

Iodine-catalyzed transformation of aryl-substituted alcohols under solvent-free and highly concentrated reaction conditions

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Characterization of known compounds

Bis(1-phenylethyl) ether¹ **2a**

Reaction conditions: 1 mmol (122 mg) **1a**, 0.03 mmol (8 mg) I₂, 16 h, 55 °C; column chromatography (SiO₂, hexane); 92 mg (81%), colorless oil as a mixture of isomers in ratio 1/3.2; IR (neat): 3064, 3030, 2856, 1495, 1452, 1360, 1095, 1071, 1024, 736, 697 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.33–7.02 (m, 20H), 4.49 (q, *J* = 6.4 Hz, 2H), 4.19 (q, *J* = 6.5 Hz, 2H): (major isomer), 1.44 (d, *J* = 6.4 Hz, 6H), 1.35 (*J* = 6.5 Hz, 6H): (major isomer); MS (EI): 107 (M – PhCH₂)⁺ (15%), 92 (100).

Bis(1,2-diphenylethyl) ether² **2b**

Reaction conditions: 2 mmol (397 mg) **1b**, 0.06 mmol (15 mg) I₂, 140 h, 25 °C; column chromatography (SiO₂, petroleum ether), 261 mg (69%), colorless solid as a mixture of stereoisomers in ratio 1/0.2. Stereoisomers were separated by preparative chromatography (SiO₂, petroleum ether/*t*-butyl methyl ether = 96/4). The minor isomer with lower R_f was a viscous colorless oil: IR (neat): 3062, 3028, 2918, 1601, 1493, 1450, 1067, 1026, 754, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.20–7.13 (m, 12H), 7.05–7.02 (m, 4H), 6.96–6.93 (m, 4H), 4.40 (dd, *J* = 7.1 Hz, *J* = 5.9 Hz, 2H), 3.02 (dd, *J* = 13.5 Hz, *J* = 7.1 Hz, 2H), 2.82 (dd, *J* = 13.5 Hz, *J* = 5.9 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 142.3, 138.4, 129.7, 128.0, 127.9, 127.1, 126.8, 126.0, 81.4, 44.3; MS *m/z* (EI): 287 (M – CH₂Ph)⁺ (23%), 181 (100), 166 (19), 103 (33), 91 (30), 77 (20).

The major isomer with higher R_f was a colorless solid, mp 131.5–132.4 °C (lit. 129.5–130.5); IR (KBr): 3059, 3028, 2920, 2867, 1494, 1452, 1088, 756, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.24–7.03 (m, 12H), 7.06–7.03 (m, 4H), 6.82–6.80 (m, 4H), 4.21, (dd, *J* = 8.4 Hz, *J* = 5.0 Hz, 2H), 2.95 (dd, *J* = 13.5 Hz, *J* = 8.4

Hz, 2H), 2.77 (dd, $J = 13.5$ Hz, $J = 5.0$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 141.8, 138.6, 129.9, 128.0, 127.8, 127.2, 126.9, 126.0, 79.5, 45.4; MS m/z (EI): 287 ($\text{M} - \text{CH}_2\text{Ph}$) $^+$ (24%), 181 (100).

Bis[1-(4-methoxyphenyl)ethyl] ether³ 2h

Reaction conditions: 1 mmol (152 mg) **1h**, 3 mmol (255 mg) CH_2Cl_2 , 0.03 mmol (8 mg) I_2 , 15 min, 25 °C; column chromatography (SiO_2 , petroleum ether), 129 mg (90%), colorless oil as a mixture of stereoisomers in ratio 1/2.9. Stereoisomers were separated by preparative chromatography (SiO_2 , petroleum ether/*tert*-butyl methyl ether = 96/4). The minor isomer with lower R_f was a colorless oily product: IR (neat): 2970, 2835, 1612, 1513, 1290, 1245, 1175, 1088, 1036, 831 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.19 (d, $J = 8.7$ Hz, 4H), 6.82 (d, $J = 8.7$ Hz, 4H), 4.46 (q, $J = 6.4$ Hz, 2H), 3.79 (s, 6H), 1.43 (d, $J = 6.4$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 158.7, 136.4, 127.4, 113.6, 73.7, 55.2, 22.8; MS m/z (EI): 286 (M^+ , 1%), 135 (100), 105 (15), 91 (17), 57 (20).

The major isomer with higher R_f was an oily product: IR (neat): 2971, 2834, 1611, 1510, 1287, 1244, 1171, 1086, 1036, 831 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.19 (d, $J = 8.7$ Hz, 4H), 6.89 (d, $J = 8.7$, 4H), 4.18 (q, $J = 6.5$ Hz, 2H), 3.82 (s, 6H), 1.34 (d, $J = 6.5$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 158.9, 136.2, 127.5, 113.8, 73.7, 55.2, 24.6; MS m/z (EI): 286 (M^+ , 1%), 135 (100), 105 (15), 91 (15), 57 (20).

Bis[2-phenyl-1-(4-methoxyphenyl)ethyl] ether² 2i

Reaction conditions: 1 mmol (228 mg) **1i**, 3 mmol (255 mg) CH_2Cl_2 , 0.03 mmol (8 mg) I_2 , 1 h, 25 °C; crystallization (petroleum ether/ $\text{CH}_2\text{Cl}_2 = 8/1$), 200 mg (91%), colorless solid, mp 149.2–151.2 °C (lit. 148–149 °C); IR (KBr): 2915, 1609, 1509, 1244, 1072, 1028, 833, 802, 738, 698 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.23–7.19 (m, 6H), 7.05–7.01 (m, 4H), 6.73 (d, $J = 8.8$ Hz, 4H), 6.67 (d, $J = 8.8$ Hz, 4H), 4.15 (dd, $J = 8.2$ Hz, $J = 5.2$ Hz, 2H), 3.78 (s, 6H), 2.93 (dd, $J = 13.6$ Hz, J

= 8.2 Hz, 2H), 2.74 (dd, $J = 13.6$ Hz, $J = 5.2$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 158.7, 138.8, 133.9, 129.9, 128.0, 127.8, 125.9, 113.4, 78.7, 55.1, 45.4; MS m/z (EI): 347 ($\text{M} - \text{CH}_2\text{Ph}$) $^+$ (2%), 211 (100), 91 (12).

Bis(4-methoxybenzyl) ether⁴ 2m

Reaction conditions: 1 mmol (138 mg) **1m**, 3 mmol (255 mg) CH_2Cl_2 , 0.03 mmol (8 mg) I_2 , 200 min, 25 °C; column chromatography (SiO_2 , petroleum ether/ CH_2Cl_2); 67 mg (52%), colorless solid; mp 37.8–38.9 °C (lit. 37–38); IR (KBr): 2843, 1611, 1514, 1458, 1350, 1302, 1248, 1174, 1059, 1028, 995, 835, 813 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.28 (d, $J = 8.7$ Hz, 4H), 6.88 (d, $J = 8.7$ Hz, 4H), 4.46 (s, 4H), 3.81 (s, 6H); MS (EI): 258 (M) $^+$ (18%), 150 (26), 137 (10), 121 (100), 77 (16).

Bis[1-(3-Methoxyphenyl)ethyl] ether⁵ 2q

Reaction conditions: 1 mmol (152 mg) **1q**, 0.03 mmol (8 mg) I_2 , 10 h, 55 °C; column chromatography (SiO_2 , petroleum ether/ CH_2Cl_2); 106 mg (74%), colorless oil as a mixture of isomers in a ratio 1/2.1; IR (neat): 2972, 2929, 2834, 1601, 1486, 1445, 1317, 1279, 1257, 1157, 1094, 1045, 877, 783, 701 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.29–7.08 (m, 4H), 6.86–6.65 (m, 12H), 4.46 (q, $J = 6.4$ Hz, 2H), 4.19 (q, $J = 6.5$ Hz, 2H), 3.80 (s, 3H), 3.72 (s, 3H), 1.43 (d, $J = 6.4$ Hz, 6H), 1.35 (d, $J = 6.5$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 159.8, 159.5, 145.9, 145.9, 129.4, 129.2, 118.7, 118.6, 112.7, 112.7, 111.6, 74.6, 74.5, 55.2, 55.1, 24.7, 23.0; MS (EI): 286 (M) $^+$ (<1%), 136 (100), 121 (15), 105 (20), 91 (20), 77 (23).

Bis[1-(4-Chlorophenyl)ethyl] ether⁶ 2r

Reaction conditions: 1 mmol (157 mg) **1r**, 0.03 mmol (8 mg) I₂, 18 h, 55 °C; column chromatography (SiO₂, petroleum ether); 140 mg (95%), colorless solid as a mixture of isomers *meso/dl* = 1/2.6); mp 54.0–57.0 °C (lit. 67–68.5 (*dl*)); IR (neat): 2977, 2928, 2889, 1595, 1487, 1410, 1371, 1292, 1204, 1090, 1014, 949, 826, 783, 722 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.33–7.10 (m, 16H), 4.42 (q, *J* = 6.4 Hz, 2H), 4.12 (q, *J* = 6.5 Hz, 2H), 1.40 (d, *J* = 6.4 Hz, 6H), 1.31 (*J* = 6.5 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 142.6, 142.4, 133.1, 132.9, 128.7, 128.4, 127.6, 127.5, 74.1, 24.5, 23.1; MS (EI): 294 (M)⁺ (<1%), 139 (100), 103 (25); HRMS: Calcd for C₁₆H₁₆Cl₂O: 294.0578; found: 294.0583.

(*E*)-Stilbene⁷ 3b

Reaction conditions: 2 mmol (397 mg) **1b**, 0.06 mmol (15 mg) I₂, 140 h, 25 °C; column chromatography (SiO₂, petroleum ether); 61 mg (17%) white solid; mp 122.5–124.0 °C (lit. 123–124); IR (neat): 1595, 1491, 1447, 1069, 961, 762, 691 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.56–7.46 (m, 4H), 7.41–7.31 (m, 4H), 7.30–7.20 (m, 2H), 7.11 (s, 2H), MS (EI): 180 (M)⁺ (24%), 165 (29).

(*E*)-1,2-Diphenylpropene⁸ 3c

Reaction conditions: 1 mmol (212 mg) **1c**, 0.03 mmol (8 mg) I₂, 20 h, 25 °C; column chromatography (SiO₂, petroleum ether); 179 mg (92%), colorless solid; mp 75.7–77.5 °C (lit. 78.5–80); IR (neat): 1593, 1487, 1444, 1074, 1022, 918, 866, 756, 739, 697 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.56–7.47 (m, 2H), 7.42–7.32 (m, 6H), 7.32–7.21 (m, 2H), 6.84 (d, *J* = 0.7 Hz, 1H), 2.28 (d, *J* = 0.7 Hz, 3H); MS (EI): 194 (M)⁺ (99%), 179 (100), 165 (27), 115 (30), 103 (15).

1,1-Diphenylethene⁹ 3d

Reaction conditions: 1 mmol (198 mg) **1d**, 0.03 mmol (8 mg) I₂, 10 min, 55 °C; column chromatography (SiO₂, petroleum ether); 169 mg (94%), colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.39–7.27 (m, 10H), 5.46 (s, 2H); IR (neat): 3080, 3056, 3025, 1607, 1572, 1491, 1444, 1328, 1027, 899, 773, 698 cm⁻¹.

1,1-Diphenylpropene⁹ 3e

Reaction conditions: 1 mmol (212 mg) **1e**, 0.03 mmol (8 mg) I₂, 3 h, 55 °C; column chromatography (SiO₂, petroleum ether); 179 mg (92%), colorless solid; mp 47.7–48.5 °C (lit. 49–50); IR (neat): 3055, 3023, 2910, 2855, 1597, 1494, 1441, 1355, 1073, 1032, 840, 757, 699, 631 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.42–7.12 (m, 10H), 6.17 (q, *J* = 7.0 Hz, 1H), 1.76 (d, *J* = 7 Hz, 3H); MS (EI): 194 (M)⁺ (100%), 179 (30), 178 (29), 115 (29).

2-Bromo-1,1-diphenylethene¹⁰ 3f

Reaction conditions: 1 mmol (277 mg) **1f**, 0.03 mmol (8 mg) I₂, 96 h, 55 °C; column chromatography (SiO₂, petroleum ether); 233 mg (90%), colorless solid; mp 40.1–40.5 °C (lit. 41–42); IR (neat): 3057, 3023, 1589, 1493, 1442, 1326, 1218, 1075, 1030, 933, 763, 739, 696, 611 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.47–7.14 (m, 10H), 6.77 (s, 1H); MS (EI): 258 (M)⁺ (55), 179 (100), 178 (90), 152 (17), 151 (18), 89 (19), 76 (21).

2-Fluoro-1,1-diphenylethene¹¹ 3g

Reaction conditions: 1 mmol (216 mg) **1g**, 0.03 mmol (8 mg) I₂, 192 h, 55 °C; column chromatography (SiO₂, petroleum ether); 105 mg (53%), colorless oil; IR (neat): 3081, 3057, 3025, 1637, 1495, 1443, 1177, 1088, 1030, 932, 827, 763, 729, 696, 655 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.35–7.17 (m, 10H), 6.92 (d, *J* = 83.3 Hz, 1H).

(E)-4-Methoxystilbene¹² 3i

Reaction conditions: 1 mmol (228 mg) **1i**, 0.03 mmol (8 mg) I₂, 230 min, 25 °C; column chromatography (SiO₂, petroleum ether); 42 mg (20%), colorless solid; mp 132.5–133.4 °C (lit. 134–136); IR (neat): 1599, 1510, 1250, 1179, 1031, 964, 813, 750, 689, 538 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.49–7.36 (m, 4H), 7.34–7.25 (m, 2H), 7.22–7.14 (m, 1H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 16.3 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H); MS (EI): 210 (M)⁺ (100%), 195 (17), 165 (23), 152 (15).

1-(4-Methoxyphenyl)-1-phenylethene¹² 3j

Reaction conditions: 1 mmol (228 mg) **1j**, 0.03 mmol (8 mg) I₂, 5 min, 25 °C; column chromatography (SiO₂, hexane); 185 mg (88%), colorless solid; mp 72.6–73.5 °C (lit. 73–75); IR (neat): 2952, 2833, 1603, 1506, 1290, 1248, 1179, 1026, 901, 839, 781, 704 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.37–7.23 (m, 7H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.40 (d, *J* = 1.1 Hz, 1H), 5.35 (d, *J* = 1.1 Hz, 1H), 3.83 (s, 3H); MS (EI): 210 (M)⁺ (100%), 195 (40), 165 (26), 152 (18).

1-(2-Methoxyphenyl)-1-phenylethene¹³ 3k

Reaction conditions: 1 mmol (228 mg) **1k**, 0.03 mmol (8 mg) I₂, 15 min, 25 °C; column chromatography (SiO₂, hexane); 189 mg (90%), colorless oil; IR (neat): 3056, 3024, 2951, 2834, 1598, 1490, 1460, 1267, 1242, 1181, 1111, 1027, 902, 780, 754, 706 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.37–7.19 (m, 7H), 7.02–6.94 (m, 1H), 6.94–6.87 (m, 1H), 5.72 (d, *J* = 1.4 Hz, 1H), 5.32 (d, *J* = 1.4 Hz, 1H), 3.63 (s, 3H); MS (EI): 210 (M)⁺ (40%), 195 (100), 167 (82), 152 (25).

1,1-Bis-(4-Methoxyphenyl)-2-phenylethene¹⁴ 3l

Reaction conditions: 1 mmol (334 mg) **1l**, 3 mmol (255 mg) CH₂Cl₂, 0.03 mmol (8 mg) I₂, 200 min, 25 °C; column chromatography (SiO₂, hexane); 282 mg (89%), viscous colorless oil; IR (neat): 3000, 2954, 2834, 1601, 1505, 1244, 1173, 1033, 832, 754, 696 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.27–7.24 (m, 2H),

7.13–7.03 (m, 7H), 6.86–6.83 (m, 5H), 3.83 (s, 3H), 3.81 (s, 3H); MS m/z (EI): 316 (M^+ , 100%), 224 (16), 210 (36), 195 (88), 167 (72), 166 (69), 152 (21), 128 (15), 91 (16), 84 (50).

(*E*)-2-(4-Methoxyphenyl)-1-phenyl-1-propene¹⁵ 3na

Reaction conditions: 1 mmol (242 mg) **1n**, 0.03 mmol (8 mg) I_2 , 0.5 h, 25 °C; column chromatography (SiO_2 , petroleum ether); 70 mg (31%), colorless solid; mp 100.6–101.4 °C (lit. 95–98); IR (neat): 2951, 2913, 2835, 1601, 1510, 1441, 1383, 1254, 1179, 1119, 1026, 918, 870, 827, 754, 719, 696, 615 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 7.47 (d, J = 8.8 Hz, 2H), 7.39–7.17 (m, 5H), 6.91 (d, J = 8.8 Hz, 2H), 6.78 (q, J = 1.2 Hz, 1H), 3.84 (s, 3H), 2.25 (d, J = 1.2 Hz, 3H); MS (EI): 224 (M^+) (100%), 209 (18), 165 (22).

2-(4-Methoxyphenyl)-3-phenyl-1-propene¹⁵ 3nb

Reaction conditions: 1 mmol (242 mg) **1n**, 3 mmol (180 mg) *i*-PrOH, 0.03 mmol (8 mg) I_2 , 0.5 h, 25 °C; preparative chromatography (Al_2O_3 , hexane); 36 mg (16%), colorless solid; mp 45.0–46.3 °C; IR (neat): 3027, 2835, 1606, 1512, 1248, 1180, 1033, 893, 835, 714, 700 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, J = 8.8 Hz, 2H), 7.26–7.23 (m, 5H), 6.81 (d, J = 8.8 Hz, 2H), 5.42 (d, J = 1.2 Hz, 1H), 4.94 (d, J = 1.2 Hz, 1H), 3.81 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 146.1, 139.7, 133.2, 128.8, 128.3, 127.2, 126.0, 113.6, 112.9, 55.2, 41.7; MS m/z (EI): 224 (M^+ , 53%), 133 (100).

9-Ethyl-9*H*-xanthen-9-ol¹⁶ 4e

Reaction conditions: 20 mmol (3.92 g) **11a**, 120 mmol (2.76 g) Na, 60 mmol (9.36 g) EtI, 40 mL toluene, 1 h, reflux; column chromatography (basic Al_2O_3 , petroleum ether), white solid (70%), mp 94.2–96.0 °C (lit. 96–97 °C); IR (KBr): 3300, 2965, 1603, 1576, 1476, 1448, 1321, 1263,

1237, 1055, 1011, 903, 754 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.67–7.64 (m, 2H), 7.32–7.25 (m, 2H), 7.18–7.08 (m, 4H), 2.44 (s, 1H), 2.00 (q, $J = 7.5$ Hz, 2H), 0.48 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 150.4, 128.7, 126.5, 126.4, 123.4, 115.9, 70.0, 39.4, 8.5; MS m/z (EI): 225 ($\text{M}^+ - \text{H}$, 1%), 197 (100).

9-Ethylidene-9H-fluorene¹⁷ 5a

Reaction conditions: 1 mmol (210 mg) **4a**, 3 mmol (255 mg) CH_2Cl_2 , 0.03 mmol (8 mg) I_2 , 23 h, 25 $^\circ\text{C}$; column chromatography (SiO_2 , petroleum ether); 181 mg (94%), colorless solid; mp 102.8–103.6 $^\circ\text{C}$ (lit. 102–104 $^\circ\text{C}$); IR (neat): 1645, 1441, 1346, 1290, 1154, 934, 830, 775, 727, 617 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.93–7.83 (m, 1H), 7.78–7.72 (m, 1H), 7.72–7.67 (m, 1H), 7.67–7.59 (m, 1H), 7.40–7.20 (m, 4H), 6.84 (q, $J = 7.6$ Hz, 1H), 2.39 (d, $J = 7.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 140.7, 139.3, 138.5, 137.7, 136.6, 127.6, 127.3, 126.8, 126.8, 125.0, 124.8, 119.8, 119.6, 119.4, 15.3; MS (EI): 192 (M^+) (100%), 165 (35).

5-Ethylidene-10,11-dihydro-5H-dibenzo[a,d]cycloheptene¹⁸ 5c

Reaction conditions: 1 mmol (238 mg) **4c**, 3 mmol (255 mg) CH_2Cl_2 , 0.03 mmol (8 mg) I_2 , 2.5 h, 25 $^\circ\text{C}$; column chromatography (SiO_2 , petroleum ether); 205 mg (93%), colorless viscous oil; IR (neat): 3060, 3016, 2913, 2855, 1483, 1441, 1358, 1161, 942, 887, 840, 750, 633 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.30–7.23 (m, 1H), 7.23–7.08 (m, 6H), 7.07–6.99 (m, 1H), 5.94 (q, $J = 7.0$ Hz, 1H), 3.72–2.49 (m, 4H), 1.74 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.1, 141.7, 139.9, 139.4, 137.1, 129.8, 128.6, 128.5, 128.1, 127.2, 126.9, 126.0, 126.0, 125.6, 33.7, 32.1, 15.3; MS (EI): 220 (M^+) (100%), 205 (70), 191 (20), 178 (21).

5-Benzylidene-10,11-dihydro-5H-dibenzo[a,d]cycloheptene¹⁹ 5d

Reaction conditions: 1 mmol (300 mg) **4d**, 3 mmol (255 mg) CH₂Cl₂, 0.03 mmol (8 mg) I₂, 2.5 h, 25 °C; column chromatography (SiO₂, petroleum ether), 257 mg (91%), colorless solid, mp 83.5–84.7 °C (lit. 85–87 °C); IR (KBr): 2876, 1485, 1442, 1356, 1261, 1155, 1027, 912, 869, 758, 692 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.49–7.46 (m, 1H), 7.27–7.00 (m, 12H), 6.78 (s, 1H), 3.82–2.44 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 143.7, 141.7, 140.4, 139.0, 137.6, 137.2, 130.1, 129.8, 129.2, 128.3, 128.2, 127.9, 127.9, 127.7, 127.3, 126.6, 126.4, 126.1, 33.5, 32.1; MS *m/z* (EI): 282 (M⁺, 100%), 267 (20), 191 (35), 69 (28), 57 (31).

9-Ethylidene-9H-xanthene²⁰ 5e

Reaction conditions: 1 mmol (226 mg) **4e**, 3 mmol (255 mg) CH₂Cl₂, 0.03 mmol (8 mg) I₂, 1 h, 25 °C; decomposition on SiO₂ and on Al₂O₃, 204 mg (98%), yellow oil; IR (neat): 3035, 2940, 2858, 1599, 1478, 1450, 1303, 1258, 1210, 814, 760 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.57–7.54 (m, 1H), 7.48–7.45 (m, 1H), 7.27–7.02 (m, 6H), 6.00 (q, *J* = 7.5 Hz, 1H), 2.13 (d, *J* = 7.5 Hz, 3H); MS *m/z* (EI): 207 (M⁺ – 1, 100%), 89 (21), 76 (40).

