Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

A Cascade Claisen Rearrangement/*o*-Quinone Methide Formation/Electrocyclization Approach to 2*H*-Chromenes

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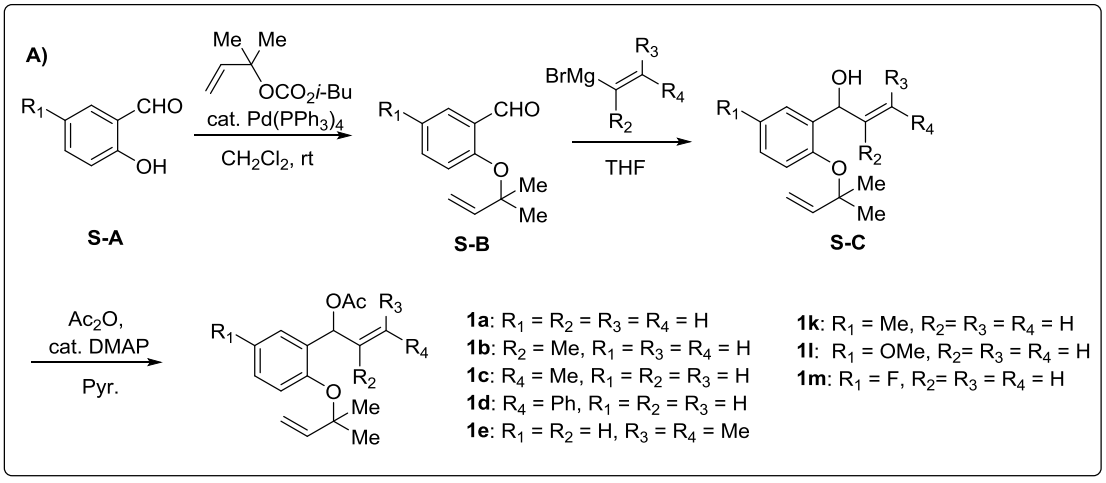
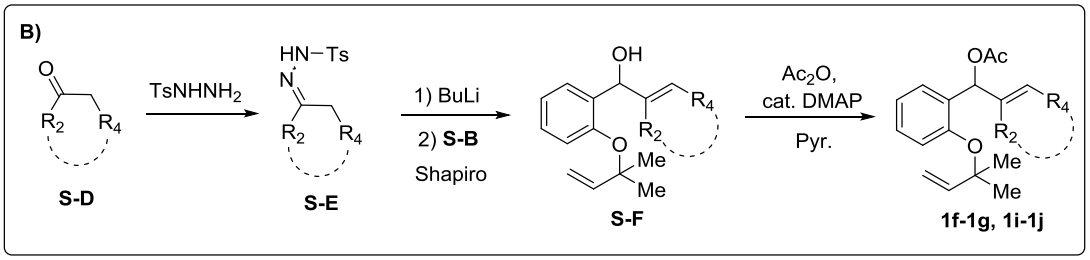
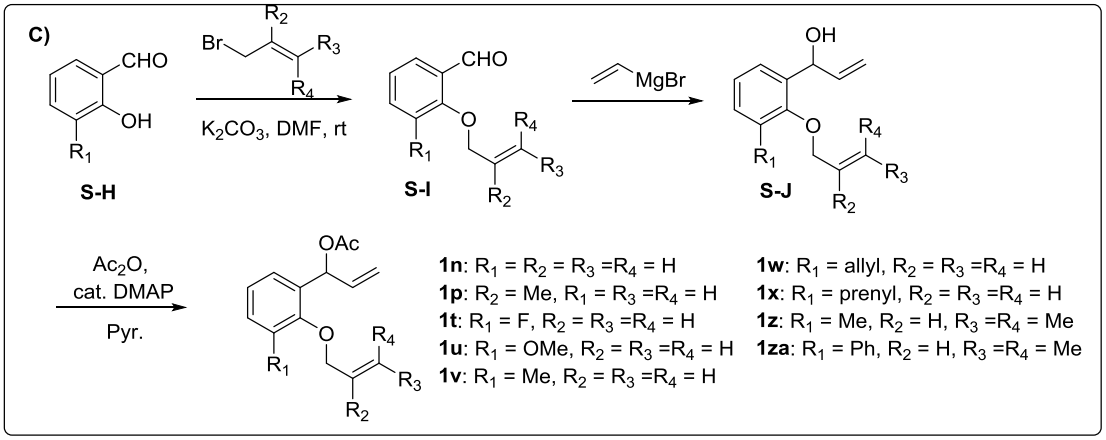
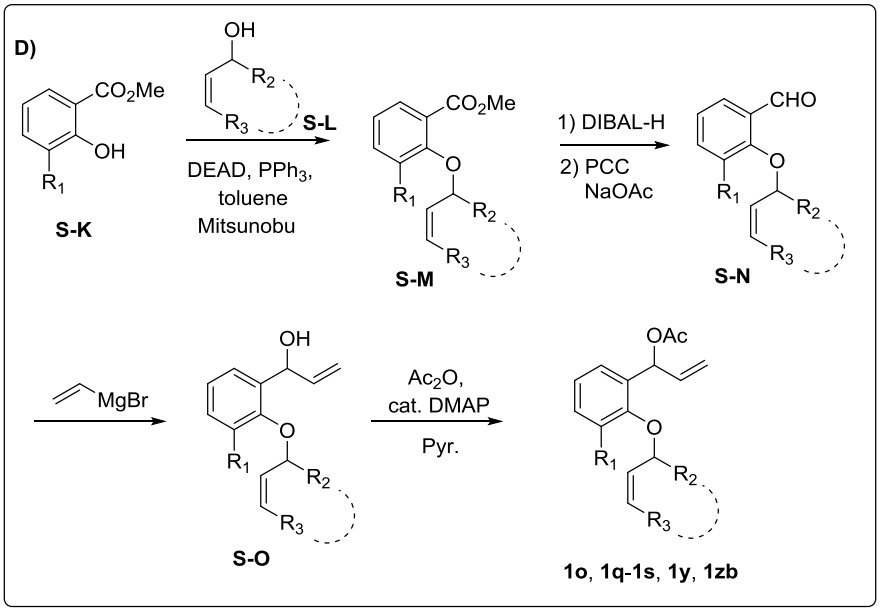
General Information: Reactions were carried out in oven or flame-dried glassware under a nitrogen atmosphere, unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled before use from sodium using benzophenone as indicator. Dichloromethane was freshly distilled before use from calcium hydride (CaH_2). All other anhydrous solvents were dried over 3Å or 4Å molecular sieves. Solvents used in workup, extraction and column chromatography were used as received from commercial suppliers without prior purification. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC, 0.25 mm) on Liangchen pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm) supplied by Liangchen. Infrared spectra were collected on a Bruker model TENSOR27 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVIII-400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C, 376 MHz for ^{19}F). Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform (7.26 ppm for ^1H and 77.16 ppm for ^{13}C) or benzene (7.16 ppm for ^1H and 128.06 ppm for ^{13}C). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High resolution mass spectra were measured at Keecloud Mass Spectrometry Service Company on either an Thermo Scientific LTQ Orbitrap XL system or a Bruker solariX System.

General Synthetic Routes to Substrates 1a-1g and 1i-1zb

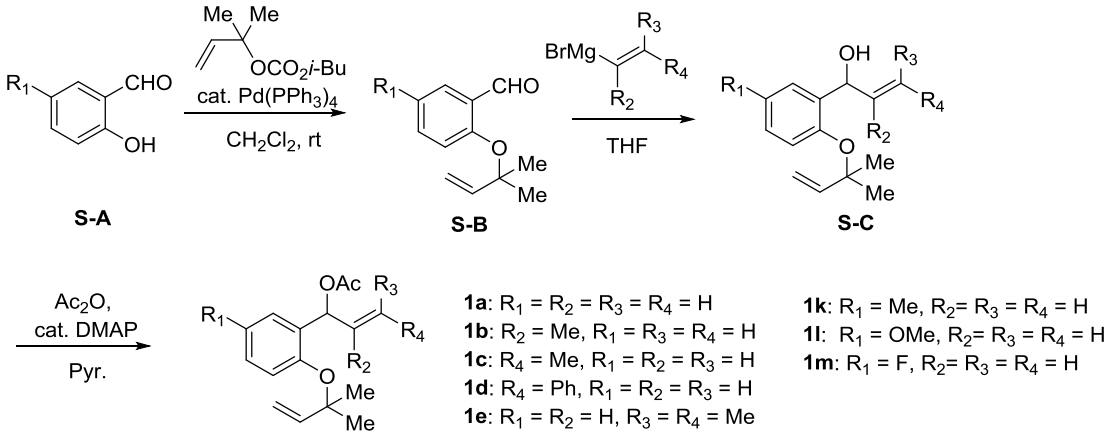



B)
TsNHNH2
1) BuLi
2) S-B
Shapiro
Ac2O,
cat. DMAP
Pyr.
S-D
S-E
S-F
1f-1g, 1i-1j


C)
K2CO3, DMF, rt
MgBr
Ac2O,
cat. DMAP
Pyr.
S-H
S-I
S-J
1n: R1 = R2 = R3 =R4 = H
1p: R2 = Me, R1 = R3 =R4 = H
1t: R1 = F, R2 = R3 =R4 = H
1u: R1 = OMe, R2 = R3 =R4 = H
1v: R1 = Me, R2 = R3 =R4 = H
1w: R1 = allyl, R2 = R3 =R4 = H
1x: R1 = prenyl, R2 = R3 =R4 = H
1z: R1 = Me, R2 = H, R3 =R4 = Me
1za: R1 = Ph, R2 = H, R3 =R4 = Me


D)
S-L
DEAD, PPh3,
toluene
Mitsunobu
1) DIBAL-H
2) PCC
NaOAc
MgBr
Ac2O,
cat. DMAP
Pyr.
S-K
S-M
S-N
S-O
1o, 1q-1s, 1y, 1zb

Syntheses of Substrates 1a-1e, 1k-1m



***Palladium-catalyzed etherification (Step 1)*:** Following the procedure developed by Shishido[1], to a solution of salicylaldehyde **S**-**A** (3.0 mmol) and isobutyl-2-methyl-3-butene-2-yl carbonate (1.12 g, 6.0 mmol) in dry dichloromethane (12 mL) at room temperature under nitrogen atmosphere was added $Pd(PPh_3)_4$ (70 mg, 0.06mmol) at one portion. The reaction mixture was stirred for 10 min, then filtered through a plug of silica gel, rinsed with dichloromethane and concentrated under reduced pressure. The resulting residue went through a short column to give the desired crude aldehyde **S**-**B**, which was used directly in the next step.

Grignard Addition to Aldehyde (Step 2, General Procedure): To a solution of the crude aldehyde **S**-**B** (2.0 mmol) in dry THF (5 mL) at -78℃ was added slowly Grignard reagent (3.0 mmol). The reaction was allowed to warm to room temperature over 60 min, and quenched with aqueous NH_4Cl (10 mL). The organic layer was collected and the aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic fractions were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude benzylic alcohol **S**-**C**, which was used without further purification for the next step.

***Acetylation of Alcohol (Step 3, General Procedure)*:** To a solution of alcohol **S**-**C** (1.0 mmol) in pyridine (1 mL) was added 4-dimethylamino pyridine (DMAP, 12 mg, 0.1 mmol). The resulting solution was cooled to 0 ℃ with ice-water bath and then acetyl anhydride (0.15 mL, 1.5 mmol) was added dropwise. After the completion of addition, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was quenched by dilution with ethyl acetate (30 mL). The organic phase was

[1]Kishuku, H; Shindo, M.; Shishido, K. *Chem. Commun*. **2003**, 350.

collected and washed with sat. aqueous $CuSO_4$ (3 × 5 mL), 1 M citric acid (3 × 5 mL), sat. aqueous $NaHCO_3$ (5 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (petroleum ether/ethyl acetate = 50/1) to give the corresponding pure acetate **1a**-**1c**, **1l**-**1m**. However, attempts to purify **1d**, **1e** and **1k** for spectroscopic characterization were unsuccessful. Therefore, the crude products **1d**, **1e** and **1k** were used directly after acetylation.

1a. 228 mg, 65% yield over 3 steps; colorless oil. R_f = 0.28 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3086, 2983, 2930, 1743, 1599, 1486, 1369, 1232, 1133. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.16-7.08 (m, 2H), 6.95 (td, *J* = 7.2, 1,2 Hz, 1H), 6.68 (d, *J* = 5.6 Hz, 1H), 6.18 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.02 (ddd, *J* = 17.2 Hz, 10.4, 5.6 Hz, 1H), 5.29-5.15 (m, 4H), 2.12 (s, 3H), 1,52 (s, 3H), 1.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ:170.0, 153.9, 144.9, 136.1, 130.5, 128.3, 127.5, 121.4, 118.6, 116.0, 113.4, 80.2, 71.3, 27.8, 27.0, 21.4. **HRMS** (ESI) *m*/*z* calculated for $C_{16}H_{20}NaO_3$ $[M+Na]^+$ 283.1305, found 283.1302.

1b. 234 mg, 69% yield over 3 steps; colorless oil. R_f = 0.43 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3086, 2982, 2934, 1741, 1599, 1486, 1453, 1370, 1232, 1133. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.33 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.16-7.09 (m, 2H), 6.95 (td, *J* = 7.6, 1.6 Hz, 1H), 6.64 (s, 1H), 6.19 (dd, *J* = 17,6, 10.8 Hz, 1H), 5.23 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.16 (dd, *J* = 10.8, 0.8 Hz, 1H), 5.04 (s, 1H), 4.97 (s, 1H), 2.12 (s, 3H), 1.72 (s, 3H), 1.53 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.9, 154.3, 144.9, 143.2, 129.9, 128.2, 127.6, 121.2, 118.5, 113.4, 112.1, 80.1, 72.9, 27.9, 26.7, 21.3, 19.4. **HRMS** (ESI) *m*/*z* calculated for $C_{17}H_{22}NaO_3$ $[M+Na]^+$ 297.1461, found 297.1457.

1c. 248 mg, 71% yield over 3 steps; colorless oil. R_f = 0.31 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3066, 2980, 2931, 1737, 1596, 1483, 1452, 1370, 1239, 1131.**^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.44 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.12-7.03 (m, 2H), 6.99-6.92 (m, 2H), 6.18 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.14 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.54 (quint, *J* = 6.4 Hz, 1H), 5.20 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.13 (dd, *J* = 11.2, 0.8 Hz, 1H), 2.08 (s, 3H), 1.46 (s, 3H), 1.45 (s, 3H), 1.41 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 170.5, 153.9, 144.7, 129.6, 128.9, 128.1, 127.3, 126.5, 122.3, 121.0, 113.4, 80.6, 71.6, 27.3, 27.1, 21.5, 20.5. **HRMS** (ESI) *m*/*z* calculated for $C_{17}H_{22}NaO_3$ $[M+Na]^+$ 297.1461, found 297.1458.

Precursor of **1d** (Inseperable Isomers). 476 mg, 81% over 2 steps, dr 2.1:1; colorless oil. R_f = 0.35 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3564, 3060, 3026,

2981,2930, 1597, 1584, 1483, 1451, 1378,1363, 1236, 1131. Major diastereomer: **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.49-7.21 (m, 3H), 7.14-6.76 (m, 7H), 6.55-6.46 (m, 1H), 6.16-5.68 (m, 2H), 4.96-4.81 (m, 2H), 2.82 (br,1H), 1.26 (s, 3H), 1.25 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 154.2, 144.9, 137.6, 134.7, 132.6, 129.6, 128.8 (2×C), 128.3, 128.1, 127.6, 126.9 (2×C), 121.9, 118.4, 113.3, 80.0, 71.5, 27.5, 27.1. Minor diastereomer: **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.49-7.21 (m, 3H), 7.14-6.76 (m, 7H), 6.55-6.46 (m, 1H), 6.16-5.68 (m, 2H), 4.96-4.81 (m, 2H), 3.02 (br,1H), 1.16 (s, 3H), 1.14 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 154.4, 144.8, 137.3, 135.4, 134.0, 131.0, 129.5 (2×C), 128.5 (2×C), 128.0, 127.4, 126.9, 122.1, 118.9, 113.3, 80.2, 67.4, 27.3, 27.0. **HRMS** (ESI) *m*/*z* calculated for $C_{20}H_{22}NaO_2$ $[M+Na]^+$ 317.1517, found 317.1519.

Precursor of **1e**. 383 mg, 81% yield over 2 steps; colorless oil. R_f = 0.39 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3421, 3065, 2976, 2926, 1483, 1451, 1376, 1363, 1275,1259, 1235, 1130. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.45 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.11-7.04 (m, 2H), 6.98-6.93 (m, 2H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.20 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.13 (dd, *J* = 10.8, 0.8 Hz, 1H), 1.80 (br, 1H), 1.46 (s, 6H), 1.43 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.7, 144.7, 137.6, 130.3, 127.7, 126.4, 122.4, 122.3, 121.2, 113.3, 80.5, 71.3, 29.8 (2×C), 27.2 (2×C). **HRMS** (ESI) *m*/*z* calculated for $C_{16}H_{22}NaO_2$ $[M+Na]^+$ 269.1517, found 269.1509.

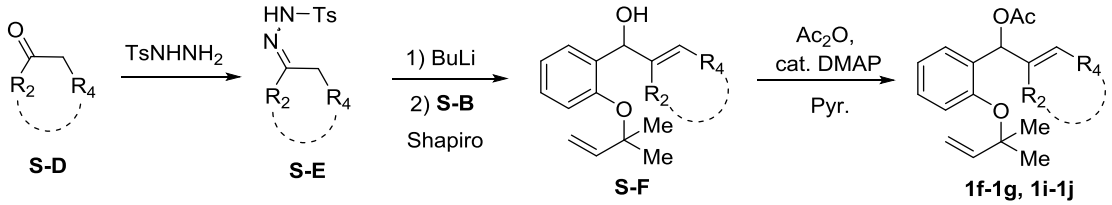
Precursor of **1k**. 368 mg, 80% yield over 2 steps; colorless oil. R_f = 0.29 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3433, 3085, 2981, 2925, 1494, 1414, 1379, 1363, 1245, 1216, 1132. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.09 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.92 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.16 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.12 (ddd, *J* = 16.8, 10.8, 5.6 Hz, 1H), 5.37-5.32 (m, 2H), 5.23 (d, *J* = 17.6 Hz, 1H), 5.17 (d, *J* = 10.8 Hz, 2H), 3.09 (d, *J* = 6.0 Hz, 1H), 2.27 (s, 3H), 1.51 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 151.6, 144.7, 140.0, 133.3, 130.9, 128.3 (2×C), 118.4, 114.3, 113.6, 80.1, 72.2, 27.7, 27.1, 20.7. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{20}NaO_2$ $[M+Na]^+$ 255.1356, found 255.1354.

1l. 243 mg, 62% yield over 3 steps; colorless oil. R_f = 0.23 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3087, 2983, 2934, 2835, 1743, 1495, 1369, 1280, 1233, 1160, 1131, 1043. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.03 (d, *J* = 9.2 Hz, 1H), 6.87 (d, *J* = 3.2 Hz, 1H), 6.68 (dd, *J* = 8.8, 3.2 Hz, 1H), 6.64 (dt, *J* = 5.6, 1,2 Hz, 1H), 6.16 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.98 (ddd, *J* = 17.6, 10.8, 5.6 Hz, 1H), 5.26 (dt, *J* = 17.6, 1.6 Hz, 1H), 5.20 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.19 (dt, *J* = 10.8, 1.2 Hz, 1H), 5.13 (dd, *J* = 10.8, 0.8 Hz, 1H), 3.76 (s, 3H), 2.12 (s, 3H), 1.47 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.8, 154.4, 147.4, 144.9, 135.9, 132.1, 120.5, 116.1, 113.3, 113.1,

112.8, 80.1, 71.1, 55.5, 27.6, 26.6, 21.2. **HRMS** (ESI) *m*/*z* calculated for $C_{17}H_{22}NaO_4$ $[M+Na]^+$ 313.1410, found 313.1411.

1m. 208 mg, 58% yield over 3 steps; colorless oil. R_f = 0.38 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3089, 2984, 2934, 1746, 1643, 1596, 1491, 1426, 1370, 1231, 1191, 1131. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.03 (ddd, *J* = 9.2, 6.4, 4.8 Hz, 2H), 6.82 (ddd, *J* = 8.8, 8.0, 3.2 Hz, 1H), 6.61 (dd, *J* = 5.2, 0.8 Hz, 1H), 6.15 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.95 (ddd, *J* = 17.2, 10.8, 5.6 Hz, 1H), 5.26 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.21 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.20 (dt, *J* = 10.8, 1.2 Hz, 1H), 5.16 (dd, *J* = 10.8, 0.8 Hz, 1H), 2.13 (s, 3H), 1.48 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.6, 157.6 (d, *J* = 238.4 Hz), 149.6 (d, *J* = 2.2 Hz), 144.6, 135.5, 132.6 (d, *J* = 6.6 Hz), 120.0 (d, *J* = 8.0 Hz), 116.4, 114.4 (d, *J* = 22.6 Hz), 113.8 (d, *J* = 23.3 Hz), 113.6, 80.5, 70.7, 27.6, 26.6, 21.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -121.4. **HRMS** (ESI) *m*/*z* calculated for $C_{16}H_{19}FNaO_3$ $[M+Na]^+$ 301.1210, found 301.1211.

Syntheses of Substrates 1f-1g, 1i-1j



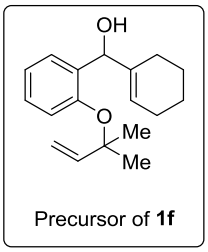
***Formation of tosylhydrozones (Step 1)*:** A suspension of the ketone **S-D** (10 mmol), *p*-toluenesulfonyl hydrazide (2.05 g, 11 mmol) and *p*-toluenesulfonic acid monohydrate (172 mg, 1 mmol) in methanol (30 mL) was heated at reflux under N_2 until thin layer chromatography (TLC) analysis indicated complete consumption of the starting material. The reaction slurry was cooled to room temperature and then immersed in an ice-water bath for 2 h. The resulting white crystals were filtered, rinsed with cold methanol and air-dried overnight. The tosylhydrazone **S-E** was used without further purification for the next step.

***Shapiro reaction*[2] *(Step 2)*:** A suspension of the tosylhydrazone (1 mmol) and dry tetramethylethylenediamine (TMEDA, 5 mL) was cooled to -78℃ under a nitrogen atmosphere. A solution of *n*-BuLi (1.6 M, 1.6 mL, 2.5 mmol) was added dropwise to the frozen suspension, and the resulting solution was kept at -78℃ for 15 min and

[2] Hamon, D. P. G.; Tuck, K. L. *J. Org. Chem*. **2000**, *65*, 7839-7846.

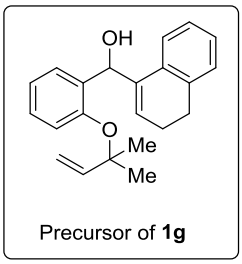
then allowed to warm to room temperature whereupon it turned a dark red color. This suspension was stirred for a further 4 h. It was cooled to -78℃ again. A solution of the aldehyde **S**-**B** (1 mmol) in dry THF (2 mL) was added to the mixture dropwise at -78 ℃ and the mixture was stirred at that temperature for 30 min. It was then poured into saturated aqueous NH_4Cl (50 mL) and extracted with diethyl ether (3×30 mL). The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (petroleum ether/ethyl acetate = 20/1) to give the benzylic alcohol **S**-**F**.

***Acetylation of alcohol S-F (Step 3)*:** Following the general procedure described for synthesis of **1a** in step 3, the alcohol obtained above was acetylated to the desired product **1f**, **1g**, **1i** and **1j**. However, attempts to purify **1f**, **1g**, **1i** and **1j** for spectroscopic characterization were unsuccessful. Therefore, the crude products **1f**, **1g**, **1i** and **1j** were used directly after acetylation.



Precursor of **1f**

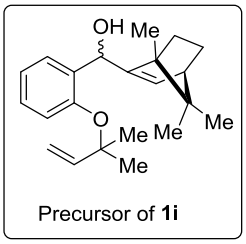
Precursor of **1f**. 152 mg, 56% yield; colorless oil. R_f = 0.28 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3434, 3061, 3033, 2981, 2927, 2857, 2835, 1598, 1584, 1483, 1451, 1141, 1378, 1363, 1235, 1135. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.26 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.12-7.05 (m, 2H), 6.92 (td, *J* = 14.0, 1.6 Hz, 1H), 6.16 (dd, *J* = 18.0, 10.8 Hz, 1H), 5.79-5.76 (m, 1H), 5.24 (s, 1H), 5.22 (d, *J* = 16.8 Hz, 1H), 5.17 (dd, *J* = 11.2, 0.4 Hz, 1H), 2.83 (br, 1H), 2.09-2.06 (m, 2H), 1.90-1.86 (m, 2H), 1.64-1.54 (m, 4H), 1.49 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 154.1, 144.7, 139.0, 133.4, 128.1, 127.4, 122.3, 121.1, 118.1, 113.4, 80.0, 74.3, 27.5, 27.1, 25.3, 25.0, 22.8, 22.6. **HRMS** (ESI) *m*/*z* calculated for $C_{18}H_{25}O_2$ $[M+H]^+$ 273.1849, found 273.1848.



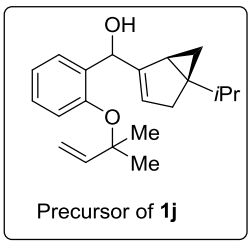
Precursor of **1g**

Precursor of **1g**. 195 mg, 61% yield; colorless oil. R_f = 0.39 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3414, 3059, 2981, 2931, 2883, 2830, 1598, 1584, 1484, 1452, 1378, 1363, 1237, 1132. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.28-7.25 (m, 2H), 7.17-7.10 (m, 5H), 6.92-6.87 (m, 1H), 6.21 (dd, *J* =17.6, 10.8 Hz, 1H), 6.18-6.15 (m, 1H), 6.10 (d, *J* = 3.6 Hz, 1H), 5.28 (d, *J* = 17.6 Hz, 1H), 5.20 (dd, *J* = 10.8, 0.8 Hz, 1H), 2.88 (d, *J* = 0.8 Hz, 1H), 2.81 (t, *J* = 8.4 Hz, 2H), 2.39-2.34 (m, 2H), 1.55 (s, 3H), 1.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 154.2, 144.6, 137.8, 136.6, 133.8, 133.5, 128.2, 127.9, 127.6, 126.7, 126.3 (2×C), 123.5,

121.4, 118.1, 113.6, 80.2, 68.8, 28.3, 27.8, 27.1, 23.1. **HRMS** (ESI) *m*/*z* calculated for $C_{22}H_{24}NaO_2$ $[M+Na]^+$ 343.1669, found 343.1672.

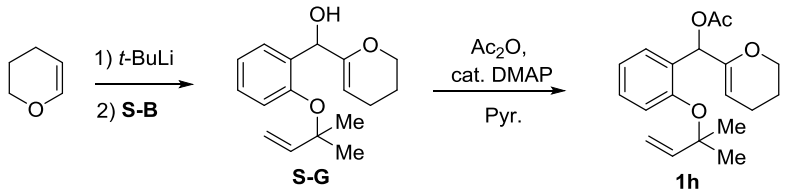


Precursor of **1i** (Inseperable Diastereomers). 189 mg, 58% yield, *dr* 1.2:1; colorless oil. R_f = 0.44 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3460, 3059, 2950, 2871, 1598, 1585, 1484, 1452, 1413, 1383, 1364, 1234, 1134. Diastereomer A: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.31-7.26 (m, 1H), 7.12-7.02 (m, 2H), 6.94-6.89 (m, 1H), 6.18-6.11 (m, 1H), 6.53-6.48 (m 2H), 5.24-5.15 (m, 2H), 2.56-2.53 (m, 1H), 2.27-2.23 (m, 1H), 1.88-1.76 (m, 1H), 1.51 (s, 6H), 1.44-1.39 (m, 1H), 1.10 (s, 3H), 1.08-1.01 (m, 1H), 0.90 (br, 1H), 0.89 (s, 3H), 0.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.7, 150.3, 144.8, 132.8, 129.7, 128.5, 127.4, 120.8, 117.6, 113.5, 79.7, 68.0, 57.1, 54.4, 51.4, 31.6, 27.8, 27.2, 25.6, 19.9, 19.7, 12.2. Diastereomer B: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.31-7.26 (m, 1H), 7.12-7.02 (m, 2H), 6.94-6.89 (m, 1H), 6.18-6.11 (m, 1H), 6.53-6.48 (m, 2H), 5.24-5.15 (m, 2H), 2.56-2.53 (m, 1H), 2.27-2.23 (m, 1H), 1.88-1.76 (m, 1H), 1.63-1.56 (m, 1H), 1.51 (s, 6H), 1.27-1.19 (m, 1H), 1.06 (s, 3H), 0.92 (br, 1H), 0.78 (s, 3H), 0.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.8, 150.5, 144.7, 132.9, 130.3, 128.4, 127.4, 120.8, 117.7, 113.6, 79.8, 68.6, 57.2, 54.2, 51.5, 32.5, 28.0, 26.9, 25.5, 19.8, 19.6, 11.4. **HRMS** (ESI) *m*/*z* calculated for $C_{22}H_{30}NaO_2$ $[M+Na]^+$ 349.2138, found 349.2142.



Precursor of **1j**. 197 mg, 63%yield; colorless oil. R_f = 0.37 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3483, 3063, 2958, 2928, 2871, 1702, 1598, 1483, 1453, 1380, 1364, 1237, 1130. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 7.6 Hz, 1H), 7.11-7.06 (m, 2H), 7.02-6.98 (m, 1H), 6.67 (s, 1H), 6.15 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.19 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 4.67 (d, *J* = 7.2 Hz, 1H), 2.10 (ddd, *J* = 14.0, 7.6, 1.2 Hz, 1H), 1.92 (dd, *J* = 8.4, 3.2 Hz, 1H), 1.74 (d, *J* = 14.0 Hz, 1H), 1.46 (s, 7H), 1.40 (hept, *J* = 6.8 Hz, 1H), 1.14 (t, *J* = 3.6 Hz, 1H), 1.03 (ddd, *J* = 8.4, 3.6, 1.6 Hz, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 154.1, 150.0, 144.8, 131.3, 129.6, 127.1, 121.9, 120.5, 119.1, 113.3, 80.4, 77.7, 39.2, 36.0, 33.1, 27.6, 27.3, 26.9, 20.8, 19.9, 19.8. **HRMS** (ESI) *m*/*z* calculated for $C_{21}H_{28}NaO_2$ $[M+Na]^+$ 335.1982, found 335.1984.

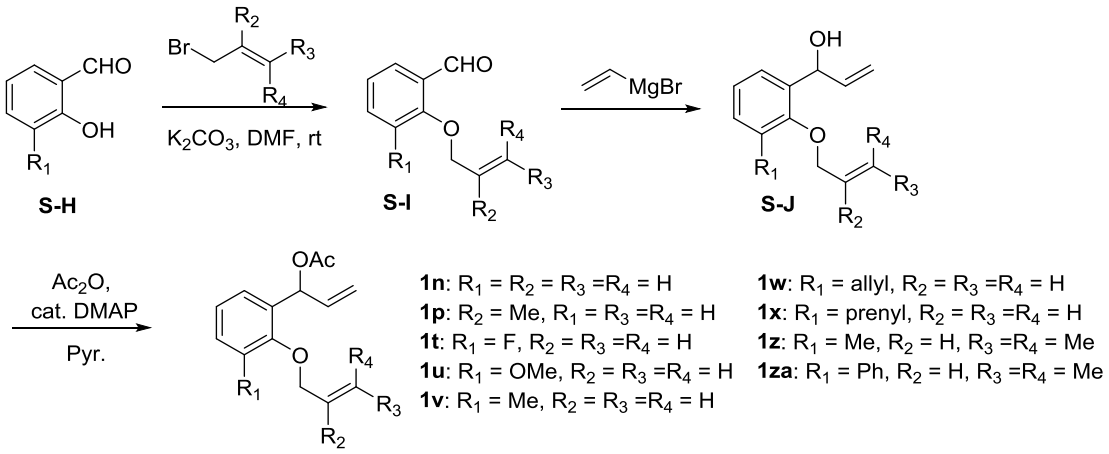
<u>Synthesis of Substrate 1h</u>



Nucleophilic addition to aldehyde (Step 1): To a solution of the dihydropyrane (DHP) (168 mg, 2 mmol) in dry THF (10 mL) was added *t*-BuLi (1.3 M, 1.4 mL, 1.8 mmol) dropwise at -78℃. The reaction mixture was allowed to warm to 0℃ over 2 hours and then cooled back to -78℃. The aldehyde **S**-**B** (285 mg, 1.5 mmol) was added dropwise at -78℃ and the resulting mixture was allowed to warm to 0℃ and quenched by addition of sat. aqueous NH_4Cl (10 mL). The organic fraction was collected and the aqueous layer was extracted with diethyl ether (3×10 mL). The combined organic fractions was washed with brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to afford the crude benzylic alcohol **S**-**G**, which were used directly for acetylation.

***Acetylation of alcohol S-G (Step 2)*:** Following the general procedure described for synthesis of **1a** in step 3, the alcohol obtained above was acetylated to the desired product **1h** (365 mg, 77% yield over 2 steps) as a colorless oil. R_f = 0.21 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3081, 2981, 2933, 2878, 1742, 1671, 1600, 1585, 1487, 1454, 1369, 1231, 1133. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.70 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.13 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.12 (s, 1H), 7.03 (td, *J* = 7.2, 1.6 Hz, 1H), 6.93 (td, *J* = 7.2, 0.8 Hz, 1H), 6.07 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.03 (dd, *J* = 17.6, 0.8 Hz, 1H), 4.90 (dd, *J* = 10.8, 0.8 Hz, 1H), 4.87 (t, *J* = 4.0 Hz, 1H), 3.70 (dd, *J* = 6.0, 4.8 Hz, 2H), 1.75-1.71 (m, 2H), 1.74 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H), 1.40-1.33 (m, 2H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 169.3, 155.0, 152.6, 145.4, 130.4, 128.7, 128.4, 121.5, 118.9, 113.1, 99.3, 80.3, 70.3, 86.3, 27.8, 26.9, 22.3, 20.8, 20.3. **HRMS** (ESI) *m*/*z* calculated for $C_{19}H_{25}O_4$ $[M+H]^+$ 317.1753, found 317.1755.

<u>Syntheses of Substrates 1n, 1p, 1t-1x, 1z-1za</u>



Alkylation with allyl bromide (Step 1): To a solution of the salicylaldehyde **S**-**H** (2 mmol) in DMF (2 mL) were added K_2CO_3 (3 mmol) and the corresponding allyl bromide (3 mmol). The suspension was stirred at room temperature overnight. The reaction was quenched by addition of water (10 mL). The organic fraction was collected and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organic fractions was washed with water (10 mL x 2) and brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to afford the crude aldehyde (**S**-**I**), which was used for the next step without further purification.

Grignard addition to aldehyde and subsequent acetylation (Step 2&3): Following the general procedure described for synthesis of **1a** in step 2&3, the aldehyde obtained above was elaborated to the desired product **1n, 1p, 1t-1x, 1z-1za**. However, attempts to purify **1v-1x**, **1z-1za** for spectroscopic characterization were unsuccessful. Therefore, the crude products **1v-1x**, **1z-1za** were used directly after acetylation.

1n. 193 mg, 73% yield over 3 steps; colorless oil. R_f = 0.34 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3084, 3019, 2987, 2926, 2857, 1742, 1602, 1589, 1491, 1453, 1370, 1287, 1233, 1162. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.36 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.28-7.23 (m, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 5.6 Hz, 1H), 6.09-5.99 (m, 2H), 5.42 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.29-5.24 (m, 2H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.58 (dt, *J* = 4.8, 1.2 Hz, 2H), 2.11 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.9, 155.6, 135.8, 133.2, 129.1, 127.8, 127.4, 120.9, 117.3, 116.1, 112.1, 70.8, 69.0, 21.3. **HRMS** (ESI) *m*/*z* calculated for $C_{14}H_{16}NaO_3$ $[M+Na]^+$ 255.0997, found 255.0993.

1p. 200 mg, 67% yield over 3 steps; colorless oil. R_f = 0.39 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3081, 3039, 2976, 2921, 2857, 1742, 1657, 1602, 1589, 1492, 1453, 1370, 1286, 1235, 1093. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.36 (dd, *J*

= 7.6, 1.6 Hz, 1H), 7.25 (td, *J* = 7.6, 1.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 5.6 Hz, 1H), 6.05 (ddd, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.26 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.20 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.11 (s, 1H), 4.99 (s, 1H), 4.47 (s, 2H), 2.11 (s, 3H), 1.84 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.8, 155.6, 140.7, 135.8, 129.1, 127.6, 127.4, 120.7, 116.1, 112.6, 111.8, 71.8, 70.8, 21.2, 19.4. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{18}NaO_3$ $[M+Na]^+$ 269.1148, found 269.1151.

1t. 195 mg, 63% yield over 3 steps; colorless oil. R_f = 0.48 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3086, 3021, 2987, 2927, 1744, 1645, 1589, 1476, 1422, 1371, 1276, 1230, 1100, 1070. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.12-7.09 (m, 1H), 7.06-7.00 (m, 2H), 6.62 (d, *J* = 5.6 Hz, 1H), 6.15-6.04 (m, 1H), 6.00 (ddd, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.40 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.27-5.20 (m, 3H), 4.65 (dd, *J* = 5.6, 0.8 Hz, 2H), 2.11 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.5, 155.3 (d, *J* = 245.7 Hz), 143.7 (d, *J* = 11.7 Hz), 135.6, 134.1 (d, *J* = 2.2 Hz), 133.5, 123.8 (d, *J* = 8.0 Hz), 122.6 (d, *J* = 3.7 Hz), 118.1, 116.7, 116.4 (d, *J* = 19.0 Hz), 74.4 (d, *J* = 5.9 Hz), 70.6 (d, *J* = 2.9 Hz), 21.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -129.1. **HRMS** (ESI) *m*/*z* calculated for $C_{14}H_{16}FO_3$ $[M+H]^+$ 251.1083, found 251.1081.

1u. 214 mg, 70% yield over 3 steps; colorless oil. R_f = 0.24 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3084, 2936, 2839, 1742, 1644, 1587, 1479, 1440, 1370, 1233, 1182, 1068. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.06 (t, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.87 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.64 (d, *J* = 5.6 Hz, 1H), 6.13 (ddt, *J* = 17.6, 10.8, 6.0 Hz, 1H), 6.01 (ddd, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.39 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.27-5.17 (m, 3H), 4.62-4.53 (m, 2H), 3.85 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.8, 152.7, 145.3, 136.1, 134.3, 133.2, 124.2, 119.1, 117.4, 116.3, 112.0, 73.8, 71.2, 55.8, 21.2. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{19}O_4$ $[M+H]^+$ 263.1283, found 263.1286.

Precursor of **1v**. 322 mg, 79% yield over 2 steps; colorless oil. R_f = 0.27 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3411, 3081, 3016, 2982, 2921, 2862, 1645, 1591, 1468, 1421, 1377, 1256, 1192, 1088. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.21 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.13 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.15-6.06 (m, 2H), 5.53-5.49 (m, 1H), 5.45 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.36 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.29 (dq, *J* = 10.4, 1.6 Hz, 1H), 5.20 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.43-4.33 (m, 2H), 2.64 (br, 1H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 155.0, 140.3, 135.8, 133.7, 131.4, 131.0, 125.5, 124.5, 117.6, 114.7, 74.3, 70.4, 16.5. **HRMS** (ESI) *m*/*z* calculated for $C_{13}H_{16}NaO_2$ $[M+Na]^+$ 227.1043, found 227.1047.

Precursor of **1w**. 354 mg, 76% yield over 2 steps; colorless oil. R_f = 0.39 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3420, 3079, 3013, 2979, 2924, 2858, 1639, 1453, 1421, 1252, 1186, 1105, 1078. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.32 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.03 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.05 (ddd, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.94-5.82 (m, 2H), 5.56 (d, *J* = 4.4 Hz, 1H), 5.36 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.33 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.07-4.98 (m, 4H), 4.18 (qdt, *J* = 12.0, 5.2, 1.6 Hz, 2H), 3.34 (d, *J* = 6.8 Hz, 2H), 2.29 (br, 1H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 155.0, 141.0, 137.5, 136.9, 134.2, 133.4, 130.2, 126.6, 124.9, 116.6, 116.0, 114.1, 75.1, 69.8, 34.2. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{19}O_2$ $[M+H]^+$ 231.1380, found 231.1379.

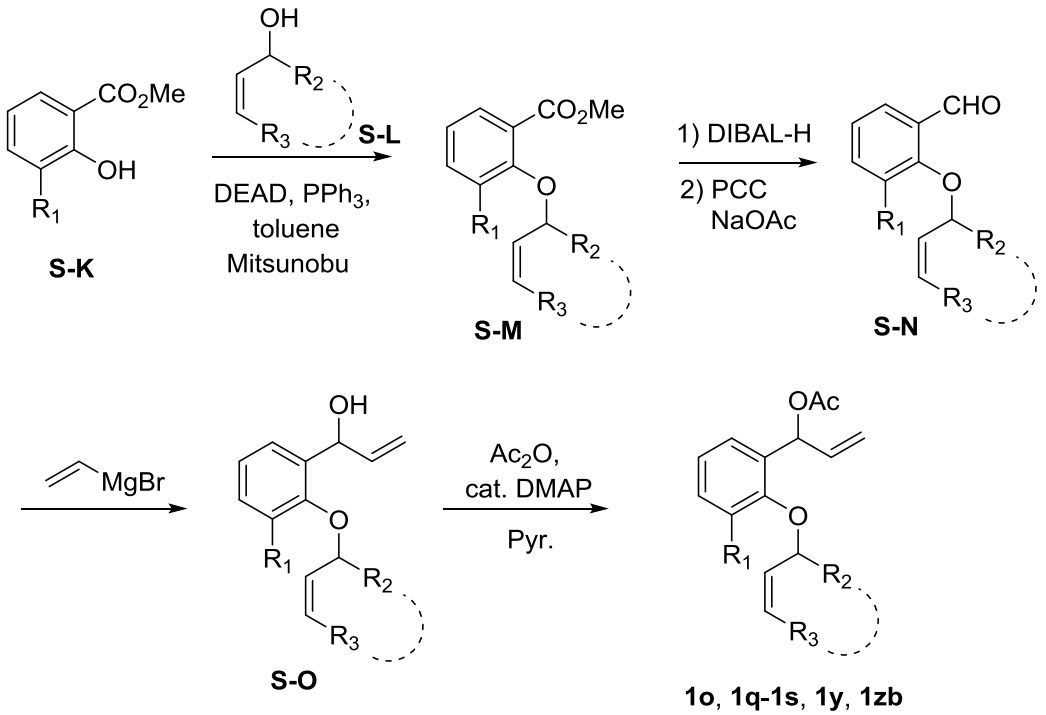
Precursor of **1x**. 382 mg, 74% yield over 2 steps; colorless oil. R_f = 0.41 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3445, 3078, 3016, 2967, 2925, 2857, 1726, 1686, 1646, 1588, 1450, 1252, 1188, 1103. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.32 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.06 (ddd, *J* = 17.2, 10.4, 8.8 Hz, 1H), 5.91 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.60-5.57 (m, 1H), 5.40-5.32 (m, 3H), 5.08-5.02 (m, 2H), 4.22 (qdt, *J* = 13.2, 5.2, 1.6 Hz, 2H), 3.40 (d, *J* = 7.6 Hz, 2H), 2.47 (d, *J* = 4.8 Hz, 1H), 1.64 (d, *J* = 1.2 Hz, 3H), 1.60 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 154.9, 141.1, 136.8, 135.2, 134.4, 132.5, 129.8, 126.3, 125.0, 123.7, 116.5, 114.0, 75.0, 69.8, 28.7, 25.8, 17.9. **HRMS** (ESI) *m*/*z* calculated for $C_{17}H_{22}KO_2$ $[M+K]^+$ 297.1257, found 297.1260.

Precursor of **1z**. 349 mg, 75% yield over 2 steps; colorless oil. R_f = 0.35 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3430, 3065, 3019, 2976, 2918, 1675, 1639, 1591, 1467, 1380, 1254, 1187, 1116, 1087. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.27 (d, *J* = 7.2 Hz, 1H), 6.97-6.90 (m, 2H), 6.12 (ddd, *J* = 16.8, 10.4, 4.8 Hz, 1H), 5.67-5.63 (m, 1H), 5.57 (t, *J* = 6.4 Hz, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 4.33-4.22 (m, 2H), 2.24 (br, 1H), 2.21 (s, 3H), 1.57 (s, 3H), 1.44 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 155.4, 141.3, 137.1, 136.9, 131.3, 130.7, 126.2, 124.5, 121.3, 114.0, 70.6, 69.8, 25.8, 18.0, 16.6. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{21}O_2$ $[M+H]^+$ 233.1536, found 233.1535.

Precursor of **1za** 418 mg, 71% yield over 2 steps; colorless oil. R_f = 0.44 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3421, 3060, 3022, 2976, 2929, 1455, 1431, 1380, 1275, 1257, 1208, 1075, 1029. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.17 (d, *J* = 7.6 Hz, 1H), 6.95 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.80-6.66 (m, 5H), 6.56 (t, *J* = 7.6 Hz, 1H), 5.74 (ddd, *J* = 17.2, 10.4, 4.8 Hz, 1H), 5.29-5.25 (m, 1H), 5.03 (dt, *J* = 17.2, 1.6 Hz, 1H), 4.90-4.85 (m, 1H), 4.66 (dt, *J* = 10.4, 1.6 Hz, 1H), 3.62-3.53 (m, 2H), 2.09 (br, 1H), 1.02 (s, 3H), 0.73 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 154.3, 141.3, 139.5, 137.6,

137.5, 135.5, 130.7, 129.5 (2×C), 128.6 (2×C), 127.6, 127.4, 124.7, 120.8, 114.1, 70.3, 70.2, 25.7, 17.7. **HRMS** (ESI) *m*/*z* calculated for $C_{20}H_{23}O_2$ $[M+H]^+$ 295.1693, found 295.1692.

Syntheses of Substrates 1o, 1q-1s, 1y, 1zb



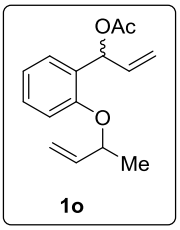
Mitsunobu reaction (Step 1): To a solution of the allyl alcohol **S**-**L** (3 mmol) in toluene (15 mL) were added triphenylphosphine (1.24 g, 4.74 mmol) and methyl salycilate **S**-**K** (3.3 mmol) at room temperature. The reaction mixture was cooled to 0℃ and diethyl azodicarboxylate (DEAD, 0.88 mL, 5.64 mmol) was added dropwise with stirring. The reaction mixture was warmed to room temperature and stirred for 3 days before quenching with 1.0 M citric acid (10 mL). The resulting mixture was stirred vigorously for 30 min. The organic layer was collected and the aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic fractions were washed with brine, dried with anhydrous Na_2SO_4 and concentrated under vacuum. Purification of the residue by short column chromatography on silica gel gave the phenolic ether **S**-**M**, which is used directly in the next step.

DIBAL-H Reduction of ester S-M (Step 2): To a solution of ester **S**-**M** (2 mmol) in dry CH_2Cl_2 (8 mL) under nitrogen at -78℃ was added diisobutylaluminium hydride (DIBAL-H, 1.0 M in hexane, 5 mL, 5 mmol) dropwise over a period of 10 min. After the addition was completed, the reaction mixture was stirred at -78℃ for 60 min and then

quenched by addition of MeOH (1 mL). The reaction mixture was stirred for additional 15 min at -78℃ and transferred to a flask containing 20 mL sat. aqueous Rochelle's salt. The resulting mixture was stirred vigorously for 3 hours. The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford the crude benzyl alcohol products, which was used for the next step without further purification.

PCC oxidation (Step 3): The above residue was dissolved in CH_2Cl_2 (10 mL). To the solution were added sodium acetate (369 mg, 4.5 mmol) and pyridinium chloromate (PCC, 648 mg, 3 mmol) portion-wise. The resulting dark mixture was stirred at room temperature for 2 hours, filtered through a pad of Florisil and rinsed with CH_2Cl_2 (3× 10 mL). The filtrate was washed with sat. aqueous $CuSO_4$ (3×5 mL), 1M citric acid (3 ×5 mL), sat. aqueous $NaHCO_3$ (5 mL) and brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford the crude aldehyde **S**-**N**, which was used directly for the next step.

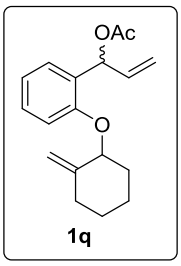
Grignard addition to aldehyde and subsequent acetylation (Step 4&5): Following the general procedure described for synthesis of **1a** in step 2&3, the aldehyde obtained above was elaborated to the desired product **1o, 1q-1s, 1y and 1zb**. However, attempts to purify **1r, 1s**, **1y and 1za** for spectroscopic characterization were unsuccessful. Therefore, the crude products **1r, 1s**, **1y and 1za** were used directly after acetylation.



1o

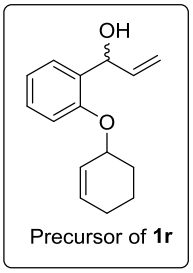
1o (Inseperable Diastereomers). 180 mg, 38% yield over 5 steps, *dr* 1.3:1; colorless oil. R_f = 0.29 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3083, 2982, 2932, 1742, 1601, 1488, 1454, 1371, 1285, 1230, 1095. Diastereomer A: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 7.6 Hz, 1H), 7.24-7.19 (m, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 5.6 Hz, 1H), 6.07-5.98 (m, 1H), 5.95-5.86 (m, 1H), 5.30-5.13 (m, 4H), 4.88-4.81 (m, 1H), 2.12 (s, 3H), 1.45 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.9, 155.0, 139.2, 135.9, 128.9, 128.2, 127.4, 120.7, 116.1, 115.6, 113.6, 75.1, 71.0, 21.5, 21.3. Diastereomer B: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 7.6 Hz, 1H), 7.24-7.19 (m, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 5.6 Hz, 1H), 6.07-5.98 (m, 1H), 5.95-5.86 (m, 1H), 5.30-5.13 (m, 4H), 4.88-4.81 (m, 1H), 2.11 (s, 3H), 1.44 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.9, 154.9, 139.0, 135.9, 128.9, 128.2, 127.3, 120.6, 116.1, 115.7, 113.5,

74.8, 70.9, 21.5, 21.3. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{18}NaO_3$ $[M+Na]^+$ 269.1148, found 269.1149.



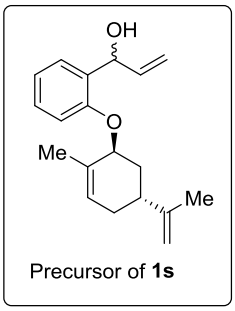
1q

1q (Inseperable Diastereomers). 210 mg, 36% yield over 5 steps, *dr* 1.3:1; colorless oil. R_f = 0.33 (petroleum ether/ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3071, 2935, 2858, 1743, 1600, 1488, 1454, 1370, 1285, 1231, 1019. Diastereomer A: **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.48-7.45 (m, 1H), 7.17-7.13 (m, 1H), 7.10-7.05 (m, 1H), 6.90-6.85 (m, 1H), 6.74 (t, *J* = 8.4 Hz, 1H), 6.16-6.06 (m, 1H), 5.40-5.32 (m, 1H), 5.11-5.05 (m, 1H), 4.97 (s, 1H), 4.77 (s, 1H), 4.45-4.38 (m, 1H), 2.39-2.28 (m, 1H), 1.89-1.72 (m, 4H), 1.70 (s, 3H), 1.45-1.18 (m, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 169.0, 155.4, 147.3, 136.7, 129.0, 128.7, 127.9, 120.8, 115.9, 113.7, 109.2, 78.2, 70.8, 34.4, 33.2, 28.3, 23.3, 20.7. Diastereomer B: **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.48-7.45 (m, 1H), 7.17-7.13 (m, 1H), 7.10-7.05 (m, 1H), 6.90-6.85 (m, 1H), 6.74 (t, *J* = 8.4 Hz, 1H), 6.16-6.06 (m, 1H), 5.40-5.32 (m, 1H), 5.11-5.05 (m, 1H), 4.93 (s, 1H), 4.77 (s, 1H), 4.45-4.38 (m, 1H), 2.39-2.28 (m, 1H), 1.89-1.72 (m, 4H), 1.71 (s, 3H), 1.45-1.18 (m, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 169.1, 155.6, 147.8, 136.8, 129.1, 128.8, 127.9, 120.9, 115.9, 113.9, 108.5, 79.0, 70.9, 34.4, 33.4, 28.2, 23.4, 20.7. **HRMS** (ESI) *m*/*z* calculated for $C_{18}H_{23}O_3$ $[M+H]^+$ 287.1642, found 287.1646.



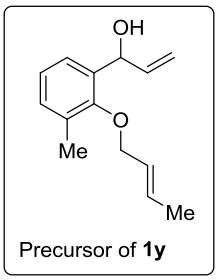
Precursor of **1r**

Precursor of **1r** (Inseperable Diastereomers). 177 mg, 39% yield over 4 steps, *dr* 1:1; colorless oil. R_f = 0.38 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3029, 2929, 2864, 1596, 1486, 1452, 1395, 1286, 1236, 1095, 1060. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.41-7.36 (m, 1H), 7.08-7.03 (m, 1H), 6.88-6.84 (m, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.24-6.15 (m, 1H), 5.76-5.70 (m, 1H), 5.68-5.63 (m, 1H), 5.58-5.53 (m, 1H), 5.46-5.39 (m, 1H), 5.10-5.05 (m, 1H), 4.51-4.48 (m, 1H), 2.57 (dd, *J* = 16.4, 2.0 Hz, 1H), 1.80-1.53 (m, 5H), 1.33-1.23 (m, 1H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 155.3/155.2, 140.7/140.6, 132.8/132.7, 132.1/132.0, 128.5, 128.1, 126.5/126.4, 121.0, 113.8/113.6, 112.8, 71.6/71.5, 70.9/70.8, 28.6/28.5, 25.2, 19.2. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{19}O_2$ $[M+H]^+$ 231.1380, found 231.1372.



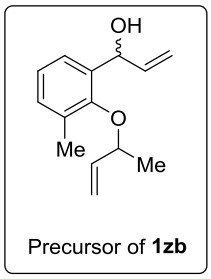
Precursor of **1s**

Precursor of **1s** (Inseperable Diastereomers). 202 mg, 41% yield over 4 steps, *dr* 4:1; colorless oil. R_f = 0.43 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3439, 3076, 3015, 2967, 2915, 1463, 1598, 1587, 1485, 1453, 1374, 1284, 1227, 1155. Major diastereomer: **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.41 (dd, *J* = 7.6, 1.6 Hz,1H), 7.10-7.05 (m, 1H), 6.88-6.83 (m, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.12 (ddd, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.60-5.51 (m, 2H), 5.36 (dt, *J* = 17.2, 1.6 Hz,1H), 5.04 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.72-4.70 (m, 2H), 4.43 (s, 1H), 2.82-2.70 (m, 1H), 2.49-2.38 (m, 1H), 2.08-1.98 (m, 2H), 1.76-1.68 (m, 4H), 1.54 (s, 3H), 1.33-1.26 (m, 1H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 155.6, 148.8, 140.7, 132.8, 131.9, 128.6, 128.2, 127.3, 121.0, 113.8, 112.4, 109.6, 74.2, 70.9, 36.4, 32.8, 31.2, 21.2, 20.9. Minor diastereomer: **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.36 (dd, *J* = 7.6, 1.6 Hz,1H), 7.10-7.05 (m, 1H), 6.88-6.83 (m, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.15 (ddd, *J* = 17.2, 9.6, 4.8 Hz, 1H), 5.60-5.51 (m, 2H), 5.34 (dt, *J* = 17.2, 1.6 Hz,1H), 5.03 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.72-4.70 (m, 2H), 4.36 (s, 1H), 2.82-2.70 (m, 1H), 2.49-2.38 (m, 1H), 2.08-1.98 (m, 2H), 1.76-1.68 (m, 4H), 1.56 (s, 3H), 1.33-1.26 (m, 1H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 155.7, 148.9, 140.9, 132.7, 131.8, 128.6, 128.2, 127.5, 121.1, 113.6, 112.5, 109.6, 74.1, 71.6, 36.3, 32.7, 31.3, 21.1, 21.0. **HRMS** (ESI) *m*/*z* calculated for $C_{19}H_{25}O_2$ $[M+H]^+$ 285.1849, found 285.1850.



Precursor of **1y**

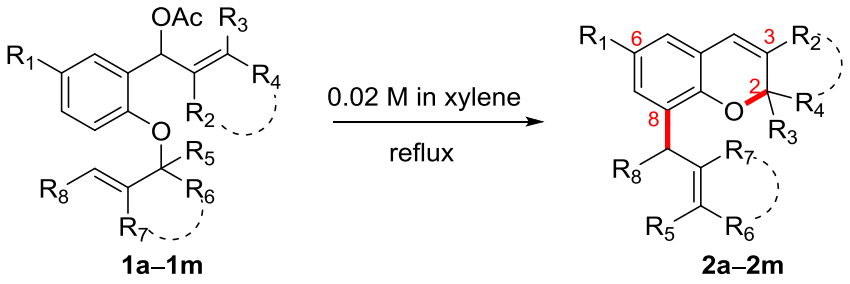
Precursor of **1y**. 168 mg, 43% yield over 4 steps; colorless oil. R_f = 0.46 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3420, 3018, 2918, 2860, 1675, 1640, 1591, 1467, 1375, 1255, 1190, 1112, 1088. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.28 (dd, *J* = 6.8, 2.4 Hz, 1H), 6.96-6.90 (m, 2H), 6.10 (ddd, *J* = 17.2, 10.4, 4.8 Hz, 1H), 5.68-5.55 (m, 3H), 5.40 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.06 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.19-4.10 (m, 2H), 2.26 (br, 1H), 2.17 (s, 3H), 1.51 (d, *J* = 5.2 Hz, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 155.3, 141.3, 136.8, 131.2, 130.7, 129.5, 127.5, 126.2, 124.5, 114.0, 74.3, 69.6, 17.8, 16.6. **HRMS** (ESI) *m*/*z* calculated for $C_{14}H_{19}O_2$ $[M+H]^+$ 219.1380, found 219.1377.



Precursor of **1zb**

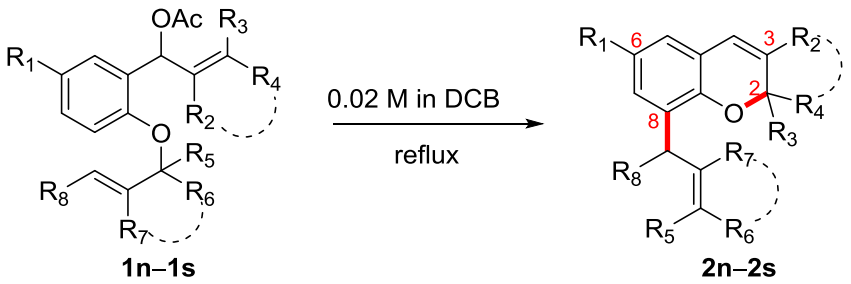
Precursor of **1zb** (Inseperable Diastereomers). 153 mg, 40% yield over 4 steps, *dr* 1.1:1; colorless oil. R_f = 0.41 (petroleum ether/ethyl acetate = 10/1). **IR** (neat, cm^{-1}): 3421, 3080, 3013, 2980, 2927, 1466, 1421, 1374, 1253, 1191, 1088, 1046. Diastereomer A. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.36 (dd, *J* = 6.4, 2.4 Hz, 1H), 6.96-6.90 (m, 2H), 6.12-6.02 (m, 1H), 5.80 (ddt, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.68 (d, *J* = 4.4 Hz, 1H), 5.46 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.08 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.98-4.82 (m, 2H), 4.40-4.27 (m, 1H), 2.15 (s, 3H), 2.11 (br, 1H), 1.22 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 153.7, 140.8, 139.4, 137.0, 131.4, 130.8, 126.3, 124.4, 116.4, 114.0, 80.8, 69.0, 21.0, 17.6. Diastereomer B. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.31 (dd, *J* = 7.2, 2.4 Hz, 1H), 6.96-6.90 (m, 2H), 6.12-6.02 (m, 1H), 5.80 (ddt, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.68 (d, *J* = 4.4 Hz, 1H), 5.46 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.09 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.98-4.82 (m, 2H), 4.40-4.27 (m, 1H), 2.15 (s, 3H), 2.11 (br, 1H), 1.24 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 153.9, 140.9, 139.5, 137.0, 131.5, 130.9, 126.3, 124.3, 116.3, 113.9, 80.7, 69.1, 20.9, 17.5. **HRMS** (ESI) *m*/*z* calculated for $C_{14}H_{19}O_2$ $[M+H]^+$ 219.1380, found 219.1379.

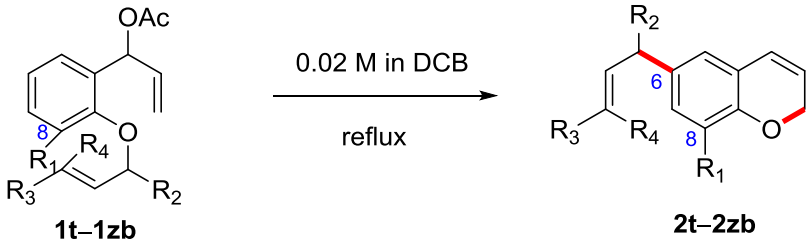
Cascade Claisen Rearrangement/*o*-quinone methide formation/6π-electrocyclization



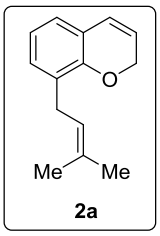
1a–1m **2a–2m**

General Procedure A: An oven-dried pressure tube under nitrogen atmosphere was charged with acetate (**1a**-**1m**, 0.2 mmol) and xylene (10 mL). The reaction mixture was heated to 140 ℃ (reflux) for 30 min and then cooled to room temperature. The solvent (xylene) was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether as the eluent to afford the desired product.

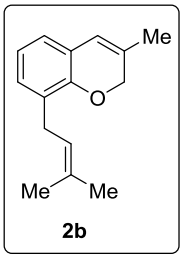




General Procedure B: An oven-dried pressure tube under nitrogen atmosphere was charged with acetate (**1n**-**1zb**, 0.2 mmol) and 1,2-dichlorobenzene (DCB, 10 mL). The reaction mixture was heated to 180 ℃ (reflux) for 30 min and cooled to room temperature. The solvent (DCB) was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether as the eluent to afford the desired product.

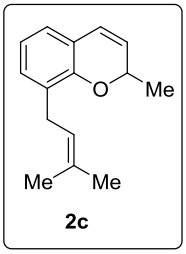


2a. General procedure A; 35 mg, 86% yield; colorless oil. R_f = 0.42 (petroleum ether). **IR** (neat, cm^{-1}): 3047, 2965, 2924, 2853, 1637, 1463, 1448, 1374, 1275, 1261, 1203, 1082, 1028. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.03 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.69 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.16 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.48-5.43 (m, 1H), 5.22 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.43 (dd, *J* = 3.6, 1.6 Hz, 2H), 3.45 (d, *J* = 7.2 Hz, 2H), 1.66 (d, *J* = 0.8 Hz, 3H), 1.62 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 152.3, 132.1, 130.0, 129.1, 125.3, 124.9, 123.4, 122.6, 121.8, 121.3, 65.5, 28.5, 25.9, 17.8. **HRMS** (ESI) *m*/*z* calculated for $C_{14}H_{17}O$ $[M+H]^+$ 201.1279, found 201.1277.



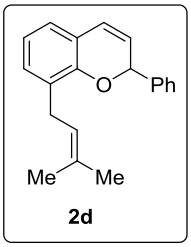
2b. General procedure A; 38 mg, 89% yield; colorless oil. R_f = 0.46 (petroleum ether). **IR** (neat, cm^{-1}): 3032, 2968, 2913, 2854, 2813, 1465, 1446, 1375, 1260, 1201, 1076, 1040. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.03 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.73 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.91 (q, *J* = 1.6 Hz, 1H), 5.52-5.47 (m, 1H), 4.37 (s, 2H), 3.49 (d, *J* = 7.2 Hz, 2H), 1.68 (d, *J* = 0.8 Hz, 3H), 1.65 (s, 3H), 1.30 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 150.8, 132.0, 130.6, 129.0, 128.6, 124.1, 123.6, 123.0,

121.2, 120.3, 69.2, 28.7, 25.9, 18.6, 17.8. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{19}O$ $[M+H]^+$ 215.1430, found 215.1427.



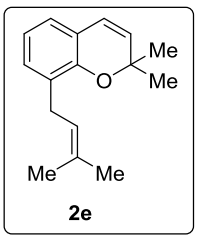
2c

2c. General procedure A; 35 mg, 81% yield; colorless oil. R_f = 0.40 (petroleum ether). **IR** (neat, cm^{-1}): 3043, 2973, 2924, 2855, 1638, 1454, 1375, 1321, 1260, 1206, 1171, 1098, 1078. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.04 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.73 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.17 (dd, *J* = 9.6, 2.0 Hz, 1H), 5.48-5.44 (m, 1H), 5.25 (dd, *J* = 9.6, 3.2 Hz, 1H), 4.74 (qdd, *J* = 6.4, 3.2, 1.6 Hz, 1H), 3.52-3.41 (m, 2H), 1.66 (d, *J* = 1.2 Hz, 3H), 1.64 (s, 3H), 1.18 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 151.6, 131.9, 130.0, 129.3, 126.6, 124.8, 124.4, 123.6, 122.0, 121.0, 71.5, 28.7, 25.9, 21.3, 17.8. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{19}O$ $[M+H]^+$ 215.1430, found 215.1426.



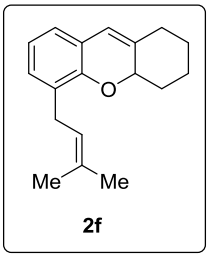
2d

2d. General procedure A; 51 mg, 92% yield; colorless oil. R_f = 0.46 (petroleum ether). **IR** (neat, cm^{-1}): 3060, 3030, 2967, 2914, 2855, 1636, 1599, 1493, 1450, 1375, 1260, 1204, 1076, 1040. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.32 (d, *J* = 6.8 Hz, 2H), 7.12-7.01 (m, 4H), 6.79-6.73 (m, 2H), 6.25 (dd, *J* = 9.6, 2.0 Hz, 1H), 5.71 (d, *J* = 1.2 Hz, 1H), 5.43 (dd, *J* = 9.6, 3.6 Hz, 1H), 5.36-5.32 (m, 1H), 3.46-3.36 (m, 2H), 1.59 (s, 3H), 1.52 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 151.3, 141.6, 131.9, 130.4, 129.2, 128.8 (2×C), 128.4, 127.2 (2×C), 124.9, 124.8, 124.5, 123.3, 121.5, 121.2, 77.4, 28.7, 25.8, 17.8. **HRMS** (ESI) *m*/*z* calculated for $C_{20}H_{21}O$ $[M+H]^+$ 277.1592, found 277.1599.



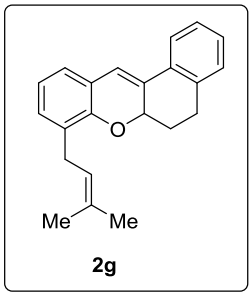
2e

2e. General procedure A; 36 mg, 78% yield; colorless oil. R_f = 0.56 (petroleum ether). **IR** (neat, cm^{-1}): 3040, 2975, 2924, 2856, 1638, 1450, 1376, 1360, 1256, 1203, 1167, 1121, 1075. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.04 (dd, *J* = 6.4, 3.2 Hz, 1H), 6.80-6.74 (m, 2H), 6.15 (d, *J* = 9.6 Hz, 1H), 5.48-5.43 (m, 1H), 5.26 (d, *J* = 10 Hz, 1H), 3.46 (d, *J* = 7.6 Hz, 2H), 1.67 (d, *J* = 0.8 Hz, 3H), 1.66 (s, 3H), 1.28 (s, 6H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 151.1, 131.6, 130.3, 130.0, 129.5, 124.6, 123.7, 123.2, 121.4, 120.8, 76.0, 28.8, 28.0 (2×C), 25.9, 17.9. **HRMS** (ESI) *m*/*z* calculated for $C_{16}H_{21}O$ $[M+H]^+$ 229.1587, found 229.1585. Note: The cascade reaction was performed on a 2.0 mmol scale to provide **2e** (324 mg) in 71% yield for total syntheses of natural products.



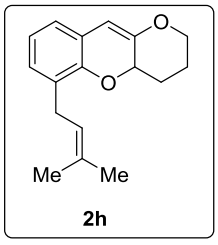
2f

2f. General procedure A; 38 mg, 75% yield; colorless oil. R_f = 0.51 (petroleum ether). **IR** (neat, cm^{-1}): 3057, 3023, 2932, 2858, 1457, 1375, 1333, 1257, 1209, 1092, 1075, 1033. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.02 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.70 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.83 (s, 1H), 5.53-5.48 (m, 1H), 4.72 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.48 (d, *J* = 7.2 Hz, 2H), 2.12-2.03 (m, 2H), 1.72-1.62 (m, 2H), 1.69 (s, 3H), 1.67 (s, 3H), 1.51-1.46 (m, 1H), 1.42-1.34 (m, 1H), 1.13-0.97 (m, 2H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 151.1, 137.2, 131.7, 129.1, 127.9, 124.1, 123.7, 121.7, 120.7, 117.4, 77.5, 35.5, 33.0, 28.7, 27.0, 25.9, 24.5, 17.9. **HRMS** (ESI) *m*/*z* calculated for $C_{18}H_{23}O$ $[M+H]^+$ 255.1743, found 255.1742.



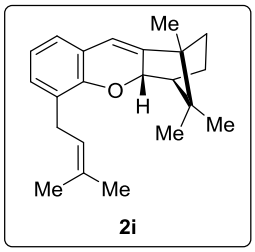
2g

2g. General procedure A; 49 mg, 81% yield; colorless oil. R_f = 0.57 (petroleum ether). **IR** (neat, cm^{-1}): 3057, 3032, 2927, 2852, 1487, 1453, 1359, 1299, 1220, 1202, 1124, 1098, 1074, 1037. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.54 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.10 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.02 (quint, *J* = 7.2 Hz, 2H), 6.95-6.83 (m, 4H), 5.54-5.49 (m, 1H), 4.76 (ddd, *J* = 11.6, 9.2, 2.4 Hz, 1H), 3.60 (dd, *J* = 15.2, 7.6 Hz, 1H), 3.51 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.49-2.39 (m, 2H), 2.22-2.16 (m, 1H), 2.11-2.01 (m, 1H), 1.69 (s, 3H), 1.67 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 152.6, 137.2, 132.2, 132.1, 131.5, 129.6, 129.2, 128.8, 127.7, 126.8, 125.3, 124.4, 124.0, 123.5, 121.7, 117.3, 75.4, 29.5, 28.6, 28.1, 25.9, 17.9. **HRMS** (ESI) *m*/*z* calculated for $C_{22}H_{23}O$ $[M+H]^+$ 303.1743, found 303.1743.



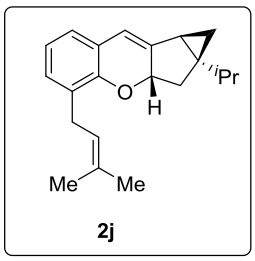
2h

2h. General procedure A; 40 mg, 77% yield; colorless oil. R_f = 0.37 (petroleum ether). **IR** (neat, cm^{-1}): 3056, 3026, 2962, 2925, 2874, 2856, 1658, 1584, 1453, 1274, 1219, 1199, 1144, 1079. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.98 (d, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.71 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.96 (d, *J* = 2.0 Hz, 1H), 5.51-5.47 (m, 1H), 4.56 (ddd, *J* = 11.2, 6.0, 2.0 Hz, 1H), 3.64-3.60 (m, 1H), 3.54 (dd, *J* = 14.8, 7.6 Hz, 1H), 3.47 (dd, *J* = 14.8, 7.6 Hz, 1H), 3.21-3.14 (m, 1H), 1.99-1.95 (m, 1H), 1.69 (s, 3H), 1.66 (s, 3H), 1.64-1.60 (m, 1H), 1.32-1.20 (m, 1H), 1.05-1.00 (m, 1H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 152.1, 149.7, 131.8, 128.3, 127.6, 124.2, 123.9, 123.7, 122.0, 102.4, 72.2, 68.1, 29.4, 28.8, 25.9, 23.8, 17.9. **HRMS** (ESI) *m*/*z* calculated for $C_{17}H_{20}NaO_2$ $[M+Na]^+$ 279.1361, found 279.1368.



