Ed.* **2015**, 54, 14815.



22s

White solid. 61 mg, 32% yield. m.p. 44-46 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.55 (s, 2H), 3.94 (d, *J* = 2.3 Hz, 2H), 2.45 (m, 1H), 1.91 (s, 6H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 186.21, 145.58, 136.74, 80.76, 74.38, 73.12, 52.99, 26.44, 15.81. ESI-MS: $[M+Na]^{\oplus}$ 213.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{12}H_{15}O_2^{\oplus}$ 191.1067, found 191.1067; IR (KBr) ν (cm^{-1}) 3291, 2977, 2926, 2864, 1675, 1391, 1211, 1077, 701.

3.2 General Procedures for the Preparation of Cyclohexadienone-Tethered Allenes

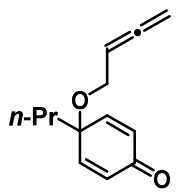


22 23 24 1

To a well-stirred solution of **22** (1.0 mmol, 1.0 eq) in dioxane (5 mL) was added paraformaldehyde **24** (150 mg, 5.0 mmol, 5 eq), CuBr (72 mg, 0.5 mmol, 0.5 eq) and diisopropylamine **23** (280 ul, 2.0 mmol, 2.0 eq) under argon atmosphere. The resulting mixture was stirred at 110 °C for 1 h. After cooled to room temperature, the reaction mixture was filtered and washed with DCM (10 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the pure substrates **1**.

(Note that compounds **1a, 1b, 1e–1k, 1m, 1n, 1p-1r** were prepared according to the corresponding report.[1])

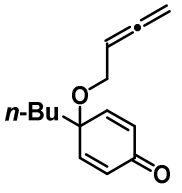
4-(buta-2,3-dien-1-yloxy)-4-propylcyclohexa-2,5-dienone (1c)



1c

Red oil. 80 mg, 39% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.79 (d, *J* = 10.0 Hz, 2H), 6.34 (d, *J* = 10.0 Hz, 2H), 5.29 – 5.13 (m, 1H), 4.68 – 4.85 (m, 2H), 3.82 – 3.94 (m, 2H), 1.77 – 1.69 (m, 2H), 1.22 – 1.34 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 209.24, 185.56, 151.29, 130.96, 88.63, 76.11, 75.93, 63.73, 41.71, 16.90, 14.28. ESI-MS: $[M+Na]^{\oplus}$ 227.2; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{17}O_2^{\oplus}$ 205.1223, found 205.1222; IR (KBr) *v* (cm^{-1}) 2962, 2935, 1957, 1671, 1466, 1381, 1174, 862.

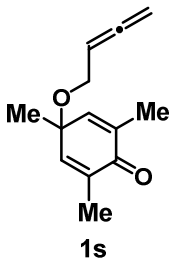
4-(buta-2,3-dien-1-yloxy)-4-butylcyclohexa-2,5-dienone (1d)



1d

Yellow oil. 94 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.78 (d, *J* = 10.1 Hz, 2H), 6.34 (d, *J* = 10.1 Hz, 2H), 5.21 (p, *J* = 6.8 Hz, 1H), 4.77 (dd, *J* = 4.0, 2.6 Hz, 2H), 3.92 – 3.84 (m, 2H), 1.80 – 1.70 (m, 2H), 1.32 – 1.18 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 209.25, 185.55, 151.25, 130.99, 88.62 , 76.09, 75.96, 63.74, 39.27, 25.56, 22.88, 13.87. ESI-MS: $[M+H]^{\oplus}$ 219.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{14}H_{19}O_2^{\oplus}$ 219.1380, found 219.1378; IR (KBr) ν (cm^{-1}) 3040, 2958, 2935, 1958, 1672, 1381, 1255, 861.

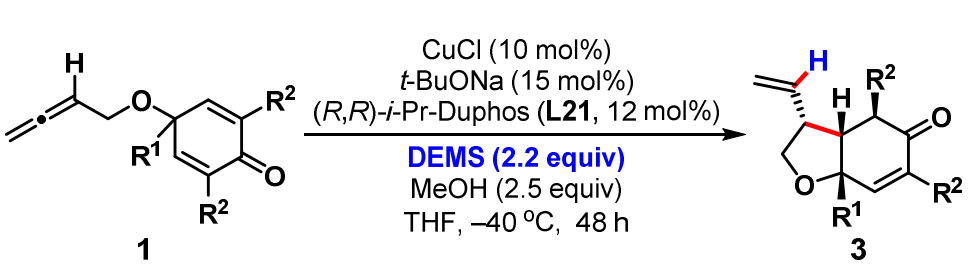
4-(buta-2,3-dien-1-yloxy)-2,4,6-trimethylcyclohexa-2,5-dienone (1s)



1s

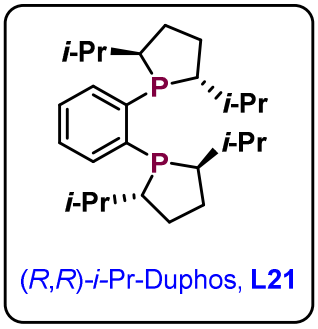
Pale yellow solid. 80 mg, 39% yield. m.p. 42-43 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.54 (s, 2H), 5.20 (p, *J* = 6.8 Hz, 1H), 4.76 (dd, *J* = 4.1, 2.4 Hz, 2H), 3.87 – 3.78 (m, 2H), 1.91 (s, 6H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 209.20, 186.65, 146.79, 136.35, 88.76, 75.88, 72.66, 63.47, 26.73, 16.04. ESI-MS: $[M+H]^{\oplus}$ 205.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{17}O_2^{\oplus}$ 205.1223, found 205.1223; IR (KBr) ν (cm^{-1}) 3263, 3060, 2976, 2922, 1956, 1675, 1369, 1069, 857.

4. Scope Of The Substrates



1 **3**

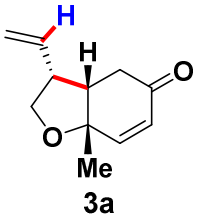
For **1a** to **1r**: R^2 = H; For **1s**: R^1 = R^2 = Me



(*R*,*R*)-*i*-Pr-Duphos, **L21**

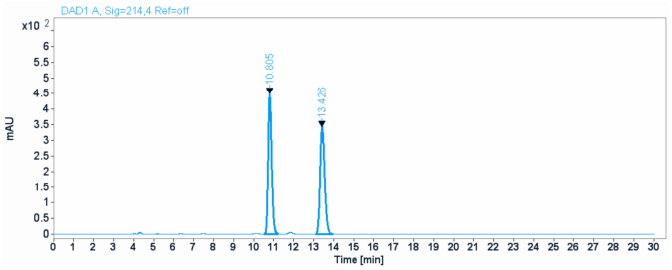
General Procedure: A dried Schlenk flask was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), ligand **L21** (10.0 mg, 0.024 mmol, 12 mol%), *t*-BuONa (3.0 mg, 0.030 mmol, 15 mol%) and anhydrous THF (2 mL) under argon atmosphere. After the mixture was stirred at –40 °C for 10 min, DEMS (70 μL, 0.44 mmol, 2.2 equiv) was added, and then stirred at –40 °C for another 10 min. A solution of substrate **1** (0.20 mmol) in anhydrous THF (2 mL) was added, followed by anhydrous MeOH (20 μL, 0.5 mmol, 2.5 equiv). The resulting mixture was stirred at –40 °C for 48 hours. Then the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel (300–400 mesh) chromatography to afford the desired products **3**. (Notice: The racemic products were prepared according to the same procedure above except for using *rac*-BINAP instead of **L21,** and the reaction was stirred under room temperature.)

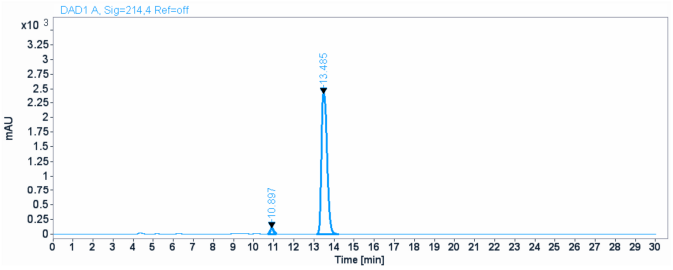
(3*R*,3a*S*,7a*S*)-7a-methyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3a)



3a

Light yellow oil. 15.2 mg, 43% yield. $[\alpha]_D^{23.0}$ +26.7 (c 0.55, $CHCl_3$) 95% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.63 (dd, *J* = 10.3, 1.2 Hz, 1H), 5.99 (d, *J* = 10.3 Hz, 1H), 5.54 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.08 (dd, *J* = 13.6, 6.3 Hz, 2H), 4.09 (dd, *J* = 9.0, 7.7 Hz, 1H), 3.56 (dd, *J* = 9.1, 6.7 Hz, 1H), 3.17 – 3.06 (m, 1H), 2.65 – 2.56 (m, 2H), 2.51 (dd, *J* = 17.7, 7.1 Hz, 1H), 1.48 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ(ppm) 197.61, 152.72, 135.75, 129.59, 118.85, 78.83, 71.15, 47.61, 46.33, 35.67, 25.27; ESI-MS: $[M+Na]^{\oplus}$ 201.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{11}H_{15}O_2^{\oplus}$ 179.1067, found 179.1066; IR (KBr) ν (cm^{-1}) 2971, 2927, 2857, 1684, 1653, 1648, 1637, 1457, 1384, 1286, 1232, 1154, 1090, 1046, 1030, 924, 864, 810; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 10.9 min (minor), 13.5 min (major).





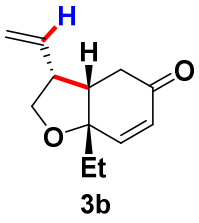
Signal: DAD1 A, Sig=214,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
10.805	0.205	5527.686	449.057	50.2967	RAC
13.426	0.265	5462.463	343.050	49.7033	

Signal: DAD1 A, Sig=214,4 Ref=off

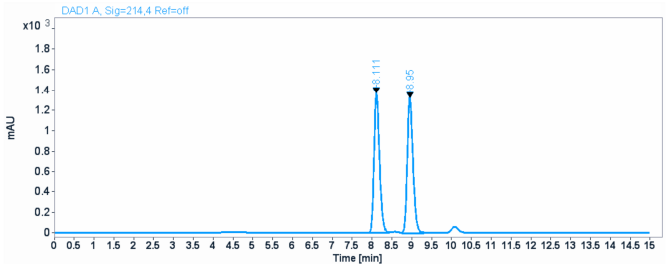
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
10.897	0.206	1209.771	97.700	2.5085	94.9
13.485	0.324	47016.484	2415.934	97.4915	

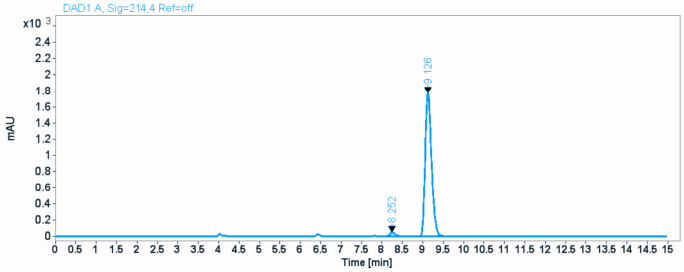
(3*R*,3a*S*,7a*S*)-7a-ethyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3b)



3b

Light yellow oil. 20 mg, 52% yield. $[\alpha]_D^{23.3}$ +25.5 (c 0.64, $CHCl_3$) for 96% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.63 (dd, *J* = 10.4, 1.2 Hz, 1H), 6.04 (d, *J* = 10.4 Hz, 1H), 5.56 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.12 – 5.02 (m, 2H), 4.03 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.58 (dd, *J* = 9.0, 6.1 Hz, 1H), 3.12 – 3.01 (m, 1H), 2.72 – 2.64 (m, 1H), 2.59 (dd, *J* = 17.7, 2.8 Hz, 1H), 2.49 (dd, *J* = 17.7, 7.0 Hz, 1H), 1.89 – 1.71 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 197.89, 151.87, 135.80, 130.19, 118.74, 81.16, 71.01, 48.13, 43.81, 36.03, 31.90, 8.29; ESI-MS: $[M+H]^{\oplus}$ 193.0; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{12}H_{17}O_2^{\oplus}$ 193.1223, found 193.1224; IR (KBr) ν (cm^{-1}) 3078, 2969, 2936, 2881, 1682, 1639, 1462, 1384, 1249, 1130, 1065, 1045, 966, 923, 735; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 8.2 min (minor), 9.1 min (major).





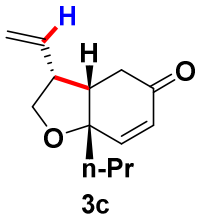
Signal: DAD1 A, Sig=214,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
8.111	0.159	13038.166	1367.130	49.5474	RAC
8.950	0.167	13276.370	1323.588	50.4526	

Signal: DAD1 A, Sig=214,4 Ref=off

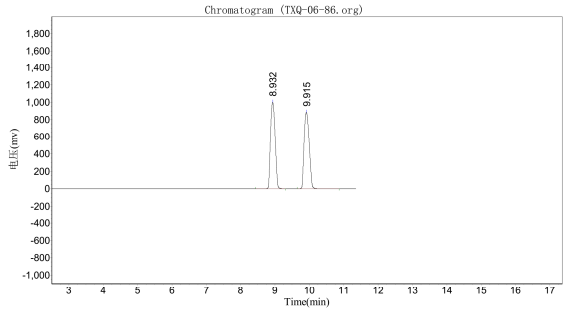
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
8.252	0.154	413.698	44.881	2.1147	95.771
9.126	0.180	19148.971	1774.164	97.8853	

(3*R*,3a*S*,7a*S*)-7a-propyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3c)



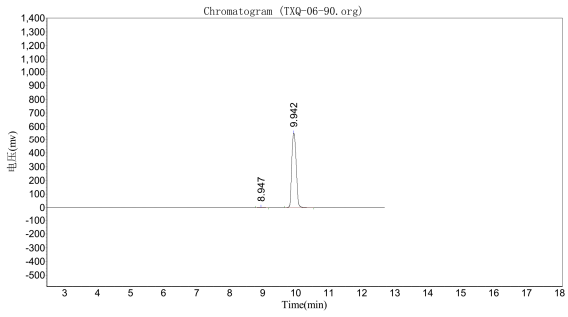
3c

Light yellow oil. 17.6 mg, 43% yield. $[\alpha]_D^{24.1}$ +25.0 (c 0.75, $CHCl_3$) for 99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 6.64 (dd, *J* = 10.4, 1.4 Hz, 1H), 6.02 (d, *J* = 10.4 Hz, 1H), 5.55 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.12 – 5.02 (m, 2H), 4.03 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.56 (dd, *J* = 9.0, 6.1 Hz, 1H), 3.12 – 2.98 (m, 1H), 2.70 – 2.63 (m, 1H), 2.54 (qd, *J* = 17.7, 4.9 Hz, 2H), 1.72 (qdd, *J* = 13.7, 10.3, 6.5 Hz, 2H), 1.51 – 1.40 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 197.79, 152.06, 135.79, 129.95, 118.68, 80.90, 70.94, 47.98, 44.37, 41.50, 35.91, 17.32, 14.55.; ESI-MS: $[M+Na]^{\oplus}$ 229.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{19}O_2^{\oplus}$ 207.1380, found 207.1378; IR (KBr) ν (cm^{-1}) 3086, 2958, 2242, 1683, 1413, 1384, 1360, 1260, 1057, 1025, 924, 796, 740; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 8.9 min (minor), 9.9 min (major).



Results

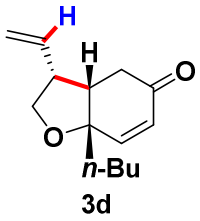
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.932	996566.813	9470160.000	50.8565
2		9.915	881466.500	9151181.000	49.1435
Total			1878033.313	18621341.000	100.0000



Results

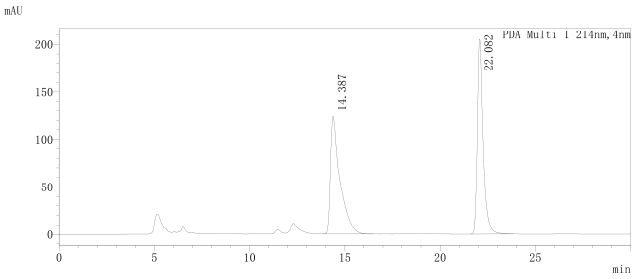
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.947	2141.808	21846.102	0.4275
2		9.942	552358.313	5088220.500	99.5725
Total			554500.120	5110066.602	100.0000

(3*R*,3a*S*,7a*S*)-7a-butyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3d)



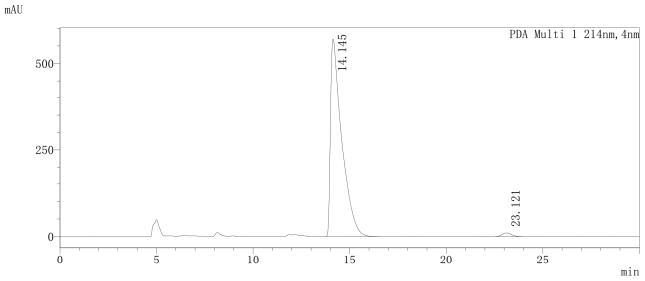
3d

Light yellow oil. 18 mg, 41% yield. $[\alpha]_D^{20.9}$ +16.2 (c 0.53, $CHCl_3$) for 97% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.64 (dd, J = 10.4, 1.2 Hz, 1H), 6.02 (d, J = 10.4 Hz, 1H), 5.55 (dt, J = 17.0, 9.8 Hz, 1H), 5.12 – 5.01 (m, 2H), 4.03 (dd, J = 9.0, 7.3 Hz, 1H), 3.57 (dd, J = 9.0, 6.2 Hz, 1H), 3.12 – 3.00 (m, 1H), 2.71 – 2.63 (m, 1H), 2.54 (qd, J = 17.7, 4.8 Hz, 2H), 1.80 (dt, J = 16.4, 7.4 Hz, 1H), 1.73 – 1.64 (m, 1H), 1.44 – 1.30 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.83, 152.09, 135.79, 129.98, 118.70, 80.92, 70.94, 48.00, 44.34, 39.01, 35.95, 26.11, 23.17, 13.96.; ESI-MS: $[M+H]^{\oplus}$ 221.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{14}H_{21}O_2^{\oplus}$ 221.1537, found 221.1535; IR (KBr) ν (cm^{-1}) 2957, 2933, 1684,1638, 1466, 1384, 1241, 1061, 983, 922, 875; HPLC: Chiracel AS-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 14.1min (major), 23.1 min (minor).



PDA Ch1 214nm

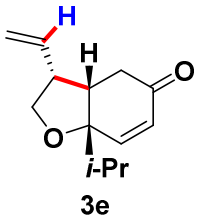
#	Ret.Time	Area	Height	Area%
1	14.387	4304817	123773	50.154
2	22.082	4278407	205203	49.846



PDA Ch1 214nm

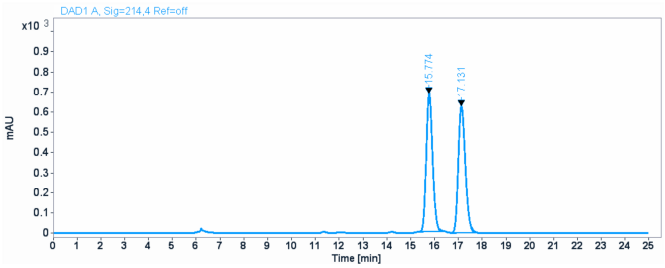
#	Ret.Time	Area	Height	Area%
1	14.145	23040955	568899	98.513
2	23.121	347765	10480	1.487

(3*R*,3a*S*,7a*S*)-7a-isopropyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3e)



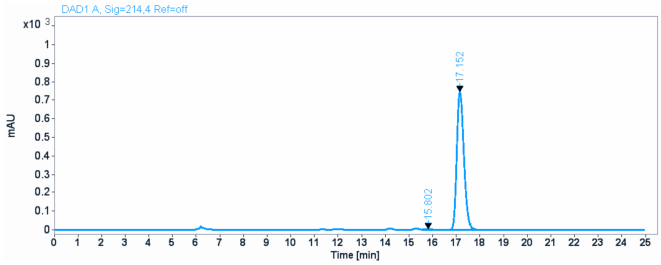
3e

Light yellow oil. 19.0 mg, 46% yield. $[\alpha]_D^{23.3}$ +32.7 (c 0.59, $CHCl_3$) for 99% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.61 (dd, J = 10.5, 1.3 Hz, 1H), 6.10 (d, J = 10.5 Hz, 1H), 5.56 (dt, J = 16.8, 9.8 Hz, 1H), 5.07 (dd, J = 9.1, 7.7 Hz, 2H), 3.95 (dd, J = 8.9, 6.6 Hz, 1H), 3.57 (dd, J = 8.9, 5.6 Hz, 1H), 3.01 (tt, J = 9.4, 6.2 Hz, 1H), 2.75 (td, J = 7.3, 1.5 Hz, 1H), 2.60 (dd, J = 17.9, 2.1 Hz, 1H), 2.49 (dd, J = 17.9, 7.3 Hz, 1H), 2.07 – 1.94 (m, 1H), 1.02 (dd, J = 6.9, 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.10, 150.44, 135.69, 130.65, 118.62, 83.08, 70.65, 49.09, 41.55, 36.88, 36.62, 17.74, 16.90; ESI-MS: $[M+H]^{\oplus}$ 207.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{19}O_2^{\oplus}$ 207.1380, found 207.1379; IR (KBr) ν (cm^{-1}) 3077, 2963, 2876, 1683, 1639, 1470, 1385, 1259, 1063, 996, 923, 781; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 99/1; flow rate = 0.5 mL/min; Retention time: 15.8 min (minor), 17.1 min (major).



Signal: DAD1 A, Sig=214,4 Ref=off

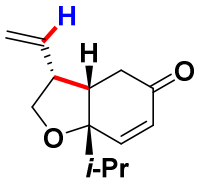
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
15.774	0.307	12617.253	685.336	49.6578	RAC
17.131	0.341	12791.151	625.843	50.3422	



Signal: DAD1 A, Sig=214,4 Ref=off

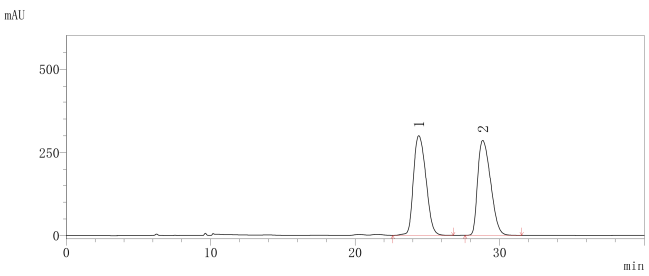
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
15.802	0.274	73.436	4.467	0.4718	99.056
17.152	0.345	15490.315	747.946	99.5282	

(3*R*,3a*S*,7a*S*)-7a-isopropyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3e)



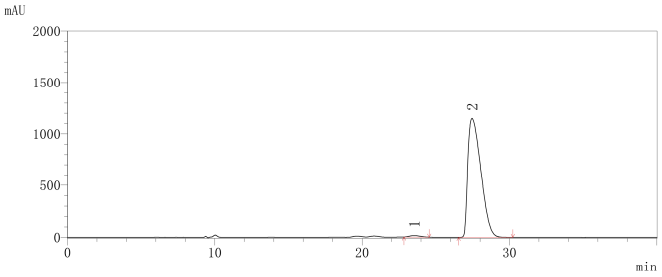
3e

For 1 mmol scale, A dried Schlenk flask was charged with CuCl (4.95 mg, 5 mol%), ligand **L21** (25.0 mg, 6 mol%), *t*-BuONa (7.2 mg, 7.5 mol%) and anhydrous THF (10 mL) under argon atmosphere. After the mixture was stirred at –40 °C for 10 min, DEMS (351 μL, 2.2 equiv) was added, and then stirred at –40 °C for another 10 min. A solution of substrate **1e** (1.0 mmol, 1.0 equiv) in anhydrous THF (10 mL) was added, followed by anhydrous MeOH (101 μL, 2.5 equiv). The resulting mixture was stirred at –40 °C for 24 hours. Then the reaction mixture was filtered, washed with EtOAc (50 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel (300–400 mesh) chromatography to afford the desired products **3e**. Light yellow oil. 104 mg, 50% yield. $[\alpha]_D^{21.4}$ +29.2 (c 1.50, $CHCl_3$) for 98% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.61 (dd, *J* = 10.5, 1.3 Hz, 1H), 6.10 (d, *J* = 10.5 Hz, 1H), 5.56 (dt, *J* = 16.8, 9.8 Hz, 1H), 5.07 (dd, *J* = 9.1, 7.7 Hz, 2H), 3.95 (dd, *J* = 8.9, 6.6 Hz, 1H), 3.57 (dd, *J* = 8.9, 5.6 Hz, 1H), 3.01 (tt, *J* = 9.4, 6.2 Hz, 1H), 2.75 (td, *J* = 7.3, 1.5 Hz, 1H), 2.60 (dd, *J* = 17.9, 2.1 Hz, 1H), 2.49 (dd, *J* = 17.9, 7.3 Hz, 1H), 2.07 – 1.94 (m, 1H), 1.02 (dd, *J* = 6.9, 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 198.10, 150.44, 135.69, 130.65, 118.62, 83.08, 70.65, 49.09, 41.55, 36.88, 36.62, 17.74, 16.90; ESI-MS: $[M+H]^{\oplus}$ 207.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{19}O_2^{\oplus}$ 207.1380, found 207.1379; IR (KBr) ν (cm^{-1}) 3077, 2963, 2876, 1683, 1639, 1470, 1385, 1259, 1063, 996, 923, 781; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 99/1; flow rate = 0.5 mL/min; Retention time: 23.5 min (minor), 27.5 min (major).



PDA Ch1 214nm

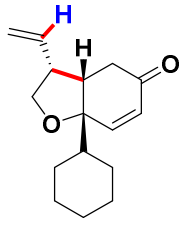
Number	Ret.Time	Area	Area%
1	24.400	18053607	50.42
2	28.828	17755180	49.58



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	23.531	701674	0.99
2	27.460	70447137	99.01

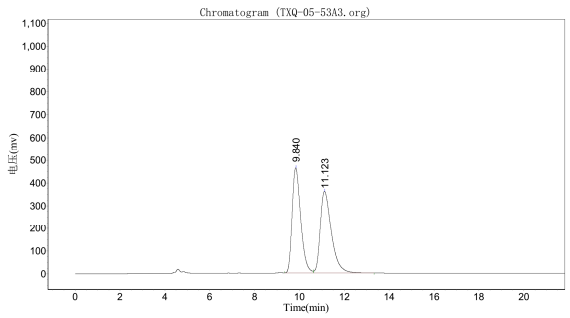
(3*R*,3a*S*,7a*S*)-7a-cyclohexyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3f)

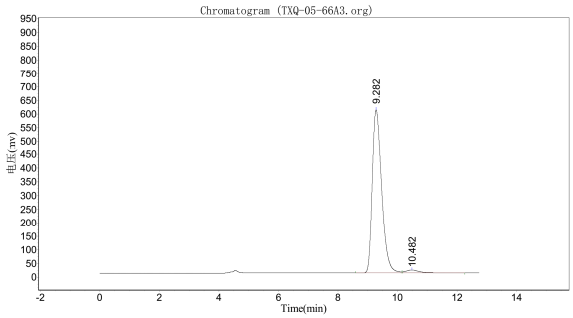


3f

Light yellow oil. 27.1 mg, 55% yield.$[\alpha]_D^{25.3}$ +10.4 (*c* 0.75 $CHCl_3$) for 95% *ee*;^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 6.60 (dd, *J* = 10.5, 1.3 Hz, 1H), 6.07 (d, *J* = 10.5 Hz, 1H), 5.56 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.06 (dd, *J* = 9.4, 7.8 Hz, 2H), 3.92 (dd, *J* = 8.9, 6.5 Hz, 1H), 3.57 (dd, *J* = 8.9, 5.4 Hz, 1H), 2.98 (tt, *J* = 9.4, 6.0 Hz, 1H), 2.78

(td, *J* = 7.1, 1.5 Hz, 1H), 2.54 (qd, *J* = 17.9, 4.8 Hz, 2H), 1.92 – 1.75 (m, 4H), 1.72 – 1.61 (m, 2H), 1.30 – 1.21 (m, 2H), 1.19 – 1.04 (m, 3H); ^{13}C NMR (10 0 MHz, $CDCl_3$) δ (ppm) δ 198.25, 151.07, 135.74, 130.27, 118.60, 82.70, 70.66, 49.09, 47.09, 41.66, 36.88, 27.88, 26.94, 26.46, 26.37, 26.28; ESI-MS: $[M+H]^{\oplus}$ 247.2; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{16}H_{23}O_2^{\oplus}$ 247.1693, found 247.1690; IR (KBr) ν (cm^{-1}) 3077, 3032, 2925, 2852, 1682, 1639, 1450, 1411, 1386, 1300, 1261, 1244, 1180, 1046, 995, 919, 820, 732; HPLC: Chiracel OJ-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 9.3 min (major), 10.5min (minor).





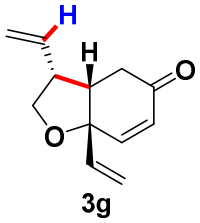
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.840	463840.594	12412100.000	47.4543
2		11.123	361065.281	12634623.000	48.3050
3		105.590	76.701	1109188.000	4.2407
Total			824982.576	26155911.000	100.0000

Results

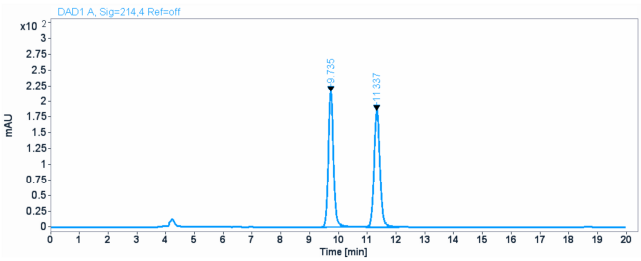
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.282	598918.188	13164325.000	97.4466
2		10.482	10782.382	344951.188	2.5534
Total			609700.569	13509276.188	100.0000

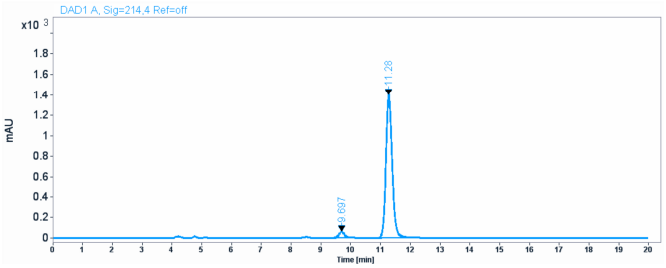
(3*R*,3a*S*,7a*S*)-3,7a-divinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3g)



3g

Light yellow oil. 14.0 mg, 37% yield. $[\alpha]_D^{23.3}$ –23.1 (c 0.385, $CHCl_3$) for 93% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.56 (dd, *J* = 10.3, 1.2 Hz, 1H), 6.11 (d, *J* = 10.3 Hz, 1H), 5.95 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.64 – 5.52 (m, 1H), 5.28 (ddd, *J* = 14.0, 11.4, 0.7 Hz, 2H), 5.13 – 5.06 (m, 2H), 4.14 (dd, *J* = 9.0, 7.5 Hz, 1H), 3.71 (dd, *J* = 9.0, 6.4 Hz, 1H), 3.17 – 3.07 (m, 1H), 2.72 – 2.65 (m, 1H), 2.53 (qd, *J* = 17.3, 5.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.65, 149.21, 139.02, 135.35, 130.60, 118.86, 115.74, 81.29, 71.53, 47.05, 45.89, 34.95; ESI-MS: $[M+H]^{\oplus}$191.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{12}H_{15}O_2^{\oplus}$ 191.1067, found 191.1066; IR (KBr) ν (cm^{-1}) 3081, 2924, 2856, 1685, 1638, 1409, 1383, 1260, 1065, 1027, 998, 928, 791; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 9.7 min (minor), 11.3 min (major).





Signal: DAD1 A, Sig=214,4 Ref=off

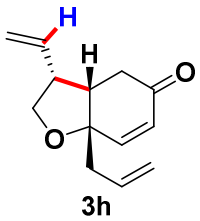
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
9.735	0.206	2665.235	215.519	50.2878	RAC
11.337	0.238	2634.729	184.430	49.7122	

Signal: DAD1 A, Sig=214,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
9.697	0.197	688.301	58.330	3.2842	93.432
11.280	0.242	20269.363	1396.788	96.7158	

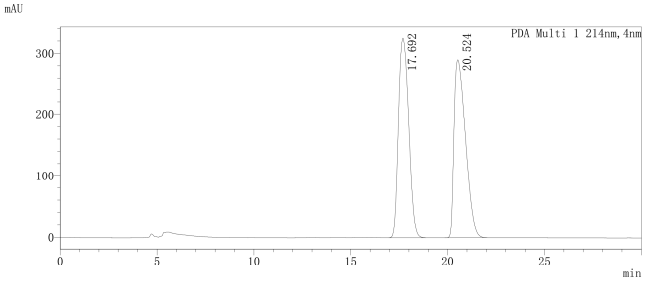
(3*R*,3a*S*,7a*S*)-7a-allyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3h)

Light yellow oil. 18.5 mg, 45% yield. $[\alpha]_D^{21.9}$ +12.0 (*c* 0.75, $CHCl_3$) for 98% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.63 (dd, *J* = 10.4, 1.4 Hz, 1H), 6.04 (d, *J* = 10.4 Hz, 1H), 5.90 – 5.77 (m, 1H), 5.55 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.17 (m, 2H), 5.07 (m, 2H), 4.04 (dd, *J* = 9.0, 7.1 Hz, 1H), 3.60 (dd, *J* = 9.0, 5.9 Hz, 1H), 3.06



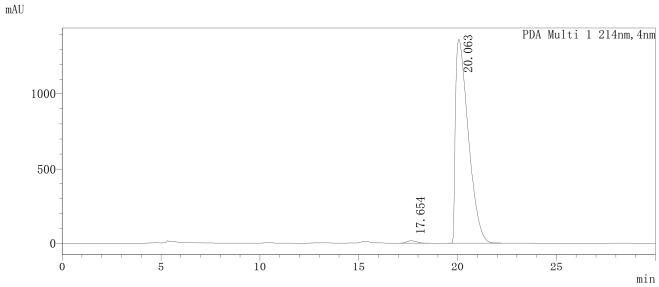
3h

(m, 1H), 2.74 – 2.67 (m, 1H), 2.60 – 2.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.62, 151.38, 135.67, 132.14, 130.15, 119.29, 118.73, 80.27, 71.04, 47.96, 43.87, 43.56, 35.84; ESI-MS: $[M+H]^{\oplus}$ 205.0; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{17}O_2^{\oplus}$ 205.1223, found 205.1223; IR (KBr) ν (cm^{-1}) 3077, 2977, 2918, 2857, 1628, 1639, 1507, 1427, 1411, 1385, 1244, 1124, 1082, 997, 922, 851; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 99/1; flow rate = 0.7 mL/min; Retention time: 20.0 min (major), 17.6 min (minor).



PDA Ch1 214nm

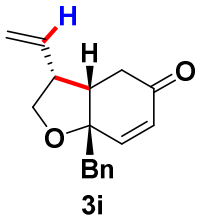
#	Ret.Time	Area	Height	Area%
1	17.692	11957928	325164	49.967
2	20.524	11973831	290295	50.033



PDA Ch1 214nm

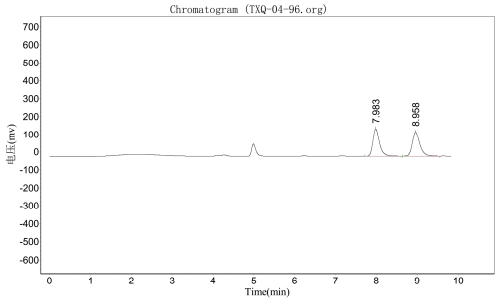
#	Ret.Time	Area	Height	Area%
1	17.654	583137	16276	0.934
2	20.063	61857083	1367059	99.066

(3*R*,3a*S*,7a*S*)-7a-benzyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3i)



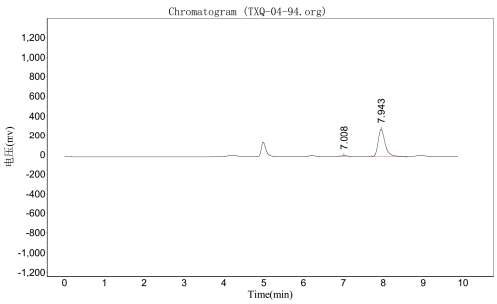
3i

Light yellow oil. 21.3 mg, 42% yield. $[\alpha]_D^{26.3}$ –5.6 (*c* 0.79, CH_3OH) for 96% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32 – 7.20 (m, 5H), 6.58 (dd, *J* = 10.4, 1.5 Hz, 1H), 6.00 (d, *J* = 10.4 Hz, 1H), 5.52 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.03 (dd, *J* = 9.4, 8.1 Hz, 2H), 3.96 (dd, *J* = 9.0, 7.0 Hz, 1H), 3.57 (dd, *J* = 9.0, 5.5 Hz, 1H), 3.08 – 2.91 (m, 3H), 2.75 – 2.65 (m, 1H), 2.47 (dd, *J* = 17.7, 1.7 Hz, 1H), 2.15 (dd, *J* = 17.7, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.57, 151.51, 135.83, 135.63, 130.31, 129.99, 128.29, 126.98, 118.67, 80.85, 70.99, 47.97, 45.14, 43.90, 35.64; ESI-MS: $[M+H]^{\oplus}$ 255.0; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{17}H_{19}O_2^{\oplus}$ 255.1380, found 255.1376; IR (KBr) ν (cm^{-1})3062, 3028, 2936, 2858, 1620, 1638, 1603, 1493, 1454, 1424, 1385, 1238, 1117, 1079, 1030, 999, 923, 849, 761, 736; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 7.0 min (minor), 7.9 min (major).



Results

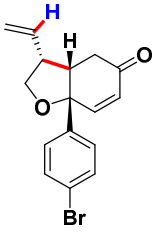
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.983	155219.422	1763011.500	50.2239
2		8.958	135236.453	1747295.375	49.7761
Total			290455.875	3510306.875	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.008	8954.514	72711.609	2.0425
2		7.943	288628.625	3487156.750	97.9575
Total			297583.139	3559868.359	100.0000

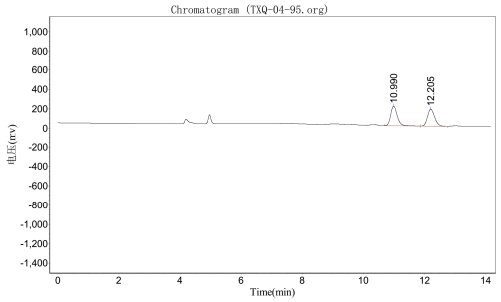
(3*R*,3a*S*,7a*S*)-7a-(4-bromophenyl)-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3j)



3j

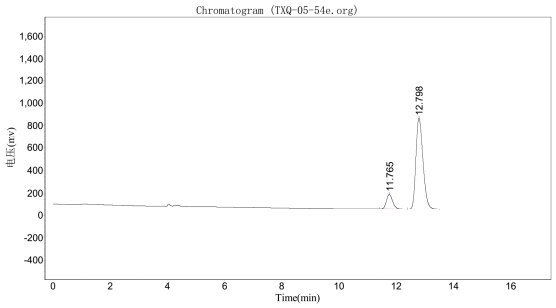
Colorless solid. m.p. 81–82 °C, 27.3 mg, 43% yield. $[\alpha]_D^{26.5}$ –38.8 (*c* 0.90, CH_3OH) for 75% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 10.2 Hz, 1H), 6.19 (d, *J* = 10.2 Hz, 1H), 5.64 (dt, *J* = 16.8, 9.7 Hz, 1H), 5.16 – 5.06 (m, 2H), 4.28 (t, *J* = 8.2 Hz, 1H), 3.95 – 3.87 (m, 1H),

3.17 – 3.06 (m, 1H), 2.80 (dd, J = 13.9, 6.3 Hz, 1H), 2.57 (qd, J = 17.2, 5.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.64, 148.78, 142.04, 134.59, 131.86, 130.09, 126.79, 121.97, 119.19, 82.31, 71.81, 48.79, 47.25, 35.31; EI-MS: $[M]^{\oplus}$ 318.0; HRMS (EI): $[M]^{\oplus}$ calcd for $C_{16}H_{15}O_2Br^{\oplus}$ 318.0250, found 318.0259; IR (KBr) ν (cm^{-1}) 3078, 2970, 2868, 1683, 1640, 1587, 1485, 1394, 1234, 1123, 1069, 1008, 926, 824, 772; HPLC: Chiracel OD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 11.8 min (minor), 12.8 min (major).



Results

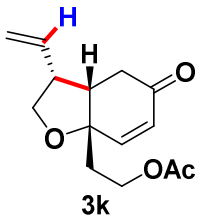
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.990	200392.125	2995346.500	51.7633
2		12.205	173924.594	2791275.500	48.2367
Total			374316.719	5786622.000	100.0000



Results

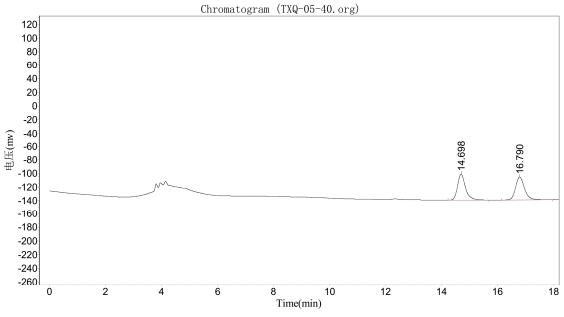
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.765	127736.656	1950316.000	12.4429
2		12.798	804717.875	13723814.000	87.5571
Total			932454.531	15674130.000	100.0000

2-((3*R*,3a*S*,7a*S*)-5-oxo-3-vinyl-3,3a,4,5-tetrahydrobenzofuran-7a(2*H*)-yl)ethyl acetate (3k)



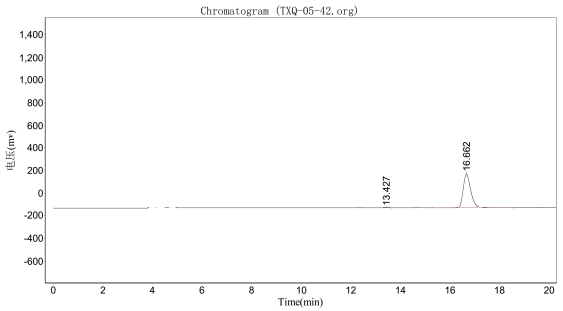
3k

Light yellow oil. 27.2 mg, 55% yield. $[\alpha]_D^{26.2}$ –10.0 (c 1.5, CH_3OH) for 99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.64 (dd, J = 10.4, 1.4 Hz, 1H), 6.04 (d, J = 10.4 Hz, 1H), 5.53 (dt, J = 17.0, 9.8 Hz, 1H), 5.13 – 5.03 (m, 2H), 4.34 – 4.18 (m, 2H), 4.05 (dd, J = 9.1, 7.4 Hz, 1H), 3.58 (dd, J = 9.1, 6.2 Hz, 1H), 3.08 (ddd, J = 16.2, 9.5, 6.9 Hz, 1H), 2.77 – 2.69 (m, 1H), 2.61 (dd, J = 17.7, 2.7 Hz, 1H), 2.53 (dd, J = 17.7, 6.7 Hz, 1H), 2.19 – 2.01 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.18, 170.75, 150.88, 135.51, 130.24, 118.99, 79.56, 71.10, 60.10, 47.65, 44.71, 37.54, 35.45, 20.93; ESI-MS: $[M+Na]^{\oplus}$ 273.2; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{14}H_{19}O_4^{\oplus}$ 251.1278, found 251.1276; IR (KBr) ν (cm^{-1}) 3079, 2939, 1736, 1682, 1640, 1424, 1387, 1367, 1241, 1037, 925, 803; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 13.4 min (minor), 16.7 min (major).



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.698	38309.078	751979.938	50.1930
2		16.790	33834.676	746198.000	49.8070
Total			72143.754	1498177.938	100.0000

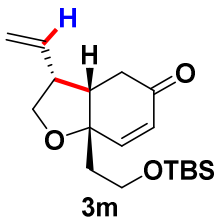


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.427	2237.718	29041.688	0.4278
2		16.662	302693.781	6759050.500	99.5722
Total			304931.499	6788092.188	100.0000

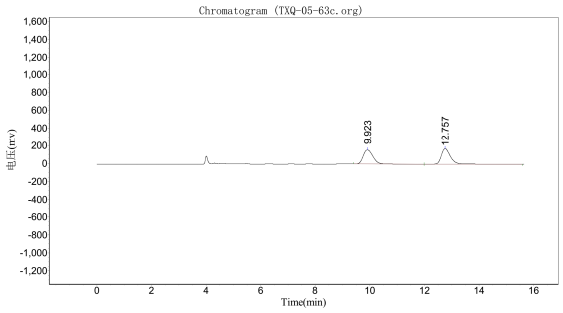
(3*R*,3a*S*,7a*S*)-7a-(2-((tert-butyldimethylsilyl)oxy)ethyl)-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3m)

Light yellow oil. 38.6 mg, 60% yield. $[\alpha]_D^{24.1}$ +54.4 (c 0.25, $CHCl_3$) for 99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.63 (dd, J = 10.4, 1.4 Hz, 1H), 6.00 (d, J = 10.4 Hz, 1H), 5.54 (dt, J = 17.0, 9.8 Hz, 1H), 5.11 –



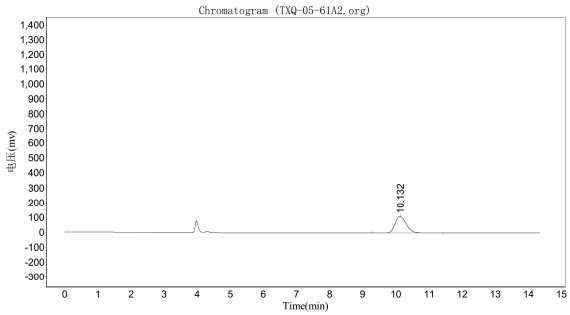
3m

5.01 (m, 2H), 4.04 (dd, J = 9.0, 7.3 Hz, 1H), 3.85 – 3.73 (m, 2H), 3.56 (dd, J = 9.0, 6.2 Hz, 1H), 3.06 (ddd, J = 16.2, 9.4, 6.9 Hz, 1H), 2.89 – 2.80 (m, 1H), 2.58 (qd, J = 17.6, 4.8 Hz, 2H), 2.02 (ddd, J = 13.1, 7.2, 5.9 Hz, 1H), 1.93 (dt, J = 14.2, 5.7 Hz, 1H), 0.87 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.02, 151.95, 135.89, 129.82, 118.64, 80.30, 70.94, 58.67, 47.82, 44.53, 41.75, 35.64, 25.83, 18.13, -5.44, -5.46; ESI-MS: $[M+H]^{\oplus}$ 323.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{18}H_{31}O_3Si^{\oplus}$ 323.2037, found 323.2036; IR (KBr) ν (cm^{-1}) 3079, 2953, 2929, 2856, 1685, 1471, 1387, 1255, 1092, 999, 920, 837, 811; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 99/1; flow rate = 0.7 mL/min; Retention time: 10.1 min (major), 12.8 min (minor).



Results

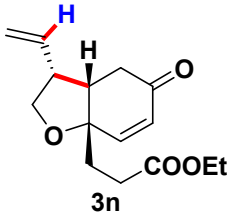
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.923	156639.281	3921438.250	50.2249
2		12.757	169940.281	3886312.750	49.7751
Total			326579.563	7807751.000	100.0000



Results

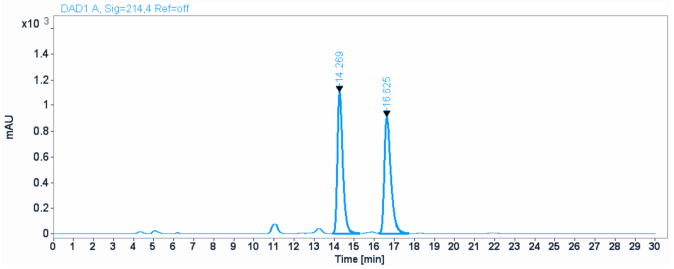
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.132	109959.406	2590919.250	100.0000
Total			109959.406	2590919.250	100.0000

Ethyl 3-((3*R*,3a*S*,7a*S*)-5-oxo-3-vinyl-3,3a,4,5-tetrahydrobenzofuran-7a(2*H*)-yl)propanoate (3n)



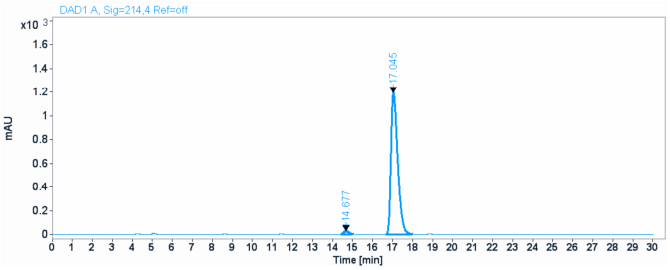
3n

Colorless oil. 23.0 mg, 44% yield. $[\alpha]_D^{23.4}$ +7.2 (c 0.84, $CHCl_3$) 97% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.62 (dd, J = 10.4, 1.3 Hz, 1H), 6.03 (d, J = 10.4 Hz, 1H), 5.54 (dt, J = 17.0, 9.8 Hz, 1H), 5.07 (dd, J = 13.5, 7.3 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 4.03 (dd, J = 9.0, 7.3 Hz, 1H), 3.58 (dd, J = 9.0, 6.0 Hz, 1H), 3.13 – 3.02 (m, 1H), 2.70 – 2.44 (m, 5H), 2.18 – 2.01 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H).^{13}C NMR (100MHz, $CDCl_3$) δ(ppm) 197.32, 173.05, 150.88, 135.59, 130.31, 118.93, 79.96, 71.20, 60.66, 47.79, 44.22, 35.60, 33.49, 28.91, 14.21; ESI-MS: $[M+H]^{\oplus}$ 265; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{15}H_{21}O_4^{\oplus}$ 265.1434, found 265.1432; IR (KBr) ν (cm^{-1}) 3358, 2921, 2852, 1730, 1681, 1632, 1469, 1445, 1424, 1382, 1266, 1179, 1029, 923, 864, 797, 737, 703; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 14.7 min (minor), 17.0 min (major).



