Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Gold(I)-Catalyzed Cyclization of 2-(1-Alkynyl)-alk-2-en-1-one Oximes: A Facile Access to Highly Substituted *N*-Alkoxypyrroles

Mei Zhang,[a] Junliang Zhang*[a,b]

[a] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 N, Zhongshan Road, Shanghai 200062 (P. R. China), Fax: (+86) 021-6223-5039 E-mail: jlzhang@chem.ecnu.edu.cn*

1. General Information

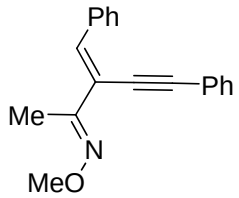
All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. ^{1}H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and intergration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Dichloromethane was freshly distilled from CaH_2; Toluene was freshly distilled from sodium metal prior to use. 4 Å molecular sieves purchased from Sinopharm Chemical Reagent Co.,Ltd were powdered and dried at 300 ºC in muffle furnace for 8-10 hours prior to use.

2. Experimental Procedures and Characterization Data

2.1 General Procedure for Synthesis of Oxime Substrates 1:

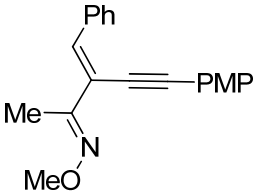
In a three necked flask, the corresponding 2-(1-alkynyl)-2-alken-1-one[1](5.0 mmol) was dissolved in 20 mL absolute ethyl alcohol under nitrogen. Potassium carbonate (2.0 equiv.) and methoxylamine hydrochloride (2.0 equiv.) was added to the solution. The resulting mixture was stirred for 5-12h and the reaction was complete determined by TLC analysis. Then the mixture was quenched by 20 mL of water and HCl (1.0 M). The layer was separated, and the aqueous layer was extracted by ethyl acetate (2×20 mL). The combined organic layer was washed with brine (20 mL), dried by anhydrous sodium sulfate. After filtration and concentration in vacuo, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the corresponding oxime product.

1. Substrate 1a.



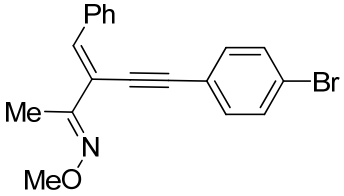
Yellow oil, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.53-7.51 (m, 2H), 7.42-7.32 (m, 6H), 7.22 (s, 1H), 4.02 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 136.3, 135.9, 131.5, 129.6, 128.9, 128.5, 128.4, 128.3, 123.2, 118.7, 97.4, 86.7, 62.0, 12.6; IR (neat): *v* 3059, 2936, 2897, 2815, 2196, 1951, 1887, 1804, 1673, 1597, 1490, 1443, 1364, 1282, 1183, 1046, 906, 848, 753, 688 cm^{-1}; MS (EI): m/z (%) = 275 (M^+, 10.54), 202 (100), 203 (96.60), 191 (62.73), 244 (33.05), 201 (29.18), 200 (29.04), 77 (22.52), 204 (16.93)；HRMS (EI): calculated for $[C_{19}H_{17}NO]^+$ 275.1310, found: 275.1311.

2. Substrate 1b.



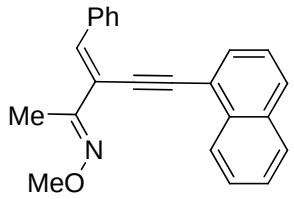
Yellow oil, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.19 (s, 1H), 6.90 (d, *J* = 7.6 Hz, 2H), 4.02 (s, 3H), 3.83 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 155.4, 136.0, 135.5, 133.0, 129.5, 128.7, 128.2, 118.9, 115.3, 114.1, 97.6, 85.5, 62.0, 55.3, 12.6; IR (neat): *v* 2936, 2837, 2541. 2195, 2036, 1956, 1604, 1568, 1509, 1463, 1444, 1364, 1290, 1248, 1171, 1046, 904, 854 cm^{-1}; MS (EI): m/z (%) = 305 (M^+, 12.68), 189 (100), 274 (69.83), 233 (65.58), 218 (65.50), 221 (41.22), 190 (37.69), 202 (34.20), 163 (21.29)；HRMS (EI): calculated for $[C_{20}H_{19}NO_2]^+$ 305.1416, found: 305.1413.

3. Substrate 1c.



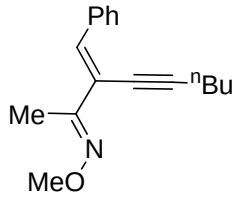
Yellow solid, 65% yield, m.p. 48-49 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.40-7.31 (m, 5H), 7.21 (s, 1H), 4.01 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 136.8, 135.8, 132.9, 131.7, 129.5, 129.0, 128.3, 122.8, 122.1, 118.5, 96.1, 87.7, 62.1, 12.5; IR (neat): *v* 2931, 2814, 1906, 1612, 1486, 1462, 1446, 1394, 1182, 1070, 1009, 922, 899, 882, 757, 689 cm^{-1}; MS (EI): m/z (%) = 353 (M^+, 4.10), 355 (M^++2, 4.10), 202 (100), 200 (29.07), 203 (19.84), 201 (18.82), 269 (17.34), 271 (16.80), 324 (11.97), 322 (11.56)； HRMS (EI): calculated for $[C_{19}H_{16}NOBr]^+$ 353.0415, found: 353.0414.

4. Substrate 1d.



Yellow solid, 91% yield, m.p. 79-80 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.86-7.83 (m, 2H), 7.72 (d, *J* = 6.8 Hz, 1H), 7.56-7.50 (m, 2H), 7.48-7.34 (m, 4H), 7.24 (d, *J* = 6.0 Hz, 1H), 4.10 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 136.3, 136.0, 133.5, 133.2, 130.3, 129.6, 129.0, 128.9, 128.3, 128.2, 126.72, 126.66, 126.5, 125.2, 121.0, 119.2, 95.8, 91.1, 62.1, 12.3; IR (neat): *v* 3059, 2935, 2897, 2813, 2199, 1951, 1584, 1461, 1446, 1364, 1046, 909, 798, 770, 750, 685 cm^{-1}; MS (EI): m/z (%) = 325 (M^+, 14.80), 252 (100), 253 (90.15), 294 (81.44), 250 (55.24), 241 (29.98), 295 (21.04), 251 (19.40), 176 (19.32)； HRMS (EI): calculated for $[C_{23}H_{19}NO]^+$ 325.1467, found: 325.1466.

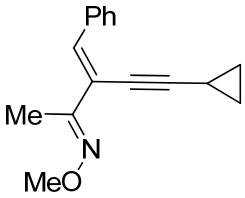
5. Substrate 1e.



Yellow oil, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.36-7.25 (m, 3H), 7.06 (s, 1H), 3.98 (s, 3H), 2.49 (t, *J* = 6.8 Hz, 2H), 2.11 (s, 3H), 1.65-1.58 (m, 2H), 1.58-1.45 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 135.9, 135.1, 129.2, 128.4, 128.0, 119.1, 99.3, 77.5, 61.8, 30.4, 21.9, 19.5, 13.5, 12.4; IR (neat): *v* 2937, 2897, 2871, 2818, 2361, 2210, 1614, 1491, 1464, 1364, 1325, 1285, 1247, 1184, 1127, 1050, 884, 757, 690 cm^{-1}; MS (EI): m/z (%) =

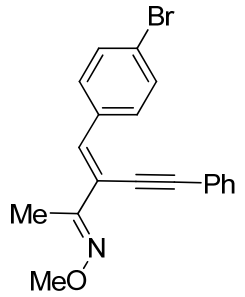
255 (M^+, 12.70), 115 (100), 139 (98.57), 141 (85.61), 140 (65.78), 128 (65.65), 77 (61.43), 91 (54.73), 43 (54.72)； HRMS (EI): calculated for $[C_{17}H_{21}NO]^+$ 255.1623, found: 255.1624.

6. Substrate 1f.



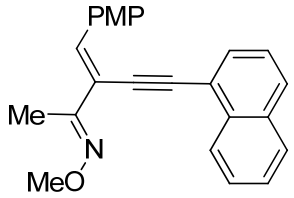
Yellow oil, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.36-7.27 (m, 3H), 7.05 (s, 1H), 3.97 (s, 3H), 2.10 (s, 3H), 1.54-1.47 (m, 1H), 0.91-0.81 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 135.9, 135.2, 129.1, 128.5, 128.0, 119.0, 102.2, 72.7, 61.8, 12.5, 8.6, 0.7; IR (neat): *v* 2937, 2816, 2214, 1613, 1491, 1446, 1366, 1283, 1183, 1151, 1047, 888, 839, 754 cm^{-1}; MS (EI): m/z (%) = 239 (M^+, 48.61), 165 (100), 208 (95.01), 152 (67.41), 139 (60.33), 167 (49.01), 239 (48.61), 180 (38.03), 115 (35.69)； HRMS (EI): calculated for $[C_{16}H_{17}NO]^+$ 239.1310, found: 239.1310.

7. Substrate 1g.



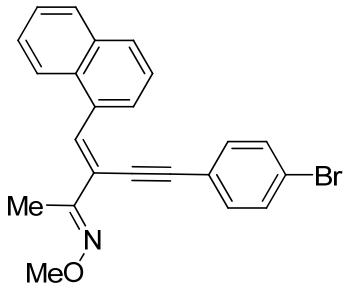
Yellow solid, 94% yield, m.p. 68-69 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.53-7.49 (m, 4H), 7.40-7.36 (m, 3H), 7.14 (s, 1H), 4.01 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 134.8, 134.7, 131.5, 131.4, 131.0, 128.8, 128.5, 122.9, 122.8, 119.4, 98.1, 86.4, ,62.1, 12.6; IR (neat): *v* 2970, 2934, 2897, 2820, 2202, 1585, 1488, 1437, 1362, 1185, 1061, 1043, 908, 887, 840, 755, 692 cm^{-1}; MS (EI): m/z (%) = 353 (M^+, 8.16), 355 (M^++2, 7.68), 202 (100), 200 (38.44), 218 (31.96), 243 (30.24), 201 (26.08), 203 (20.80), 189 (16.30), 269 (14.78)； HRMS (EI): calculated for $[C_{19}H_{16}NOBr]^+$ 353.0415, found: 353.0417.

8. **Substrate 1h.**



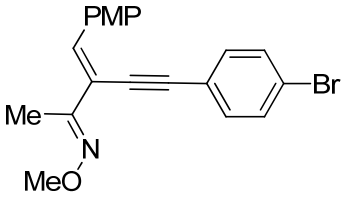
Yellow solid, 92% yield, m.p. 99-100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.86 (t, *J* = 7.4 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.58-7.52 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.19 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.10 (s, 3H), 3.86 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 155.5, 136.0, 133.5, 133.2, 131.3, 130.2, 128.8, 128.2, 126.7, 126.5, 125.3, 121.2, 116.8, 113.8, 95.6, 91.5, 62.1, 55.3, 12.3; IR (neat): *v* 3016, 2930, 2835, 2814, 2360, 2192, 1602, 1509, 1254, 1181, 1048, 909, 800, 771 cm^{-1}; MS (EI): m/z (%) = 355 (M^+, 50.24), 239 (100), 324 (82.26), 283 (58.53), 355 (50.24), 252 (41.95), 271 (40.47), 240 (37.06), 268 (32.12)； HRMS (EI): calculated for $[C_{24}H_{21}NO_2]^+$ 355.1572, found: 355.1576.

9. Substrate 1i.



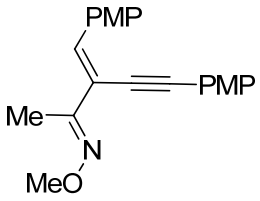
Yellow solid, 94% yield, m.p. 78-79 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.2 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.93 (s, 1H), 7.88 (t, *J* = 8.4 Hz, 2H), 7.57-7.51 (m, 3H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.06 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 134.5, 133.4, 132.8, 132.6, 131.7, 131.4, 129.2, 128.6, 127.2, 126.3, 125.8, 124.9, 123.8, 122.6, 122.0, 121.0, 94.7, 87.6, 62.1, 12.5; IR (neat): *v* 2049, 2934, 2817, 1897, 1587, 1506, 1393, 1042, 903, 819, 769, 758, 680 cm^{-1}; MS (EI): m/z (%) = 403 (M^+, 3.52), 405 (M^++2, 3.52), 252 (100), 250 (36.89), 372 (24.16), 253 (22.24), 374 (20.92), 251 (11.54), 126 (10.37), 239 (8.88)； HRMS (EI): calculated for $[C_{23}H_{18}NOBr]^+$ 403.0572, found: 403.0583.

10. **Substrate 1j.**



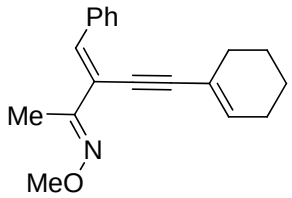
Yellow solid, 82% yield, m.p. 62-63 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.17 (s, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.00 (s, 3H), 3.85 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 155.2, 136.5, 132.8, 131.7, 131.2, 128.6, 122.7, 122.3, 116.0, 113.7, 95.8, 88.2, 62.0, 55.3, 12.5; IR (neat): *v* 2936, 2838, 2027, 1894, 1760, 1605, 1591, 1509, 1486, 1305, 1255, 1177, 1114, 1039, 908, 820 cm^{-1}; MS (EI): m/z (%) = 383 (M^+, 19.24), 385 (M^++2, 19.78), 232 (100), 189 (92.46), 187 (32.34), 299 (31.62), 217 (30.01), 188 (29.29), 301(29.27), 233 (22.66)； HRMS (EI): calculated for $[C_{20}H_{18}NO_2Br]^+$ 383.0521, found: 383.0533.

11. **Substrate 1k.**



Yellow solid, 88% yield, m.p. 96-97 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 6.90 (t, *J* = 8.6 Hz, 4H), 4.00 (s, 3H), 3.84 (d, *J* = 3.6 Hz, 6H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 159.8, 155.7, 135.2, 132.9, 131.1, 128.9, 116.4, 115.5, 114.1, 113.6, 97.2, 85.8, 61.9, 55.29, 55.26, 12.7; IR (neat): *v* 2966, 2935, 2838, 2361, 2197, 1602, 1508, 1255, 1245, 1169, 1051, 1026, 879, 832, 808 cm^{-1}; MS (EI): m/z (%) = 335 (M^+, 55.71), 176 (100), 304 (88.93), 202 (86.99), 263 (83.83), 251 (80.49), 203 (66.26), 151(63.44), 189 (61.34)； HRMS (EI): calculated for $[C_{21}H_{21}NO_2]^+$ 335.1572, found: 335.1574.

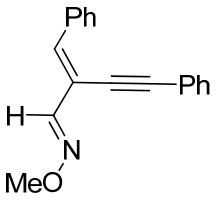
12. **Substrate 1l.**



Yellow oil, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.6 Hz, 2H),

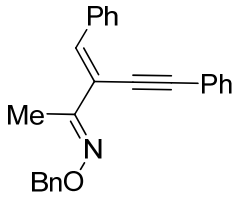
7.37-7.30 (m, 2H), 7.30-7.25 (m, 1H), 7.10 (s, 1H), 6.21 (bs, 1H), 3.98 (s, 3H), 2.24 （s, 2H), 2.23-2.07 (m, 5H), 1.71-1.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 136.0, 135.8, 135.0, 129.4, 128.5, 128.1, 120.9, 118.9, 99.6, 84.2, 61.9, 28.6, 25.8, 22.2, 21.4, 12.6; IR (neat): *v* 3023, 2934, 2190, 1947, 1610, 1491, 1446, 1365, 1176, 1049, 918, 896, 862, 754, 690 cm^{-1}; MS (EI): m/z (%) = 279 (M^+, 16.28), 248 (100), 165 (50.43), 152 (32.09), 178 (32.03), 115 (29.09), 179 (25.63), 139 (24.05), 77 (23.63)； HRMS (EI): calculated for $[C_{19}H_{21}NO]^+$ 279.1623, found: 279.1624.

13. **Substrate 1m.**



Yellow oil, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.91 (s, 1H), 7.60-7.56 (m, 2H), 7.44-7.34 (m, 6H), 6.92 (s, 1H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 140.9, 135.5, 131.7, 129.5, 129.3, 128.7, 128.4, 128.3, 123.0, 115.6, 98.1, 84.4, 62.1; IR (neat): *v* 3060, 2937, 2899, 2816, 2498, 2207, 1956, 1885, 1675, 1597, 1490, 1463, 1444, 1170, 1049, 938, 917, 754, 730, 688 cm^{-1}; MS (EI): m/z (%) = 261 (M^+, 25.67), 202 (100), 203 (93.86), 230 (89.88), 191 (38.22), 115 (26.18), 261 (25.67), 201 (24.42), 200 (22.01)； HRMS (EI): calculated for $[C_{18}H_{15}NO]^+$ 261.1154, found: 261.1152.

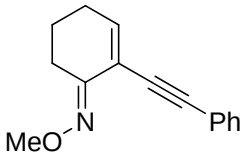
14. **Substrate 1n.**



Yellow solid, 75% yield, m.p. 93-94 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.53-7.33 (m, 13H), 7.22 (s, 1H), 5.28 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 137.8, 136.3, 135.8, 131.5, 129.6, 128.8, 128.5, 128.4, 128.3, 128.2, 127.8, 123.2, 118.7, 97.4, 86.7, 76.3, 12.8; IR (neat): *v* 3025, 2945, 2889, 2358, 1490, 1371, 1279, 1215, 1025, 995, 941, 750, 687 cm^{-1}; MS (EI): m/z (%) = 351 (M^+, 11.90), 191 (100), 91 (80.02), 202 (50.03), 203 (39.28), 77 (24.57), 200 (23.71), 189 (21.85), 230 (18.38)； HRMS (EI): calculated for $[C_{25}H_{21}NO]^+$ 351.1623,

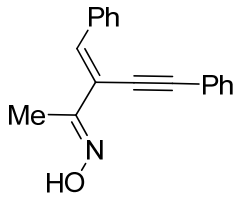
found: 351.1624.

15. **Substrate 1o.**



Yellow oil, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.49 (m, 2H), 7.34-7.30 (m, 3H), 6.69 (t, J = 4.6 Hz, 1H), 3.99 (s, 3H), 2.62 (t, J = 6.6 Hz, 2H), 2.32-2.27 (m, 2H), 1.79-1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 142.7, 131.6, 128.1, 128.0, 123.4, 119.3, 90.3, 85.4, 62.0, 25.6, 22.7, 20.3; IR (neat): v 2937, 2817, 2220, 1968, 1596, 1489, 1442, 1045, 921, 866, 755, 691 cm^{-1}; MS (EI): m/z (%) = 225 (M^+, 65.63), 77 (100), 210 (81.86), 79 (79.76), 182 (65.75), 225 (65.63), 115 (58.92), 139 (56.84), 107 (45.34)；HRMS (EI): calculated for $[C_{15}H_{15}NO]^+$ 225.1154, found: 225.1152.

16. **Substrate 1p.**

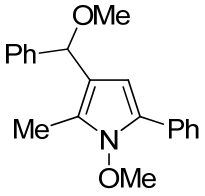


White solid, 23% yield, m.p. 161-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.79 (s, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.61(t, J = 2.6 Hz, 2H), 7.43-7.35 (m, 6H), 7.16 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 136.9, 135.8, 131.8, 129.7, 129.0, 128.5, 128.30, 128.27, 123.1, 119.4, 97.6, 85.8, 11.0; IR (neat): v 3675, 2989, 2902, 2198, 1662, 1597, 1442, 1276, 1014, 938, 914, 758, 749, 685 cm^{-1}; MS (EI): m/z (%) = 261 (M^+, 22.62), 203 (100), 202 (91.69), 191 (41.19), 244 (36.50), 201 (23.33), 200 (22.91), 261 (22.62), 77 (21.49)；HRMS (EI): calculated for $[C_{18}H_{15}NO]^+$ 261.1154, found: 261.1153.

2.2 General Procedure for Gold(I)-Catalyzed Cyclization of Oximes 1 and Nucleophiles:

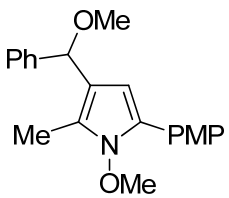
In a dry Schlenk tube, a mixture of IPrAuCl (12.4 mg, 0.02 mmol, 5 mol %) and $AgSbF_6$ (6.9 mg, 0.02 mmol, 5 mol %) in DCM (2 mL) was stirred at room temperature under nitrogen for 20 mins to generate the gold catalyst. The premixed catalyst solution was added sequentially to a solution of oxime **1** (0.4 mmol), methanol **2a** (5.0 eq.) and 100 mg of activated 4Å molecular sieves powder (MS) in DCM (2 mL) at room temperature under nitrogen. After stirring for 5 h, the reaction was complete determined by TLC analysis. The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by flash column chromatography on neutral aluminum oxide or silica gel (hexanes/ethyl acetate=20:1) to afford the pure product **3**.

17. 1-methoxy-3-(methoxy(phenyl)methyl)-2-methyl-5-phenyl-1H-pyrrole (3a).



Yellow oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (t, *J* = 4.2 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.36-7.29 (m, 4H), 7.25 (t, *J* = 6.8 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.00 (s, 1H), 5.22 (s, 1H), 3.68 (s, 3H), 3.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 131.3, 128.4, 128.2, 127.1, 126.7, 126.2, 126.1, 126.0, 123.8, 116.8, 102.8, 79.3, 65.3, 56.6, 8.7; IR (neat): *v* 2935, 2817, 1602, 1516, 1450, 1086, 971, 756 cm^{-1}; MS (EI): m/z (%) = 307 (M^+, 79.59), 276 (100), 307 (79.59), 102 (59.54), 244 (44.66), 77 (42.68), 245 (38.87), 202 (36.09), 203 (32.61)； HRMS (EI): calculated for $[C_{20}H_{21}NO_2]^+$ 307.1572, found: 307.1570.

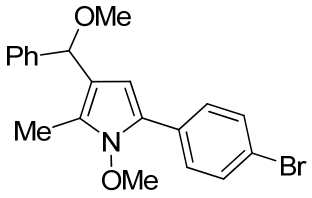
18. 1-methoxy-3-(methoxy(phenyl)methyl)-5-(4-methoxyphenyl)-2-methyl-1H-py rrole (3b).



Yellow oil, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.8 Hz, 2H), 7.41

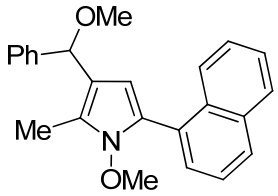
(d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 5.90 (s, 1H), 5.21 (s, 1H), 3.78 (s, 3H), 3.65 (s, 3H), 3.35 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 142.1, 128.2, 127.4, 127.0, 126.7, 126.1, 124.1, 122.9, 116.5, 113.8, 101.6, 79.3, 65.1, 56.5, 55.1, 8.7; IR (neat): v 2979, 2934, 2835, 2818, 2039, 1889, 1526, 1484, 1452, 1246, 1179, 1106, 1085, 972, 832, 790, 701 cm^{-1}; MS (EI): m/z (%) = 337 (M^+, 100.00), 337 (100), 306 (97.10), 250 (48.34), 275 (38.79), 265 (35.30), 274 (27.00), 307 (24.00), 338 (23.81)；HRMS (EI): calculated for $[C_{21}H_{23}NO_3]^+$ 337.1678, found: 337.1675.

19. 5-(4-bromophenyl)-1-methoxy-3-(methoxy(phenyl)methyl)-2-methyl-1H-pyrr ole (3c).



Yellow oil, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 8.4 Hz, 2H), 7.26 (t, J = 4.8 Hz, 1H), 6.00 (s, 1H), 5.21 (s, 1H), 3.68 (s, 3H), 3.36 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 131.5, 130.2, 128.3, 127.4, 127.2, 126.7, 125.0, 124.3, 119.8, 117.2, 103.1, 79.2, 65.4, 56.6, 8.7; IR (neat): v 2976, 2934, 2817, 2363, 1901, 1595, 1511, 1451, 1217, 1185, 1085, 1008, 827, 793 cm^{-1}; MS (EI): m/z (%) = 385 (M^+, 75.84), 387 (M^++2, 75.90), 354 (100), 356 (98.28), 387 (75.90), 385 (75.84), 202 (58.27), 101 (41.12), 102 (37.53), 77 (34.75)；HRMS (EI): calculated for $[C_{20}H_{20}NO_2Br]^+$ 385.0677, found: 385.0677.

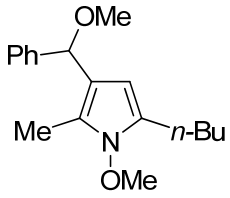
20. 1-methoxy-3-(methoxy(phenyl)methyl)-2-methyl-5-(naphthalen-1-yl)-1H-pyrr ole (3d).



Yellow solid, 87% yield, m.p. 97-98 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 9.2 Hz, 1H), 7.83-7.80 (m, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 6.8 Hz, 1H), 7.46-7.40 (m, 5H), 7.33 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 5.97 (s, 1H), 5.30

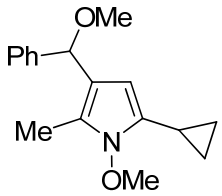
(s, 1H), 3.45 (s, 3H), 3.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 133.7, 132.0, 129.0, 128.2, 128.0, 127.9, 127.7, 127.1, 126.9, 126.5, 125.9, 125.6, 125.1, 124.5, 122.8, 116.4, 105.4, 79.6, 65.7, 56.6, 8.8; IR (neat): *v* 3047, 2939, 2930, 2815, 2360, 1953, 1841, 1736, 1590, 1498, 1454, 1383, 1066 cm^{-1}; MS (EI): m/z (%) = 357 (M^+, 100), 357 (100), 326 (97.00), 294 (83.73), 253 (58.95), 252 (45.15), 77 (40.13), 295 (31.37), 152 (30.84)；HRMS (EI): calculated for $[C_{24}H_{23}NO_2]^+$ 357.1729, found: 357.1727.

21. 5-butyl-1-methoxy-3-(methoxy(phenyl)methyl)-2-methyl-1H-pyrrole (3e).



Brown oil, 80% yield (NMR yield, because of the instability of **3e**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 6.4 Hz, 1H), 5.46 (s, 1H), 5.15 (s, 1H), 3.86 (s, 3H), 3.31 (s, 3H), 2.52-2.48 (m, 2H), 2.24 (s, 3H), 1.59-1.51 (m, 2H), 1.40-1.33 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 128.1, 127.5, 126.9, 126.7, 120.5, 115.1, 99.4, 78.4, 65.6, 56.4, 30.7, 24.6, 22.5, 13.9, 8.5; IR (neat): *v* 2956, 2933, 2871, 2816, 1601, 1492, 1451, 1380, 1186, 1082, 1030, 979, 700, 659 cm^{-1}; MS (EI): m/z (%) = 287 (M^+, 52.73), 256 (100), 287 (52.73), 183 (45.99), 115 (32.92), 141 (31.56), 182 (24.46), 257 (24.45), 244 (21.72)； HRMS (EI): calculated for $[C_{18}H_{25}NO_2]^+$ 287.1885, found: 287.1885.

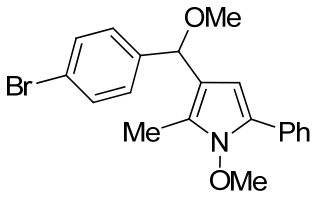
22. 5-cyclopropyl-1-methoxy-3-(methoxy(phenyl)methyl)-2-methyl-1H-pyrrole (3f).



Yellow oil, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.22 (m, 4H), 7.16-7.12 (m, 1H), 5.21 (s, 1H), 5.05 s, 1H), 3.87 (d, *J* = 1.6 Hz, 3H), 3.22 (d, *J* = 2.0 Hz, 3H), 2.16 (d, *J* = 1.6 Hz, 3H), 1.73-1.66 (m, 1H), 0.72-0.69 (m, 2H), 0.51-0.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 129.4, 128.1, 126.9, 126.7, 121.1, 114.7, 97.3, 79.3, 65.5, 56.4, 8.5, 6.8, 6.0, 5.7; IR (neat): *v* 3086, 3004, 2938, 2816, 1493, 1450, 1323, 1187, 1162, 1081, 1027, 978, 739, 701 cm^{-1}; MS (EI): m/z (%) = 271 (M^+,

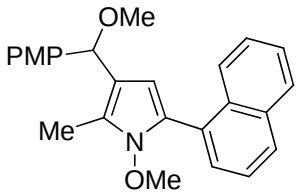
60.85), 240 (100), 208 (80.28), 150 (72.32), 77 (64.42), 271 (60.85), 115 (45.66), 121 (41.52), 91 (37.50)；HRMS (EI): calculated for $[C_{17}H_{21}NO_2]^+$ 271.1572, found: 271.1571.

23. 3-((4-bromophenyl)(methoxy)methyl)-1-methoxy-2-methyl-5-phenyl-1H-pyrrole (3g).



Yellow oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 8.4Hz, 2H), 7.37-7.30 (m, 4H), 7.21 (t, *J* = 7.4Hz, 1H), 5.98 (s, 1H), 5.20 (s, 1H), 3.70 (s, 3H), 3.37 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 131.3, 131.1, 128.46, 128.45, 126.3, 126.2, 126.0, 123.9, 120.9, 116.2, 102.7, 78.6, 65.4, 56.5, 8.7; IR (neat): *v* 2979, 2935, 2817, 1903, 1602, 1517, 1484, 1448, 1397, 1217, 1185, 1152, 1070, 1010, 970, 794, 756, 723, 695 cm^{-1}; MS (EI): m/z (%) = 385 (M^+, 17.66), 387 (M^++2, 17.77), 84 (100), 86 (67.78), 49 (60.42), 332 (47.41), 101 (45.68), 75 (45.50), 51 (39.40), 128 (36.75)；HRMS (EI): calculated for $[C_{20}H_{20}NO_2Br]^+$ 385.0677, found: 385.6076.

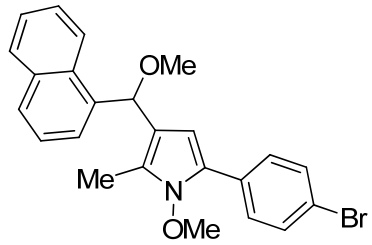
24. 1-methoxy-3-(methoxy(4-methoxyphenyl)methyl)-2-methyl-5-(naphthalen-1-yl)-1H-pyrrole (3h).



Yellow oil, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.6 Hz, 1H), 7.87-7.81 (m, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.50-7.44 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.00 (s, 1H), 5.28 (s, 1H), 3.81 (s, 3H), 3.50 (s, 3H), 3.41 (s, 3H), 2.39 (s, 3H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 134.2, 133.7, 132.1, 129.0, 128.1, 128.0, 127.9, 127.7, 126.5, 125.9, 125.6, 125.1, 124.4, 122.6, 116.7, 113.6, 105.4, 79.2, 65.7, 56.4, 55.2, 8.8; IR (neat): *v* 2935, 2835, 1611, 1583, 1526, 1510, 1483, 1463, 1440, 1302, 1285, 1244, 1173, 1107, 1082, 1032, 971 cm^{-1}; MS

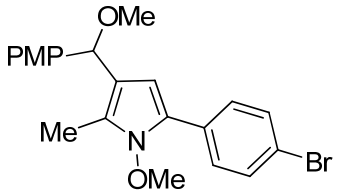
(EI): m/z (%) = 387 (M^+, 0.20), 336 (100), 367 (58.19), 305 (39.94), 337 (24.79), 132 (23.90), 280 (16.04), 135 (14.19), 368 (14.11)；HRMS (EI): calculated for $[C_{25}H_{25}NO_3]^+$ 387.1834, found: 387.1835.

25. 5-(4-bromophenyl)-1-methoxy-3-(methoxy(naphthalen-1-yl)methyl)-2-methyl -1H-pyrrole (3i).



Yellow oil, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.02 (m, 1H), 7.88-7.86 (m, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.48-7.45 (m, 6H), 5.91 (s, 1H), 5.89 (s, 1H), 3.69 (s, 3H), 3.46 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 133.9, 131.4, 131.1, 130.1, 128.7, 127.9, 127.3, 125.8, 125.3, 124.8, 124.5, 124.1, 123.8, 119.7, 116.5, 103.7, 76.8, 65.4, 56.8, 8.9; IR (neat): *v* 2935, 2817, 2243, 1946, 1595, 1510, 1437, 1216, 1185, 1152, 1077, 1008, 970, 908, 829, 779, 730 cm^{-1}; MS (EI): m/z (%) = 435 (M^+, 87.31), 437 (M^++2, 86.83), 406 (100), 404 (96.45), 435 (87.31), 437 (86.83), 252 (71.55), 374 (59.68), 127 (59.64), 152 (58.98)；HRMS (EI): calculated for $[C_{24}H_{22}NO_2Br]^+$ 435.0834, found: 435.0833.

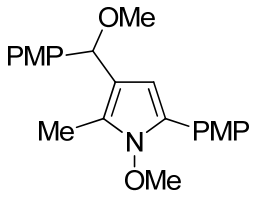
26. 5-(4-bromophenyl)-1-methoxy-3-(methoxy(4-methoxyphenyl)methyl)-2-meth yl-1H-pyrrole (3j).



Yellow oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz,, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.91] g (d, *J* = 8.8 Hz, 2H), 6.05 (s, 1H), 5.19 (s, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 134.0, 131.5, 130.2, 127.9, 127.3, 124.9, 124.1, 119.7, 117.4, 113.6, 103.0, 78.8, 65.3, 56.4, 55.1, 8.7; IR (neat): *v* 2934, 2816, 2022, 1890, 1611,

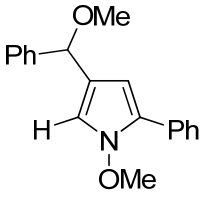
1509, 1463, 1439, 1302, 1244, 1171, 1079, 1034, 1008, 969, 827, 796 cm^{-1}; MS (EI): m/z (%) = 415 (M^+, 44.90), 417 (M^++2, 43.97), 386 (100), 384 (99.69), 415 (44.90), 417 (43.97), 189 (36.89), 355 (36.89), 353 (32.14), 151 (31.56)；HRMS (EI): calculated for $[C_{21}H_{22}NO_3Br]^+$ 415.0783, found: 415.07854.

27. 1-methoxy-3-(methoxy(4-methoxyphenyl)methyl)-5-(4-methoxyphenyl)-2-methyl-1H-pyrrole (3k).



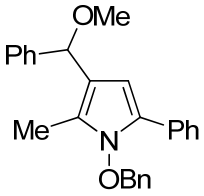
Yellow oil, 71% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 4H), 5.92 (s, 1H), 5.18 (s, 1H), 3.81 (s, 6H), 3.67 (s, 3H), 3.35 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 158.1, 134.3, 128.0, 127.4, 126.1, 124.2, 122.8, 116.8, 113.8, 113.6, 101.6, 79.0, 65.2, 56.4, 55.2, 8.7; IR (neat): *v* 29.35, 2834, 1612, 1583, 1527, 1510, 1483, 1303, 1285, 1244, 1173, 1083, 1033, 971, 833, 735 cm^{-1}; MS (EI): m/z (%) = 367 (M^+, 60.93), 305 (100), 336 (94.92), 367 (60.93), 132 (30.97), 306 (29.14), 290 (26.62), 337 (24.66), 249 (23.09)；HRMS (EI): calculated for $[C_{22}H_{25}NO_4]^+$ 367.1784, found: 367.1786.

28. 1-methoxy-4-(methoxy(phenyl)methyl)-2-phenyl-1H-pyrrole (3m).



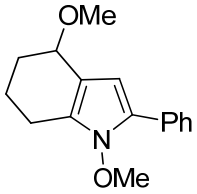
Yellow oil, 57% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.38-7.21 (m, 6H), 6.68 (s, 1H), 6.15 (s, 1H), 5.19 (s, 1H), 3.75 (s, 3H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 130.9, 128.4, 128.3, 128.1, 127.4, 126.9, 126.6, 121.5, 115.2, 103.3, 80.2, 66.6, 56.7; IR (neat): *v* 3063, 2934, 2817, 1953, 1884, 1813, 1602, 1509, 1452, 1345, 1263, 1186, 1124, 1087, 1005, 994, 914, 797, 759, 695, 663 cm^{-1}; MS (EI): m/z (%) = 293 (M^+, 74.96), 262 (100), 293 (74.96), 115 (48.91), 77 (47.71), 230 (42.17), 102 (37.19), 128 (30.14), 231 (29.93)；HRMS (EI): calculated for $[C_{19}H_{19}NO_2]^+$ 293.1416, found: 293.1414.

29. 1-(benzyloxy)-3-(methoxy(phenyl)methyl)-2-methyl-5-phenyl-1H-pyrrole (3n).



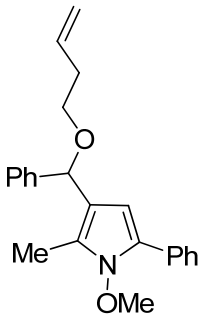
Yellow oil, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.36-7.18 (m, 11H), 6.06 (s, 1H), 5.20 (s, 1H), 4.74-4.69 (m, 2H), 3.35 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 133.7, 131.5, 129.8, 129.1, 128.5, 128.4, 128.2, 127.1, 126.7, 126.6, 126.3, 126.2, 124.6, 116.4, 102.9, 80.1, 79.2, 56.5, 9.0; IR (neat): *v* 3031, 2816, 1602, 1516, 1493, 1452, 1215, 1086, 1029, 952, 907, 752, 695 cm^{-1}; MS (EI): m/z (%) = 383 (M^+, 40.90), 91 (100), 77 (43.27), 383 (40.90), 352 (30.86), 115 (18.61), 102 (17.56), 65 (17.36), 202 (16.66)；HRMS (EI): calculated for $[C_{26}H_{25}NO_2]^+$ 383.1885, found: 383.1883.

30. 1,4-dimethoxy-2-phenyl-4,5,6,7-tetrahydro-1H-indole (3o).



