

Electronic Supplementary Material

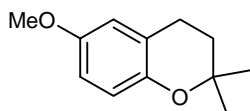
A Recyclable Copper(II) Catalyst for the Annulation of Phenols with 1,3-Dienes

Luis A. Adrio and King Kuok (Mimi) Hii

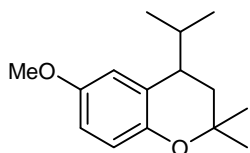
Department of Chemistry, Imperial College London, Exhibition Road, South Kensington SW7 2AZ, United Kingdom.

General Experimental. All precursors, catalysts and reagents were procured commercially and used as received. Catalytic reactions were generally performed in air, using a Radley's 12-place reaction carousel. All products were purified by column chromatography, using a mixture of CH₂Cl₂ : n-hexane (15:85) as eluent. NMR spectra were recorded on Bruker AVANCE 400 MHz machines in CDCl₃ at room temperature. Melting points were recorded using an Electrothermal Gallenham apparatus, and were uncorrected. Infrared spectra were recorded using a Perkin Elmer Spectrum One Spectrometer, equipped with a beam-condensing accessory (samples were sandwiched between diamond compressor cells).

Typical catalytic reaction: A Radley's reaction tube was charged with a stir bar, phenol (1 mmol.), Cu(OTf)₂ (18 mg, 0.05 mmol.) and 2,2'-bipyridyl (4 mg, 0.025 mmol.). DCE (1 mL) was added, followed by the corresponding diene (1.5 mmol.). The tube was positioned in a carousel and left to stir at 50 °C for 18 h, before it was centrifuged. The decanted liquid was evaporated and purified by column chromatography.

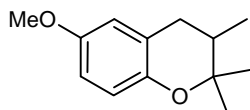


6-Methoxy-2,2-dimethyl-chroman (1).¹ Pale yellow oil. δ_{H} (CDCl₃, 400 MHz): 1.33 (6H, s), 1.80 (2H, t, $J = 6.8$ Hz), 2.77 (2H, t, $J = 6.8$ Hz), 3.76 (3H, s), 6.63 (1H, d, $J = 2.8$ Hz), 6.70 (1H, dd, $J = 2.8, 8.8$ Hz), 6.72 (1H, d, $J = 8.8$ Hz). δ_{C} (CDCl₃, 100.6 MHz): 22.8 (CH₂), 26.7 (2 x CH₃), 32.8 (CH₂), 55.7 (CH₃), 73.8 (C), 113.4 (CH), 113.9 (CH), 117.7 (CH), 121.4 (C), 148.0 (C), 152.9 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 2974, 2930, 1612, 1497, 1382, 1367, 1247, 1202, 1157, 1123, 1042, 947, 890, 844, 812, 723. m/z (EI) 192 (M⁺, 100%), 177 (27), 137 (92), 108 (25).

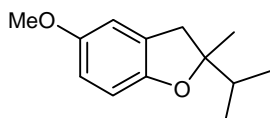


6-Methoxy-2,2-dimethyl-4-isopropyl-chroman (2). Yellow-orange oil. δ_{H} (CDCl₃, 400 MHz): 0.69 (3H, d, $J = 6.8$ Hz), 1.07 (3H, d, $J = 6.9$ Hz), 1.19 (3H, s), 1.43 (3H, s), 1.64 (2H, m), 2.48 (1H, m), 2.86 (1H, m), 3.76 (3H, s), 6.67 (1H, dd, $J = 2.8, 8.8$ Hz), 6.72 (1H, d, $J = 8.8$ Hz), 6.80 (1H, d, $J = 2.8$ Hz). δ_{C} (CDCl₃, 100.6 MHz): 15.6 (CH₃), 20.7 (CH₃), 23.7 (CH₃), 29.3 (CH₃), 30.5 (CH), 32.4 (CH₂), 36.9 (CH), 55.7 (CH₃), 73.9 (C), 112.3 (CH), 112.6 (CH), 117.9 (CH), 125.5 (C), 148.5 (C), 153.3 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 2954, 1614, 1496, 1466, 1426, 1383, 1368, 1276, 1249, 1202, 1179, 1153, 1114, 1088, 1046, 934, 913, 867, 806, 775. m/z (EI) 234 (M⁺, 54%), 191 (100), 163 (24), 137 (29).

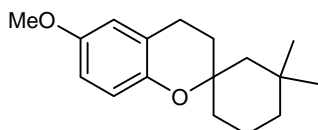
Compounds **3** and **4** were obtained as a mixture from the reaction, which are separated by column chromatography.



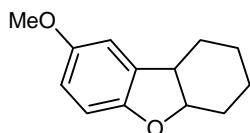
6-Methoxy-2,2,3-trimethyl-chroman (3). Yellow oil. δ_{H} (CDCl_3 , 400 MHz): 1.00 (3H, d, $J = 6.9$ Hz), 1.14 (3H, s), 1.37 (3H, s), 1.90 (1H, m), 2.44 (1H, dd, $J = 10.1, 16.8$ Hz), 2.73 (1H, dd, $J = 5.5, 16.8$ Hz), 3.74 (3H, s), 6.58 (1H, d, $J = 2.8$ Hz), 6.67 (1H, dd, $J = 2.8, 8.8$ Hz), 6.71 (1H, d, $J = 8.8$ Hz). δ_{C} (CDCl_3 , 100.6 MHz): 16.6 (CH_3), 20.0 (CH_3), 27.4 (CH_3), 31.4 (CH_2), 35.5 (CH), 55.7 (CH_3), 77.2 (C), 113.2 (CH), 113.8 (CH), 117.5 (CH), 122.1 (C), 147.7 (C), 152.9 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 2975, 2938, 2907, 2833, 1614, 1497, 1466, 1431, 1368, 1261, 1228, 1151, 1043, 943, 878, 811, 745. m/z (EI) 206 (M^+ , 90%), 163 (73), 137 (100), 108 (17).



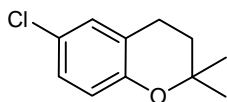
5-Methoxy-2-isopropyl-2-methyl-chroman (4). Orange-brown oil. δ_{H} (CDCl_3 , 400 MHz): 0.94 (3H, d, $J = 6.8$ Hz), 0.99 (3H, d, $J = 6.8$ Hz), 1.33 (3H, s), 1.99 (1H, septet, $J = 6.8$ Hz), 2.77 (1H, d, $J = 15.7$ Hz), 3.12 (1H, d, $J = 15.7$ Hz), 3.75 (3H, s), 6.61-6.70 (2H, m), 6.73 (1H, m). δ_{C} (CDCl_3 , 100.6 MHz): 17.4 (CH_3), 17.5 (CH_3), 23.2 (CH_3), 37.0 (CH), 39.4 (CH_2), 56.0 (CH_3), 91.7 (C), 109.0 (CH), 111.4 (CH), 112.7 (CH), 128.0 (C), 153.3 (C), 153.6 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 2969, 2941, 2910, 2878, 2832, 1604, 1491, 1467, 1432, 1374, 1236, 1141, 1035, 900, 859, 810, 774, 729. m/z (EI) 206 (M^+ , 77%), 163 (100), 137 (72), 108 (16).



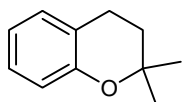
6-Methoxy-3',3'-dimethylspiro[chroman-2,1'-cyclohexane] (5). Yellow oil. δ_{H} (CDCl_3 , 400 MHz): 0.88 (3H, s), 1.06 (3H, s), 1.19 (4H, m), 1.49 (2H, m), 1.70 (2H, m), 1.89 (2H, m), 3.10 (2H, m), 3.76 (3H, s), 6.60 (1H, d, $J = 2.7$ Hz), 6.68 (1H, dd, $J = 2.7, 8.9$ Hz), 6.72 (1H, d, $J = 8.9$ Hz). δ_{C} (CDCl_3 , 100.6 MHz): 18.3 (CH_2), 22.1 (CH_2), 26.6 (CH_3), 30.7 (C), 33.9 (CH_2), 33.9 (CH_3), 36.0 (CH_2), 39.4 (CH_2), 45.2 (CH_2), 55.7 (CH_3), 74.9 (C), 113.3 (CH), 113.8 (CH), 117.9 (CH), 121.9 (C), 147.7 (C), 152.9 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 2918, 1613, 1493, 1465, 1431, 1364, 1303, 1268, 1227, 1176, 1149, 1042, 963, 906, 842, 801, 718. m/z (EI) 260 (M^+ , 100%), 137 (85), 123 (44), 109 (33).



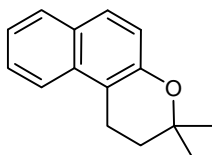
8-Methoxy-1,2,3,4,9a,9b-hexahydrodibenzo[b,d]furan (6).² Orange oil. δ_{H} (CDCl_3 , 400 MHz): 1.64 (2H, m), 1.80 (1H, m), 2.01 (2H, m), 2.12 (2H, m), 3.55 (1H, m), 3.76 (3H, s), 5.79 (1H, dd, $J = 2.1, 10.0$ Hz), 6.04 (1H, m), 6.66 (1H, dd, $J = 3.0, 8.6$ Hz), 6.70 (1H, d, $J = 3.0$ Hz), 6.73 (1H, d, $J = 8.6$ Hz). δ_{C} (CDCl_3 , 100.6 MHz): 20.7 (CH_2), 22.2 (CH_2), 27.6 (CH_2), 28.3 (CH_2), 41.1 (CH), 56.0 (CH_3), 82.7 (CH), 109.8 (CH), 110.3 (CH), 112.1 (CH), 134.6 (C), 153.4 (C), 154.1 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 2933, 2857, 1736, 1602, 1483, 1449, 1433, 1373, 1266, 1214, 1177, 1134, 1087, 1031, 950, 885, 855, 813, 746. m/z (EI) 204 (M^+ , 100%), 161 (42), 150 (74), 137 (25).



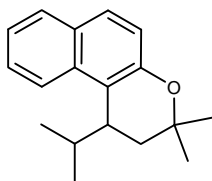
6-Chloro-2,2-dimethylchroman (7).¹ Yellow oil. δ_{H} (CDCl₃, 400 MHz): 1.32 (6H, s), 1.78 (2H, t, $J = 6.8$ Hz), 2.74 (2H, t, $J = 6.8$ Hz), 6.7 (1H, d, $J = 9.2$ Hz), 7.04 (2H, m). δ_{C} (CDCl₃, 100.6 MHz): 22.4 (CH₂), 26.8 (2 x CH₃), 32.4 (CH₂), 74.5 (C), 118.6 (CH), 122.5 (C), 124.2 (C), 127.2 (CH), 129.0 (CH), 152.6 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 2976, 2931, 1717, 1477, 1452, 1417, 1385, 1370, 1295, 1262, 1182, 1158, 1123, 1085, 946, 887, 814, 773, 683. m/z (EI) 196 (M⁺, 82%), 181 (55), 161 (40), 143 (46), 141 (100), 77 (33).



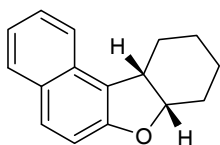
2,2-Dimethylchroman (8).¹ Yellow oil. δ_{H} (CDCl₃, 400 MHz): 1.37 (6H, s), 1.84 (2H, t, $J = 6.8$ Hz), 2.81 (2H, t, $J = 6.8$ Hz), 6.82 (1H, d, $J = 8.1$ Hz), 6.85 (1H, t, $J = 7.3$ Hz), 7.10 (2H, m). δ_{C} (CDCl₃, 100.6 MHz): 22.5 (CH₂), 26.9 (2 x CH₃), 32.8 (CH₂), 74.1 (C), 117.3 (CH), 119.6 (CH), 120.9 (C), 127.3 (CH), 129.5 (CH), 154.0 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 2975, 2932, 2852, 1716, 1610, 1582, 1489, 1456, 1383, 1368, 1347, 1306, 1256, 1220, 1157, 1123, 1037, 948, 931, 884, 833, 709. m/z (EI) 162 (M⁺, 53%), 147 (50), 107 (100).



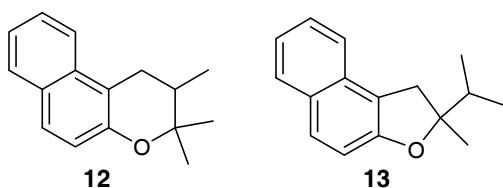
3,3-Dimethyl-2,3-dihydro-1H-benzo[f]chromene (9).³ Pale yellow solid. m.p. 108-109 °C (lit.³ 110 °C). δ_{H} (CDCl₃, 400 MHz): 1.59 (6H, s), 2.09 (2H, t, $J = 6.8$ Hz), 3.17 (2H, t, $J = 6.8$ Hz), 7.31 (1H, d, $J = 8.8$ Hz), 7.55 (1H, t, $J = 8.0$ Hz), 7.70 (1H, t, $J = 8.0$ Hz), 7.83 (1H, d, $J = 8.8$ Hz), 7.96 (1H, d, $J = 8.0$ Hz), 8.01 (1H, d, $J = 8.0$ Hz). δ_{C} (CDCl₃, 100.6 MHz): 19.3 (CH₂), 26.5 (2 x CH₃), 32.7 (CH₂), 74.0 (C), 111.4 (C), 119.8 (CH), 121.9 (CH), 122.9 (CH), 126.2 (CH), 127.7 (CH), 128.4 (CH), 128.7 (C), 133.1 (C), 151.4 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 3049, 2975, 2927, 2853, 1760, 1619, 1597, 1509, 1466, 1433, 1395, 1367, 1318, 1236, 1158, 1121, 1079, 971, 895, 814, 749, 684. m/z (EI) 212 (M⁺, 67%), 157 (100), 128 (39).



1-Isopropyl-3,3-dimethyl-2,3-dihydro-1H-benzo[f]chromene (10): Pale-yellow solid. mp 70-72 °C. δ_{H} (CDCl₃, 400 MHz): 0.62 (3H, d, $J = 6.8$ Hz), 1.21 (3H, d, $J = 6.9$ Hz), 1.29 (3H, s), 1.66 (3H, s), 2.06 (1H, dd, $J = 8.9, 13.9$ Hz), 2.15 (1H, dd, $J = 8.9, 13.9$ Hz), 2.81 (1H, m), 3.62 (1H, dt, $J = 4.2, 8.9$ Hz), 7.20 (1H, d, $J = 8.8$ Hz), 7.44 (1H, t, $J = 8.0$ Hz), 7.57 (1H, t, $J = 8.0$ Hz), 7.72 (1H, d, $J = 8.0$ Hz), 7.89 (1H, d, $J = 8.0$ Hz), 8.01 (1H, d, $J = 8.4$ Hz). δ_{C} (CDCl₃, 100.6 MHz): 15.7 (CH₃), 21.2 (CH₃), 23.6 (CH₃), 30.4 (CH₃), 30.8 (CH), 35.0 (CH), 35.3 (CH₂), 74.8 (C), 119.3 (C), 120.1 (CH), 122.9 (CH), 123.6 (CH), 125.5 (CH), 127.8 (CH), 128.9 (CH), 130.0 (C), 132.4 (C), 152.7 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 3062, 2967, 2931, 2869, 1620, 1598, 1512, 1461, 1390, 1368, 1313, 1268, 1242, 1199, 1138, 1075, 1019, 985, 942, 903, 813, 748, 709, 665. m/z (EI) 254 (M⁺, 33%), 211 (100), 181 (25), 169 (31).



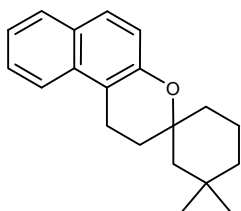
(7aS,11aS)-7a,8,9,10,11,11a-Hexahydrobenzo[d]naphtho[2,1-b]furan (11):⁴ Pale yellow oil. δ_{H} (CDCl_3 , 400 MHz): 1.27 (1H, m), 1.34 (1H, m), 1.61 (1H, m), 1.71 (2H, m), 1.88 (1H, m), 2.21 (1H, m), 2.39 (1H, m), 3.46 (1H, dt, $J = 6.5, 10.5$ Hz), 4.81 (1H, m), 7.18 (1H, d, $J = 8.8$ Hz), 7.31 (1H, t, $J = 8.0$ Hz), 7.47 (1H, t, $J = 8.0$ Hz), 7.68-7.71 (2H, m), 7.83 (1H, d, $J = 8.8$ Hz). δ_{C} (CDCl_3 , 100.6 MHz): 20.4 (CH_2), 22.6 (CH_2), 27.4 (CH_2), 29.1 (CH_2), 39.8 (CH), 83.5 (CH), 112.6 (CH), 122.7 (2C) (CH), 126.4 (CH), 126.8 (C), 128.5 (CH), 128.9 (CH), 129.5 (C), 130.3 (C), 156.7 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 3056, 3023, 2934, 2859, 1629, 1593, 1520, 1462, 1445, 1374, 1353, 1248, 1218, 1203, 1162, 1098, 1068, 974, 940, 883, 855, 814, 776, 746. m/z (EI) 224 (M^+ , 95%), 181 (100), 152 (20).



2,3,3-Trimethyl-2,3-dihydro-1H-benzo[f]chromene (12) and 2-isopropyl-2-methyl-1,2-dihydronaphtho[2,1-b]furan (13). Obtained as an inseparable mixture of isomers in a ratio of 40:60, as a yellow-orange oil.

