Electronic Supplementary Material (ESI) for RSC Advances.


# Multicomponent Bicyclization Reaction of Isocyanide, Allenoate, Imine and Water to Synthesize Pyrrolidine-Fused Rings

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## Supporting Information

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# 1 General Information:

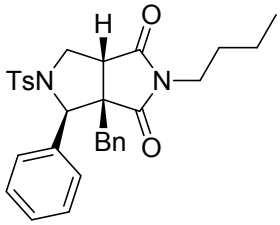
The NMR spectra were recorded on Bruker AC – 500 spectrometer (500 MHz for $^{1}H$ NMR and 125 MHz for $^{13}C$ NMR) with $CDCl_3$ as the solvent and TMS as internal reference. $^{1}H$ NMR spectral data were reported as follows: chemical shift (δ, ppm), multiplicity, integration, and coupling constant (Hz). $^{13}C$ NMR spectral data were reported in terms of the chemical shift. The following abbreviations were used to indicate multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Low-resolution mass spectra were obtained on a Shimadzu LCMS-2010EV spectrometer in ESI mode and reported as m/z. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. Melting points were obtained on a X-4 digital melting point apparatus without correction. Chemical yields referred to pure isolated product. Purification of products was accomplished by column chromatography packed with silica gel. Unless otherwise stated, all reagents were commercially purchased and used without further purification. Aromatic isocyanides **1** were prepared from the corresponding anilines according to the method disclosed by Ugi with a slight modification.[1]

# 2 General Procedure

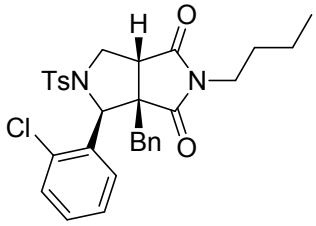
To a solution of isocyanide **1** (0.5 mmol), and substituted allenoate **2** (0.6 mmol) in a mixed solvent (5 mL; toluene/$H_2O$, v/v = 6:1), imine **3** (0.5 mmol) was added. The reaction mixture was stirred under reflux for several hours and the progress was monitored using TLC detection. After completion of present reaction, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel [silica: 200-300; eluant: petroleum ether/ethyl acetate] to afford the product **4-6**.

# 3 Characterization Data

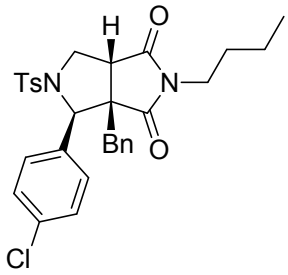
## Spectroscopic Data of All Compounds



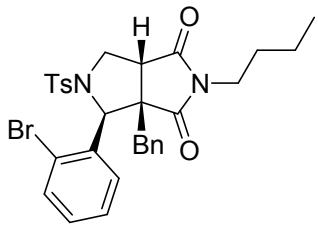

**(4a)**: white solid: m. p. 168-169 °C. $^{1}$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.43 (d, *J* = 8.0 Hz, 1H), 7.37-7.31 (m, 3H), 7.26 (d, *J* = 2.5 Hz, 1H), 7.15-7.14 (m, 5H), 6.91 (dd, *J* = 8.0, 2.5 Hz, 2H), 5.34 (s, 1H), 4.10-4.06 (m, 1H), 3.97-3.95 (m, 1H), 3.22 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.94-2.91 (m, 2H), 2.71 (dd, *J* = 14.0 Hz, 1H), 2.36 (s, 3H), 2.08 (dd, *J* = 14.0 Hz, 1H), 1.02-0.94 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.4, 176.3, 143.5, 137.1, 135.2, 134.8, 129.5, 129.4, 128.8, 127.8, 127.5, 127.1, 69.3, 61.3, 50.1, 48.3, 39.1, 39.0, 29.2, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{30}H_{33}N_2O_4S$ $[M+H]^+$ 517.2161, Found 517.2158.



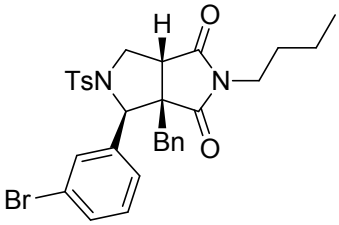

**(4b)**: white solid: m. p. 204-206 °C. $^{1}$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.58 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.46-7.44 (m, 1H), 7.23-7.22 (m, 5H), 7.46-7.13 (m, 3H), 6.92-6.91 (m, 2H), 5.95 (s, 1H), 4.25-4.20 (m, 1H), 3.96 (dd , *J* = 12.0, 3.0 Hz, 1H), 3.22 (dd, *J* = 9.5, 3.0 Hz, 1H), 2.90 (d, *J* = 13.5 Hz, 1H), 2.79-2.76 (m, 1H), 2.38 (s, 3H), 2.09 (d, *J* = 13.5 Hz, 1H), 0.95-0.74 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 178.3, 175.9, 143.8, 136.3, 134.9, 134.5, 133.7, 130.3, 129.8, 129.6, 128.7, 127.6, 127.4, 127.2, 65.0, 61.9, 51.0, 48.6, 38.9, 38.3, 29.1, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{30}H_{32}ClN_2O_4S$ $[M+H]^+$ 551.1771, Found 551.1760.



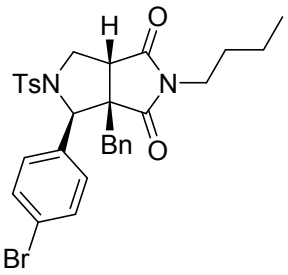

**(4c)**: white solid: m. p. 210-212 °C. $^{1}$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.45 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 9.0 Hz, 2H), 7.22-7.15 (m, 7H), 6.91-6.89 (m, 2H), 5.26 (s, 1H), 4.08-4.04 (m, 1H), 3.95 (dd, *J* = 7.0, 3.0 Hz, 1H), 3.22-3.19 (m, 1H), 2.94-2.69 (m ,2H), 2.70 (d, *J* = 14.0 Hz, 1H), 2.38 (s, 3H), 2.06 (d, *J* = 13.5 Hz, 1H), 1.02-0.76 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.1, 176.0, 143.8, 135.7, 134.9, 134.5, 134.4, 129.6, 129.5, 129.1, 128.9, 128.8, 127.7, 127.2, 68.7, 61.1, 50.4, 48.1, 39.1, 39.0, 29.2, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{30}H_{32}ClN_2O_4S$ $[M+H]^+$ 551.1771, Found 551.1768.



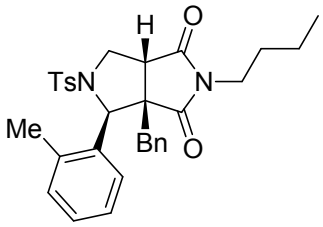

**(4d)**: white solid: m. p. 176-177 °C. $^{1}$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.63-7.58 (m, 3H), 7.29-7.12 (m, 8H), 6.91 (d, *J* = 3.0 Hz, 2H), 5.96 (s, 1H), 4.27-4.22 (m, 1H), 3.92 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.26 (dd, *J* = 9.5, 3.0 Hz, 1H), 2.88-2.79 (m, 3H), 2.37 (s, 3H), 2.08 (d, *J* = 13.0 Hz, 1H), 0.94-0.73 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 178.2, 175.9, 143.8, 137.9, 134.9, 134.4, 133.6, 129.8, 129.6, 128.7, 128.3, 128.0, 127.6, 127.2, 124.1, 67.3, 62.1, 51.2, 48.6, 38.9, 38.7, 29.1, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{30}H_{32}BrN_2O_4S$ $[M+H]^+$ 595.1266, Found 595.1268.



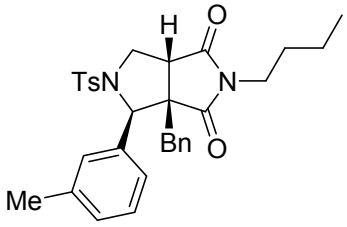
(**4e**): white solid: m. p. 171-172 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.44-7.42 (m, 3H), 7.28-7.14 (m, 8H), 6.93-6.91 (m, 2H), 5.27 (s, 1H), 4.08-4.03 (m, 1H), 4.00 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.22 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.95-2.91 (m, 1H), 2.71 (d, *J* = 13.5 Hz, 1H), 2.38 (s, 3H), 2.05 (d, *J* = 14.0 Hz, 1H), 1.02-0.76 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.1, 176.0, 143.9, 139.3, 134.5, 131.5, 130.5, 130.3, 129.7, 129.5, 128.8, 127.7, 127.1, 126.7, 123.0, 68.7, 61.2, 50.6, 48.1, 39.1, 30.9, 29.2, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{30}H_{32}BrN_2O_4S$ $[M+H]^+$ 595.1266, Found 595.1268.



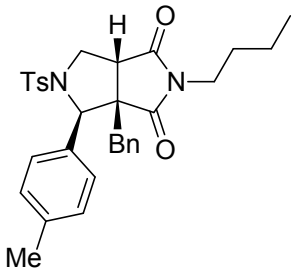
(**4f**): white solid: m. p. 145-147 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.47-7.43 (m, 4H), 7.18-7.14 (m, 7H), 6.91-6.89 (m, 2H), 5.24 (s, 1H), 4.07-4.03 (m, 1H), 3.95 (dd, *J* = 7.0, 3.0 Hz, 1H), 3.20 (dd, *J* = 8.5, 3.0 Hz, 6H), 2.94-2.90 (m, 2H), 2.70 (d, *J* = 13.5 Hz, 1H), 2.05 (s, 3H), 2.07 (d, *J* = 13.5 Hz, 1H), 1.02-0.76 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.1, 176.0, 143.8, 136.2, 134.9, 134.5, 131.9, 129.6, 129.5, 128.8, 127.6, 127.2, 122.5, 68.7, 61.1, 50.5, 48.1, 39.1, 39.0, 29.2, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{30}H_{32}BrN_2O_4S$ $[M+H]^+$ 595.1266, Found 595.1261.



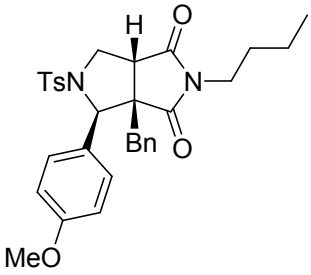
(**4g**): white solid: m. p. 183-184 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.43 (d, *J* = 8.5 Hz, 2H), 7.23-7.12 (m, 7H), 7.07 (t, *J* = 7.0 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.92-6.90 (m, 2H), 5.71 (s, 1H), 4.16-4.12 (m, 1H), 4.03 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.26 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.91 (t, *J* = 7.5 Hz, 1H), 2.65 (s, 3H), 2.56 (d, *J* = 13.5 Hz, 1H), 2.36 (s, 3H), 2.14 (d, *J* = 13.5 Hz, 1H), 1.01-0.76 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.7, 176.4, 143.5, 136.6, 136.2, 135.4, 134.7, 131.1, 129.6, 129.5, 128.7, 128.1, 127.5, 127.1, 126.6, 126.4, 64.9, 61.7, 50.8, 48.9, 39.0, 38.8, 29.2, 21.4, 19.9, 19.8, 13.5. HRMS: Calcd for $C_{31}H_{35}N_2O_4S$ $[M+H]^+$ 531.2318, Found 531.2315.



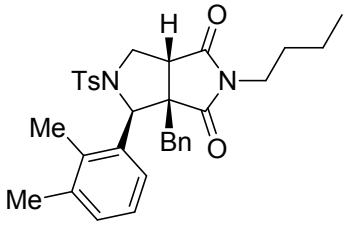
(**4h**): white solid: m. p. 170-172 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.42-7.39 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.15-7.11 (m, 5H), 7.09-6.91 (m, 5H), 5.31 (s, 1H), 4.09-4.05 (m, 1H), 3.96 (dd, *J* = 7.0, 2.5 Hz, 1H), 3.23 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.95-2.92 (m, 2H), 2.73 (s, 3H), 2.71 (d, *J* = 13.5 Hz, 1H), 2.31 (s, 3H), 2.09 (d, *J* = 13.5 Hz, 1H), 1.00-0.76 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.5, 176.4, 143.4, 138.5, 136.9, 135.3, 134.9, 129.5, 129.4, 129.1, 128.7, 128.6, 127.5, 127.1, 69.3, 61.3, 50.6, 48.3, 39.1, 39.0, 29.2, 21.5, 21.4, 19.2, 13.5. HRMS: Calcd for $C_{31}H_{35}N_2O_4S$ $[M+H]^+$ 531.2318, Found 531.2316.



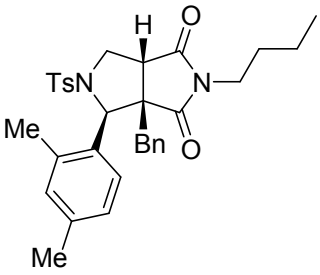

(**4i**): white solid: m. p. 185-187 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.41 (d, *J* = 8.5 Hz, 2H), 7.14-7.11 (m, 9H), 6.92-6.90 (m, 2H), 5.29 (s, 1H), 4.09-4.05 (m, 1H), 3.93 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.22 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.94-2.90 (m, 2H), 2.71 (d, *J* = 13.5 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 2.12 (d, *J* = 13.5 Hz, 1H), 1.01-0.76 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.5, 176.4, 143.4, 138.2, 135.3, 134.9, 134.0, 129.5, 129.44, 129.41, 128.7, 127.8, 127.5, 127.2, 69.1, 61.3, 50.5, 48.2, 39.1, 38.9, 29.2, 21.5, 21.1, 19.8, 13.5. HRMS: Calcd for $C_{31}H_{35}N_2O_4S$ $[M+H]^+$ 531.2318, Found 531.2311.



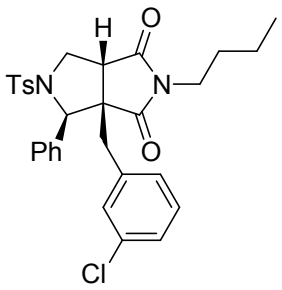

(**4j**): white solid: m. p. 167-169 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.41 (d, *J* = 8.5 Hz, 2H), 7.16-7.12 (m, 7H), 6.92-6.90 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.28 (s, 1H), 4.06-4.02 (m, 1H), 3.92 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.80 (s, 3H), 3.22 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.95-2.92 (m, 2H), 2.69 (d, *J* = 14.0 Hz, 1H), 2.35 (s, 3H), 2.14 (d, *J* = 14.0 Hz, 1H), 1.03-0.79 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.5, 176.4, 159.6, 143.4, 135.2, 134.9, 129.5, 129.4, 129.1, 129.0, 128.7, 127.5, 127.2, 114.1, 68.9, 61.4, 55.3, 50.4, 48.1, 39.1, 38.9, 29.2, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{31}H_{35}N_2O_5S$ $[M+H]^+$ 547.2267, Found 547.2265.



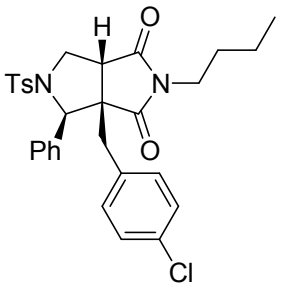

(**4k**): white solid: m. p. 195-196 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.47 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.14-7.09 (m, 4H), 7.03-6.99 (m, 1H), 6.91-6.89 (m, 3H), 5.80 (s, 1H), 4.18-4.13 (m, 1H), 4.02 (dd,, *J* = 12.0, 2.5 Hz, 1H), 3.23 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.89-2.86 (m, 2H), 2.60 (d, *J* = 13.5 Hz, 1H), 2.54 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H), 2.12 (d, *J* = 13.5 Hz, 1H), 1.02-0.76 (m, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.8, 176.4, 143.5, 137.6, 136.2, 135.5, 135.0, 134.8, 129.7, 129.6, 129.5, 128.7, 127.5, 127.1, 125.8, 124.2, 65.3, 61.7, 50.8, 48.9, 39.0, 38.8, 29.2, 21.5, 21.1, 19.8, 15.4, 13.5. HRMS: Calcd for $C_{32}H_{37}N_2O_4S$ $[M+H]^+$ 545.2474, Found 545.2473.



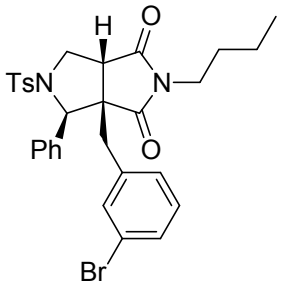

(**4l**): white solid: m. p. 206-207 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.45 (d, *J* = 8.5 Hz, 2H), 7.17-7.15 (m, 5H), 7.05 (s, 1H), 6.94-6.93 (m, 2H), 6.89 (s, 2H), 5.68 (s, 1H), 4.17-4.13 (m, 1H), 4.03 (dd, *J* = 12.0, 2.5Hz, 1H), 3.27 (dd, *J* = 9.0, 2.5 Hz,1H), 2.95-2.92 (m, 2H), 2.62 (s, 3H), 2.58 (d, *J* = 13.5 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 2.20 (d, *J* = 13.5 Hz, 1H), 1.05-0.95 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.8, 176.4, 143.4, 137.8, 136.4, 135.5, 134.8, 133.1, 131.8, 129.6, 129.5, 128.7, 127.5, 127.1, 127.0, 126.5, 64.7, 61.6, 50.8, 48.8, 39.0, 38.9, 29.2, 21.4, 21.0, 19.9, 19.8, 13.5. HRMS: Calcd for $C_{32}H_{37}N_2O_4S$ $[M+H]^+$ 545.2474, Found 545.2469.



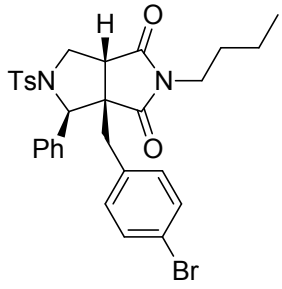
(**5a**): white solid: m. p. 201-203 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.43 (d, *J* = 8.5 Hz, 2H), 7.34-7.32 (m, 3H), 7.26-7.24 (m, 2H), 7.16-7.08 (m, 4H), 6.92-6.91 (m, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 5.32 (s, 1H), 4.10-4.06 (m, 1H), 4.00 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.17 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.98-2.94 (m, 2H), 2.70 (d, *J* = 13.5 Hz, 1H), 2.37 (s, 3H), 2.05 (d, *J* = 13.5 Hz, 1H), 1.02-0.79 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.2, 176.0, 143.6, 136.9, 135.2, 134.6, 129.9, 129.7, 128.9, 128.5, 127.8, 127.7, 127.6, 127.1, 69.3, 61.0, 50.6, 48.2, 39.2, 38.7, 29.3, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{30}H_{32}ClN_2O_4S$ $[M+H]^+$ 551.1771, Found 551.1766.



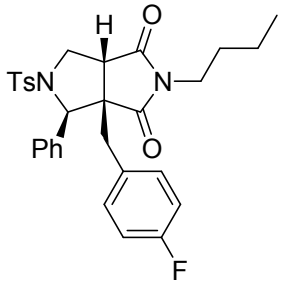
(**5b**): white solid: m. p. 141-142 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.41 (d, *J* = 8.0 Hz, 2H), 7.33-7.31 (m, 3H), 7.25-7.23 (m, 2H), 7.15-7.12 (m, 4H), 6.87-6.85 (m, 2H), 5.32 (s, 1H), 4.09-4.06 (m, 1H), 3.97 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.18 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.97-2.93 (m, 2H), 2.67 (d, *J* = 14.0 Hz, 1H), 2.36 (s, 3H), 2.07 (d, *J* = 13.5 Hz, 1H), 1.02-0.92 (m 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.3, 176.5, 143.7, 136.3, 135.4, 133.7, 130.8, 129.5, 128.9, 128.8, 127.8, 127.1, 69.2, 61.1, 50.6, 48.3, 39.1, 38.4, 29.3, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{30}H_{32}ClN_2O_4S$ $[M+H]^+$ 551.1771, Found 551.1764.



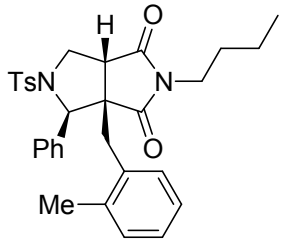
(**5c**): white solid: m. p. 198-199 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.44 (d, *J* = 8.0 Hz, 2H), 7.36-7.26 (m, 6H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.09-7.03 (m, 2H), 6.87 (d, *J* = 7.5 Hz, 1H), 5.34 (s, 1H), 4.12-4.08 (m, 1H), 4.01 (d, *J* = 12.0, 2.5 Hz, 1H), 3.20 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.00-2.96 (m, 2H), 2.70 (d, *J* = 13.5 Hz, 1H), 2.38 (s, 3H), 2.06 (d, *J* = 13.5 Hz, 1H), 1.13-0.85 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.1, 176.0, 143.6, 137.2, 136.9, 136.2, 132.5, 130.7, 129.7, 129.6, 128.8, 128.5, 128.1, 127.8, 127.1, 126.5, 122.8, 69.3, 61.0, 50.6, 48.1, 39.2, 38.6, 29.3, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{30}H_{32}BrN_2O_4S$ $[M+H]^+$ 595.1266, Found 595.1265.