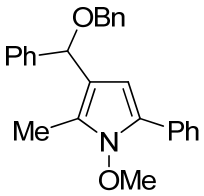
Yellow oil, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.25-7.20 (m, 1H), 6.23 (s, 1H), 4.28 (t, *J* = 3.8 Hz, 1H), 3.70 (s, 3H), 3.44 (s, 3H), 2.79-2.72 (m, 1H), 2.64-2.56 (m, 1H), 2.09-1.98 (m, 2H), 1.85-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.4, 128.5, 127.1, 126.7, 126.2, 113.8, 102.9, 72.6, 65.4, 56.0, 28.7, 20.7, 18.3; IR (neat): *v* 3062, 2934, 2816, 1602, 1484, 1397, 1329, 1217, 1070, 1010, 970, 795, 756, 723, 695 cm^{-1}; MS (EI): m/z (%) = 257 (M^+, 33.66), 194 (100), 226 (53.29), 257 (33.66), 193 (31.56), 91 (28.58), 225 (24.70), 165 (23.35), 195 (23.05)； HRMS (EI): calculated for $[C_{16}H_{19}NO_2]^+$ 257.1416, found: 257.1417.

31. 3-((but-3-enyloxy)(phenyl)methyl)-1-methoxy-2-methyl-5-phenyl-1H-pyrrole (3q).



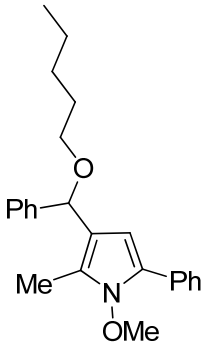
White solid, 68% yield, m.p. 54-55 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.59 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.35-7.24 (m, 5H), 7.19-7.15 (m, 1H), 5.95 (s, 1H), 5.87-5.82 (m, 1H), 5.34 (s, 1H), 5.10-5.01 (m, 2H), 3.68 (s, 3H), 3.53-3.47 (m, 2H), 2.44-2.39 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 135.6, 131.4, 128.4, 128.2, 127.1, 126.9, 126.04, 125.97, 123.8, 117.0, 116.1, 103.1, 77.8, 68.1, 65.3, 34.4, 8.8 ; IR (neat): *v* 3086, 2978, 2930, 2852, 2361, 1642, 1602, 1517, 1492, 1448, 1301, 1185, 1149, 1111, 990, 910,762, 746, 698 cm^{-1}; MS (EI): m/z (%) = 347 (M^+, 73.13), 276 (100), 347 (73.13), 102 (65.26), 244 (53.57), 202 (44.66), 245 (43.84), 246 (40.20), 203 (37.37)；HRMS (EI): calculated for $[C_{23}H_{25}NO_2]^+$ 347.1885, found: 347.1888.

32. 3-(benzyloxy(phenyl)methyl)-1-methoxy-2-methyl-5-phenyl-1H-pyrrole (3r).



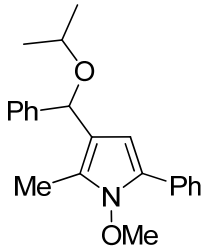
White solid, 89% yield, m.p. 83-84 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 1.2 Hz, 2H), 7.60 (d, *J* = 1.2 Hz, 2H), 7.46-7.23 (m, 11H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.03 (s, 1H), 5.41 (s, 1H), 4.60-4.50 (m, 2H), 3.68 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 138.6, 131.3, 128.4, 128.2, 127.9, 127.4, 127.1, 126.9, 126.1, 126.0, 125.9, 124.0, 116.6, 103.2, 76.3, 70.1, 65.3, 8.7; IR (neat): *v* 3031, 2853, 1601, 1515, 1494, 1448, 1303, 1217, 1149, 1107, 1055, 965, 749, 699 cm^{-1}; MS (EI): m/z (%) = 383 (M^+, 33.88), 91 (100), 246 (81.64), 77 (62.58), 102 (57.15), 245 (45.83), 276 (40.25), 202 (39.45), 383 (33.88)；HRMS (EI): calculated for $[C_{26}H_{25}NO_2]^+$ 383.1885, found: 383.1885.

33. 1-methoxy-2-methyl-3-(pentyloxy(phenyl)methyl)-5-phenyl-1H-pyrrole (3s).



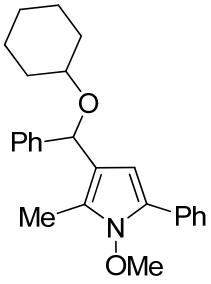
Yellow oil, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.59 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.35-7.24 (m, 5H), 7.23-7.15 (m, 1H), 5.94 (s, 1H), 5.31 (s, 1H), 3.68 (s, 3H), 3.47-3.40 (m, 2H), 2.32 (s, 3H), 1.66-1.61 (m, 2H), 1.38-1.30 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 131.4, 128.4, 128.2, 127.0, 126.9, 126.00, 125.95, 123.7, 117.3, 103.1, 77.7, 68.9, 65.3, 29.6, 28.5, 22.5, 14.0, 8.8; IR (neat): *v* 3062, 2932, 2858, 1949, 1720, 1603, 1516, 1451, 1217, 1088, 1029, 973, 756 cm^{-1}; MS (EI): m/z (%) = 363 (M^+, 59.65), 276 (100), 363 (59.65), 244 (37.21), 246 (36.81), 102 (27.29), 245 (27.17), 277 (24.64), 105 (19.42)；HRMS (EI): calculated for $[C_{24}H_{29}NO_2]^+$ 363.2198, found: 363.2198.

34. 3-(isopropoxy(phenyl)methyl)-1-methoxy-2-methyl-5-phenyl-1H-pyrrole (3t).



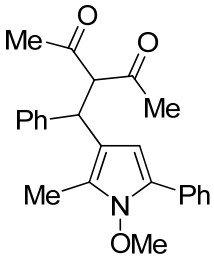
White solid, 79% yield, m.p. 37-38 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.35-7.29 (m, 4H), 7.25-7.21 (m, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 5.94 (s, 1H), 5.47 (s, 1H), 3.68-3.62 (m, 4H), 2.33 (s, 3H), 1.24(d, *J* = 6.0 Hz, 3H), 1.19 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 131.4, 128.4, 128.1, 126.9, 126.0, 125.92, 125.87, 123.5, 117.4, 103.2, 74.4, 68.3, 65.3, 22.6, 21.8, 8.7 ; IR (neat): *v* 3059, 2970, 2937, 1601, 1515, 1493, 1450, 1370, 1118, 1037, 1026, 974, 760 cm^{-1}; MS (EI): m/z (%) = 335 (M^+, 89.62), 276 (100), 335 (89.62), 246 (64.03), 244 (52.35), 102 (50.46), 105 (39.22), 245 (33.28), 77 (30.21)；HRMS (EI): calculated for $[C_{22}H_{25}NO_2]^+$ 335.1885, found: 335.1887.

35. 4-(cyclohexyloxy(phenyl)methyl)-1-methoxy-2-phenyl-1H-pyrrole (3u).



Yellow oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.34-7.19 (m, 5H), 7.15 (t, *J* = 7.4 Hz, 1H), 5.90 (s, 1H), 5.54 (s, 1H), 3.66 (s, 3H), 3.35-3.29 (m, 1H), 2.32 (s, 3H), 2.06 (d, *J* = 11.6 Hz, 1H), 1.90 (d, *J* = 11.6 Hz, 1H), 1.81-1.72 (m, 2H), 1.54-1.44 (m, 1H), 1.41-1.35 (m, 2H), 1.26-1.12 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 131.4, 128.3, 128.1, 127.0, 126.9, 125.9, 125.8, 123.5, 117.5, 103.3, 74.6, 74.0, 65.3, 32.8, 32.3, 25.8, 24.4, 24.3, 8.7; IR (neat): *v* 2930, 2855, 1948, 1811, 1602, 1449, 1069, 1026, 972, 756 cm^{-1}; MS (EI): m/z (%) = 375 (M^+, 30.38), 276 (100), 102 (58.27), 107 (55.86), 244 (46.04), 245 (45.51), 307 (44.37), 55 (41.84), 77 (41.35)；HRMS (EI): calculated for $[C_{25}H_{29}NO_2]^+$ 375.2198, found: 375.2195.

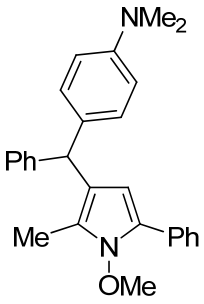
36. 3-((1-methoxy-2-methyl-5-phenyl-1H-pyrrol-3-yl)(phenyl)methyl)pentane-2,4-dione (3v).



Brown solid, 99% yield, m.p. 87-88 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.29-7.24 (m, 4H), 7.22-7.18 (m, 1H), 7.17-7.14 (m, 1H), 6.14 (s, 1H), 4.67-4.61 (m, 2H), 3.61 (s, 3H), 2.26 (s, 3H), 2.09 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.4, 203.2, 142.1, 131.1, 128.7, 128.5, 127.7, 126.6, 126.5, 126.2, 125.9, 122.5, 115.8, 101.5, 74.6, 65.3, 43.2, 30.1, 29.5, 8.4; IR (neat): *v* 2938, 2361, 2342, 1733, 1698, 1602, 1352, 1221, 1188, 1159, 968, 909, 754, 677 cm^{-1}; MS (EI): m/z (%) = 375 (M^+, 38.82), 276 (100), 43 (54.50), 244

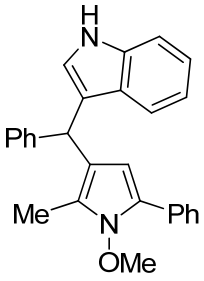
(42.61), 375 (38.82), 245 (26.76), 202 (24.47), 102 (23.57), 277 (20.983); HRMS (EI): calculated for $[C_{24}H_{25}NO_3]^+$ 375.1834, found: 375.1837. Enantiomeric excess was determined by HPLC with a Chiral AD-H column (hexanes:2-propanol = 99:1, 0.8 mL/min, 254 nm); major enantiomer t_r = 16.4 min, minor enantiomer t_r = 18.9 min (51% *ee*, 85% yield).

37. 4-((1-methoxy-2-methyl-5-phenyl-1H-pyrrol-3-yl)(phenyl)methyl)-N,N-dimethylaniline (3w).



Yellow oil, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.31-7.23 (m, 4H), 7.20-7.12 (m, 4H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 5.86 (s, 1H), 5.23 (s, 1H), 3.68 (s, 3H), 2.90 (s, 6H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 145.4, 132.8, 131.6, 129.6, 128.9, 128.4, 128.0, 125.71, 125.67, 125.4, 122.9, 119.1, 112.5, 104.6, 65.3, 47.9, 40.7, 8.8; IR (neat): *v* 2933, 2852, 2798, 1951, 1602, 1517, 1447, 1345, 1161, 1072, 972, 802, 756, 696 cm^{-1}; MS (EI): m/z (%) = 396 (M^+, 72.97), 365 (100), 396 (72.97), 366 (30.63), 397 (21.9), 202 (21.70), 203 (15.21), 77 (15.07), 319 (14.77); HRMS (EI): calculated for $[C_{27}H_{28}N_2O]^+$ 396.2202, found: 396.2202.

38. 3-((1-methoxy-2-methyl-5-phenyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-indole (3x).



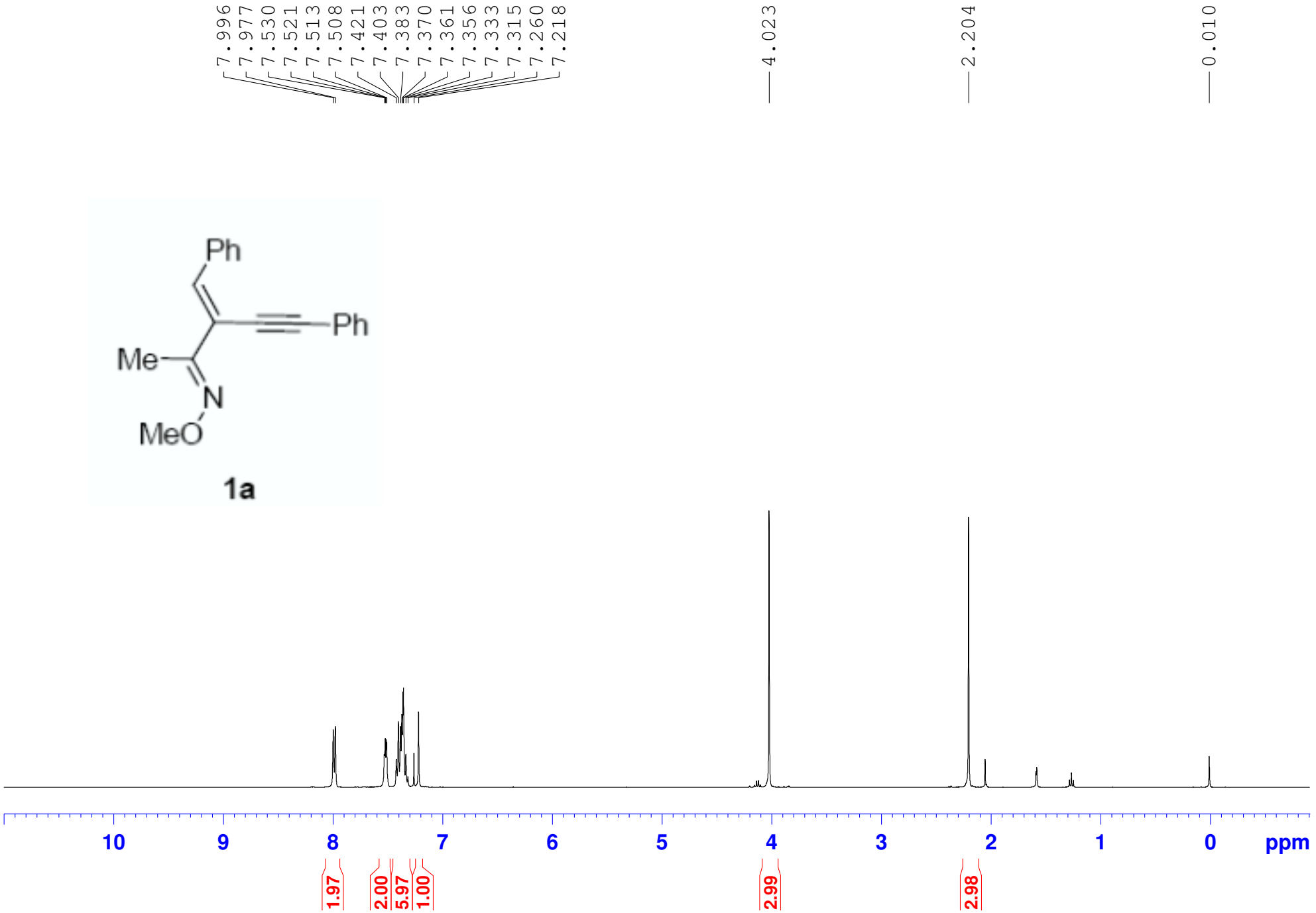
Brown solid, 83% yield, m.p. 79-81 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (bs, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.31-7.22 (m, 8H), 7.20-7.11 (m, 3H), 6.97 (t, *J* = 7.6 Hz,

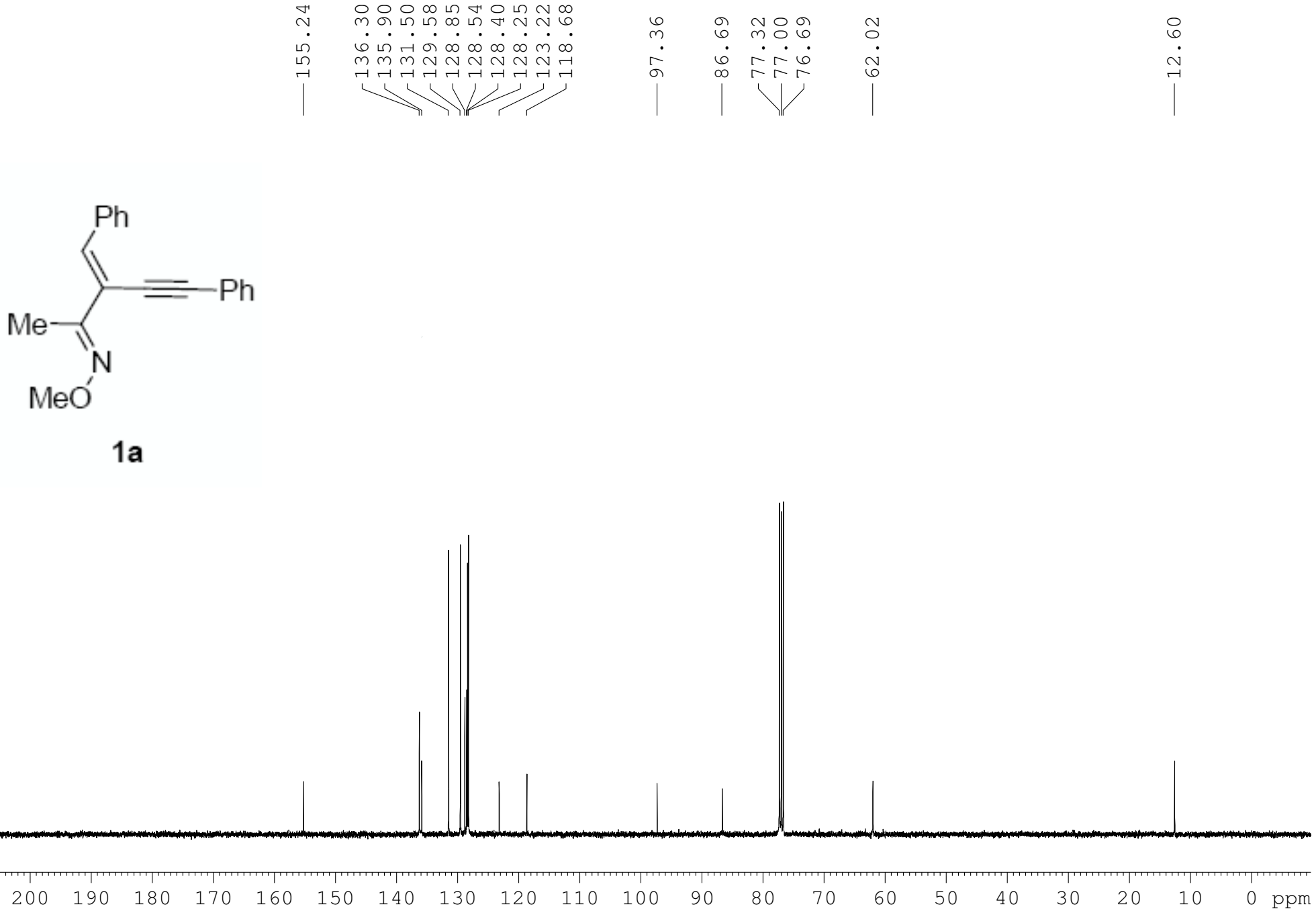
1H), 6.71 (s, 1H), 5.94 (s, 1H), 5.48 (s, 1H), 3.68 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 136.7, 131.6, 128.6, 128.4, 128.1, 127.1, 125.9, 125.72, 125.65, 125.5, 123.5, 122.7, 121.8, 120.1, 119.9, 119.1, 118.7, 110.9, 104.3, 65.3, 40.6, 8.7; IR (neat): *v* 3568, 3413, 3024, 2937, 1882, 1810, 1601, 1513, 1492, 1337, 1217, 1184, 1147, 970, 913, 845, 756, 743, 702 cm^{-1}; MS (EI): m/z (%) = 392 (M^+, 100), 392 (100), 361 (90.82), 393 (30.42), 362 (30.04), 77 (25.38), 243 (22.73), 242 (21.41), 241 (21.40)； HRMS (EI): calculated for $[C_{27}H_{24}N_2O]^+$ 392.1889, found: 392.8818.

Reference.

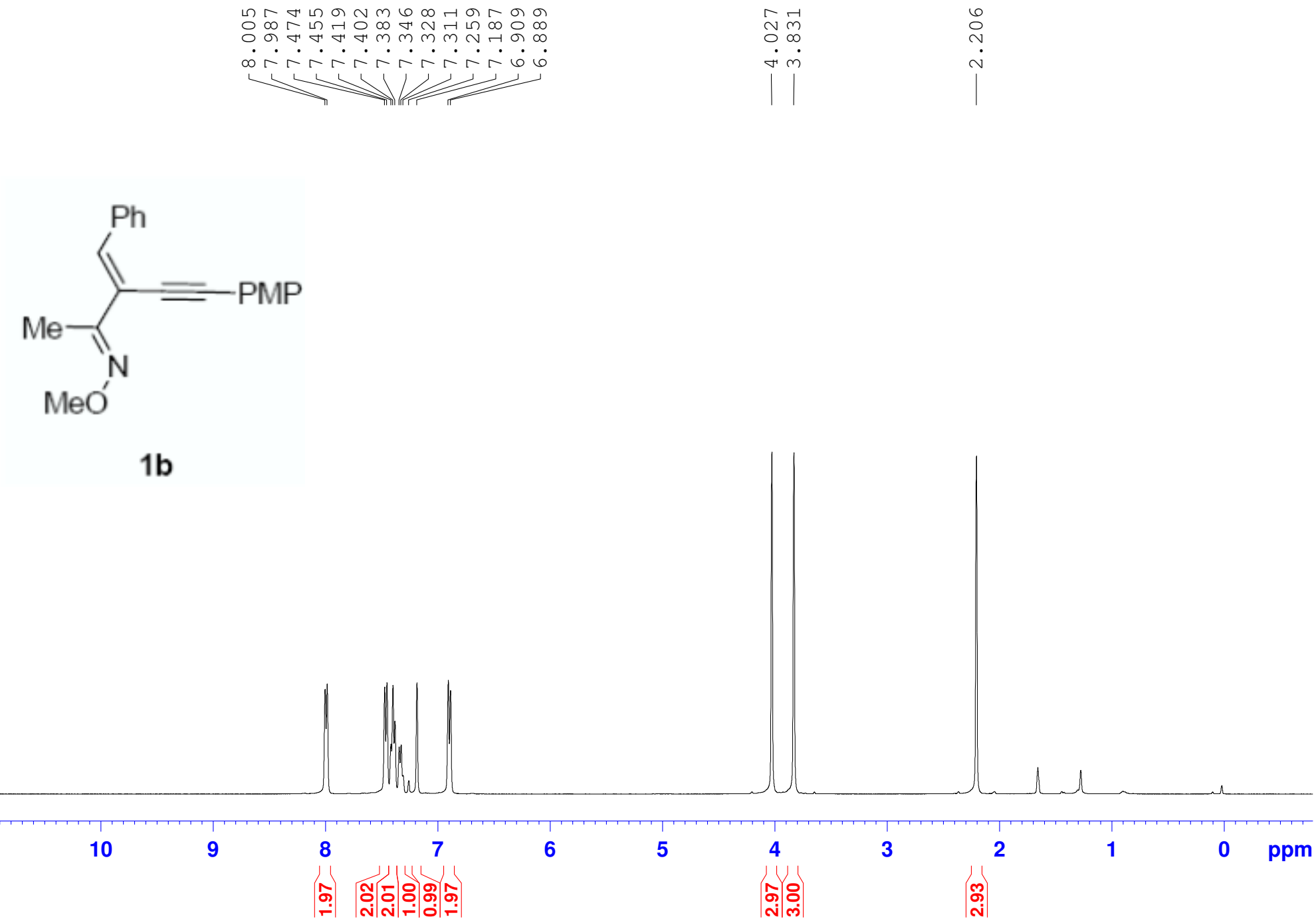
1. T. Yao, X. Zhang and R. C. Larock, *J. Am. Chem. Soc*. 2004, **126**, 111645.

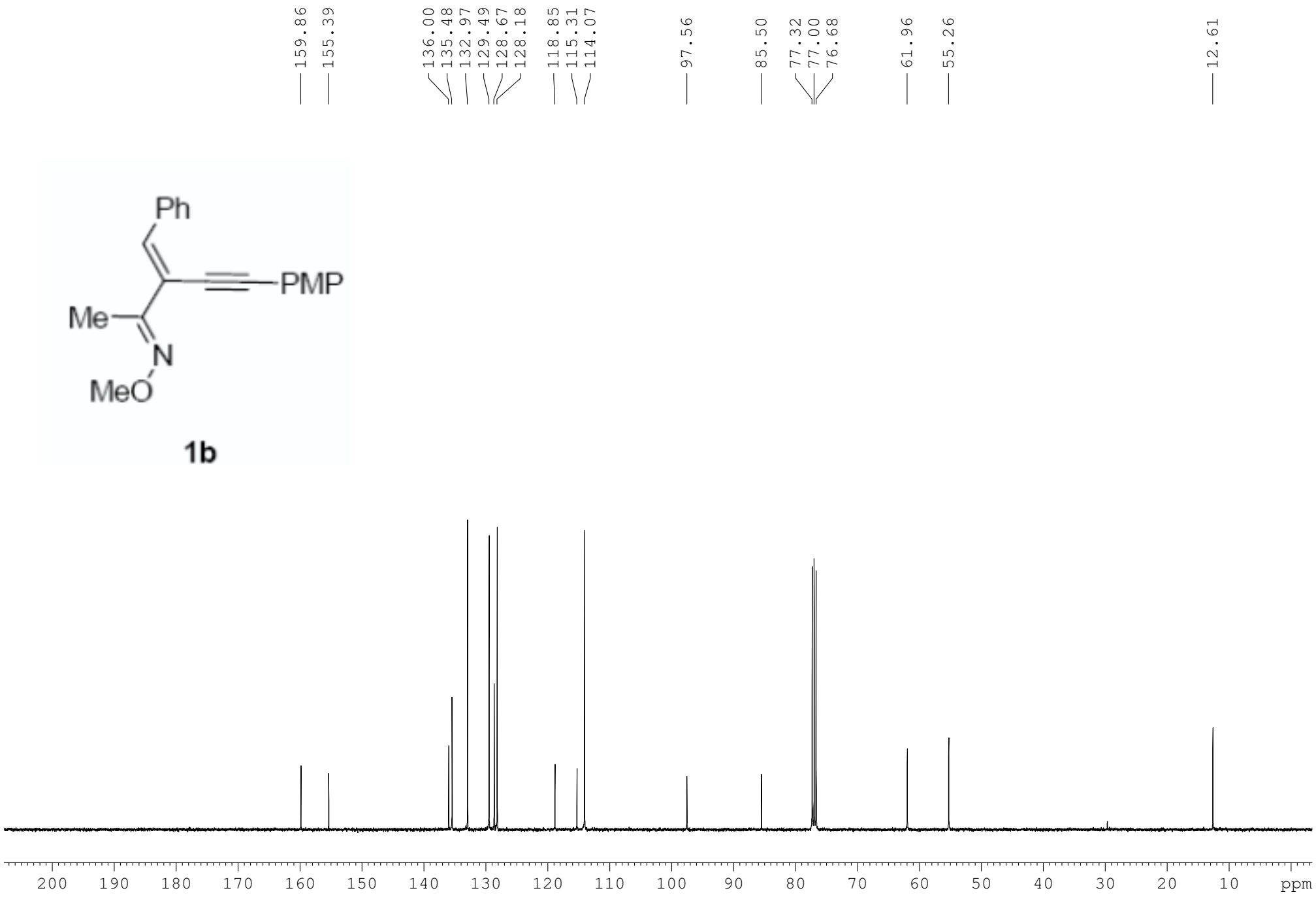
3. ^{1}H and ^{13}C NMR Spectra for New Compounds





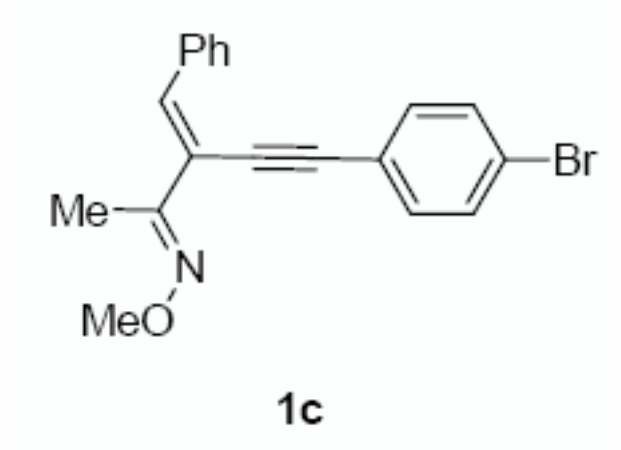
1a



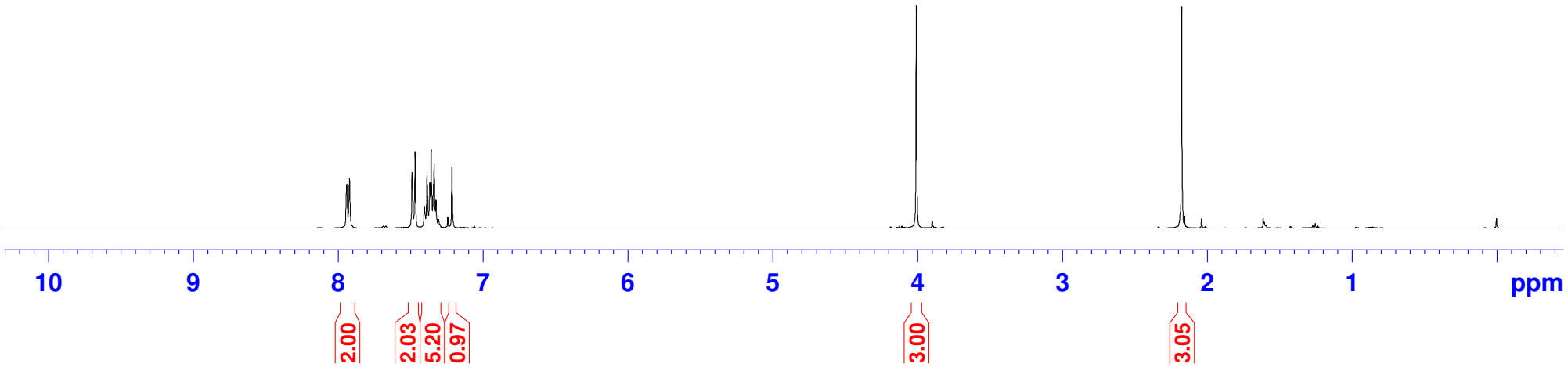


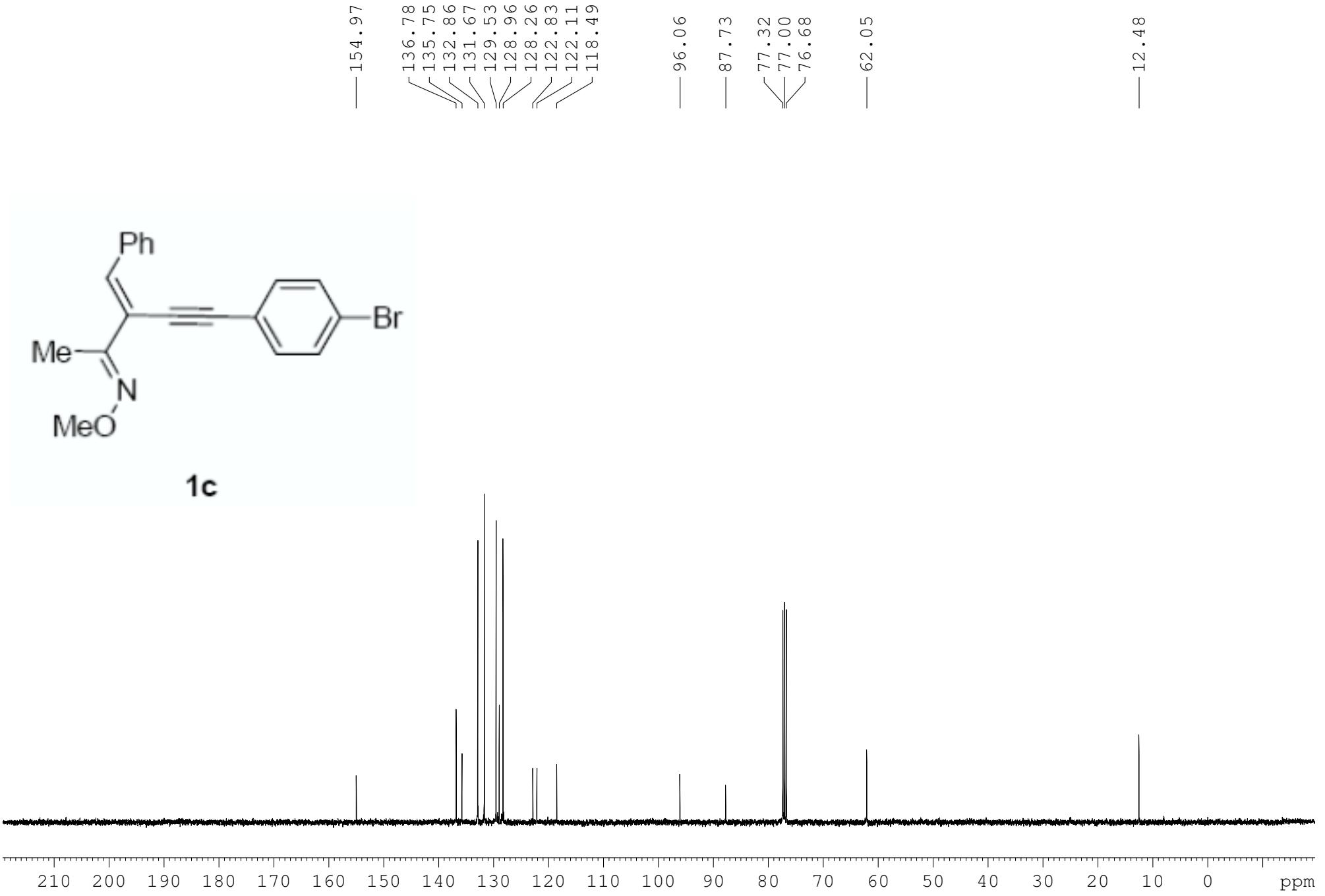
zm-c-82 H

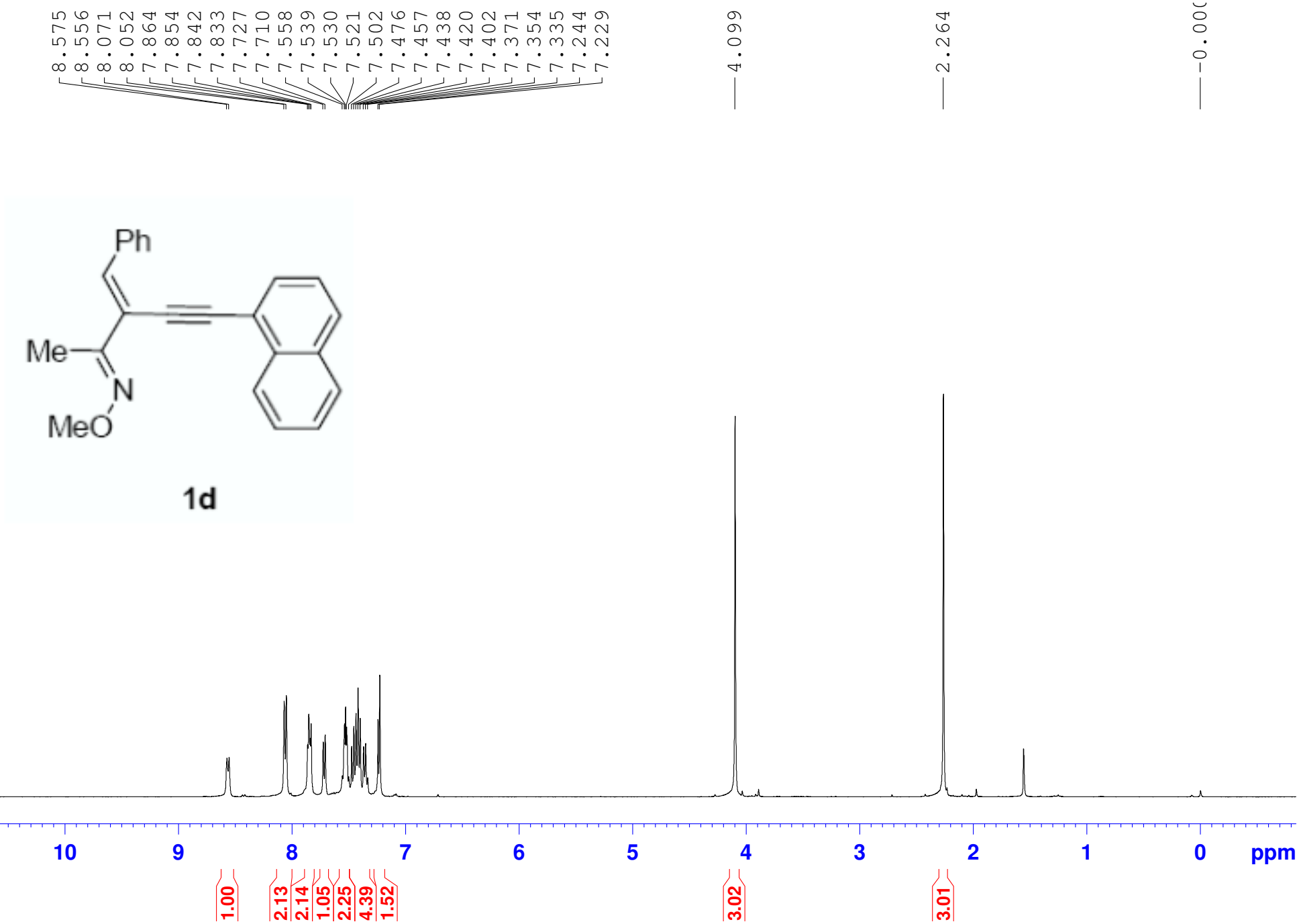
7.940
7.921
7.489
7.468
7.403
7.385
7.366
7.357
7.341
7.336
7.324
7.306
7.243
7.213
4.007
2.174
0.000