Signal: DAD1 A, Sig=214,4 Ref=off

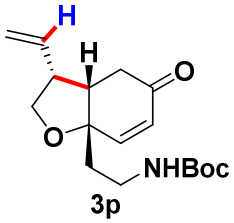
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
14.269	0.308	20386.855	1104.151	49.9825	RAC
16.625	0.376	20401.156	904.324	50.0175	



Signal: DAD1 A, Sig=214,4 Ref=off

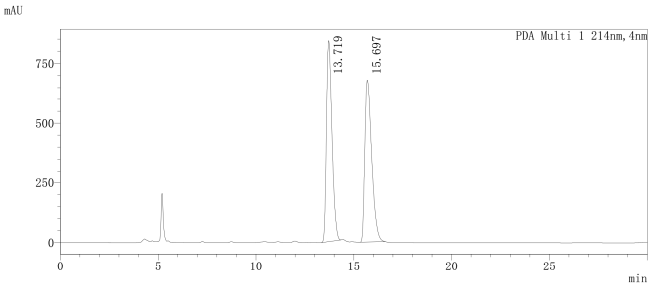
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
14.677	0.274	454.286	27.656	1.6033	96.793
17.045	0.391	27880.920	1189.898	98.3967	

Tert-butyl(2-((3*R*,3a*S*,7a*S*)-5-oxo-3-vinyl-3,3a,4,5-tetrahydrobenzofuran-7a(2*H*)-yl)ethyl)carbamate (3p)

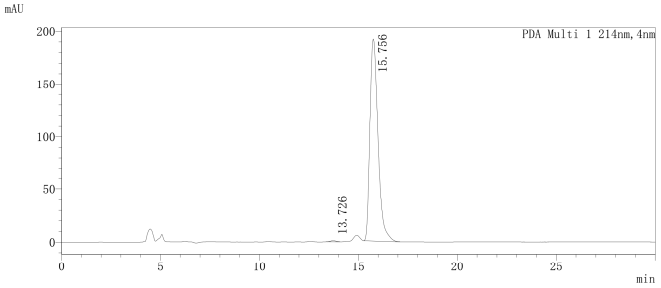


3p

Colorless oil. 14.5 mg, 47% yield (0.1 mmol). $[\alpha]_D^{23.3}$ +8.3 (c 0.71, $CHCl_3$) >99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.67 (dd, *J* = 10.4, 1.2 Hz, 1H), 6.03 (d, *J* = 10.4 Hz, 1H), 5.51 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.14 – 4.93 (m, 3H), 4.07 (dd, *J* = 9.0, 7.6 Hz, 1H), 3.56 (dd, *J* = 9.1, 6.2 Hz, 1H), 3.32 (d, *J* = 5.9 Hz, 2H), 3.12 – 3.00 (m, 1H), 2.70 (t, *J* = 7.6 Hz, 1H), 2.61 (dd, *J* = 17.8, 2.2 Hz, 1H), 2.50 (dd, *J* = 17.8, 6.8 Hz, 1H), 2.03 (dt, *J* = 13.3, 4.9 Hz, 1H), 1.90 (dt, *J* = 14.3, 7.2 Hz, 1H), 1.45 (s, 9H).^{13}C NMR (100MHz, $CDCl_3$) δ(ppm) 197.15, 155.90, 150.84, 135.65, 130.44, 119.08, 80.48, 79.37, 71.31, 47.41, 44.80, 38.20, 36.35, 35.53, 28.44; ESI-MS: $[M+Na]^{\oplus}$ 330; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{17}H_{26}NO_4^{\oplus}$ 308.1856, found 308.1854; IR (KBr) ν (cm^{-1}) 3356, 2975, 2929, 1684, 1516, 1390, 1365, 1270, 1250, 1171, 1039, 998, 923, 866, 781; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 13.7 min (minor), 15.7 min (major).

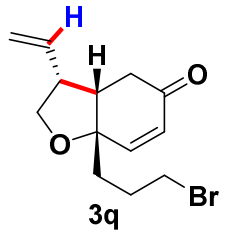


PDA Ch1 214nm				
#	Ret.Time	Area	Height	Area%
1	13.719	16500771	838938	49.893
2	15.697	16571796	678382	50.107



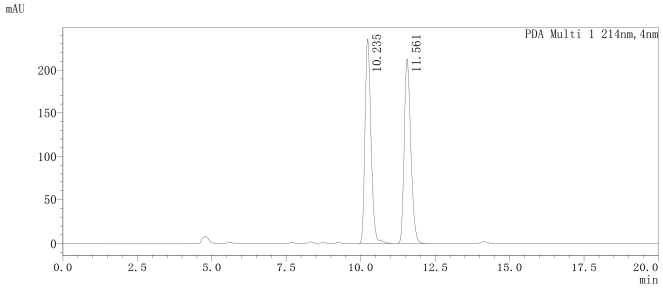
PDA Ch1 214nm				
#	Ret.Time	Area	Height	Area%
1	13.726	21768	1042	0.398
2	15.756	5450731	191614	99.602

(3*R*,3a*S*,7a*S*)-7a-(3-bromopropyl)-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3q)

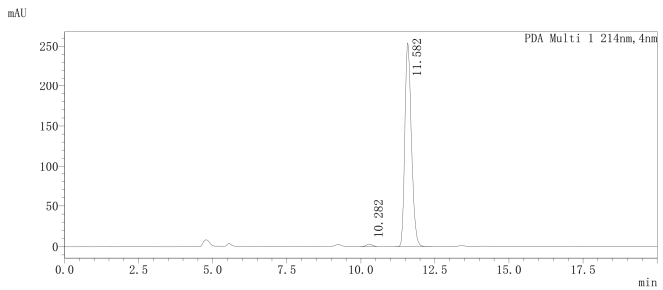


3q

Light yellow oil. 23.1 mg, 41% yield. $[\alpha]_D^{20.6}$ +1.9 (*c* 0.47, $CHCl_3$) for 98% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 6.63 (dd, *J* = 10.4, 1.4 Hz, 1H), 6.04 (dd, *J* = 10.4, 0.6 Hz, 1H), 5.54 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.08 (ddd, *J* = 8.5, 2.0, 1.2 Hz, 2H), 4.04 (dd, *J* = 9.1, 7.3 Hz, 1H), 3.58 (dd, *J* = 9.1, 6.1 Hz, 1H), 3.46 (t, *J* = 6.4 Hz, 2H), 3.08 (ddd, *J* = 16.1, 9.4, 6.9 Hz, 1H), 2.72 – 2.44 (m, 3H), 2.08 – 1.91 (m, 3H), 1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 197.32, 151.17, 135.57, 130.31, 118.95, 80.28, 71.13, 47.77, 44.45, 37.51, 35.69, 33.59, 27.28; ESI-MS: $[M+H]^{\oplus}$ 285.0; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{18}O_2Br^{\oplus}$ 285.0485, found 285.0485; IR (KBr) ν (cm^{-1}) 3076, 2927, 2855, 1688, 1638, 1438, 1410, 1385, 1256, 1063, 921, 792; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 10.3 min (minor), 11.6 min (major).

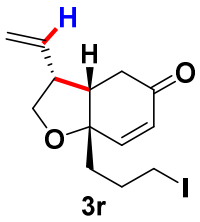


PDA Ch1 214nm				
#	Ret.Time	Area	Height	Area%
1	10.235	3289835	235336	50.249
2	11.561	3257234	212814	49.751



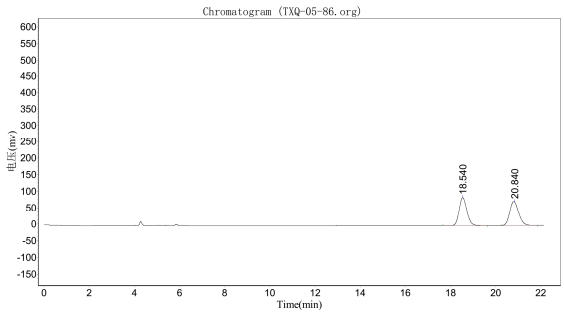
PDA Ch1 214nm				
#	Ret.Time	Area	Height	Area%
1	10.282	39020	2783	0.992
2	11.582	3893223	253686	99.008

(3*R*,3a*S*,7a*S*)-7a-(3-iodopropyl)-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3r)



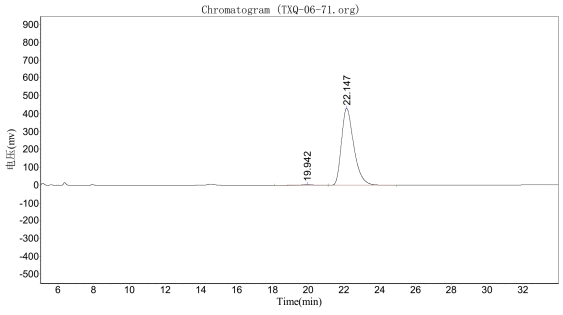
3r

Light yellow oil. 33.8 mg, 51% yield. $[\alpha]_D^{26.0}$–27.3 (*c* 0.8, $CHCl_3$) for 99% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.62 (dd, *J* = 10.4, 1.3 Hz, 1H), 6.03 (d, *J* = 10.4 Hz, 1H), 5.53 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.08 (dd, *J* = 13.9, 5.1 Hz, 2H), 4.04 (dd, *J* = 9.0, 7.3 Hz, 1H), 3.57 (dd, *J* = 9.1, 6.1 Hz, 1H), 3.23 (t, *J* = 6.7 Hz, 2H), 3.07 (ddd, *J* = 16.1, 9.4, 6.9 Hz, 1H), 2.71 – 2.45 (m, 3H), 2.04 – 1.74 (m, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.31, 151.18, 135.55, 130.27, 118.92, 80.19, 71.11, 47.75, 44.44, 39.78, 35.68, 27.99, 6.36; EI-MS: $[M]^{\oplus}$ 332.0; HRMS (EI): $[M]^{\oplus}$ calcd for $C_{13}H_{17}O_2I^{\oplus}$ 332.0268, found 332.0269; IR (KBr) ν (cm^{-1}) 3078, 2959, 2932, 2872, 1683, 1639,1466, 1384, 1245, 1122, 1085, 998, 922, 792; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 19.9 min (minor), 22.1 min (major).



Results

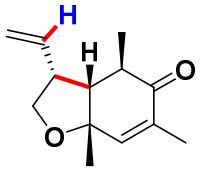
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.540	85200.000	2042356.750	50.3140
2		20.840	73581.000	2016864.000	49.6860
Total			158781.000	4059220.750	100.0000



Results

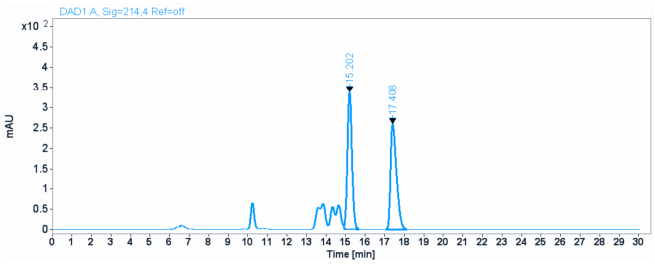
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.942	3743.530	158437.844	0.7664
2		22.147	429715.094	20513472.000	99.2336
Total			433458.624	20671909.844	100.0000

(3*R*,3a*R*,4*R*,7a*R*)-4,6,7a-trimethyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3s)



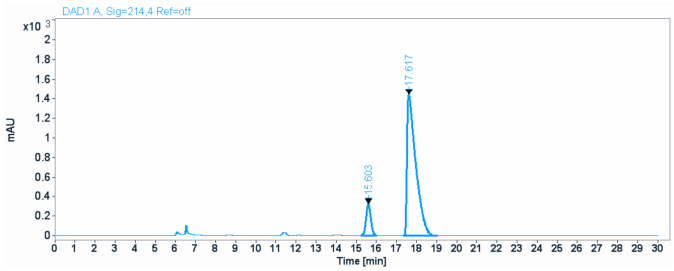
3s

Light yellow oil. 39.0 mg, 95% yield. $[\alpha]_D^{23.4}$ +26.6 (*c* 0.96, $CHCl_3$) for 79% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ 6.33 (s, 1H), 5.52 (dt, *J* = 17.0, 10.0 Hz, 1H), 5.09 – 4.90 (m, 2H), 4.00 (dd, *J* = 8.7, 6.5 Hz, 1H), 3.58 (dd, *J* = 8.8, 3.3 Hz, 1H), 3.11 – 2.99 (m, 1H), 2.71 – 2.50 (m, 2H), 1.78 (s, 3H), 1.45 (s, 3H), 1.29 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 200.07, 146.79, 136.51, 134.59, 118.10, 79.89, 71.58, 54.24, 46.83, 40.55, 24.87, 15.76, 12.87.; ESI-MS: $[M+H]^{\oplus}$ 207.2; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{19}O_2^{\oplus}$ 207.1380, found 207.1378; IR (KBr) ν (cm^{-1}) 2973, 2925, 2855, 1682, 1639, 1446, 1373, 1352, 1193, 1125, 1086, 1036, 998, 918, 876; HPLC: Chiracel IC-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.5 mL/min; Retention time: 15.6 min (minor), 17.6 min (major).



Signal: DAD1 A, Sig=214,4 Ref=off

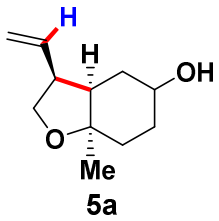
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
15.202	0.270	5464.255	337.245	49.9017	RAC
17.408	0.353	5485.782	258.910	50.0983	



Signal: DAD1 A, Sig=214,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
15.603	0.271	5147.313	316.452	10.6430	78.714
17.617	0.500	43216.016	1441.639	89.3570	

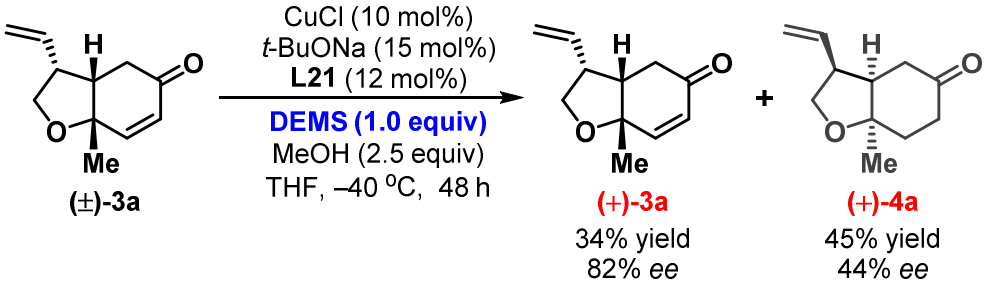
(3*S*,3*a*R,7a*R*)-7a-methyl-3-vinyloctahydrobenzofuran-5-ol (5a)



5a

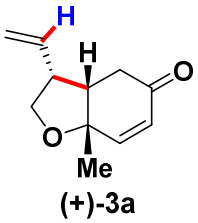
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.84 – 5.73 (m, 1H), 5.10 (dd, J = 13.6, 7.8 Hz, 2H), 3.99 (t, J = 8.8 Hz, 1H), 3.76 (t, J = 9.0 Hz, 1H), 3.61 – 3.52 (m, 1H), 3.40 – 3.31 (m, 1H), 1.95 (ddd, J = 18.4, 11.5, 4.3 Hz, 2H), 1.82 – 1.65 (m, 4H), 1.58 – 1.45 (m, 2H), 1.17 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 135.58, 117.15, 80.80, 69.97, 68.72, 46.66, 46.20, 34.23, 33.74, 30.93, 26.88; ESI-MS: $[M+H]^{\oplus}$ 182.9; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{11}H_{19}O_2^{\oplus}$ 183.1380, found 183.1379;IR (KBr) ν (cm^{-1}) 3385, 3071, 2967, 2934, 2869, 1639, 1481,1367, 1300, 1265, 1140, 1054, 1029, 998, 917, 884, 793;

5. THE KINETIC RESOLUTION of (±)-3a

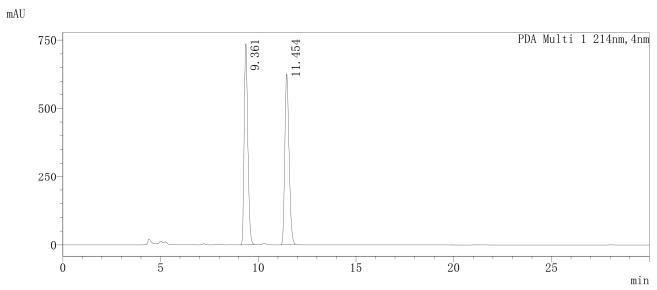


A dried Schlenk flask was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), ligand **L21** (10.0 mg, 0.024 mmol, 12 mol%), *t*-BuONa (3.0 mg, 0.030 mmol, 15 mol%) and anhydrous THF (2 mL) under argon atmosphere. After the mixture was stirred at –40 °C for 10 min, DEMS (32 μL, 0.2 mmol, 1.0 equiv) was added, and then stirred at –40 °C for another 10 min. A solution of substrate **(±)-3a** (0.20 mmol) in anhydrous THF (2 mL) was added, followed by anhydrous MeOH (20 μL, 0.5 mmol, 2.5 equiv). The resulting mixture was stirred at –40 °C for 48 hours. Then the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel (300–400 mesh) chromatography to afford the desired products **(+)-3a** and **(+)-4a**. (Notice: The racemic **4a** were prepared according to the same procedure above except for using rac-BINAP instead of **L21,** and the reaction was stirred under room temperature.)

(3*R*,3a*S*,7a*S*)-7a-methyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one ((+)-3a)

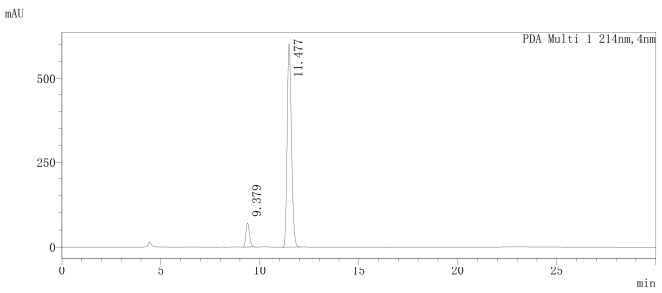


Light yellow oil. 12 mg, 34% yield. $[\alpha]_D^{24.0}$ +41.3 (c 0.4, $CHCl_3$) 82% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.63 (dd, *J* = 10.3, 1.2 Hz, 1H), 5.99 (d, *J* = 10.3 Hz, 1H), 5.54 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.08 (dd, *J* = 13.6, 6.3 Hz, 2H), 4.09 (dd, *J* = 9.0, 7.7 Hz, 1H), 3.56 (dd, *J* = 9.1, 6.7 Hz, 1H), 3.17 – 3.06 (m, 1H), 2.65 – 2.56 (m, 2H), 2.51 (dd, *J* = 17.7, 7.1 Hz, 1H), 1.48 (s, 3H).^{13}C NMR (100MHz, $CDCl_3$) δ(ppm) 197.61, 152.72, 135.75, 129.59, 118.85, 78.83, 71.15, 47.61, 46.33, 35.67, 25.27; ESI-MS: $[M+Na]^{\oplus}$ 201.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{11}H_{15}O_2^{\oplus}$ 179.1067, found 179.1066; IR (KBr) ν (cm^{-1}) 2971, 2927, 2857, 1684, 1653, 1648, 1637, 1457, 1384, 1286, 1232, 1154, 1090, 1046, 1030, 924, 864, 810; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 9.4 min (minor), 11.5 min (major).



PDA Ch1 214nm

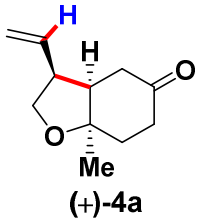
#	Ret.Time	Area	Height	Area%
1	9.361	9472056	735701	50.180
2	11.454	9404281	626406	49.820



PDA Ch1 214nm

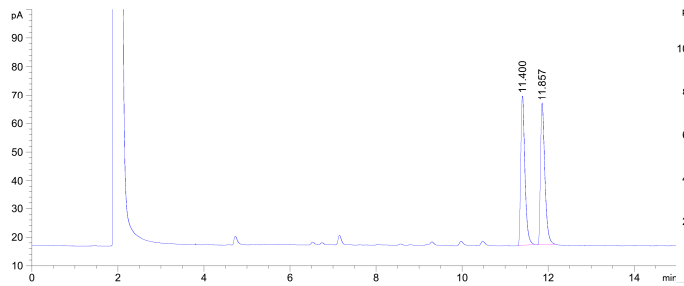
#	Ret.Time	Area	Height	Area%
1	9.379	870493	69962	8.761
2	11.477	9065819	601026	91.239

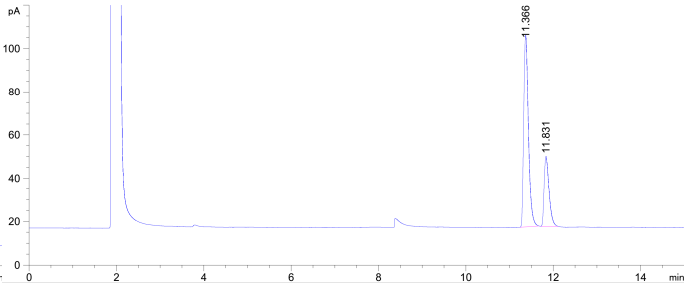
(3*S*,3a*R*,7a*R*)-7a-methyl-3-vinylhexahydrobenzofuran-5(4*H*)-one ((+)4a)



(+)-4a

Colorless oil. 16 mg, 45% yield. $[\alpha]_D^{24.0}$ +22.1 (*c* 0.52, $CHCl_3$) for 44% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.75 – 5.63 (m, 1H), 5.12 (t, *J* = 13.5 Hz, 2H), 4.02 (dd, *J* = 8.8, 7.5 Hz, 1H), 3.73 (t, *J* = 8.8 Hz, 1H), 3.26 – 3.16 (m, 1H), 2.54 – 2.43 (m, 1H), 2.42 – 2.25 (m, 3H), 2.15 (tdd, *J* = 12.5, 8.0, 4.6 Hz, 2H), 2.02 – 1.92 (m, 1H), 1.33 (s, 3H).;^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 212.85, 134.42, 118.05, 81.58, 69.80, 47.00, 46.81, 38.86, 35.66, 33.85, 27.17.; ESI-MS: $[M+Na]^{\oplus}$ 203.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{11}H_{17}O_2^{\oplus}$ 181.1223, found 181.1224; IR (KBr) ν (cm^{-1}) 3087, 2967, 2870, 1717, 1639, 1514, 1375, 1420, 1246, 1180, 1052, 919, 685; Chiral GC Cyclosil-B(30×0.25×0.25, 15min, 150 °C), Retention time: 11.8 min (minor), 11.4 min (major).



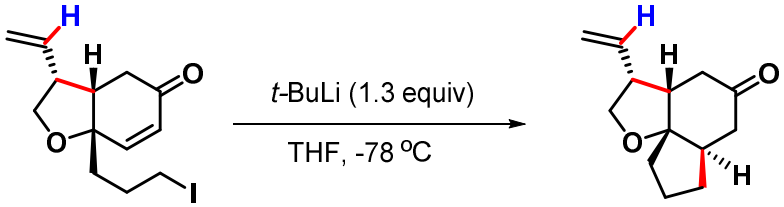


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	11.400	BB	0.1018	351.56497	52.73799	50.12593
2	11.857	BB	0.1102	349.79852	49.63801	49.87407
Totals :				701.36349	102.37600	

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	11.366	BB	0.1151	662.10822	88.72452	72.41962
2	11.831	BB	0.1198	252.15813	32.41627	27.58038
Totals :				914.26634	121.14079	

6. TRANSFORMATION OF THE CYCLIZATION PRODUCTS

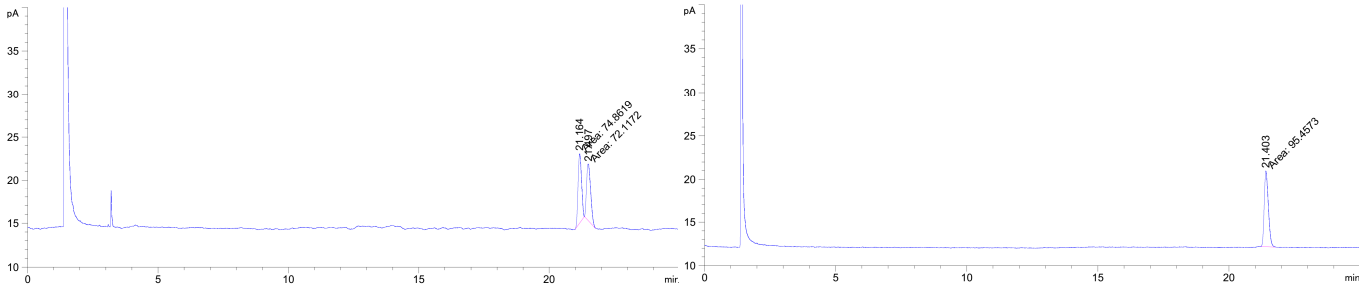
6.1 The Transformation of Cyclization Product 3r.



3r, 99% *ee* **6r**, 99% *ee*

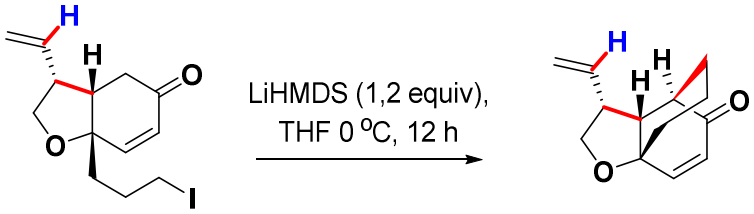
(3*R*,3a*S*,6a*R*,9a*S*)-3-vinyloctahydroindeno[3a,4-b]furan-5(6*H*)-one (6r)To a solution of **3r** (66 mg, 0.2 mmol) in dry THF (4 mL) was added *t*-BuLi(1.3M in pentane, 0.20 mL, 1.3 equiv) in 10 minutes at -78 °C. The resulting mixture was stirred for 10 min. The reaction mixture was quenched by MeOH (0.2 mL) and water (10 mL), extracted with EtOAc (10 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 15/1) to afford **6r** (17.7 mg, 43%) as colorless oil. $[\alpha]_D^{27.5}$ –51.7 (*c* 0.20, $CHCl_3$) for 99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.78 – 5.61 (m, 1H), 5.18 – 5.07 (m, 2H), 4.00 (t, *J* = 8.6 Hz, 1H), 3.76 (t, *J* = 9.0 Hz, 1H), 3.34 – 3.18 (m, 1H), 2.45 (dd, *J* = 16.2, 5.3 Hz, 1H), 2.42 – 2.31 (m, 2H), 2.30 – 2.17 (m, 2H), 2.17 – 2.05 (m, 1H), 2.03 – 1.91 (m, 2H), 1.73 (qdd, *J* = 12.2, 8.5, 4.4 Hz, 2H), 1.60 – 1.54 (m, 1H), 1.32 – 1.22 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 212.77, 134.60, 117.83, 93.05, 68.93, 46.35, 45.22, 43.65, 42.41, 38.04, 37.64, 31.21, 22.90; ESI-MS: $[M+Na]^{\oplus}$ 229.2; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{19}O_2^{\oplus}$ 207.1380, found 207.1378; IR (KBr) ν (cm^{-1}) 3078, 2924, 2868, 1716, 1653, 1418, 1261, 1030, 918, 901. Chiral GC Cyclosil-B(30×0.25×0.25, 25min, 150 °C), Retention time: 21.1 min (minor), 21.4 min (major).



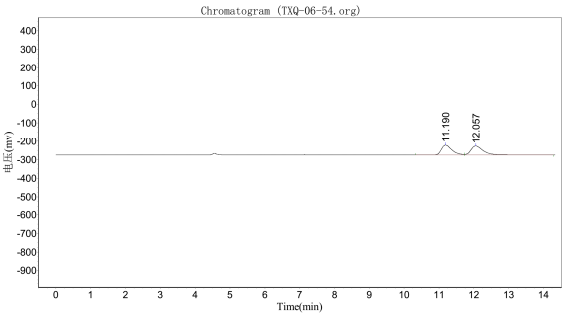
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	21.164	MM	0.1540	74.86190	8.09972	50.93370
2	21.497	MM	0.1824	72.11722	6.58993	49.06630
Totals :				146.97912	14.68964	

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	21.403	MM	0.1804	95.45729	8.81930	1.000e2
Totals :				95.45729	8.81930	



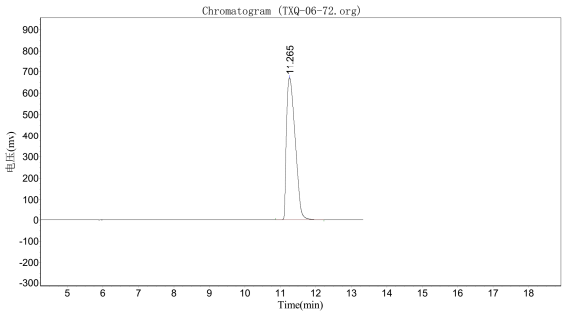
3r, 99% *ee* **7r**, 99% *ee*

(3*R*,3a*R*,4*R*,7a*S*)-3-vinyl-2,3,3a,4-tetrahydro-5*H*-4,7a-propanobenzofuran-5-one (7r) To a solution of **3r** (66 mg, 0.2 mmol) in dry THF (4 mL) was added a solution of LiHMDS (1 M THF solution, 0.24 ml, 1.0 equiv) at 0 °C. The resulting mixture was stirred at 0 °C for 12 h. The reaction mixture was quenched by aqueous saturated NH_4Cl (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 15/1) to afford **7r** (34.7 mg, 85%) as white solid . White solid. m. p. 52–54°C. $[\alpha]_D^{27.5}$ –14.0 (*c* 0.45, $CHCl_3$) for 99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.65 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.17 (dd, *J* = 10.1, 1.0 Hz, 1H), 5.62 – 5.48 (m, 1H), 4.98 (dd, *J* = 19.7, 13.6 Hz, 2H), 4.25 (dd, *J* = 9.4, 8.5 Hz, 1H), 3.60 (dd, *J* = 9.5, 5.9 Hz, 1H), 3.13 – 3.02 (m, 1H), 2.83 (s, 1H), 2.13 (dt, *J* = 10.4, 2.0 Hz, 1H), 1.89 (dd, *J* = 12.3, 4.6 Hz, 1H), 1.84 – 1.77 (m, 2H), 1.65 – 1.57 (m, 2H), 1.50 – 1.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.64, 152.89, 137.44, 133.67, 118.07, 80.27, 72.68, 54.11, 45.76, 44.01, 31.81, 29.64, 19.78; ESI-MS: $[M+H]^{\oplus}$ 205.1; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{13}H_{17}O_2^{\oplus}$ 205.1224, found 205.1223; IR (KBr) ν (cm^{-1}) 3068, 3043, 2930, 2857, 1670, 1634, 1616, 1470 ,1284, 1254, 1064, 1051, 995, 929, 829, 821, 755; HPLC: Chiracel OJ-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time:11.0 min (major), 12.1 min (minor).



Results

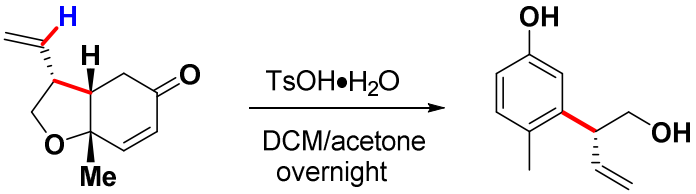
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.190	52774.730	1122739.875	48.5515
2		12.057	48202.461	1189731.125	51.4485
Total			100977.191	2312471.000	100.0000



Results

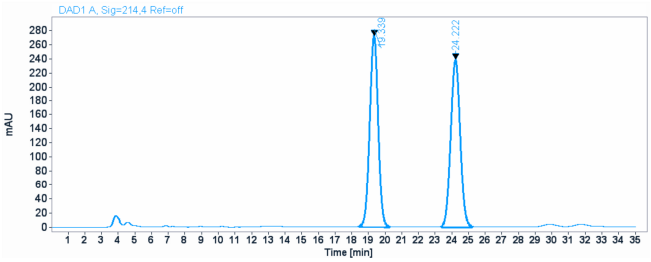
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.265	670822.563	11492316.000	100.0000
Total			670822.563	11492316.000	100.0000

6.2 The Transformation of Cyclization Product 3a.



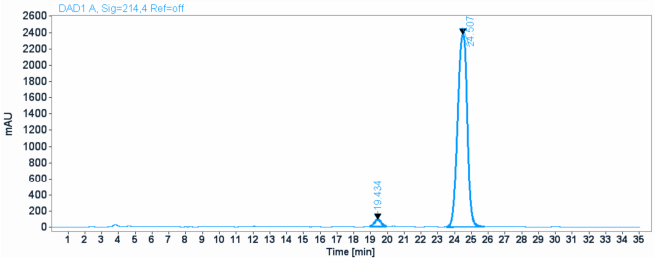
3a. 95% *ee* **8a**, 95% *ee*

(*R*)-3-(1-hydroxybut-3-en-2-yl)-4-methylphenol (8a) *p*-Toluenesulfonic acid monohydrate (45.6 mg, 0.24mmol) was added to a solution of **3a** (21.4mg, 0.12mmol) in DCM/acetone (0.5 mL/0.5 mL). The mixture was stirred at room temperature overnight. Then it was quenched by aqueous saturated $NaHCO_3$ (10 mL), extracted with EtOAc (10 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 2/1) to afford **8a** (13 mg, 61%) as light yellow solid, m.p. 46-47°C. $[\alpha]_D^{23.8}$ –40.8 (c 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.02 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 6.62 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.88 (ddd, *J* = 17.4, 10.3, 7.2 Hz, 1H), 5.63 (s, 1H), 5.15 (dd, *J* = 21.7, 13.7 Hz, 2H), 3.81 (d, *J* = 6.7 Hz, 2H), 3.73 (dd, *J* = 13.7, 7.1 Hz, 1H), 2.25 (s, 3H), 1.84 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ(ppm) 154.16, 139.81, 137.76, 131.70, 128.53, 117.17, 113.66, 113.59, 65.16, 47.75, 18.67; ESI-MS: $[M-H]^-$ 177; HRMS (ESI): $[M-H]^-$ calcd for $C_{11}H_{13}O_2^-$ 177.0921, found 177.0921; IR (KBr) ν (cm^{-1}) 3362, 3145, 3023, 2921, 2882, 2359, 1659, 1638, 1612, 1510, 1469, 1388, 1262, 1060, 1021, 997, 915, 868, 810, 738. HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 19.4 min (minor), 24.5 min (major).



Signal: DAD1 A, Sig=214,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
19.339	0.583	9509.078	271.636	50.3338	RAC
24.222	0.656	9382.962	238.488	49.6662	

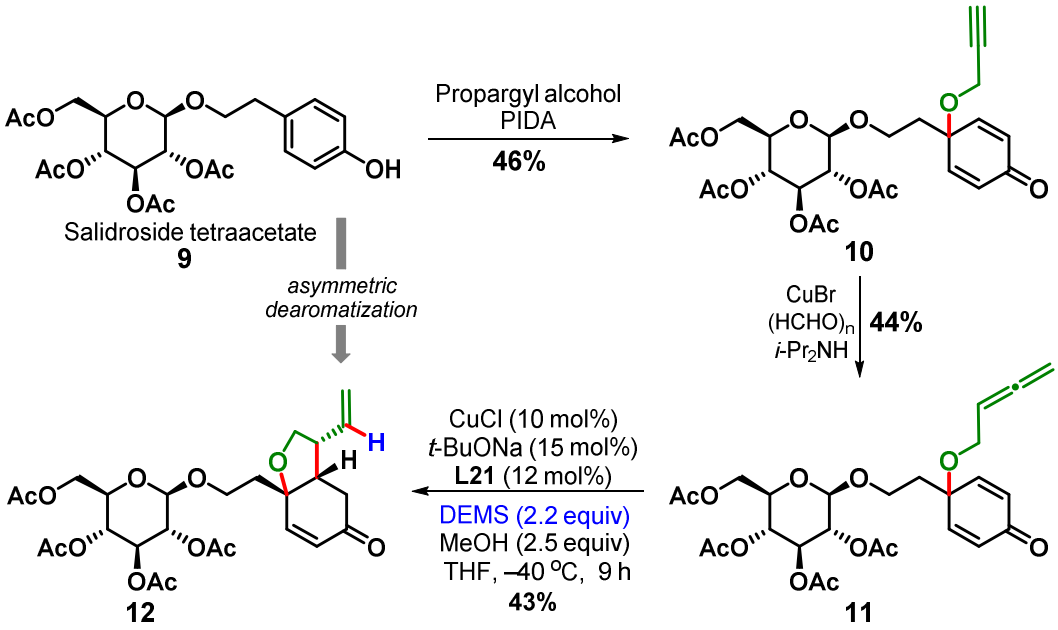


Signal: DAD1 A, Sig=214,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
19.434	0.462	2394.584	86.464	2.4962	95.0
24.507	0.657	93533.289	2371.170	97.5038	

7. ASYMMETRIC DEAROMATIZATION MODIFICATION Of 9 And 13

7.1 ASMMETRIC DEAROMATIZATION MODIFICATION OF 9

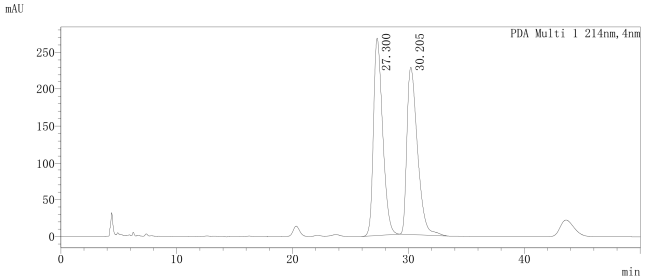


(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(2-(4-oxo-1-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-yl)ethoxy) tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (10) Salidroside tetraacetate **9** (7.0 mmol, 1.0 eq) was dissolved in 4 mL DCM, then 4mL propargyl alcohol (10 eq) was added, the mixture was cooled to 0 °C and treated with phenyliodine (III) diacetate (PIDA, 3.38g, 1.5 eq) in several portions. The resulting mixture was warmed to room temperature and stirred 1.5h. Then it was diluted with water (30 mL) and extracted with DCM (30 mL × 3). The combined organic phases were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 1/1) to afford the desired product **10**. yellow oil, 46% yield, $[\alpha]_D^{30.3}$ -9.0 (c 2.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.86 – 6.76 (m, 2H), 6.37 – 6.30 (m, 2H), 5.17 (t, *J* = 9.5 Hz, 1H), 5.07 (t, *J* = 9.7 Hz, 1H), 4.95 (dd, *J* = 9.4, 8.0 Hz, 1H), 4.45 (d, *J* = 7.9 Hz, 1H), 4.25 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.13 (dd, *J* = 12.3, 2.3 Hz, 1H), 4.01 – 3.90 (m, 3H), 3.70 – 3.56 (m, 2H), 2.46 (t, *J* = 2.4 Hz, 1H), 2.10 – 1.98 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 184.87, 170.57, 170.16, 169.34, 169.14, 149.31, 149.29, 131.21, 131.18, 100.39, 80.26, 75.09, 74.64, 72.76, 71.75, 71.18, 68.31, 64.29, 61.82, 53.34, 39.40, 20.67, 20.62, 20.52. ESI-MS: $[M+Na]^{\oplus}$ 545.2; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{25}H_{31}O_{12}^{\oplus}$ 523.1810, found 523.1803; IR (KBr) ν (cm^{-1}) 2940, 2383, 2348, 2328, 1755, 1670, 1631, 1431, 1369, 1228, 1040, 906, 860, 757, 600.

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(2-(1-(buta-2,3-dien-1-yloxy)-4-oxocyclohexa-2,5-dien-1-yl)etho xy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (11) To a well-stirred solution of **10** (0.2 mmol, 1.0 eq) in dioxane (2 mL) was added paraformaldehyde (30 mg, 1.0 mmol, 5 eq), CuBr (14.3 mg, 0.1 mmol, 0.5 eq) and diisopropylamine (56 ul, 0.4 mmol, 2.0 eq) under argon atmosphere. The resulting mixture was stirred at 110 °C for 30min. After cooled to room temperature, the reaction mixture was filtered and washed with

DCM (10 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 2/1) to afford the pure substrates **11**. yellow oil, 43.6% yield, $[\alpha]_D^{30.3}$ -10.6 (c 1.825, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.80 – 6.70 (m, 2H), 6.27 (ddd, *J* = 10.2, 4.4, 1.8 Hz, 2H), 5.19 – 5.09 (m, 2H), 5.02 (t, *J* = 9.7 Hz, 1H), 4.91 (dd, *J* = 9.5, 8.0 Hz, 1H), 4.73 (dt, *J* = 6.5, 2.5 Hz, 2H), 4.41 (d, *J* = 7.9 Hz, 1H), 4.20 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.08 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.90 (dt, *J* = 10.1, 6.2 Hz, 1H), 3.82 (dt, *J* = 6.8, 2.5 Hz, 2H), 3.63 (ddd, *J* = 9.9, 4.7, 2.4 Hz, 1H), 3.55 (dt, *J* = 10.1, 6.4 Hz, 1H), 2.04 (s, 3H), 2.02 – 1.94 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 209.18, 185.15, 170.61, 170.22, 169.37, 169.17, 150.48, 150.43, 130.75, 130.69, 100.48, 88.48, 76.19, 74.04, 72.81, 71.80, 71.22, 68.34, 64.46, 63.55, 61.85, 39.53, 20.71, 20.67, 20.57. ESI-MS: $[M+Na]^{\oplus}$ 559.2; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{26}H_{33}O_{12}^{\oplus}$ 537.1967, found 537.1958; IR (KBr) ν (cm^{-1}) 2958, 2860, 2376, 2348, 2315, 1755, 1670, 1630, 1432, 1368, 1226, 1038, 906, 860, 672, 665, 600.

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(2-((3*R*,3a*S*,7a*S*)-5-oxo-3-vinyl-3,3a,4,5-tetrahydrobenzofuran-7a(2H)-yl)ethoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (12) The reaction was carried out in 0.1mmol accroding to general procedure to afford **12** (23 mg, 43% yield) as yellow oil. $[\alpha]_D^{30.4}$ -8.2 (c 0.84, $CHCl_3$) for d.r. = 97:3; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 6.57 (dd, *J* = 10.4, 1.1 Hz, 1H), 6.00 (d, *J* = 10.4 Hz, 1H), 5.53 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.19 (t, *J* = 9.5 Hz, 1H), 5.11 – 5.04 (m, 3H), 4.97 (dd, *J* = 9.4, 8.0 Hz, 1H), 4.51 (d, *J* = 7.9 Hz, 1H), 4.26 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.15 (dd, *J* = 12.3, 2.3 Hz, 1H), 4.05 (m, 2H), 3.73 – 3.66 (m, 2H), 3.57 (dd, *J* = 9.0, 6.1 Hz, 1H), 3.11 – 3.01 (m, 1H), 2.78 (m, 1H), 2.57 – 2.51 (m, 2H), 2.09 (s, 3H), 2.06 – 1.99 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.72, 170.74, 170.36, 169.52, 169.36, 151.30, 135.80, 130.17, 118.95, 100.68, 79.96, 72.98, 72.02, 71.40, 71.18, 68.53, 65.36, 62.02, 47.92, 44.57, 38.59, 35.63, 20.85, 20.81, 20.71. ESI-MS: $[M+Na]^{\oplus}$ 561.2; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{26}H_{35}O_{12}^{\oplus}$ 539.2123, found 539.2117; IR (KBr) ν (cm^{-1}) 2920, 2851, 2378, 2348, 2302, 1755, 1679, 1631, 1368, 1224, 1038, 906, 676, 664. HPLC: Chiracel OD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 27.7 min (minor), 30.3 min (major).



PDA Ch1 214nm

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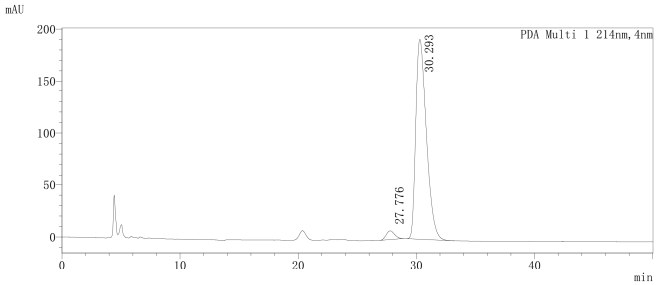
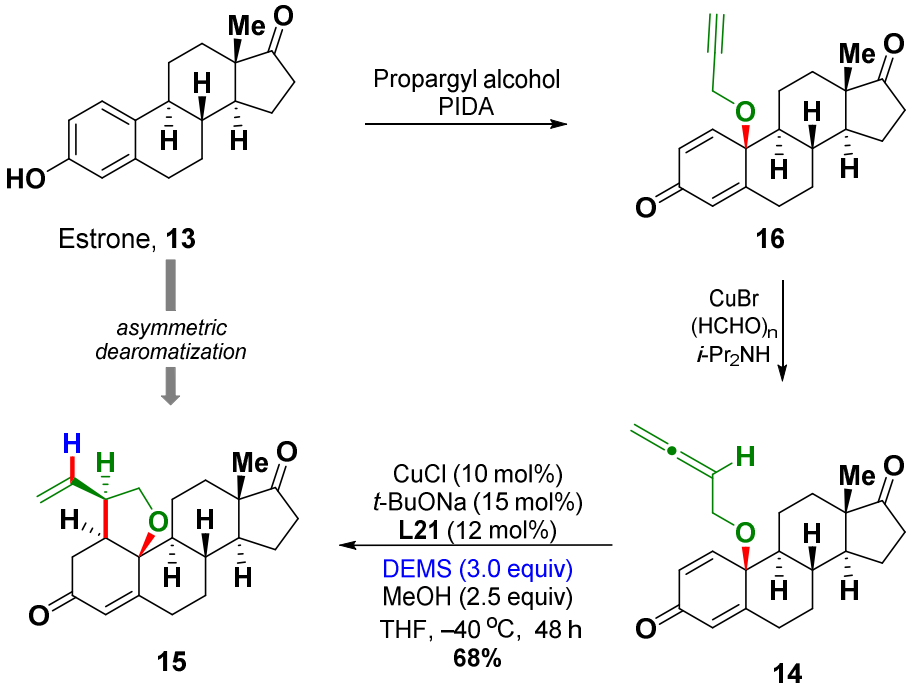
1	27.300	14761288	267452	50.521
2	30.205	14457056	227329	49.479



PDA Ch1 214nm

#	Ret.Time	Area	Height	Area%
1	27.776	416841	8355	3.356
2	30.293	12005183	192390	96.644

7.2 ASMMETRIC DEAROMATIZATION MODIFICATION OF 13



(8*S*,9*S*,10*S*,13*S*,14*S*)-13-methyl-10-(prop-2-yn-1-yloxy)-7,8,9,10,11,12,13,14,15,16-decahydro-3*H*-cyclopenta[a]phenanthrene-3,17(6*H*)-dione (16) Estrone **13** (8.0 mmol, 1.0 eq) was dissolved in 5 mL DCM, then 4.65mL propargyl alcohol (10 eq) was added, the mixture was cooled to 0 °C and treated with phenyliodine (III) diacetate (PIDA, 3.86g, 1.5 eq) in several portions. The resulting mixture was warmed to room temperature and stirred 2h. Then it was diluted with water (30 mL) and extracted with DCM (30 mL × 3). The combined organic phases were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 2/1) to afford the desired product **16**. light yellow solid, m.p. 137-138 °C, 38.5% yield, d.r.= 91:9. $[\alpha]_D^{24.2}$ +24.8 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.06 (d, *J* = 10.3 Hz, 1H), 6.36 (dd, *J* = 10.3, 1.7 Hz, 1H), 6.20 (s, 1H), 3.86 (d, *J* = 2.2 Hz, 2H), 2.62 (td, *J* = 12.7, 4.3 Hz, 1H), 2.53 – 2.34 (m, 3H), 2.26 – 2.02 (m, 4H), 2.00 – 1.91 (m, 1H), 1.90 – 1.83 (m, 1H), 1.82 – 1.74 (m, 1H), 1.69 – 1.56 (m, 1H), 1.31 – 1.11 (m, 4H), 0.98 (s, 3H).^{13}C NMR (100MHz, $CDCl_3$) δ(ppm) 220.23, 185.07, 163.26, 149.35, 131.62, 126.61, 80.13, 76.40, 74.64, 55.31, 52.78, 50.20, 47.80, 35.65, 34.63, 32.55, 32.19, 31.13, 22.17, 22.01, 13.87; EI-MS: $[M]^{\oplus}$ 324; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{21}H_{25}O_3^{\oplus}$ 325.1798, found 325,1799; IR (KBr) ν (cm^{-1}) 2943, 2856, 2374, 2348, 2301, 1737, 1632, 1610, 1453, 1374, 1289, 1074, 1019, 890, 753, 663.

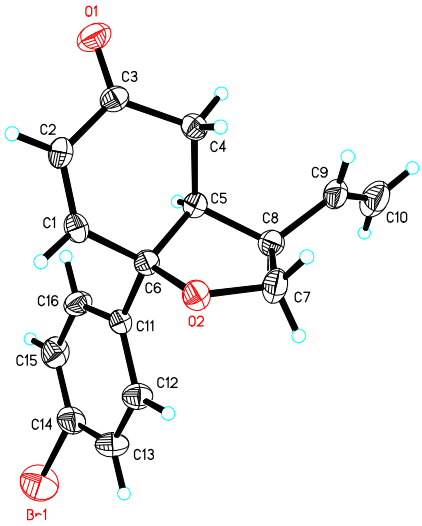
(8*S*,9*S*,10*S*,13*S*,14*S*)-10-(buta-2,3-dien-1-yloxy)-13-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-3*H*-cyclopenta[a]phenanthrene-3,17(6*H*)-dione (14) To a well-stirred solution of **16** (3.0 mmol, 1.0 eq) in dioxane (25 mL) was added paraformaldehyde (450 mg, 15 mmol, 5 eq), CuBr (219 mg, 1.5 mmol, 0.5 eq) and diisopropylamine (840 ul, 6.0 mmol, 2.0 eq) under argon atmosphere. The resulting mixture was stirred at 110 °C for 1 h. After cooled to room temperature, the reaction mixture was filtered and washed with DCM (30 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc

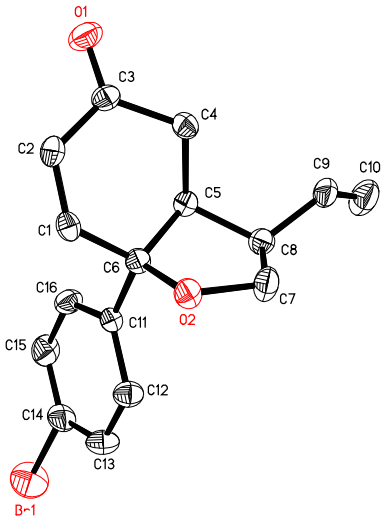
= 2/1) to afford the pure substrates **14**. yellow oil, 38.8% yield, d.r.=91:9. $[\alpha]_D^{24.2}$ +22.1 (c 1.375, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.03 (d, *J* = 10.3 Hz, 1H), 6.34 (d, *J* = 10.1 Hz, 1H), 6.18 (s, 1H), 5.26 – 5.15 (m, 1H), 4.84 – 4.74 (m, 2H), 3.78 – 3.63 (m, 2H), 2.61 – 2.33 (m, 3H), 2.22 (m, 1H), 2.16 – 2.02 (m, 3H), 1.95 (dd, *J* = 15.7, 10.9 Hz, 1H), 1.86 (d, *J* = 13.1 Hz, 1H), 1.76 (d, *J* = 13.7 Hz, 1H), 1.64 – 1.52 (m, 1H), 1.29 – 1.12 (m, 4H), 0.96 (s, 3H).^{13}C NMR (100MHz, $CDCl_3$) δ(ppm) 220.47, 208.86, 185.38, 164.53, 150.63, 131.06, 126.08, 88.52, 76.30, 75.78, 62.22, 55.56, 50.12, 47.83, 35.67, 34.63, 32.59, 32.17, 31.14, 22.24, 22.04, 13.76; EI-MS: $[M]^{\oplus}$ 338; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{22}H_{27}O_3^{\oplus}$ 339.1955, found 339.1955; IR (KBr) ν (cm^{-1}) 2936, 2856, 2349, 1957, 1738, 1669, 1608, 1455, 1374, 1288, 1076, 1049, 1030, 890, 855, 754.