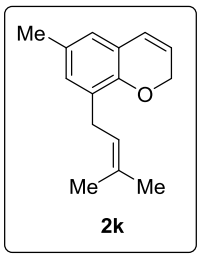
2i

2i (Inseperable Diastereomers). General procedure A; 49 mg, 79% yield, dr 5.6:1; colorless oil. R_f = 0.50 (petroleum ether). **IR** (neat, cm^{-1}): 3034, 2956, 2927, 2870, 1474, 1447, 1389, 1375, 1284, 1255, 1198, 1097, 1077, 1036. Major Diastereomer: **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.06 (d, *J* = 7.6 Hz, 1H), 6.94-6.84 (m, 2H), 5.97 (s, 1H), 5.52-5.45 (m, 1H), 4.30 (s, 1H), 3.62-3.46 (m, 2H), 2.09 (d, *J* = 4.8 Hz, 1H), 1.70-1.60 (m, 1H), 1.67 (s, 3H), 1.66 (s, 3H), 1.47 (td, *J* = 12.0, 3.6 Hz, 1H), 1.35-1.24 (m, 1H), 1.08 (s, 3H), 0.98-0.93 (m, 1H), 0.92 (s, 3H), 0.76 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 151.7, 147.3, 131.8, 129.4, 128.9, 125.4, 125.1, 123.7, 121.4, 113.2, 82.2, 50.9, 50.7, 49.5, 32.2, 29.1, 26.0, 25.9, 20.6, 20.1, 17.9, 11.7. Minor Diastereomer: **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.08 (d, *J* = 7.6 Hz, 1H), 6.94-6.84 (m, 2H), 6.08 (s, 1H), 5.52-5.45 (m, 1H), 4.66 (s, 1H), 3.62-3.46 (m, 2H), 2.21-2.15 (m, 1H), 1.70-1.60 (m, 1H), 1.67 (s, 3H), 1.66 (s, 3H), 1.47 (td, *J* = 12.0, 3.6 Hz, 1H), 1.35-1.24 (m, 1H), 0.98-0.93 (m, 1H), 0.92 (s, 3H), 0.74 (s, 3H), 0.66 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 153.5, 148.3, 131.9, 129.7, 128.7, 125.7, 125.1, 123.6, 121.5, 114.2, 78.1, 51.7, 49.3, 46.1, 38.5, 29.2, 26.0, 25.9, 20.2, 19.1, 18.6, 11.6. **HRMS** (ESI) *m*/*z* calculated for $C_{22}H_{29}O$ $[M+H]^+$ 309.2213, found 309.2220. The relative stereochemistry of **2i** was established based on the 2D NOESY experiments. The NOESY spectrum was provided at page S-111.



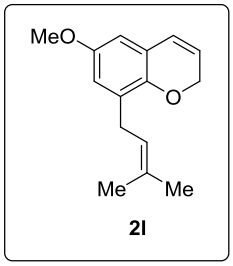
2j

2j. General procedure A; 40 mg, 68% yield; colorless oil. R_f = 0.56 (petroleum ether). **IR** (neat, cm^{-1}): 3057, 3033, 2960, 2929, 2872, 1667, 1585, 1450, 1382, 1364, 1259, 1200, 1152, 1081, 1038. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.06-7.02 (m, 1H), 6.87-6.84 (m, 2H), 6.16 (d, *J* = 2.4 Hz, 1H), 5.53-5.48 (m, 1H), 4.47 (dt, *J* = 7.2, 2.0 Hz, 1H), 3.59 (dd, *J* = 15.2, 7.6 Hz, 1H), 3.48 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.17 (dd, *J* = 12.4, 7.6 Hz, 1H), 2.10 (ddd, *J* = 12.4, 7.6, 1.2 Hz, 1H), 1.68 (s, 3H), 1.66 (s, 3H), 1.56 (dd, *J* = 8.8, 3.6 Hz, 1H), 1.15 (hept, *J* = 6.8 Hz, 1H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H), 0.44 (dd, *J* = 7.2, 4.8 Hz, 1H), 0.36 (dd, *J* = 4.8, 4.0 Hz, 1H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 150.7, 141.7, 131.9, 129.0, 128.4, 124.4, 124.1, 123.7, 121.5, 114.0, 76.3, 36.5, 35.3, 33.3, 28.9, 27.0, 25.9, 19.7, 19.6, 17.8, 16.8. **HRMS** (ESI) *m*/*z* calculated for $C_{21}H_{27}O$ $[M+H]^+$ 295.2056, found 295.2063. The relative stereochemistry of **2i** was established based on the nOe experiment. The nOe spectrum was provided at page S-114



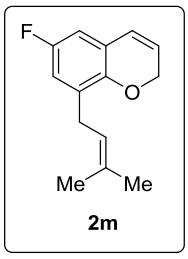
2k

2k. General procedure A; 35 mg, 82% yield; colorless oil. R_f = 0.42 (petroleum ether). **IR** (neat, cm^{-1}): 3047, 2967, 2918, 2858, 1641, 1590, 1471, 1377, 1264, 1210, 1152, 1064, 1032. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.88 (s, 1H), 6.51 (d, *J* = 1.6 Hz, 1H), 6.19 (dt, *J* = 10.0, 1.6 Hz, 1H), 5.52-5.48 (m, 1H), 5.27 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.45 (dd, *J* = 3.6, 1.6 Hz, 2H), 3.47 (d, *J* = 7.6 Hz, 2H), 2.10 (s, 3H), 1.67 (s, 3H), 1.65 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 150.2, 131.8, 130.6, 130.0, 128.8, 125.5, 125.4, 123.7, 122.5, 121.9, 65.4, 28.6, 25.9, 20.7, 17.8. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{19}O$ $[M+H]^+$ 215.1430, found 215.1428.



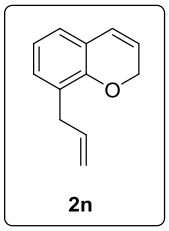
2l

2l. General procedure A; 39 mg, 85% yield; colorless oil. R_f = 0.32 (petroleum ether). **IR** (neat, cm^{-1}): 3048, 2962, 2927, 2854, 1642, 1590, 1470, 1376, 1324, 1302, 1201, 1153, 1070. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.78 (d, *J* = 3.2 Hz, 1H), 6.39 (d, *J* = 2.8 Hz, 1H), 6.16 (dt, *J* = 9.6, 1.6 Hz, 1H), 5.48-5.44 (m, 1H), 5.31 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.43 (dd, *J* = 3.6, 2.0 Hz, 2H), 3.45 (d, *J* = 7.2 Hz, 2H), 3.37 (s, 3H), 1.64 (s, 3H), 1.61 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 154.6, 146.3, 132.3, 132.2, 128.3, 125.5, 123.3, 122.8, 115.7, 109.6, 65.4, 55.2, 28.7, 25.8, 17.8. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{19}O_2$ $[M+H]^+$ 231.1380, found 231.1379.



2m

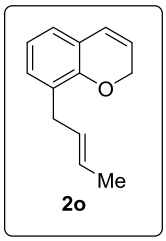
2m. General procedure A; 41 mg, 93% yield; colorless oil. R_f = 0.58 (petroleum ether). **IR** (neat, cm^{-1}): 3054, 2970, 2924, 2856, 1591, 1467, 1378, 1313, 1203, 1168, 1132, 1063. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.80 (dd, *J* = 9.6, 3.2 Hz, 1H), 6.39 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.92 (d, *J* = 9.6 Hz, 1H), 5.34-5.30 (m, 1H), 5.18 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.31 (dd, *J* = 3.6, 2.0 Hz, 2H), 3.32 (d, *J* = 7.6 Hz, 2H), 1.61 (s, 3H), 1.53 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 157.8 (d, *J* = 236.2 Hz), 148.0 (d, *J* = 2.2 Hz), 133.1, 130.9 (d, *J* = 6.5 Hz), 124.6 (d, *J* = 2.2 Hz), 123.4 (d, *J* = 8.8 Hz), 123.2, 122.3, 115.8 (d, *J* = 23.4 Hz), 110.7 (d, *J* = 23.4 Hz), 65.4, 28.2, 25.8, 17.7. **^{19}F NMR** (376 MHz, C_6D_6) δ: -123.2. **HRMS** (ESI) *m*/*z* calculated for $C_{14}H_{16}FO$ $[M+H]^+$ 219.1180, found 219.1180.



2n

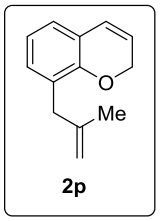
2n. General procedure B; 27 mg, 79% yield; colorless oil. R_f = 0.48 (petroleum ether). **IR** (neat, cm^{-1}): 3076, 3005, 2977, 2919, 2850, 1638, 1602, 1456, 1317, 1259, 1199, 1160, 1087, 1025. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.94 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.68 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.14 (dt, *J* = 9.6, 1.6 Hz, 1H), 6.01 (ddt, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.20 (dt, *J* = 9.6, 3.6 Hz, 1H), 5.08 (dd, *J* = 17.2, 1.6

Hz, 1H), 5.02 (dd, *J* = 10.0, 1.2 Hz, 1H), 4.39 (dd, *J* = 3.6, 2.0 Hz, 2H), 3.39 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 152.2, 137.3, 130.4, 127.5, 125.2, 125.1, 122.6, 121.9, 121.3, 115.5, 65.4, 34.2. **HRMS** (ESI) *m*/*z* calculated for $C_{12}H_{13}O$ $[M+H]^+$ 173.0966, found 173.0958.



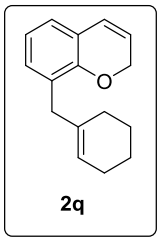
2o

2o. General procedure B; 29 mg, 77% yield; colorless oil. R_f = 0.49 (petroleum ether). **IR** (neat, cm^{-1}): 3014, 2963, 2917, 2854, 1644, 1600, 1455, 1376, 1260, 1202, 1086, 1058. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.99 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.69 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.43 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.66 (dtq, *J* = 15.2, 10.4, 1.6 Hz, 1H), 5.46 (dqt, *J* = 15.2, 6.4, 1.6 Hz, 1H), 5.21 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.41 (dd, *J* = 3.6, 2.0 Hz, 2H), 3.40 (d, *J* = 6.4 Hz, 2H), 1.57 (dq, *J* = 6.4, 1.6 Hz, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 152.2, 130.3, 130.0, 128.5, 126.0, 125.2, 125.0, 122.6, 121.8, 121.2, 65.5, 33.0, 18.0. **HRMS** (ESI) *m*/*z* calculated for $C_{13}H_{15}O$ $[M+H]^+$ 187.1117, found 187.1114. The alkene geometry of 2**o** was determined by the large coupling constant of the *trans*-alkene protons (15.2 Hz).



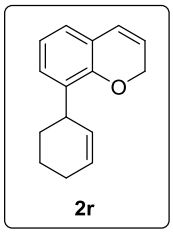
2p

2p. General procedure B; 29 mg, 78% yield; colorless oil. R_f = 0.53 (petroleum ether). **IR** (neat, cm^{-1}): 3074, 2968, 2919, 2852, 1645, 1601, 1456, 1374, 1312, 1259, 1203, 1086. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.97 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.69 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.15 (dt, *J* = 9.6, 1.6 Hz, 1H), 5.21 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.86 (d, *J* = 0.8 Hz, 1H), 4.83 (s, 1H), 4.40 (dd, *J* = 3.6, 1.6 Hz, 2H), 3.38 (s, 2H), 1.70 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 152.6, 144.8, 130.8, 127.2, 125.3, 125.2, 122.7, 121.9, 121.2, 111.7, 65.4, 37.7, 22.6. **HRMS** (ESI) *m*/*z* calculated for $C_{13}H_{15}O$ $[M+H]^+$ 187.1117, found 187.1116.

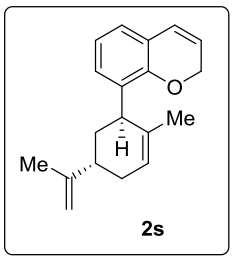


2q

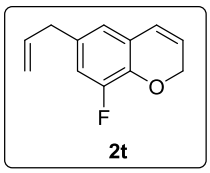
2q. General procedure B; 38 mg, 83% yield; colorless oil. R_f = 0.49 (petroleum ether). **IR** (neat, cm^{-1}): 3046, 2996, 2925, 2833, 1667, 1598, 1462, 1392, 1371, 1341, 1241, 1207, 1158, 1083, 1027. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.02 (d, *J* = 7.6 Hz, 1H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.70 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.17 (dt, *J* = 9.6, 1.6 Hz, 1H), 5.52 (s, 1H), 5.22 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.42 (dd, *J* = 3.6, 1.6 Hz, 2H), 3.38 (s, 2H), 1.97-1.95 (m, 4H), 1.54-1.43 (m, 4H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 152.7, 137.0, 130.8, 127.7, 125.3, 125.1, 122.7, 122.6, 121.9, 121.2, 65.4, 37.7, 28.7, 25.7, 23.4, 22.9. **HRMS** (ESI) *m*/*z* calculated for $C_{16}H_{19}O$ $[M+H]^+$ 227.1430, found 227.1433.



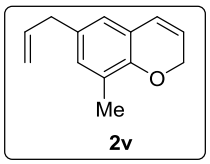
2r. General procedure B; 28 mg, 66% yield; colorless oil. R_f = 0.42 (petroleum ether). **IR** (neat, cm^{-1}): 3018, 2926, 2855, 2834, 1698, 1652, 1558, 1541, 1507, 1457, 1447, 1197, 1084. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.17 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.81 (*J* = 7.6 Hz, 1H), 6.71 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.18 (dt, *J* = 10.0, 1.6 Hz, 1H), 5.89-5.84 (m, 1H), 5.80-5.76 (m, 1H), 5.23 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.40 (dd, *J* = 3.6, 1.6 Hz, 2H), 4.07-4.02 (m, 1H), 2.13-2.05 (m, 1H), 2.00-1.89 (m, 2H), 1.69-1.48 (m, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 151.9, 133.6, 130.5, 129.0, 128.7, 125.4, 125.0, 122.7, 121.8, 121.2, 65.4, 34.6, 30.8, 25.5, 21.3. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{17}O$ $[M+H]^+$ 213.1279, found 213.1275.



2s. General procedure B; 34 mg, 63% yield; colorless oil. R_f = 0.55 (petroleum ether). **IR** (neat, cm^{-1}): 3079, 3034, 2962, 2915, 2855, 2837, 1645, 1448, 1375, 1196, 1159, 1086, 1027. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.70 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.15 (dt, *J* = 9.6, 2.0 Hz, 1H), 5.71-5.68 (m, 1H), 5.20 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.75 (d, *J* = 0.8 Hz, 1H), 4.72 (t, *J* = 1.6 Hz, 1H), 4.43-4.41 (m, 2H), 3.99 (d, *J* = 5.6 Hz, 1H), 2.36-2.28 (m, 1H), 2.24-2.17 (m, 1H), 2.14-2.10 (m, 1H), 2.01-1.92 (m, 2H), 1.65 (t, *J* = 0.8 Hz, 3H), 1.55 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 152.3, 149.8, 134.2, 131.6, 129.5, 125.3, 125.2, 124.9, 122.8, 121.7, 120.9, 109.0, 65.5, 38.9, 35.8, 34.8, 31.7, 22.9, 21.0. **HRMS** (ESI) *m*/*z* calculated for $C_{19}H_{23}O$ $[M+H]^+$ 267.1743, found 267.1747. The relative stereochemistry of **2s** was established based on the nOe experiment. The nOe spectrum was provided at page S-132.

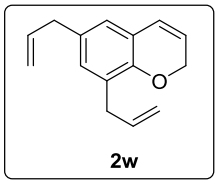


2t. General procedure B; 12 mg, 32% yield; colorless oil. R_f = 0.67 (petroleum ether). **IR** (neat, cm^{-1}): 3079, 3004, 2978, 2921, 2851, 1639, 1587, 1492, 1445, 1394, 1299, 1221, 1139, 1075. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.64 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.31 (s, 1H), 6.02 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.73 (ddt, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.15 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.96-4.90 (m, 2H), 4.32 (dd, *J* = 3.6, 1.6 Hz, 2H), 2.96 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 151.3 (d, *J* = 243.6 Hz), 140.4 (d, *J* = 11.7 Hz), 137.3, 133.1 (d, *J* = 6.5 Hz), 124.7 (d, *J* = 2.9 Hz), 124.1 (d, *J* = 4.4 Hz), 123.2, 122.0 (d, *J* = 2.9 Hz), 116.7 (d, *J* = 18.2 Hz), 116.0, 65.5, 39.4 (d, *J* = 1.5 Hz). **^{19}F NMR** (376 MHz, C_6D_6) δ: -137.5. **HRMS** (ESI) *m*/*z* calculated for $C_{12}H_{12}FO$ $[M+H]^+$ 191.0872, found 191.0865.



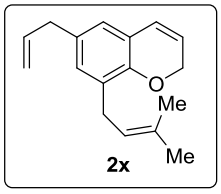
2v

2v. General procedure B; 27 mg, 73% yield; colorless oil. R_f = 0.47 (petroleum ether). **IR** (neat, cm^{-1}): 3077, 3056, 3005, 2975, 2921, 2852, 1639, 1593, 1479, 1434, 1312, 1210, 1152, 1076. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.74 (d, *J* = 1.6 Hz, 1H), 6.56 (d, *J* = 2.0 Hz, 1H), 6.17 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.91 (ddt, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.23 (dt, *J* = 10.0, 3.6 Hz, 1H), 5.07-4.99 (m, 2H), 4.44 (dd, *J* = 3.2, 2.0 Hz, 2H), 3.15 (d, *J* = 6.8 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 151.1, 138.4, 132.1, 131.4, 125.3, 125.1, 124.9, 122.2, 121.8, 115.4, 65.5, 39.8, 15.7. **HRMS** (ESI) *m*/*z* calculated for $C_{13}H_{15}O$ $[M+H]^+$ 187.1117, found 187.1120.



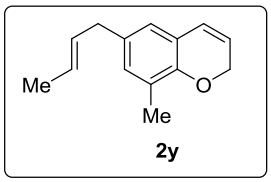
2w

2w. General procedure B; 30 mg, 70% yield; colorless oil. R_f = 0.53 (petroleum ether). **IR** (neat, cm^{-1}): 3077, 3005, 2977, 2904, 2832, 1638, 1474, 1432, 1215, 1151, 1091, 1028. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.82 (s, 1H), 6.57 (s, 1H), 6.16 (d, *J* = 9.6 Hz, 1H), 6.02 (dddt, *J* = 16.8, 10.4, 6.4, 1.2 Hz, 1H), 5.88 (dddt, *J* = 16.8, 10.4, 6.4, 1.2 Hz, 1H), 5.25 (dt, *J* = 9.6, 3.6 Hz, 1H), 5.11-4.98 (m, 4H), 4.41 (dd, *J* = 3.6, 1.6 Hz, 2H), 3.40 (dd, *J* = 6.4, 0.8 Hz, 2H), 3.14 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 150.6, 138.3, 137.4, 132.5, 130.5, 127.3, 125.4, 125.2, 122.6, 122.0, 115.5, 115.4, 65.5, 39.8, 34.3. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{17}O$ $[M+H]^+$ 213.1274, found 213.1277.



2x

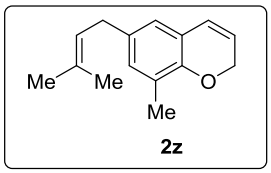
2x. General procedure B; 33 mg, 68% yield; colorless oil. R_f = 0.57 (petroleum ether). **IR** (neat, cm^{-1}): 3077, 3050, 2973, 2923, 2855, 1638, 1474, 1436, 1211, 1146, 1101, 1029. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.93 (d, *J* = 2.0 Hz, 1H), 6.58 (d, *J* = 2.0 Hz, 1H), 6.19 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.90 (ddt, *J* = 16.8, 10.0, 6.4 Hz, 1H), 5.51-5.46 (m, 1H), 5.25 (dt, *J* = 10.0, 3.6 Hz, 1H), 5.06-4.98 (m, 2H), 4.44 (dd, *J* = 3.6, 2.0 Hz, 2H), 3.46 (d, *J* = 7.2 Hz, 2H), 3.17 (d, *J* = 6.8 Hz, 2H), 1.66 (s, 3H), 1.64 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 150.7, 138.4, 132.5, 131.9, 130.2, 129.0, 125.4, 125.0, 123.6, 122.6, 121.9, 115.4, 65.5, 39.9, 28.7, 25.9, 17.8. **HRMS** (ESI) *m*/*z* calculated for $C_{17}H_{21}O$ $[M+H]^+$ 241.1587, found 241.1592.



2y

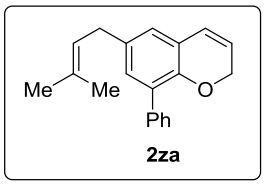
2y. General procedure B; 34 mg, 84% yield; colorless oil. R_f = 0.48 (petroleum ether). **IR** (neat, cm^{-1}): 3046, 3019, 2960, 2917, 2853, 1638, 1592, 1478, 1449, 1212, 1151, 1066, 1029. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.79 (d, *J* = 1.2 Hz, 1H), 6.61 (d, *J* = 2.0 Hz, 1H), 6.19 (dt, *J* = 9.6, 1.6 Hz, 1H), 5.58 (dtq, *J* = **15.2**, 6.8, 1.6 Hz，1H), 5.43 (dqt, *J* = **15.2**, 6.4, 1.6 Hz, 1H), 5.24 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.45 (dd, *J* = 3.6, 2.0 Hz, 2H), 3.17 (d, *J* = 6.4 Hz, 2H), 2.22 (s, 3H), 1.59 (dq, *J* = 6.4, 1.2 Hz, 3H). **^{13}C NMR**

(100 MHz, C_6D_6) δ: 151.0, 133.2, 131.4, 131.3, 125.8, 125.4, 125.0, 124.8, 122.2, 121.8, 65.5, 38.7, 18.0, 15.8. **HRMS** (ESI) *m*/*z* calculated for $C_{14}H_{17}O$ $[M+H]^+$ 201.1279, found 201.1274. The alkene geometry of 2**y** was determined by the large coupling constant of the *trans*-alkene protons (15.2 Hz).



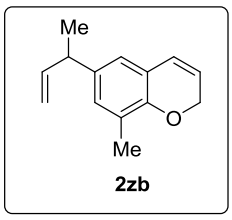
2z

2z. General procedure B; 35 mg, 82% yield; colorless oil. R_f = 0.51 (petroleum ether). **IR** (neat, cm^{-1}): 3047, 2968, 2916, 2853, 1638, 1478, 1449, 1376, 1265, 1211, 1150, 1102, 1030. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.82 (s, 1H), 6.64 (s, 1H), 6.20 (dt, *J* = 9.6, 1.6 Hz, 1H), 5.43-5.39 (m, 1H), 5.25 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.45 (dd, *J* = 3.6, 1.6 Hz, 2H), 3.23 (d, *J* = 7.2 Hz, 2H), 2.23 (s, 3H), 1.67 (s, 3H), 1.61 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 150.9, 134.0, 131.7, 131.2, 125.4, 125.0, 124.6 (2×C), 122.3, 121.8, 65.5, 34.0, 25.8, 17.8, 15.8. **HRMS** (ESI) *m*/*z* calculated for $C_{15}H_{19}O$ $[M+H]^+$ 215.1430, found 215.1431.



2za

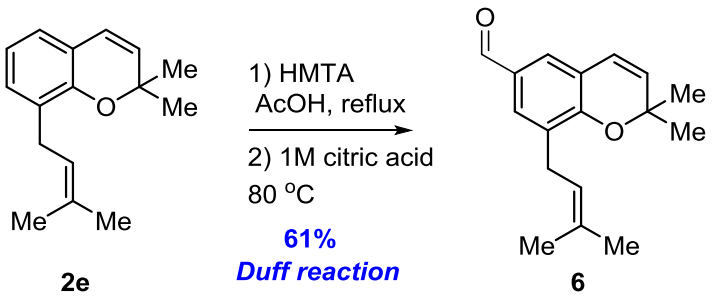
2za. General procedure B; 39 mg, 71% yield; colorless oil. R_f = 0.41 (petroleum ether). **IR** (neat, cm^{-1}): 3082, 3048, 3030, 2967, 2914, 2853, 1638, 1601, 1468, 1442, 1426, 1214, 1129, 1036, 1018. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.66-7.63 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.16-7.12 (m, 2H), 6.74 (d, *J* = 1.6 Hz, 1H), 6.22 (d, *J* = 9.6 Hz, 1H), 5.44-5.39 (m, 1H), 5.25 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.31 (dd, *J* = 3.6, 1.6 Hz, 2H), 3.26 (d, *J* = 7.2 Hz, 2H), 1.66 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 149.8, 138.9, 134.7, 132.1, 130.9, 130.0, 129.9 (2×C), 127.9 (2×C), 127.1, 126.2, 125.4, 124.3, 123.5, 122.4, 65.4, 34.0, 25.8, 17.8. **HRMS** (ESI) *m*/*z* calculated for $C_{20}H_{21}O$ $[M+H]^+$ 277.1587, found 277.1589.



2zb

2zb. General procedure B; 30 mg, 75% yield; colorless oil. R_f = 0.46 (petroleum ether). **IR** (neat, cm^{-1}): 3080, 2964, 2927, 2871, 1638, 1479, 1371, 1280, 1213, 1146, 1092, 1028. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.81 (d, *J* = 2.0 Hz, 1H), 6.63 (d, *J* = 2.0 Hz, 1H), 6.19 (dt, *J* = 9.6, 1.6 Hz, 1H), 5.99 (ddd, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.24 (dt, *J* = 9.6, 3.6 Hz, 1H), 5.05 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.00 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.44 (dd, *J* = 3.6, 1.6 Hz, 2H), 3.29-3.22 (m, 1H), 2.21 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 151.1, 144.0, 137.8, 130.1, 125.4, 125.1, 123.5, 122.2, 121.8, 112.8, 65.5, 42.8, 21.1, 15.8. **HRMS** (ESI) *m*/*z* calculated for $C_{14}H_{17}O$ $[M+H]^+$ 201.1279, found 201.1274.

Synthesis of Aldehyde 6



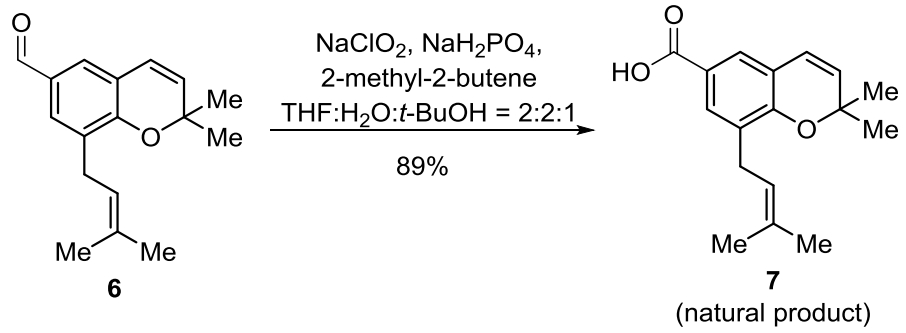
2e **6**

Duff reaction[3]: An oven-dried pressure tube under nitrogen atmosphere was charged with 2*H*-chromene **2e** (114 mg, 0.5 mmol), hexamethylenetetramine (140 mg, 1mmol) and glacial acetic acid (2 mL). The reaction mixture was heated to 120℃ (reflux) for 3 hours and cooled to room temperature. A 1 M citric acid solution (5 mL) was added and the resulting solution was heated at 80℃ for 1 hour and then cooled to room temperature before diluted with water (20 mL). The mixture was extracted with diethyl ether (3×50 mL) and the combined organic phase was washed with sat. aqueous $NaHCO_3$ (2×10 mL) and brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel using eluents (petroleum ether/ethyl acetate = 100/1) to afford the desired aldehyde **6**[4] (78 mg, 61% yield) as a colorless oil. R_f = 0.48 (petroleum ether / ethyl acetate = 20/1). **IR** (neat, cm^{-1}): 3044, 2975, 2925, 2856, 2731, 1690, 1641, 1595, 1461, 1440, 1375, 1282, 1210, 1135. **^{1}H NMR** (400 MHz, C_6D_6) δ: 9.70 (s, 1H), 7.54 (d, *J* = 1.2 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 5.97 (d, *J* = 10.0 Hz, 1H), 5.34-5.30 (m, 1H), 5.16 (d, *J* = 10.0 Hz, 1H), 3.32 (d, *J* = 7.6 Hz, 2H), 1.64 (s, 3H), 1.60 (s, 3H), 1.17 (s, 6H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 190.1, 156.2, 132.6, 131.7, 130.9, 130.5, 130.1, 126.4, 122.5, 122.1, 121.1, 77.6, 28.6, 28.2 (2×C), 25.8, 17.9. **HRMS** (ESI) *m*/*z* calculated for $C_{17}H_{21}O_2$ $[M+H]^+$ 257.1536, found 257.1541.

Total Synthesis of 2.2-Dimethyl-8-(3-methyl-2-butenyl)-2*H*-chromene-6-carboxylic acid (7)

[3] a) Zhou, G.; Corey, E. J. *J. Am. Chem. Soc*. **2005**, *127*, 11958-11959. b) Masurier, N.; Moreau, E.; Lartigue, C.; Gaumet, V.; Chezal, J.-M.; Heitz, A.; Teulade, J.-C.; Chavignon, O. *J. Org. Chem.* **2008**, *73*, 5989–5992.

[4] Damodar, K; Kim, J.-K.; Jun, J.-G. *Chin. Chem. Lett.* **2016**, *27*, 698–702.



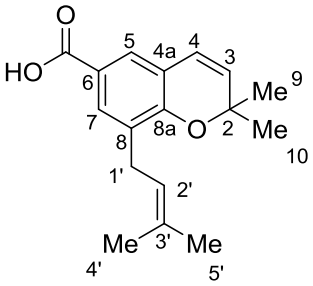
***Pinnick Oxidation*[5]:** To a solution of aldehyde **6** (51 mg, 0.2 mmol) in THF (2 mL), water (2 mL), *t*-BuOH (0.5 mL) and 2-methyl-2-butene (0.5 mL) was added $NaH_2PO_4{\cdot}2H_2O$ (250 mg, 1.6 mmol) and sodium chlorite (72 mg, 0.8 mmol). The reaction mixture was stirred vigoriously. After TLC analysis indicated complete consumption of the starting material (3 h), the reacion mixture was diluted with sat. aqueous NH_4Cl (10 mL) and then extracted with ethyl acetate (3 × 20 mL). The combined organic fractions were washed with brine and dried with anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure and the resulting residue was purified by flash chromatography on silica gel using eluents (petroleum ether/ethyl acetate = 5:1) to give the desired product **7** (49 mg, 89% yield) as a colorless oil. R_f = 0.21 (petroleum ether/ethyl acetate = 2/1). **IR** (neat, cm^{-1}): 2968, 2923, 2852, 1683, 1653, 1637, 1601, 1541, 1436, 1409, 1284, 1252, 1204, 1167, 1123. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 2.0 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 6.35 (d, *J* = 9.6 Hz, 1H), 5.65 (d, *J* = 9.6 Hz, 1H), 5.28 (t, *J* = 7.2 Hz, 1H), 3.29 (d, *J* = 7.2 Hz, 2H), 1.74 (s, 6H), 1.45 (s, 6H), (OH, not observed). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.9, 155.6, 132.7, 131.8, 130.8, 129.4, 126.7, 122.0, 121.9, 120.9, 120.4, 77.5, 28.4 (2×C), 28.2, 25.8, 17.9. **HRMS** (ESI) *m*/*z* calculated for $C_{17}H_{21}O_3$ $[M+H]^+$ 273.1485, found 273.1491.

Other Physical Properties comparison:

	Synthetic **7**	Natural **7**6
Morphology	Colorless oil.	Clear oil.
IR	2923, 1683, 1601, 1409, 1284, 1252, 1204, 1123	2920,1680, 1600, 1410, 1280, 1250, 1200, 1120
HRMS $[M]^+$ $C_{17}H_{20}O_3$ = 272.1412 $[M+H]^+$ $C_{17}H_{21}O_3$ = 273.1485	(ESI) 273.1491	(EI) 272

[5] Bal, B. S.; Childers, W. E. Jr.; Pinnick, H. W. *Tetrahedron* **1981**, *37*, 2091-2096.

Comparison of NMR data of synthetic 7 with those reported for natural 7[6]



7

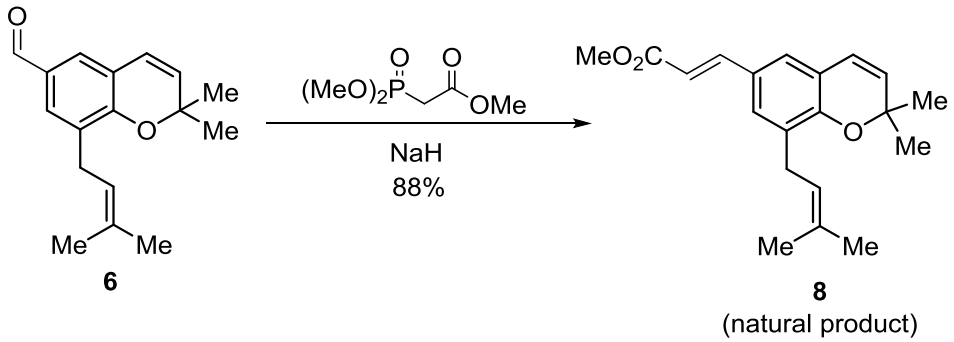
No.	^{1}H NMR ($CDCl_3$)		^{13}C NMR ($CDCl_3$)	
	Natural **7**[a]	Synthetic **7**[b]	Natural **7**[a]	Synthetic **7**[b]
2	--	--	77.6	77.5
3	5.65 (d, *J* = 9.8 Hz, 1H)	5.65 (d, *J* = 9.6 Hz, 1H)	130.8	130.8
4	6.35 (d, *J* = 9.8 Hz, 1H)	6.35 (d, *J* = 9.6 Hz, 1H)	121.9	121.9
4a	--	--	120.8	120.9
5	7.60 (d, *J* = 2.0 Hz, 1H)	7.61 (d, *J* = 2.0 Hz, 1H)	126.7	126.7
6	--	--	120.4	120.4
7	7.75 (d, *J* = 2.0 Hz, 1H)	7.75 (d, *J* = 2.0 Hz, 1H)	131.8	131.8
8	--	--	129.4	129.4
8a	--	--	155.6	155.6
9	1.45 (s, 3H)	1.45 (s, 3H)	28.4	28.4
10	1.45 (s, 3H)	1.45 (s, 3H)	28.4	28.4
1'	3.29 (d, *J* = 7.3 Hz, 2H)	3.29 (d, *J* = 7.2 Hz, 2H)	28.2	28.2
2'	5.28 (t, *J* = 7.2 Hz, 1H)	5.28 (t, *J* = 7.2 Hz, 1H)	122.0	122.0
3'	--	--	132.7	132.7
4'	1.74 (s, 3H)	1.74 (s, 3H)	25.8	25.8
5'	1.74 (s, 3H)	1.74 (s, 3H)	17.9	17.9
COOH	Not observed.	Not observed.	171.3	171.9

[6] a) Cabanillas, B. J.; Lamer, A. C. L.; Castillo, D.; Arevalo, J.; Estevez, Y.; Rojas, R.; Valadeau, C.; Bourdy, G.; Sauvain, M. Fabre, N. *Planta Med.* **2012**, *78*, 914-918. b) Orjala, J.; Erdelmeier, C. A. J.; Wright, A. D.; Rali, T.; Sticher, O. *Phytochemistry* **1993**, *34*, 813–818.

[a] ^{1}H NMR spectra were recorded at 500 MHz; ^{13}C NMR spectra were recorded at 125 MHz.

[b] ^{1}H NMR spectra were recorded at 400 MHz; ^{13}C NMR spectra were recorded at 100 MHz.

Total Synthesis of 8-(3',3'-Dimethylallyl)-werneria chromene (8)

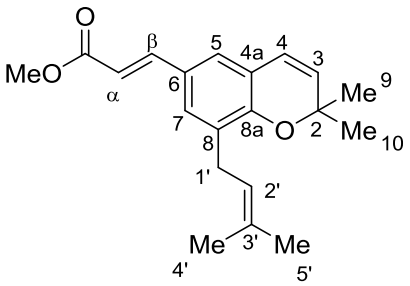


Horner-Wadsworth-Emmons (HWE) Reaction: To a suspension of NaH (10 mg of 60% oil dispersion, 0.24 mmol) in dry THF (1 mL) under nitrogen at -10℃ was added trimethyl phosphonoacetate (55 mg, 0.3 mmol) and the mixture was stirred for 30 min. A solution of the aldehyde **6** (51 mg, 0.2 mmol) in THF (1 mL) was added to the mixture dropwise at -10℃ and the mixture was stirred at that temperature for 60 min. Sat. aqueous NH_4Cl (10 mL) was added to quench the reaction. THF was removed in vacuum and the aqueous mixture was extracted with diethyl ether (3×20 mL). The combined organic fractions were washed with brine, dried over anhydrous $MgSO_4$ and evaporated by rotavap under reduced pressure. The resulting residue was purified by flash chromatography on silica gel using eluents (petroleum ether/ethyl acetate = 20:1) to afford **8** (55 mg, 88% yield) as a colorless oil. R_f = 0.28 (petroleum ether/ethyl acetate = 5/1). **IR** (neat, cm^{-1}): 3043, 2969, 2926, 2855, 1718, 1629, 1597, 1465, 1438, 1376, 1267, 1169, 1147, 1118. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 16.0 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.30 (d, *J* = 10.0 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 5.63 (d, *J* = 10.0 Hz, 1H), 5.25 (t, *J* = 7.6 Hz, 1H), 3.77 (s, 3H), 3.25 (d, *J* = 7.6 Hz, 2H), 1.73 (s, 3H), 1.72 (s, 3H), 1.42 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 167.9, 152.9, 145.1, 132.6, 131.0, 129.7, 129.5, 126.6, 124.1, 122.1, 122.0, 121.0, 114.6, 76.9, 51.5, 28.2 (2×C), 28.1, 25.8, 17.8. **HRMS** (ESI) *m/z* calculated for $C_{20}H_{25}O_3$ $[M+H]^+$ 313.1798, found 313.1799.

Other Physical Properties comparison:

	Synthetic **8** (Reported by Stratakis)	**Synthetic 8 (Our Sample)**	Natural **8** (Reported by Robinson)
Morphology	Not available	**Colorless oil.**	Colorless gum.
IR		**1718, 1629, 1597**	1725, 1635, 1595
HRMS $[M]^+$ = 312.1725 $[M+H]^+$ = 313.1798		**(ESI) 313.1799**	(EI) 312.173

Comparison of NMR data of our synthetic 8 with those reported for 8[7]



8

No.	^{1}H NMR ($CDCl_3$)		
	Synthetic **8**[a] (Reported by Stratakis)	**Synthetic 8[b] (our Sample)**	Natural **8**[b] (Reported by Robinson)
2	--	**--**	--
3	5.63 (d, *J* = 10.0 Hz, 1H)	**5.63 (d, *J* = 10.0 Hz, 1H)**	5.57 (d, *J* = 10.0 Hz, 1H)
4	6.30 (d, *J* = 10.0 Hz, 1H)	**6.30 (d, *J* = 10.0 Hz, 1H)**	6.24 (d, *J* = 10.0 Hz, 1H)
4a	--	**--**	--
5	7.15 (d, *J* = 1.5 Hz, 1H)	**7.15 (d, *J* = 2.0 Hz, 1H)**	7.09 (d, *J* = 2.0 Hz, 1H)
6	--	**--**	--
7	7.01 (d, *J* = 1.5 Hz, 1H)	**7.00 (d, *J* = 2.0 Hz, 1H)**	6.94 (d, *J* = 2.0 Hz, 1H)
8	--	**--**	--
8a	--	**--**	--
9	1.42 (s, 3H)	**1.42 (s, 3H)**	1.36 (s, 3H)
10	1.42 (s, 3H)	**1.42 (s, 3H)**	1.36 (s, 3H)
α	6.26 (d, *J* = 15.5 Hz, 1H)	**6.26 (d, *J* = 16.0 Hz, 1H)**	6.19 (d, *J* = 16.0 Hz, 1H)
β	7.58 (d, *J* = 16.0 Hz, 1H)	**7.58 (d, *J* = 16.0 Hz, 1H)**	7.52 (d, *J* = 16.0 Hz, 1H)
1'	3.25 (d, *J* = 7.5 Hz, 2H)	**3.25 (d, *J* = 7.6 Hz, 2H)**	3.19 (d, *J* = 7.5 Hz, 2H)
2'	5.25 (br. t, *J* = 7.5 Hz, 1H)	**5.25 (t, *J* = 7.6 Hz, 1H)**	5.19 (tqq, *J* = 7.5, 1.0, 1.0 Hz, 1H)
3'	--	**--**	--
4'	1.73 (br. s, 3H)	**1.73 (s, 3H)**	1.67 (d, *J* = 1.0 Hz, 3 H)
5'	1.72 (br. s, 3H)	**1.72 (s, 3H)**	1.66 (d, *J* = 1.0 Hz, 3 H)

[7] a) Bohlmann, F.; Zdero, C.; King, R. M.; Robinson, H. *Phytochemistry* **1984**, *23*, 1135–1137. b) Lynkakis, I. N.; Efe, C.; Gryparis, C.; Stratakis, M. *Eur. J. Org. Chem.* **2011**, 2334–2338.

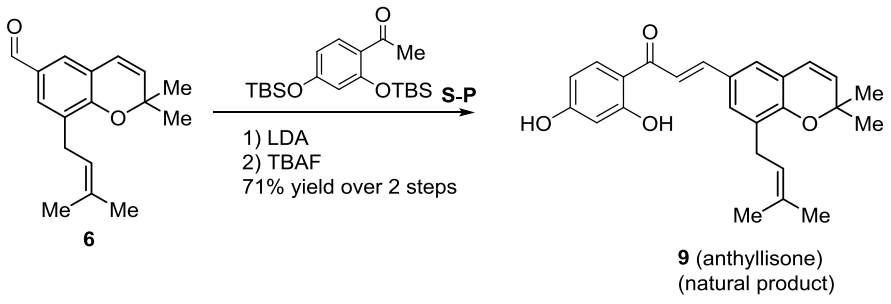
OMe	3.78 (s, 3H)	**3.77 (s, 3H)**	3.71 (s, 3H)
C=O	--	**--**	--

[a] Measured with 300 MHz Spectrometer. [b] Measured with 400 MHz Spectrometer.

^{13}C NMR ($CDCl_3$)[a]		
Synthetic **8**[b] (Reported by Stratakis)	**Synthetic 8[c] (our Sample)**	Natural **8** (Reported by Robinson)
167.9	**167.9**	
152.8	**152.9**	
145.1	**145.1**	
132.6	**132.6**	
131.0	**131.0**	
129.7	**129.7**	
129.5	**129.5**	
126.6	**126.6**	
124.1	**124.1**	
122.1	**122.1**	Not available
122.0	**122.0**	
121.0	**121.0**	
114.6	**114.6**	
76.9	**76.9**	
51.5	**51.5**	
28.2	**28.2**	
28.1	**28.1**	
25.8	**25.8**	
17.8	**17.8**	

[a] Peaks not assigned. [b] Measured with 75 MHz Spectrometer. [c] Measured with 100 MHz Spectrometer.

Total Synthesis of anthyllisone (9)



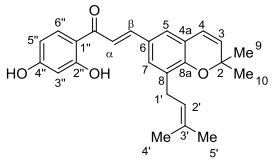
***Di-silylation of 2,4-dihydroxyacetophenone*:** To a solution of 2,4-dihydroxyacetophenone (760 mg, 5 mmol) in dry CH_2Cl_2 (20 mL) were added imidazole (1.02 g, 15 mmol) and 4-dimethylamino pyridine (DMAP, 30 mg, 0.25 mmol). The resulting solution was cooled to 0 ℃ with an ice-water bath and then *tert*-butyldimethylsilyl chloride (TBSCl, 1.88 g, 12.5 mmol) dissolved in CH_2Cl_2 (10 mL) was added dropwise. After the completion of addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched by addition of water (20 mL). The organic fractions were collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic fractions were washed with water (20 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by short column chromatography on silica gel using petroleum ether as the eluent to afford bis-silylether **S-P** (1.88 g, 99% yield) as a colorless oil. This compound was used directly in the next step.

LDA-mediated Claisen-Schmidt condensation: To a solution of the acetophenone **S-P** (190 mg, 0.5 mmol) in dry THF (1 mL) under nitrogen was added Lithium Diisopropylamide (LDA, 1.0 M, 0.4 mL, 0.4 mmol) dropwise at -78℃. The reaction mixture was allowed to warm to -20℃ over 30 min, and then cooled to -78℃. The solution of aldehyde **6** (51 mg, 0.2 mmol) in dry THF (1 mL) was added dropwise at -78℃ and the resulting reaction mixture was allowed to warm to 0℃ and quenched by addition of sat. aqueous NH_4Cl (5 mL). The organic fraction was collected and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organic fractions was washed with brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to afford the crude TBS-masked anthyllisone, which were used directly for desilylation.

***Desilylation*:** The above residue was dissolved in THF (5 mL) and tetrabutylammonium fluoride (TBAF, 1.0 M, 2.0 mL, 2.0 mmol) was added. The resulting reaction mixture was stirred at room temperature for 1 hr and quenched by addition of water (5 mL). The organic fraction was collected and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic fractions was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (petroleum ether/ethyl acetate=5/1) to furnish anthyllisone (**9**) (55 mg, 71% yield over 2 steps) as a yellow solid, mp = 158-162℃.R_f = 0.43 (petroleum ether/ethyl acetate = 2/1). **IR** (neat, cm^{-1}): 3178, 2961, 2972, 2924, 2853, 1625, 1596, 1542, 1507, 1491, 1458, 1434, 1371, 1274, 1263, 1224, 1206, 1137, 1032. **^{1}H NMR** (400 MHz, MeOH-d_4) δ: 7.95 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 15.2 Hz, 1H), 7.58 (d, *J* = 15.2 Hz, 1H), 7.31

(s, 1H), 7.28 (s, 1H), 6.40 (d, *J* = 9.6 Hz, 2H), 6.27 (s, 1H), 5.72 (d, *J* = 9.6 Hz, 1H), 5.25 (t, *J* = 6.8 Hz, 1H), 3.26 (d, *J* = 7.2 Hz, 2H), 1.75 (s, 3H), 1.72 (s, 3H), 1.41 (s, 6H), (OH×2, not observed). **^{13}C NMR** (100 MHz, MeOH-d_4) δ: 192.2, 166.3, 165.1, 153.3, 144.4, 132.2, 131.8, 131.1, 130.5, 129.8, 127.4, 124.5, 122.4, 121.9, 121.5, 117.6, 113.5, 107.9, 102.6, 77.0, 28.1, 27.2 (2×C), 24.7, 16.8. **HRMS** (ESI) *m*/*z* calculated for $C_{25}H_{27}O_4$ $[M+H]^+$ 391.1904, found 391.1904.

Comparison of NMR data of our synthetic anthyllisone (9) with those reported for anthyllisone[8]



9

No.	^{1}H NMR (MeOH-d_4)		
	Synthetic anthyllisone[a] (Reported by Jun)	**Synthetic anthyllisone[b] (our Sample)**	Natural anthyllisone[c] (Reported by Mele)
2	--	**--**	--
3	5.72 (d, *J* = 8.7 Hz, 1H)	**5.72 (d, *J* = 9.6 Hz, 1H)**	5.75 (d, *J* = 8.9 Hz, 1H)
4	6.39 (d, *J* = 8.7 Hz, 1H)	**6.40 (d, *J* = 9.6 Hz, 1H)**	6.41 (d, *J* = 8.9 Hz, 1H)
4a	--	**--**	--
5	7.28 (d, *J* = 1.8 Hz, 1H)	**7.28 (s, 1H)**	7.32 (br s, 1H)
6	--	**--**	--
7	7.31 (d, *J* = 1.8 Hz, 1H)	**7.31 (s, 1H)**	7.35 (br s, 1H)
8	--	**--**	--
8a	--	**--**	--
9	1.42 (s, 3H)	**1.41 (s, 3H)**	1.43 (s, 3H)
10	1.42 (s, 3H)	**1.41 (s, 3H)**	1.43 (s, 3H)
1'	3.26 (d, *J* = 7.2 Hz, 2H)	**3.26 (d, *J* = 7.2 Hz, 2H)**	3.25 (m, 2H)
2'	5.27-5.22 (m, 1H)	**5.25 (t, *J* = 6.8 Hz, 1H)**	5.27 (m, 1H)
3'	--	**--**	--
4'	1.76 (s, 3H)	**1.75 (s, 3H)**	1.77 (br s, 3H)
5'	1.72 (s, 3H)	**1.72 (s, 3H)**	1.74 (br s, 3H)
1''	--	**--**	--
2''	--	**--**	--
3''	6.26 (d, *J* = 2.1 Hz, 1H)	**6.27 (s, 1H)**	6.29 (d, *J* = 2.2 Hz, 1H)
4''	--	**--**	--
5''	6.40 (dd, *J* = 8.8, 2.1 Hz, 1H)	**6.40 (d, *J* = 9.6 Hz, 1H)**	6.42 (dd, *J* = 8.8, 2.2 Hz, 1H)
6''	7.96 (d, *J* = 8.7 Hz, 1H)	**7.95 (d, *J* = 8.8 Hz, 1H)**	7.98 (d, *J* = 8.8 Hz, 1H)

[8] a) Pistelli, L.; Spera, K.; Flamini, G.; Mele, S.; Morelli, I. *Phytochemistry* **1996**, *42*, 1455–1458.

α	7.58 (d, *J* = 15.3 Hz, 1H)	**7.58 (d, *J* = 15.2 Hz, 1H)**	7.61 (d, *J* = 15.3 Hz, 1H)
β	7.70 (d, *J* = 15.3 Hz, 1H)	**7.71 (d, *J* = 15.2 Hz, 1H)**	7.75 (d, *J* = 15.3 Hz, 1H)
C=O	**--**	**--**	--
OH-2'	Not observed	**Not observed**	13.6 (s, 1H)
OH-4'	Not observed	**Not observed**	Not observed

[a] Measured with 300 MHz Spectrometer [b] Measured with 400 MHz Spectrometer. [c] Measured with 200 MHz Spectrometer.

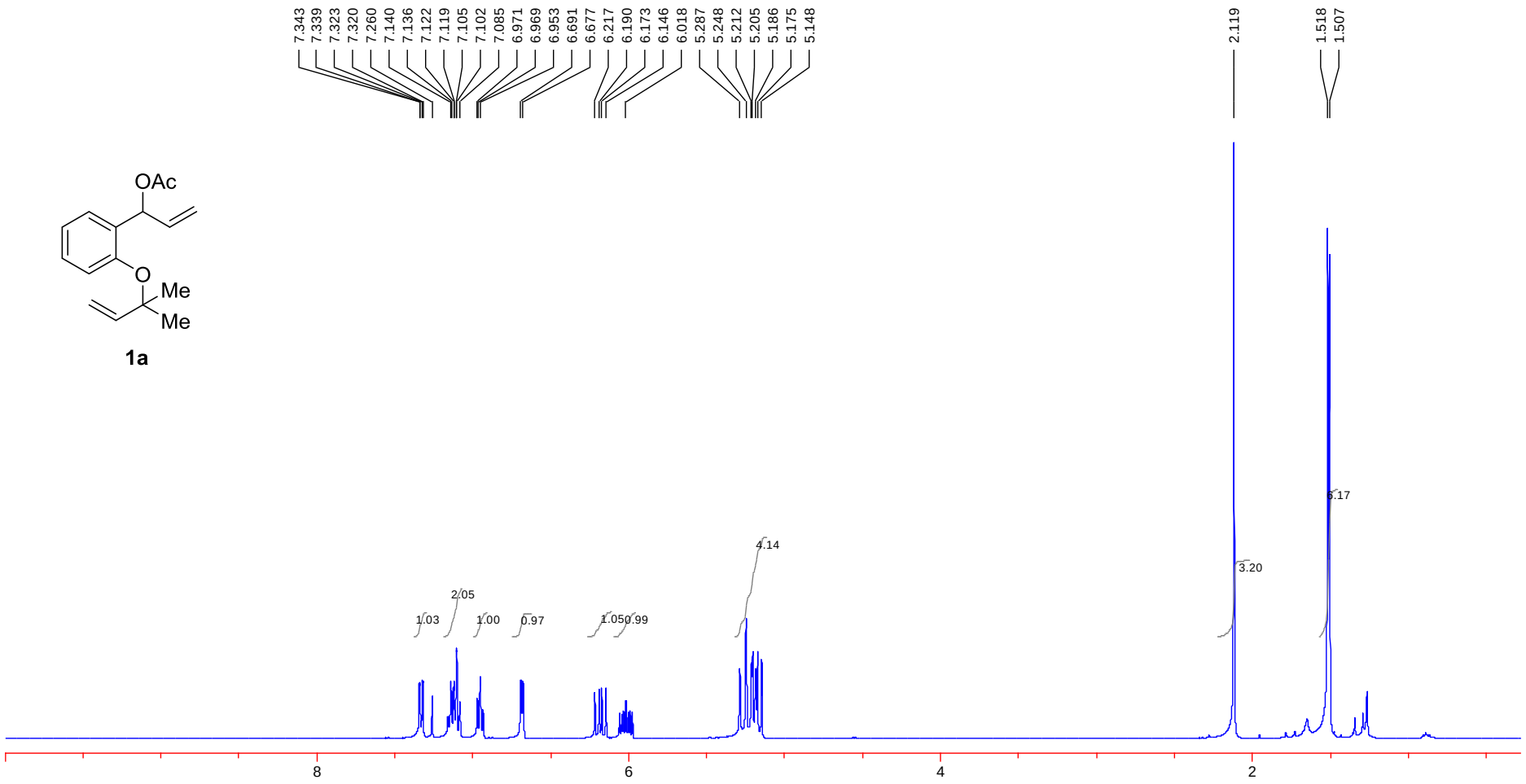
No.	^{13}C NMR (MeOH-d_4)		
	Synthetic anthyllisone[a] (Reported by Jun)	**Synthetic anthyllisone[b] (our Sample)**	Natural anthyllisone[c] (Reported by Mele)
2	77.1	**77.0**	78.3
3	131.1	**131.1**	131.7
4	122.5	**122.4**	123.1
4a	127.4	**127.4**	128.7
5	131.8	**131.8**	132.3
6	130.6	**130.5**	131.0
7	124.5	**124.5**	125.7
8	121.5	**121.5**	122.7
8a	153.3	**153.3**	154.6
9	27.4	**27.2**	28.4
10	27.4	**27.2**	28.4
1'	28.3	**28.1**	29.3
2'	121.9	**121.9**	123.6
3'	129.8	**129.8**	129.8
4'	24.9	**24.7**	25.9
5'	17.1	**16.8**	18.0
1''	113.5	**113.5**	114.7
2''	165.1	**165.1**	166.4
3''	102.6	**102.6**	103.8
4''	166.3	**166.3**	167.5
5''	108.0	**107.9**	109.2
6''	132.2	**132.2**	133.4
α	117.6	**117.6**	118.9
β	144.4	**144.4**	145.6
C=O	192.0	**192.2**	193.5

[a] Measured with 75 MHz Spectrometer [b] Measured with 100 MHz Spectrometer. [c] Measured with 50 MHz Spectrometer.

Other Physical Properties comparison:

	Synthetic anthyllisone (Reported by Jun)	**Synthetic anthyllisone (our Sample)**	Natural anthyllisone (Reported by Mele)
Morphology	Yellow solid	Yellow solid	Not available

mp	161-163℃	158-162℃	Not available
IR	Not available	**3178, 1625, 1542, 1371**	3350, 1640, 1530, 1380
HRMS $[M]^+$ = 390.1831 $[M+H]^+$ = 391.1904	(EI) 390	**(ESI) 391.1904**	(EI) 390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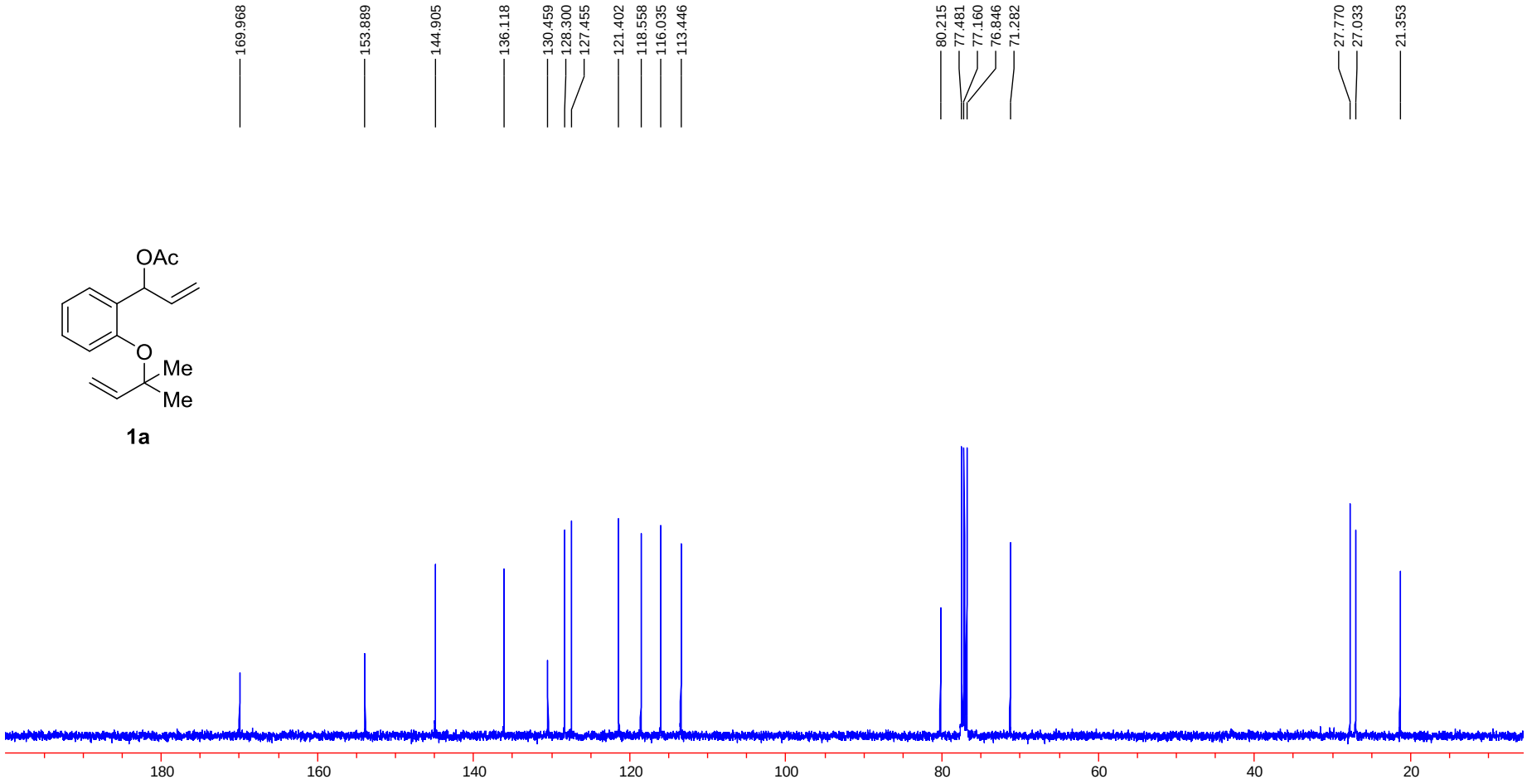
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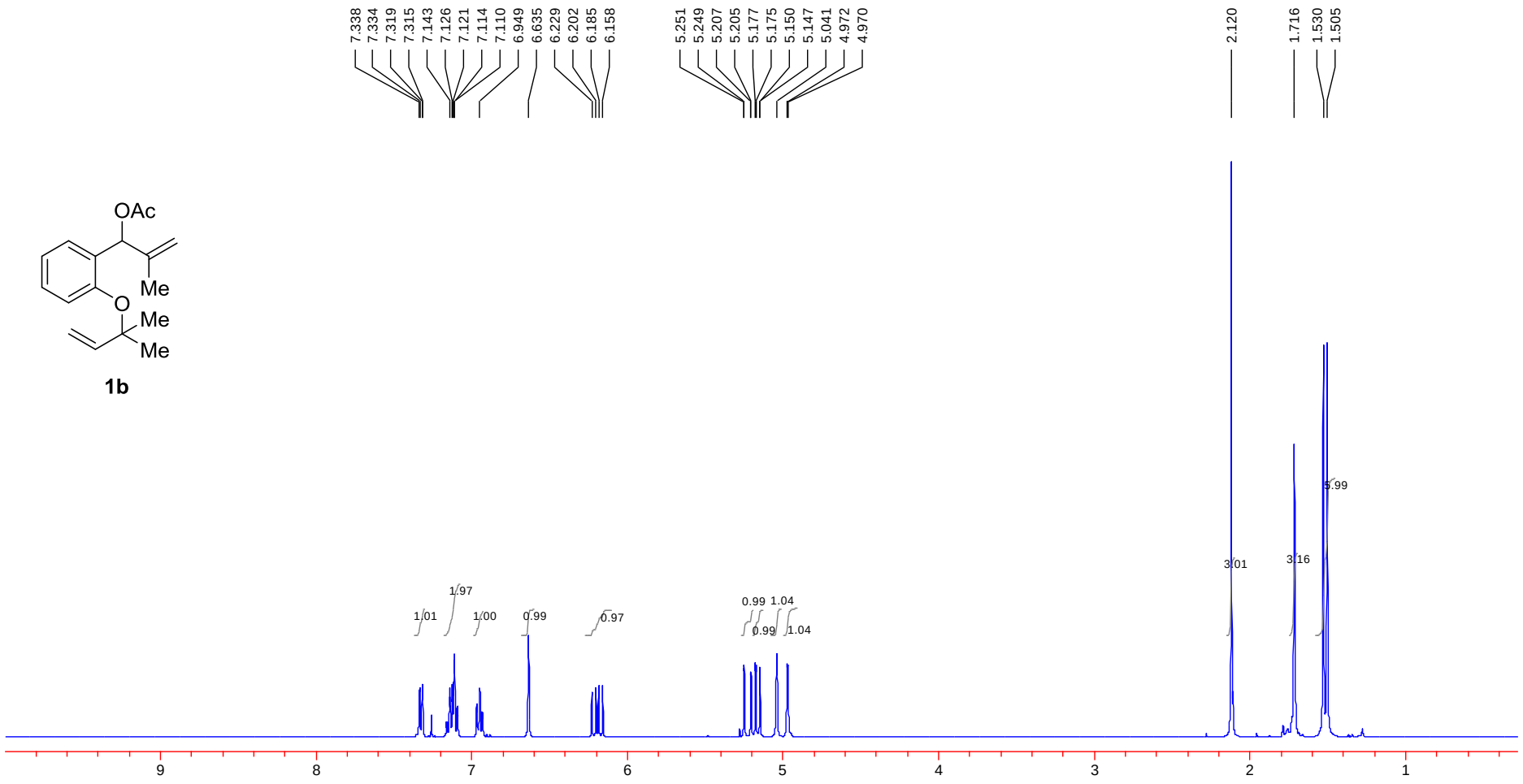
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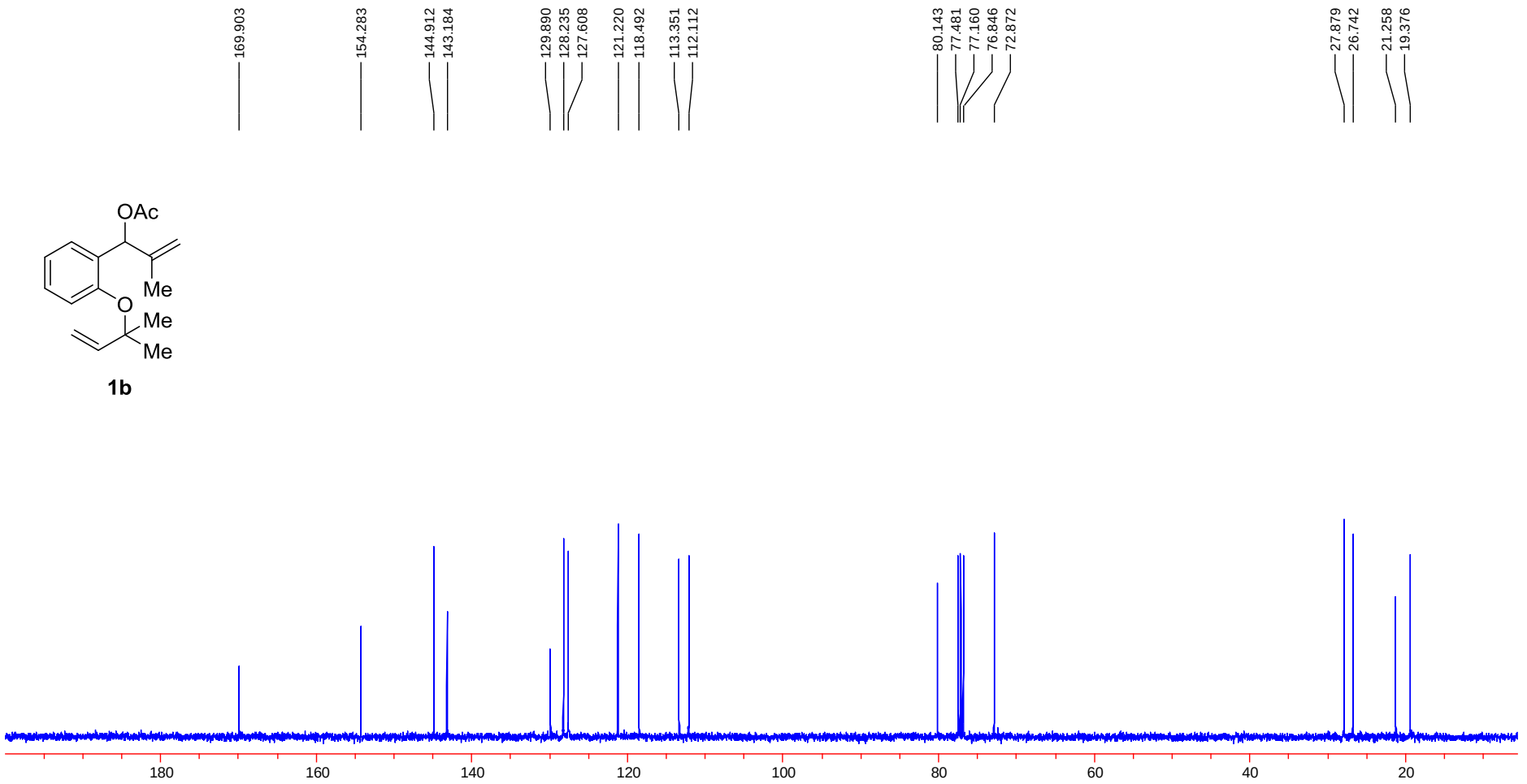
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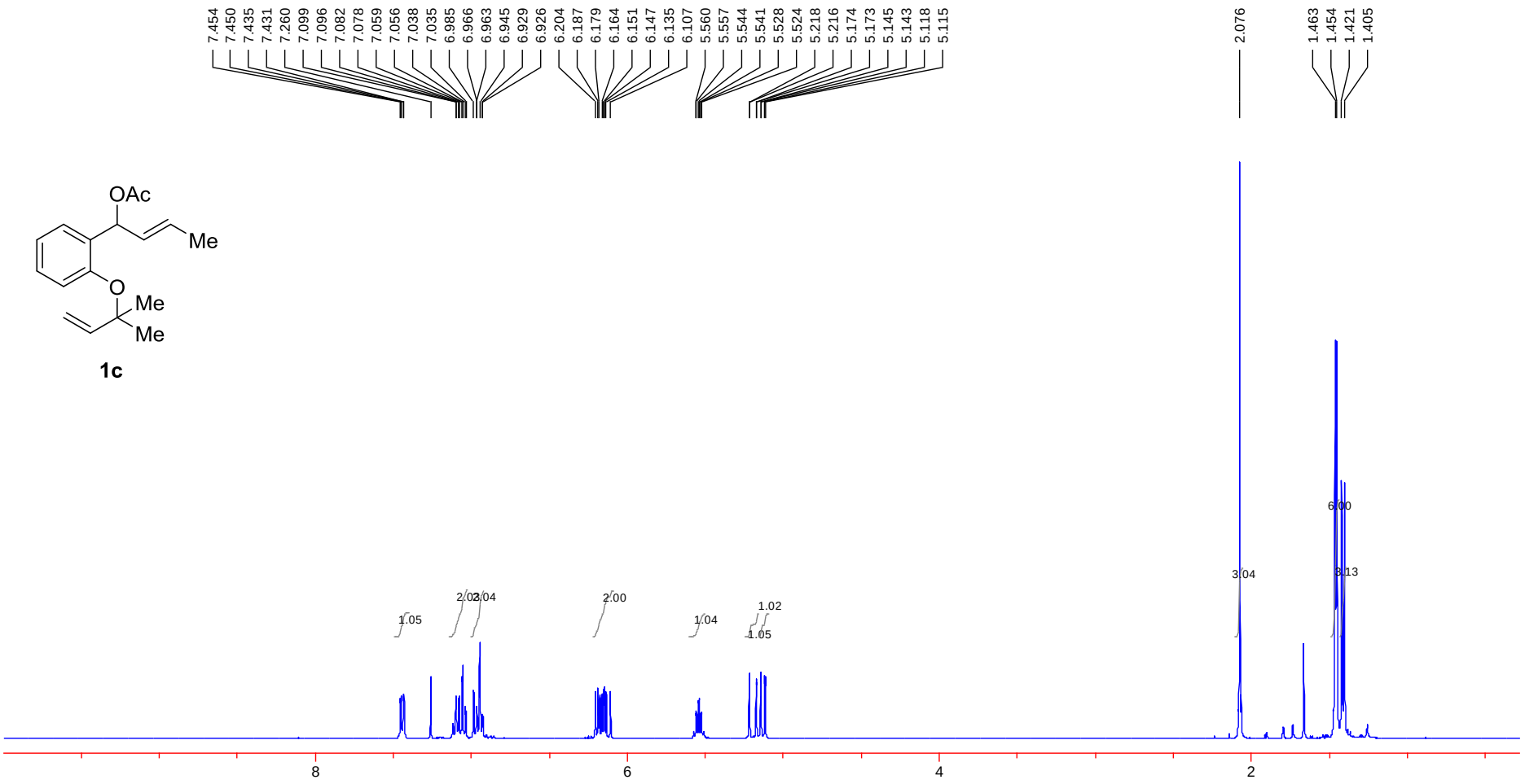
1b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Me
O
Me
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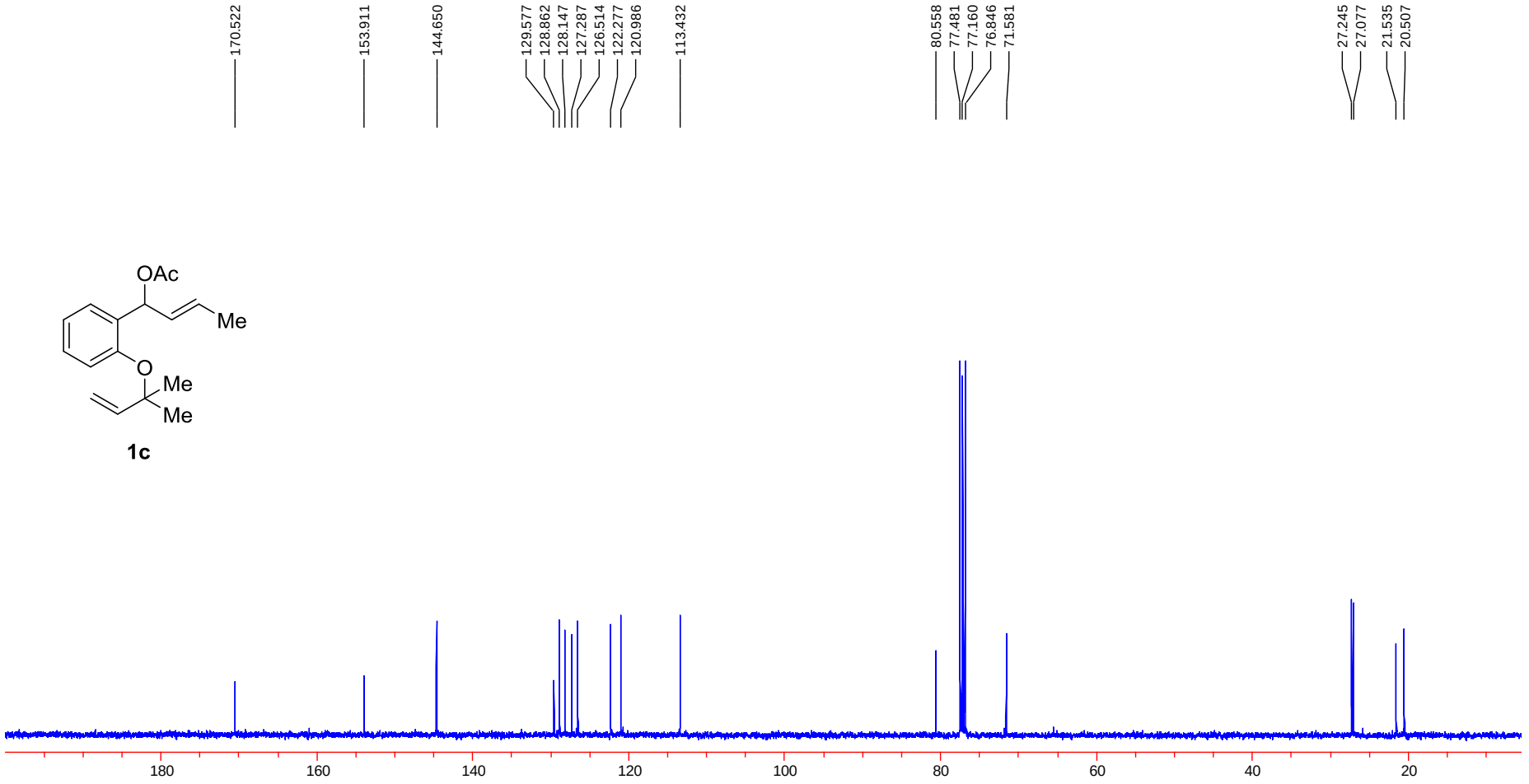
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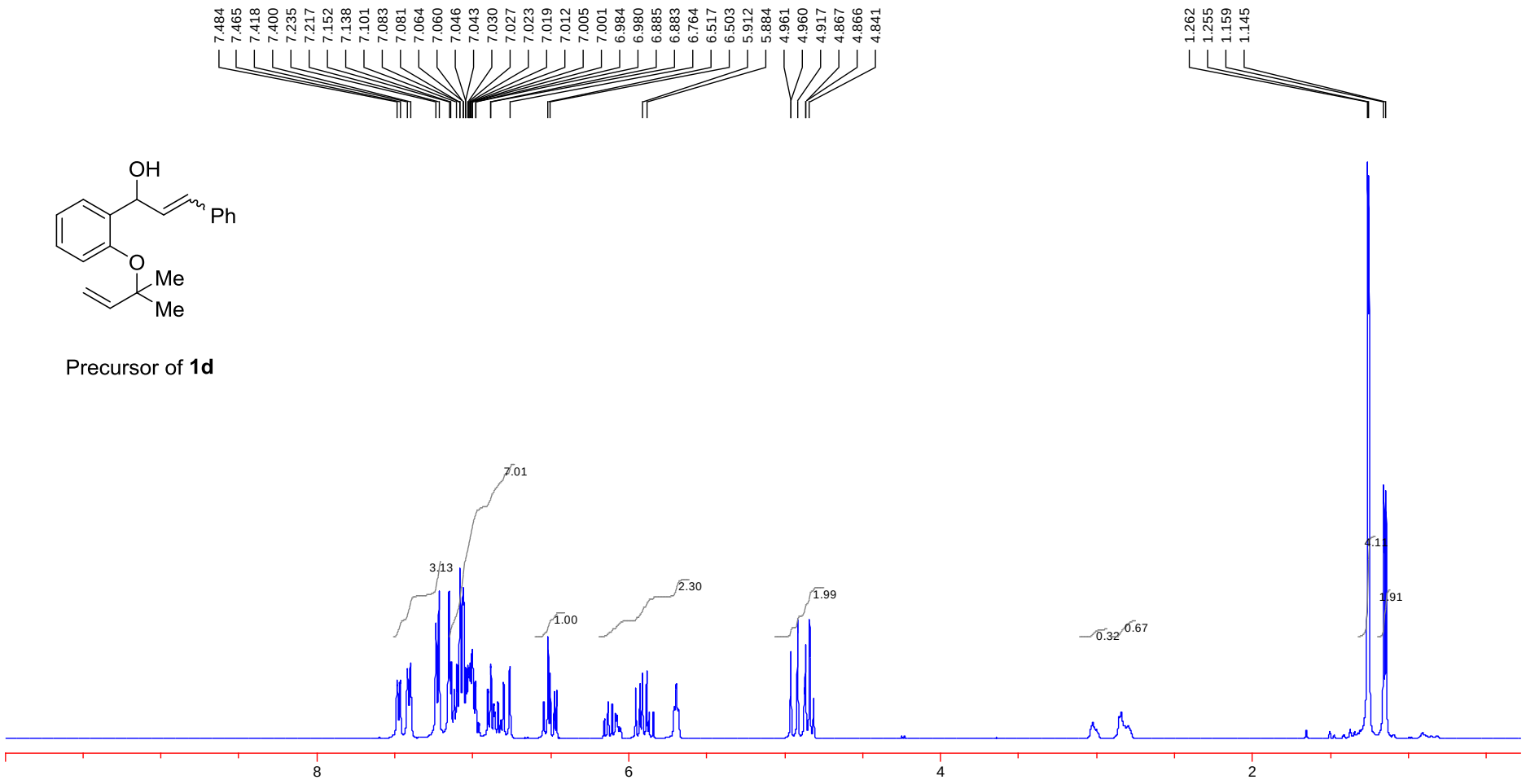