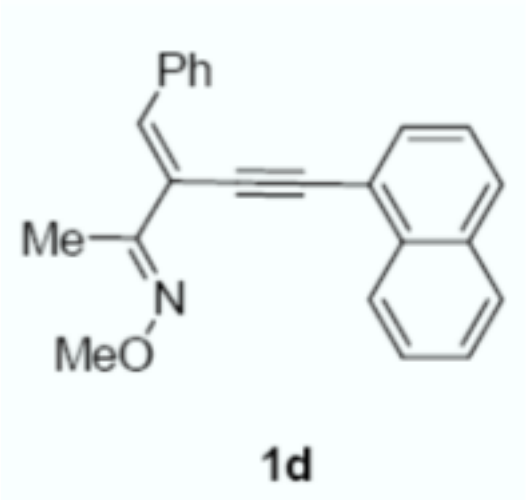
1c



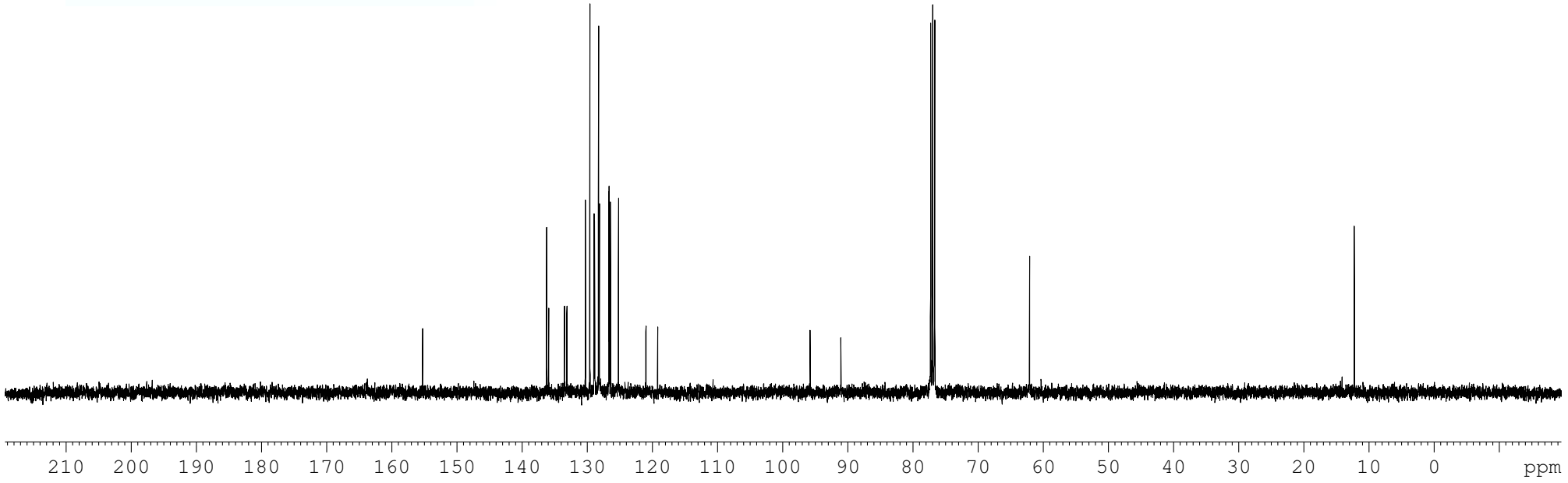


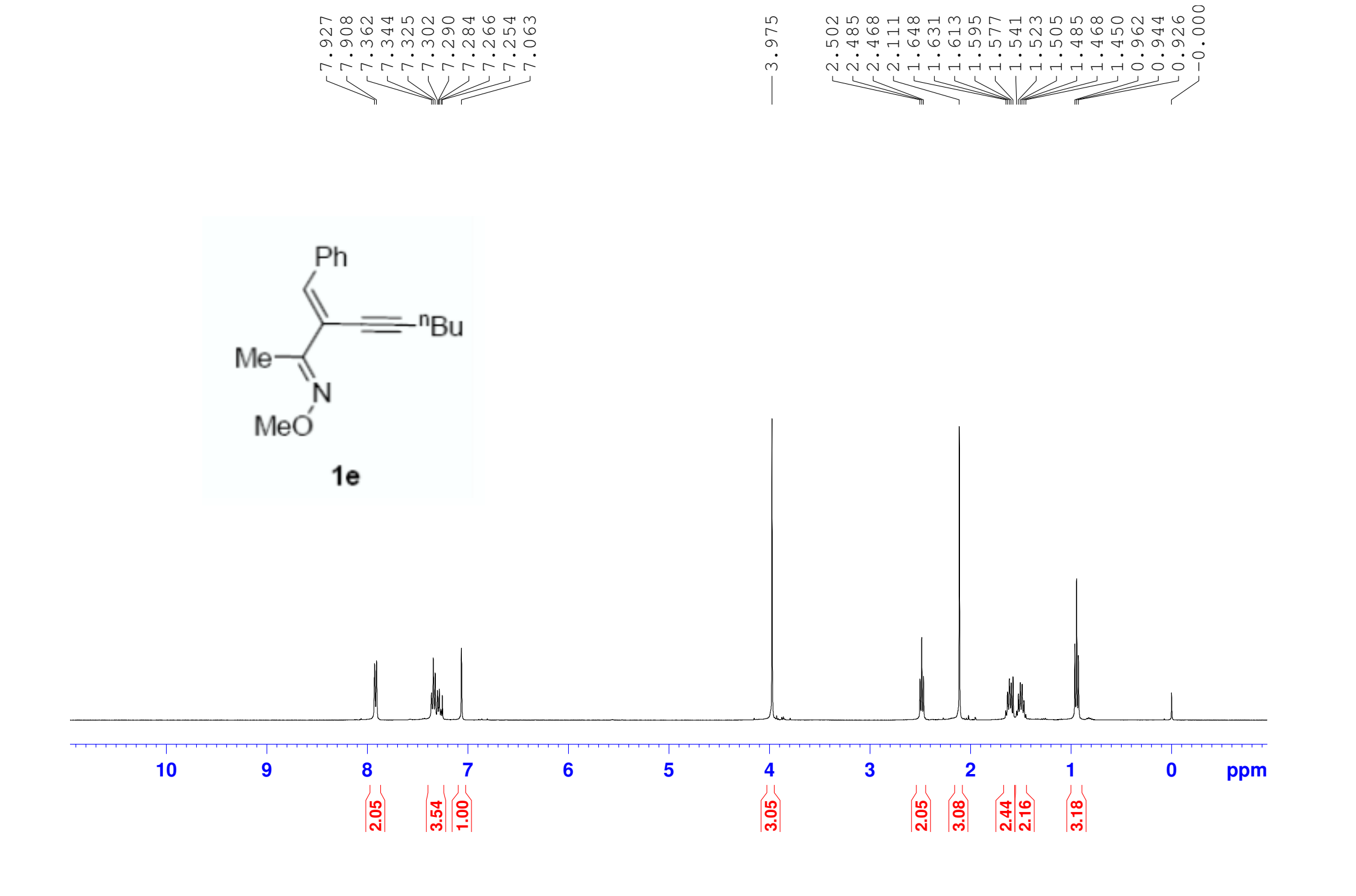


155.29
136.27
135.95
133.51
133.17
130.32
129.64
128.99
128.90
128.30
128.17
126.72
126.66
126.46
125.24
121.03
119.23
95.84
91.12
77.32
77.00
76.68
62.13
12.28

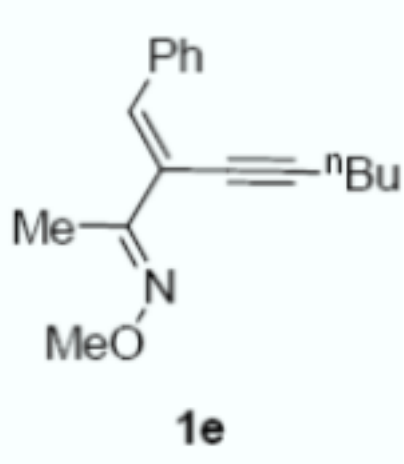


1d

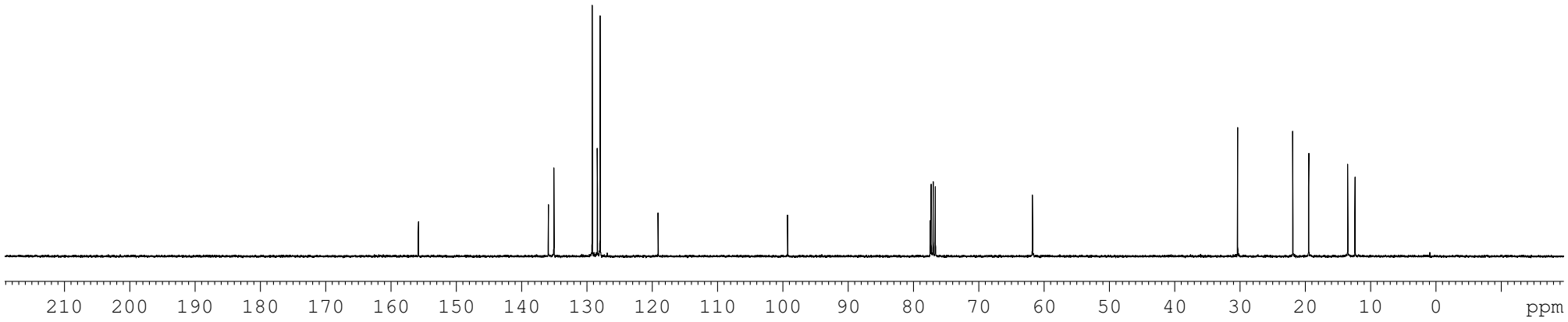


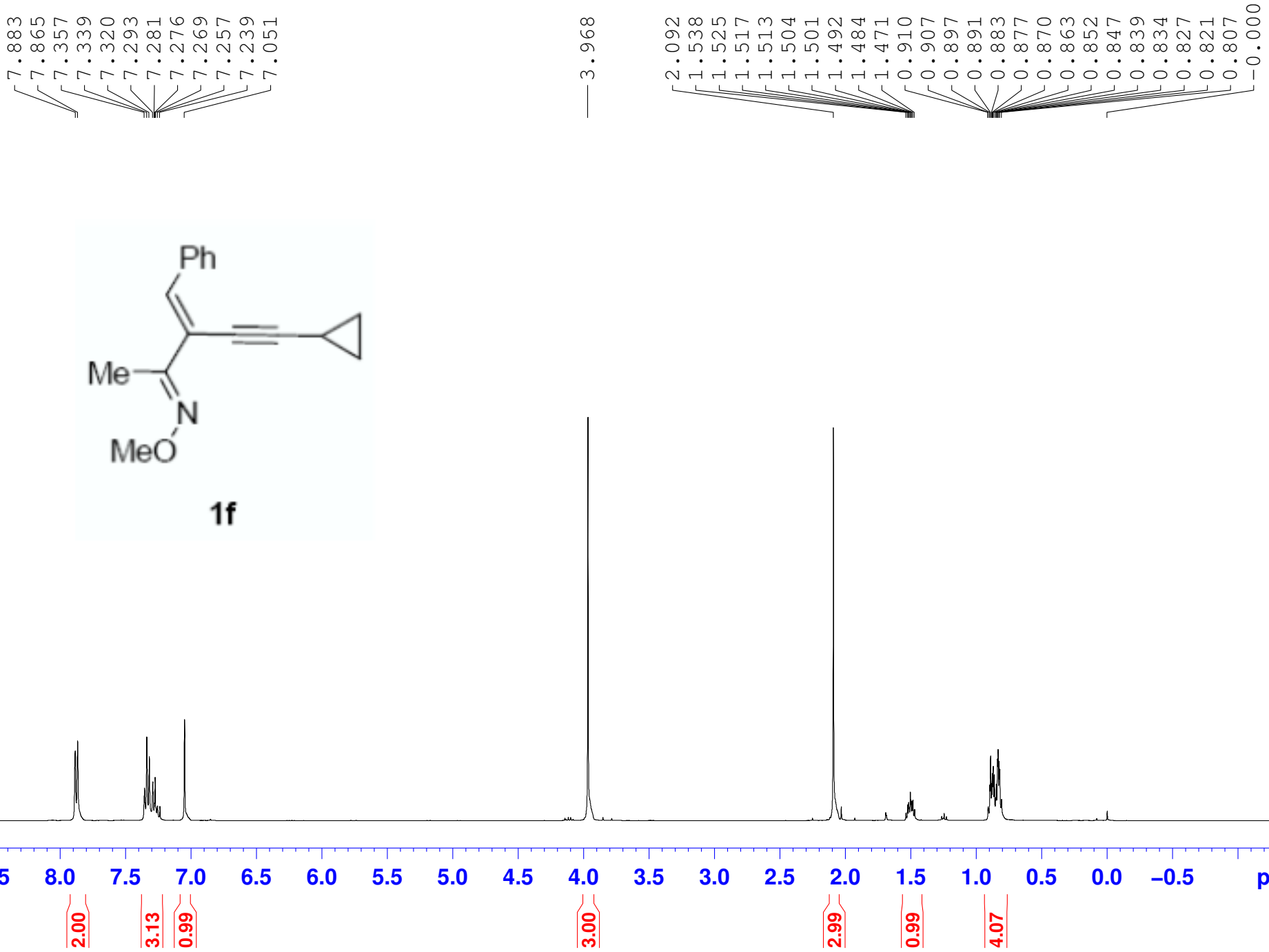


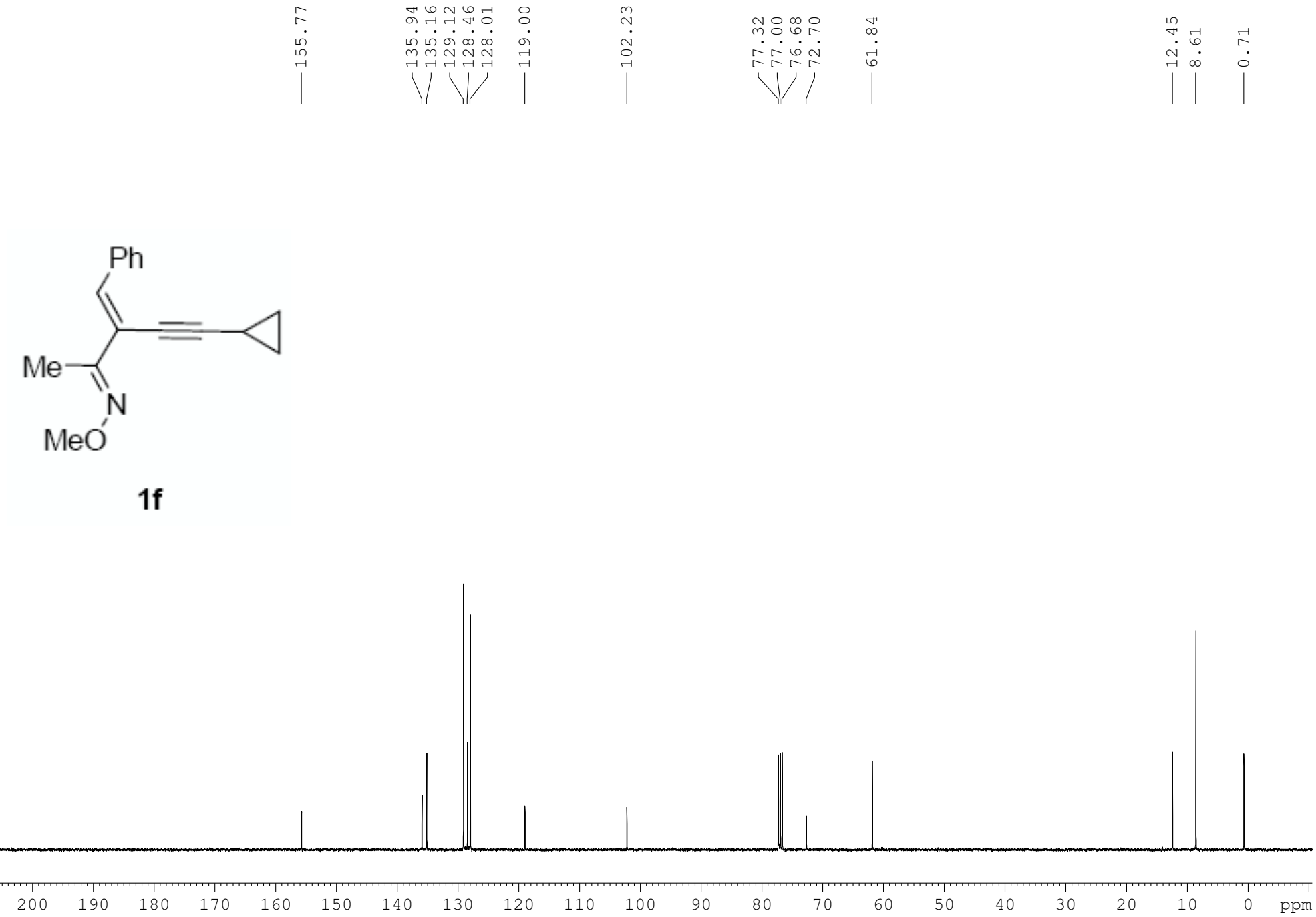
155.84
135.94
135.08
129.22
128.43
128.01
119.14
99.30
77.47
77.32
77.00
76.68
61.81
30.39
21.94
19.50
13.53
12.42