9-Benzylidene-9H-xanthene²¹ 5f

Reaction conditions: 1 mmol (288 mg) **4f**, 3 mmol (255 mg) CH₂Cl₂, 0.03 mmol (8 mg) I₂, 30 min, 25 °C; column chromatography (SiO₂, hexane), 259 mg (96%), yellow solid, mp 112.0–114.0 °C (lit. 108–110 °C); IR (neat): 3058, 1620, 1593, 1476, 1451, 1252, 1207, 1140, 1101, 940, 835, 755, 695 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.80–7.71 (m, 1H), 7.40–7.11 (m, 11H), 6.94 (s, 1H), 6.84–6.75 (m, 1H); MS (EI): 270 (M⁺) (100%), 239 (16), 134 (15).

1-(4-Methoxyphenyl)-1-methoxyethane²² 6ha

Reaction conditions: 1 mmol (152 mg) **1h**, 3 mmol (96 mg) MeOH, 0.03 mmol (8 mg) I₂, 3 h, 25 °C; column chromatography (SiO₂, petroleum ether), 145 mg (87%), colorless oil; IR (neat): 2975, 2931, 2836, 2819, 1612, 1512, 1444, 1371, 1288, 1247, 1174, 1106, 1084, 1037, 832, 809 cm⁻¹; ¹H NMR (300 MHz,

CDCl₃): δ 7.23 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.25 (q, J = 6.4 Hz, 1H), 3.81 (s, 3H), 3.20 (s, 3H), 1.42 (d, J = 6.4 Hz, 3H); MS (EI): 166 (M)⁺ (11%), 151 (100), 135 (36).

1-(4-Methoxyphenyl)ethyl ethyl ether²³ 6hb

Reaction conditions: 1 mmol (152 mg) **1h**, 3 mmol (138 mg) EtOH, 0.03 mmol (8 mg) I₂, 25 h, 25 °C; column chromatography (SiO₂, petroleum ether), 137 mg (76%), colorless oil; IR (neat): 2974, 2930, 1612, 1512, 1300, 1287, 1245, 1174, 1098, 1037, 832, 810 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.24 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.36 (q, J = 6.5 Hz, 1H), 3.80 (s, 3H), 3.33 (q, J = 7.0 Hz, 2H), 1.42 (d, J = 6.5 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H); MS (EI): 180 (M)⁺ (17%), 165 (100), 137 (75), 135 (54), 109 (25), 105 (15), 77 (15).

1-(1-Isopropoxyethyl)-4-methoxybenzene²⁴ 6hc

Reaction conditions: 1 mmol (152 mg) **1h**, 3 mmol (180 mg) *i*-PrOH, 0.03 mmol (8 mg) I₂, 25 h, 25 °C; column chromatography (SiO₂, petroleum ether), 105 mg (54%), colorless oil; IR (neat): 2972, 2930, 2835, 1613, 1511, 1464, 1368, 1245, 1173, 1088, 1038, 832 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.24 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz), 4.48 (q, J = 6.5 Hz, 1H), 3.80 (s, 3H), 3.47 (septet, J = 6.1 Hz, 1H), 1.39 (d, J = 6.5 Hz, 3H), 1.14 (d, J = 6.1 Hz, 3H), 1.08 (d, J = 6.1 Hz, 3H); MS (EI): 194 (M)⁺ (10%), 179 (39), 137 (100), 135 (43), 109 (16).

1-(4-Methoxyphenyl)ethyl trifluoroethyl ether²⁵ 6hd

Reaction conditions: 1 mmol (152 mg) **1h**, 3 mmol (300 mg) CF₃CH₂OH, 0.03 mmol (8 mg) I₂, 2.5 h, 25 °C; column chromatography (SiO₂, petroleum ether), 199 mg (85%), colorless oil (85%); IR (neat): 2980, 2936, 2839, 1613, 1514, 1279, 1247, 1173, 1037, 967, 833 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.24 (d, J =

8.7 Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 2H), 4.53 (q, $J = 6.4$ Hz, 1H), 3.81 (s, 3H), 3.71–3.53 (m, 2H), 1.48 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 159.5, 133.7, 127.6, 124.2 (q, $J = 279$ Hz), 114.1, 79.0, 65.5 (q, $J = 34$ Hz), 55.3, 23.7; MS m/z (EI): 234 (M^+ , 28%), 219 (100), 135 (71).

1-(4-Methoxyphenyl)ethyl acetate²⁶ 6he

Reaction conditions: 1 mmol (152 mg) **1h**, 3 mmol (180 mg) acetic acid, 0.03 mmol (8 mg) I_2 , 6 h, 25 °C; column chromatography (SiO_2 , petroleum ether/ CH_2Cl_2), 113 mg (58%), colorless oil; IR (neat): 2979, 2935, 2837, 1736, 1613, 1514, 1459, 1371, 1296, 1241, 1177, 1061, 1034, 944, 831 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.29 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 5.85 (q, $J = 6.6$ Hz, 1H), 3.80 (s, 3H), 2.04 (s, 3H), 1.52 (d, $J = 6.8$ Hz, 3H); MS (EI): 194 (M^+) (27%), 135 (100), 121 (21), 91 (20), 77 (17).

1-Methoxy-1-(4-methoxyphenyl)-2-phenylethane²⁷ 6ia

Reaction conditions: 1 mmol (228 mg) **1i**, 3 mmol (96 mg) MeOH, 0.03 mmol (8 mg) I_2 , 20 h, 25 °C; column chromatography (SiO_2 , petroleum ether), 199 mg (82%), colorless solid, mp 46.5–47.1 °C (lit. 46–47 °C); IR (neat): 3028, 2932, 1611, 1511, 1454, 1300, 1247, 1173, 1097, 1034, 831, 737, 699 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.20–6.95 (m, 7H), 6.77 (d, $J = 8.7$ Hz, 2H), 4.18 (dd, $J = 7.2$ Hz, $J = 6.1$ Hz, 1H), 3.78 (s, 3H), 3.12 (s, 3H), 3.05 (dd, $J = 13.6$ Hz, $J = 7.2$ Hz, 1H), 2.79 (dd, $J = 13.6$ Hz, $J = 6.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 159.0, 138.5, 133.6, 129.4, 128.0, 128.0, 126.0, 113.6, 84.6, 56.5, 55.2, 44.7; MS (EI): 241 ($\text{M} - 1$)⁺ (<1%), 227 (<1), 211 (3), 151 (100), 135 (16), 91 (10).

4-Methoxybenzyl methyl ether²⁸ 6ma

Reaction conditions: 1 mmol (138 mg) **1m**, 3 mmol (96 mg) MeOH, 0.03 mmol (8 mg) I₂, 8 h, 55 °C; column chromatography (SiO₂, petroleum ether), 140 mg (92%), colorless oil; IR (neat): 2932, 2836, 1612, 1513, 1462, 1381, 1302, 1248, 1174, 1097, 1035, 819 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.39 (s, 2H), 3.81 (s, 3H), 3.36 (s, 3H); MS (EI): 152 (M)⁺ (30%), 121 (100), 77 (15).

Ethyl 4-methoxybenzyl ether²⁹ 6mb

Reaction conditions: 1 mmol (138 mg) **1m**, 3 mmol (138 mg) EtOH, 0.03 mmol (8 mg) I₂, 8 h, 55 °C; column chromatography (SiO₂, petroleum ether), 145 mg (87%), colorless oil; IR (neat): 2974, 2934, 2863, 2838, 1612, 1512, 1462, 1373, 1352, 1302, 1248, 1173, 1097, 1036, 822 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.51 (q, *J* = 7.0 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H); MS (EI): 166 (M)⁺ (27%), 121 (100), 77 (15).

1-Isopropoxymethyl-4-methoxybenzene³⁰ 6mc

Reaction conditions: 1 mmol (138 mg) **1m**, 3 mmol (180 mg) *i*-PrOH, 0.03 mmol (8 mg) I₂, 8 h, 55 °C; column chromatography (SiO₂, petroleum ether), 121 mg (67%), colorless oil; IR (neat): 2971, 1612, 1512, 1300, 1464, 1248, 1172, 1126, 1037, 820 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.66 (septet, *J* = 6.1 Hz, 1H), 1.20 (d, *J* = 6.1 Hz, 6H); MS *m/z* (EI): 180 (M⁺, 21%), 137 (18), 121 (100), 109 (18).

1-(4-Methoxyphenyl)ethyl formate³¹ 7ha

Reaction conditions: 1 mmol (152 mg) **1h**, 3 mmol (138 mg) formic acid, 0.03 mmol (8 mg) I₂, 30 min, 25 °C; column chromatography (SiO₂, petroleum ether), 142 mg (79%), colorless oil; IR (neat): 2981, 2934, 2837, 1721, 1612, 1514, 1459, 1249, 1171, 1034, 831 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.06 (s,

1H), 7.31 (d, $J = 8.7$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 5.98 (q, $J = 6.6$ Hz, 1H), 3.81 (s, 3H), 1.57 (d, $J = 6.6$ Hz, 3H); MS m/z (EI): 180 (M^+ , 30%), 135 (100), 134 (46), 121 (25), 119 (15), 105 (21), 91 (18), 77 (15); HRMS: Calcd for $C_{10}H_{12}O_3$ 180.0786; found 180.0791.

Bis(4-methoxyphenyl)methane³² 8

Reaction conditions: 1 mmol (138 mg) **1m**, 3 mmol (255 mg) CH_2Cl_2 , 0.03 mmol (8 mg) I_2 , 200 min, 25 °C; column chromatography (SiO_2 , petroleum ether), 15 mg (13%), white solid, mp 48.0–49.2 °C (lit. 51–52 °C); IR (neat): 2959, 2906, 2837, 1609, 1584, 1457, 1509, 1298, 1246, 1176, 1105, 1027, 809 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 7.07 (d, $J = 8.7$ Hz, 4H), 6.81 (d, $J = 8.7$ Hz, 4H), 3.86 (s, 2H), 3.77 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.9, 133.7, 129.7, 113.9, 55.3, 40.1; MS (EI): 228 (M^+) (100%), 197 (68), 121 (33).

9H-Xanthene-9-on³³ 11a

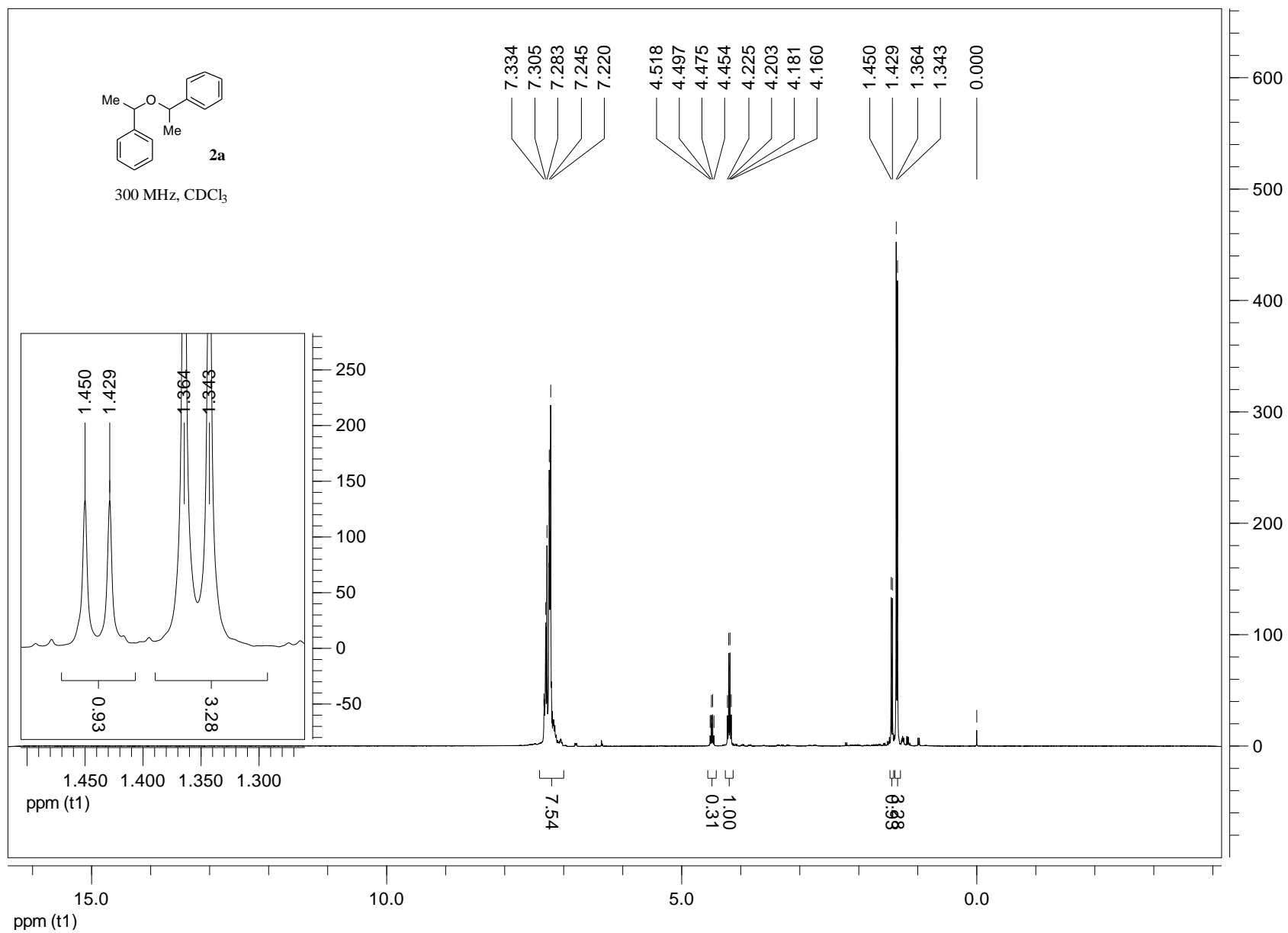
Reaction conditions: 1 mmol (198 mg) **10**, 0.03 mmol (8 mg) I_2 , 15 min, 25 °C; column chromatography (SiO_2 , petroleum ether), 82 mg (84%), white solid, mp 174.9–175.4 °C (lit. 172–174 °C); IR (neat): 1656, 1607, 1456, 1332, 1236, 1210, 1146, 1097, 1023, 930, 880, 804, 759, 667, 623 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 8.39–8.26 (m, 2H), 7.75–7.63 (m, 2H), 7.51–7.42 (m, 2H), 7.41–7.31 (m, 2H);

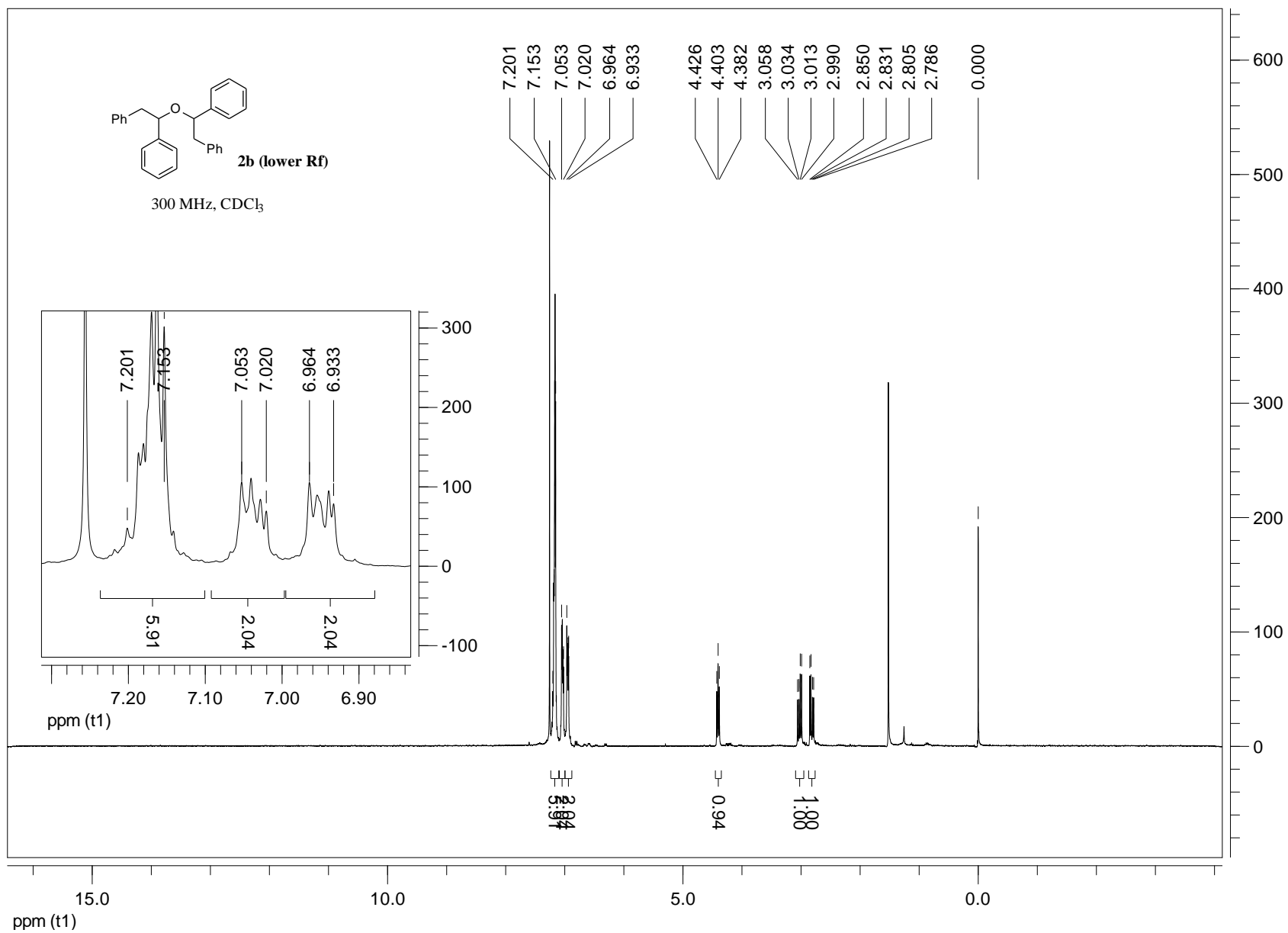
9H-Xanthene³³ 11b

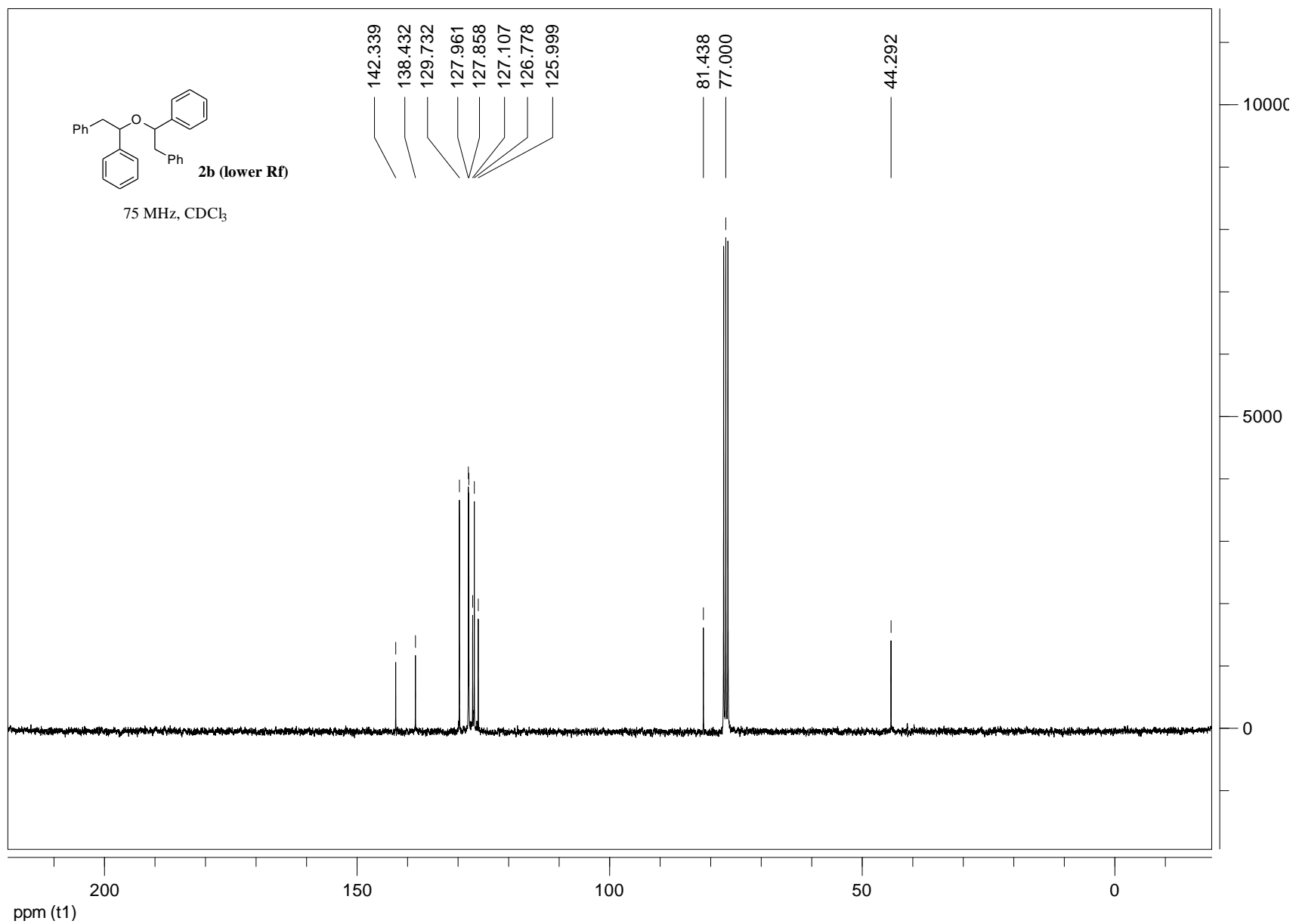
Reaction conditions: 1 mmol (198 mg) **10**, 0.03 mmol (8 mg) I_2 , 15 min, 25 °C; column chromatography (SiO_2 , petroleum ether), 89 mg (98%), colorless solid, mp 100.8–101.4 °C (lit. 101–102 °C); IR (neat): 1598, 1574, 1483, 1454, 1302, 1265, 1213, 1187, 1115, 1090, 1030, 966, 925, 891, 860, 747, 694 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 7.20–7.07 (m, 4H), 7.04–6.93 (m, 4H), 4.05 (s, 2H).

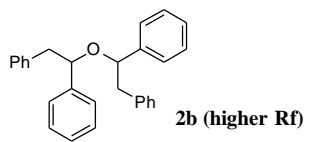
9-Methoxy-9*H*-xanthene³⁴ 11c

Reaction conditions: 1 mmol (198 mg) **10**, 3 mmol (96 mg) MeOH, 0.03 mmol (8 mg) I₂, 5 min, 25 °C; decomposition on SiO₂ and on Al₂O₃, 180 mg (85%), colorless oil; IR (neat): 3043, 2933, 2816, 1605, 1576, 1479, 1459, 1256, 1061, 904, 753 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.49–7.46 (m, 2H), 7.34–7.29 (m, 2H), 7.14–7.10 (m, 4H), 5.74 (s, 1H), 2.86 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 152.5, 130.0, 129.6, 123.2, 119.6, 116.6, 70.8, 51.5; MS *m/z* (EI): 211 (M⁺ – H, 20%), 196 (18), 181 (100), 152 (16).