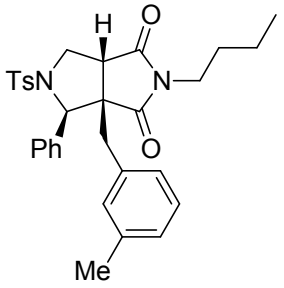
(**5d**): white solid: m. p. 173-175 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.41 (d, *J* = 8.0 Hz, 2H), 7.33-7.23 (m, 7H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 3.5 Hz, 2H), 5.32 (s, 1H), 4.09-4.06 (m, 1H), 3.98 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.18 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.98-2.94 (m, 2H), 2.65 (d, *J* = 14.0 Hz, 1H), 2.36 (s, 3H), 2.05 (d, *J* = 13.5 Hz, 1H), 1.02-0.97 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.1, 176.1, 143.5, 136.9, 135.1, 133.8, 131.9, 131.2, 129.5, 128.8, 128.5, 127.8, 127.1, 121.7, 69.2, 61.0, 50.6, 48.3, 39.1, 38.5, 29.3, 21.5, 19.8, 13.6. $C_{30}H_{32}BrN_2O_4S$ $[M+H]^+$ 595.1266, Found 595.1271.



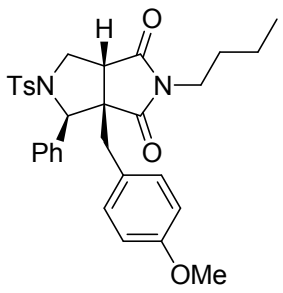
(**5e**): white solid: m. p. 163-165 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.42 (d, *J* = 8.5 Hz, 1H), 7.33-7.23 (m, 6H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 1.5 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 1H), 4.08-4.00 (m, 1H), 3.98 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.17 (d, *J* = 9.0, 2.5 Hz, 1H), 2.98-2.94 (m, 2H), 2.68 (d, *J* = 14.0 Hz, 1H), 2.36 (s, 3H), 2.04 (d, *J* = 14.0 Hz, 1H), 1.00-0.80 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.1, 176.0, 143.6, 137.2, 136.9, 135.2, 132.5, 130.7, 130.2, 129.6, 120.8, 128.5, 128.1, 127.8, 127.1, 122.8, 69.3, 61.0, 50.6, 48.1, 39.2, 38.6, 29.3, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{30}H_{32}FN_2O_4S$ $[M+H]^+$ 535.2067, Found 535.2071.



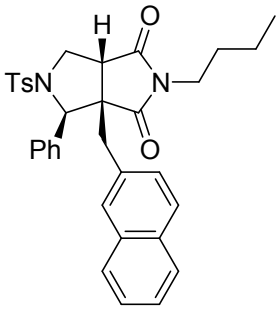
(**5f**): white solid: m. p. 185-186 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.44-7.42 (m, 2H), 7.35-7.32 (m, 3H), 7.29-7.27 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 4.0 Hz, 2H), 6.95 (t, *J* = 4.0 Hz, 2H), 6.84 (d, *J* = 7.5 Hz, 1H), 5.31 (s, 1H), 4.08-4.04 (m, 1H), 3.98 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.10 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.02-2.98 (m, 2H), 2.73 (d, *J* = 14.0 Hz, 1H), 2.36 (s, 3H), 2.24 (d, *J* = 14.0 Hz, 1H), 2.10 (s, 3H), 1.08-0.79 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.9, 176.4, 143.5, 137.4, 136.3, 135.0, 133.5, 131.1, 129.5, 129.4, 128.8, 128.4, 127.7, 127.5, 127.2, 126.2, 69.7, 61.4, 50.7, 48.1, 39.1, 34.6, 29.2, 21.5, 19.84, 19.82, 13.5. HRMS: Calcd for $C_{31}H_{35}N_2O_4S$ $[M+H]^+$ 531.2318, Found 531.2310.



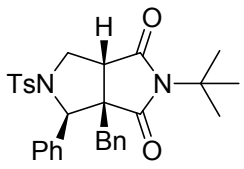
(**5g**): white solid: m. p. 218-219 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.43 (d, *J* = 8.0 Hz, 2H), 7.33-7.31 (m, 3H), 7.26-7.25 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 5.33 (s, 1H), 4.10-4.06 (m, 1H), 3.96 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.33 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.94-2.91 (m, 2H), 2.68 (d, *J* = 13.5 Hz, 1H), 2.36 (s, 3H), 2.19 (s, 3H), 2.04 (d, *J* = 14.0 Hz, 1H), 1.03-0.78 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.5, 176.4, 143.5, 138.3, 137.1, 135.2, 130.2, 129.5, 128.7, 128.6, 128.3, 128.2, 127.8, 127.2, 126.5, 69.2, 61.3, 50.5, 48.3, 39.0, 29.3, 21.5, 21.3, 19.8, 13.5. HRMS: Calcd for $C_{31}H_{35}N_2O_4S$ $[M+H]^+$ 531.2318, Found 531.2311.



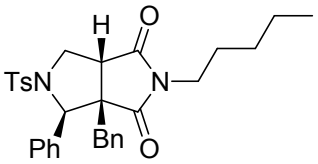
(**5h**): white solid: m. p. 181-183 °C. $^1$H NMR (500 MHz, $CDCl_3$): 7.42 (d, *J* = 8.5 Hz, 2H), 7.33-7.24 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 2H), 5.32 (s, 1H), 4.09-4.06 (m, 1H), 3.96 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.69 (s, 3H), 3.21 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.96-2.92 (m, 2H), 2.66 (d, *J* = 14.0 Hz, 1H), 2.36 (s, 3H),2.03 (d, *J* = 14.0 Hz, 1H), 1.04-0.92 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.5, 176.4, 158.9, 143.4, 137.1, 135.2, 130.5, 129.5, 128.8, 128.3, 127.8, 127.1, 126.6, 114.1, 69.2, 61.5, 55.1, 50.5, 48.3, 39.0, 38.3, 29.3, 21.5, 19.8, 13.5. HRMS: Calcd for $C_{31}H_{35}N_2O_5S$ $[M+H]^+$ 547.2267, Found 547.2262.



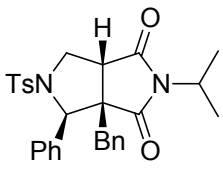
(**5i**): white solid: m. p. 166-168 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.72-7.63 (m, 3H), 7.45-7.30 (m, 10H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.02 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.38 (s, 1H), 4.15-4.10 (m, 1H), 4.00 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.33 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.91-2.85 (m, 3H), 2.36 (s, 3H), 2.26 (d, *J* = 13.5 Hz, 1H), 0.82-0.49 (m, 7H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.4, 176.2, 143.5, 137.2, 135.2, 133.2, 129.5, 128.8, 128.6, 128.5, 127.9, 127.6, 127.5, 127.2, 127.1, 126.4, 126.1, 69.3, 61.5, 50.6, 48.4, 39.3, 39.0, 29.2, 21.4, 19.6, 13.2. HRMS: Calcd for C34H35N2O4S $[M+H]^+$ 567.2318, Found 567.2311.



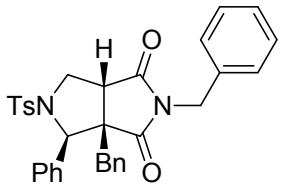
(**6a**): white solid. m. p. 190-192 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.44 (d, *J* = 8.0 Hz, 2H), 7.34-7.30 (m, 3H), 7.24-7.23 (m, 2H), 7.18-7.13 (m, 5H), 6.96-6.94 (m, 2H), 5.34 (s, 1H), 4.09-4.05 (m, 1H), 3.81 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.16 (dd, *J* = 14.0, 2.5 Hz, 1H), 2.66 (d, *J* = 13.5 Hz, 1H), 2.35 (s, 3H), 2.06 (d, *J* = 13.5 Hz, 1H), 1.15 (s, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 180.1, 177.4, 143.5, 137.5, 135.3, 134.9, 129.6, 129.5, 128.7, 128.3, 127.8, 127.5, 127.3, 69.7, 60.7, 58.6, 50.9, 48.1, 39.4, 27.6, 21.4. HRMS: Calcd for C30H33N2O4S $[M+H]^+$ 517.2161, Found 517.2152.



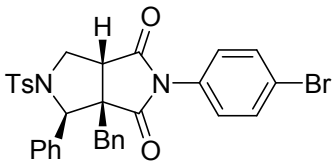
**(6b)**: white solid: m. p. 164-165 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.41 (d, *J* = 8.5 Hz, 2H),7.34-7.24 (m, 5H), 7.14-7.13 (m, 5H), 6.92-6.90 (m, 2H), 5.34 (s, 1H), 4.10-4.06 (m, 1H), 3.97 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.23 (d, *J* = 9.0, 2.5 Hz, 1H), 2.93-2.88 (m, 2H), 2.71 (d, *J* = 13.5 Hz, 1H), 2.36 (s, 3H), 2.08 (d, *J* = 13.5 Hz, 1H), 1.19-0.89 (m, 6H), 0.83-0.80 (m, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.4, 176.3, 143.5, 137.1, 135.2, 129.5, 129.4, 128.8, 128.7, 128.4, 127.8, 127.5, 127.1, 69.3, 61.3, 50.5, 48.3, 39.2, 39.1, 28.6, 26.8, 22.1, 21.5, 13.8. HRMS: Calcd for C31H35N2O4S $[M+H]^+$ 531.2318, Found 531.2310.



(**6c**): white solid: m. p. 188-189 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.41-7.39 (m, 2H), 7.33-7.31 (m, 3H), 7.23-7.22 (m, 2H), 7.18-7.10 (m, 5H), 6.95-6.93 (m, 2H), 5.36 (s, 1H), 4.07-4.03 (m, 1H), 3.99-3.94 (m, 1H), 3.84 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.23 (dd, *J* = 9.5, 3.0 Hz, 1H), 2.70 (d, *J* = 13.5 Hz, 1H), 2.34 (s, 3H), 2.12 (d, *J* = 13.5 Hz, 1H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.3, 176.3, 143.5, 137.1, 135.3, 134.8, 129.5, 129.4, 128.8, 128.4, 127.9, 127.5, 127.2, 69.3, 60.9, 50.5, 48.1, 44.2, 39.1, 21.5,18.6, 18.5. HRMS: Calcd for C29H31N2O4S $[M+H]^+$ 503.2005, Found 503.1999.



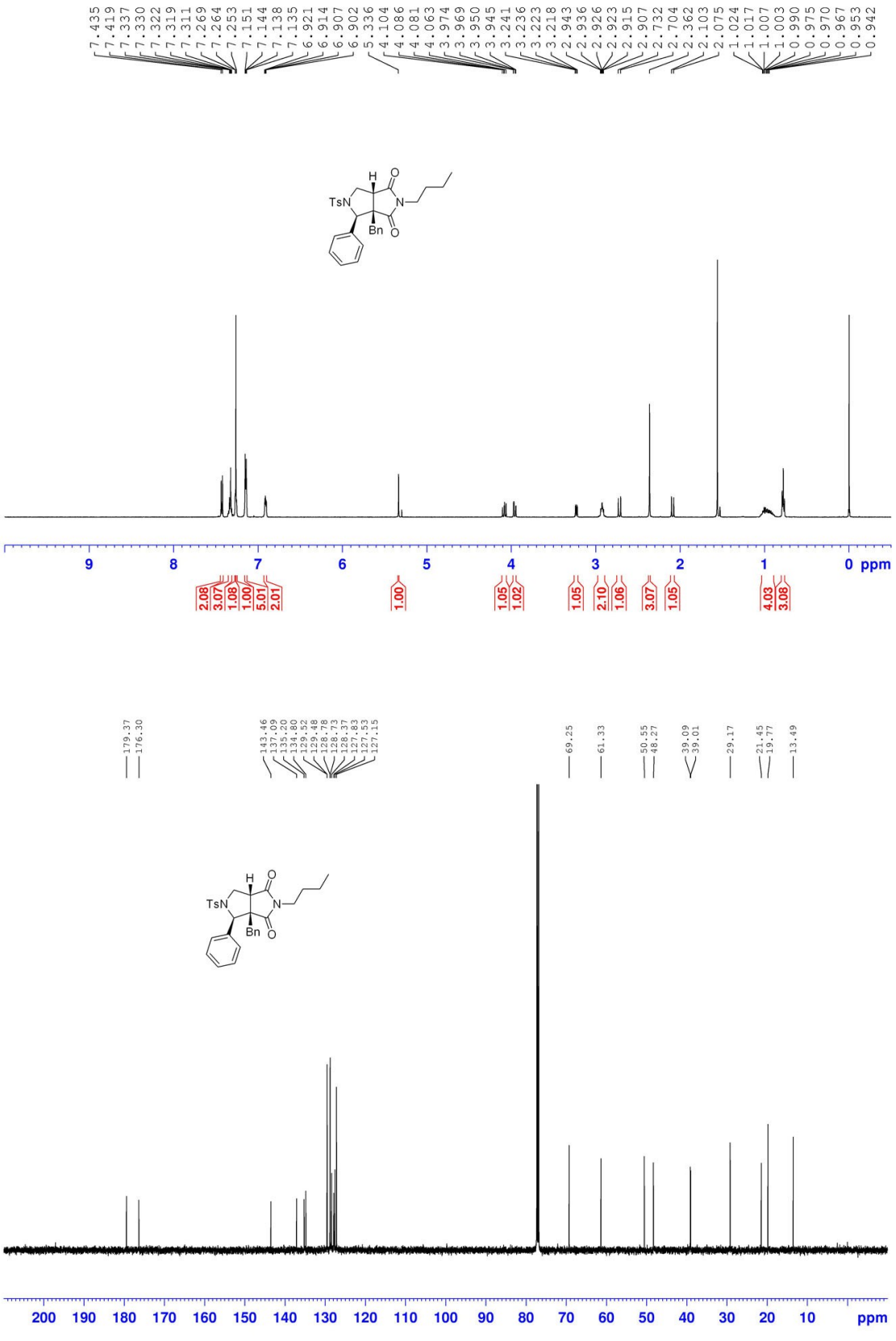

(**6d**): white solid: m. p. 174-175 °C. $^{1}$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.42 (d, *J* = 8.0 Hz, 2H), 7.32-7.14 (m, 10H), 7.02-6.97 (m, 3H), 6.89-6.86 (m, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 5.35 (s, 1H), 4.18 (d, *J* = 14.5 Hz, 1H), 4.12 (d, *J* = 14.5 Hz, 1H), 4.08-4.01 (m, 2H), 3.21 (d, *J* = 9.0, 3.0 Hz, 1H), 2.73 (d, *J* = 13.5 Hz, 1H), 2.38 (s, 3H), 2.06 (d, *J* = 13.5 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.4, 175.9, 143.5, 136.9, 135.1, 134.6, 134.4, 129.6, 129.2, 128.8, 128.6, 128.5, 128.4, 128.3, 127.8, 127.7, 127.3, 127.2, 69.5, 61.3, 50.4, 48.2, 42.8, 38.8, 21.5. HRMS: Calcd for $C_{33}H_{31}N_2O_4S$ $[M+H]^+$ 551.2005, Found 551.1999.



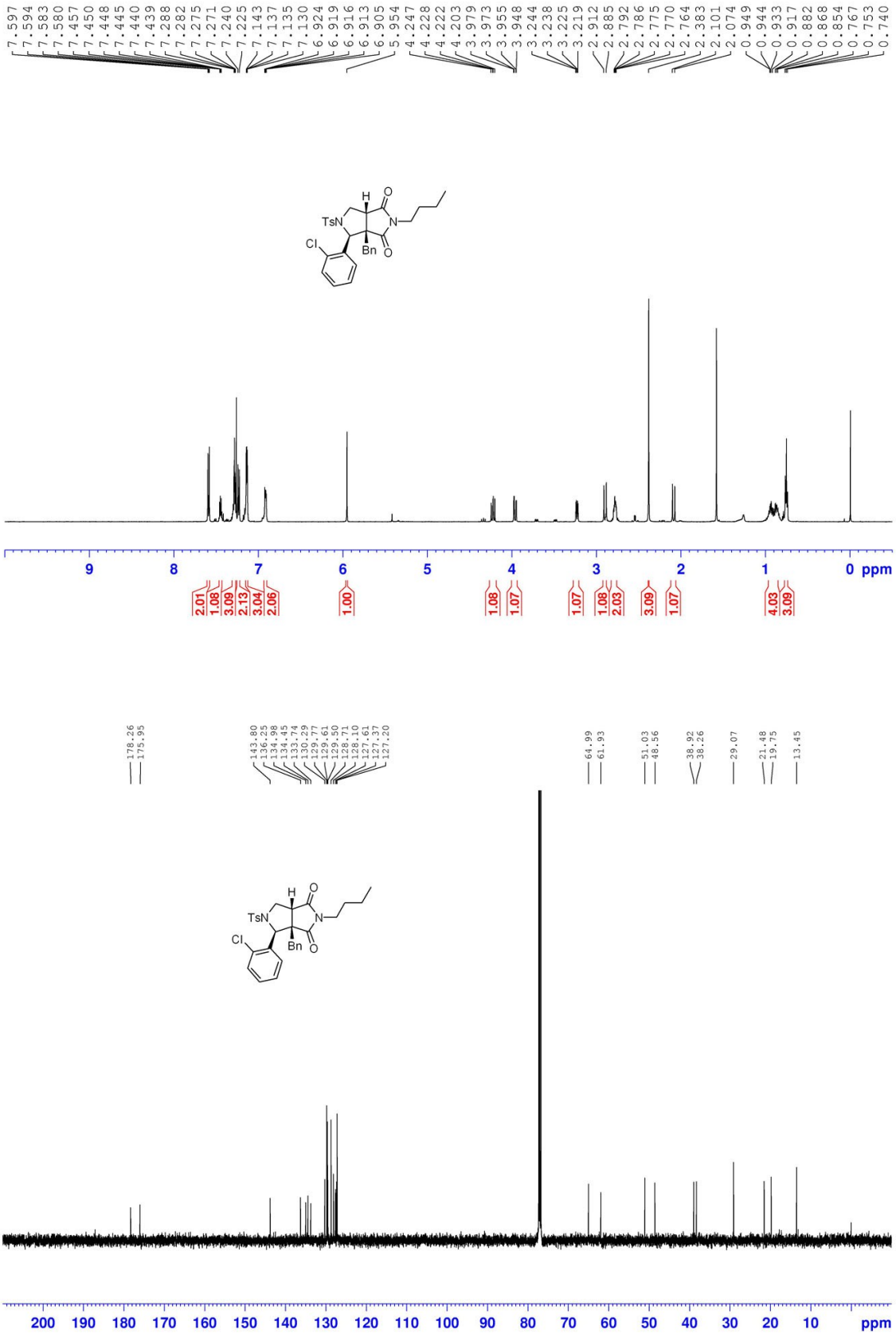

(**6e**): white solid: m. p. 195-196 °C. $^{1}$H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.45-7.43 (m, 4H), 7.37-7.33 (m, 3H), 7.28-7.20 (m, 5H), 7.13-7.12 (m, 2H), 6.99-6.97 (m, 2H), 6.48 (d, *J* = 9.0 Hz, 2H), 5.55 (s, 1H), 4.19-4.15 (m, 1H), 4.00 (d, *J* = 9.0, 3.0 Hz, 1H), 3.46 (dd, *J* = 9.5, 2.5 Hz, 1H), 2.82 (d, *J* = 13.5 Hz, 1H), 2.35 (s, 3H), 2.20 (d, *J* = 13.5 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) = 178.2, 174.9, 143.7, 136.9, 135.2, 134.7, 132.1, 130.0, 129.6, 129.4, 129.0, 128.9, 128.6, 127.8, 127.7, 127.3, 122.7, 69.1, 62.2, 50.6, 48.6, 39.5, 21.5. HRMS: Calcd for $C_{32}H_{28}BrN_2O_4S$ $[M+H]^+$ 615.0953, Found 615.0949.

