

Iron-Catalyzed unprecedented formation of Benzo[d]imidazo [2,1-b]thiazoles  
under Solvent-Free Conditions.

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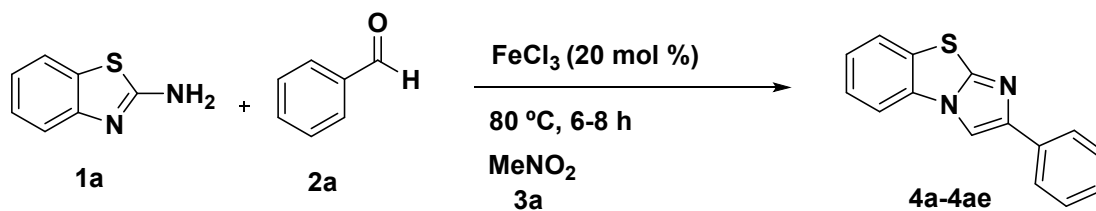
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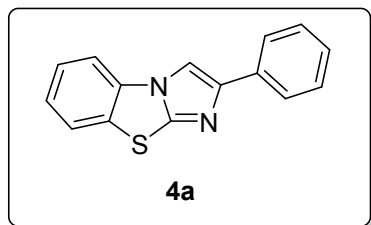
## General procedures for the Synthesis of 2-phenylbenzo[d]imidazo[2,1-b]thiazole (4a)



### Procedure: Synthesis of 2-phenylbenzo[d]imidazo[2,1-b]thiazole (4a).

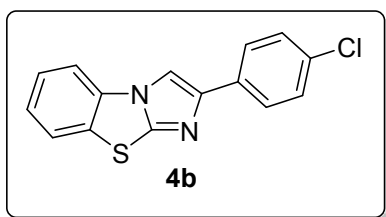
A mixture of 2-Aminobenzothiazole (**1a**, 1.0mmol), and benzaldehyde (**2a**,1.1mmol), was dissolved in 3 mL of nitromethane (**3a**) in a round-bottom flask, FeCl<sub>3</sub> (20 mol%) was added, the mixture was heated at 80 °C until full consumption of 2-aminobenzothiazole as monitored through TLC. Upon completion (6–8 h) of the reaction, the mixture was filtered on Celite. The filtrate was concentrated under reduced pressure to give the crude material, which was purified by column chromatography on silica gel (eluent:EtOAc/hexane) and afforded 2-phenylbenzo[d]imidazo[2,1-b]thiazole (**4a**) in 89 % yield. Compounds **4a-4ae** were also synthesized by adopting this procedure.

2-Phenylbenzo[d]imidazo[2,1-b]thiazole (**4a**)



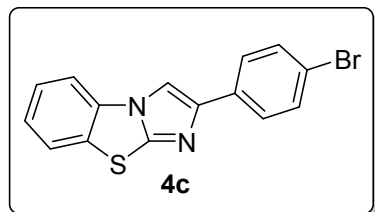
Yield 89 %; Off White solid; Mp:106-108 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (s, 1H), 7.86 – 7.83 (m, 2H), 7.61 (d,  $J = 7.4$  Hz, 1H), 7.50 (d,  $J = 8.5$  Hz, 1H), 7.41 – 7.35 (m, 3H), 7.29 – 7.27 (m, 1H), 7.26 – 7.24 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.07, 147.61, 133.83, 132.12, 130.24, 128.77, 127.55, 126.21, 125.21, 124.88, 124.35, 112.65, 106.93; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{10}\text{N}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 250.0565, found: 250.0556.

2-(4-Chlorophenyl)benzo[d]imidazo[2,1-b]thiazole (**4b**)



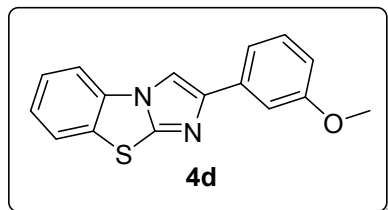
Yield 91 %; yellow solid; Mp: 160-162 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (s, 1H), 7.79 – 7.78 (m, 1H), 7.77 – 7.76 (m, 1H), 7.69 – 7.66 (m, 1H), 7.57 (dd,  $J = 8.1, 1.1$  Hz, 1H), 7.46 – 7.41 (m, 1H), 7.38 – 7.36 (m, 1H), 7.35 – 7.34 (m, 1H), 7.32 (dd,  $J = 7.5, 1.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.38, 146.66, 133.22, 132.45, 132.16, 130.38, 128.99, 126.50, 126.38, 125.13, 124.54, 112.77, 107.10; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{15}\text{H}_9\text{ClN}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 284.0175, found: 284.0162.

2-(4-Bromophenyl)benzo[d]imidazo[2,1-b]thiazole (**4c**)



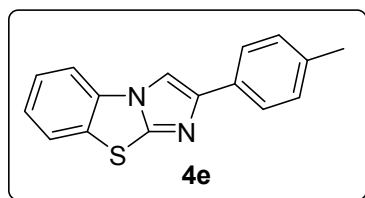
Yield 88 %; brown solid; Mp: 164-166 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (s, 1H), 7.72 – 7.69 (m, 2H), 7.67 (d,  $J = 8.0$  Hz, 1H), 7.56 (d,  $J = 8.6$  Hz, 1H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 1H), 7.35 – 7.30 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.39, 146.63, 132.87, 132.13, 131.91, 130.38, 126.79, 126.39, 125.15, 124.54, 121.35, 112.78, 107.16; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{15}\text{H}_9\text{BrN}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 327.9670, found: 327.9658.

2-(3-Methoxyphenyl)benzo[d]imidazo[2,1-b]thiazole (**4d**)



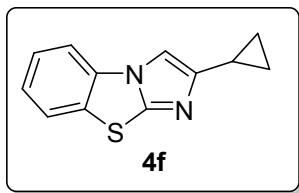
Yield 90 %; white solid; Mp: 170-172 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (s, 1H), 7.65 (d,  $J = 9.1$  Hz, 1H), 7.55 (d,  $J = 7.6$  Hz, 1H), 7.47 – 7.45 (m, 1H), 7.43 – 7.38 (m, 2H), 7.33 – 7.27 (m,  $J = 8.0, 2.3$  Hz, 2H), 6.84 (dd,  $J = 8.2, 3.6$  Hz, 1H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.14 (s), 148.07, 147.60, 135.32, 132.19, 130.34, 129.79, 126.27, 124.96, 124.43, 117.68, 113.82, 112.72, 110.28, 107.20, 55.44; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{OS}$  ( $\text{M}+\text{H}^+$ ) 280.0670, found: 280.0580.

2-(P-tolyl)benzo[d]imidazo[2,1-b]thiazole (**4e**)



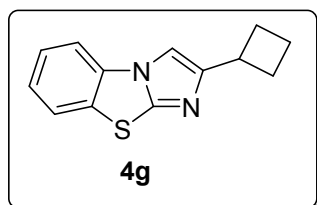
Yield 94 %; yellow solid; Mp: 147-149 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.66 (s, 1H), 7.96 (dd,  $J = 19.8, 8.1$  Hz, 2H), 7.75 (d,  $J = 8.1$  Hz, 2H), 7.57 – 7.35 (m, 2H), 7.21 (d,  $J = 8.3$  Hz, 2H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  146.71, 146.43, 136.42, 131.79, 131.12, 129.25, 129.13, 126.57, 124.98, 124.90, 124.60, 113.19, 108.47, 20.79; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 264.0721, found: 264.0742.

2-Cyclopropylbenzo[d]imidazo[2,1-b]thiazole (**4f**)



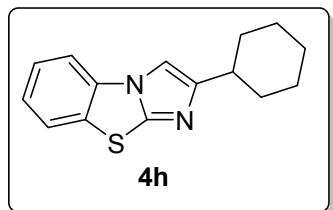
Yield 95 %; yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 9.2$  Hz, 1H), 7.61 (d,  $J = 9.7$  Hz, 1H), 7.56 (s, 1H), 7.47 – 7.42 (m, 1H), 7.36 – 7.31 (m, 1H), 2.04 – 1.94 (m, 1H), 1.00 – 0.89 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.10, 146.46, 131.96, 130.02, 126.53, 125.10, 124.46, 112.85, 107.57, 29.77, 9.41, 7.82, HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 214.0565, found: 214.0554.

#### 2-Cyclobutylbenzo[d]imidazo[2,1-b]thiazole (**4g**)



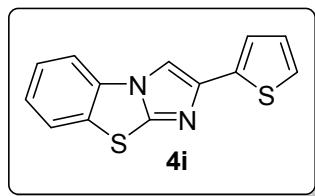
Yield 93 %; yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 8.5$  Hz, 1H), 7.50 (d,  $J = 8.0$  Hz, 1H), 7.43 (s, 1H), 7.41 – 7.37 (m, 1H), 7.30 – 7.25 (m, 1H), 3.67 – 3.57 (m, 1H), 2.42 – 2.26 (m, 4H), 2.10 – 1.89 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.26, 147.24, 132.44, 130.22, 129.44, 126.08, 124.45, 124.38, 112.42, 106.79, 34.97, 29.13, 18.72; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 228.0721, found: 228.0734.

#### 2-Cyclohexylbenzo[d]imidazo[2,1-b]thiazole (**4h**)



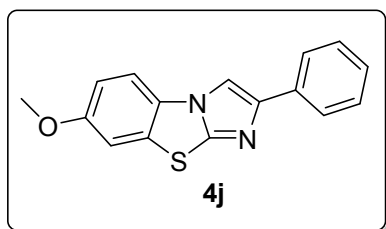
Yield 94 %; yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J = 8.0$  Hz, 1H), 7.48 (d,  $J = 7.6$  Hz, 1H), 7.40 – 7.34 (m, 2H), 7.28 – 7.23 (m, 1H), 2.75 – 2.63 (m, 1H), 2.16 – 2.07 (m,  $J = 10.5$  Hz, 2H), 1.87 – 1.69 (m, 3H), 1.52 – 1.24 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.82, 146.79, 132.48, 130.16, 126.00, 124.35, 124.31, 112.36, 106.26, 38.44, 32.96, 26.38, 26.32; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 256.1034, found: 256.1027.

2-(Thiophen-2-yl)benzo[d]imidazo[2,1-b]thiazole (**4i**)



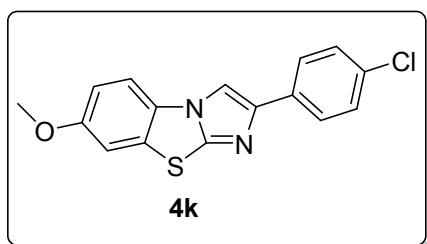
Yield 87 %; gummy mass;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (s, 1H), 7.61 (d,  $J = 8.5$  Hz, 1H), 7.49 (d,  $J = 7.4$  Hz, 1H), 7.40 – 7.34 (m, 2H), 7.28 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.04 (dd,  $J = 5.0, 3.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.98, 142.46, 137.44, 131.93, 130.17, 127.72, 126.26, 124.95, 124.33, 124.20, 122.77, 112.63, 106.32; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{13}\text{H}_8\text{N}_2\text{S}_2$  ( $\text{M}+\text{H}^+$ ) 256.1034, found: 256.1027.

7-Methoxy-2-phenylbenzo[d]imidazo[2,1-b]thiazole (**4j**)



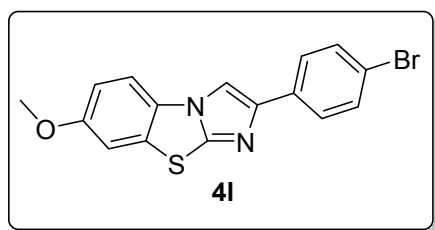
Yield 93 %; gummy mass;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 1H), 7.83 (s, 1H), 7.46 – 7.36 (m, 4H), 7.27 (d,  $J = 13.9$  Hz, 1H), 7.15 (d,  $J = 2.4$  Hz, 1H), 6.97 – 6.94 (m, 1H), 3.83 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.32, 147.56, 147.27, 134.00, 131.57, 128.81, 127.47, 126.52, 125.18, 113.48, 113.20, 108.84, 106.94, 56.02; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{OS}$  ( $\text{M}+\text{H}^+$ ) 280.0670, found: 280.0662.

2-(4-Chlorophenyl)-7-methoxybenzo[d]imidazo[2,1-b]thiazole (**4k**)



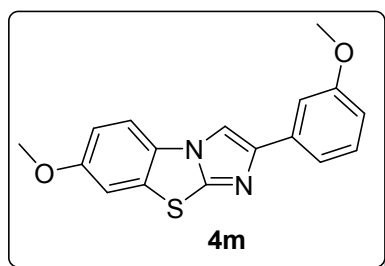
Yield 88 %; brown solid; Mp: 158-160 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (s, 1H), 7.77 (d,  $J$  = 8.5 Hz, 2H), 7.48 (d,  $J$  = 8.8 Hz, 1H), 7.36 (d,  $J$  = 8.5 Hz, 2H), 7.20 (d,  $J$  = 2.4 Hz, 1H), 7.00 (dd,  $J$  = 8.8, 2.5 Hz, 1H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.50, 146.31, 140.72, 136.49, 133.06, 132.57, 131.56, 130.89, 128.99, 126.42, 113.61, 113.28, 108.93, 107.09, 56.08; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{11}\text{ClN}_2\text{OS}$  ( $\text{M}+\text{H}^+$ ) 314.0281, found: 314.0272.

2-(4-Bromophenyl)-7-methoxybenzo[d]imidazo[2,1-b]thiazole (**4l**)



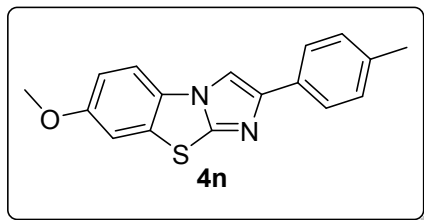
Yield 92 %; brown solid; Mp: 161-163 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 1H), 7.69 (d,  $J$  = 8.6 Hz, 2H), 7.50 (d,  $J$  = 8.6 Hz, 2H), 7.45 (d,  $J$  = 8.8 Hz, 1H), 7.18 (d,  $J$  = 2.4 Hz, 1H), 6.98 (dd,  $J$  = 8.8, 2.5 Hz, 1H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.46, 147.81, 146.25, 133.05, 131.90, 131.62, 126.69, 126.42, 121.14, 113.59, 113.26, 108.90, 107.11, 56.06; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{11}\text{BrN}_2\text{OS}$  ( $\text{M}+\text{H}^+$ ) 357.9775, found: 357.9764.

7-Methoxy-2-(3-methoxyphenyl)benzo[d]imidazo[2,1-b]thiazole (**4m**)



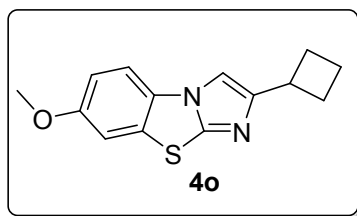
Yield 90 %; gummy mass;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (s, 1H), 7.48 (d,  $J$  = 8.8 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.31 (t,  $J$  = 7.9 Hz, 1H), 7.19 (d,  $J$  = 2.5 Hz, 1H), 6.99 (dd,  $J$  = 8.8, 2.5 Hz, 1H), 6.84 (dd,  $J$  = 8.2, 2.6 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.18, 157.39, 147.53, 147.24, 135.48, 131.64, 129.81, 126.51, 117.64, 113.74, 113.53, 113.25, 110.22, 108.90, 107.21, 56.06, 55.48; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 310.0776, found: 310.0784.

7-Methoxy-2-(p-tolyl)benzo[d]imidazo[2,1-b]thiazole (**4n**)



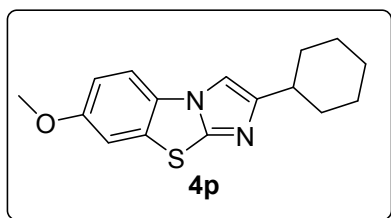
Yield 88 %; brown solid; Mp:161-163 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (s, 1H), 7.70 (d,  $J$  = 8.2 Hz, 2H), 7.33 (d,  $J$  = 8.8 Hz, 1H), 7.17 (d,  $J$  = 8.2 Hz, 2H), 7.09 (d,  $J$  = 2.5 Hz, 1H), 6.88 (dd,  $J$  = 8.8, 2.5 Hz, 1H), 3.77 (s, 3H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.12, 147.28, 147.24, 137.07, 131.36, 131.20, 129.40, 126.38, 124.98, 113.26, 113.01, 108.68, 106.43, 55.88, 21.29; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{OS}$  ( $\text{M}+\text{H}^+$ ) 294.0827, found: 294.0835.

2-Cyclobutyl-7-methoxybenzo[d]imidazo[2,1-b]thiazole (**4o**)



Yield 92 %; yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J$  = 8.8 Hz, 1H), 7.38 (s, 1H), 7.18 (d,  $J$  = 2.5 Hz, 1H), 6.97 (dd,  $J$  = 8.8, 2.5 Hz, 1H), 3.86 (s, 3H), 3.65 – 3.55 (m, 1H), 2.40 – 2.25 (m, 4H), 2.08 – 1.93 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.03, 152.75, 146.64, 131.47, 126.82, 113.36, 112.94, 108.89, 106.81, 56.06, 34.96, 29.24, 18.73; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{OS}$  ( $\text{M}+\text{H}^+$ ) 258.0827, found: 258.0818.

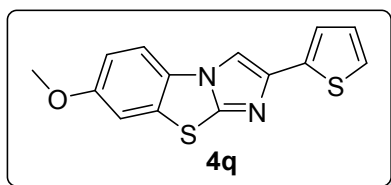
2-Cyclohexyl-7-methoxybenzo[d]imidazo[2,1-b]thiazole (**4p**)





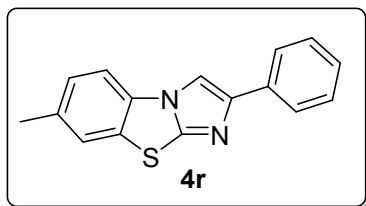
Yield 94 %; yellow oil ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (dd,  $J = 8.8, 2.7$  Hz, 1H), 7.33 – 7.31 (m, 1H), 7.16 (t,  $J = 2.6$  Hz, 1H), 6.97 – 6.92 (m, 1H), 3.84 (s, 3H), 2.73 – 2.63 (m, , 1H), 2.14 – 2.06 (m, 2H), 1.85 – 1.71 (m, 3H), 1.51 – 1.29 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.91, 154.40, 146.17, 131.40, 126.87, 113.23, 112.86, 108.83, 106.25, 56.01, 38.45, 33.05, 26.43, 26.36; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{OS}$  ( $\text{M}+\text{H}^+$ ) 286.1140, found: 286.1152.

7-Methoxy-2-(thiophen-2-yl)benzo[d]imidazo[2,1-b]thiazole (**4q**)



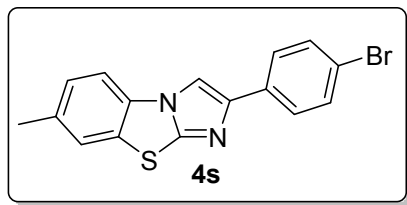
Yield 88 %; gummy mass;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (s, 1H), 7.46 (d,  $J = 8.8$  Hz, 1H), 7.36 (dd,  $J = 3.6, 1.1$  Hz, 1H), 7.23 (d,  $J = 6.2$  Hz, 1H), 7.18 (d,  $J = 2.5$  Hz, 1H), 7.06 (d,  $J = 8.6$  Hz, 1H), 6.98 (dd,  $J = 8.8, 2.5$  Hz, 1H), 3.85 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.42, 137.71, 131.61, 127.78, 124.11, 122.65, 122.44, 115.88, 113.59, 113.23, 108.90, 106.40, 56.07; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{OS}_2$  ( $\text{M}+\text{H}^+$ ) 286.0235, found: 286.0248.