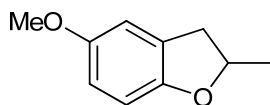
Observable signals attributed to the major isomer (**13**): δ_{H} (CDCl_3 , 400 MHz): 1.08 (3H, d, $J = 6.8$ Hz), 1.14 (3H, d, $J = 6.8$ Hz), 1.52 (3H, s), 2.15 (1H, m), 3.14 (1H, d, $J = 15.5$ Hz), 3.45 (1H, d, $J = 15.5$ Hz), 7.18 (1H, d, $J = 8.7$ Hz), 7.36 (1H, t, $J = 8.0$ Hz), 7.54 (1H, t, $J = 8.2$ Hz), 7.65 (1H, d, $J = 8.0$ Hz), 7.74 (1H, d, $J = 8.7$ Hz), 7.87 (1H, d, $J = 7.8$ Hz). δ_{C} (CDCl_3 , 100.6 MHz): 17.5 (2 x CH_3), 24.1 (CH_3), 37.3 (CH), 37.6 (CH_2), 92.8 (C), 112.4 (CH), 119.6 (CH), 122.6 (CH), 122.7 (CH), 126.6 (CH), 127.8 (CH), 128.8 (C), 129.0 (C), 131.2 (C), 156.6 (C).

Observable signals attributed to the minor isomer (**12**): δ_{H} (CDCl_3 , 400 MHz): 1.19 (3H, d, $J = 6.9$ Hz), 1.28 (3H, s), 1.53 (3H, s), 2.13 (1H, m), 2.70 (1H, dd, $J = 10.0, 16.8$ Hz), 3.16 (1H, dd, $J = 5.7, 16.8$ Hz), 7.14 (1H, d, $J = 8.9$ Hz), 7.41 (1H, t, $J = 8.0$ Hz), 7.56 (1H, t, $J = 8.4$ Hz), 7.69 (1H, d, $J = 8.9$ Hz), 7.83 (1H, d, $J = 8.0$ Hz), 7.89 (1H, d, $J = 8.0$ Hz). δ_{C} (CDCl_3 , 100.6 MHz): 17.0 (CH_3), 19.8 (CH_3), 27.4 (CH_3), 28.2 (CH_2), 35.6 (CH), 77.6 (C), 118.2 (C), 119.6 (CH), 122.0 (CH), 122.6 (CH), 123.0 (CH), 126.3 (CH), 128.5 (CH), 131.1 (C), 133.0 (C), 151.1 (C). $\nu_{\text{max}}/\text{cm}^{-1}$: 3058, 2963, 2872, 1715, 1629, 1597, 1520, 1464, 1372, 1249, 1169, 1076, 978, 924, 811, 747. m/z (EI) 226 (M^+ , 90%), 183 (80), 157 (100), 129 (31).



3',3'-Dimethyl-3,4-dihydrospiro[benzo[g]chromene-2,1'-cyclohexane] (14): Pale yellow oil. δ_{H} (CDCl_3 , 400 MHz): 0.98 (3H, s), 1.18 (3H, s), 1.34 (4H, m), 1.59 (2H, m), 1.86 (2H, m), 1.95 (2H, m), 3.10 (2H, m), 7.15 (1H, d, $J = 8.8$ Hz), 7.42 (1H, t, $J = 8.0$ Hz), 7.57 (1H, t, $J = 8.0$ Hz), 7.71 (1H, d, $J = 8.8$ Hz), 7.85 (1H, d, $J = 8.8$ Hz), 7.90 (1H, d, $J = 8.0$ Hz). δ_{C} (CDCl_3 , 100.6 MHz): 17.2 (C), 18.4 (CH_2), 18.8 (CH_2), 26.7 (CH_3), 30.8 (C), 33.8 (CH_2), 34.1 (CH_3), 35.9 (CH_2), 39.5 (CH_2), 45.0

(CH₂), 75.3 (C), 112.9 (C), 120.1 (CH), 121.9 (CH), 123.0 (CH), 126.2 (CH), 127.8 (CH), 128.5 (CH), 133.2 (C), 151.2 (C). $\nu_{\max}/\text{cm}^{-1}$: 3060, 2945, 2867, 1623, 1599, 1514, 1466, 1435, 1397, 1364, 1263, 1237, 1176, 1099, 1056, 981, 883, 811, 745, 685. m/z (EI) 280 (M⁺, 73%), 195 (18), 157 (100).

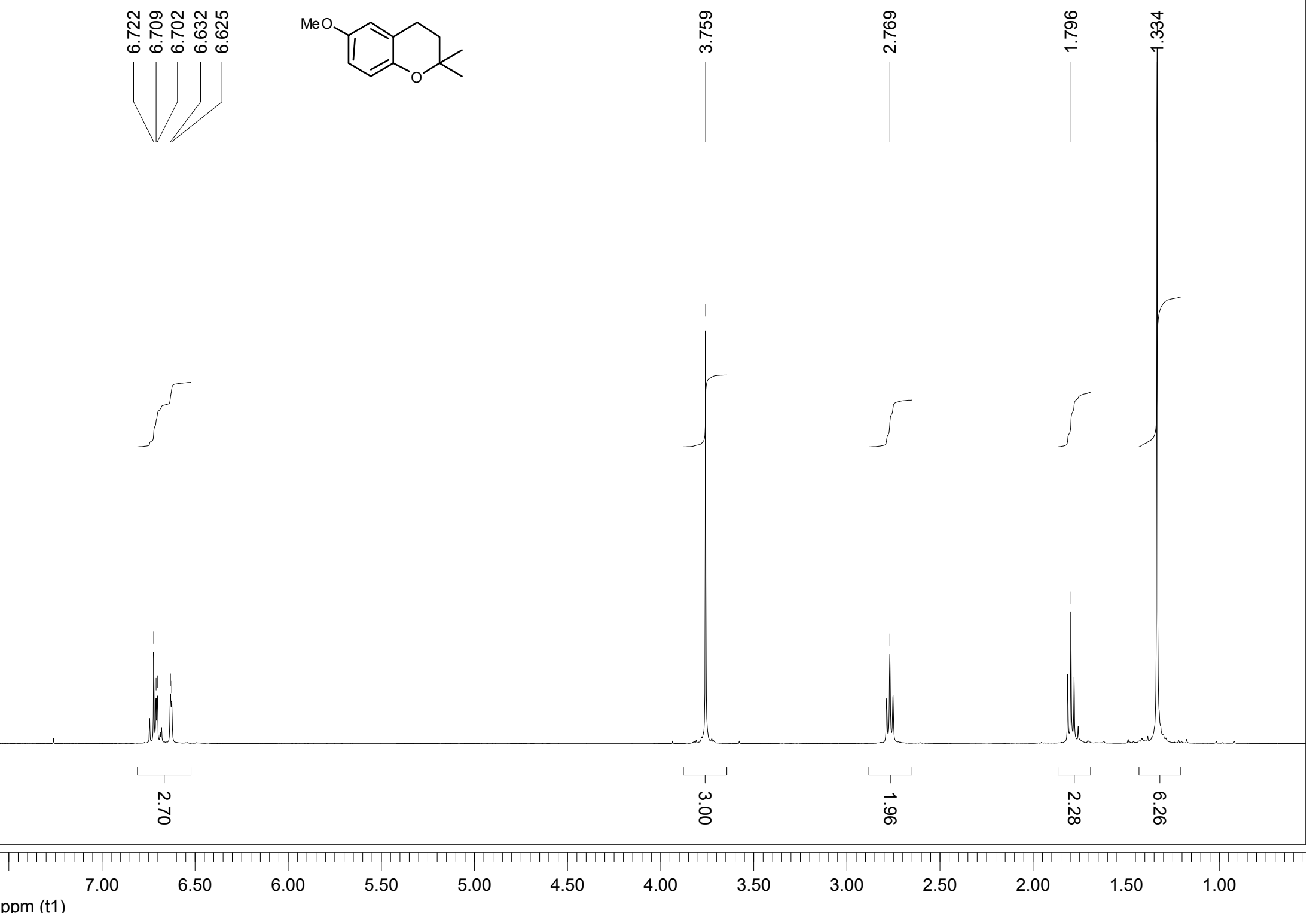
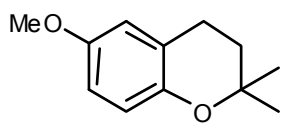


5-Methoxy-2-methyl-2,3-dihydrobenzofuran (18b):⁵ Yellow oil. δ_{H} (CDCl₃, 400 MHz): 1.45 (3H, d, $J = 6.3$ Hz), 2.79 (1H, dd, $J = 7.8, 15.5$ Hz), 3.27 (1H, dd, $J = 8.7, 15.5$ Hz), 3.75 (3H, s), 4.90 (1H, m), 6.65 (2H, m), 6.75 (1H, s).

References

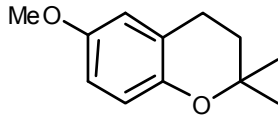
1. Youn, S. W.; Eom, J. I. *J. Org. Chem.* **2006**, *71*, 6705.
2. Core, S. K.; Lotspeich, F. J. *J. Org. Chem.* **1971**, *36*, 399.
3. Paradkar, M. V.; Godbole, H. M.; Ranade, A. A.; Joseph, A. R. *J. Chem. Res. Synop.* **1998**, 318.
4. Kovacs, P.; Kolonits, P.; Kaleta, Z.; Parkanyi, L.; Szabo, E.; Novak, L. *Synthesis* **2003**, 1043.
5. Grant, V. H.; Liu, B. *Tetrahedron Lett.* **2005**, *46*, 1237.

6.722
6.709
6.702
6.632
6.625



152.879
147.967

121.466
117.734
113.949
113.390



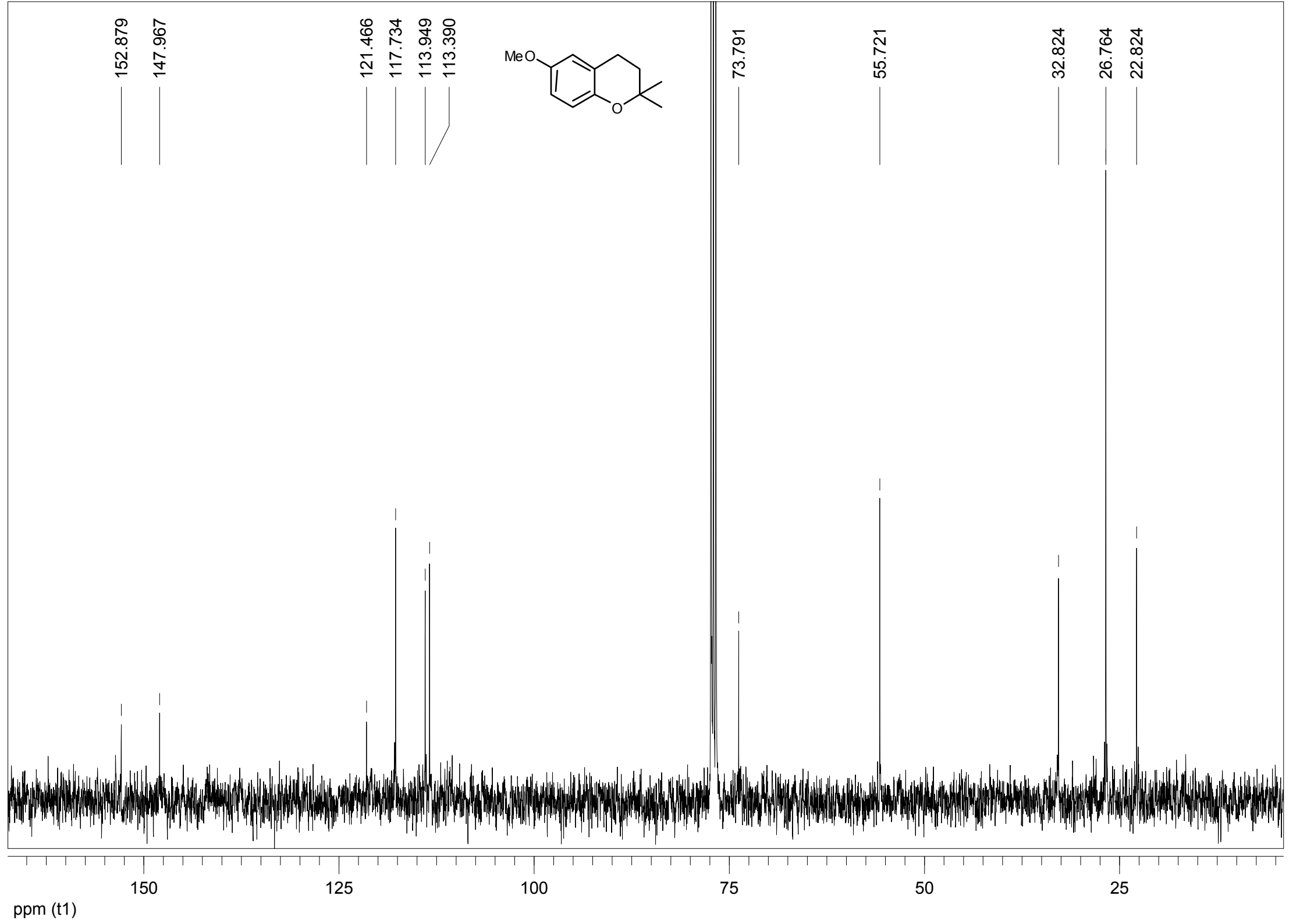
73.791

55.721

32.824

26.764

22.824



ppm (t1)

