Supporting Information

Enantioselective reductive cyclization of alkynals via cobalt catalysis

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1. General Information

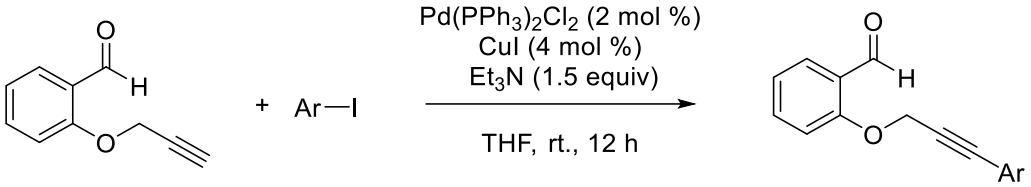
All reagents were purchased and used without further purification unless otherwise specified. Flash column chromatography was performed over silica gel (300-400 mesh) purchased from Shanghai Titan Scientific Co., Ltd. Commercial reagents were purchased from J&K, Energy, Titan, Bide Pharmatech or Haohong Scientific and used as received unless otherwise stated.

^{1}H, ^{13}C, ^{19}F NMR spectra were collected on a Bruker AV 400 MHz and 600 MHz NMR spectrometer using residue solvent peaks as an internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm, acetone-d_6 at 2.05 ppm, ^{13}C NMR: $CDCl_3$ at 77.0 ppm, $(CD_3)_2CO$ at 29.8 ppm). The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant *J* (Hz), and integration. High resolution mass spectra were acquired by Agilent 6545 Accurate-Mass Q-TOF LC/MS System. Specific Rotation was measured on Rudolph Research Analytical AUTOPOL IV Automatic Polarimeter. Enantiomeric excess was determined by chiral HPLC analysis on Shimadzu LC 40 and Agilent 1260 Infinity II LC System.

2. Substrate Preparation

Alkynals **1a-1b**[1], **1c**[2], **1d**[1], **1f-1g**[1], **1h**[3],**1j**[2],**1l**[3], **1m-1o**[1], **1q**[1], **1t**[1], **1w-1z**[1], **1aa**[2], **3a**[4], **3b**[5]and **3c**[6] are known compounds. They were prepared according to the literatures.

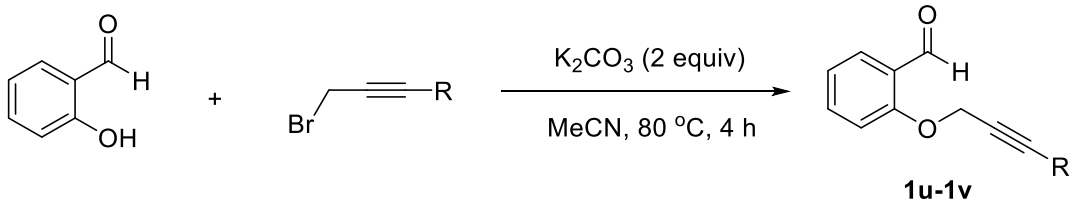
General Procedure A:



1e, 1i, 1k, 1p, 1r-1s

To a 100 mL flask equipped with a stir bar was added 2-(prop-2-yn-1-yloxy)benzaldehyde[7] (5.0 mmol, 1.0 equiv), aryl iodide (5.5 mmol, 1.1 equiv), $Pd(PPh_3)_2Cl_2$ (0.1 mmol, 0.02 equiv) and CuI (0.2 mmol, 0.04 equiv) under N_2 atmosphere. Then, triethylamine (7.5 mmol, 1.5 equiv) and THF (10 ml) were added to the reaction. The resulting mixture was stirred at room temperature for 12 hours. The reaction solution was quenched by saturated NH_4Cl (aq), extracted with EtOAc. The organic layer was washed with brine for three times. The resulting organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product.

General Procedure B:

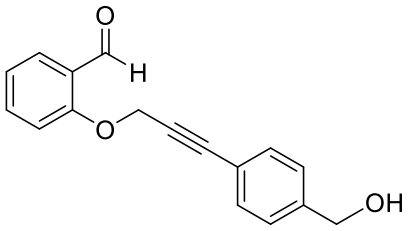


1u-1v

To a 100 mL flask equipped with a stir bar was charged with propargylic bromide (6.0 mmol, 1.2 equiv), salicylaldehyde (5.0 mmol, 1.0 equiv), K_2CO_3 (10

mmol, 2.0 equiv), and MeCN (10 mL). The mixture was initially stirred at 80 °C for 4 hours. After the reaction was complete, the reaction mixture was cooled to room temperature, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product

2-((3-(4-(Hydroxymethyl)phenyl)prop-2-yn-1-yl)oxy)benzaldehyde (1e)



1e

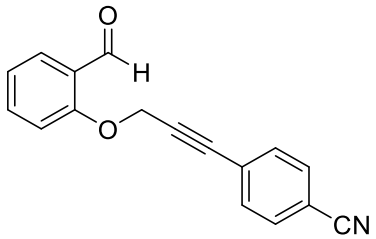
General Procedure A, R_f = 0.2 (petroleum ether/ethyl acetate = 5/1), yellow solid (711,9 mg, 53% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.52 (s, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 5.05 (s, 2H), 4.69 (s, 2H), 1.85 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 189.7, 160.1, 141.8, 135.7, 132.0, 128.5, 126.7, 125.5, 121.5, 121.0, 113.4, 87.9, 82.9, 64.8, 57.3.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{17}H_{15}O_3^{\oplus}$ 267.1016, found 267.1014.

4-(3-(2-Formylphenoxy)prop-1-yn-1-yl)benzonitrile (1i)



1i

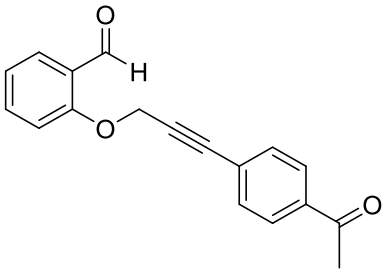
General Procedure A, R_f = 0.3 (petroleum ether/ethyl acetate = 5/1), yellow solid (1.008 g, 77% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.51 (s, 1H), 7.88 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.52 – 7.48 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.07 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 189.5, 159.7, 135.7, 132.3, 132.0, 128.7, 126.7, 125.6, 121.8, 118.2, 113.2, 112.3, 87.3, 86.2, 57.0.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{11}NNaO_2^{\oplus}$ 284.0682, found 284.0684.

2-((3-(4-Acetylphenyl)prop-2-yn-1-yl)oxy)benzaldehyde (1k)



1k

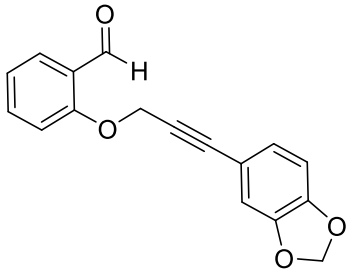
General Procedure A, R_f = 0.2 (petroleum ether/ethyl acetate = 5/1), yellow solid (1.045 g, 75% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.53 (s, 1H), 7.91 – 7.87 (m, 3H), 7.61 – 7.57 (m, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.08 (s, 2H), 2.59 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.2, 189.6, 159.9, 136.8, 135.8, 131.9, 128.7, 128.2, 126.6, 125.5, 121.7, 113.3, 87.1, 86.1, 57.1, 26.6.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{18}H_{15}O_3^{\oplus}$ 279.1016, found 279.1018.

2-((3-(Benzo[*d*][1,3]dioxol-5-yl)prop-2-yn-1-yl)oxy)benzaldehyde (1p)



1p

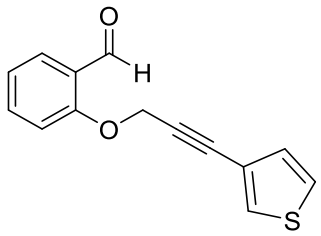
General Procedure A, R_f = 0.5 (petroleum ether/ethyl acetate = 5/1), yellow solid (860 mg, 61% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.52 (s, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.21 – 7.17 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.86 (d, *J* = 1.5 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 5.97 (s, 2H), 5.02 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 189.7, 160.1, 148.4, 147.4, 135.7, 128.5, 126.7, 125.6, 121.5, 115.0, 113.4, 111.7, 108.5, 101.4, 88.0, 81.3, 57.3.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{12}NaO_4^{\oplus}$ 303.0628, found 303.0631.

2-((3-(Thiophen-3-yl)prop-2-yn-1-yl)oxy)benzaldehyde (1r)



1r

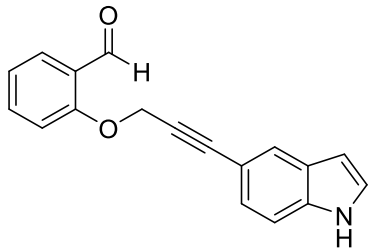
General Procedure A, R_f = 0.6 (petroleum ether/ethyl acetate = 5/1), yellow solid (856.2 mg, 71% yield).

^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 10.49 (s, 1H), 7.78 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.69 – 7.66 (m, 1H), 7.53 – 7.49 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.16 – 7.11 (m, 2H), 5.20 (s, 2H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 189.3, 161.0, 136.7, 131.0, 130.5, 128.5, 127.1, 126.5, 122.3, 121.9, 115.0, 84.0, 83.5, 58.0.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{14}H_{10}NaO_2S^{\oplus}$ 265.0294, found 265.0297.

2-((3-(1*H*-Indol-5-yl)prop-2-yn-1-yl)oxy)benzaldehyde (1s)



1s

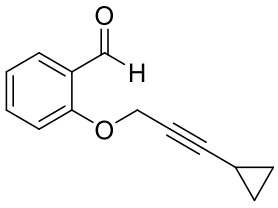
General Procedure A, R_f = 0.2 (petroleum ether/ethyl acetate = 10/1), yellow solid (311.3 mg, 23% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.55 (s, 1H), 8.35 (s, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.76 (s, 1H), 7.61 – 7.56 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.26 – 7.24 (m, 2H), 7.23 – 7.21 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.54 – 6.49 (m, 1H), 5.07 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 189.9, 160.3, 135.8, 135.7, 128.4, 127.6, 125.6, 125.5, 125.3, 125.0, 121.3, 113.6, 112.9, 111.1, 102.8, 89.8, 80.4, 57.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{13}NNaO_2^{\oplus}$ 298.0838, found 298.0843.

2-((3-Cyclopropylprop-2-yn-1-yl)oxy)benzaldehyde (1u)



1u

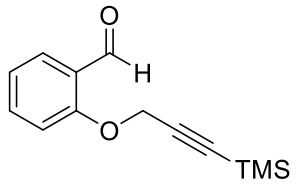
General Procedure B, R_f = 0.6 (petroleum ether/ethyl acetate = 10/1), yellow solid (717 mg, 72% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.48 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.12 – 7.03 (m, 2H), 4.77 (d, *J* = 1.8 Hz, 2H), 1.31 – 1.20 (m, 1H), 0.81 – 0.73 (m, 2H), 0.73 – 0.65 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 189.8, 160.2, 135.6, 128.3, 125.4, 121.3, 113.4, 92.4, 69.3, 57.2, 8.3, -0.6.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{13}H_{13}O_2^{\oplus}$ 201.0910, found 201.0913.

2-((3-(Trimethylsilyl)prop-2-yn-1-yl)oxy)benzaldehyde (1v)



1v

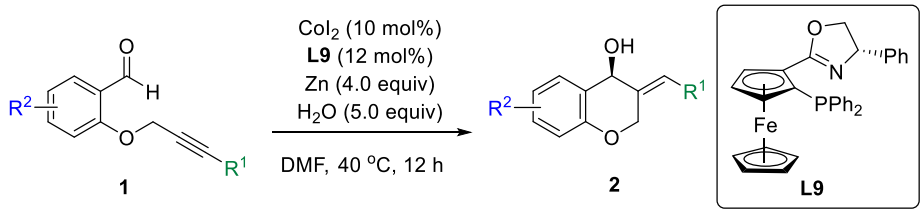
General Procedure B, R_f = 0.6 (petroleum ether/ethyl acetate = 20/1), yellow solid (1.124 g, 97% yield)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.48 (s, 1H), 7.85 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 4.80 (s, 2H), 0.16 (s, 9H).

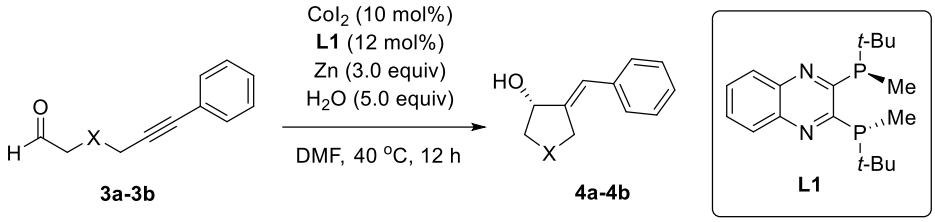
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 189.7, 160.0, 135.6, 128.3, 125.5, 121.5, 113.5, 99.0, 94.0, 57.4, -0.4.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{13}H_{17}O_2Si^{\oplus}$ 233.0992, found 233.0997.

3. Substrate Scope of Alkynals

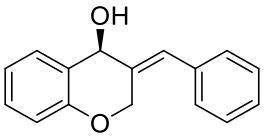


General Procedure C: In a glove box, an oven-dried 4-mL vial was charged with alkynals **1** (0.2 mmol, 1.0 equiv), CoI_2 (0.02 mmol, 0.1 equiv), **L9** (0.024 mmol, 0.12 equiv), Zn (0.8 mmol, 4.0 equiv), H_2O (1.0 mmol, 5.0 equiv) and DMF (2.0 mL). The vial was capped and removed from the glove box. The reaction mixture was placed in a pre-heated block and stirred at 40 °C for 12 h. Then the reaction mixture was cooled to room temperature, water was added and the organic layer was extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product **2**.



General Procedure D: In a glove box, an oven-dried 4-mL vial was charged with alkynals **3a-3b** (0.2 mmol, 1.0 equiv), CoI_2 (0.02 mmol, 0.1 equiv), **L1** (0.024 mmol, 0.12 equiv), Zn (0.6 mmol, 3.0 equiv), H_2O (1.0 mmol, 5.0 equiv) and DMF (2.0 mL). The vial was capped and removed from the glove box. The reaction mixture was placed in a pre-heated block and stirred at 40 °C for 12 h. Then the reaction mixture was cooled to room temperature and the organic layer was extracted with EtOAc. Then the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired products **4a-4b**.

(*S*,*E*)-3-Benzylidenechroman-4-ol (2a)



2a

General Procedure C, R_f = 0.4 (petroleum ether/ethyl acetate = 5/1), yellow solid (45.6 mg, 96% yield).

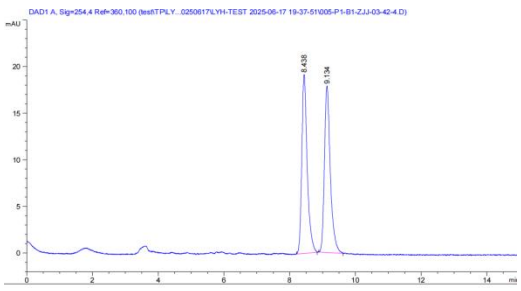
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.39 (d, *J* = 6.2 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.30 – 7.26 (m, 1H), 7.23 – 7.19 (m, 3H), 6.96 (td, *J* = 7.5, 1.1 Hz, 1H), 6.90 (s, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 5.16 (s, 1H), 4.92 – 4.86 (m, 2H), 2.33 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 154.4, 135.6, 134.6, 129.7, 129.03, 128.96, 128.8, 128.4, 127.5, 124.9, 121.1, 116.9, 69.2, 62.7.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{14}NaO_2^{\oplus}$ 261.0886, found 261.0885.

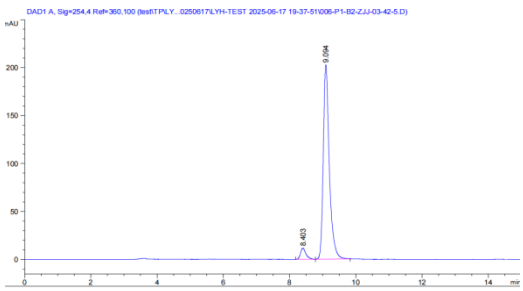
Specific Rotation: $[\alpha]_D^{26.1}$ –116.4 (*c* 0.71, MeOH) for 90% *ee*.

Chiral HPLC analysis: Chiralpak IG-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 0.5 mL/min; Retention time: 9.1 min (major), 8.4 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

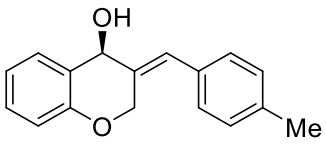
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.438	BB	0.1618	220.05583	19.18101	49.6965
2	9.134	BB	0.1763	222.74364	17.87976	50.3035



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.403	BB	0.1481	132.85924	11.68987	4.9393
2	9.094	BB	0.1893	2556.99512	202.52792	95.0607

(*S*,*E*)-3-(4-Methylbenzylidene)chroman-4-ol (2b)



2b

General Procedure C, R_f = 0.4 (petroleum ether/ethyl acetate = 5/1), white solid (43 mg, 85% yield).

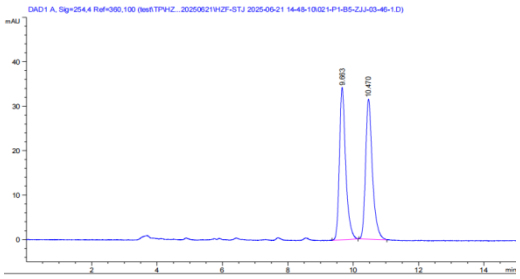
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.86 (s, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 5.14 (s, 1H), 4.92 (d, *J* = 12.4 Hz, 1H), 4.88 (d, *J* = 12.4 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 154.4, 137.4, 133.9, 132.7, 129.7, 129.09, 129.07, 129.01, 128.8, 125.0, 121.0, 116.9, 69.3, 62.8, 21.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{16}NaO_2^{\oplus}$ 275.1043, found 275.1042.

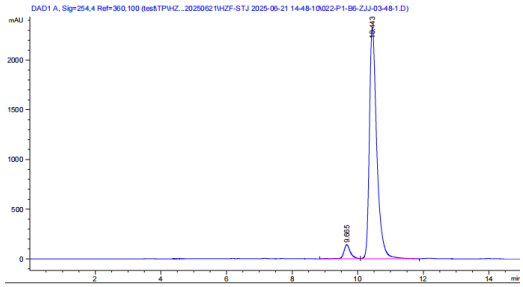
Specific Rotation: $[\alpha]_D^{26.9}$ –139.5 (*c* 0.87, MeOH) for 90% *ee*.

Chiral HPLC analysis: Chiralpak IG-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 0.5 mL/min; Retention time: 10.4 min (major), 9.7 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

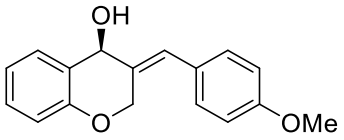
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.663	BB	0.1935	457.06085	34.28341	49.9932
2	10.470	BB	0.2050	457.18433	31.47582	50.0068



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.665	VV R	0.2060	1963.09119	140.90947	5.1244
2	10.443	VB	0.2091	3.63458e4	2321.66235	94.8756

(*S*,*E*)-3-(4-Methoxybenzylidene)chroman-4-ol (2c)



2c

General Procedure C, R_f = 0.3 (petroleum ether/ethyl acetate = 5/1), yellow solid (50.6 mg, 94% yield).

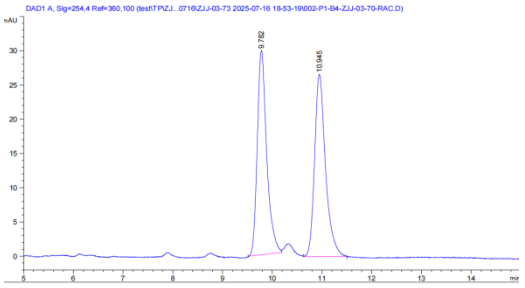
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.19 – 7.15 (m, 1H), 6.97 – 6.95 (m, 2H), 6.93 (td, *J* = 7.5, 1.1 Hz, 1H), 6.89 (s, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.19 (d, *J* = 5.4 Hz, 1H), 4.95 (d, *J* = 0.9 Hz, 2H), 4.76 (d, *J* = 5.5 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 160.0, 155.3, 135.2, 131.0, 130.0, 129.7, 129.4, 127.8, 127.4, 121.3, 117.1, 114.7, 69.2, 63.7, 55.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{16}NaO_3^{\oplus}$ 291.0992, found 291.0991.

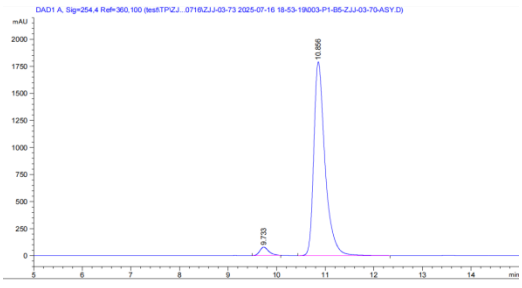
Specific Rotation: $[\alpha]_D^{27.1}$ –135.5 (*c* 1.14, MeOH) for 93% *ee*.

Chiral HPLC analysis: Chiralpak IG-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 70/30; flow rate = 0.5 mL/min; Retention time: 10.9 min (major), 9.7 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

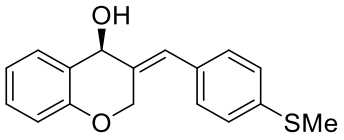
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.782	MM R	0.2195	392.69614	29.81519	49.2177
2	10.945	BV R	0.2152	405.17896	26.60192	50.7823



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.733	MM R	0.2155	1014.19873	78.45162	3.4119
2	10.856	VB	0.2371	2.87114e4	1790.44519	96.5881

(*S*,*E*)-3-(4-(Methylthio)benzylidene)chroman-4-ol (2d)



2d

General Procedure C, R_f = 0.3 (petroleum ether/ethyl acetate = 5/1), yellow solid (45.3 mg, 80% yield).

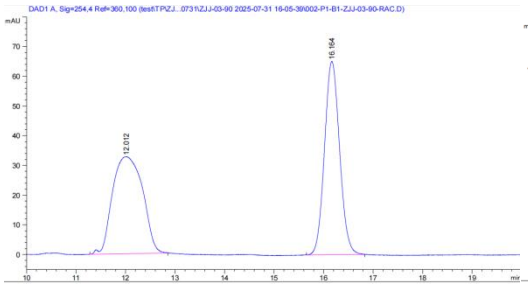
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.43 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.26 – 7.22 (m, 2H), 7.19 – 7.15 (m, 1H), 6.93 (td, *J* = 7.5, 1.1 Hz, 1H), 6.91 (s, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.22 (s, 1H), 4.97 – 4.91 (m, 2H), 2.51 (s, 3H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.3, 138.9, 136.6, 133.7, 130.3, 129.9, 129.7, 127.43, 127.38, 126.9, 121.4, 117.0, 69.1, 63.7, 15.3.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{16}NaO_2S^{\oplus}$ 307.0763, found 307.0766.

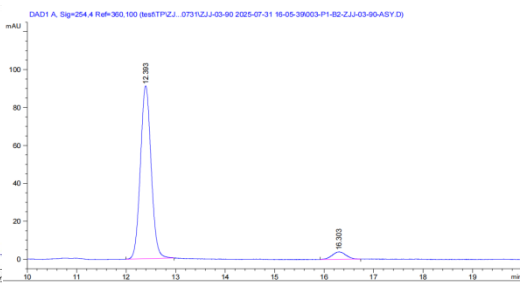
Specific Rotation: $[\alpha]_D^{26.0}$ –117.1 (*c* 0.52, MeOH) for 90% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 12.4 min (major), 16.3 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

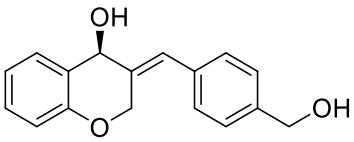
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.012	VB R	0.4951	1382.88977	32.61965	50.0945
2	16.164	BV R	0.2755	1377.67017	65.07388	49.9055



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.393	BV R	0.2253	1372.75525	91.09546	94.8184
2	16.303	BV R	0.2249	75.01808	3.93484	5.1816

(*S*,*E*)-3-(4-(Hydroxymethyl)benzylidene)chroman-4-ol (2e)



2e

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 2/1), yellow solid (40.6 mg, 76% yield).

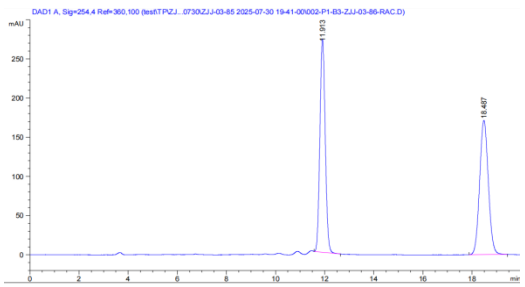
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.44 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.15 (m, 1H), 6.96 – 6.91 (m, 2H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.23 (s, 1H), 4.95 (d, *J* = 12.5 Hz, 1H), 4.93 (d, *J* = 12.5 Hz, 1H), 4.65 (s, 2H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.2, 142.6, 136.4, 135.7, 129.9, 129.7, 129.5, 127.9, 127.5, 127.4 ,121.4, 117.0, 69.1, 64.3, 63.7.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{16}NaO_3^{\oplus}$ 291.0992, found 291.0987.

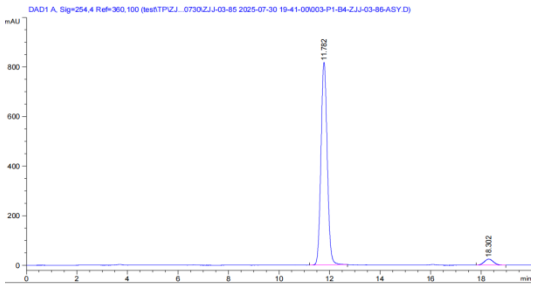
Specific Rotation: $[\alpha]_D^{27.0}$ –124.5 (*c* 0.20, MeOH) for 92% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 0.5 mL/min; Retention time: 11.8 min (major), 18.3 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

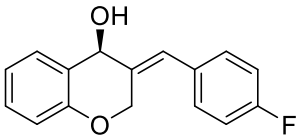
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.913	BV R	0.2345	4115.43848	271.98370	49.4751
2	18.487	VV R	0.3370	4202.76123	171.44339	50.5249



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.782	BV R	0.2678	1.41065e4	817.72516	95.8324
2	18.302	BB	0.2976	613.47406	24.29711	4.1676

(*S*,*E*)-3-(4-Fluorobenzylidene)chroman-4-ol (2f)



2f

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 5/1), white solid (44.5 mg, 87% yield).

^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.44 (d, *J* = 6.5 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.20 – 7.14 (m, 3H), 6.95 – 6.91 (m, 2H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.23 (s, 1H), 4.93 (d, *J* = 12.5 Hz, 1H), 4.89 (d, *J* = 12.5 Hz, 1H).

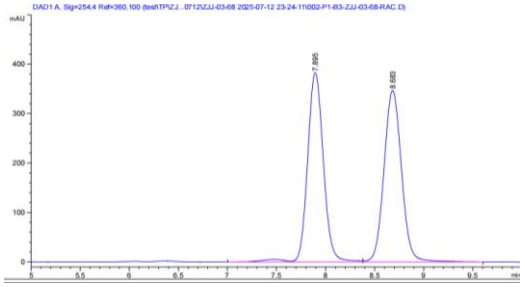
^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 162.8 (d, *J* = 243.7 Hz), 155.2, 137.0, 133.4 (d, *J* = 3.2 Hz), 131.7 (d, *J* = 7.8 Hz), 129.9, 129.7, 127.4, 126.8, 121.5, 117.1, 116.1 (d, *J* = 21.6 Hz), 69.0, 63.6.

^{19}F NMR (376 MHz, Acetone-d_6) δ (ppm) -116.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{13}FNaO_2^{\oplus}$ 279.0792, found 279.0789.

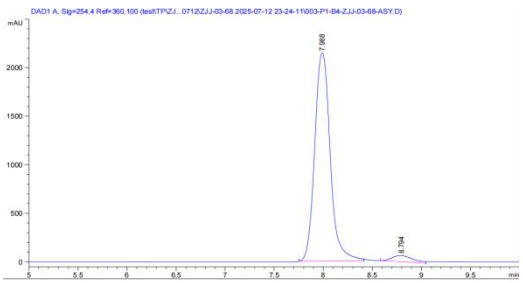
Specific Rotation: $[\alpha]_D^{26.2}$ –118.7 (*c* 0.57, MeOH) for 93% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 8.0 min (major), 8.8 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

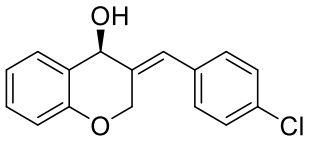
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.895	VV R	0.1714	4324.05127	382.87643	50.1070
2	8.683	VB	0.1924	4305.58301	346.55066	49.8930



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.988	MM R	0.1829	2.35240e4	2143.10156	96.2798
2	8.794	MM R	0.2410	908.96790	62.86190	3.7202

(*S*,*E*)-3-(4-Chlorobenzylidene)chroman-4-ol (2g)



2g

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 5/1), white solid (50 mg, 92% yield).

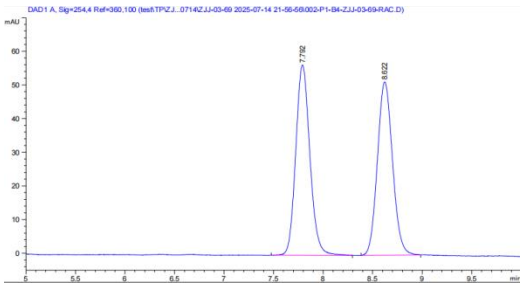
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.45 – 7.41 (m, 3H), 7.31 – 7.29 (m, 2H), 7.19 – 7.15 (m, 1H), 6.95 – 6.92 (m, 2H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.25 (d, *J* = 5.7 Hz, 1H), 4.95 – 4.87 (m, 3H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.2, 137.8, 135.9, 133.5, 131.4, 129.8, 129.7, 129.4, 127.4, 126.5, 121.5, 117.0, 69.0, 63.7.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{13}ClNaO_2^{\oplus}$ 295.0496, found 295.0498.

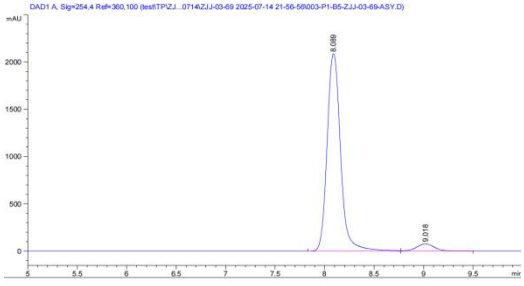
Specific Rotation: $[\alpha]_D^{25.7}$ –116.2 (*c* 0.55, MeOH) for 91% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 8.1 min (major), 9.0 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

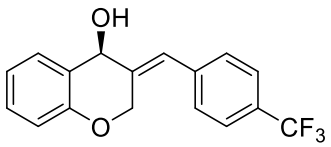
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.792	BV R	0.1510	562.61060	56.58480	50.6804
2	8.622	BV R	0.1644	547.50446	51.54173	49.3196



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.089	MF R	0.1534	1.96979e4	2086.55469	95.3825
2	9.018	FM R	0.2097	953.58167	75.77769	4.6175

(*S*,*E*)-3-(4-(Trifluoromethyl)benzylidene)chroman-4-ol (2h)



2h

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 5/1), white solid (49.2 mg, 80% yield).

^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.75 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.03 (s, 1H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 5.31 (s, 1H), 4.96 (d, *J* = 12.7 Hz, 1H), 4.90 (d, *J* = 12.7 Hz, 1H).

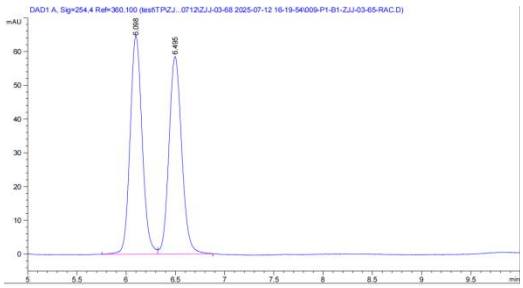
^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.2, 141.3, 139.2, 130.4, 129.8, 129.7, 129.5 (q, *J* = 31.8 Hz), 127.4, 126.22, 126.19 (q, *J* = 4.2 Hz), 125.4 (q, *J* = 269.5 Hz), 121.6, 117.1, 68.9, 63.8.

^{19}F NMR (376 MHz, Acetone-d_6) δ (ppm) -63.0.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{13}F_3NaO_2^{\oplus}$ 329.0760, found 329.0757.

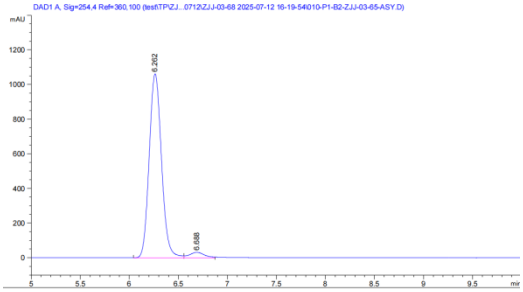
Specific Rotation: $[\alpha]_D^{26.5}$ –85.3 (*c* 0.22, MeOH) for 93% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 6.3 min (major), 6.7 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

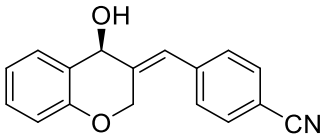
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.098	VV R	0.1316	549.41528	64.68705	51.0609
2	6.495	VB	0.1390	526.58569	58.52719	48.9391



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.262	MF R	0.1456	9287.74902	1063.19568	96.2991
2	6.688	FM R	0.1808	356.94504	32.90912	3.7009

(*S*,*E*)-4-((4-Hydroxychroman-3-ylidene)methyl)benzonitrile (2i)



2i

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 3/1), yellow solid (41.3 mg, 79% yield).

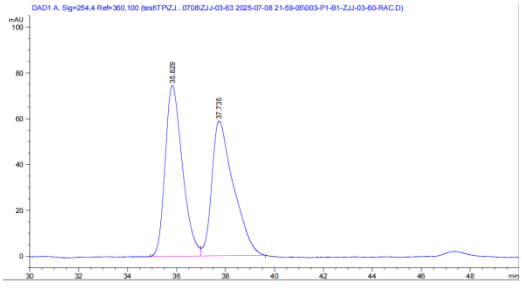
^{1}H NMR (400 MHz, Acetone-d_6) δ (ppm) 7.80 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 7.1 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.01 (s, 1H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.31 (d, *J* = 4.6 Hz, 1H), 4.98 (s, 1H), 4.95 (d, *J* = 12.7 Hz, 1H), 4.89 (d, *J* = 12.7 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ (ppm) 155.1, 142.0, 139.9, 133.1, 130.6, 129.8, 129.6, 127.4, 126.0, 121.7, 119.3, 117.0, 111.6, 68.9, 63.9.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{13}NNaO_2^{\oplus}$ 286.0838, found 286.0839.

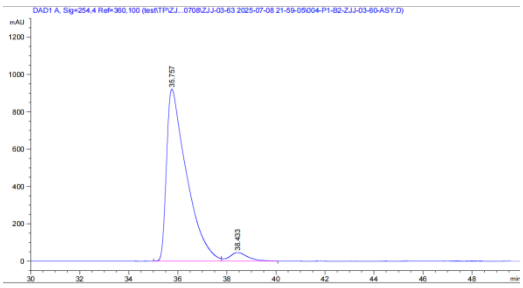
Specific Rotation: $[\alpha]_D^{27.3}$ –83.5 (*c* 0.43, MeOH) for 91% *ee*.

Chiral HPLC analysis: Chiralpak ID-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 35.8 min (major), 38.4 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

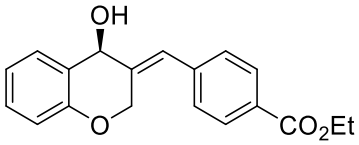
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.829	BV	0.5748	3655.15210	74.70382	50.2073
2	37.735	VB	0.7220	3624.97217	58.82319	49.7927



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.757	MF R	0.9441	5.21389e4	920.41180	95.6215
2	38.433	FM R	0.8668	2387.42847	45.90590	4.3785

Ethyl (*S*,*E*)-4-((4-hydroxychroman-3-ylidene)methyl)benzoate (2j)



2j

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 5/1), yellow solid (55.6 mg, 90% yield).

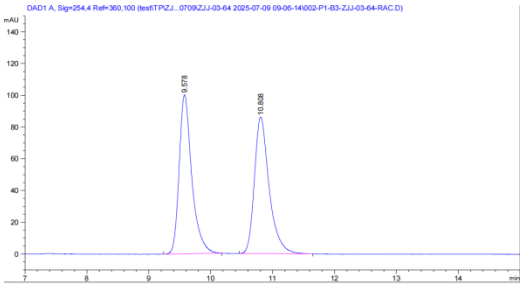
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 8.06 – 8.02 (m, 2H), 7.46 (d, *J* = 6.5 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.15 (m, 1H), 7.02 (s, 1H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.29 (s, 1H), 4.97 (d, *J* = 12.6 Hz, 1H), 4.92 (d, *J* = 12.6 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 166.5, 155.2, 141.8, 138.9, 130.3, 130.2, 129.8, 129.73, 129.69, 127.4, 126.7, 121.6, 117.0, 69.0, 63.9, 61.5, 14.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{18}NaO_4^{\oplus}$ 333.1097, found 333.1100.

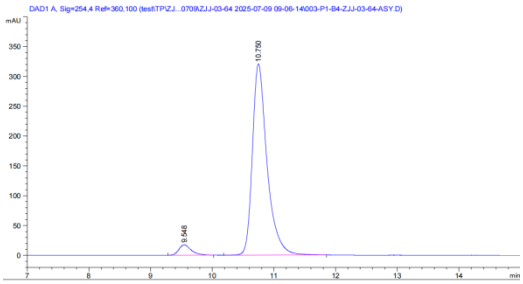
Specific Rotation: $[\alpha]_D^{26.5}$ –84.8 (*c* 0.45, MeOH) for 91% *ee*.

Chiral HPLC analysis: Chiralpak IG-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 70/30; flow rate = 0.5 mL/min; Retention time: 10.8 min (major), 9.5 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

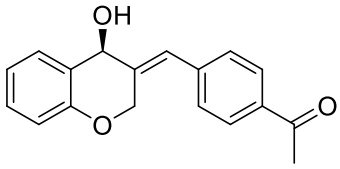
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.578	BB	0.2082	1422.09082	100.12384	49.9967
2	10.808	BB	0.2431	1422.27881	86.13542	50.0033



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.548	BB	0.1992	246.15276	17.49060	4.4409
2	10.750	BB	0.2488	5296.66699	320.51617	95.5591

(*S*,*E*)-1-(4-((4-Hydroxychroman-3-ylidene)methyl)phenyl)ethan-1-one (2k)



2k

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 5/1), white solid (44.7 mg, 80% yield).

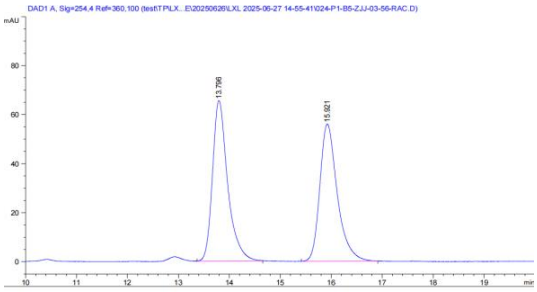
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 8.01 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 6.7 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.17 (m, 1H), 7.01 (s, 1H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 5.29 (d, *J* = 5.7 Hz, 1H), 4.97 (d, *J* = 12.7 Hz, 1H), 4.95 (d, *J* = 5.8 Hz, 1H), 4.92 (d, *J* = 12.7 Hz, 1H), 2.59 (s, 3H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 197.5, 155.2, 141.8, 138.9, 136.9, 129.9, 129.74, 129.68, 129.5, 127.4, 126.8, 121.6, 117.0, 69.0, 63.9, 26.7

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{16}NaO_3^{\oplus}$ 303.0992, found 303.0990.

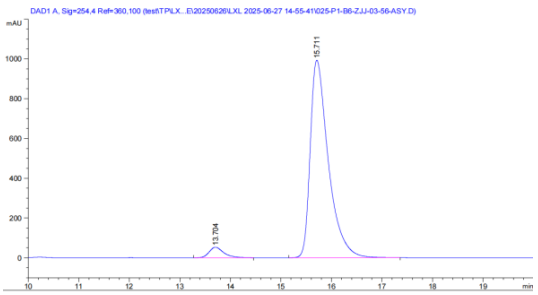
Specific Rotation: $[\alpha]_D^{26.8}$ –89.5 (*c* 0.22, MeOH) for 92% *ee*.

Chiral HPLC analysis: Chiralpak IG-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 70/30; flow rate = 0.5 mL/min; Retention time: 15.7 min (major), 13.7 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

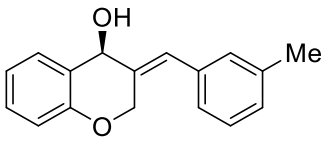
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.796	BB	0.2986	1352.61499	65.44310	50.4080
2	15.921	BV R	0.3108	1330.71692	55.98386	49.5920



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.704	BB	0.2720	1064.87305	52.98423	4.1399
2	15.711	BB	0.3631	2.46574e4	993.28900	95.8601

(*S*,*E*)-3-(3-Methylbenzylidene)chroman-4-ol (2l)



2l

General Procedure C, R_f = 0.3 (petroleum ether/ethyl acetate = 5/1), yellow solid (40.4 mg, 80% yield).

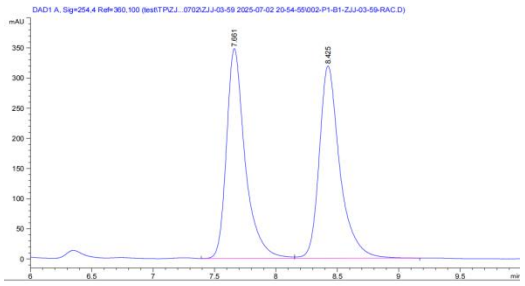
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.44 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.95 – 6.91 (m, 2H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.23 (s, 1H), 4.95 (d, *J* = 12.4 Hz, 1H), 4.92 (d, *J* = 12.4 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.3, 138.8, 137.0, 136.6, 130.3, 129.9, 129.7, 129.2, 128.8, 128.1, 127.4, 126.8, 121.4, 117.0, 69.1, 63.7, 21.4.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{16}NaO_2^{\oplus}$ 275.1043, found 275.1042.

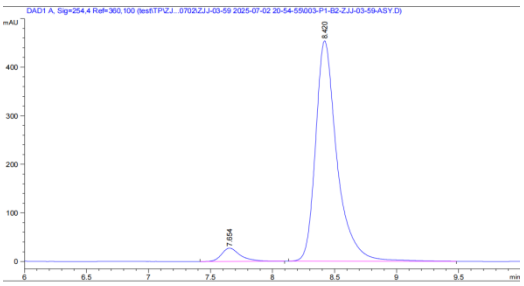
Specific Rotation: $[\alpha]_D^{26.0}$ –97.3 (*c* 0.65, MeOH) for 90% *ee*.

Chiral HPLC analysis: Chiralpak IG-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 0.5 mL/min; Retention time: 8.4 min (major), 7.7 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

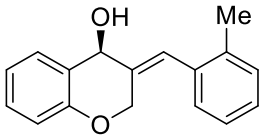
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.661	VV	0.1568	3680.14282	348.09549	49.7359
2	8.425	VB	0.1740	3719.22583	319.07211	50.2641



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.654	BB	0.1539	285.94928	27.37024	4.9885
2	8.420	BB	0.1786	5446.25586	453.54535	95.0115

(*S*,*E*)-3-(2-Methylbenzylidene)chroman-4-ol (2m)



2m

General Procedure C, R_f = 0.4 (petroleum ether/ethyl acetate = 5/1), white solid (42.3 mg, 84% yield).

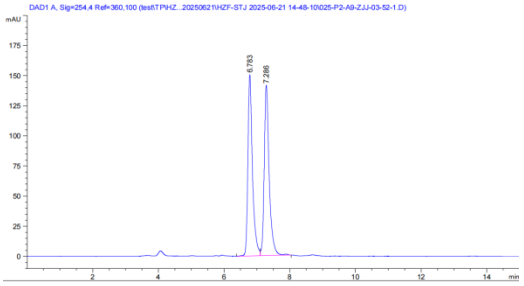
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.41 (d, *J* = 6.7 Hz, 1H), 7.23 – 7.16 (m, 4H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.90 (s, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 5.19 (s, 1H), 4.78 (d, *J* = 12.3 Hz, 1H), 4.72 (d, *J* = 12.3 Hz, 1H), 2.36 (s, 1H), 2.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 154.4, 136.6, 134.6, 134.5, 130.0, 129.7, 129.2, 128.3, 127.8, 125.7, 124.8, 121.0, 116.9, 68.9, 62.8, 19.9.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{16}NaO_2^{\oplus}$ 275.1043, found 275.1041.

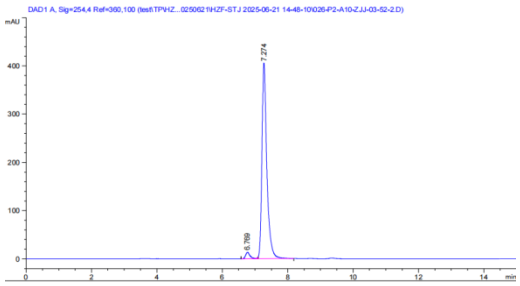
Specific Rotation: $[\alpha]_D^{26.0}$ –126.4 (*c* 0.45, MeOH) for 94% *ee*.

Chiral HPLC analysis: Chiralpak IG-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 0.5 mL/min; Retention time: 7.3 min (major), 6.8 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

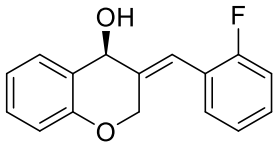
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.783	BV	0.1432	1453.63391	150.48924	49.5446
2	7.286	VV R	0.1556	1480.35400	141.47134	50.4554



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.769	BV E	0.1385	131.34909	13.61605	2.9947
2	7.274	VB R	0.1555	4254.64307	405.34253	97.0053

(*S*,*E*)-3-(2-Fluorobenzylidene)chroman-4-ol (2n)



2n

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 5/1), white solid (43.7 mg, 85% yield).

^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.47 (d, *J* = 7.3 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.15 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.93 (s, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 5.32 (d, *J* = 5.0 Hz, 1H), 4.98 (d, *J* = 5.7 Hz, 1H), 4.89 (d, *J* = 12.5 Hz, 1H), 4.80 (d, *J* = 12.5 Hz, 1H).

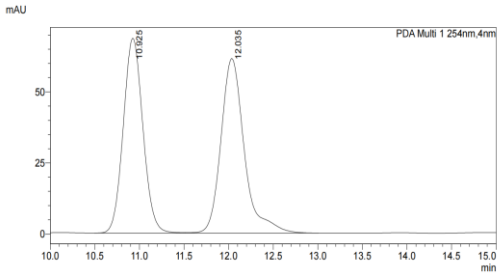
^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 161.0 (d, *J* = 244.3 Hz), 155.2, 139.1 ,131.82 (d, *J* = 2.9 Hz), 130.5 (d, *J* = 8.3 Hz), 129.8, 129.7, 127.2, 125.1 (d, *J* = 3.2 Hz), 124.6 (d, *J* = 14.9 Hz), 121.5, 120.4 (d, *J* = 2.1 Hz), 117.0, 116.3 (d, *J* = 22.0 Hz), 68.8, 64.0.

^{19}F NMR (565 MHz, Acetone-d_6) δ (ppm) -116.3.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{13}FNaO_2^{\oplus}$ 279.0792, found 279.0792.

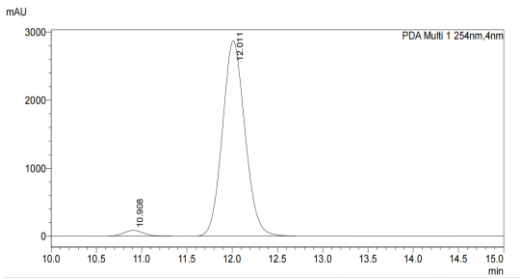
Specific Rotation: $[\alpha]_D^{21.5}$ –91.2 (*c* 0.61, MeOH) for 95% *ee*.

Chiral HPLC analysis: Chiralpak AD-H Column (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 1 mL/min; Retention time: 12.0 min (major), 10.9 min (minor).



PDA Ch1 254nm

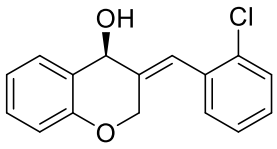
Peak#	Ret. Time	Area	Area%
1	10.925	1049364	48.454
2	12.035	1116339	51.546



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.908	1294738	2.547
2	12.011	49537263	97.453

(*S*,*E*)-3-(2-Chlorobenzylidene)chroman-4-ol (2o)



2o

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 5/1), white solid (46.9 mg, 86% yield).

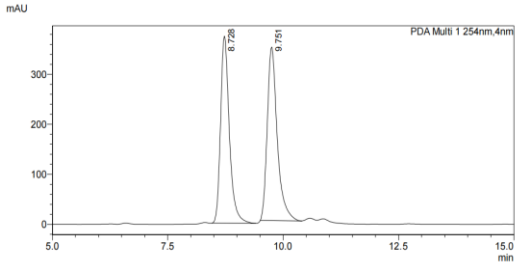
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.48 (t, *J* = 7.3 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.01 (s, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.34 (d, *J* = 5.2 Hz, 1H), 4.97 (d, *J* = 5.8 Hz, 1H), 4.87 (d, *J* = 12.4 Hz, 1H), 4.76 (d, *J* = 12.4 Hz, 1H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.2, 138.5, 135.3, 134.3, 131.9, 130.4, 130.1, 129.9, 129.7, 127.9, 127.2, 124.8, 121.5, 117.0, 68.8, 63.8.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{13}ClNaO_2^{\oplus}$ 295.0496, found 295.0494.

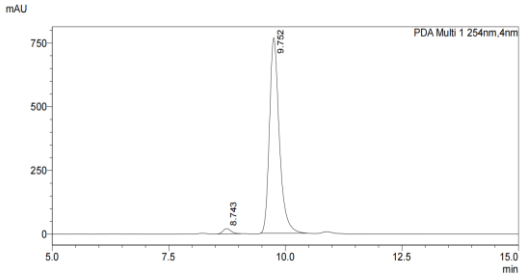
Specific Rotation: $[\alpha]_D^{22.0}$ –73.9 (*c* 0.40, MeOH) for 96% *ee*.

Chiral HPLC analysis: Chiralpak IA Column (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 1.0 mL/min; Retention time: 9.8 min (major), 8.7 min (minor).



PDA Ch1 254nm

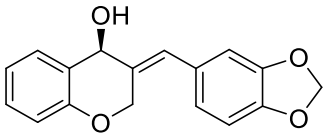
Peak#	Ret. Time	Area	Area%
1	8.728	4942363	48.557
2	9.751	5236085	51.443



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.743	241415	2.098
2	9.752	11267992	97.902

(*S*,*E*)-3-(Benzo[*d*][1,3]dioxol-5-ylmethylene)chroman-4-ol (2p)



2p

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 5/1), yellow solid (50 mg, 89% yield).

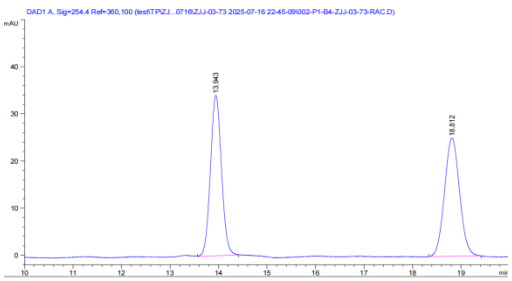
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.42 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.14 (m, 1H), 6.93 (td, *J* = 7.5, 1.2 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.86 (s, 1H), 6.80 – 6.75 (m, 3H), 6.02 (s, 2H), 5.19 (s, 1H), 4.96 – 4.91 (m, 2H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.3, 148.8, 147.9, 135.8, 131.0, 129.9, 129.7, 127.8, 127.4, 123.5, 121.4, 117.1, 109.8, 109.0, 102.2, 69.1, 63.7

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{14}NaO_4^{\oplus}$ 305.0784, found 305.0785.

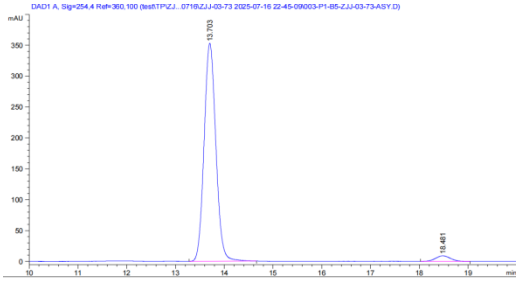
Specific Rotation: $[\alpha]_D^{27.6}$ –129.3 (*c* 0.86, MeOH) for 94% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 13.7 min (major), 18.5 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

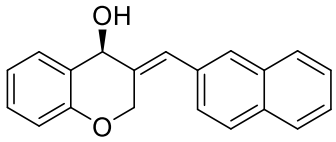
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.943	BB	0.1997	536.05688	34.05160	49.8655
2	18.812	BV R	0.2604	538.94818	25.11045	50.1345



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.703	BB	0.2598	5908.39355	352.99463	96.8484
2	18.481	VV R	0.2511	192.26656	9.02331	3.1516

(*S*,*E*)-3-(Naphthalen-2-ylmethylene)chroman-4-ol (2q)



2q

General Procedure C, R_f = 0.3 (petroleum ether/ethyl acetate = 5/1), yellow solid (43.1 mg, 75% yield).

