Electronic Supplementary Information

Synthesis of Perinaphthenones through Rhodium-Catalyzed Dehydrative Annulation of 1-Naphthoic Acids with Alkynes

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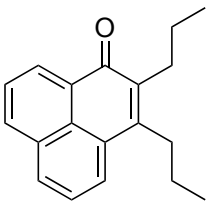
General information

^{1}H NMR spectra were recorded with a JEOL ECS-400 (400 MHz) spectrometers in $CDCl_3$, and are referenced at 0.00 ppm for TMS. ^{13}C NMR spectra were recorded with a JEOL ECS-400 (100 MHz) spectrometers in $CDCl_3$, and are referenced at 77.16 ppm for $CDCl_3$. Chemical shifts are reported in parts per million (δ). Infrared spectra were obtained on a JASCO FT/IR-4100 spectrometer; absorptions were reported in reciprocal centimeters. Both conventional and high-resolution mass spectra were recorded with a JEOL MS-700 spectrometer. Melting point was measured by BÜCHI Melting Point B-540. GC analysis was performed on a Shimadzu GC-2014 instrument equipped with an FID detector using a J&W Scientific DB-1 column under the following conditions: initial oven temp. 60 ºC, hold at this temperature for 5 min, first ramp 20 ºC/min to 250 ºC, hold at this temperature for 5 min. The products were purified by flash chromatography on silica gel (Kanto Chem. Co. Silica Gel 60N (spherical, neutral, 40-50 mm). $[RhCl(cod)]_2$ was prepared according to the literature procedure.[1] Structures of the regioisomers, **1c**, **1c'**, **3d**, **3d'**, **3e**, **3e'**, **3i**, **3i'**, **3k**, **3k'**, **3l'**, and **3m'** were determined by HMBC analysis. Structure of **3f** was determined by NOESY analysis.

Typical Procedure for the Rhodium-Catalyzed Dehydrative Annulation of 1-Naphthoic Acids with Alkynes

To a 5 mL screw capped test tube were added 1-naphthoic acid (**1a**, 86.1 mg, 0.50 mmol), $[RhCl(cod)]_2$ (6.2 mg, 0.0125 mmol), bis(diphenylphosphino)methane (DPPM, 9.6 mg, 0.025 mmol), KI (41.5 mg, 0.25 mmol), Piv_2O (279.4 mg, 1.50 mmol), 4-octyne (**2a**, 154.3 mg, 1.5 mmol), 1,4-dioxane (1 mL), and a magnetic stirring bar. The test tube was purged with argon and sealed. The mixture was heated with oil bath at 160 °C for 30 h. After cooling to room temperature, the reaction mixture was diluted with $CHCl_3$, passed through a pad of Celite, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give phenalenone as a yellow solid (**2a**, 115.9 mg, 88%).

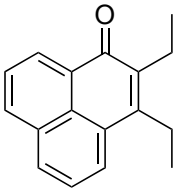
2,3-Dipropyl-1H-phenalen-1-one (3a)



3a

Yellow solid; mp 96-97 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (t, *J* = 7.4 Hz, 3H), 1.14 (t, *J* = 7.4 Hz, 3H), 1.53-1.62 (m, 2H), 1.69-1.78 (m, 2H), 2.69-2.73 (m, 2H), 2.91-2.95 (m, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.94-7.97 (m, 2H), 8.14 (dd, *J* = 1.4, 8.2 Hz, 1H), 8.63 (dd, *J* = 1.4, 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.65, 14.74, 23.96, 24.37, 28.76, 31.42, 126.42, 126.6, 127.38, 127.61, 128.49, 128.95, 130.16, 130.59, 132.12, 134.39, 138.21, 148.07, 184.81; IR (KBr) 2959, 1631, 1612, 1569, 1366, 788 cm^{-1}; EIMS m/z (relative intensity) 264 (M^+, 51), 221 (100), 165 (15); HRMS (EI) m/z calcd for $C_{19}H_{20}O$: 264.1514, found: 264.1518.

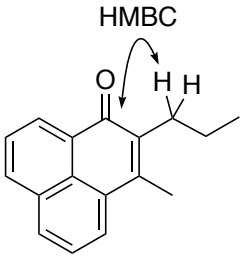
2,3-Diethyl-1H-phenalen-1-one(3b)



3b

Yello solid; mp 55-56 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (t, *J* = 7.4 Hz, 3H), 1.36 (t, *J* = 7.4 Hz, 3H), 2.76 (q, *J* = 7.4 Hz, 2H), 3.00 (q, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.97 (t, *J* = 6.9, 7.3 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 8.63 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.09, 15.26, 19.72, 22.20, 126.43, 126.58, 127.48, 128.11, 128.94, 130.12, 130.61, 132.14, 134.41, 139.12, 149.14, 184.64; IR (KBr) 2961, 1631, 1615, 1577, 1571, 1407, 786 cm^{-1}; EIMS m/z (relative intensity) 236 (M^+, 44), 235 (54), 212 (95), 156 (34), 129 (74), 115 (100); HRMS (EI) m/z calcd for $C_{17}H_{16}O$: 236.1201, found: 236.1202.

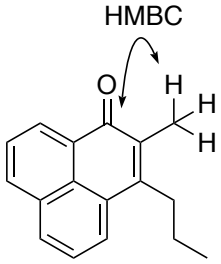
2-Propyl-3-methyl-1H-phenalen-1-one (3c)



3c

Yellow solid; mp 74-75 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (t, *J* = 7.4 Hz, 3H), 1.53-1.59 (m, 2H), 2.56 (s, 3H), 2.75 (t, *J* = 7.8 Hz, 2H), 7.56-7.60 (m, 1H), 7.69-7.73 (m, 1H), 7.93-7.97 (m, 2H), 8.12-8.13 (m, 1H), 8.60-8.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.22, 14.55, 23.32, 31.57, 126.41, 126.59, 127.22, 127.41, 128.36, 128.73, 130.21, 130.64, 132.11, 133.72, 134.46, 148.25, 185.06; IR (KBr) 2959, 1632, 1615, 1571, 1409, 1377, 784 cm^{-1}; EIMS m/z (relative intensity) 236 (M^+, 28), 221 (100), 208 (31), 179 (34), 152 (14); HRMS (EI) m/z calcd for $C_{17}H_{16}O$: 236.1201, found: 236.1199.

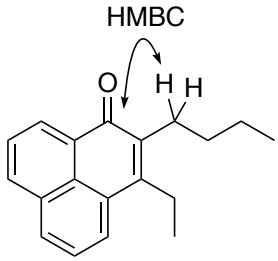
3-Propyl-2-methyl-1H-phenalen-1-one (3c')



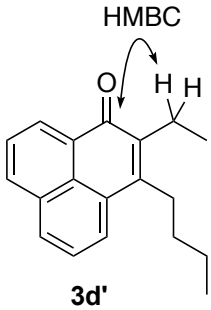
3c'

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (t, *J* = 7.4 Hz, 3H), 1.69-1.75 (m, 2H), 2.26 (s, 3H), 2.93-2.97 (m, 2H), 7.58-7.62 (m, 1H), 7.70-7.73 (m, 1H), 7.93-7.97 (m, 2H), 8.12-8.13 (m, 1H), 8.60-8.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.41, 15.73, 22.55, 28.60, 126.38, 126.61, 127.10, 127.41, 128.85, 129.61, 130.19, 130.60, 131.90, 134.31, 138.55, 143.81, 184.53; IR (KBr) 2961, 1631, 1612, 1571, 1457, 1330, 779 cm^{-1}; EIMS m/z (relative intensity) 236 (M^+, 61), 235 (77), 221 (100), 178 (33), 165 (23); HRMS (EI) m/z calcd for $C_{17}H_{16}O$: 236.1201, found: 236.1198.

2-Butyl-3-ethyl-1H-phenalen-1-one (3d) and 3-Butyl-2-ethyl-1H-phenalen-1-one (3d')



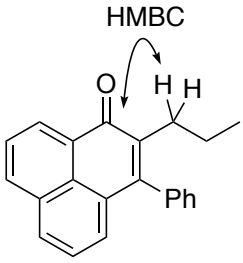
3d



3d'

These compounds were obtained as an inseparable mixture. Pale yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96-1.05 (m), 1.17-1.20 (m), 1.33-1.37 (m), 1.45-1.74 (m), 2.71-2.79 (m), 2.92-3.02 (m), 7.58-7.62 (m, 1H), 7.70-7.74 (m, 1H), 7.94-7.97 (m, 2H), 8.13-8.15 (m, 1H), 8.61-8.64 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 13.91, 14.00, 15.17, 19.82, 22.25, 23.27, 23.35, 26.29, 28.93, 31.89, 33.15, 126.35, 126.37, 126.49, 127.27, 127.34, 127.43, 127.49, 128.02, 128.39, 128.84, 128.88, 130.03, 130.50, 130.55, 132.04, 132.07, 134.32, 137.90, 139.28, 147.91, 149.26, 184.52, 184.76; IR (KBr) 2958, 1631, 1614, 1572, 1376, 786 cm^{-1}; EIMS m/z (relative intensity) 264 (M^+, 24), 235 (100), 221 (19), 181 (22), 131 (21); HRMS (EI) m/z calcd for $C_{19}H_{20}O$: 264.1514, found: 264.1509.

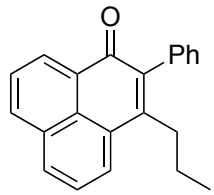
3-Phenyl-2-propyl-1H-phenalen-1-one (3e)



3e

Orange solid; mp 109-110 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, *J* = 7.4 Hz, 3H), 1.50-1.42 (m, 2H), 2.43-2.37 (m, 2H), 7.21-7.17 (m, 1H), 7.33-7.26 (m, 2H), 7.55-7.41 (m, 4H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.71 (dd, *J* = 7.4, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.51, 22.81, 30.08, 126.40, 126.85, 127.73, 128.25, 129.03, 129.14, 129.86, 130.35, 130.66, 131.15, 131.96, 134.64, 137.43, 138.65, 149.28, 184.93; IR (KBr) 2959, 1630, 1616, 1570, 1334, 788 cm^{-1}; EIMS m/z (relative intensity) 298 (M^+, 48), 297 (46), 269 (40), 239 (30), 69 (100); HRMS (EI) m/z calcd for $C_{22}H_{18}O$: 298.1358, found: 298.1360.

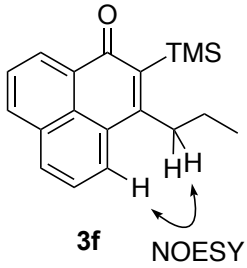
2-Phenyl-3-propyl-1H-phenalen-1-one (3e')



3e'

Orange solid; mp = 200-201 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.4 Hz, 3H), 1.62-1.73 (m, 2H), 2.71-2.76 (m, 2H), 7.24-7.27 (m, 2H), 7.38-7.49 (m, 3H), 7.62-7.67 (m, 1H), 7.73-7.78 (m, 1H), 8.02-8.05 (m, 2H), 8.18-8.21 (m, 1H), 8.62-8.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.54, 24.73, 32.56, 126.44, 126.81, 127.29, 127.82, 128.11, 128.12, 128.62, 129.14, 129.68, 130.43, 131.38, 132.24, 134.64, 136.81, 139.39, 149.62, 184.31; IR (KBr) 2955, 1629, 1610, 1570, 1560, 1407, 706 cm^{-1}; EIMS m/z (relative intensity) 298 (M^+, 88), 297 (100), 269 (36), 255 (38), 149 (12); HRMS (EI) m/z calcd for $C_{22}H_{18}O$: 298.1358, found: 298.1350.

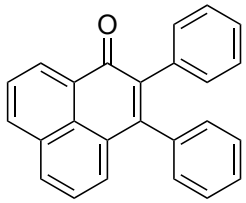
3-Propyl-2-trimethlsilyl-1H-phenalen-1-one (3f)



3f

Yellow solid; mp = 95-96 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35 (s, 9H), 1.14 (t, *J* = 7.3 Hz, 3H), 1.59-1.66 (m, 2H), 2.89-2.93 (m, 2H), 7.61-7.65 (m, 1H), 7.68-7.72 (m, 1H), 7.81-7.84 (m, 2H), 7.96-7.94 (m, 1H), 8.05-8.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.23, 14.76, 22.36, 35.98, 121.06, 121.62, 125.11, 127.81, 128.53, 130.84, 131.20, 132.89, 135.01, 140.17, 141.44; IR (KBr) 2960, 1774, 1750, 1736, 1719, 1458, 777 cm^{-1}; EIMS m/z (relative intensity) 279 (M^+, 75), 235 (37), 205 (35), 189 (100), 164 (70), 163 (79); HRMS (EI) m/z calcd for $C_{18}H_{17}O$ (M^+-CH_3), 279.1205, found: 279.1203.

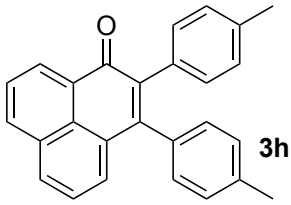
2,3-Diphenyl-1H-phenalen-1-one (3g)



3g

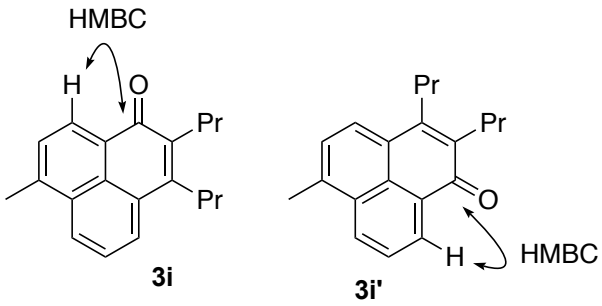
Orange solid; mp 193-194 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08-7.29 (m, 10H), 7.48-7.51 (m, 2H), 7.83 (t, *J* = 7.8 Hz, 1H), 8.03 (dd, *J* = 7.4, 1.8, 1H), 8.25 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.74 (dd, *J* = 7.3, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 126.45, 126.76, 127.07, 127.38, 127.47, 127.73, 129.33, 129.37, 130.11, 130.66, 130.74, 131.51, 132.12, 134.90, 135.75, 136.95, 138.83, 150.12, 184.09; IR (KBr) 3055, 1631, 1615, 1570, 1271,801, 699, 788 cm^{-1}; EIMS m/z (relative intensity) 332 (M^+, 47), 331 (58), 255 (17), 213 (34), 149 (63); HRMS (EI) m/z calcd for $C_{25}H_{16}O$: 332.1201, found: 332.1195.

2,3-Di-*p*-tolyl-1H-phenalen-1-one (3h)



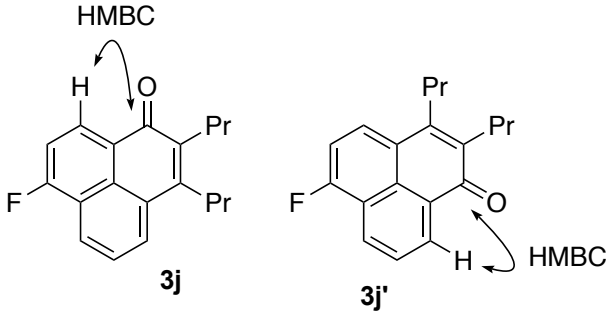
Orange solid; mp 231.2-232.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.34 (s, 3H), 6.99 (s, 4H), 7.06-7.11 (m, 4H), 7.46-7.51 (m, 2H), 7.79-7.83 (m, 1H), 8.00-8.02 (m, 1H), 8.23-8.25 (m, 1H), 8.72-7.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.44, 126.57, 127.14, 127.51, 128.33, 128.61, 129.56, 129.80, 130.17, 130.69, 130.80, 131.43, 132.18, 132.26, 132.95, 134.24, 134.91, 136.34, 137.17, 138.88, 150.13, 184.45; IR (KBr) 1632, 1610, 1569, 1361, 799 cm^{-1}; EIMS m/z (relative intensity) 360 (M^+, 55), 345 (100), 295 (18), 269 (12), 257 (11); HRMS (EI) m/z calcd for $C_{27}H_{20}O$: 360.1514, found: 360.1509.

7-Methyl-2,3-dipropyl-1H-phenalen-1-one (3i) and 6-Methyl-2,3-dipropyl-1H-phenalen-1-one (3i')



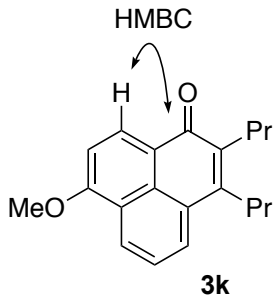
These compounds were obtained as an inseparable mixture. Yellow solid, mp = 91-93 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): for **3i**; δ 1.04 (t, *J* = 7.4 Hz, 3H), 1.14 (t, *J* = 7.4 Hz, 3H), 1.52-1.62 (m, 2H), 1.69-1.75 (m, 2H), 2.67-2.72 (m, 2H), 2.83 (s, 3H), 2.88-2.94 (m, 2H), 7.52-7.63 (m, 2H), 7.95 (d, *J* = 7.4 Hz, 1H), 8.14 (d, *J* = 9.2 Hz, 1H), 8.52 (d, *J* = 7.3, Hz, 1H); for **3i'**; δ 1.05 (d, *J* = 7.4 Hz,3H), 1.15 (t, *J* = 7.4 Hz, 3H), 1.52-1.62 (m, 2H), 1.69-1.75 (m, 2H), 2.67-2.72 (m, 2H), 2.79 (s, 3H), 2.88-2.94 (m, 2H), 7.41 (d, *J* = 6.4 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.4 Hz, 1H), 8.33 (dd, *J* = 1.4, 8.3 Hz, 1H), 8.64 (d, *J* = 7.3, Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.62, 14.68, 19.49, 20.07, 22.94, 24.29, 24.39, 28.67, 28.71, 31.27, 31.41, 125.97, 126.20, 126.71, 127.13, 127.26, 127.47, 127.53, 127.58, 127.74, 128.77, 129.31, 129.73, 130.12, 130.42, 131.19, 131.59, 137.01, 137.91, 138.17, 142.47, 147.86, 148.28, 184.64, 184.84; IR (KBr) 2959, 1626, 1610, 1570, 1362, 781 cm^{-1}; EIMS m/z (relative intensity) 278 (M^+, 54), 263 (100), 235 (71), 189 (12), 149 (12); HRMS (EI) m/z calcd for $C_{20}H_{22}O$: 278.1671, found: 278.1670.