150

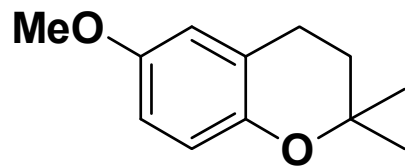
125

100

75

50

25



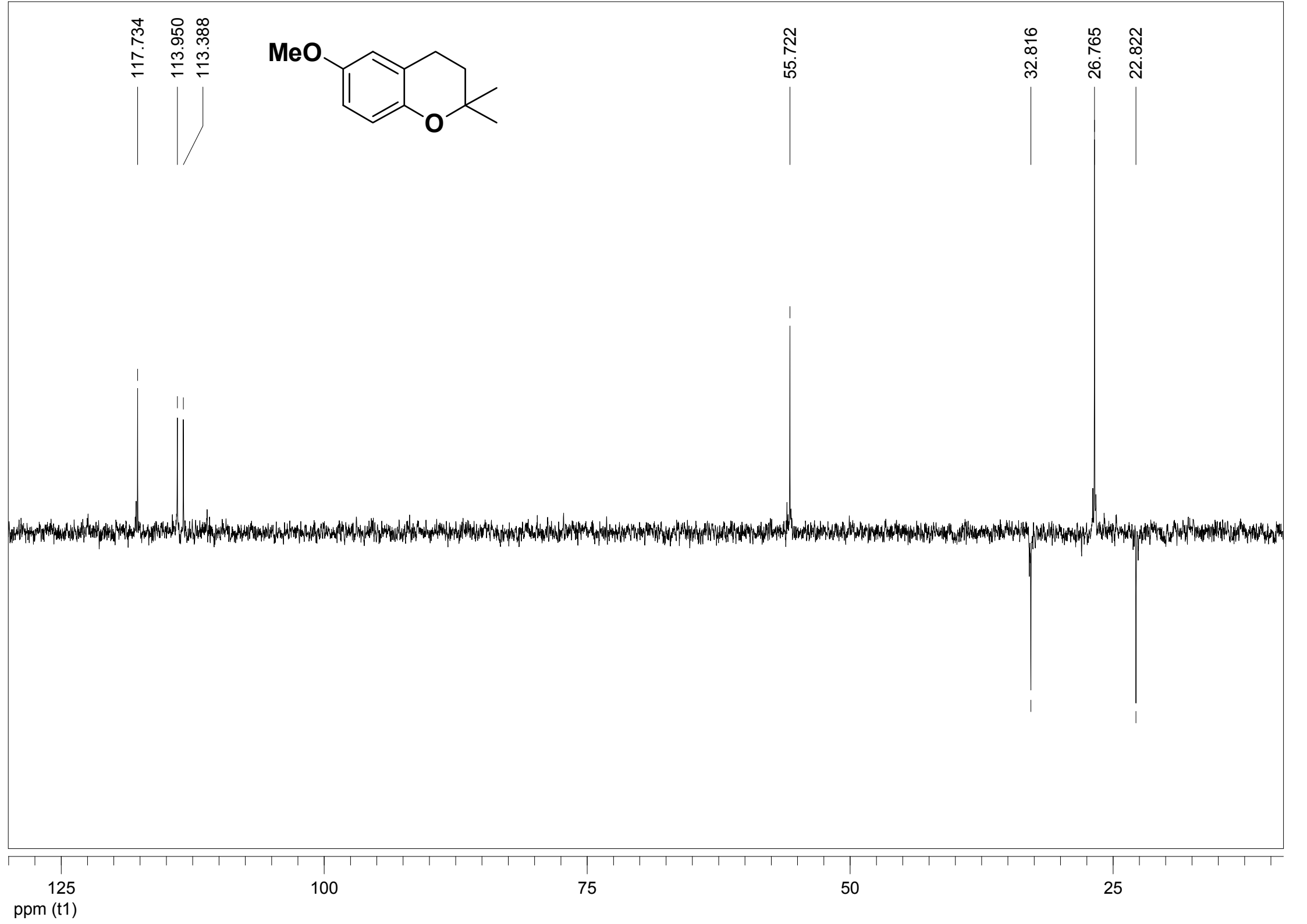
117.734
113.950
113.388

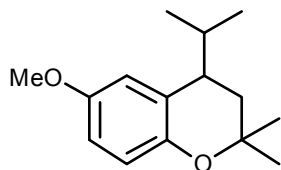
55.722

32.816

26.765

22.822





6.795
6.710

3.756

2.863

2.491
2.481

1.651
1.634
1.433

1.192
1.077
1.060

0.701
0.684

2.92

3.00

0.98

0.96

2.15

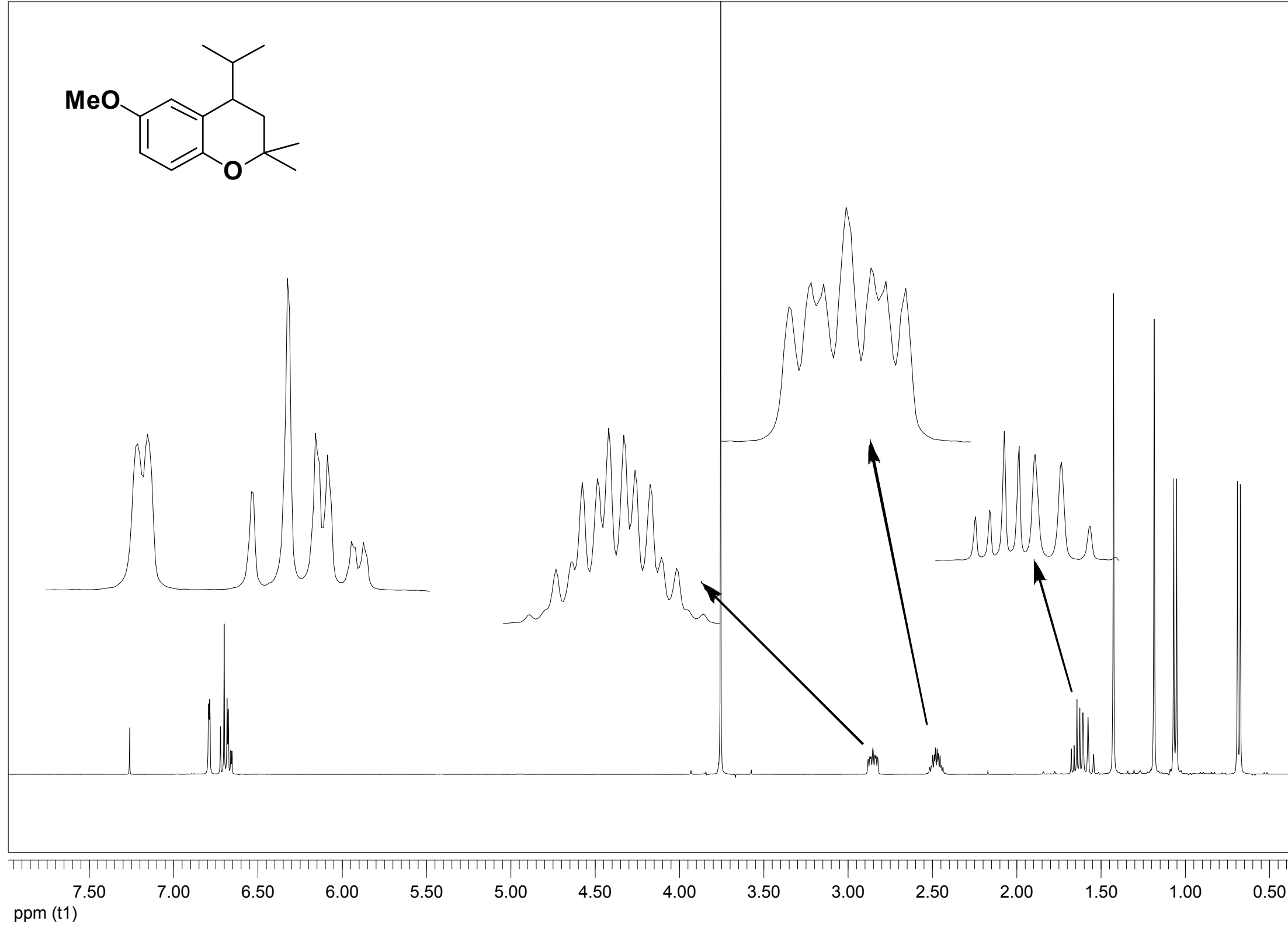
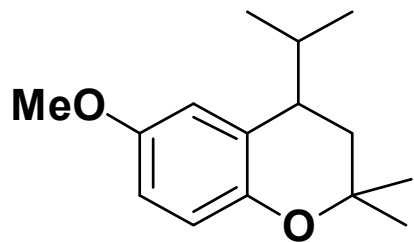
3.05

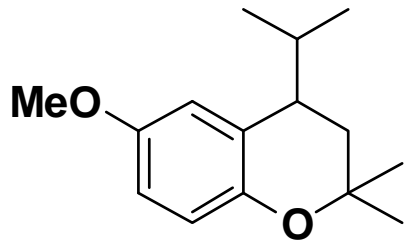
3.00

3.10

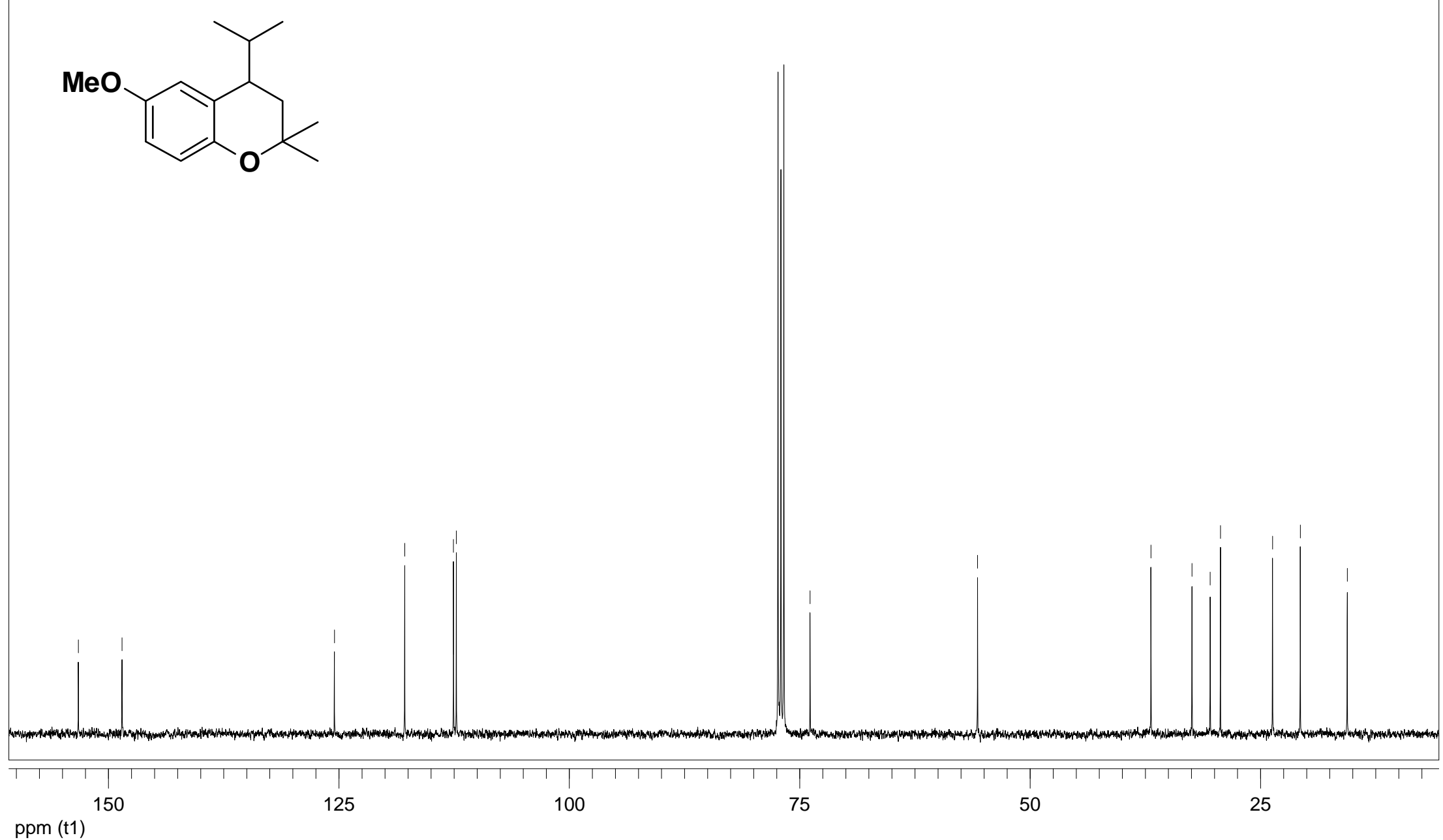
3.01

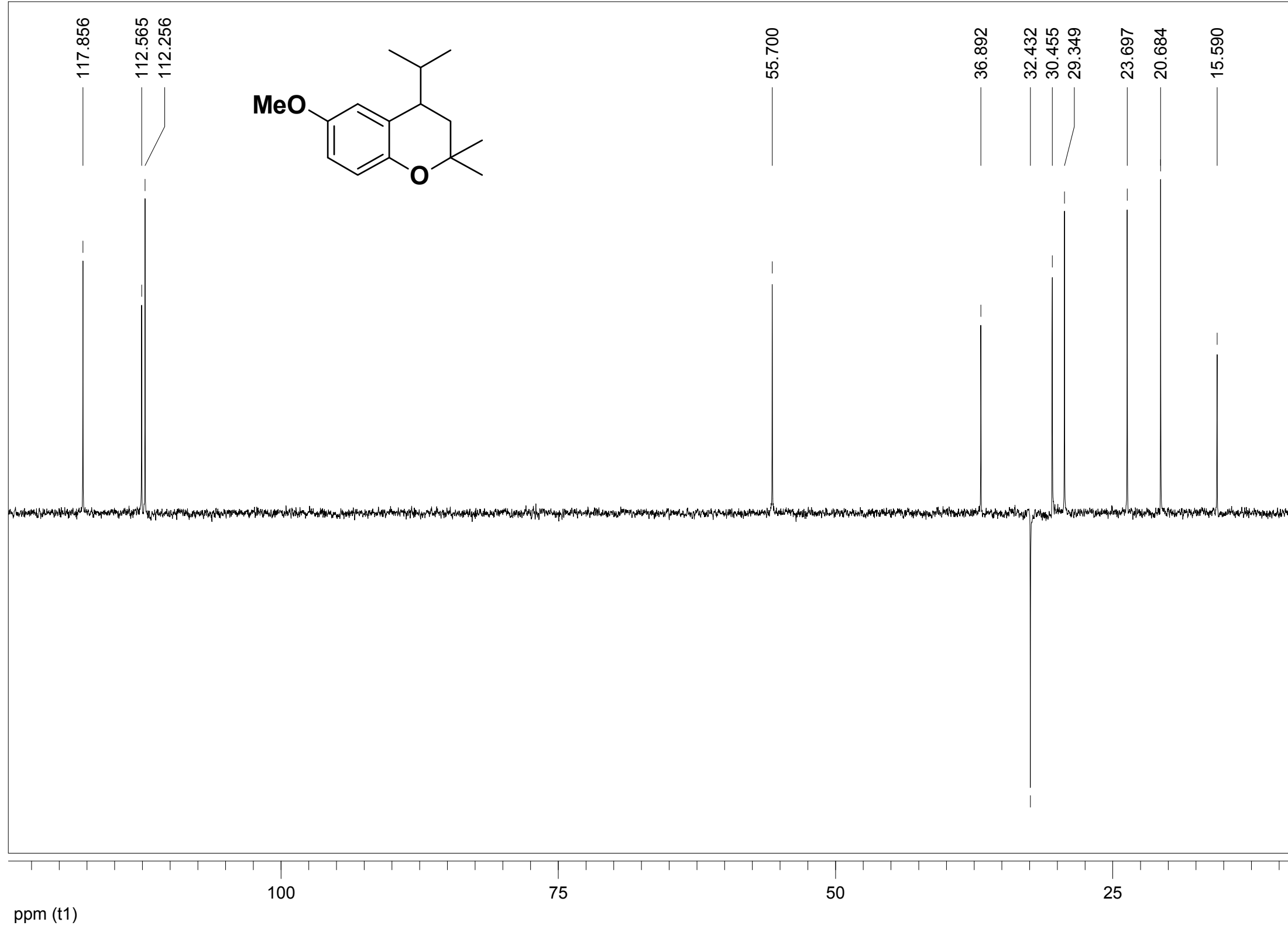
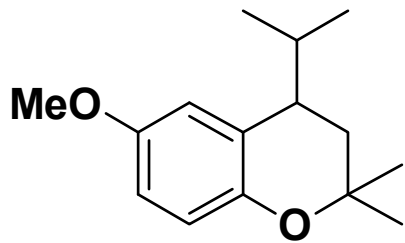
7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50
ppm (t1)



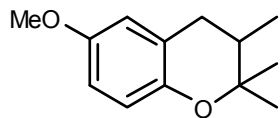


153.268
148.532
125.487
117.856
112.565
112.257
73.876
55.702
36.892
32.436
30.463
29.349
23.698
20.685
15.591





6.700
6.684
6.677
6.584



3.744

2.761
2.747
2.719
2.705
2.480
2.455
2.438
2.413
1.936
1.919
1.911
1.905
1.897
1.368
1.140
1.015
0.998

0.94

1.01

0.32

0.31

0.30

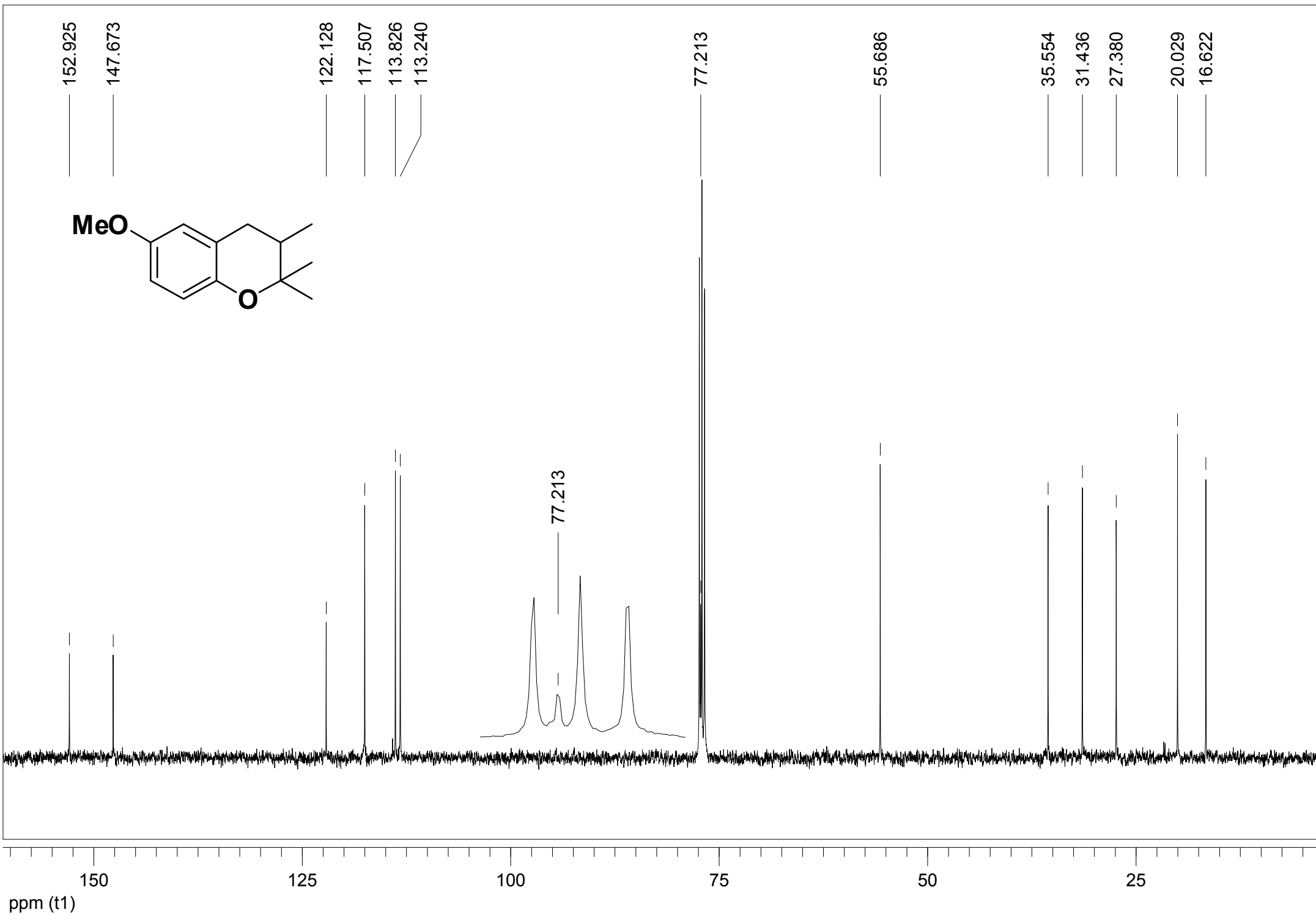
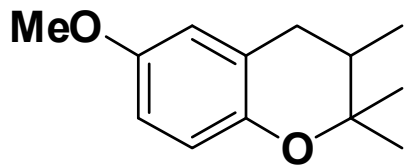
1.03