## 4 $^{1}$H NMR and $^{13}$C NMR Spectra of All Compounds

Compound **4a**



Compound **4b**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7.445
7.440
7.439
7.288
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7.275
7.271
7.240
7.225
7.143
7.137
7.135
7.130
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6.919
6.916
6.913
6.905
5.954
4.247
4.228
4.222
4.203
3.979
3.973
3.955
3.948
3.244
3.238
3.225
3.219
2.912
2.885
2.792
2.786
2.775
2.770
2.764
2.383
2.101
2.074
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0.944
0.933
0.917
0.882
0.868
0.854
0.767
0.753
0.740
TsN
Cl
Bn
9
8
7
6
5
4
3
2
1
0 ppm
2.01
1.08
3.09
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2.06
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1.08
1.07
1.07
1.08
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136.25
134.98
134.45
133.74
130.29
129.77
129.61
128.90
128.71
128.10
127.61
127.37
127.20
64.99
61.93
51.03
48.56
38.92
38.26
29.07
21.48
19.75
13.45
200
190
180
170
160
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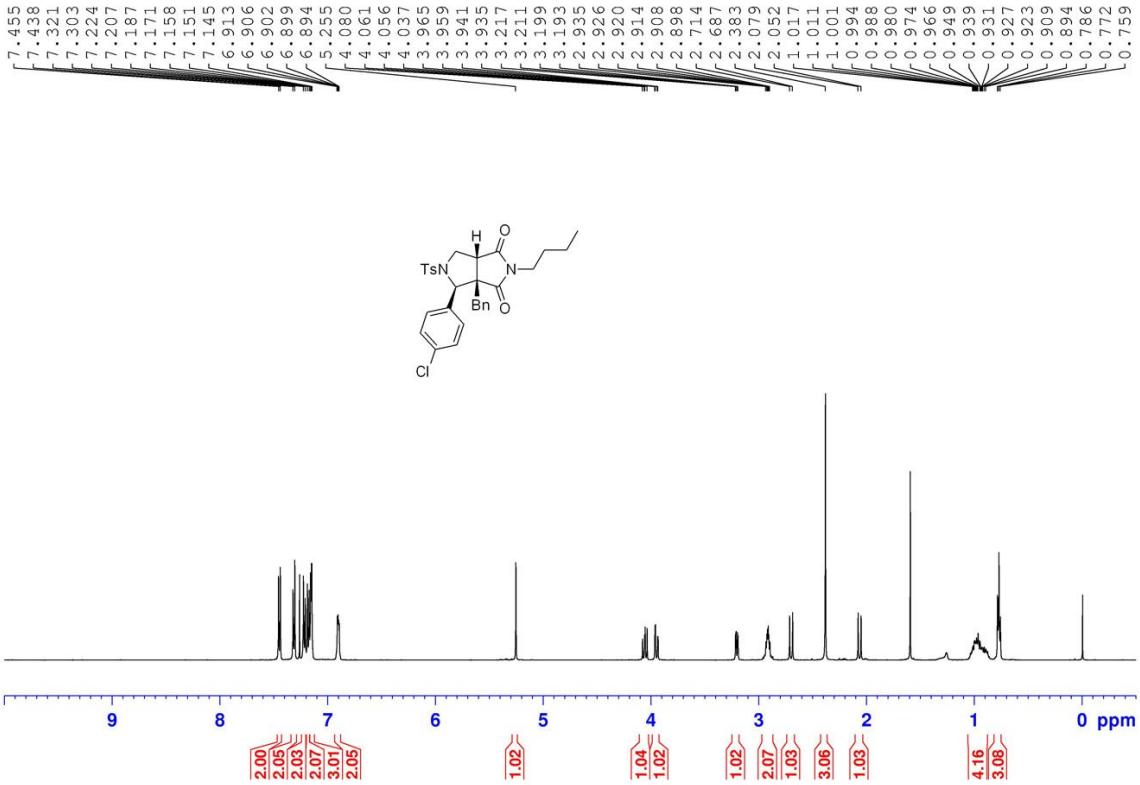
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **4c**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7.145
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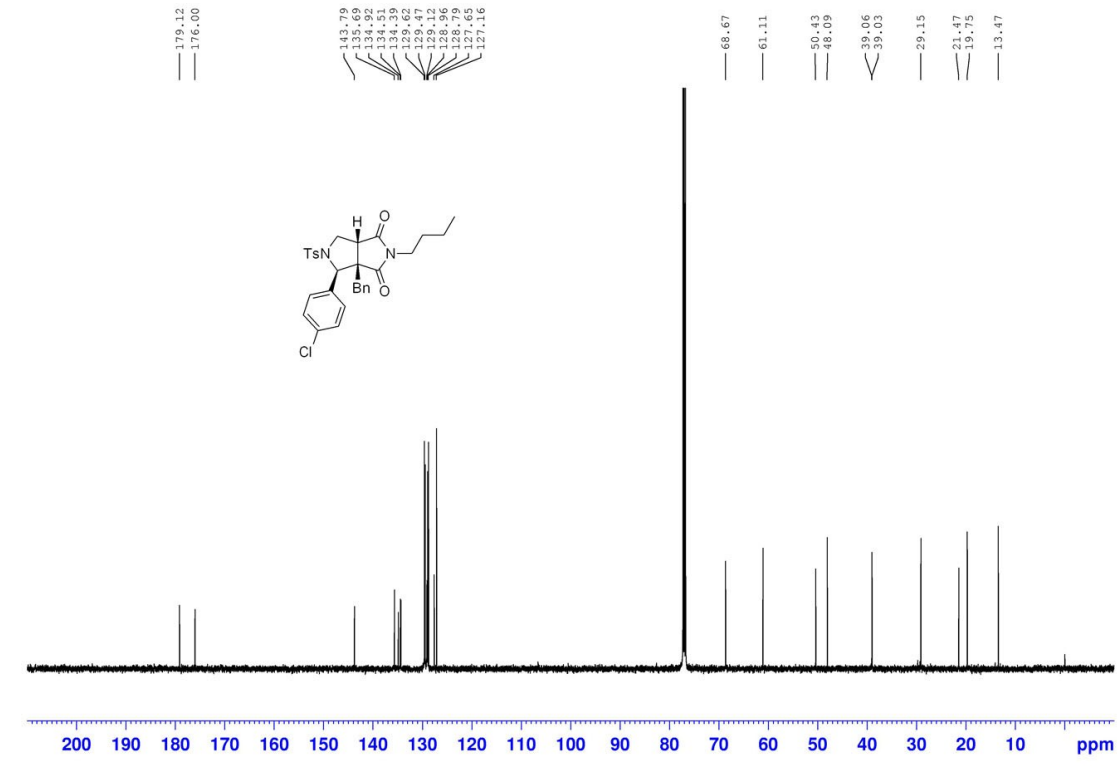
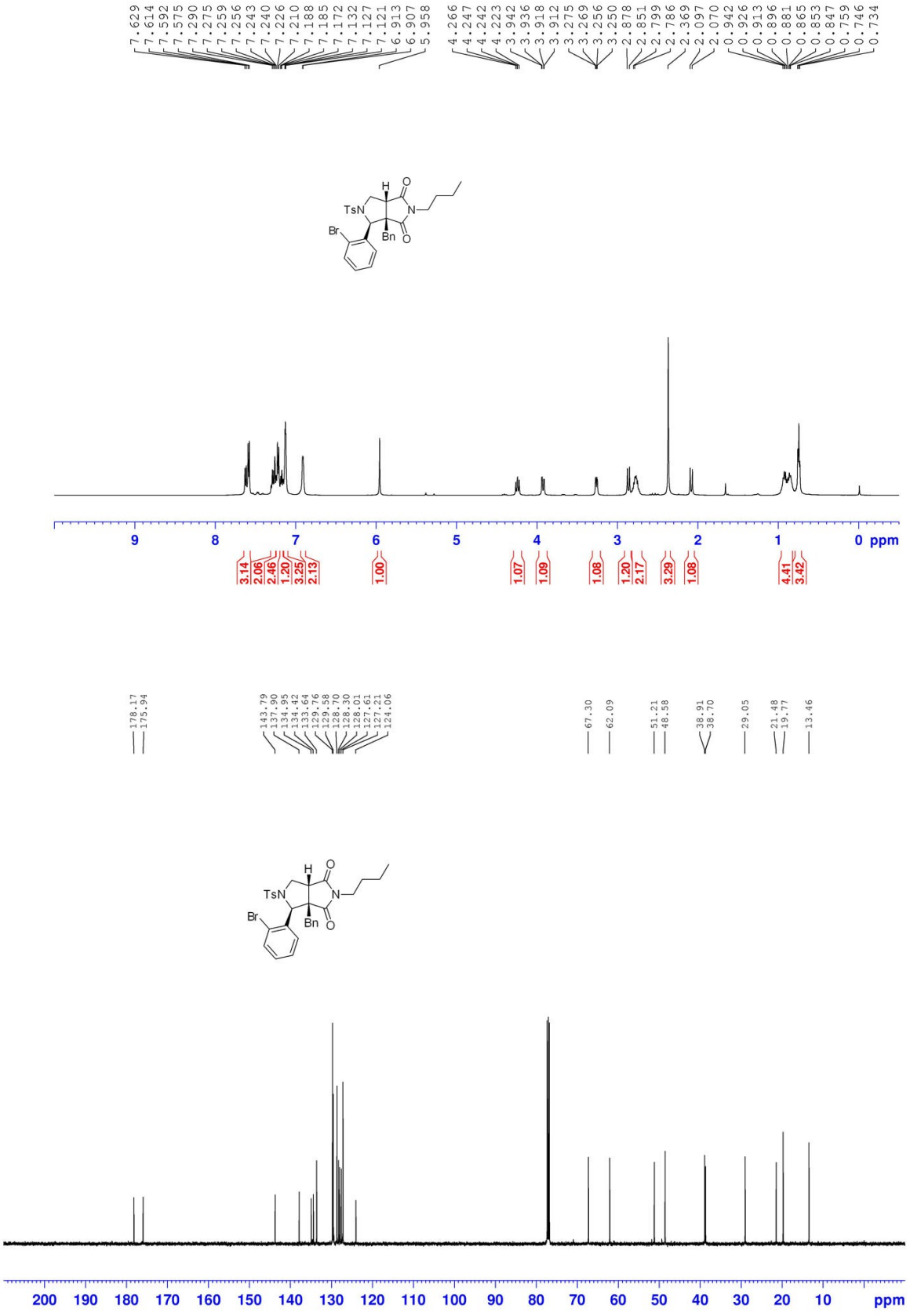
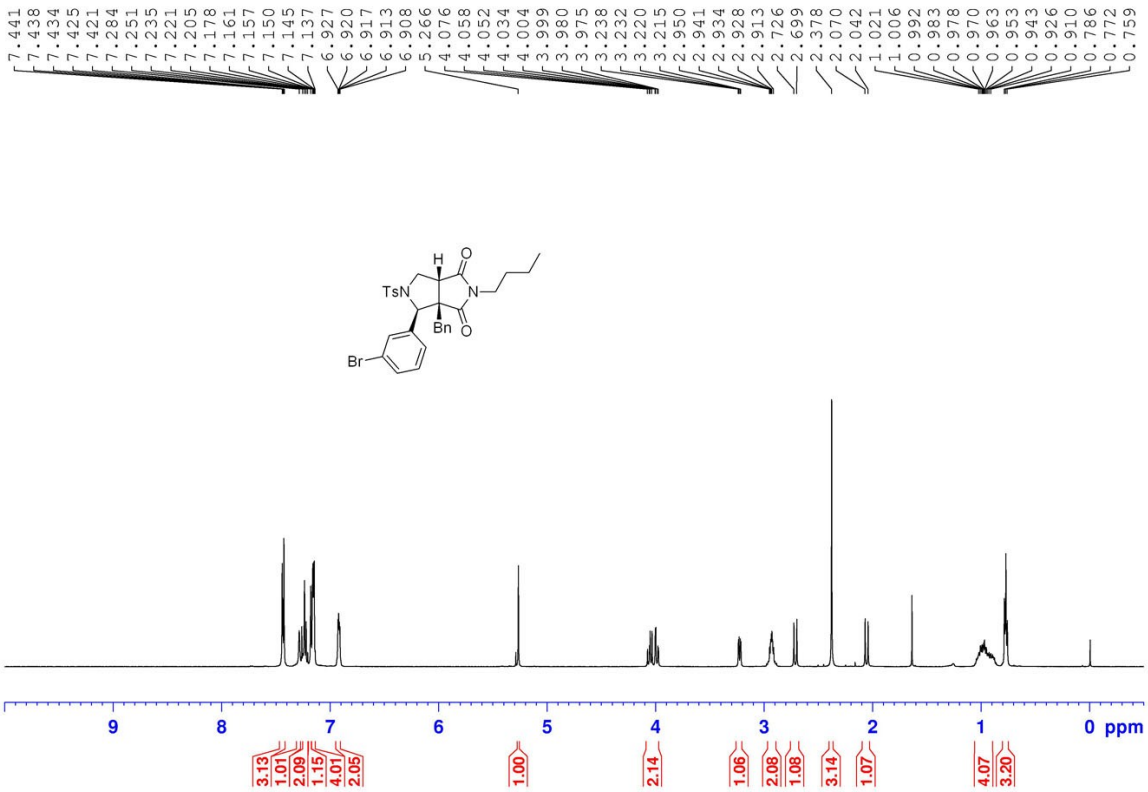
6.902
6.899
6.894
5.255
4.080
4.061
4.056
4.037
3.965
3.959
3.941
3.935
3.217
3.211
3.199
3.193
2.935
2.926
2.920
2.914
2.908
2.898
2.714
2.687
2.383
2.079
2.052
1.017
1.011
1.001
0.994
0.988
0.980
0.974
0.966
0.949
0.939
0.931
0.927
0.923
0.909
0.894
0.786
0.772
0.759
H
O
TsN
N
Bn
O
Cl
9
8
7
6
5
4
3
2
1
0 ppm
2.00
2.05
2.03
2.07
3.01
2.05
1.02
1.04
1.02
1.02
2.07
1.03
3.06
1.03
4.16
3.08

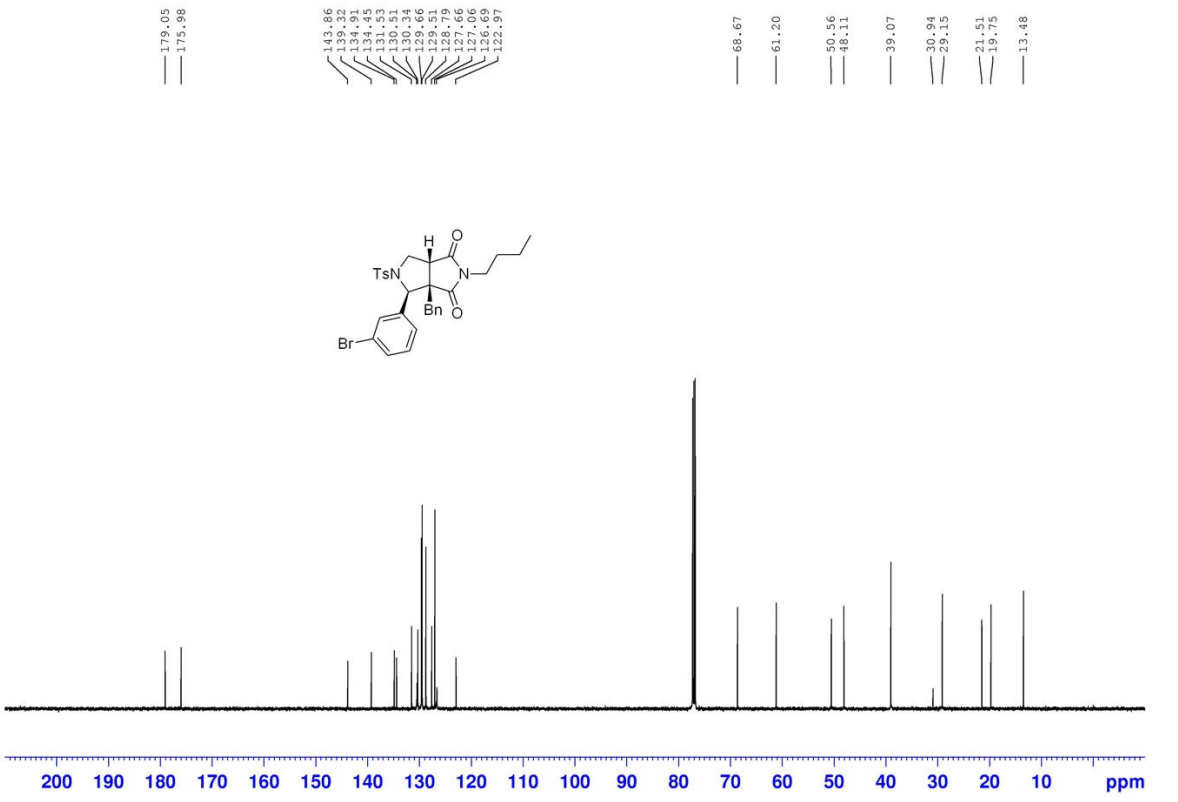

179.12
176.00
143.79
135.69
134.92
134.51
134.39
129.62
129.47
129.12
128.96
128.79
127.65
127.16
68.67
61.11
50.43
48.09
39.06
39.03
29.15
21.47
19.75
13.47
H
O
TsN
N
Bn
O
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **4d**

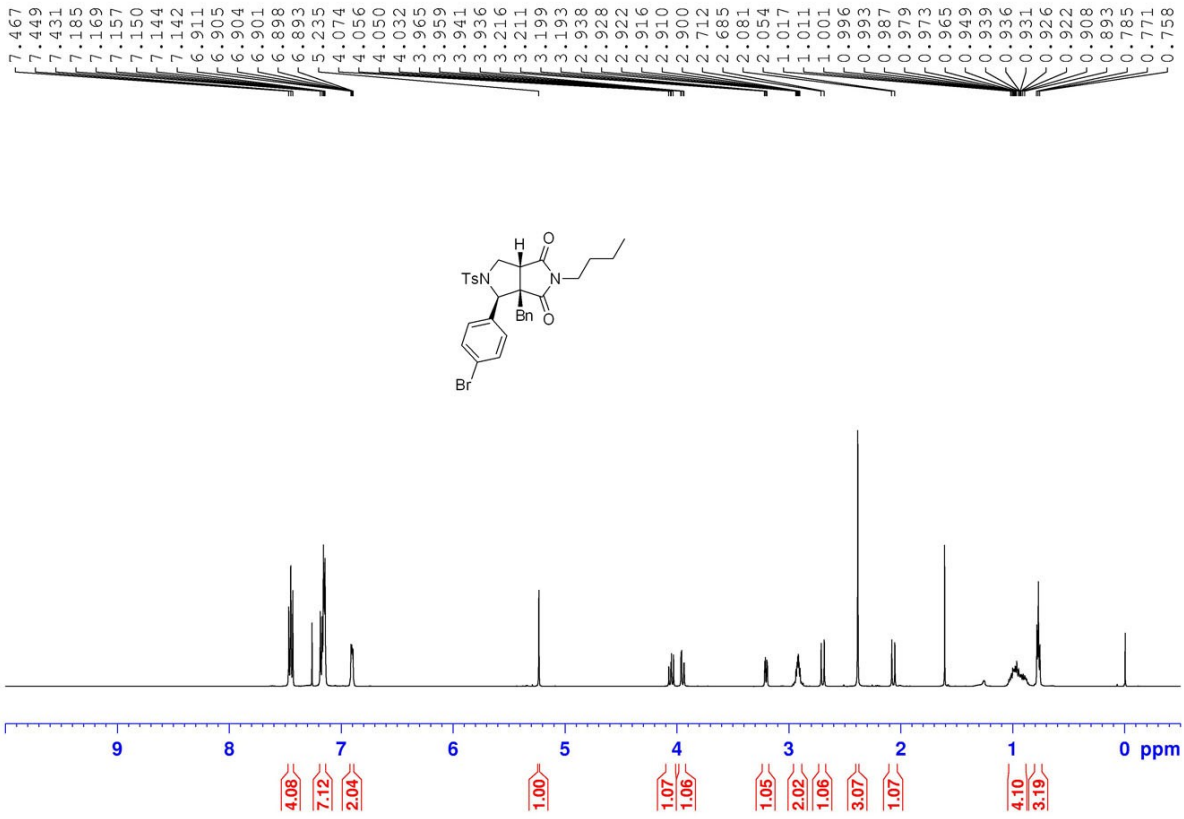

7.629
7.614
7.592
7.575
7.290
7.275
7.259
7.256
7.243
7.240
7.226
7.210
7.188
7.185
7.172
7.132
7.127
7.121
6.913
6.907
5.958
4.266
4.247
4.242
4.223
3.942
3.936
3.918
3.912
3.275
3.269
3.256
3.250
2.878
2.851
2.799
2.786
2.369
2.097
2.070
0.942
0.926
0.913
0.896
0.881
0.865
0.853
0.847
0.759
0.746
0.734
TsN
Br
Bn
9
8
7
6
5
4
3
2
1
0 ppm
3.14
2.06
2.46
1.20
3.25
2.13
1.00
1.07
1.09
1.08
1.20
2.17
3.29
1.08
4.41
3.42
178.17
175.94
143.79
137.90
134.95
134.42
133.64
129.76
129.58
128.70
128.30
128.01
127.61
127.21
124.06
67.30
62.09
51.21
48.58
38.91
38.70
29.05
21.48
19.77
13.46
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

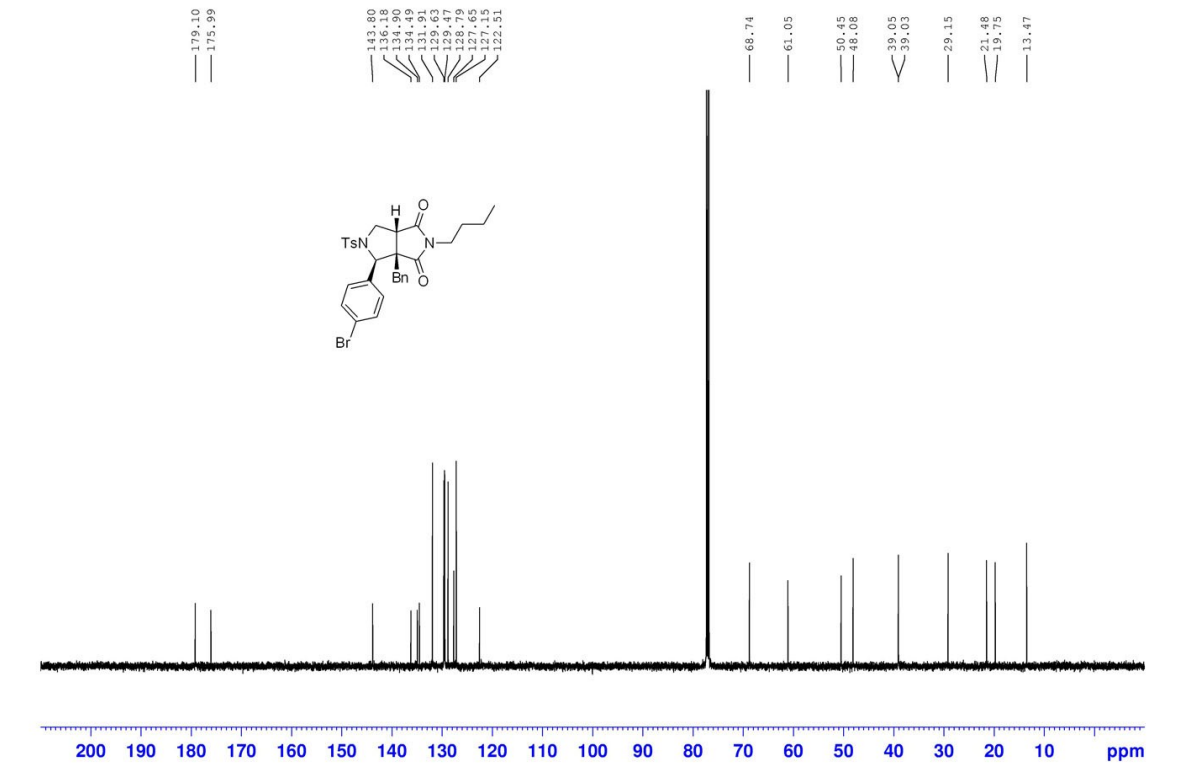
Compound **4e**


7.441
7.438
7.434
7.425
7.421
7.284
7.251
7.235
7.221
7.205
7.178
7.161
7.157
7.150
7.145
7.137
6.927
6.920
6.917
6.913
6.908
5.266
4.076
4.058
4.052
4.034
4.004
3.999
3.980
3.975
3.238
3.232
3.220
3.215
2.950
2.941
2.934
2.928
2.913
2.726
2.699
2.378
2.070
2.042
1.021
1.006
0.992
0.983
0.978
0.970
0.963
0.953
0.943
0.926
0.910
0.786
0.772
0.759
TsN
N
Bn
Br
9
8
7
6
5
4
3
2
1
0 ppm
3.13
1.01
2.09
1.15
4.01
2.05
1.00
2.14
1.06
2.08
1.08
3.14
1.07
4.07
3.20