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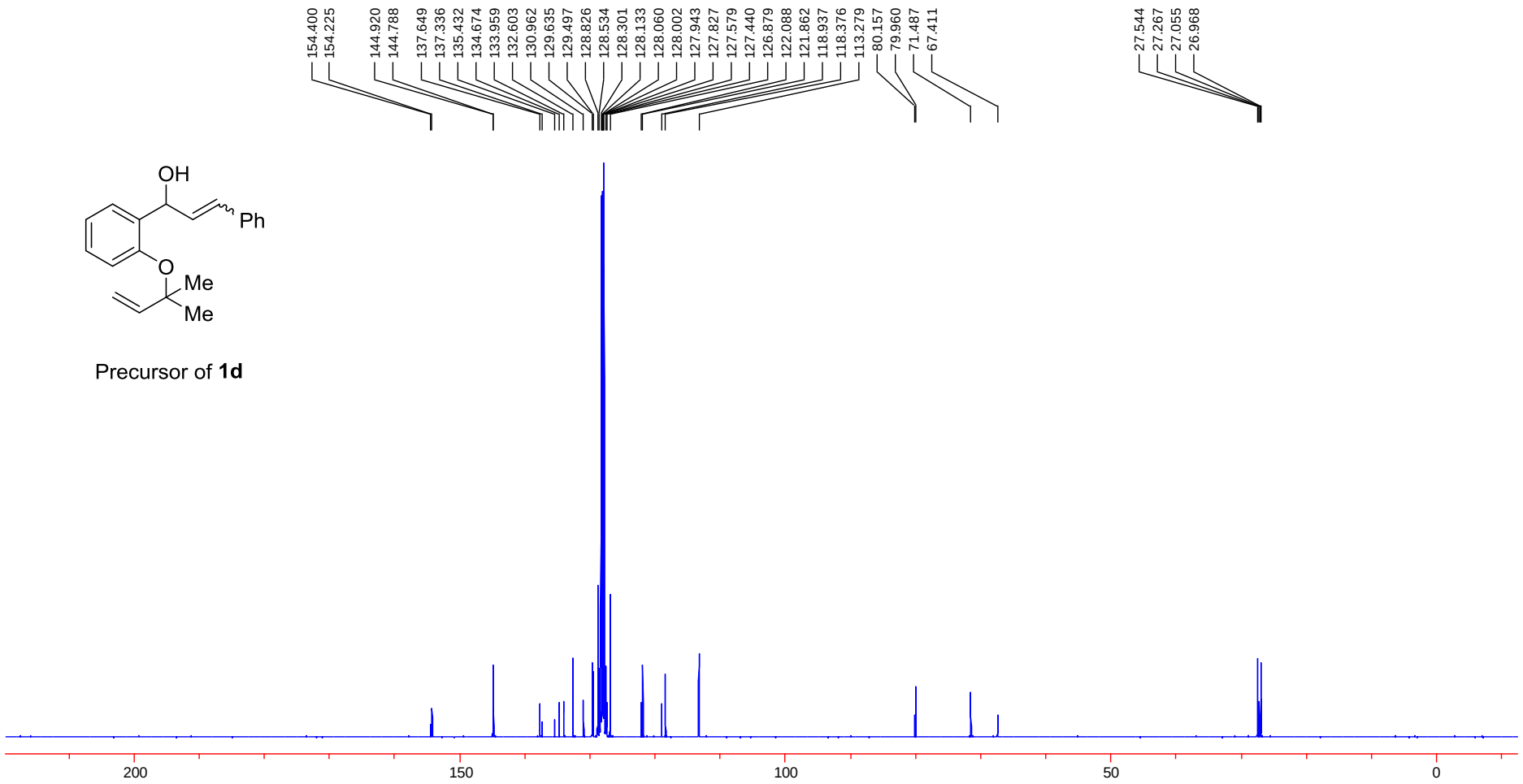

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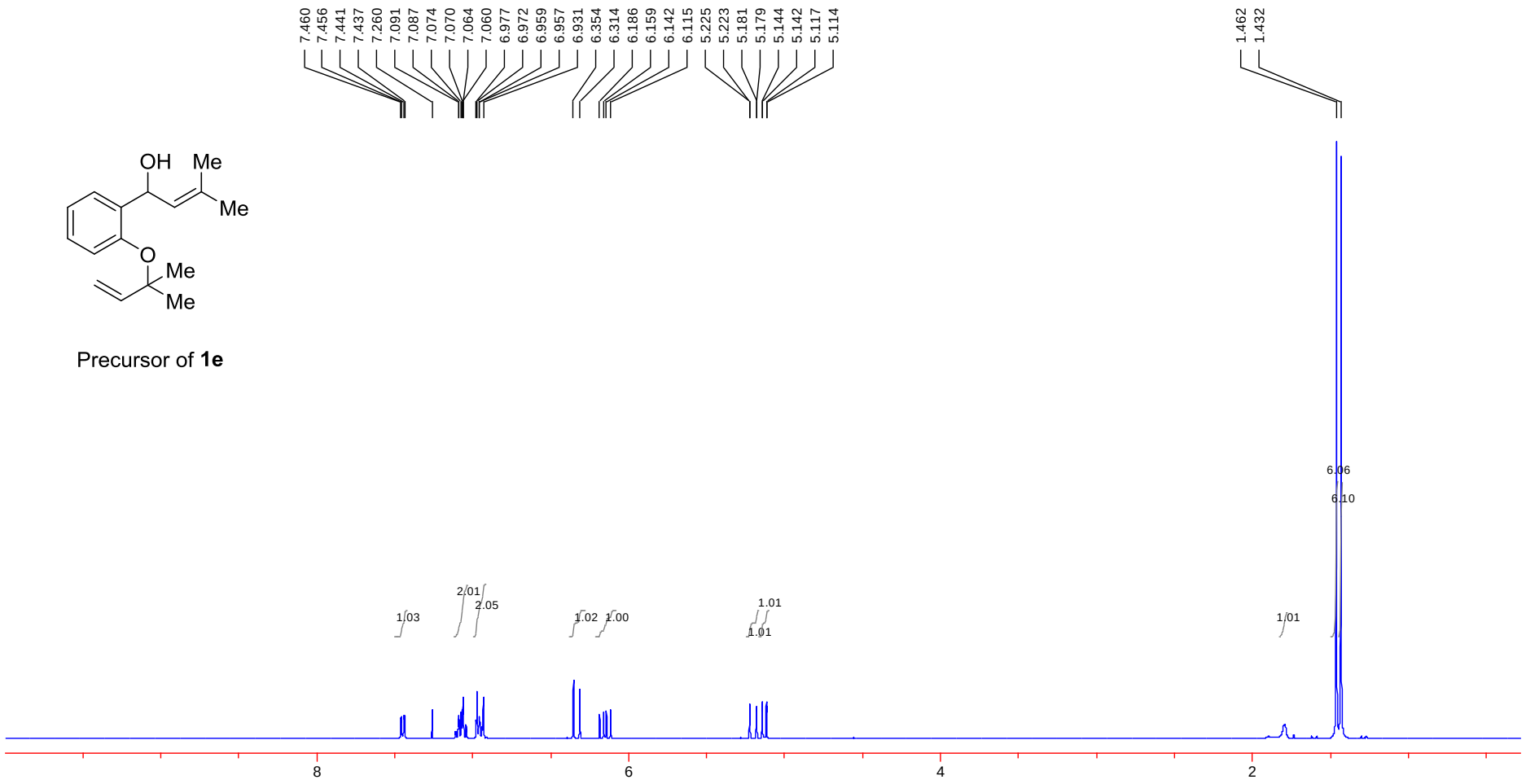
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5.114
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1.432
OH
Me
Me
O
Me
Me
Precursor of 1e
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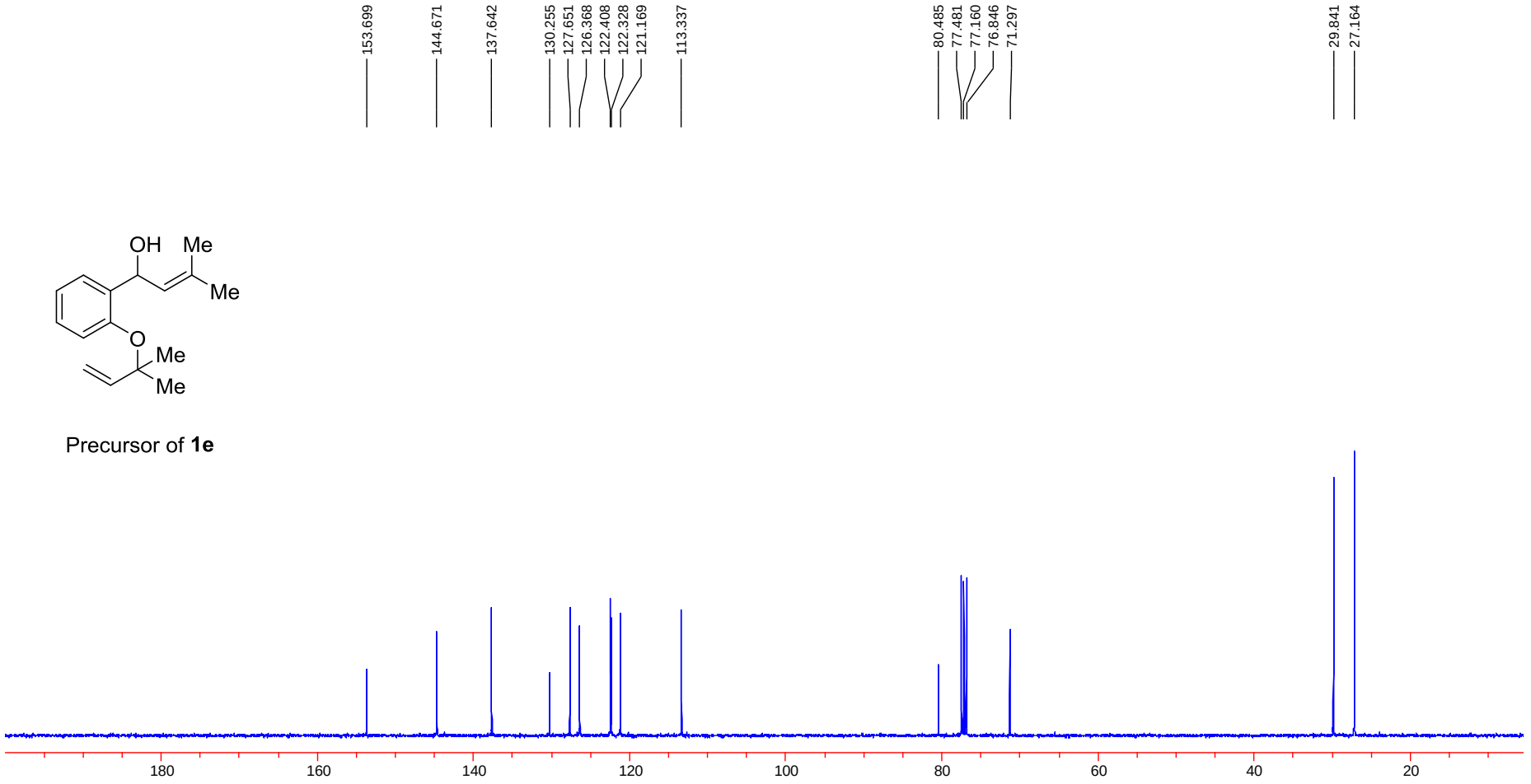

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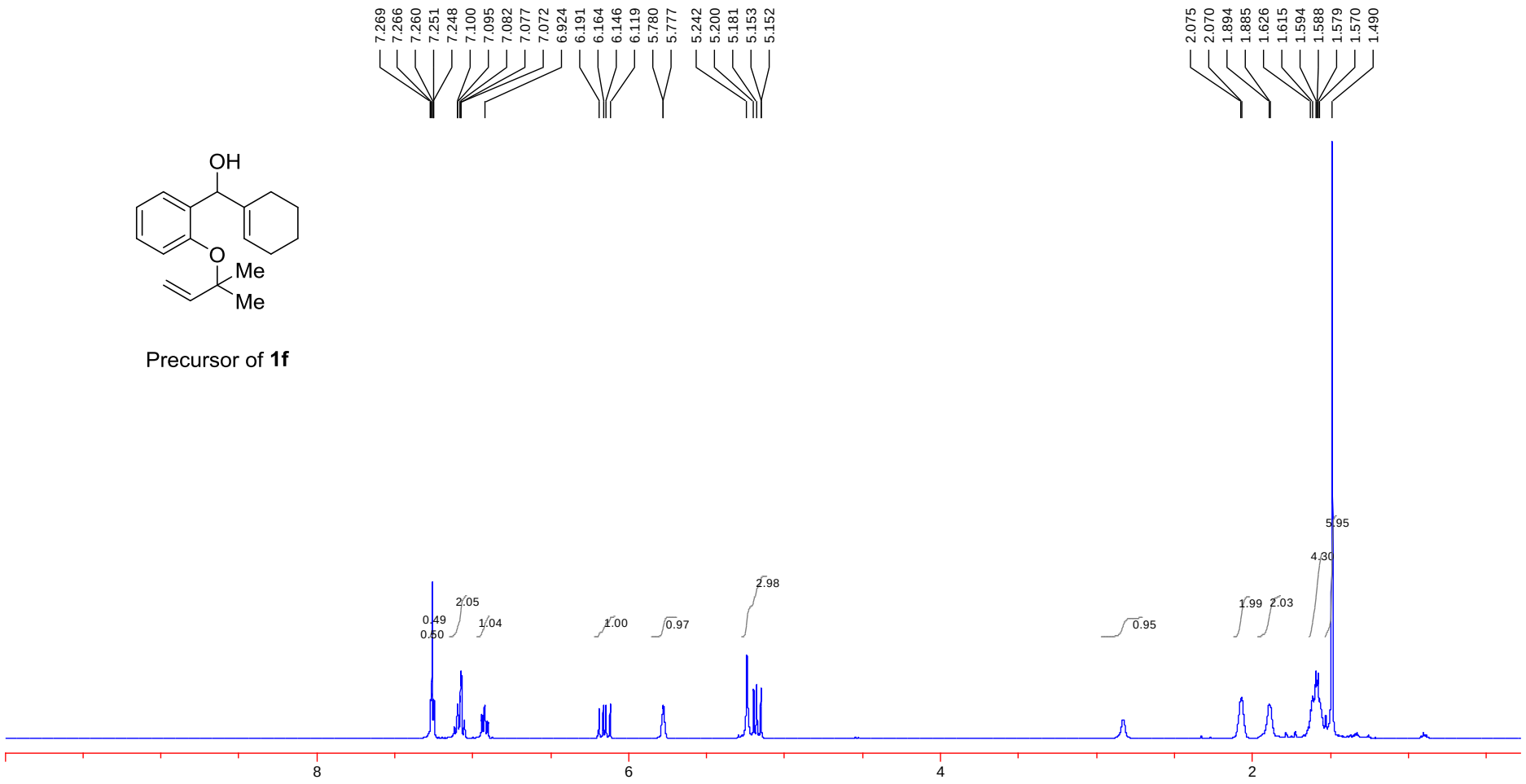

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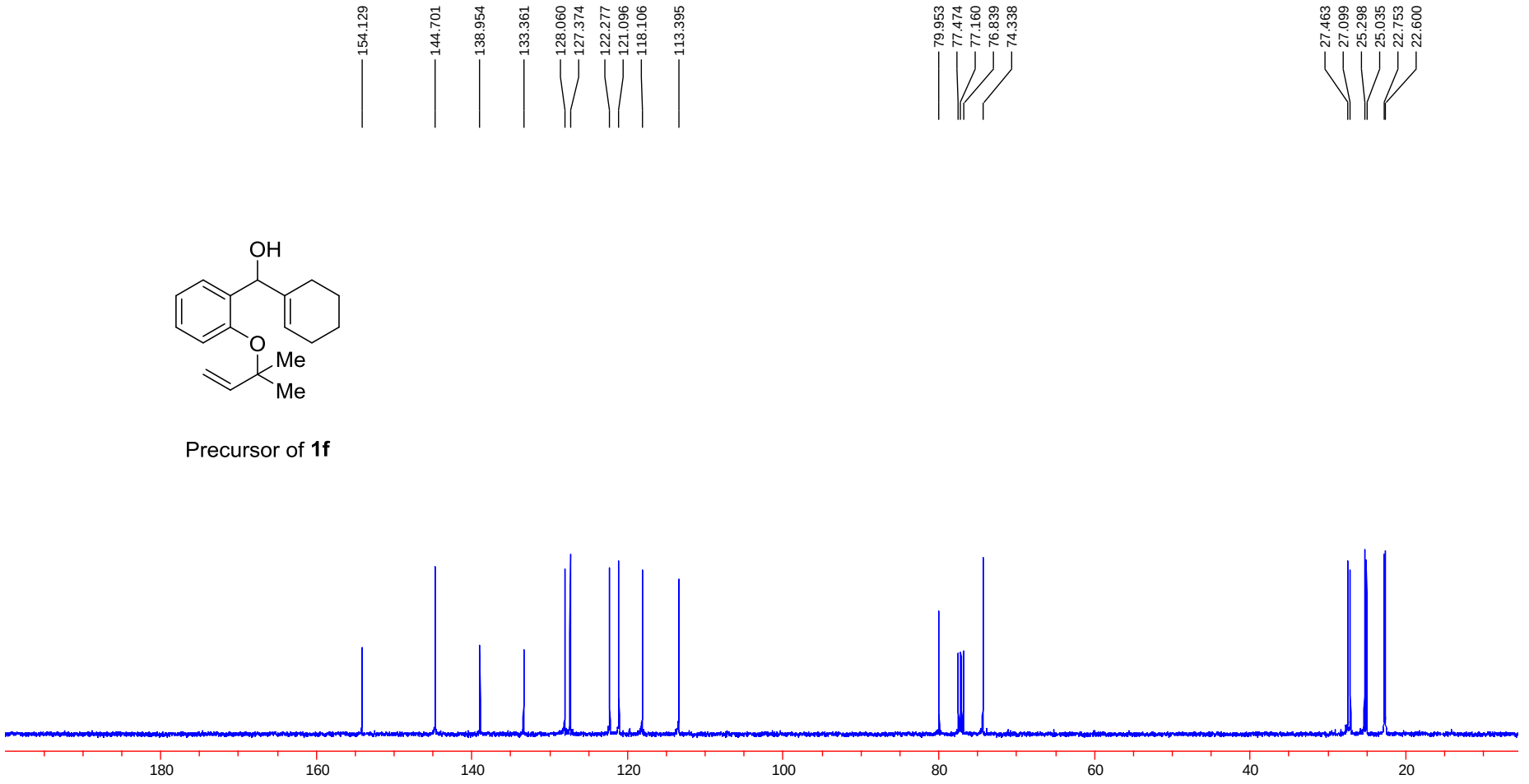

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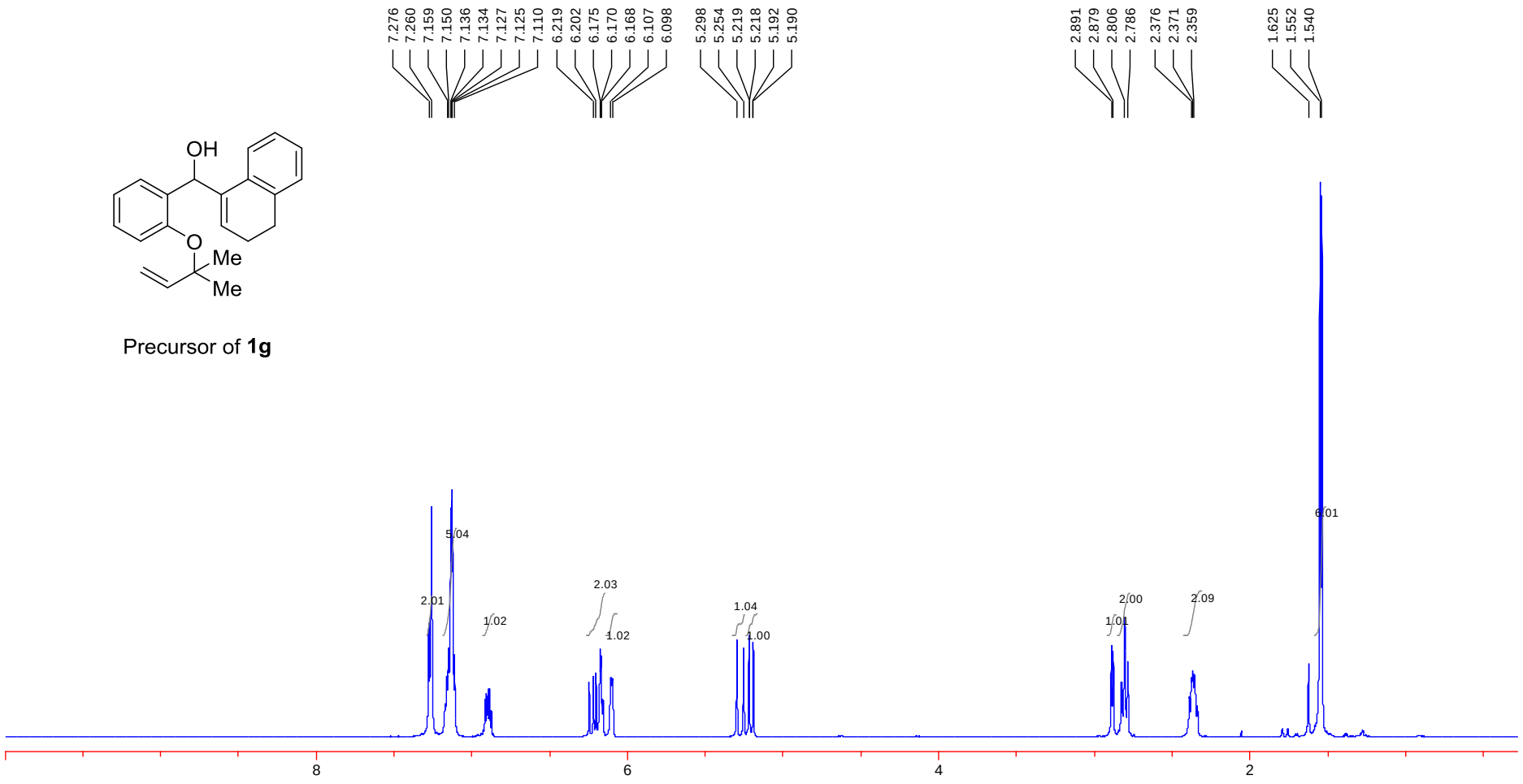

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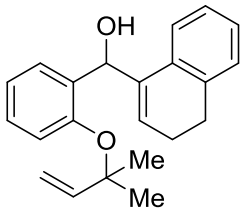

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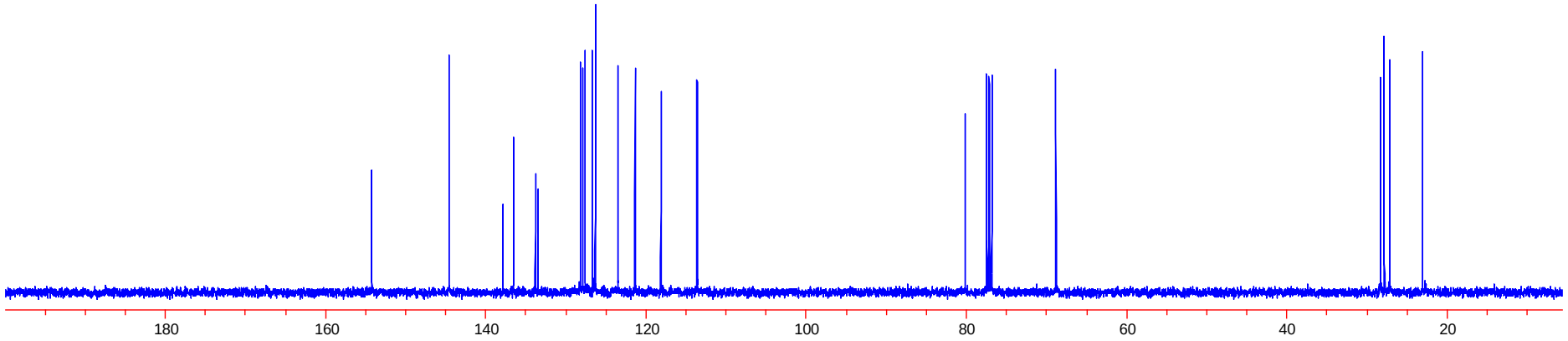

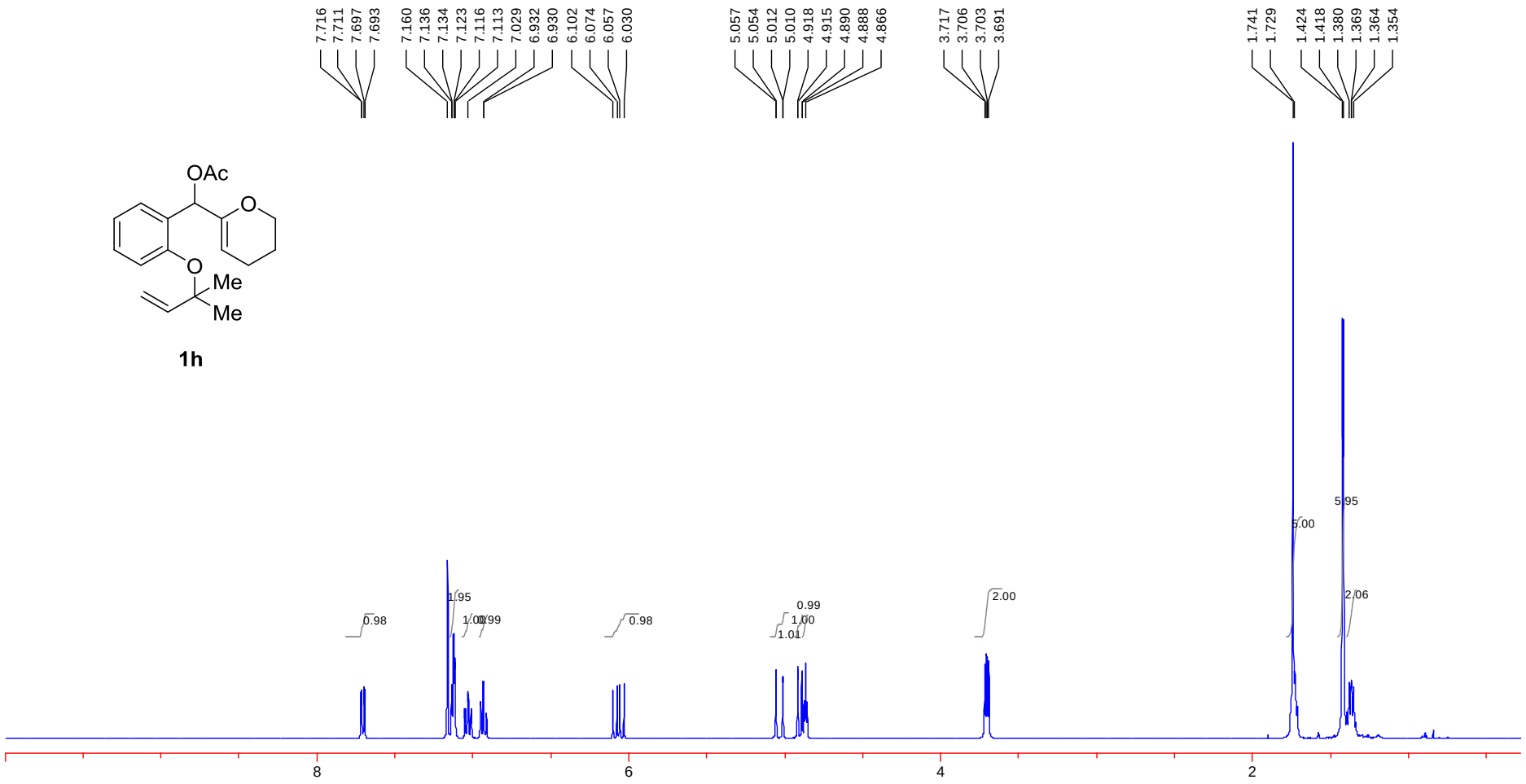
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3.703
3.691
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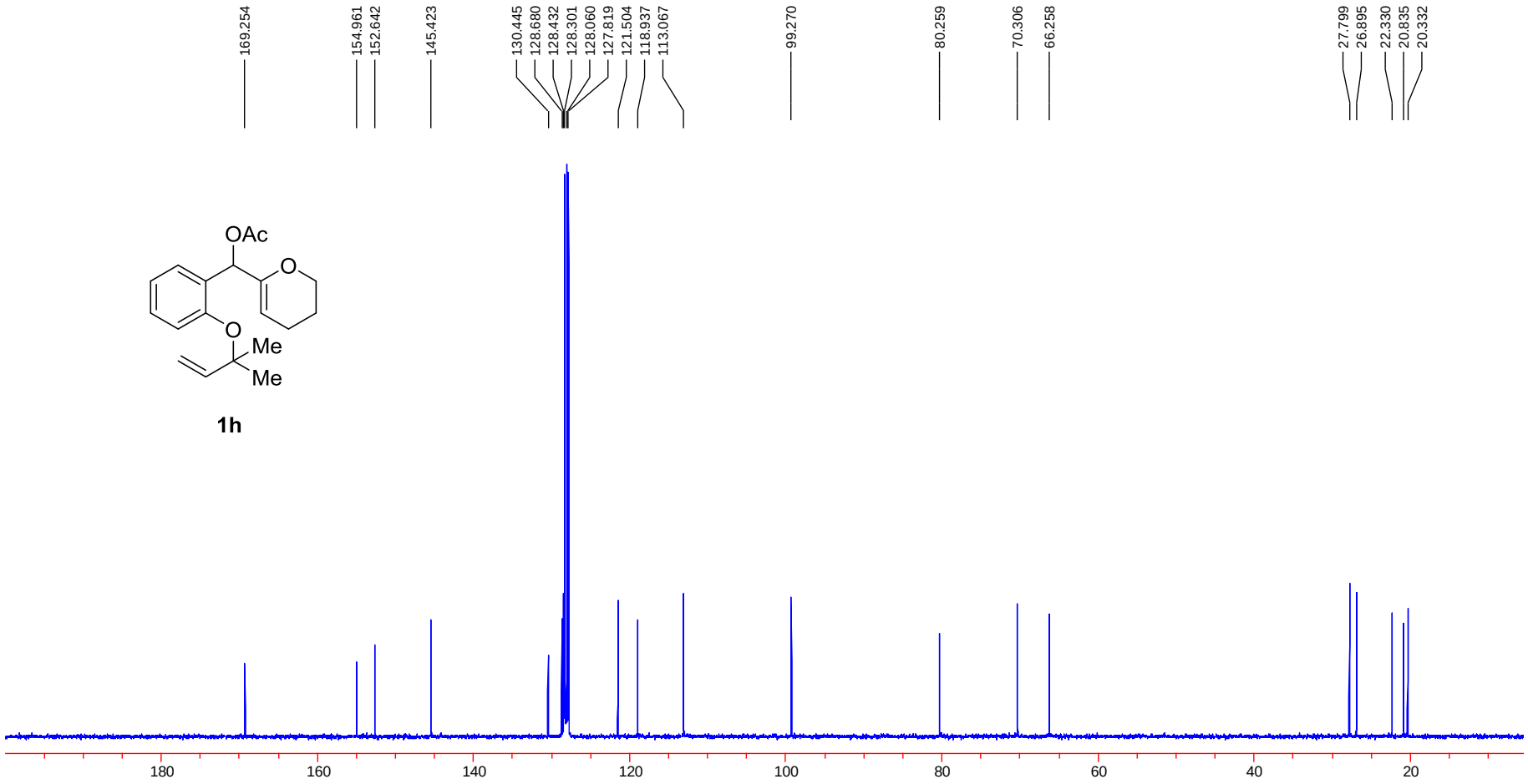
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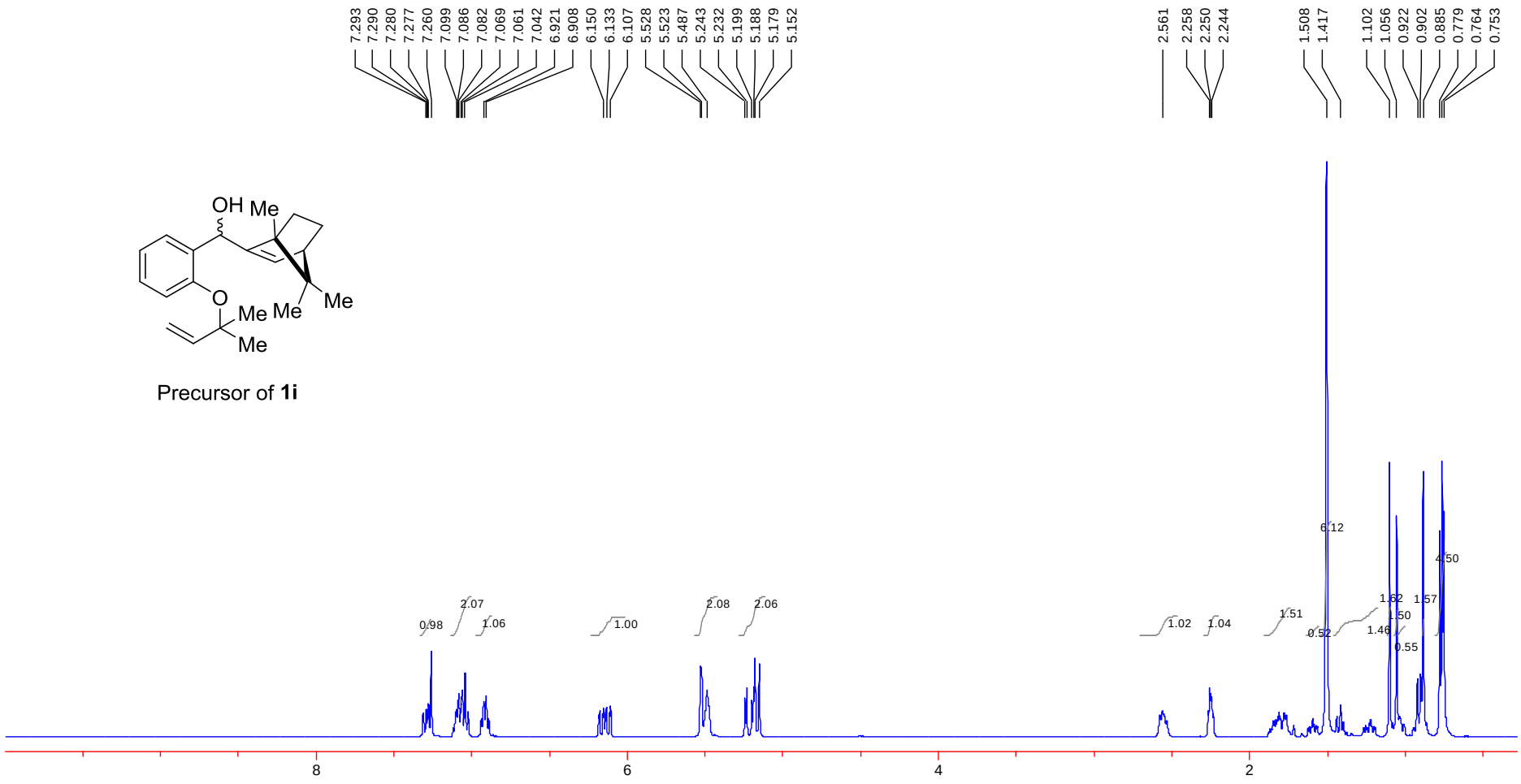
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Precursor of 1i
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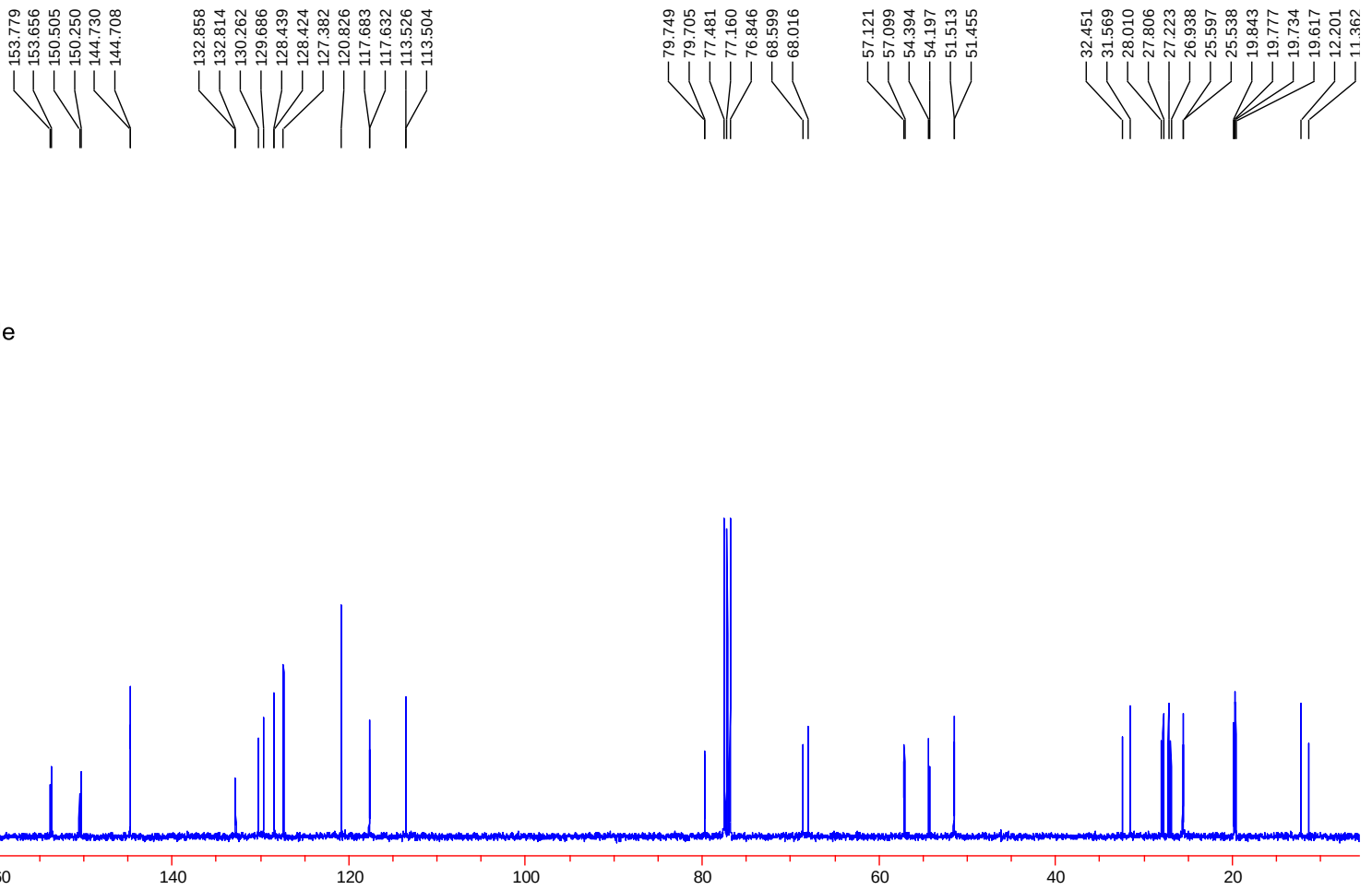

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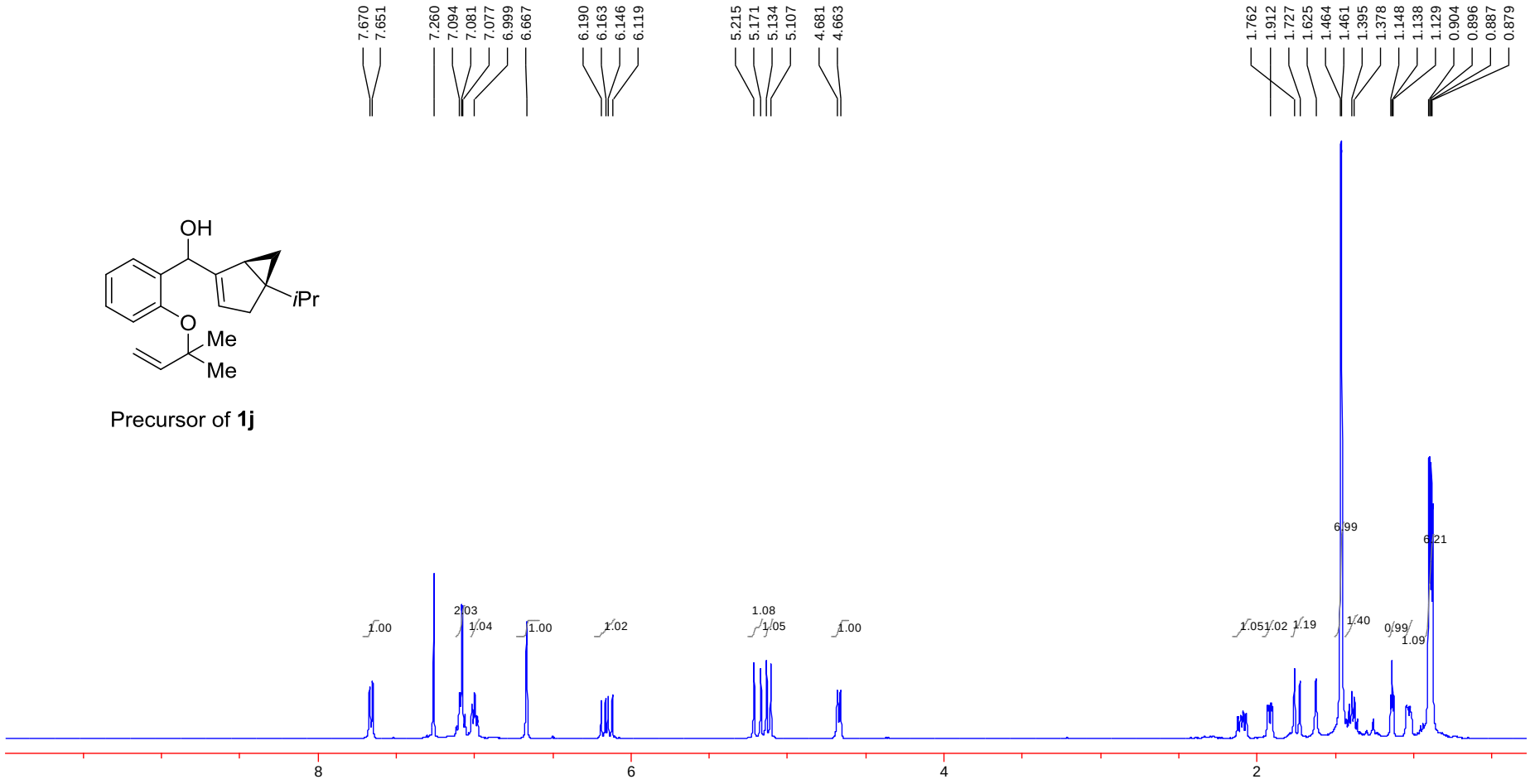
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5.134
5.107
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4.663
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1.464
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OH
O
Me
Me
iPr
Precursor of 1j
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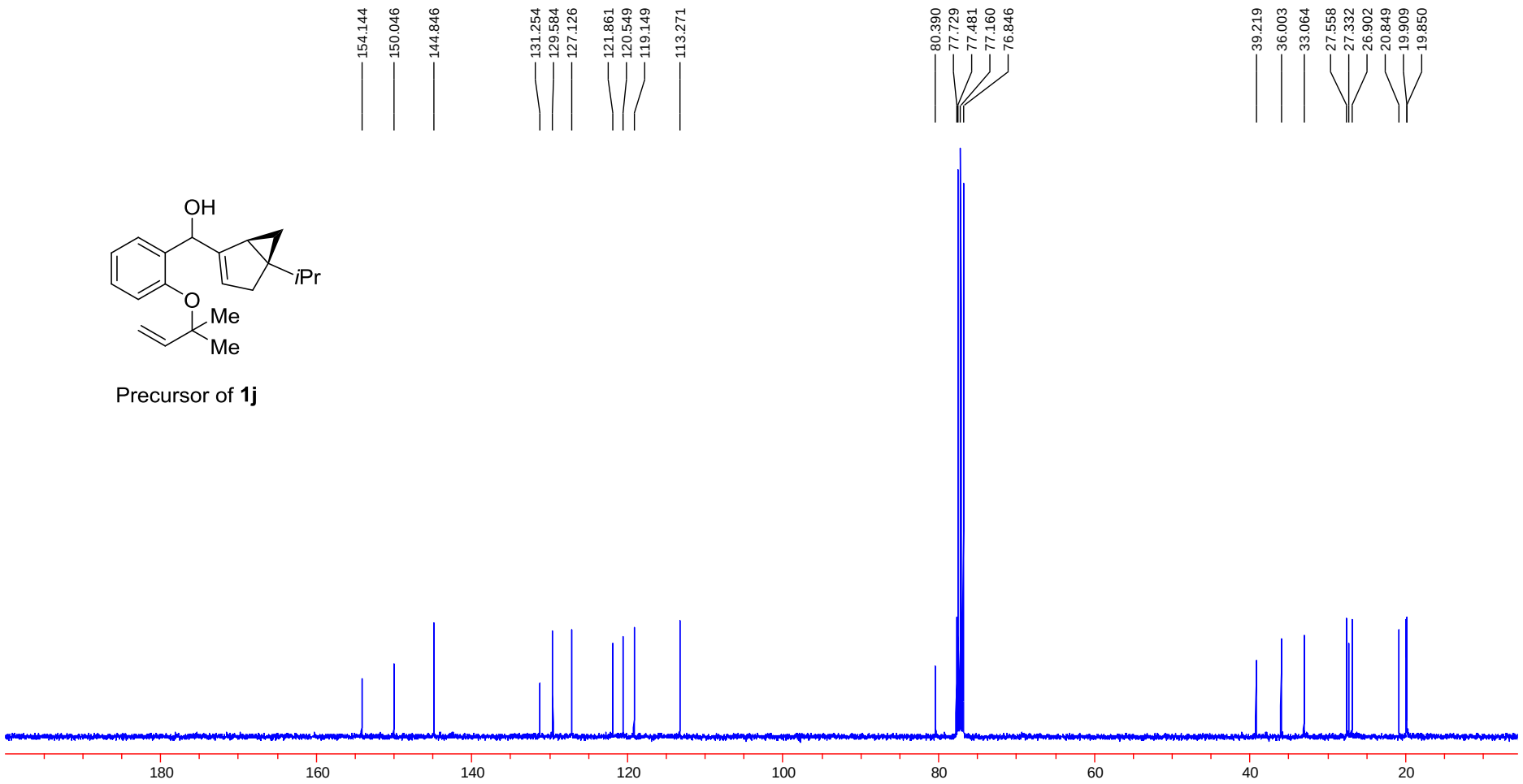

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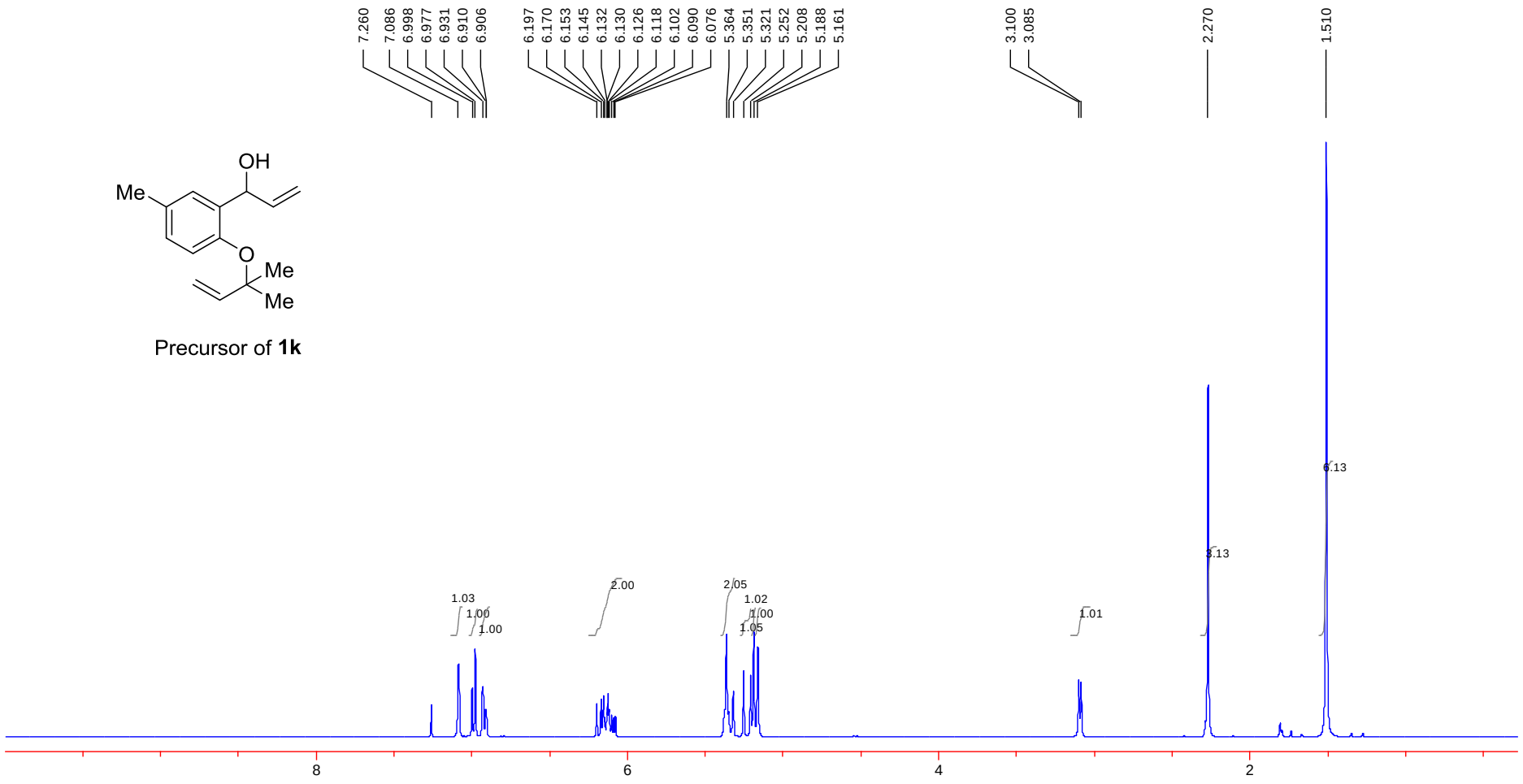

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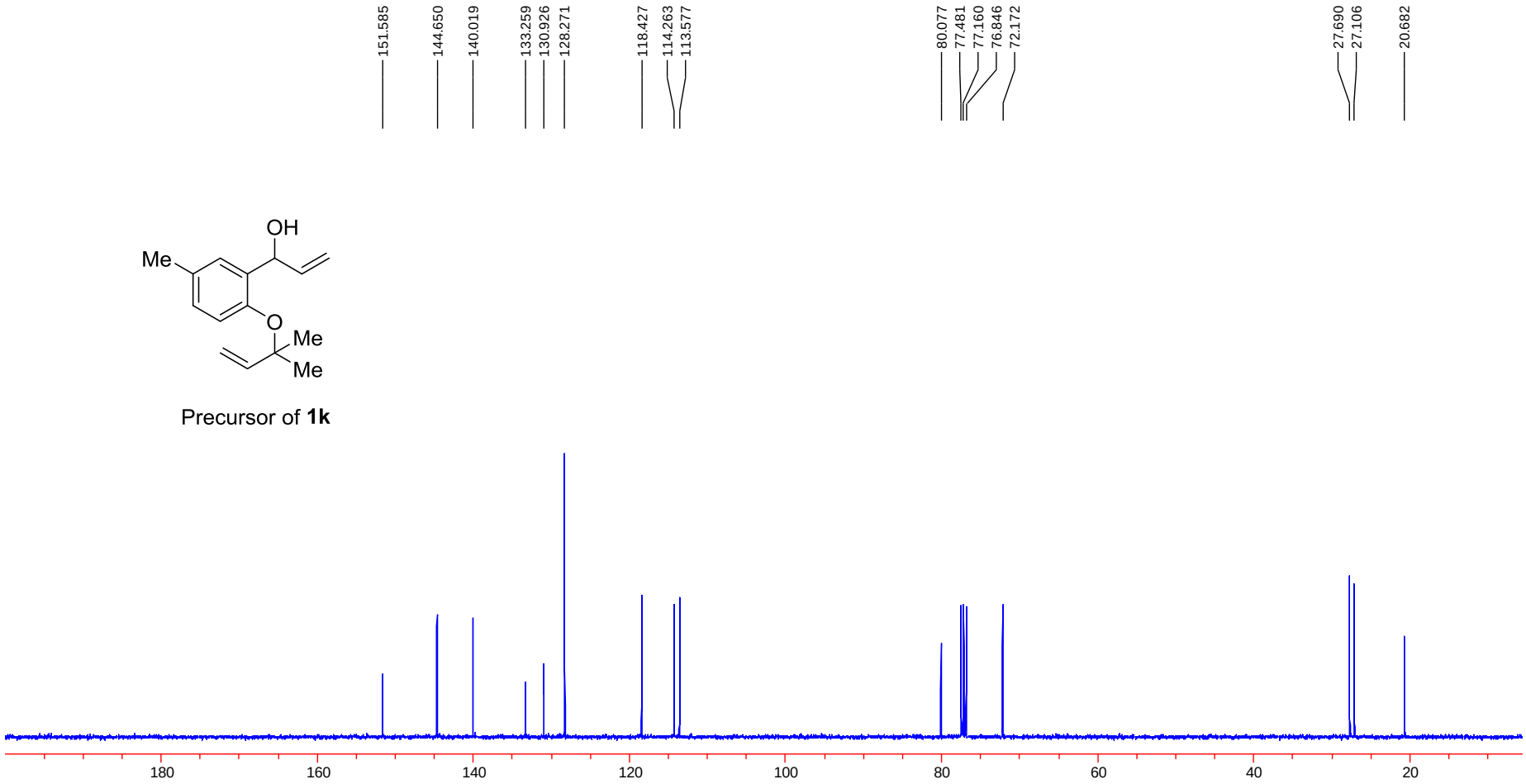