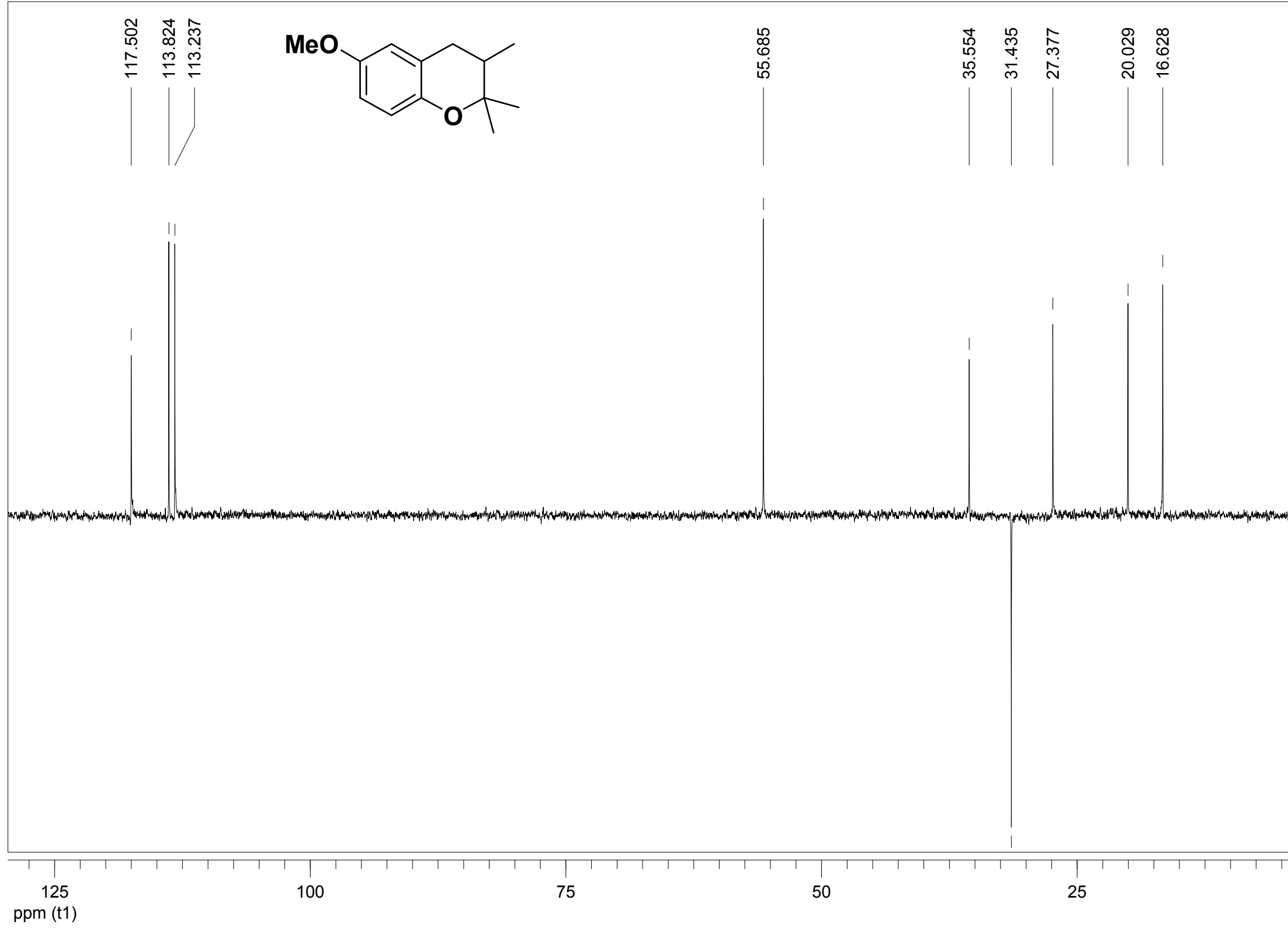
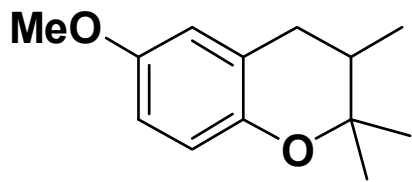
1.00

1.06

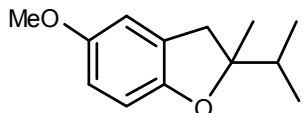
ppm (t1)

7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50





6.726
6.699
6.635



3.746

3.140
3.101

2.790
2.751

2.009
1.992
1.975

1.328

1.003
0.986
0.949
0.932

99.7

00.0

48.0

88.0

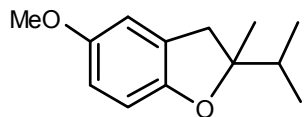
06.0

88.3

96.5

ppm (t1)

7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00



153.616
153.340

128.001

112.723
111.446
109.017

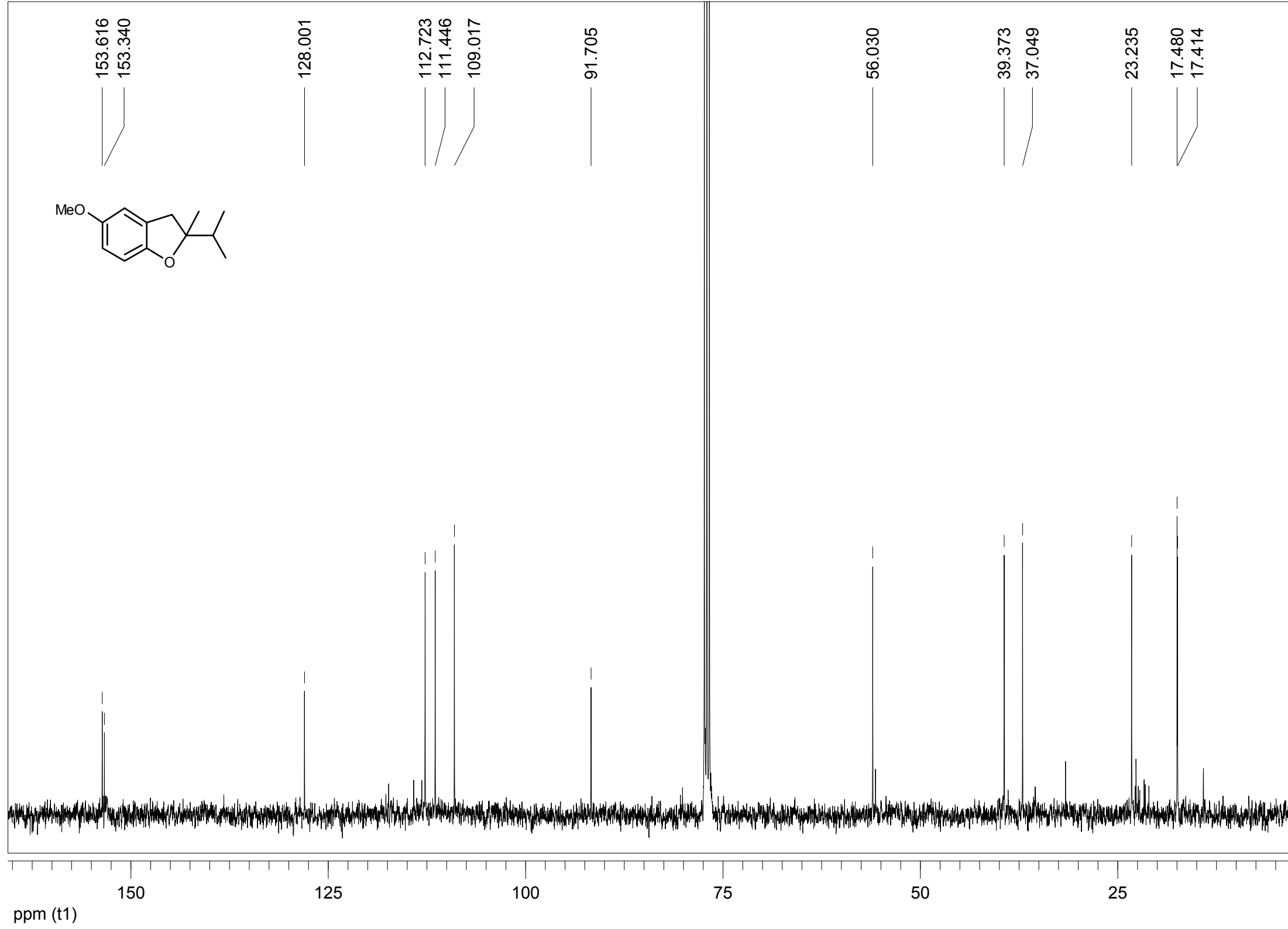
91.705

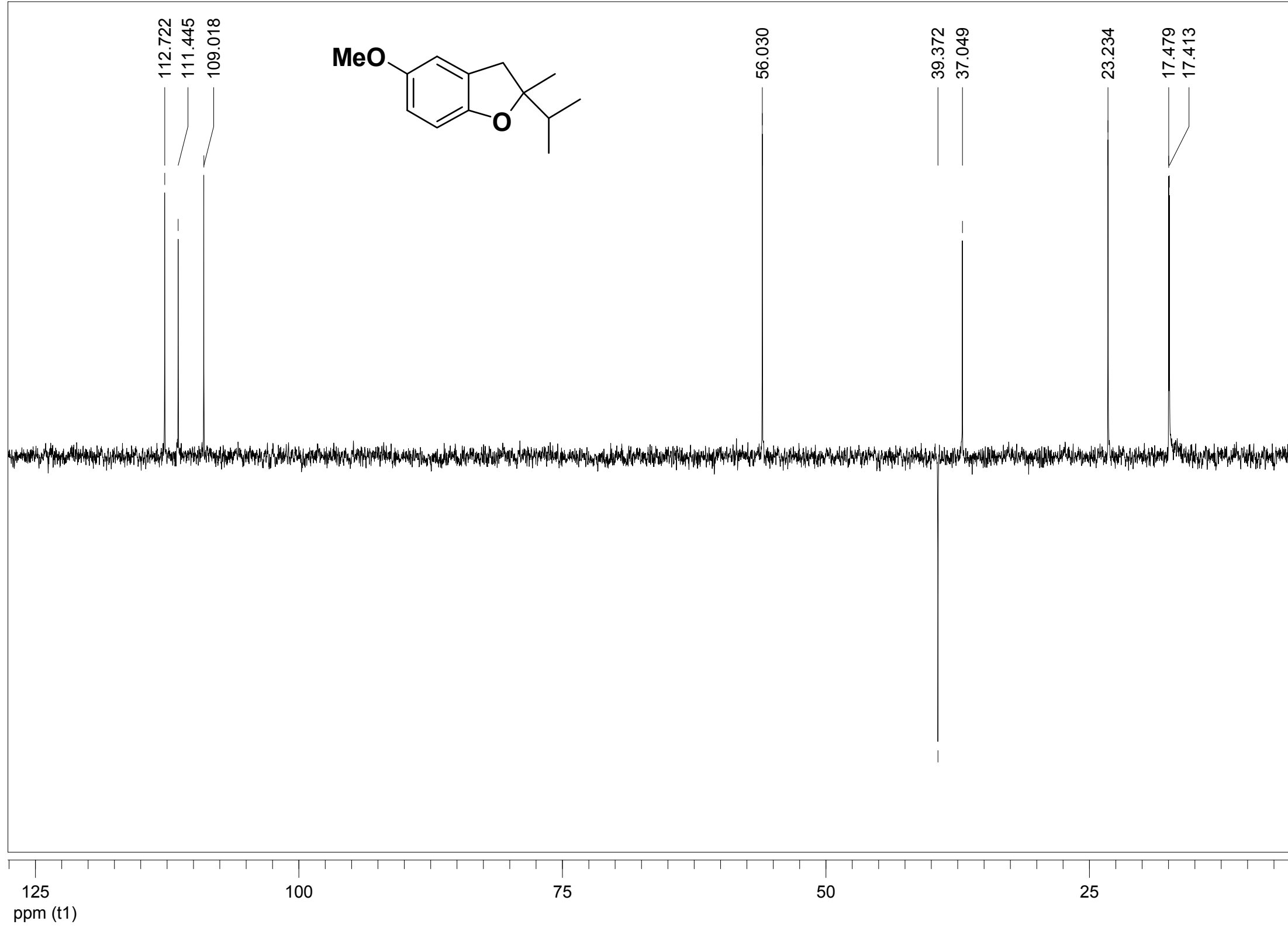
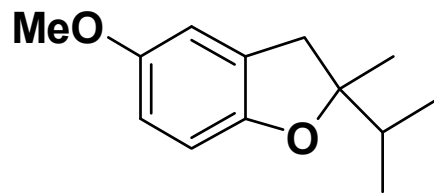
56.030

39.373
37.049

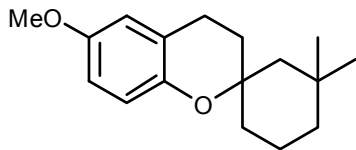
23.235

17.480
17.414





6.709
6.694
6.687
6.609



3.756

2.731

1.900
1.874
1.839
1.703
1.499
1.470
1.065
0.883

2.83

2.95

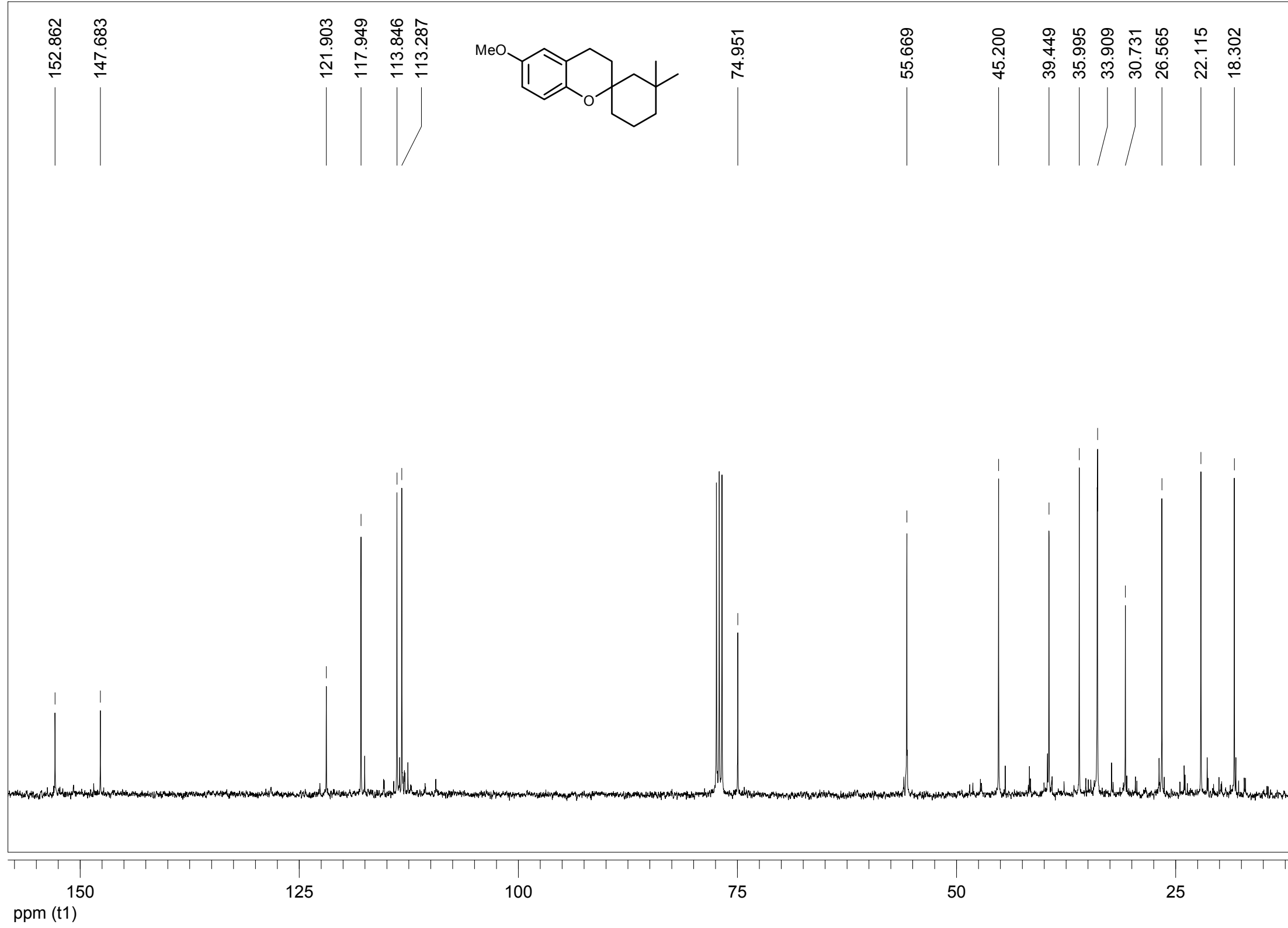
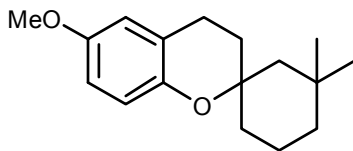
1.75