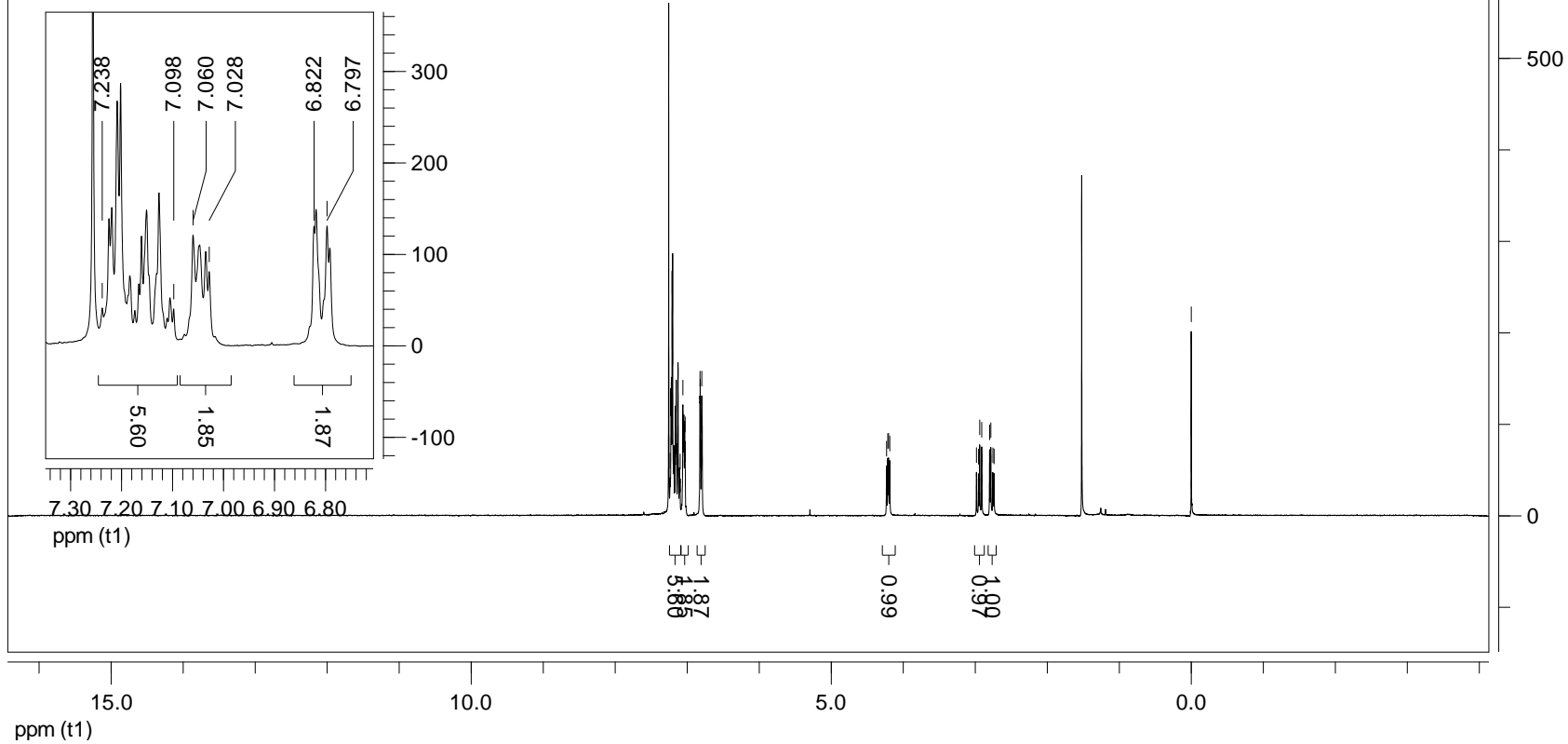


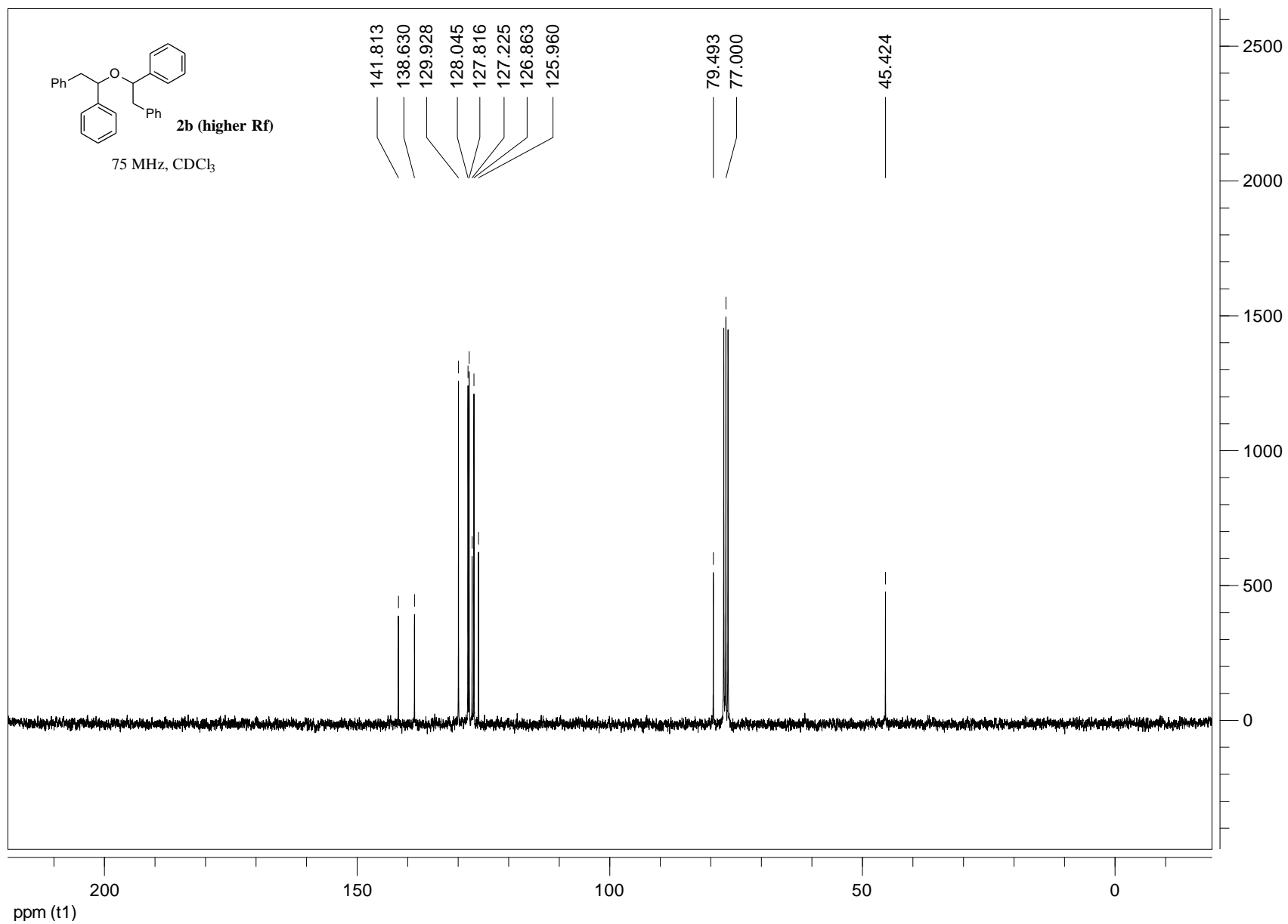


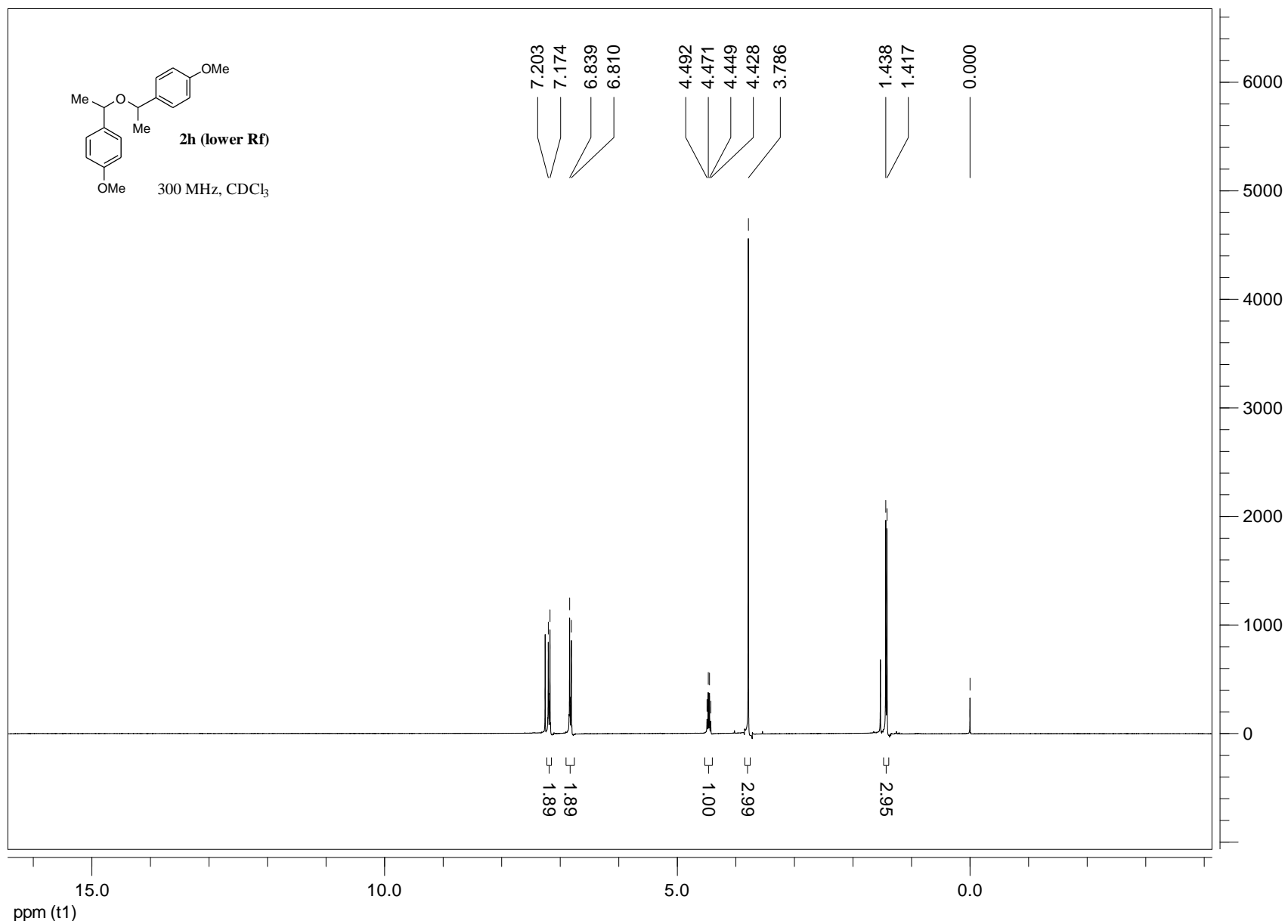


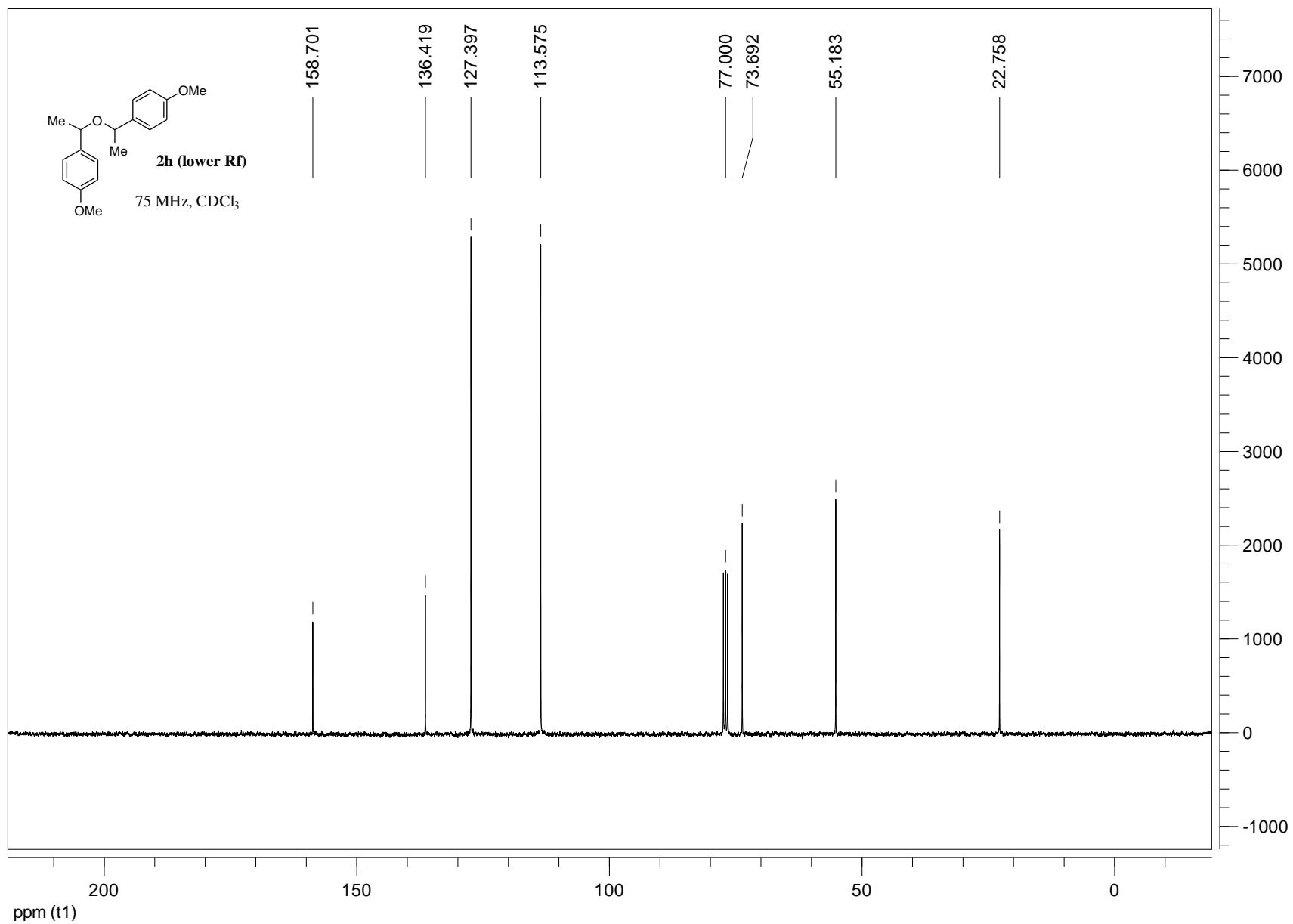
300 MHz, CDCl₃

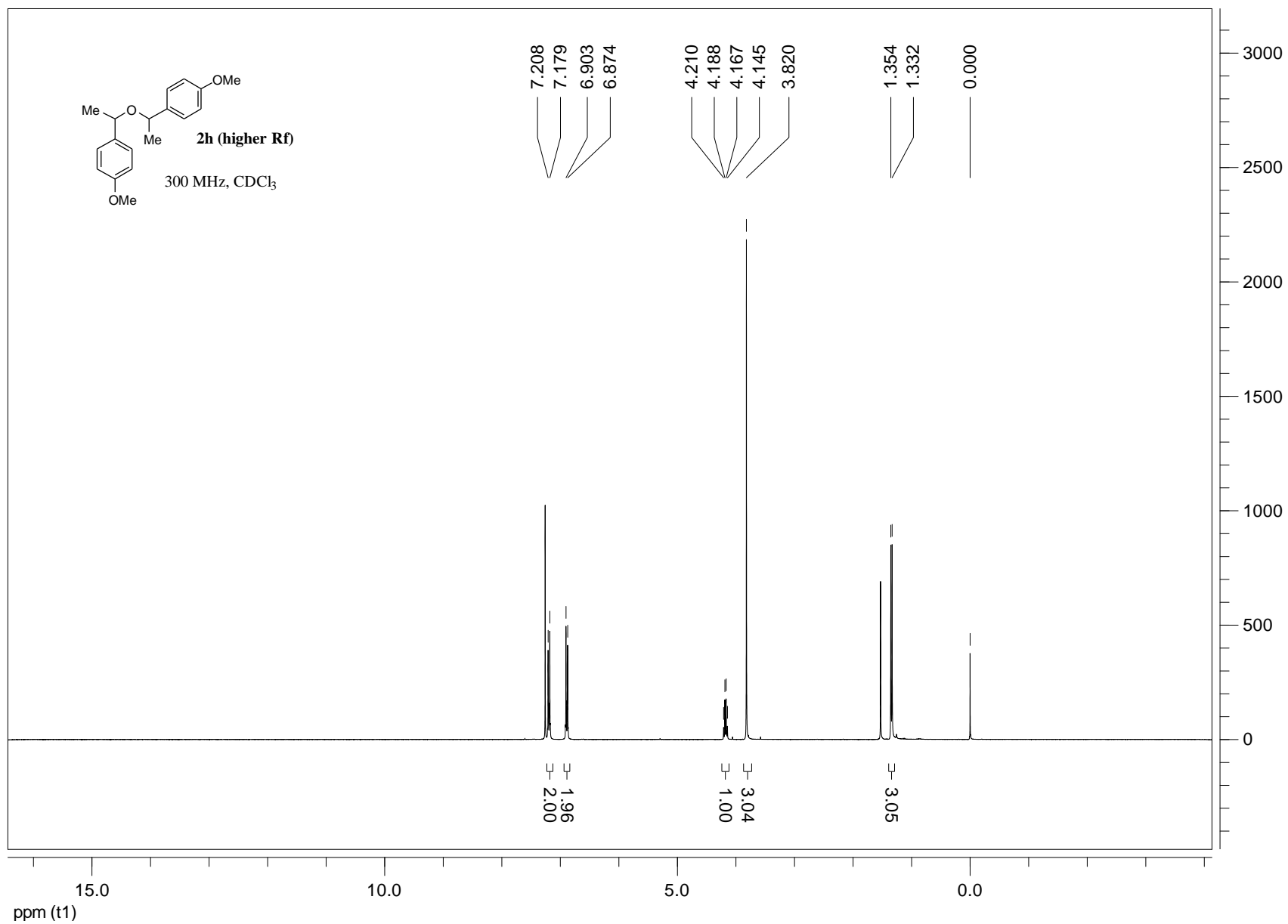
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 4.231
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 2.738
 0.000

