Rhodium(III)-Catalyzed Selective C-H Acetoxylation and Hydroxylation Reactions

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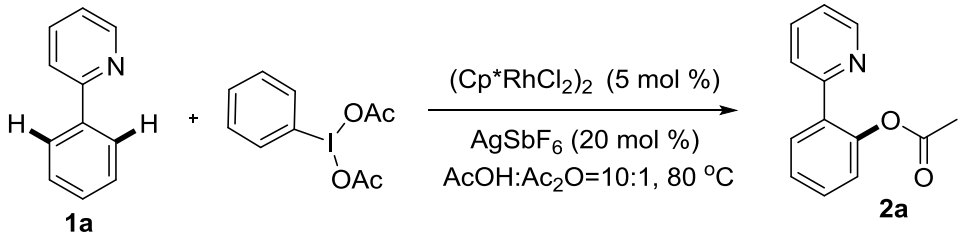
General methods:

^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (125, 100 MHz) spectra were determined with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in ppm from internal TMS (δ). All coupling constants (J values) were reported in hertz (Hz). High-resolution mass spectra were recorded using the EI method with a double focusing magnetic mass analyzer. Reactions were monitored by thin-layer chromatography or LC-MS analysis. Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh).

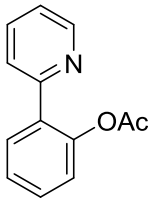
Materials:

All reagents were purchased from *adamas-beta* in China and used without further purification, unless otherwise indicated. $[Cp^*RhCl_2]_2$[S1] was prepared according to the previously reported synthetic methods.

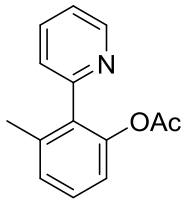
General procedure for the synthesis of 2 (taking 2a as an example):



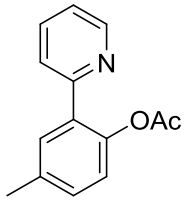
1a (0.2 mmol), $PhI(OAc)_2$ (0.24 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), AcOH (2 mL) and Ac_2O (0.2 mL) were added to a test tube. The reaction mixture was stirred at 80 ^{o}C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (5:1) to afford the title compound **2a**.



Compound **2a** was obtained as a white amorphous solid in 83% yield (35.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.54 (dt, J = 7.9, 1.0 Hz, 1H), 7.43 (ddd, J = 8.0, 7.5, 1.8 Hz, 1H), 7.35 (td, J = 7.5, 1.3 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.16 (dd, J = 8.0, 1.3 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.57, 155.97, 149.72, 148.21, 136.47, 133.23, 130.95, 129.88, 126.52, 123.81, 123.35, 122.36, 21.09; HRMS (EI) Calcd for $C_{13}H_{11}NO_2$ $[M]^+$ 213.0790, found 213.0793.

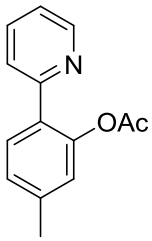


Compound **2b** was obtained as a white amorphous solid in 71% yield (32.3 mg),^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (d, J = 5.1 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 7.36 – 7.15 (m, 4H), 6.98 (d, J = 7.8 Hz, 1H), 2.15 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.26, 156.61, 150.28, 149.11, 138.91, 136.73, 134.34, 129.58, 128.74, 125.46, 122.82, 120.69, 21.28, 20.62; HRMS (EI) Calcd for $C_{14}H_{13}NO_2$ $[M]^+$ 227.0946, found 227.0949.

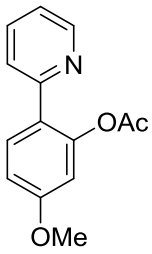


Compound **2c** was obtained as a white amorphous solid in 77% yield (35 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (d, J = 4.6 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 7.57-7.50 (m, 2H), 7.26 – 7.18 (m, 2H), 7.04 (d, J = 8.3 Hz, 1H), 2.40 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.37, 156.55, 150.26, 146.54, 136.95, 136.81,

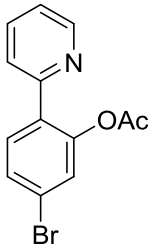
133.36, 131.97, 131.06, 124.35, 123.59, 122.86, 21.67, 21.62; HRMS (EI) Calcd for $C_{14}H_{13}NO_2$ $[M]^+$ 227.0946, found 227.0941.



Compound **2d** was obtained as a white amorphous solid in 80% yield (36.4 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, J = 4.4 Hz, 1H), 7.70 (q, J = 7.2 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.25 – 7.13 (m, 2H), 6.97 (s, 1H), 2.40 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.57, 155.84, 149.47, 147.88, 140.19, 136.25, 130.52, 130.15, 127.25, 123.67, 123.46, 121.95, 21.14, 20.98; HRMS (EI) Calcd for $C_{14}H_{13}NO_2$ $[M]^+$ 227.0946, found 227.0944.

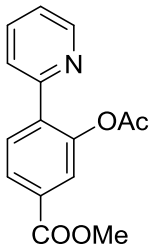


Compound **2e** was obtained as a white amorphous solid in 61% yield (29.7 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (d, J = 4.2 Hz, 1H), 7.73-7.63 (m, 2H), 7.50 (d, J = 7.9 Hz, 1H), 7.24 – 7.14 (m, 1H), 6.90 (dd, J = 8.6, 2.1 Hz, 1H), 6.70 (d, J = 2.1 Hz, 1H), 3.84 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.48, 160.81, 155.84, 149.62, 149.15, 136.37, 131.61, 125.78, 123.36, 121.82, 112.51, 108.90, 55.70, 21.16; HRMS (EI) Calcd for $C_{14}H_{13}NO_3$ $[M]^+$ 243.0895, found 243.0893.

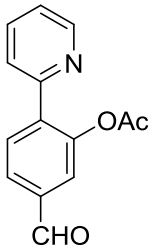


Compound **2f** was obtained as a yellow amorphous solid in 72% yield (42 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (d, J = 4.1 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.60 (d,

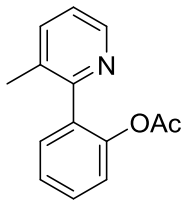
J = 8.3 Hz, 1H), 7.55-7.46 (m, 2H), 7.35 (s, 1H), 7.26 (t, *J* = 6.2 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.10, 155.00, 149.86, 148.62, 136.55, 132.34, 132.04, 129.76, 126.74, 123.60, 122.78, 122.61, 21.01； HRMS (EI) Calcd for $C_{13}H_{10}BrNO_2$ $[M]^+$ 290.9895, found 290.9894.



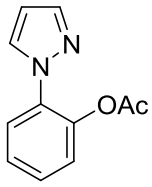
Compound **2g** was obtained as a white amorphous solid in 74% yield (40.1 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (d, J = 4.2 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.87-7.72 (m, 3H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.27 (m, 1H), 3.94 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.31, 166.09, 154.96, 149.92, 148.12, 137.51, 136.59, 131.62, 131.08, 127.54, 124.83, 123.89, 122.94, 52.53, 21.05; HRMS (EI) Calcd for $C_{15}H_{13}NO_4$ $[M]^+$ 271.0845, found 271.0849.



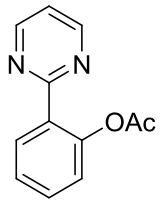
Compound **2h** was obtained as a white amorphous solid in 71% yield (34.3 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.73 (d, *J* = 4.7 Hz, 1H), 7.91 – 7.74 (m, 3H), 7.69 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.28 (m, 1H), 2.19 (s, *J* = 14.7 Hz, 3H)； ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.98, 169.18, 154.68, 150.01, 148.81, 138.90, 137.54, 136.64, 131.84, 127.54, 124.46, 123.97, 123.15, 21.03； HRMS (EI) Calcd for $C_{14}H_{11}NO_3$ $[M]^+$ 241.0739, found 241.0733.



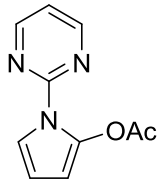
Compound **2i** was obtained as a white amorphous solid in 70% yield (31.8 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, J = 4.3 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.47 – 7.27 (m, 3H), 7.22-7.12 (m, 2H), 2.21 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.05, 155.68, 148.28, 146.83, 138.06, 133.64, 132.35, 130.61, 129.40, 126.04, 122.86, 122.63, 20.76, 19.21; HRMS (EI) Calcd for $C_{14}H_{13}NO_2$ $[M]^+$ 227.0946, found 227.0948.



Compound **2j** was obtained as a yellow amorphous solid in 65% yield (26.2 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 2H), 7.67 – 7.58 (m, 1H), 7.42 – 7.31 (m, 2H), 7.22 (d, J = 9.3 Hz, 1H), 6.44 (s, 1H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.88, 143.43, 141.15, 133.25, 130.28, 128.50, 126.93, 125.80, 124.11, 107.13, 20.89; HRMS (EI) Calcd for $C_{11}H_{10}N_2O_2$ $[M]^+$ 202.0742, found 202.0741.

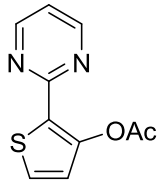


Compound **2k** was obtained as a white amorphous solid in 75% yield (32.1 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (d, J = 4.8 Hz, 2H), 8.23 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.25 – 7.14 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.24, 164.02, 157.10, 149.50, 131.76, 131.52, 130.62, 126.44, 124.05, 119.18, 21.29; HRMS (EI) Calcd for $C_{12}H_{10}N_2O_2$ $[M]^+$ 214.0742, found 214.0746.

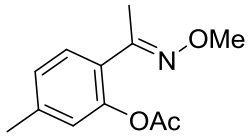


Compound **2l** was obtained as a yellow amorphous solid in 64% yield (26 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (d, J = 4.8 Hz, 2H), 7.47-7.43 (m, 1H), 7.17 (d, J =

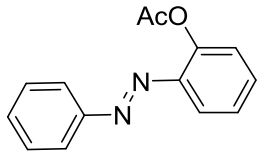
6.2 Hz, 1H), 7.08 (t, *J* = 4.9 Hz, 1H), 6.36 (d, *J* = 6.0 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.09, 167.39, 158.47, 156.02, 143.22, 129.92, 117.18, 82.43, 20.93; HRMS (EI) Calcd for $C_{10}H_9N_3O_2$ $[M]^+$ 203.0695, found 203.0694.



Compound **2m** was obtained as a white amorphous solid in 54% yield (23.8 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.6 Hz, 2H), 7.44 (d, *J* = 5.4 Hz, 1H), 7.11 (t, *J* = 5.1 Hz, 1H), 6.94 (d, *J* = 5.2 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.26, 160.59, 156.95, 147.40, 127.93, 127.53, 124.40, 118.34, 21.10; HRMS (EI) Calcd for $C_{10}H_8N_2O_2S$ $[M]^+$ 220.0306, found 220.0307.

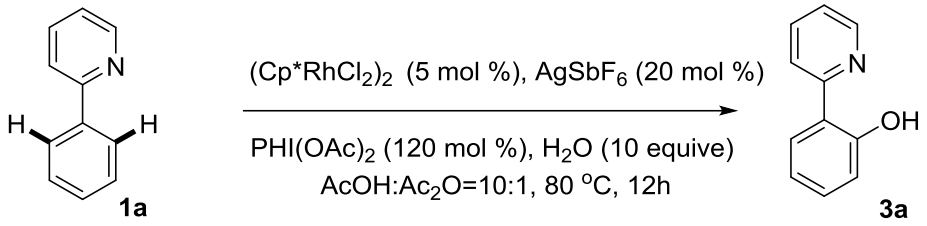


Compound **2n** was obtained as a white amorphous solid in 56% yield (24.8 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.91 (s, 1H), 3.95 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.29, 155.26, 149.66, 142.10, 131.06, 129.20, 128.79, 125.61, 63.76, 23.00, 16.88; HRMS (EI) Calcd for $C_{12}H_{15}NO_3$ $[M]^+$ 221.1052, found 221.1056.

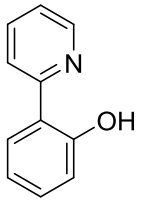


Compound **2o** was obtained as a red amorphous solid in 70% yield (33.6 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.84 – 7.81 (m, 1H), 7.54 – 7.48 (m, 4H), 7.35 (ddd, *J* = 8.1, 7.4, 1.4 Hz, 1H), 7.27 – 7.24 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.72, 152.94, 149.07, 144.07, 132.19, 131.48, 129.22, 126.70, 123.45, 123.11, 117.77, 20.88; HRMS (EI) Calcd for $C_{14}H_{12}N_2O_2$ $[M]^+$ 240.0899, found 240.0894.

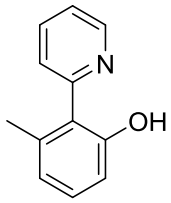
General procedure for the synthesis of 3 (taking 3a as an example):



1a (0.2 mmol), $PhI(OAc)_2$ (0.24 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), H_2O (2 mmol, 10 equiv), AcOH (2 mL) and Ac_2O (0.2 mL) were added to a test tube. The reaction mixture was stirred at 80 ^oC for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (5:1) to afford the title compound **3a**.

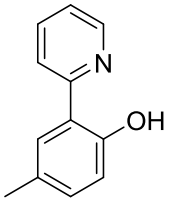


Compound **3a** was obtained as a yellow oil in 82% yield (28.1 mg), ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (ddd, J = 5.0, 1.8, 0.9 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.34 – 7.28 (m, 1H), 7.26 – 7.22 (m, 1H), 7.04 (dd, J = 8.3, 1.2 Hz, 1H), 6.94 – 6.88 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.04, 157.88, 145.82, 137.81, 131.53, 126.12, 121.52, 119.08, 118.79, 118.66; HRMS (EI) Calcd for $C_{11}H_9NO$ $[M]^+$ 171.0684, found 171.0685.

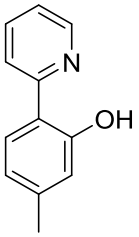


Compound **3b** was obtained as a yellow oil in 76% yield (28.2 mg), ^1H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, J = 4.4 Hz, 1H), 7.84 (t, J = 7.9 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.28 (d, J = 9.2 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.62, 157.24, 147.39, 137.13, 136.36, 130.14, 125.85, 122.97, 122.38, 121.73, 115.38, 22.59;

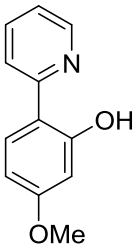
HRMS (EI) Calcd for $C_{12}H_{11}NO$ $[M]^+$ 185.0841, found 185.0839.



Compound **3c** was obtained as a yellow oil in 70% yield (25.9 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.10 (s, 1H), 8.51 (d, J = 4.2 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.82 (t, J = 7.9 Hz, 1H), 7.60 (s, 1H), 7.26 – 7.18 (m, 1H), 7.12 (d, J = 8.2 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.37, 158.11, 146.32, 138.05, 132.72, 128.07, 126.68, 121.75, 119.39, 118.77, 21.15; HRMS (EI) Calcd for $C_{12}H_{11}NO$ $[M]^+$ 185.0841, found 185.0844.

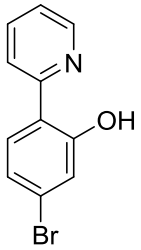


Compound **3d** was obtained as a yellow oil in 85% yield (31.5 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.34 (s, 1H), 8.48 (d, J = 4.6 Hz, 1H), 7.91 – 7.75 (m, 2H), 7.68 (d, J = 7.9 Hz, 1H), 7.23 – 7.16 (m, 1H), 6.85 (s, 1H), 6.73 (d, J = 7.9 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.06, 158.15, 145.93, 142.25, 137.77, 126.05, 121.19, 120.05, 119.03, 118.84, 116.37, 21.56; HRMS (EI) Calcd for $C_{12}H_{11}NO$ $[M]^+$ 185.0841, found 185.0845.

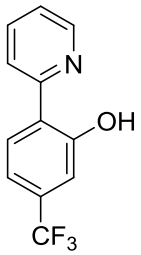


Compound **3e** was obtained as a white amorphous solid in 65% yield (26.2 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.71 (s, 1H), 8.46 (s, 1H), 7.80 (s, 2H), 7.70 (d, J = 8.7 Hz, 1H), 7.22-7.17(m, 1H), 6.58 – 6.47 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.25, 163.81, 159.79, 147.46, 139.51, 129.02, 122.42, 120.14, 113.95, 108.51, 104.03, 57.23; HRMS (EI) Calcd for $C_{12}H_{11}NO_2$ $[M]^+$ 201.0790, found

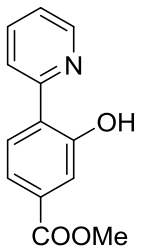
201.0794.



Compound **3f** was obtained as a yellow amorphous solid in 85% yield (42.5 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.65 (s, 1H), 8.50 (d, J = 4.9 Hz, 1H), 7.90 – 7.81 (m, 2H), 7.64 (d, J = 8.5 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.20 (d, J = 1.7 Hz, 1H), 7.03 (dd, J = 8.6, 1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.97, 157.23, 145.97, 138.12, 127.26, 125.04, 122.09, 121.99, 121.79, 119.14, 117.88; HRMS (EI) Calcd for $C_{11}H_8BrNO$ $[M]^+$ 248.9789, found 248.9791.

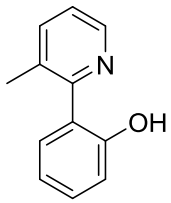


Compound **3g** was obtained as a white amorphous solid in 76% yield (36.4 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.61 (s, 1H), 8.56 (d, J = 5.2 Hz, 1H), 8.01 – 7.85 (m, 3H), 7.40 – 7.30 (m, 1H), 7.27 (s, 1H), 7.14 (d, J = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.09, 156.62, 146.05, 138.16, 133.14 (q, J =32.5 Hz), 126.61, 123.74 (d, J = 272.4 Hz), 122.54, 121.50, 119.59, 115.85 (d, J = 3.9 Hz), 115.07 (d, J = 3.7 Hz); HRMS (EI) Calcd for $C_{12}H_8F_3NO$ $[M]^+$ 239.0558, found 239.0556.

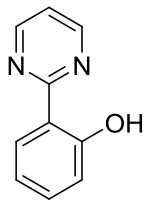


Compound **3h** was obtained as a white amorphous solid in 83% yield (38.1 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.42 (s, 1H), 8.56 (d, J = 4.6 Hz, 1H), 8.01 – 7.83 (m, 3H), 7.69 (s, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.31 (dd, J = 13.3, 7.2 Hz, 1H), 3.93 (s,

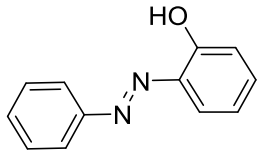
3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.71, 159.82, 156.87, 146.08, 138.06, 132.56, 126.11, 122.52, 122.47, 119.92, 119.81, 119.57, 52.27; HRMS (EI) Calcd for $C_{13}H_{11}NO_3$ $[M]^+$ 229.0739, found 229.0741.



Compound **3i** was obtained as a yellow oil in 80% yield (29.6 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.40 (s, 1H), 8.55 (d, *J* = 5.0 Hz, 1H), 8.11 (dd, *J* = 22.4, 8.3 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.90-7.81 (m, 1H), 7.69 (s, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.28 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.41, 147.68, 141.33, 139.19, 131.53, 129.64, 128.85, 128.62, 122.78, 20.77; HRMS (EI) Calcd for $C_{12}H_{11}NO$ $[M]^+$ 185.0841, found 185.0845.

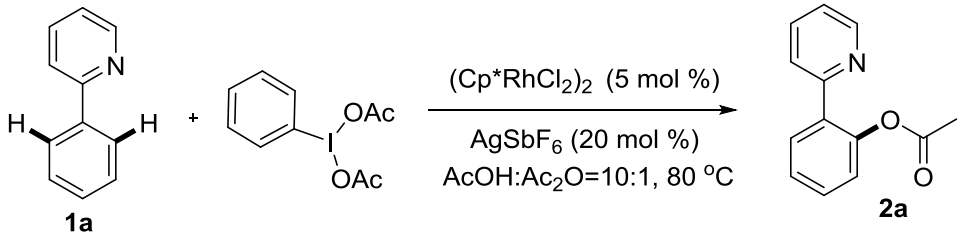


Compound **3j** was obtained as a yellow oil in 75% yield (25.8 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.06 (s, 1H), 8.79 (d, *J* = 4.9 Hz, 2H), 8.49 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 4.9 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.97, 161.32, 156.82, 134.10, 129.85, 119.86, 119.41, 119.02, 118.73; HRMS (EI) Calcd for $C_{10}H_8N_2O$ $[M]^+$ 172.0637, found 172.0633.