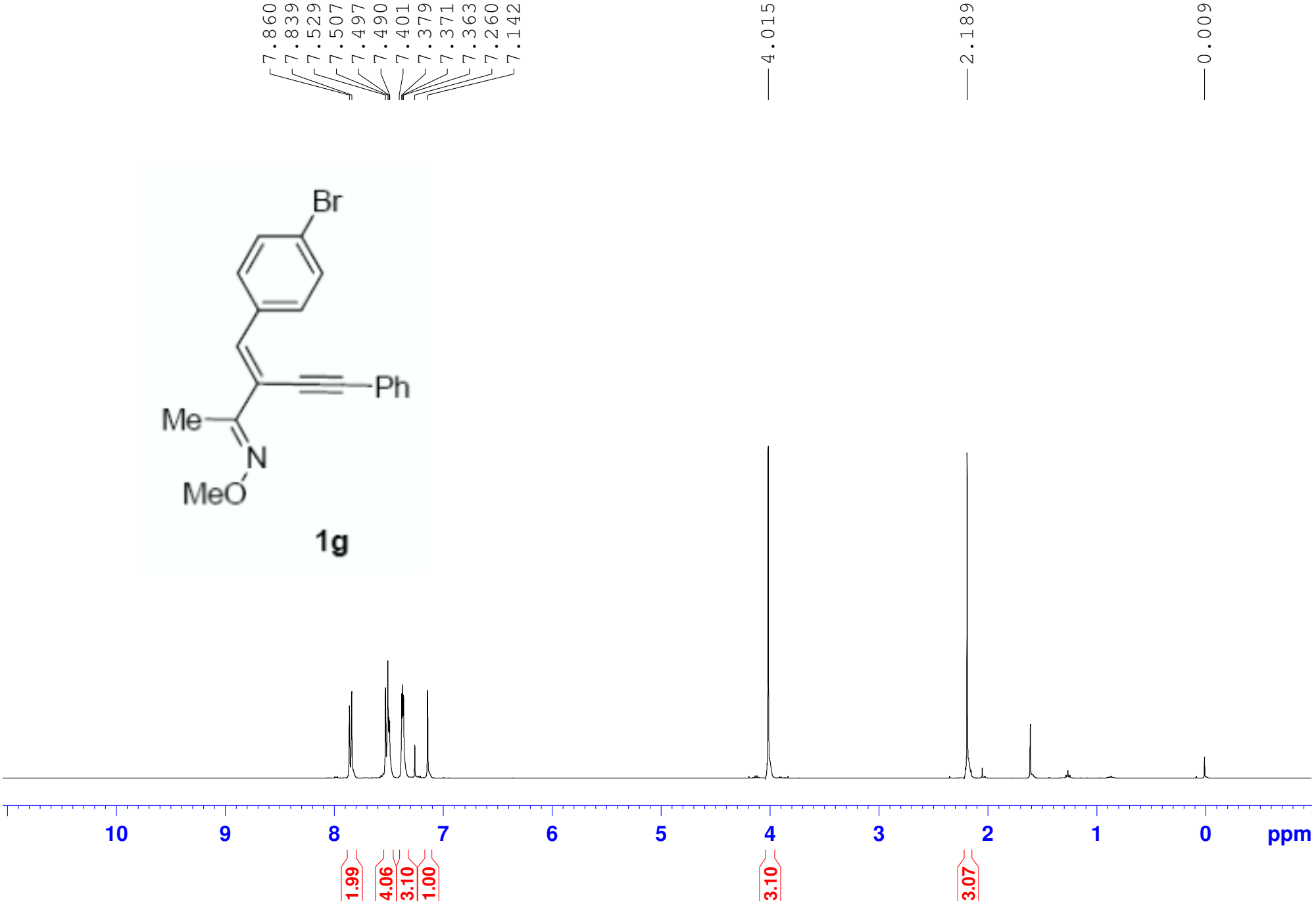


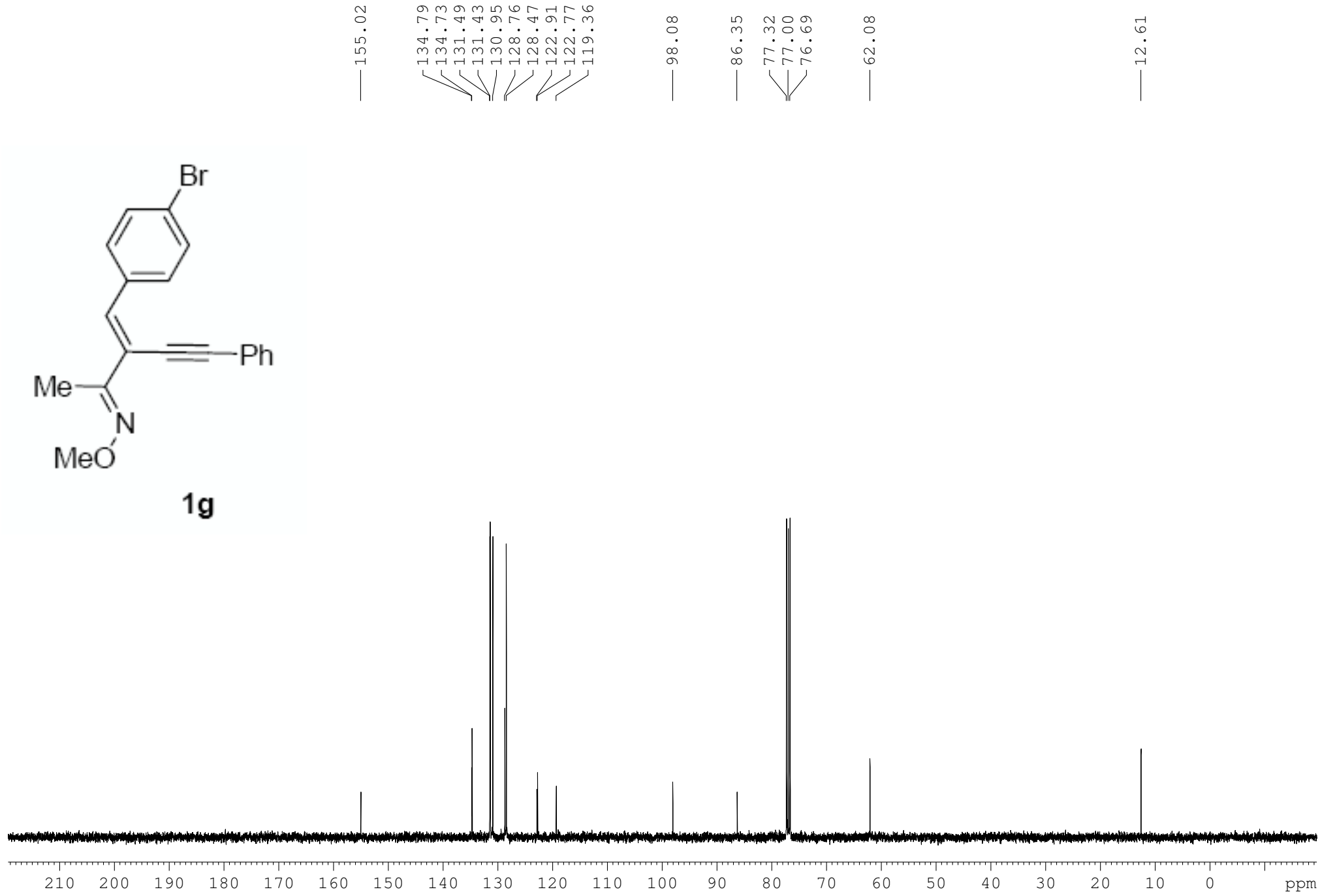
1e

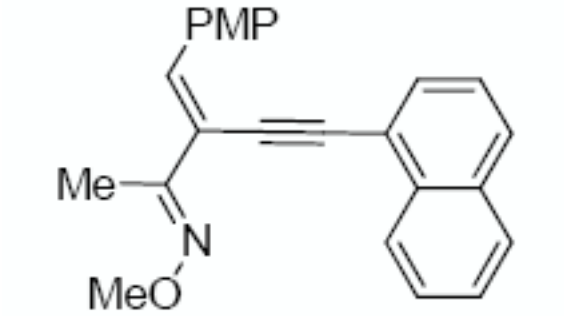




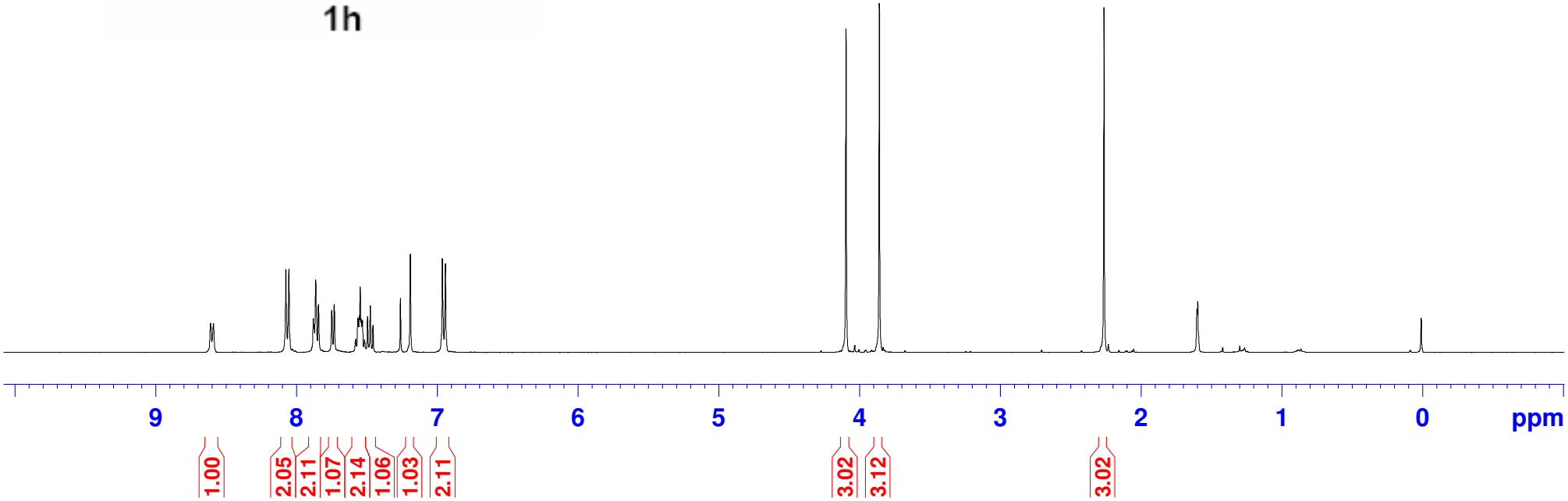


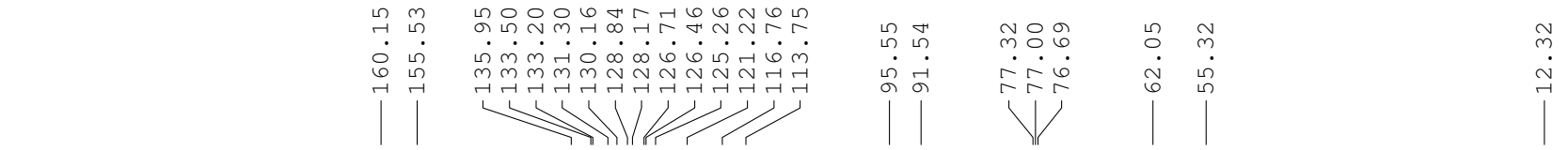


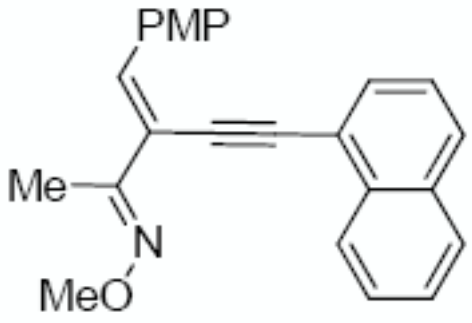




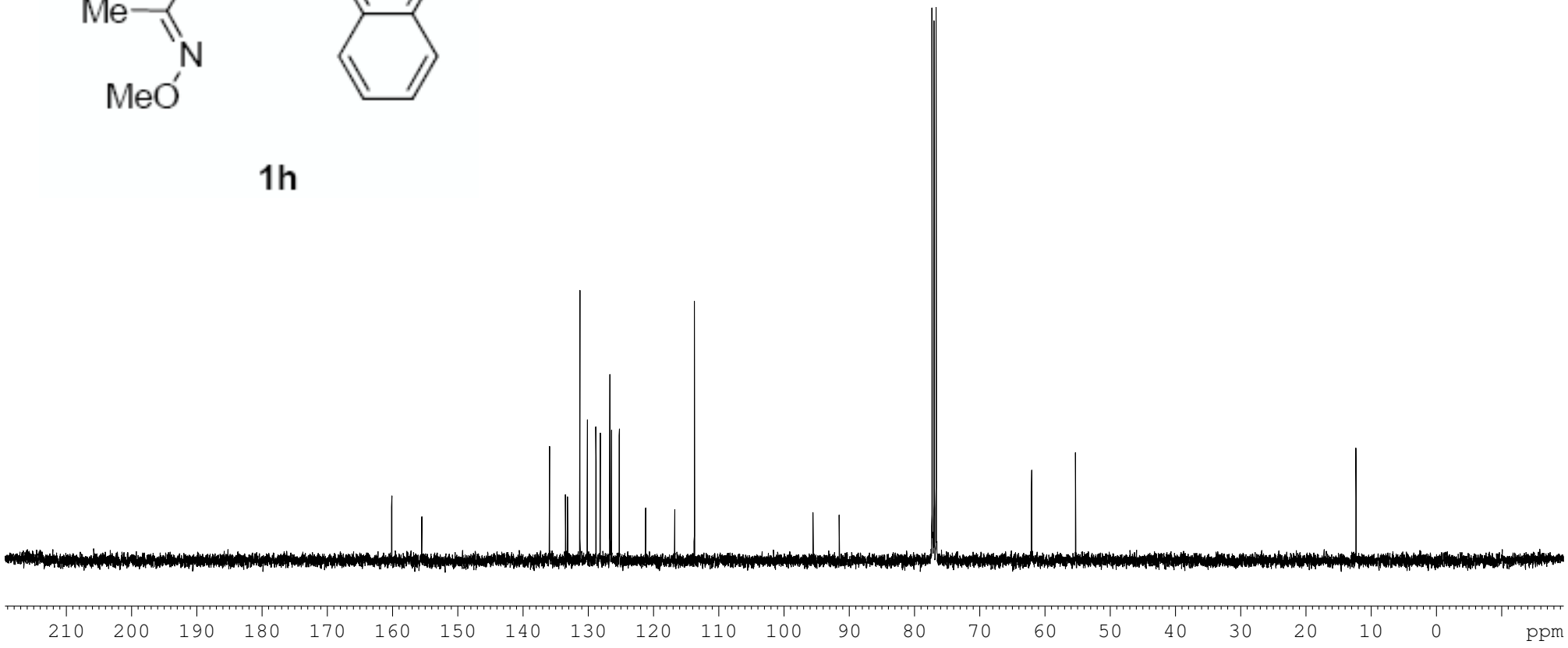
1h

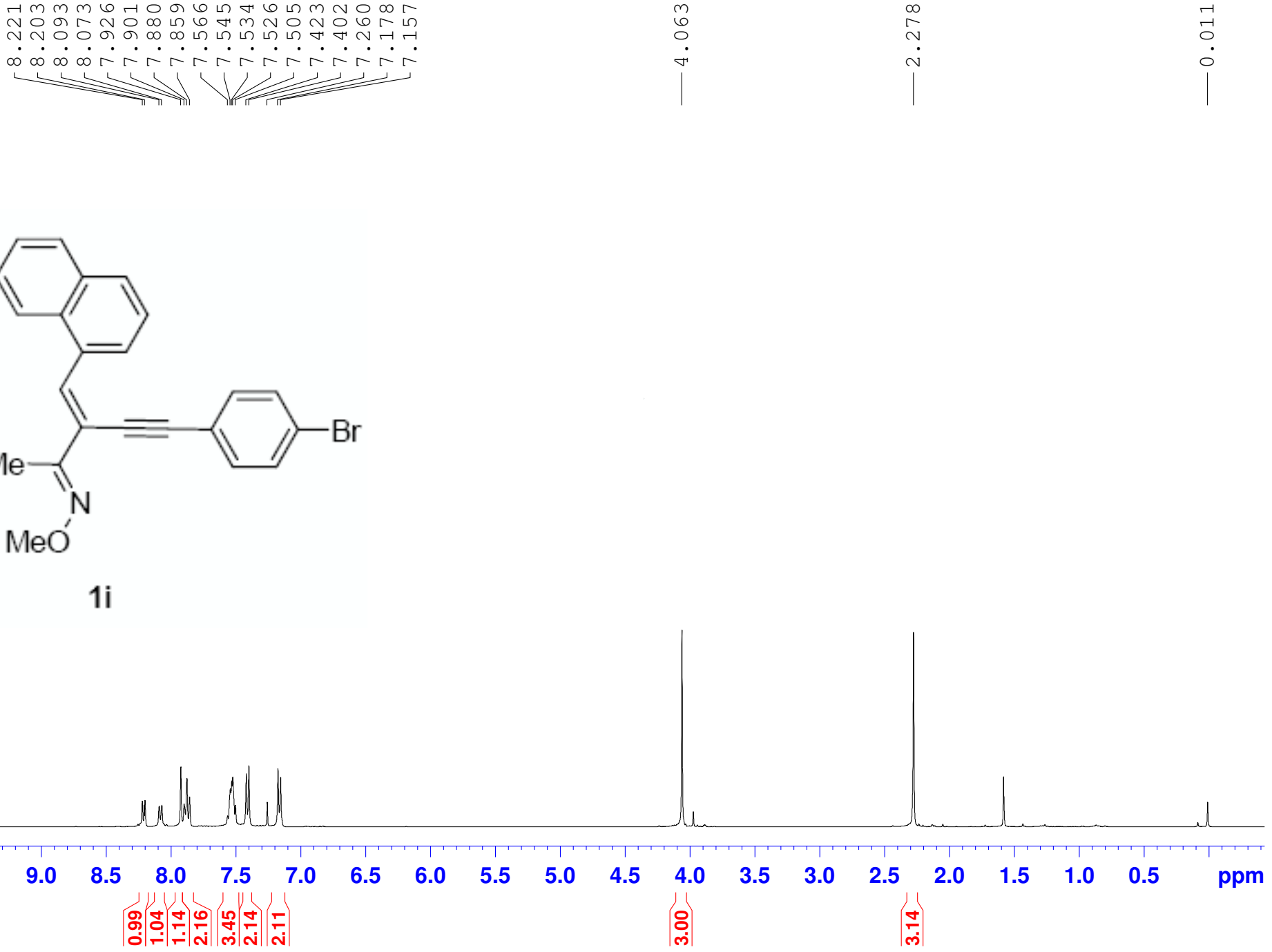


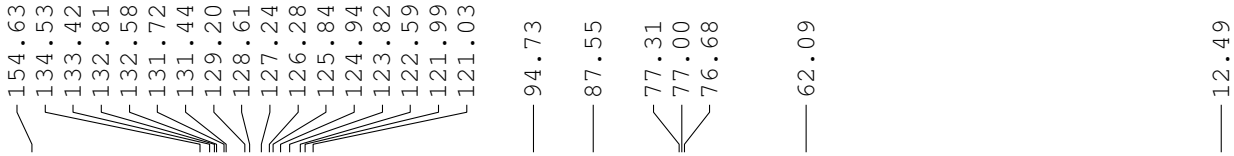


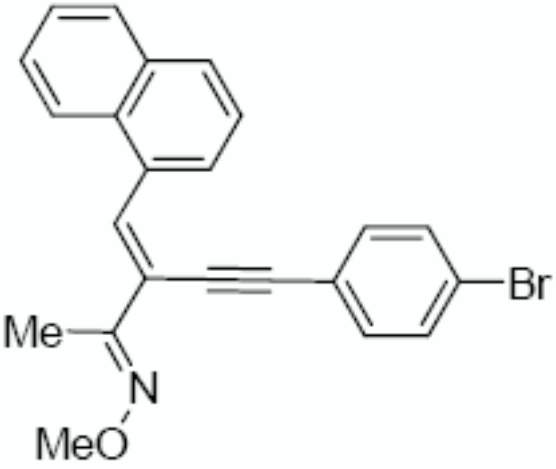


1h

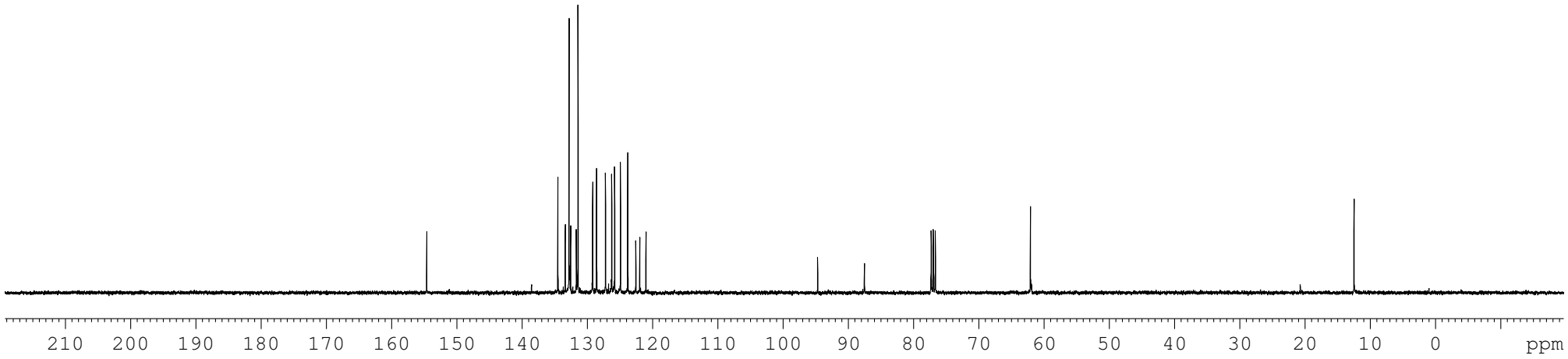


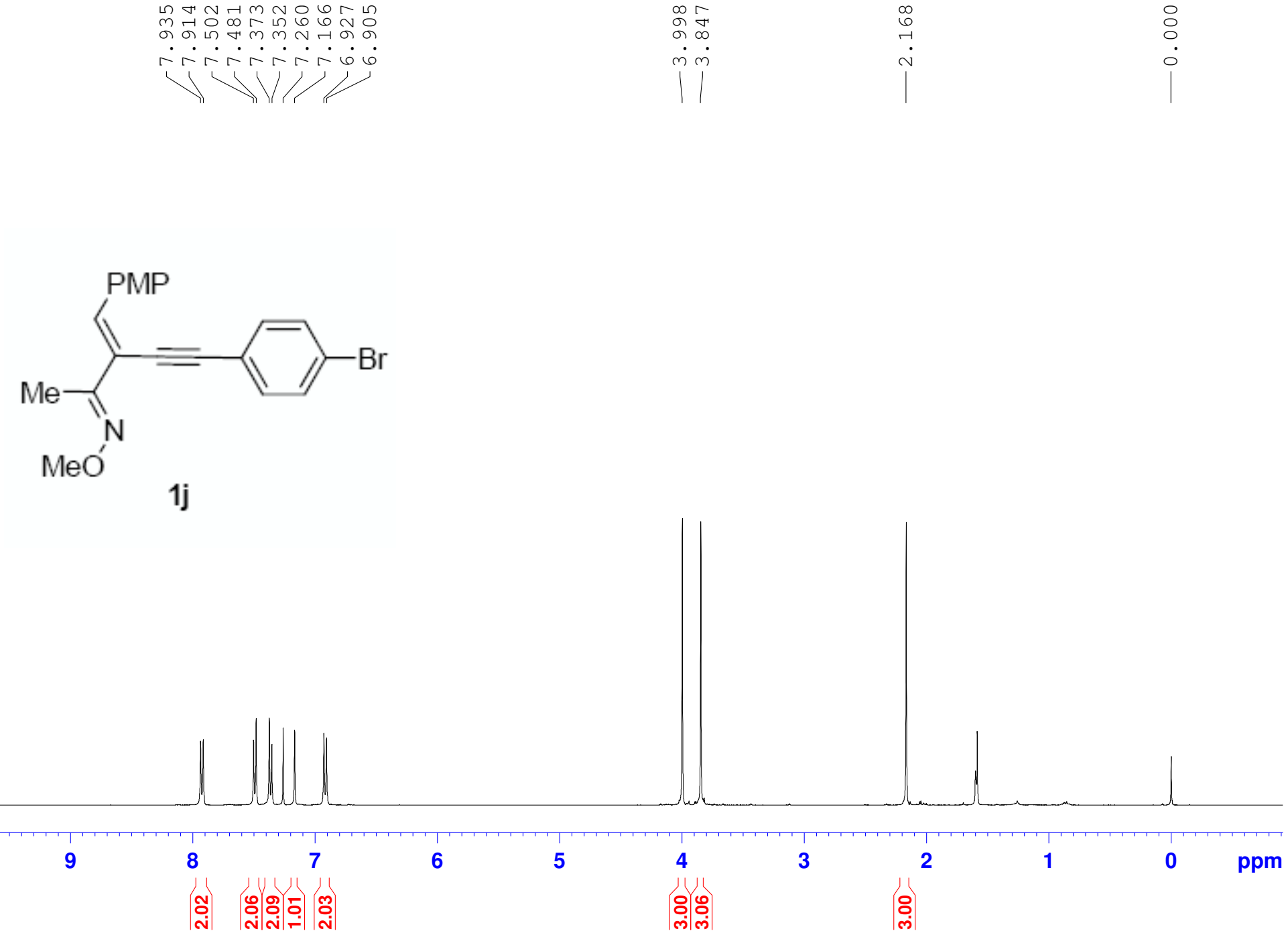






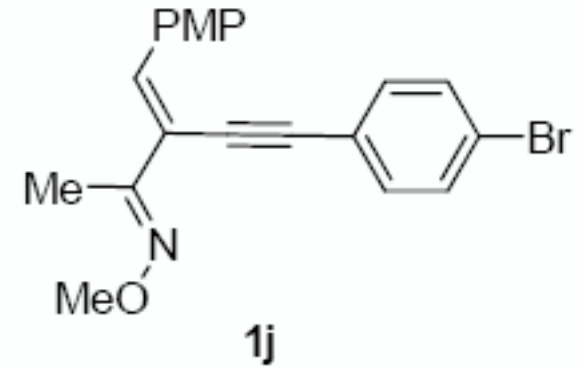
1i



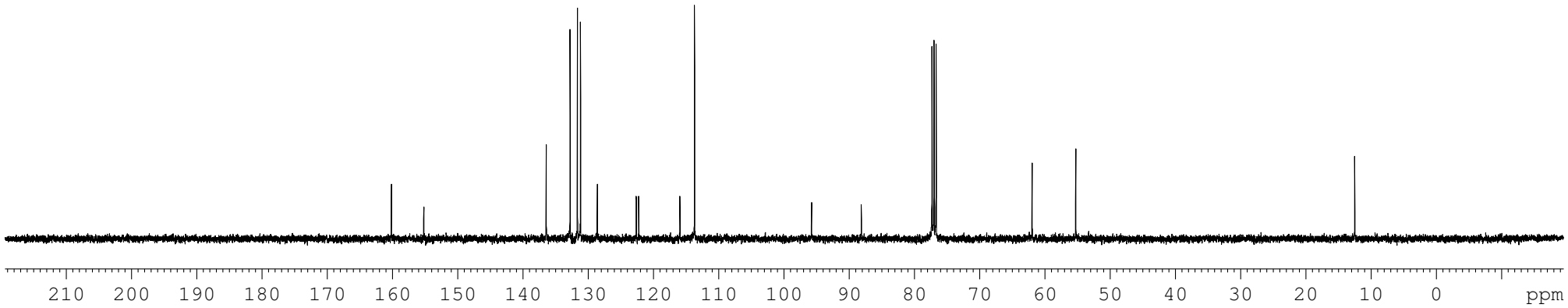


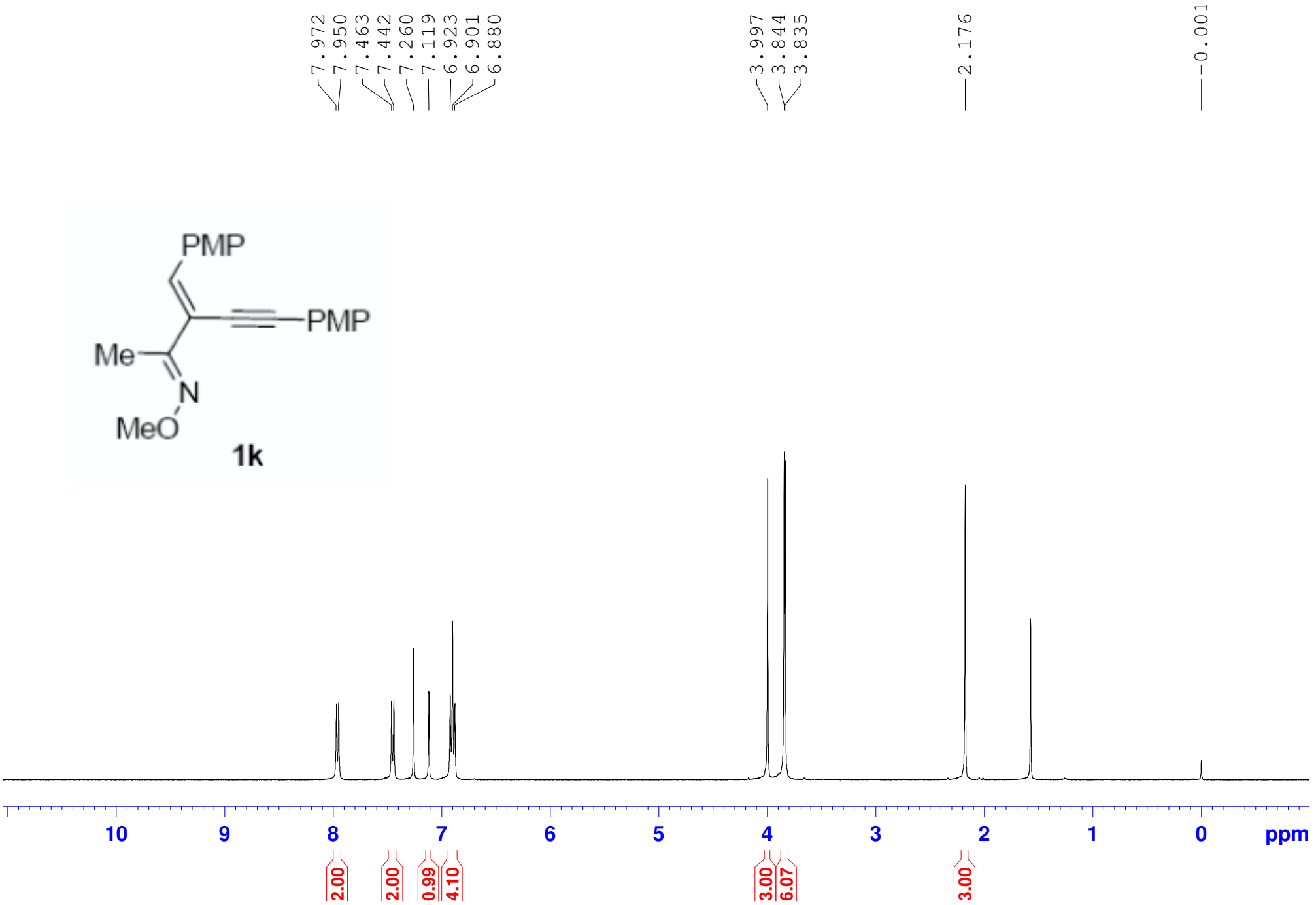
zm-c-59 C

160.17
155.22
136.45
132.79
131.67
131.19
128.60
122.65
122.28
115.97
113.72
95.78
88.15
77.32
77.00
76.68
61.96
55.28
12.51

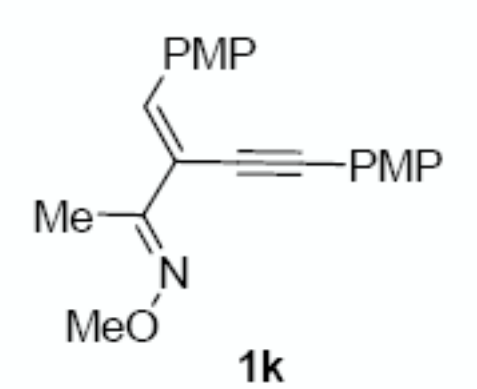


1j

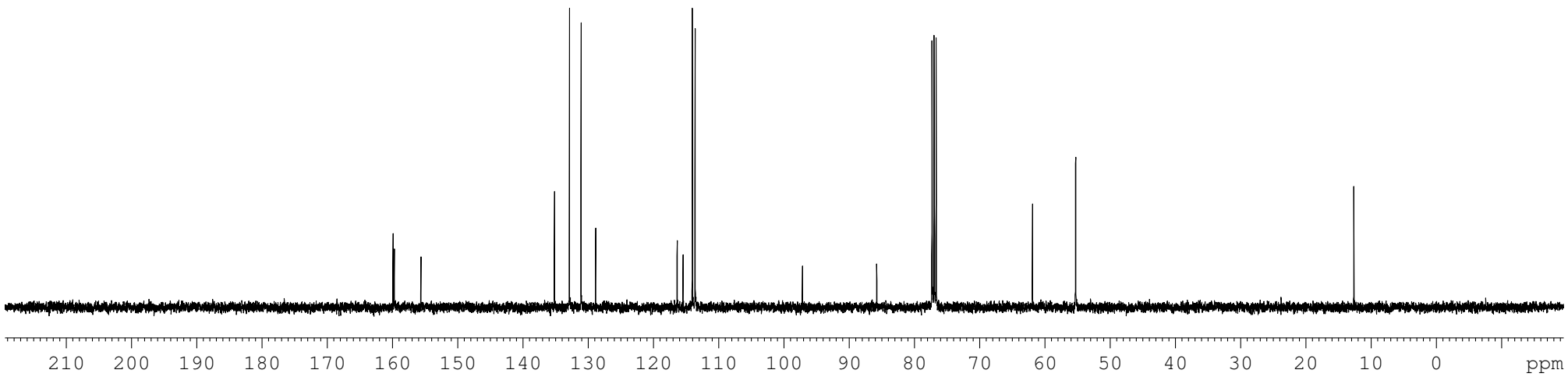


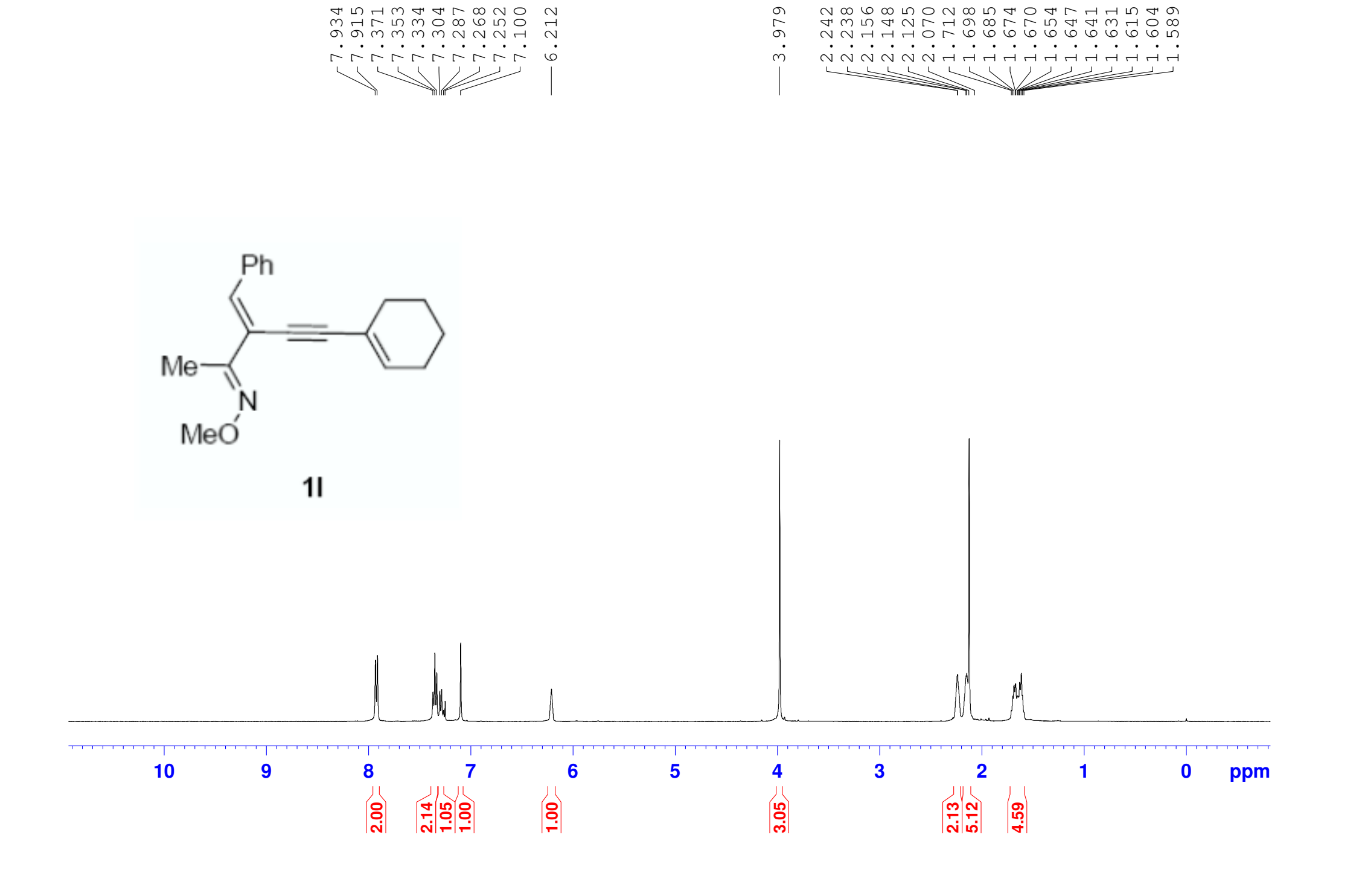


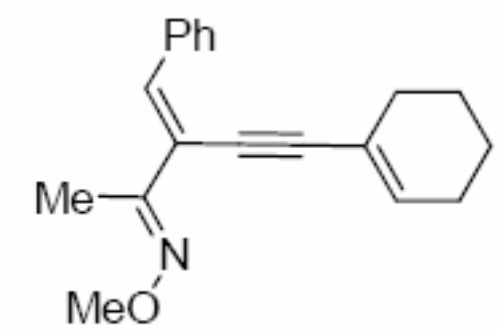
159.95
159.75
155.66
135.19
132.90
131.12
128.88
116.39
115.49
114.06
113.64
97.17
85.79
77.32
77.00
76.69
61.91
55.29
55.26
12.65



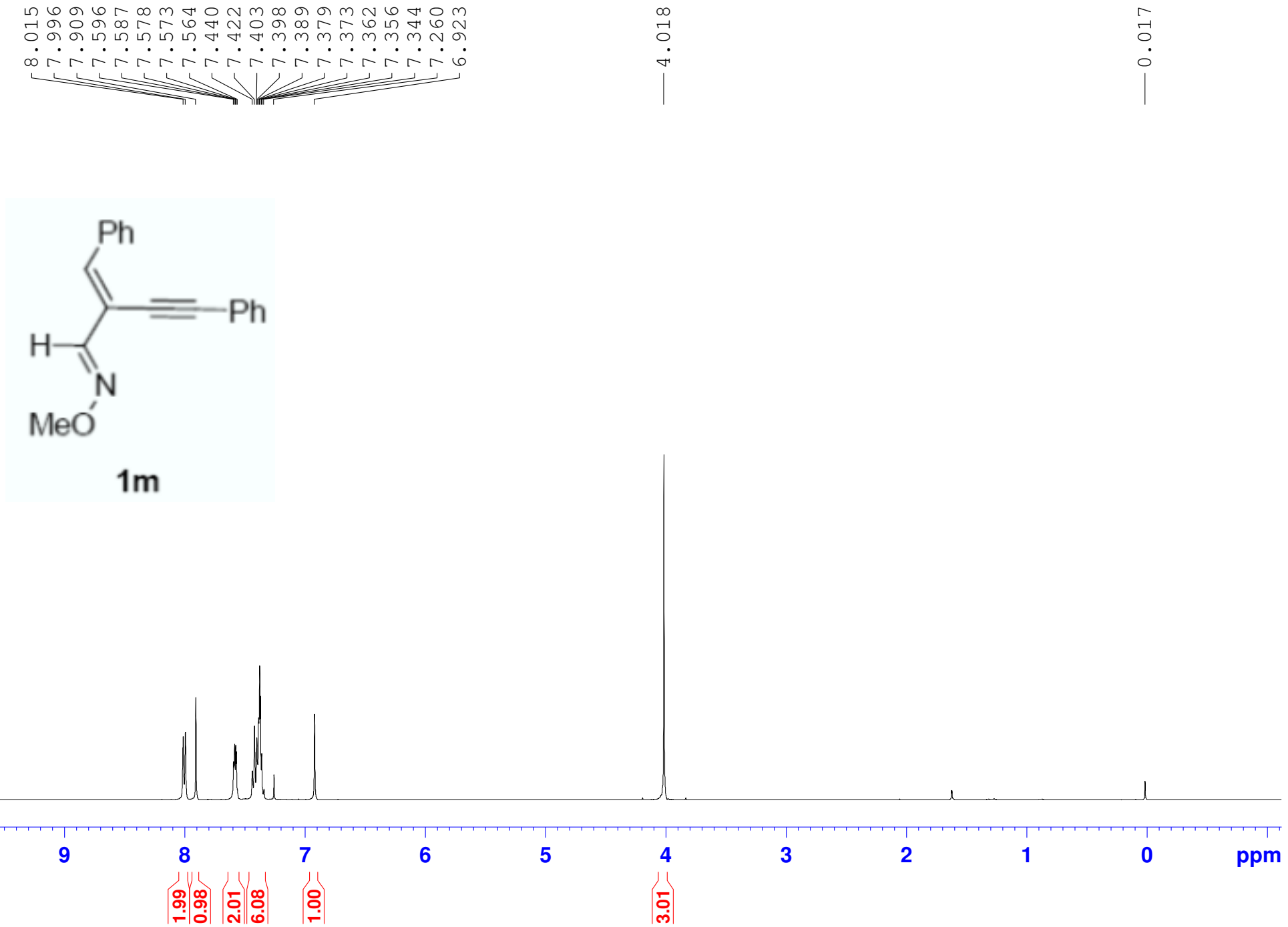
1k

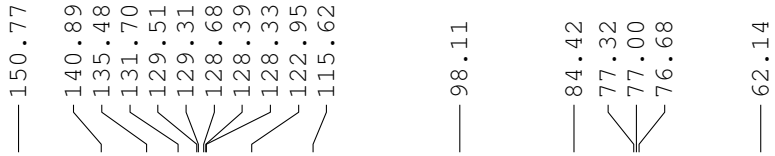


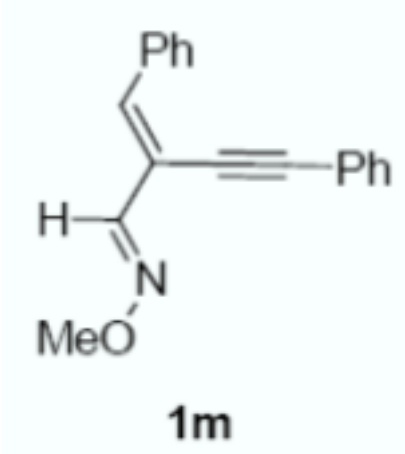




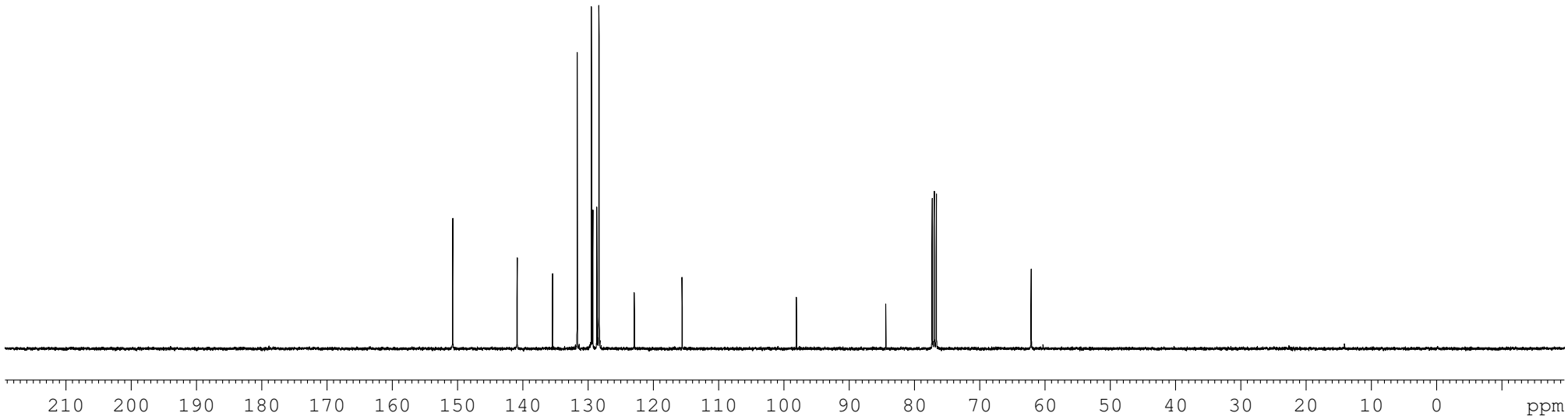
1l

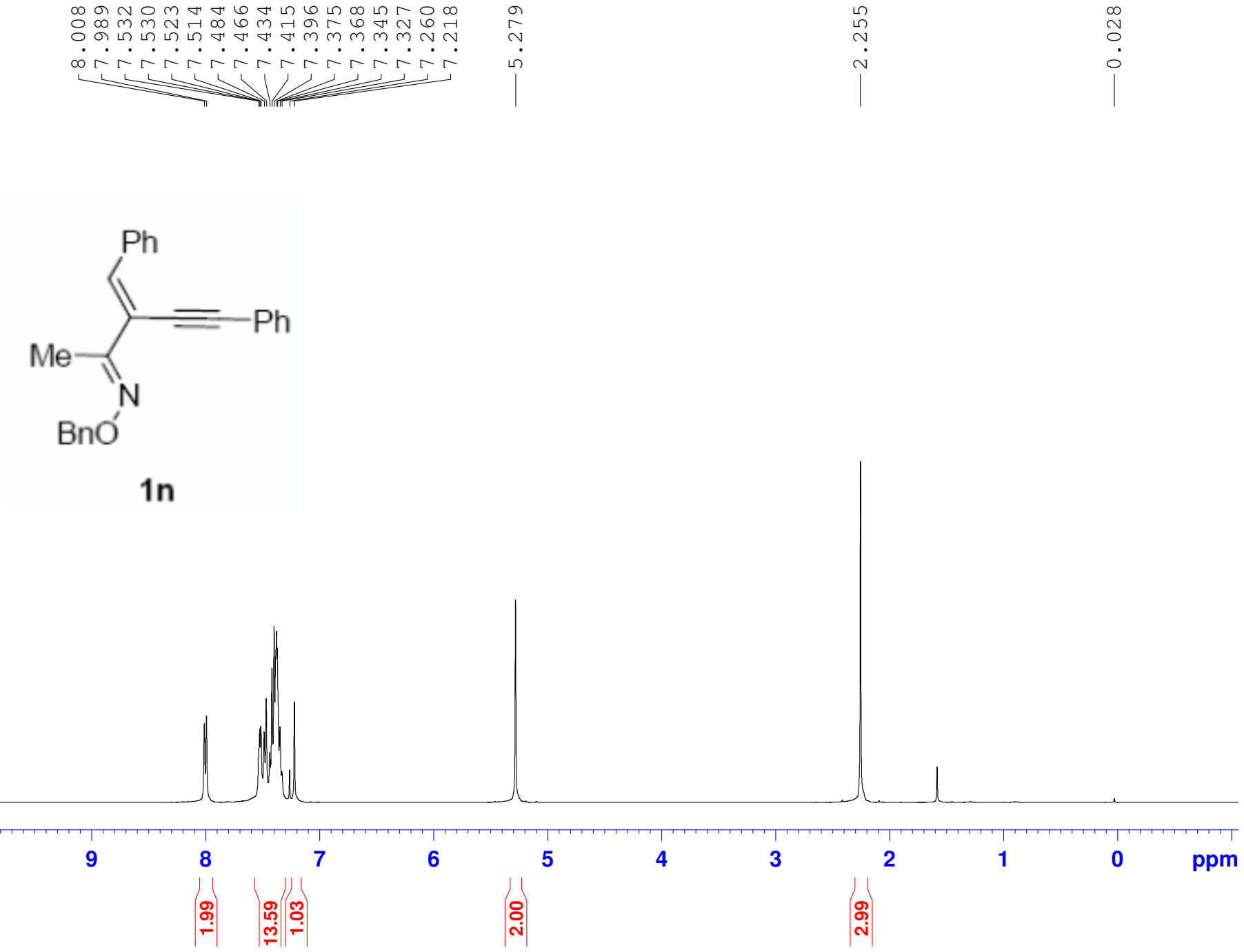


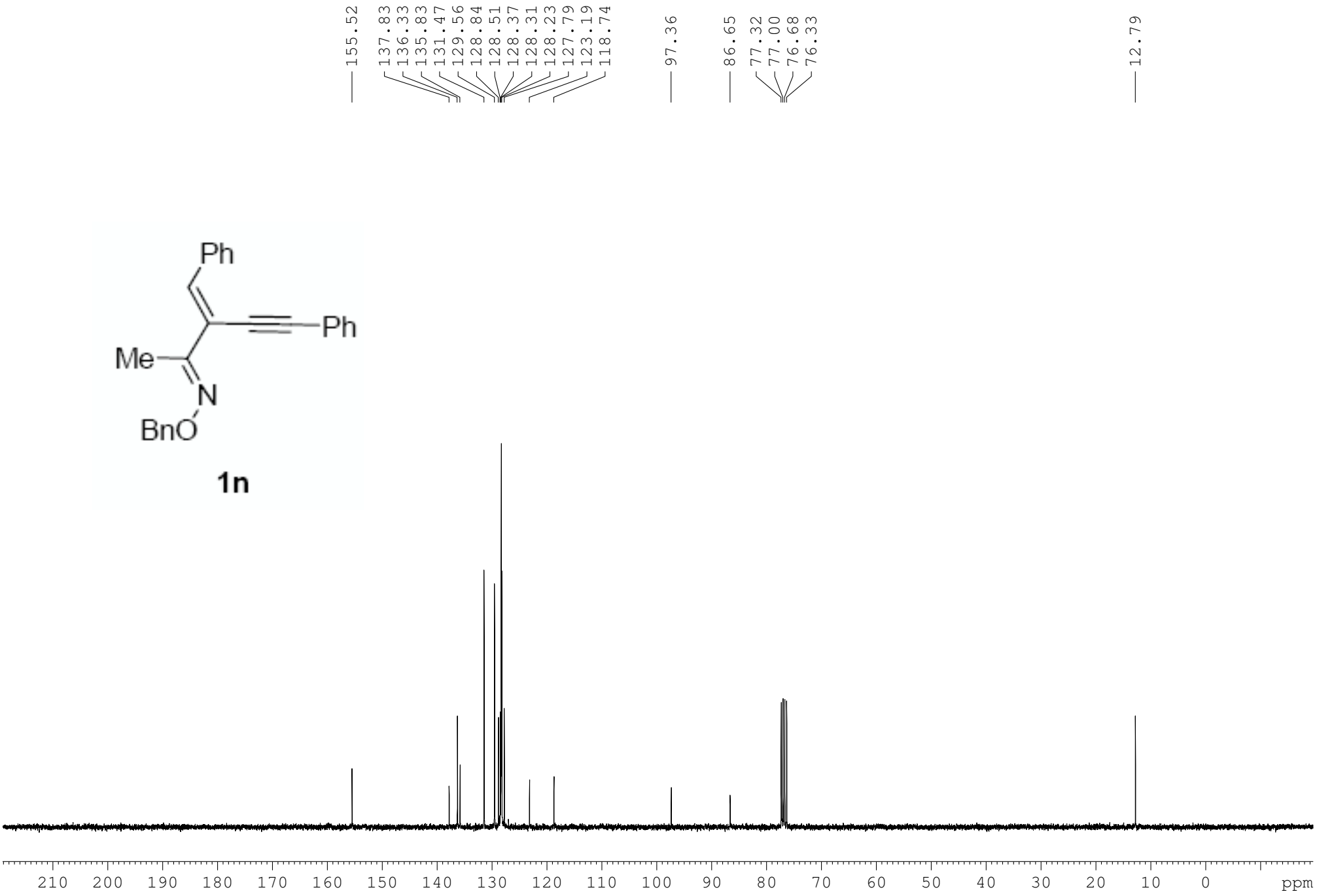


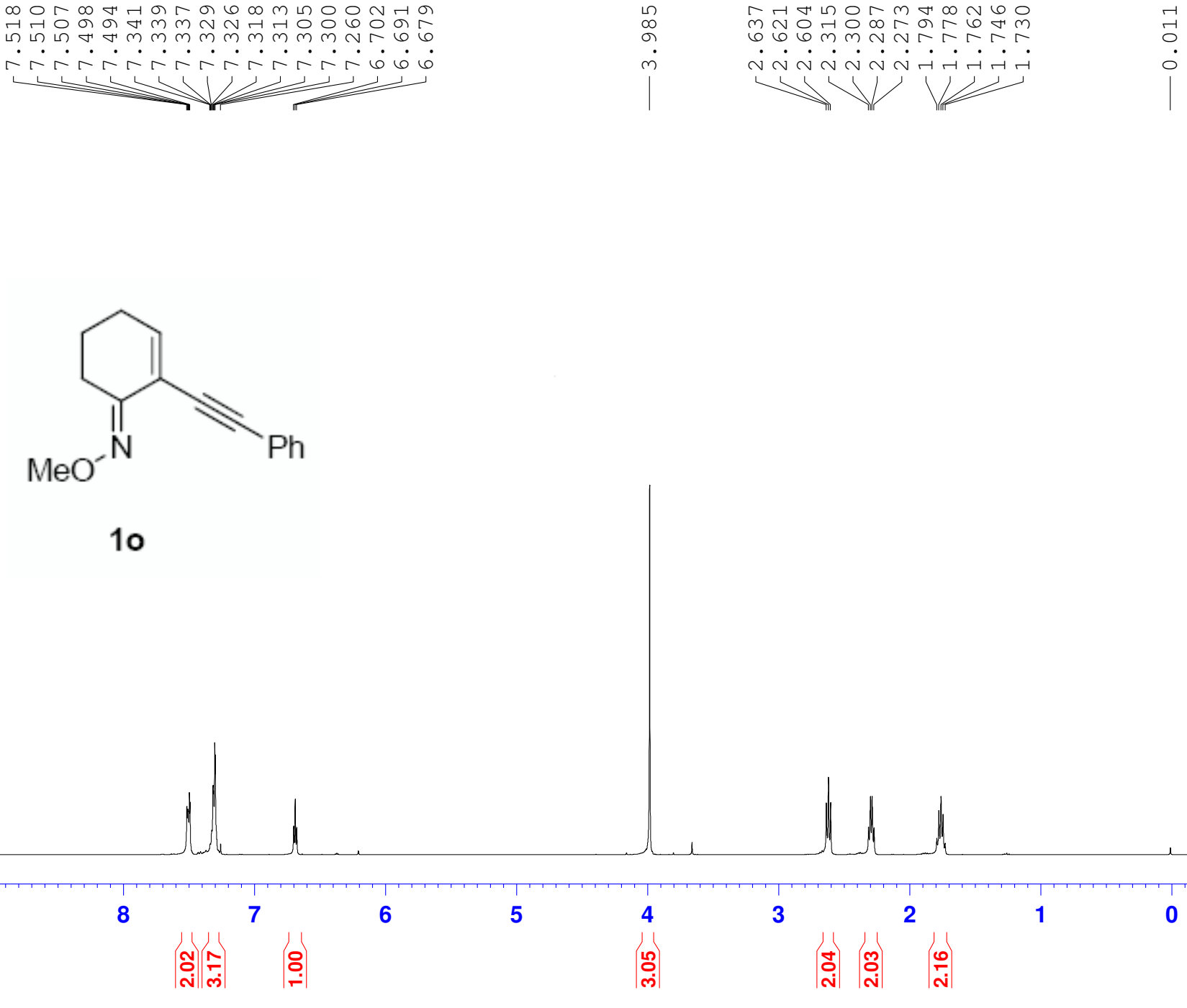


1m

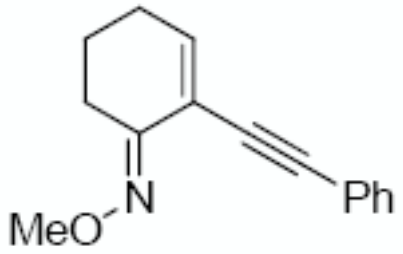




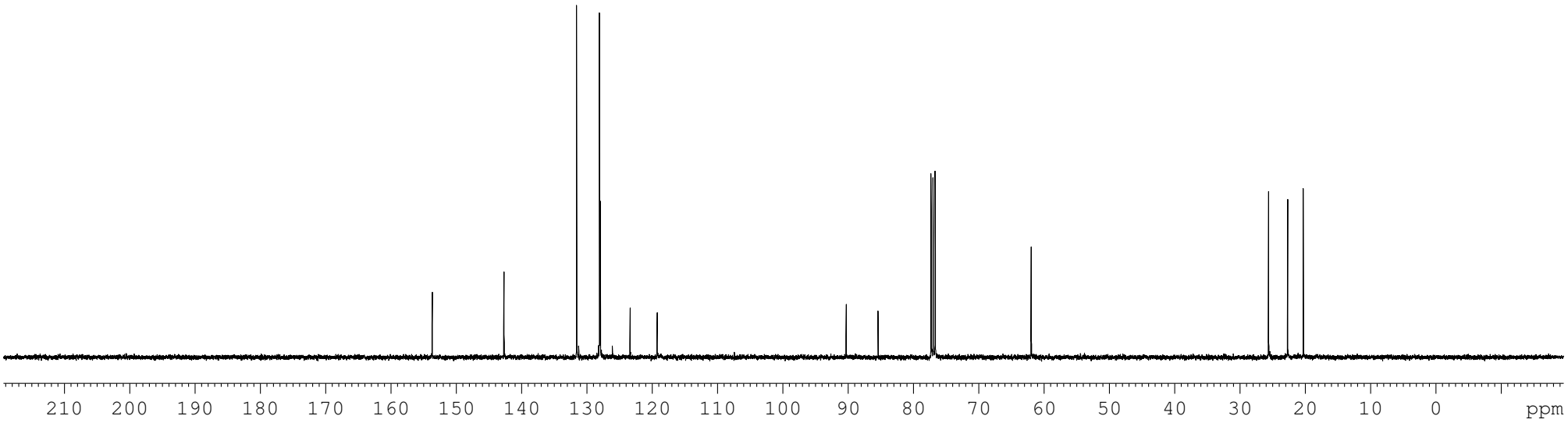


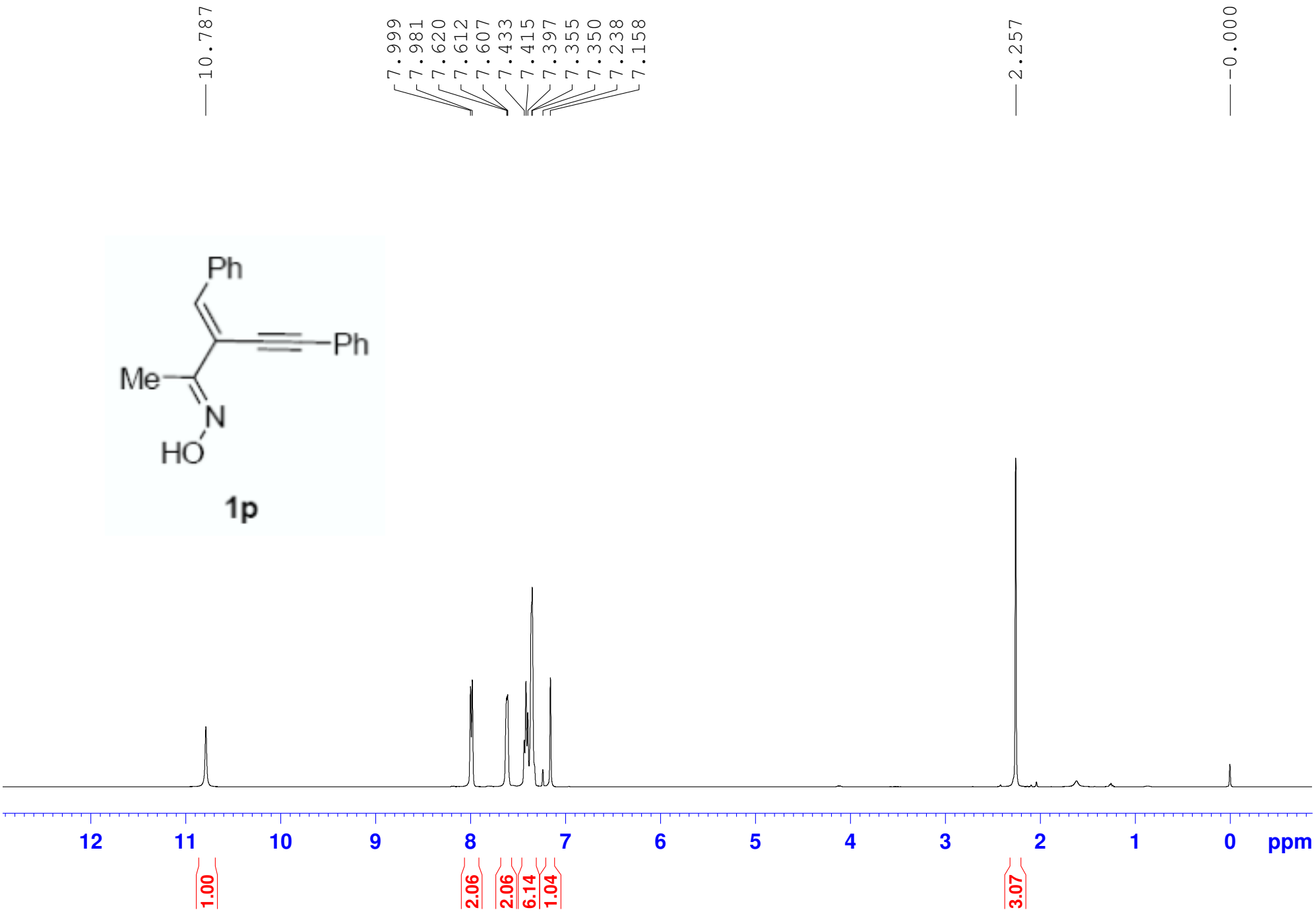


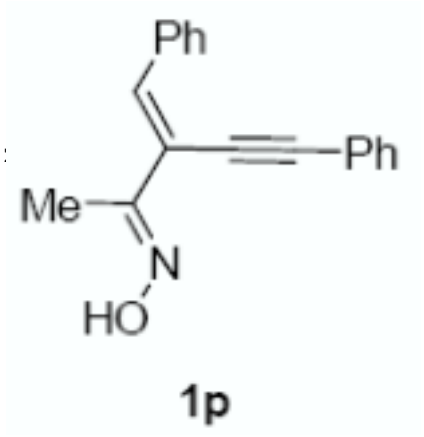
153.71
142.71
131.59
128.10
127.97
123.41
119.26
90.31
85.44
77.31
77.00
76.68
61.97
25.62
22.70
20.31