(3aS,5aS,5bR,8R,8aS,13aS,13bS)-3a-methyl-8-vinyl-1,2,3a,4,5,5a,7,8,8a,9,12,13,13a,13b-tetradecahydrocyclopenta[7,8]phenanthro[4a,4-b]furan-3,10-dione (15) The reaction was carried out accroding to general procedure to afford **15** (46.2 mg, 68% yield) as light yellow solid, m.p. 144-145 °C, d.r.=95:5(the d.r. was determined by ^1H-NMR (400 MHz)). $[\alpha]_D^{24.1}$ +46.4 (c 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ(ppm) 5.87 (s, 1H), 5.53 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.10 – 5.00 (m, 2H), 4.00 (dd, *J* = 8.8, 7.3 Hz, 1H), 3.46 (dd, *J* = 8.9, 6.1 Hz, 1H), 3.03 (ddd, *J* = 16.1, 9.5, 6.9 Hz, 1H), 2.96 – 2.87 (m, 1H), 2.76 (td, *J* = 12.3, 3.6 Hz, 1H), 2.60 – 2.37 (m, 3H), 2.26 – 2.18 (m, 1H), 2.16 – 2.01 (m, 3H), 2.00 – 1.84 (m, 2H), 1.83 – 1.67 (m, 2H), 1.61 – 1.52 (m, 1H), 1.41 – 1.26 (m, 3H), 1.20 – 1.07 (m, 1H), 0.95 (s, 3H).^{13}C NMR (100MHz, $CDCl_3$) δ(ppm) 220.36, 197.27, 166.39, 136.27, 125.48, 118.68, 82.71, 70.93, 50.78, 50.40, 47.93, 47.89, 40.03, 36.59, 35.91, 35.82, 32.13, 32.07, 31.13, 21.79, 21.27, 13.90; ESI-MS: $[M+H]^{\oplus}$ 341.2; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{22}H_{27}O_3^{\oplus}$ 341.2111, found 341.2111; IR (KBr) ν (cm^{-1}) 2925, 2853, 2381, 1738, 1672, 1640, 1630, 1564, 1468, 1452, 1263, 1123, 1040, 1000, 915, 758.

8. Absolute Configuration Confirmation Of 3j and 15

8.1 The Single Crystal Data of 3j (CCDC 1572373).





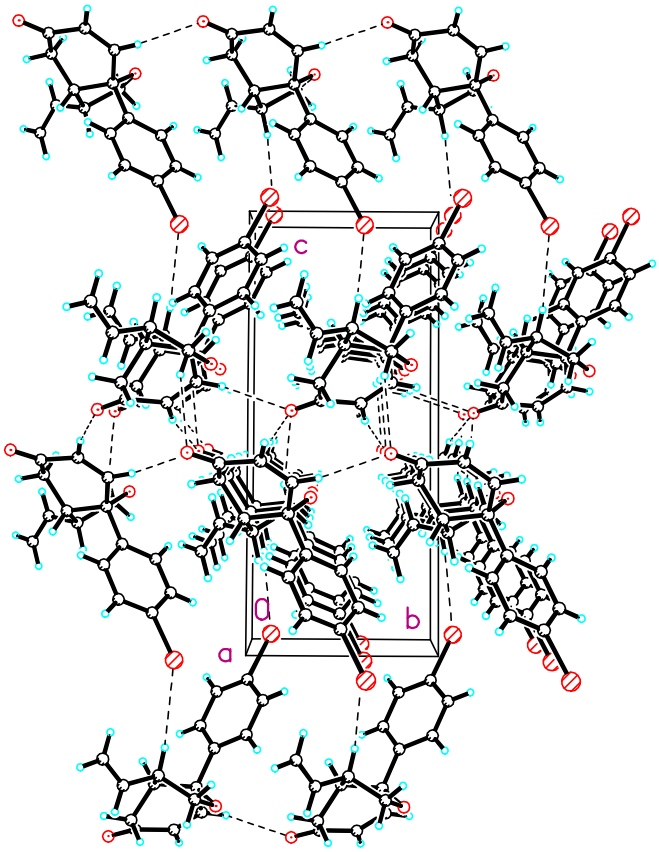
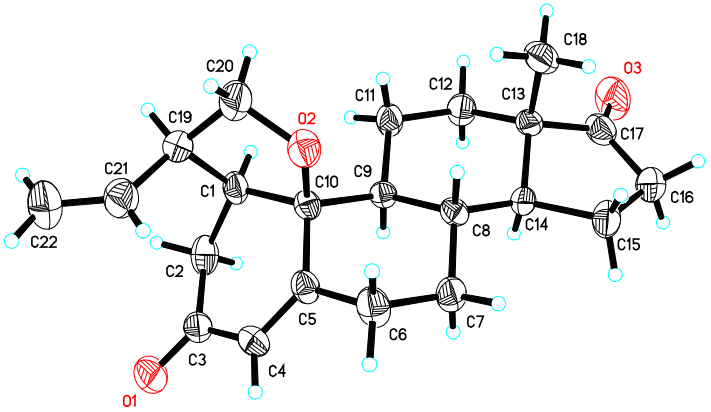
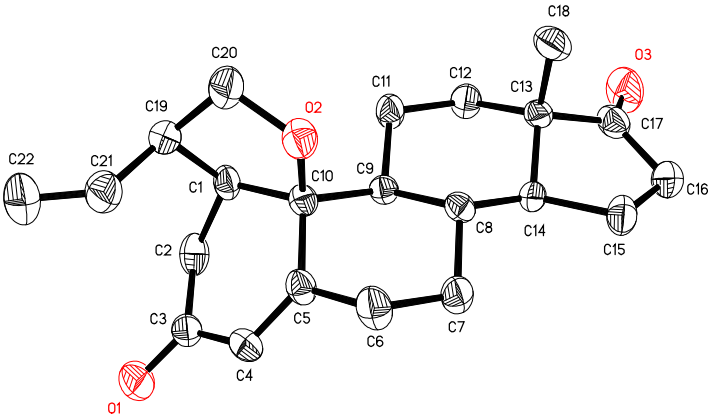


Table S3: Crystal data and structure refinement for mo_dm15677_0m.

Identification code	mo_dm15677_0m	
Empirical formula	C_{16} H_{15} Br O_2	
Formula weight	319.19	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.1968(15) Å	α= 90°.
	b = 6.4943(14) Å	β= 96.738(4)°.
	c = 15.208(3) Å	γ = 90°.
Volume	705.9(3) $Å^3$	
Z	2	
Density (calculated)	1.202 Mg/m^3	
Absorption coefficient	2.907 mm^{-1}	
F(000)	324	
Crystal size	0.230 x 0.160 x 0.110 mm^3	
Theta range for data collection	2.697 to 25.982°.	
Index ranges	-7<=h<=8, -7<=k<=8, -18<=l<=18	
Reflections collected	5161	
Independent reflections	2643 [R(int) = 0.0266]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5630	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2643 / 1 / 172	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0810	
R indices (all data)	R1 = 0.0610, wR2 = 0.0887	
Absolute structure parameter	0.032(11)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.195 and -0.439 $e.Å^{-3}$	

8.2 The Single Crystal Data of 15 (CCDC 1572374).





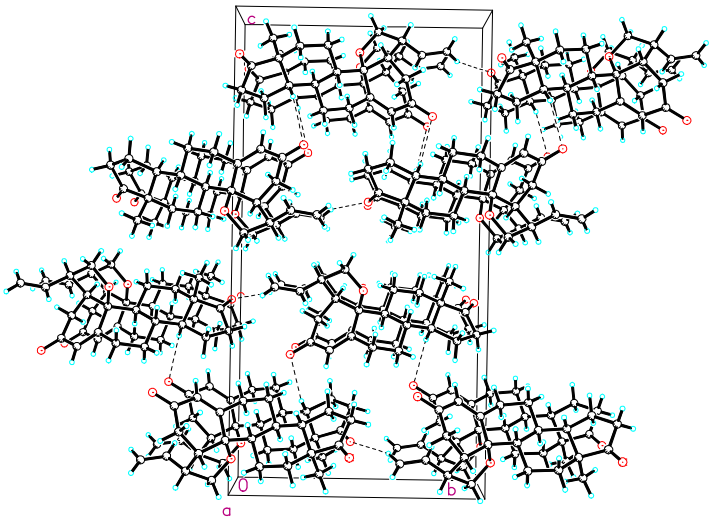
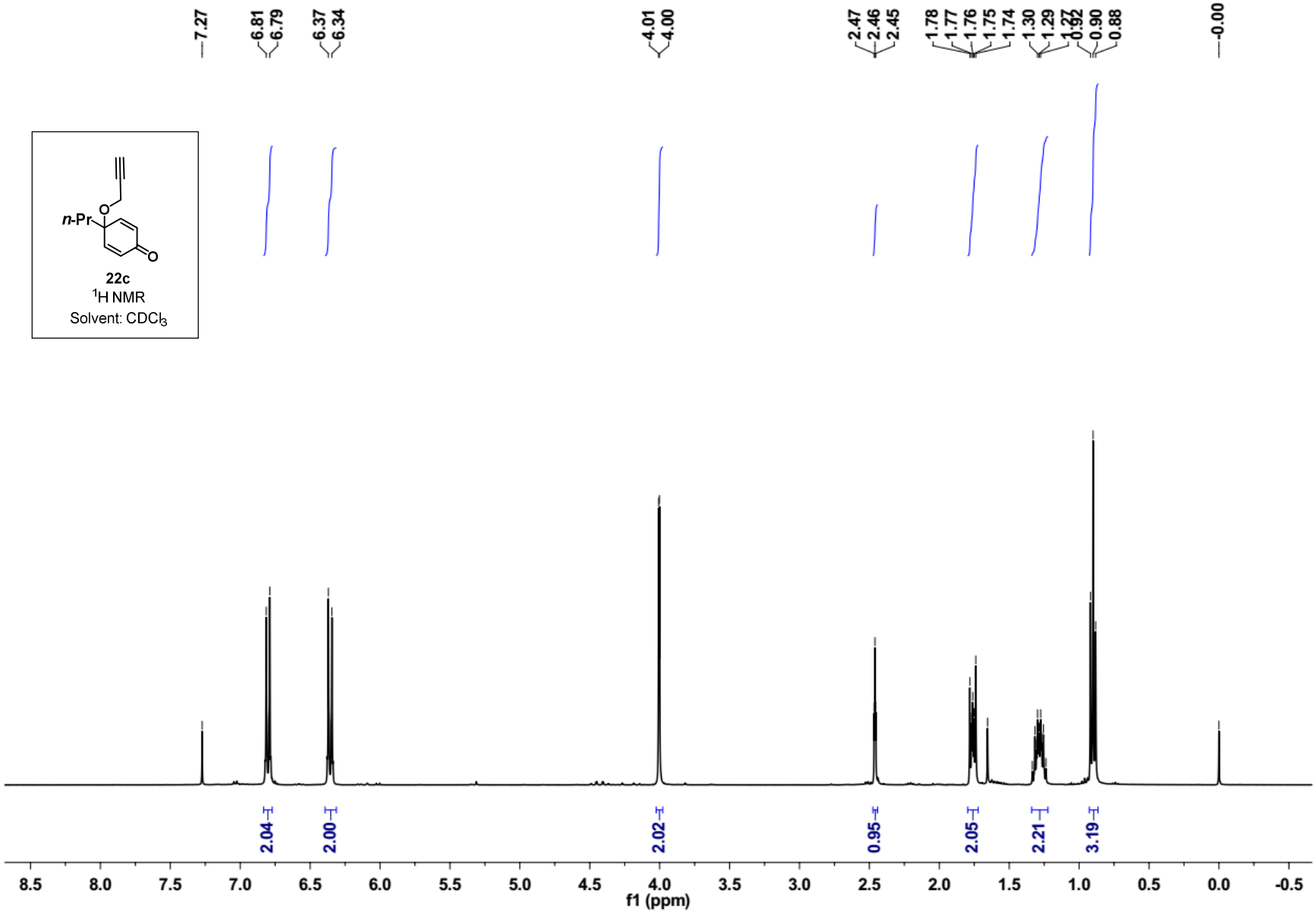


Table S4: Crystal data and structure refinement for 15

Identification code	cd16742	
Empirical formula	C22 H28 O3	
Formula weight	340.44	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.1385(5) Å	α= 90°.
	b = 12.6387(10) Å	β= 90°.
	c = 24.081(2) Å	γ = 90°.
Volume	1868.3(3) $Å^3$	
Z	4	
Density (calculated)	1.210 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	736	
Crystal size	0.150 x 0.100 x 0.060 mm^3	
Theta range for data collection	1.820 to 24.993°.	
Index ranges	-7<=h<=6, -14<=k<=15, -28<=l<=28	
Reflections collected	10334	
Independent reflections	3286 [R(int) = 0.0835]	
Completeness to theta = 25.242°	97.3 %	
Absorption correction	Multi-scam	
Max. and min. transmission	0.7456 and 0.5860	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3286 / 0 / 227	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0636, wR2 = 0.1387	
R indices (all data)	R1 = 0.1092, wR2 = 0.1542	
Absolute structure parameter	-0.5(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.280 and -0.266 $e.Å^{-3}$	

9. ^{1}H NMR, ^{13}C NMR, HSQC , COSY, NOSEY, HMBC, DEPT90, DEPT135 COPIES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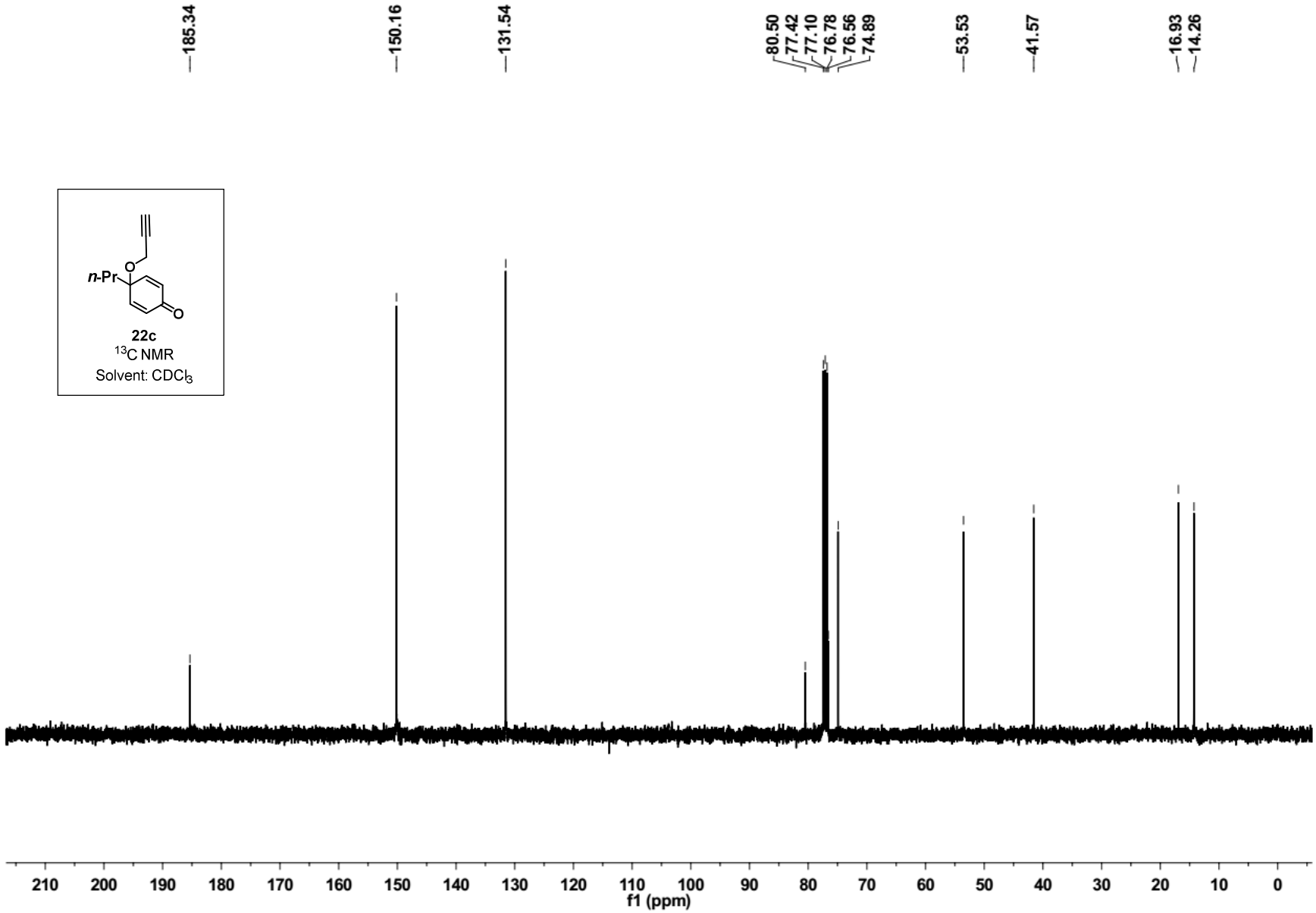
6.81
6.79
6.37
6.34
4.01
4.00
2.47
2.46
2.45
1.78
1.77
1.76
1.75
1.74
1.30
1.29
0.92
0.90
0.88
-0.00
n-Pr
O
O
22c
1H NMR
Solvent: CDCl3
2.04
2.00
2.02
0.95
2.05
2.21
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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80.50
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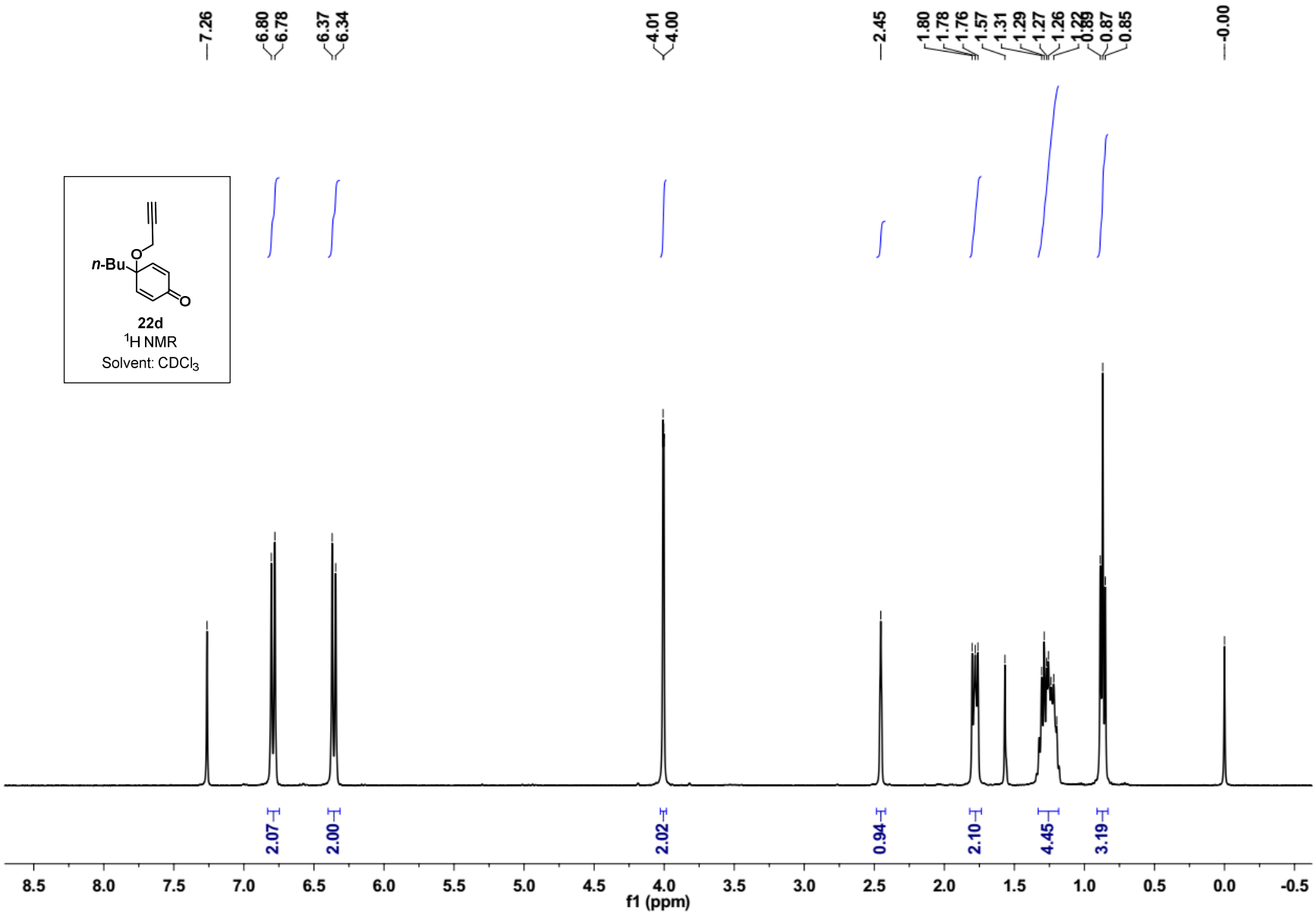
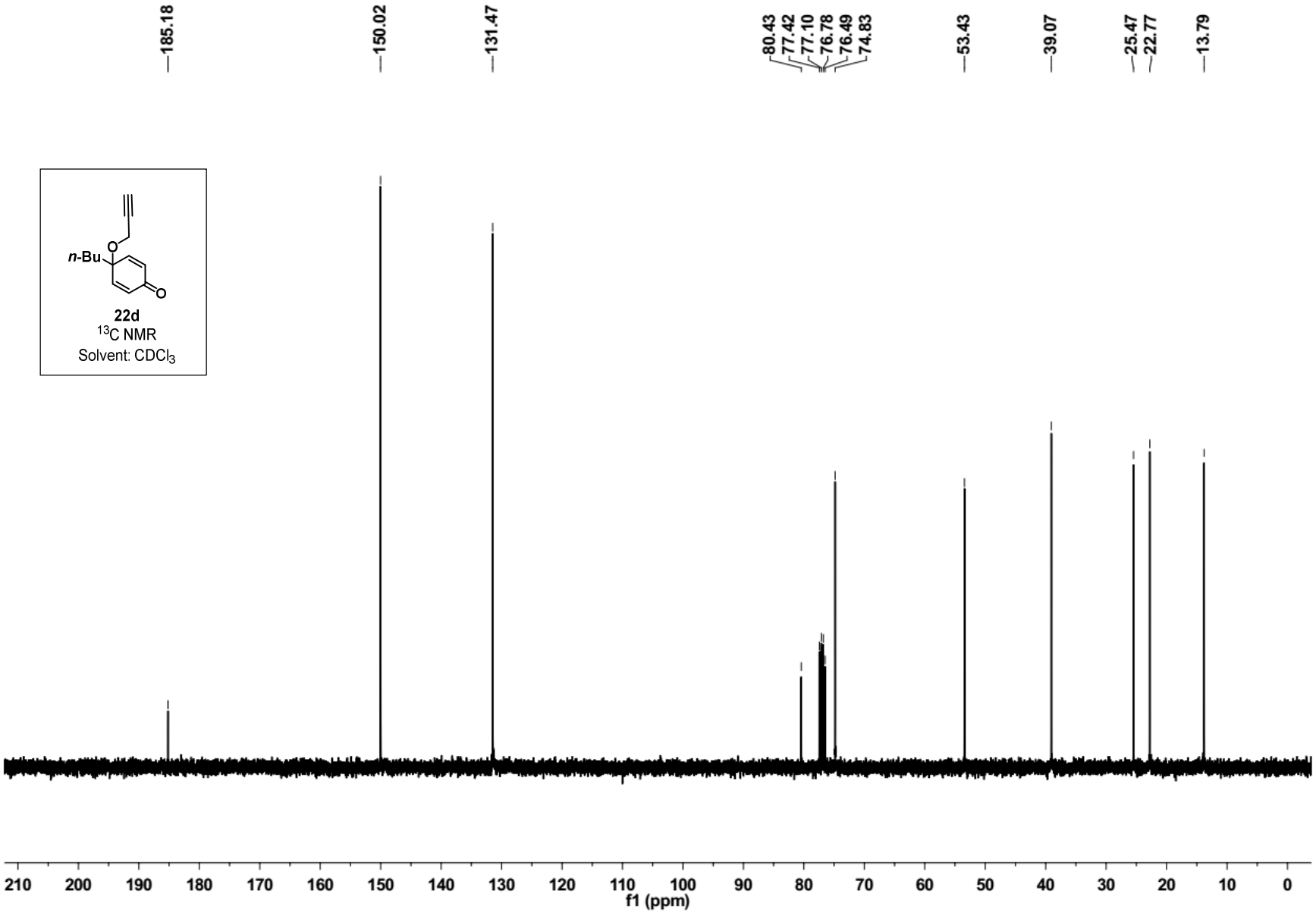
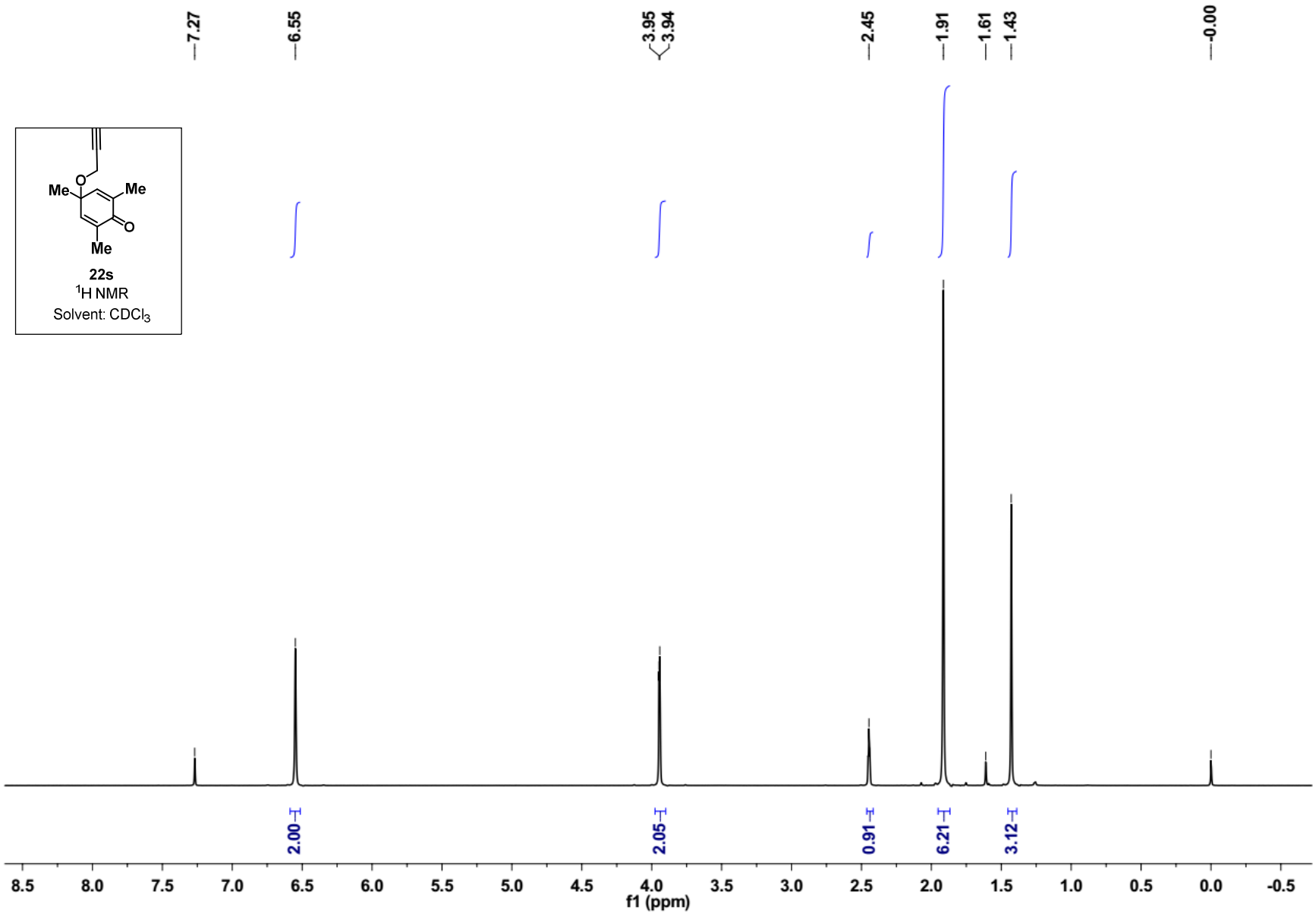
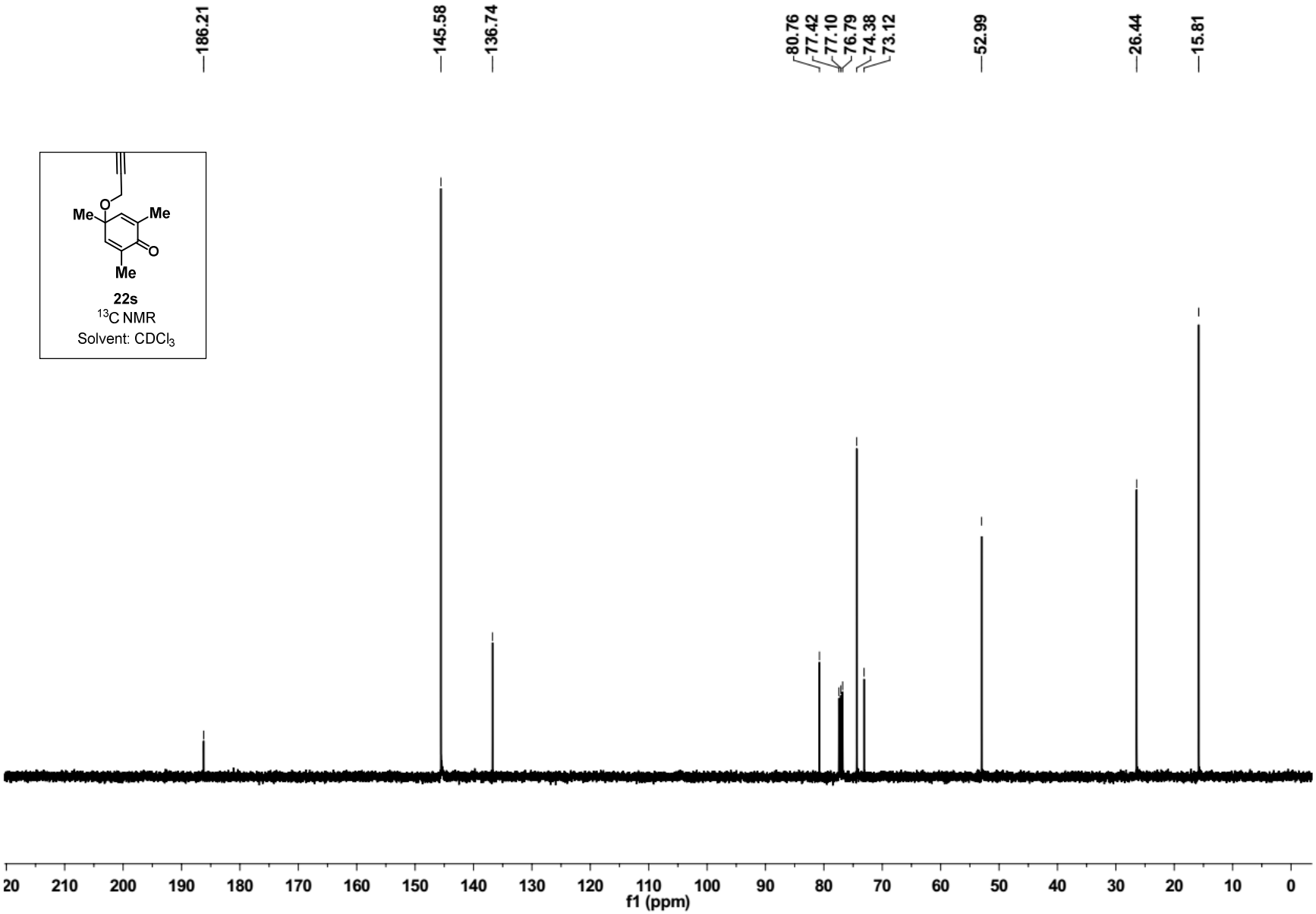
77.10
76.78
76.56
74.89
53.53
41.57
16.93
14.26
n-Pr
O
O
22c
13C NMR
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
6.80
6.78
6.37
6.34
4.01
4.00
2.45
1.80
1.78
1.76
1.57
1.31
1.29
1.27
1.26
0.87
0.85
0.00
n-Bu
O
O
22d
1H NMR
Solvent: CDCl3
2.07
2.00
2.02
0.94
2.10
4.45
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


185.18
150.02
131.47
80.43
77.42
77.10
76.78
76.49
74.83
53.43
39.07
25.47
22.77
13.79
n-Bu
O
O
22d
13C NMR
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27
6.55
3.95
3.94
2.45
1.91
1.61
1.43
0.00
Me
Me
Me
O
O
22s
1H NMR
Solvent: CDCl3
2.00
2.05
0.91
6.21
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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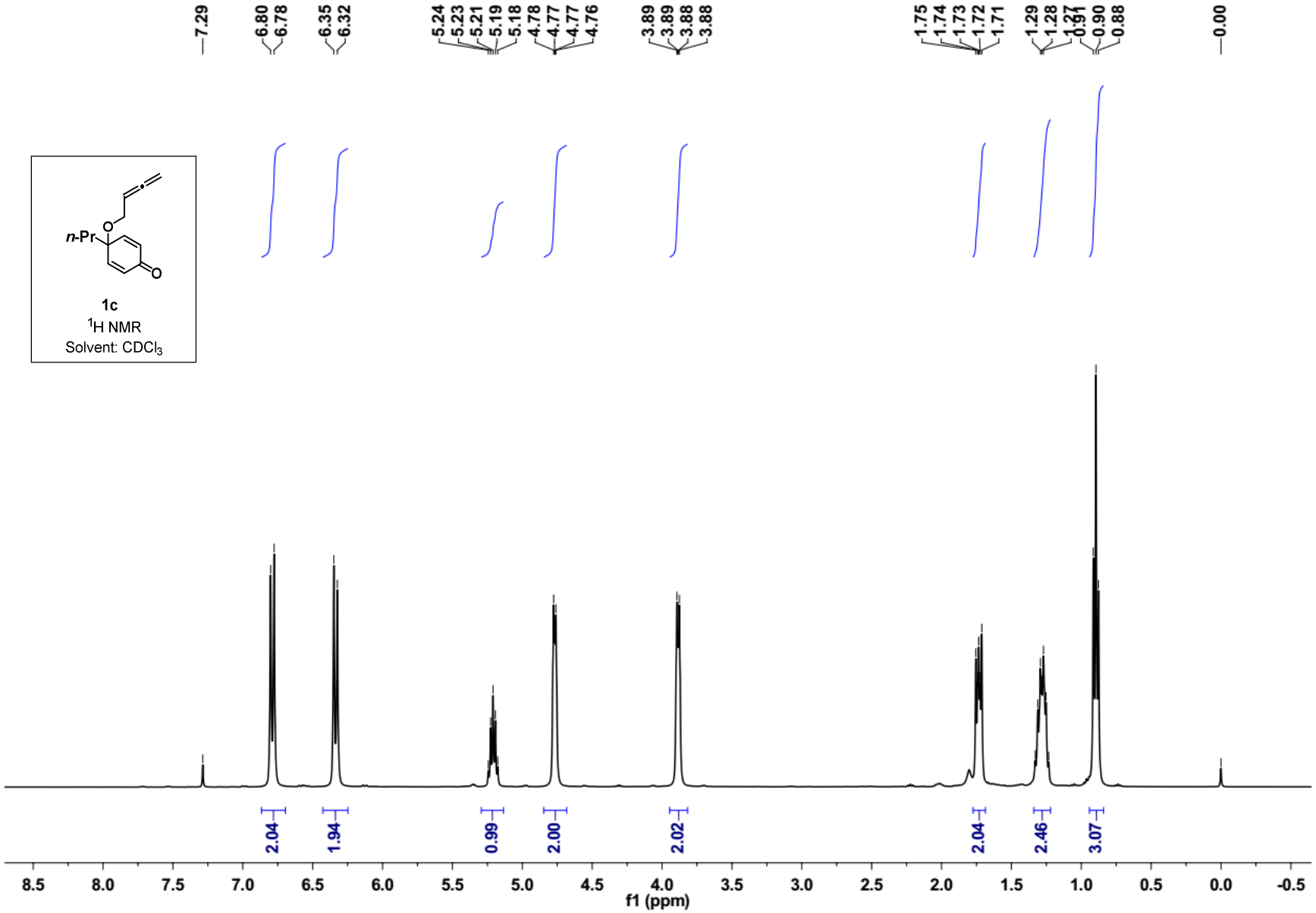
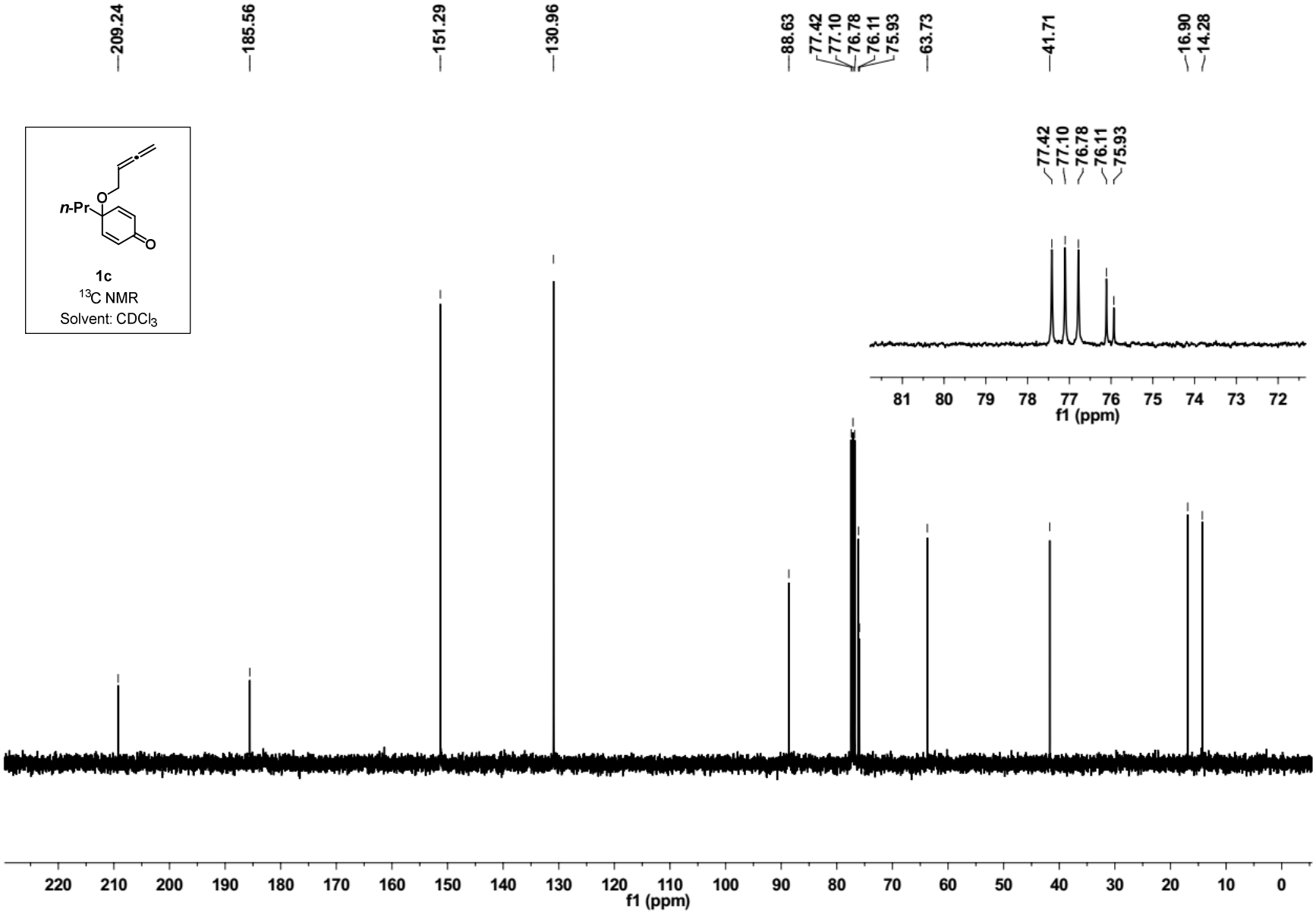
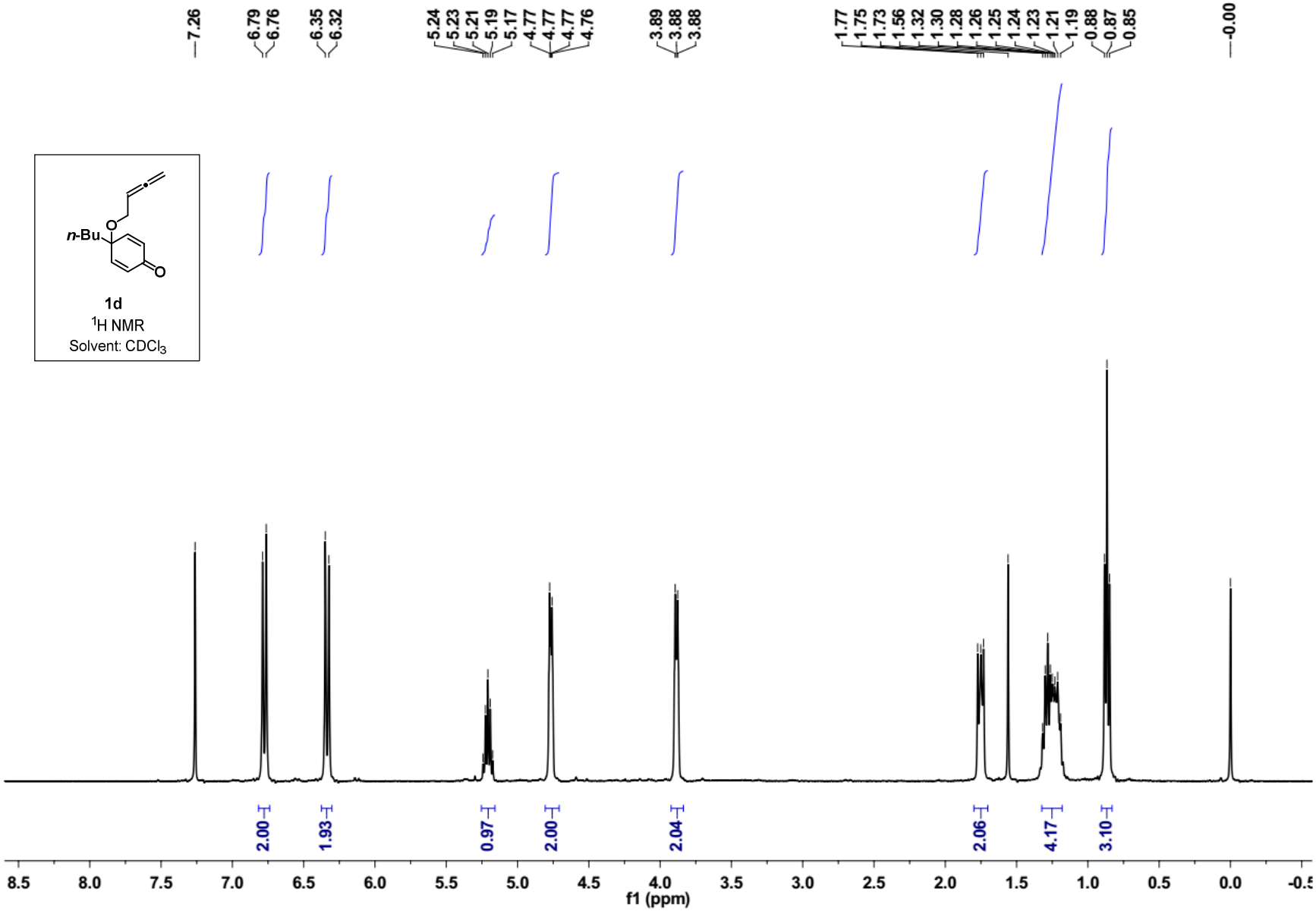
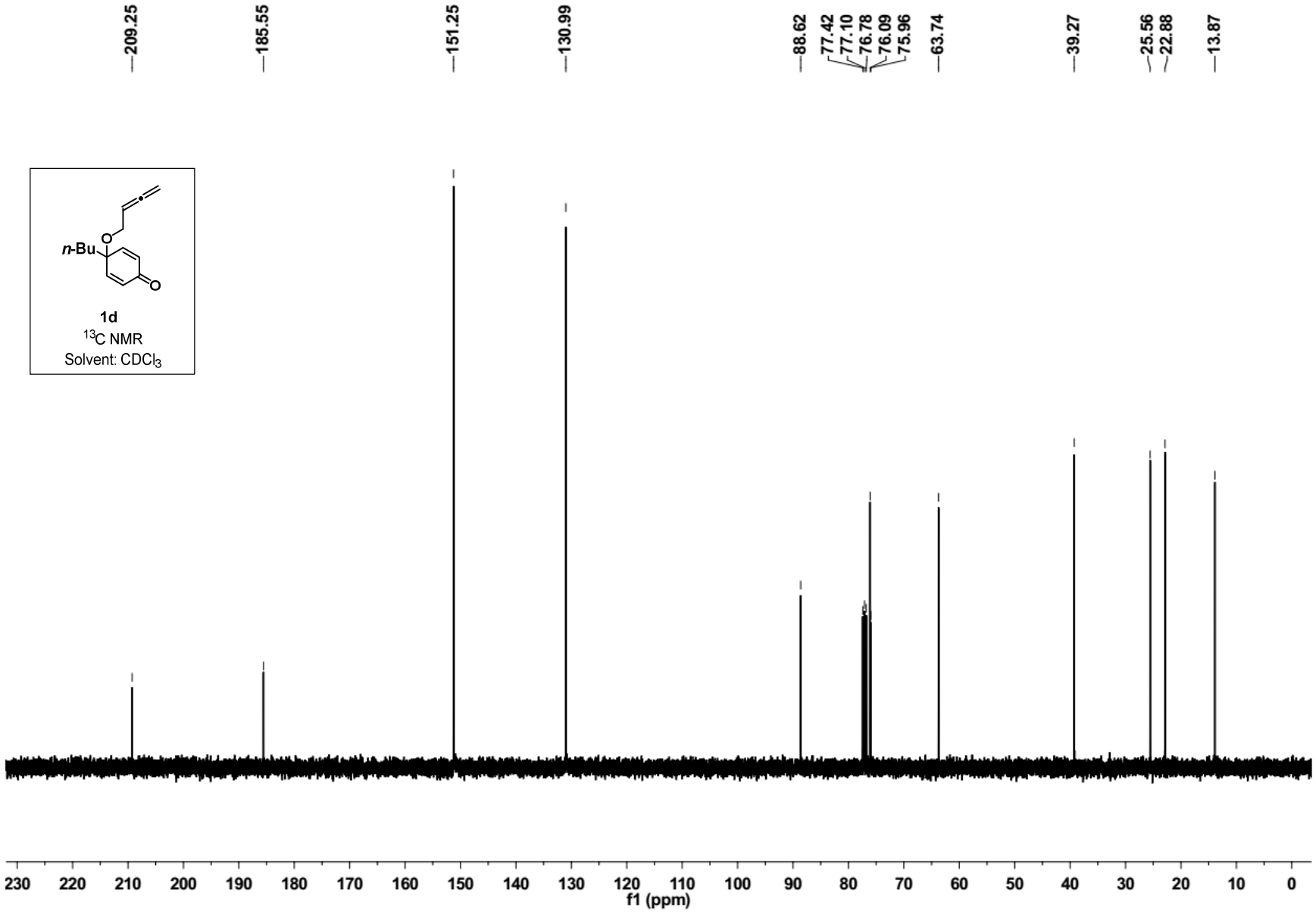
145.58
136.74
80.76
77.42
77.10
76.79
74.38
73.12
52.99
26.44
15.81
Me
Me
Me
O
O
22s
13C NMR
Solvent: CDCl3
f1 (ppm)


7.29
6.80
6.78
6.35
6.32
5.24
5.23
5.21
5.19
5.18
4.78
4.77
4.77
4.76
3.89
3.89
3.88
3.88
1.75
1.74
1.73
1.72
1.71
1.29
1.28
0.91
0.90
0.88
0.00
n-Pr
O
O
1c
1H NMR
Solvent: CDCl3
2.04
1.94
0.99
2.00
2.02
2.04
2.46
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


209.24
185.56
151.29
130.96
88.63
77.42
77.10
76.78
76.11
75.93
63.73
41.71
16.90
14.28
n-Pr
O
O
1c
13C NMR
Solvent: CDCl3
f1 (ppm)
f1 (ppm)