7-Methyl-2-phenylbenzo[d]imidazo[2,1-b]thiazole (**4r**)



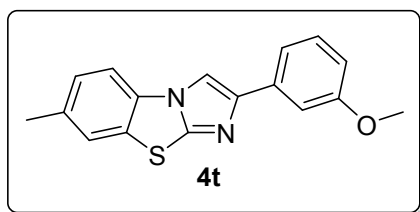
Yield 90 %; yellow solid; Mp:158-160 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 1.4$  Hz, 1H), 7.82 (s, 1H), 7.82 (s, 1H), 7.41 – 7.35 (m, 4H), 7.30 – 7.24 (m, 1H), 7.14 (d,  $J = 8.2$  Hz, 1H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.93, 147.37, 135.00, 133.99, 130.23, 130.08, 128.75, 127.43, 127.15, 125.16, 124.38, 112.22, 106.86, 21.39; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 264.0721, found: 264.0732.

2-(4-Bromophenyl)-7-methylbenzo[d]imidazo[2,1-b]thiazole (**4s**)



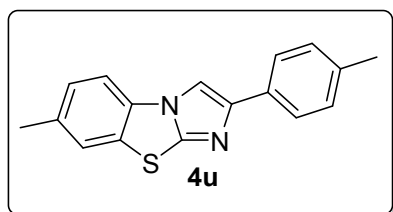
Yield 89 %; yellow solid; Mp: 178-180 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (s, 1H), 7.72 – 7.68 (m, 2H), 7.50 (d,  $J$  = 8.4 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.22 (d,  $J$  = 8.2 Hz, 1H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.28, 146.38, 135.31, 131.89, 130.39, 130.10, 127.34, 126.73, 124.58, 121.21, 112.38, 107.12, 21.51; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{11}\text{BrN}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 341.9826, found: 341.9831.

2-(3-Methoxyphenyl)-7-methylbenzo[d]imidazo[2,1-b]thiazole (**4t**)



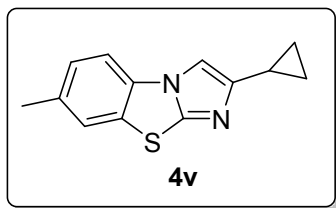
Yield 91 %; yellow solid; Mp: 172-174 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (s, 1H), 7.44 – 7.42 (m, 1H), 7.40 – 7.34 (m, 3H), 7.29 (d,  $J$  = 8.0 Hz, 1H), 7.14 (d,  $J$  = 8.9 Hz, 1H), 6.82 (d,  $J$  = 5.5 Hz, 1H), 3.86 (s, 3H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.07, 147.83, 147.20, 135.38, 135.02, 130.21, 130.03, 129.71, 127.15, 124.35, 117.56, 113.62, 112.23, 110.14, 107.11, 55.37, 21.37; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{OS}$  ( $\text{M}+\text{H}^+$ ) 294.0827, found: 294.0818.

7-Methyl-2-(p-tolyl)benzo[d]imidazo[2,1-b]thiazole (**4u**)



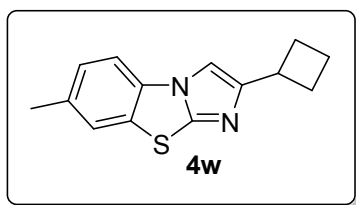
Yield 94 %; yellow solid; Mp: 152-154 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (s, 1H), 7.72 (d,  $J$  = 8.1 Hz, 2H), 7.38 (s, 1H), 7.35 (d,  $J$  = 8.2 Hz, 1H), 7.16 (dd,  $J$  = 19.4, 8.0 Hz, 3H), 2.38 (s, 3H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.77, 147.51, 137.16, 134.87, 131.22, 130.23, 130.15, 129.44, 127.11, 125.07, 124.36, 112.18, 106.43, 21.38, 21.32; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 278.0878, found: 278.0867.

2-Cyclopropyl-7-methylbenzo[d]imidazo[2,1-b]thiazole (**4v**)



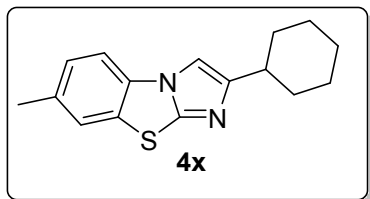
Yield 94 %; yellow oil ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (s, 1H), 7.42 (s, 1H), 7.40 (d,  $J = 8.2$  Hz, 1H), 7.20 (d,  $J = 8.2$  Hz, 1H), 2.44 (s, 3H), 2.01 – 1.93 (m, 1H), 0.97 – 0.91 (m, 2H), 0.91 – 0.86 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.88, 146.59, 134.79, 130.19, 130.13, 127.22, 124.44, 112.15, 107.12, 21.42, 9.76, 7.64; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 228.0721, found: 228.0736.

2-Cyclobutyl-7-methylbenzo[d]imidazo[2,1-b]thiazole (**4w**)



Yield 93 %; yellow oil ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (s, 1H), 7.39 (s, 1H), 7.36 (d,  $J = 8.2$  Hz, 1H), 7.17 (d,  $J = 8.2$  Hz, 1H), 3.66 – 3.55 (m,  $J = 8.9$  Hz, 1H), 2.42 (s, 3H), 2.37 – 2.25 (m, 4H), 2.08 – 1.91 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.85, 147.06, 134.50, 130.37, 130.16, 127.01, 124.39, 112.01, 106.74, 34.92, 29.16, 21.38, 18.69; HRMS (ESI,  $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 242.0878, found: 242.0863.

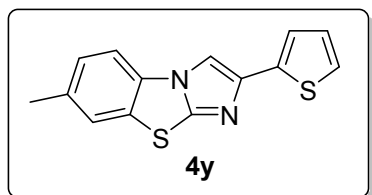
2-Cyclohexyl-7-methylbenzo[d]imidazo[2,1-b]thiazole (**4x**)



Yield 90 %; yellow oil ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (s, 1H), 7.38 – 7.32 (m, 2H), 7.16 (d,  $J = 7.5$  Hz, 1H), 2.74 – 2.61 (m, 1H), 2.41 (s, 3H), 2.15 – 2.07 (m, 2H), 1.86 – 1.69 (m, 3H), 1.53 – 1.27 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.60, 146.66, 134.38, 130.50, 130.20,

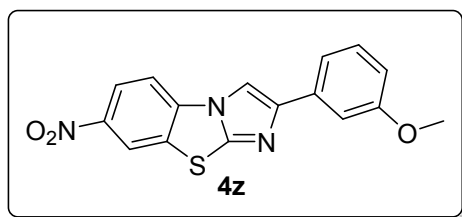
126.95, 124.39, 111.99, 106.20, 38.47, 33.01, 26.42, 26.36, 21.39; HRMS (ESI, m/z): calcd for  $C_{16}H_{18}N_2S$  ( $M+H^+$ ) 270.1191, found: 270.1183.

7-Methyl-2-(thiophen-2-yl)benzo[d]imidazo[2,1-b]thiazole (**4y**)



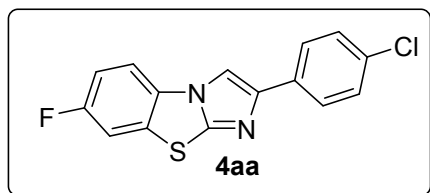
Yield 88 %; gummy mass;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.71 (s, 1H), 7.37 (s, 1H), 7.35 – 7.32 (m, 2H), 7.21 (d,  $J = 5.0$  Hz, 1H), 7.14 (d,  $J = 8.2$  Hz, 1H), 7.03 (dd,  $J = 4.9, 3.7$  Hz, 1H), 2.38 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  147.82, 142.22, 137.63, 135.10, 130.15, 129.88, 127.69, 127.20, 124.33, 124.02, 122.58, 112.18, 106.26, 21.36; HRMS (ESI, m/z): calcd  $C_{14}H_{10}N_2S_2$  ( $M+H^+$ ) 270.0285, found: 270.0298.

2-(3-Methoxyphenyl)-7-nitrobenzo[d]imidazo[2,1-b]thiazole (**4z**)



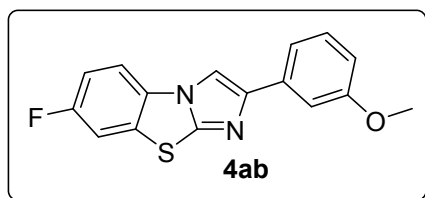
Yield 84 %; yellow solid; Mp: 228-230 °C;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  9.09 (d,  $J = 2.3$  Hz, 1H), 8.88 (s, 1H), 8.44 (dd,  $J = 8.9, 2.3$  Hz, 1H), 8.13 (d,  $J = 8.9$  Hz, 1H), 7.45 – 7.32 (m, 3H), 6.88 (d,  $J = 8.0$  Hz, 1H), 3.82 (s, 3H);  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ )  $^{13}C$  NMR  $\delta$  159.64, 148.75, 147.13, 144.09, 135.90, 134.68, 130.66, 129.90, 122.65, 121.57, 117.21, 113.49, 113.44, 110.01, 109.86, 55.07; HRMS (ESI, m/z): calcd  $C_{16}H_{11}N_3O_3S$  ( $M+H^+$ ) 325.0521, found: 325.0535.

2-(4-Chlorophenyl)-7-fluorobenzo[d]imidazo[2,1-b]thiazole (**4aa**)



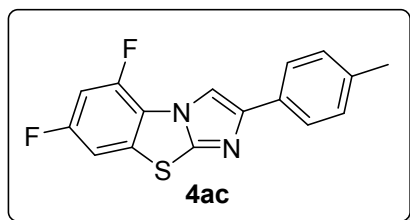
Yield 89 %; yellow solid; Mp: 162-164 °C;  $^1\text{H}$  NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.79 (s, 1H), 8.03 – 7.97 (m, 2H), 7.85 (d,  $J$  = 8.5 Hz, 2H), 7.51 – 7.42 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  159.17 ( $^1J_{\text{C-F}}$  = 242 Hz), 147.15, 145.06, 132.70, 131.57, 130.89, 130.83 ( $J_{\text{C-F}}$  = 12 Hz), 128.78, 128.61, 128.59, 126.26, 114.42 ( $J_{\text{C-F}}$  = 10 Hz), 114.11, 112.14 ( $J_{\text{C-F}}$  = 28 Hz), 109.68; HRMS (ESI,  $m/z$ ): calcd C<sub>15</sub>H<sub>8</sub>ClFN<sub>2</sub>S (M+H<sup>+</sup>) 302.0081, found: 302.0076.

7-Fluoro-2-(3-methoxyphenyl)benzo[d]imidazo[2,1-b]thiazole (**4ab**)



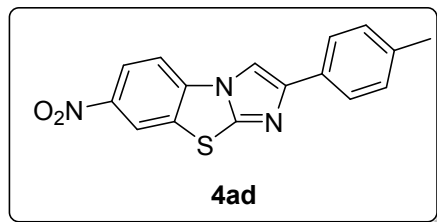
Yield 86 %; yellow solid; Mp: 168-170 °C;  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (s, 1H), 7.52 (dd,  $J$  = 8.8, 4.3 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.31 (t,  $J$  = 7.9 Hz, 1H), 7.16 (td,  $J$  = 8.7, 2.5 Hz, 1H), 6.85 (dd,  $J$  = 8.5, 2.9 Hz, 1H), 3.88 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.17, 159.85 ( $^1J_{\text{C-F}}$  = 244 Hz), 147.78, 135.16, 131.7 ( $J_{\text{C-F}}$  = 10 Hz), 129.85, 128.81, 117.69, 114.11, 113.39 ( $J_{\text{C-F}}$  = 10 Hz), 113.34, 111.59 ( $J_{\text{C-F}}$  = 28 Hz), 110.37, 107.31, 55.47; HRMS (ESI,  $m/z$ ): calcd C<sub>16</sub>H<sub>11</sub>FN<sub>2</sub>OS (M+H<sup>+</sup>) 298.0576, found: 298.0585.

5,7-Difluoro-2-(p-tolyl)benzo[d]imidazo[2,1-b]thiazole (**4ac**)



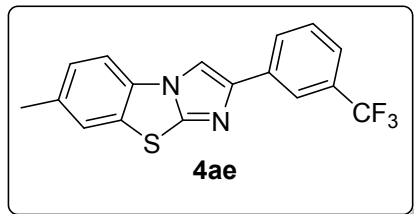
Yield 90 %; white solid; Mp: 216-218 °C;  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d,  $J$  = 1.9 Hz, 1H), 7.72 (d,  $J$  = 8.1 Hz, 2H), 7.21 (d,  $J$  = 8.0 Hz, 3H), 7.00 – 6.94 (m, 1H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.26 ( $^1J_{\text{C-F}}$  = 248 Hz), 159.16 ( $^1J_{\text{C-F}}$  = 247 Hz), 150.69 ( $J_{\text{C-F}}$  = 13 Hz), 148.22 ( $J_{\text{C-F}}$  = 7 Hz), 146.95, 137.59, 133.22 ( $J_{\text{C-F}}$  = 4 Hz, 13 Hz), 130.80, 129.54, 125.19, 109.23 ( $J_{\text{C-F}}$  = 3 Hz), 107.11 ( $J_{\text{C-F}}$  = 4 Hz), 102.52 ( $J_{\text{C-F}}$  = 21 Hz), 102.38 ( $J_{\text{C-F}}$  = 21 Hz), 21.38; HRMS (ESI,  $m/z$ ): calcd C<sub>16</sub>H<sub>10</sub>F<sub>2</sub>N<sub>2</sub>S (M+H<sup>+</sup>) 300.0533, found: 300.0546.

7-Nitro-2-(p-tolyl)benzo[d]imidazo[2,1-b]thiazole (**4ad**)



Yield 82 %; yellow solid, Mp: 245-247 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- *d*6)  $\delta$  9.12 (d,  $J$  = 2.2 Hz, 1H), 8.85 (s, 1H), 8.46 (m, , 1H), 8.29 (s, 1H), 8.16 (d,  $J$  = 8.9 Hz, 1H), 7.78 – 7.76 (m, 1H), 7.27 – 7.25 (m, 1H), 6.82 (s, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO-*d*6)  $\delta$  147.44, 143.93, 136.66, 136.41, 135.65, 130.36, 128.94, 127.54, 124.61, 122.16, 121.03, 113.08, 108.54, 20.41; HRMS (ESI,  $m/z$ ): calcd  $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 309.0572, found: 309.0586.

7-Methyl-2-(3-(trifluoromethyl)phenyl)benzo[d]imidazo[2,1-b]thiazole (**4ae**)

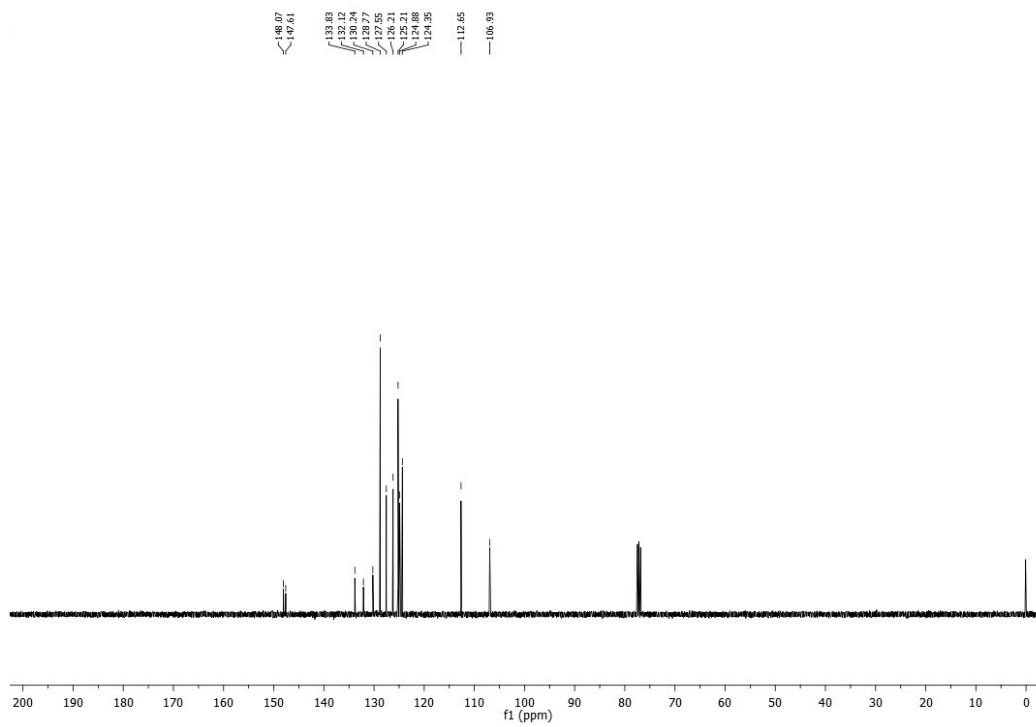
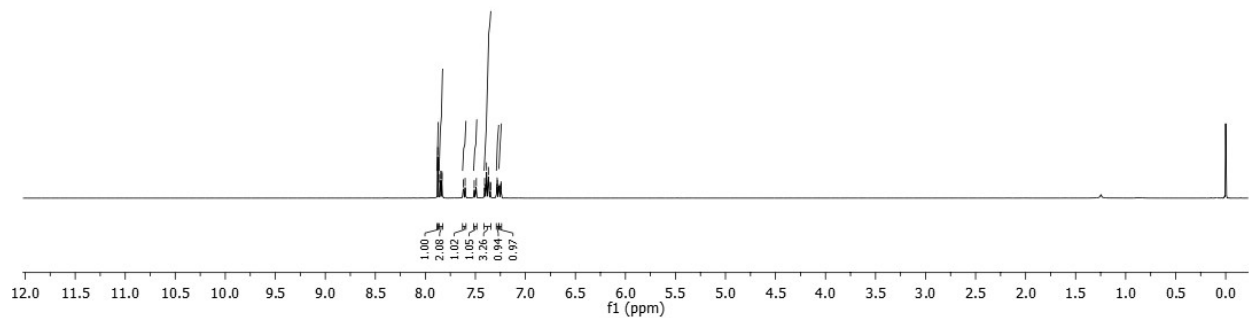
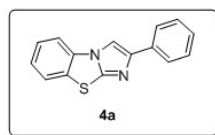


Yield 89 %; gummy mass,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (s, 1H), 8.04 – 8.00 (m, 1H), 7.97 (s, 1H), 7.52 (dd,  $J$  = 4.9, 2.1 Hz, 2H), 7.50 – 7.47 (m, 2H), 7.26 – 7.23 (m, 1H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.47, 146.03, 135.50, 134.85, 131.94, 130.7 (q,  $^2J_{\text{C-F}}$  = 32 Hz), 129.27, 128.28, 128.27, 127.43, 124.0 (q,  $^3J_{\text{C-F}}$  = 4 Hz), 122.0 (q,  $^1J_{\text{C-F}}$  = 270 Hz), 112.47, 107.62, 21.51; HRMS (ESI,  $m/z$ ): calcd  $\text{C}_{17}\text{H}_{11}\text{F}_3\text{N}_2\text{S}$  ( $\text{M}+\text{H}^+$ ) 332.0595, found: 332.0623.

