Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Facile One-Pot Synthesis of Three Different Substituted Thiazoles from Propargylic Alcohols

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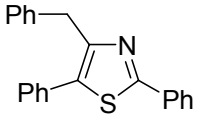
Experimental

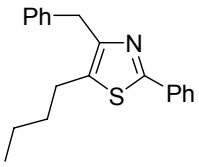
General methods and materials. Melting points were uncorrected. NMR spectra were in $CDCl_3$ (^1H at 400 MHz and ^{13}C at 100 MHz). Column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification.

General procedure for synthesis of substituted thiazoles 3 and 4. To a 5-mL flask, propargylic alcohols **1** (0.5 mmol), thioamides **2** (0.6 mmol), chlorobenzene (2.0 mL), and AgOTf (0.05 mmol) were successively added. The reaction mixture was stirred at reflux, and monitored periodically by TLC. Upon completion, the chlorobenzene was removed under reduced pressure, and then the residue was purified by silica gel column chromatography (EtOAc/hexane) to afford corresponding substituted thiazoles **3 (**or two regioisomers **3** and **4)**.

General Procedure for Synthesis of Substituted Thiazoles 6. To a 5-mL flask, propargylic alcohols **1** (0.5 mmol), amides **5** (0.55 mmol), acetonitrile (2.0 mL) and $FeCl_3$ (0.05 mmol) were successively added. The reaction was allowed to stir at 70-80 ^oC, and monitored periodically by TLC. Upon reaction completion, acetonitrile was removed in vacuo, followed by the addition of toluene (2 mL) and Lawesson's reagent (0.55 mmol). The reaction mixture was heated to reflux temperature for an additional 10 h until completion. Upon completion, the toluene was removed under reduced pressure, and then the residue was purified by silica gel column chromatography (EtOAc/hexane) to afford corresponding substituted thiazoles **6**.

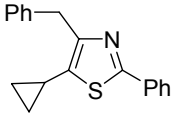


4-benzyl-2,5-diphenylthiazole (3aa): a white solid (mp 108-109 ^oC). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.24 (s, 2H), 7.20-7.26 (m, 1H), 7.30-7.32 (m, 4H), 7.36-7.49 (m, 8H), 7.96-8.01 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 35.5, 126.1, 126.4, 128.2, 128.5, 128.6, 128.8, 128.9, 129.4, 129.9, 131.9, 133.7, 133.8, 139.9, 150.9, 165.6; **IR** (film): 3026, 1600, 1485 cm^{-1}; **ESI-MS**: *m/z* (%) = 328 (100) $[M+H]^+$. **Anal** calcd for $C_{22}H_{17}NS$: C, 80.70; H, 5.23; N, 4.28. Found: C, 80.98; H, 5.04; N, 4.51.

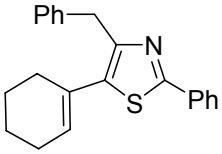


4-benzyl-5-butyl-2-phenylthiazole (3ba): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.90 (t, *J* =

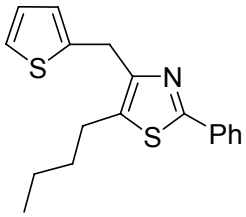
7.2 Hz, 3H), 1.32-1.41 (m, 2H), 1.55-1.62 (m, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 4.12 (s, 2H), 7.15-7.23 (m, 1H), 7.25-7.30 (m, 4H), 7.32-7.42 (m, 3H), 7.86-7.91 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.8, 22.3, 26.3, 34.0, 35.3, 126.1, 126.2, 128.4, 128.6, 128.8, 129.4, 134.1, 134.5, 139.8, 151.1, 163.9; **IR** (film): 3061, 1601, 1494 cm^{-1}; **ESI-MS**: *m/z* (%) = 308 (100) $[M+H]^+$, 330 (46) $[M+Na]^+$. **Anal** calcd for $C_{20}H_{21}NS$: C, 78.13; H, 6.88; N, 4.56. Found: C, 78.42; H, 6.62; N, 4.81.



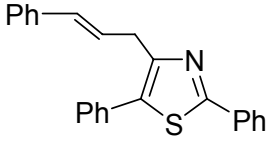
4-benzyl-5-cyclopropyl-2-phenylthiazole (3ca): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.69-0.74 (m, 2H), 1.02-1.08 (m, 2H), 1.94-2.01 (m, 1H), 4.24 (s, 2H), 7.18-7.23 (m, 1H), 7.28-7.42 (m, 7H), 7.85-7.89 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 7.9, 9.8, 35.6, 126.0, 126.1, 128.3, 128.6, 128.7, 129.3, 134.0, 137.3, 139.7, 152.6, 162.7; **IR** (film): 3027, 1602, 1496 cm^{-1}; **ESI-MS**: *m/z* (%) = 292 (100) $[M+H]^+$, 314 (32) $[M+Na]^+$. **Anal** calcd for $C_{19}H_{17}NS$: C, 78.31; H, 5.88; N, 4.81. Found: C, 78.02; H, 5.54; N, 5.06.



4-benzyl-5-cyclohexenyl-2-phenylthiazole (3da): a pale yellow solid (mp 91-92 °C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.62-1.69 (m, 2H), 1.72-1.79 (m, 2H), 2.15-2.21 (m, 2H), 2.28-2.35 (m, 2H), 4.23 (s, 2H), 5.93-5.96 (m, 1H), 7.18-7.24 (m, 1H), 7.27-7.33 (m, 4H), 7.36-7.44 (m, 3H), 7.91-7.94 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.7, 22.9, 25.6, 31.2, 36.0, 125.9, 126.3, 128.3, 128.6, 128.7, 129.0, 129.5, 129.6, 134.0, 136.8, 140.2, 150.0, 163.9; **IR** (film): 3024, 1616, 1491 cm^{-1}; **ESI-MS**: *m/z* (%) = 332 (100) $[M+H]^+$, 354 (20) $[M+Na]^+$. **Anal** calcd for $C_{22}H_{21}NS$: C, 79.72; H, 6.39; N, 4.23. Found: C, 79.47; H, 6.74; N, 4.01.

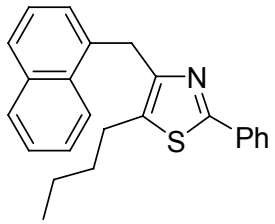


5-butyl-2-phenyl-4-(thiophen-2-ylmethyl)thiazole (3ea): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.34-1.43 (m, 2H), 1.58-1.65 (m, 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 4.26 (d, *J* = 0.8 Hz, 2H), 6.84-6.86 (m, 1H), 6.89 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.11 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.31-7.41 (m, 3H), 7.87-7. 91 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.8, 22.2, 26.2, 29.7, 33.9, 123.8, 124.8, 126.2, 126.6, 128.7, 129.4, 133.9, 134.5, 142.4, 150.3, 164.1; **IR** (film): 3012, 1604, 1495 cm^{-1}; **ESI-MS**: *m/z* (%) = 314 (100) $[M+H]^+$, 336 (29) $[M+Na]^+$. **Anal** calcd for $C_{18}H_{19}NS_2$: C, 68.97; H, 6.11; N, 4.47. Found: C, 69.22; H, 6.35; N, 4.26.

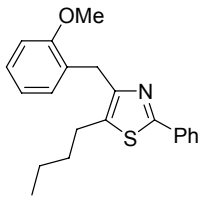


4-cinnamyl-2,5-diphenylthiazole (3fa): a pale yellow solid (mp 93-94 °C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.77 (dd, *J* = 6.0, 1.6 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.54 (dt, *J* = 16.0, 6.0 Hz, 1H), 7.16-7.21 (m,

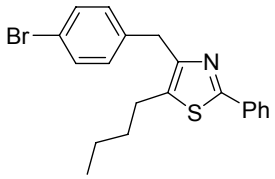
1H), 7.25-7.30 (m, 2H), 7.34-7.45 (m, 8H), 7.49-7.52 (m, 2H), 7.94-7.98 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 33.5, 126.2, 126.5, 127.1, 128.1, 128.2, 128.5, 128.8, 128.9, 129.4, 129.9, 131.2, 131.9, 133.3, 133.8, 137.6, 150.6, 165.7; **IR** (film): 3025, 1598, 1509 cm^{-1}; **ESI-MS**: *m/z* (%) = 354 (100) $[M+H]^+$. **Anal** calcd for $C_{24}H_{19}NS$: C, 81.55; H, 5.42; N, 3.96. Found: C, 81.74; H, 5.75; N, 3.72.



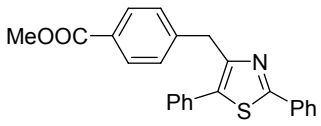
5-butyl-4-(naphthalen-1-ylmethyl)-2-phenylthiazole (3ga): a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.31-1.41 (m, 2H), 1.55-1.63 (m, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 4.63 (s, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.37-7.45 (m, 4H), 7.50-7.61 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.93-7.97 (m, 2H), 8.34 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 22.3, 26.4, 32.8, 33.9, 124.1, 125.5, 125.6, 125.9, 126.0, 126.2, 127.0, 128.7, 128.8, 129.4, 132.2, 133.9, 134.2, 135.3, 135.7, 150.5, 163.9; **IR** (film): 3065, 1616, 1503 cm^{-1}; **ESI-MS**: *m/z* (%) = 358 (100) $[M+H]^+$, 380 (70) $[M+Na]^+$. **Anal** calcd for $C_{24}H_{23}NS$: C, 80.63; H, 6.48; N, 3.92. Found: C, 80.47; H, 6.69; N, 3.67.



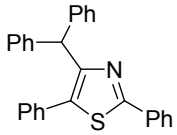
4-(2-methoxybenzyl)-5-butyl-2-phenylthiazole (3ha): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.6 Hz, 3H), 1.32-1.42 (m, 2H), 1.54-1.65 (m, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 3.86 (s, 3H), 4.09 (s, 2H), 6.84-6.87 (m, 2H), 7.07-7.10 (m, 1H), 7.15-7.19 (m, 1H), 7.31-7.40 (m, 3H), 7.86-7.90 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.8, 22.3, 26.2, 28.8, 34.1, 55.3, 110.0, 120.5, 126.2, 127.2, 128.2, 128.7, 129.3, 129.8, 134.2, 134.6, 150.8, 157.0, 163.7; **IR** (film): 3058, 1600, 1493 cm^{-1}; **ESI-MS**: *m/z* (%) = 338 (100) $[M+H]^+$, 360 (71) $[M+Na]^+$. **Anal** calcd for $C_{21}H_{23}NOS$: C, 74.74; H, 6.87; N, 4.15. Found: C, 75.01; H, 6.53; N, 4.41.



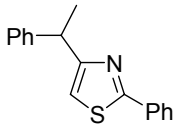
4-(4-bromobenzyl)-5-butyl-2-phenylthiazole (3ia): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.32-1.41 (m, 2H), 1.55-1.63 (m, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 4.05 (s, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.34-7.42 (m, 5H), 7.85-7.89 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.8, 22.3, 26.3, 34.0, 34.6, 119.9, 126.2, 128.8, 129.5, 130.3, 131.4, 133.9, 134.6, 138.8, 150.4, 164.2; **IR** (film): 3061, 1613, 1518 cm^{-1}; **ESI-MS**: *m/z* (%) = 386 (100) $[M+H]^+$, 408 (49) $[M+Na]^+$. **Anal** calcd for $C_{20}H_{20}BrNS$: C, 62.18; H, 5.22; N, 3.63. Found: C, 61.95; H, 5.51; N, 3.87.



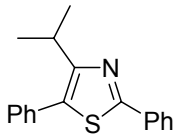
methyl 4-((2,5-diphenylthiazol-4-yl)methyl)benzoate (3ja): a pale yellow solid (mp 121-122 °C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.89 (s, 3H), 4.26 (s, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.37-7.45 (m, 8H), 7.94-7.97 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 35.5, 52.0, 126.4, 128.1, 128.4, 128.7, 128.8, 128.9, 129.4, 129.8, 130.1, 131.5, 133.5, 134.1, 145.2, 149.9, 165.9, 167.1; **IR** (film): 3028, 1717, 1616, 1509 cm^{-1}; **ESI-MS**: *m/z* (%) = 386 (100) $[M+H]^+$, 408 (73) $[M+Na]^+$. **Anal** calcd for $C_{24}H_{19}NO_2S$: C, 74.78; H, 4.97; N, 3.63. Found: C, 75.03; H, 4.65; N, 3.82.



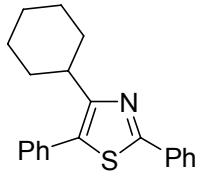
4-benzhydryl-2,5-diphenylthiazole (3ka): a white solid (mp 93-94 °C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.60 (s, 1H), 7.20-7.25 (m, 2H), 7.28-7.34 (m, 4H), 7.38-7.48 (m, 12H), 7.95-7.99 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 50.3, 126.3, 126.5, 128.2, 128.3, 128.8, 129.3, 129.7, 129.8, 131.8, 133.9, 134.0, 143. 6, 152.9, 165.4; **IR** (film): 3055, 1613, 1491 cm^{-1}; **ESI-MS**: *m/z* (%) = 404 (100) $[M+H]^+$. **Anal** calcd for $C_{28}H_{21}NS$: C, 83.34; H, 5.25; N, 3.47. Found: C, 83.05; H, 5.41; N, 3.18.



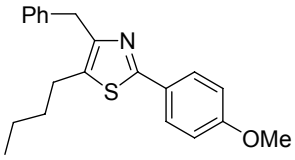
2-phenyl-4-(1-phenylethyl)thiazole (3la): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.75 (d, *J* = 7.2 Hz, 3H), 4.38 (q, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 0.8 Hz, 1H), 7.22-7.25 (m, 1H), 7.31-7.38 (m, 4H), 7.39-7.45 (m, 3H), 7.93-7.97 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.6, 42.3, 113.2, 126.4, 126.6, 127.7, 128.5, 128.8, 129.8, 133.9, 144.9, 162.4, 167.6; **IR** (film): 3030, 1616, 1509 cm^{-1}; **ESI-MS**: *m/z* (%) = 266 (100) $[M+H]^+$, 288 (31) $[M+Na]^+$. **Anal** calcd for $C_{17}H_{15}NS$: C, 76.94; H, 5.70; N, 5.28. Found: C, 76.70; H, 5.44; N, 5.43.



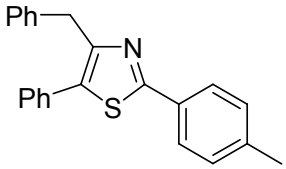
4-isopropyl-2,5-diphenylthiazole (3na): a white solid (mp 81-82 °C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.37 (d, *J* = 6.4 Hz, 6H), 3.23 (sep, *J* = 6.8 Hz, 1H), 7.35-7.48 (m, 8H), 8.96-7.00 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 23.0, 28.4, 126.4, 127.8, 128.7, 128.8, 129.6, 129.7, 130.7, 132.3, 134.2, 158.7, 165.4; **IR** (film): 3061, 1613, 1509 cm^{-1}; **ESI-MS**: *m/z* (%) = 280 (100) $[M+H]^+$. **Anal** calcd for $C_{18}H_{17}NS$: C, 77.38; H, 6.13; N, 5.01. Found: C, 77.05; H, 6.43; N, 5.07.



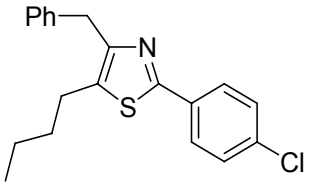
4-cyclohexyl-2,5-diphenylthiazole (3oa): a pale yellow solid (mp 97-98 °C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.23-1.43 (m, 3H), 1.70-1.95 (m, 7H), 2.81-2.88 (m, 1H), 7.36-7.46 (m, 8H), 7.95-7.99 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 25.9, 26.5, 33.0, 38.4, 126.4, 127.8, 128.7, 128.8, 129.6, 129.7, 131.0, 132.3, 134.2, 158.2, 165.2; **IR** (film): 3051, 1613, 1506 cm^{-1}; **ESI-MS**: *m/z* (%) = 320 (100) $[M+H]^+$. **Anal** calcd for $C_{21}H_{21}NS$: C, 78.95; H, 6.63; N, 4.38. Found: C, 79.22; H, 6.41; N, 4.15.



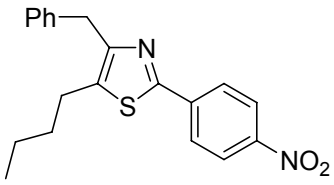
4-benzyl-5-butyl-2-(4-methoxyphenyl)thiazole (3bb): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.33-1.43 (m, 2H), 1.55-1.63 (m, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 3.84 (s, 3H), 4.12 (s, 2H), 6.92 (d, *J* = 9.2 Hz, 2H), 7.17-7.23 (m, 1H), 7.26-7.31 (m, 4H), 7.84 (d, *J* = 9.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.8, 22.3, 26.3, 34.0, 35.2, 55.4, 114.1, 126.0, 127.1, 127.7, 128.3, 128.6, 133.4, 139.9, 150.7, 160.7, 163.9; **IR** (film): 3028, 1607, 1491 cm^{-1}; **ESI-MS**: *m/z* (%) = 338 (100) $[M+H]^+$, 360 (29) $[M+Na]^+$. **Anal** calcd for $C_{21}H_{23}NOS$: C, 74.74; H, 6.87; N, 4.15. Found: C, 74.52; H, 7.06; N, 4.39.



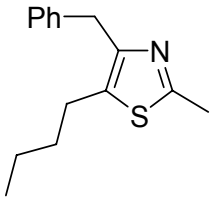
4-benzyl-5-phenyl-2-p-tolylthiazole (3ac): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 4.13 (s, 2H), 7.10-7.18 (m, 4H), 7.19-7.24 (m, 4H), 7.25-7.38 (m, 5H), 7.77 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.4, 35.4, 126.1, 126.4, 128.0, 128.4, 128.6, 128.7, 129.4, 129.5, 131.1, 131.9, 133.2, 139.9, 140.1, 150.7, 165.8; **IR** (film): 3025, 1613, 1509 cm^{-1}; **ESI-MS**: *m/z* (%) = 342 (100) $[M+H]^+$, 364 (38) $[M+Na]^+$. **Anal** calcd for $C_{23}H_{19}NS$: C, 80.90; H, 5.61; N, 4.10. Found: C, 80.68; H, 5.87; N, 4.33.



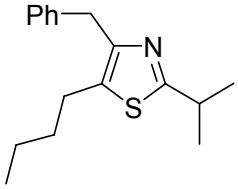
4-benzyl-5-butyl-2-(4-chlorophenyl)thiazole (3bd): a pale yellow solid (mp 43-44 °C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.32-1.41 (m, 2H), 1.54-1.62 (m, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 4.10 (s, 2H), 7.16-7.21 (m, 1H), 7.23-7.30 (m, 4H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.8, 22.3, 26.3, 34.0, 35.2, 126.1, 127.4, 128.4, 128.6, 128.9, 132.6, 134.9, 135.2, 139.7, 151.4, 162.5; **IR** (film): 3028, 1616, 1497 cm^{-1}; **ESI-MS**: *m/z* (%) = 342 (100) $[M+H]^+$, 364 (37) $[M+Na]^+$. **Anal** calcd for $C_{20}H_{20}ClNS$: C, 70.26; H, 5.90; N, 4.10. Found: C, 70.52; H, 6.17; N, 4.41.



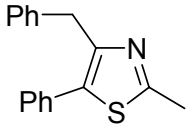
4-benzyl-5-butyl-2-(4-nitrophenyl)thiazole (3be): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.34-1.43 (m, 2H), 1.57-1.66 (m, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 4.14 (s, 2H), 7.18-7.22 (m, 1H), 7.24-7.32 (m, 4H), 8.04 (d, *J* = 9.2 Hz, 2H), 8.25 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.7, 22.3, 26.4, 33.9, 35.3, 124.2, 126.3, 126.6, 128.5, 128.6, 137.3, 139.3, 139.6, 148.0, 152.6, 160.8; **IR** (film): 3028, 1611, 1593, 1507 cm^{-1}; **ESI-MS**: *m/z* (%) = 353 (100) $[M+H]^+$, 375 (40) $[M+Na]^+$. **Anal** calcd for $C_{20}H_{20}N_2O_2S$: C, 68.16; H, 5.72; N, 7.95. Found: C, 67.88; H, 5.97; N, 7.73.



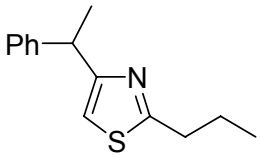
4-benzyl-5-butyl-2-methylthiazole (3bf): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.29-1.39 (m, 2H), 1.49-1.57 (m, 2H), 2.61 (s, 3H), 2.70 (t, *J* = 7.6 Hz, 2H), 4.01 (s, 2H), 7.14-7.20 (m, 3H), 7.23-7.35 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.8, 19.2, 22.3, 26.1, 34.1, 35.0, 126.0, 128.4, 128.5, 133.4, 139.9, 149.2, 162.1; **IR** (film): 3030, 1613, 1494 cm^{-1}; **ESI-MS**: *m/z* (%) = 246 (100) $[M+H]^+$, 268 (12) $[M+Na]^+$. **Anal** calcd for $C_{15}H_{19}NS$: C, 73.42; H, 7.80; N, 5.71. Found: C, 73.71; H, 7.55; N, 5.88.



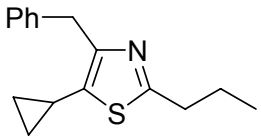
4-benzyl-5-butyl-2-isopropylthiazole (3bg): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.25-1.41 (m, 8H), 1.47-1.56 (m, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 3.23 (sep, *J* = 6.8 Hz, 1H), 4.03 (s, 2H), 7.13-7.20 (m, 3H), 7.23-7.28 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.8, 22.3, 23.3, 26.2, 33.3, 34.0, 35.1, 125.9, 128.3, 128.5, 132.4, 140.0, 148.8, 174.0; **IR** (film): 3028, 1619, 1503 cm^{-1}; **ESI-MS**: *m/z* (%) = 274 (100) $[M+H]^+$, 296 (10) $[M+Na]^+$. **Anal** calcd for $C_{17}H_{23}NS$: C, 74.67; H, 8.48; N, 5.12. Found: C, 74.39; H, 8.72; N, 5.32.



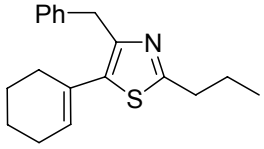
4-benzyl-2-methyl-5-phenylthiazole (3af): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.69 (s, 3H), 4.12 (s, 2H), 7.16-7.21 (m, 3H), 7.25-7.30 (m, 2H), 7.31-7.42 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.3, 35.2, 126.1, 127.9, 128.4, 128.5, 128.7, 129.4, 132.0, 133.0, 139.9, 149.3, 163.9; **IR** (film): 3025, 1619, 1598, 1491 cm^{-1}; **ESI-MS**: *m/z* (%) = 266 (100) $[M+H]^+$, 288 (22) $[M+Na]^+$. **Anal** calcd for $C_{17}H_{15}NS$: C, 76.94; H, 5.70; N, 5.28. Found: C, 77.17; H, 5.46; N, 5.54.



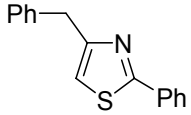
4-(1-phenylethyl)-2-propylthiazole (3mh): a pale yellow oil. **1H NMR** (400 MHz, $CDCl_3$): δ 0.99 (t, *J* = 7.2 Hz, 3H), 1.66 (d, *J* = 7.2 Hz, 3H), 1.71-1.84 (m, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 4.28 (q, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 0.8 Hz, 1H), 7.17-7.22 (m, 1H), 7.24-7.32 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.6, 21.6, 23.5, 35.5, 42.1, 112.1, 126.3, 127.6, 128.4, 145.0, 160.7, 170.9; **IR** (film): 3027, 1613, 1506 cm^{-1}; **ESI-MS**: *m/z* (%) = 232 (100) $[M+H]^+$, 254 (11) $[M+Na]^+$. **Anal** calcd for $C_{14}H_{17}NS$: C, 72.68; H, 7.41; N, 6.05. Found: C, 72.91; H, 7.18; N, 6.23.



4-benzyl-5-cyclopropyl-2-propylthiazole (3ch): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.59-0.63 (m, 2H), 0.93-0.99 (m, 5H), 1.68-1.78 (m, 2H), 1.84-1.92 (m, 1H), 2.84 (t, *J* = 7.2 Hz, 2H), 4.12 (s, 2H), 7.14-7.18 (m, 1H), 7.21-7.28 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 7.6, 9.4, 13.6, 23.5, 35.3, 35.4, 125.9, 128.3, 128.5, 135.6, 139.8, 150.5, 166.4; **IR** (film): 3031, 1616, 1494 cm^{-1}; **ESI-MS**: *m/z* (%) = 258 (100) $[M+H]^+$, 280 (36) $[M+Na]^+$. **Anal** calcd for $C_{16}H_{19}NS$: C, 74.66; H, 7.44; N, 5.44. Found: C, 74.41; H, 7.72; N, 5.28.

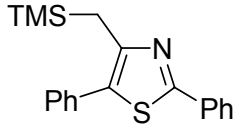


4-benzyl-5-cyclohexenyl-2-propylthiazole (3dh): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.99 (t, *J* = 7.6 Hz, 3H), 1.56-1.63 (m, 2H), 1.65-1.73 (m, 2H), 1.73-1.81 (m, 2H), 2.08-2.15 (m, 2H), 2.15-2.25 (m, 2H), 2.89 (t, *J* = 7.2 Hz, 2H), 4.10 (s, 2H), 5.81-5.85 (m, 1H), 7.12-7.19 (m, 3H), 7.22-7.27 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.6, 21.7, 22.9, 23.5, 25.6, 31.2, 35.4, 35.7, 125.8, 128.2, 128.4, 128.9, 129.2, 135.6, 140.3, 148.0, 167.6; **IR** (film): 3030, 1604, 1494 cm^{-1}; **ESI-MS**: *m/z* (%) = 298 (100) $[M+H]^+$. **Anal** calcd for $C_{19}H_{23}NS$: C, 76.72; H, 7.79; N, 4.71. Found: C, 76.56; H, 8.02; N, 7.45.

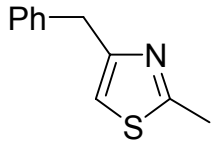


4-benzyl-2-phenylthiazole (3pa): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.19 (d, *J* = 0.4 Hz, 2H), 6.72 (t, *J* = 0.8 Hz, 1H), 7.21-7.27 (m, 1H), 7.28-7.34 (m, 4H), 7.35-7.44 (m, 3H), 7.91-7.95 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 38.1, 114.4, 126.5, 126.6, 128.6, 128.9, 129.2, 129.9, 133.8, 139.1, 157.6, 167.9; **IR** (film): 3021, 1619, 1494 cm^{-1}; **ESI-MS**: *m/z* (%) = 252 (68) $[M+H]^+$, 274 (100) $[M+Na]^+$.

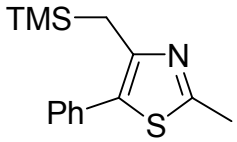
Data are in accordance with previously reported results.[1]



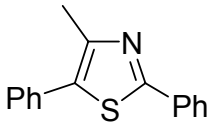
2,5-diphenyl-4-((trimethylsilyl)methyl)thiazole (4pa): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.05 (s, 9H), 2.40 (s, 2H), 7.32-7.36 (m, 1H), 7.39-7.46 (m, 5H), 7.47-7.50 (m, 2H), 7.93-7.97 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ -1.0, 20.3, 126.2, 127.6, 128.7, 128.9, 129.3, 129.5, 129.6, 132.8, 134.0, 151.7, 164.4; **IR** (film): 3061, 1619, 1598, 1482 cm^{-1}; **ESI-MS**: *m/z* (%) = 324 (100) $[M+H]^+$, 346 (37) $[M+Na]^+$. **Anal** calcd for $C_{19}H_{21}NSSi$: C, 70.54; H, 6.54; N, 4.33. Found: C, 70.77; H, 6.39; N, 4.61.



4-benzyl-2-methylthiazole (3pf): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.68 (s, 3H), 4.08 (s, 2H), 6.60 (t, *J* = 0.8 Hz, 1H), 7.20-7.33 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.2, 37.9,113.7, 126.4, 128.5, 129.0, 139.1, 155.9, 165.8; **IR** (film): 3025, 1617, 1496 cm^{-1}; **ESI-MS**: *m/z* (%) = 190 (100) $[M+H]^+$. **Anal** calcd for $C_{11}H_{11}NS$: C, 69.80; H, 5.86; N, 7.40. Found: C, 69.53; H, 6.04; N, 7.16.

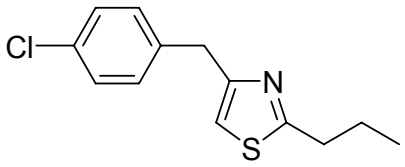


2-methyl-5-phenyl-4-((trimethylsilyl)methyl)thiazole (4pf): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ -0.05 (s, 9H), 2.33 (s, 2H), 2.66 (s, 3H), 7.27-7.33 (m, 1H), 7.36-7.42 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ -1.2, 19.1, 20.2, 127.3, 127.9, 128.6, 129.4, 133.1, 150.1, 162.7; **IR** (film): 3059, 1597, 1494 cm^{-1}; **ESI-MS**: *m/z* (%) = 262 (100) $[M+H]^+$, 284 (42) $[M+Na]^+$. **Anal** calcd for $C_{14}H_{19}NSSi$: C, 64.31; H, 7.32; N, 5.36. Found: C, 64.57; H, 7.08; N, 5.54.

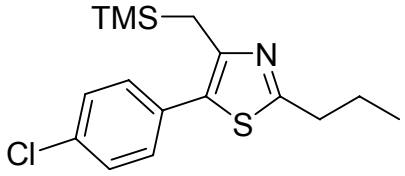


4-methyl-2,5-diphenylthiazole (4qa): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.56 (s, 3H), 7.33-7.37 (m, 1H), 7.39-7.46 (m, 5H), 7.47-7.50 (m, 2H), 7.92-7.96 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 16.4, 126.3, 127.8, 128.7, 128.9, 129.2, 129.8, 132.2, 133.7, 148.8, 165.1; **IR** (film): 3027, 1616, 1506 cm^{-1}; **ESI-MS**: *m/z* (%) = 252 (100) $[M+H]^+$, 274 (27) $[M+Na]^+$.

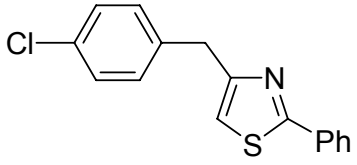
Data are in accordance with previously reported results.[2]



4-(4-chlorobenzyl)-2-propylthiazole (3rh): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.01 (t, *J* = 7.2 Hz, 3H), 1.75-1.85 (m, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 4.06 (s, 2H), 6.62 (s, 1H), 7.19 (d, *J* = 4.8 Hz, 2H), 7.27 (d, *J* = 4.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.6, 23.5, 35.5, 37.2, 113.5, 128.6, 130.3, 132.2, 137.7, 155.1, 171.5; **IR** (film): 3062, 1599, 1491 cm^{-1}; **ESI-MS**: *m/z* (%) = 252 (100) $[M+H]^+$. **Anal** calcd for $C_{13}H_{14}ClNS$: C, 62.02; H, 5.60; N, 5.56. Found: C, 61.77; H, 5.74; N, 5.27.



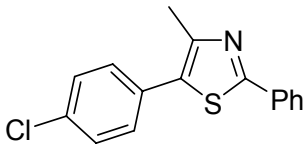
5-(4-chlorophenyl)-2-propyl-4-((trimethylsilyl)methyl)thiazole (4rh): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ -0.05 (s, 9H), 1.02 (t, *J* = 7.2 Hz, 3H), 1.77-1.86 (m, 2H), 2.30 (s, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 7.31-7.37 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ -1.2, 13.6, 20.3, 23.4, 35.4, 126.2, 128.8, 130.6, 131.7, 133.2, 150.4, 168.3; **IR** (film): 3060, 1609, 1501 cm^{-1}; **ESI-MS**: *m/z* (%) = 324 (100) $[M+H]^+$. **Anal** calcd for $C_{16}H_{22}ClNSSi$: C, 59.32; H, 6.84; N, 4.32. Found: C, 59.61; H, 6.55; N, 4.58.



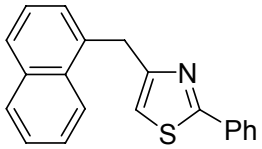
4-(4-chlorobenzyl)-2-phenylthiazole (3sa): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.15 (s, 2H), 6.76 (s, 1H), 7.23-7.31 (m, 4H), 7.38-7.46 (m, 3H), 7.89-7.96 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$):

δ 37.3, 114.4, 126.5, 128.6, 128.9, 129.9, 130.4, 132.3, 133.7, 137.6, 156.8, 168.2; **IR** (film): 3061, 1613, 1506 cm^{-1}; **ESI-MS**: *m/z* (%) = 286 (100) $[M+H]^+$.

Data are in accordance with previously reported results.[1]

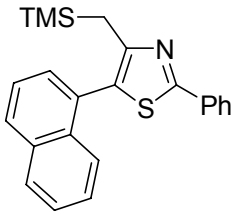


5-(4-chlorophenyl)-4-methyl-2-phenylthiazole (4sa): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.54 (s, 3H), 7.37-7.48 (m, 7H), 7.91-7.94 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 16.3, 126.3, 128.6, 128.9, 129.9, 130.4, 130.7, 130.9, 133.6, 133.8, 149.2, 165.4; **IR** (film): 3058, 1616, 1506 cm^{-1}; **ESI-MS**: *m/z* (%) = 286 (100) $[M+H]^+$. **Anal** calcd for $C_{16}H_{12}ClNS$: C, 67.24; H, 4.23; N, 4.90. Found: C, 67.01; H, 4.45; N, 4.72.

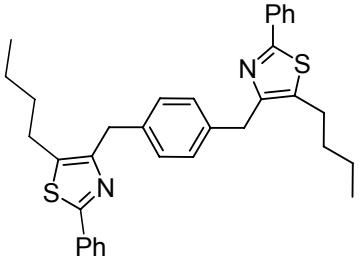


4-(naphthalen-1-ylmethyl)-2-phenylthiazole (3ta): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.73 (s, 2H), 6.56 (s, 1H), 7.43-7.56 (m, 7H), 7.86 (dd, *J* = 6.8, 2.8 Hz, 1H), 7.91-7.96 (m, 1H), 8.01-8.06 (m, 2H), 8.09-8.14 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 35.6, 114.7, 124.3, 125.6, 126.0, 126.4, 127.3, 127.5, 128.6, 128.8, 129.8, 131.9, 133.7, 133.9, 135.0, 157.1, 167.6; **IR** (film): 3058, 1616, 1595, 1506 cm^{-1}; **ESI-MS**: *m/z* (%) = 302 (100) $[M+H]^+$.

Data are in accordance with previously reported results.[1]

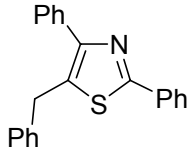


5-(naphthalen-1-yl)-2-phenyl-4-((trimethylsilyl)methyl)thiazole (4ta): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ -0.03 (s, 9H), 2.10 (s, 2H), 7.41-7.56 (m, 7H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.90-7.94 (m, 2H), 7.98-8.01 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ -1.1, 20.5, 125.23, 125.24, 126.0, 126.1, 126.2, 126.5, 128.38, 128.39, 128.9, 129.6, 129.7, 132.5, 133.8, 134.03, 134.04, 153.9, 165.7; **IR** (film): 3055, 1613, 1503 cm^{-1}; **ESI-MS**: *m/z* (%) = 374 (100) $[M+H]^+$, 396 (29) $[M+Na]^+$. **Anal** calcd for $C_{23}H_{23}NSSi$: C, 73.94; H, 6.21; N, 3.75. Found: C, 74.19; H, 5.97; N, 3.46.

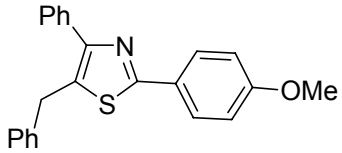


4-(4-((5-butyl-2-phenylthiazol-4-yl)methyl)benzyl)-5-butyl-2-phenylthiazole (3ua): a white solid (mp 87-88 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.2 Hz, 6H), 1.33-1.42 (m, 4H), 1.56-1.63 (m, 4H),

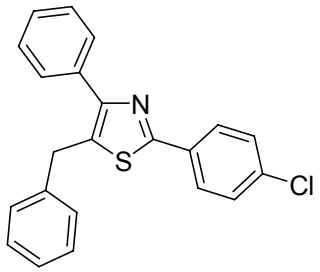
2.77 (t, J = 7.6 Hz, 4H), 4.09 (s, 4H), 7.20 (s, 4H), 7.33-7.42 (m, 6H), 7.87-7.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 22.3, 26.3, 34.0, 34.9, 126.2, 128.6, 128.8, 129.4, 134.1, 134.3, 137.5, 151.3, 163.9; **IR** (film): 3061, 1613, 1509 cm^{-1}; **ESI-MS**: *m/z* (%) = 537 (85) $[M+H]^+$, 559 (100) $[M+Na]^+$. **Anal** calcd for $C_{34}H_{36}N_2S_2$: C, 76.07; H, 6.76; N, 5.22. Found: C, 75.85; H, 6.49; N, 5.51.



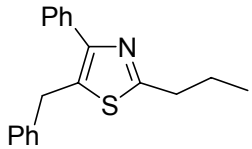
5-benzyl-2,4-diphenylthiazole (6aa): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.32 (s, 2H), 7.25-7.30 (m, 3H), 7.32-7.36 (m, 2H), 7.39-7.43 (m, 4H), 7.44-7.50 (m, 2H), 7.72-7.75 (m, 2H), 7.95-7.98 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 33.3, 126.3, 126.8, 127.9, 128.4, 128.5, 128.7, 128.8, 129.8, 133.0, 133.8, 135.0, 140.0, 152.6, 165.1; **IR** (film): 3059, 1599, 1498 cm^{-1}; **ESI-MS**: *m/z* (%) = 328 (100) $[M+H]^+$, 350 (35) $[M+Na]^+$. **Anal** calcd for $C_{22}H_{17}NS$: C, 80.70; H, 5.23; N, 4.28. Found: C, 80.93; H, 5.08; N, 4.50.



5-benzyl-2-(4-methoxyphenyl)-4-phenylthiazole (6ab): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 4.29 (s, 2H), 6.92 (d, J = 9.2 Hz, 2H), 7.23-7.29 (m , 3H), 7.31-7.40 (m, 3H), 7.42-7.48 (m, 2H), 7.69-7.73 (m, 2H), 7.85 (d, J = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 33.2, 55.4, 114.2, 126.7, 126.8, 127.8, 128.4, 128.5, 128.7, 128.8, 132.0, 135.1, 140.2, 152.3, 161.0, 165.1; **IR** (film): 3025, 1606, 1496 cm^{-1}; **ESI-MS**: *m/z* (%) = 358 (100) $[M+H]^+$, 380 (33) $[M+Na]^+$, **Anal** calcd for $C_{23}H_{19}NOS$: C, 77.28; H, 5.36; N, 3.92. Found: C, 77.08; H, 5.56; N, 4.15.

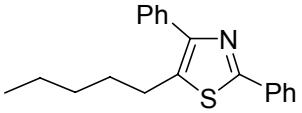


5-benzyl-2-(4-chlorophenyl)-4-phenylthiazole (6ac): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.30 (s, 2H), 7.22-7.27 (m, 3H), 7.30-7.34 (m, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.39-7.40 (m, 1H), 7.43-7.47 (m, 2H), 7.68-7.71 (m, 2H), 7.88 (d, J = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 33.3, 126.8, 127.5, 128.0, 128.3, 128.5, 128.7, 128.8, 129.0, 132.3, 133.5, 134.8, 135.7, 139.9, 152.7, 163.7; **IR** (film): 3026, 1599, 1493 cm^{-1}; **ESI-MS**: *m/z* (%) = 362 (100) $[M+H]^+$, 384 (56) $[M+Na]^+$. **Anal** calcd for $C_{22}H_{16}ClNS$: C, 73.02; H, 4.46; N, 3.87. Found: C, 73.15; H, 4.20; N, 4.12.

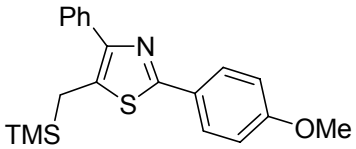


5-benzyl-4-phenyl-2-propylthiazole (6ad): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.02 (t, J = 7.6 Hz, 3H), 1.76-1.85 (m, 2H), 2.93 (t, J = 7.2 Hz, 2H), 4.22 (s, 2H), 7.17-7.25 (m, 3H), 7.27-7.35 (m, 3H), 7.37-7.42 (m, 2H), 7.58-7.64 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.7, 23.4, 33.0, 35.5, 126.6,

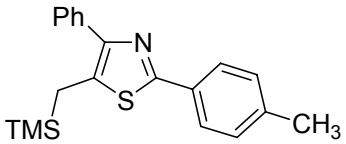
127.6, 128.3, 128.4, 128.6, 128.9, 131.5, 135.1, 140.2, 150.9, 168.7; **IR** (film): 3060, 1601, 1494 cm^{-1}; **ESI-MS**: *m/z* (%) = 294 (100) $[M+H]^+$, 316 (78) $[M+Na]^+$. **Anal** calcd for $C_{19}H_{19}NS$: C, 77.77; H, 6.53; N, 4.77. Found: C, 77.53; H, 6.71; N, 4.66.



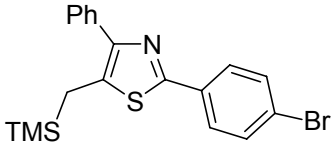
5-pentyl-2,4-diphenylthiazole (6ba): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.36-1.46 (m, 4H), 1.75-1.83 (m, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 7.40-7.46 (m, 3H), 7.46-7.54 (m, 3H), 7.75-7.78 (m, 2H), 8.03-8.07 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.9, 22.3, 27.2, 31.3, 31.9, 126.2, 127.5, 128.3, 128.68, 128.70, 129.5, 133.9, 135.1, 135.3, 151.6, 163.7; **IR** (film): 3060, 1598, 1483 cm^{-1}; **ESI-MS**: *m/z* (%) = 308 (100) $[M+H]^+$. **Anal** calcd for $C_{20}H_{21}NS$: C, 78.13; H, 6.88; N, 4.56. Found: C, 78.25; H, 6.76; N, 4.79.



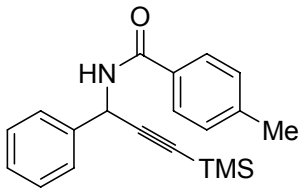
2-(4-methoxyphenyl)-4-phenyl-5-((trimethylsilyl)methyl)thiazole (6pb): a pale yellow solid (mp 105-106 °C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.05 (s, 9H), 2.46 (s, 2H), 3.85 (s, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.31-7.39 (m, 1H), 7.42-7.49 (m, 2H), 7.63-7.71 (m, 2H), 7.91 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ -1.5, 17.0, 55.3, 114.1, 126.9, 127.2, 127.6, 128.3, 128.8, 131.3, 135.8, 150.3, 160.6, 162.0; **IR** (film): 3058, 1605, 1495 cm^{-1}; **ESI-MS**: *m/z* (%) = 354 (100) $[M+H]^+$, 376 (24) $[M+Na]^+$. **Anal** calcd for $C_{20}H_{23}NOSSi$: C, 67.94; H, 6.56; N, 3.96. Found: C, 67.75; H, 6.75; N, 3.70.



4-phenyl-2-p-tolyl-5-((trimethylsilyl)methyl)thiazole (6pe): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.05 (s, 9H), 2.40 (s, 3H), 2.47 (s, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.32-7.37 (m, 1H), 7.42-7.48 (m, 2H), 7.65-7.70 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ -1.5, 17.1, 21.3, 126.1, 127.3, 128.3, 128.9, 129.4, 131.3, 131.8, 135.8, 139.5, 150.5, 162.3 ; **IR** (film): 3022, 1601, 1496 cm^{-1}; **ESI-MS**: *m/z* (%) = 338 (100) $[M+H]^+$, 360 (71) $[M+Na]^+$. **Anal** calcd for $C_{20}H_{23}NSSi$: C, 71.16; H, 6.87; N, 4.15. Found: C, 71.33; H, 6.75; N, 4.30.