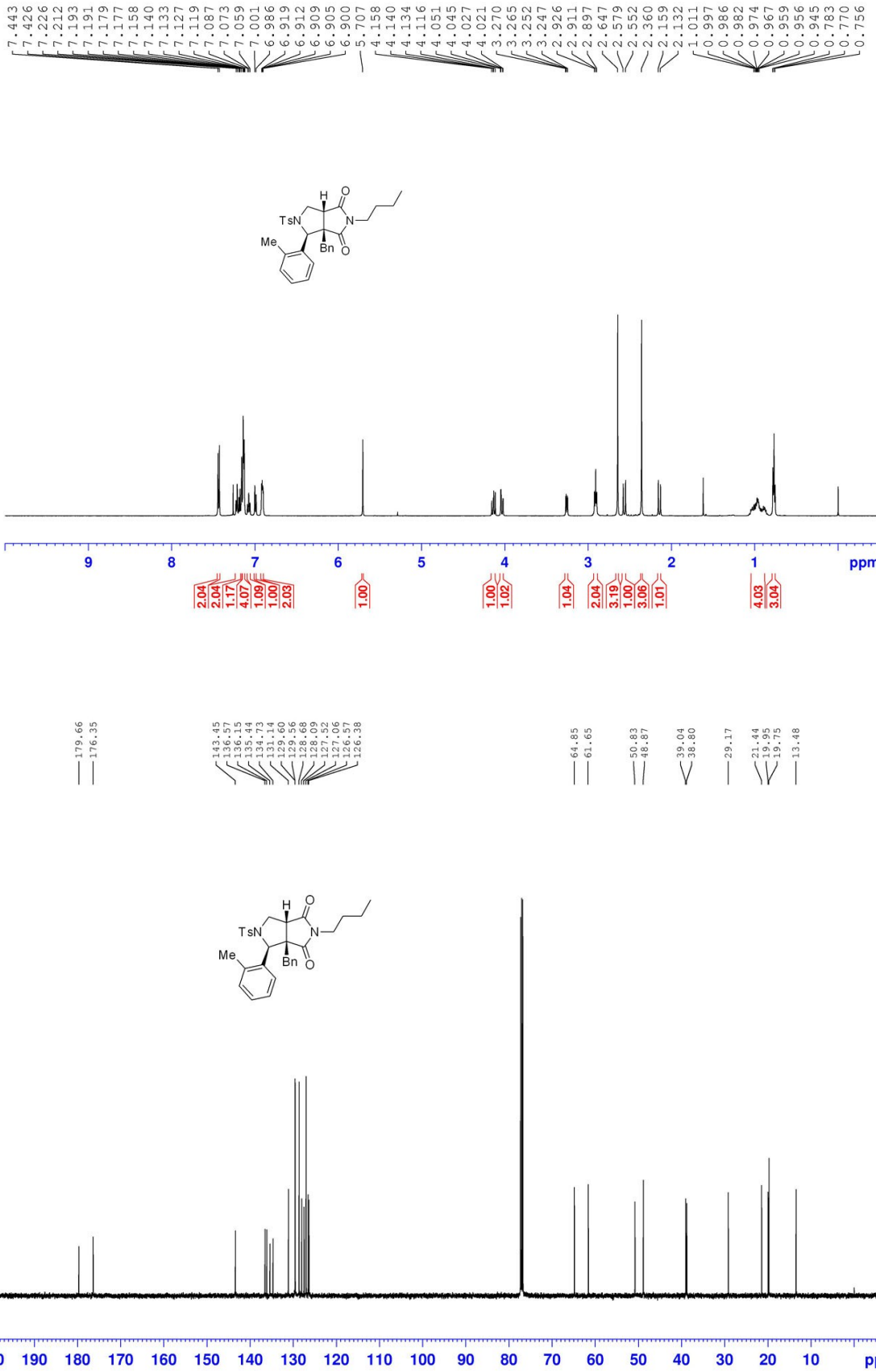

179.05
175.98
143.86
139.32
134.91
134.45
131.53
130.51
130.34
129.66
129.51
128.79
127.66
127.06
126.69
122.97
68.67
61.20
50.56
48.11
39.07
30.94
29.15
21.51
19.75
13.48
TsN
N
Bn
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **4f**

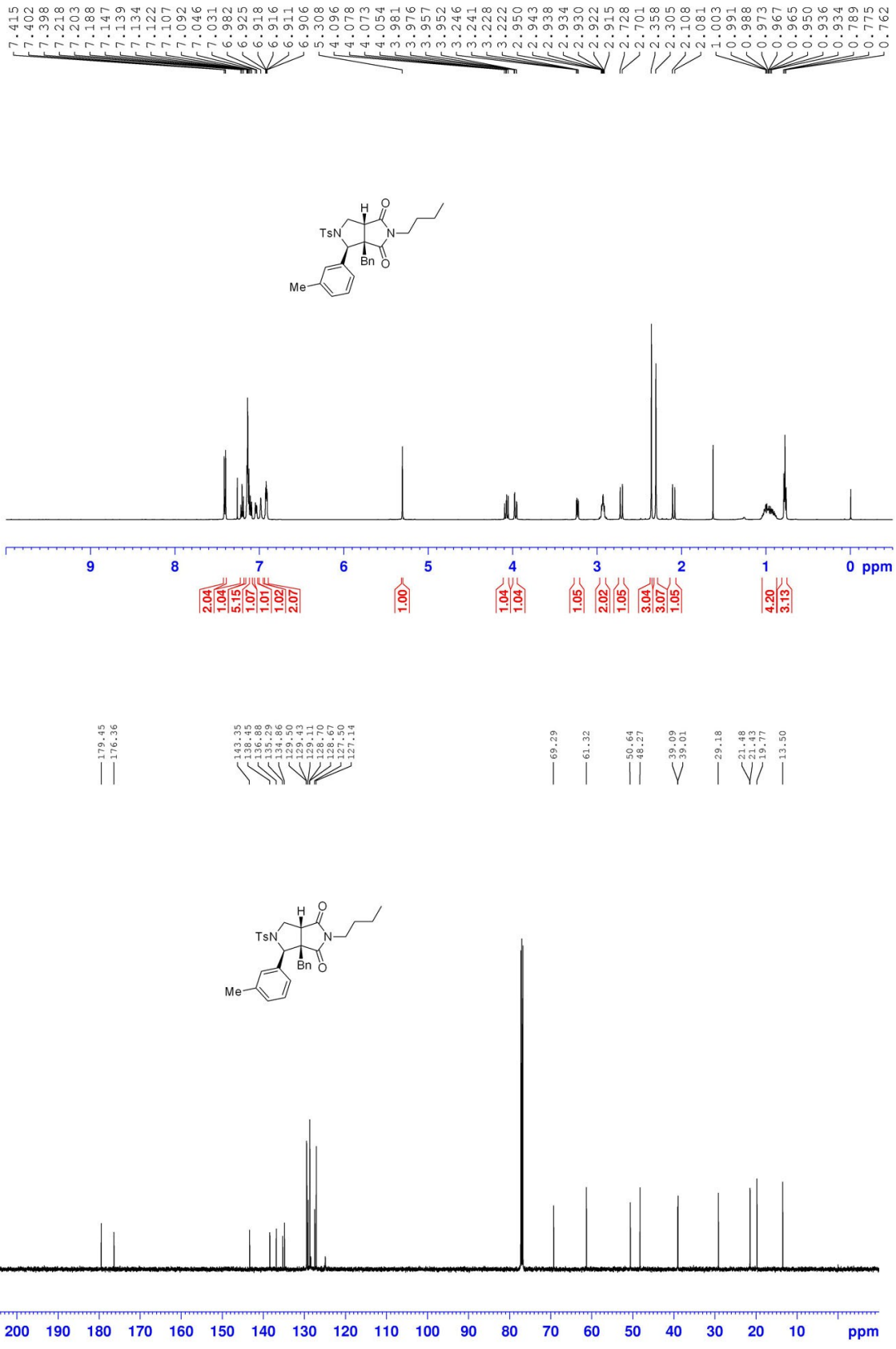

7.467
7.449
7.431
7.185
7.169
7.157
7.150
7.144
7.142
6.911
6.905
6.904
6.901
6.898
6.893
5.235
4.074
4.056
4.050
4.032
3.965
3.959
3.941
3.936
3.216
3.211
3.199
3.193
2.938
2.928
2.922
2.916
2.910
2.900
2.712
2.685
2.081
2.054
1.017
1.011
1.001
0.996
0.993
0.987
0.979
0.973
0.965
0.949
0.939
0.936
0.931
0.926
0.922
0.908
0.893
0.785
0.771
0.758
H
O
TsN
N
Bn
O
Br
9
8
7
6
5
4
3
2
1
0 ppm
4.08
7.12
2.04
1.00
1.07
1.06
1.05
2.02
1.06
3.07
1.07
4.10
3.19


179.10
175.99
143.80
136.18
134.90
134.49
131.91
129.63
129.47
128.79
127.65
127.15
122.51
68.74
61.05
50.45
48.08
39.05
39.03
29.15
21.48
19.75
13.47
H
O
TsN
N
Bn
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

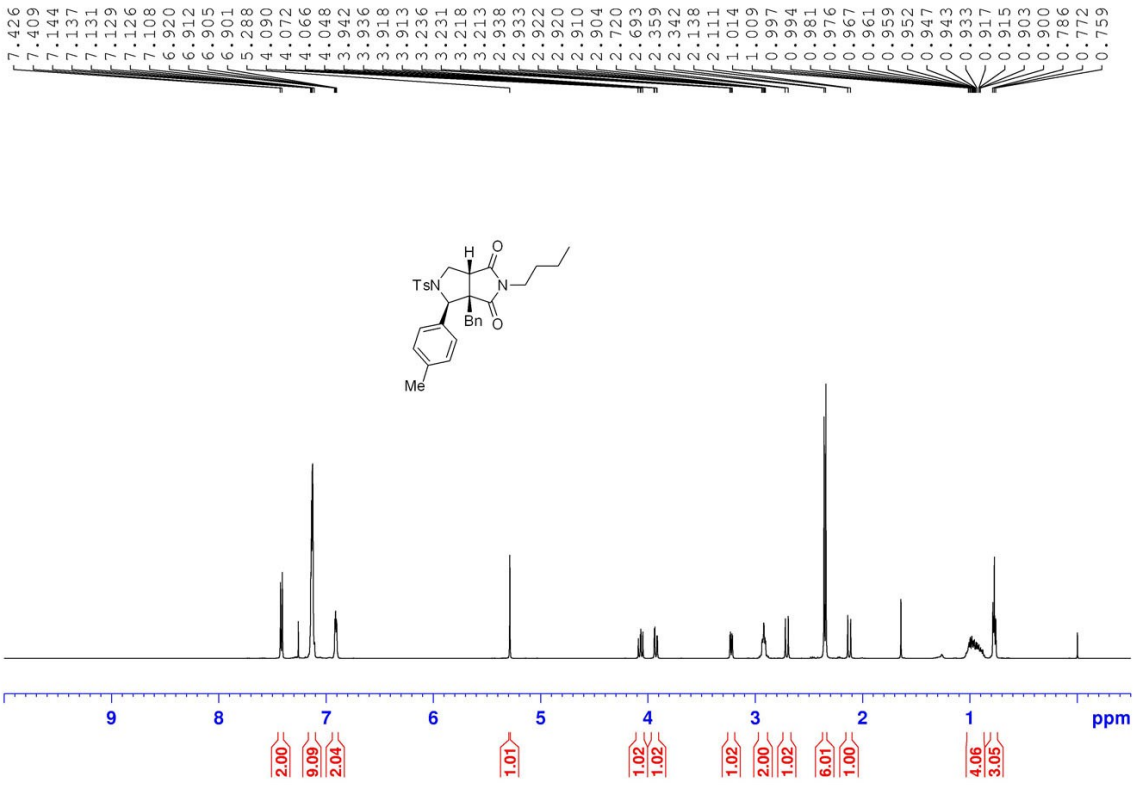
Compound **4g**

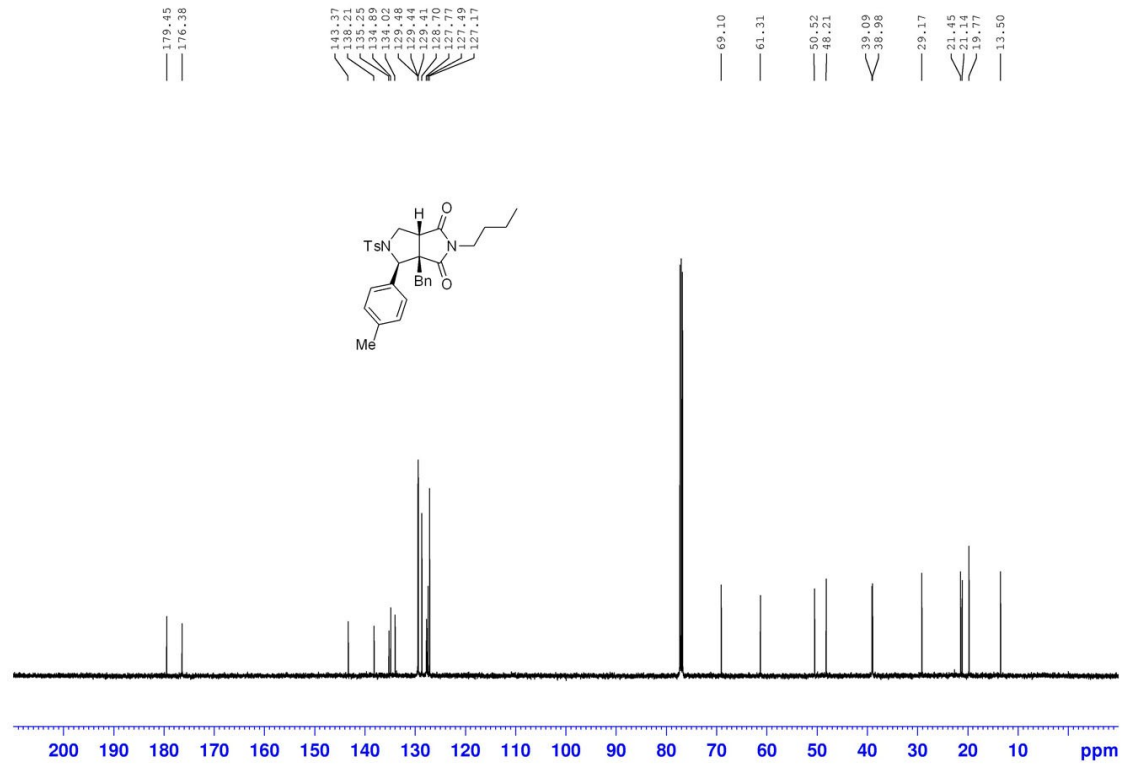

7.443
7.426
7.226
7.212
7.193
7.191
7.179
7.177
7.158
7.140
7.133
7.127
7.119
7.087
7.073
7.059
7.001
6.986
6.919
6.912
6.909
6.905
6.900
5.707
4.158
4.140
4.134
4.116
4.051
4.045
4.027
4.021
3.270
3.265
3.252
3.247
2.926
2.911
2.897
2.647
2.579
2.552
2.360
2.159
2.132
1.011
0.997
0.986
0.982
0.974
0.967
0.959
0.956
0.945
0.783
0.770
0.756
H
O
TsN
N
Me
Bn
O
9
8
7
6
5
4
3
2
1
ppm
2.04
2.04
1.17
4.07
1.09
1.00
2.03
1.00
1.00
1.02
1.04
2.04
3.19
1.00
3.06
1.01
4.03
3.04
179.66
176.35
143.45
136.57
136.15
135.44
134.73
134.14
131.60
129.56
128.68
128.09
127.52
127.06
126.57
126.38
64.85
61.65
50.83
48.87
39.04
38.80
29.17
21.44
19.95
19.75
13.48
H
O
TsN
N
Me
Bn
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **4h**

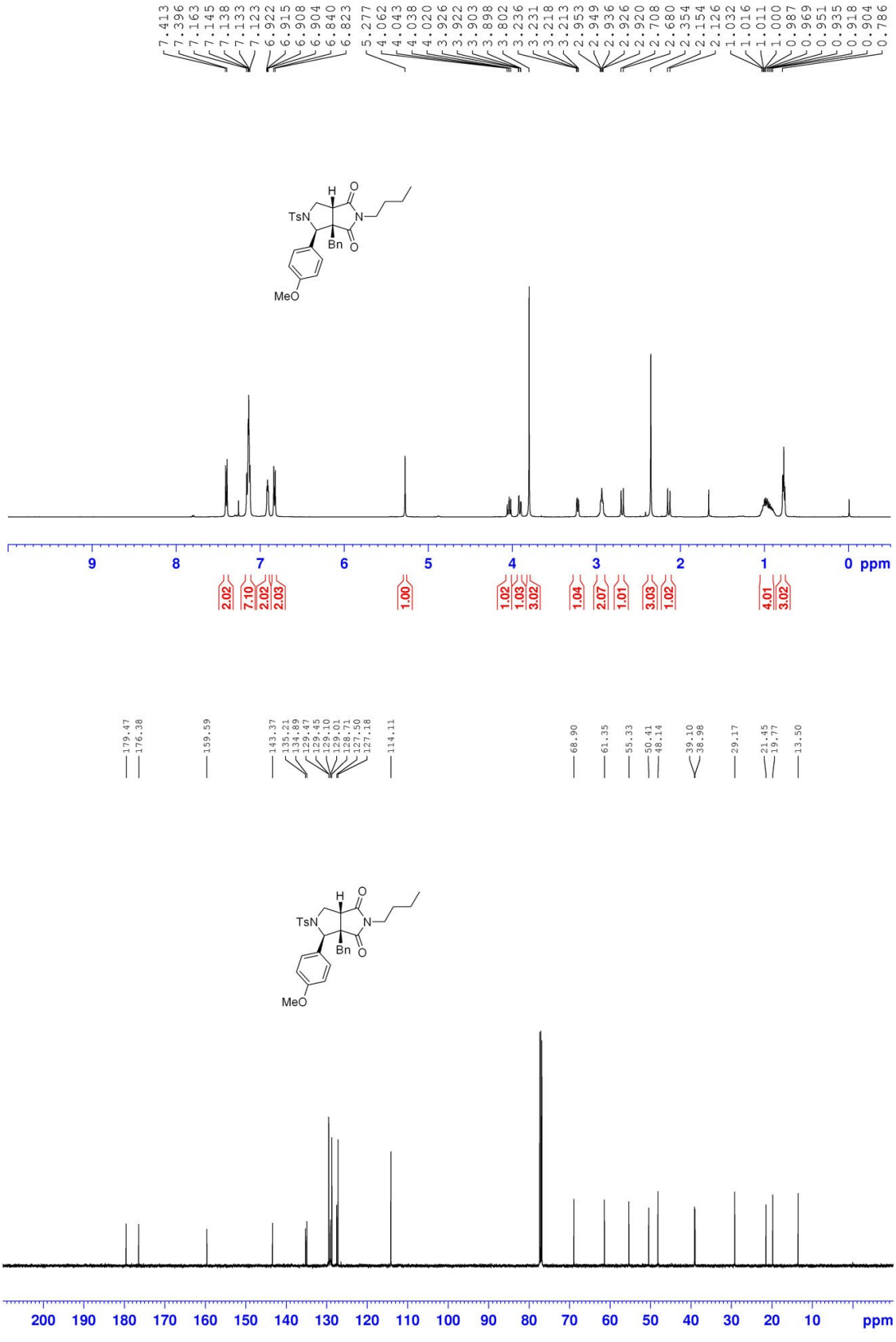

7.415
7.402
7.398
7.218
7.203
7.188
7.147
7.139
7.134
7.122
7.107
7.092
7.046
7.031
6.982
6.925
6.918
6.916
6.911
6.906
5.308
4.096
4.078
4.073
4.054
3.981
3.976
3.957
3.952
3.246
3.241
3.228
3.222
2.950
2.943
2.938
2.934
2.930
2.922
2.915
2.728
2.701
2.358
2.305
2.108
2.081
1.003
0.991
0.988
0.973
0.967
0.965
0.950
0.936
0.934
0.789
0.775
0.762
TsN
Bn
Me
9
8
7
6
5
4
3
2
1
0 ppm
2.04
1.04
5.15
1.07
1.01
1.02
2.07
1.00
1.04
1.04
1.05
2.02
1.05
3.04
3.07
1.05
4.20
3.13
179.45
176.36
143.35
138.45
136.88
135.29
134.86
129.50
129.43
129.11
128.70
128.67
127.50
127.14
69.29
61.32
50.64
48.27
39.09
39.01
29.18
21.48
21.43
19.77
13.50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **4i**