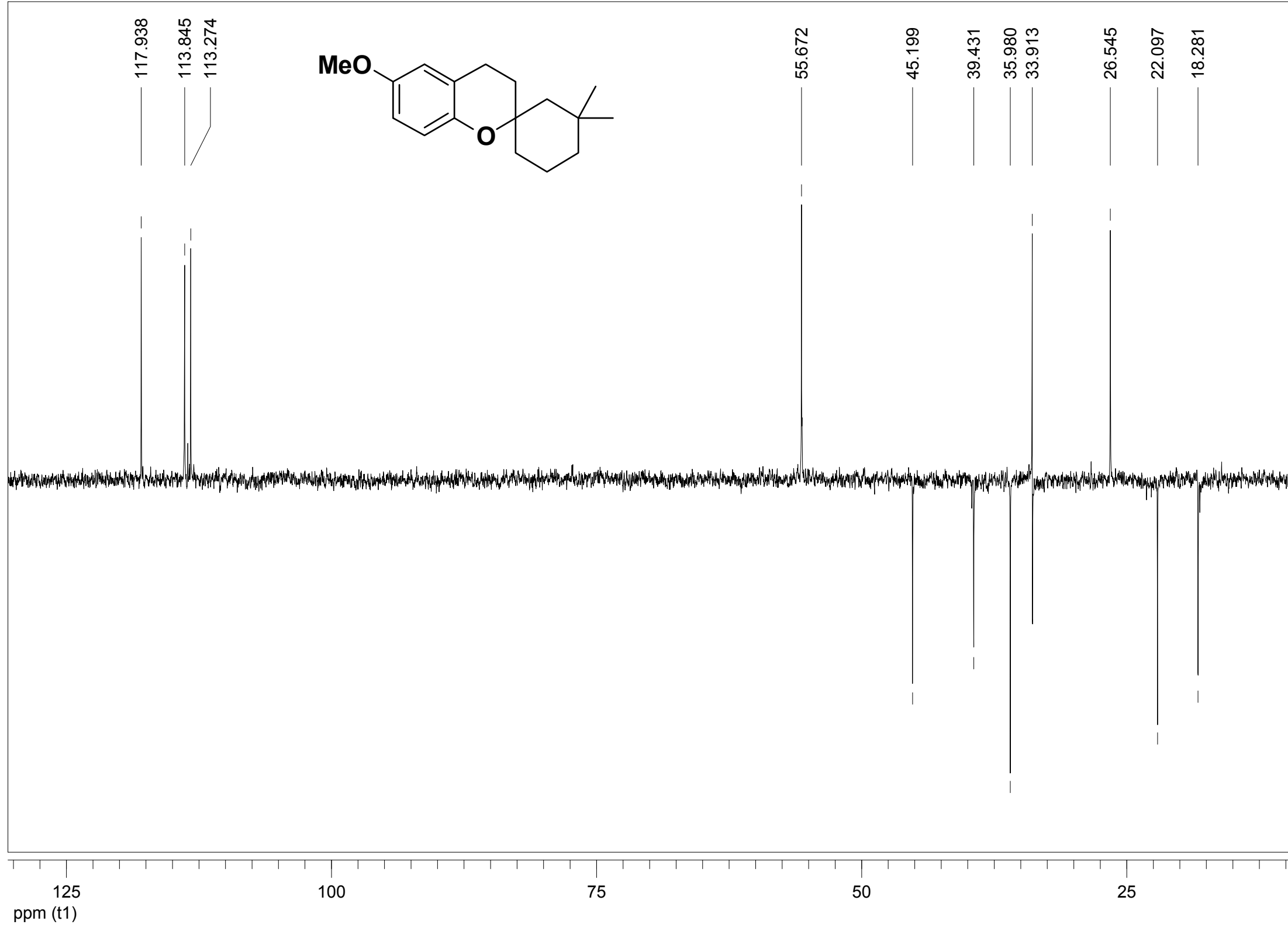
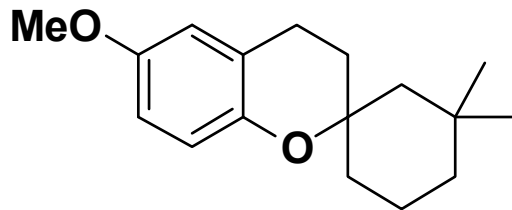
12.00

3.34

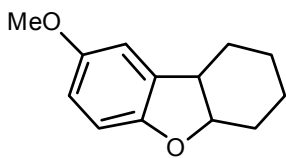
2.87

7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (t1)



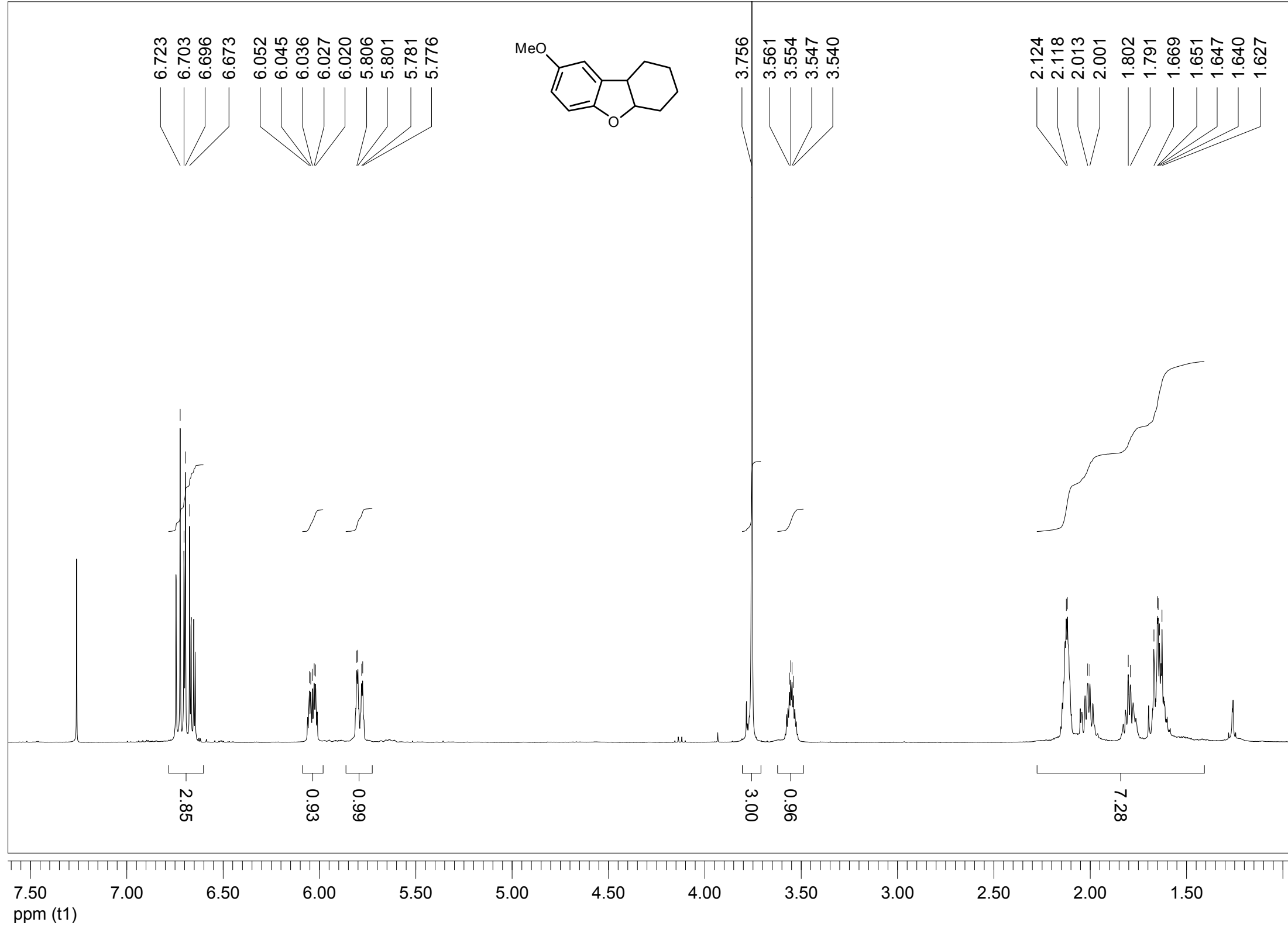


6.723
6.703
6.696
6.673
6.052
6.045
6.036
6.027
6.020
5.806
5.801
5.781
5.776

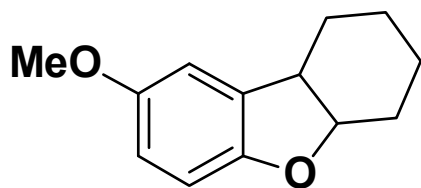


3.756
3.561
3.554
3.547
3.540

2.124
2.118
2.013
2.001
1.802
1.791
1.669
1.651
1.647
1.640
1.627



7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50
ppm (t1)



154.112
153.375

134.651

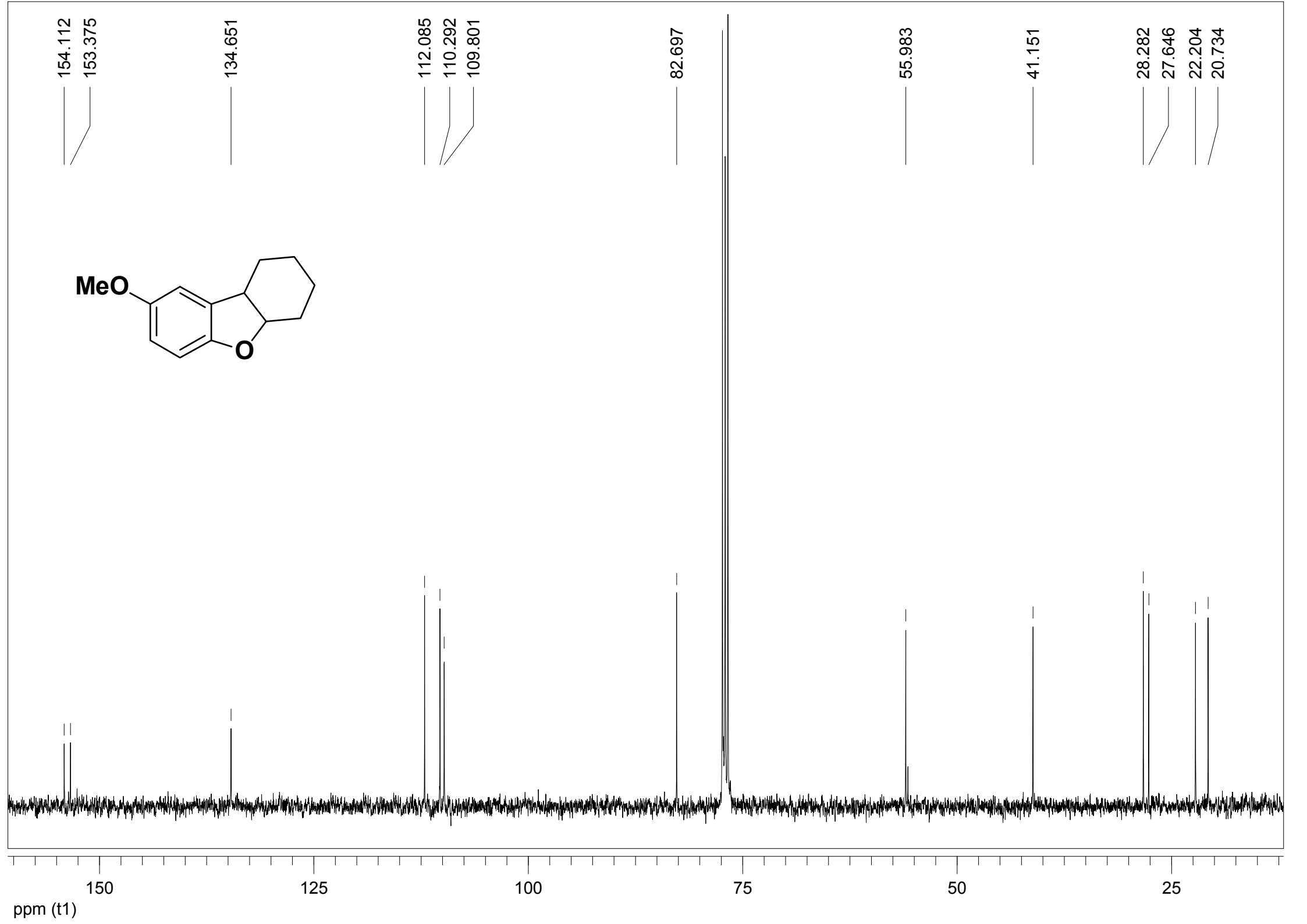
112.085
110.292
109.801

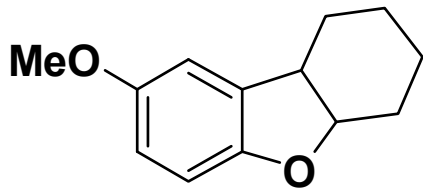
82.697

55.983

41.151

28.282
27.646
22.204
20.734





112.084
110.291
109.807

82.697

55.981

41.150

28.280

27.647

22.202

20.733

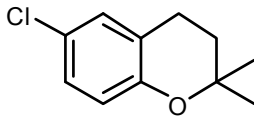
ppm (t1)

100

75

50

25



7.039

6.716

6.693

2.745

1.785

1.324

1.99

1.01

1.97

2.24

6.00

7.50
ppm (t1)

7.00

6.50

6.00

5.50

5.00

4.50

4.00

3.50

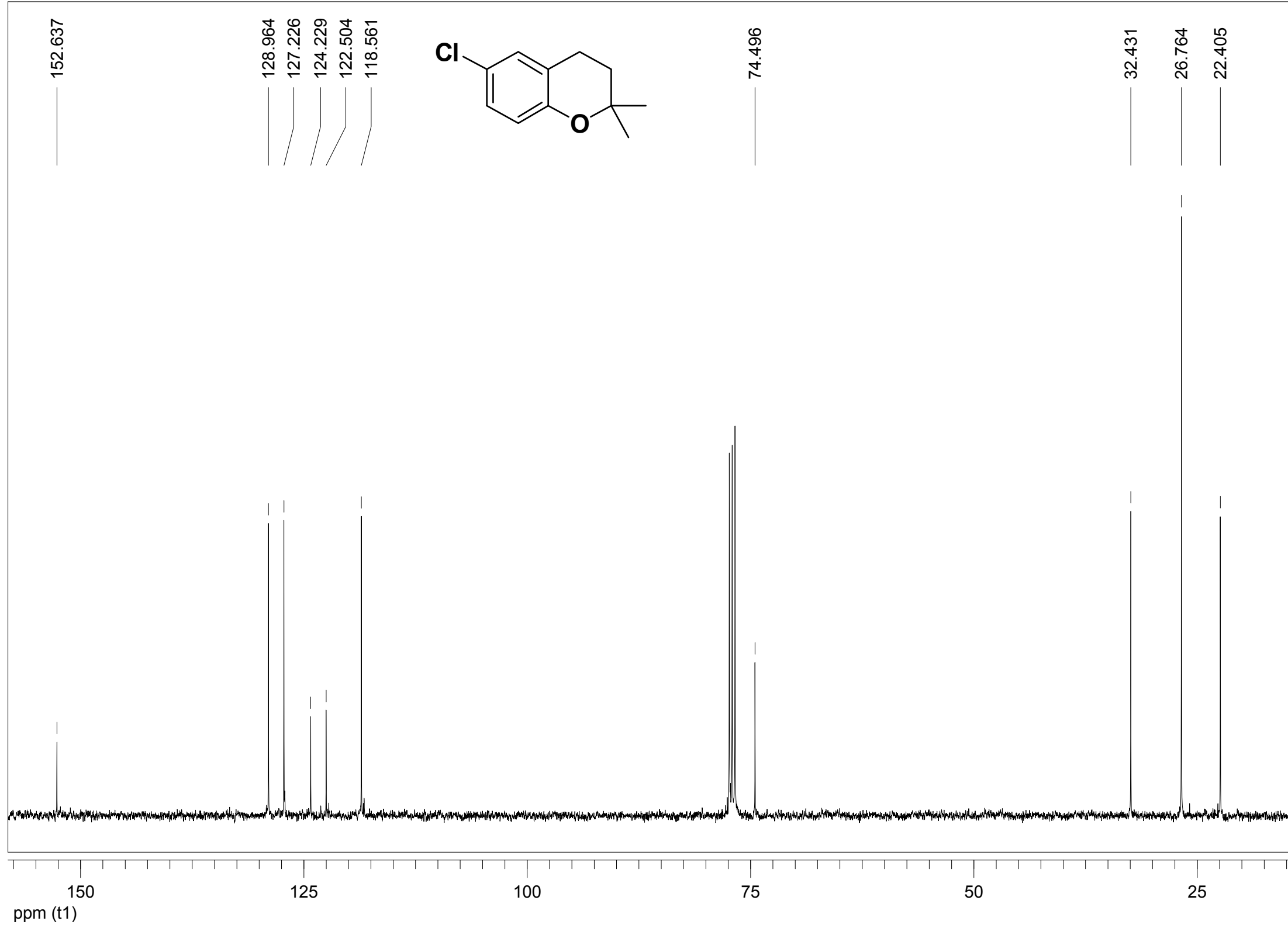
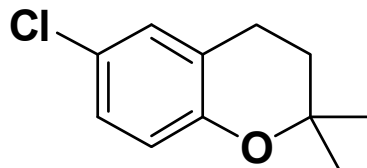
3.00

2.50

2.00

1.50

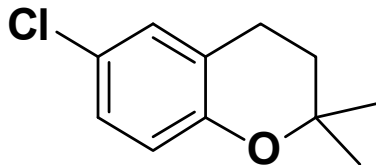
1.00



128.965

127.226

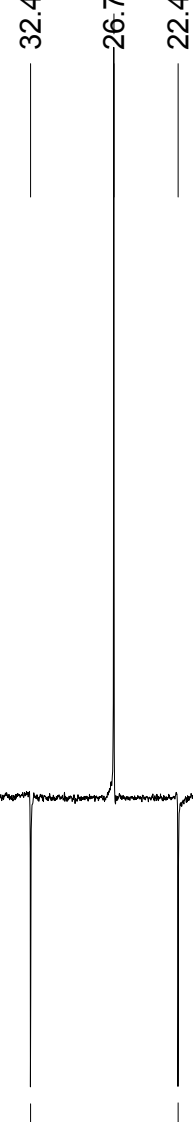
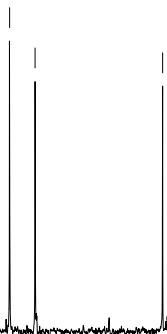
118.561



32.429

26.765

22.403



125

100

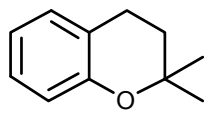
75

50

25

ppm (t1)

7.098
6.851
6.829
6.808



3.63

2.802

1.92

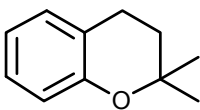
1.837

1.93

1.372

6.00

7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00
ppm (t1)



154.031

129.489

127.290

120.950

119.644

117.281

74.119

32.848

26.938

22.501

ppm (t1)