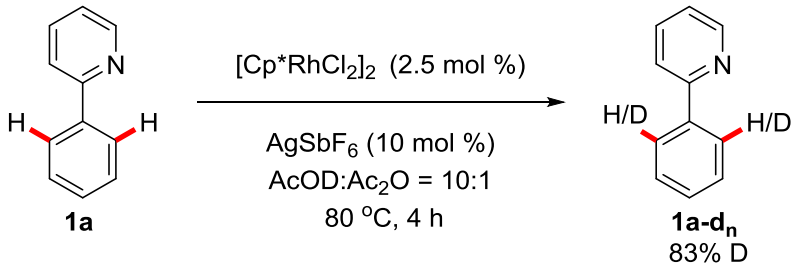
Compound **3k** was obtained as a red amorphous solid in 71% yield (28.2 mg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.95 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.60-7.48 (m, 3H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.13-7.03 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.78, 150.54, 137.37, 133.31, 133.28, 131.20, 129.39, 122.27, 119.96, 118.22; HRMS (EI) Calcd for $C_{12}H_{10}N_2O$ $[M]^+$ 198.0793, found 198.0796.

Scale-up of the reaction.

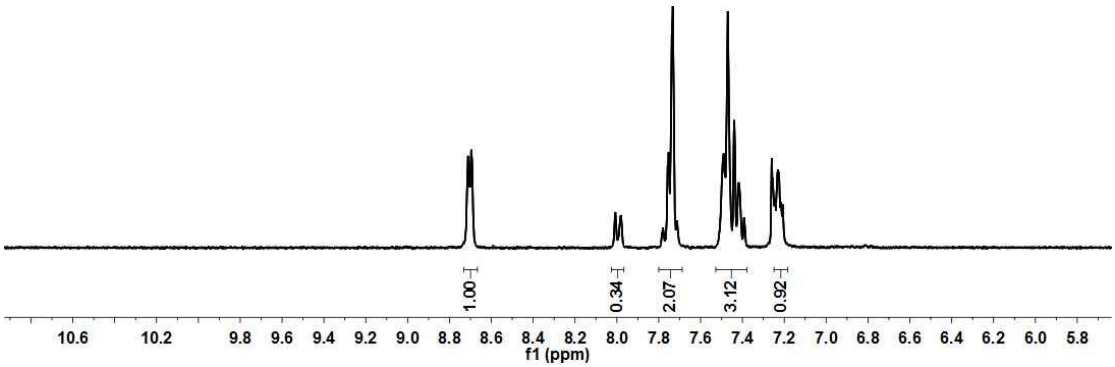


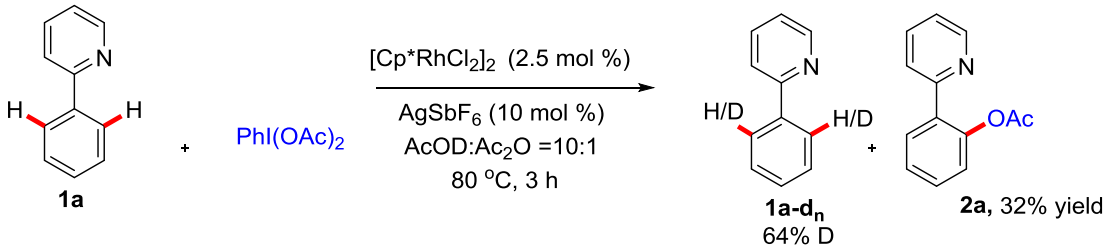
1a (5 mmol, 775 mg), $PhI(OAc)_2$ (6 mmol, 1.2 equiv, 1930 mg), $[Cp^*RhCl_2]_2$ (5 mol %, 154 mg), $AgSbF_6$ (20 mol %, 343mg), AcOH (50 mL) and Ac_2O (5 mL) were added to a 150 mL round-bottom flask. The reaction mixture was refluxed at 80 ^oC for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (5:1) to afford the title compound **2a** 872 mg (yield 81.8%).

Mechanistic study

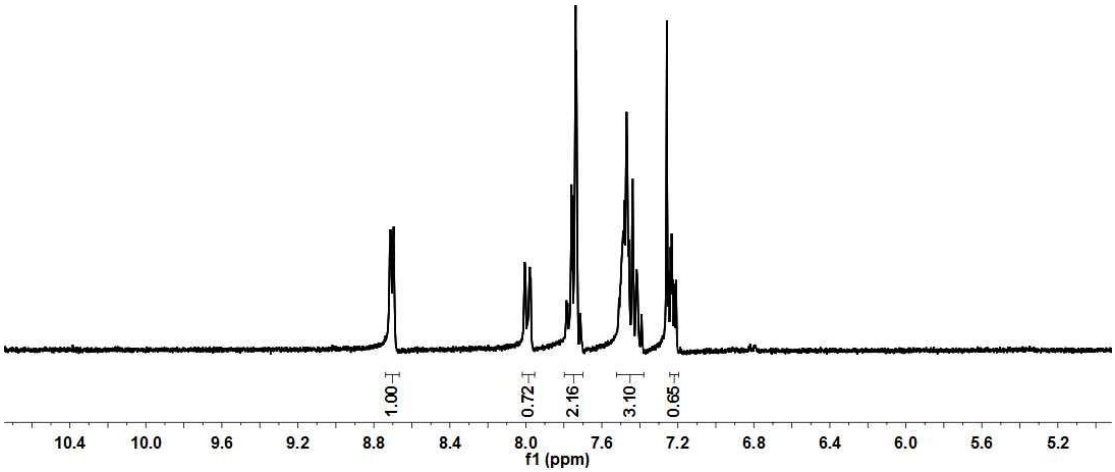


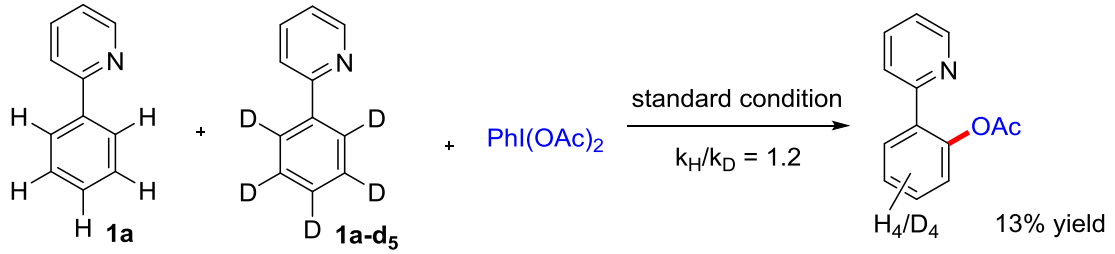
A mixture of **1a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), were dissolved in Acetic acid-d_1:Ac_2O (10:1) (2 mL) in a pressure tube. The reaction mixtures was stirred at 80 ℃ for overnight. The solvent was rapidly removed under reduced pressure and the residues of the reaction was purified by silica gel chromatography using EA/PE to afford the mixture of **1a** : **1a-d_n** .



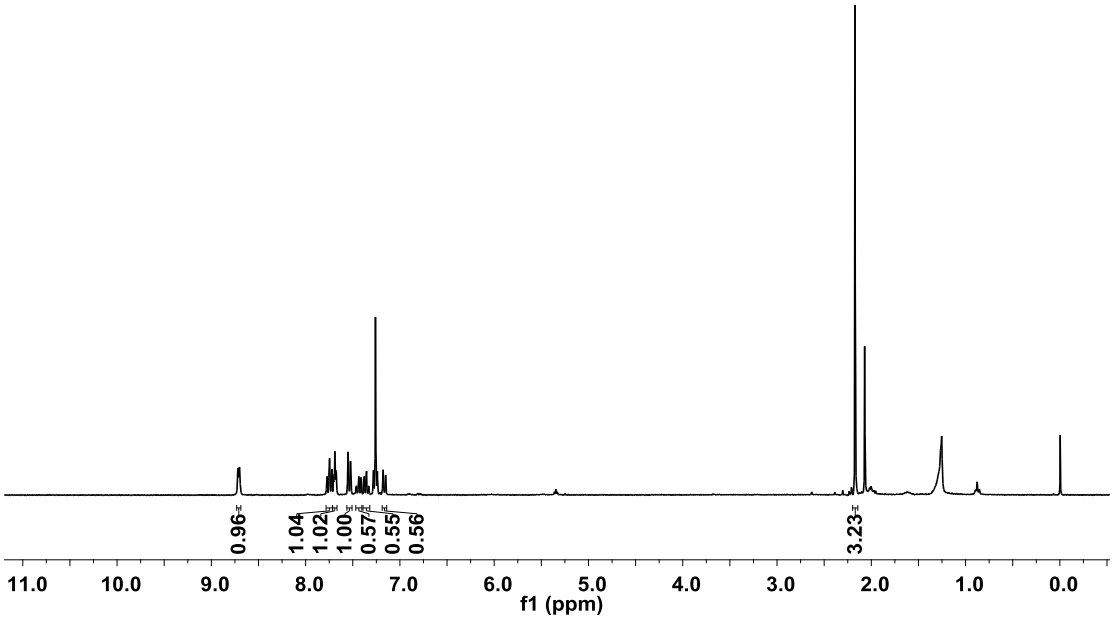


A mixture of **1a** (0.2 mmol), $PhI(OAc)_2$ (0.24 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), were dissolved in $AcOD:Ac_2O$(10:1) (2 mL) in a pressure tube, The reaction mixtures was stirred at 80 ℃ for 3 h. The solvent was rapidly removed under reduced pressure and the residues of the reaction was purified by silica gel chromatography using EA/PE to re-isolate **1a**.

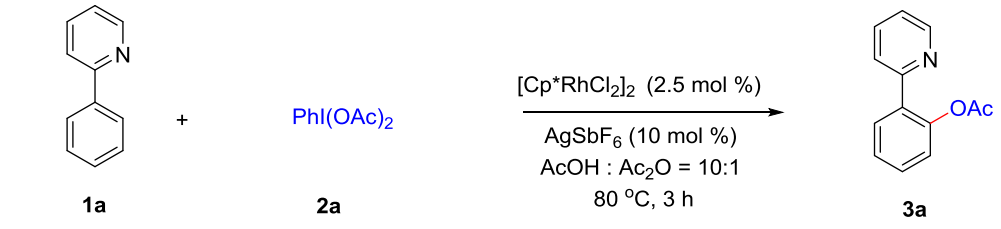


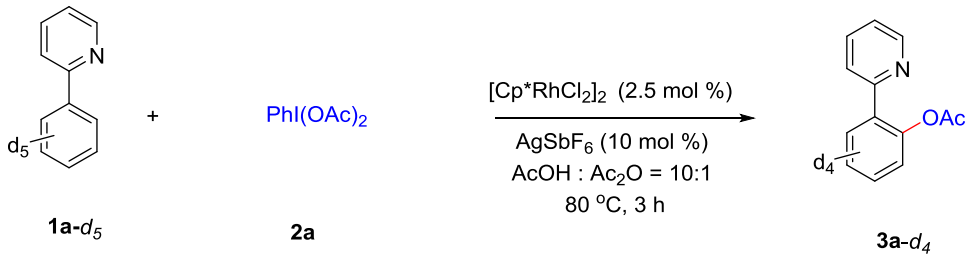


An equimolar mixture of **1a** (0.2 mmol, 31 mg), **1a-d$_5$** (0.2 mmol, 32 mg), PhI(OAc)$_2$ (0.2 mmol, 64mg), [Cp*RhCl$_2$]$_2$ (2.5 mol %), AgSbF$_6$ (10 mol %), were dissolved in Acetic acid:Ac$_2$O (10:1) (2 mL) in a pressure tube,. The reaction mixtures were stirred at 80 ℃ for 1 h. The solvent was rapidly removed under reduced pressure and the residue of the reaction was purified by silica gel chromatography using EA/PE to afford the products. KIE value (k_H/k_D = 1.2) was determined on the basis of ^{1}H NMR analysis.



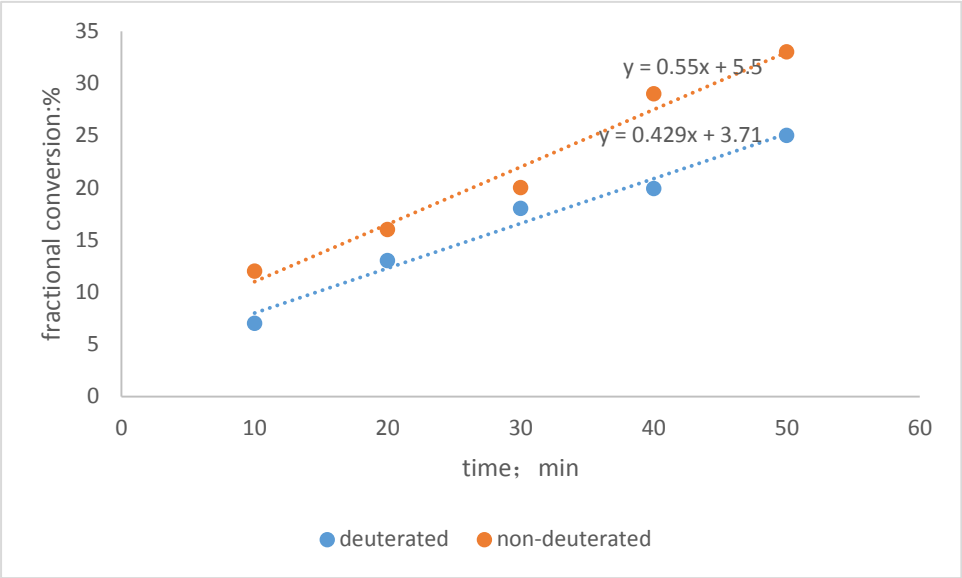
Kinetic Isotope Effect Experiments





A mixture of **1a** (0.2 mmol, 31 mg) or **1a-d$_5$** (0.2 mmol, 32 mg), PhI(OAc)$_2$ (0.2 mmol, 64mg), [Cp*RhCl$_2$]$_2$ (2.5 mol %), AgSbF$_6$ (10 mol %), were dissolved in AcOH:Ac$_2$O(10:1) (2 mL) in a pressure tube,. The resulting mixture was stirred at 80 ℃ for designated time (10 min, 20 min, 30 min, 40 min, and 50 min). The solution was concentrated and submitted to HPLC to provide the following yield.

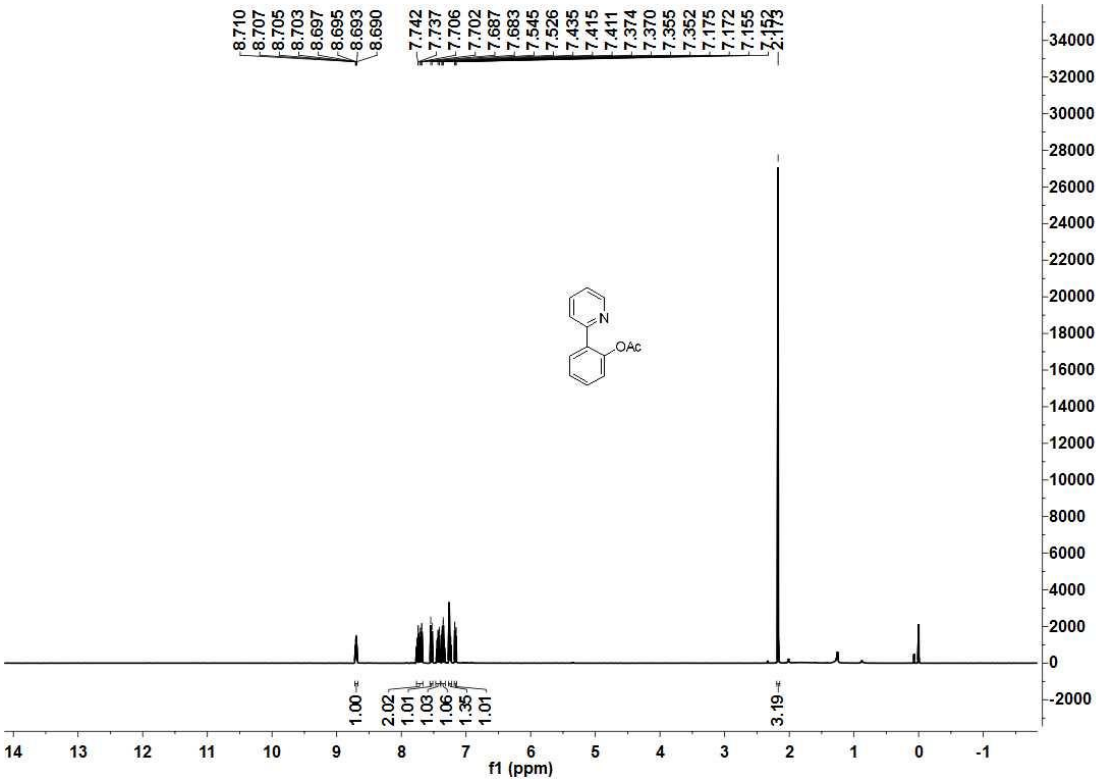
Time (min)	10	20	30	40	50
3a (%)	12	16	20	29	33
3a-d$_4$ (%)	7	13	18	20	25