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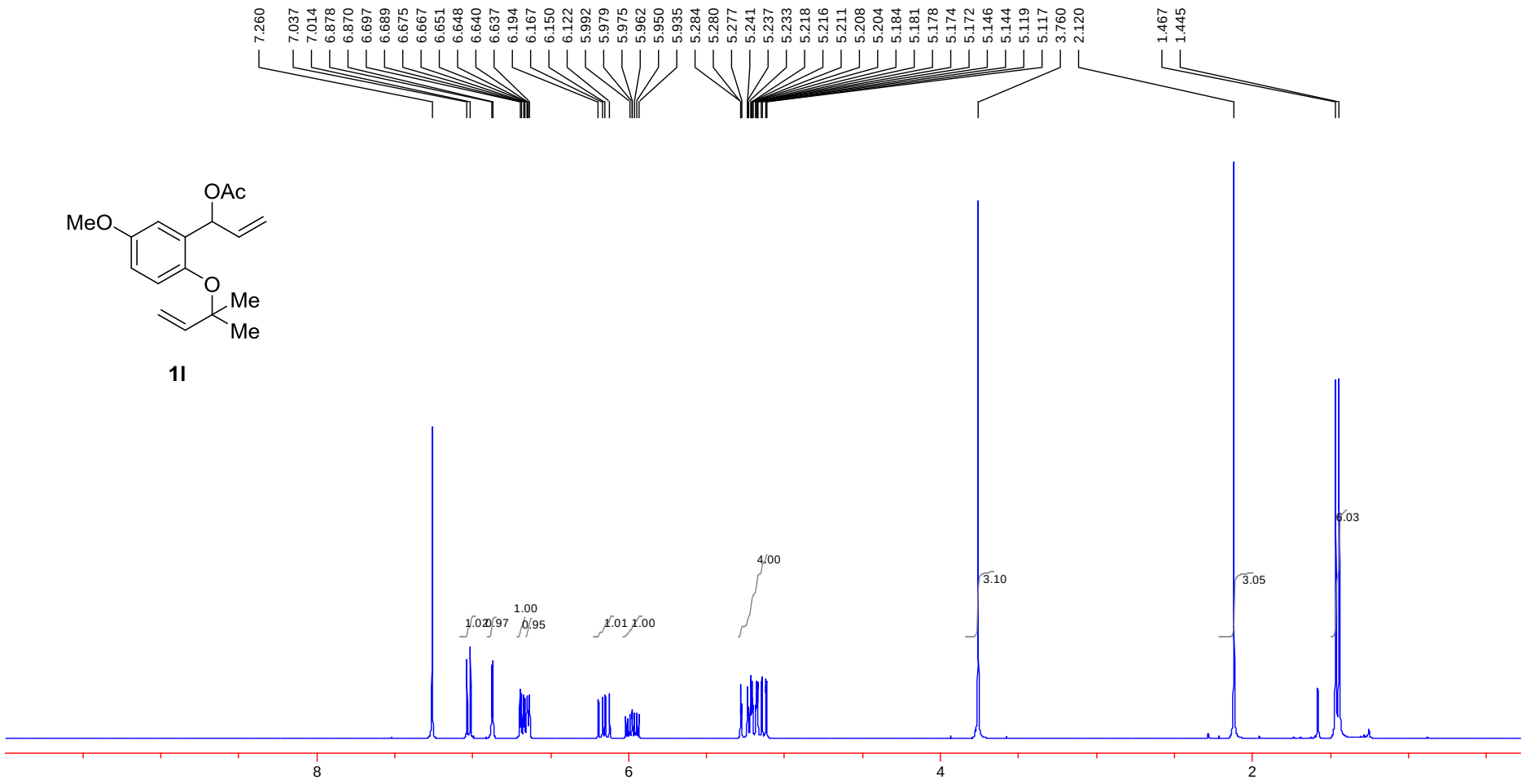
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5.216
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5.208
5.204
5.184
5.181
5.178
5.174
5.172
5.146
5.144
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5.117
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1.445
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MeO
O
Me
Me
1l
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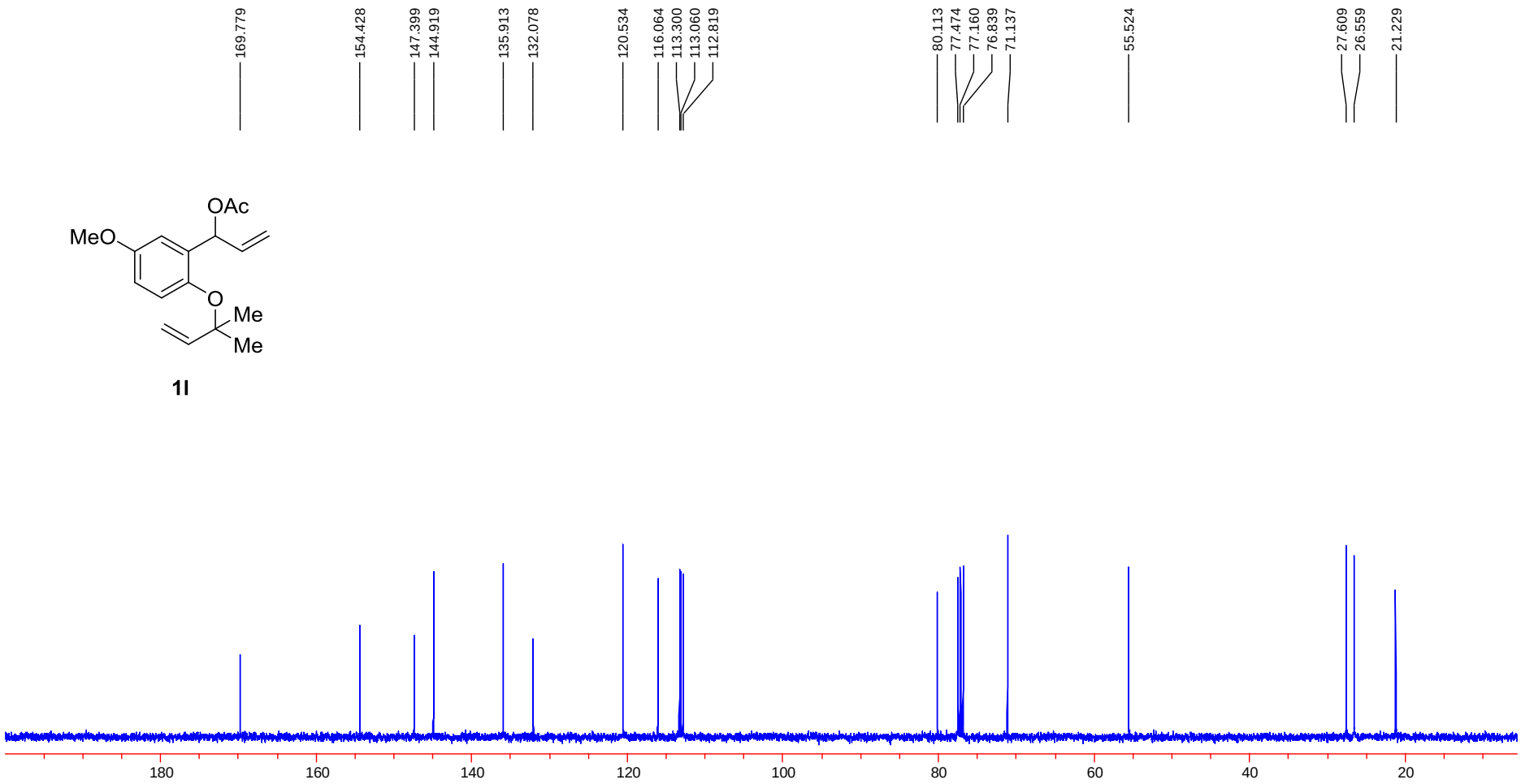
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76.839
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Me
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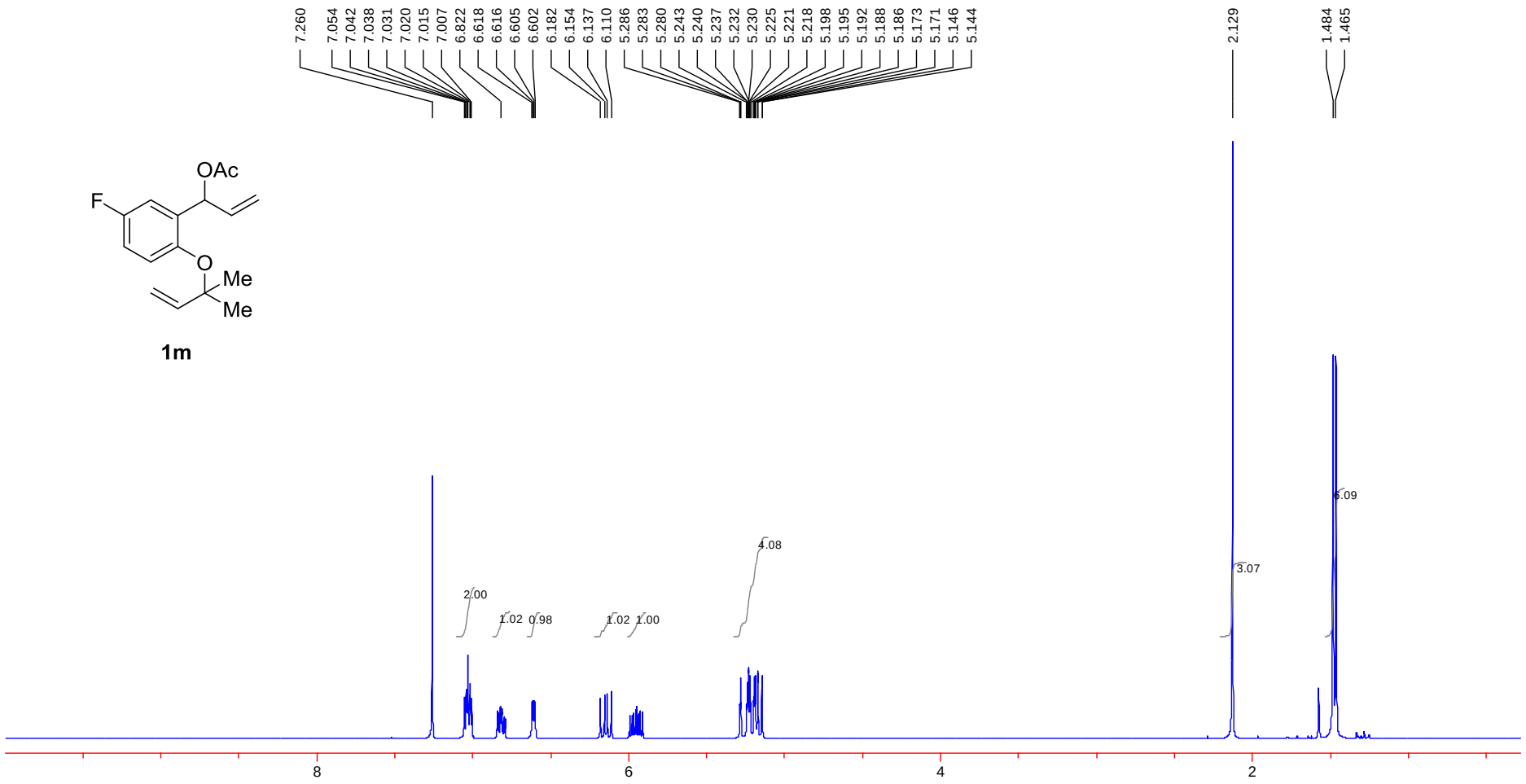
1l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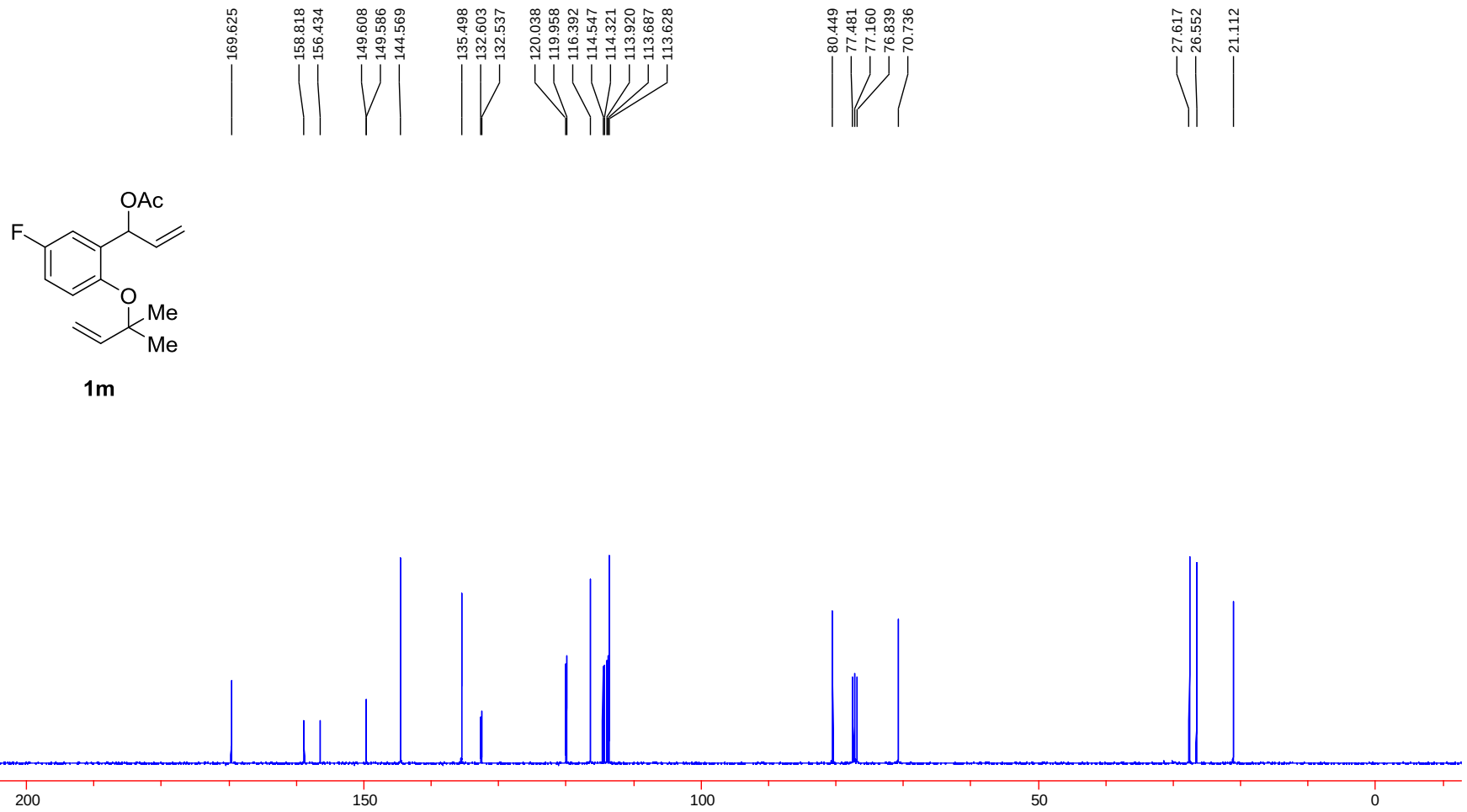
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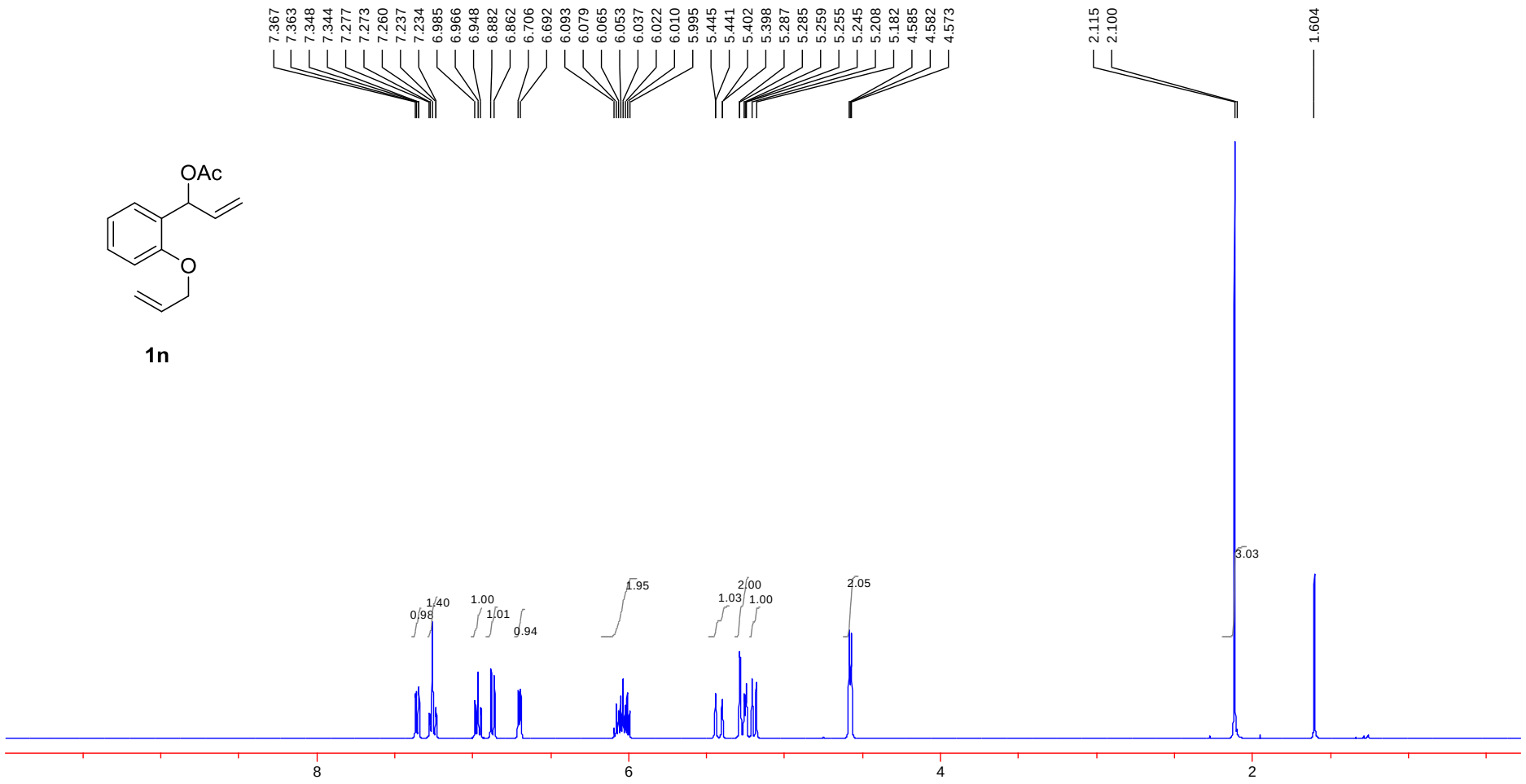
1m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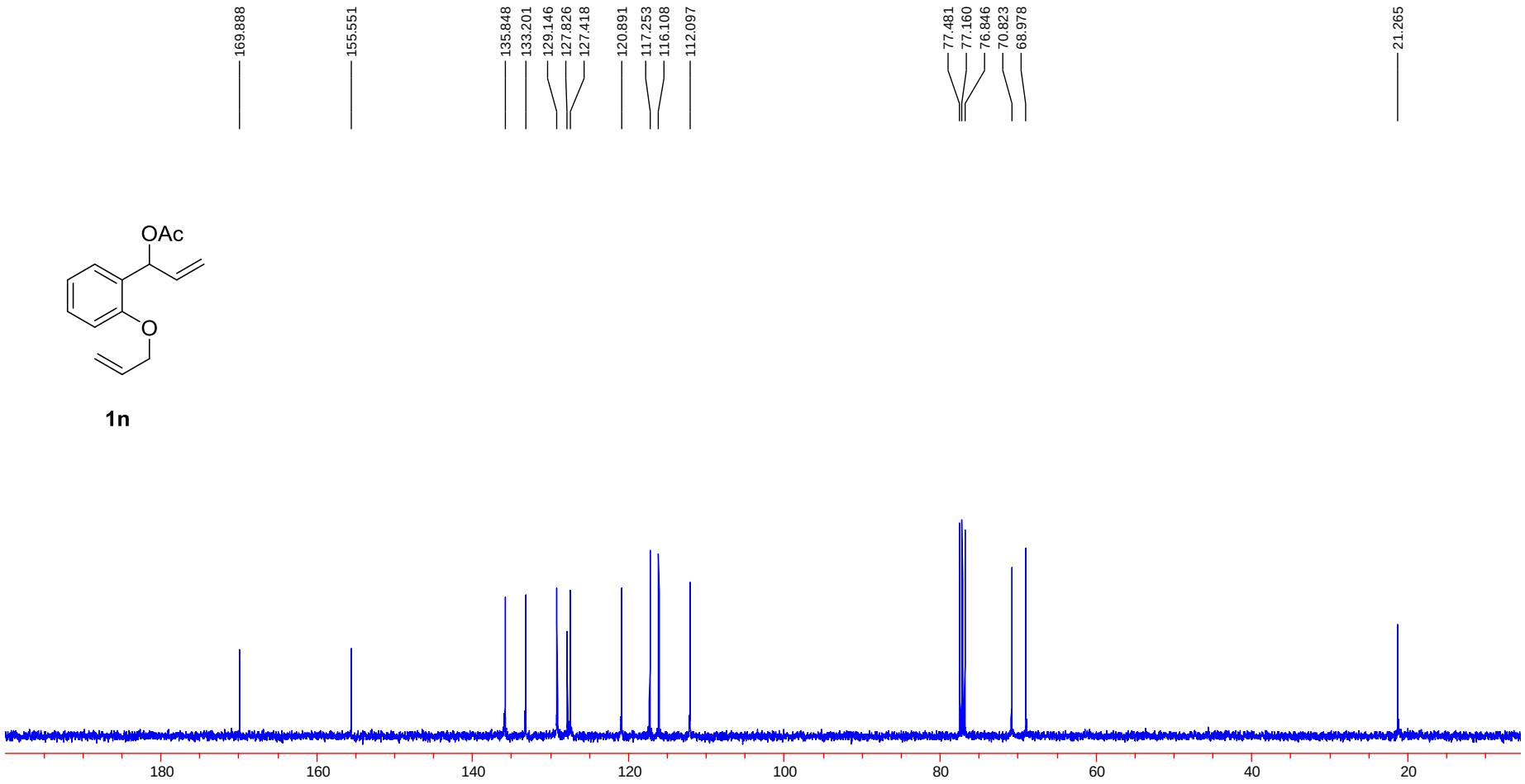
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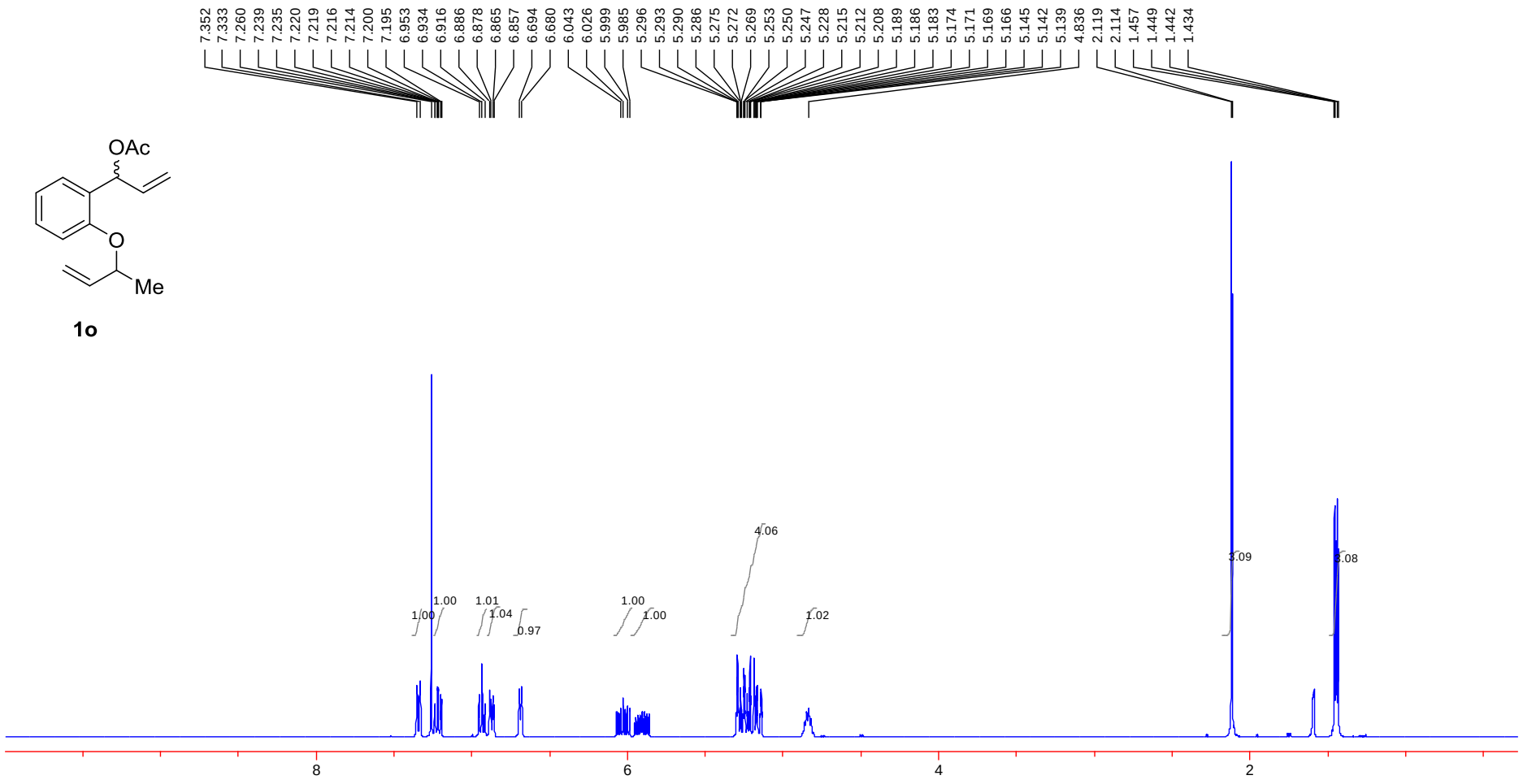
1n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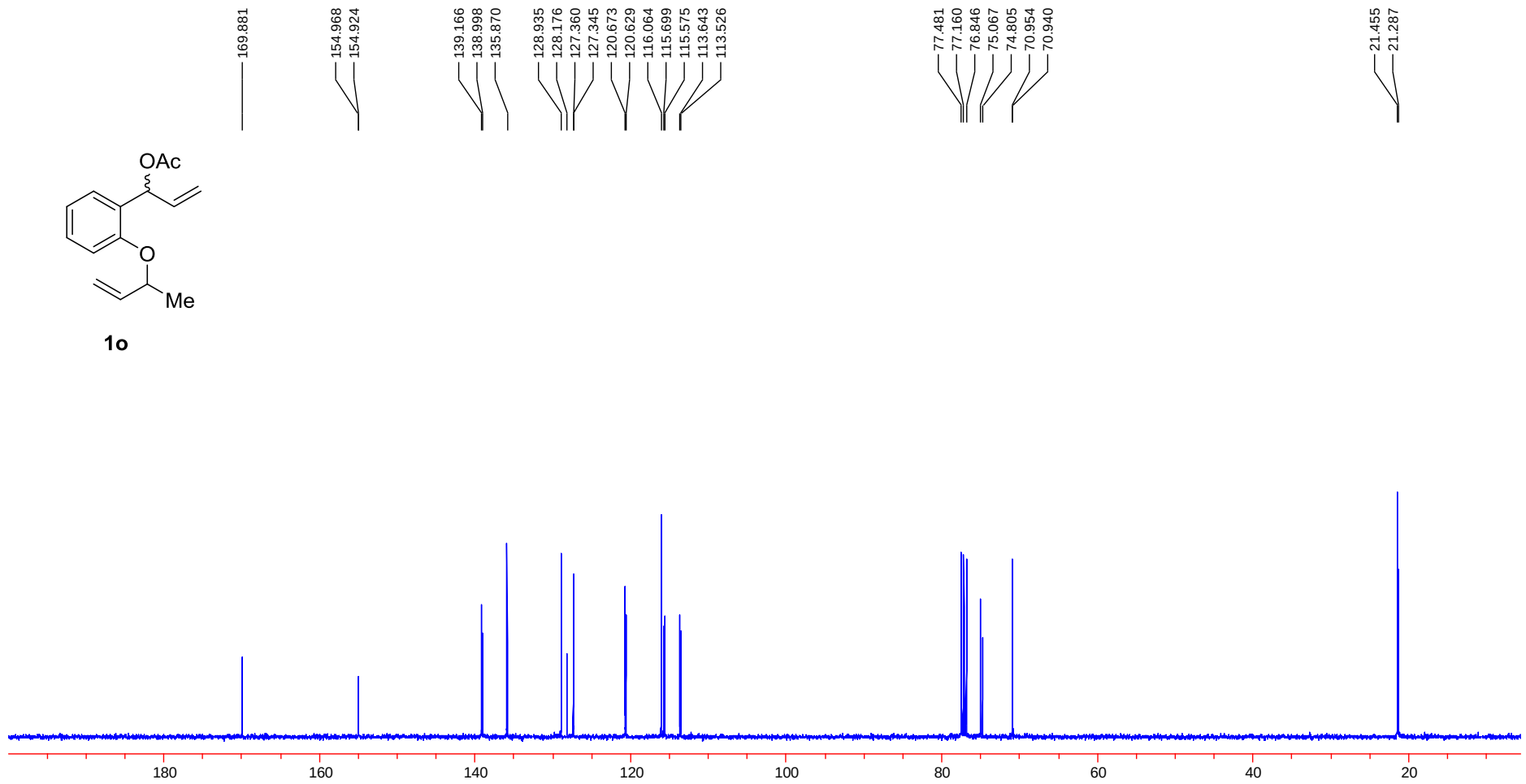
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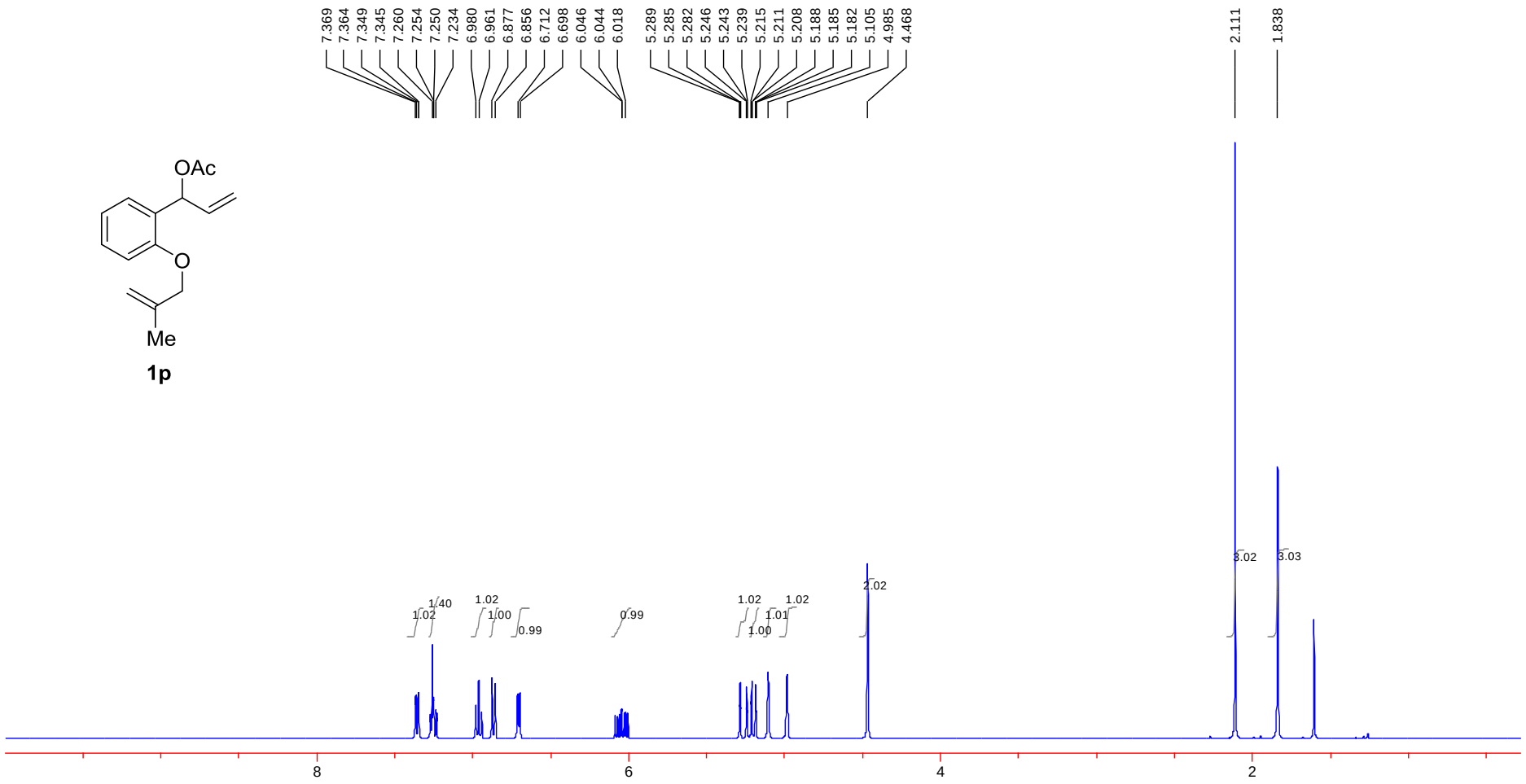
1o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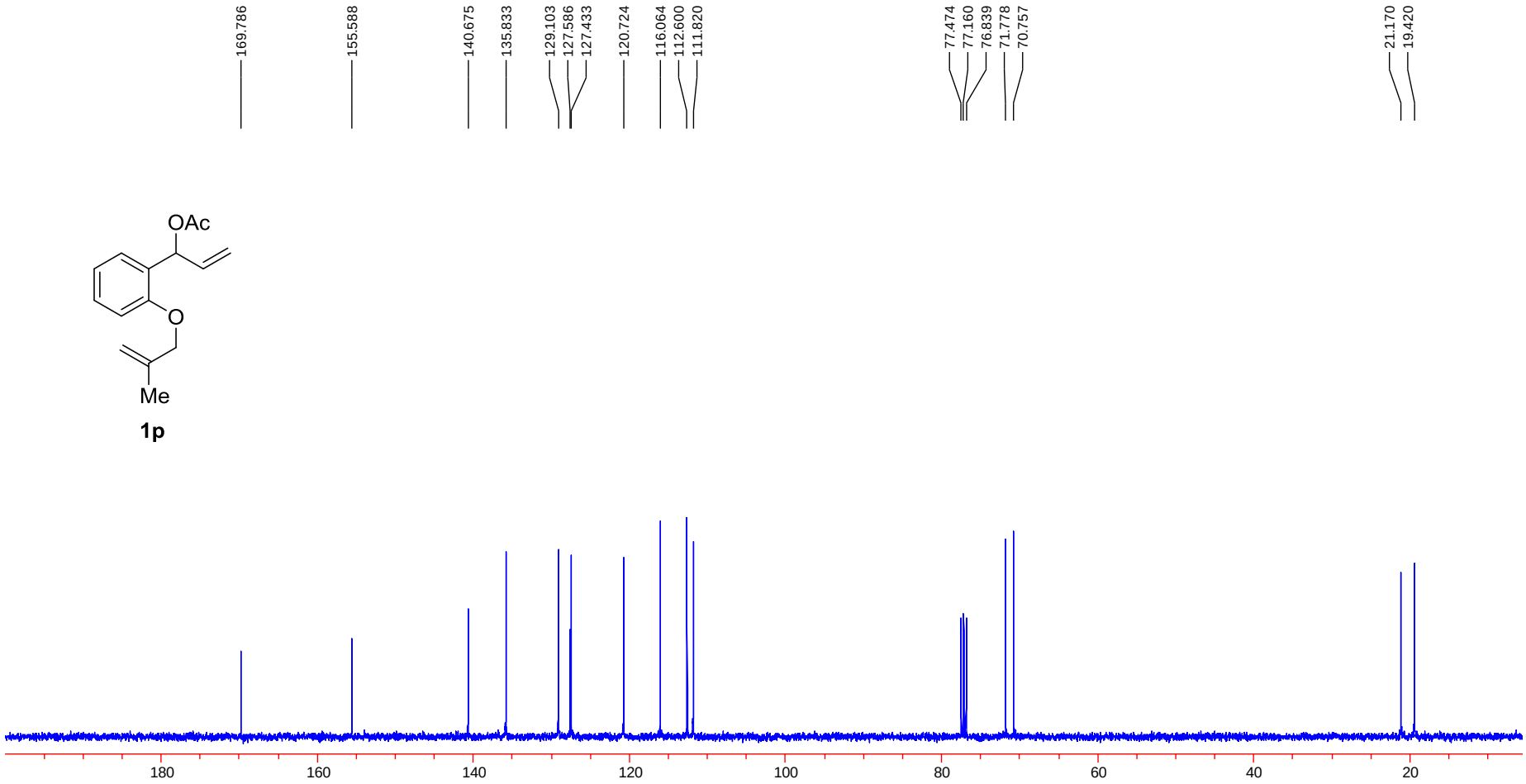
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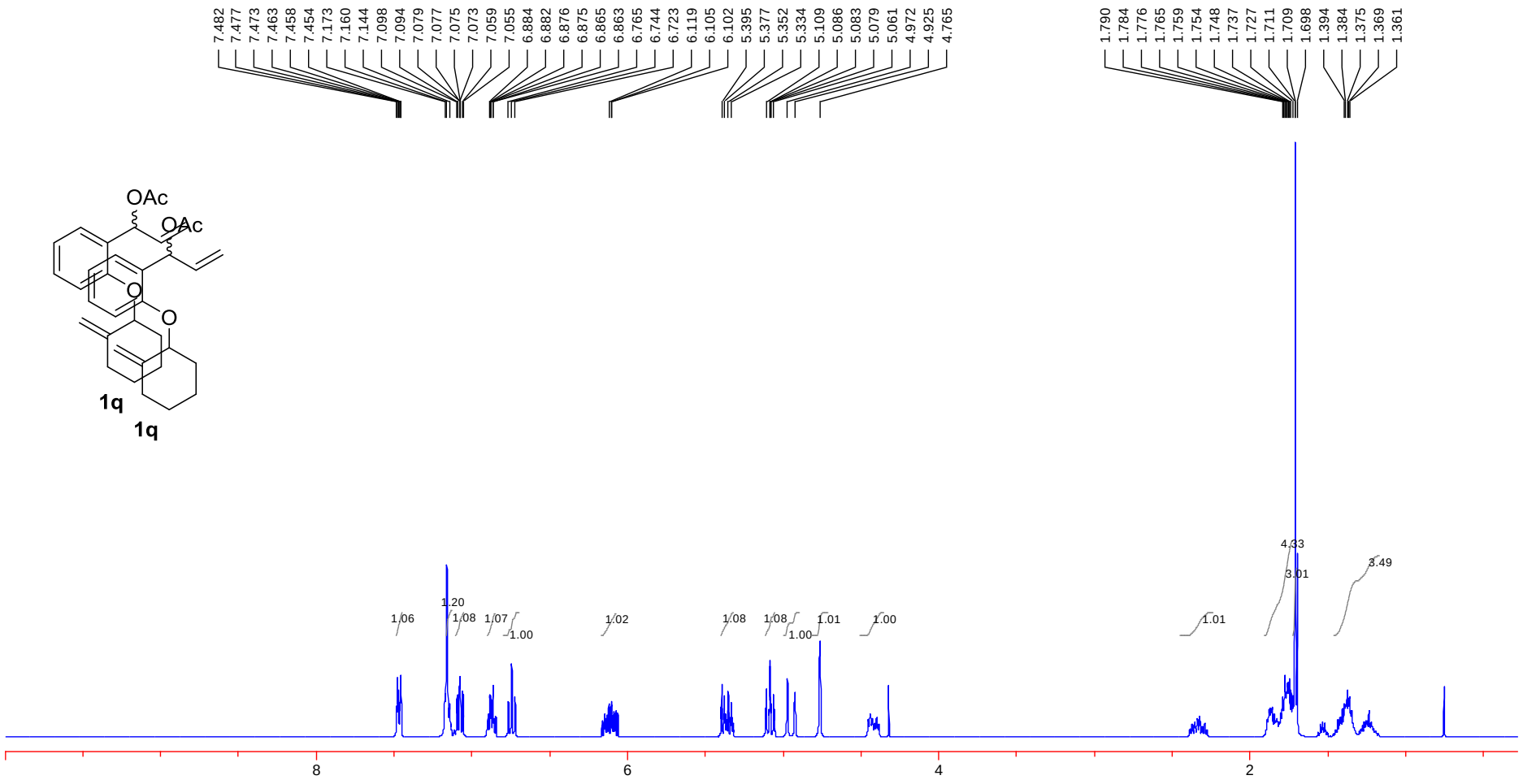
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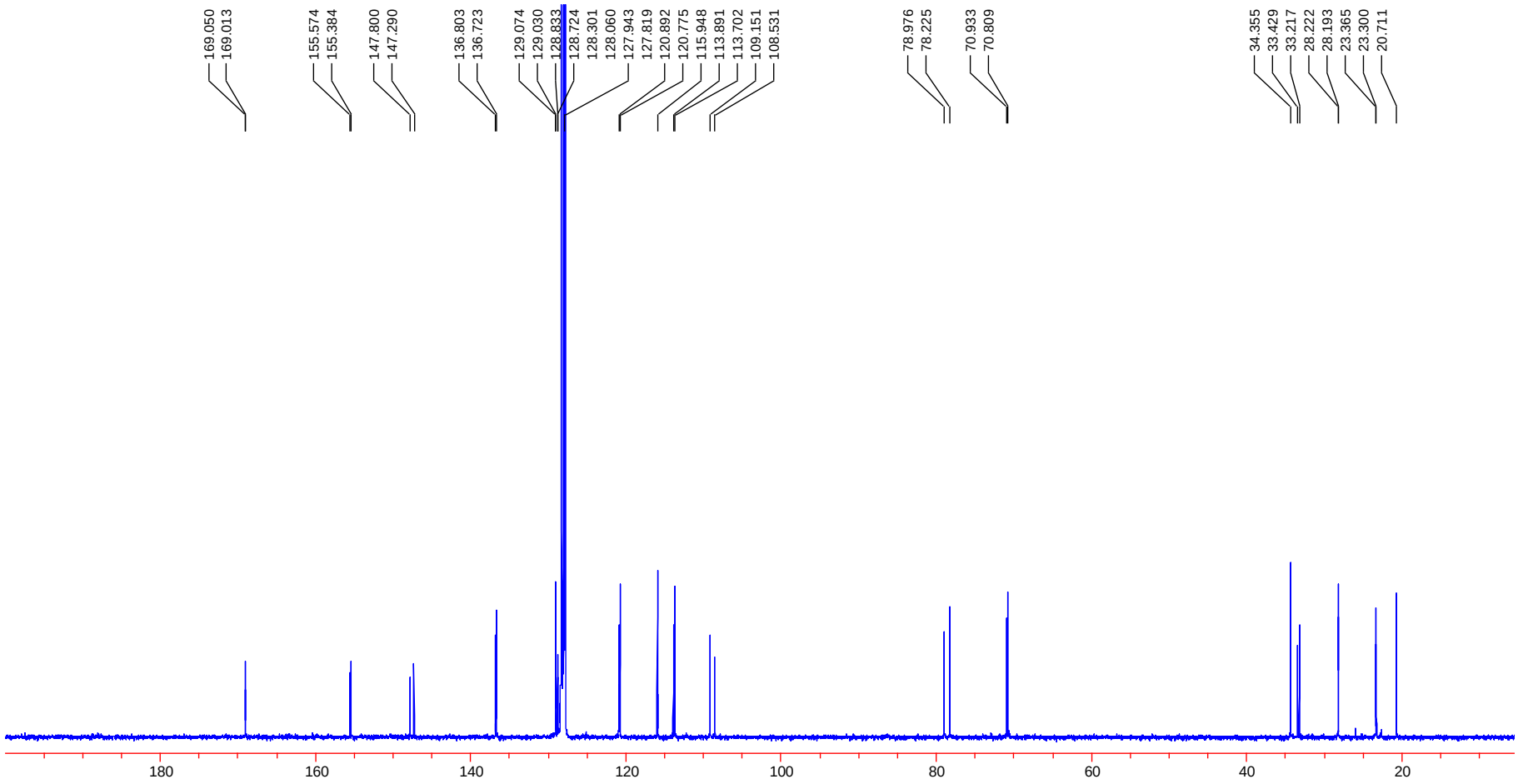
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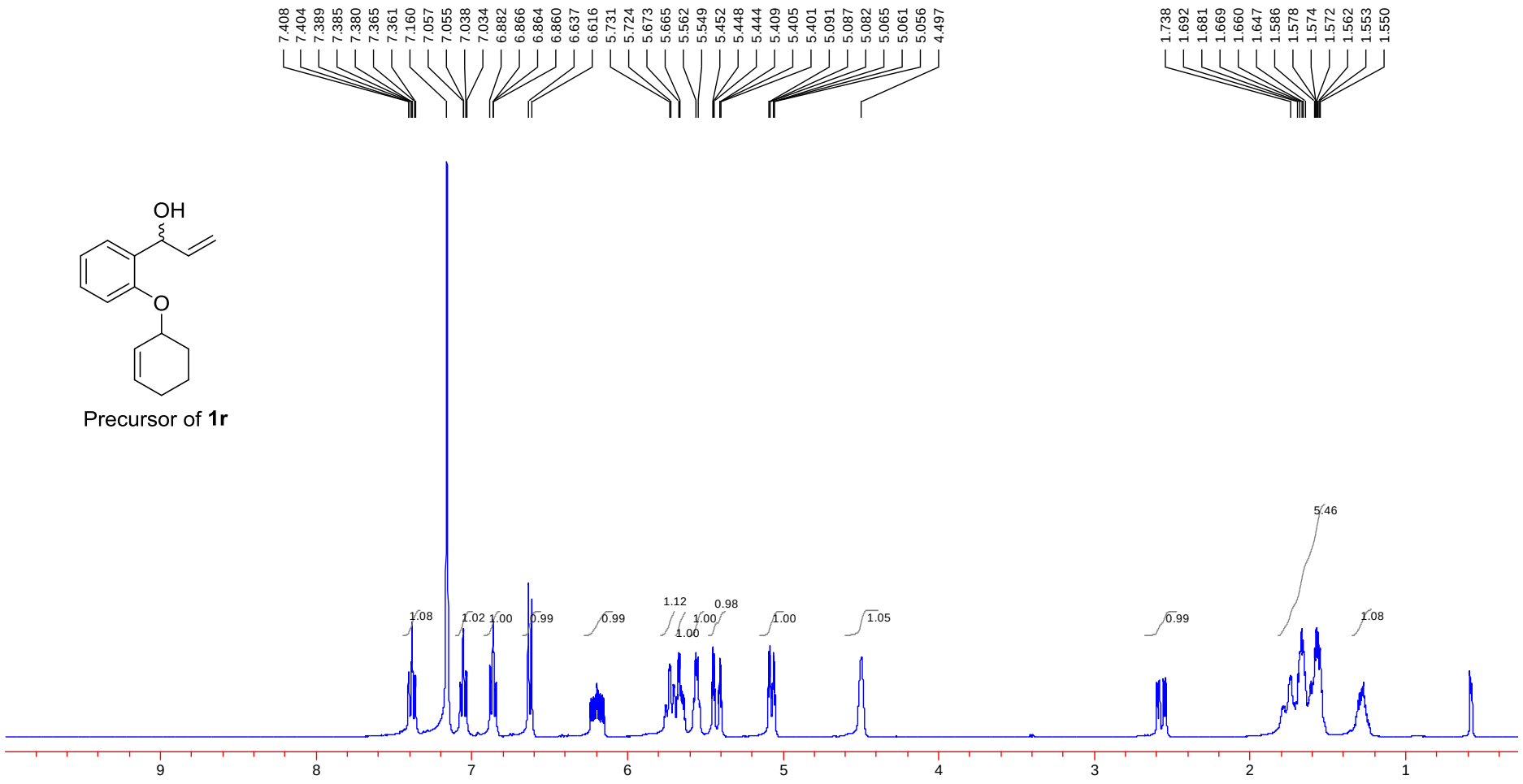
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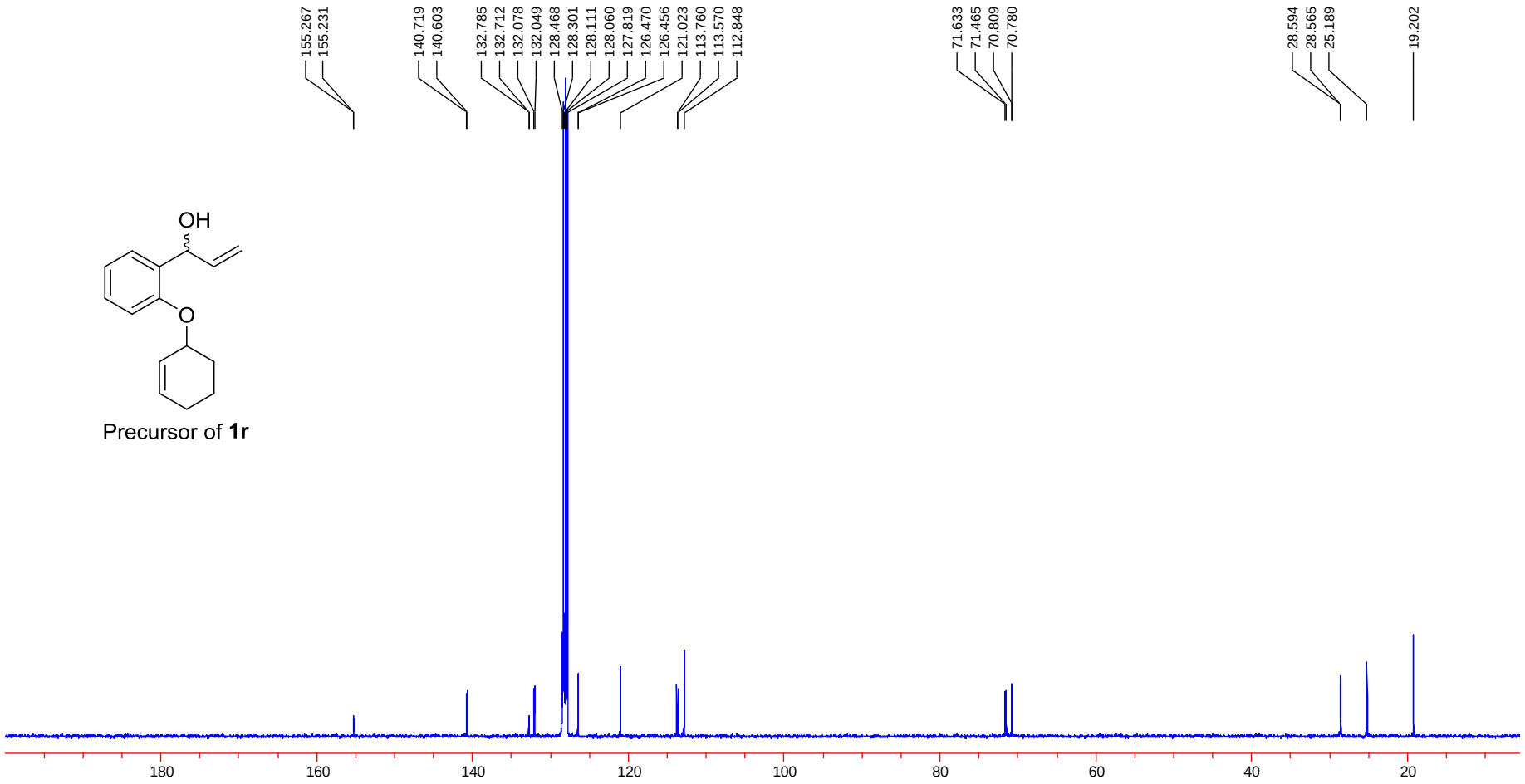
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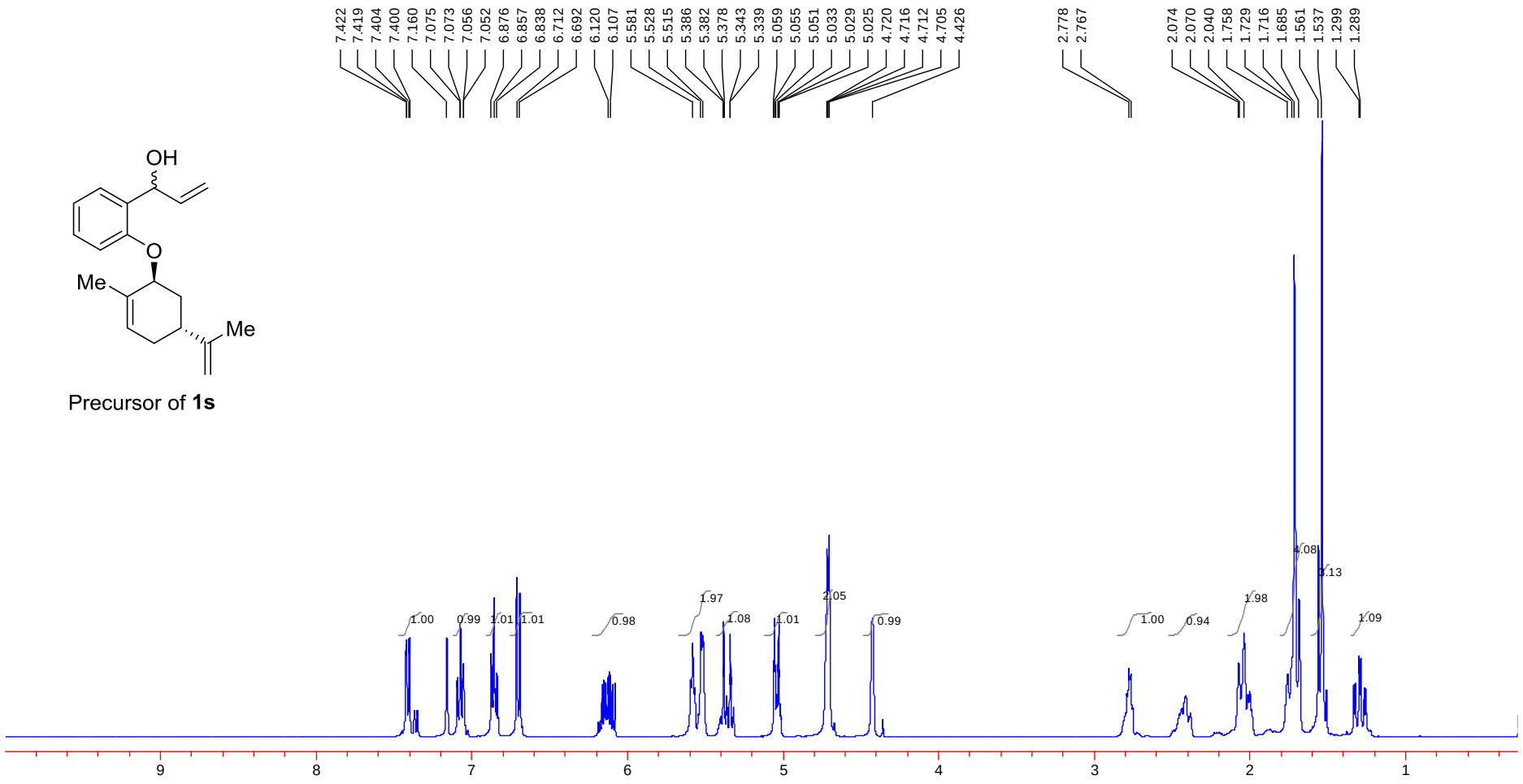

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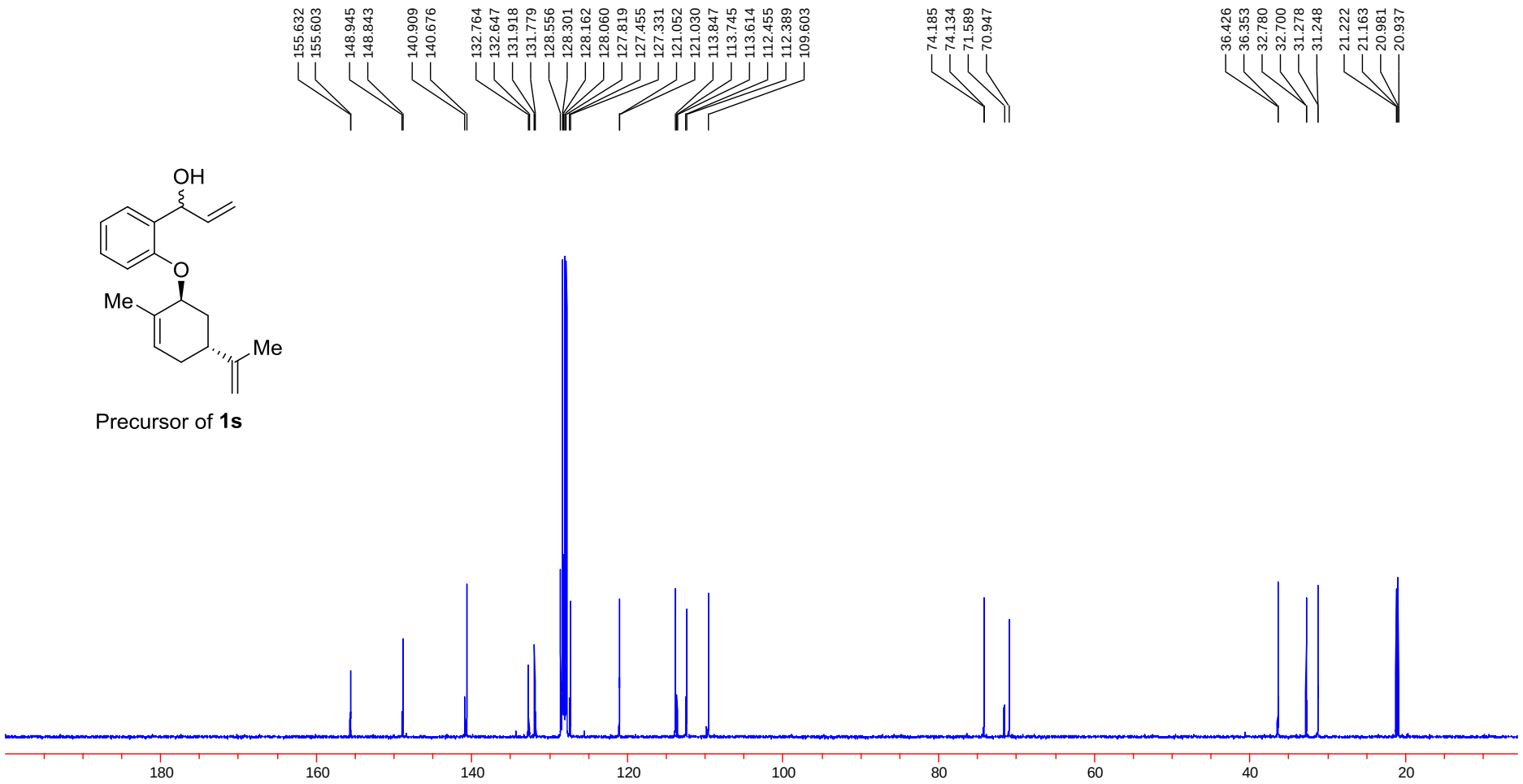

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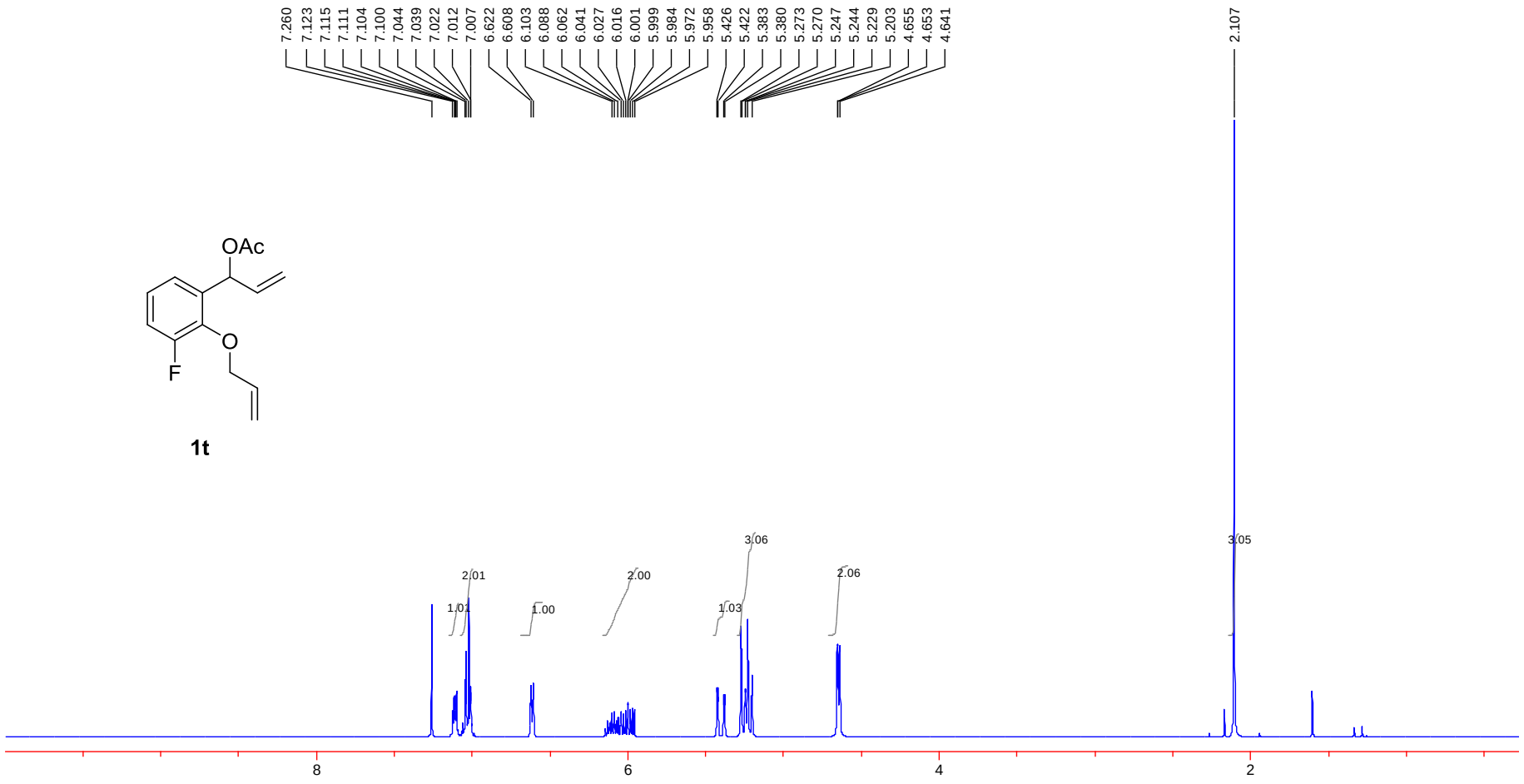
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6.088
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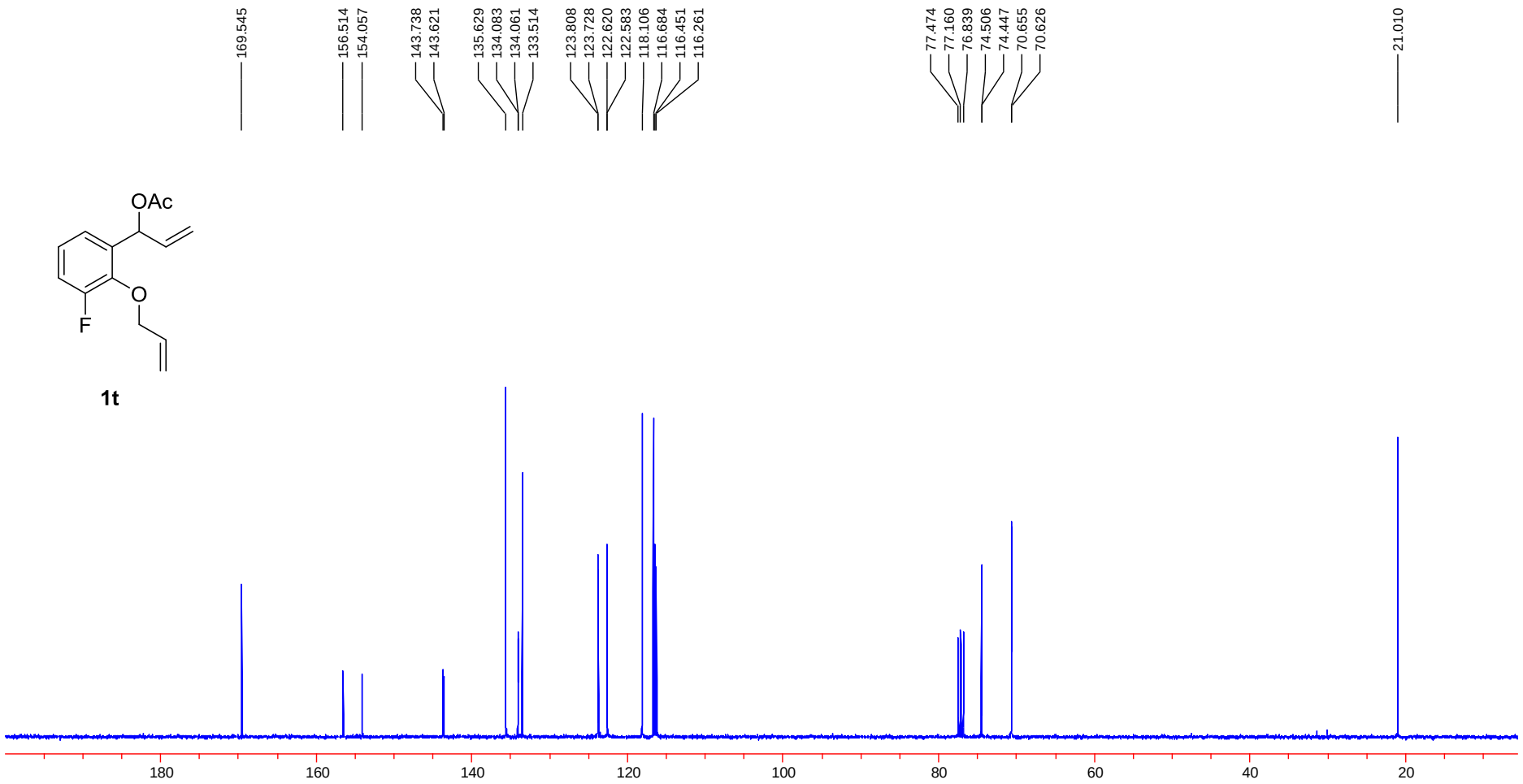
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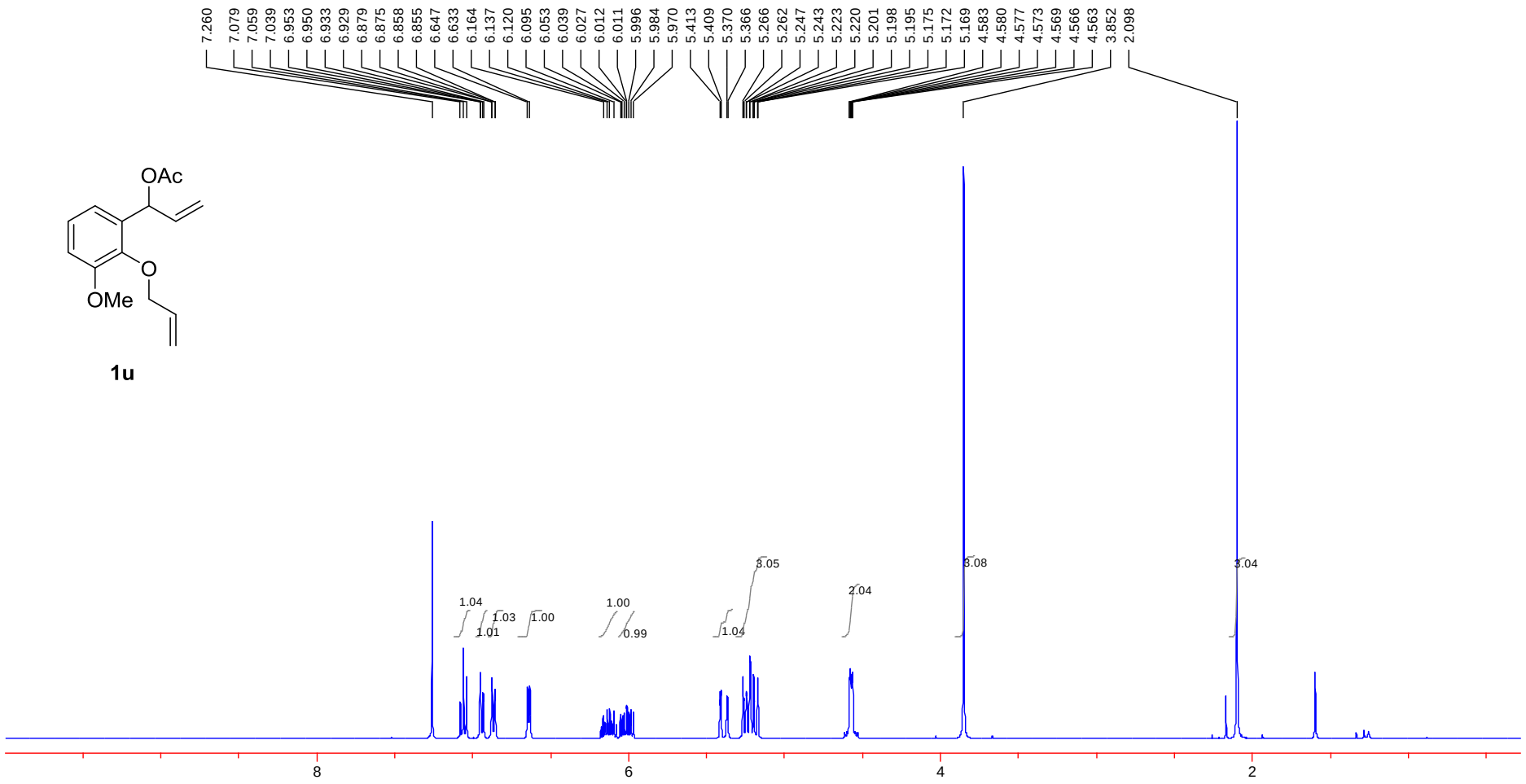
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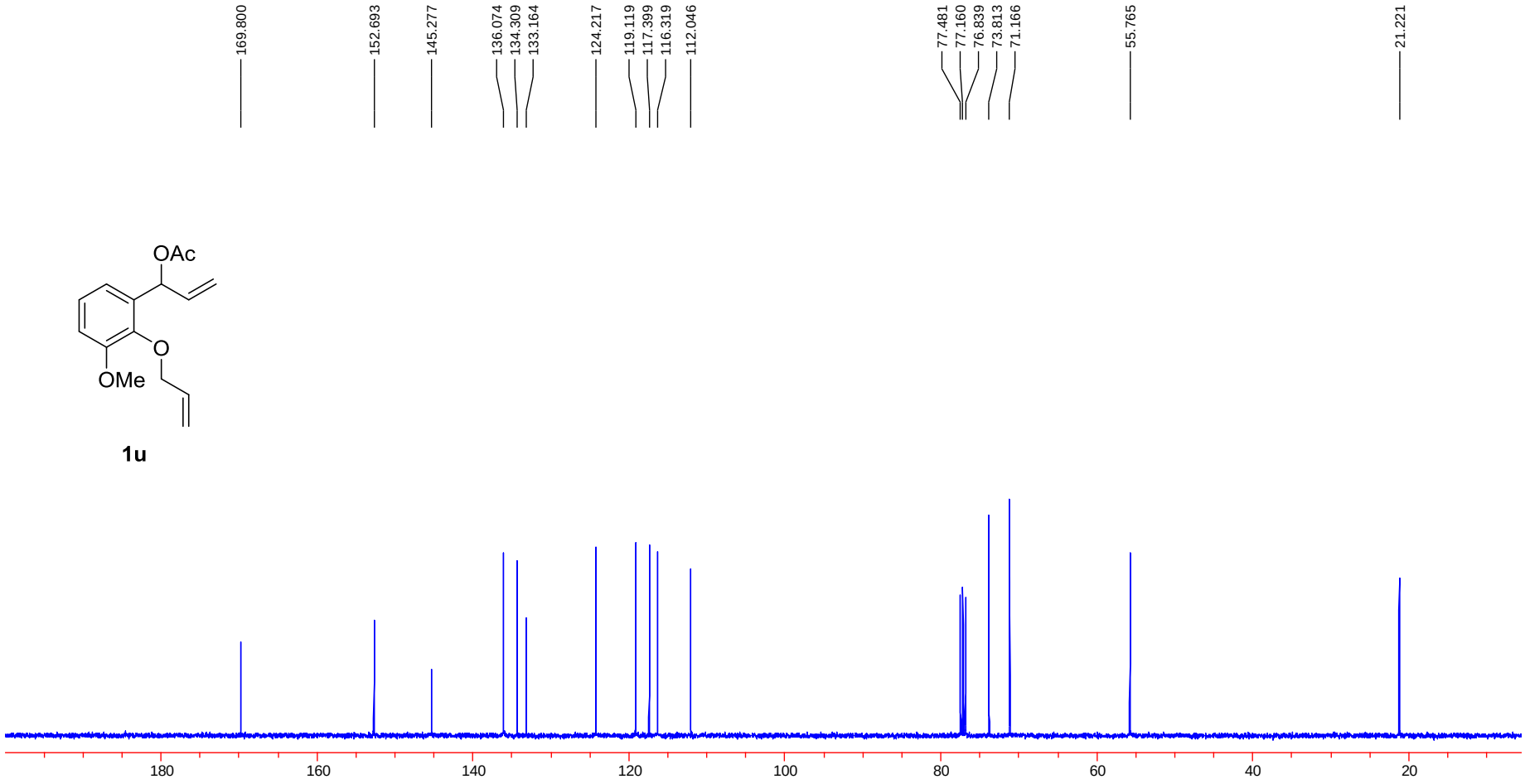
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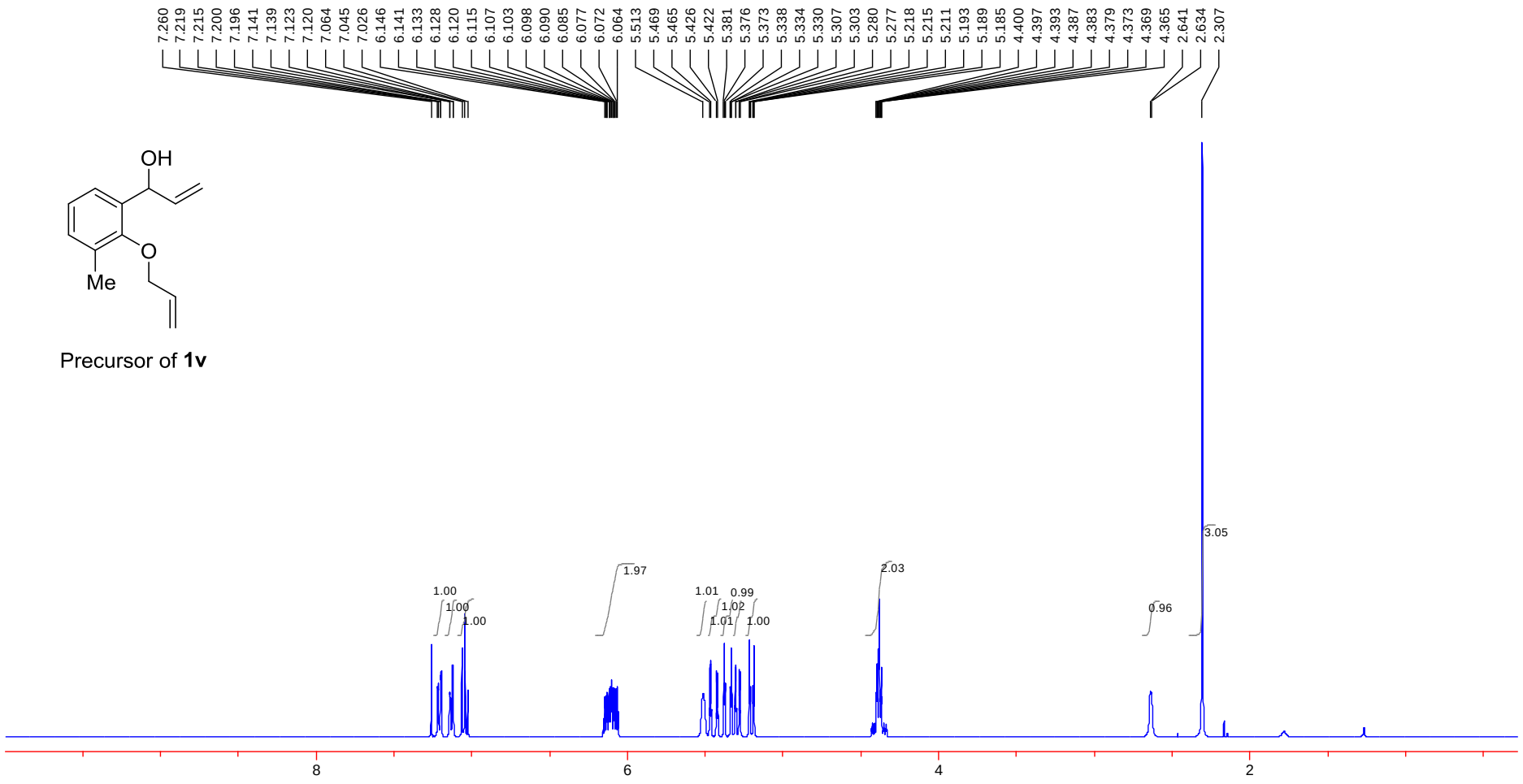
1u



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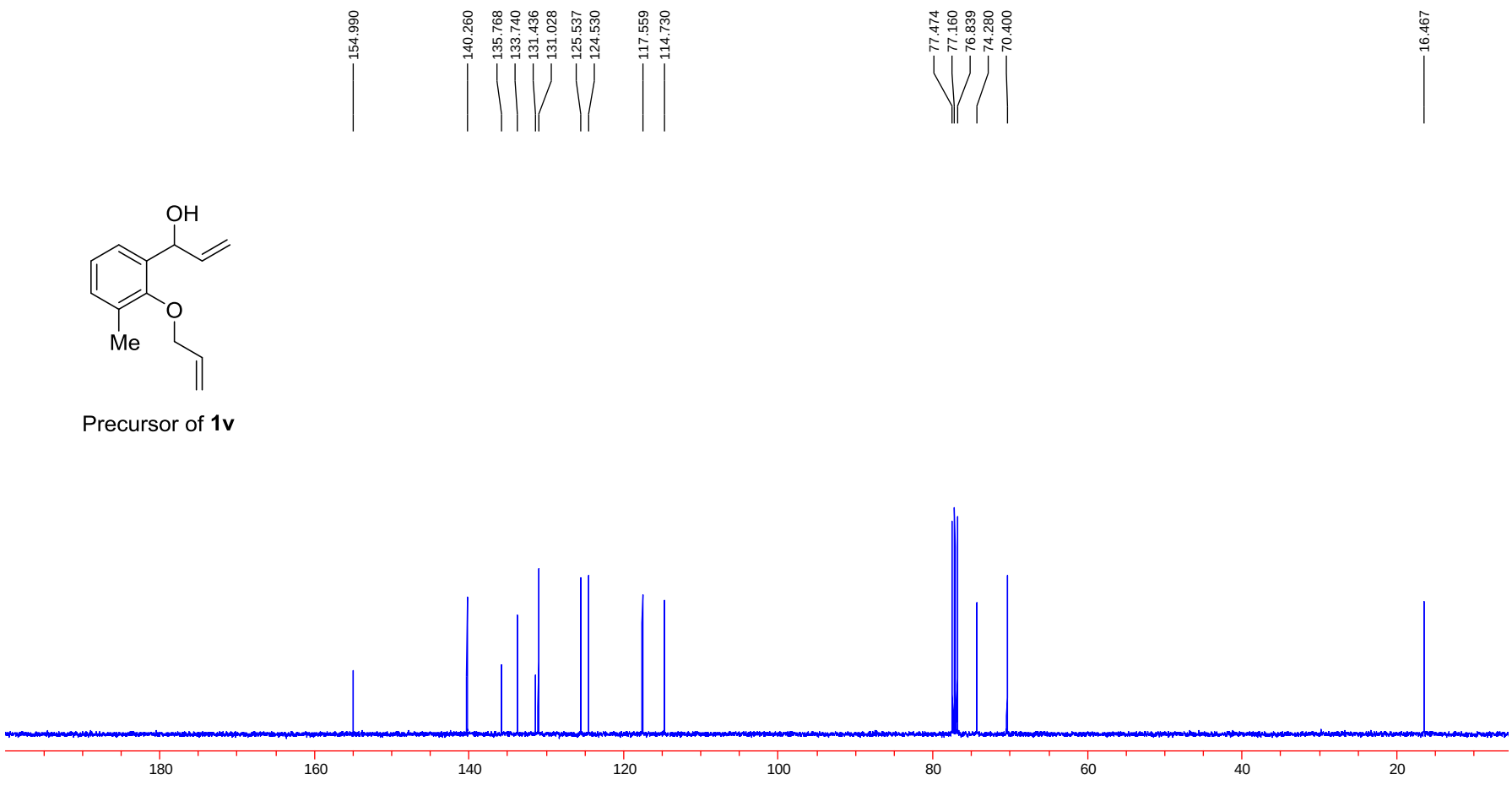

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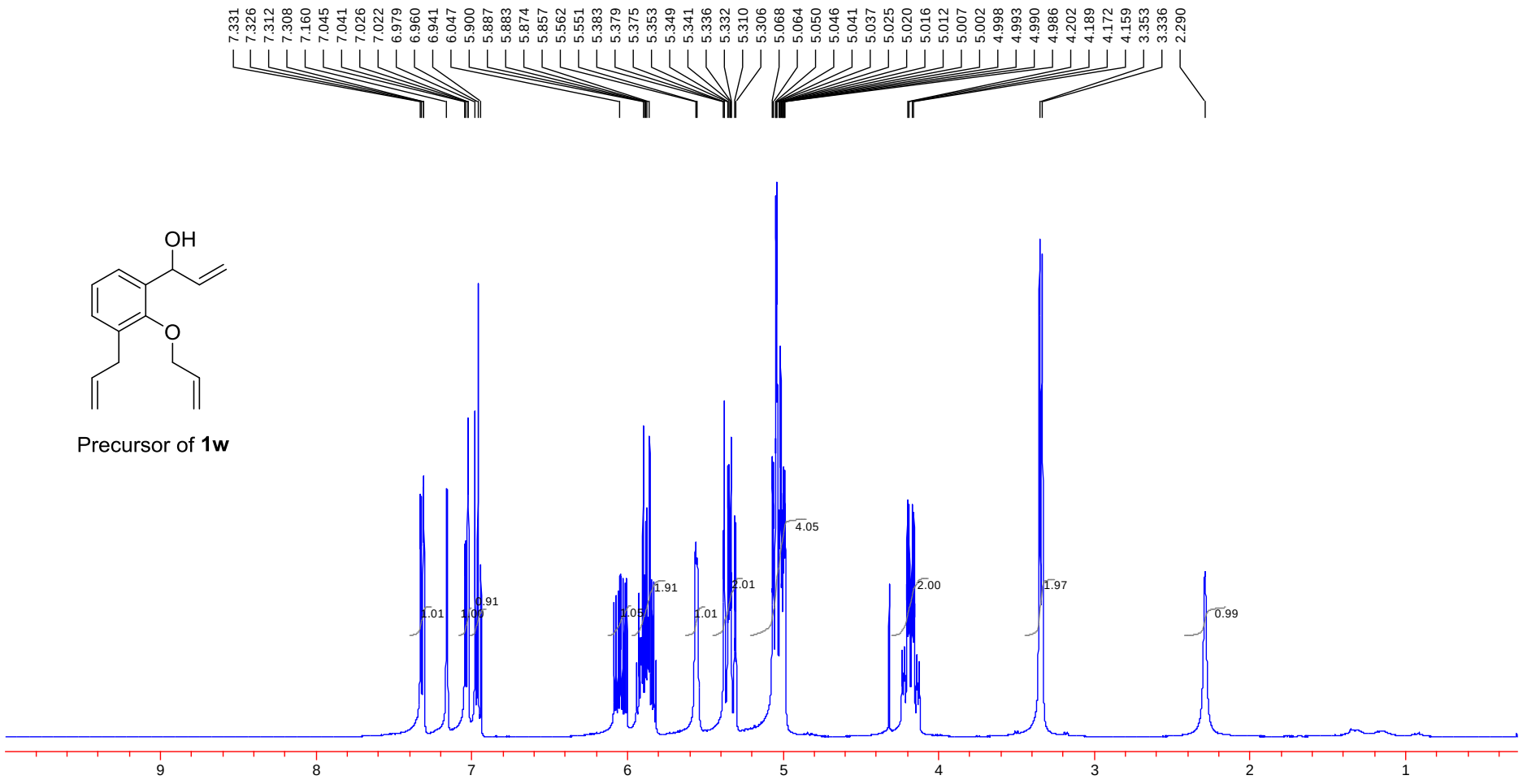
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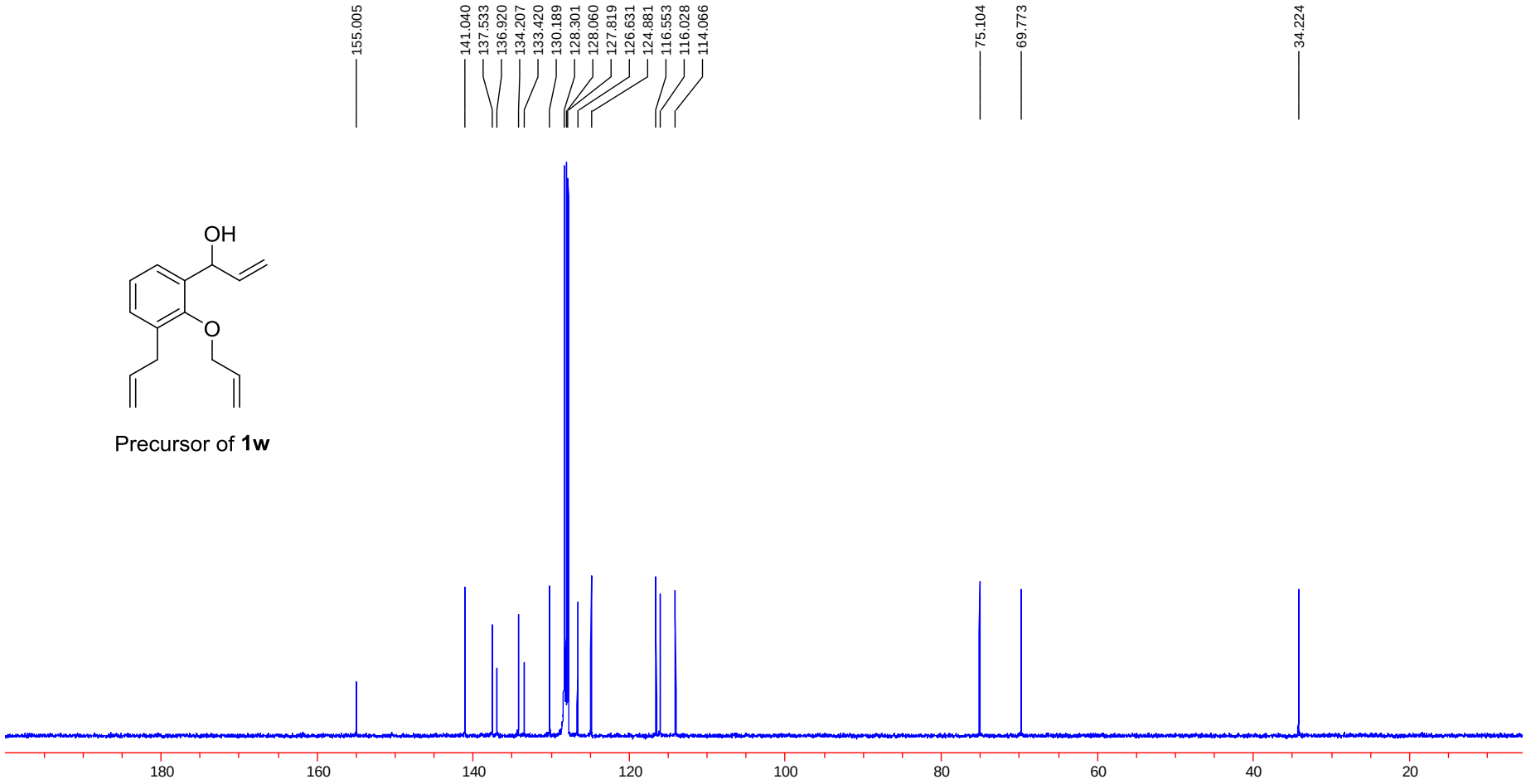