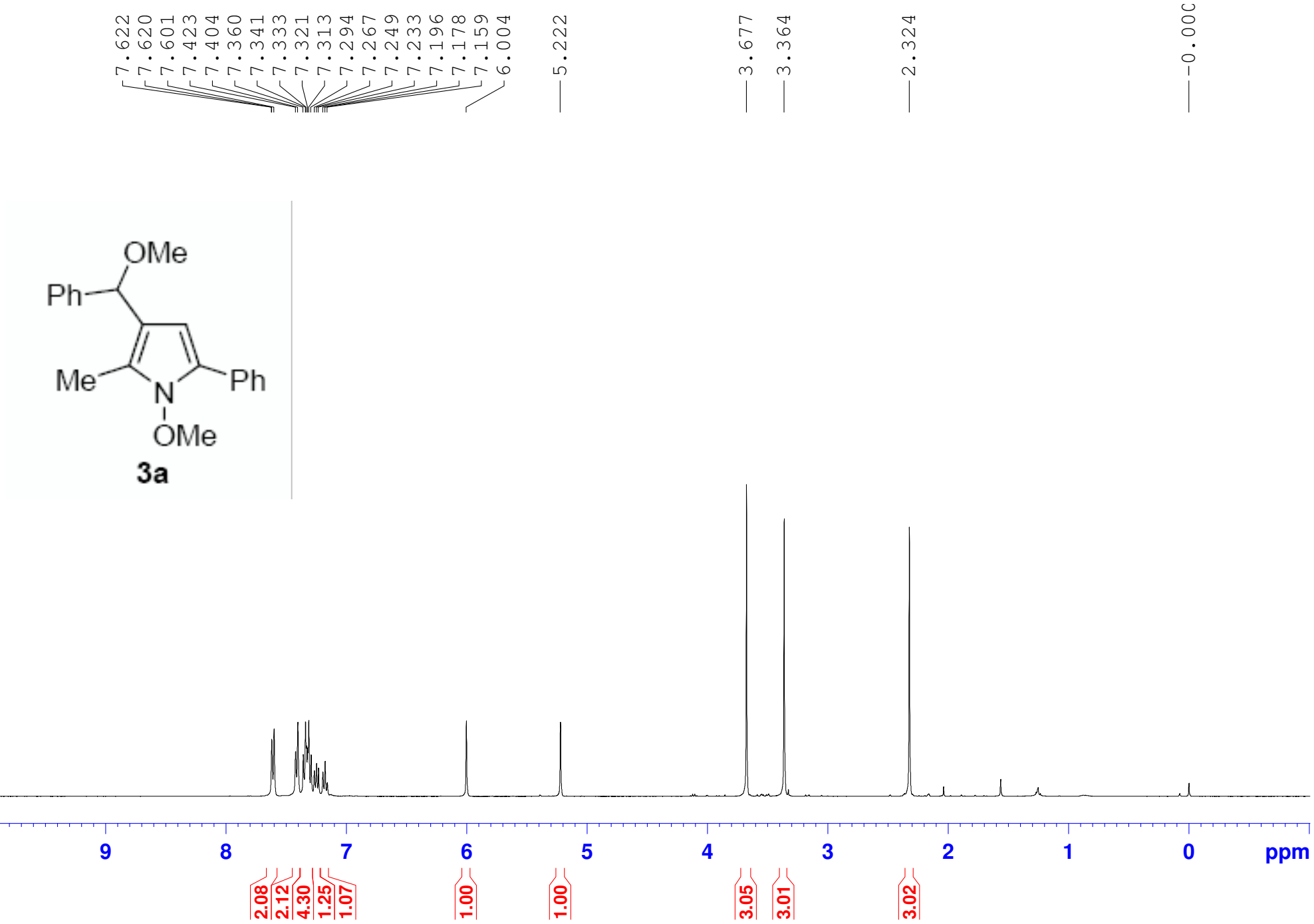
1o

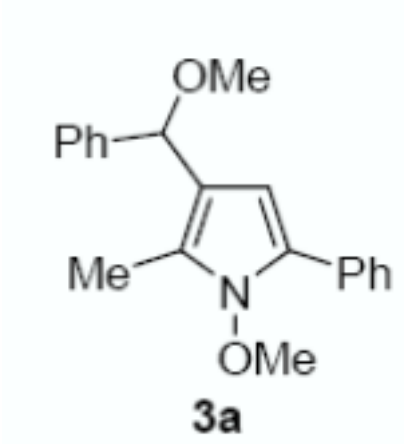




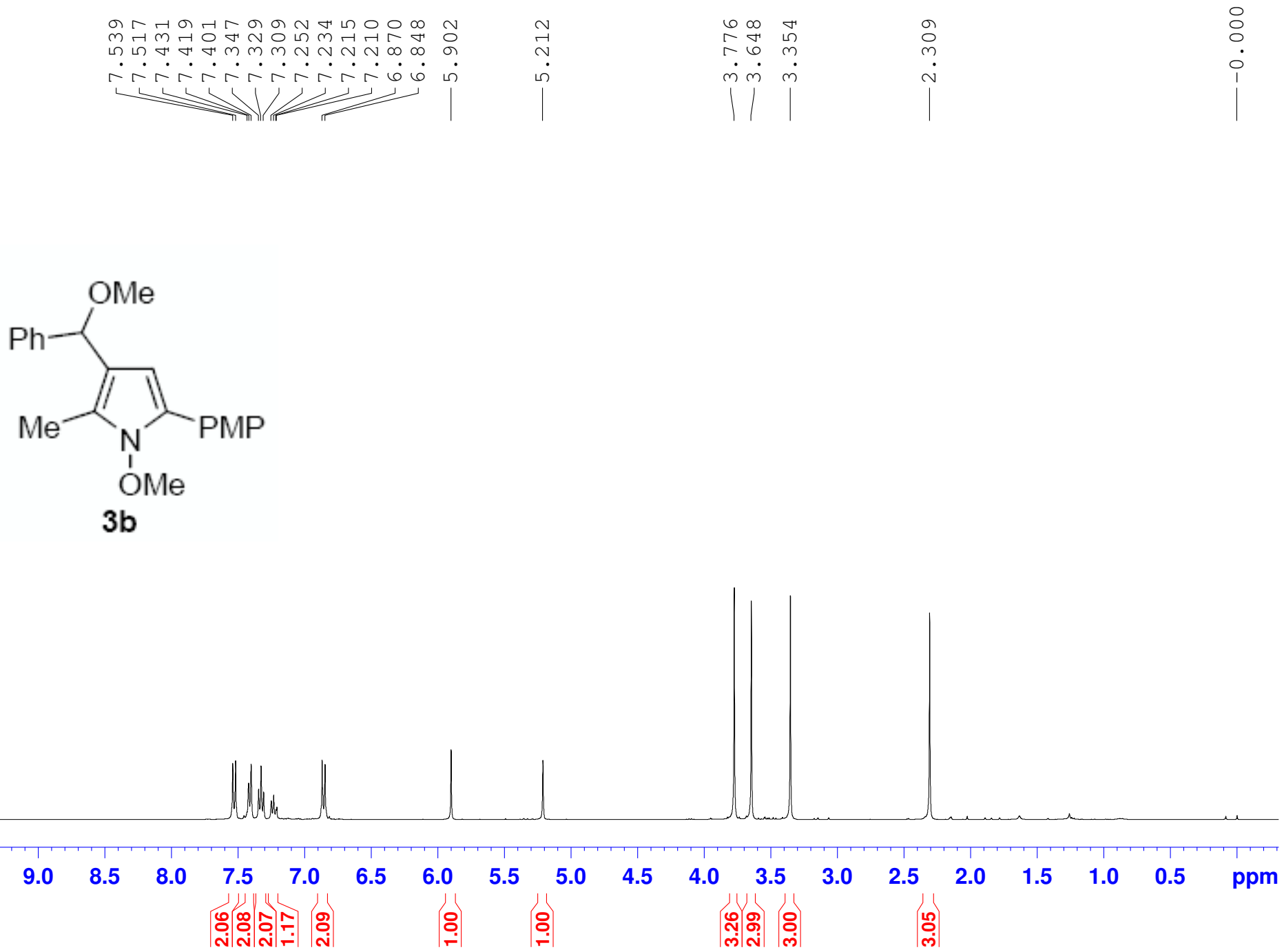


1p

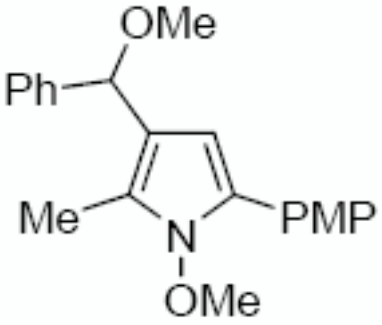




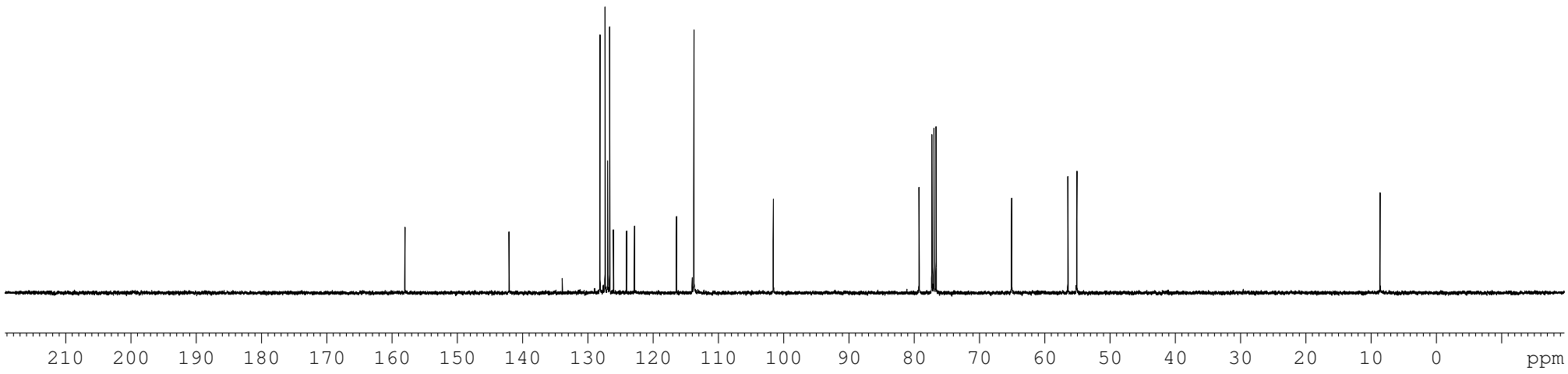
3a

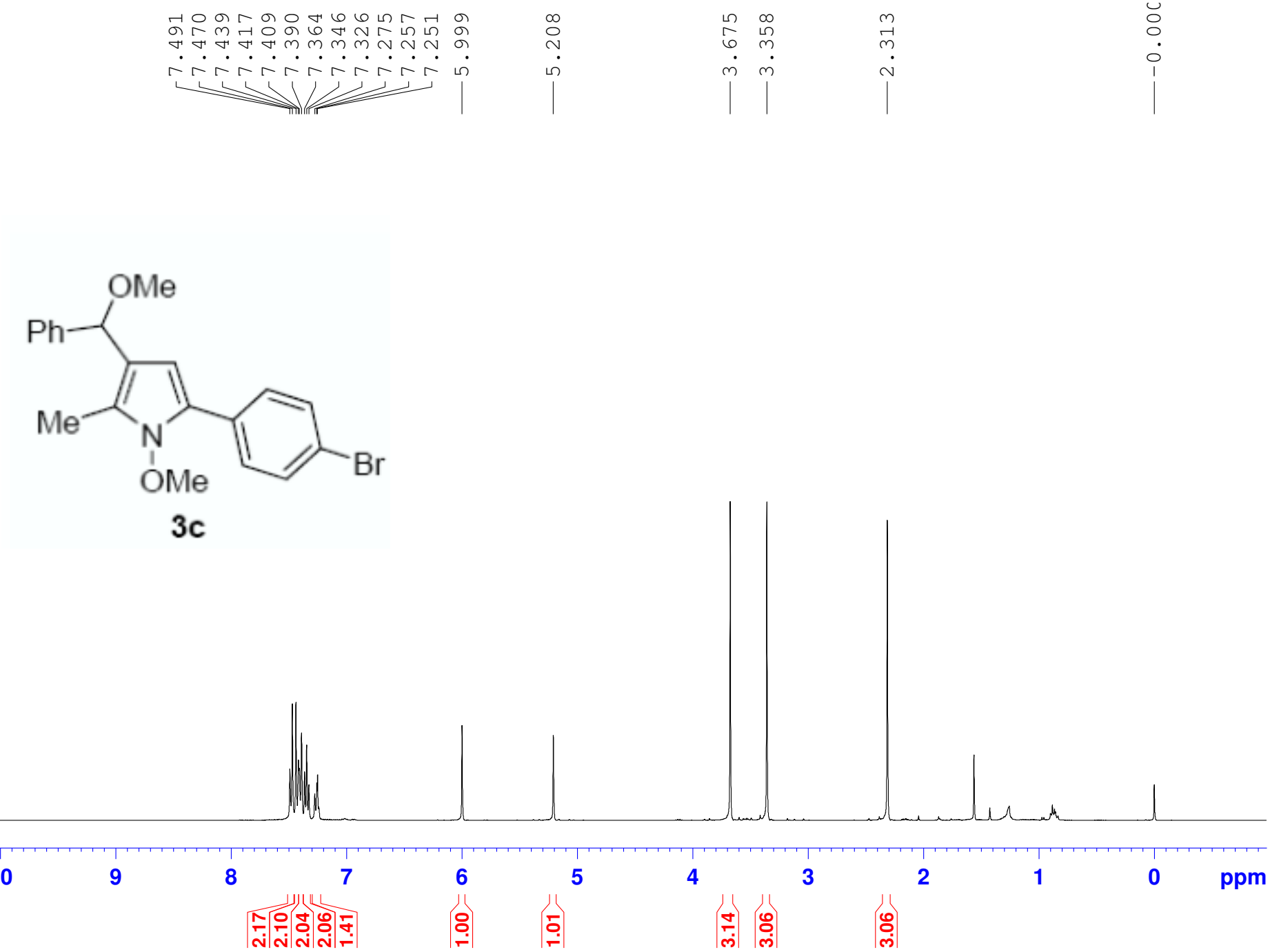


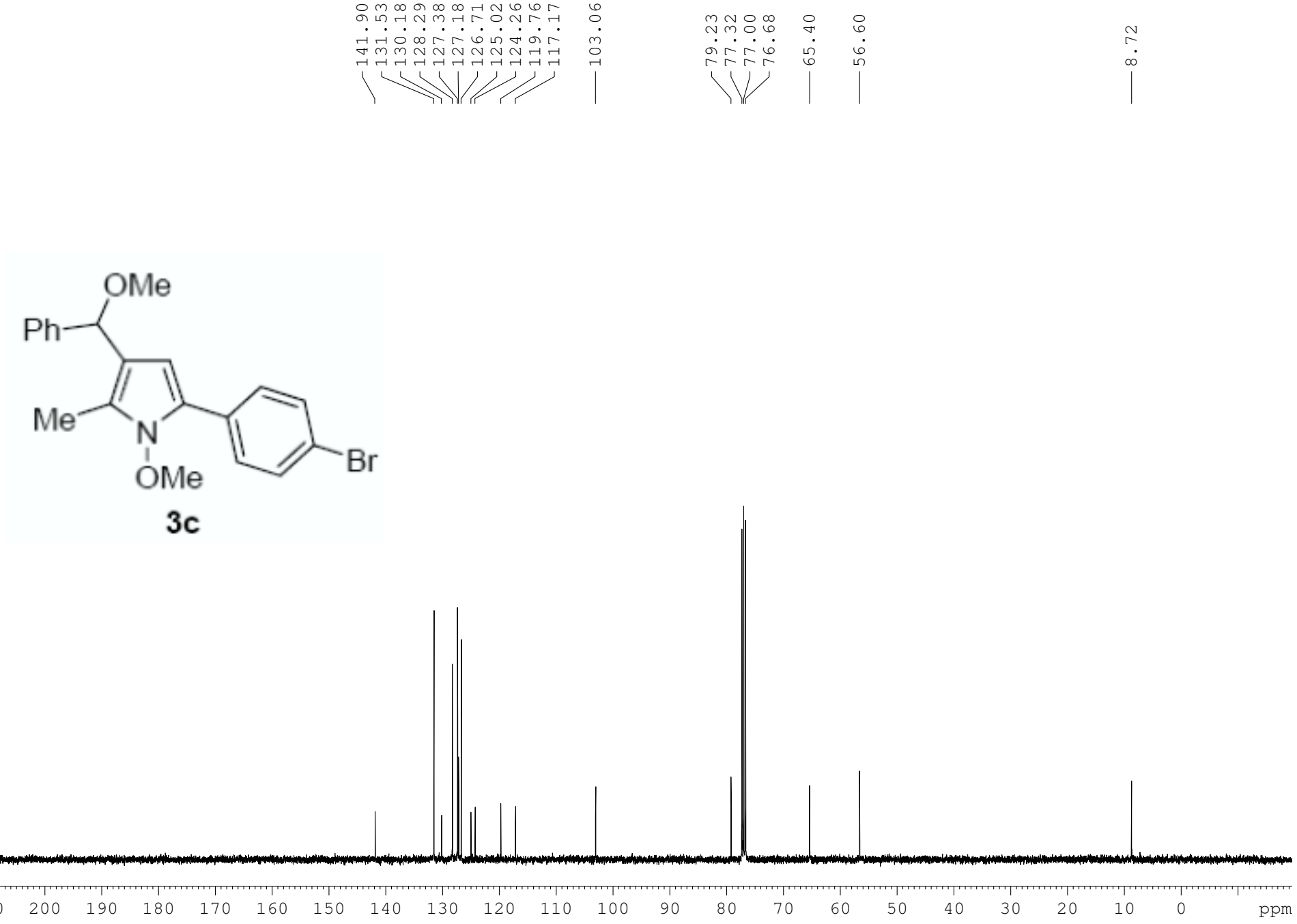
158.05
142.11
128.17
127.39
127.00
126.69
126.11
124.10
122.88
116.46
113.78
101.62
79.29
77.32
77.00
76.68
65.11
56.48
55.11
8.65

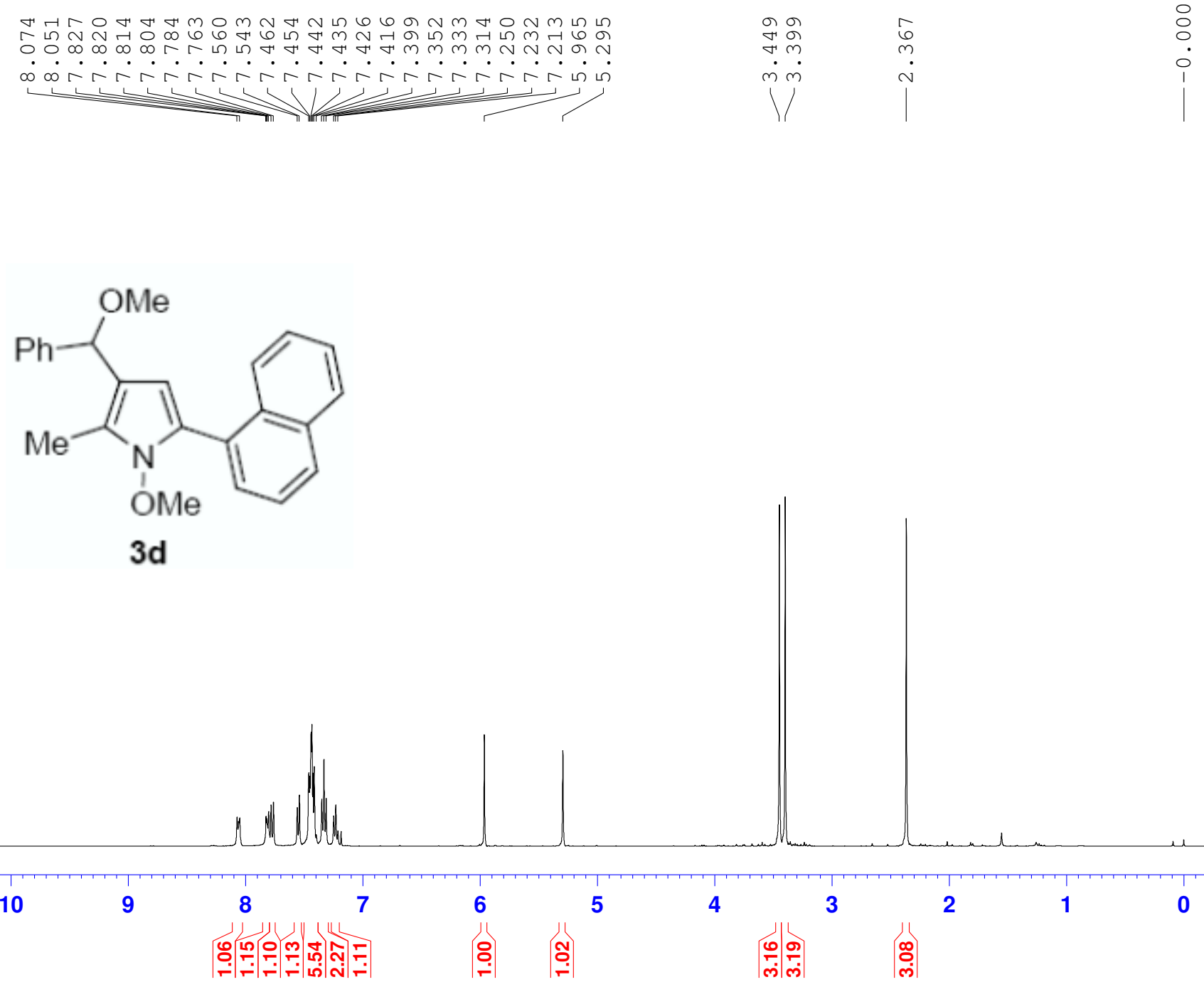


3b

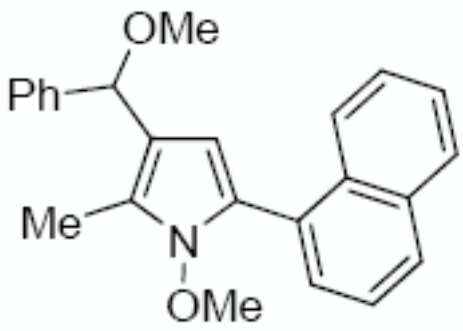




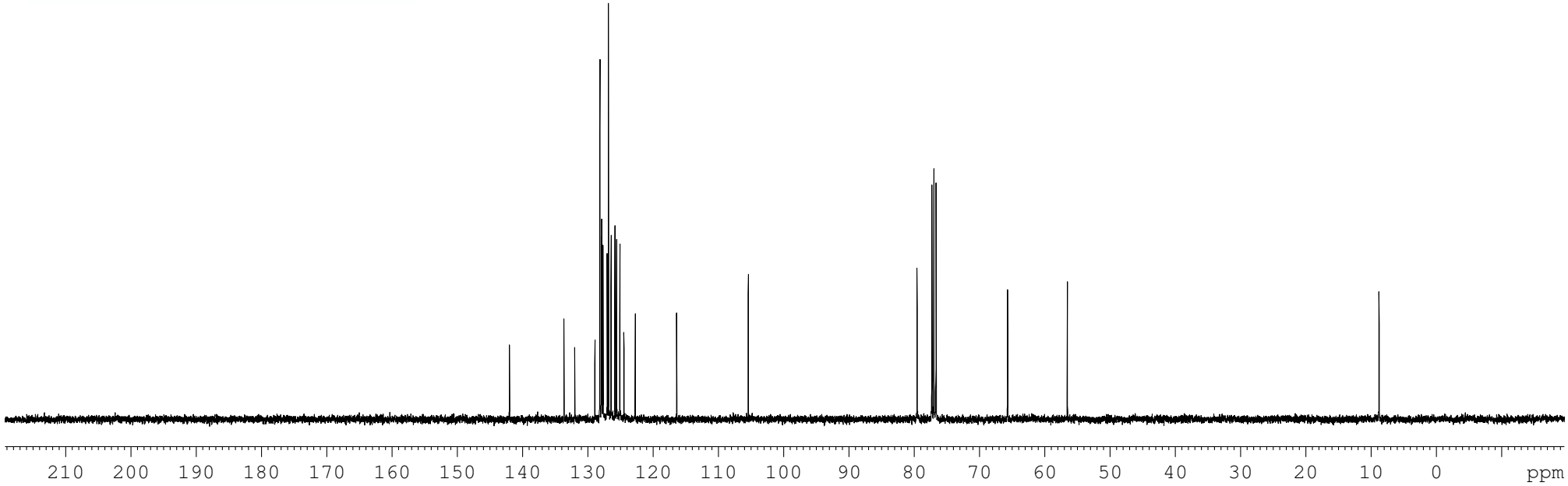


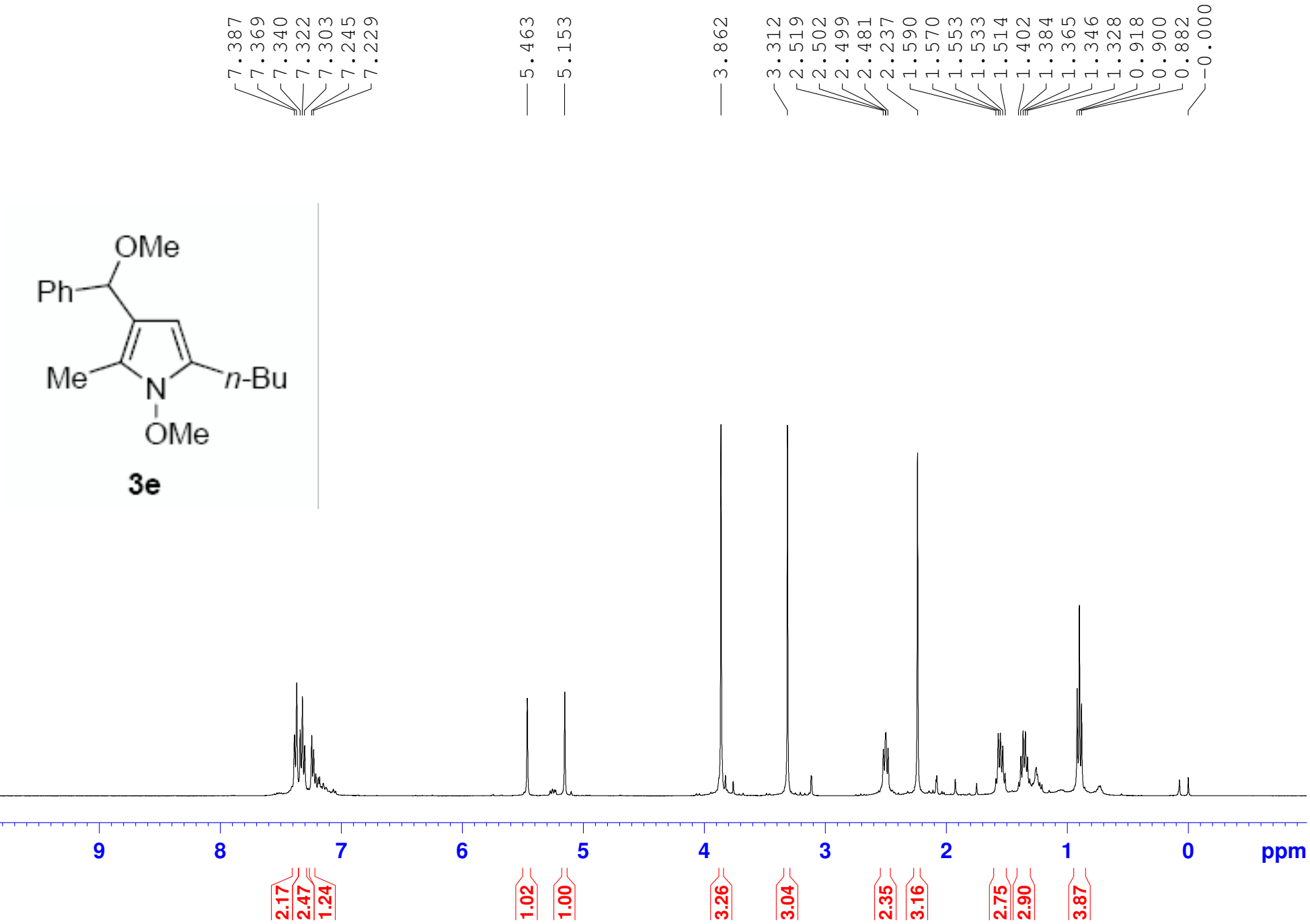


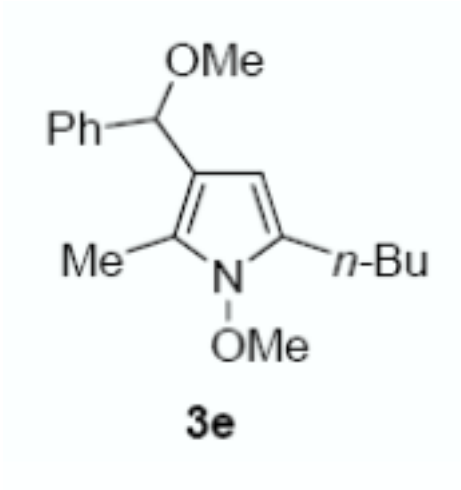
142.05
133.69
132.04
128.96
128.19
127.96
127.90
127.71
127.07
126.87
126.47
125.89
125.64
125.13
124.50
122.76
116.42
105.44
79.59
77.32
77.00
76.68
65.71
56.56
8.80



