Supporting Information

Rh-catalyzed aziridine ring expansions to dehydropiperazines

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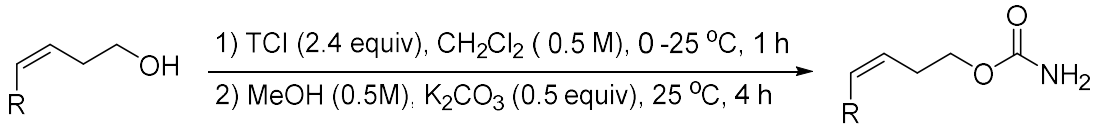
I. General information

Unless otherwise specified, all reactions were conducted under an inert atmosphere of N_2. Glassware was either oven-dried overnight at 130 °C or flame-dried under a stream of dry nitrogen prior to use. Unless otherwise specified, reagents were used as obtained from the vendor without further purification. Purification of compounds was conducted following "Purification of Laboratory Chemicals".[1] Dichloromethane and acetonitrile were dried over CaH_2 and freshly distilled prior to use. All other solvents were purified in accordance with methods reported in "Purification of Laboratory Chemicals".[1] Analytical thin layer chromatography (TLC) was performed utilizing pre-coated silica gel 60 F_{254} plates containing a fluorescent indicator, while preparative chromatography was performed using SilicaFlash P60 silica gel (230-400 mesh) via Still's method.[2] Columns were typically run using a gradient method. Potassium permanganate stain, CAM stain, and UV lamp were employed to visualize material. ^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker Avance-400 or Bruker Avance-500 NMR spectrometers. ^{1}H NMR chemical shifts are reported relative to residual solvent peaks (δ 7.26, 2.49, 7.15 and 4.80 ppm for $CDCl_3$, $(CD_3)_2SO$, C_6D_6 and CD_3OD respectively). ^{13}C NMR chemical shifts are reported relative to residual solvent peaks (δ 77.1, 39.5, 128.0 and 49.0 ppm for $CDCl_3$, $(CD_3)_2SO$, C_6D_6, and CD_3OD, respectively). Accurate mass measurements were acquired at the University of Wisconsin, Madison using a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact methods). The NMR and Mass Spectrometry facilities are funded by the NSF (CHE-1048642), the NIH (S10 OD012245, 1S10 OD020022-1), the Bender Fund, UW2020, and the University of Wisconsin-Madison.

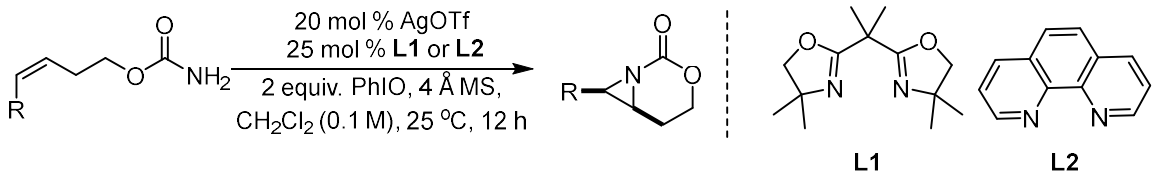
II. Carbamate synthesis

All carbamates were synthesized according to reported literature procedures using the general reaction scheme shown below.[3]



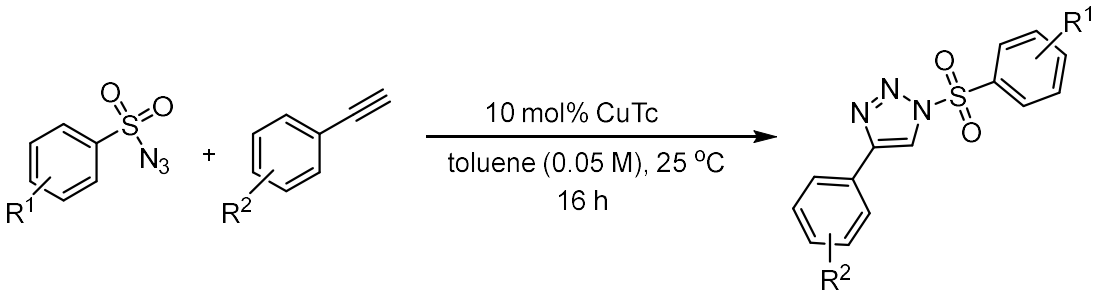
III. Preparation of aziridine precursors

All aziridines were synthesized according to reported literature procedures using the general reaction scheme shown below.[3,4]

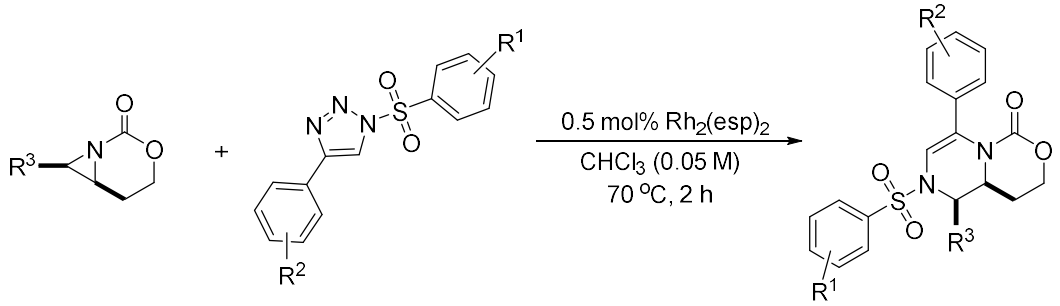


IV. Preparation of triazoles

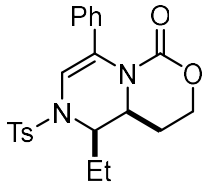
All triazole compounds were synthesized according to the reported literature procedures (CuTc = copper(I) thiophene-2-carboxylate).[5]



V. General procedure for piperazine synthesis

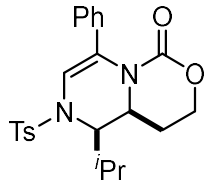


A flame-dried round bottom flask was placed under nitrogen and charged with the aziridine (1 equiv), $Rh_2(esp)_2$ (0.005 equiv), triazole (2 equiv for the aziridine scope studies and 3 equiv for the triazole scope studies) and $CHCl_3$ (0.05 M). The reaction mixture was heated at 70 ºC using an oil bath for 2 h. Conversion of the reaction was determined by both TLC (60% Ether/Hexanes or 40% EtOAc/Hexanes) and ^{1}H NMR ($CDCl_3$). Once complete conversion of the aziridine was determined to have occurred, the reaction was cooled down to room temperature, concentrated and loaded directly onto a silica gel column for purification by column chromatography (60% Ether/Hexanes or 40% EtOAc/Hexanes).

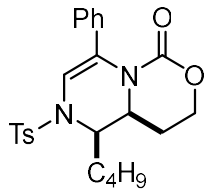


Compound 6ab. Following the general procedure, the carbene transfer to access **6ab** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% Et_2O/hexanes, 10% increments) to yield **6ab** as a yellow solid (119.8 mg, 82% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.19 (m, 5H), 6.99 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.08 (s, 1H), 4.81 (dd, *J* = 11.0, 6.2 Hz, 1H), 3.89 (td, *J* = 11.3, 6.0 Hz, 1H), 2.34 (s, 3H), 1.77 – 1.62 (m, 2H), 1.58 (ddd, *J* = 10.3, 6.4, 2.1 Hz, 1H), 1.08 – 0.99 (m, 1H), 0.90 – 0.74 (m, 2H), 0.60 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.2, 147.3, 143.3, 134.0, 131.8, 127.9, 127.7, 127.5, 127.2, 116.4, 64.1, 42.9, 41.2, 29.3, 28.7, 24.5, 20.6, 20.0, 10.3. HRMS (ESI) *m/z* calculated for $C_{22}H_{24}N_2O_4S$ $[M+H]^+$ 413.1530; found, 413.1516.

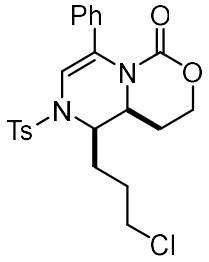
Large-scale synthesis of compound 6ab. A pre-dried 250-mL round-bottom flask equipped with a magnetic stir bar was charged with aziridine **1a** (0.500 mg, 3.54 mmol, 1 equiv), $Rh_2(esp)_2$ (13.4 mg, 0.018 mmol, 0.005 equiv), triazole **5b** (3.18 g, 10.6 mmol, 3 equiv), and anhydrous $CHCl_3$ (70 mL, 0.05 M). The reaction mixture was heated at 70 ºC using an oil bath for 2 h. Conversion of the reaction was determined by both TLC (40% EtOAc/Hexanes) and ^1H NMR ($CDCl_3$). Once complete conversion of the aziridine was determined to have occurred, the reaction was cooled down to room temperature and concentrated. The crude mixture was purified by silica gel column chromatography (0→40% EtOAc/hexanes) to afford dehydropiperazine **6ab** as a yellow solid (1.10 g, 75%). Characterization data is given above.



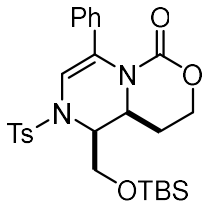
Compound 6bb. Following the general procedure, the carbene transfer to access **6bb** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% EtOAc/hexanes, 10% increments) to yield **6bb** as a yellow solid (113.8 mg, 83% yield, >19:1 *dr*). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.29 (m, 5H), 7.10 – 7.04 (m, 2H), 6.16 (s, 1H), 4.89 (dd, *J* = 11.0, 6.5 Hz, 1H), 3.98 (td, *J* = 11.7, 5.7 Hz, 1H), 2.42 (s, 3H), 1.89 – 1.72 (m, 2H), 1.69 (ddd, *J* = 10.7, 6.5, 1.8 Hz, 1H), 1.56 (dd, *J* = 9.5, 6.5 Hz, 1H), 0.97 (dp, *J* = 9.4, 6.7 Hz, 1H), 0.68 (dd, *J* = 10.7, 6.7 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.1, 148.1, 144.4, 135.1, 132.8, 129.1, 129.1, 128.6, 128.6, 128.2, 117.3, 65.0, 47.6, 44.0, 27.8, 25.6, 21.6, 20.5, 19.3. HRMS (ESI) *m/z* calculated for $C_{23}H_{27}N_2O_4S$ $[M+H]^+$ 427.1686; found, 427.1683.



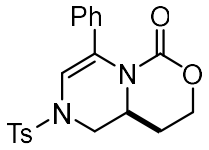
Compound 6cb. Following the general procedure, the carbene transfer to access **6cb** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% EtOAc/hexanes, 10% increments) to yield **6cb** as a yellow solid (92.3 mg, 71% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) Dehydropiperazine product: δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.34 (m, 3H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.07 (m, 2H), 6.19 (s, 1H), 4.91 (dd, *J* = 11.0, 6.5 Hz, 1H), 4.02 – 3.95 (m, 1H), 2.44 (s, 3H), 1.86 (ddt, *J* = 10.4, 7.5, 4.1 Hz, 1H), 1.83 – 1.76 (m, 1H), 1.76 – 1.70 (m, 1H), 1.67 (ddd, *J* = 10.8, 6.5, 1.8 Hz, 1H), 1.19 – 1.12 (m, 2H), 1.07 (qd, *J* = 7.1, 4.6 Hz, 3H), 0.97 – 0.87 (m, 1H), 0.84 (t, *J* = 7.2 Hz, 3H). Triazole impurity: δ 8.31 (s, 1H), 8.04 – 8.02 (m, 1H), 7.84 – 7.81 (m, 1H), 7.51 – 7.37 (m, 5H), 2.45 (s, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) Dehydropiperazine product: δ 153.2, 148.0, 144.2, 135.3, 133.0, 130.5, 129.0, 128.9, 128.8, 128.2, 117.5, 65.1, 43.7, 40.9, 29.4, 27.6, 25.7, 22.5, 21.7, 13.9. Triazole impurity: δ 147.4, 133.1, 130.5, 129.1, 129.0, 128.7, 128.6, 126.1, 118.9, 21.8. HRMS (ESI) *m/z* calculated for $C_{24}H_{29}N_2O_4S[M+H]^+$ 441.1843; found, 441.1838.



Compound 6db. Following the general procedure, the carbene transfer to access **6db** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% EtOAc/hexanes, 10% increments) to yield **6db** as a yellow solid (84.7 mg, 70% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.97 (m, 2H), 7.39 – 7.32 (m, 5H), 7.08 – 7.03 (m, 2H), 6.19 (s, 1H), 4.94 – 4.87 (m, 1H), 3.99 (td, *J* = 10.9, 6.9 Hz, 1H), 3.30 (tt, *J* = 7.4, 3.7 Hz, 2H), 2.45 (s, 3H), 1.86 (dt, *J* = 8.0, 5.7 Hz, 1H), 1.82 – 1.69 (m, 3H), 1.60 – 1.44 (m, 2H), 1.25 (ddt, *J* = 15.6, 9.6, 5.6 Hz, 1H), 1.02 (dddd, *J* = 13.8, 9.8, 8.0, 5.6 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.2, 147.6, 144.6, 135.1, 132.7, 129.1, 129.0, 128.8, 128.8, 128.4, 117.8, 65.0, 44.4, 43.6, 40.0, 30.4, 25.7, 25.4, 21.8. HRMS (ESI) *m/z* calculated for $C_{23}H_{26}ClN_2O_4S[M+H]^+$ 461.1296; found, 461.1292.

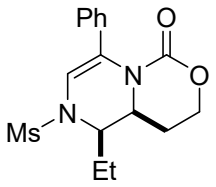


Compound 6eb. Following the general procedure, the carbene transfer to access **6eb** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% EtOAc/hexanes, 10% increments) to yield **6eb** as a yellow solid (169.2 mg, 90% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) Dehydropiperazine product: δ 8.00 – 7.95 (m, 2H), 7.45 – 7.34 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.12 (m, 1H), 6.23 (s, 1H), 4.92 (dd, *J* = 11.7, 4.9 Hz, 1H), 3.98 (td, *J* = 10.4, 5.4 Hz, 1H), 3.27 (dd, *J* = 10.9, 5.9 Hz, 1H), 3.13 (dd, *J* = 11.0, 6.4 Hz, 1H), 2.45 (s, 3H), 2.19 (dt, *J* = 10.5, 5.2 Hz, 1H), 1.84 – 1.70 (m, 3H), 0.86 (s, 9H), -0.00 (s, 6H). Triazole impurity: δ 8.31 (s, 1H), 8.05 – 8.01 (m, 2H), 7.82 (dt, J = 6.3, 1.4 Hz, 2H), 7.41 (dt, J = 23.2, 7.3 Hz, 5H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) Dehydropiperazine product: δ 153.3, 146.9, 144.4, 135.4, 132.9, 130.6, 129.1, 129.1, 128.9, 128.4, 126.2, 117.8, 65.2, 61.4, 43.4, 41.9, 26.0, 26.0, 21.9, 18.3, -5.2, -5.4. Triazole impurity: δ 147.5, 133.2, 129.2, 129.1, 129.0, 128.9, 128.8, 126.2, 119.0, 22.0. HRMS (ESI) *m/z* calculated for $C_{27}H_{36}N_2O_5SSi$ $[M+H]^+$ 529.2187; found, 529.2189.

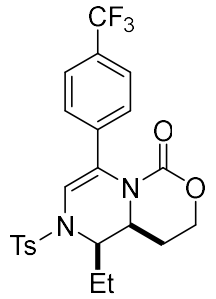


Compound 6fb. Following the general procedure, the carbene transfer to access **6fb** was conducted on a 0.55 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% EtOAc/hexanes, 10% increments) to yield **6fb** as a yellow solid (184.8 mg, 87% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.30 (m, 5H), 7.13 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.25 (s, 1H), 4.84 (dd, *J* = 11.2, 6.2 Hz, 1H), 4.05 (td, *J* = 11.6, 5.2 Hz, 1H), 2.44 (s, 3H), 1.97 (dd, *J* = 13.0, 5.2 Hz, 1H), 1.82 (d, *J* = 5.7 Hz, 1H), 1.71 – 1.58 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 146.7, 144.4, 135.4, 132.9, 129.1, 128.9, 128.6, 128.6, 128.3, 117.3, 65.0, 38.5,

30.4, 30.3, 21.7. HRMS (ESI) *m/z* calculated for $C_{20}H_{21}N_2O_4S[M+H]^+$ 385.1217; found, 385.1212.

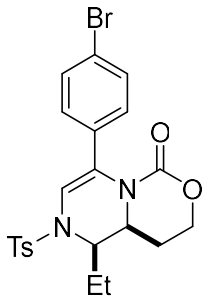


Compound 6aa. Following the general procedure, the carbene transfer to access **6aa** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% Et_2O/hexanes, 10% increments) to yield **6aa** as a yellow solid (98.9 mg, 83% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.35 (m, 3H), 7.17 – 7.13 (m, 2H), 6.04 (s, 1H), 5.01 (dd, *J* = 11.0, 6.8 Hz, 1H), 4.07 (ddd, *J* = 12.4, 11.0, 5.4 Hz, 1H), 3.33 (s, 3H), 2.12 – 2.06 (m, 2H), 1.91 (ddd, *J* = 14.1, 5.3, 1.6 Hz, 1H), 1.81 (ddd, *J* = 11.2, 6.6, 1.5 Hz, 1H), 1.50 – 1.43 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 148.1, 132.5, 129.2, 128.7, 128.2, 117.5, 77.3, 77.1, 76.8, 65.4, 44.4, 42.6, 38.6, 25.7, 21.4, 11.8. HRMS (ESI) *m/z* calculated for $C_{16}H_{20}N_2O_4S$ [M+H]+ 337.1217; found, 337.1215.

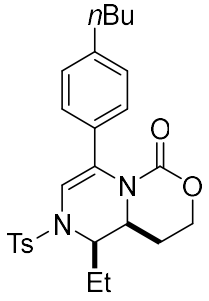


Compound 6ac. Following the general procedure, the carbene transfer to access **6ac** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% EtOAc/hexanes, 10% increments) to yield **6ac** as a yellow solid (81.7 mg, 48% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.96 (m, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.20 (s, 1H), 4.93 – 4.88 (m, 1H), 3.99 (td, *J* = 11.2, 6.3 Hz, 1H), 2.44 (s, 3H), 1.84 – 1.74 (m, 3H), 1.69 (ddd, *J* = 10.0, 6.5, 2.4 Hz, 1H), 1.16 (dtd, *J* = 14.9, 7.4, 5.4 Hz, 1H), 1.03 –

0.92 (m, 1H), 0.71 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 146.8, 144.6, 136.8, 136.8, 135.0, 129.3, 129.1, 128.7, 125.3, 125.3, 125.3, 125.2, 118.3, 77.3, 77.1, 76.8, 65.1, 44.4, 42.6, 25.6, 21.6, 21.1, 11.3. HRMS (ESI) *m/z* calculated for $C_{23}H_{24}F_3N_2O_4S[M+H]^+$ 481.1403; found, 481.1399.

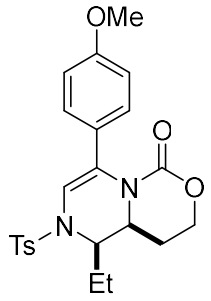


Compound 6ad. Following the general procedure, the carbene transfer to access **6ad** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% EtOAc/hexanes, 10% increments) to yield **6ad** as a yellow solid (149.3 mg, 86% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 (dd, J = 8.8, 2.2 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.31 (d, J = 8.3 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.18 (s, 1H), 4.93 – 4.88 (m, 1H), 3.98 (td, J = 11.2, 6.2 Hz, 1H), 2.43 (s, 3H), 1.85 – 1.72 (m, 3H), 1.65 (ddd, J = 9.7, 6.6, 2.4 Hz, 1H), 1.20 – 1.09 (m, 1H), 1.00 – 0.91 (m, 1H), 0.69 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 147.0, 144.5, 134.9, 131.8, 131.4, 130.5, 129.0, 128.6, 122.9, 117.7, 65.1, 44.1, 42.3, 25.5, 21.6, 21.0, 11.3. HRMS (ESI) *m/z* calculated for $C_{22}H_{24}BrN_2O_4S$ $[M+H]^+$ 491.0635; found, 491.0645.

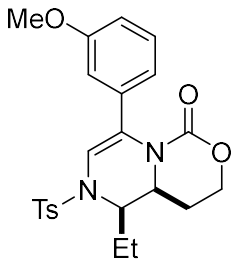


Compound 6ae. Following the general procedure, the carbene transfer to access **6ae** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% Et_2O/hexanes, 10% increments) to yield **6ae** as a yellow solid (116.2 mg, 70% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, J = 8.1

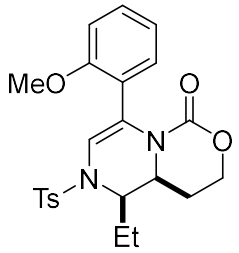
Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 7.7 Hz, 2H), 6.14 (s, 1H), 4.88 (dd, *J* = 11.0, 6.1 Hz, 1H), 3.97 (td, *J* = 11.3, 6.0 Hz, 1H), 2.60 (t, *J* = 7.8 Hz, 2H), 2.42 (s, 3H), 1.85 (dt, *J* = 7.8, 5.8 Hz, 1H), 1.74 (qq, *J* = 11.2, 6.1 Hz, 2H), 1.65 (ddd, *J* = 13.2, 7.9, 3.6 Hz, 1H), 1.62 – 1.56 (m, 2H), 1.36 (sextet, *J* = 7.4 Hz, 2H), 1.10 (tq, *J* = 12.9, 7.4, 6.5 Hz, 1H), 0.96 – 0.89 (m, 4H), 0.68 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 148.4, 144.3, 143.5, 135.0, 130.1, 128.9, 128.9, 128.7, 128.2, 117.2, 65.1, 43.9, 42.2, 35.4, 33.5, 25.6, 22.4, 21.6, 21.1, 14.0, 11.4. HRMS (ESI) *m/z* calculated for $C_{26}H_{32}N_2O_4S$ $[M+H]^+$ 469.2156; found, 469.2154.



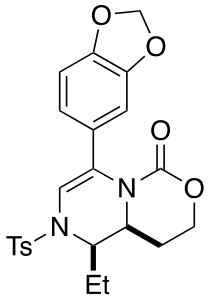
Compound 6af. Following the general procedure, the carbene transfer to access **6af** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% Et_2O/hexanes, 10% increments) to yield **6af** as a yellow solid (105.1 mg, 67% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.02 – 6.99 (m, 2H), 6.90 – 6.83 (m, 2H), 6.14 (s, 1H), 4.89 (dd, *J* = 10.5, 6.2 Hz, 1H), 3.97 (td, *J* = 11.6, 5.9 Hz, 1H), 3.81 (s, 3H), 2.43 (s, 3H), 1.87 – 1.68 (m, 3H), 1.64 (ddd, *J* = 10.4, 6.5, 2.1 Hz, 1H), 1.18 – 1.06 (m, 1H), 0.98 – 0.85 (m, 1H), 0.68 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 153.2, 147.9, 144.3, 135.1, 130.2, 128.9, 128.7, 125.1, 117.1, 113.6, 65.1, 55.3, 43.7, 42.0, 25.6, 21.6, 21.0, 11.4. HRMS (ESI) *m/z* calculated for $C_{23}H_{26}N_2O_5S$ $[M+H]^+$ 443.1635; found, 443.1637.



