

**Supporting Information**  
**General Method for the Preparation of Electron Deficient Imidazo[1,2-  
a]pyridines and Related Heterocycles**

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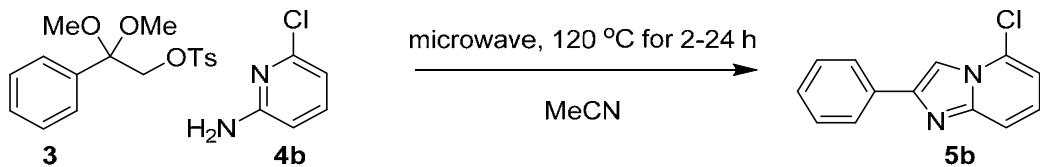
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## General Information

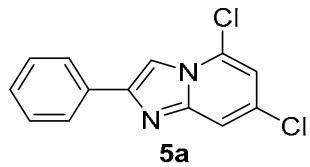
Methanol, dichloroethane, acetonitrile, dioxane, and toluene obtained from Aldrich in Sure/Seal<sup>TM</sup> bottles and used directly. Toluenesulfonic acid monohdrate and scandium triflate obtained from Aldrich and used directly. Pyridyl amines **4a-s**, 2-chloro-1-phenylethanone (**S1**), 2-bromo-1-phenylethanone (**S2**), hydroxy(phenyl)-l3-iodanyl 4-methylbenzenesulfonate (**S3**), acetaphenone (**S4**), 1-cyclohexylethan-1-one (**S6**), cyclohexanone (**S8**), and propiophenone (**S10**) purchased commercially and used as received. NMR spectra obtained on Bruker 400 MHz or 500 MHz NMR spectrometers. The chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR signals are cited relative to internal CHCl<sub>3</sub> ( $\delta$  = 7.26) and CDCl<sub>3</sub> ( $\delta$  = 77.0). LCMS obtained on Shimadzu LCMS 2020 system run with 2%-98% MeCN/water gradient [0.05% TFA].

### General Procedure

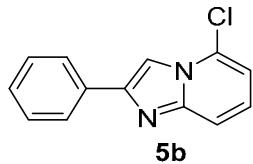


To a solution of 6-chloropyridin-2-amine (**3**) (100 mg, 0.778 mmol, 1 equiv) and 2,2-dimethoxy-2-phenylethyl 4-methylbenzenesulfonate (**4b**) (314 mg, 0.933 mmol, 1.2 equiv) in acetonitrile (7.8 mL) was added scandium triflate (19 mg, 0.039 mmol, 0.05 equiv). The reaction vial was sealed and heated at 120 °C for 24 h. Upon cooling to ambient temperature, the reaction was added to a saturated aqueous sodium bicarbonate solution and extracted with DCM (x2). The combined DCM extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified *via* silica gel flash chromatography (0-100% EtOAc/hexane) to provide the product (176 mg, 99%) as a white solid.

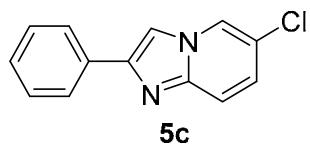
## Characterization of 5a-q, 7a-d, 9a-c, 11a, 11c



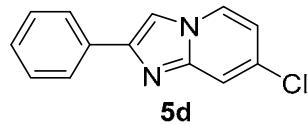
5,7-Dichloro-2-phenylimidazo[1,2-*a*]pyridine (**5a**). Prepared in 71% (146 mg white solid) from 4,6-dichloropyridin-2-amine (**4a**) and ketal **3** following the standard procedure or in 96% (155 mg of a white solid) following the standard procedure at 80 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (s, 1H), 8.00 - 7.96 (m, 2H), 7.63 (d, *J* = 1.3 Hz, 1H), 7.51 - 7.44 (m, 2H), 7.42 - 7.36 (m, 1H), 6.94 (d, *J* = 2.0 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.6, 145.2, 132.5, 130.3, 128.4 (s, 2C), 128.2, 125.9, 125.8 (s, 2C), 114.3, 112.8, 106.8; LCMS (ESI, M+1): 262.95.



5-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5b**). Prepared in 99% (177 mg white solid) from 6-chloropyridin-2-amine (**4b**) and ketal **3** following the standard procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (s, 1H), 7.98 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.48 - 7.41 (m, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.18 - 7.11 (m, 1H), 6.87 (d, *J* = 7.3 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.5, 146.2, 133.3, 128.8 (s, 2C), 128.3, 126.3 (s, 2C), 125.9, 124.7, 115.7, 111.9, 107.1; LCMS (ESI, M+1): 229.0.



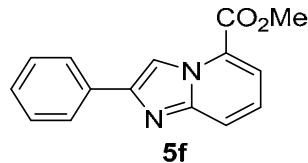
6-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5c**). Prepared in 96% (171 mg white solid) from 5-chloropyridin-2-amine (**4c**) and ketal **3** following the standard procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (d, *J* = 1.0 Hz, 1H), 8.02 - 7.93 (m, 2H), 7.87 (s, 1H), 7.61 (d, *J* = 9.5 Hz, 1H), 7.53 - 7.45 (m, 2H), 7.41 - 7.35 (m, 1H), 7.17 (dd, *J* = 9.5, 2.0 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.9, 144.1, 133.3, 128.8 (s, 2C), 128.3, 126.1 (s, 2C), 126.0, 123.4, 120.6, 117.9, 108.5; LCMS (ESI, M+1): 228.95.



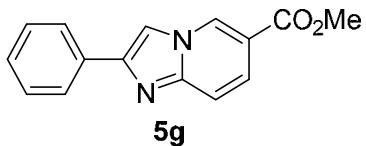
**7-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5d**).** Prepared in 79% (141 mg white solid) from 4-chloropyridin-2-amine (**4d**) and ketal **3** following the standard procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 - 8.01 (m, 1H), 7.95 (d,  $J = 8.3$  Hz, 2H), 7.93 - 7.80 (m, 1H), 7.72 - 7.61 (m, 1H), 7.47 (t,  $J = 7.2$  Hz, 2H), 7.41 - 7.34 (m, 1H), 6.81 (br d,  $J = 7.0$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 145.5, 133.3, 131.0, 128.8 (s, 2C), 128.3, 126.1 (s, 2C), 125.8, 116.4, 114.1, 108.2; LCMS (ESI, M+1): 229.0.



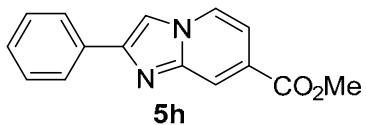
**8-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5e**).** Prepared in 64% (115 mg white solid) from 3-chloropyridin-2-amine (**4e**) and ketal **3** following the standard procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 - 8.08 (m, 1H), 8.05 - 8.00 (m, 2H), 7.95 (s, 1H), 7.50 - 7.44 (m, 2H), 7.40 - 7.34 (m, 1H), 7.28 - 7.25 (m, 1H), 6.76 (t,  $J = 7.0$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.5, 143.1, 133.2, 128.7 (s, 2C), 128.3, 126.4 (s, 2C), 124.4, 123.6, 123.3, 112.0, 109.7; LCMS (ESI, M+1): 229.05.



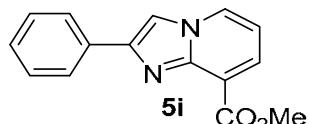
**Methyl 2-phenylimidazo[1,2-*a*]pyridine-5-carboxylate (**5f**).** Prepared in 69% (137 mg white solid) from methyl 6-aminopicolinate (**4f**) and ketal **3** following the standard procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.16 (s, 1H), 8.09 - 7.99 (m, 2H), 7.89 (d,  $J = 8.8$  Hz, 1H), 7.76 (dd,  $J = 7.3, 1.3$  Hz, 1H), 7.49 - 7.41 (m, 2H), 7.38 - 7.30 (m, 1H), 7.22 (dd,  $J = 8.8, 7.3$  Hz, 1H), 4.02 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4, 147.2, 146.4, 133.7, 128.8 (s, 2C), 128.3, 126.3 (s, 2C), 125.5, 122.5, 122.4, 118.8, 111.0, 52.8; LCMS (ESI, M+1): 253.0.



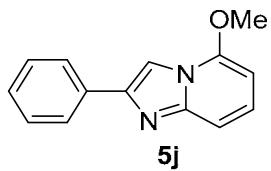
Methyl 2-phenylimidazo[1,2-*a*]pyridine-6-carboxylate (**5g**). Prepared in 64% (126 mg white solid) from methyl 5-aminopicolinate (**4g**) and ketal **3** following the standard procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.89 (dd, *J* = 1.5, 1.0 Hz, 1H), 7.98 - 7.93 (m, 2H), 7.91 (s, 1H), 7.74 - 7.68 (m, 1H), 7.64 - 7.58 (m, 1H), 7.48 - 7.41 (m, 2H), 7.38 - 7.31 (m, 1H), 3.95 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.3, 147.8, 146.2, 133.1, 129.8, 128.8 (s, 2C), 128.5, 126.3 (s, 2C), 124.4, 116.8, 116.5, 108.9, 52.4; LCMS (ESI, M+1): 253.0.



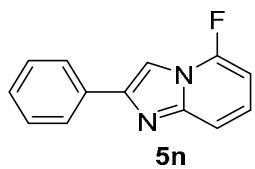
Methyl 2-phenylimidazo[1,2-*a*]pyridine-7-carboxylate (**5h**). Prepared in 60% (119 mg white solid) from methyl 4-aminopicolinate (**4h**) and ketal **3** following the standard procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.42 - 8.29 (m, 1H), 8.12 (dd, *J* = 7.2, 0.9 Hz, 1H), 8.00 - 7.88 (m, 3H), 7.50 - 7.42 (m, 2H), 7.39 - 7.30 (m, 2H), 3.95 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.7, 148.3, 144.6, 133.2, 128.9 (s, 2C), 128.5, 126.2 (s, 2C), 126.0, 125.0, 120.2, 111.8, 109.6, 52.6; LCMS (ESI, M+1): 253.0.



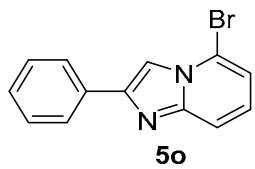
Methyl 2-phenylimidazo[1,2-*a*]pyridine-8-carboxylate (**5i**). Prepared in 49% (98 mg white solid) from methyl 3-aminopicolinate (**4i**) and ketal **3** following the standard procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (dd, *J* = 6.8, 1.3 Hz, 1H), 8.04 - 7.99 (m, 2H), 7.95 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.92 (s, 1H), 7.47 - 7.39 (m, 2H), 7.36 - 7.29 (m, 1H), 6.84 (t, *J* = 6.9 Hz, 1H), 4.06 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.3, 147.1, 143.0, 133.3, 129.4, 129.3, 128.6 (s, 2C), 128.3, 126.5 (s, 2C), 119.7, 111.3, 108.6, 52.7; LCMS (ESI, M+1): 253.0.



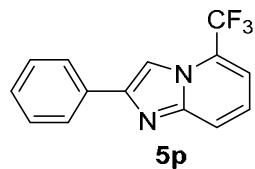
**5-Methoxy-2-phenylimidazo[1,2-a]pyridine (5j).** Prepared in 82% (144 mg white solid) from 6-methoxypyridin-2-amine (**4j**) and ketal **3** following the standard procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 - 7.94 (m, 2H), 7.91 (s, 1H), 7.46 - 7.38 (m, 2H), 7.33 - 7.25 (m, 2H), 7.19 - 7.12 (m, 1H), 6.00 (d,  $J = 7.5$  Hz, 1H), 4.09 - 4.00 (m, 3H)  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.5, 146.9, 145.3, 134.1, 128.7 (s, 2C), 127.8, 126.1 (s, 2C), 125.9, 109.5, 103.6, 87.8, 56.3; LCMS (ESI, M+1): 225.05.



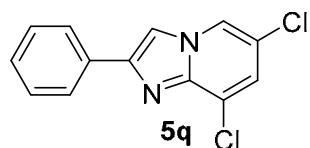
**5-Fluoro-2-phenylimidazo[1,2-a]pyridine (5n).** Prepared in 87% (144 mg white solid) from 6-fluoropyridin-2-amine (**4n**) and ketal **3** following the standard procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 - 7.90 (m, 3H), 7.49 - 7.41 (m, 3H), 7.38 - 7.31 (m, 1H), 7.26 - 7.16 (m, 1H), 6.45 (dd,  $J = 7.4, 4.9$  Hz, 1H), 1.78 (br s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1 (d,  $J_{\text{CF}} = 265.9$  Hz, 1C), 147.5 (d,  $J_{\text{CF}} = 4.6$  Hz, 1C), 146.6, 133.3, 128.8 (s, 2C), 128.4, 126.3 (s, 2C), 125.4 (d,  $J_{\text{CF}} = 6.2$  Hz, 1C), 113.1 (d,  $J_{\text{CF}} = 5.4$  Hz, 1C), 102.7, 92.4 (d,  $J_{\text{CF}} = 15.4$  Hz, 1C); LCMS (ESI, M+1): 213.05.



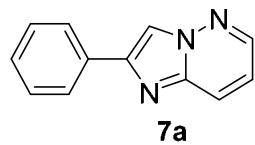
**5-Bromo-2-phenylimidazo[1,2-a]pyridine (5o).** Prepared in 76% (161 mg white solid) from 6-bromopyridin-2-amine (**4o**) and ketal **3** following the standard procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 0.5$  Hz, 1H), 8.05 - 7.99 (m, 2H), 7.65 (dt,  $J = 8.8, 0.9$  Hz, 1H), 7.51 - 7.45 (m, 2H), 7.41 - 7.34 (m, 1H), 7.14 - 7.08 (m, 1H), 7.07 - 7.03 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 145.4, 133.0, 128.4 (s, 2C), 127.9, 125.8 (s, 2C), 124.5, 115.8, 113.6, 108.9; LCMS (ESI, M+1): 272.95.



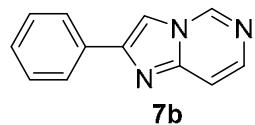
**5-Trifluoromethyl-2-phenylimidazo[1,2-*a*]pyridine (5p).** Prepared in 73% (150 mg white solid) from 6-(trifluoromethyl)pyridin-2-amine (**4p**) and ketal **3** following the standard procedure for 24 h at 120 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (s, 1H), 8.01 (d, *J* = 7.0 Hz, 2H), 7.90 - 7.83 (m, 1H), 7.52 - 7.45 (m, 2H), 7.42 - 7.35 (m, 1H), 7.27 - 7.26 (m, 2H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -69.44 (s, 3F); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.9, 145.5, 132.6, 128.4 (s, 2C), 128.2, 125.9 (s, 2C), 124.9 (q, *J*<sub>CF</sub> = 36.2 Hz, 1C), 122.2, 120.9, 120.4 (d, *J*<sub>CF</sub> = 271.3 Hz, 1C), 111.9 (q, *J*<sub>CF</sub> = 4.6 Hz, 1C), 107.5 (d, *J*<sub>CF</sub> = 1.5 Hz, 1C); LCMS (ESI, M+1): 263.00.



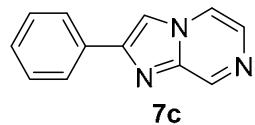
**6,8-Dichloro-2-phenylimidazo[1,2-*a*]pyridine (5q).** Prepared in 62% (127 mg white solid) from 3,5-dichloropyridin-2-amine (**4q**) and ketal **3** following the standard procedure for 24 h at 120 °C or in 97% (156 mg of a white solid) following the standard procedure at 80 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 1.5 Hz, 1H), 8.02 - 7.96 (m, 2H), 7.90 (s, 1H), 7.49 - 7.43 (m, 2H), 7.41 - 7.35 (m, 1H), 7.29 (d, *J* = 1.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.9, 141.2, 132.4, 128.4 (s, 2C), 128.2, 125.9 (s, 2C), 124.3, 123.2, 121.8, 119.1, 109.7; LCMS (ESI, M+1): 262.90.



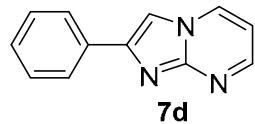
**2-Phenylimidazo[1,2-*b*]pyridazine (7a).** Prepared in 61% (126 mg tan solid) from pyridazin-3-amine (**6a**) and ketal **3** following the standard procedure for 12 h at 140 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.35 - 8.28 (m, 2H), 8.05 - 7.94 (m, 3H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 - 7.35 (m, 1H), 7.06 (dd, *J* = 9.2, 4.4 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.5, 142.6, 139.1, 132.9, 128.5 (s, 2C), 128.1, 125.7 (s, 2C), 124.7, 116.5, 112.3; LCMS (ESI, M+1): 195.90.



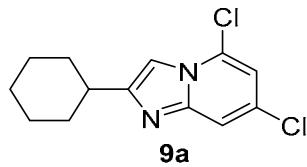
**2-Phenylimidazo[1,2-*c*]pyrimidine (7b).** Prepared in 26% (54 mg tan solid) from pyrimidin-4-amine (**6b**) and ketal **3** following the standard procedure for 6 h at 140 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.05 (s, 1H), 7.99 (d, *J* = 7.3 Hz, 2H), 7.96 - 7.92 (m, 2H), 7.55 (d, *J* = 6.5 Hz, 1H), 7.52 - 7.46 (m, 2H), 7.43 - 7.38 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.1, 144.6, 139.1, 138.6, 132.3, 128.5 (s, 2C), 128.4, 126.0 (s, 2C), 111.9, 104.9; LCMS (ESI, M+1): 195.95.



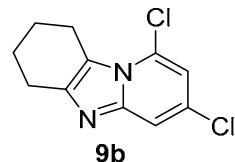
**2-Phenylimidazo[1,2-*a*]pyrazine (7c).** Prepared in 91% (186 mg pale red solid) from pyrazin-2-amine (**6c**) and ketal **3** following the standard procedure for 2 h at 120 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.13 (s, 1H), 8.13 - 8.06 (m, 1H), 8.03 - 7.96 (m, 3H), 7.90 (d, *J* = 4.5 Hz, 1H), 7.54 - 7.46 (m, 2H), 7.45 - 7.38 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.4, 143.1, 140.5, 132.4, 129.2, 128.5 (s, 2C), 128.5, 125.9 (s, 2C), 118.3, 108.9; LCMS (ESI, M+1): 196.10.



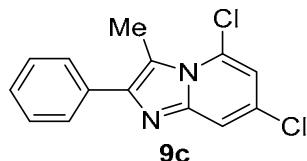
**2-Phenylimidazo[1,2-*a*]pyrimidine (7d).** Prepared in 54% (110 mg pale tan solid) from pyrimidin-2-amine (**6d**) and ketal **3** following the standard procedure for 9 h at 120 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.56 (br. s., 1H), 8.45 (d, *J* = 6.8 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 2H), 7.85 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.43 - 7.34 (m, 1H), 6.88 (dd, *J* = 6.9, 4.1 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.4, 148.3, 146.8, 132.8, 132.8, 128.4 (s, 2C), 128.2, 125.9 (s, 2C), 108.4, 106.0; LCMS (ESI, M+1): 195.95.



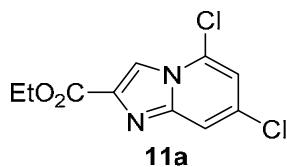
**5,7-Dichloro-2-cyclohexylimidazo[1,2-*a*]pyridine (**9a**)**. Prepared in 64% (212 mg off white solid) from 4,6-dichloropyridin-2-amine (**4a**) and ketal **8a** following the standard procedure for 2 h at 120 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52 (s, 1H), 7.48 (s, 1H), 6.87 (s, 1H), 2.79 (br. s., 1H), 2.14 (d, *J* = 12.0 Hz, 2H), 1.87 (d, *J* = 11.5 Hz, 2H), 1.77 (d, *J* = 13.1 Hz, 1H), 1.50 - 1.27 (m, 5H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.3, 144.4, 129.4, 125.7, 113.8, 111.9, 106.4, 37.8, 32.4 (s, 2C), 25.9 (s, 2C), 25.8; LCMS (ESI, M+1): 268.95.



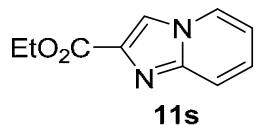
**1,3-Dichloro-6,7,8,9-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (**9b**)**. Prepared in 45% (66 mg off white solid) from 4,6-dichloropyridin-2-amine (**4a**) and ketal **8b** following the standard procedure for 2 h at 80 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 1.8 Hz, 1H), 6.73 (d, *J* = 1.8 Hz, 1H), 3.34 (t, *J* = 6.1 Hz, 2H), 2.83 (t, *J* = 5.9 Hz, 2H), 2.02 - 1.79 (m, 4H); LCMS (ESI, M+1): 240.95; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.0, 144.3, 128.4, 126.4, 121.1, 114.0, 112.9, 25.1, 24.3, 23.0, 22.0.



**5,7-Dichloro-3-methyl-2-phenylimidazo[1,2-*a*]pyridine (**9c**)**. Prepared in 56% (95 mg white solid) from 4,6-dichloropyridin-2-amine (**4a**) and ketal **8c** following the standard procedure for 2 h at 120 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.44 - 7.37 (m, 1H), 6.82 (d, *J* = 2.0 Hz, 1H), 2.97 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.3, 145.2, 133.6, 129.1, 128.7 (s, 2C), 128.1 (s, 2C), 127.5, 127.0, 119.0, 114.8, 114.2, 13.3; LCMS (ESI, M+1): 276.95.

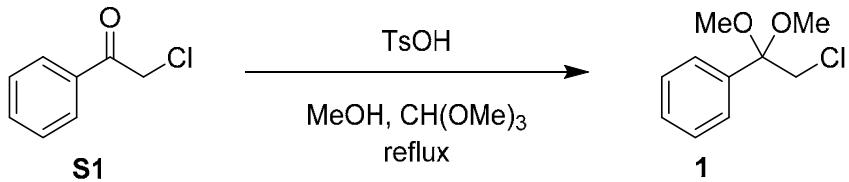


Ethyl 5,7-dichloroimidazo[1,2-*a*]pyridine-2-carboxylate (**11a**). Prepared in 60% (100 mg peach colored solid) from 4,6-dichloropyridin-2-amine (**4a**) and ethyl bromopyruvate (**10**) following the standard procedure for 2 h at 120 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.35 (s, 1H), 7.68 (s, 1H), 7.03 (s, 1H), 4.49 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.4, 144.7, 137.4, 132.7, 126.7, 115.6, 115.4, 114.4, 61.0, 14.0; LCMS (ESI, M+1): 259.0.

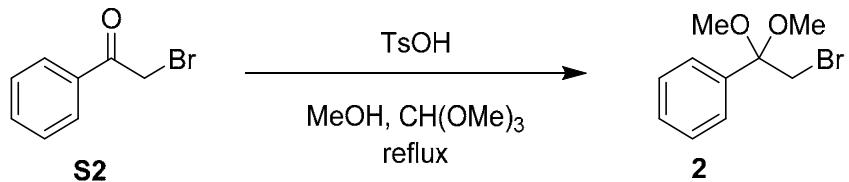


Ethyl imidazo[1,2-*a*]pyridine-2-carboxylate (**11s**). Prepared in 46% (92 mg off white solid) from pyridin-2-amine (**4a**) and ethyl bromopyruvate (**10**) following the standard procedure for 2 h at 120 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>2</sub>) δ 8.20 (s, 1H), 8.14 (d, *J* = 6.8 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.25 (d, *J* = 9.3 Hz, 1H), 6.89 (t, *J* = 6.8 Hz, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.8, 144.8, 136.4, 125.8, 125.6, 118.5, 116.5, 113.4, 60.6, 14.0; LCMS (ESI, M+1): 191.0.

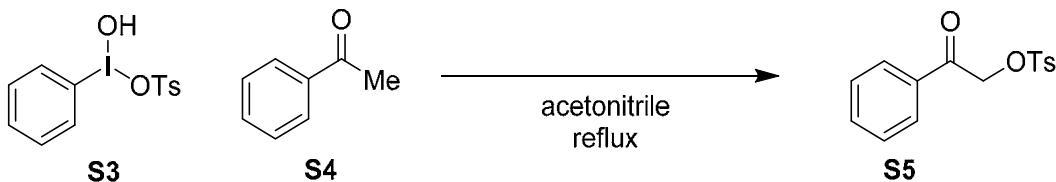
### Ketal 1-3, 8a-c preparation



(2-Chloro-1,1-dimethoxyethyl)benzene (**1**). A solution of 2-chloro-1-phenylethanone (20.8 g, 135 mmol, 1 equiv), trimethyl orthoformate (30 mL, 269 mmol, 2 equiv), TsOH monohydrate (1.40 g, 6.7 mmol, 0.05 equiv) in MeOH (270 mL) was heated to reflux for 4 h. Upon cooling to ambient temperature, the reaction was diluted with ether, washed with 10% K<sub>2</sub>CO<sub>3</sub>, dried (MgSO<sub>4</sub>), and concentrated *in vacuo* to provide a colorless oil which slowly solidified. The crude product was recrystallized from hexane to provide the product (21.5 g, 80%) as a white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.54 (d, *J* = 7.7 Hz, 2H), 7.45 - 7.34 (m, 3H), 3.77 (s, 2H), 3.27 (s, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 138.4, 128.4, 128.1 (s, 2C), 127.3 (s, 2C), 101.9, 49.2 (s, 2C), 46.6.

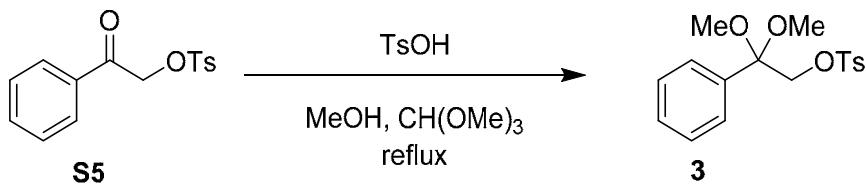


(2-Bromo-1,1-dimethoxyethyl)benzene (**2**). A solution of 2-bromo-1-phenylethanone (21.8 g, 110 mmol, 1 equiv), trimethyl orthoformate (24 mL, 219 mmol, 2 equiv), TsOH monohydrate (1.14 g, 5.5 mmol, 0.05 equiv) in MeOH (200 mL) was heated to reflux for 4 h. Upon cooling to ambient temperature, the reaction was diluted with ether, washed with 10% K<sub>2</sub>CO<sub>3</sub>, dried (MgSO<sub>4</sub>), and concentrated *in vacuo* to provide the product (22.9 g, 85%) as colorless oil that crystallized to a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 - 7.47 (m, 2H), 7.45 - 7.32 (m, 3H), 3.65 (s, 2H), 3.25 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.2, 128.0, 127.6 (s, 2C), 126.9 (s, 2C), 101.0, 49.0 (s, 2C), 35.1.

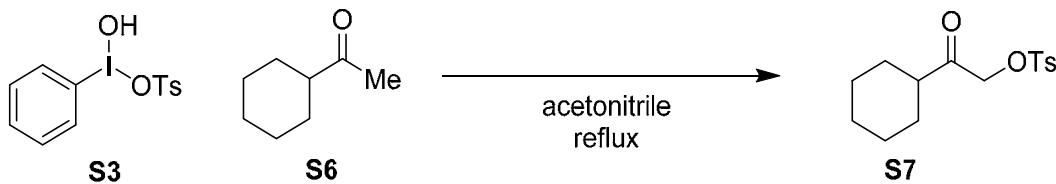


2-Oxo-2-phenylethyl 4-methylbenzenesulfonate (**S5**). A solution of hydroxy(phenyl)-λ3-iodanyl 4-methylbenzenesulfonate (**S3**) (32.6 g, 83 mmol, 1 equiv) and acetophenone (**S4**) (9.7 mL, 83 mmol, 1 equiv) in acetonitrile (208 mL) was heated to reflux for 2 h. Upon cooling to ambient temperature, the

yellow solution was added to water and extracted with DCM (x3). The combined DCM extractions were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (0-50% EtOAc/hexane) to provide the product (22.0 g, 91%) as a white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (t,  $J = 7.3$  Hz, 4H), 7.67 - 7.58 (m, 1H), 7.54 - 7.45 (m, 2H), 7.37 (d,  $J = 8.0$  Hz, 2H), 5.28 (s, 2H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.0, 145.0, 133.9, 133.4, 132.3, 129.6 (s, 2C), 128.6 (s, 2C), 127.8 (s, 2C), 127.6 (s, 2C), 69.6 (s, 2C), 21.3.

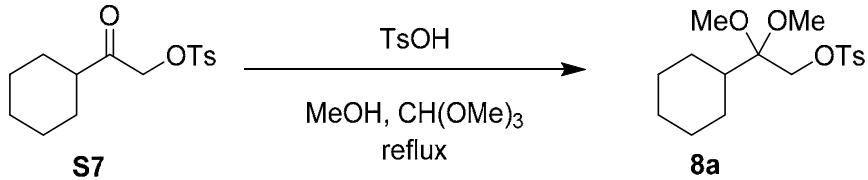


**2,2-Dimethoxy-2-phenylethyl 4-methylbenzenesulfonate (6).** A solution of 2-oxo-2-phenylethyl 4-methylbenzenesulfonate (**S5**) (22 g, 76 mmol, 1 equiv), trimethyl orthoformate (17 mL, 152 mmol, 2 equiv), TsOH monohydrate (0.79 g, 3.8 mmol, 0.05 equiv) in MeOH (200 mL) was heated to reflux for 18 h. Upon cooling to ambient temperature, the reaction mixture was cooled in refrigerator. The crystals that formed were filtered to provide the product (18.7 g, 73%) as large colorless needle shaped crystals.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 8.3$  Hz, 2H), 7.38 - 7.33 (m, 2H), 7.31 - 7.28 (m, 3H), 7.18 (d,  $J = 8.0$  Hz, 2H), 4.14 (s, 2H), 3.19 (s, 6H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 137.3, 131.9, 129.3 (s, 2C), 128.0, 127.7 (s, 2C), 127.3 (s, 2C), 126.8 (s, 2C), 99.9, 69.1, 48.5 (s, 2C), 21.1.

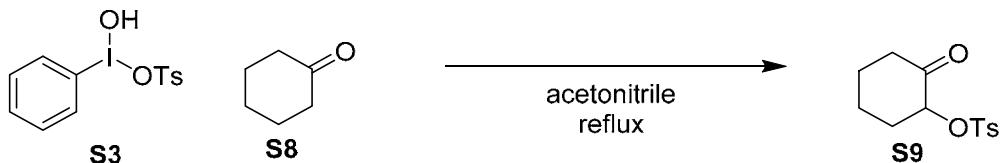


**2-Cyclohexyl-2-oxoethyl 4-methylbenzenesulfonate (S7).** Prepared following the procedure of Handy, S. T.; Okello, M. *Synlett* **2002**, 489. A solution of hydroxy(phenyl)- $\lambda^3$ -iodanyl 4-methylbenzenesulfonate (**S3**) (5.2 g, 13.3 mmol, 1 equiv) and 1-cyclohexylethan-1-one (**S6**) (16 mL) in acetonitrile (100 mL) was sonicated for 20 min in a 60 °C water bath. During this time, the reaction turned yellow and became homogenous. Upon cooling to ambient temperature, the reaction was concentrated *in vacuo*. The residue was taken up in DCM and washed with saturated aqueous sodium bicarbonate. The DCM layer was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated *in vacuo*. The crude product was put

under high vacuum overnight. The crude product was then triturated from cold hexane (16 mL) and filtered to provide the product (2.4 g, 61%) as an off white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.3$  Hz, 2H), 7.38 (d,  $J = 8.0$  Hz, 2H), 4.61 (s, 2H), 2.54 (t,  $J = 10.8$  Hz, 1H), 2.47 (s, 3H), 1.83 - 1.69 (m, 4H), 1.42 - 1.16 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  204.7, 145.0, 132.2, 129.6 (s, 2C), 127.6 (s, 2C), 70.2, 46.4, 27.5 (s, 2C), 25.2, 25.0 (s, 2C), 21.3; LCMS (ESI, M+1): 297.00.

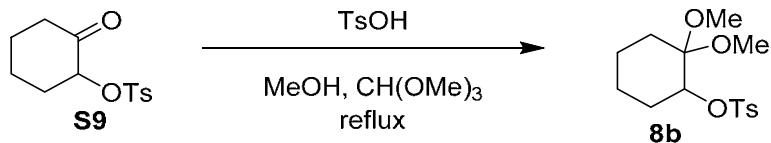


**2-Cyclohexyl-2,2-dimethoxyethyl 4-methylbenzenesulfonate (8a).** A solution of 2-cyclohexyl-2-oxoethyl 4-methylbenzenesulfonate (**S7**) (2.4 g, 8.1 mmol, 1 equiv), trimethyl orthoformate (2.7 mL, 24.3 mmol, 3 equiv), TsOH monohydrate (0.17 g, 0.81 mmol, 0.1 equiv) in MeOH (25 mL) was heated to reflux for 18 h. Upon cooling to ambient temperature, the reaction was diluted with ethyl acetate, washed with saturated aqueous sodium bicarbonate, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated *in vacuo* to provide the product (2.5 g, 90%) as a tan oil that slowly solidified.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 8.3$  Hz, 2H), 7.37 (d,  $J = 8.3$  Hz, 2H), 3.95 (s, 2H), 3.14 (s, 6H), 2.47 (s, 3H), 1.79 - 1.65 (m, 5H), 1.19 - 0.92 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 132.2, 129.4 (s, 2C), 127.7 (s, 2C), 100.2, 66.2, 47.9 (s, 2C), 42.3, 27.0 (s, 2C), 26.4 (s, 2C), 26.0, 21.2.

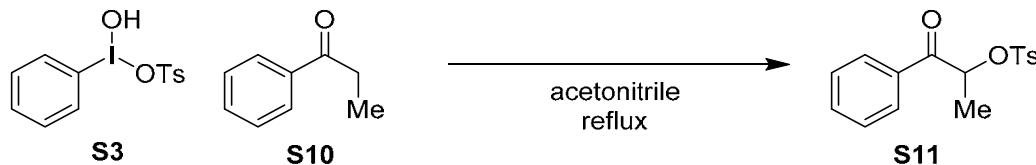


**2-Oxocyclohexyl 4-methylbenzenesulfonate (S10).** Prepared following the procedure of Handy, S. T.; Okello, M. *Synlett* **2002**, 489. A solution of hydroxy(phenyl)- $\lambda$ 3-iodanyl 4-methylbenzenesulfonate (**S3**) (5.2 g, 13.3 mmol, 1 equiv) and cyclohexanone (**S8**) (16 mL) in acetonitrile (100 mL) was sonicated for 20 min in a 60 °C water bath. During this time, the reaction turned yellow and became homogenous. Upon cooling to ambient temperature, the reaction was concentrated *in vacuo*. The residue was taken up in DCM and washed with saturated aqueous sodium bicarbonate. The DCM layer was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated *in vacuo*. The crude product was put under high vacuum overnight. The crude product was then triturated from cold hexane (16 mL) and filtered to provide the product (1.2 g, 35%) as an off white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.3$  Hz, 2H), 7.35 (d,  $J = 8.0$  Hz, 2H), 4.91 (dd,  $J = 10.8, 4.8$  Hz, 1H), 2.54 (t,  $J = 10.8$  Hz, 1H), 2.47 (s, 3H), 1.83 - 1.69 (m, 4H), 1.42 - 1.16 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  204.7, 145.0, 132.2, 129.6 (s, 2C), 127.6 (s, 2C), 70.2, 46.4, 27.5 (s, 2C), 25.2, 25.0 (s, 2C), 21.3; LCMS (ESI, M+1): 297.00.