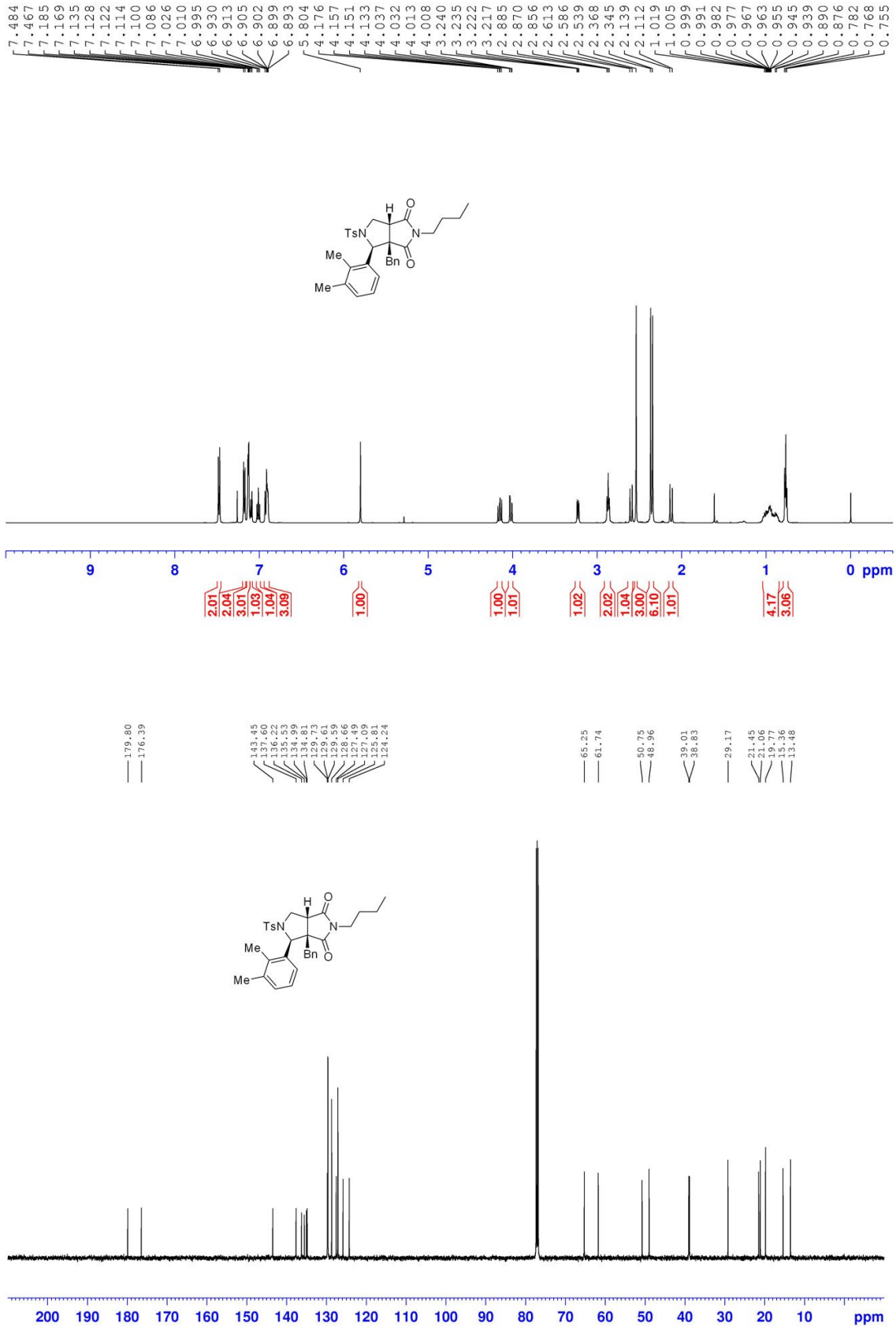

7.426
7.409
7.144
7.137
7.131
7.129
7.126
7.108
6.920
6.912
6.905
6.901
5.288
4.090
4.072
4.066
4.048
3.942
3.936
3.918
3.913
3.236
3.231
3.218
3.213
2.938
2.933
2.922
2.920
2.910
2.904
2.720
2.693
2.359
2.342
2.138
2.111
1.014
1.009
0.997
0.994
0.981
0.976
0.967
0.961
0.959
0.952
0.947
0.943
0.933
0.917
0.915
0.903
0.900
0.786
0.772
0.759
H
O
TsN
N
Bn
O
Me
9
8
7
6
5
4
3
2
1
ppm
2.00
9.09
2.04
1.01
1.02
1.02
1.02
2.00
1.02
6.01
1.00
4.06
3.05


179.45
176.38
143.37
138.21
135.25
134.89
134.02
130.48
129.44
129.41
128.70
127.77
127.49
127.17
69.10
61.31
50.52
48.21
39.09
38.98
29.17
21.45
21.14
19.77
13.50
H
O
TsN
N
Bn
O
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

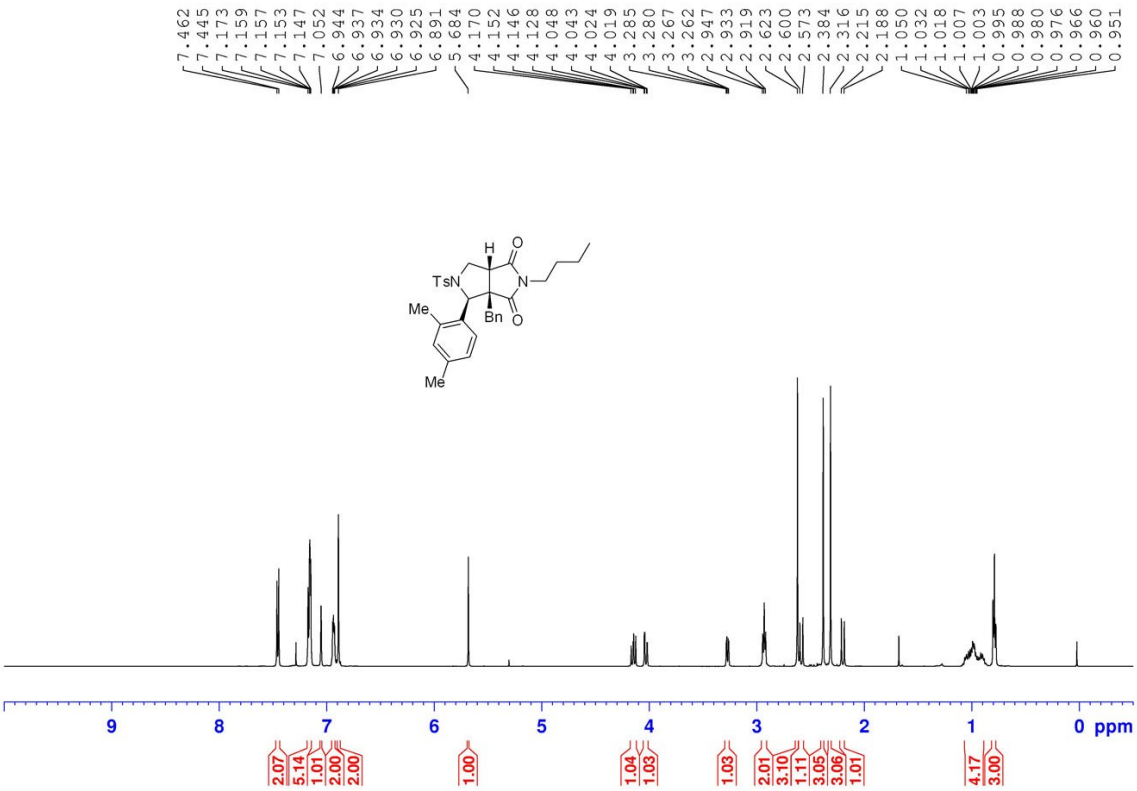
Compound **4j**

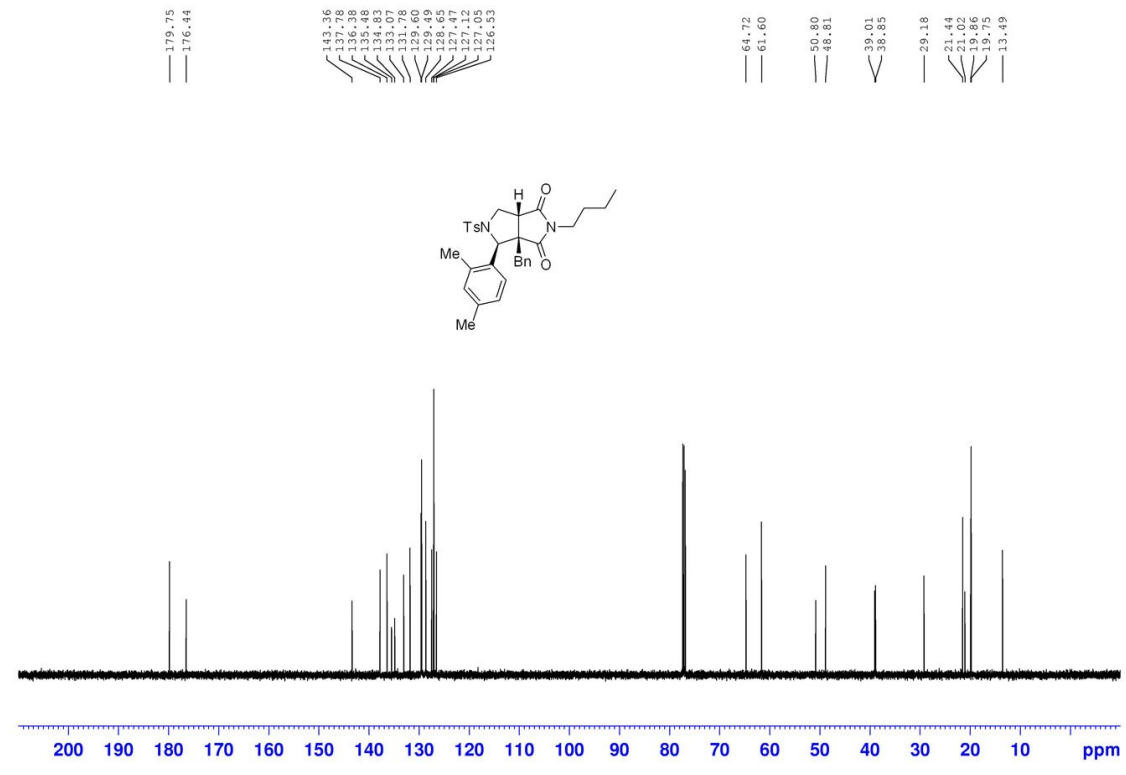

7.413
7.396
7.163
7.145
7.138
7.133
7.123
6.922
6.915
6.908
6.904
6.840
6.823
5.277
4.062
4.043
4.038
4.020
3.926
3.922
3.903
3.898
3.802
3.236
3.231
3.218
3.213
2.953
2.949
2.936
2.926
2.920
2.708
2.680
2.354
2.154
2.126
1.032
1.016
1.011
1.000
0.987
0.969
0.951
0.935
0.918
0.904
0.786
TsN
Bn
MeO
9 8 7 6 5 4 3 2 1 0 ppm
2.02 7.10 2.02 2.03 1.00 1.02 1.03 3.02 1.04 2.07 1.01 3.03 1.02 4.01 3.02
179.47
176.38
159.59
143.37
135.21
134.89
129.47
129.45
129.10
129.01
128.71
127.50
127.18
114.11
68.90
61.35
55.33
50.41
48.14
39.10
38.98
29.17
21.45
19.77
13.50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Compound **4k**

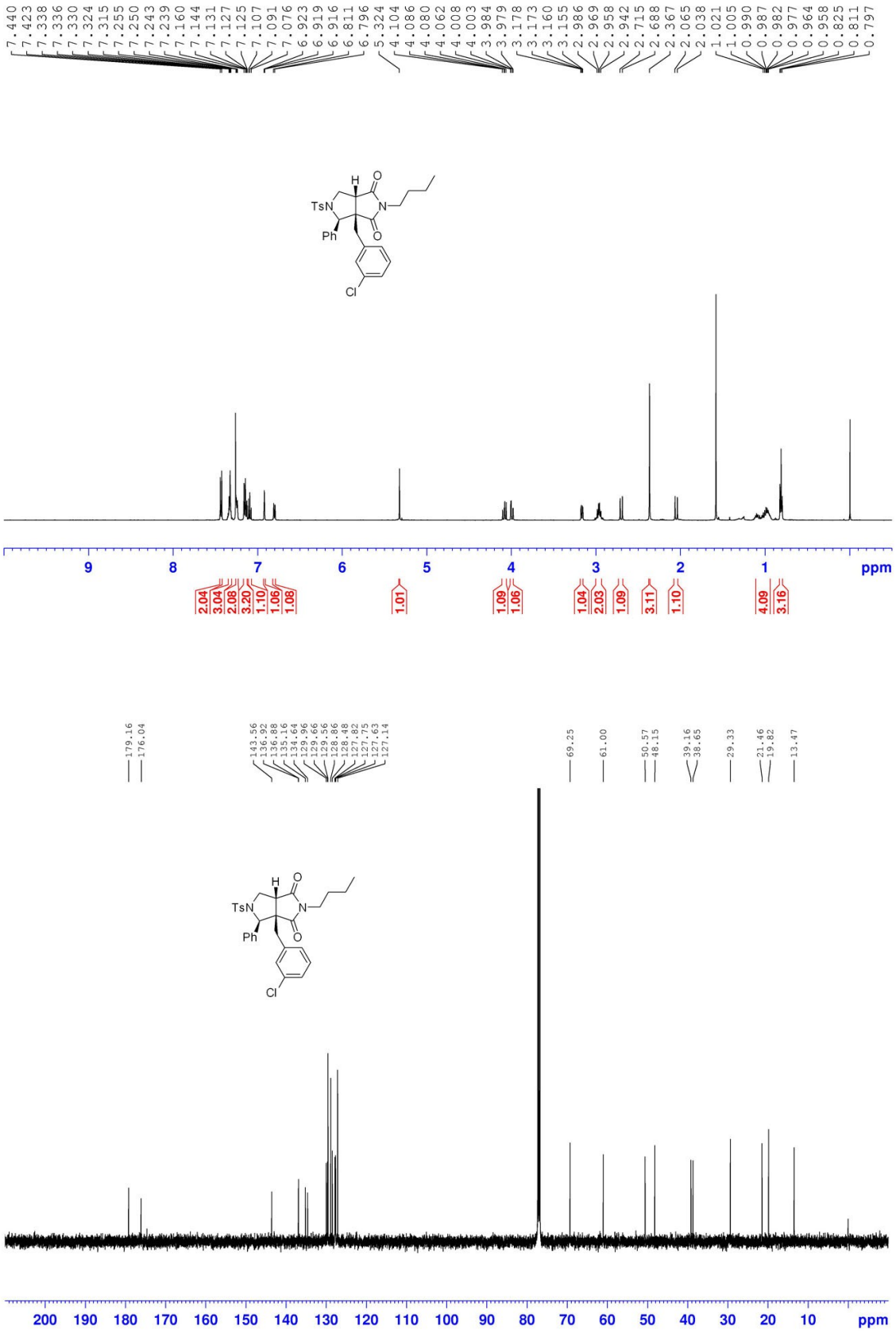

7.484
7.467
7.185
7.169
7.135
7.128
7.122
7.114
7.100
7.086
7.026
7.010
6.995
6.930
6.913
6.905
6.902
6.899
6.893
5.804
4.176
4.157
4.151
4.133
4.037
4.032
4.013
4.008
3.240
3.235
3.222
3.217
2.885
2.870
2.856
2.613
2.586
2.539
2.368
2.345
2.139
2.112
1.019
1.005
0.999
0.991
0.982
0.977
0.967
0.963
0.955
0.945
0.939
0.890
0.876
0.782
0.768
0.755
H
O
TsN
N
Bn
O
Me
Me
9
8
7
6
5
4
3
2
1
0 ppm
2.01
2.04
3.01
1.03
1.04
3.09
1.00
1.00
1.01
1.02
2.02
1.04
3.00
6.10
1.01
4.17
3.06
179.80
176.39
143.45
137.60
136.22
135.53
134.89
134.81
129.73
129.61
129.59
128.66
127.49
127.09
125.81
124.24
65.25
61.74
50.75
48.96
39.01
38.83
29.17
21.45
21.06
19.77
15.36
13.48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **4l**

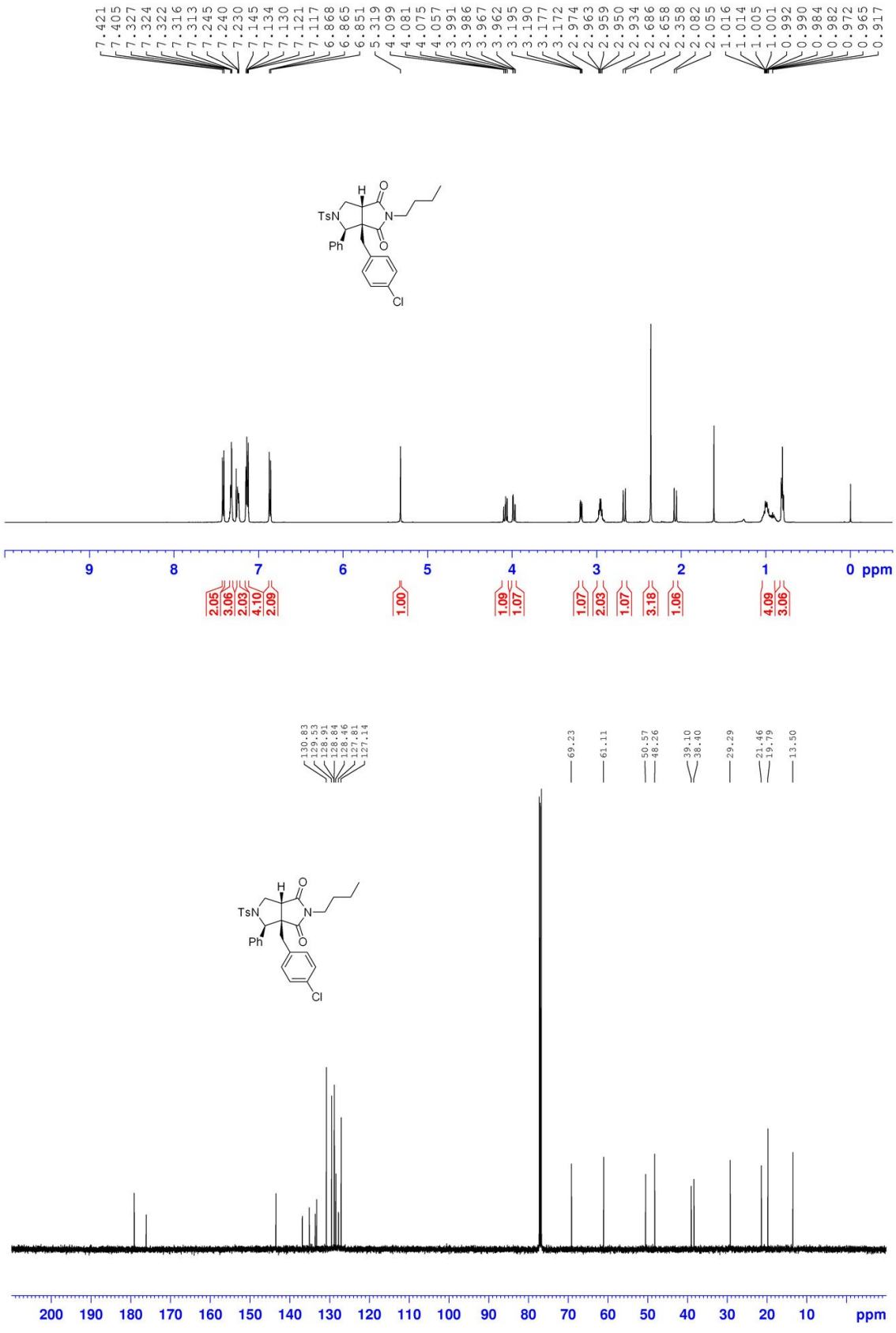

7.462
7.445
7.173
7.159
7.157
7.153
7.147
7.052
6.944
6.937
6.934
6.930
6.925
6.891
5.684
4.170
4.152
4.146
4.128
4.048
4.043
4.024
4.019
3.285
3.280
3.267
3.262
2.947
2.933
2.919
2.623
2.600
2.573
2.384
2.316
2.215
2.188
1.050
1.032
1.018
1.007
1.003
0.995
0.988
0.980
0.976
0.966
0.960
0.951
H
O
TsN
N
Me
Bn
O
Me
9
8
7
6
5
4
3
2
1
0 ppm
2.07
5.14
1.01
2.00
2.00
1.00
1.04
1.03
1.03
2.01
3.10
1.11
3.05
3.06
1.01
4.17
3.00