7.26
6.79
6.76
6.35
6.32
5.24
5.23
5.21
5.19
5.17
4.77
4.77
4.77
4.76
3.89
3.88
3.88
1.77
1.75
1.73
1.56
1.32
1.30
1.28
1.26
1.25
1.24
1.23
1.21
1.19
0.88
0.87
0.85
0.00
n-Bu
O
O
1d
1H NMR
Solvent: CDCl3
2.00
1.93
0.97
2.00
2.04
2.06
4.17
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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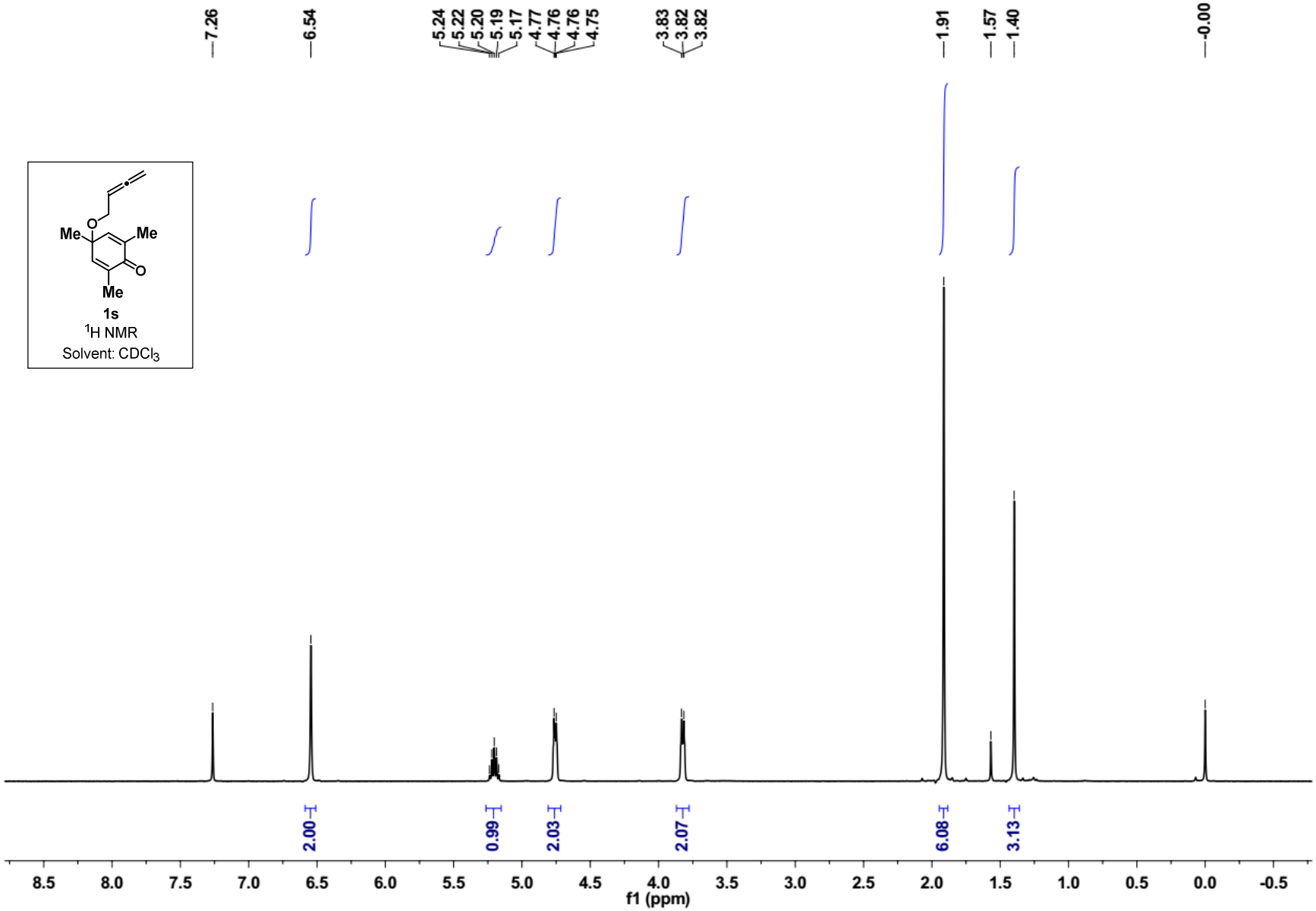
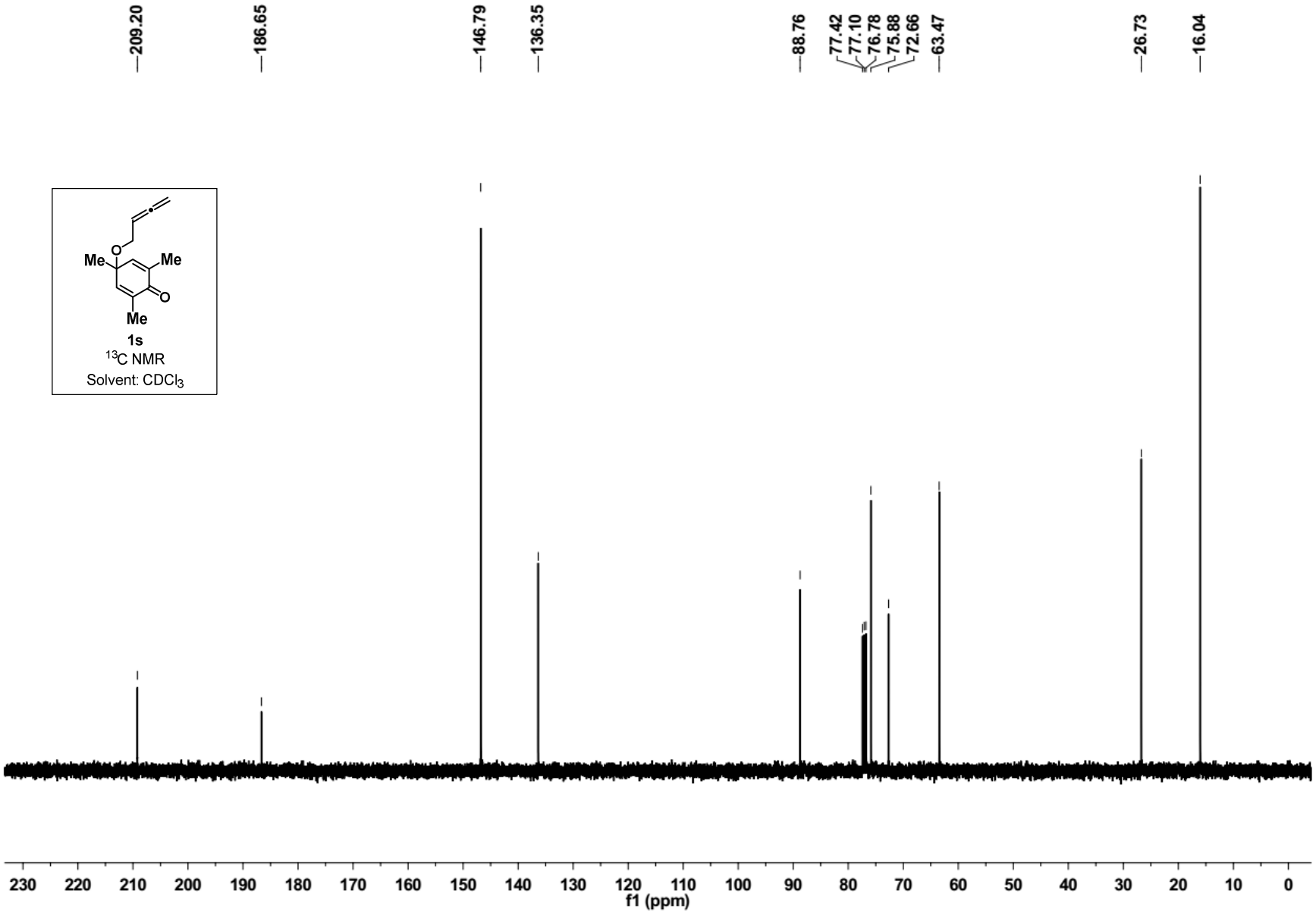
185.55
151.25
130.99
88.62
77.42
77.10
76.78
76.09
75.96
63.74
39.27
25.56
22.88
13.87
n-Bu
O
O
1d
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
6.54
5.24
5.22
5.20
5.19
5.17
4.77
4.76
4.76
4.75
3.83
3.82
3.82
1.91
1.57
1.40
0.00
Me
Me
Me
O
O
1s
1H NMR
Solvent: CDCl3
2.00
0.99
2.03
2.07
6.08
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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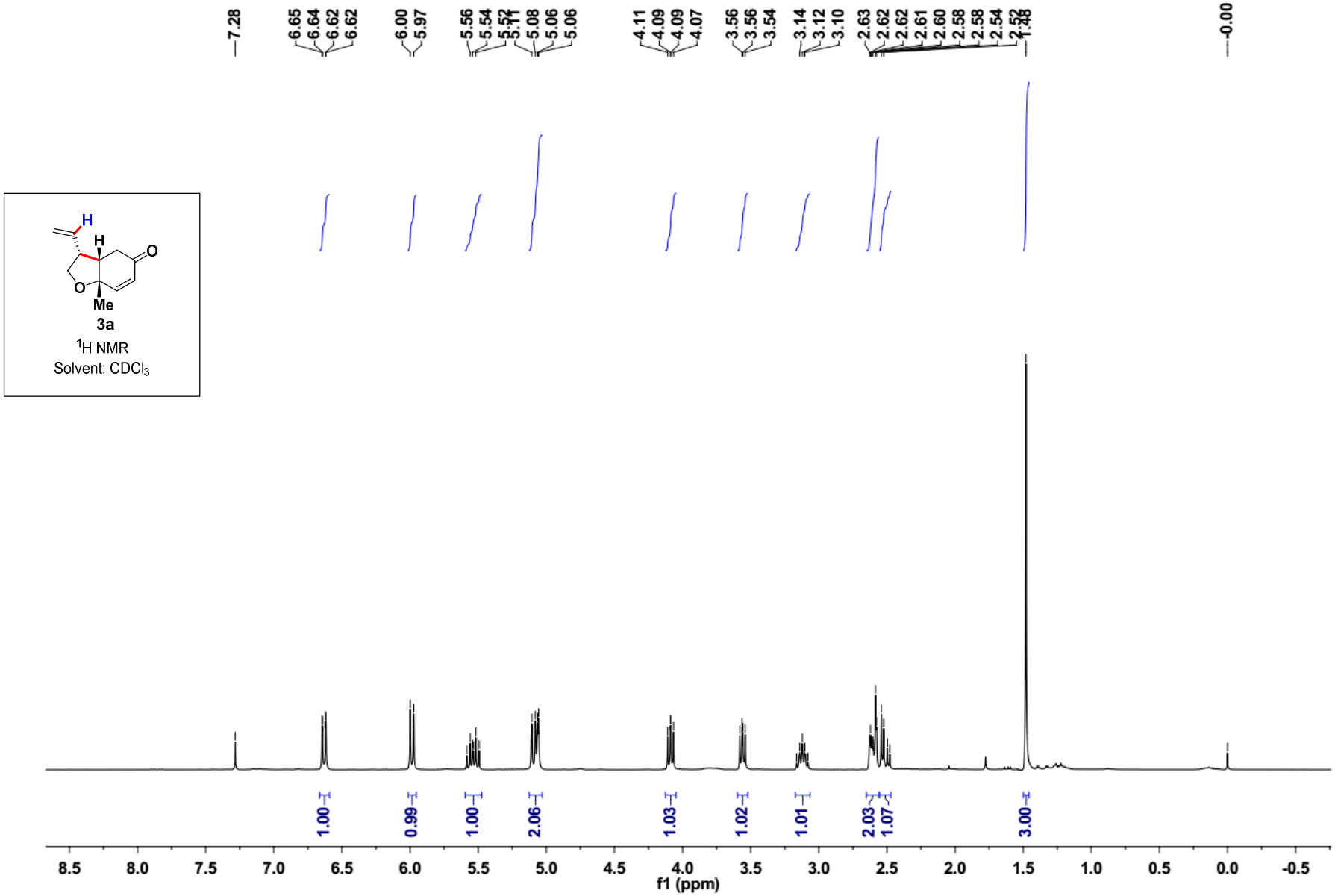
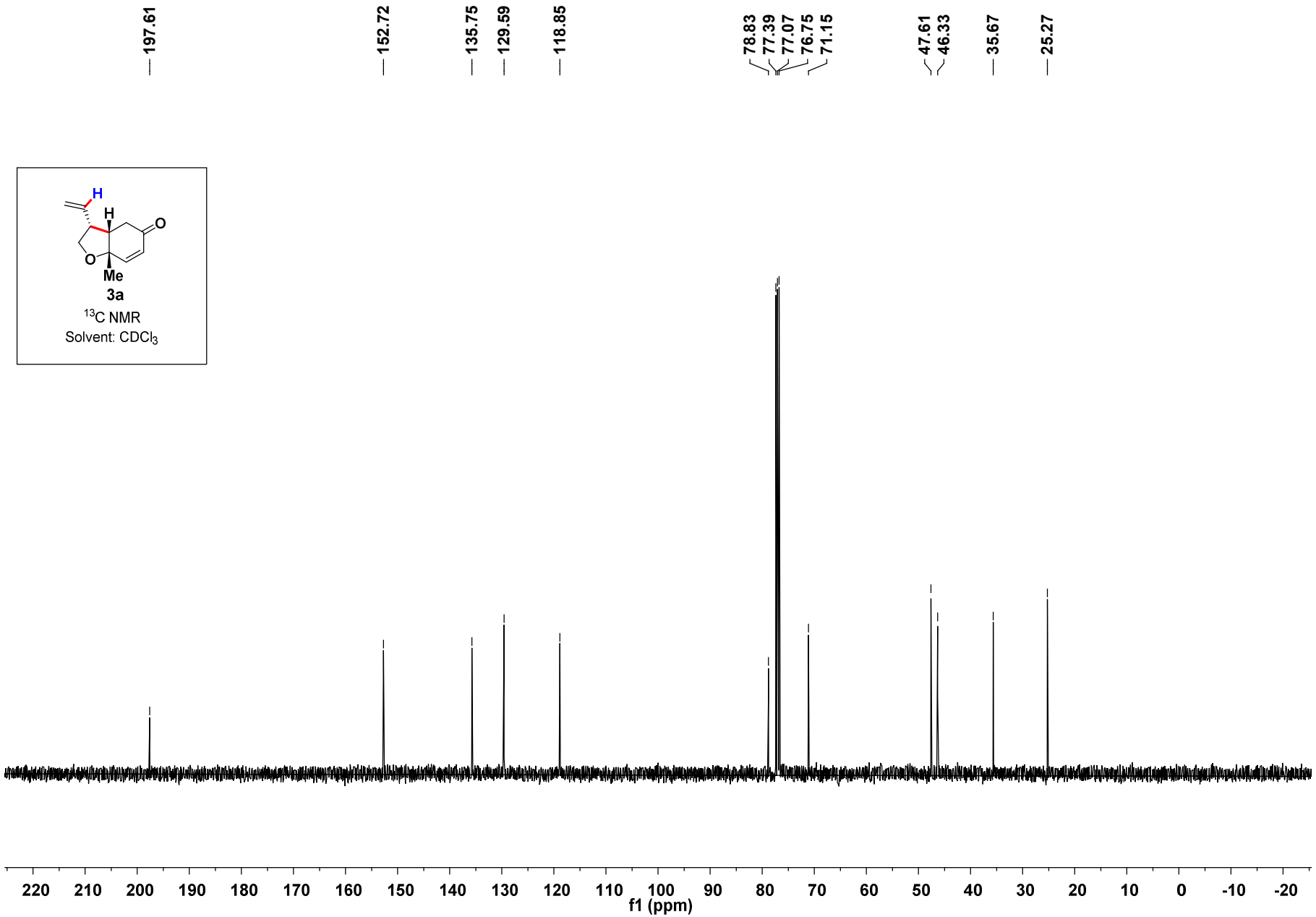
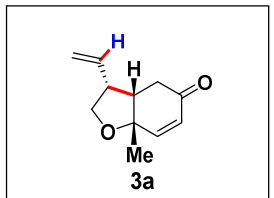
186.65
146.79
136.35
88.76
77.42
77.10
76.78
75.88
72.66
63.47
26.73
16.04
Me
Me
Me
O
O
1s
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

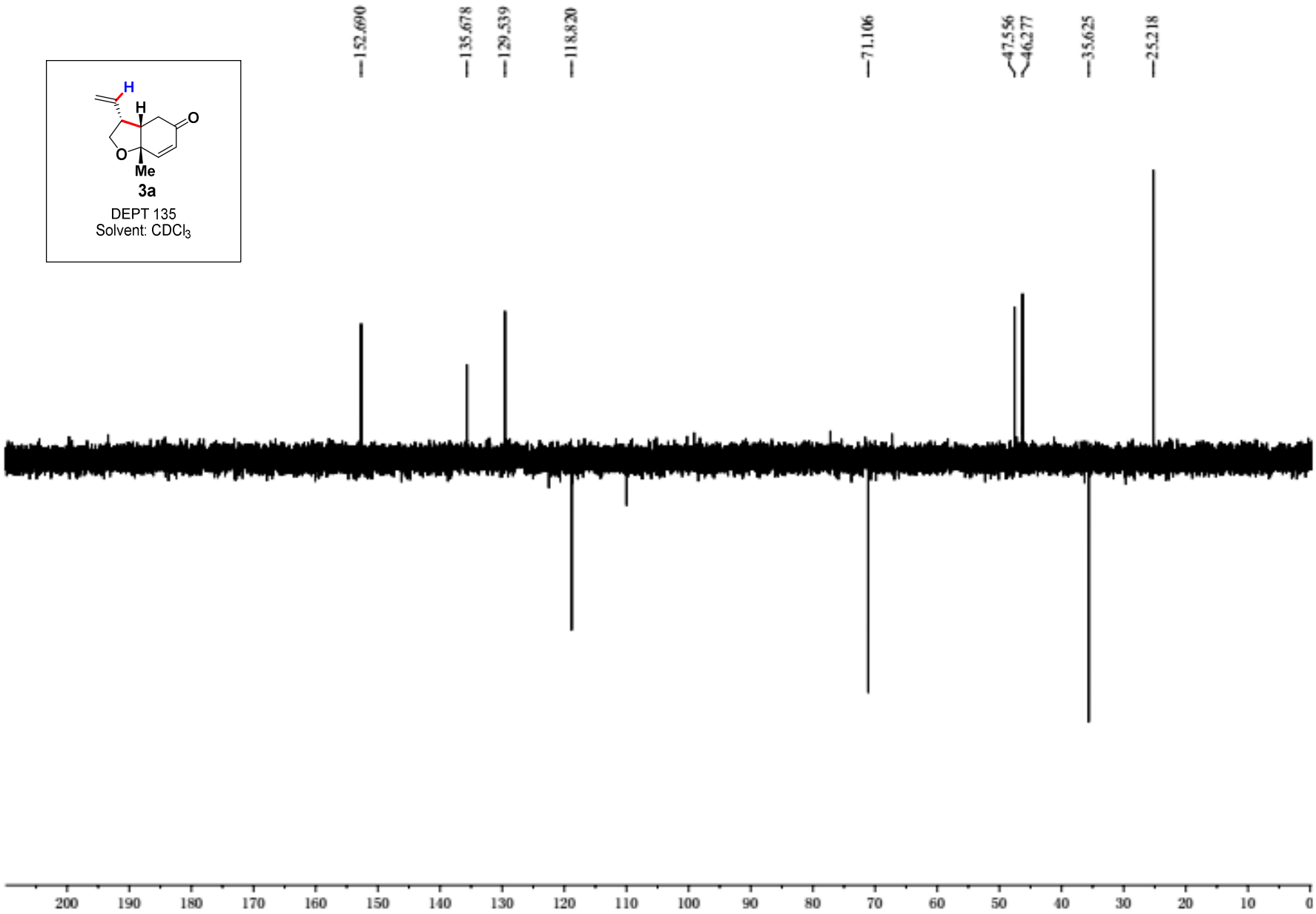

7.28
6.65
6.64
6.62
6.62
6.00
5.97
5.56
5.54
5.08
5.06
5.06
4.11
4.09
4.09
4.07
3.56
3.56
3.54
3.14
3.12
3.10
2.63
2.62
2.62
2.61
2.60
2.58
2.58
2.54
0.00
H
H
O
O
Me
3a
1H NMR
Solvent: CDCl3
1.00
0.99
1.00
2.06
1.03
1.02
1.01
2.03
1.07
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

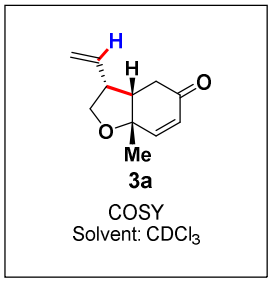

197.61
152.72
135.75
129.59
118.85
78.83
77.39
77.07
76.75
71.15
47.61
46.33
35.67
25.27
H
H
O
O
Me
3a
13C NMR
Solvent: CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



3a

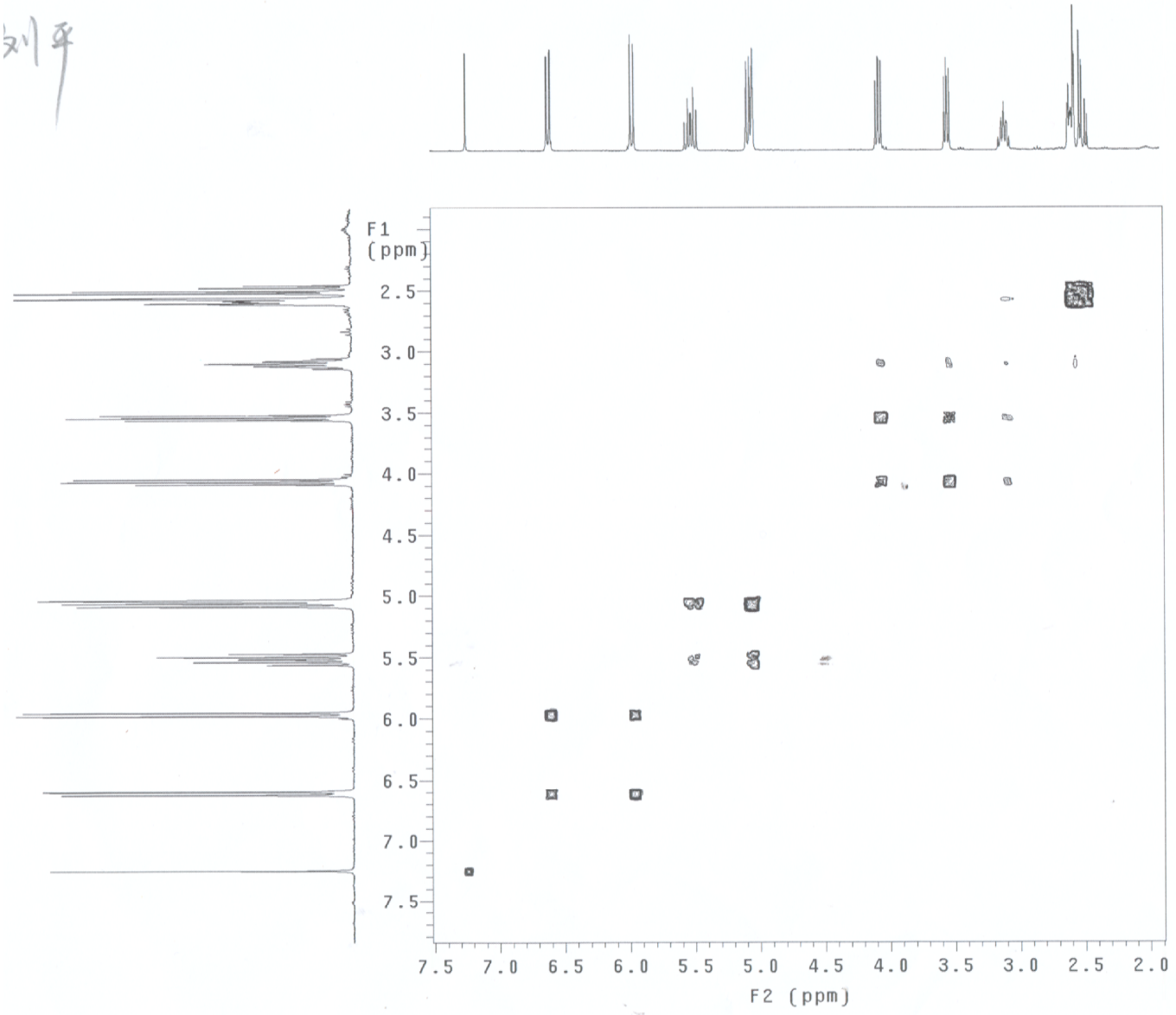
DEPT 90
Solvent: $CDCl_3$

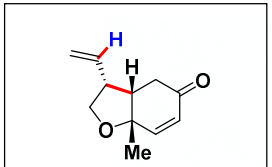

152.690
135.678
129.539
118.820
71.106
47.556
46.277
35.625
25.218
H
H
O
O
Me
3a
DEPT 135
Solvent: CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



3a

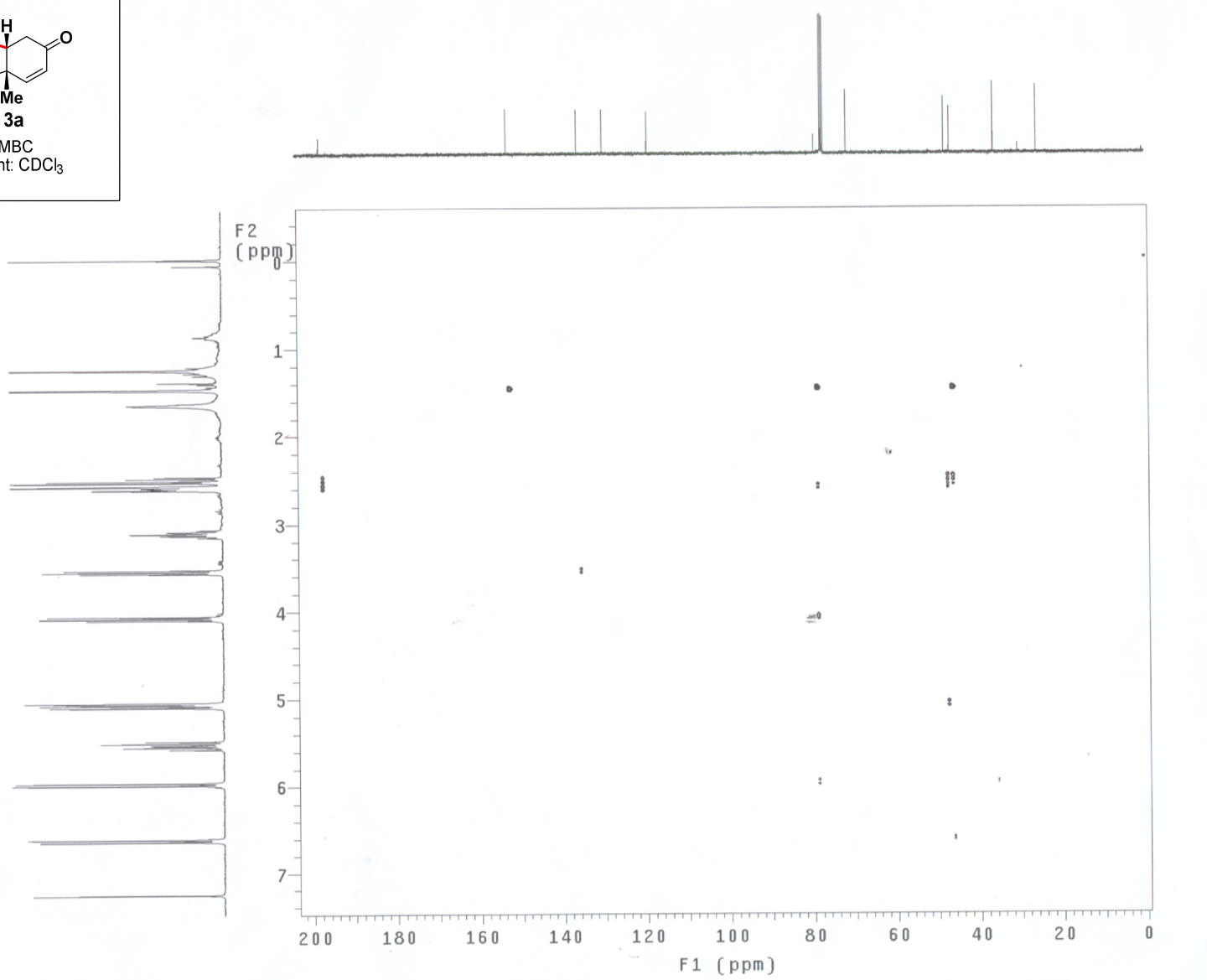
COSY
Solvent: $CDCl_3$

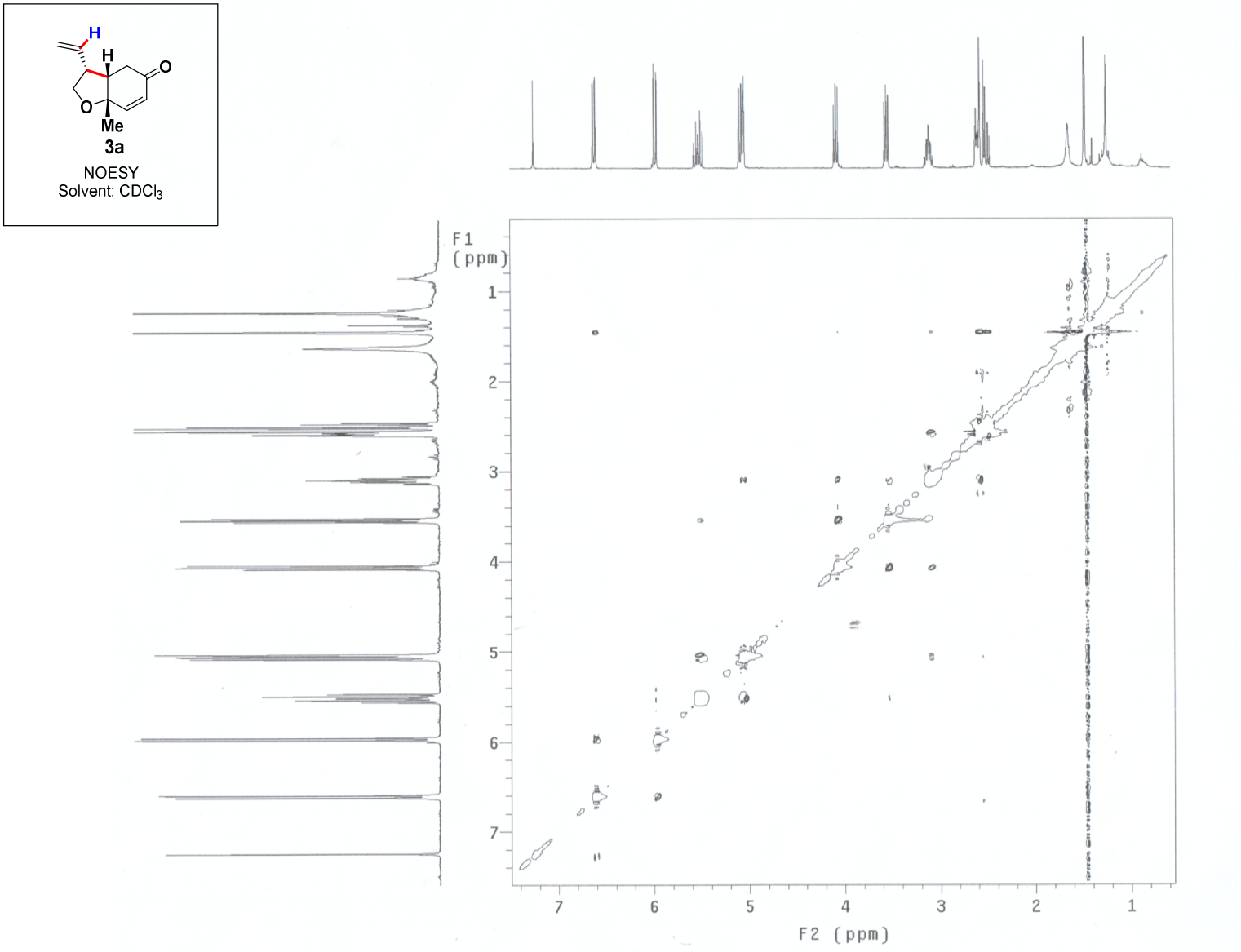


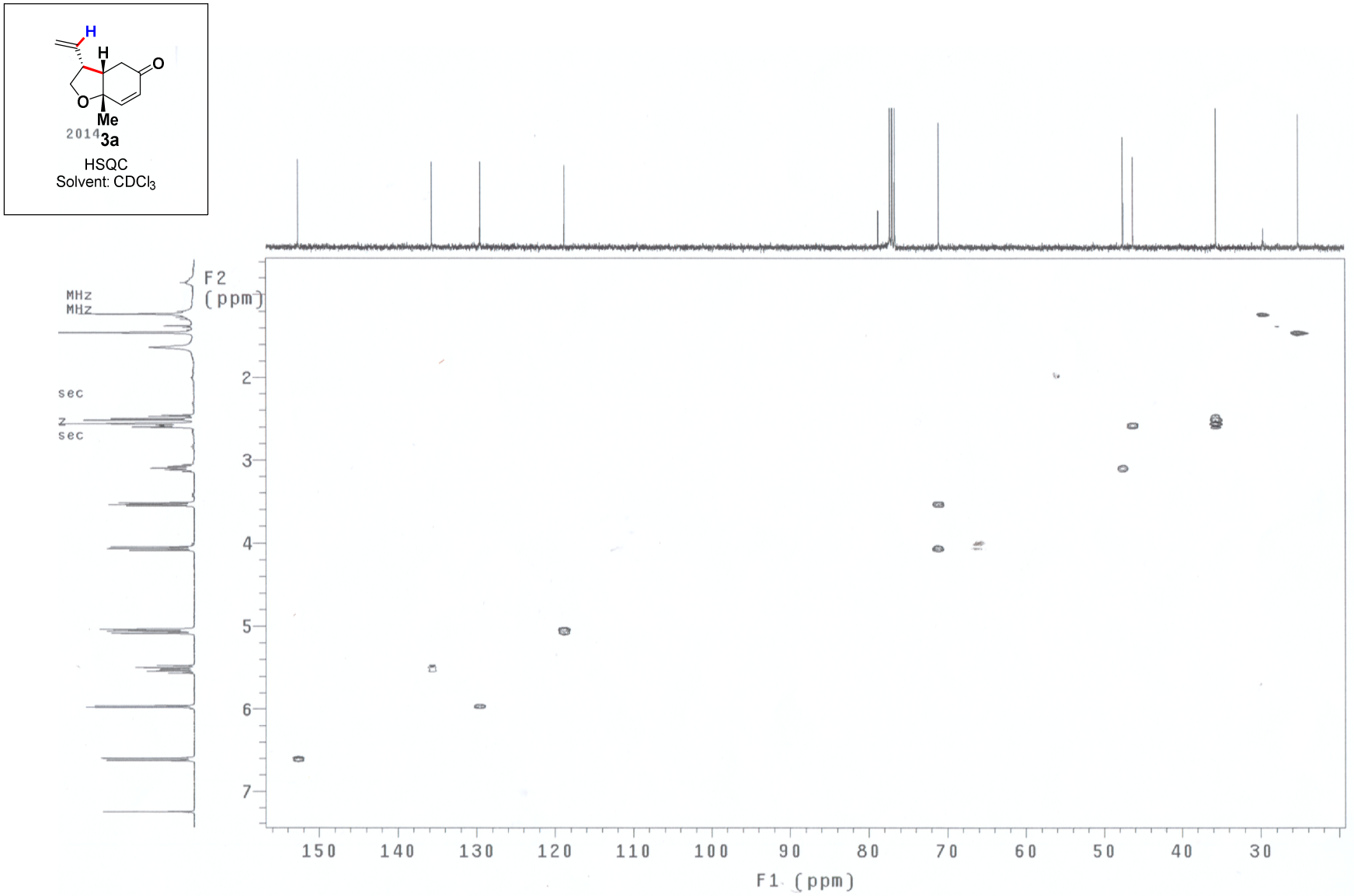


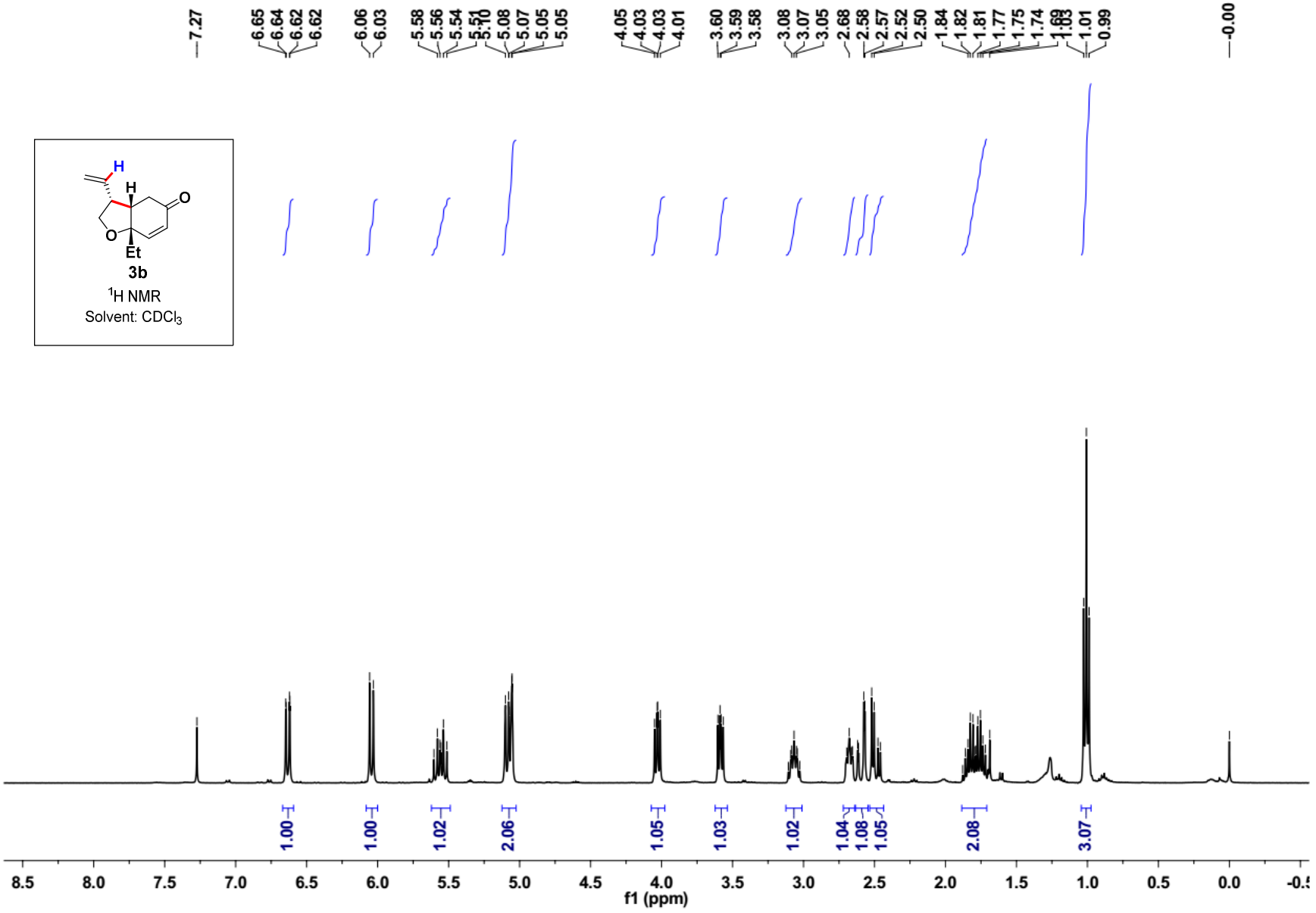
3a

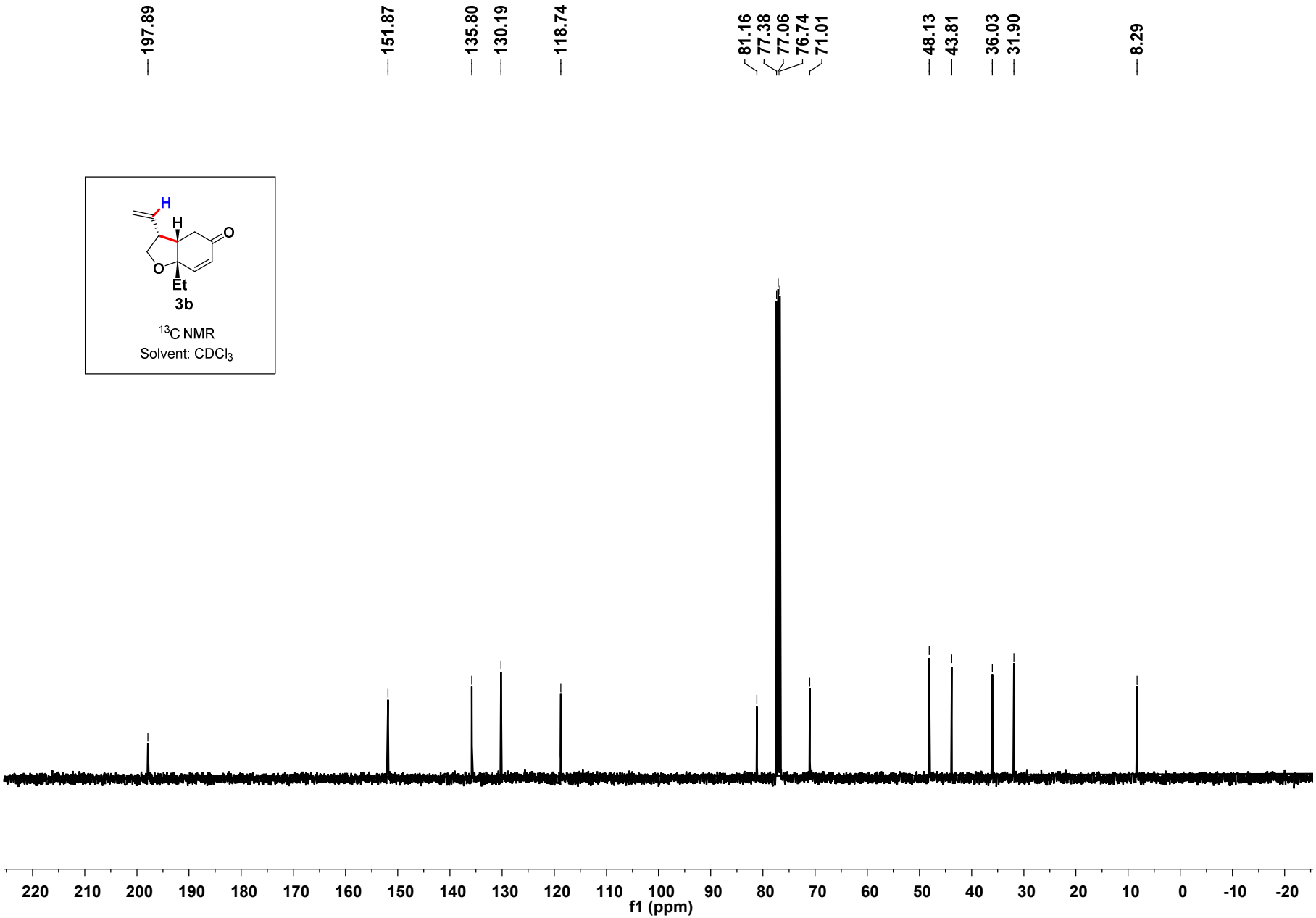
HMBC
Solvent: $CDCl_3$

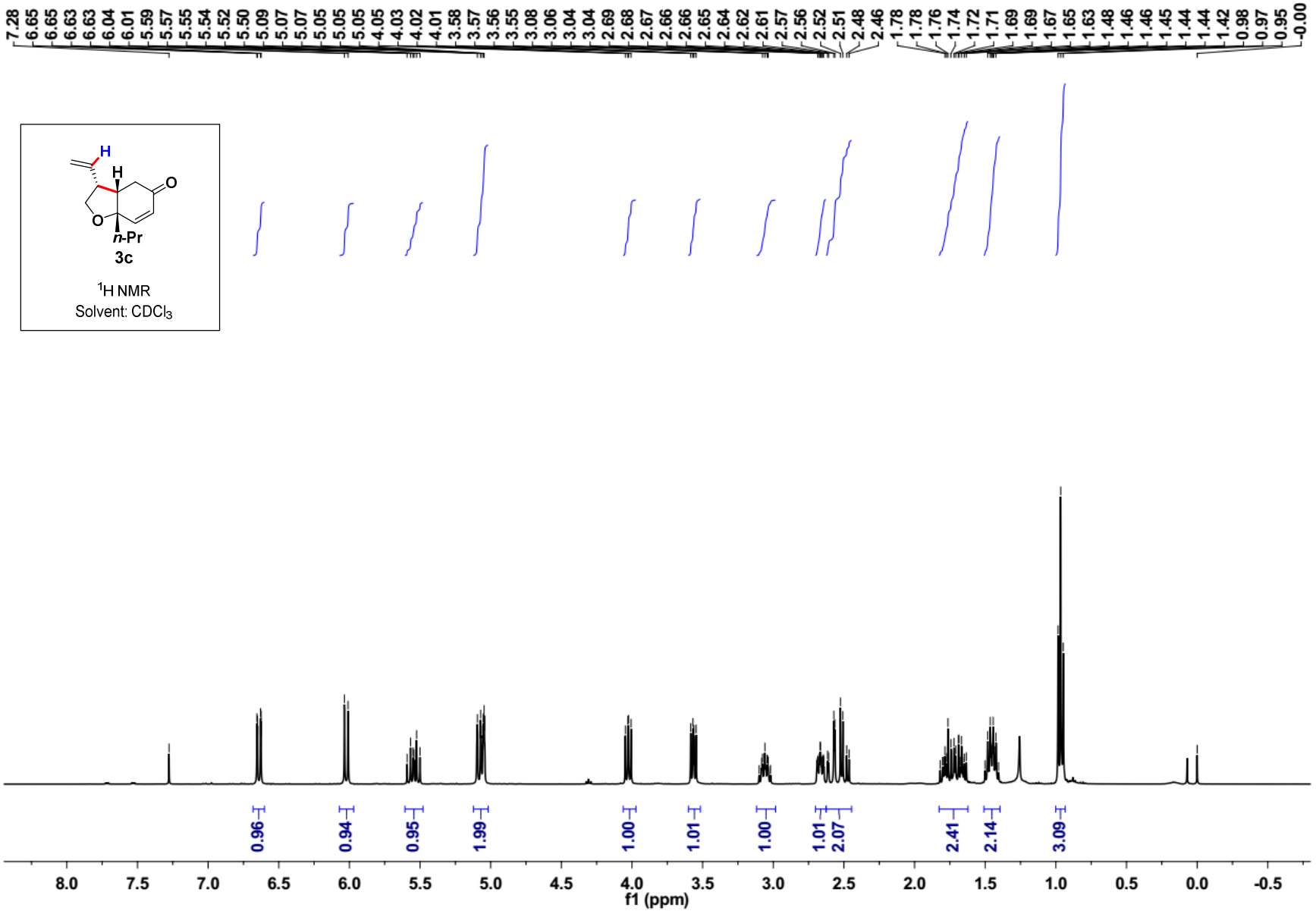


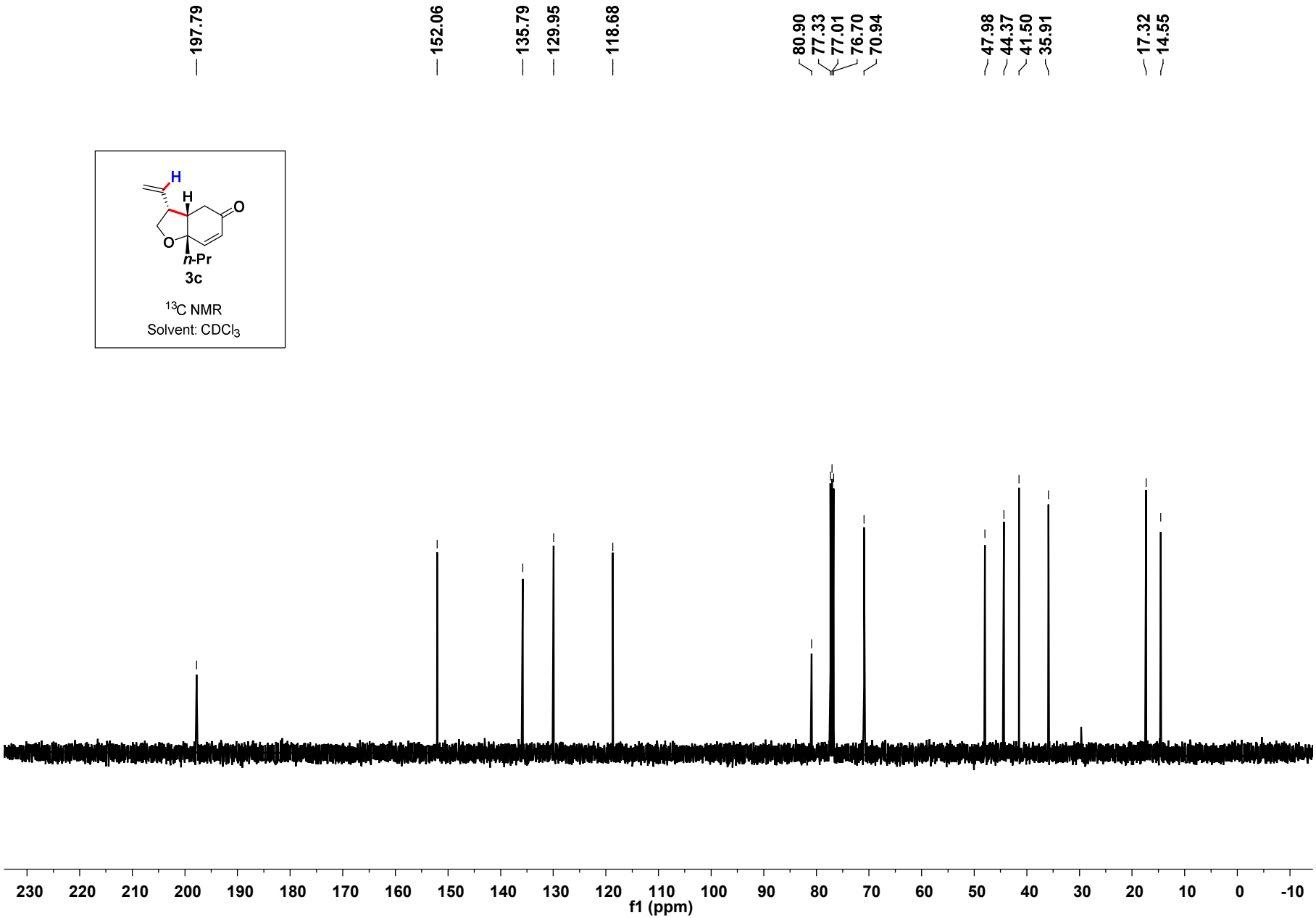

H
H
O
O
Me
3a
NOESY
Solvent: CDCl3
F1
(ppm)
1
2
3
4
5
6
7
7
6
5
4
3
2
1
F2 (ppm)


H
H
O
O
Me
2014
3a
HSQC
Solvent: CDCl3
MHz
MHz
sec
z
sec
F2
(ppm)
2
3
4
5
6
7
150
140
130
120
110
100
90
80
70
60
50
40
30
F1 (ppm)