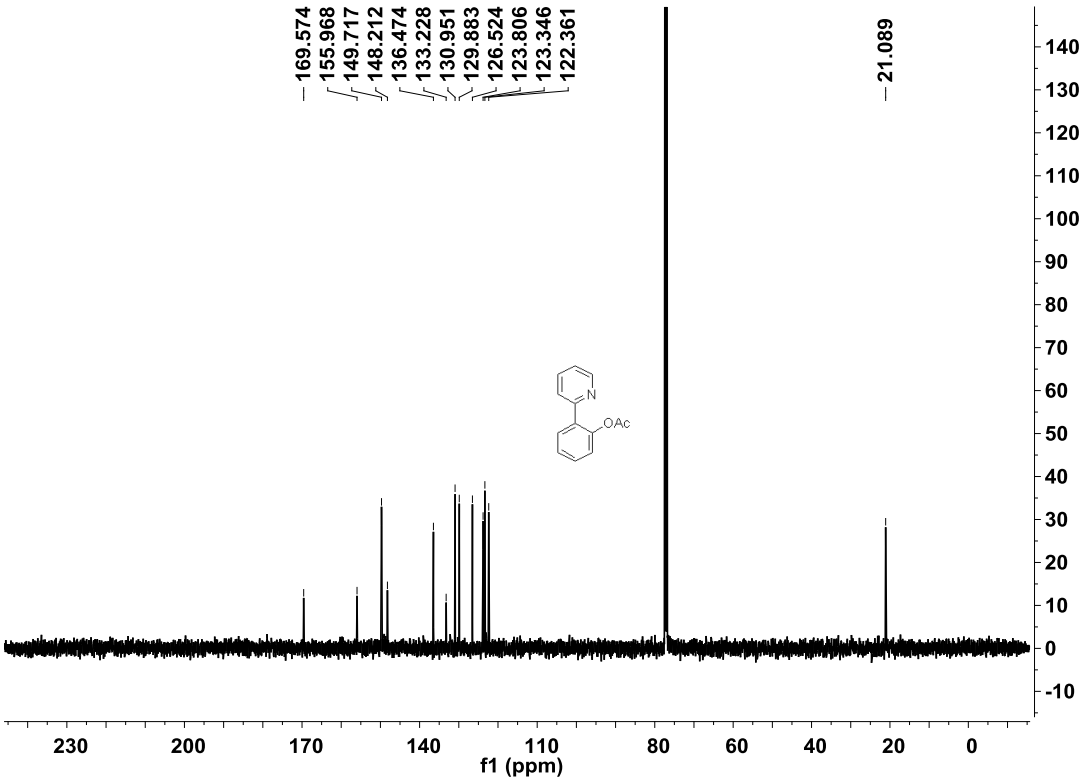


KIE = 0.55/0.429 = 1.28

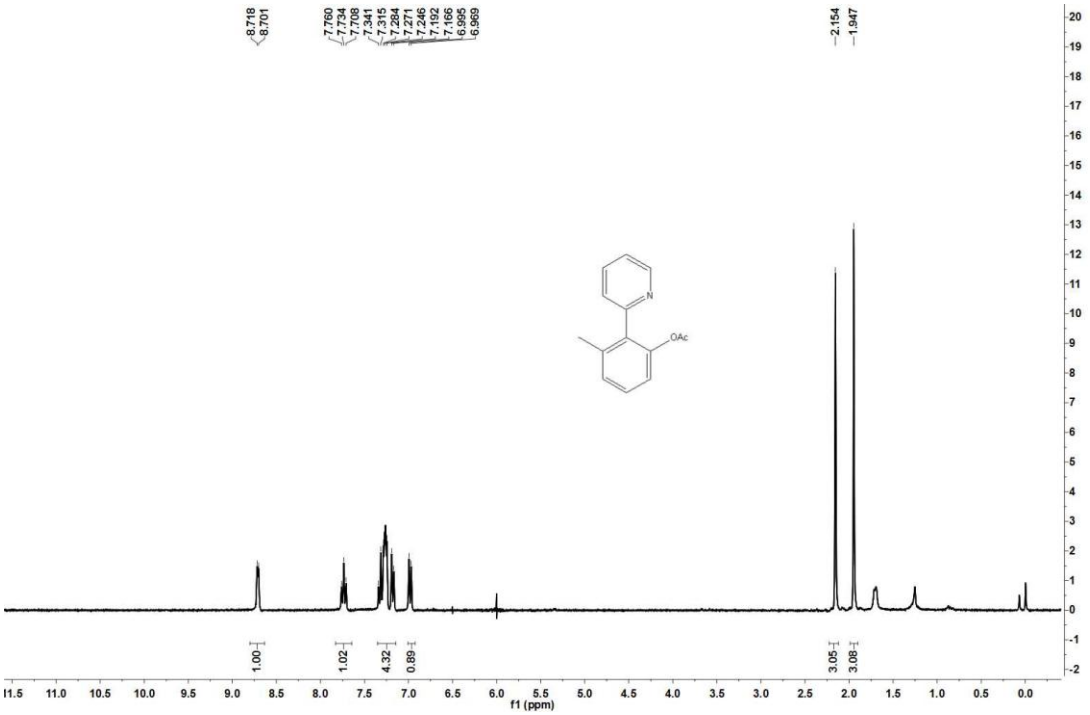
^{1}H NMR and ^{13}C NMR

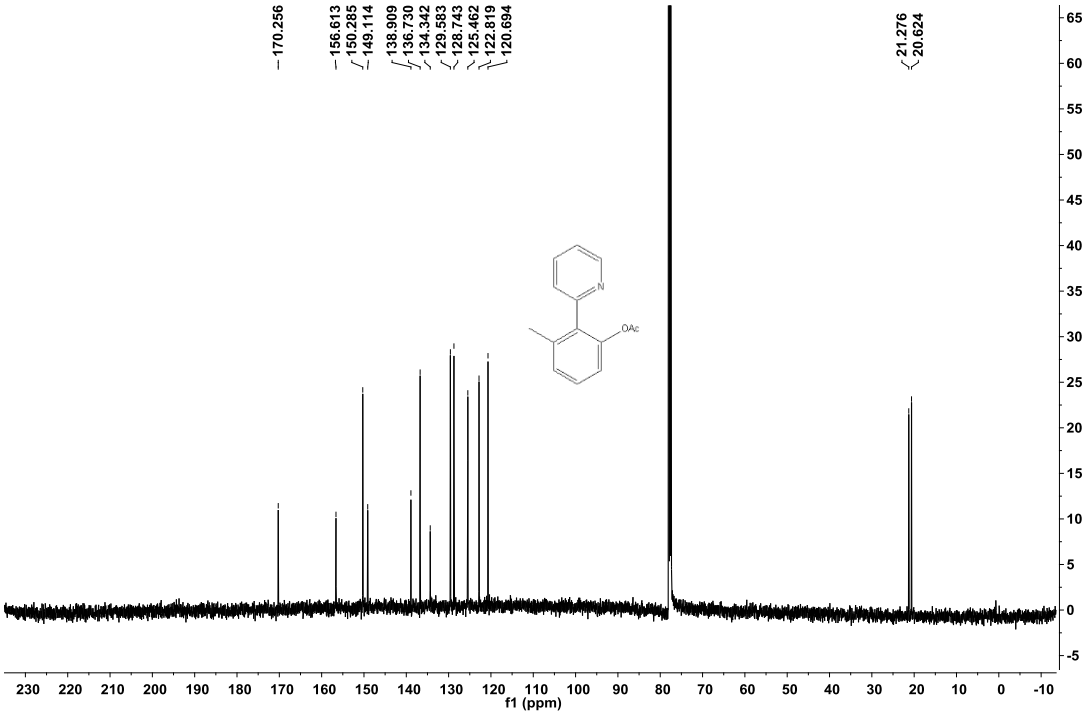
Compound **2a**



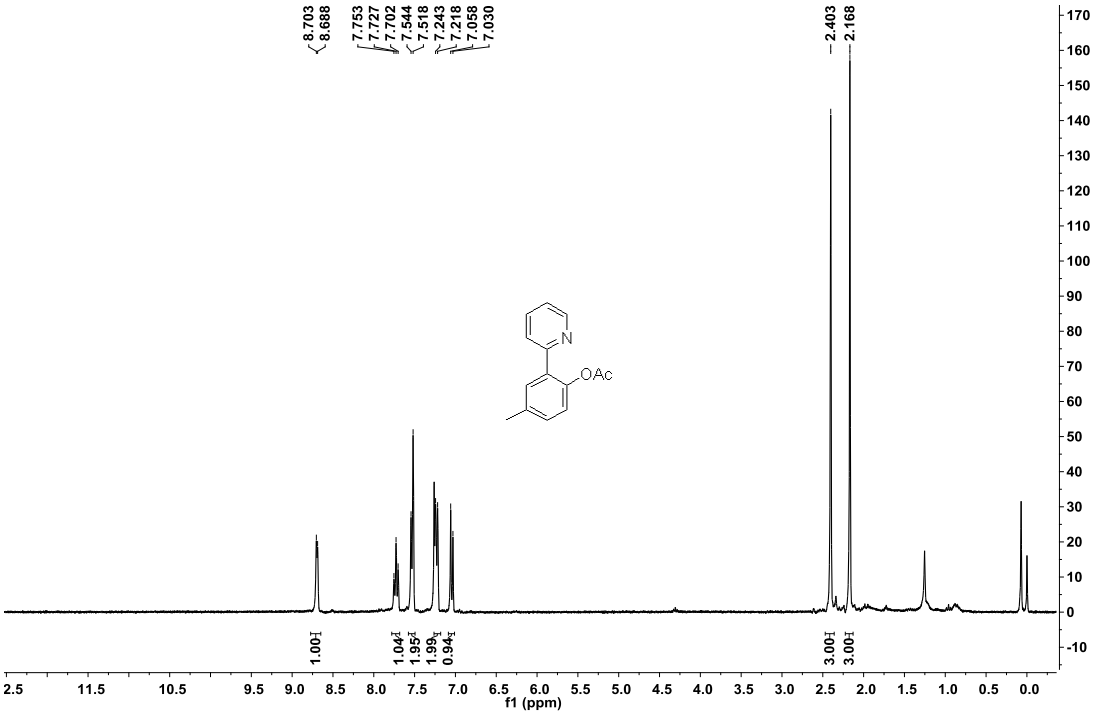


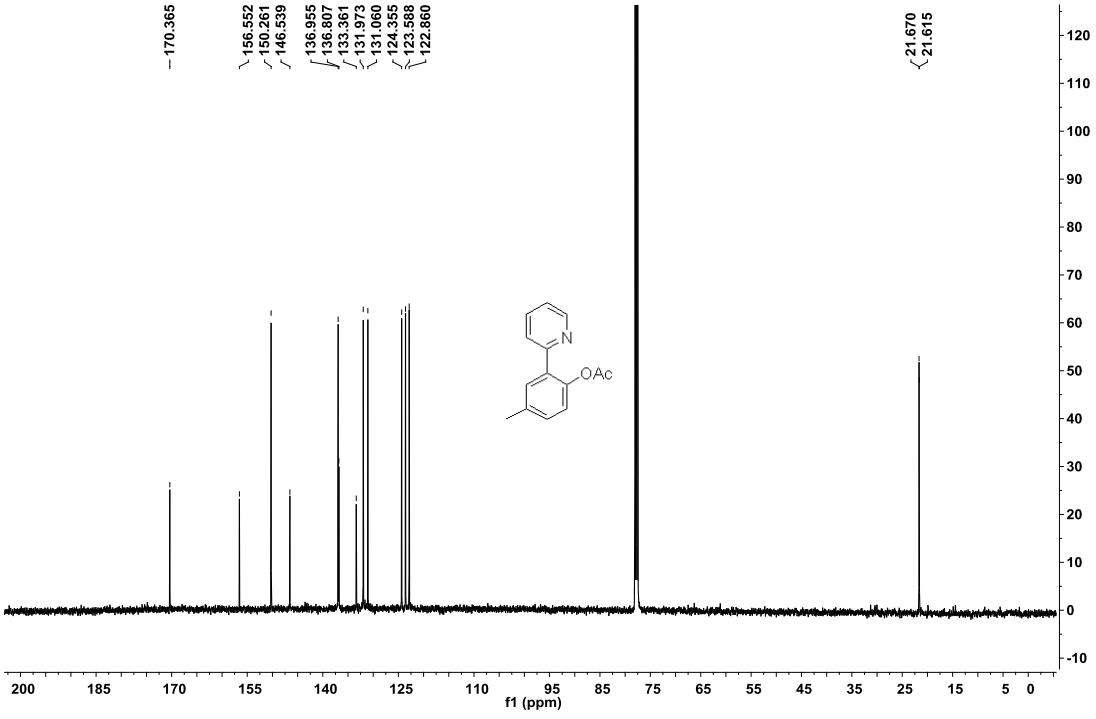
Compound **2b**


8.718
8.701
7.760
7.734
7.708
7.341
7.315
7.284
7.271
7.246
7.192
7.166
6.995
6.969
2.154
1.947
1.00
1.02
4.32
0.89
3.05
3.08
f1 (ppm)

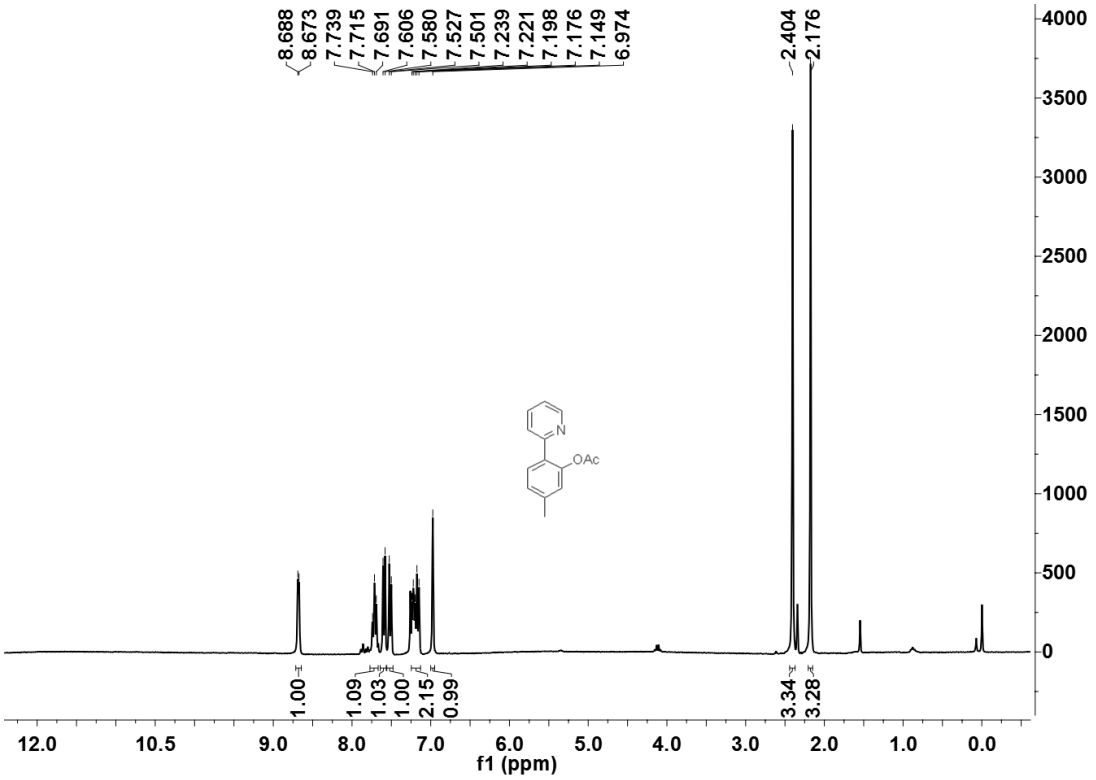

170.256
156.613
150.285
149.114
138.909
136.730
134.342
129.583
128.743
125.462
122.819
120.694
21.276
20.624
f1 (ppm)

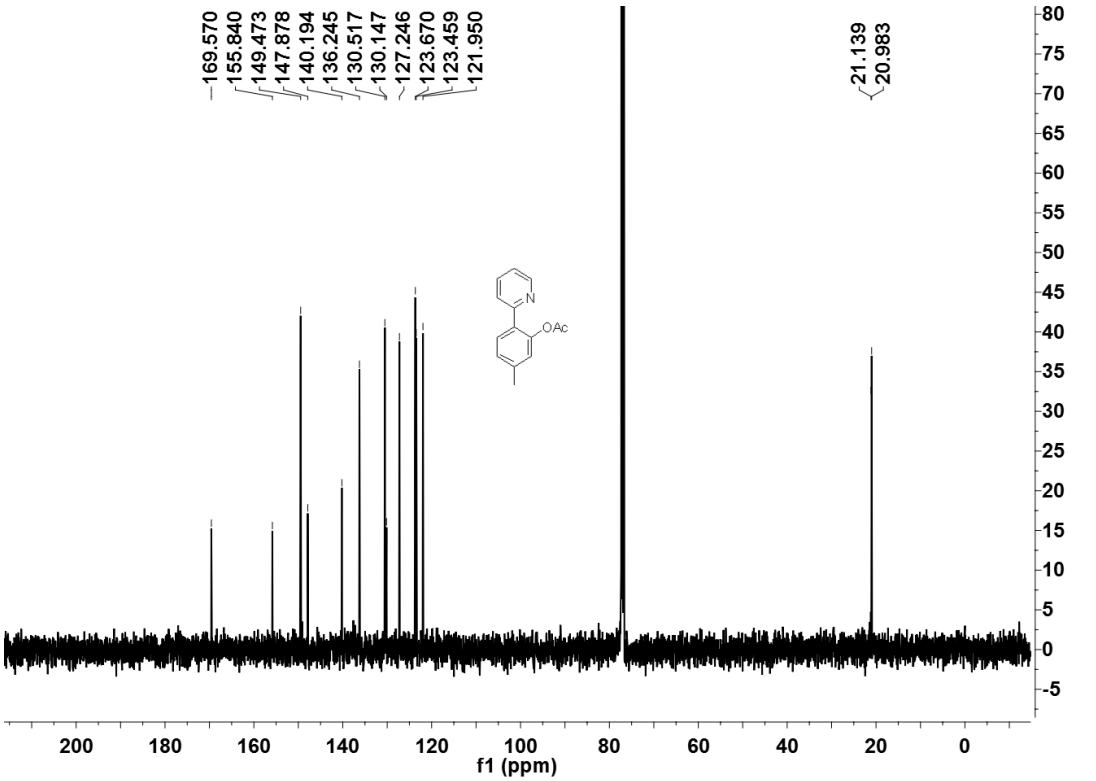
Compound **2c**


8.703
8.688
7.753
7.727
7.702
7.544
7.518
7.243
7.218
7.058
7.030
2.403
2.168
N
OAc
1.00
1.04
1.95
1.99
0.94
3.00
3.00
f1 (ppm)

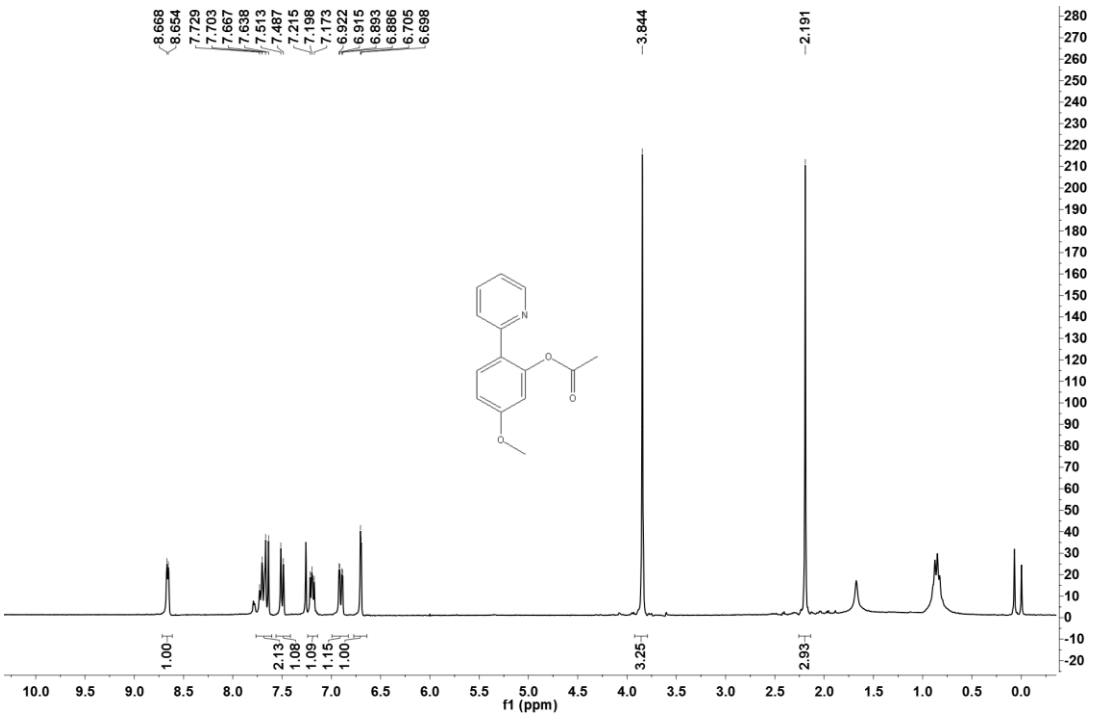

170.365
156.552
150.261
146.539
136.955
136.807
133.361
131.973
131.060
124.355
123.588
122.860
21.670
21.615
N
OAc
f1 (ppm)

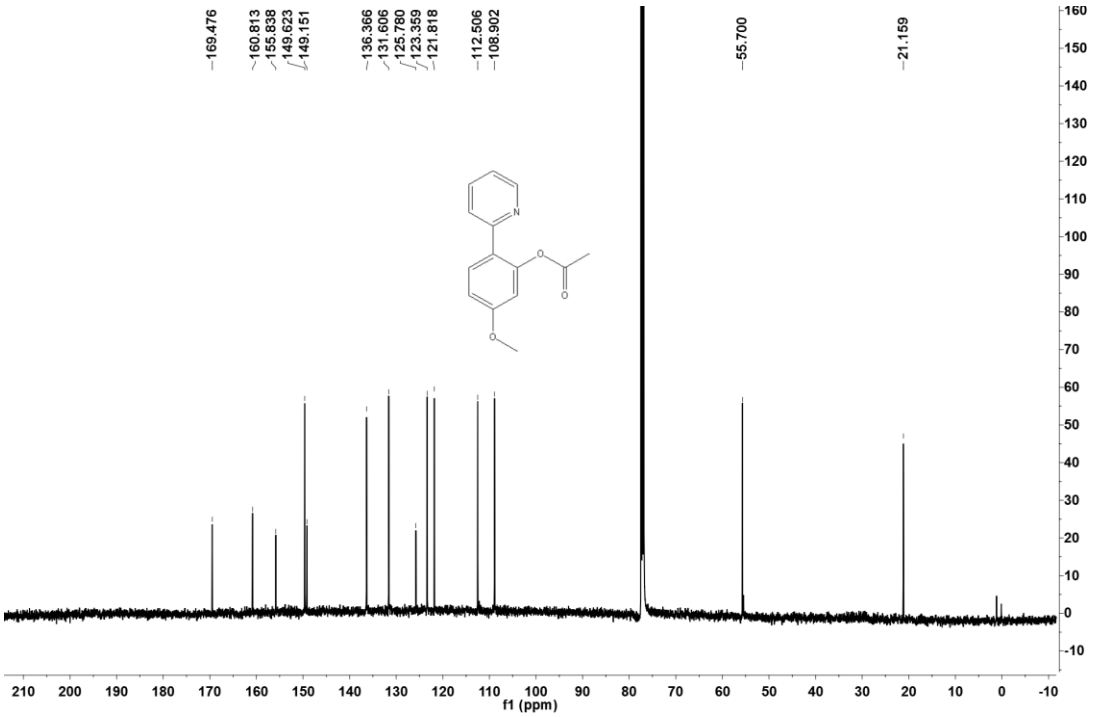
Compound **2d**


8.688
8.673
7.739
7.715
7.691
7.606
7.580
7.527
7.501
7.239
7.221
7.198
7.176
7.149
6.974
2.404
2.176
1.00
1.09
1.03
1.00
2.15
0.99
3.34
3.28
OAc
f1 (ppm)