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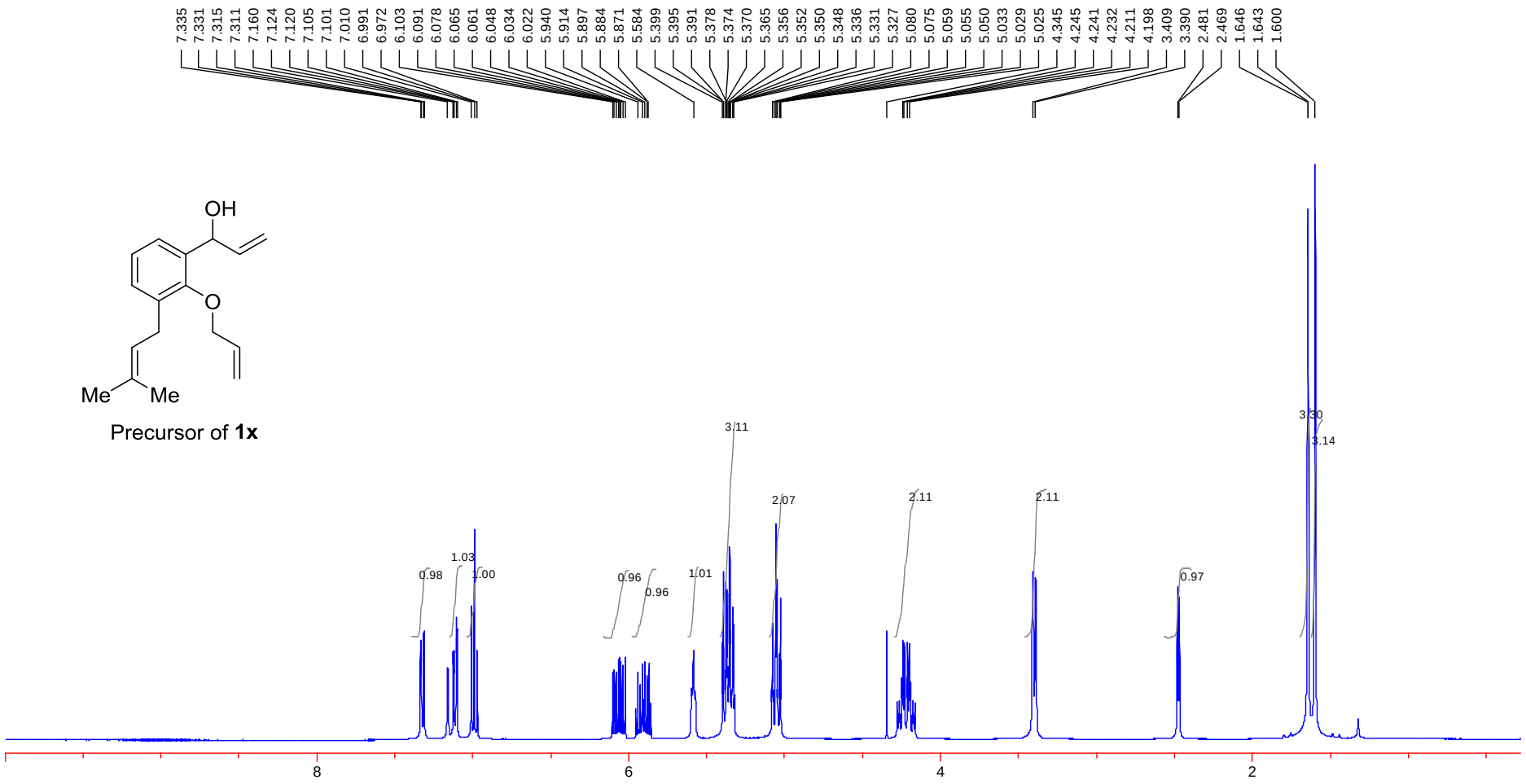
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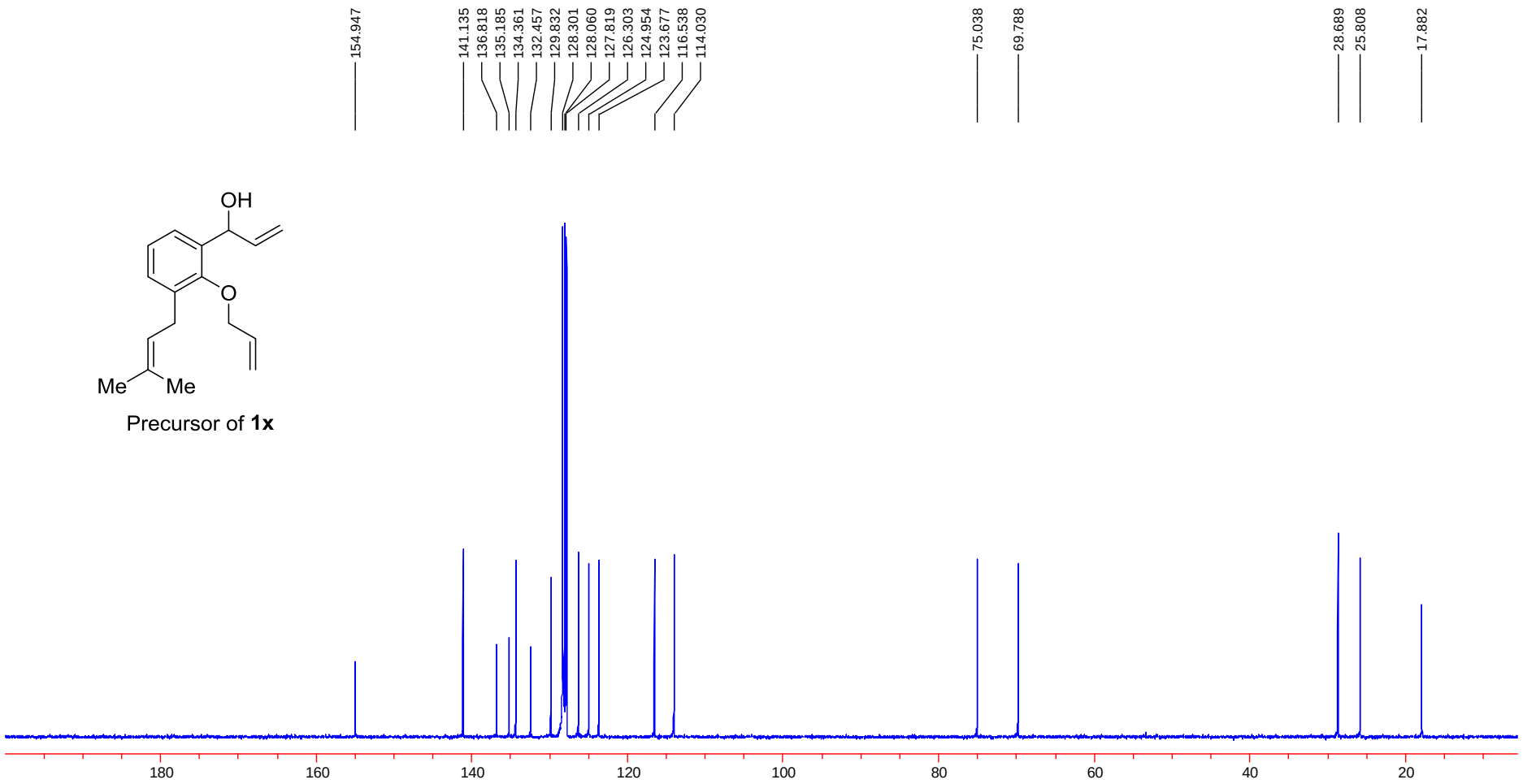

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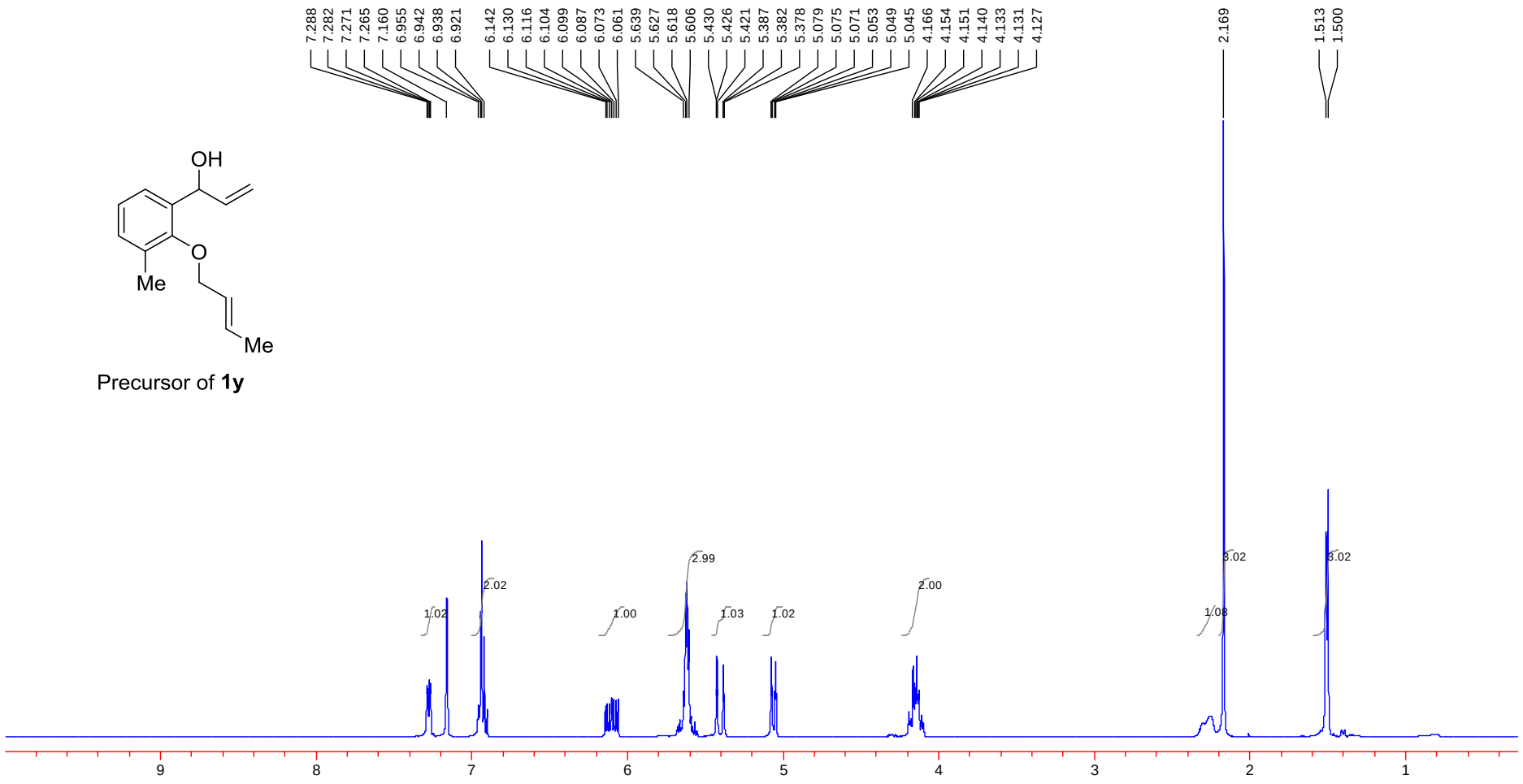

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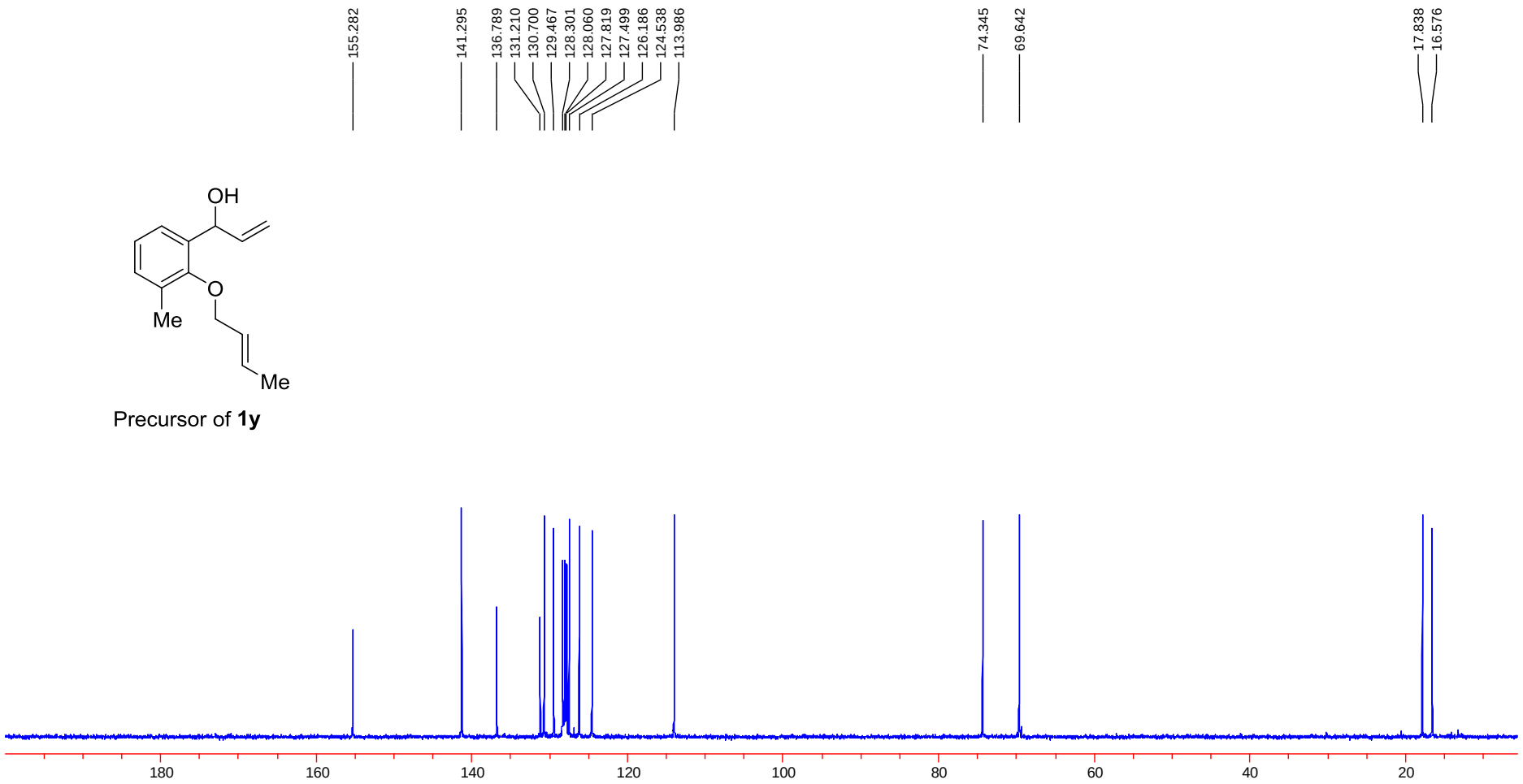

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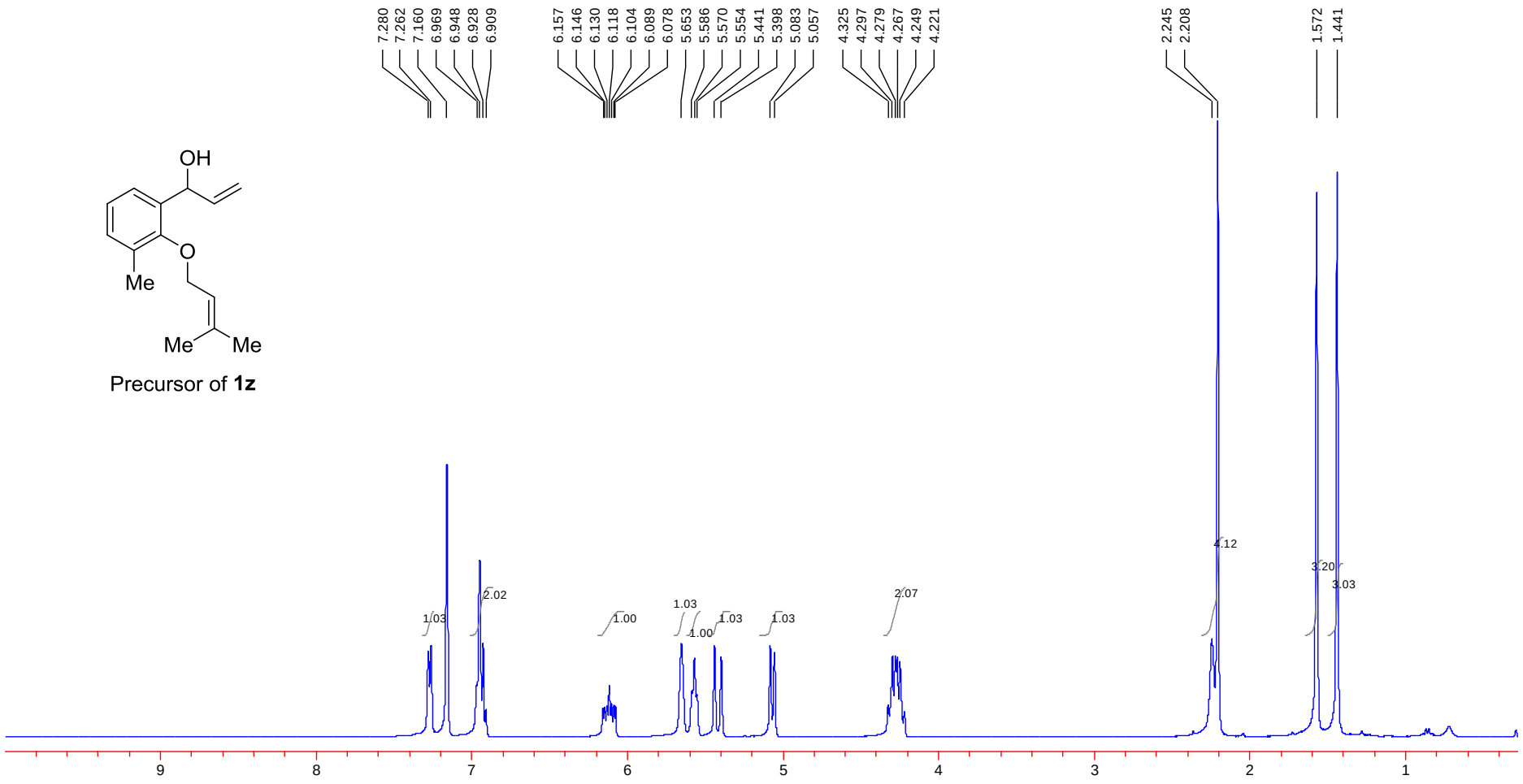

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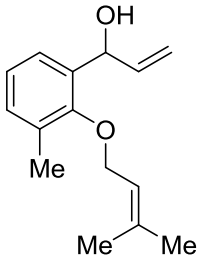

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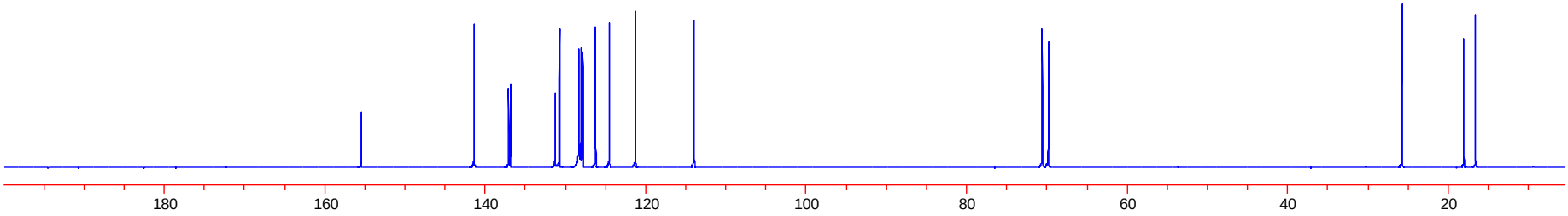

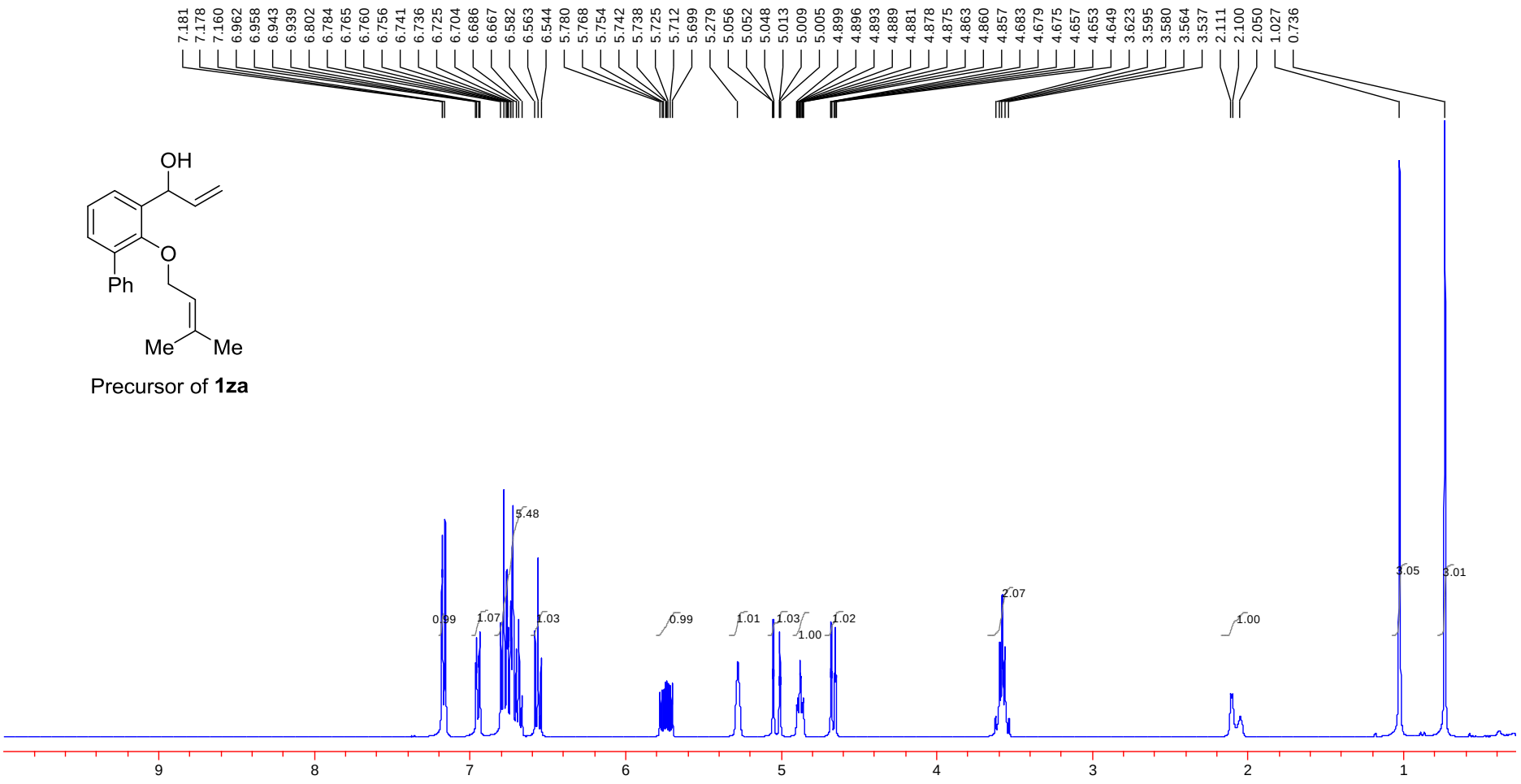
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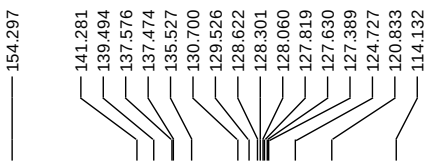

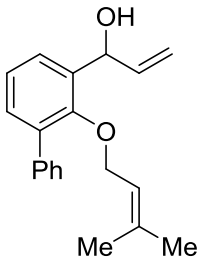

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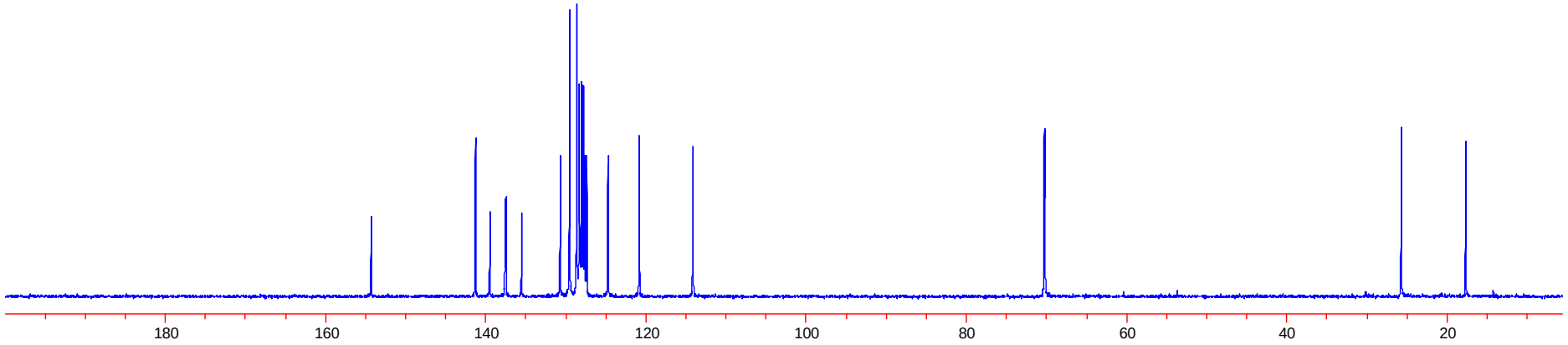

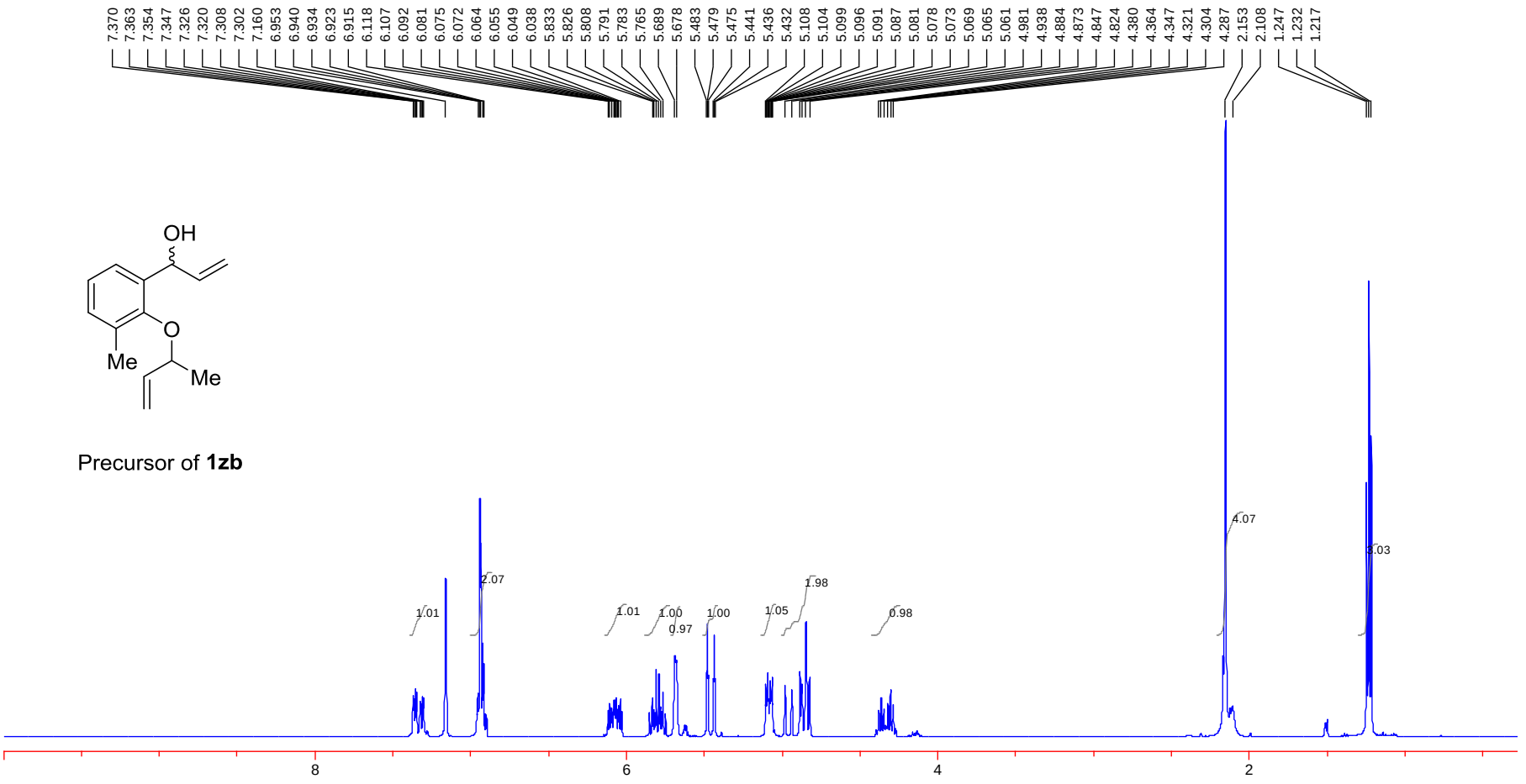

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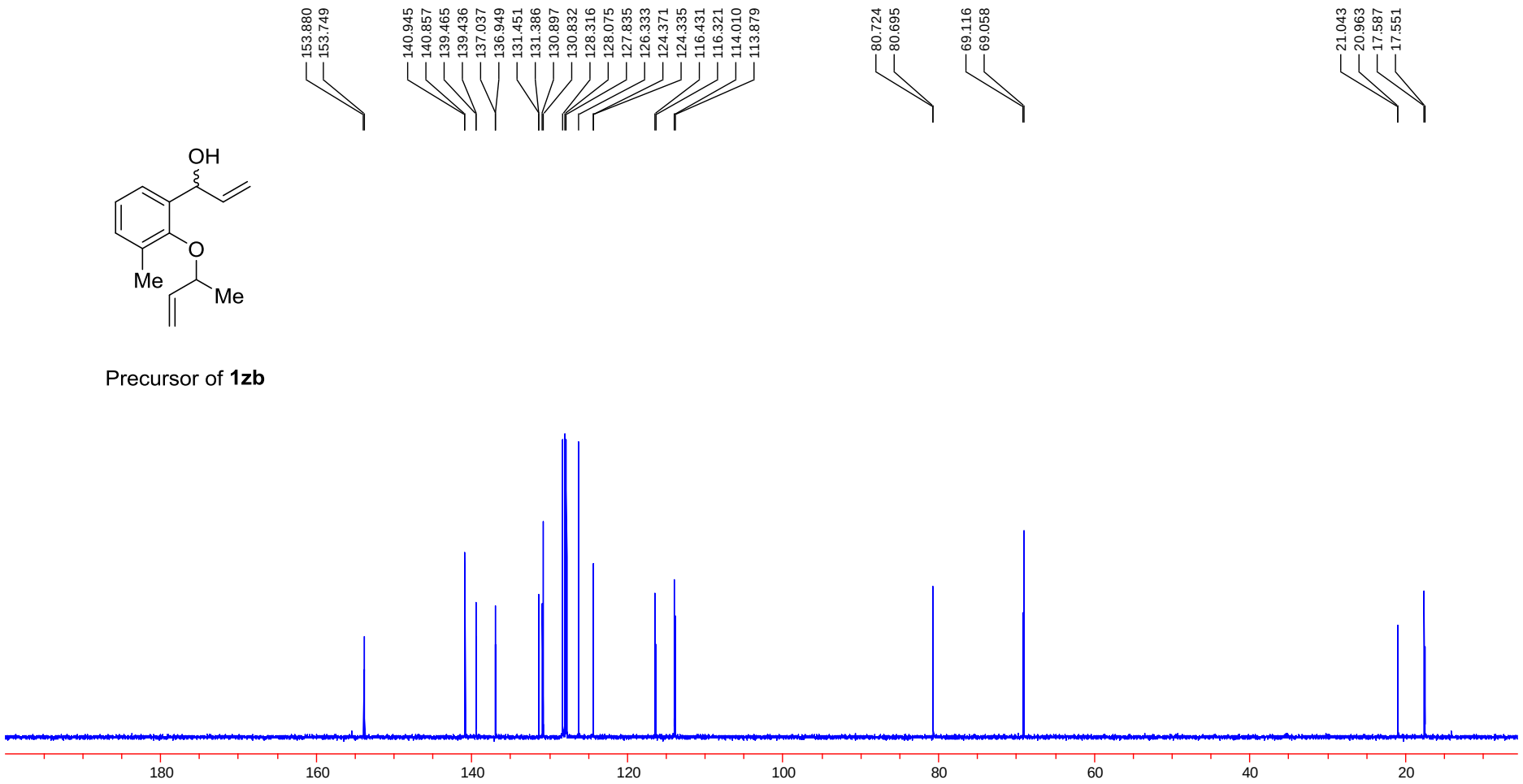

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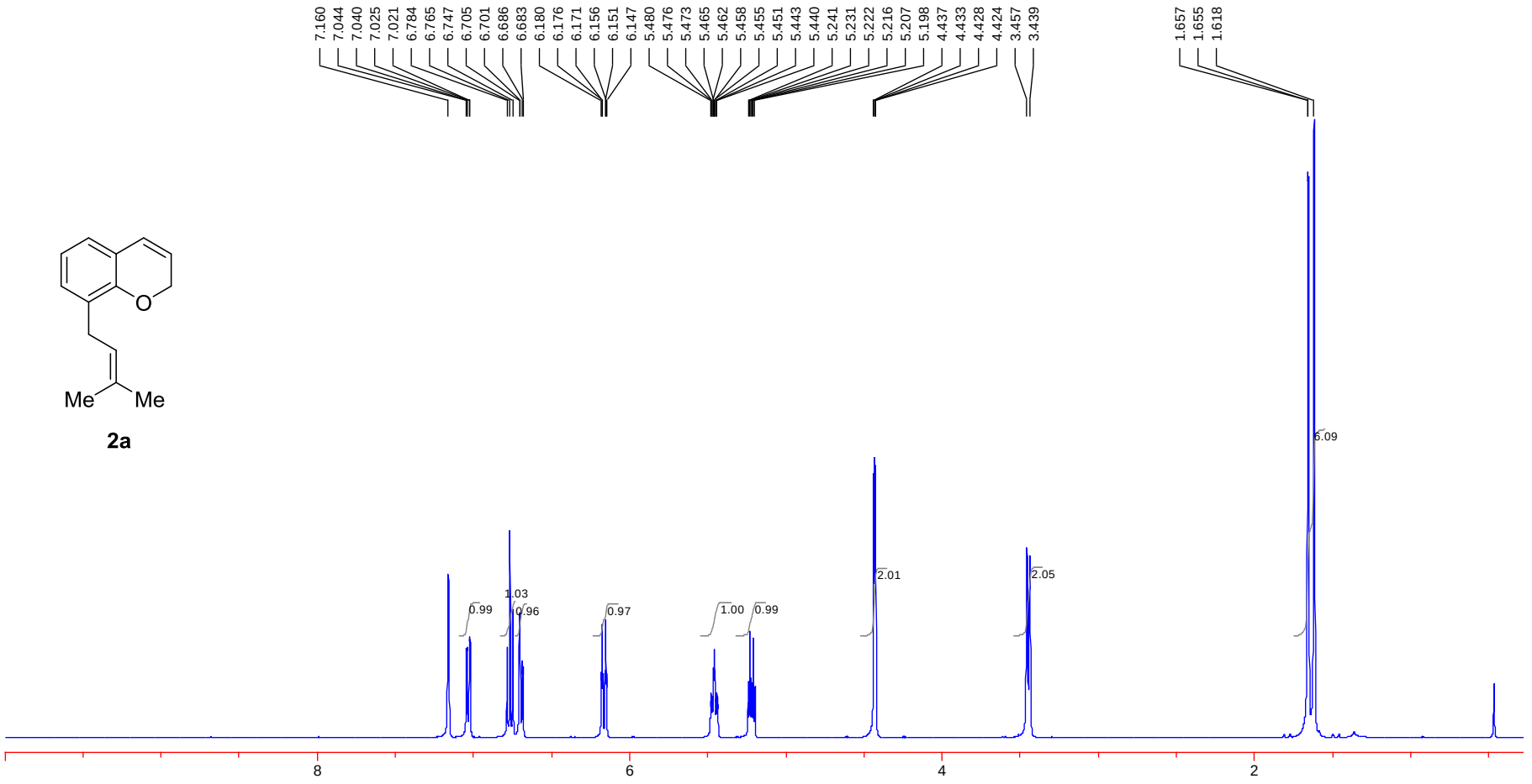
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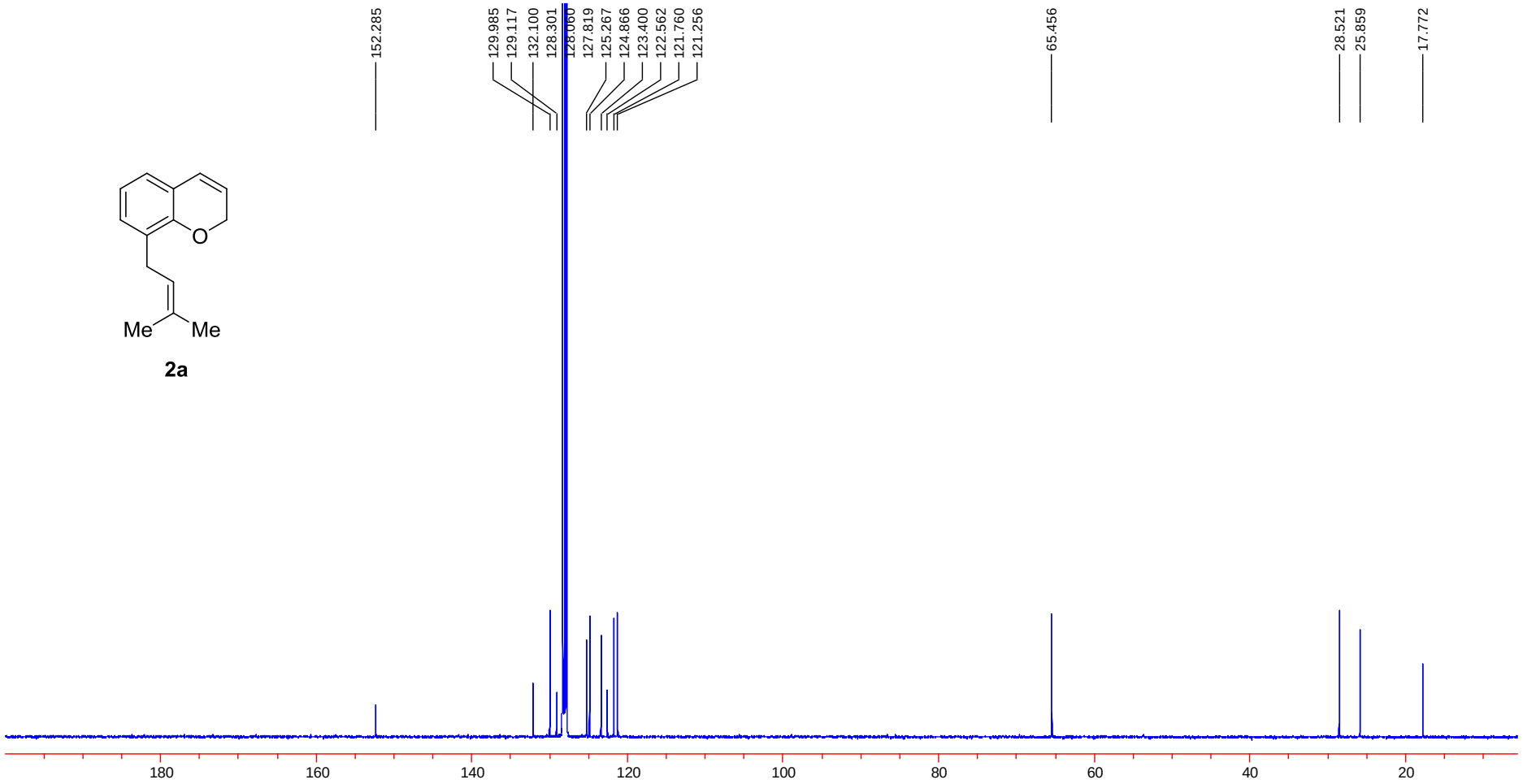
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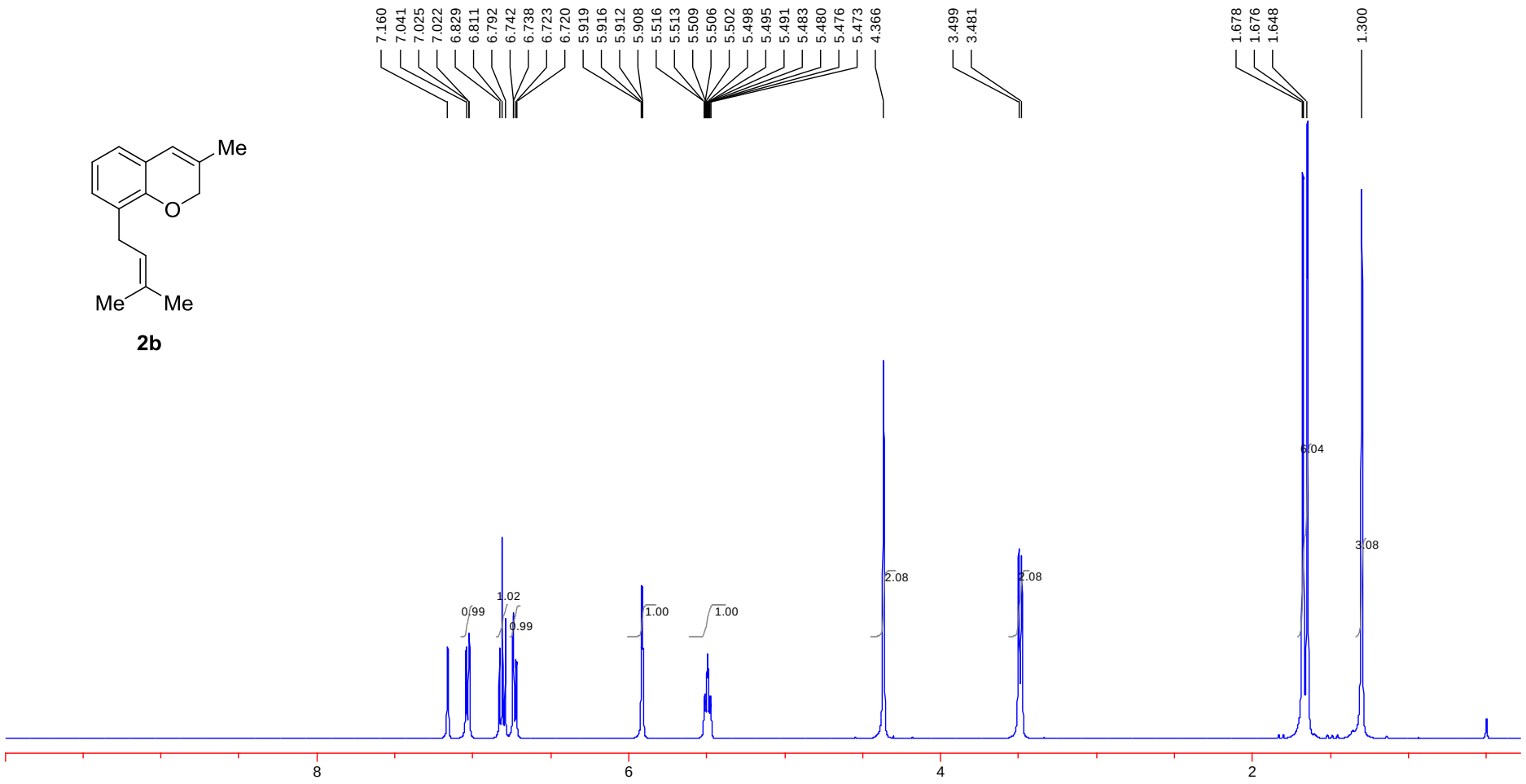
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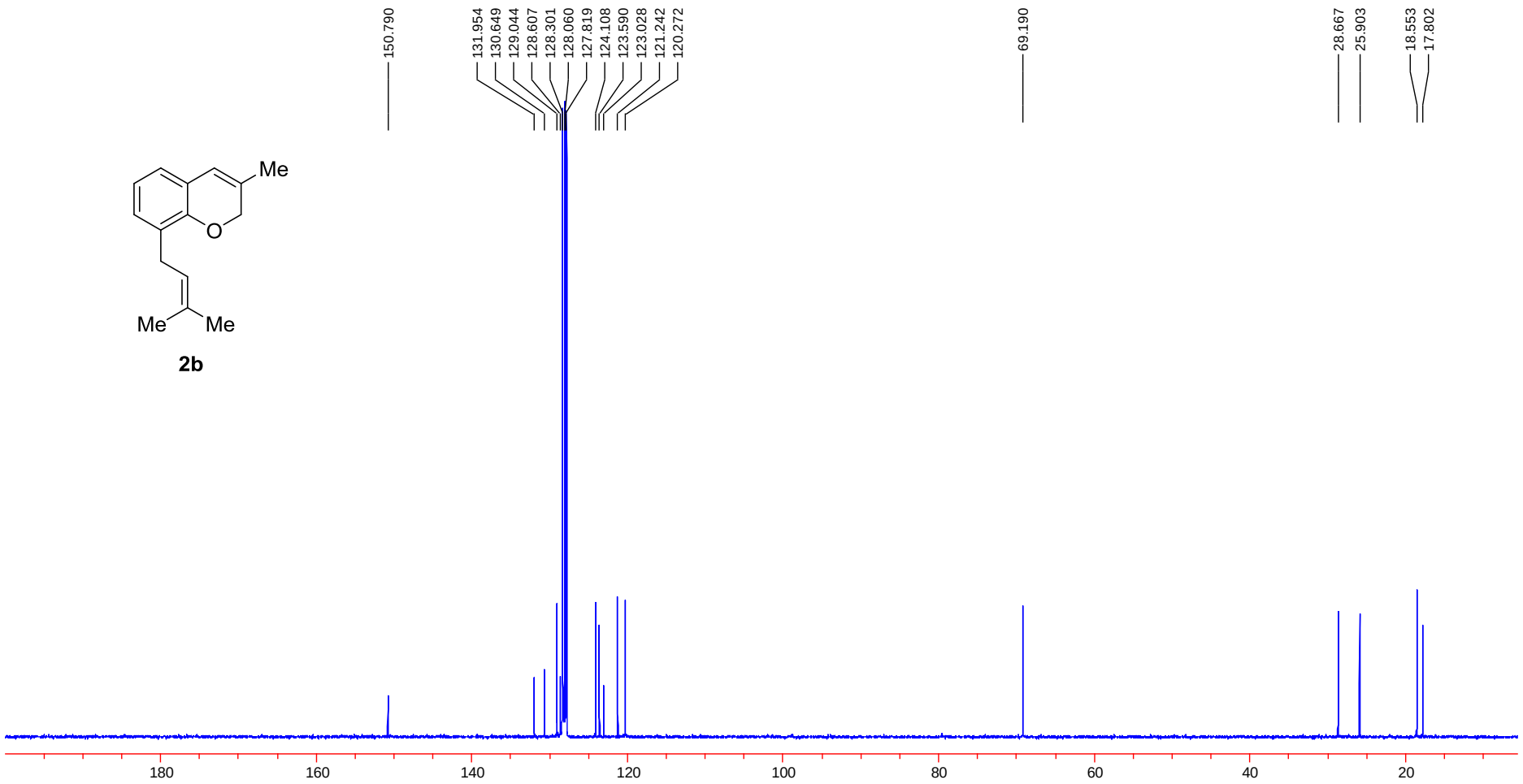
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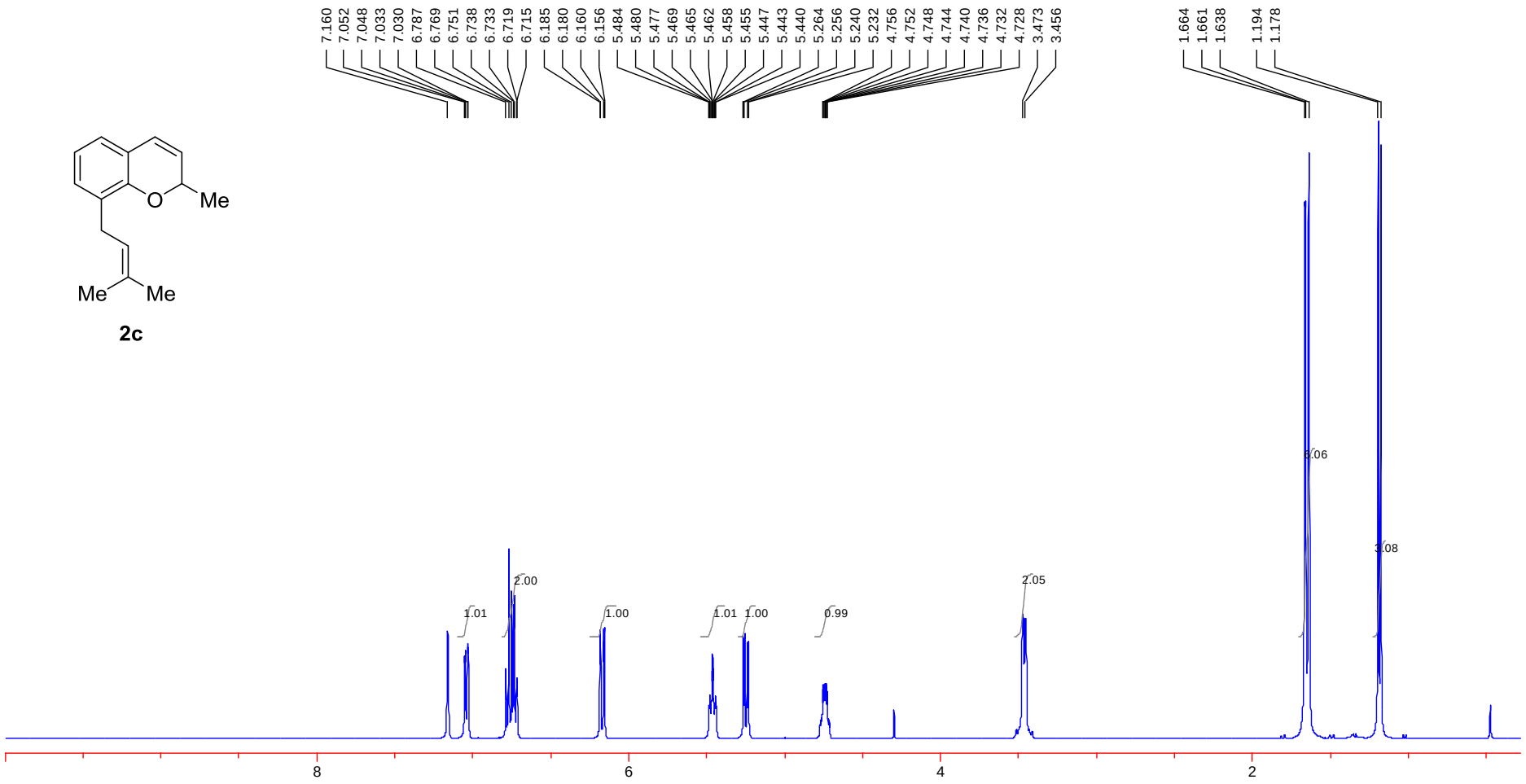
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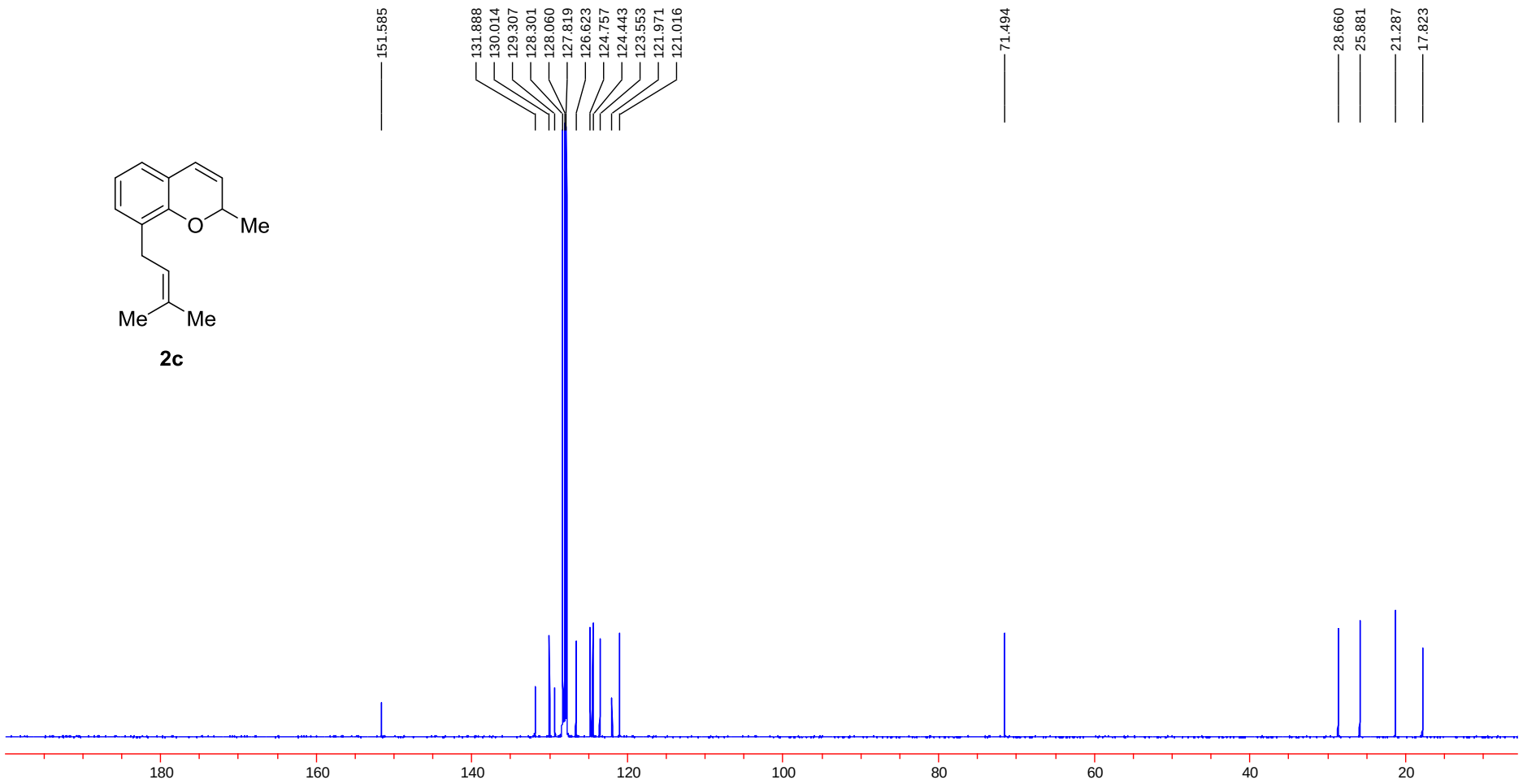
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28.660
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17.823
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Me
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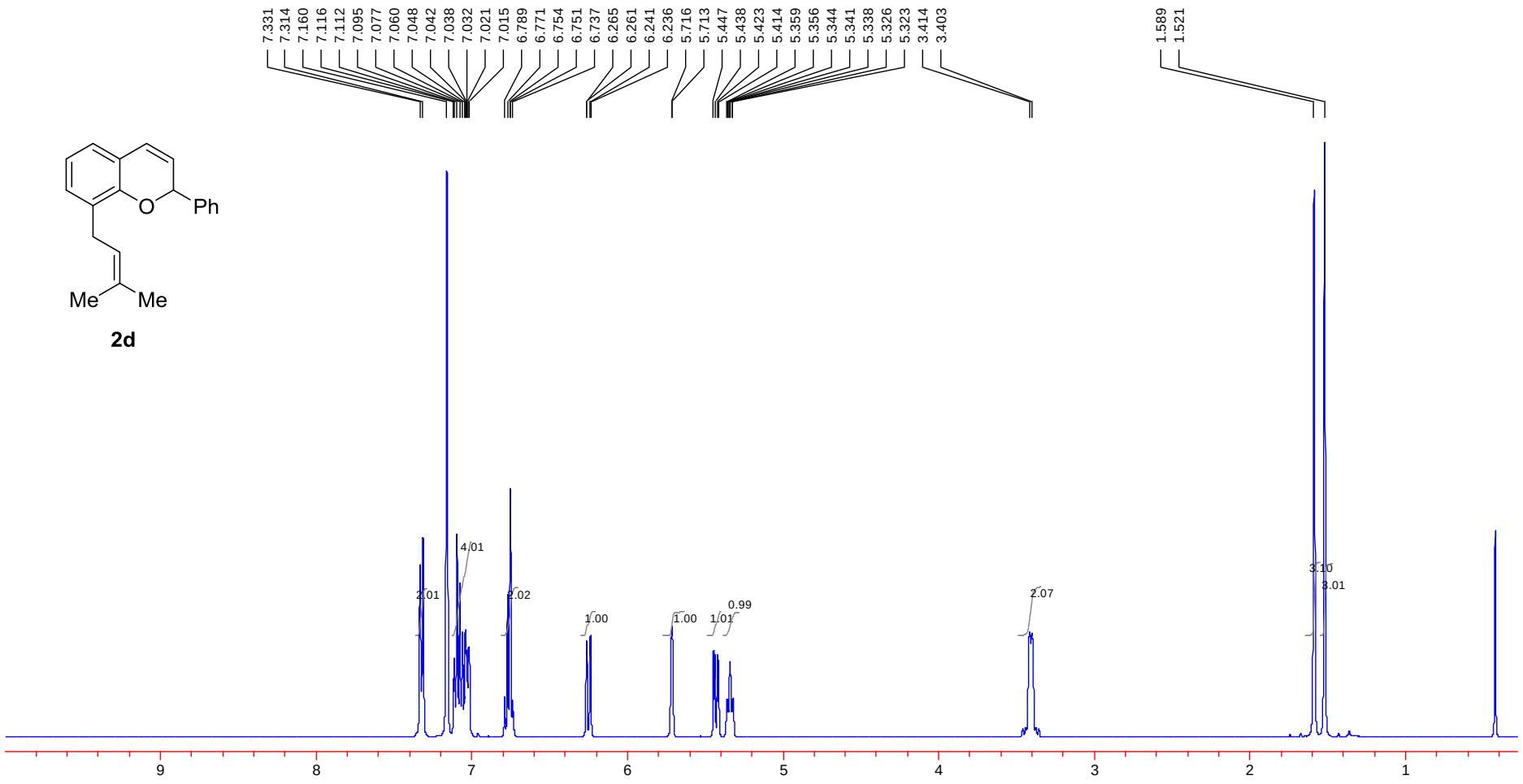
20

2c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7.077
7.060
7.048
7.042
7.038
7.032
7.021
7.015
6.789
6.771
6.754
6.751
6.737
6.265
6.261
6.241
6.236
5.716
5.713
5.447
5.438
5.423
5.414
5.359
5.356
5.344
5.341
5.338
5.326
5.323
3.414
3.403
1.589
1.521
O
Ph
Me
Me
2d
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4.01
2.02
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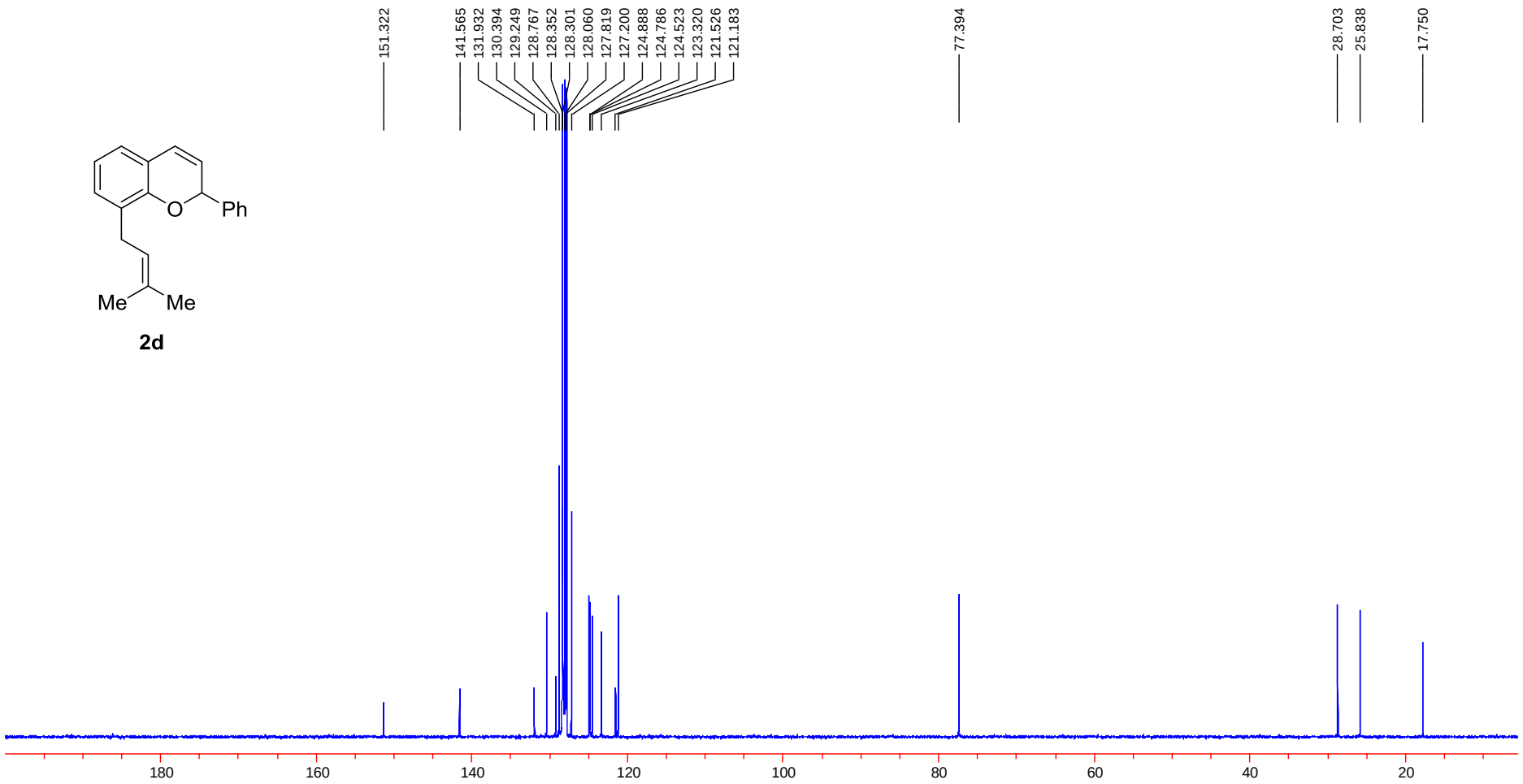
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121.526
121.183
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Me
Me
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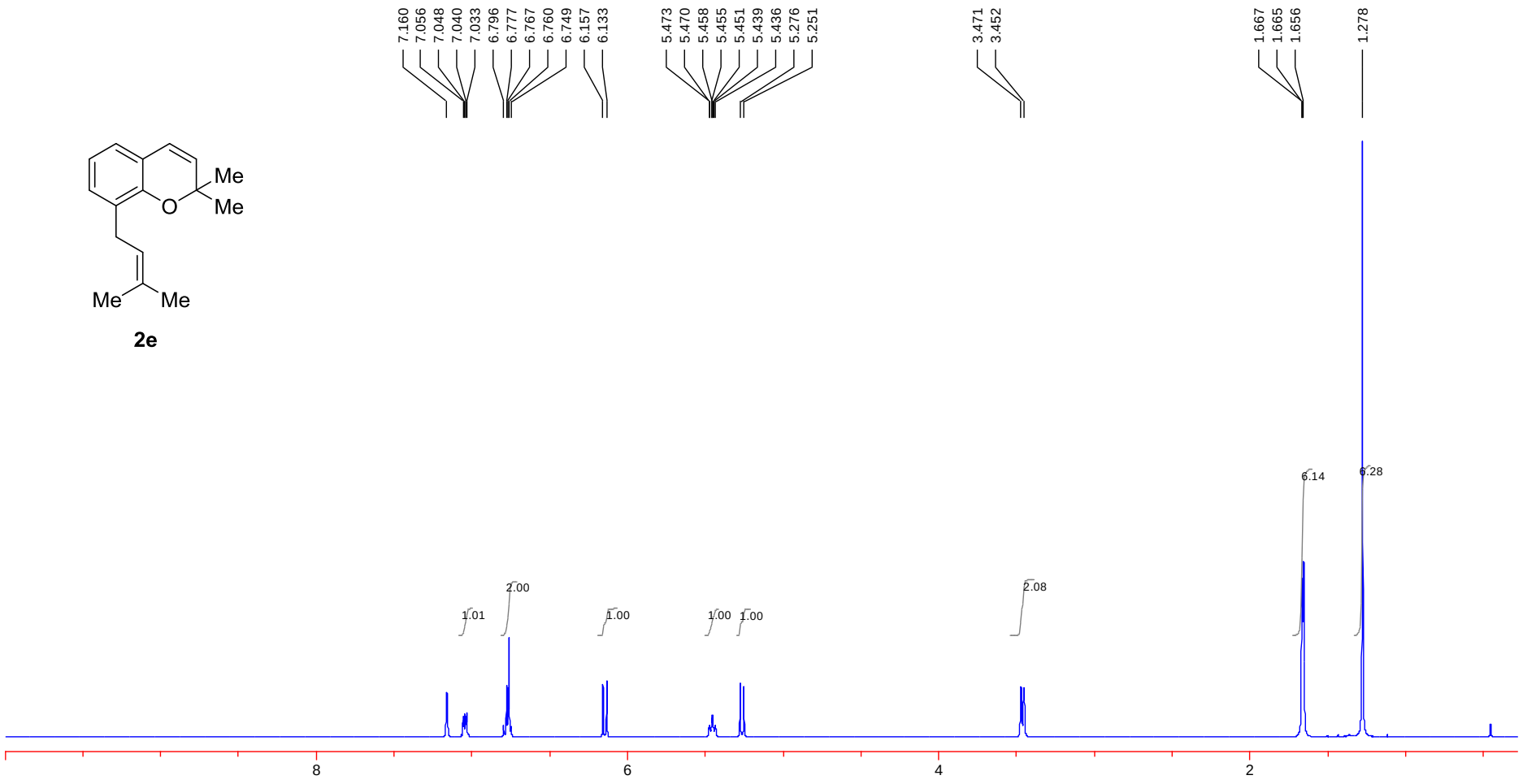
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6.767
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6.133
5.473
5.470
5.458
5.455
5.451
5.439
5.436
5.276
5.251
3.471
3.452
1.667
1.665
1.656
1.278
Me
Me
O
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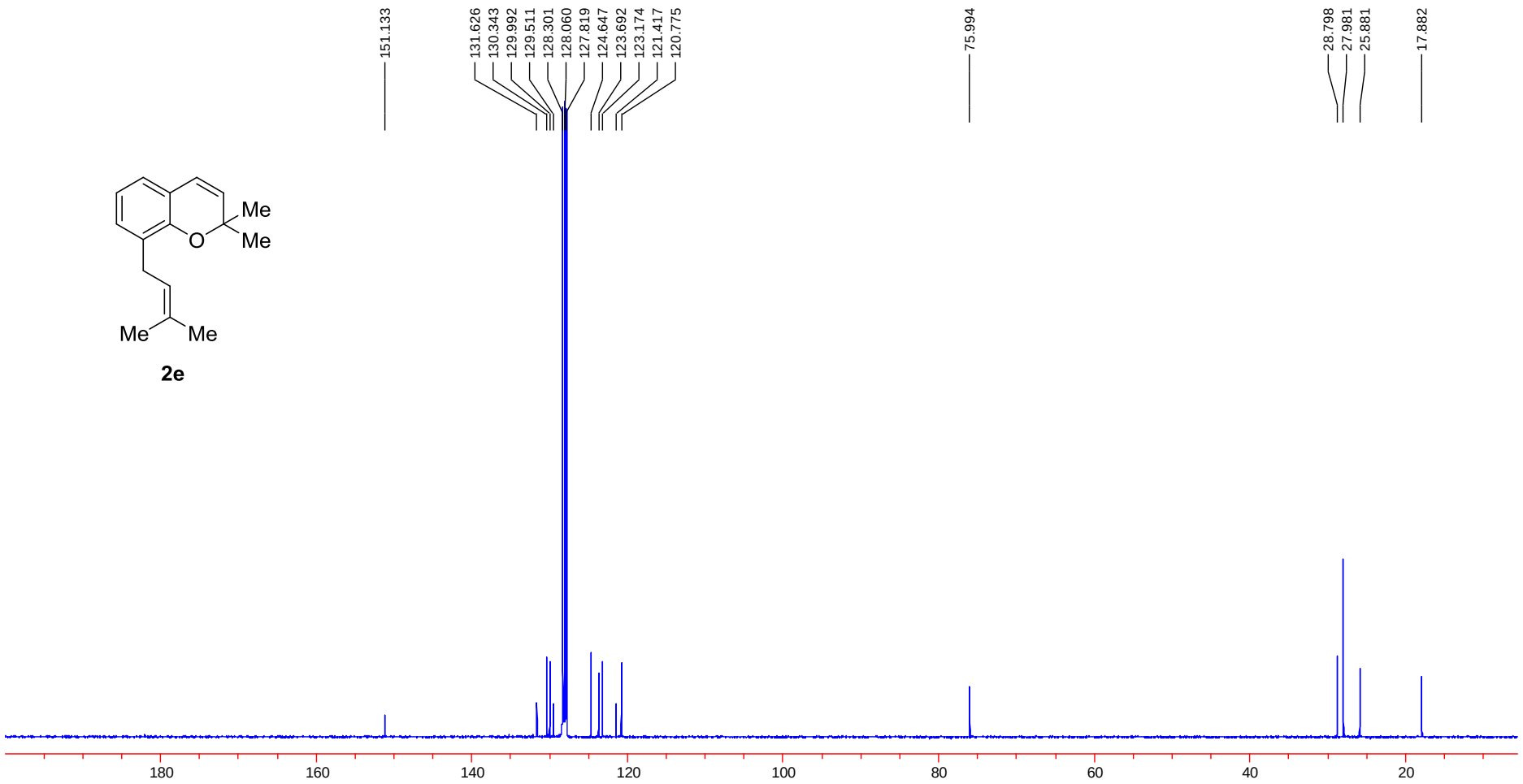
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120.775
75.994
28.798
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Me
O
Me
Me
2e
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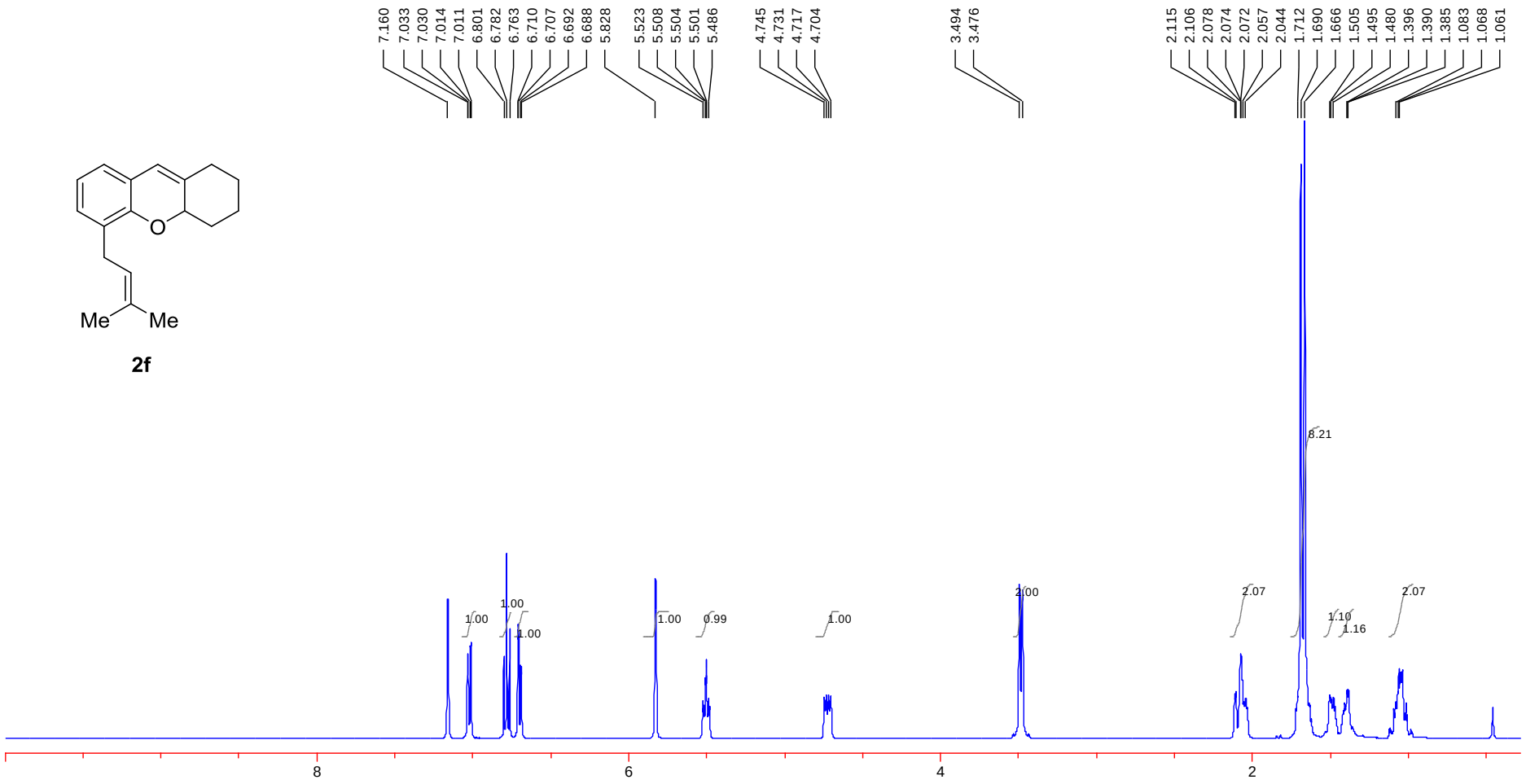
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6.763
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6.707
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6.688
5.828
5.523
5.508
5.504
5.501
5.486
4.745
4.731
4.717
4.704
3.494
3.476
2.115
2.106
2.078
2.074
2.072
2.057
2.044
1.712
1.690
1.666
1.505
1.495
1.480
1.396
1.390
1.385
1.083
1.068
1.061
O
Me
Me
1.00
1.00
1.00
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1.16
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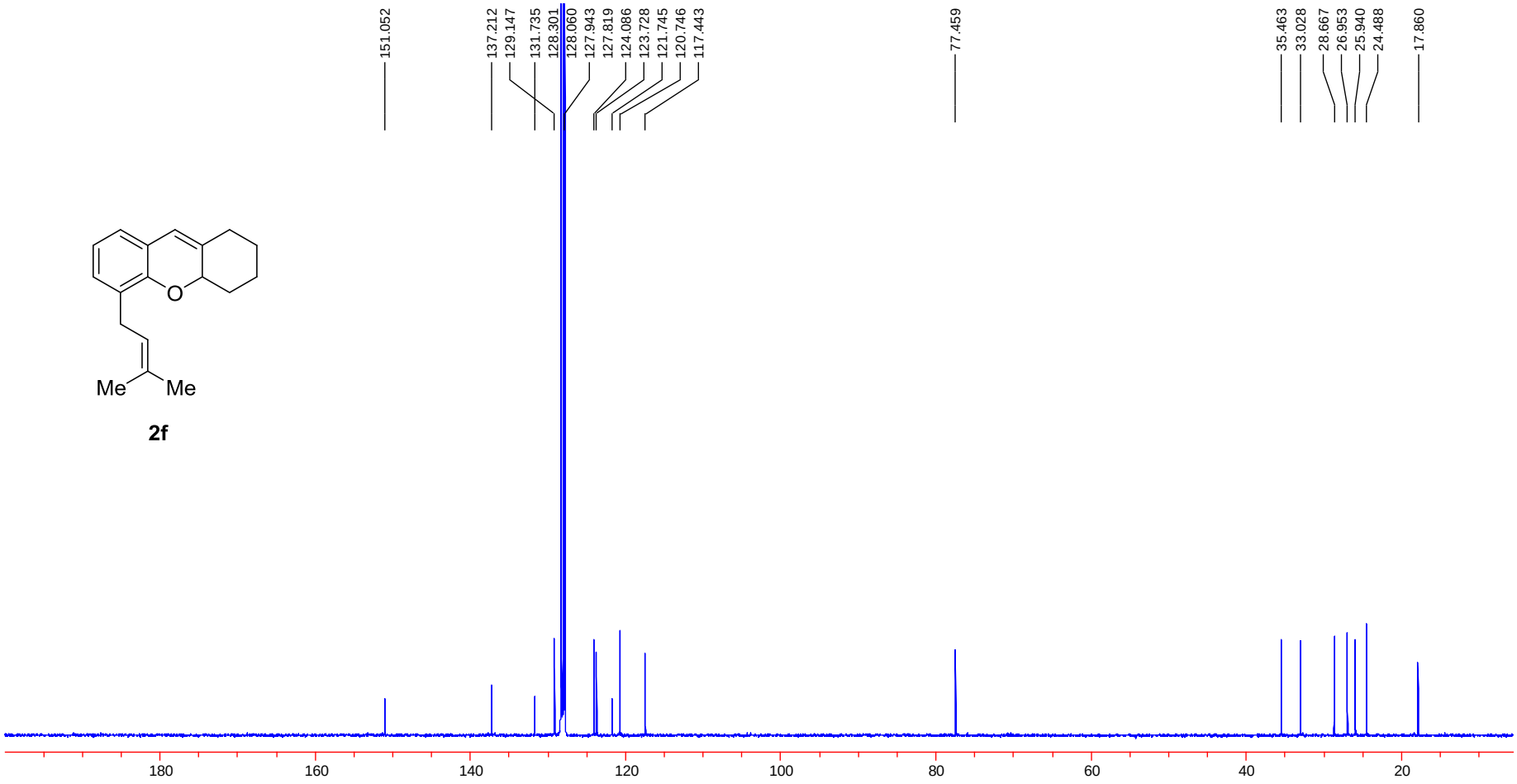
2