7-Fluoro-2,3-dipropyl-1H-phenalen-1-one (3j) and 6-Fluoro-2,3-dipropyl-1H-phenalen-1-one (3j')



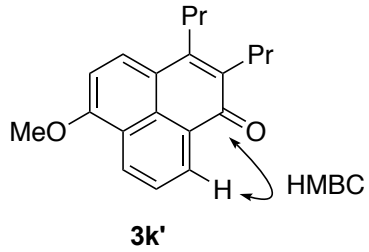
These compounds were obtained as an inseparable mixture. Yellow solid, mp = 108-109 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): for **3j**; δ 1.04-1.07 (m, 3H), 1.57 (t, *J* = 7.4 Hz, 3H), 1.54-1.59 (m, 2H), 1.69-1.75 (m, 2H), 2.66-2.71 (m, 2H), 2.88-2.94 (m, 2H), 7.36 (dd, *J* = 8.3, 10.1 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 8.59 (dd, *J* = 5.5, 8.3 Hz, 1H); for **3j'**; δ 1.04-1.07 (m, 3H), 1.56 (dt, *J* = 7.4 Hz, 3H), 1.54-1.59 (m, 2H), 1.69-1.75 (m, 2H), 2.66-2.71 (m, 2H), 2.88-2.94 (m, 2H), 7.22 (d, *J* = 9.2 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.87 (dd, *J* = 5.5, 8.3 Hz, 1H), 8.41 (d, *J* = 6.9, 1H), 8.66 (d, *J* = 7.4, Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.57, 14.62, 22.87, 24.14, 24.21, 28.61, 28.68, 31.29, 31.39, 110.07 (d, J_{CF} = 20.2 Hz), 111.21 (d, J_{CF} = 20.2 Hz), 120.80 (d, J_{CF} = 16.3 Hz), 122.47 (d, J_{CF} = 16.3 Hz), 122.93 (d, J_{CF} = 4.9 Hz), 124.86 (d, J_{CF} = 4.8 Hz), 125.39 (d, J_{CF} = 3.8 Hz), 126.53, 126.65, 126.76 (d, J_{CF} = 3.9 Hz), 127.90 (d, J_{CF} = 8.7 Hz), 128.05, 128.32, 128.36, 128.65, 128.70, 130.73, 131.57 (d, J_{CF} = 10.6 Hz), 137.02 (d, J_{CF} = 2.9 Hz), 138.37, 147.51, 147.73, 160.22 (d, J_{CF} = 261.1 Hz), 162.72 (d, J_{CF} = 262.9 Hz), 183.51, 184.51; ^{19}F NMR (100MHz, $CDCl_3$): for **3j**; δ -111.13; for **3j'**; d -117.90 ; IR (KBr) 2962, 1637, 1616, 1592, 1571, 1479, 1376, 781 cm^{-1}; EIMS m/z (relative intensity) 282 (M^+, 62), 239 (100), 173 (32); HRMS (EI) m/z calcd for $C_{19}H_{19}FO$: 282.1420, found: 282.1425.

6-Methoxy-2,3-dipropyl-1H-phenalen-1-one (3k)



Yellow solid; mp = 153-154 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, *J* = 7.4 Hz, 3H), 1.14 (t, *J* = 7.4 Hz, 3H), 1.52-1.62 (m, 2H), 1.67-1.77 (m, 2H), 2.68-2.72 (m, 2H), 2.89-2.93 (m, 2H), 4.10 (s, 3H), 7.05 (d, *J* = 8.2 Hz, 1H), 7.54-7.58 (m, 1H), 7.95 (d, *J* = 7.3 Hz, 1H), 8.36 (d, *J* = 8.3, Hz, 1H), 8.62 (d, *J* = 8.2, Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.80, 14.84, 23.12, 24.40, 28.91, 31.58, 56.11, 105.70, 122.60, 123.69, 124.81, 125.46, 127.94, 128.16, 128.56, 132.91, 138.29, 147.67, 161.27, 183.90; IR (KBr) 2956, 1628, 1605, 1577, 1362, 1263, 1067, 1366, 1067, 777 cm^{-1}; EIMS m/z (relative intensity) 294 (M^+, 76), 293 (91), 279 (52), 251 (100), 221 (32), 165 (23); HRMS (EI) m/z calcd for $C_{20}H_{22}O_2$: 294.1620, found: 294.1611.

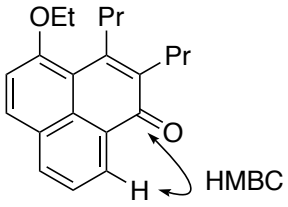
6-Methoxy-2,3-dipropyl-1H-phenalen-1-one (3k')



3k'

Orange solid; mp = 142-143 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (t, *J* = 7.4 Hz, 3H), 1.13 (t, *J* = 7.4 Hz, 3H), 1.54-1.60 (m, 2H), 1.68-1.74 (m, 2H), 2.66-2.70 (m, 2H), 2.87-2.91 (m, 2H), 6.88-6.90 (m, 1H), 7.69-7.73 (m, 1H), 7.86-7.88 (m, 1H), 8.56-8.59 (m, 1H), 8.65-8.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.81, 14.90, 23.14, 24.70, 28.82, 31.56, 55.97, 104.40, 121.53, 124.84, 126.00, 128.48, 128.55, 129.11, 129.38, 130.68, 135.84, 148.42, 158.47, 185.01; IR (KBr) 2963, 1629, 1608, 1578, 1571, 1258, 1088, 781 cm^{-1}; EIMS m/z (relative intensity) 294 (M^+, 30), 279 (41), 263 (100), 251 (63), 221 (26), 165 (18), 149 (41); HRMS (EI) m/z calcd for $C_{20}H_{22}O_2$: 294.1620, found: 294.1616.

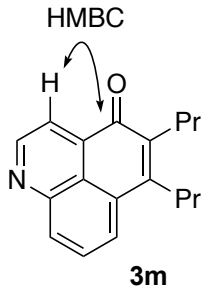
4-Ethoxy-2,3-dipropyl-1H-phenalen-1-one (3l')



3l'

Orange solid; mp = 100.4-101.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02-1.11 (m, 6H), 1.51-1.72 (m, 7H), 2.72-2.77 (m, 2H), 3.13-3.18 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 7.34 (d, *J* = 9.2 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 9.2 Hz, 1H), 8.05 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.71 (dd, *J* = 7.4, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.68, 14.76, 14.95, 23.05, 23.71, 28.48, 34.91, 65.11, 114.02, 115.16, 124.31, 126.54, 127.75, 128.35, 128.50, 128.98, 131.33, 133.40, 134.19, 138.26, 149.79, 158.97, 183.56; IR (KBr) 2960, 1626, 1603, 1588, 1559, 1389, 1051, 813 cm^{-1}; EIMS m/z (relative intensity) 308 (M^+, 21), 279 (100), 265 (44), 235(18), 149(27); HRMS (EI) m/z calcd for $C_{21}H_{24}O_2$ (M^+-C_2H_5): 279.1385, found: 279.1393.

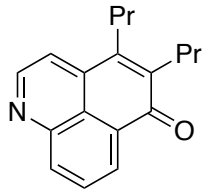
5,6-Dipropyl-4H-benzo[*de*]quinolin-4-one (3m)



3m

Yellow solid; mp = 105-107 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (t, *J* = 7.4 Hz, 3H), 1.15 (t, *J* = 7.4 Hz, 3H), 1.51-1.60 (m, 2H), 1.68-1.78 (m, 2H), 2.65-2.69 (m, 2H), 2.89-2.93 (m, 2H), 7.77-7.81 (m, 1H), 7.91-7.93 (m, 1H), 8.16-8.18 (m, 1H), 8.23 (d, *J* = 4.6 Hz, 1H), 9.21 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.55, 14.68, 22.86, 24.18, 28.52, 31.42, 120.42, 122.41, 127.60, 129.04, 129.93, 131.64, 134.00, 138.00, 148.41, 148.80, 151.20, 184.64; IR (KBr) 2962, 1631, 1580, 1561, 1255, 790 cm^{-1}; EIMS m/z (relative intensity) 265 (M^+, 51), 222 (32), 174 (64), 148 (100) 122 (44); HRMS (EI) m/z calcd for $C_{18}H_{19}NO$: 265.1467, found: 265.1469.

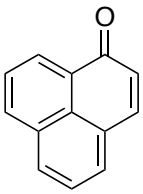
4,5-Dipropyl-6H-benzo[*de*]quinolin-6-one (3m')



3m'

Yellow solid; mp = 101-103 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04-1.08 (t, *J* = 7.4 Hz, 3H), 1.15 (t, *J* = 7.4 Hz, 3H), 1.52-1.62 (m, 2H), 1.66-1.74 (m, 2H), 2.68-2.72 (m, 2H), 2.86-2.90 (m, 2H), 7.65 (d, *J* = 4.6 Hz, 1H), 7.86-7.90 (m, 1H), 8.35-8.37 (m, 1H), 8.53-8.55 (m, 1H), 9.04 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.59, 14.62, 22.92, 23.89, 28.85, 30.85, 119.48, 123.06, 128.74, 129.49, 129.81, 135.70, 142.36, 145.81, 146.74, 183.54; IR (KBr) 2959, 1636, 1610, 1585, 1349, 789 cm^{-1}; EIMS m/z (relative intensity) 265 (M^+, 100), 250 (48), 222 (64), 207 (29) 166 (15); HRMS (EI) m/z calcd for $C_{18}H_{19}NO$: 265.1467, found: 265.1468.

1H-Phenalen-1-one (3n)[2]



3n

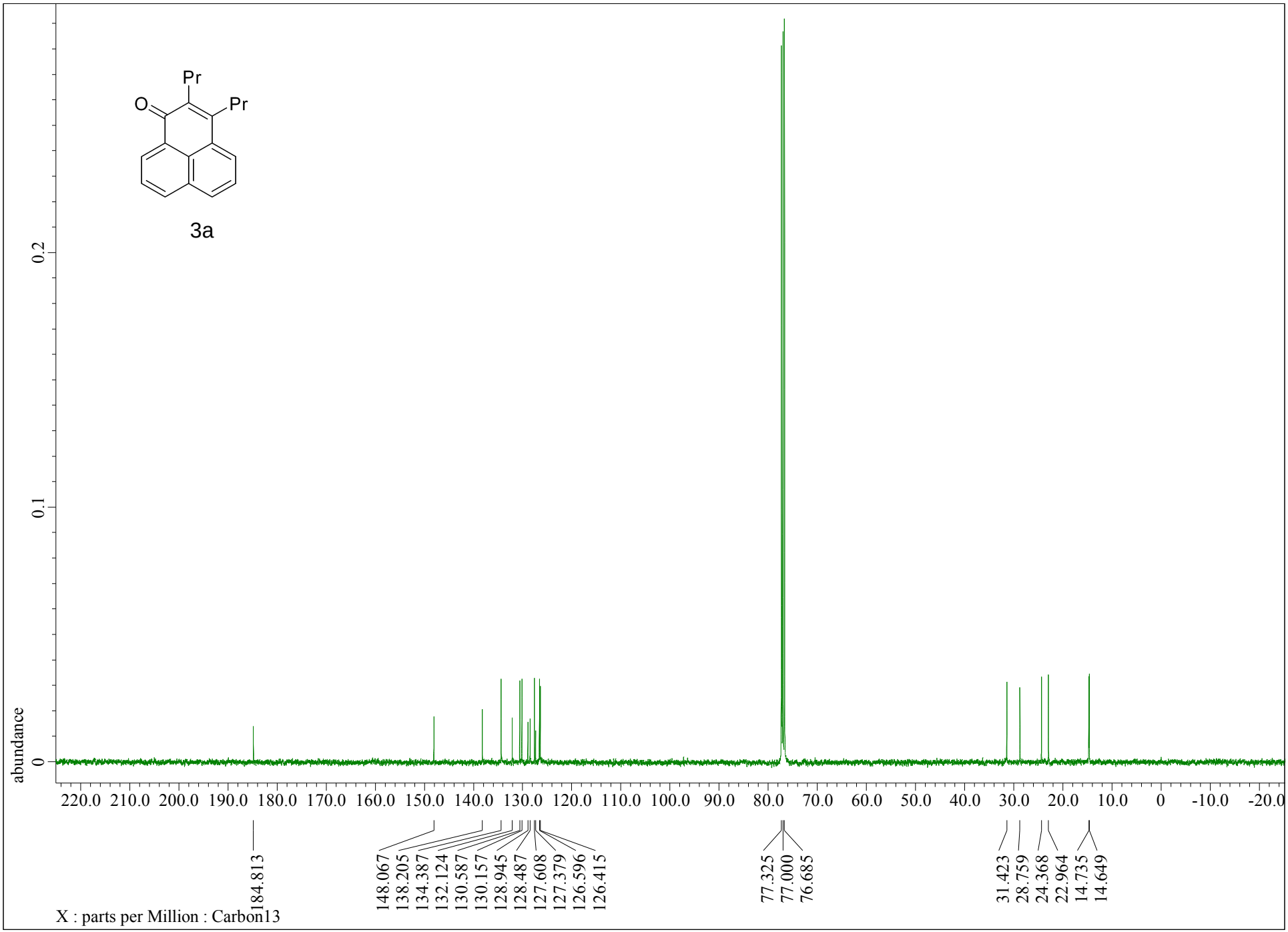
Yellow solid; mp = 148-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 7.6 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.78-7.71 (m, 3H), 7.57 (t, *J* =7.6 Hz, 1H), 6.72 (d, *J* =9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): d 185.6, 141.7, 134.9, 132.1, 131.9, 131.3, 130.3, 129.3, 129.2, 127.8, 127.5, 127.1, 126.6

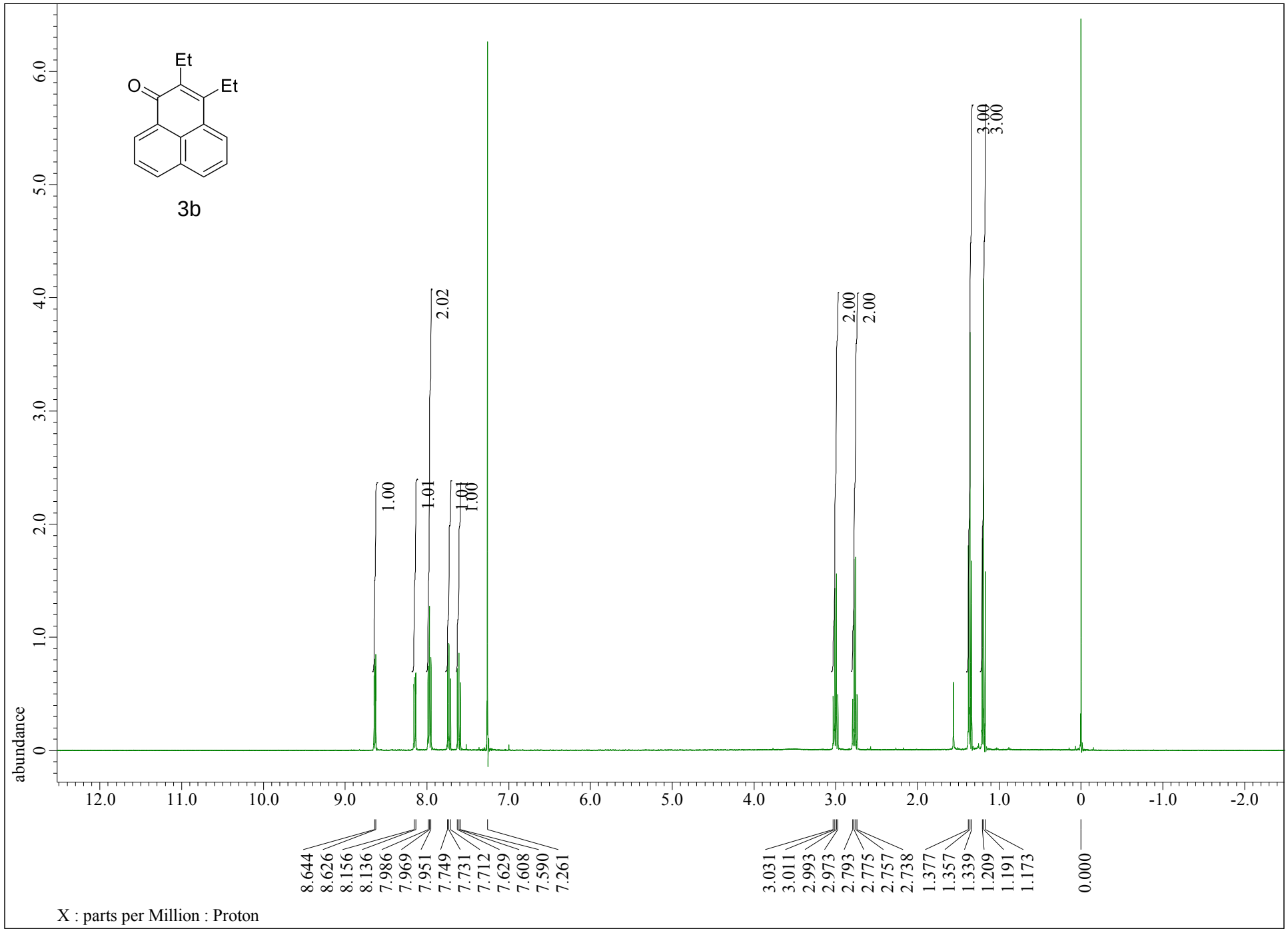
Procedure for the reaction of 1b and 2a under ^{13}CO