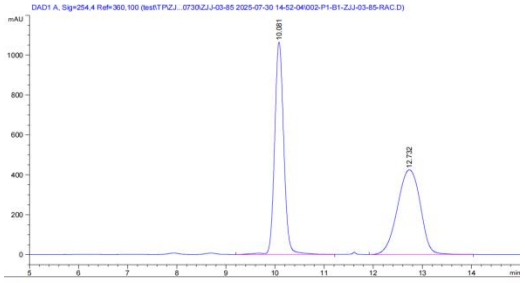
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.93 – 7.88 (m, 3H), 7.78 (s, 1H), 7.53 – 7.49 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.12 (s, 1H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.30 (s, 1H), 5.05 (d, *J* = 12.6 Hz, 1H), 5.02 (d, *J* = 12.6 Hz, 1H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.2, 137.3, 134.6, 134.3, 133.4, 129.9, 129.7, 128.9, 128.8, 128.5, 128.4, 127.9, 127.8, 127.4, 127.2, 127.0, 121.4, 117.1, 69.1, 63.9.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{20}H_{16}NaO_2^{\oplus}$ 3111.1043, found 311.1042.

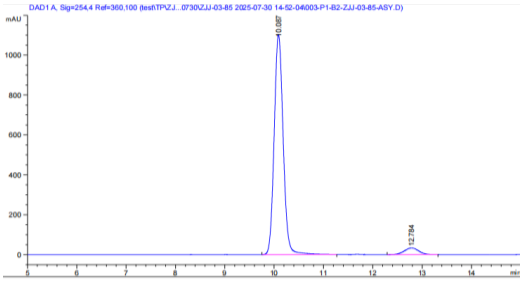
Specific Rotation: $[\alpha]_D^{26.8}$ –148.5 (*c* 0.30, MeOH) for 91% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 10.1 min (major), 12.8 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

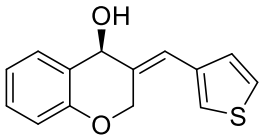
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.081	VB R	0.1984	1.37120e4	1064.76196	49.9190
2	12.732	BB	0.4787	1.37565e4	424.39777	50.0810



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.087	BV R	0.1958	1.39521e4	1101.55066	95.5082
2	12.784	BB	0.2382	656.16998	32.76242	4.4918

(*S*,*E*)-3-(Thiophen-3-ylmethylene)chroman-4-ol (2r)



2r

General Procedure C, R_f = 0.3 (petroleum ether/ethyl acetate = 5/1), yellow solid (30 mg, 61% yield).

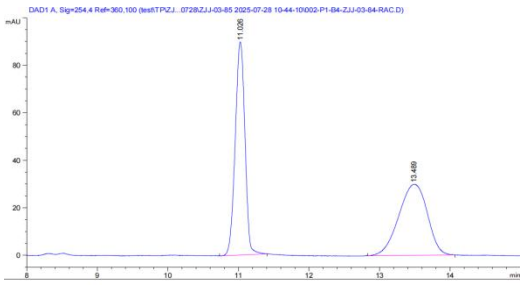
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.52 – 7.49 (m, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.19 – 7.15 (m, 1H), 7.14 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.93 (td, *J* = 7.5, 1.1 Hz, 1H), 6.86 (s, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.20 (s, 1H), 5.03 (d, *J* = 12.8 Hz, 1H), 4.99 (d, *J* = 12.8 Hz, 1H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.2, 138.0, 136.2, 129.62, 129.61, 129.3, 127.6, 126.8, 124.8, 121.8, 121.4, 117.0, 68.9, 64.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{14}H_{12}NaO_2S^{\oplus}$ 267.0450, found 267.0450.

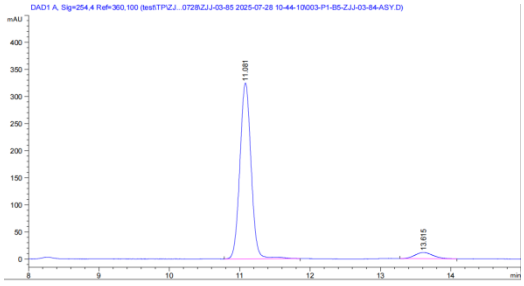
Specific Rotation: $[\alpha]_D^{27.9}$ –118.9 (*c* 0.33, MeOH) for 89% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 11.1 min (major), 13.6 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

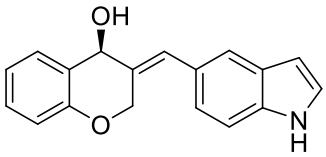
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.026	BB	0.1505	857.92041	89.80215	50.5048
2	13.489	BB	0.3310	840.77124	29.90263	49.4952



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.081	BV R	0.1697	3580.81494	324.54877	94.5621
2	13.615	BV R	0.2136	205.92032	11.56954	5.4379

(*S*,*E*)-3-((1H-indol-5-yl)methylene)chroman-4-ol (2s)



2s

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 3/1), yellow solid (48.3 mg, 87% yield).

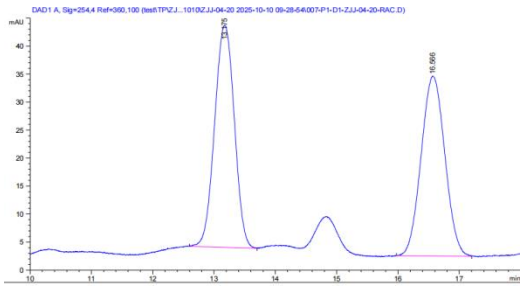
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 10.34 (s, 1H), 7.50 (s, 1H), 7.47 – 7.42 (m, 2H), 7.37 – 7.34 (m, 1H), 7.18 – 7.14 (m, 1H), 7.08 – 7.04 (m, 2H), 6.92 (td, *J* = 7.5, 1.1 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.52 – 6.49 (m, 1H), 5.21 (s, 1H), 5.06 (d, *J* = 12.3 Hz, 1H), 5.00 (d, *J* = 12.3 Hz, 1H), 4.75 (s, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ (ppm) 155.4, 136.5, 134.1, 130.2, 130.0, 129.7, 129.2, 128.1, 127.5, 126.4, 123.5, 121.6, 121.2, 117.1, 112.1, 102.6, 69.5, 63.8.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{15}NNaO_2^{\oplus}$ 300.0995, found 300.0994.

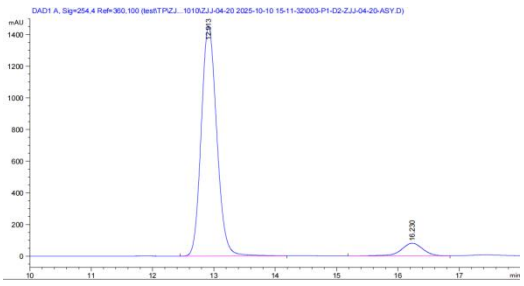
Specific Rotation: $[\alpha]_D^{26.5}$ –97.0 (*c* 0.31, MeOH) for 86% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 85/15; flow rate = 0.5 mL/min; Retention time: 12.8 min (major), 16.2 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

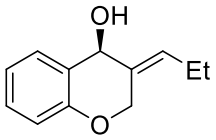
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.175	VV R	0.2624	884.82288	39.63683	50.5983
2	16.566	BV R	0.3171	863.89819	32.13615	49.4017



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.913	VV R	0.2614	2.55088e4	1452.45752	92.9126
2	16.230	VB R	0.2958	1945.81763	79.83850	7.0874

(*S*,*E*)-3-Propylidenechroman-4-ol (2t)



2t

General Procedure C, R_f = 0.3 (petroleum ether/ethyl acetate = 10/1), yellow solid (28.5 mg, 75% yield).

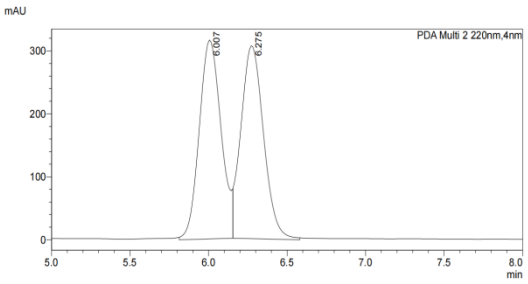
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.35 (d, J = 7.6 Hz, 1H), 7.17 – 7.11 (m, 1H), 6.88 (t, J = 7.4 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 5.81 (t, J = 7.5 Hz, 1H), 4.96 (s, 1H), 4.76 (d, J = 12.1 Hz, 1H), 4.72 (d, J = 12.1 Hz, 1H), 4.51 (s, 1H), 2.23 – 2.14 (m, 2H), 1.00 (t, J = 7.5 Hz, 3H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.5, 133.6, 130.6, 130.3, 129.6, 127.3, 121.1, 117.0, 69.0, 62.6, 21.1, 14.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{12}H_{14}NaO_2^{\oplus}$ 213.0886, found 213.0887.

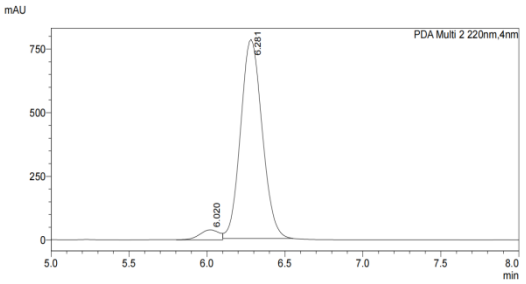
Specific Rotation: $[\alpha]_D^{26.0}$ –59.1 (c 0.42, MeOH) for 91% *ee*.

Chiral HPLC analysis: Chiralcel OD-H Column (250 mm); detected at 220 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 1.0 mL/min; Retention time: 6.3 min (major), 6.0 min (minor).



PDA Ch2 220nm

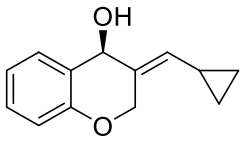
Peak#	Ret. Time	Area	Area%
1	6.007	3079257	50.225
2	6.275	3051669	49.775



PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	6.020	352632	4.482
2	6.281	7514255	95.518

(*S*,*E*)-3-(Cyclopropylmethylene)chroman-4-ol (2u)



2u

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 10/1), yellow solid (34.6 mg, 86% yield).

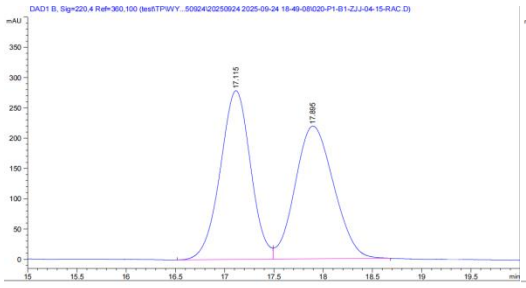
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.33 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 7.7 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 5.16 (d, J = 10.1 Hz, 1H), 4.92 (s, 1H), 4.90 (d, J = 12.0 Hz, 1H), 4.82 (d, J = 12.0 Hz, 1H), 4.46 (s, 1H), 1.76 – 1.67 (m, 1H), 0.84 – 0.76 (m, 2H), 0.44 – 0.36 (m, 2H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.5, 133.7, 132.1, 130.4, 129.5, 127.3, 121.0, 117.1, 68.9, 63.1, 10.2, 7.5, 7.4.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{14}NaO_2^{\oplus}$ 225.0886, found 225.0885.

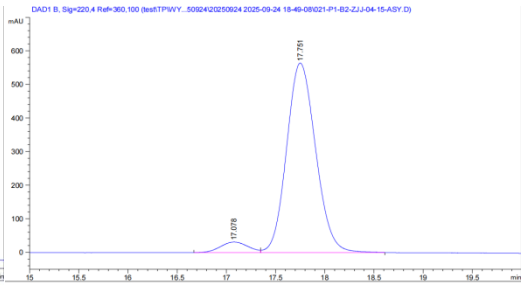
Specific Rotation: $[\alpha]_D^{26.2}$ –166.4 (c 0.23, MeOH) for 90% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 220 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.5 mL/min; Retention time: 17.8 min (major), 17.1 min (minor).



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

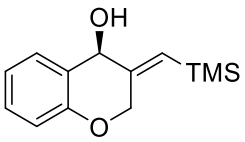
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.115	BV	0.2960	5972.80811	278.72760	50.0604
2	17.895	VV R	0.3663	5958.39697	219.43736	49.9396



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.078	MF R	0.3228	607.95477	31.39205	4.9967
2	17.751	FM R	0.3138	1.15592e4	564.47980	95.0033

(*R*,*E*)-3-((Trimethylsilyl)methylene)chroman-4-ol (2v)



2v

General Procedure C, R_f = 0.5 (petroleum ether/ethyl acetate = 10/1), yellow solid (42.6 mg, 91% yield).

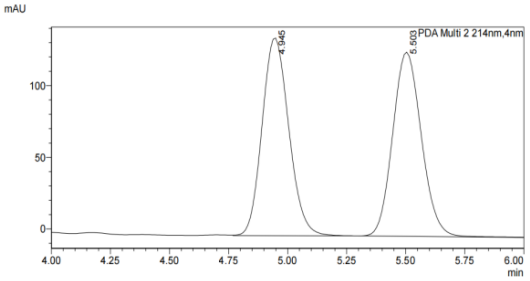
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.40 (d, J = 7.6 Hz, 1H), 7.17 – 7.13 (m, 1H), 6.90 (td, J = 7.5, 1.1 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 5.99 (d, J = 1.4 Hz, 1H), 5.10 (s, 1H), 4.82 (d, J = 12.2 Hz, 1H), 4.70 (d, J = 12.2 Hz, 1H), 0.18 (s, 9H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.2, 151.7, 129.5, 129.4, 127.8, 126.1, 121.3, 116.8, 70.2, 67.3, 0.3.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{18}NaO_2Si^{\oplus}$ 257.0968, found 257.0968.

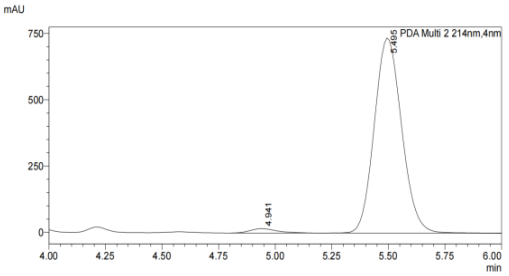
Specific Rotation: $[\alpha]_D^{26.5}$ –50.5 (c 0.48, MeOH) for 96% *ee*.

Chiral HPLC analysis: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 1.0 mL/min; Retention time: 5.5 min (major), 4.9 min (minor).



PDA Ch2 214nm

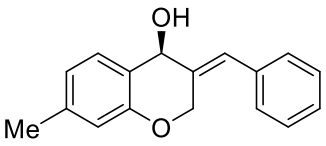
Peak#	Ret. Time	Area	Area%
1	4.945	1086990	50.048
2	5.503	1084907	49.952



PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	4.941	134627	2.131
2	5.495	6183849	97.869

(*S*,*E*)-3-Benzylidene-7-methylchroman-4-ol (2w)



2w

General Procedure C, R_f = 0.3 (petroleum ether/ethyl acetate = 10/1), yellow solid (45.7 mg, 91% yield).

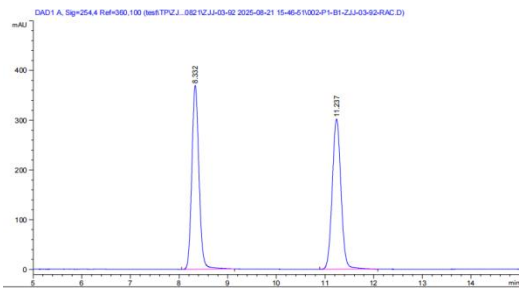
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) δ 7.41 – 7.38 (m, 2H), 7.32 – 7.27 (m, 3H), 7.24 (d, *J* = 1.7 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.95 (s, 1H), 6.66 (d, *J* = 8.3 Hz, 1H), 5.19 (s, 1H), 4.91 (d, *J* = 12.4 Hz, 1H), 4.87 (d, *J* = 12.4 Hz, 1H), 2.26 (s, 3H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 153.1, 137.2, 130.34, 130.29, 130.1, 129.7, 129.3, 128.1, 127.8, 127.1, 116.8, 69.1, 63.6, 20.6

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{16}NaO_2^{\oplus}$ 275.1043, found 275.1041.

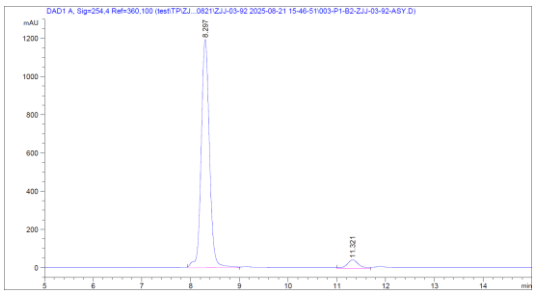
Specific Rotation: $[\alpha]_D^{29.3}$ –81.5 (*c* 0.90, MeOH) for 90% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 8.3 min (major), 11.3 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

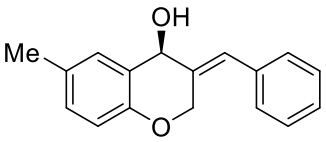
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.332	BB	0.1587	3775.94580	369.42740	49.9701
2	11.237	VV R	0.1956	3780.45776	301.95557	50.0299



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.297	MM R	0.1956	1.40016e4	1192.94031	95.2556
2	11.321	MM R	0.2665	697.37897	43.61827	4.7444

(*S*,*E*)-3-Benzylidene-6-methylchroman-4-ol (2x)



2x

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 10/1), yellow solid (37.2 mg, 74% yield).

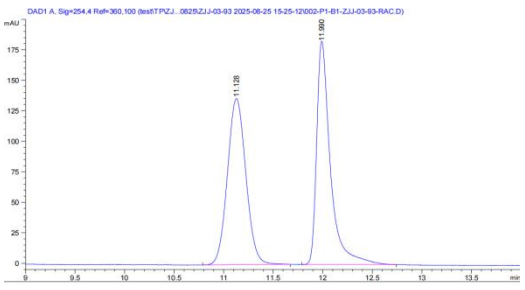
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.42 – 7.38 (m, 2H), 7.33 – 7.26 (m, 4H), 6.94 (s, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.60 (s, 1H), 5.18 (s, 1H), 4.92 (d, J = 12.4 Hz, 1H), 4.88 (d, J = 12.4 Hz, 1H), 4.73 (s, 1H) 2.25 (s, 3H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 155.1, 139.6, 137.2, 137.1, 129.8, 129.7, 129.3, 128.1, 127.9, 124.4, 122.3, 117.3, 69.0, 63.5, 21.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{16}NaO_2^{\oplus}$ 275.1043, found 275.1042.

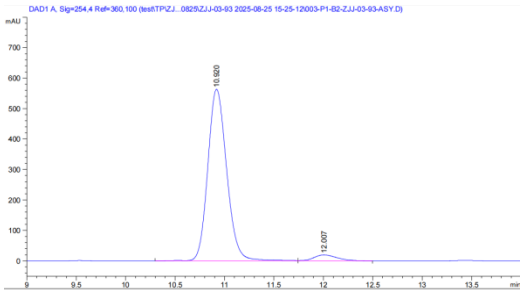
Specific Rotation: $[\alpha]_D^{27.8}$ –122.9 (c 0.43, MeOH) for 92% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 10.9 min (major), 12.0 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

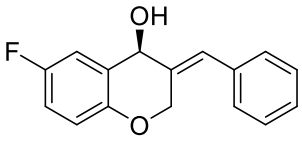
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.128	BV R	0.2019	1760.97229	136.13960	50.0057
2	11.990	VV R	0.1412	1760.57092	183.04100	49.9943



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.920	VV R	0.2038	7484.91602	563.22888	95.9639
2	12.007	VV R	0.1967	314.80353	19.36015	4.0361

(*S*,*E*)-3-Benzylidene-6-fluorochroman-4-ol (2y)



2y

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 10/1), yellow solid (41.3 mg, 81% yield).

^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.40 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.21 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.99 (s, 1H), 6.95 (td, *J* = 8.6, 3.1 Hz, 1H), 6.81 – 6.77 (m, 1H), 5.28 (s, 1H), 5.09 (s, 1H), 4.94 (d, *J* = 12.6 Hz, 1H), 4.90 (d, *J* = 12.6 Hz, 1H).

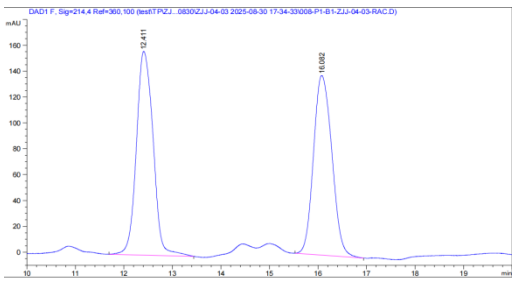
^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 157.9 (d, *J* = 235.2 Hz), 151.4, 137.0, 136.2, 129.7, 129.3, 129.08 (d, *J* = 6.6 Hz), 128.2, 128.0, 118.3 (d, *J* = 8.2 Hz), 116.3 (d, *J* = 24.0 Hz), 115.1 (d, *J* = 23.6 Hz), 68.6, 64.2.

^{19}F NMR (376 MHz, Acetone-d_6) δ (ppm) -125.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{13}FNaO_2^{\oplus}$ 279.0792, found 279.0791.

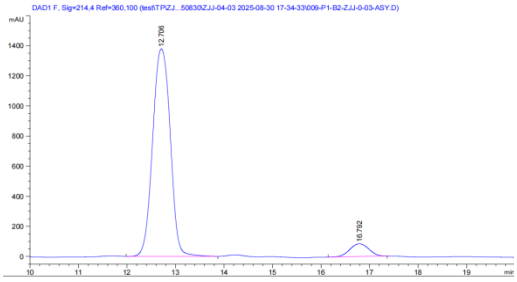
Specific Rotation: $[\alpha]_D^{26.8}$ –79.1 (*c* 0.28, MeOH) for 88% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.5 mL/min; Retention time: 12.7 min (major), 16.8 min (minor).



Signal 1: DAD1 F, Sig=214,4 Ref=360,100

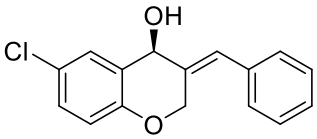
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.411	VV R	0.3123	3770.13525	157.47617	50.8074
2	16.082	BV R	0.3137	3650.30322	138.83319	49.1926



Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.706	VV R	0.2960	3.47229e4	1380.15417	93.7519
2	16.792	VV R	0.3234	2314.10596	84.53734	6.2481

(*S*,*E*)-3-Benzylidene-6-chlorochroman-4-ol (2z)



2z

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 10/1), yellow solid (45.3 mg, 83% yield).

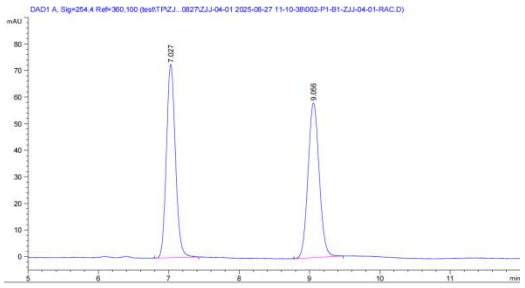
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.45 (d, *J* = 2.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.18 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.00 (s, 1H), 6.79 (d, *J* = 8.7 Hz, 1H), 5.28 (s, 1H), 5.08 (s, 1H), 4.97 (d, *J* = 12.5 Hz, 1H), 4.92 (d, *J* = 12.5 Hz, 1H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 154.0, 136.9, 135.7, 129.7, 129.5, 129.4, 129.3, 129.1, 128.30, 128.26, 125.7, 118.8, 68.5, 64.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{13}ClNaO_2^{\oplus}$ 295.0496, found 295.0492.

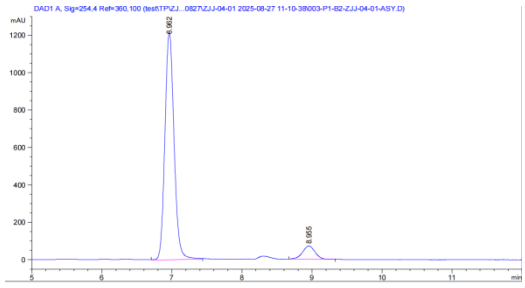
Specific Rotation: $[\alpha]_D^{29.5}$ –86.2 (*c* 0.40, MeOH) for 85% *ee*.

Chiral HPLC analysis: Chiralpak IC-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 7.0 min (major), 9.0 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

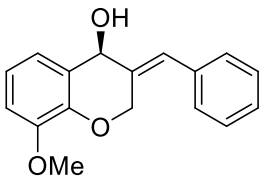
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.027	BV R	0.1382	646.48175	72.71841	50.1570
2	9.056	BV R	0.1697	642.43549	58.23264	49.8430



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.962	MM R	0.1508	1.09959e4	1215.45422	92.6981
2	8.955	MM R	0.2050	866.15594	70.41100	7.3019

(*S*,*E*)-3-Benzylidene-8-methoxychroman-4-ol (2aa)



2aa

General Procedure C, R_f = 0.2 (petroleum ether/ethyl acetate = 10/1), yellow solid (41.1 mg, 77% yield).

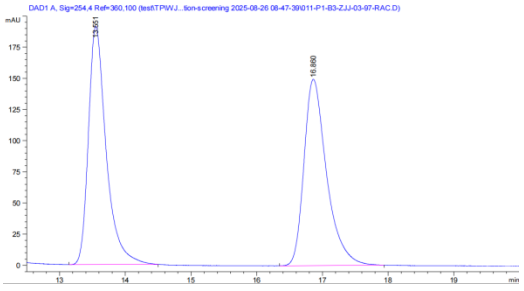
^{1}H NMR (600 MHz, Acetone-d_6) δ (ppm) 7.40 (t, J = 7.6 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.06 – 7.02 (m, 1H), 6.95 (s, 1H), 6.89 – 6.84 (m, 2H), 5.22 (s, 1H), 4.97 – 4.90 (m, 2H), 3.76 (s, 3H).

^{13}C NMR (150 MHz, Acetone-d_6) δ (ppm) 149.3, 145.0, 137.1, 137.0, 129.7, 129.3, 128.12, 128.10, 127.9, 121.5, 121.1, 112.2, 69.1, 63.7, 56.1.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{16}NaO_3^{\oplus}$ 291.0992, found 291.0991.

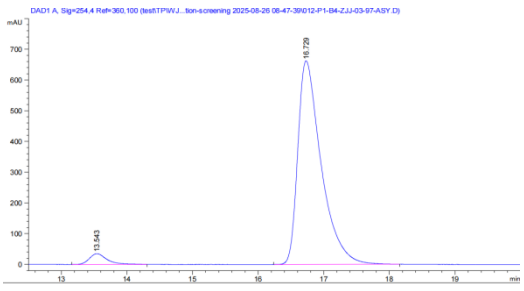
Specific Rotation: $[\alpha]_D^{27.0}$ –102.2 (*c* 0.56, MeOH) for 92% *ee*.

Chiral HPLC analysis: Chiralpak ID-3 Column (150 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 0.5 mL/min; Retention time: 16.7 min (major), 13.5 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

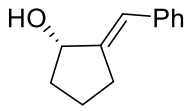
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.551	BV R	0.2780	3594.74194	191.08583	50.1391
2	16.860	BB	0.3410	3574.79443	149.50772	49.8609



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.543	VV R	0.2342	655.12115	35.03550	3.8462
2	16.729	BV R	0.3590	1.63779e4	662.39636	96.1538

(*S*,*E*)-2-Benzylidenecyclopentan-1-ol (4a)



4a

General Procedure D, R_f = 0.4 (petroleum ether/ethyl acetate = 5/1), white solid (20.9 mg, 60% yield).

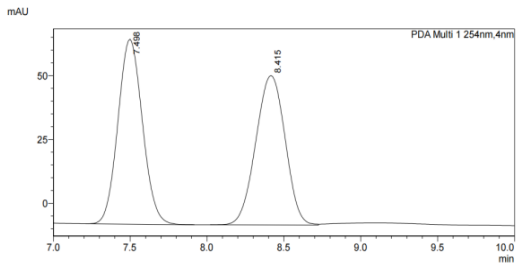
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 – 7.30 (m, 4H), 7.24 – 7.17 (m, 1H), 6.58 (s, 1H), 4.65 – 4.53 (m, 1H), 2.82 – 2.49 (m, 2H), 2.04 – 1.88 (m, 2H), 1.78 – 1.63 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.8, 137.7, 131.5, 128.4, 128.3, 126.6, 123.7, 34.8, 29.3, 22.5.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{12}H_{14}NaO^{\oplus}$ 197.0937, found 197.0934

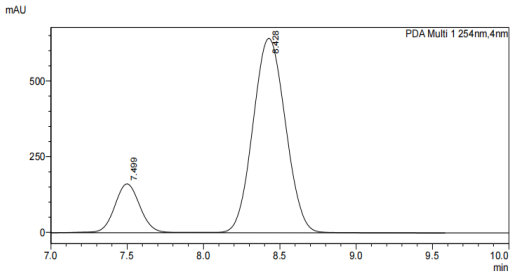
Specific Rotation: $[\alpha]_D^{25.3}$ +30.7 (*c* 0.33, MeOH) for 67% *ee*.

Chiral HPLC analysis: Chiralcel OD-H Column (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 1.0 mL/min; Retention time: 8.4 min (major), 7.5 min (minor).



PDA Ch1 254nm

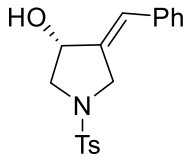
Peak#	Ret. Time	Area	Area%
1	7.498	803345	50.790
2	8.415	778350	49.210



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.499	1879704	16.508
2	8.428	9506926	83.492

(*R*,*E*)-4-Benzylidene-1-tosylpyrrolidin-3-ol (4b)



4b

General Procedure D, R_f = 0.5 (petroleum ether/ethyl acetate = 5/1), white solid (48.8 mg, 74% yield).

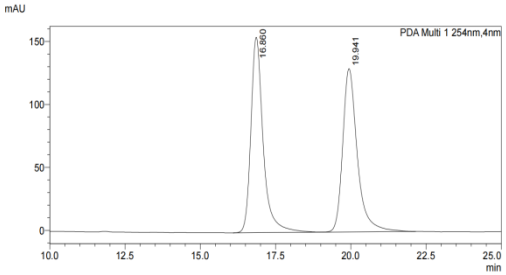
^{1}H NMR (400 MHz, Acetone-d_6) δ (ppm) 7.75 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.34 (m, 4H), 7.30 – 7.23 (m, 3H), 6.59 (s, 1H), 4.68 (s, 2H), 4.20 (d, *J* = 15.1 Hz, 1H), 4.13 (d, *J* = 15.1 Hz, 1H), 3.59 – 3.51 (m, 1H), 3.01 – 2.96 (m, 1H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ (ppm) 144.6, 140.4, 137.1, 133.9, 130.6, 129.4, 129.2, 128.6, 128.2, 125.1, 73.3, 54.8, 50.2, 21.4.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{18}H_{20}NO_3S^{\oplus}$ 330.1158, found 330.1160.

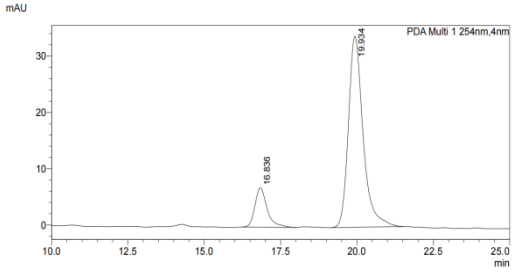
Specific Rotation: $[\alpha]_D^{25.3}$ +17.3 (*c* 0.63, MeOH) for 70% *ee*.

Chiral HPLC analysis: Chiralpak IA Column (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 85/15; flow rate = 1.0 mL/min; Retention time: 19.9 min (major), 16.8 min (minor).



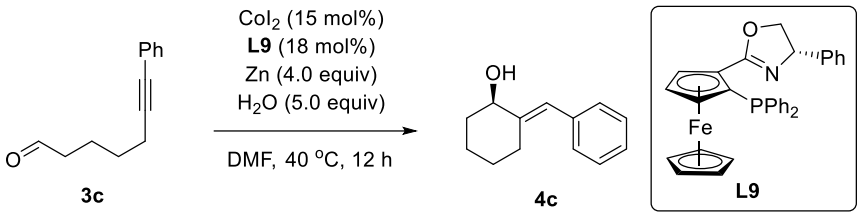
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.860	4411083	50.180
2	19.941	4379375	49.820



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.836	194290	14.614
2	19.934	1135197	85.386



(*R*,*E*)-2-Benzylidenecyclohexan-1-ol (4c) In a glove box, an oven-dried 4-mL vial was charged with alkynals **3c** (0.1 mmol, 1.0 equiv), CoI_2 (0.015 mmol, 0.15 equiv), **L9** (0.018 mmol, 0.18 equiv), Zn (0.4 mmol, 4.0 equiv), H_2O (0.5 mmol, 5.0 equiv) and DMF (1.0 mL). The vial was capped and removed from the glove box. The reaction mixture was placed in a pre-heated block and stirred at 40 °C for 12 h. Then the reaction mixture was cooled to room temperature and the organic layer was extracted with EtOAc. Then the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product **4c** as a white solid (R_f = 0.2, petroleum ether/ethyl acetate = 5/1, 8.5 mg, 45% yield).

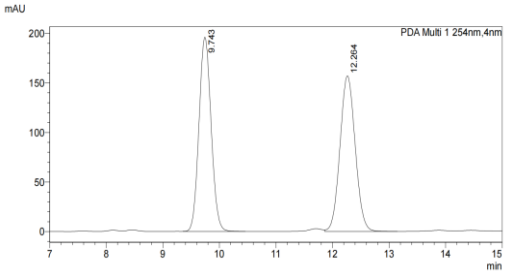
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.35 – 7.30 (m, 2H), 7.23 – 7.19 (m, 3H), 6.53 (s, 1H), 4.28 – 4.21 (m, 1H), 2.77 – 2.68 (m, 1H), 2.17 – 2.08 (m, 1H), 2.05 – 1.98 (m, 1H), 1.91 – 1.83 (m, 1H), 1.68 – 1.65 (m, 1H), 1.64 – 1.54 (m, 3H), 1.51 – 1.42 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 144.3, 137.6, 128.9, 128.1, 126.2, 120.8, 73.7, 36.6, 27.3, 27.0, 23.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{16}NaO^{\oplus}$ 211.1093, found 211.1087.

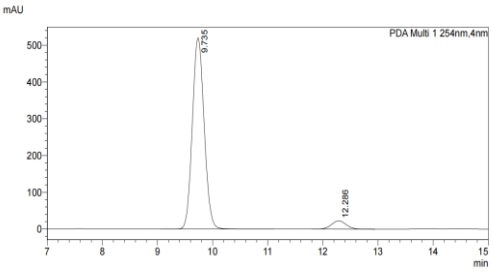
Specific Rotation: $[\alpha]_D^{22.9}$ +31.5 (*c* 0.13, MeOH) for 90% *ee*.

Chiral HPLC analysis: Chiralpak OD-H Column (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 1 mL/min; Retention time: 9.7 min (major), 12.3 min (minor).



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.743	2928595	49.915
2	12.264	2938525	50.085

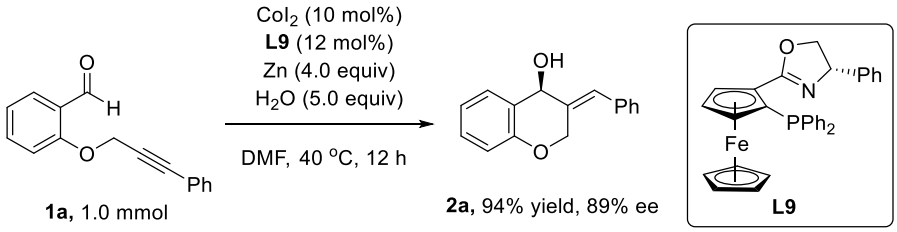


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.735	7744461	94.889
2	12.286	417129	5.111

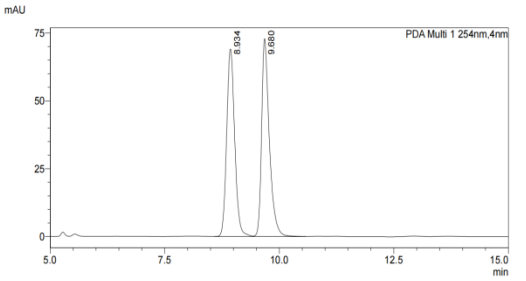
4. Scale-up Reaction and Deuterium Labeling Experiment

1.0-mmol Scale Reaction:



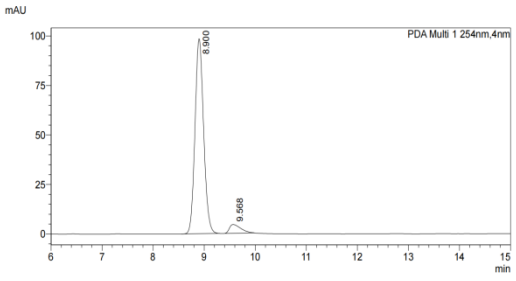
In a glove box, a 100-mL oven-dried Schlenk flask was charged with alkynals **1a** (236 mg, 1.0 mmol, 1.0 equiv), CoI_2 (31.3 mg, 0.1 mmol, 0.1 equiv), **L9** (61.1 mg, 0.12 mmol, 0.12 equiv), Zn (260 mg, 4.0 mmol, 4.0 equiv), H_2O (90μL, 5.0 mmol, 5.0 equiv) and DMF (10 mL). The flask was capped and removed from the glove box. The reaction mixture was placed in a pre-heated oil bath and stirred at 40 °C for 12 h. Then the reaction mixture was cooled to room temperature, water was added and the organic layer was extracted with EtOAc (20 mL×3). The combined organic layers were washed brine, dried over Na_2SO_4, filtered and evaporated. The residue was purified by silica gel flash column chromatography to afford the desired product **2a** as a yellow solid (eluent: petroleum ether/ethyl acetate = 10:1, 223.2 mg, 94% yield, 89% *ee*).

Chiral HPLC analysis: Chiralpak IH Column (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 1.0 mL/min; Retention time: 8.9 min (major), 9.6 min (minor).



PDA Ch1 254nm

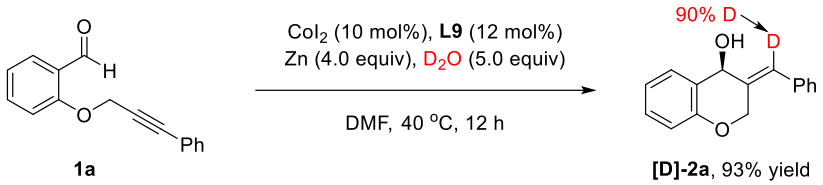
Peak#	Ret. Time	Area	Area%
1	8.934	841857	49.580
2	9.680	856112	50.420



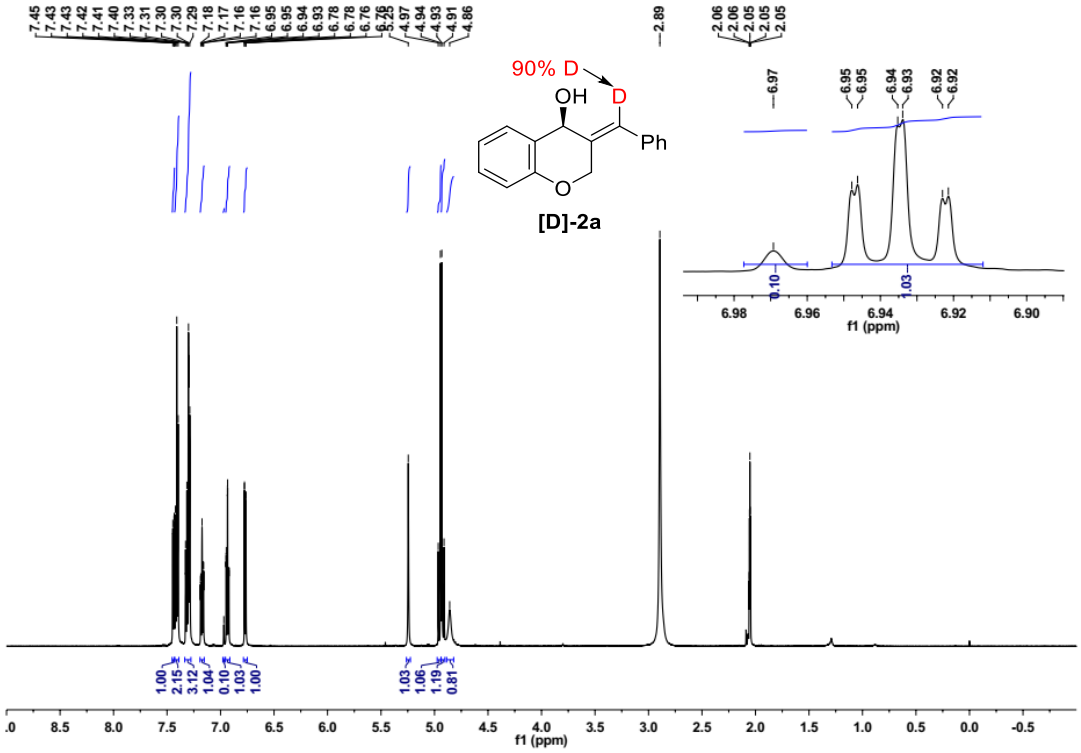
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.900	1155318	94.528
2	9.568	66885	5.472

Deuterium labeling experiment

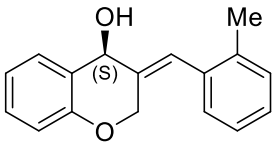


In a glove box, an oven-dried 4-mL vial was charged with alkynals **1a** (0.1 mmol, 1.0 equiv), CoI_2 (0.01 mmol, 0.1 equiv), **L9** (0.012 mmol, 0.12 equiv), Zn (0.4 mmol, 4.0 equiv), D_2O (0.5 mmol, 5.0 equiv) and DMF (1.0 mL). The vial was capped and removed from the glove box. The reaction mixture was placed in a pre-heated block and stirred at 40 °C for 12 h. Then the reaction mixture was cooled to room temperature, water was added and the organic layer was extracted with EtOAc (5 mL×3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product **[D]-2a** as a yellow solid. (R_f = 0.2, petroleum ether/ethyl acetate = 5/1, 22.3 mg, 93% yield).



5. Absolute Configuration Determination of the Products

Compound **2m** was assigned the (*S*)-configuration by comparison of its specific rotation with literature data[1].

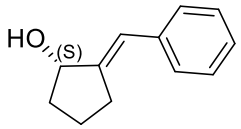


2m

Literature data: $[\alpha]_D^{RT}$ –106.4 (*c* 1.0, $CHCl_3$) for 92% *ee*, (*S*)-configuration;

2m: $[\alpha]_D^{26.0}$ –126.4 (*c* 0.45, MeOH) for 94% *ee*, (*S*)-configuration.

Compound **4a** was assigned the (*S*)-configuration by comparison of its specific rotation with literature data[8].

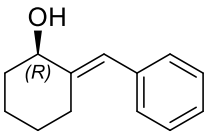


4a

Literature data: $[\alpha]_D^{20}$ +28.5 (*c* 1.08, EtOH) for 96% *ee*, (*S*)-configuration;

4a: $[\alpha]_D^{25.3}$ +30.7 (*c* 0.33, MeOH) for 67% *ee.*, (*S*)-configuration.

Compound **4c** was assigned the (*R*)-configuration by comparison of its specific rotation with literature data[8].

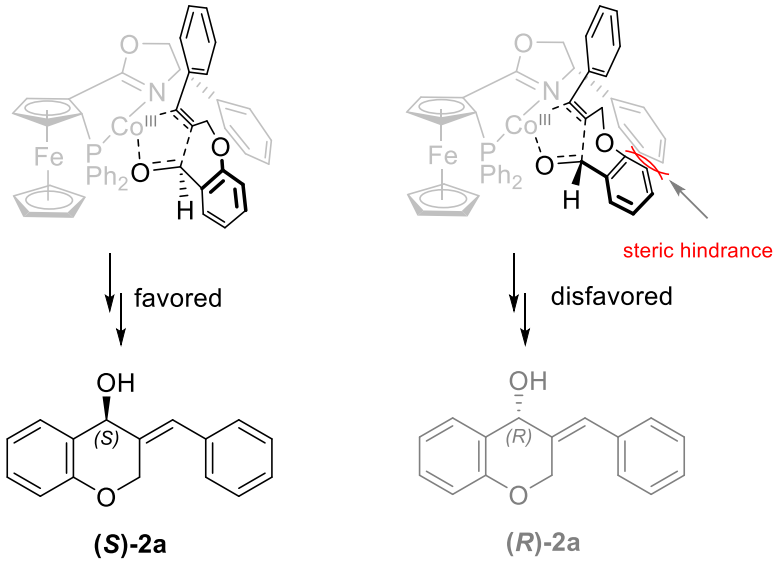


4c

Literature data: $[\alpha]_D^{20}$ –43.0 (*c* 0.76, EtOH) for 97% *ee*, (*S*)-configuration;

4c: $[\alpha]_D^{22.9}$ +31.5 (*c* 0.13, MeOH) for 90% *ee*, (*R*)-configuration.

6. Proposed Model for Stereochemical Induction



Scheme S1. Proposed model for stereochemical induction.

7. Preliminary Bioactivity Studies

Compounds were firstly dissolved in DMSO to obtain 10 mM stock solutions and diluted using DMEM for analysis. Human hepatocellular carcinomas (HepG2) cells were purchased from the Cell Bank of Shanghai Institute of Cell Biology, Chinese Academy of Sciences and cultured in high glucose Dulbecco's Modified Eagle Medium (Meilun Biotechnology, Dalian, China) supplemented with 10% fetal bovine serum (Tuona Biotechnology, Shanghai, China), and penicillin/streptomycin (Meilun Biotechnology, Dalian, China) at 37 °C under 5% CO_2. The cells were seeded in 96-well culture plates at a density of 5000 cells per well (100 μL/well) and grown for 8 h. Then, compounds were added to the plates and the plates were incubated at 37 °C for 48 h. After incubation, a volume of 10 uL of Cell Counting Kit-8 (CCK-8, Titan Scientific, Shanghai, China) was added per well, and the plate was incubated in the 37 °C incubator for 1 h. The samples absorbance was measured at the wavelength of 450 nm using a microplate reader. Each treatment was performed in triplicate. The half inhibitory concentration IC_{50} values were calculated by GraphPad Prism 10.6.0.

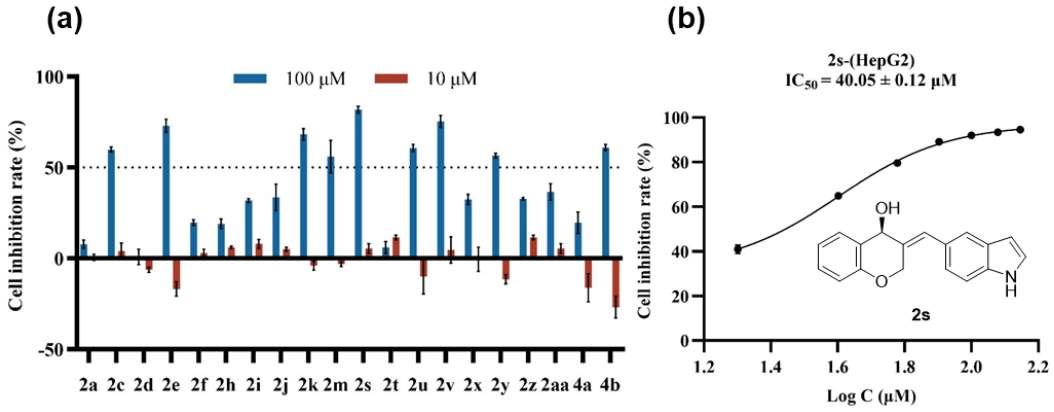


Figure S1. Preliminary bioactivity studies. (a) Evaluating the inhibitory activity of reductive cyclization products against Human hepatocellular carcinomas (HepG2) cells. (b) Inhibition curve for compound **2s** against HepG2 cells.