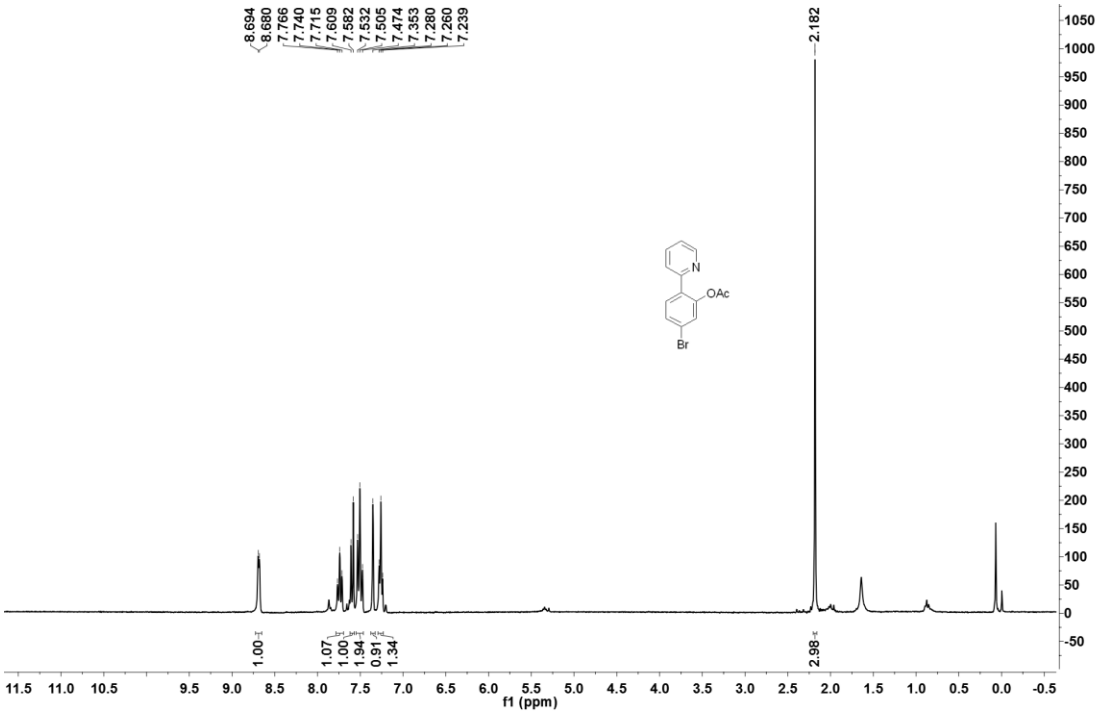

169.570
155.840
149.473
147.878
140.194
136.245
130.517
130.147
127.246
123.670
123.459
121.950
21.139
20.983
OAc
f1 (ppm)

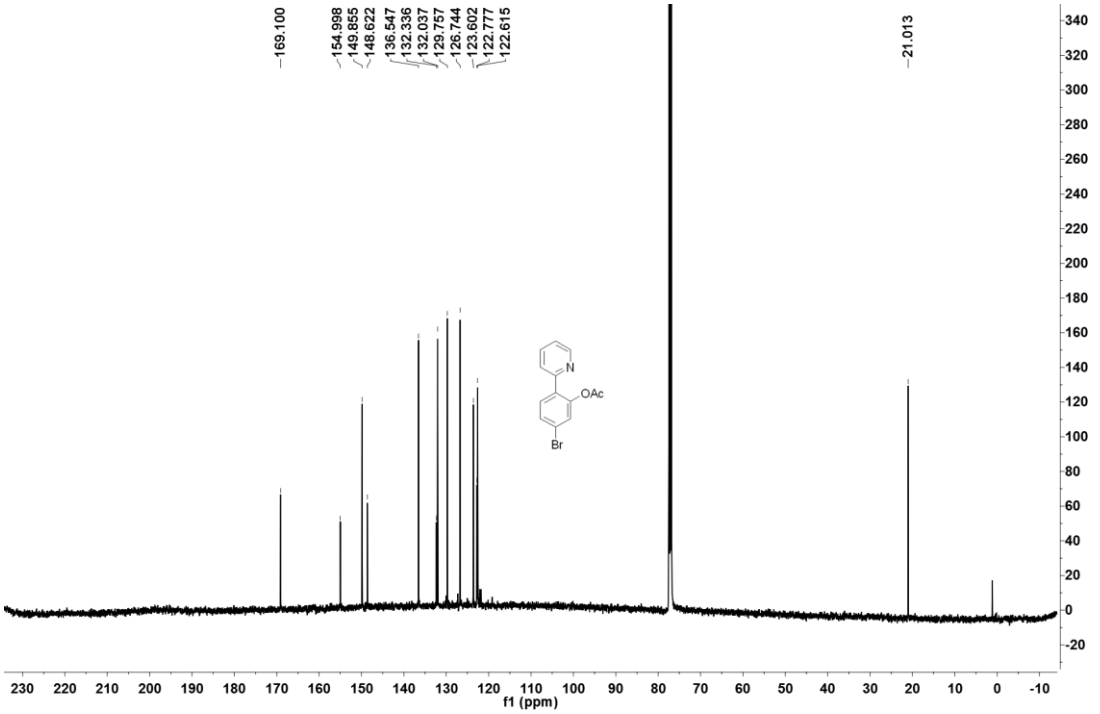
Compound **2e**


8.668
8.654
7.729
7.703
7.667
7.638
7.513
7.487
7.215
7.198
7.173
6.922
6.915
6.893
6.886
6.705
6.698
3.844
2.191
1.00
2.13
1.08
1.09
1.15
1.00
3.25
2.93
f1 (ppm)

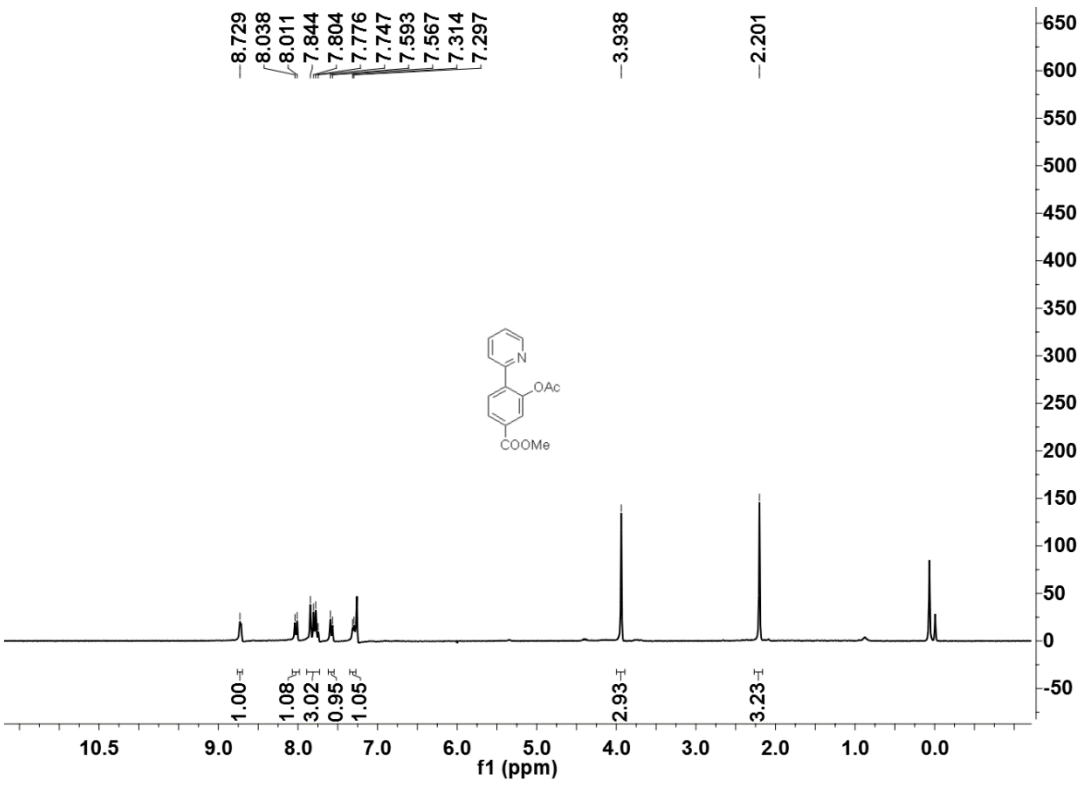

169.476
160.813
155.838
149.623
149.151
136.366
131.606
125.780
123.359
121.818
112.506
108.902
55.700
21.159
f1 (ppm)

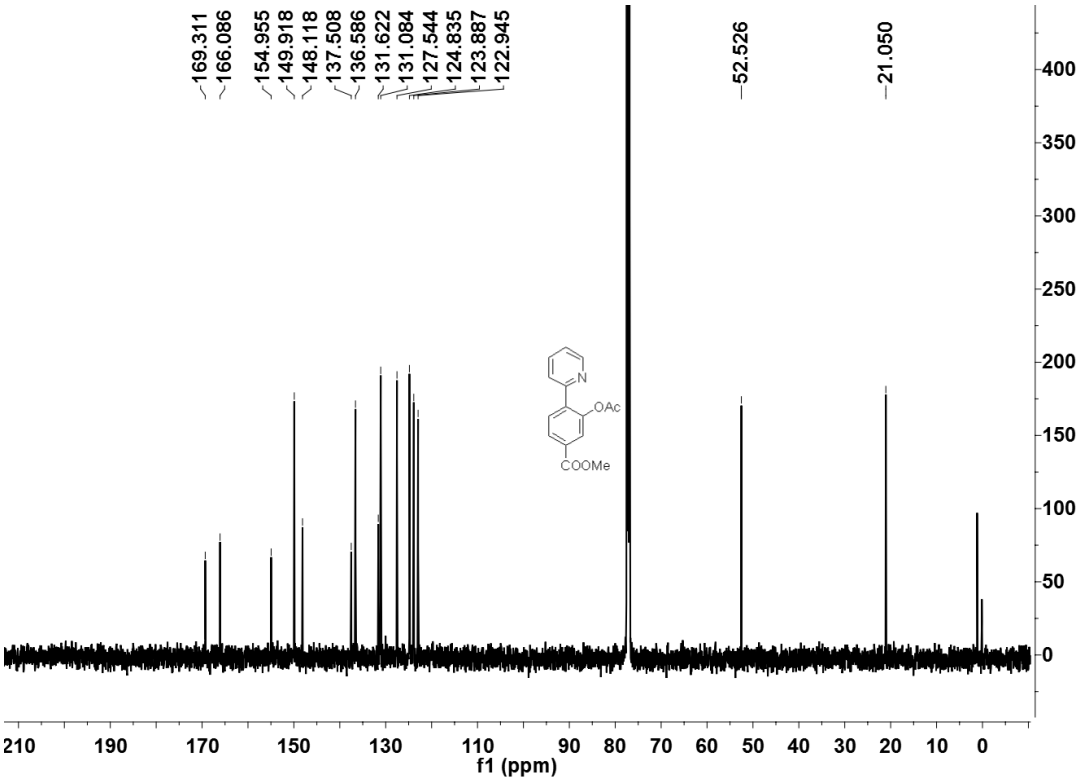
Compound **2f**


8.694
8.680
7.766
7.740
7.715
7.609
7.582
7.532
7.505
7.474
7.353
7.280
7.260
7.239
2.182
1.00
1.07
1.00
1.94
0.91
1.34
2.98
N
OAc
Br
f1 (ppm)

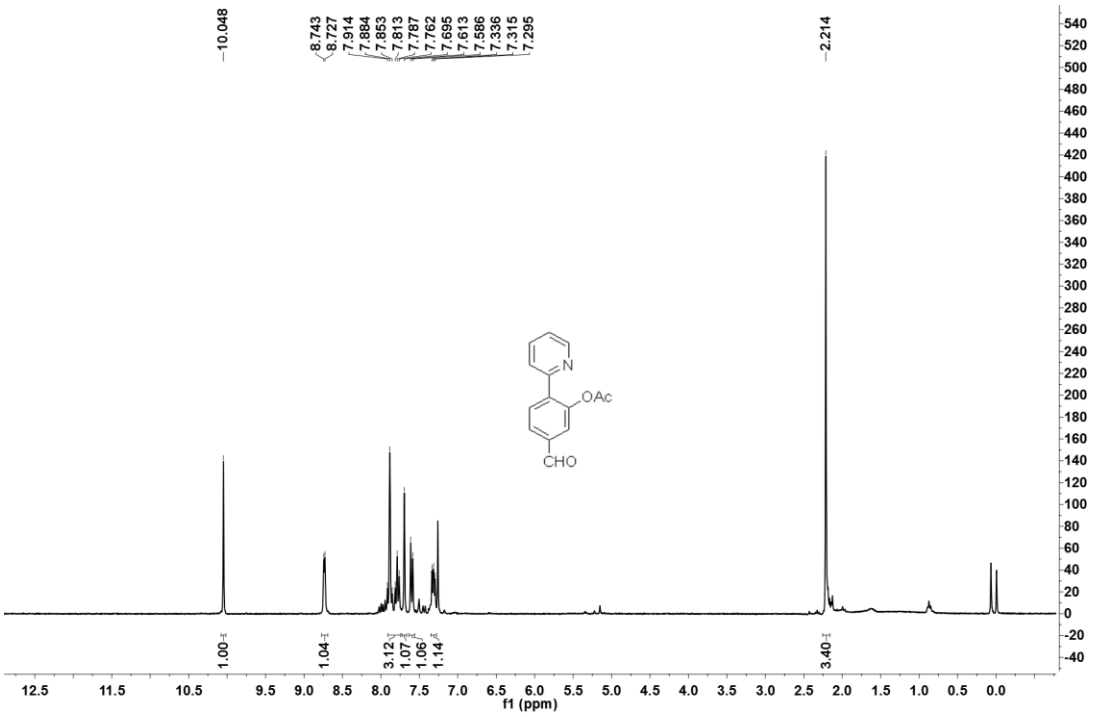

169.100
154.998
149.855
148.622
136.547
132.336
132.037
129.757
126.744
123.602
122.777
122.615
21.013
N
OAc
Br
f1 (ppm)

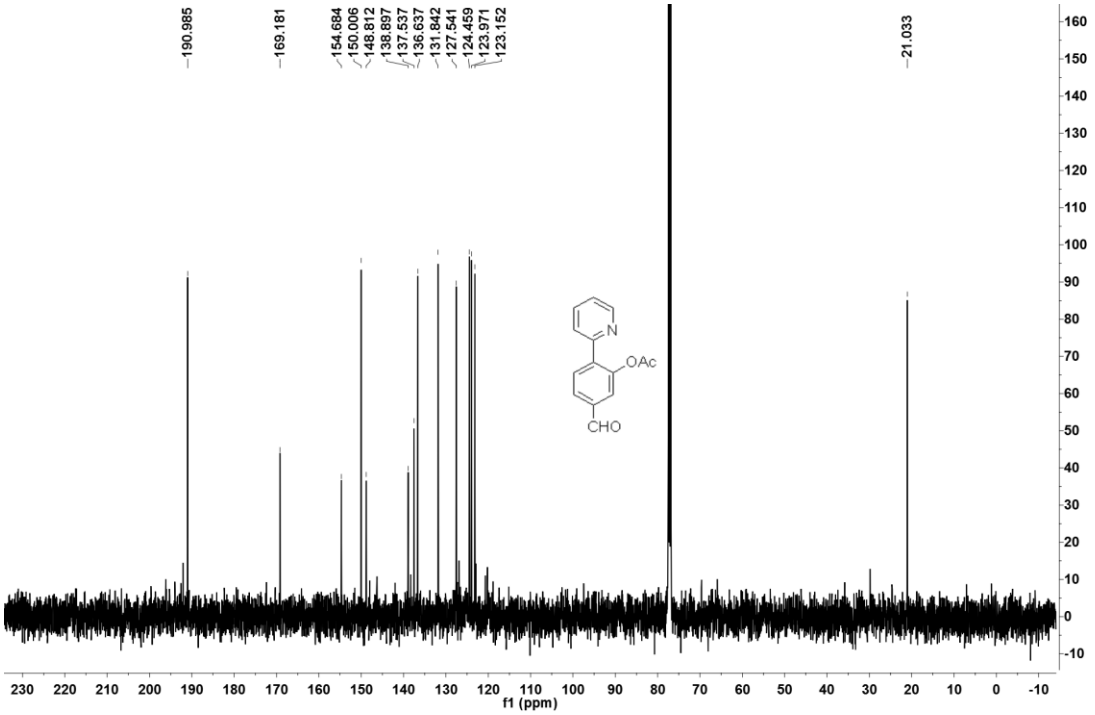
Compound **2g**


8.729
8.038
8.011
7.844
7.804
7.776
7.747
7.593
7.567
7.314
7.297
3.938
2.201
OAc
COOMe
1.00
1.08
3.02
0.95
1.05
2.93
3.23
f1 (ppm)

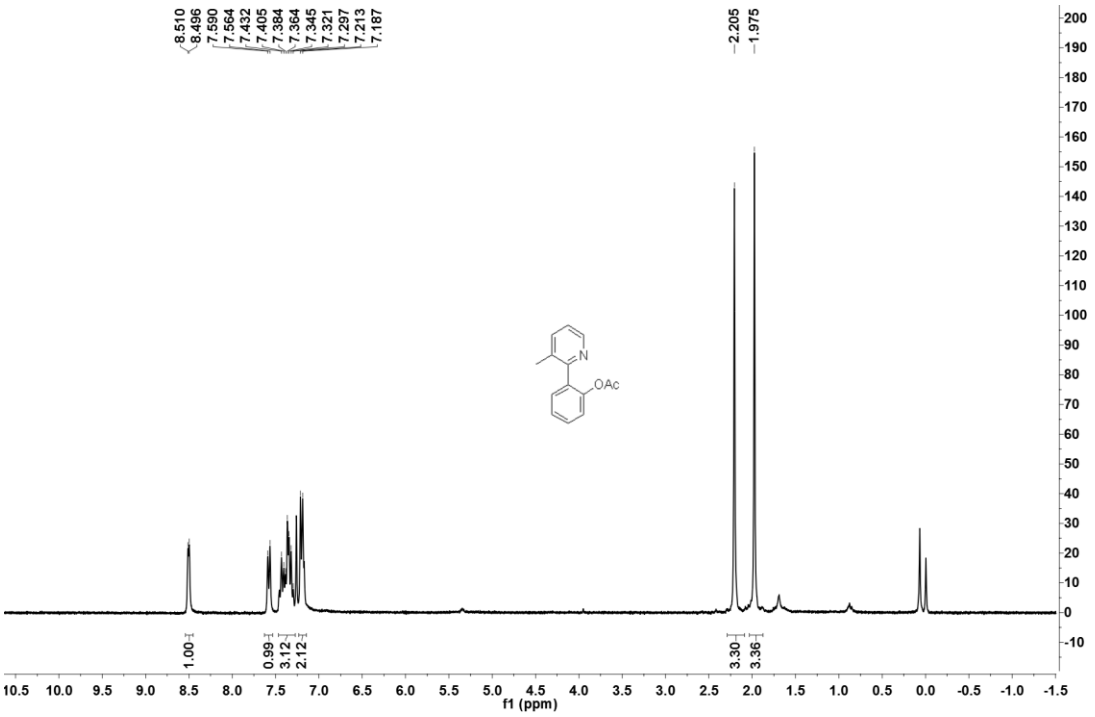

169.311
166.086
154.955
149.918
148.118
137.508
136.586
131.622
131.084
127.544
124.835
123.887
122.945
52.526
21.050
OAc
COOMe
f1 (ppm)