## **$^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of the compounds**

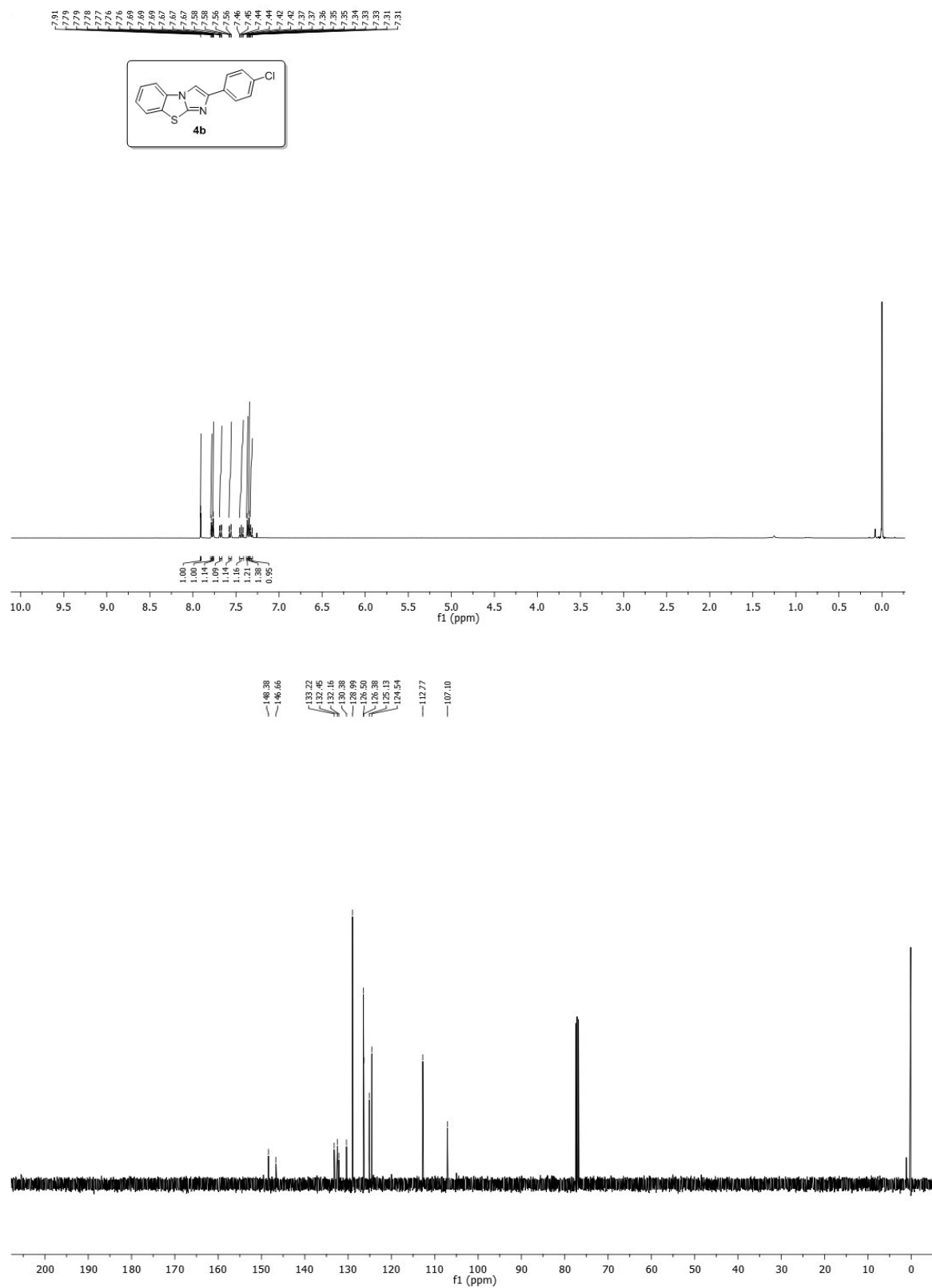
# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of compound (4a)

7.68  
7.66  
7.65  
7.65  
7.64  
7.63  
7.62  
7.60  
7.51  
7.49  
7.41  
7.40  
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7.24  
7.24

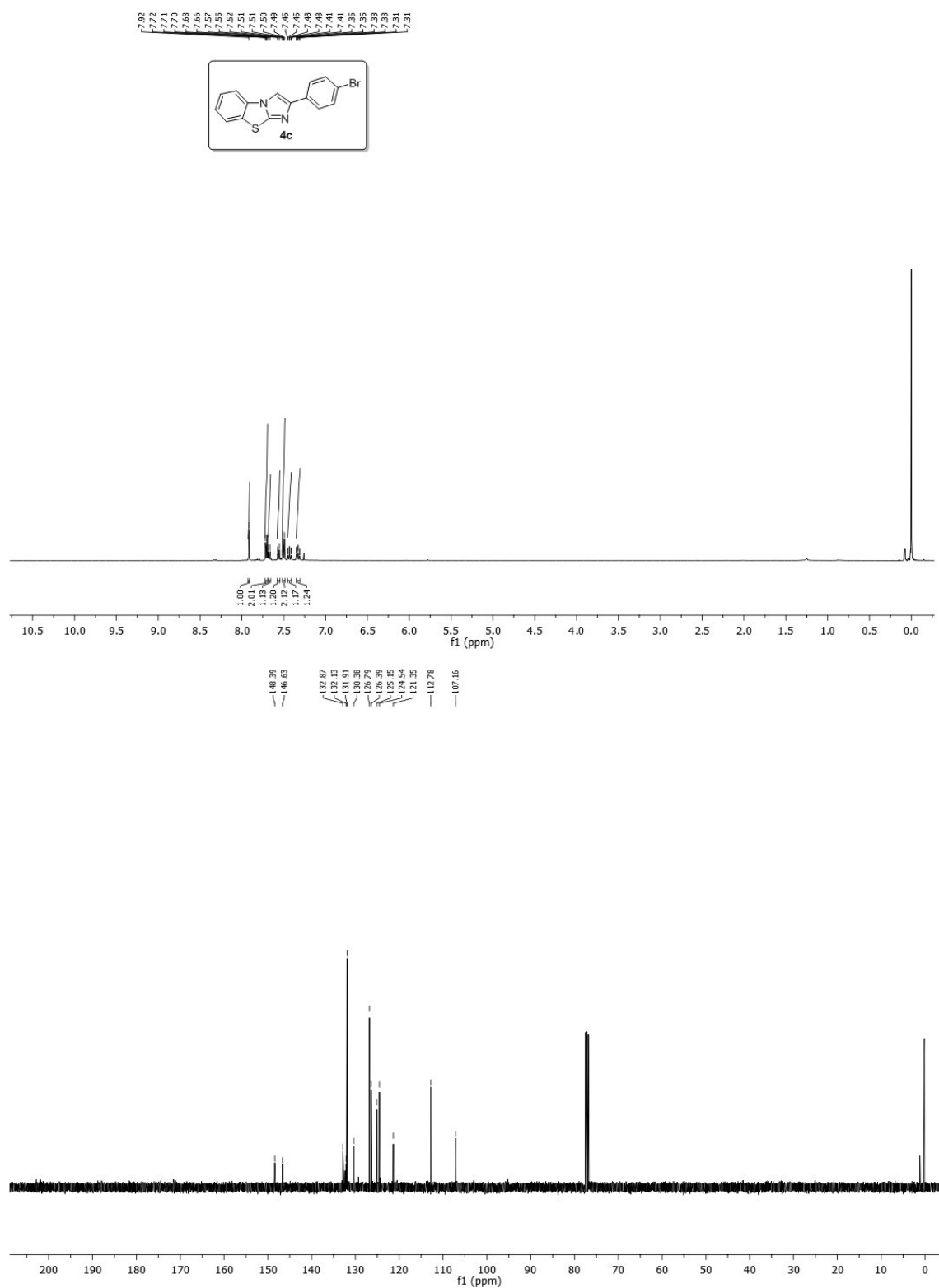




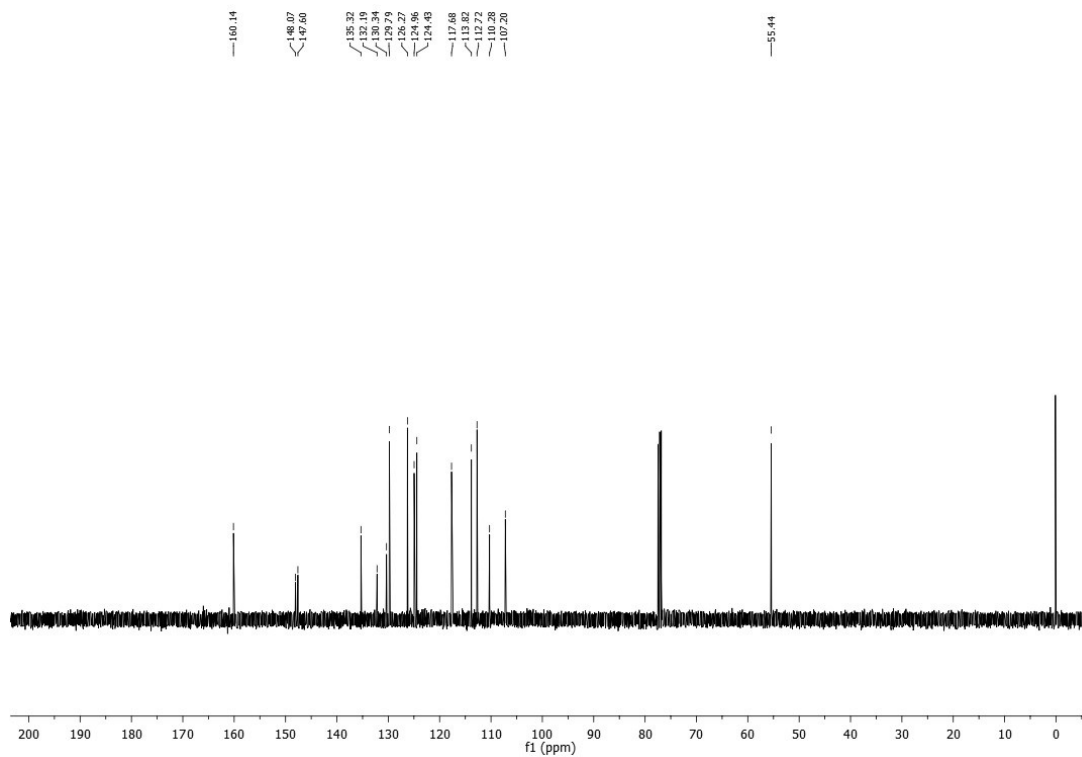
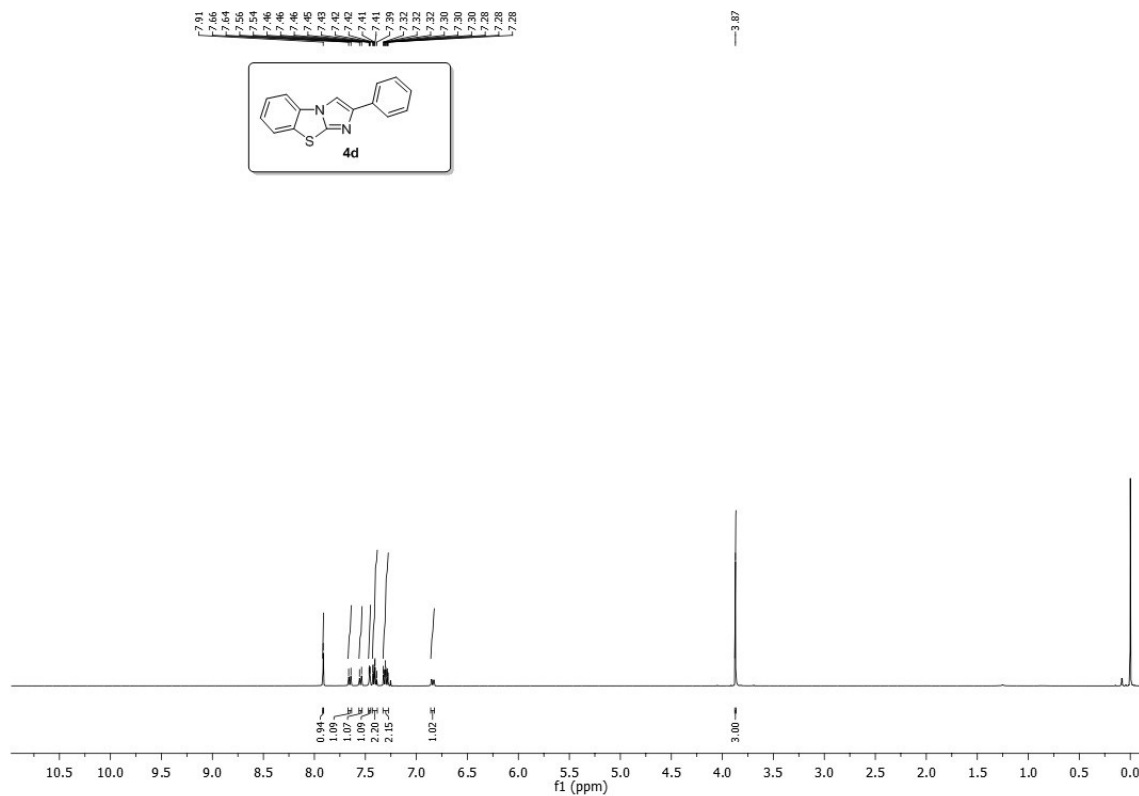
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4b**)



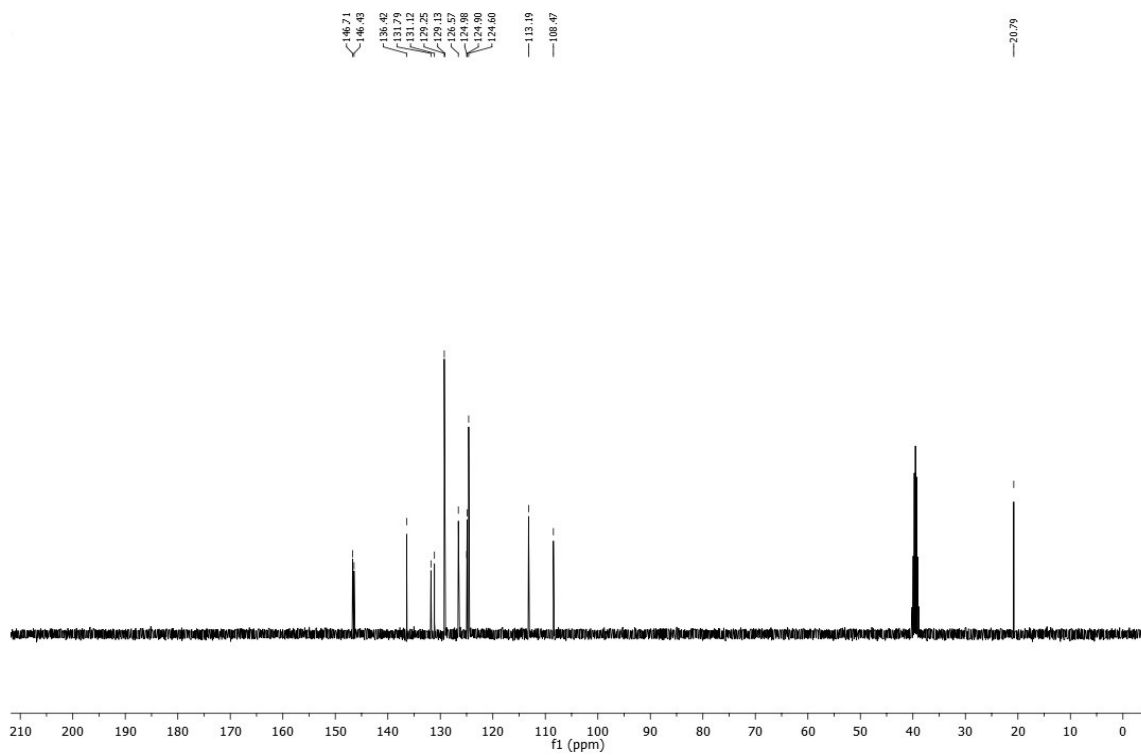
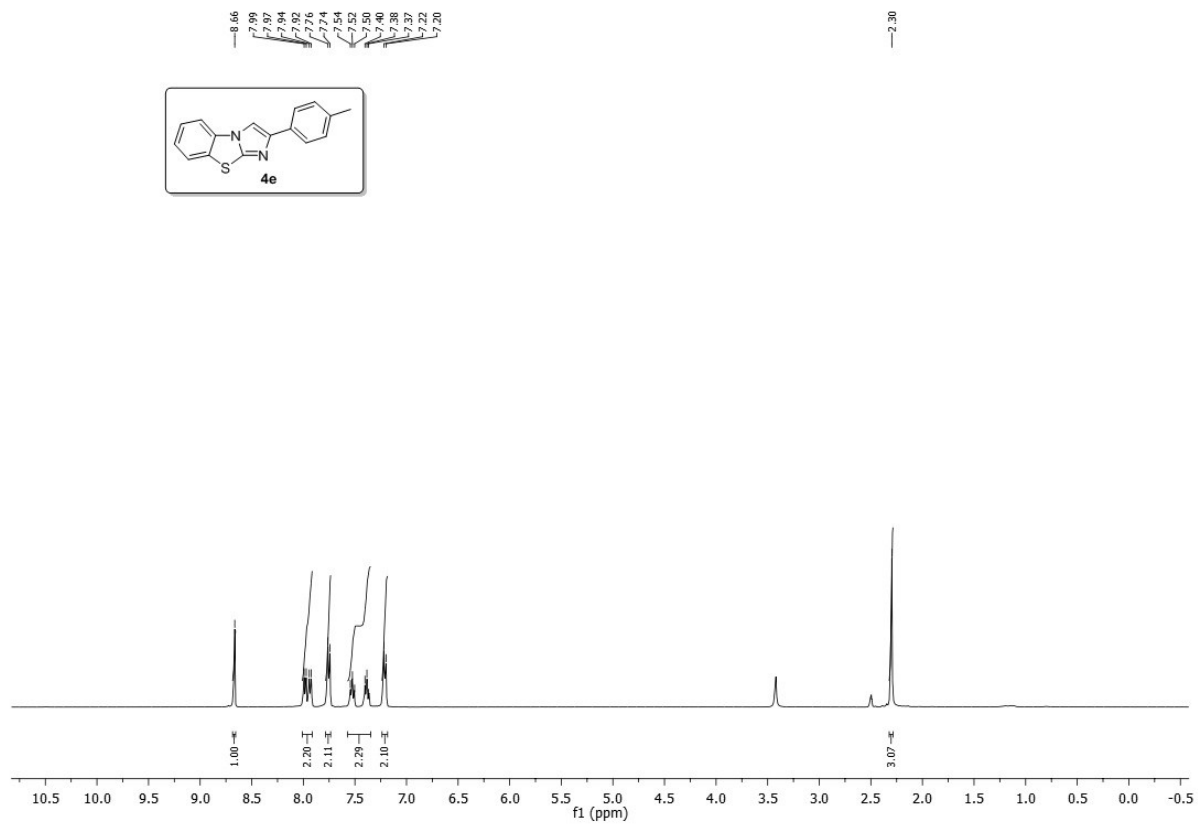
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4c**)