Compound 6ag. Following the general procedure, the carbene transfer to access **6ag** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% EtOAc/hexanes, 10% increments) to yield **6ag** as a yellow solid (98.2 mg, 63% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 1H), 6.89 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.66 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.61 (t, *J* = 2.1 Hz, 1H), 6.19 (s, 1H), 4.90 (dd, *J* = 10.9, 6.2 Hz, 1H), 3.98 (td, *J* = 11.4, 5.9 Hz, 1H), 3.82 (s, 3H), 2.43 (s, 3H), 1.87 (dt, *J* = 7.8, 5.6 Hz, 1H), 1.81 – 1.70 (m, 1H), 1.68 (ddd, *J* = 10.4, 6.4, 2.0 Hz, 1H), 1.18 – 1.09 (m, 1H), 0.98 – 0.89 (m, 1H), 0.69 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CF_3COOD) δ 163.6, 157.4, 152.3, 148.6, 139.3, 138.5, 133.6, 133.2, 125.6, 121.6, 119.2, 118.0, 69.3, 59.6, 48.4, 46.6, 29.8, 25.9, 25.3, 15.6. HRMS (ESI) *m/z* calculated for $C_{23}H_{26}N_2O_5S$ $[M+H]^+$ 443.1635; found, 443.1634.

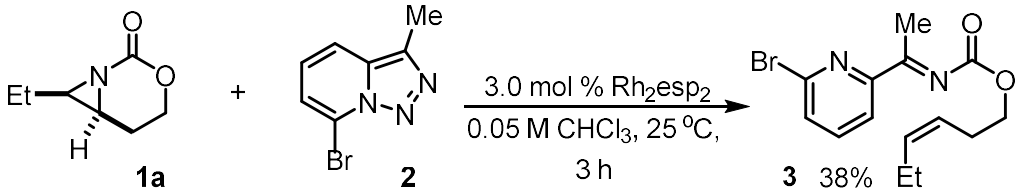


Compound 6ah. Following the general procedure, the carbene transfer to access **6ah** was conducted on 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% EtOAc/hexanes, 10% increments) to yield **6ah** as a yellow solid (137.9 mg, 88% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 – 8.06 (m, 2H), 7.34 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.97 (dd, *J* = 7.3, 1.9 Hz, 1H), 6.92 – 6.85 (m, 2H), 6.14 (s, 1H), 4.88 (dt, *J* = 10.5, 3.6 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.83 (s, 3H), 2.42 (s, 3H), 1.72 – 1.66 (m, 2H), 1.49 (q, *J* = 6.4 Hz, 1H), 1.07 – 0.92 (m, 2H), 0.64 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 153.4, 144.0, 135.6, 131.6, 130.5, 130.0, 129.6, 128.9, 128.8, 120.2, 117.9, 110.2, 65.2, 55.2, 42.4, 25.4, 21.6, 21.2, 11.2. HRMS (ESI) *m/z* calculated for $C_{23}H_{26}N_2O_5S$ [M+H]+ 443.1635; found, 443.1623.



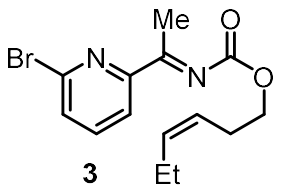
Compound 6ai. Following the general procedure, the carbene transfer to access **6ai** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% Et_2O/hexanes, 10% increments) to yield **6ai** as a yellow solid (122.9 mg, 76% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.55 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.52 (d, *J* = 1.7 Hz, 1H), 6.14 (s, 1H), 5.98 (q, *J* = 1.5 Hz, 2H), 4.88 (dd, *J* = 10.3, 5.8 Hz, 1H), 3.96 (td, *J* = 11.2, 6.3 Hz, 1H), 2.42 (s, 3H), 1.85 (dt, *J* = 7.8, 5.7 Hz, 1H), 1.80 – 1.70 (m, 2H), 1.65 (ddd, *J* = 9.7, 6.6, 2.5 Hz, 1H), 1.10 (tq, *J* = 12.9, 7.4, 6.5 Hz, 1H), 0.96 – 0.86 (m, 1H), 0.67 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 147.9, 147.8, 147.4, 144.4, 135.0, 129.0, 128.7, 126.5, 122.9, 117.3, 109.2, 108.1, 101.4, 65.1, 43.9, 42.2, 25.5, 21.6, 21.0, 11.4. HRMS (ESI) *m/z* calculated for $C_{23}H_{25}N_2O_6S$ [M+H]+ 457.1428; found, 457.1429.

VI. General procedure for cheletropic extrusion.



A flame-dried round bottom flask was placed under nitrogen and charged with the aziridine (1 equiv), $Rh_2(esp)_2$ (0.03 equiv), triazole (3 equiv) and $CHCl_3$ (0.05 M). The reaction mixture stirred at 25 °C for 2 h. The conversion of the reaction was determined by both TLC (60% Ether/Hexanes or 40% EtOAc/Hexanes) and ^{1}H NMR ($CDCl_3$). Once complete conversion of the aziridine was observed, the reaction was cooled down to

room temperature, concentrated and loaded directly onto silica gel for purification by column chromatography (60% Ether/Hexanes or 40% EtOAc/Hexanes).

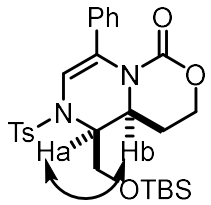


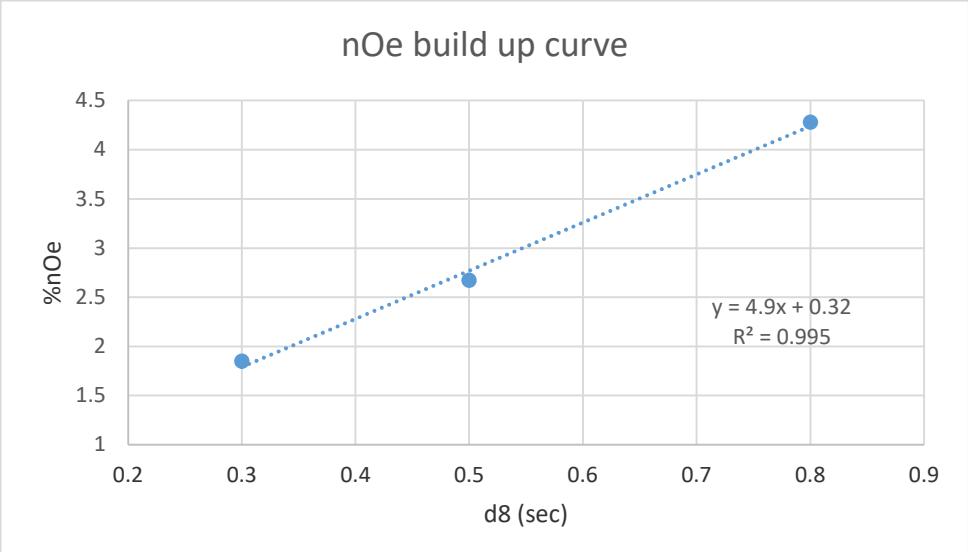
3

Compound 3. Following the general procedure, the carbene transfer to access **3** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 60% EtOAc/hexanes, 10% increments) to yield **3** as a yellow solid (43.8 mg, 38% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 – 7.64 (m, 1H), 7.64 – 7.54 (m, 1H), 7.46 – 7.35 (m, 1H), 5.60 – 5.45 (m, 1H), 5.35 (dddd, *J* = 14.1, 8.6, 7.1, 3.5 Hz, 1H), 4.27 (t, *J* = 6.9 Hz, 2H), 2.69 (s, 3H), 2.48 (d, *J* = 3.3 Hz, 2H), 2.07 (qd, *J* = 7.4, 3.4 Hz, 2H), 0.97 (dt, *J* = 8.9, 7.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.72, 154.27, 141.35, 139.15, 134.99, 131.78, 130.40, 123.27, 120.47, 66.19, 26.86, 25.75, 20.66, 14.18. HRMS (ESI) *m/z* calculated for $C_{14}H_{18}BrN_2O_2$ $[M+H]^+$ 325.0546; found, 325.0543.

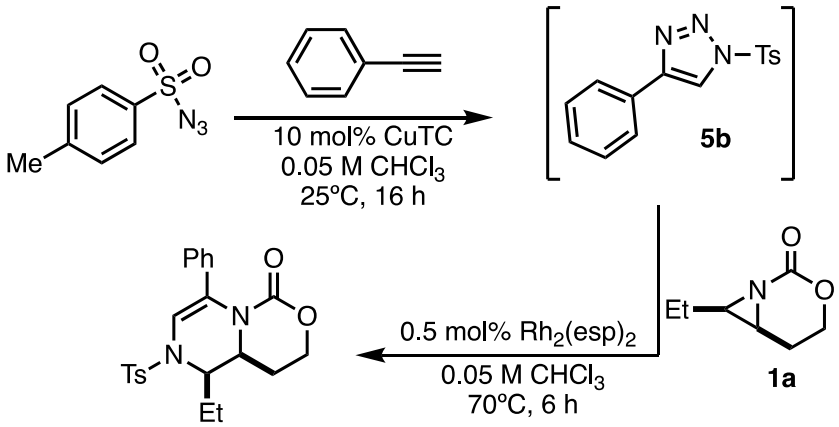
VII. NOESY experiment

A selective 1-D NOESY experiment was carried out to determine the relative stereochemistry for **3eb**. All other compounds are assumed to display the same stereochemical relationship.



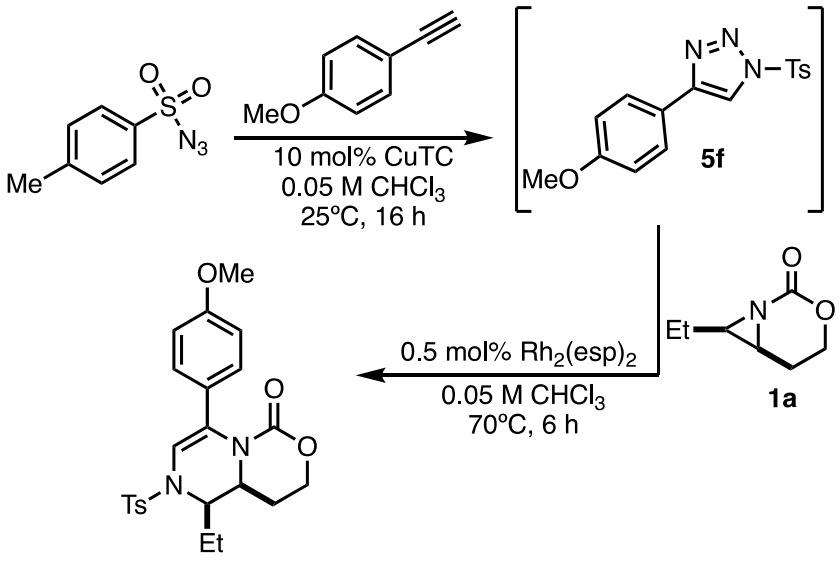


VIII. One-pot CuAAC-carbene transfer reactions



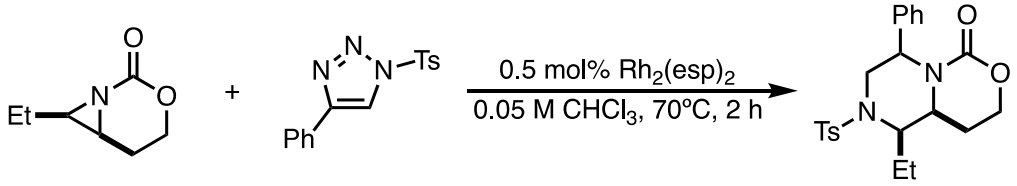
A flame-dried round bottom flask was placed under nitrogen and charged with phenylacetylene (109 mg, 1.06 mmol, 3.00 equiv), CuTC (6.75 mg, 0.035 mmol, 0.10 equiv) and chloroform (10 mL, 0.04 M). The tosyl azide (210 mg, 1.06 mmol, 3.00 equiv) was added slowly as the limiting reagent to avoid a run-away exotherm. The mixture was stirred at room temperature for 16 h (NMR aliquots were used to determine when the reaction was complete). Once the initial reaction was completed, the reaction flask was fitted with a reflux condenser. To the reaction flask was added $Rh_2(esp)_2$ (1.34 mg, 0.00177 mmol, 0.005 equiv) and the aziridine (50 mg, 0.35 mmol, 1.00 equiv) in a solution of chloroform. The mixture was stirred at 70 °C for 2 h. Conversion of the reaction was determined by both TLC (40% EtOAc/Hexanes) and ^1H NMR ($CDCl_3$).

Once the reaction was complete, it was cooled down to room temperature, concentrated, and loaded directly onto silica gel for purification by column chromatography (40% EtOAc/Hexanes).



Compound 6af. Following the general procedure, the one-pot CuAAC and carbene transfer reaction to furnish **6af** was conducted on a 0.35 mmol scale. The product was purified by silica gel flash column chromatography (0 to 40% EtOAc/Hexanes, 10% increments) to yield **6af** as a yellow solid (111.4 mg, 71% yield, >19:1 *dr*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.11 (s, 1H), 4.86 (dd, *J* = 10.9, 5.9 Hz, 1H), 3.95 (td, *J* = 11.3, 6.2 Hz, 1H), 3.78 (s, 3H), 2.41 (s, 3H), 1.81 (dt, *J* = 7.7, 5.8 Hz, 1H), 1.77 – 1.68 (m, 2H), 1.63 (ddd, *J* = 9.8, 6.5, 2.4 Hz, 1H), 1.10 (ddd, *J* = 13.8, 7.7, 5.8 Hz, 1H), 0.90 (dq, *J* = 14.7, 7.5 Hz, 1H), 0.67 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 153.2, 147.9, 144.3, 135.1, 130.2, 128.9, 128.7, 125.1, 117.1, 113.6, 65.1, 55.3, 43.7, 42.0, 25.6, 21.6, 21.0, 11.4. HRMS (ESI) *m/z* calculated for $C_{23}H_{26}N_2O_5S$ $[M+H]^+$ 443.1635; found, 443.1637.

IX. Catalyst recycle experiment.



A flame-dried round bottom flask was placed under nitrogen and charged with the aziridine (0.35 mmol, 1 equiv), $Rh_2(esp)_2$ (0.005 equiv), triazole (3 equiv) and $CHCl_3$ (0.05 M). The reaction mixture was heated at 70ºC using an oil bath for 2 h. Conversion of the reaction was determined by both TLC (40% EtOAc/Hexanes) and ^1H NMR ($CDCl_3$). Once the initial reaction was complete, the aziridine (1 equiv) and triazole (3 equiv) were added and the reaction mixture was heated at 70 ºC using an oil bath for 2 h. Once complete conversion of the second reaction was reached, the reaction was cooled down to room temperature and concentrated. The crude material was loaded directly onto silica gel for purification by column chromatography (40% EtOAc/Hexanes) to yield **6ab** as a yellow solid (111.4 mg, 83% yield, >19:1 *dr*). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.96 (m, 2H), 7.36 – 7.30 (m, 6H), 7.07 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.16 (s, 1H), 4.92 – 4.85 (m, 1H), 3.97 (td, *J* = 11.3, 6.1 Hz, 1H), 2.42 (s, 3H), 1.84 – 1.78 (m, 1H), 1.74 (tdd, *J* = 12.9, 5.5, 3.9 Hz, 1H), 1.67 (ddd, *J* = 10.2, 6.5, 2.2 Hz, 1H), 1.21 – 1.07 (m, 2H), 0.97 – 0.89 (m, 1H), 0.68 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 147.2, 143.3, 134.0, 131.8, 127.9, 127.7, 127.5, 127.2, 116.4, 64.1, 42.9, 41.2, 29.3, 28.7, 24.5, 20.6, 20.0, 10.3. HRMS (ESI) *m/z* calculated for $C_{22}H_{24}N_2O_4S$ $[M+H]^+$ 413.1530; found, 413.1516.

X. Computational studies

All the calculations reported in this paper were performed with the Gaussian 09 suite of programs.[6] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[7] in conjunction with the D3 dispersion correction suggested by Grimme et al.[8] using the standard double-ζ quality def2-SVP[9] basis set for all atoms. The SMD continuum model was used to model the effects of the solvent. This level is denoted SMD(solvent)-B3LYP-D3/def2-SVP. Geometries were fully optimized in solution without any geometry or symmetry constraints. Reactants, intermediates, and products were characterized by frequency calculations,[10] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[11]

Table S1. Cartesian coordinates (in Å) and energies (in free energies, in a.u.) of all the stationary points discussed in the text in Figure 2. All calculations have been performed at the SMD(solvent)-B3LYP-D3/def2-SVP level.

1a, G = -438.809908

N	0.262344000	-0.539114000	-0.948473000
C	0.848806000	0.795236000	-0.891354000
C	1.583461000	-0.383547000	-0.320214000
H	1.209079000	1.138283000	-1.868937000
C	0.104868000	1.866386000	-0.112266000
C	-1.045236000	1.299079000	0.724484000
O	-1.687216000	0.161318000	0.109043000
C	-0.886730000	-0.877142000	-0.241211000
O	-1.217593000	-2.017801000	-0.020856000
H	-0.707954000	0.995664000	1.728914000
H	-1.838113000	2.046650000	0.858032000
H	0.784812000	2.436048000	0.541734000
H	-0.304495000	2.575161000	-0.847857000
H	2.392151000	-0.783004000	-0.945054000
C	1.781988000	-0.639707000	1.151603000
H	1.020096000	-0.160260000	1.780849000
H	1.754373000	-1.722168000	1.356808000
H	2.769158000	-0.262542000	1.463080000

5a-Rh_2, G = -2085.528421

Rh	-0.369407000	0.178166000	-0.080001000
C	1.407358000	1.106241000	-0.294528000
Rh	-2.528829000	-0.972175000	0.134636000
O	-2.132390000	-1.882293000	-1.670332000
C	-1.036215000	-1.657950000	-2.255117000
O	-0.137902000	-0.846286000	-1.851391000
O	-3.378195000	0.638132000	-0.836665000
C	-2.648908000	1.588573000	-1.234526000
O	-1.386105000	1.668109000	-1.073769000
O	-1.513068000	-2.502283000	1.078535000
C	-0.265196000	-2.409454000	1.257303000
O	0.452223000	-1.414254000	0.914222000
O	-2.762262000	0.017552000	1.929645000
C	-1.877631000	0.826665000	2.324840000
O	-0.793389000	1.095731000	1.706961000
C	-2.081937000	1.529518000	3.640351000
H	-3.111536000	1.400324000	3.997254000
H	-1.383537000	1.103951000	4.379463000
H	-1.842417000	2.597828000	3.534968000
C	0.448733000	-3.537824000	1.951104000
H	0.272688000	-3.445882000	3.036082000

H	0.035008000	-4.502162000	1.623351000
H	1.528185000	-3.481598000	1.757052000
C	-3.296204000	2.719673000	-1.988960000
H	-4.384332000	2.711554000	-1.845715000
H	-2.870616000	3.681200000	-1.668006000
H	-3.074177000	2.596399000	-3.061964000
C	-0.727028000	-2.407434000	-3.523040000
H	-1.599863000	-2.977172000	-3.865591000
H	-0.398788000	-1.702890000	-4.301679000
H	0.110217000	-3.096462000	-3.325879000
C	2.376900000	0.066176000	-0.552774000
H	2.236237000	-0.523020000	-1.478525000
N	3.229738000	-0.270701000	0.354113000
S	4.018635000	-1.771771000	0.087255000
O	3.812393000	-2.584206000	1.294897000
O	3.663002000	-2.343550000	-1.226243000
C	5.725038000	-1.241497000	0.046697000
H	5.947153000	-0.717757000	0.985908000
H	6.329798000	-2.155255000	-0.043718000
H	5.871167000	-0.588104000	-0.823901000
C	1.729791000	2.488586000	-0.200295000
C	3.043815000	2.951358000	-0.513866000
C	0.755162000	3.439762000	0.223009000
C	3.362399000	4.297506000	-0.409261000
C	1.089115000	4.783546000	0.331209000
C	2.386272000	5.213523000	0.014473000
H	3.801913000	2.236074000	-0.837968000
H	-0.247065000	3.097541000	0.471017000
H	4.369050000	4.643810000	-0.654144000
H	0.341114000	5.506722000	0.663855000
H	2.640853000	6.273532000	0.098101000

TS1, G = -2524.325505

Rh	-0.809316000	-0.230595000	0.202137000
C	1.172173000	-0.066772000	0.948226000
N	2.576762000	-0.532600000	-0.931835000
C	3.462559000	0.480802000	-1.545166000
C	2.182510000	0.100503000	-2.214578000
H	3.400631000	1.426053000	-1.003890000
C	4.871764000	0.075251000	-1.921874000
C	5.062159000	-1.433470000	-1.998974000
O	4.304305000	-2.128363000	-0.985485000
C	2.978346000	-1.888996000	-0.891357000
O	2.210684000	-2.790478000	-0.680421000
H	4.768155000	-1.838602000	-2.979890000
H	6.109296000	-1.713092000	-1.824541000

H	5.163636000	0.533255000	-2.880749000
H	5.543791000	0.482750000	-1.150890000
Rh	-3.143821000	-0.301820000	-0.567767000
O	-3.530464000	1.271351000	0.713566000
C	-2.624032000	1.650388000	1.508074000
O	-1.474009000	1.113560000	1.616394000
O	-3.504957000	-1.674376000	0.928802000
C	-2.534012000	-2.126821000	1.600690000
O	-1.322123000	-1.756101000	1.490777000
O	-2.625846000	1.086184000	-2.006577000
C	-1.479751000	1.616464000	-1.960798000
O	-0.561588000	1.306369000	-1.135982000
O	-2.585930000	-1.844537000	-1.817197000
C	-1.356948000	-2.129784000	-1.929483000
O	-0.408404000	-1.575916000	-1.292807000
C	-0.977070000	-3.197060000	-2.924282000
H	-1.736387000	-3.991816000	-2.933420000
H	-0.948409000	-2.747726000	-3.930793000
H	0.012987000	-3.607364000	-2.689024000
C	-1.126563000	2.683369000	-2.961405000
H	-0.497562000	2.230404000	-3.746403000
H	-2.028420000	3.103147000	-3.425728000
H	-0.534467000	3.462713000	-2.460301000
C	-2.816770000	-3.227803000	2.590149000
H	-3.840835000	-3.143488000	2.978406000
H	-2.724986000	-4.194128000	2.066068000
H	-2.086297000	-3.210094000	3.410088000
C	-2.884324000	2.826306000	2.410304000
H	-3.858334000	3.284233000	2.196666000
H	-2.853424000	2.491370000	3.459483000
H	-2.070271000	3.555269000	2.272872000
H	1.362476000	0.803292000	-2.047719000
C	2.034843000	-0.713905000	-3.470573000
H	2.844960000	-1.437491000	-3.634214000
H	1.084698000	-1.264590000	-3.432904000
H	2.004716000	-0.034568000	-4.337591000
C	1.294827000	1.363453000	1.081299000
H	0.720856000	1.701931000	1.969033000
N	1.805072000	2.229321000	0.275605000
S	1.390617000	3.853083000	0.586797000
O	0.838224000	4.402599000	-0.660470000
O	0.605515000	3.998597000	1.830969000
C	3.005319000	4.575743000	0.851109000
H	3.615138000	4.403172000	-0.045467000
H	2.841969000	5.651604000	1.008734000
H	3.458936000	4.115772000	1.739399000