2-(4-bromophenyl)-4-phenyl-5-((trimethylsilyl)methyl)thiazole (6pf): a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.03 (s, 9H), 2.47 (s, 2H), 7.32-7.39 (m, 1H), 7.42-7.48 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.62-7.69 (m, 2H), 7.82 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ -1.5, 17.3, 123.5, 127.5, 127.6, 128.4, 128.9, 131.9, 132.9, 133.0, 135.5, 151.0, 160.8; **IR** (film): 3054, 1600, 1588, 1500 cm^{-1}; **ESI-MS**: *m/z* (%) = 402 (100) $[M+H]^+$. **Anal** calcd for $C_{19}H_{20}BrNSSi$: C, 56.71; H, 5.01; N, 3.48. Found: C, 56.58; H, 5.23; N, 3.64.



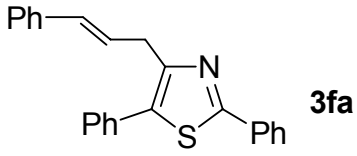
4-Methyl-N-(1-phenyl-3-(trimethylsilyl)prop-2-ynyl)benzamide (14a): a white solid (mp 136-138 ^{o}C). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 0.22 (s, 9H), 2.39 (s, 3H), 6.28 (d, 1H, *J* = 8.4 Hz), 6.60 (d, 1H, *J* = 8.8 Hz), 7.22 (d, 2H, *J* = 8.0 Hz), 7.29-7.39 (m, 3H), 7.54-7.59 (m, 2H) , 7.69 (d, 2H, *J* = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ -0.09, 21.5, 45.5, 90.0, 103.2, 127.15, 127.17, 128.1, 128.7, 129.3, 131.0, 139.0, 142.3, 166.0; **IR** (film): 3208, 3046, 1635, 1604, 1587, 1492 cm^{-1}; **ESI-MS**: *m/z* (%) = 322 (100) [M+H^{+}]. **Anal** calcd for $C_{19}H_{21}NOSi$: C, 74.72; H, 7.21; N, 4.36. Found: C,74.54; H, 7.47; N, 4.19.

References

1 M. Yoshimatsu, T. Yamamoto, A. Sawa, T. Kato, G. Tanabe, and O. Muraoka, *Org. Lett.*, 2009, **11**, 2952.

2 T. Nishio and M. Ori, *Helv. Chim. Acta*, 2001, **84**, 2347.

X-ray data for compound 3fa.



3fa

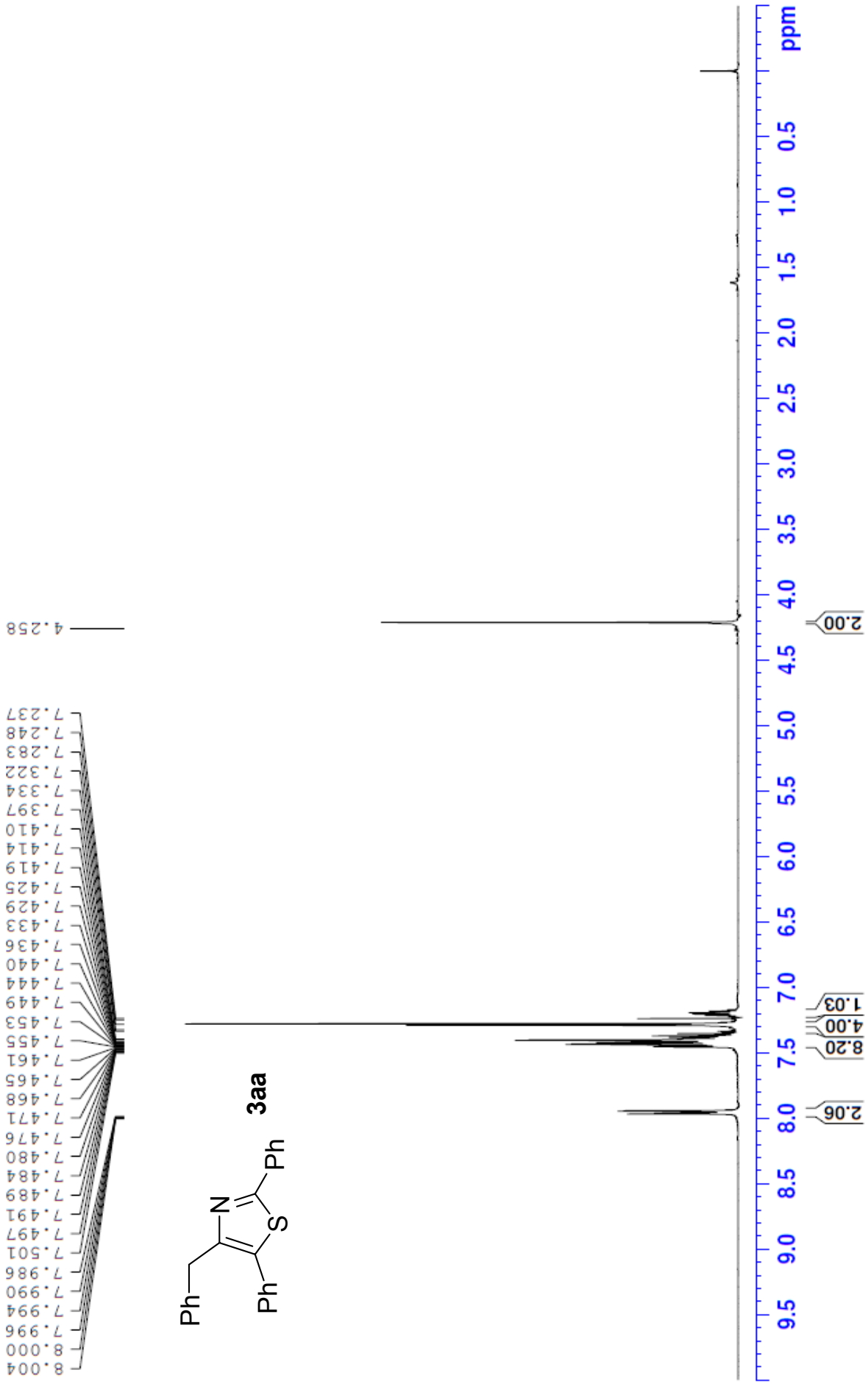
Table 1. Crystal data and structure refinement for **3fa**.

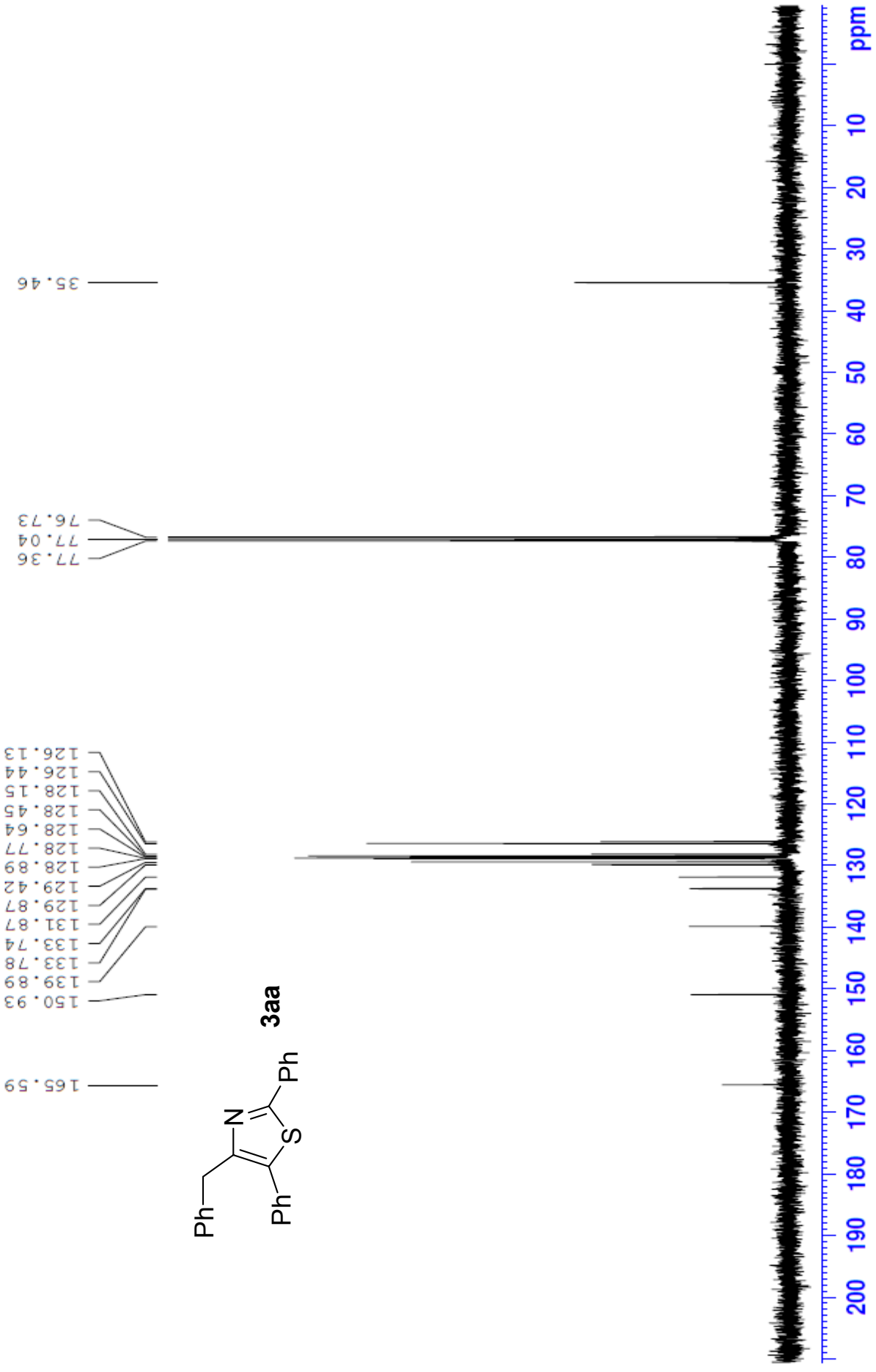
Identification code	p	
Empirical formula	$C_{24}H_{19}NS$	
Formula weight	353.46	
Temperature	273 (2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Fdd2	
Unit cell dimensions	a = 17.699(4) Å	α = 90°
	b = 74.502(18) Å	β = 90°
	c = 5.7208(14) Å	γ = 90°
Volume	7544(3) $Å^3$	
Z	16	
Absorption coefficient	0.178 mm^{-1}	
F(000)	2976	
Crystal size	0.13 x 0.41 x 0.15 mm	
Theta range for data collection	1.09–26°	
Index ranges	$-21 \le h \le 21$, $-90 \le k \le 90$, $-7 \le l \le 7$	
Reflections collected	14565	
Independent reflections	3678 [R(int) = 0.1042]	
Absorption correction	none	
R indices	$R[F^2 > 2\sigma(F^2)]$ = 0.0722	$wR(F^2)$ = 0.2081
Largest diff. peak and hole	0.366 and -0.347 e $Å^{-3}$	
Flack value	0.02(18)	

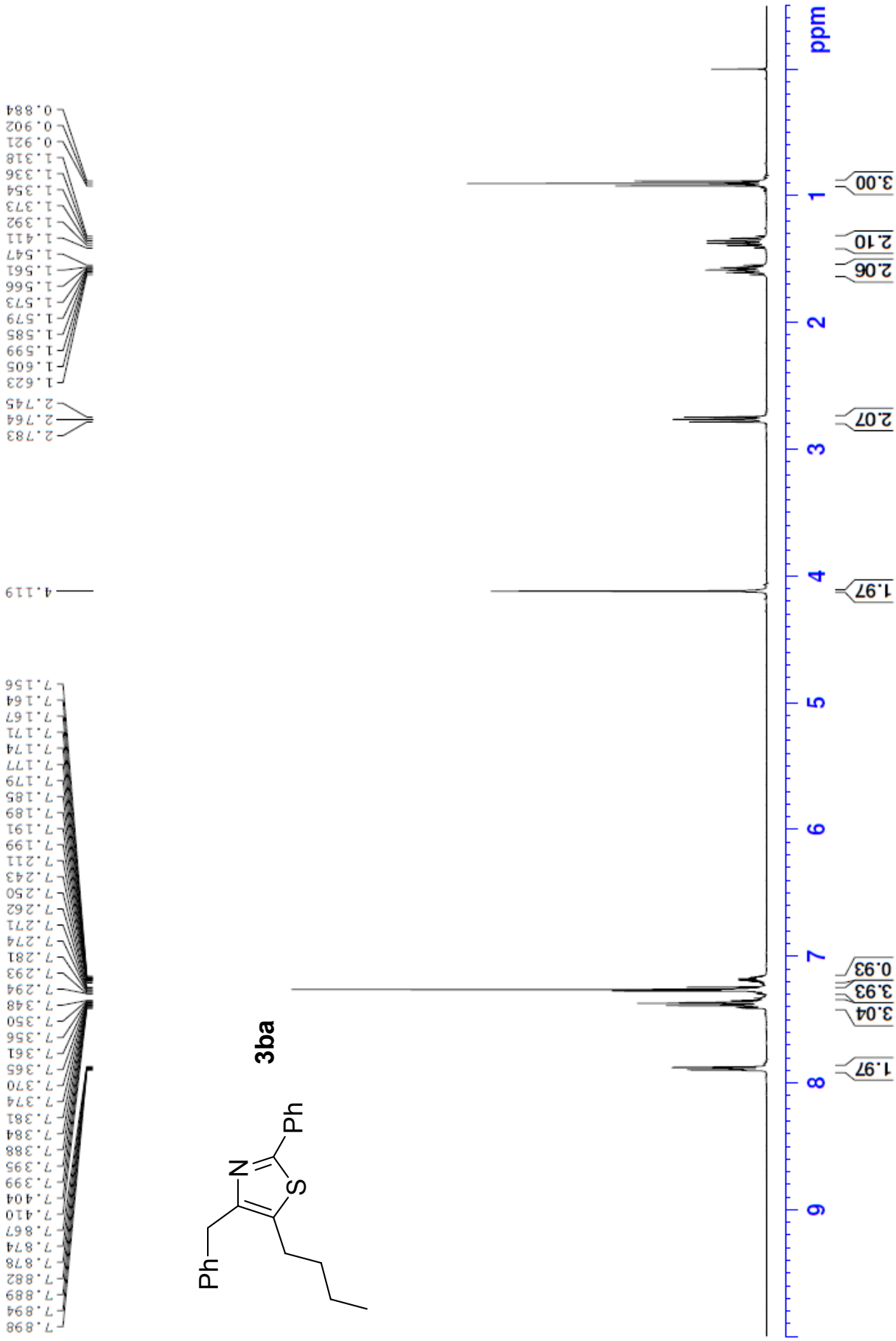
Table 2. Bond lengths [Å] and angles [°] for **3fa**.

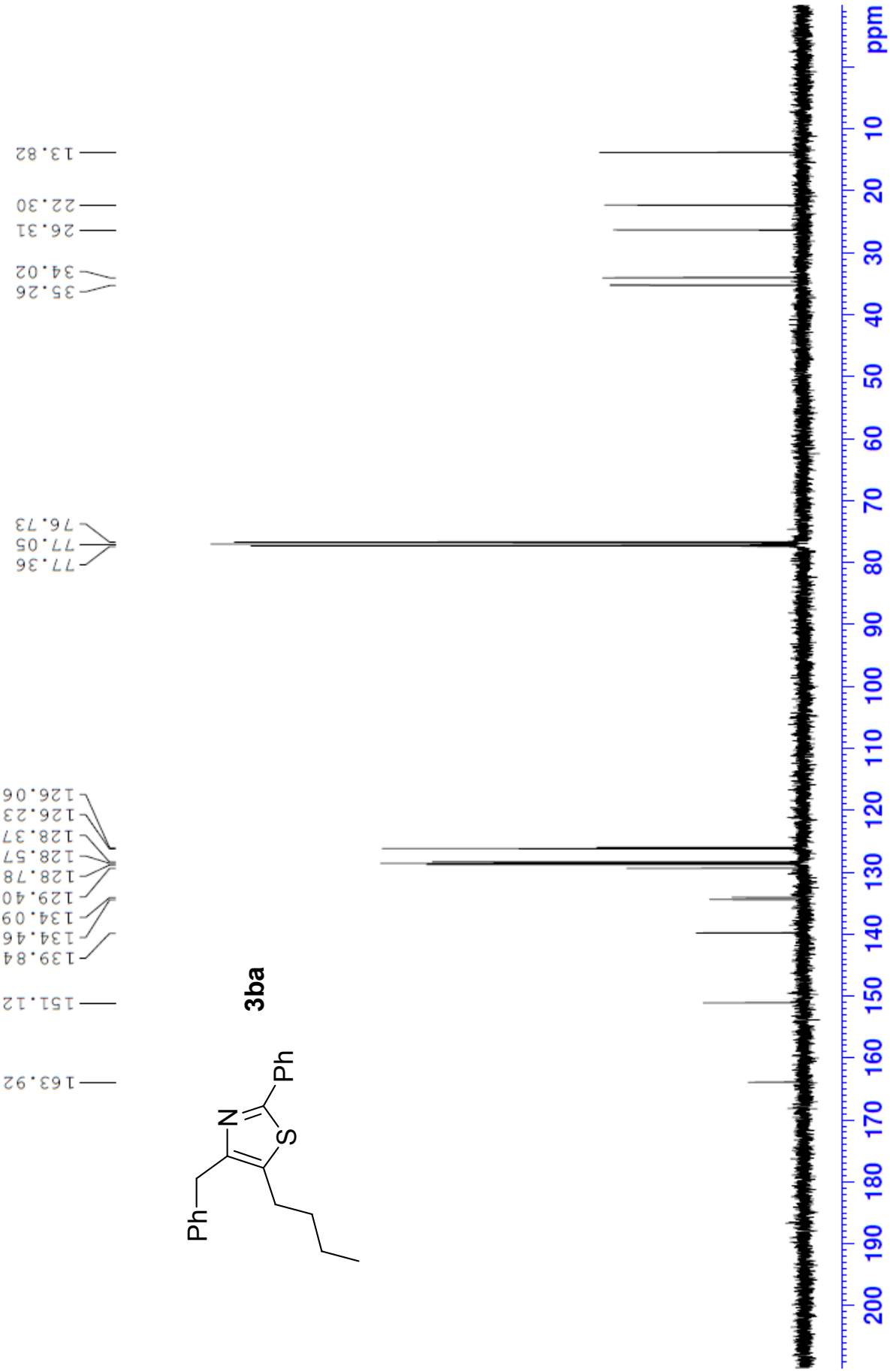
S1-C11	1.717(5)	S1-C12	1.756(5)
N1-C12	1.274(6)	N1-C10	1.391(6)
C13-C14	1.400(8)	C13-C15	1.366(7)
C13-C12	1.447(7)	C19-C21	1.386(7)
C19-C20	1.373(7)	C19-C11	1.484(7)
C20-C22	1.392(7)	C11-C10	1.346(7)
C10-C9	1.478(7)	C7-C8	1.276(7)
C7-C6	1.459(8)	C6-C4	1.361(8)
C6-C5	1.373(8)	C23-C24	1.371(8)
C23-C21	1.367(7)	C8-C9	1.529(7)
C24-C22	1.373(8)	C5-C3	1.361(8)
C18-C16	1.321(8)	C18-C17	1.366(9)
C14-C16	1.383(8)	C3-C1	1.338(9)
C15-C17	1.369(8)	C4-C2	1.383(9)
C2-C1	1.344(10)		
C11-S1-C12	89.7(3)	C12-N1-C10	112.0(4)
C14-C13-C15	117.6(6)	C14-C13-C12	118.6(5)
C15-C13-C12	123.7(5)	C21-C19-C20	118.7(5)
C21-C19-C11	120.3(5)	C20-C19-C11	121.0(5)
C19-C20-C22	120.2(5)	C10-C11-C19	131.0(5)
C10-C11-S1	109.4(4)	C19-C11-S1	119.6(4)
C11-C10-N1	115.6(5)	C11-C10-C9	126.3(5)
N1-C10-C9	117.9(5)	C8-C7-C6	128.8(6)
N1-C12-C13	128.2(5)	N1-C12-S1	113.2(4)
C13-C12-S1	118.5(4)	C4-C6-C5	117.6(6)
C4-C6-C7	119.3(6)	C5-C6-C7	123.0(6)
C24-C23-C21	120.6(6)	C7-C8-C9	126.0(6)

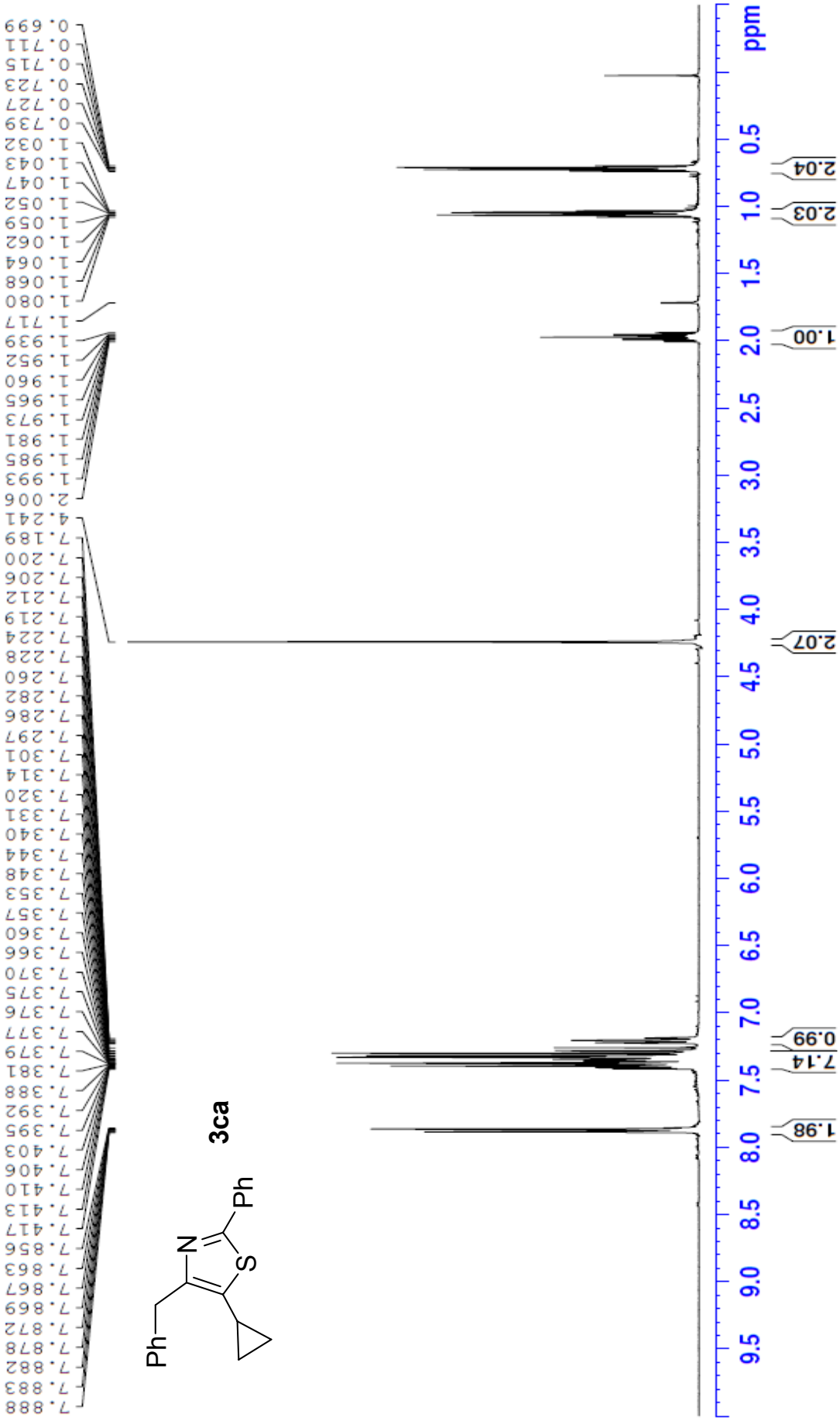
C23-C24-C22	119.2(6)	C19-C21-C23	120.9(6)
C3-C5-C6	120.0(6)	C16-C18-C17	120.6(6)
C16-C14-C13	119.0(5)	C24-C22-C20	120.4(6)
C18-C16-C14	121.7(6)	C10-C9-C8	112.9(4)
C5-C3-C1	121.3(6)	C17-C15-C13	122.0(6)
C6-C4-C2	121.9(6)	C1-C2-C4	118.5(7)
C15-C17-C18	119.1(6)	C2-C1-C3	120.6(7)