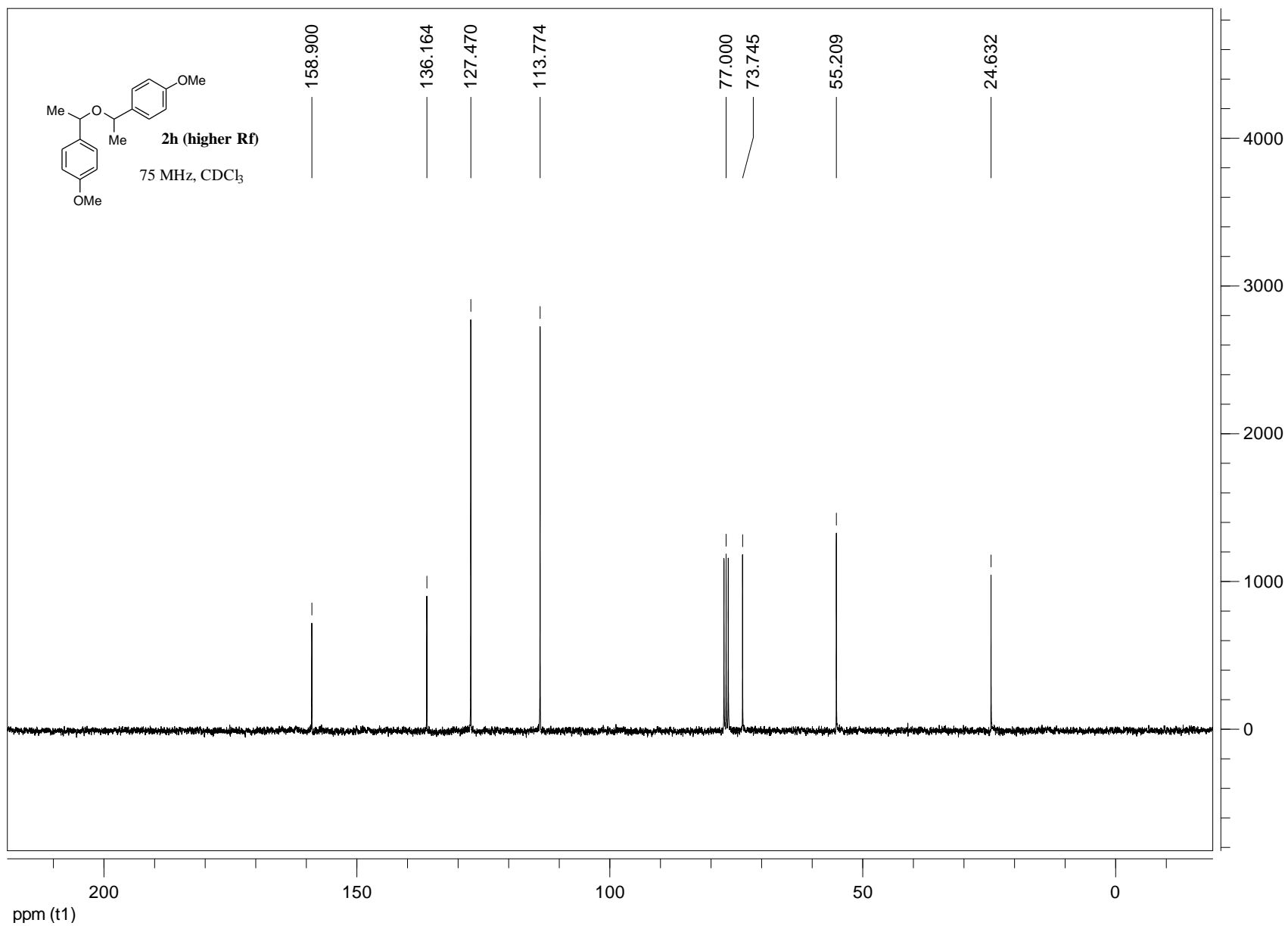


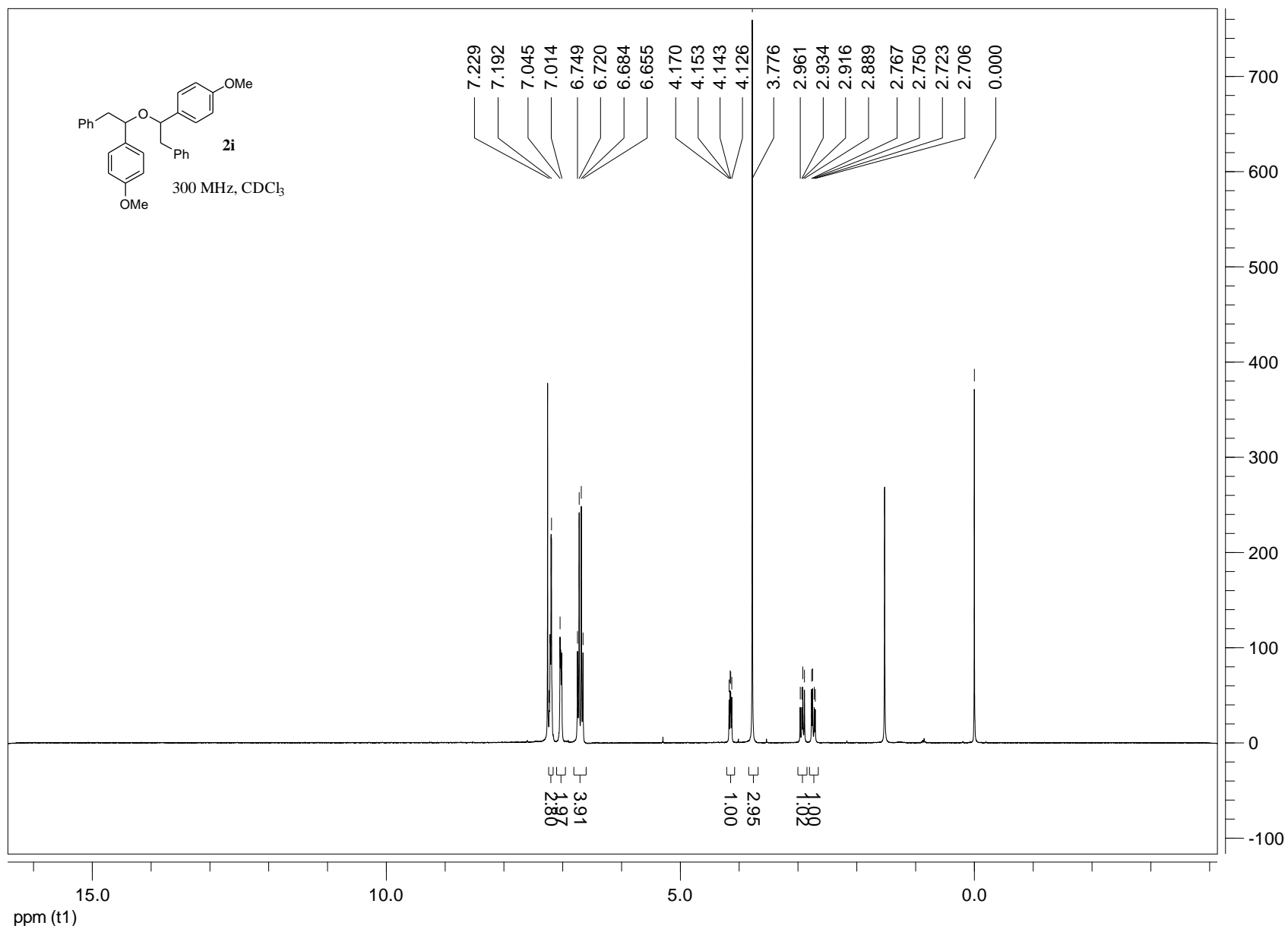


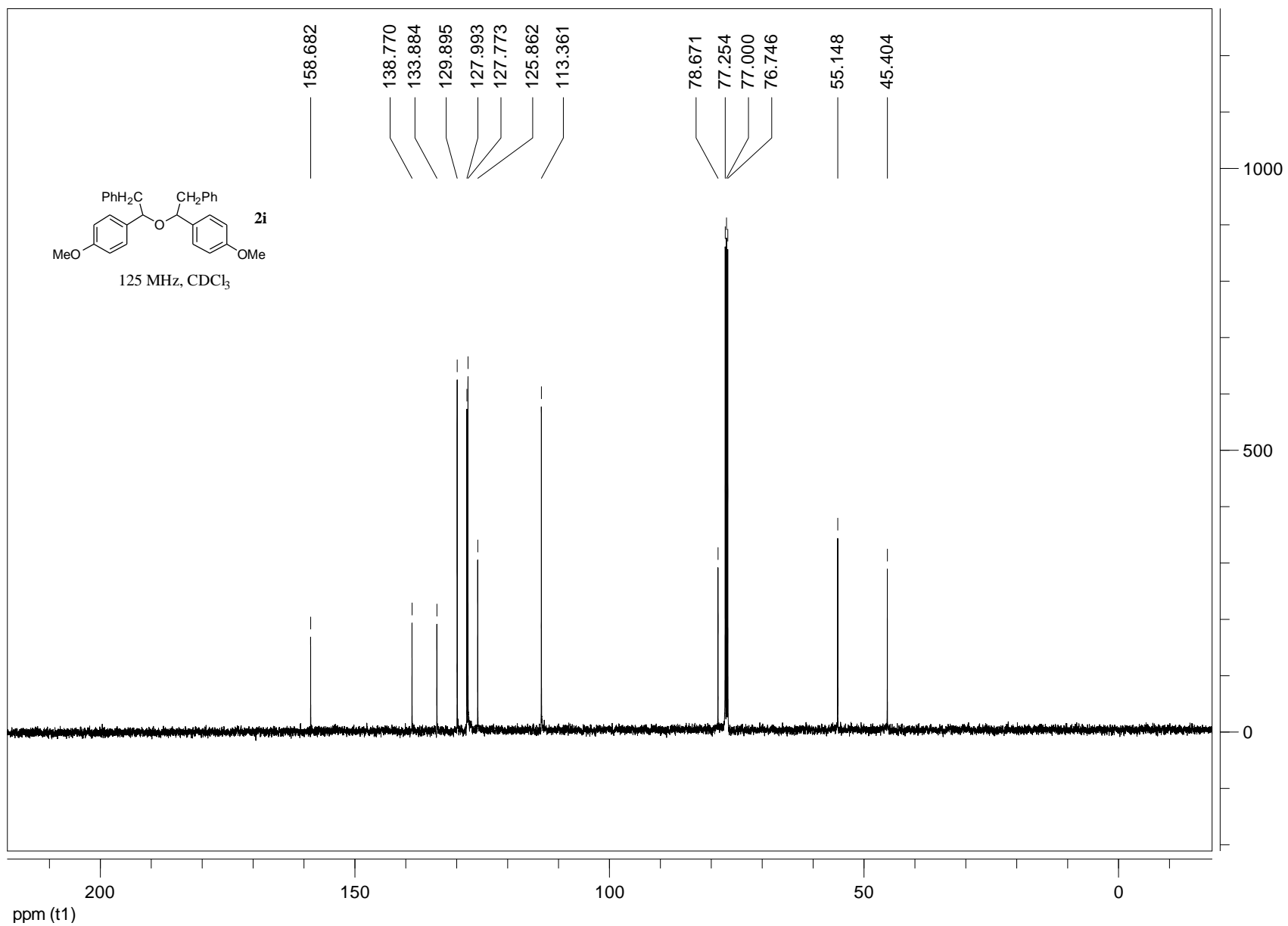


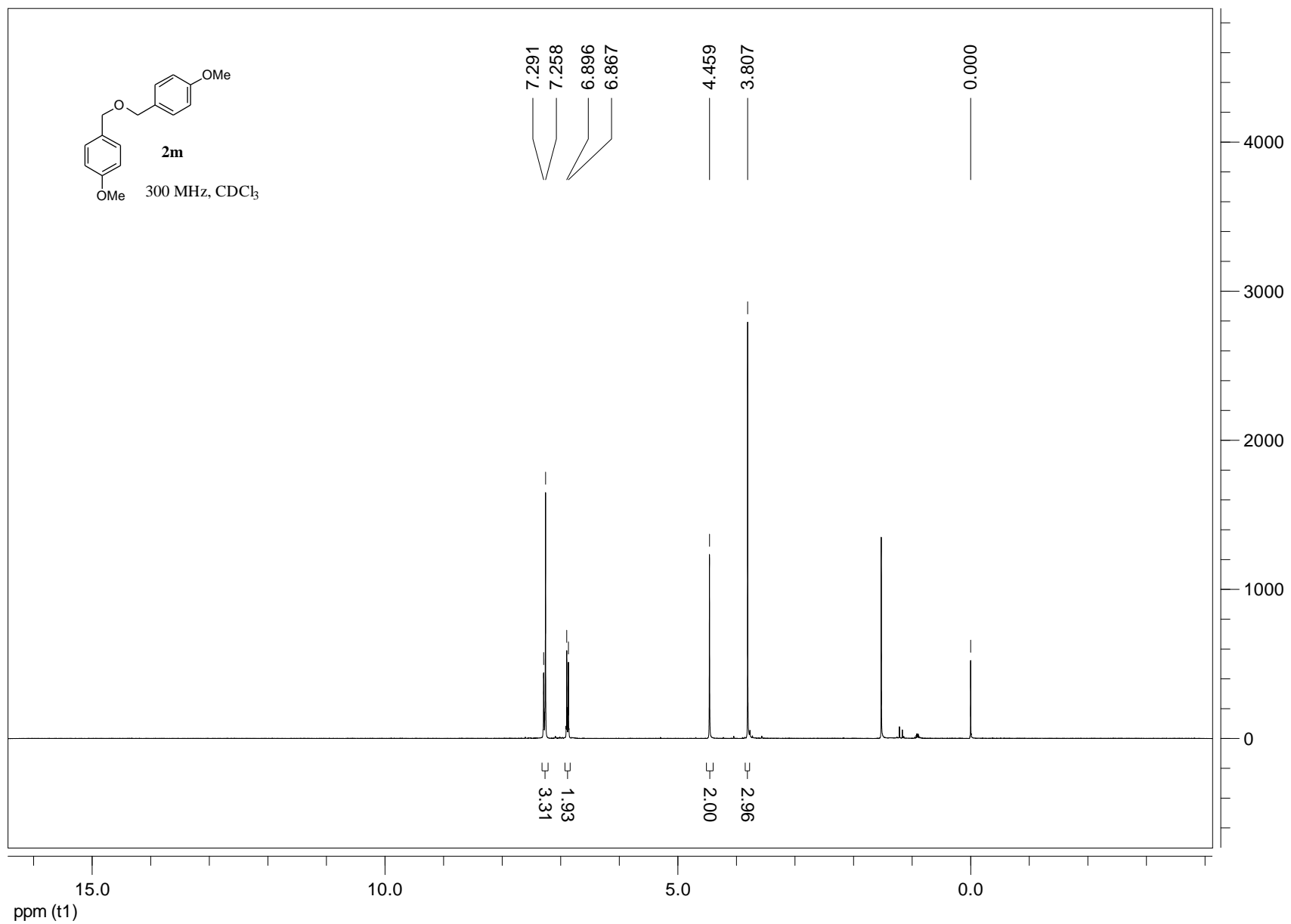


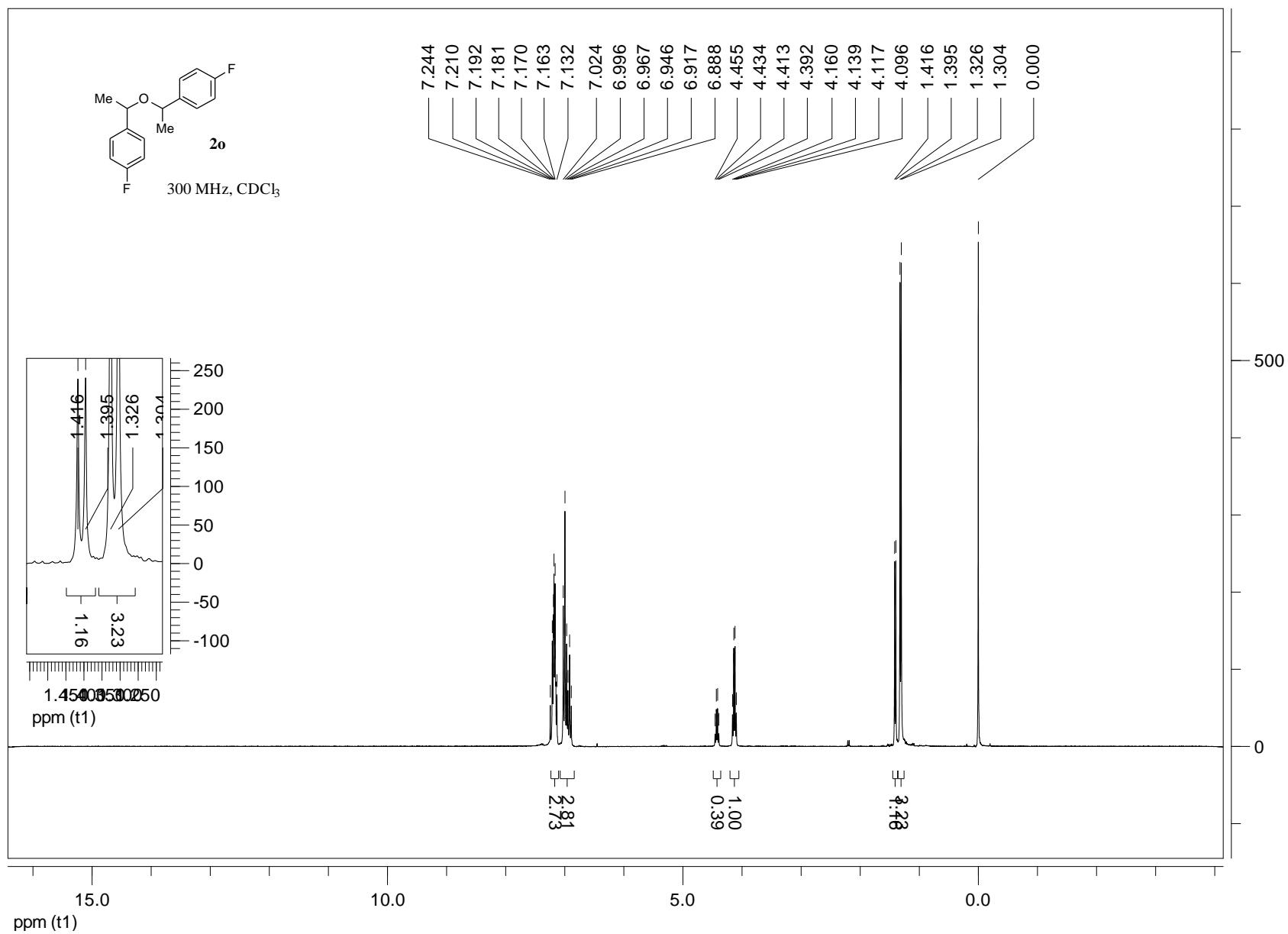


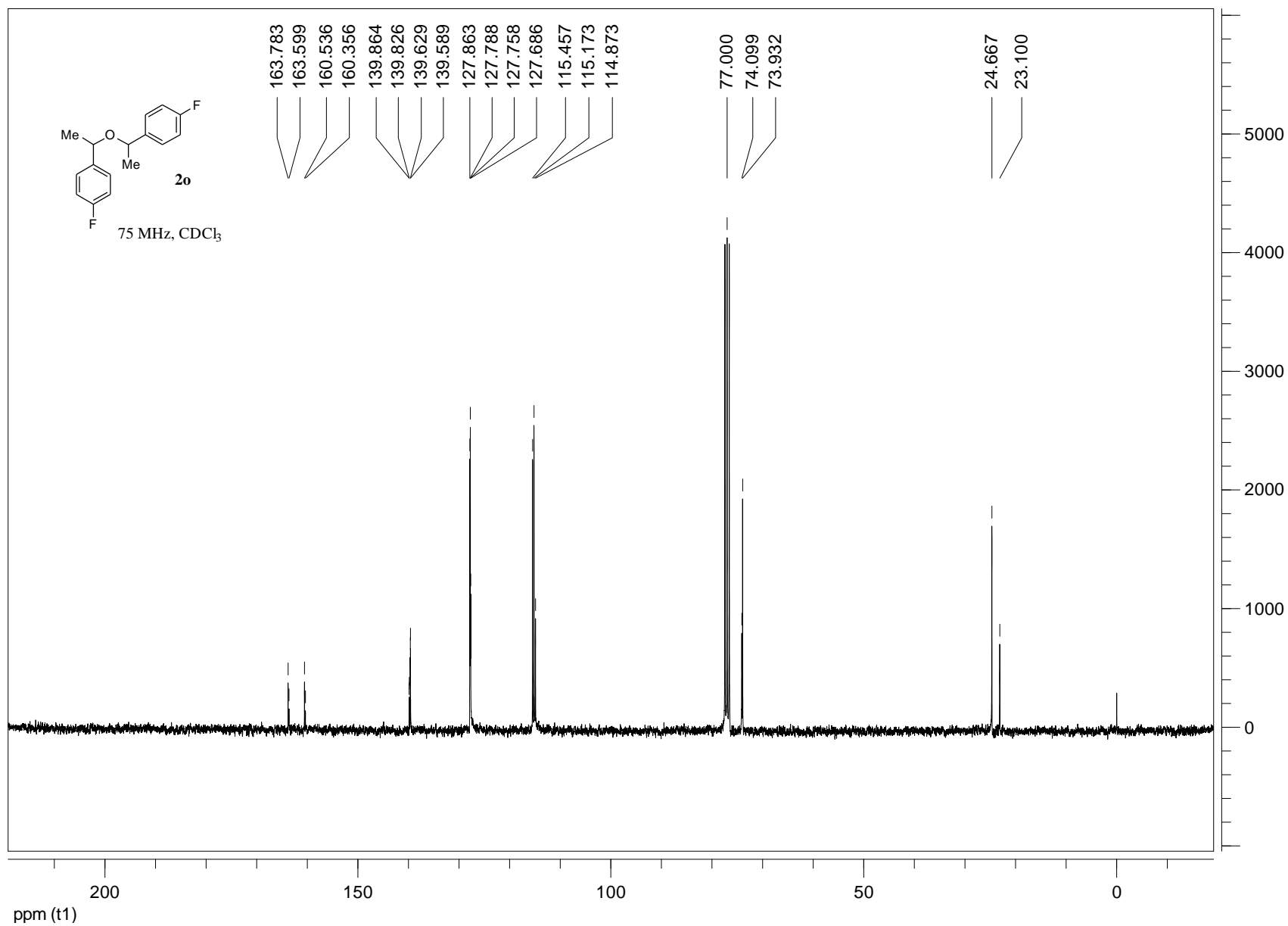


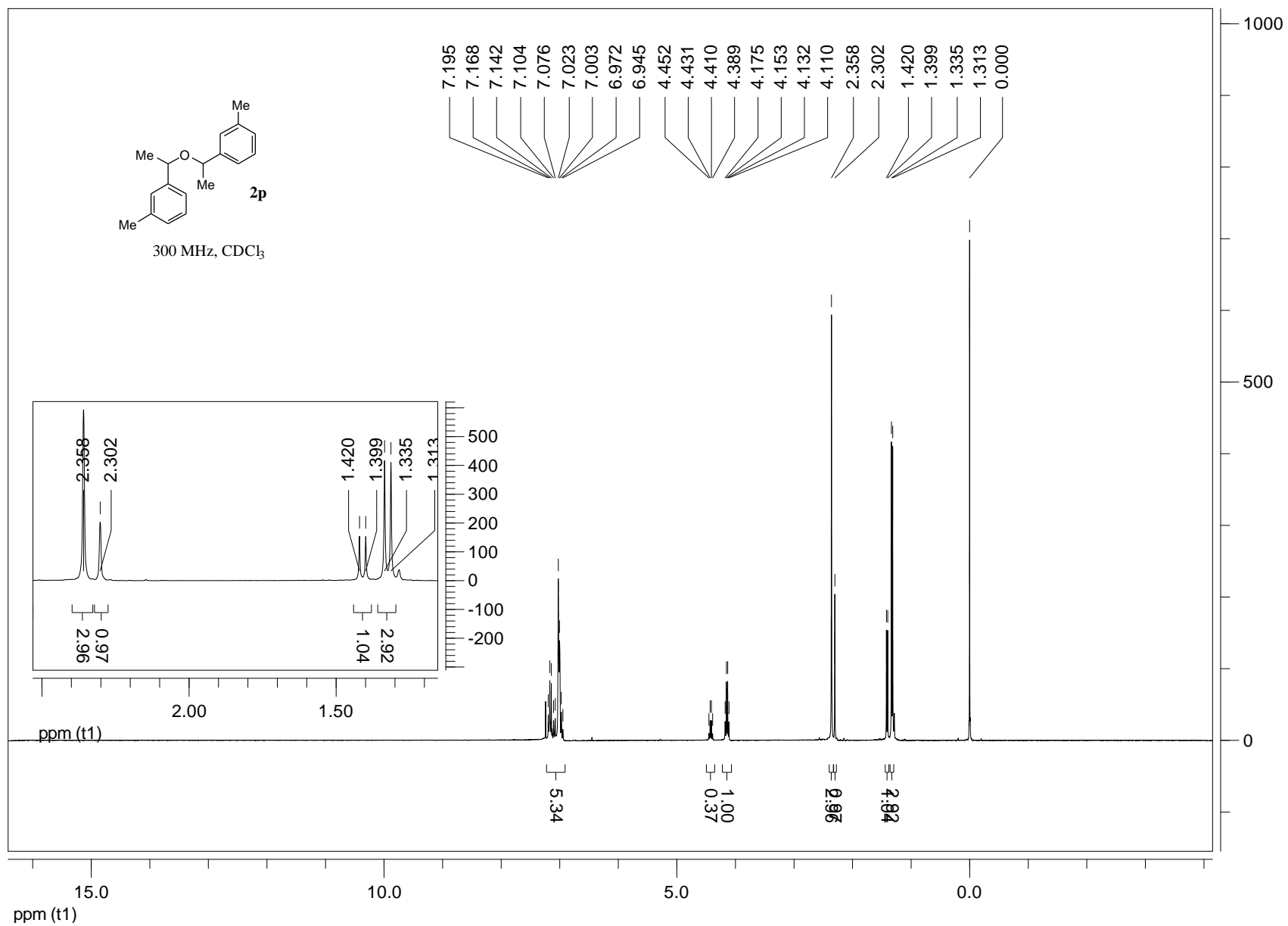