C	1.885142000	-0.938063000	1.858077000
C	2.979527000	-0.438096000	2.614343000
C	1.534112000	-2.302215000	2.000604000
C	3.679548000	-1.262533000	3.487075000
C	2.238744000	-3.123478000	2.879367000
C	3.307472000	-2.609375000	3.621194000
H	3.275245000	0.608264000	2.503586000
H	0.708288000	-2.695332000	1.417313000
H	4.516284000	-0.863895000	4.065946000
H	1.957501000	-4.174342000	2.981968000
H	3.857543000	-3.258940000	4.307501000

INT1, G = -2524.355466

Rh	-0.610812000	-0.335719000	0.099929000
C	1.822417000	0.166652000	0.483627000
N	2.474385000	-0.259442000	-0.795523000
C	3.466707000	0.648665000	-1.534218000
C	2.122584000	0.469442000	-2.116539000
H	3.587963000	1.583969000	-0.981909000
C	4.751940000	0.011984000	-1.975408000
C	4.528907000	-1.355934000	-2.573178000
O	3.609884000	-2.147574000	-1.775285000
C	2.705835000	-1.735711000	-0.901185000
O	2.108570000	-2.492246000	-0.206215000
H	4.117721000	-1.300720000	-3.589911000
H	5.453610000	-1.945772000	-2.607602000
H	5.230535000	0.665178000	-2.721951000
H	5.428009000	-0.044894000	-1.107550000
Rh	-2.981653000	-0.721757000	-0.285337000
O	-3.372227000	0.760389000	1.098949000
C	-2.402252000	1.344722000	1.665656000
O	-1.179126000	1.038368000	1.514401000
O	-2.903835000	-2.141822000	1.202021000
C	-1.802383000	-2.376079000	1.786749000
O	-0.699082000	-1.804117000	1.535468000
O	-2.931786000	0.734909000	-1.738853000
C	-1.829763000	1.308576000	-1.988904000
O	-0.728507000	1.049647000	-1.416145000
O	-2.442880000	-2.139091000	-1.680068000
C	-1.215695000	-2.319918000	-1.941739000
O	-0.248450000	-1.726184000	-1.377044000
C	-0.870647000	-3.287188000	-3.044890000
H	-1.638470000	-4.067870000	-3.131232000
H	-0.837765000	-2.730119000	-3.996507000
H	0.117489000	-3.734182000	-2.871302000
C	-1.796446000	2.386593000	-3.037733000

H	-1.061592000	2.119379000	-3.813440000
H	-2.784436000	2.532908000	-3.492527000
H	-1.450806000	3.310789000	-2.550316000
C	-1.810009000	-3.392191000	2.900057000
H	-2.545117000	-4.182752000	2.695205000
H	-0.808690000	-3.820134000	3.041859000
H	-2.106341000	-2.882524000	3.832384000
C	-2.680045000	2.493628000	2.596709000
H	-3.732345000	2.801151000	2.548883000
H	-2.430870000	2.190486000	3.626694000
H	-2.010239000	3.324596000	2.328282000
H	1.457949000	1.296823000	-1.860430000
C	1.660875000	-0.279167000	-3.337275000
H	2.035280000	-1.302685000	-3.441293000
H	0.565387000	-0.317985000	-3.315589000
H	1.977005000	0.298900000	-4.220471000
C	1.429582000	1.523415000	0.670859000
H	1.119930000	1.715221000	1.706252000
N	1.379872000	2.514446000	-0.188131000
S	0.572812000	3.886403000	0.333582000
O	-0.705330000	4.026975000	-0.394713000
O	0.514464000	3.991850000	1.810324000
C	1.674667000	5.161402000	-0.271097000
H	1.787623000	5.040119000	-1.356571000
H	1.200742000	6.124733000	-0.035225000
H	2.640832000	5.065479000	0.242128000
C	2.421923000	-0.447596000	1.719421000
C	3.758908000	-0.886056000	1.771339000
C	1.665789000	-0.513124000	2.906594000
C	4.310310000	-1.396203000	2.950840000
C	2.220898000	-1.008873000	4.087291000
C	3.545086000	-1.461519000	4.118181000
H	4.398250000	-0.827788000	0.888293000
H	0.625616000	-0.188778000	2.895835000
H	5.350130000	-1.734570000	2.954274000
H	1.605731000	-1.052081000	4.990441000
H	3.974344000	-1.859860000	5.041240000

INT2, G = -1389.843480

C	0.371268000	0.505018000	-0.228338000
N	0.633905000	-0.937091000	-0.138549000
C	1.238024000	-1.731307000	-1.308170000
C	-0.201243000	-1.876636000	-1.043269000
H	1.506250000	-1.048091000	-2.115528000
C	2.250208000	-2.805111000	-0.949985000
C	2.825666000	-2.576568000	0.434200000

O	1.768236000	-2.367010000	1.408462000
C	0.847107000	-1.434102000	1.253504000
O	0.174373000	-1.014419000	2.141723000
H	3.371373000	-3.454238000	0.799376000
H	3.493561000	-1.703503000	0.471273000
H	1.780558000	-3.798339000	-1.001597000
H	3.071580000	-2.786858000	-1.680168000
H	-0.868782000	-1.274302000	-1.658415000
C	-0.860799000	-3.072310000	-0.425753000
H	-0.211216000	-3.643497000	0.250836000
H	-1.755940000	-2.738756000	0.116644000
H	-1.176902000	-3.742595000	-1.240644000
C	-0.957241000	0.892147000	-0.180059000
N	-1.987843000	0.057542000	-0.042555000
H	-1.153428000	1.968014000	-0.295569000
S	-3.503073000	0.676421000	-0.200243000
O	-3.514198000	2.137102000	-0.465924000
O	-4.265958000	-0.186876000	-1.124701000
C	-4.198594000	0.431349000	1.438854000
H	-3.625836000	1.030811000	2.159567000
H	-5.245224000	0.766613000	1.399049000
H	-4.144452000	-0.636925000	1.687769000
C	1.516334000	1.420219000	-0.167127000
C	1.339664000	2.766956000	0.245984000
C	2.836314000	1.034425000	-0.502765000
C	2.404718000	3.664316000	0.292986000
C	3.905163000	1.933713000	-0.436795000
C	3.702720000	3.258817000	-0.044623000
H	0.353504000	3.112985000	0.559817000
H	3.050939000	0.024710000	-0.846209000
H	2.219982000	4.692155000	0.618324000
H	4.907224000	1.588333000	-0.706998000
H	4.538055000	3.961645000	0.005742000

TS2, G = -1389.826804

C	0.238833000	0.556526000	0.189927000
N	0.582050000	-0.726055000	0.409020000
C	1.167534000	-2.093740000	-1.509489000
C	-0.014697000	-1.995579000	-0.747641000
H	1.352432000	-1.313742000	-2.253933000
C	2.256183000	-3.061147000	-1.208533000
C	3.044702000	-2.576109000	0.014434000
O	2.163353000	-2.313068000	1.122825000
C	1.595721000	-1.094696000	1.299037000
O	1.857654000	-0.426569000	2.269574000
H	3.741705000	-3.352132000	0.363350000

H	3.627216000	-1.669630000	-0.214506000
H	1.850509000	-4.062157000	-0.986793000
H	2.956175000	-3.152167000	-2.054011000
H	-0.812603000	-1.398923000	-1.196779000
C	-0.577613000	-3.123626000	0.077731000
H	0.180675000	-3.645368000	0.673382000
H	-1.352551000	-2.727607000	0.748601000
H	-1.053667000	-3.851950000	-0.600460000
C	-1.155775000	0.857592000	0.033782000
N	-2.075737000	-0.051522000	0.190780000
H	-1.425619000	1.879369000	-0.271965000
S	-3.660339000	0.385099000	-0.213737000
O	-3.791041000	1.829459000	-0.493985000
O	-4.108459000	-0.570646000	-1.238653000
C	-4.507068000	0.023735000	1.320399000
H	-4.117310000	0.689638000	2.102278000
H	-5.574536000	0.216202000	1.139163000
H	-4.337327000	-1.031451000	1.571545000
C	1.247723000	1.613284000	-0.019745000
C	0.965433000	2.964491000	0.281081000
C	2.522804000	1.302730000	-0.536685000
C	1.922172000	3.958410000	0.073097000
C	3.475278000	2.300189000	-0.749360000
C	3.182513000	3.633759000	-0.443554000
H	-0.001510000	3.239146000	0.708284000
H	2.764274000	0.271791000	-0.797085000
H	1.684027000	4.995189000	0.325043000
H	4.453445000	2.032878000	-1.158142000
H	3.931365000	4.414036000	-0.601752000

TS2', G = -1389.836249

C	-0.674267000	-0.536029000	0.177490000
N	-0.577867000	0.882969000	0.107231000
C	-0.820185000	1.610773000	-1.192482000
C	0.619280000	1.416067000	-1.408104000
H	-1.435815000	0.967648000	-1.830974000
C	-1.480903000	2.952548000	-0.970420000
C	-0.777470000	3.766440000	0.095768000
O	-0.314909000	2.959786000	1.203926000
C	-0.302065000	1.623728000	1.287552000
O	-0.084401000	1.084165000	2.338947000
H	0.099993000	4.294331000	-0.301389000
H	-1.450407000	4.517596000	0.532701000
H	-1.504491000	3.518239000	-1.913938000
H	-2.522064000	2.749331000	-0.677491000
H	0.874415000	0.458255000	-1.862919000

C	1.753403000	2.328872000	-1.161626000
H	2.694445000	1.775898000	-1.274421000
H	1.706148000	3.162443000	-1.889413000
H	1.734620000	2.784924000	-0.160576000
C	0.538605000	-1.204766000	0.224245000
N	1.687481000	-0.522594000	0.207869000
H	0.546166000	-2.302894000	0.208262000
S	3.081737000	-1.325282000	-0.130376000
O	3.745657000	-0.612286000	-1.246176000
O	2.900887000	-2.789184000	-0.274719000
C	4.068264000	-1.041063000	1.340858000
H	3.577847000	-1.533620000	2.191535000
H	5.059634000	-1.479291000	1.155384000
H	4.145876000	0.041523000	1.507057000
C	-2.004378000	-1.134826000	0.060275000
C	-3.168640000	-0.342799000	0.199030000
C	-2.187245000	-2.516194000	-0.194606000
C	-4.445032000	-0.899346000	0.080776000
C	-3.462964000	-3.068582000	-0.295756000
C	-4.605271000	-2.266312000	-0.165018000
H	-3.073864000	0.722476000	0.422538000
H	-1.319125000	-3.166020000	-0.322455000
H	-5.322669000	-0.256665000	0.194900000
H	-3.567218000	-4.139795000	-0.490671000
H	-5.603251000	-2.703399000	-0.251508000

INT3, G = -1389.876371

C	0.723007000	0.430631000	0.184552000
N	0.557260000	-0.773616000	0.572745000
C	-1.243168000	-2.690894000	-1.255010000
C	-2.019902000	-2.477561000	-0.182576000
H	-1.500185000	-2.156025000	-2.178492000
C	-0.005322000	-3.549760000	-1.338091000
C	1.325312000	-2.812177000	-1.140597000
O	1.726130000	-2.737841000	0.248455000
C	1.450106000	-1.704534000	1.058357000
O	1.864794000	-1.688261000	2.195012000
H	2.140750000	-3.378277000	-1.612611000
H	1.306221000	-1.808551000	-1.593465000
H	-0.031456000	-4.383885000	-0.618369000
H	0.040992000	-4.006749000	-2.341214000
H	-2.858405000	-1.780810000	-0.300179000
C	-1.817959000	-3.011608000	1.201564000
H	-1.005450000	-3.750182000	1.270094000
H	-1.564846000	-2.175583000	1.878279000
H	-2.740900000	-3.471113000	1.596703000

C	-0.542367000	1.170638000	-0.149539000
N	-1.643045000	0.822445000	0.389576000
H	-0.479642000	1.979026000	-0.896742000
S	-3.067812000	1.602788000	-0.200424000
O	-2.742348000	2.760820000	-1.049392000
O	-3.903813000	0.527481000	-0.749697000
C	-3.761905000	2.171798000	1.340802000
H	-3.079544000	2.911566000	1.781076000
H	-4.729136000	2.630662000	1.089005000
H	-3.898821000	1.303421000	1.998234000
C	2.013331000	1.137735000	-0.012892000
C	2.065909000	2.541287000	0.101407000
C	3.200864000	0.431654000	-0.289104000
C	3.278763000	3.218135000	-0.038311000
C	4.407808000	1.112824000	-0.441468000
C	4.451070000	2.506374000	-0.312774000
H	1.160698000	3.111333000	0.323925000
H	3.187989000	-0.652272000	-0.409689000
H	3.307155000	4.305427000	0.065984000
H	5.319517000	0.553424000	-0.664486000
H	5.399151000	3.037334000	-0.430459000

TS3, G = -1389.838872

N	0.580569000	0.965697000	-0.510758000
C	-0.393881000	1.721851000	1.229463000
C	-1.713847000	1.238173000	1.119101000
H	0.260705000	1.156970000	1.897297000
C	-0.062845000	3.189786000	1.080588000
C	0.204859000	3.635203000	-0.350331000
O	1.424473000	3.093345000	-0.858124000
C	1.557853000	1.770075000	-1.070479000
O	2.448329000	1.376392000	-1.794872000
H	-0.625300000	3.363624000	-1.020903000
H	0.340547000	4.724977000	-0.388797000
H	-0.888255000	3.807013000	1.473425000
H	0.829455000	3.424067000	1.681310000
H	-2.021122000	0.487013000	1.847776000
C	-2.798655000	2.009930000	0.441464000
H	-2.532493000	2.237134000	-0.602498000
H	-3.740220000	1.448128000	0.455063000
H	-2.966402000	2.974332000	0.955601000
N	-1.595197000	-0.487782000	-0.233318000
C	-0.421813000	-1.102111000	-0.157466000
H	-0.356112000	-2.150944000	0.153909000
C	0.761298000	-0.345328000	-0.314839000
S	-2.961563000	-1.522782000	0.005887000

O	-2.551441000	-2.929149000	0.162257000
O	-3.824709000	-0.930334000	1.040403000
C	-3.755965000	-1.331721000	-1.583653000
H	-3.972021000	-0.267147000	-1.741988000
H	-3.082559000	-1.721941000	-2.358657000
H	-4.683630000	-1.920793000	-1.537617000
C	2.070548000	-0.975278000	-0.002267000
C	3.052842000	-0.274863000	0.722903000
C	2.340377000	-2.298316000	-0.400128000
C	4.270010000	-0.879562000	1.038441000
C	3.562678000	-2.899221000	-0.090449000
C	4.531851000	-2.193178000	0.630751000
H	2.856917000	0.746894000	1.055695000
H	1.595875000	-2.854210000	-0.975628000
H	5.019339000	-0.322683000	1.607260000
H	3.760081000	-3.923508000	-0.417304000
H	5.487527000	-2.664484000	0.874503000

Product 6aa, G = -1389.928213

N	-0.657551000	1.114901000	-0.140576000
C	0.524341000	1.540816000	-0.907829000
C	1.805826000	1.020774000	-0.208409000
H	0.477925000	1.010449000	-1.871729000
C	0.475069000	3.039272000	-1.198992000
C	-0.052535000	3.835545000	-0.022645000
O	-1.277726000	3.279263000	0.477505000
C	-1.434132000	1.948422000	0.646129000
O	-2.277187000	1.545216000	1.417788000
H	0.666748000	3.884689000	0.808265000
H	-0.293475000	4.866119000	-0.317976000
H	1.473747000	3.402998000	-1.484534000
H	-0.192363000	3.199859000	-2.059765000
H	2.645299000	1.213859000	-0.890462000
C	2.115366000	1.631090000	1.155255000
H	1.272629000	1.511735000	1.854287000
H	2.999007000	1.144297000	1.593543000
H	2.353240000	2.699995000	1.059840000
N	1.645293000	-0.447963000	-0.120038000
C	0.375989000	-1.022481000	-0.043469000
H	0.347674000	-2.110009000	-0.095434000
C	-0.770367000	-0.299619000	-0.007049000
S	2.995565000	-1.470718000	-0.225915000
O	2.591710000	-2.673395000	-0.962397000
O	4.107760000	-0.641158000	-0.700114000
C	3.323927000	-1.962831000	1.464317000
H	3.594471000	-1.075788000	2.050954000

H	2.425538000	-2.449264000	1.868004000
H	4.160316000	-2.675745000	1.422874000
C	-2.101379000	-0.945757000	-0.046992000
C	-3.150821000	-0.378868000	-0.796653000
C	-2.340319000	-2.161297000	0.621429000
C	-4.390121000	-1.013784000	-0.884924000
C	-3.580351000	-2.799035000	0.527148000
C	-4.612567000	-2.229477000	-0.225796000
H	-2.986225000	0.565910000	-1.319834000
H	-1.552729000	-2.600792000	1.238539000
H	-5.189578000	-0.556748000	-1.474768000
H	-3.744203000	-3.740750000	1.058405000
H	-5.585249000	-2.723933000	-0.292654000

Table S2. Cartesian coordinates (in Å) and energies (in free energies, in a.u.) of all the stationary points discussed in the text in Scheme 2B. All calculations have been performed at the SMD(solvent)-B3LYP-D3/def2-SVP level.

INT2, G = -3337.426184

C	1.064642000	1.381236000	-0.412297000
N	1.661879000	0.057248000	-0.250306000
C	2.553843000	-0.520242000	-1.335154000
C	1.211725000	-1.107045000	-1.111799000
H	2.635656000	0.190109000	-2.161008000
C	3.850863000	-1.113332000	-0.829575000
C	4.335051000	-0.275400000	0.340569000
O	3.346856000	-0.278992000	1.401445000
C	2.041478000	-0.232634000	1.159772000
O	1.216624000	-0.343364000	2.015166000
H	5.243206000	-0.686230000	0.799699000
H	4.527366000	0.768102000	0.046182000
H	3.729118000	-2.158808000	-0.509331000
H	4.602340000	-1.093119000	-1.632034000
H	0.437365000	-0.759918000	-1.795514000
C	0.916975000	-2.423839000	-0.457232000
H	1.684180000	-2.744754000	0.261412000
H	-0.050266000	-2.346736000	0.059234000
H	0.838852000	-3.194250000	-1.240448000
C	-0.326629000	1.475460000	-0.222201000
N	-1.075925000	0.322257000	-0.137735000
C	2.040877000	2.515292000	-0.309480000
H	2.316747000	2.797384000	0.730252000
H	2.983123000	2.284564000	-0.837764000
H	1.641554000	3.424351000	-0.785460000
C	-2.370763000	0.398558000	-0.027820000

Br	-3.319359000	-1.314575000	0.072734000
C	-1.018319000	2.736632000	-0.145855000
H	-0.458347000	3.672330000	-0.174571000
C	-3.140787000	1.560646000	0.031425000
H	-4.224648000	1.543035000	0.134030000
C	-2.395624000	2.757769000	-0.028328000
H	-2.918204000	3.717770000	0.030887000

TS2, G = -3337.418396

C	1.028425000	1.590797000	-0.059810000
N	1.723866000	0.366568000	-0.028639000
C	2.532673000	-0.104816000	-1.254727000
C	1.319378000	-0.906887000	-1.346392000
H	2.583649000	0.736737000	-1.950185000
C	3.887644000	-0.736574000	-0.947771000
C	4.186653000	-0.600625000	0.531913000
O	3.049532000	-1.030264000	1.310419000
C	1.910472000	-0.321611000	1.220379000
O	1.129837000	-0.270270000	2.123516000
H	5.019629000	-1.240993000	0.848776000
H	4.425028000	0.441495000	0.801884000
H	3.881941000	-1.798195000	-1.234426000
H	4.676626000	-0.238470000	-1.529359000
H	0.467662000	-0.448759000	-1.849545000
C	1.138168000	-2.306123000	-0.889386000
H	1.979887000	-2.697829000	-0.304507000
H	0.211241000	-2.381808000	-0.298219000
H	1.005487000	-2.948873000	-1.779955000
C	-0.379649000	1.566031000	-0.007482000
N	-1.024739000	0.350570000	0.019030000
C	1.825522000	2.829649000	-0.371672000
H	1.682233000	3.616779000	0.391704000
H	2.905636000	2.613613000	-0.380713000
H	1.571478000	3.292397000	-1.346975000
C	-2.327001000	0.317741000	0.016194000
Br	-3.138771000	-1.464545000	0.010467000
C	-1.172468000	2.764015000	-0.041647000
H	-0.687163000	3.740532000	-0.072744000
C	-3.190970000	1.414669000	0.004813000
H	-4.274467000	1.305823000	0.022099000
C	-2.552427000	2.671827000	-0.028266000
H	-3.159262000	3.582365000	-0.045273000

INT3, G = -3337.499048

C	0.925974000	2.078810000	-0.637318000
N	1.972783000	1.584230000	-0.093090000

C	2.324462000	-1.765812000	-1.212220000
C	1.130679000	-2.100374000	-0.697570000
H	2.358719000	-1.437055000	-2.258240000
C	3.629727000	-1.716016000	-0.462622000
C	3.894622000	-0.351767000	0.176873000
O	2.918348000	-0.081832000	1.199198000
C	1.923213000	0.805505000	1.075861000
O	1.144828000	0.962568000	1.990179000
H	4.868024000	-0.351360000	0.691926000
H	3.887244000	0.451920000	-0.571688000
H	3.667762000	-2.481421000	0.329269000
H	4.472283000	-1.920292000	-1.145138000
H	0.256542000	-2.033021000	-1.354170000
C	0.832696000	-2.515345000	0.711283000
H	1.735625000	-2.685996000	1.313944000
H	0.244837000	-1.729291000	1.215740000
H	0.215194000	-3.429588000	0.733466000
C	-0.489516000	1.760007000	-0.226523000
N	-0.880023000	0.480697000	-0.316477000
C	1.074206000	3.038793000	-1.778728000
H	0.550054000	3.983608000	-1.557154000
H	2.134087000	3.241333000	-1.982691000
H	0.595017000	2.618435000	-2.679737000
C	-2.116663000	0.181584000	0.012348000
Br	-2.661553000	-1.654496000	-0.191753000
C	-1.349196000	2.777949000	0.201493000
H	-1.004034000	3.811677000	0.256848000
C	-3.059718000	1.103855000	0.484899000
H	-4.069069000	0.794581000	0.758116000
C	-2.648857000	2.432549000	0.580491000
H	-3.342440000	3.195041000	0.943227000

TS3, G = -3337.427814

N	-1.823074000	0.332181000	-0.226959000
C	-1.488584000	-0.635228000	1.299301000
C	-0.144431000	-1.131083000	1.254053000
H	-1.615308000	0.178103000	2.019309000
C	-2.647530000	-1.624613000	1.343082000
C	-3.070861000	-2.086520000	-0.037042000
O	-3.660004000	-1.010732000	-0.763722000
C	-2.998489000	0.151230000	-0.933740000
O	-3.430420000	0.947719000	-1.744280000
H	-2.225935000	-2.495368000	-0.612968000
H	-3.850548000	-2.858650000	0.025705000
H	-2.376545000	-2.501746000	1.952568000
H	-3.516723000	-1.150320000	1.824414000