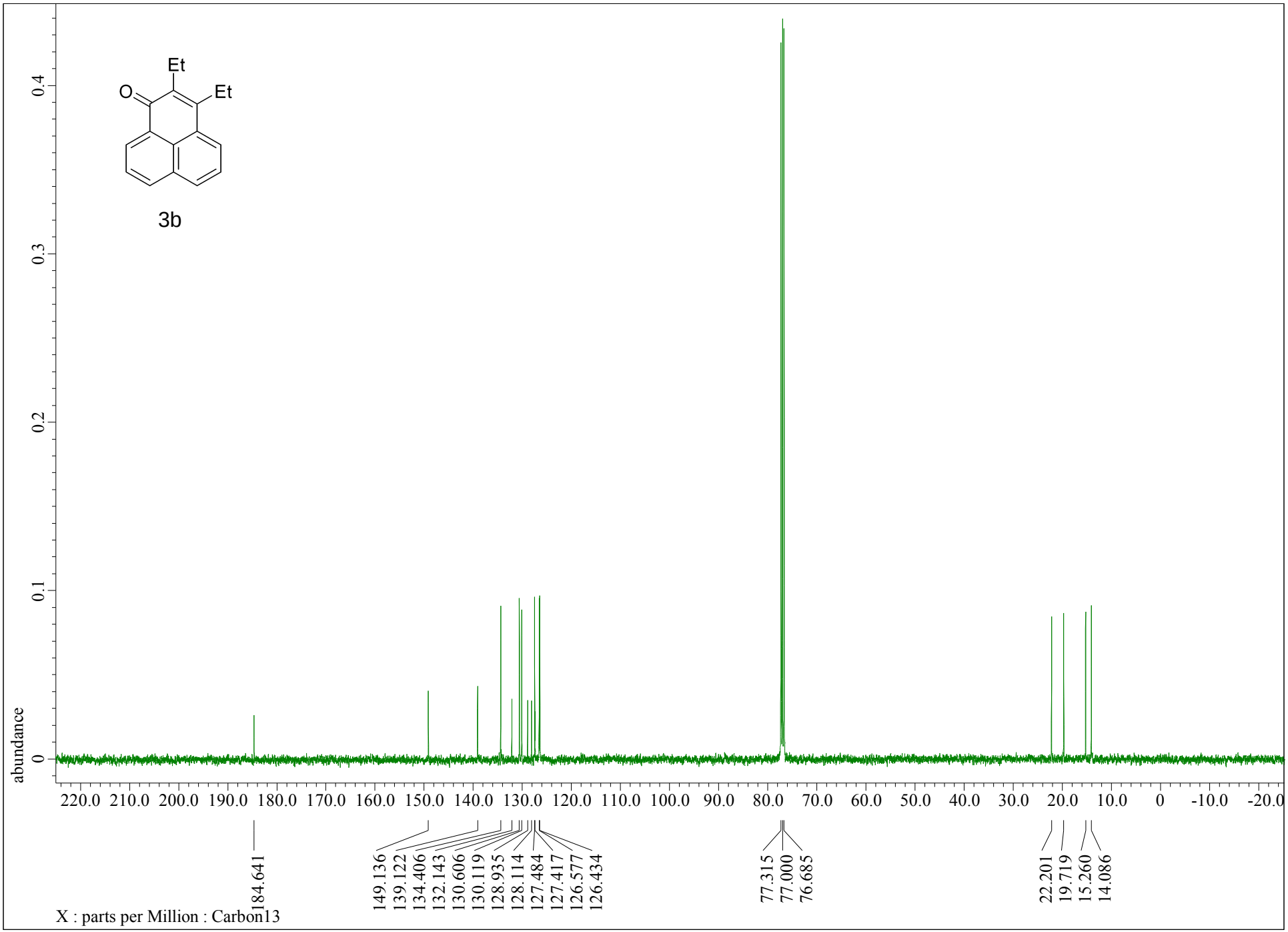
4-methyl-1-naphthoic acid (**1b**, 94.6 mg, 0.50 mmol), 4-octyne (**2a**, 163.5 mg, 1.5 mmol), $[RhCl(cod)]_2$ (6.1 mg, 0.01 mmol), DPPM (9.9 mg, 0.025 mmol), KI (41.9 mg, 0.25 mmol), Piv_2O (278.8 mg, 1.50 mmol), dioxane (1 mL), and a magnetic stirring bar were added in a screw-capped test tube (A). Sulfuric acid (168 mg, 1.7 mmol) was added in a screw-capped test tube (B). The two test tubes were connected with cannula and tightly closed. The test tube B was stirred at room temperature then ^{13}C-formic acid (120 mg, 1.2 mmol) was added in the B, and generated ^{13}CO was introduced to test tube A. After finishing the generation of ^{13}CO, the cannula was removed and test tube A was shealed. The reactor A was allowed to stir at 160 °C for 18 h. The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give non-labeled phenalenones **3i** and **3i'** as a mixture. No ^{13}CO incorporation was determined by ^{13}C-NMR analysis.

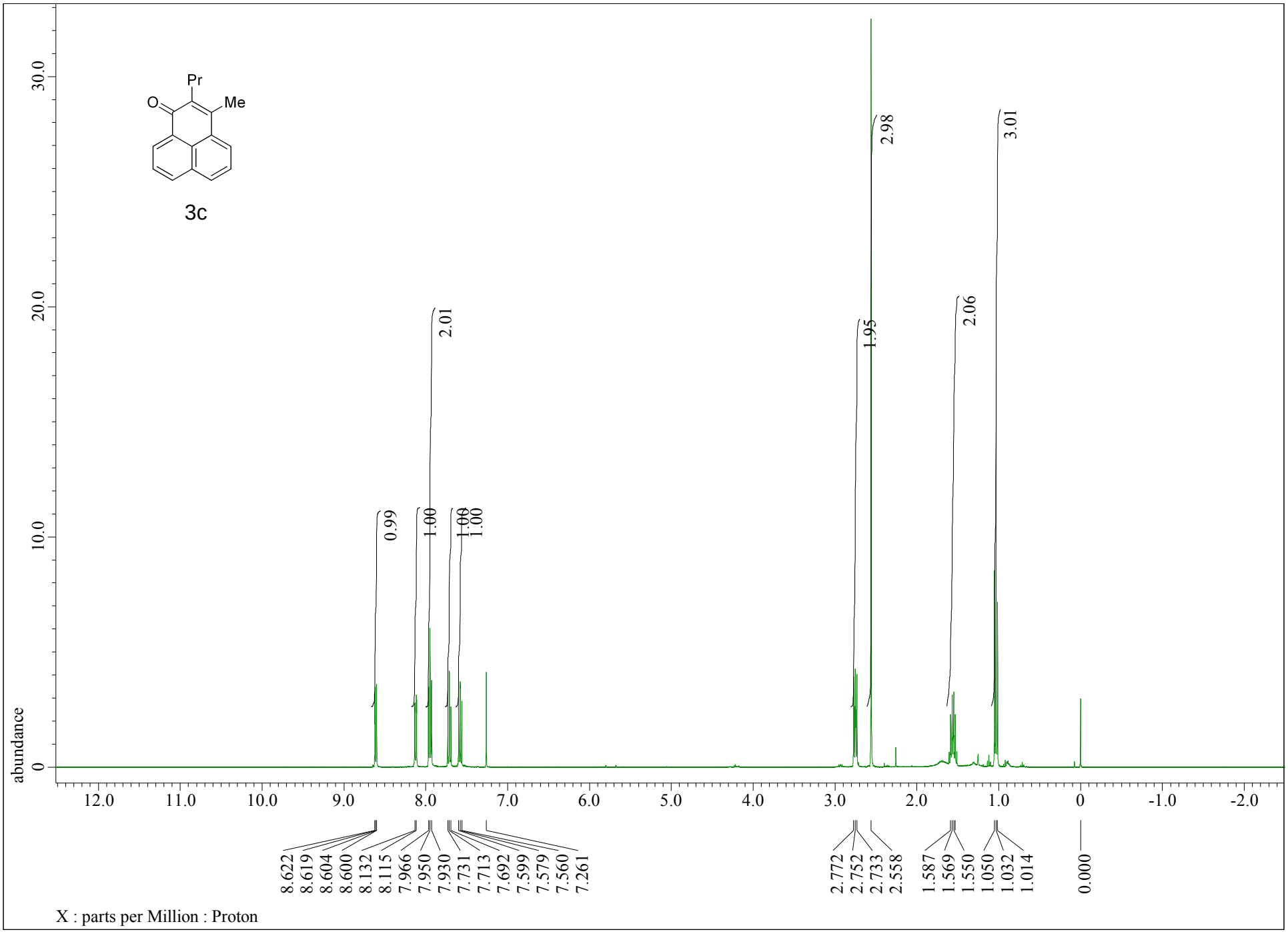
1 Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.

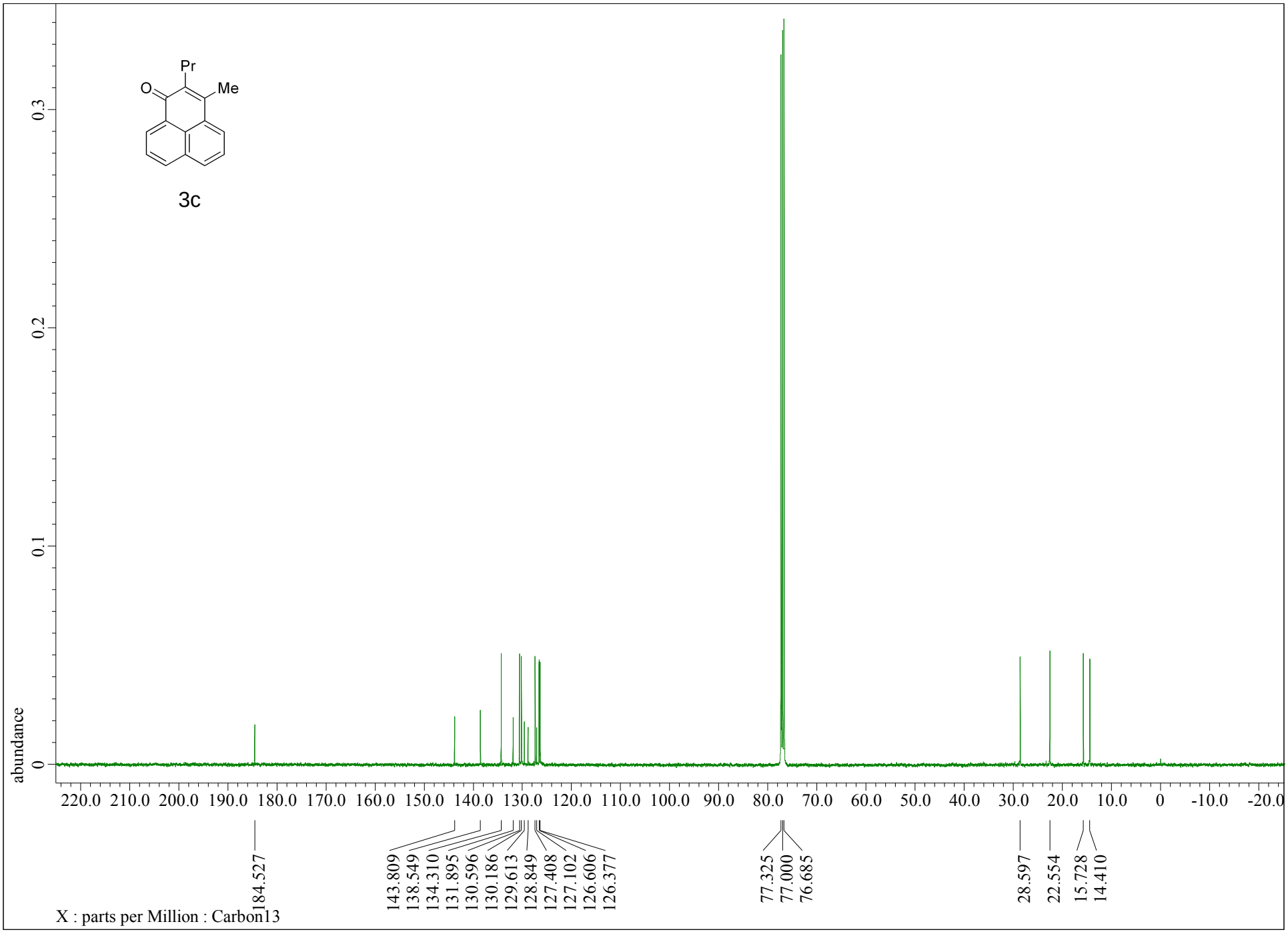
2 Andreas, S.; Christoph, L.; Fabian, C.; Karin, L.; Johannes, R.; Karl-Anton, H.; Wolfgang, B.; Gottfried, S.; Tim, M. *Eur. J. Med. Chem.* **2014**, *57*, 5157.

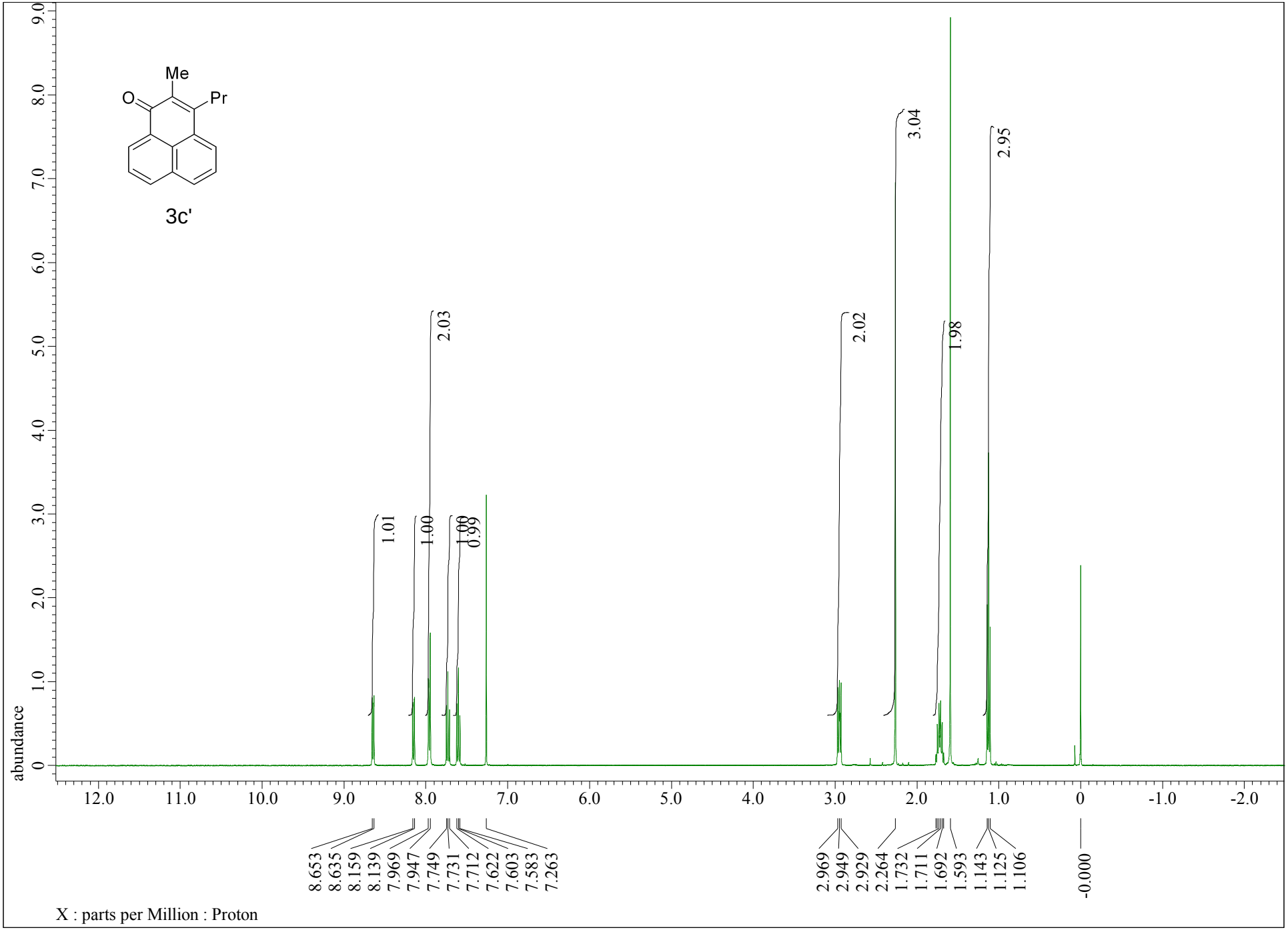

Pr
O
Pr
3a
abundance
0
0.1
0.2
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.813
148.067
138.205
134.387
132.124
130.587
130.157
128.945
128.487
127.608
127.379
126.596
126.415
77.325
77.000
76.685
31.423
28.759
24.368
22.964
14.735
14.649
X : parts per Million : Carbon13

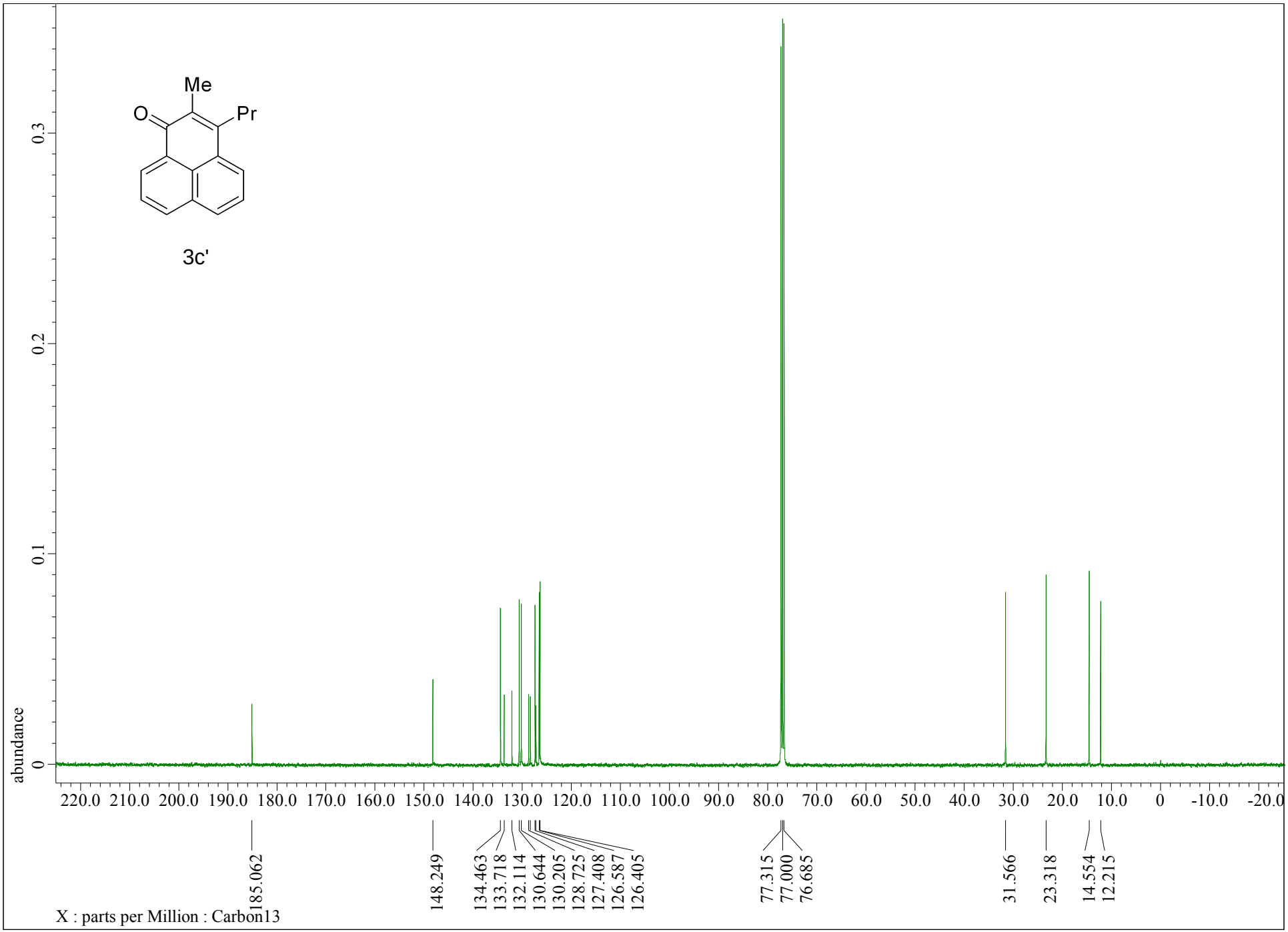

Et
O
Et
3b
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
1.00
1.01
2.02
1.01
1.00
2.00
2.00
3.00
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.644
8.626
8.156
8.136
7.986
7.969
7.951
7.749
7.731
7.712
7.629
7.608
7.590
7.261
3.031
3.011
2.993
2.973
2.793
2.775
2.757
2.738
1.377
1.357
1.339
1.209
1.191
1.173
0.000
X : parts per Million : Proton