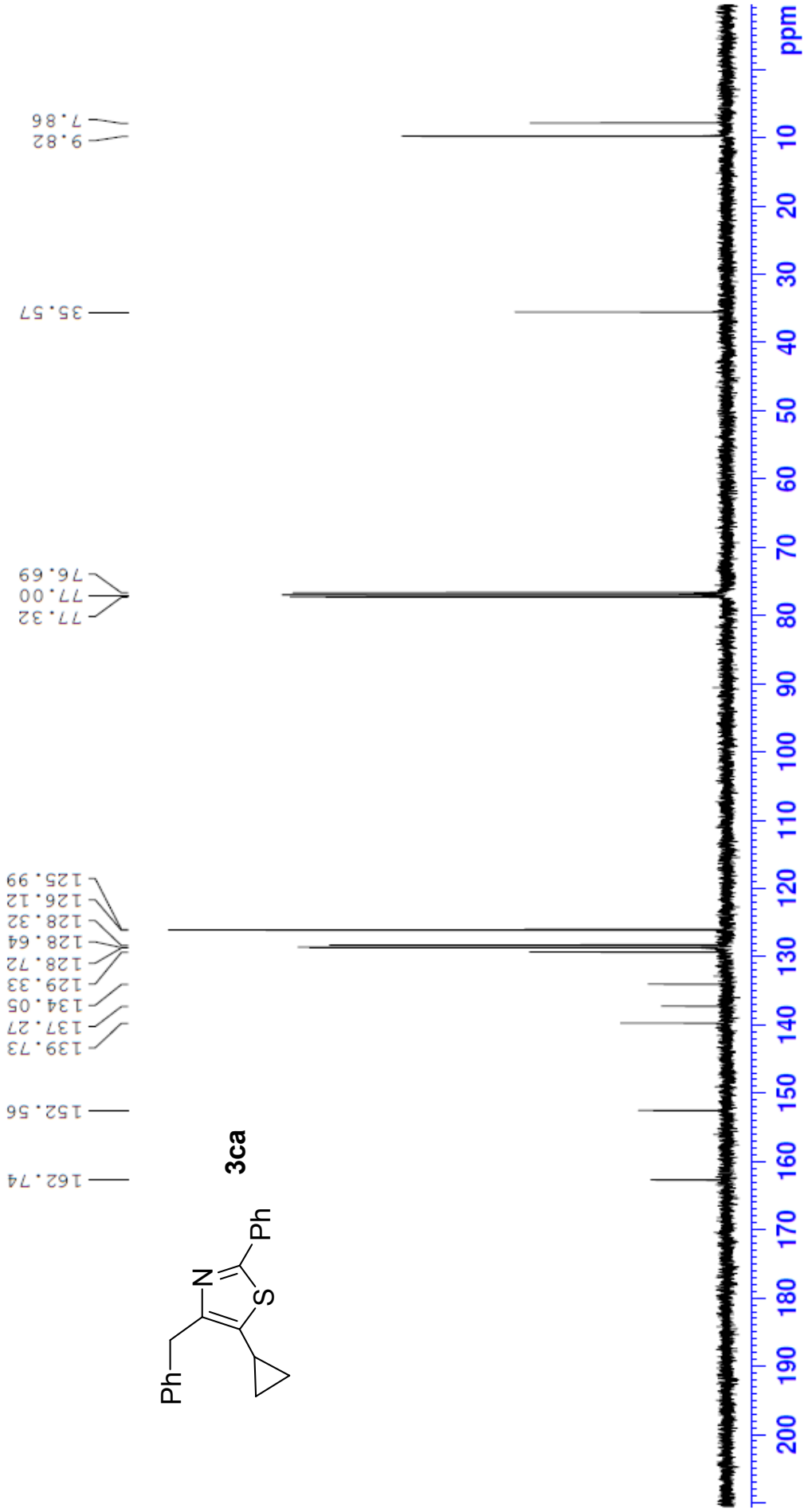


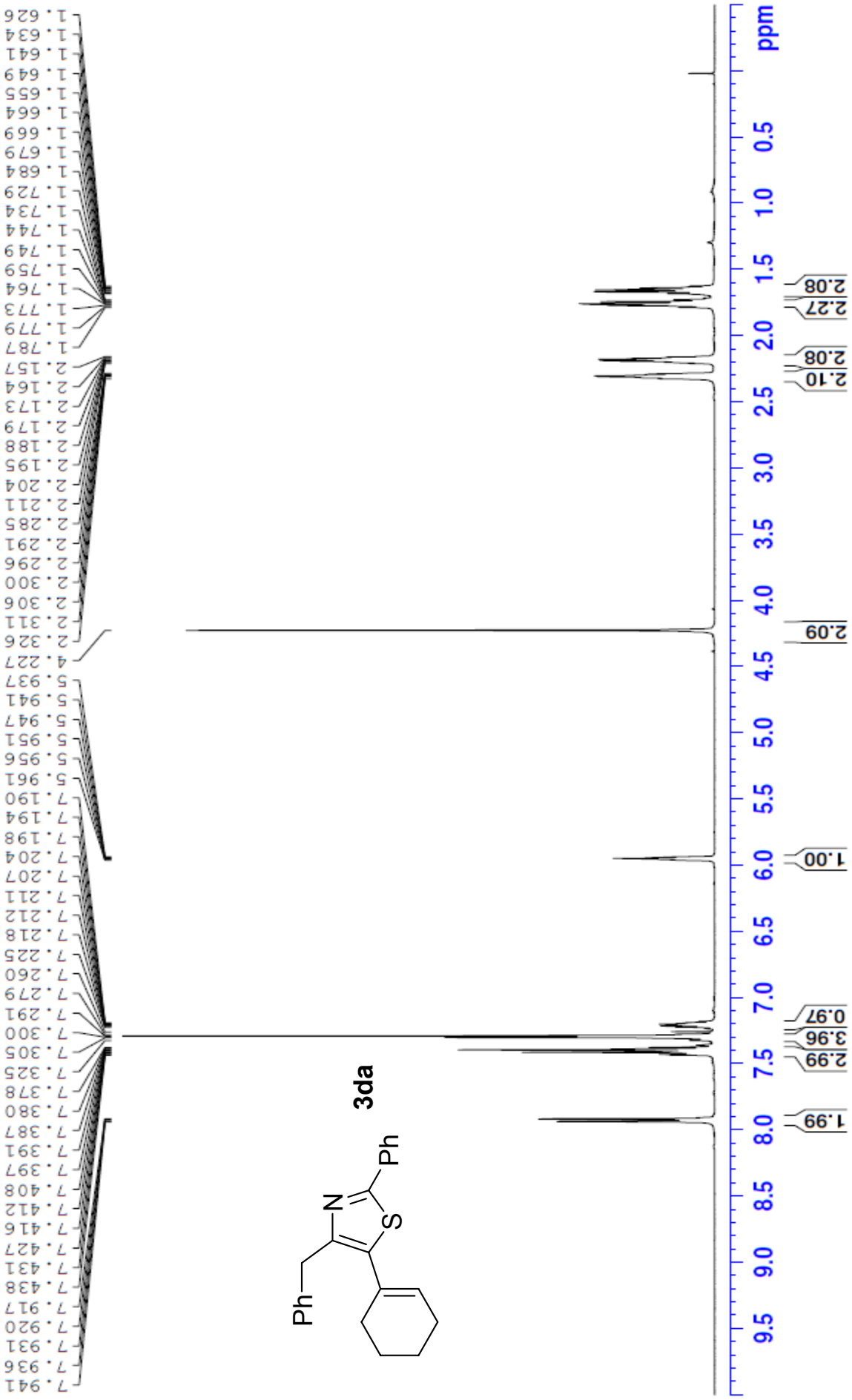


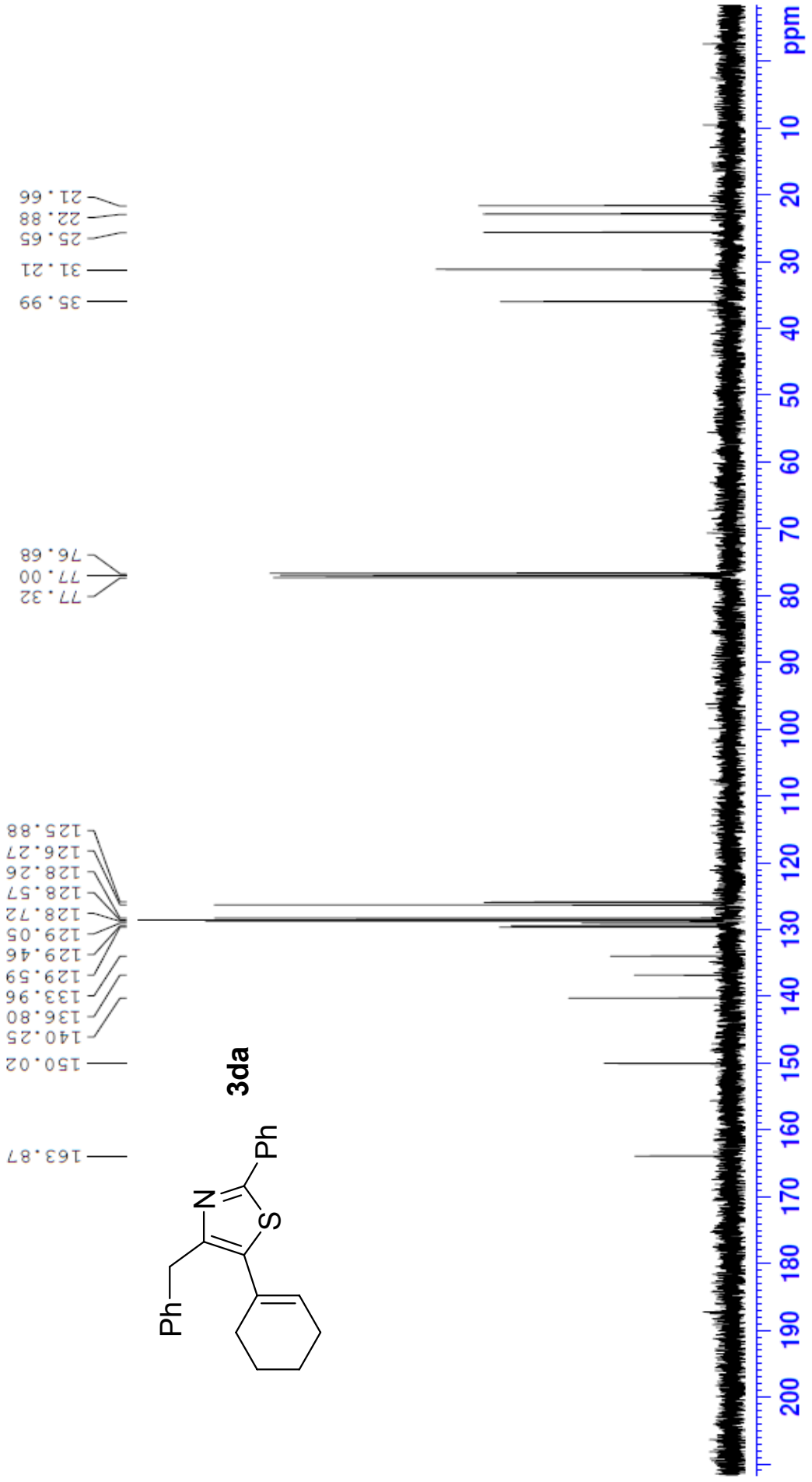


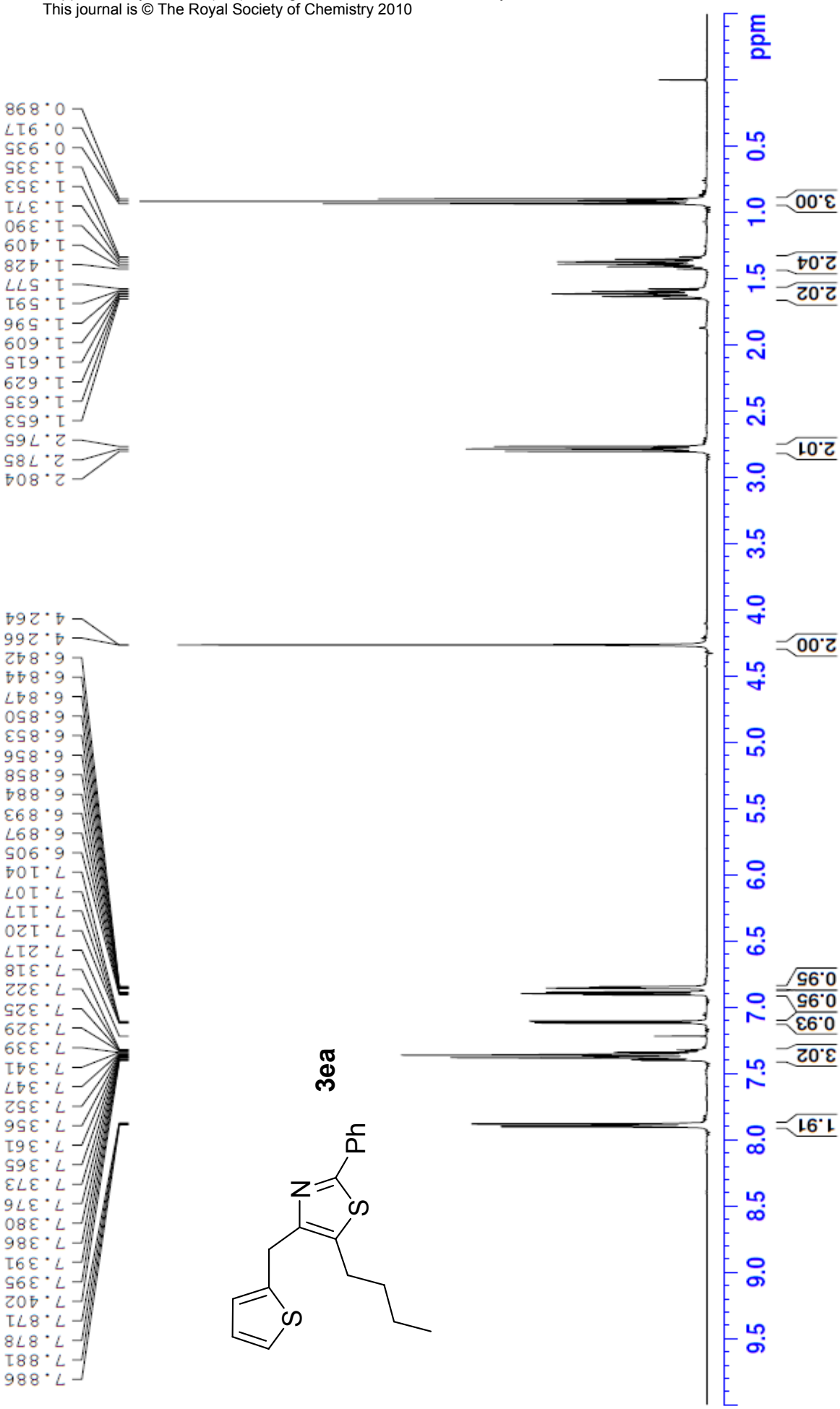


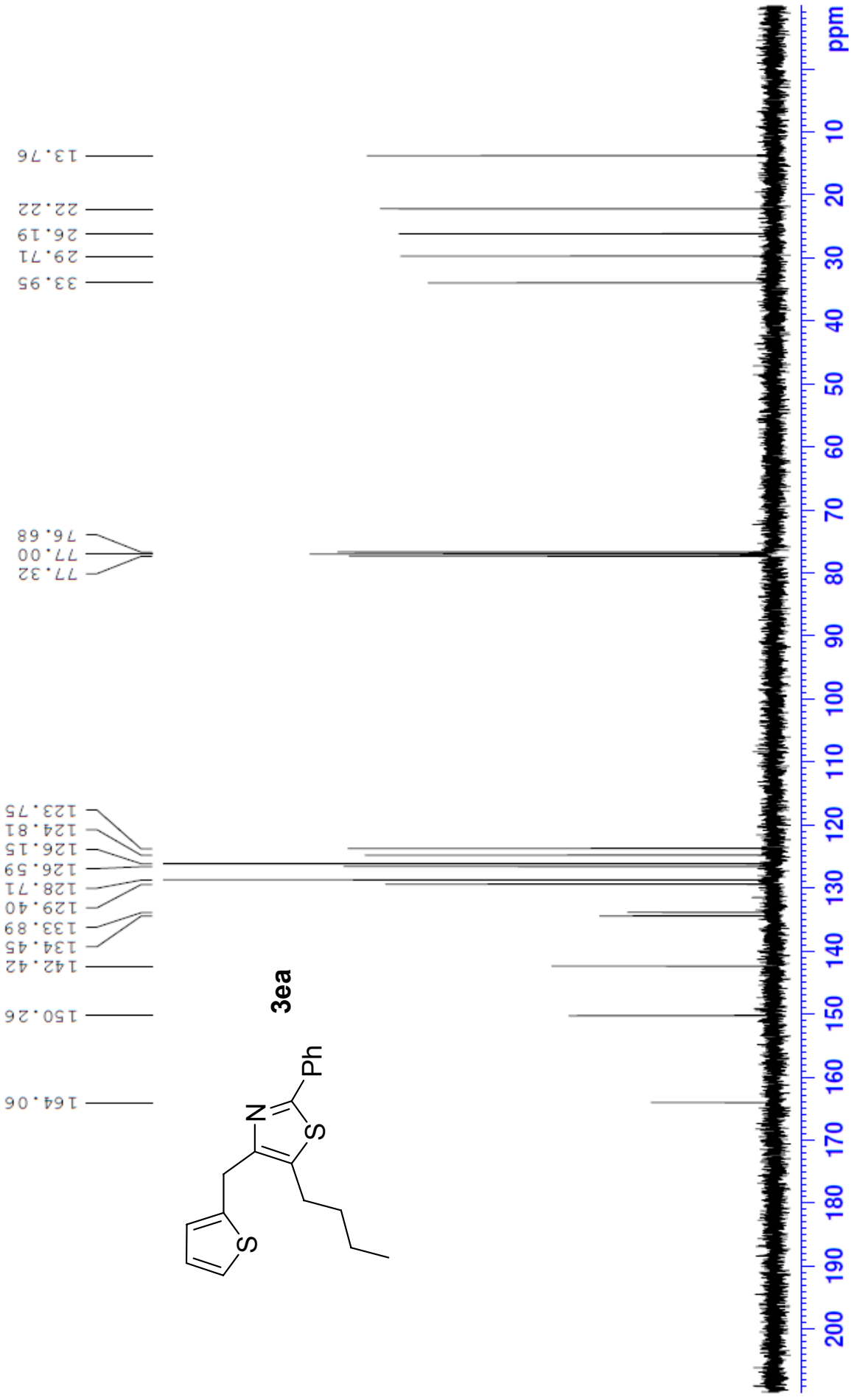


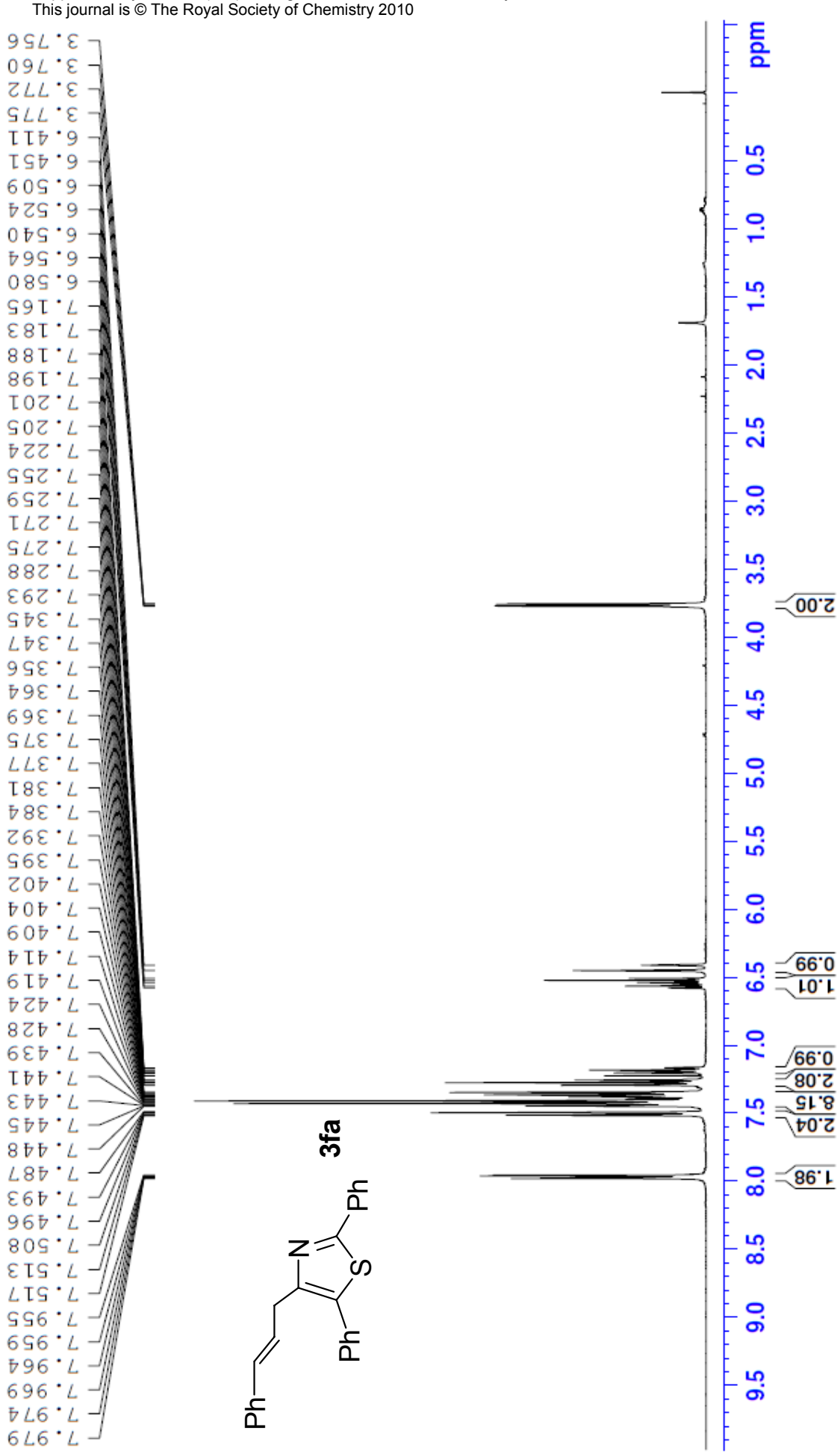


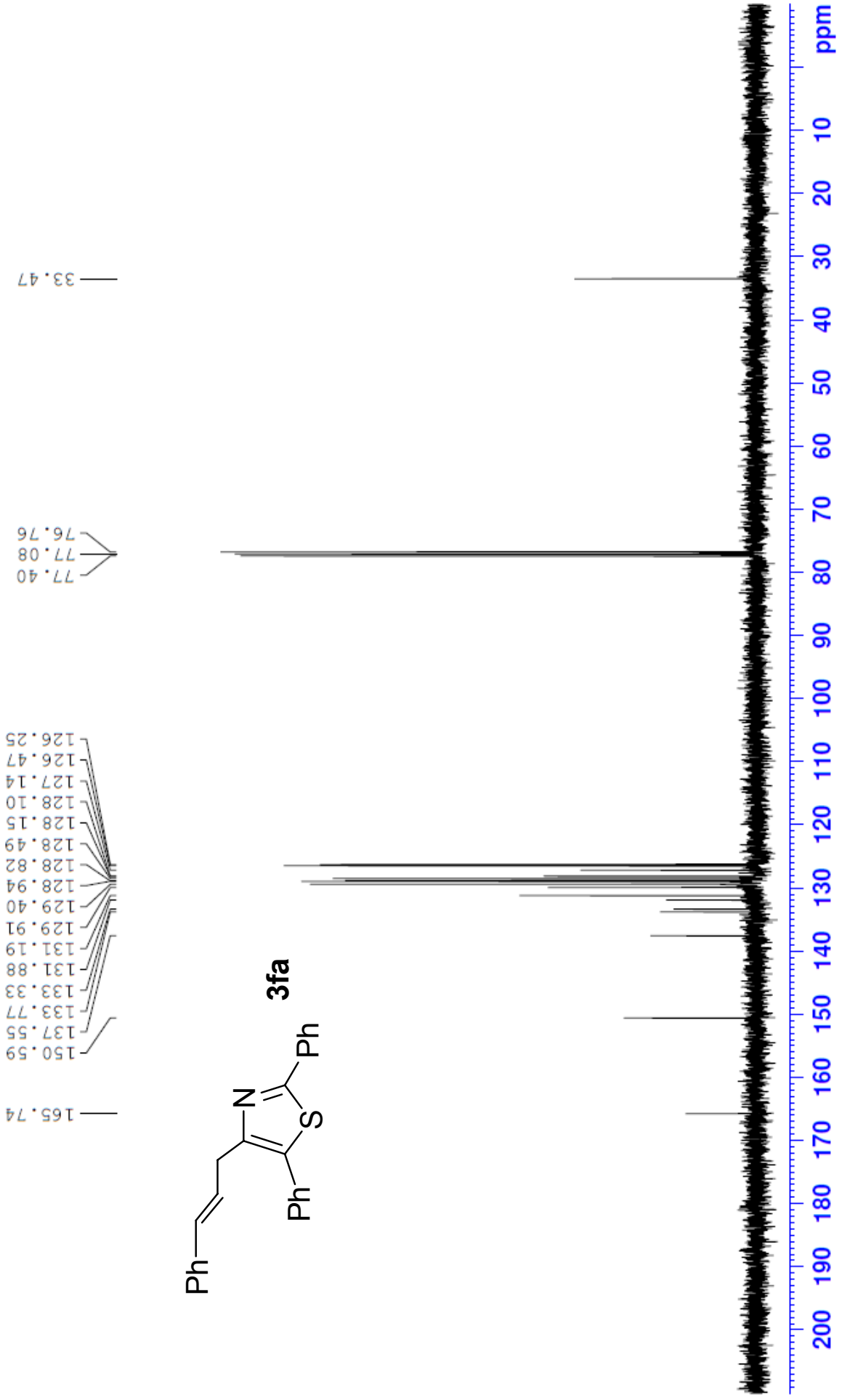


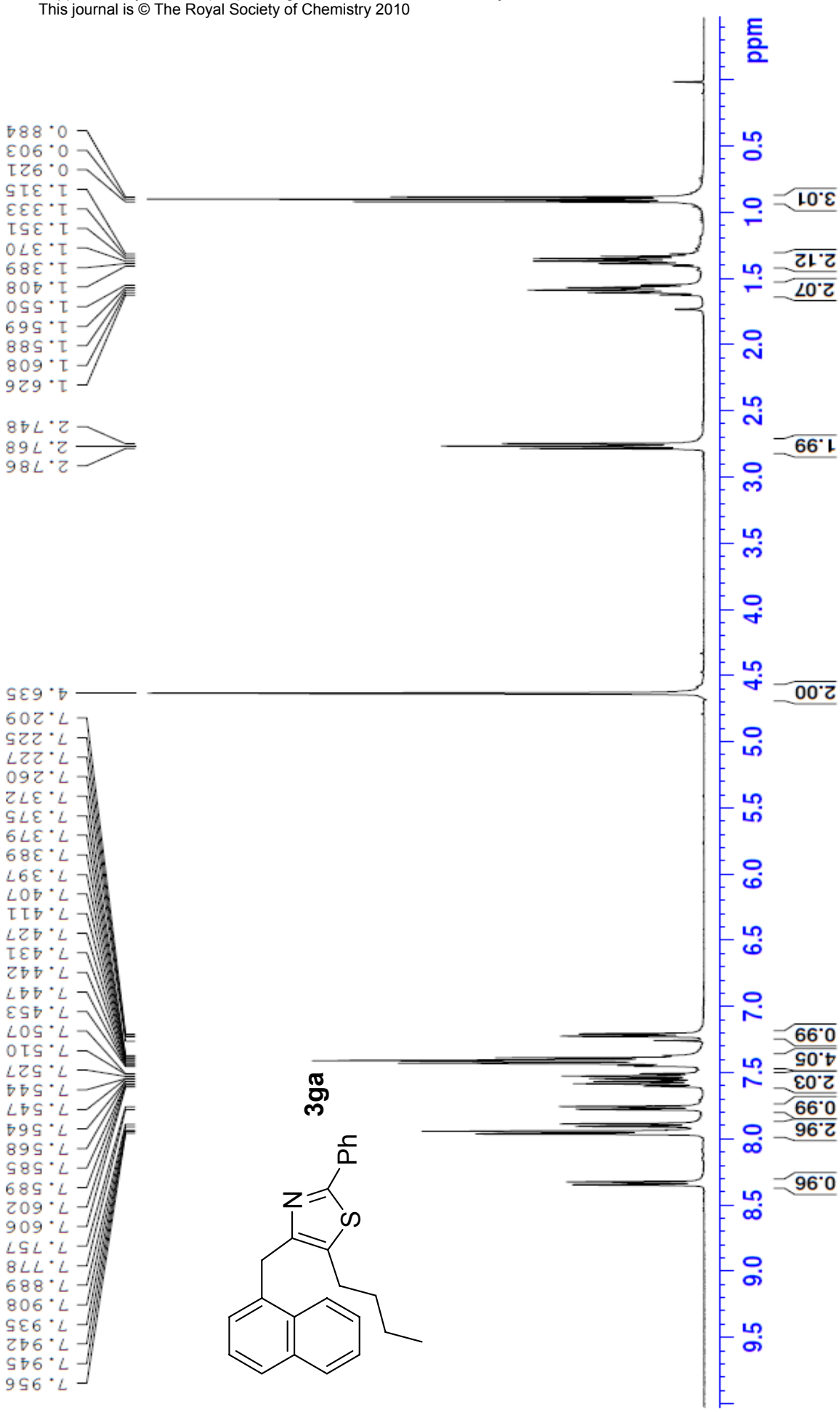


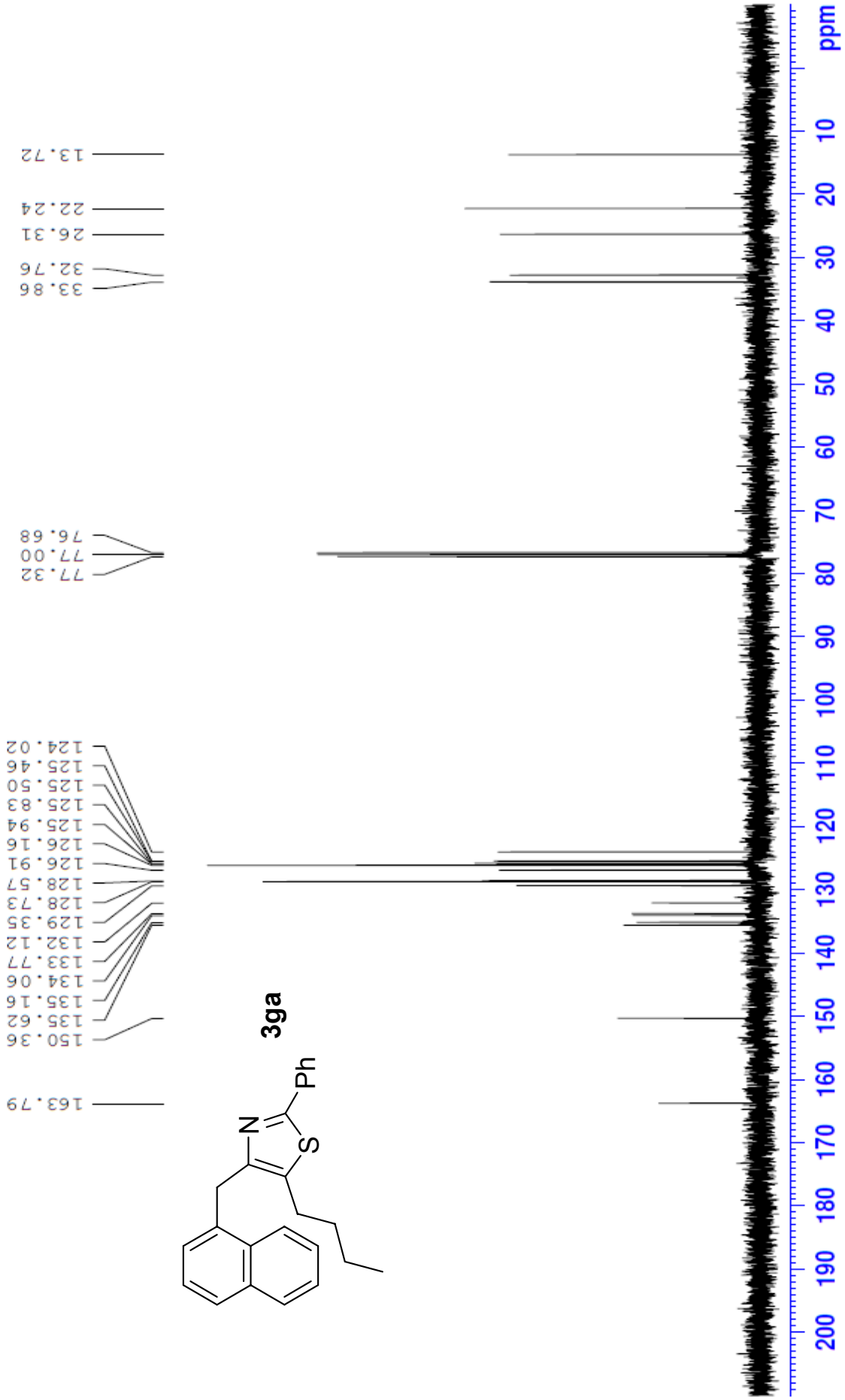


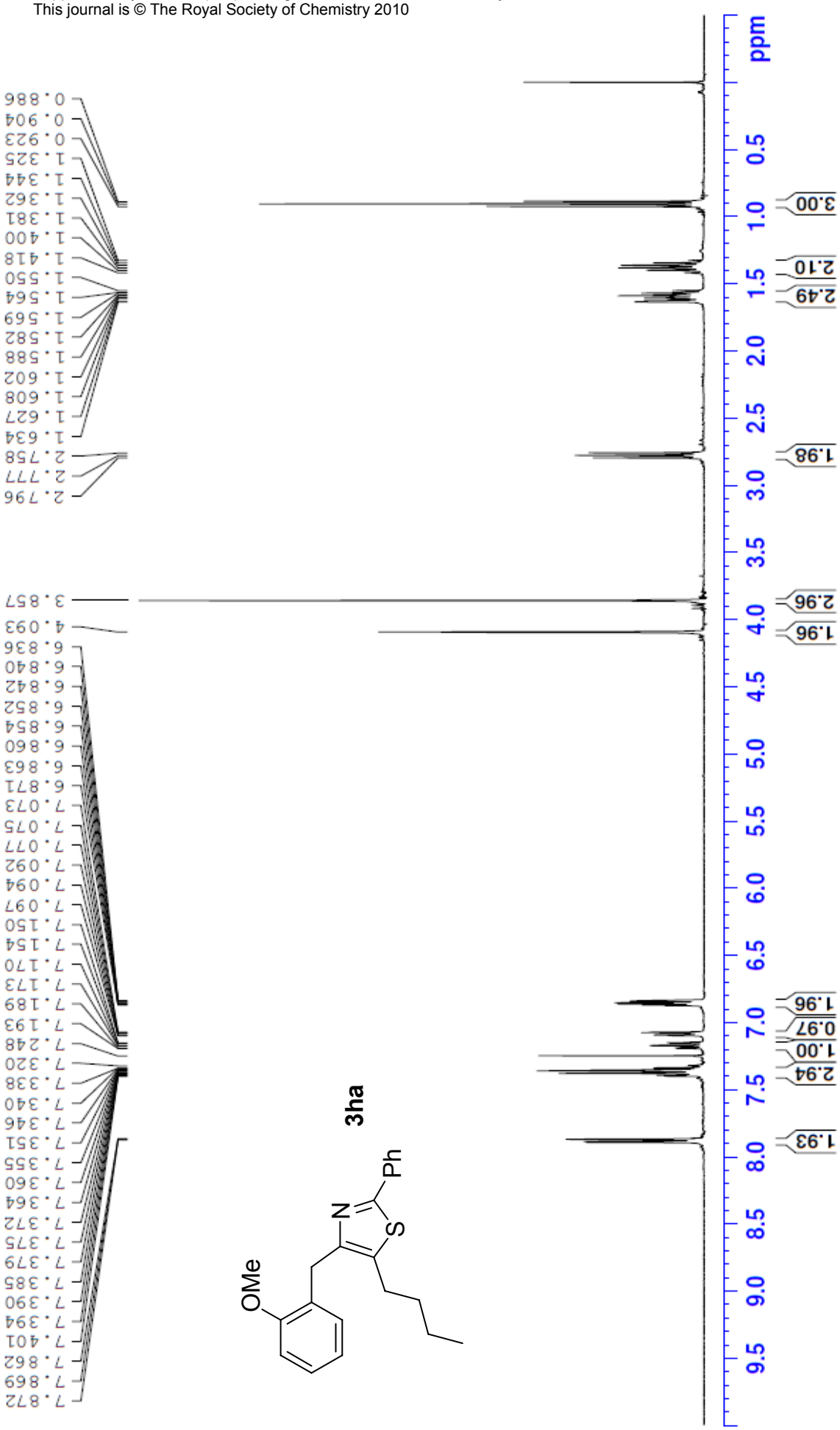


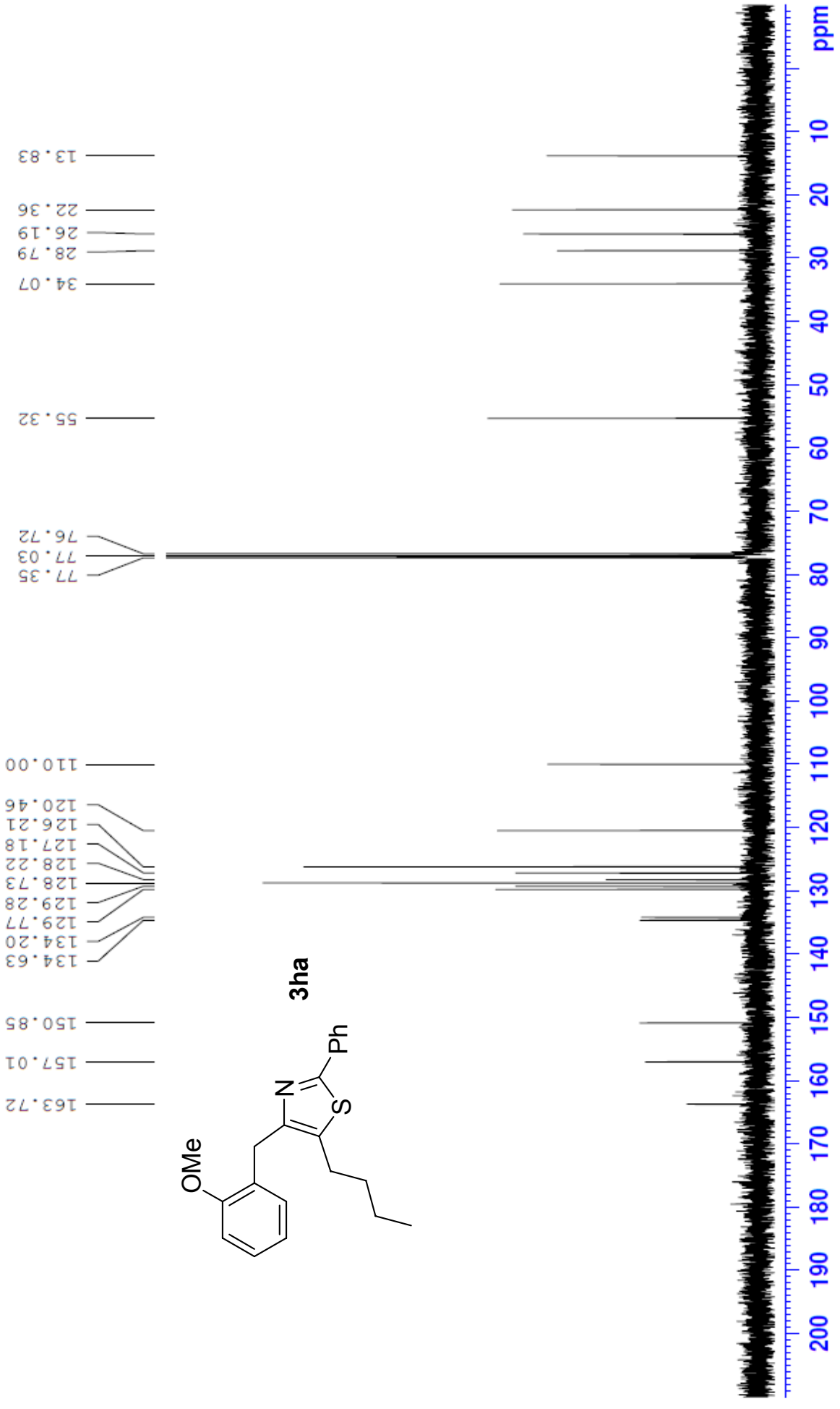


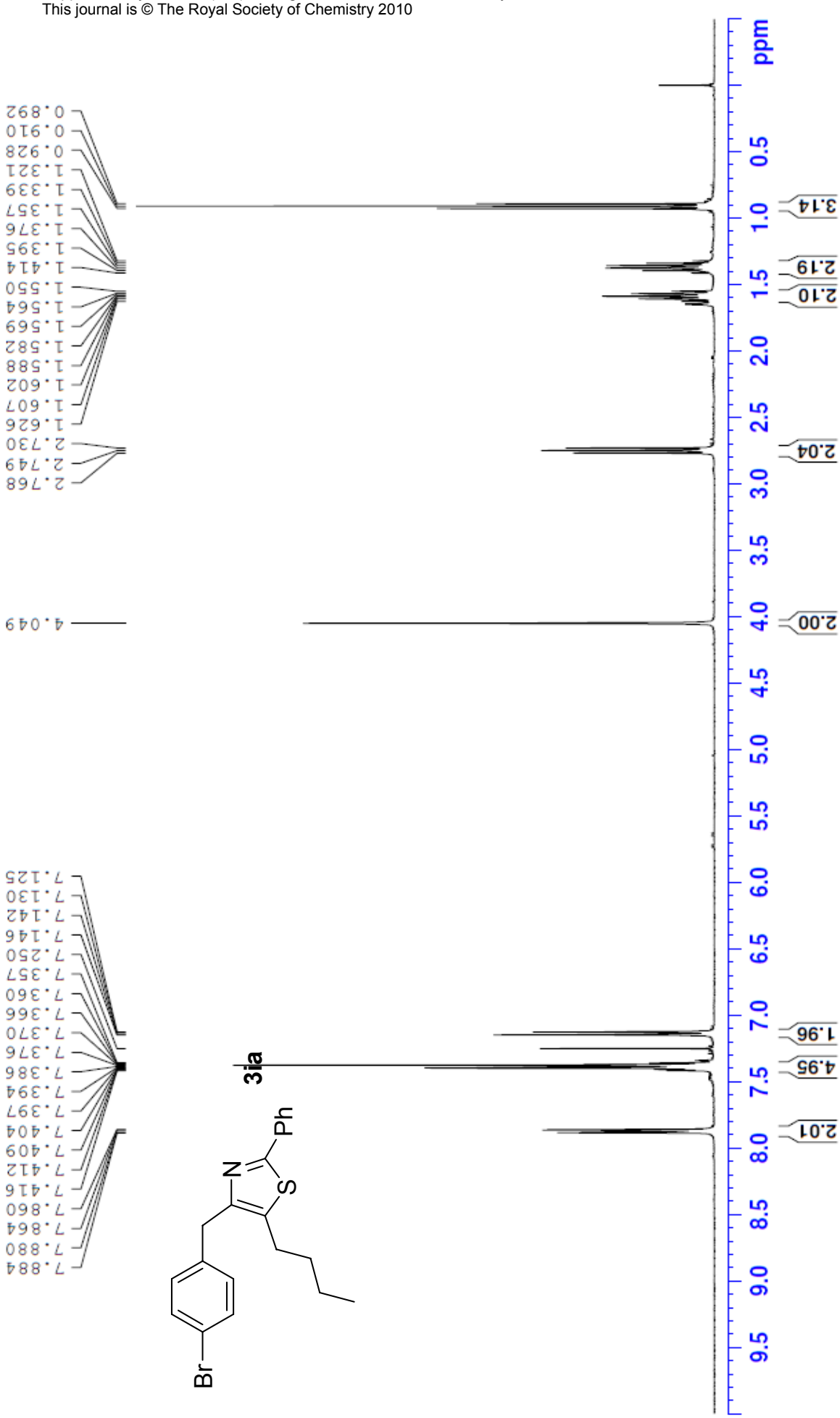


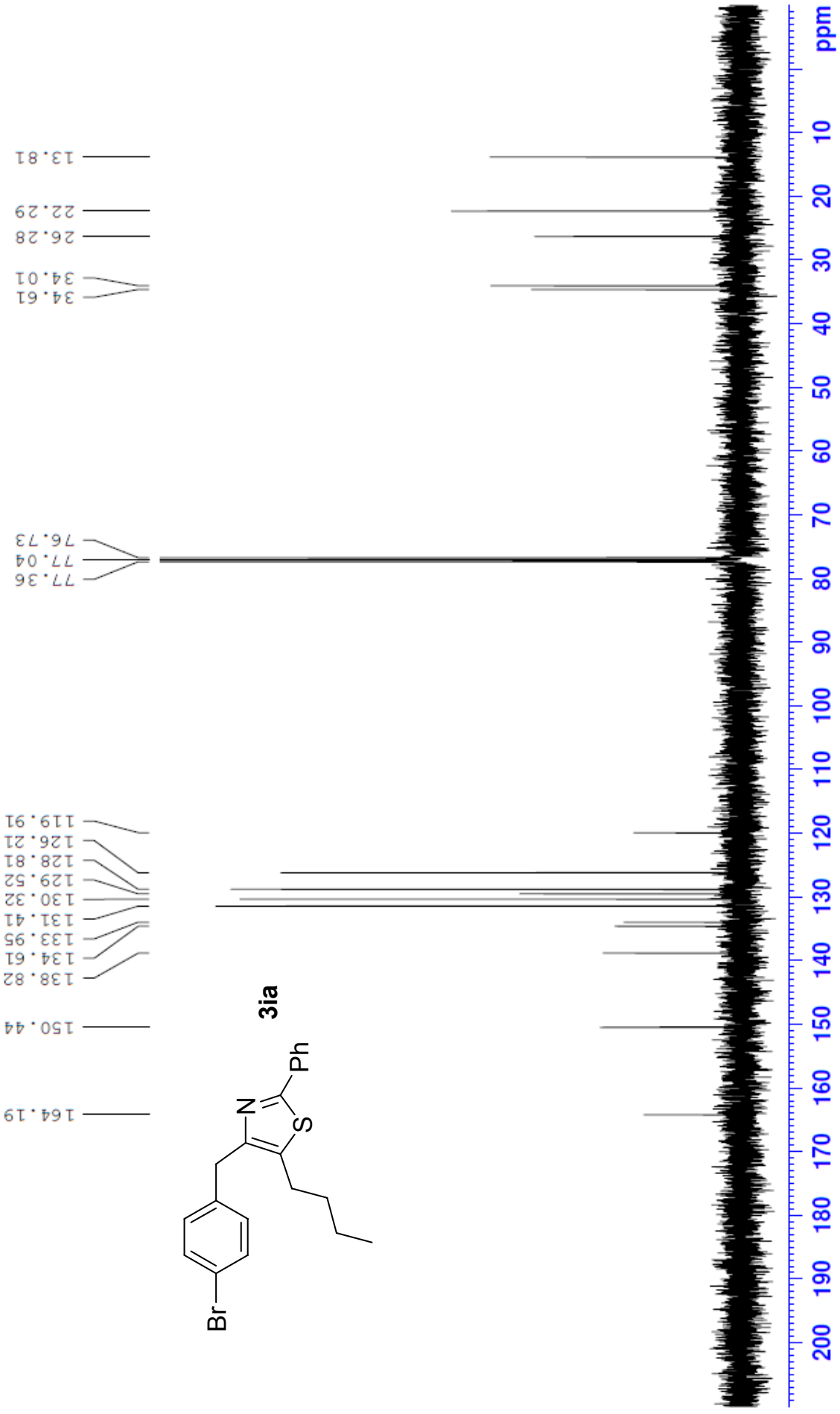