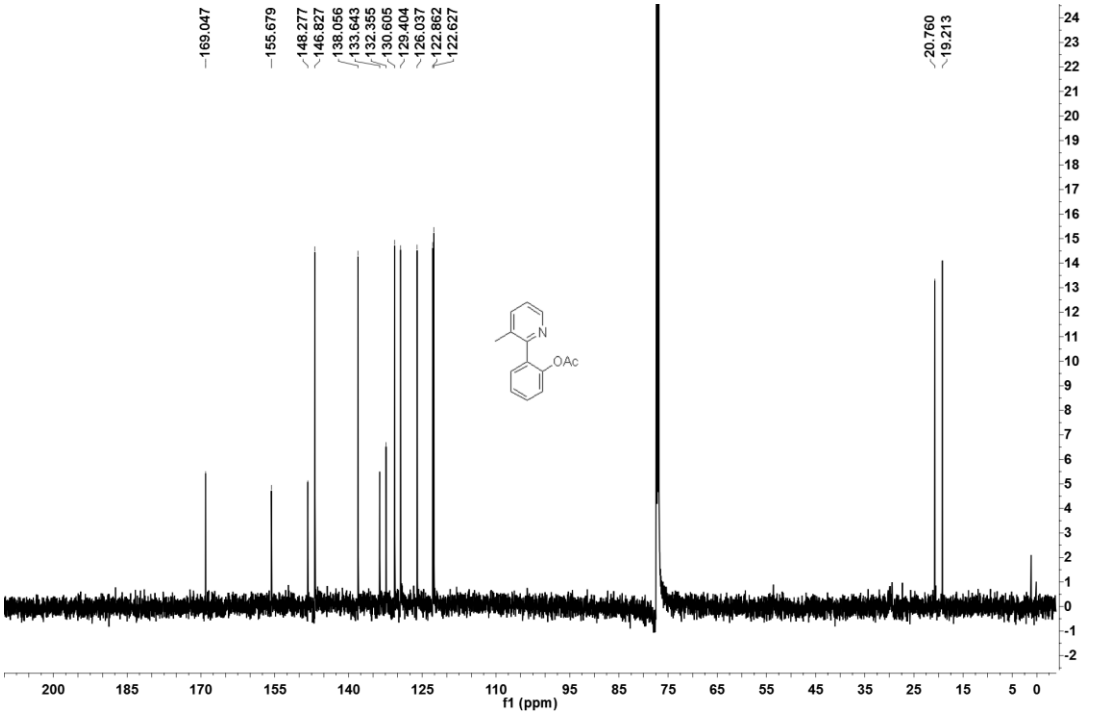
Compound **2h**


10.048
8.743
8.727
7.914
7.884
7.853
7.813
7.787
7.762
7.695
7.613
7.586
7.336
7.315
7.295
2.214
1.00
1.04
3.12
1.07
1.06
1.14
3.40
N
OAc
CHO
f1 (ppm)

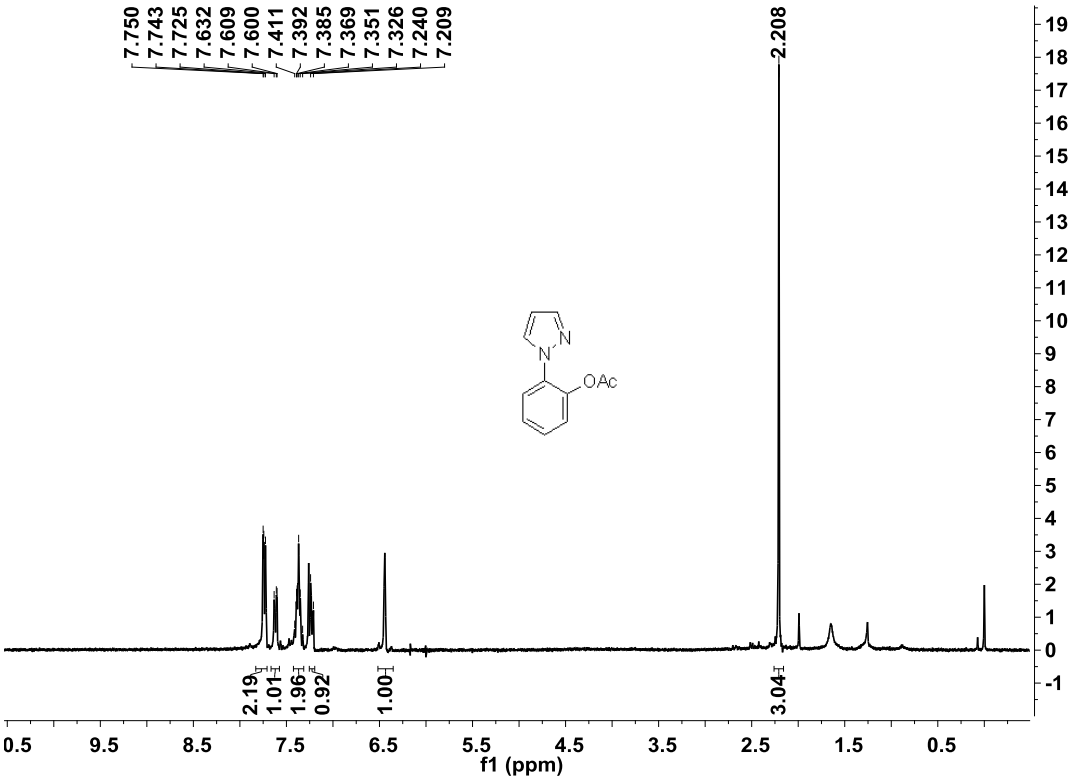

190.985
169.181
154.684
150.006
148.812
138.897
137.537
136.637
131.842
127.541
124.459
123.971
123.152
21.033
N
OAc
CHO
f1 (ppm)

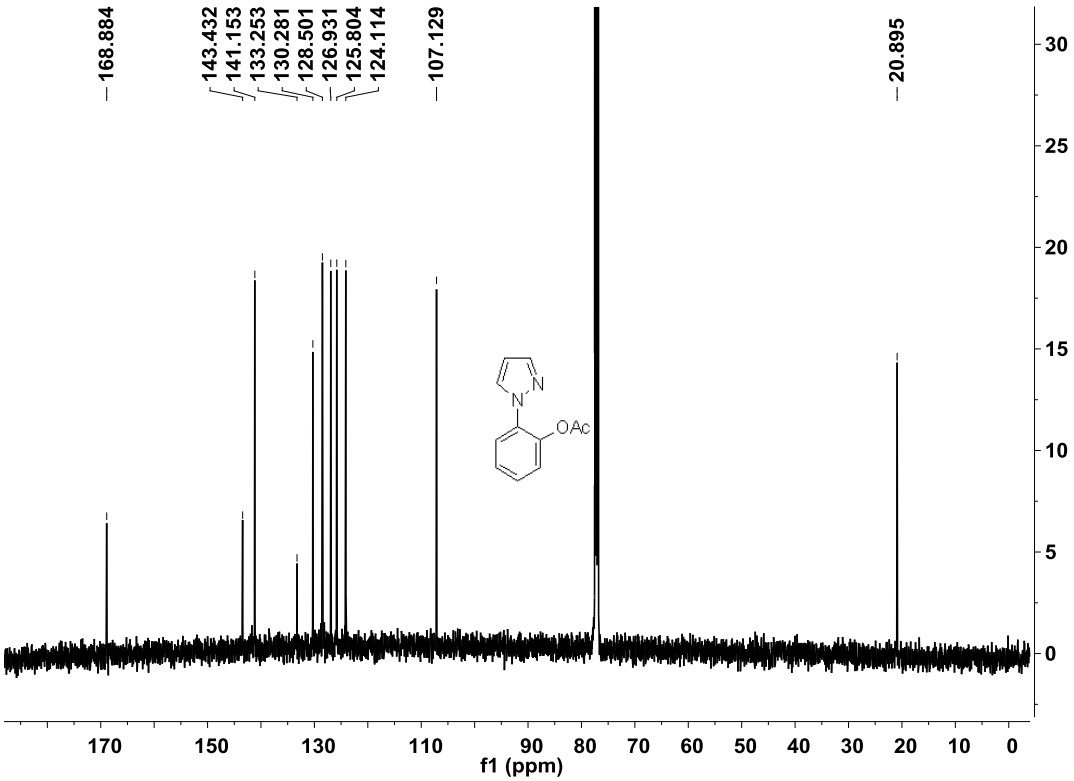
Compound **2i**


8.510
8.496
7.590
7.564
7.432
7.405
7.384
7.364
7.345
7.321
7.297
7.213
7.187
2.205
1.975
N
OAc
1.00
0.99
3.12
2.12
3.30
3.36
f1 (ppm)

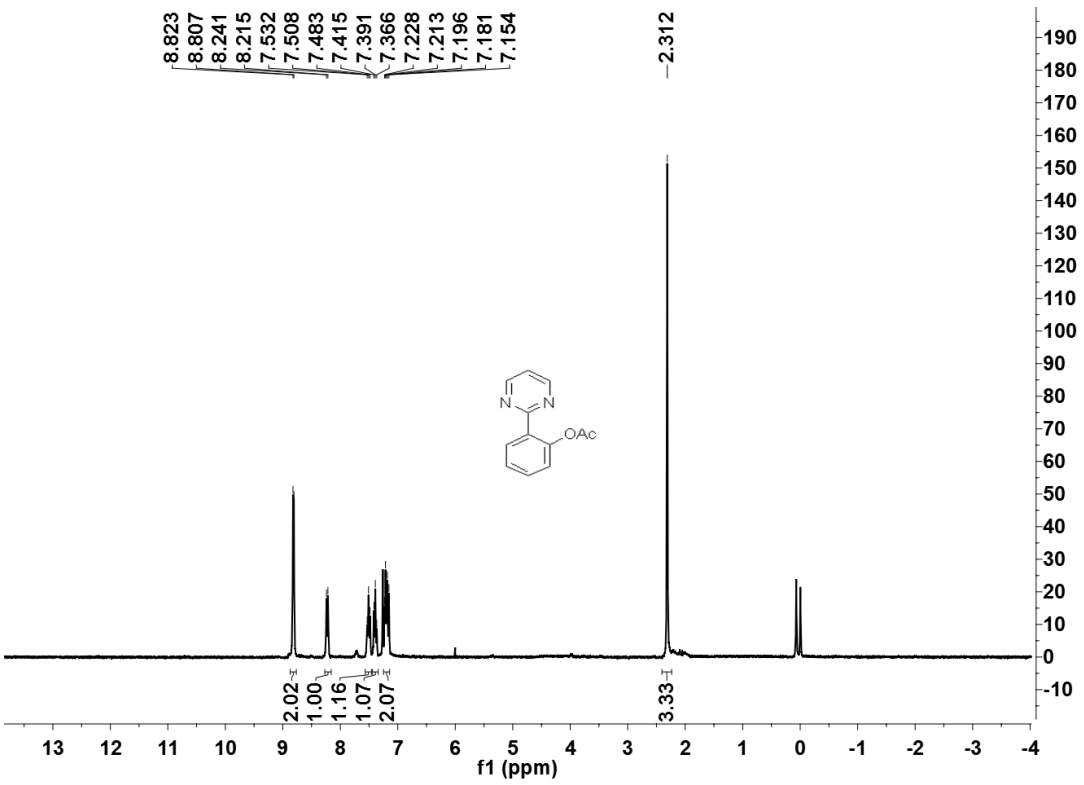

169.047
155.679
148.277
146.827
138.056
133.643
132.355
130.605
129.404
126.037
122.862
122.627
20.760
19.213
N
OAc
f1 (ppm)

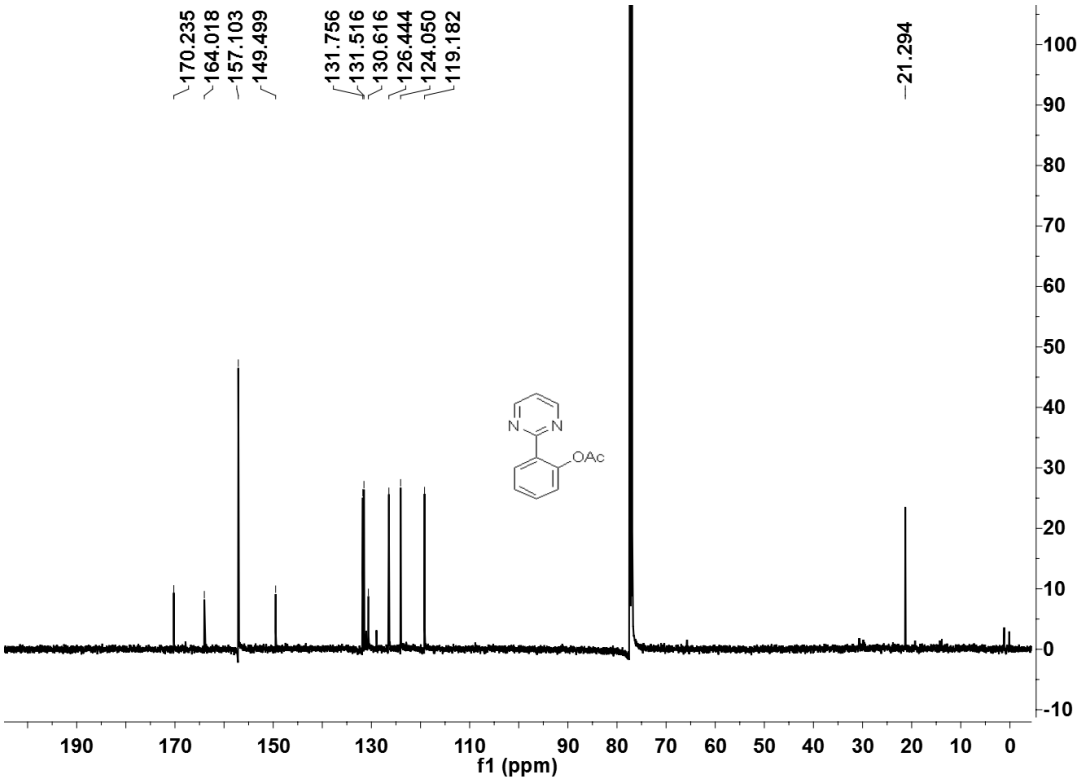
Compound **2j**


7.750
7.743
7.725
7.632
7.609
7.600
7.411
7.392
7.385
7.369
7.351
7.326
7.240
7.209
2.208
OAc
2.19
1.01
1.96
0.92
1.00
3.04
f1 (ppm)

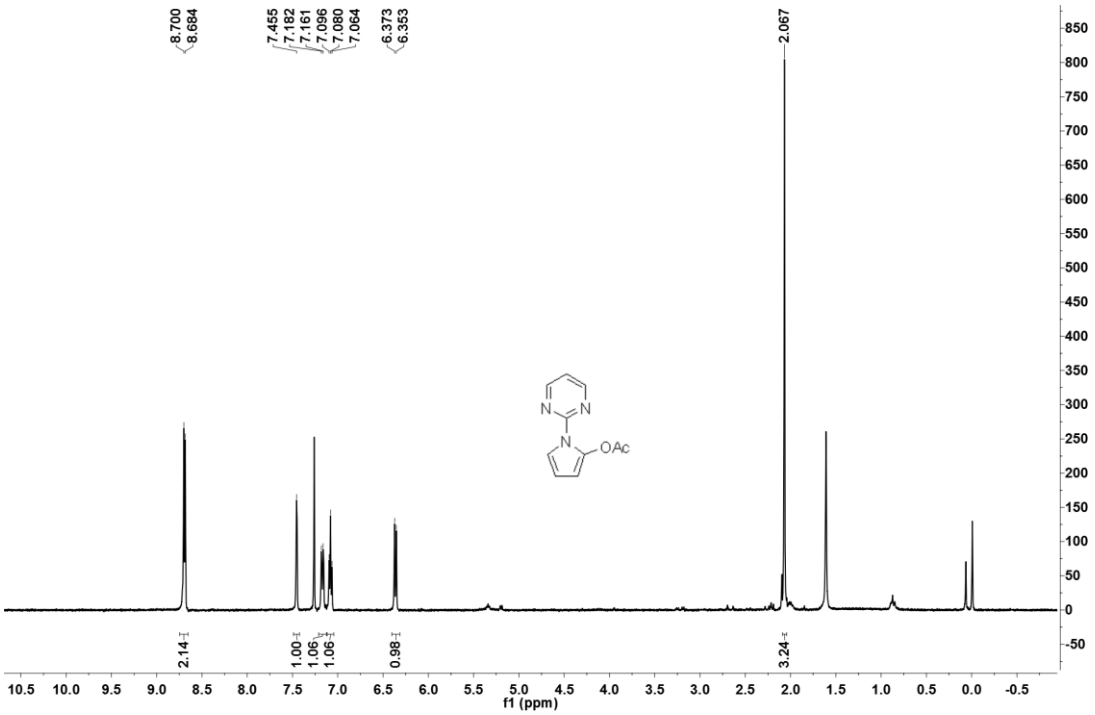

168.884
143.432
141.153
133.253
130.281
128.501
126.931
125.804
124.114
107.129
20.895
OAc
f1 (ppm)

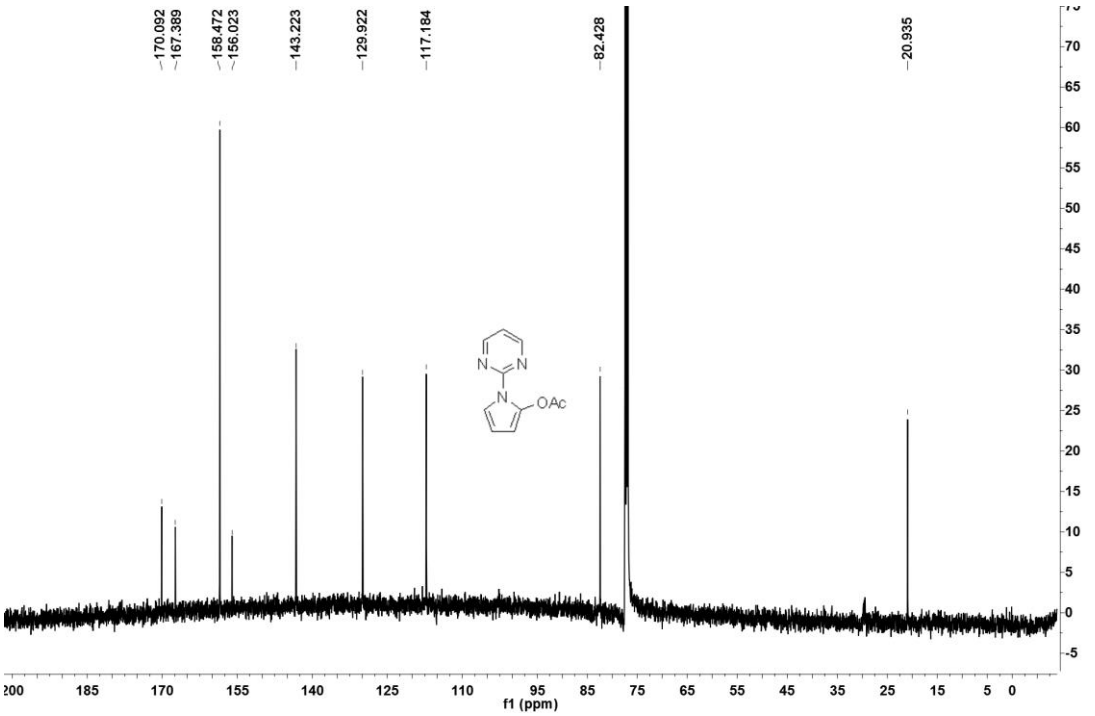
Compound **2k**


8.823
8.807
8.241
8.215
7.532
7.508
7.483
7.415
7.391
7.366
7.228
7.213
7.196
7.181
7.154
2.312
OAc
2.02
1.00
1.16
1.07
2.07
3.33
f1 (ppm)