7.27
6.65
6.64
6.62
6.62
6.06
6.03
5.58
5.56
5.54
5.51
5.10
5.08
5.07
5.05
5.05
4.05
4.03
4.03
4.01
3.60
3.59
3.58
3.08
3.07
3.05
2.68
2.58
2.57
2.52
2.50
1.84
1.82
1.81
1.77
1.75
1.74
1.01
0.99
0.00
H
H
O
O
Et
3b
1H NMR
Solvent: CDCl3
1.00
1.00
1.02
2.06
1.05
1.03
1.02
1.04
1.08
1.05
2.08
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.89
151.87
135.80
130.19
118.74
81.16
77.38
77.06
76.74
71.01
48.13
43.81
36.03
31.90
8.29
H
H
O
O
Et
3b
13C NMR
Solvent: CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.28 6.65 6.65 6.63 6.63 6.04 6.01 5.59 5.57 5.55 5.54 5.52 5.50 5.09 5.07 5.07 5.05 5.05 5.05 4.05 4.03 4.02 4.01 3.58 3.57 3.56 3.55 3.08 3.06 3.04 3.04 2.69 2.68 2.67 2.66 2.66 2.65 2.64 2.62 2.61 2.57 2.56 2.52 2.51 2.48 2.46 1.78 1.78 1.76 1.74 1.72 1.71 1.69 1.69 1.67 1.65 1.63 1.48 1.46 1.46 1.45 1.44 1.44 1.42 0.98 0.97 0.95 -0.00
H
H
O
O
n-Pr
3c
1H NMR
Solvent: CDCl3
0.96 0.94 0.95 1.99 1.00 1.01 1.00 1.01 2.07 2.41 2.14 3.09
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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152.06
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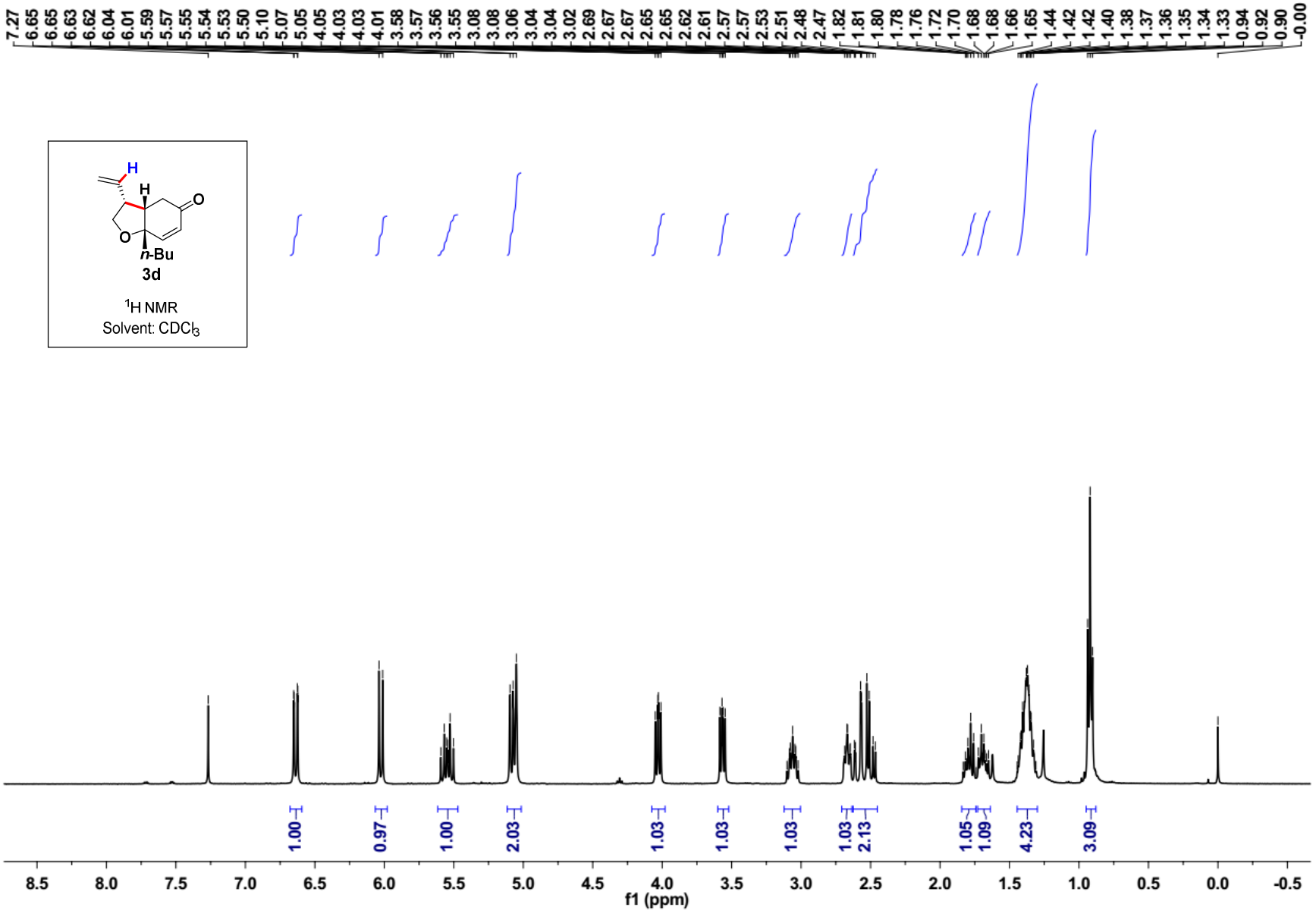
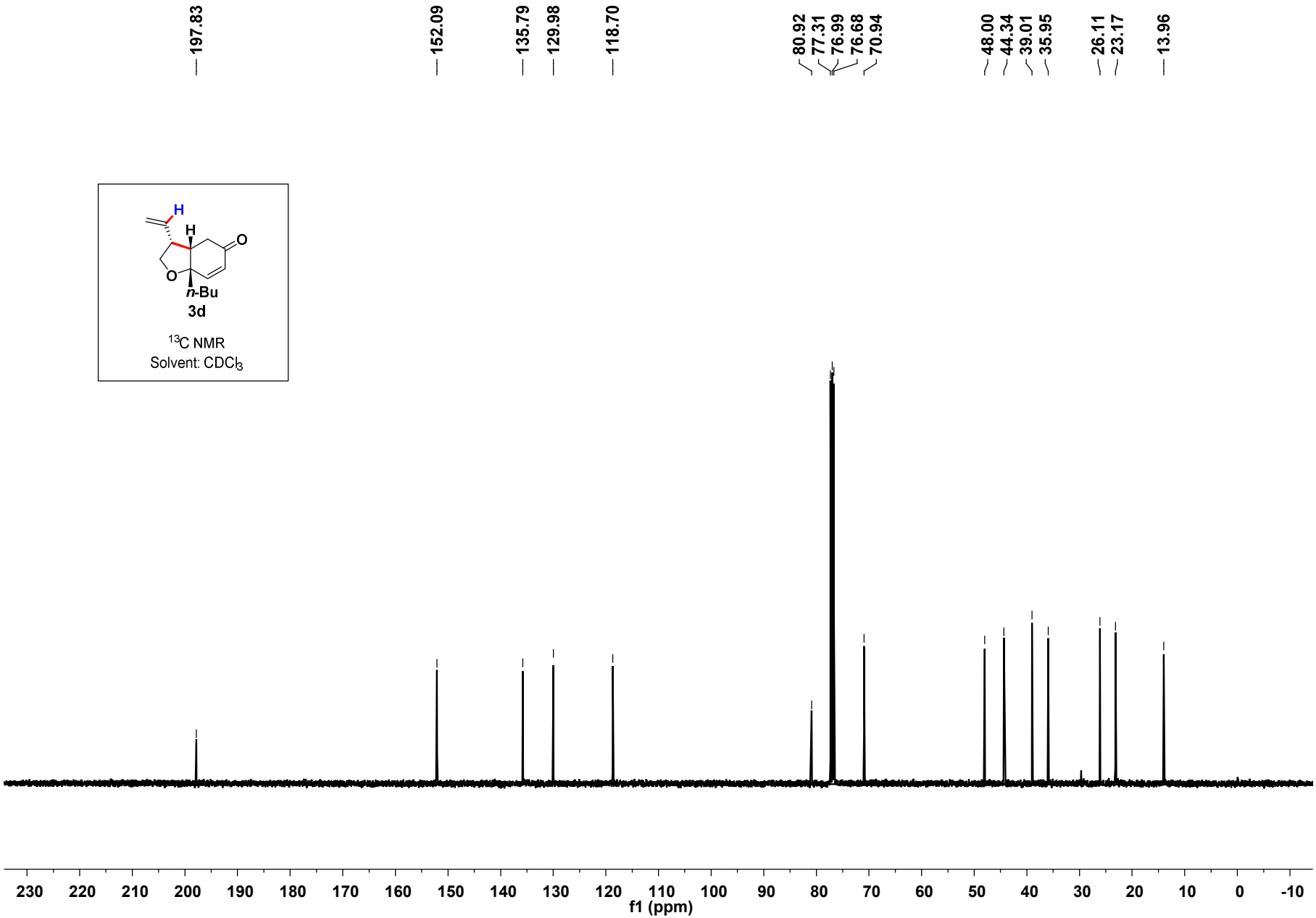
118.68
80.90
77.33
77.01
76.70
70.94
47.98
44.37
41.50
35.91
17.32
14.55
H
H
O
O
n-Pr
3c
13C NMR
Solvent: CDCl3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.27 6.65 6.65 6.63 6.62 6.04 6.01 5.59 5.57 5.55 5.54 5.53 5.50 5.10 5.07 5.05 4.05 4.03 4.03 4.01 3.58 3.57 3.56 3.55 3.08 3.08 3.06 3.04 3.04 3.02 2.69 2.67 2.67 2.65 2.65 2.62 2.61 2.57 2.57 2.53 2.51 2.48 2.47 1.82 1.81 1.80 1.78 1.76 1.72 1.70 1.68 1.68 1.66 1.65 1.44 1.42 1.42 1.40 1.38 1.37 1.36 1.35 1.34 1.33 0.94 0.92 0.90 -0.00
H
H
O
O
n-Bu
3d
1H NMR
Solvent: CDCl3
1.00 0.97 1.00 2.03 1.03 1.03 1.03 1.03 2.13 1.05 1.09 4.23 3.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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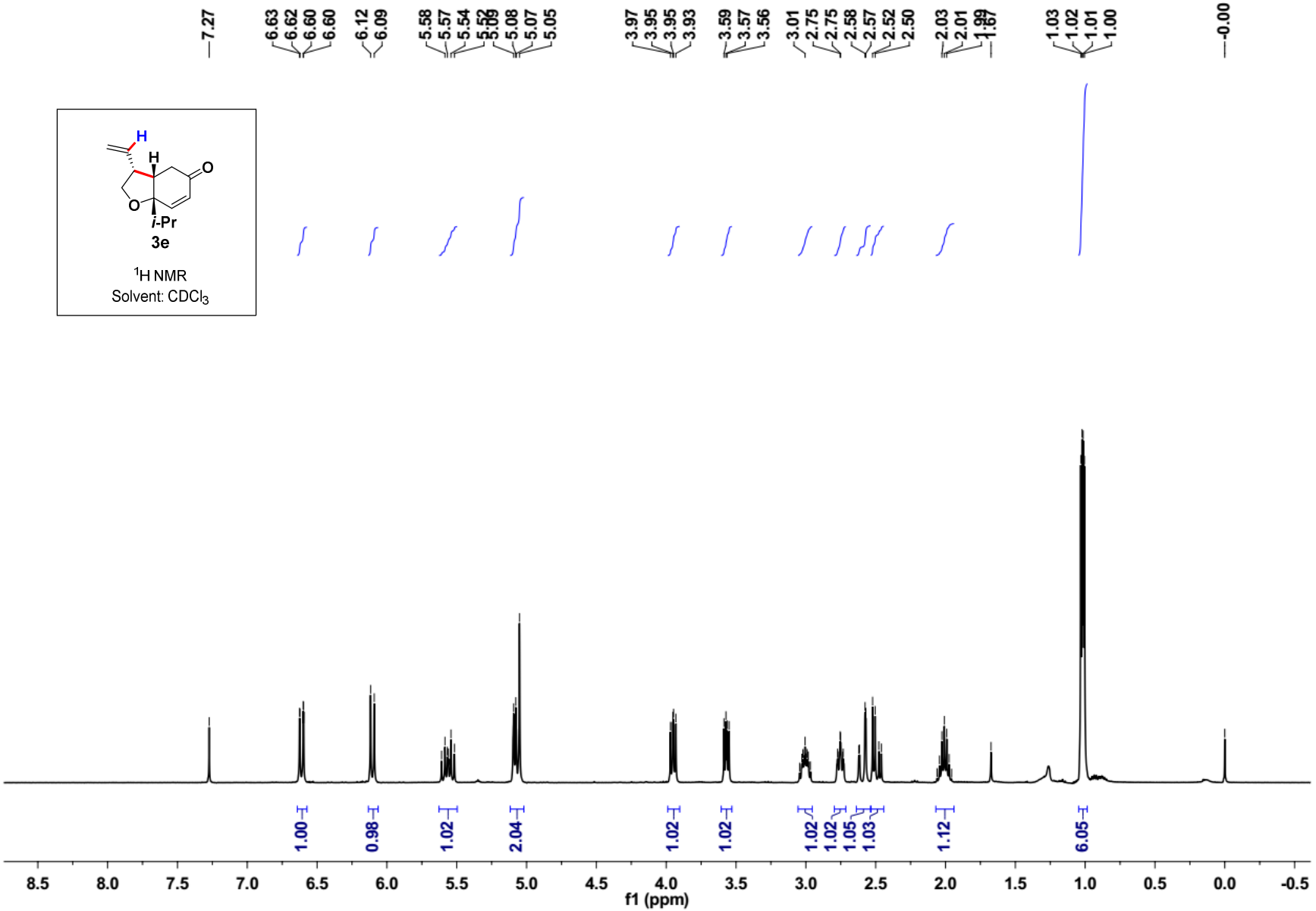
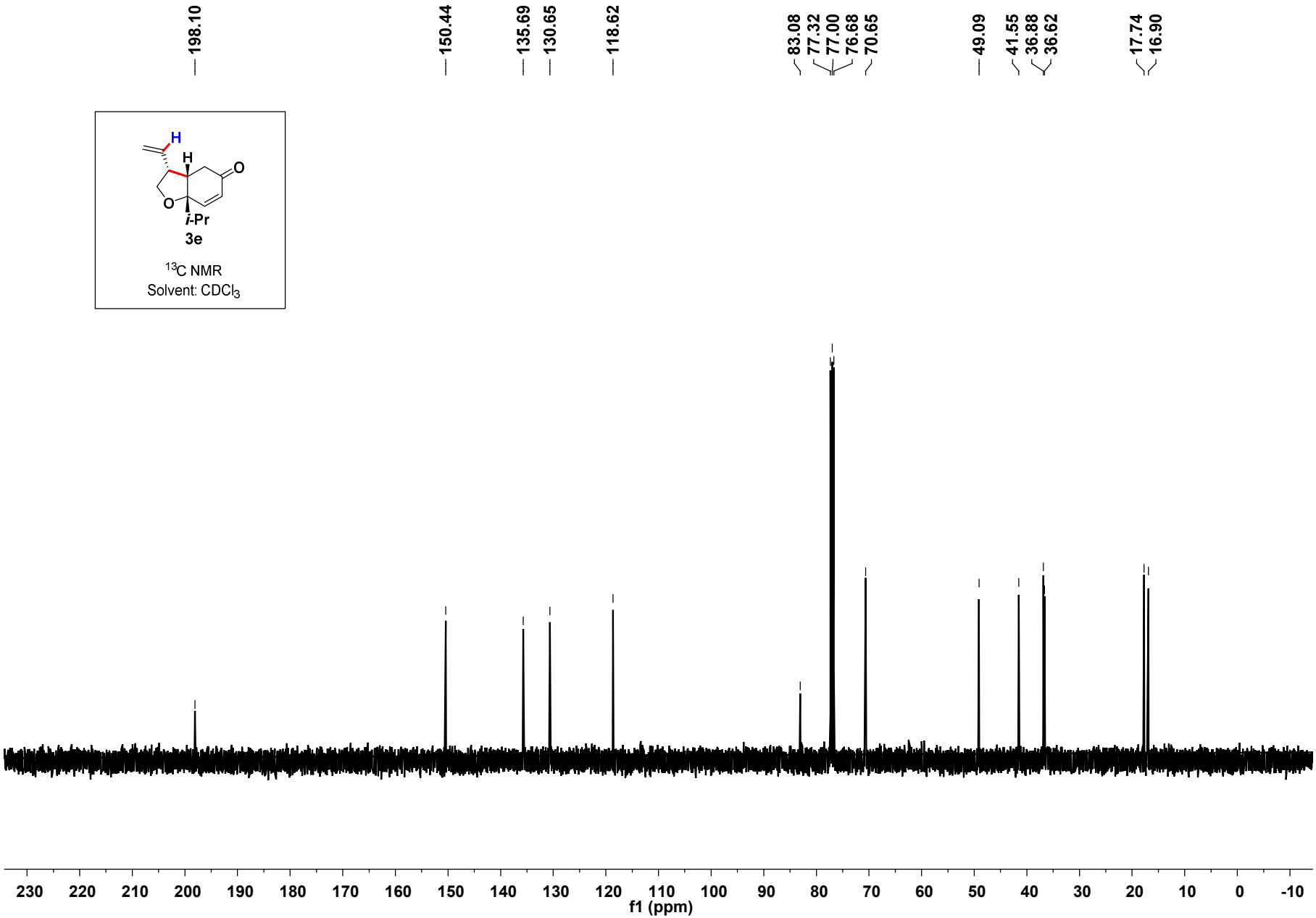
152.09
135.79
129.98
118.70
80.92
77.31
76.99
76.68
70.94
48.00
44.34
39.01
35.95
26.11
23.17
13.96
H
H
O
O
n-Bu
3d
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.27
6.63
6.62
6.60
6.60
6.12
6.09
5.58
5.57
5.54
5.08
5.07
5.05
3.97
3.95
3.95
3.93
3.59
3.57
3.56
3.01
2.75
2.75
2.58
2.57
2.52
2.50
2.03
2.01
1.03
1.02
1.01
1.00
-0.00
H
H
O
O
i-Pr
3e
1H NMR
Solvent: CDCl3
1.00
0.98
1.02
2.04
1.02
1.02
1.02
1.05
1.03
1.12
6.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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77.32
77.00
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70.65
49.09
41.55
36.88
36.62
17.74
16.90
H
H
O
O
i-Pr
3e
13C NMR
Solvent: CDCl3
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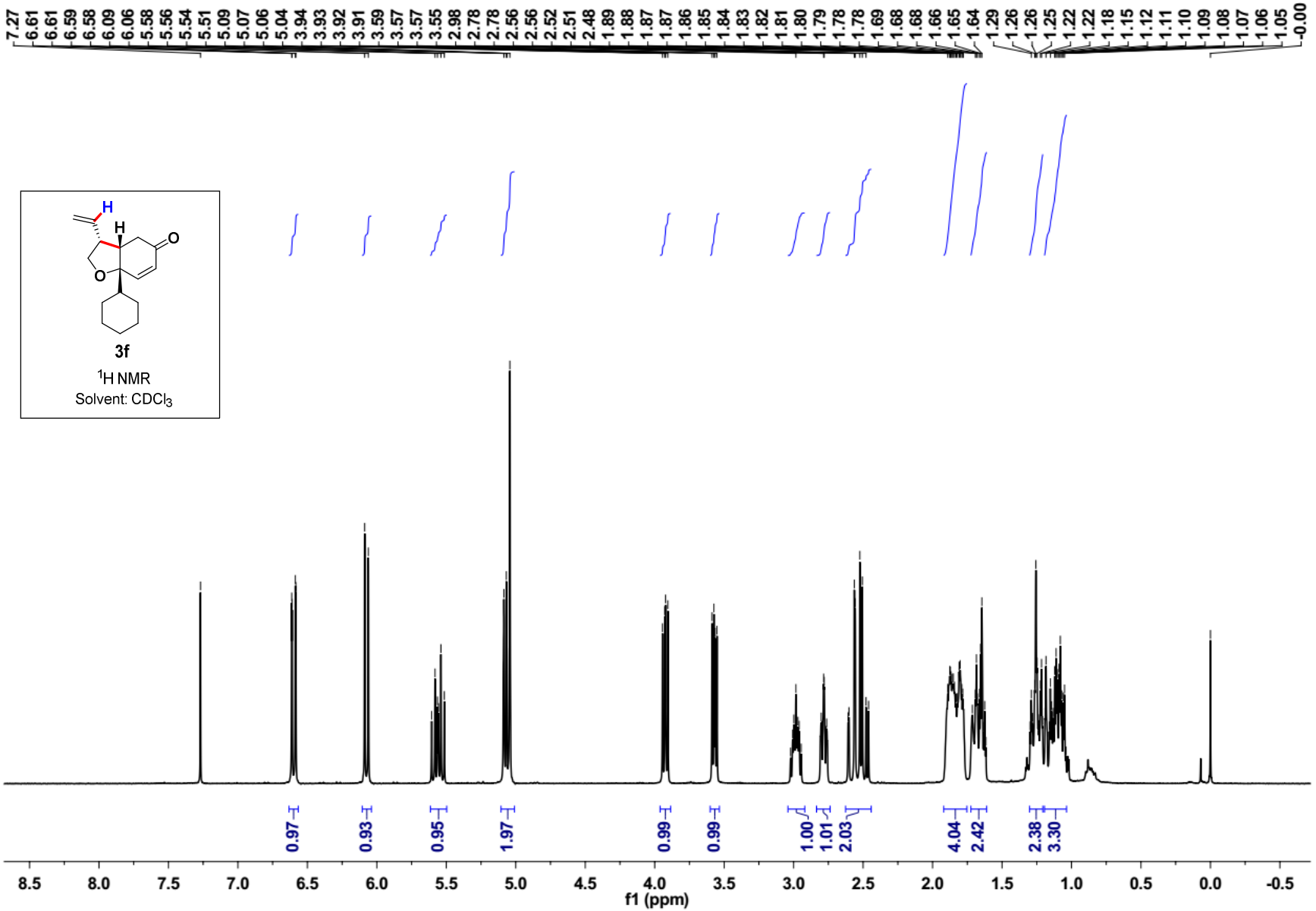
f1 (ppm)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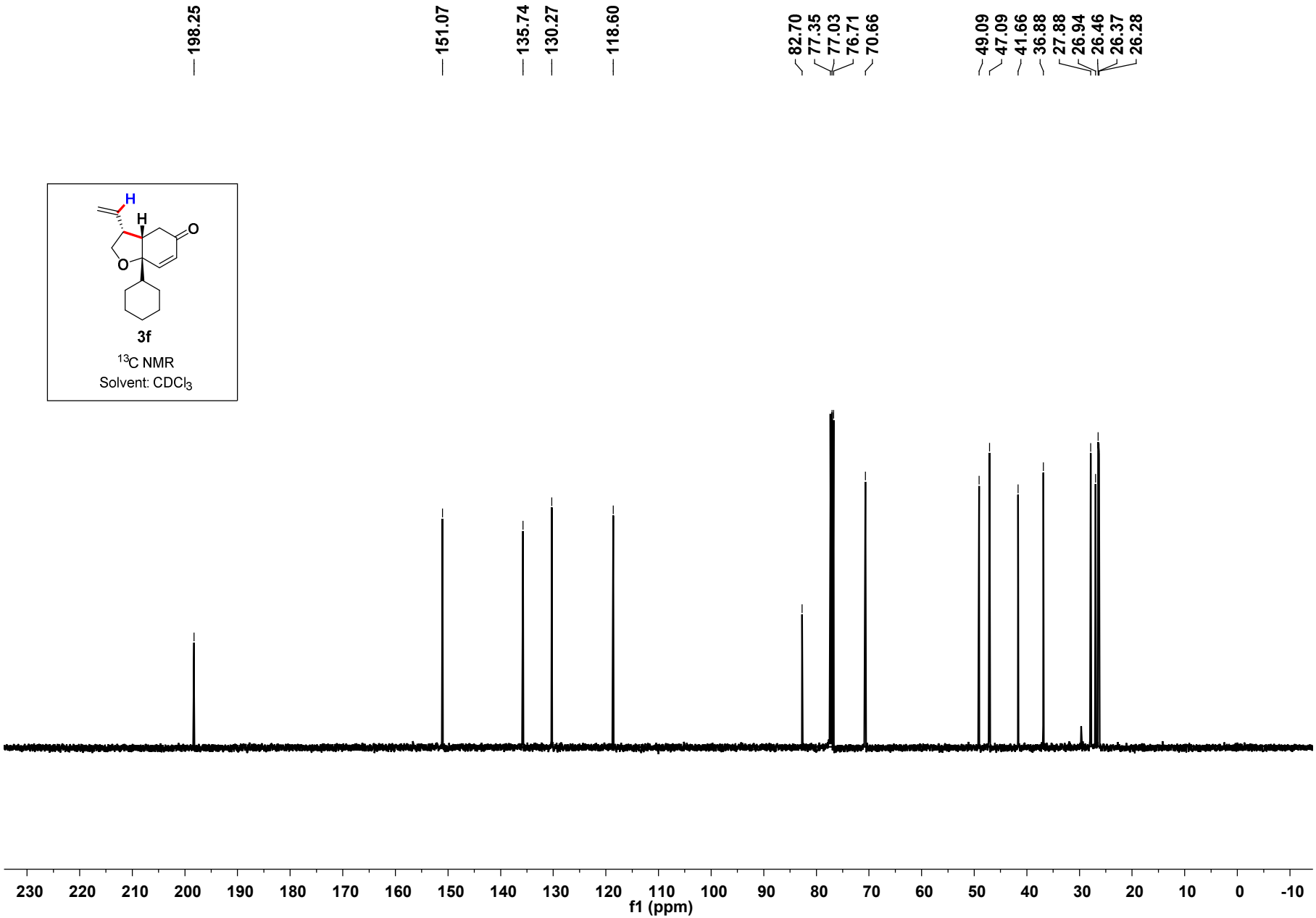
H
H
O
O
3f
1H NMR
Solvent: CDCl3
0.97 0.93 0.95 1.97 0.99 0.99 1.00 1.01 2.03 4.04 2.42 2.38 3.30
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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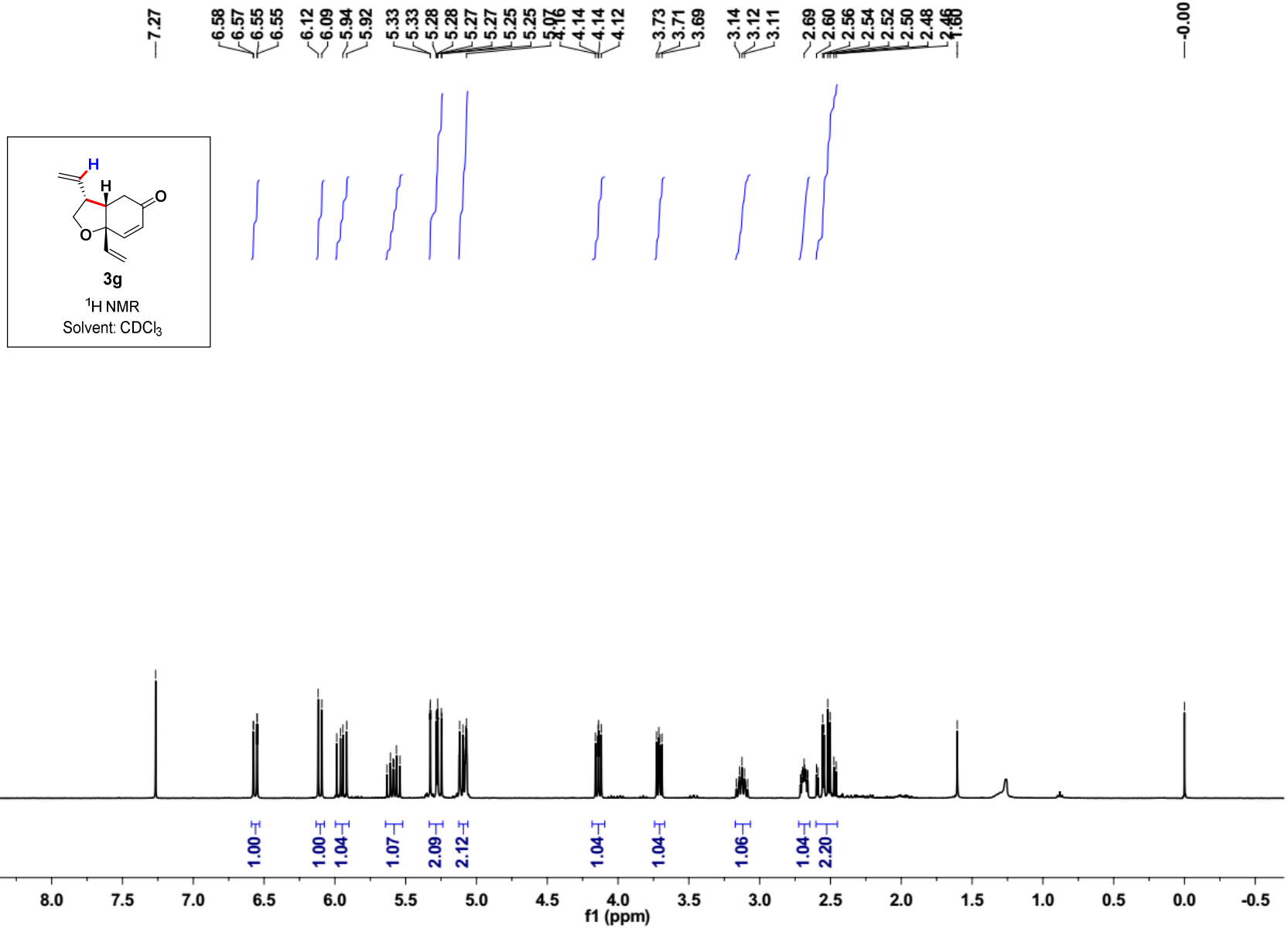
41.66
36.88
27.88
26.94
26.46
26.37
26.28
H
H
O
O
3f
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.58
6.57
6.55
6.55
6.12
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5.94
5.92
5.33
5.33
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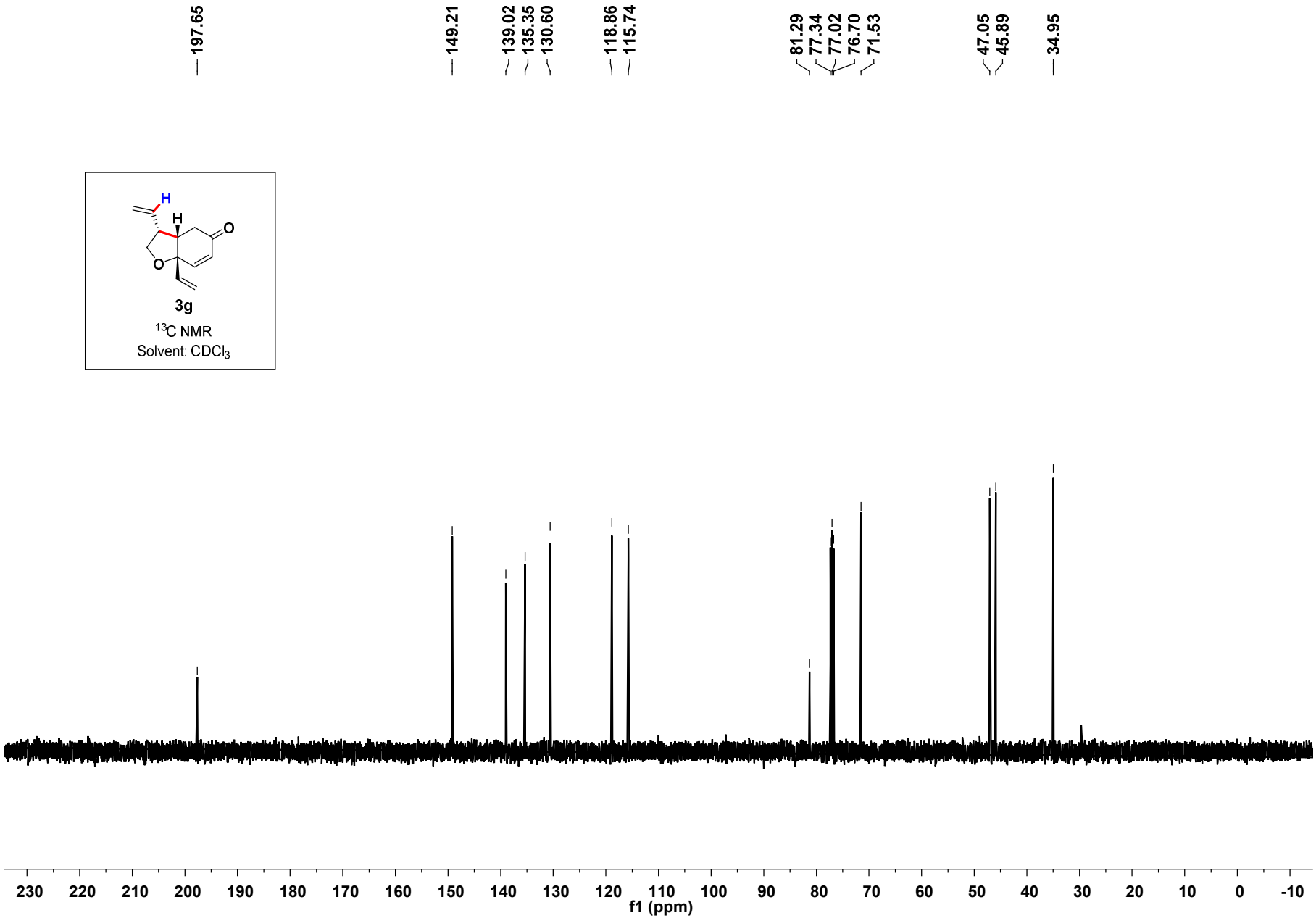
5.28
5.27
5.27
5.25
5.25
5.07
4.16
4.14
4.14
4.12
3.73
3.71
3.69
3.14
3.12
3.11
2.69
2.60
2.56
2.54
2.52
2.50
2.48
2.46
1.60
0.00
H
H
O
O
3g
1H NMR
Solvent: CDCl3
1.00
1.00
1.04
1.07
2.09
2.12
1.04
1.04
1.06
1.04
2.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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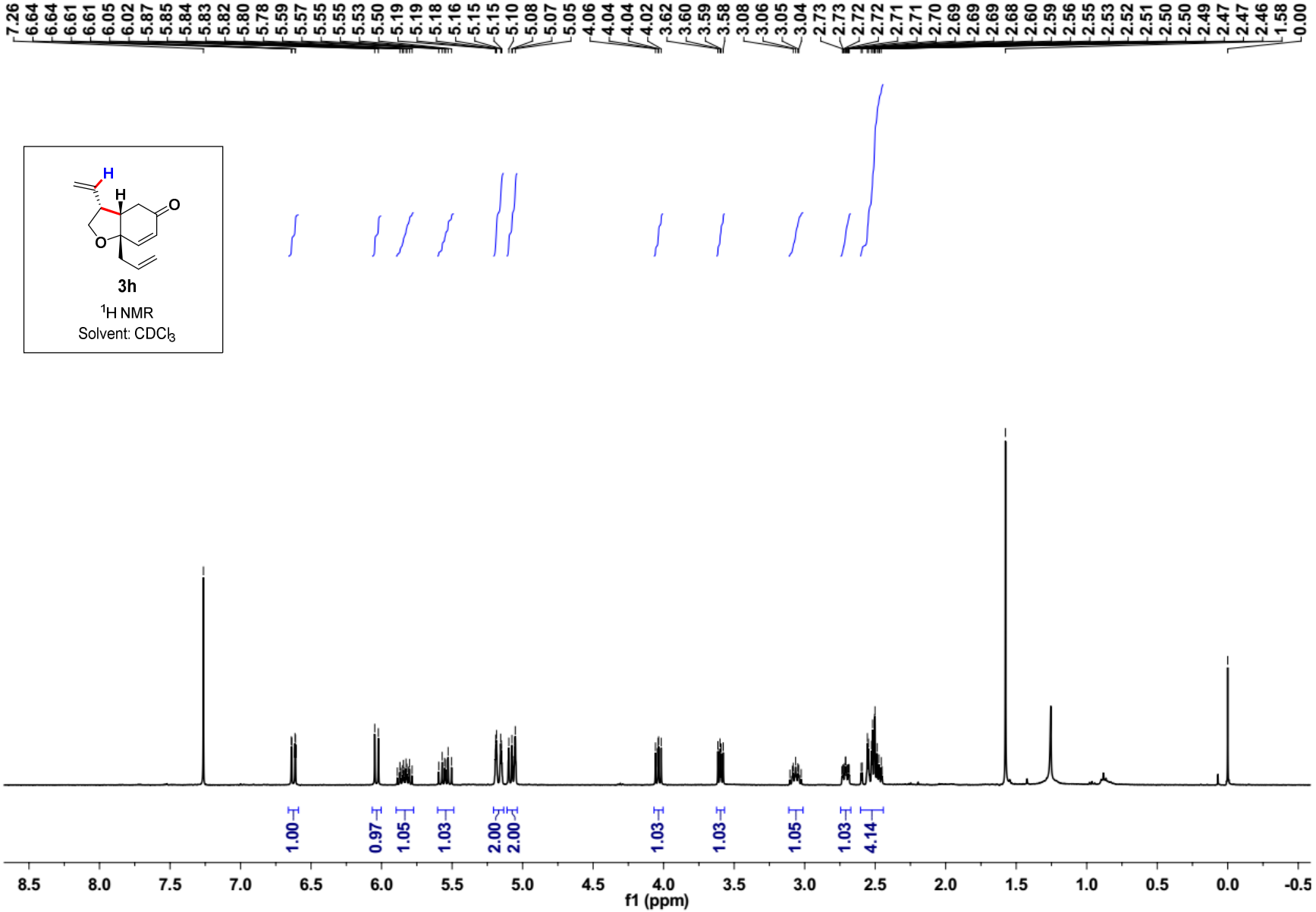
76.70
71.53
47.05
45.89
34.95
H
H
O
O
3g
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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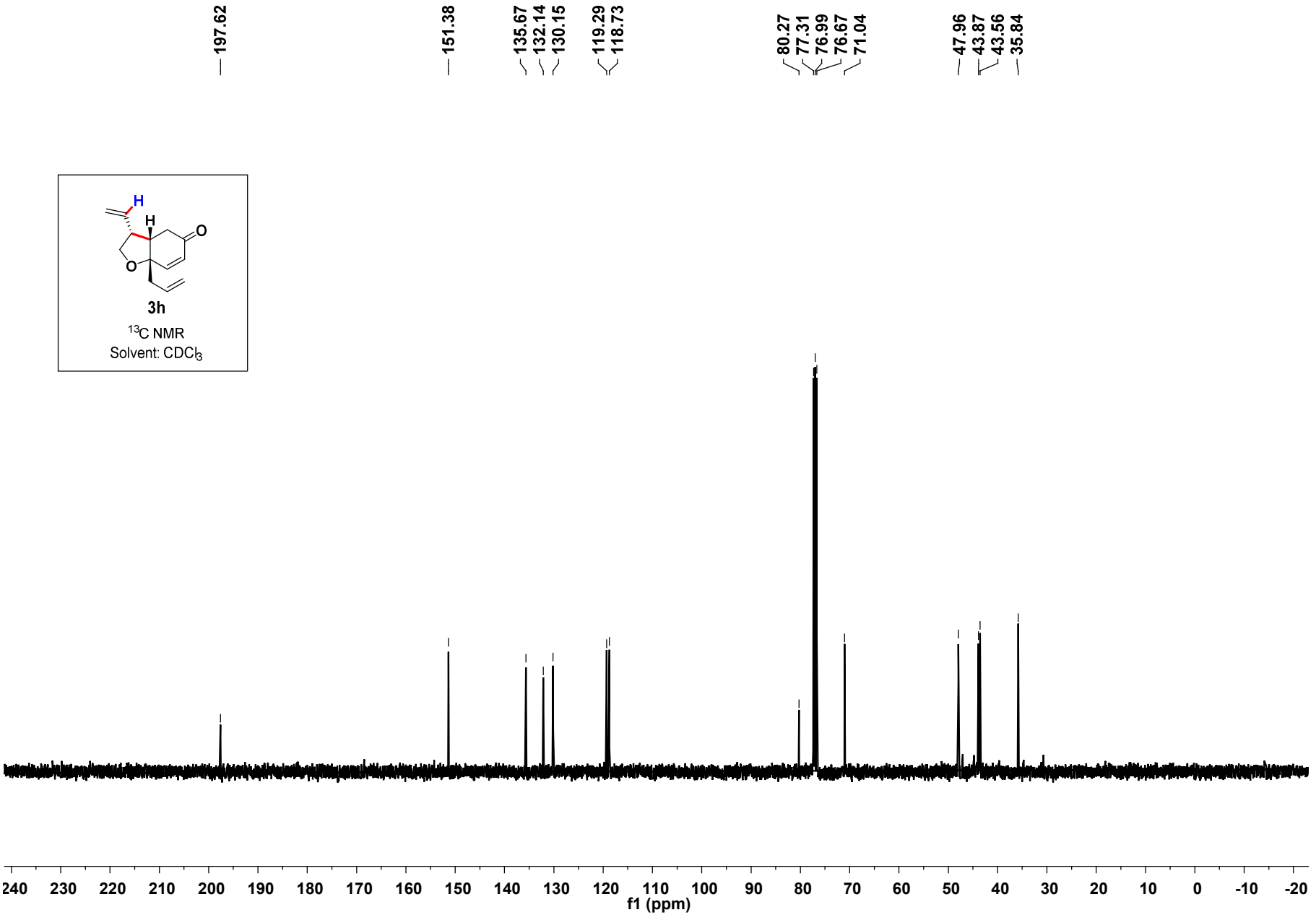
H
H
O
O
3h
1H NMR
Solvent: CDCl3
1.00 0.97 1.05 1.03 2.00 2.00 1.03 1.03 1.05 1.03 4.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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119.29
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80.27
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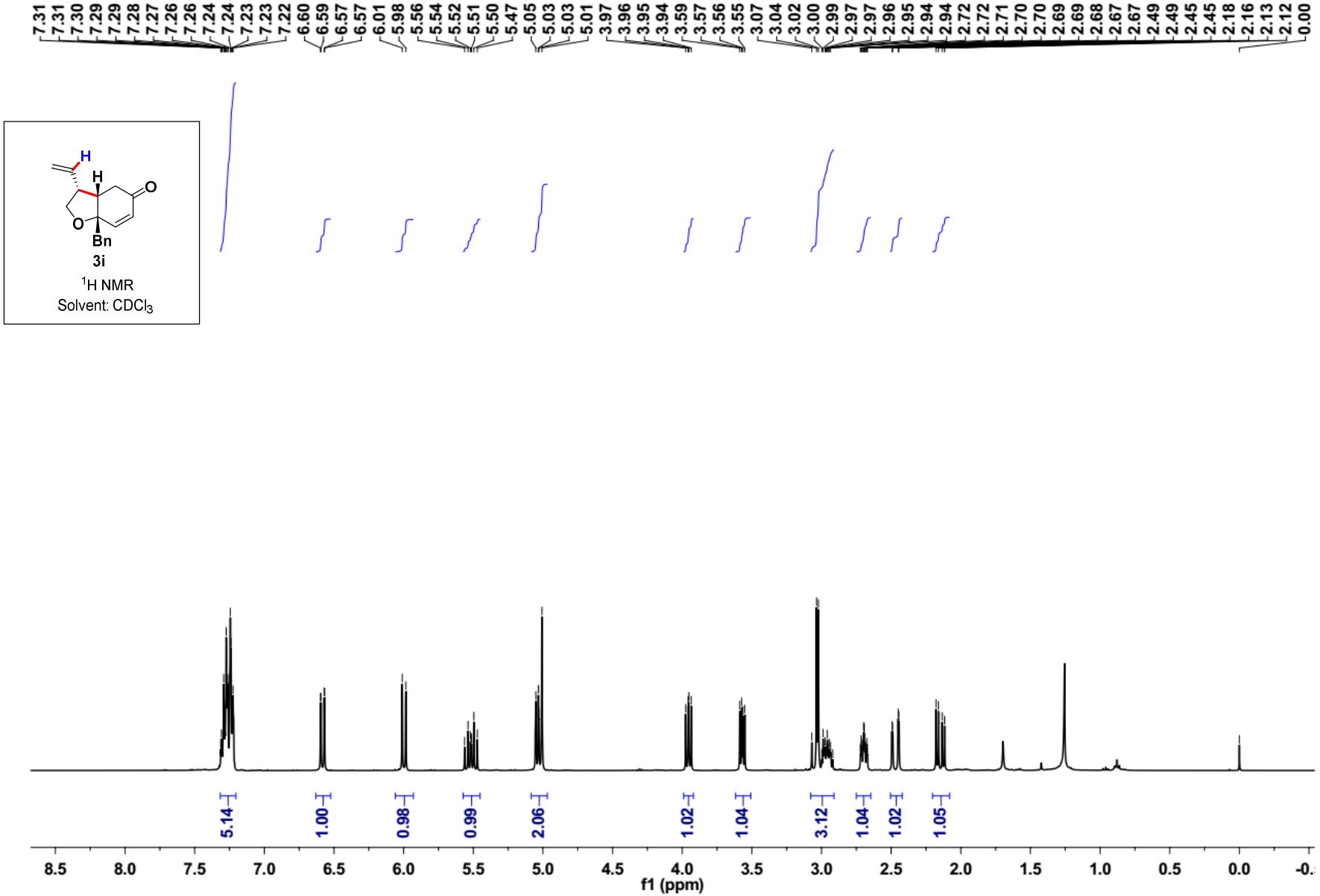
76.99
76.67
71.04
47.96
43.87
43.56
35.84
H
H
O
O
3h
13C NMR
Solvent: CDCl3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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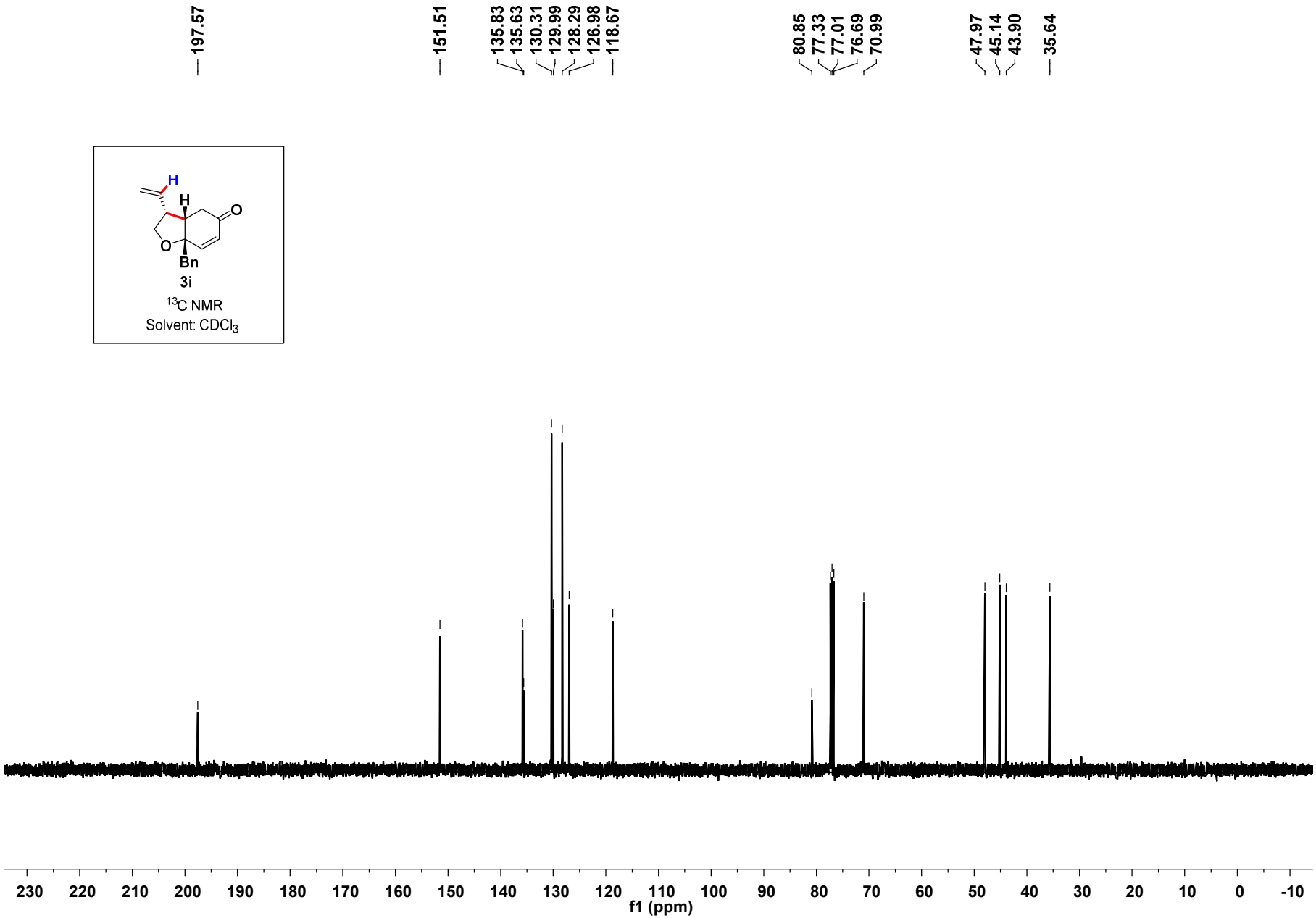
H
H
O
O
Bn
3i
1H NMR
Solvent: CDCl3
5.14
1.00
0.98
0.99
2.06
1.02
1.04
3.12
1.04
1.02
1.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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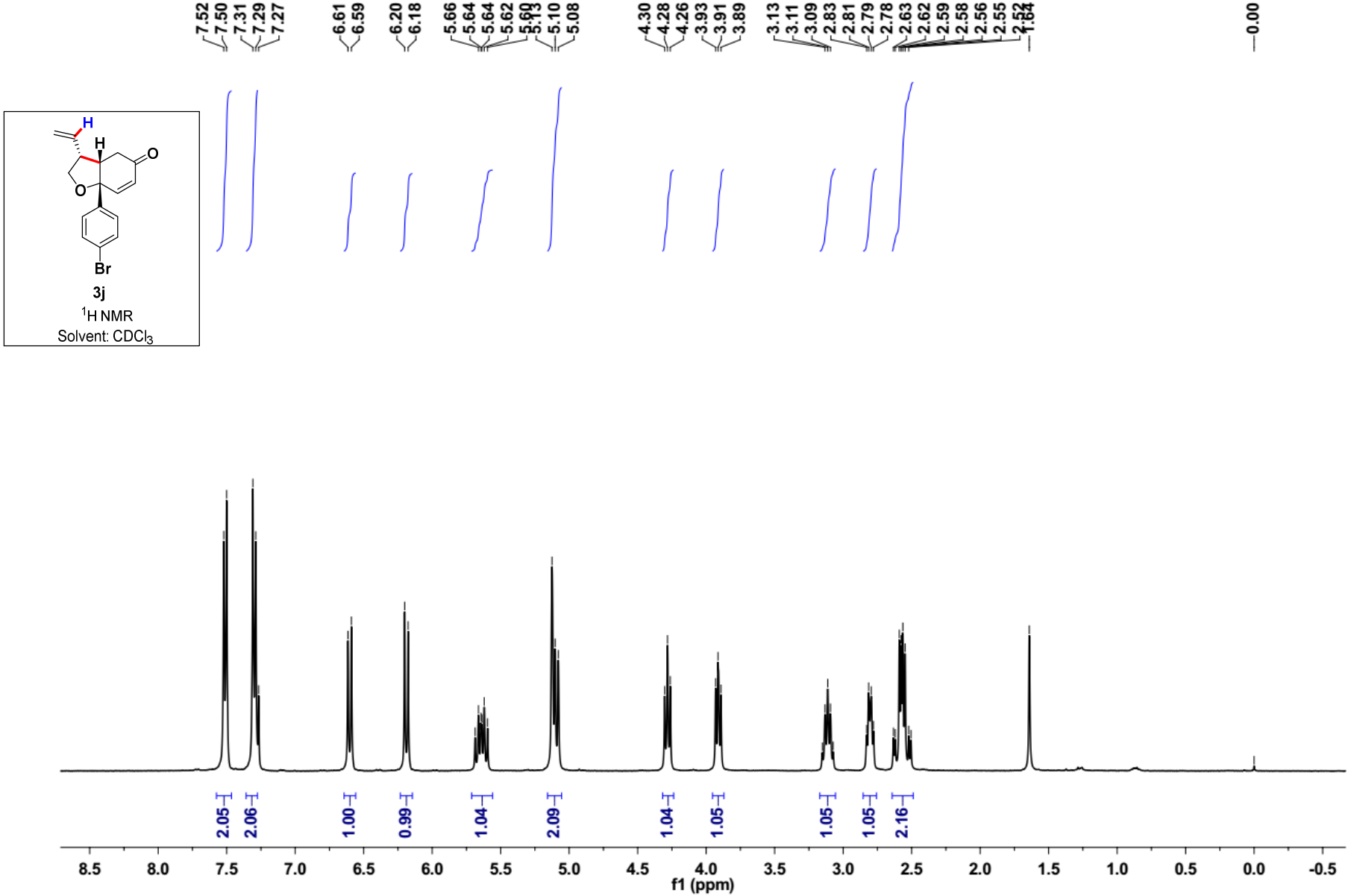
126.98
118.67
80.85
77.33
77.01
76.69
70.99
47.97
45.14
43.90
35.64
H
H
O
O
Bn
3i
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.31