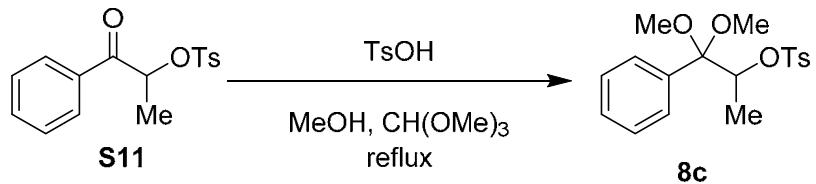
= 10.9, 5.9 Hz, 1H), 2.56 (bd,  $J$  = 13.8 Hz, 1H), 2.46 (s, 3H), 2.40 - 2.25 (m, 2H), 2.06 - 1.88 (m, 3H), 1.79 - 1.65 (m, 2H).



**2,2-Dimethoxycyclohexyl 4-methylbenzenesulfonate (8b).** A solution of 2-oxocyclohexyl 4-methylbenzenesulfonate (**S9**) (1.25 g, 4.7 mmol, 1 equiv), trimethyl orthoformate (1.5 mL, 14.0 mmol, 3 equiv), and TsOH monohydrate (0.048 g, 0.23 mmol, 0.05 equiv) in MeOH (10 mL) was heated to reflux for 1 h. Upon cooling to ambient temperature, the reaction was diluted with ethyl acetate, washed with saturated aqueous sodium bicarbonate, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated *in vacuo* to provide the product (1.2 g, 90%) as a viscous brown oil which was used as is.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J$  = 8.3 Hz, 2H), 7.33 (d,  $J$  = 8.0 Hz, 2H), 4.77 (d,  $J$  = 2.0 Hz, 1H), 3.15 (s, 3H), 3.07 (s, 3H), 1.95 - 1.87 (m, 1H), 1.79 - 1.27 (m, 7H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 134.7, 129.2 (s, 2C), 127.2 (s, 2C), 98.3, 77.6, 47.2 (s, 2C), 27.9, 27.7, 21.2, 21.1, 19.0.



**1-Oxo-1-phenylpropan-2-yl 4-methylbenzenesulfonate (S11).** A solution of hydroxy(phenyl)- $\lambda$ 3-iodanyl 4-methylbenzenesulfonate (**S3**) (20.0 g, 51 mmol, 1 equiv) and propiophenone (**S10**) (13.7 g, 102 mmol, 2 equiv) in acetonitrile (200 mL) was heated to reflux for 6 h. Upon cooling to ambient temperature, the yellow solution was added to water and extracted with DCM (x3). The combined DCM extractions were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (0-60% EtOAc/hexane) to provide the product (13.1 g, 84%) as a viscous yellow oil that crystallized to a white waxy solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J$  = 7.8 Hz, 2H), 7.77 (d,  $J$  = 8.3 Hz, 2H), 7.65 - 7.56 (m, 1H), 7.51 - 7.43 (m, 2H), 7.31 - 7.25 (m, 2H), 5.80 (q,  $J$  = 6.9 Hz, 1H), 1.61 (d,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.4, 144.7, 133.5, 133.4, 133.1, 129.4 (s, 2C), 128.4 (s, 2C), 128.3 (s, 2C), 127.5 (s, 2C), 77.0, 21.2, 18.4.

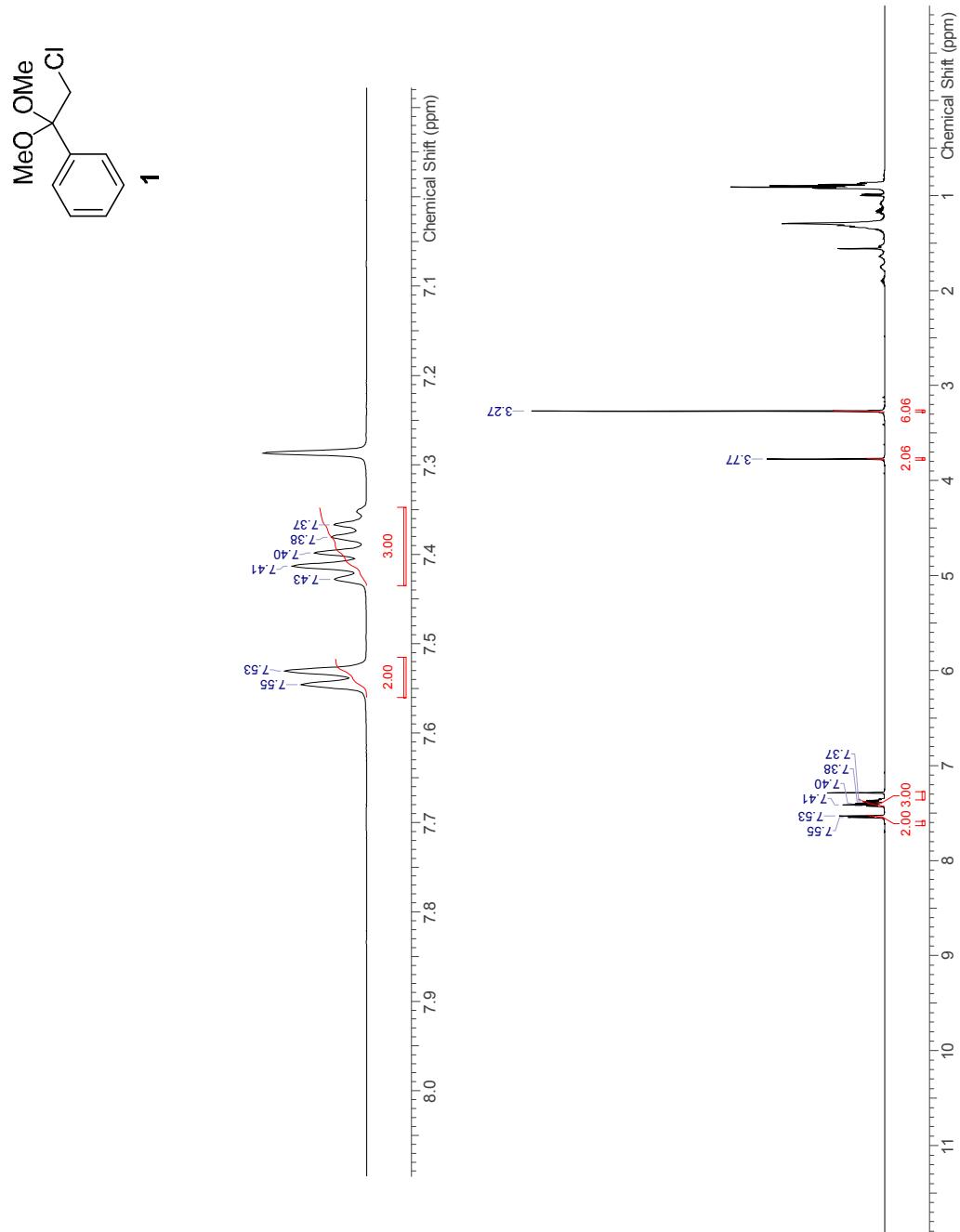


**1,1-Dimethoxy-1-phenylpropan-2-yl 4-methylbenzenesulfonate (8c).** A solution of 1-oxo-1-phenylpropan-2-yl 4-methylbenzenesulfonate (**S11**) (9.6 g, 31.5 mmol, 1 equiv), trimethyl orthoformate (10.5 mL, 95 mmol, 3 equiv), TsOH monohydrate (0.33 g, 1.58 mmol, 0.05 equiv) in MeOH (100 mL) was heated to reflux. After 3 h, NMR of an aliquot showed <5% conversion. Scandium triflate (0.31 g, 0.63 mmol, 0.02 equiv) was added and reflux continued for 48 h. Upon cooling to ambient temperature, the reaction was diluted with ethyl acetate, washed with saturated aqueous sodium bicarbonate, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated *in vacuo*. The crude product was purified by flash chromatography on triethylamine deactivated silica gel (0-60% PhH/hexane) to provide the product (3.4 g, 31%) as a yellow glass. Product contains ~10% of an unidentified impurity which does not interfere with the subsequent annulation reaction.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 8.3$  Hz, 2H), 7.42 - 7.30 (m, 7H), 5.00 (q,  $J = 6.5$  Hz, 1H), 3.19 (s, 3H), 3.12 (s, 3H), 2.46 (s, 3H), 1.10 (d,  $J = 6.5$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 136.0, 134.7, 129.0 (s, 2C), 128.0, 127.8 (s, 2C), 127.4 (s, 2C), 127.4 (s, 2C), 101.7, 79.2, 49.3, 48.8, 21.2, 15.9.

<sup>1</sup>H and <sup>13</sup>C NMR spectra

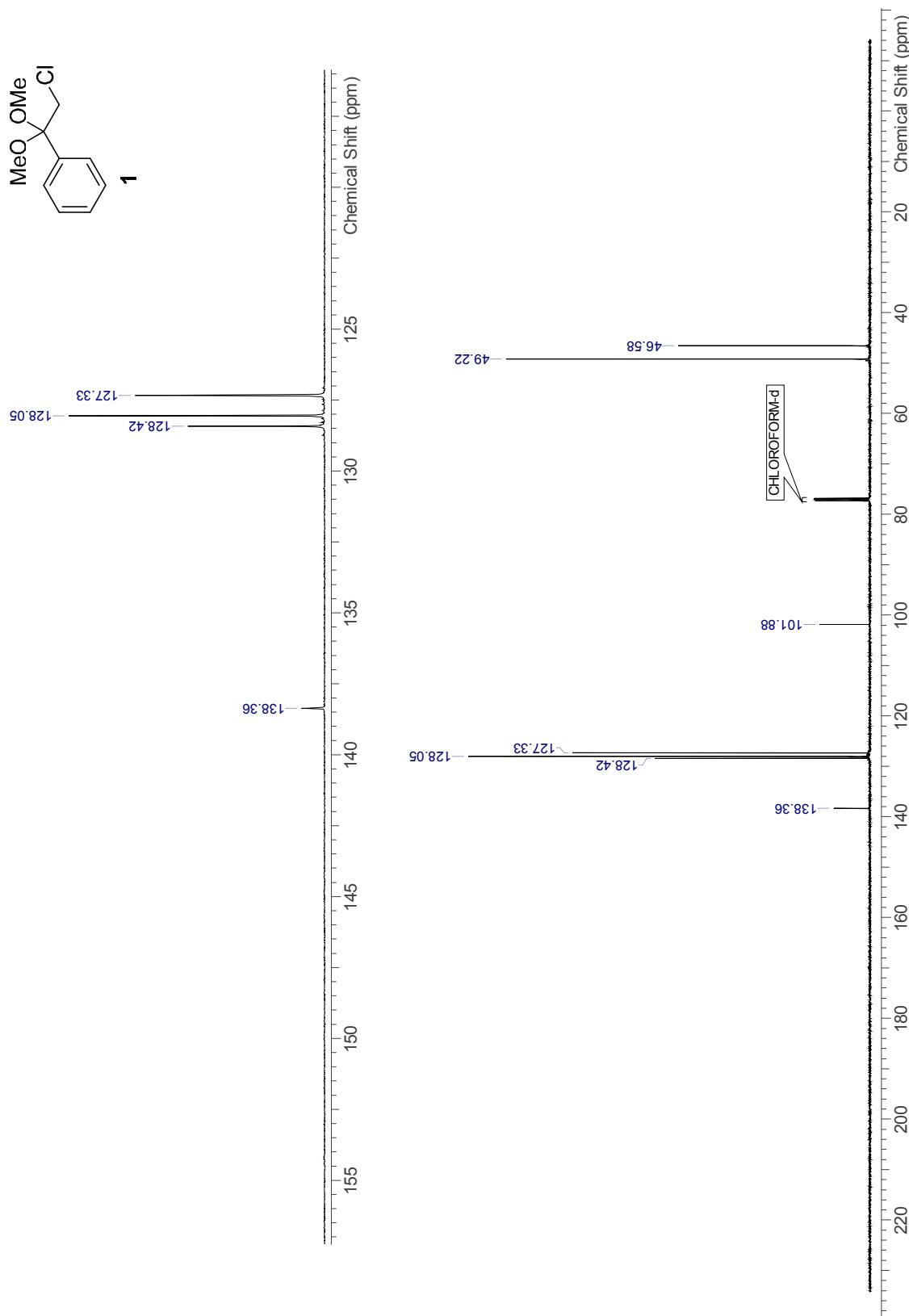
(2-Chloro-1,1-dimethoxyethyl)benzene (**1**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



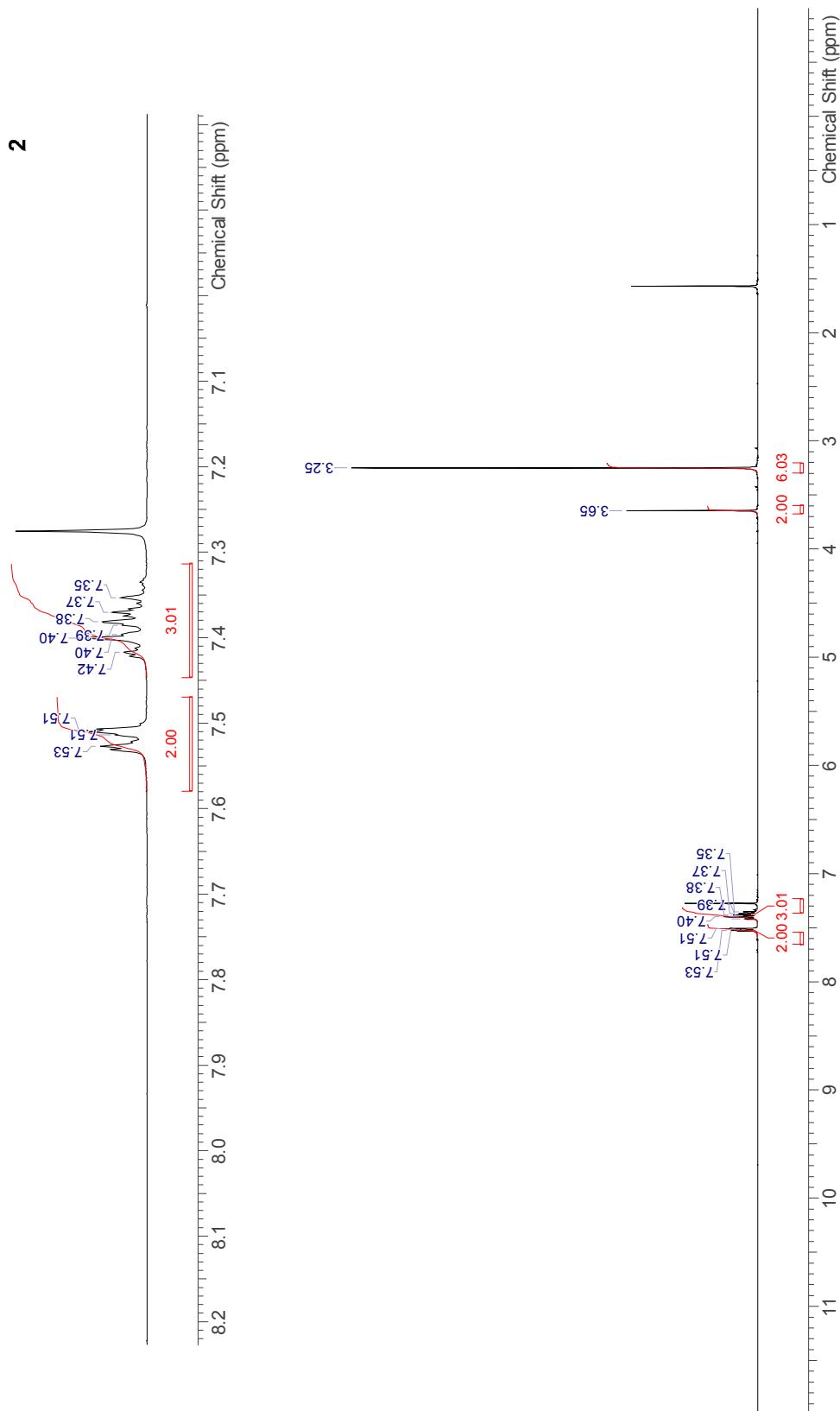
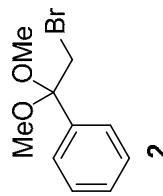
(2-Chloro-1,1-dimethoxyethyl)benzene (**1**)

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )



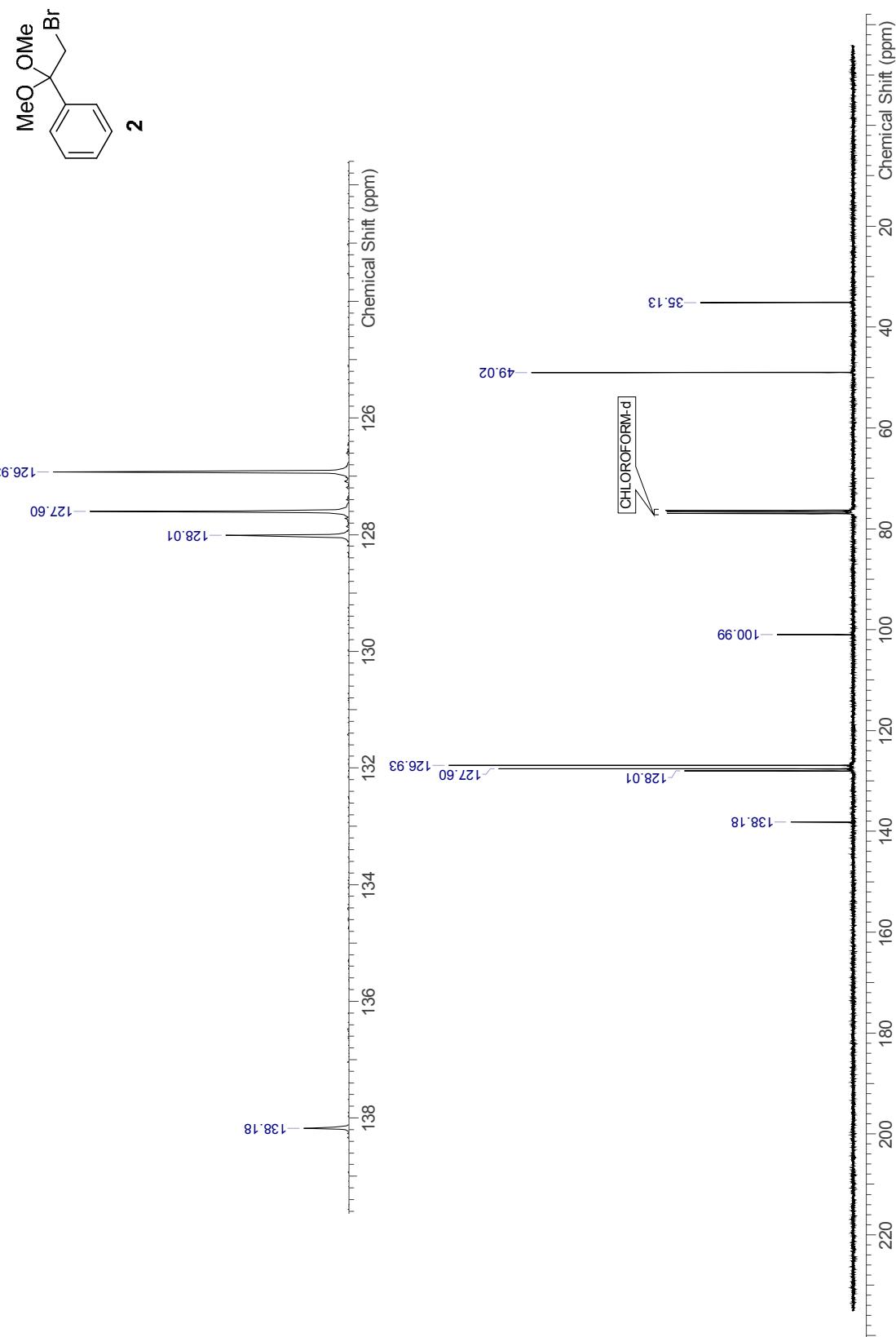
### (2-Bromo-1,1-dimethoxyethyl)benzene (**2**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



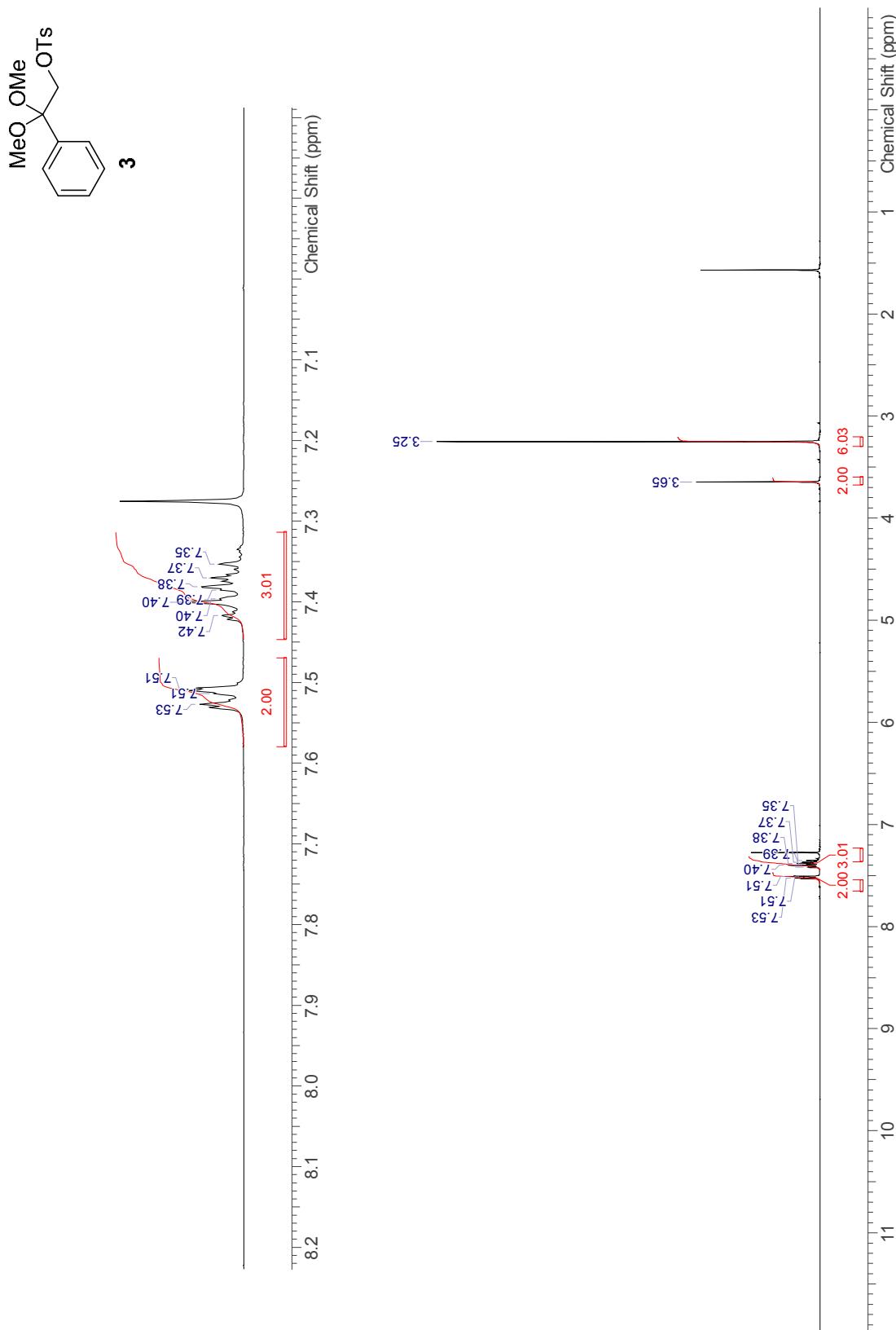
(2-Bromo-1,1-dimethoxyethyl)benzene (**2**)

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )



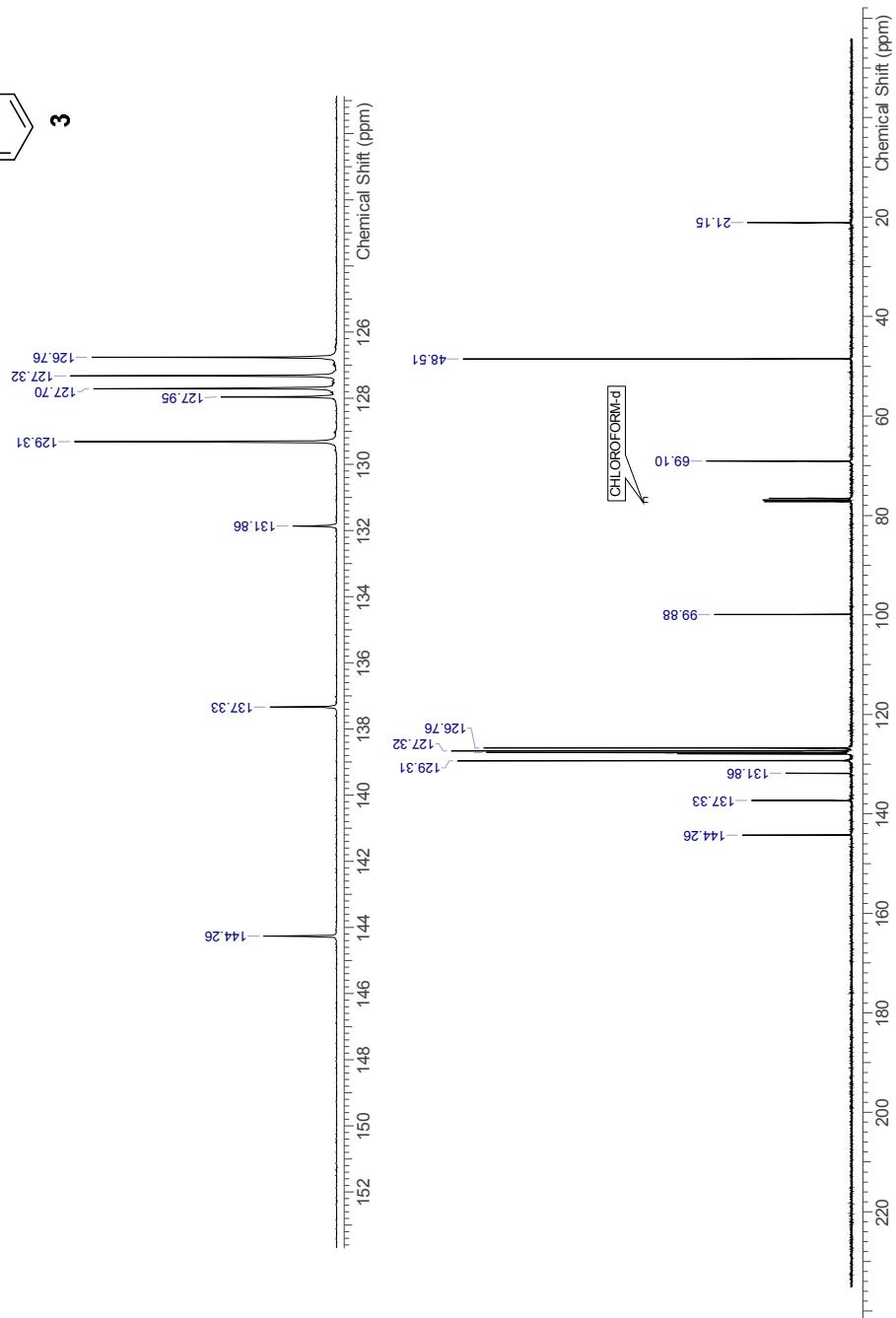
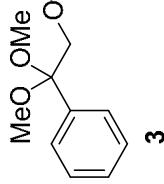
2,2-Dimethoxy-2-phenylethyl 4-methylbenzenesulfonate (**3**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



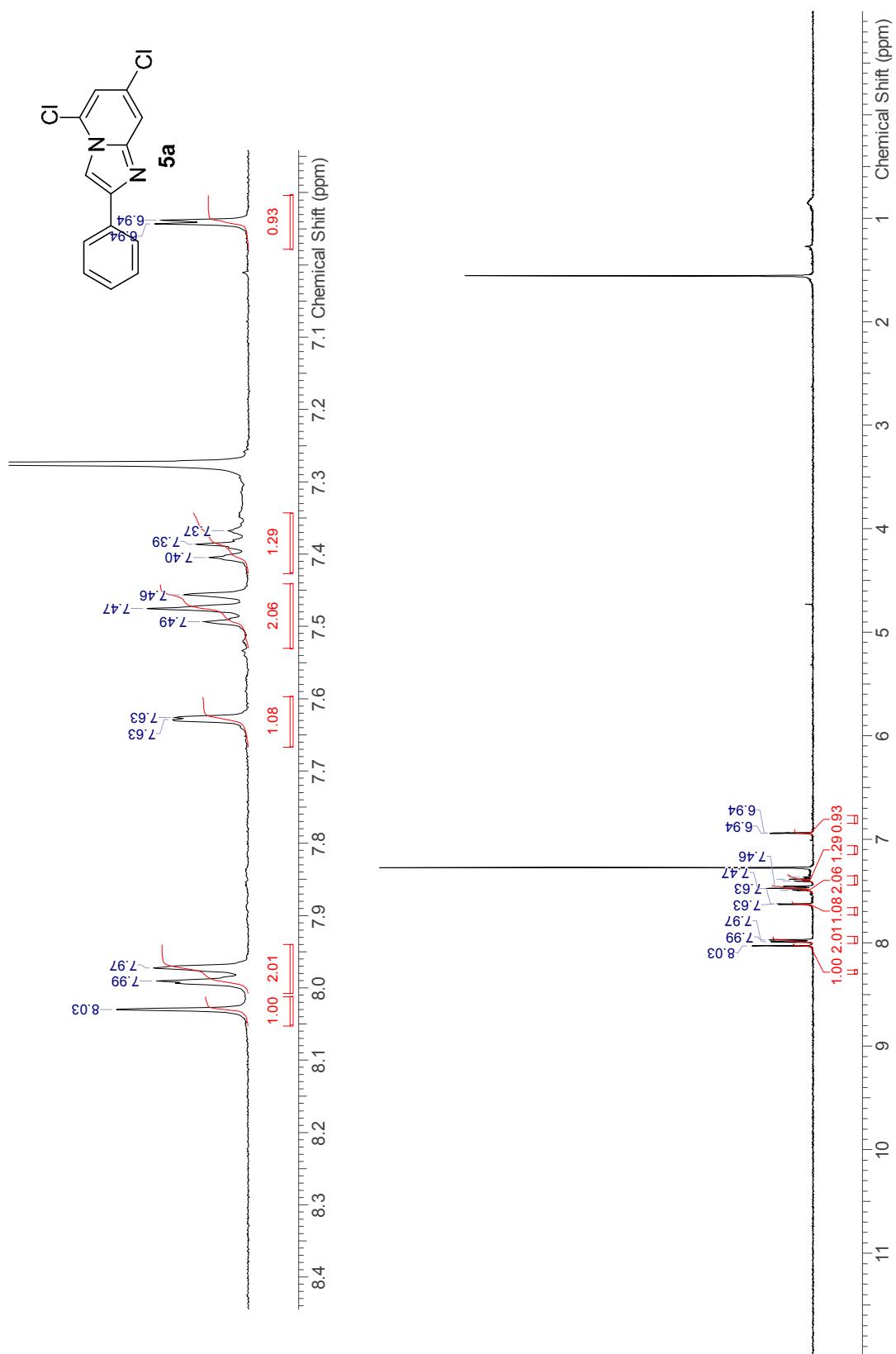
### 2,2-Dimethoxy-2-phenylethyl 4-methylbenzenesulfonate (**3**)

<sup>13</sup>C NMR ( $\delta$ , 26 MHz, CDCl<sub>3</sub>)



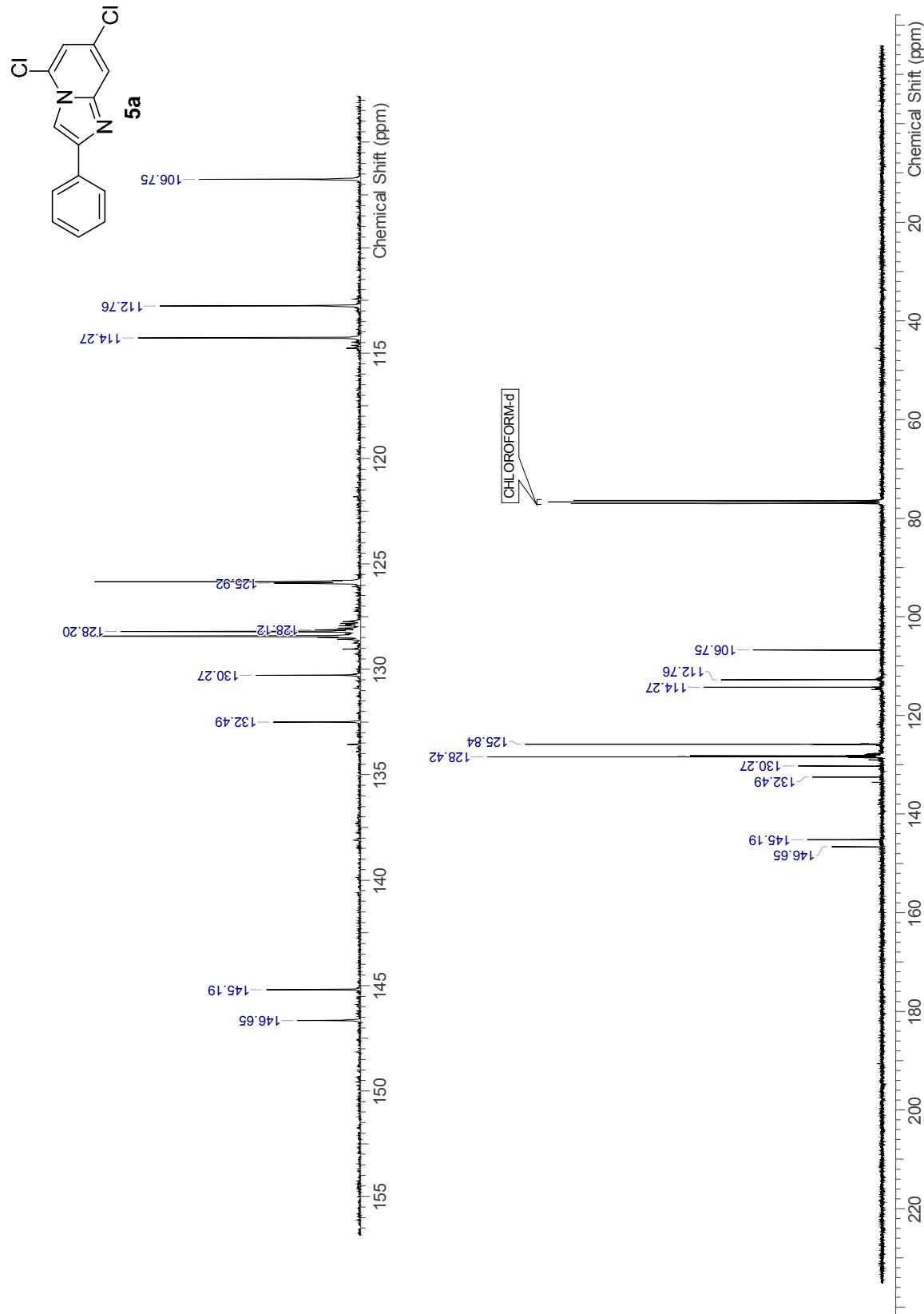
5,7-Dichloro-2-phenylimidazo[1,2-*a*]pyridine (**5a**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