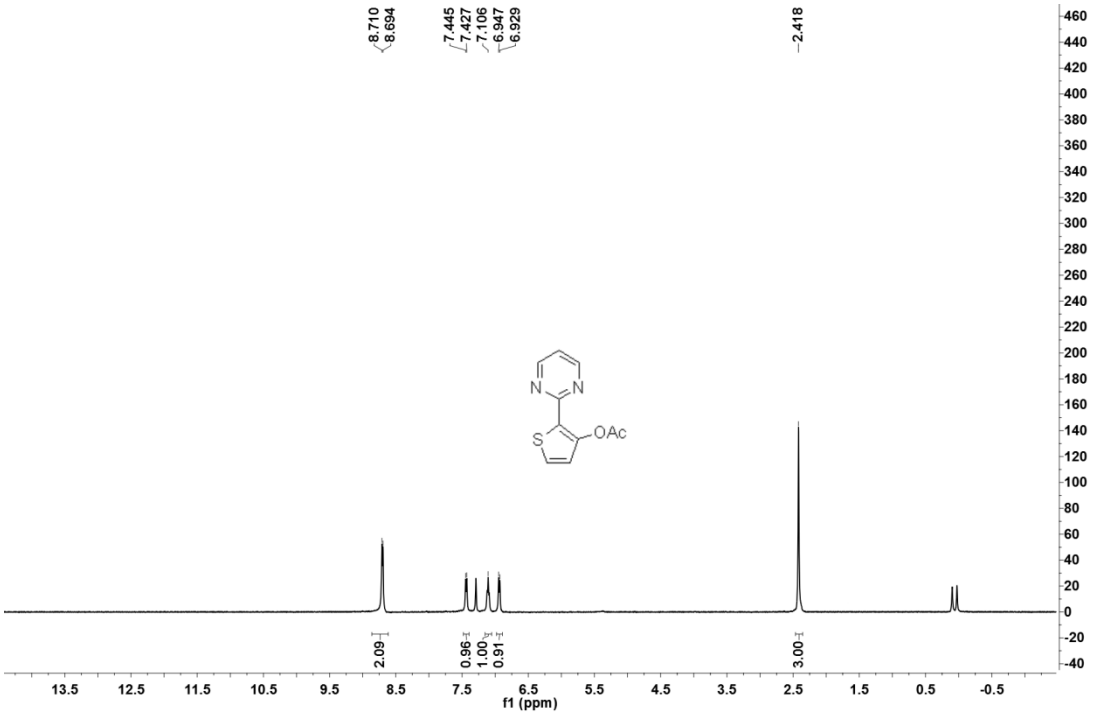

170.235
164.018
157.103
149.499
131.756
131.516
130.616
126.444
124.050
119.182
21.294
OAc
f1 (ppm)

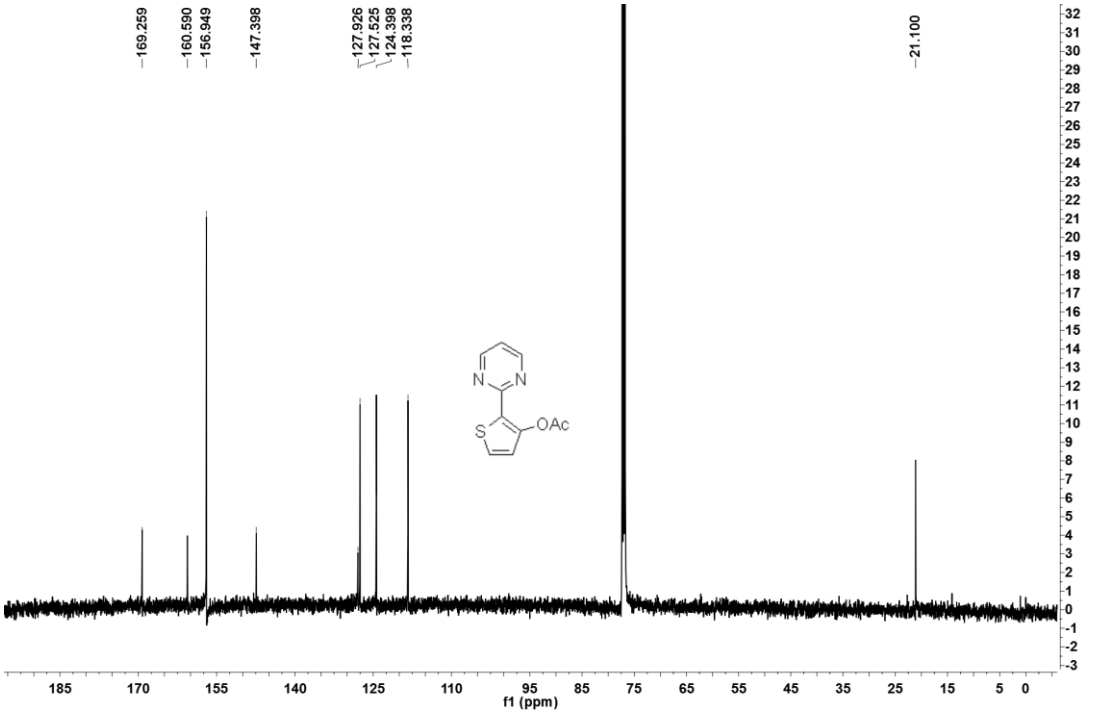
Compound **2l**


8.700
8.684
7.455
7.182
7.161
7.096
7.080
7.064
6.373
6.353
2.067
OAc
2.14
1.00
1.06
1.06
0.98
3.24
f1 (ppm)

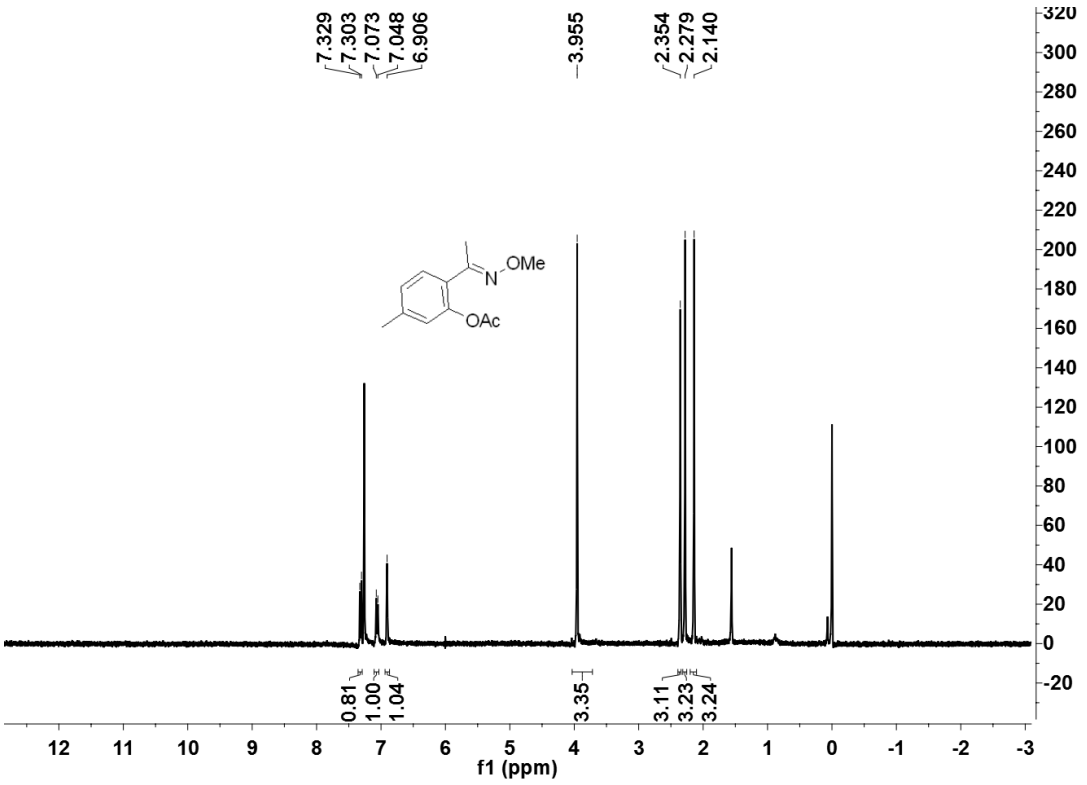

170.092
167.389
158.472
156.023
143.223
129.922
117.184
82.428
20.935
OAc
f1 (ppm)

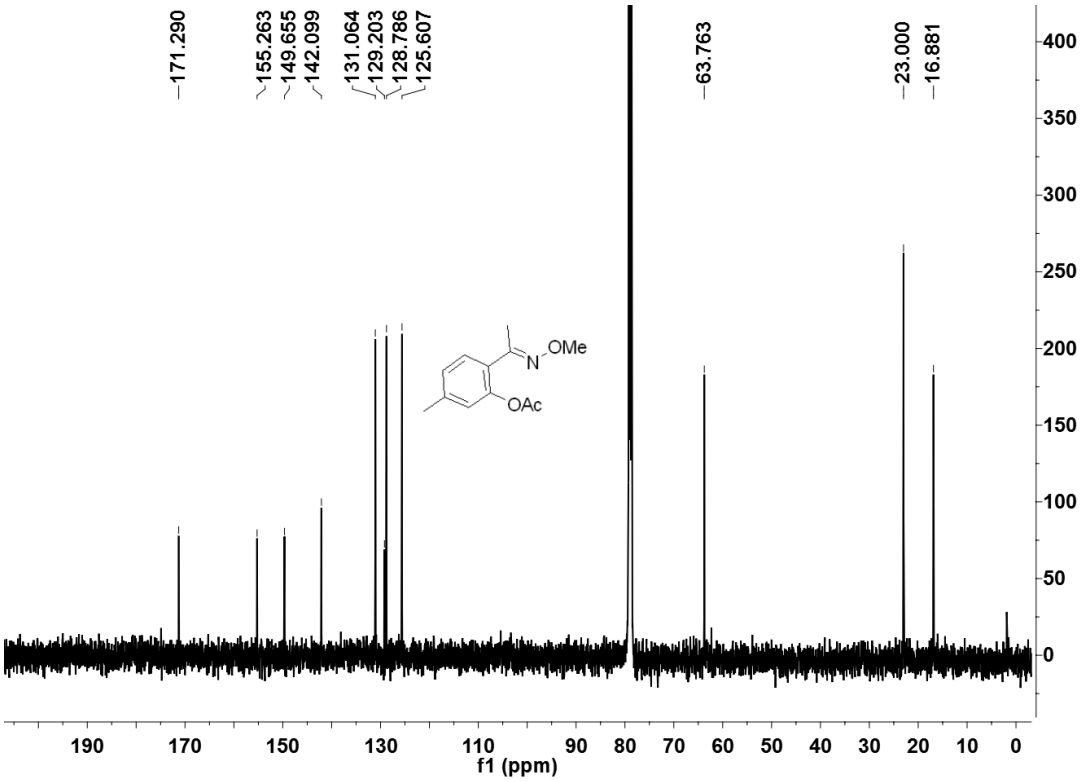
Compound **2m**


8.710
8.694
7.445
7.427
7.106
6.947
6.929
2.418
N
N
S
OAc
2.09
0.96
1.00
0.91
3.00
f1 (ppm)

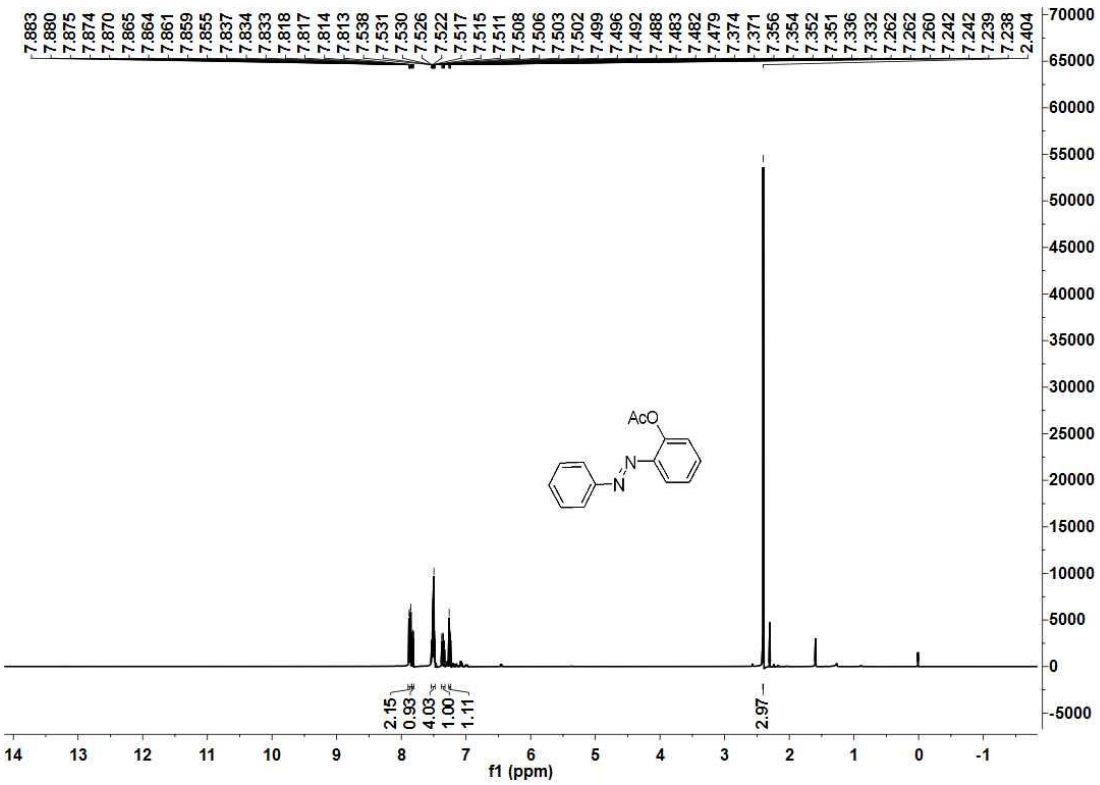

169.259
160.590
156.949
147.398
127.926
127.525
124.398
118.338
21.100
N
N
S
OAc
f1 (ppm)

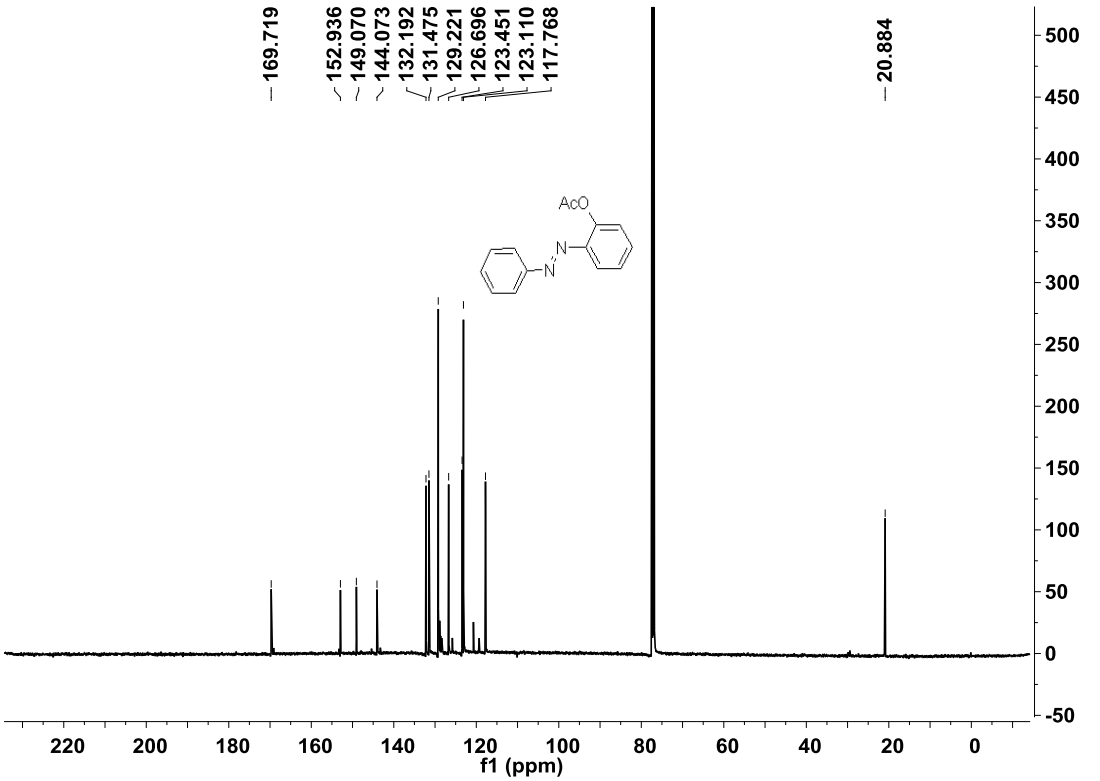
Compound **2n**


7.329
7.303
7.073
7.048
6.906
3.955
2.354
2.279
2.140
OMe
N
OAc
0.81
1.00
1.04
3.35
3.11
3.23
3.24
f1 (ppm)

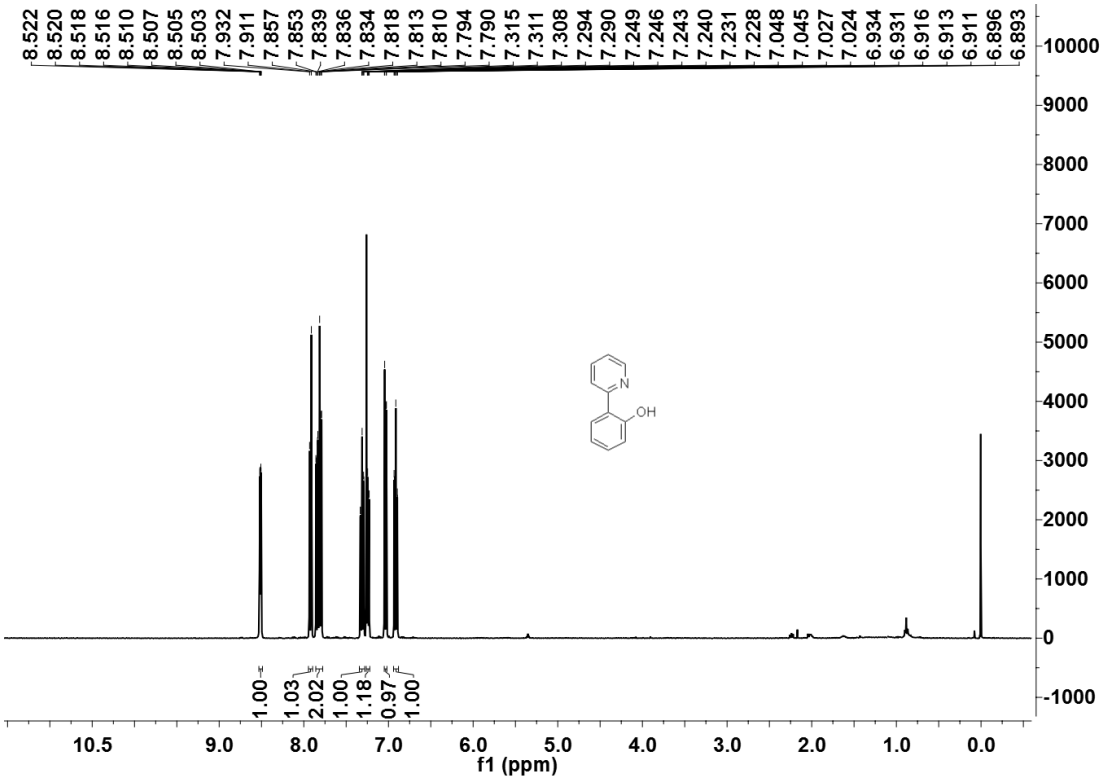

171.290
155.263
149.655
142.099
131.064
129.203
128.786
125.607
63.763
23.000
16.881
OMe
N
OAc
f1 (ppm)