2f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120.746
117.443
77.459
35.463
33.028
28.667
26.953
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24.488
17.860
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Me
Me
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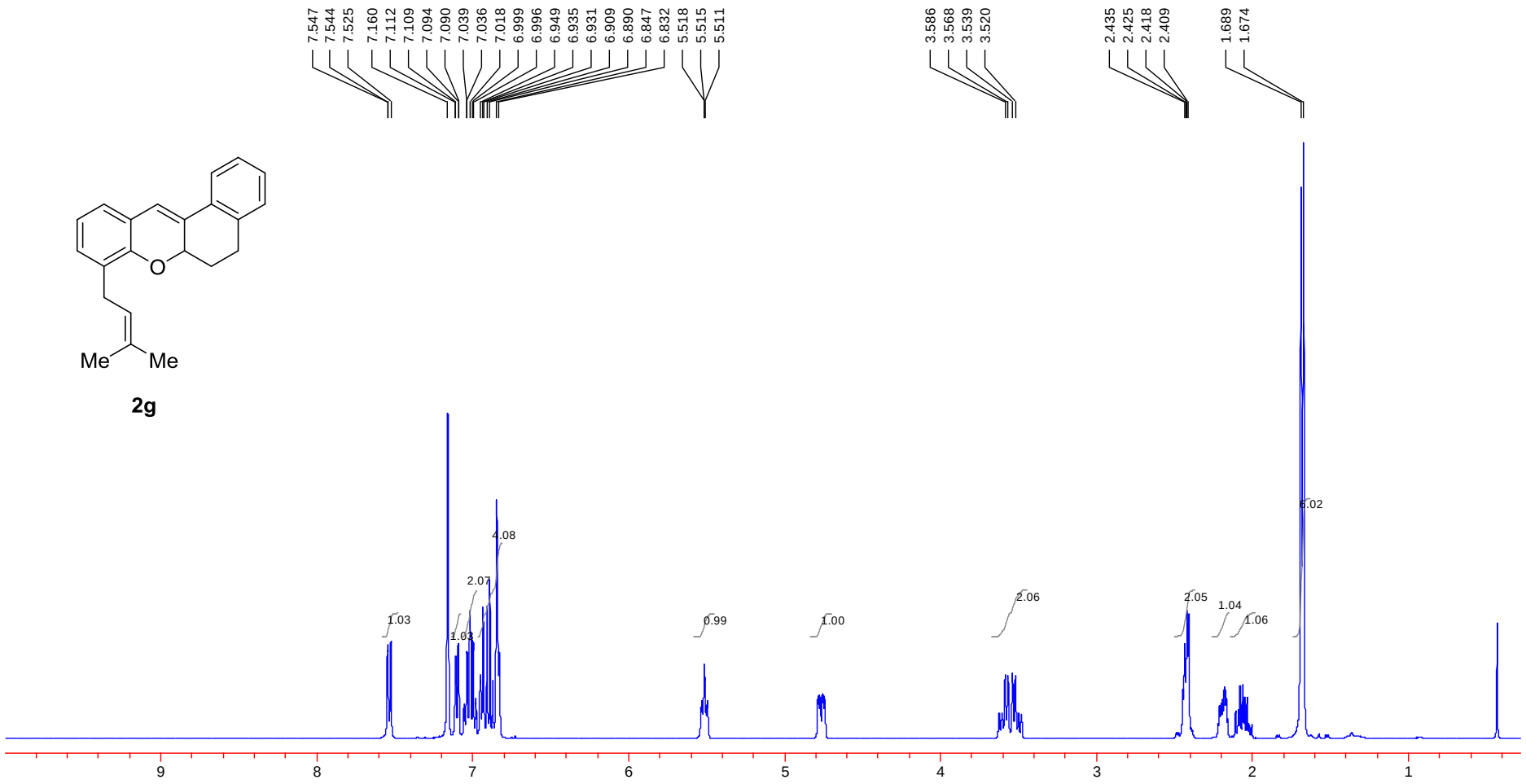
140
120
100
80
60
40
20

2f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7.094
7.090
7.039
7.036
7.018
6.999
6.996
6.949
6.935
6.931
6.909
6.890
6.847
6.832
5.518
5.515
5.511
3.586
3.568
3.539
3.520
2.435
2.425
2.418
2.409
1.689
1.674
O
Me
Me
2g
1.03
1.01
2.07
4.08
0.99
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2.05
1.04
1.06
6.02
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6
5
4
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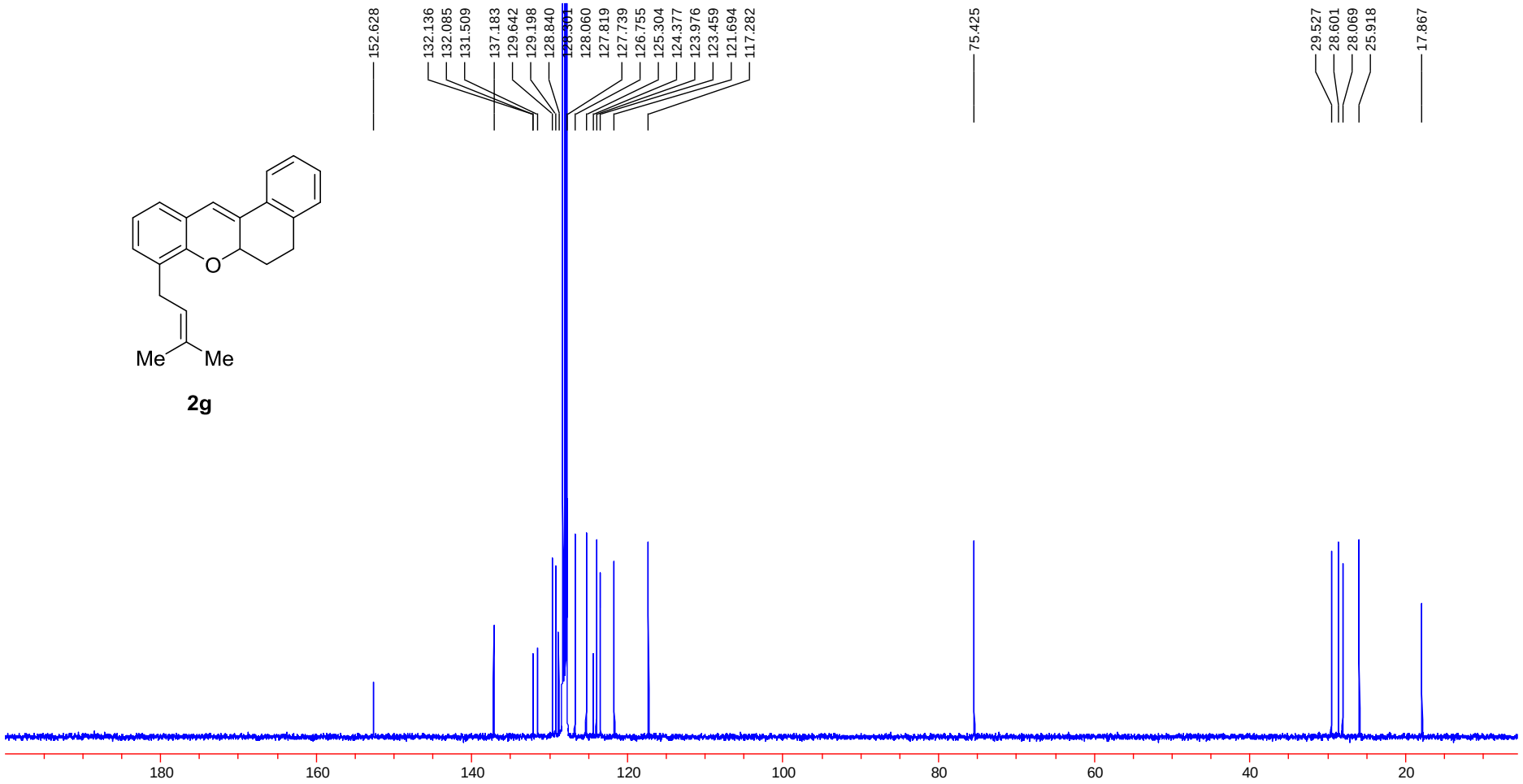
1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128.301
128.060
127.819
127.739
126.755
125.304
124.377
123.976
123.459
121.694
117.282
75.425
29.527
28.601
28.069
25.918
17.867
O
Me
Me
2g
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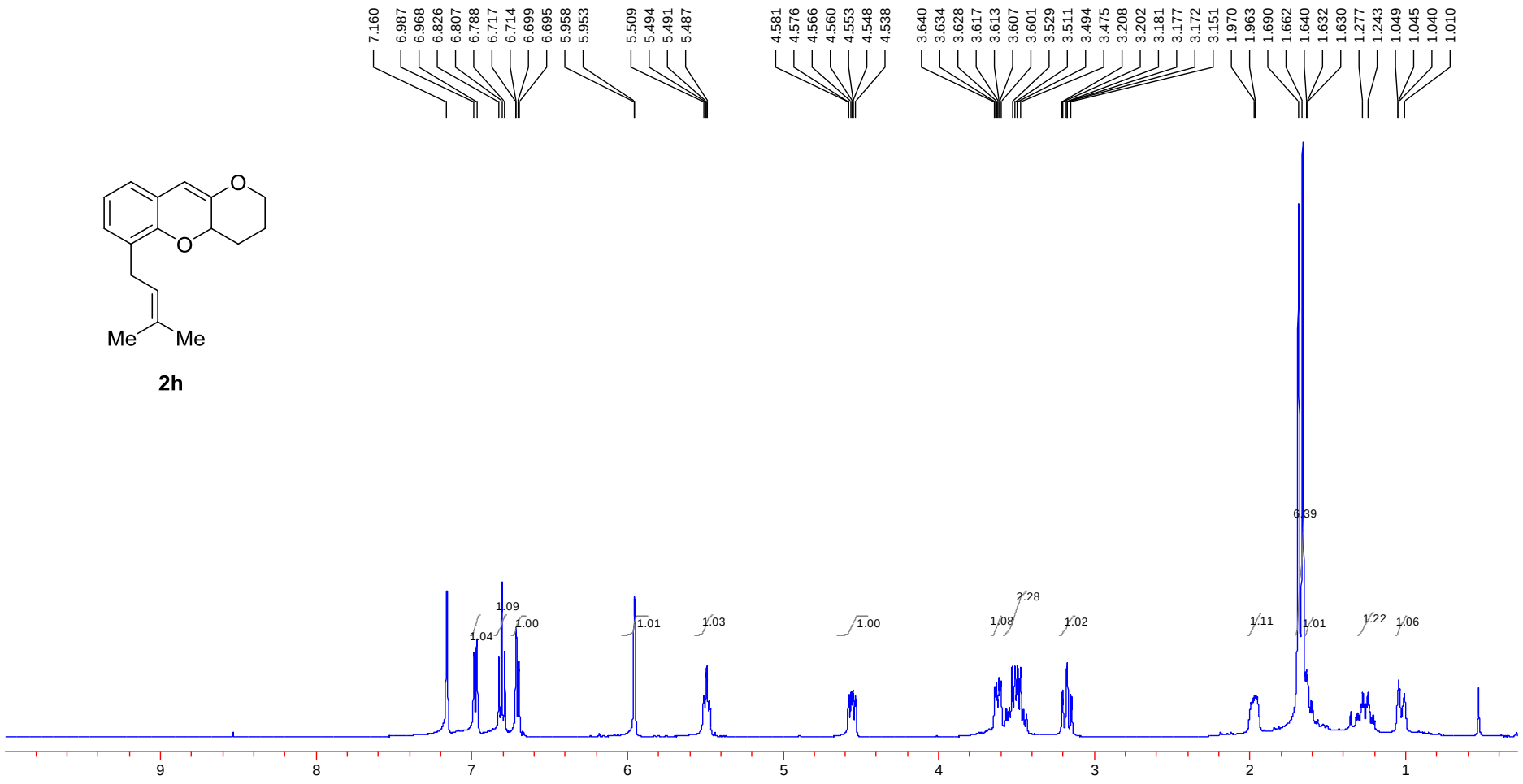
160
140
120
100
80
60
40
20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6.699
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5.953
5.509
5.494
5.491
5.487
4.581
4.576
4.566
4.560
4.553
4.548
4.538
3.640
3.634
3.628
3.617
3.613
3.607
3.601
3.529
3.511
3.494
3.475
3.208
3.202
3.181
3.177
3.172
3.151
1.970
1.963
1.690
1.662
1.640
1.632
1.630
1.277
1.243
1.049
1.045
1.040
1.010
O
O
Me
Me
2h
6.39
2.28
1.09
1.04
1.00
1.01
1.03
1.00
1.08
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1.11
1.01
1.22
1.06
9
8
7
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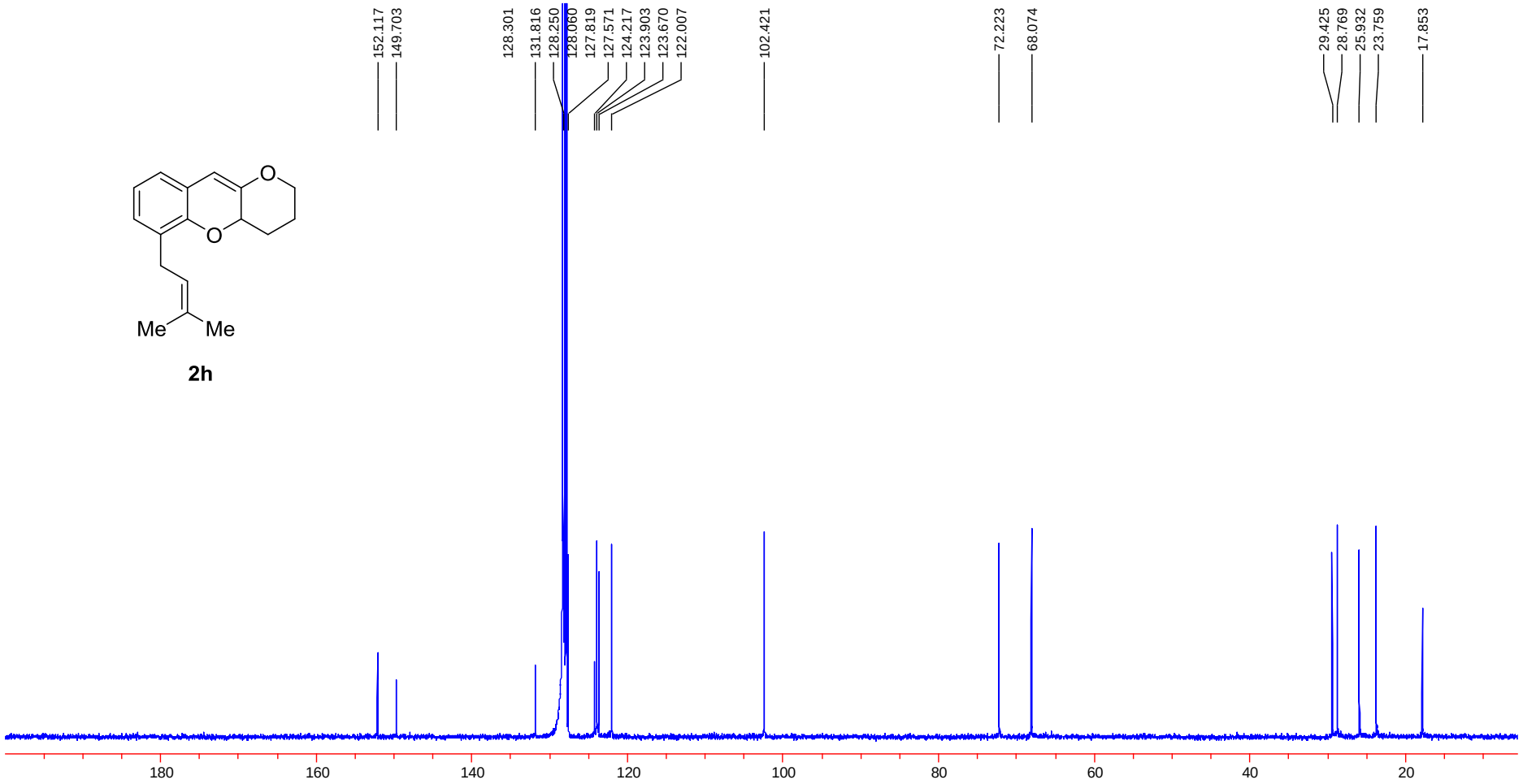
5
4
3
2
1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123.670
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102.421
72.223
68.074
29.425
28.769
25.932
23.759
17.853
O
O
Me
Me
2h
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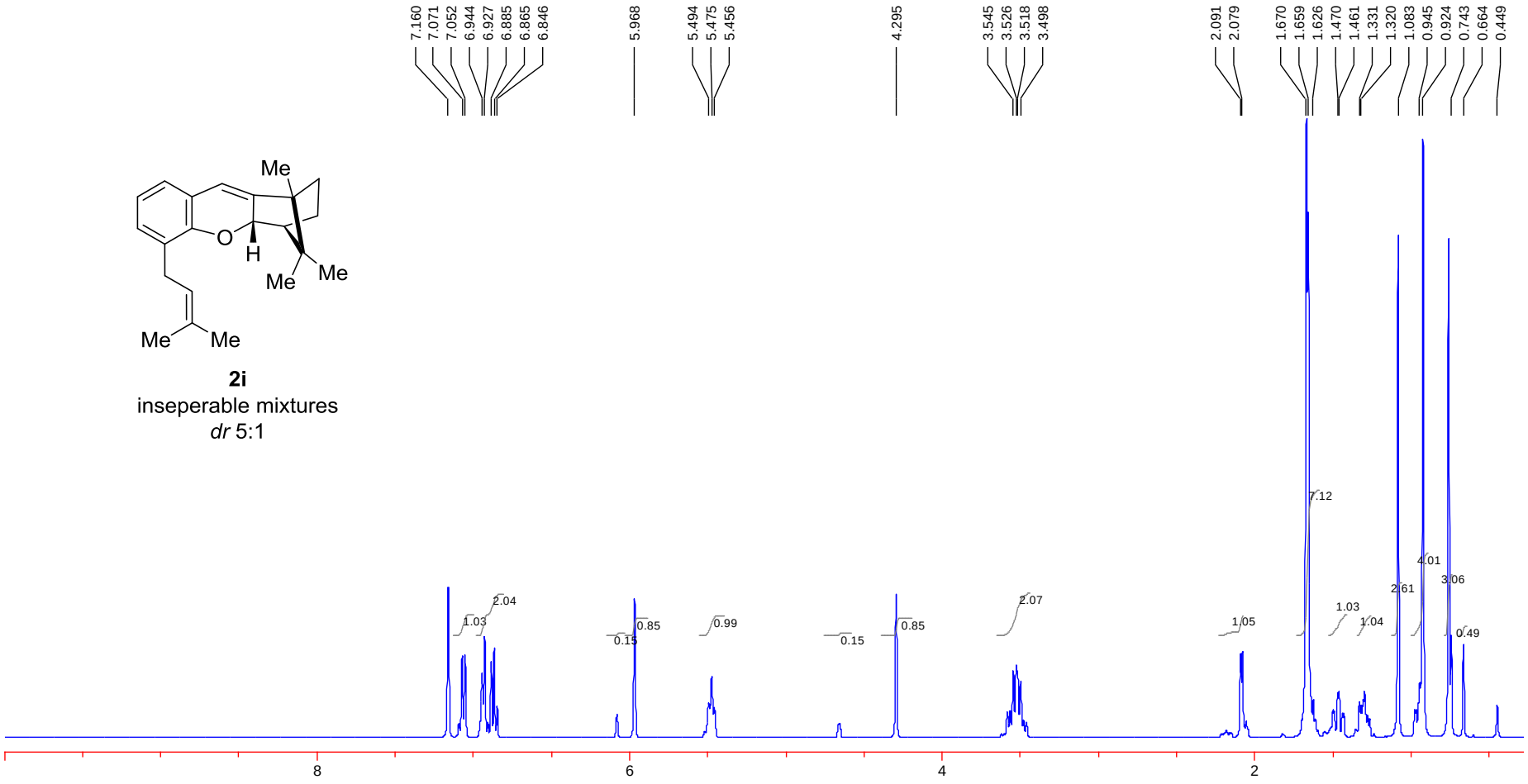
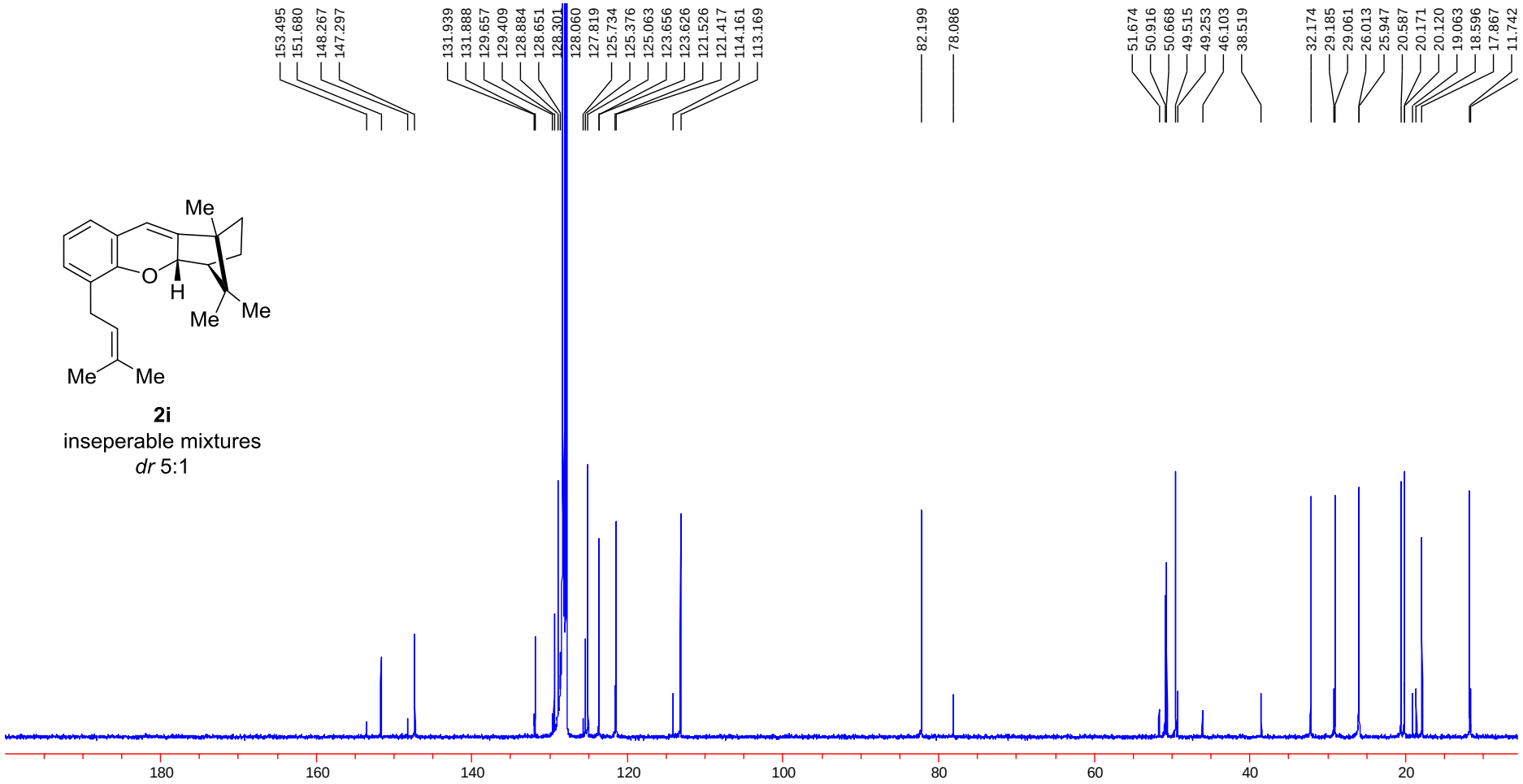
160
140
120
100
80
60
40
20

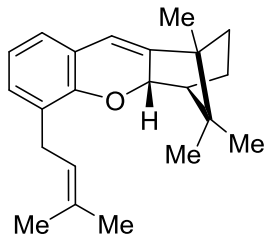


2i
inseperable mixtures
dr 5:1

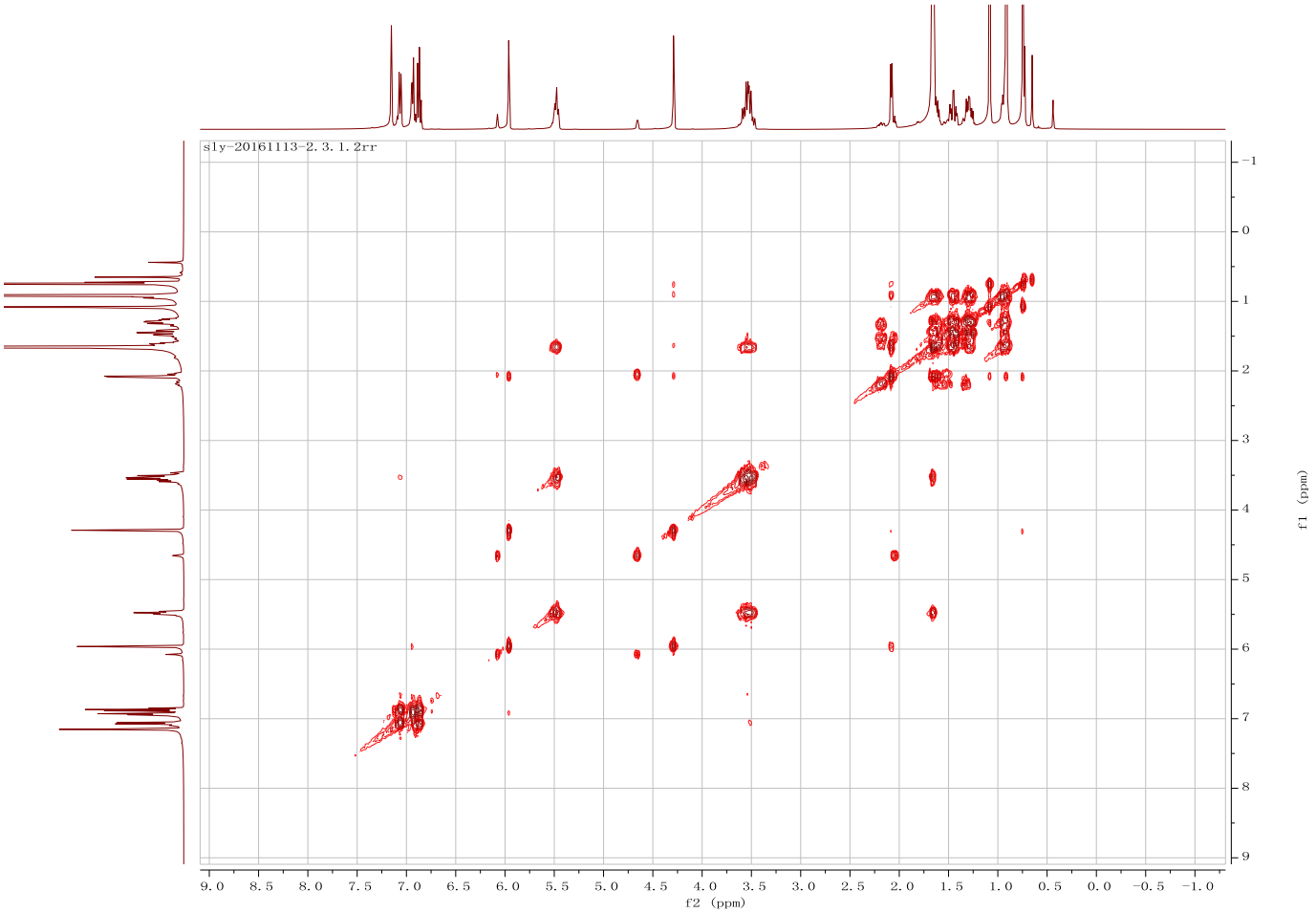


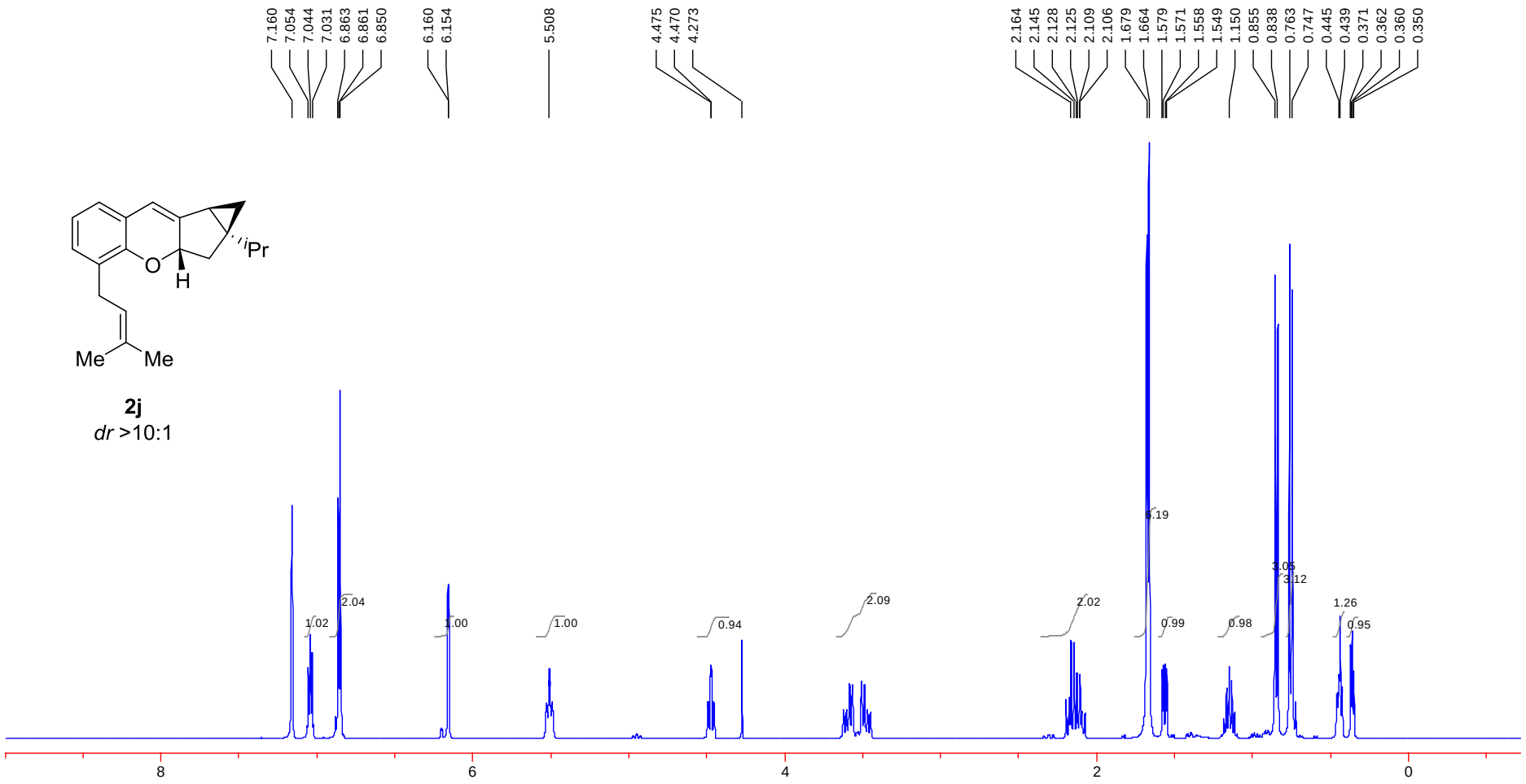
2i
inseperable mixtures
dr 5:1

2-D NOESY experiment for compound 2i



2i

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6.861
6.850
6.160
6.154
5.508
4.475
4.470
4.273
2.164
2.145
2.128
2.125
2.109
2.106
1.679
1.664
1.579
1.571
1.558
1.549
1.150
0.855
0.838
0.763
0.747
0.445
0.439
0.371
0.362
0.360
0.350
O
H
iPr
Me
Me
2j
dr >10:1
1.02
2.04
1.00
1.00
0.94
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0.99
0.98
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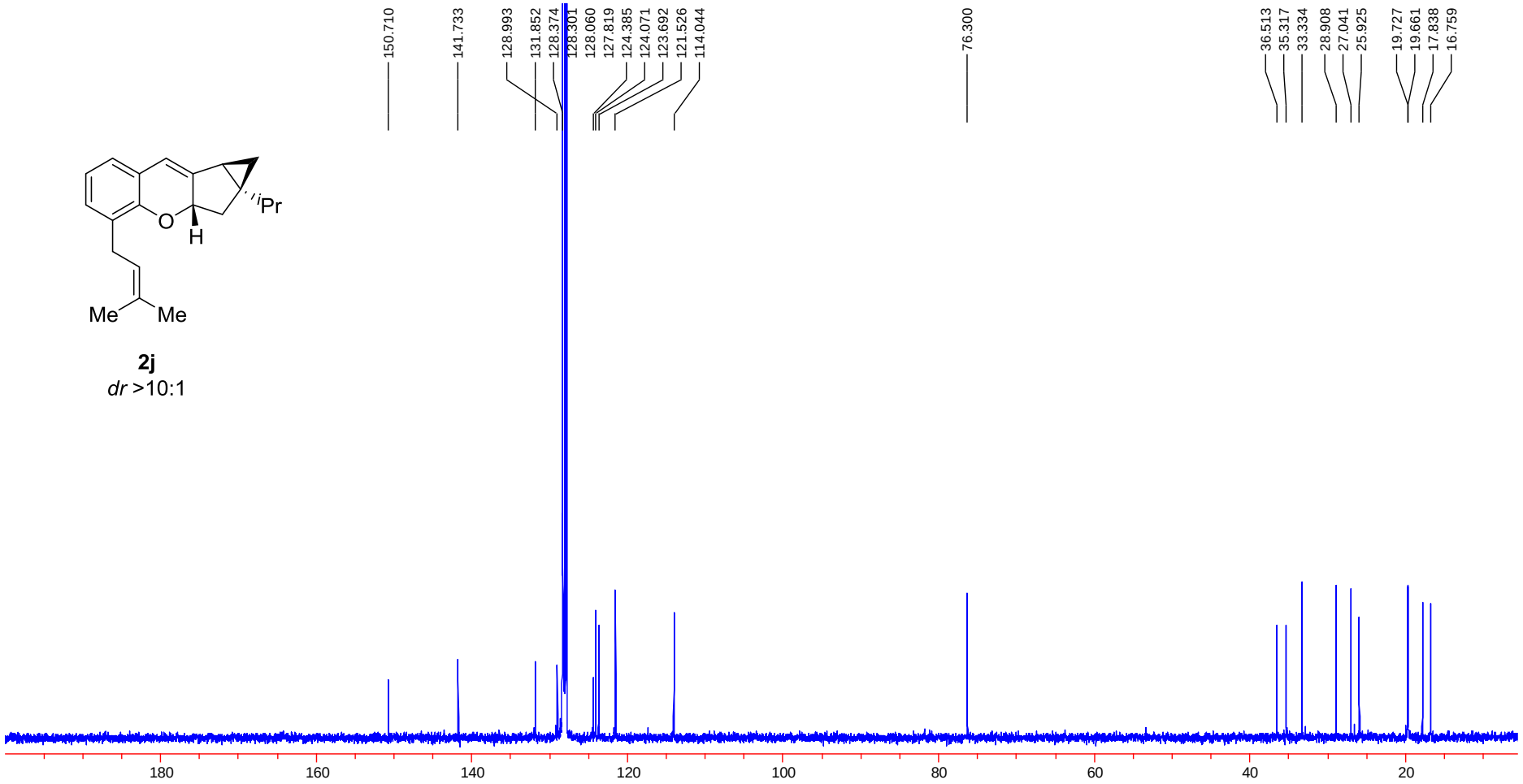
1.26
0.95
8
6
4
2
0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124.071
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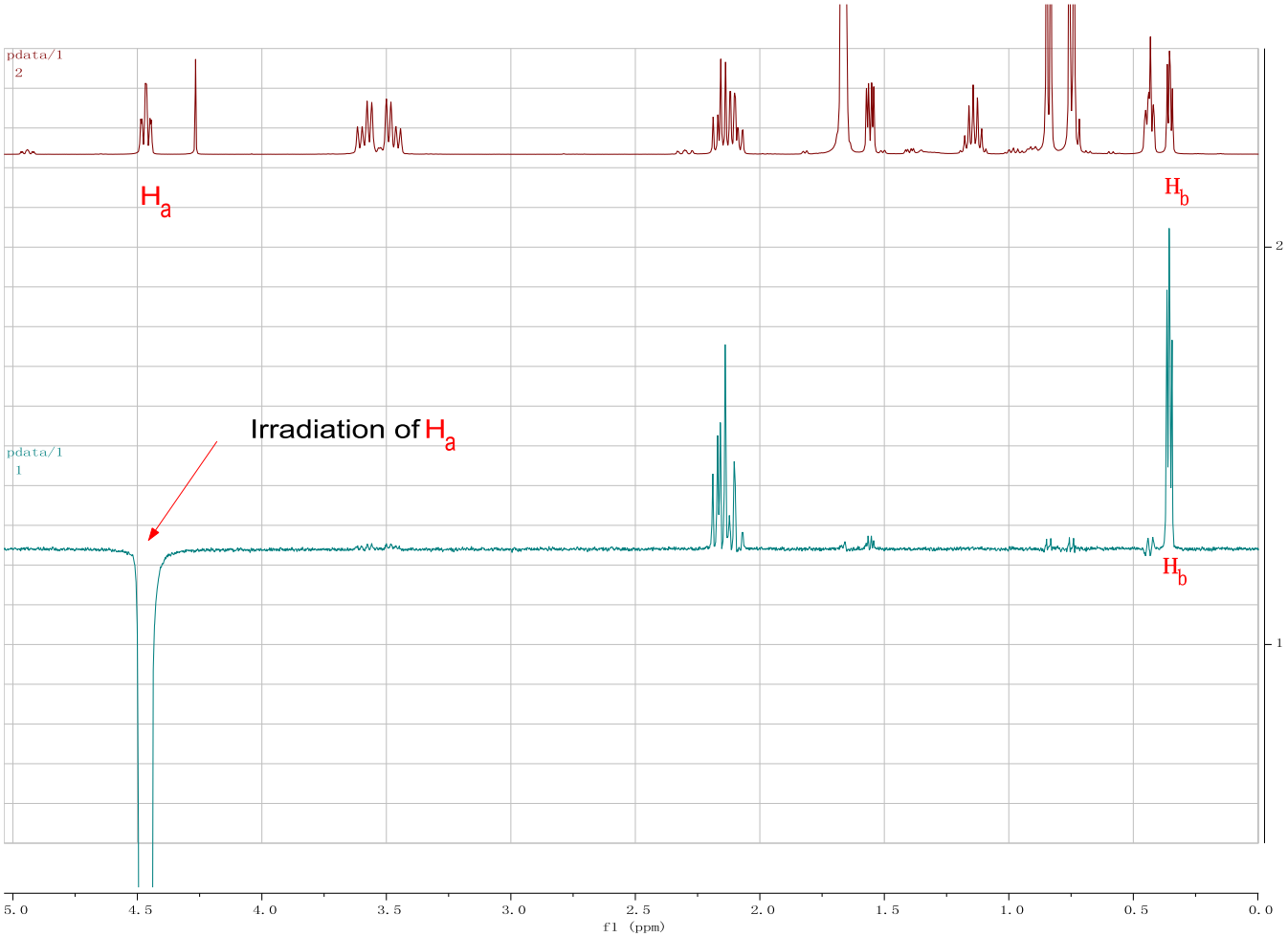
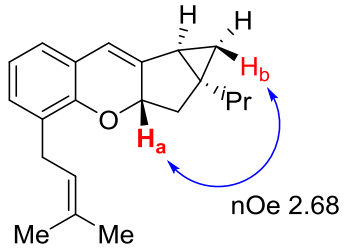
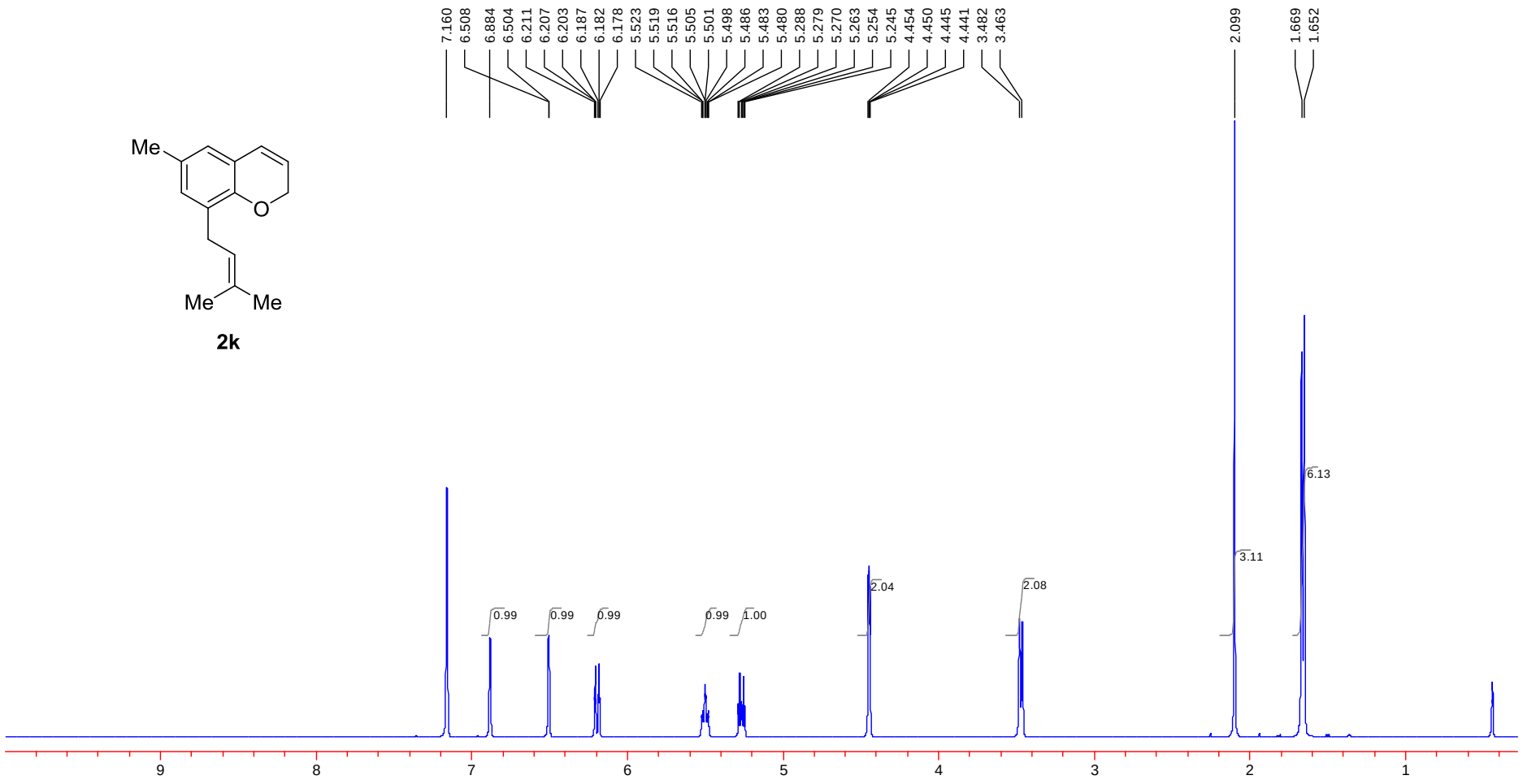
114.044
76.300
36.513
35.317
33.334
28.908
27.041
25.925
19.727
19.661
17.838
16.759
O
H
iPr
Me
Me
180
160
140
120
100
80
60
40
20