7.29
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6.61
6.59
6.20
6.18
5.66
5.64
5.64
5.62
5.10
5.08
4.30
4.28
4.26
3.93
3.91
3.89
3.13
3.11
3.09
2.83
2.81
2.79
2.78
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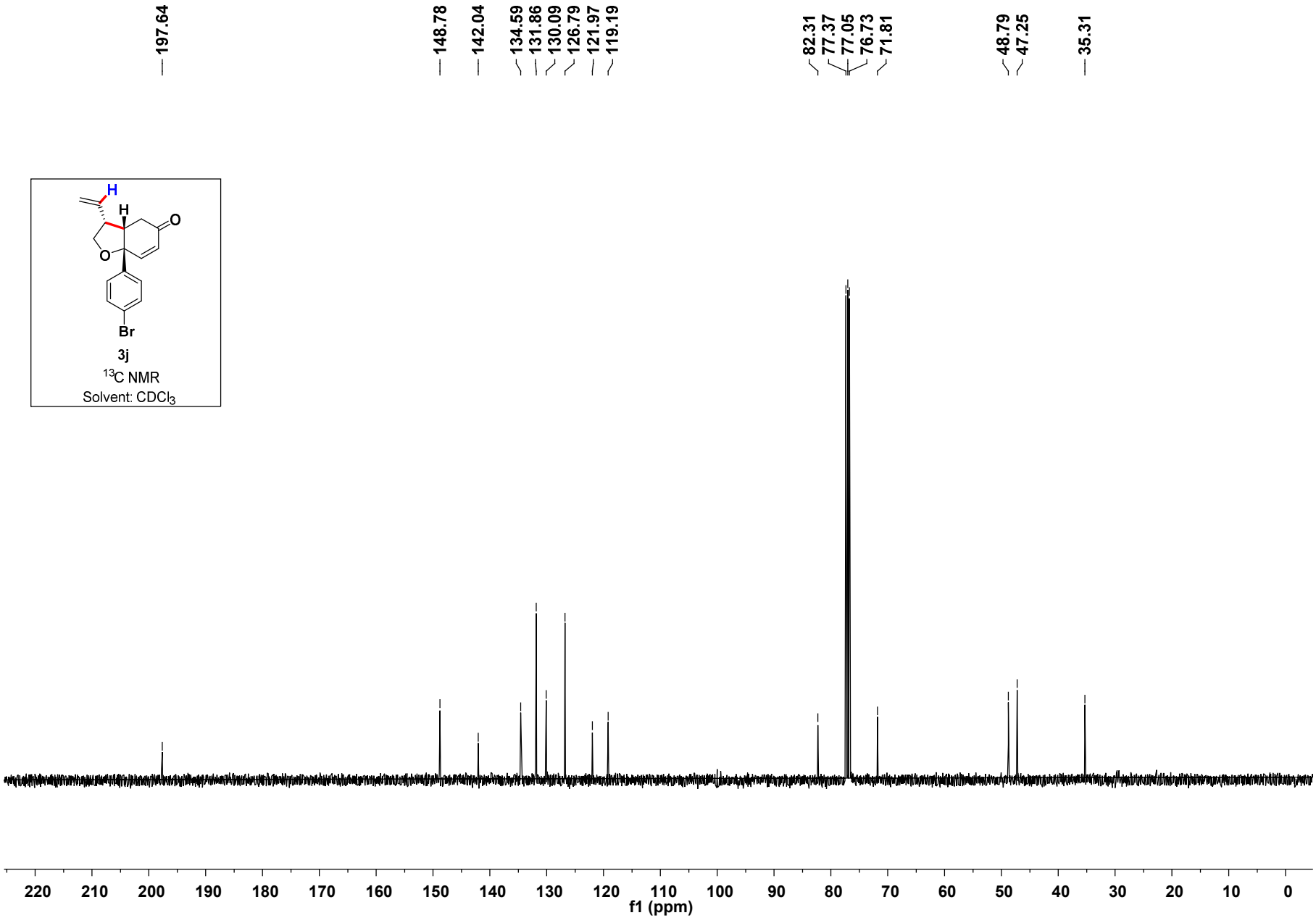
2.62
2.59
2.58
2.56
2.55
0.00
H
H
O
O
Br
3j
1H NMR
Solvent: CDCl3
2.05
2.06
1.00
0.99
1.04
2.09
1.04
1.05
1.05
1.05
2.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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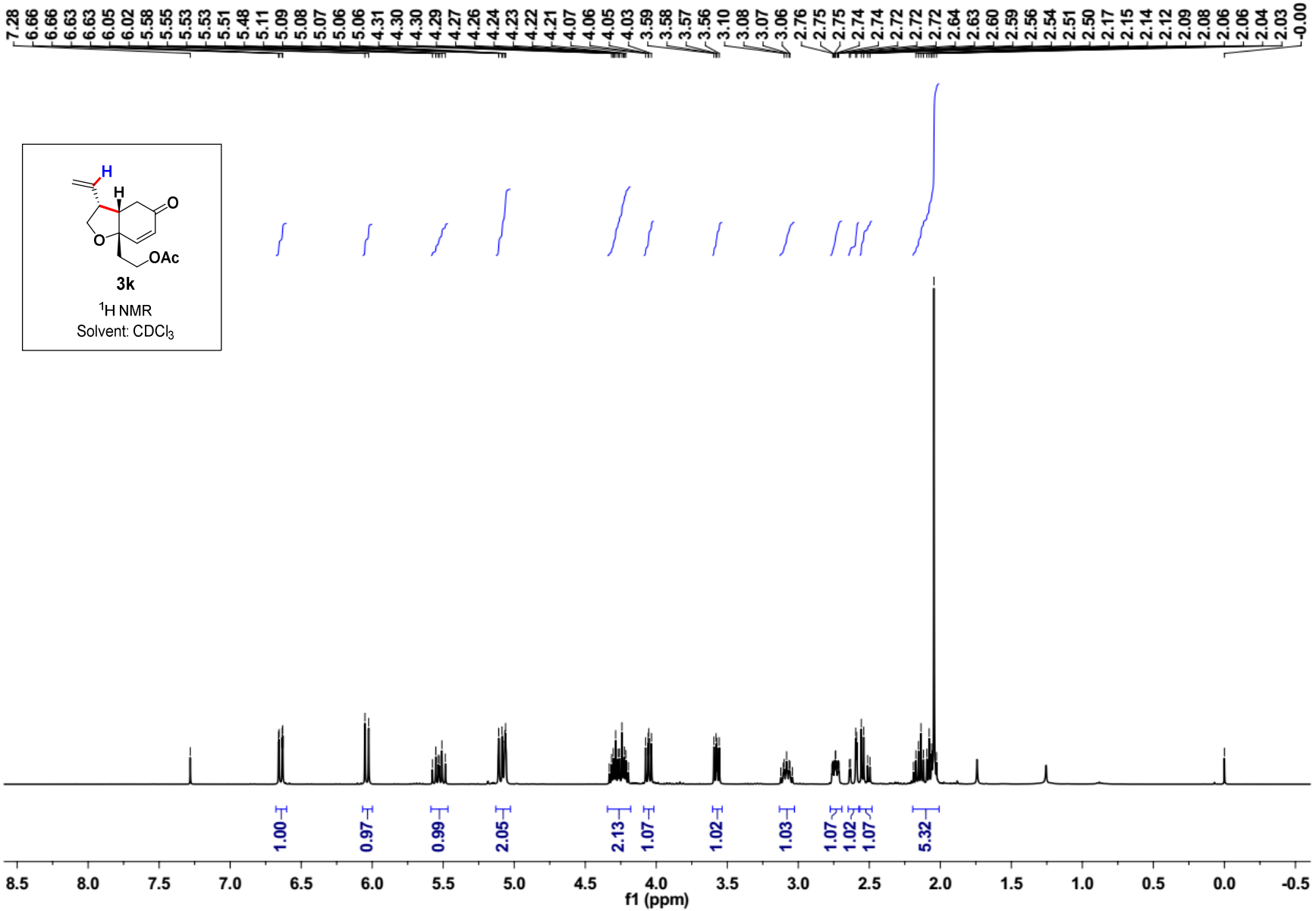
130.09
126.79
121.97
119.19
82.31
77.37
77.05
76.73
71.81
48.79
47.25
35.31
H
H
O
O
Br
3j
13C NMR
Solvent: CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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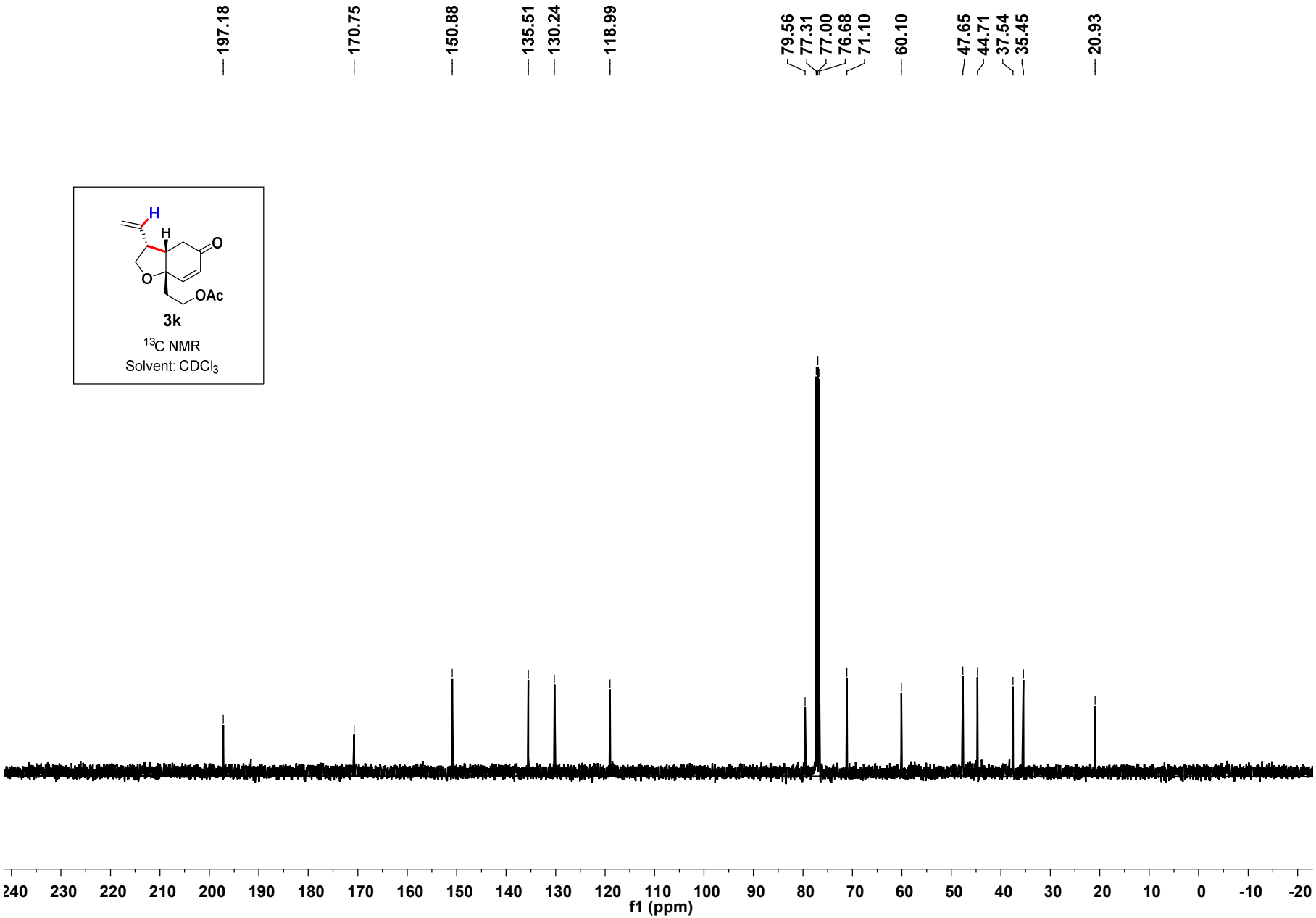
H
H
O
O
OAc
3k
1H NMR
Solvent: CDCl3
1.00 0.97 0.99 2.05 2.13 1.07 1.02 1.03 1.07 1.02 1.07 5.32
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.31
77.00
76.68
71.10
60.10
47.65
44.71
37.54
35.45
20.93
H
H
O
O
OAc
3k
13C NMR
Solvent: CDCl3
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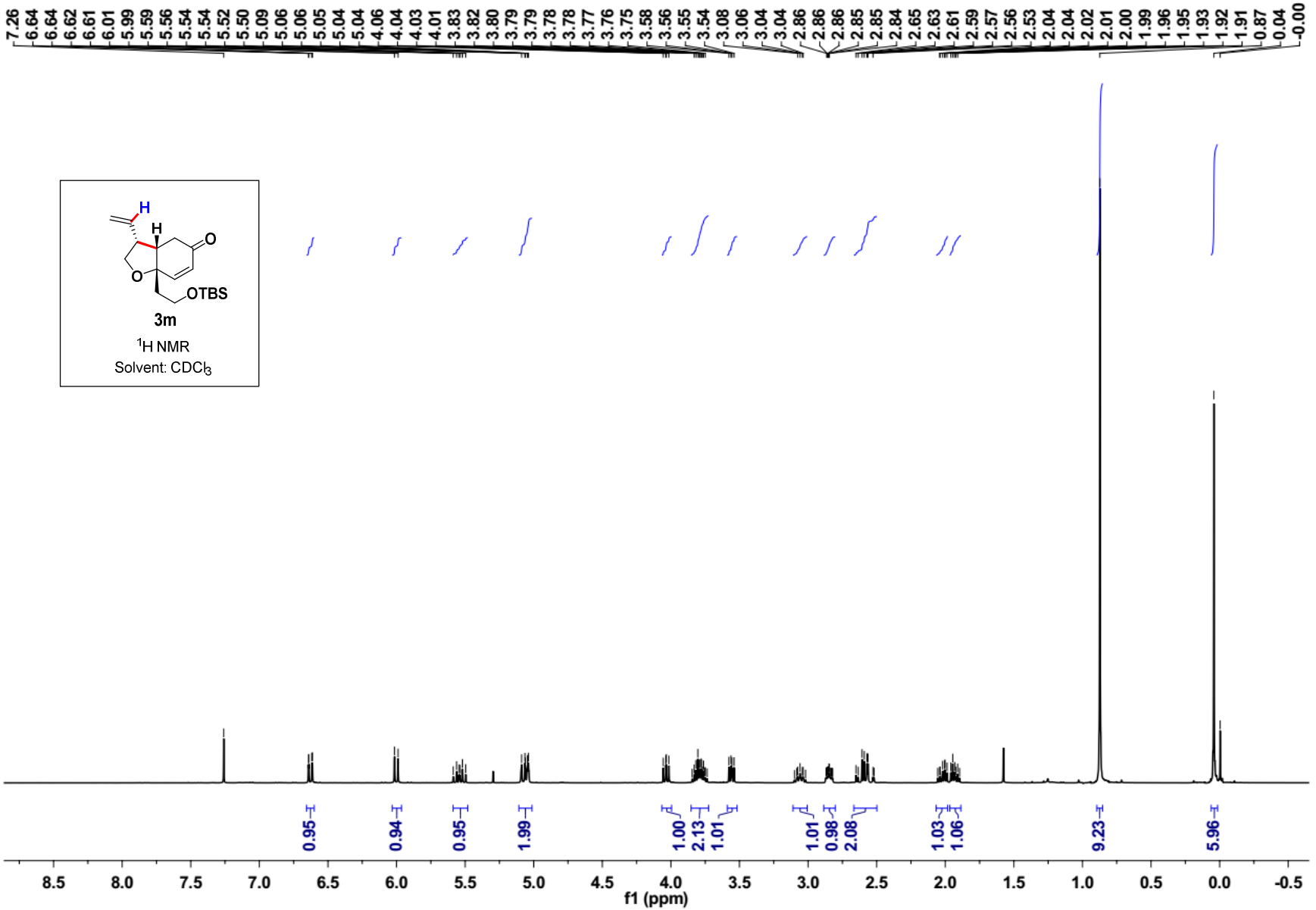
f1 (ppm)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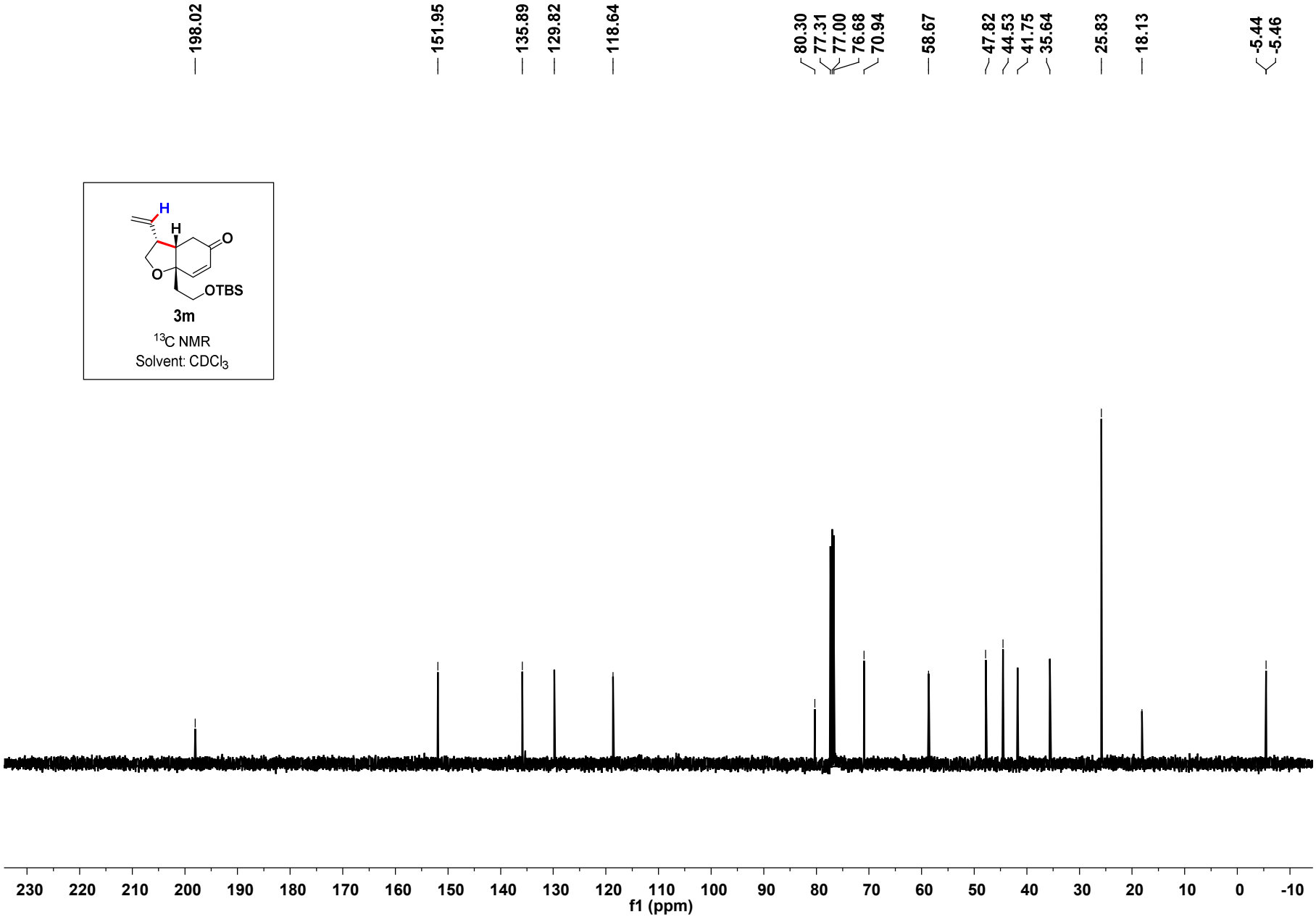
H
H
O
O
OTBS
3m
1H NMR
Solvent: CDCl3
0.95 0.94 0.95 1.99 1.00 2.13 1.01 1.01 0.98 2.08 1.03 1.06 9.23 5.96
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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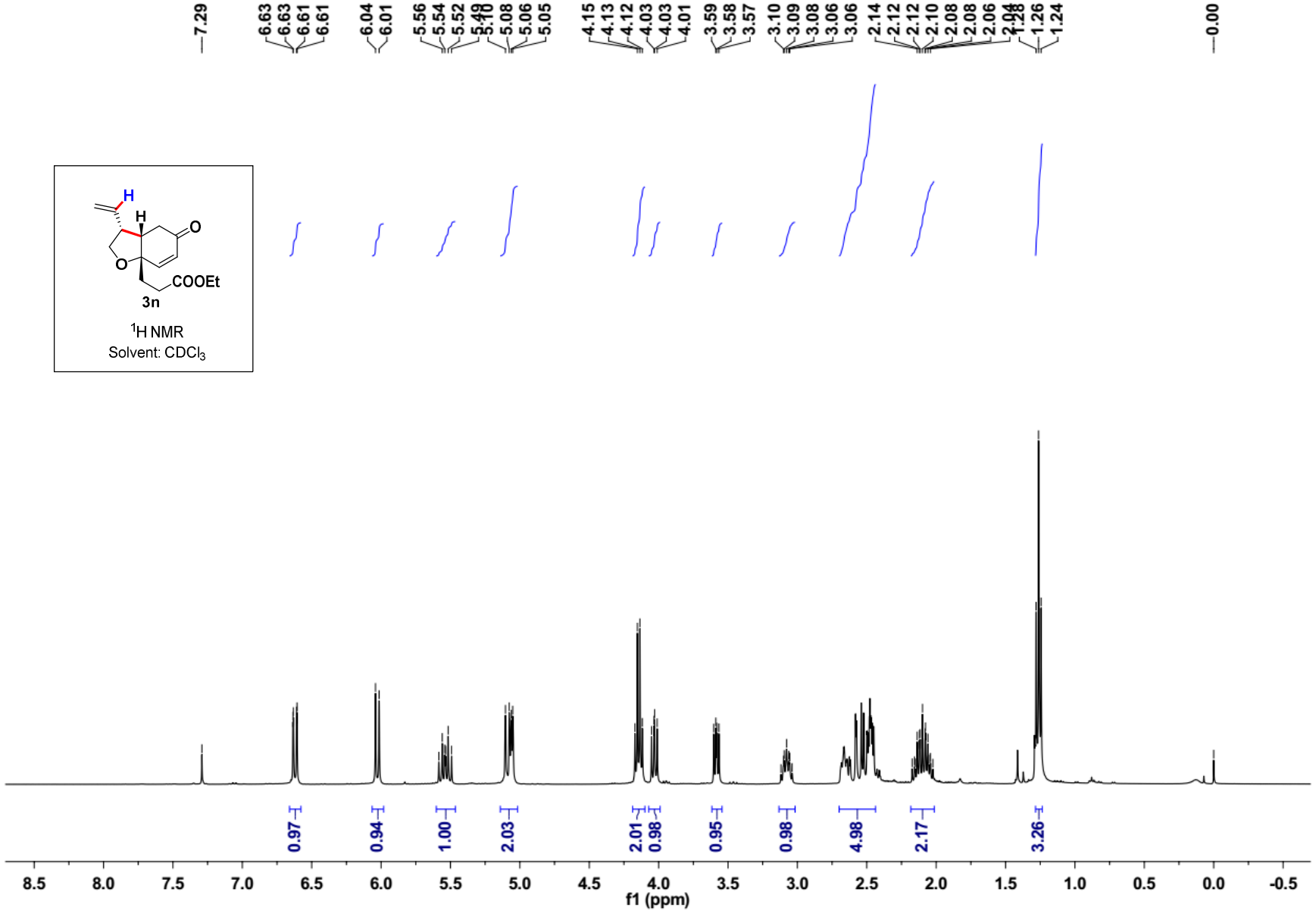
77.00
76.68
70.94
58.67
47.82
44.53
41.75
35.64
25.83
18.13
-5.44
-5.46
H
H
O
O
OTBS
3m
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.61
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6.04
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5.56
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5.52
5.08
5.06
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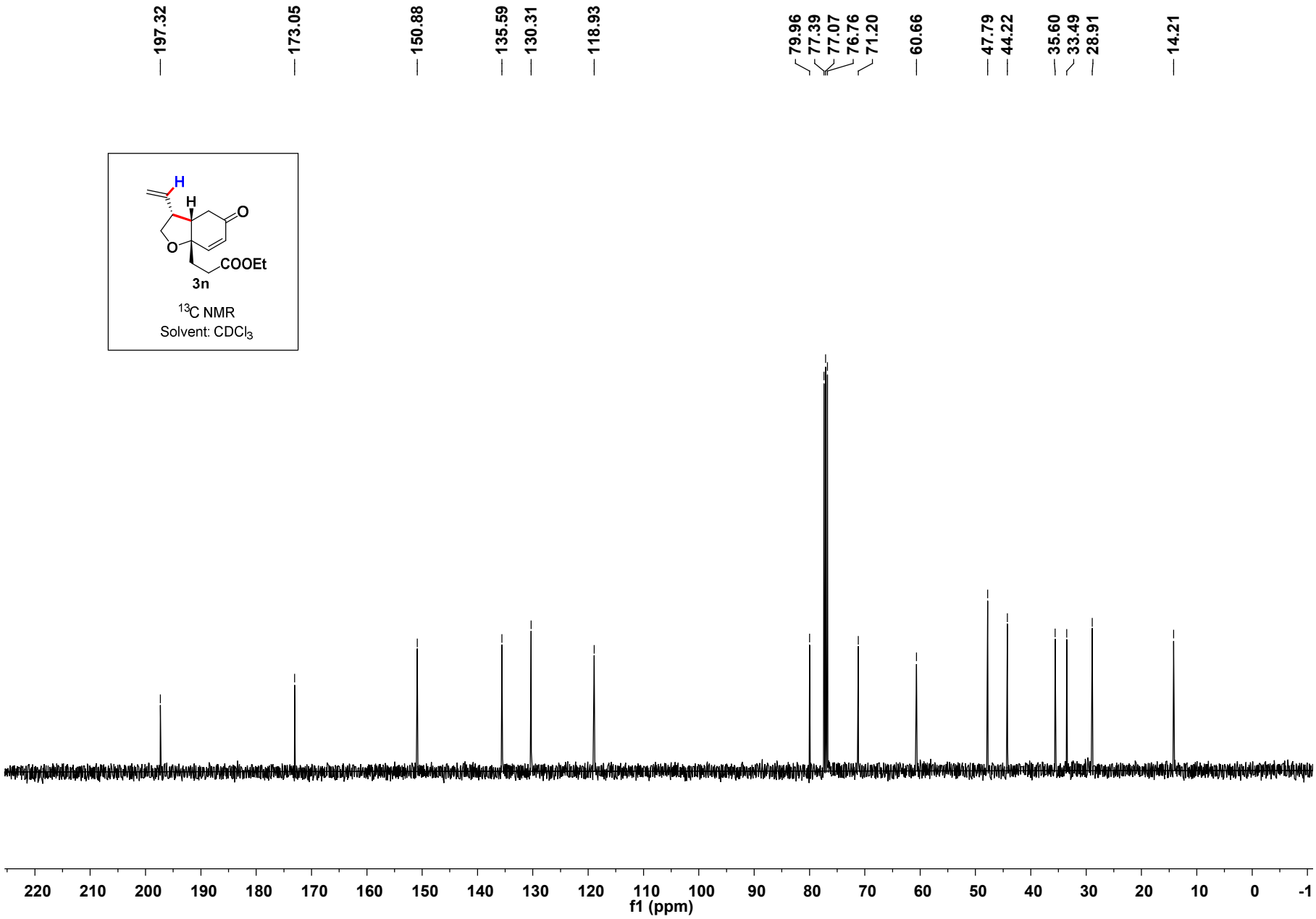
4.13
4.12
4.03
4.03
4.01
3.59
3.58
3.57
3.10
3.09
3.08
3.06
3.06
2.14
2.12
2.12
2.10
2.08
2.08
2.06
1.26
1.24
0.00
H
H
O
O
COOEt
3n
1H NMR
Solvent: CDCl3
0.97
0.94
1.00
2.03
2.01
0.98
0.95
0.98
4.98
2.17
3.26
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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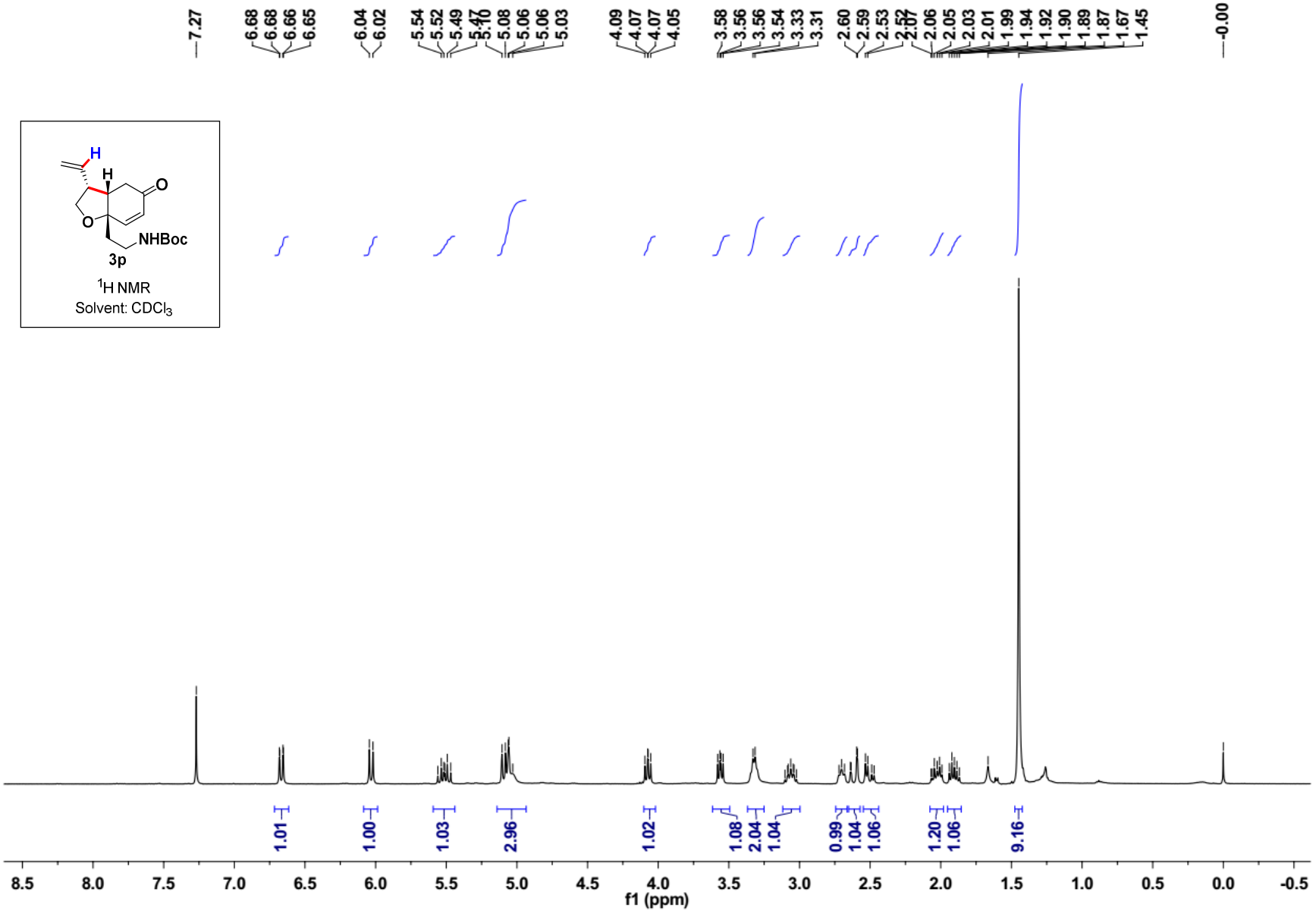
76.76
71.20
60.66
47.79
44.22
35.60
33.49
28.91
14.21
H
H
O
O
COOEt
3n
13C NMR
Solvent: CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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5.49
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5.08
5.06
5.06
5.03
4.09
4.07
4.07
4.05
3.58
3.56
3.56
3.54
3.33
3.31
2.60
2.59
2.53
2.52
2.07
2.06
2.05
2.03
2.01
1.99
1.94
1.92
1.90
1.89
1.87
1.67
1.45
0.00
H
H
O
O
NHBoc
3p
1H NMR
Solvent: CDCl3
1.01
1.00
1.03
2.96
1.02
1.08
2.04
1.04
0.99
1.04
1.06
1.20
1.06
9.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
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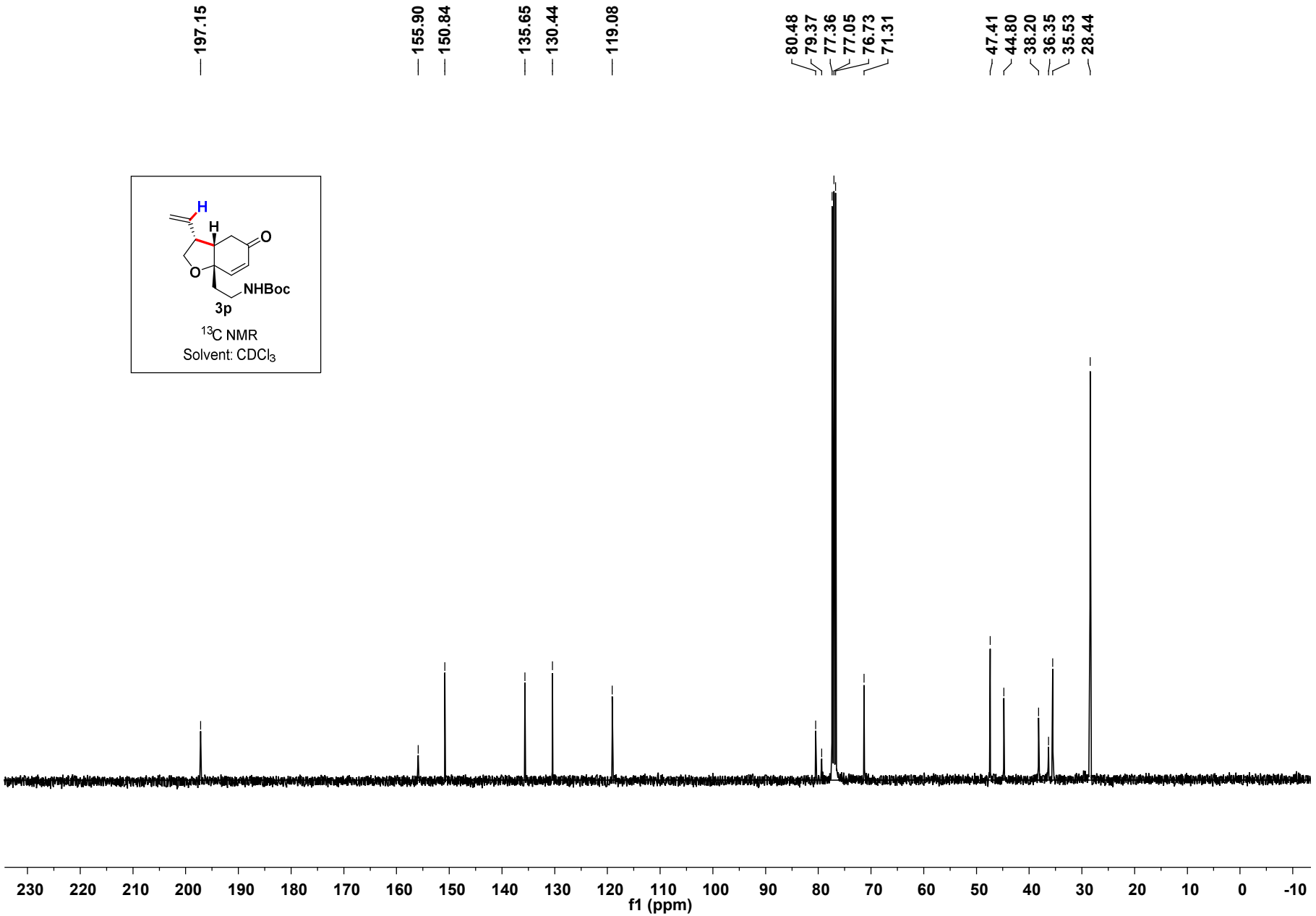
0.5
0.0
-0.5
f1 (ppm)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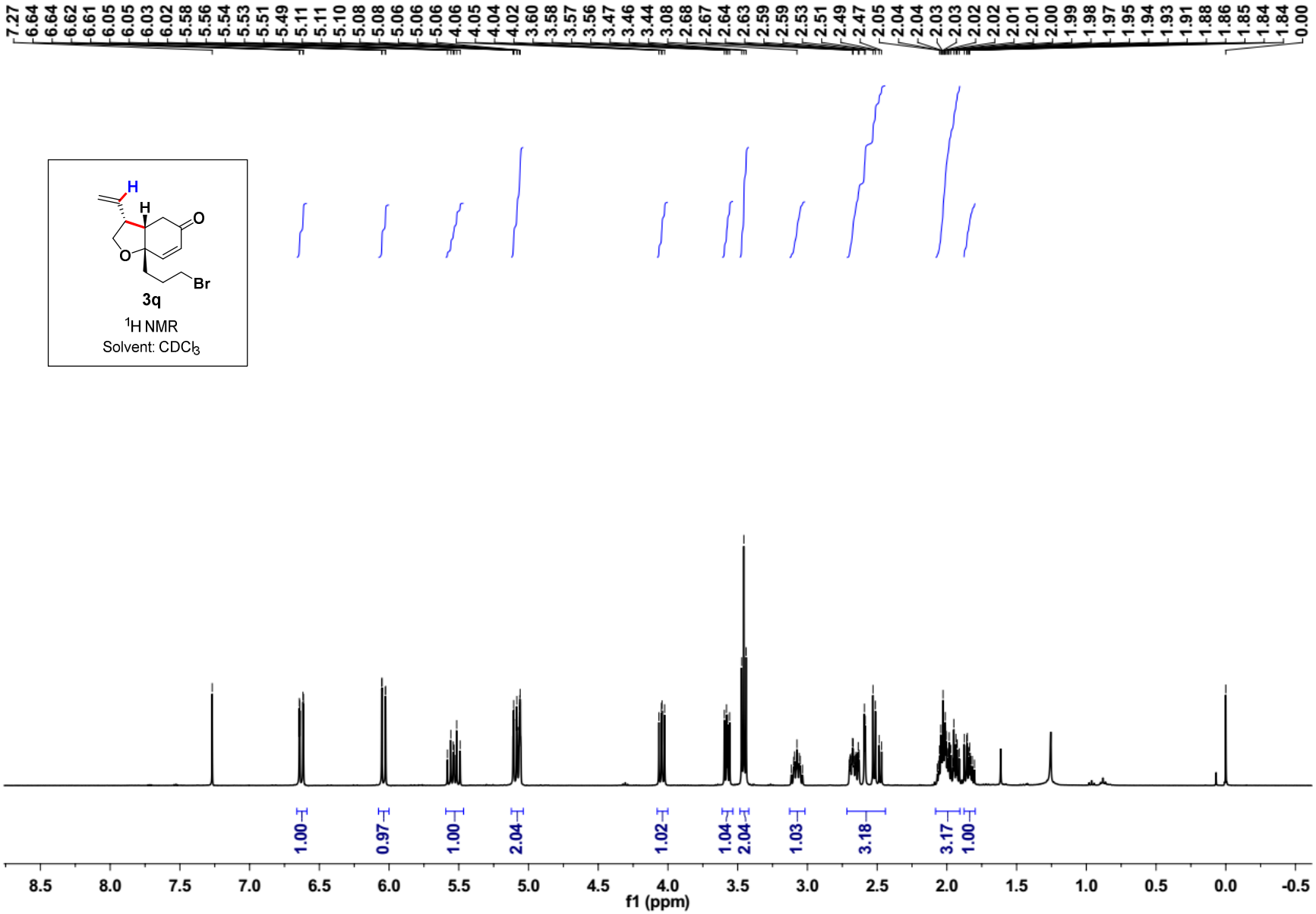
77.05
76.73
71.31
47.41
44.80
38.20
36.35
35.53
28.44
H
H
O
O
NHBoc
3p
13C NMR
Solvent: CDCl3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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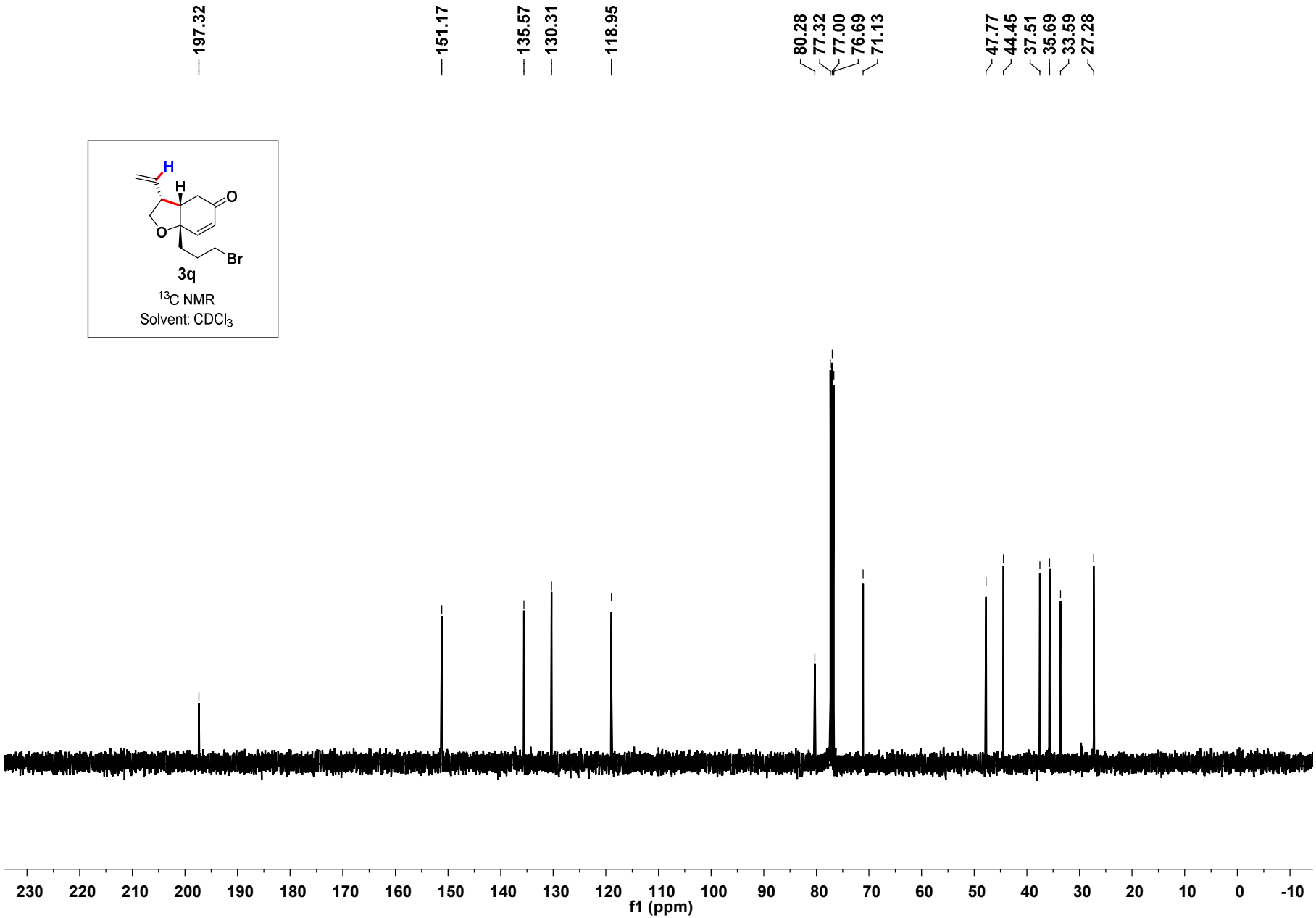
H
H
O
O
Br
3q
1H NMR
Solvent: CDCl3
1.00
0.97
1.00
2.04
1.02
1.04
2.04
1.03
3.18
3.17
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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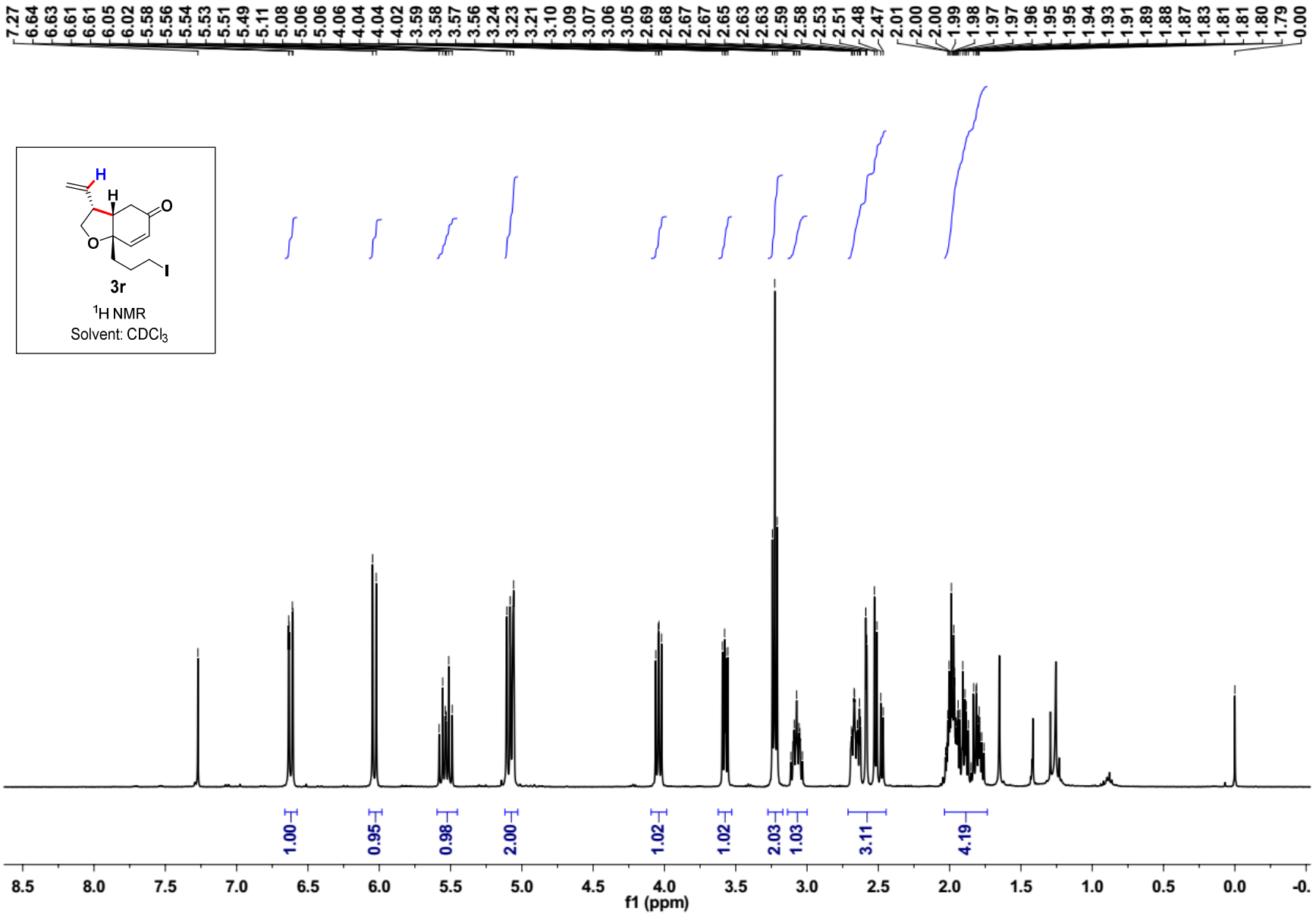
77.00
76.69
71.13
47.77
44.45
37.51
35.69
33.59
27.28
H
H
O
O
Br
3q
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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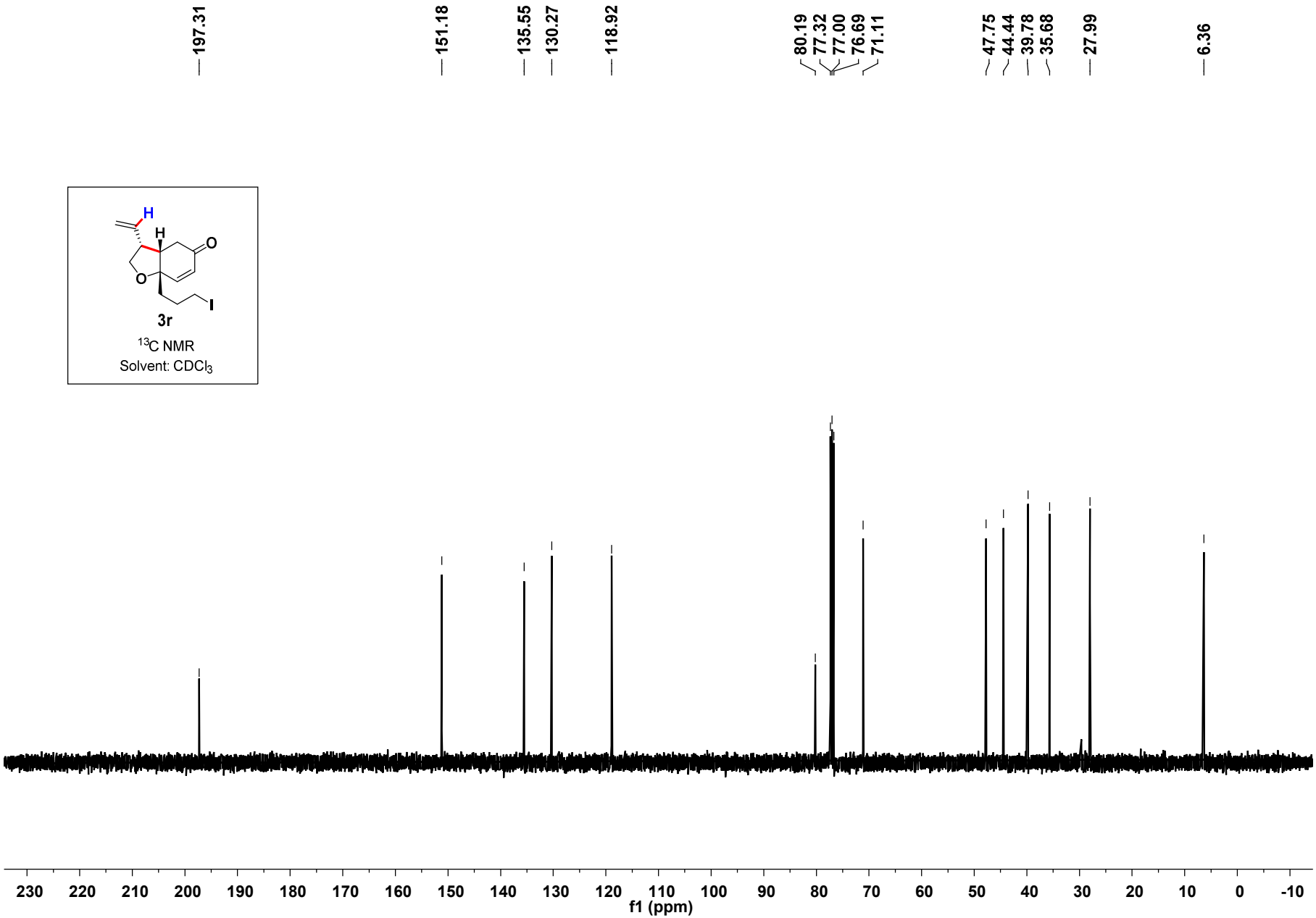
H
H
O
O
I
3r
1H NMR
Solvent: CDCl3
1.00
0.95
0.98
2.00
1.02
1.02
2.03
1.03
3.11
4.19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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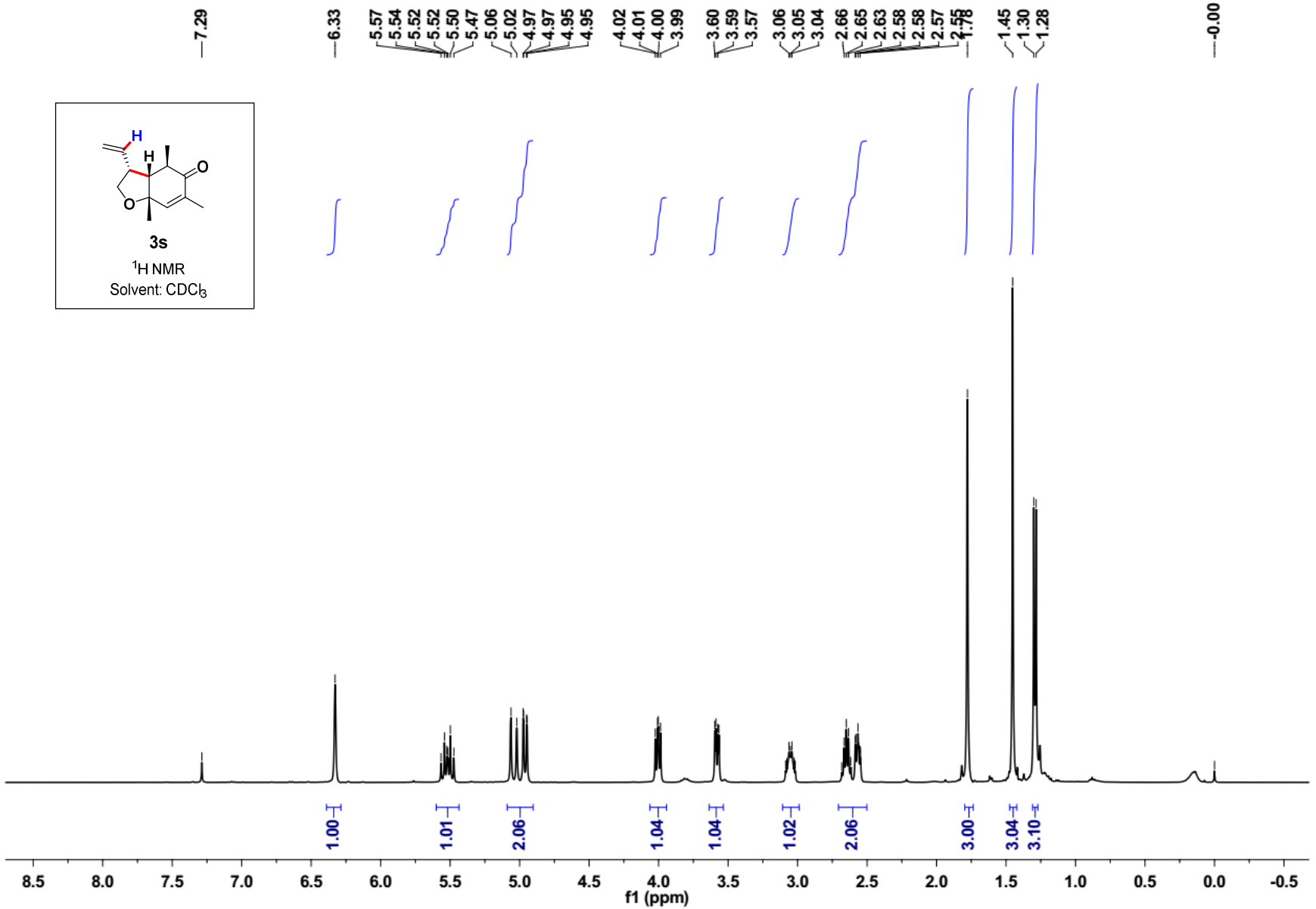
77.32
77.00
76.69
71.11
47.75
44.44
39.78
35.68
27.99
6.36
H
H
O
O
I
3r
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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5.47
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5.02
4.97
4.97
4.95
4.95
4.02
4.01
4.00
3.99
3.60
3.59
3.57
3.06
3.05
3.04
2.66
2.65
2.63
2.58
2.58
2.57
2.55
1.78
1.45
1.30
1.28
0.00
H
H
O
O
3s
1H NMR
Solvent: CDCl3
1.00
1.01
2.06
1.04
1.04
1.02
2.06
3.00
3.04
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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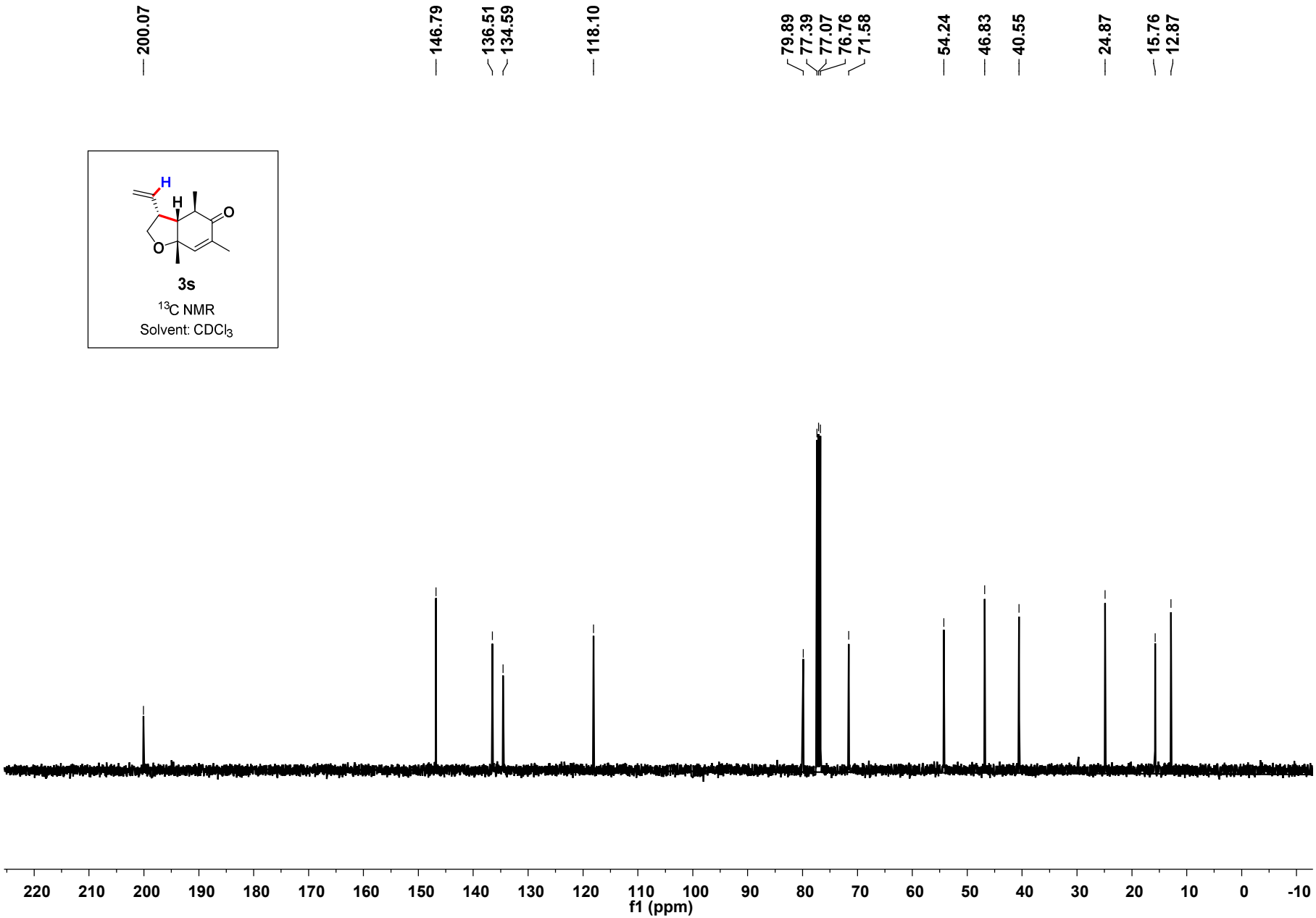
-0.5
f1 (ppm)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146.79
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77.07
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71.58
54.24
46.83
40.55
24.87
15.76
12.87
H
H
O
O
3s
13C NMR
Solvent: CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