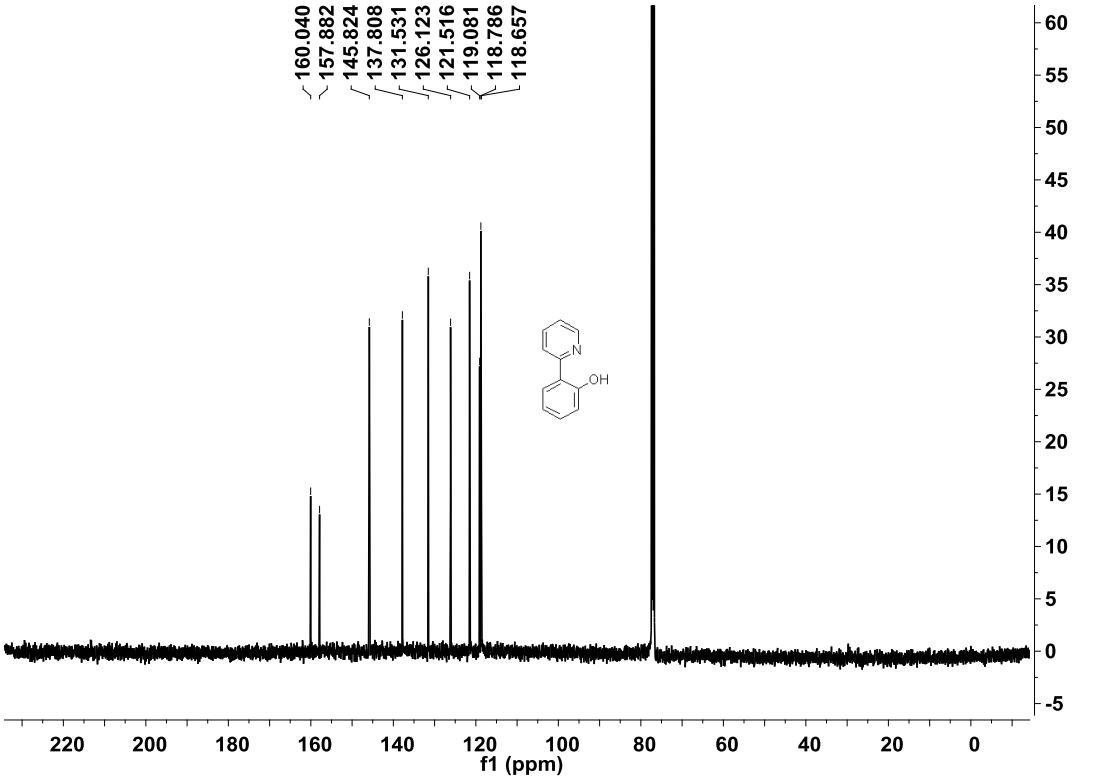
Compound **2o**


7.883
7.880
7.875
7.874
7.870
7.865
7.864
7.861
7.859
7.855
7.837
7.834
7.833
7.818
7.817
7.814
7.813
7.538
7.531
7.530
7.526
7.522
7.517
7.515
7.511
7.508
7.506
7.503
7.502
7.499
7.496
7.492
7.488
7.483
7.482
7.479
7.374
7.371
7.356
7.354
7.352
7.351
7.336
7.332
7.262
7.262
7.260
7.242
7.242
7.239
7.238
2.404
AcO
N
N
2.15
0.93
4.03
1.00
1.11
2.97
f1 (ppm)

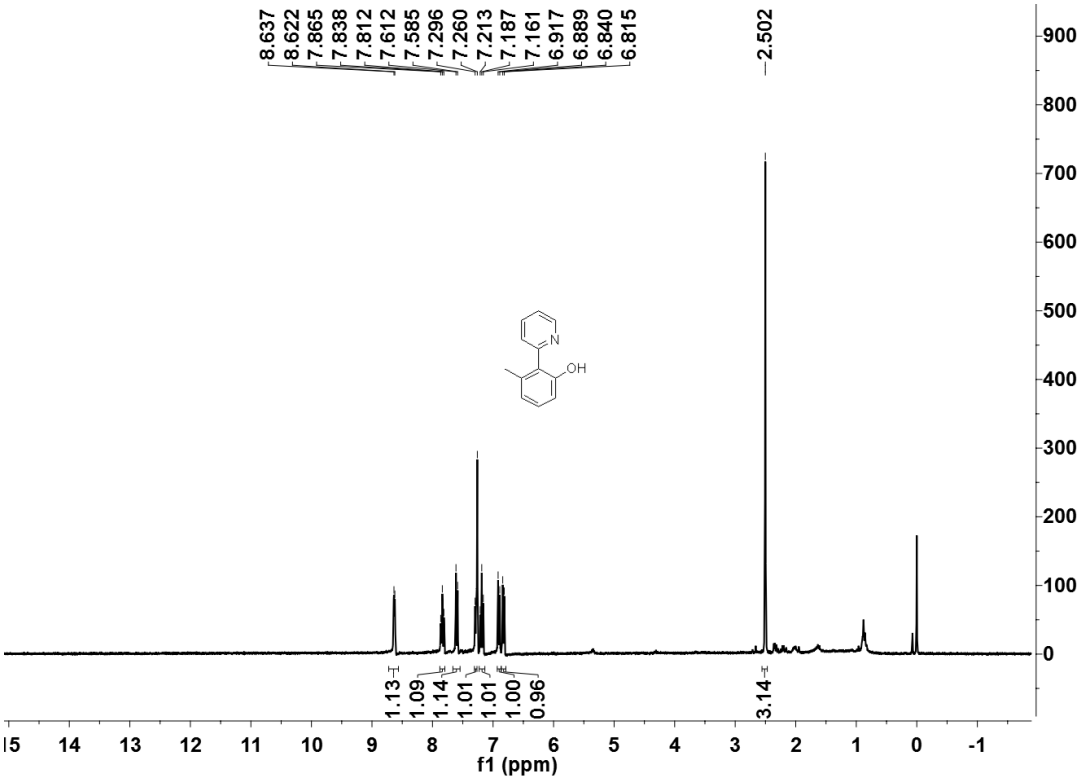

169.719
152.936
149.070
144.073
132.192
131.475
129.221
126.696
123.451
123.110
117.768
20.884
AcO
N
N
f1 (ppm)

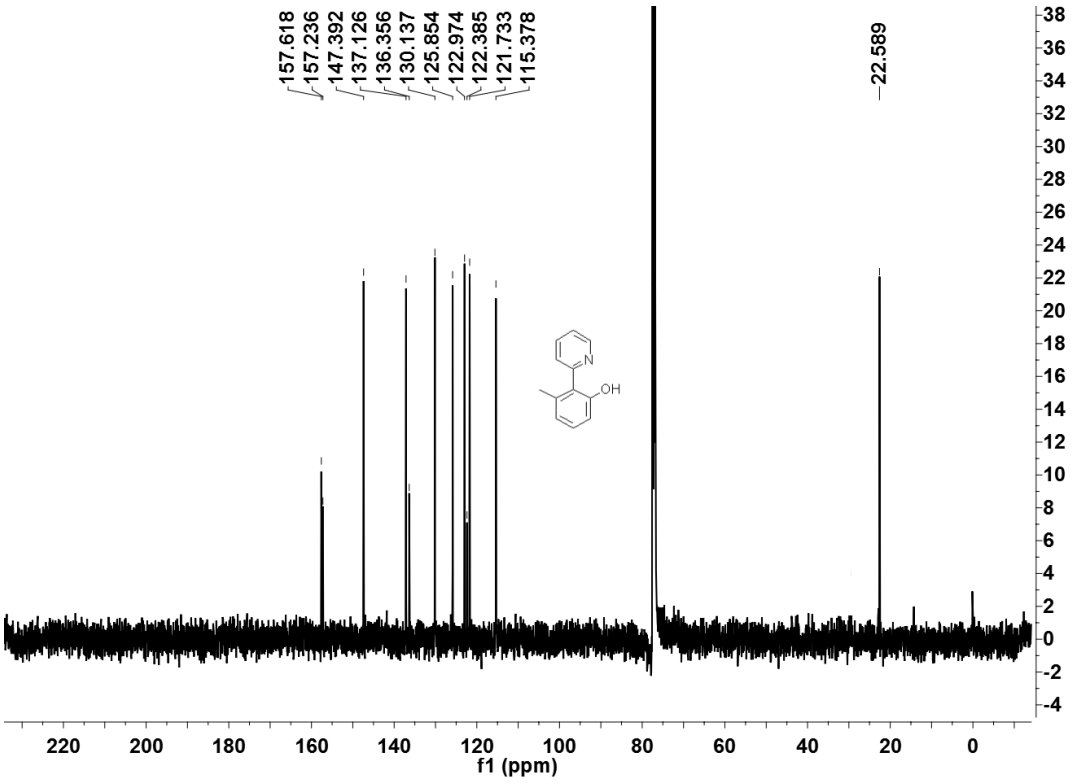
Compound **3a**


8.522
8.520
8.518
8.516
8.510
8.507
8.505
8.503
7.932
7.911
7.857
7.853
7.839
7.836
7.834
7.818
7.813
7.810
7.794
7.790
7.315
7.311
7.308
7.294
7.290
7.249
7.246
7.243
7.240
7.231
7.228
7.048
7.045
7.027
7.024
6.934
6.931
6.916
6.913
6.911
6.896
6.893
1.00
1.03
2.02
1.00
1.18
0.97
1.00
f1 (ppm)

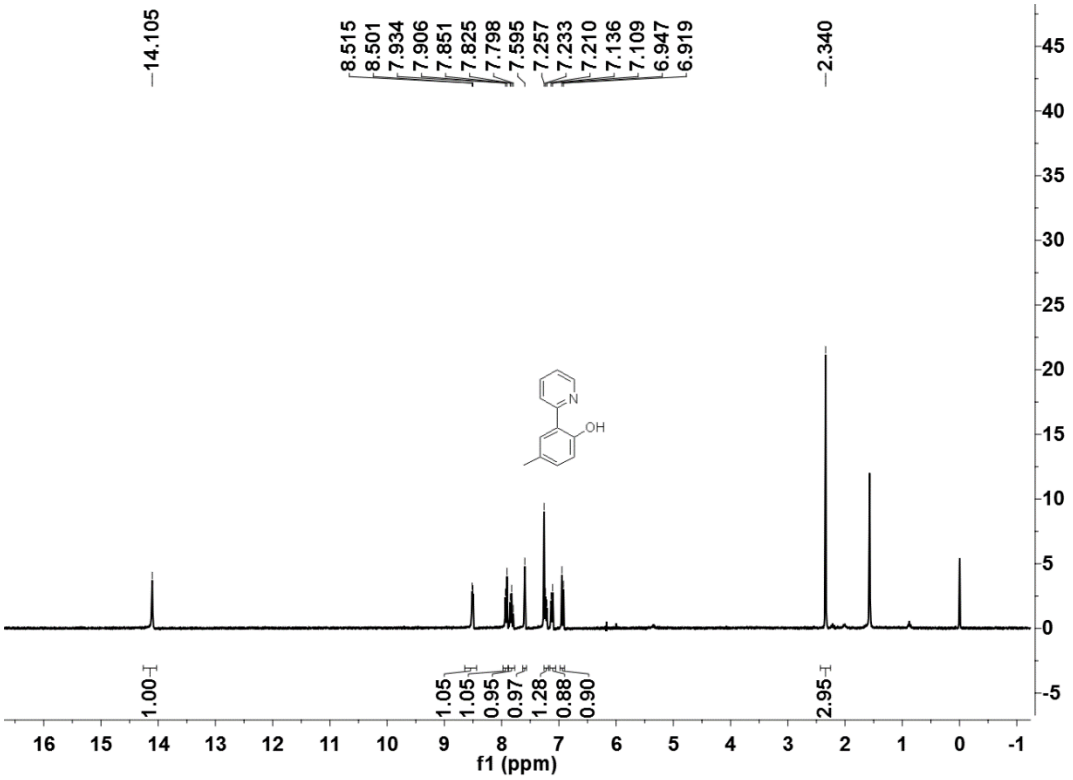

160.040
157.882
145.824
137.808
131.531
126.123
121.516
119.081
118.786
118.657
f1 (ppm)

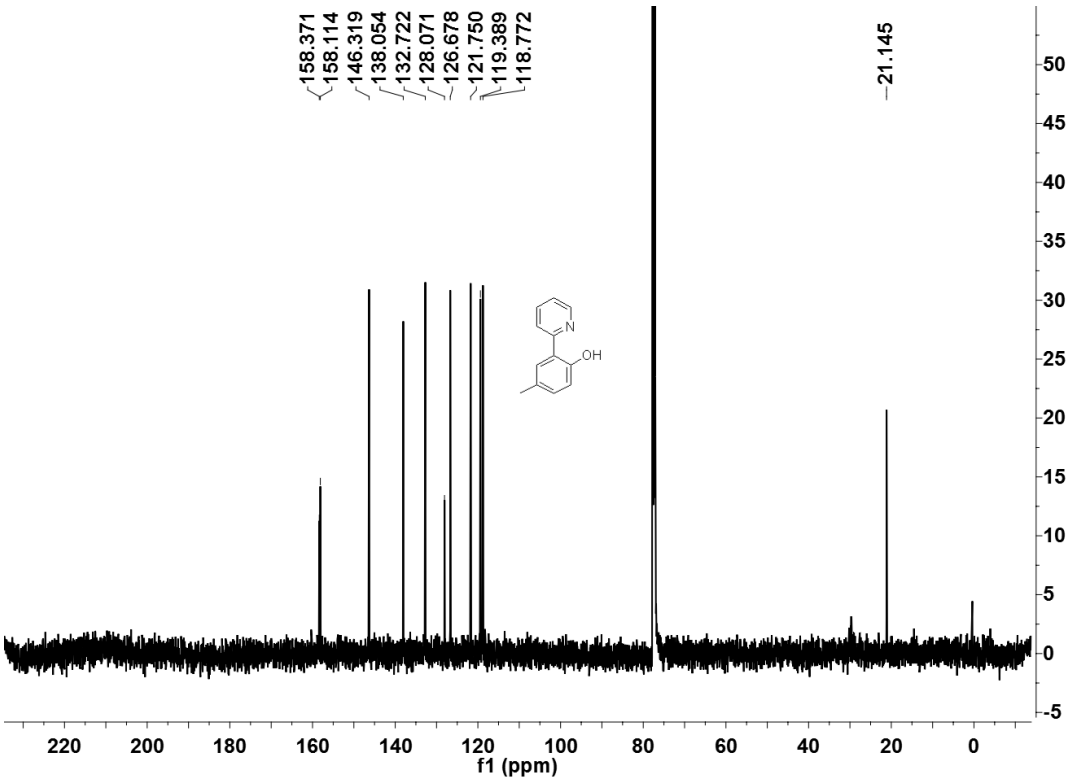
Compound **3b**


8.637
8.622
7.865
7.838
7.812
7.612
7.585
7.296
7.260
7.213
7.187
7.161
6.917
6.889
6.840
6.815
2.502
1.13
1.09
1.14
1.01
1.01
1.00
0.96
3.14
f1 (ppm)

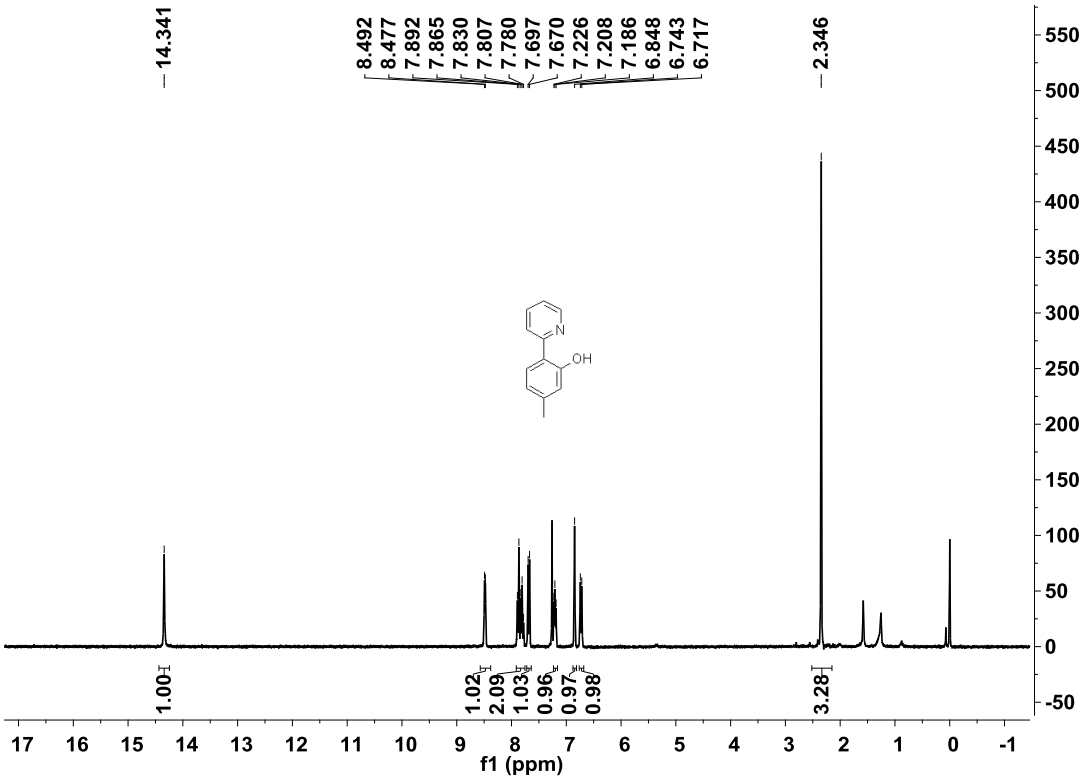

157.618
157.236
147.392
137.126
136.356
130.137
125.854
122.974
122.385
121.733
115.378
22.589
f1 (ppm)

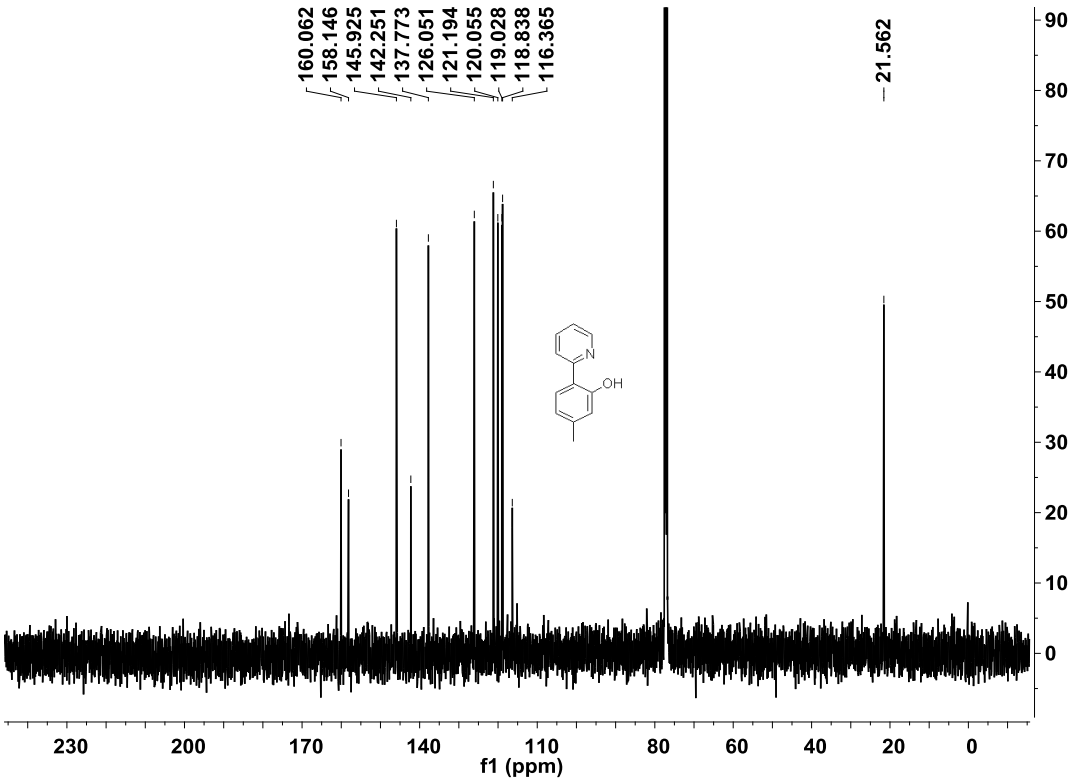
Compound **3c**


14.105
8.515
8.501
7.934
7.906
7.851
7.825
7.798
7.595
7.257
7.233
7.210
7.136
7.109
6.947
6.919
2.340
1.00
1.05
1.05
0.95
0.97
1.28
0.88
0.90
2.95
N
OH
f1 (ppm)