179.75
176.44
143.36
137.78
136.38
135.48
134.83
133.07
131.78
131.60
129.49
128.65
127.47
127.12
127.05
126.53
64.72
61.60
50.80
48.81
39.01
38.85
29.18
21.44
21.02
19.86
19.75
13.49
H
O
TsN
N
Me
Bn
O
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

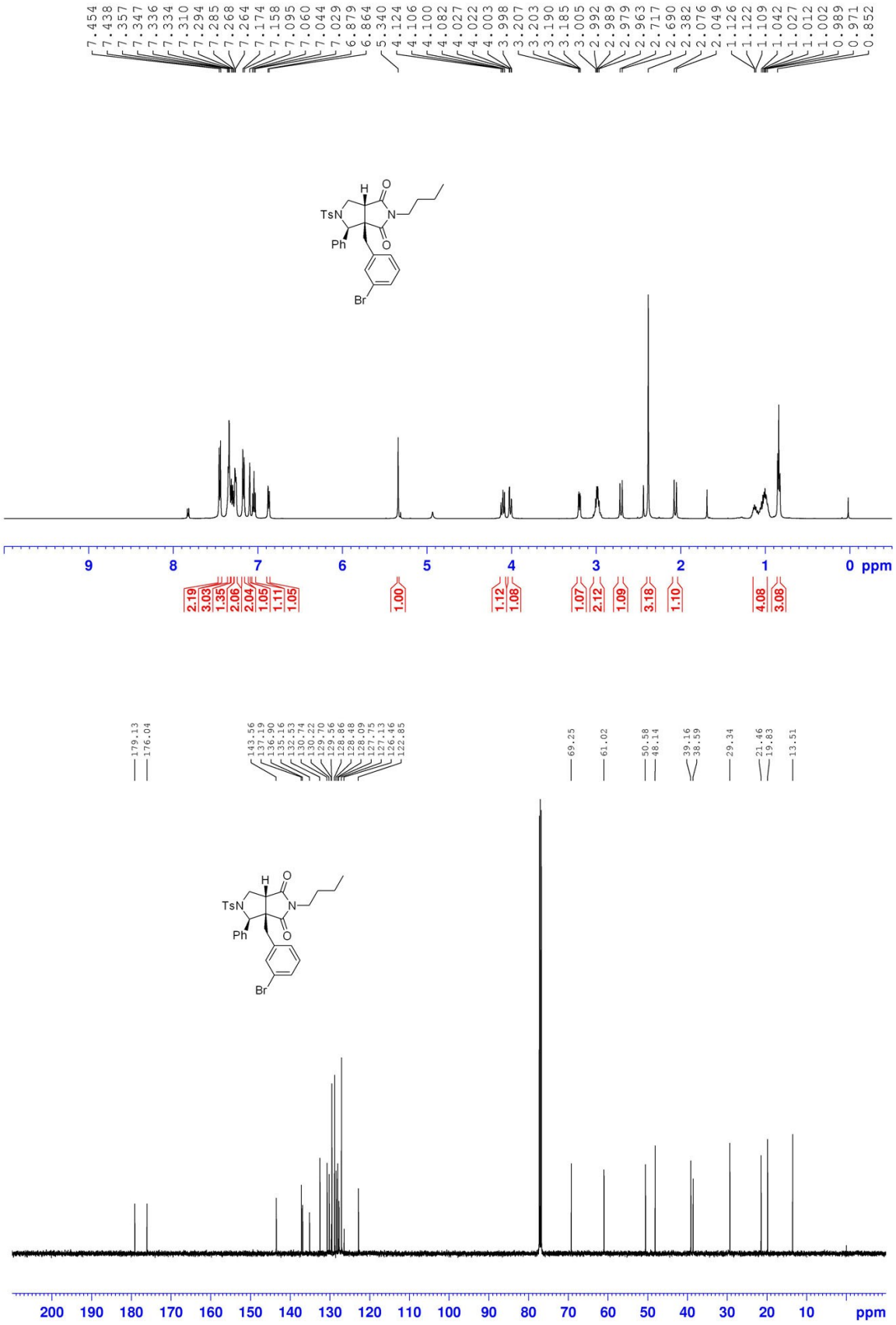
Compound **5a**


7.440
7.423
7.338
7.336
7.330
7.324
7.315
7.255
7.250
7.243
7.239
7.160
7.144
7.131
7.127
7.125
7.107
7.091
7.076
6.923
6.919
6.916
6.811
6.796
5.324
4.104
4.086
4.080
4.062
4.008
4.003
3.984
3.979
3.178
3.173
3.160
3.155
2.986
2.969
2.958
2.942
2.715
2.688
2.367
2.065
2.038
1.021
1.005
0.990
0.987
0.982
0.977
0.964
0.958
0.825
0.811
0.797
TsN
Ph
Cl
ppm
2.04
3.04
2.08
3.20
1.10
1.06
1.08
1.01
1.09
1.06
1.04
2.03
1.09
3.11
1.10
4.09
3.16
179.16
176.04
143.56
136.92
136.88
135.16
134.64
129.66
129.56
128.86
128.48
127.82
127.75
127.63
127.14
69.25
61.00
50.57
48.15
39.16
38.65
29.33
21.46
19.82
13.47

Compound **5b**


7.421
7.405
7.327
7.324
7.322
7.316
7.313
7.245
7.240
7.230
7.145
7.134
7.130
7.121
7.117
6.868
6.865
6.851
5.319
4.099
4.081
4.075
4.057
3.991
3.986
3.967
3.962
3.195
3.190
3.177
3.172
2.974
2.963
2.959
2.950
2.934
2.686
2.658
2.358
2.082
2.055
1.016
1.014
1.005
1.001
0.992
0.990
0.984
0.982
0.972
0.965
0.917
TsN
Ph
N
O
H
Cl
9
8
7
6
5
4
3
2
1
0 ppm
2.05
3.06
2.03
4.10
2.09
1.00
1.09
1.07
1.07
2.03
1.07
3.18
1.06
4.09
3.06
130.83
129.53
128.91
128.84
128.46
127.81
127.14
69.23
61.11
50.57
48.26
39.10
38.40
29.29
21.46
19.79
13.50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **5c**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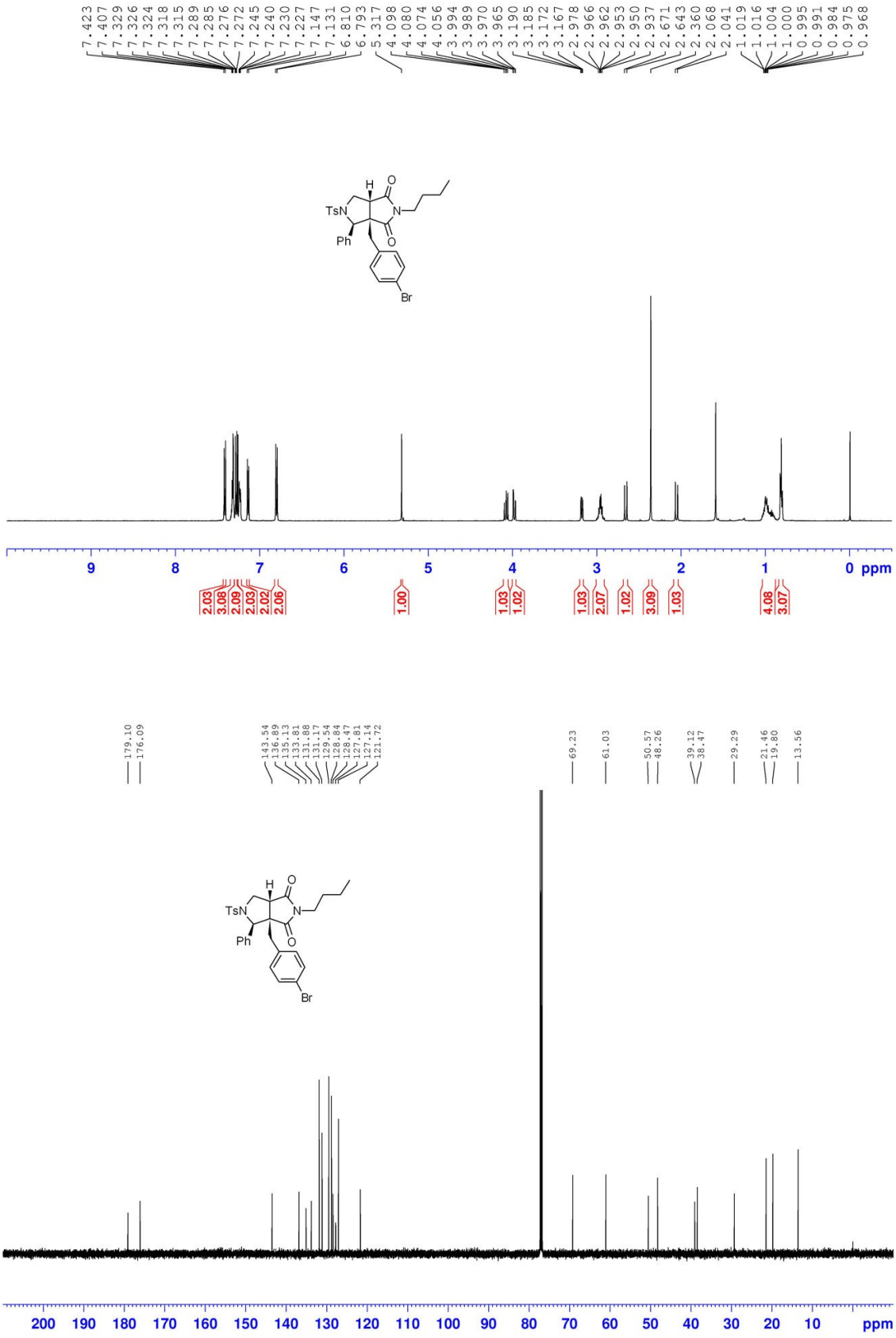
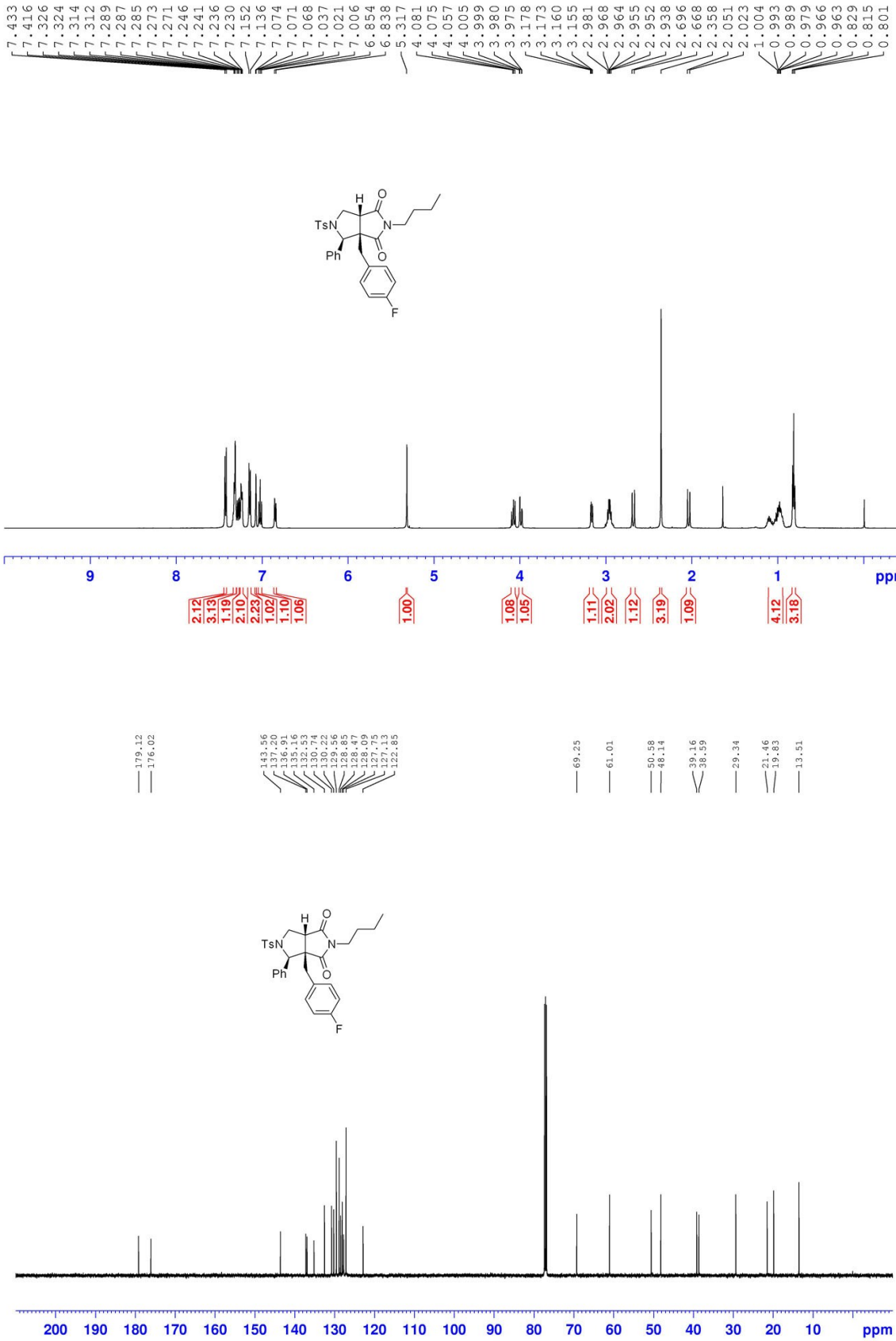
7.438
7.357
7.347
7.336
7.334
7.310
7.294
7.285
7.268
7.264
7.174
7.158
7.095
7.060
7.044
7.029
6.879
6.864
5.340
4.124
4.106
4.100
4.082
4.027
4.022
4.003
3.998
3.207
3.203
3.190
3.185
3.005
2.992
2.989
2.979
2.963
2.717
2.690
2.382
2.076
2.049
1.126
1.122
1.109
1.042
1.027
1.012
1.002
0.989
0.971
0.852
TsN
Ph
Br
9 8 7 6 5 4 3 2 1 0 ppm
2.19 3.03 1.35 2.06 2.04 1.05 1.11 1.05 1.00 1.12 1.08 1.07 2.12 1.09 3.18 1.10 4.08 3.08
179.13
176.04
143.56
137.19
136.90
135.16
132.53
130.74
130.22
129.70
129.56
128.86
128.48
128.09
127.75
127.13
126.46
122.85
69.25
61.02
50.58
48.14
39.16
38.59
29.34
21.46
19.83
13.51
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

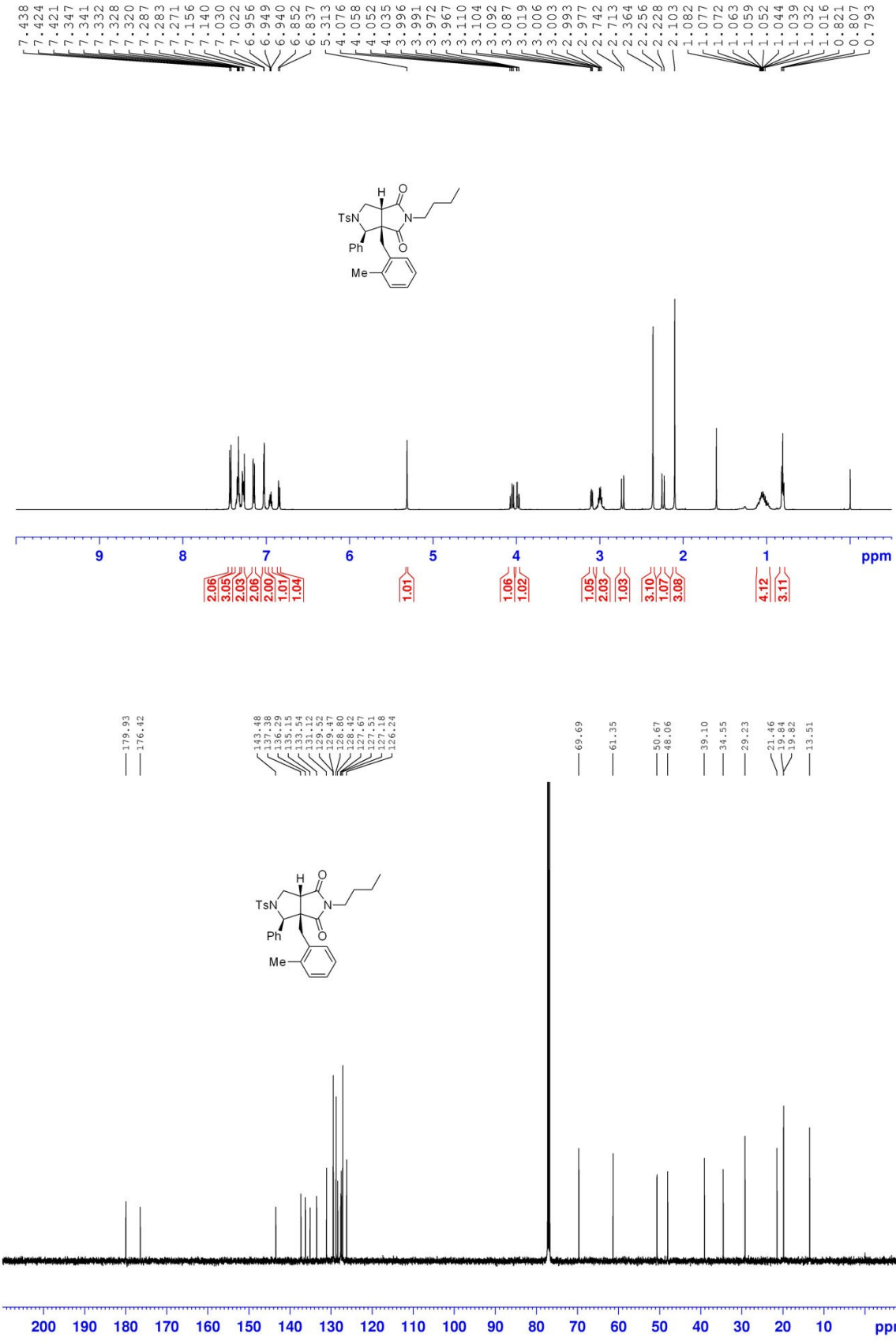
Compound **5d**


7.423
7.407
7.329
7.326
7.324
7.318
7.315
7.289
7.285
7.276
7.272
7.245
7.240
7.230
7.227
7.147
7.131
6.810
6.793
5.317
4.098
4.080
4.074
4.056
3.994
3.989
3.970
3.965
3.190
3.185
3.172
3.167
2.978
2.966
2.962
2.953
2.950
2.937
2.671
2.643
2.360
2.068
2.041
1.019
1.016
1.004
1.000
0.995
0.991
0.984
0.975
0.968
H
O
TsN
N
Ph
O
Br
9
8
7
6
5
4
3
2
1
0 ppm
2.03
3.08
2.09
2.03
2.02
2.06
1.00
1.03
1.02
1.03
2.07
1.02
3.09
1.03
4.08
3.07
179.10
176.09
143.54
136.89
135.13
133.81
131.88
131.17
130.54
128.84
128.47
127.81
127.14
121.72
69.23
61.03
50.57
48.26
39.12
38.47
29.29
21.46
19.80
13.56
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