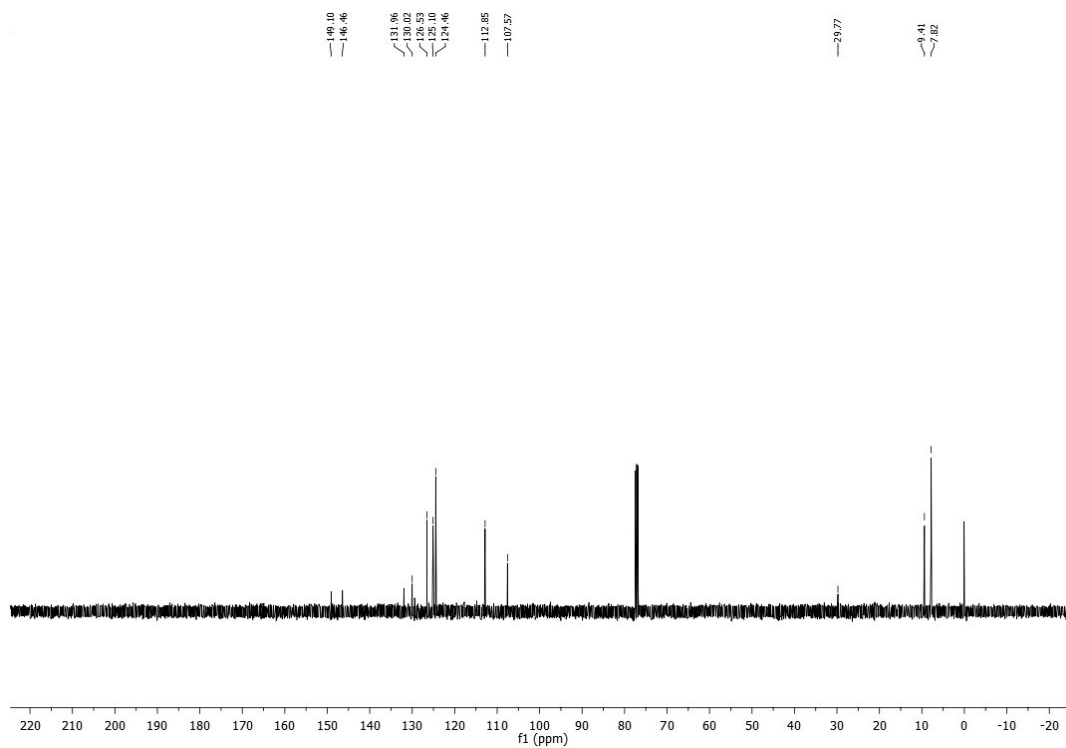
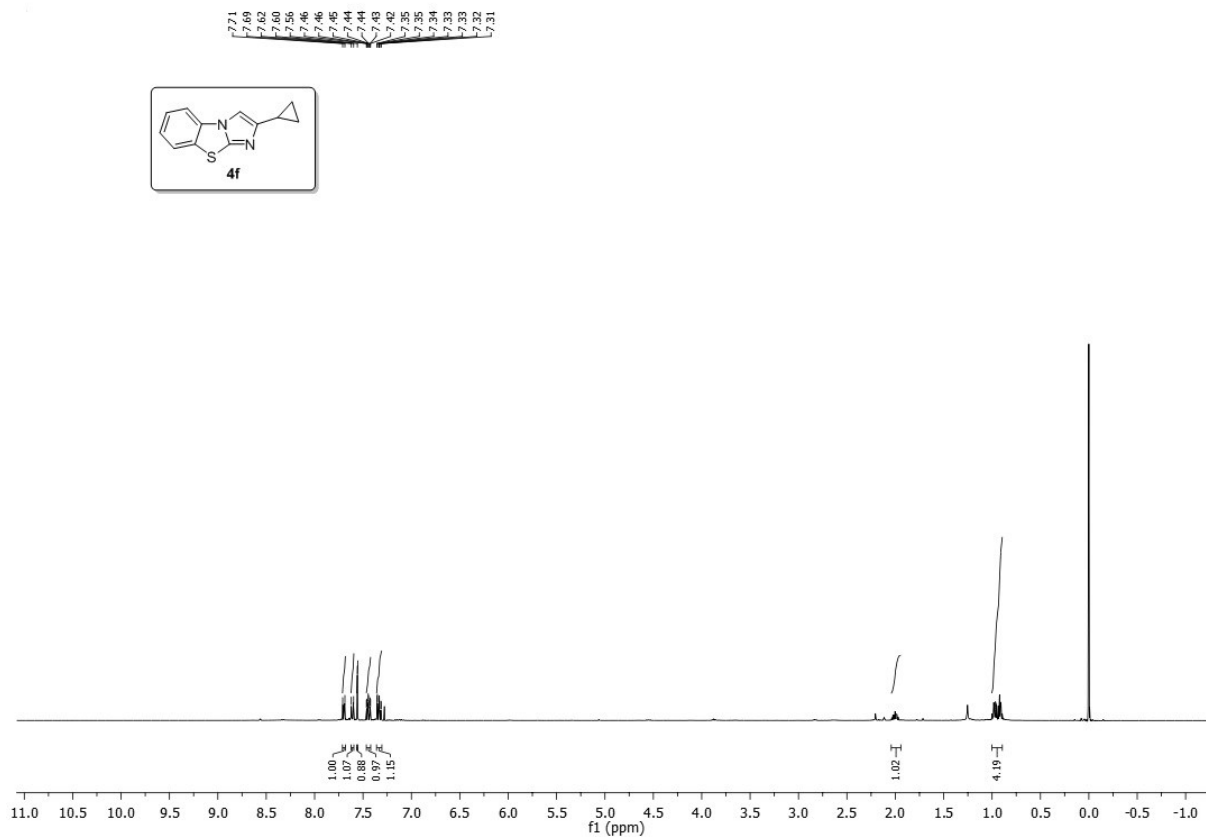
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4d**)



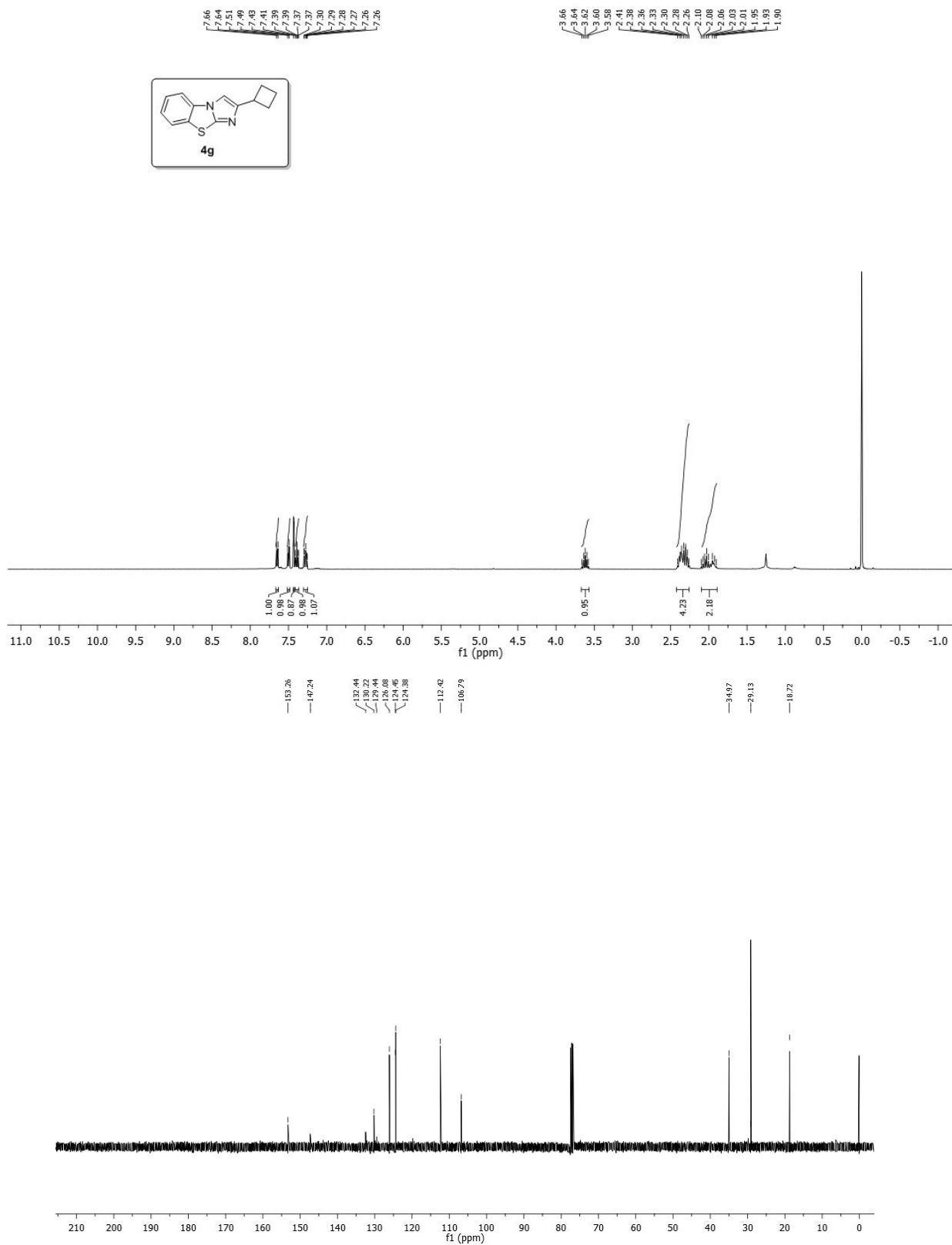
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4e**)



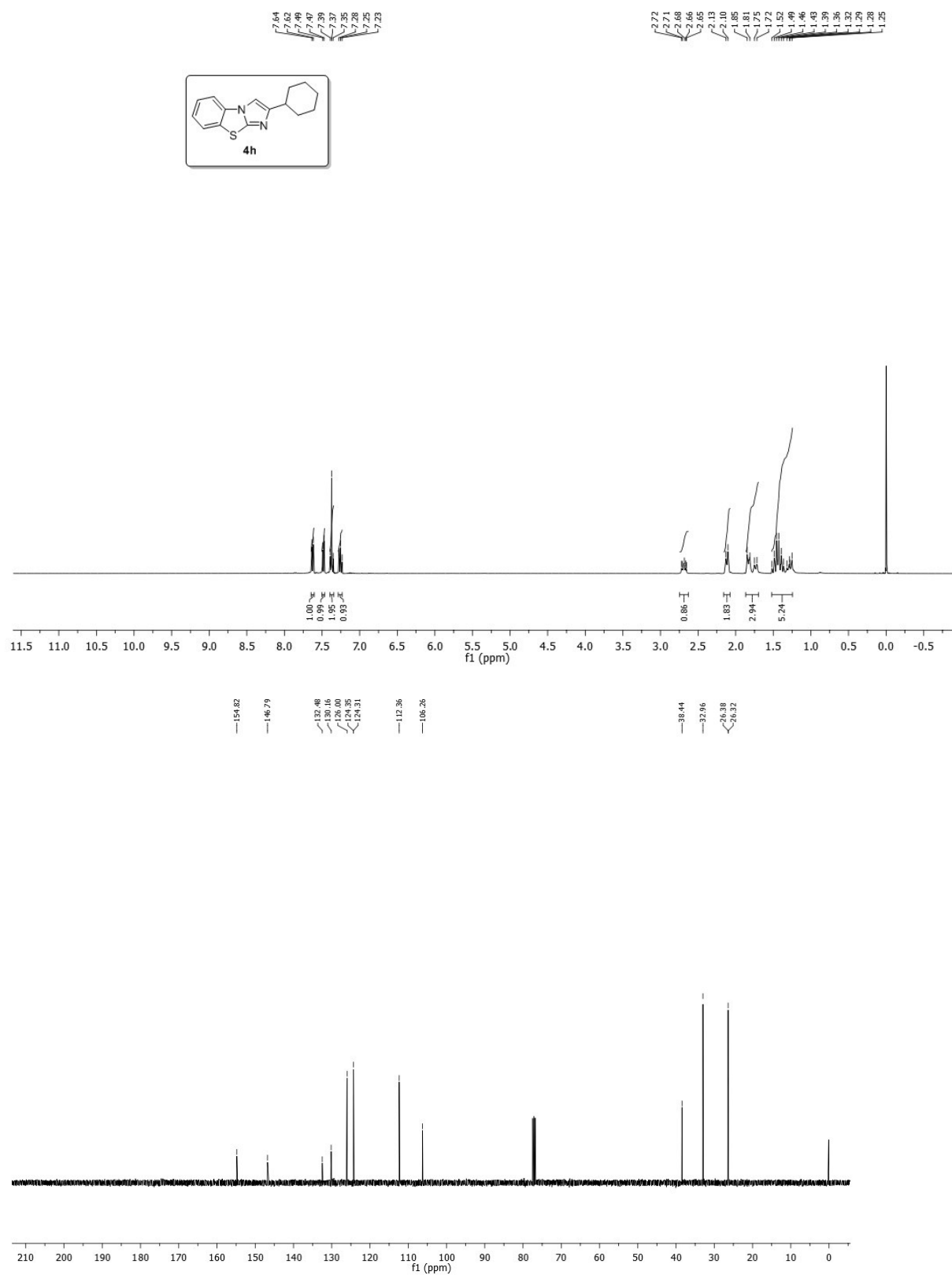
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (4f)



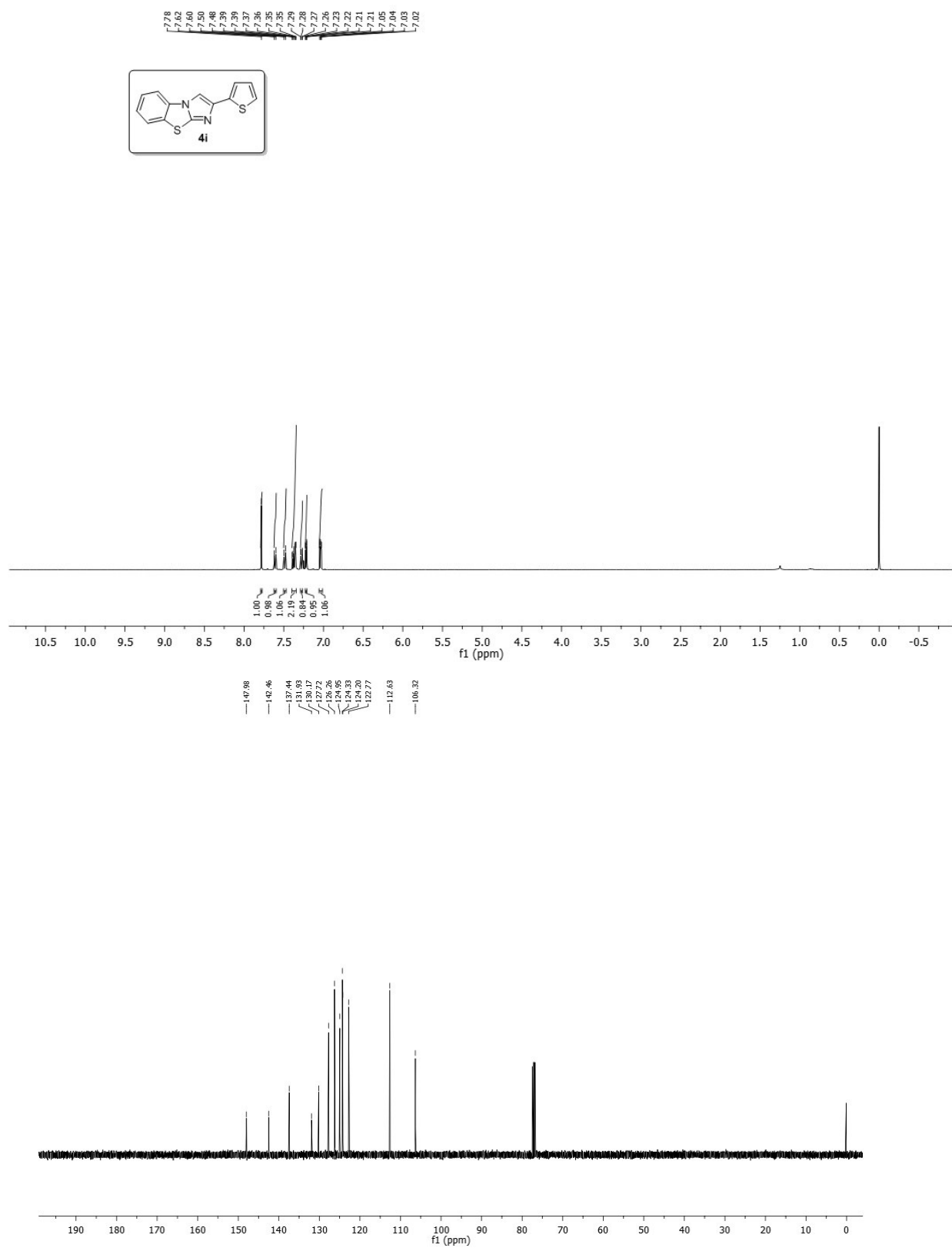
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4g**)



$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4h**)

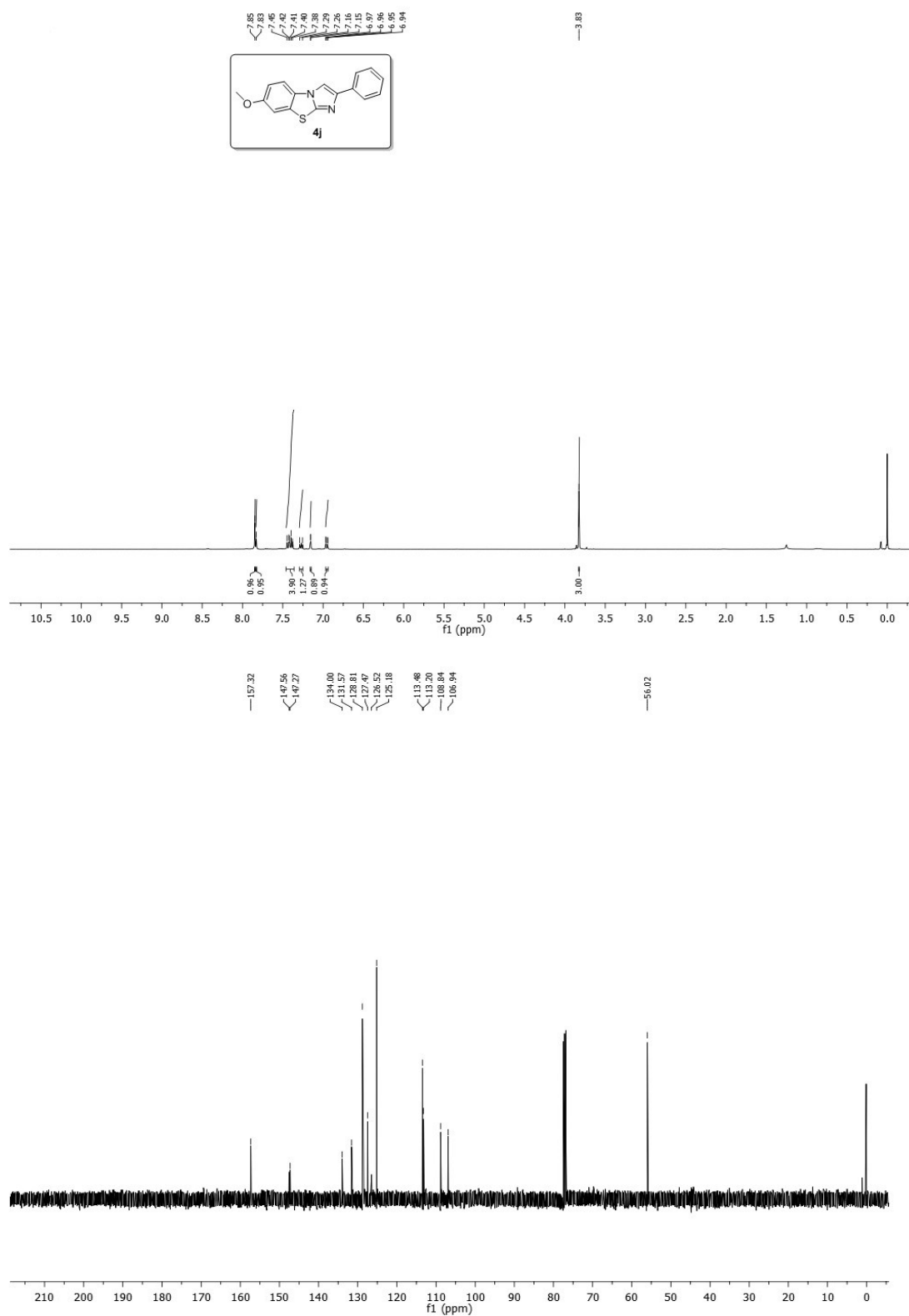


$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4i**)