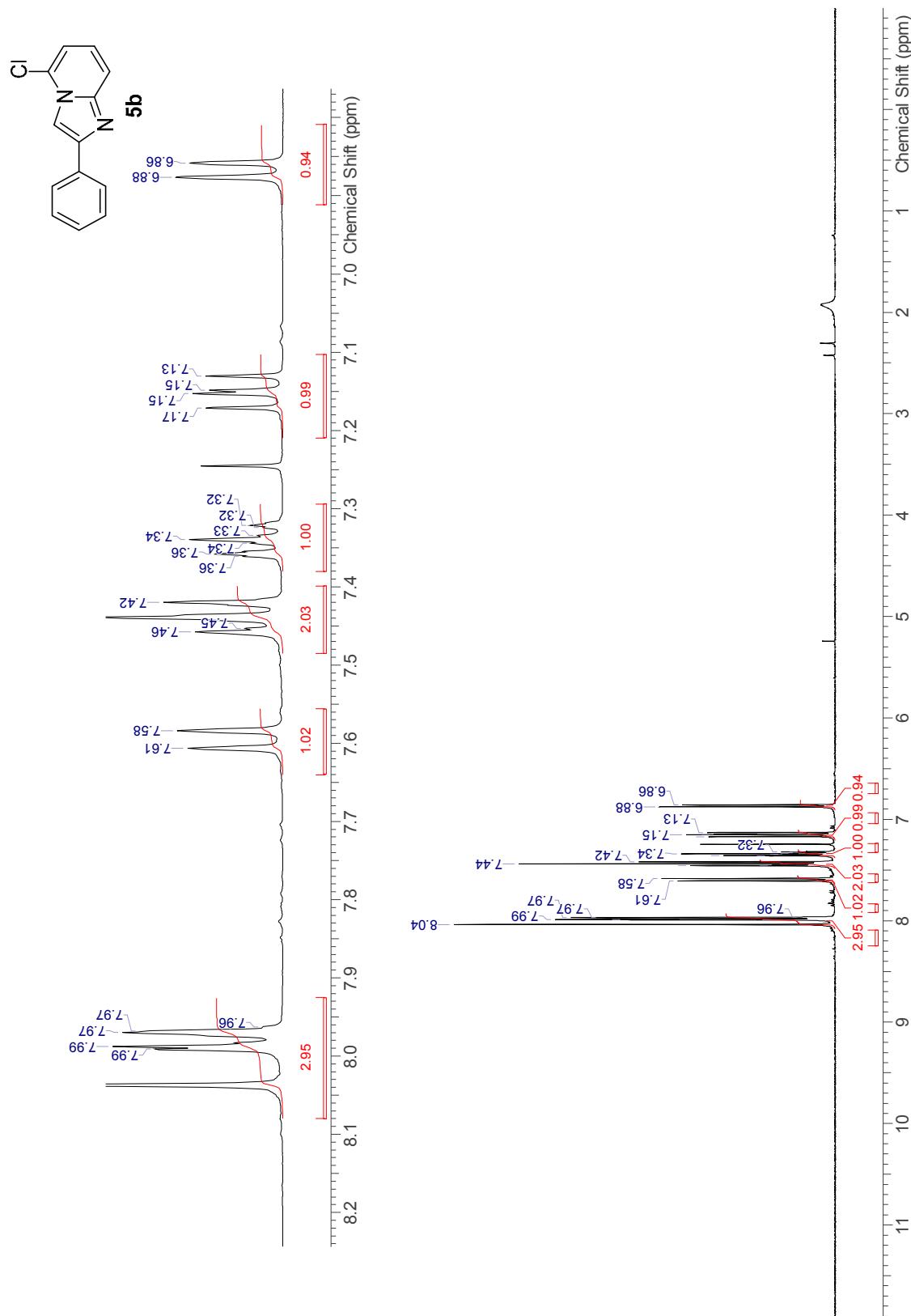
**5,7-Dichloro-2-phenylimidazo[1,2-*a*]pyridine (**5a**)**

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



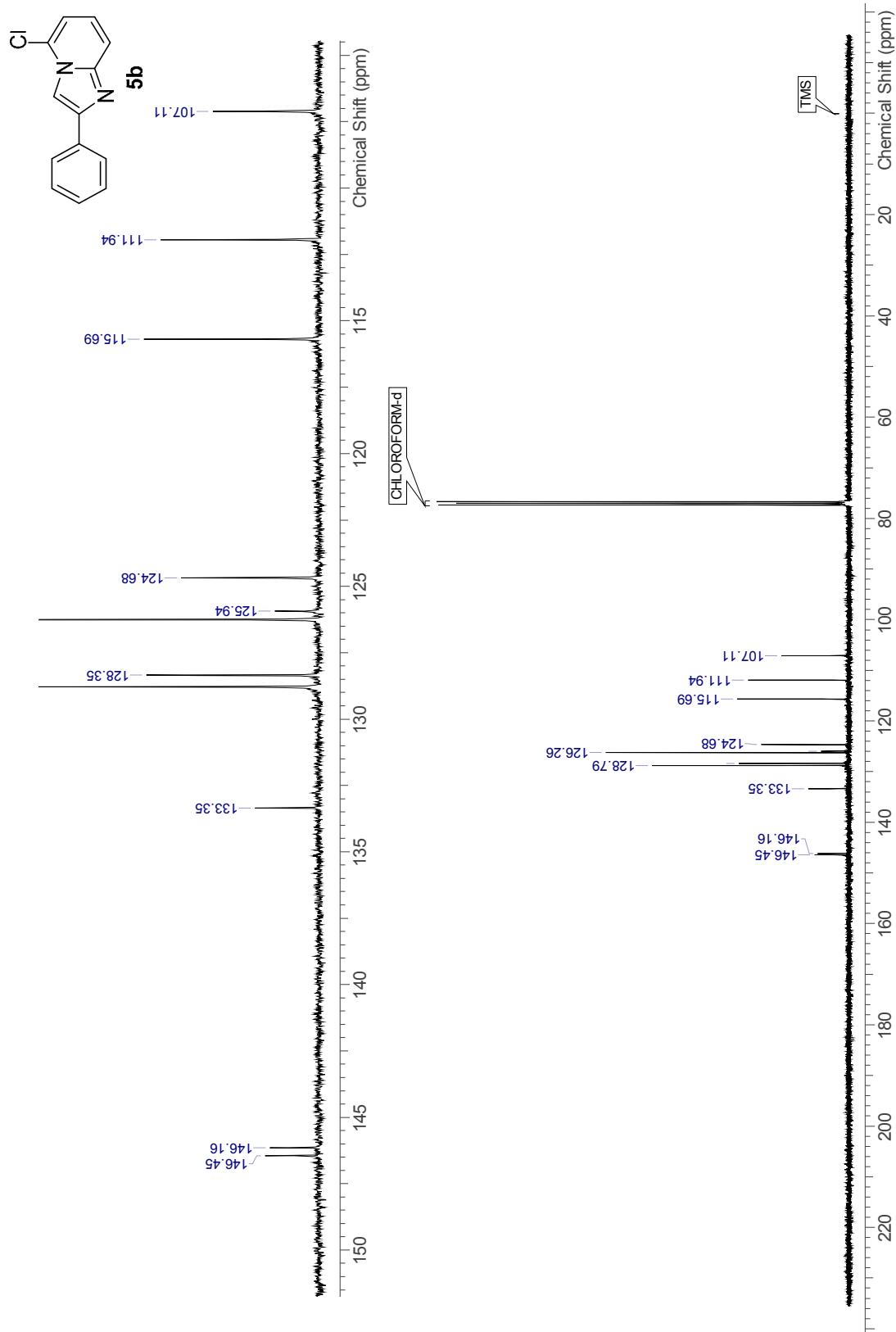
### 5-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5b**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



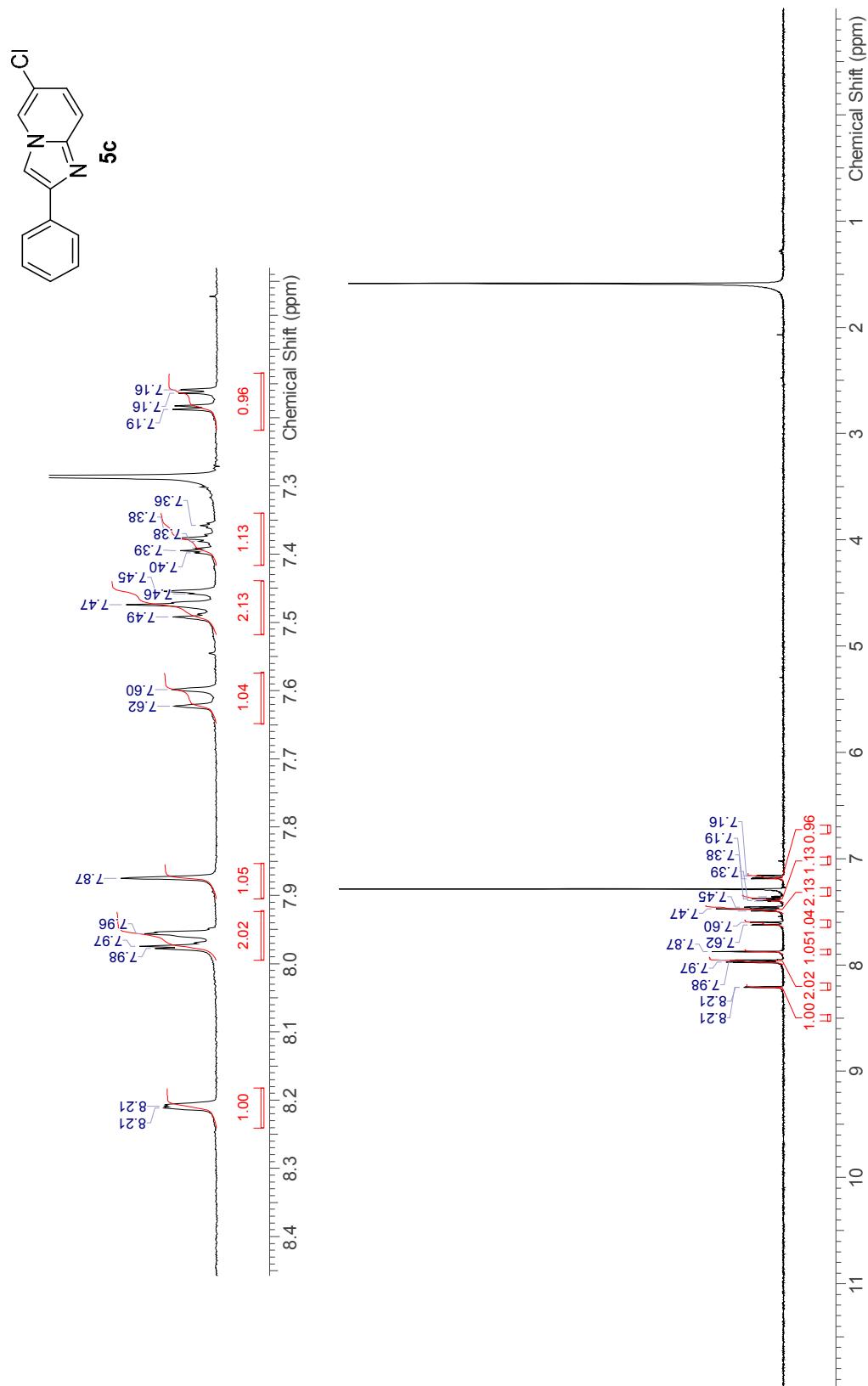
5-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5b**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



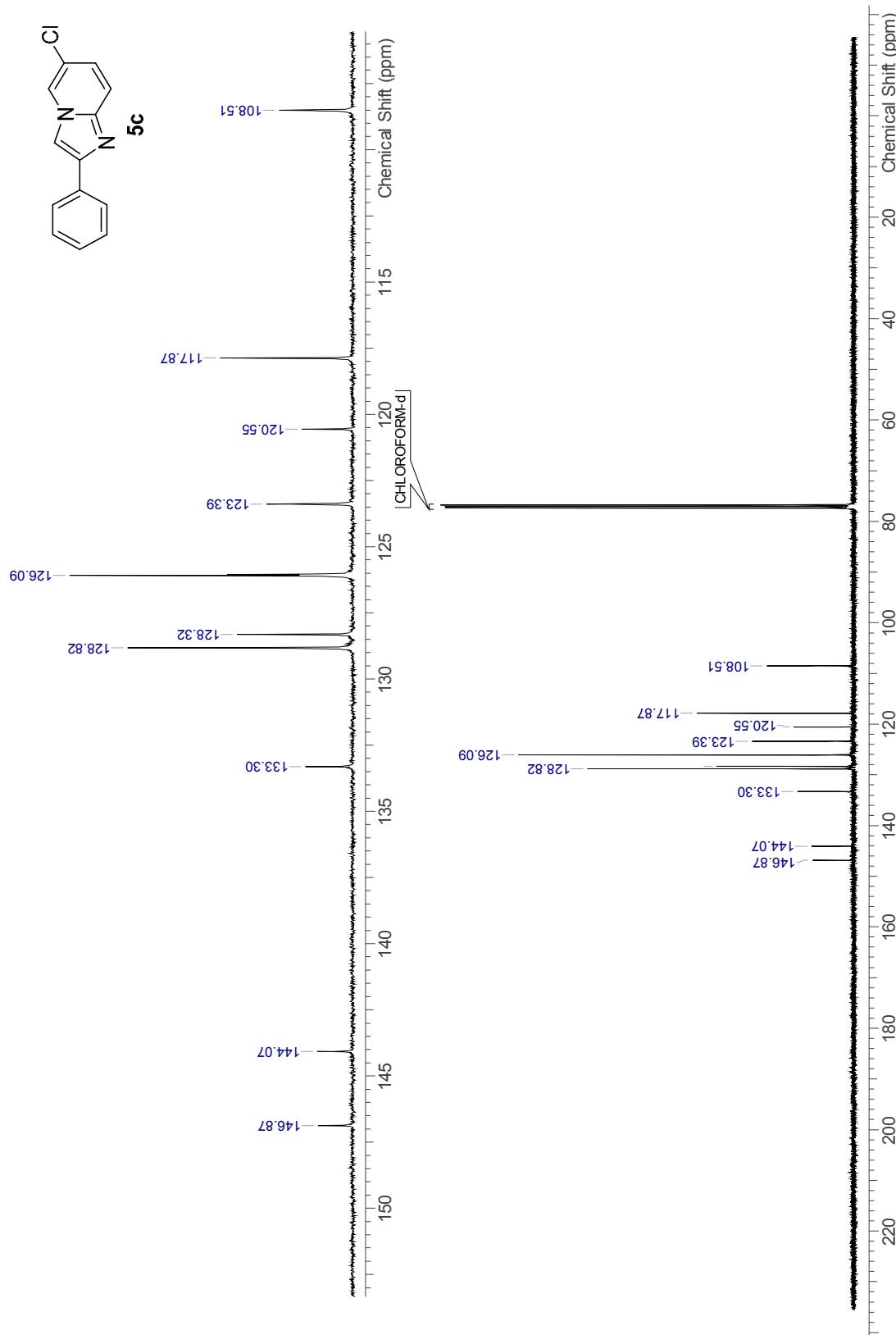
### 6-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5c**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



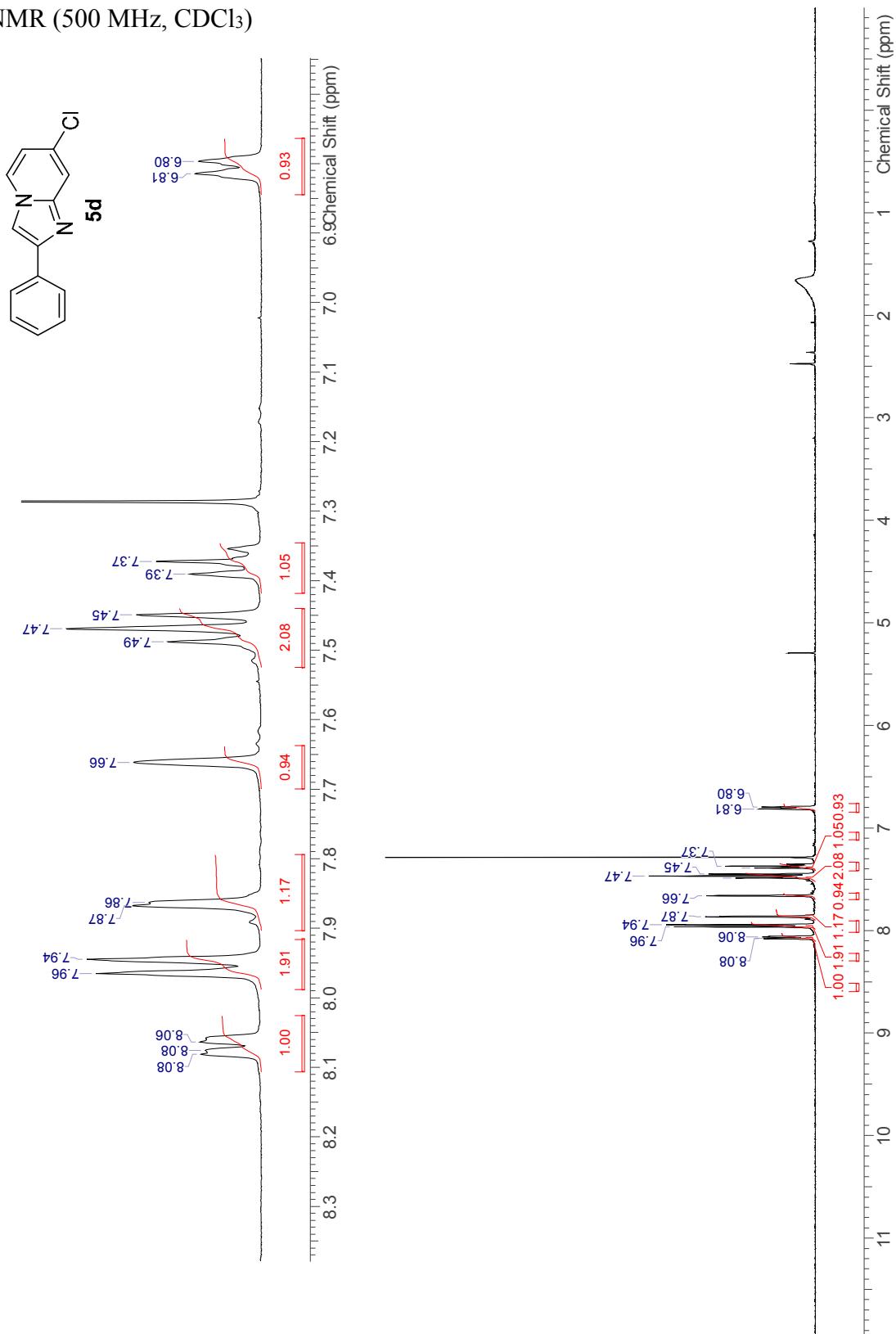
6-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5c**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



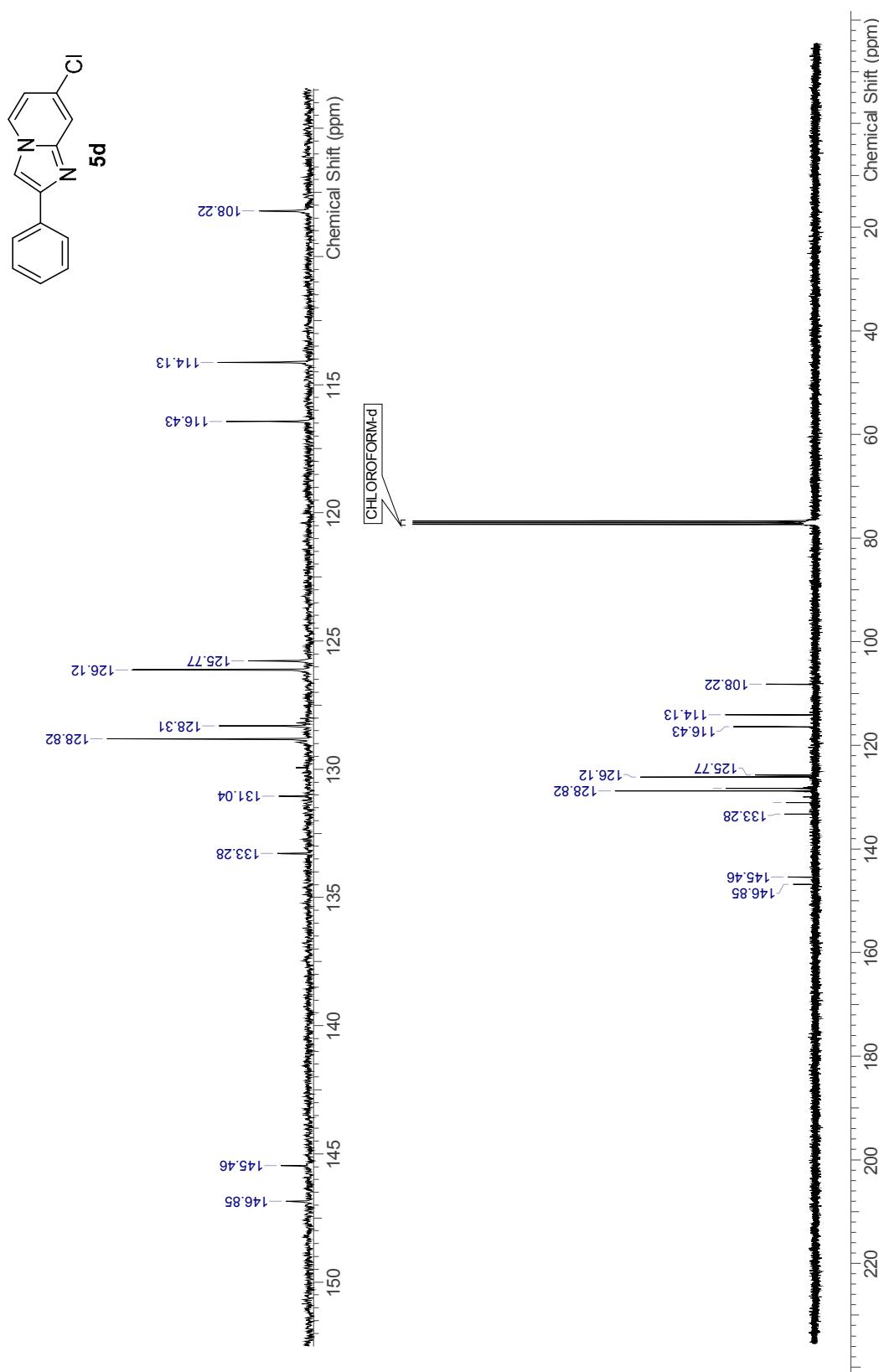
7-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5d**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



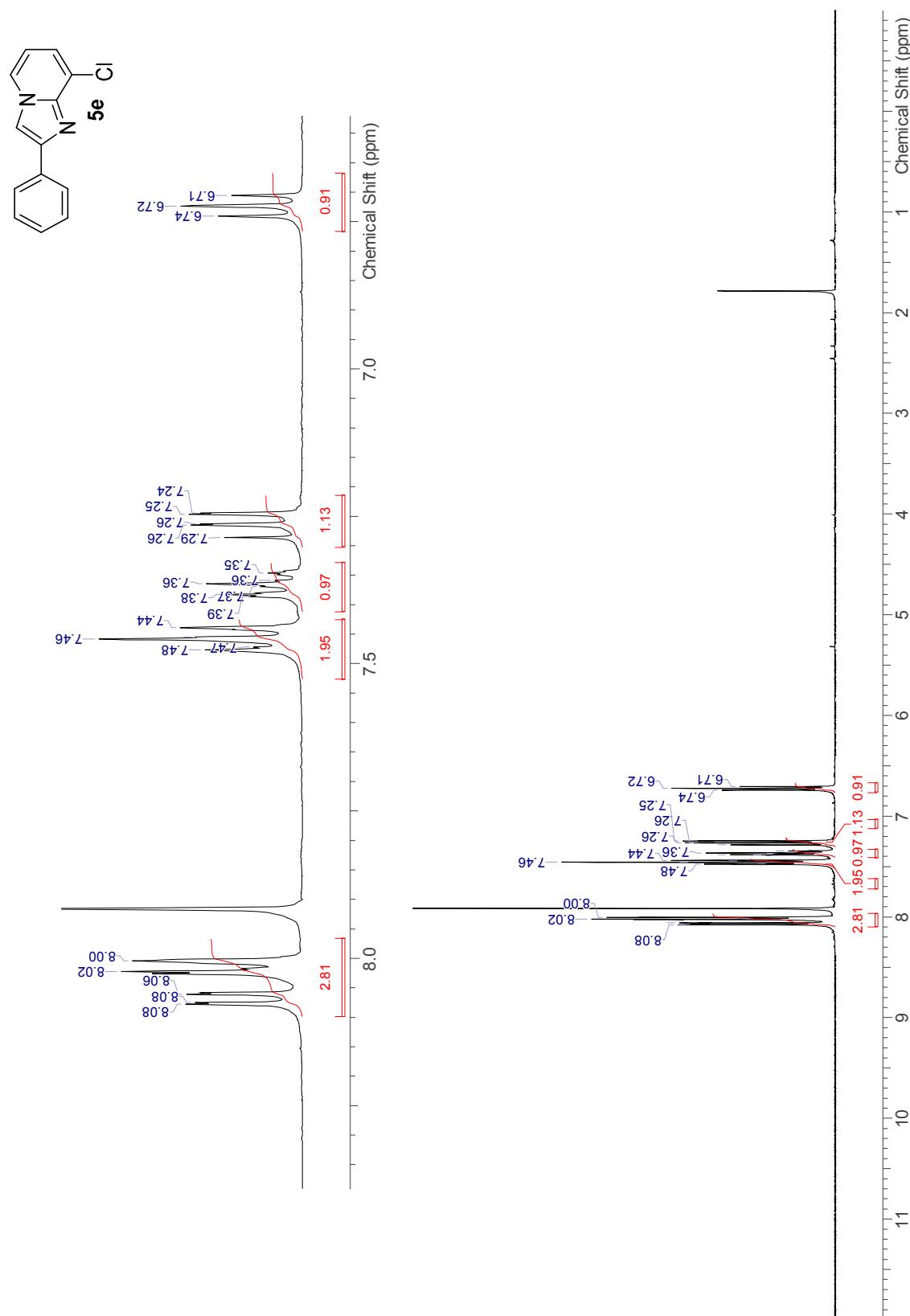
7-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5d**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



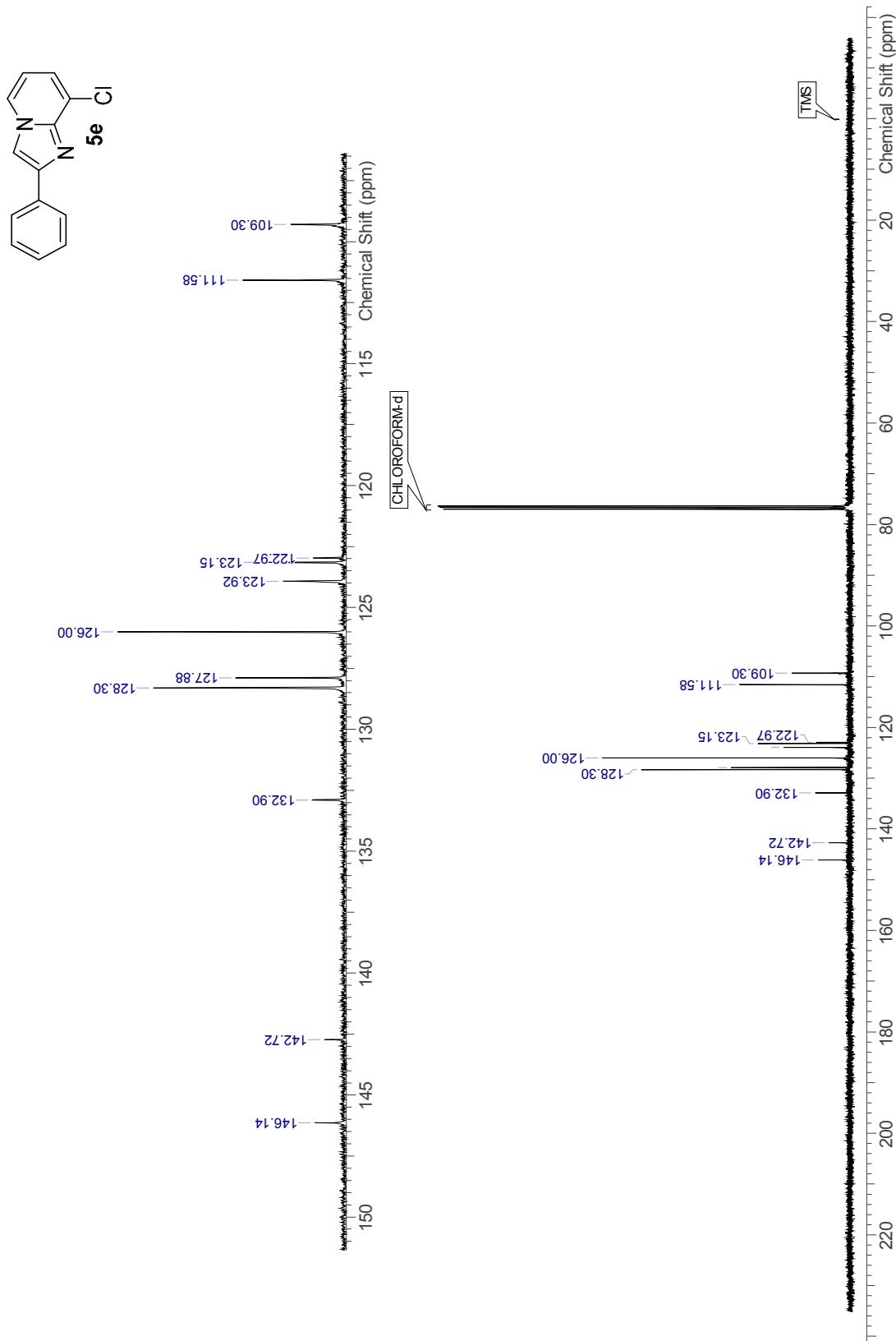
8-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5e**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



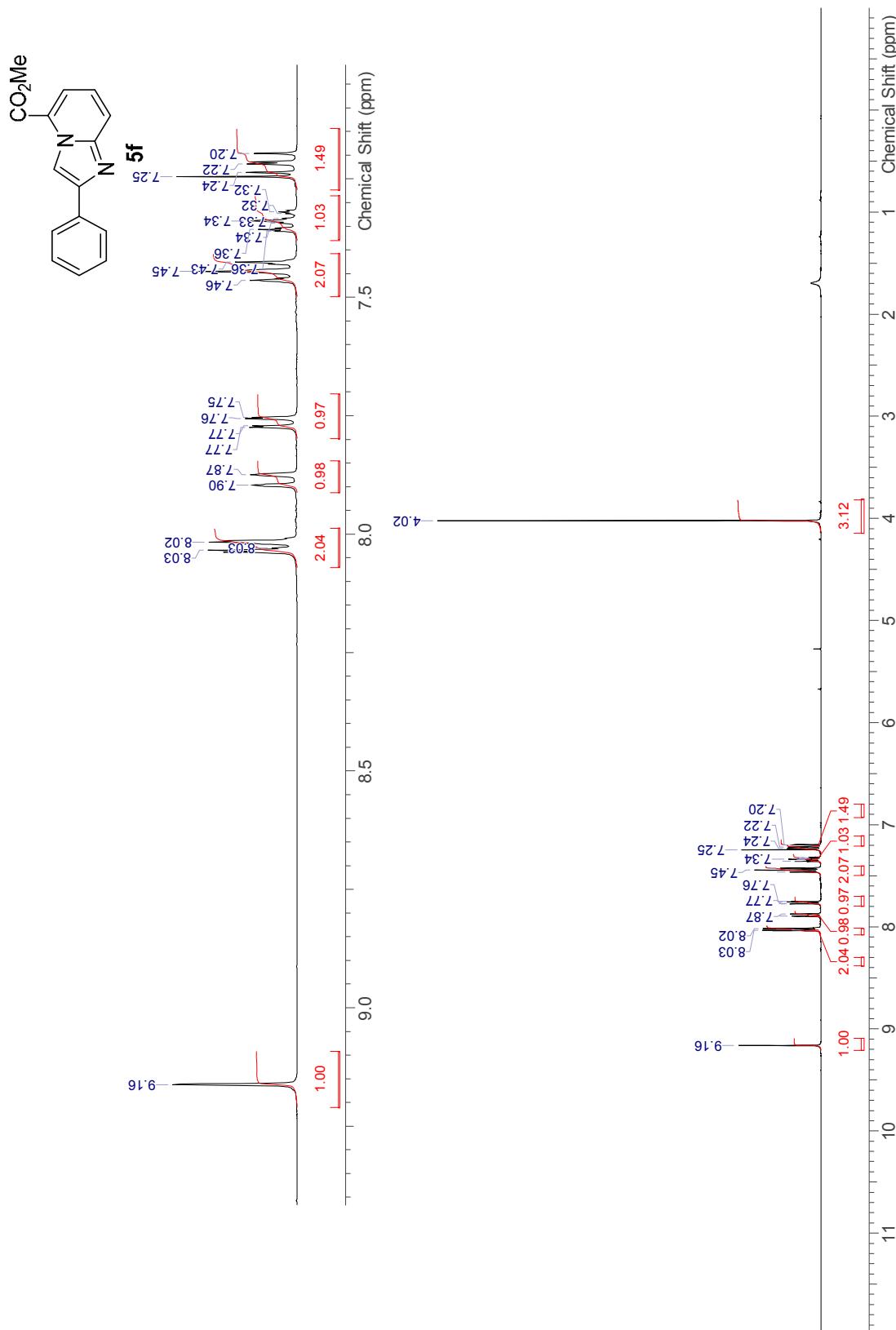
8-Chloro-2-phenylimidazo[1,2-*a*]pyridine (**5e**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



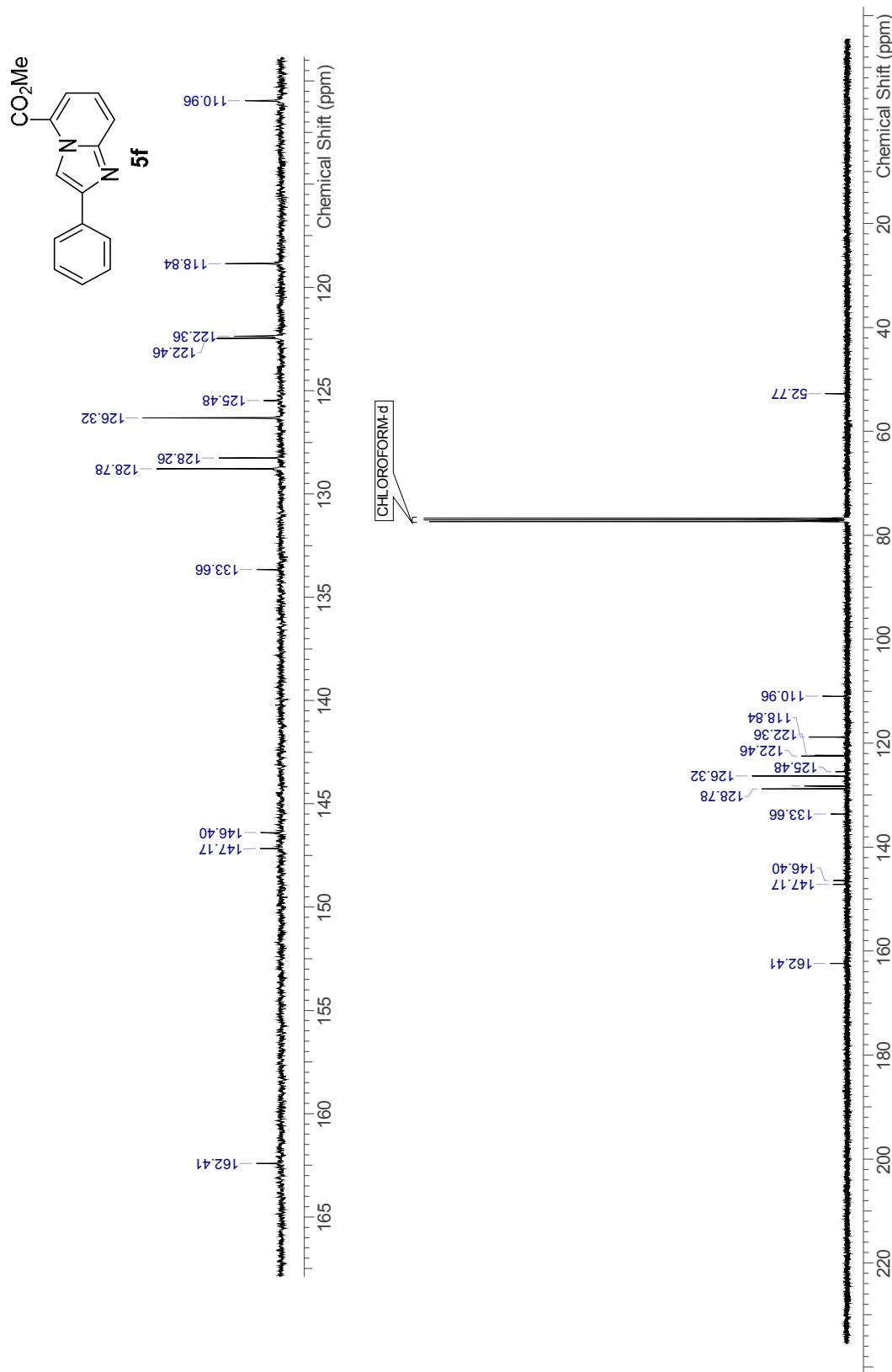
Methyl 2-phenylimidazo[1,2-*a*]pyridine-5-carboxylate (**5f**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