8. References

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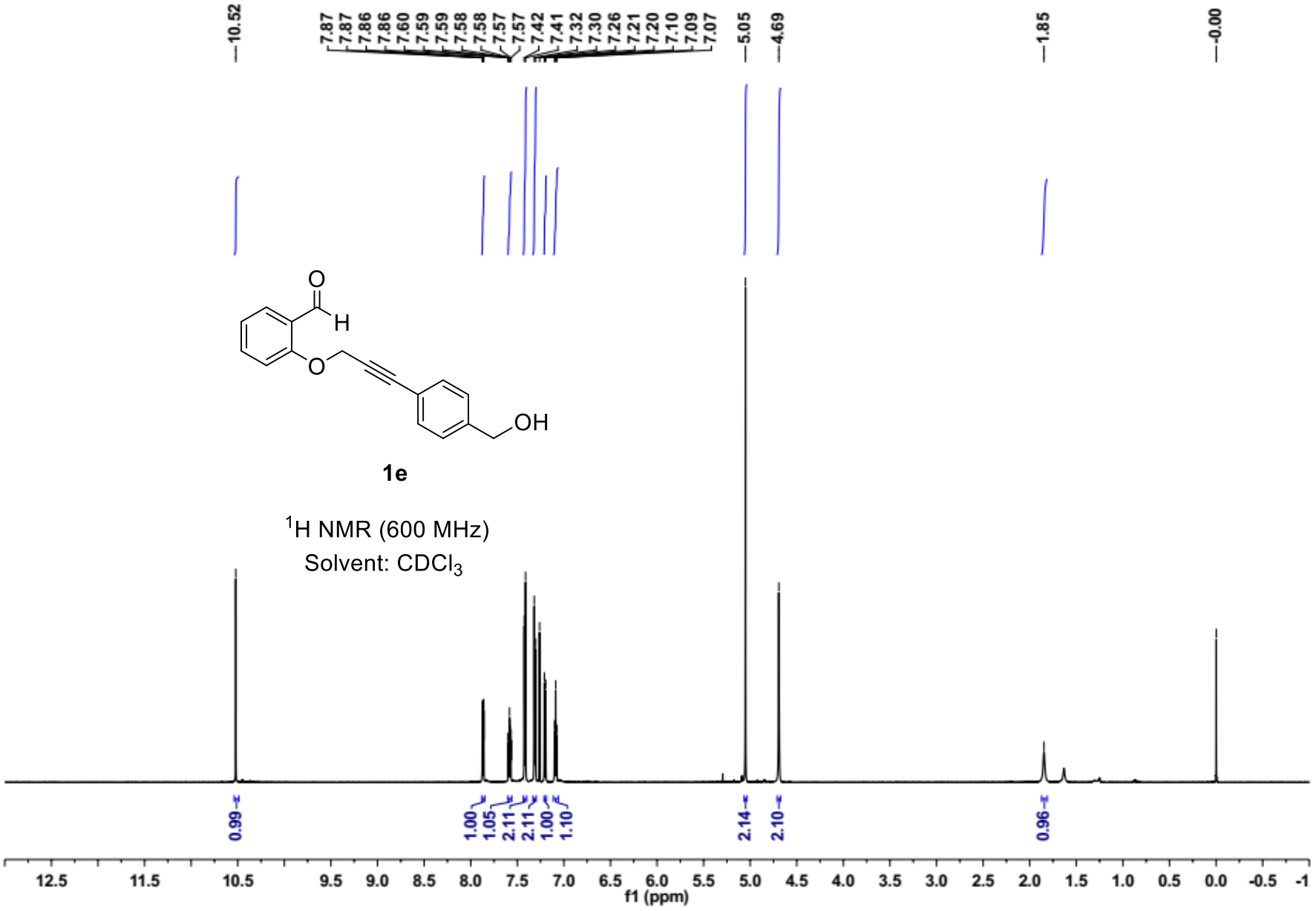
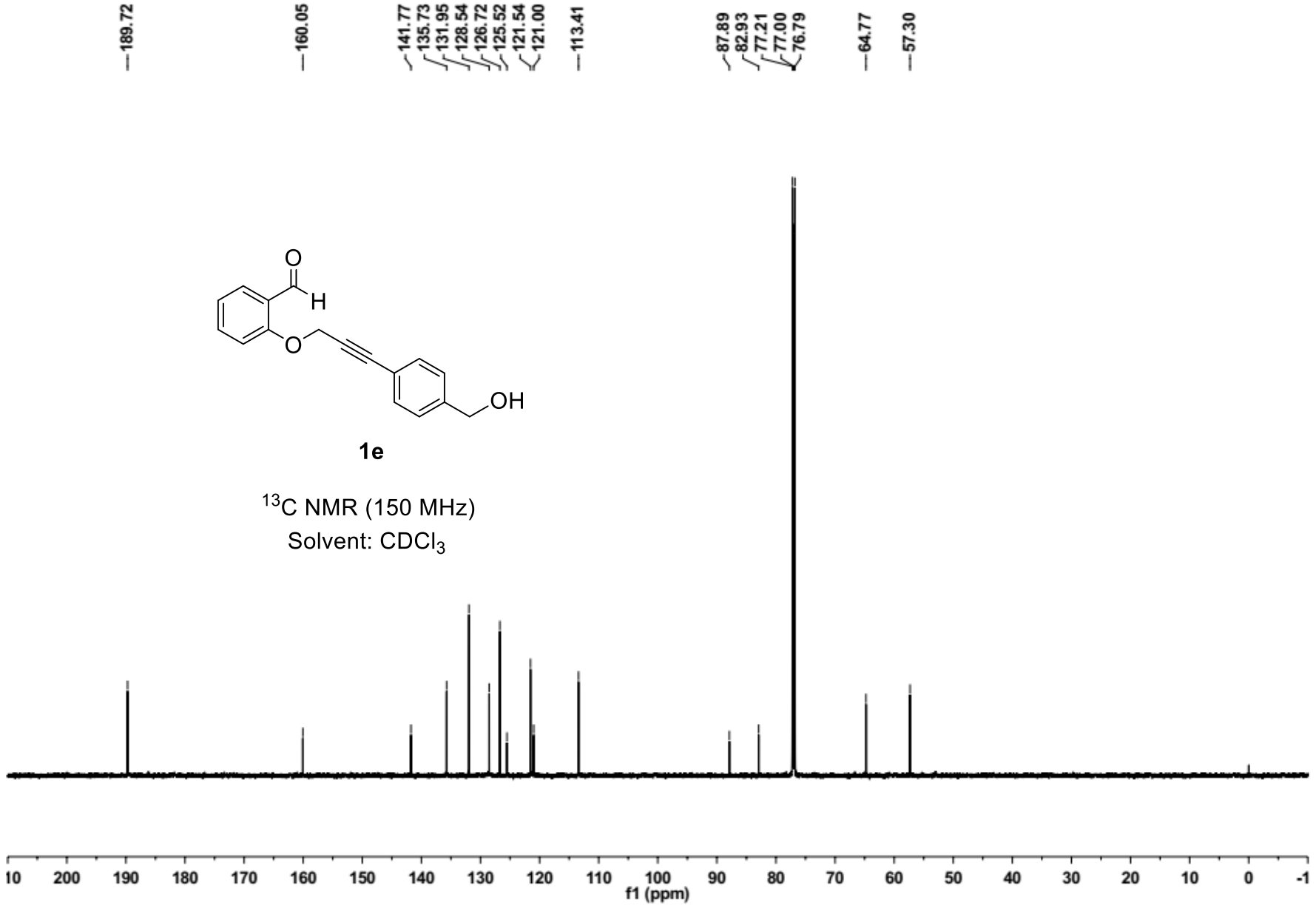
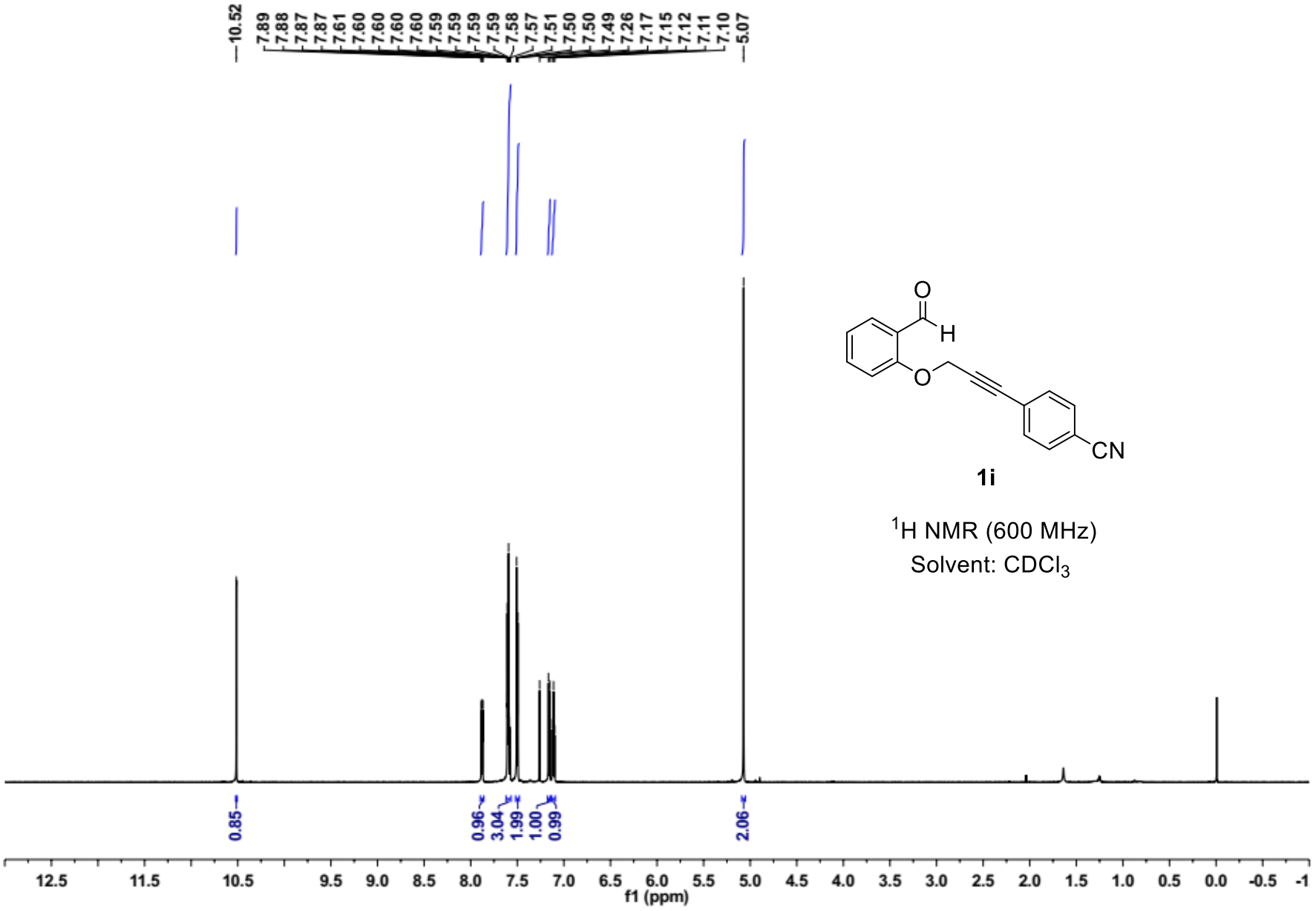
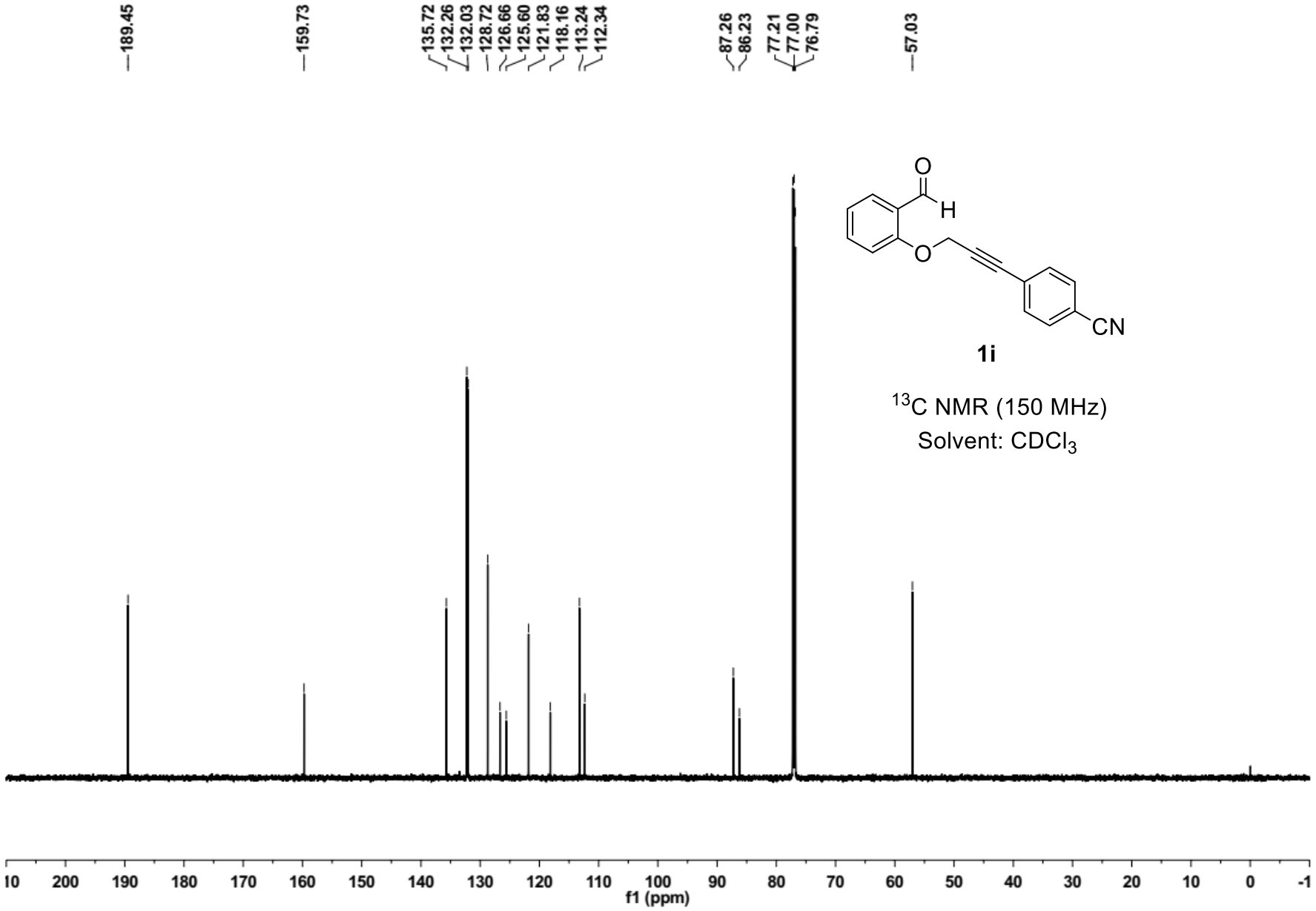
(8) J.-B. Xie, J.-H. Xie, X.-Y. Liu, W.-L. Kong, S. Li and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2010, **132**, 4538−4539.

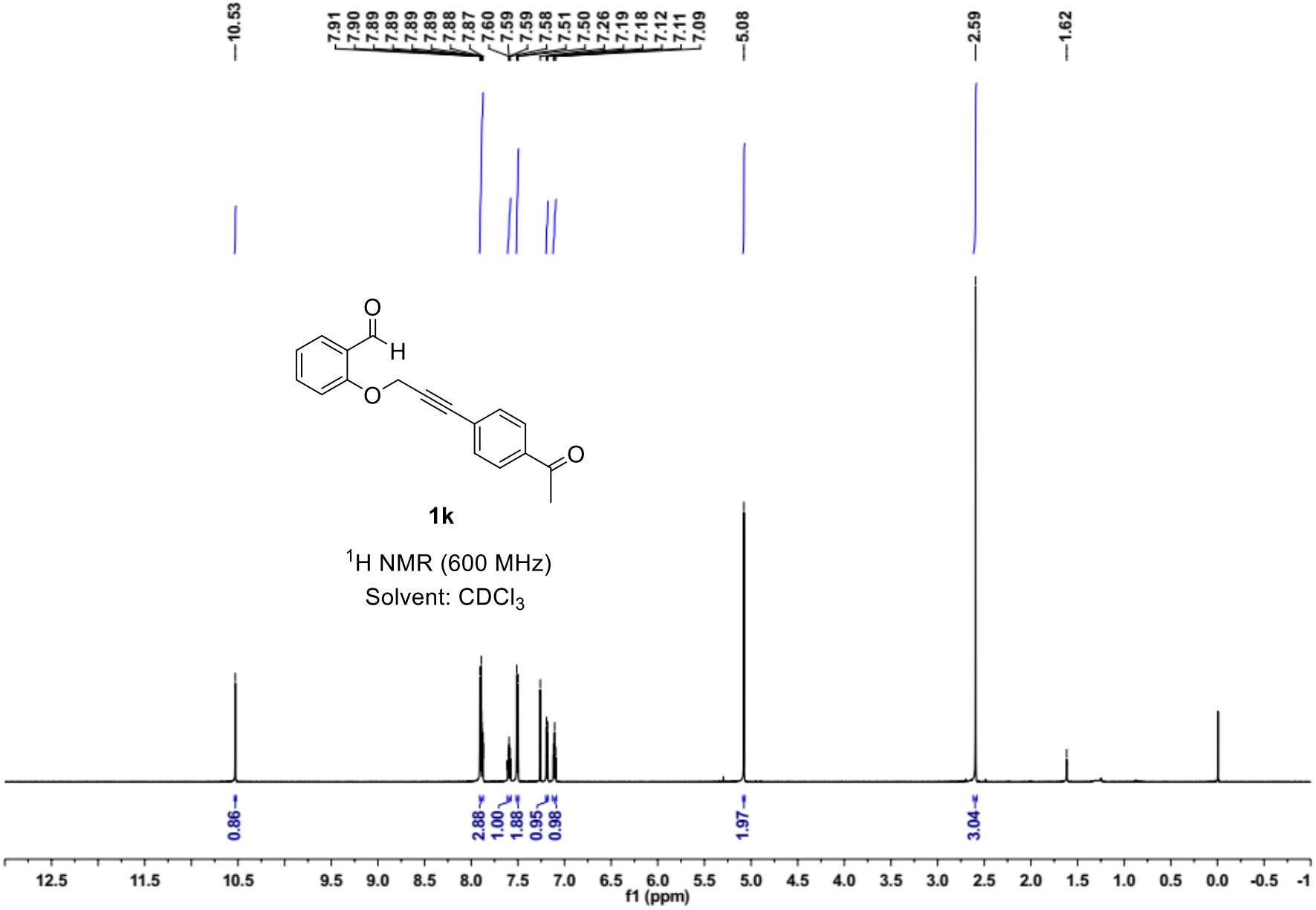
9. NMR Spectra

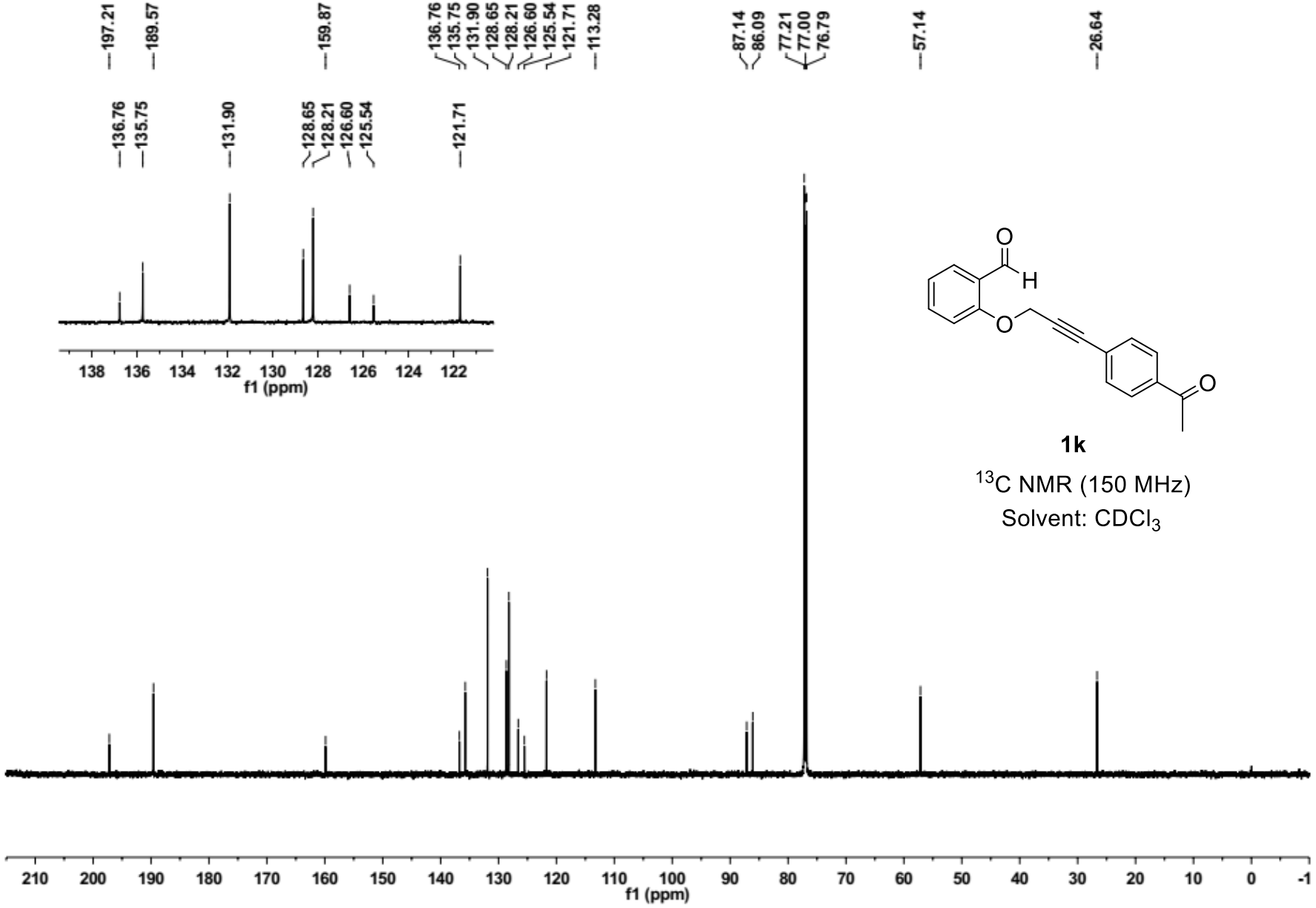

10.52
7.87
7.87
7.86
7.86
7.60
7.59
7.59
7.58
7.58
7.57
7.57
7.42
7.41
7.32
7.30
7.26
7.21
7.20
7.10
7.09
7.07
5.05
4.69
1.85
-0.00
O
H
O
OH
1e
1H NMR (600 MHz)
Solvent: CDCl3
0.99
1.00
1.05
2.11
2.11
1.00
1.10
2.14
2.10
0.96
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

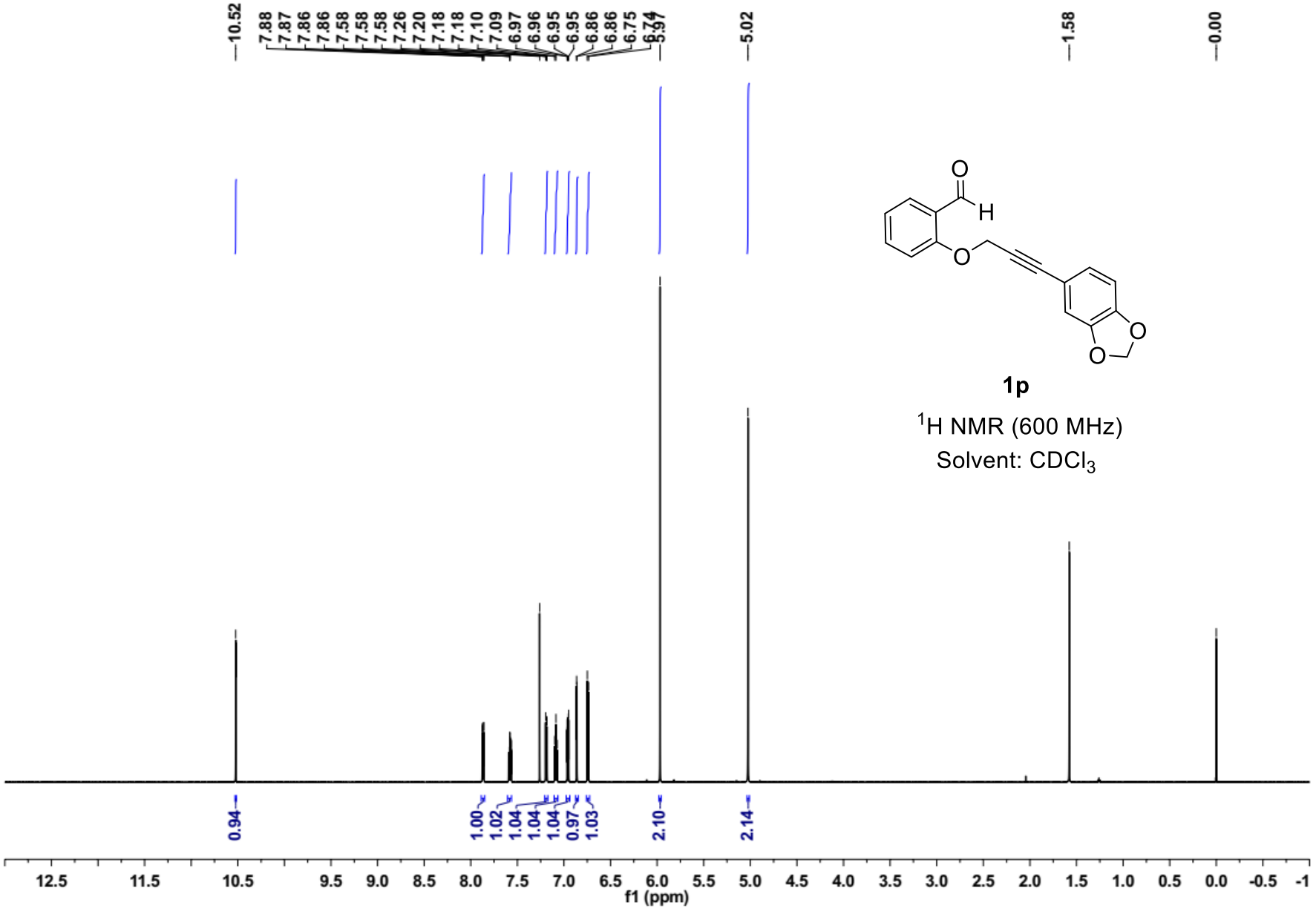

189.72
160.05
141.77
135.73
131.95
128.54
126.72
125.52
121.54
121.00
113.41
87.89
82.93
77.21
77.00
76.79
64.77
57.30
O
H
O
OH
1e
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)

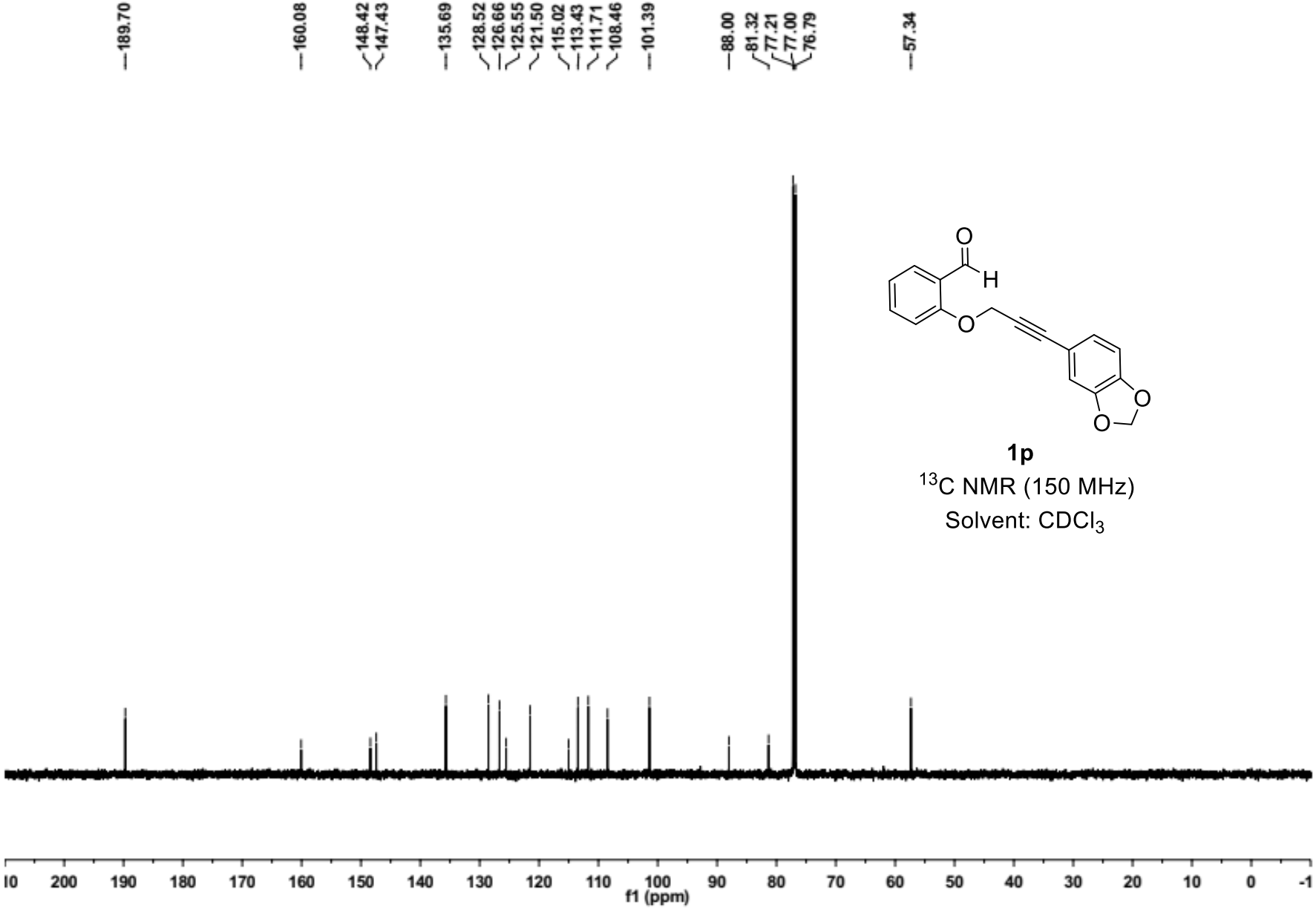

10.52
7.89
7.88
7.87
7.87
7.61
7.60
7.60
7.60
7.60
7.59
7.59
7.59
7.59
7.58
7.57
7.51
7.50
7.50
7.49
7.26
7.17
7.15
7.12
7.11
7.10
5.07
O
H
O
CN
1i
^{1}H NMR (600 MHz)
Solvent: $CDCl_3$
0.85
0.96
3.04
1.99
1.00
0.99
2.06
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

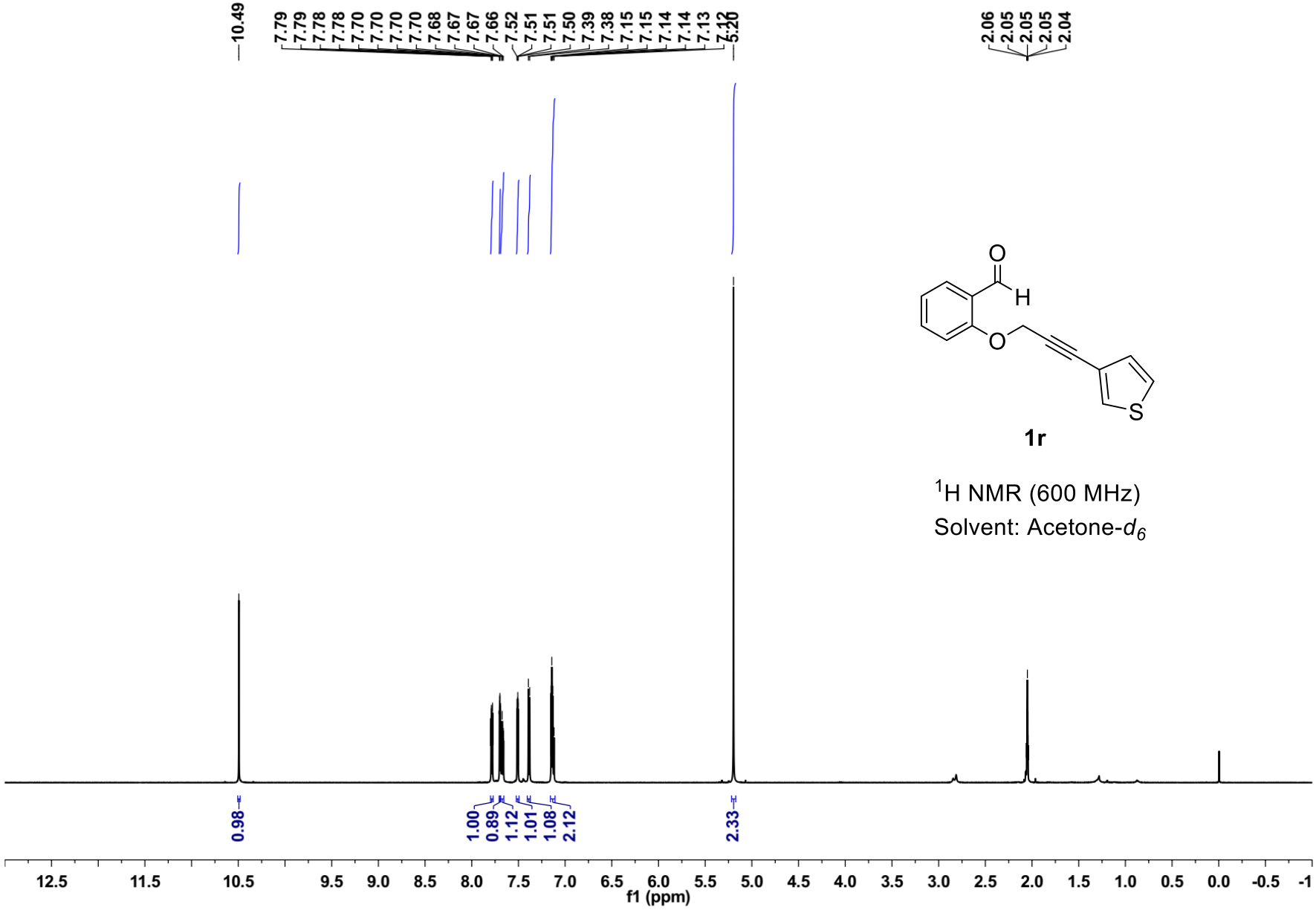

189.45
159.73
135.72
132.26
132.03
128.72
126.66
125.60
121.83
118.16
113.24
112.34
87.26
86.23
77.21
77.00
76.79
57.03
O
H
O
CN
1i
^{13}C NMR (150 MHz)
Solvent: $CDCl_3$
f1 (ppm)

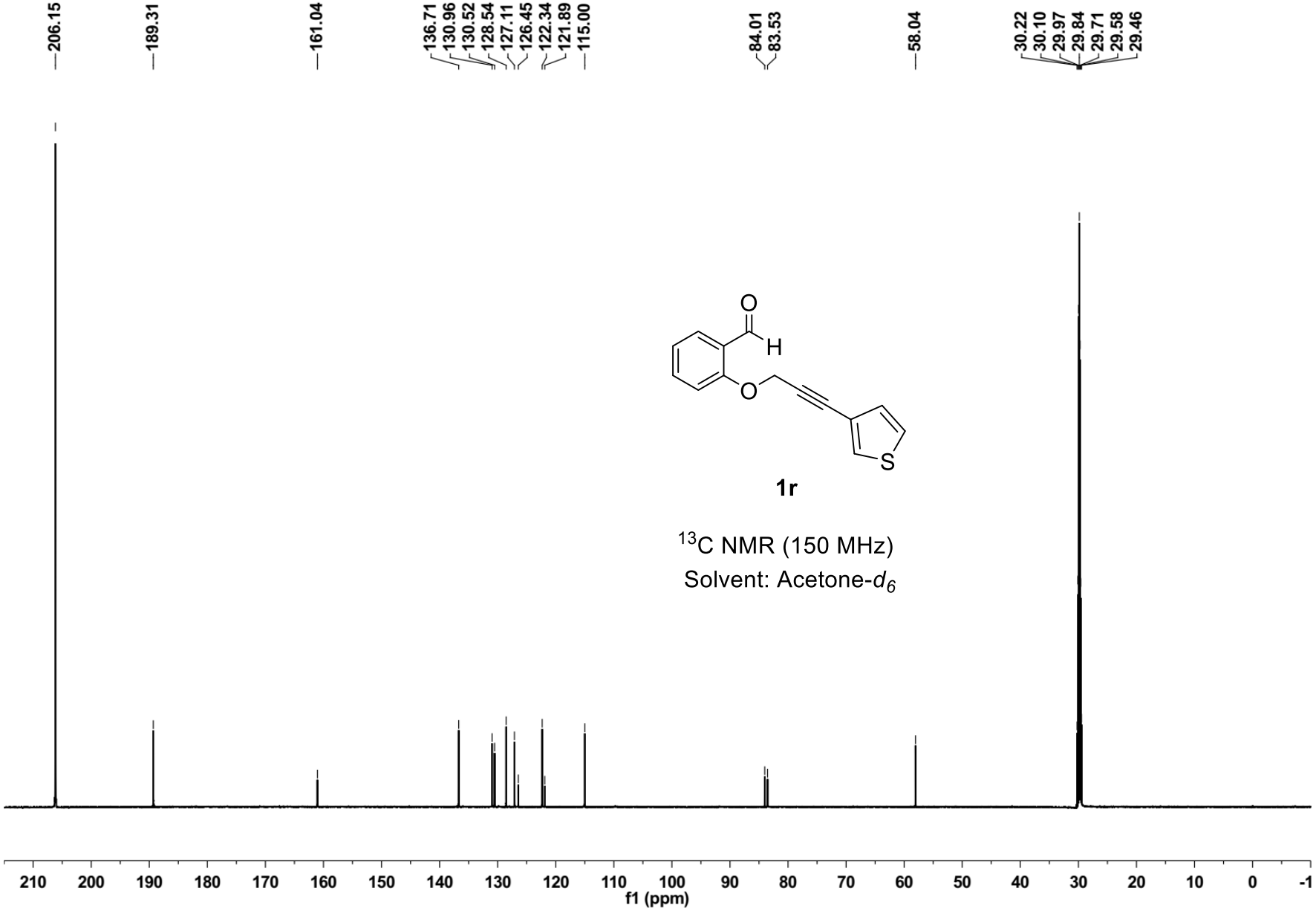

10.53
7.91
7.90
7.89
7.89
7.89
7.89
7.88
7.87
7.60
7.59
7.59
7.58
7.51
7.50
7.26
7.19
7.18
7.12
7.11
7.09
5.08
2.59
1.62
O
H
O
O
1k
1H NMR (600 MHz)
Solvent: CDCl3
0.86
2.88
1.00
1.88
0.95
0.98
1.97
3.04
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

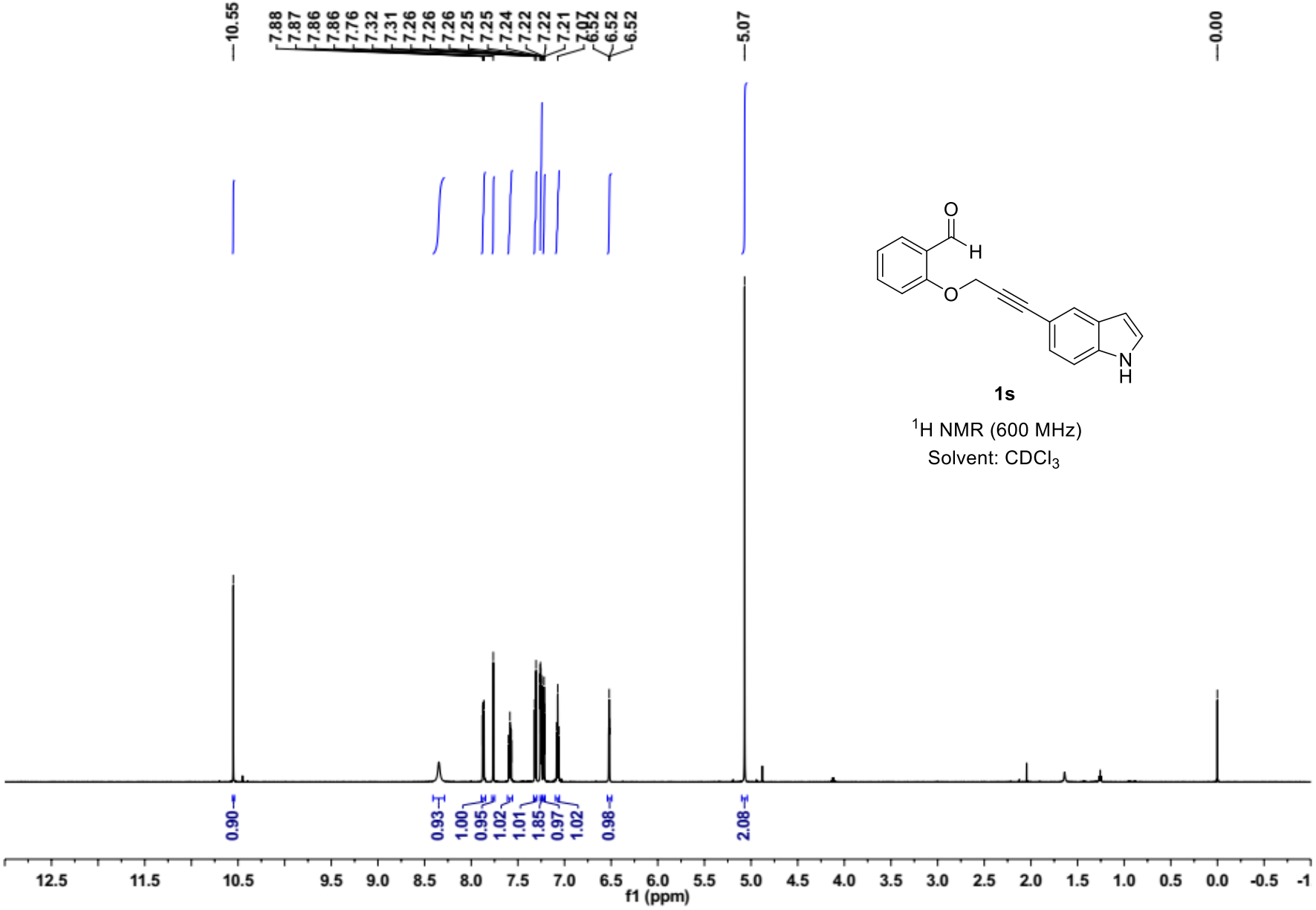

197.21
189.57
159.87
136.76
135.75
131.90
128.65
128.21
126.60
125.54
121.71
113.28
87.14
86.09
77.21
77.00
76.79
57.14
26.64
f1 (ppm)
O
H
O
O
1k
13C NMR (150 MHz)
Solvent: CDCl3


10.52
7.88
7.87
7.86
7.86
7.58
7.58
7.58
7.26
7.20
7.18
7.18
7.10
7.09
6.97
6.96
6.95
6.95
6.86
6.86
6.75
6.74
5.97
5.02
1.58
0.00
O
H
O
O
O
1p
1H NMR (600 MHz)
Solvent: CDCl3
0.94
1.00
1.02
1.04
1.04
1.04
0.97
1.03
2.10
2.14
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


189.70
160.08
148.42
147.43
135.69
128.52
126.66
125.55
121.50
115.02
113.43
111.71
108.46
101.39
88.00
81.32
77.21
77.00
76.79
57.34
O
H
O
O
O
1p
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)


10.49
7.79
7.79
7.78
7.78
7.70
7.70
7.70
7.70
7.68
7.67
7.67
7.66
7.52
7.51
7.51
7.50
7.39
7.38
7.15
7.15
7.14
7.14
7.13
7.12
5.20
2.06
2.05
2.05
2.05
2.04
O
H
O
S
1r
1H NMR (600 MHz)
Solvent: Acetone-d6
0.98
1.00
0.89
1.12
1.01
1.08
2.12
2.33
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

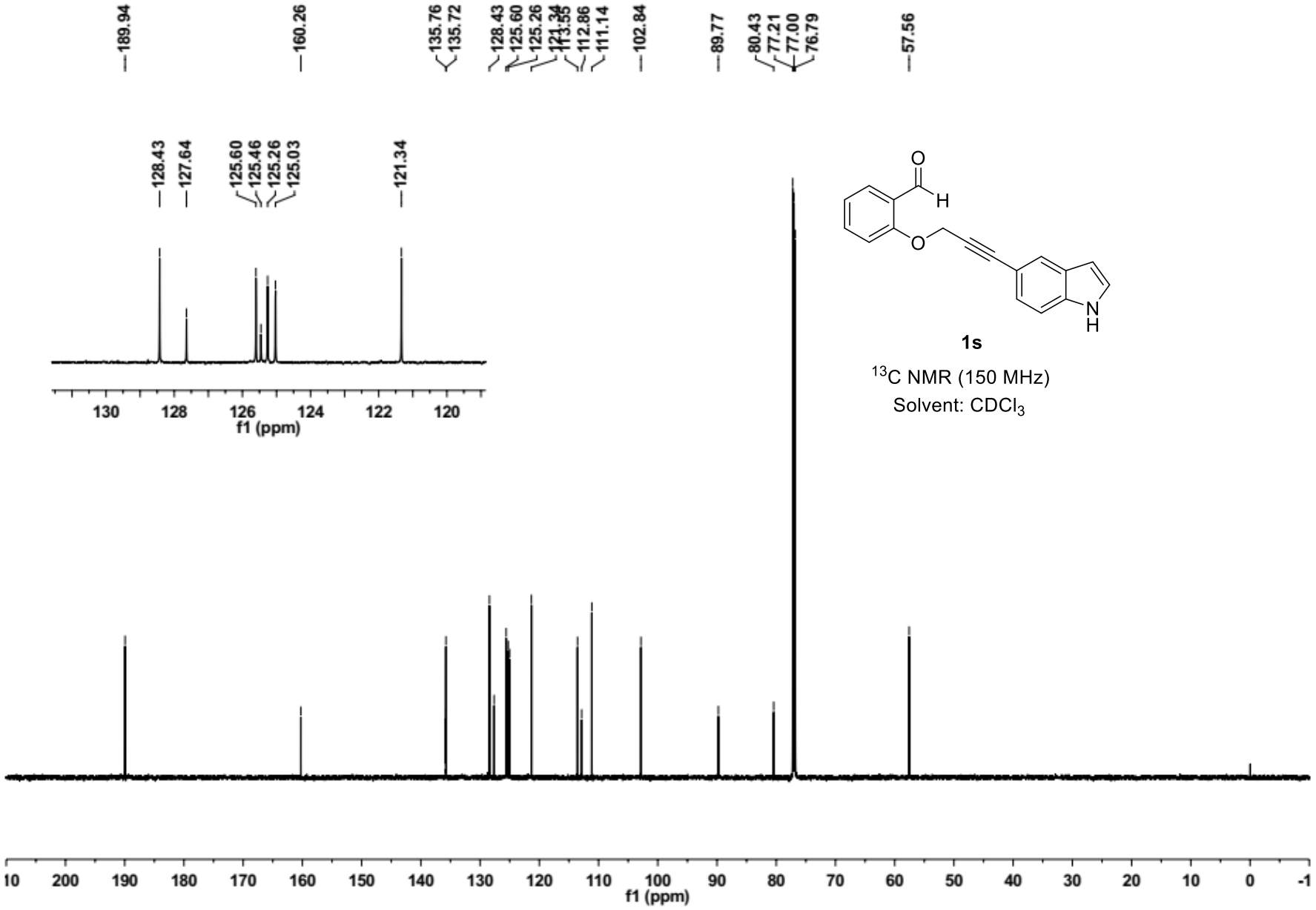

206.15
189.31
161.04
136.71
130.96
130.52
128.54
127.11
126.45
122.34
121.89
115.00
84.01
83.53
58.04
30.22
30.10
29.97
29.84
29.71
29.58
29.46
O
H
O
S
1r
^{13}C NMR (150 MHz)
Solvent: Acetone-d_6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



1s

^{1}H NMR (600 MHz)

Solvent: $CDCl_3$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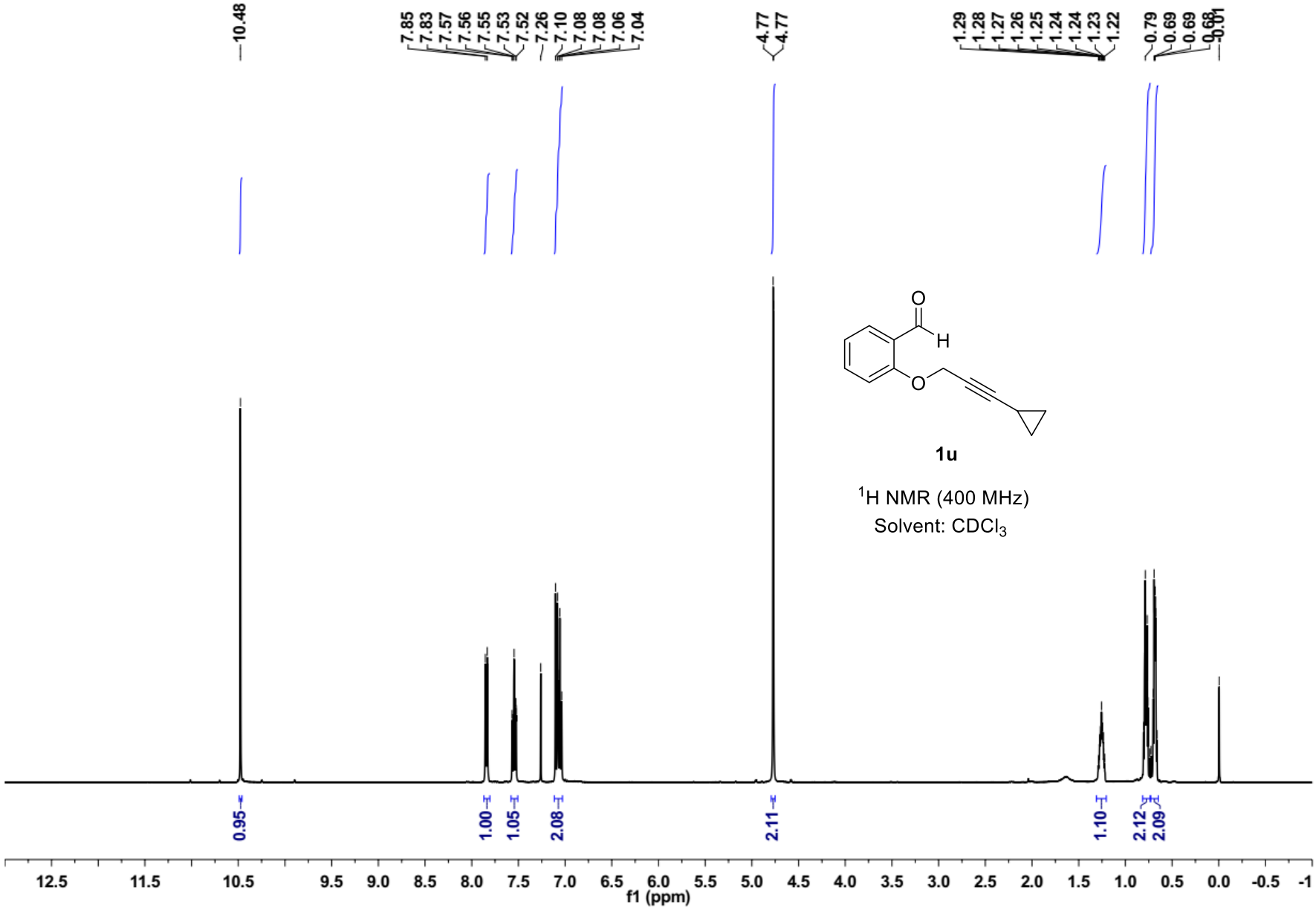
135.72
128.43
125.60
125.26
121.34
113.55
112.86
111.14
102.84
89.77
80.43
77.21
77.00
76.79
57.56
128.43
127.64
125.60
125.46
125.26
125.03
121.34
130
128
126
124
122
120
f1 (ppm)
O
H
O
N
H
1s
13C NMR (150 MHz)
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


10.48
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7.83
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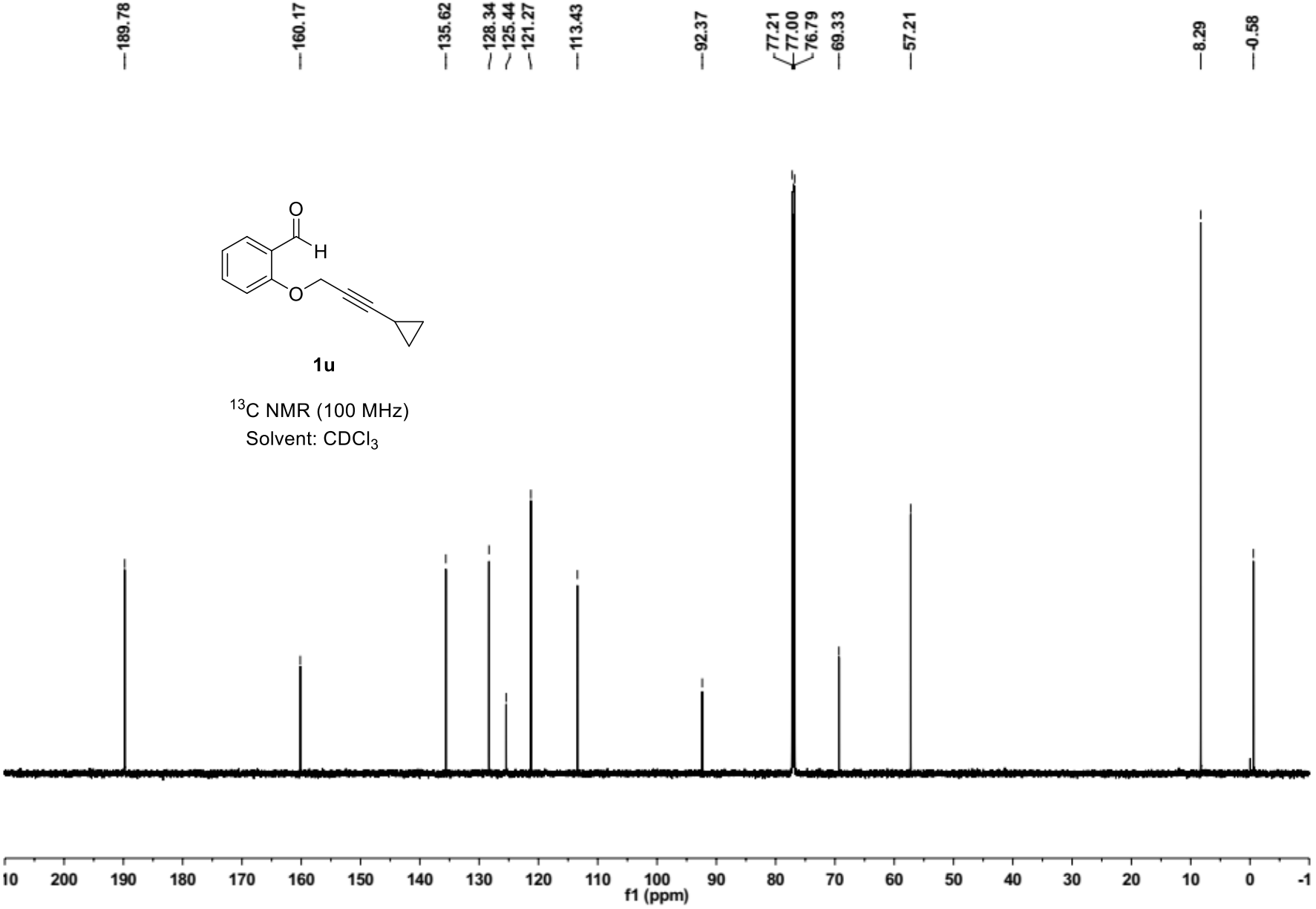
7.56
7.55
7.53
7.52
7.26
7.10
7.08
7.08
7.06
7.04
4.77
4.77
1.29
1.28
1.27
1.26
1.25
1.24
1.24
1.23
1.22
0.79
0.69
0.69
0.68
0.01
O
H
O
1u
1H NMR (400 MHz)
Solvent: CDCl3
0.95
1.00
1.05
2.08
2.11
1.10
2.12
2.09
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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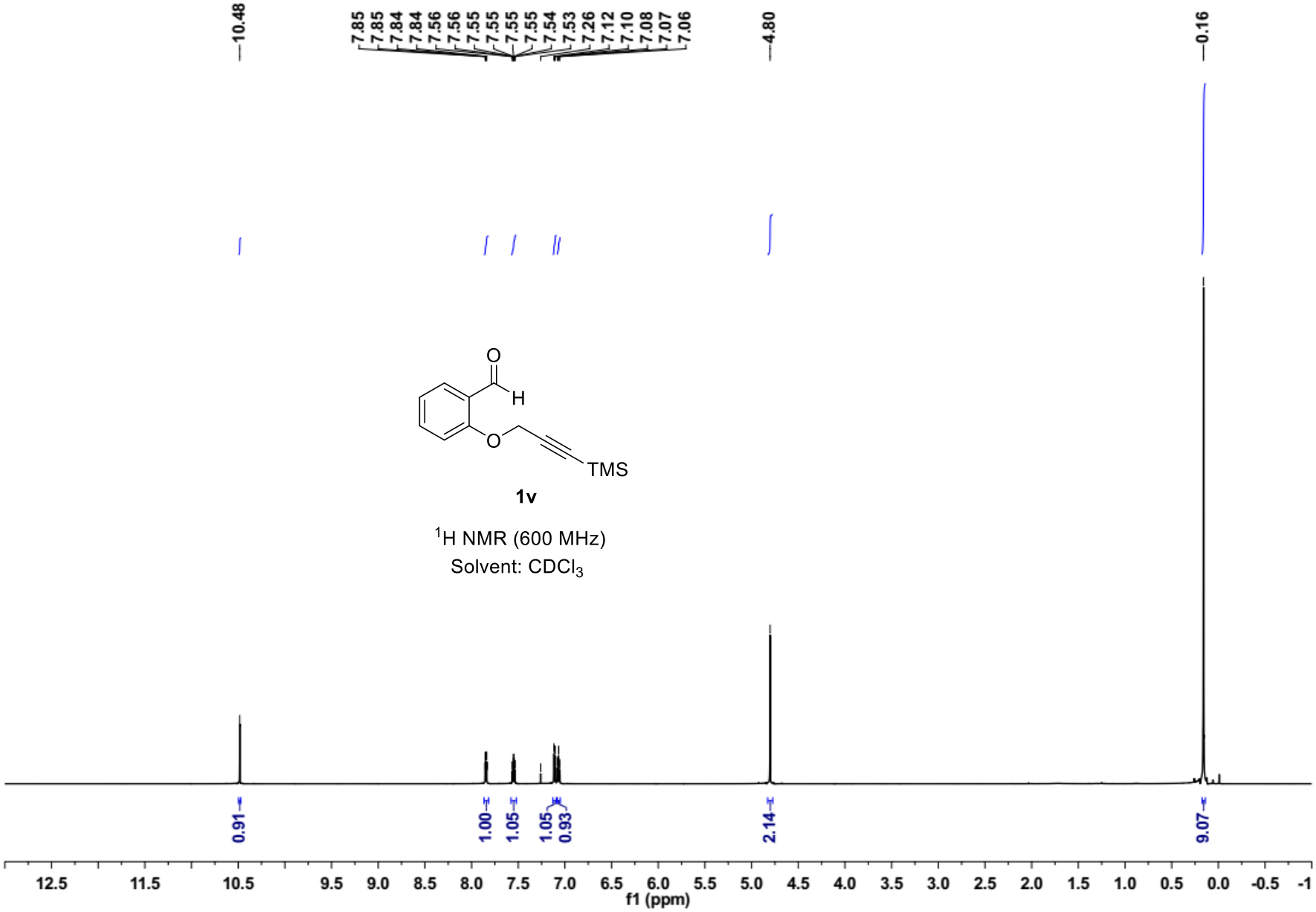
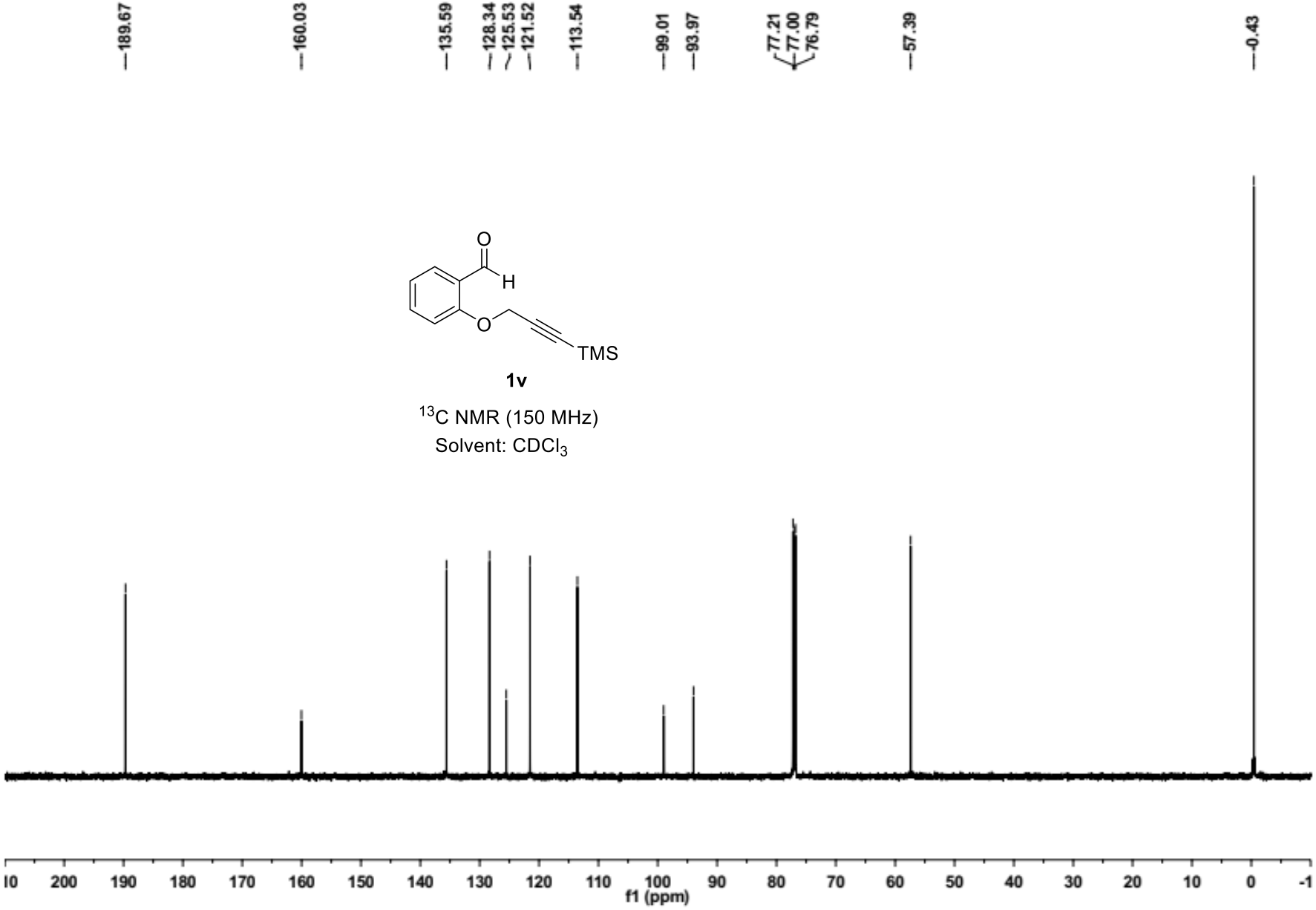
125.44
121.27
113.43
92.37
77.21
77.00
76.79
69.33
57.21
8.29
-0.58
O
H
O
1u
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)