150

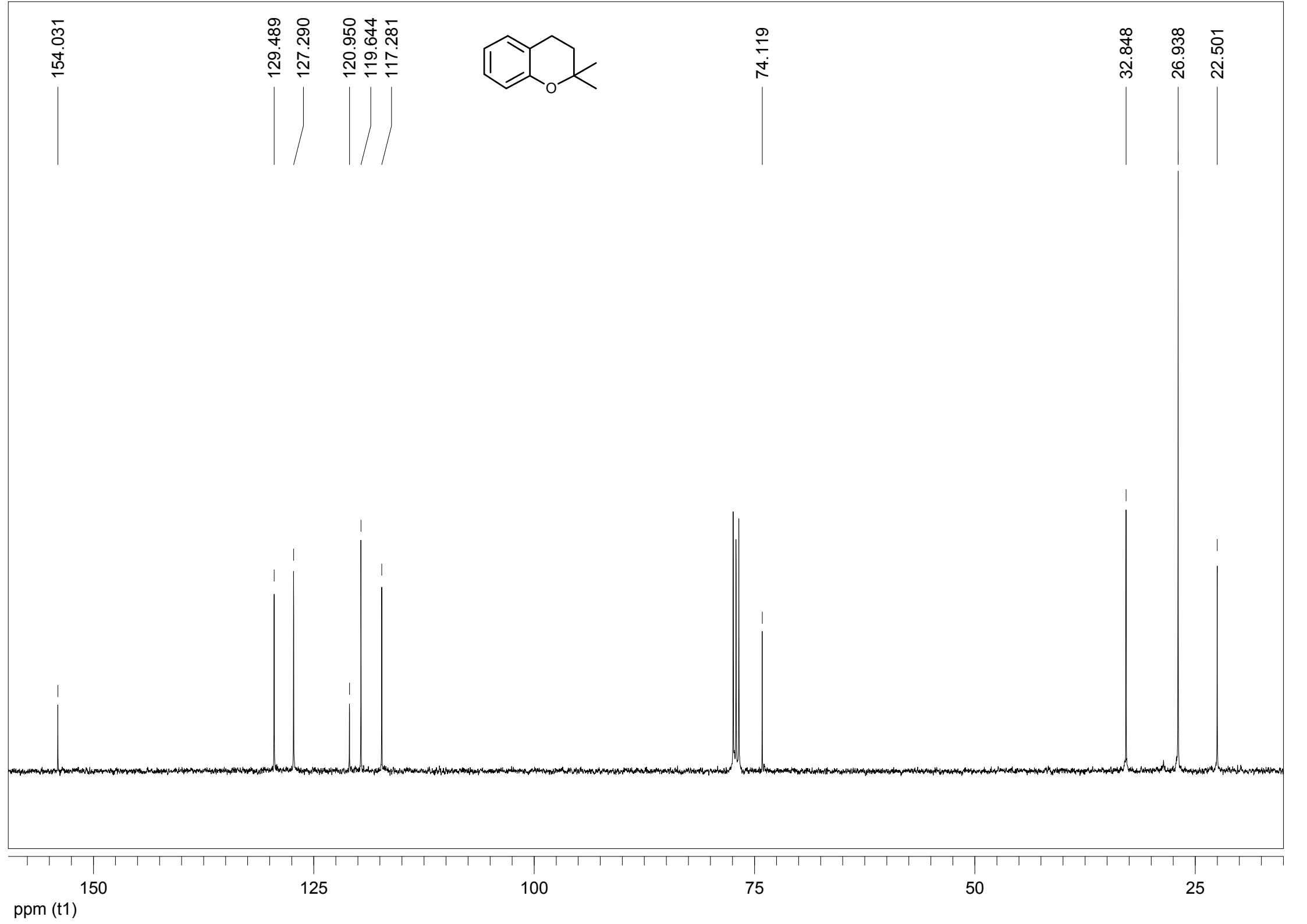
125

100

75

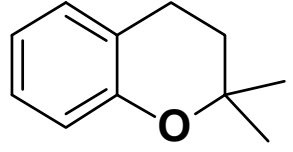
50

25



129.498
127.292

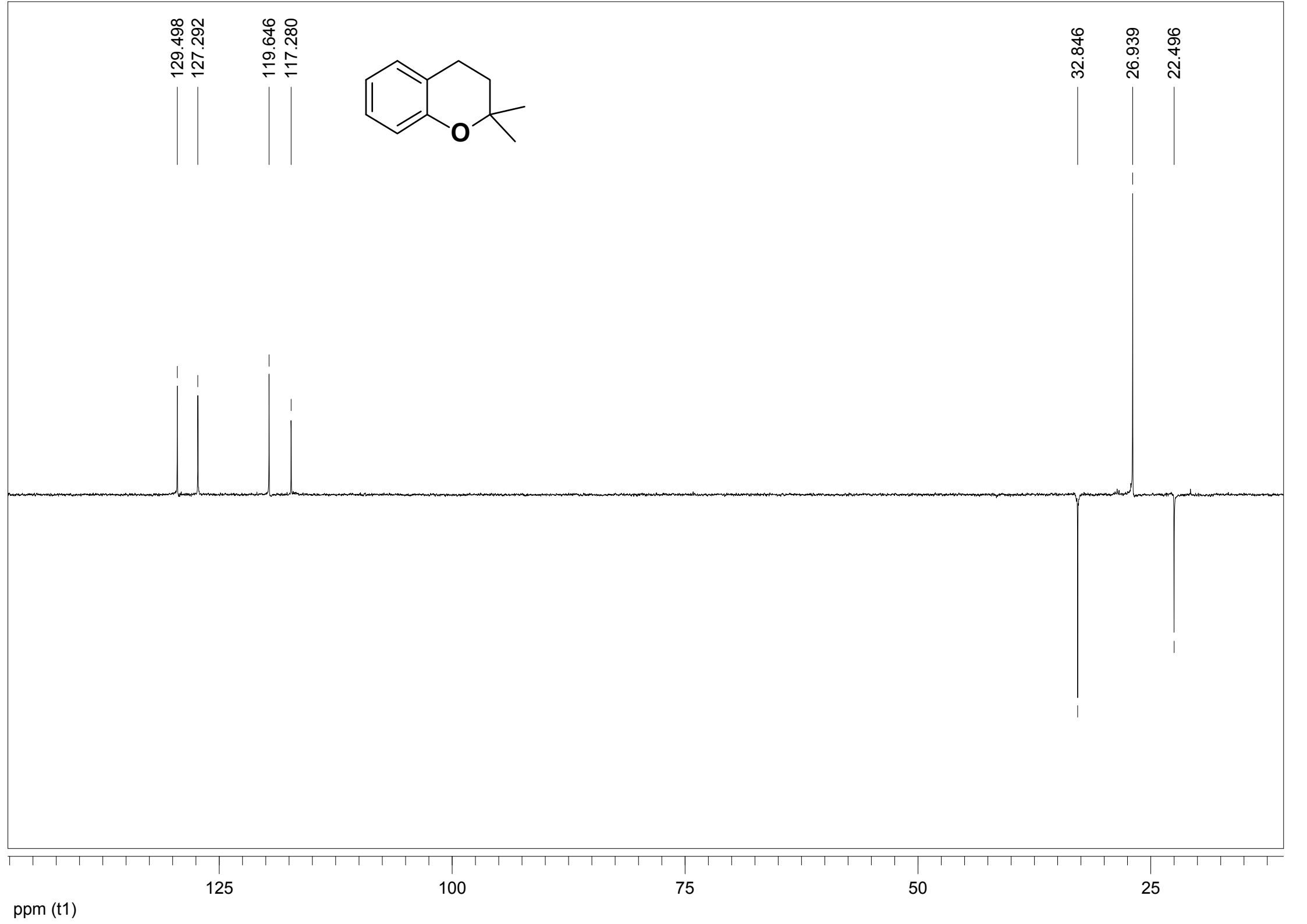
119.646
117.280



32.846

26.939

22.496



ppm (t1)

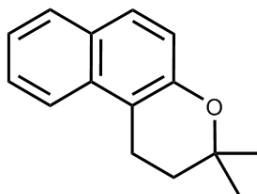
125

100

75

50

25



8.020
7.999
7.973
7.952
7.842
7.820
7.720
7.700
7.682
7.571
7.551
7.531
7.321
7.299

3.172

2.095

1.592



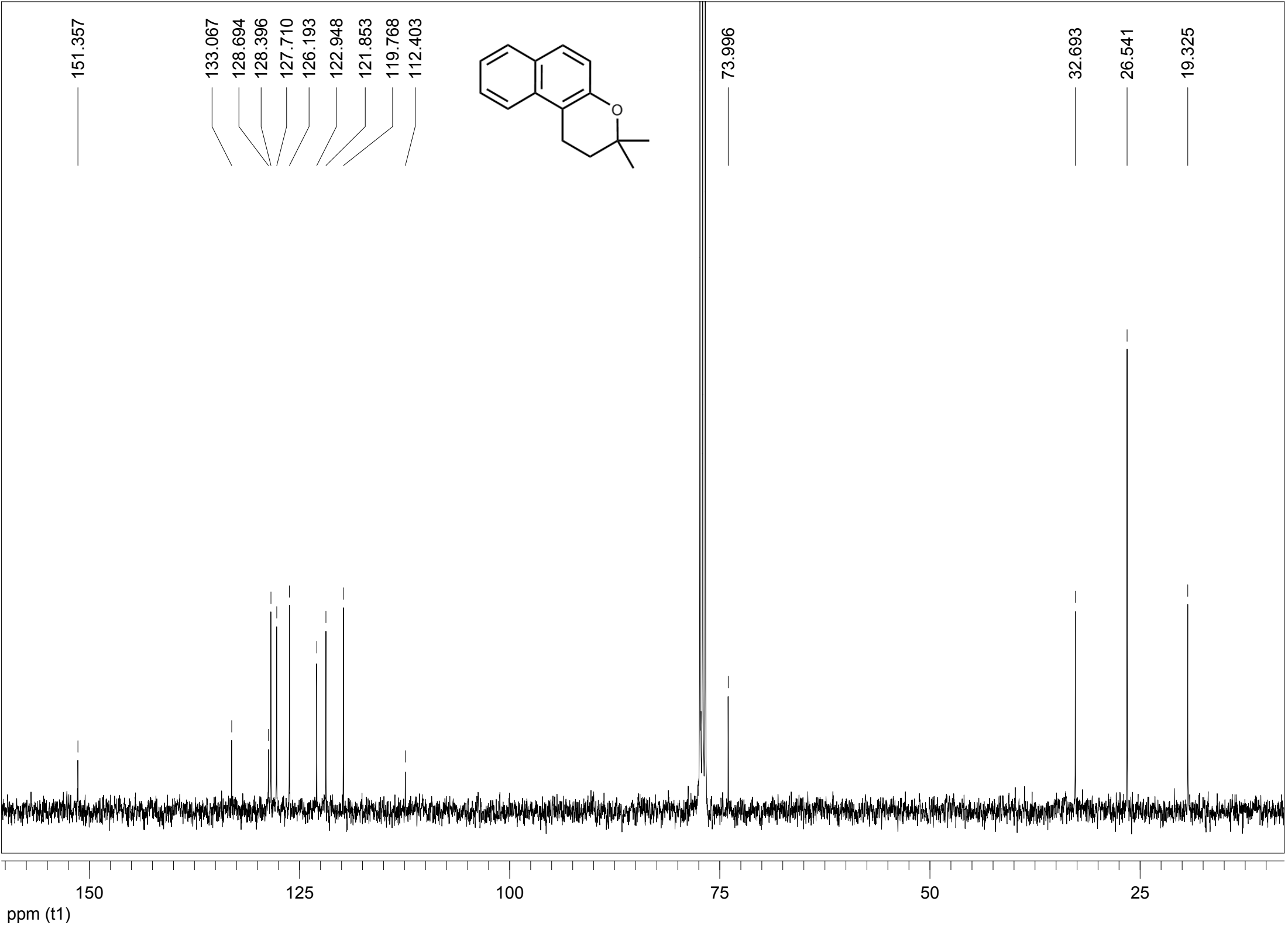
1.79
0.92
0.91
0.92
0.90

1.92

2.05

6.00

8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50
ppm (t1)



151.357

133.067

128.694

128.396

127.710

126.193

122.948

121.853

119.768

112.403

73.996

32.693

26.541

19.325

ppm (t1)

150

125

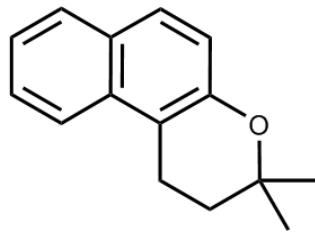
100

75

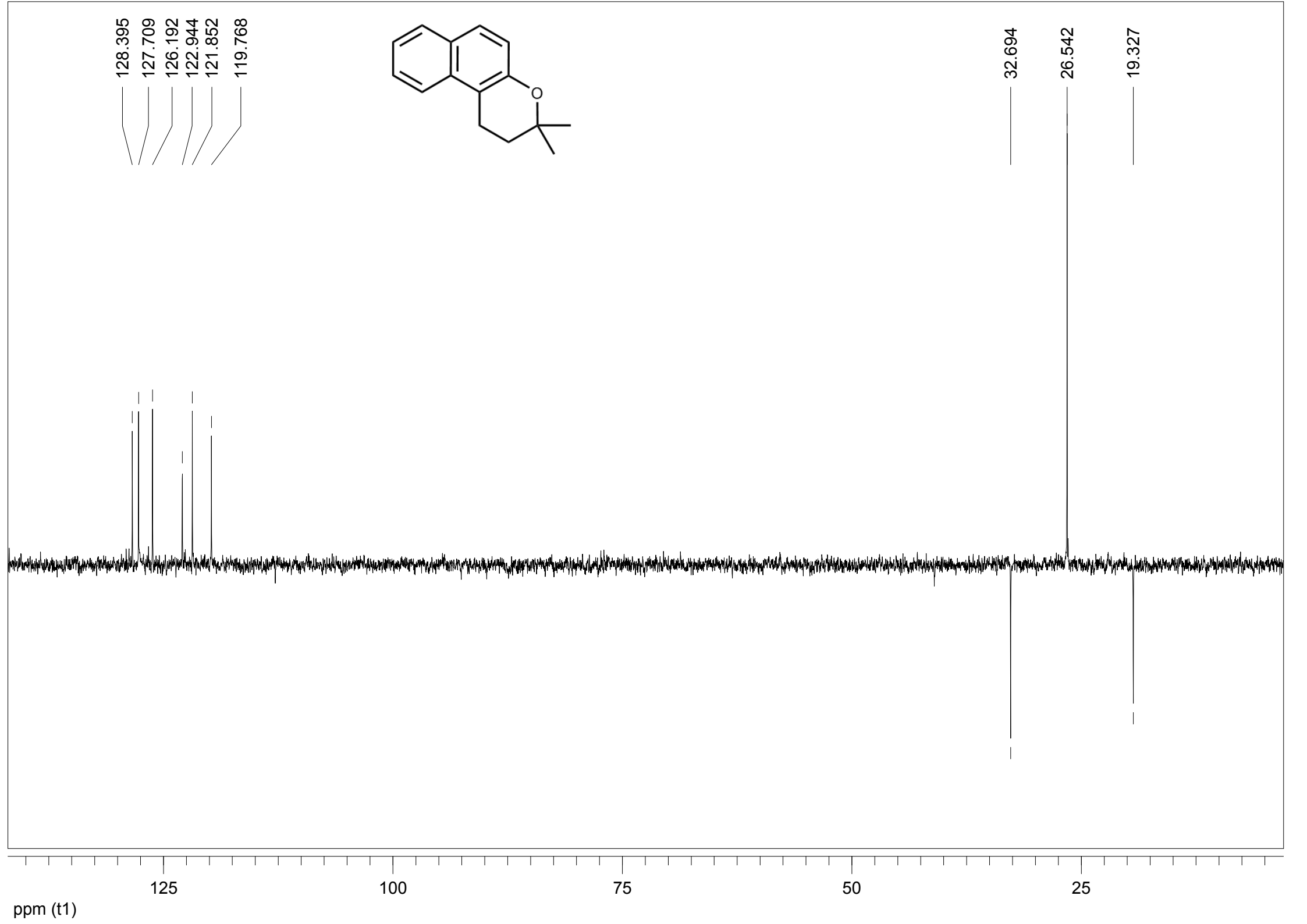
50

25

128.395
127.709
126.192
122.944
121.852
119.768



32.694
26.542
19.327



ppm (t1)