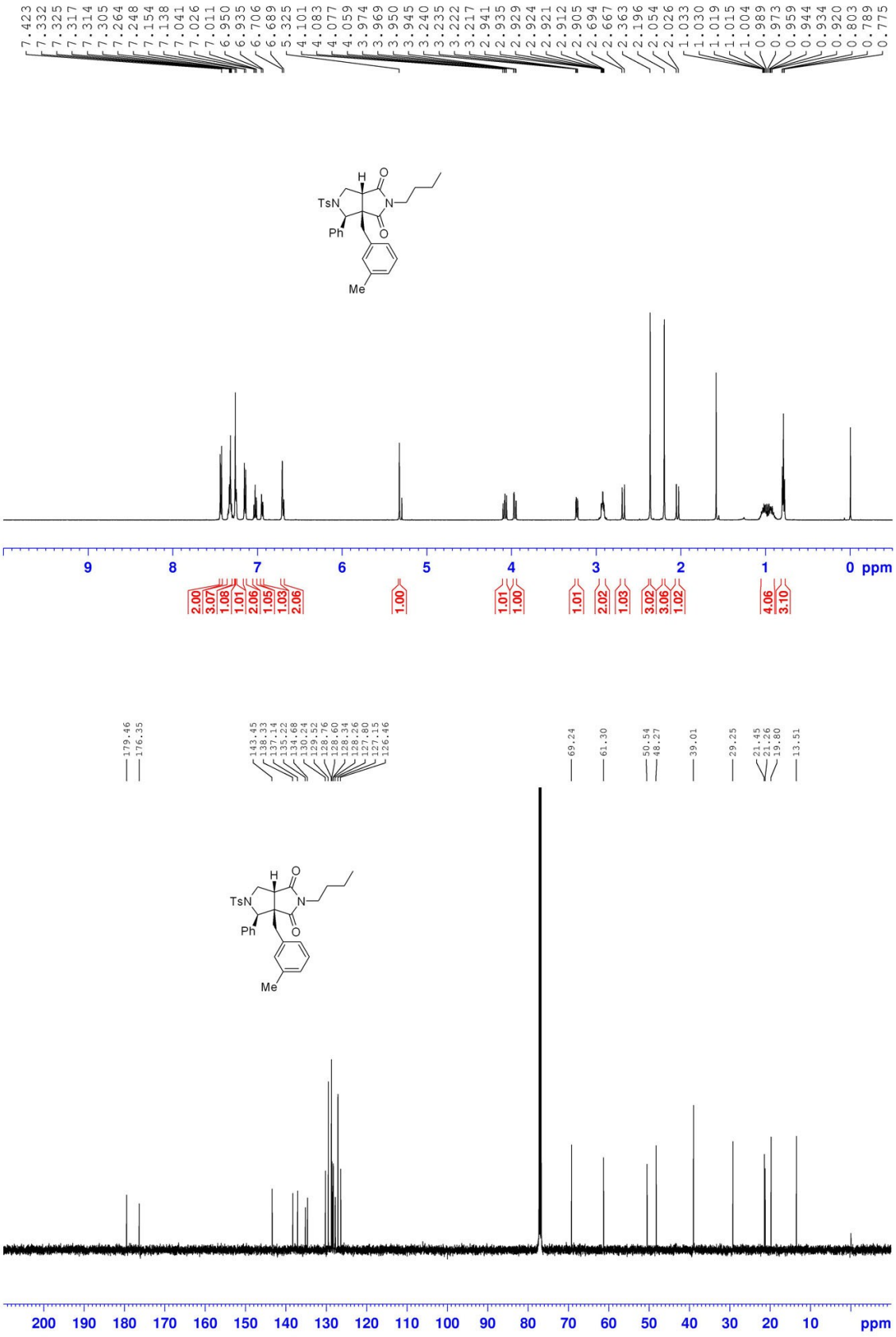
Compound **5e**


7.433
7.416
7.326
7.324
7.314
7.312
7.289
7.287
7.285
7.273
7.271
7.246
7.241
7.236
7.230
7.152
7.136
7.074
7.071
7.068
7.037
7.021
7.006
6.854
6.838
5.317
4.081
4.075
4.057
4.005
3.999
3.980
3.975
3.178
3.173
3.160
3.155
2.981
2.968
2.964
2.955
2.952
2.938
2.696
2.668
2.358
2.051
2.023
1.004
0.993
0.989
0.979
0.966
0.963
0.829
0.815
0.801
TsN
Ph
O
H
N
F
9
8
7
6
5
4
3
2
1
ppm
2.12
3.13
1.19
2.10
2.23
1.02
1.10
1.06
1.00
1.08
1.05
1.11
2.02
1.12
3.19
1.09
4.12
3.18
179.12
176.02
143.56
137.20
136.91
135.16
132.53
130.74
130.22
129.56
128.85
128.47
128.09
127.75
127.13
122.85
69.25
61.01
50.58
48.14
39.16
38.59
29.34
21.46
19.83
13.51
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

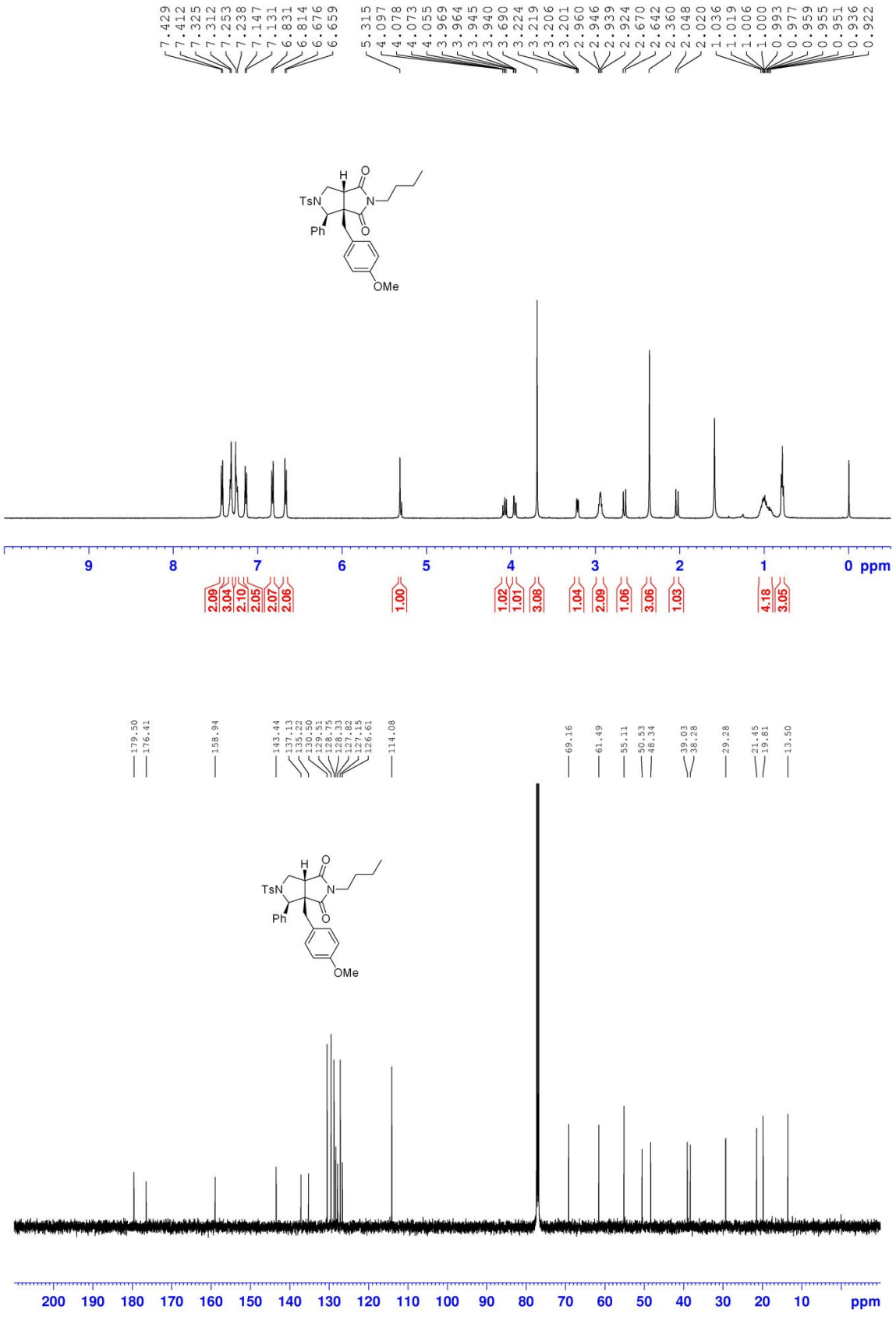
Compound **5f**


7.438
7.424
7.421
7.347
7.341
7.332
7.328
7.320
7.287
7.283
7.271
7.156
7.140
7.030
7.022
6.956
6.949
6.940
6.852
6.837
5.313
4.076
4.058
4.052
4.035
3.996
3.991
3.972
3.967
3.110
3.104
3.092
3.087
3.019
3.006
3.003
2.993
2.977
2.742
2.713
2.364
2.256
2.228
2.103
1.082
1.077
1.072
1.063
1.059
1.052
1.044
1.039
1.032
1.016
0.821
0.807
0.793
TsN
H
O
N
Ph
O
Me
9
8
7
6
5
4
3
2
1
ppm
2.06
3.05
2.03
2.06
2.00
1.01
1.04
1.01
1.06
1.02
1.05
2.03
1.03
3.10
1.07
3.08
4.12
3.11
179.93
176.42
143.48
137.38
136.29
135.15
133.54
131.12
129.52
129.47
128.80
128.42
127.67
127.51
127.18
126.24
69.69
61.35
50.67
48.06
39.10
34.55
29.23
21.46
19.84
19.82
13.51
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

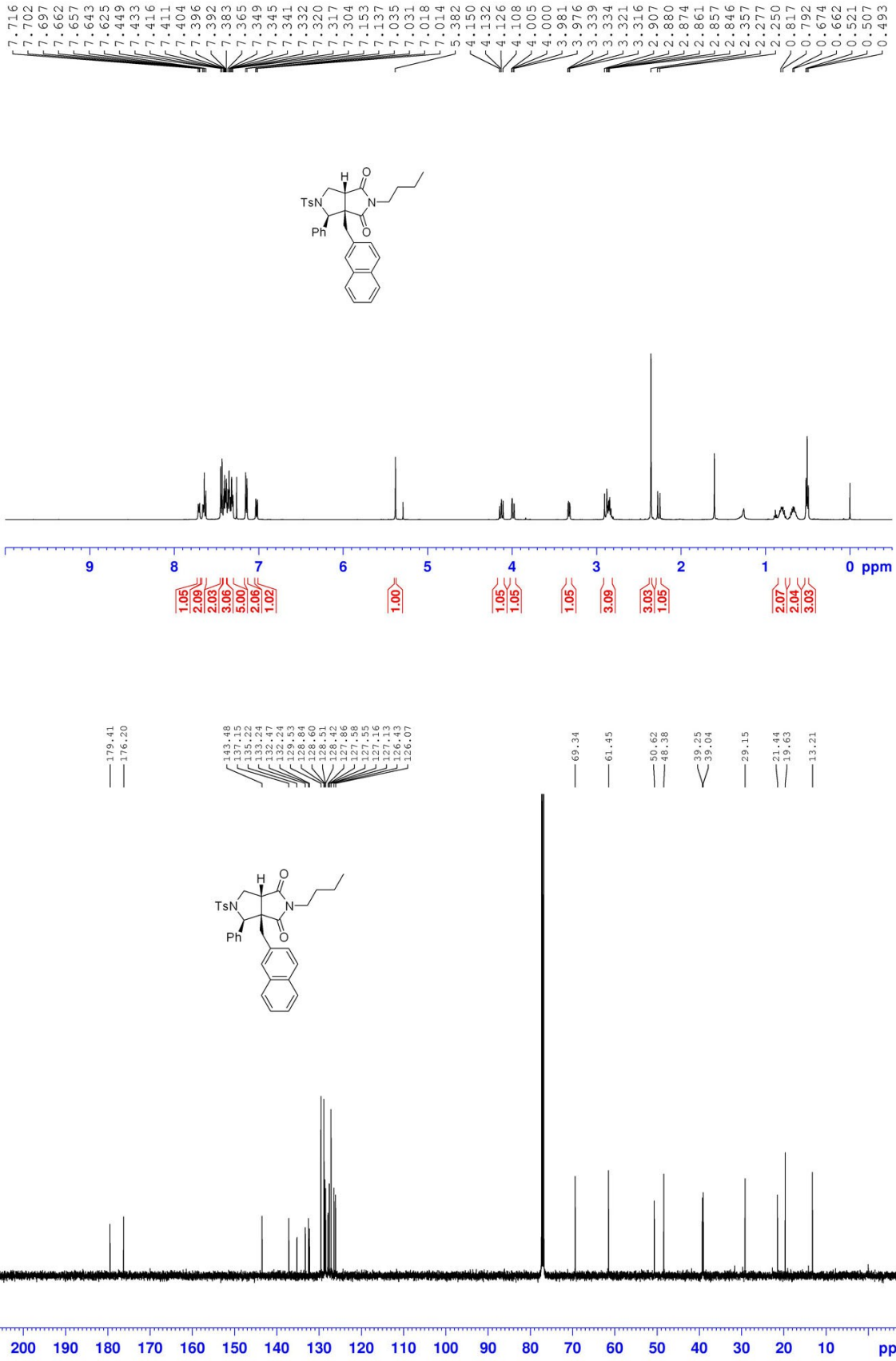
Compound **5g**


7.423
7.332
7.325
7.317
7.314
7.305
7.264
7.248
7.154
7.138
7.041
7.026
7.011
6.950
6.935
6.706
6.689
5.325
4.101
4.083
4.077
4.059
3.974
3.969
3.950
3.945
3.240
3.235
3.222
3.217
2.941
2.935
2.929
2.924
2.921
2.912
2.905
2.694
2.667
2.363
2.196
2.054
2.026
1.033
1.030
1.019
1.015
1.004
0.989
0.973
0.959
0.944
0.934
0.920
0.803
0.789
0.775
TsN
Ph
Me
9 8 7 6 5 4 3 2 1 0 ppm
2.00 3.07 1.08 1.01 2.06 1.05 1.03 2.06 1.00 1.01 1.00 1.01 2.02 1.03 3.02 3.06 1.02 4.06 3.10
179.46
176.35
143.45
138.33
137.14
135.22
134.68
130.24
129.52
128.76
128.60
128.34
128.26
127.80
127.15
126.46
69.24
61.30
50.54
48.27
39.01
29.25
21.45
21.26
19.80
13.51
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Compound **5h**


7.429
7.412
7.325
7.312
7.253
7.238
7.147
7.131
6.831
6.814
6.676
6.659
5.315
4.097
4.078
4.073
4.055
3.969
3.964
3.945
3.940
3.690
3.224
3.219
3.206
3.201
2.960
2.946
2.939
2.924
2.670
2.642
2.360
2.048
2.020
1.036
1.019
1.006
1.000
0.993
0.977
0.959
0.955
0.951
0.936
0.922
TsN
Ph
H
O
N
O
OMe
9
8
7
6
5
4
3
2
1
0 ppm
2.09
3.04
2.10
2.05
2.07
2.06
1.00
1.02
1.01
3.08
1.04
2.09
1.06
3.06
1.03
4.18
3.05
179.50
176.41
158.94
143.44
137.13
135.22
130.50
129.51
128.75
128.33
127.82
127.15
126.61
114.08
69.16
61.49
55.11
50.53
48.34
39.03
38.28
29.28
21.45
19.81
13.50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **5i**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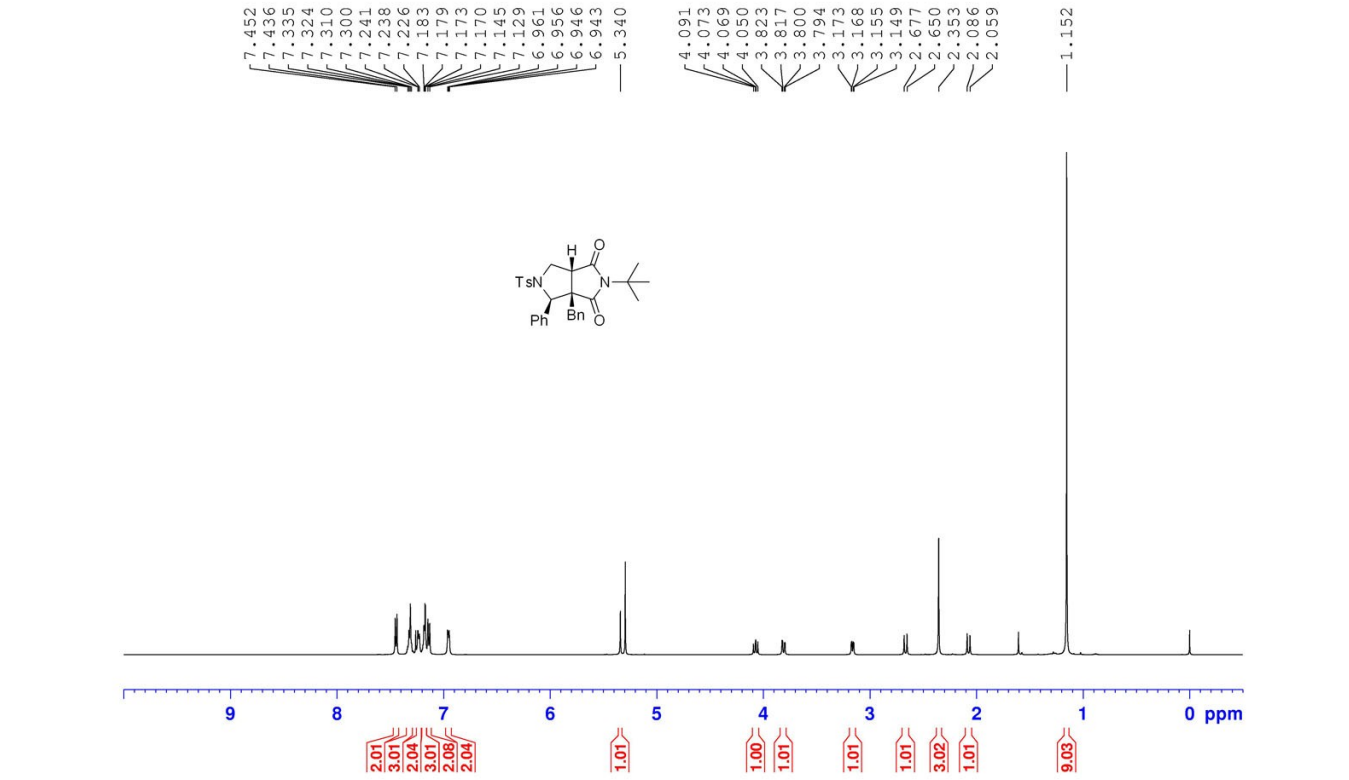
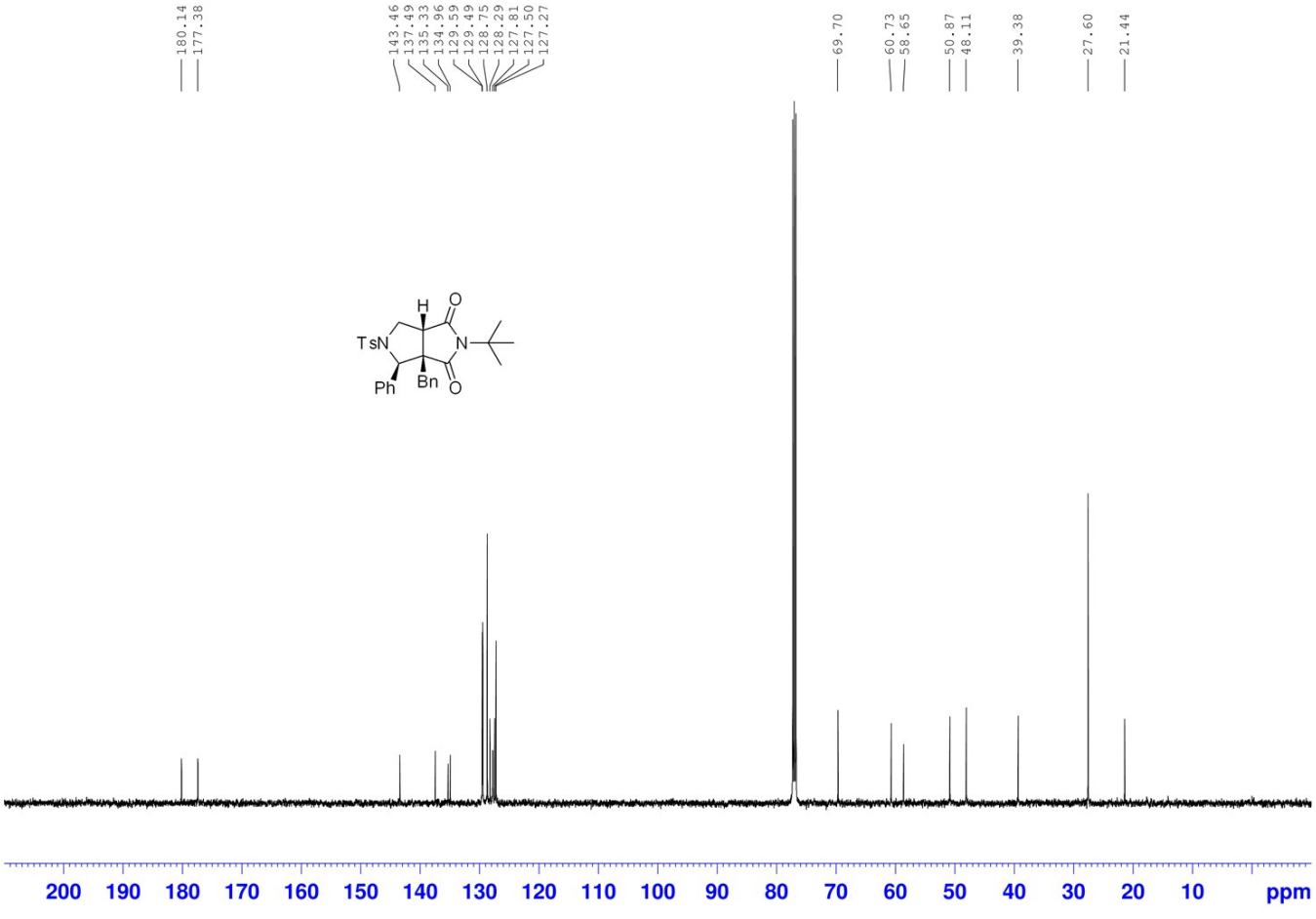
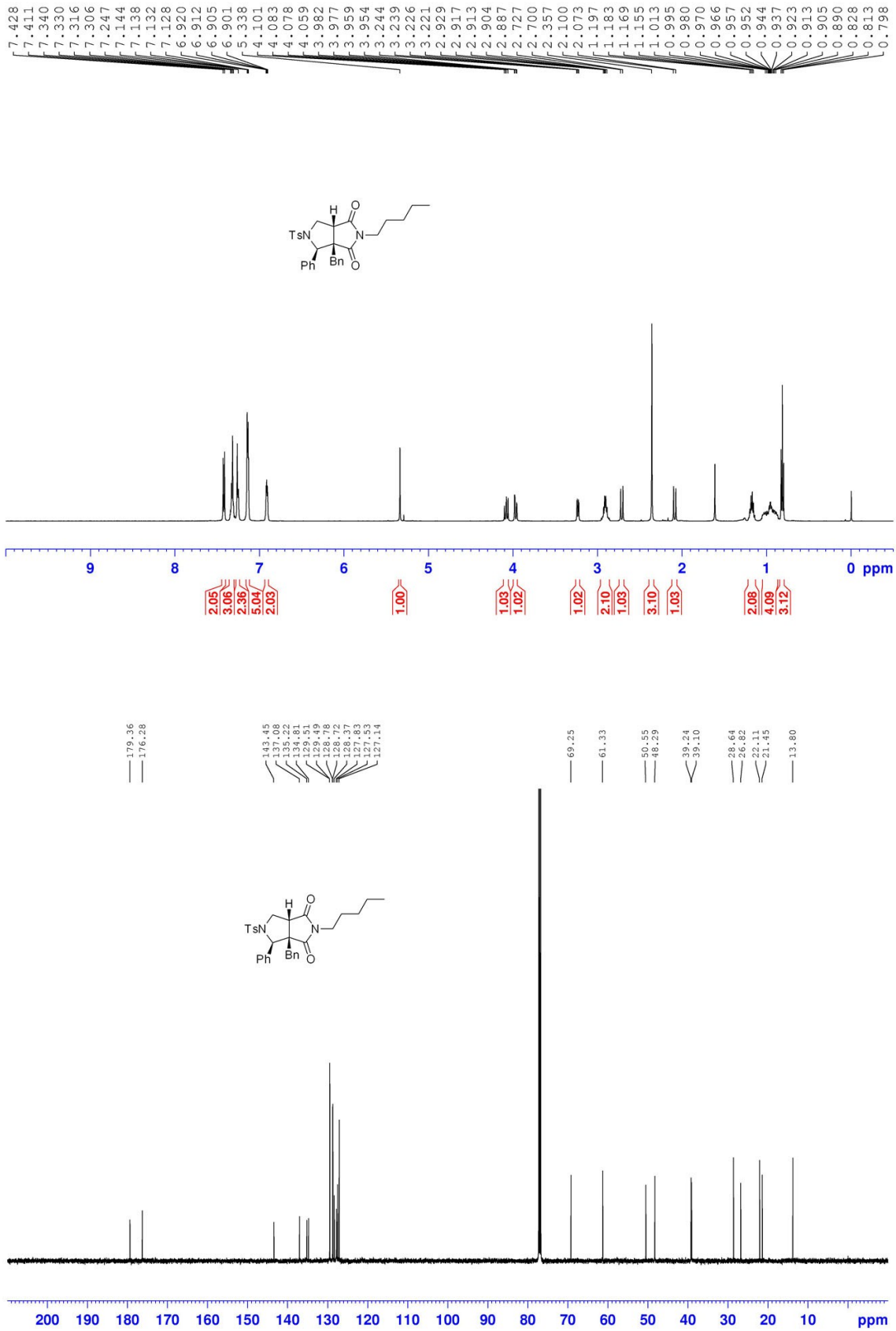
7.702
7.697
7.662
7.657
7.643
7.625
7.449
7.433
7.416
7.411
7.404
7.396
7.392
7.383
7.365
7.349
7.345
7.341
7.332
7.320
7.317
7.304
7.153
7.137
7.035
7.031
7.018
7.014
5.382
4.150
4.132
4.126
4.108
4.005
4.000
3.981
3.976
3.339
3.334
3.321
3.316
2.907
2.880
2.874
2.861
2.857
2.846
2.357
2.277
2.250
0.817
0.792
0.674
0.662
0.521
0.507
0.493
TsN
Ph
9
8
7
6
5
4
3
2
1
0 ppm
1.05
2.09
2.03
3.06
5.00
2.06
1.02
1.00
1.05
1.05
1.05
3.09
3.03
1.05
2.07
2.04
3.03
179.41
176.20
143.48
137.15
135.22
133.24
133.17
132.24
129.53
128.84
128.60
128.51
128.42
127.86
127.58
127.55
127.16
127.13
126.43
126.07
69.34
61.45
50.62
48.38
39.25
39.04
29.15
21.44
19.63
13.21
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **6a**