10.48
7.85
7.85
7.84
7.84
7.56
7.56
7.55
7.55
7.55
7.55
7.54
7.53
7.26
7.12
7.10
7.08
7.07
7.06
4.80
0.16
O
H
O
TMS
1v
1H NMR (600 MHz)
Solvent: CDCl3
0.91
1.00
1.05
1.05
0.93
2.14
9.07
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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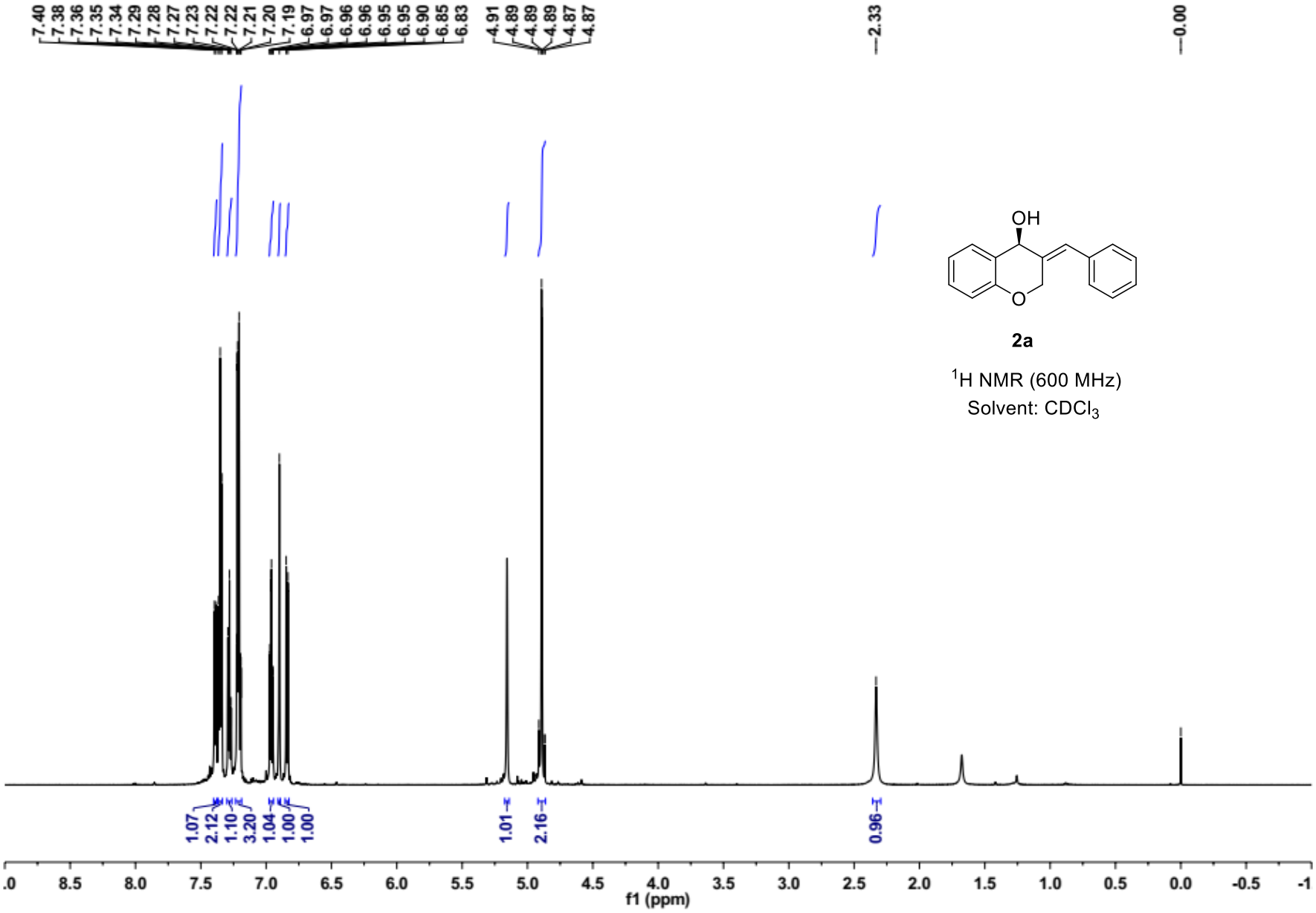
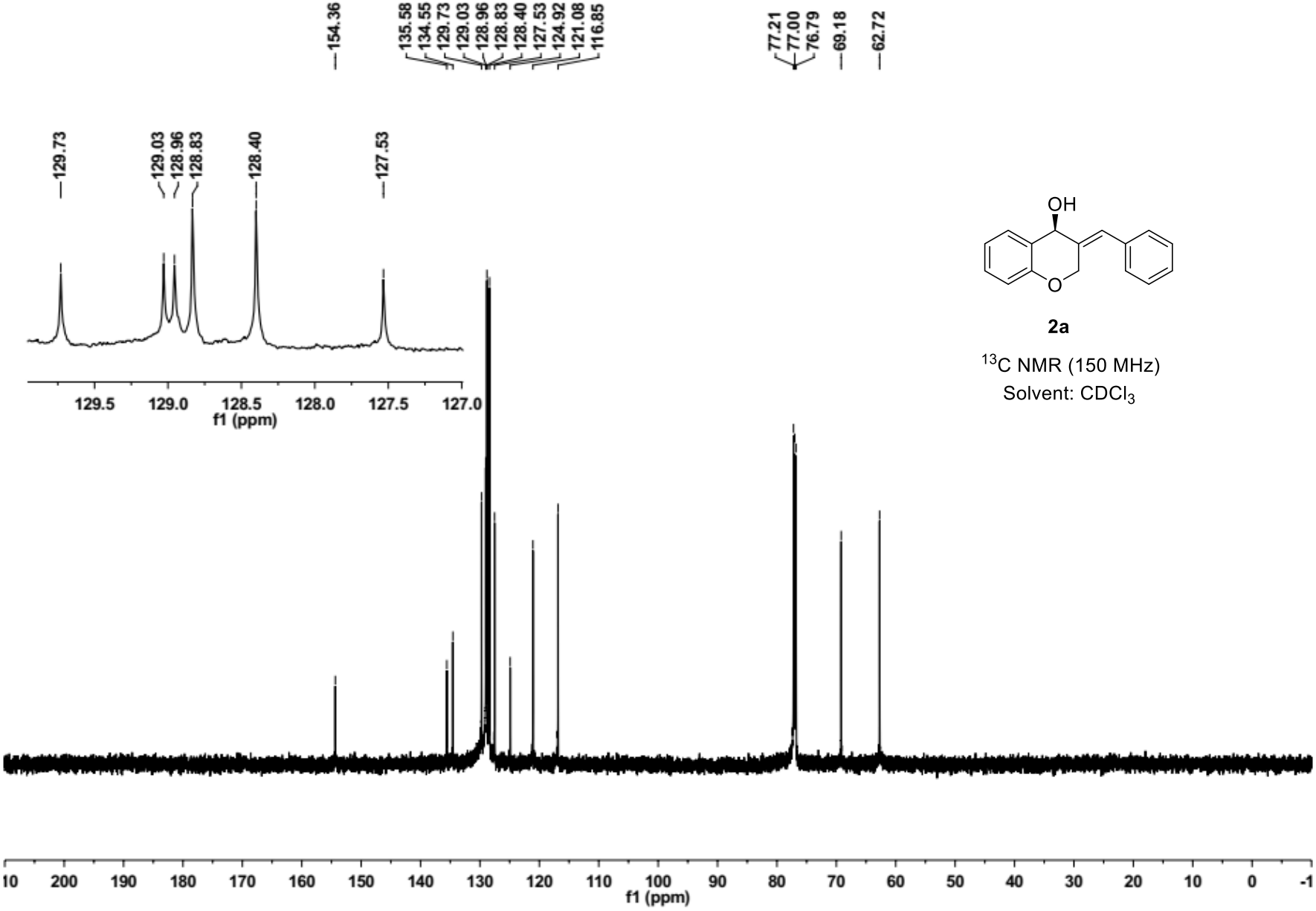
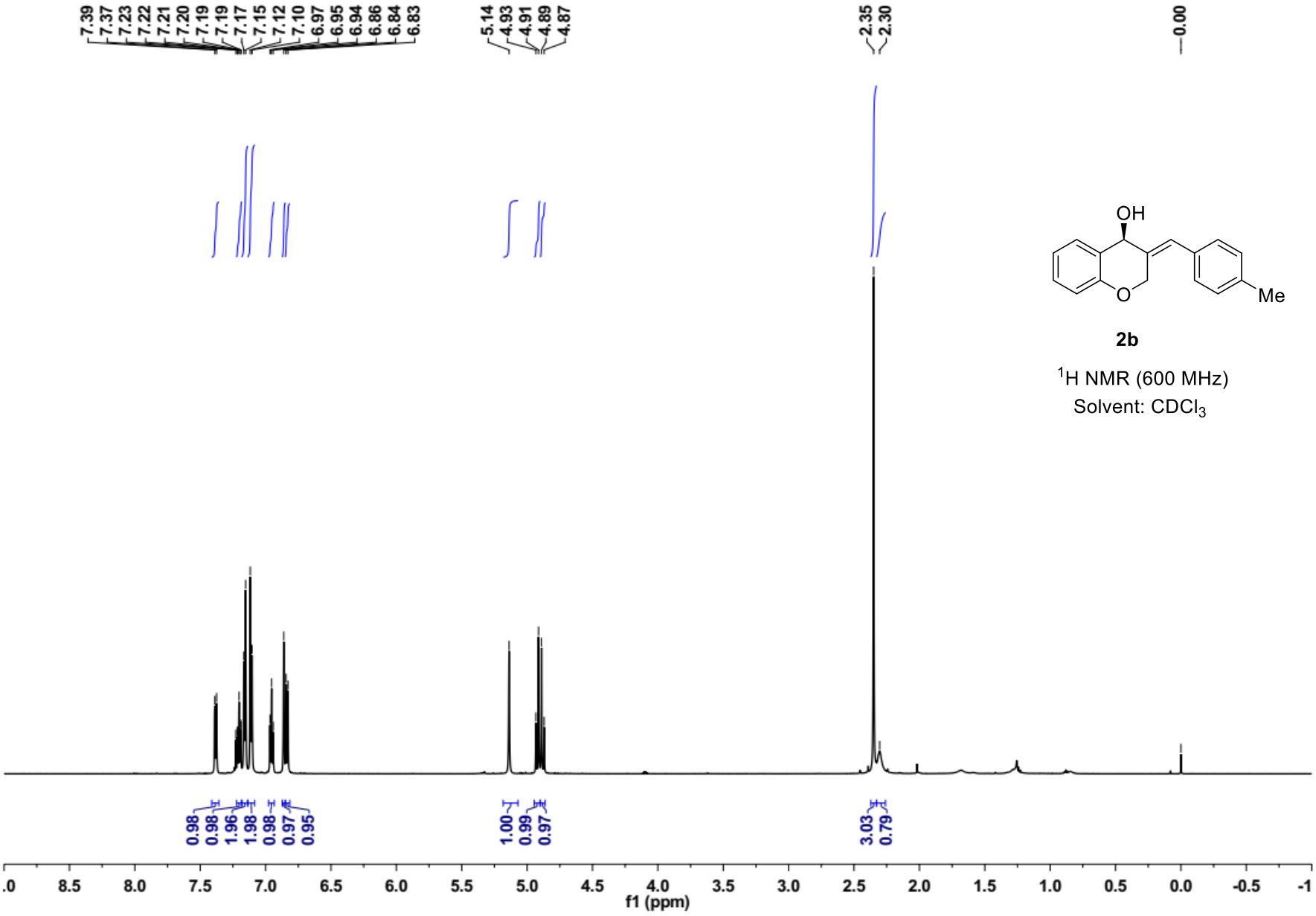
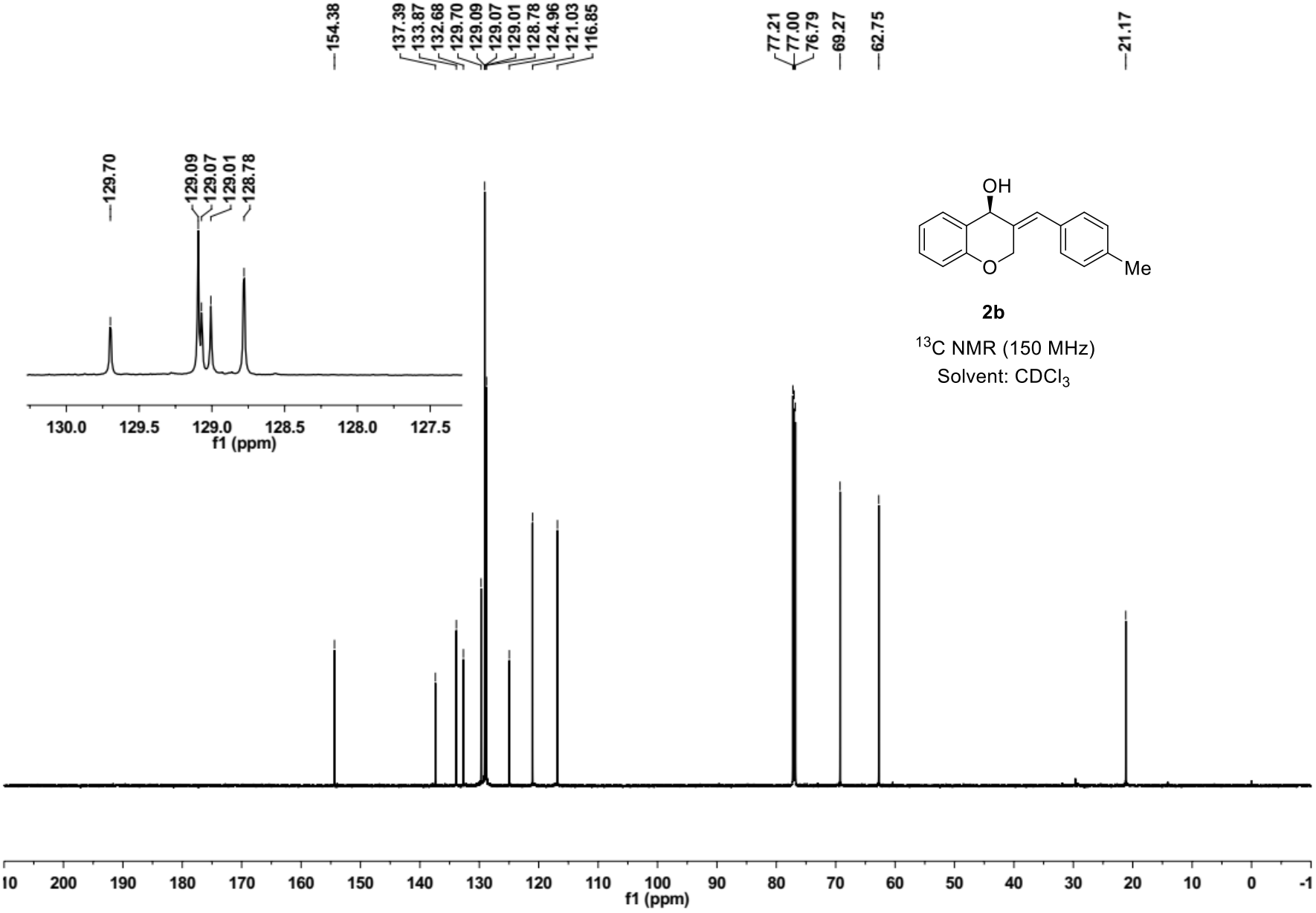
160.03
135.59
128.34
125.53
121.52
113.54
99.01
93.97
77.21
77.00
76.79
57.39
-0.43
O
H
O
TMS
1v
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)


7.40
7.38
7.36
7.35
7.34
7.29
7.28
7.27
7.23
7.22
7.22
7.21
7.20
7.19
6.97
6.97
6.96
6.96
6.95
6.95
6.90
6.85
6.83
4.91
4.89
4.89
4.89
4.87
4.87
2.33
0.00
OH
O
2a
1H NMR (600 MHz)
Solvent: CDCl3
1.07
2.12
1.10
3.20
1.04
1.00
1.00
1.01
2.16
0.96
f1 (ppm)


154.36
135.58
134.55
129.73
129.03
128.96
128.83
128.40
127.53
124.92
121.08
116.85
77.21
77.00
76.79
69.18
62.72
129.73
129.03
128.96
128.83
128.40
127.53
129.5
129.0
128.5
128.0
127.5
127.0
f1 (ppm)
OH
O
2a
13C NMR (150 MHz)
Solvent: CDCl3
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)


7.39
7.37
7.23
7.22
7.21
7.20
7.19
7.19
7.17
7.15
7.12
7.10
6.97
6.95
6.94
6.86
6.84
6.83
5.14
4.93
4.91
4.89
4.87
2.35
2.30
0.00
OH
O
Me
2b
1H NMR (600 MHz)
Solvent: CDCl3
0.98
0.98
1.96
1.98
0.98
0.97
0.95
1.00
0.99
0.97
3.03
0.79
f1 (ppm)


154.38
137.39
133.87
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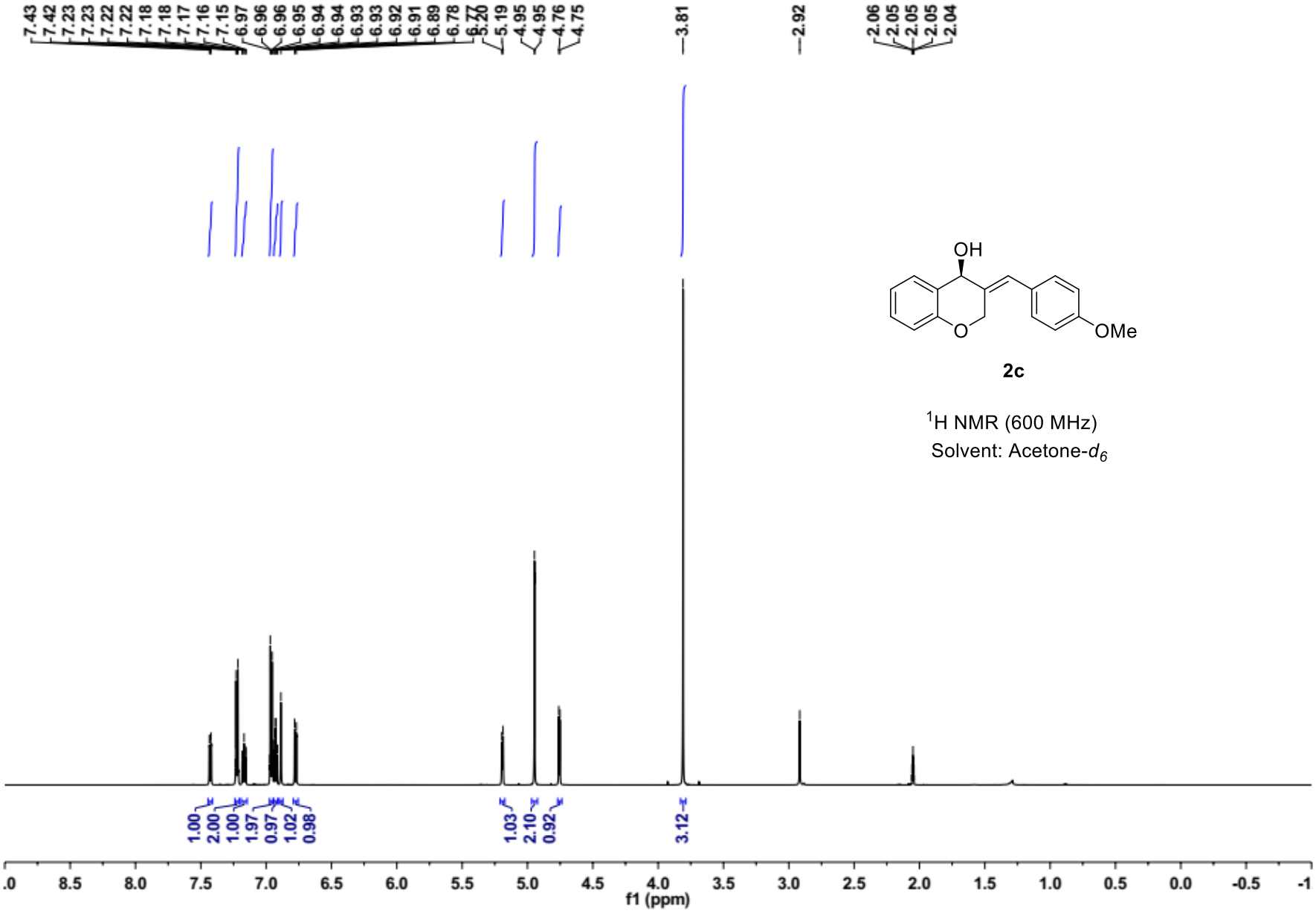
129.09
129.07
129.01
128.78
124.96
121.03
116.85
77.21
77.00
76.79
69.27
62.75
21.17
129.70
129.09
129.07
129.01
128.78
130.0
129.5
129.0
128.5
128.0
127.5
f1 (ppm)
OH
O
Me
2b
13C NMR (150 MHz)
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.42
7.23
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7.18
7.18
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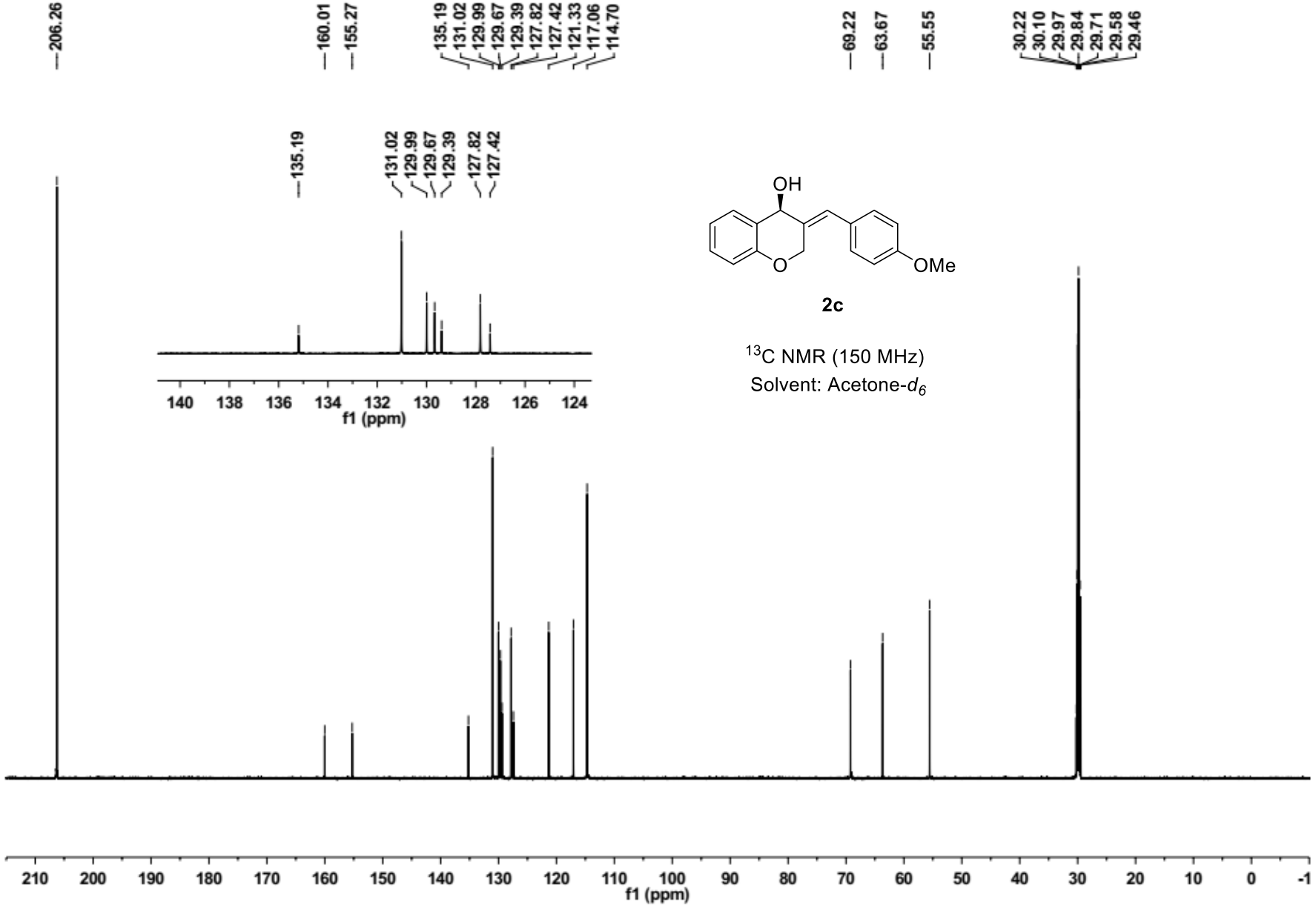
6.96
6.96
6.95
6.94
6.94
6.93
6.93
6.92
6.91
6.89
6.78
6.77
5.20
5.19
4.95
4.95
4.76
4.75
3.81
2.92
2.06
2.05
2.05
2.05
2.04
OH
O
OMe
2c
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
2.00
1.00
1.97
0.97
1.02
0.98
1.03
2.10
0.92
3.12
f1 (ppm)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135.19
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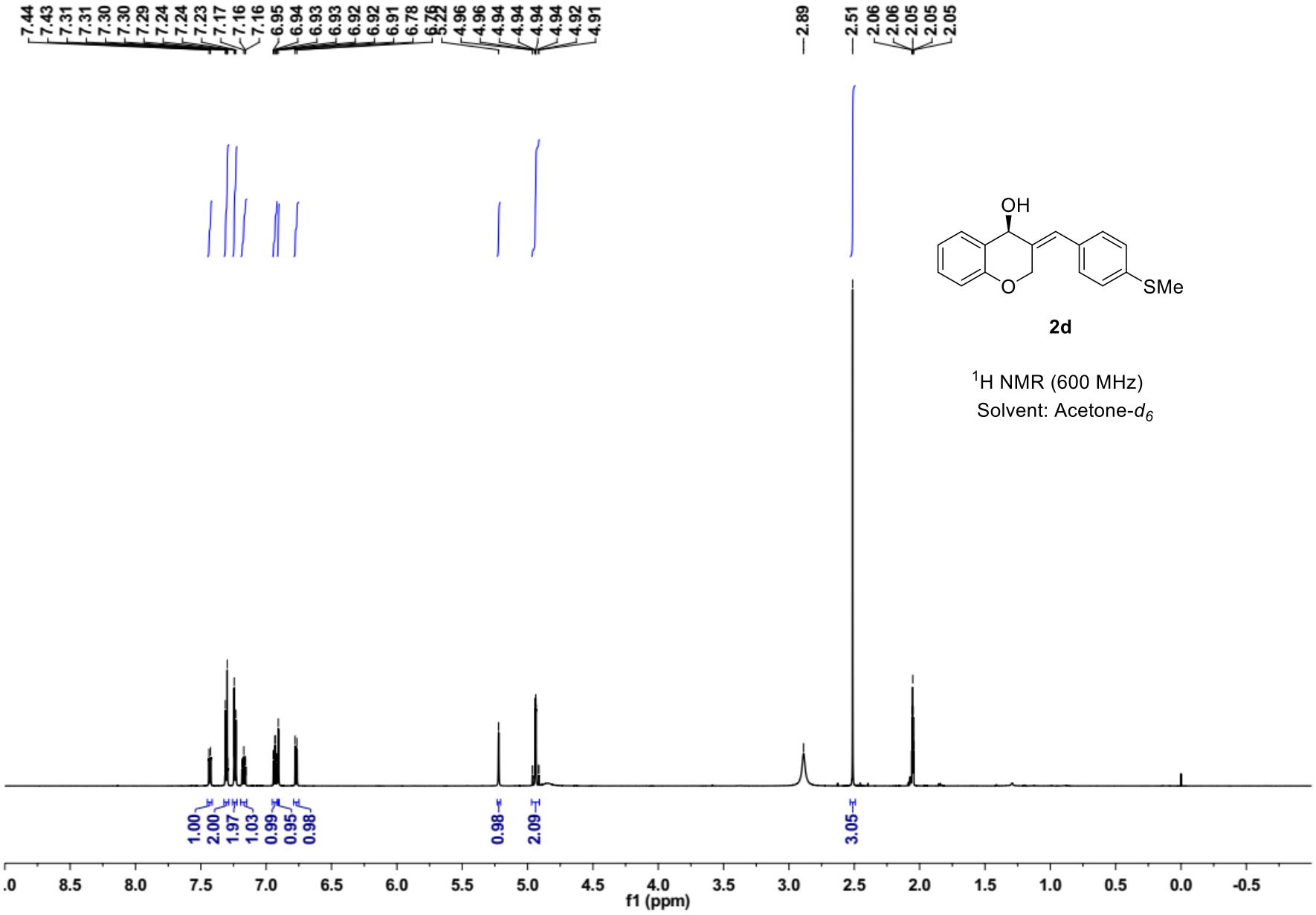
129.67
129.39
127.82
127.42
121.33
117.06
114.70
69.22
63.67
55.55
30.22
30.10
29.97
29.84
29.71
29.58
29.46
OH
O
OMe
2c
^{13}C NMR (150 MHz)
Solvent: Acetone-d_6
f1 (ppm)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7.43
7.31
7.31
7.30
7.30
7.29
7.24
7.24
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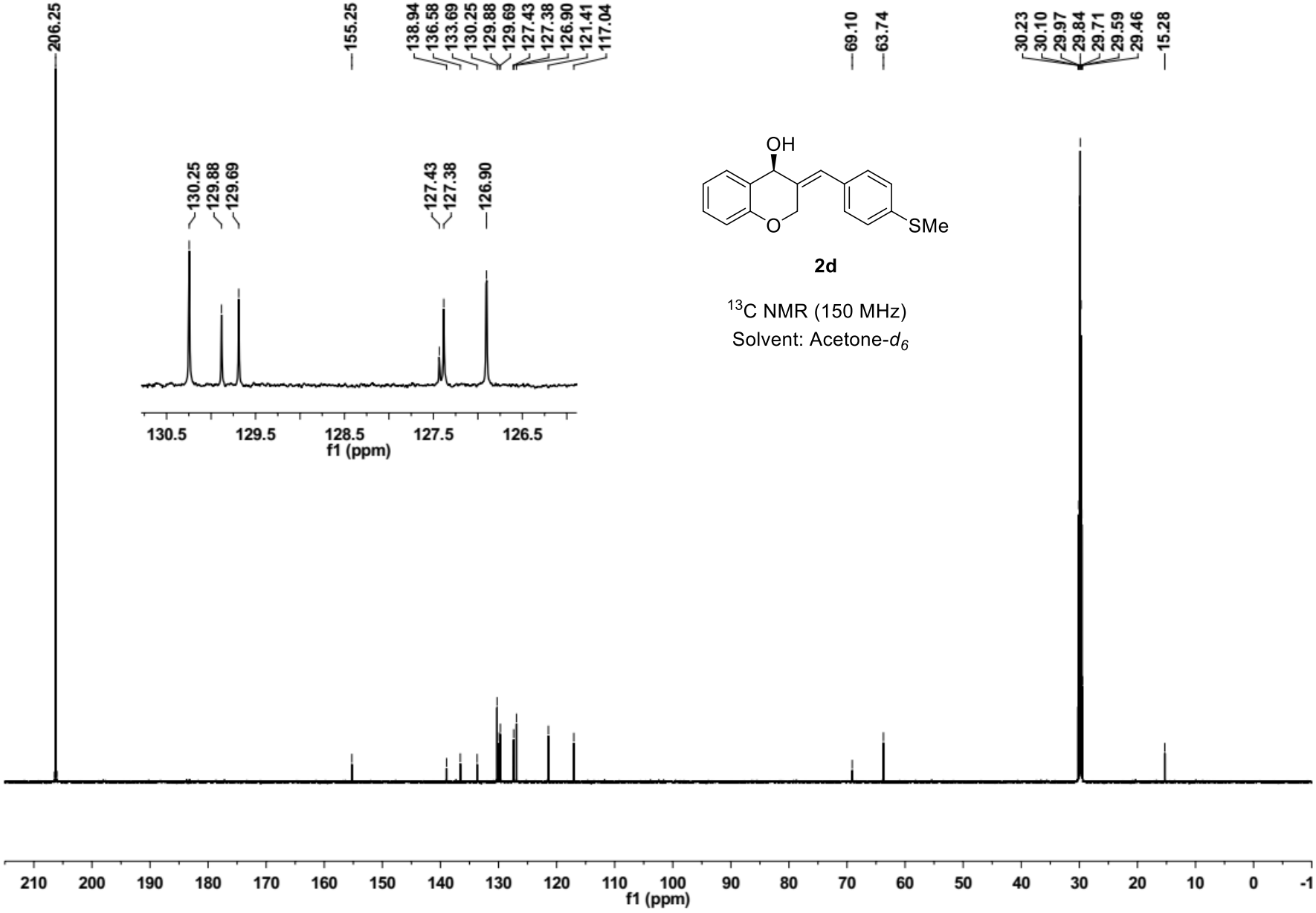
7.17
7.16
7.16
6.95
6.94
6.93
6.93
6.92
6.92
6.91
6.78
6.76
5.22
4.96
4.96
4.94
4.94
4.94
4.94
4.92
4.91
2.89
2.51
2.06
2.06
2.05
2.05
2.05
OH
O
SMe
2d
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
2.00
1.97
1.03
0.99
0.95
0.98
0.98
2.09
3.05
f1 (ppm)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136.58
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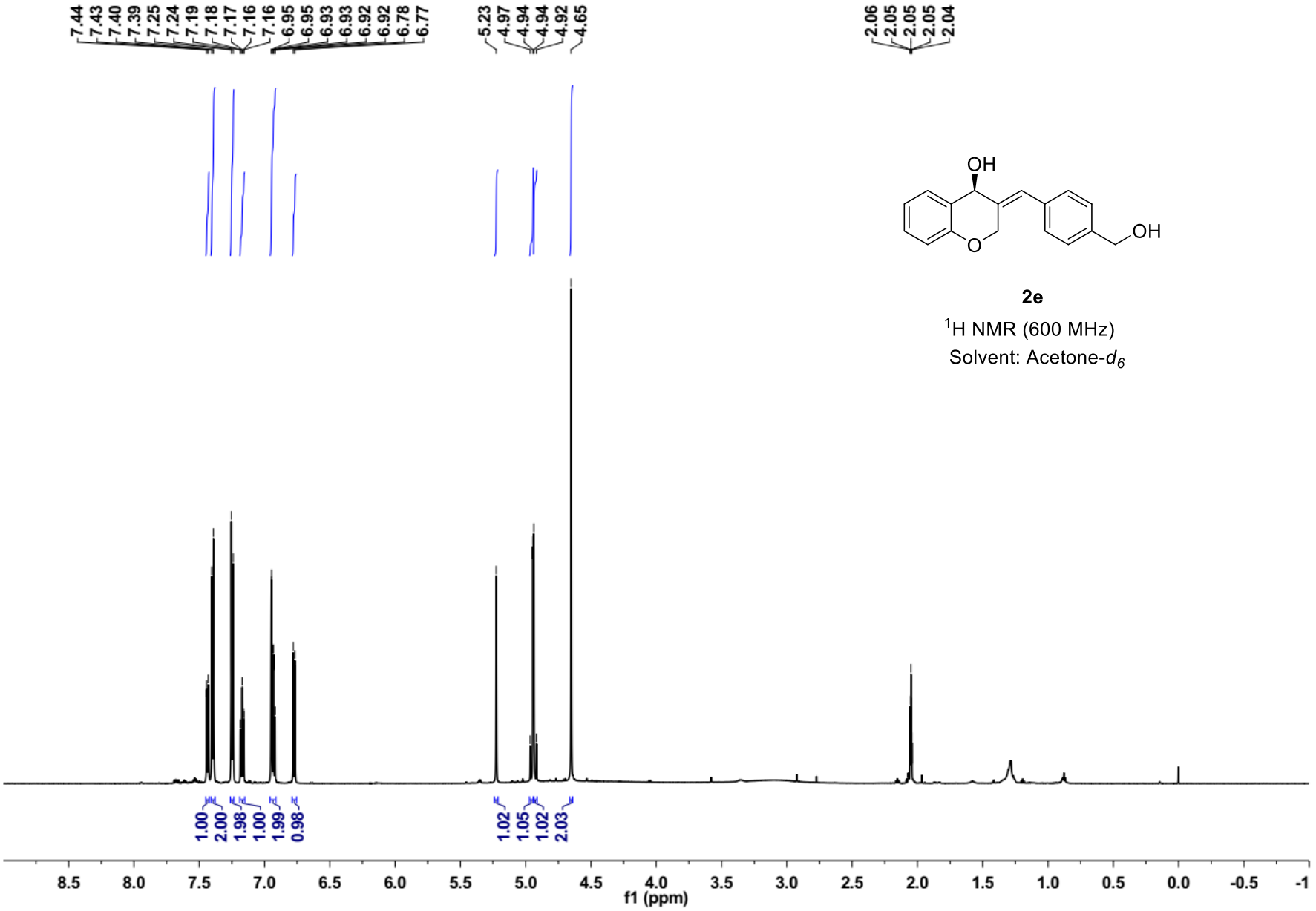
130.25
129.88
129.69
127.43
127.38
126.90
121.41
117.04
69.10
63.74
30.23
30.10
29.97
29.84
29.71
29.59
29.46
15.28
130.25
129.88
129.69
127.43
127.38
126.90
130.5
129.5
128.5
127.5
126.5
f1 (ppm)
OH
O
SMe
2d
13C NMR (150 MHz)
Solvent: Acetone-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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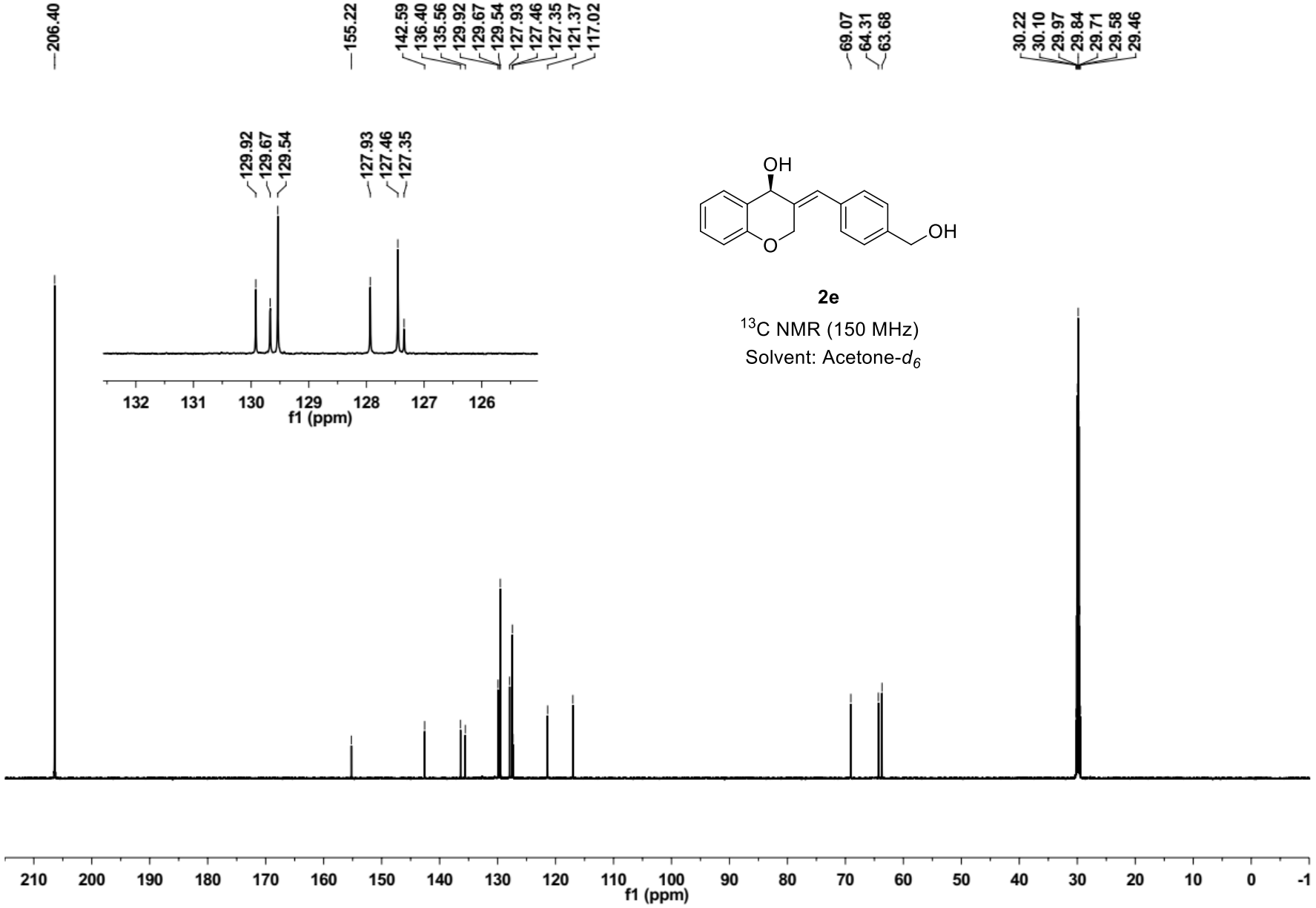
7.43
7.40
7.39
7.25
7.24
7.19
7.18
7.17
7.16
7.16
6.95
6.95
6.93
6.93
6.92
6.92
6.78
6.77
5.23
4.97
4.94
4.94
4.92
4.65
2.06
2.05
2.05
2.05
2.04
OH
OH
O
2e
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
2.00
1.98
1.00
1.99
0.98
1.02
1.05
1.02
2.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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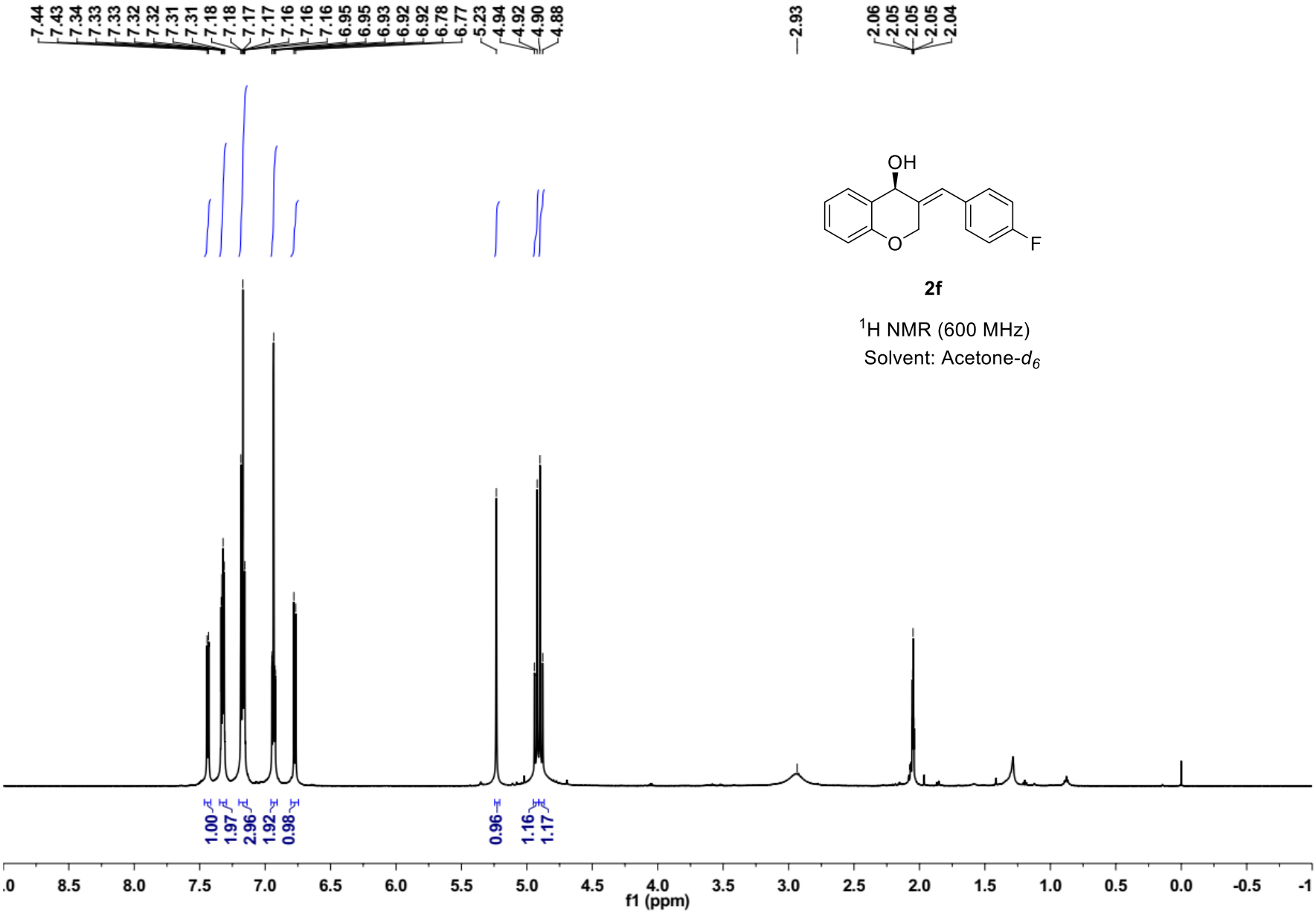
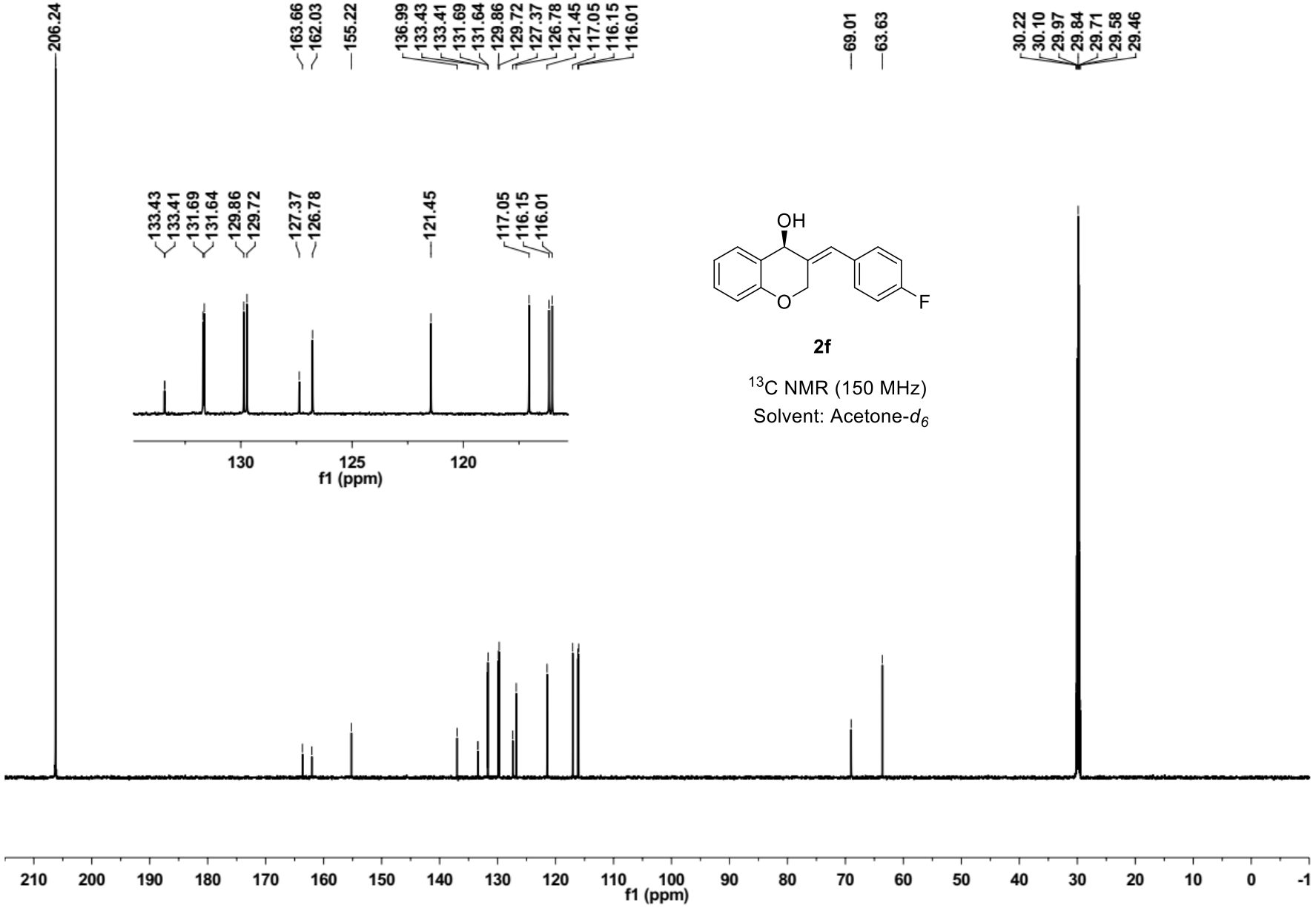
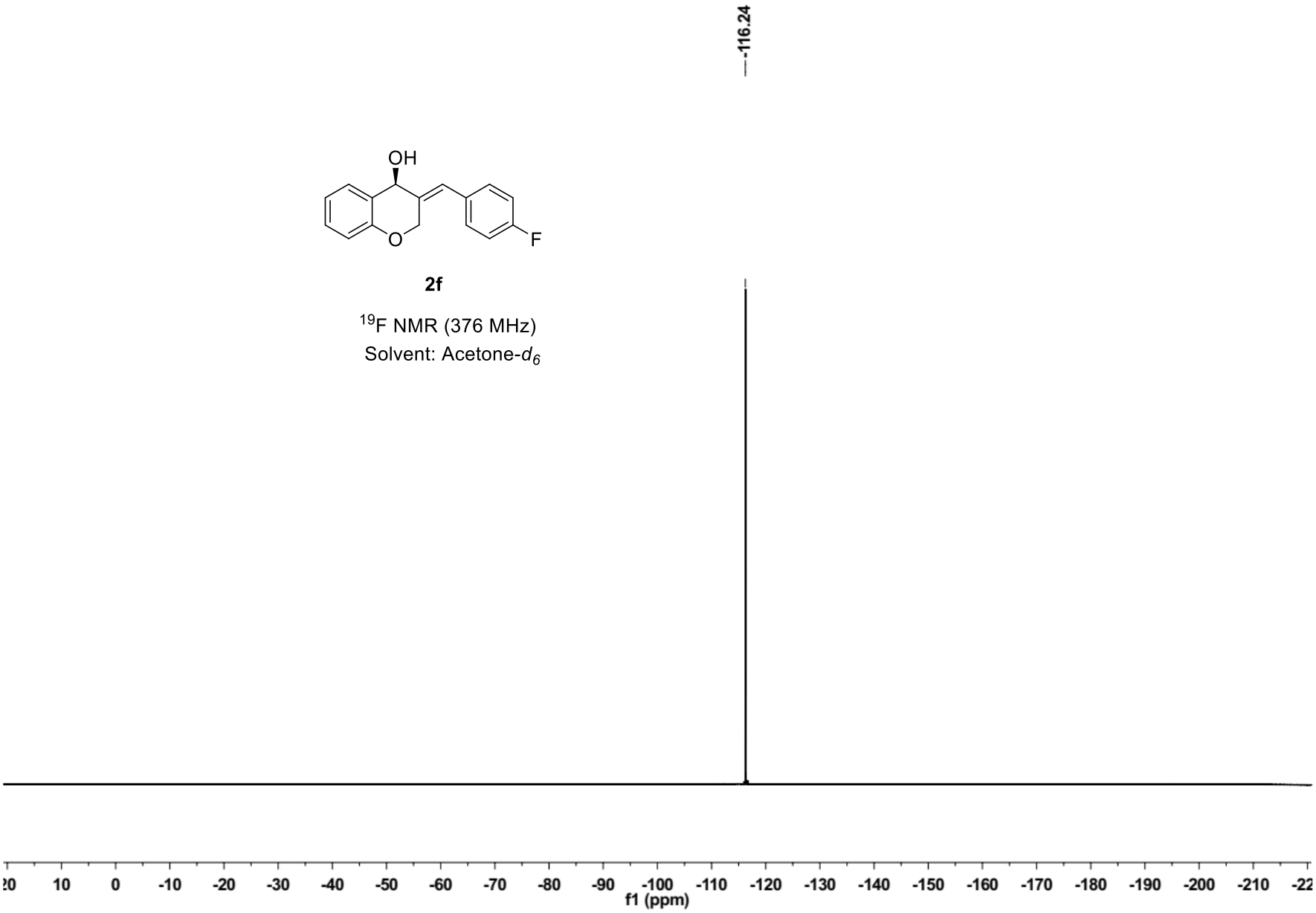
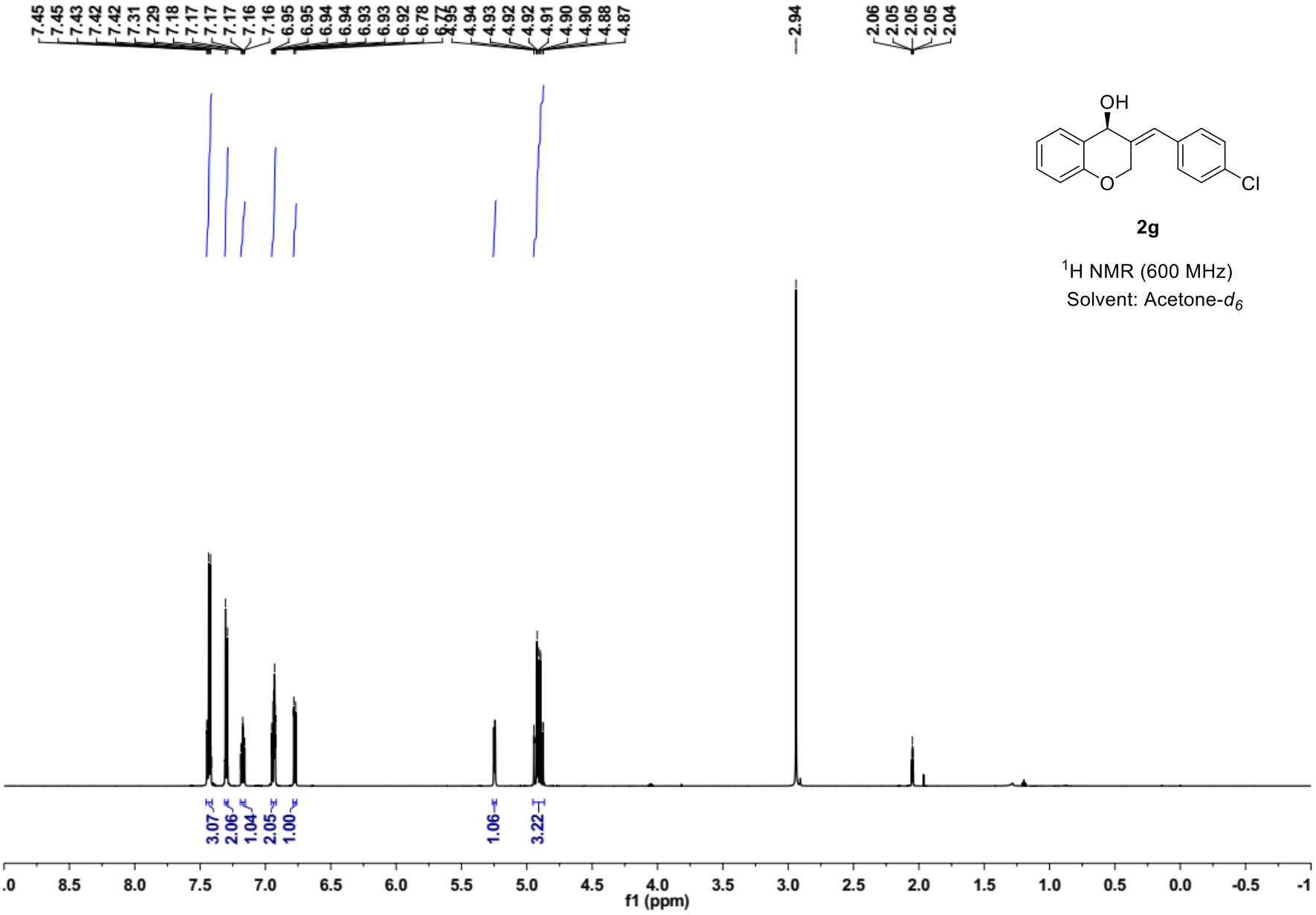
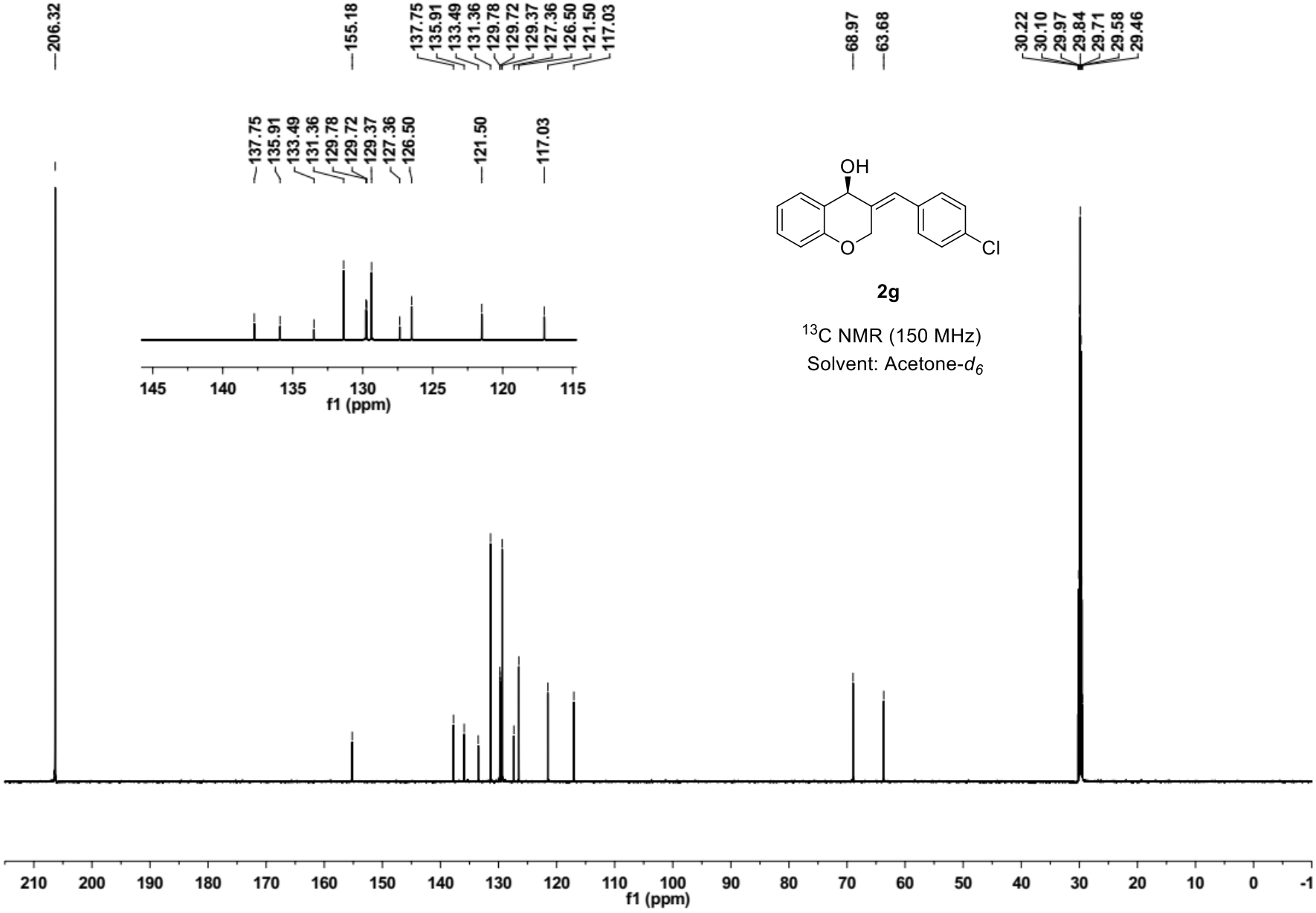
155.22
142.59
136.40
135.56
129.92
129.67
129.54
127.93
127.46
127.35
121.37
117.02
69.07
64.31
63.68
30.22
30.10
29.97
29.84
29.71
29.58
29.46
OH
OH
O
2e
13C NMR (150 MHz)
Solvent: Acetone-d6
f1 (ppm)
f1 (ppm)