125

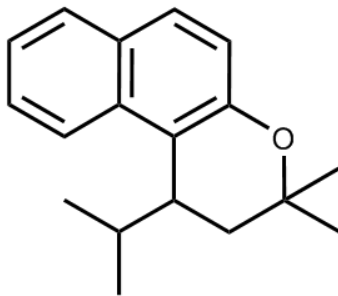
100

75

50

25

8.027
8.005
7.902
7.882
7.737
7.715
7.570
7.436
7.215
7.193



3.623
3.613

2.813
2.802
2.796

2.149
2.126
2.083
2.061

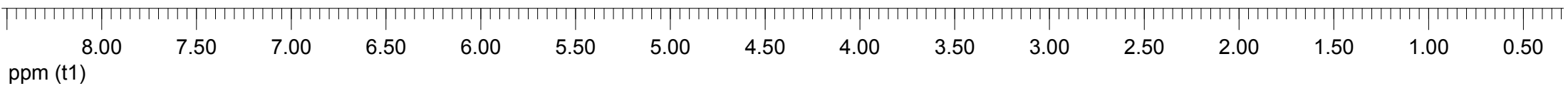
1.660

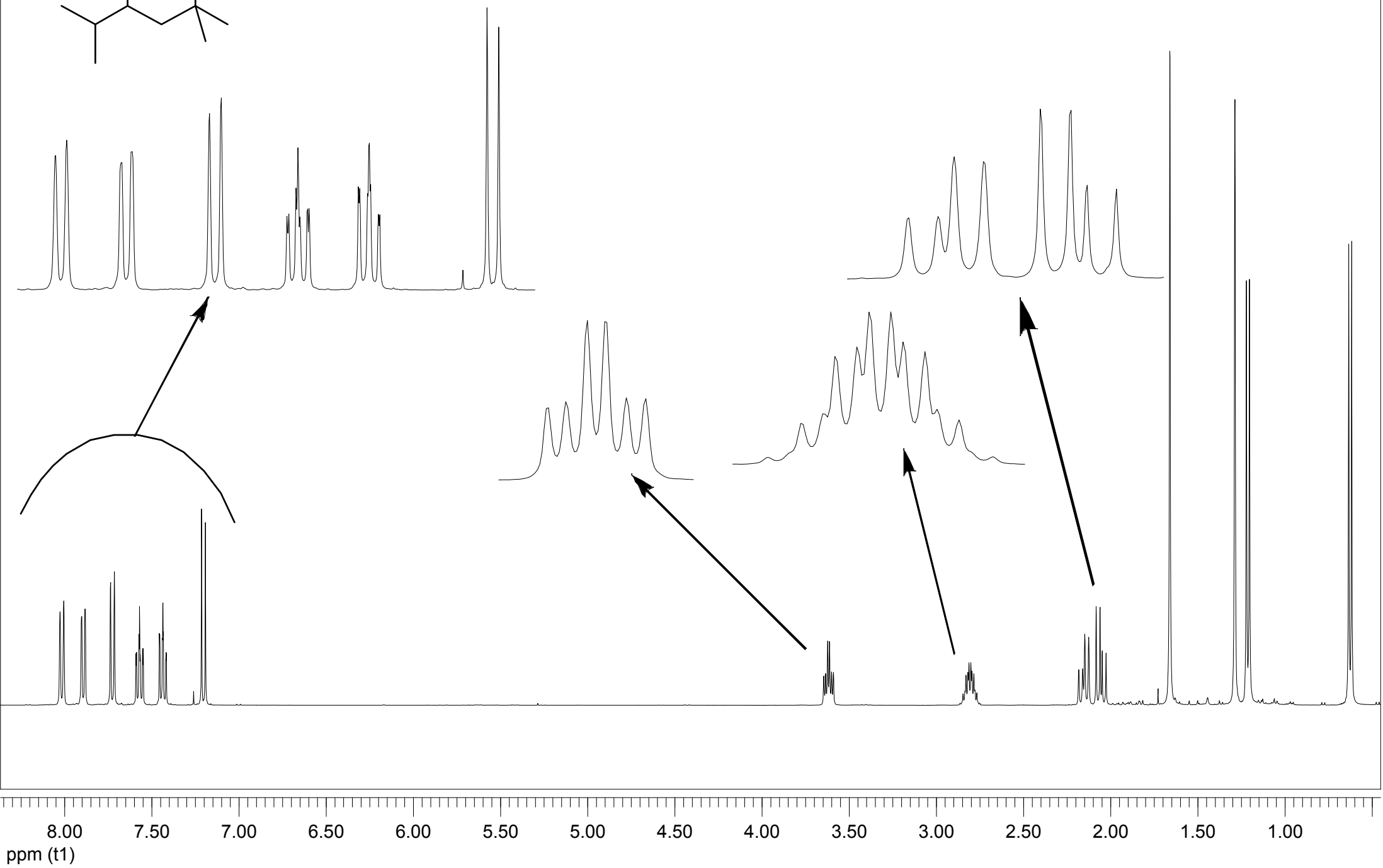
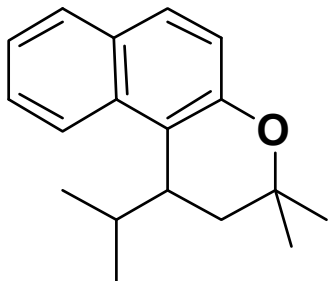
1.287
1.221
1.204

0.635
0.618

0.33
0.33
0.33
0.33
0.33
2.00

0.33
0.33
0.69
1.01
1.03
1.00





152.738

132.375

130.035

128.897

127.773

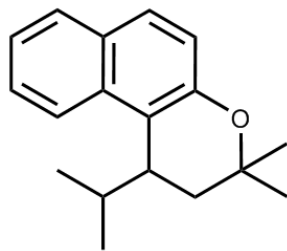
125.538

123.557

122.923

120.106

119.303



74.844

35.317

34.983

30.769

30.442

23.639

21.160

15.742

ppm (t1)

150

125

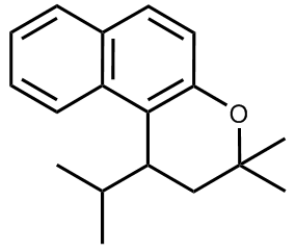
100

75

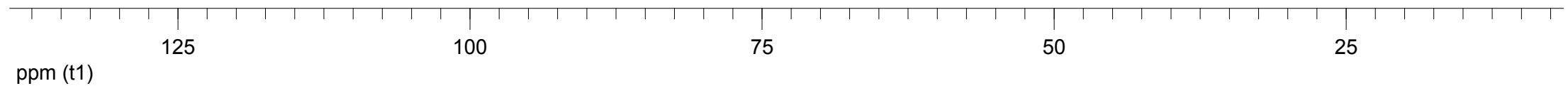
50

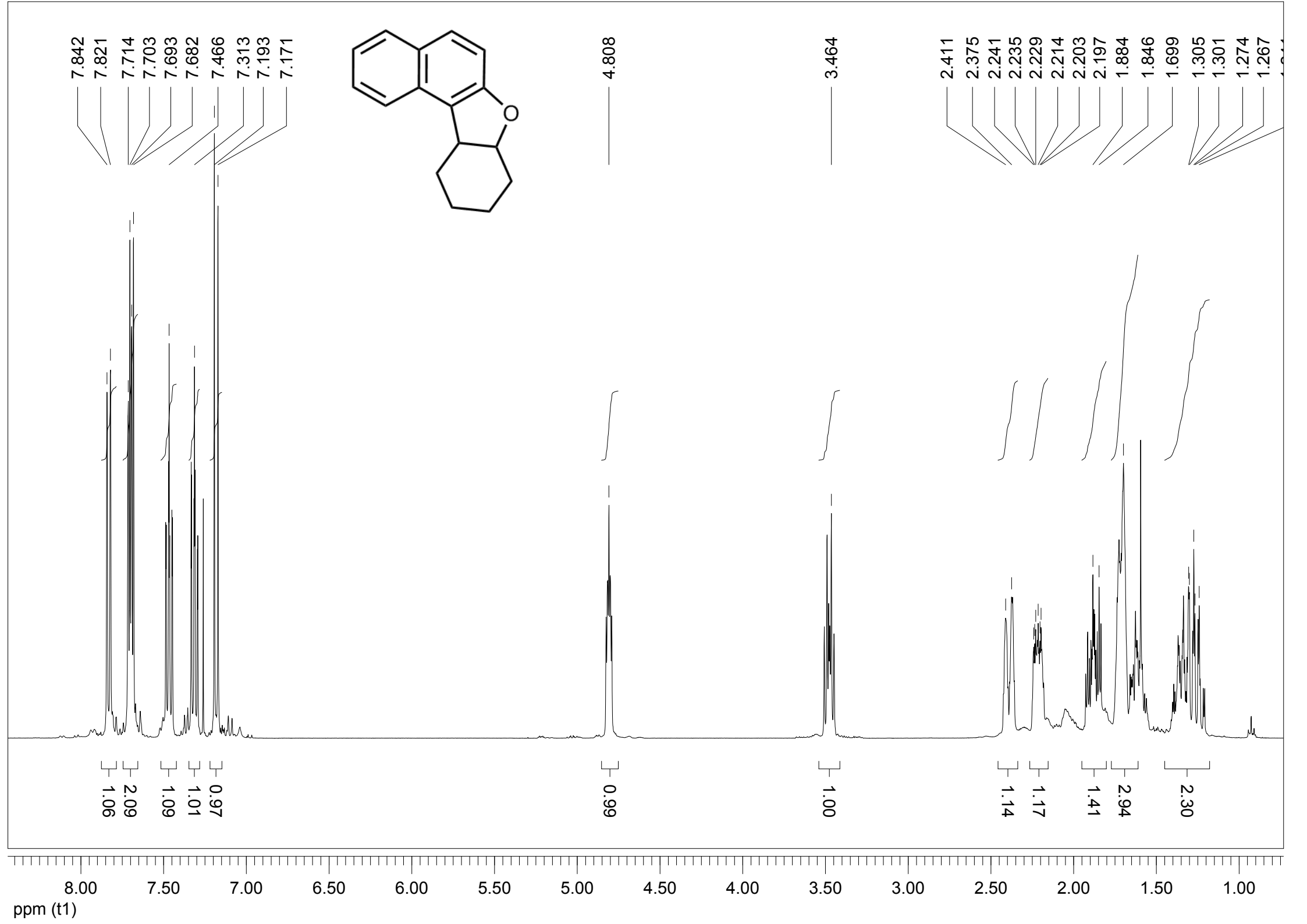
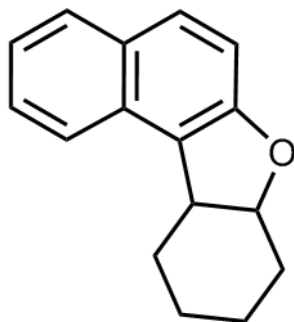
25

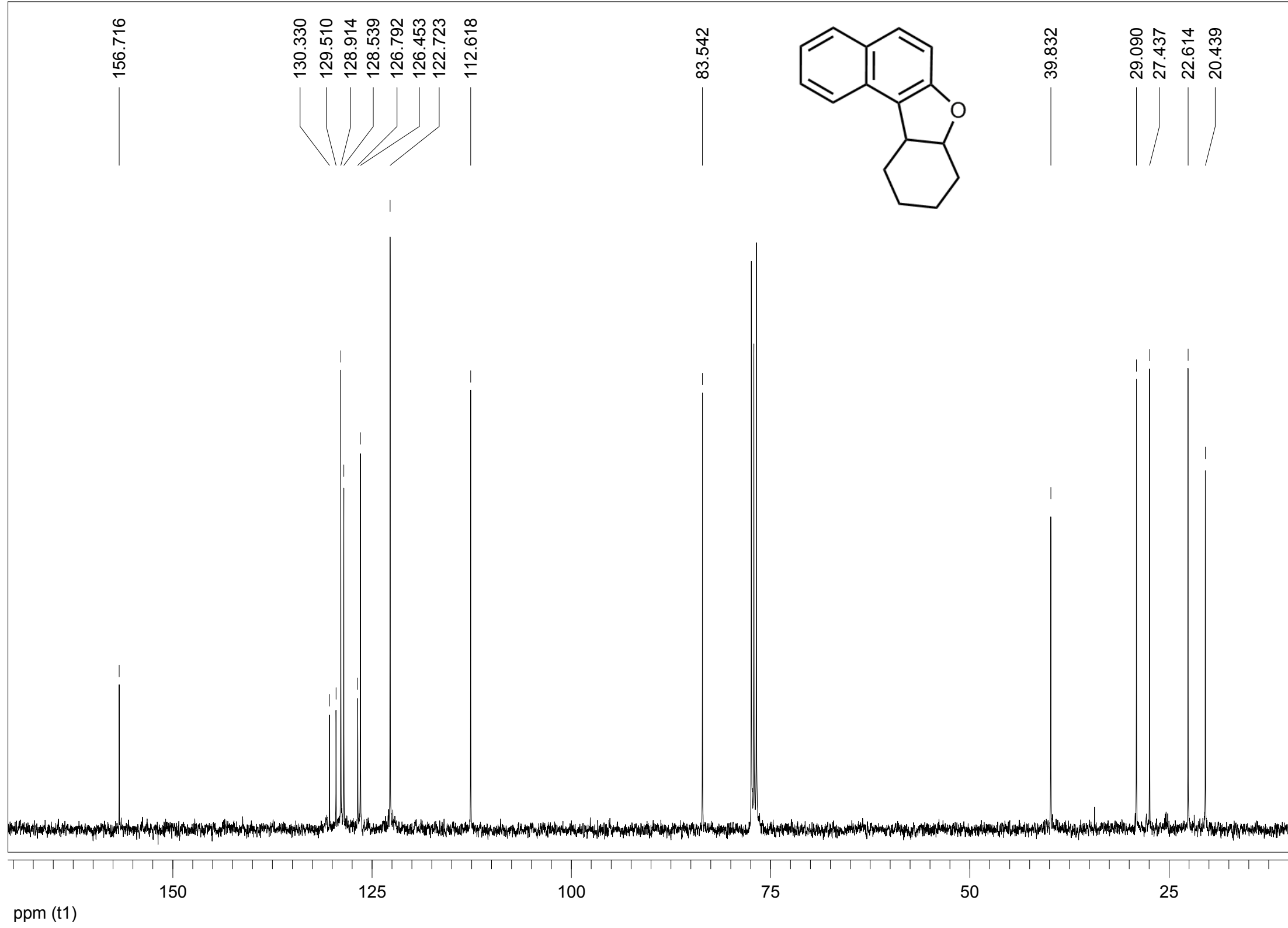
128.897
127.774
125.539
123.559
122.925
120.105

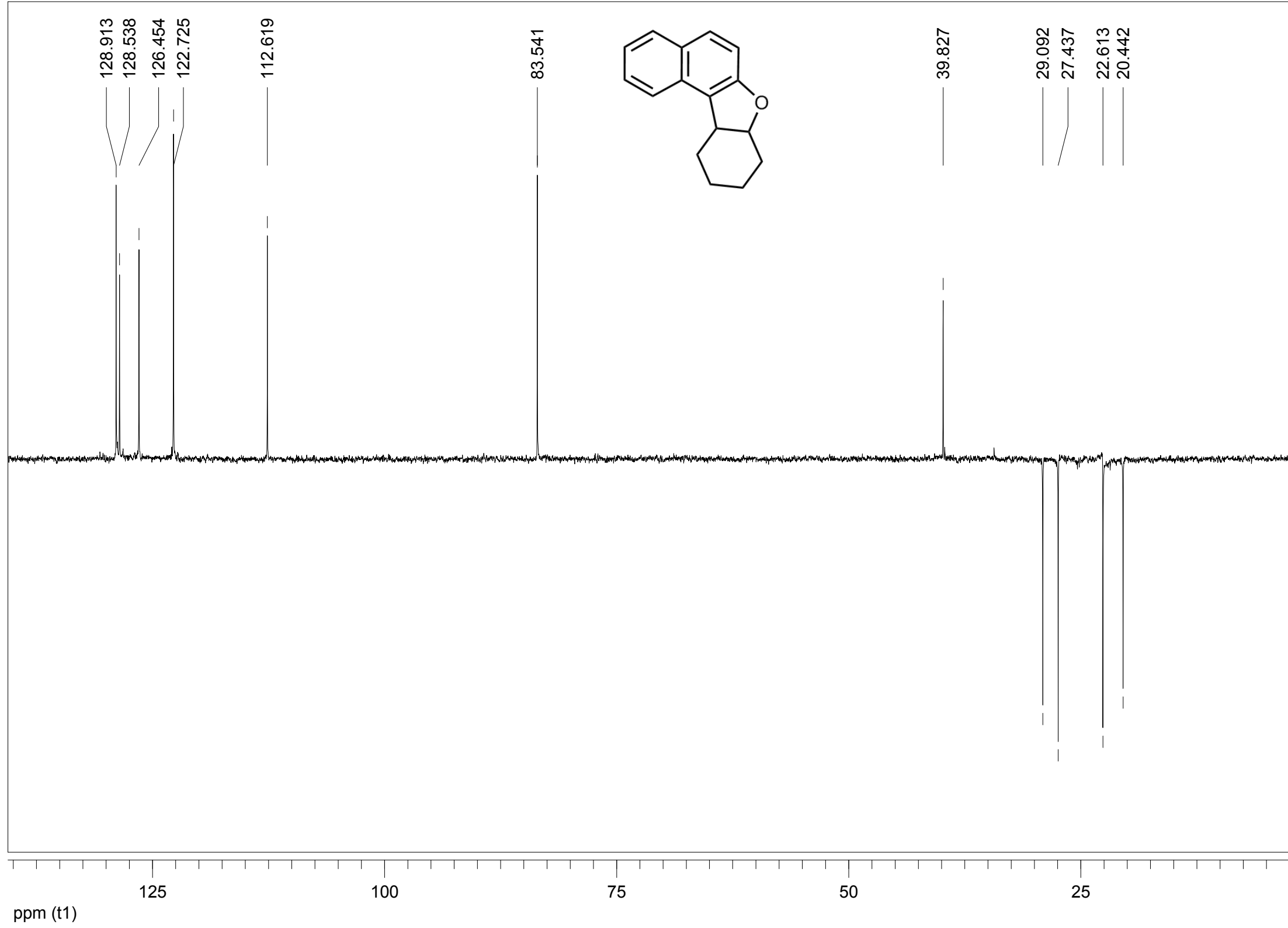
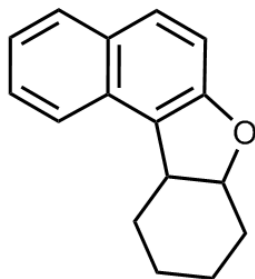