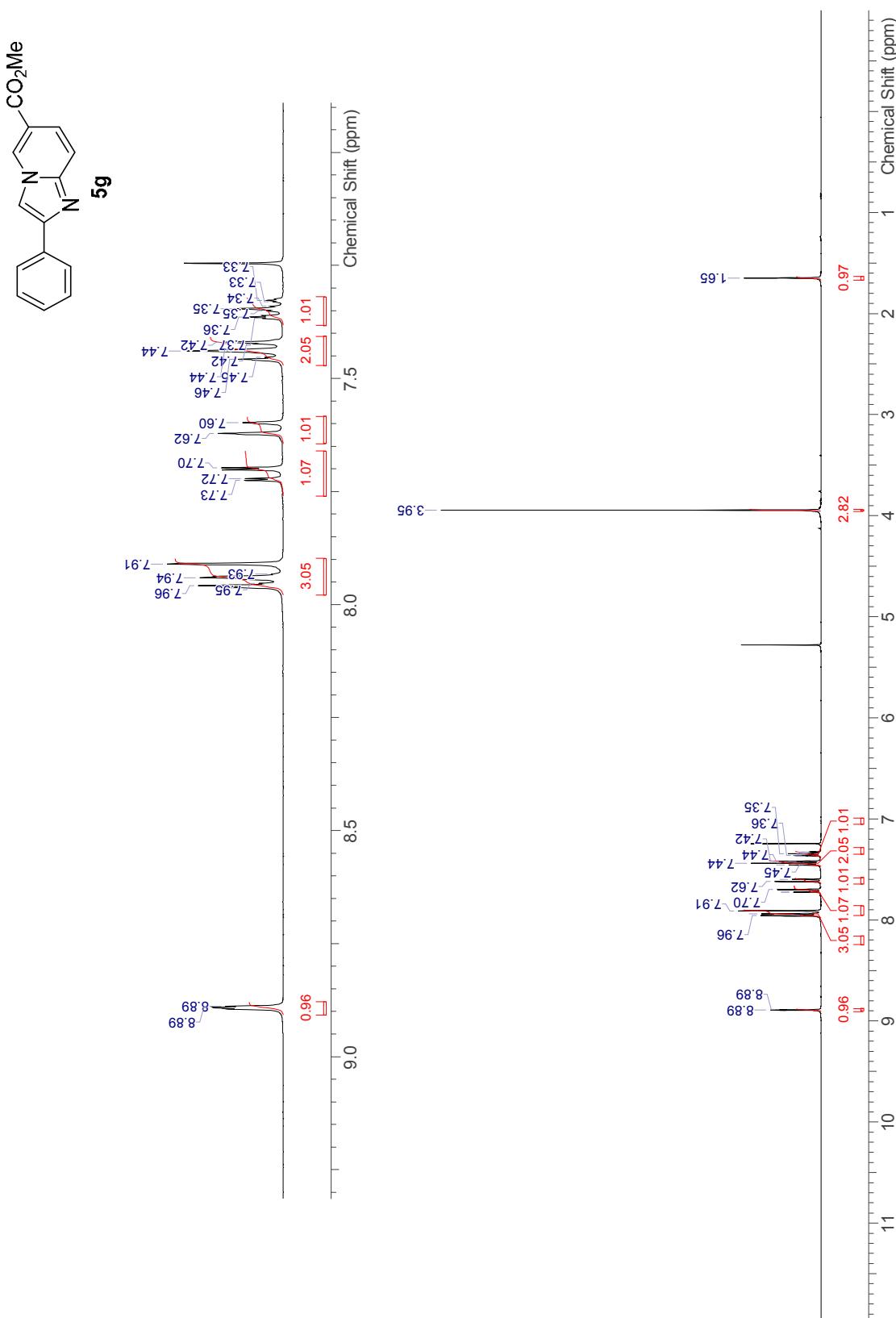
Methyl 2-phenylimidazo[1,2-*a*]pyridine-5-carboxylate (**5f**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



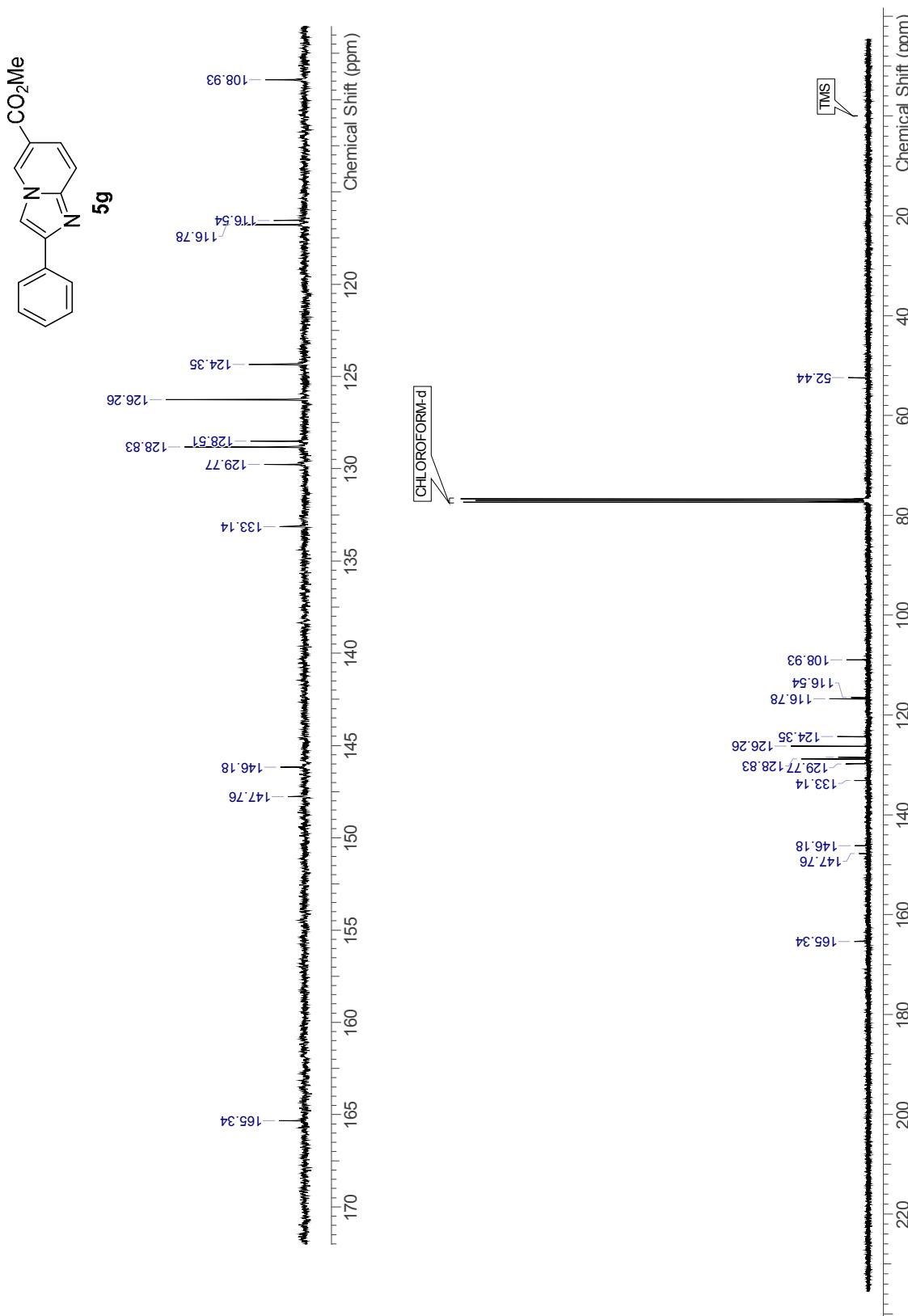
Methyl 2-phenylimidazo[1,2-*a*]pyridine-6-carboxylate (**5g**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

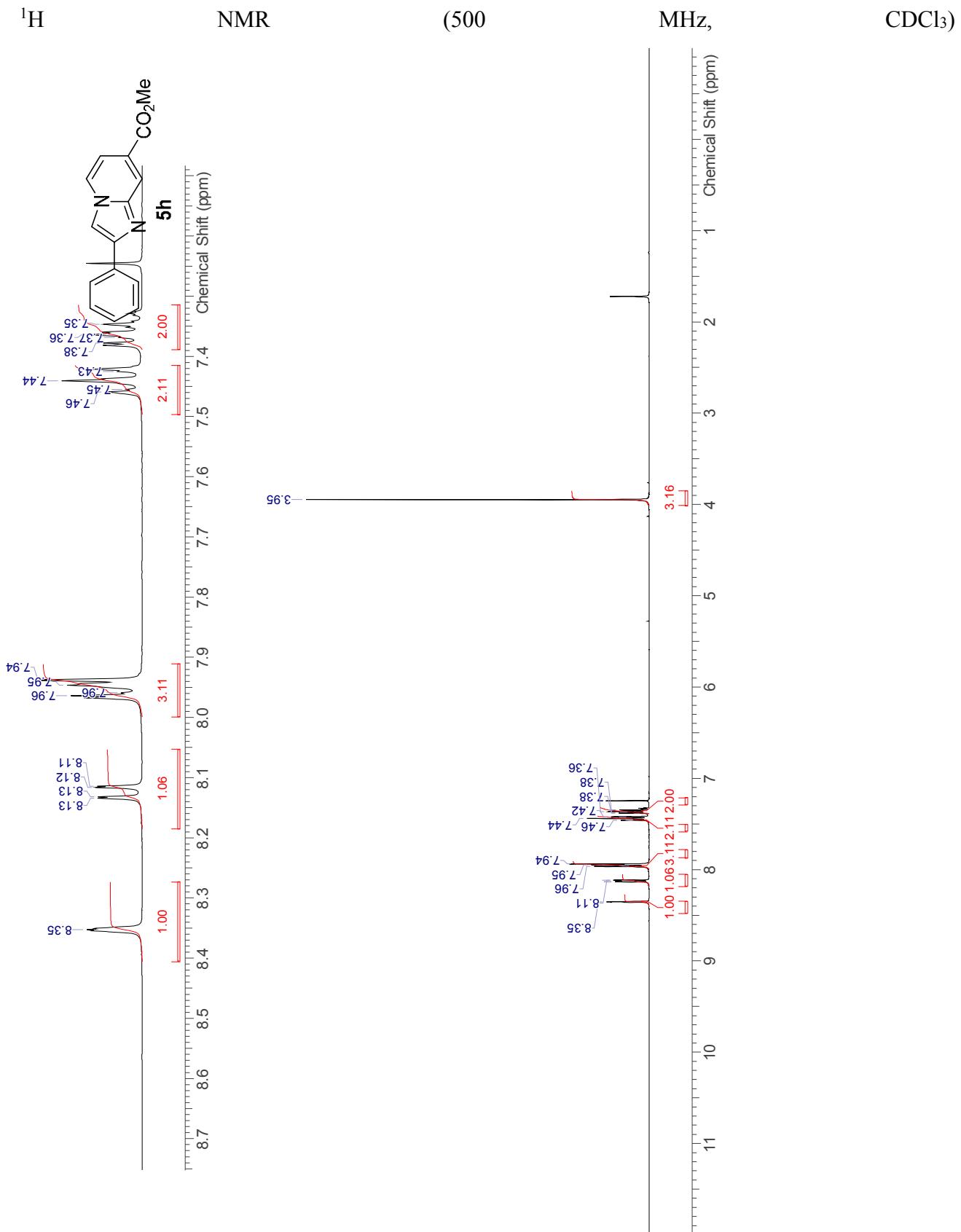


Methyl 2-phenylimidazo[1,2-*a*]pyridine-6-carboxylate (**5g**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

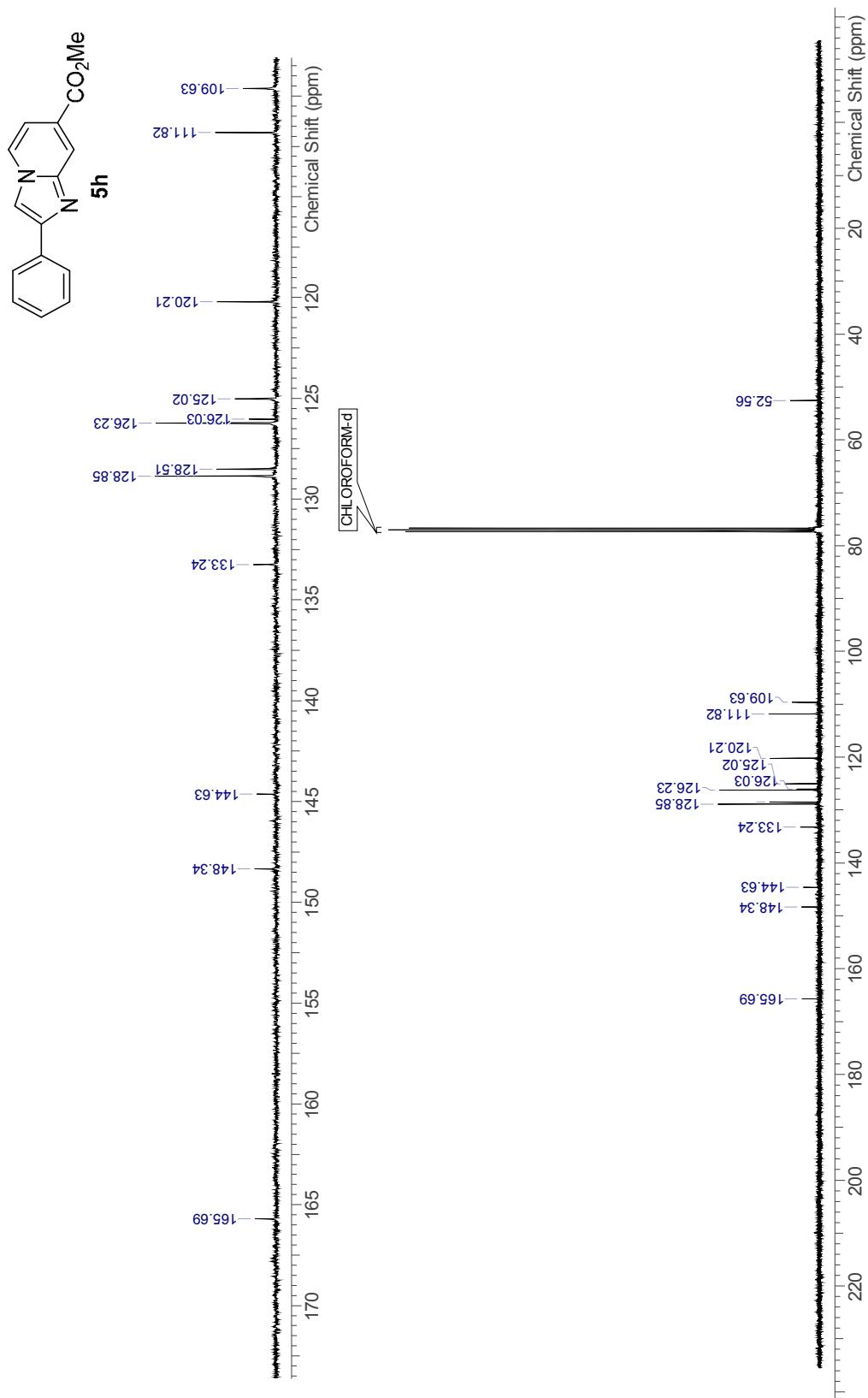


Methyl 2-phenylimidazo[1,2-*a*]pyridine-7-carboxylate (**5h**)



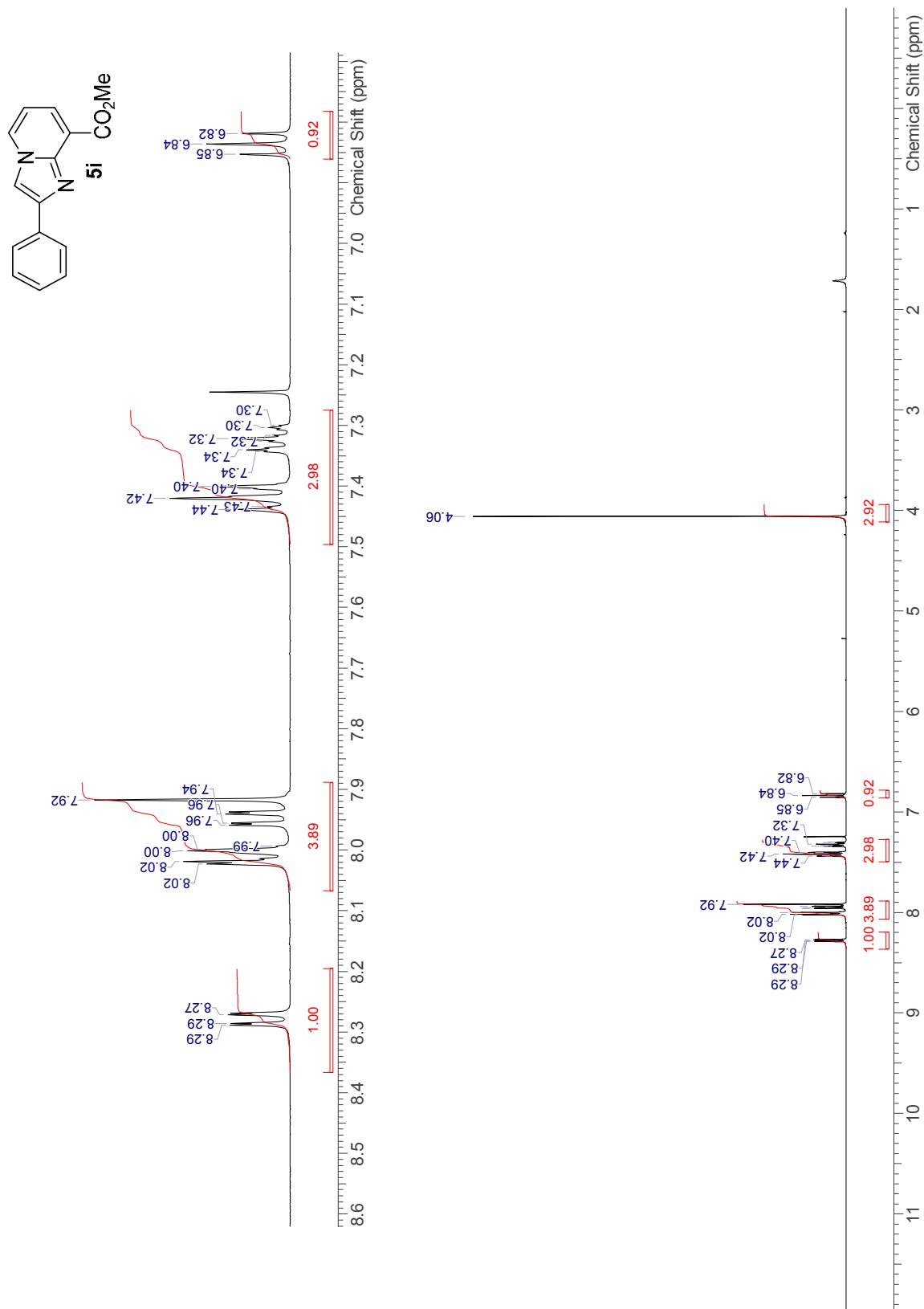
Methyl 2-phenylimidazo[1,2-*a*]pyridine-7-carboxylate (**5h**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



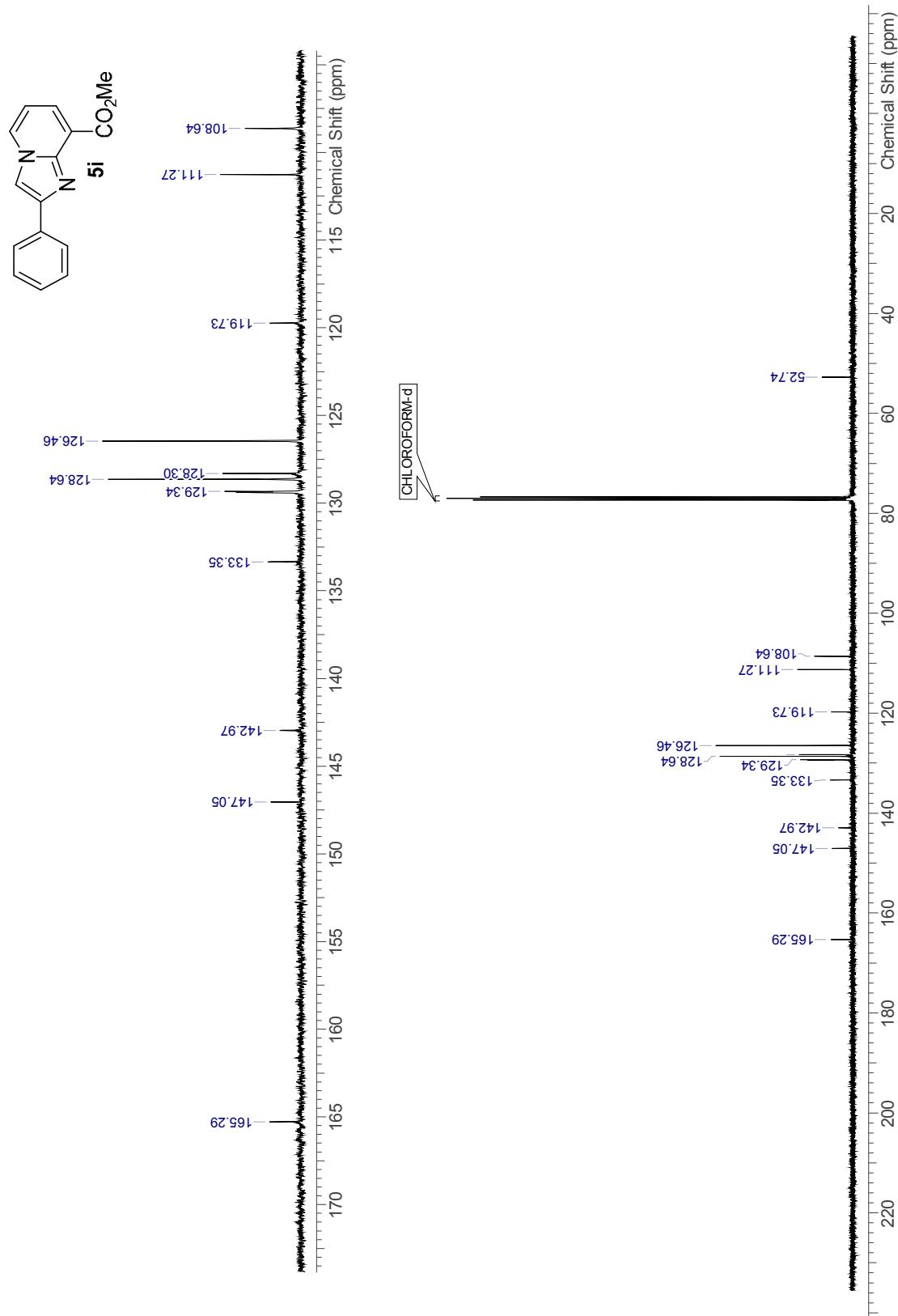
### Methyl 2-phenylimidazo[1,2-*a*]pyridine-8-carboxylate (**5i**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



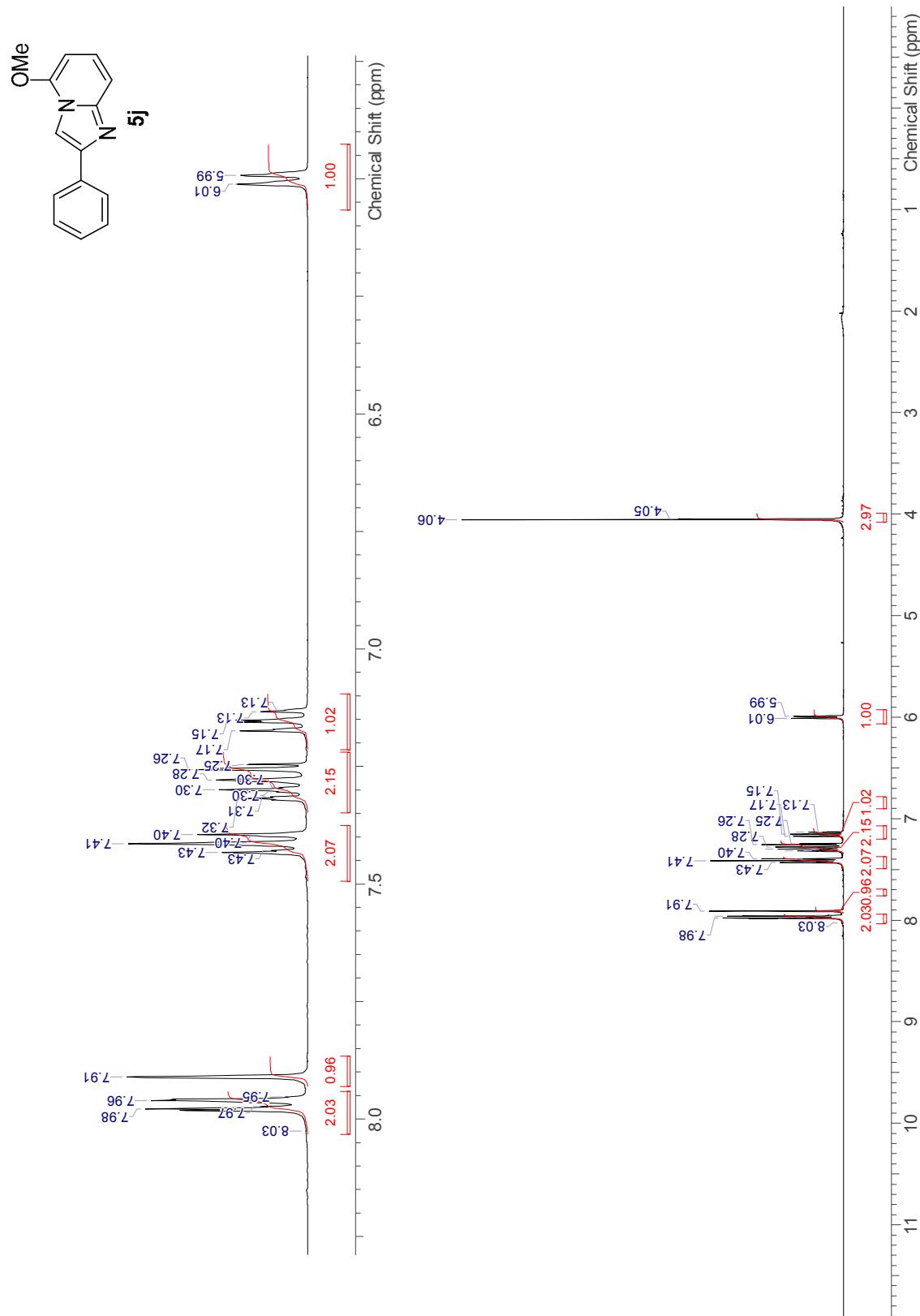
Methyl 2-phenylimidazo[1,2-*a*]pyridine-8-carboxylate (**5i**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



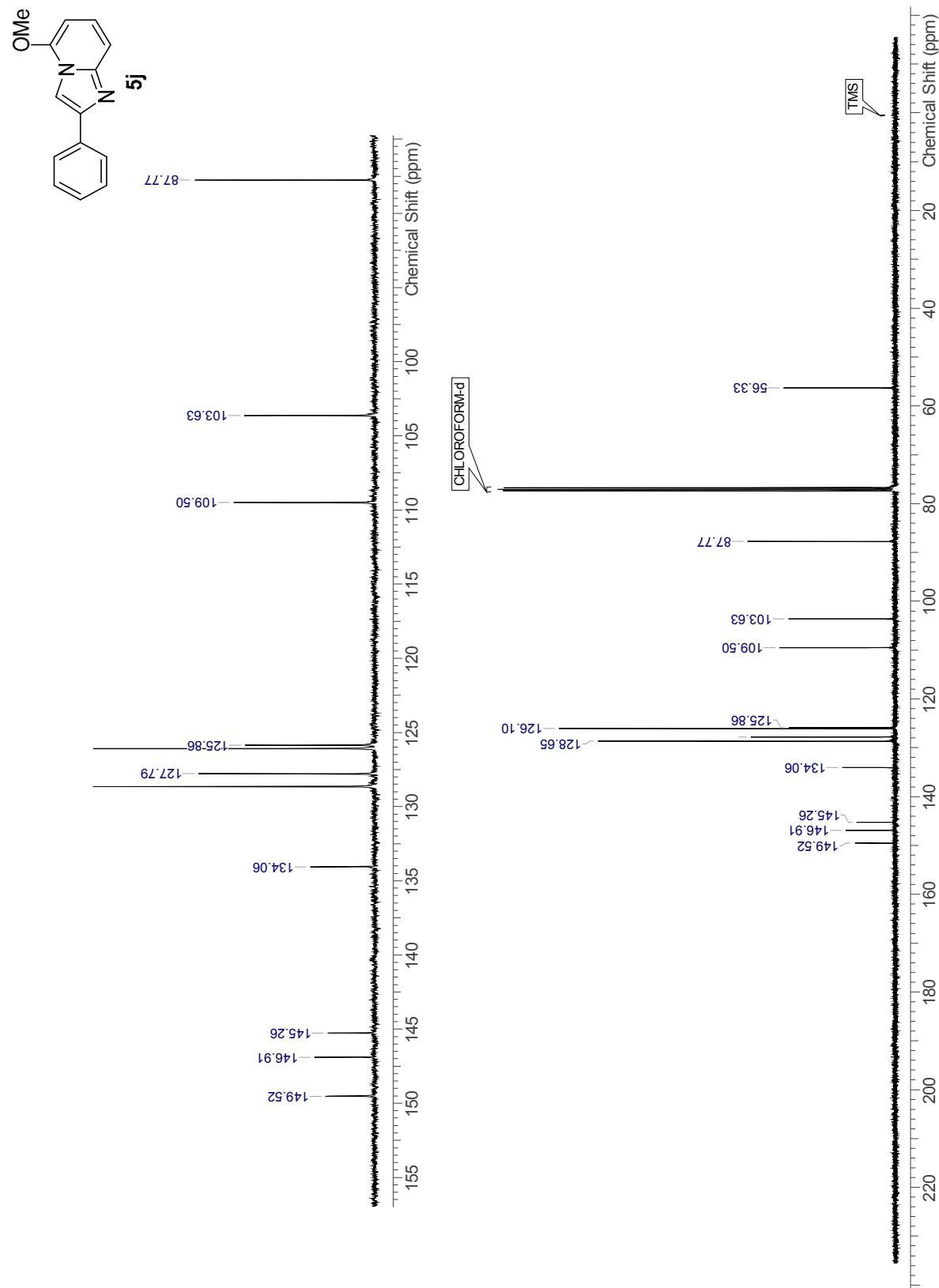
5-Methoxy-2-phenylimidazo[1,2-a]pyridine (**5j**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



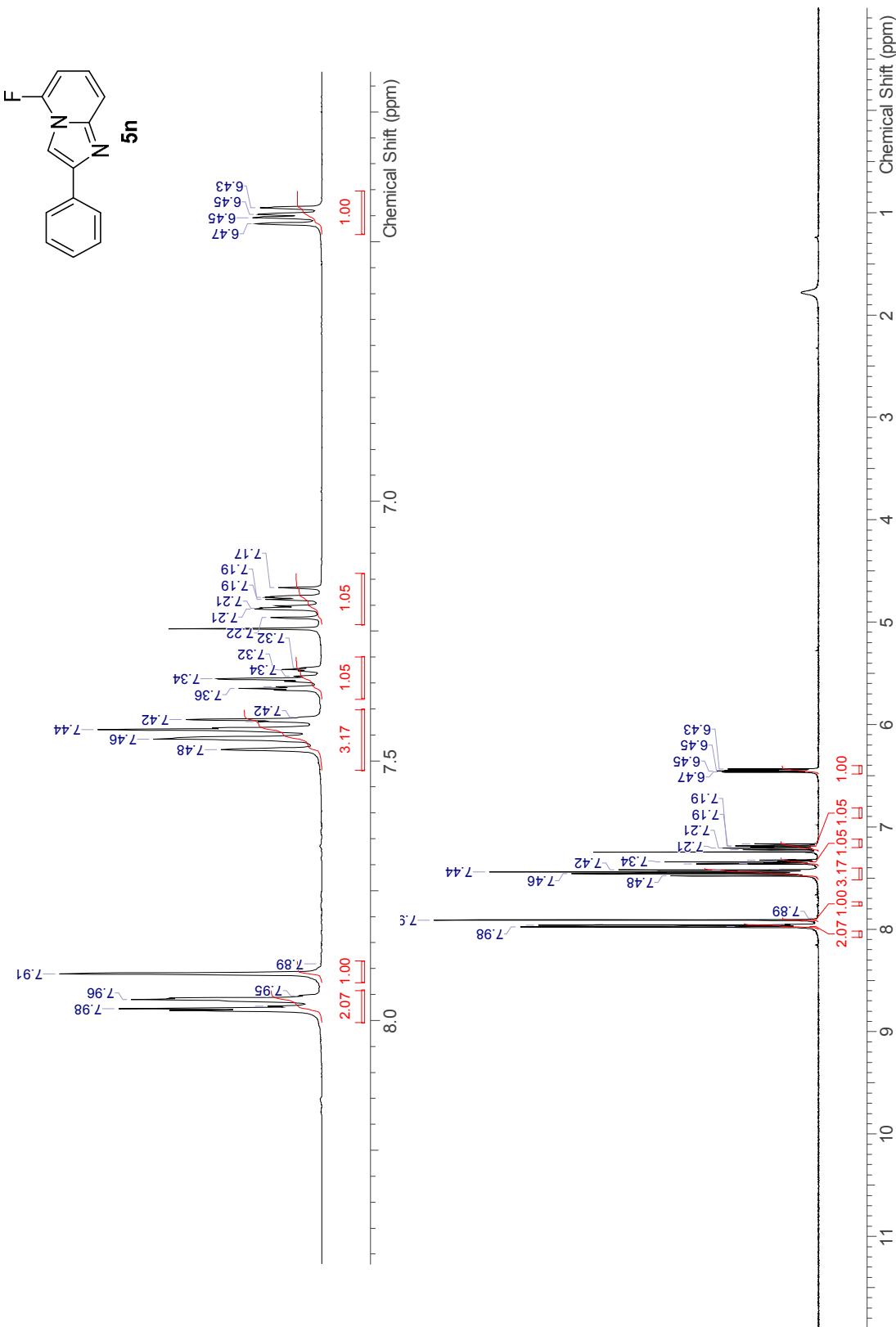
5-Methoxy-2-phenylimidazo[1,2-a]pyridine (**5j**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