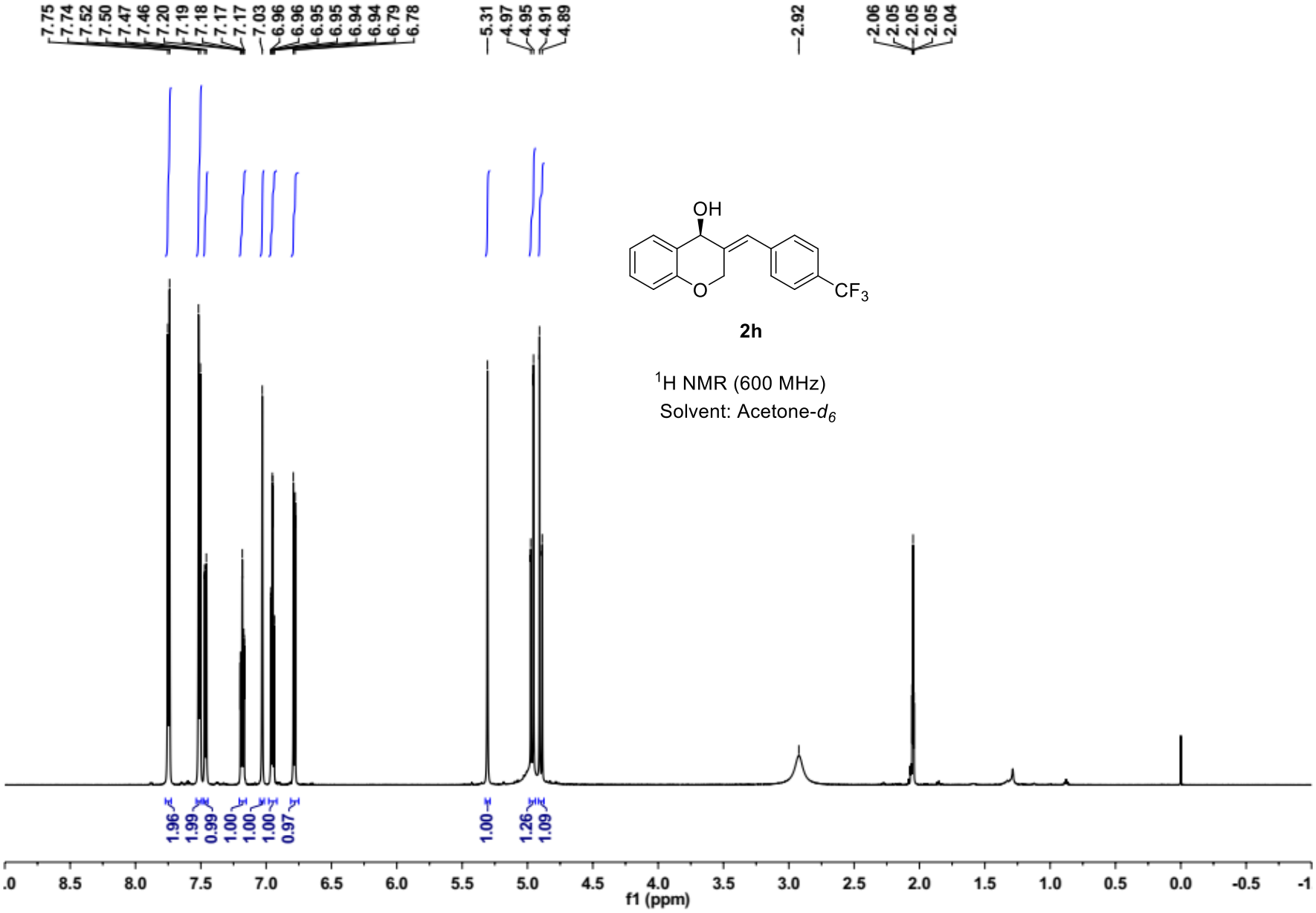

7.44
7.43
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.18
7.18
7.17
7.17
7.16
7.16
7.16
6.95
6.95
6.93
6.92
6.92
6.78
6.77
5.23
4.94
4.92
4.90
4.88
2.93
2.06
2.05
2.05
2.05
2.04
OH
O
F
2f
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
1.97
2.96
1.92
0.98
0.96
1.16
1.17
f1 (ppm)

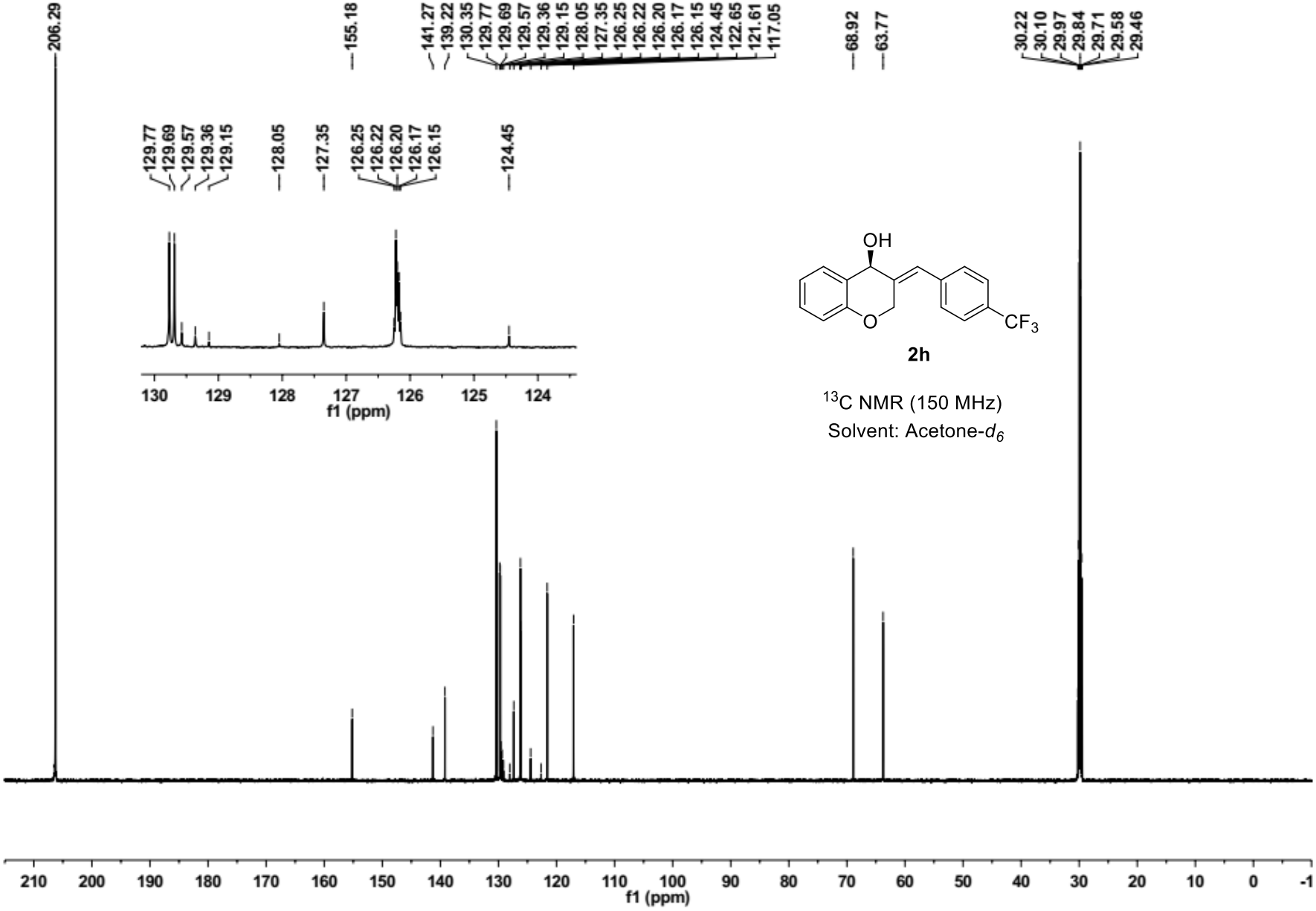

206.24
163.66
162.03
155.22
136.99
133.43
133.41
131.69
131.64
129.86
129.72
127.37
126.78
121.45
117.05
116.15
116.01
69.01
63.63
30.22
30.10
29.97
29.84
29.71
29.58
29.46
OH
O
F
2f
13C NMR (150 MHz)
Solvent: Acetone-d6
f1 (ppm)


-116.24
OH
O
F
2f
19F NMR (376 MHz)
Solvent: Acetone-d6
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)


7.45
7.45
7.43
7.42
7.42
7.31
7.29
7.18
7.17
7.17
7.17
7.16
7.16
6.95
6.95
6.94
6.94
6.93
6.93
6.92
6.78
6.77
4.95
4.94
4.93
4.92
4.92
4.91
4.90
4.90
4.88
4.87
2.94
2.06
2.05
2.05
2.05
2.04
OH
O
Cl
2g
1H NMR (600 MHz)
Solvent: Acetone-d6
3.07
2.06
1.04
2.05
1.00
1.06
3.22
f1 (ppm)


206.32
155.18
137.75
135.91
133.49
131.36
129.78
129.72
129.37
127.36
126.50
121.50
117.03
68.97
63.68
30.22
30.10
29.97
29.84
29.71
29.58
29.46
OH
O
Cl
2g
^{13}C NMR (150 MHz)
Solvent: Acetone-d_6
f1 (ppm)


7.75
7.74
7.52
7.50
7.47
7.46
7.20
7.19
7.18
7.17
7.17
7.03
6.96
6.96
6.95
6.95
6.94
6.94
6.79
6.78
5.31
4.97
4.95
4.91
4.89
2.92
2.06
2.05
2.05
2.05
2.04
OH
O
CF3
2h
1H NMR (600 MHz)
Solvent: Acetone-d6
1.96
1.99
0.99
1.00
1.00
1.00
0.97
1.00
1.26
1.09
f1 (ppm)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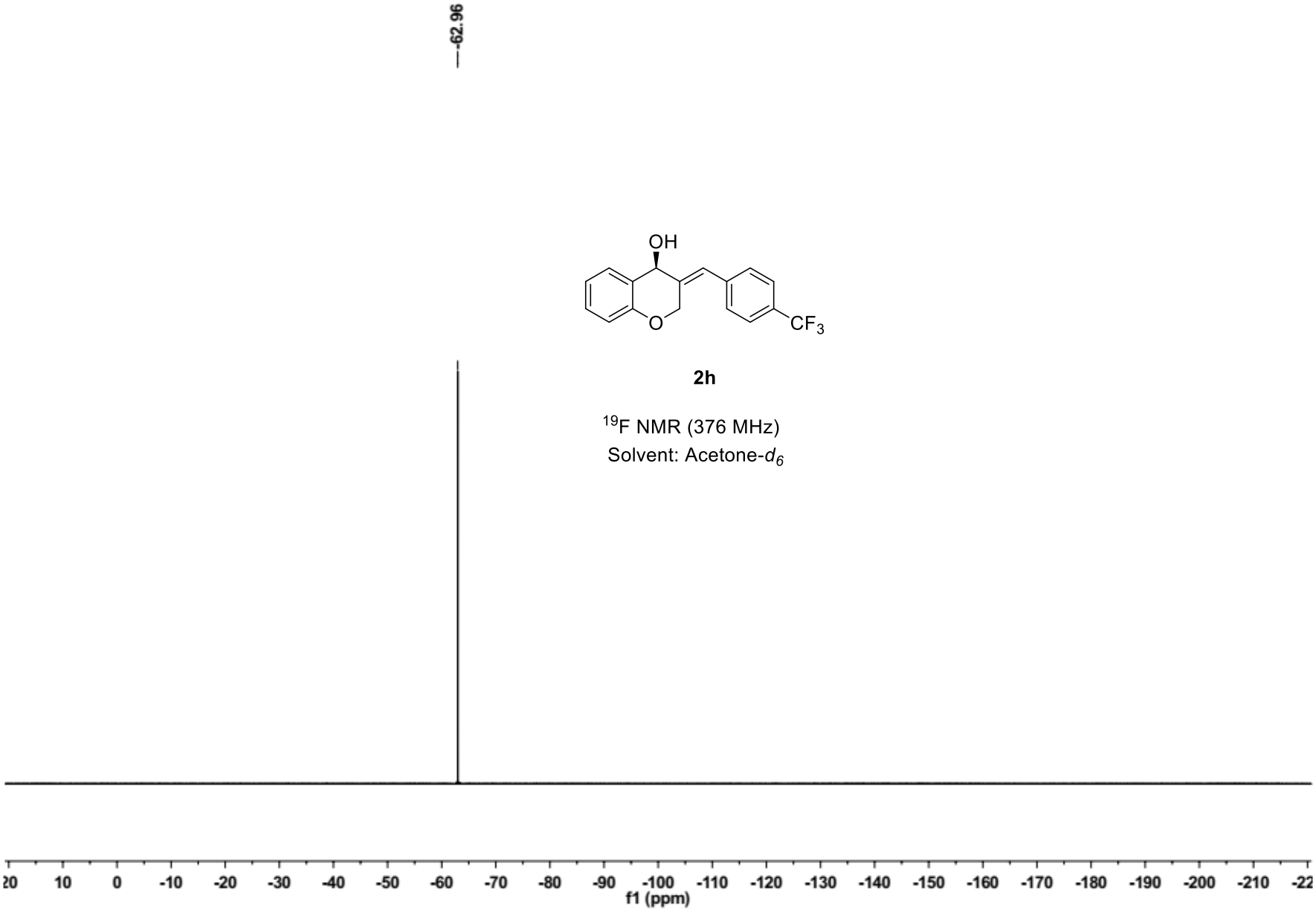
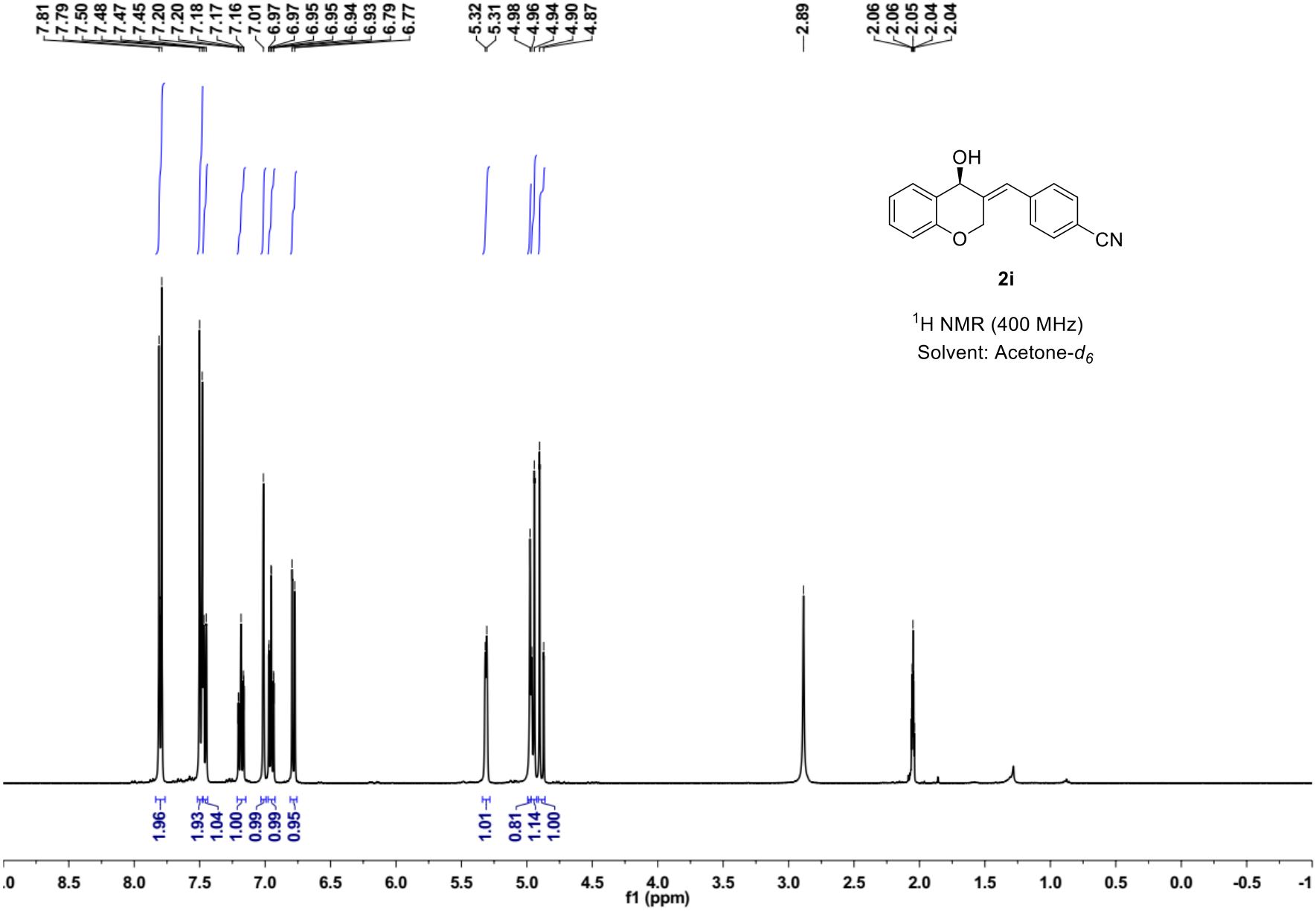
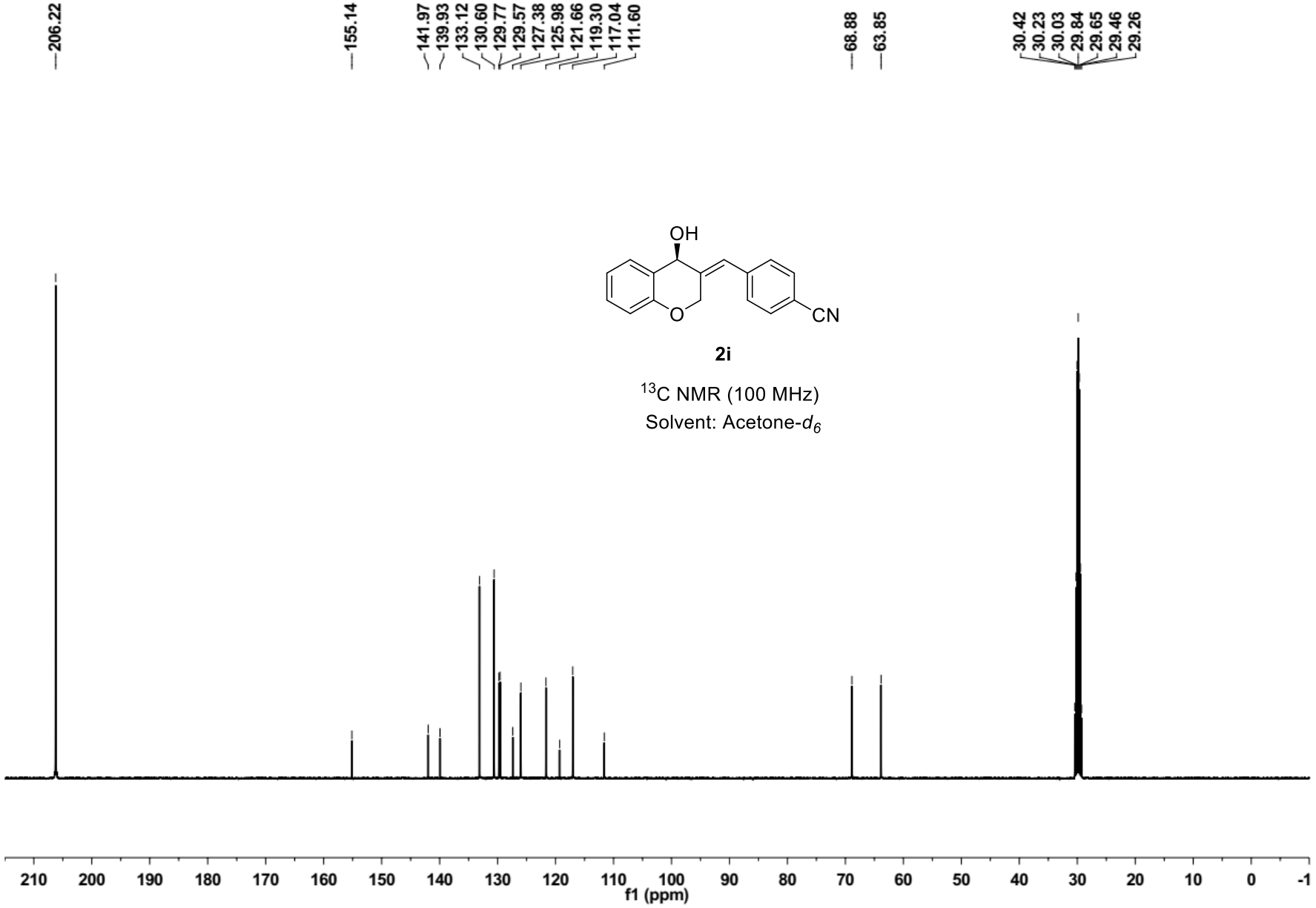
155.18
141.27
139.22
130.35
129.77
129.69
129.57
129.36
129.15
128.05
127.35
126.25
126.22
126.20
126.17
126.15
124.45
122.65
121.61
117.05
68.92
63.77
30.22
30.10
29.97
29.84
29.71
29.58
29.46
OH
O
CF3
2h
13C NMR (150 MHz)
Solvent: Acetone-d6
f1 (ppm)


-62.96
OH
O
CF3
2h
19F NMR (376 MHz)
Solvent: Acetone-d6
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)


7.81
7.79
7.50
7.48
7.47
7.45
7.20
7.20
7.18
7.17
7.16
7.01
6.97
6.97
6.95
6.95
6.94
6.93
6.79
6.77
5.32
5.31
4.98
4.96
4.94
4.90
4.87
2.89
2.06
2.06
2.05
2.04
2.04
OH
O
CN
2i
1H NMR (400 MHz)
Solvent: Acetone-d6
1.96
1.93
1.04
1.00
0.99
0.99
0.95
1.01
0.81
1.14
1.00
f1 (ppm)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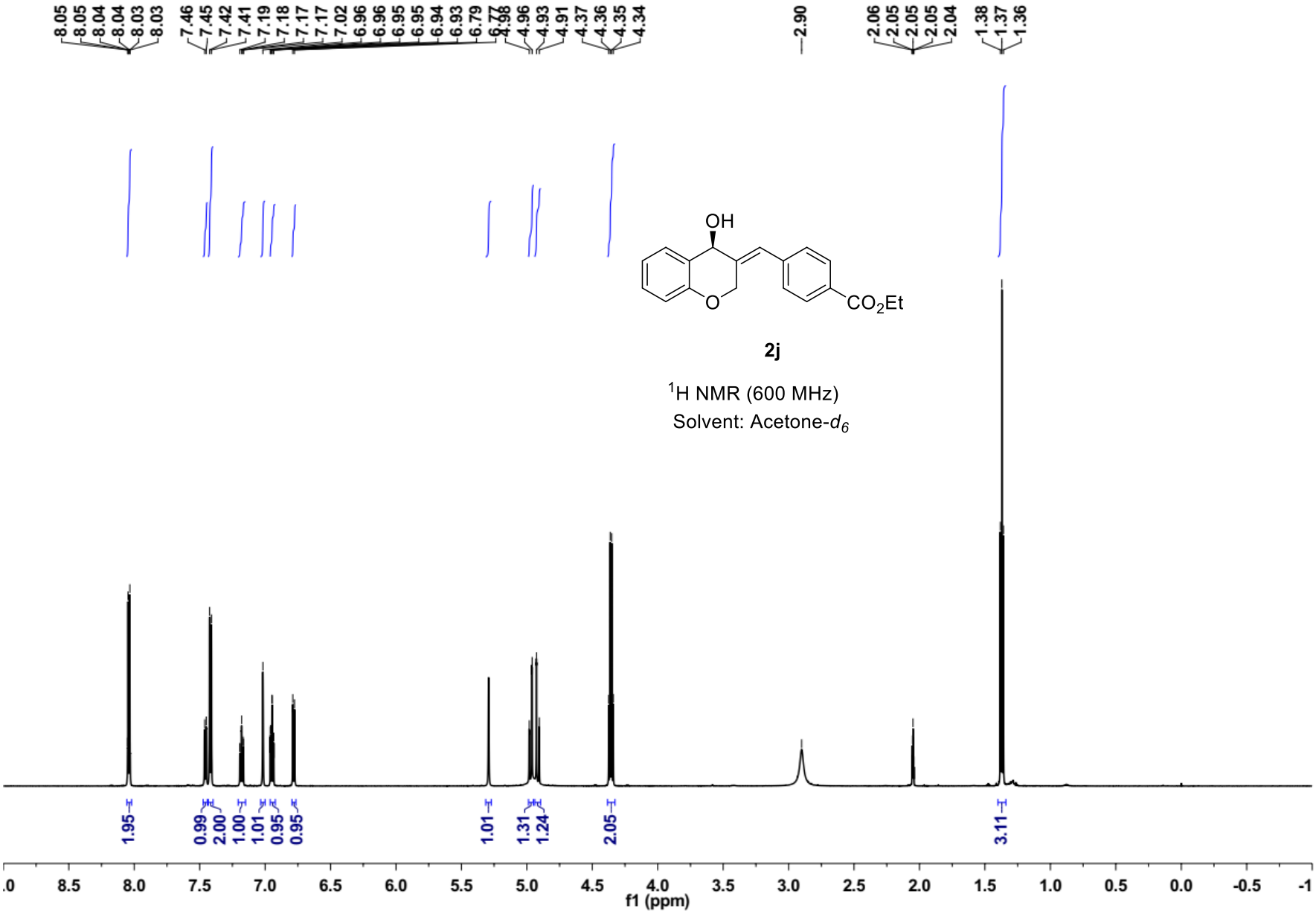
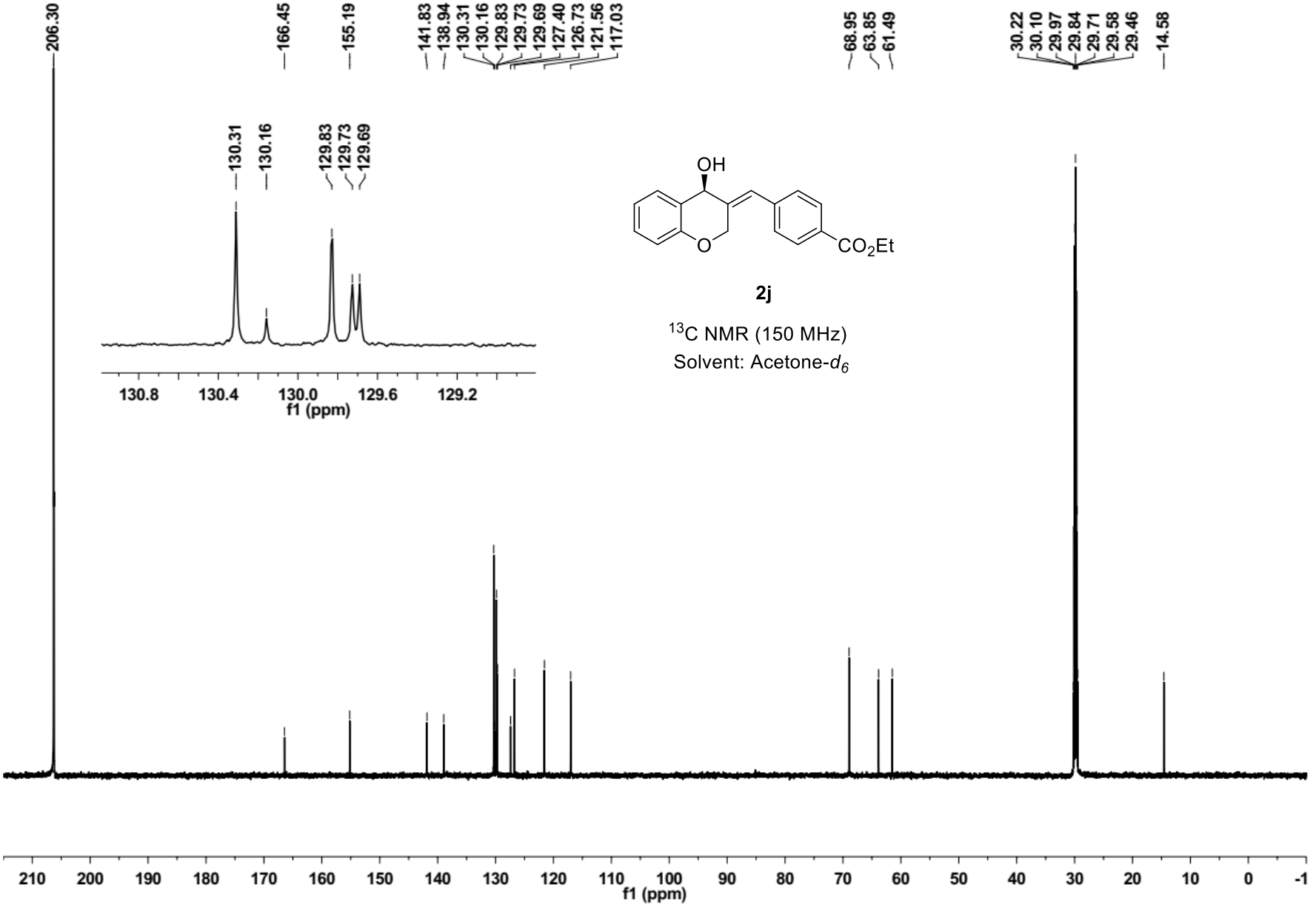
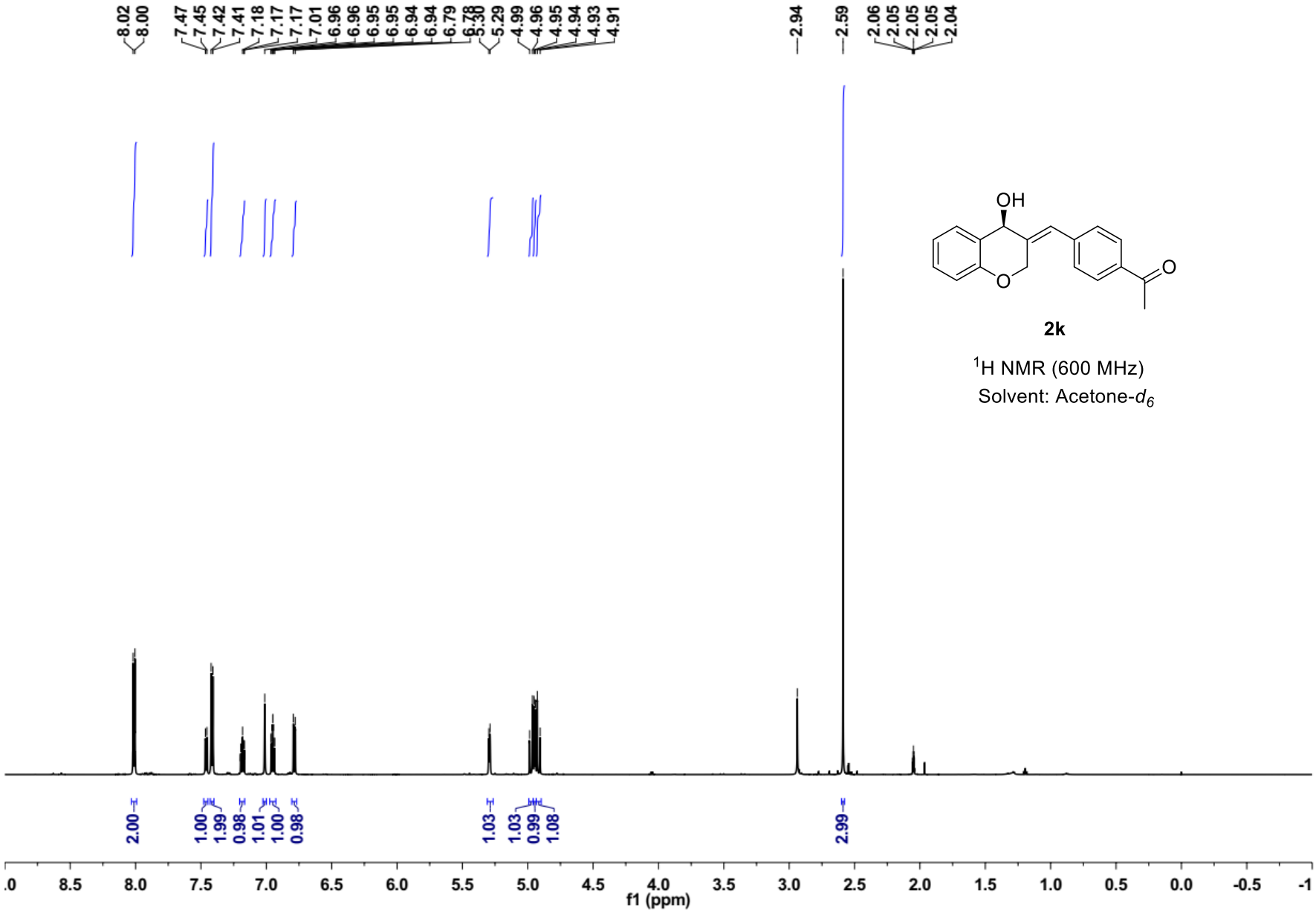
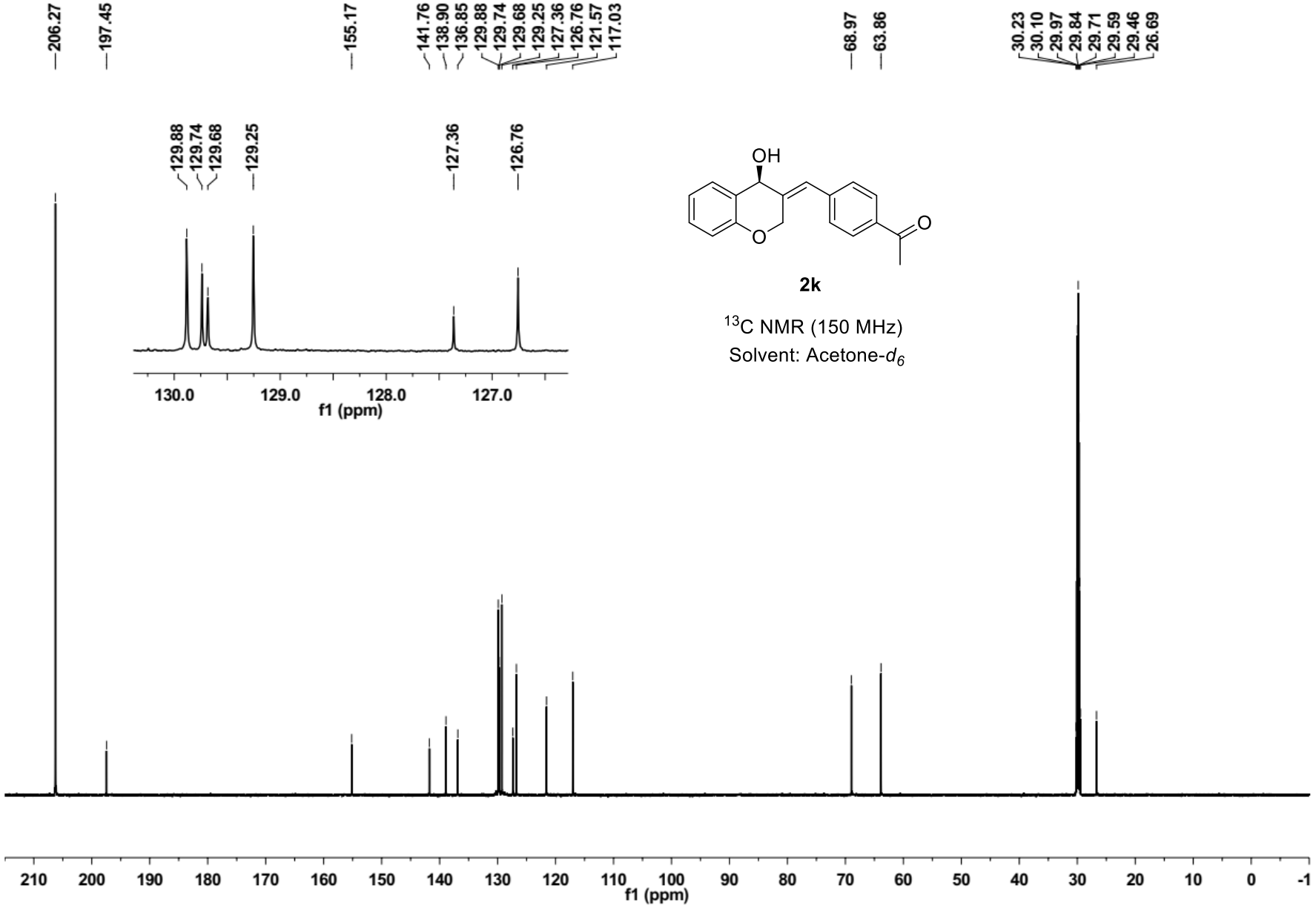
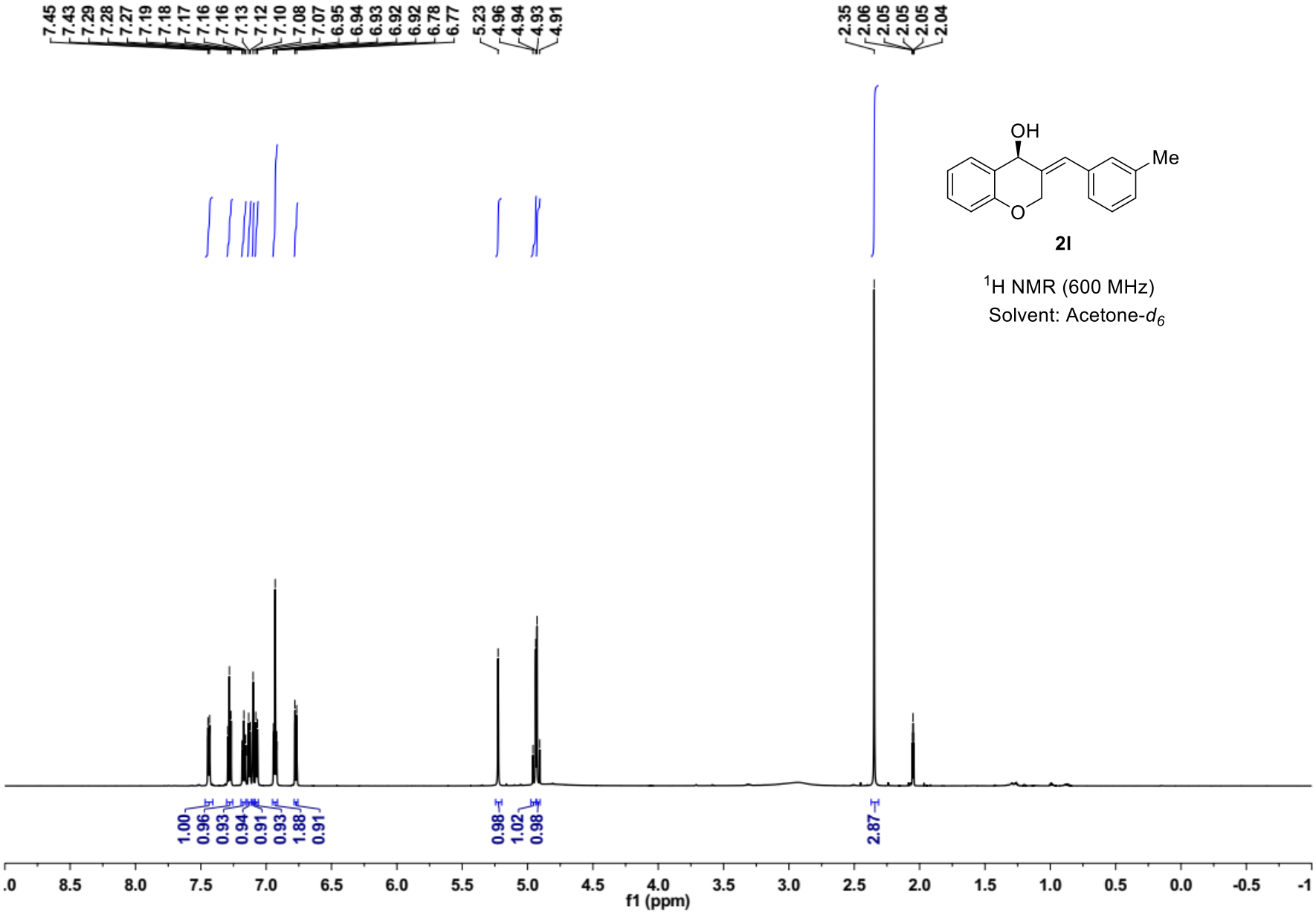
155.14
141.97
139.93
133.12
130.60
129.77
129.57
127.38
125.98
121.66
119.30
117.04
111.60
68.88
63.85
30.42
30.23
30.03
29.84
29.65
29.46
29.26
OH
O
CN
2i
13C NMR (100 MHz)
Solvent: Acetone-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