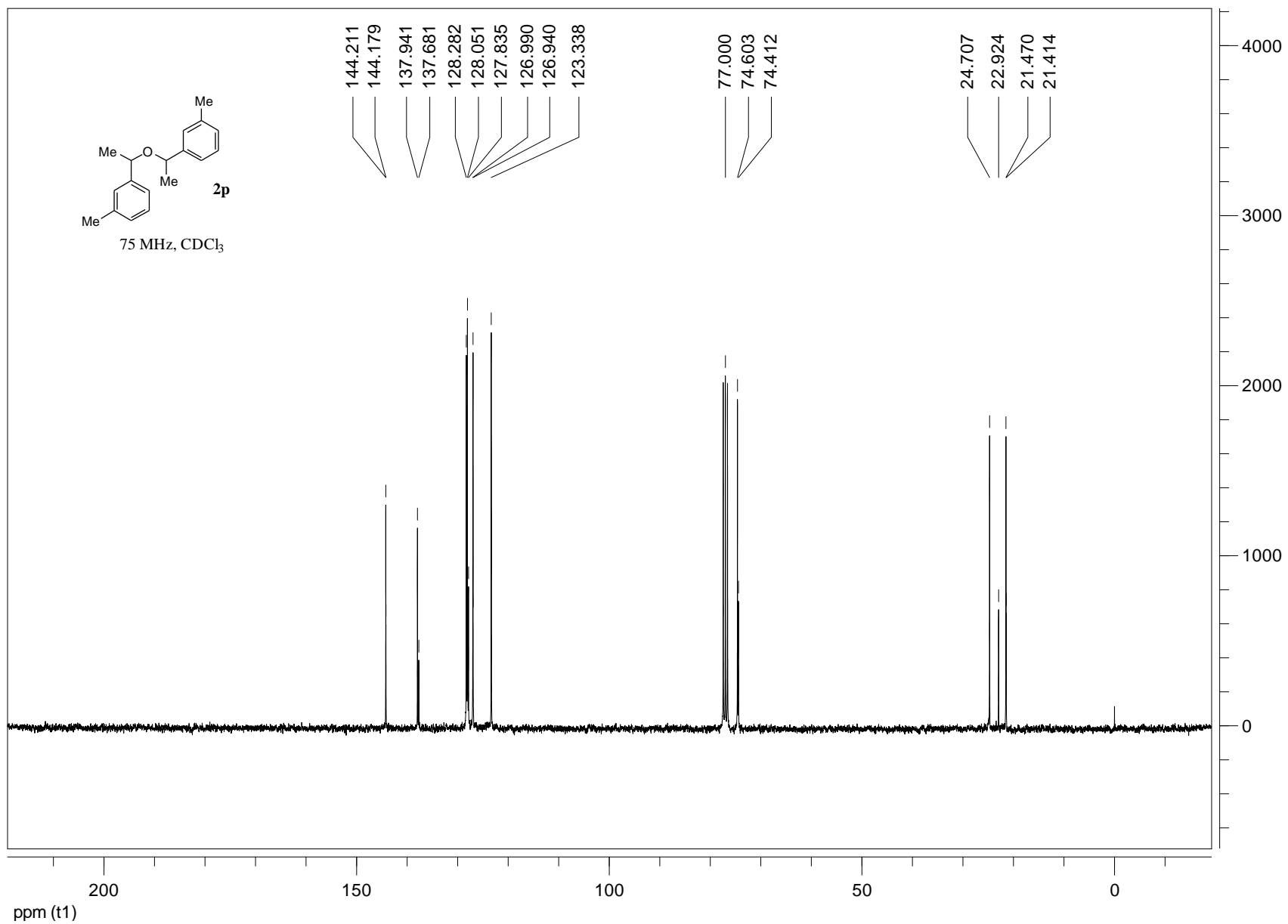


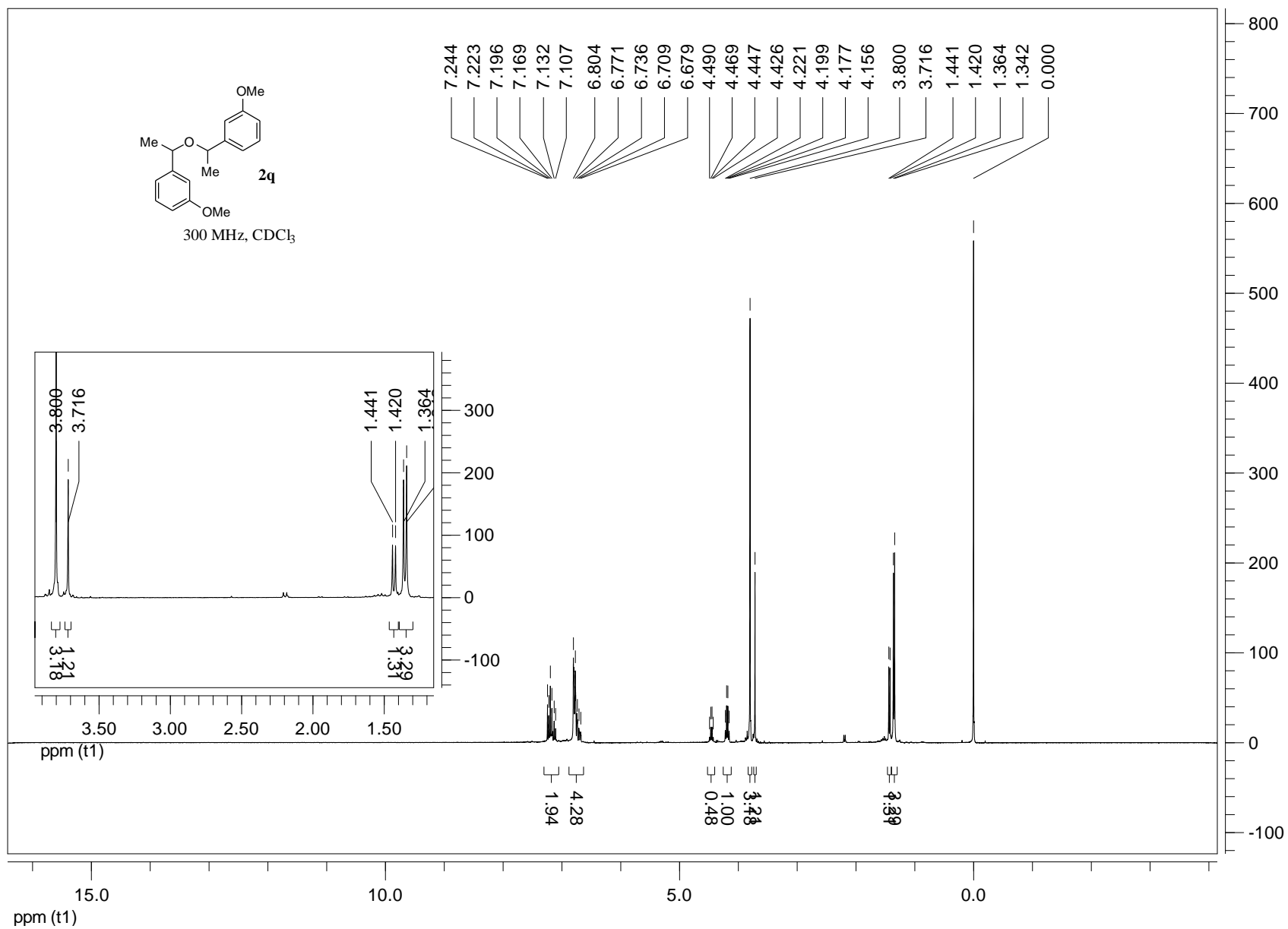


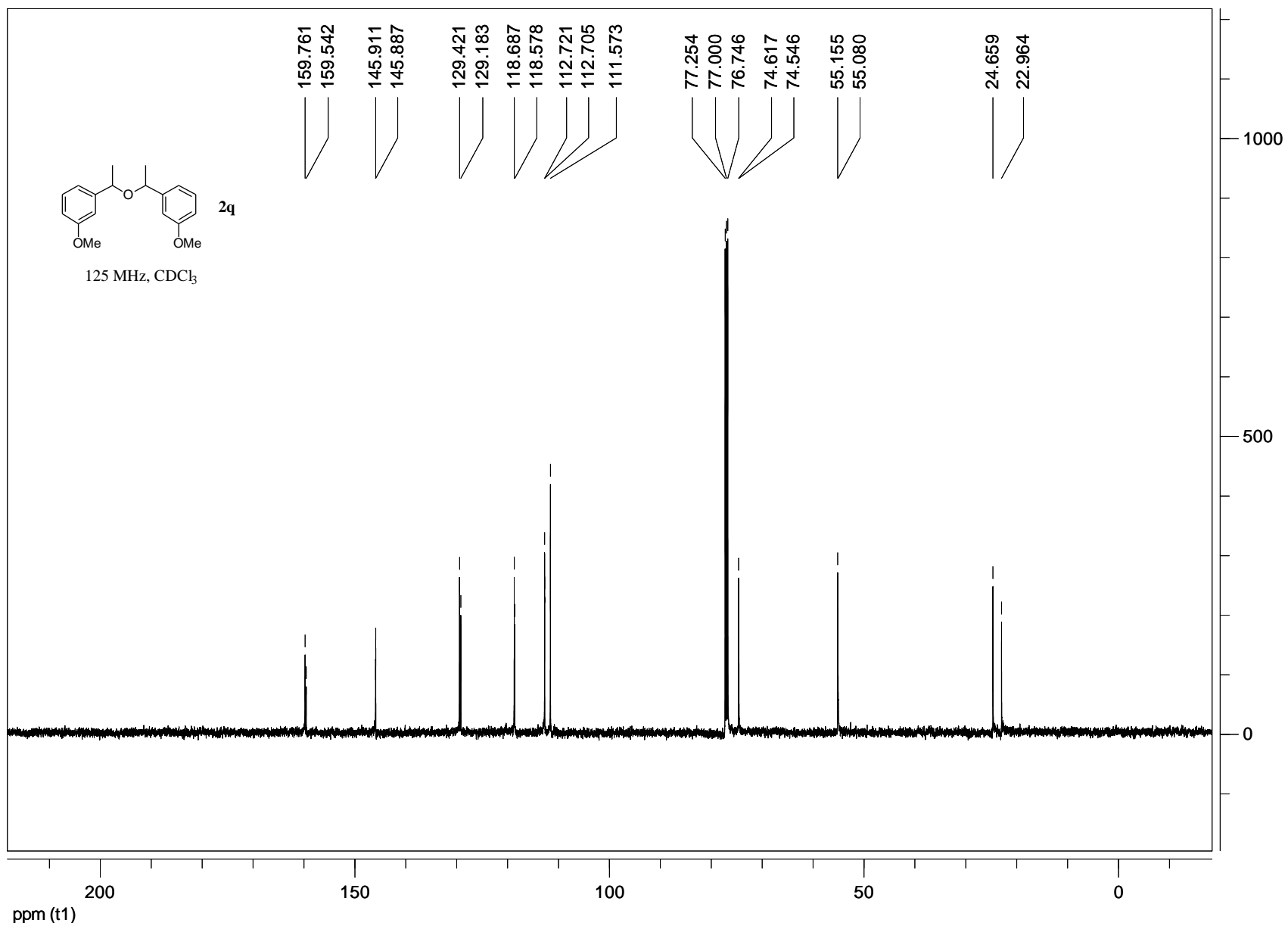


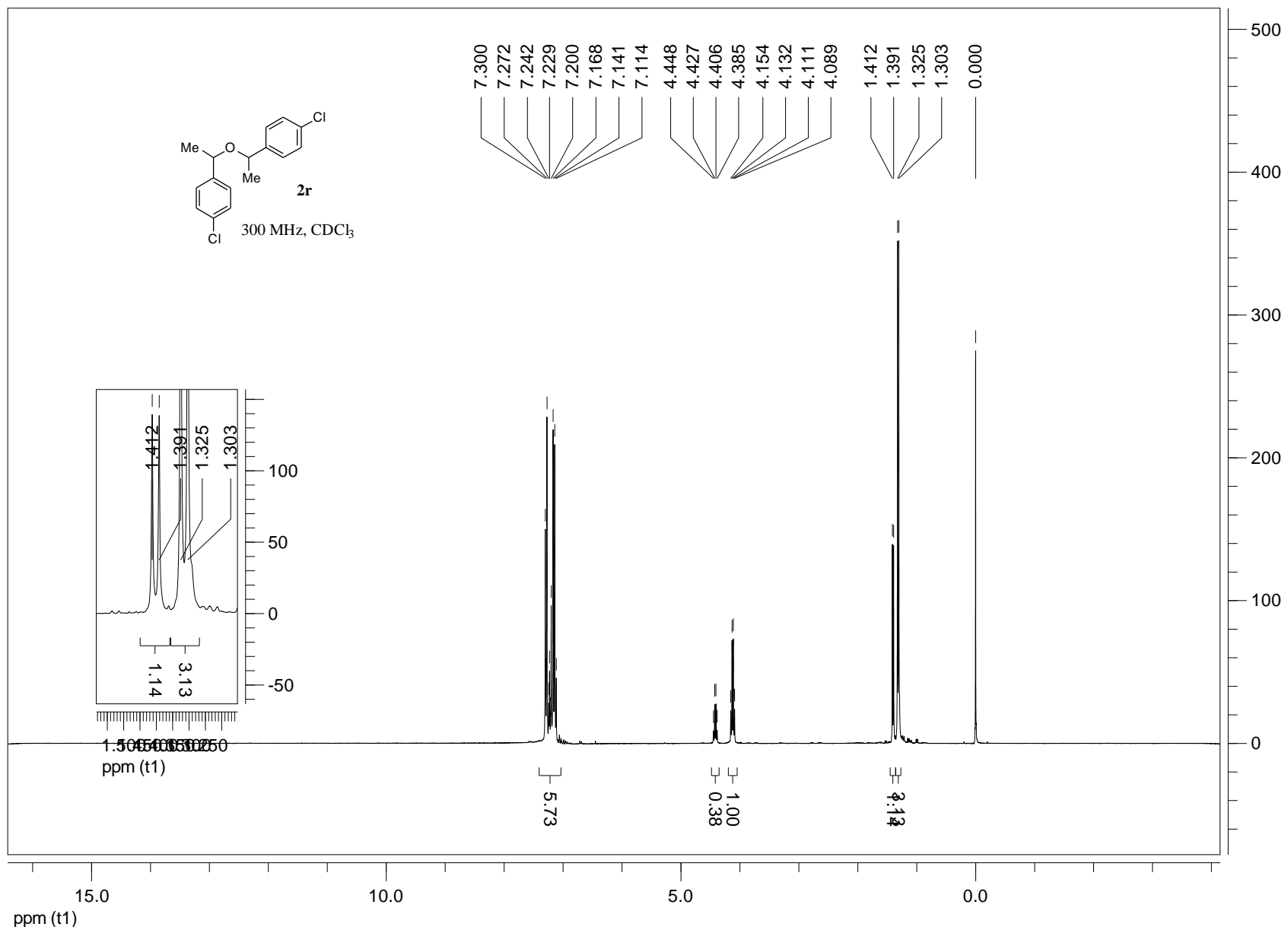


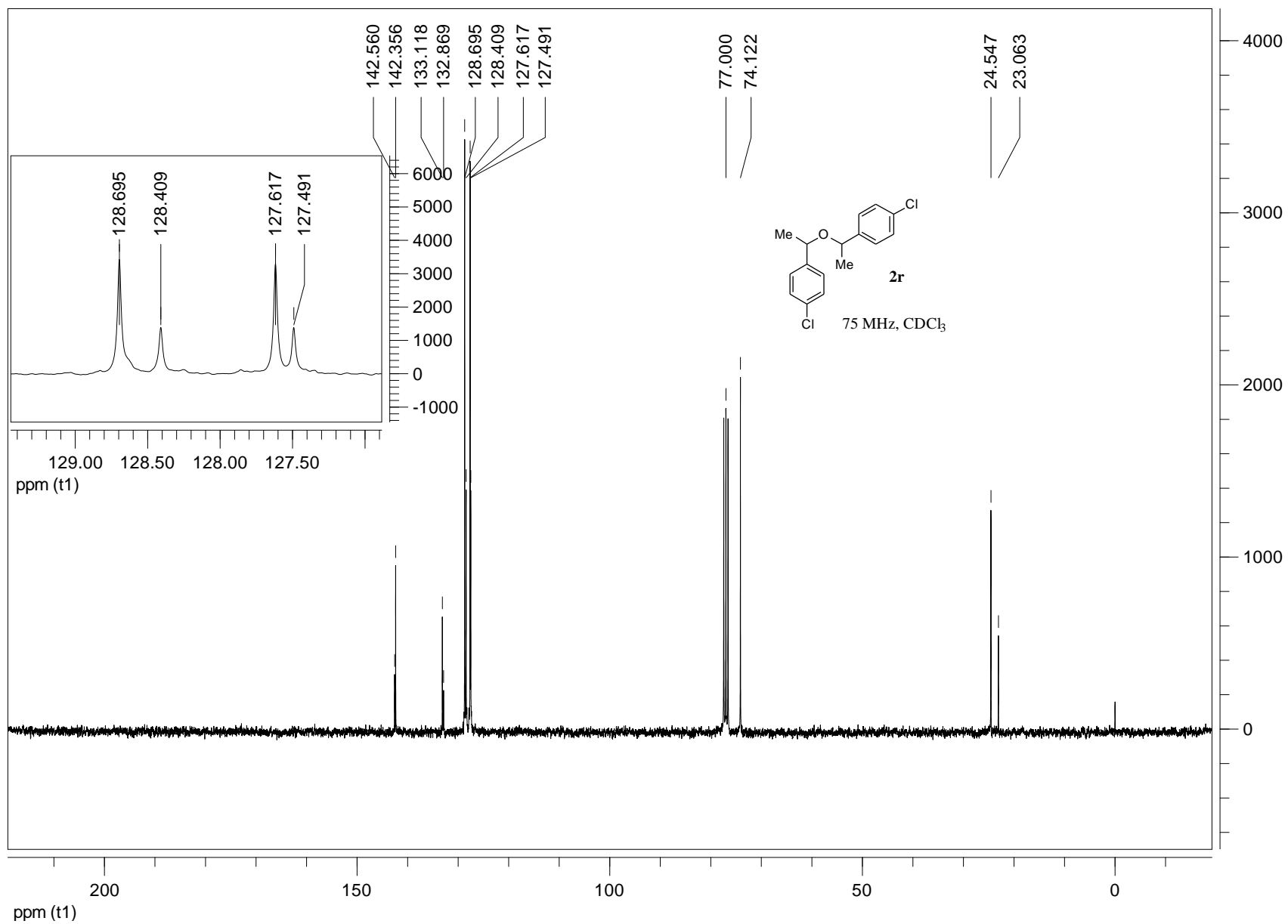


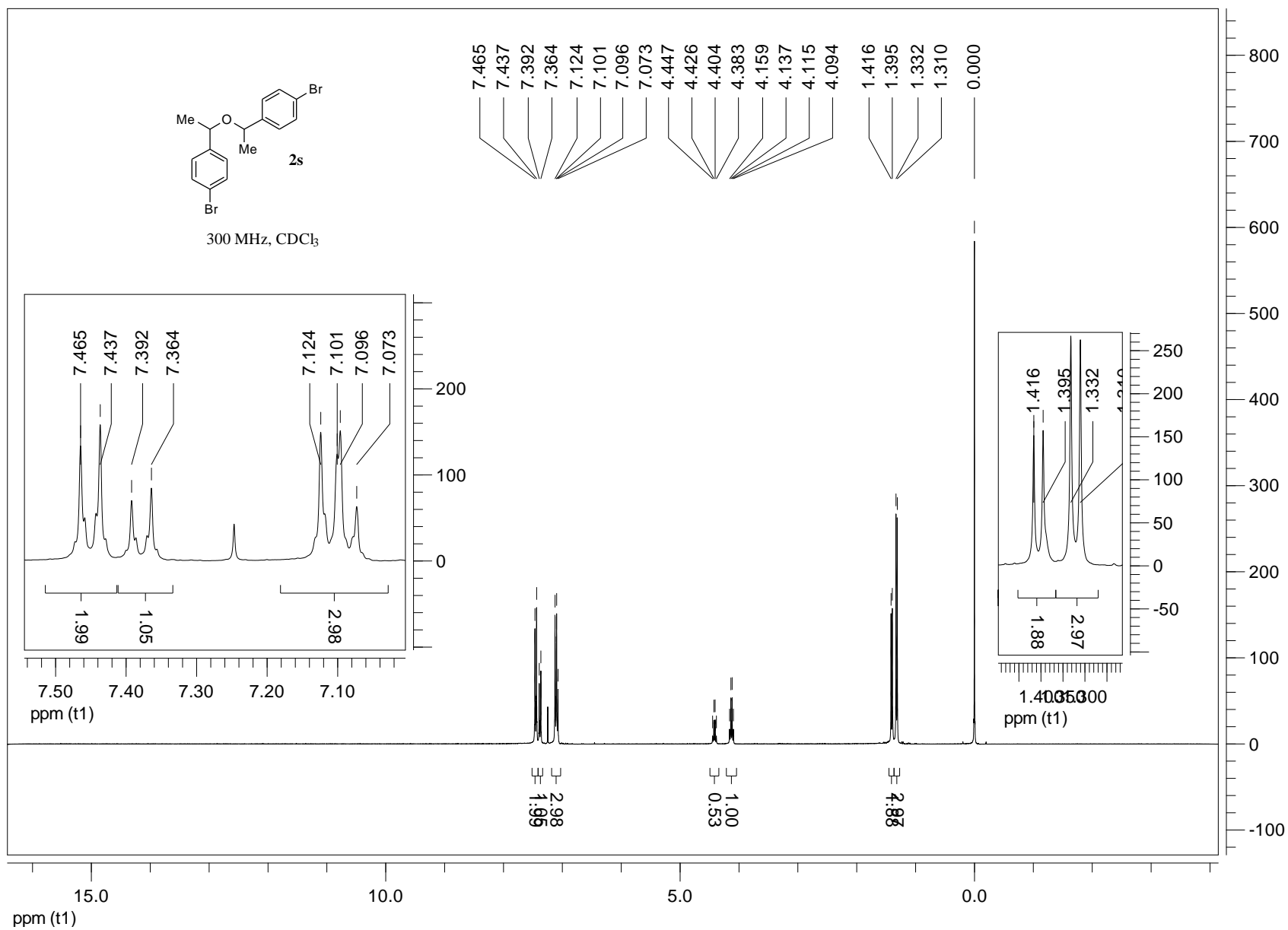