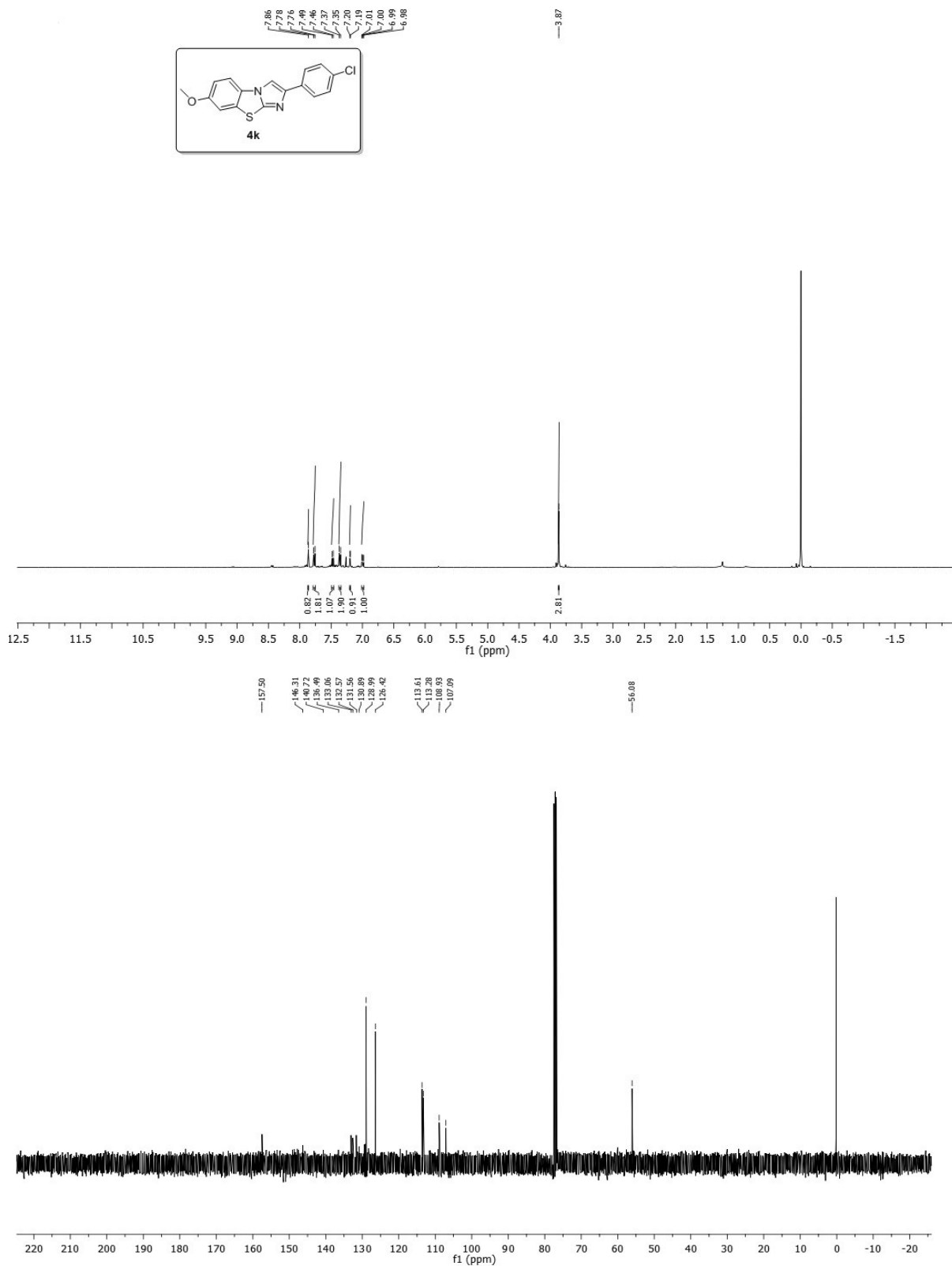




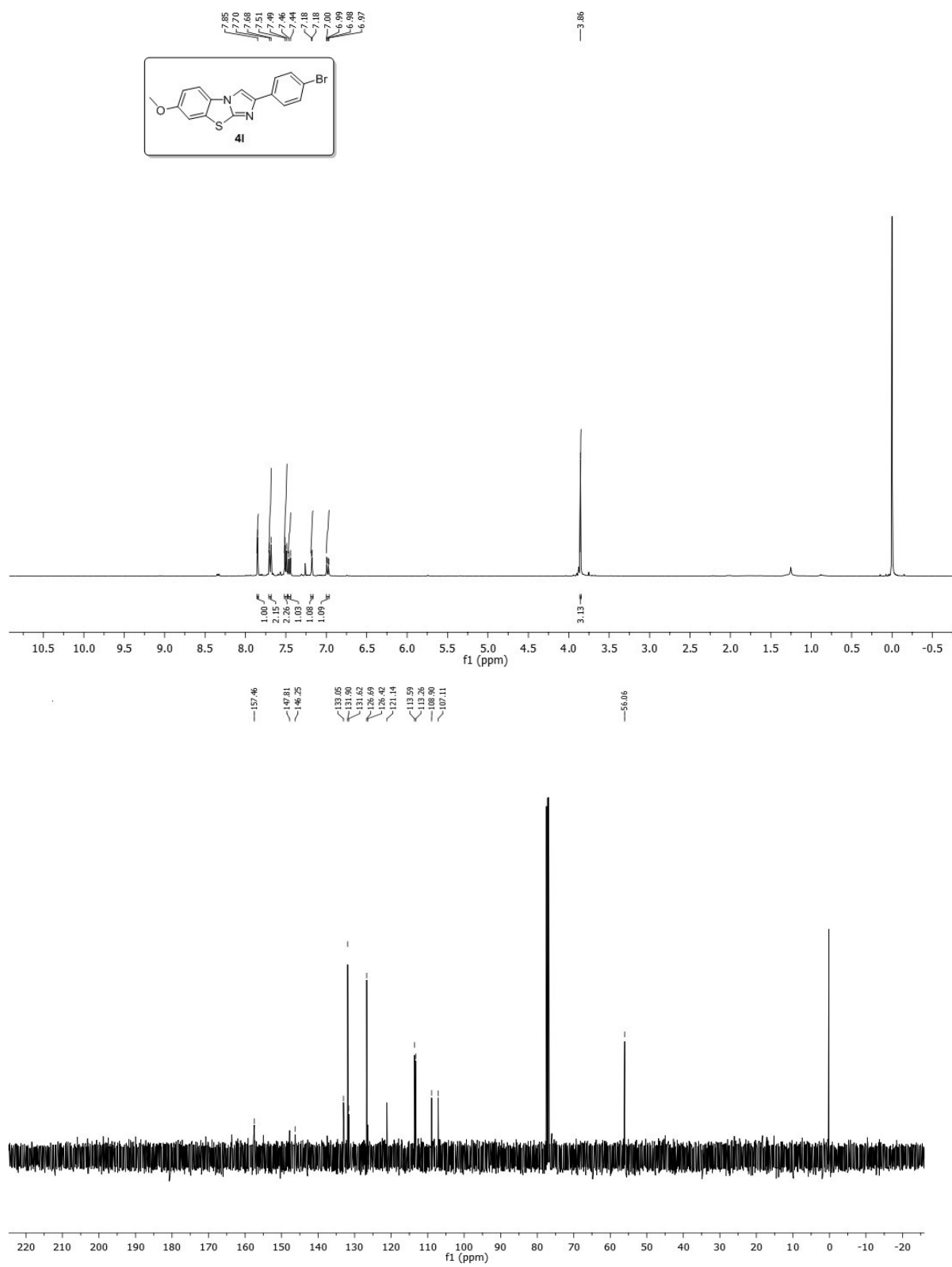
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (4j)



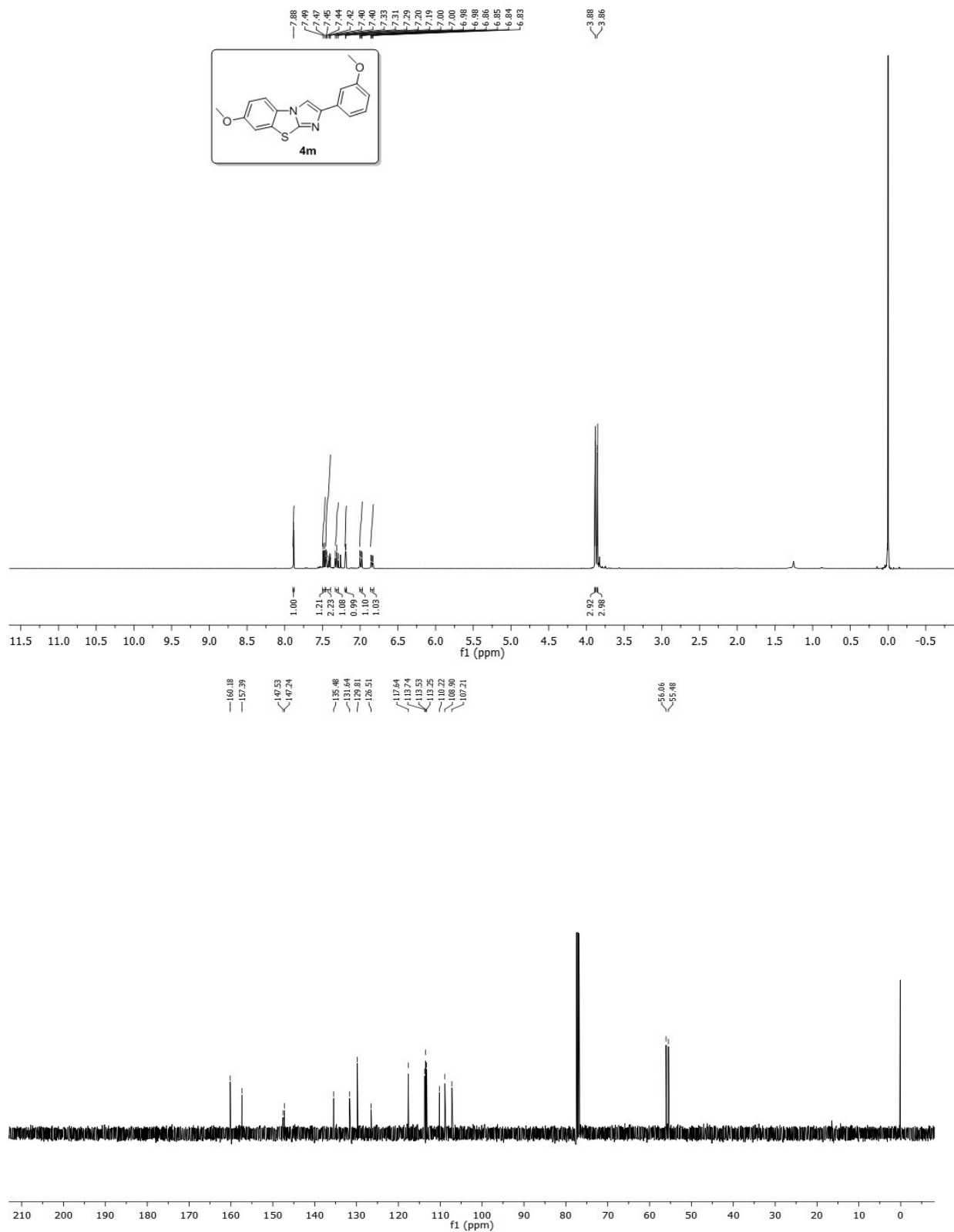
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4k**)



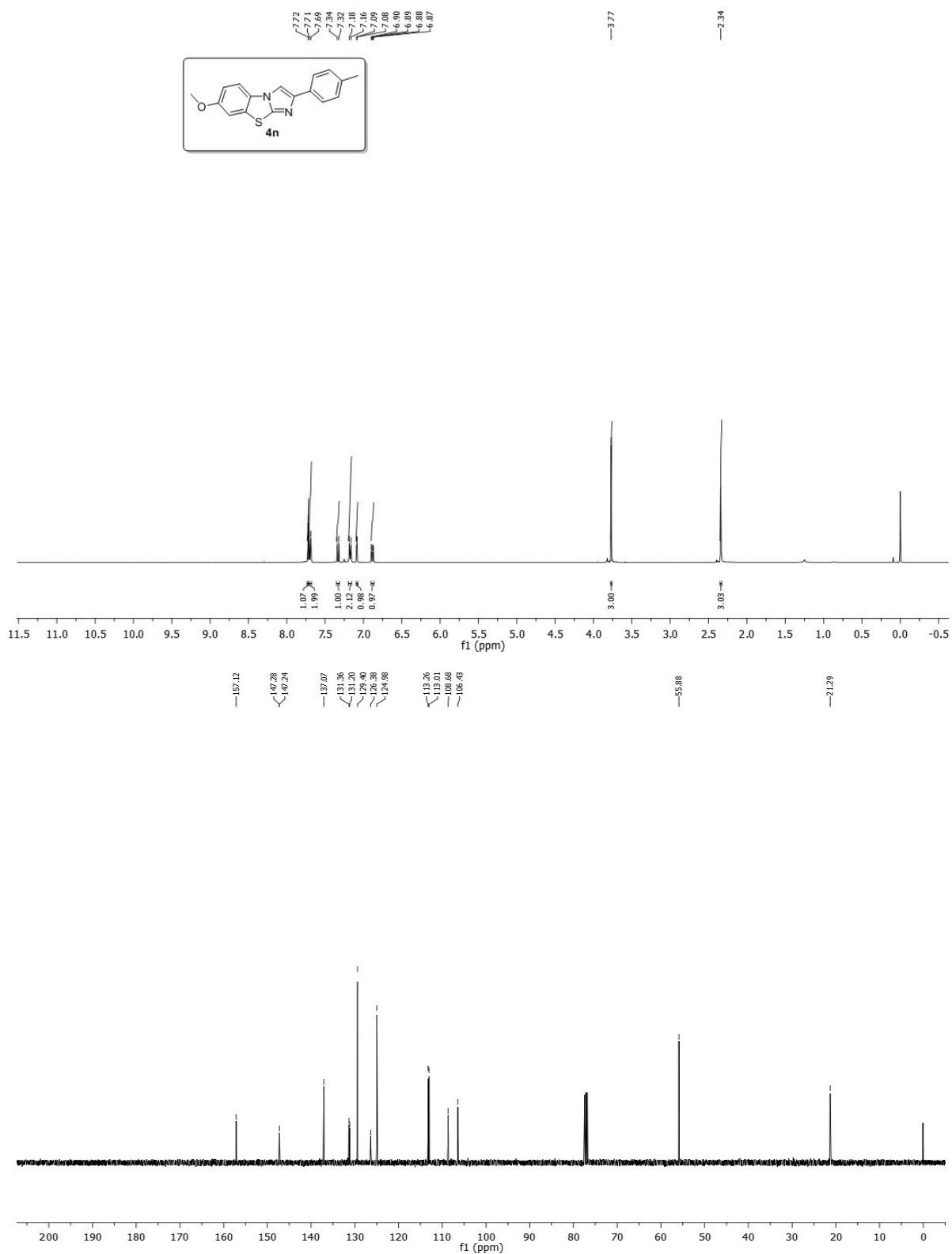
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4I**)



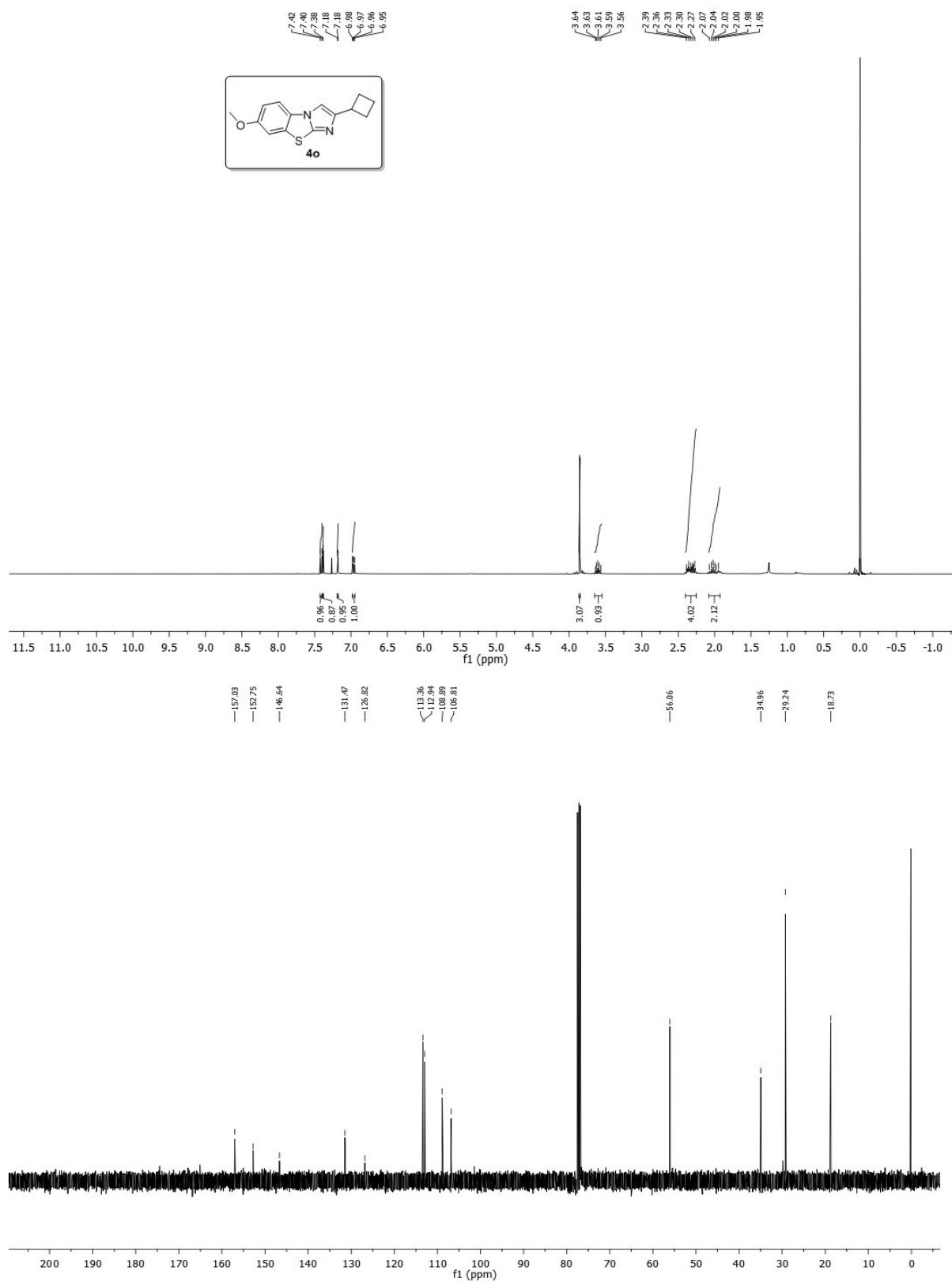
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4m**)