H	0.544317000	-0.728932000	1.998700000
C	0.187656000	-2.440724000	0.621190000
H	0.102975000	-2.378676000	-0.477639000
H	1.205740000	-2.766420000	0.863093000
H	-0.506192000	-3.235276000	0.954638000
N	0.800638000	0.416261000	-0.134122000
C	0.117583000	1.603509000	0.059788000
C	-1.286065000	1.571539000	-0.093708000
C	-2.134772000	2.778863000	0.208605000
H	-1.821617000	3.650104000	-0.388037000
H	-3.189849000	2.588711000	-0.016077000
H	-2.051153000	3.067001000	1.273274000
C	0.810859000	2.775527000	0.506888000
H	0.250046000	3.676030000	0.756755000
C	2.132811000	0.462550000	-0.055103000
C	2.883697000	1.574433000	0.279848000
H	3.973275000	1.547957000	0.256257000
C	2.180753000	2.757232000	0.615097000
H	2.731346000	3.645128000	0.934993000
Br	3.113453000	-1.128941000	-0.548084000

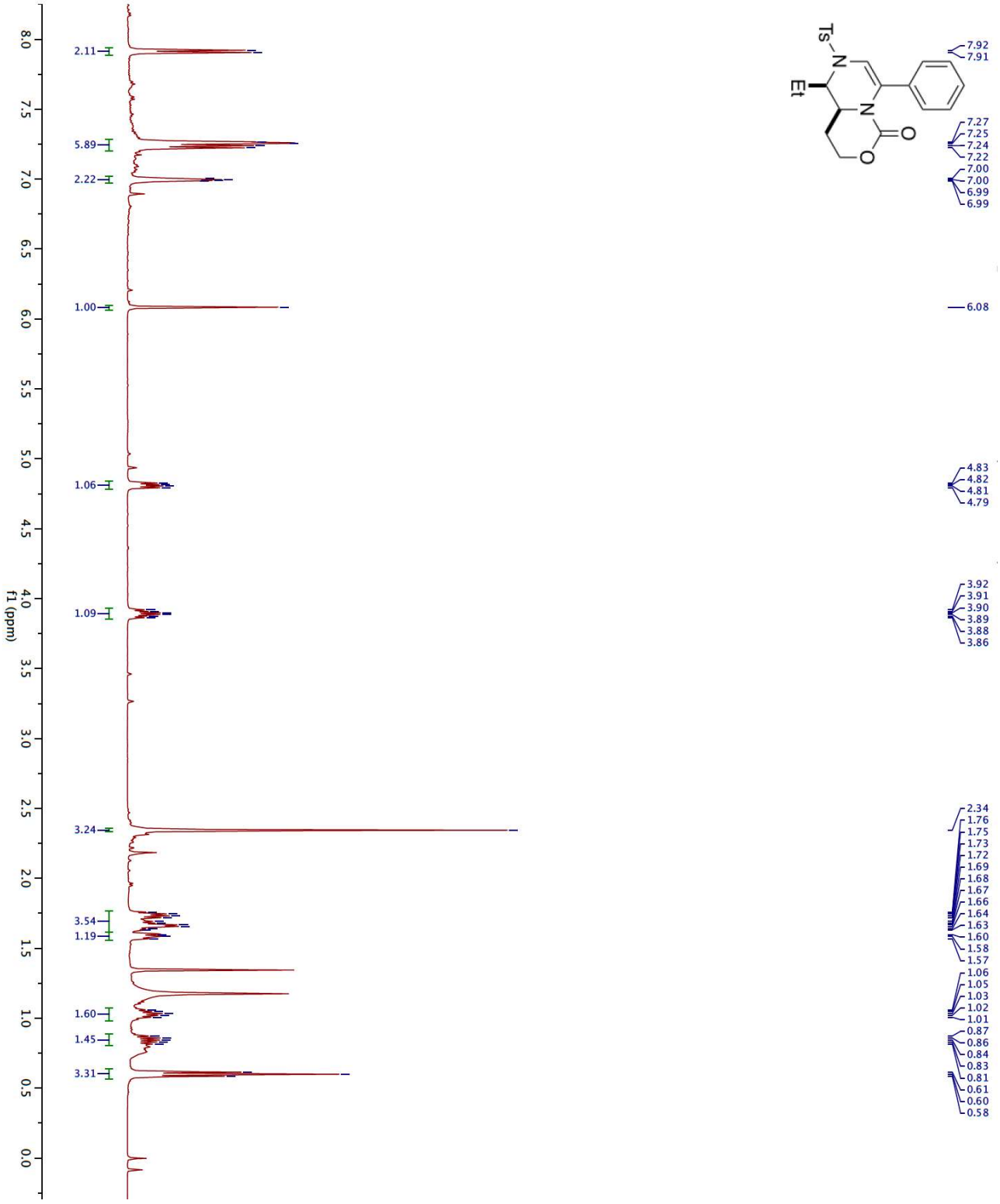
Product 4, G = -3337.500212

N	2.022950000	0.278435000	-0.292514000
C	1.192323000	-0.762562000	-0.896527000
C	-0.082513000	-0.926327000	-0.041282000
H	0.851170000	-0.375698000	-1.870582000
C	1.987117000	-2.040461000	-1.161089000
C	2.990161000	-2.321024000	-0.060632000
O	3.791327000	-1.165402000	0.204315000
C	3.226595000	0.060571000	0.343035000
O	3.830886000	0.913303000	0.960647000
H	2.506629000	-2.636793000	0.876777000
H	3.693804000	-3.112029000	-0.356175000
H	1.305892000	-2.896293000	-1.285553000
H	2.535202000	-1.915974000	-2.107883000
H	-0.712768000	-1.656260000	-0.564283000
C	0.148342000	-1.395887000	1.395703000
H	0.883831000	-0.760891000	1.912812000
H	-0.794515000	-1.354670000	1.960005000
H	0.498937000	-2.437780000	1.416349000
N	-0.796807000	0.366666000	-0.060969000
C	-0.006220000	1.567592000	-0.091807000
C	1.363373000	1.540936000	-0.192267000
C	2.194296000	2.790310000	-0.353515000
H	1.669384000	3.550249000	-0.952989000
H	2.478884000	3.250766000	0.606885000

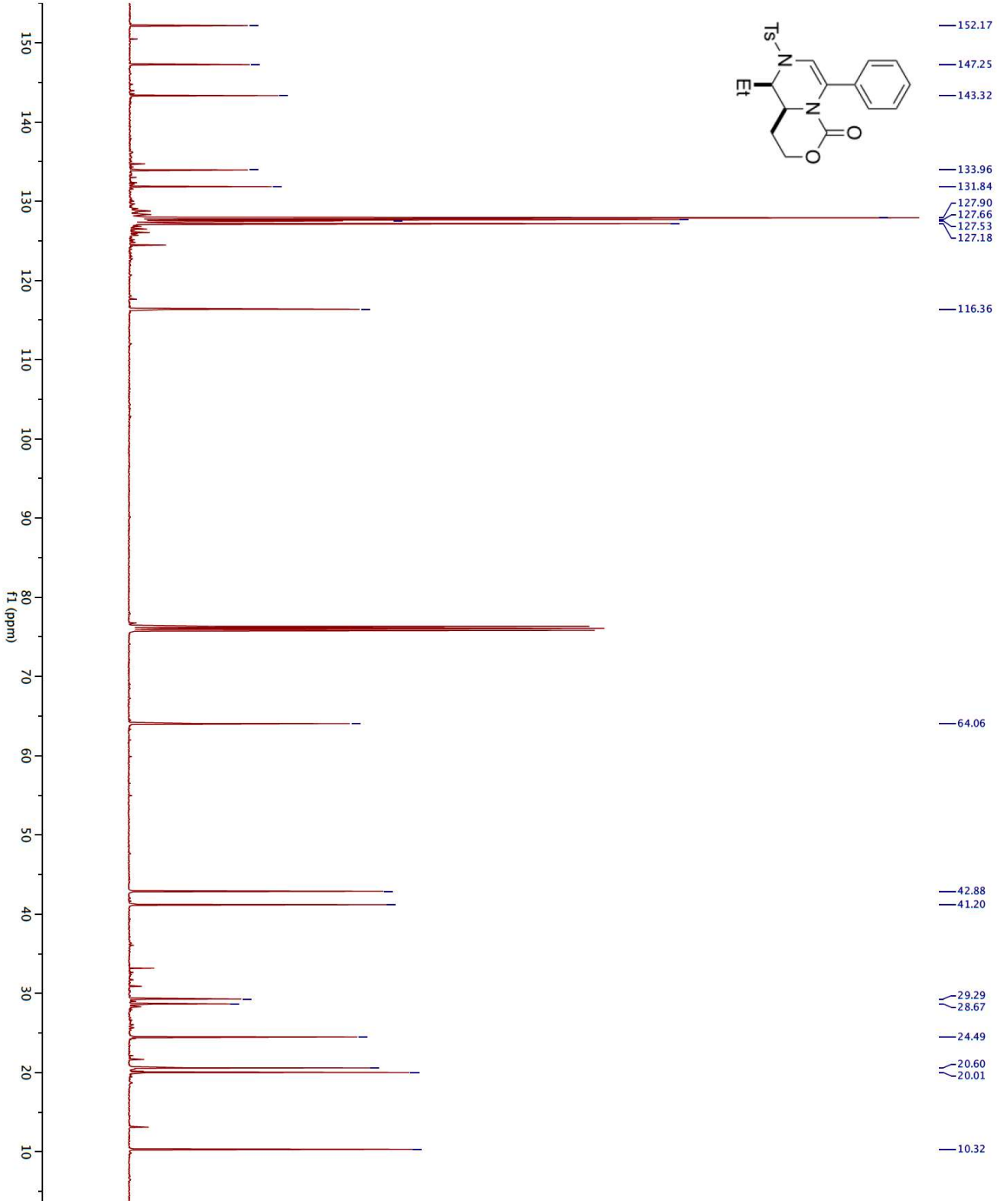
H	3.130257000	2.552751000	-0.876928000
C	-0.755197000	2.813820000	-0.034634000
H	-0.190887000	3.744501000	-0.010900000
C	-2.172398000	0.446018000	-0.012889000
C	-2.864891000	1.618227000	0.018548000
H	-3.952547000	1.619006000	0.057071000
C	-2.110428000	2.842075000	0.017729000
H	-2.641896000	3.795283000	0.071034000
Br	-3.185298000	-1.178995000	0.019909000

XI. NMR Spectra

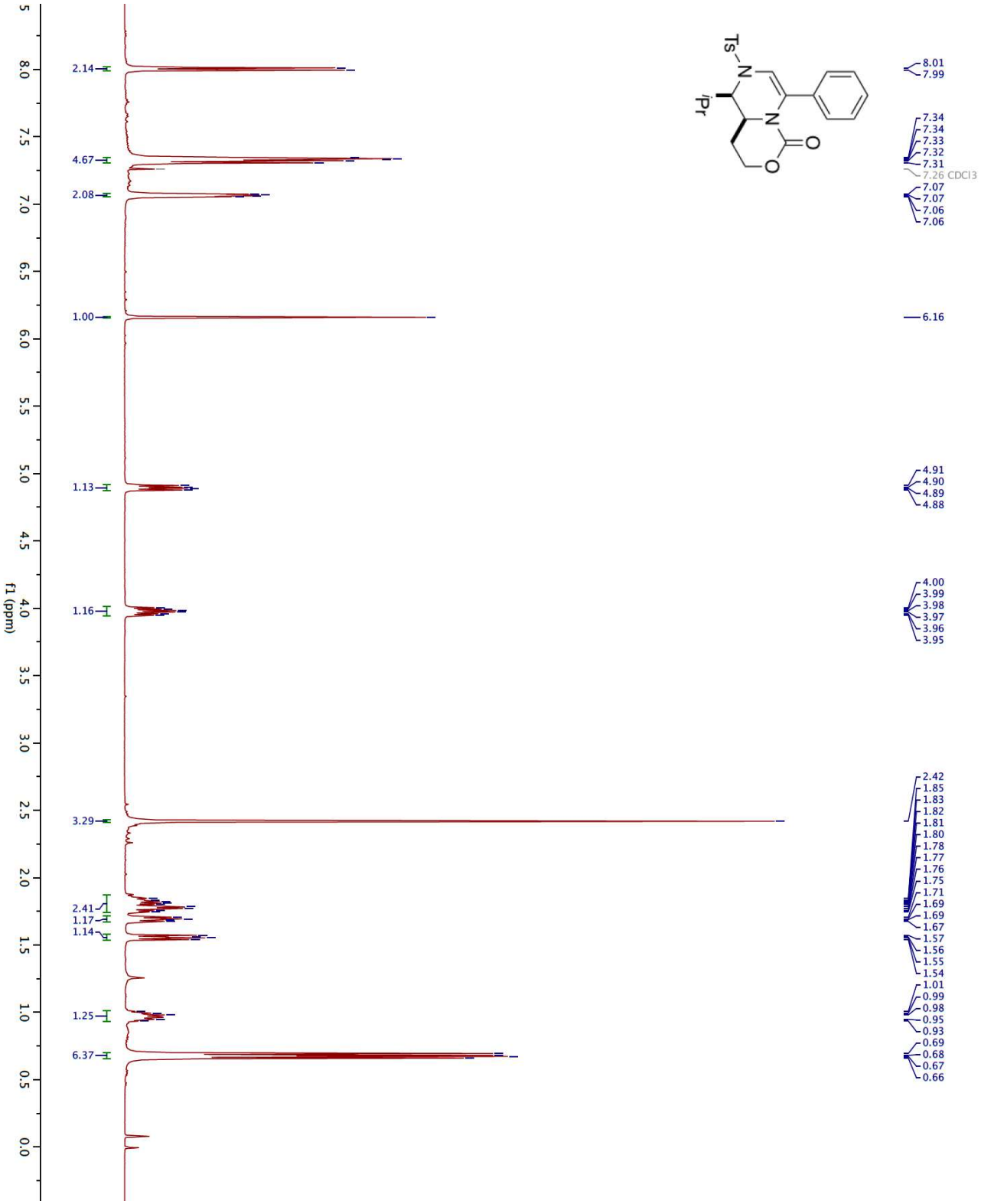
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6ab**



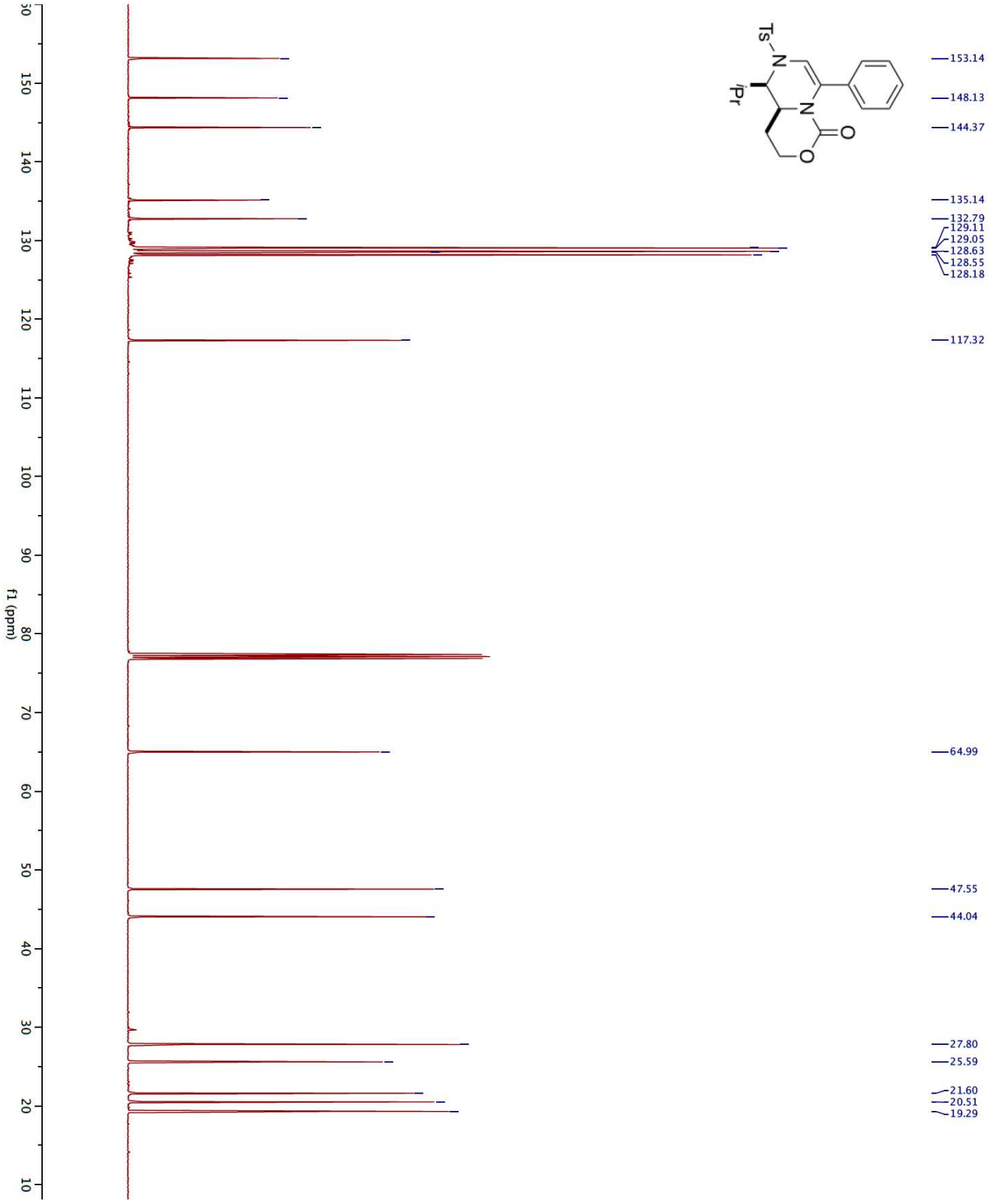
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6ab**



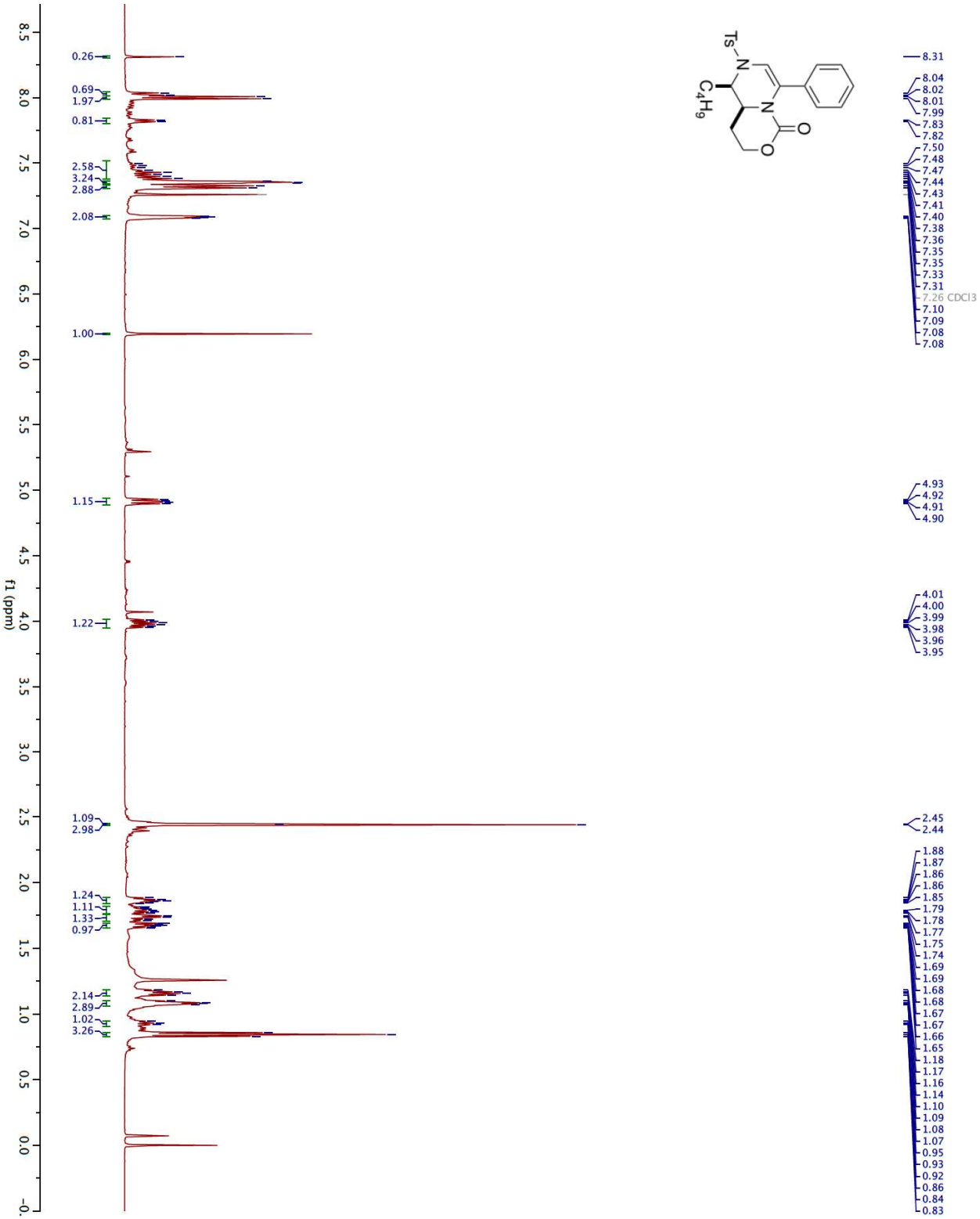
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6bb**