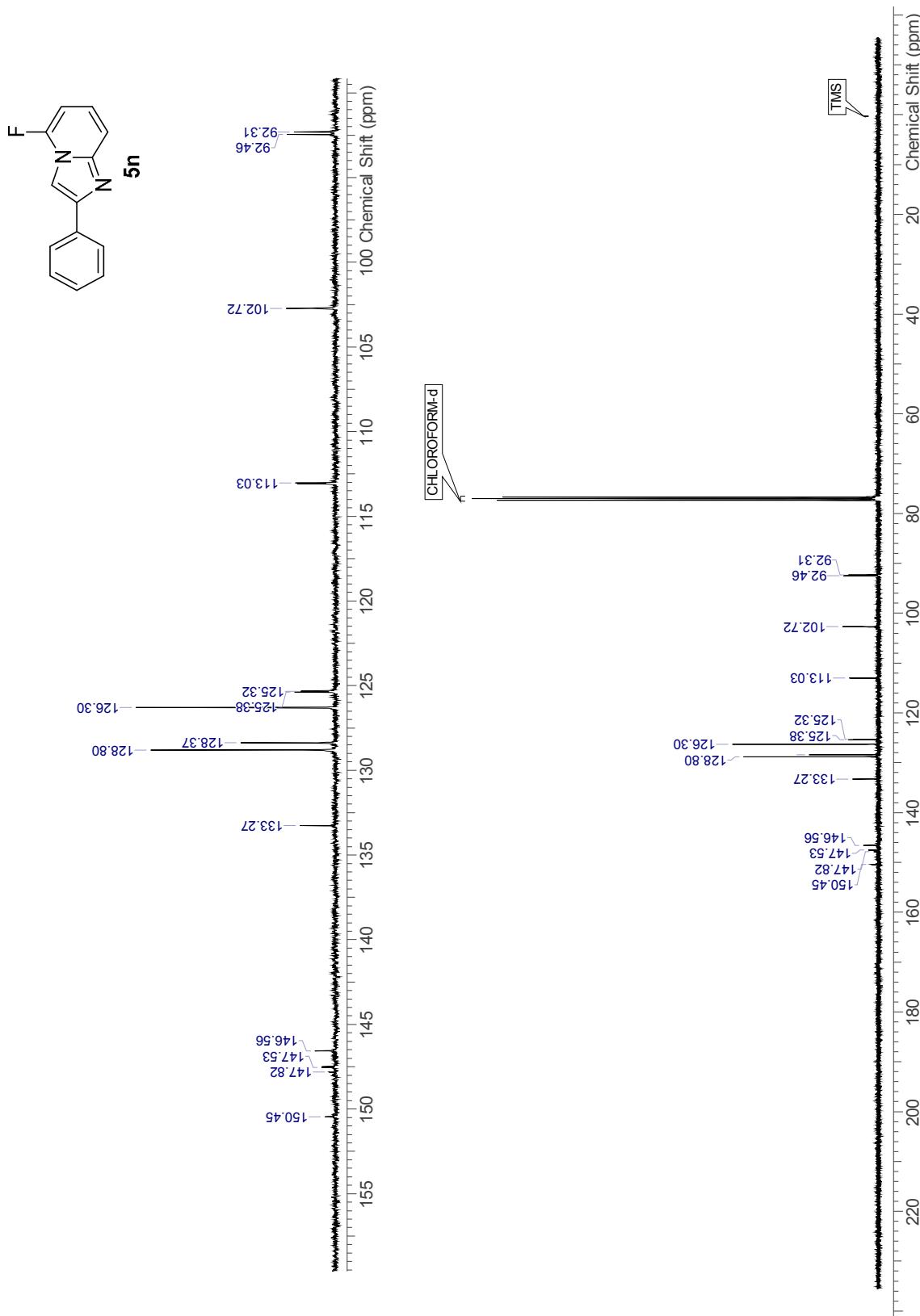
### 5-Fluoro-2-phenylimidazo[1,2-*a*]pyridine (**5n**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



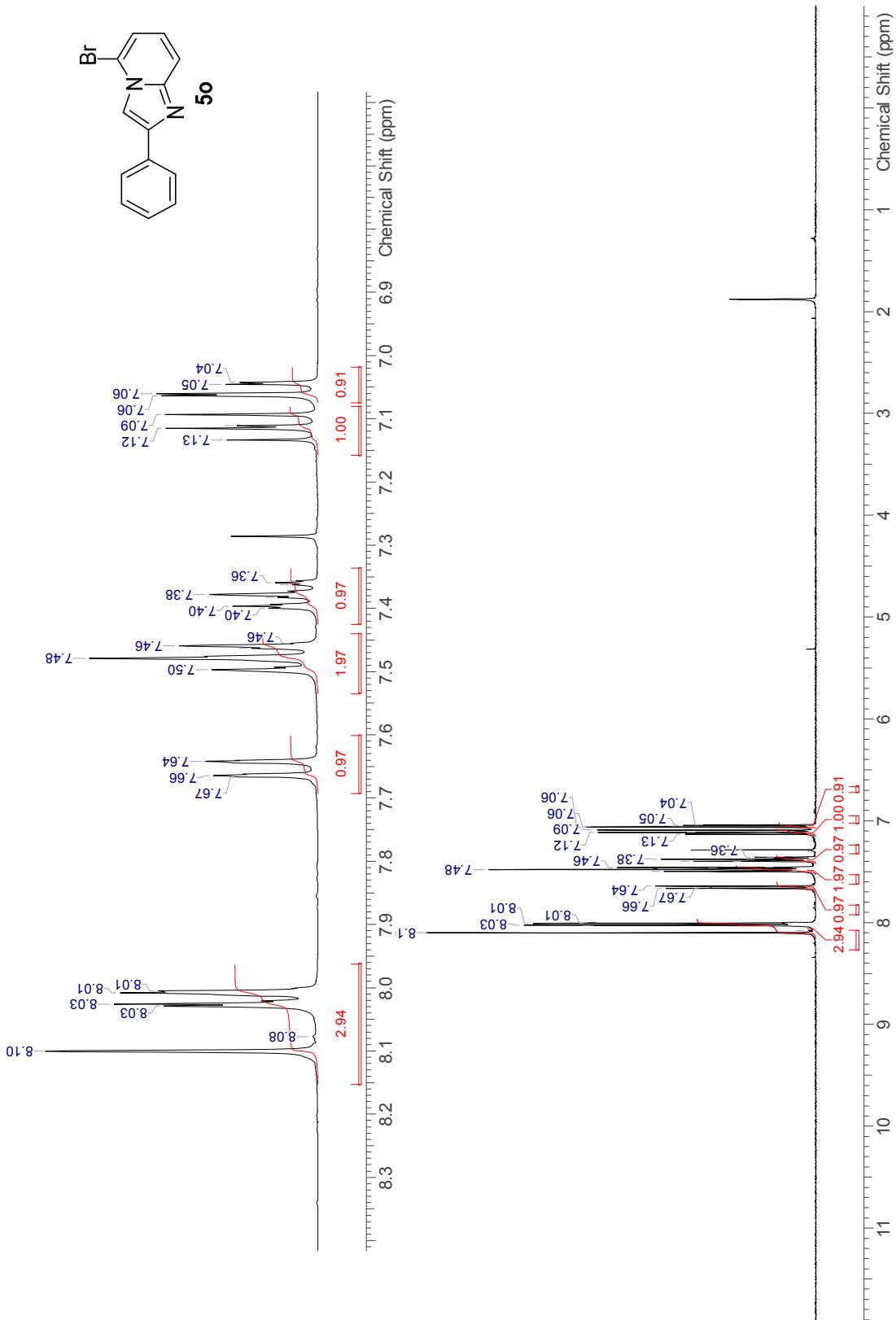
5-Fluoro-2-phenylimidazo[1,2-*a*]pyridine (**5n**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



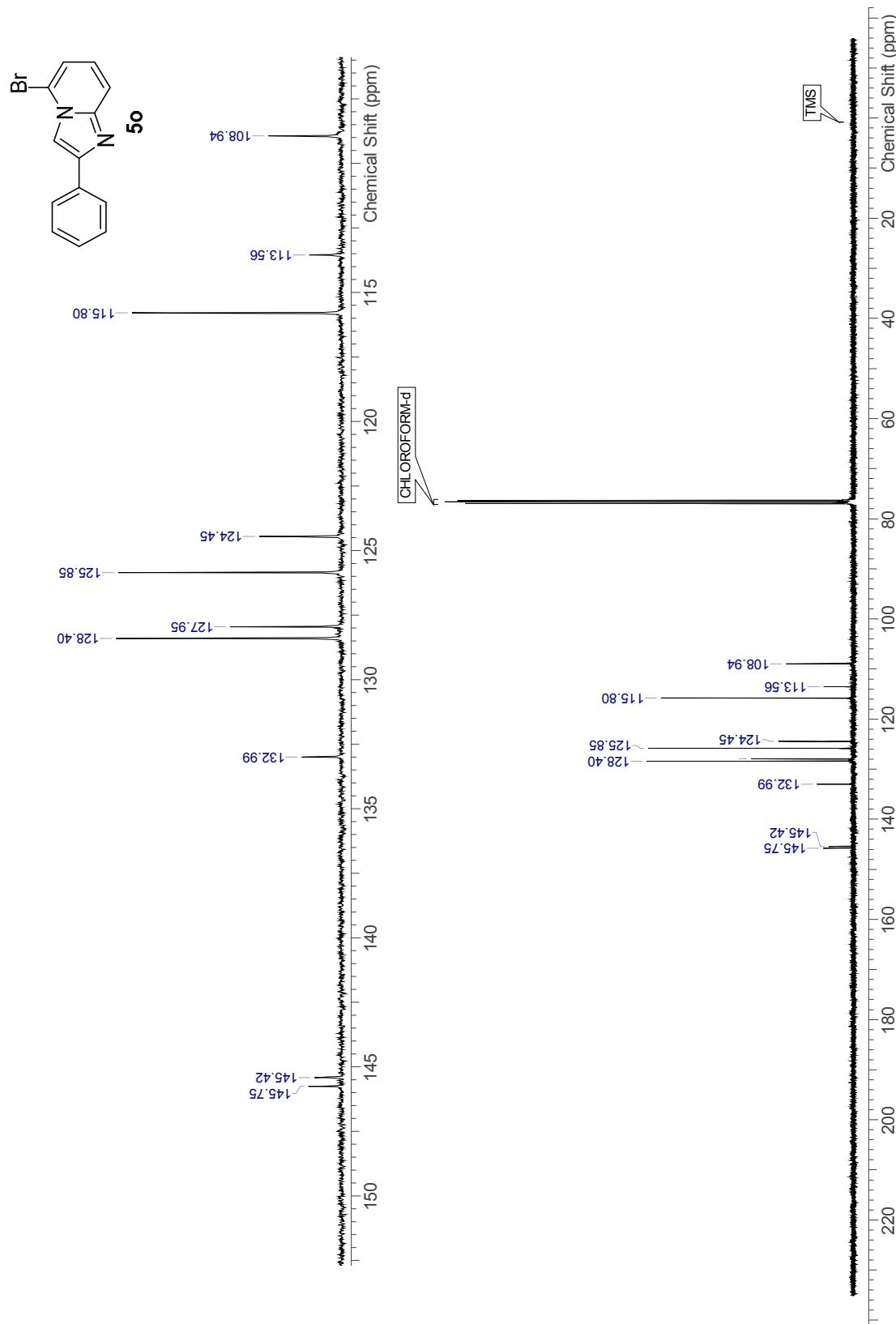
5-Bromo-2-phenylimidazo[1,2-*a*]pyridine (**5o**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



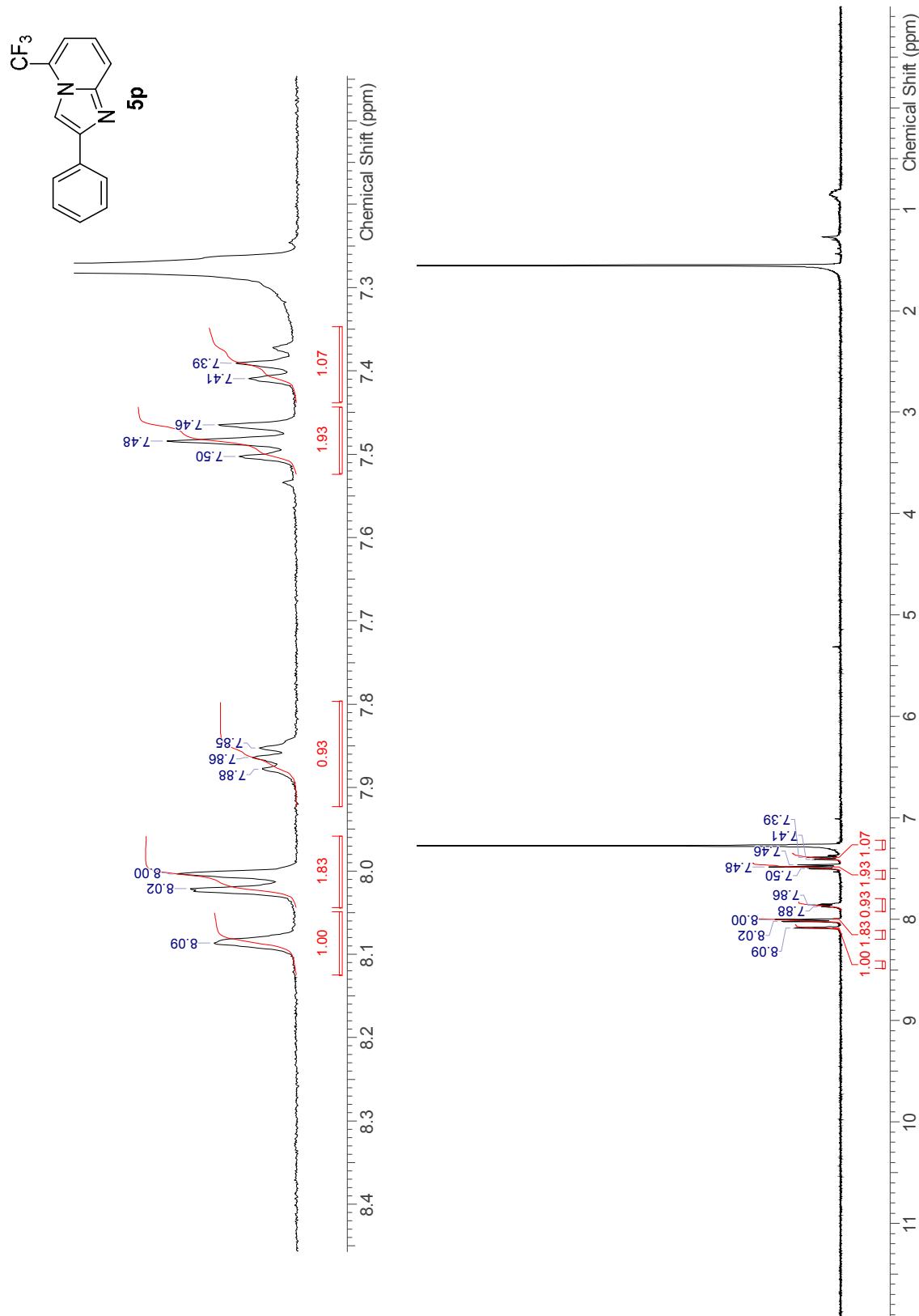
5-Bromo-2-phenylimidazo[1,2-*a*]pyridine (**5o**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

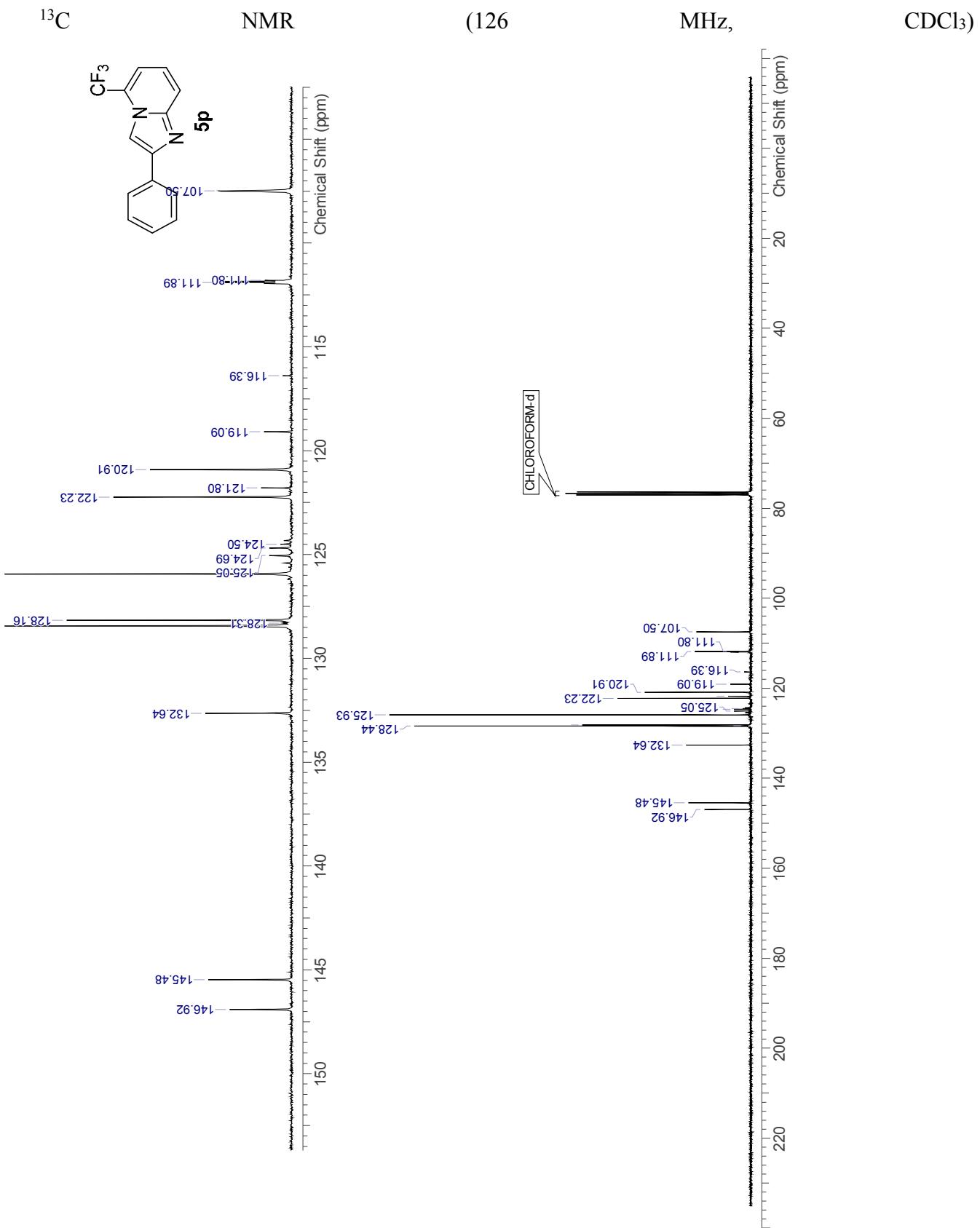


5-Trifluoromethyl-2-phenylimidazo[1,2-*a*]pyridine (**5p**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

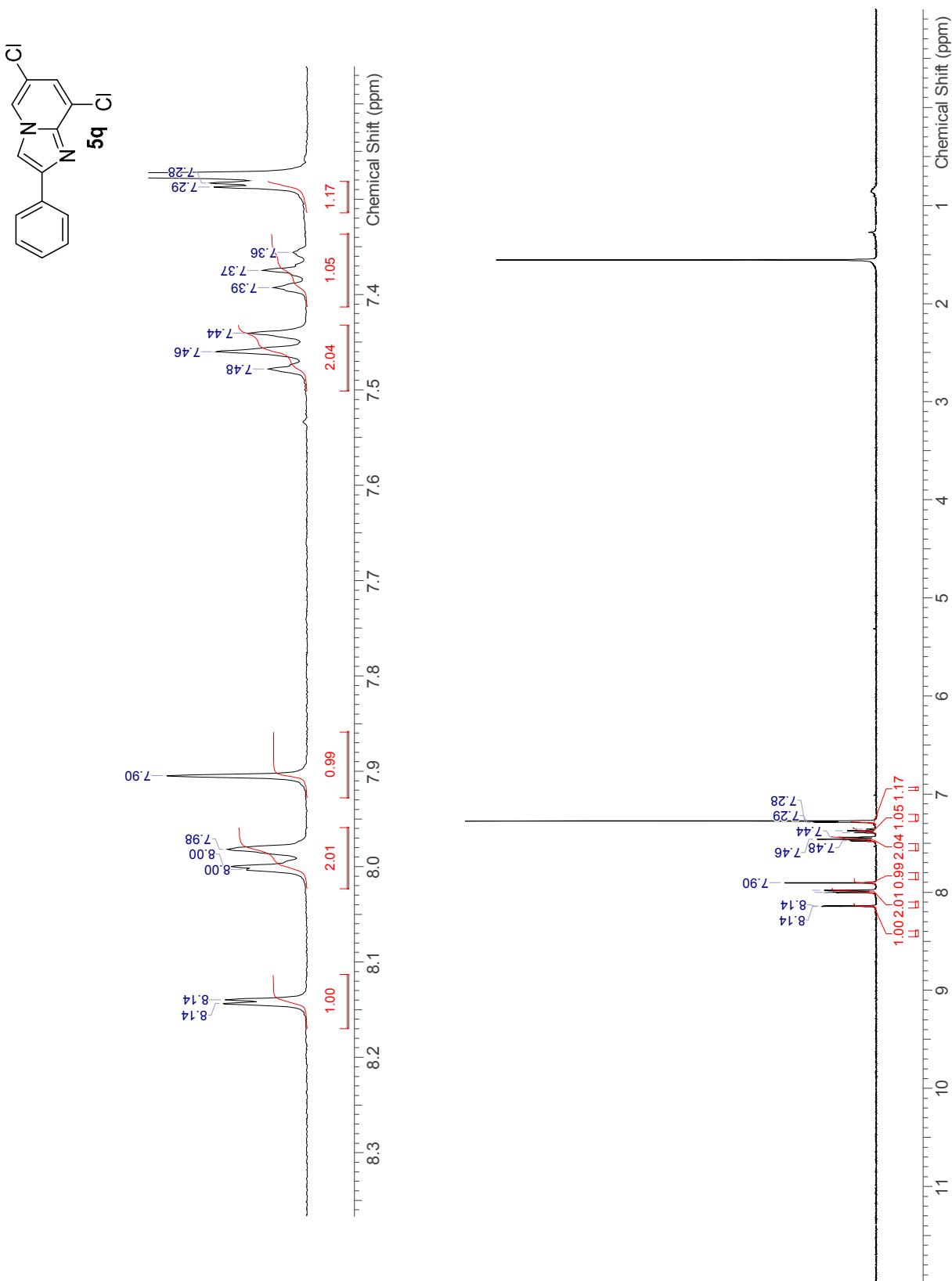


### 5-Trifluoromethyl-2-phenylimidazo[1,2-*a*]pyridine (**5p**)



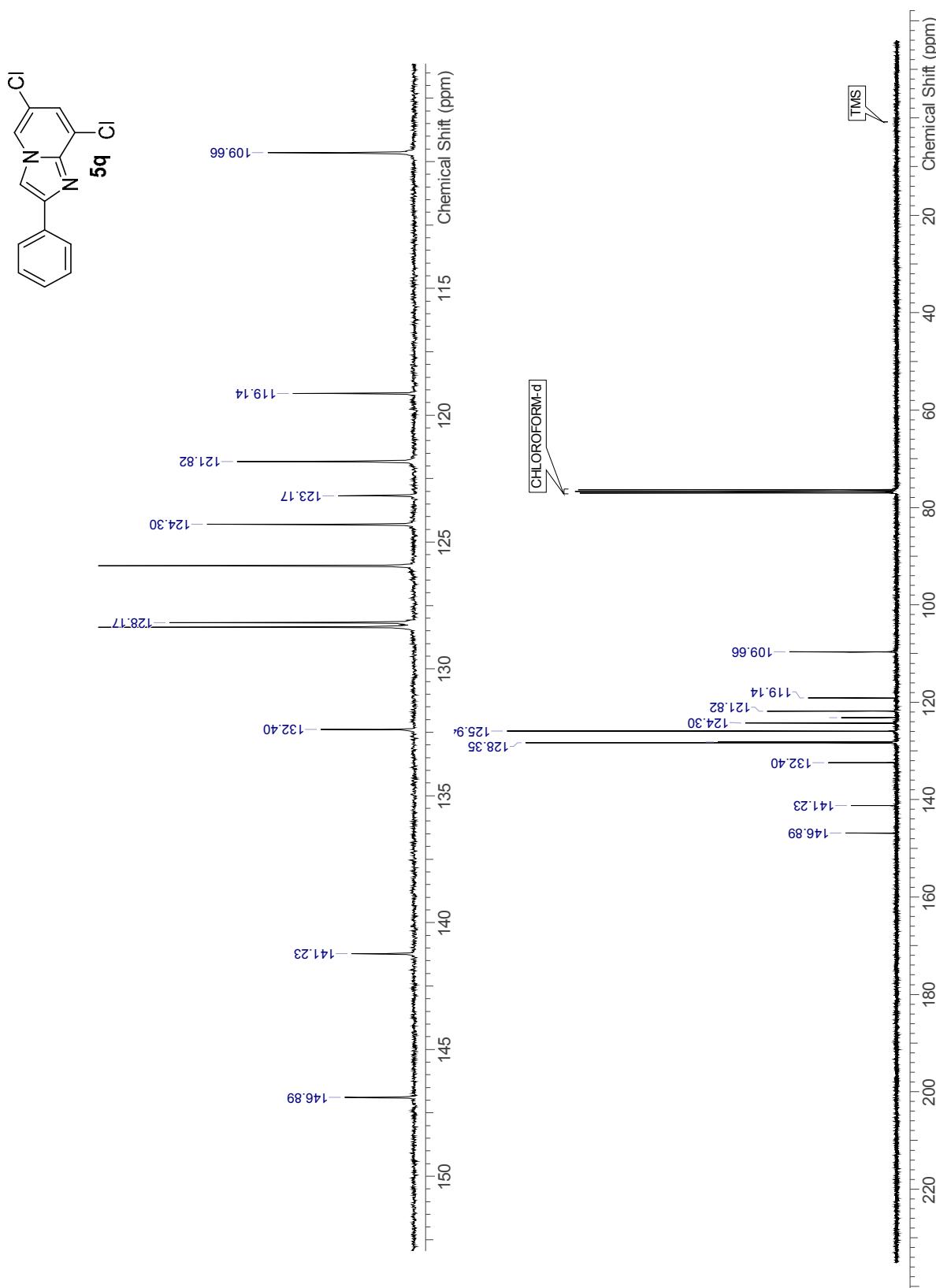
6,8-Dichloro-2-phenylimidazo[1,2-a]pyridine (**5q**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



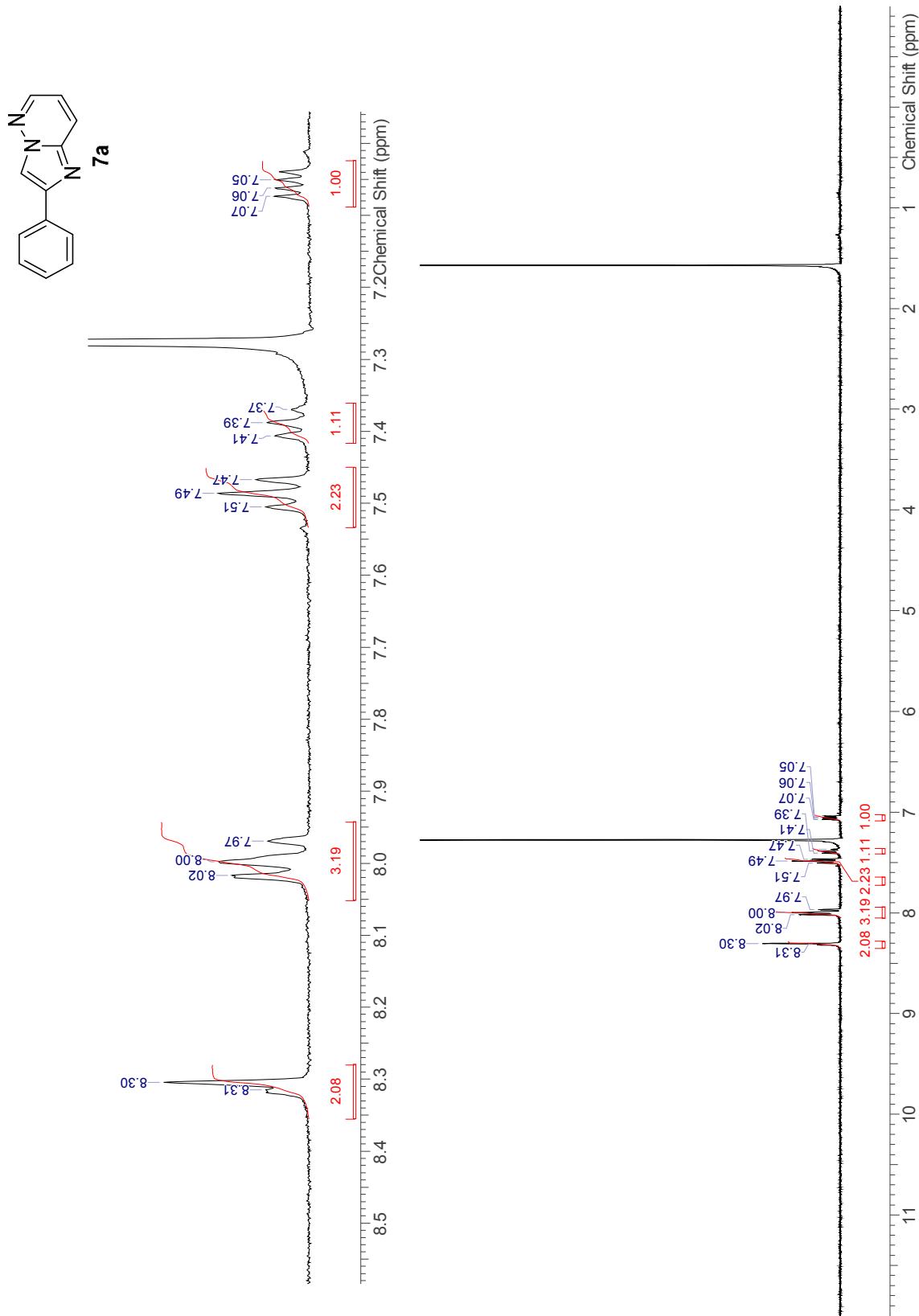
**6,8-Dichloro-2-phenylimidazo[1,2-a]pyridine (**5q**)**

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )

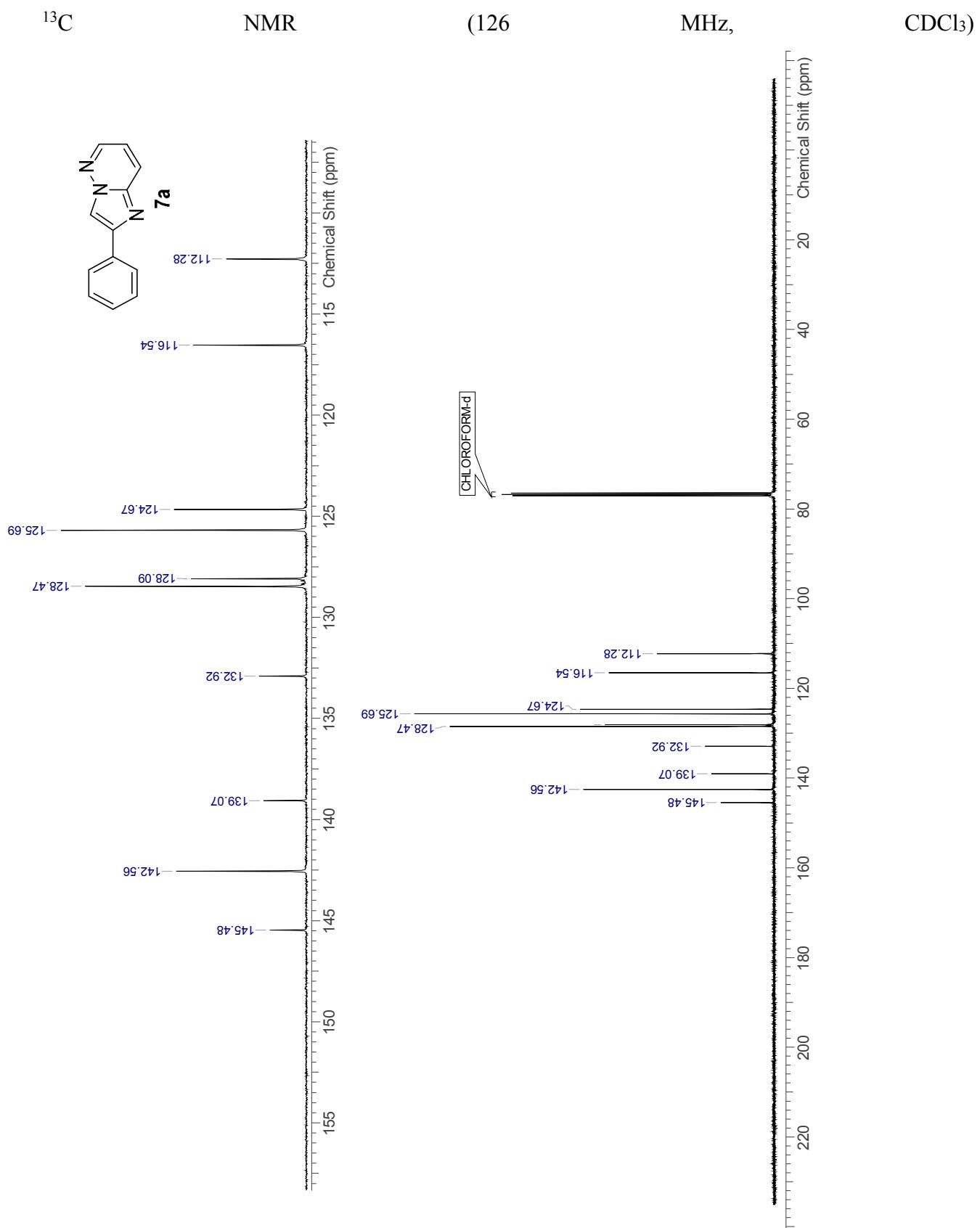


2-Phenylimidazo[1,2-*b*]pyridazine (**7a**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