Et
O
Et
3b
abundance
0
0.1
0.2
0.3
0.4
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.641
149.136
139.122
134.406
132.143
130.606
130.119
128.935
128.114
127.484
127.417
126.577
126.434
77.315
77.000
76.685
22.201
19.719
15.260
14.086
X : parts per Million : Carbon13


Pr
O
Me
3c
abundance
30.0
20.0
10.0
0
0.99
1.00
2.01
1.00
1.00
1.95
2.98
2.06
3.01
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.622
8.619
8.604
8.600
8.132
8.115
7.966
7.950
7.930
7.731
7.713
7.692
7.599
7.579
7.560
7.261
2.772
2.752
2.733
2.558
1.587
1.569
1.550
1.050
1.032
1.014
0.000
X : parts per Million : Proton


Pr
O
Me
3c
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.527
143.809
138.549
134.310
131.895
130.596
130.186
129.613
128.849
127.408
127.102
126.606
126.377
77.325
77.000
76.685
28.597
22.554
15.728
14.410
X : parts per Million : Carbon13


Me
O
Pr
3c'
abundance
1.01
1.00
2.03
1.00
0.99
2.02
3.04
1.98
2.95
8.653
8.635
8.159
8.139
7.969
7.947
7.749
7.731
7.712
7.622
7.603
7.583
7.263
2.969
2.949
2.929
2.264
1.732
1.711
1.692
1.593
1.143
1.125
1.106
-0.000
X : parts per Million : Proton


Me
O
Pr
3c'
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
185.062
148.249
134.463
133.718
132.114
130.644
130.205
128.725
127.408
126.587
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77.315
77.000
76.685
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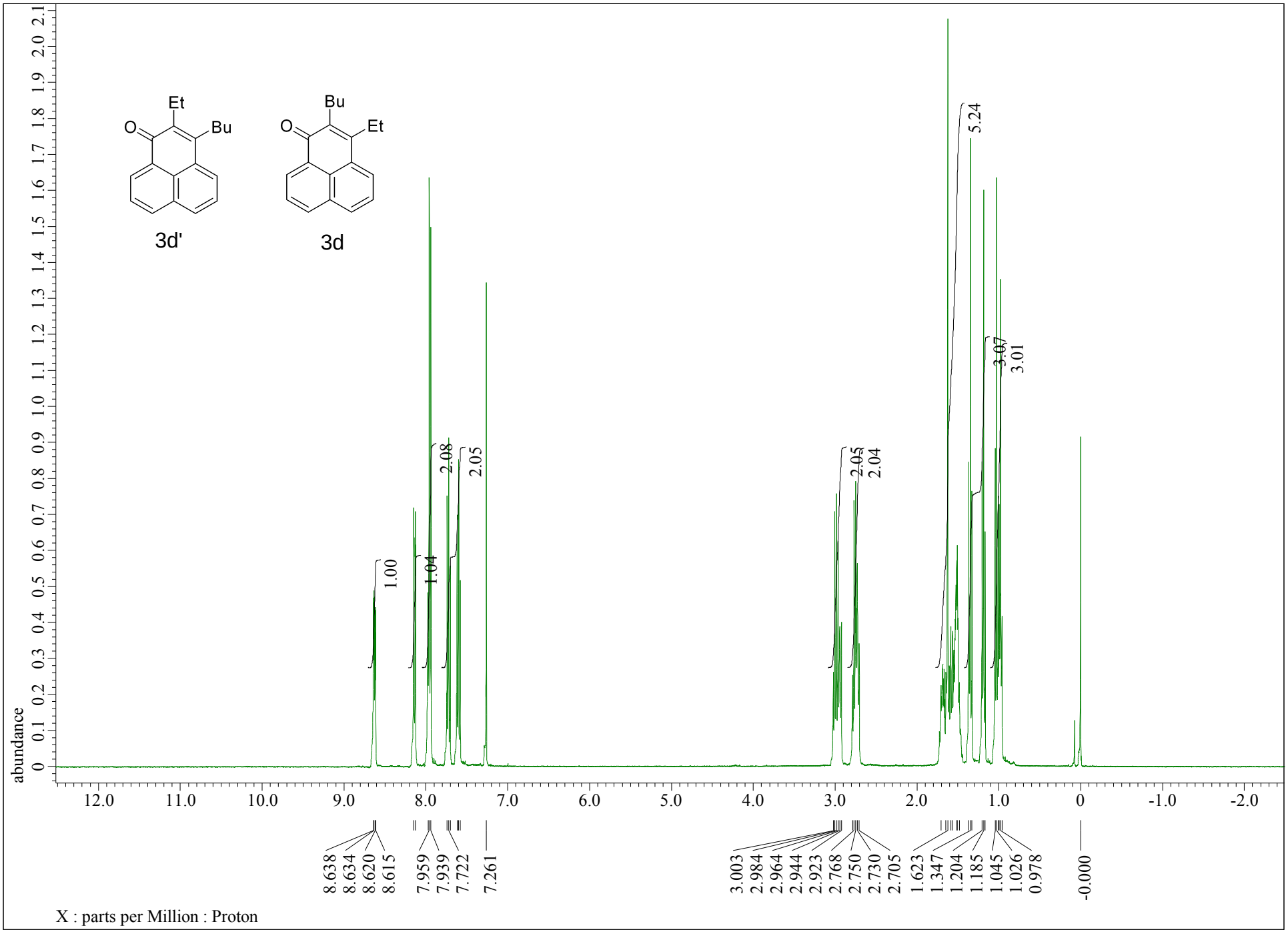
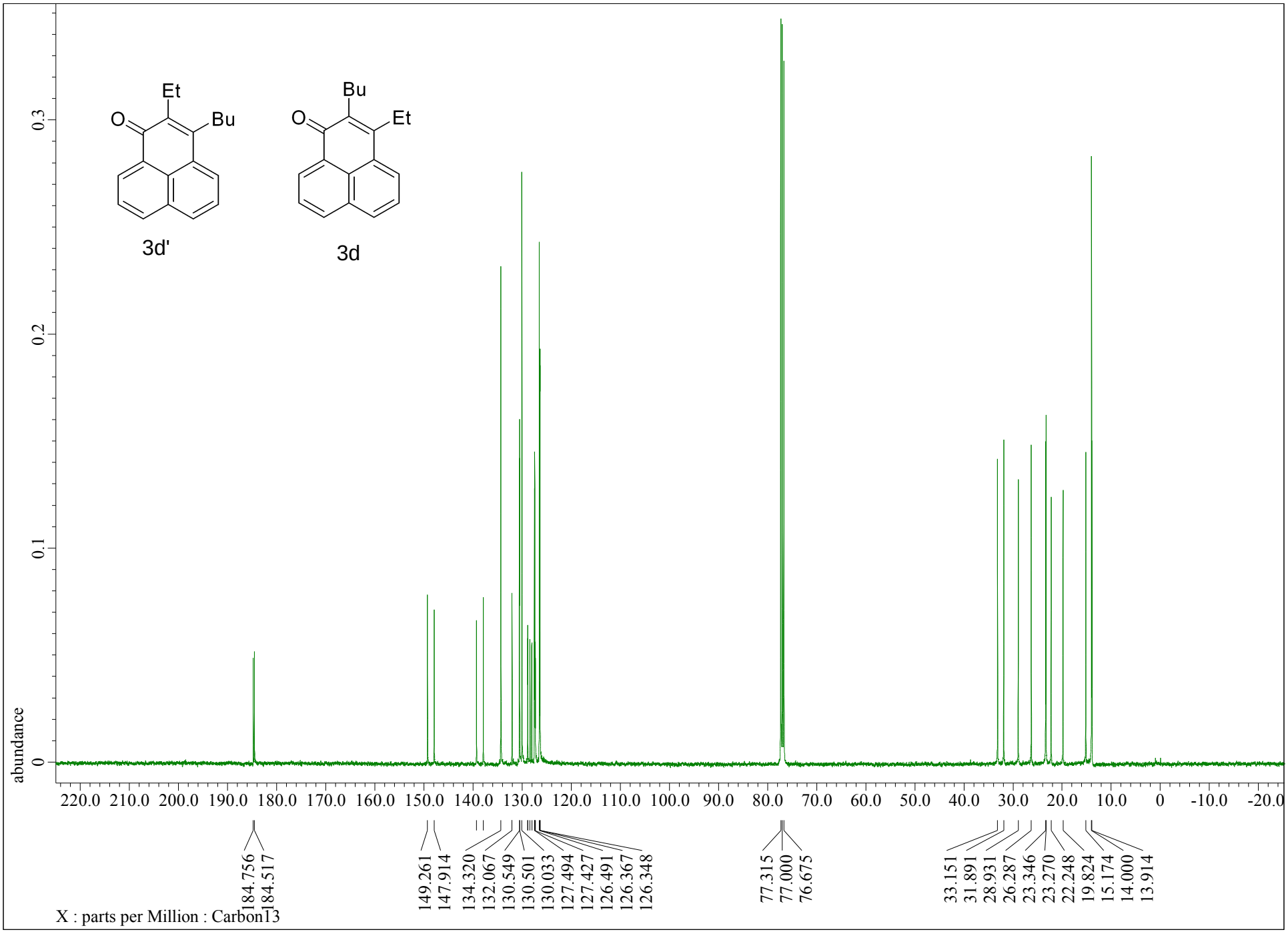
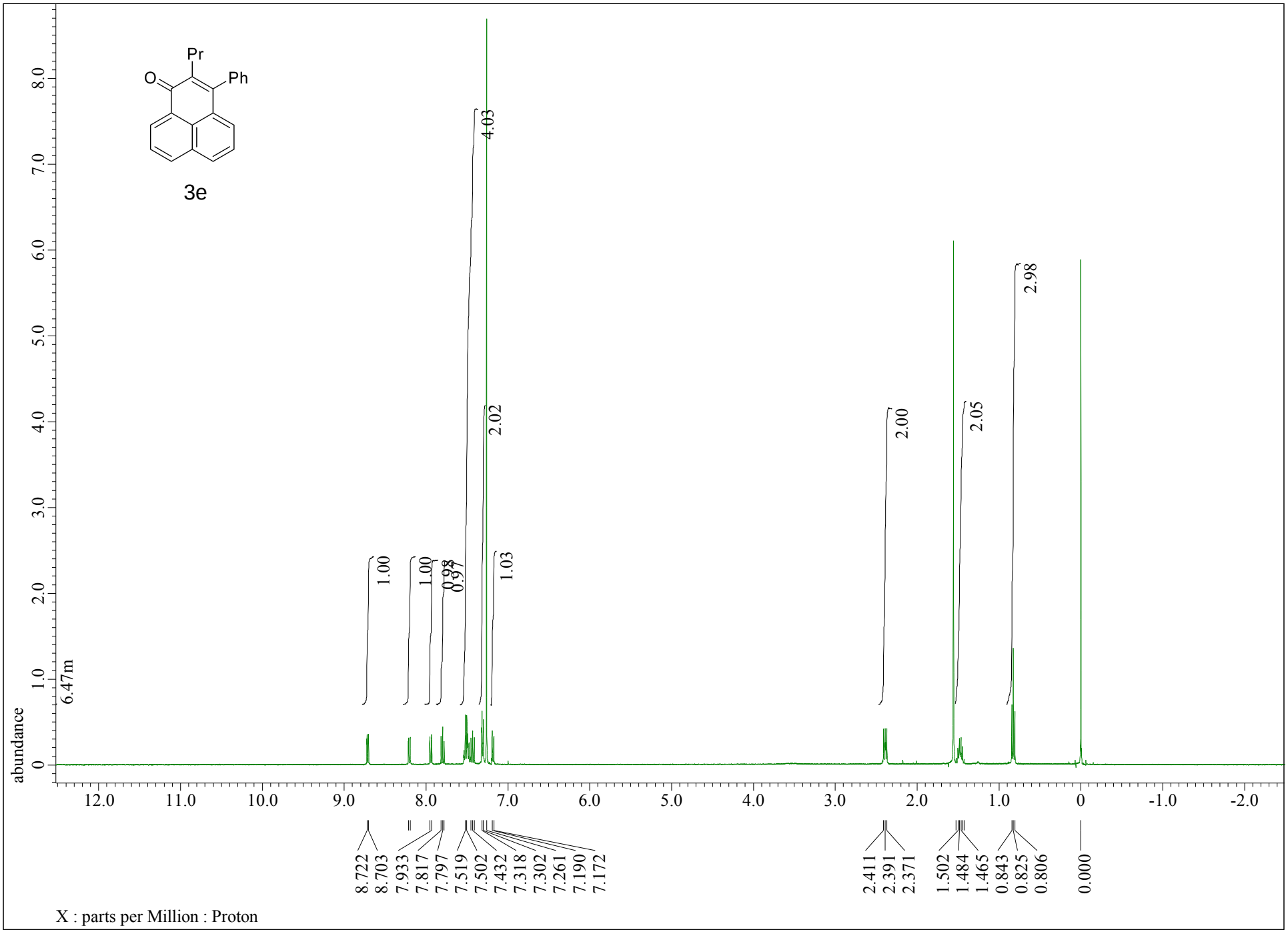
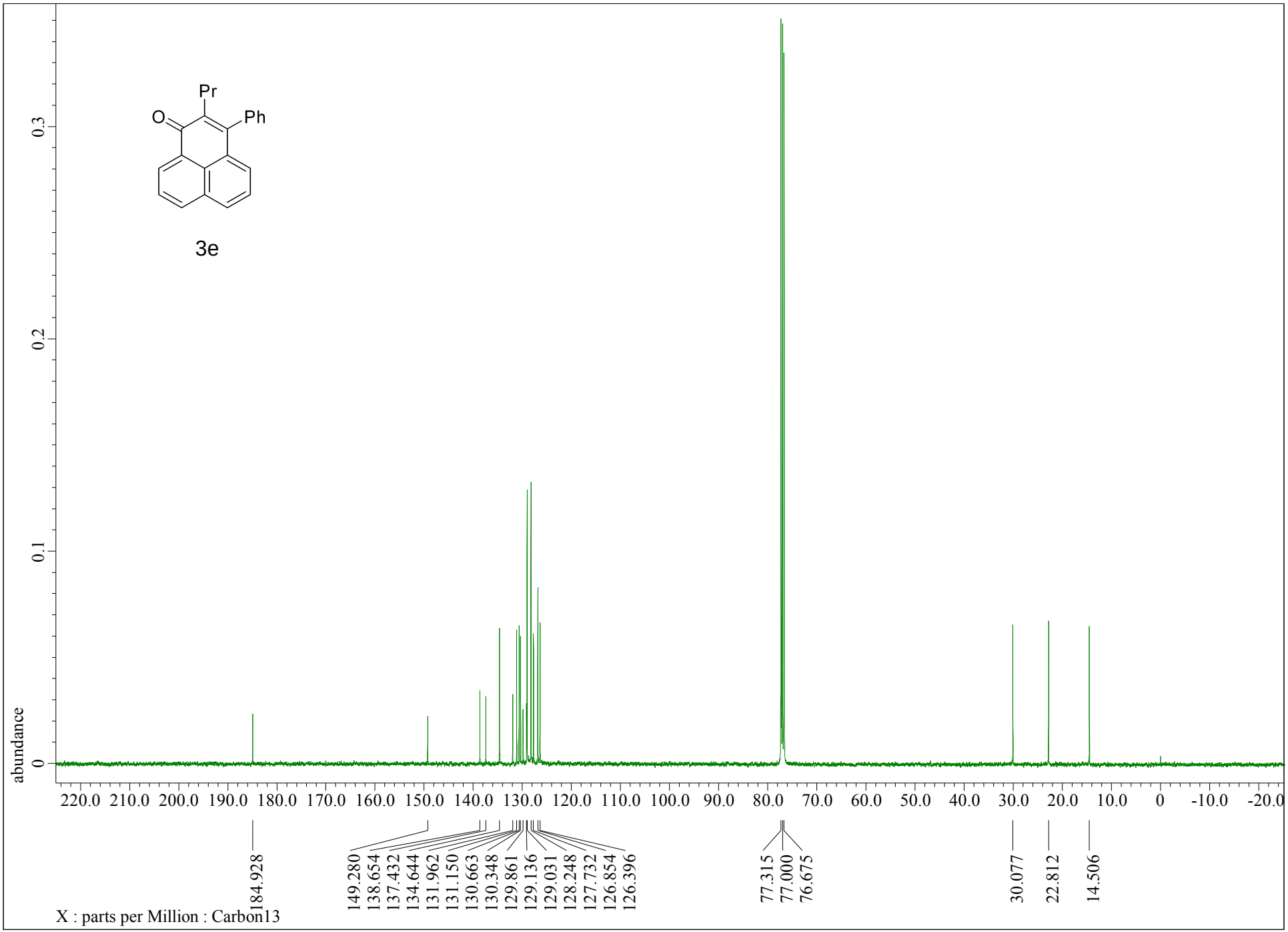
23.318
14.554
12.215
X : parts per Million : Carbon13


Et
O
Bu
3d'
Bu
O
Et
3d
abundance
1.00
1.04
2.08
2.05
2.05
2.04
5.24
3.07
3.01
8.638
8.634
8.620
8.615
7.959
7.939
7.722
7.261
3.003
2.984
2.964
2.944
2.923
2.768
2.750
2.730
2.705
1.623
1.347
1.204
1.185
1.045
1.026
0.978
-0.000
X : parts per Million : Proton


Et
O
Bu
3d'
Bu
O
Et
3d
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.756
184.517
149.261
147.914
134.320
132.067
130.549
130.501
130.033
127.494
127.427
126.491
126.367
126.348
77.315
77.000
76.675
33.151
31.891
28.931
26.287
23.346
23.270
22.248
19.824
15.174
14.000
13.914
X : parts per Million : Carbon13


Pr
O
Ph
3e
abundance
6.47m
1.00
1.00
0.98
0.97
4.03
2.02
1.03
2.00
2.05
2.98
8.722
8.703
7.933
7.817
7.797
7.519
7.502
7.432
7.318
7.302
7.261
7.190
7.172
2.411
2.391
2.371
1.502
1.484
1.465
0.843
0.825
0.806
0.000
X : parts per Million : Proton