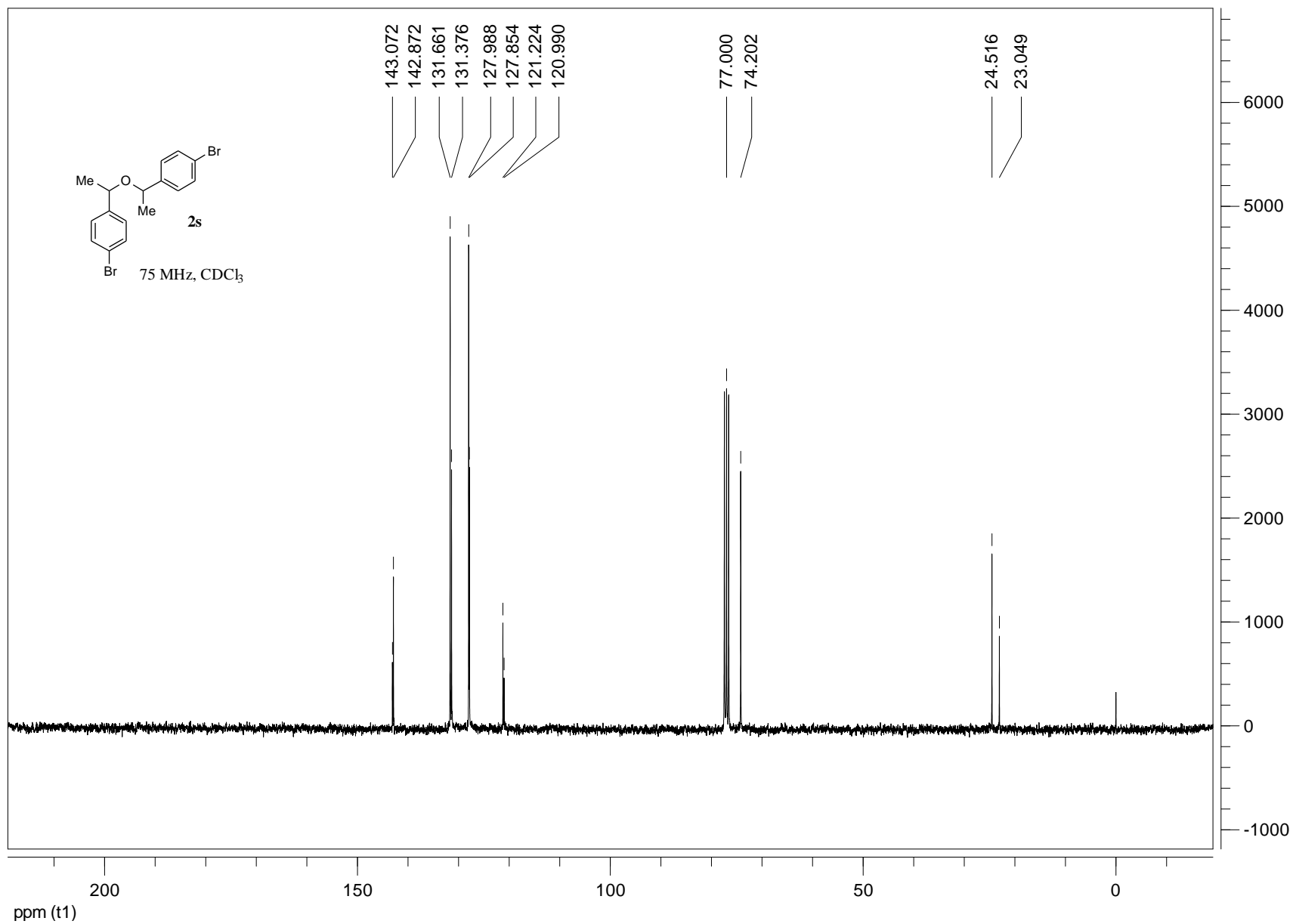


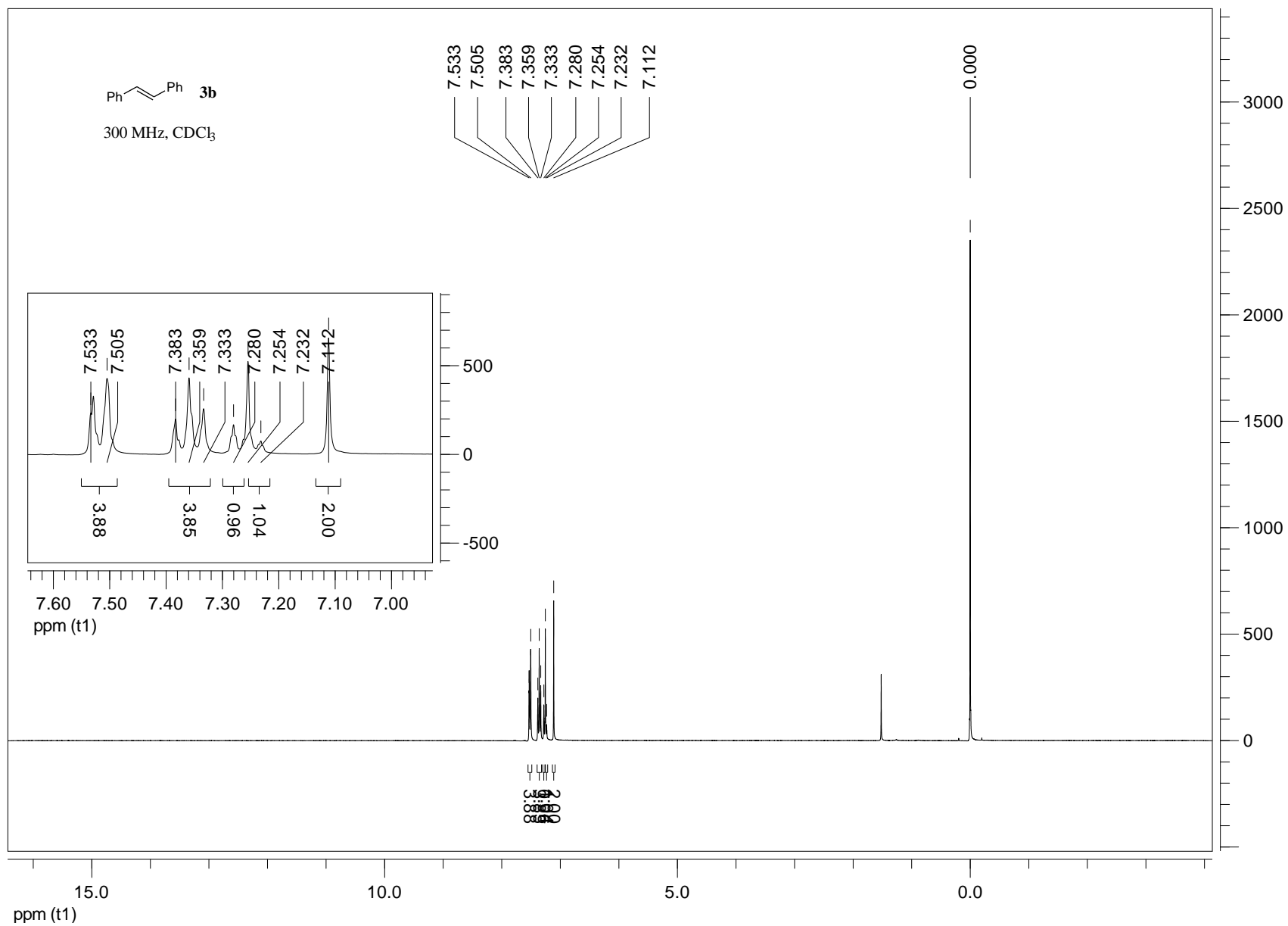


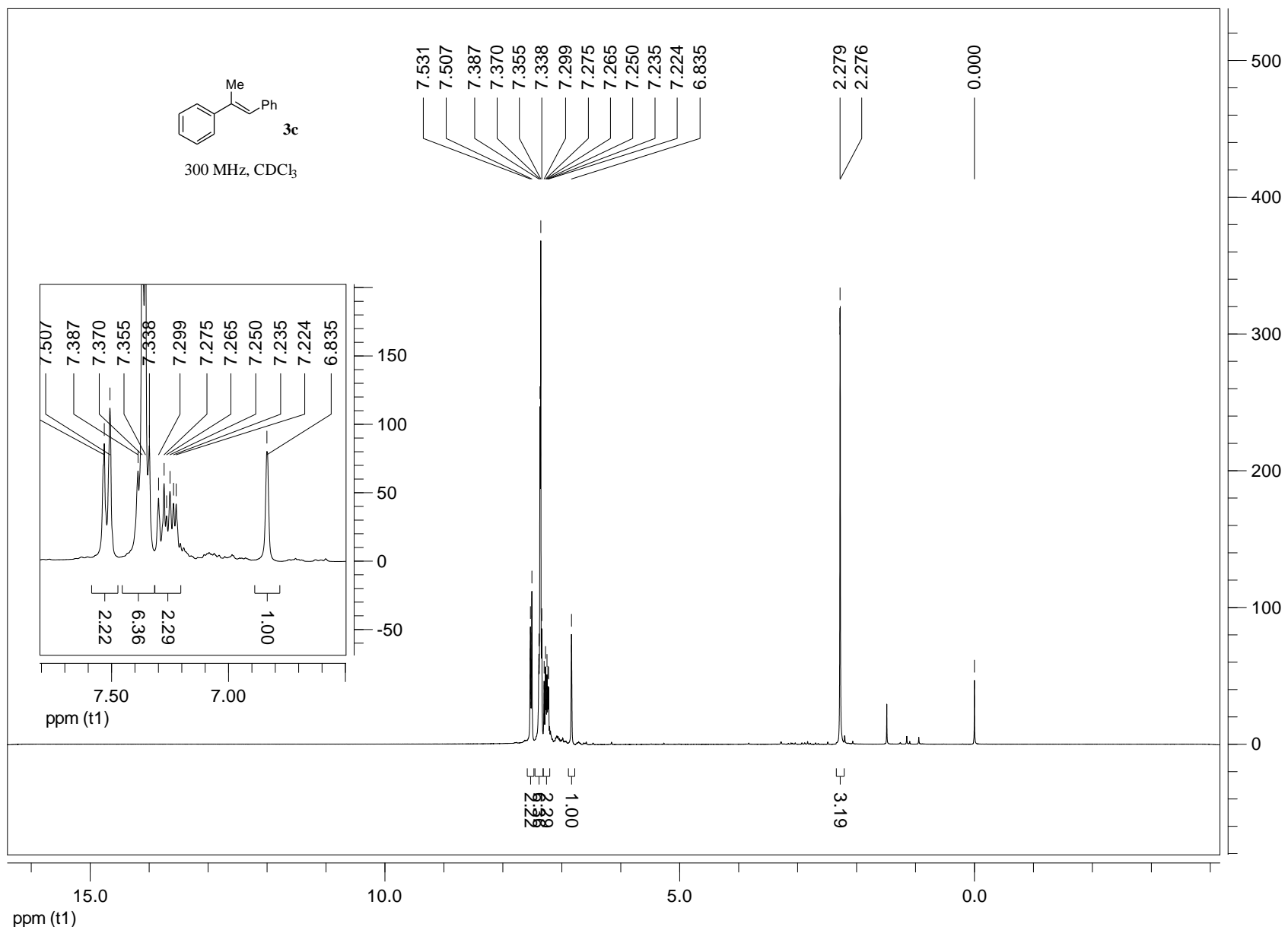


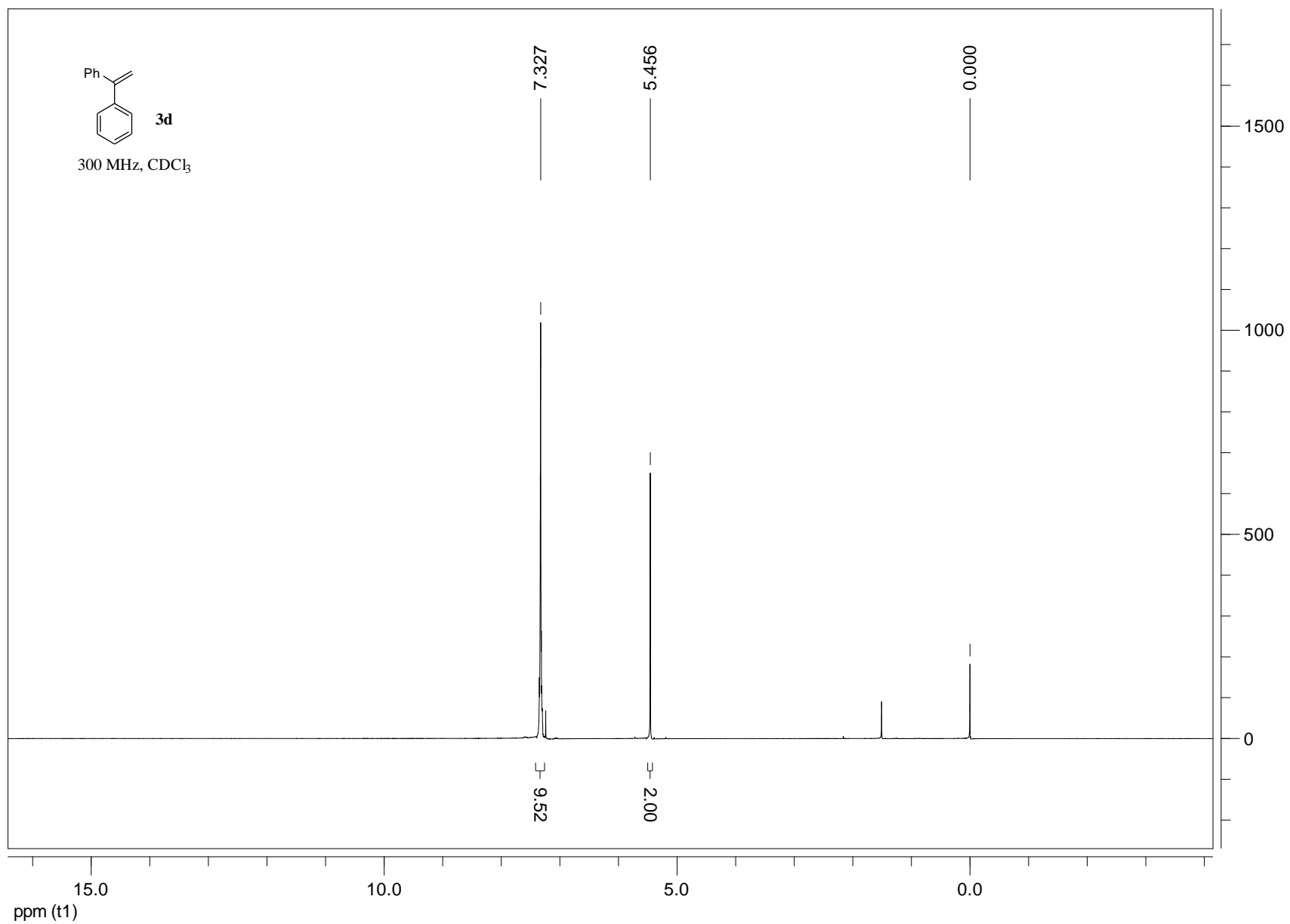


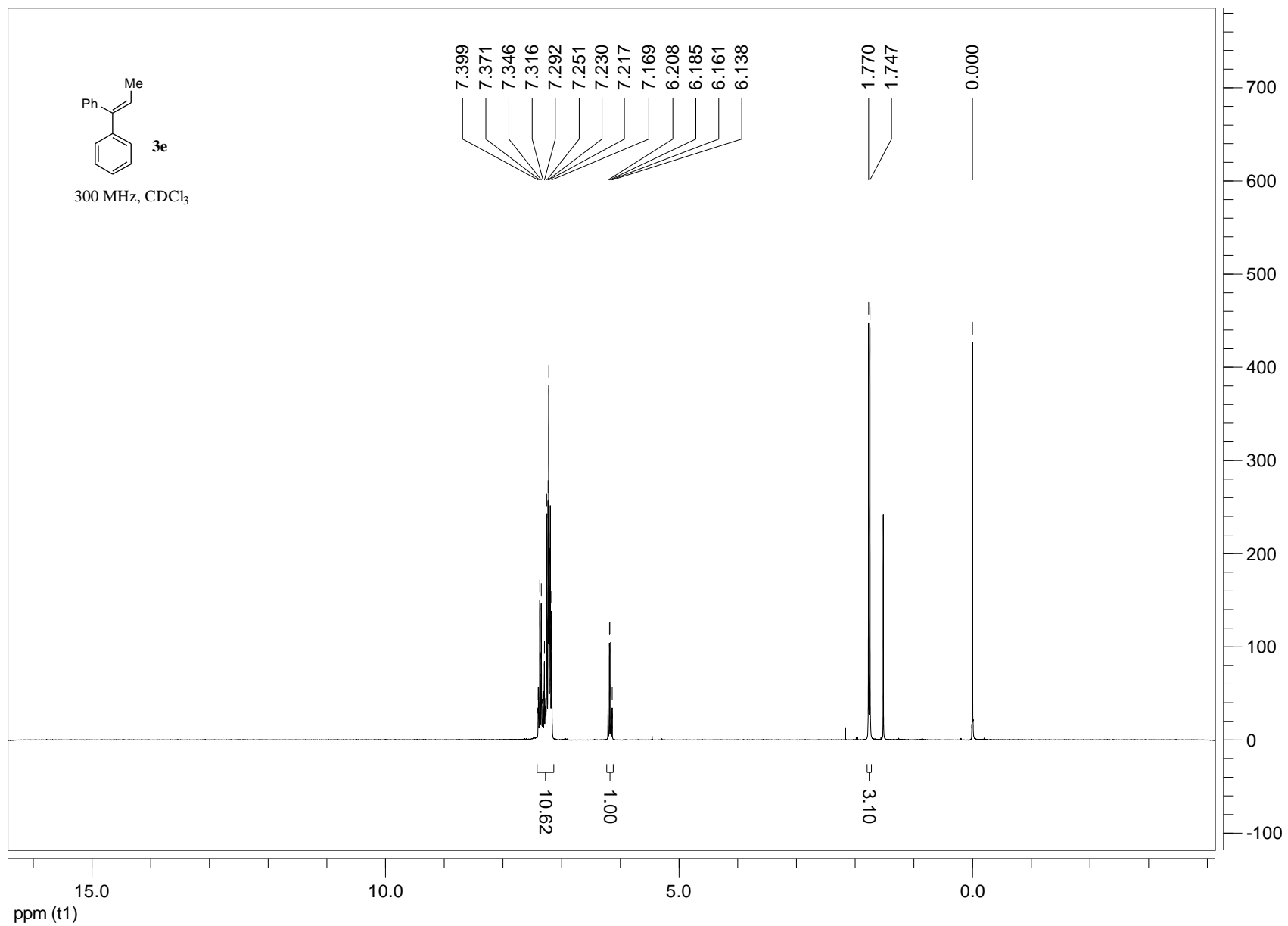


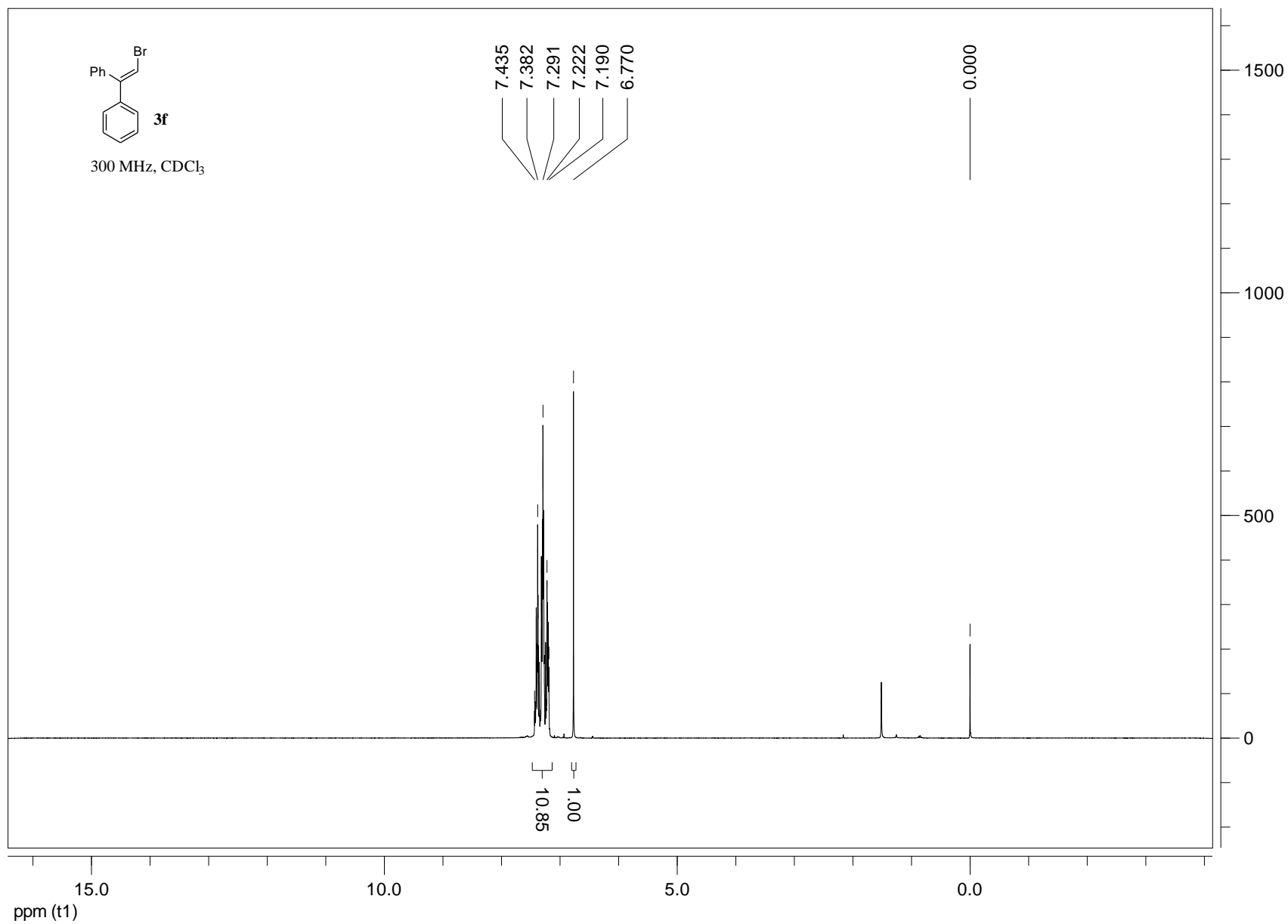


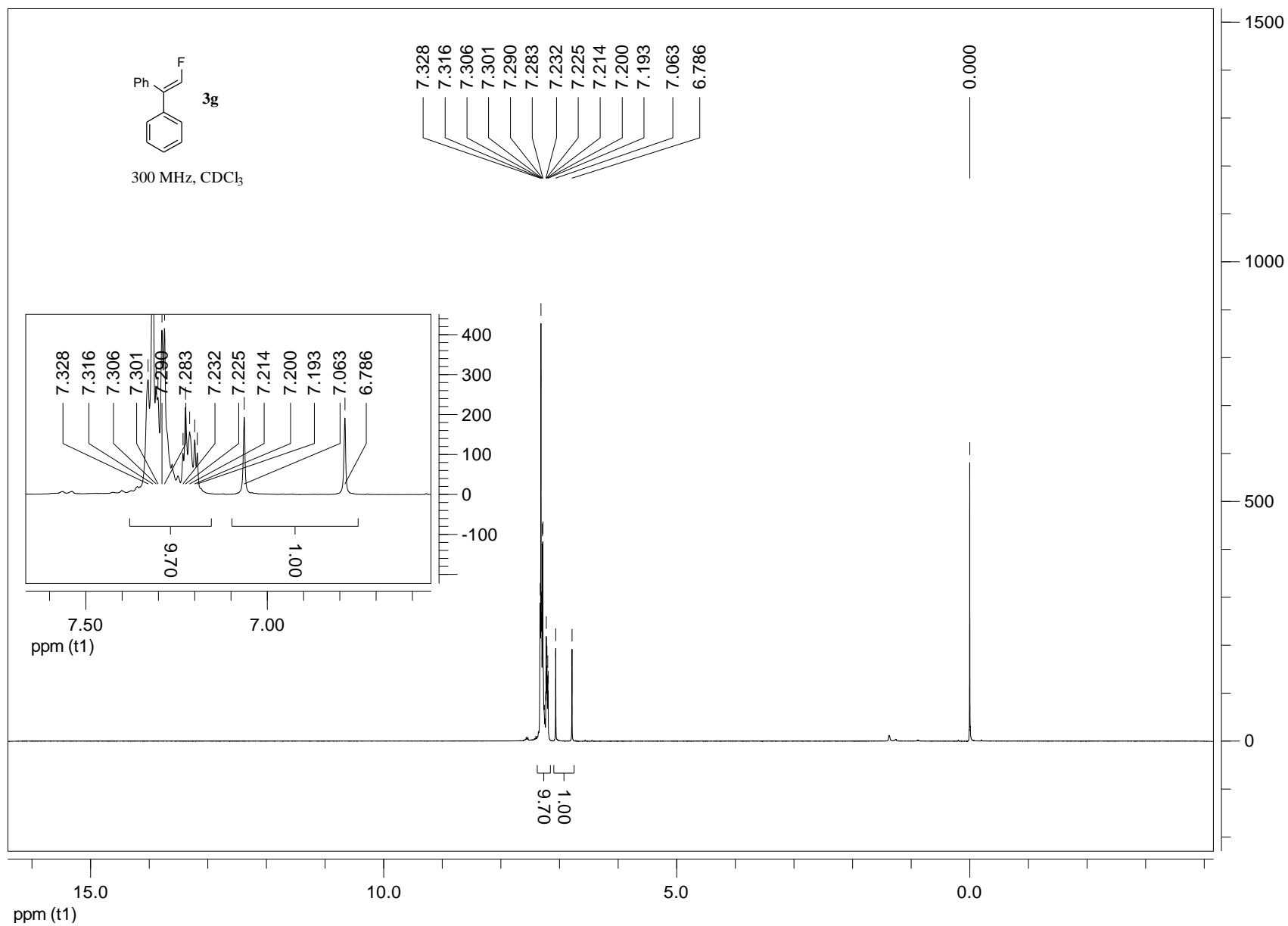