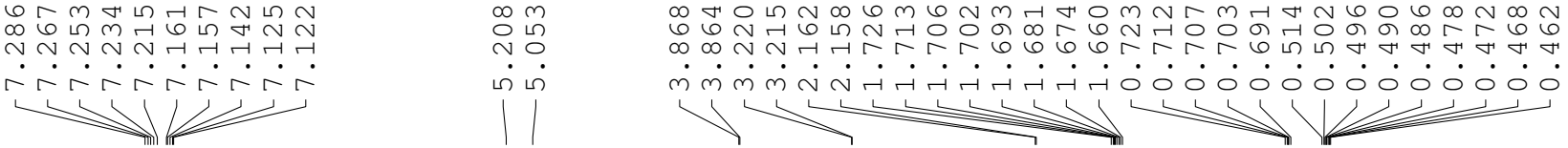
3d

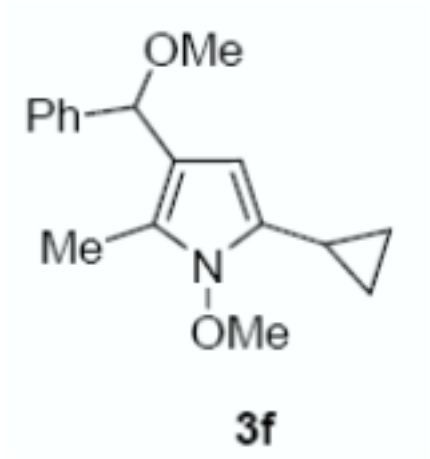




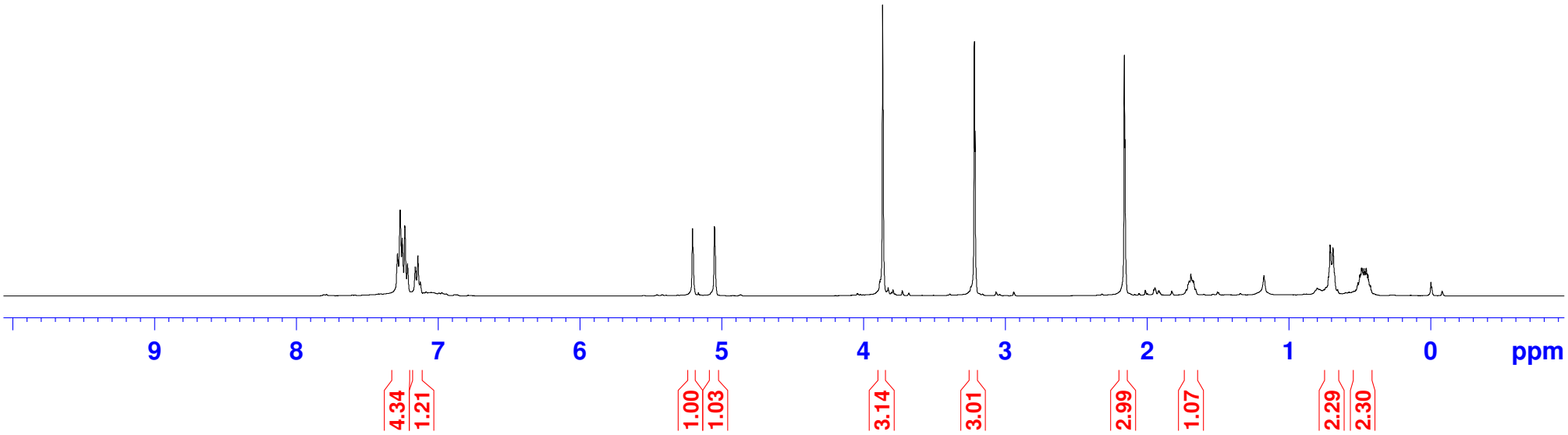


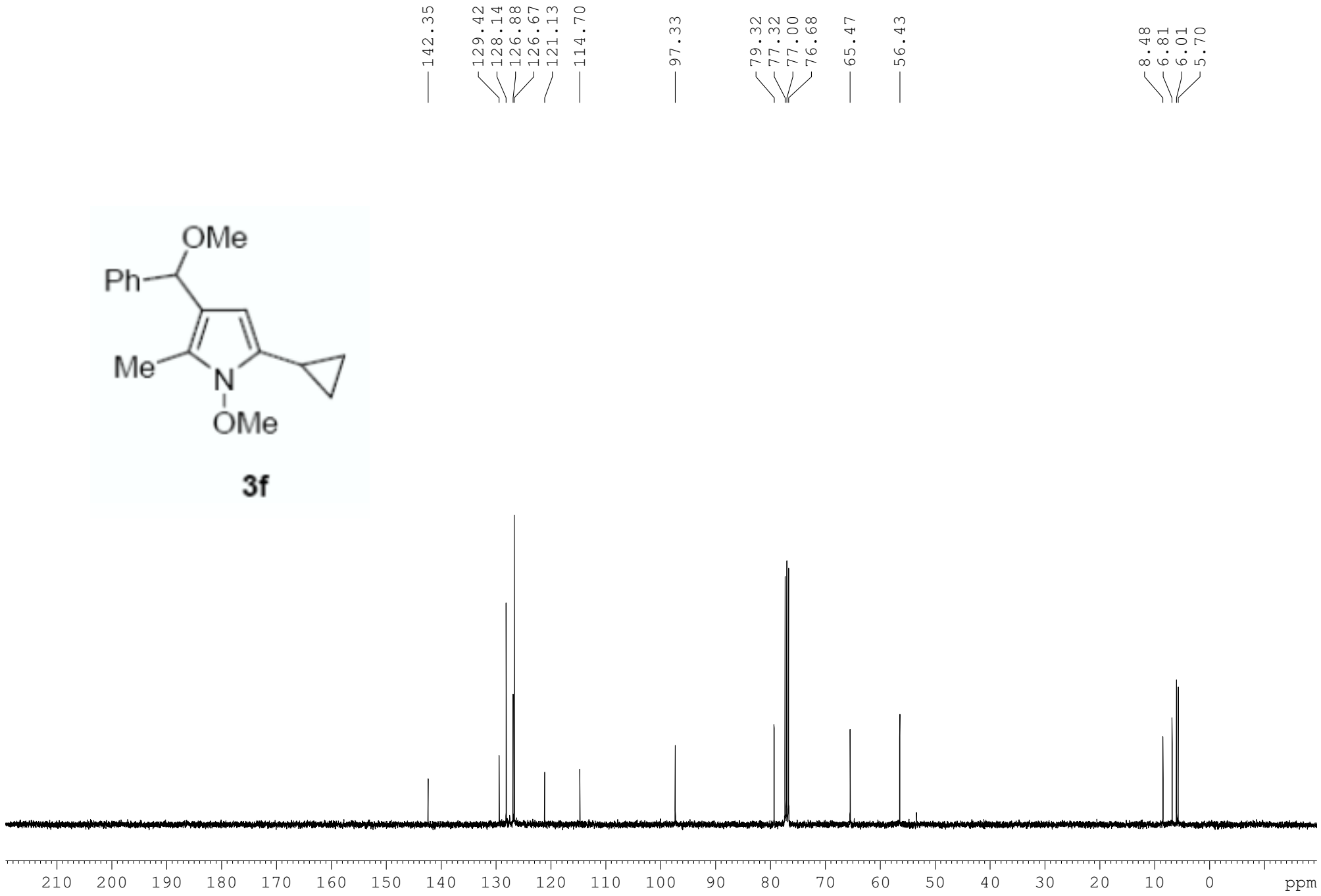
3e

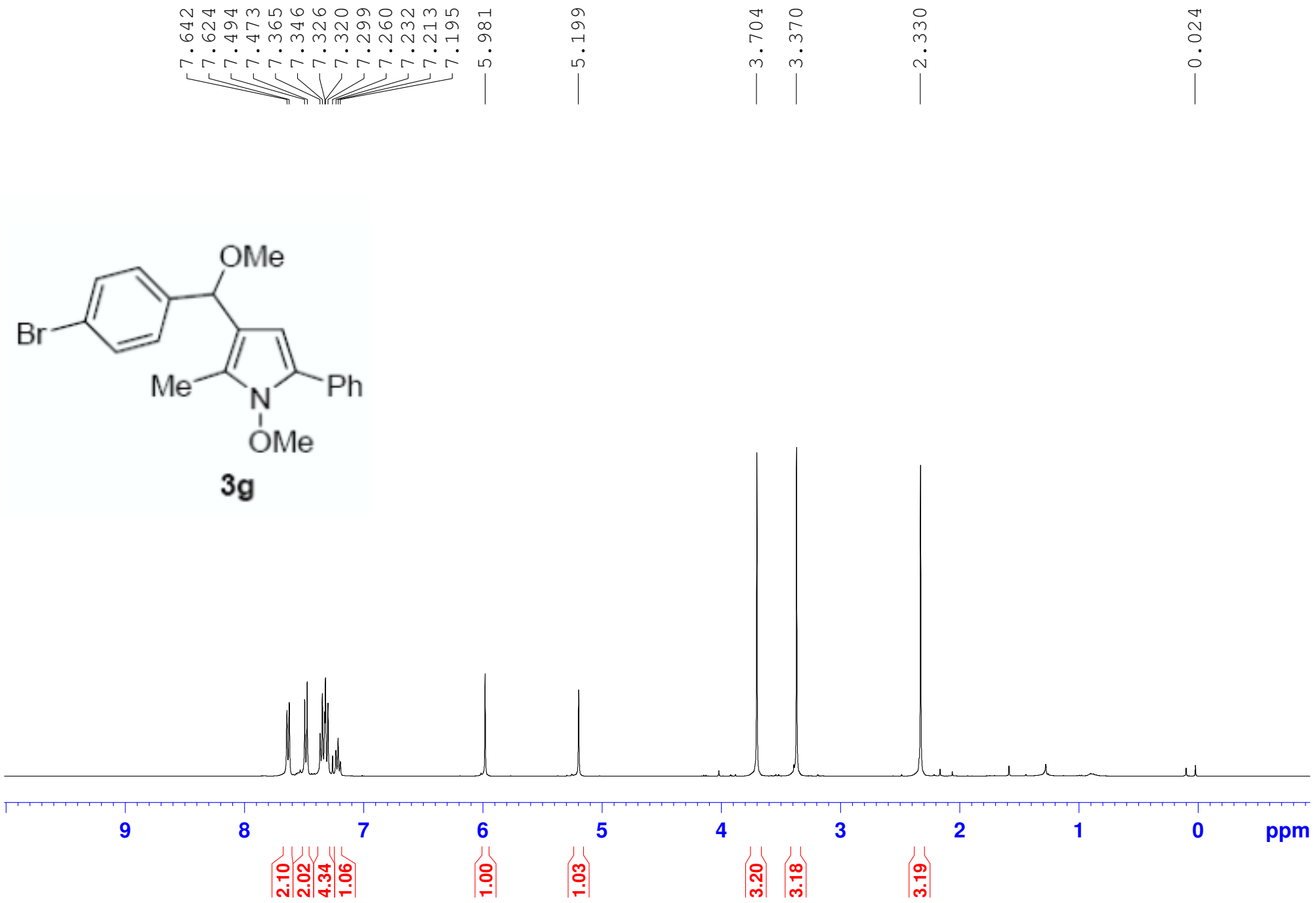




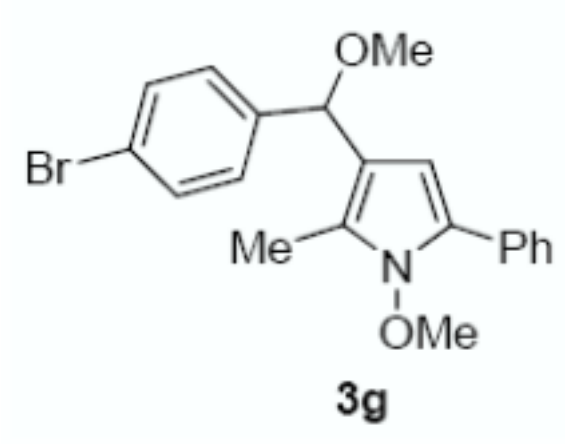
3f



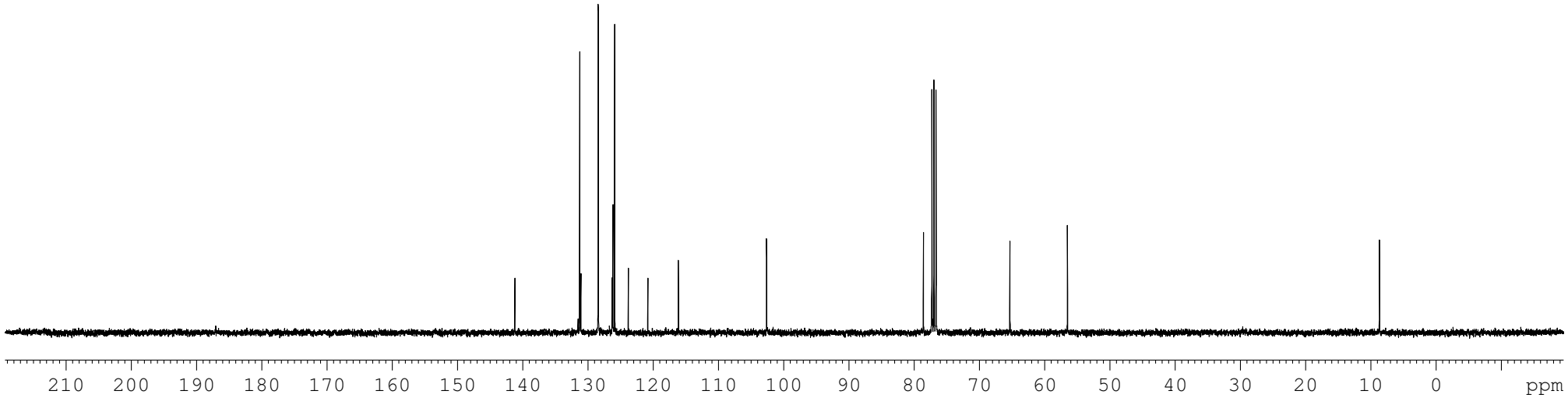


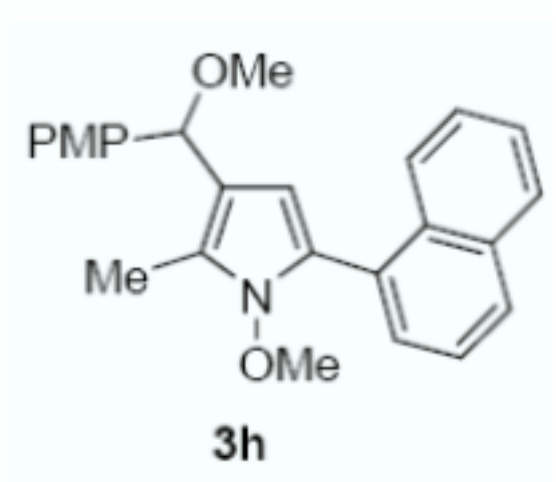


141.23
131.30
131.12
128.46
128.45
126.33
126.21
125.96
123.85
120.85
116.17
102.65
78.62
77.32
77.00
76.68
65.36
56.53
8.71



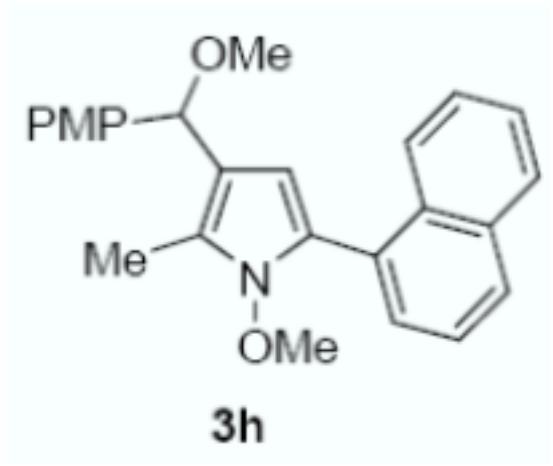
3g



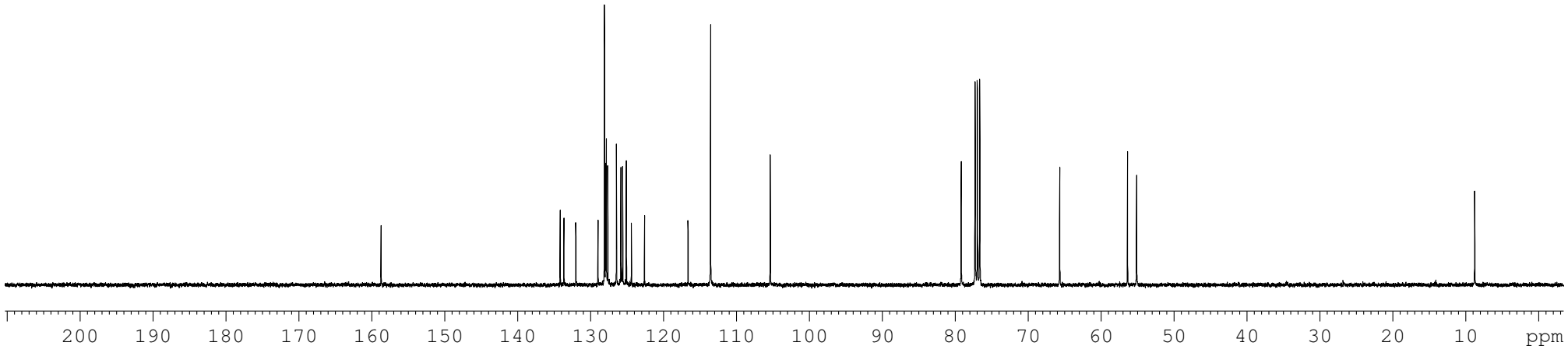


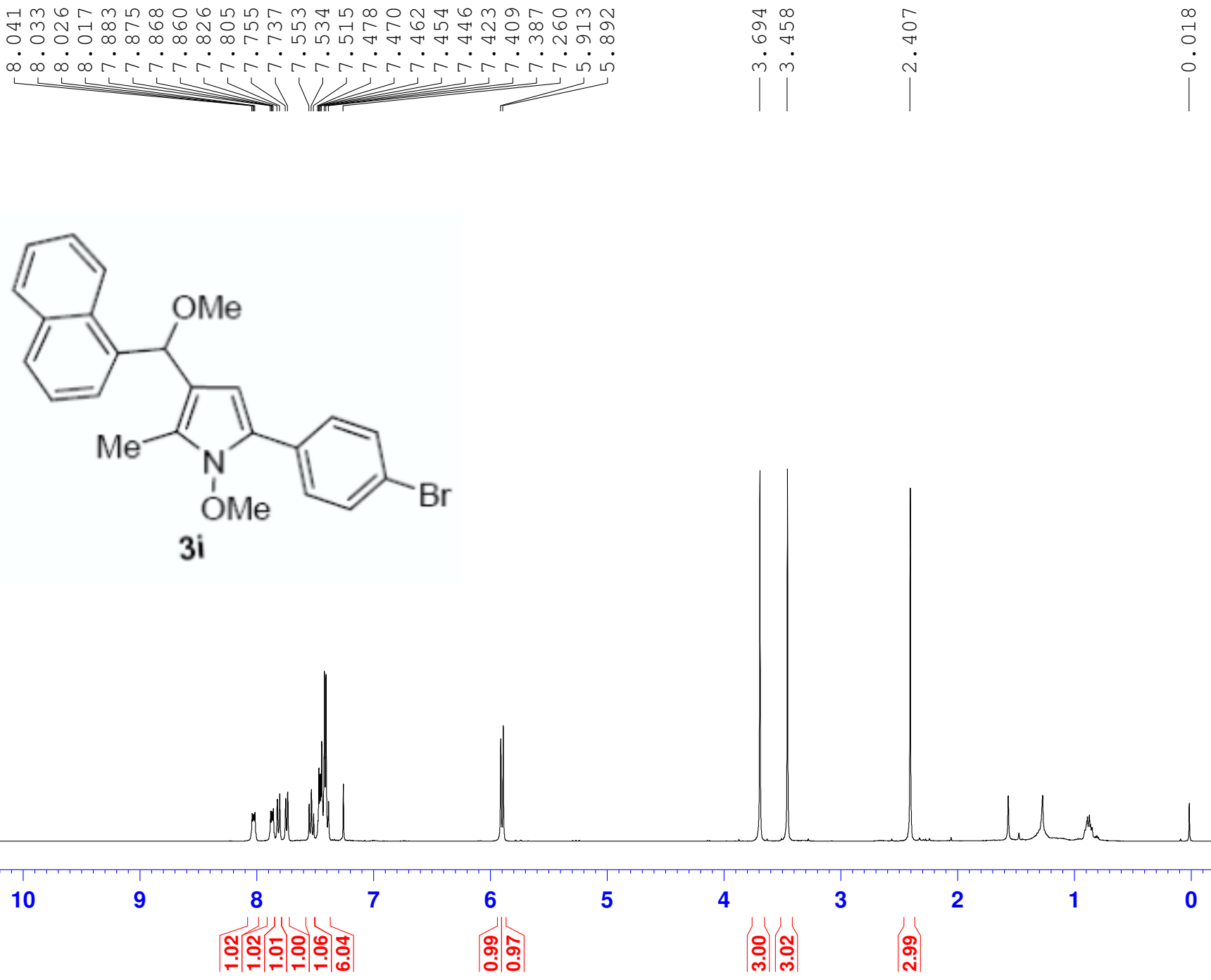
3h

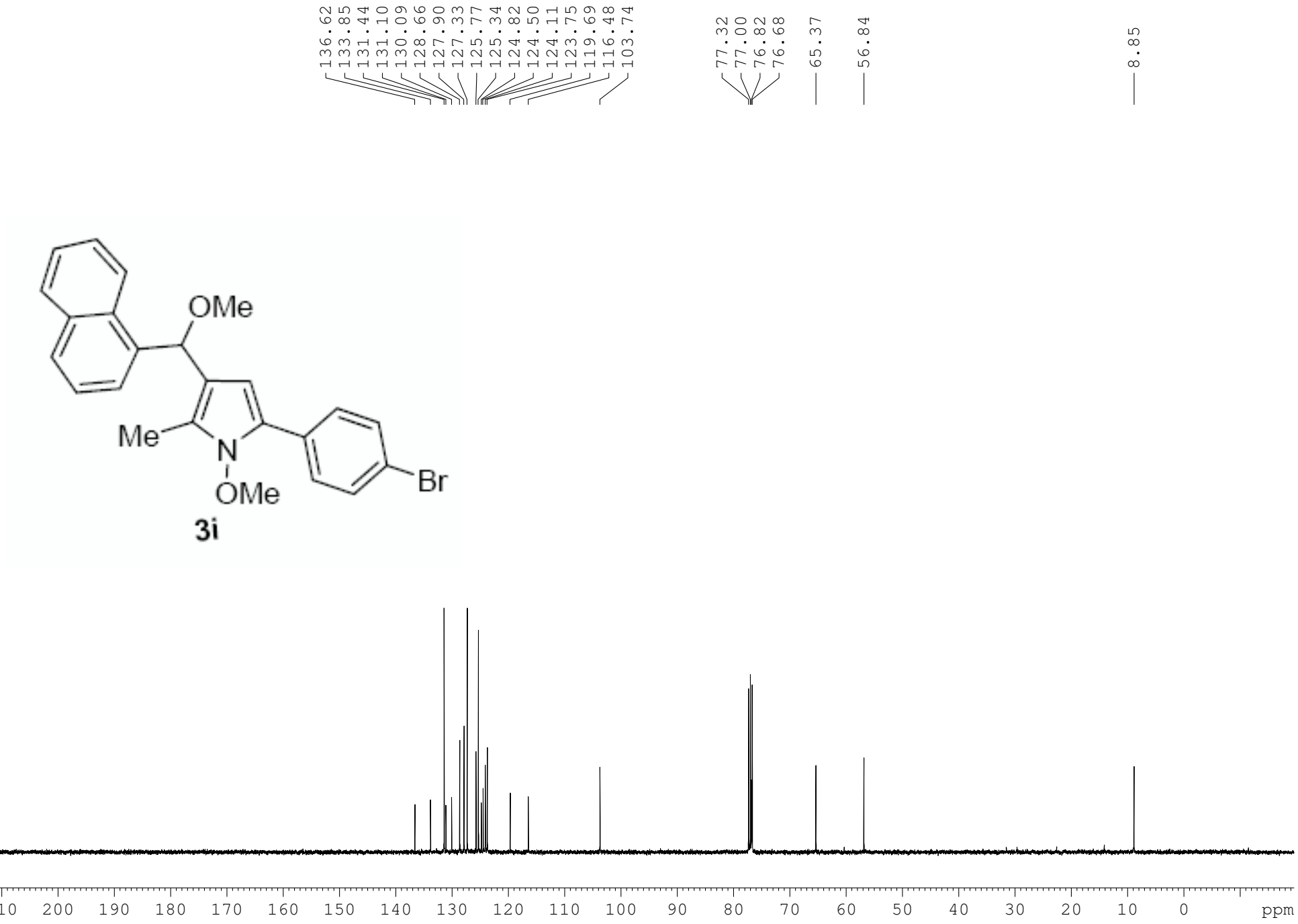
158.70
134.21
133.70
132.06
129.01
128.12
127.95
127.89
127.68
126.49
125.88
125.63
125.13
124.44
122.64
116.68
113.58
105.40
79.21
77.31
77.00
76.68
65.70
56.39
55.15
8.79