Pr
O
Ph
3e
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.928
149.280
138.654
137.432
134.644
131.962
131.150
130.663
130.348
129.861
129.136
129.031
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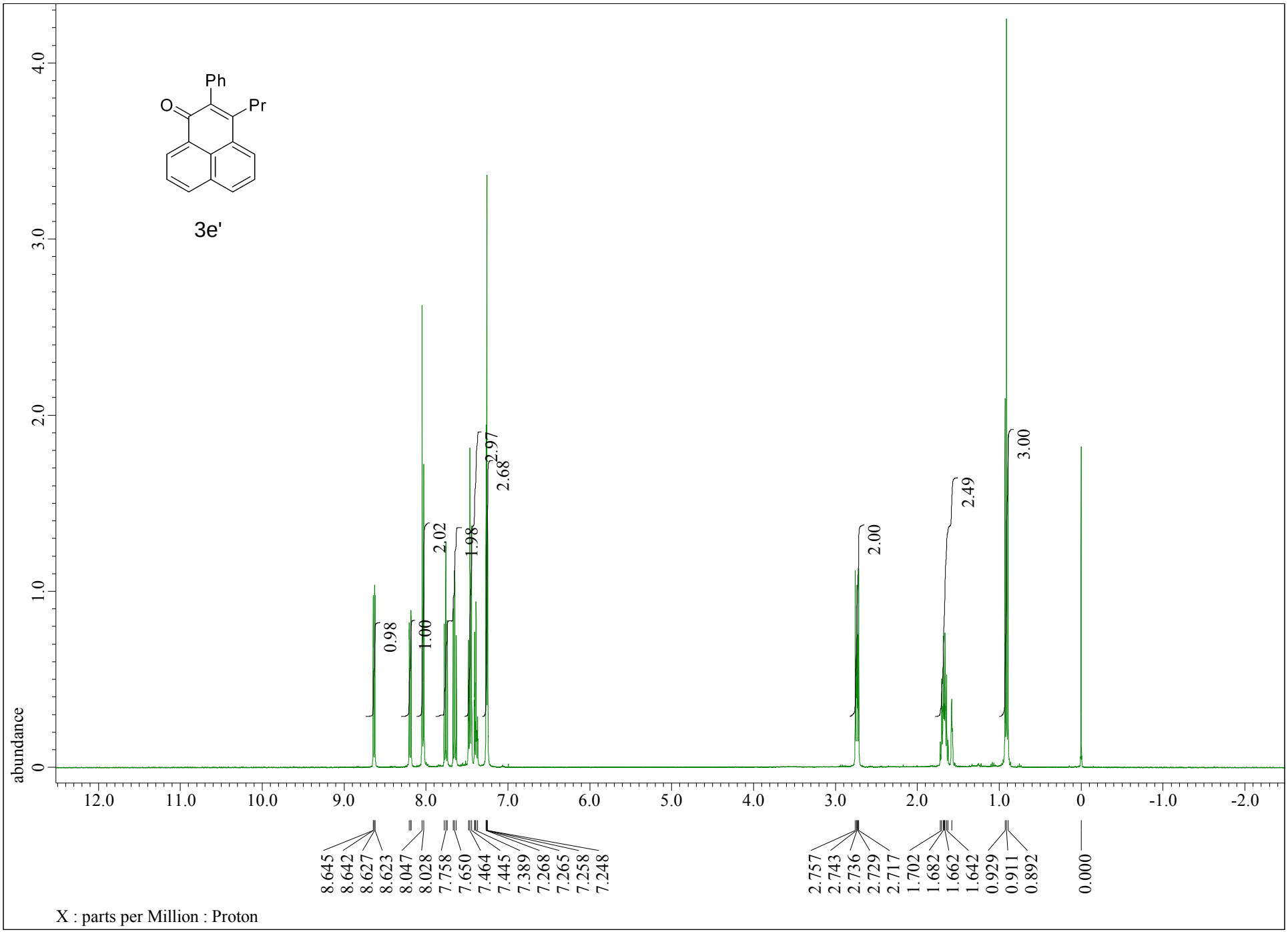
76.675
30.077
22.812
14.506
X : parts per Million : Carbon13


Ph
O
Pr
3e'
abundance
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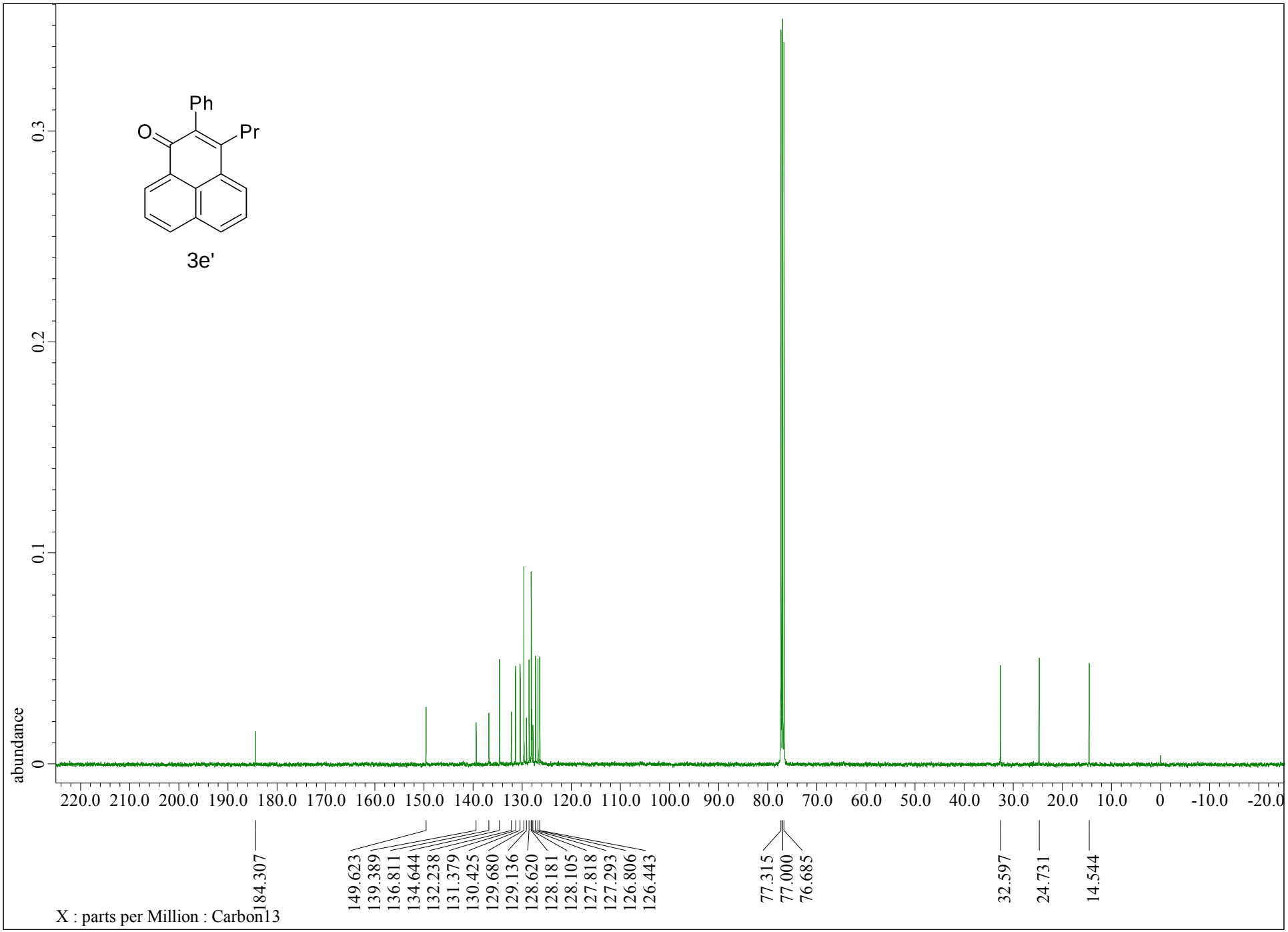
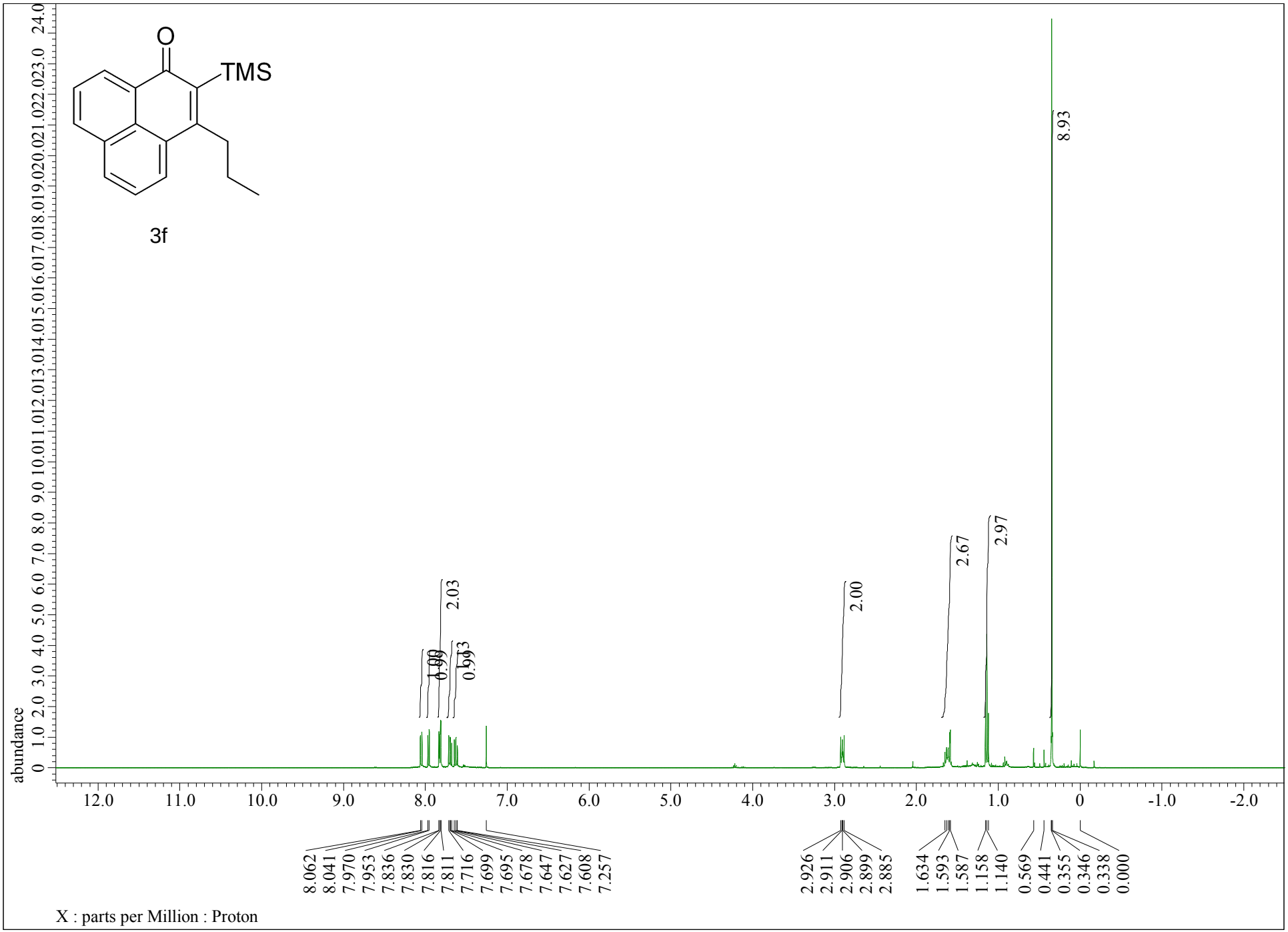
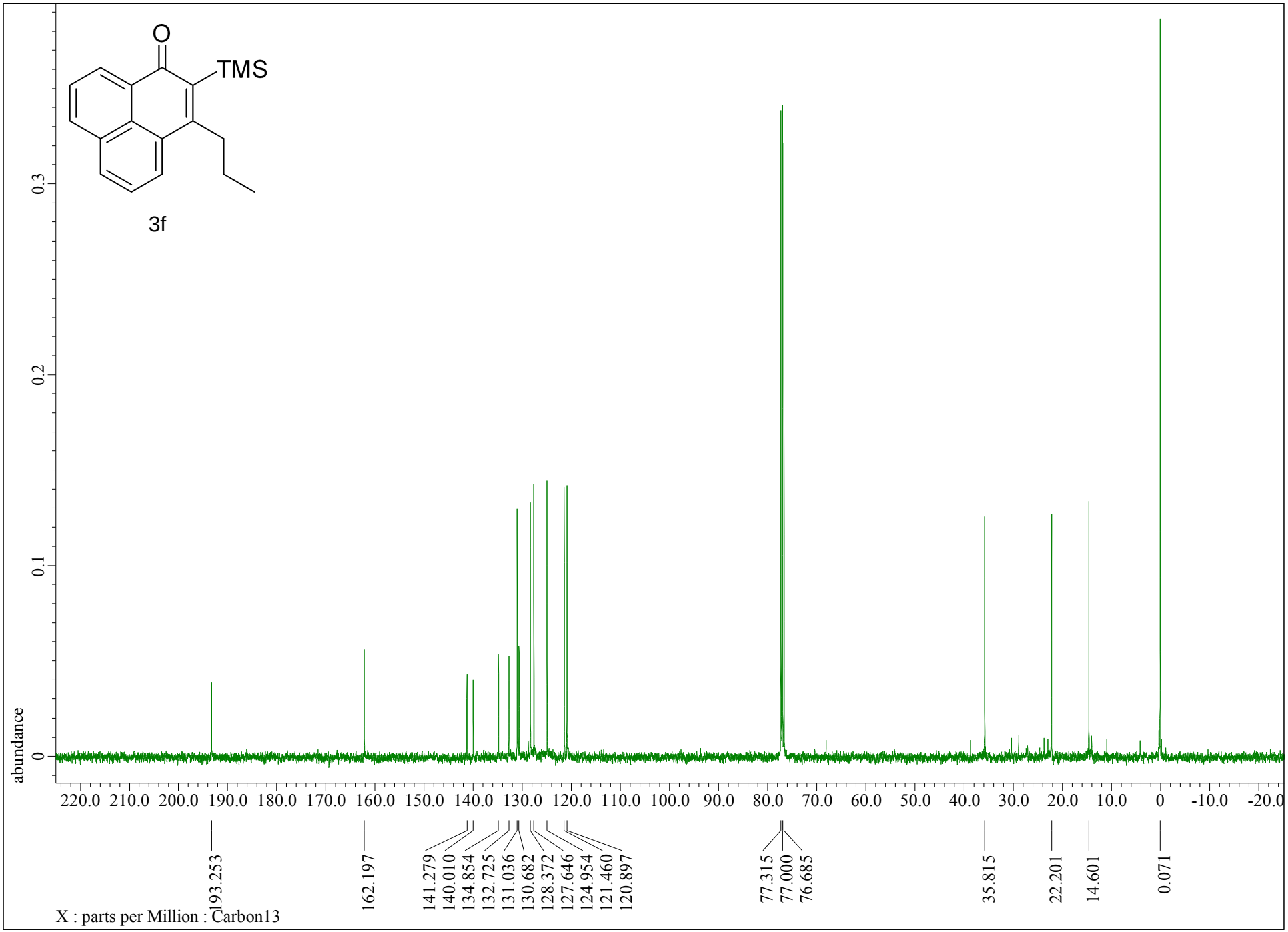
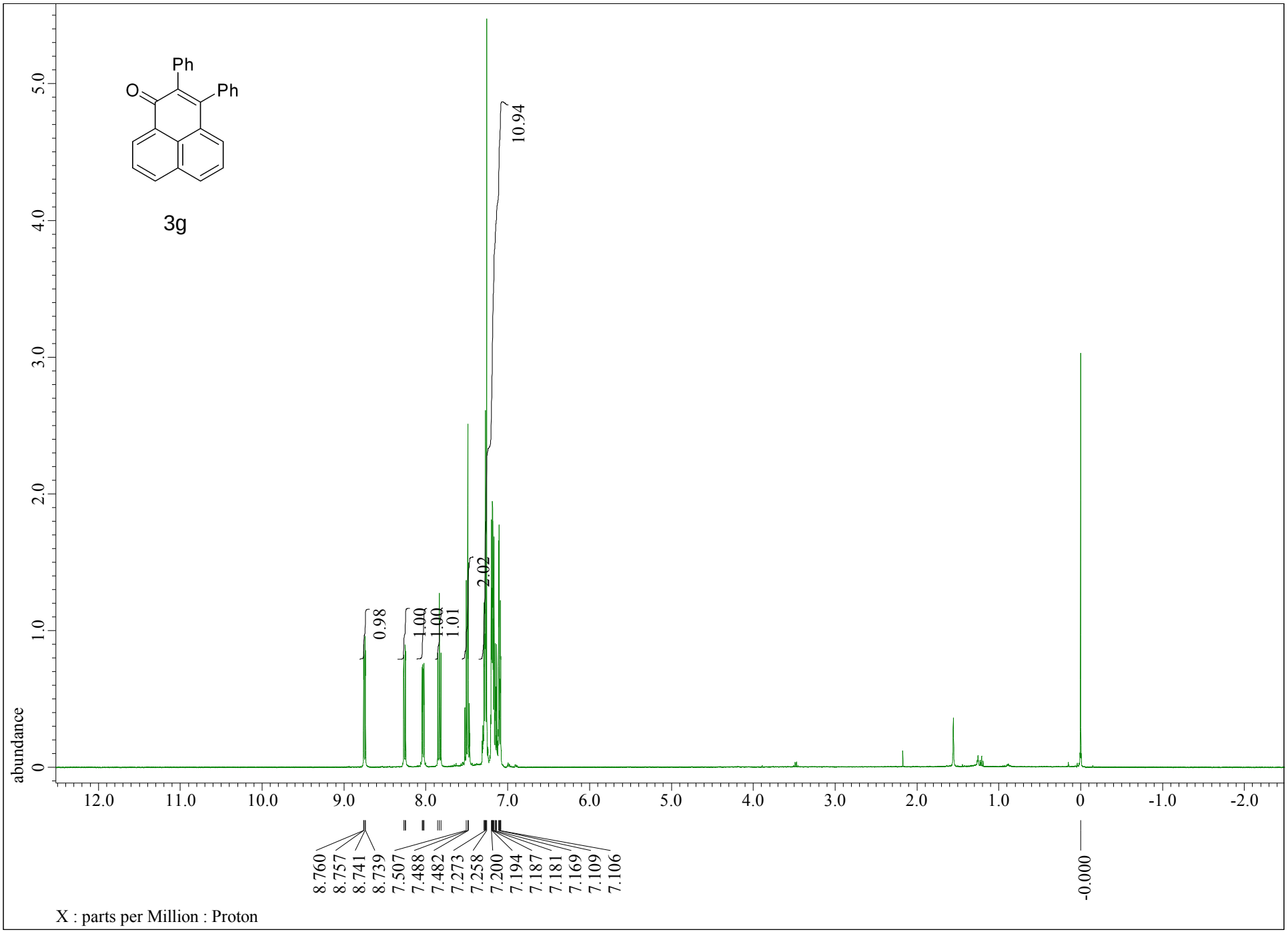
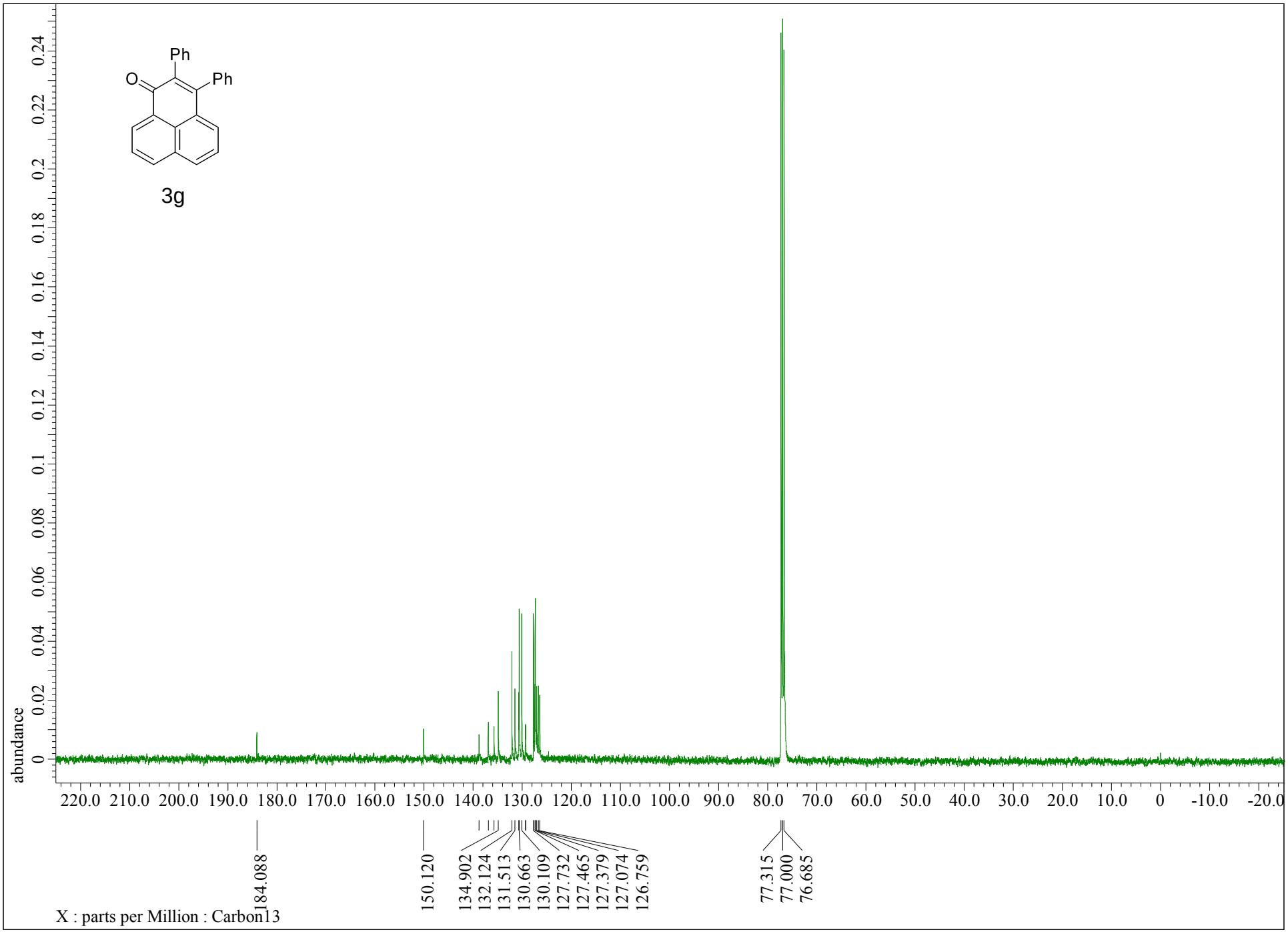
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
0.98
1.00
2.02
1.98
2.97
2.68
2.00
2.49
3.00
8.645
8.642
8.627
8.623
8.047
8.028
7.758
7.650
7.464
7.445
7.389
7.268
7.265
7.258
7.248
2.757
2.743
2.736
2.729
2.717
1.702
1.682
1.662
1.642
0.929
0.911
0.892
0.000
X : parts per Million : Proton