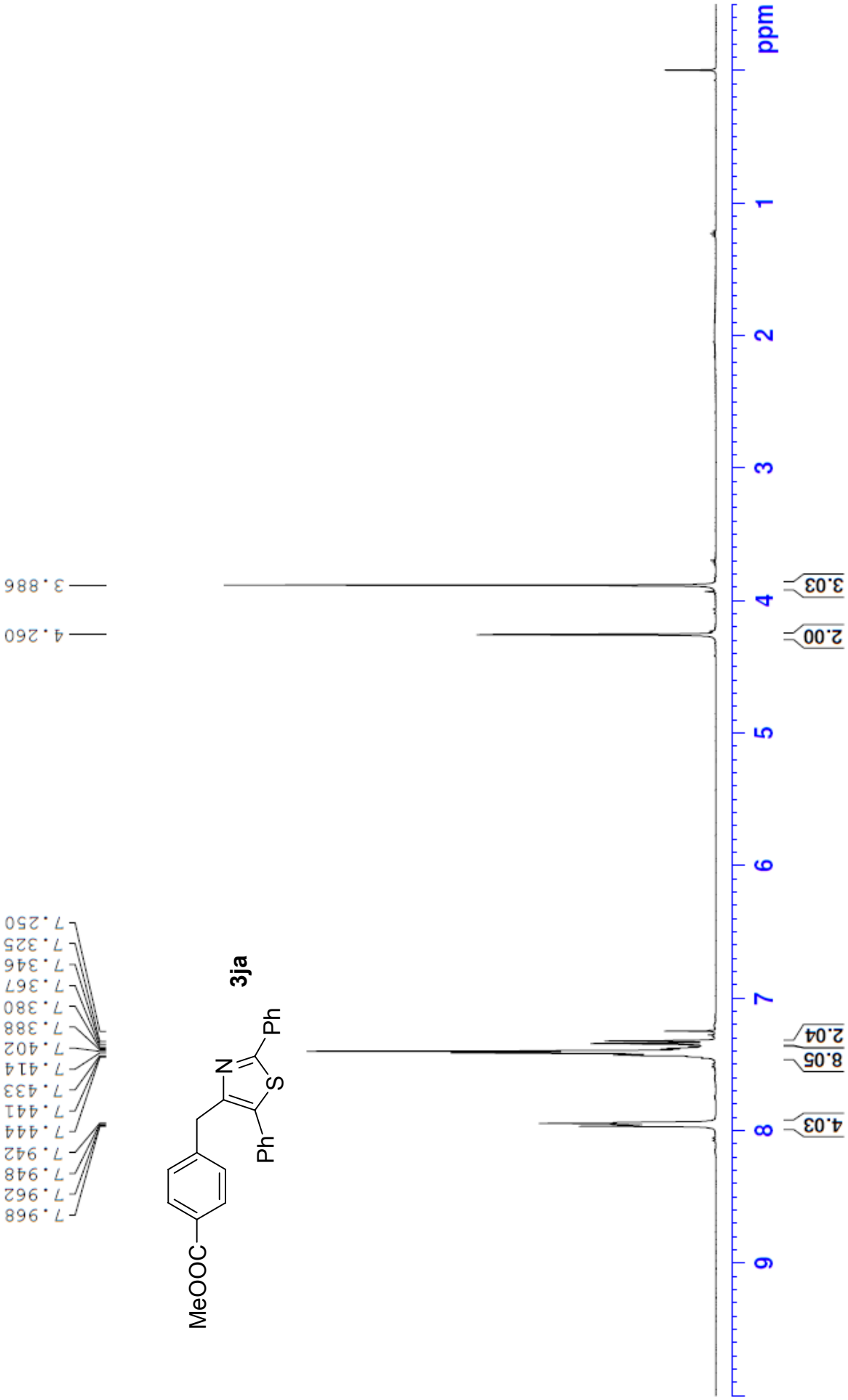


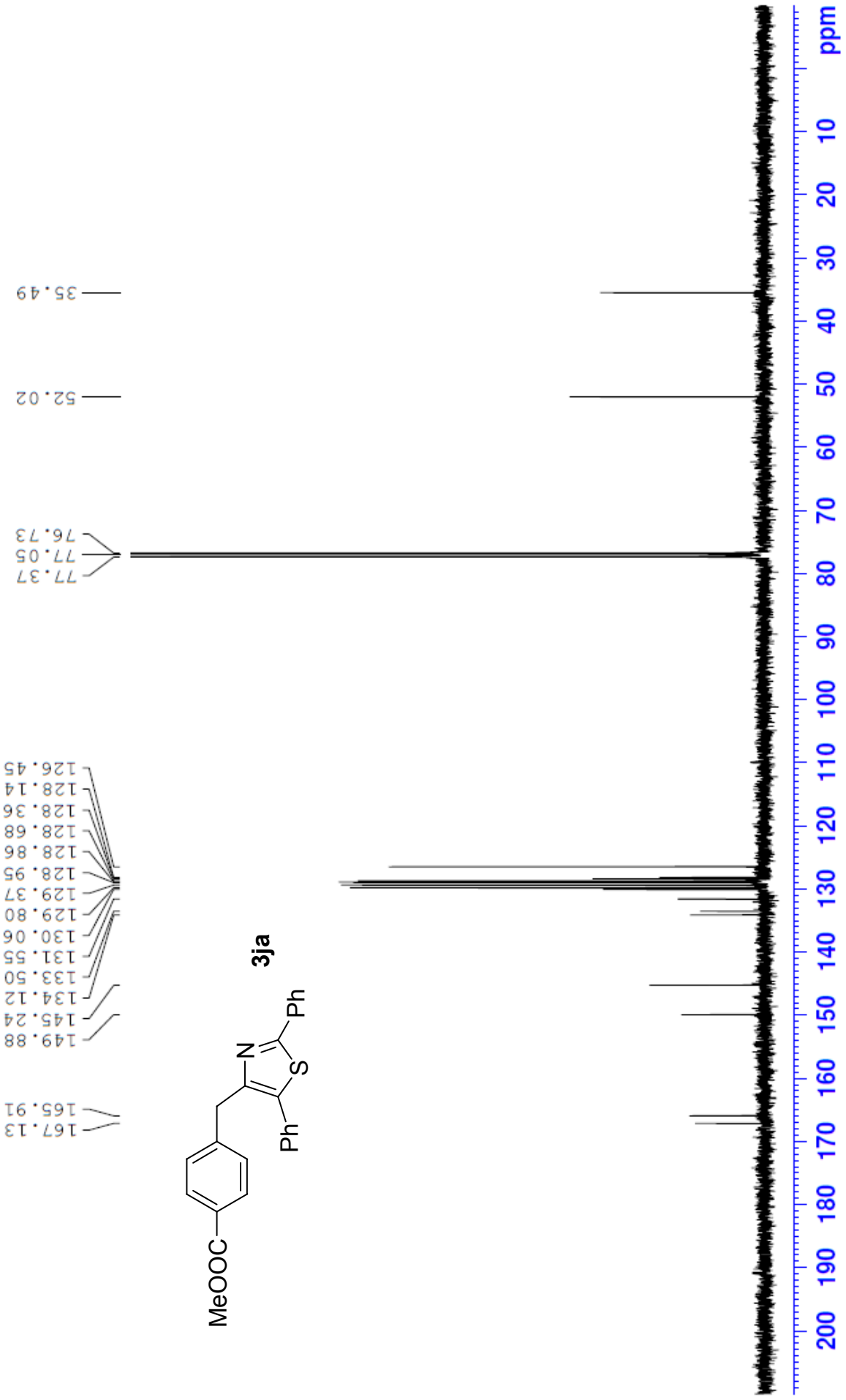


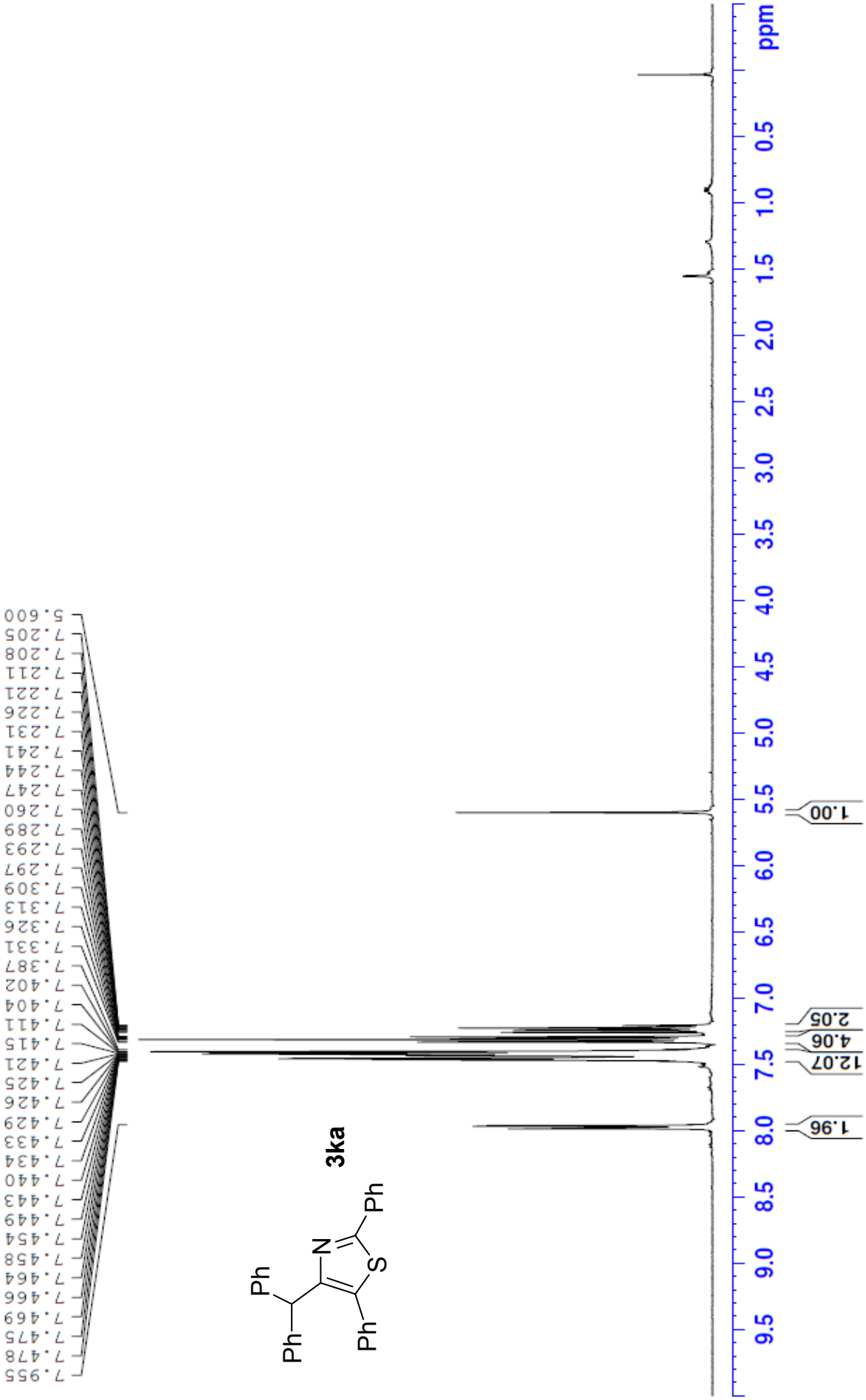


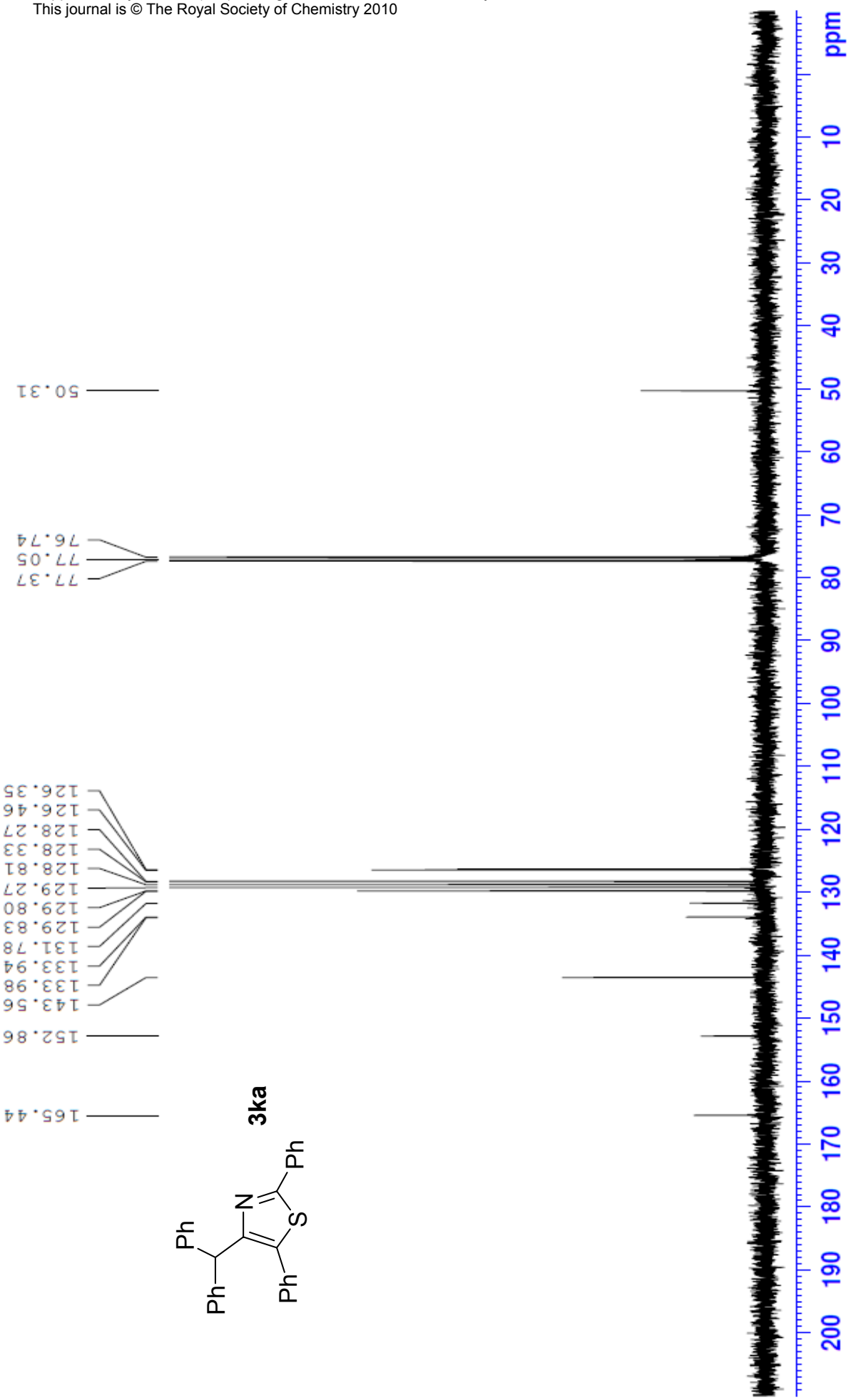


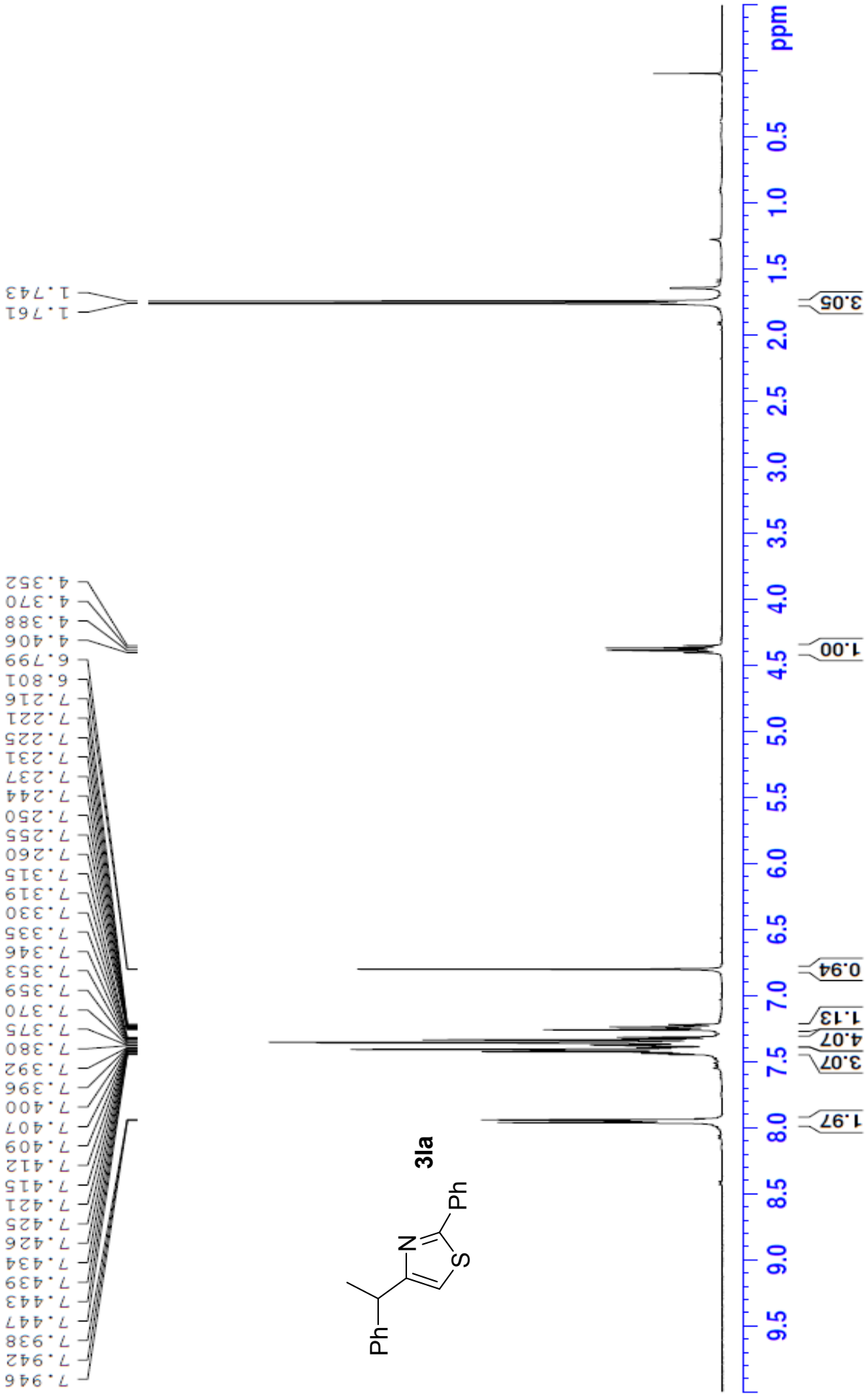


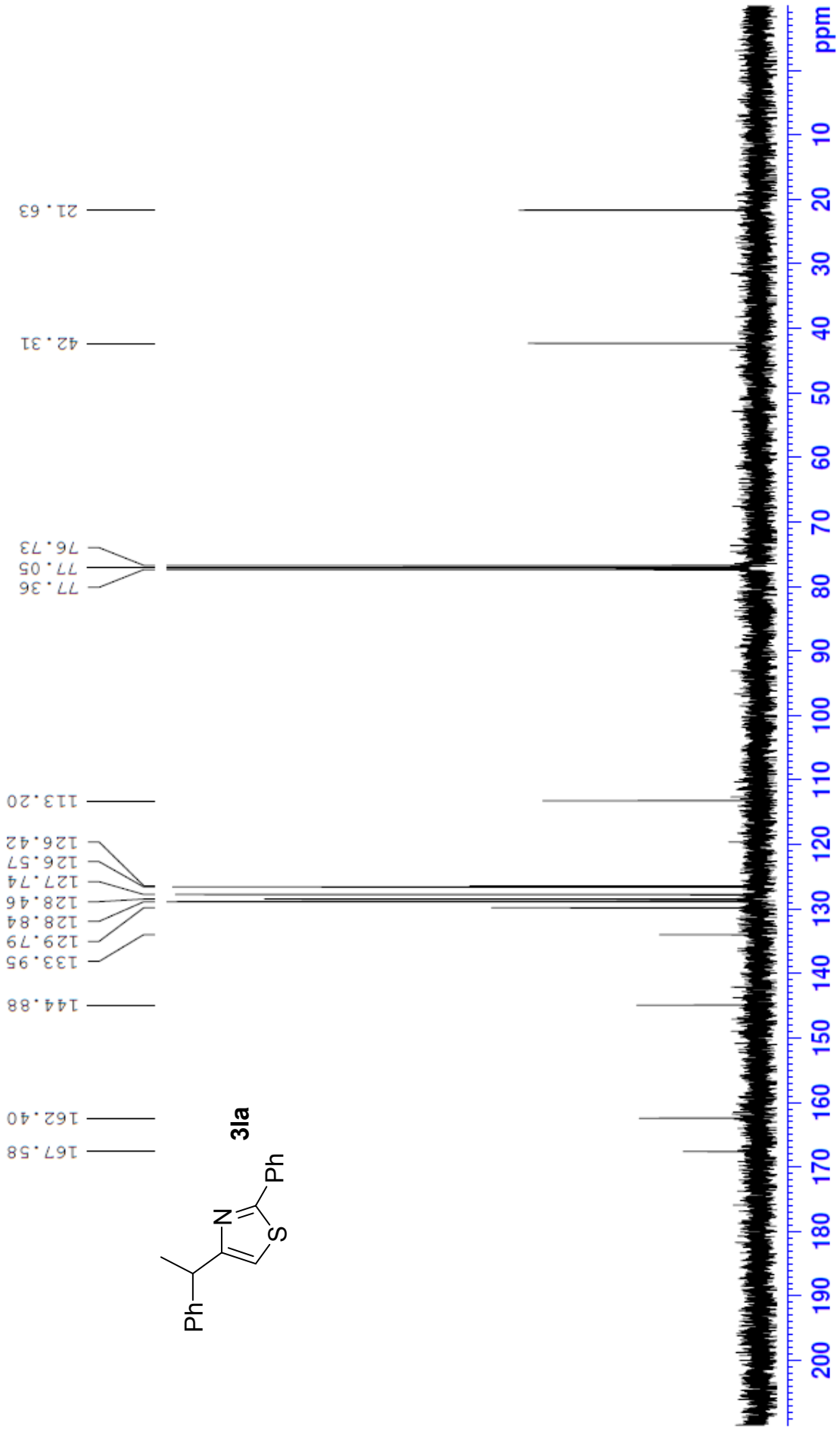


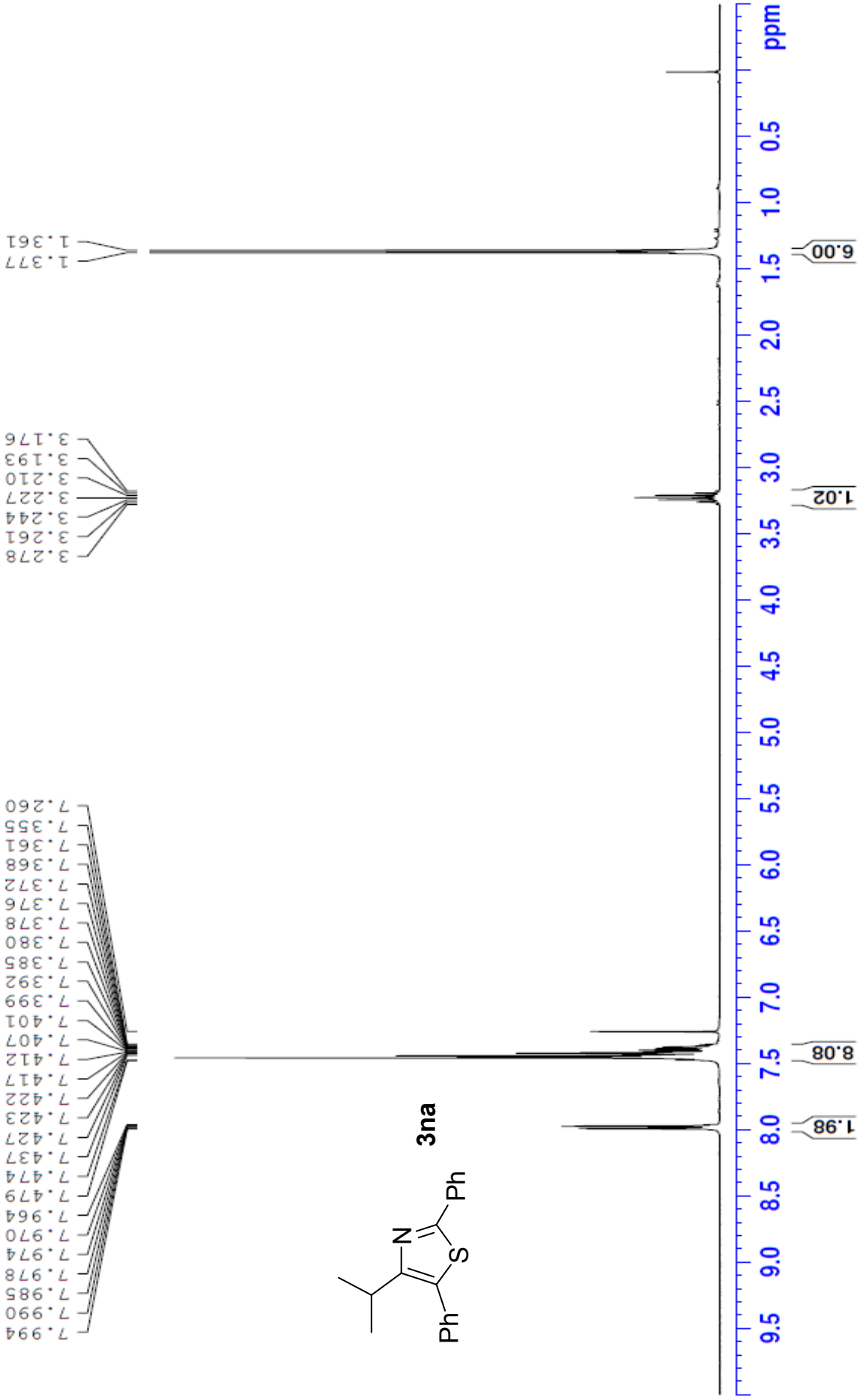


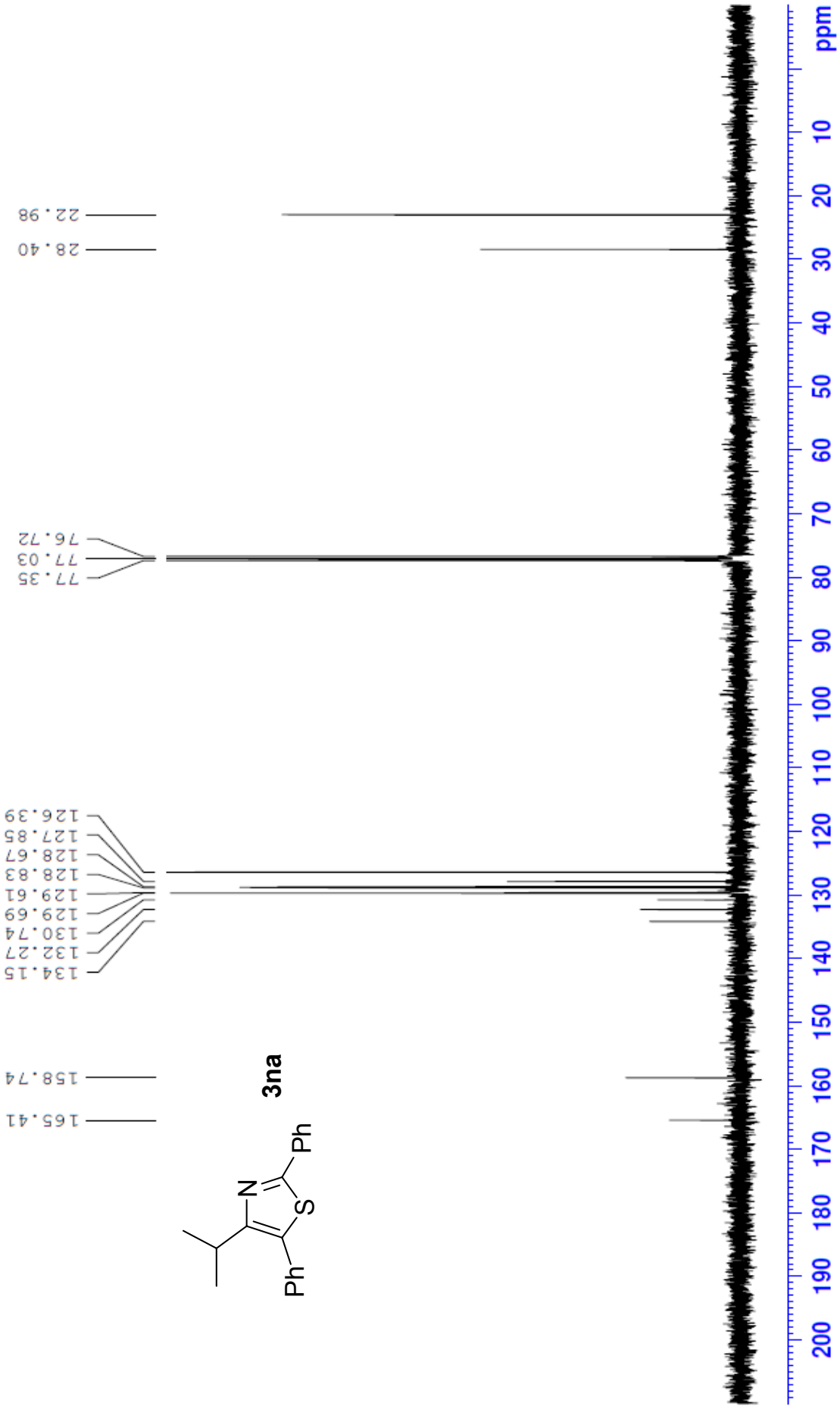


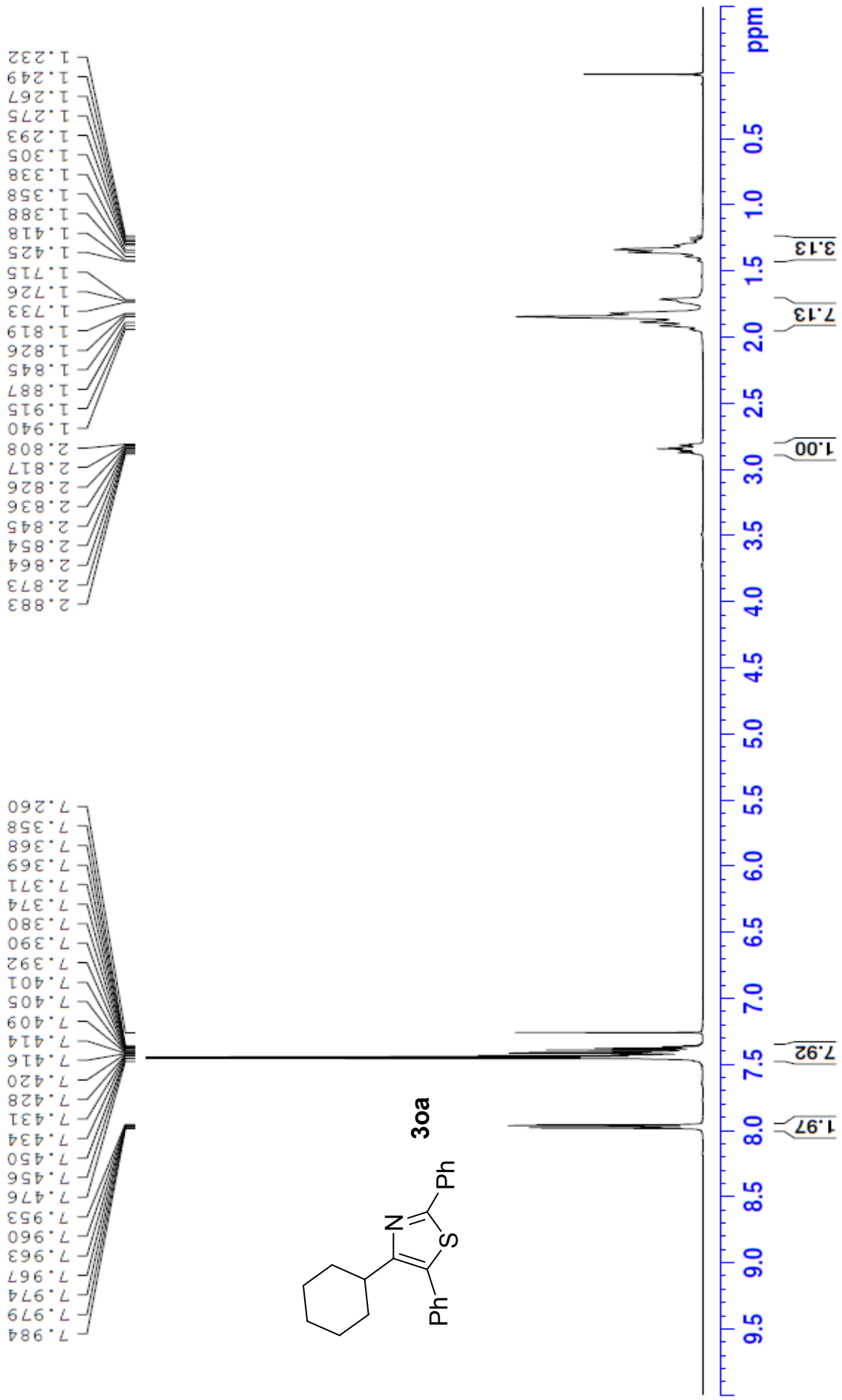


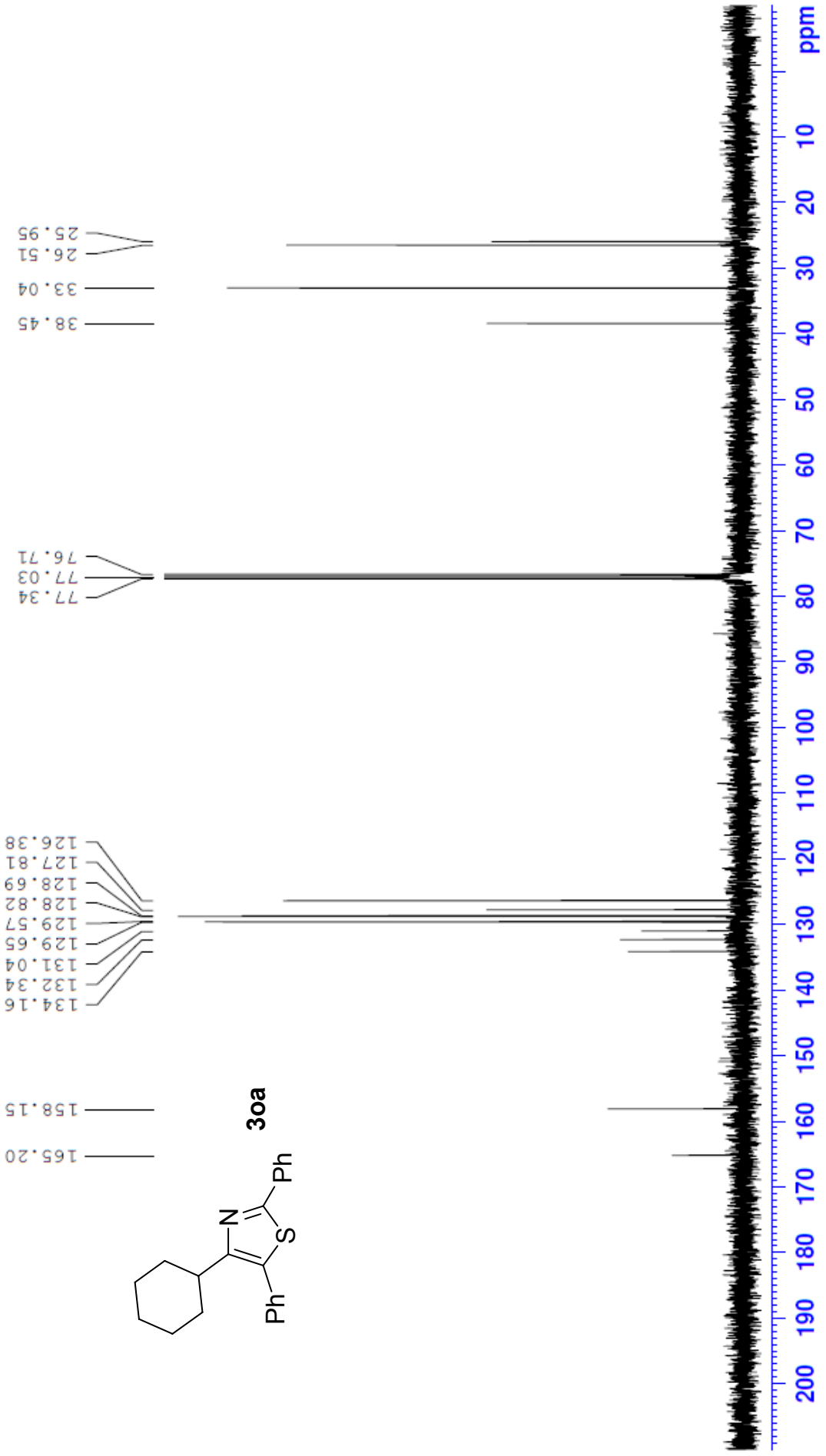


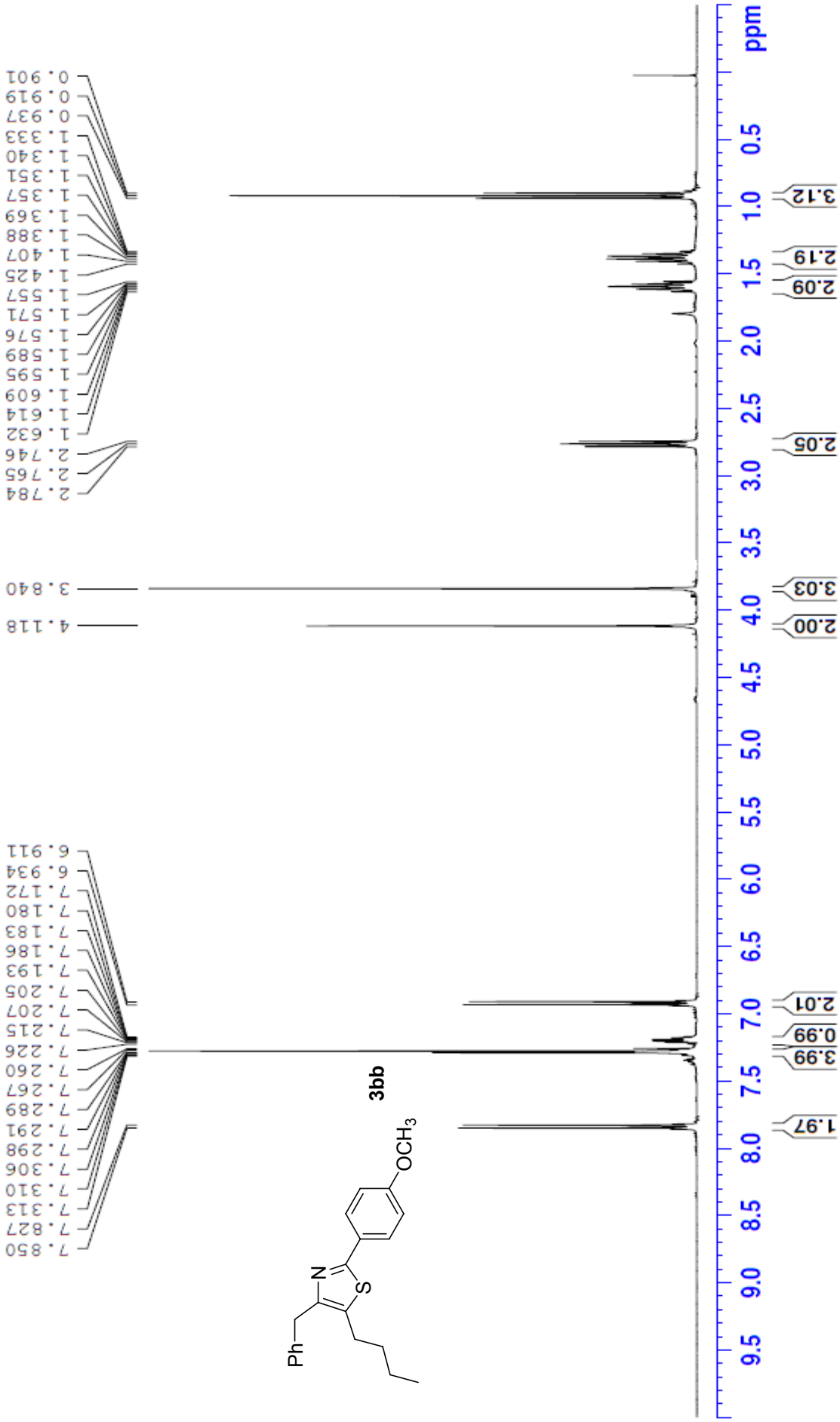


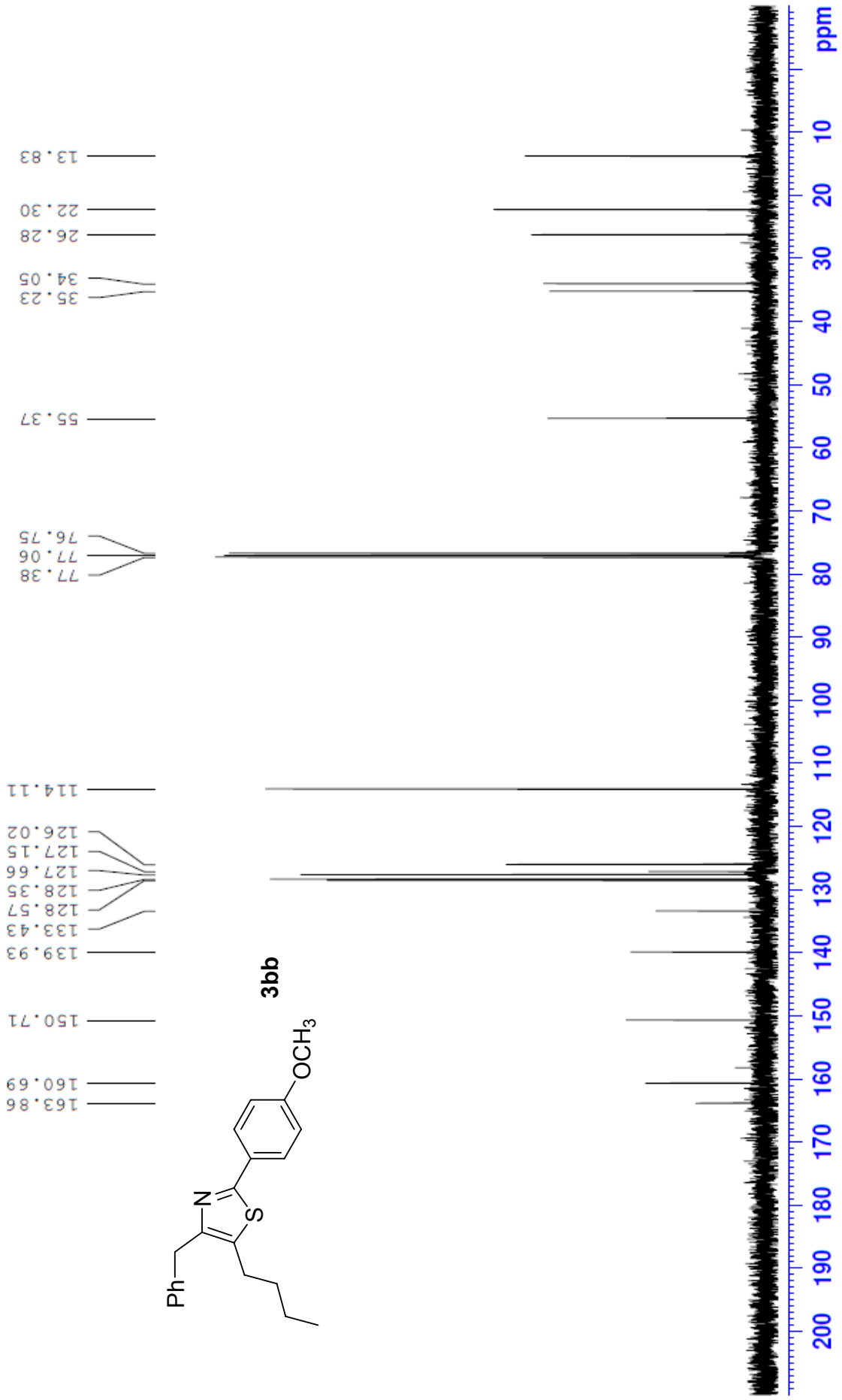


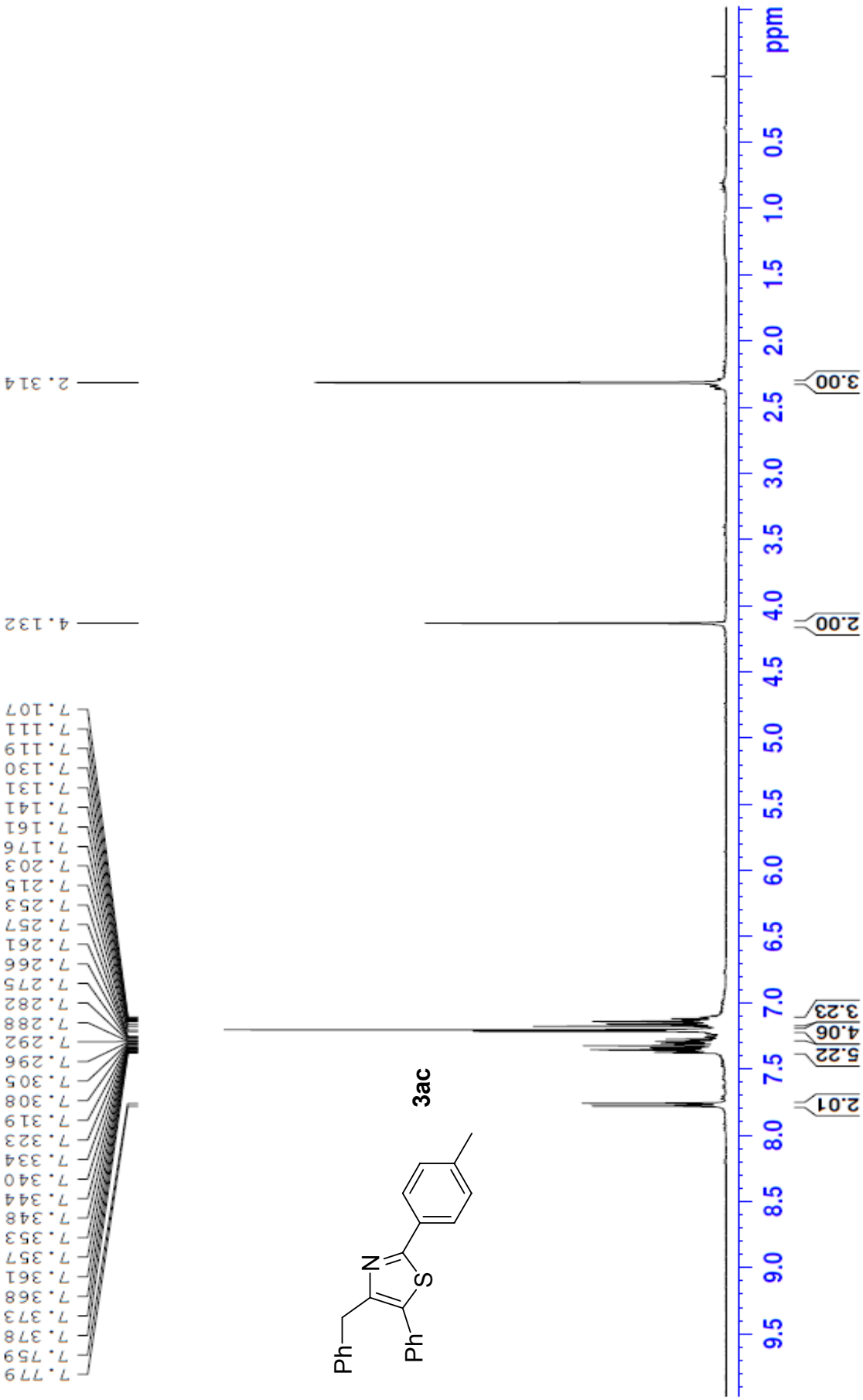


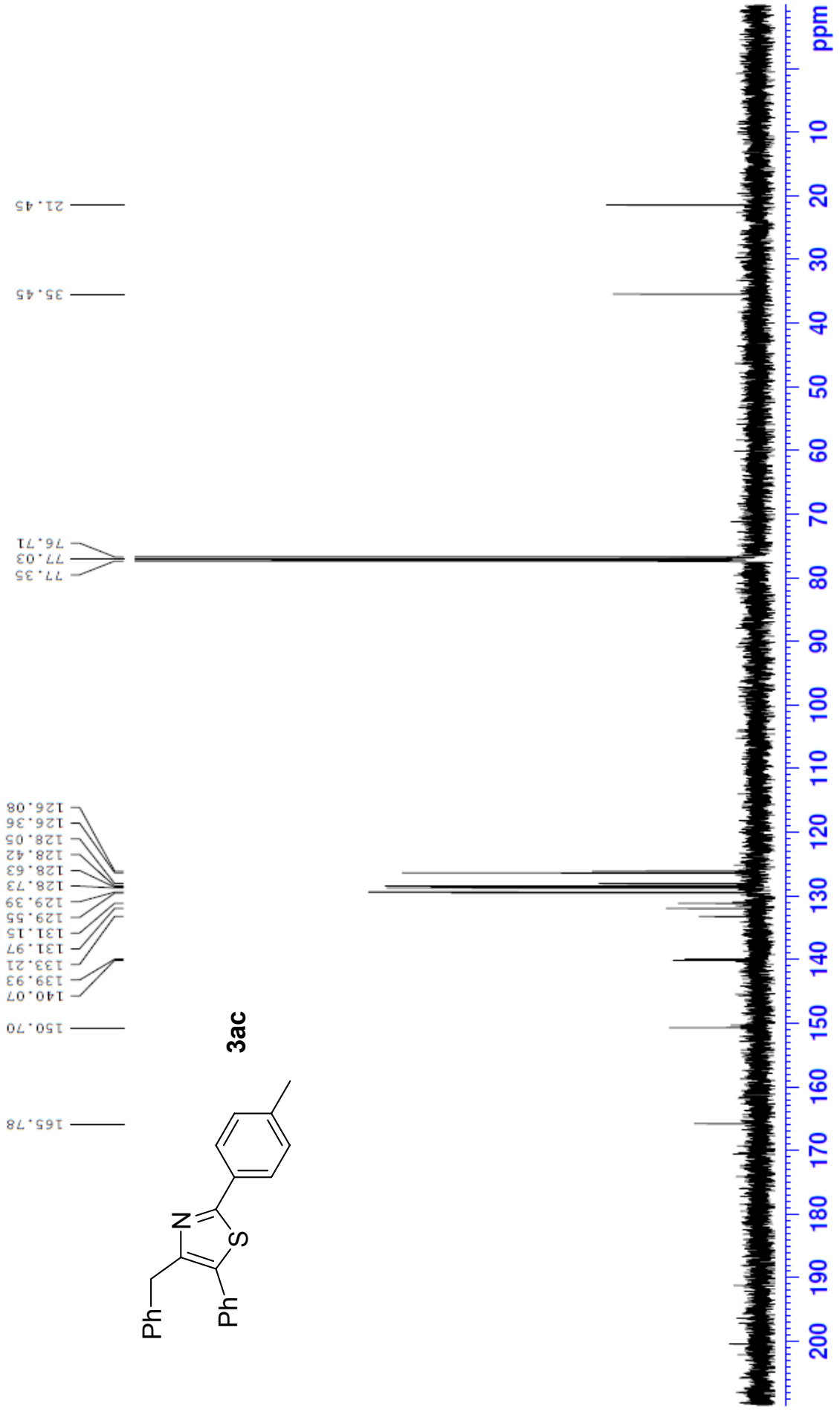