2j
dr >10:1

1-D nOe experiment for compound 2j



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6.178
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5.519
5.516
5.505
5.501
5.498
5.486
5.483
5.480
5.288
5.279
5.270
5.263
5.254
5.245
4.454
4.450
4.445
4.441
3.482
3.463
2.099
1.669
1.652
Me
O
Me
Me
2k
0.99
0.99
0.99
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3.11
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4
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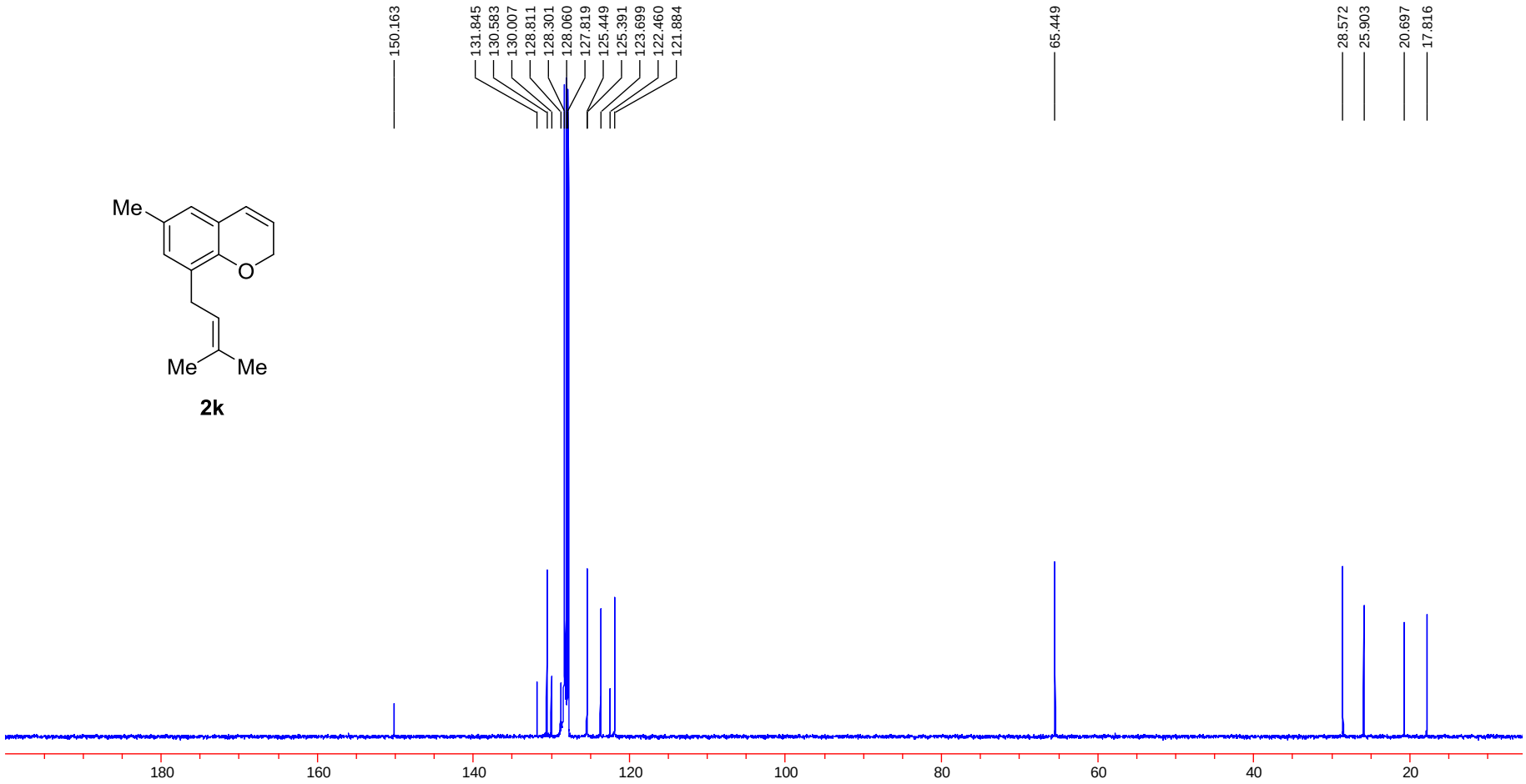
2
1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125.391
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121.884
65.449
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17.816
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O
Me
Me
2k
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160
140
120
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80
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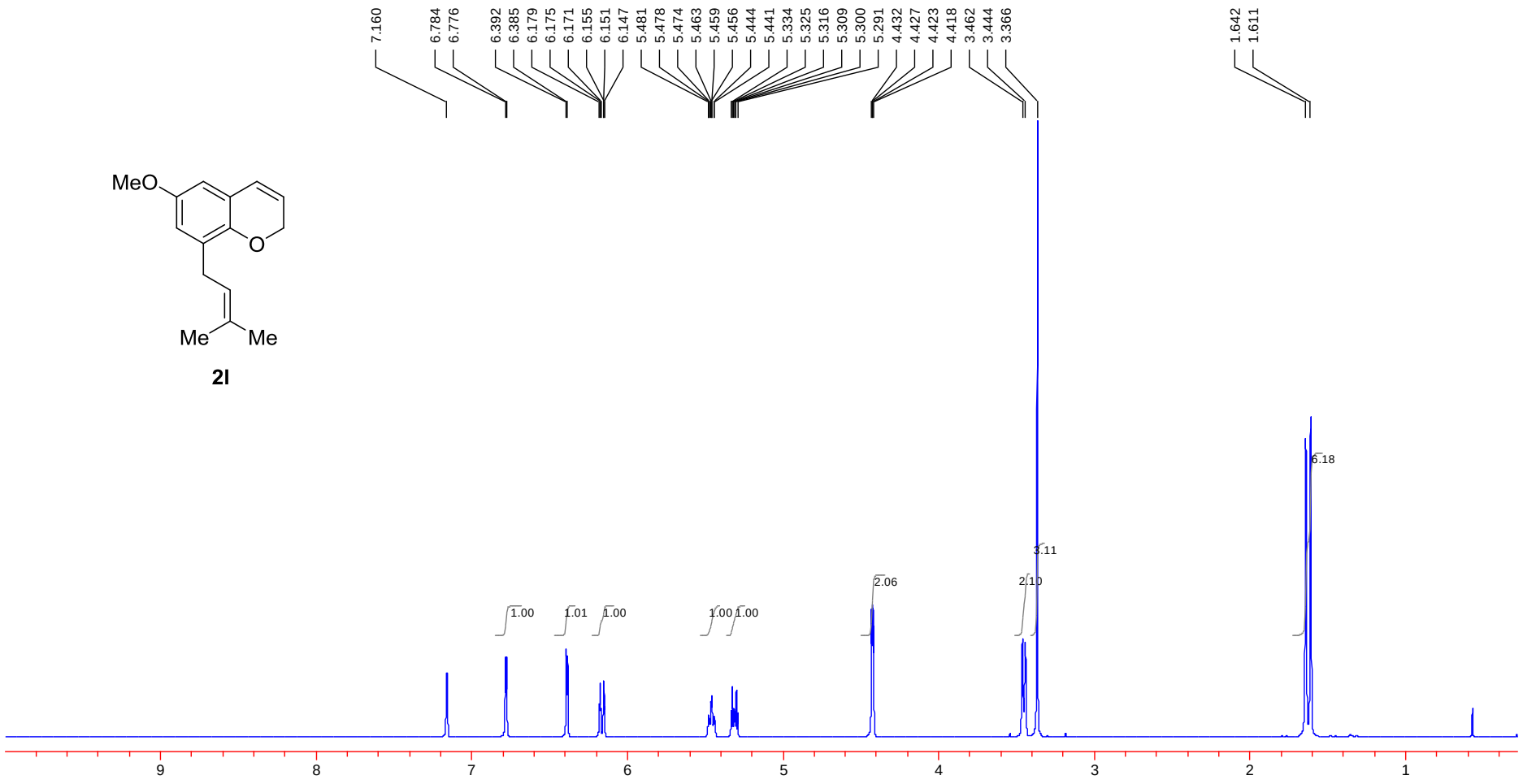
40
20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6.171
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6.151
6.147
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5.478
5.474
5.463
5.459
5.456
5.444
5.441
5.334
5.325
5.316
5.309
5.300
5.291
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4.427
4.423
4.418
3.462
3.444
3.366
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1.611
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Me
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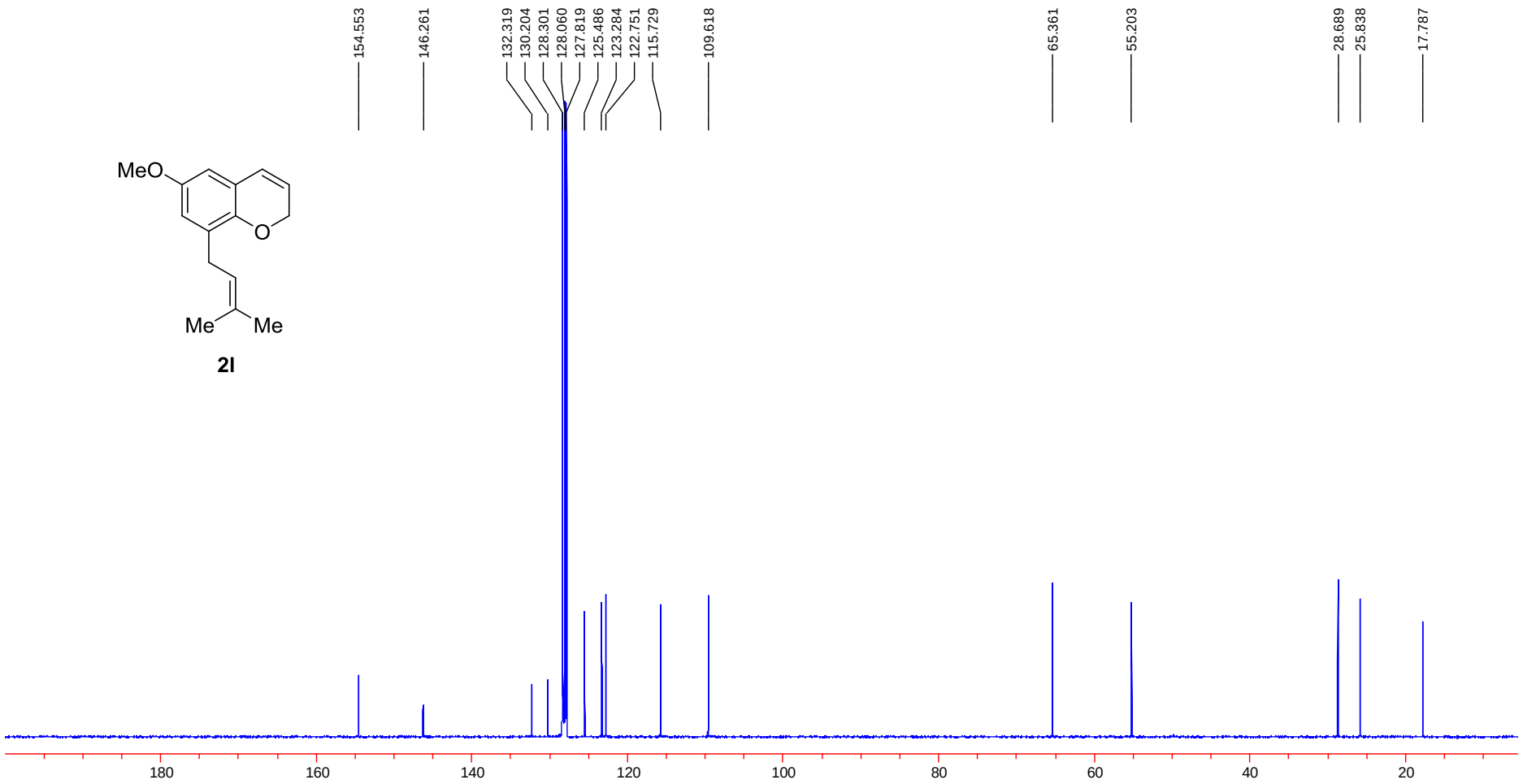
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65.361
55.203
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Me
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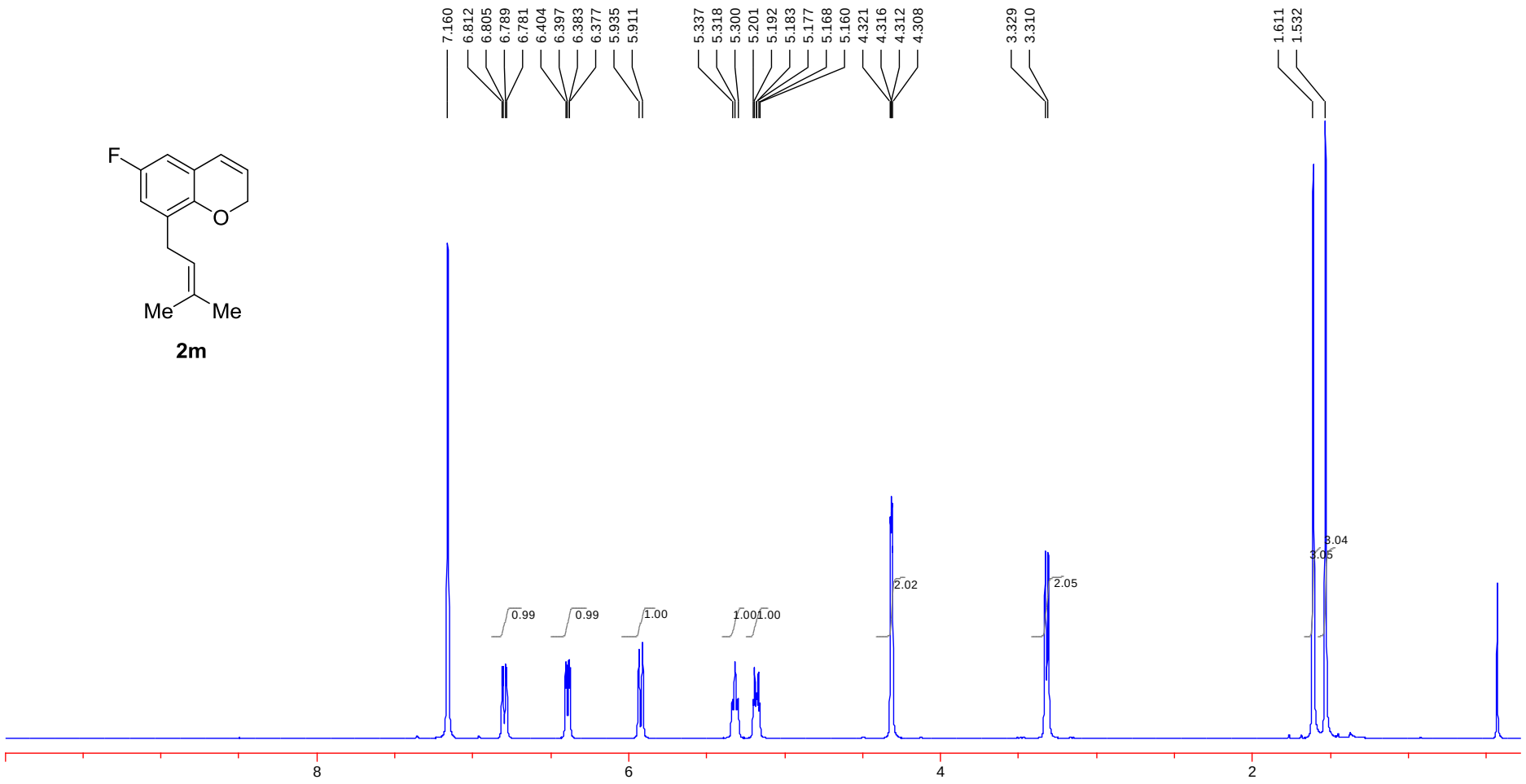
40
20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5.300
5.201
5.192
5.183
5.177
5.168
5.160
4.321
4.316
4.312
4.308
3.329
3.310
1.611
1.532
F
O
Me
Me
2m
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1.00
1.00
1.00
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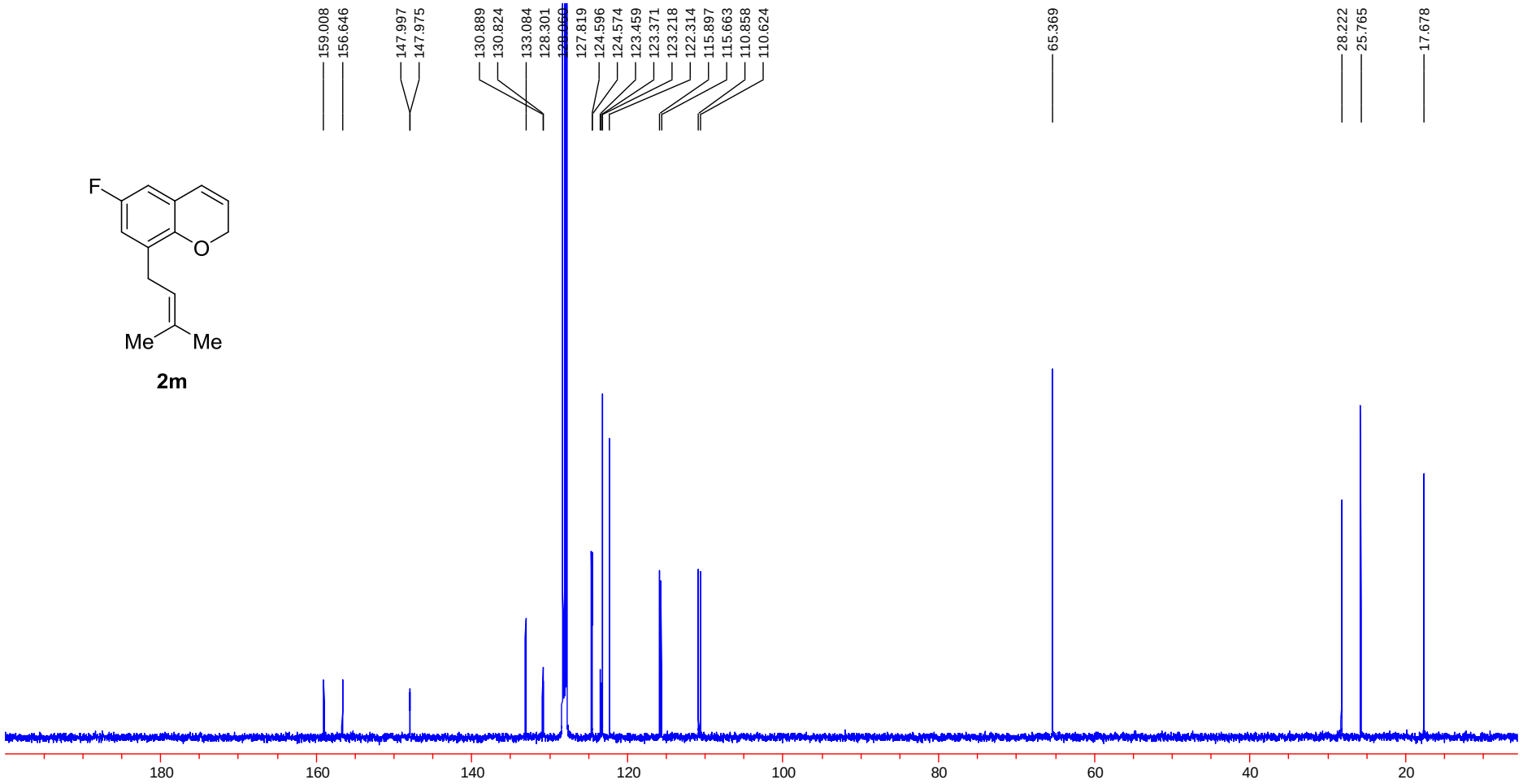
2.05
3.04
3.05
8
6
4
2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123.371
123.218
122.314
115.897
115.663
110.858
110.624
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Me
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2m
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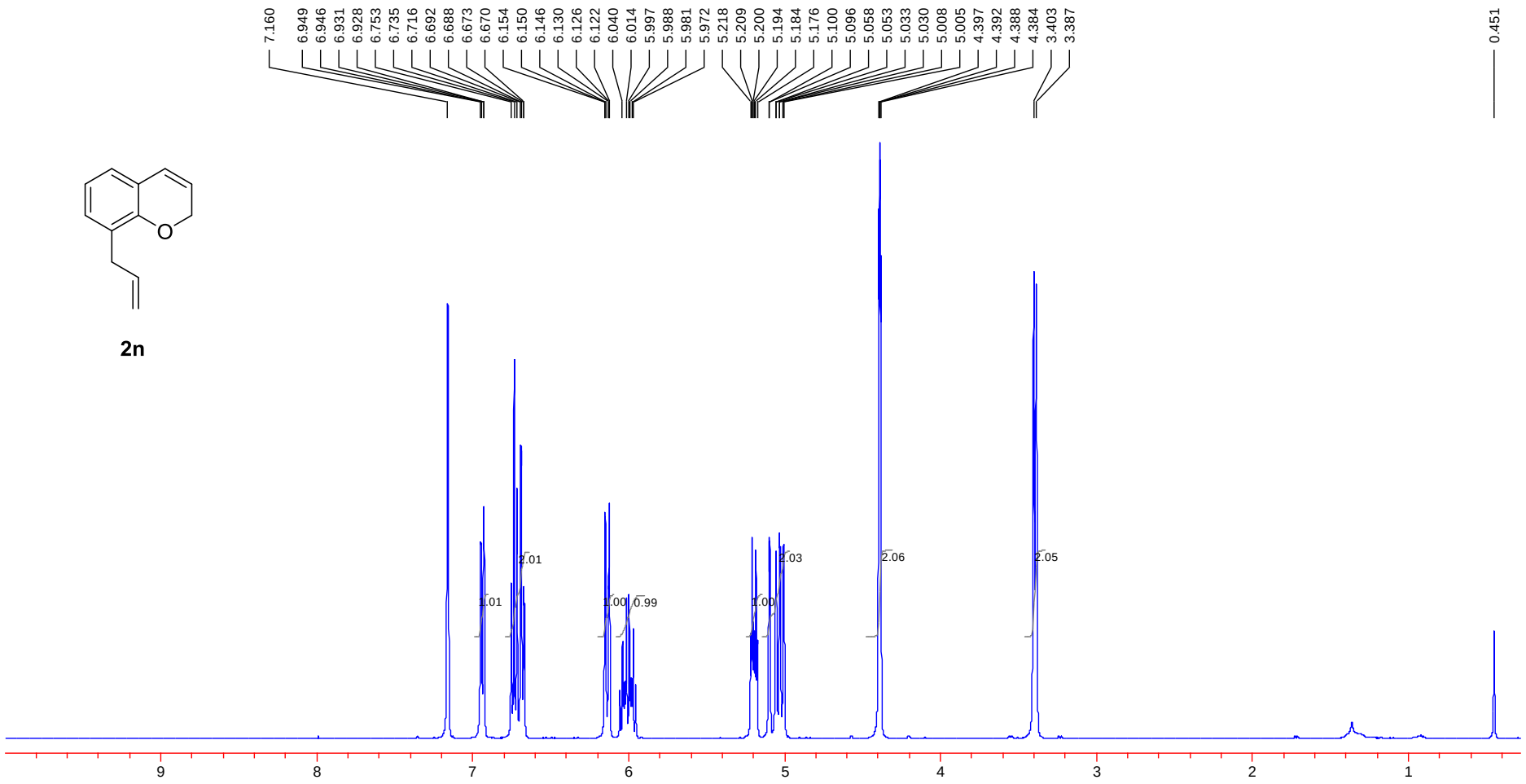
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6.150
6.146
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6.122
6.040
6.014
5.997
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5.981
5.972
5.218
5.209
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5.184
5.176
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5.033
5.030
5.008
5.005
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4.392
4.388
4.384
3.403
3.387
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2n
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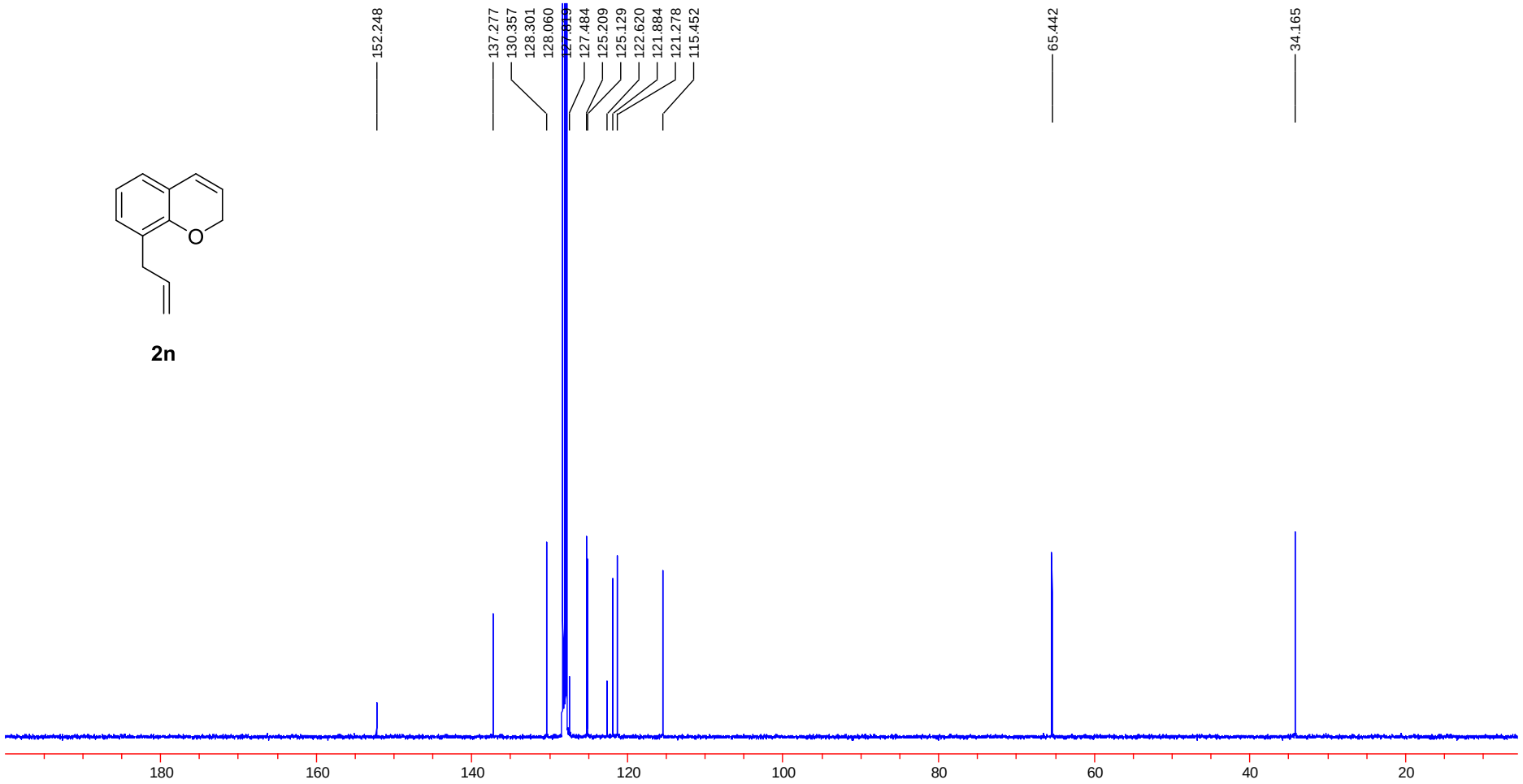
2
1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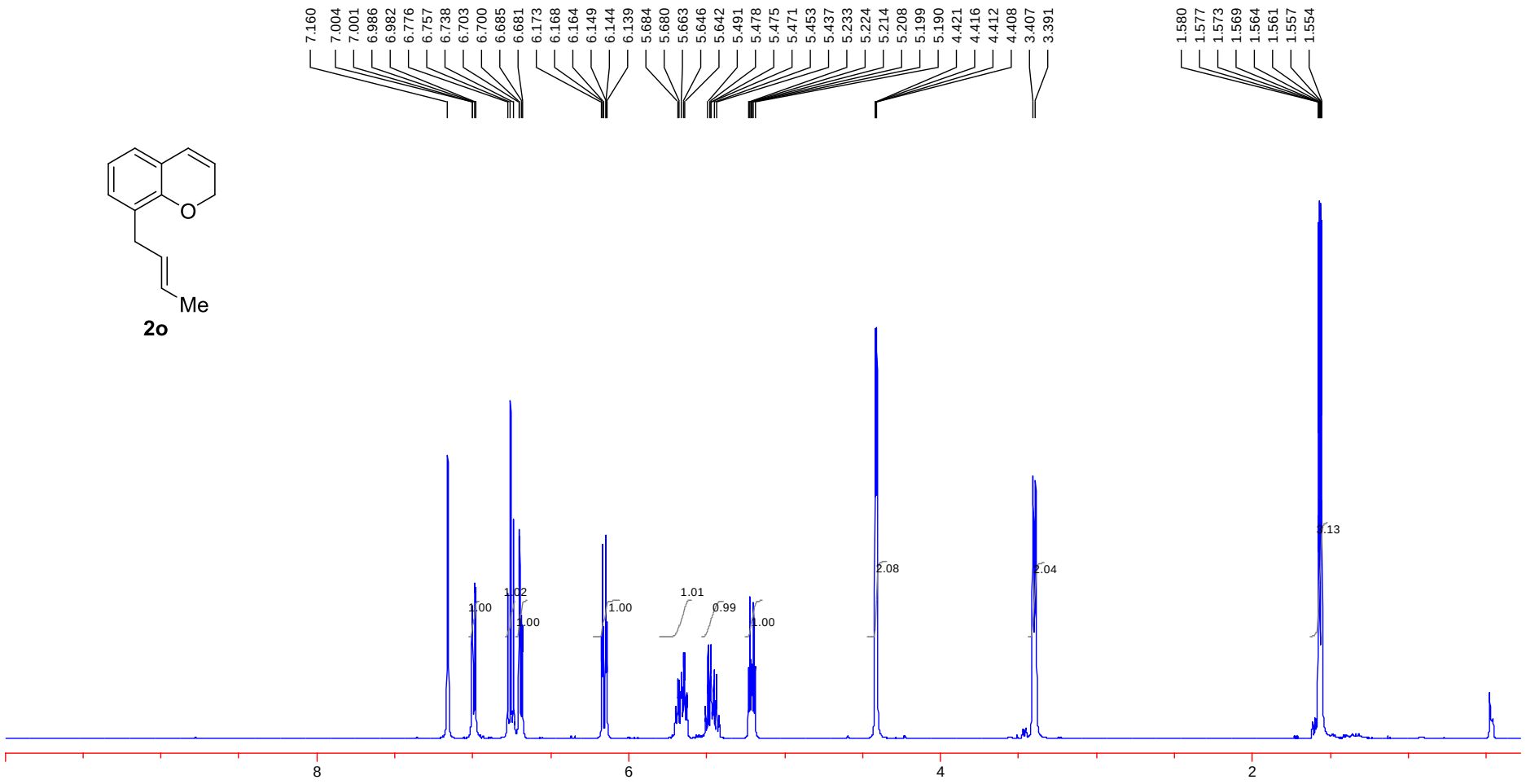
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6.168
6.164
6.149
6.144
6.139
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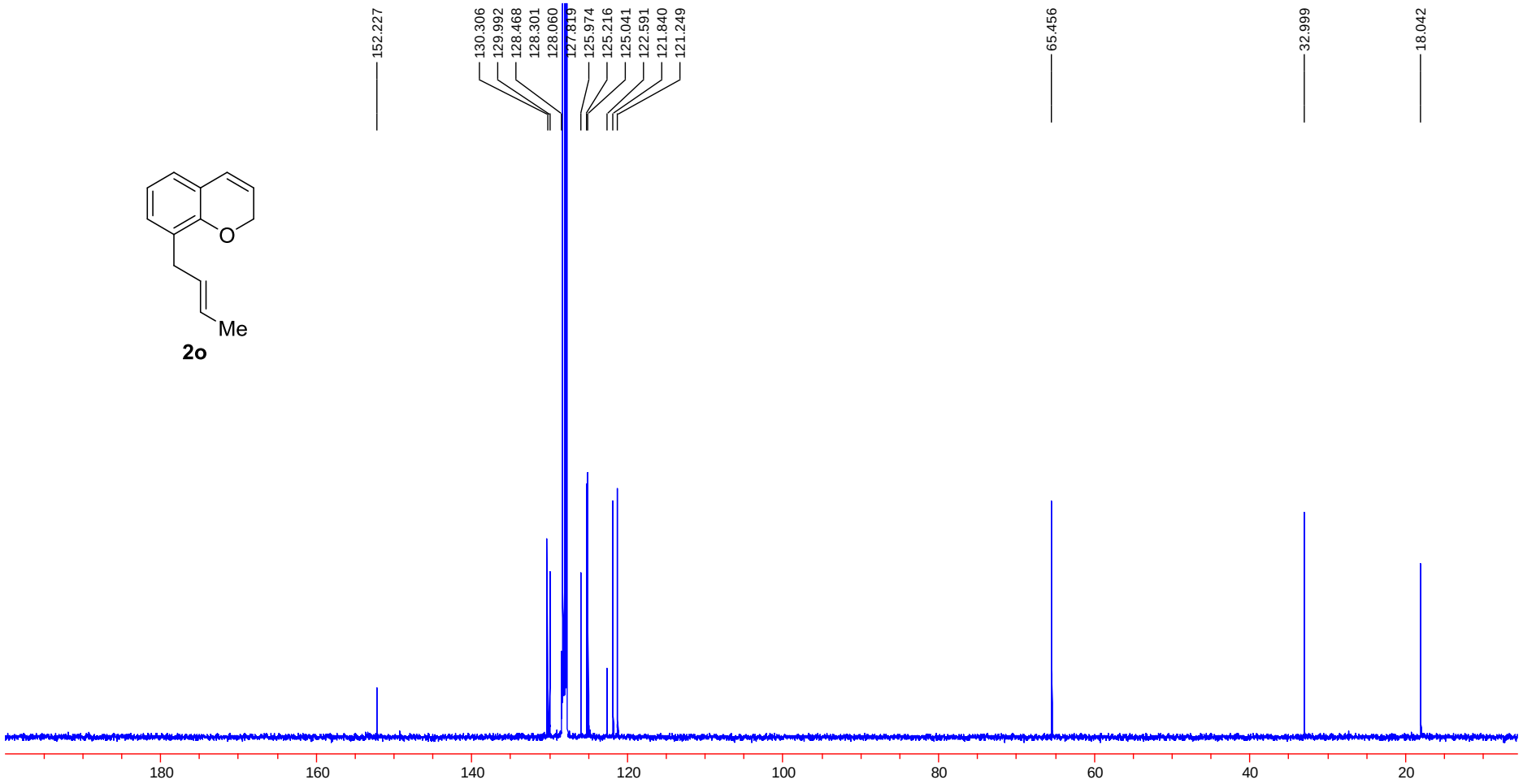
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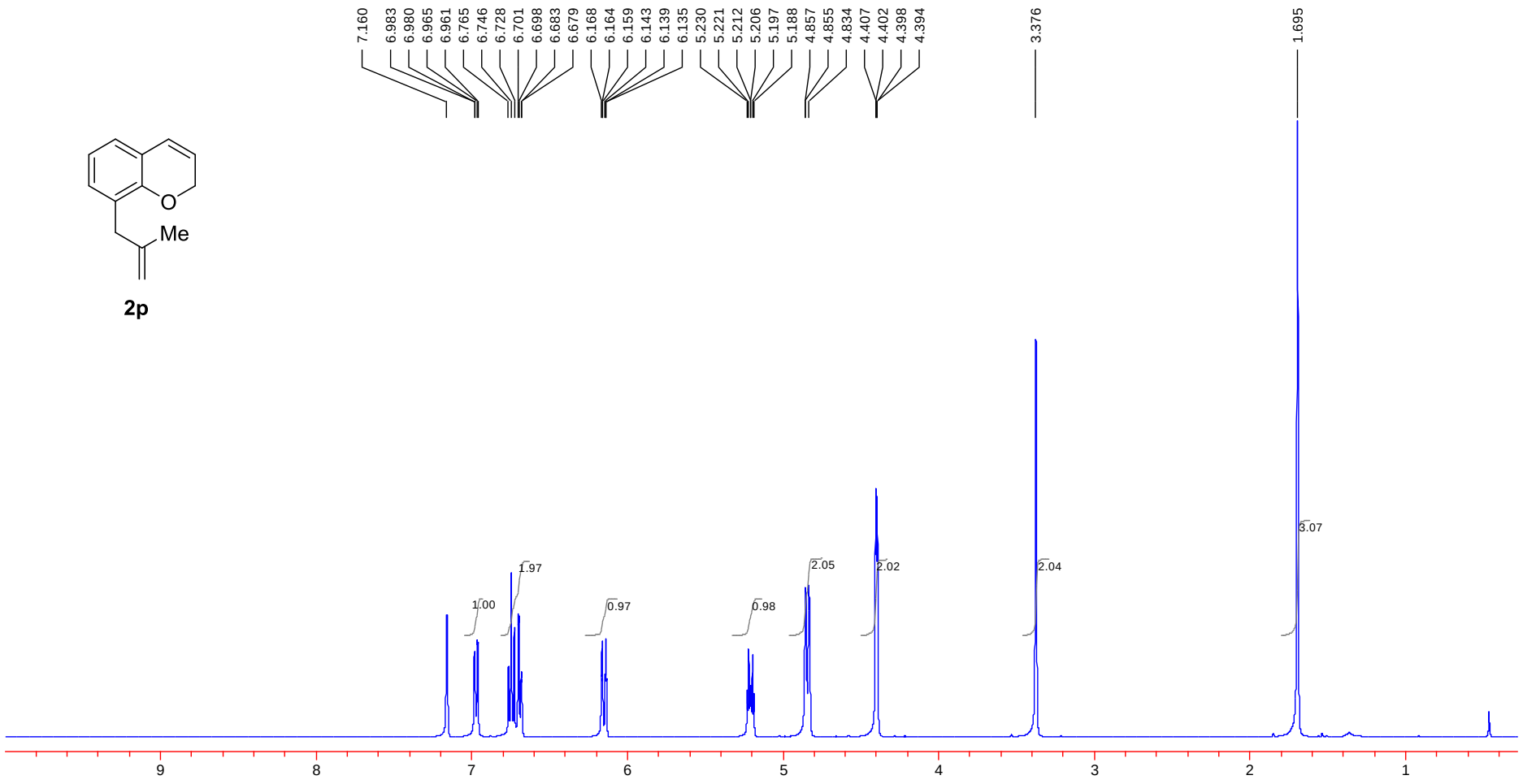
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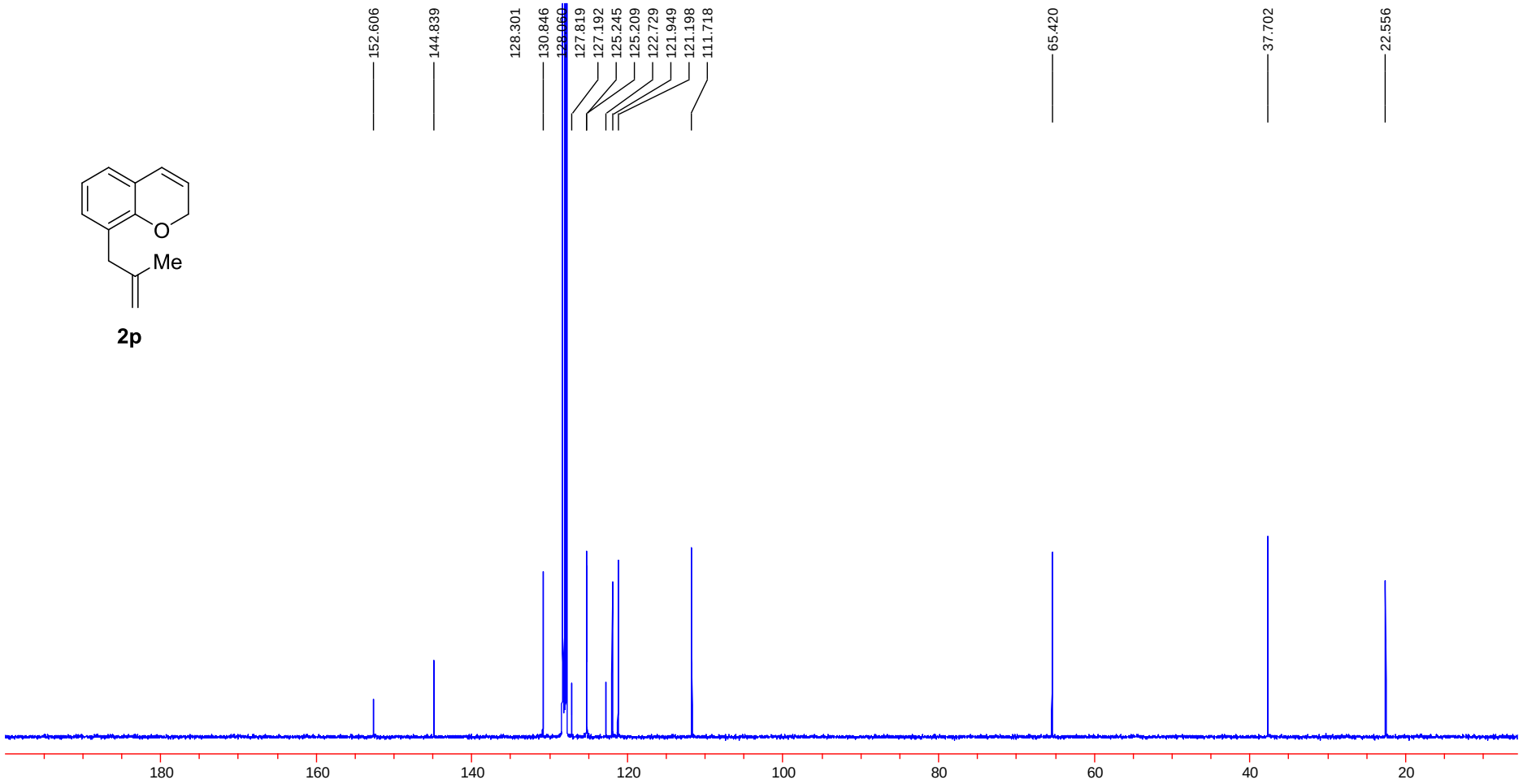
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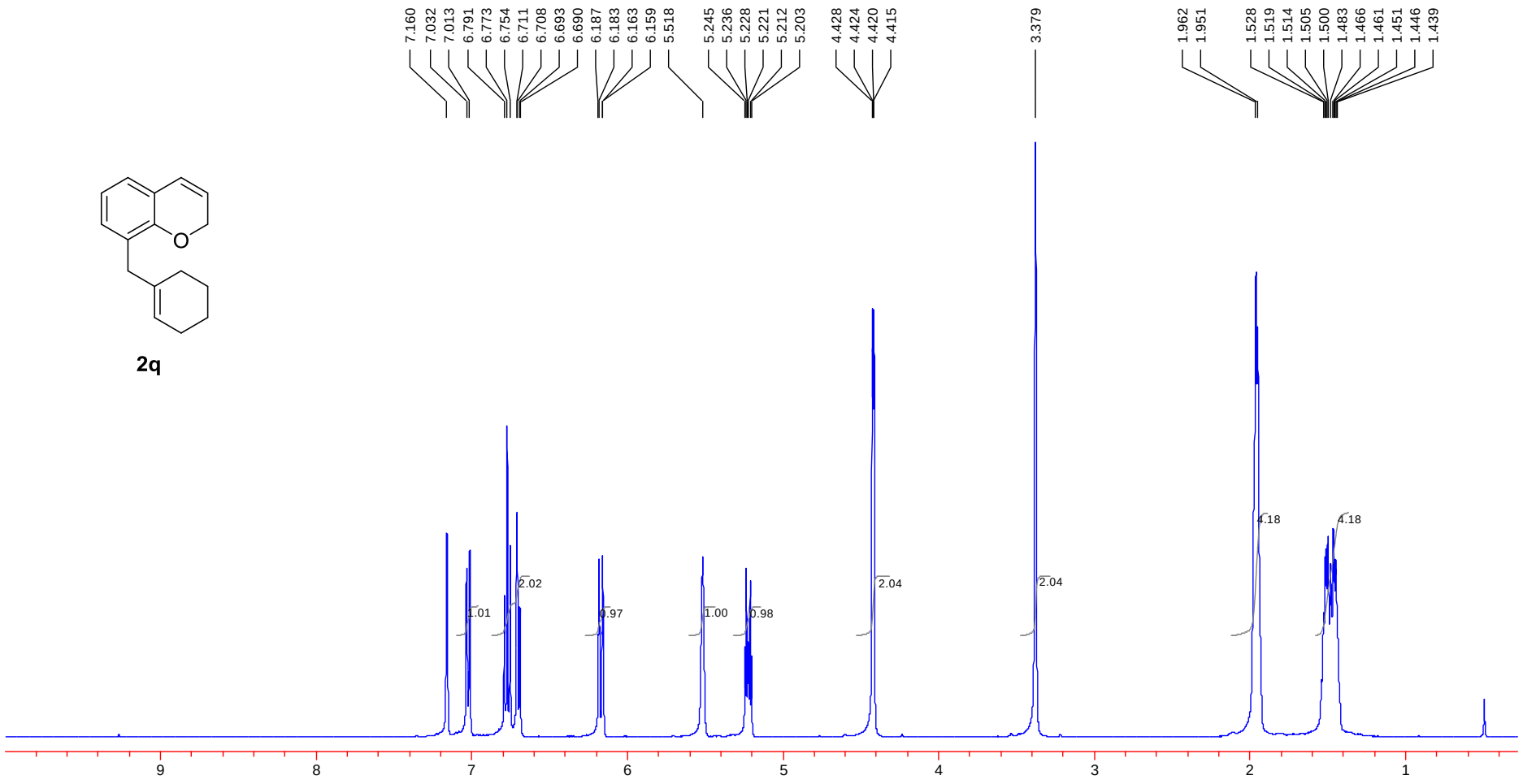
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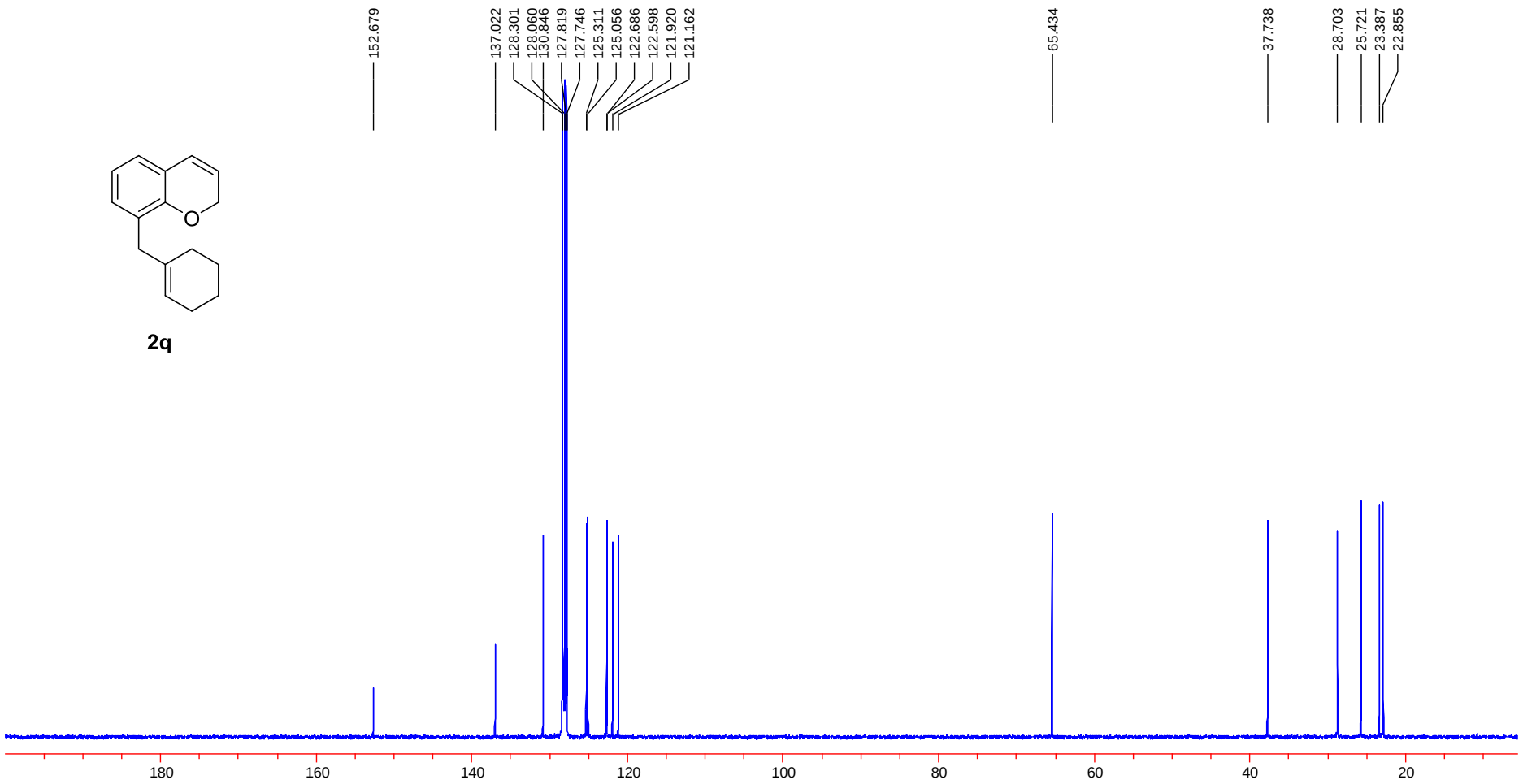
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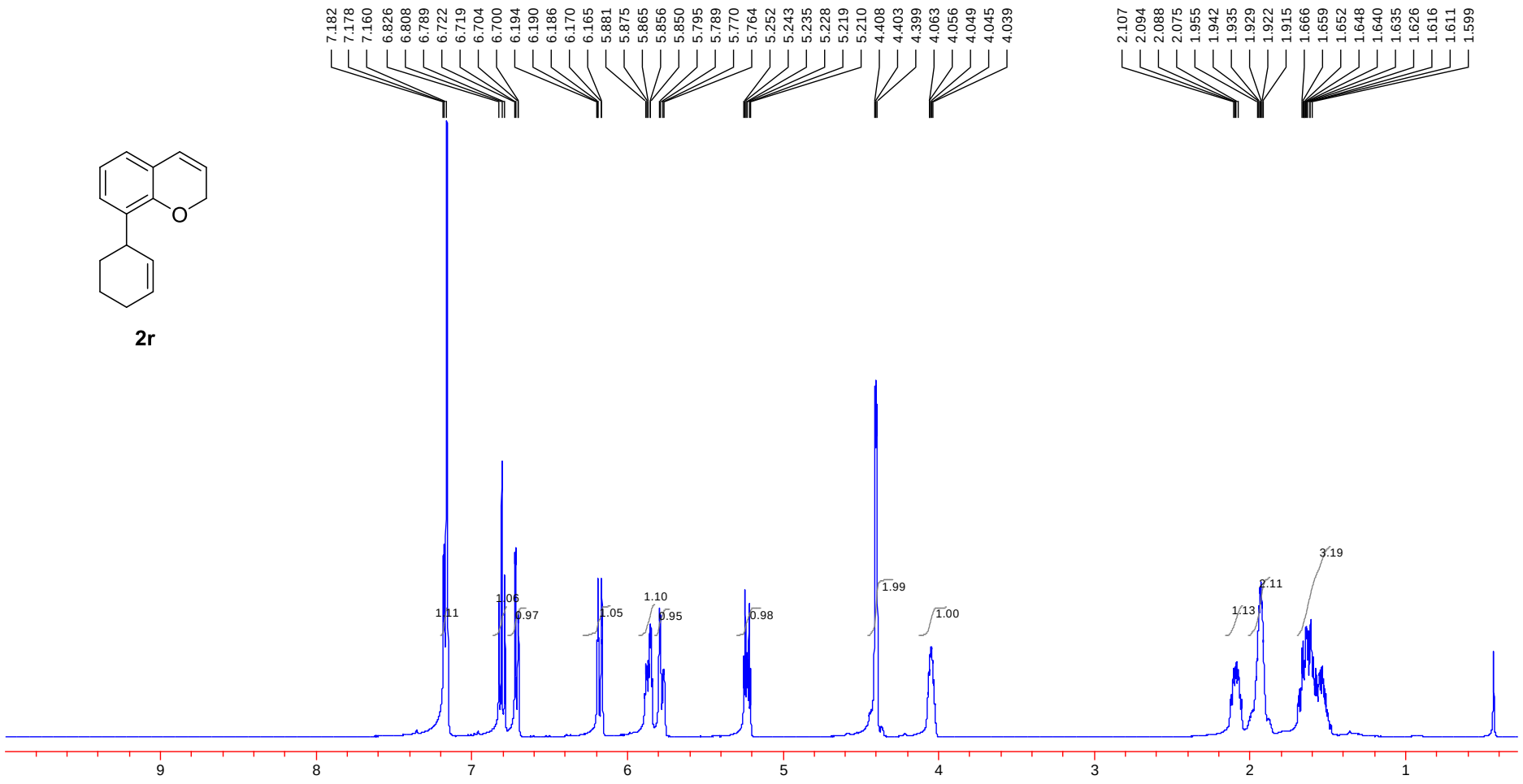
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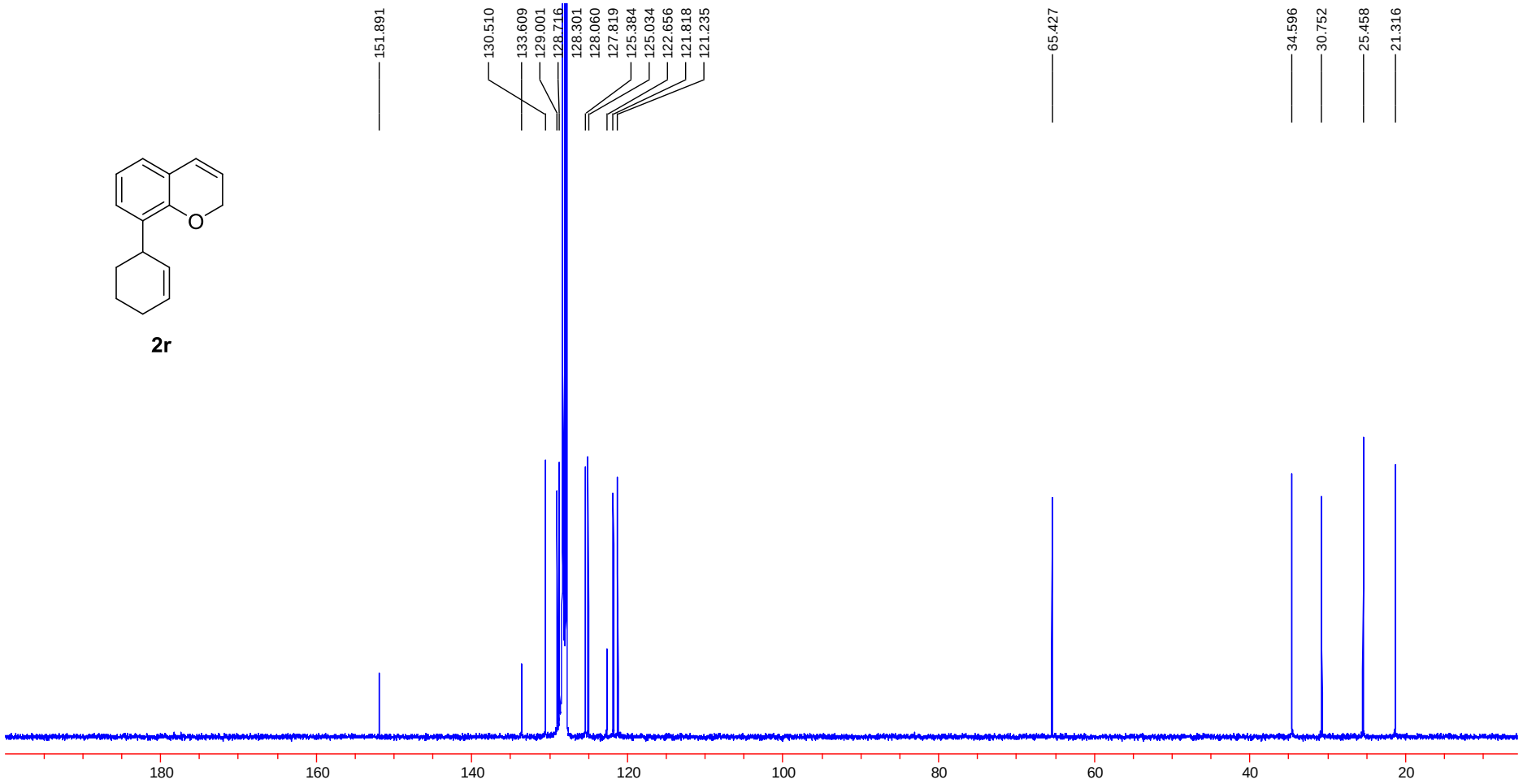
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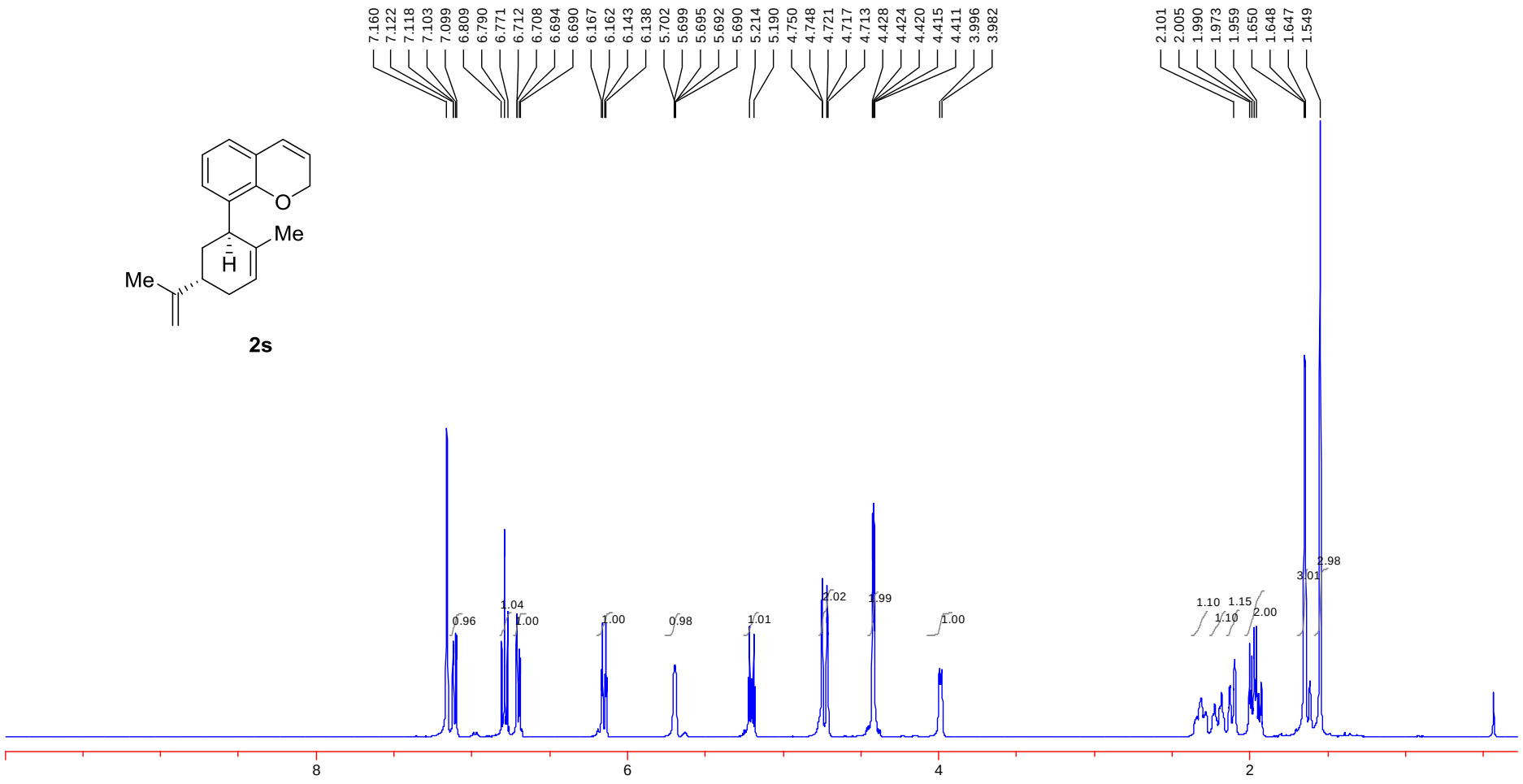
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6.143
6.138
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5.695
5.692
5.690
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5.190
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1.648
1.647
1.549
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Me
H
Me
2s
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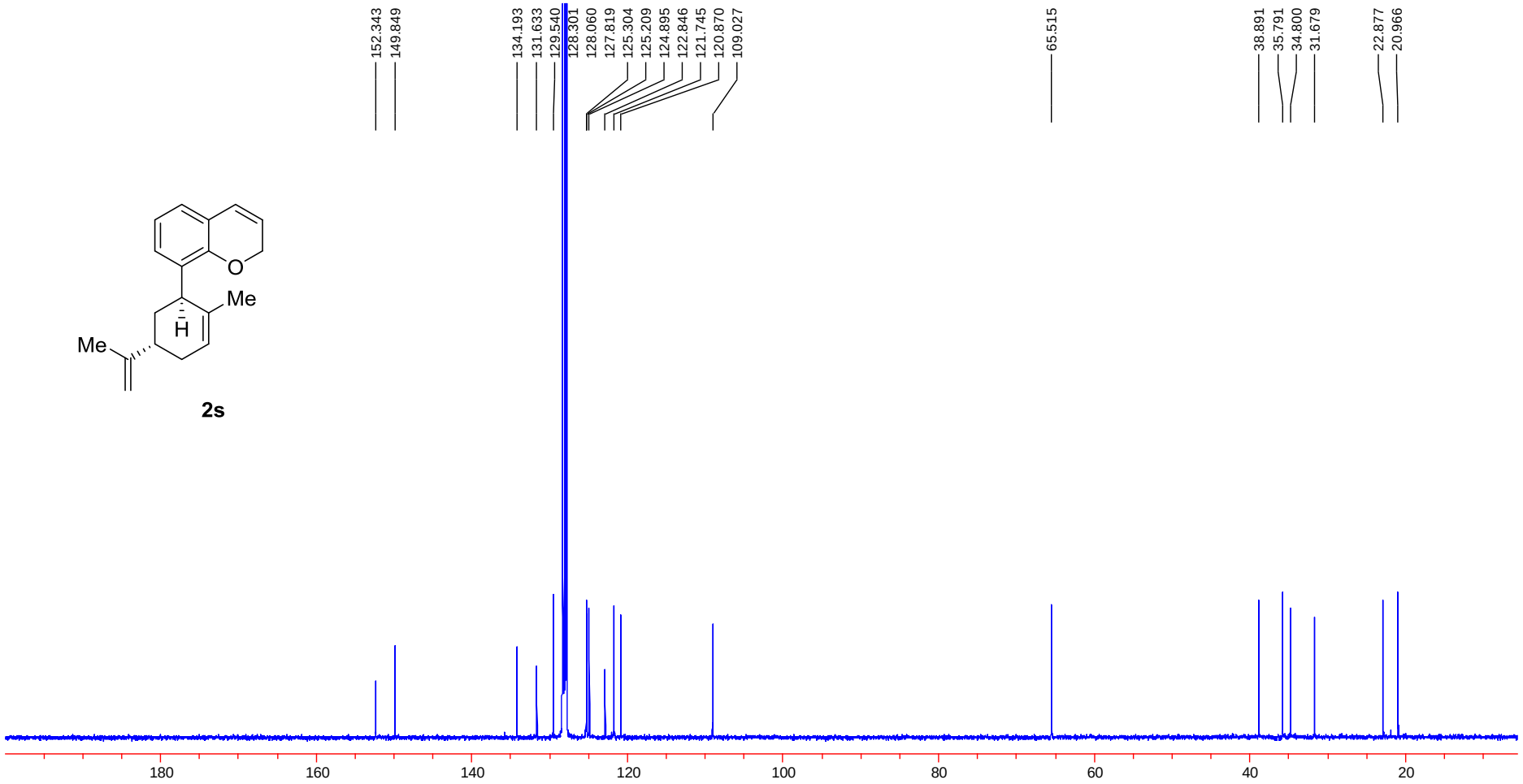
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22.877
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H
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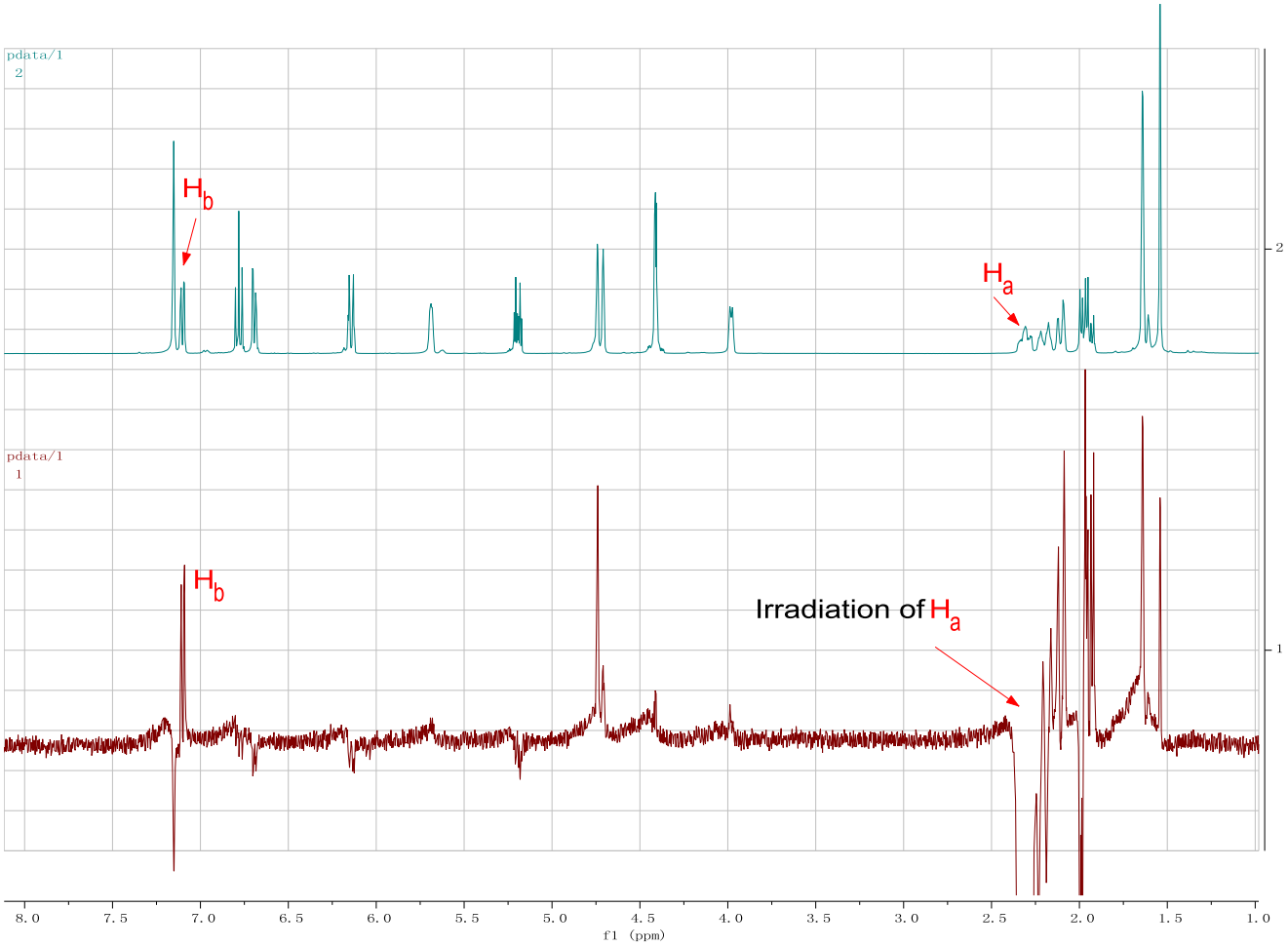
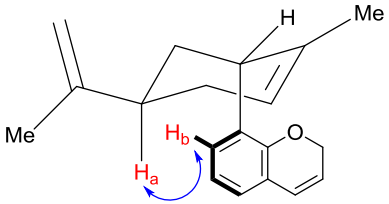
1-D nOe experiment for compound 2s