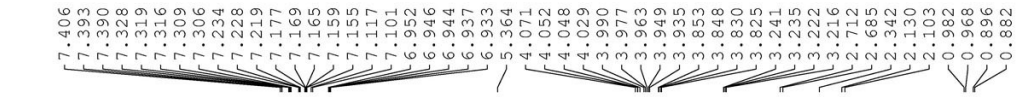

7.452
7.436
7.335
7.324
7.310
7.300
7.241
7.238
7.226
7.183
7.179
7.173
7.170
7.145
7.129
6.961
6.956
6.946
6.943
5.340
4.091
4.073
4.069
4.050
3.823
3.817
3.800
3.794
3.173
3.168
3.155
3.149
2.677
2.650
2.353
2.086
2.059
1.152
TsN
Ph
Bn
9
8
7
6
5
4
3
2
1
0 ppm
2.01
3.01
2.04
3.01
2.08
2.04
1.01
1.00
1.01
1.01
1.01
3.02
1.01
9.03

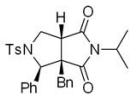

180.14
177.38
143.46
137.49
135.33
134.96
129.59
129.49
128.75
128.29
127.81
127.50
127.27
69.70
60.73
58.65
50.87
48.11
39.38
27.60
21.44
TsN
Ph
Bn
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

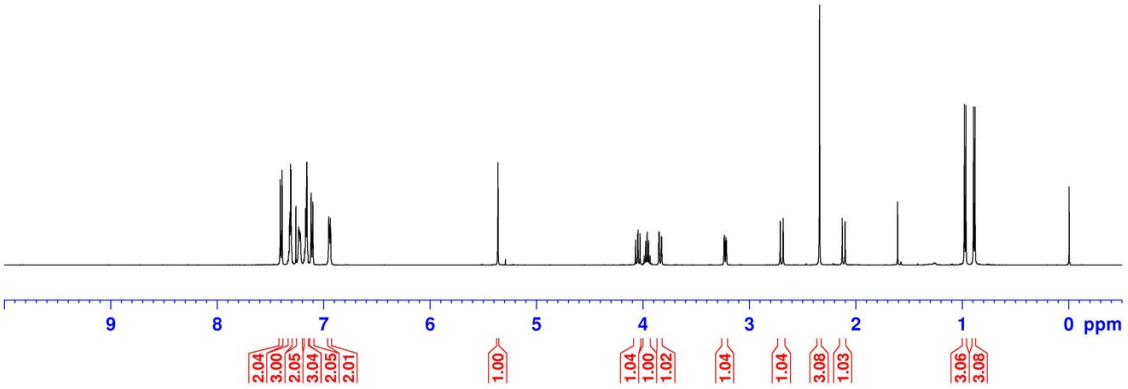
Compound **6b**


7.428
7.411
7.340
7.330
7.316
7.306
7.247
7.144
7.138
7.132
7.128
6.920
6.912
6.905
6.901
5.338
4.101
4.083
4.078
4.059
3.982
3.977
3.959
3.954
3.244
3.239
3.226
3.221
2.929
2.917
2.913
2.904
2.887
2.727
2.700
2.357
2.100
2.073
1.197
1.183
1.169
1.155
1.013
0.995
0.980
0.970
0.966
0.957
0.952
0.944
0.937
0.923
0.913
0.905
0.890
0.828
0.813
0.798
TsN
Ph
Bn
9
8
7
6
5
4
3
2
1
0 ppm
2.05
3.06
2.36
5.04
2.03
1.00
1.03
1.02
1.02
2.10
1.03
3.10
1.03
2.08
4.09
3.12
179.36
176.28
143.45
137.08
135.22
134.81
129.51
129.49
128.78
128.72
128.37
127.83
127.53
127.14
69.25
61.33
50.55
48.29
39.24
39.10
28.64
26.82
22.11
21.45
13.80
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **6c**


7.406
7.393
7.390
7.328
7.319
7.316
7.309
7.306
7.234
7.228
7.219
7.177
7.169
7.165
7.159
7.155
7.117
7.101
6.952
6.946
6.944
6.937
6.933
5.364
4.071
4.052
4.048
4.029
3.990
3.977
3.963
3.949
3.935
3.853
3.848
3.830
3.825
3.241
3.235
3.222
3.216
2.712
2.685
2.342
2.130
2.103
0.982
0.968
0.896
0.882


H
O
TsN
N
Ph
Bn
O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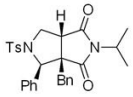
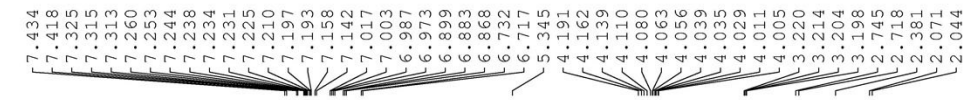
8
7
6
5
4
3
2
1
0 ppm
2.04
3.00
2.05
3.04
2.05
2.01
1.00
1.04
1.00
1.02
1.04
1.04
3.08
1.03
3.06
3.08


179.29
176.28
143.50
137.11
135.32
134.83
129.51
129.44
128.78
128.36
127.90
127.53
127.23
69.34
60.89
50.53
48.06
44.20
39.07
21.45
18.60
18.53


H
O
TsN
N
Ph
Bn
O


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **6d**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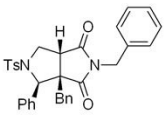
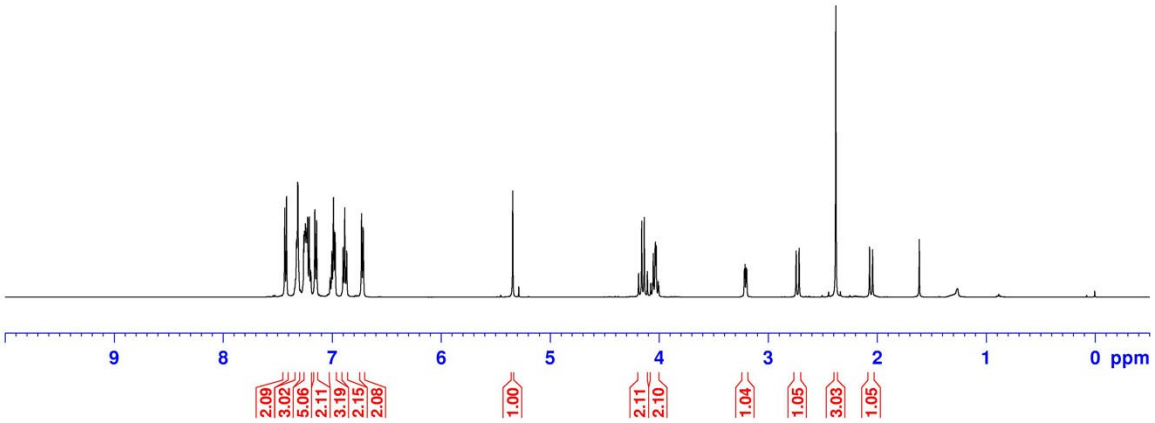
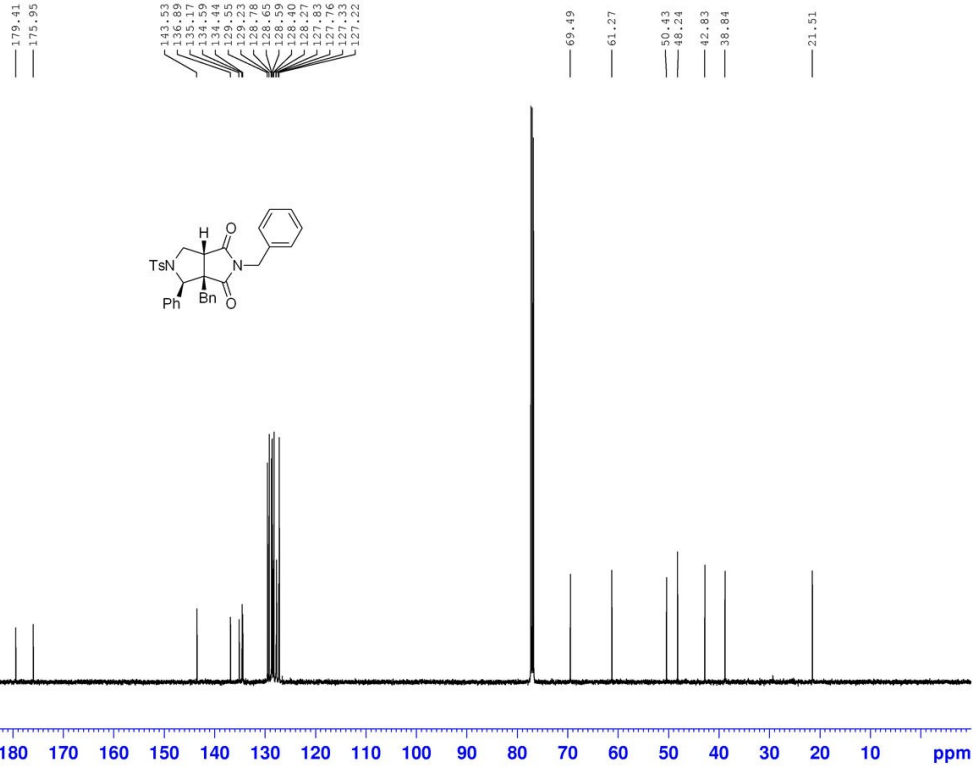
7.418
7.325
7.315
7.313
7.260
7.253
7.244
7.238
7.234
7.231
7.225
7.210
7.197
7.193
7.158
7.142
7.017
7.003
6.987
6.973
6.899
6.883
6.868
6.732
6.717
5.345
4.191
4.162
4.139
4.110
4.080
4.063
4.056
4.039
4.035
4.029
4.011
4.005
3.220
3.214
3.204
3.198
2.745
2.718
2.381
2.071
2.044


H
O
TsN
N
Ph
Bn
O


9
8
7
6
5
4
3
2
1
0 ppm
2.09
3.02
5.06
2.11
3.19
2.15
2.08
1.00
2.11
2.10
1.04
1.05
3.03
1.05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175.95
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134.59
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129.55
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128.78
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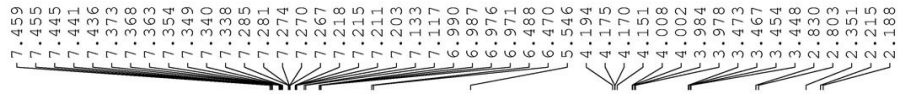
128.27
127.83
127.76
127.33
127.22
69.49
61.27
50.43
48.24
42.83
38.84
21.51
H
O
TsN
N
Ph
Bn
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **6e**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7.373
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7.363
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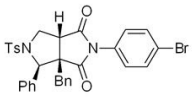
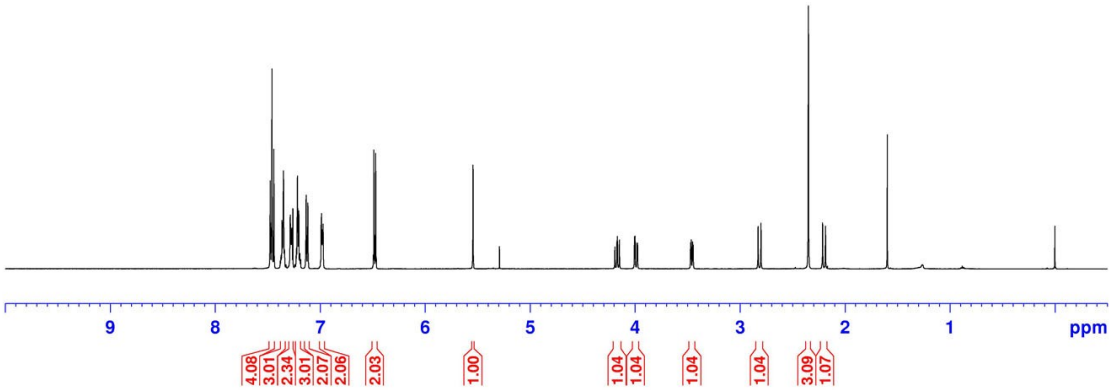
7.349
7.340
7.338
7.285
7.281
7.274
7.270
7.267
7.218
7.215
7.211
7.203
7.133
7.117
6.990
6.987
6.976
6.971
6.488
6.470
5.546
4.194
4.175
4.170
4.151
4.008
4.002
3.984
3.978
3.473
3.467
3.454
3.448
2.830
2.803
2.351
2.215
2.188


H
O
TsN
N
Br
Ph
Bn
O


9
8
7
6
5
4
3
2
1
ppm
4.08
3.01
2.34
3.01
2.07
2.06
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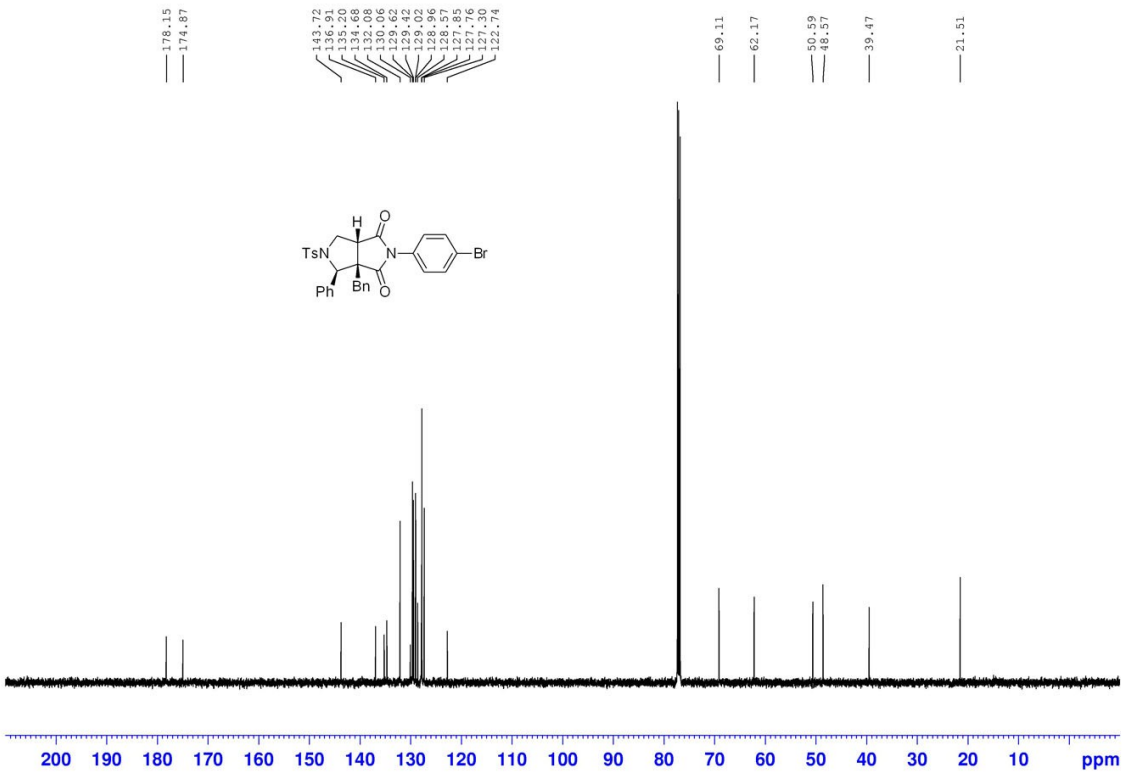
1.04
1.04
1.04
1.04
3.09
1.07


178.15
174.87
143.72
136.91
135.20
134.68
132.08
130.06
129.62
129.42
129.02
128.96
128.57
127.85
127.76
127.30
122.74
69.11
62.17
50.59
48.57
39.47
21.51
H
O
TsN
N
Br
Ph
Bn
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

# 5 Crystal Structure of Compound 4a

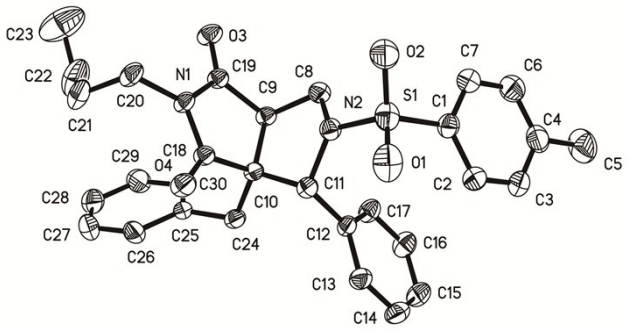



**Figure 1** Single Crystal X-Ray structure for **4a**

Table 1 Crystal data and structure refinement for **4a**

| | |
|---|---|
| Empirical formula | C30 H32 N2 O4S |
| Formula weight | 516.64 |
| Temperature | 296(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 8.337(9) Å alpha = 90 °.<br>b = 26.49(3) Å beta = 101.240(14) °.<br>c = 12.243(14) Å gamma = 90 °. |
| Volume | 2652(5) Å $^3$ |
| Z, Calculated density | 4, 1.294 Mg/m$^3$ |
| Absorption coefficient | 0.161 mm$^{-1}$ |
| F(000) | 1096 |
| Crystal size | 0.200 x 0.100x 0.080 mm |
| Theta range for data collection | 2.29 to 27.59° |
| Limiting indices | -10<=h<=10, -34<=k<=28, -15<=l<=12 |
| Reflections collected / unique | 15548 / 5995 [R(int) = 0.0388] |
| Completeness to theta = 25.05 | 97.7 % |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 5995 / 0 / 337 |
| Goodness-of-fit on F^2 | 1.037 |
| Final R indices [I>2sigma(I)] | R1 = 0.0779, wR2 = 0.1980 |
| R indices (all data) | R1 = 0.1318, wR2 = 0.2284 |
| Extinction coefficient | 0.0068(13) |
| Largest diff. peak and hole | 0.596 and -0.470 e. Å $^{-3}$ |