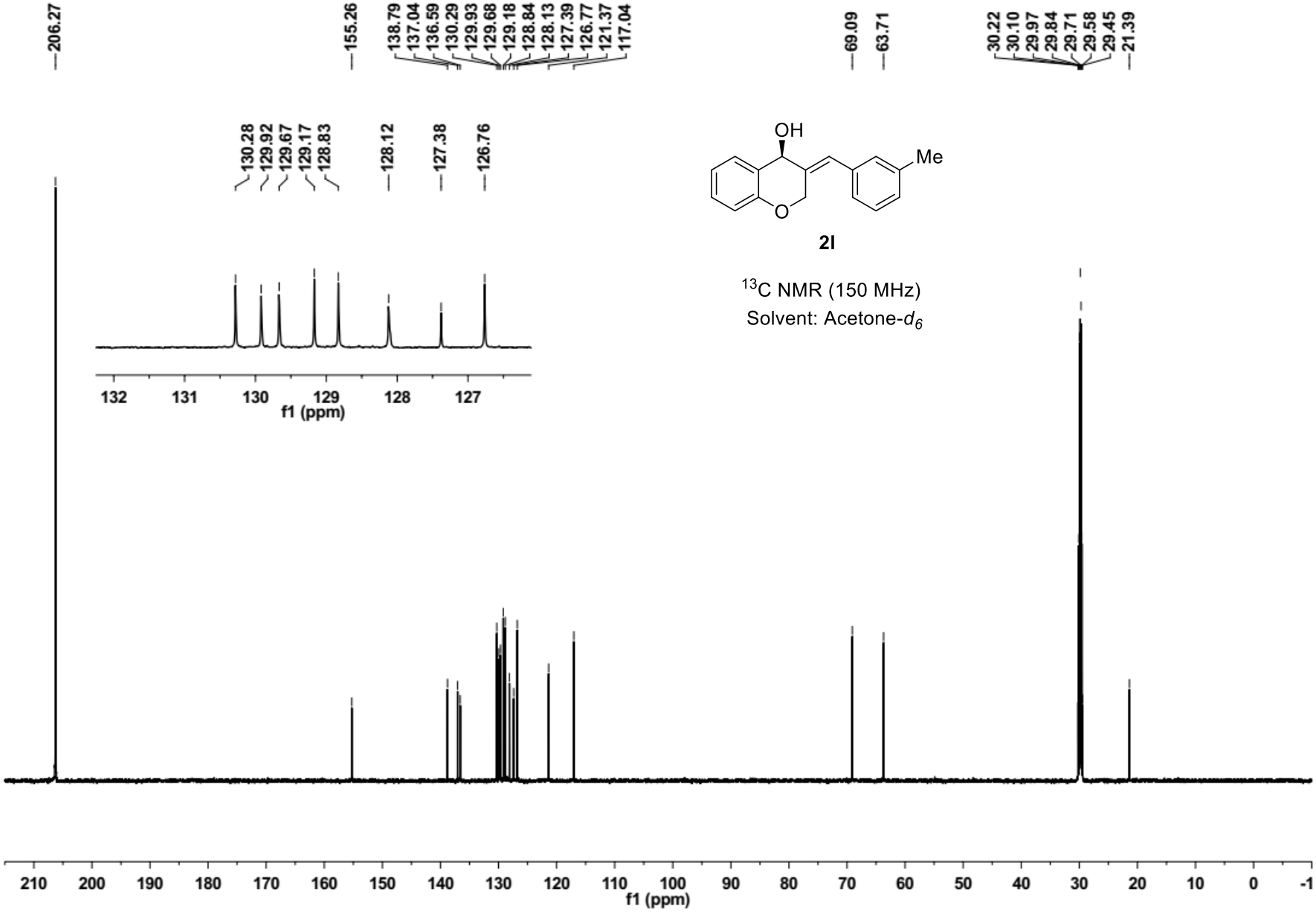

8.05
8.05
8.04
8.04
8.03
8.03
7.46
7.45
7.42
7.41
7.19
7.18
7.17
7.17
7.02
6.96
6.96
6.95
6.95
6.94
6.93
6.79
4.96
4.93
4.91
4.37
4.36
4.35
4.34
2.90
2.06
2.05
2.05
2.05
2.04
1.38
1.37
1.36
OH
O
CO2Et
2j
1H NMR (600 MHz)
Solvent: Acetone-d6
1.95
0.99
2.00
1.00
1.01
0.95
0.95
1.01
1.31
1.24
2.05
3.11
f1 (ppm)


206.30
166.45
155.19
141.83
138.94
130.31
130.16
129.83
129.73
129.69
127.40
126.73
121.56
117.03
68.95
63.85
61.49
30.22
30.10
29.97
29.84
29.71
29.58
29.46
14.58
130.31
130.16
129.83
129.73
129.69
130.8
130.4
130.0
129.6
129.2
f1 (ppm)
OH
O
CO2Et
2j
13C NMR (150 MHz)
Solvent: Acetone-d6
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)


8.02
8.00
7.47
7.45
7.42
7.41
7.18
7.17
7.17
7.01
6.96
6.96
6.95
6.95
6.94
6.94
6.79
6.78
5.30
5.29
4.99
4.96
4.95
4.94
4.93
4.91
2.94
2.59
2.06
2.05
2.05
2.05
2.04
OH
O
O
2k
1H NMR (600 MHz)
Solvent: Acetone-d6
2.00
1.00
1.99
0.98
1.01
1.00
0.98
1.03
1.03
0.99
1.08
2.99
f1 (ppm)


206.27
197.45
155.17
141.76
138.90
136.85
129.88
129.74
129.68
129.25
127.36
126.76
121.57
117.03
68.97
63.86
30.23
30.10
29.97
29.84
29.71
29.59
29.46
26.69
OH
O
O
2k
13C NMR (150 MHz)
Solvent: Acetone-d6
f1 (ppm)


7.45
7.43
7.29
7.28
7.27
7.19
7.18
7.17
7.16
7.16
7.13
7.12
7.10
7.08
7.07
6.95
6.94
6.93
6.92
6.92
6.78
6.77
5.23
4.96
4.94
4.93
4.91
2.35
2.06
2.05
2.05
2.05
2.04
OH
Me
O
2l
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
0.96
0.93
0.94
0.91
0.93
1.88
0.91
0.98
1.02
0.98
2.87
f1 (ppm)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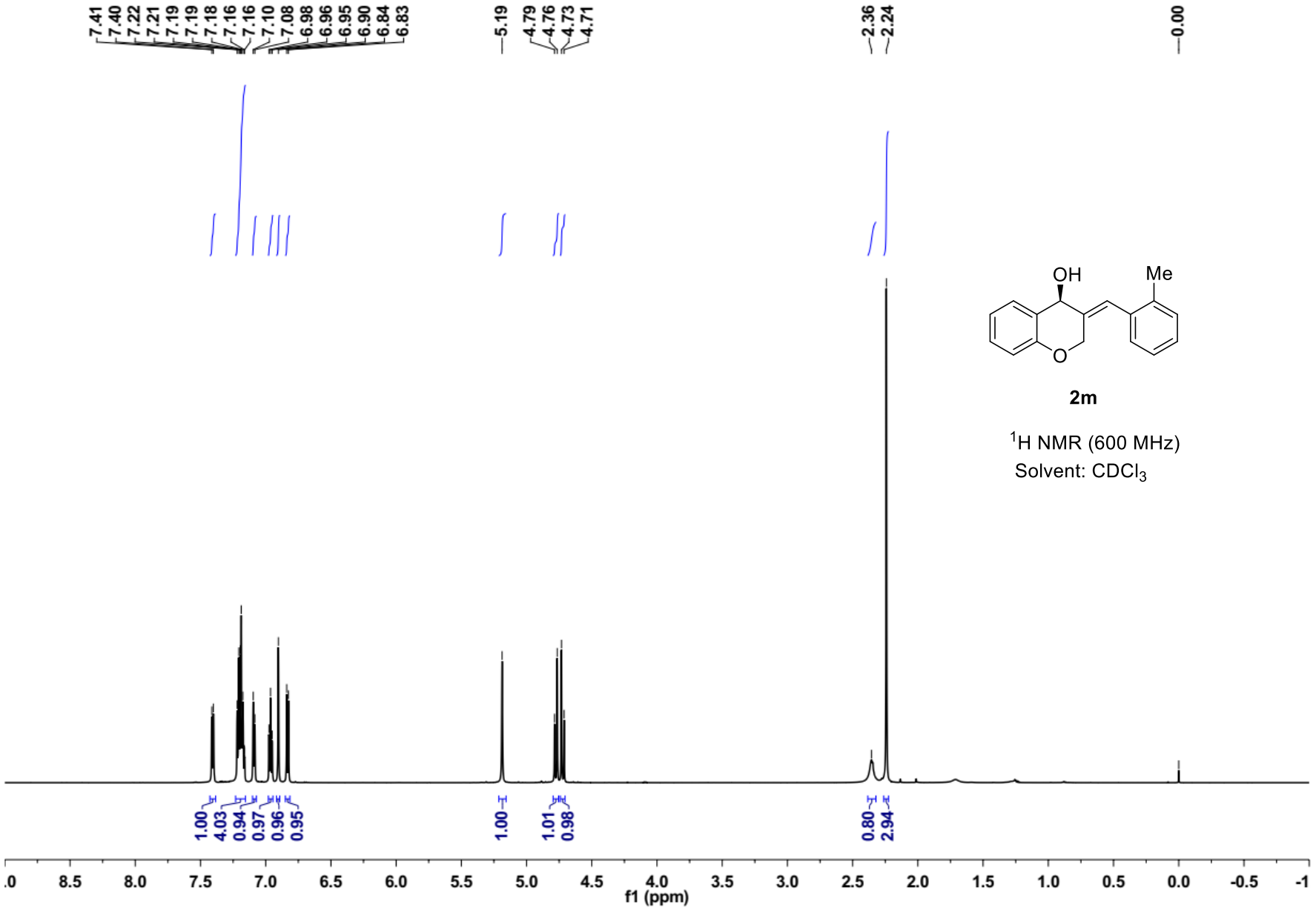
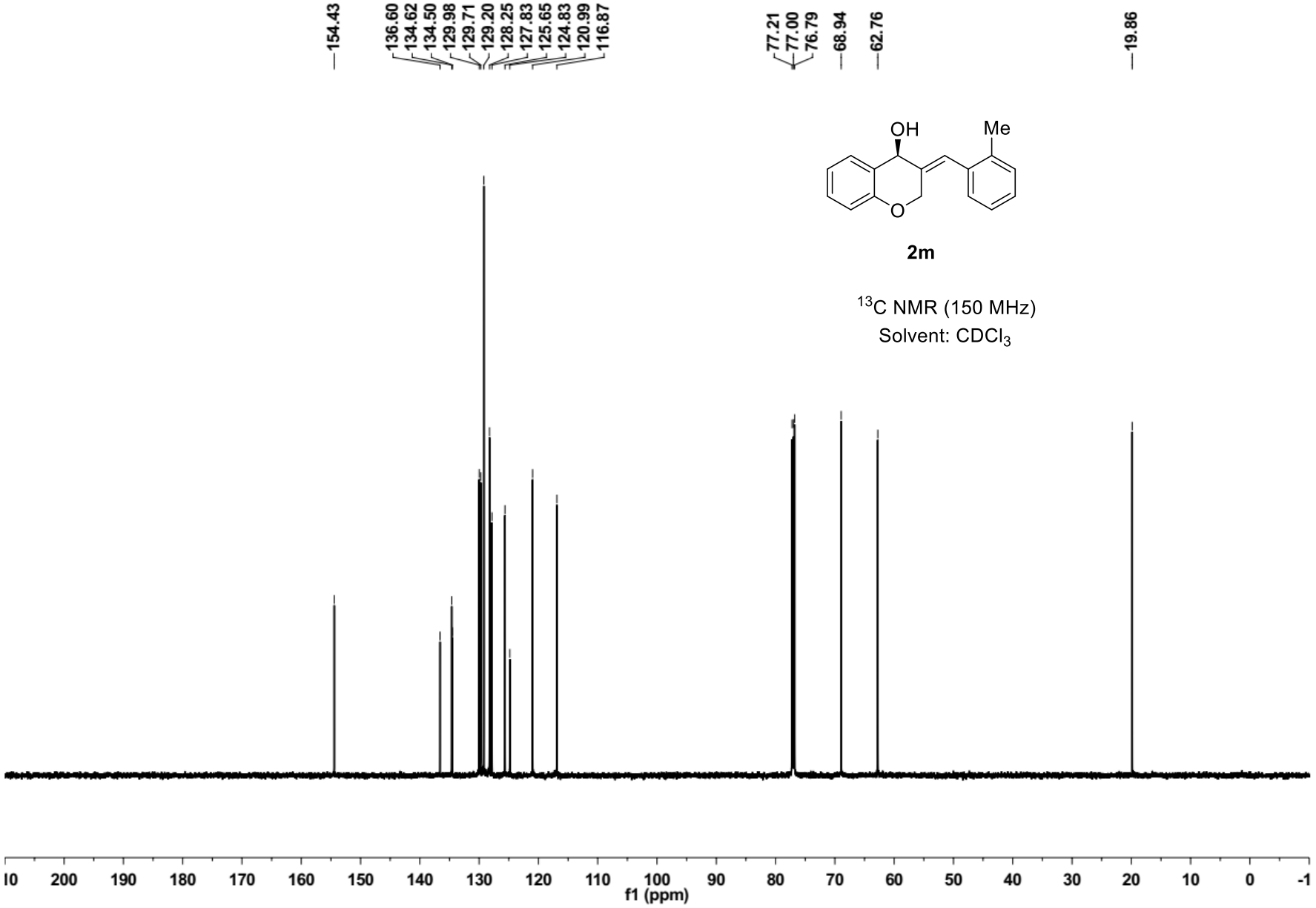
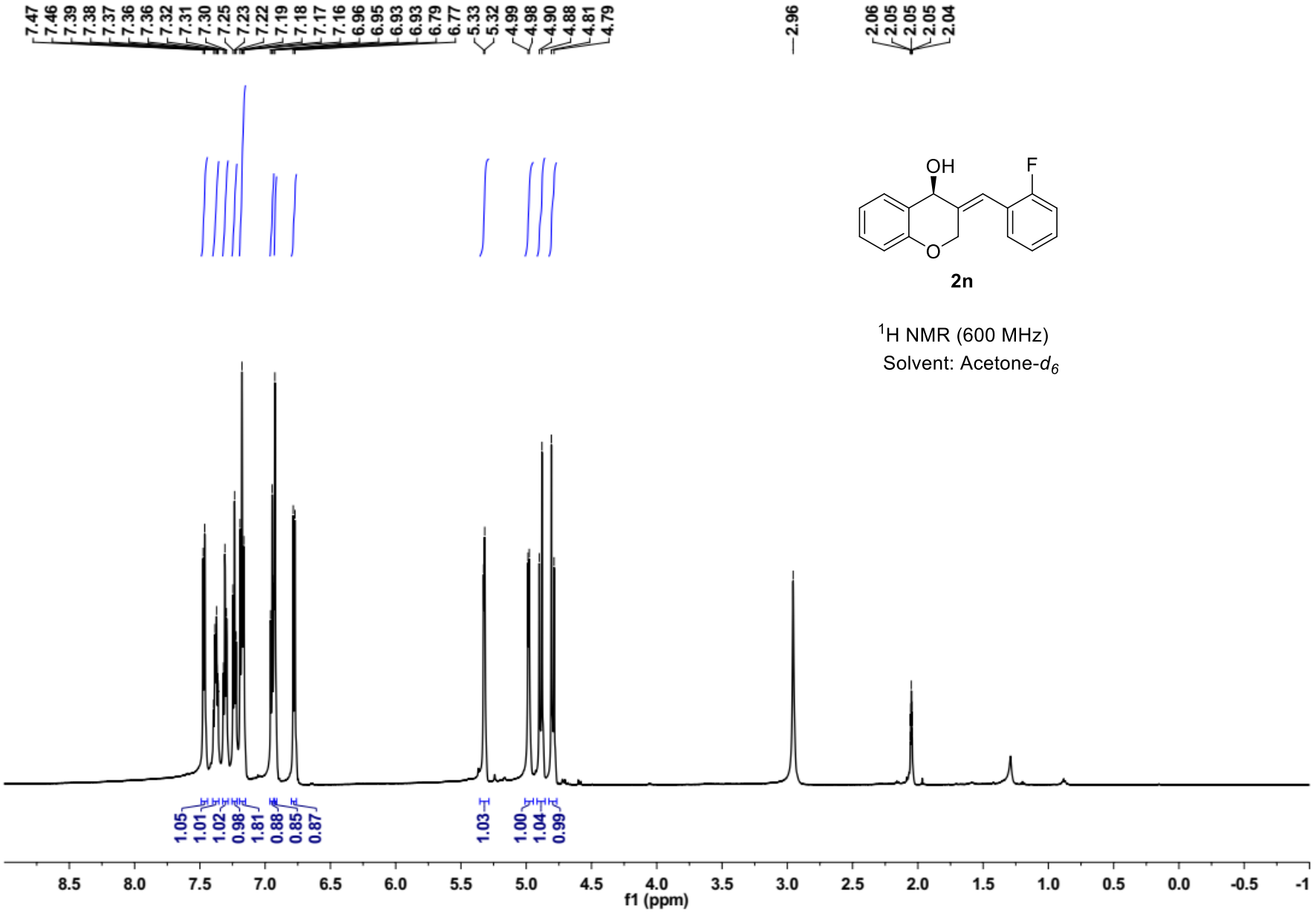
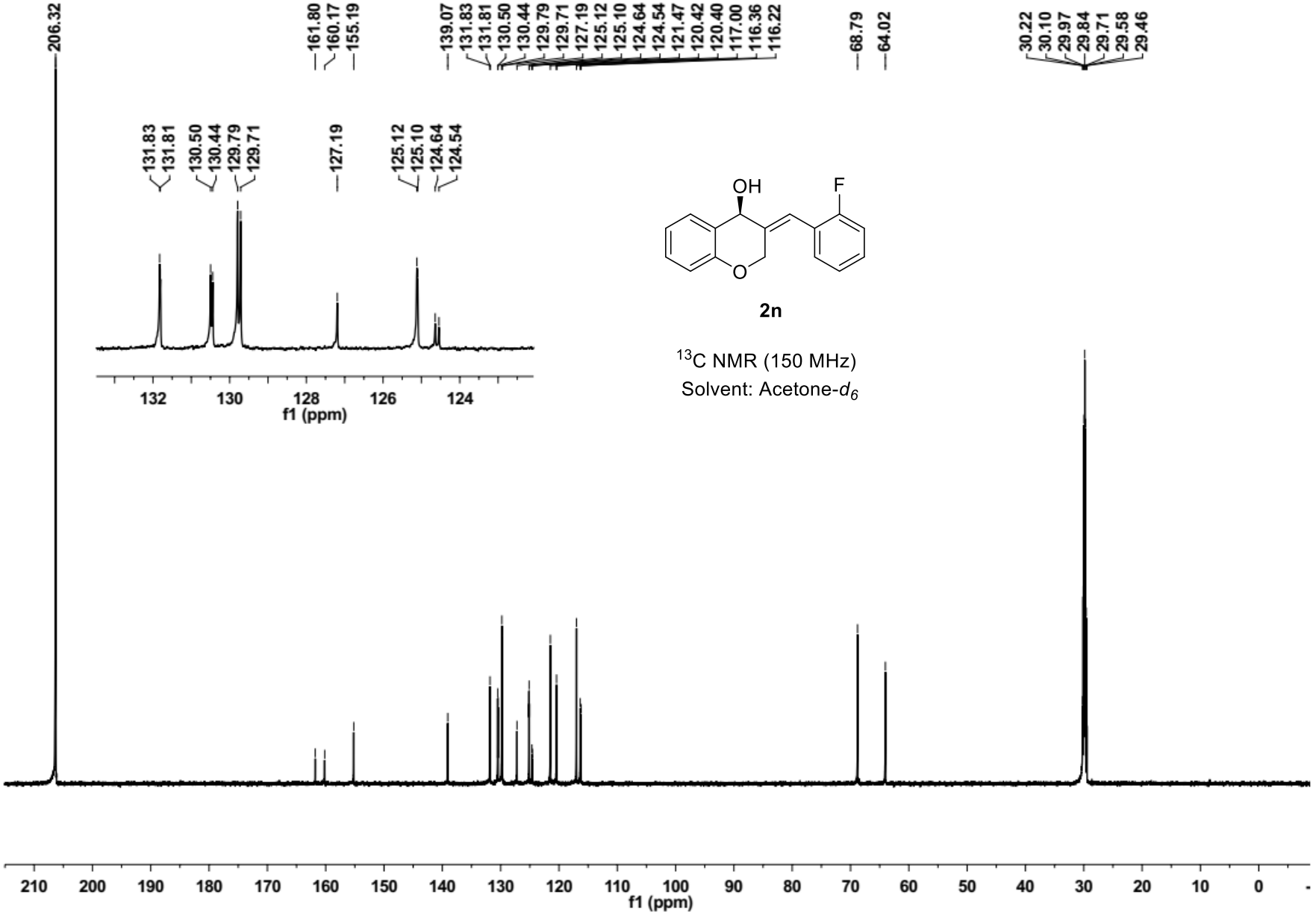
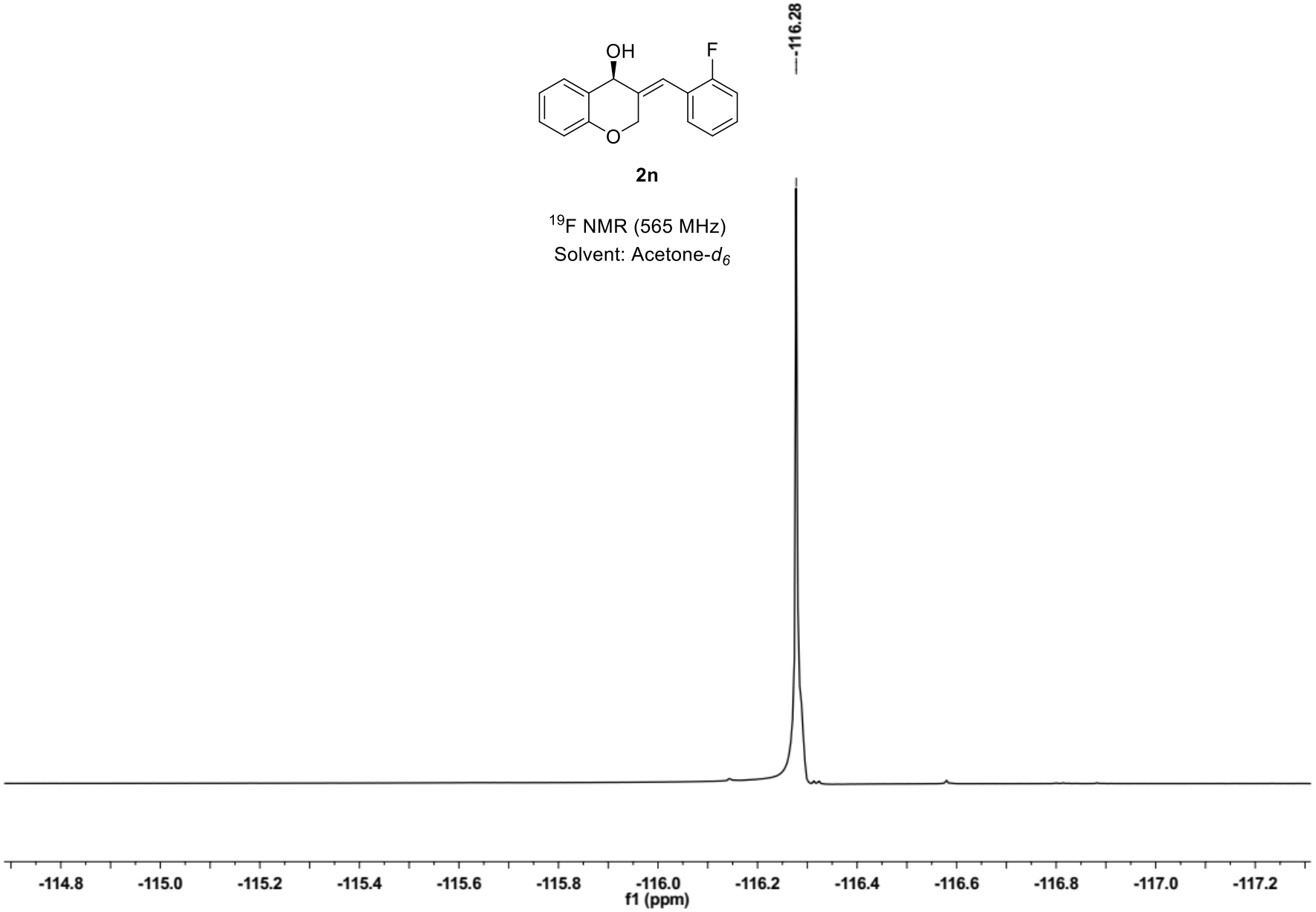
155.26
138.79
137.04
136.59
130.29
129.93
129.68
129.18
128.84
128.13
127.39
126.77
121.37
117.04
69.09
63.71
30.22
30.10
29.97
29.84
29.71
29.58
29.45
21.39
130.28
129.92
129.67
129.17
128.83
128.12
127.38
126.76
OH
Me
O
2l
^{13}C NMR (150 MHz)
Solvent: Acetone-d_6
132
131
130
129
128
127
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.41
7.40
7.22
7.21
7.19
7.19
7.18
7.16
7.16
7.10
7.08
6.98
6.96
6.95
6.90
6.84
6.83
5.19
4.79
4.76
4.73
4.71
2.36
2.24
0.00
OH
Me
O
2m
1H NMR (600 MHz)
Solvent: CDCl3
1.00
4.03
0.94
0.97
0.96
0.95
1.00
1.01
0.98
0.80
2.94
f1 (ppm)


154.43
136.60
134.62
134.50
129.98
129.71
129.20
128.25
127.83
125.65
124.83
120.99
116.87
77.21
77.00
76.79
68.94
62.76
19.86
OH
Me
O
2m
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)

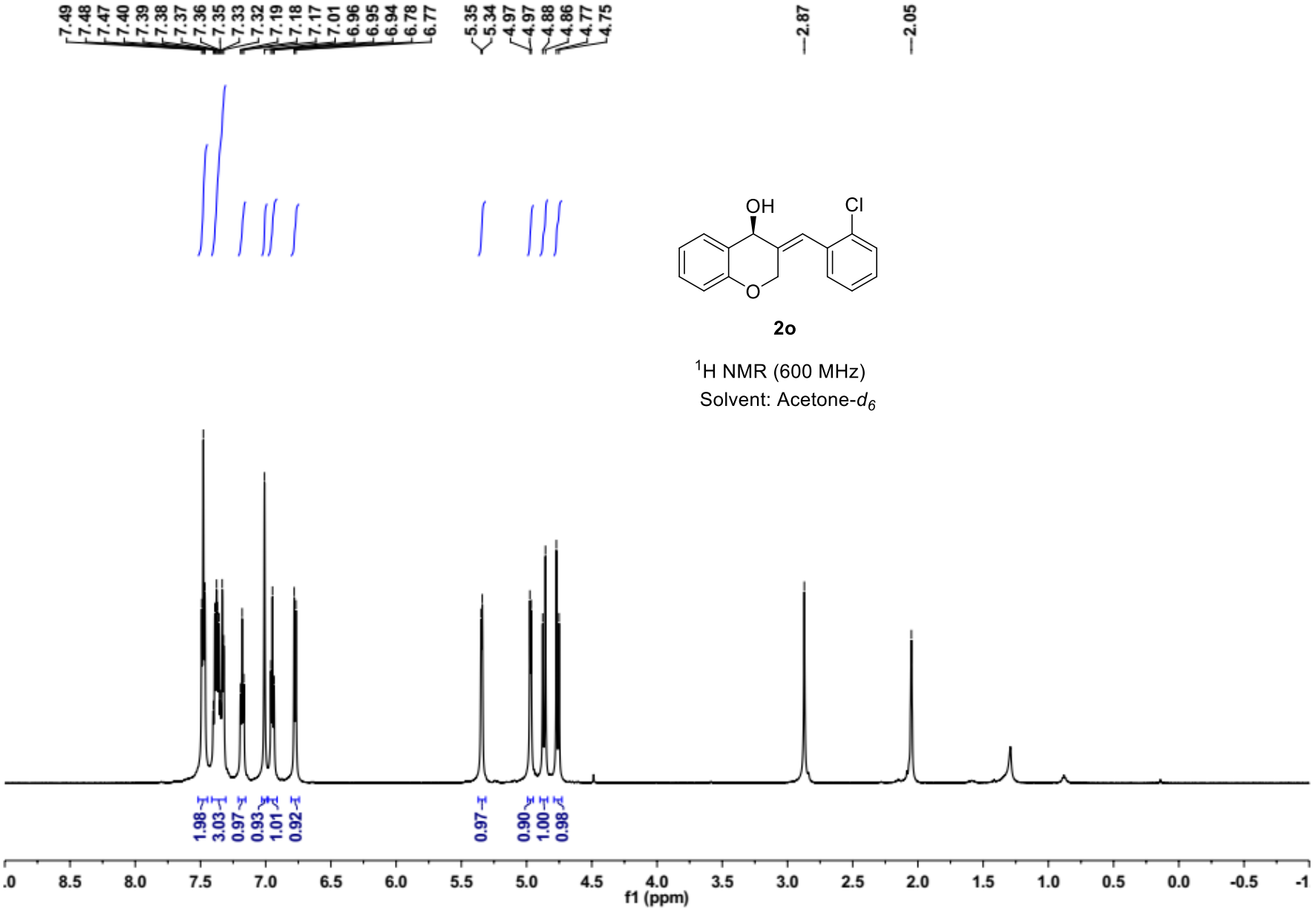

7.47
7.46
7.39
7.38
7.37
7.36
7.36
7.32
7.31
7.30
7.25
7.23
7.22
7.19
7.18
7.17
7.16
6.96
6.95
6.93
6.93
6.79
6.77
5.33
5.32
4.99
4.98
4.90
4.88
4.81
4.79
2.96
2.06
2.05
2.05
2.05
2.04
OH
F
O
2n
1H NMR (600 MHz)
Solvent: Acetone-d6
1.05
1.01
1.02
0.98
1.81
0.88
0.85
0.87
1.03
1.00
1.04
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


206.32
161.80
160.17
155.19
139.07
131.83
131.81
130.50
130.44
129.79
129.71
127.19
125.12
125.10
124.64
124.54
121.47
120.42
120.40
117.00
116.36
116.22
68.79
64.02
30.22
30.10
29.97
29.84
29.71
29.58
29.46
OH
F
O
2n
^{13}C NMR (150 MHz)
Solvent: Acetone-d_6
f1 (ppm)



2n

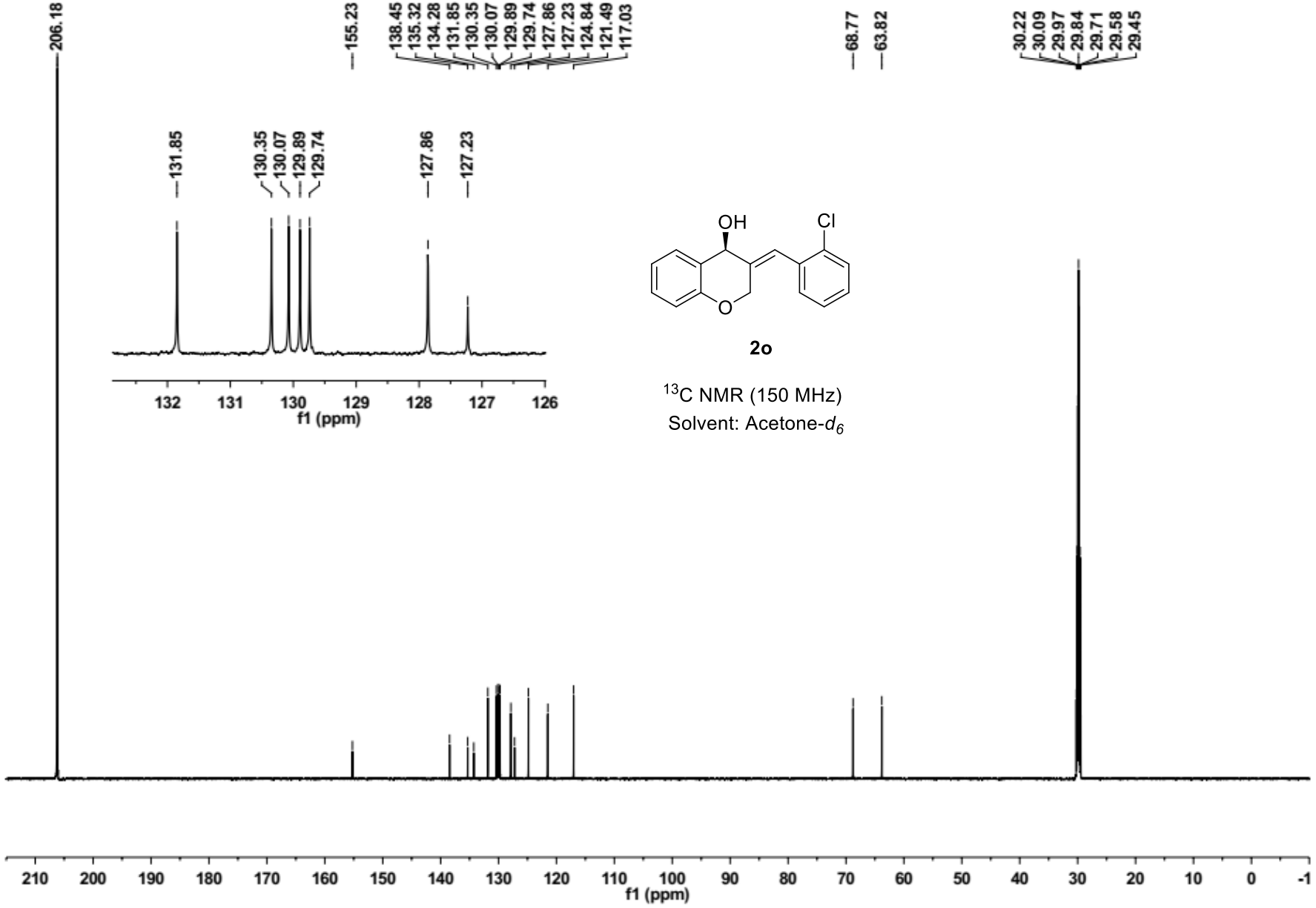
^{19}F NMR (565 MHz)
Solvent: Acetone-d_6

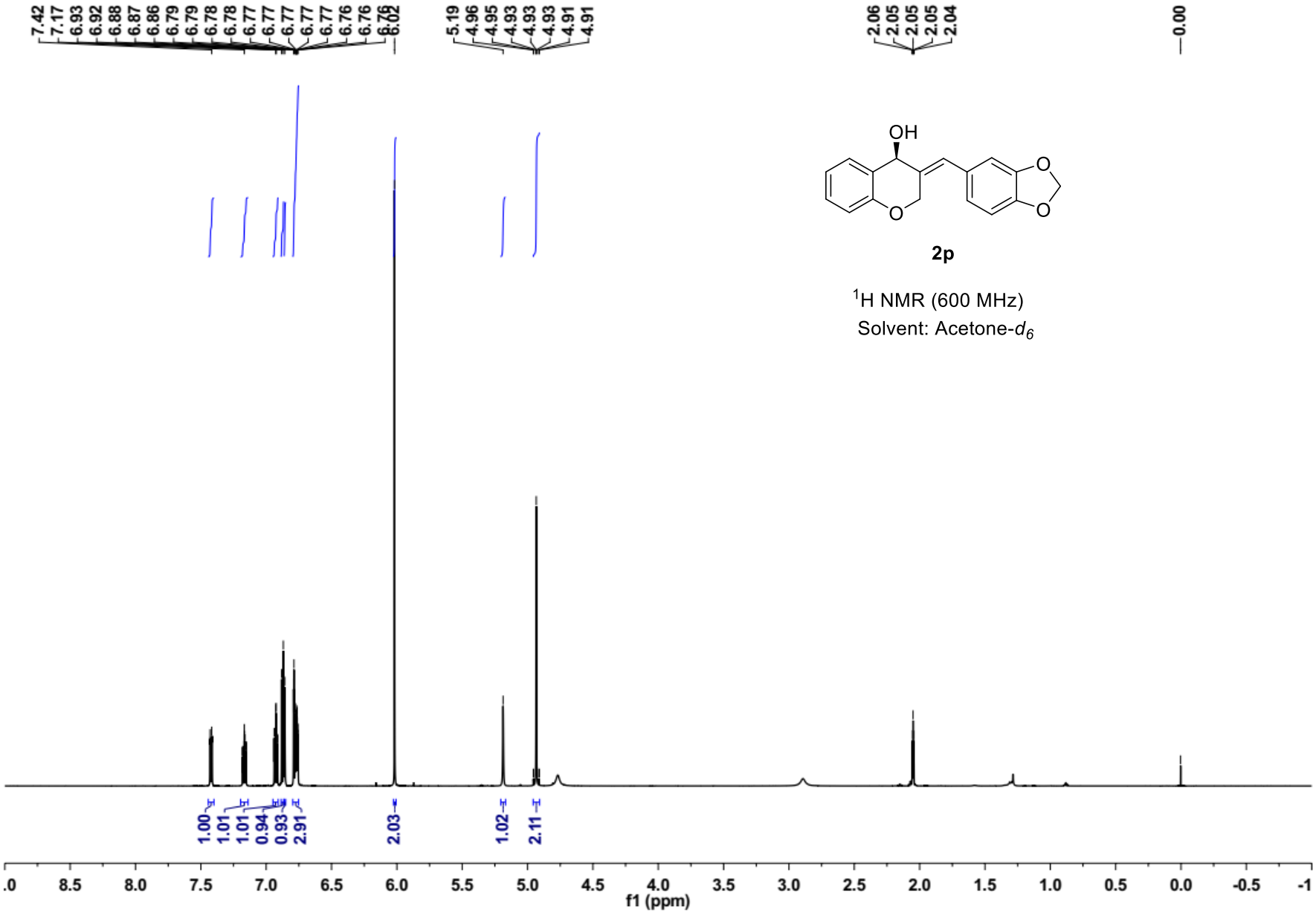


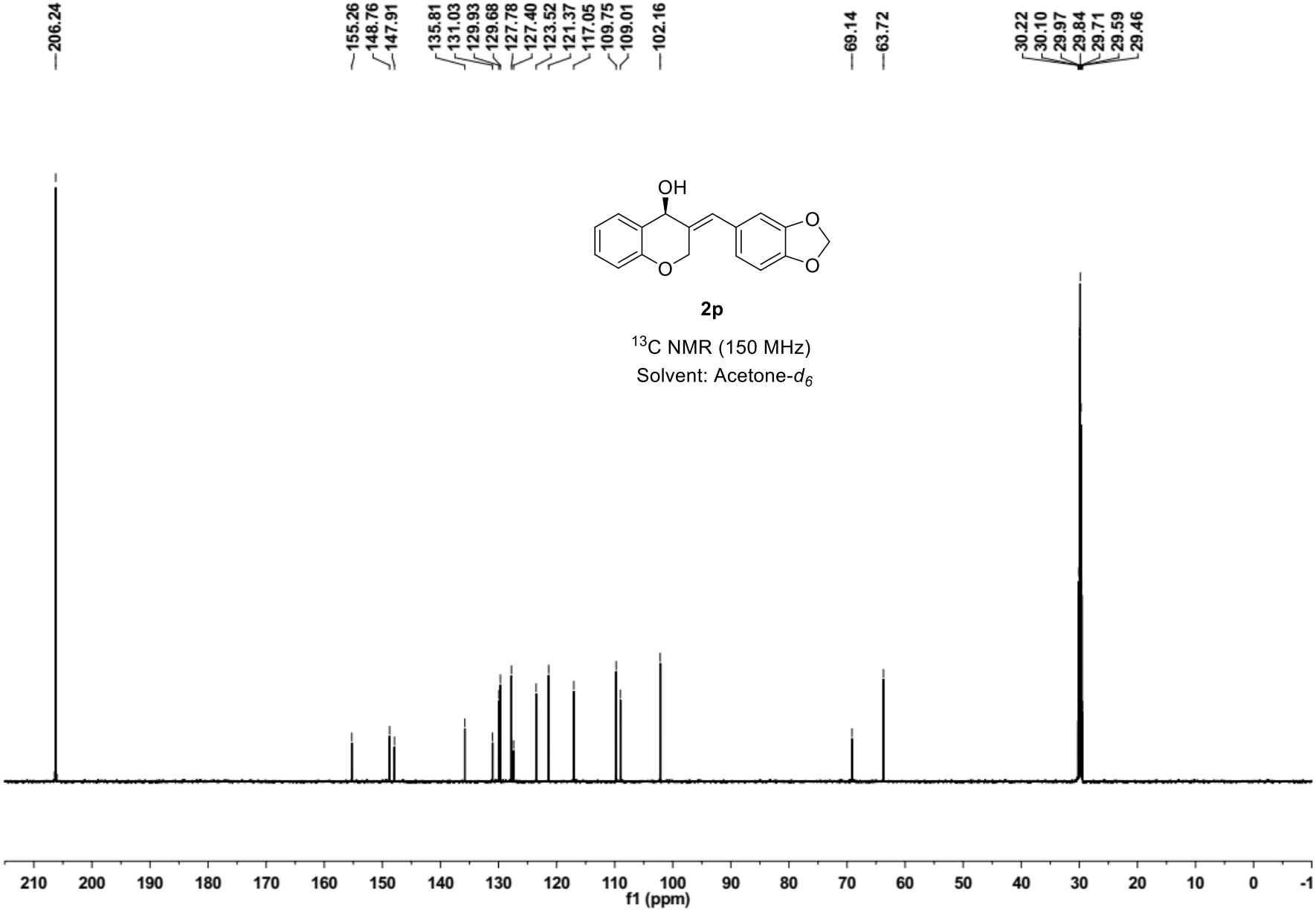
2o

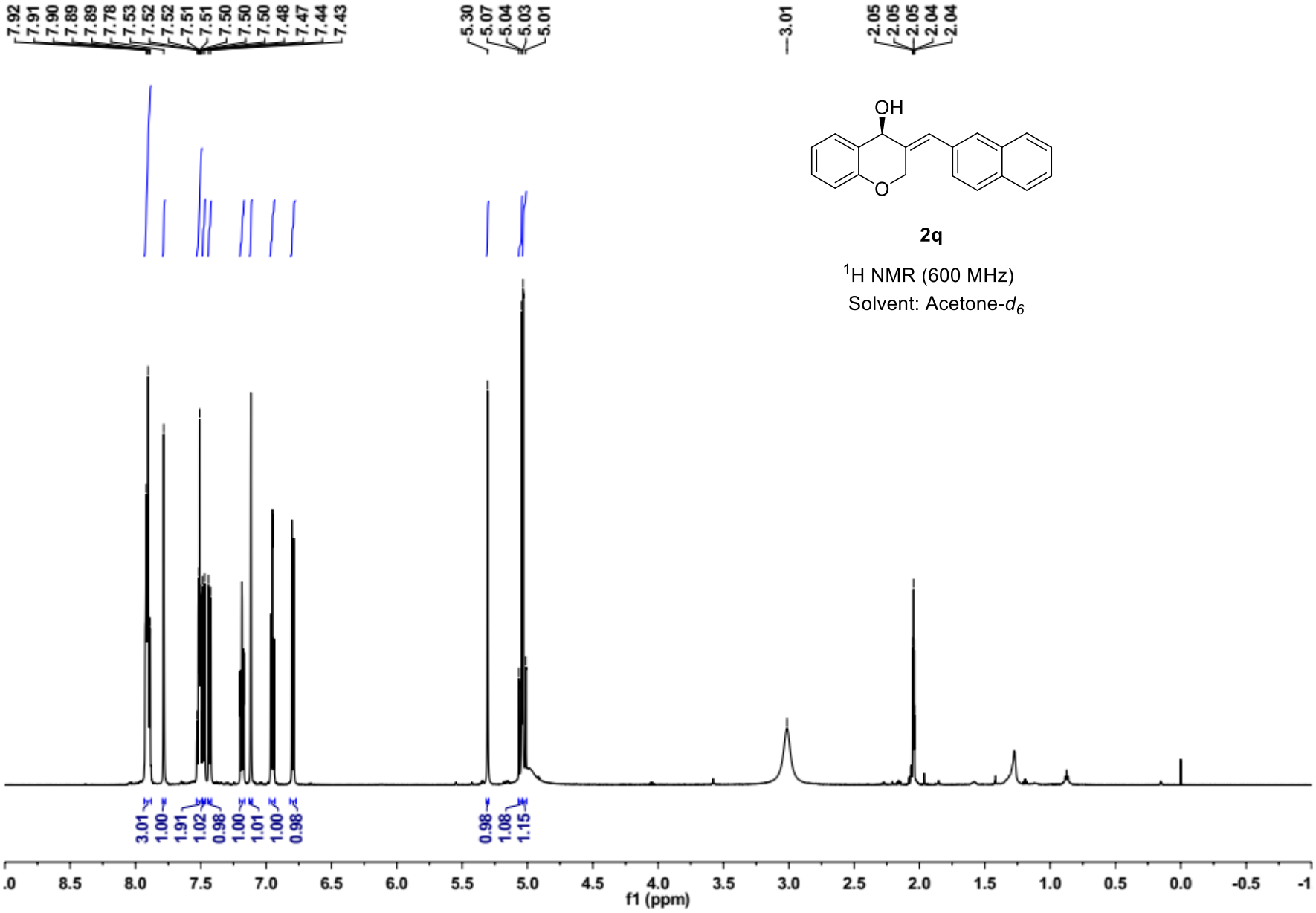
^{1}H NMR (600 MHz)

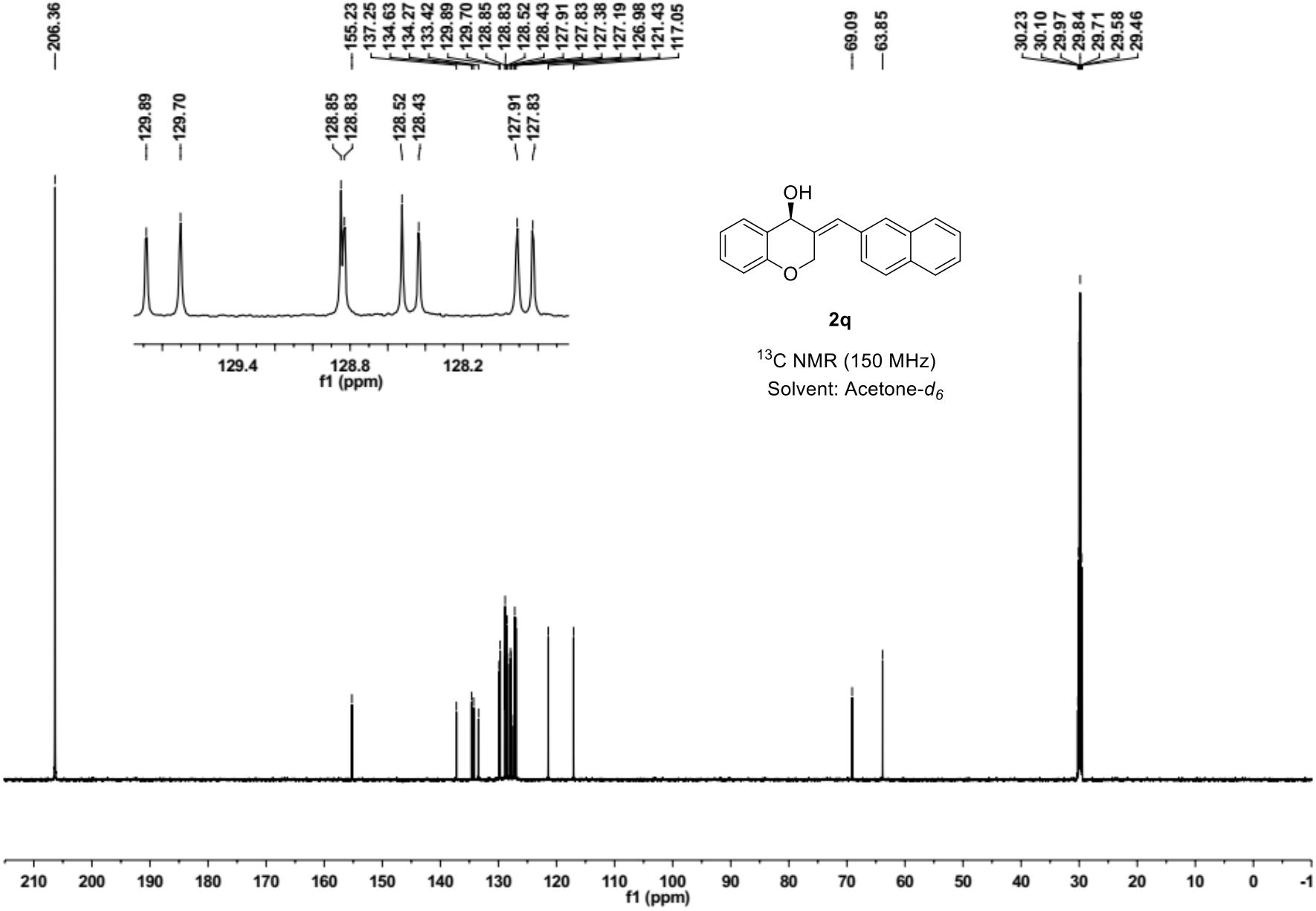
Solvent: Acetone-d_6

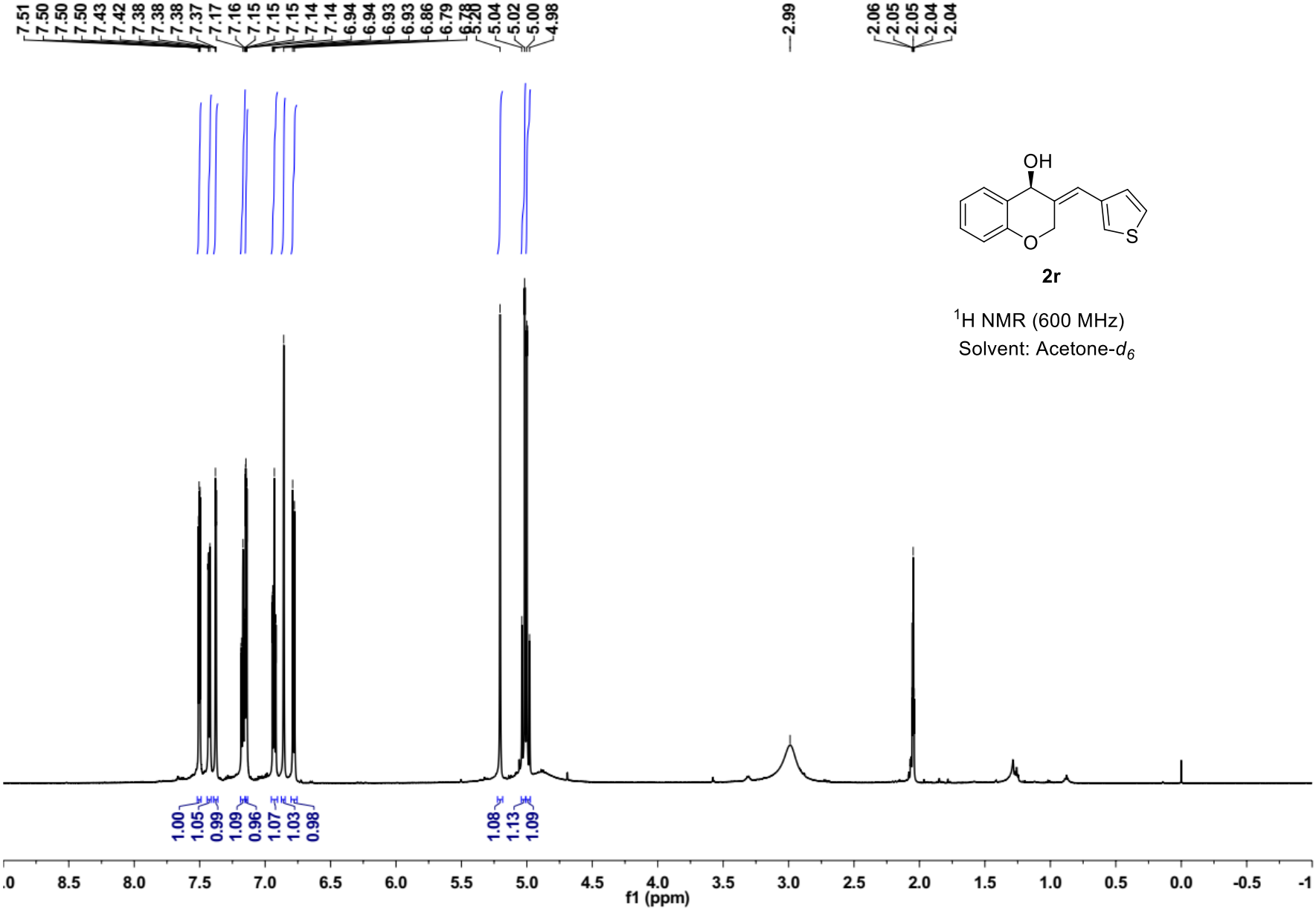

206.18
155.23
138.45
135.32
134.28
131.85
130.35
130.07
129.89
129.74
127.86
127.23
124.84
121.49
117.03
68.77
63.82
30.22
30.09
29.97
29.84
29.71
29.58
29.45
131.85
130.35
130.07
129.89
129.74
127.86
127.23
132
131
130
129
128
127
126
f1 (ppm)
OH
Cl
O
2o
^{13}C NMR (150 MHz)
Solvent: Acetone-d_6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