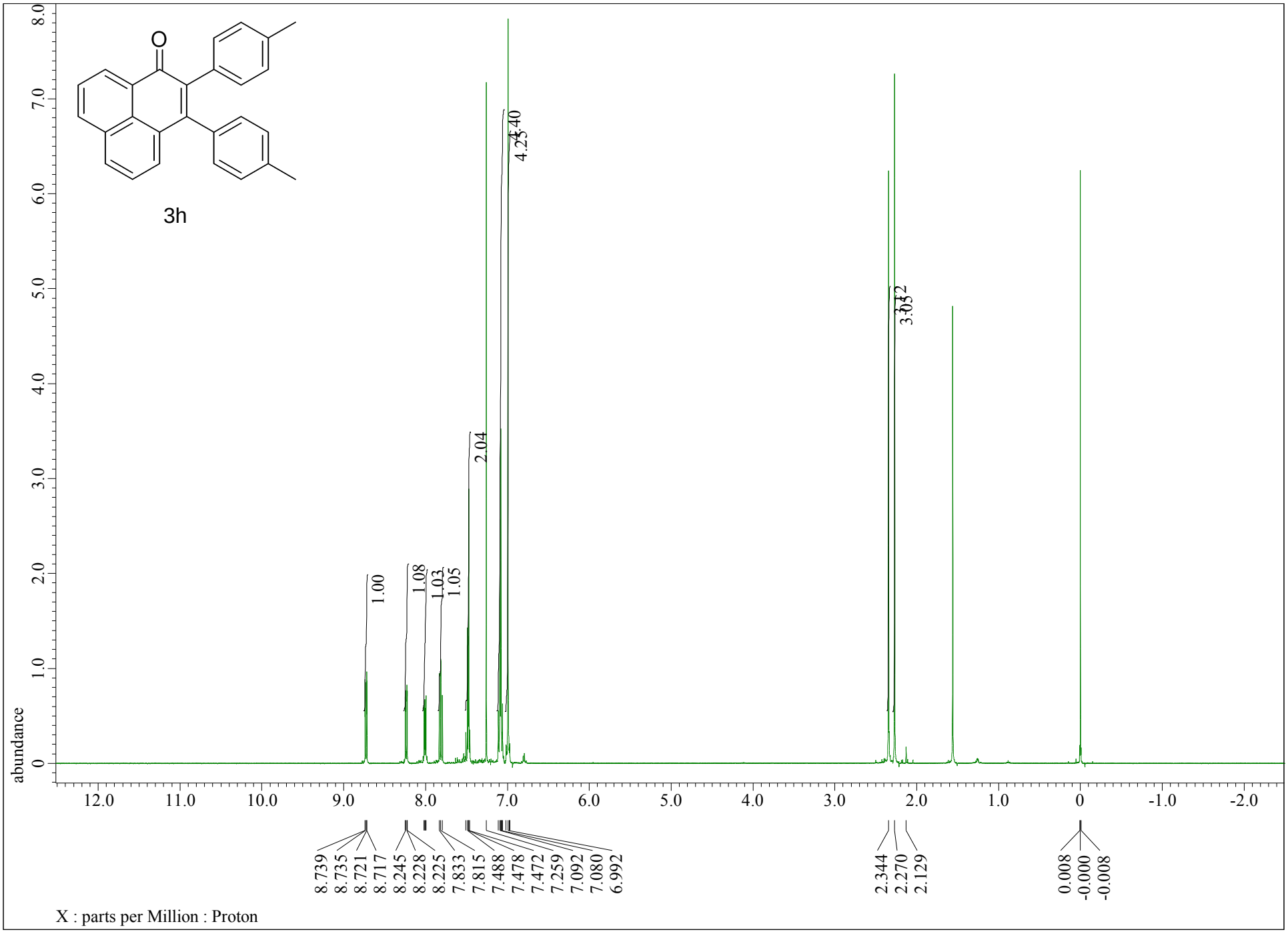

Ph
O
Pr
3e'
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.307
149.623
139.389
136.811
134.644
132.238
131.379
130.425
129.680
129.136
128.620
128.181
128.105
127.818
127.293
126.806
126.443
77.315
77.000
76.685
32.597
24.731
14.544
X : parts per Million : Carbon13

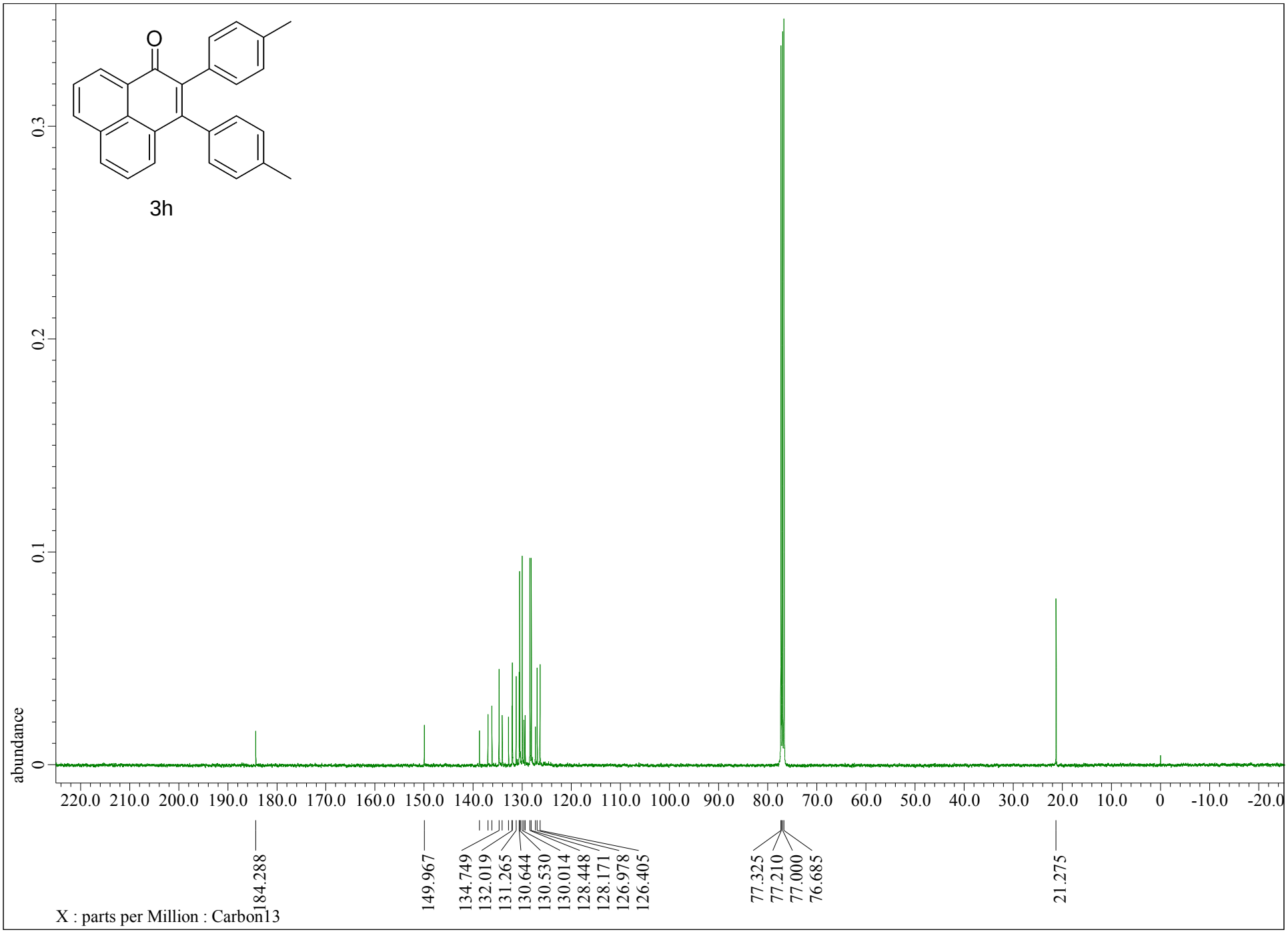

O
TMS
3f
abundance
X : parts per Million : Proton
2.03
1.00
0.99
1.13
0.93
2.00
2.67
2.97
8.93
8.062
8.041
7.970
7.953
7.836
7.830
7.816
7.811
7.716
7.699
7.695
7.678
7.647
7.627
7.608
7.257
2.926
2.911
2.906
2.899
2.885
1.634
1.593
1.587
1.158
1.140
0.569
0.441
0.355
0.346
0.338
0.000

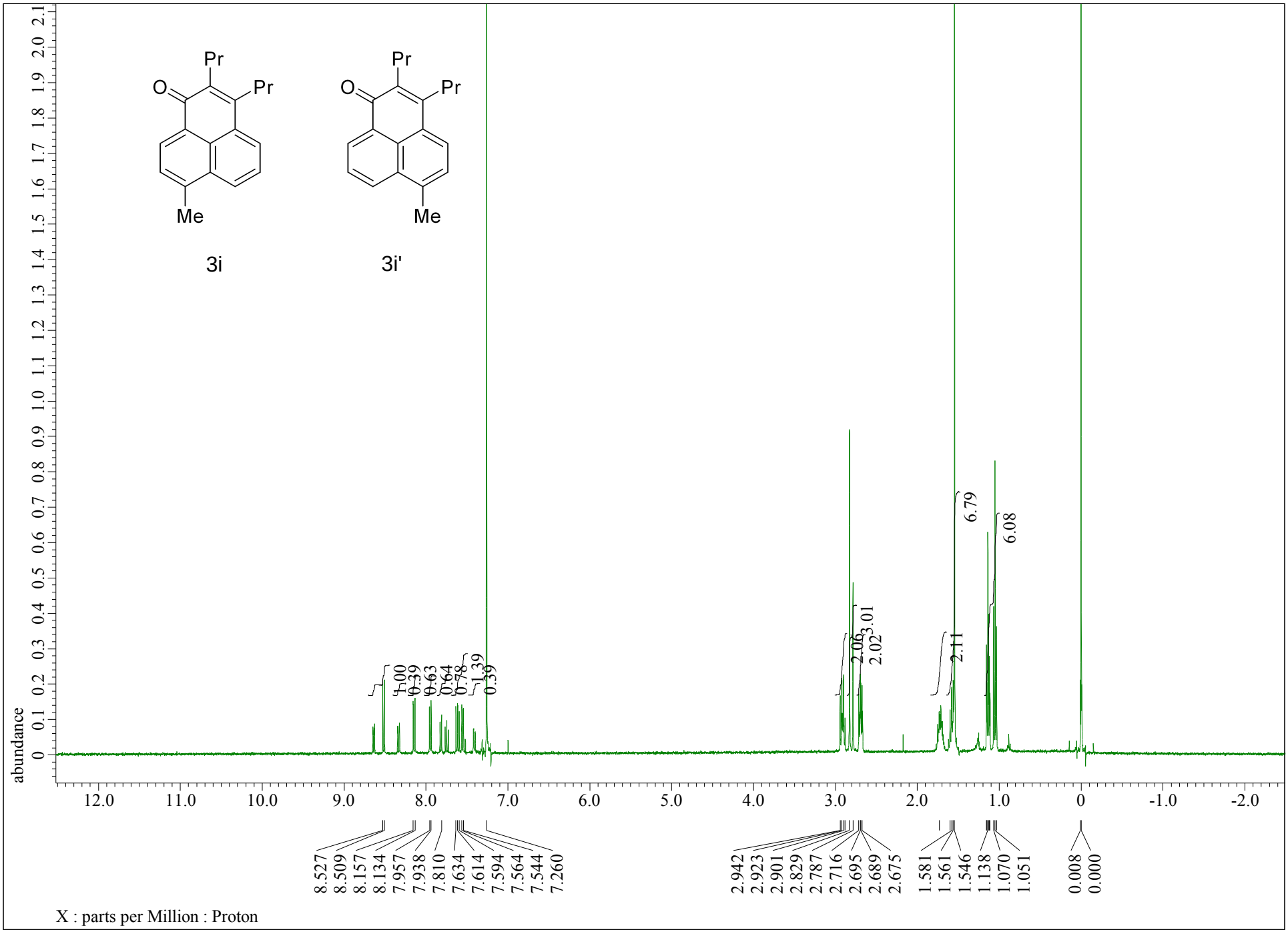

O
TMS
3f
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
193.253
162.197
141.279
140.010
134.854
132.725
131.036
130.682
128.372
127.646
124.954
121.460
120.897
77.315
77.000
76.685
35.815
22.201
14.601
0.071
X : parts per Million : Carbon13