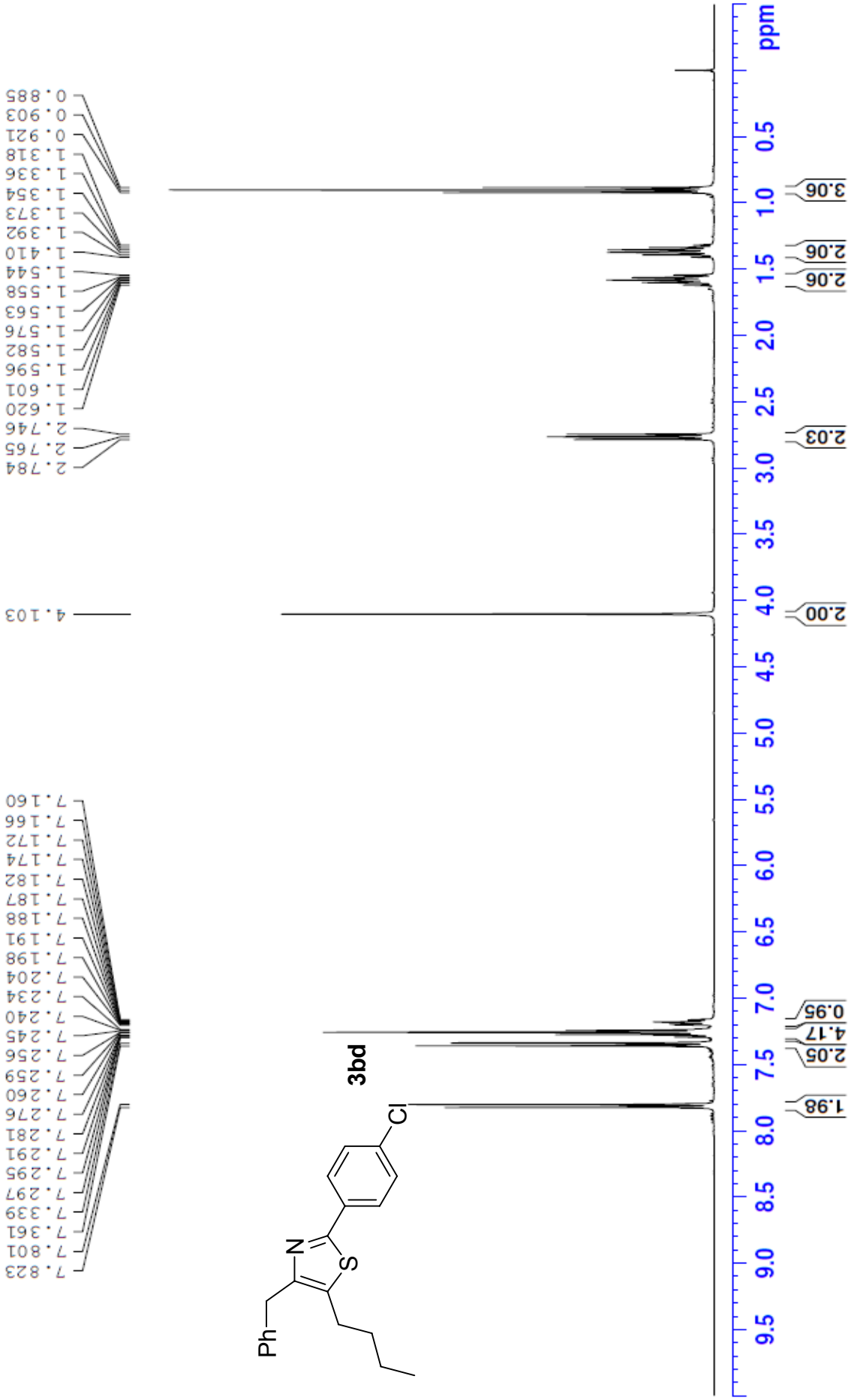


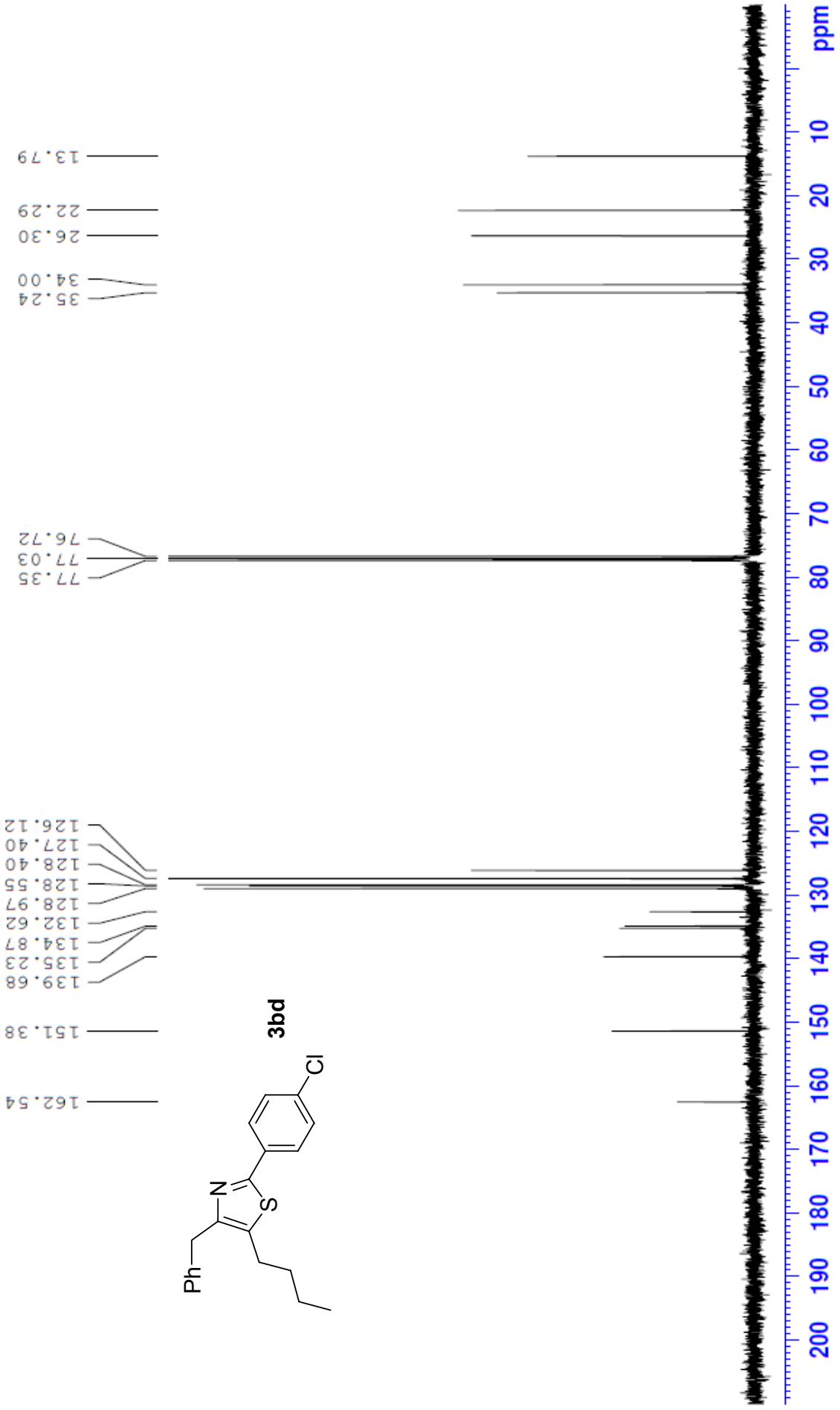


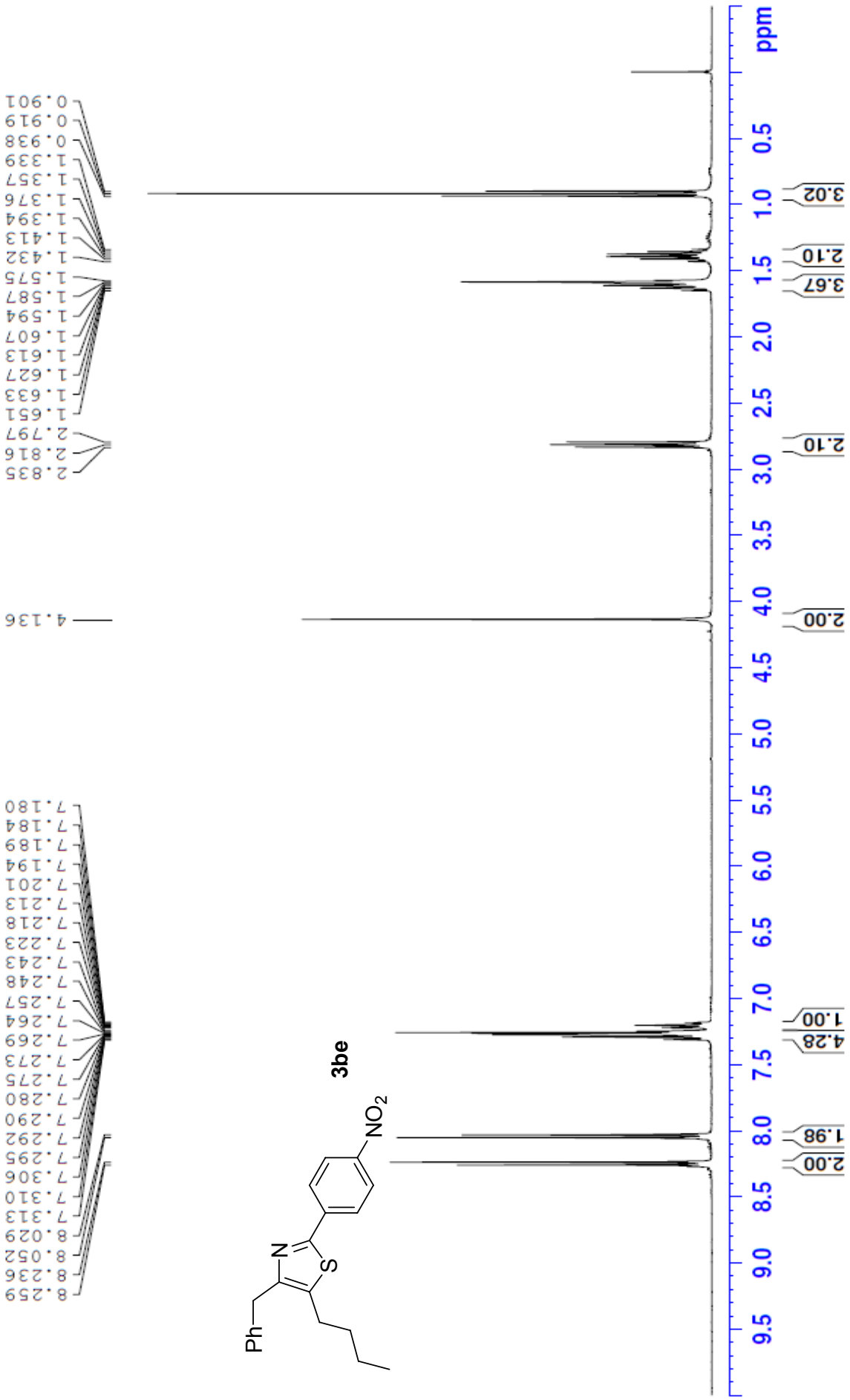


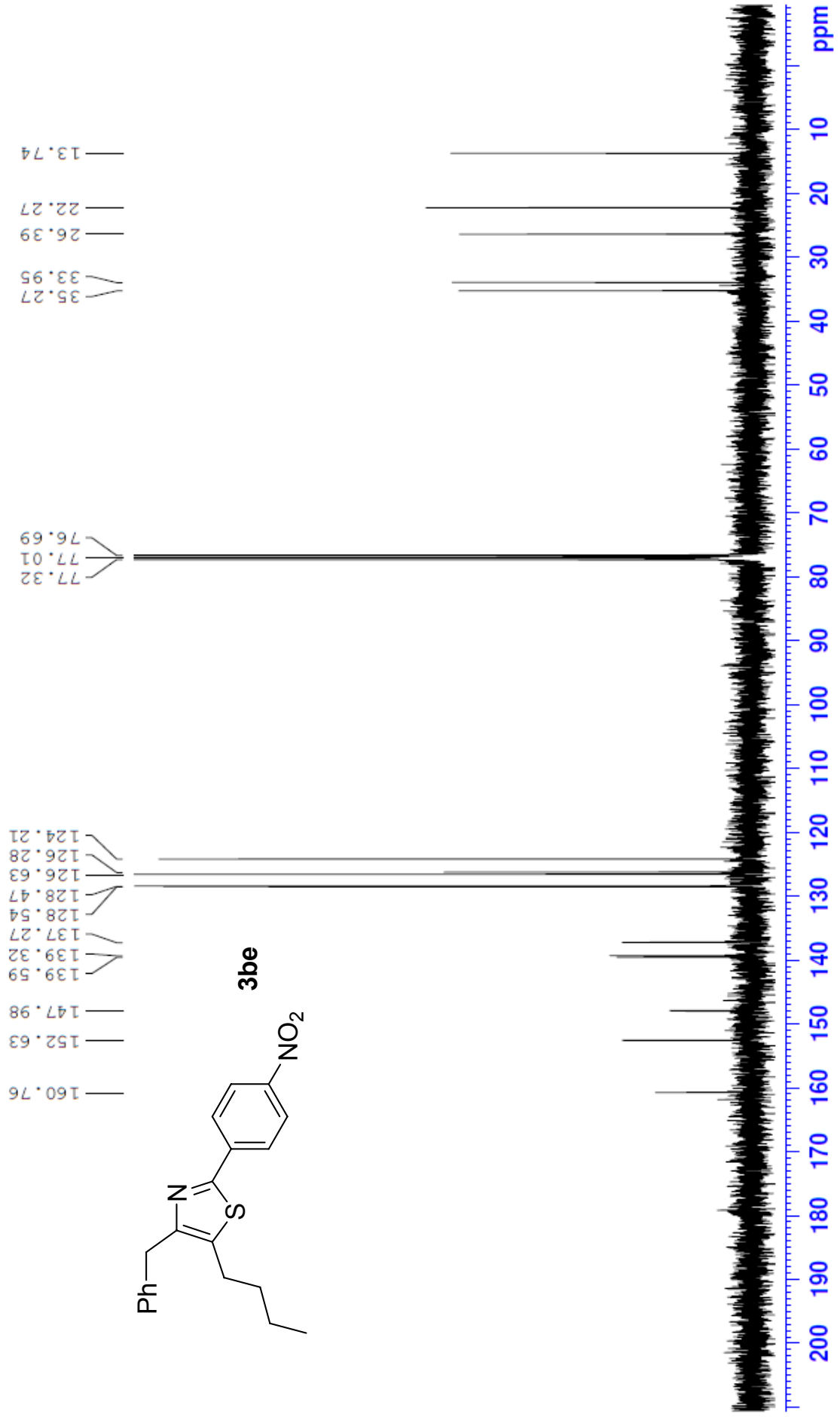


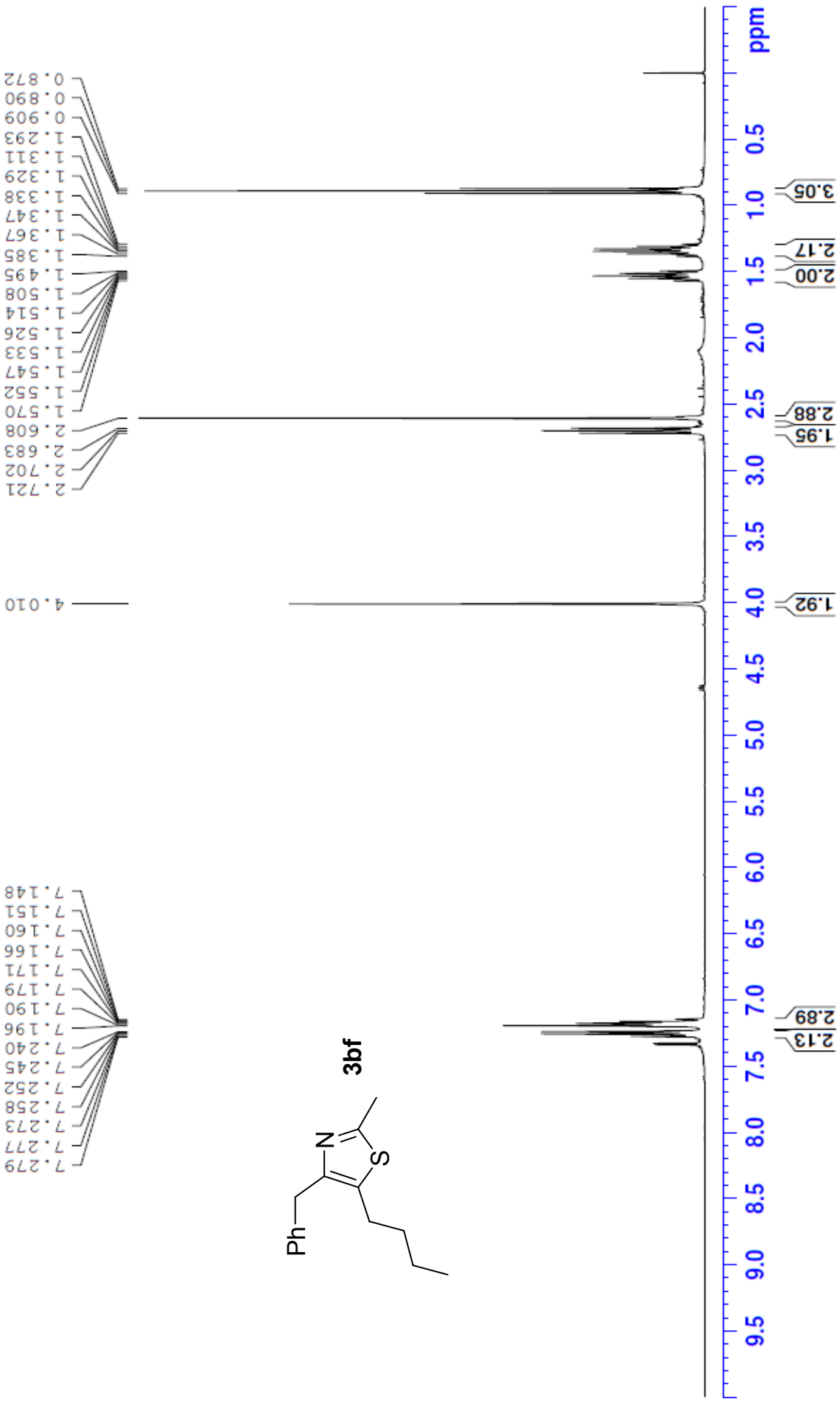


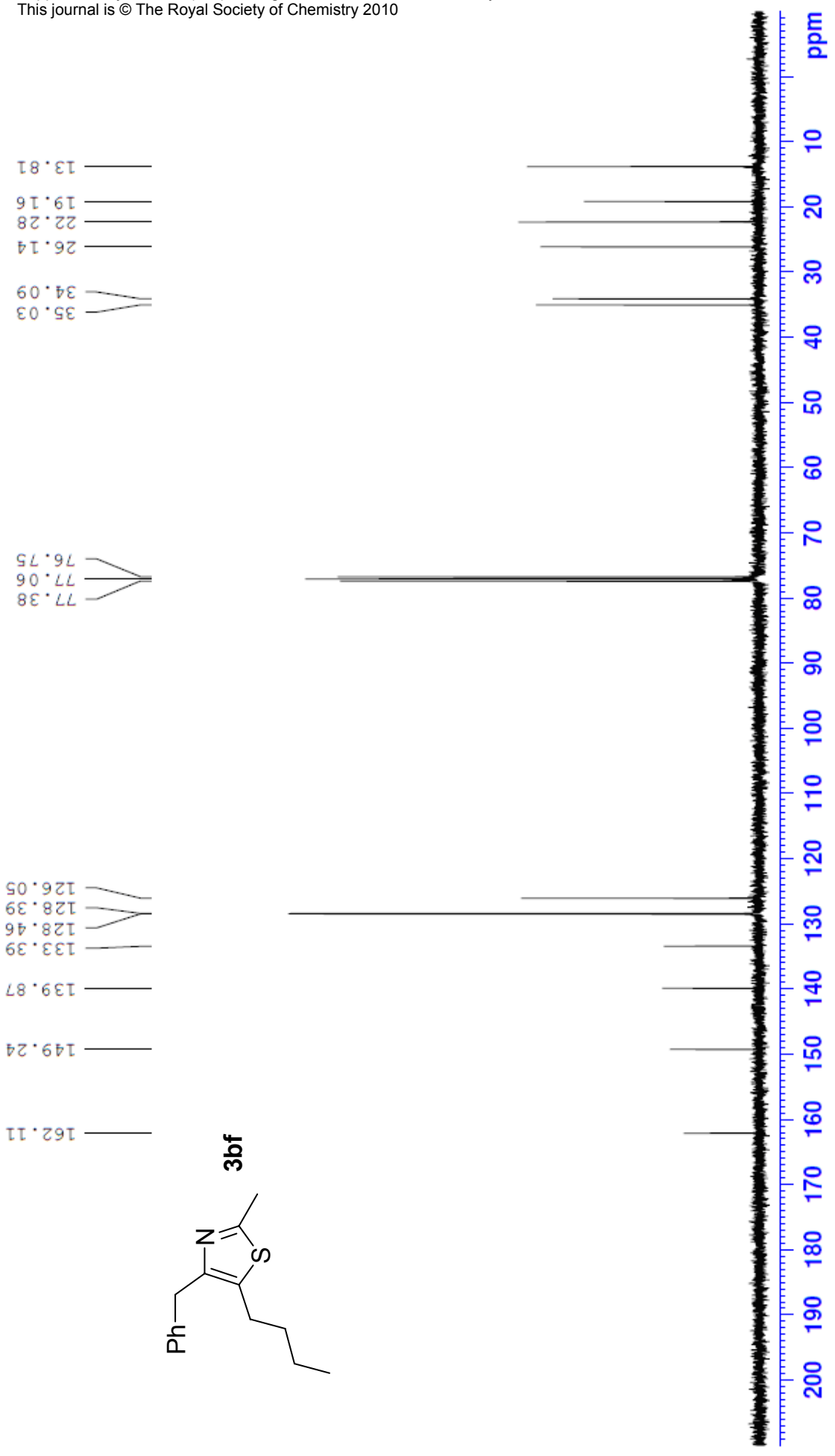


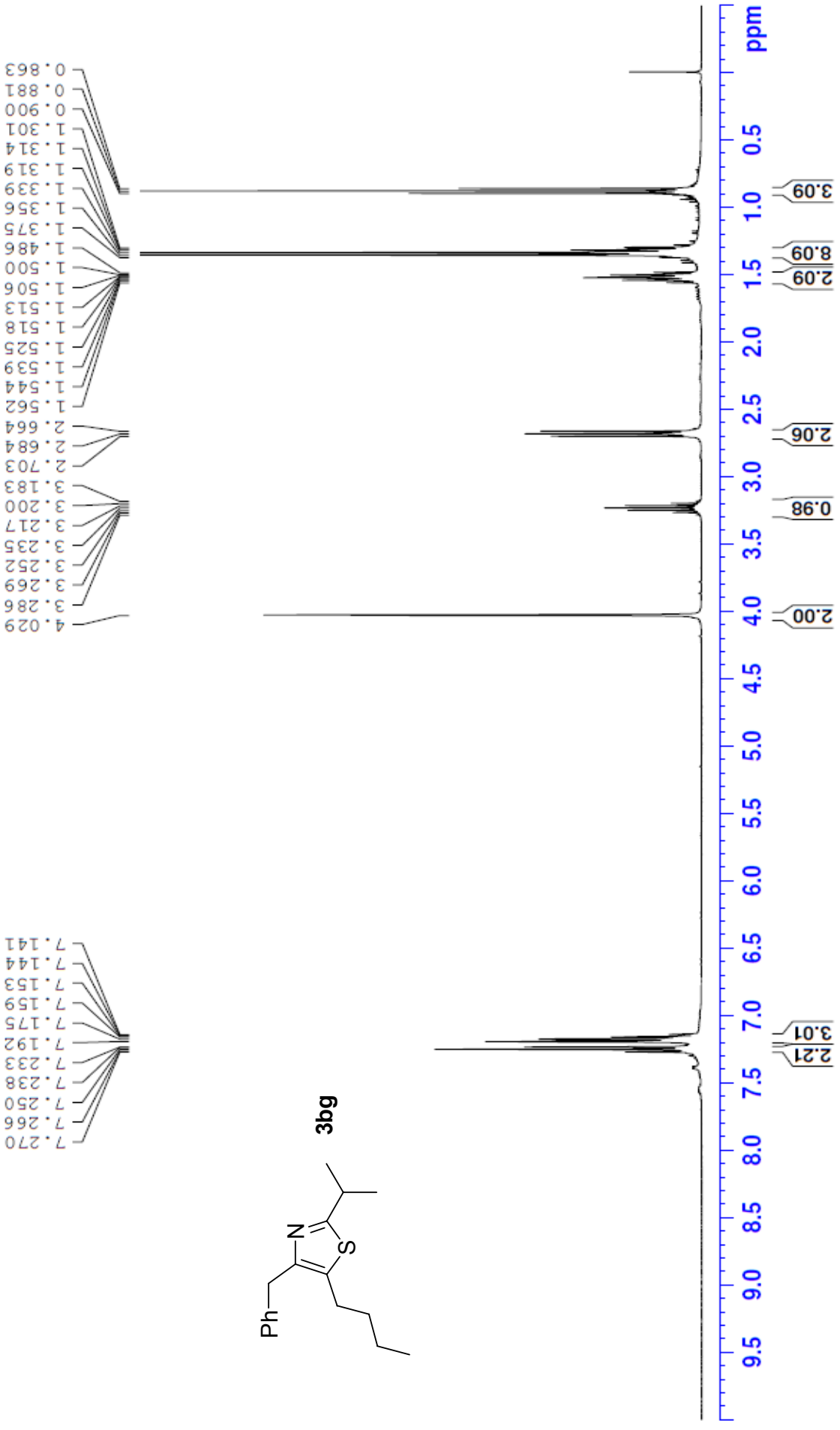


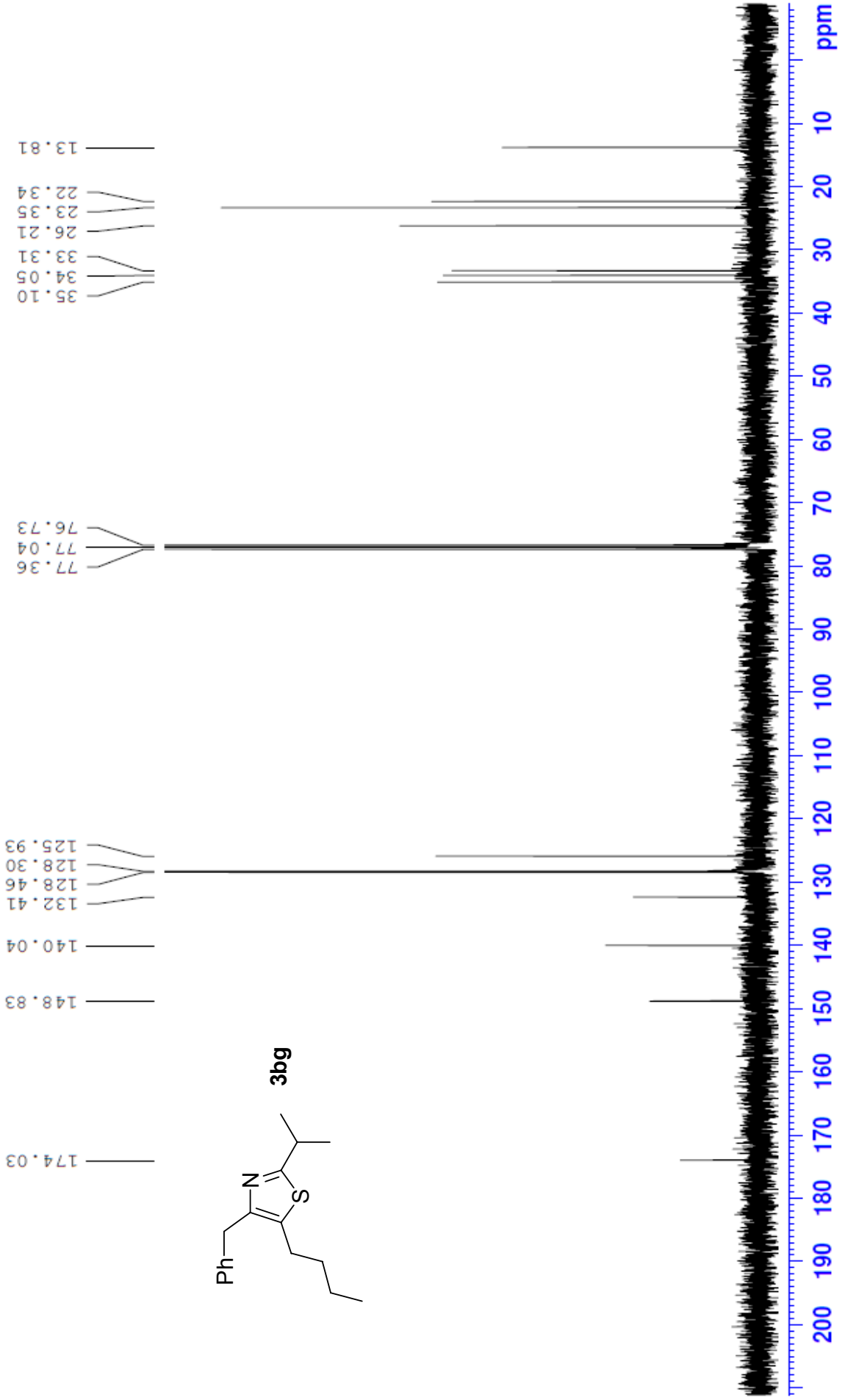


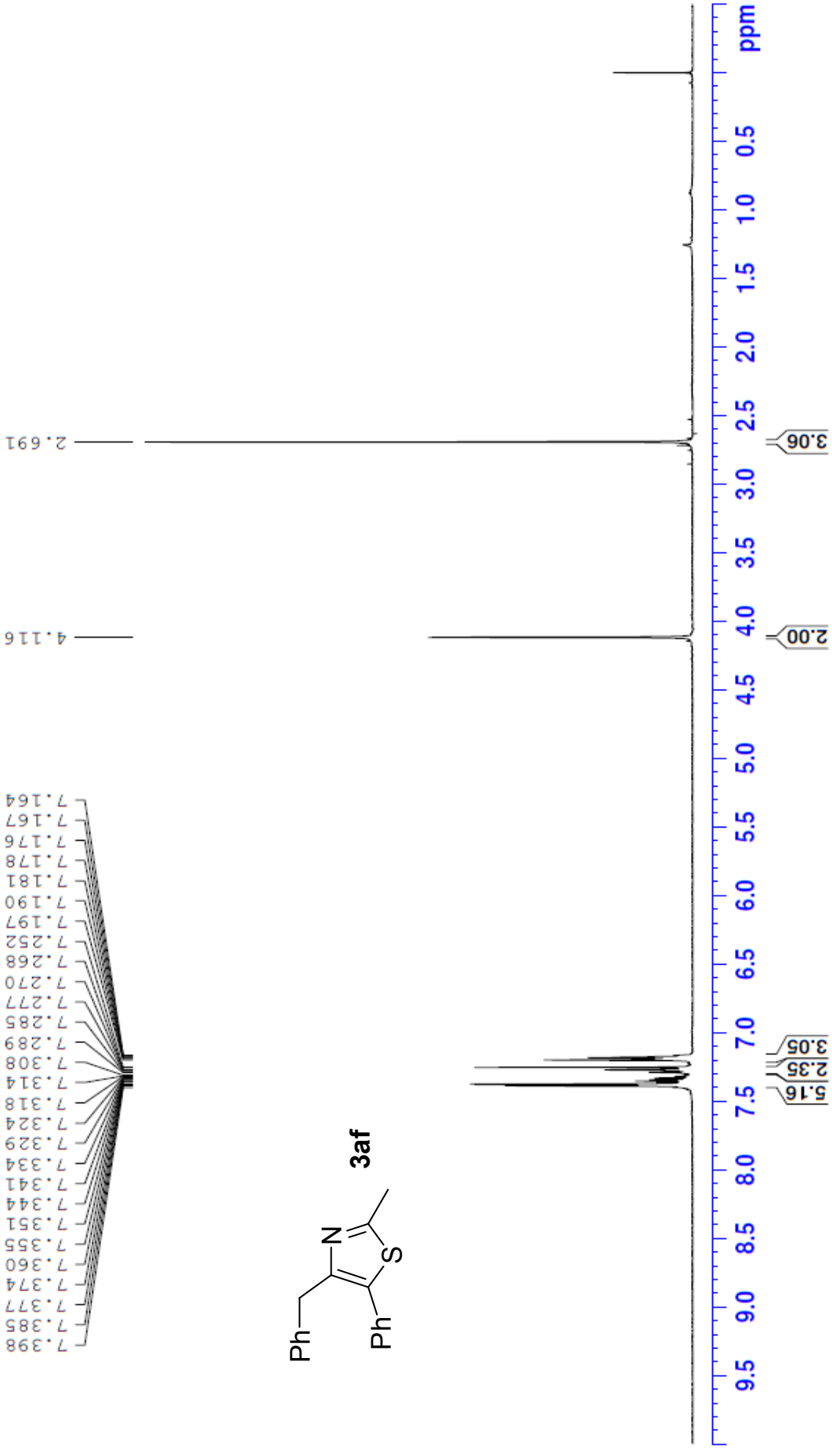


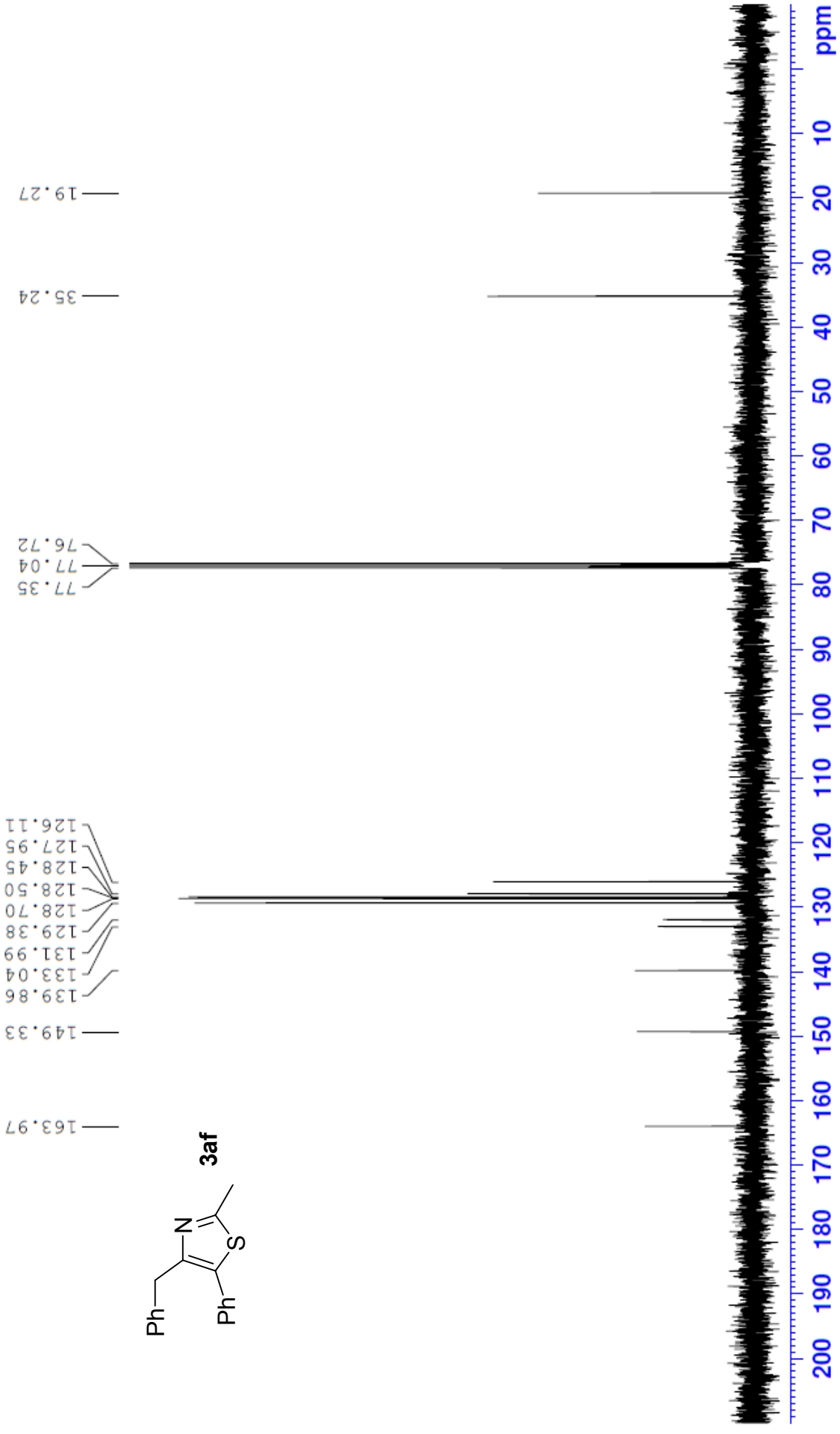


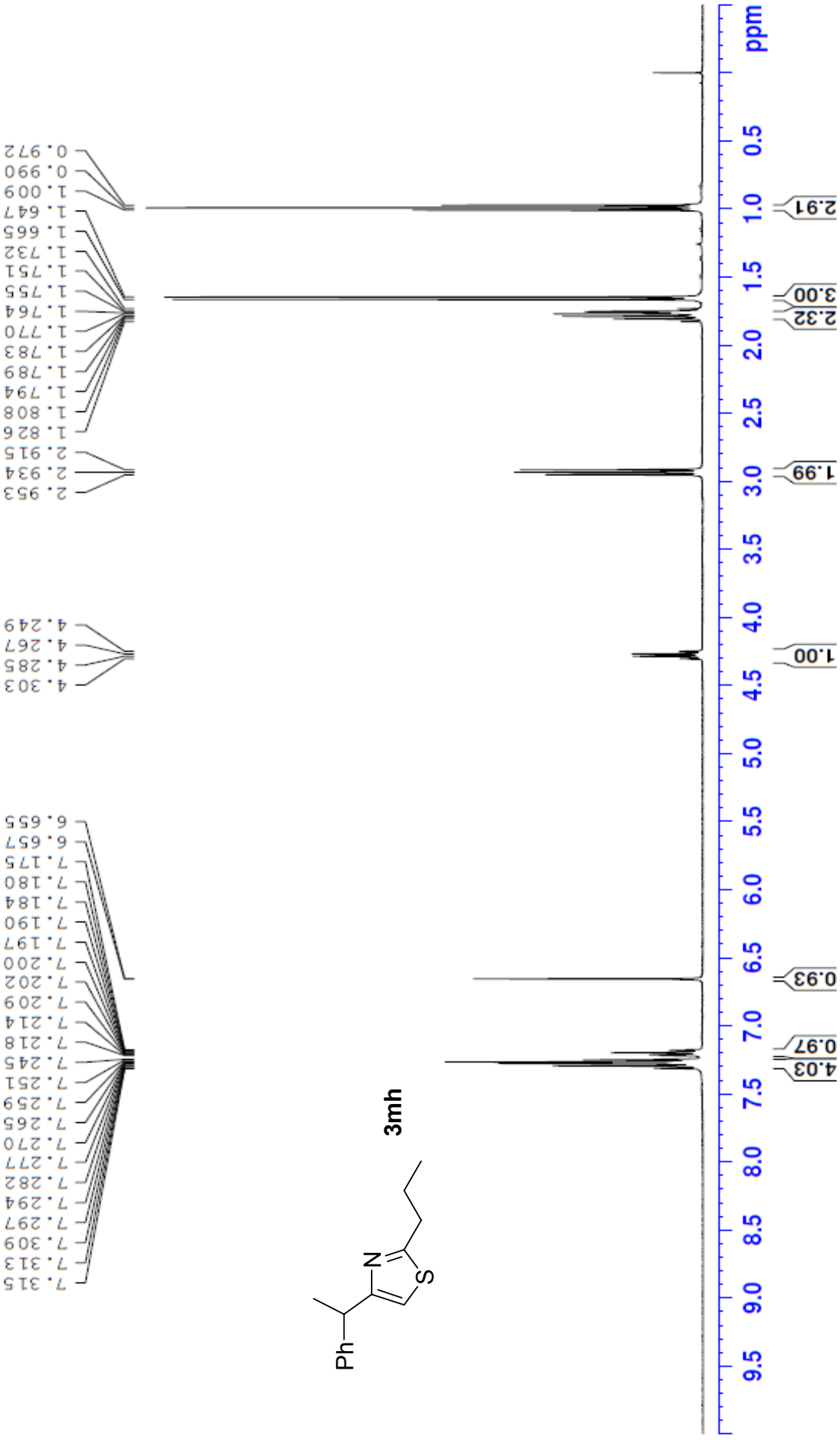


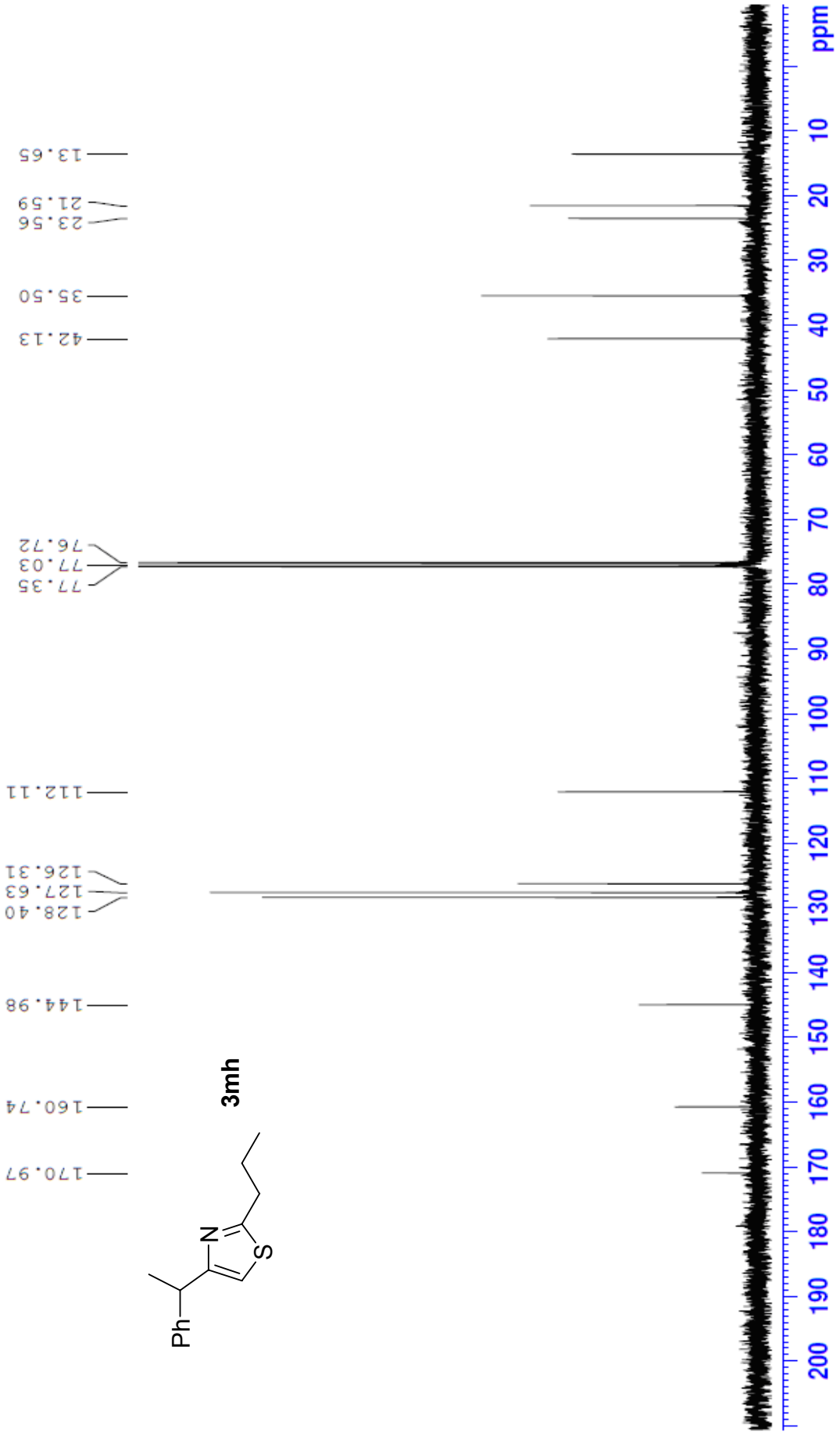


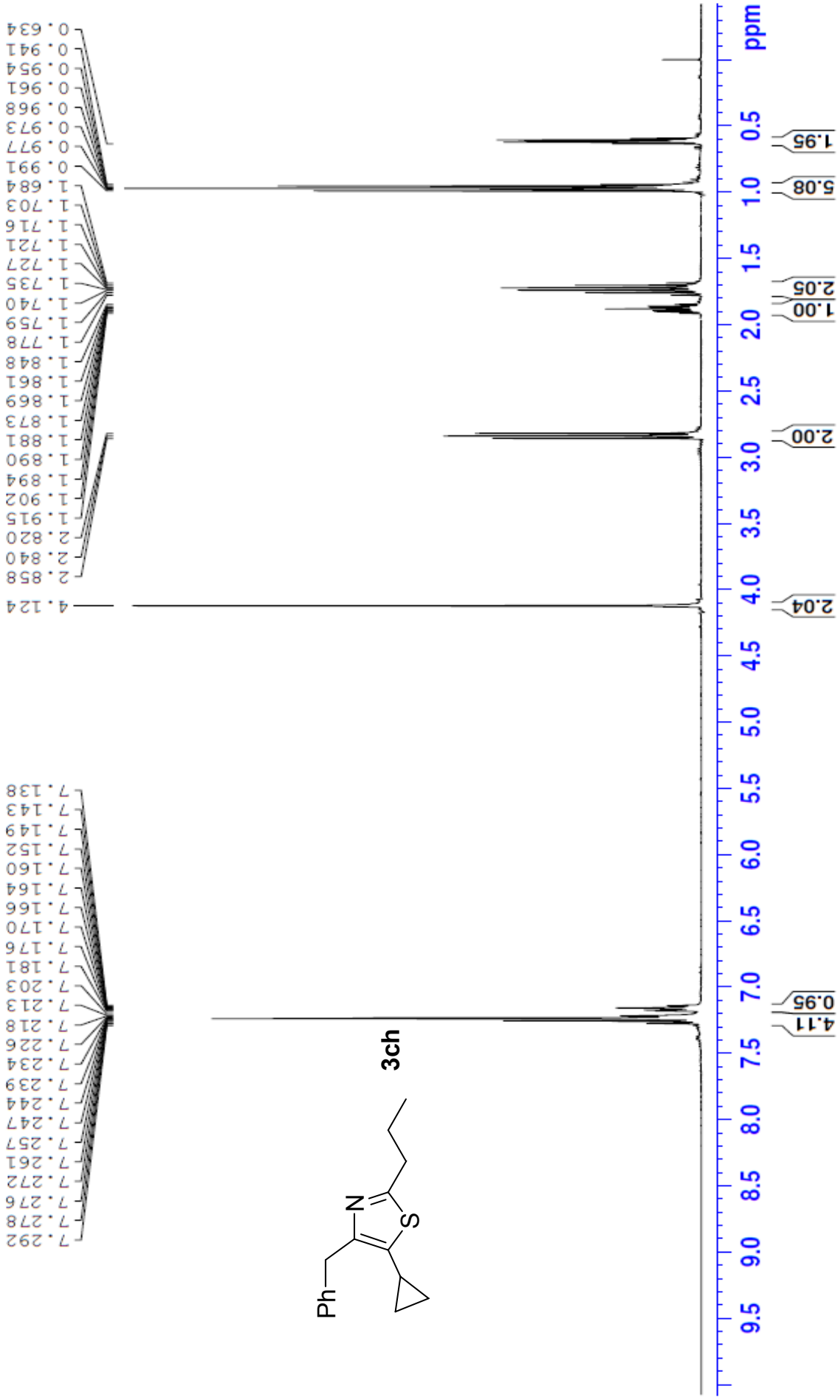