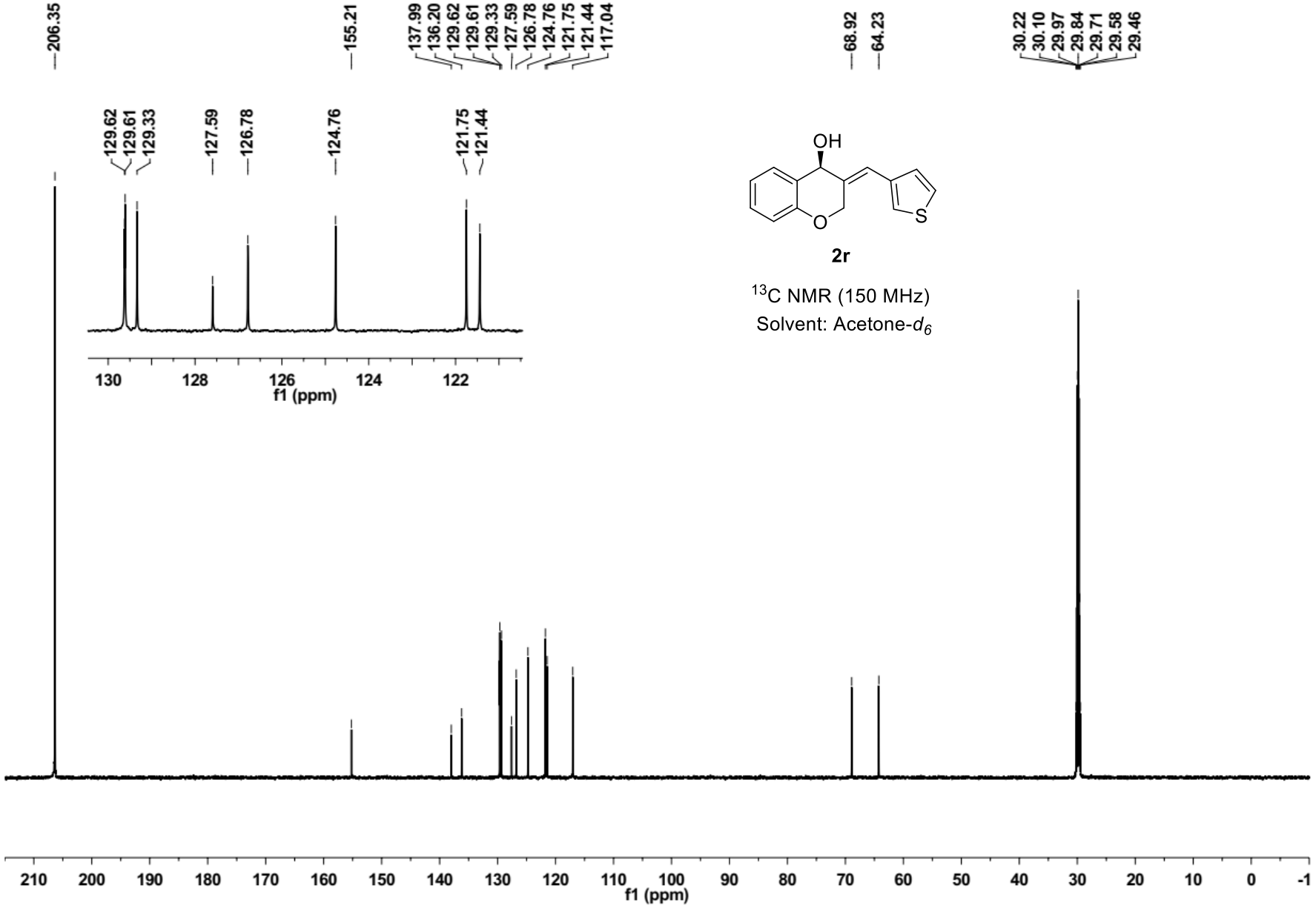

7.42
7.17
6.93
6.92
6.88
6.87
6.86
6.79
6.78
6.78
6.77
6.77
6.77
6.77
6.76
6.76
6.02
5.19
4.96
4.95
4.93
4.93
4.93
4.91
4.91
2.06
2.05
2.05
2.05
2.04
0.00
OH
O
O
O
2p
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
1.01
1.01
0.94
0.93
2.91
2.03
1.02
2.11
f1 (ppm)


206.24
155.26
148.76
147.91
135.81
131.03
129.93
129.68
127.78
127.40
123.52
121.37
117.05
109.75
109.01
102.16
69.14
63.72
30.22
30.10
29.97
29.84
29.71
29.59
29.46
OH
O
O
O
2p
13C NMR (150 MHz)
Solvent: Acetone-d6
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)


7.92
7.91
7.90
7.89
7.89
7.78
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.50
7.48
7.47
7.44
7.43
5.30
5.07
5.04
5.03
5.01
3.01
2.05
2.05
2.05
2.04
2.04
OH
O
2q
1H NMR (600 MHz)
Solvent: Acetone-d6
3.01
1.00
1.91
1.02
0.98
1.00
1.01
1.00
0.98
0.98
1.08
1.15
f1 (ppm)


206.36
155.23
137.25
134.63
134.27
133.42
129.89
129.70
128.85
128.83
128.52
128.43
127.91
127.83
127.38
127.19
126.98
121.43
117.05
69.09
63.85
30.23
30.10
29.97
29.84
29.71
29.58
29.46
129.89
129.70
128.85
128.83
128.52
128.43
127.91
127.83
129.4
128.8
128.2
f1 (ppm)
OH
O
2q
13C NMR (150 MHz)
Solvent: Acetone-d6
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)


7.51
7.50
7.50
7.50
7.43
7.42
7.38
7.38
7.38
7.37
7.17
7.16
7.15
7.15
7.15
7.14
7.14
6.94
6.94
6.93
6.93
6.86
6.79
6.78
5.20
5.04
5.02
5.00
4.98
2.99
2.06
2.05
2.05
2.04
2.04
OH
O
S
2r
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
1.05
0.99
1.09
0.96
1.07
1.03
0.98
1.08
1.13
1.09
f1 (ppm)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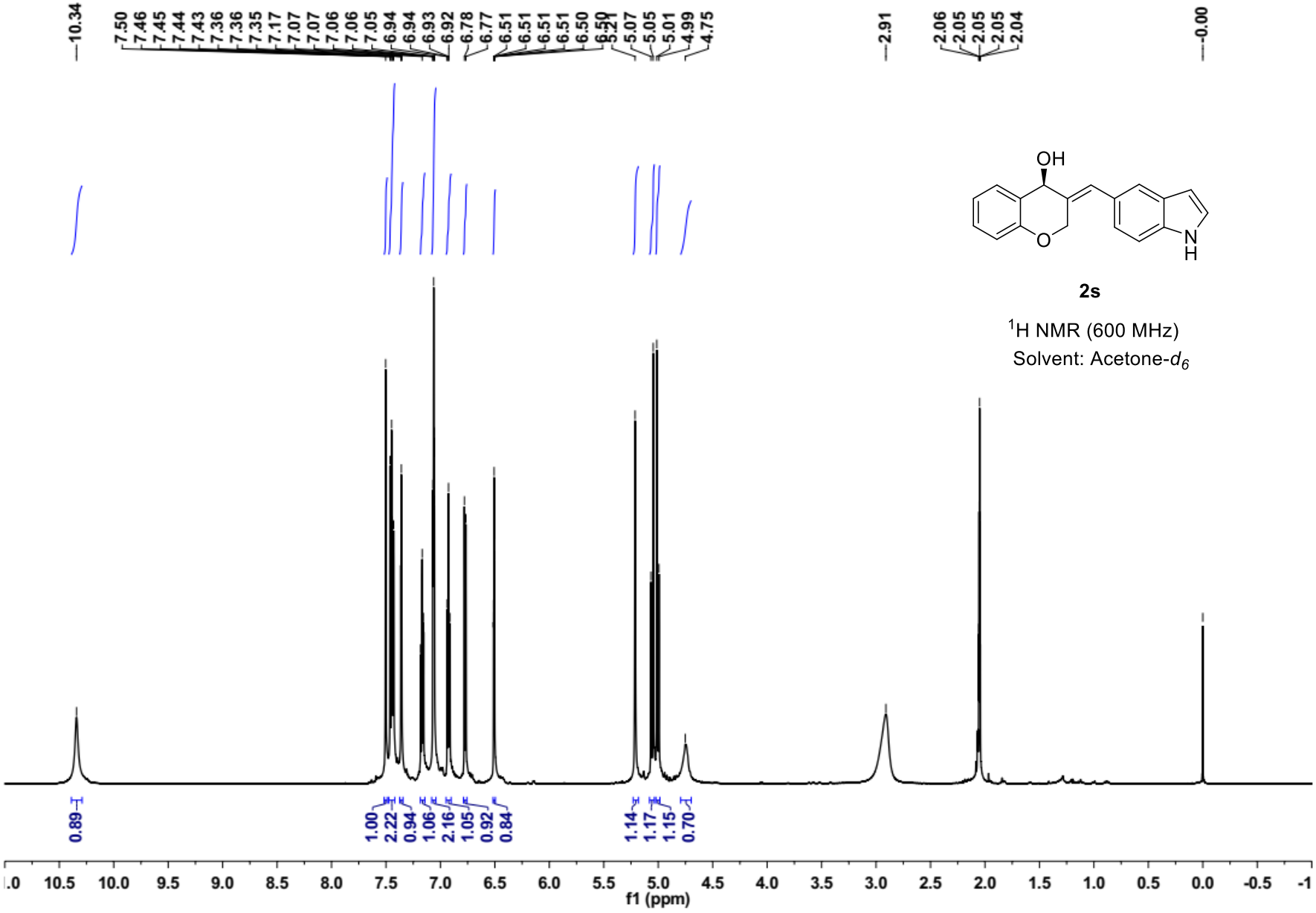
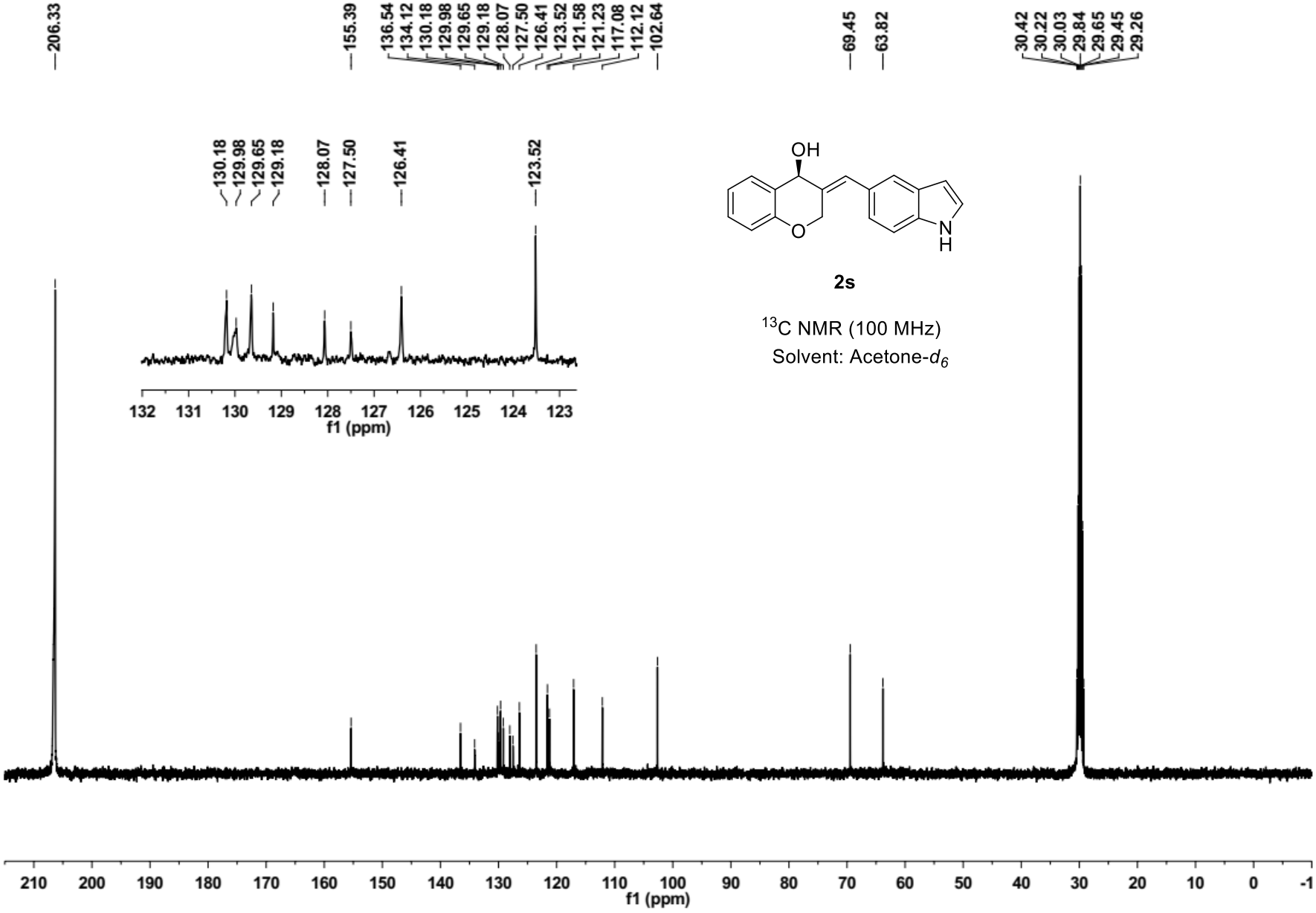
155.21
137.99
136.20
129.62
129.61
129.33
127.59
126.78
124.76
121.75
121.44
117.04
68.92
64.23
30.22
30.10
29.97
29.84
29.71
29.58
29.46
OH
O
S
2r
13C NMR (150 MHz)
Solvent: Acetone-d6
f1 (ppm)


10.34
7.50
7.46
7.45
7.44
7.43
7.36
7.36
7.35
7.17
7.07
7.07
7.06
7.06
7.05
6.94
6.94
6.93
6.92
6.78
6.77
6.51
6.51
6.51
6.51
6.50
6.50
5.21
5.07
5.05
5.01
4.99
4.75
2.91
2.06
2.05
2.05
2.05
2.04
0.00
OH
O
N
H
2s
1H NMR (600 MHz)
Solvent: Acetone-d6
0.89
1.00
2.22
0.94
1.06
2.16
1.05
0.92
0.84
1.14
1.17
1.15
0.70
f1 (ppm)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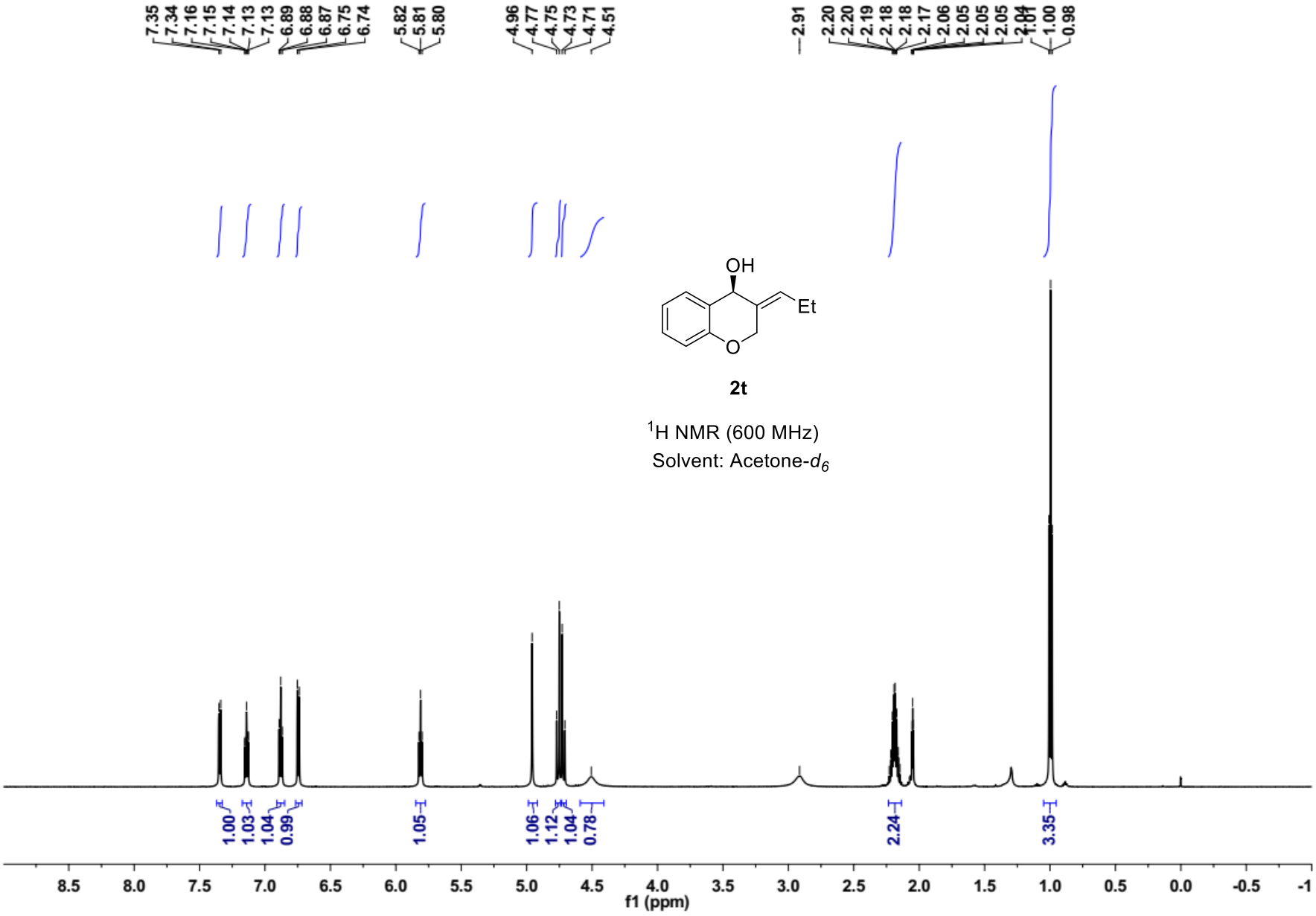
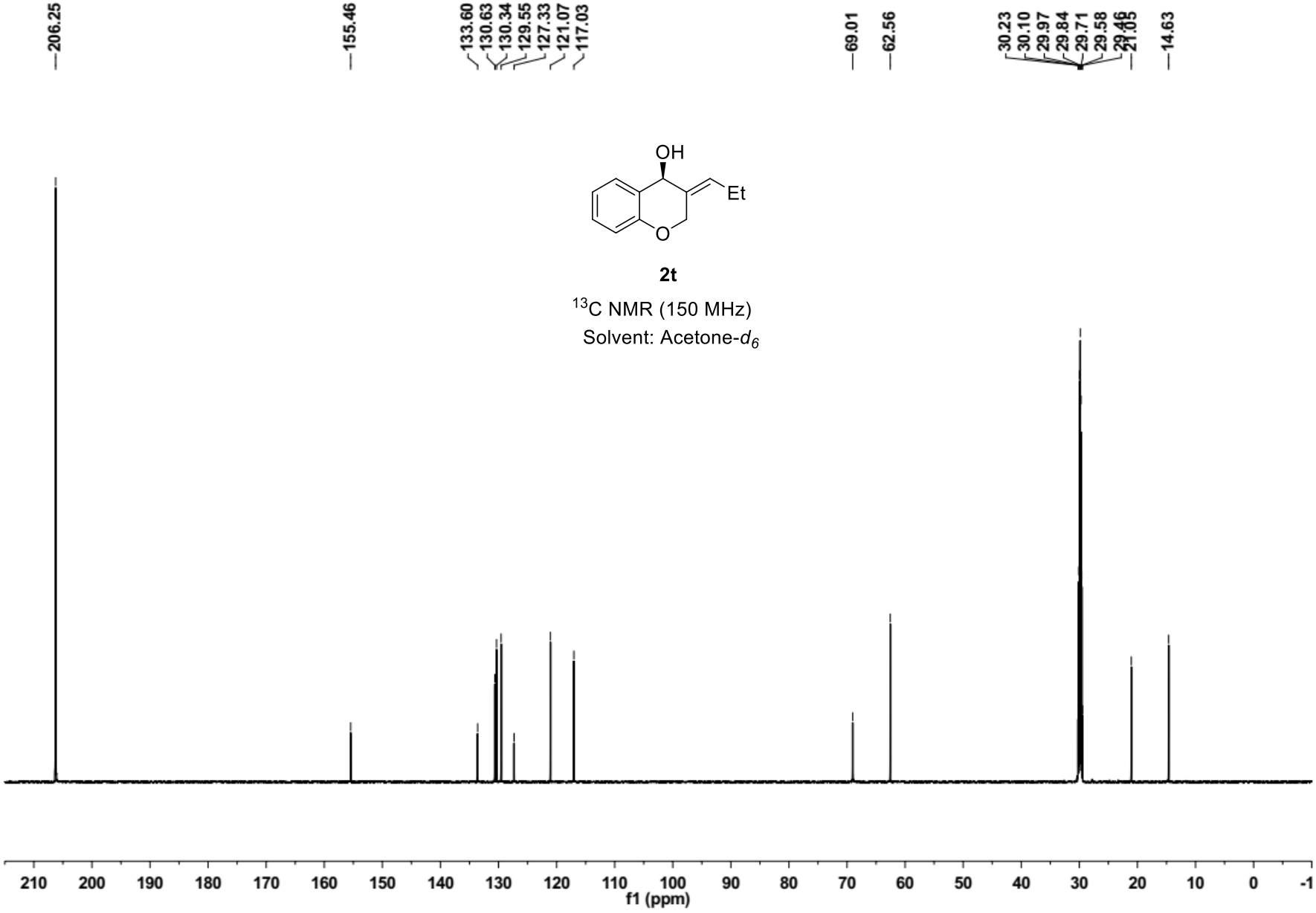
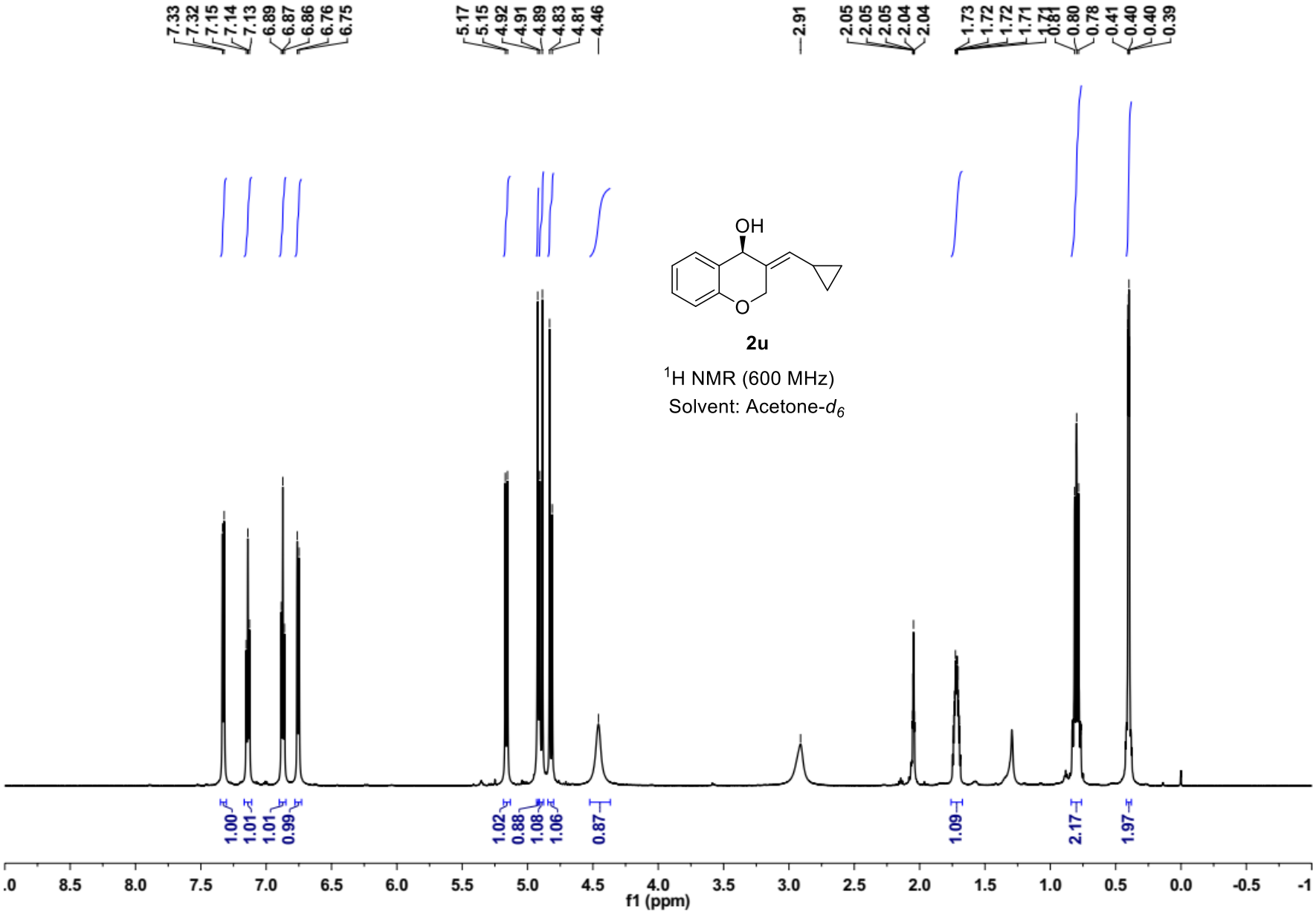
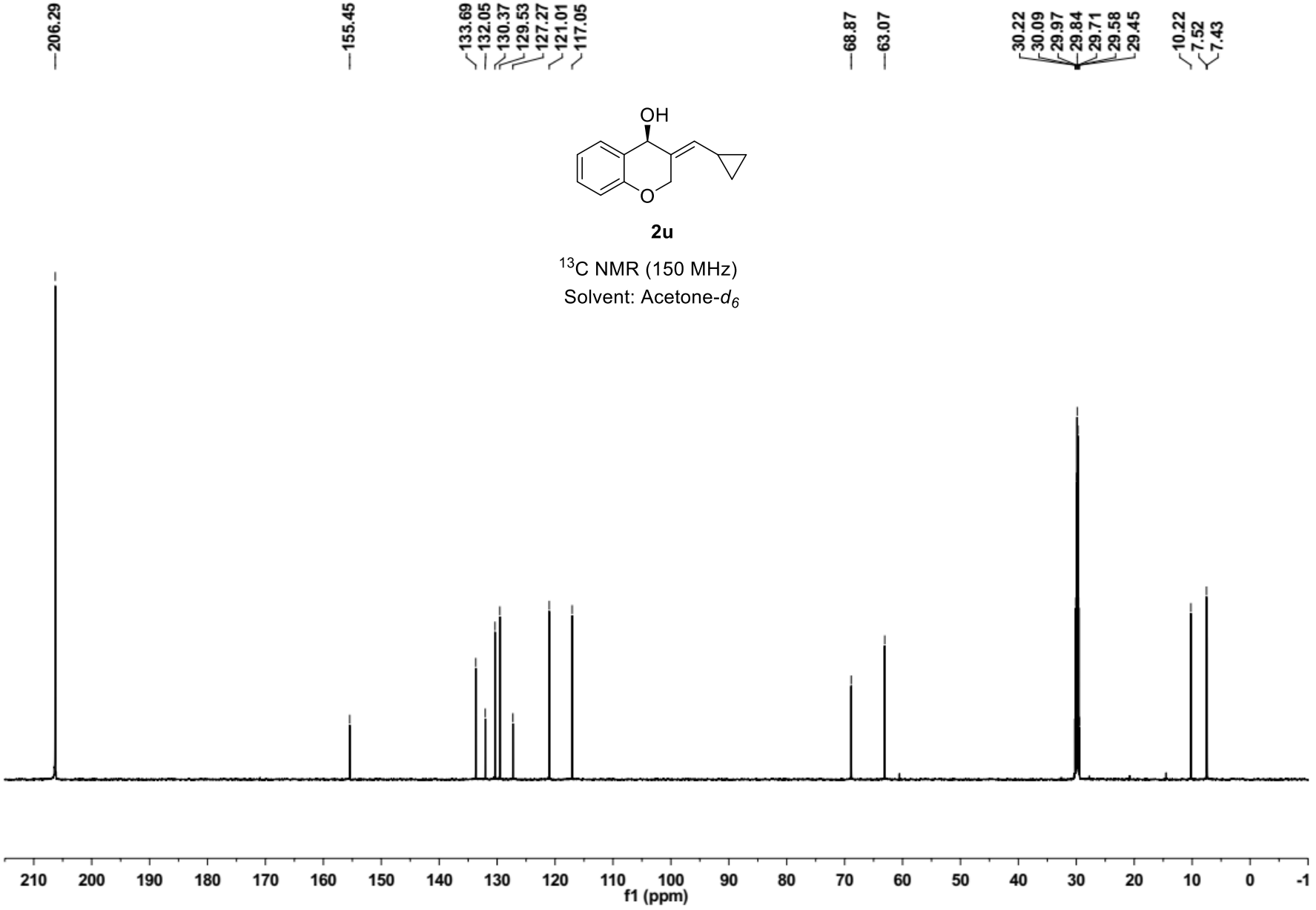
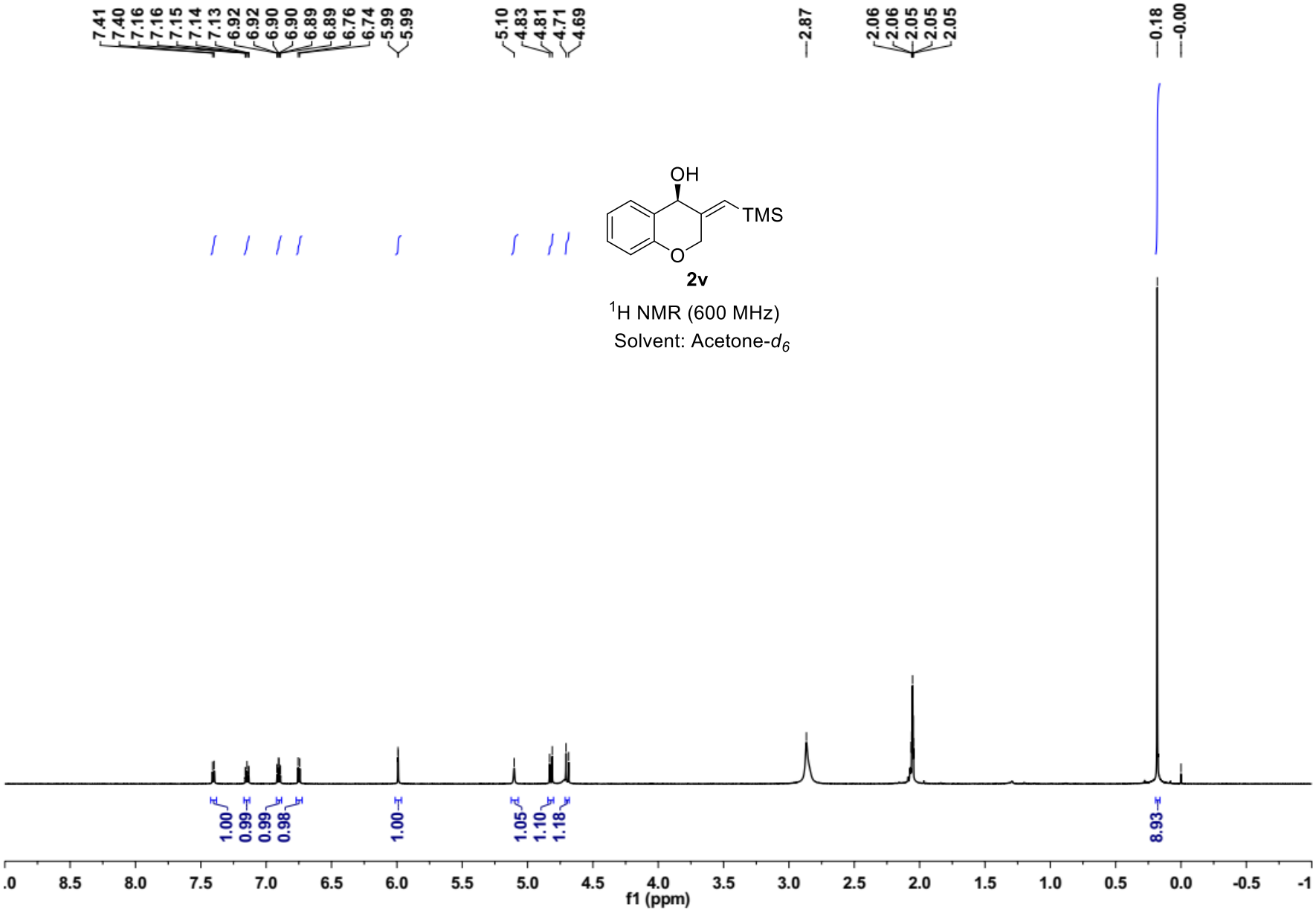
155.39
136.54
134.12
130.18
129.98
129.65
129.18
128.07
127.50
126.41
123.52
121.58
121.23
117.08
112.12
102.64
69.45
63.82
30.42
30.22
30.03
29.84
29.65
29.45
29.26
OH
O
N
H
2s
13C NMR (100 MHz)
Solvent: Acetone-d6
f1 (ppm)
f1 (ppm)

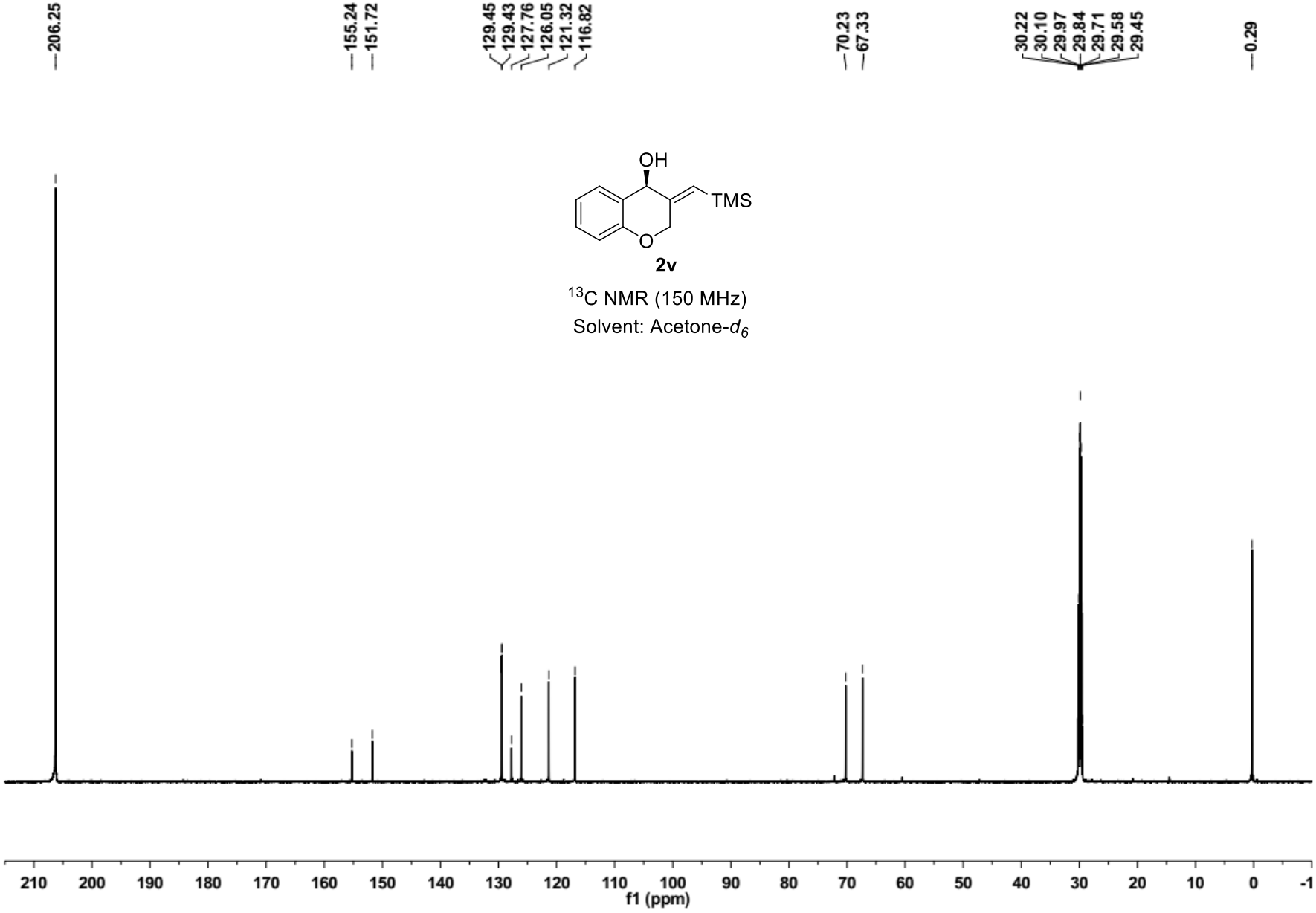

7.35
7.34
7.16
7.15
7.14
7.13
7.13
6.89
6.88
6.87
6.75
6.74
5.82
5.81
5.80
4.96
4.77
4.75
4.73
4.71
4.51
2.91
2.20
2.20
2.19
2.18
2.18
2.17
2.06
2.05
2.05
2.04
1.01
1.00
0.98
OH
Et
O
2t
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
1.03
1.04
0.99
1.05
1.06
1.12
1.04
0.78
2.24
3.35
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

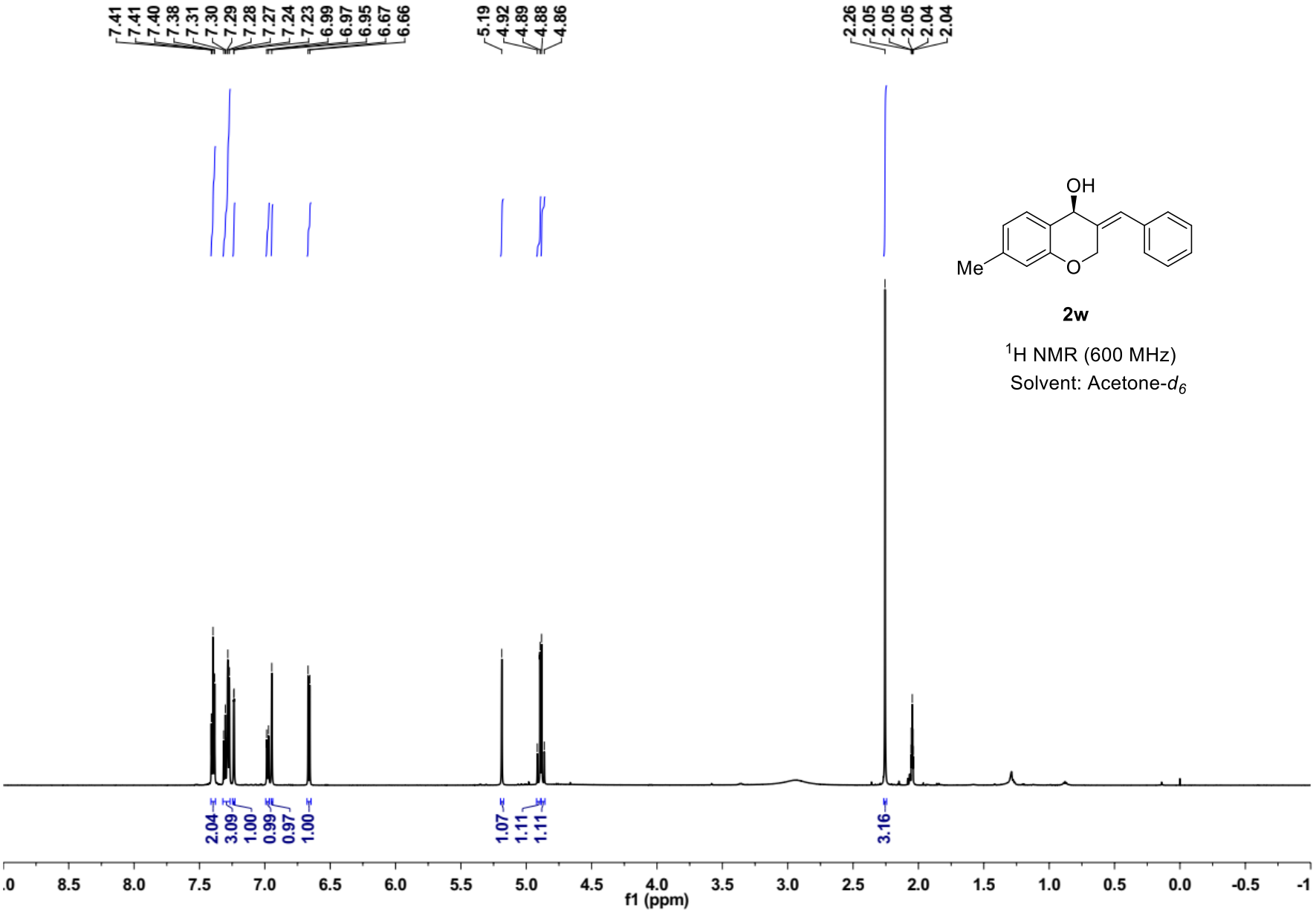

206.25
155.46
133.60
130.63
130.34
129.55
127.33
121.07
117.03
69.01
62.56
30.23
30.10
29.97
29.84
29.71
29.58
29.46
21.05
14.63
OH
Et
O
2t
13C NMR (150 MHz)
Solvent: Acetone-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

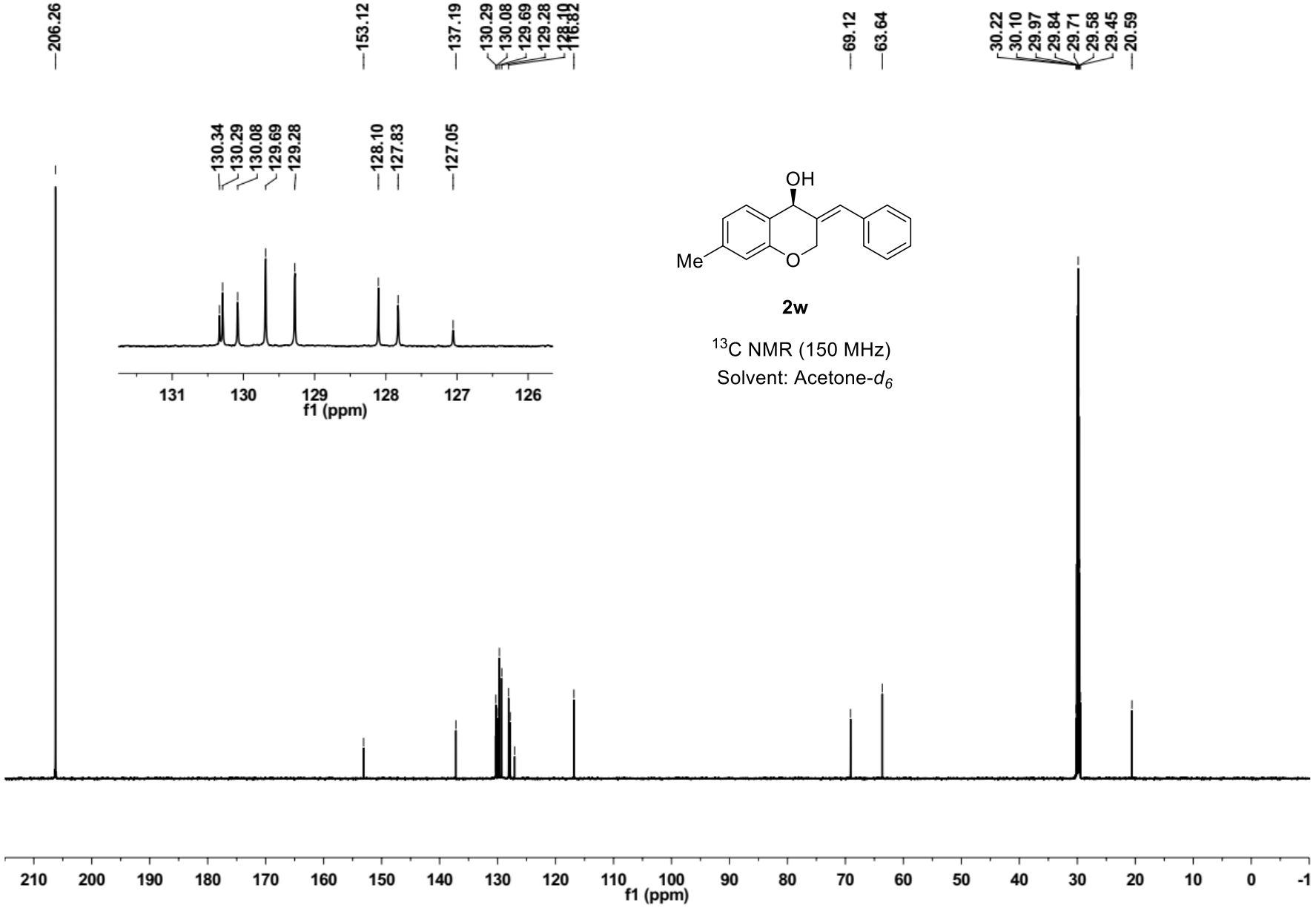

7.33
7.32
7.15
7.14
7.13
6.89
6.87
6.86
6.76
6.75
5.17
5.15
4.92
4.91
4.89
4.83
4.81
4.46
2.91
2.05
2.05
2.05
2.04
2.04
1.73
1.72
1.72
1.71
1.71
0.81
0.80
0.78
0.41
0.40
0.40
0.39
OH
O
2u
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
1.01
1.01
0.99
1.02
0.88
1.08
1.06
0.87
1.09
2.17
1.97
f1 (ppm)

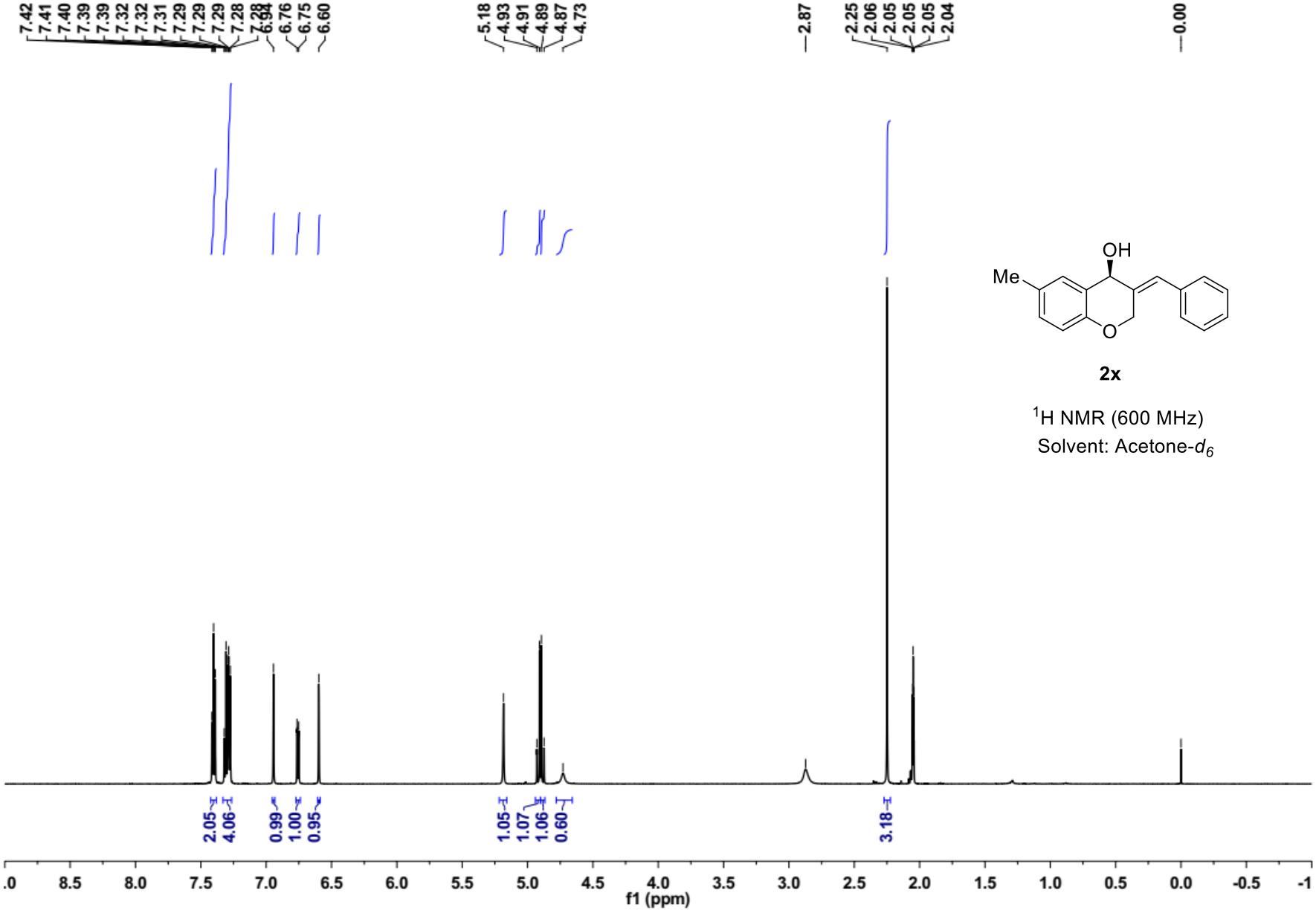

206.29
155.45
133.69
132.05
130.37
129.53
127.27
121.01
117.05
68.87
63.07
30.22
30.09
29.97
29.84
29.71
29.58
29.45
10.22
7.52
7.43
OH
O
2u
13C NMR (150 MHz)
Solvent: Acetone-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

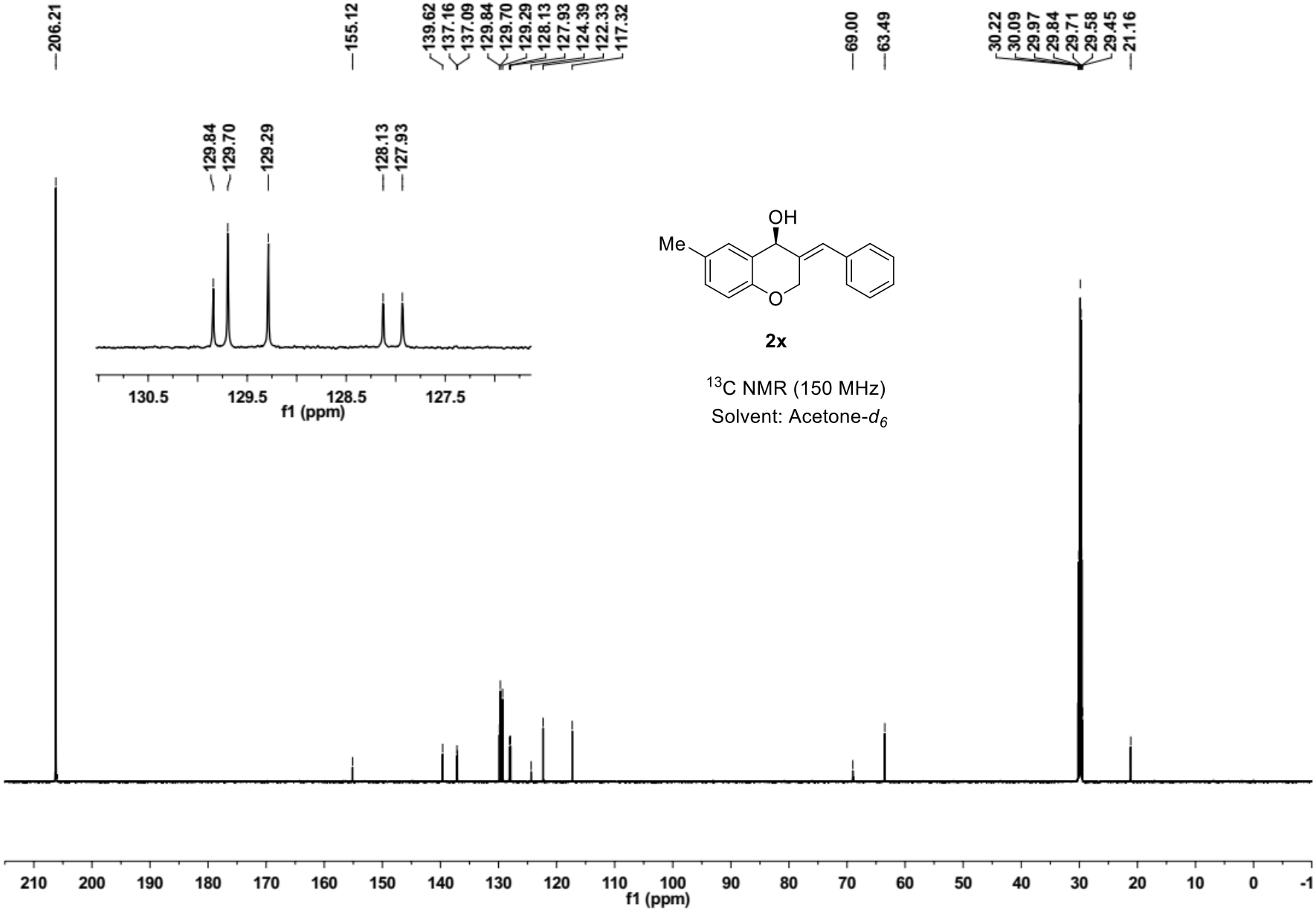

7.41
7.40
7.16
7.16
7.15
7.14
7.13
6.92
6.92
6.90
6.90
6.89
6.89
6.76
6.74
5.99
5.99
5.10
4.83
4.81
4.71
4.69
2.87
2.06
2.06
2.05
2.05
2.05
0.18
0.00
OH
TMS
O
2v
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
0.99
0.99
0.98
1.00
1.05
1.10
1.18
8.93
f1 (ppm)