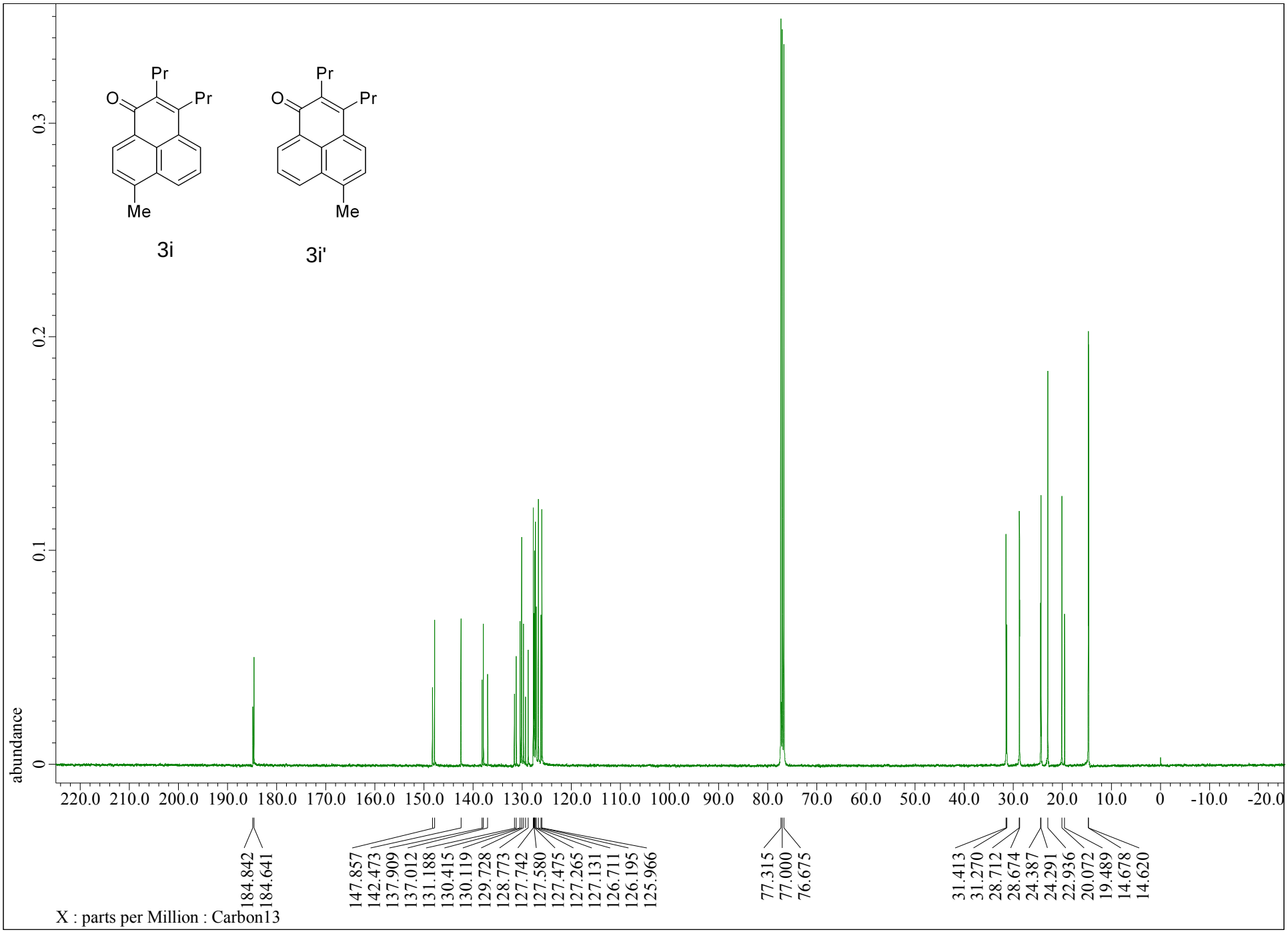

Ph
O
Ph
3g
10.94
2.02
1.01
1.00
1.00
0.98
abundance
5.0
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.760
8.757
8.741
8.739
7.507
7.488
7.482
7.273
7.258
7.200
7.194
7.187
7.181
7.169
7.109
7.106
-0.000
X : parts per Million : Proton

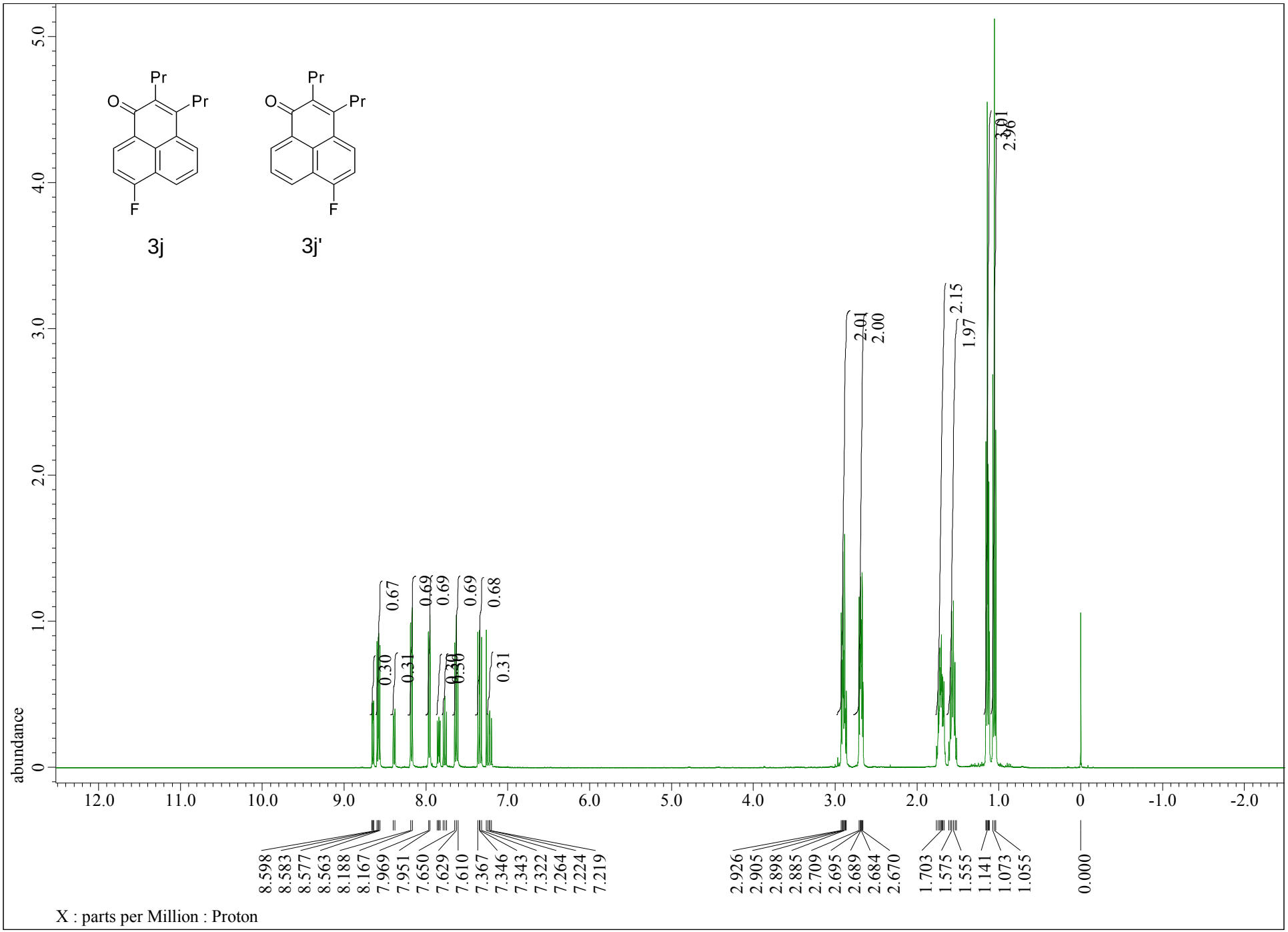

Ph
O
Ph
3g
abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.088
150.120
134.902
132.124
131.513
130.663
130.109
127.732
127.465
127.379
127.074
126.759
77.315
77.000
76.685
X : parts per Million : Carbon13

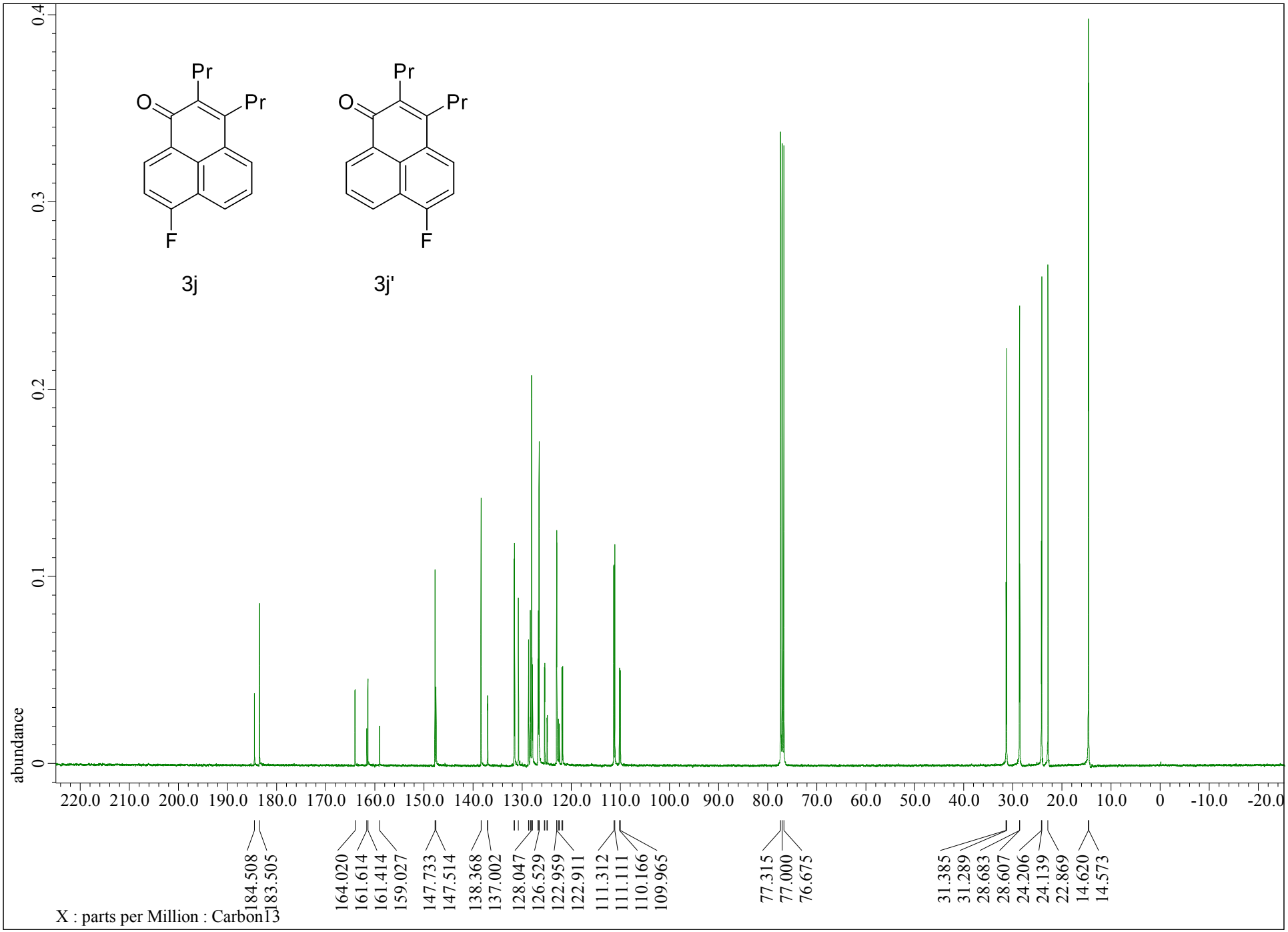

O
3h
abundance
X : parts per Million : Proton
1.00
1.08
1.03
1.05
2.04
4.25
4.40
3.03
3.12
8.739
8.735
8.721
8.717
8.245
8.228
8.225
7.833
7.815
7.488
7.478
7.472
7.259
7.092
7.080
6.992
2.344
2.270
2.129
0.008
-0.000
-0.008

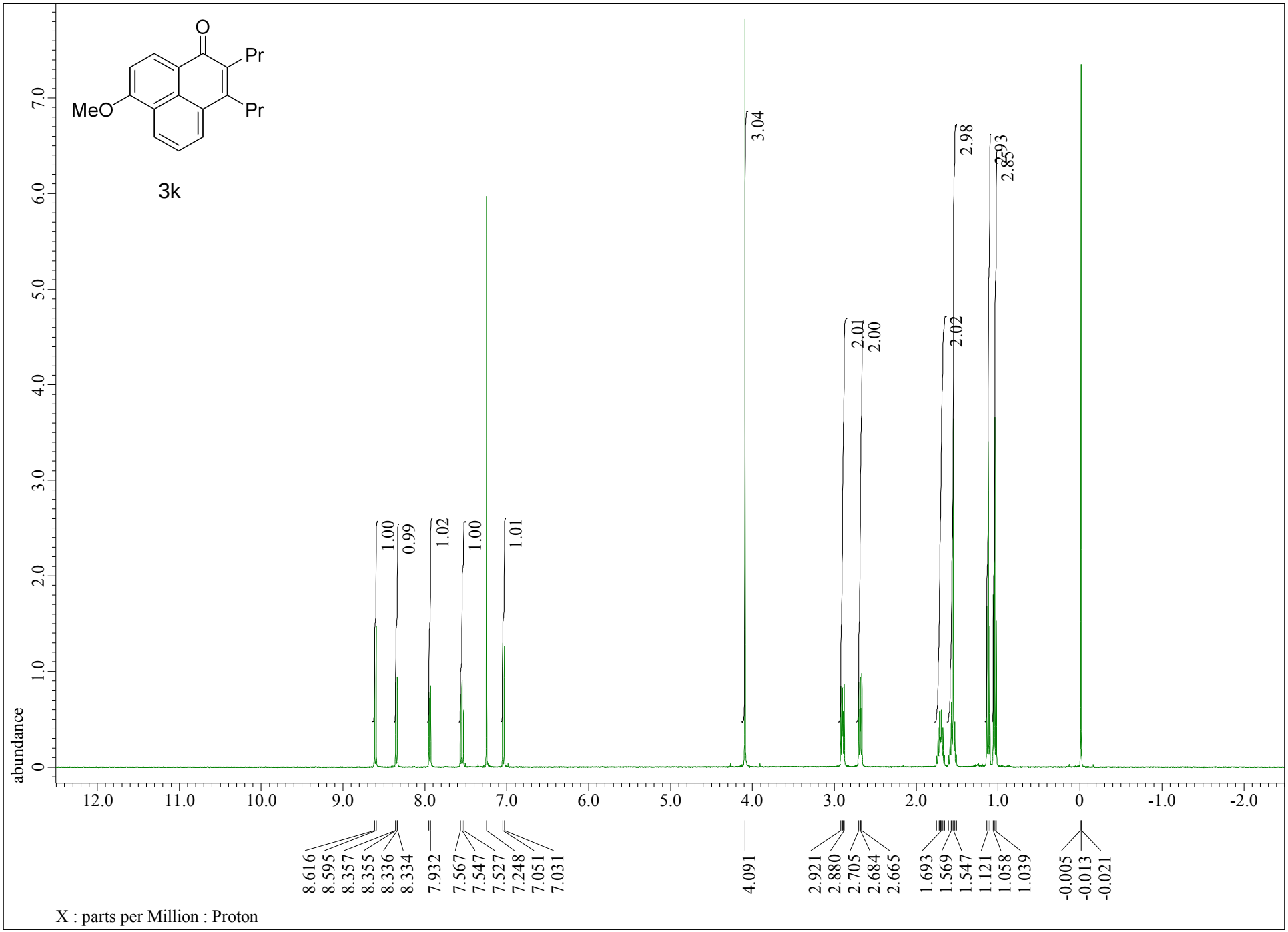

O
3h
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.288
149.967
134.749
132.019
131.265
130.644
130.530
130.014
128.448
128.171
126.978
126.405
77.325
77.210
77.000
76.685
21.275
X : parts per Million : Carbon13

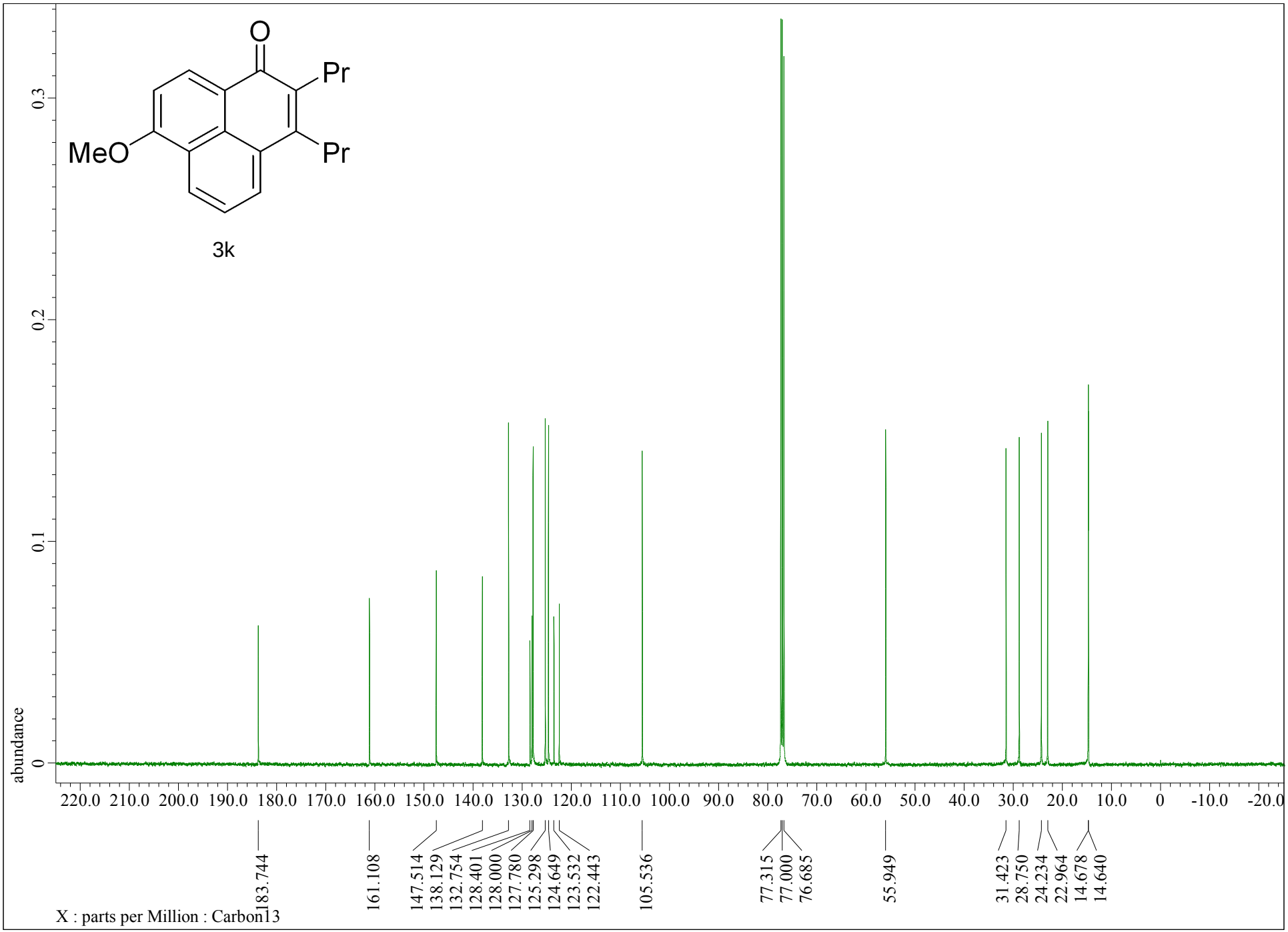

Pr
O
Pr
Me
3i
Pr
O
Pr
Me
3i'
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
1.00
0.39
0.63
0.64
0.78
1.39
0.39
2.06
3.01
2.02
2.11
6.79
6.08
8.527
8.509
8.157
8.134
7.957
7.938
7.810
7.634
7.614
7.594
7.564
7.544
7.260
2.942
2.923
2.901
2.829
2.787
2.716
2.695
2.689
2.675
1.581
1.561
1.546
1.138
1.070
1.051
0.008
0.000
X : parts per Million : Proton