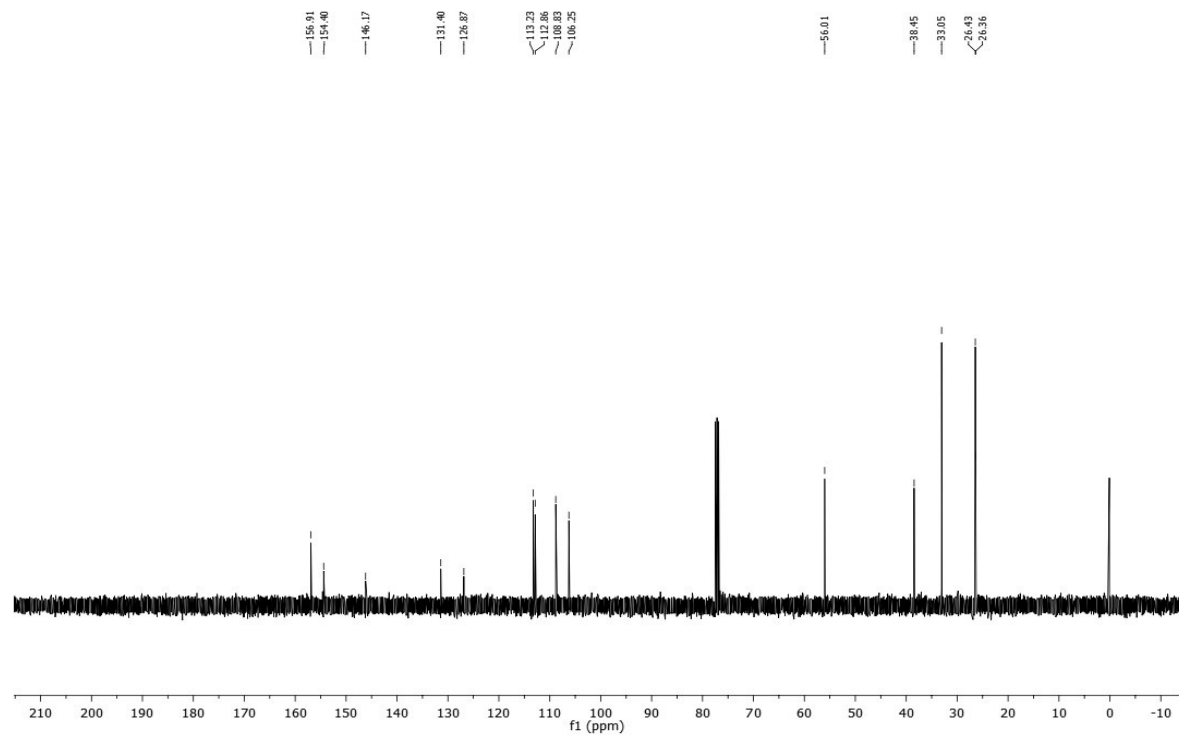
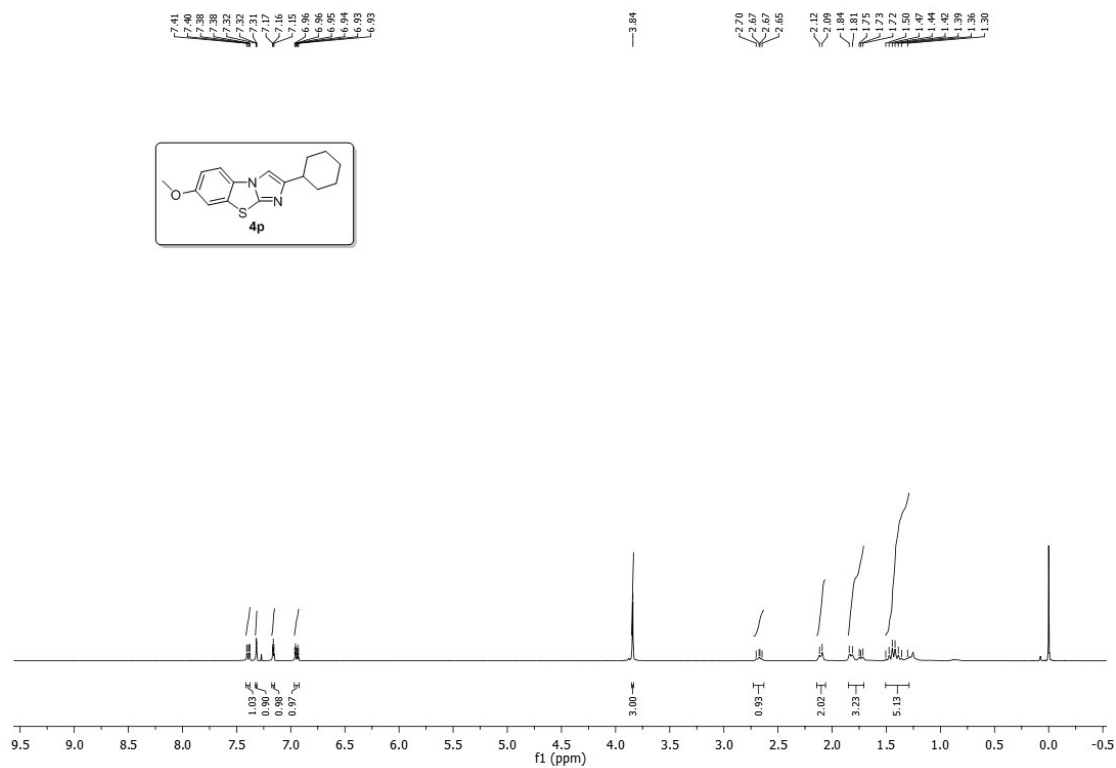
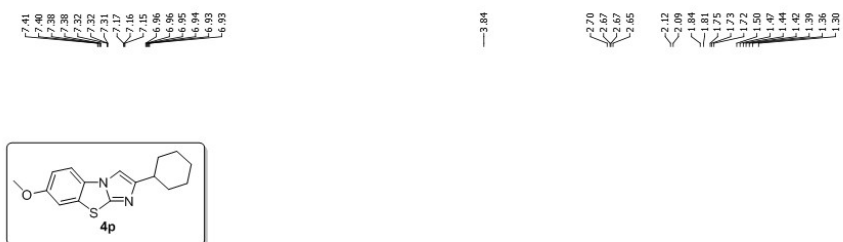
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4n**)



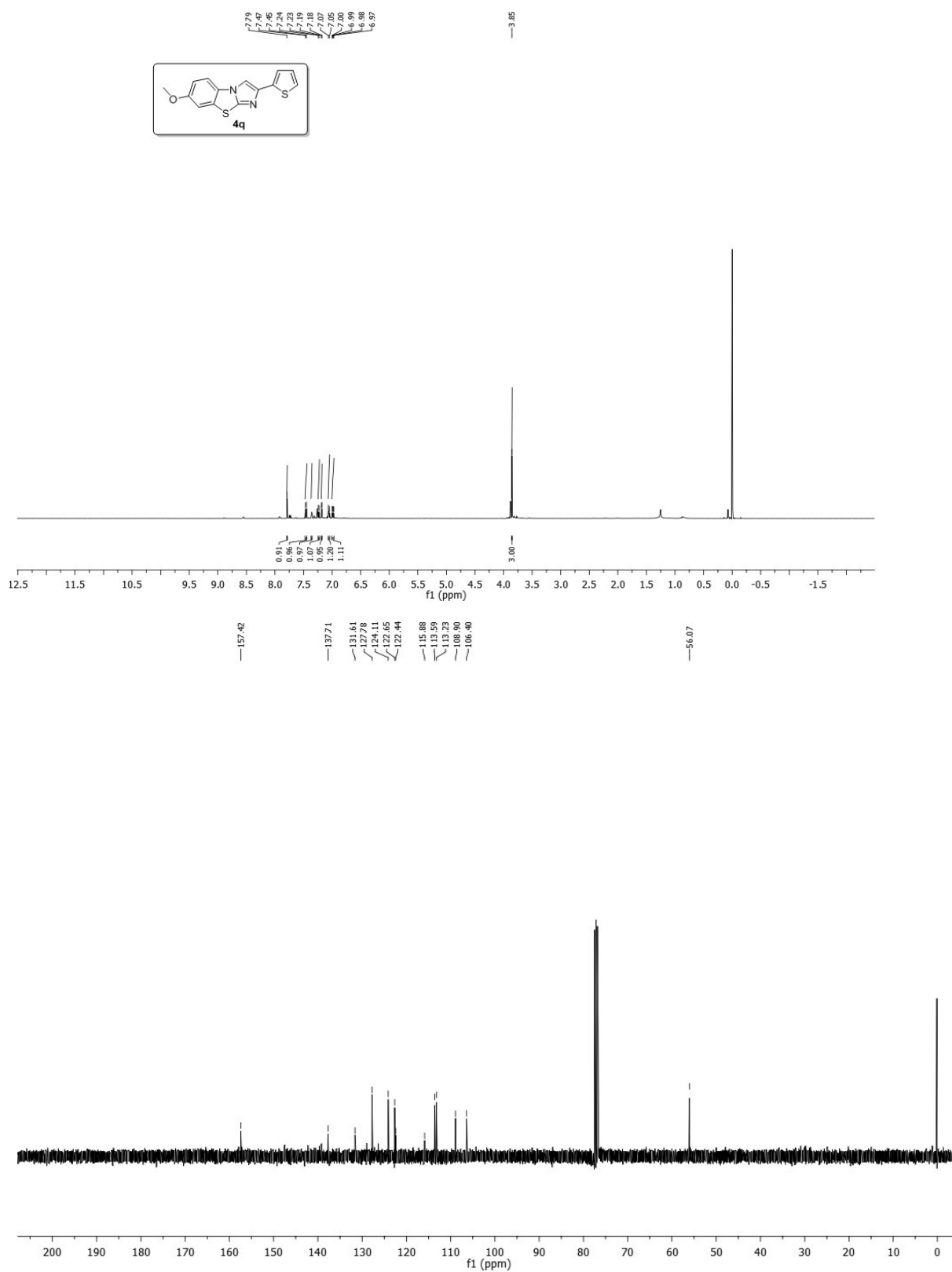
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4o**)



$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4p**)

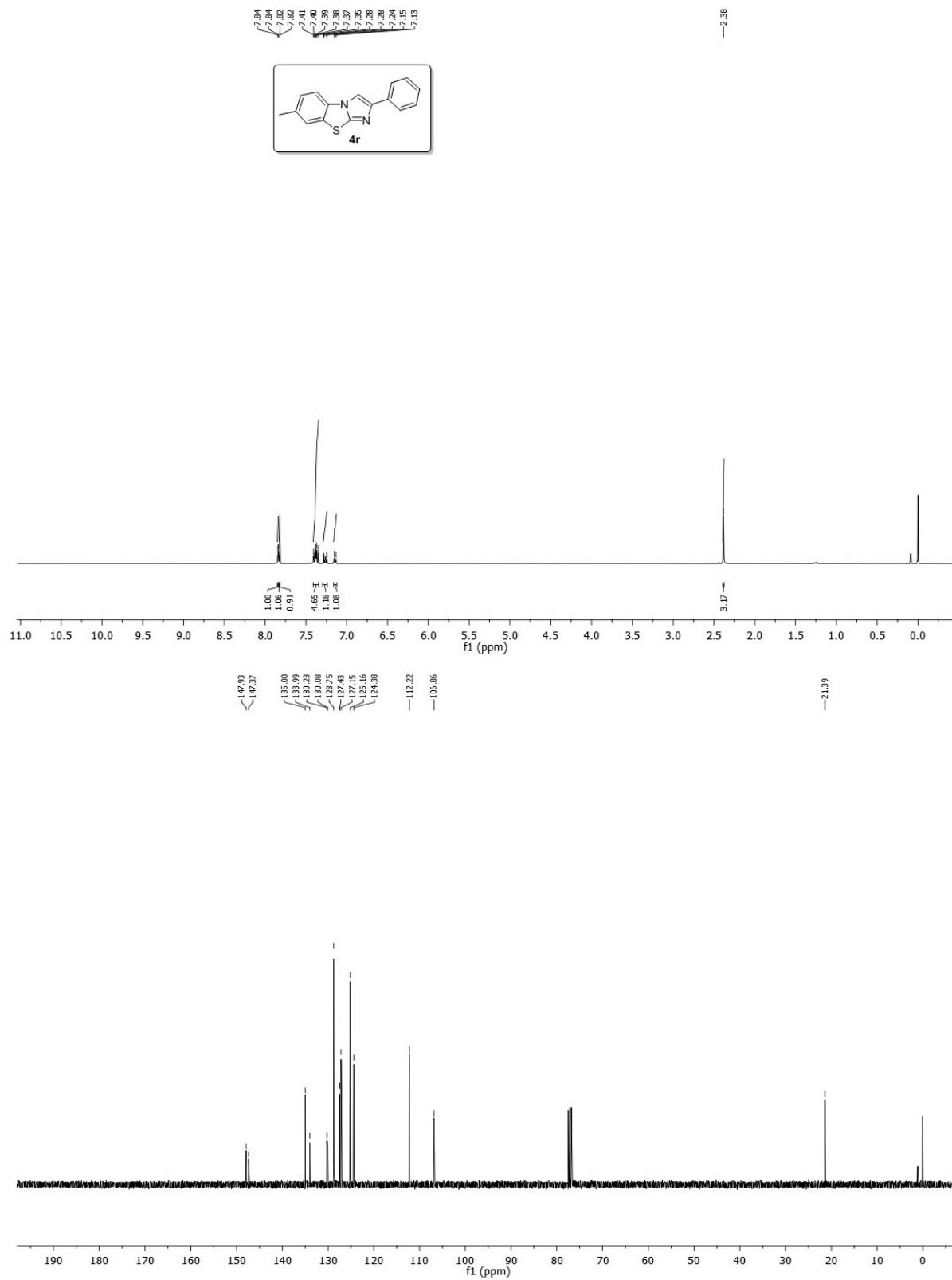


$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (4q)

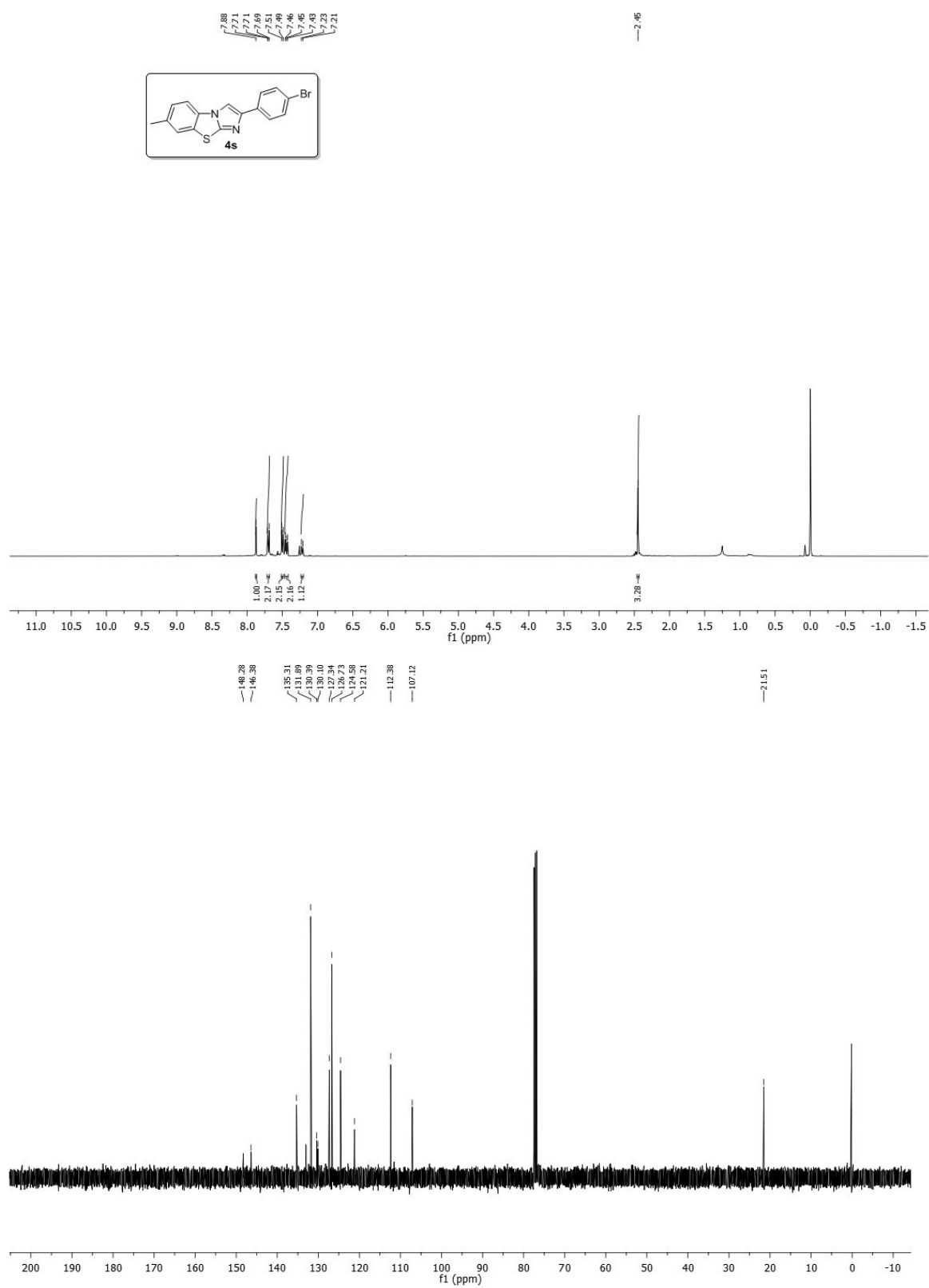




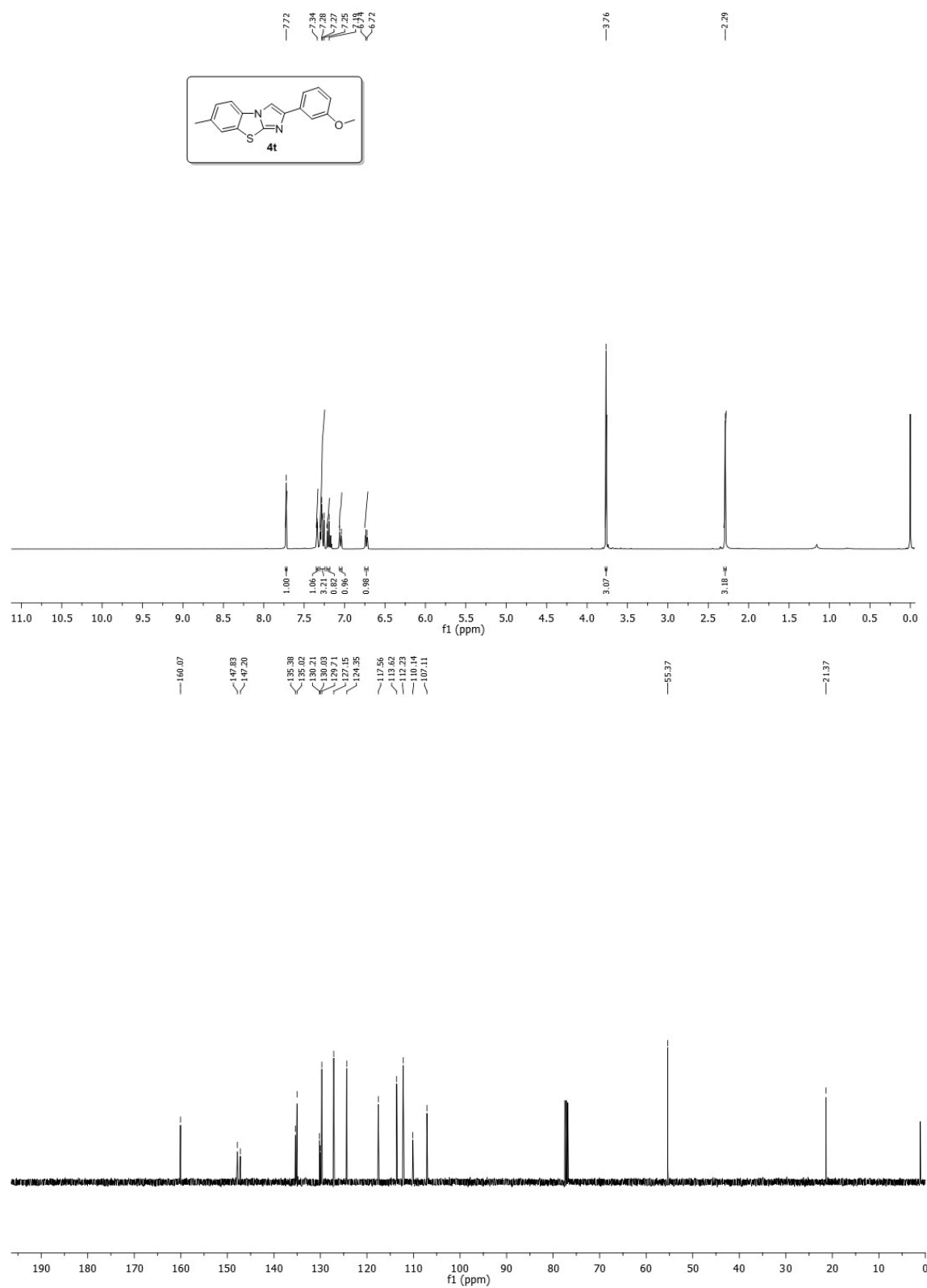
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4r**)