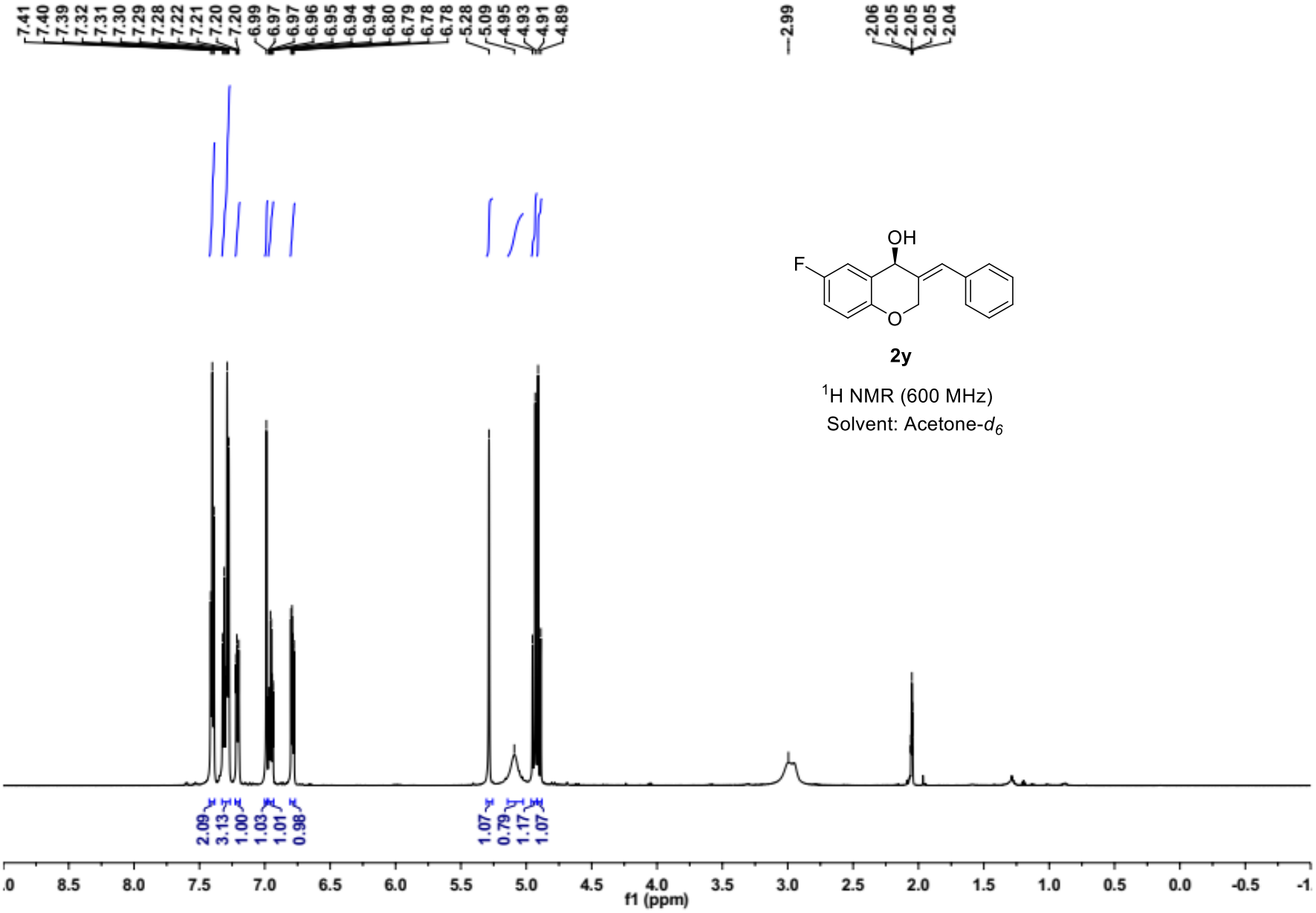

206.25
155.24
151.72
129.45
129.43
127.76
126.05
121.32
116.82
70.23
67.33
30.22
30.10
29.97
29.84
29.71
29.58
29.45
0.29
OH
TMS
O
2v
13C NMR (150 MHz)
Solvent: Acetone-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

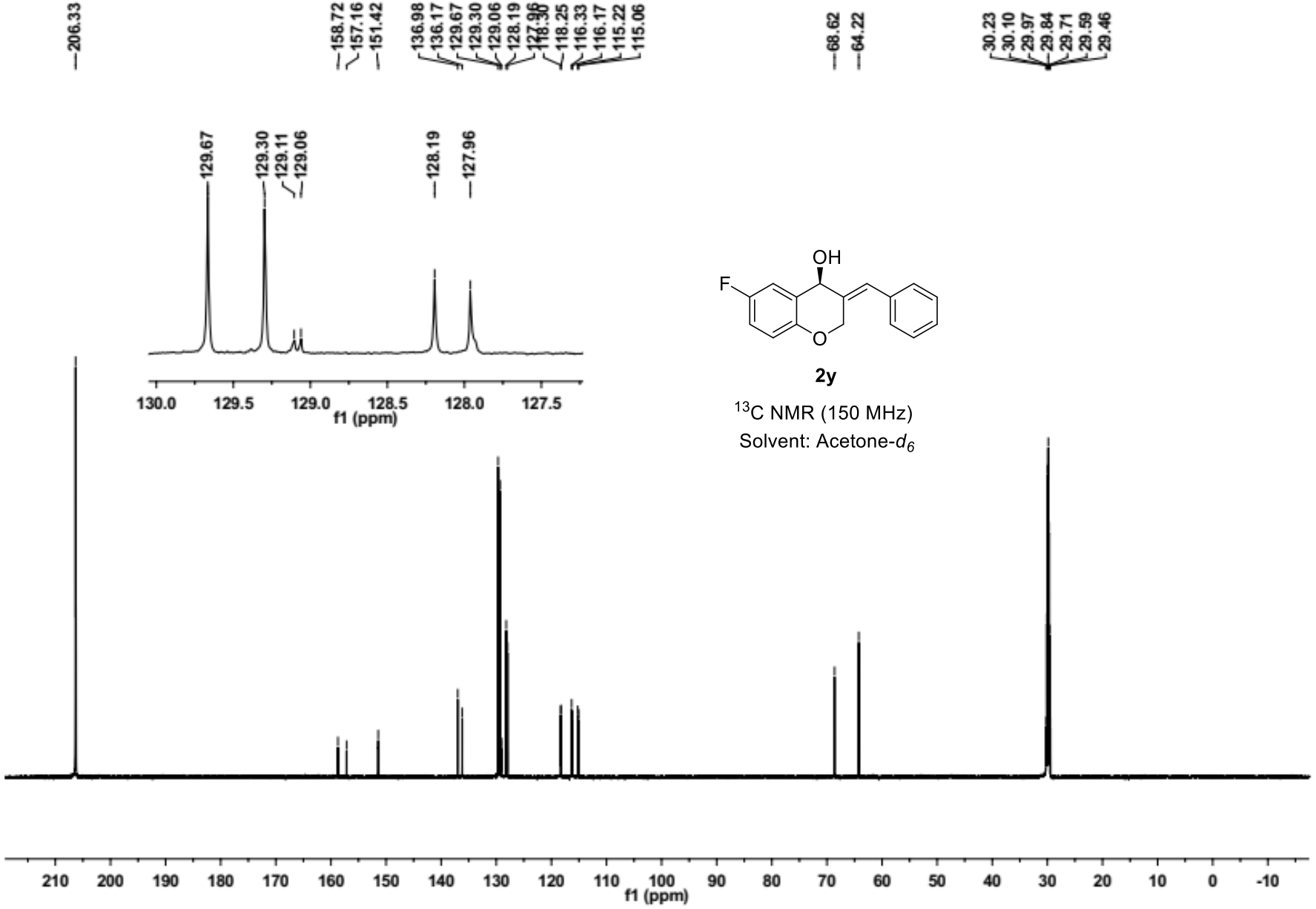

7.41
7.41
7.40
7.38
7.31
7.30
7.29
7.28
7.27
7.24
7.23
6.99
6.97
6.95
6.67
6.66
5.19
4.92
4.89
4.88
4.86
2.26
2.05
2.05
2.05
2.04
2.04
OH
Me
O
2w
1H NMR (600 MHz)
Solvent: Acetone-d6
2.04
3.09
1.00
0.99
0.97
1.00
1.07
1.11
1.11
3.16
f1 (ppm)

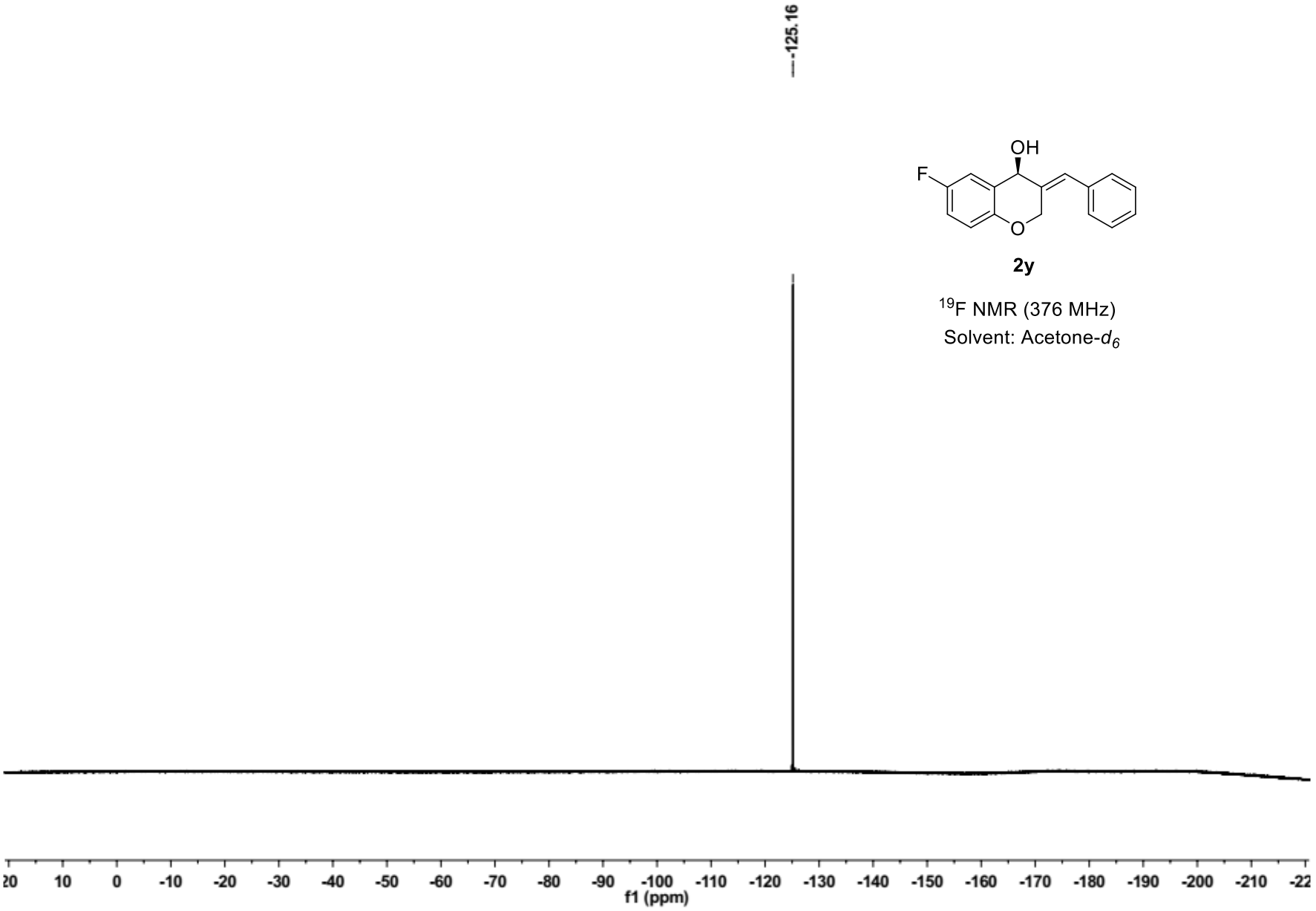

206.26
153.12
137.19
130.29
130.08
129.69
129.28
69.12
63.64
30.22
30.10
29.97
29.84
29.71
29.58
29.45
20.59
130.34
130.29
130.08
129.69
129.28
128.10
127.83
127.05
131
130
129
128
127
126
f1 (ppm)
OH
Me
O
2w
13C NMR (150 MHz)
Solvent: Acetone-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

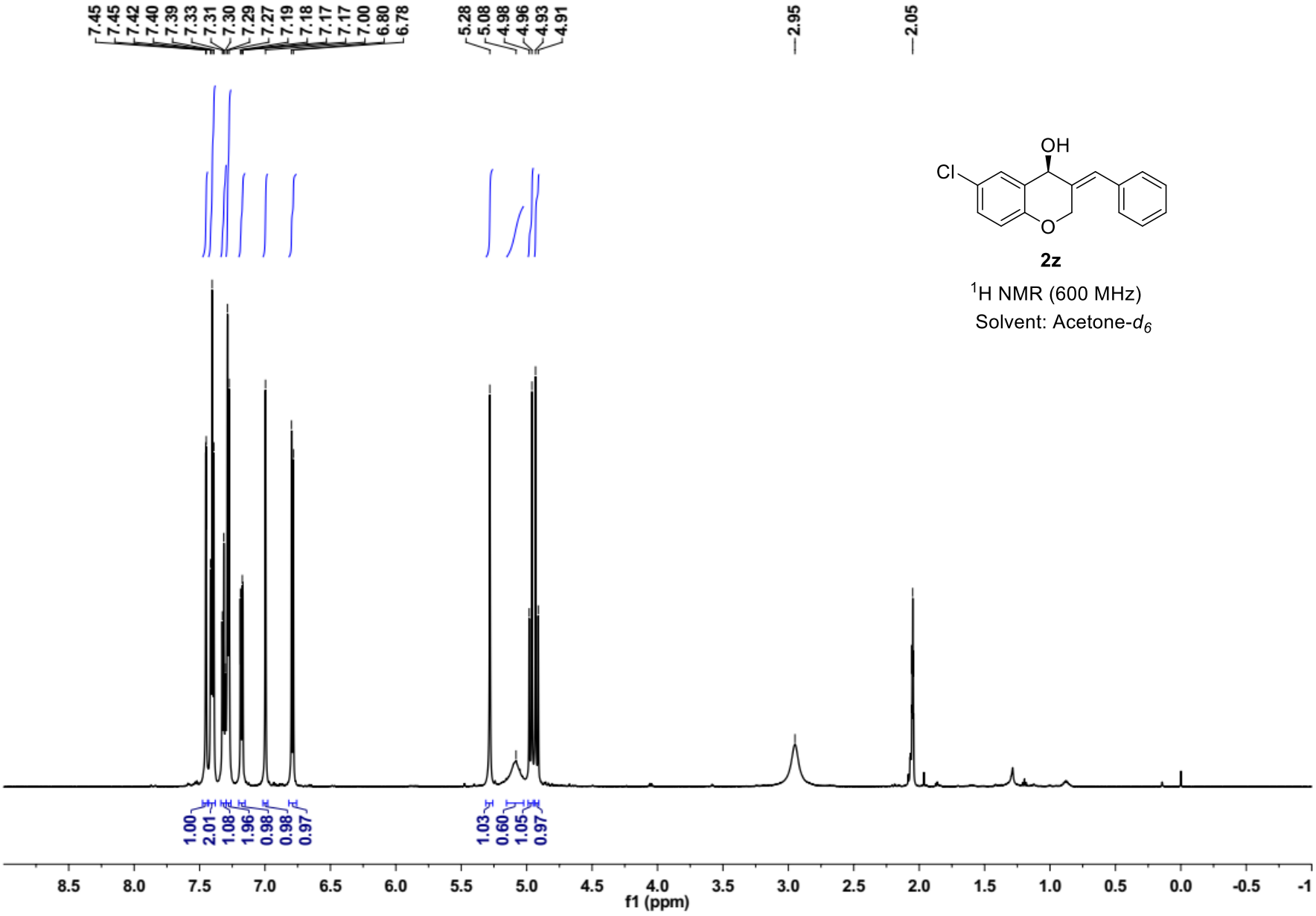

7.42
7.41
7.40
7.39
7.39
7.32
7.32
7.31
7.29
7.29
7.29
7.28
6.76
6.75
6.60
5.18
4.93
4.91
4.89
4.87
4.73
2.87
2.25
2.06
2.05
2.05
2.05
2.04
0.00
OH
Me
O
2x
1H NMR (600 MHz)
Solvent: Acetone-d6
2.05
4.06
0.99
1.00
0.95
1.05
1.07
1.06
0.60
3.18
f1 (ppm)

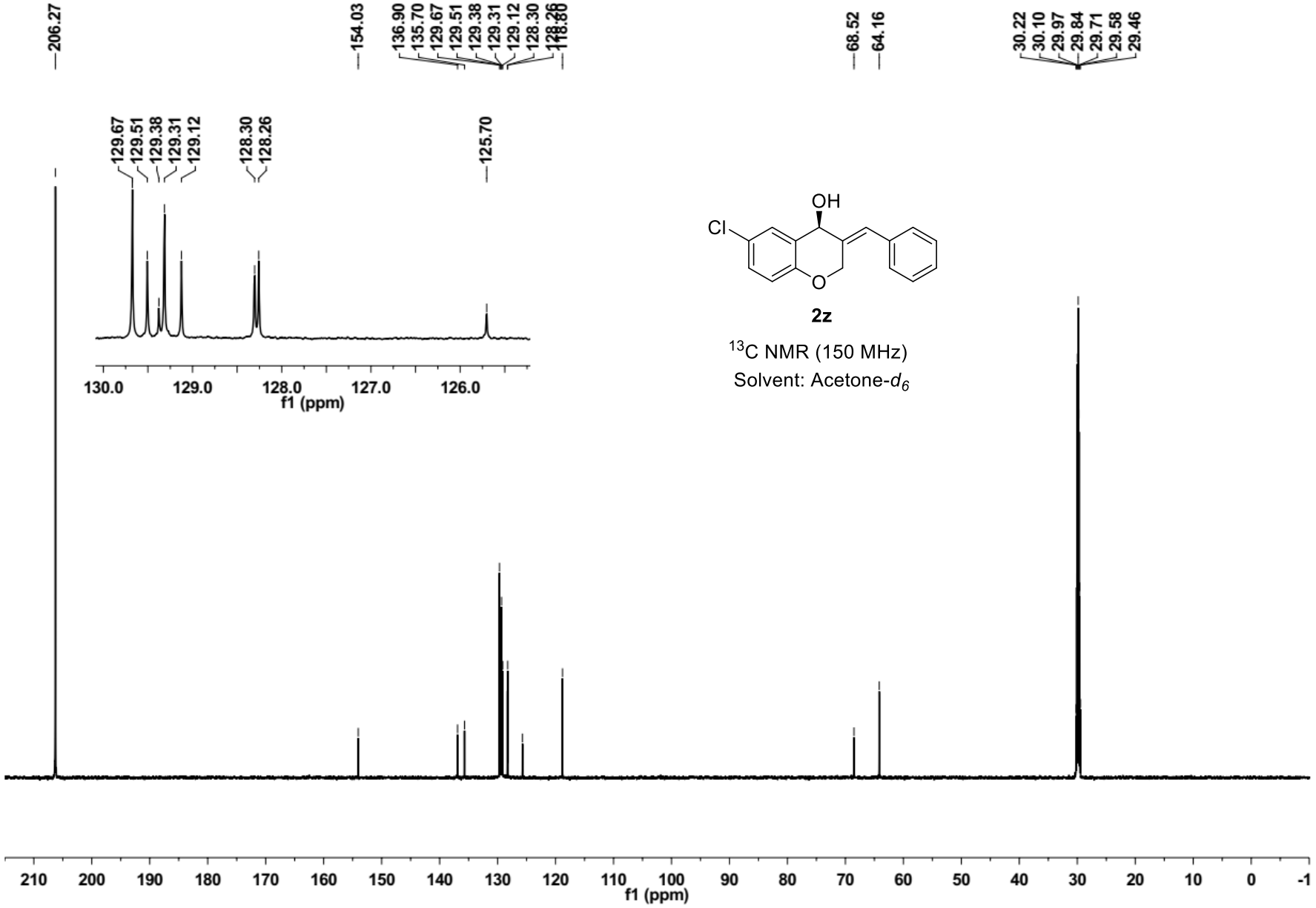

206.21
155.12
139.62
137.16
137.09
129.84
129.70
129.29
128.13
127.93
124.39
122.33
117.32
69.00
63.49
30.22
30.09
29.97
29.84
29.71
29.58
29.45
21.16
129.84
129.70
129.29
128.13
127.93
130.5
129.5
128.5
127.5
f1 (ppm)
OH
Me
O
2x
13C NMR (150 MHz)
Solvent: Acetone-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

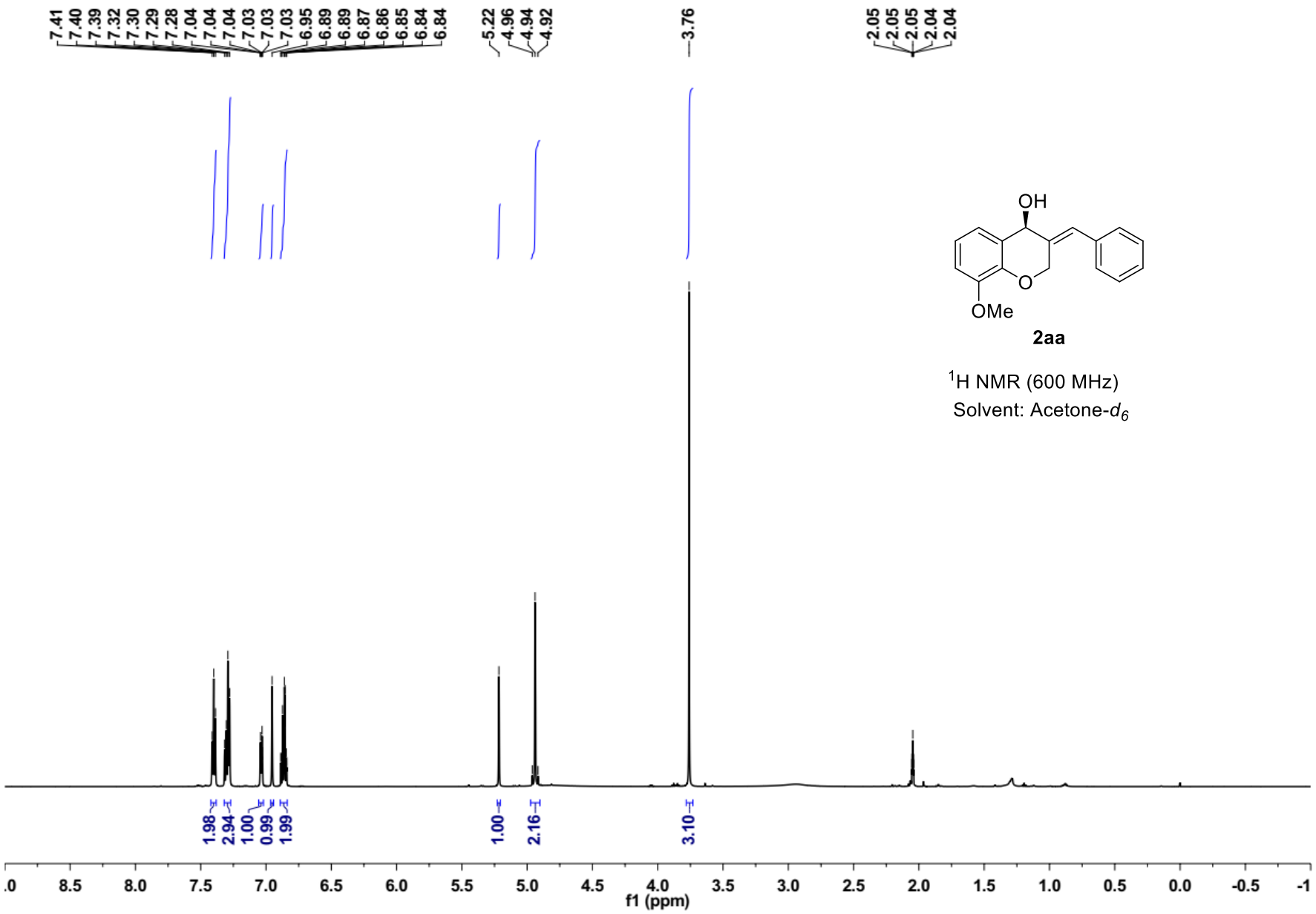

7.41
7.40
7.39
7.32
7.31
7.30
7.29
7.28
7.22
7.21
7.20
7.20
6.99
6.97
6.97
6.96
6.95
6.94
6.94
6.80
6.79
6.78
6.78
5.28
5.09
4.95
4.93
4.91
4.89
2.99
2.06
2.05
2.05
2.05
2.04
OH
F
O
2y
1H NMR (600 MHz)
Solvent: Acetone-d6
2.09
3.13
1.00
1.03
1.01
0.98
1.07
0.79
1.17
1.07
f1 (ppm)

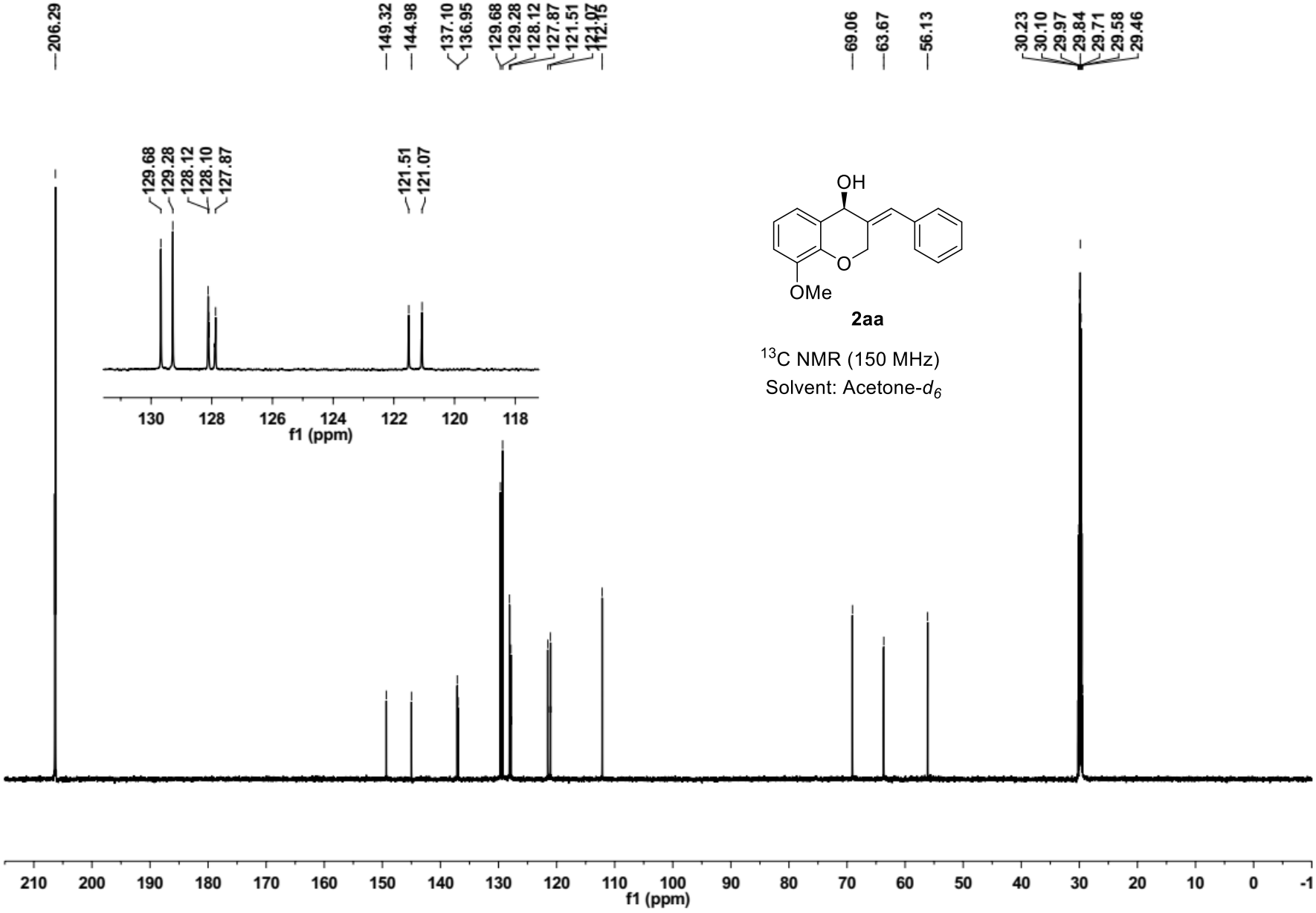

206.33
158.72
157.16
151.42
136.98
136.17
129.67
129.30
129.06
128.19
127.96
118.30
118.25
116.33
116.17
115.22
115.06
68.62
64.22
30.23
30.10
29.97
29.84
29.71
29.59
29.46
129.67
129.30
129.11
129.06
128.19
127.96
130.0
129.5
129.0
128.5
128.0
127.5
f1 (ppm)
OH
F
O
2y
13C NMR (150 MHz)
Solvent: Acetone-d6
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)

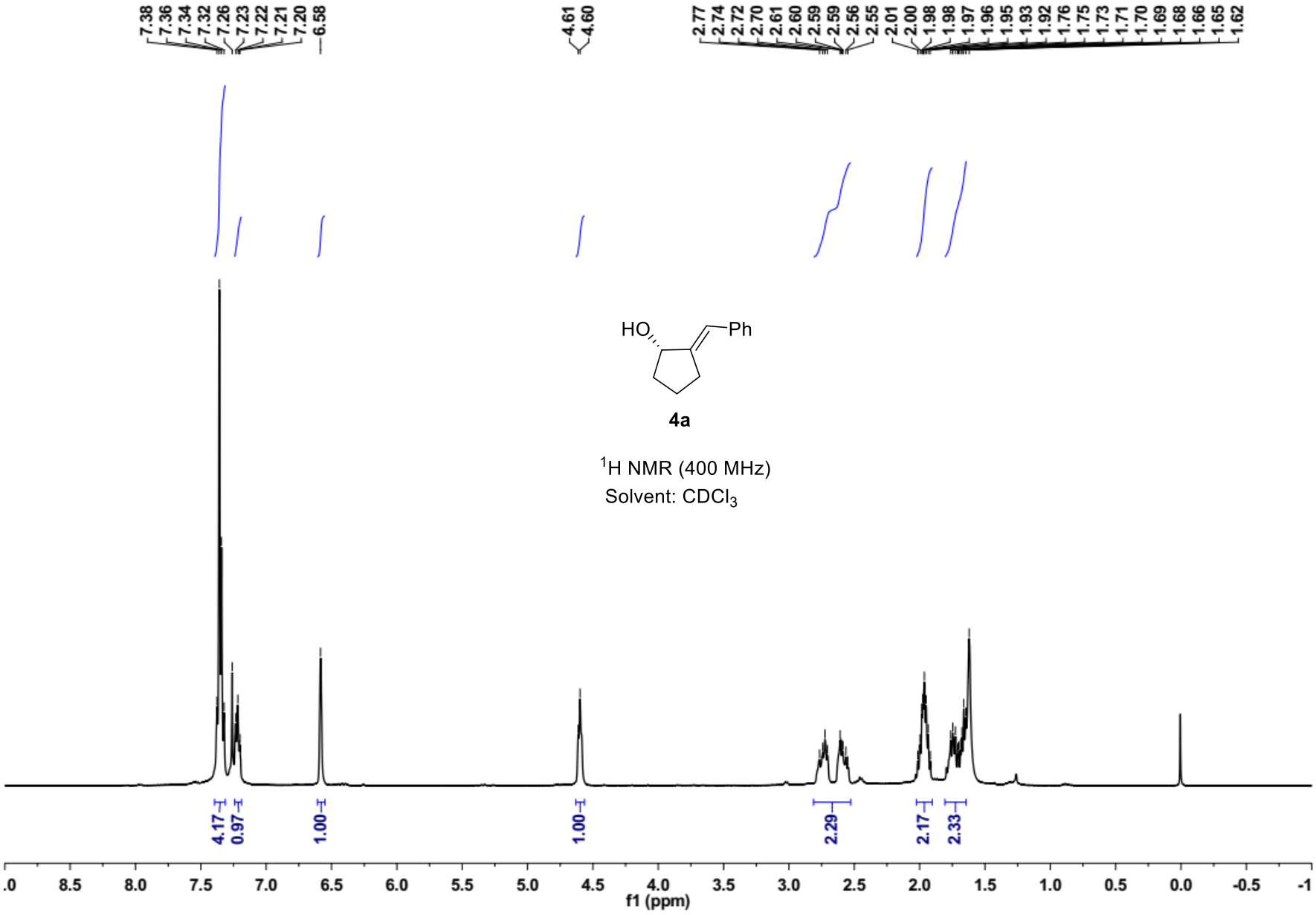

-125.16
OH
F
O
2y
19F NMR (376 MHz)
Solvent: Acetone-d6
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

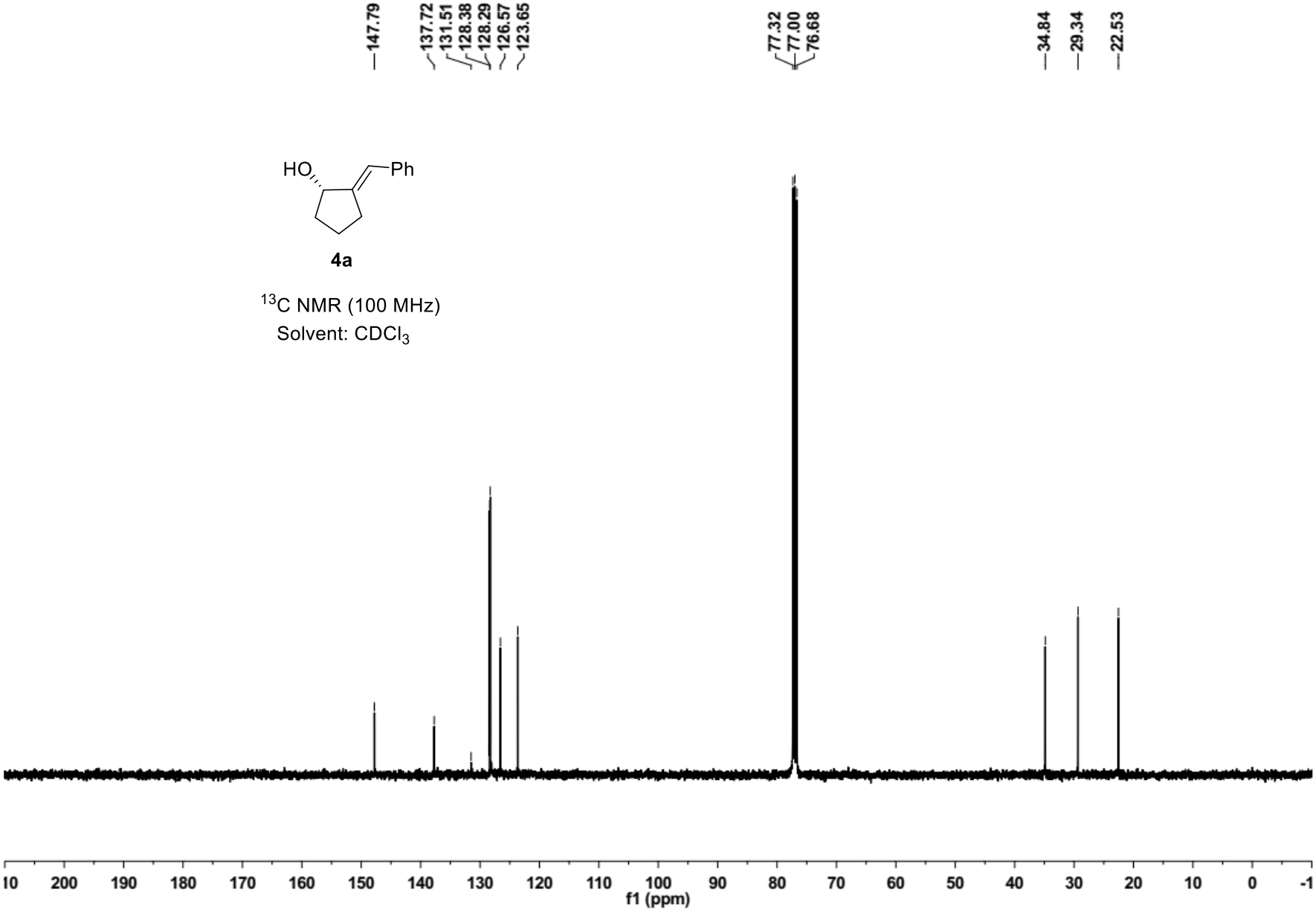

7.45
7.45
7.42
7.40
7.39
7.33
7.31
7.30
7.29
7.27
7.19
7.18
7.17
7.17
7.00
6.80
6.78
5.28
5.08
4.98
4.96
4.93
4.91
2.95
2.05
OH
Cl
O
2z
1H NMR (600 MHz)
Solvent: Acetone-d6
1.00
2.01
1.08
1.96
0.98
0.98
0.97
1.03
0.60
1.05
0.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

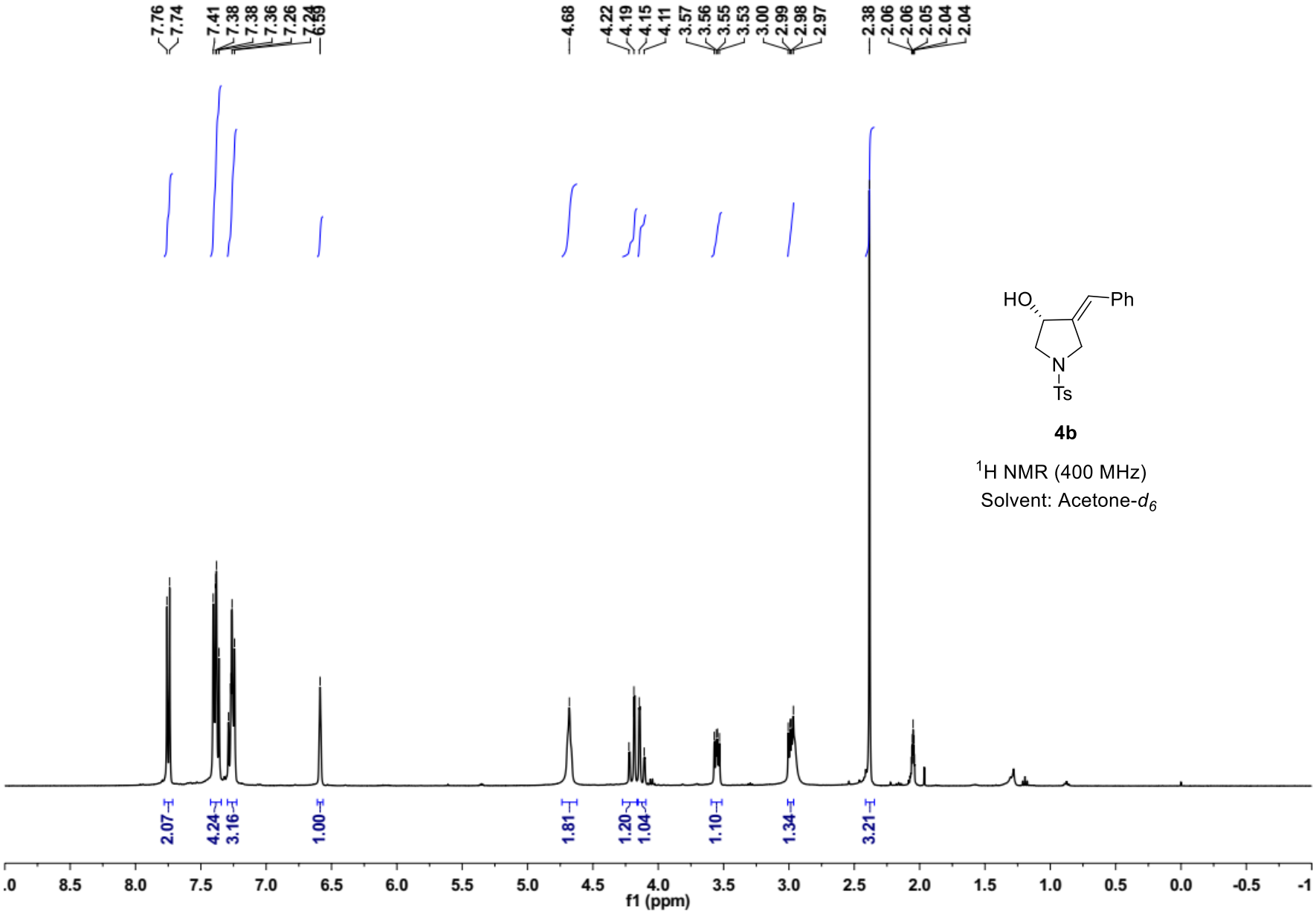

206.27
154.03
136.90
135.70
129.67
129.51
129.38
129.31
129.12
128.30
128.26
118.80
68.52
64.16
30.22
30.10
29.97
29.84
29.71
29.58
29.46
125.70
OH
Cl
O
2z
^{13}C NMR (150 MHz)
Solvent: Acetone-d_6
f1 (ppm)

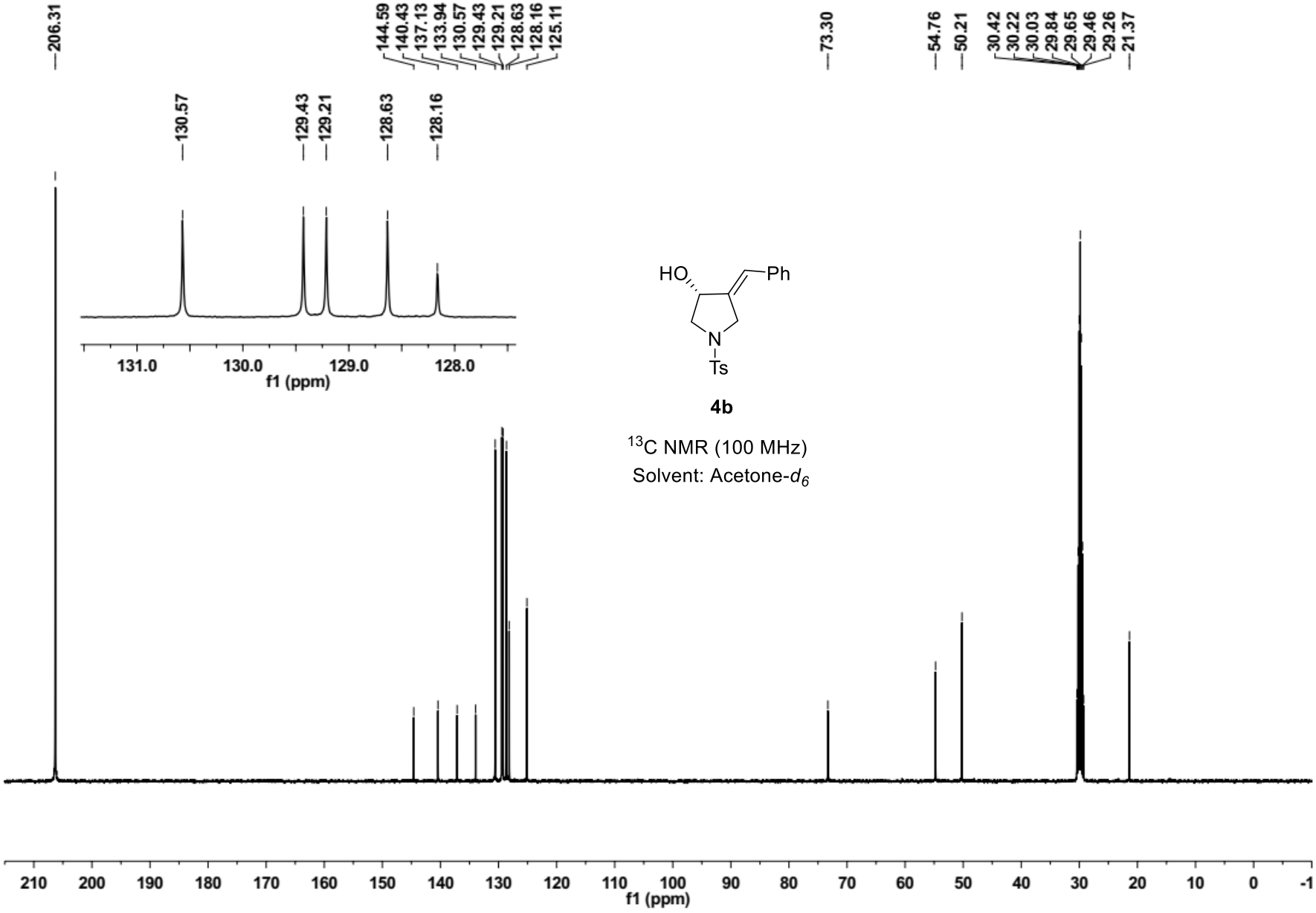

7.41
7.40
7.39
7.32
7.30
7.29
7.28
7.04
7.04
7.04
7.03
7.03
7.03
6.95
6.89
6.89
6.87
6.86
6.85
6.84
6.84
5.22
4.96
4.94
4.92
3.76
2.05
2.05
2.05
2.04
2.04
OH
O
OMe
2aa
1H NMR (600 MHz)
Solvent: Acetone-d6
1.98
2.94
1.00
0.99
1.99
1.00
2.16
3.10
f1 (ppm)

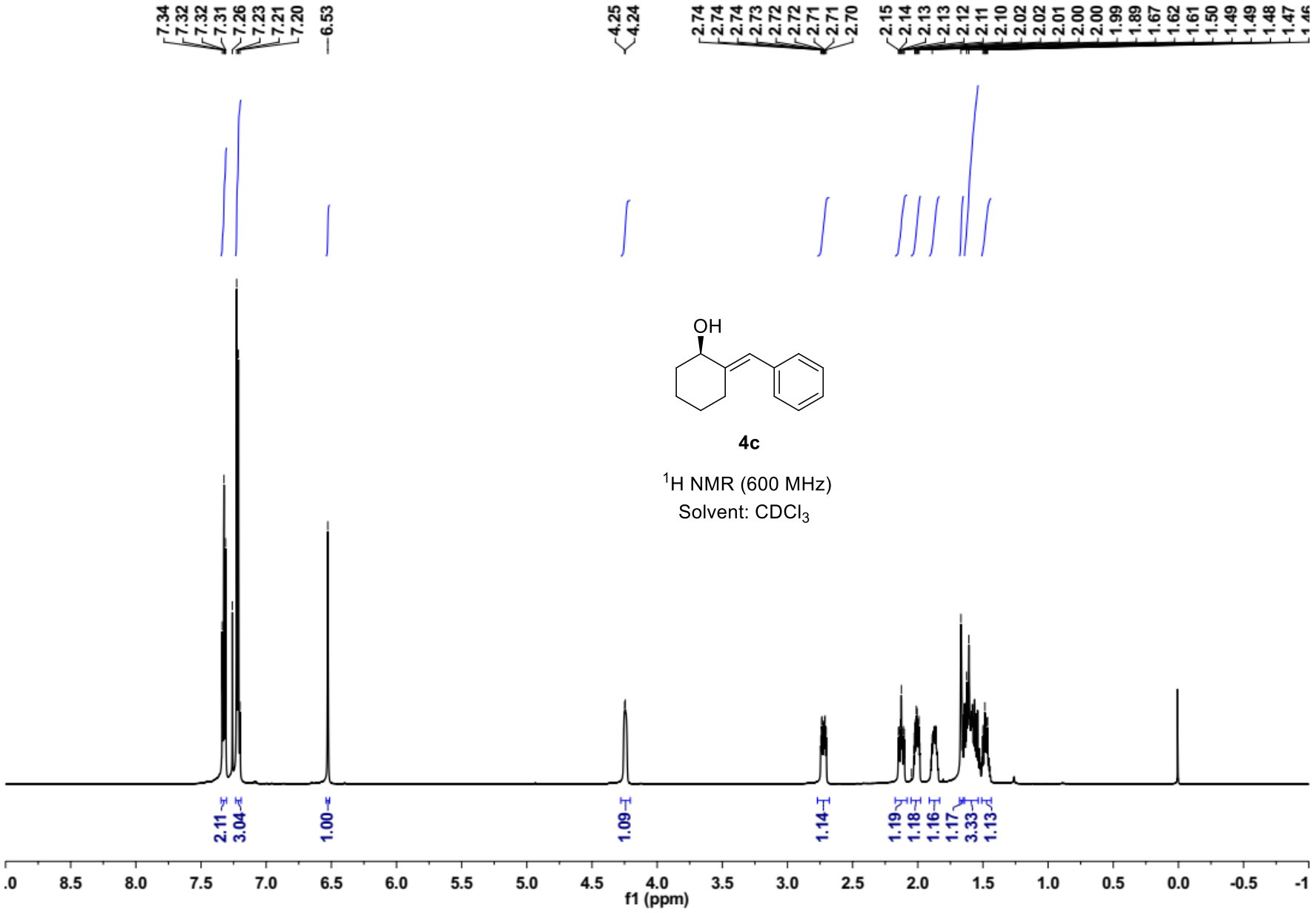

206.29
149.32
144.98
137.10
136.95
129.68
129.28
128.12
127.87
121.51
121.07
112.15
69.06
63.67
56.13
30.23
30.10
29.97
29.84
29.71
29.58
29.46
129.68
129.28
128.12
128.10
127.87
121.51
121.07
130
128
126
124
122
120
118
f1 (ppm)
OH
O
OMe
2aa
13C NMR (150 MHz)
Solvent: Acetone-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

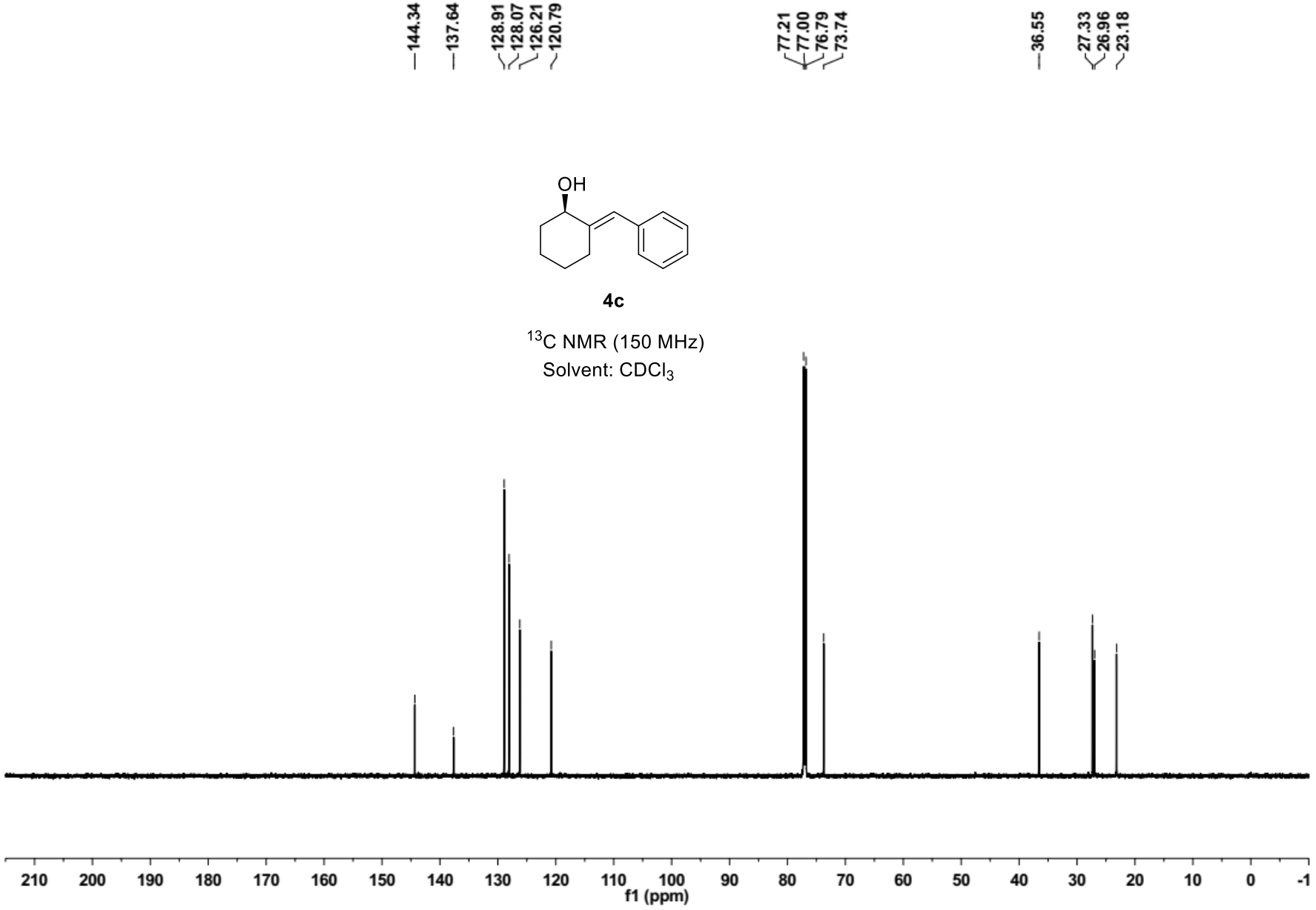

7.38
7.36
7.34
7.32
7.26
7.23
7.22
7.21
7.20
6.58
4.61
4.60
2.77
2.74
2.72
2.70
2.61
2.60
2.59
2.59
2.56
2.55
2.01
2.00
1.98
1.98
1.97
1.96
1.95
1.93
1.92
1.76
1.75
1.73
1.71
1.70
1.69
1.68
1.66
1.65
1.62
HO
Ph
4a
1H NMR (400 MHz)
Solvent: CDCl3
4.17
0.97
1.00
1.00
2.29
2.17
2.33
f1 (ppm)


147.79
137.72
131.51
128.38
128.29
126.57
123.65
77.32
77.00
76.68
34.84
29.34
22.53
HO
Ph
4a
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)


7.76
7.74
7.41
7.38
7.38
7.36
7.26
7.24
6.59
4.68
4.22
4.19
4.15
4.11
3.57
3.56
3.55
3.53
3.00
2.99
2.98
2.97
2.38
2.06
2.06
2.05
2.04
2.04
HO
Ph
N
Ts
4b
1H NMR (400 MHz)
Solvent: Acetone-d6
2.07
4.24
3.16
1.00
1.81
1.20
1.04
1.10
1.34
3.21
f1 (ppm)


206.31
144.59
140.43
137.13
133.94
130.57
129.43
129.21
128.63
128.16
125.11
73.30
54.76
50.21
30.42
30.22
30.03
29.84
29.65
29.46
29.26
21.37
130.57
129.43
129.21
128.63
128.16
131.0
130.0
129.0
128.0
f1 (ppm)
HO
Ph
N
Ts
4b
13C NMR (100 MHz)
Solvent: Acetone-d6
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)


7.34
7.32
7.32
7.31
7.26
7.23
7.21
7.20
6.53
4.25
4.24
2.74
2.74
2.74
2.73
2.72
2.72
2.71
2.71
2.70
2.15
2.14
2.13
2.13
2.12
2.11
2.10
2.02
2.02
2.01
2.00
2.00
1.99
1.89
1.67
1.62
1.61
1.50
1.49
1.49
1.48
1.47
OH
4c
1H NMR (600 MHz)
Solvent: CDCl3
2.11
3.04
1.00
1.09
1.14
1.19
1.18
1.16
1.17
3.33
1.13
f1 (ppm)


144.34
137.64
128.91
128.07
126.21
120.79
77.21
77.00
76.79
73.74
36.55
27.33
26.96
23.18
OH
4c
13C NMR (150 MHz)
Solvent: CDCl3
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)