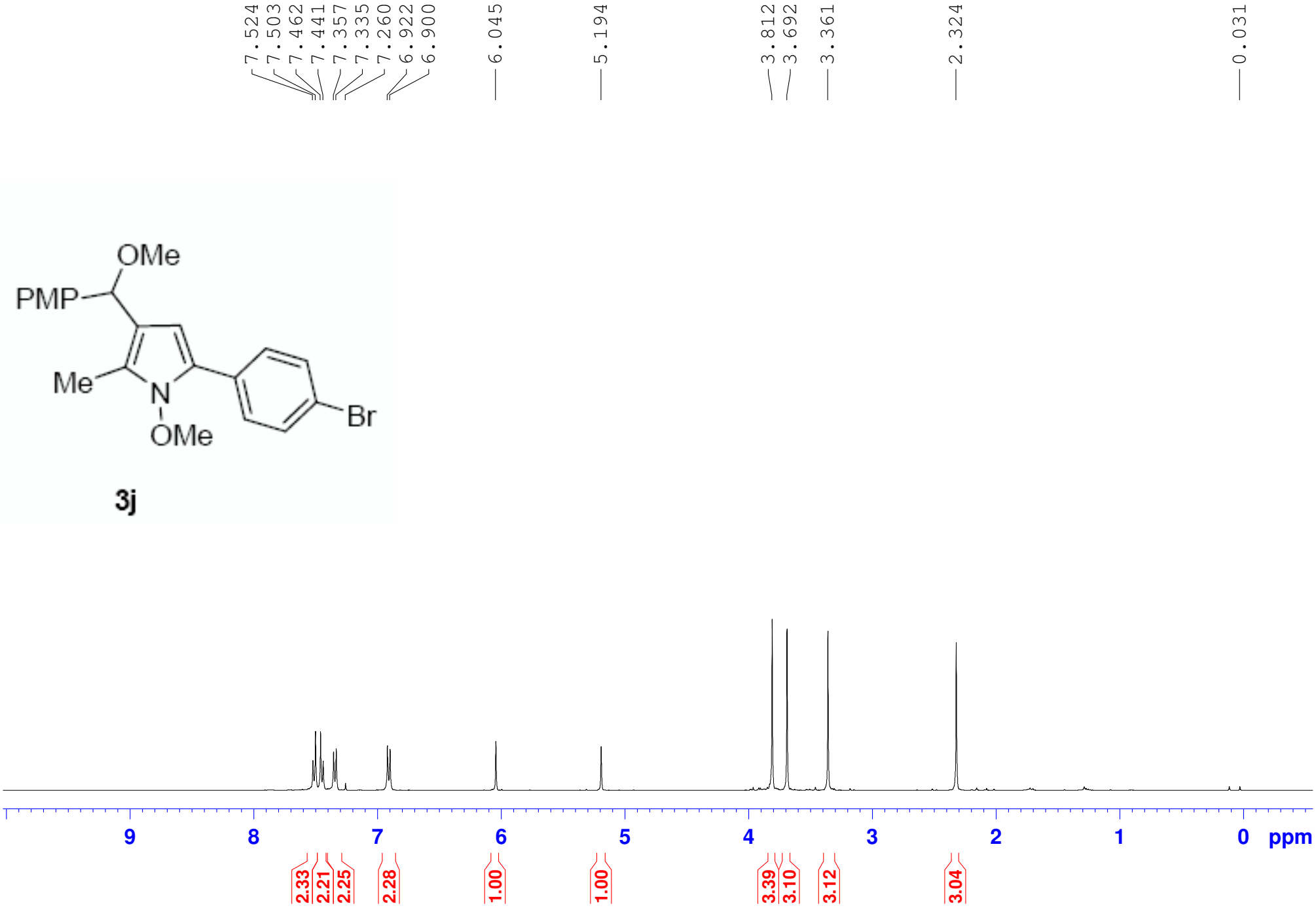


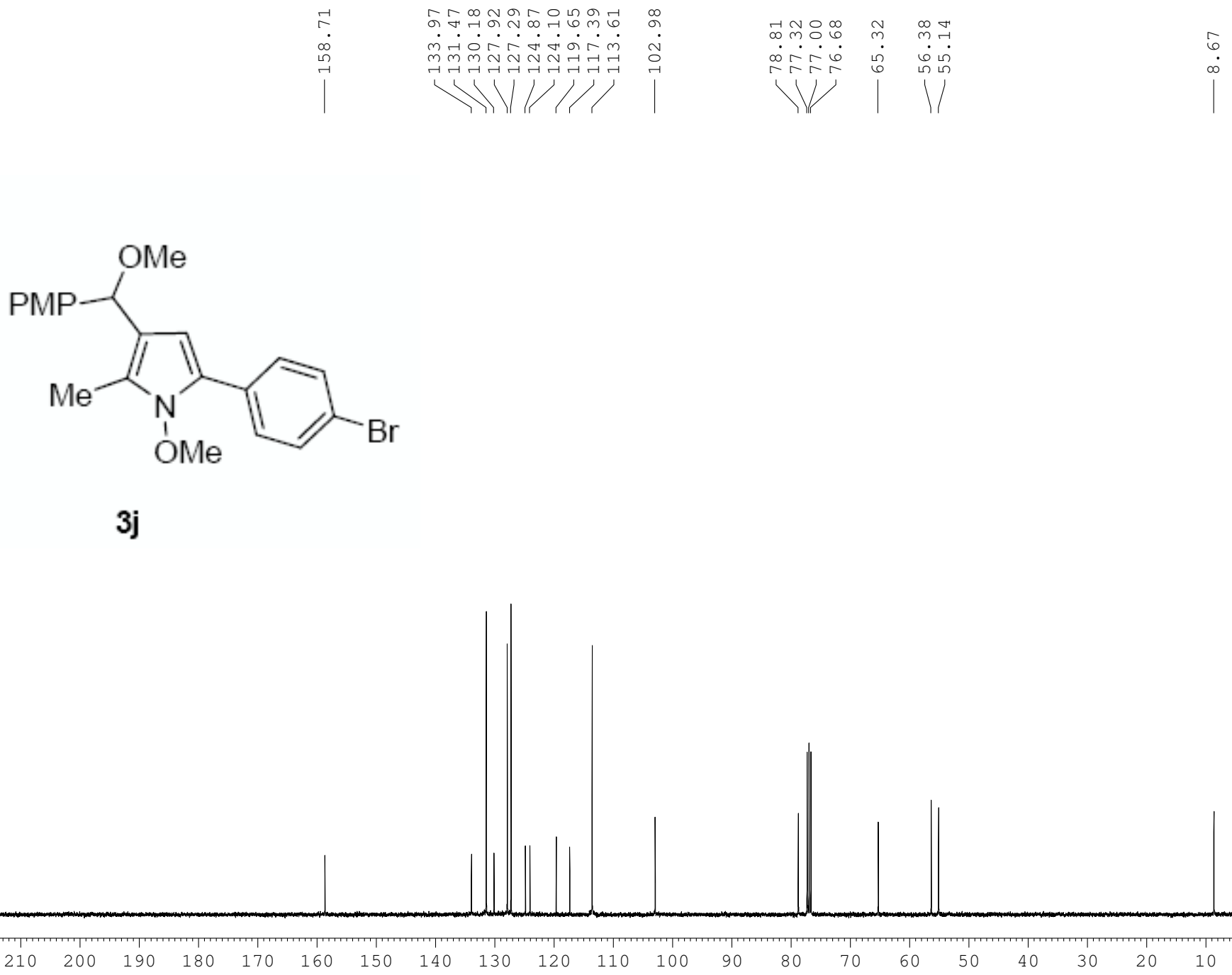
3h

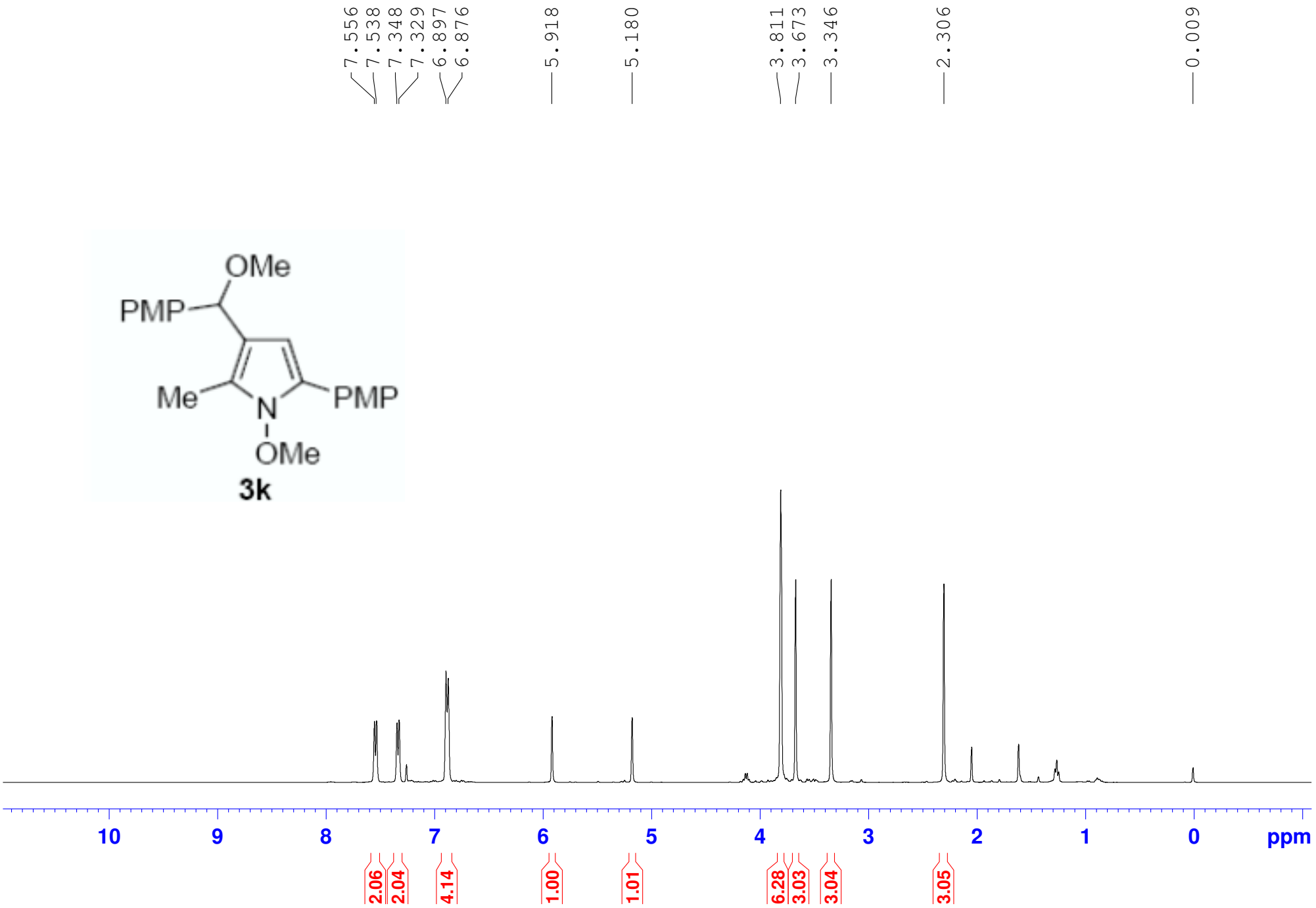


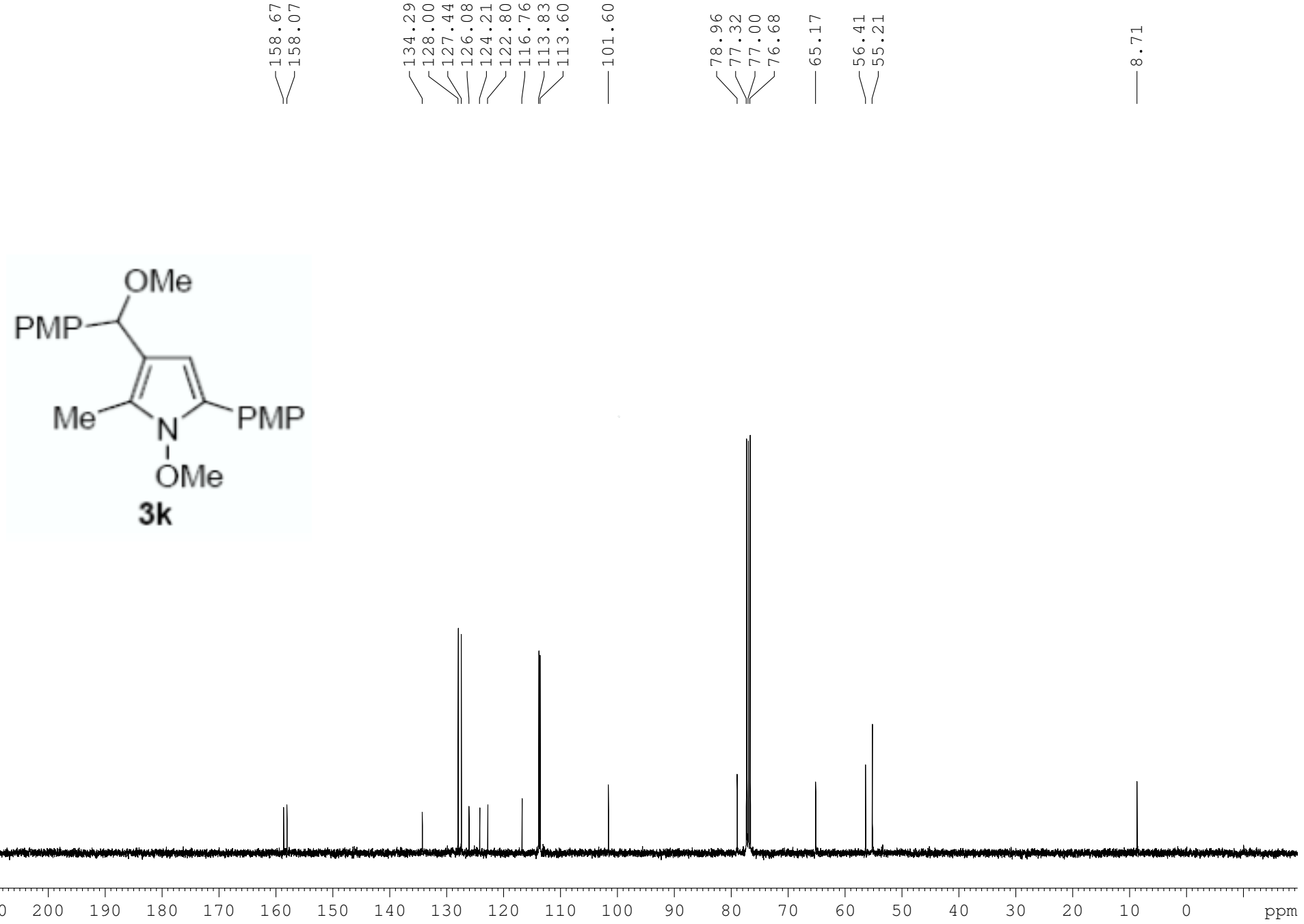


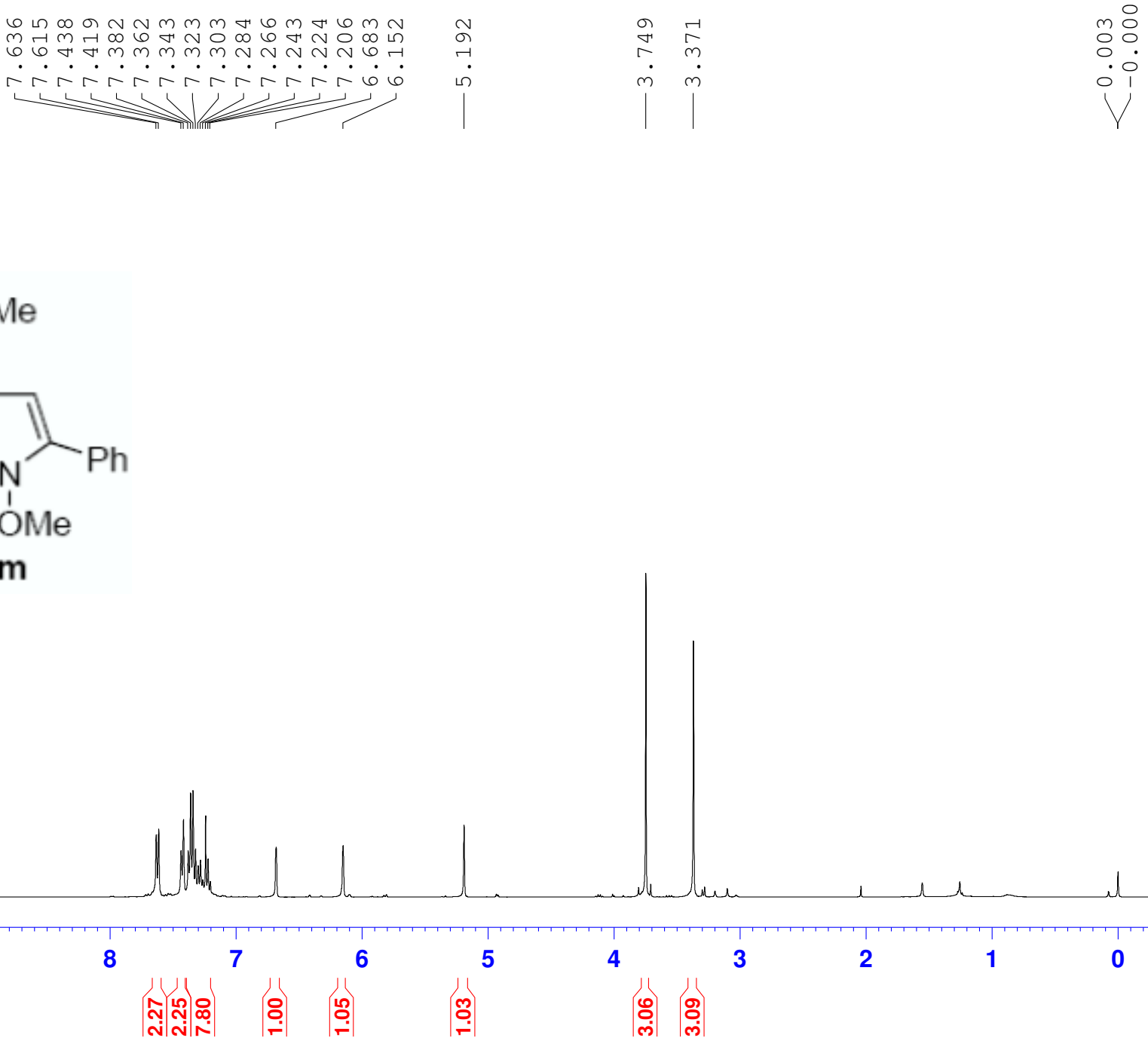


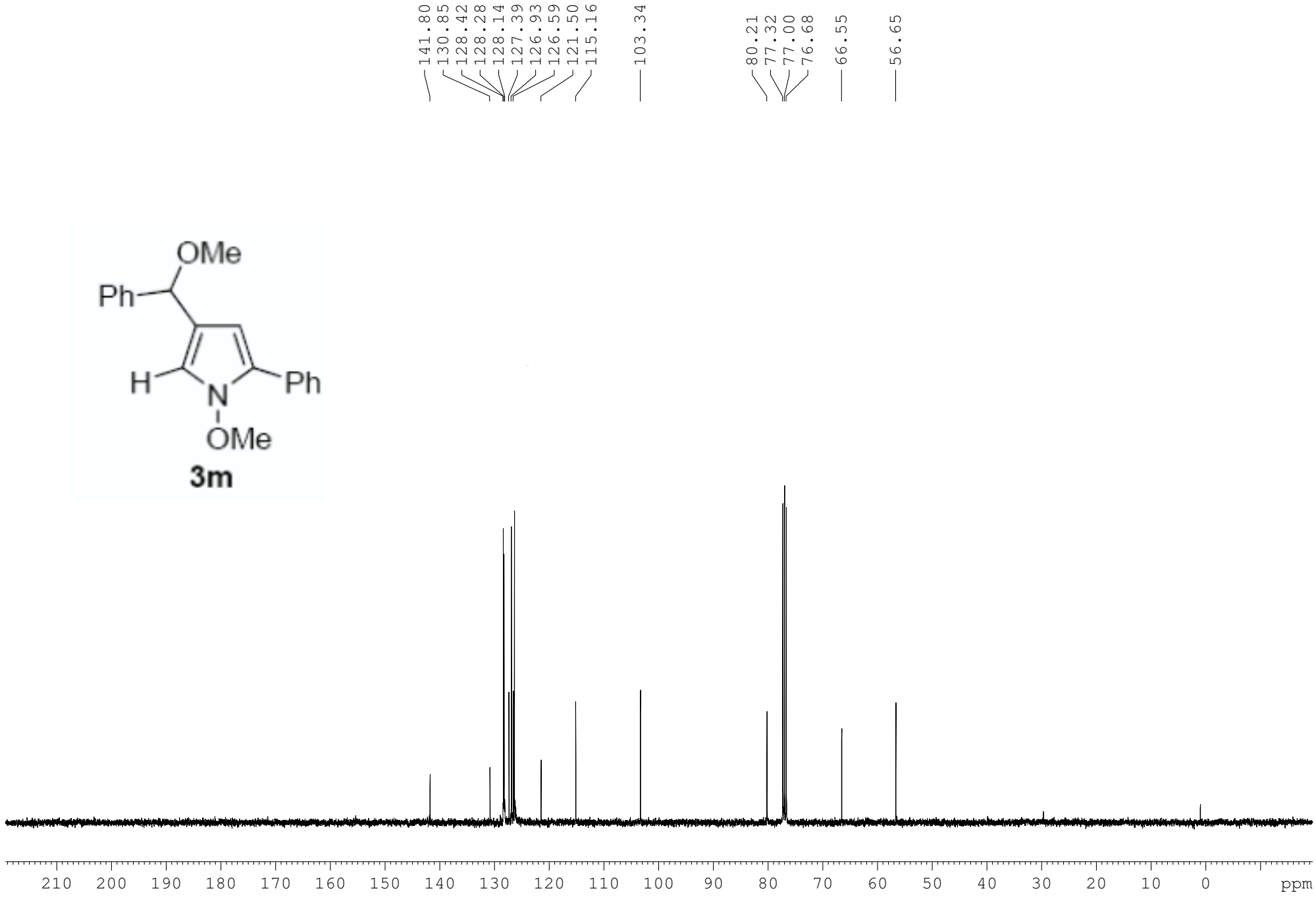


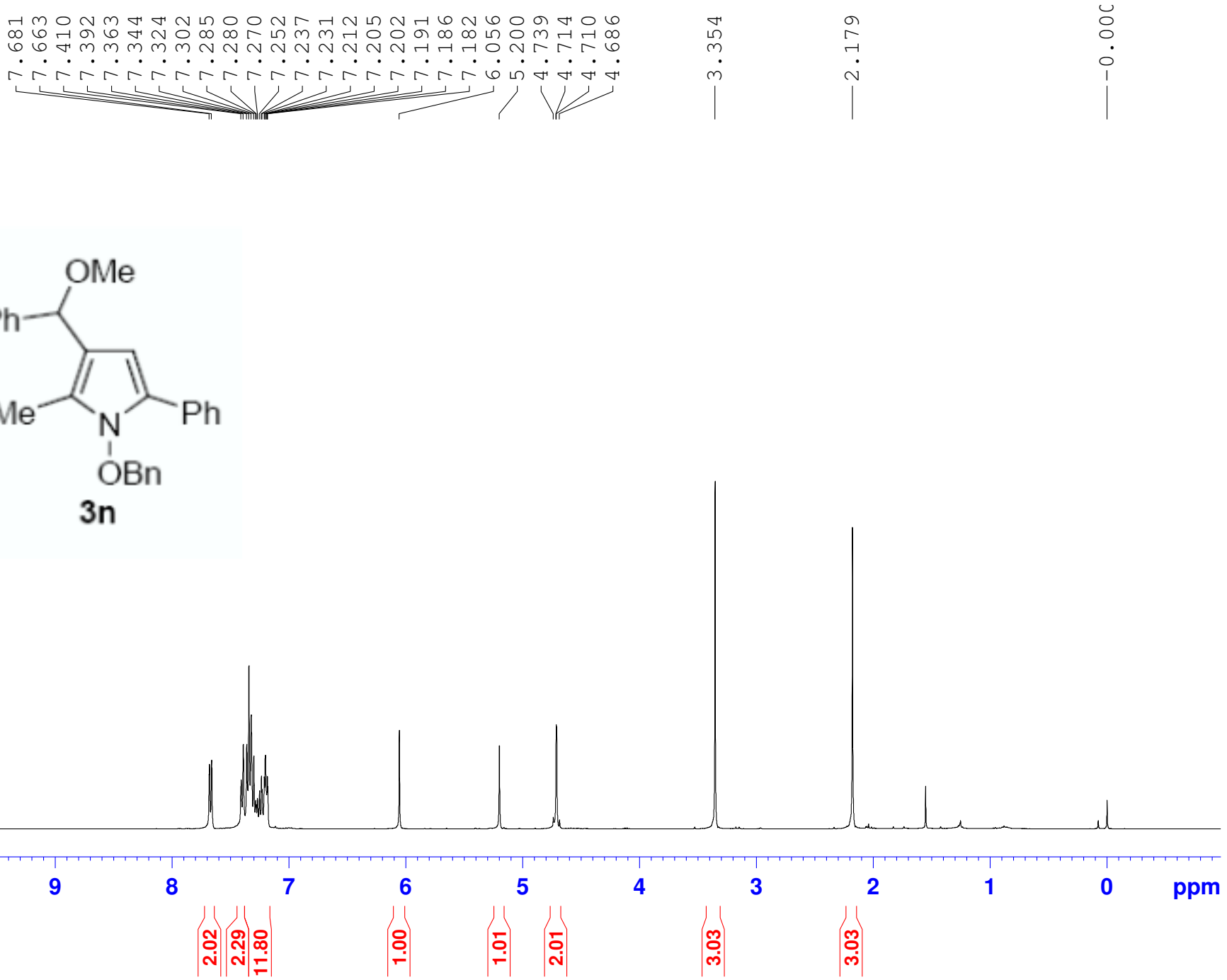




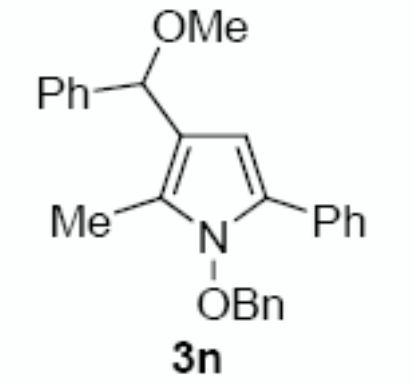




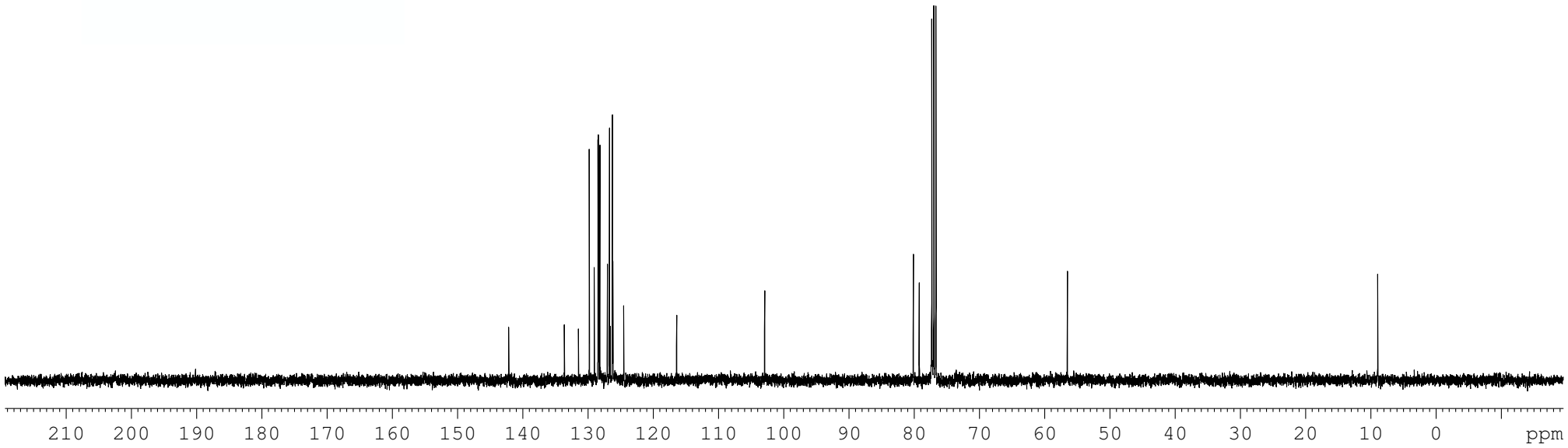


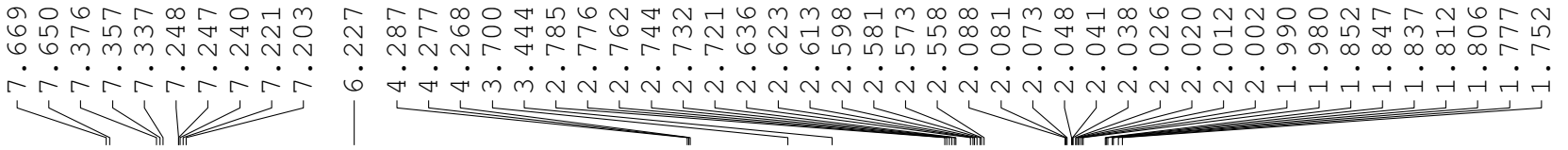


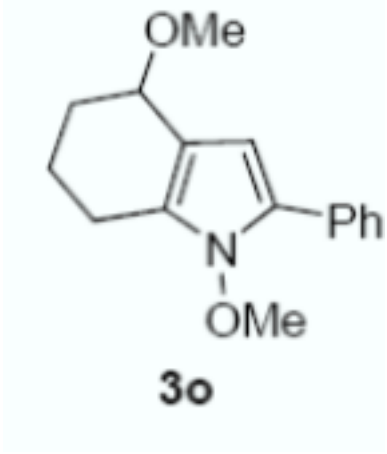
142.20
133.65
131.49
129.83
129.07
128.50
128.42
128.21
127.05
126.73
126.61
126.29
126.21
124.55
116.43
102.94
80.14
79.24
77.32
77.00
76.68
56.52
8.95