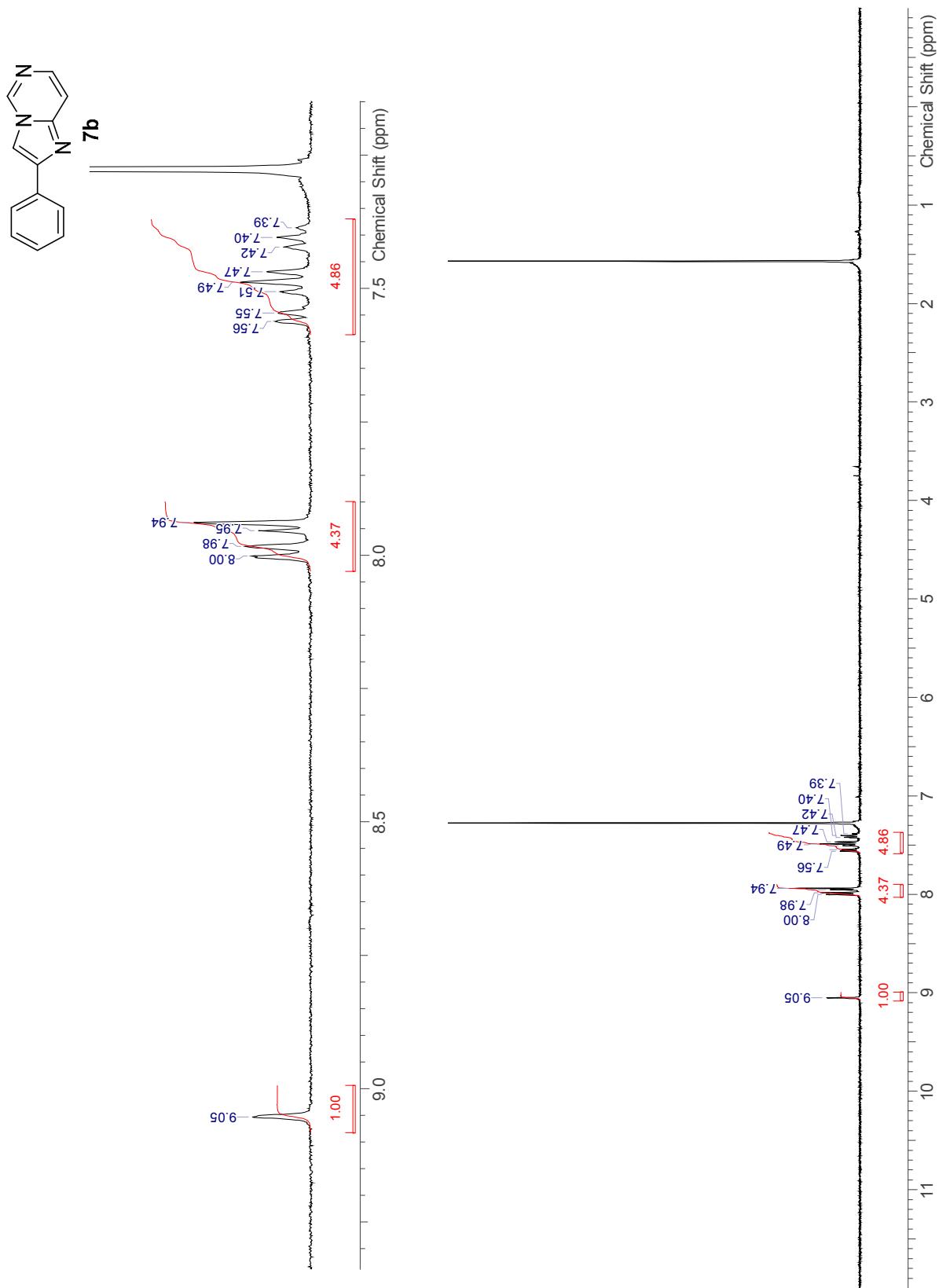


2-Phenylimidazo[1,2-*b*]pyridazine (**7a**)



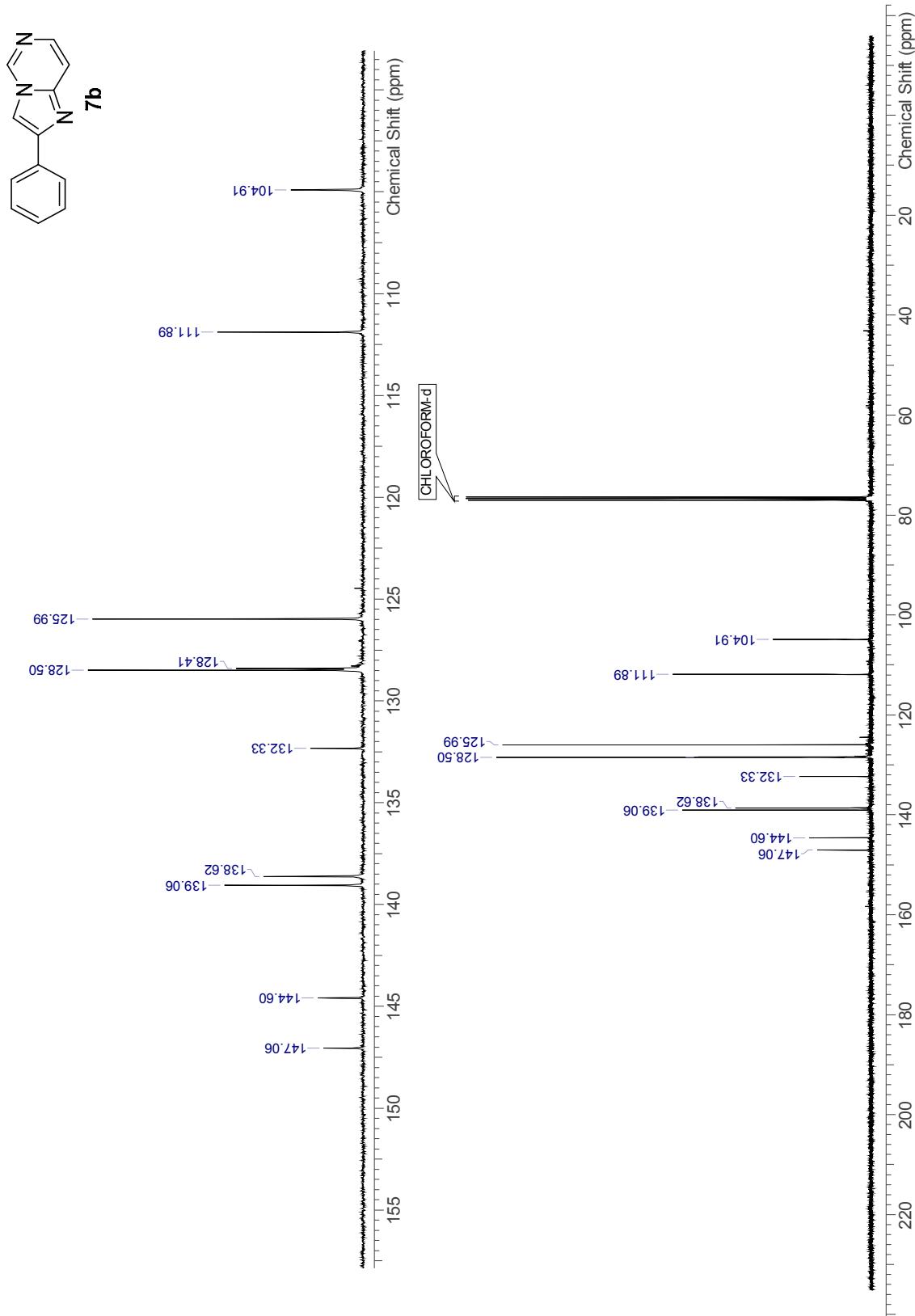
2-Phenylimidazo[1,2-*c*]pyrimidine (**7b**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



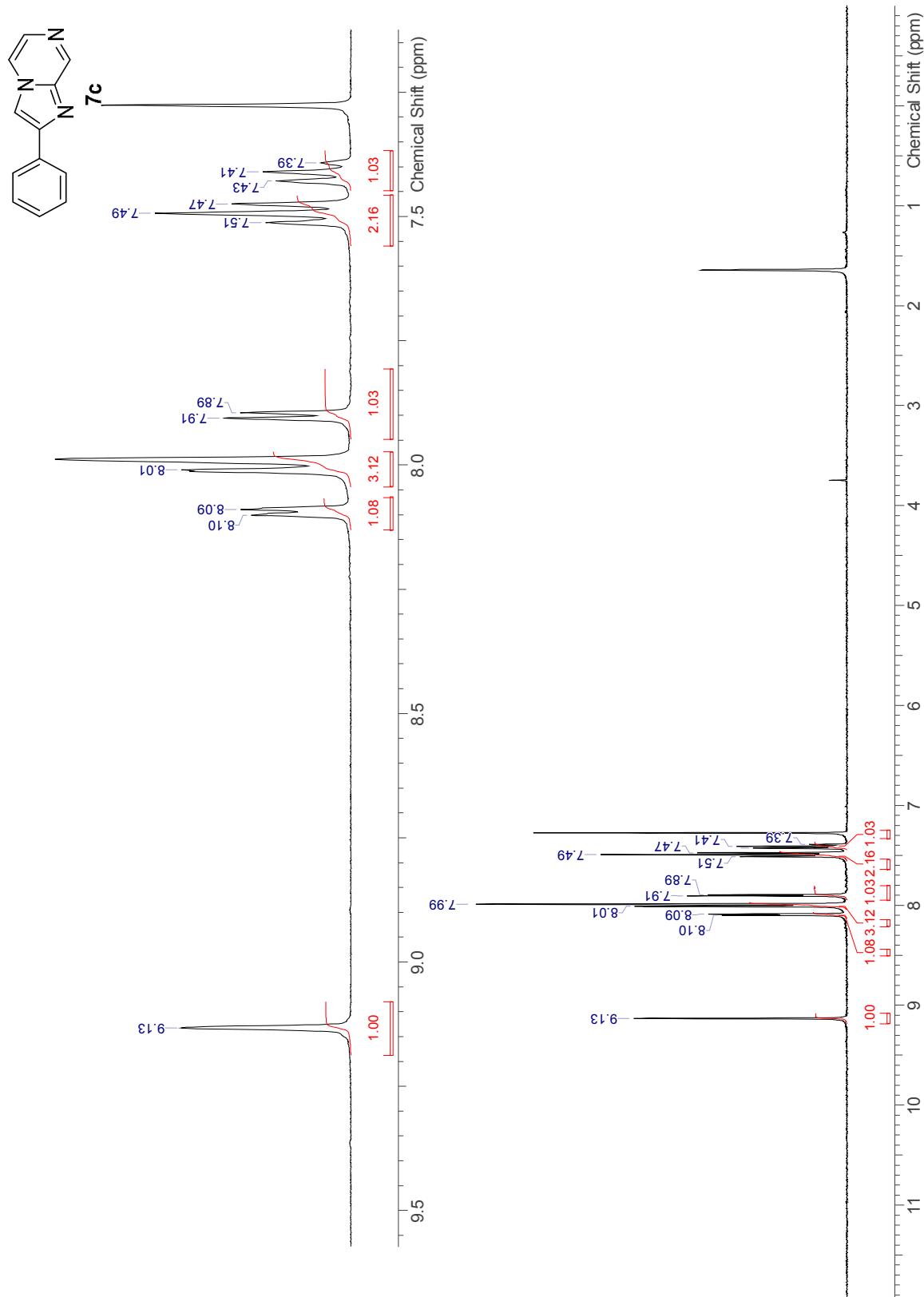
2-Phenylimidazo[1,2-*c*]pyrimidine (**7b**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



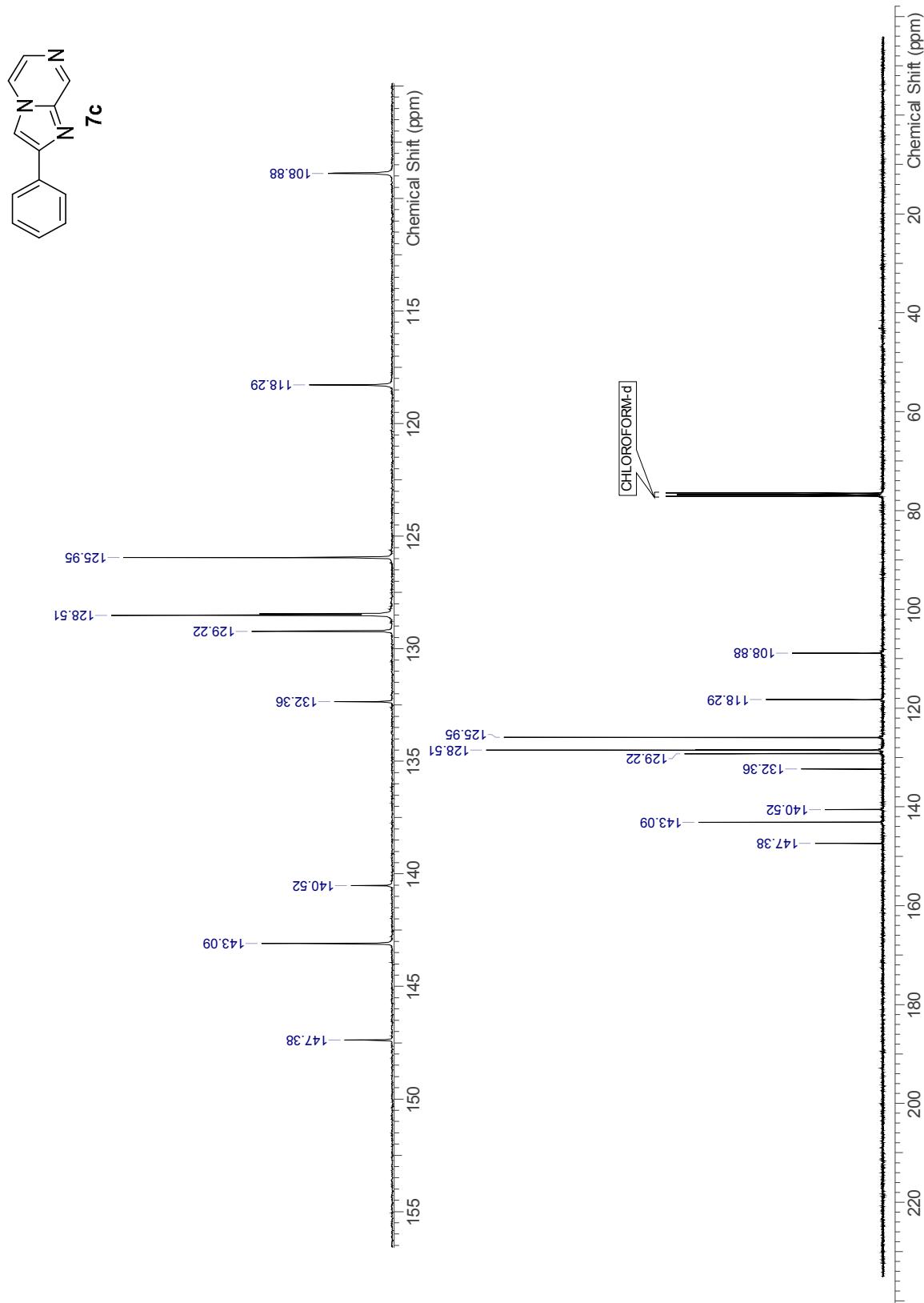
2-Phenylimidazo[1,2-*a*]pyrazine (**7c**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

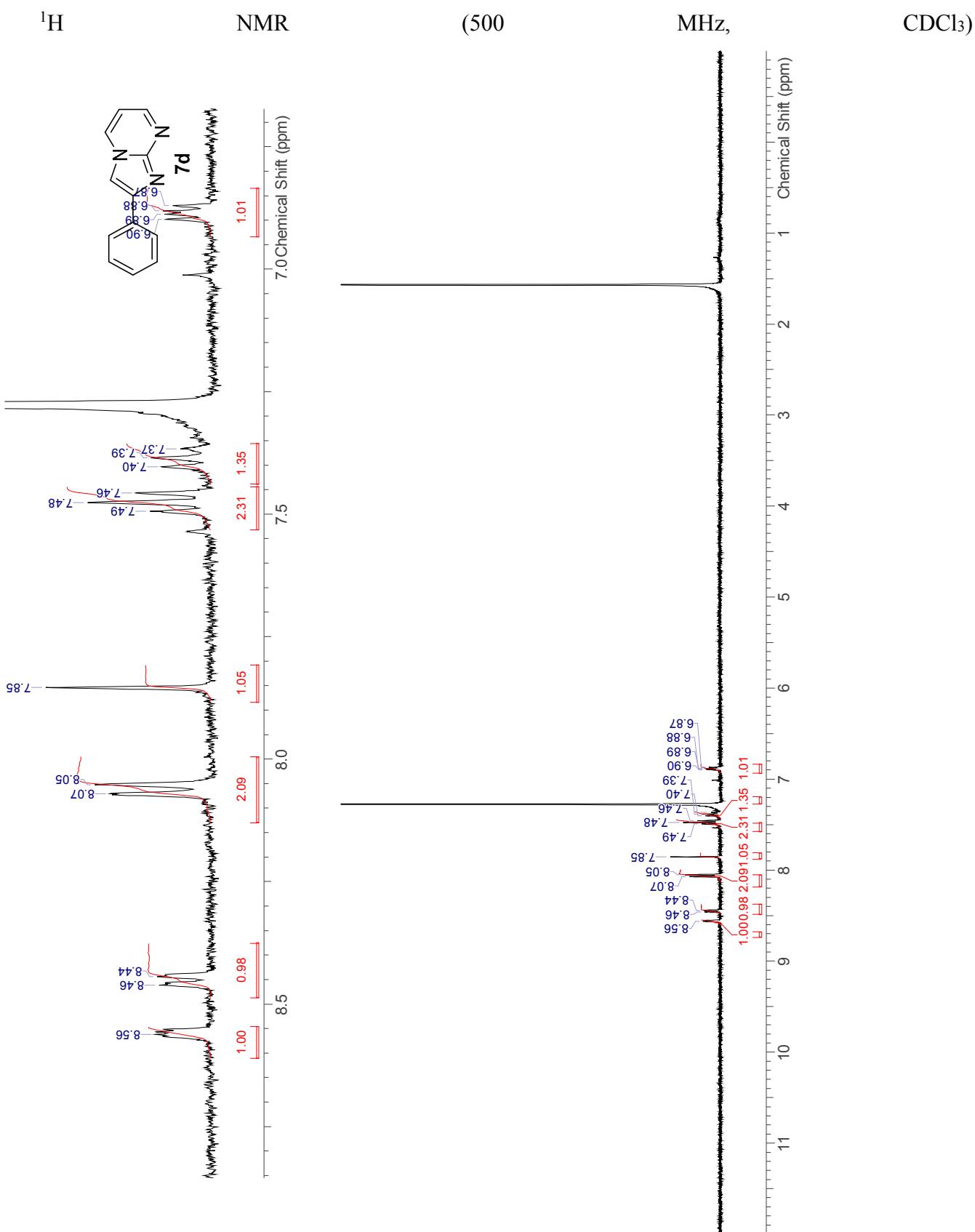


2-Phenylimidazo[1,2-*a*]pyrazine (**7c**)

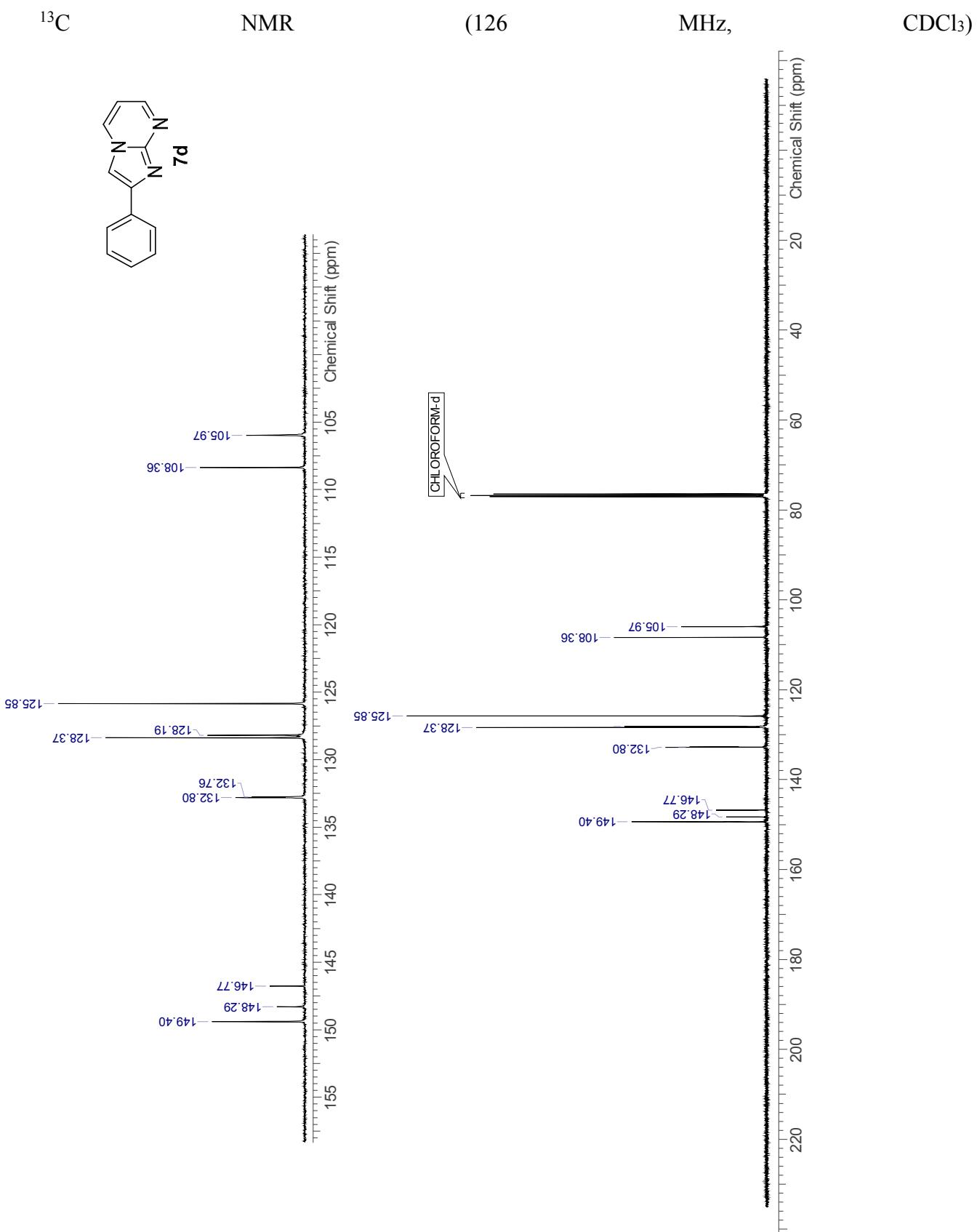
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



### 2-Phenylimidazo[1,2-*a*]pyrimidine (**7d**)

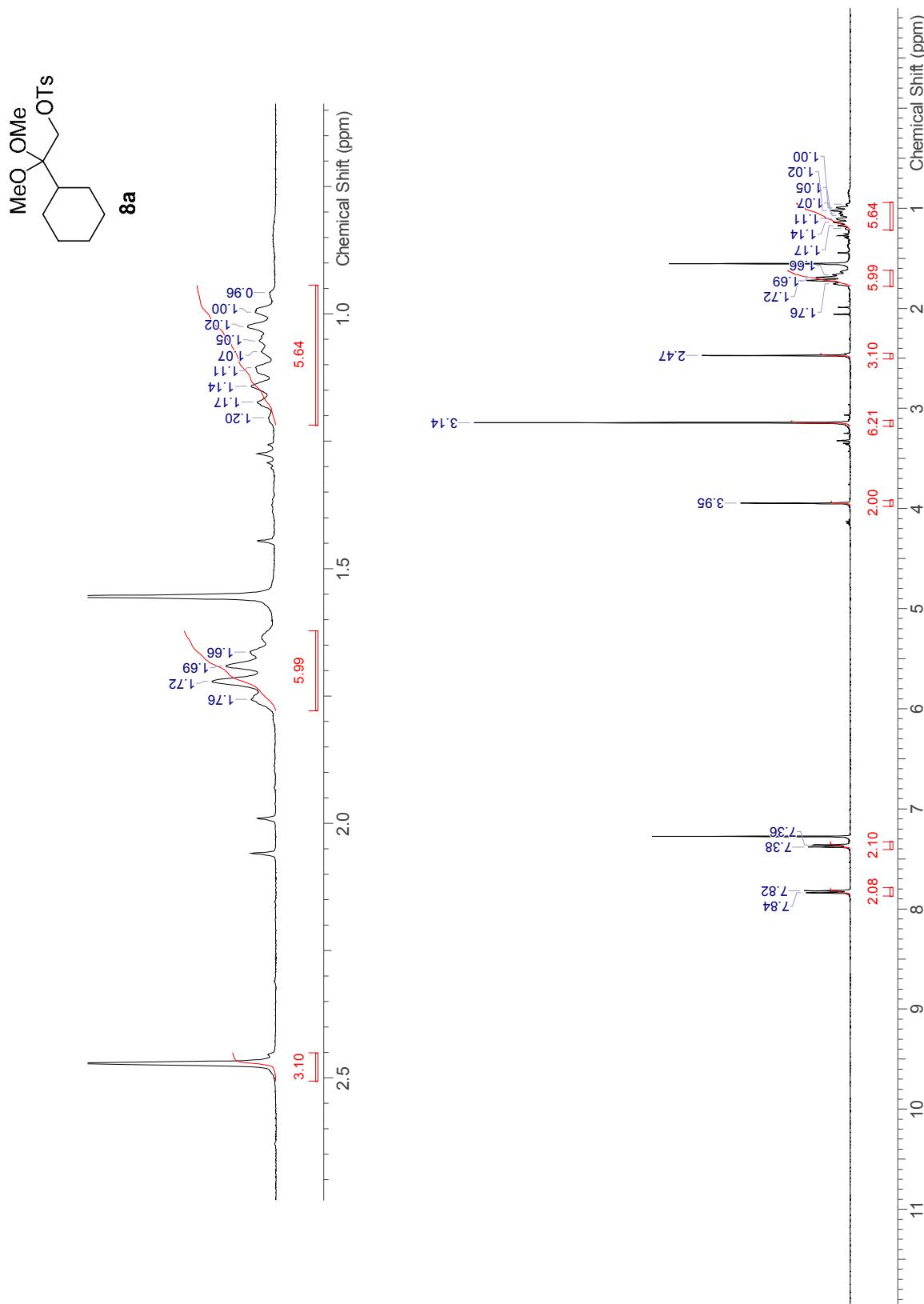


### 2-Phenylimidazo[1,2-*a*]pyrimidine (**7d**)



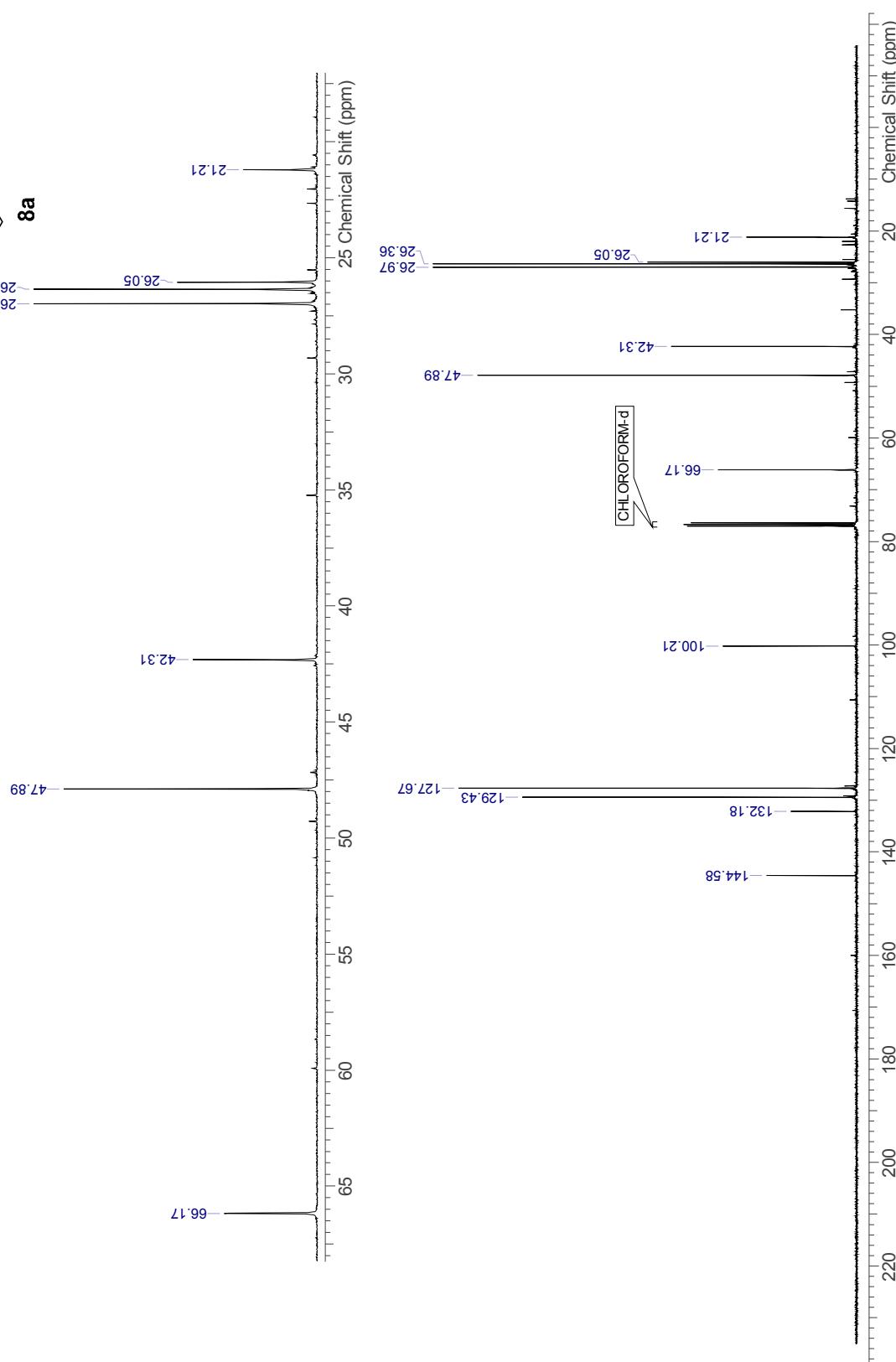
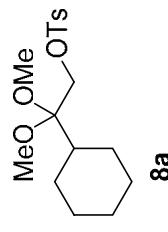
2-Cyclohexyl-2,2-dimethoxyethyl 4-methylbenzenesulfonate (**8a**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



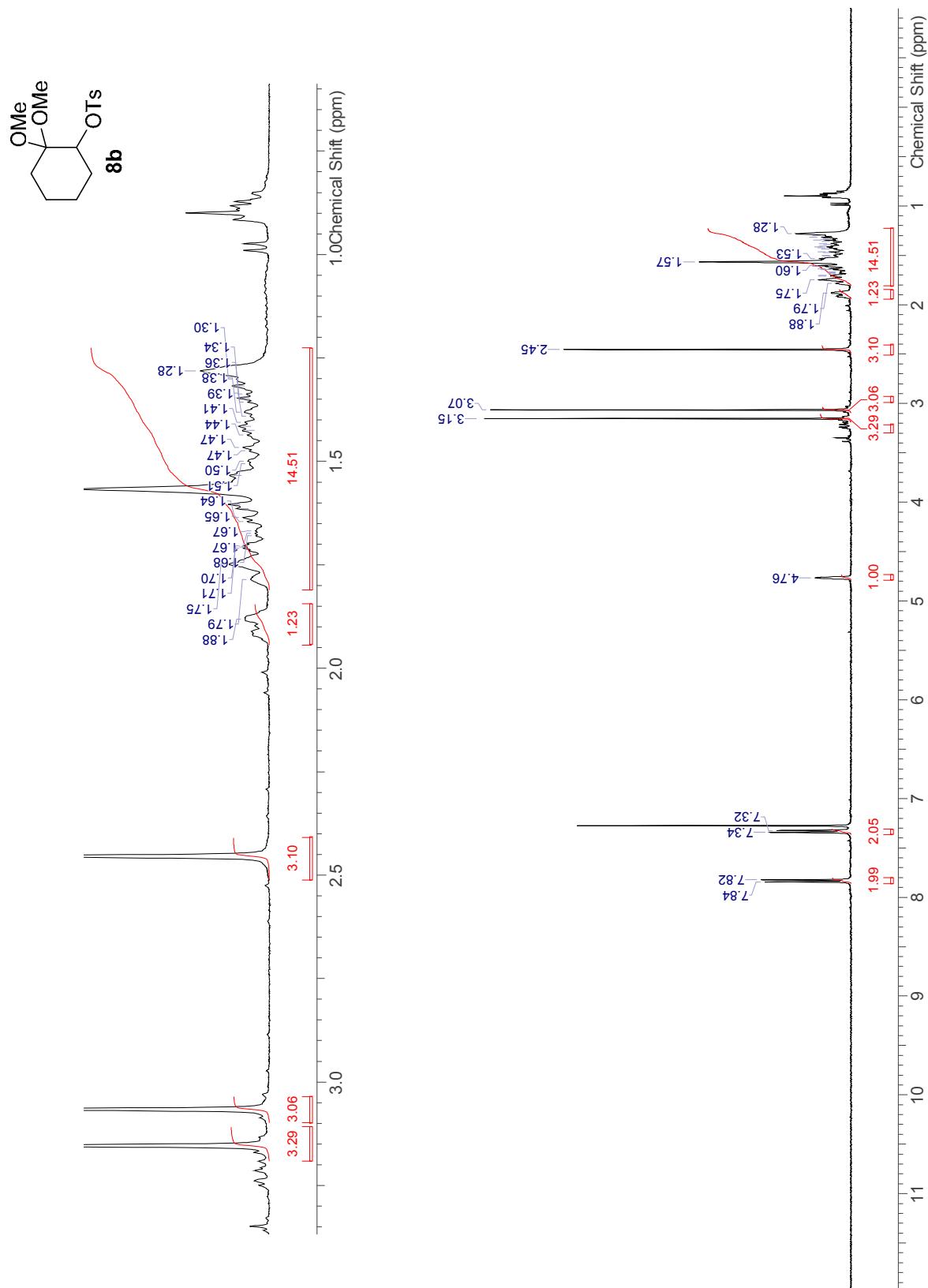
### 2-Cyclohexyl-2,2-dimethoxyethyl 4-methylbenzenesulfonate (**8a**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