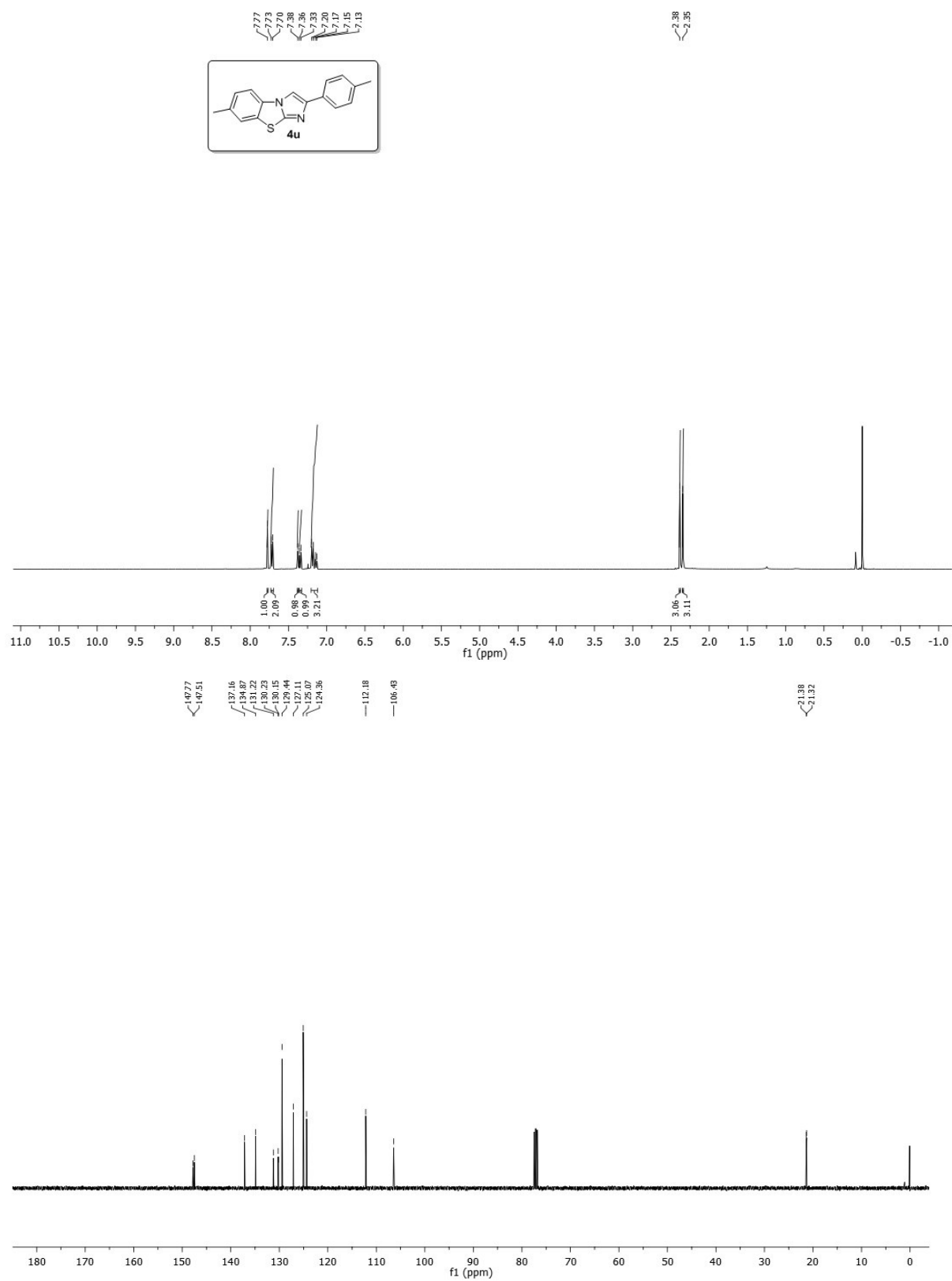
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (4s)



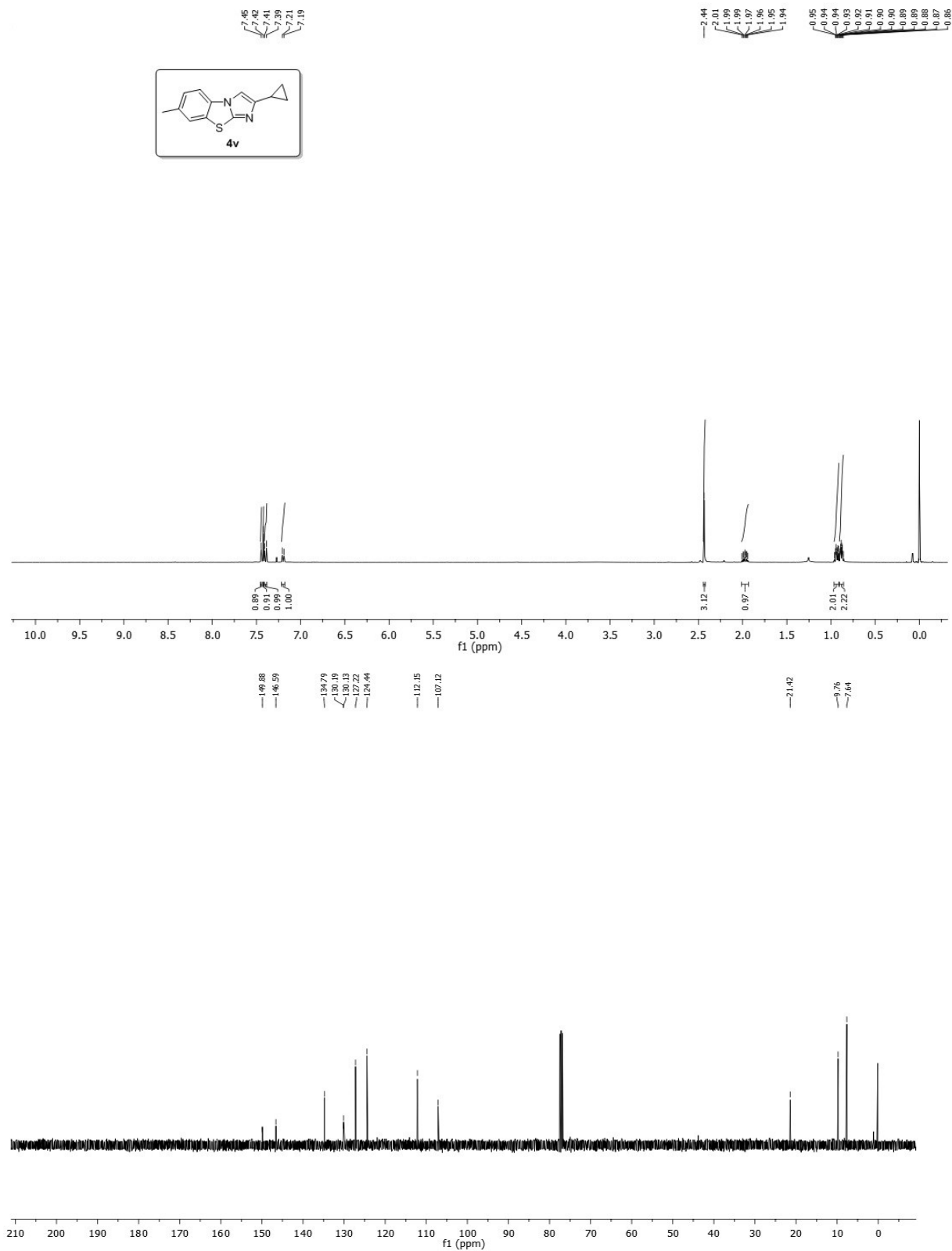
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4t**)



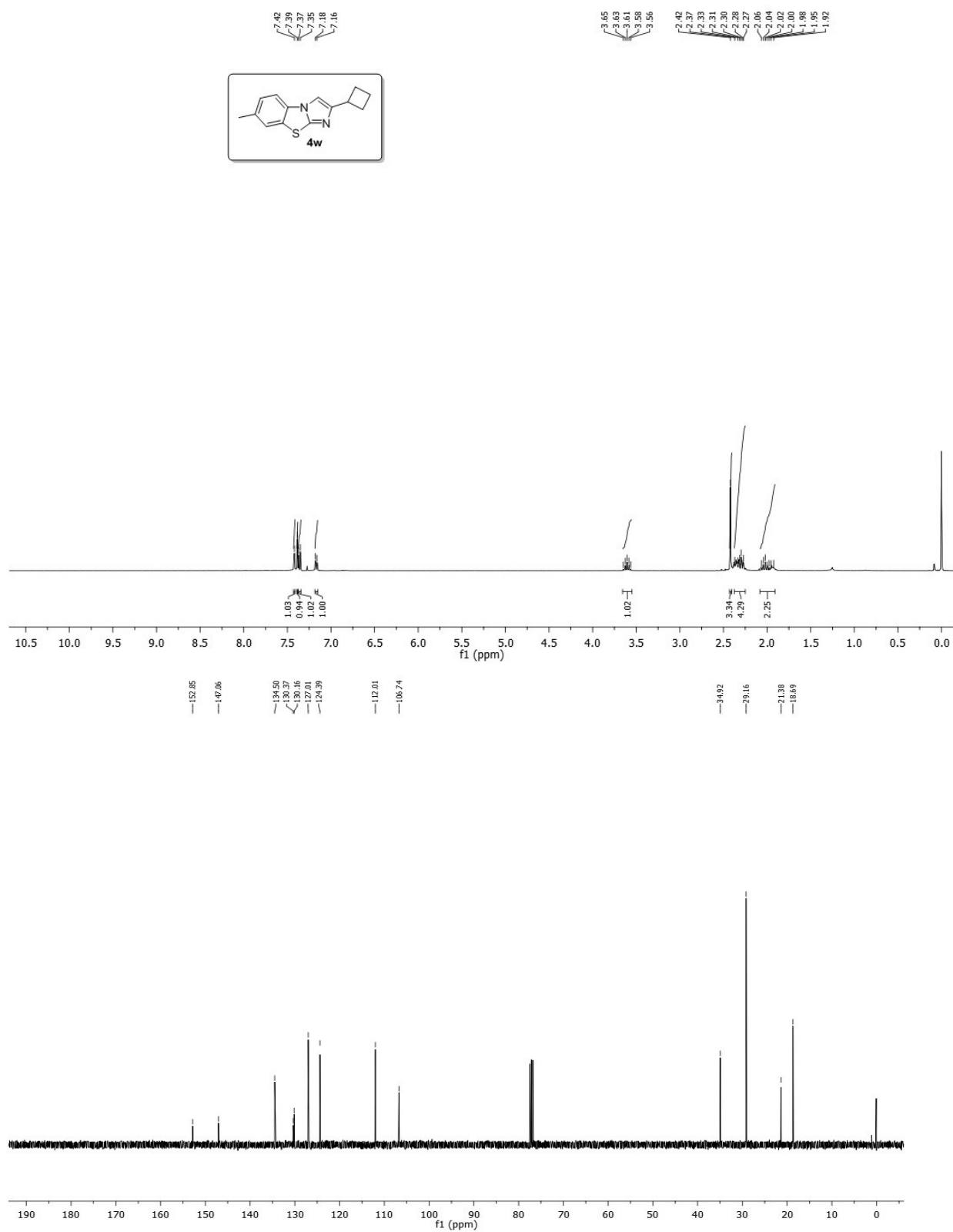
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4u**)



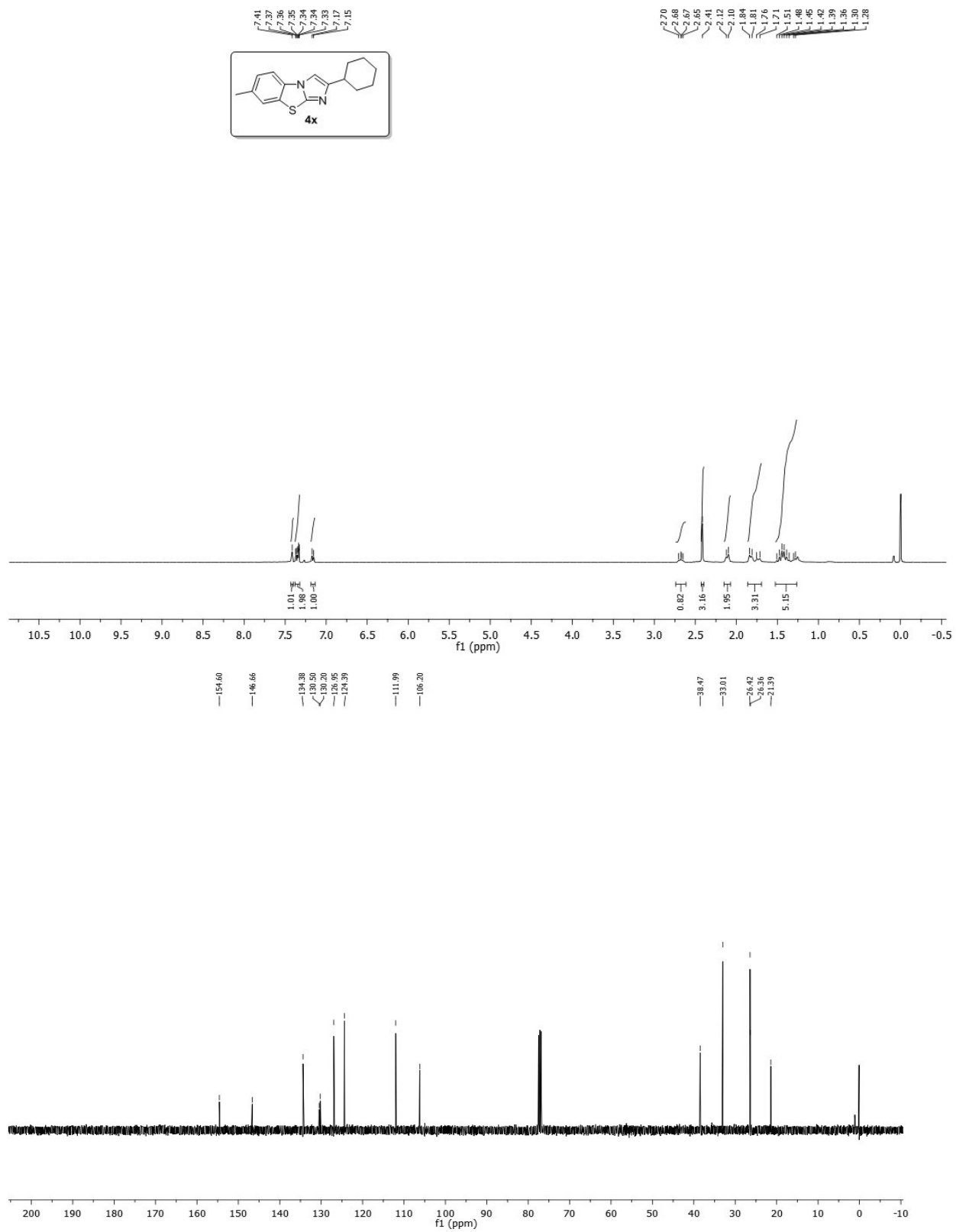
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4v**)



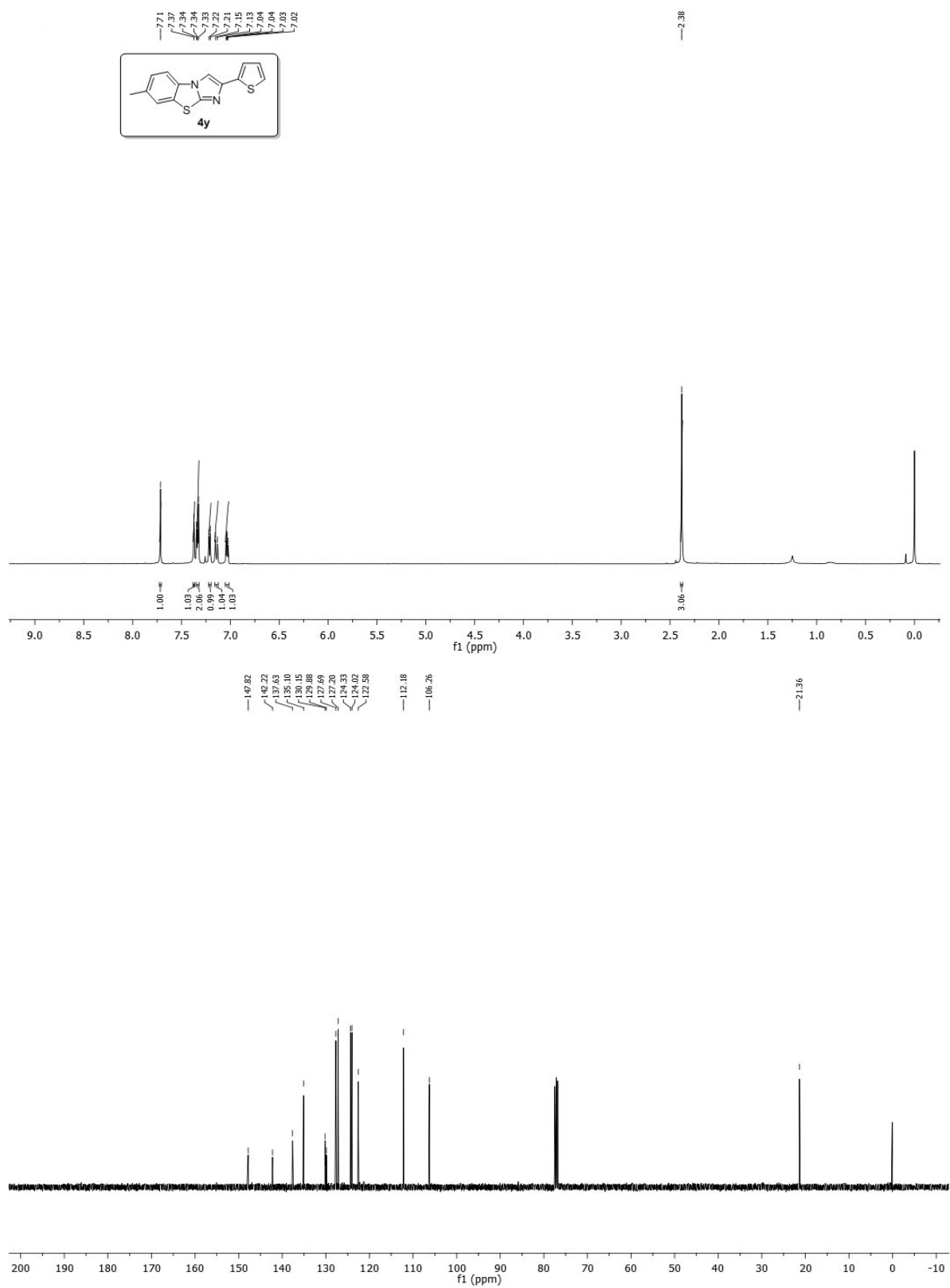
# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of compound (4w)



$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4x**)