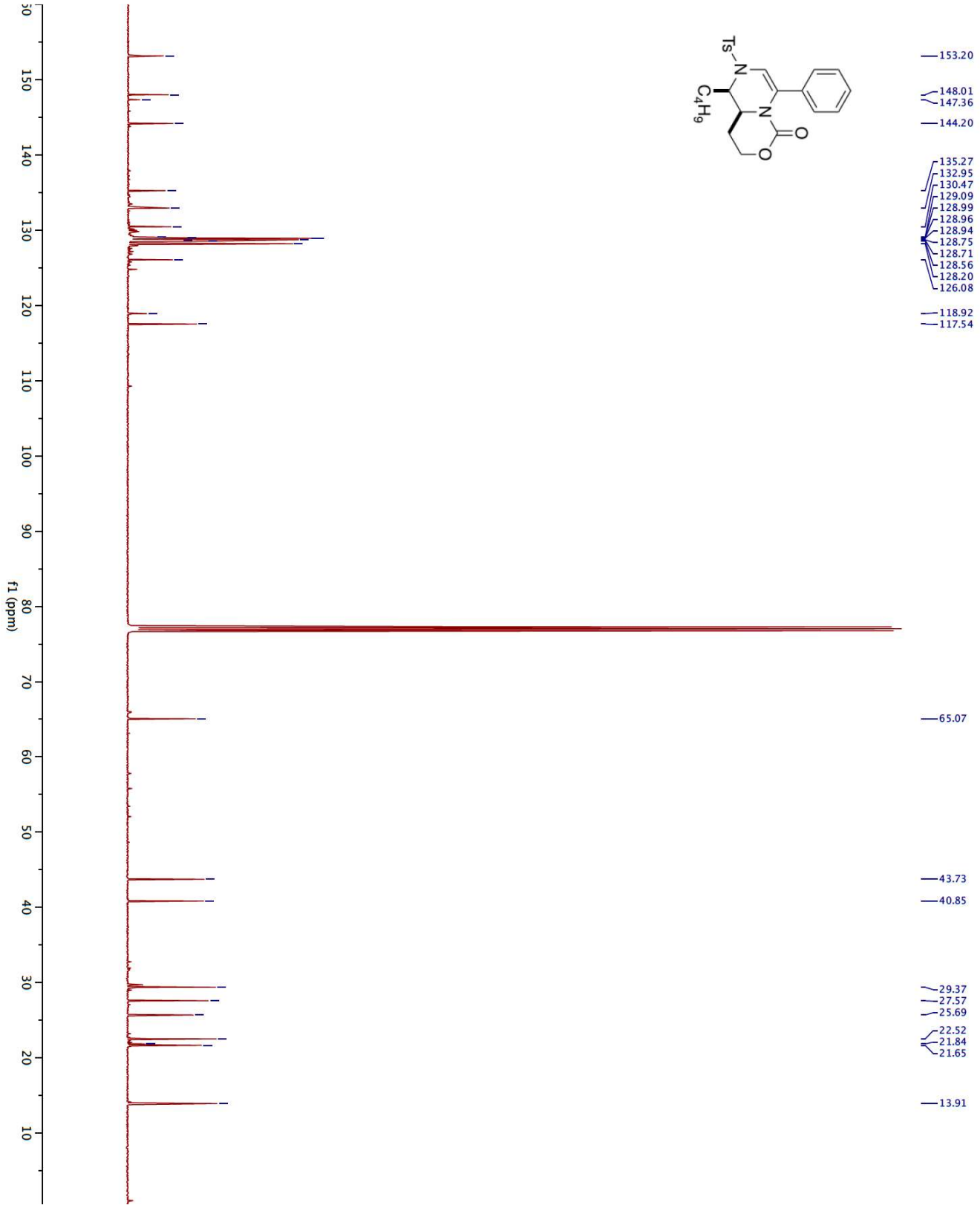
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6bb**



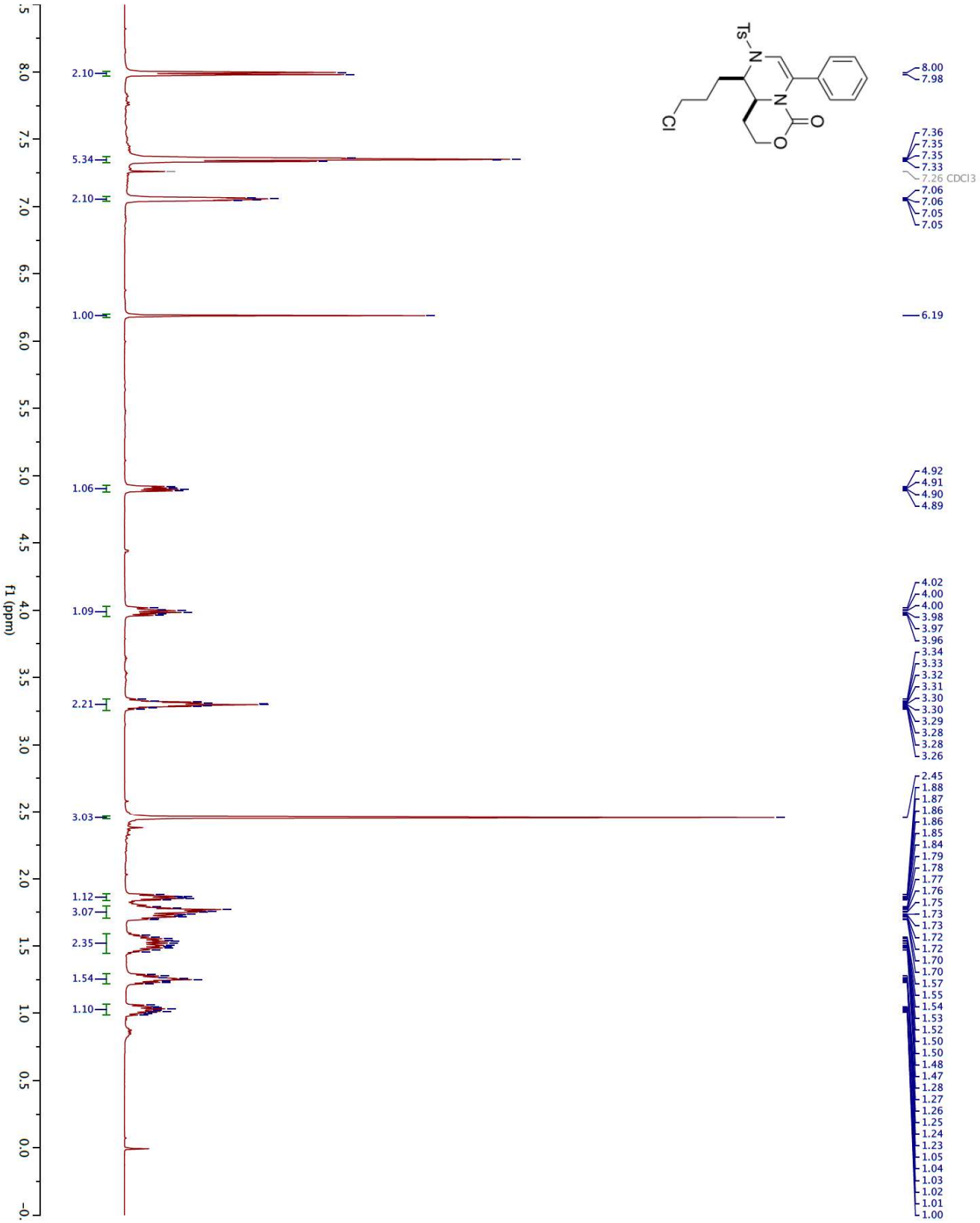
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6cb (+ triazole 5b impurity)**



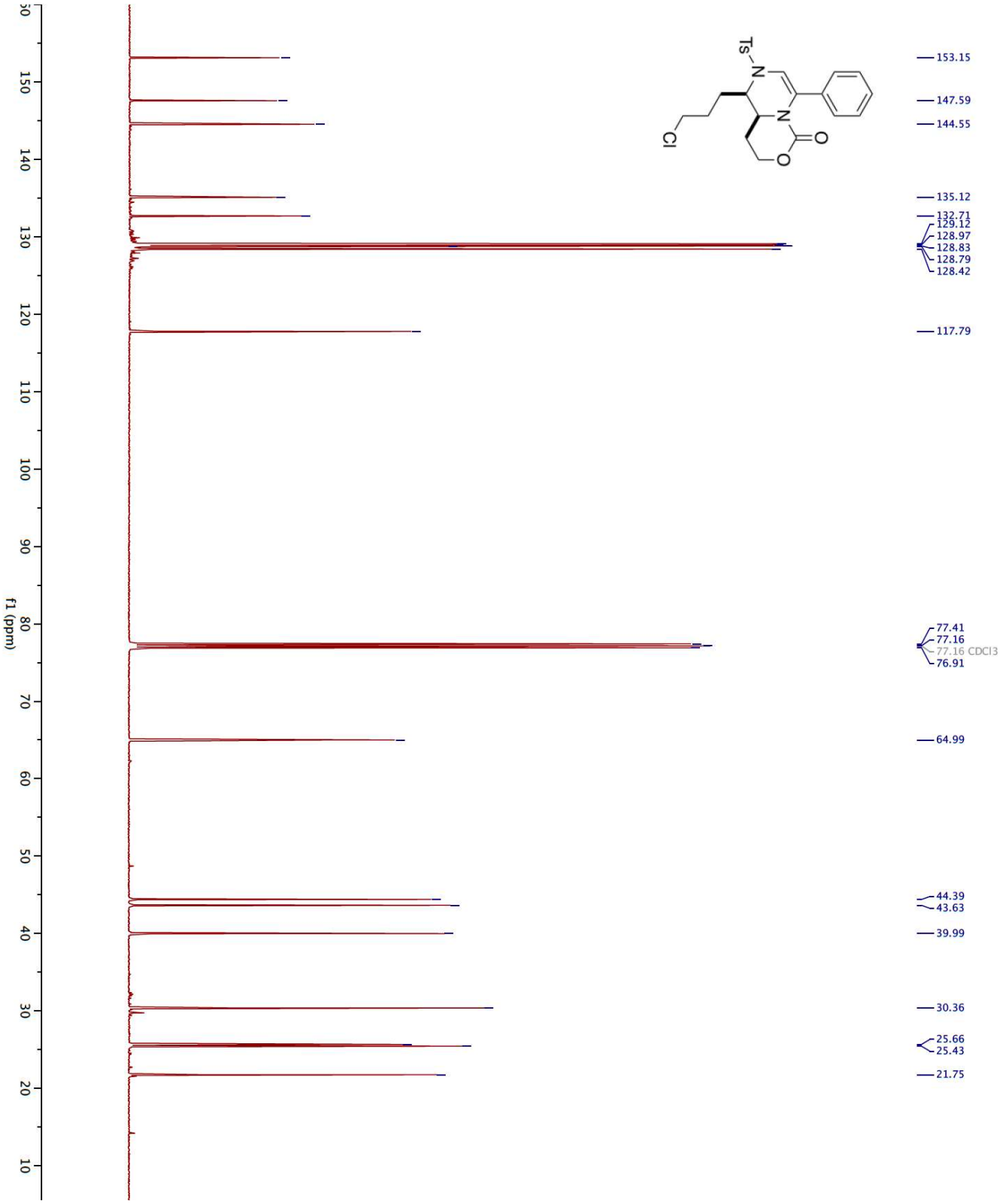
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6cb (+ triazole 5b impurity)**



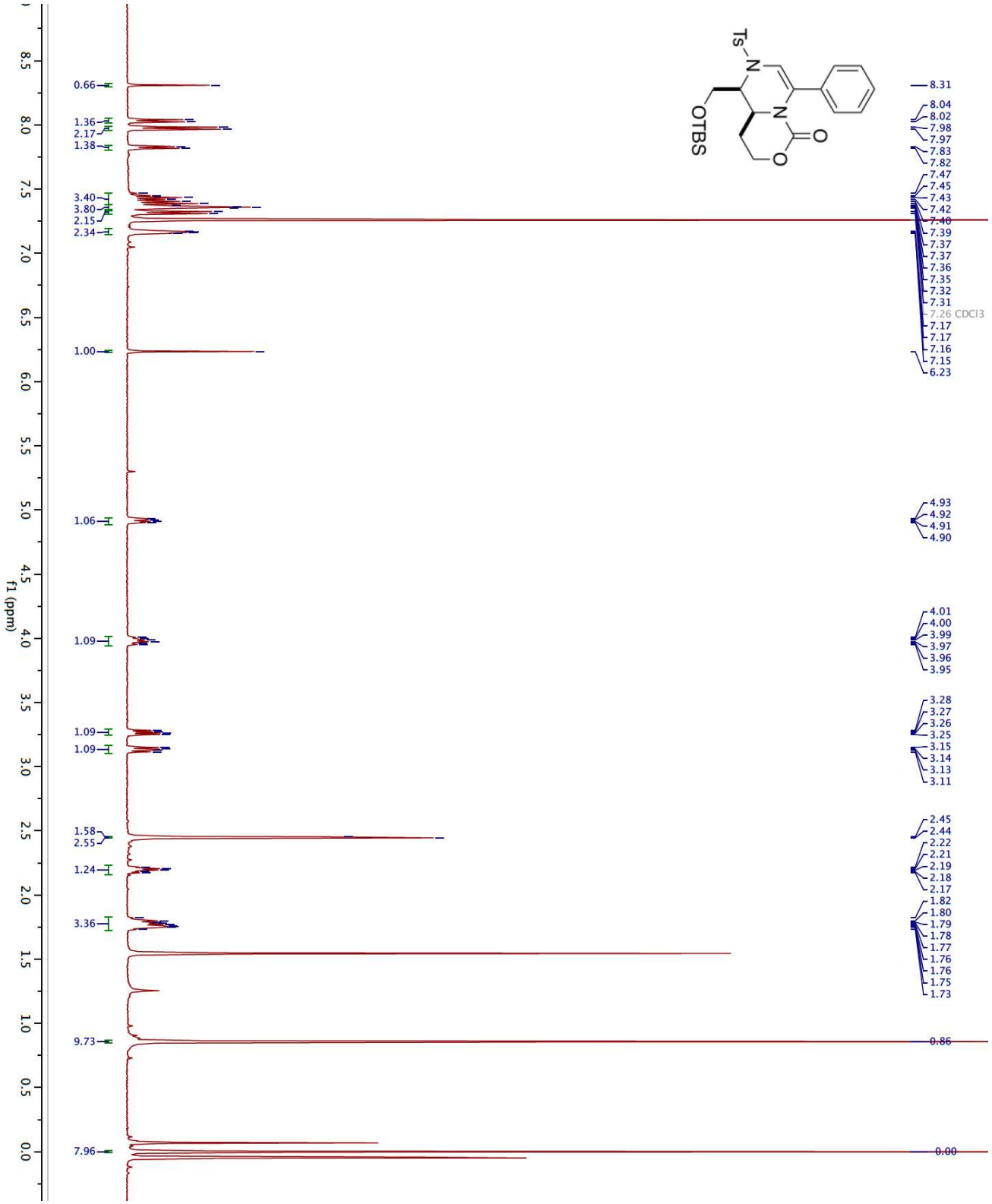
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6db**



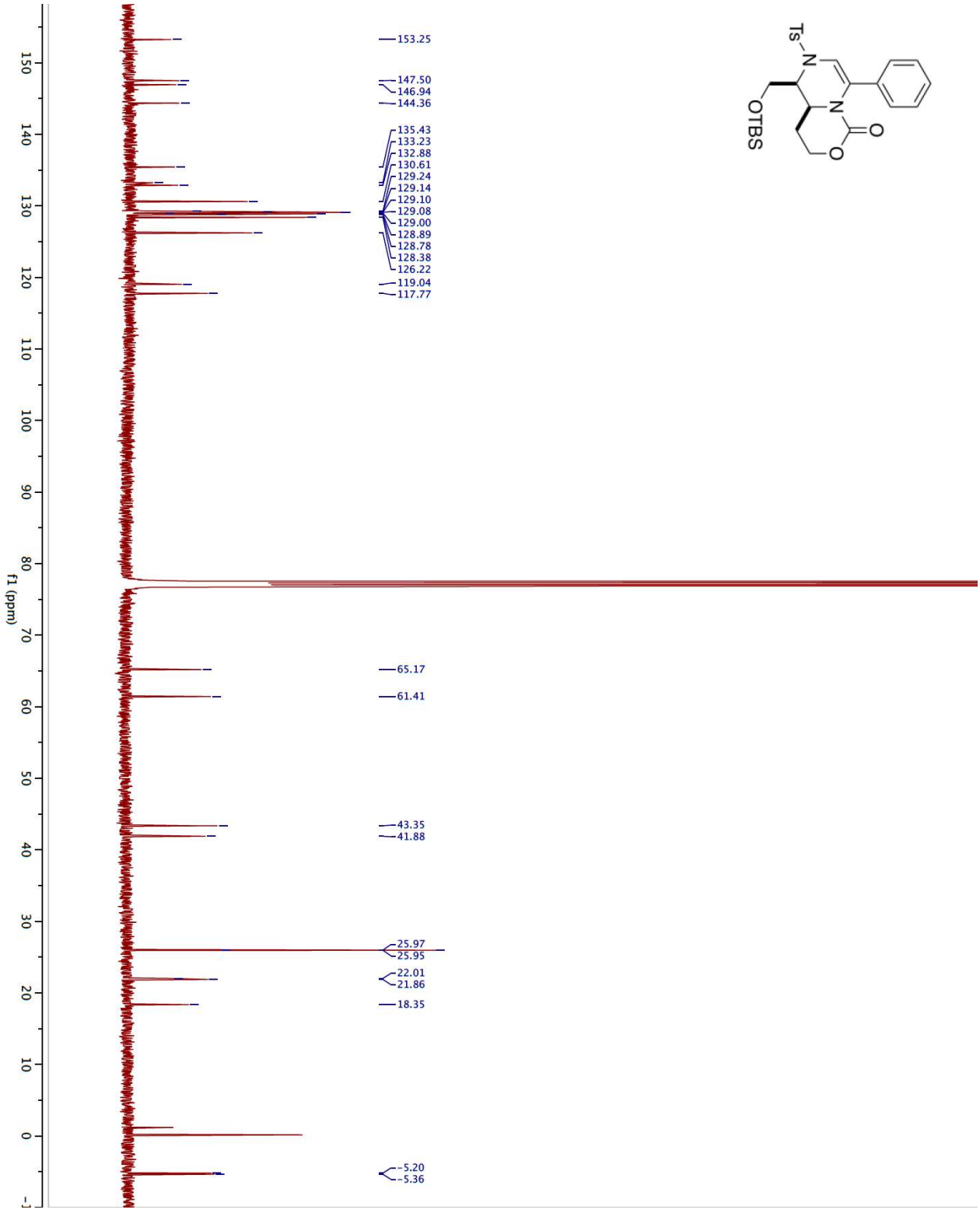
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6db**



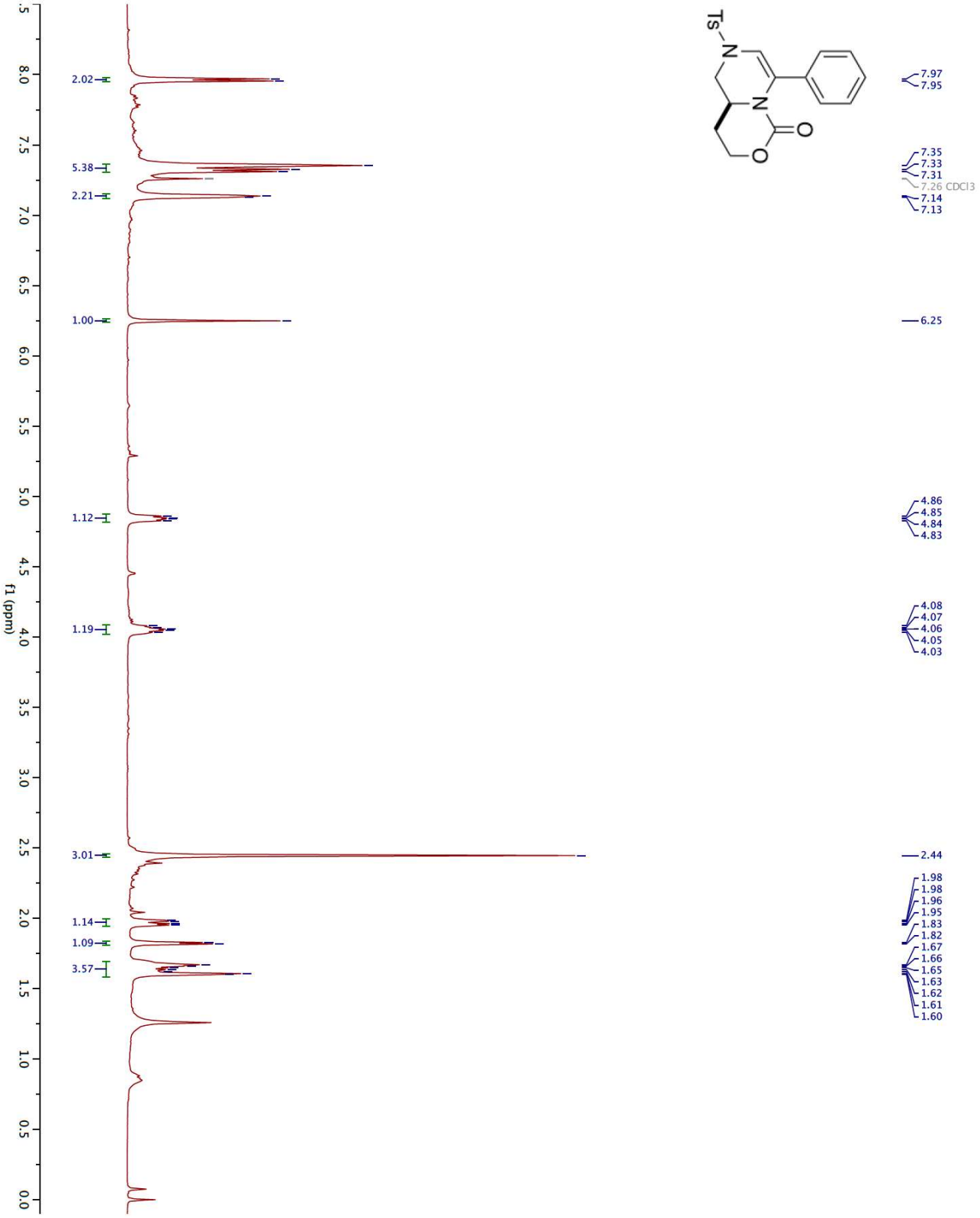
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6eb (+ triazole 5b impurity)**



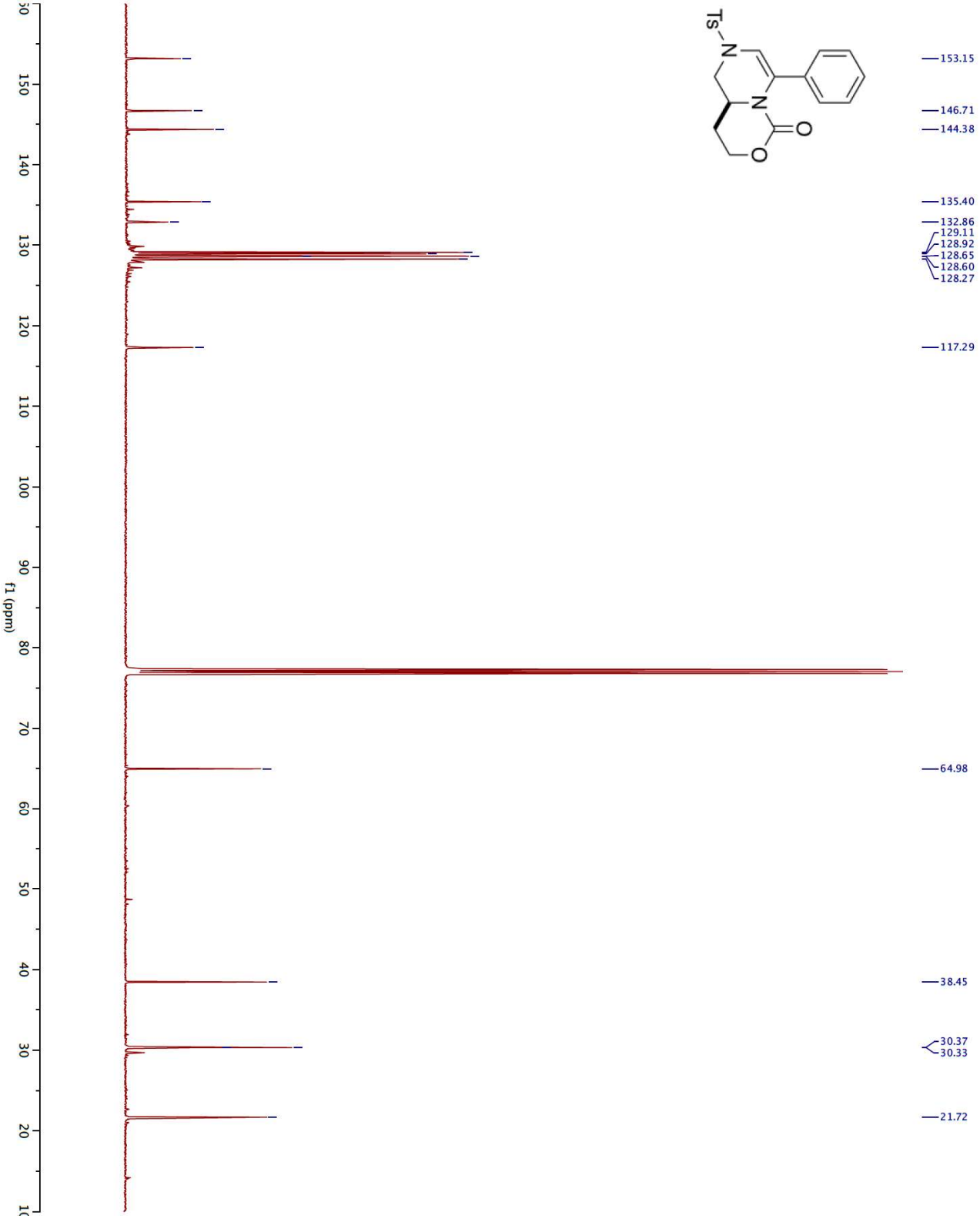
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6eb (+ triazole 5b impurity)**