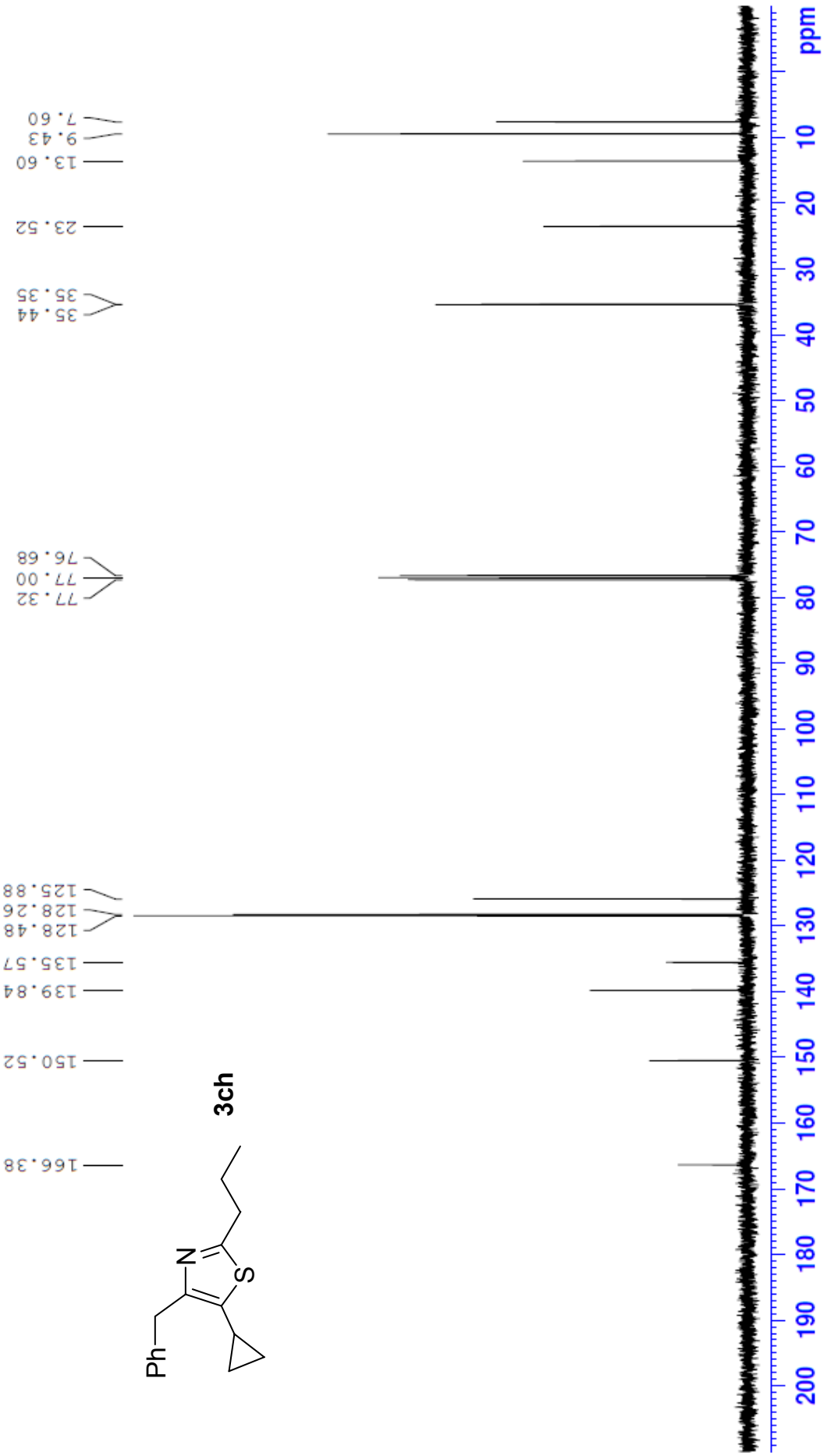


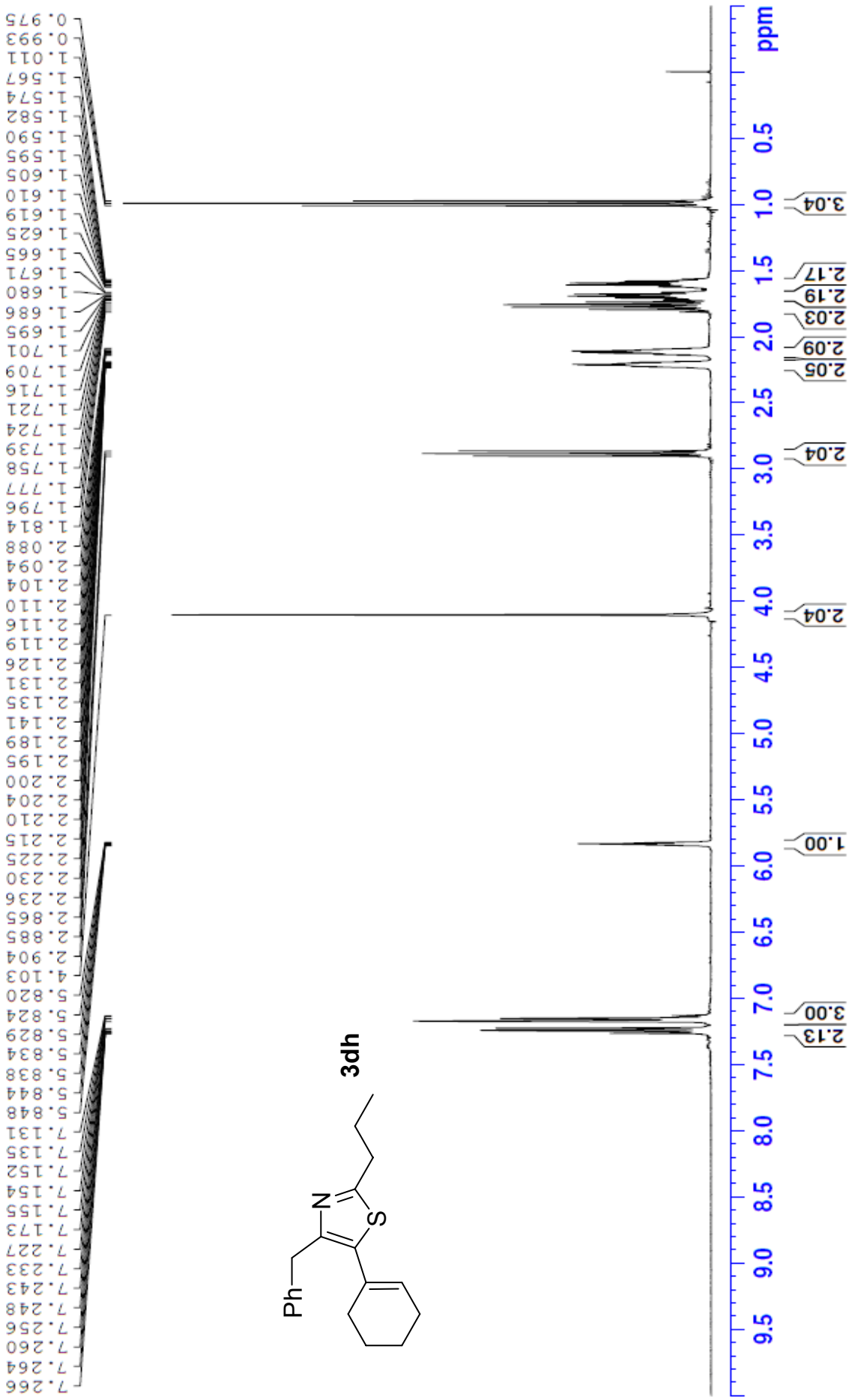


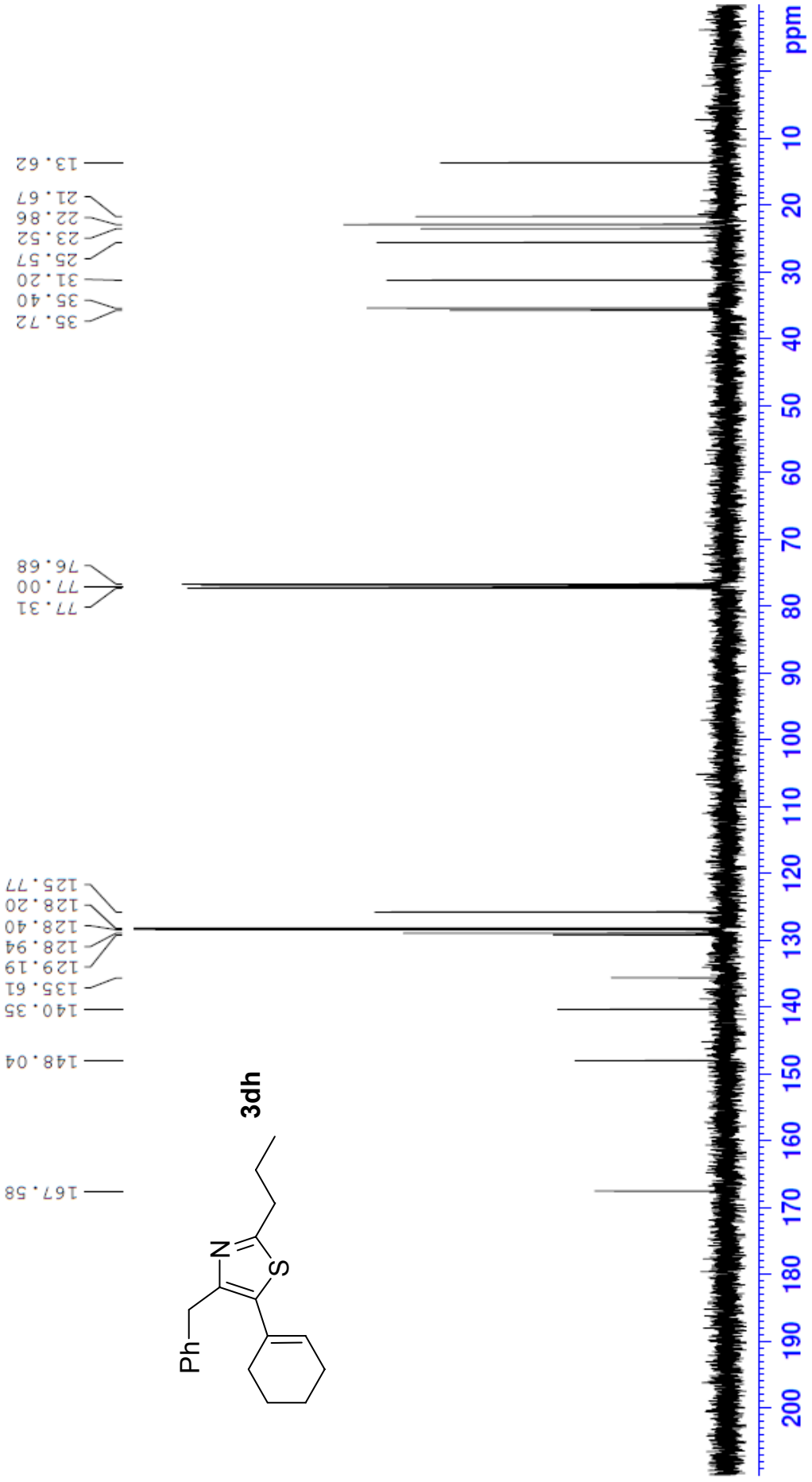


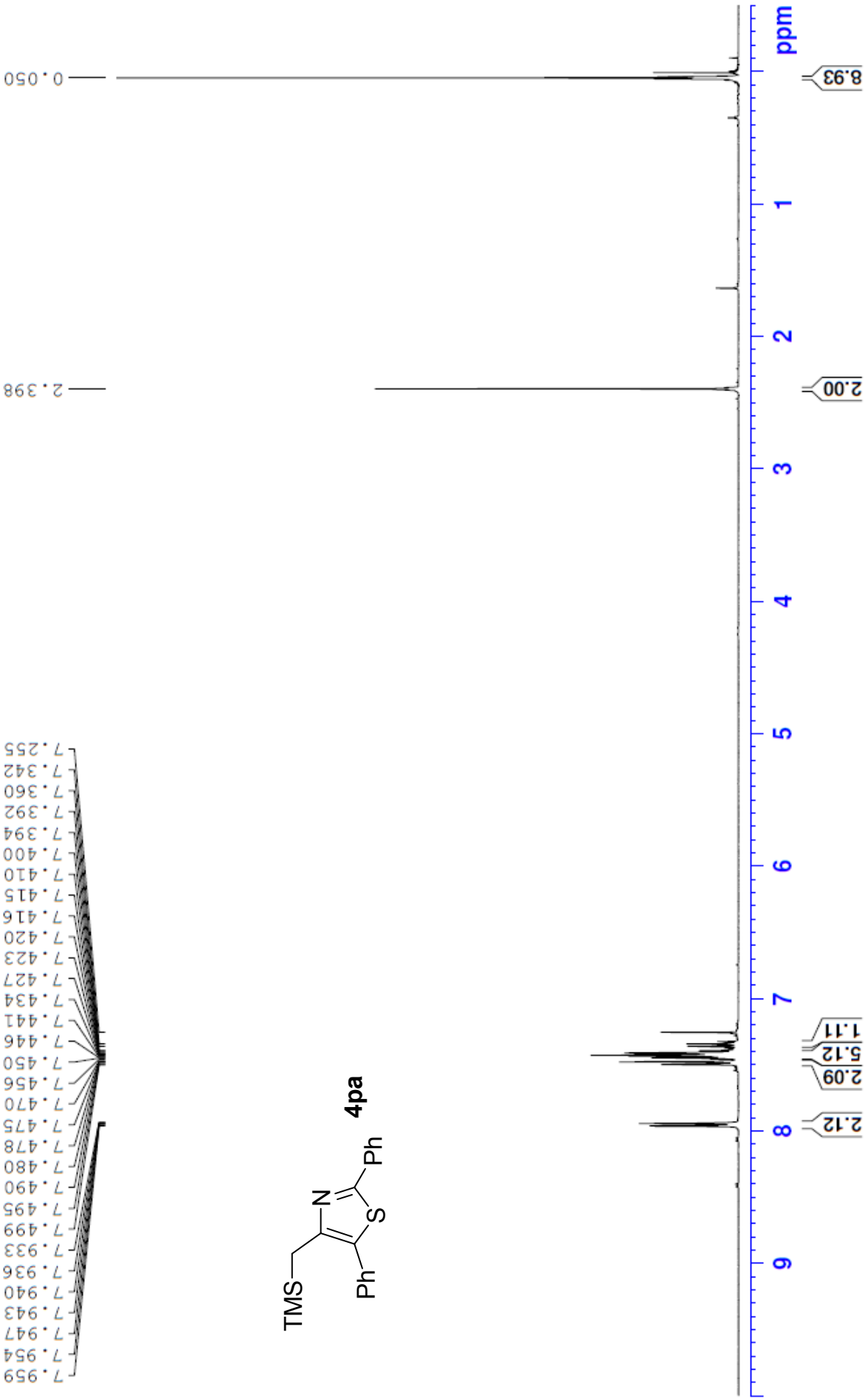


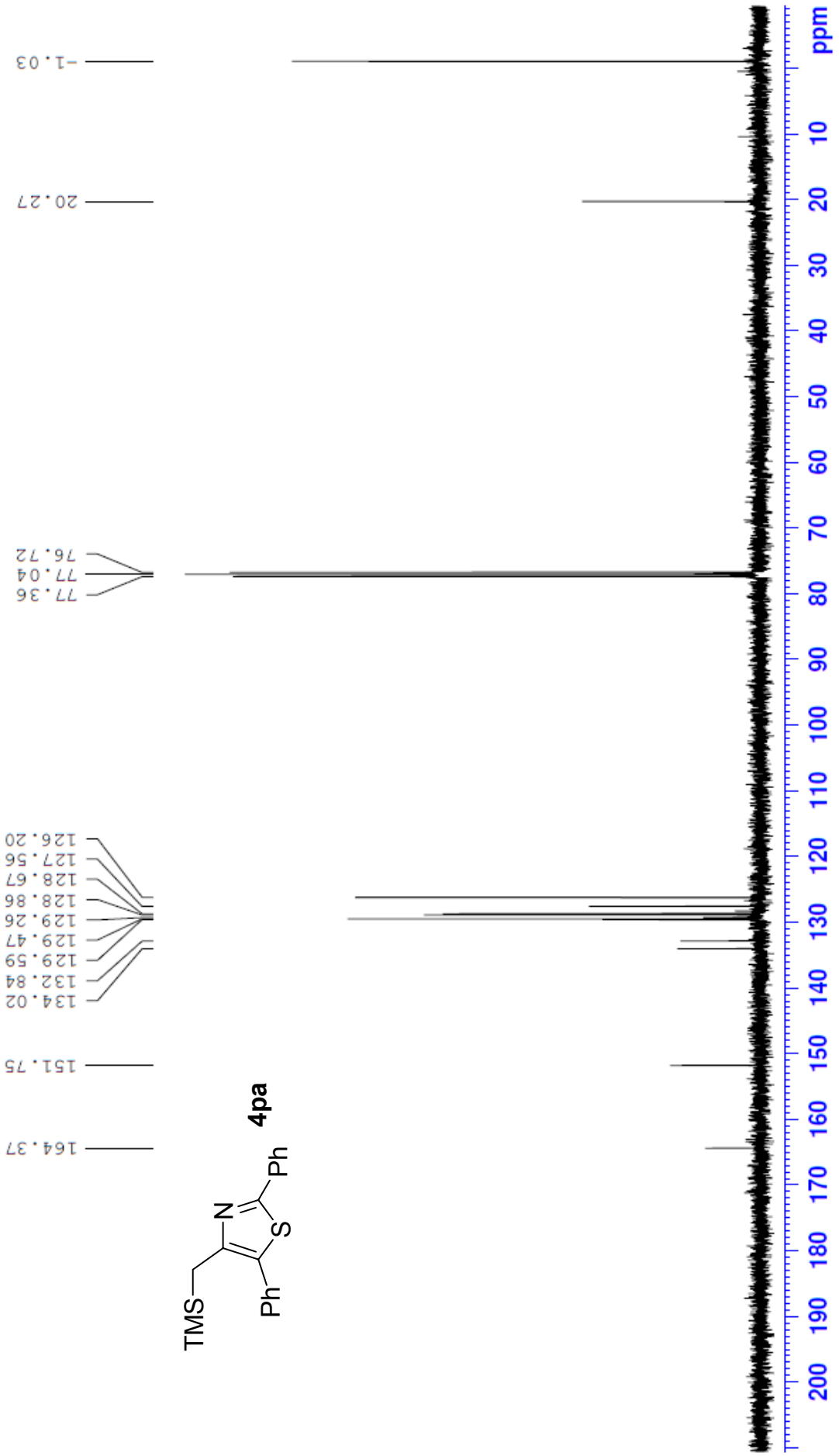


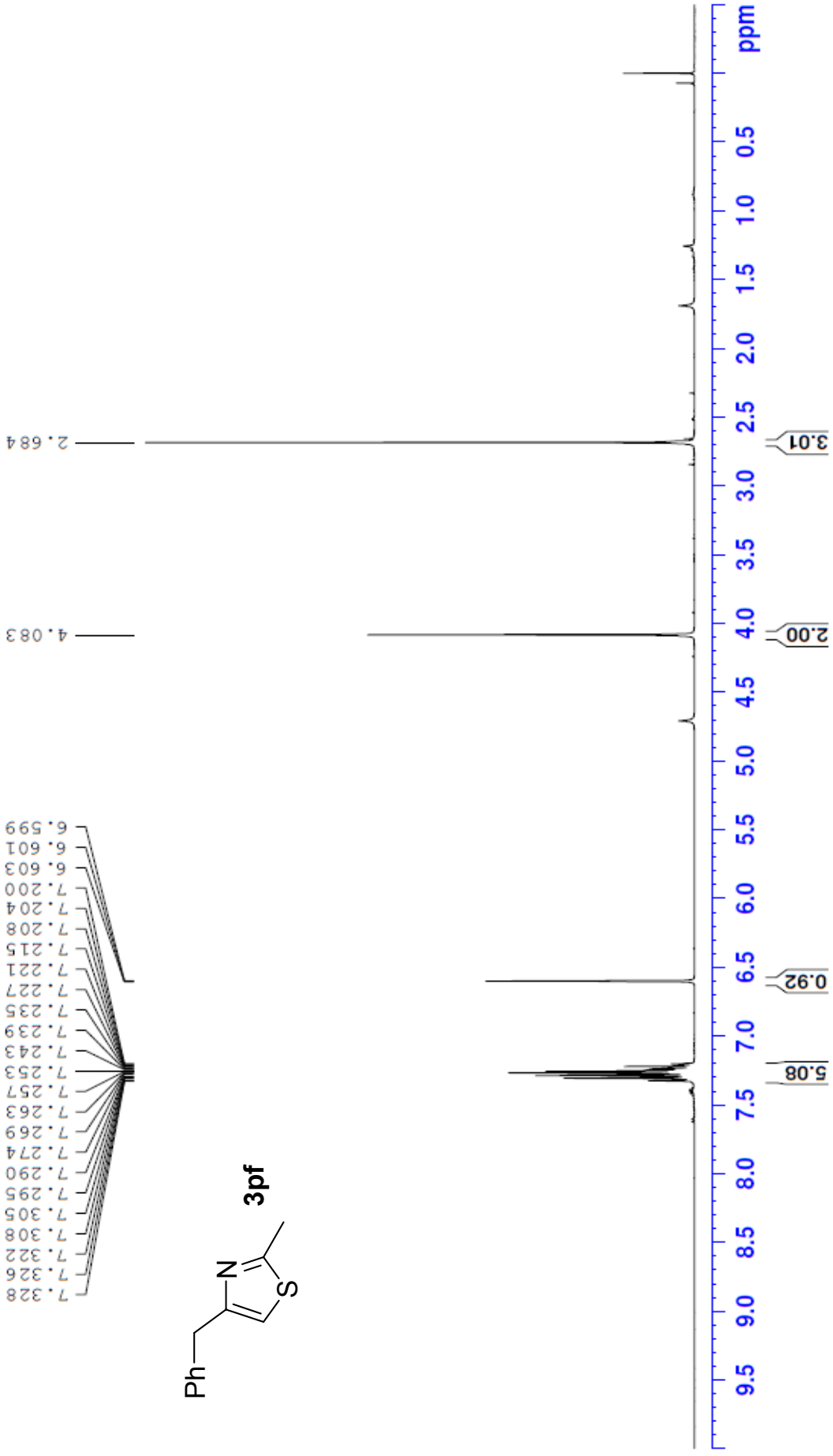


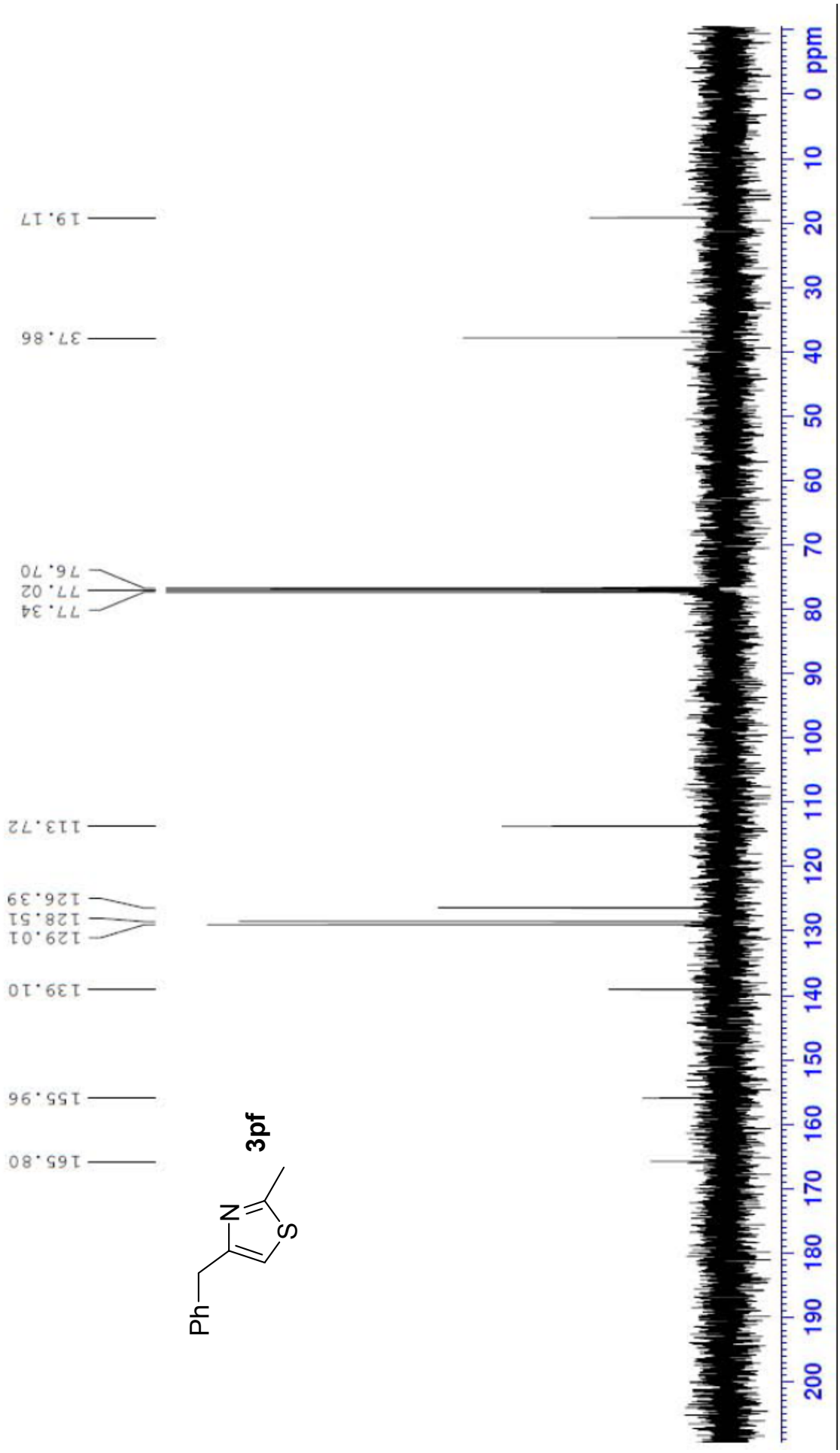


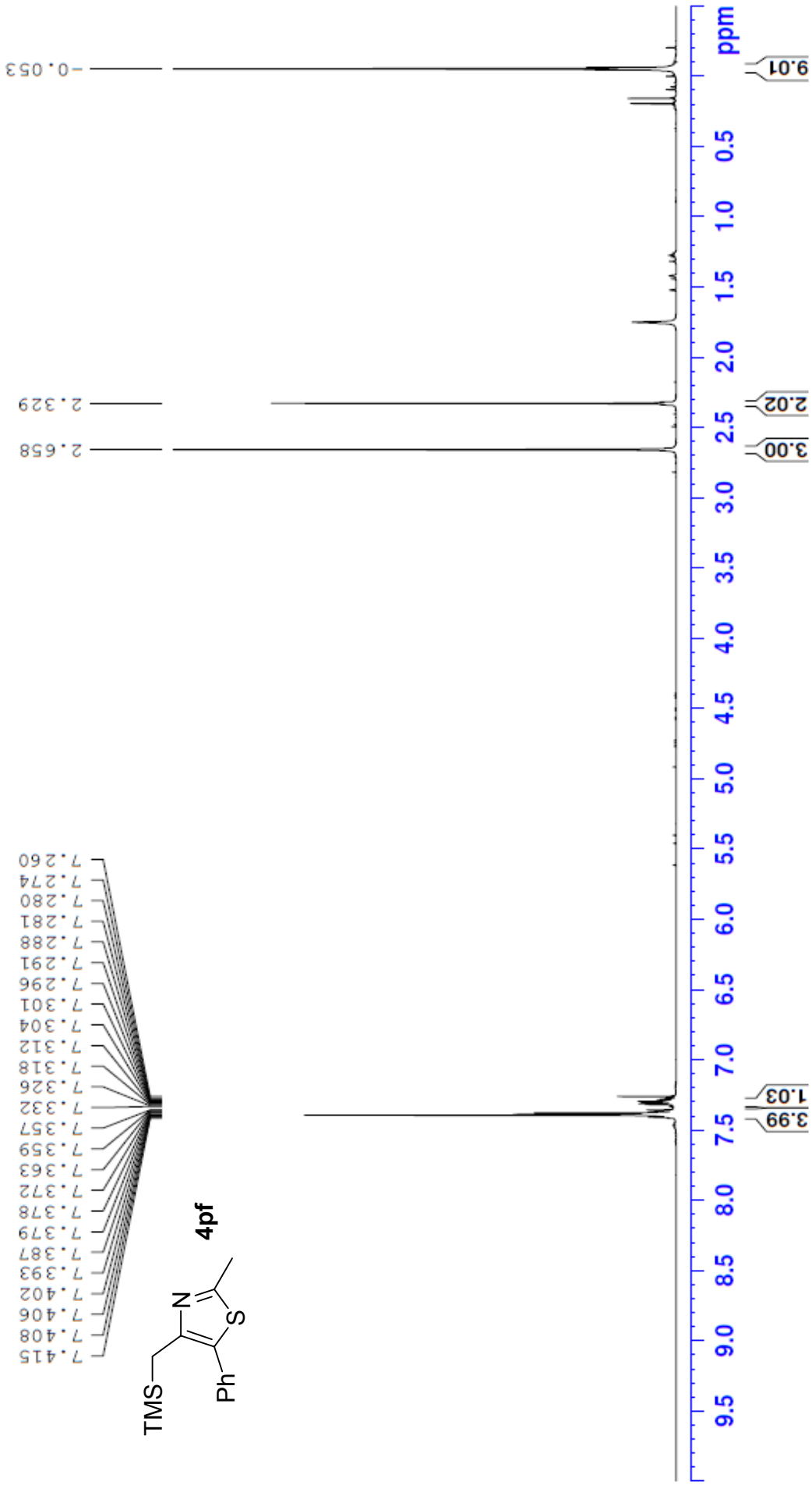


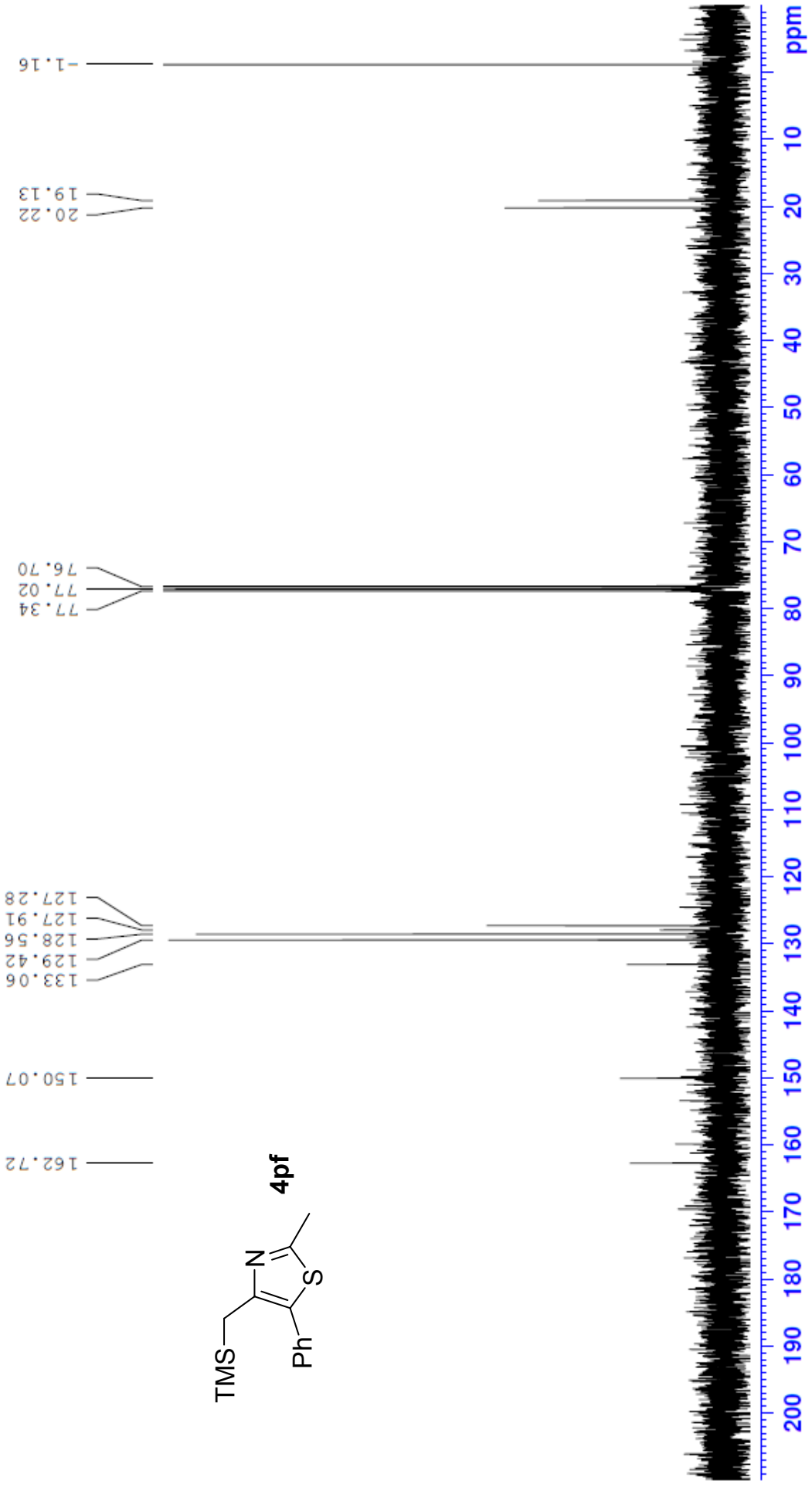


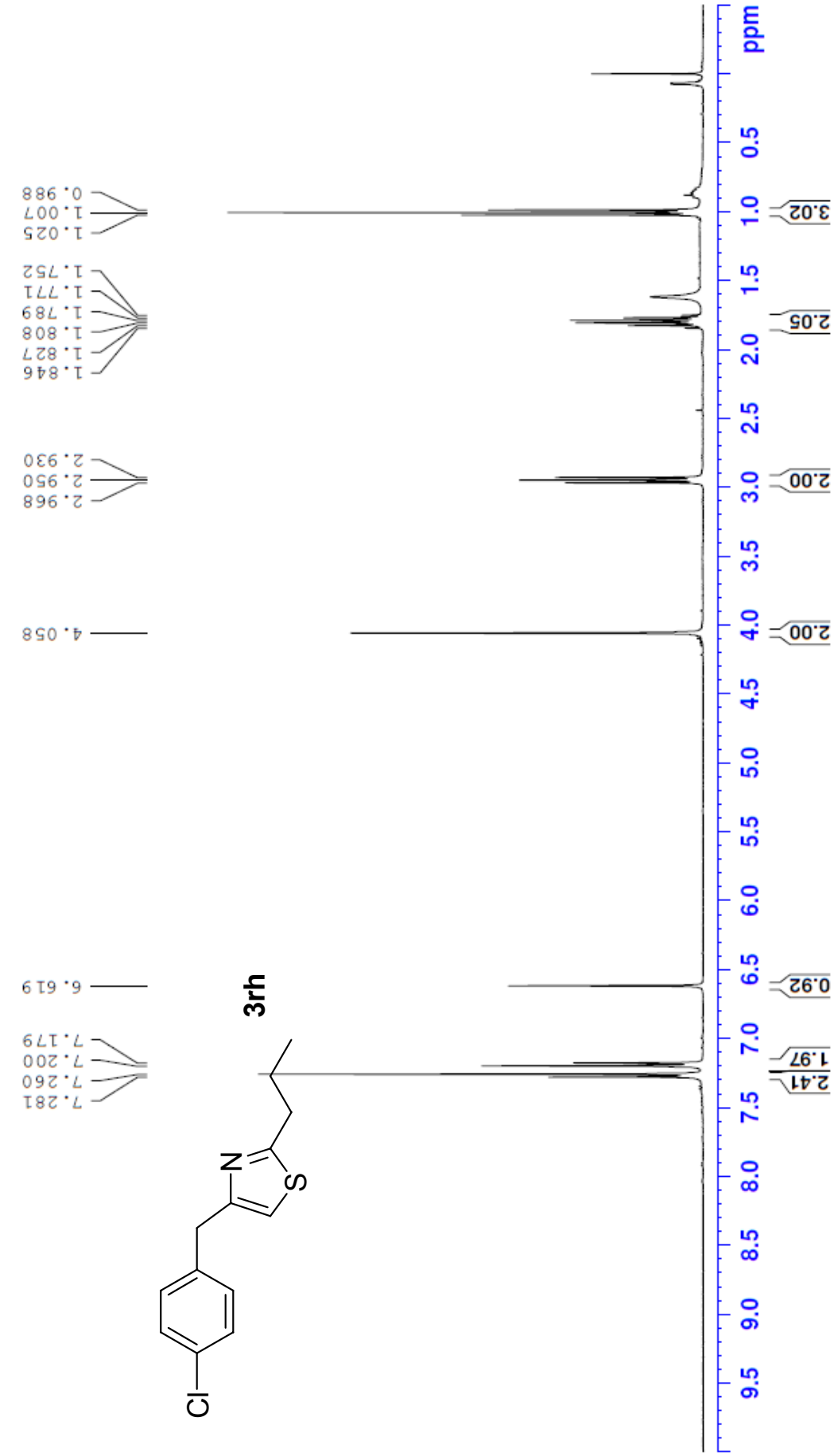


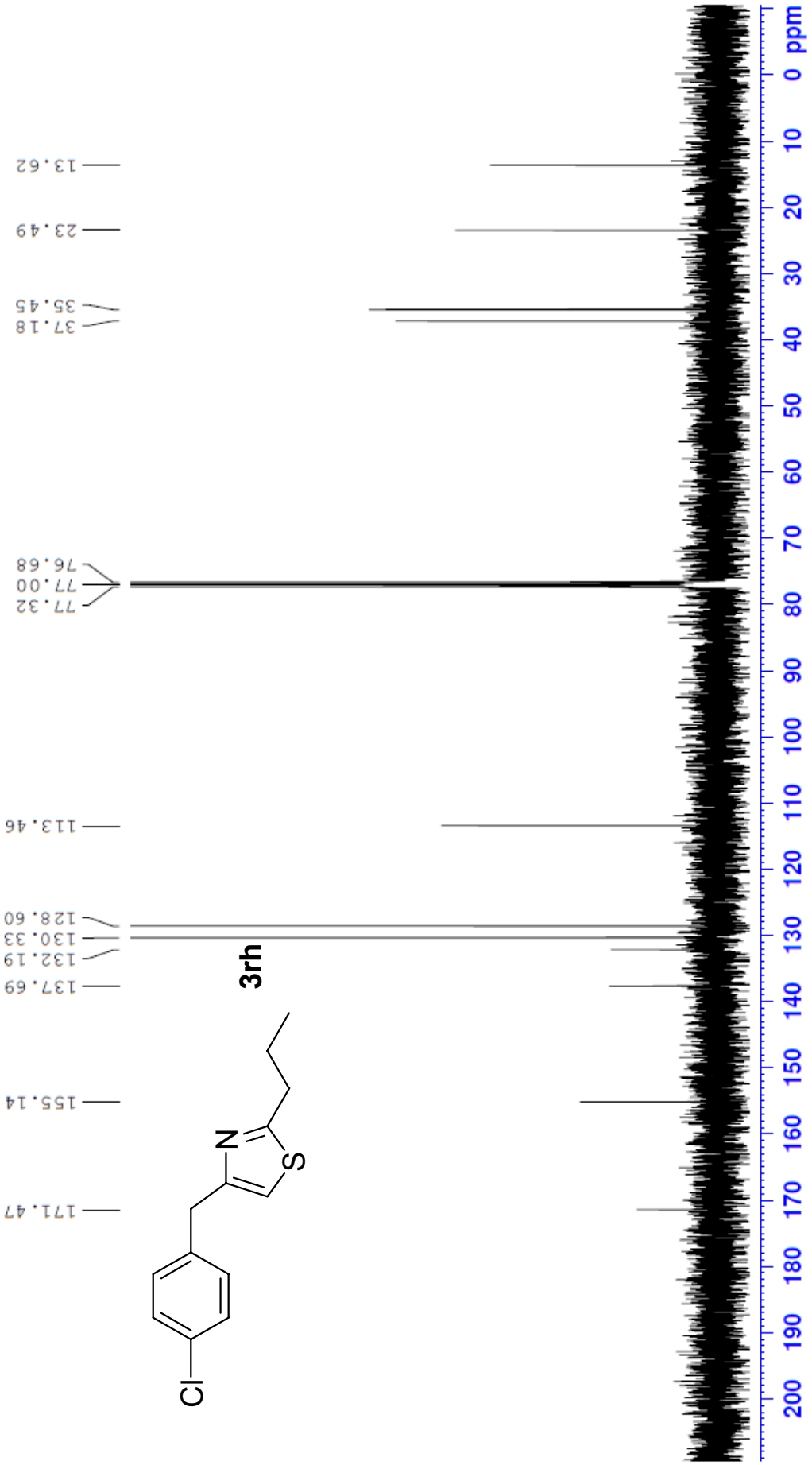


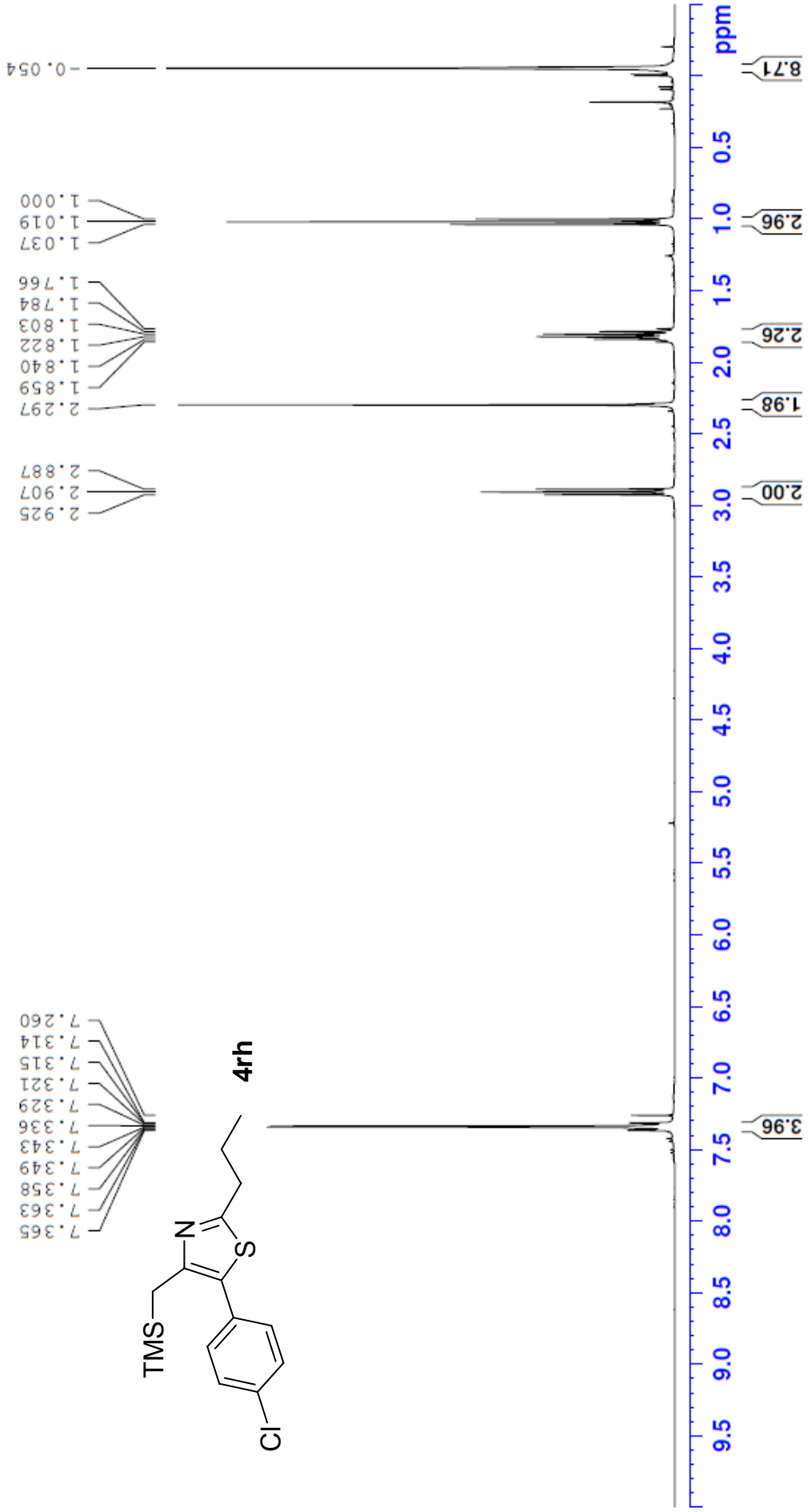


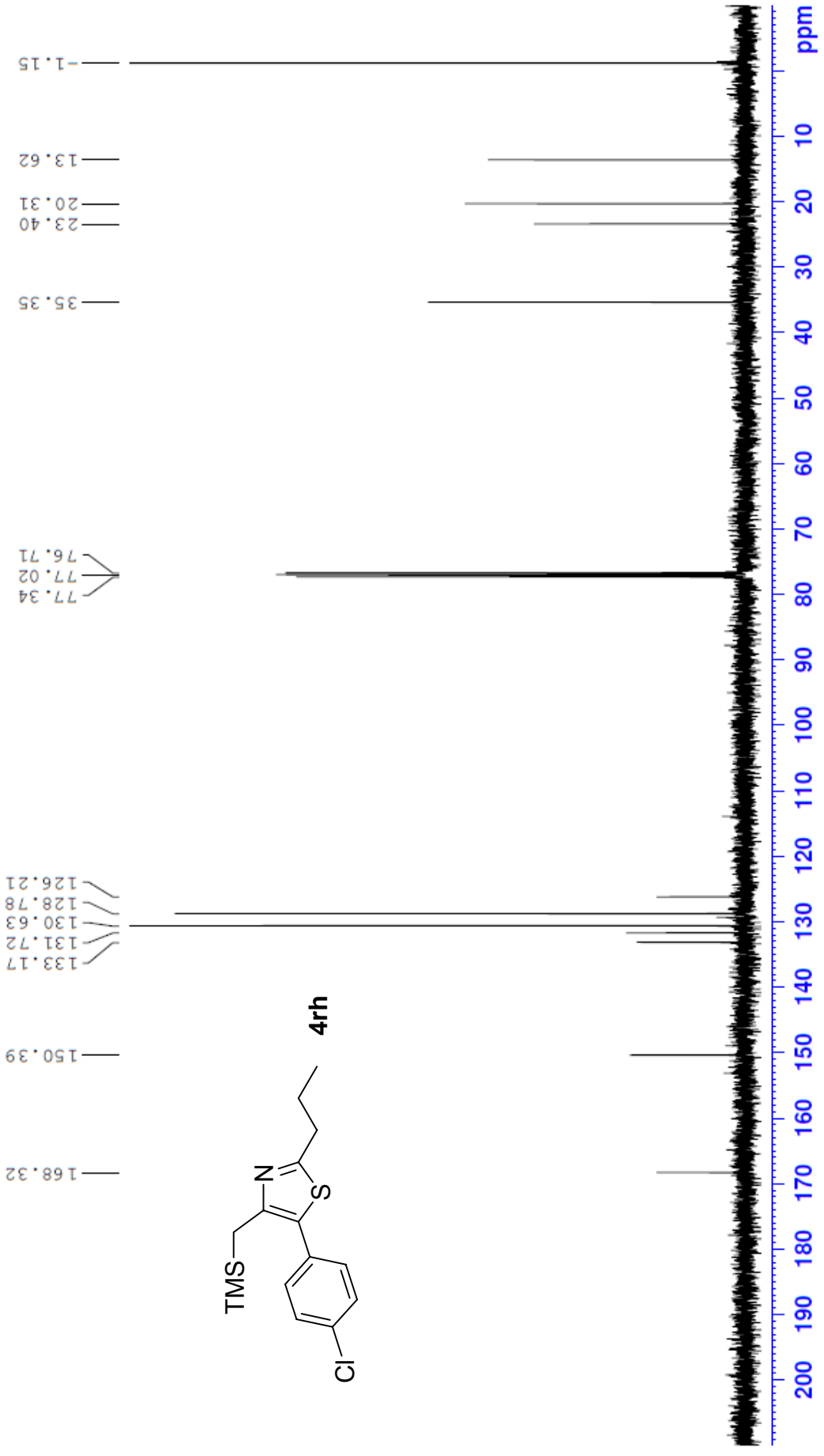


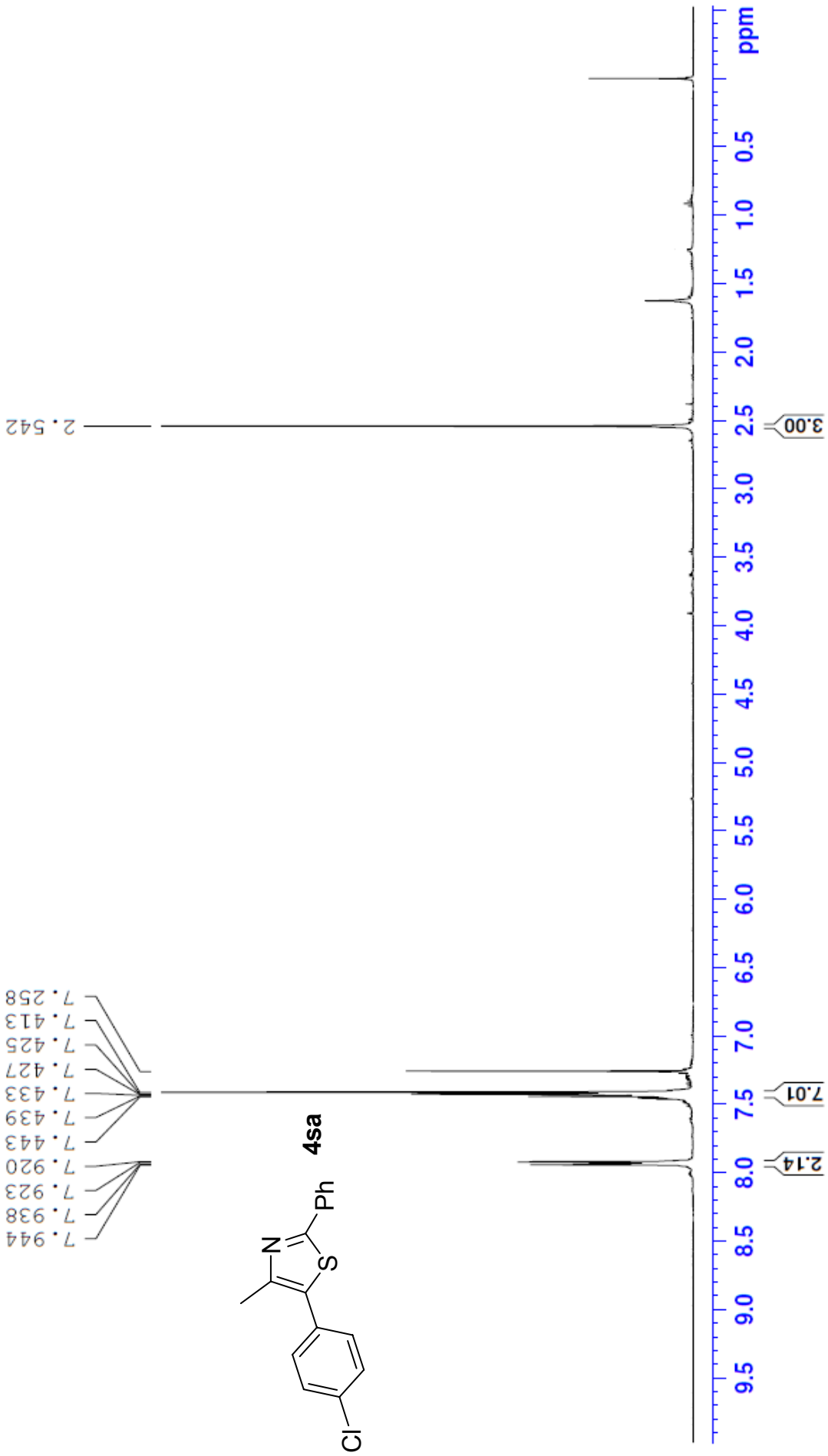