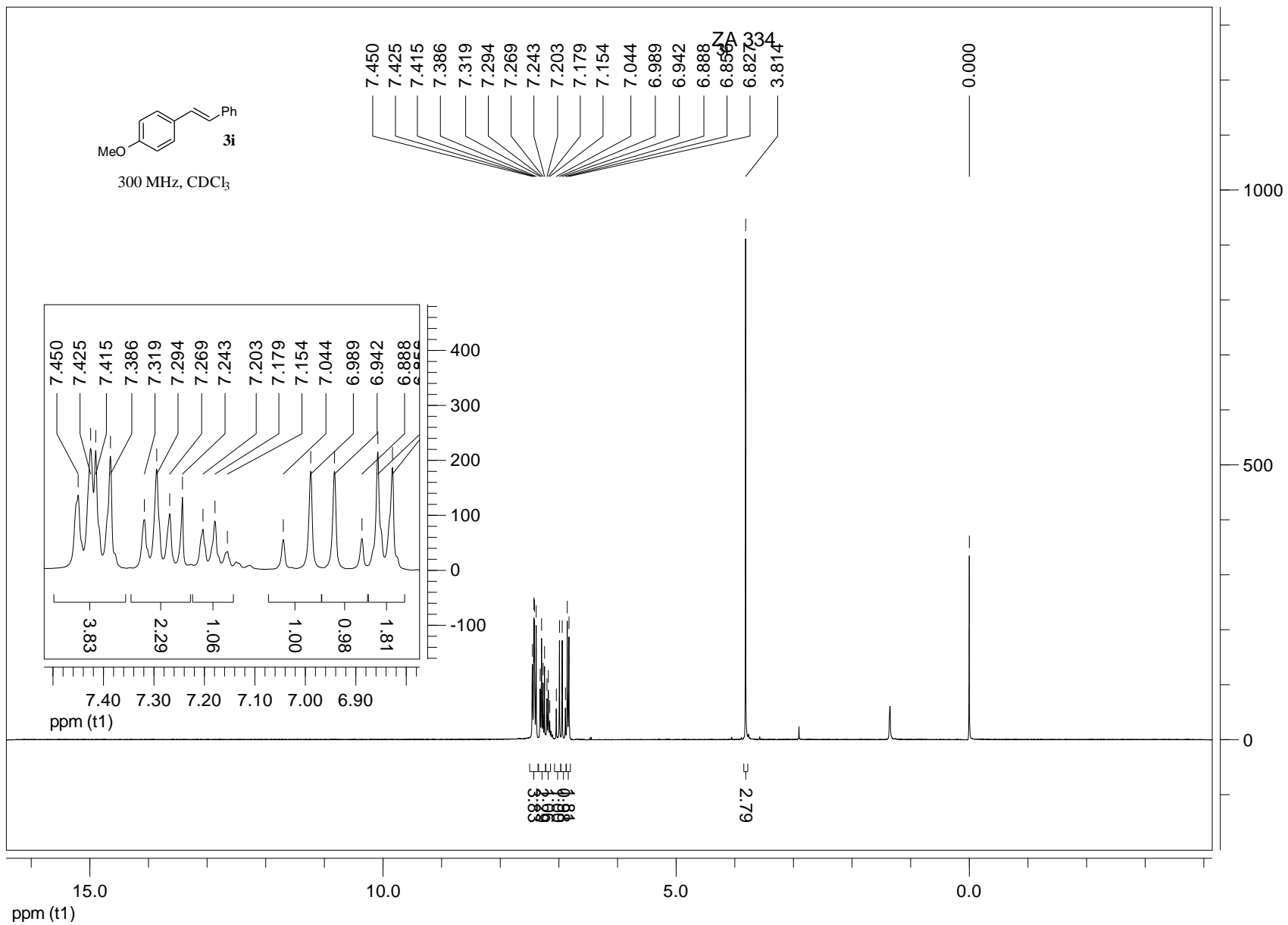


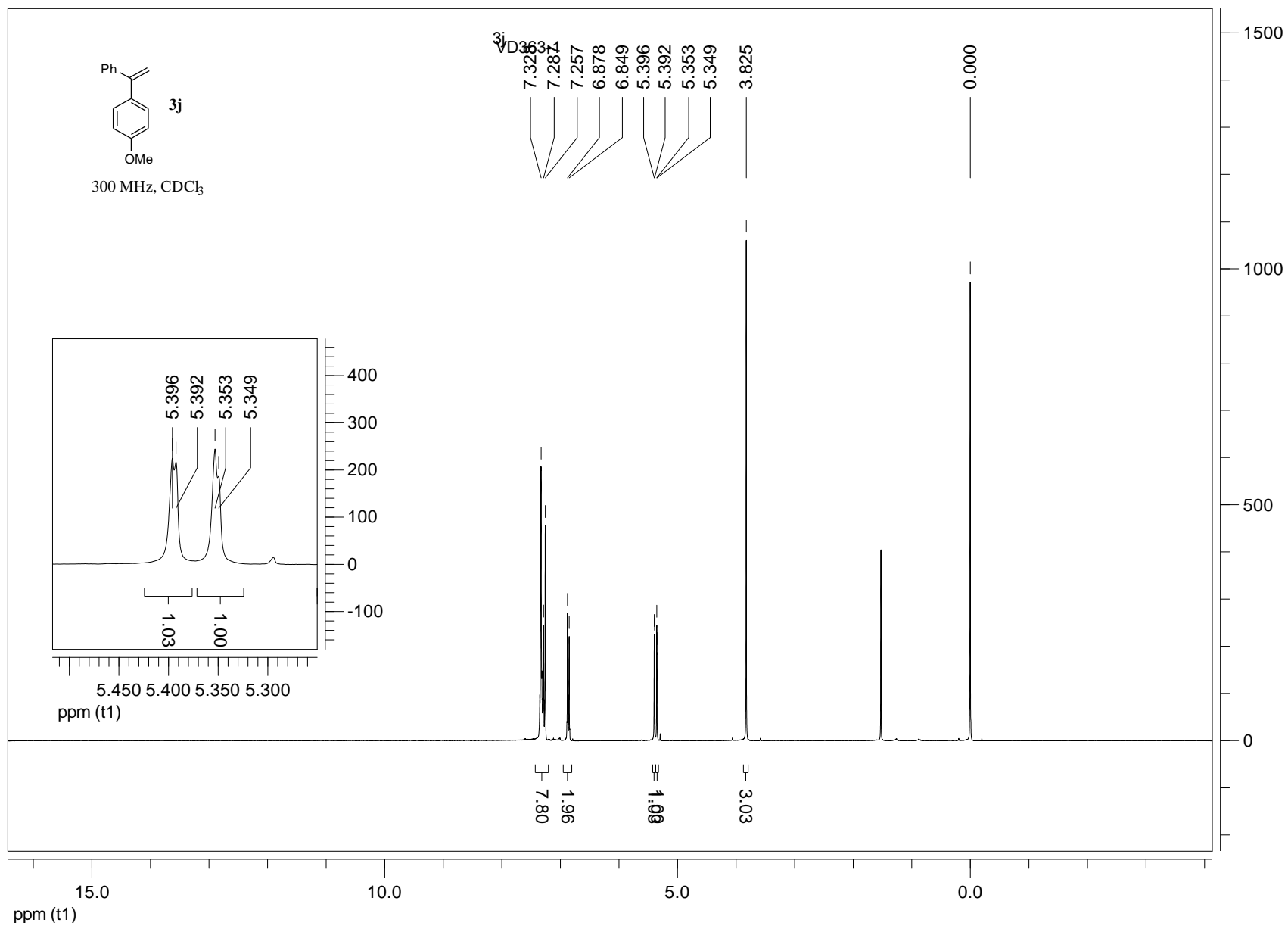


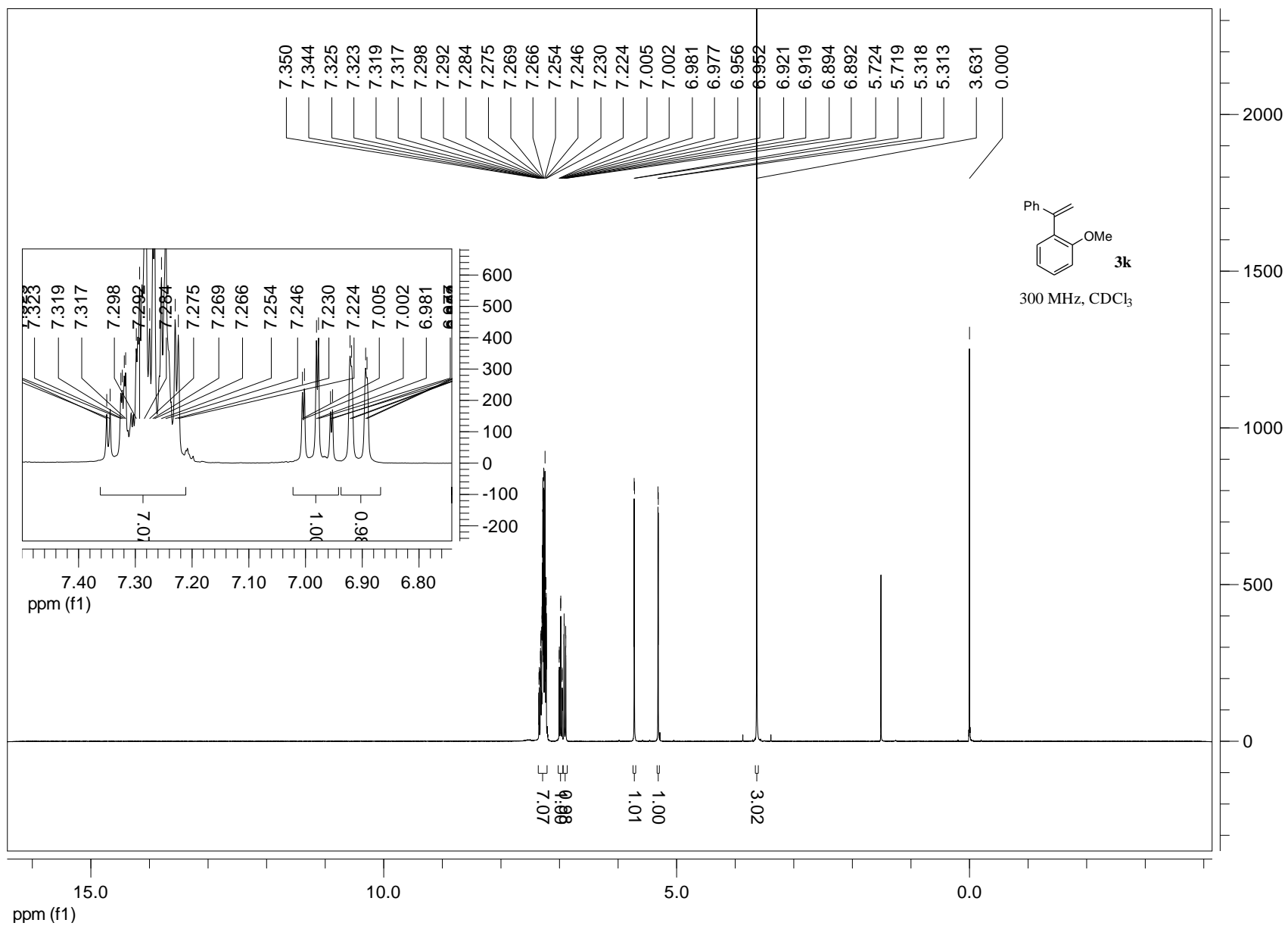


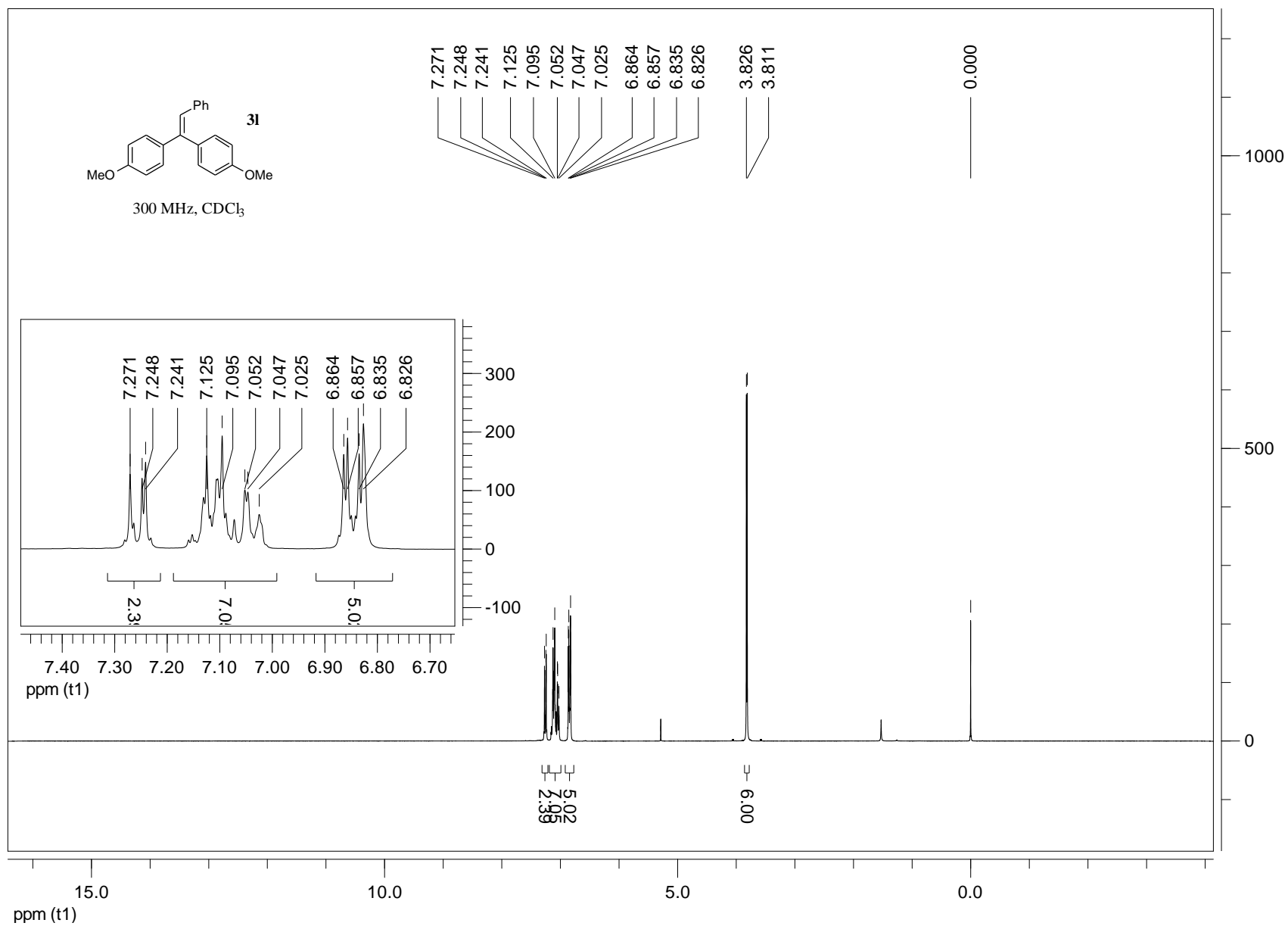


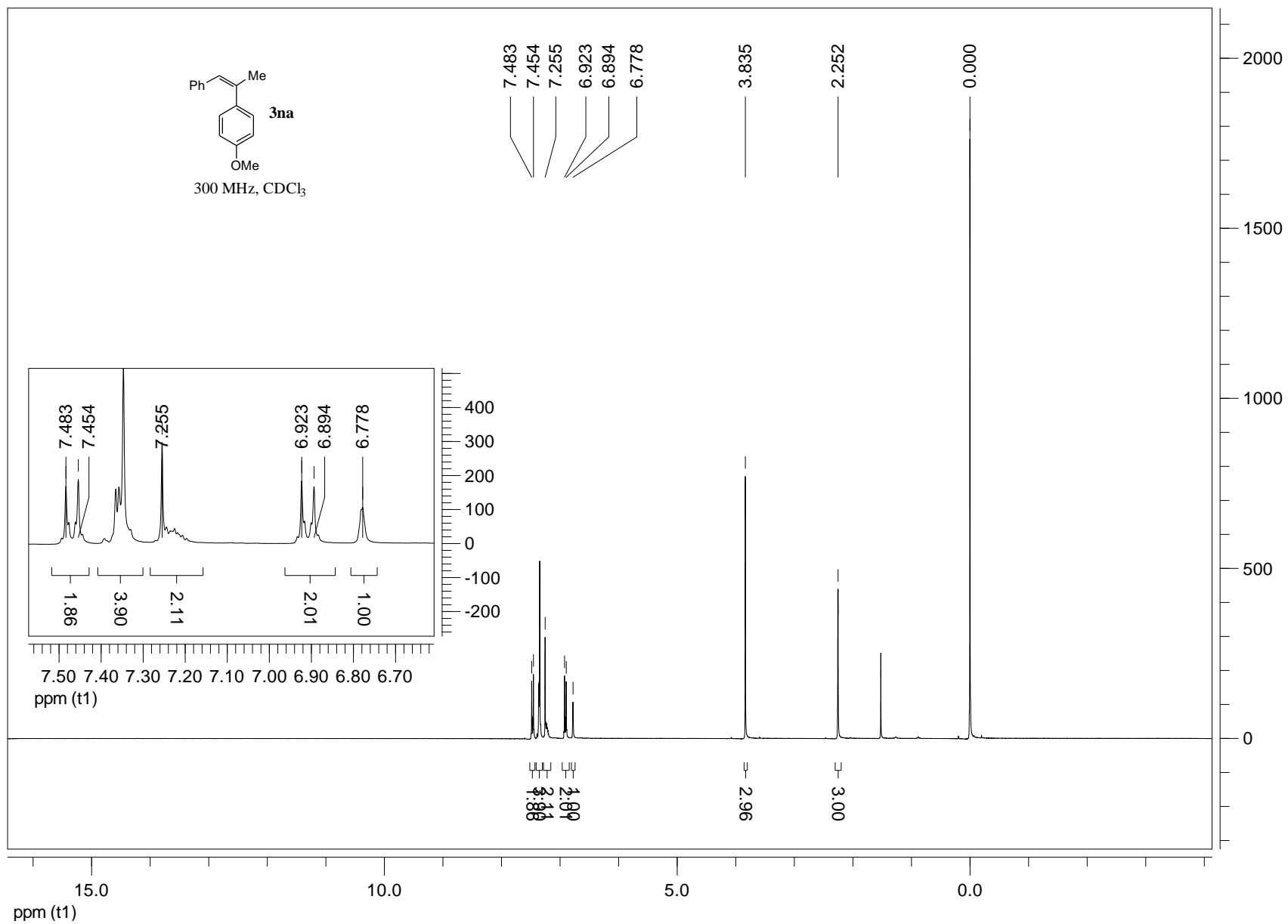


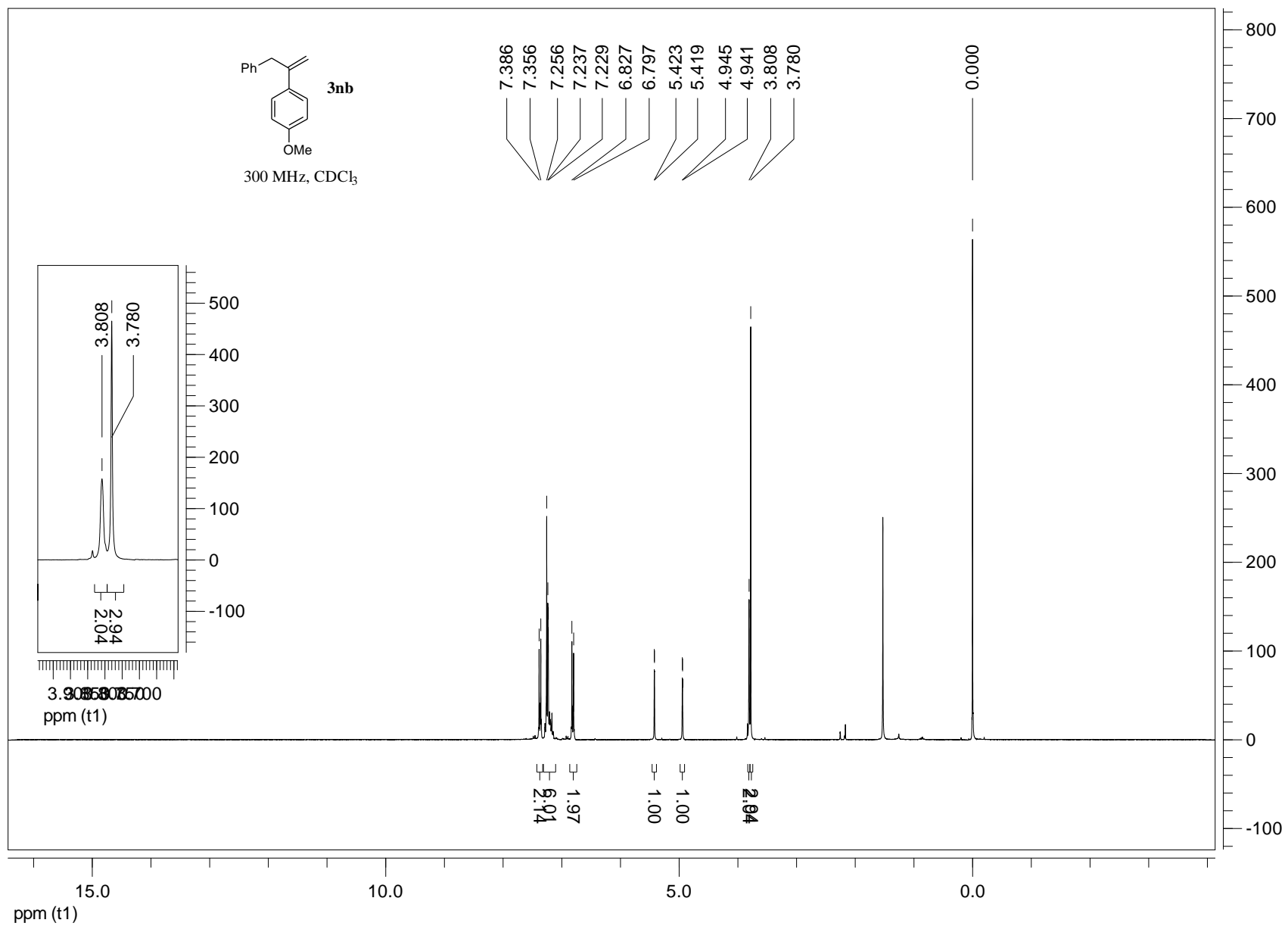


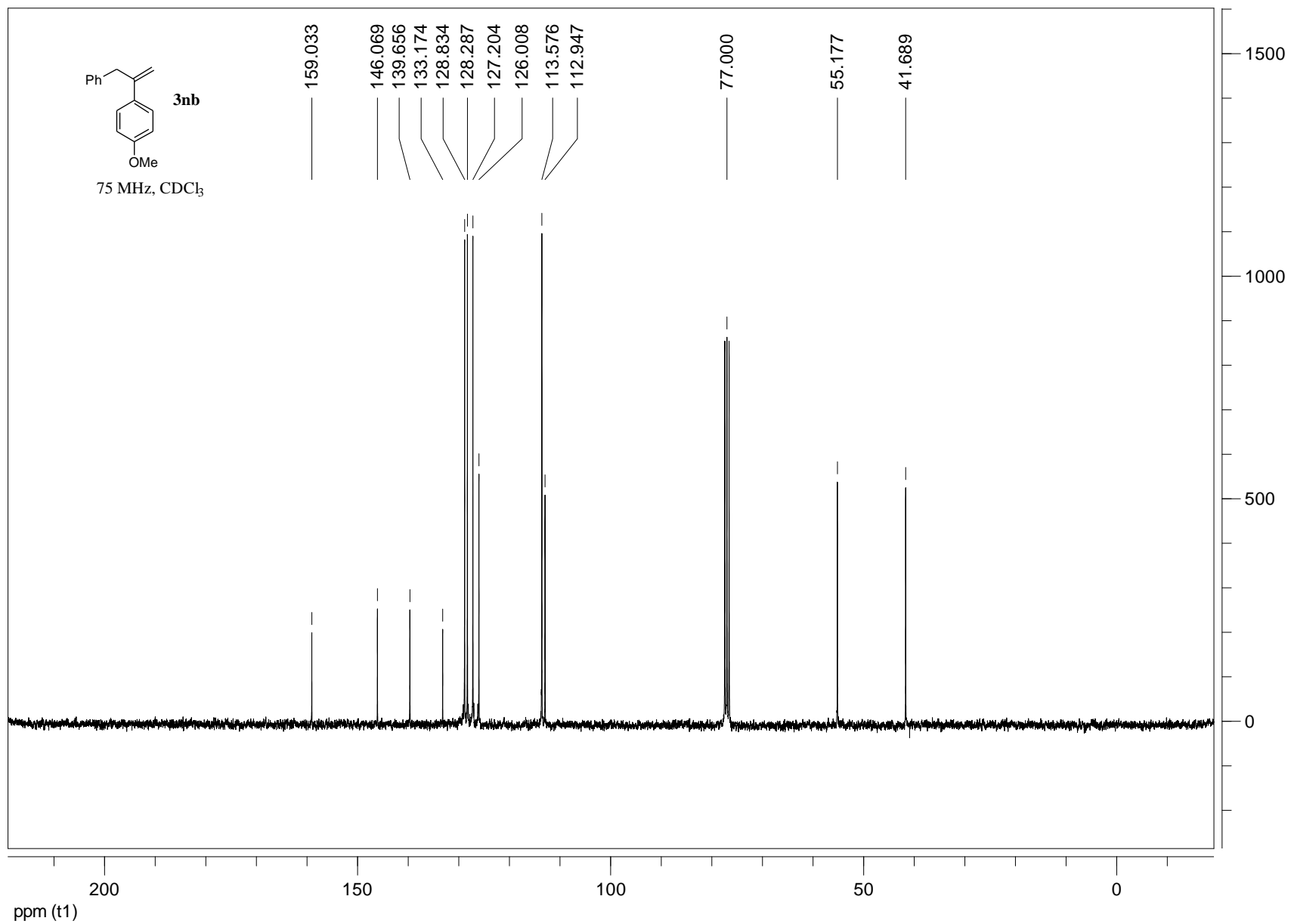