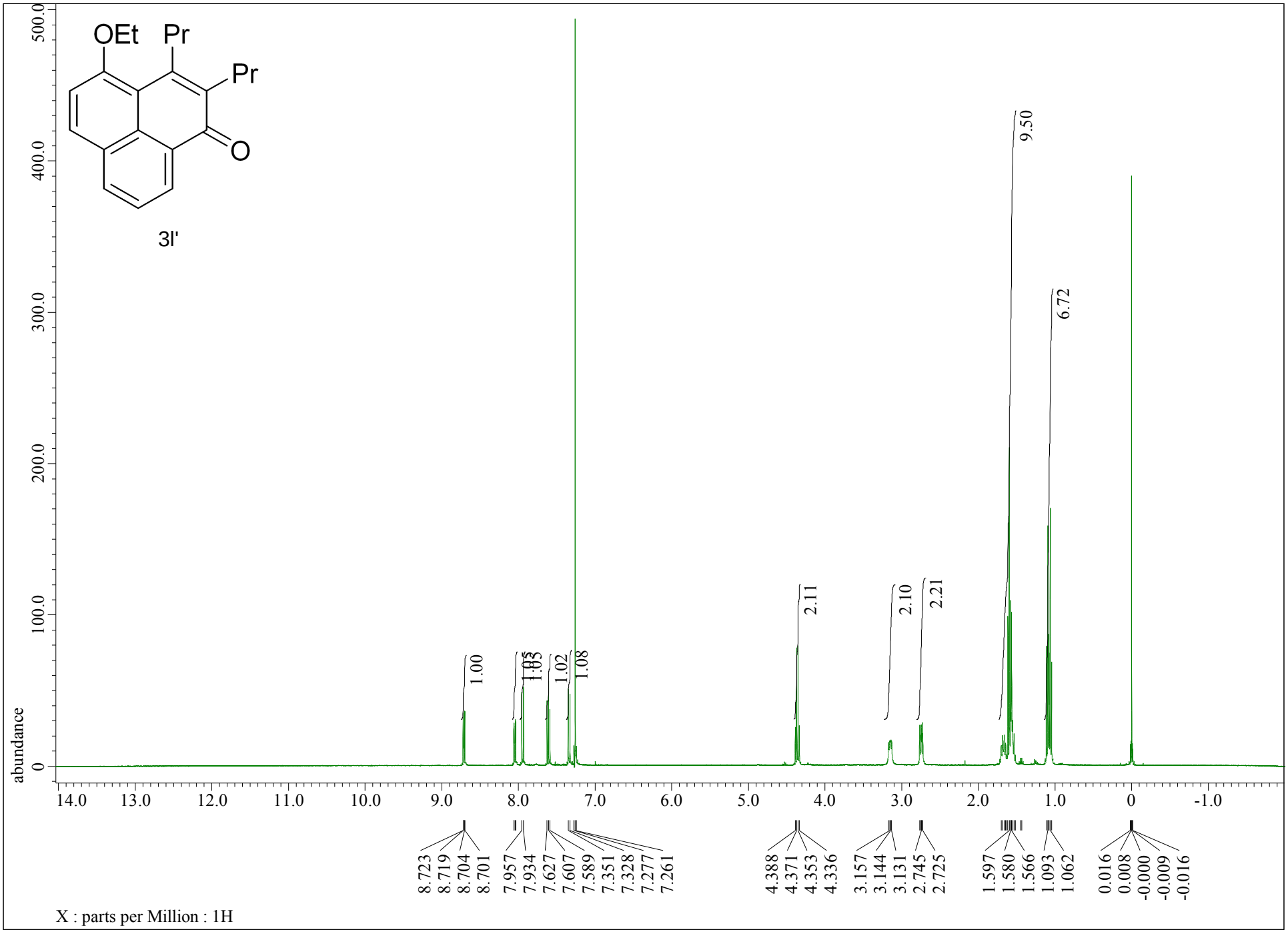

Pr
O
Pr
Me
3i
Pr
O
Pr
Me
3i'
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.842
184.641
147.857
142.473
137.909
137.012
131.188
130.415
130.119
129.728
128.773
127.742
127.580
127.475
127.265
127.131
126.711
126.195
125.966
77.315
77.000
76.675
31.413
31.270
28.712
28.674
24.387
24.291
22.936
20.072
19.489
14.678
14.620
X : parts per Million : Carbon13

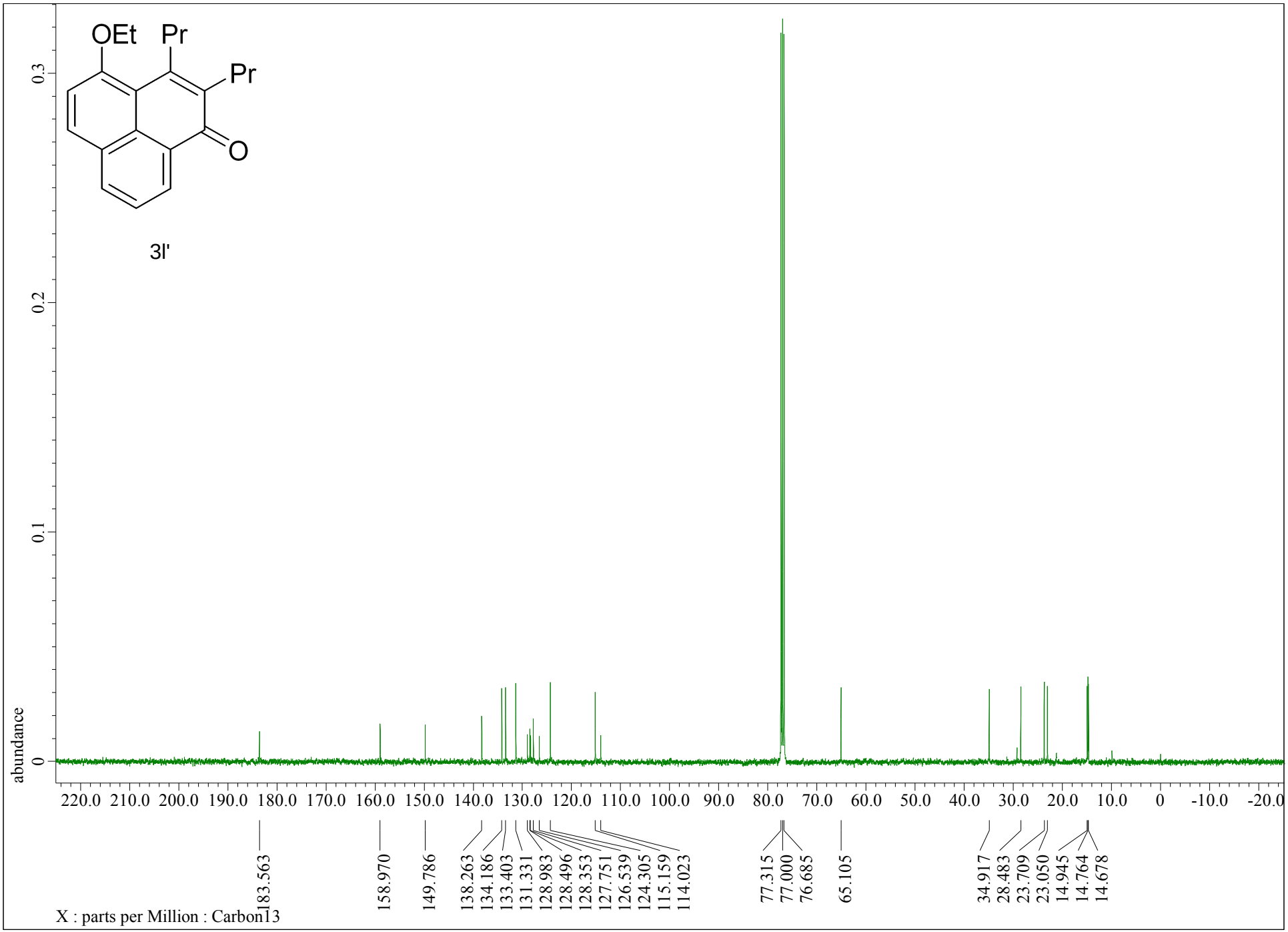

Pr
Pr
O
F
3j
Pr
Pr
O
F
3j'
abundance
X : parts per Million : Proton
8.598
8.583
8.577
8.563
8.188
8.167
7.969
7.951
7.650
7.629
7.610
7.367
7.346
7.343
7.322
7.264
7.224
7.219
2.926
2.905
2.898
2.885
2.709
2.695
2.689
2.684
2.670
1.703
1.575
1.555
1.141
1.073
1.055
0.000

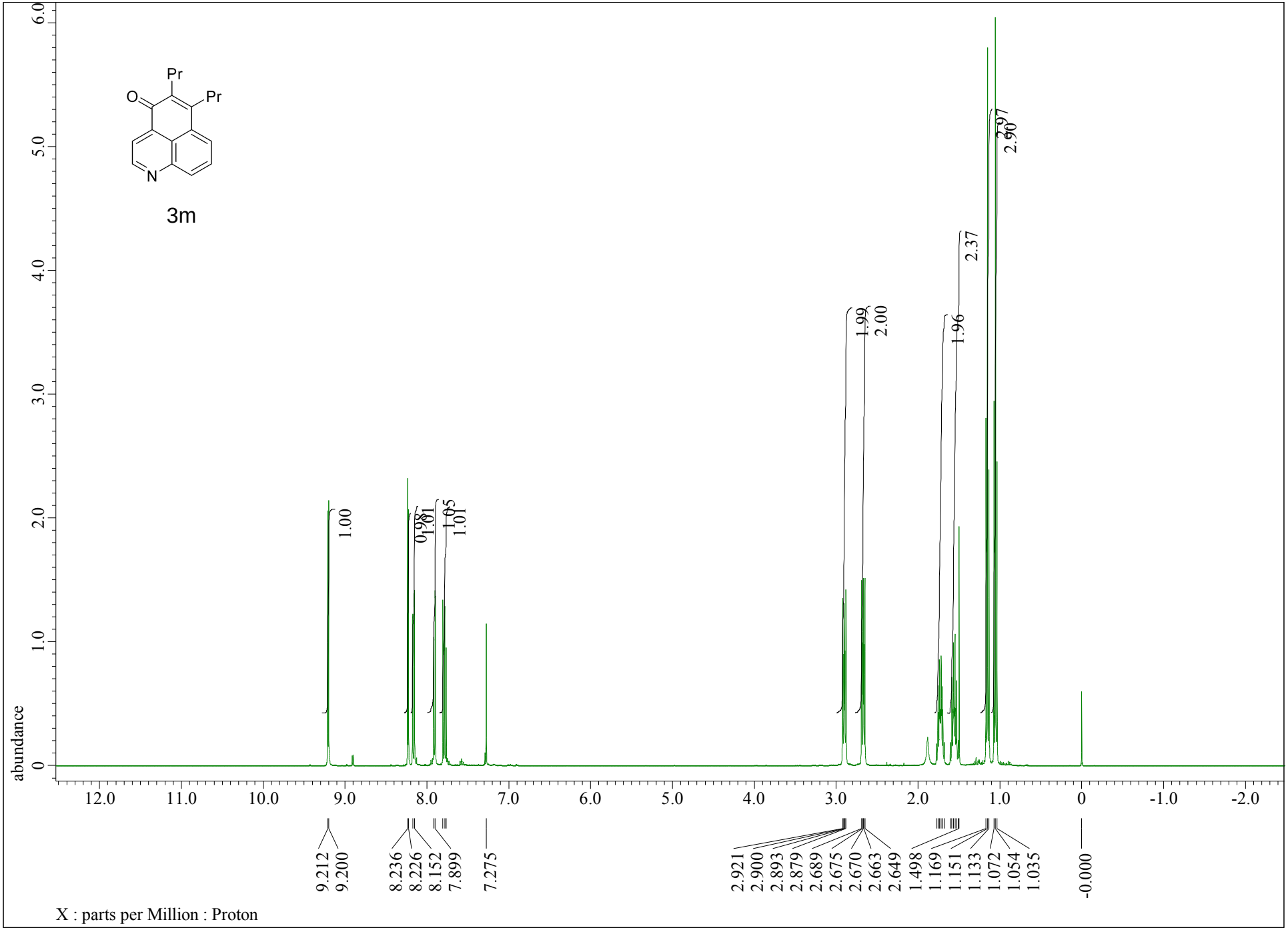

Pr
Pr
O
F
3j
Pr
Pr
O
F
3j'
abundance
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.508
183.505
164.020
161.614
161.414
159.027
147.733
147.514
138.368
137.002
128.047
126.529
122.959
122.911
111.312
111.111
110.166
109.965
77.315
77.000
76.675
31.385
31.289
28.683
28.607
24.206
24.139
22.869
14.620
14.573
X : parts per Million : Carbon13

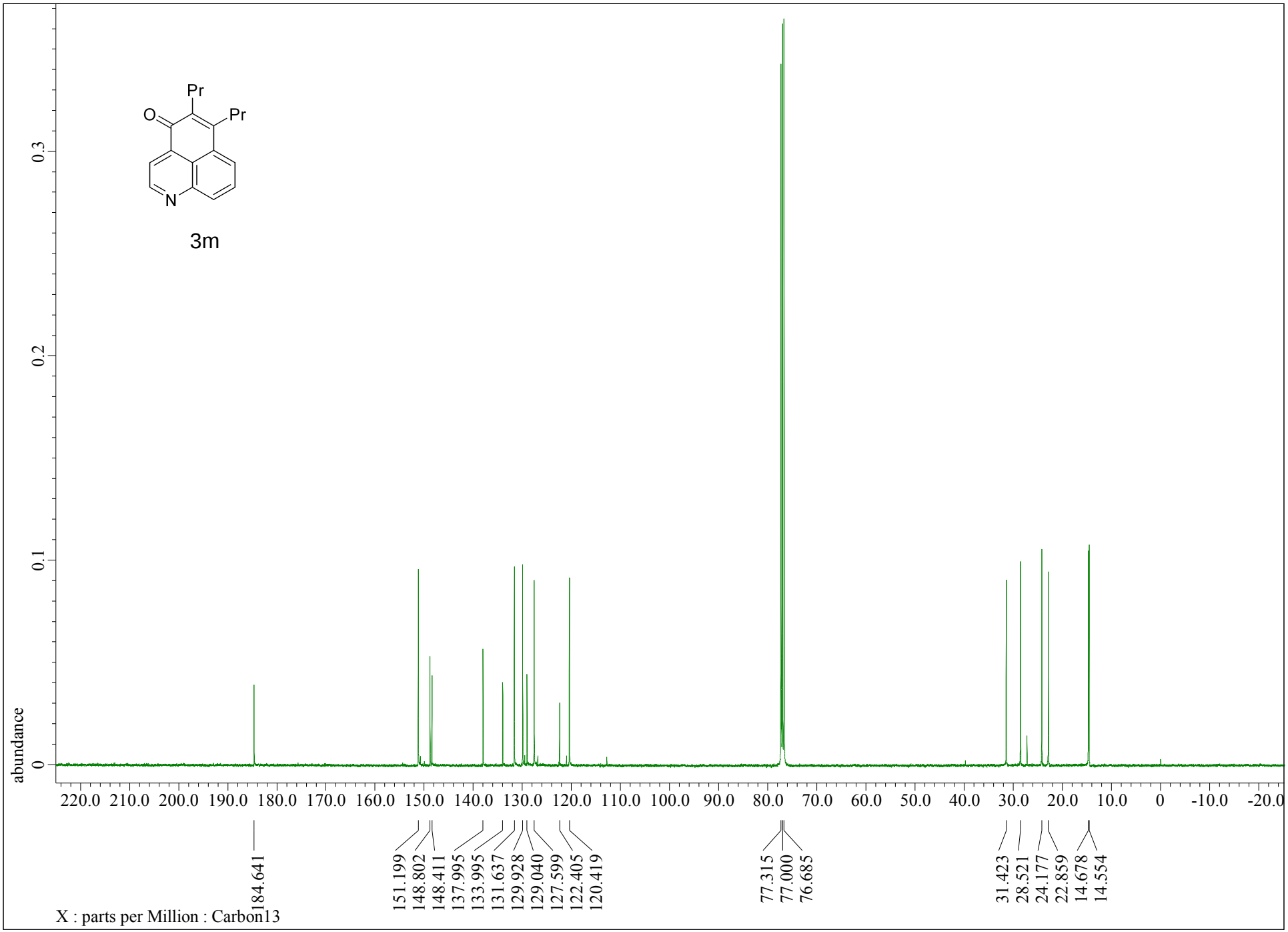

O
Pr
MeO
Pr
3k
abundance
X : parts per Million : Proton
1.00
0.99
1.02
1.00
1.01
3.04
2.01
2.00
2.02
2.98
2.93
2.85
8.616
8.595
8.357
8.355
8.336
8.334
7.932
7.567
7.547
7.527
7.248
7.051
7.031
4.091
2.921
2.880
2.705
2.684
2.665
1.693
1.569
1.547
1.121
1.058
1.039
-0.005
-0.013
-0.021


O
Pr
MeO
Pr
3k
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
183.744
161.108
147.514
138.129
132.754
128.401
128.000
127.780
125.298
124.649
123.532
122.443
105.536
77.315
77.000
76.685
55.949
31.423
28.750
24.234
22.964
14.678
14.640
X : parts per Million : Carbon13


OEt
Pr
Pr
O
3l'
abundance
500.0
400.0
300.0
200.0
100.0
0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
1.00
1.03
1.02
1.08
2.11
2.10
2.21
9.50
6.72
8.723
8.719
8.704
8.701
7.957
7.934
7.627
7.607
7.589
7.351
7.328
7.277
7.261
4.388
4.371
4.353
4.336
3.157
3.144
3.131
2.745
2.725
1.597
1.580
1.566
1.093
1.062
0.016
0.008
-0.000
-0.009
-0.016
X : parts per Million : 1H


OEt
Pr
Pr
O
3l'
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
183.563
158.970
149.786
138.263
134.186
133.403
131.331
128.983
128.496
128.353
127.751
126.539
124.305
115.159
114.023
77.315
77.000
76.685
65.105
34.917
28.483
23.709
23.050
14.945
14.764
14.678
X : parts per Million : Carbon13


Pr
O
Pr
N
3m
abundance
1.00
0.98
1.01
1.05
1.01
1.99
2.00
1.96
2.37
2.97
2.90
9.212
9.200
8.236
8.226
8.152
7.899
7.275
2.921
2.900
2.893
2.879
2.689
2.675
2.670
2.663
2.649
1.498
1.169
1.151
1.133
1.072
1.054
1.035
-0.000
X : parts per Million : Proton


Pr
Pr
O
N
3m
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
184.641
151.199
148.802
148.411
137.995
133.995
131.637
129.928
129.040
127.599
122.405
120.419
77.315
77.000
76.685
31.423
28.521
24.177
22.859
14.678
14.554
X : parts per Million : Carbon13