35.310
34.982
30.769
30.438
23.633
21.165
15.741









128.913
128.538
126.454
122.725

112.619

83.541

39.827

29.092
27.437

22.613
20.442

125

100

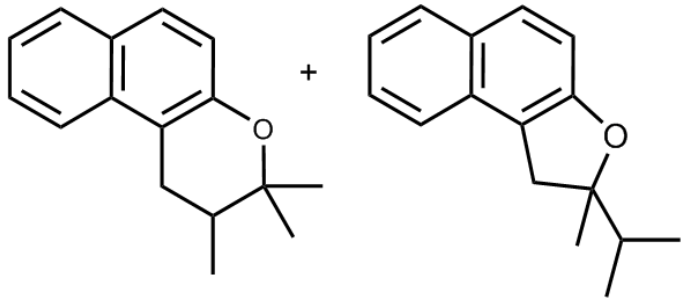
75

50

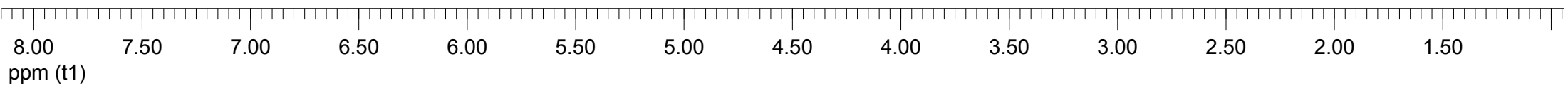
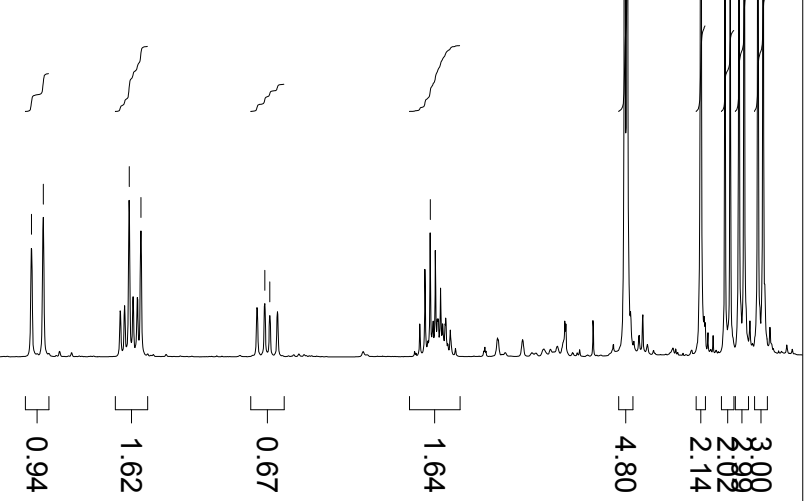
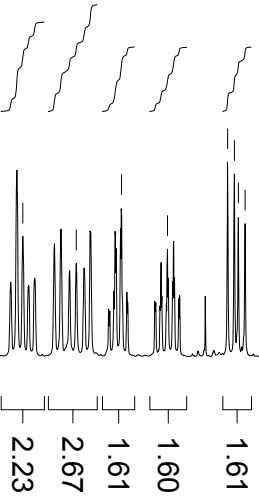
25

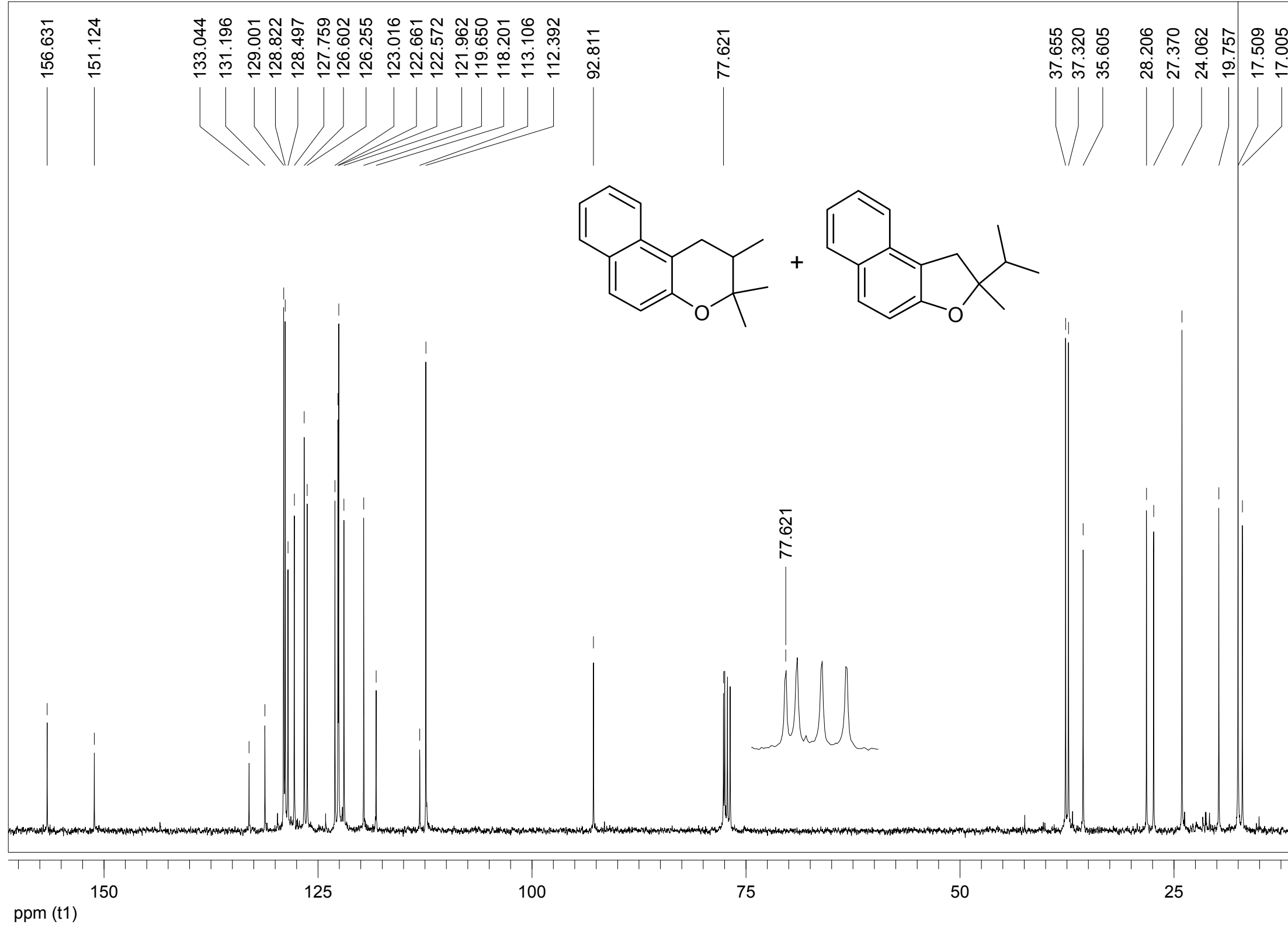
ppm (t1)

7.860
7.684
7.536
7.385
7.187
7.165
7.152
7.129

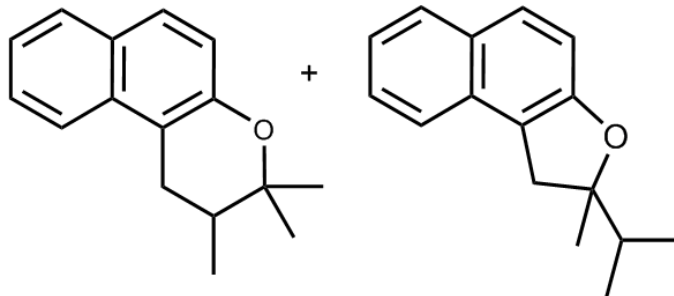


3.477
3.439
3.156
3.118
2.711
2.694
2.167
1.528
1.520
1.277
1.198
1.152
1.135

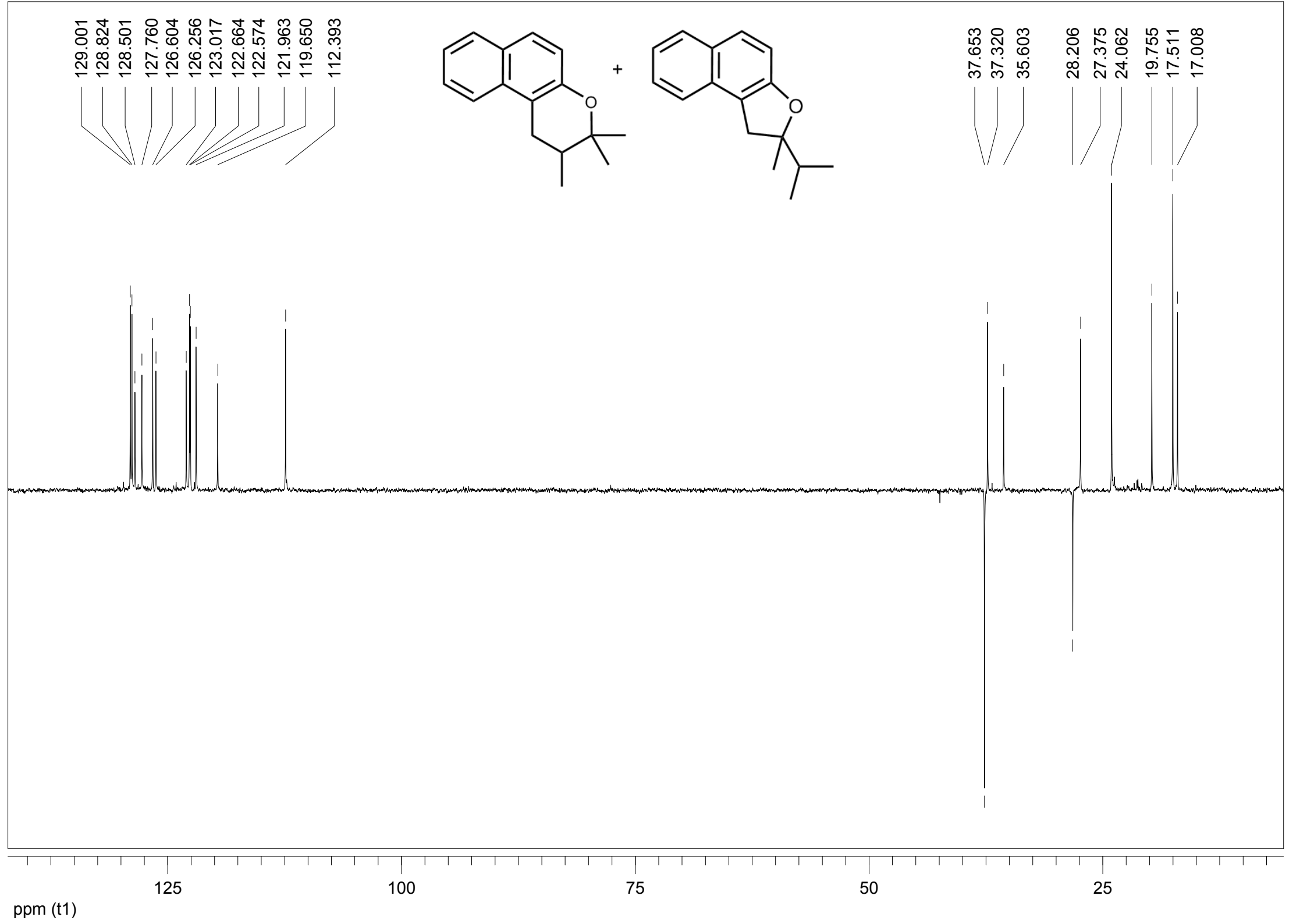


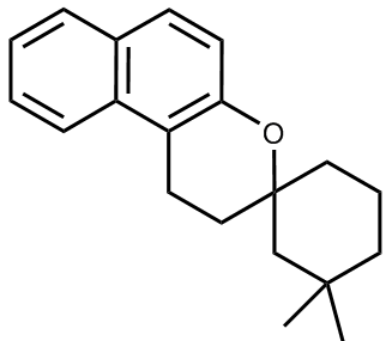


129.001
128.824
128.501
127.760
126.604
126.256
123.017
122.664
122.574
121.963
119.650
112.393



37.653
37.320
35.603
28.206
27.375
24.062
19.755
17.511
17.008





7.916
7.896
7.861
7.841
7.723
7.701
7.574
7.554
7.423
7.167
7.144

3.099
3.094

1.946

1.622

1.594

1.584

1.336

1.179

0.981

2.13
1.04
1.05
0.98
0.84

1.77

11.80

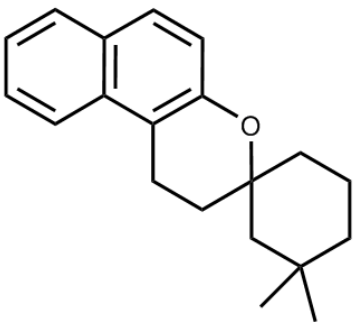
3.00

2.98

ppm (t1)

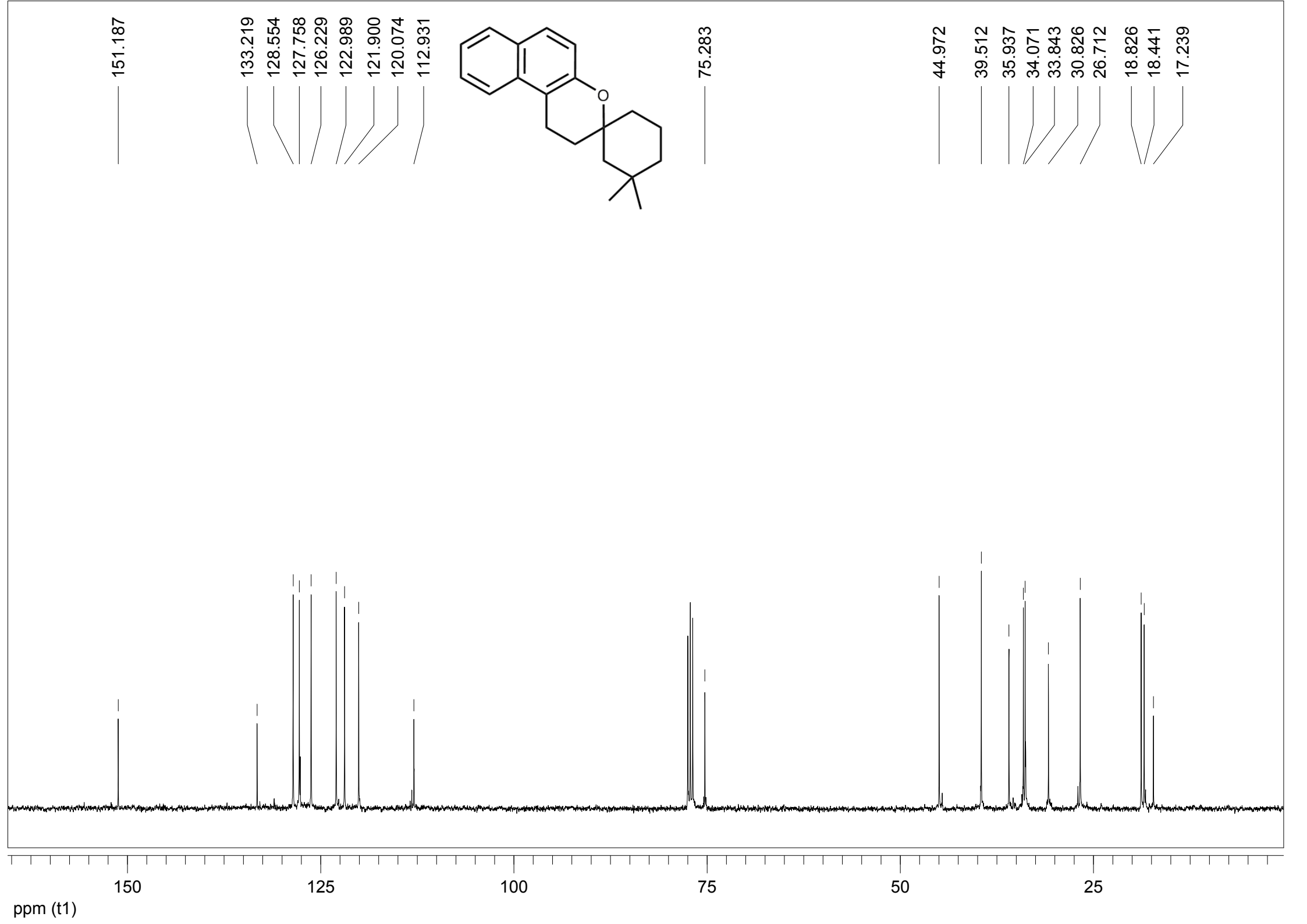
8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50

151.187
133.219
128.554
127.758
126.229
122.989
121.900
120.074
112.931

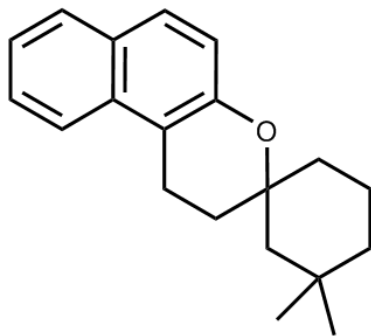


75.283

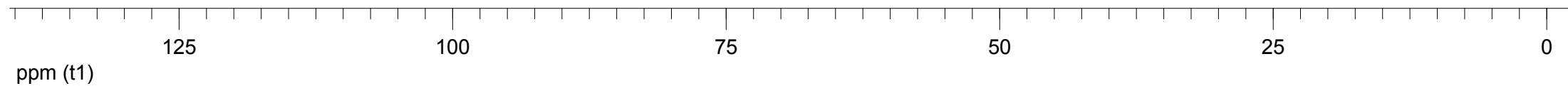
44.972
39.512
35.937
34.071
33.843
30.826
26.712
18.826
18.441
17.239

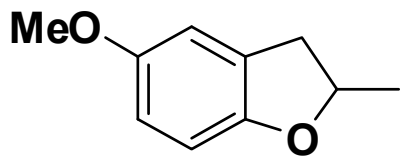


128.518
127.759
126.231
122.990
121.902
120.076



44.969
39.511
35.943
34.077
33.841
26.712
18.828
18.439





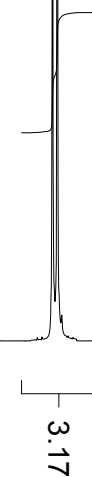
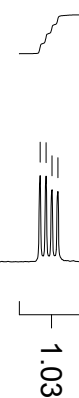
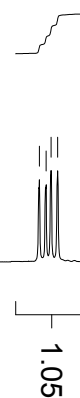
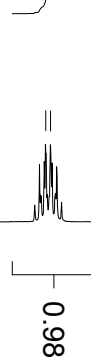
6.749
6.651

4.900
4.884

3.749

3.304
3.282
3.265
3.244
2.823
2.804
2.785
2.765

1.461
1.445



0.95
1.90

0.96

3.00

1.05

1.03

3.17

ppm (t1)

7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50