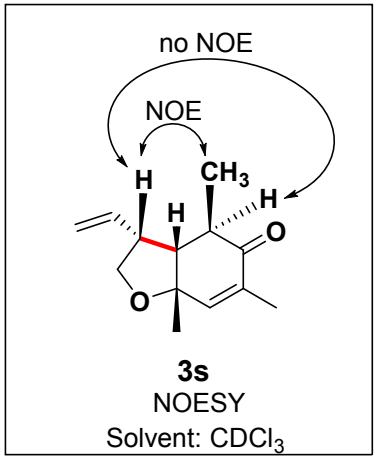
2013227txq05-47

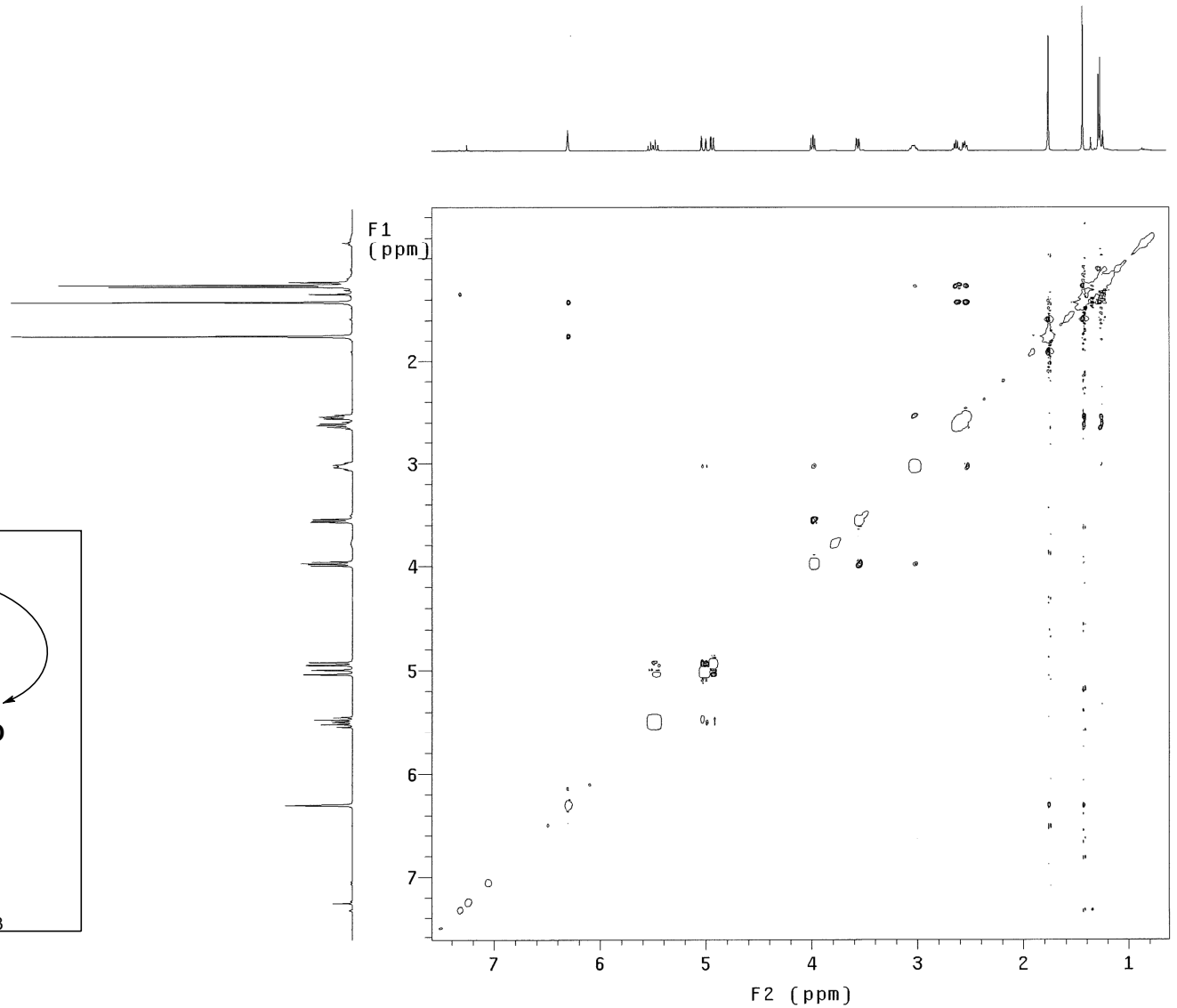
Sample Name:
2013227txq05-47
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2013227txq05-47_20150708_01
FidFile: NOESY_01

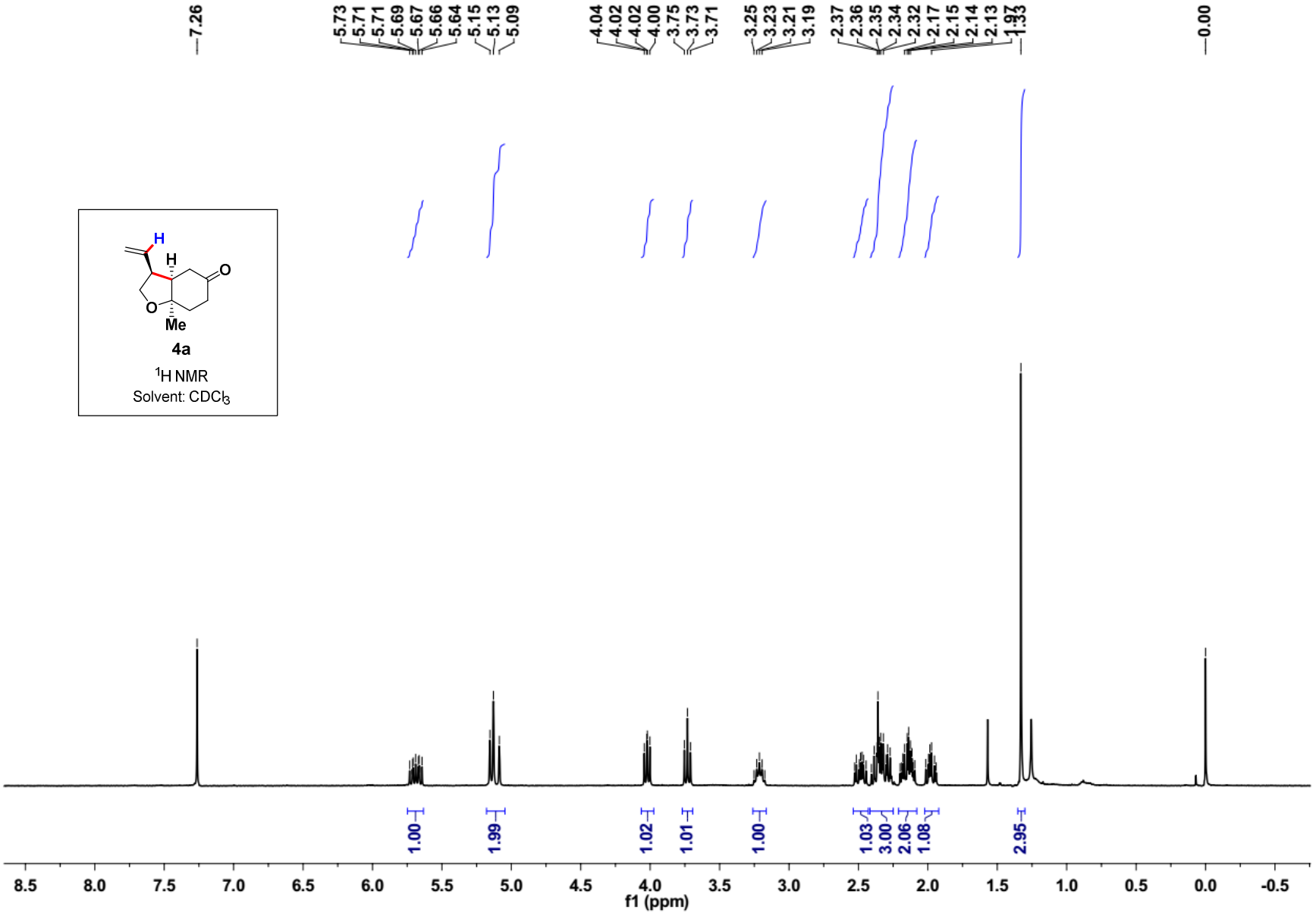
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Jul 8 2015

Temp. 25.0 C / 298.1 K
Operator: sioc

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3858.0 Hz
2D Width 3858.0 Hz
8 repetitions
2 x 200 increments
OBSERVE H1, 399.6538482 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.048 sec
FT size 2048 x 2048
Total time 1 hr, 41 min