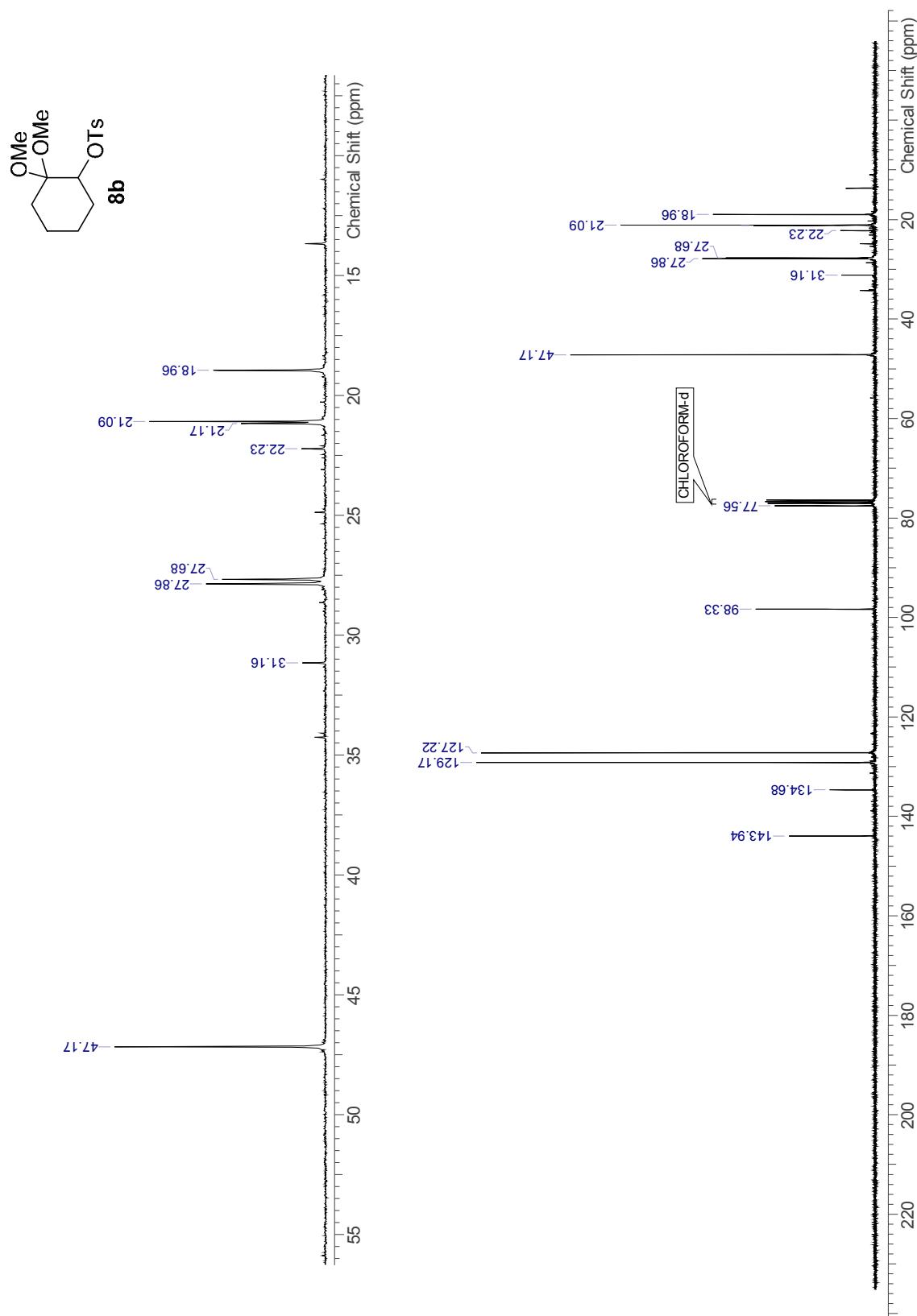
### 2,2-Dimethoxycyclohexyl 4-methylbenzenesulfonate (**8b**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

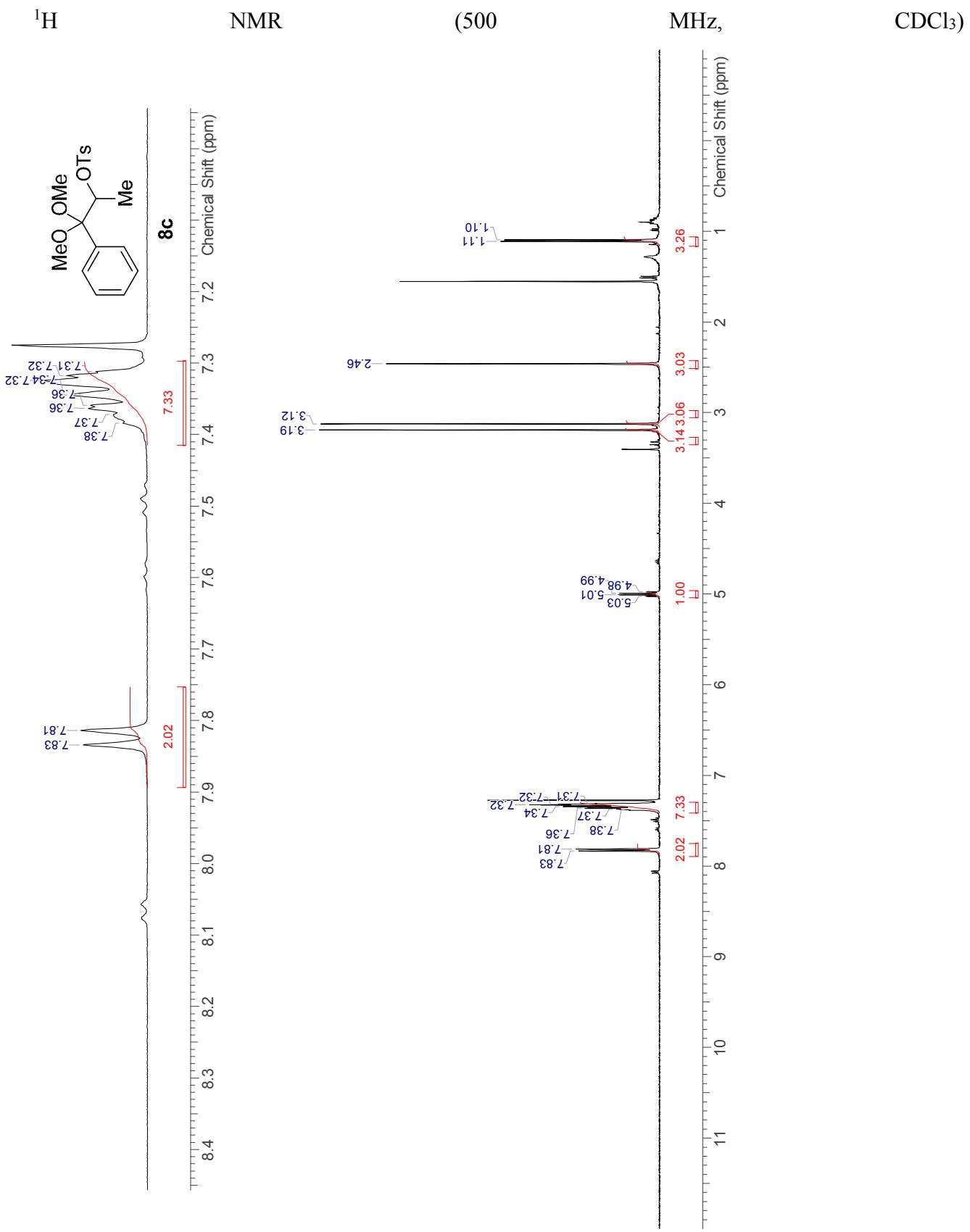


### 2,2-Dimethoxycyclohexyl 4-methylbenzenesulfonate (**8b**)

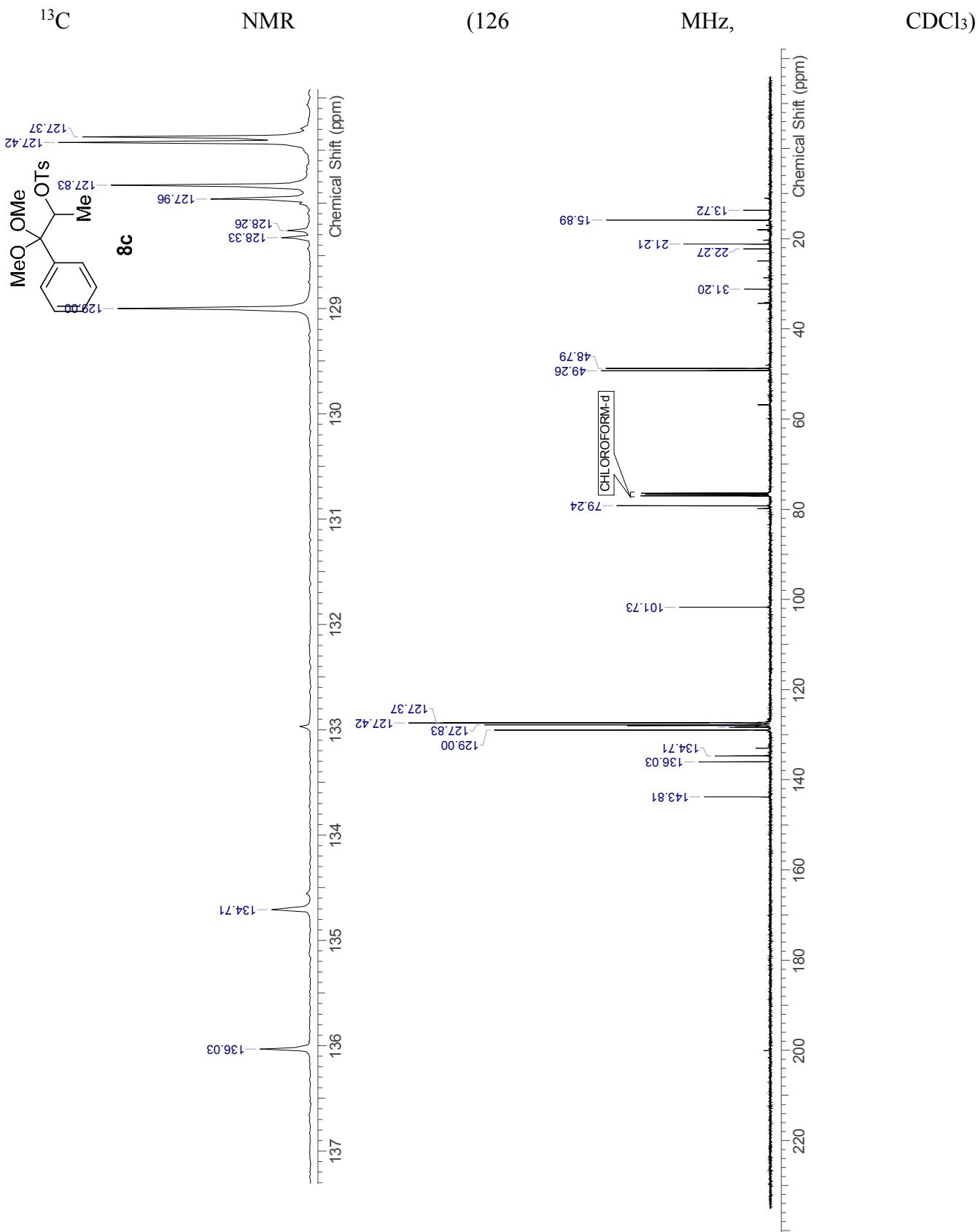
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



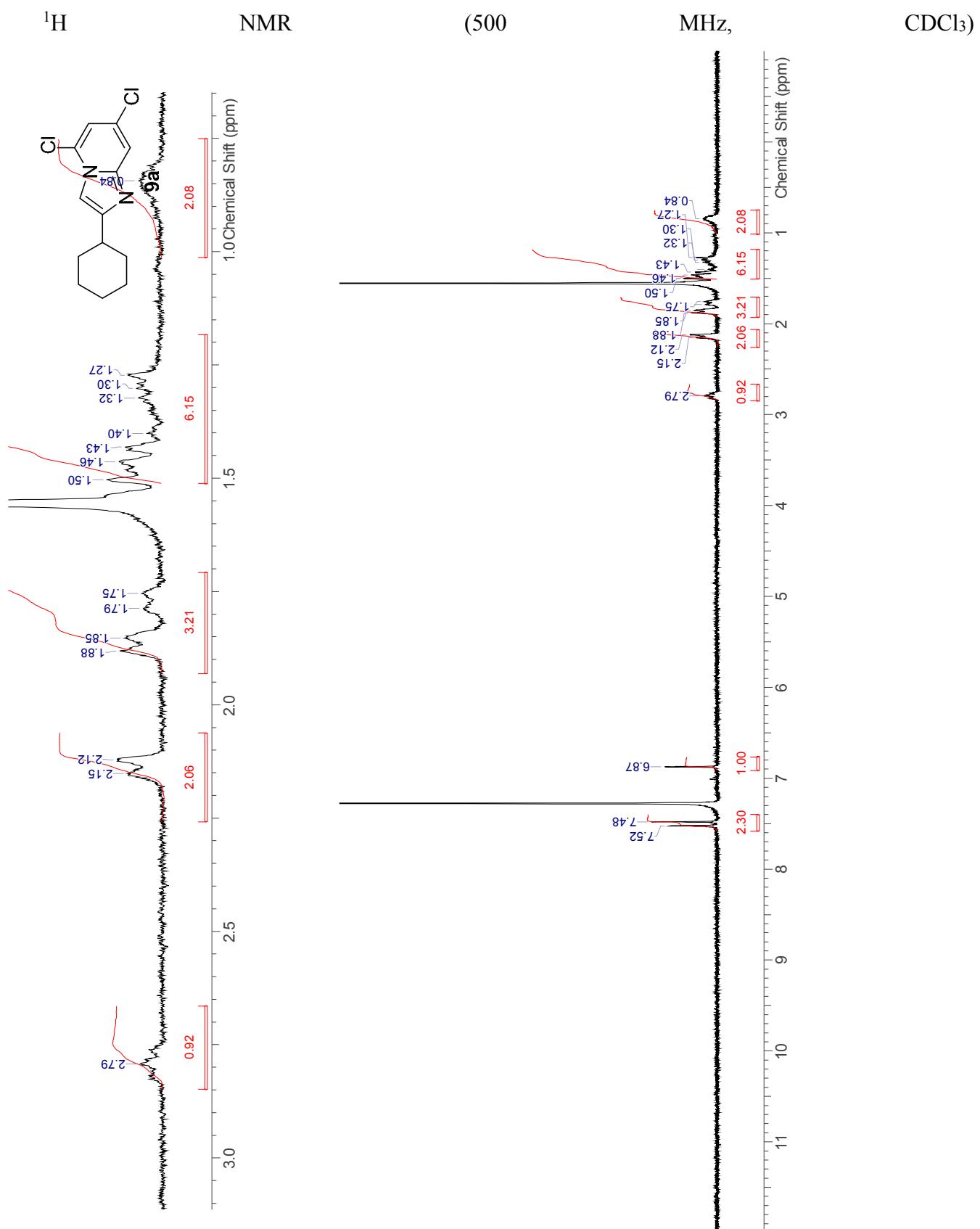
1,1-Dimethoxy-1-phenylpropan-2-yl 4-methylbenzenesulfonate (**8c**)



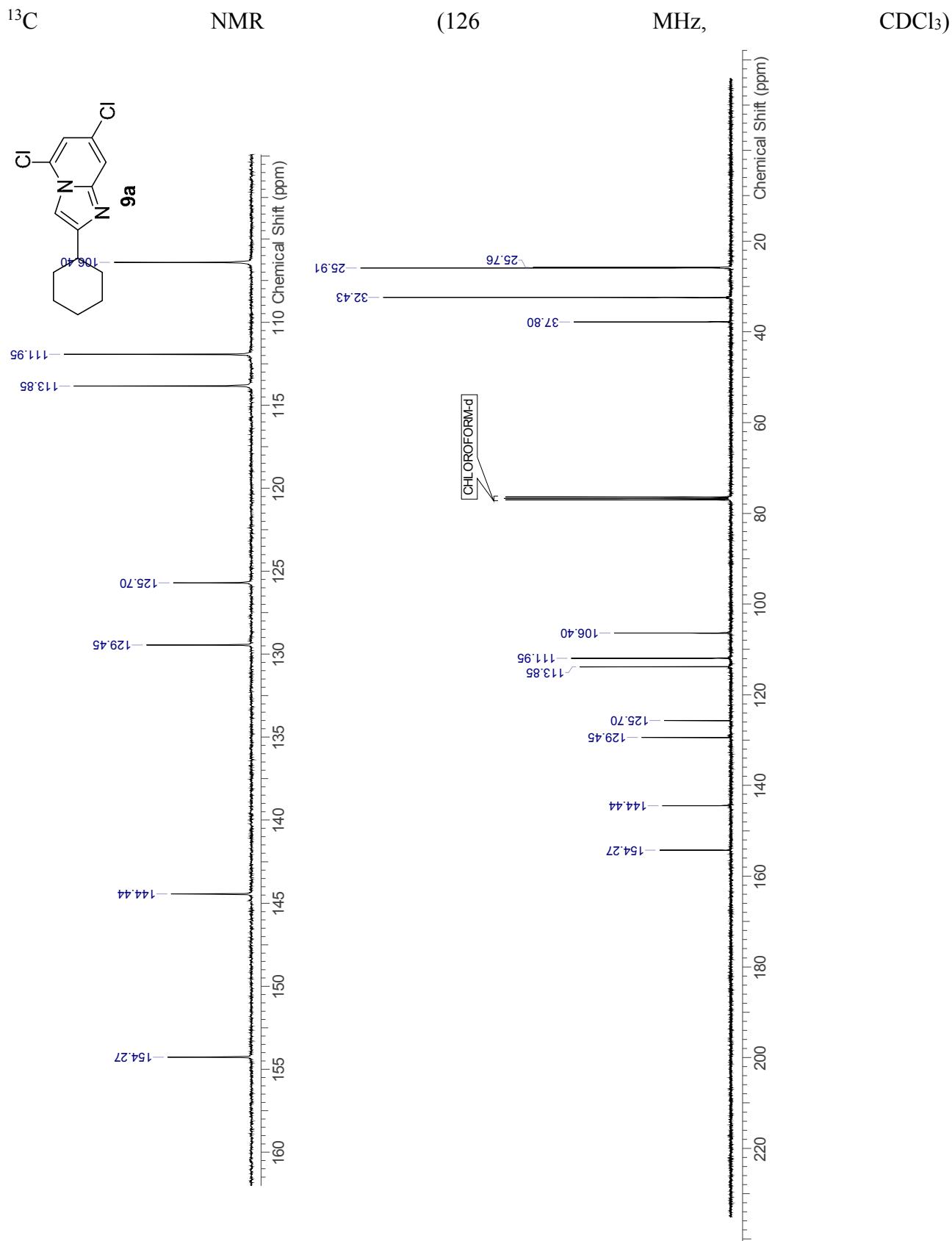
1,1-Dimethoxy-1-phenylpropan-2-yl 4-methylbenzenesulfonate (**8c**)



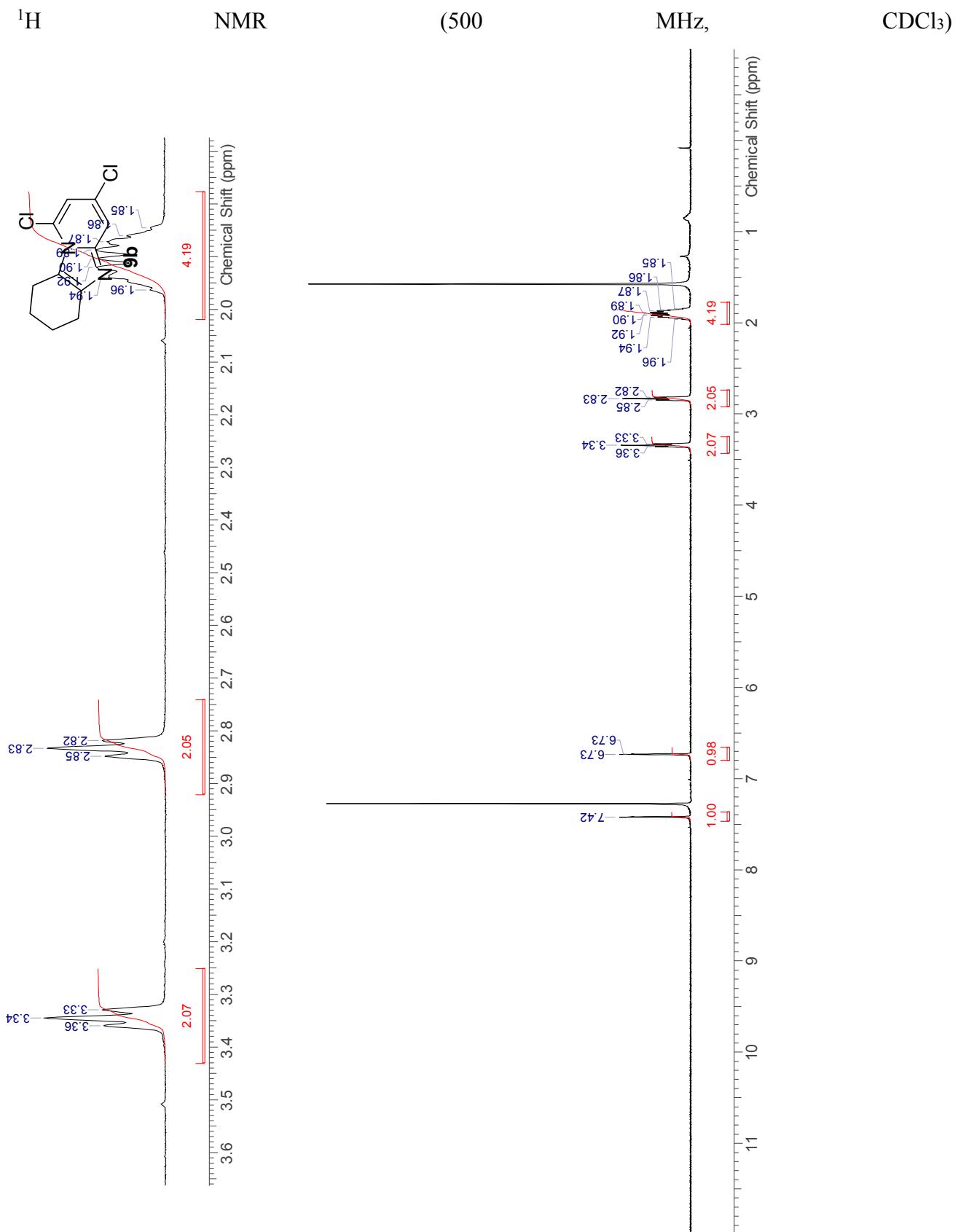
5,7-Dichloro-2-cyclohexylimidazo[1,2-*a*]pyridine (**9a**)



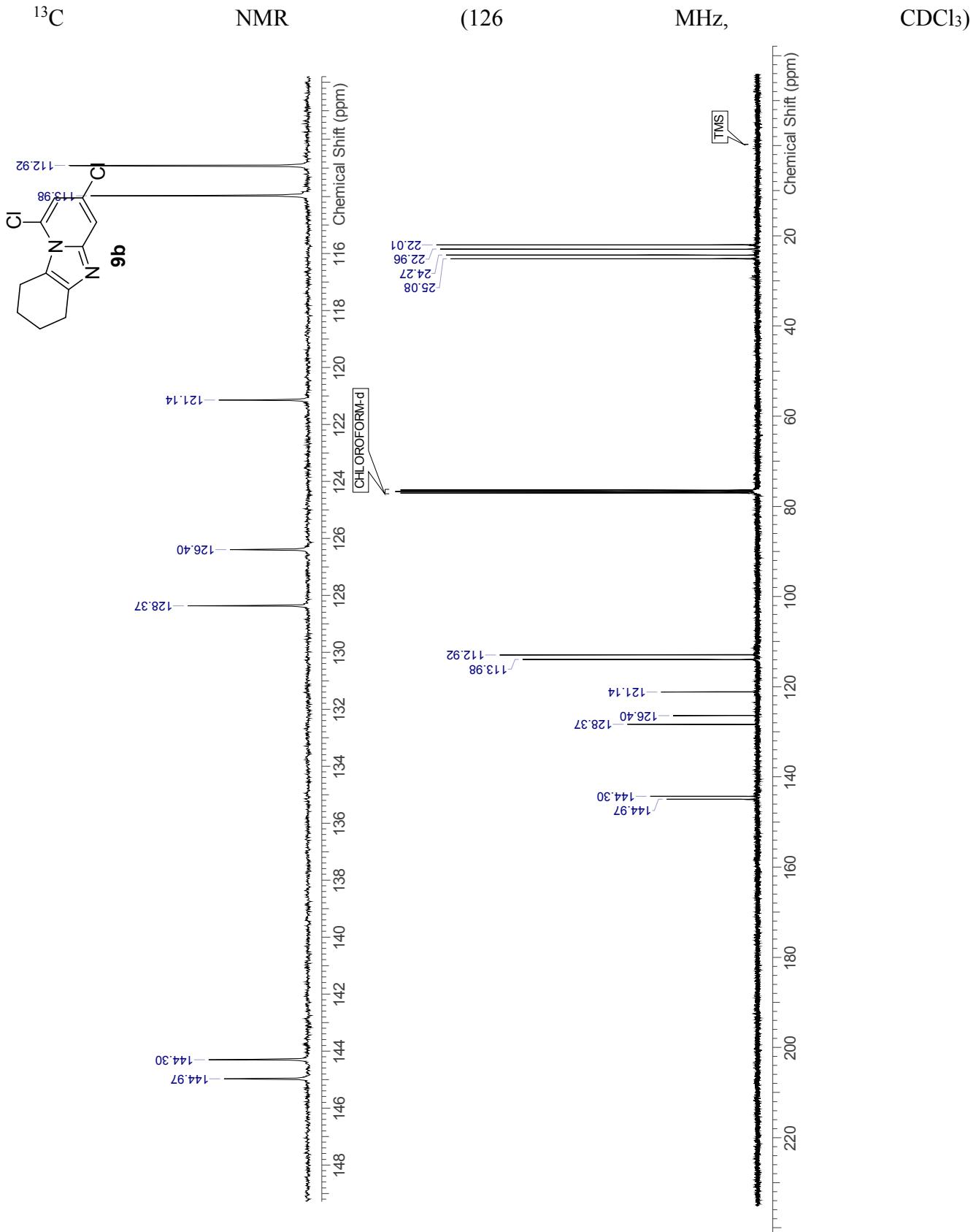
### 5,7-Dichloro-2-cyclohexylimidazo[1,2-*a*]pyridine (**9a**)



### 1,3-Dichloro-6,7,8,9-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (**9b**)

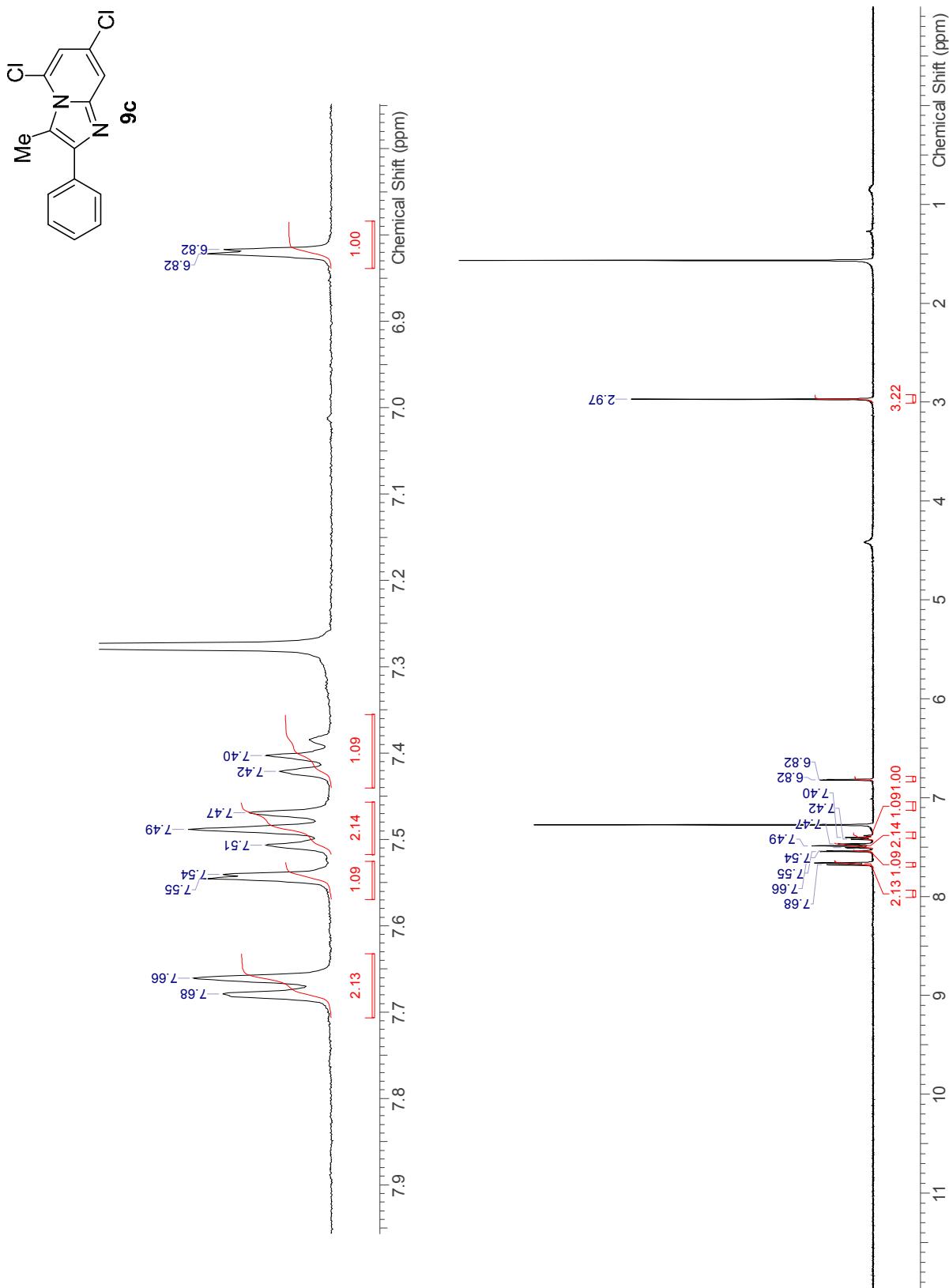


1,3-Dichloro-6,7,8,9-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (**9b**)



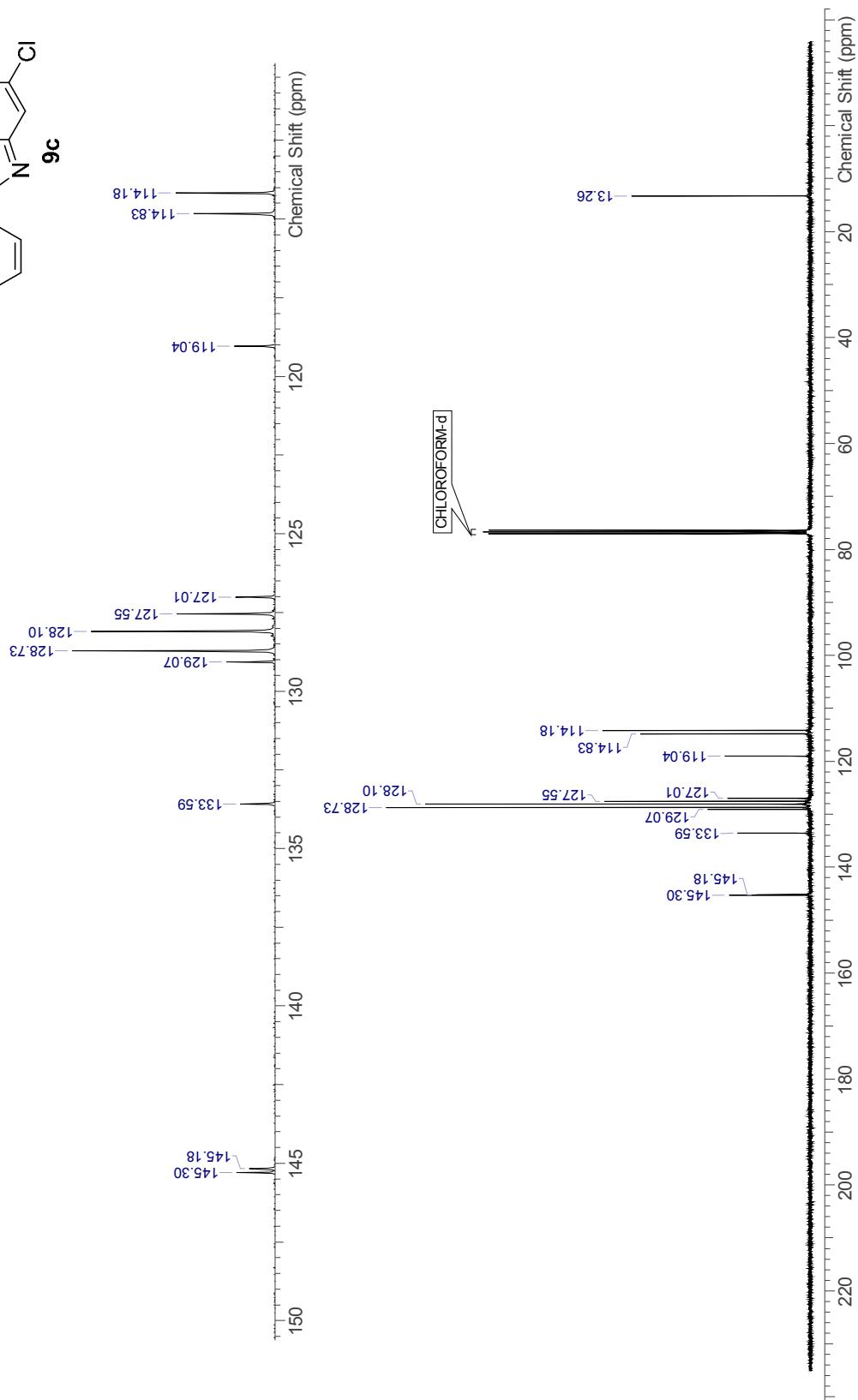
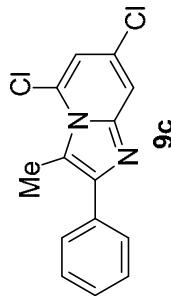
5,7-Dichloro-3-methyl-2-phenylimidazo[1,2-*a*]pyridine (**9c**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



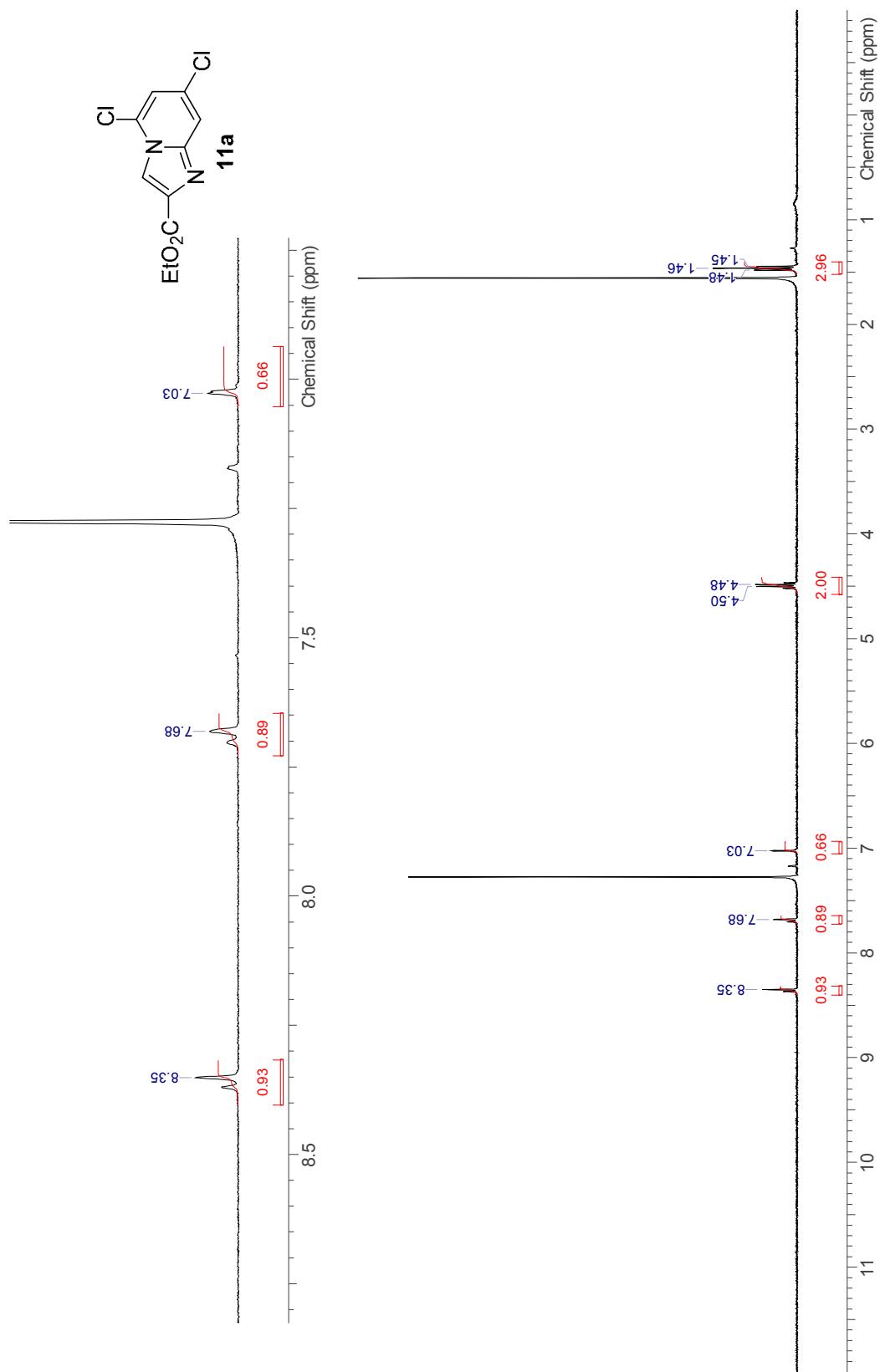
### 5,7-Dichloro-3-methyl-2-phenylimidazo[1,2-*a*]pyridine (**9c**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