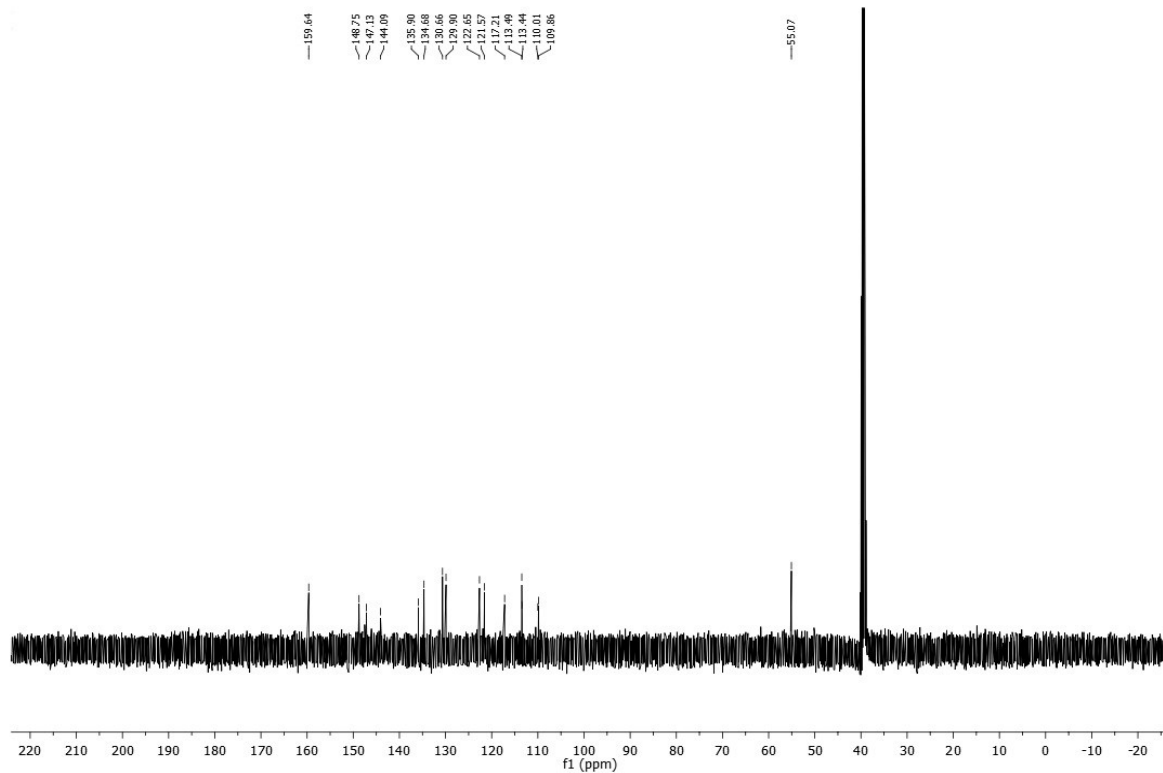
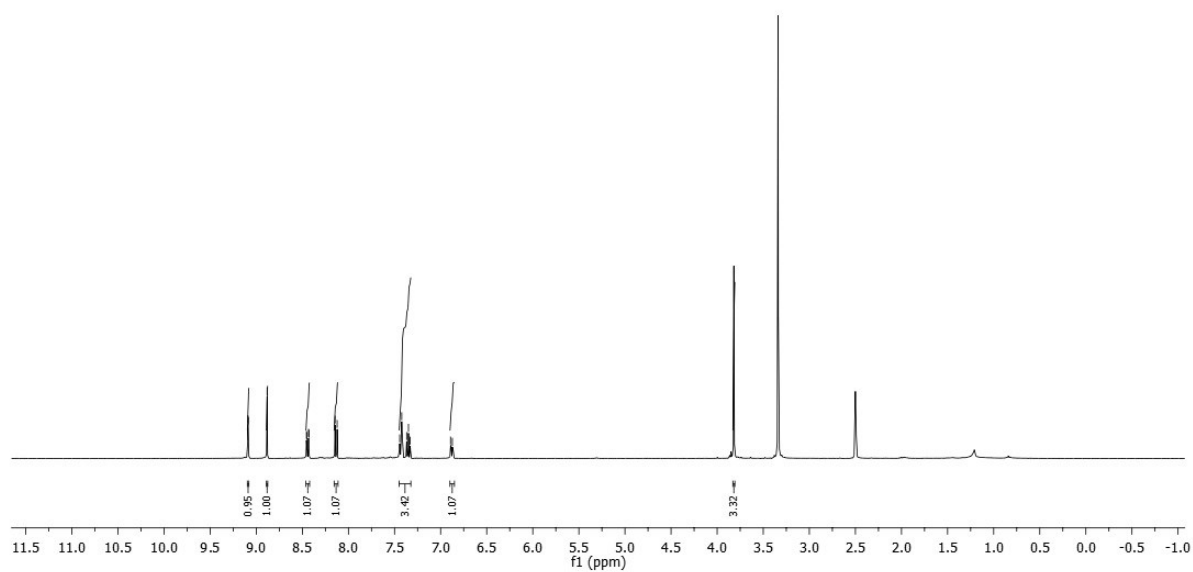
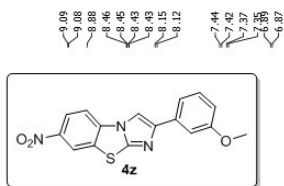


$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4y**)

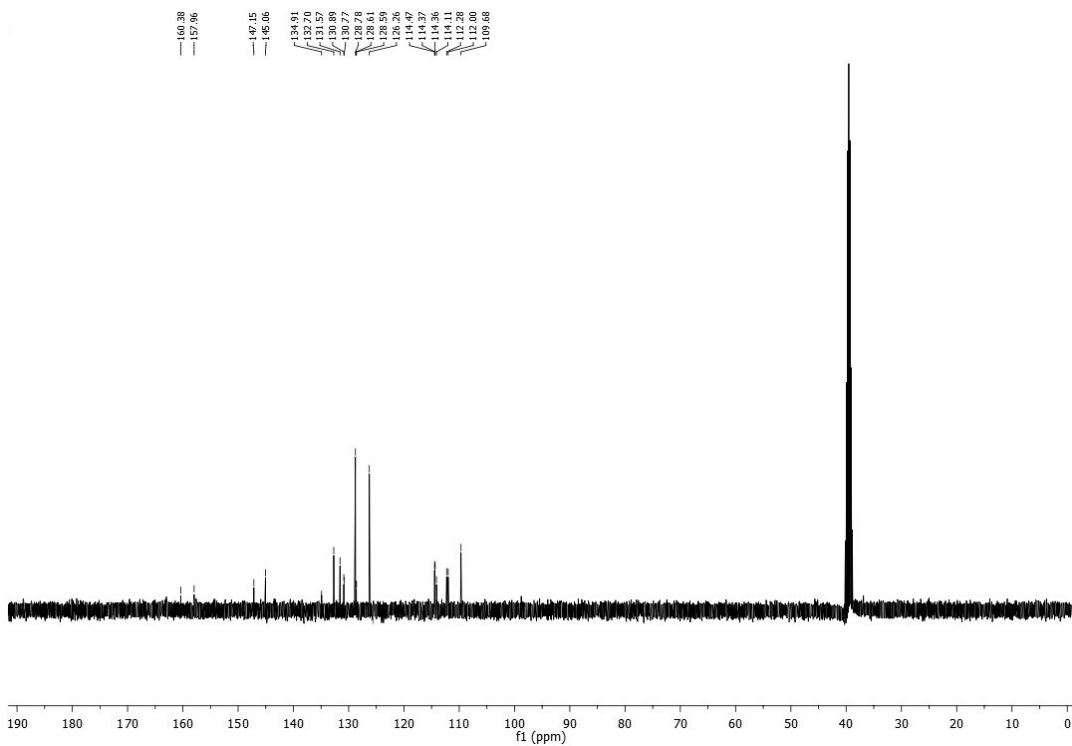
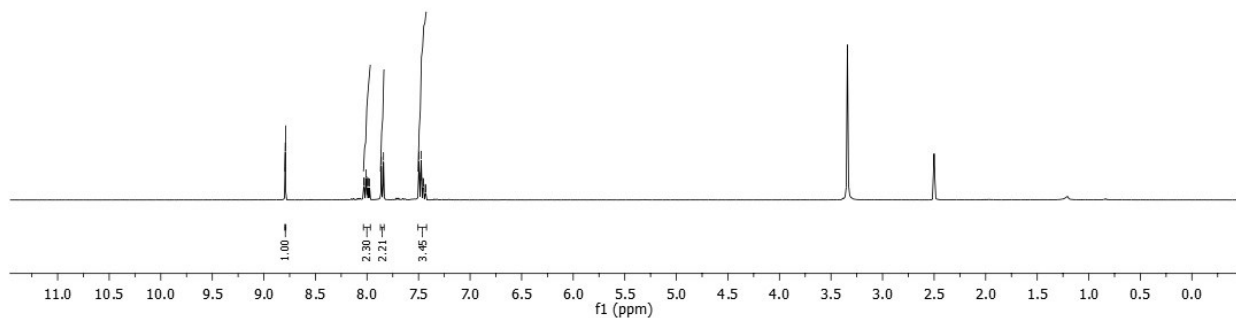
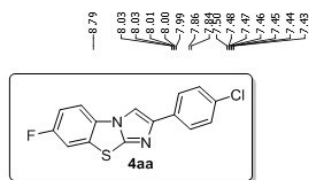




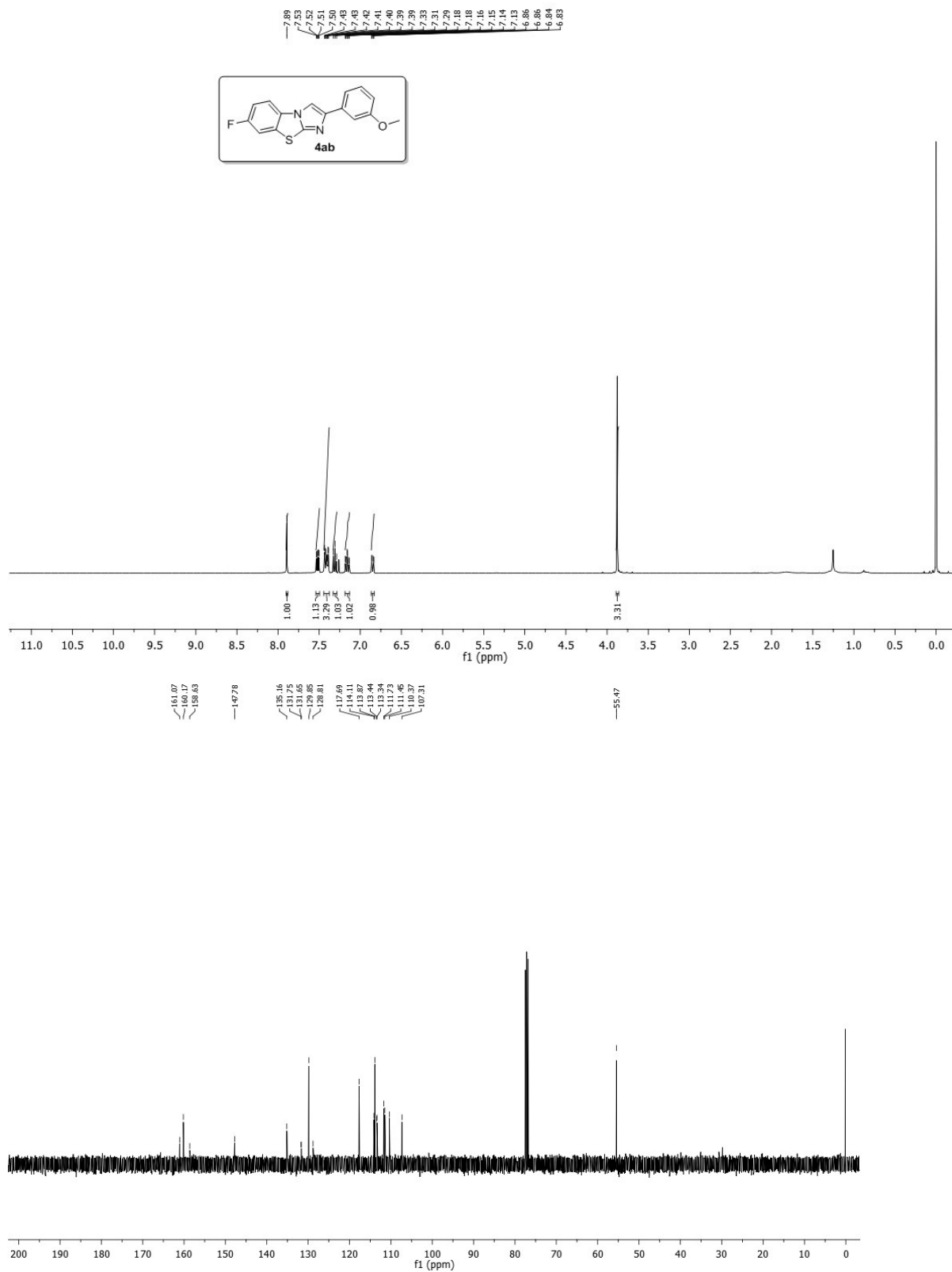
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4z**)



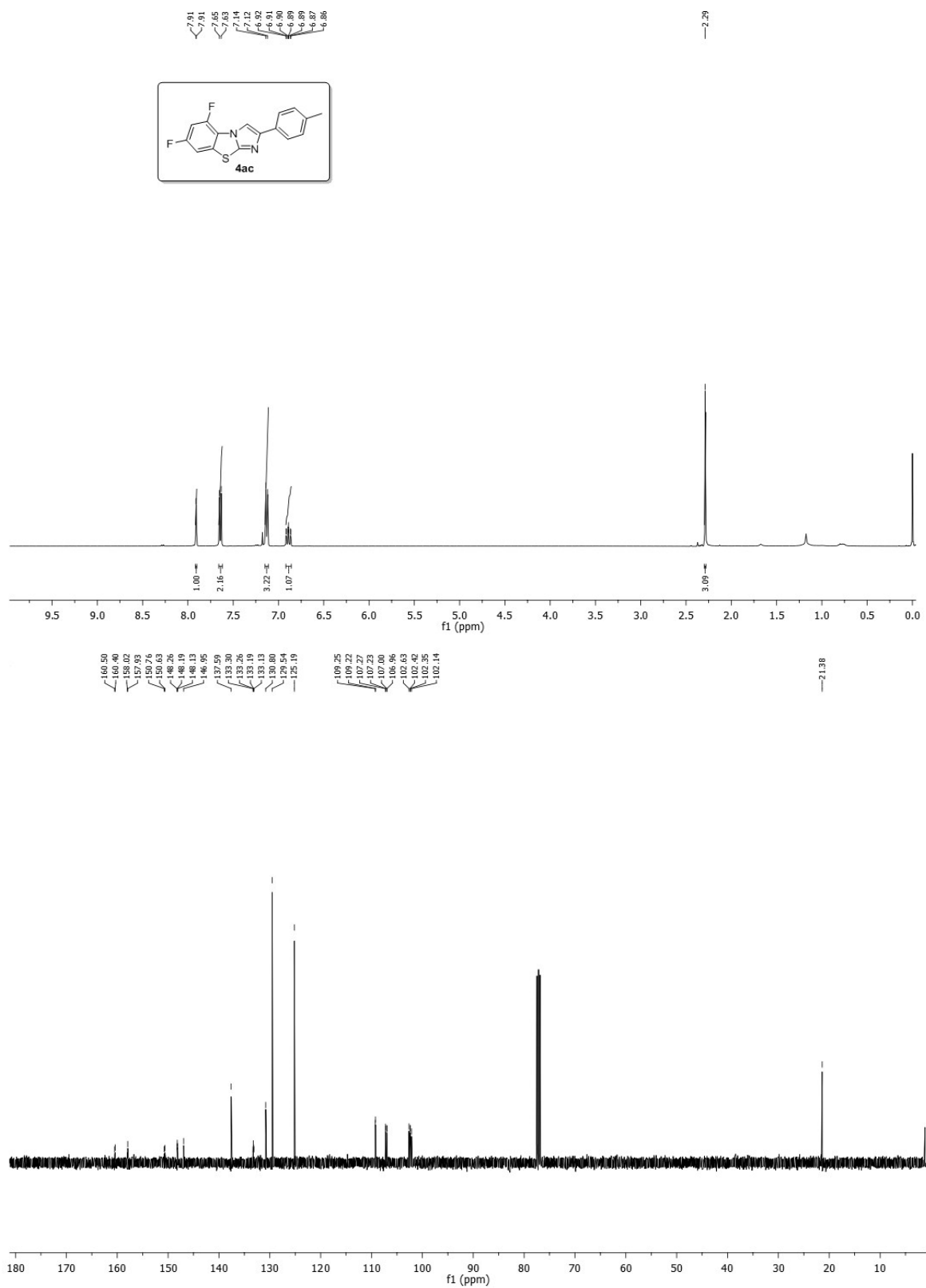
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4aa**)



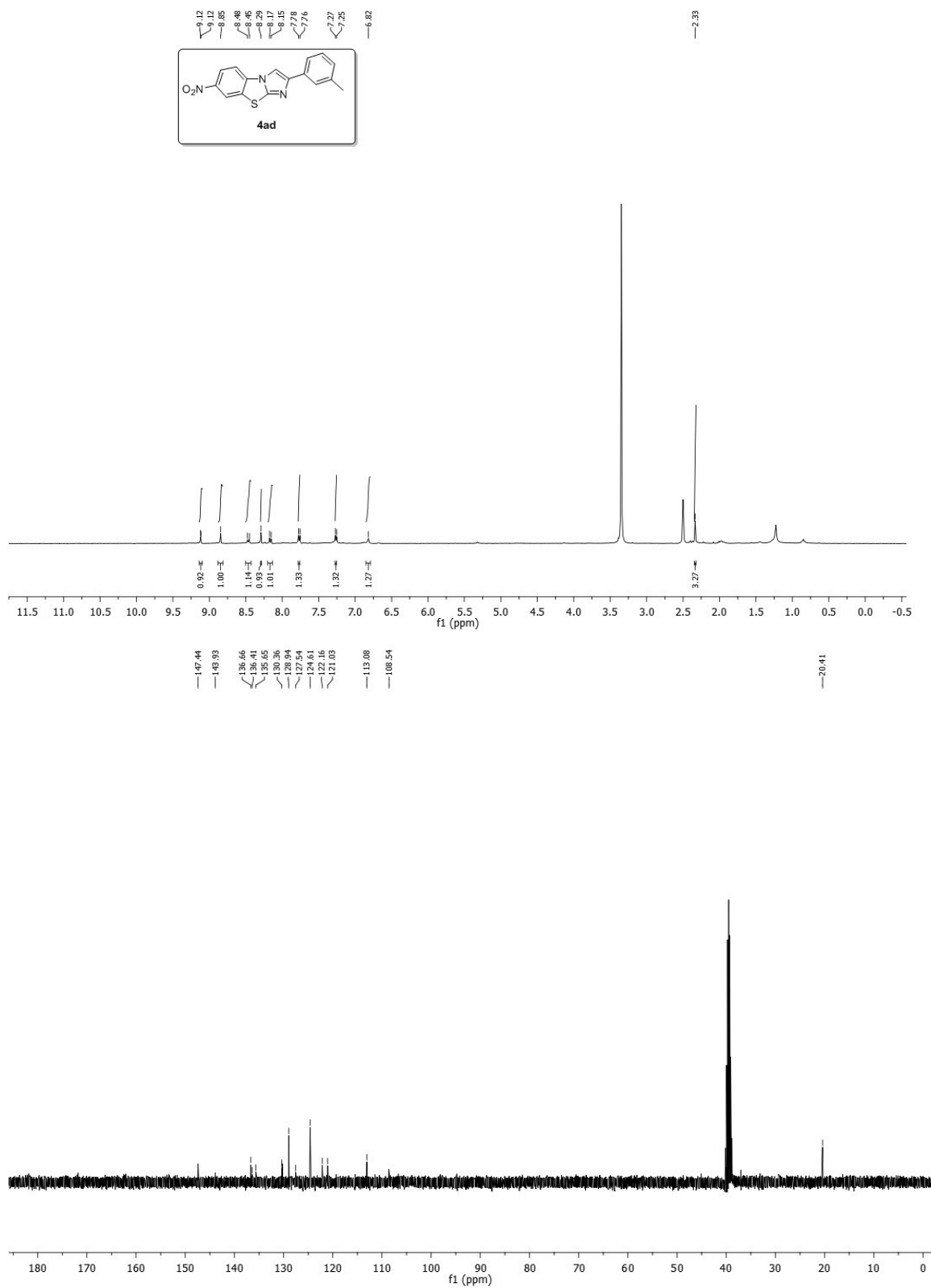
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4ab**)



$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of compound (**4ac**)



# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of compound (4ad)



# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of compound (4ae)