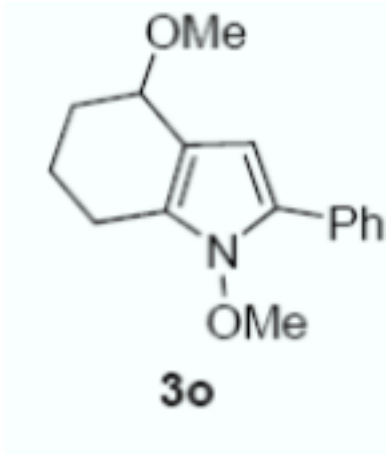
3n



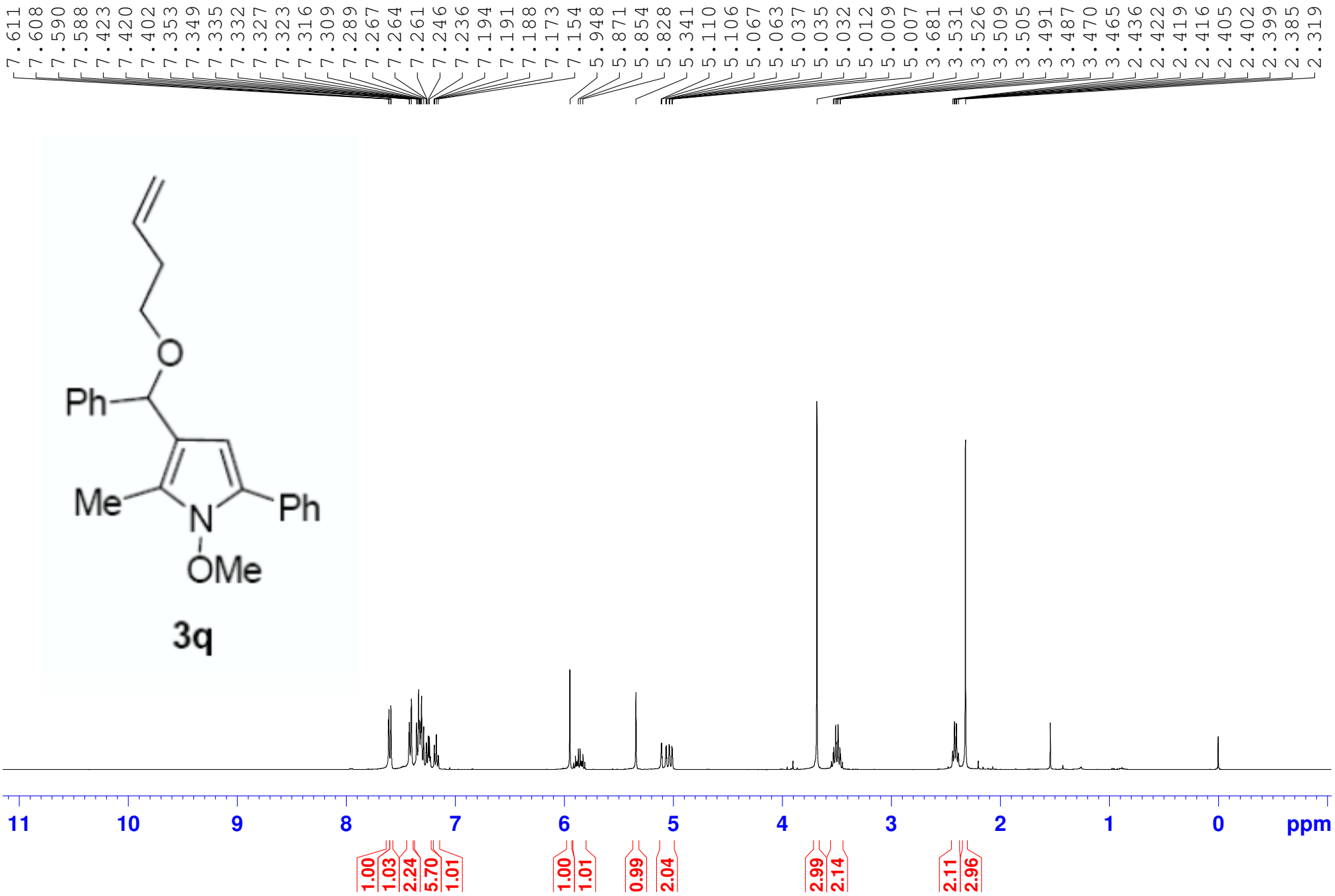


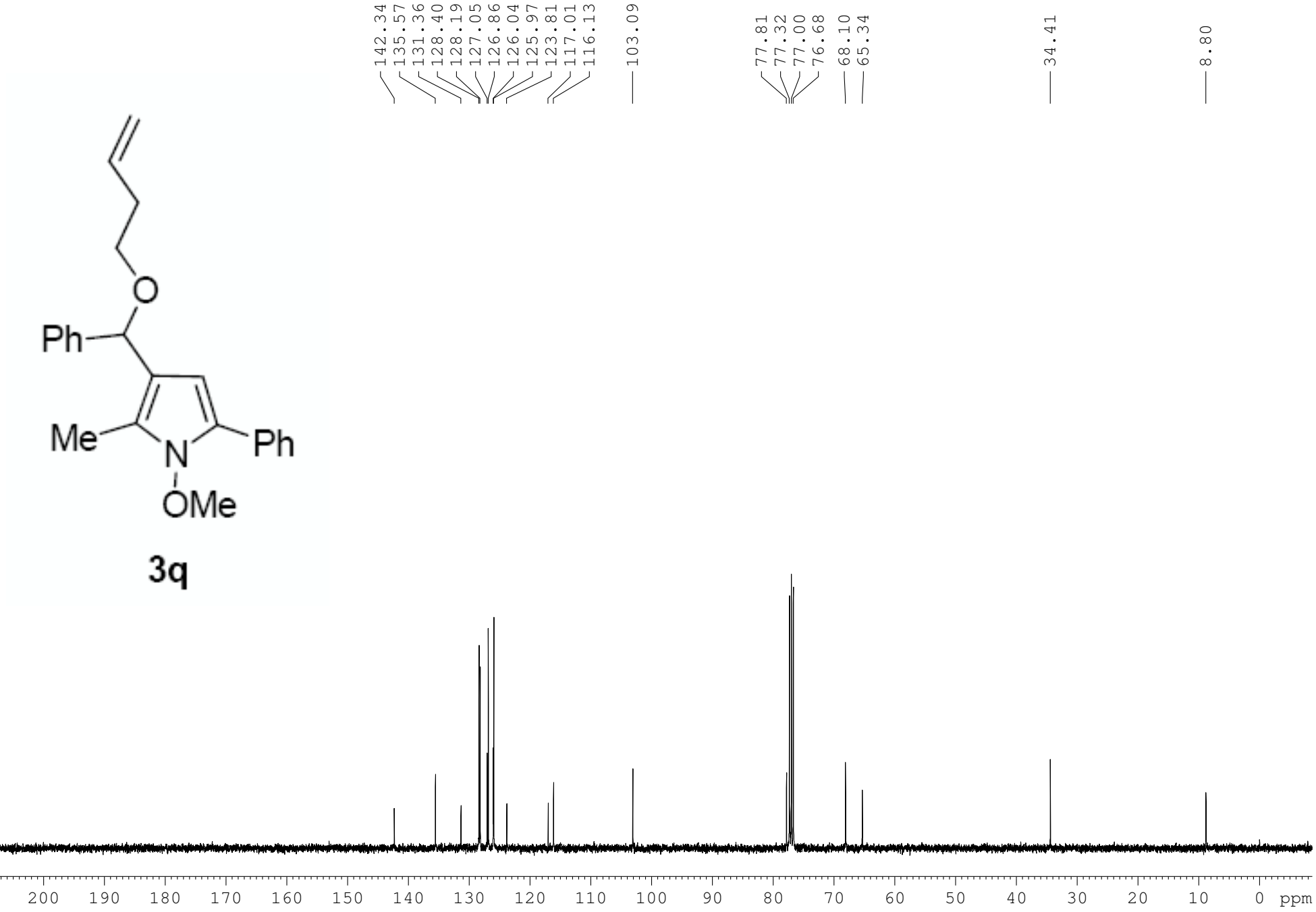


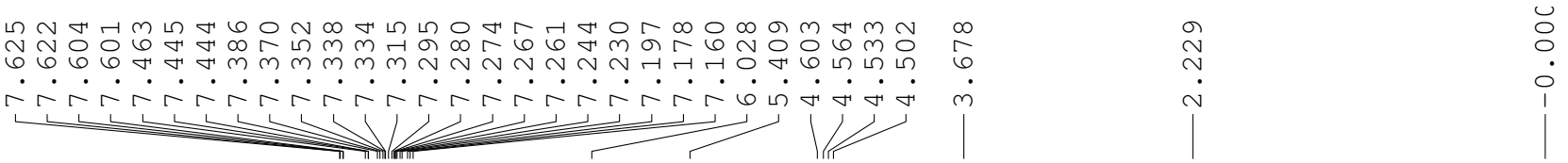
3o

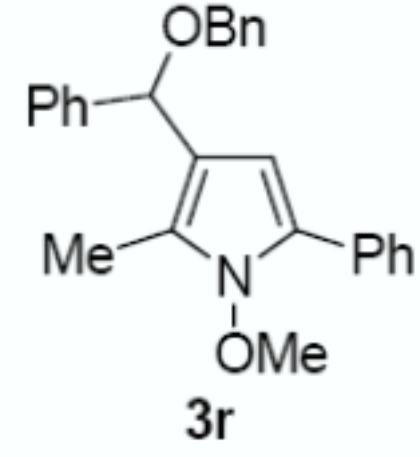


3o

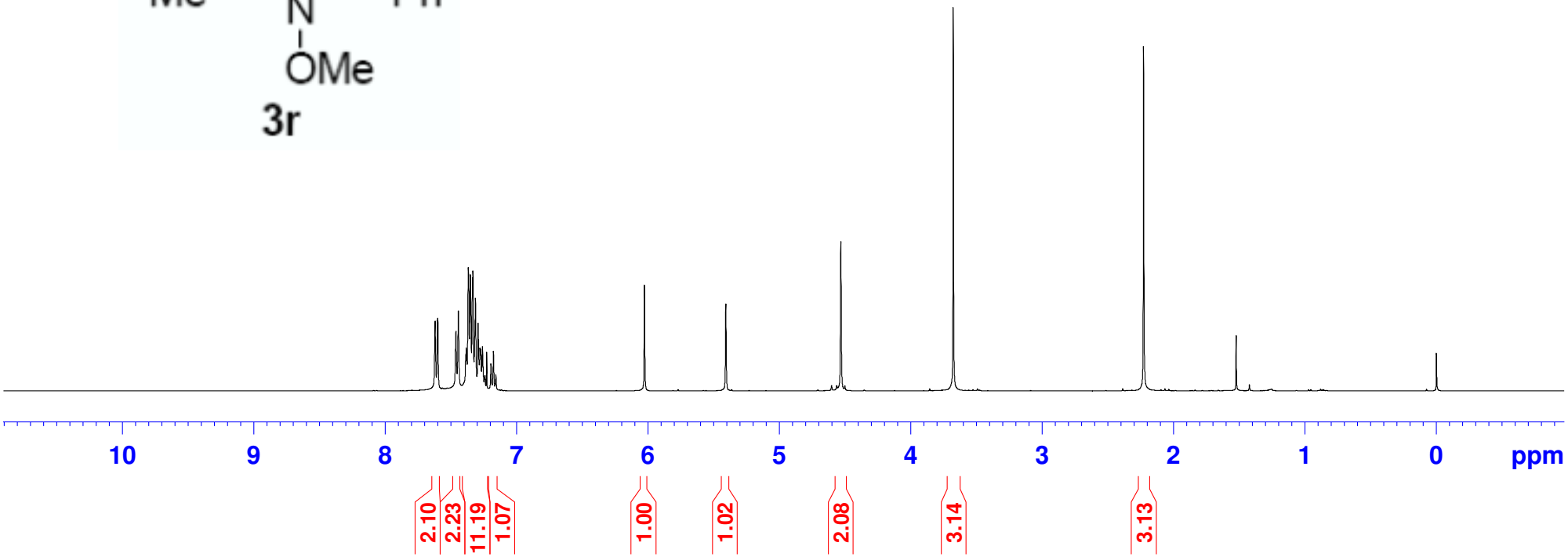


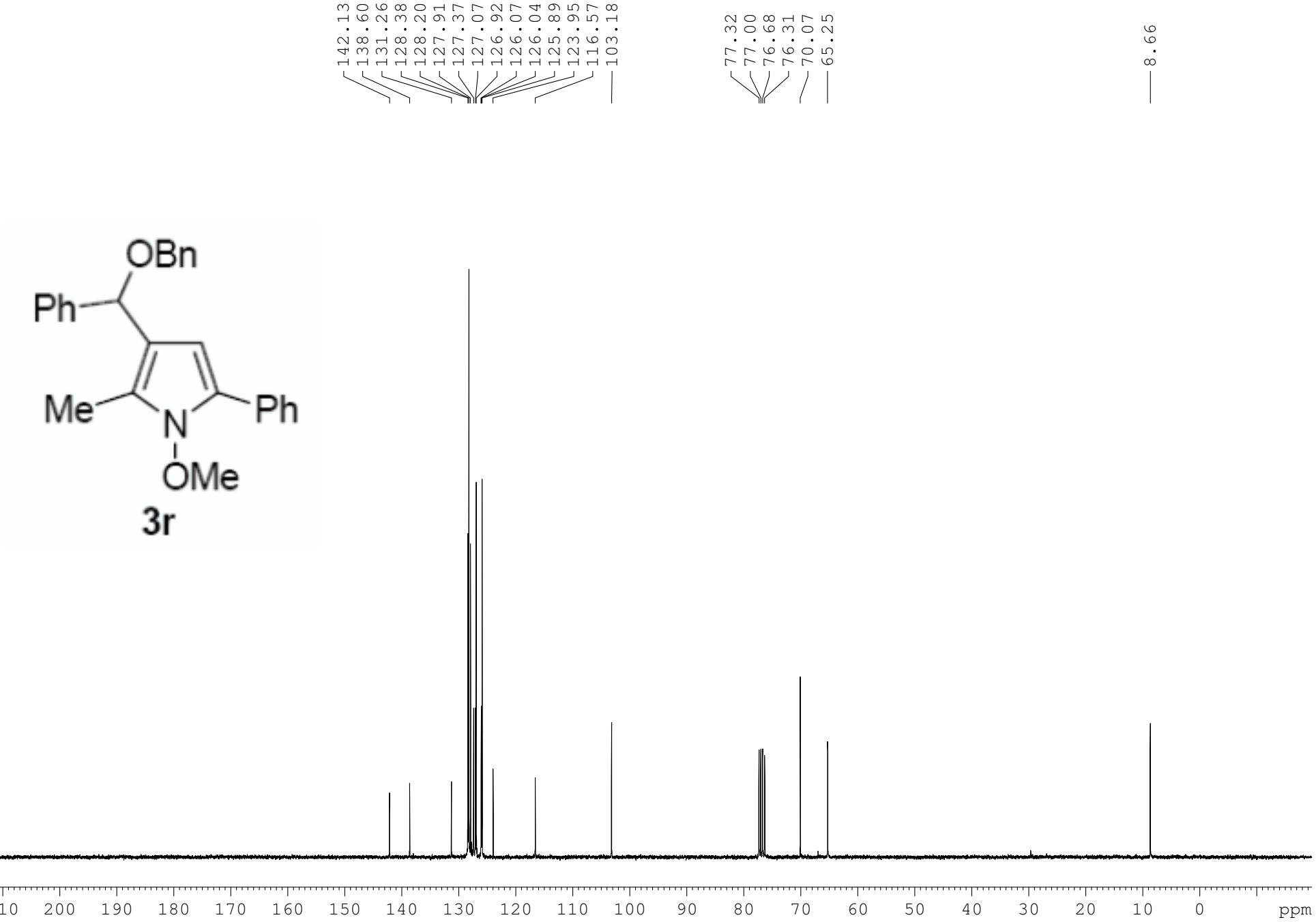


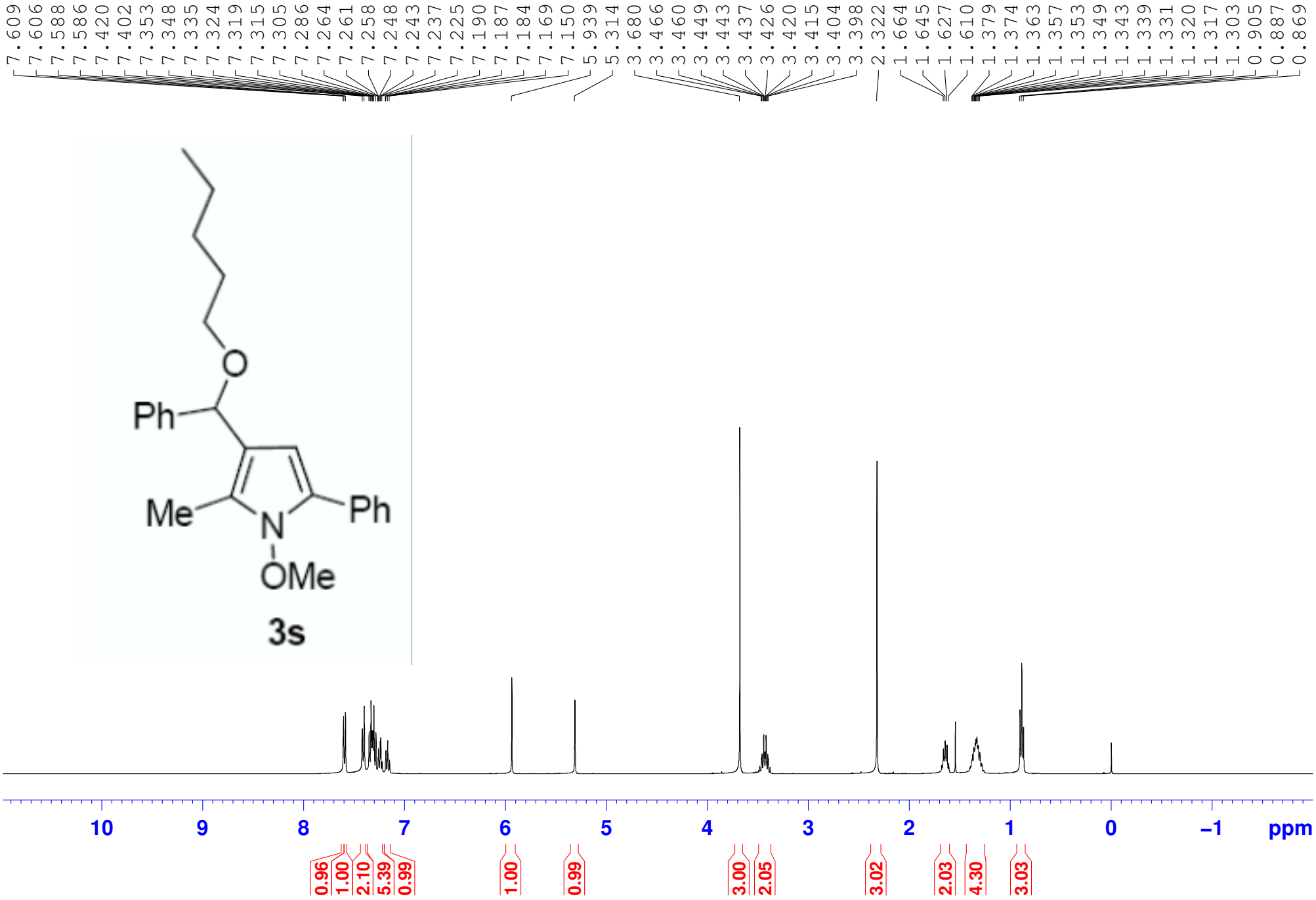


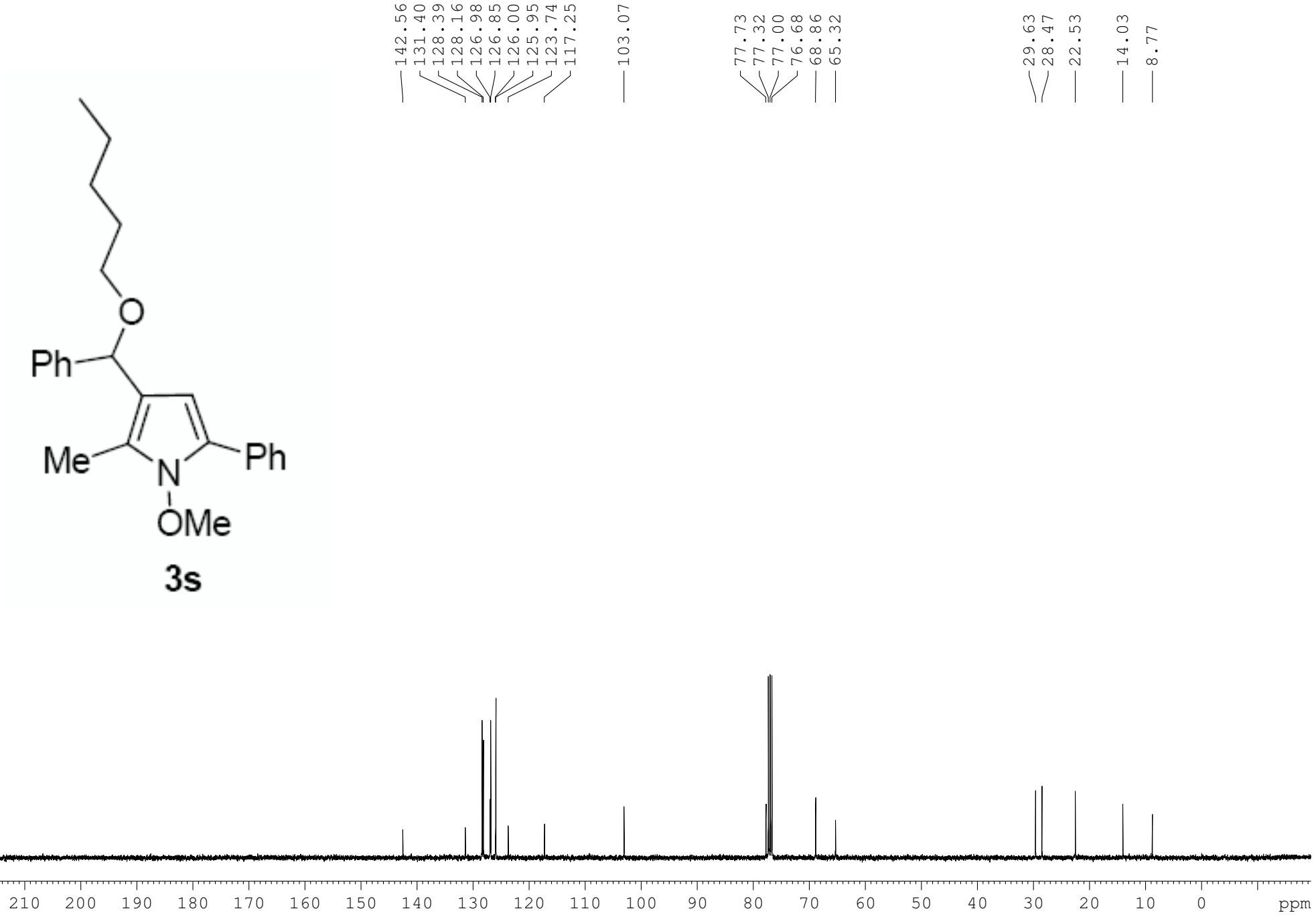


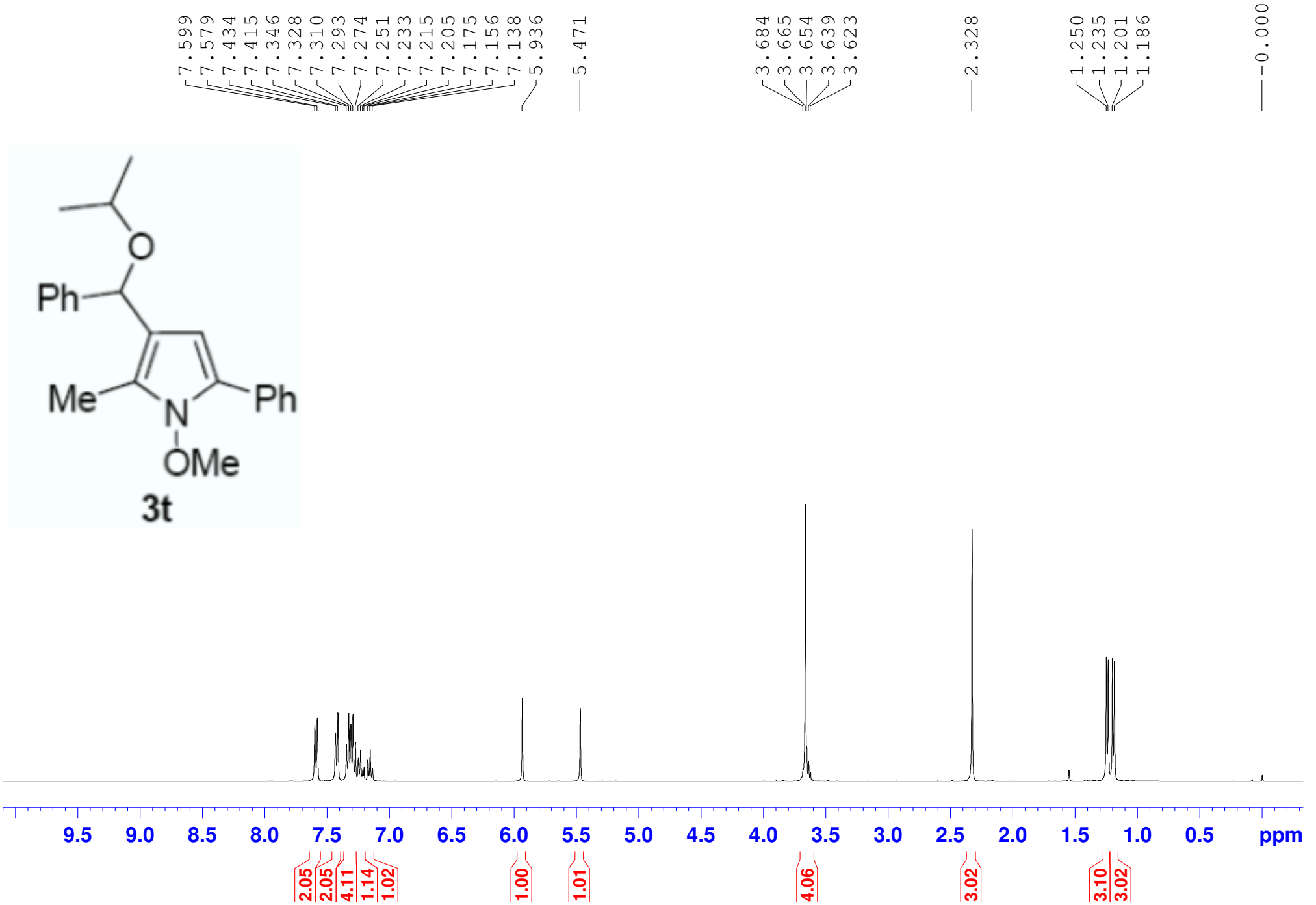
3r

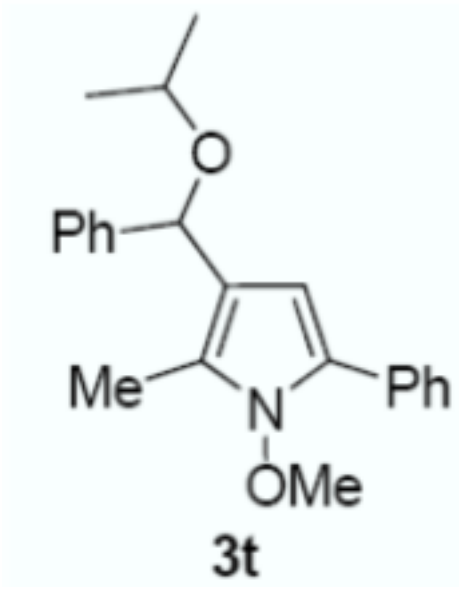




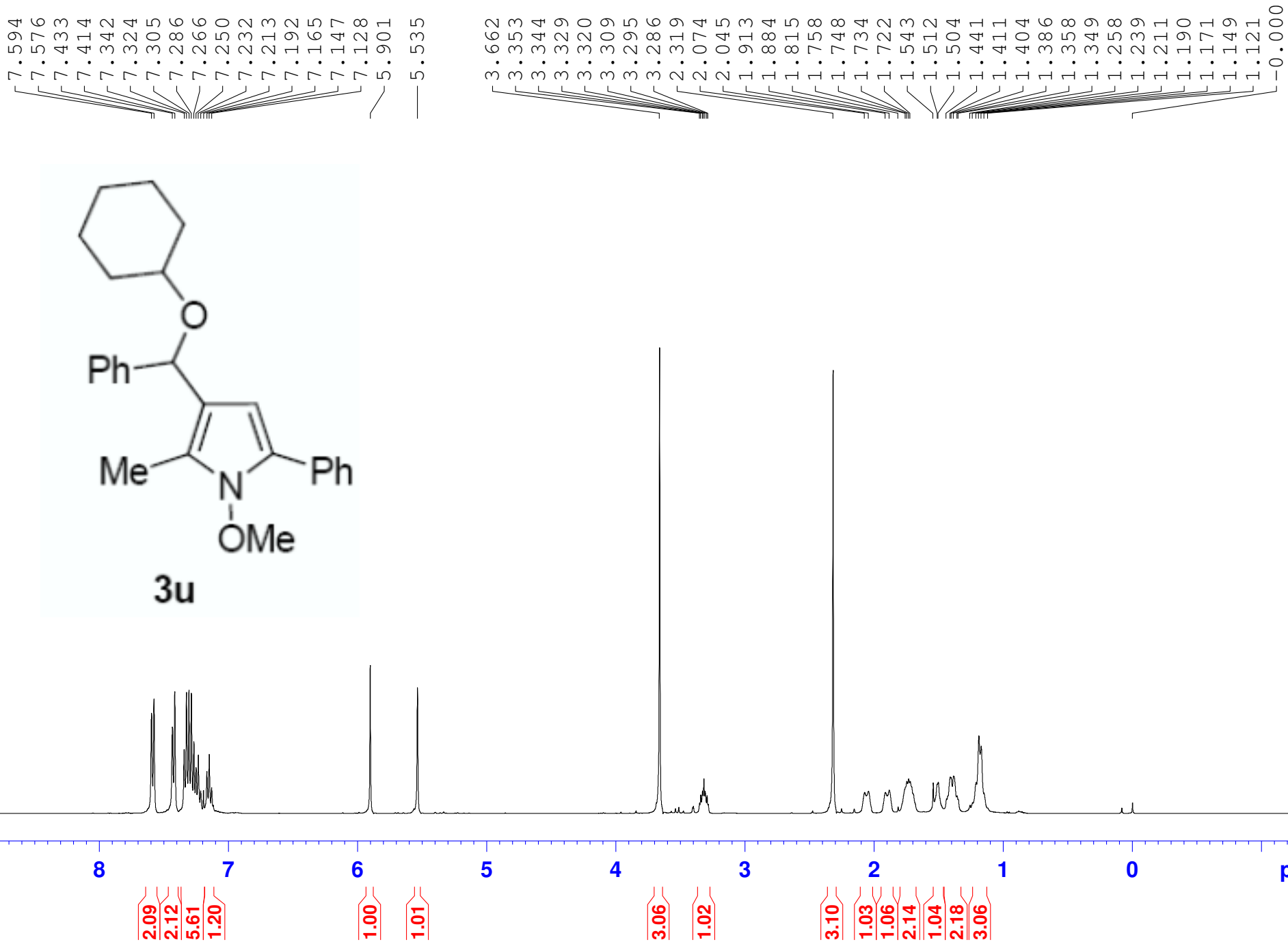


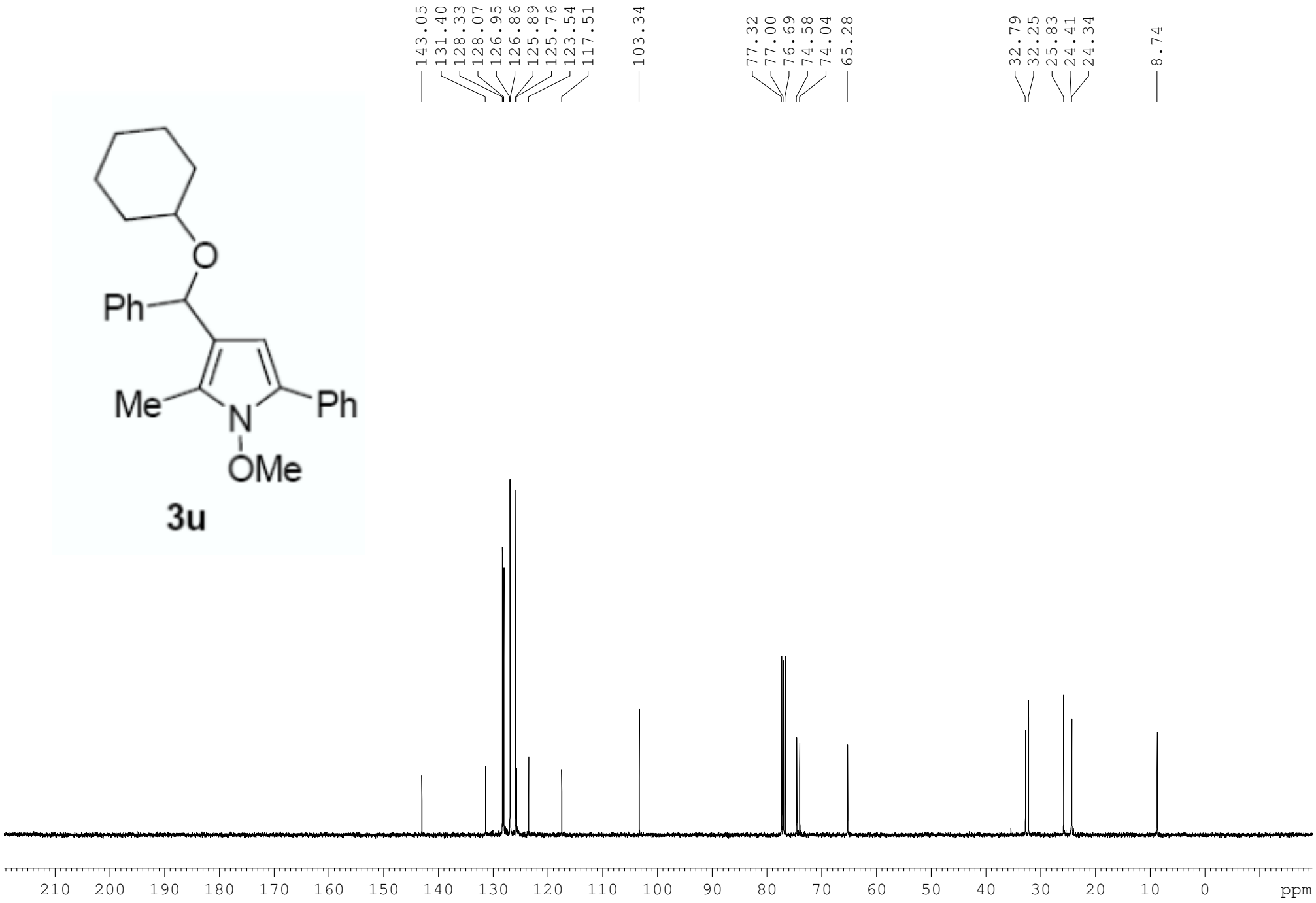


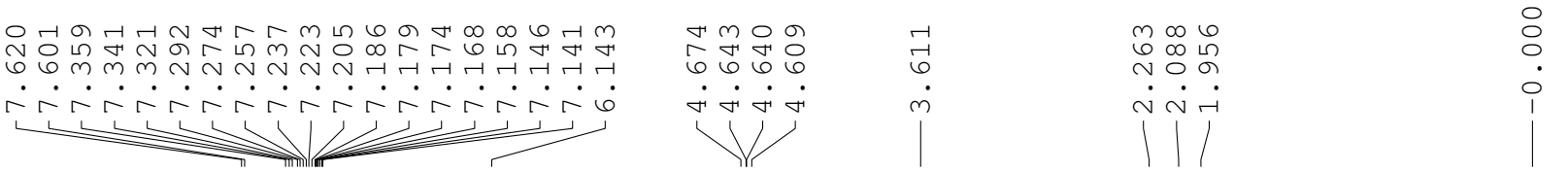


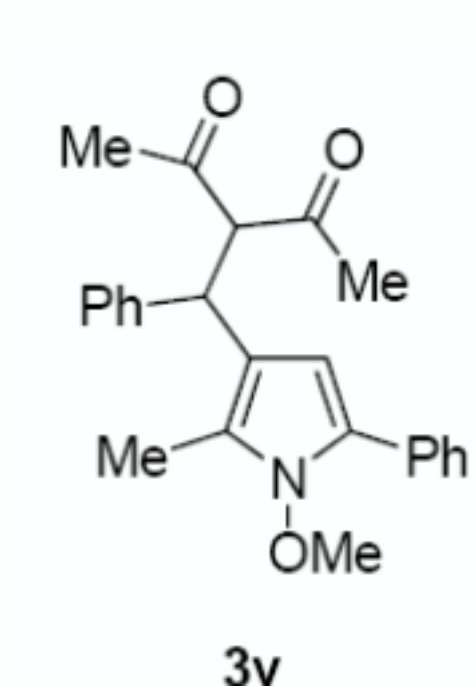


3t

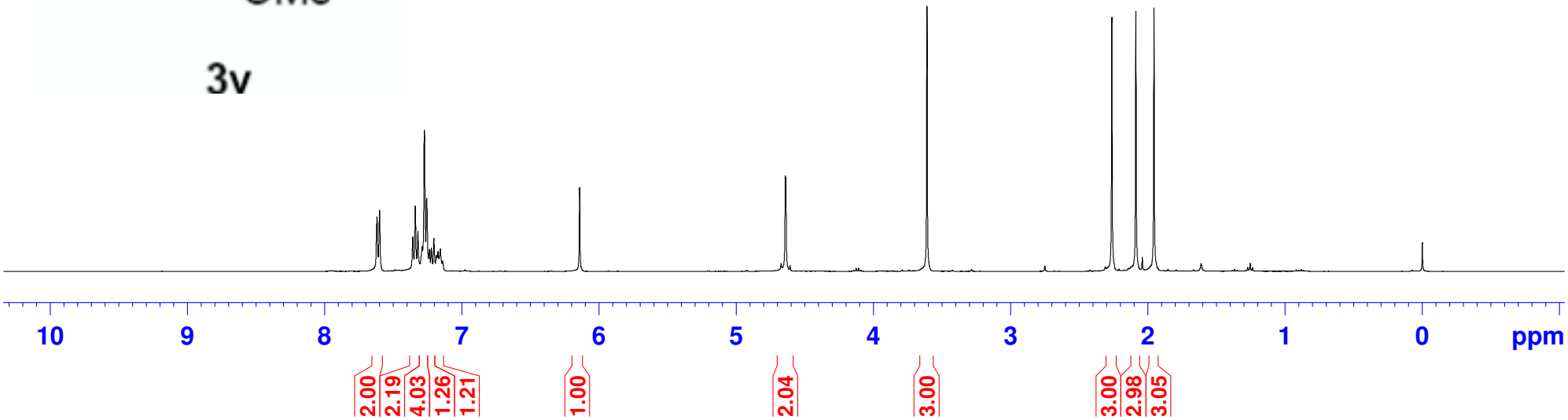


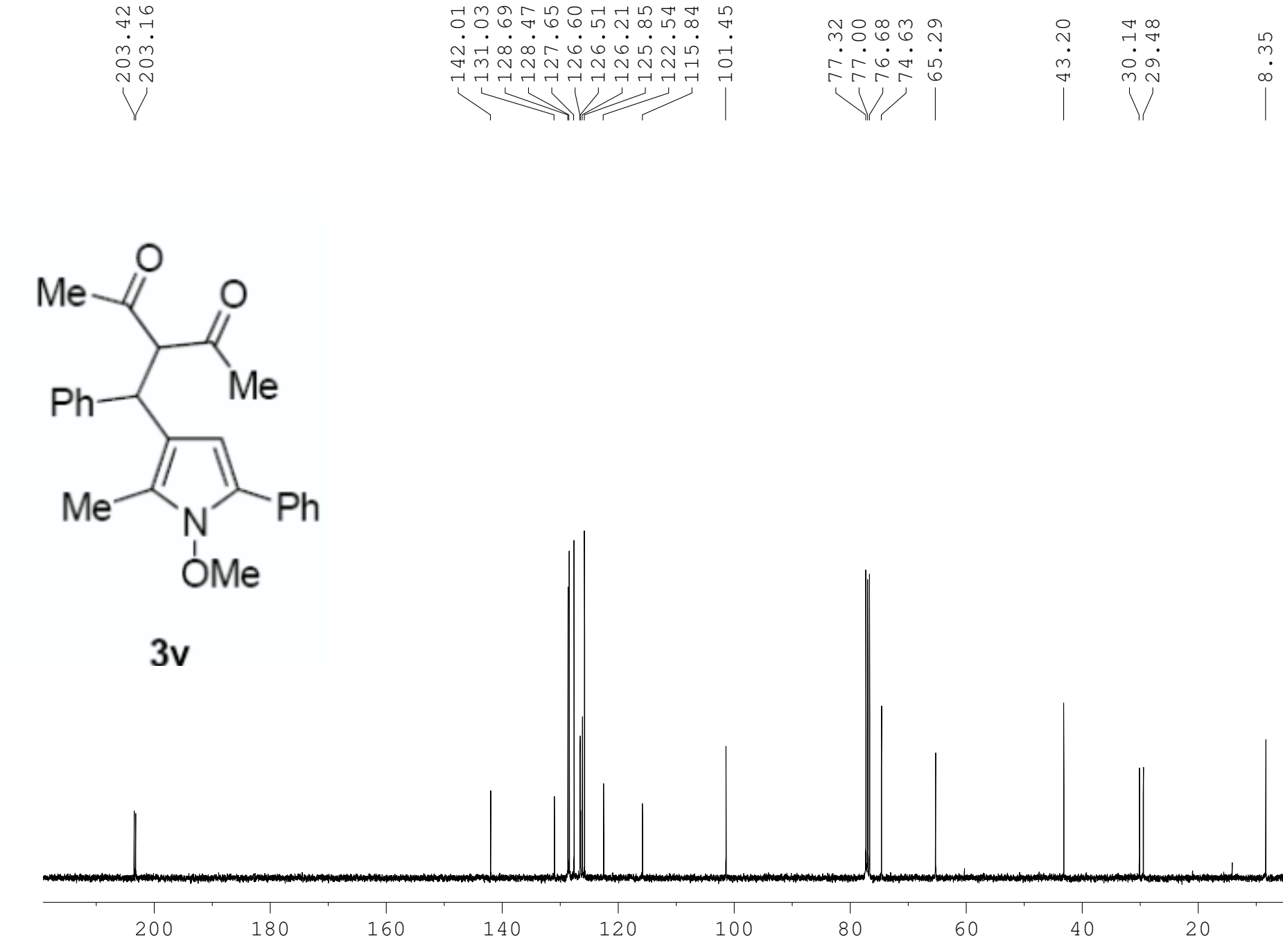


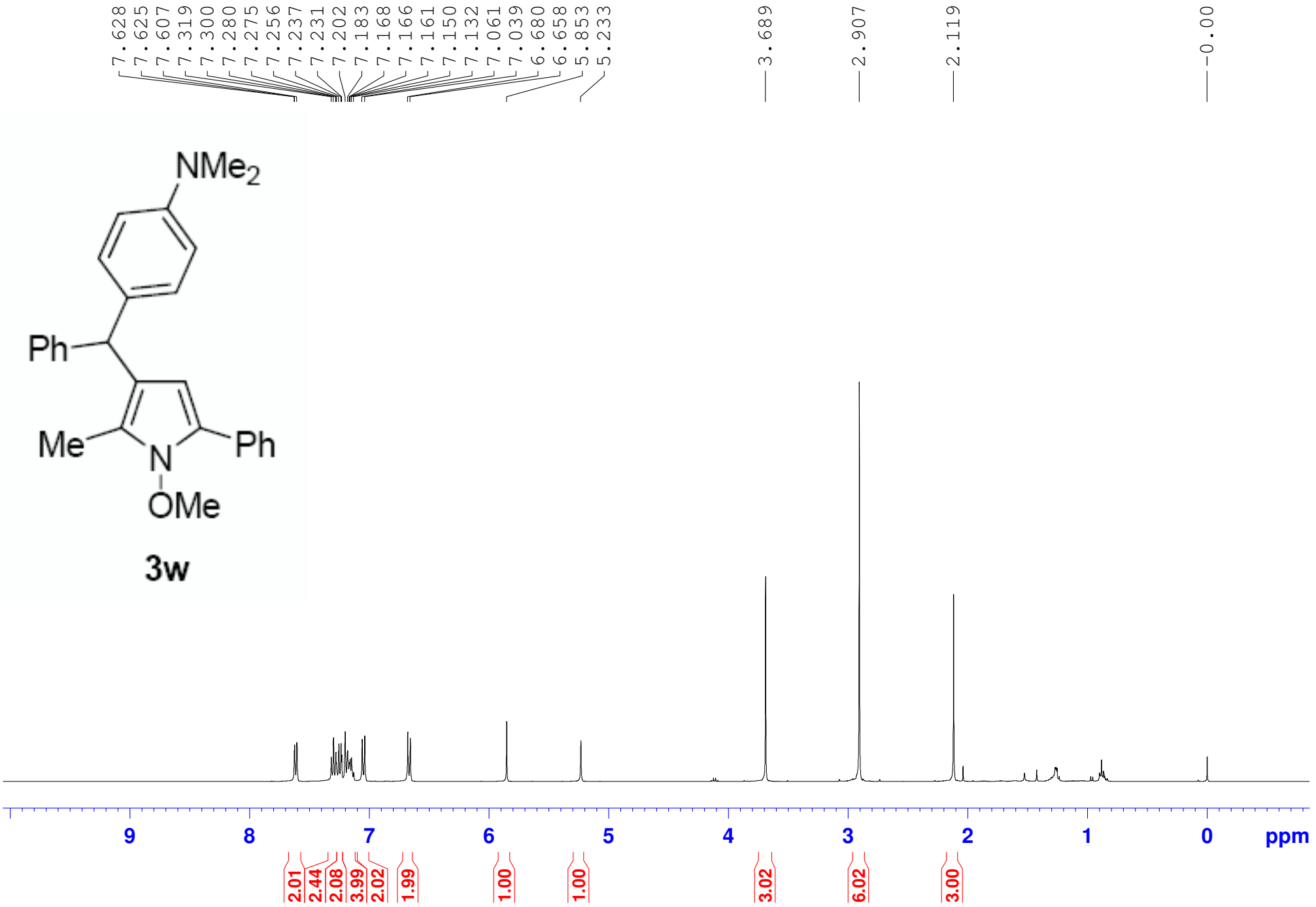


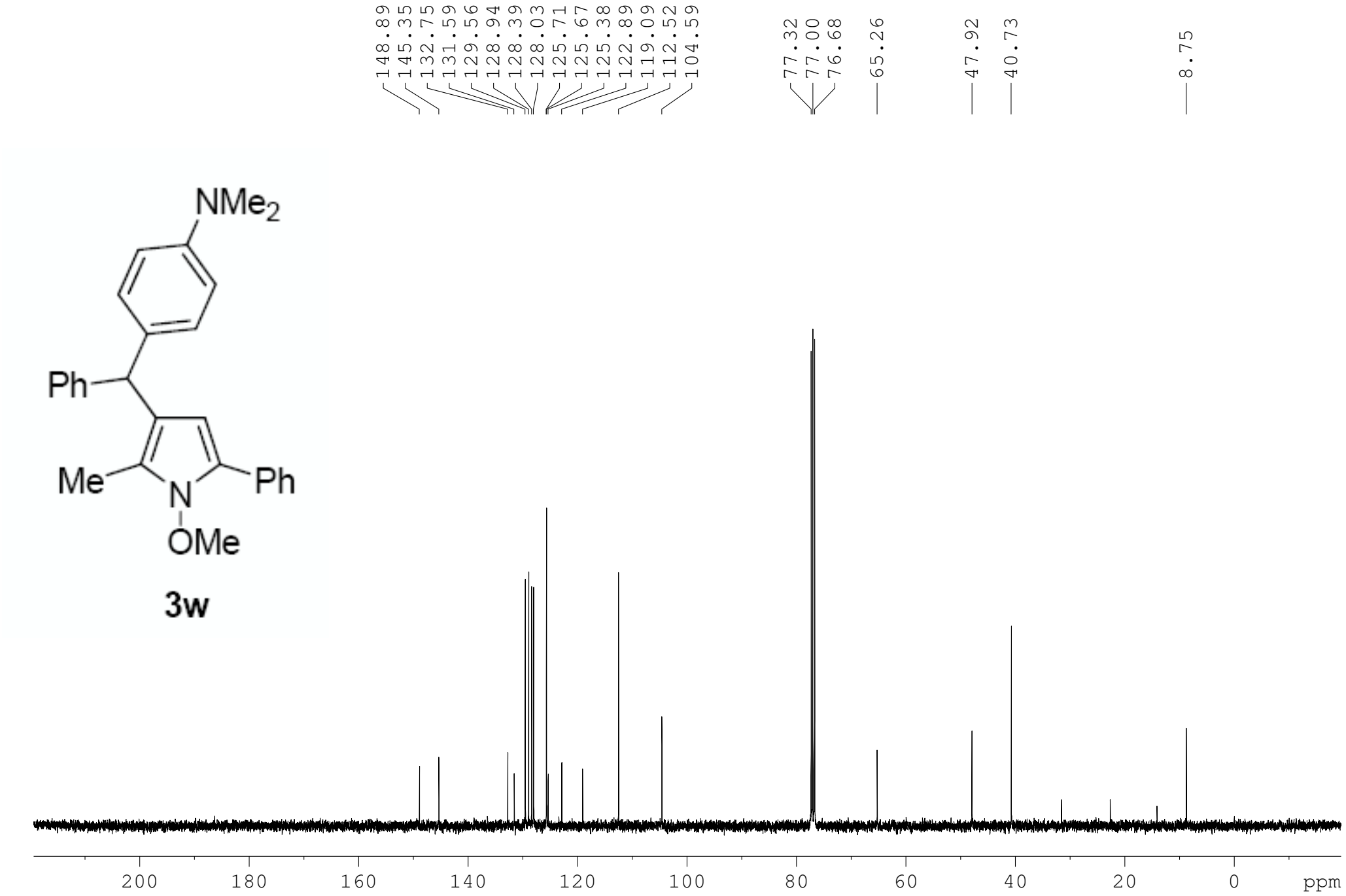


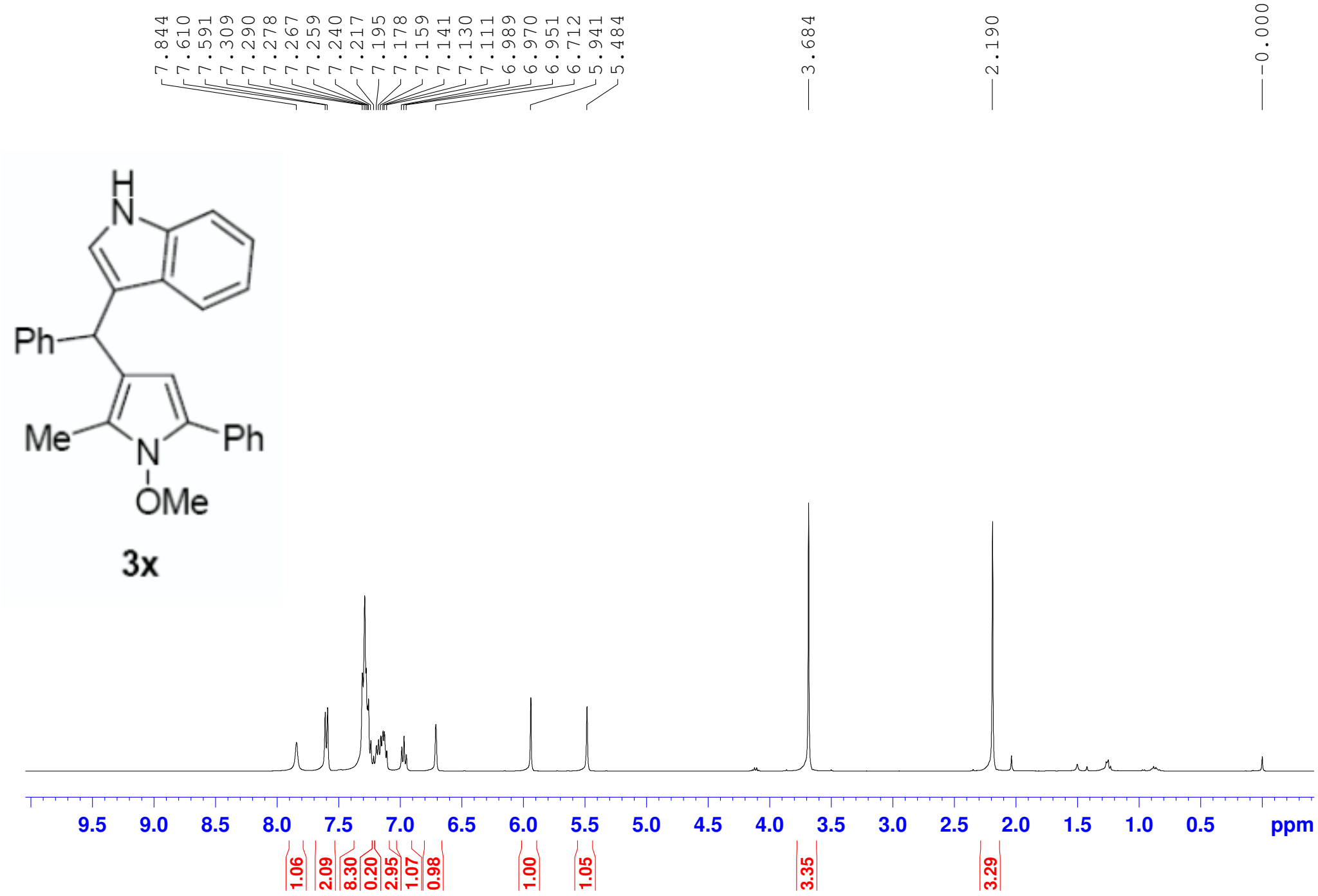
3v

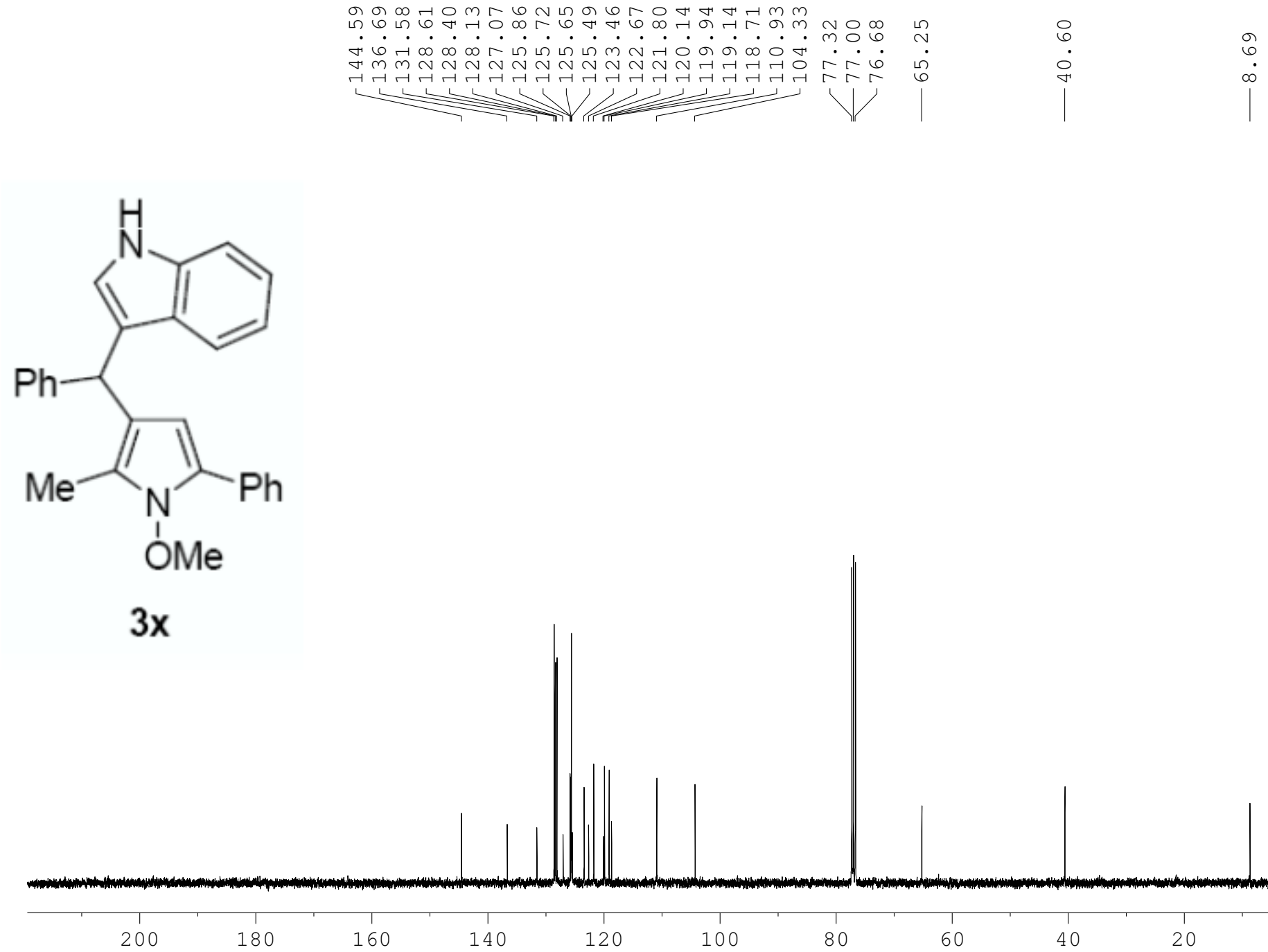


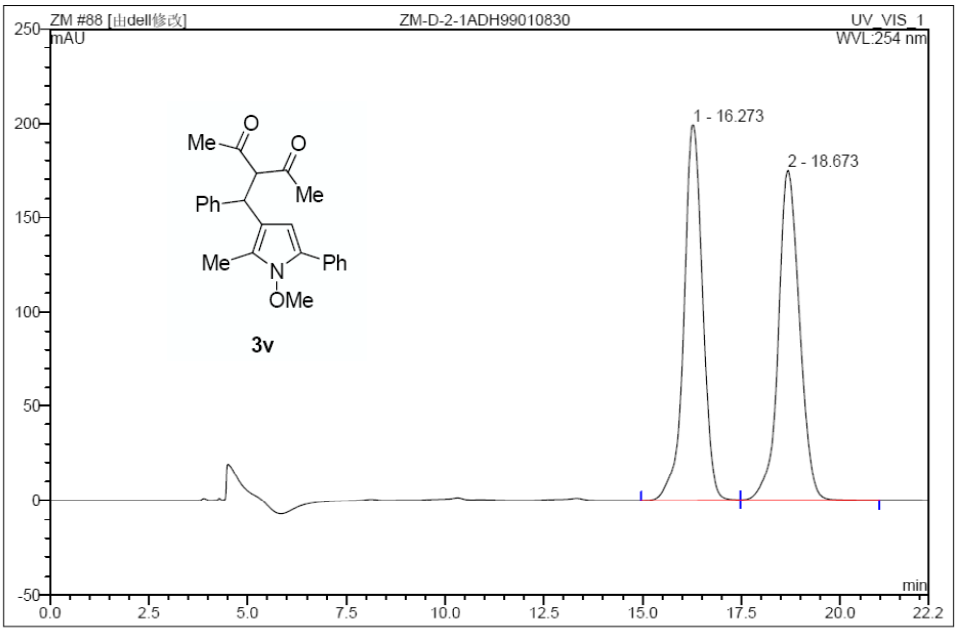




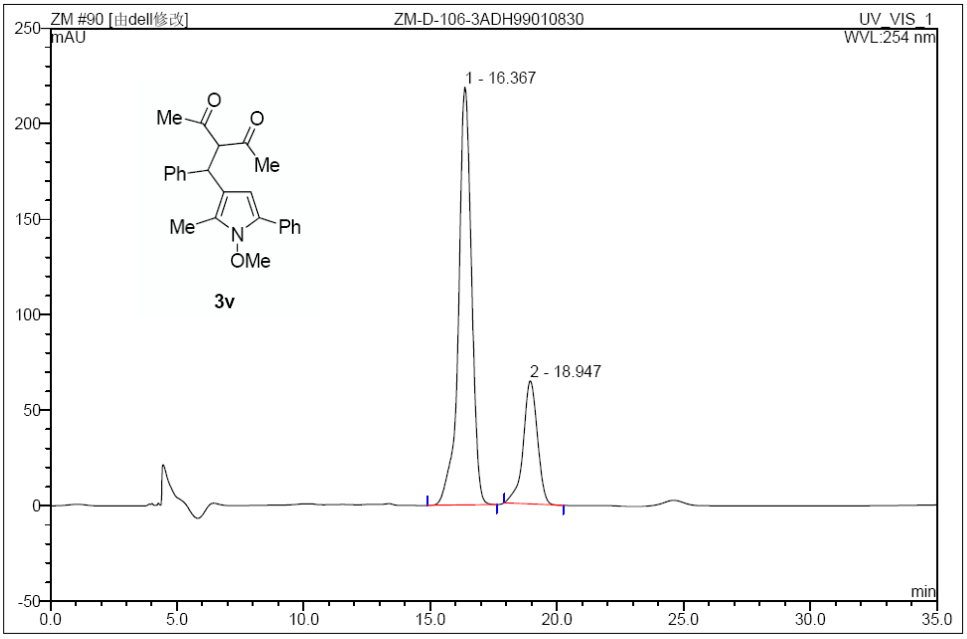








序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	16.27	n.a.		199.555	108.932	49.95	n.a.	BM
2	18.67	n.a.		174.801	109.133	50.05	n.a.	MB
总和:				374.356	218.065	100.00	0.000	



序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	16.37	n.a.		218.796	130.639	75.78	n.a.	BMB*
2	18.95	n.a.		64.421	41.747	24.22	n.a.	BMB*
总和:				283.218	172.386	100.00	0.000	