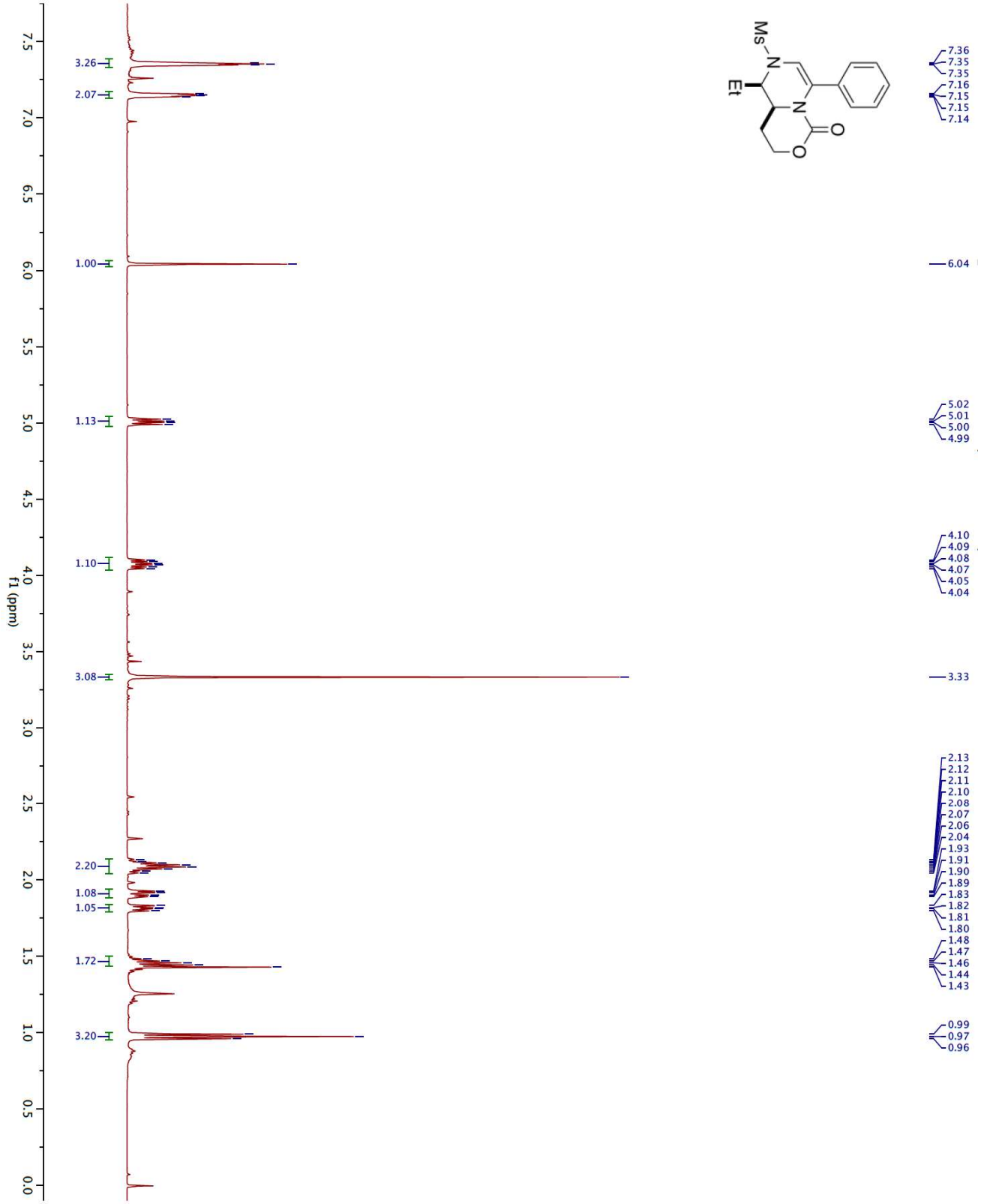
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6fb**



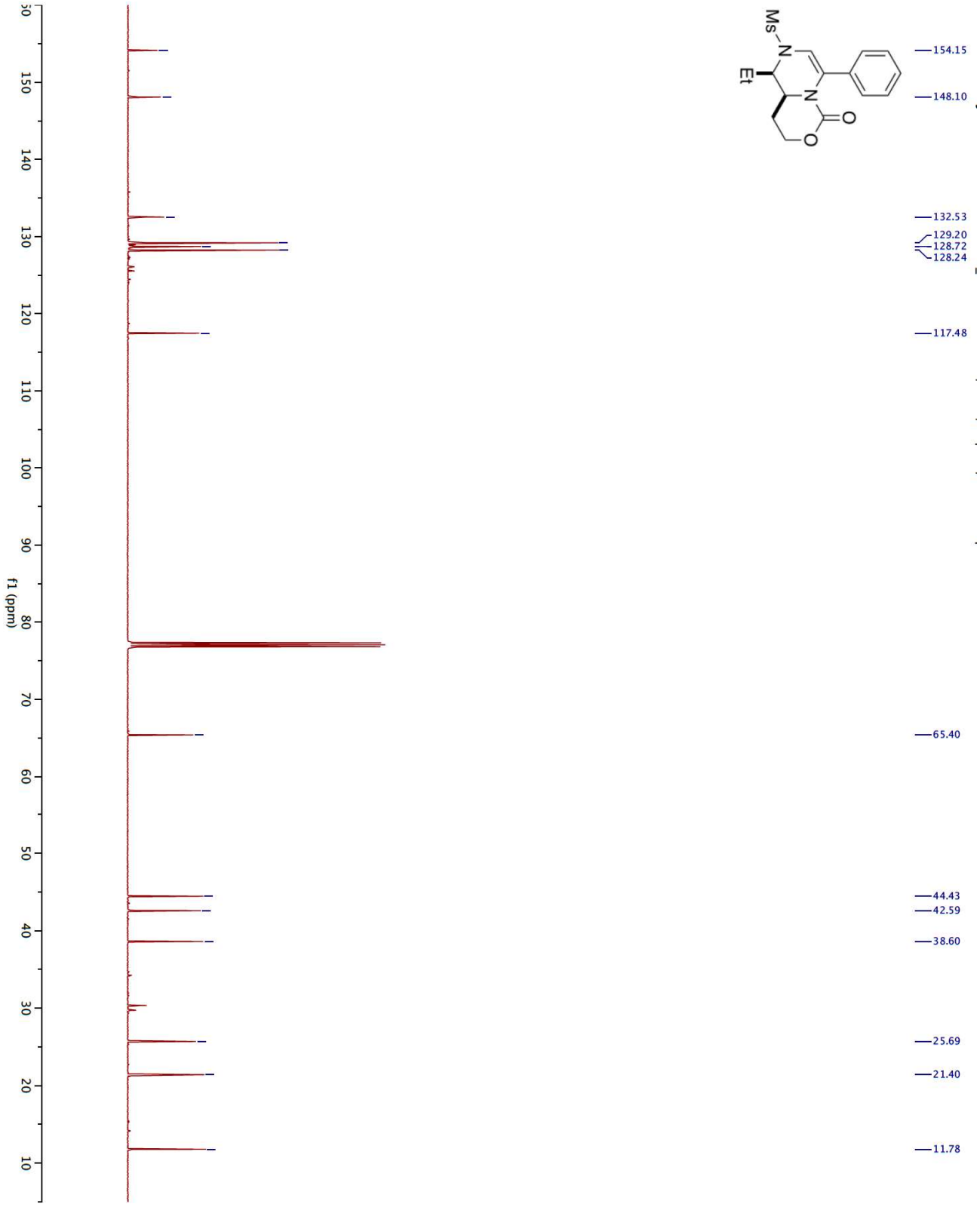
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6fb**



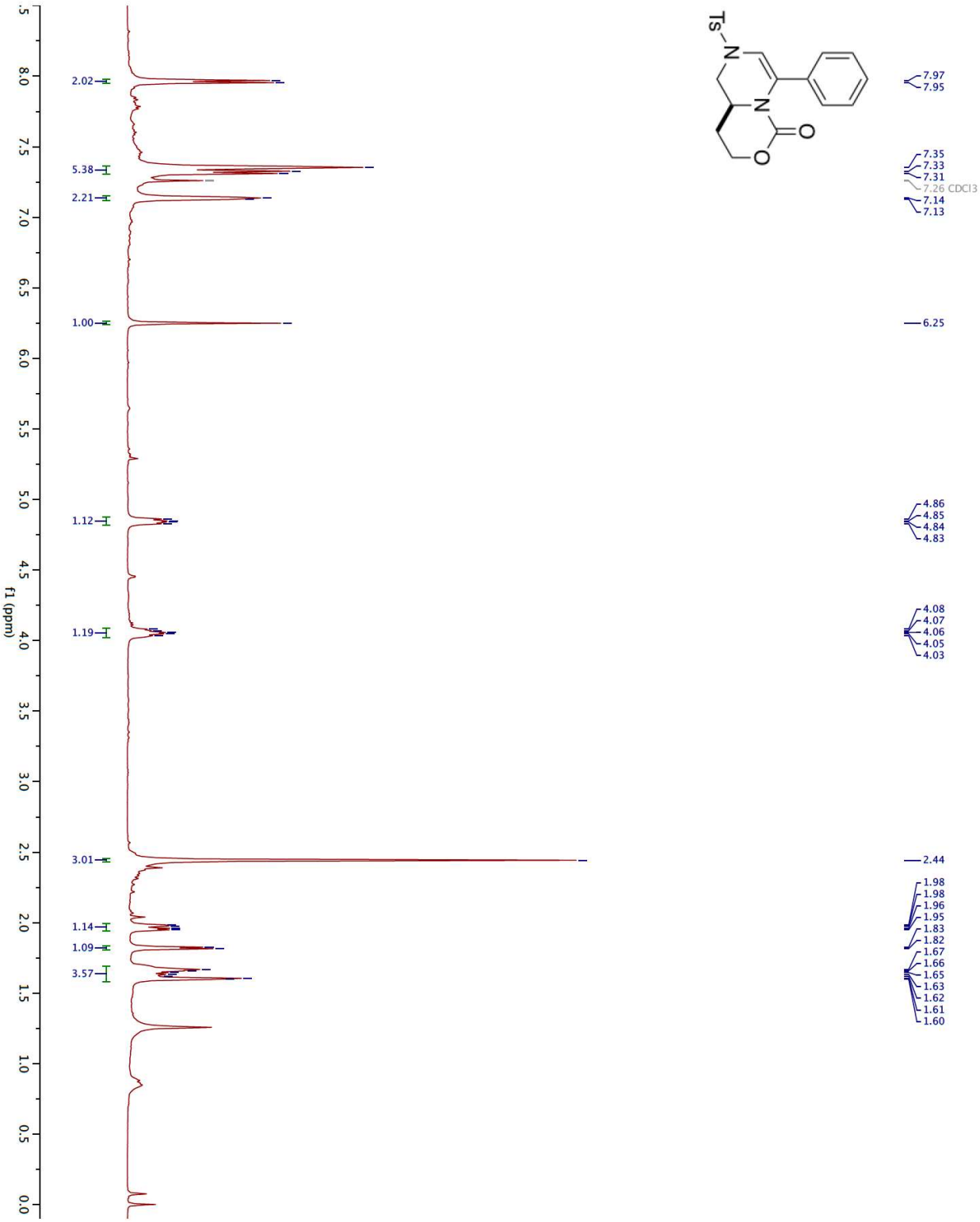
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6aa**



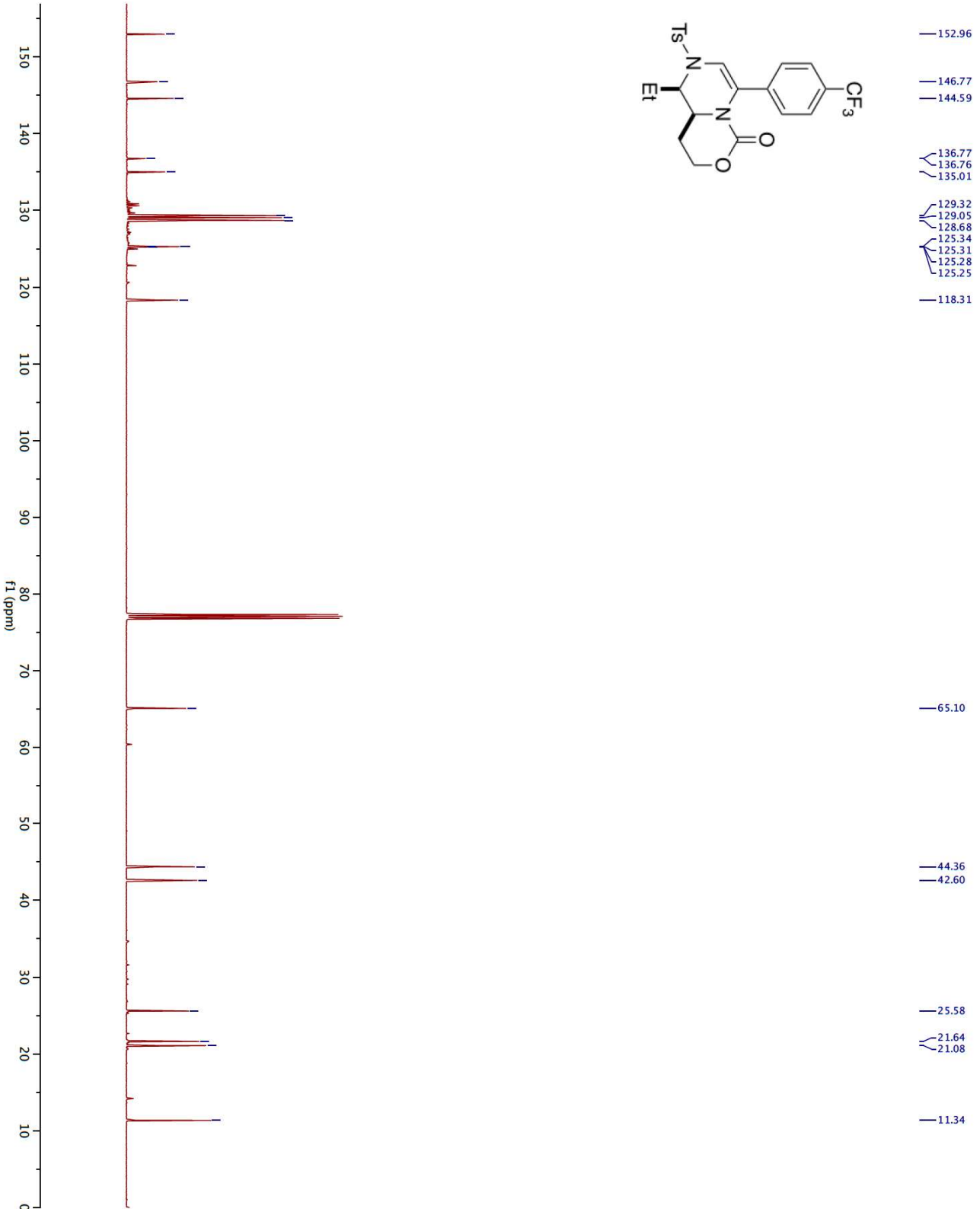
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6aa**



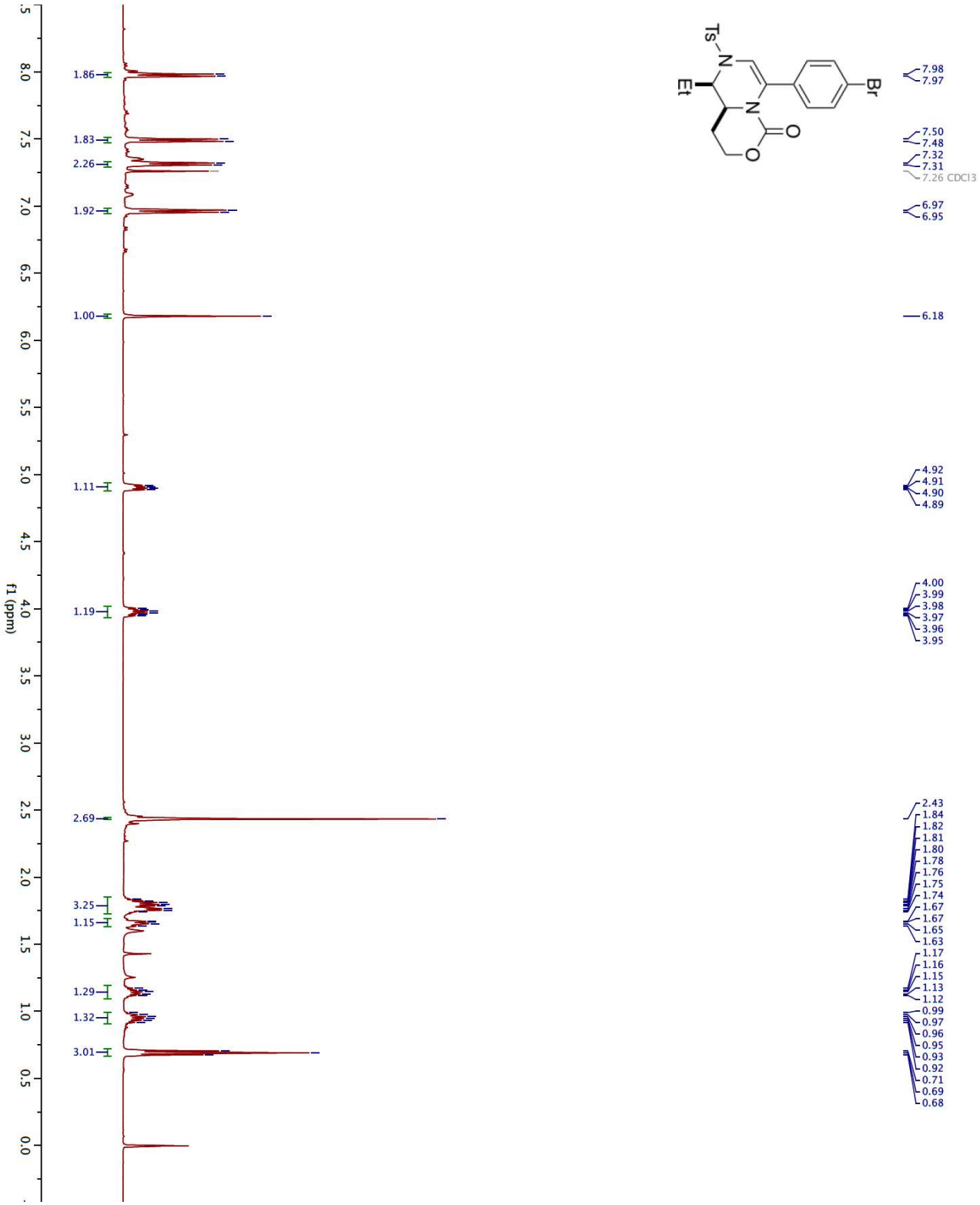
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6ac**



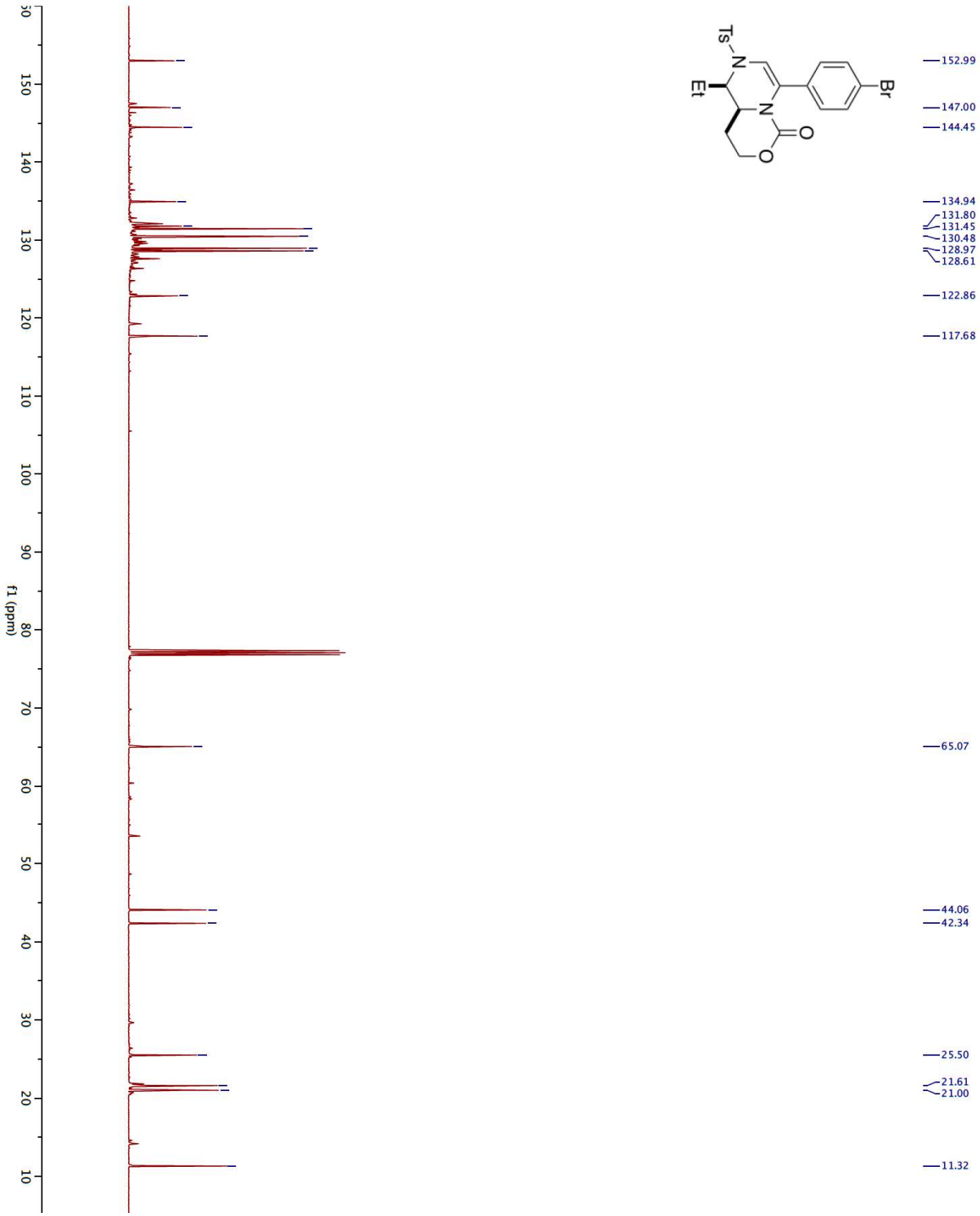
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6ac**