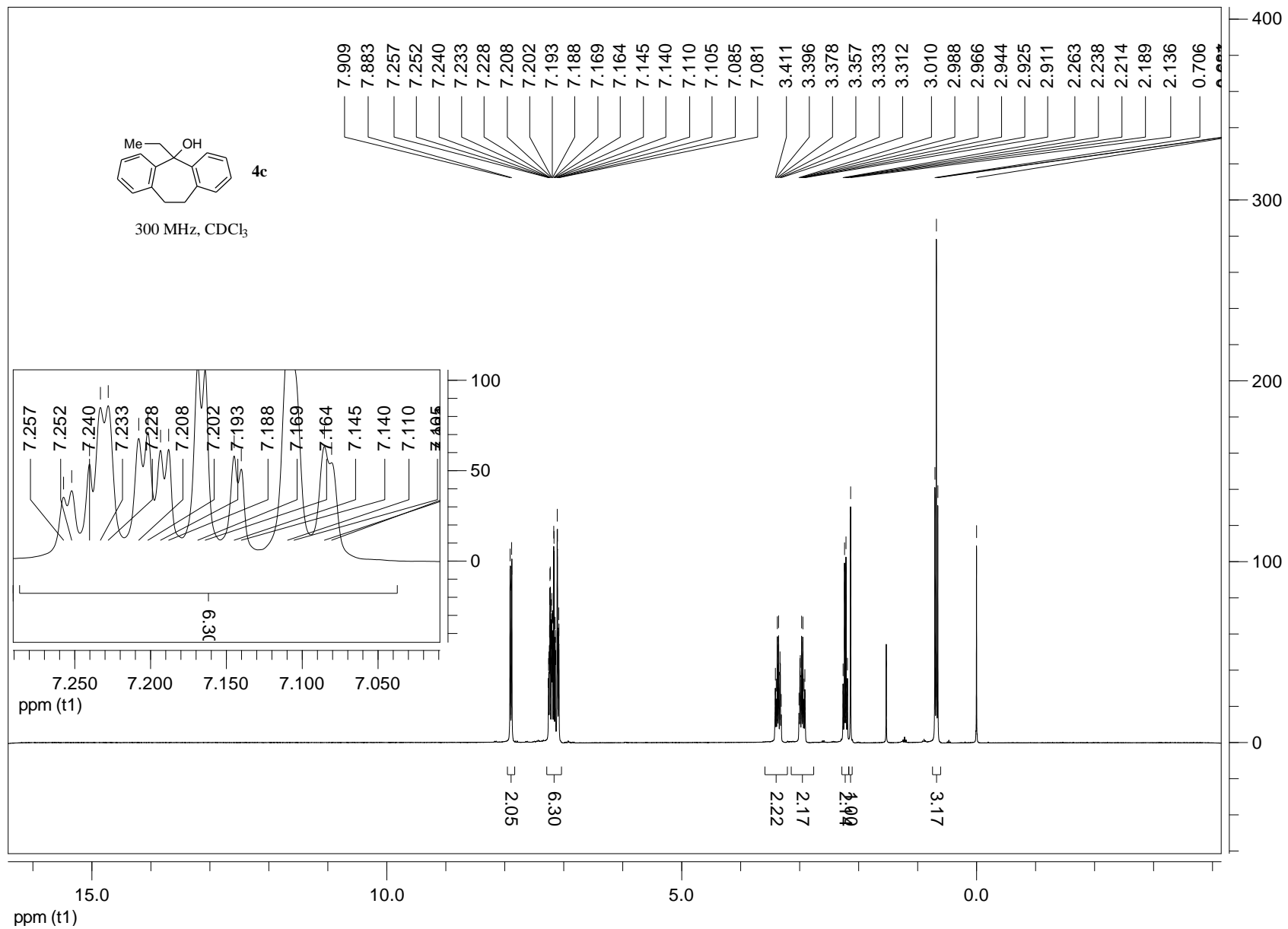


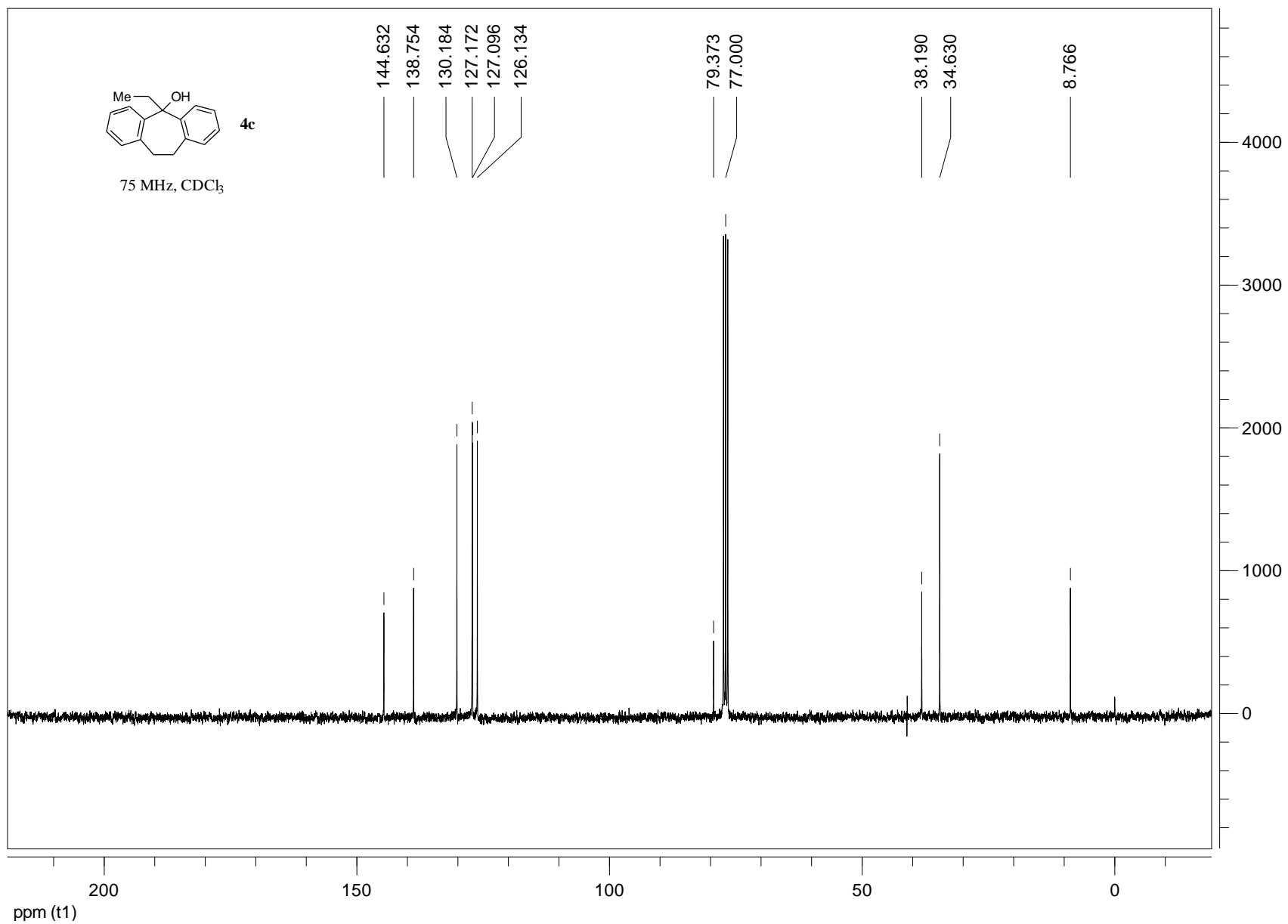


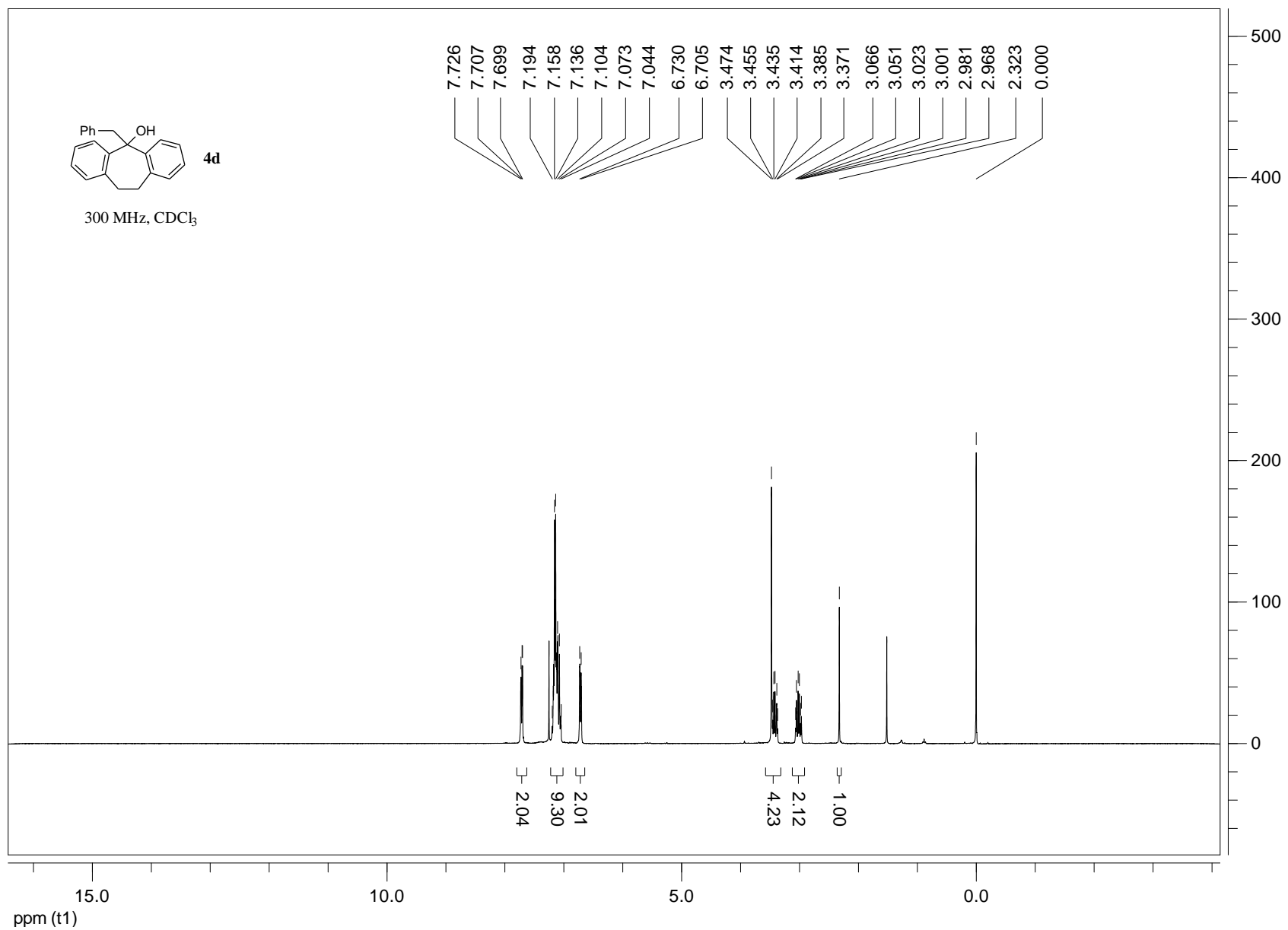


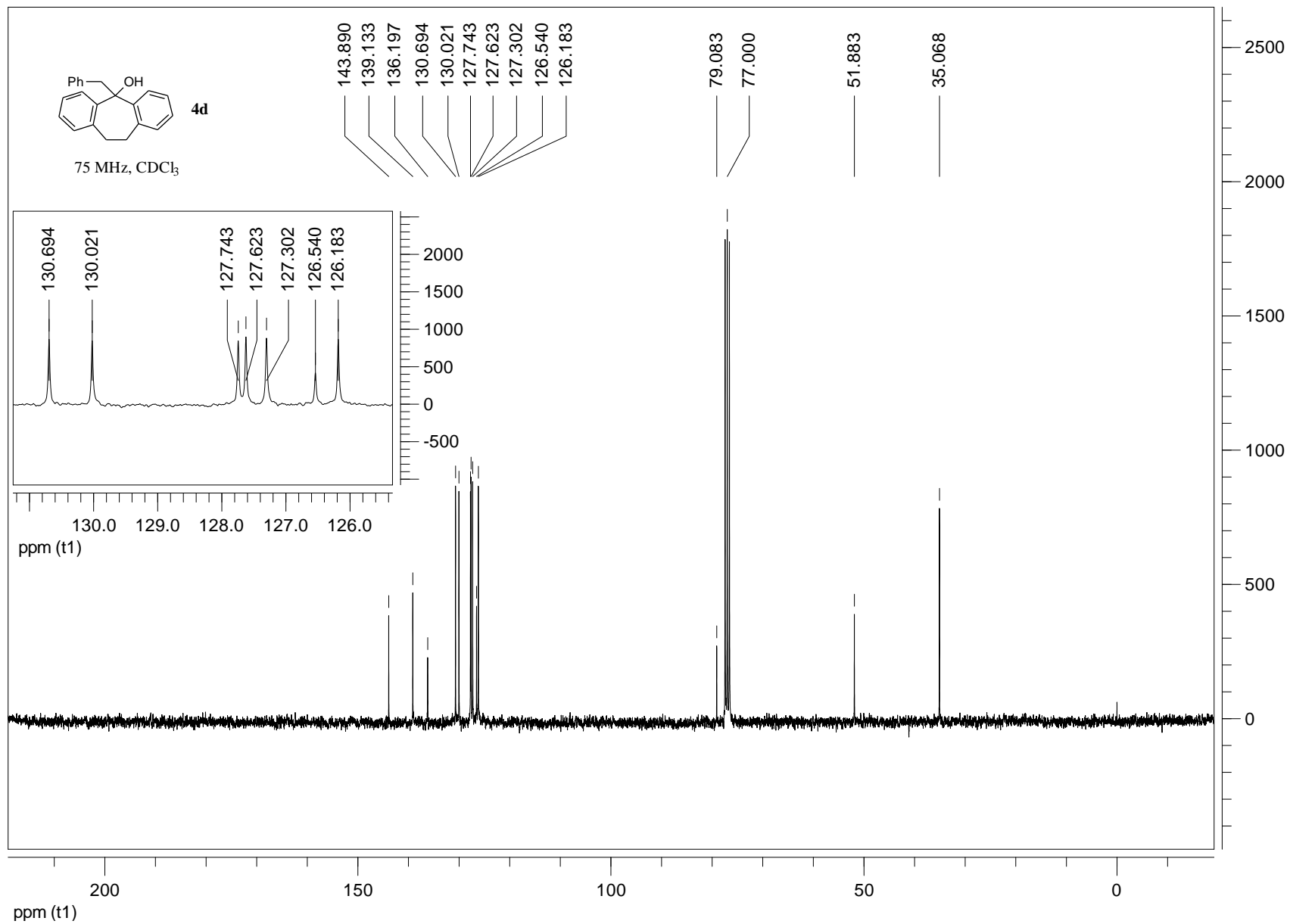


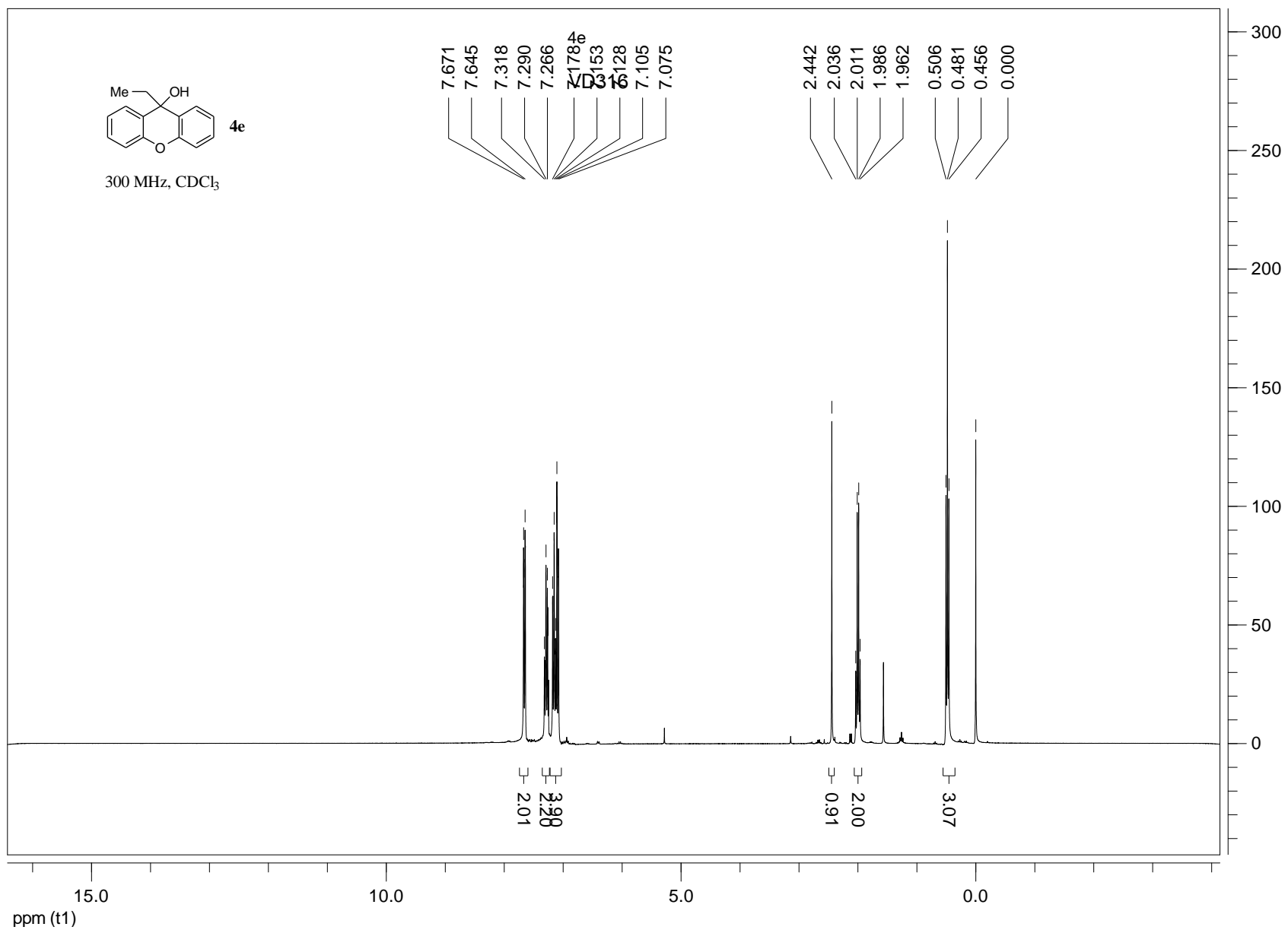












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