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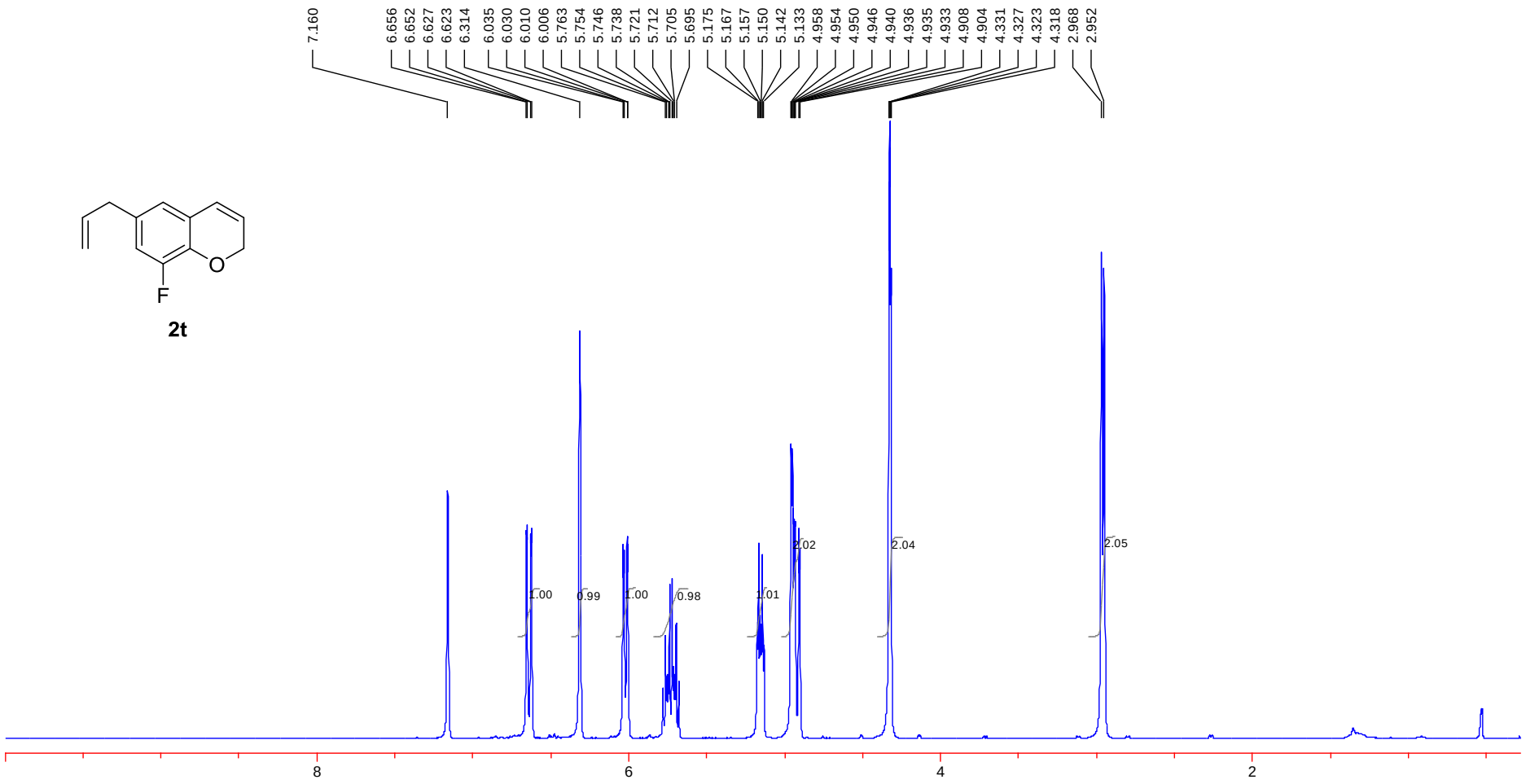
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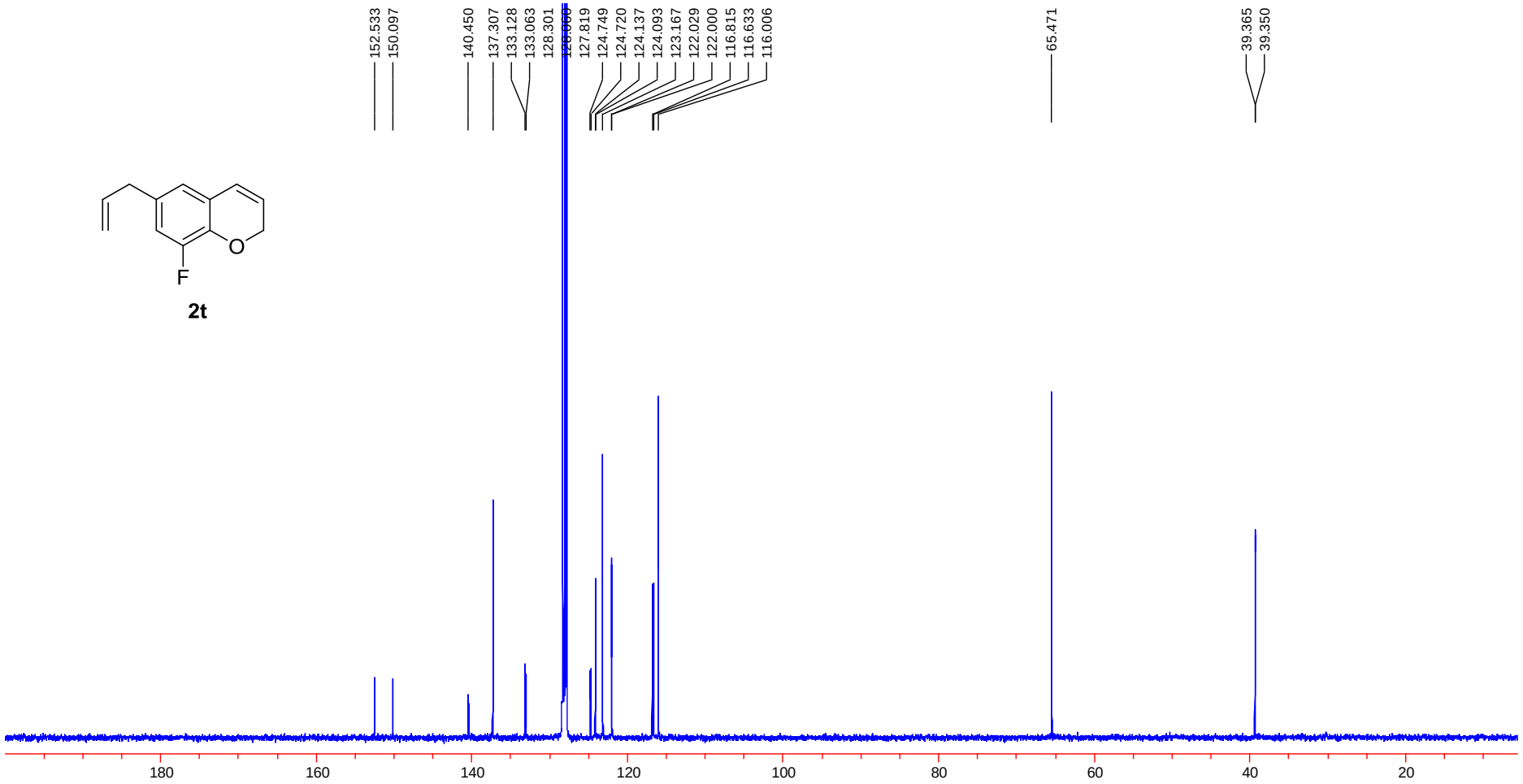
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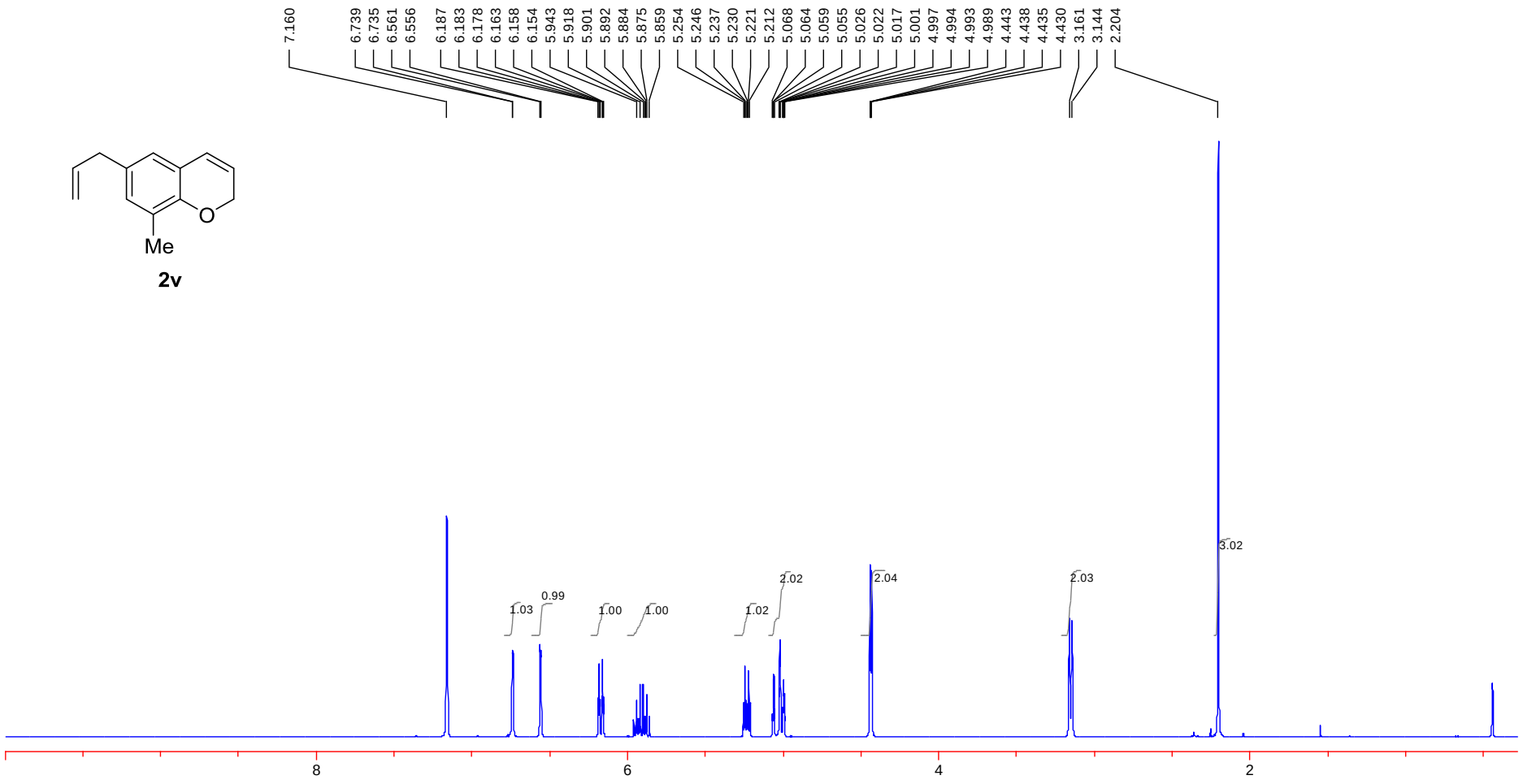
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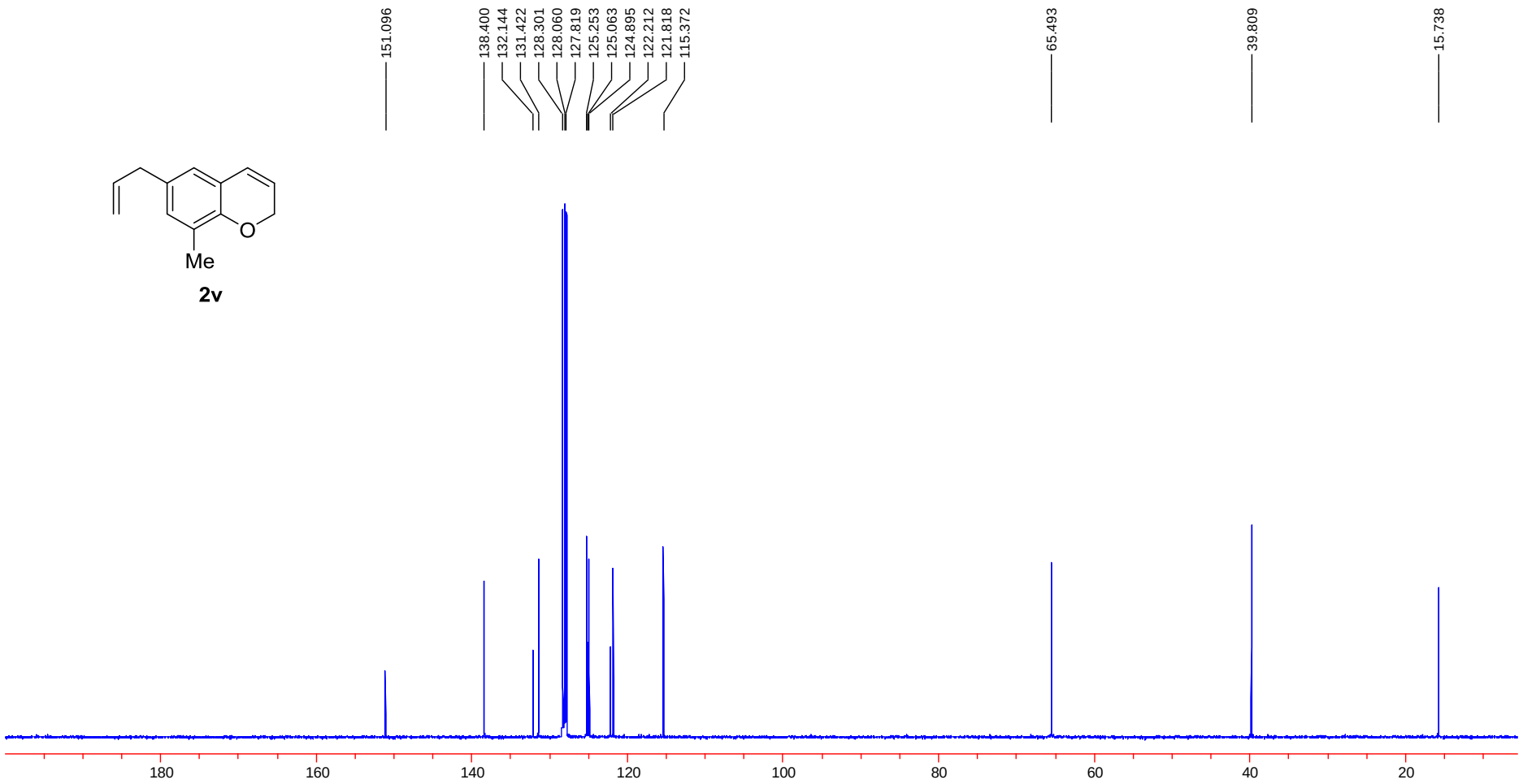
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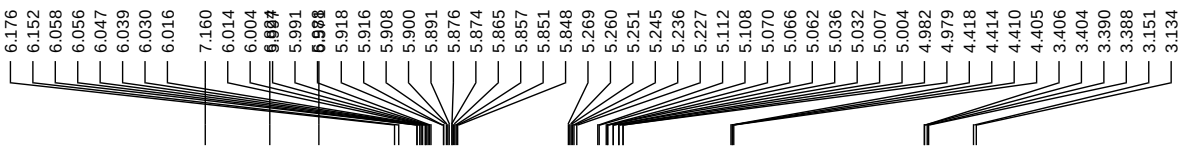
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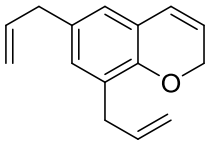
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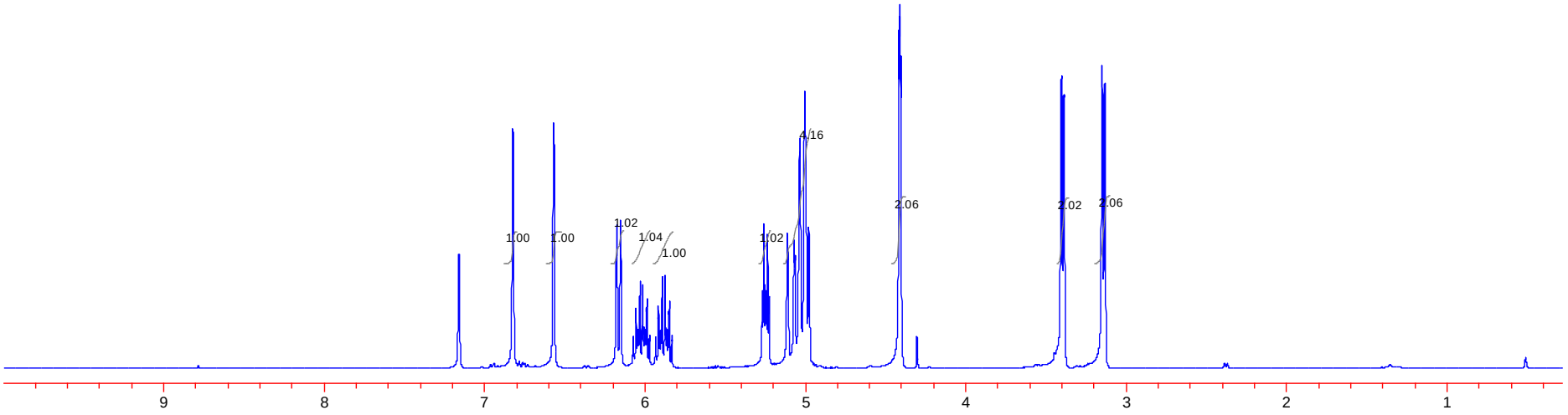
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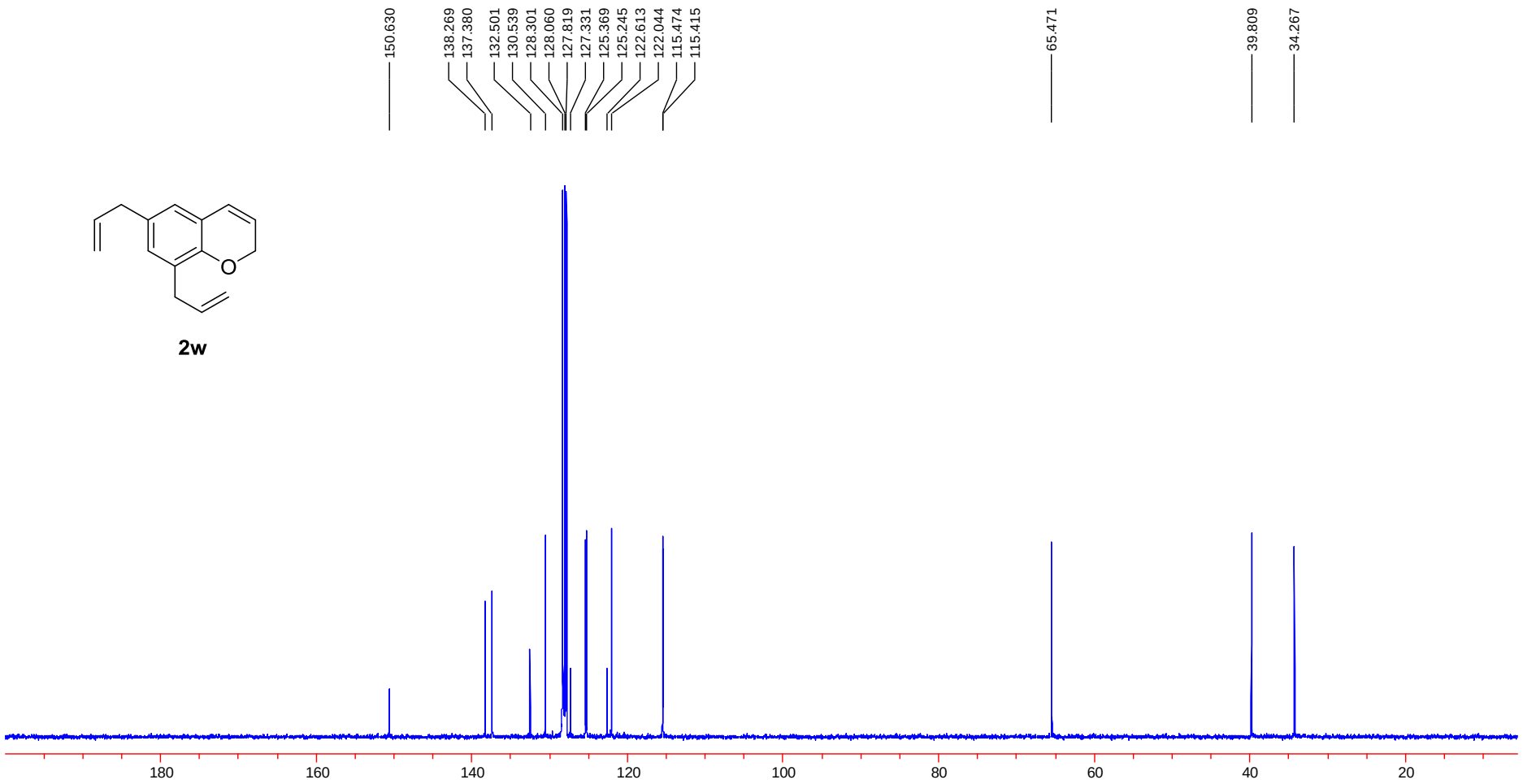
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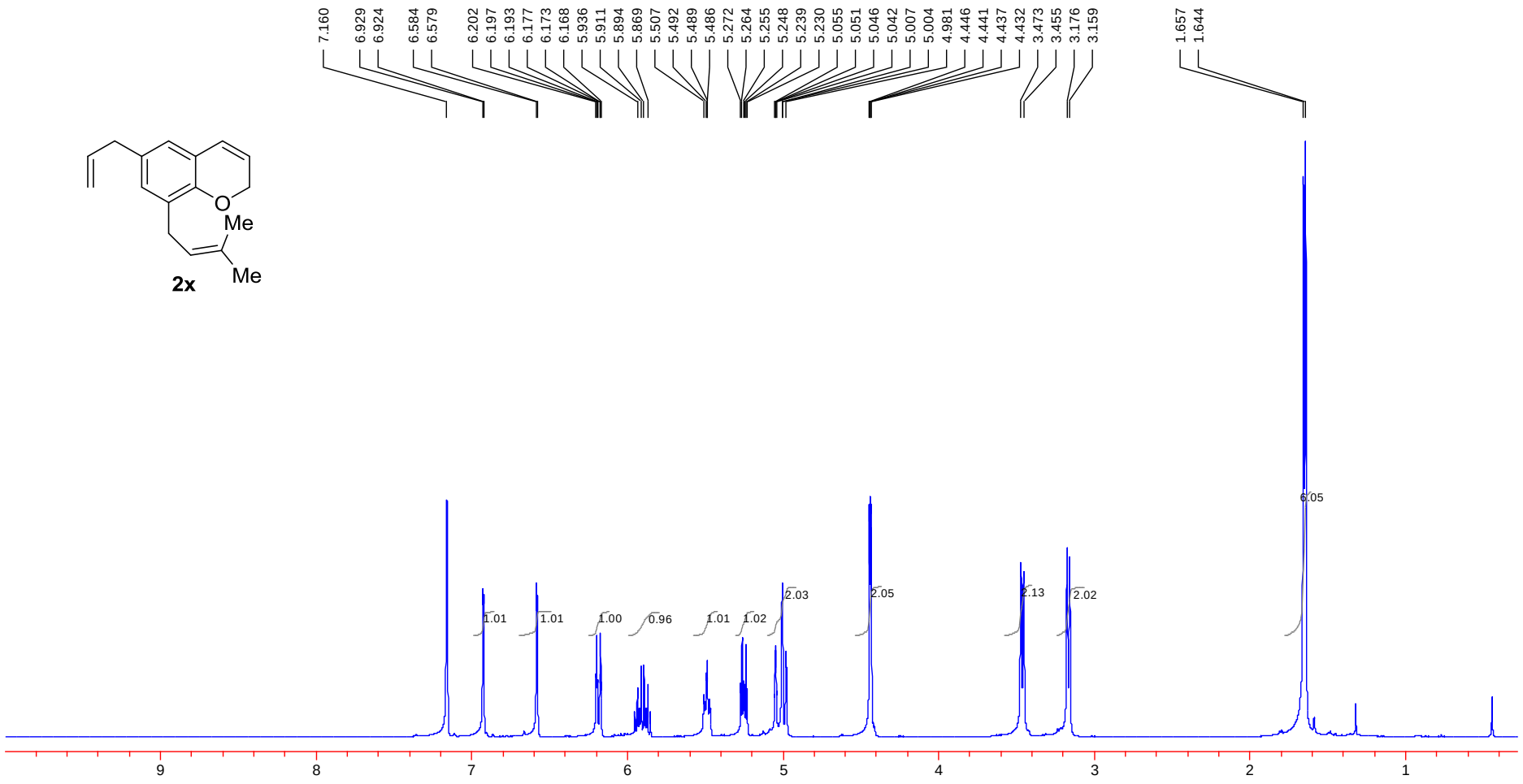
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Me
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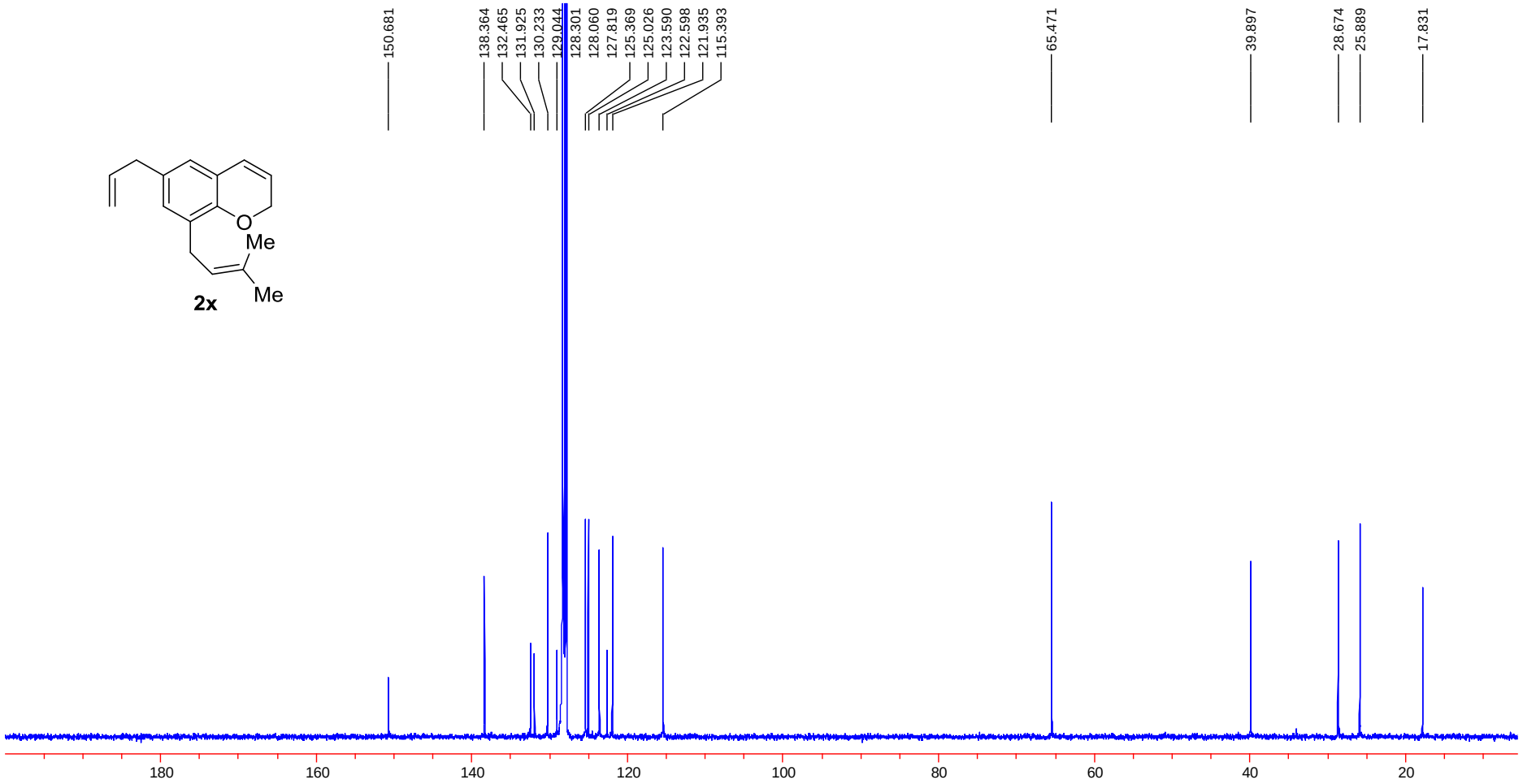
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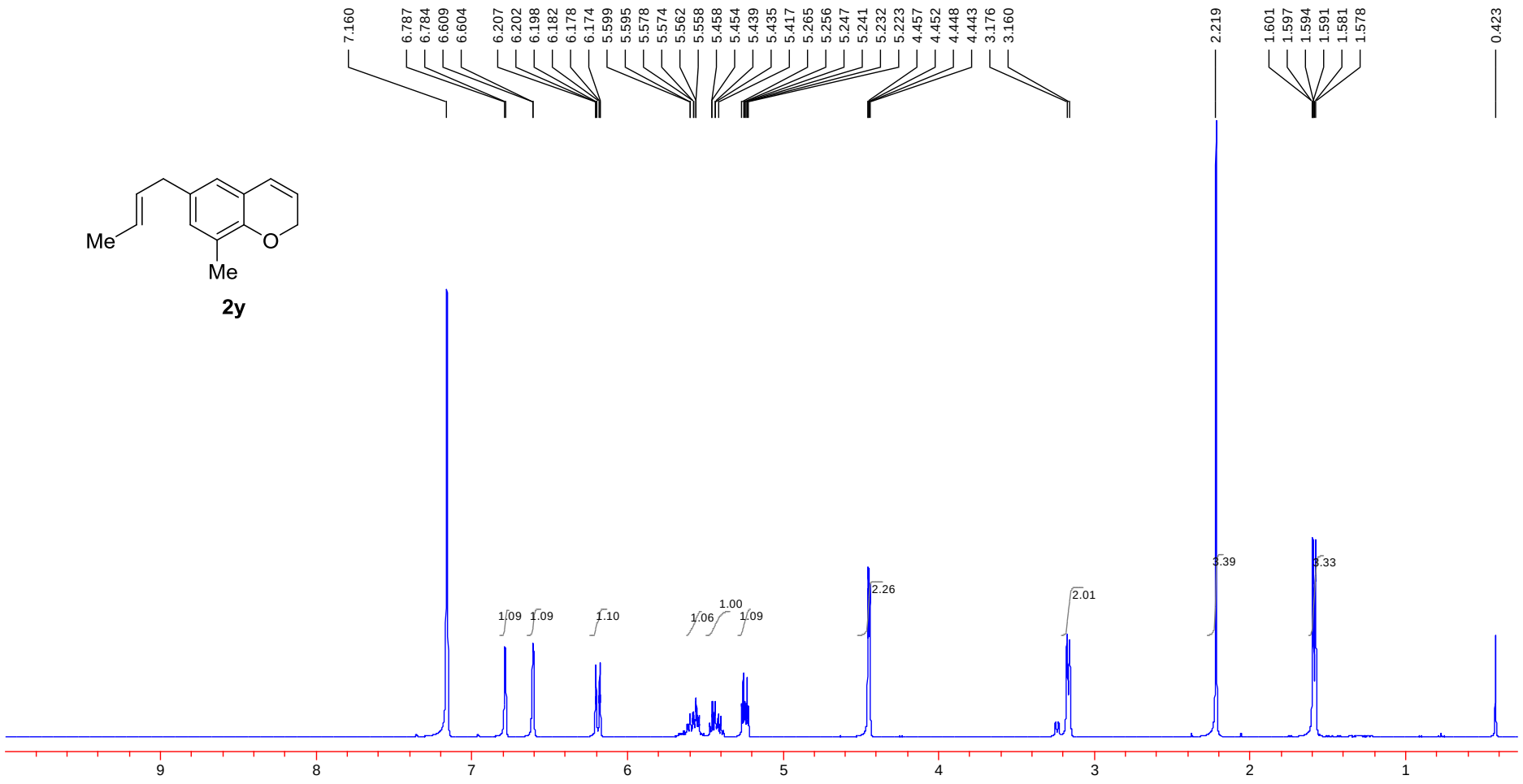
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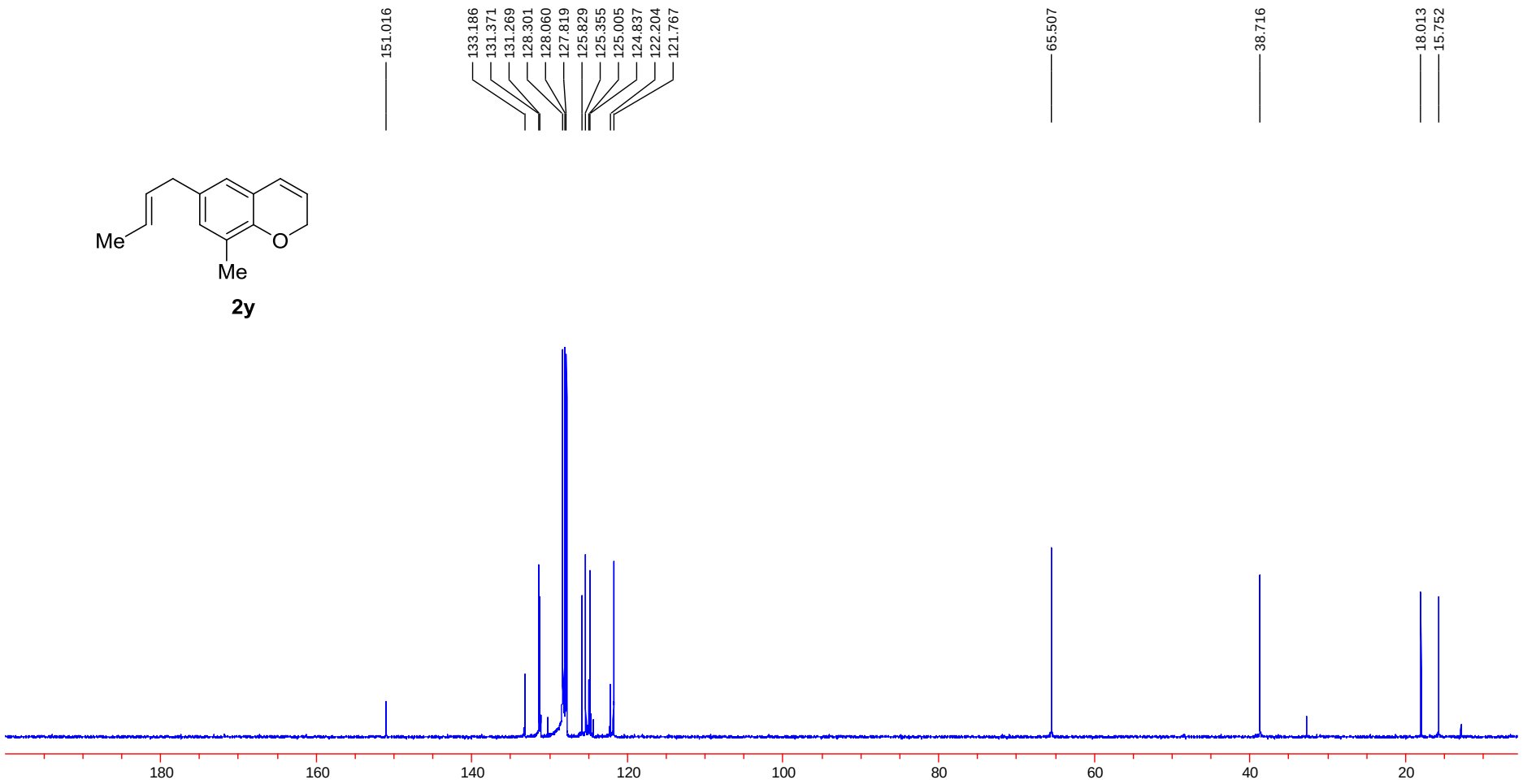
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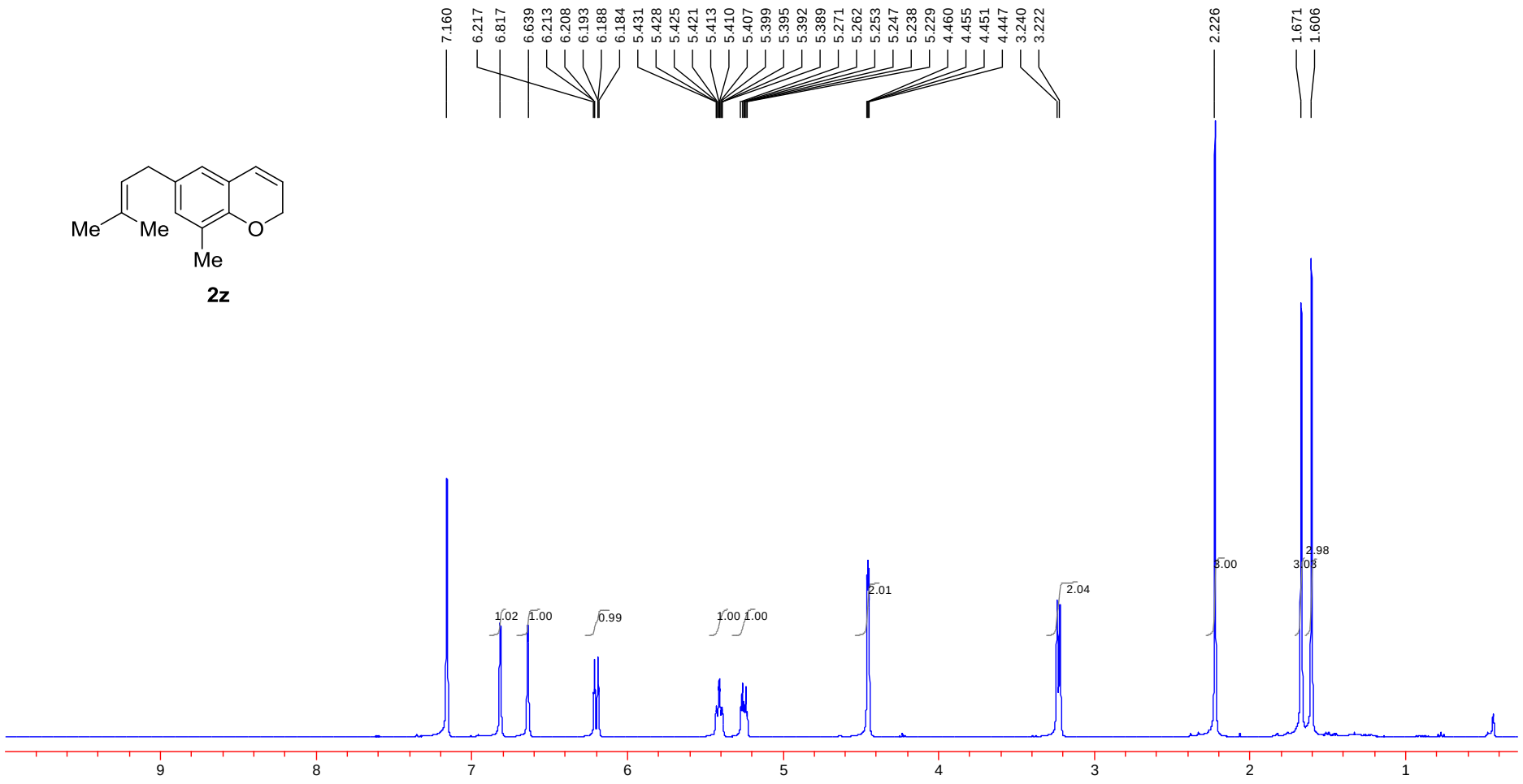
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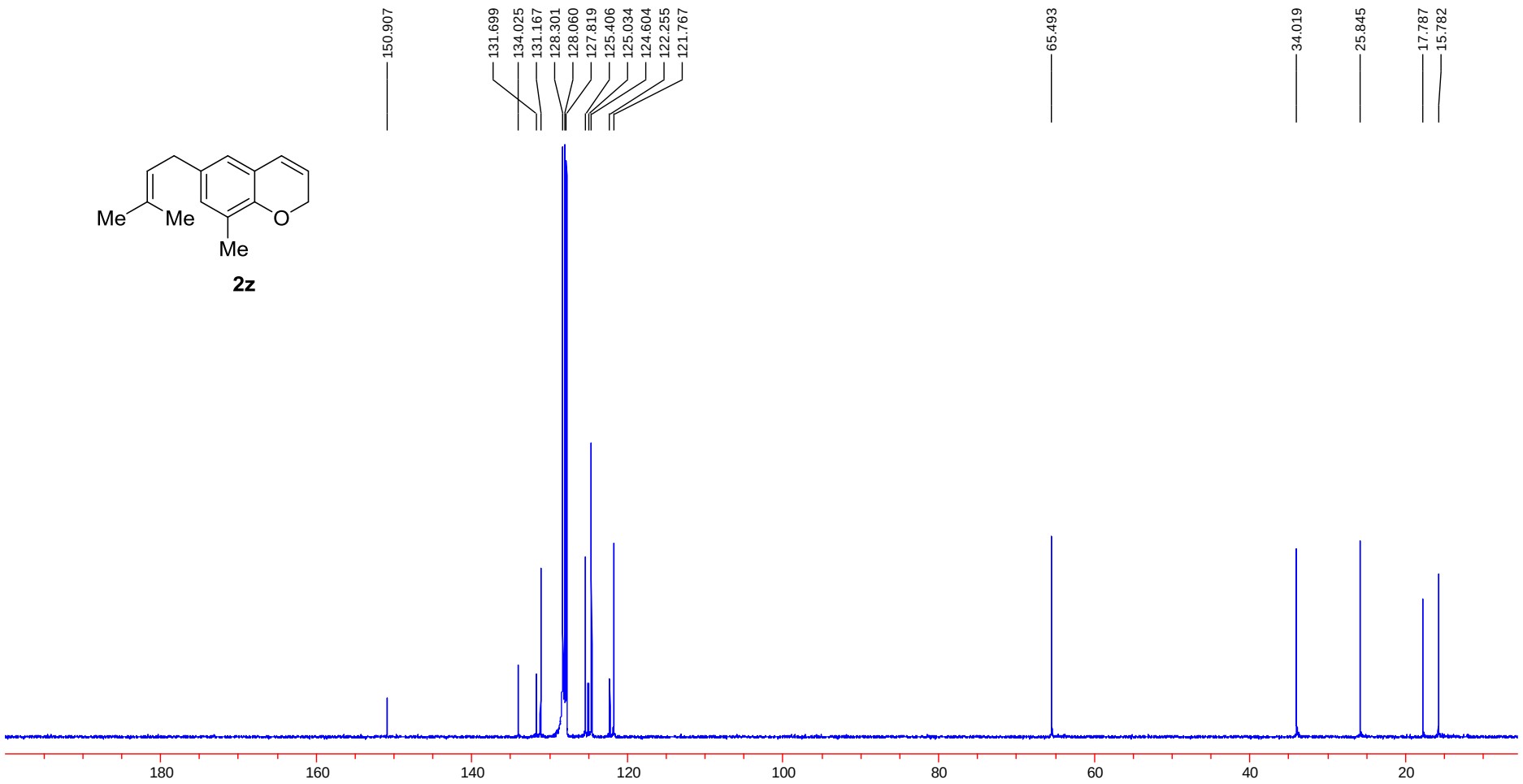
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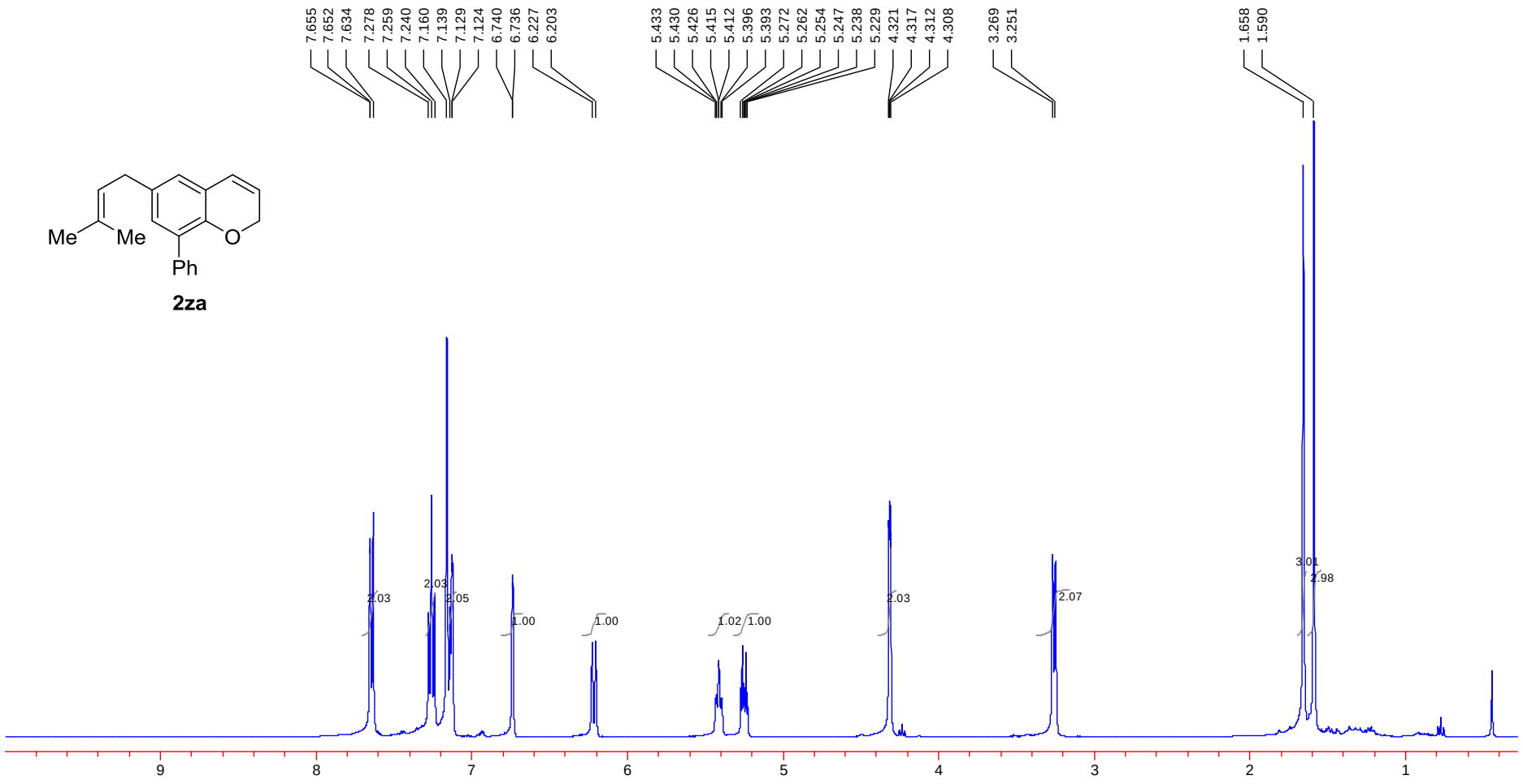
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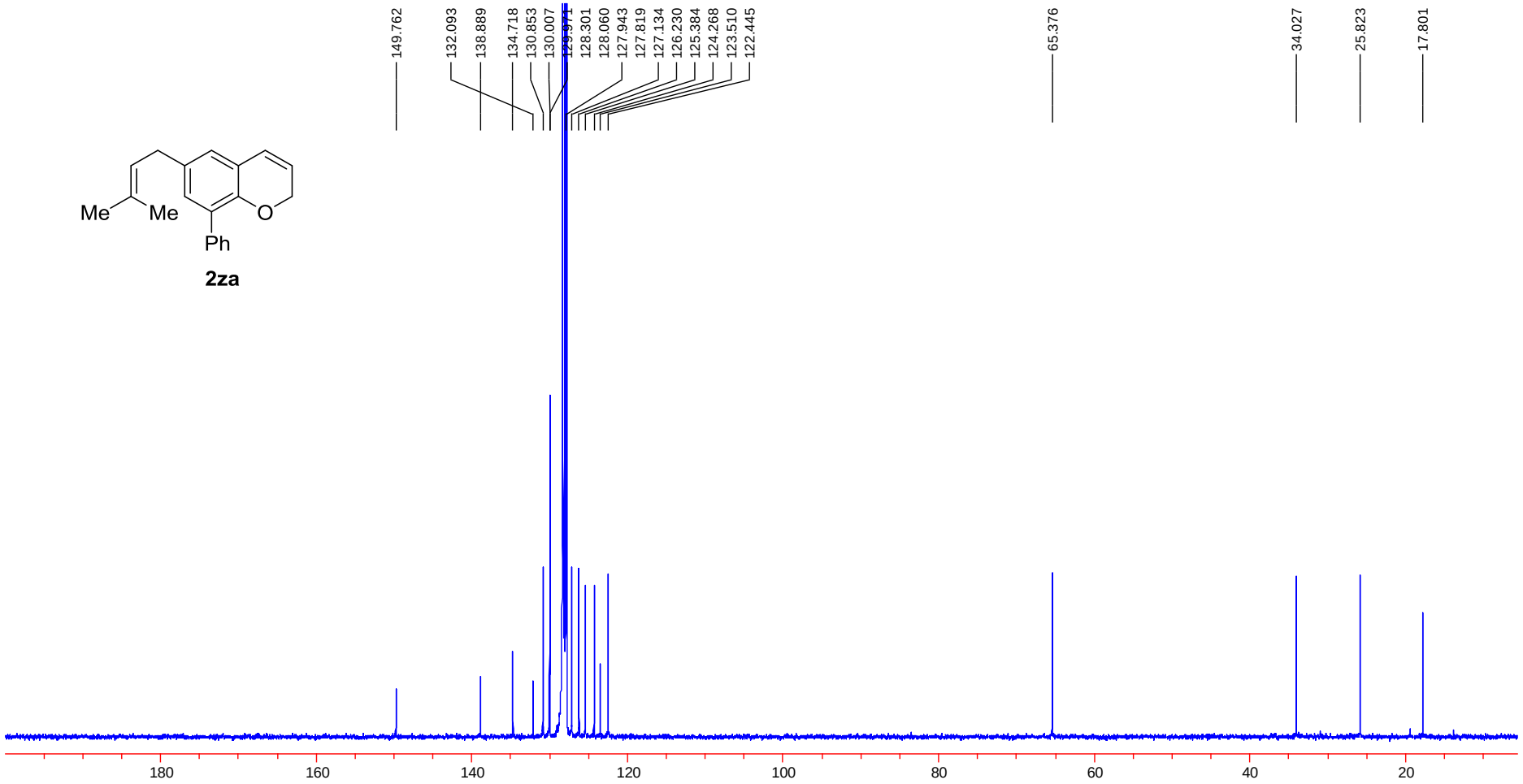
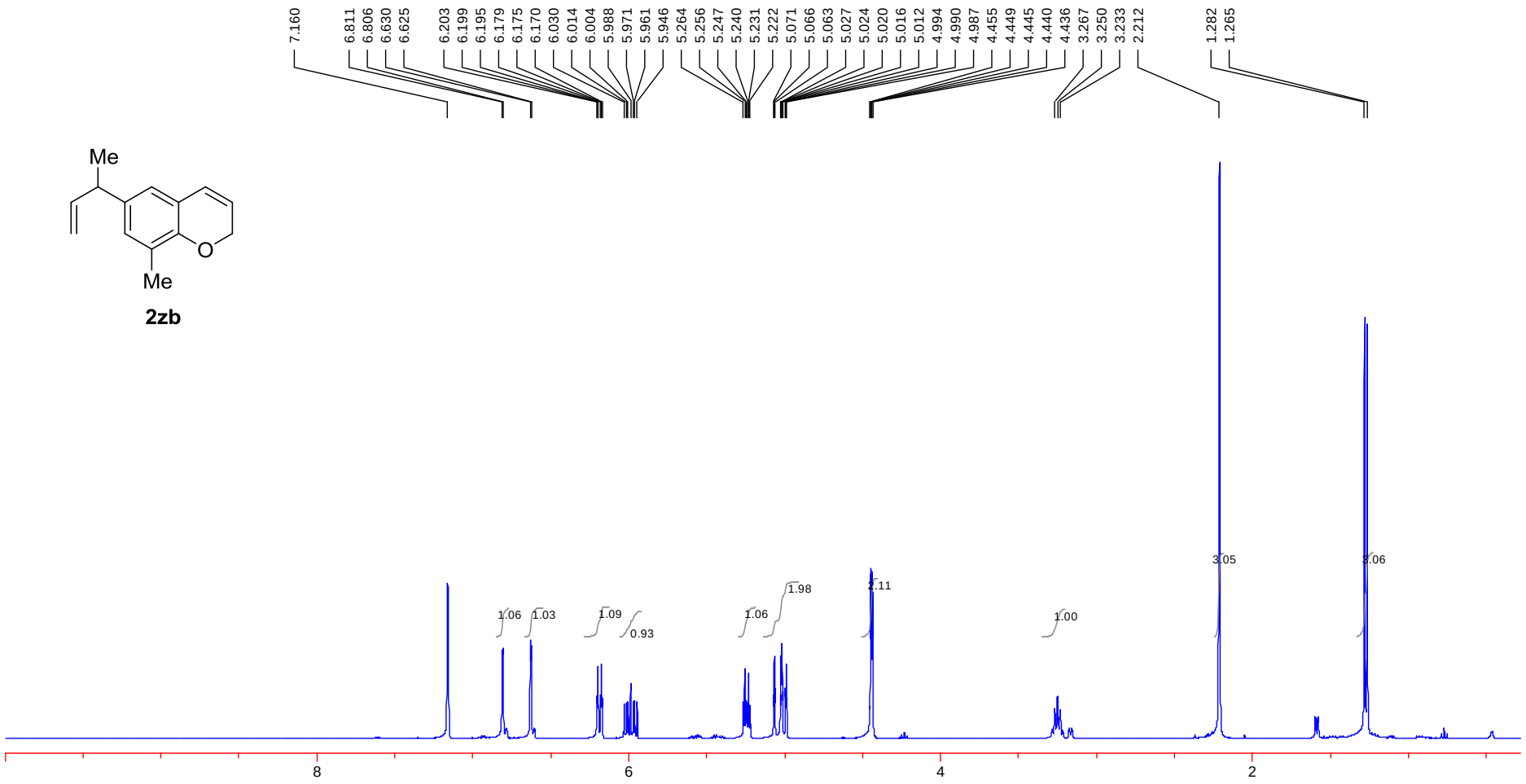
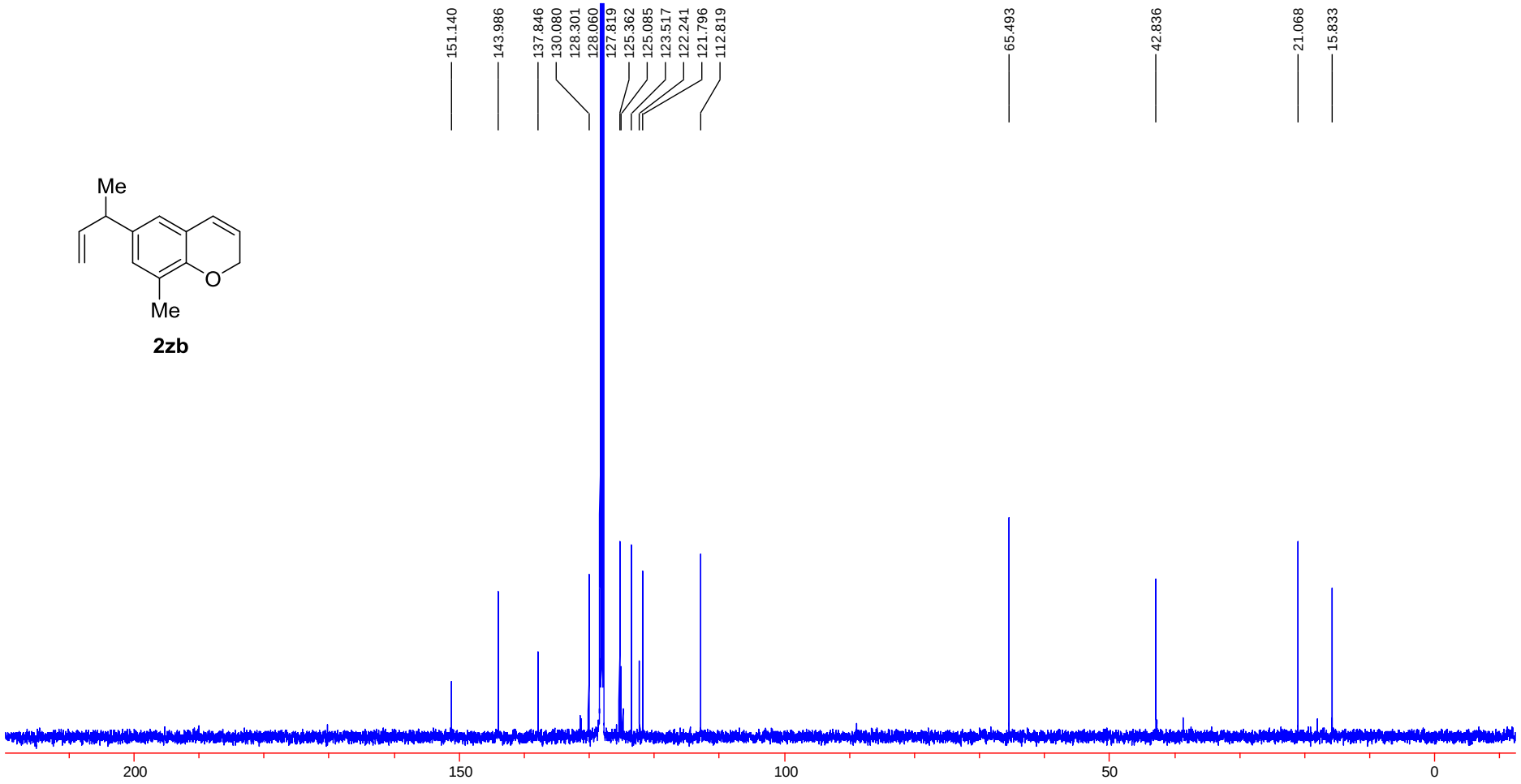
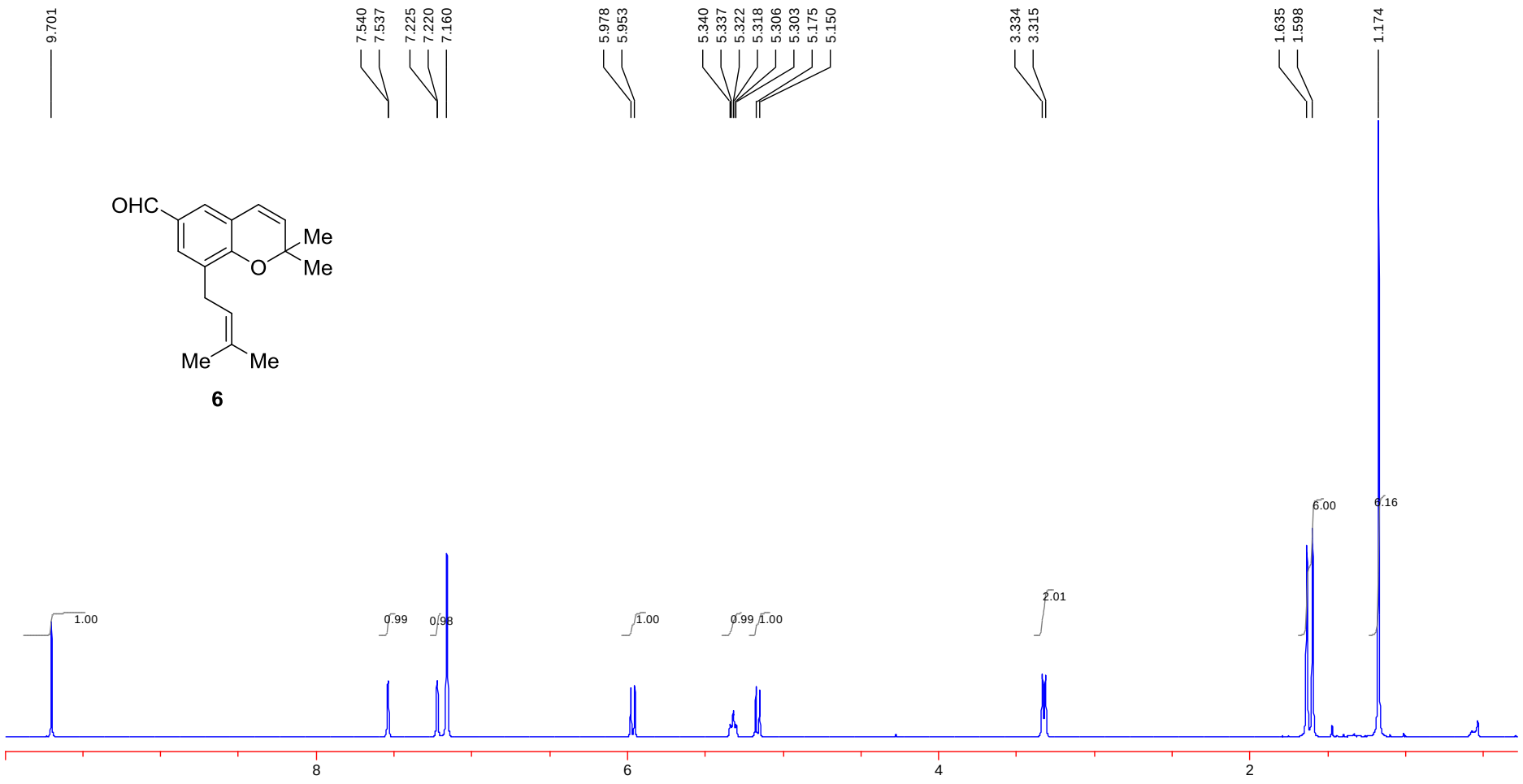
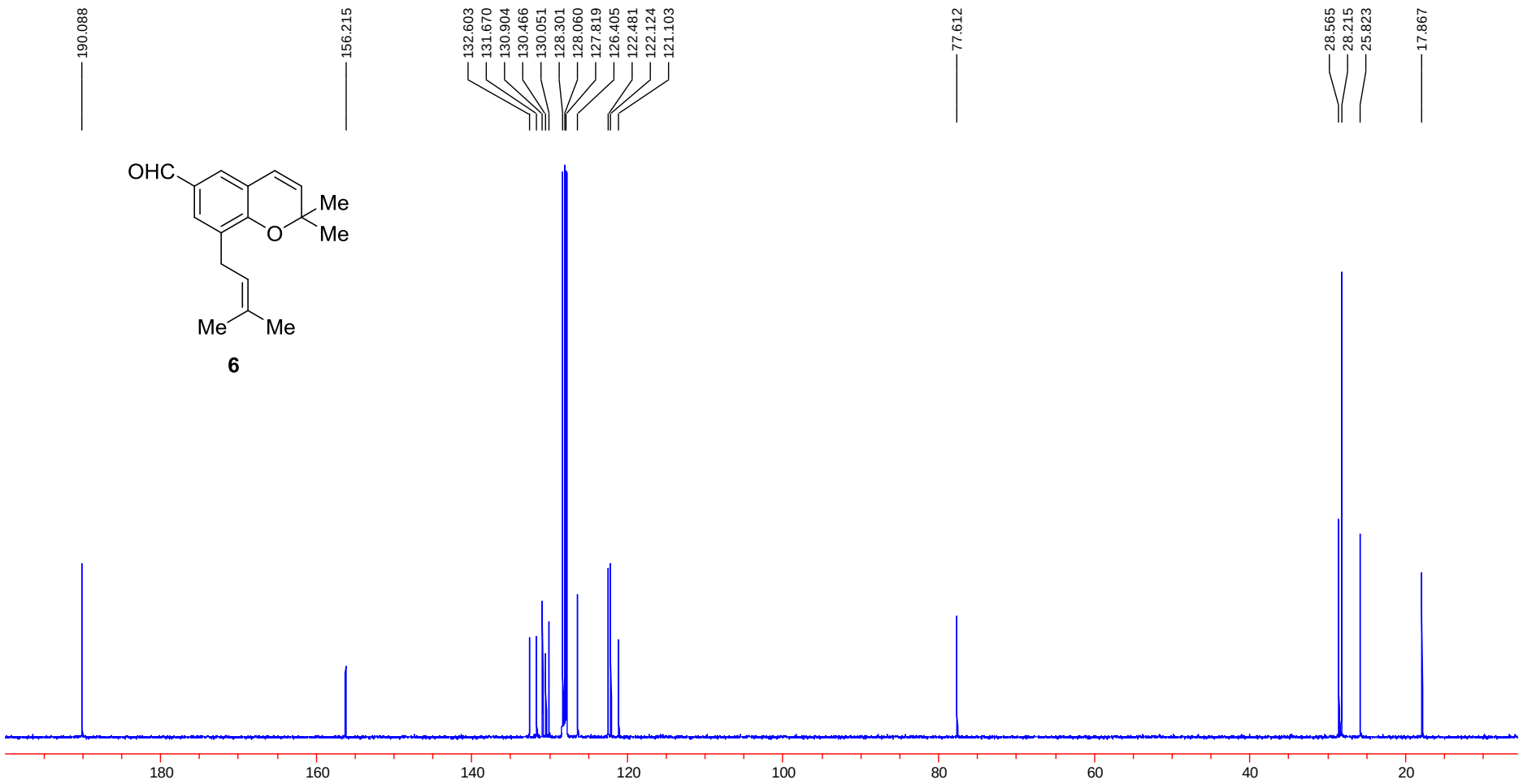
5.393
5.272
5.262
5.254
5.247
5.238
5.229
4.321
4.317
4.312
4.308
3.269
3.251
1.658
1.590
Me
Me
O
Ph
2za
2.03
2.03
2.05
1.00
1.00
1.02
1.00
2.03
2.07
3.01
2.98
9
8
7
6
5
4
3
2
1

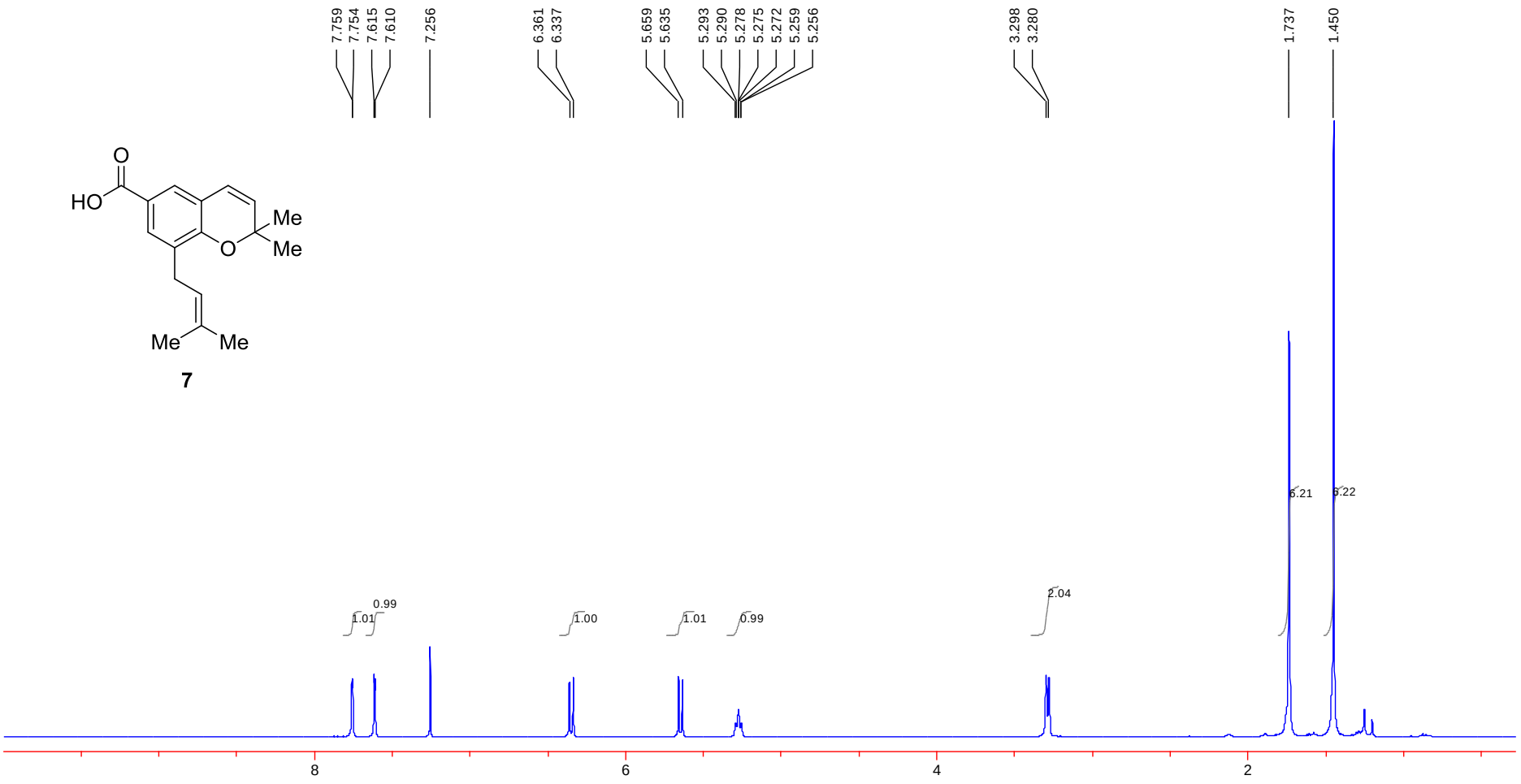

149.762
132.093
138.889
134.718
130.853
130.007
129.071
128.301
128.060
127.943
127.819
127.134
126.230
125.384
124.268
123.510
122.445
65.376
34.027
25.823
17.801
Me
Me
O
Ph
2za
180
160
140
120
100
80
60
40
20

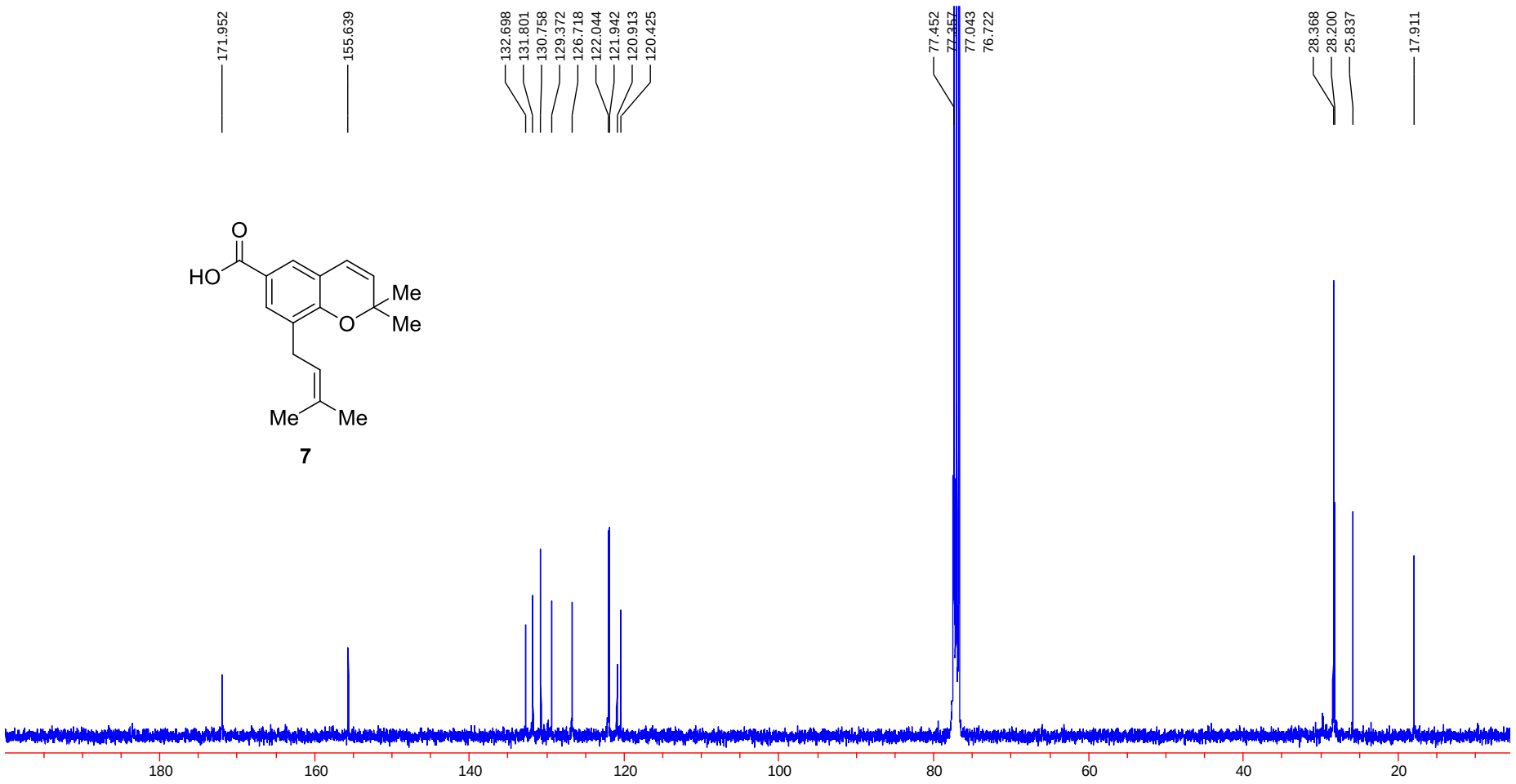

7.160
6.811
6.806
6.630
6.625
6.203
6.199
6.195
6.179
6.175
6.170
6.030
6.014
6.004
5.988
5.971
5.961
5.946
5.264
5.256
5.247
5.240
5.231
5.222
5.071
5.066
5.063
5.027
5.024
5.020
5.016
5.012
4.994
4.990
4.987
4.455
4.449
4.445
4.440
4.436
3.267
3.250
3.233
2.212
1.282
1.265
Me
O
Me
2zb
1.06
1.03
1.09
0.93
1.06
1.98
2.11
1.00
3.05
3.06
8
6
4
2


151.140
143.986
137.846
130.080
128.301
128.060
127.819
125.362
125.085
123.517
122.241
121.796
112.819
65.493
42.836
21.068
15.833
Me
O
Me
2zb
200
150
100
50
0

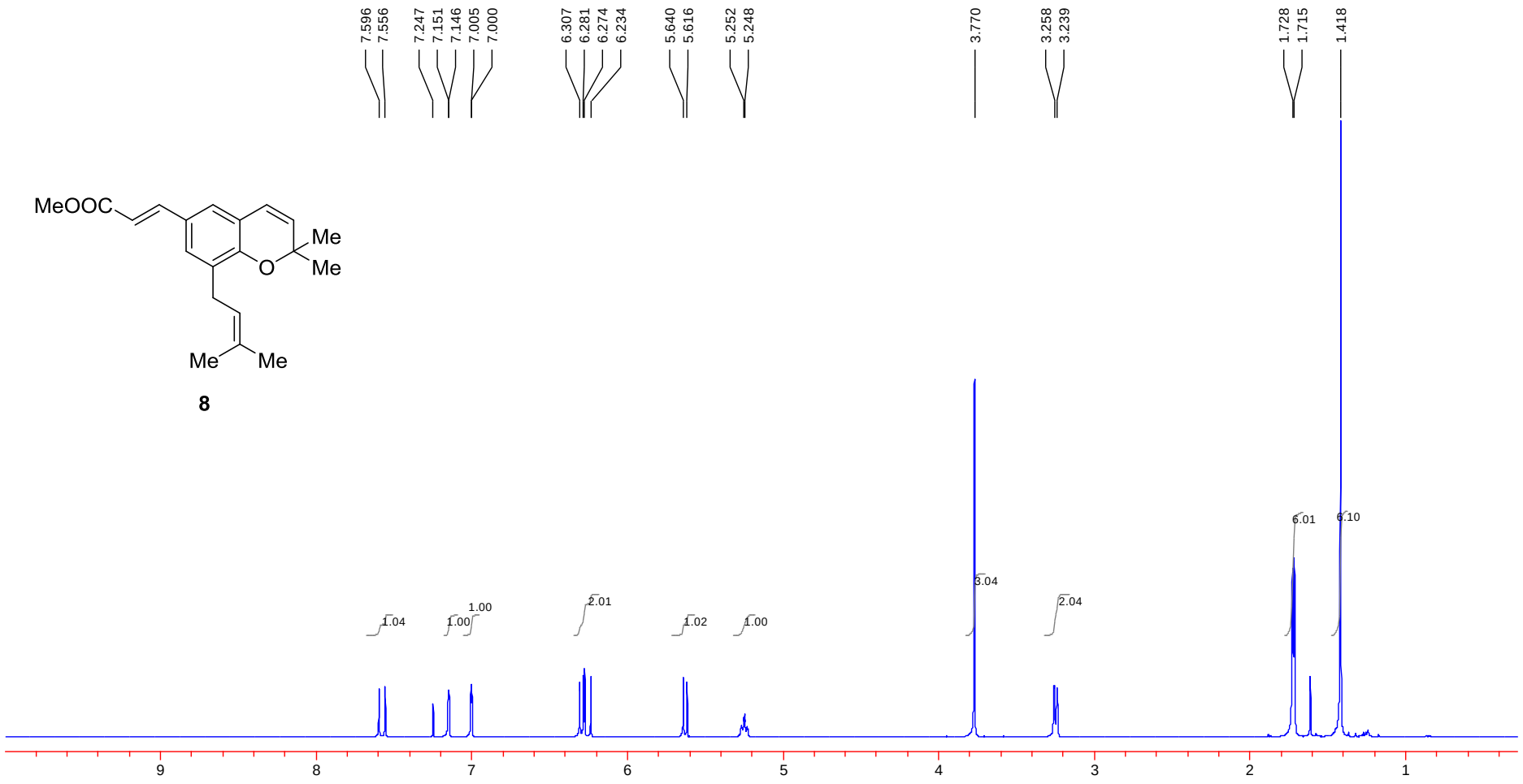

9.701
7.540
7.537
7.225
7.220
7.160
5.978
5.953
5.340
5.337
5.322
5.318
5.306
5.303
5.175
5.150
3.334
3.315
1.635
1.598
1.174
OHC
Me
Me
O
Me
Me
6
1.00
0.99
0.98
1.00
0.99
1.00
2.01
6.00
6.16
8
6
4
2

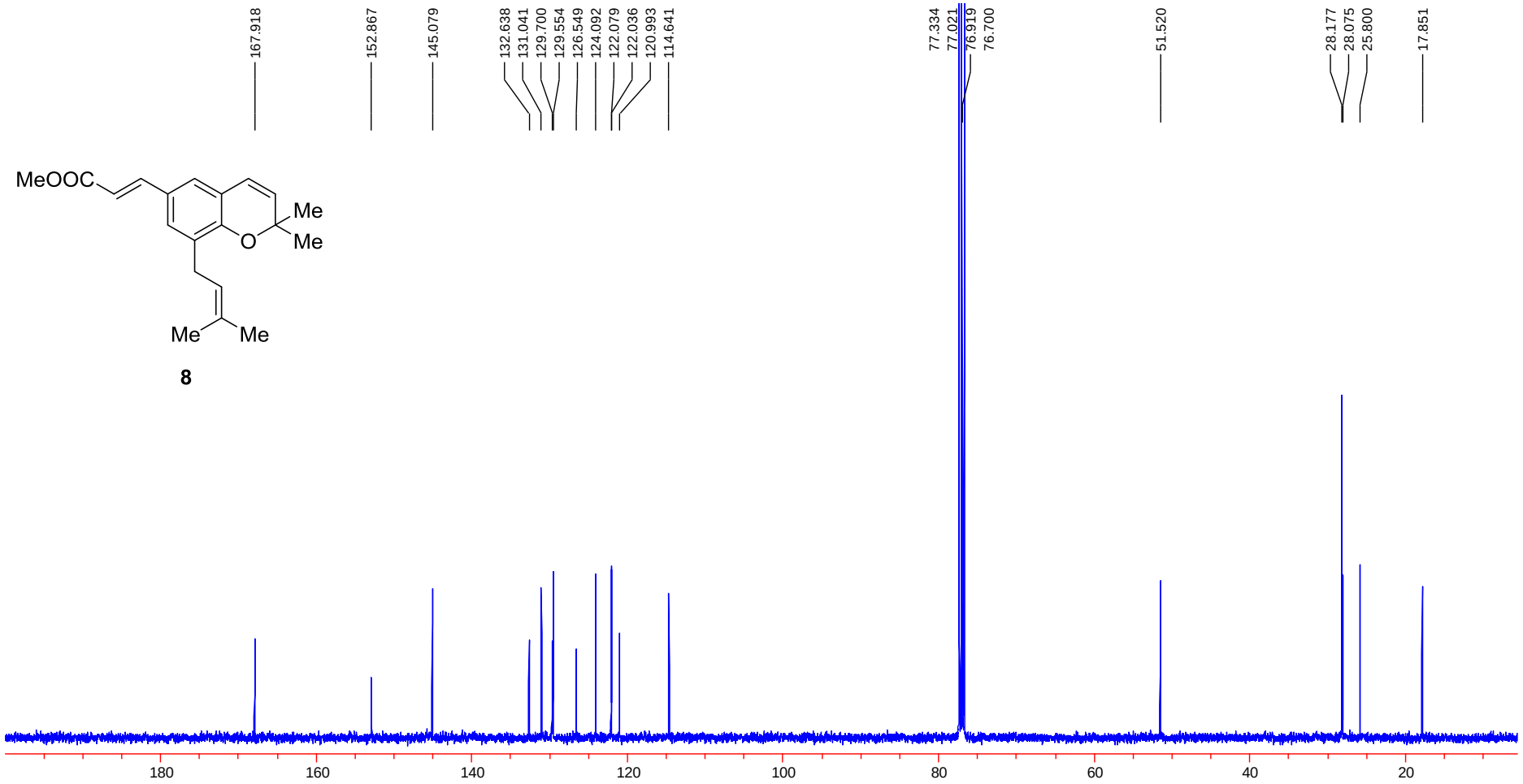

190.088
156.215
132.603
131.670
130.904
130.466
130.051
128.301
128.060
127.819
126.405
122.481
122.124
121.103
77.612
28.565
28.215
25.823
17.867
OHC
Me
Me
O
Me
Me
6
180
160
140
120
100
80
60
40
20


7.759
7.754
7.615
7.610
7.256
6.361
6.337
5.659
5.635
5.293
5.290
5.278
5.275
5.272
5.259
5.256
3.298
3.280
1.737
1.450
HO
O
Me
Me
O
Me
Me
7
1.01
0.99
1.00
1.01
0.99
2.04
6.21
6.22
8
6
4
2


171.952
155.639
132.698
131.801
130.758
129.372
126.718
122.044
121.942
120.913
120.425
77.452
77.357
77.043
76.722
28.368
28.200
25.837
17.911
HO
O
Me
Me
O
Me
Me
180
160
140
120
100
80
60
40
20

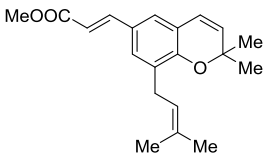
7


7.596
7.556
7.247
7.151
7.146
7.005
7.000
6.307
6.281
6.274
6.234
5.640
5.616
5.252
5.248
3.770
3.258
3.239
1.728
1.715
1.418
MeOOC
Me
Me
O
Me
Me
8
1.04
1.00
1.00
2.01
1.02
1.00
3.04
2.04
6.01
6.10
9
8
7
6
5
4
3
2
1


167.918
152.867
145.079
132.638
131.041
129.700
129.554
126.549
124.092
122.079
122.036
120.993
114.641
77.334
77.021
76.919
76.700
51.520
28.177
28.075
25.800
17.851
MeOOC
Me
Me
O
Me
Me
180
160
140
120
100
80
60
40
20

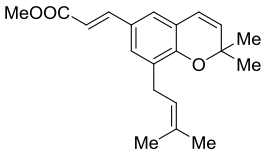
8

^{1}H NMR (300 MHz, $CDCl_3$)

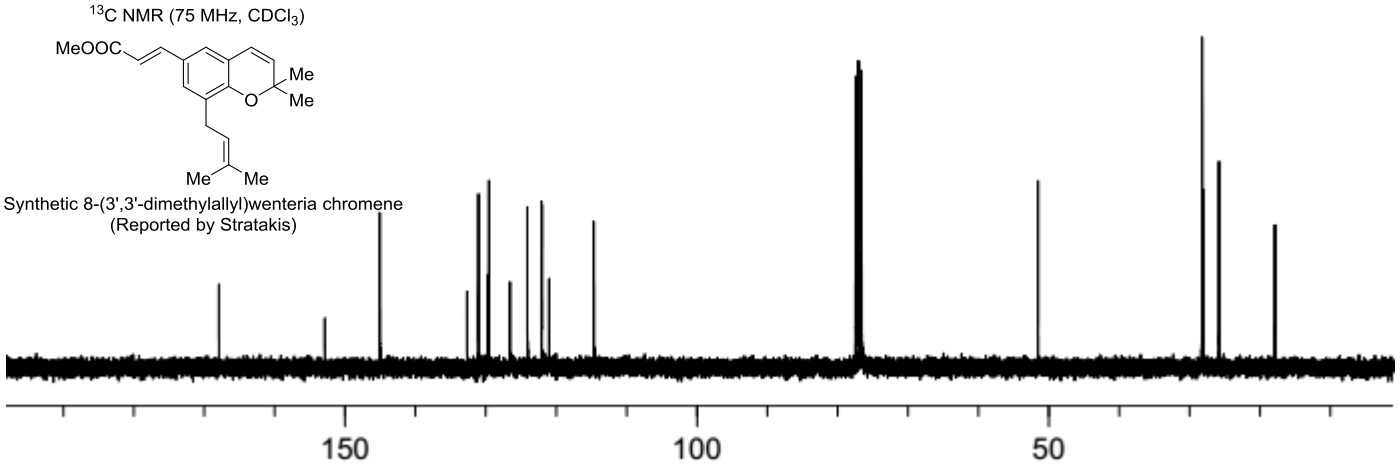


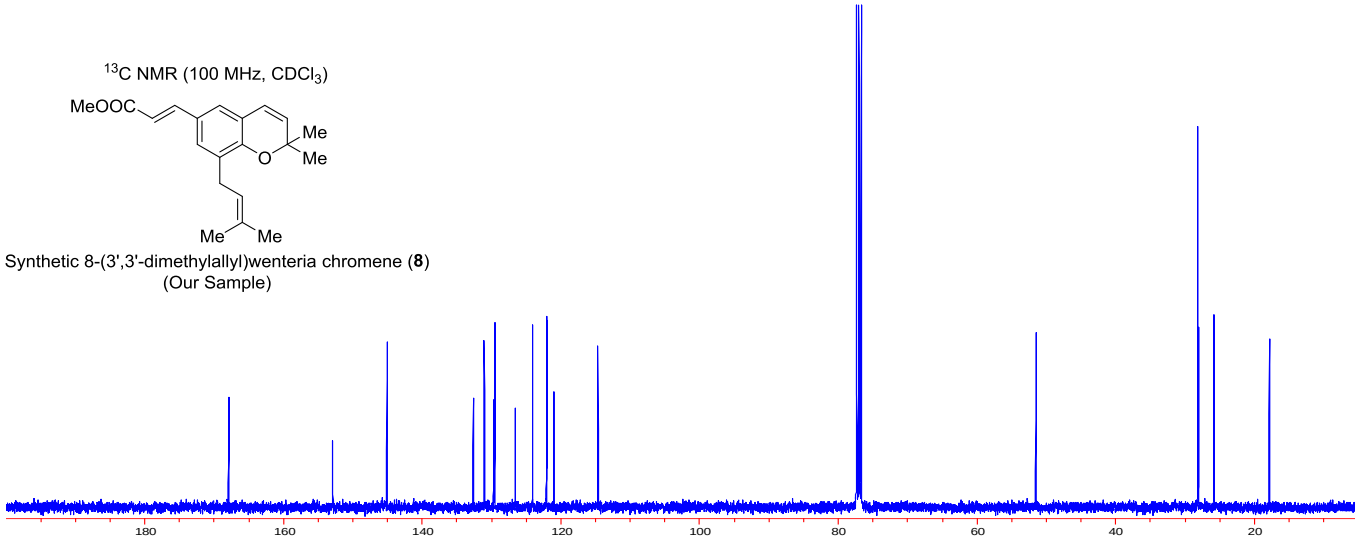
Synthetic 8-(3',3'-dimethylallyl)wenteria chromene
(Reported by Stratakis)

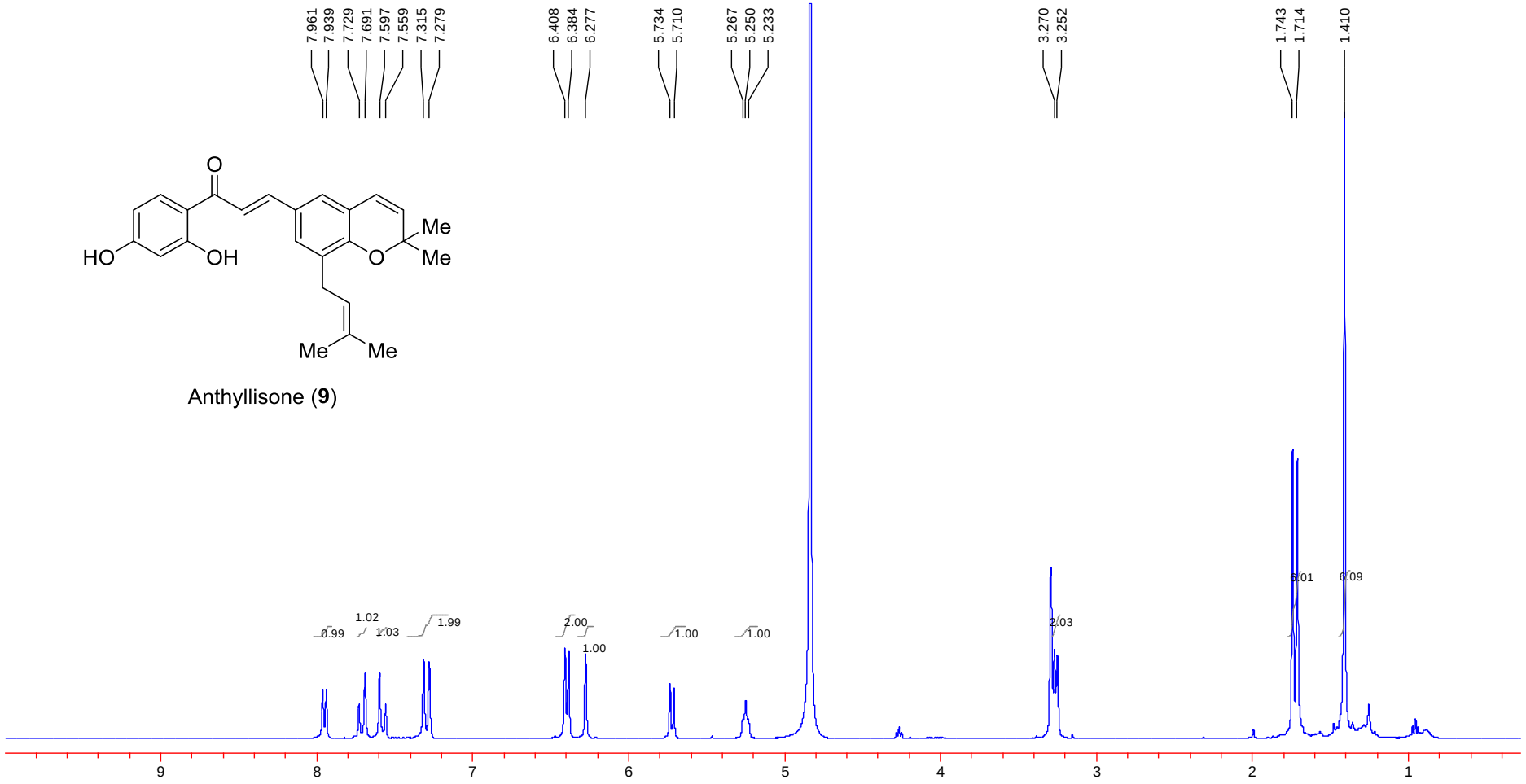
^{1}H NMR (400 MHz, $CDCl_3$)



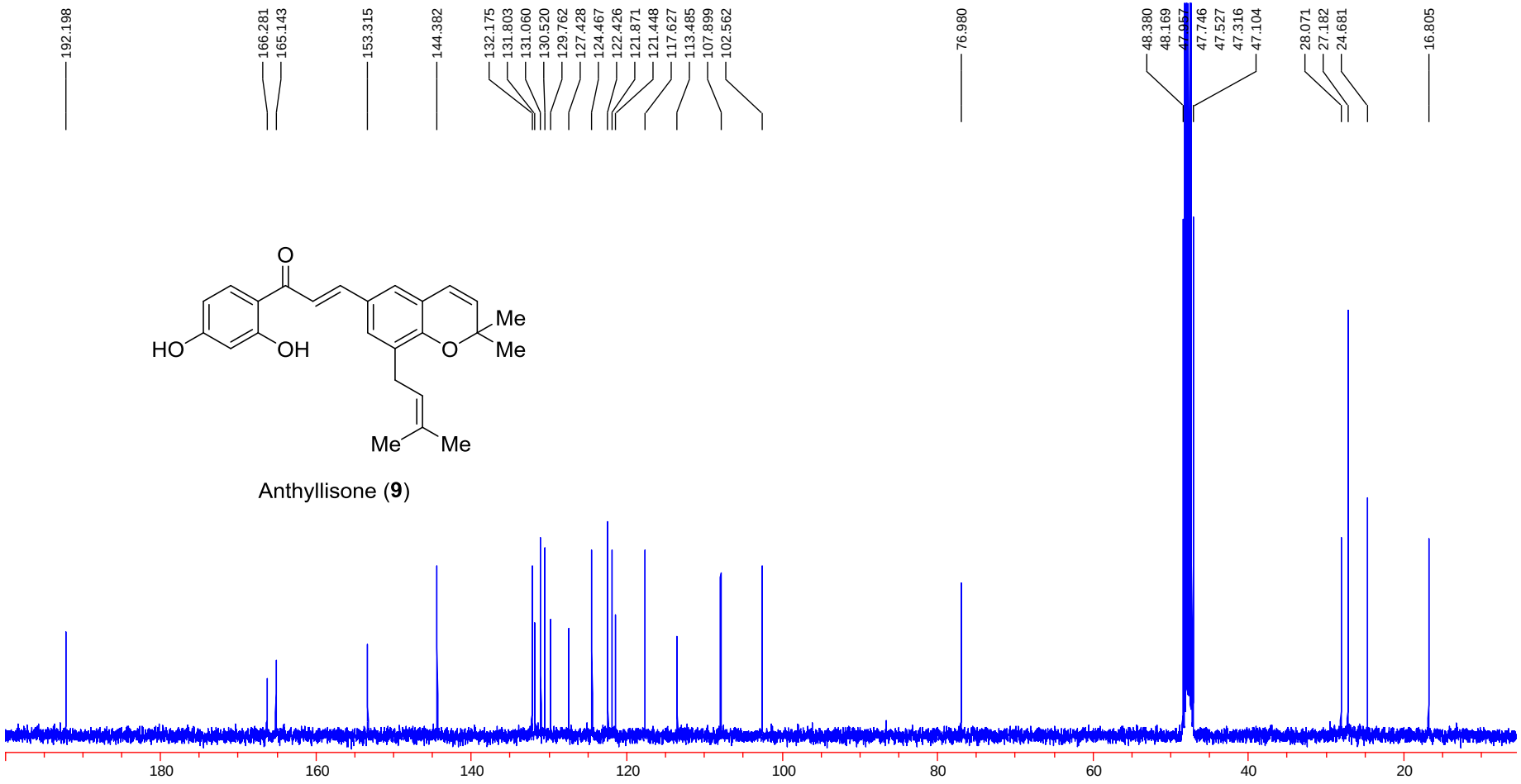
Synthetic 8-(3',3'-dimethylallyl)wenteria chromene (**8**)
(Our Sample)


^{13}C NMR (75 MHz, $CDCl_3$)
MeOOC
Me
Me
O
Me
Me
Synthetic 8-(3',3'-dimethylallyl)wenteria chromene
(Reported by Stratakis)
150
100
50


^{13}C NMR (100 MHz, $CDCl_3$)
MeOOC
Me
Me
O
Me
Me
Synthetic 8-(3',3'-dimethylallyl)wenteria chromene (**8**)
(Our Sample)
180
160
140
120
100
80
60
40
20

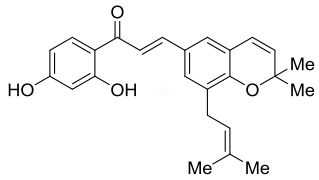


Anthyllisone (**9**)



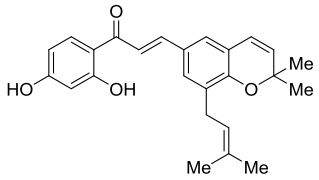
Anthyllisone (**9**)

^{1}H NMR (300 MHz, $CDCl_3$)

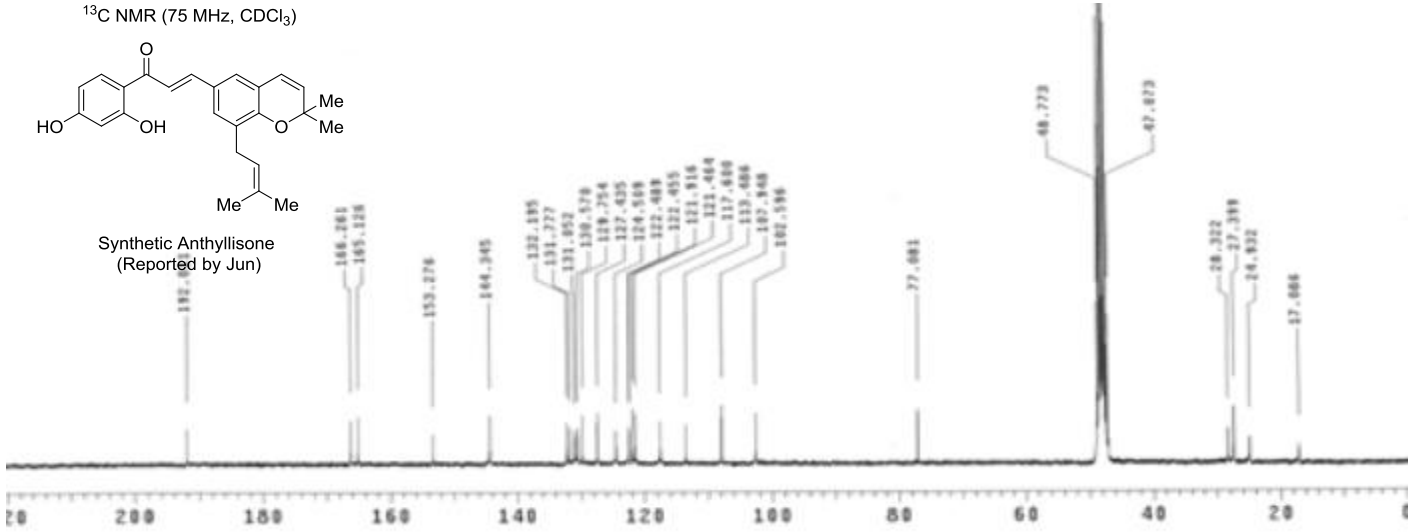


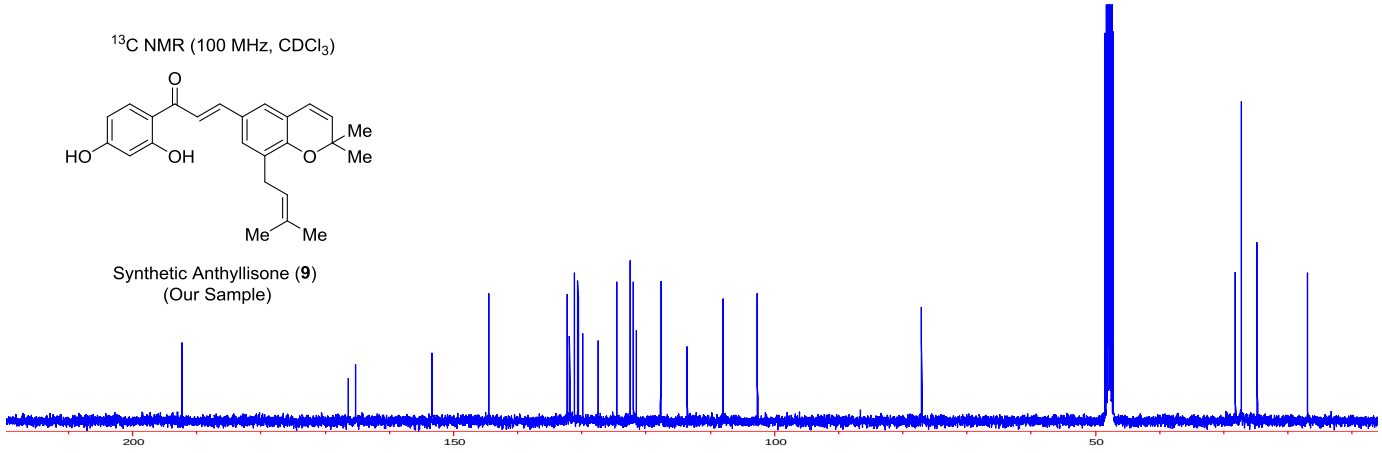
Synthetic Anthyllisone
(Reported by Jun)

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



Synthetic Anthyllisone (**9**)
(Our Sample)


^{13}C NMR (75 MHz, CDCl$_3$)
Synthetic Anthyllisone
(Reported by Jun)


^{13}C NMR (100 MHz, CDCl$_3$)
Synthetic Anthyllisone (**9**)
(Our Sample)