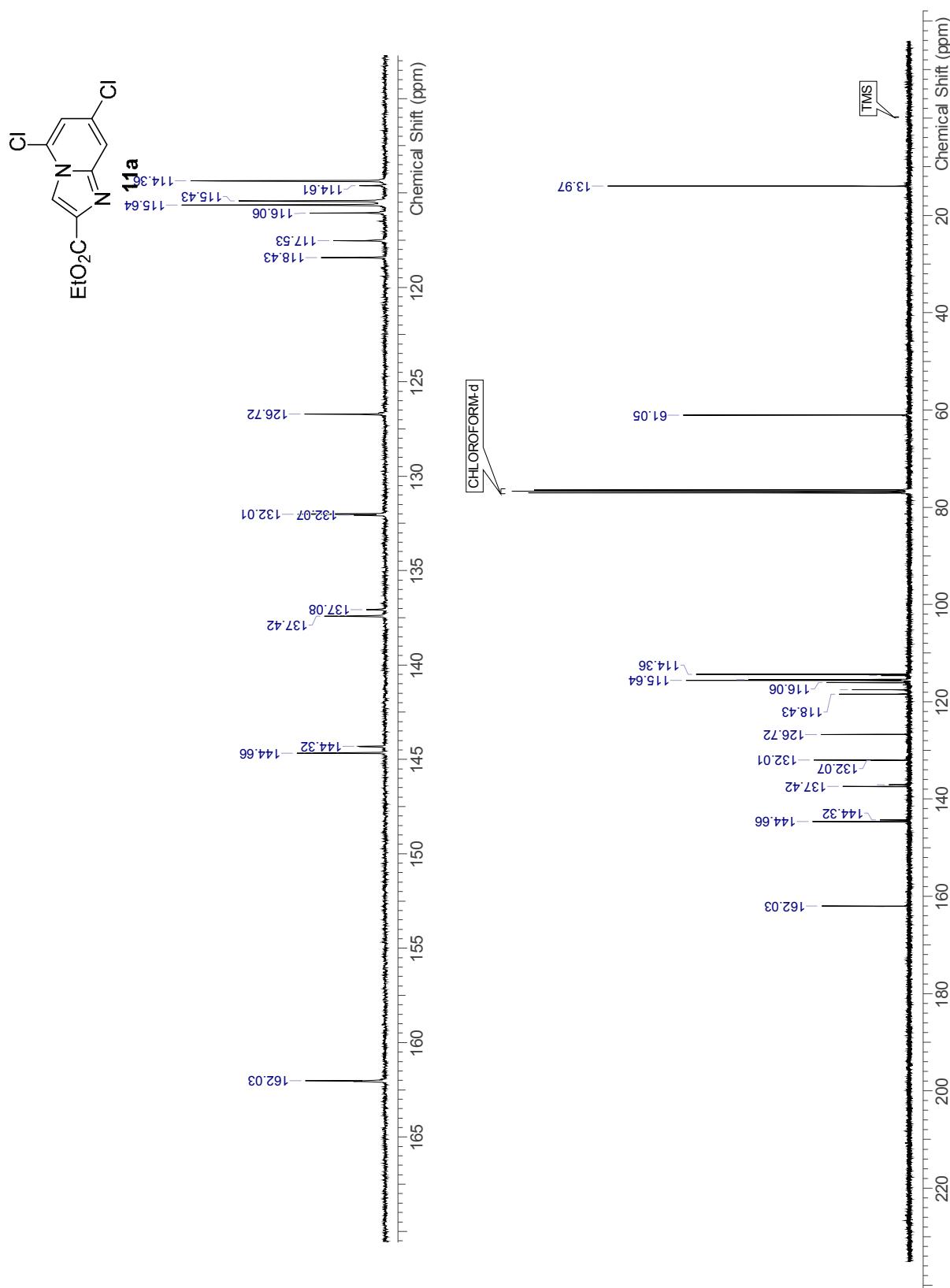
Ethyl 5,7-dichloroimidazo[1,2-*a*]pyridine-2-carboxylate (**11a**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



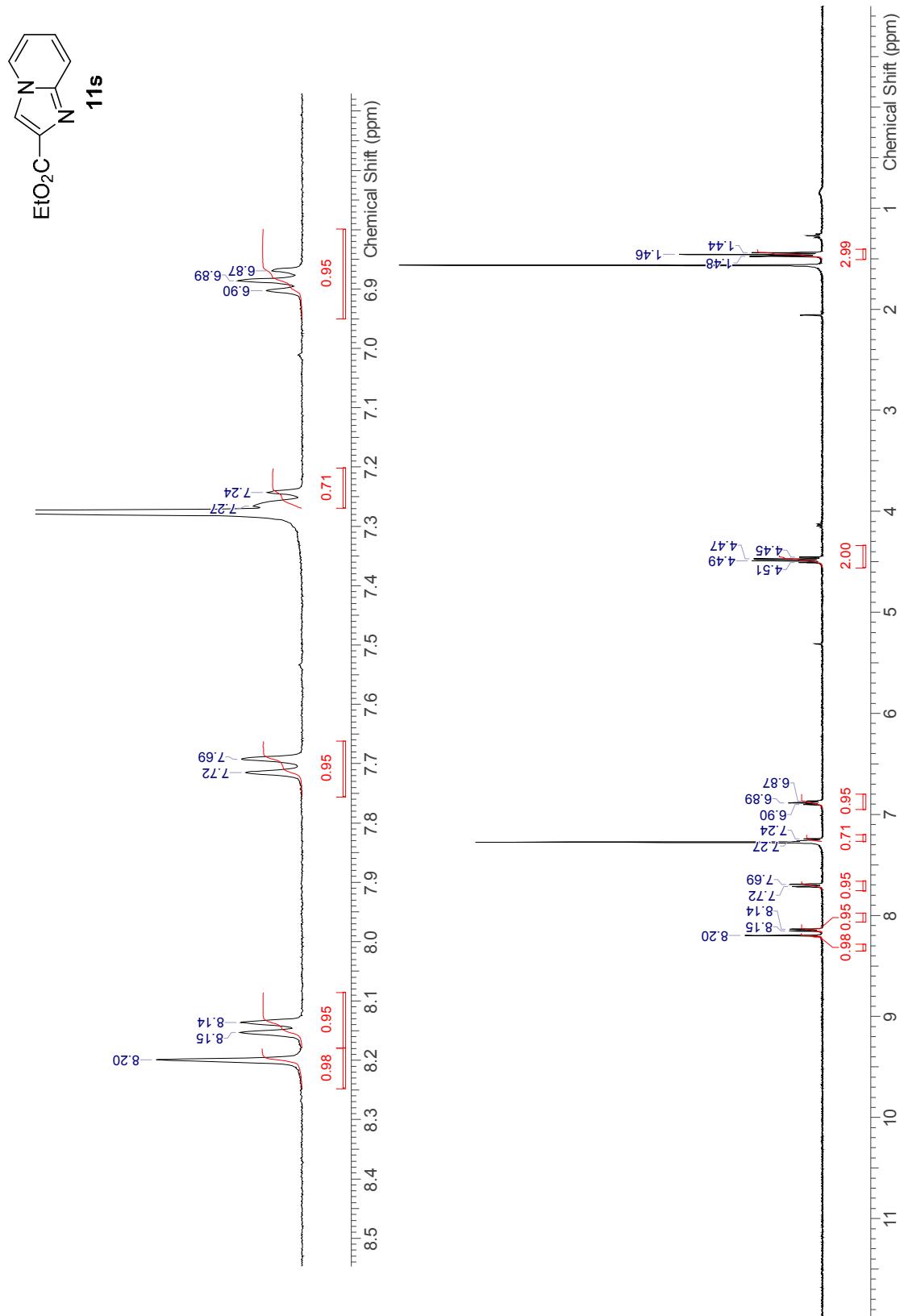
### Ethyl 5,7-dichloroimidazo[1,2-*a*]pyridine-2-carboxylate (**11a**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



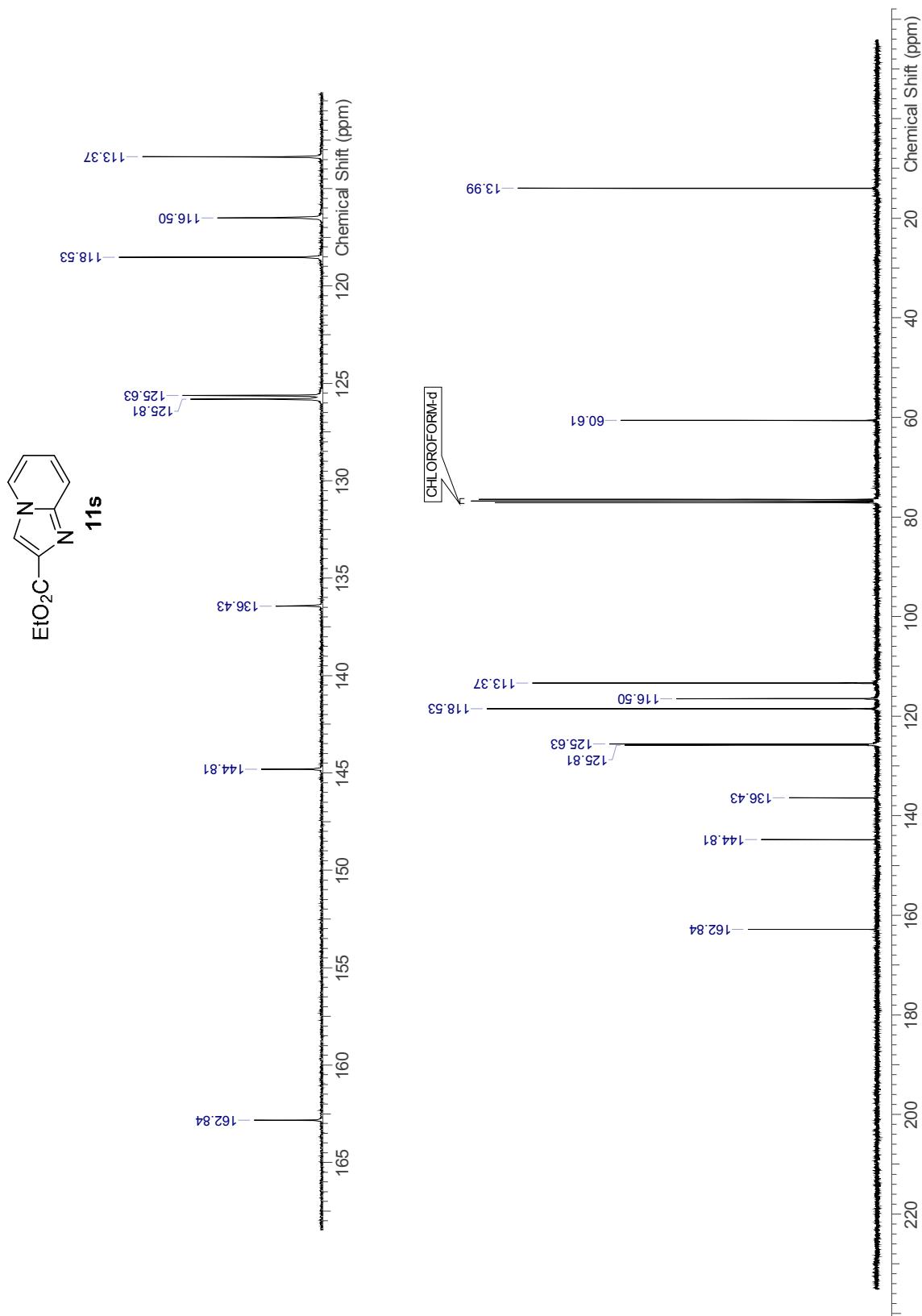
Ethyl imidazo[1,2-*a*]pyridine-2-carboxylate (**11s**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



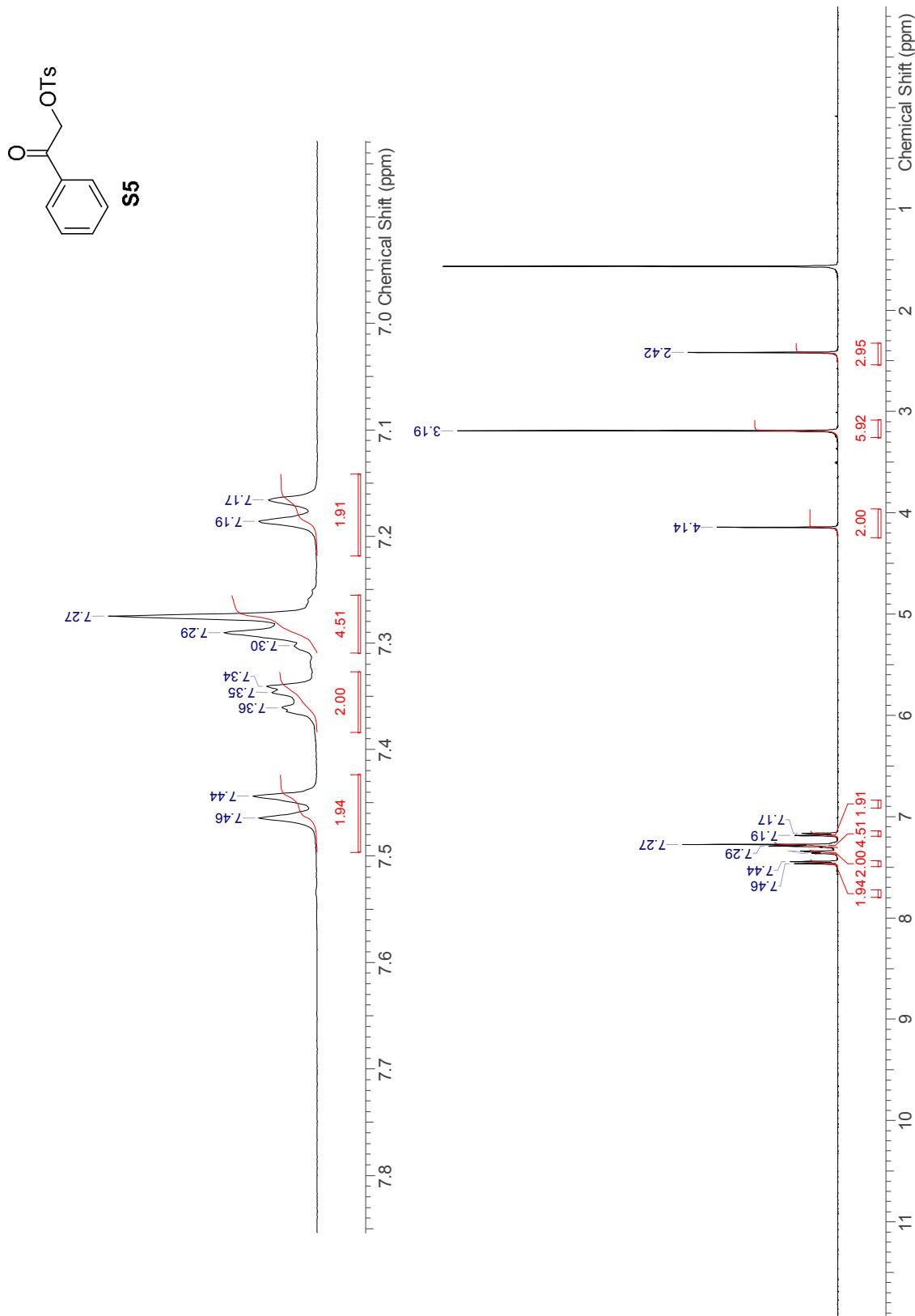
Ethyl imidazo[1,2-*a*]pyridine-2-carboxylate (**11s**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



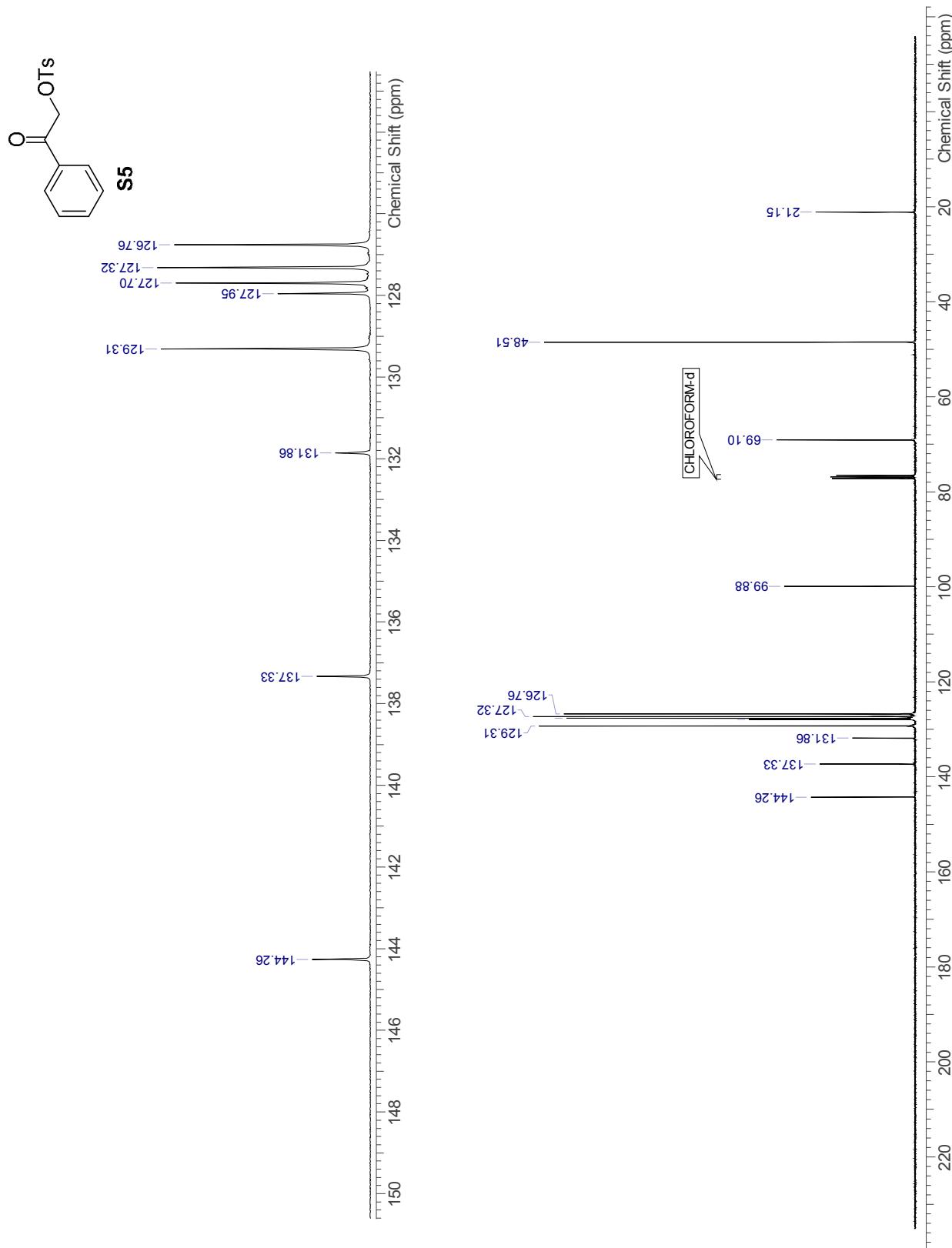
**2-Oxo-2-phenylethyl 4-methylbenzenesulfonate (**S5**)**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



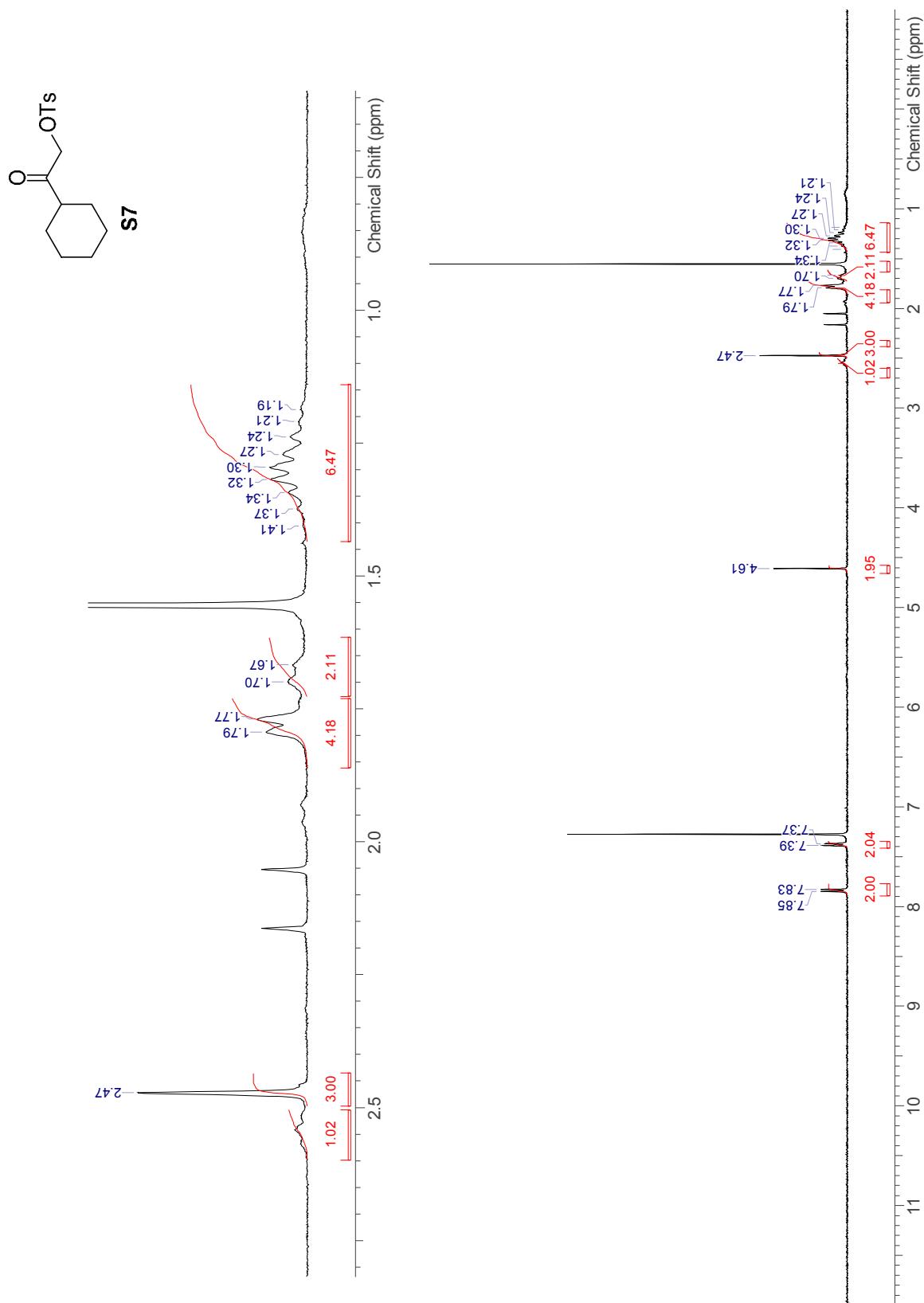
2-Oxo-2-phenylethyl 4-methylbenzenesulfonate (**S5**)

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

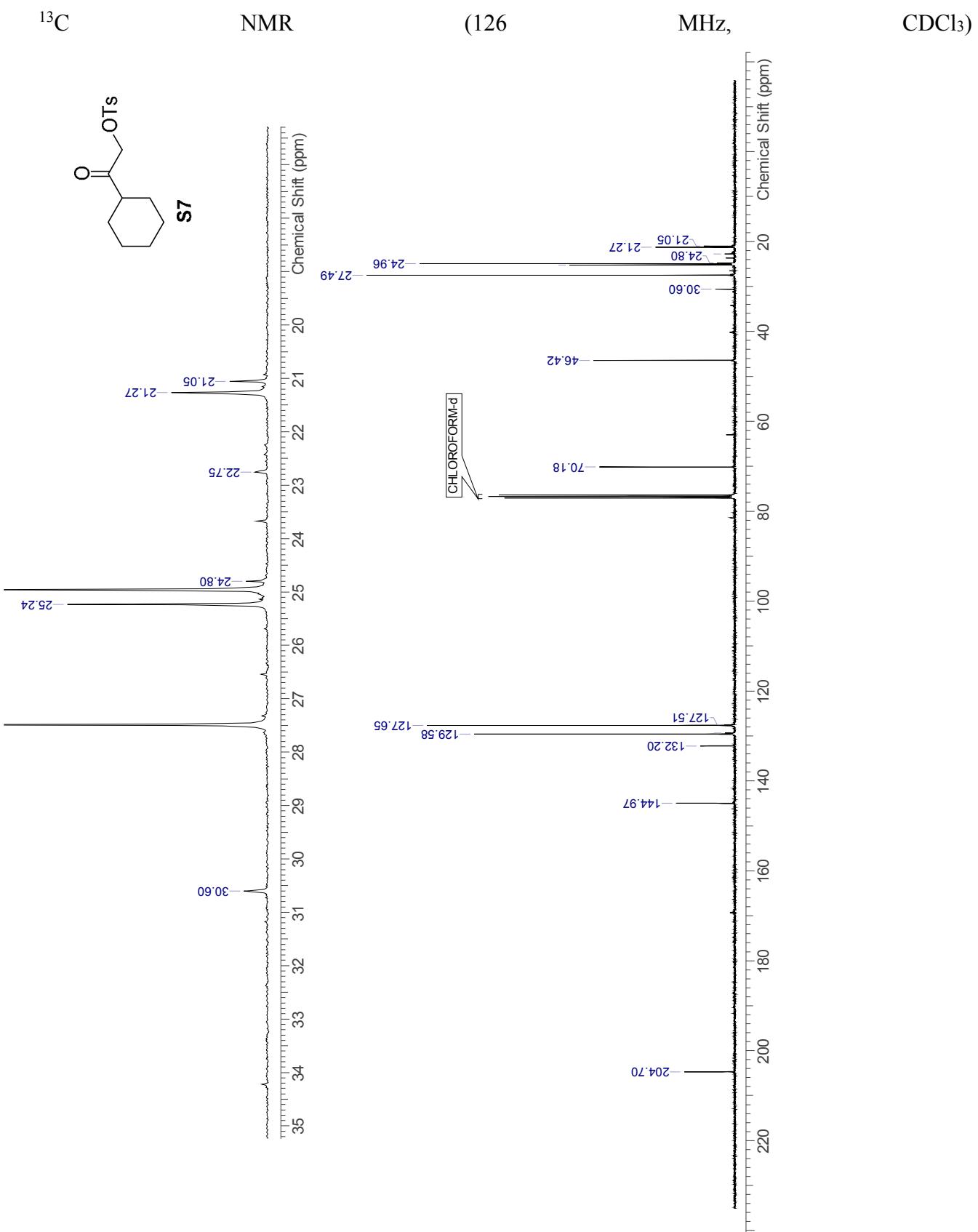


### 2-Cyclohexyl-2-oxoethyl 4-methylbenzenesulfonate (**S7**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

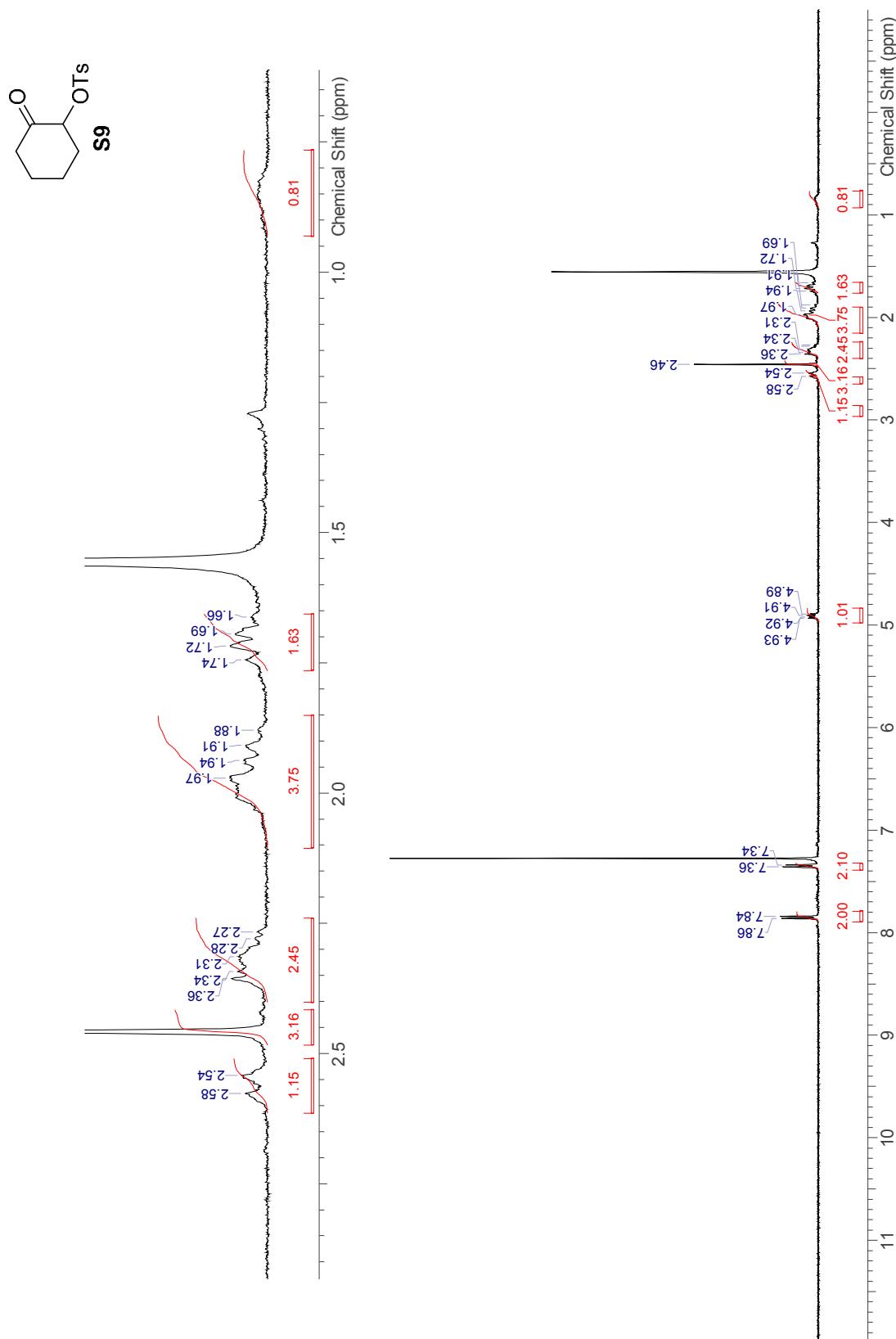


### 2-Cyclohexyl-2-oxoethyl 4-methylbenzenesulfonate (**S7**)



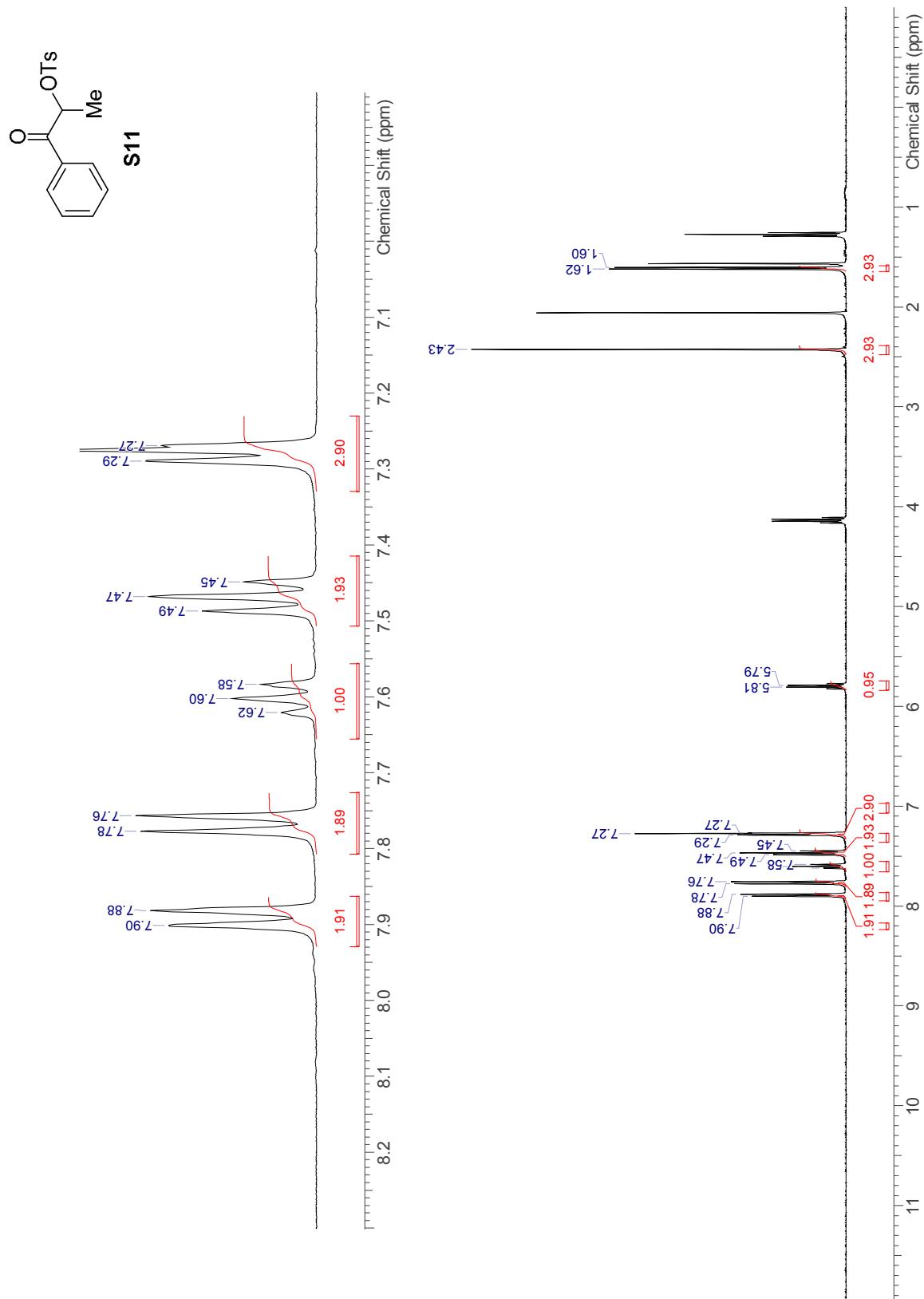
### 2-Oxocyclohexyl 4-methylbenzenesulfonate (**S9**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



1-Oxo-1-phenylpropan-2-yl 4-methylbenzenesulfonate (**S11**)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



1-Oxo-1-phenylpropan-2-yl 4-methylbenzenesulfonate (**S11**)

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )