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5.71
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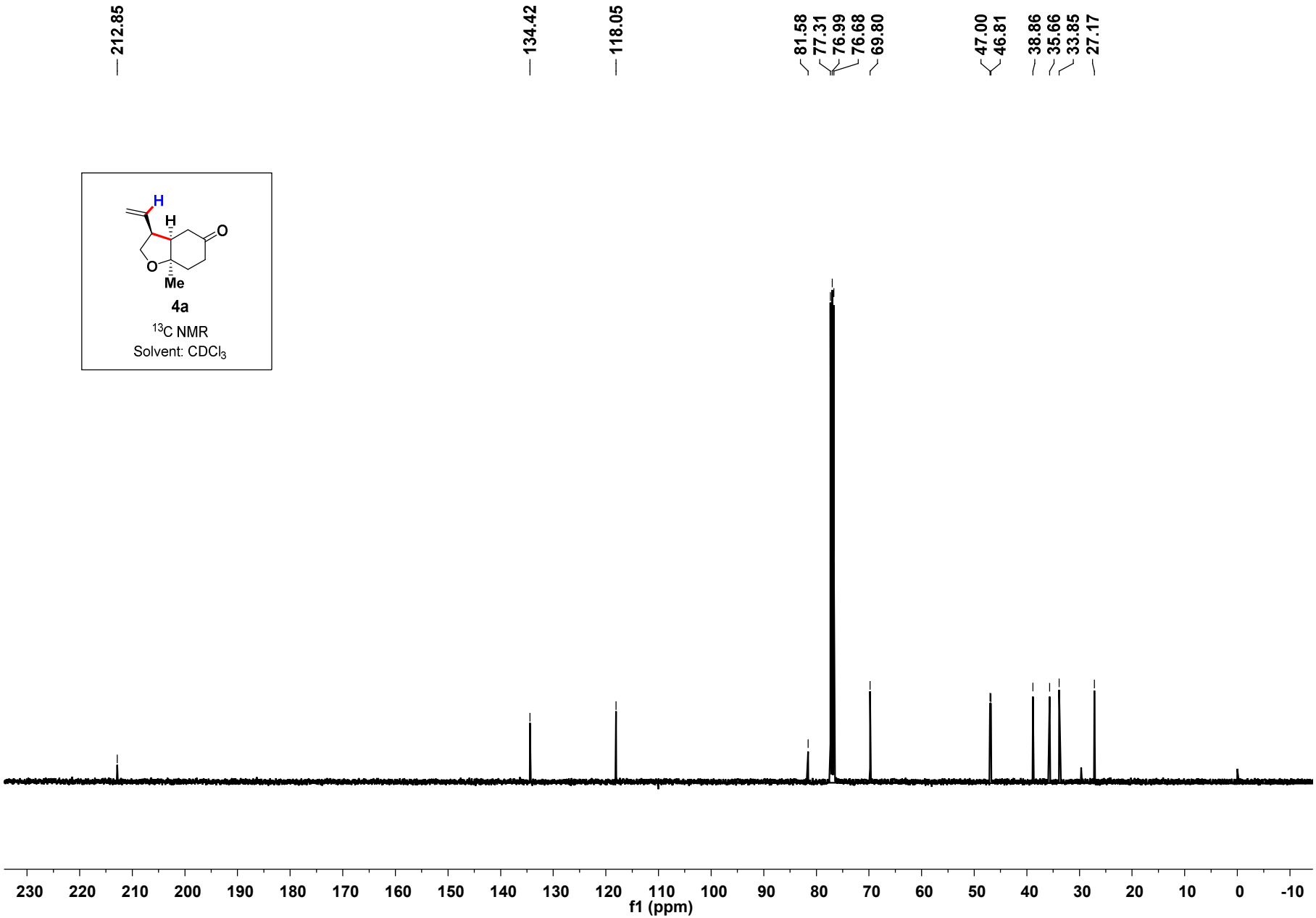
5.67
5.66
5.64
5.15
5.13
5.09
4.04
4.02
4.02
4.00
3.75
3.73
3.71
3.25
3.23
3.21
3.19
2.37
2.36
2.35
2.34
2.32
2.17
2.15
2.14
2.13
1.97
1.33
0.00
H
H
O
O
Me
4a
1H NMR
Solvent: CDCl3
1.00
1.99
1.02
1.01
1.00
1.03
3.00
2.06
1.08
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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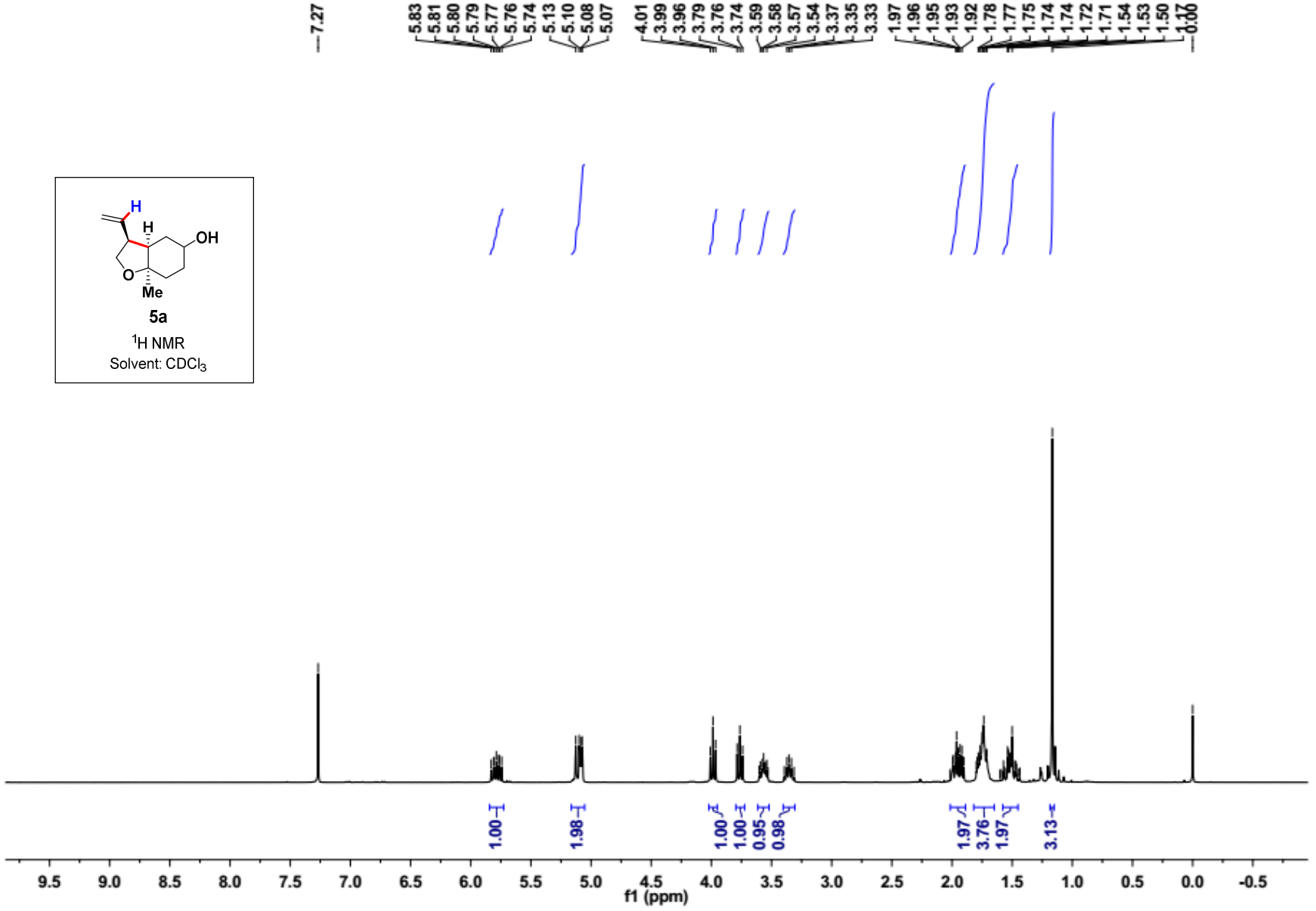
69.80
47.00
46.81
38.86
35.66
33.85
27.17
H
H
O
O
Me
4a
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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5.74
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5.08
5.07
4.01
3.99
3.96
3.79
3.76
3.74
3.59
3.58
3.57
3.54
3.37
3.35
3.33
1.97
1.96
1.95
1.93
1.92
1.78
1.77
1.75
1.74
1.74
1.72
1.71
1.54
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1.17
0.00
H
H
OH
O
Me
5a
1H NMR
Solvent: CDCl3
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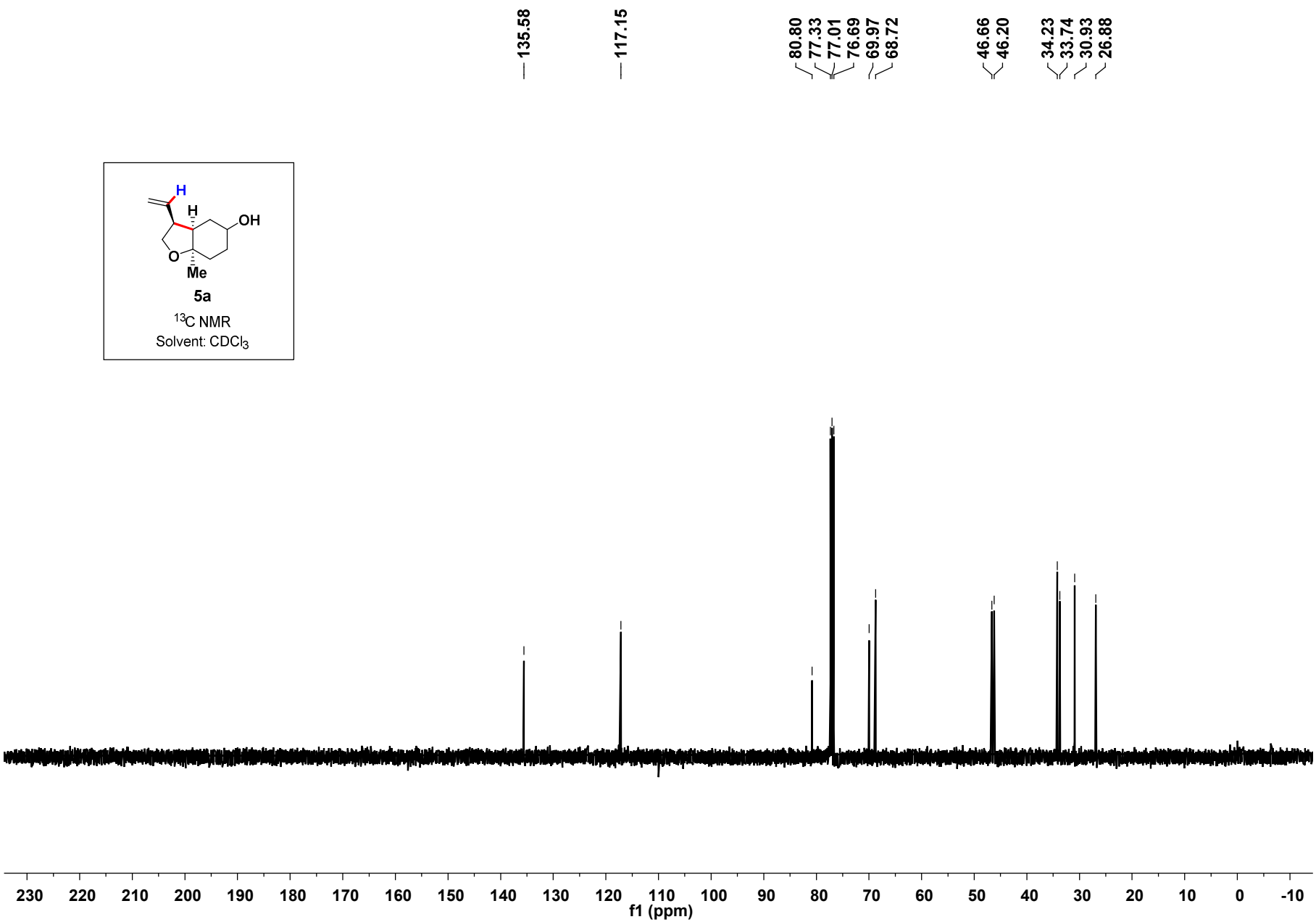
1.98
1.00
1.00
0.95
0.98
1.97
3.76
1.97
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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117.15
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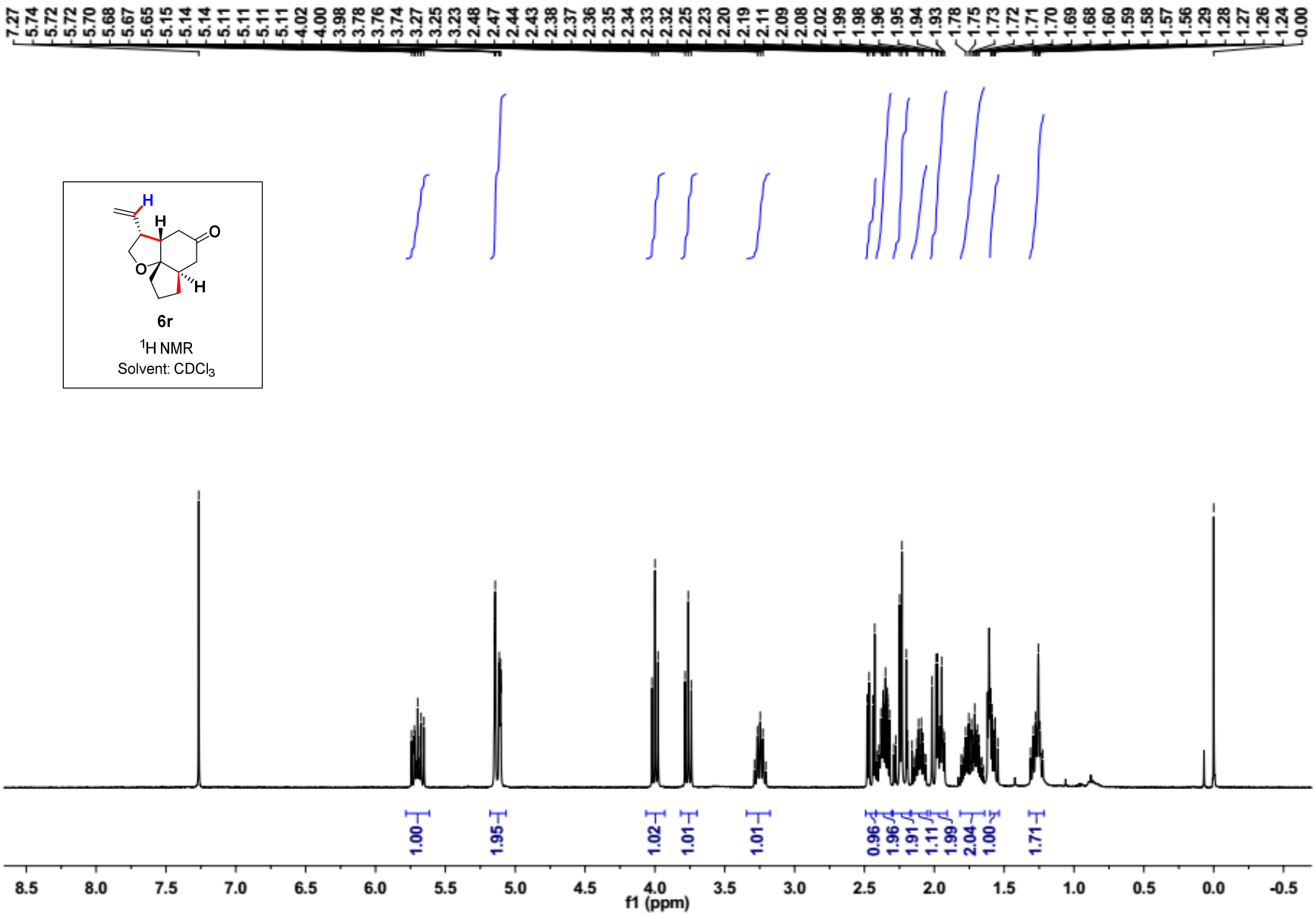
76.69
69.97
68.72
46.66
46.20
34.23
33.74
30.93
26.88
H
H
OH
O
Me
5a
13C NMR
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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5.14
5.11
5.11
5.11
5.11
4.02
4.00
3.98
3.78
3.76
3.74
3.27
3.25
3.23
2.48
2.47
2.44
2.43
2.38
2.37
2.36
2.35
2.34
2.33
2.32
2.25
2.23
2.20
2.19
2.11
2.09
2.08
2.02
1.99
1.98
1.96
1.95
1.94
1.93
1.78
1.75
1.73
1.72
1.71
1.70
1.69
1.68
1.60
1.59
1.58
1.57
1.56
1.29
1.28
1.27
1.26
1.24
0.00
H
H
O
O
H
6r
1H NMR
Solvent: CDCl3
1.00
1.95
1.02
1.01
1.01
0.96
1.96
1.91
1.11
1.99
2.04
1.00
1.71
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
2.0
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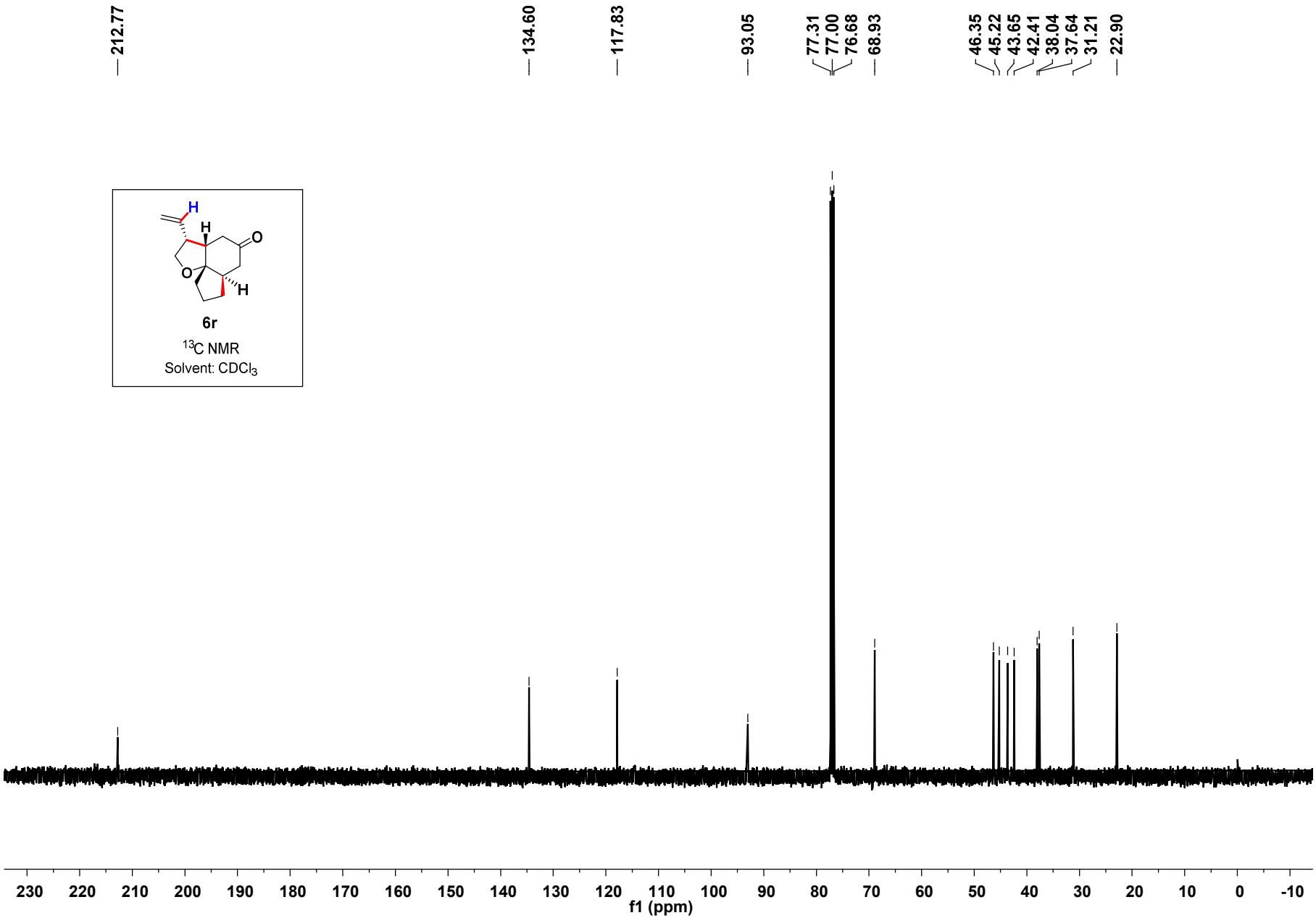
0.5
0.0
-0.5
f1 (ppm)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68.93
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45.22
43.65
42.41
38.04
37.64
31.21
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6r
13C NMR
Solvent: CDCl3
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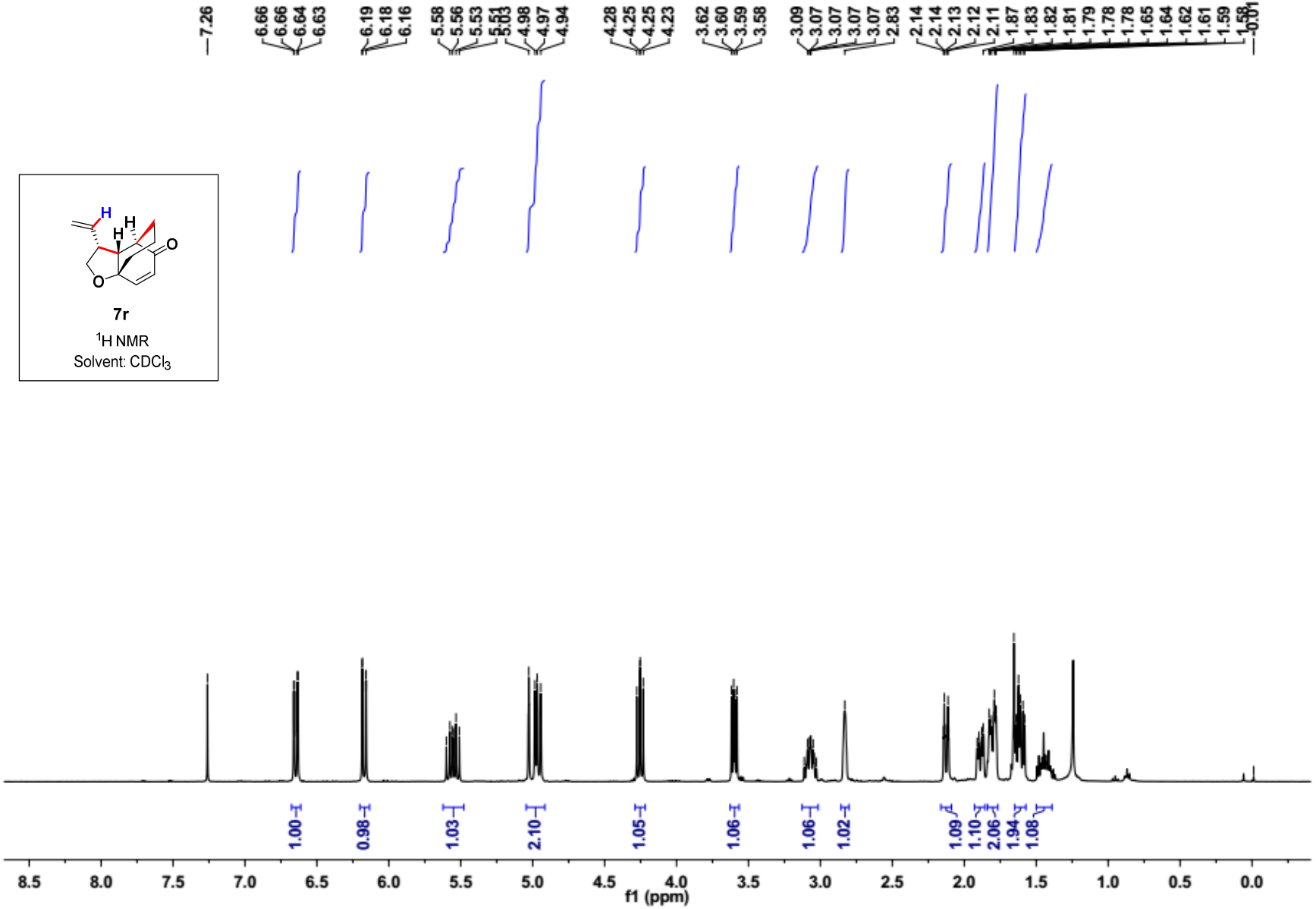
f1 (ppm)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5.03
4.98
4.97
4.94
4.28
4.25
4.25
4.23
3.62
3.60
3.59
3.58
3.09
3.07
3.07
3.07
3.07
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1.83
1.82
1.81
1.79
1.78
1.78
1.65
1.64
1.62
1.61
1.59
1.58
0.01
H
H
H
O
O
7r
1H NMR
Solvent: CDCl3
1.00
0.98
1.03
2.10
1.05
1.06
1.06
1.02
1.09
1.10
2.06
1.94
1.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
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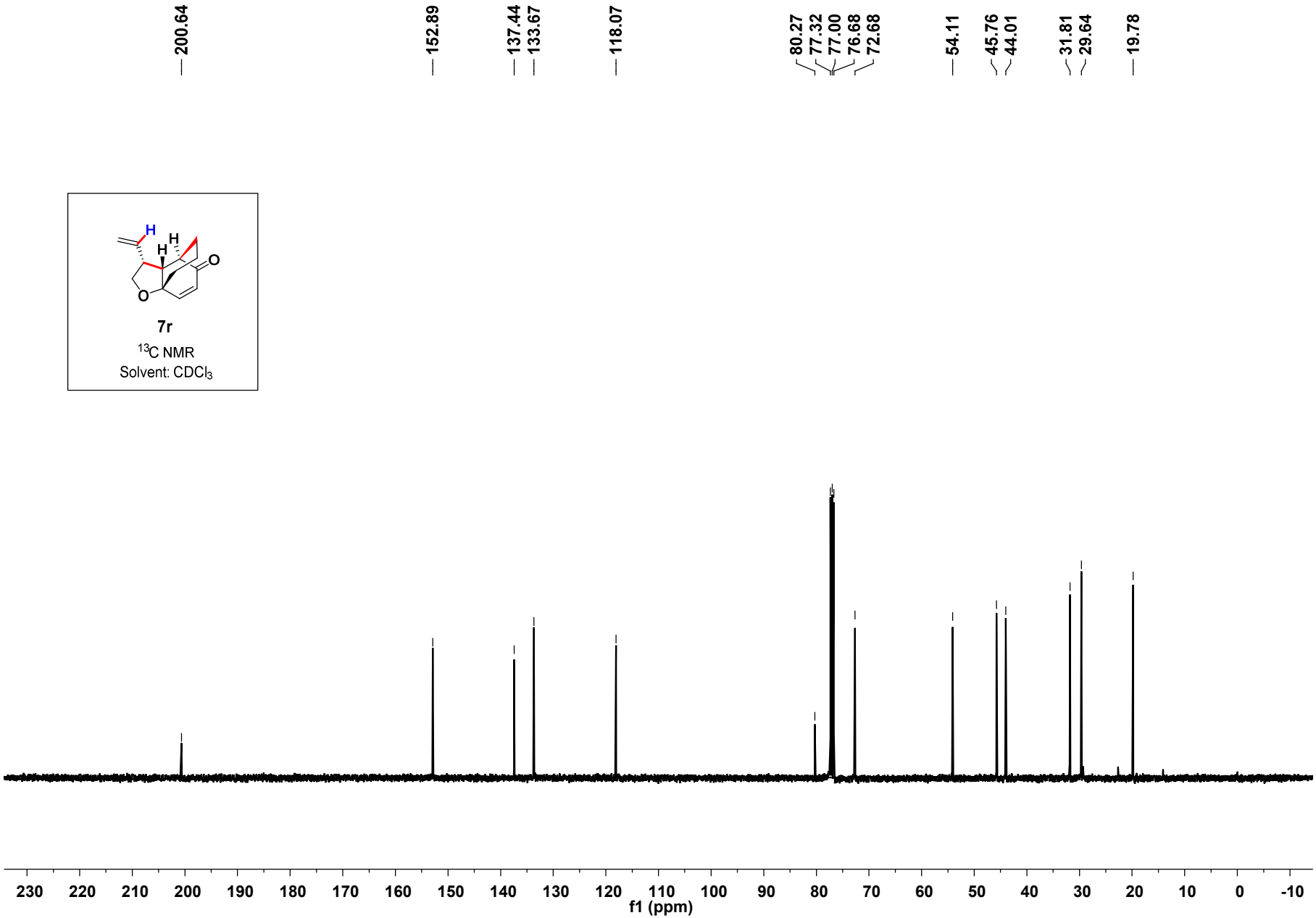
0.0
f1 (ppm)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72.68
54.11
45.76
44.01
31.81
29.64
19.78
7r
13C NMR
Solvent: CDCl3
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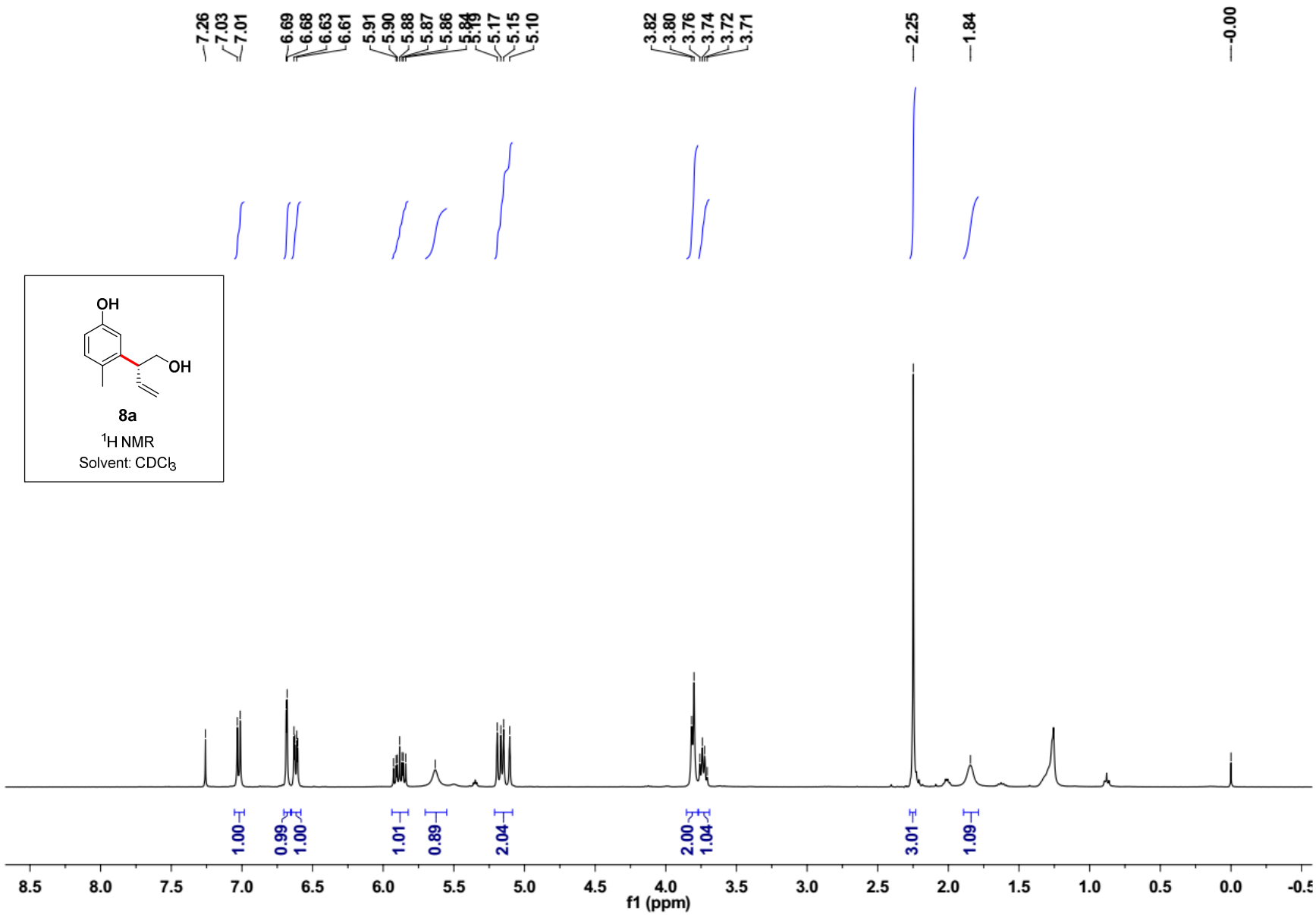
f1 (ppm)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5.17
5.15
5.10
3.82
3.80
3.76
3.74
3.72
3.71
2.25
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0.00
OH
OH
8a
1H NMR
Solvent: CDCl3
1.00
0.99
1.00
1.01
0.89
2.04
2.00
1.04
3.01
1.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
1.5
1.0
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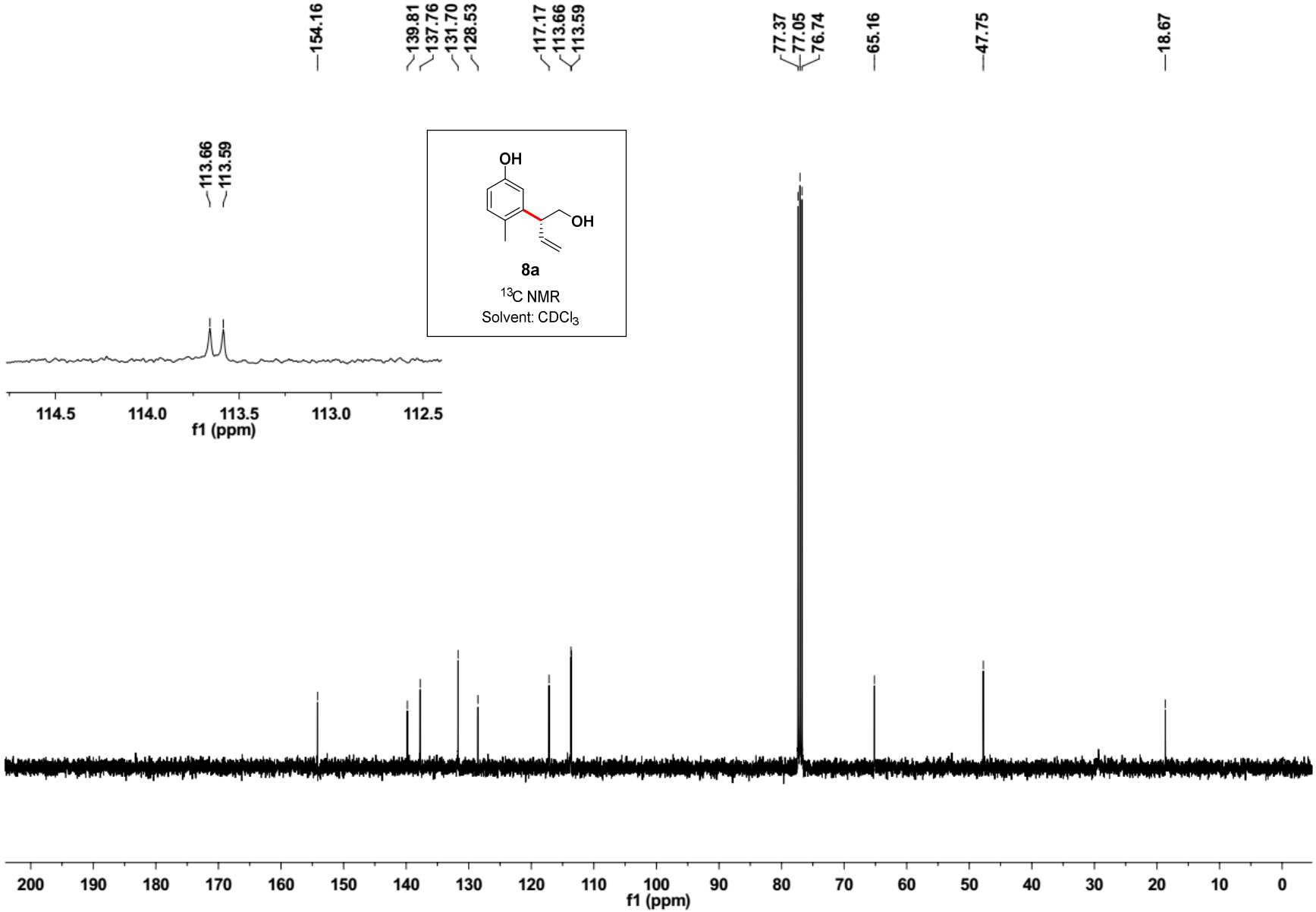
0.0
f1 (ppm)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113.66
113.59
77.37
77.05
76.74
65.16
47.75
18.67
OH
OH
8a
13C NMR
Solvent: CDCl3
114.5
114.0
113.5
113.0
112.5
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
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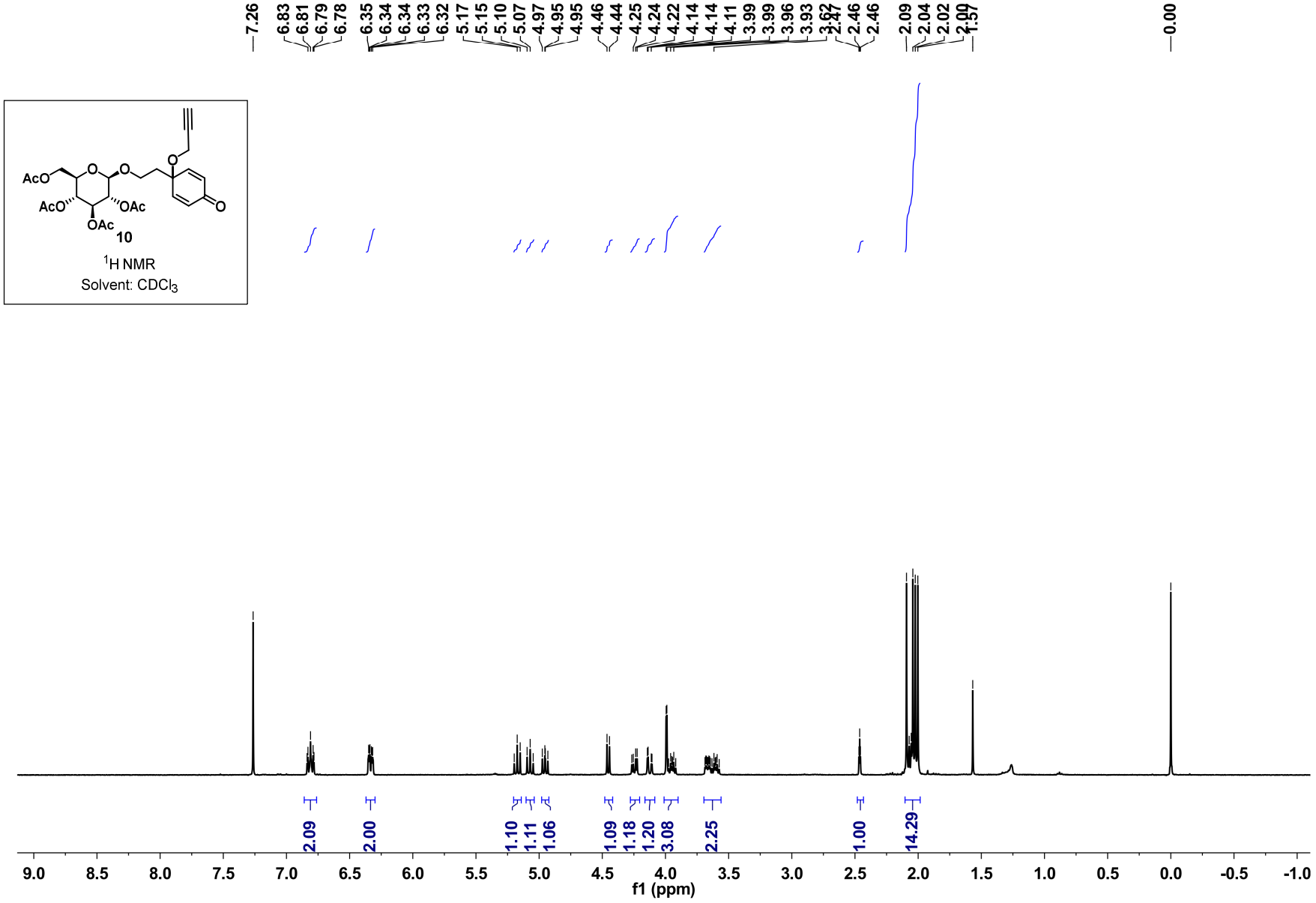
70
60
50
40
30
20
10
0
f1 (ppm)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5.10
5.07
4.97
4.95
4.95
4.46
4.44
4.25
4.24
4.22
4.14
4.14
4.11
3.99
3.99
3.96
3.93
2.47
2.46
2.46
2.09
2.04
2.02
2.00
1.57
0.00
AcO
AcO
OAc
OAc
O
O
O
O
10
1H NMR
Solvent: CDCl3
2.09
2.00
1.10
1.11
1.06
1.09
1.18
1.20
3.08
2.25
1.00
14.29
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8.5
8.0
7.5
7.0
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6.0
5.5
5.0
4.5
4.0
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0.0
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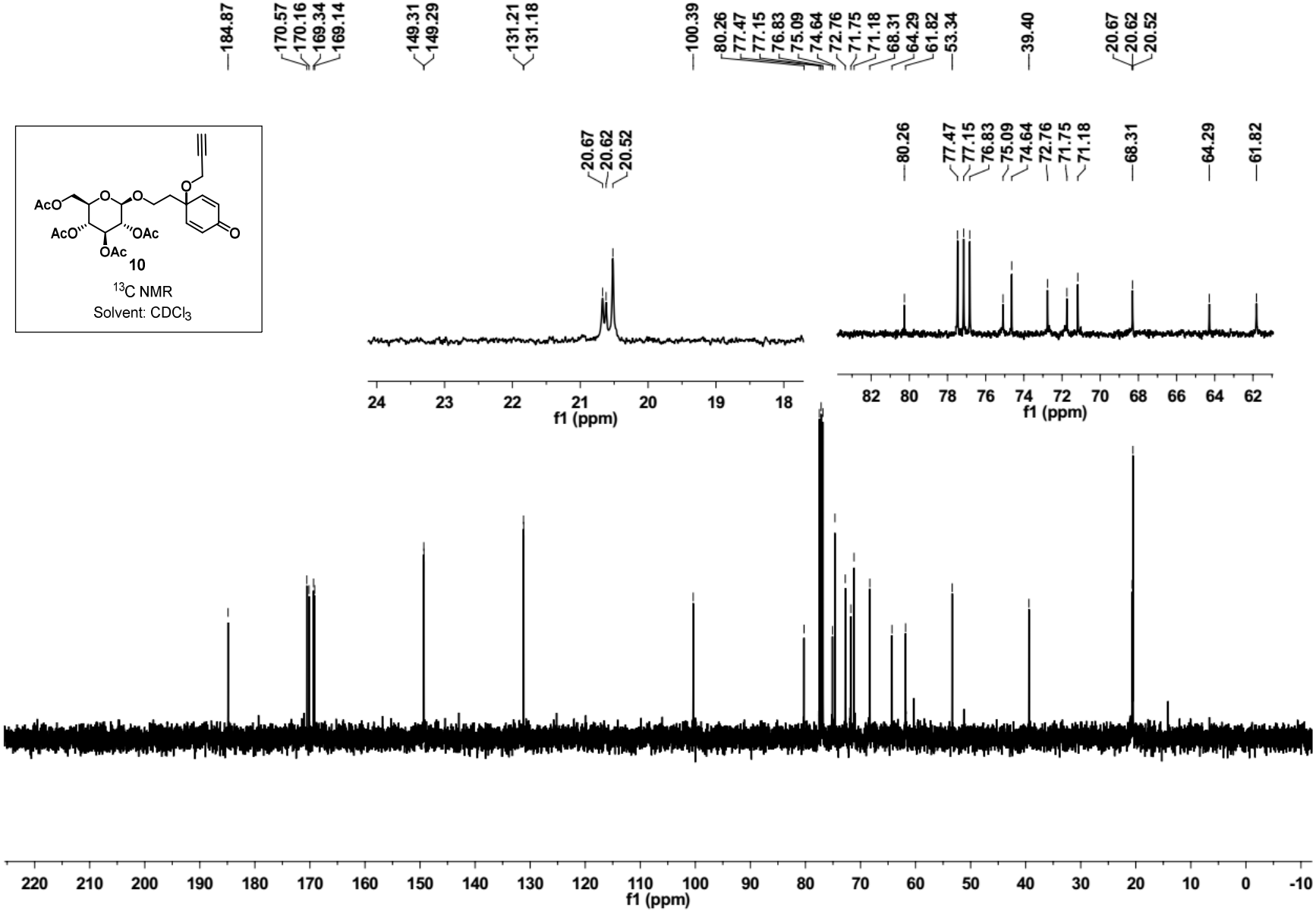
f1 (ppm)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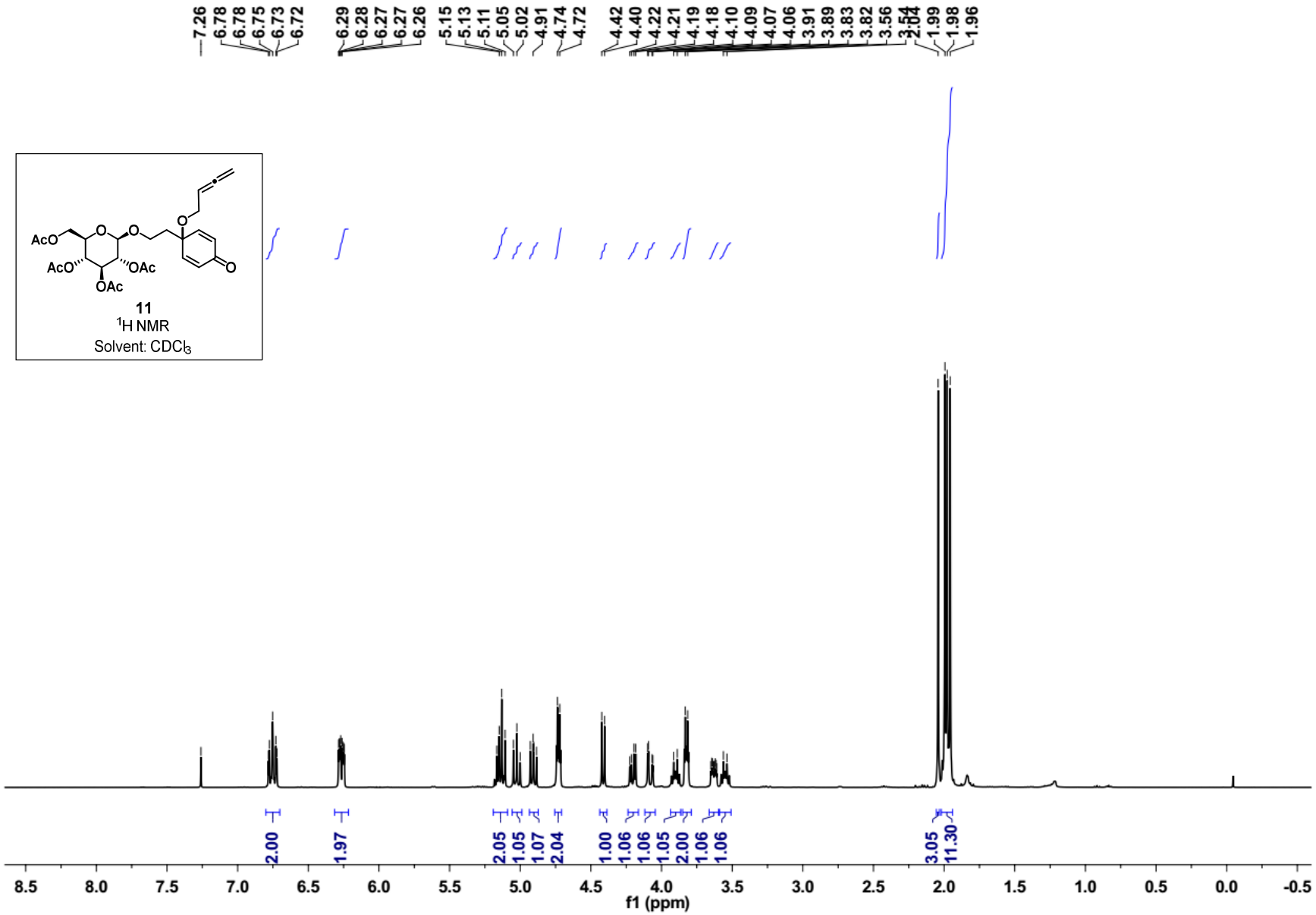
76.83
75.09
74.64
72.76
71.75
71.18
68.31
64.29
61.82
53.34
39.40
20.67
20.62
20.52
AcO
AcO
OAc
OAc
O
O
O
O
10
13C NMR
Solvent: CDCl3
f1 (ppm)
f1 (ppm)
f1 (ppm)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4.22
4.21
4.19
4.18
4.10
4.09
4.07
4.06
3.91
3.89
3.83
3.82
3.56
3.54
2.04
1.99
1.98
1.96
AcO
AcO
OAc
OAc
O
O
O
O
11
1H NMR
Solvent: CDCl3
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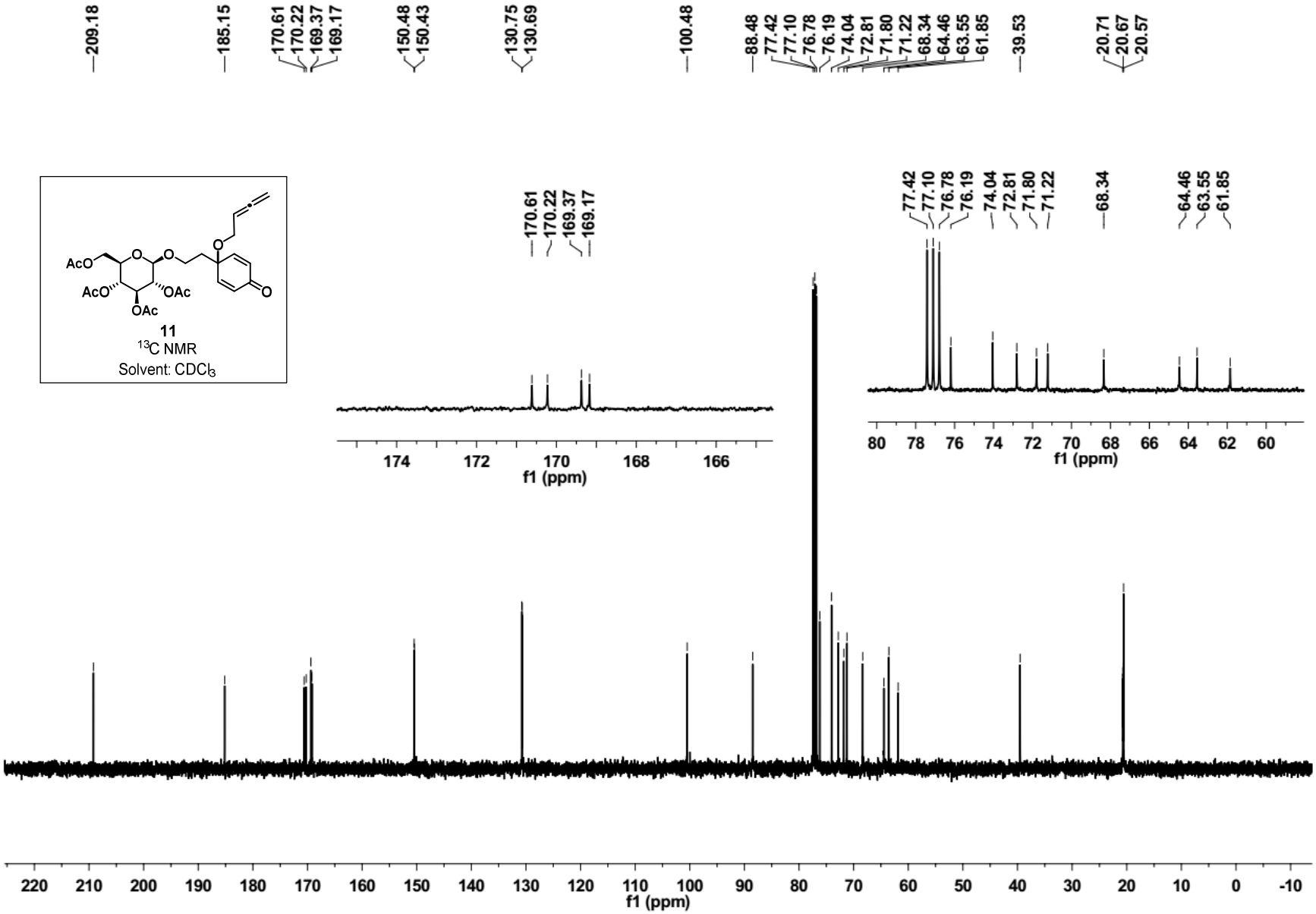
1.97
2.05
1.05
1.07
2.04
1.00
1.06
1.06
1.05
2.00
1.06
1.06
3.05
11.30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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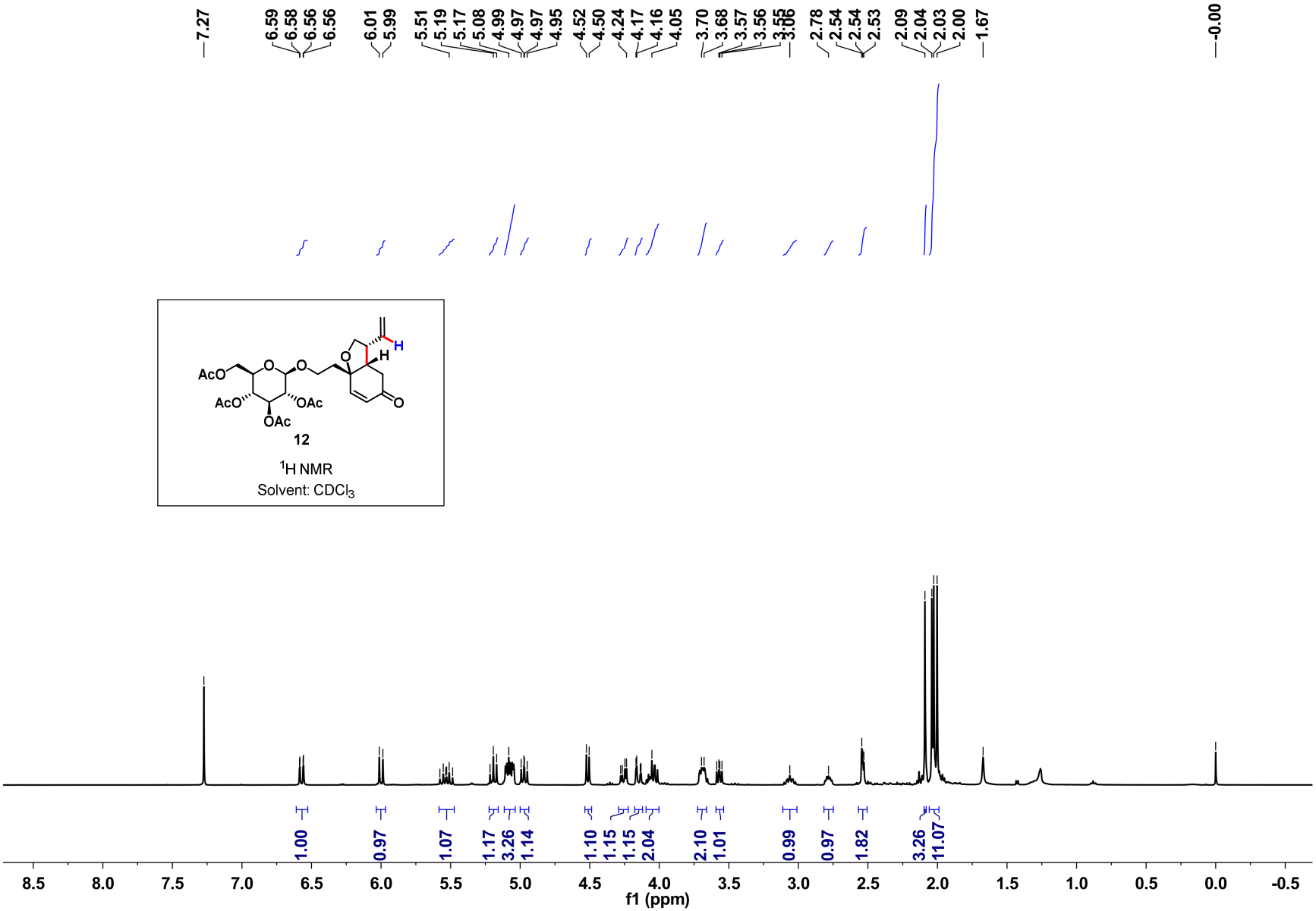
74.04
72.81
71.80
71.22
68.34
64.46
63.55
61.85
39.53
20.71
20.67
20.57
AcO
AcO
OAc
OAc
O
O
O
O
11
13C NMR
Solvent: CDCl3
f1 (ppm)
f1 (ppm)
f1 (ppm)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6.59
6.58
6.56
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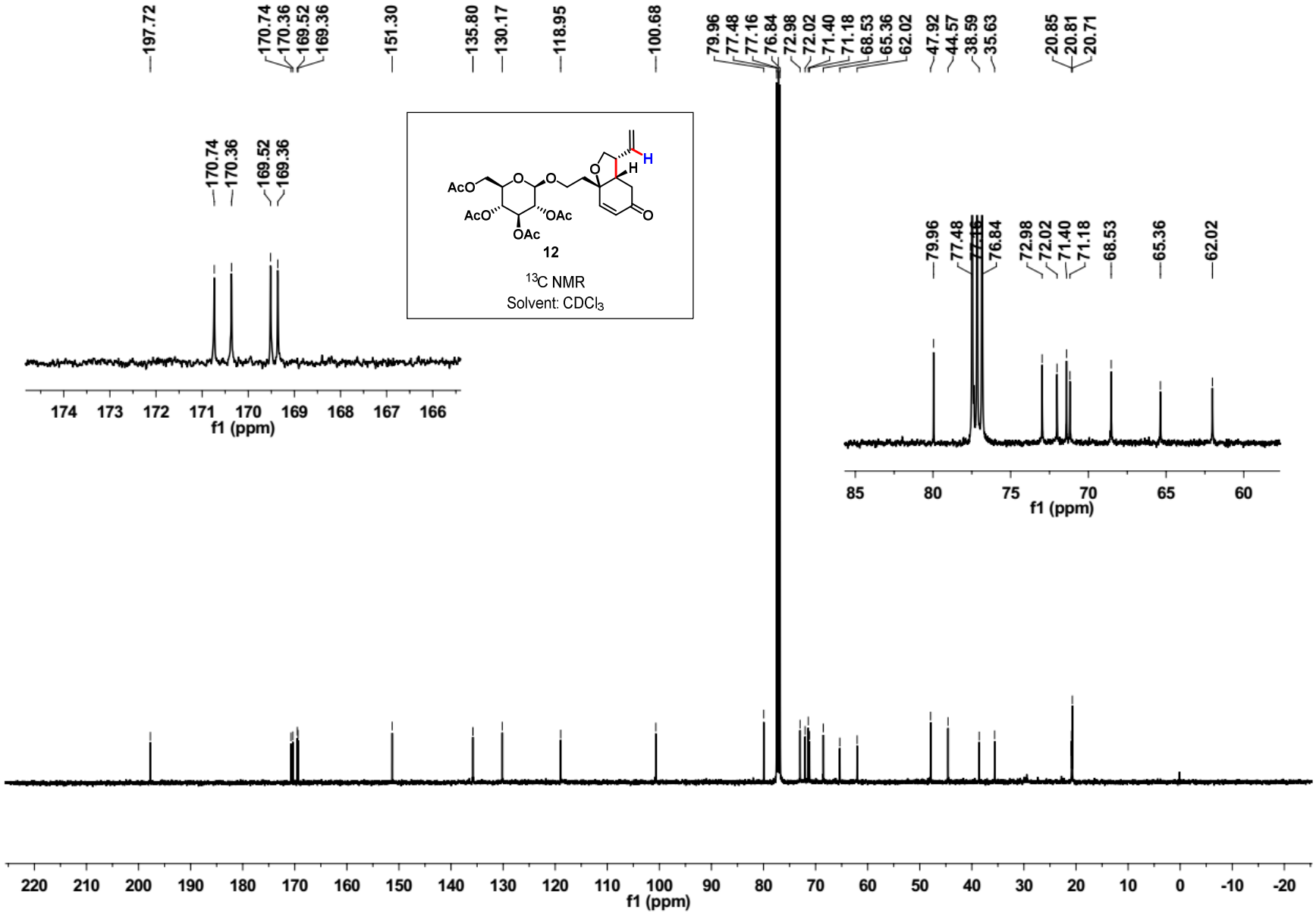
6.01
5.99
5.51
5.19
5.17
5.08
4.99
4.97
4.97
4.95
4.52
4.50
4.24
4.17
4.16
4.05
3.70
3.68
3.57
3.56
3.55
3.06
2.78
2.54
2.54
2.53
2.09
2.04
2.03
2.00
1.67
0.00
AcO
AcO
OAc
OAc
O
O
O
O
H
H
12
1H NMR
Solvent: CDCl3
1.00
0.97
1.07
1.17
3.26
1.14
1.10
1.15
1.15
2.04
2.10
1.01
0.99
0.97
1.82
3.26
11.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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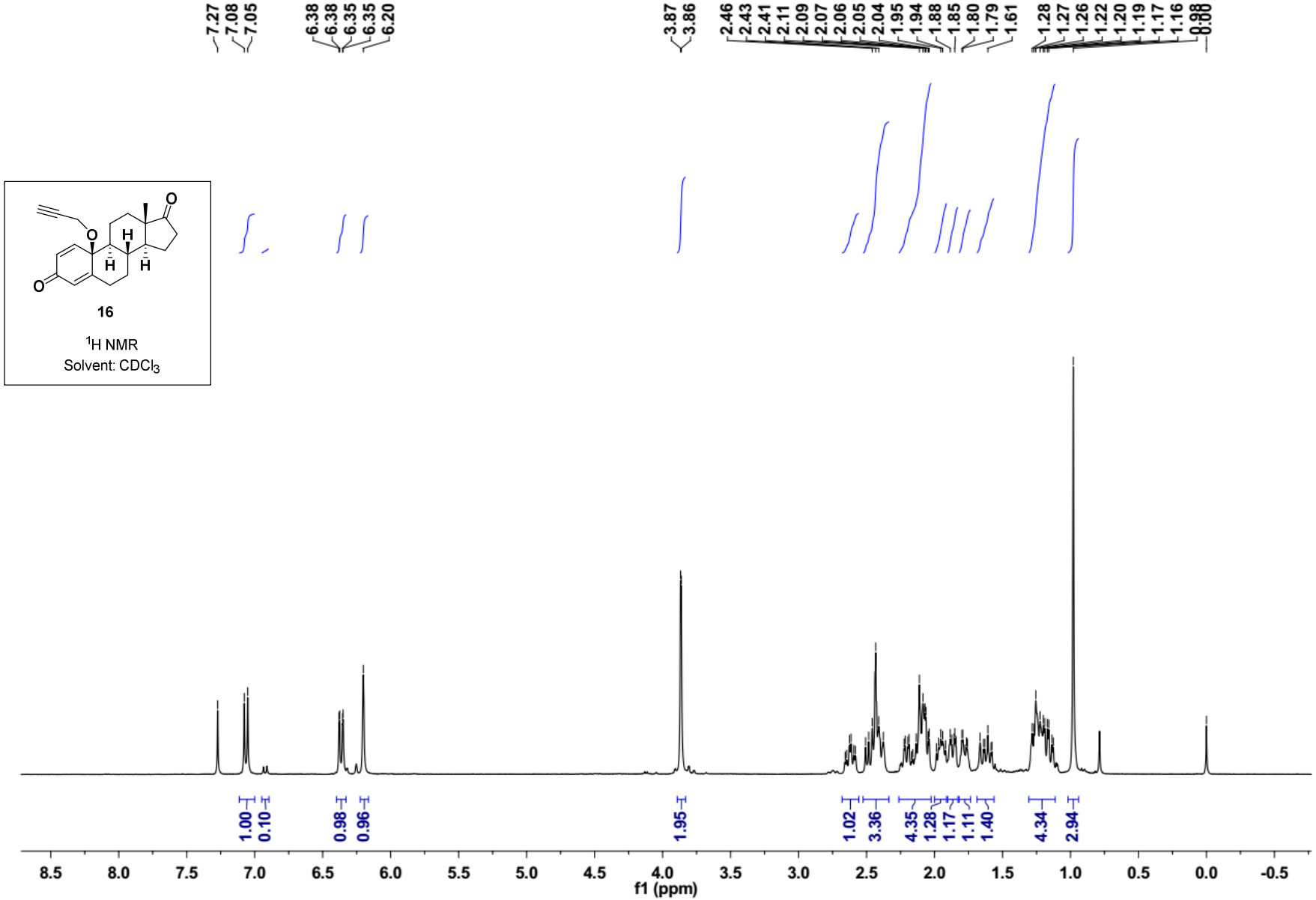
170.74
170.36
169.52
169.36
151.30
135.80
130.17
118.95
100.68
79.96
77.48
77.16
76.84
72.98
72.02
71.40
71.18
68.53
65.36
62.02
47.92
44.57
38.59
35.63
20.85
20.81
20.71
AcO
AcO
OAc
OAc
O
O
O
O
H
H
12
13C NMR
Solvent: CDCl3
f1 (ppm)
f1 (ppm)
f1 (ppm)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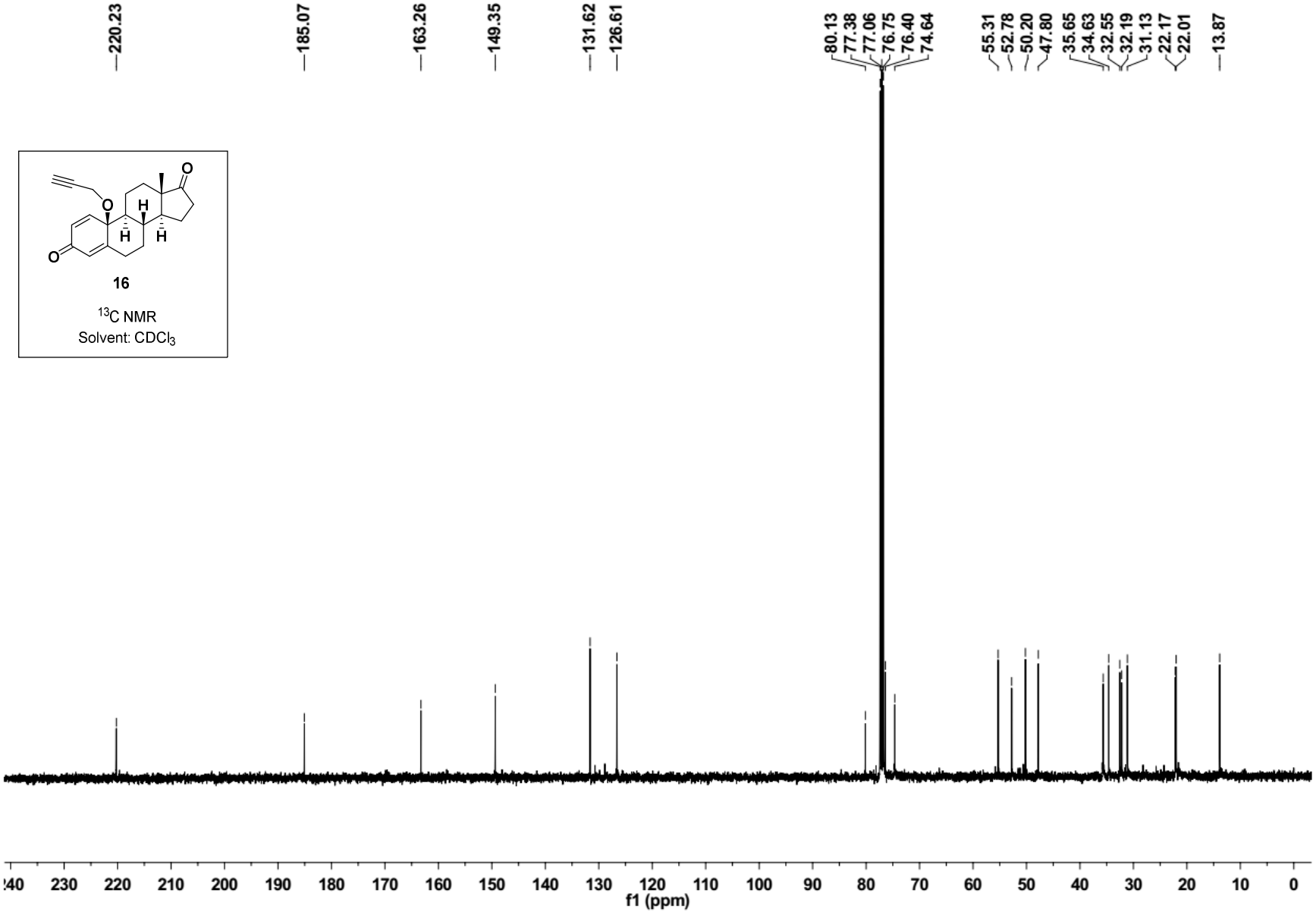
7.08
7.05
6.38
6.38
6.35
6.35
6.20
3.87
3.86
2.46
2.43
2.41
2.11
2.09
2.07
2.06
2.05
2.04
1.95
1.94
1.88
1.85
1.80
1.79
1.61
1.28
1.27
1.26
1.22
1.20
1.19
1.17
1.16
0.98
0.88
O
O
H
H
H
O
16
1H NMR
Solvent: CDCl3
1.00
0.10
0.98
0.96
1.95
1.02
3.36
4.35
1.28
1.17
1.11
1.40
4.34
2.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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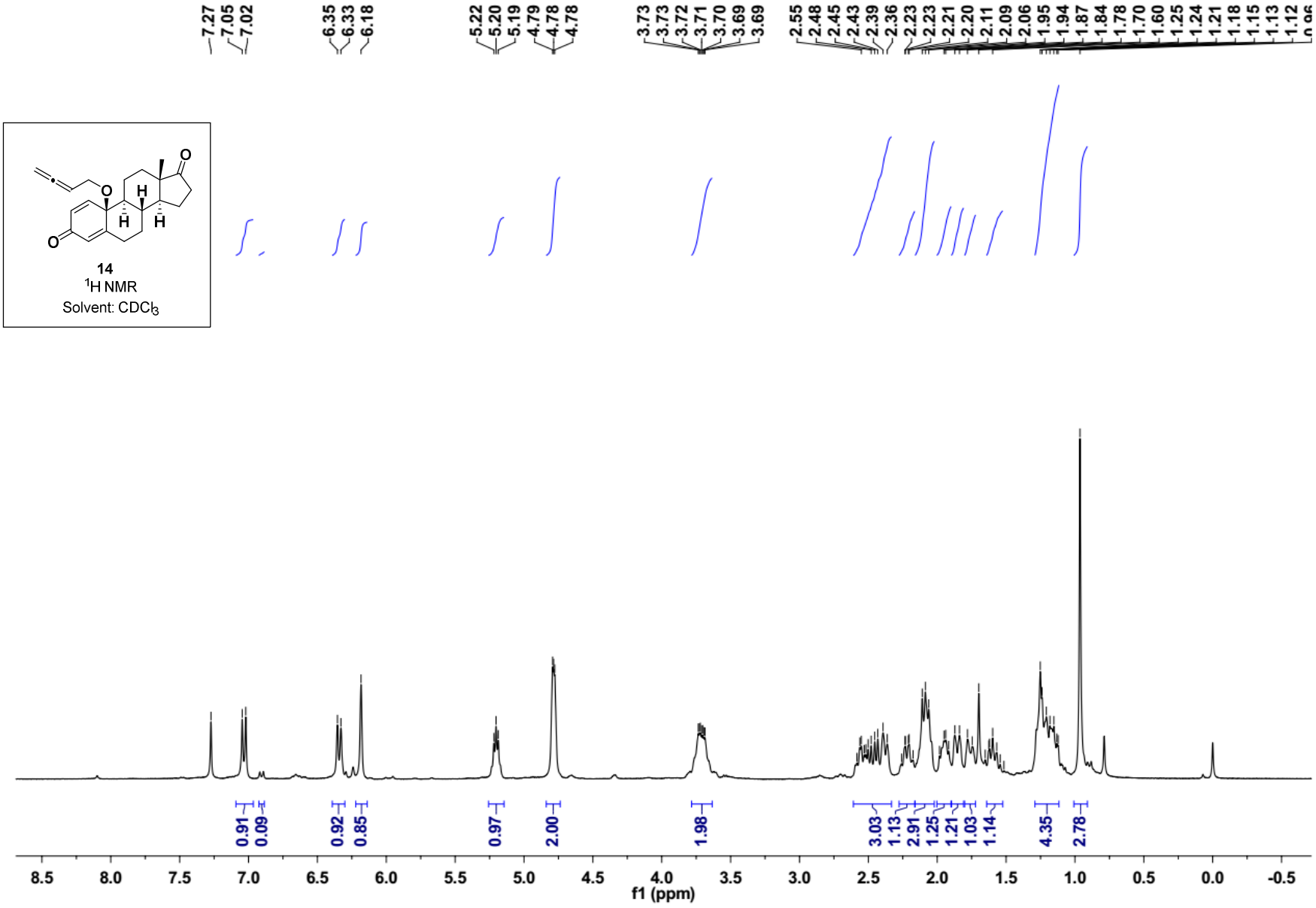
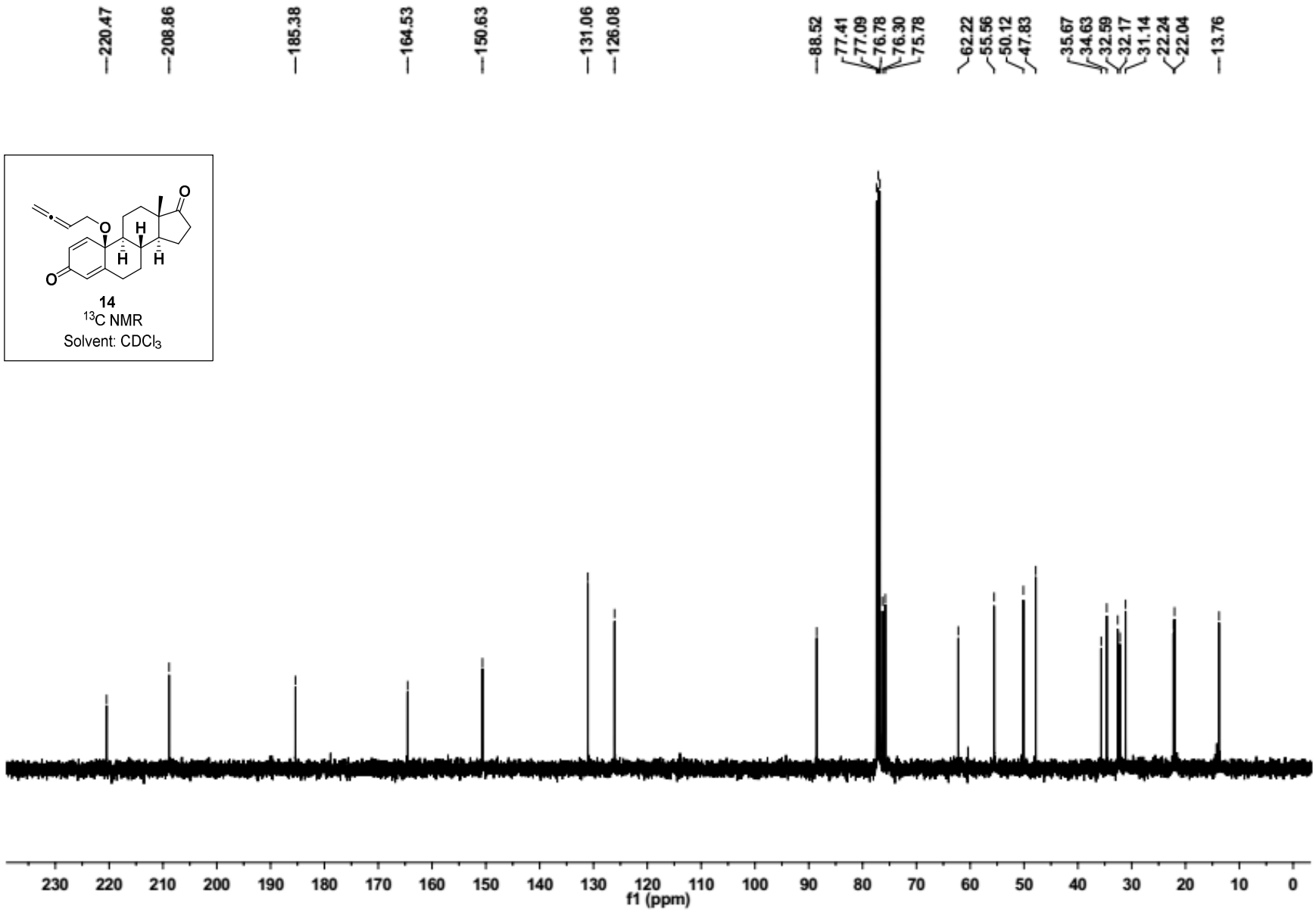
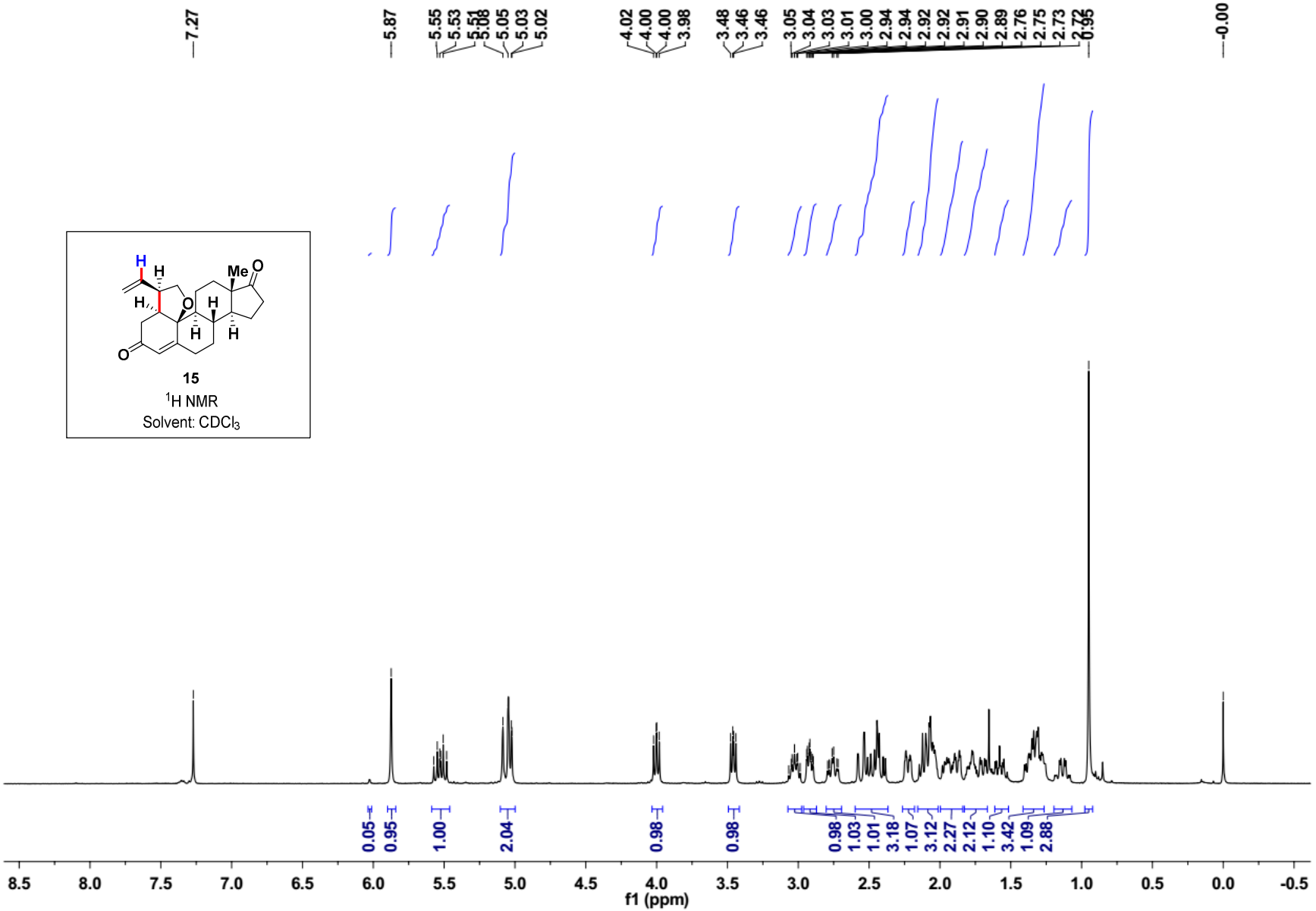
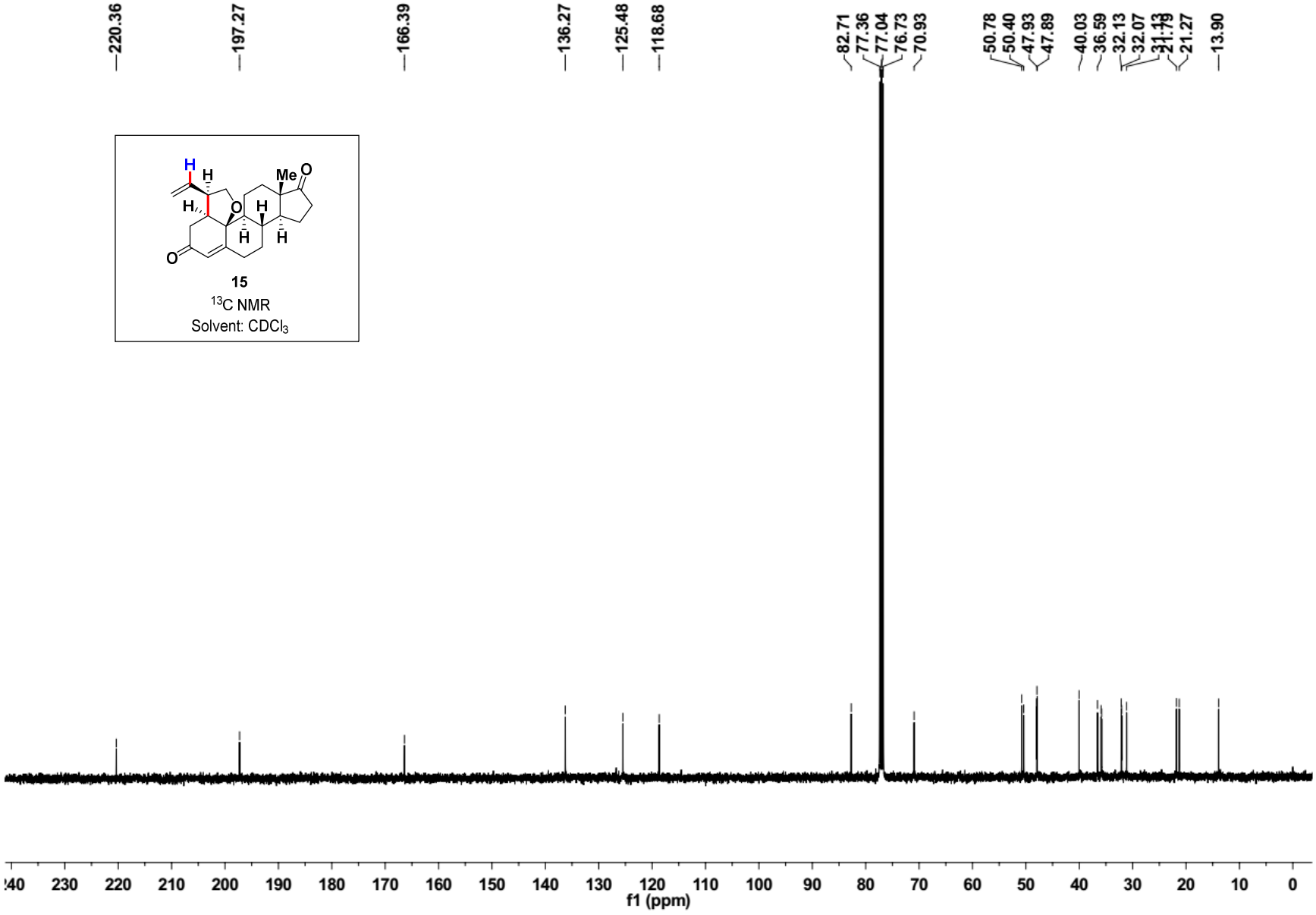
185.07
163.26
149.35
131.62
126.61
80.13
77.38
77.06
76.75
76.40
74.64
55.31
52.78
50.20
47.80
35.65
34.63
32.55
32.19
31.13
22.17
22.01
13.87
O
O
H
H
H
O
16
13C NMR
Solvent: CDCl3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.27
7.05
7.02
6.35
6.33
6.18
5.22
5.20
5.19
4.79
4.78
4.78
3.73
3.73
3.72
3.71
3.70
3.69
3.69
2.55
2.48
2.45
2.43
2.39
2.36
2.23
2.23
2.21
2.20
2.11
2.09
2.06
1.95
1.94
1.87
1.84
1.78
1.70
1.60
1.25
1.24
1.21
1.18
1.15
1.13
1.12
O
O
H
H
H
O
14
1H NMR
Solvent: CDCl3
0.91
0.09
0.92
0.85
0.97
2.00
1.98
3.03
1.13
2.91
1.25
1.21
1.03
1.14
4.35
2.78
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


220.47
208.86
185.38
164.53
150.63
131.06
126.08
88.52
77.41
77.09
76.78
76.30
75.78
62.22
55.56
50.12
47.83
35.67
34.63
32.59
32.17
31.14
22.24
22.04
13.76
O
O
H
H
H
O
14
13C NMR
Solvent: CDCl3
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)


7.27
5.87
5.55
5.53
5.51
5.08
5.05
5.03
5.02
4.02
4.00
4.00
3.98
3.48
3.46
3.46
3.05
3.04
3.03
3.01
3.00
2.94
2.94
2.92
2.92
2.91
2.90
2.89
2.76
2.75
2.73
2.72
0.95
-0.00
15
1H NMR
Solvent: CDCl3
0.05
0.95
1.00
2.04
0.98
0.98
0.98
1.03
1.01
3.18
1.07
3.12
2.27
2.12
1.10
3.42
1.09
2.88
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


220.36
197.27
166.39
136.27
125.48
118.68
82.71
77.36
77.04
76.73
70.93
50.78
50.40
47.93
47.89
40.03
36.59
32.13
32.07
31.13
21.79
21.27
13.90
H
H
H
Me
O
O
H
O
H
H
H
O
15
13C NMR
Solvent: CDCl3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)