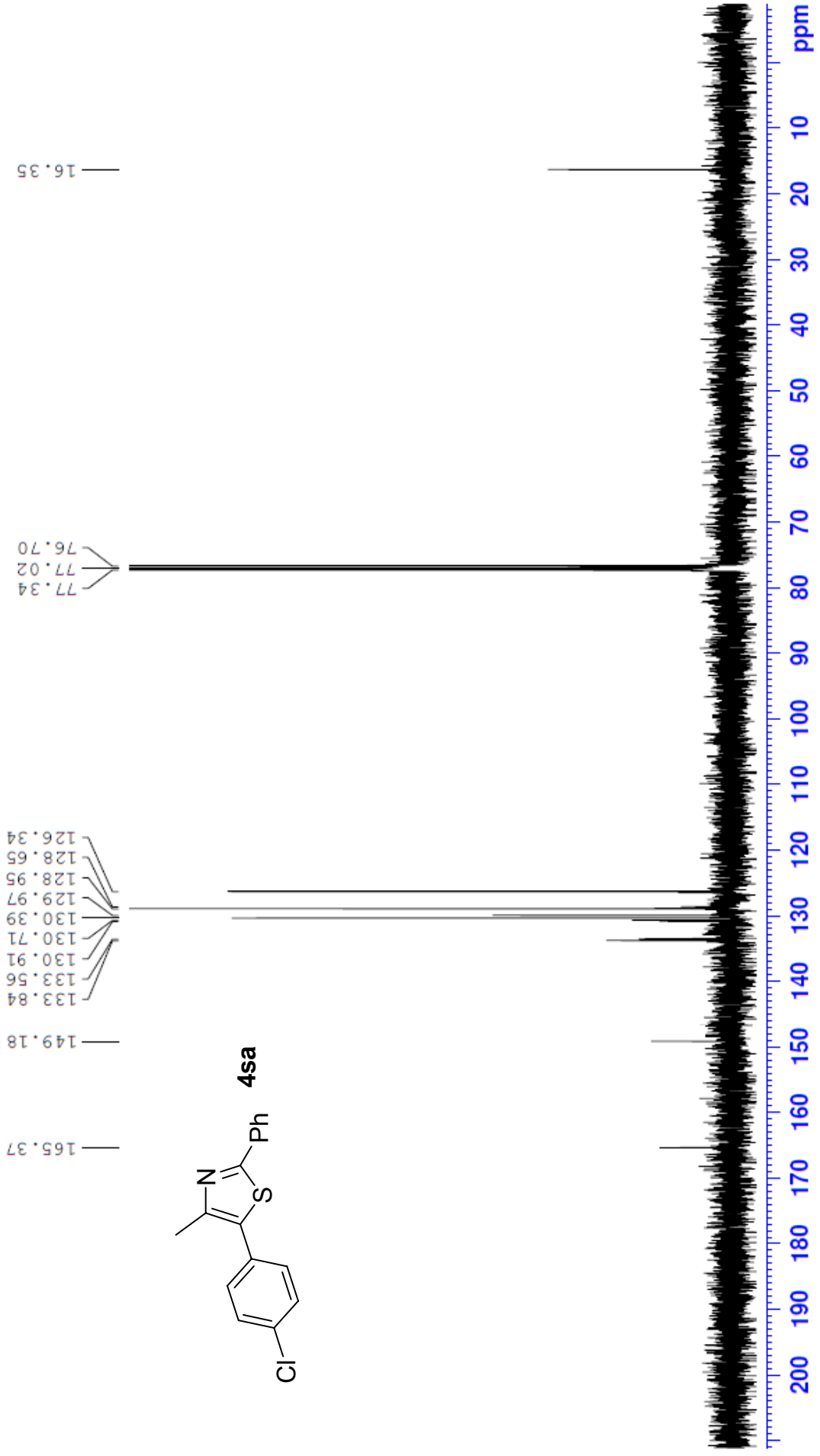


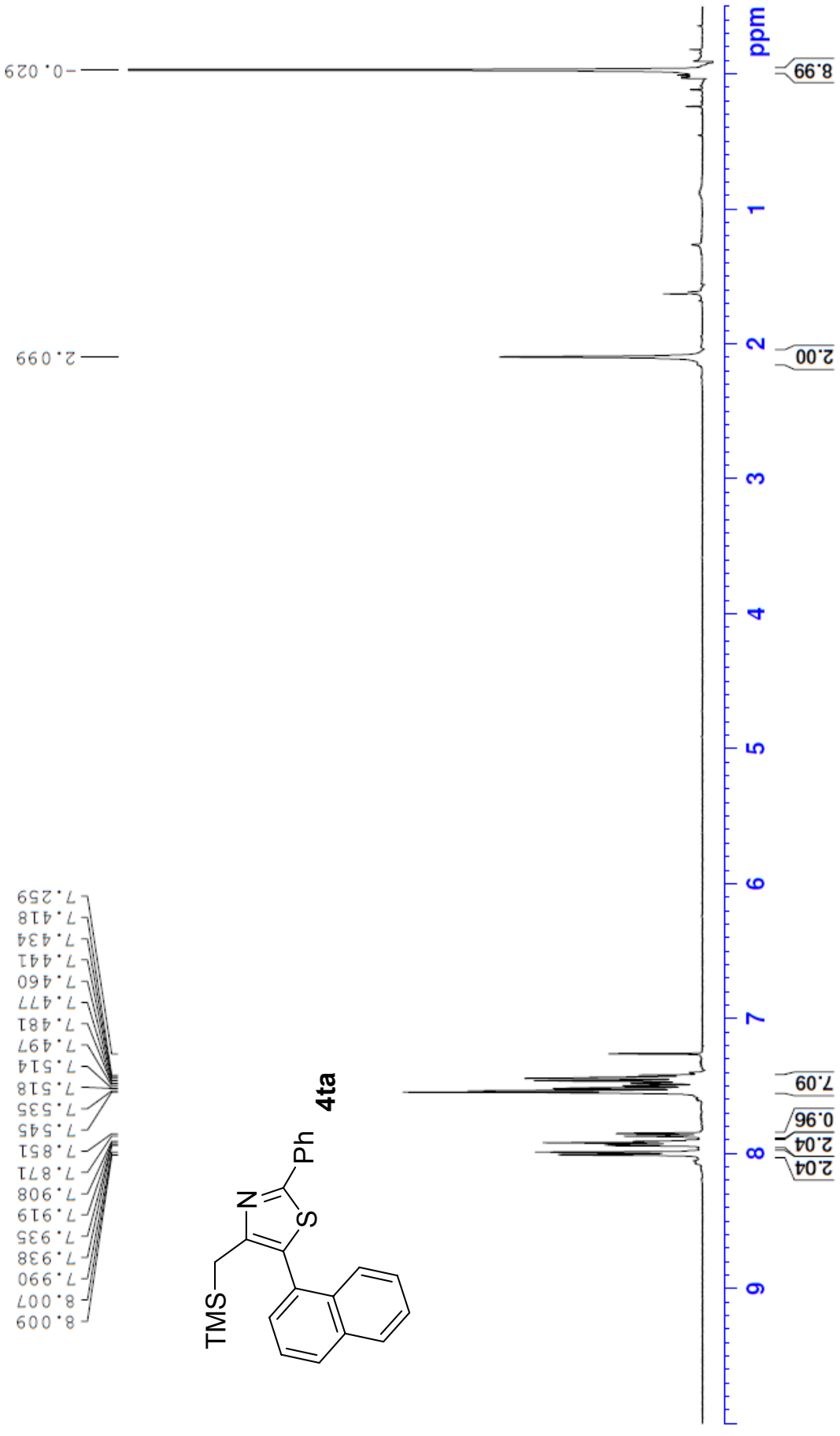


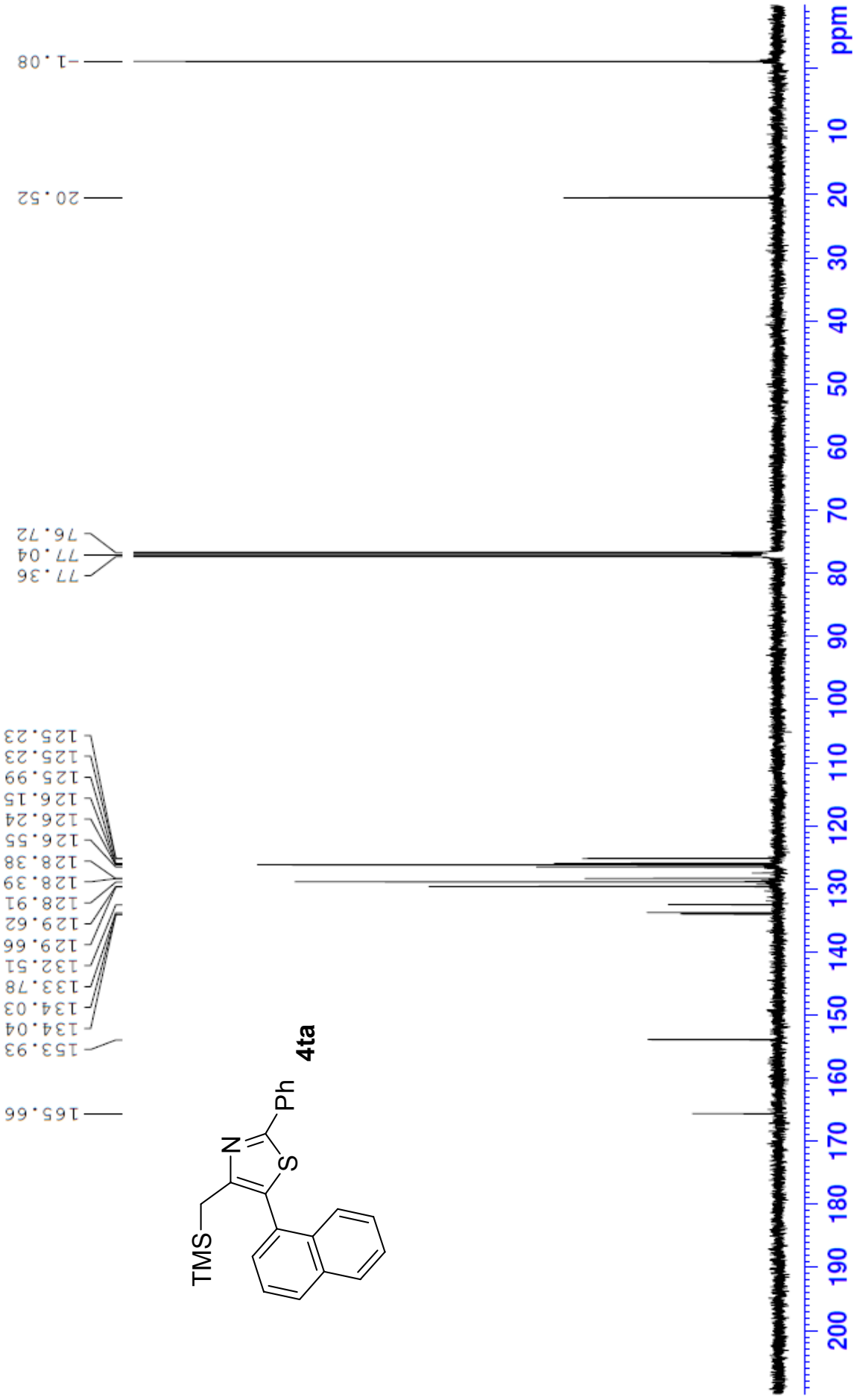


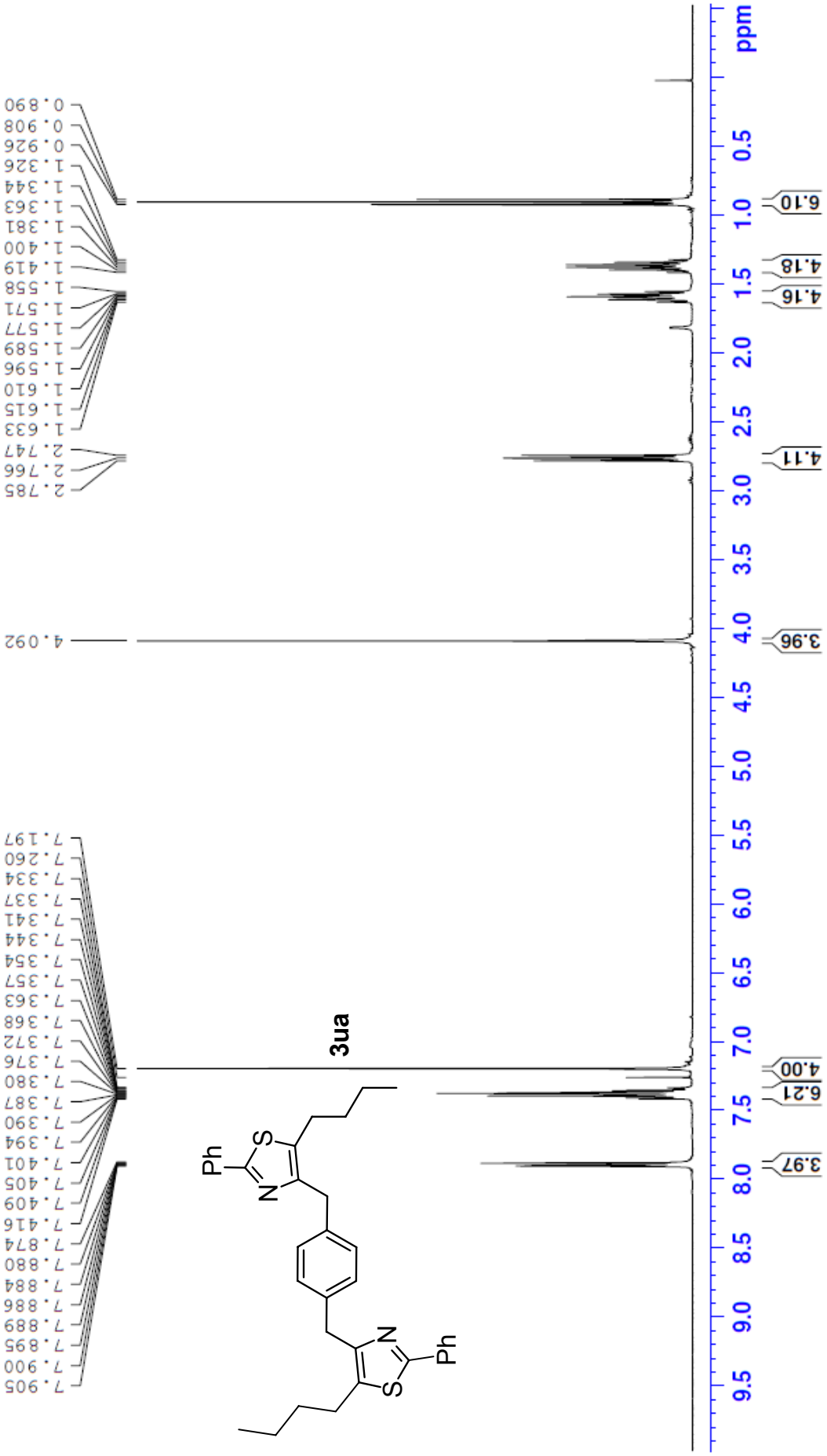


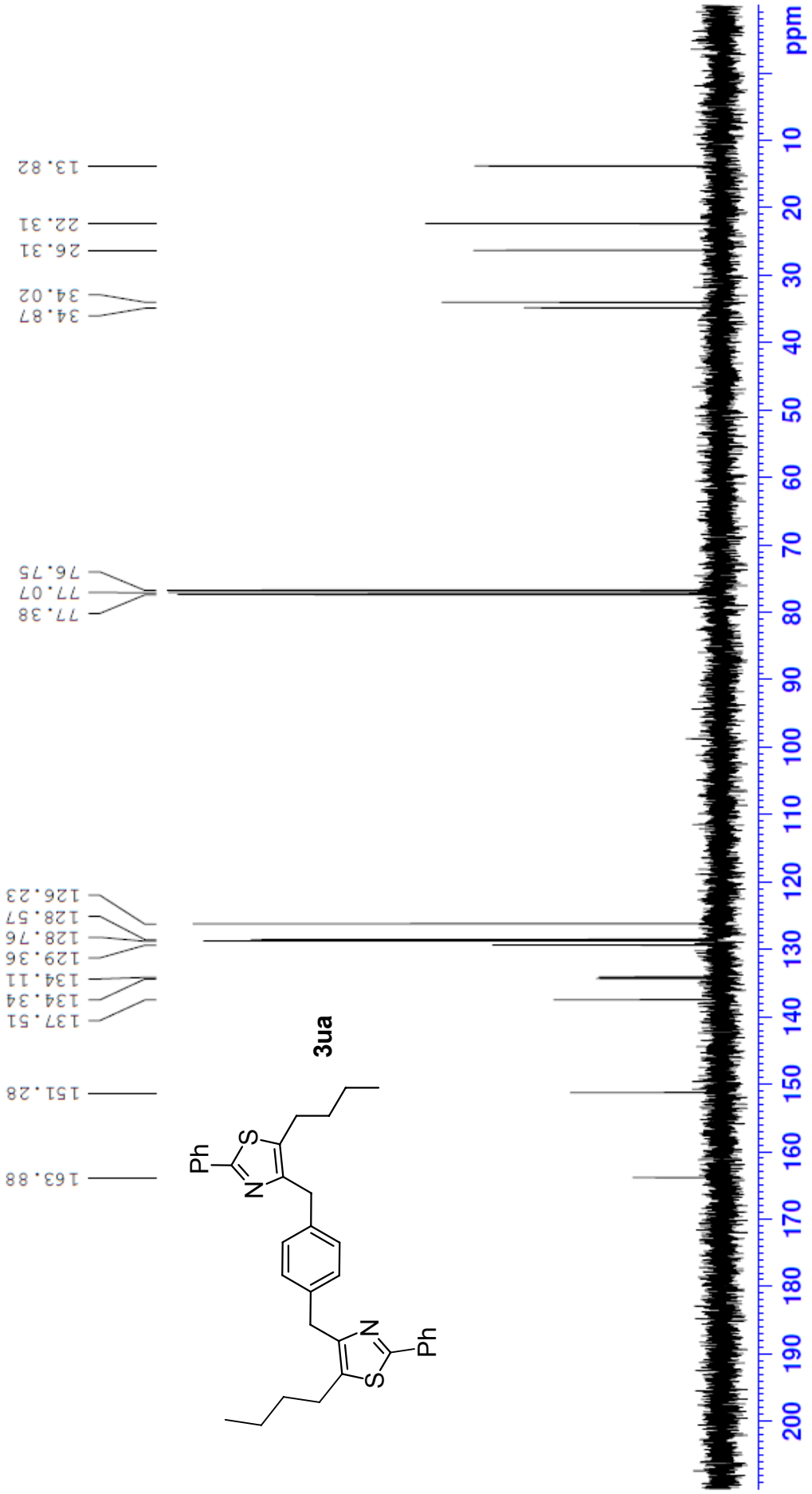


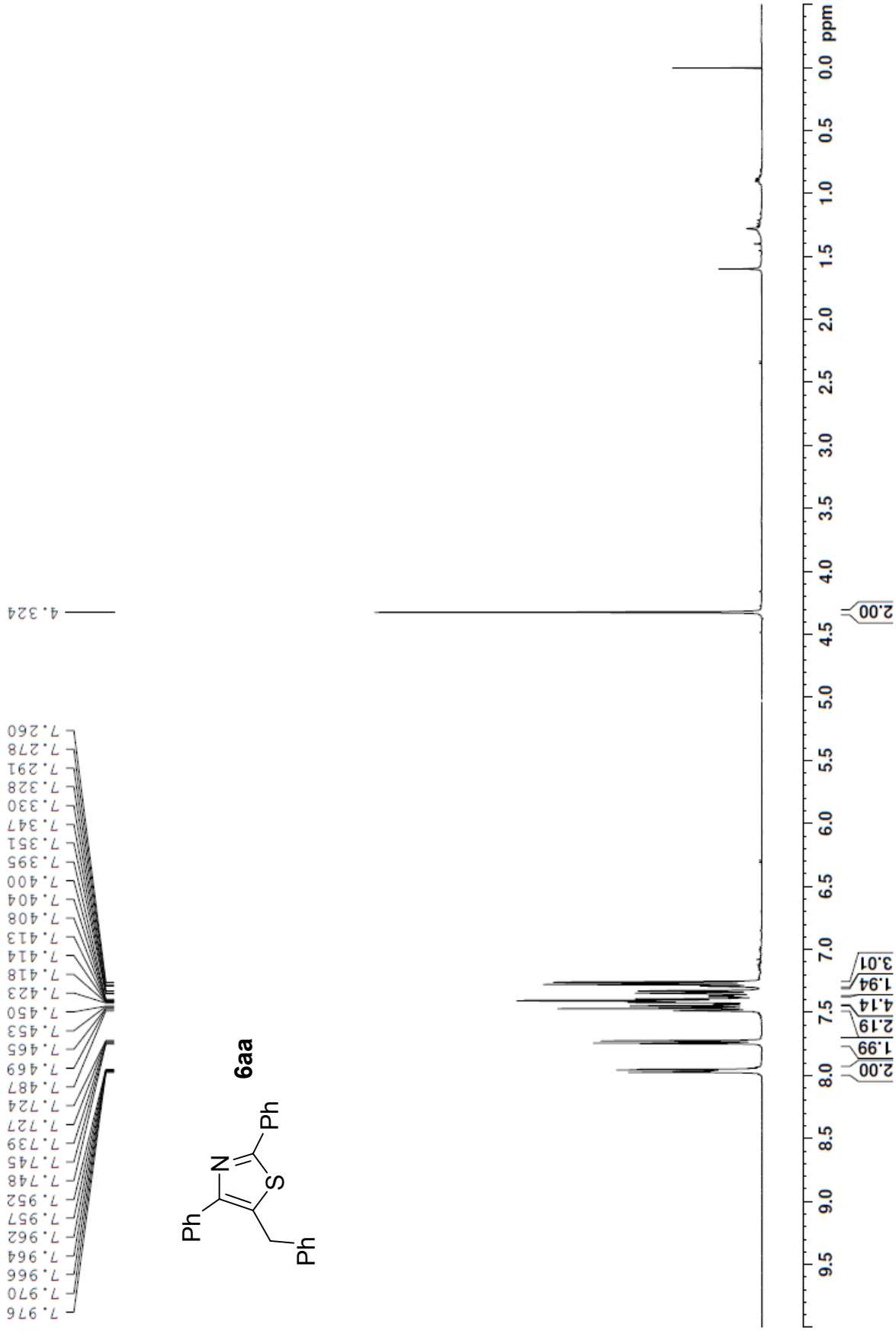


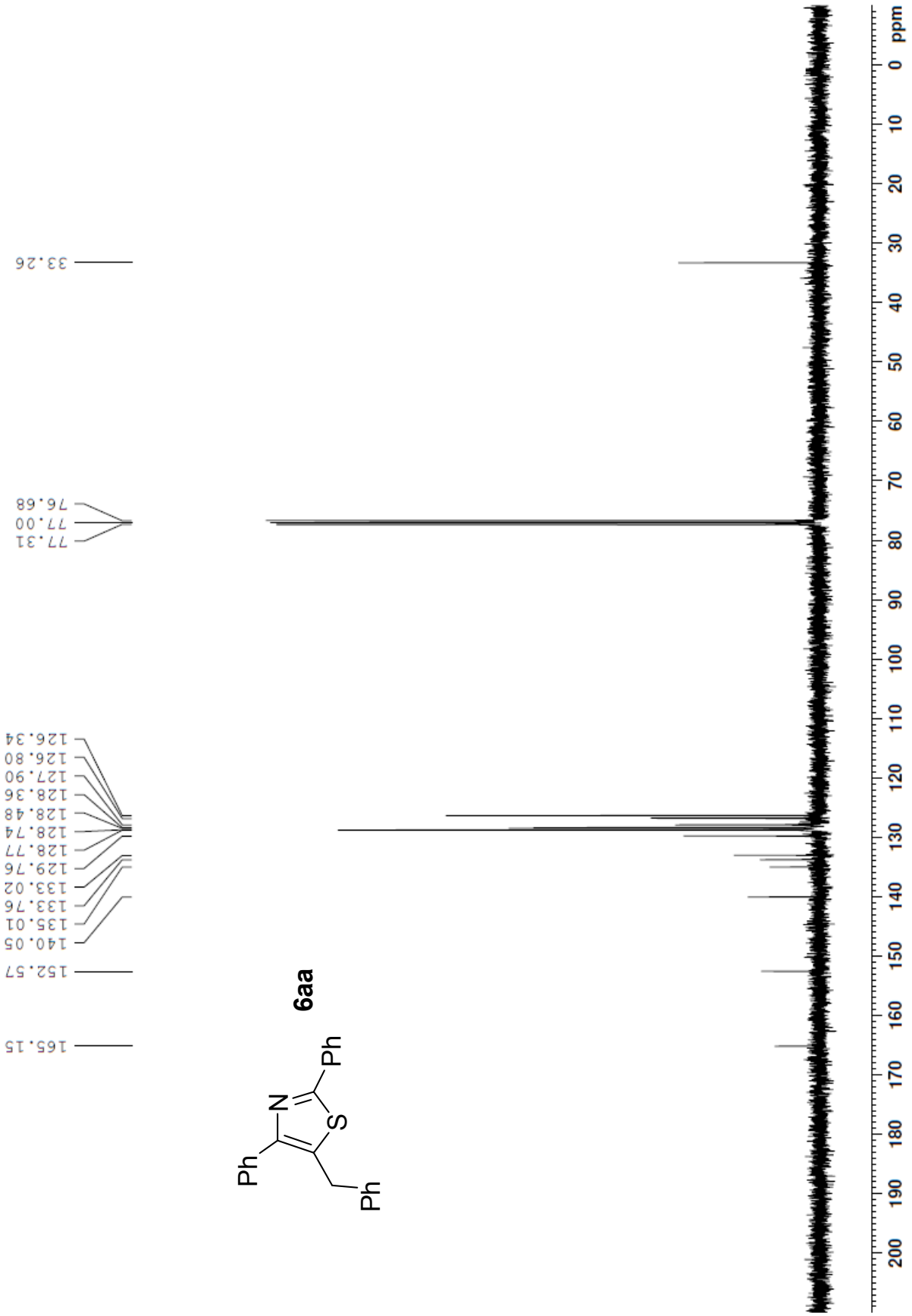


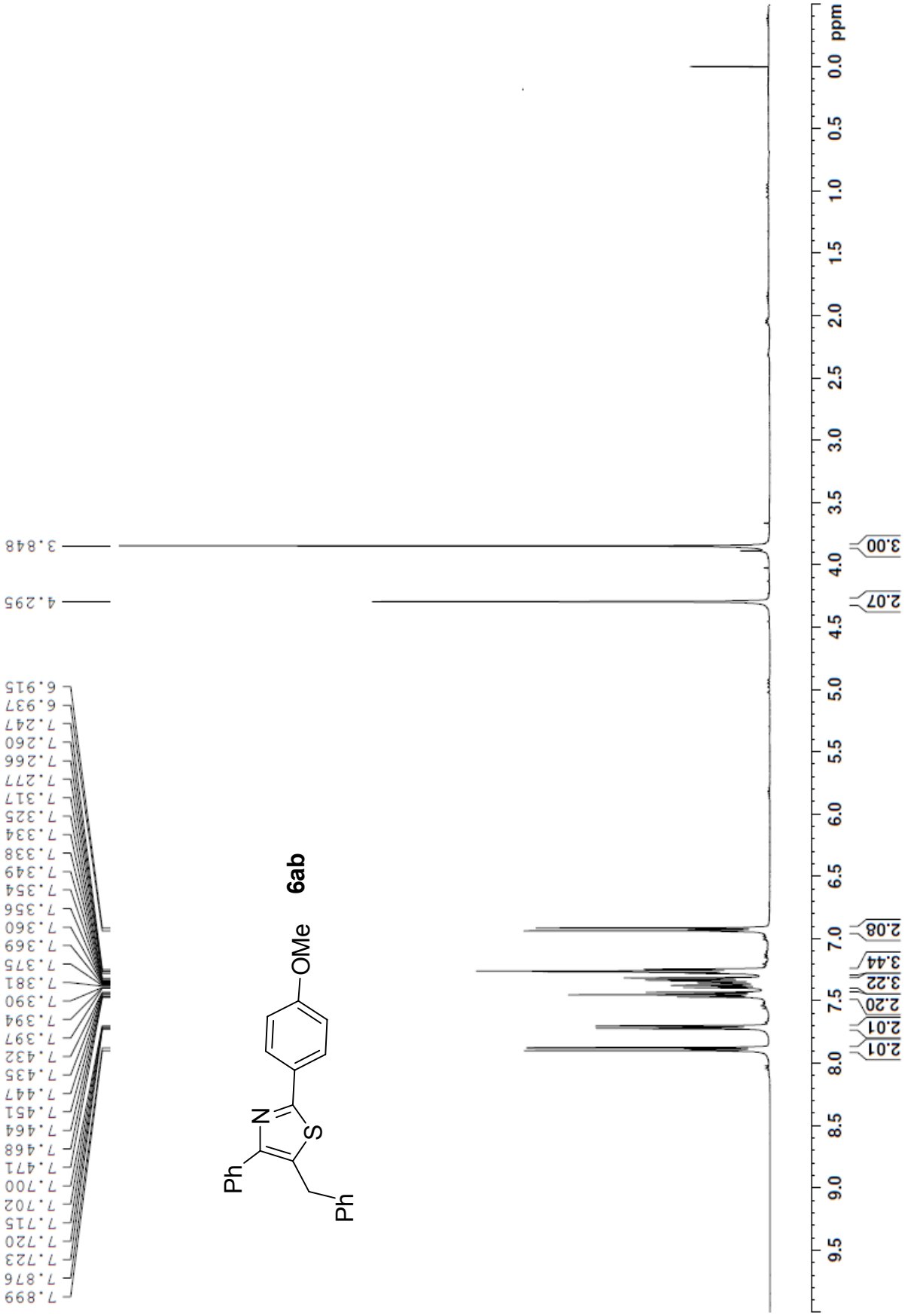


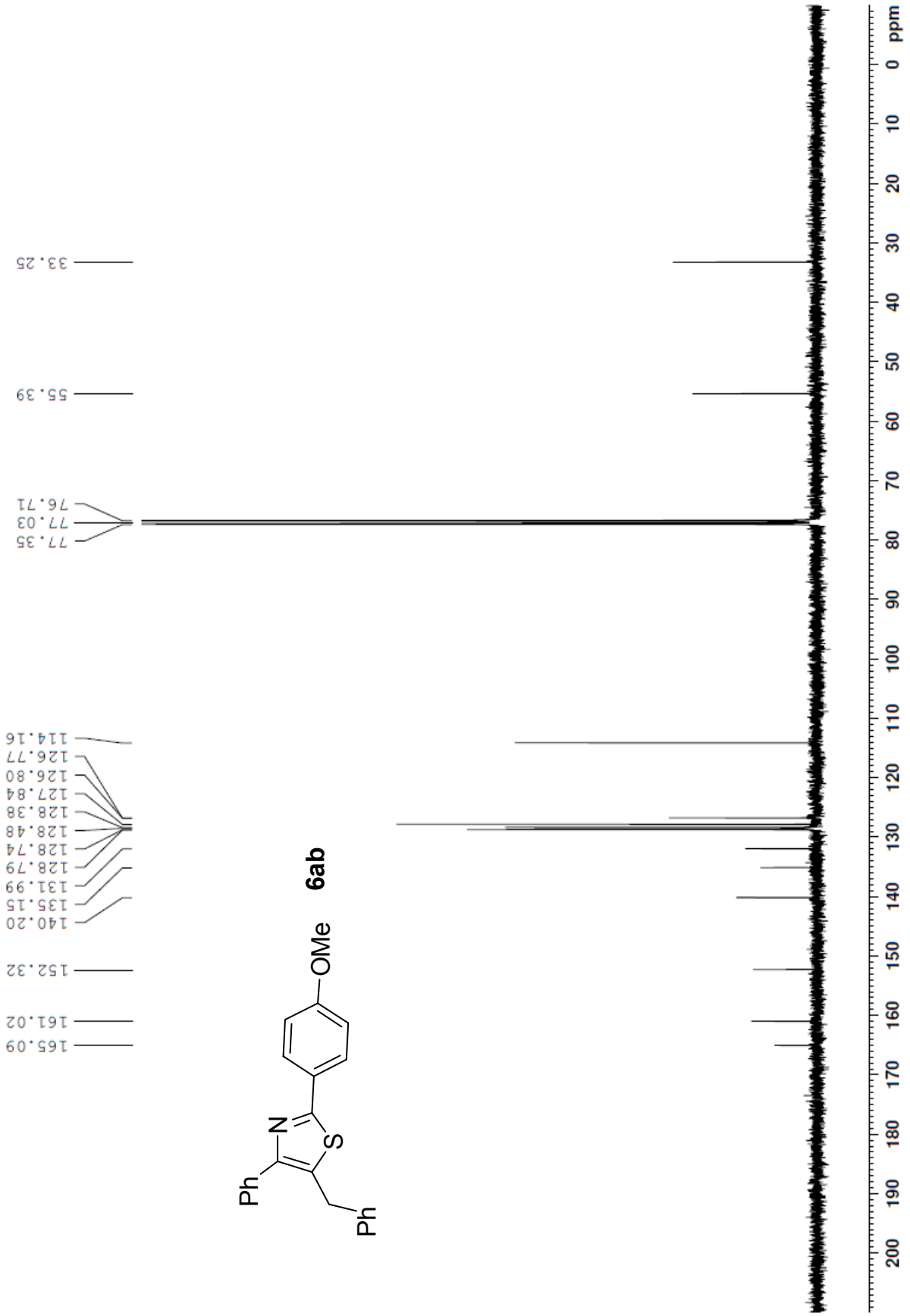


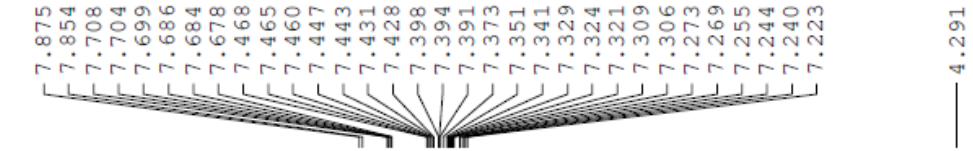


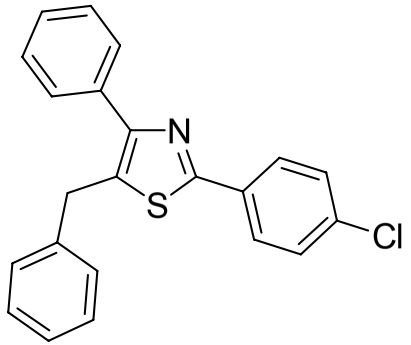












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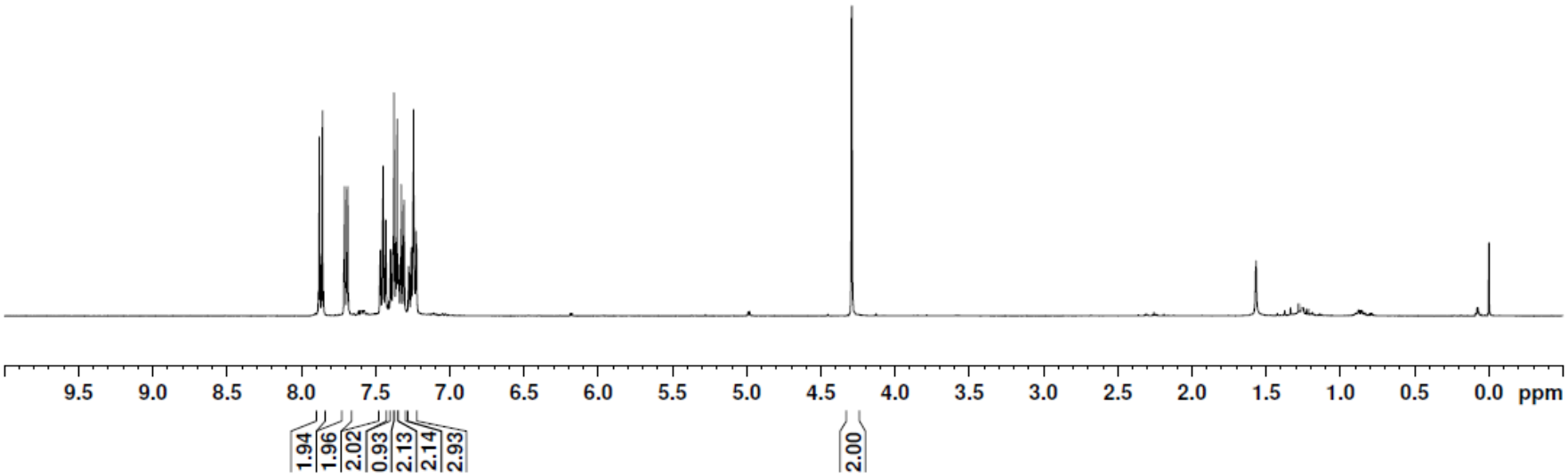