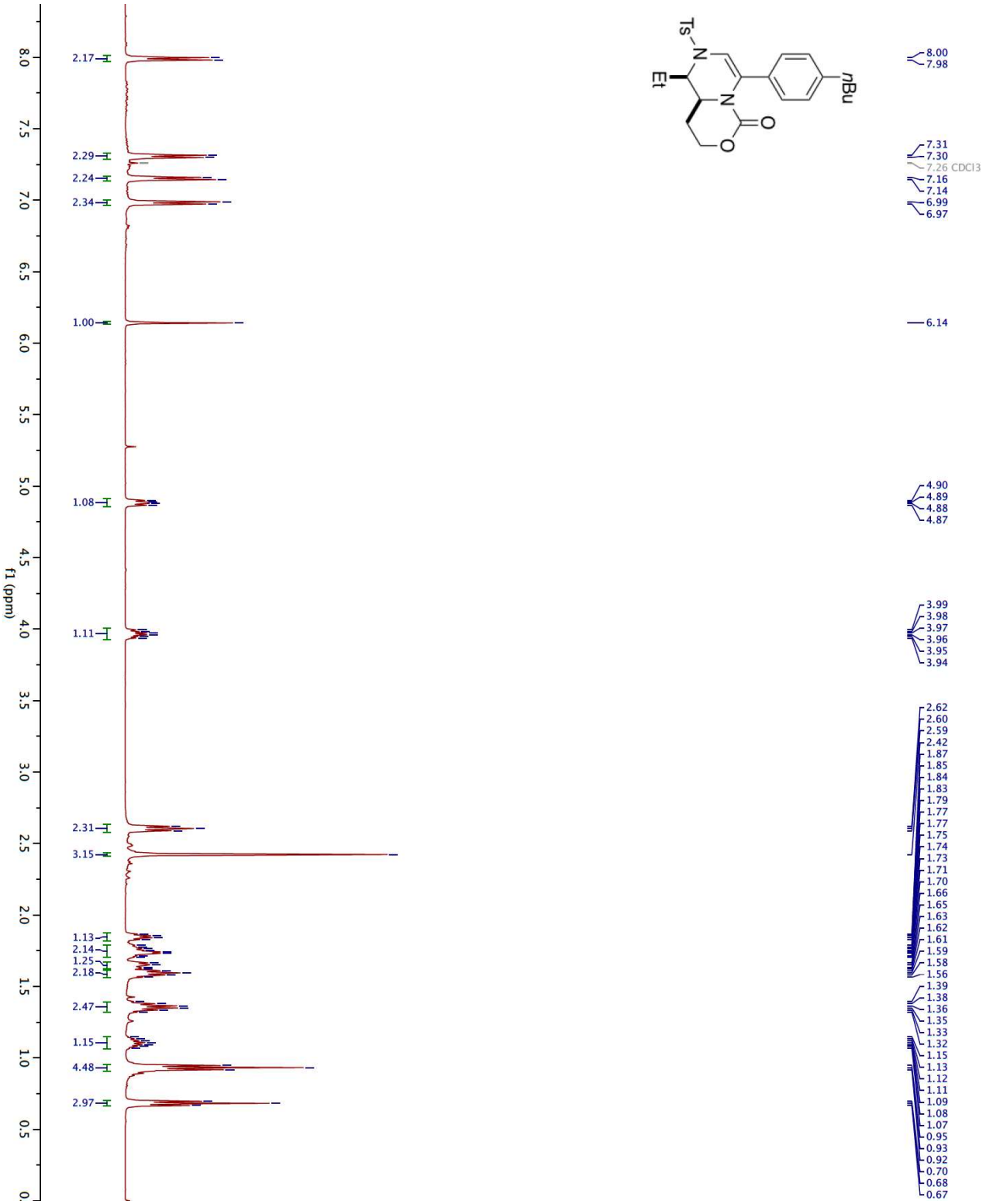
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6ad**



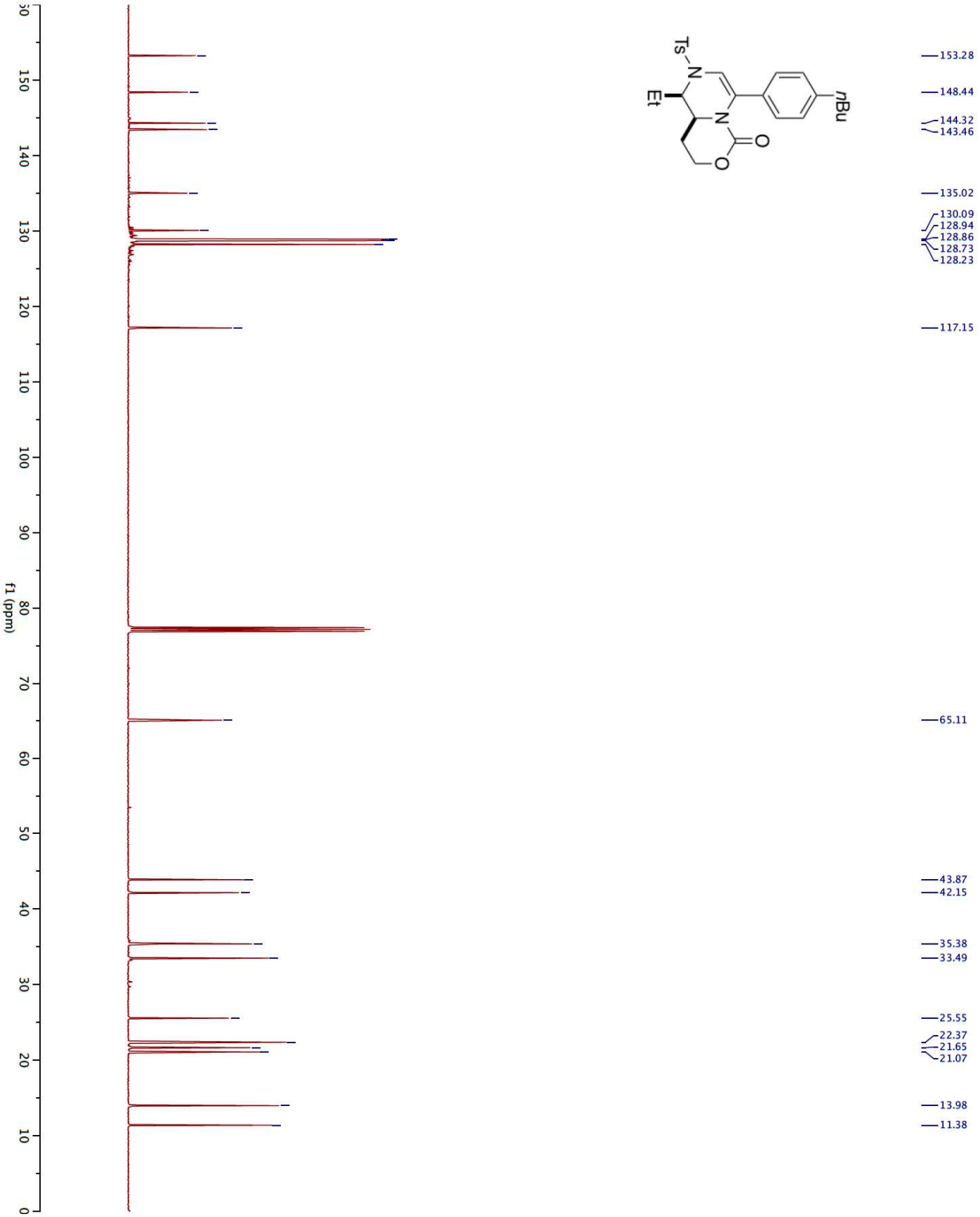
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6ad**



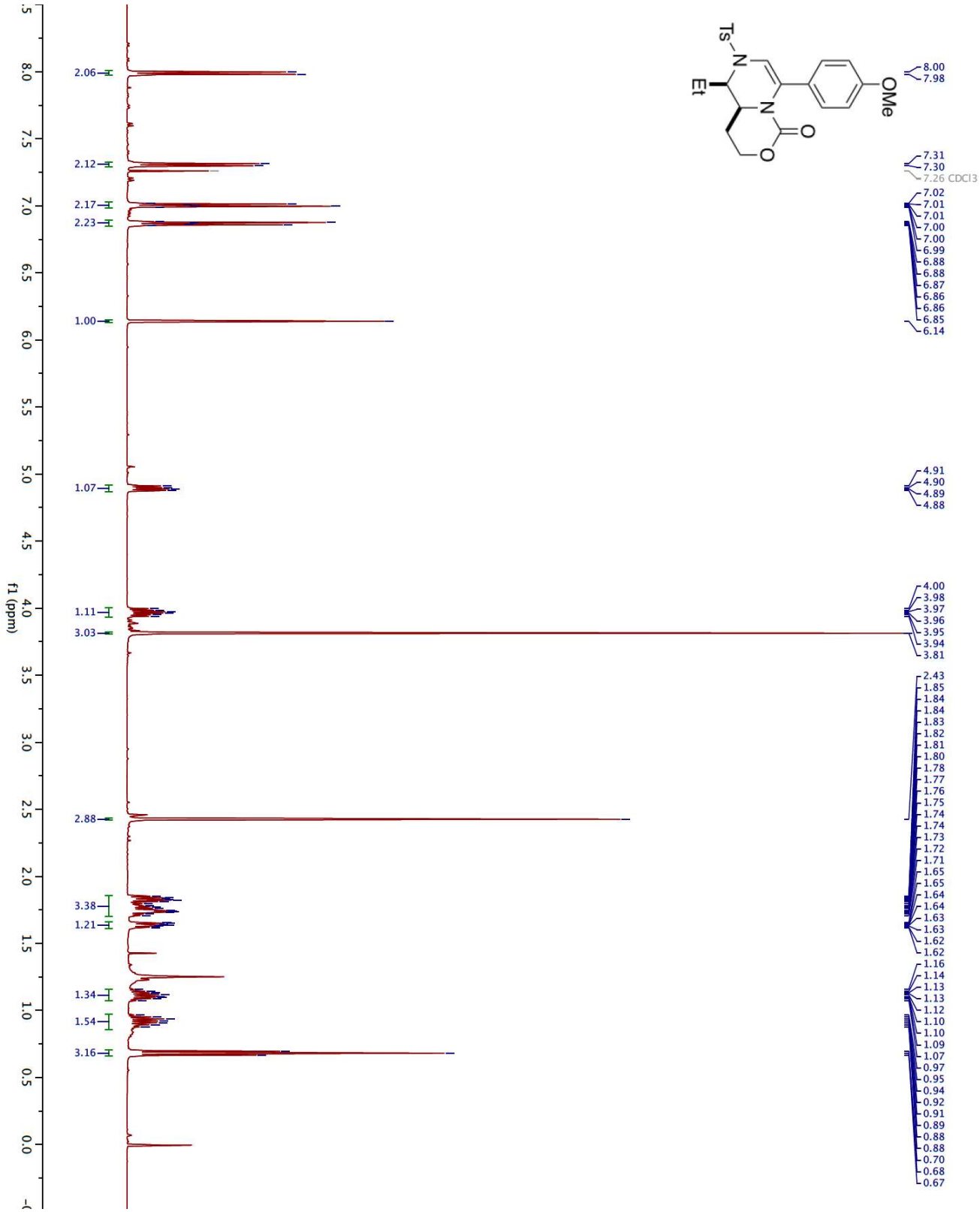
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6ae**



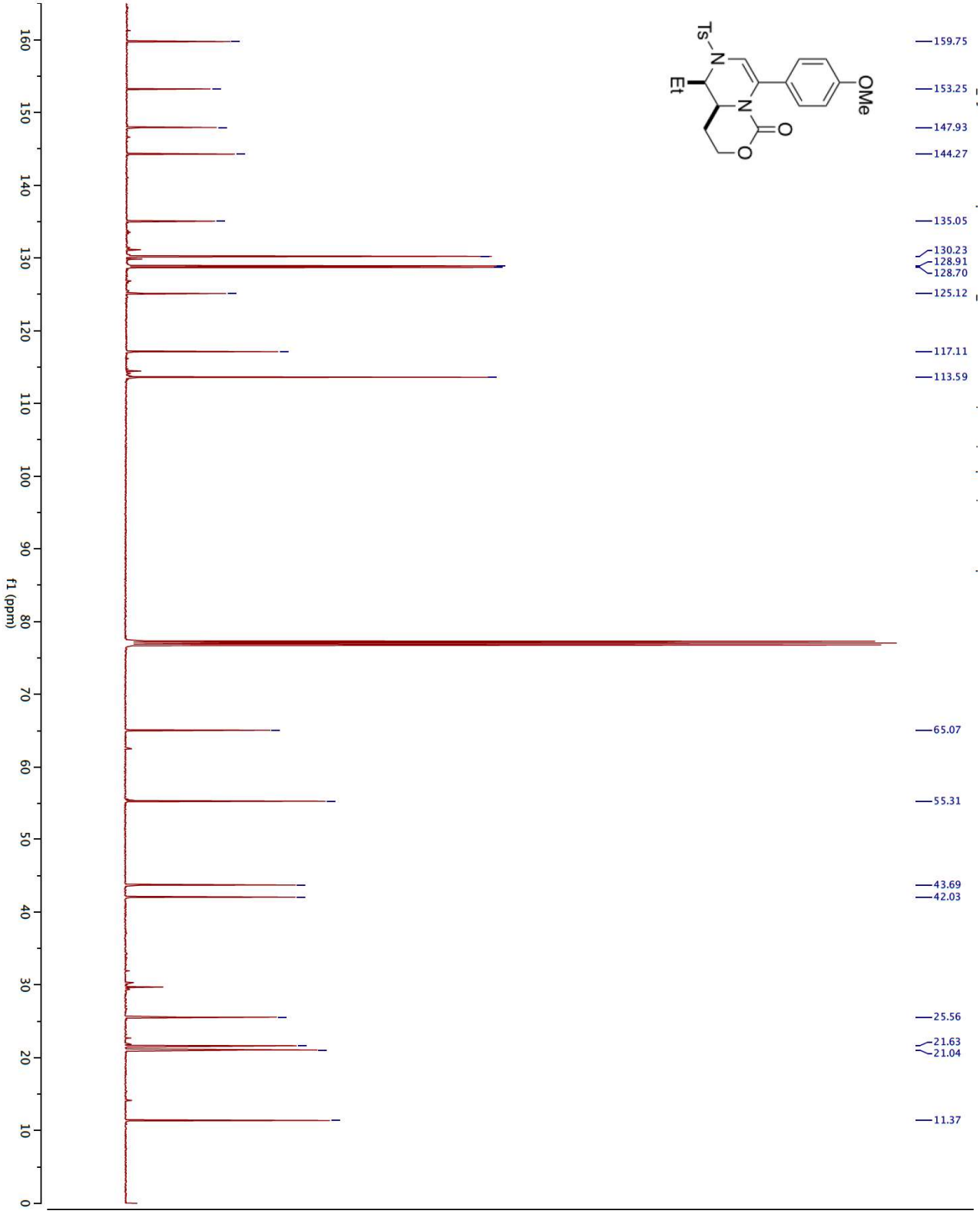
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6ae**



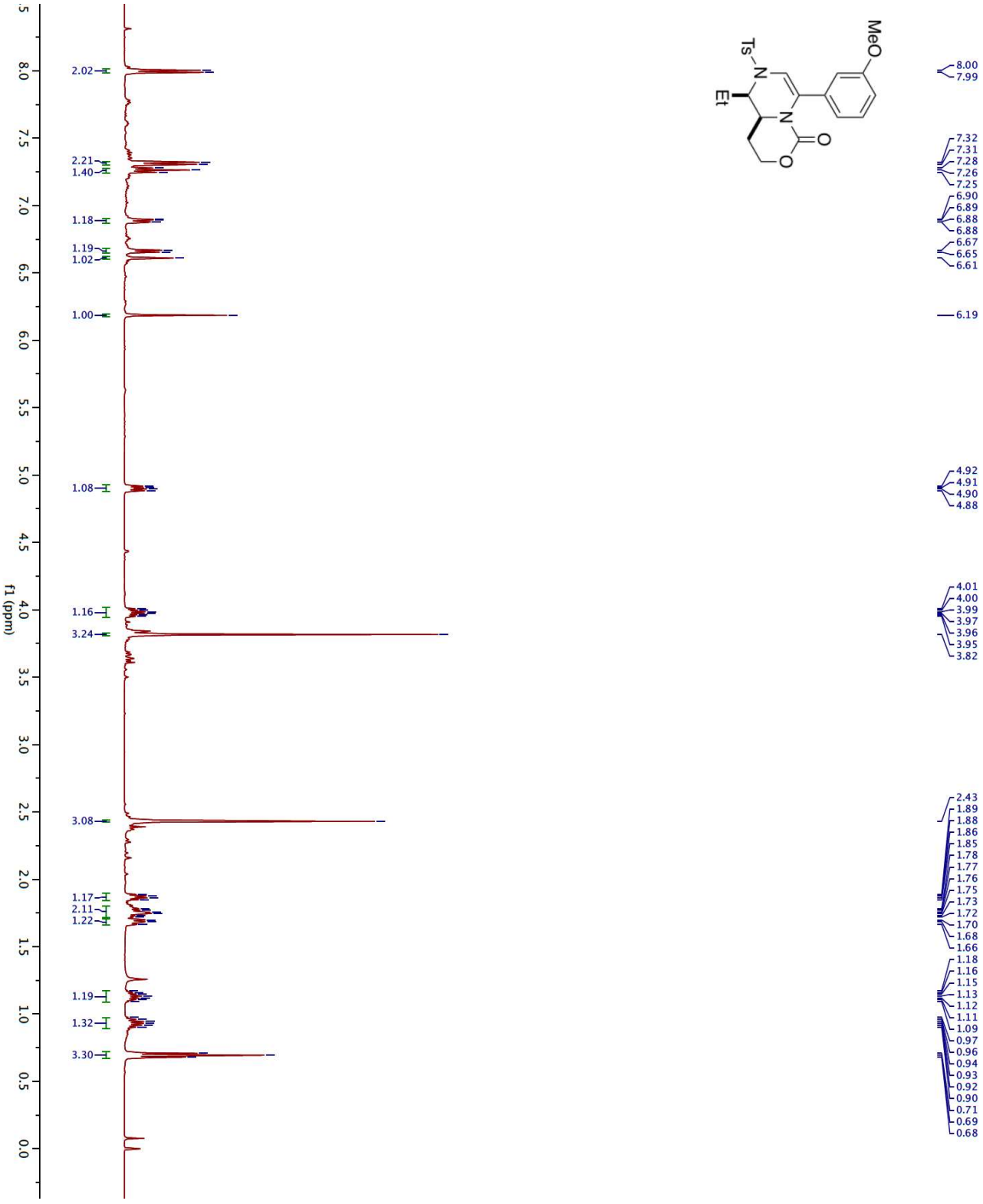
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6af**



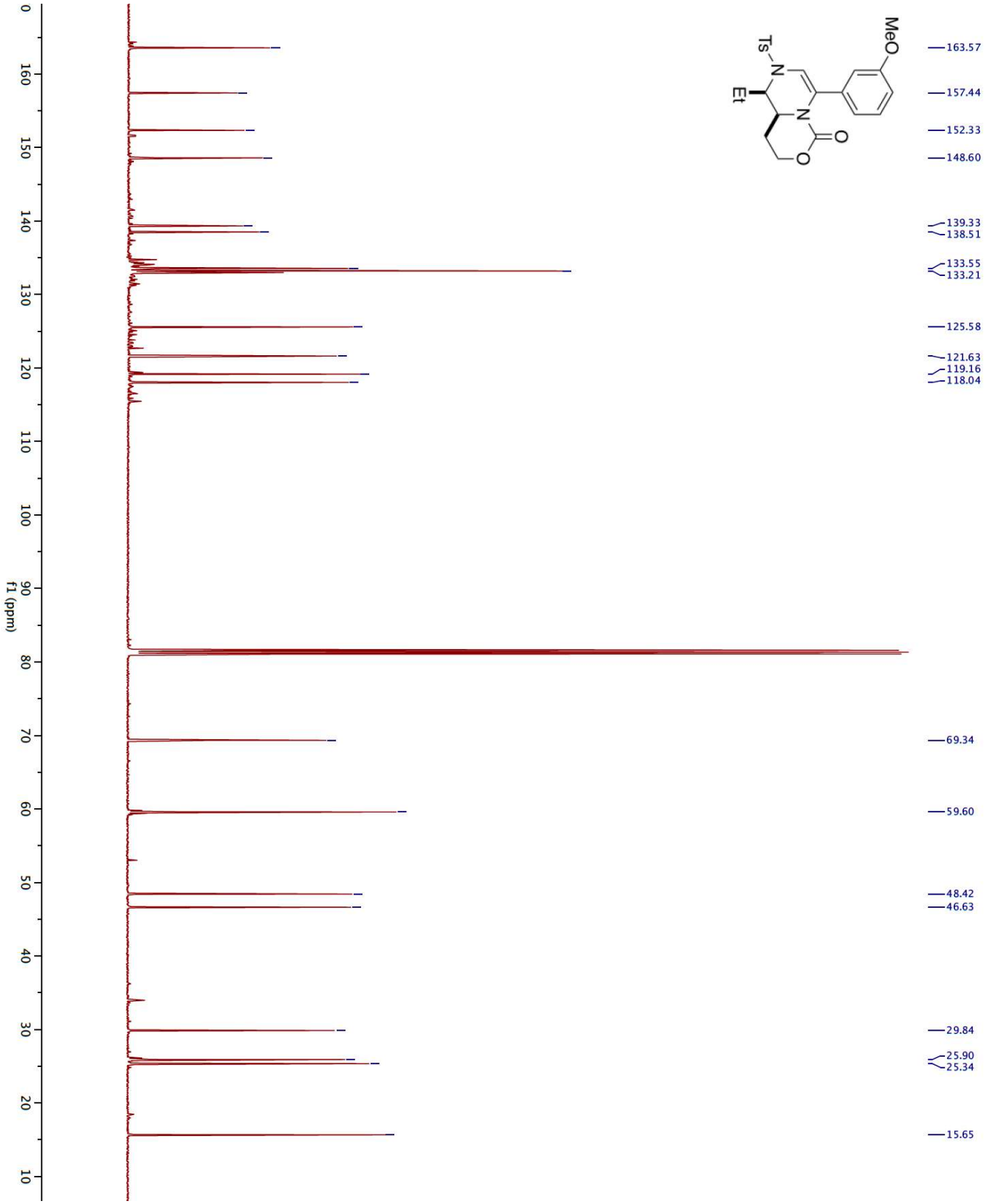
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6af**