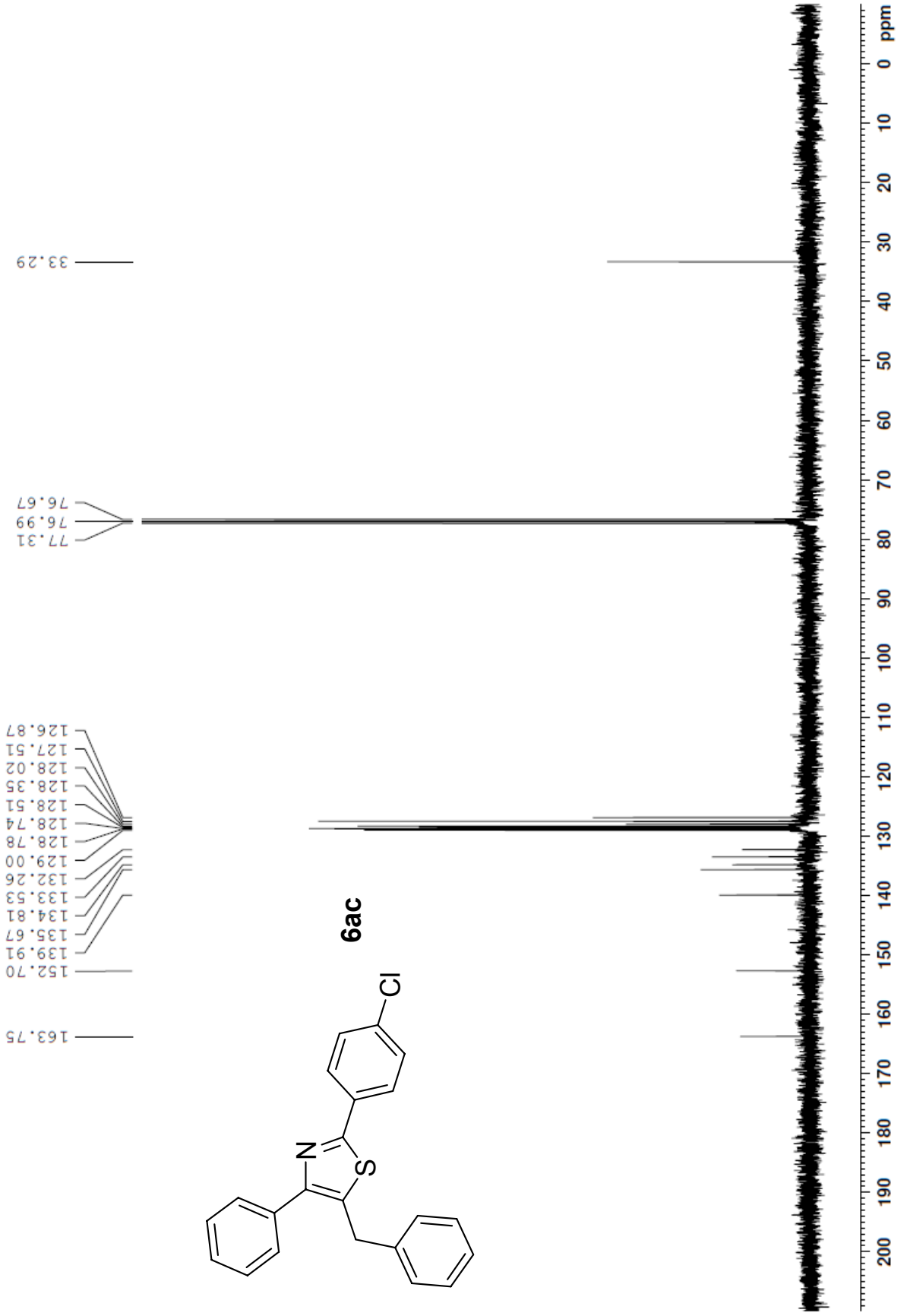

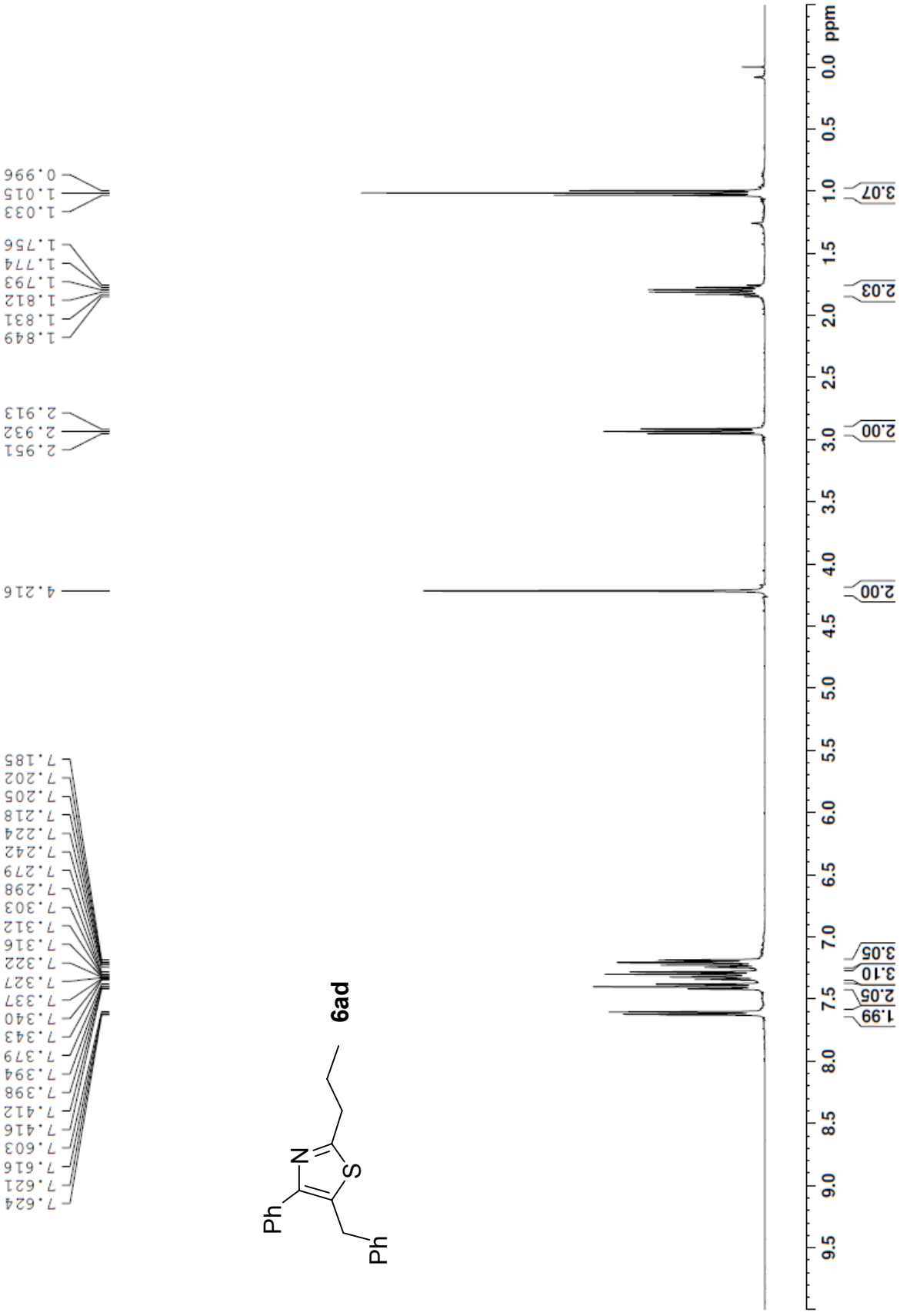

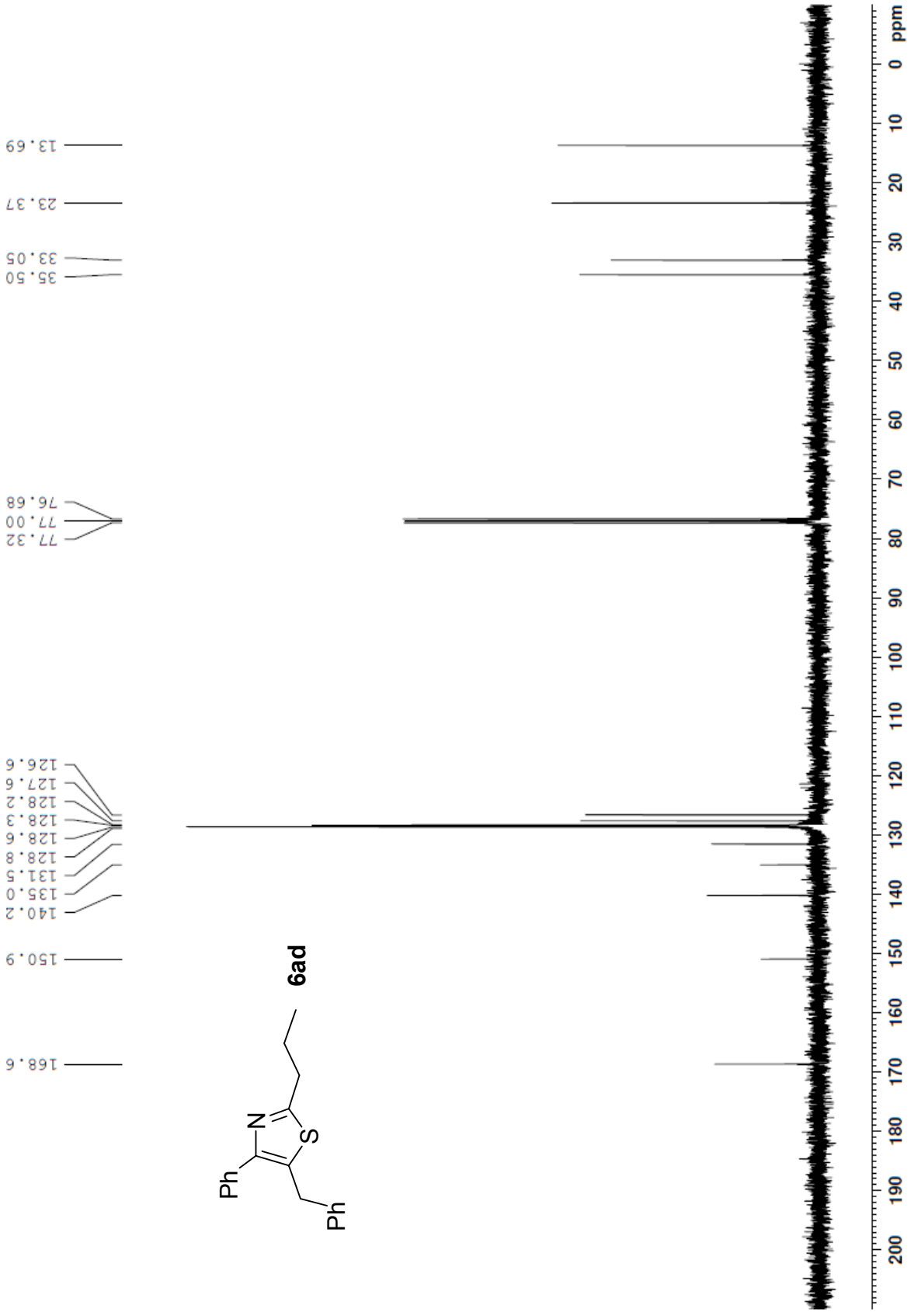

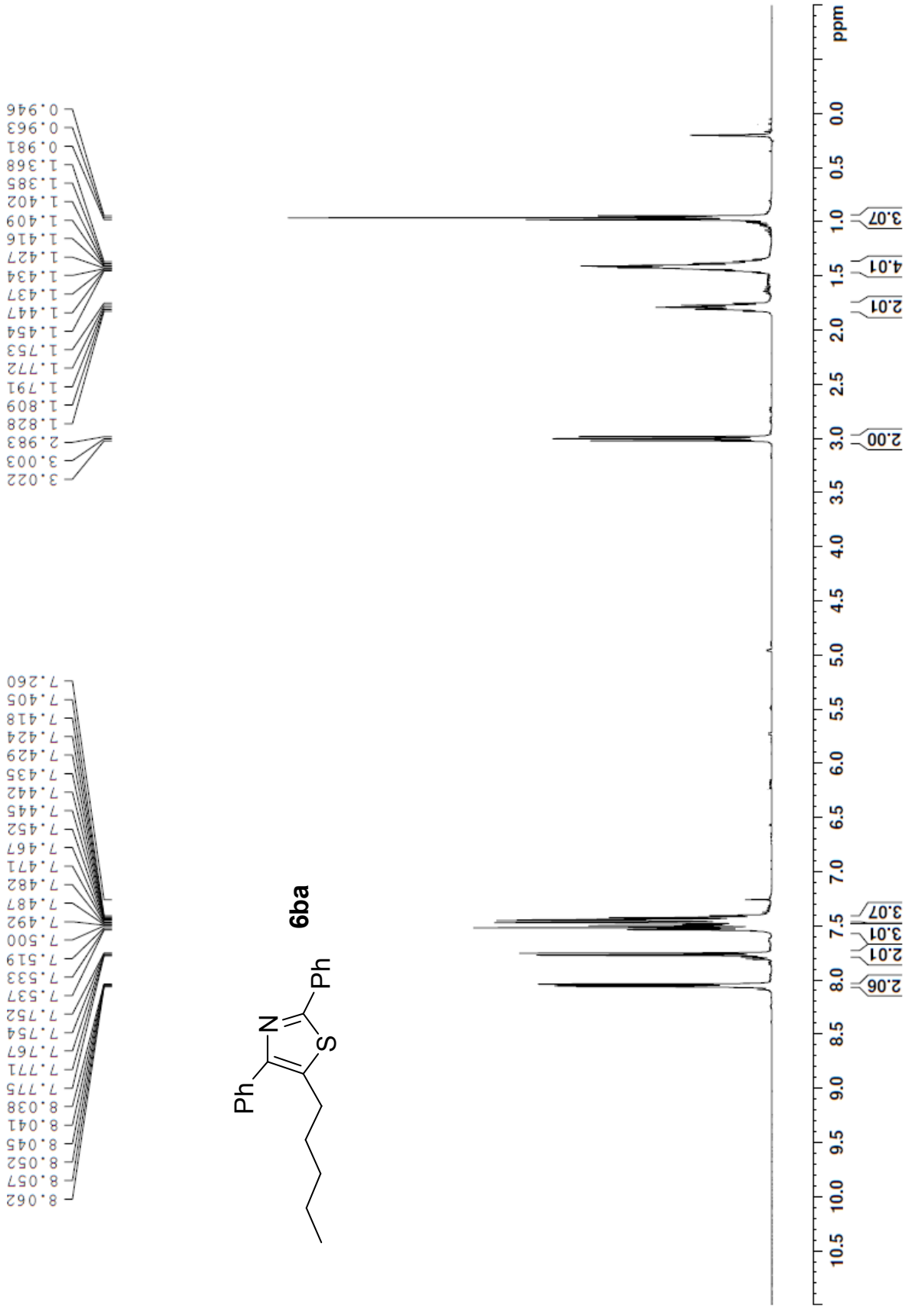

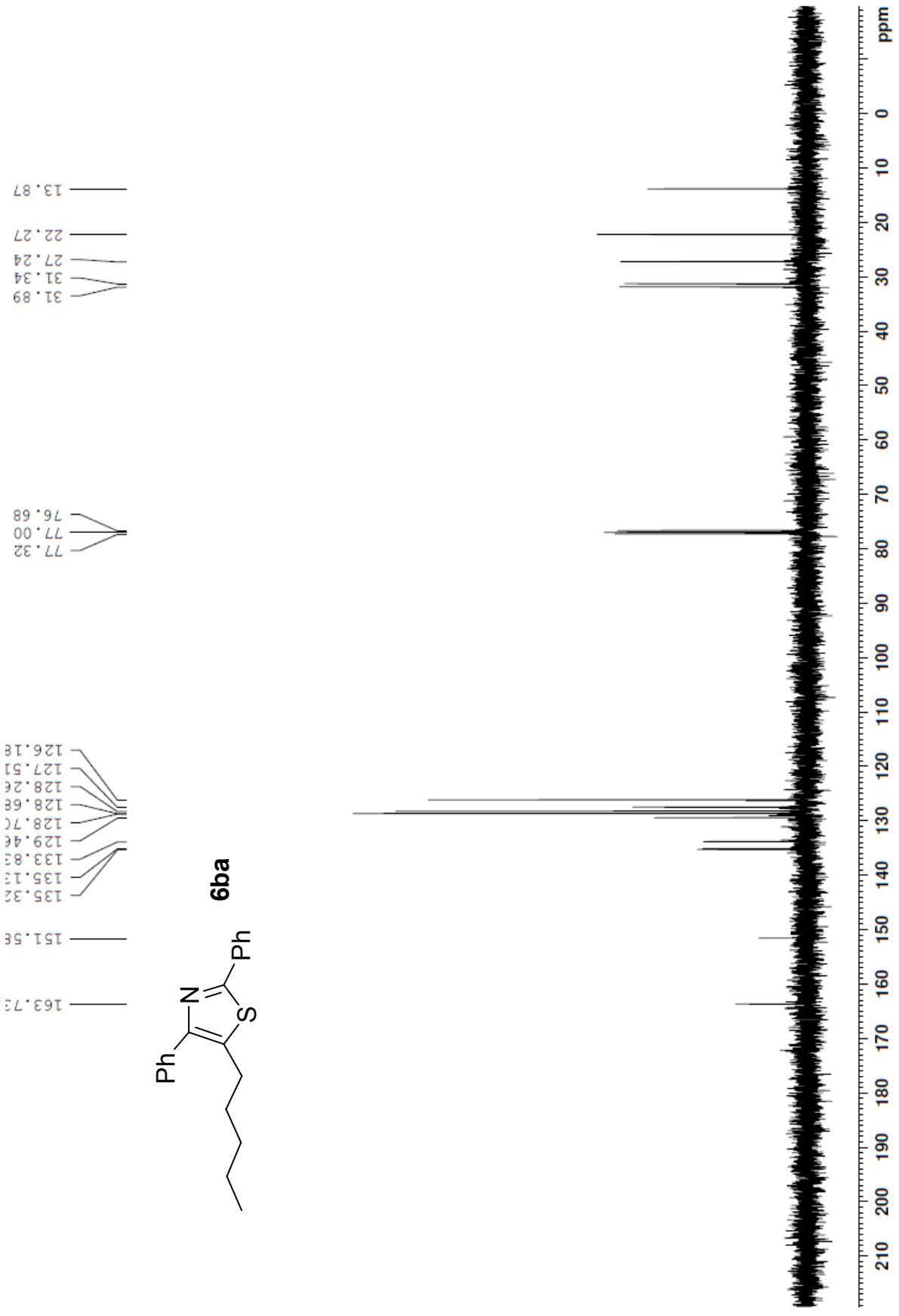

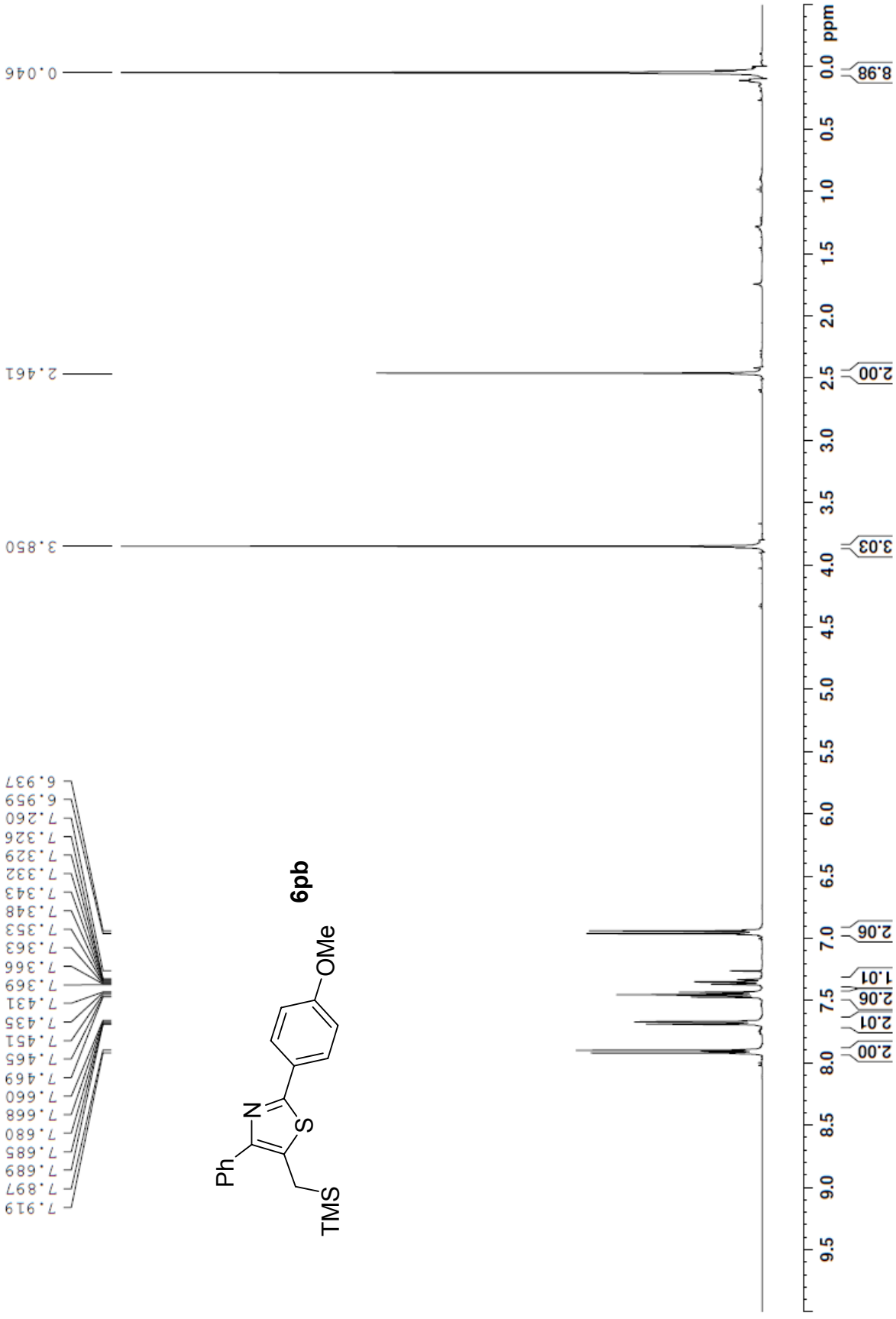

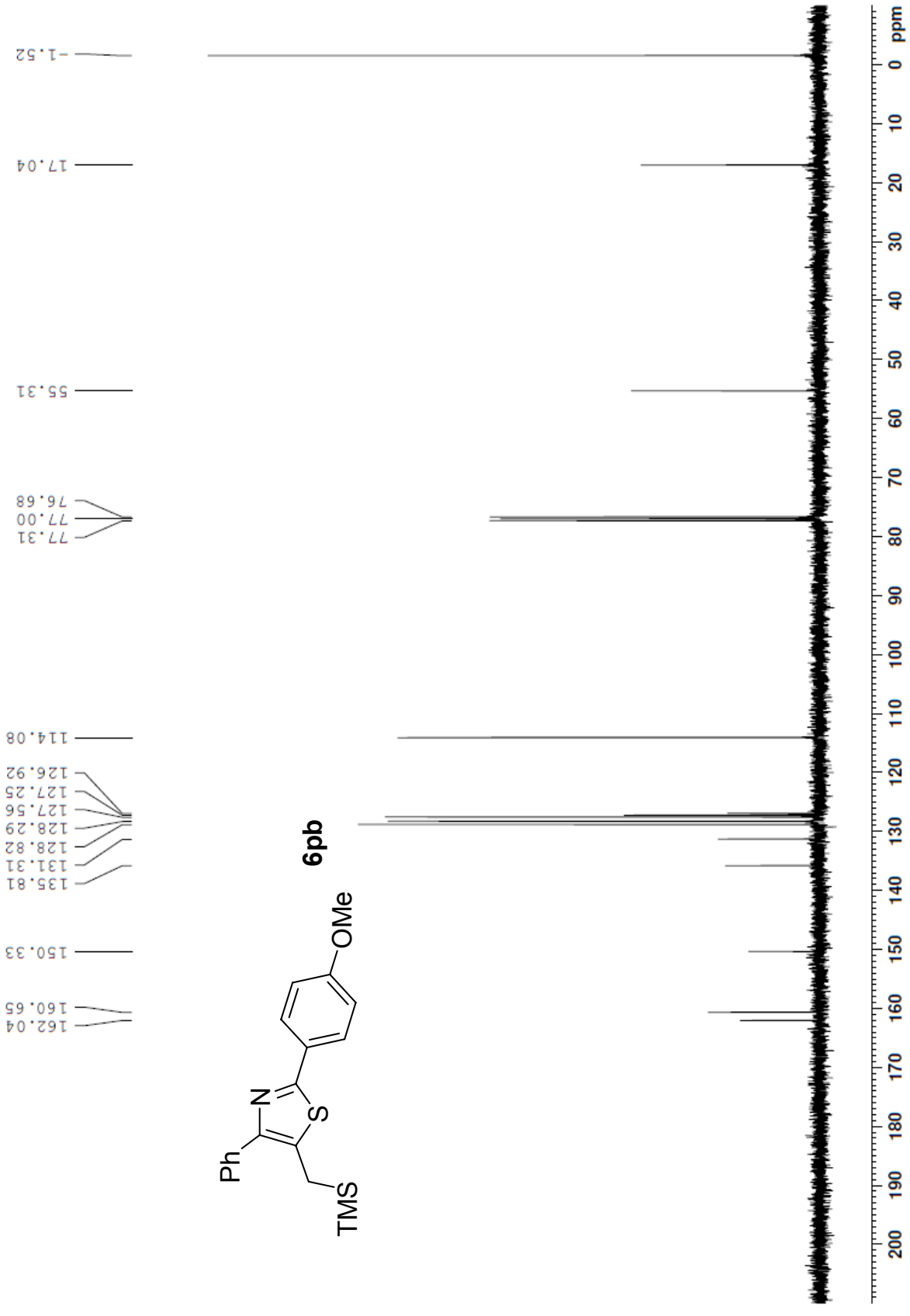

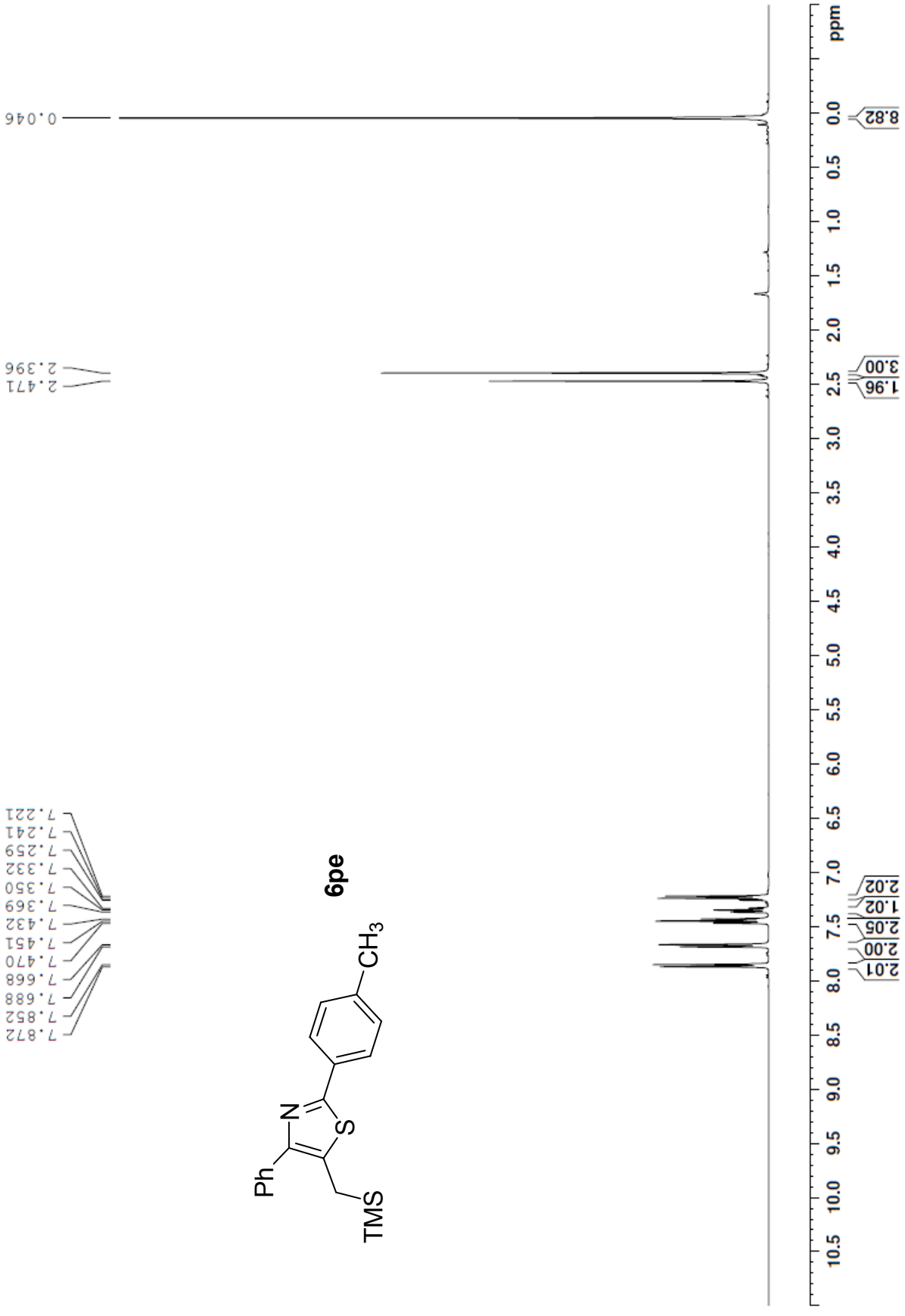
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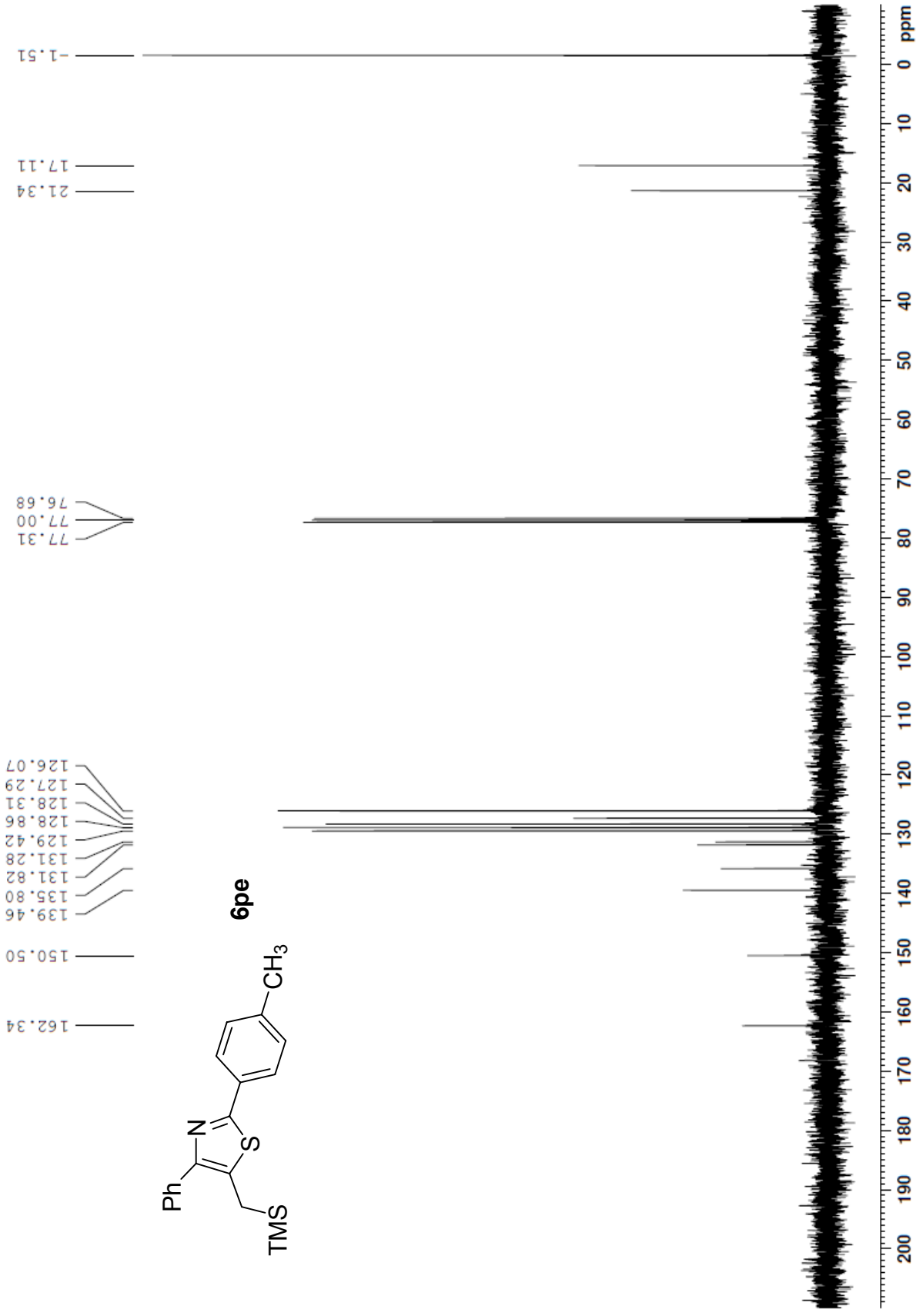

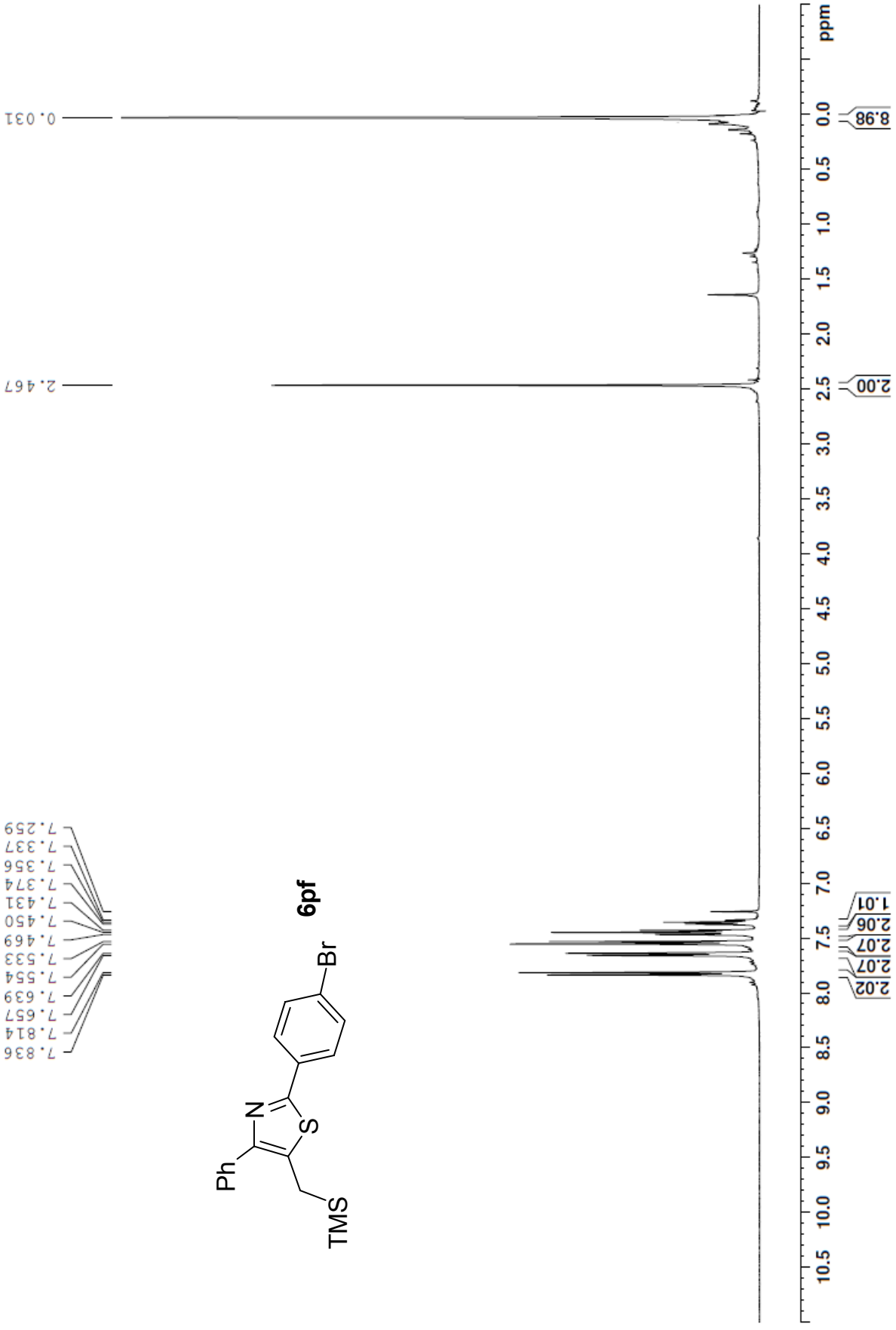
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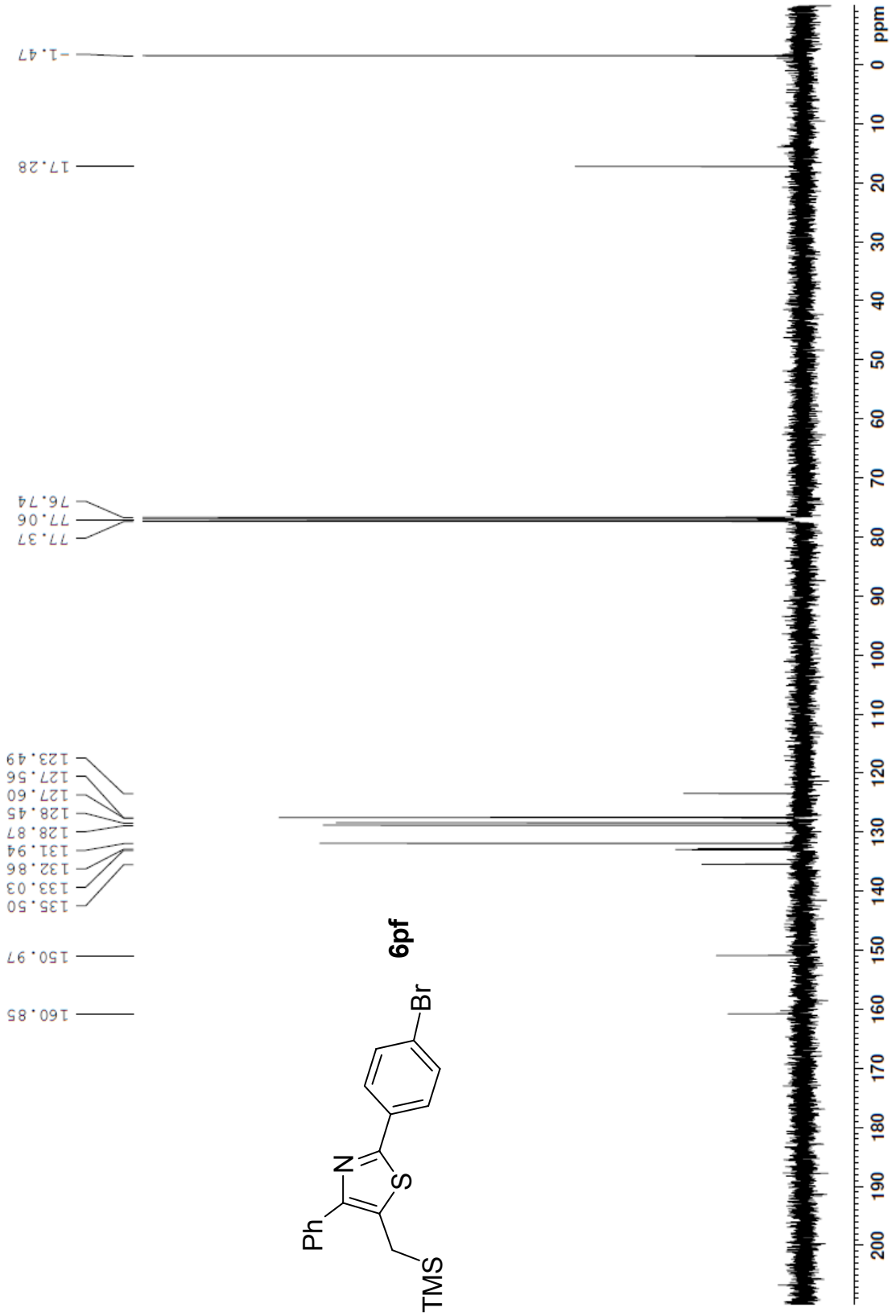

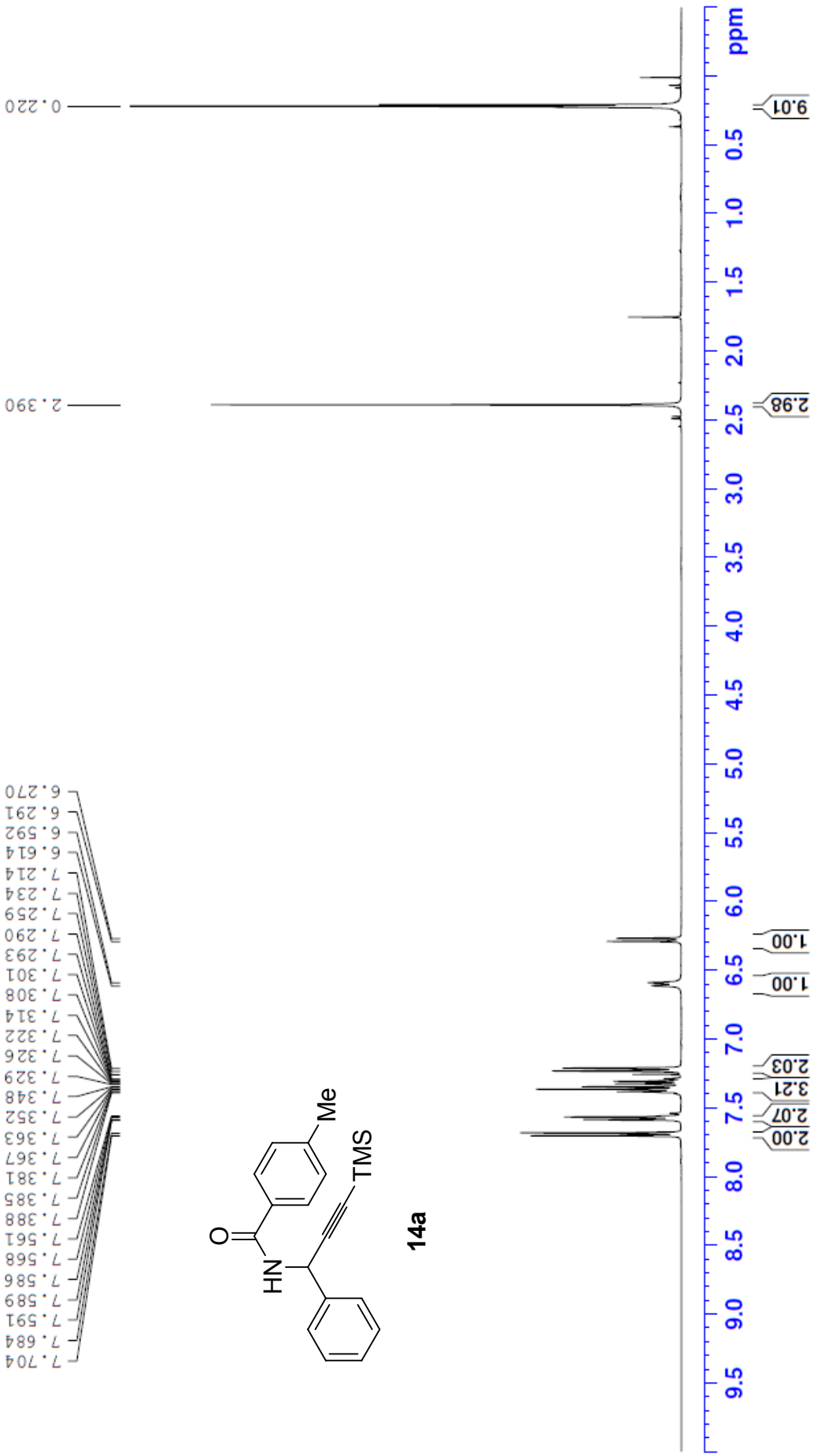

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