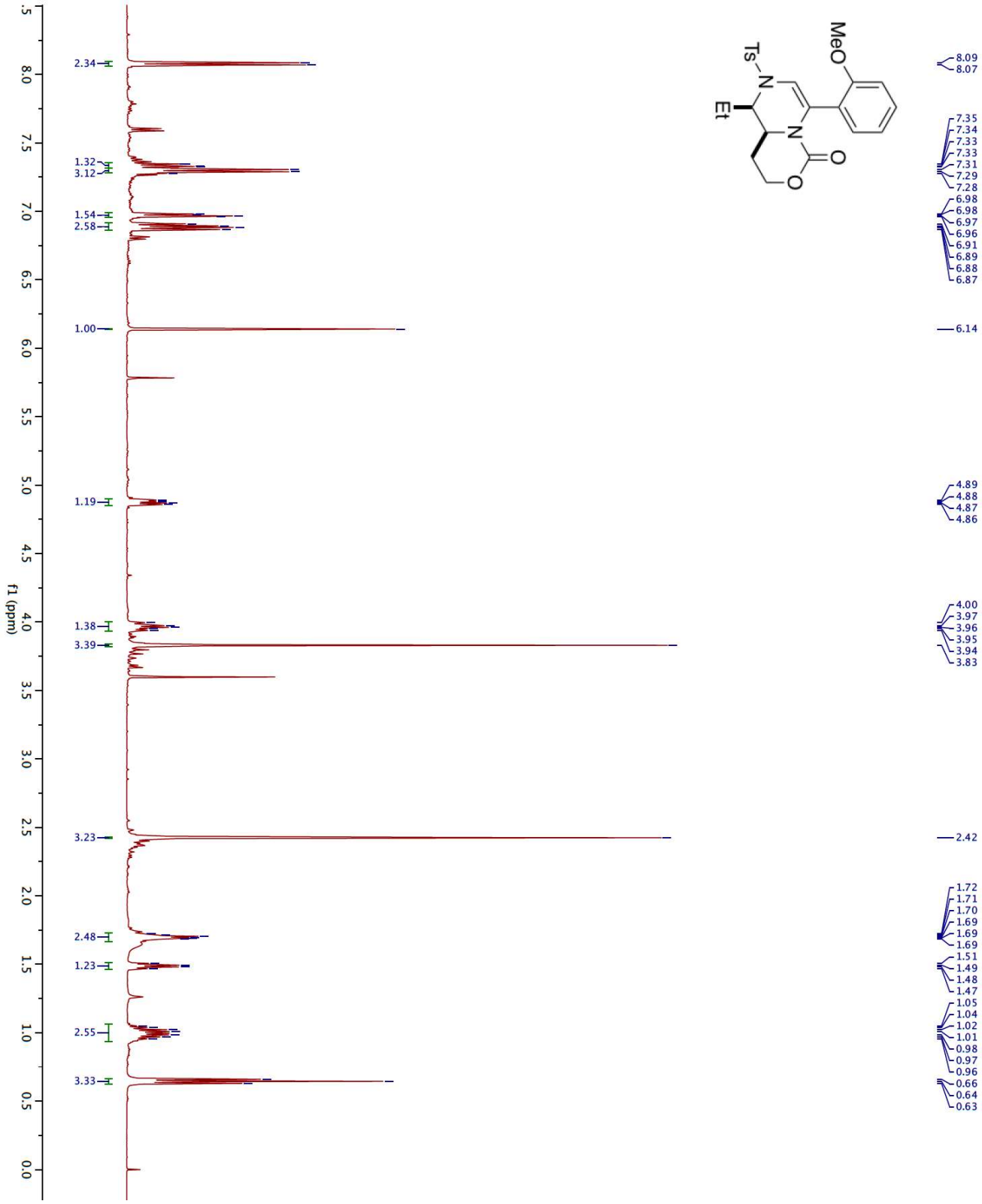
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6ag**



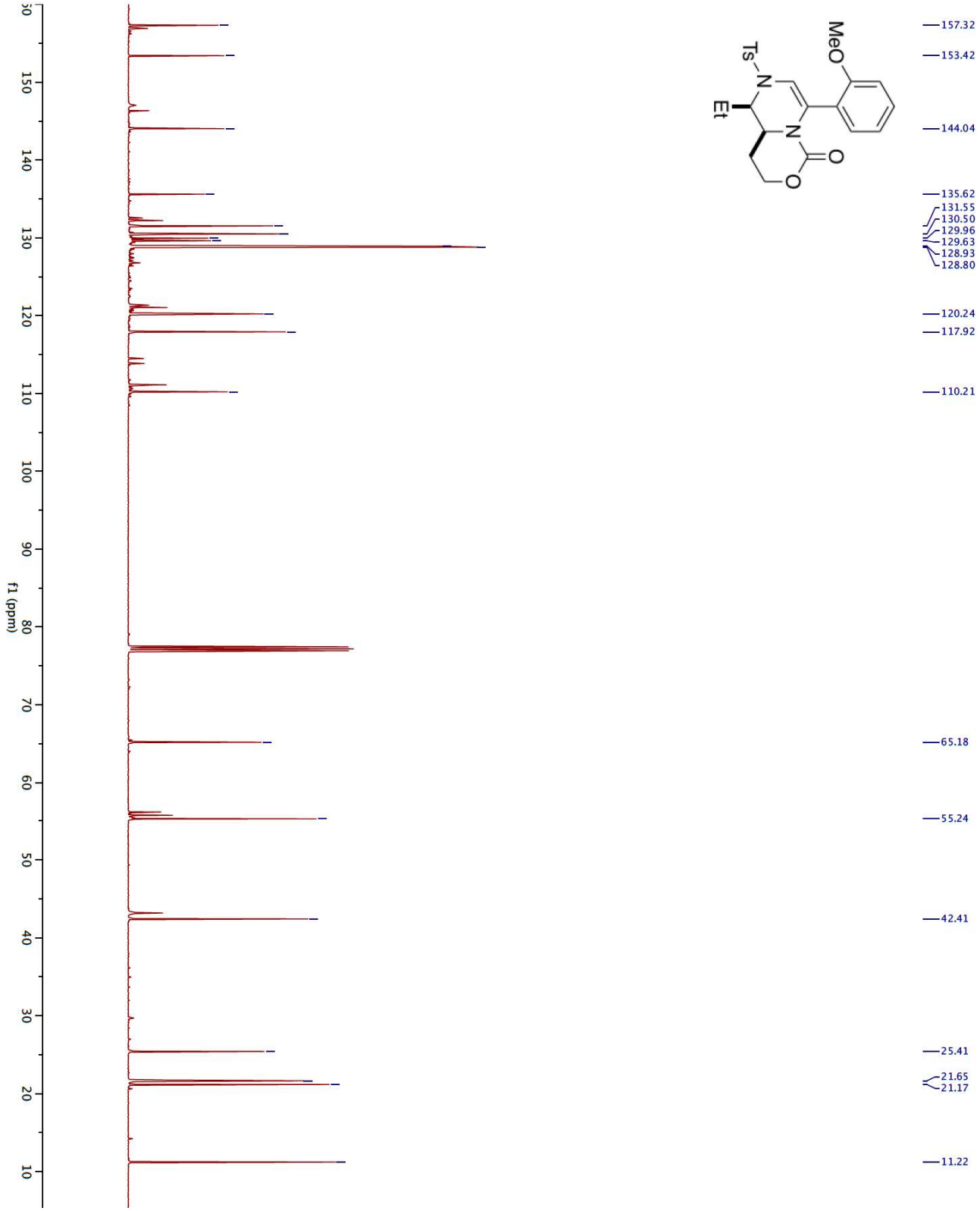
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6ag**



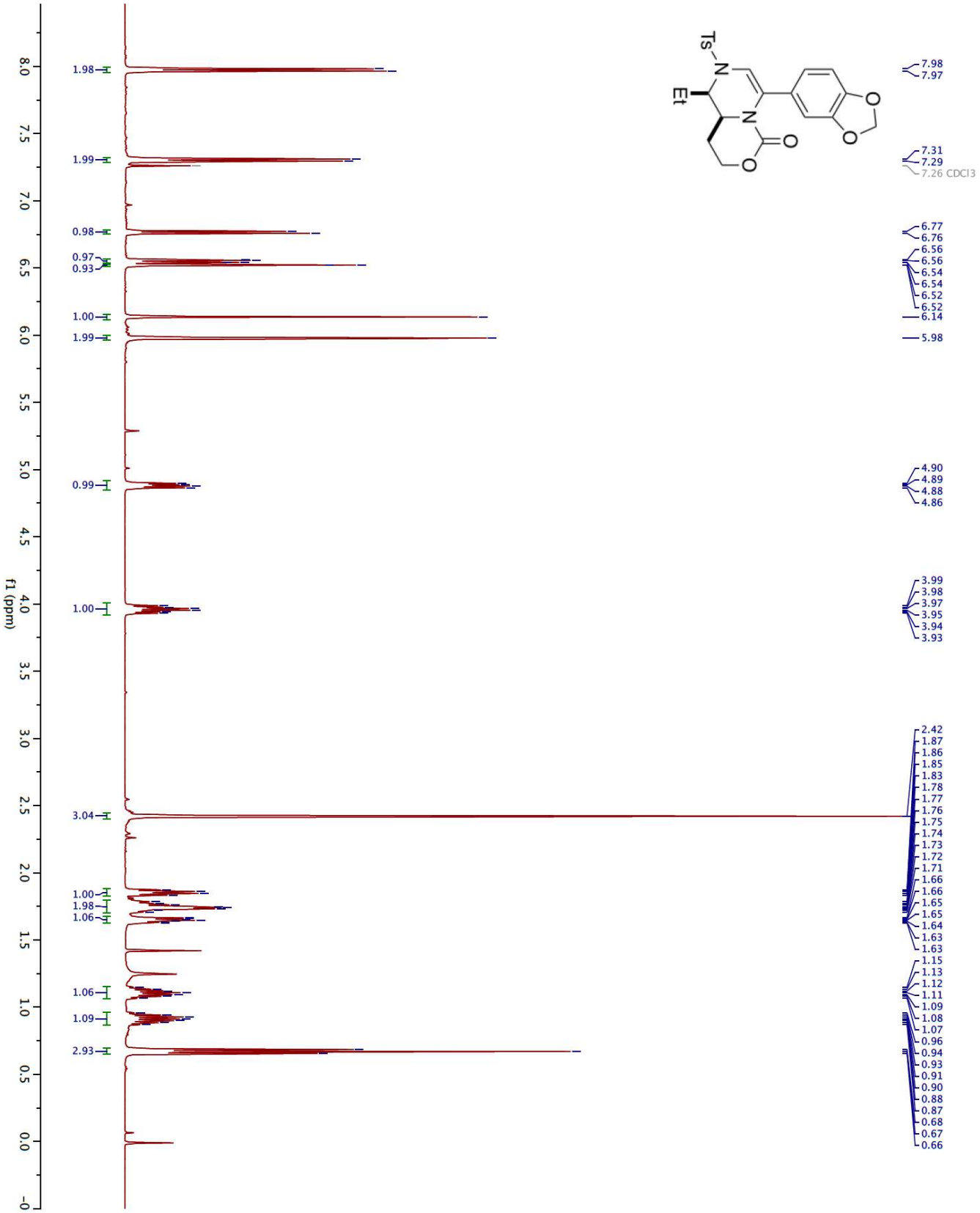
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6ah**



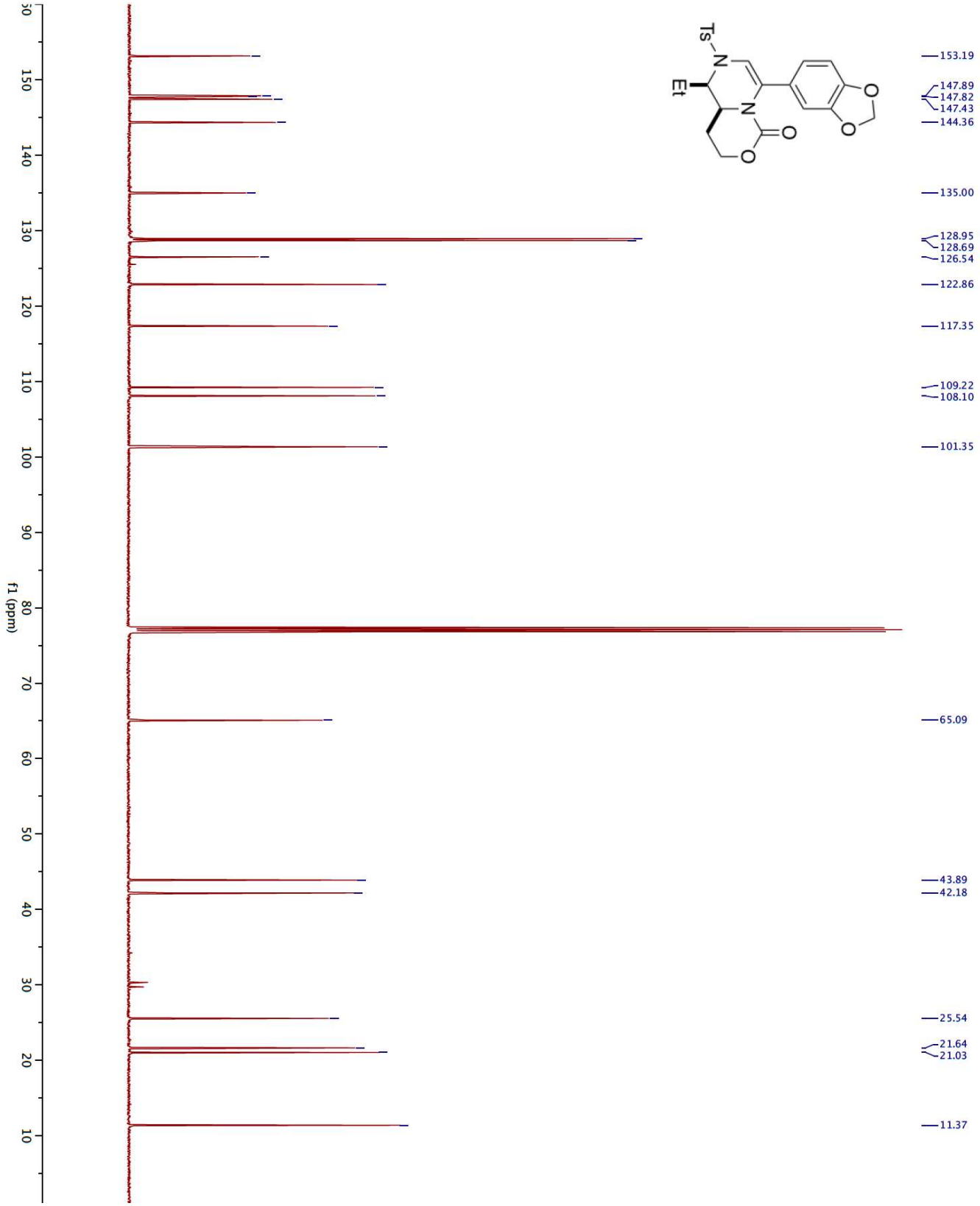
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6ah**



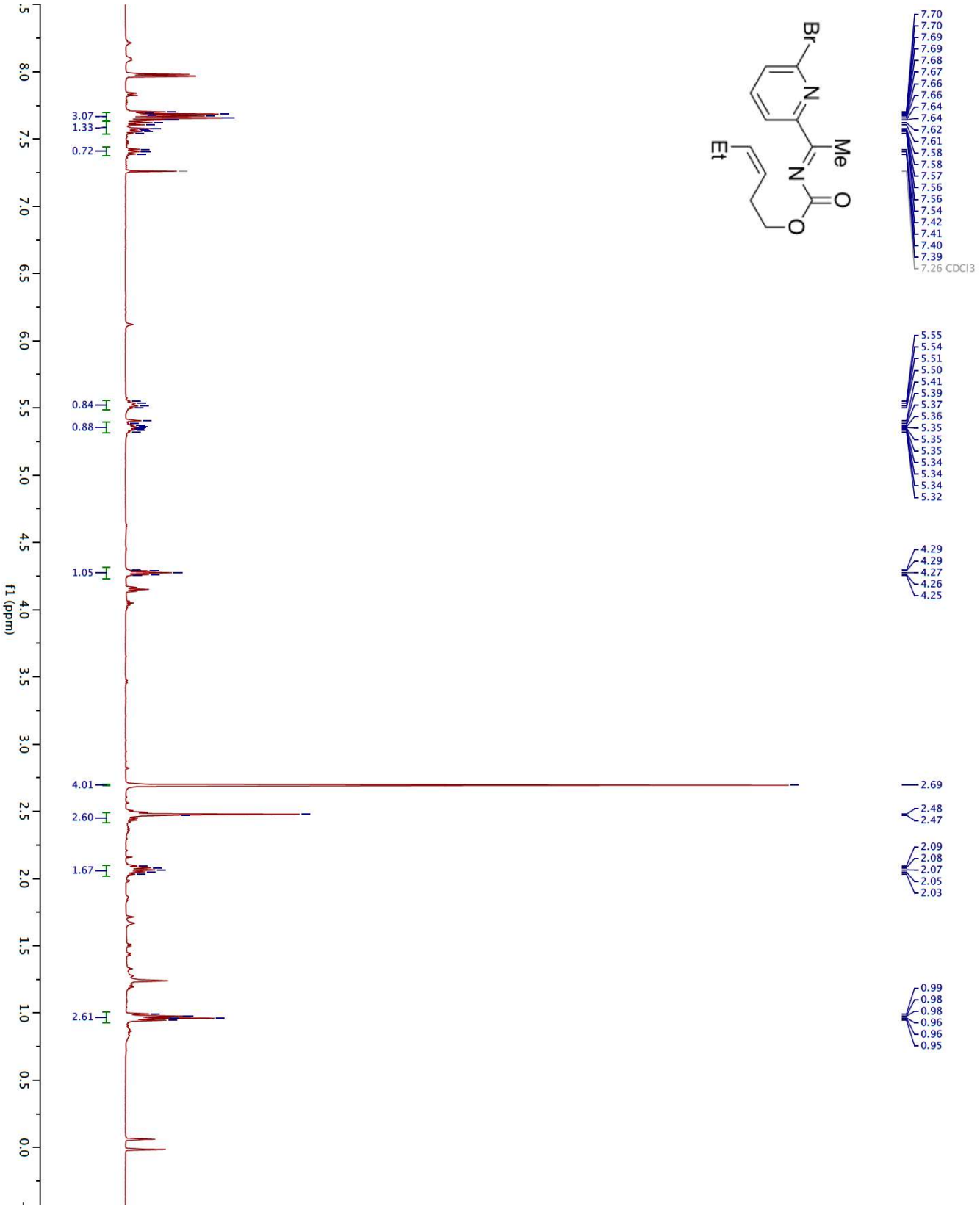
^{1}H NMR (500 MHz, $CDCl_3$) for compound **6a**



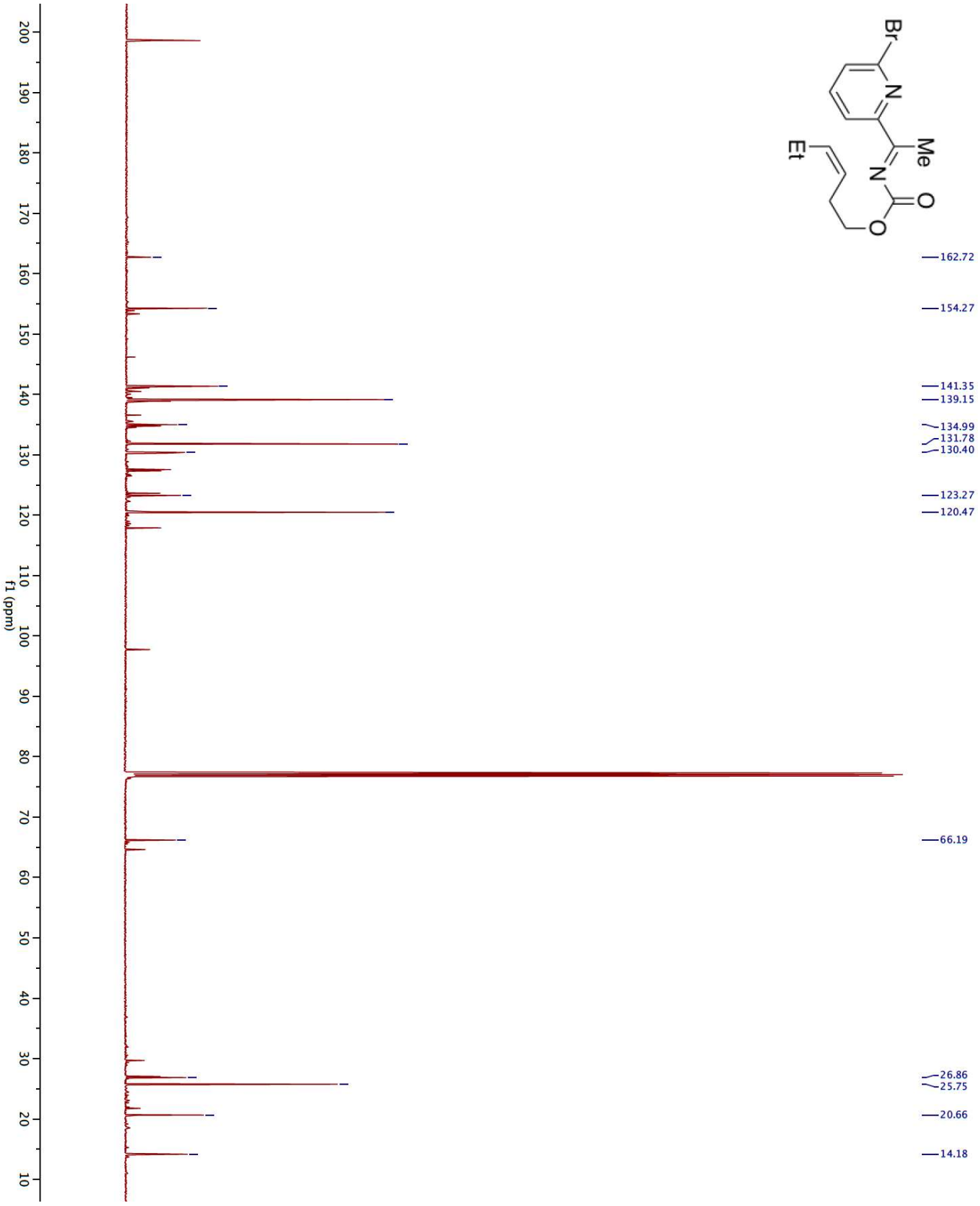
^{13}C NMR (126 MHz, $CDCl_3$) for compound **6ai**



^{1}H NMR (500 MHz, $CDCl_3$) for compound **3**



^{13}C NMR (126 MHz, $CDCl_3$) for compound **3**



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