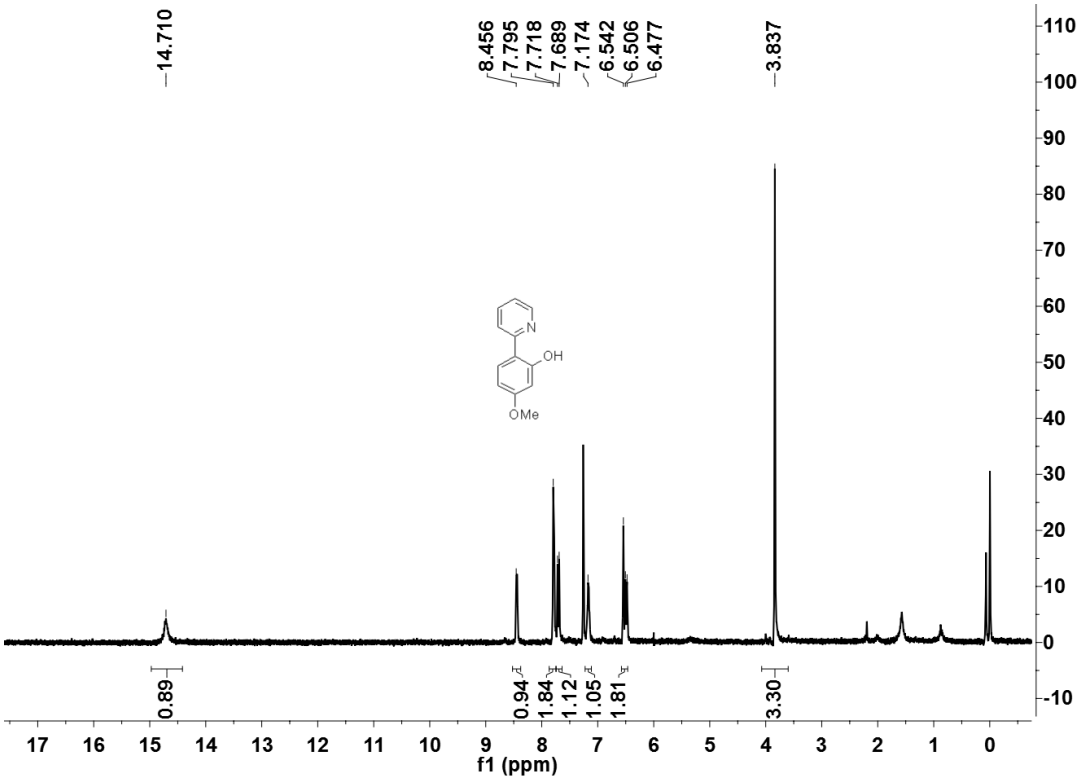

158.371
158.114
146.319
138.054
132.722
128.071
126.678
121.750
119.389
118.772
21.145
N
OH
f1 (ppm)

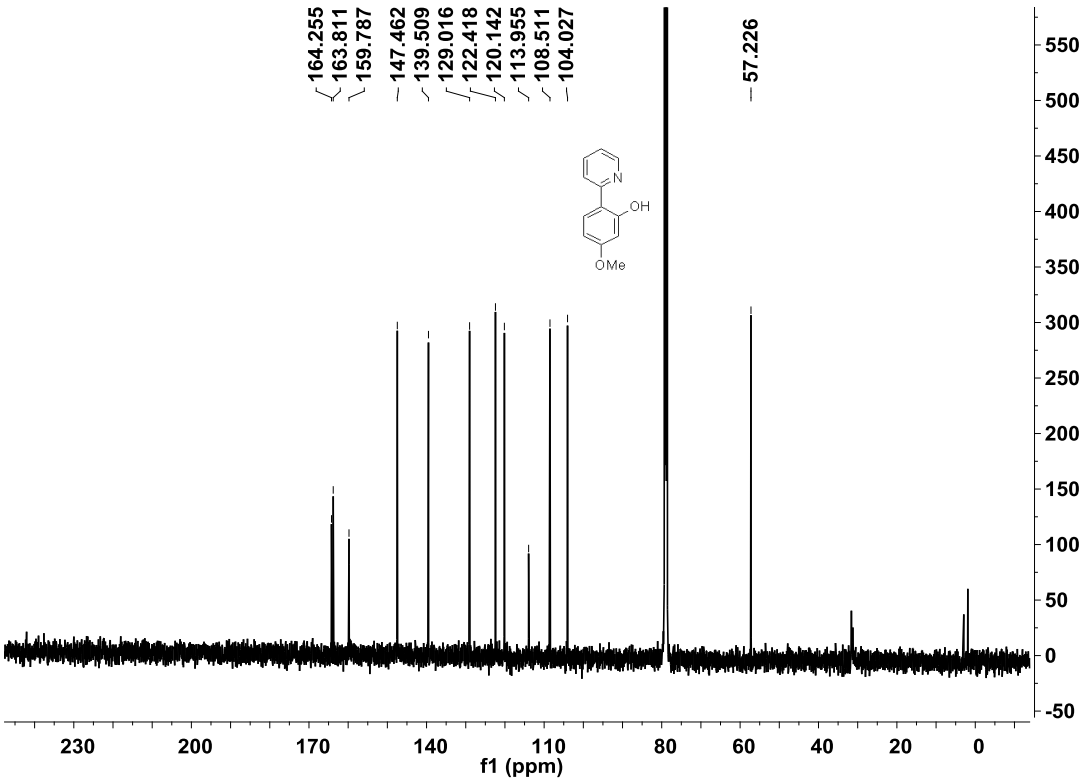
Compound **3d**


14.341
8.492
8.477
7.892
7.865
7.830
7.807
7.780
7.697
7.670
7.226
7.208
7.186
6.848
6.743
6.717
2.346
1.00
1.02
2.09
1.03
0.96
0.97
0.98
3.28
f1 (ppm)

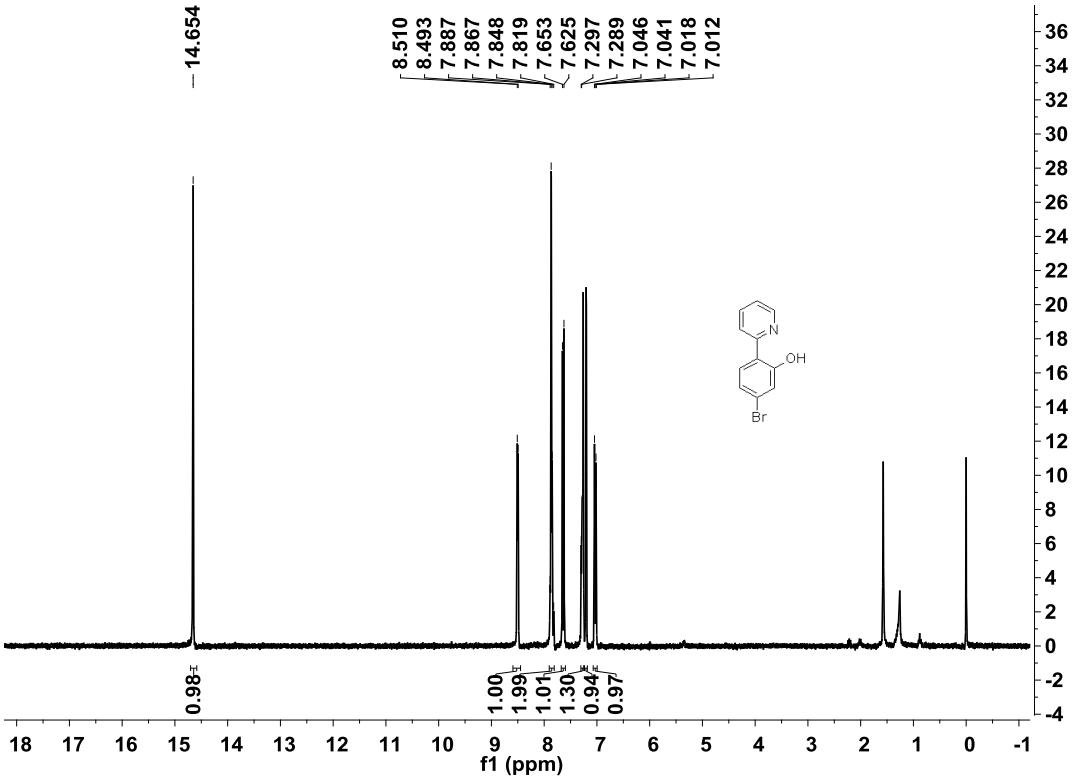

160.062
158.146
145.925
142.251
137.773
126.051
121.194
120.055
119.028
118.838
116.365
21.562
f1 (ppm)

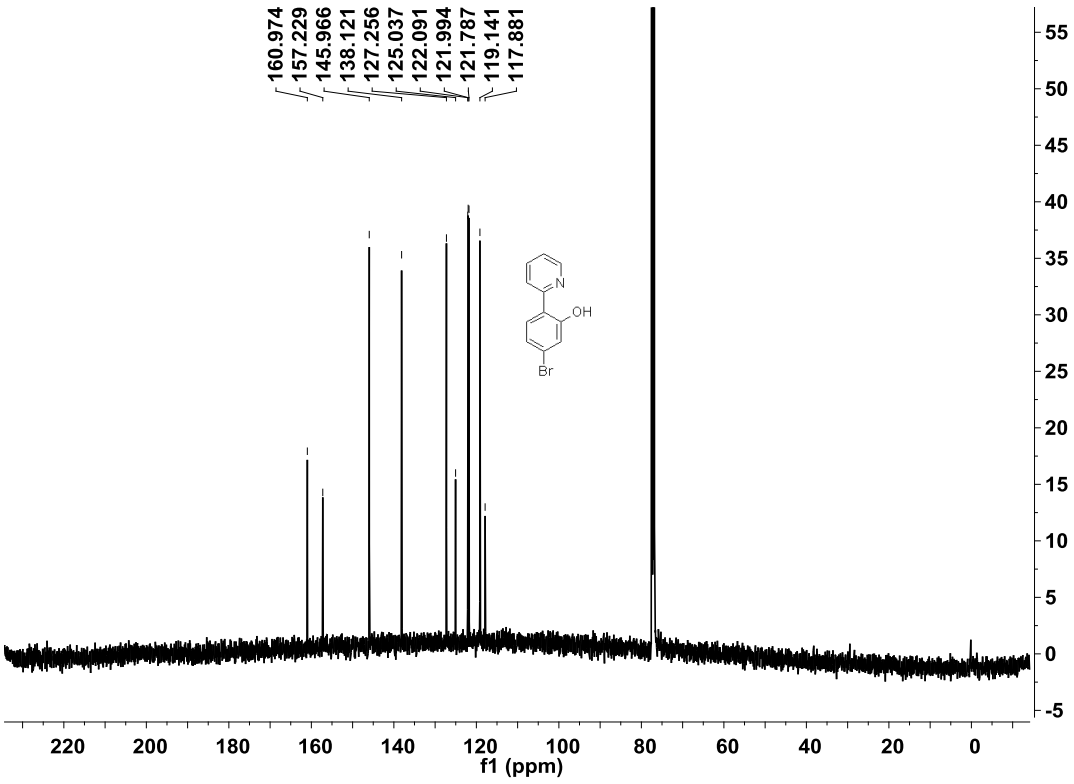
Compound **3e**


14.710
8.456
7.795
7.718
7.689
7.174
6.542
6.506
6.477
3.837
OH
N
OMe
0.89
0.94
1.84
1.12
1.05
1.81
3.30
f1 (ppm)

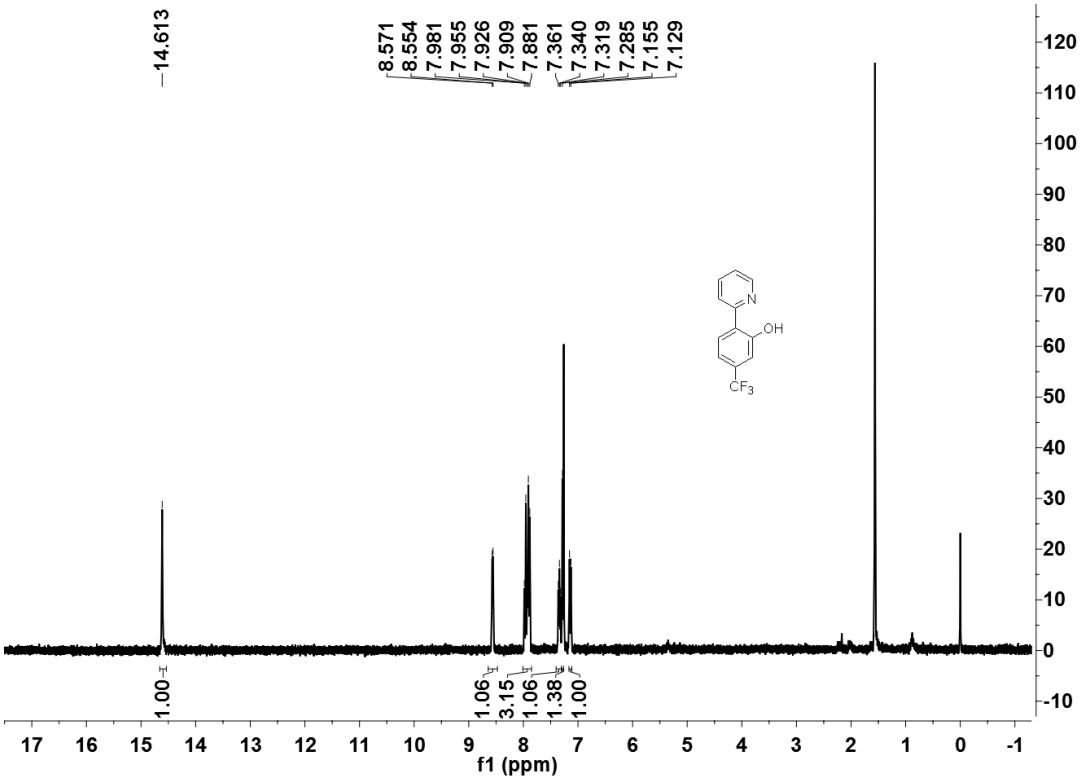

164.255
163.811
159.787
147.462
139.509
129.016
122.418
120.142
113.955
108.511
104.027
57.226
OH
N
OMe
f1 (ppm)

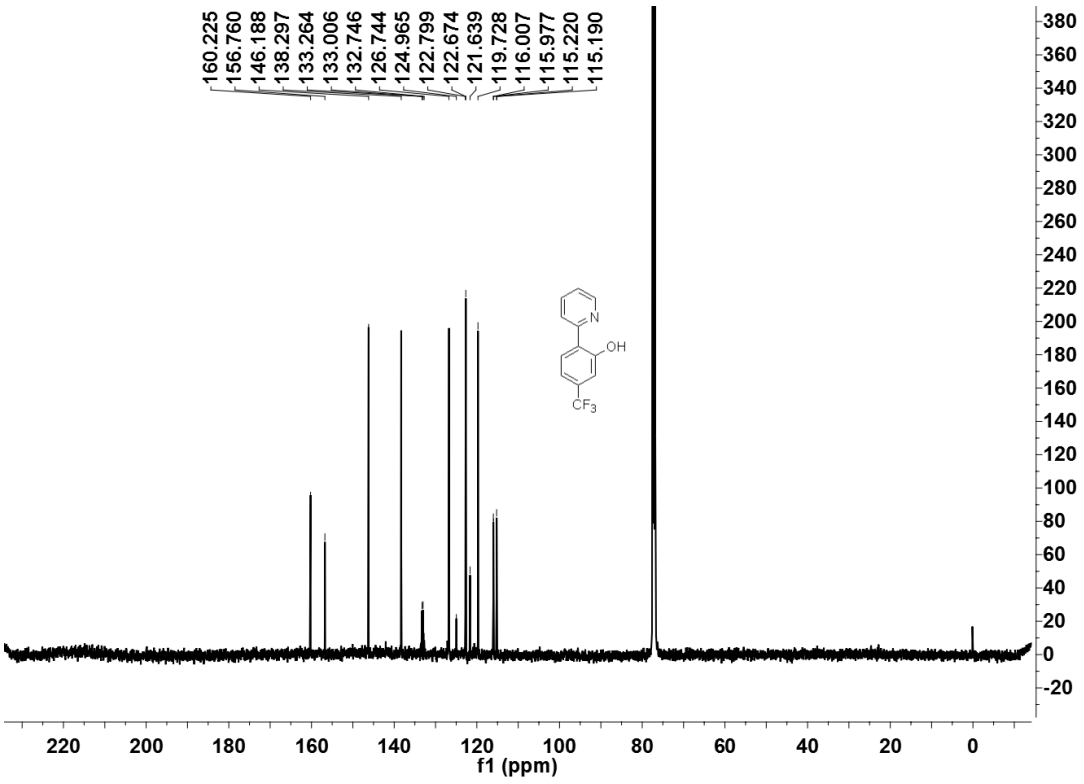
Compound **3f**


14.654
8.510
8.493
7.887
7.867
7.848
7.819
7.653
7.625
7.297
7.289
7.046
7.041
7.018
7.012
0.98
1.00
1.99
1.01
1.30
0.94
0.97
f1 (ppm)

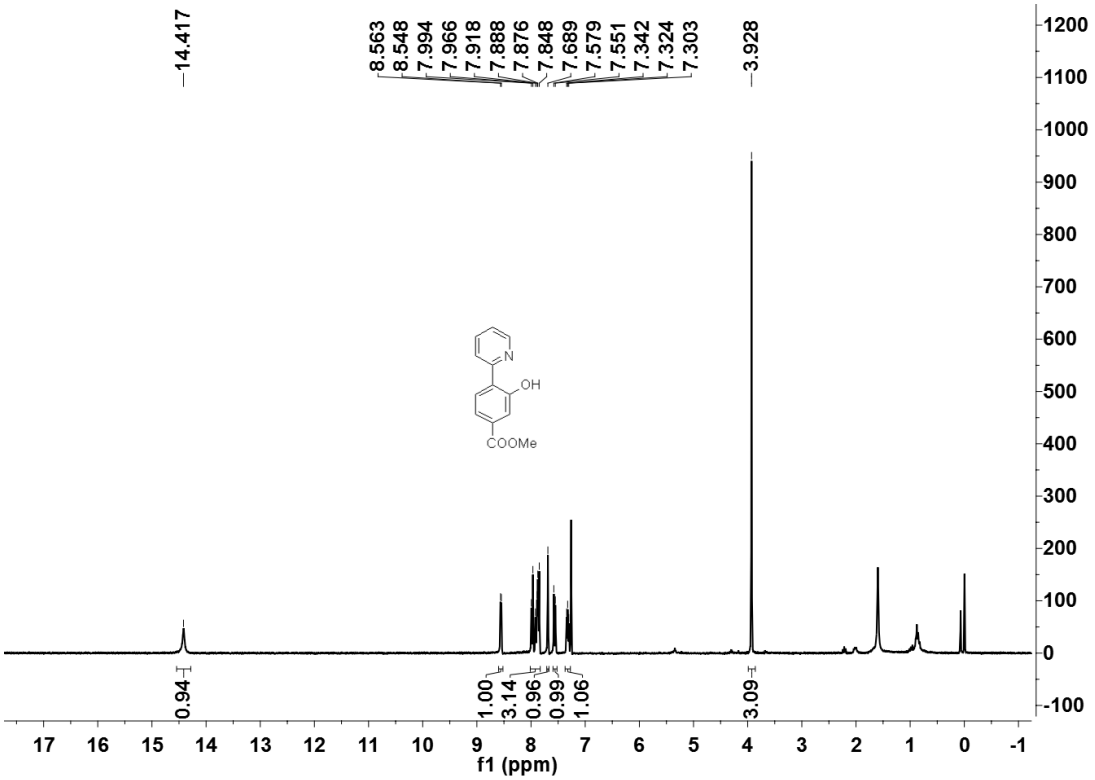

160.974
157.229
145.966
138.121
127.256
125.037
122.091
121.994
121.787
119.141
117.881
f1 (ppm)

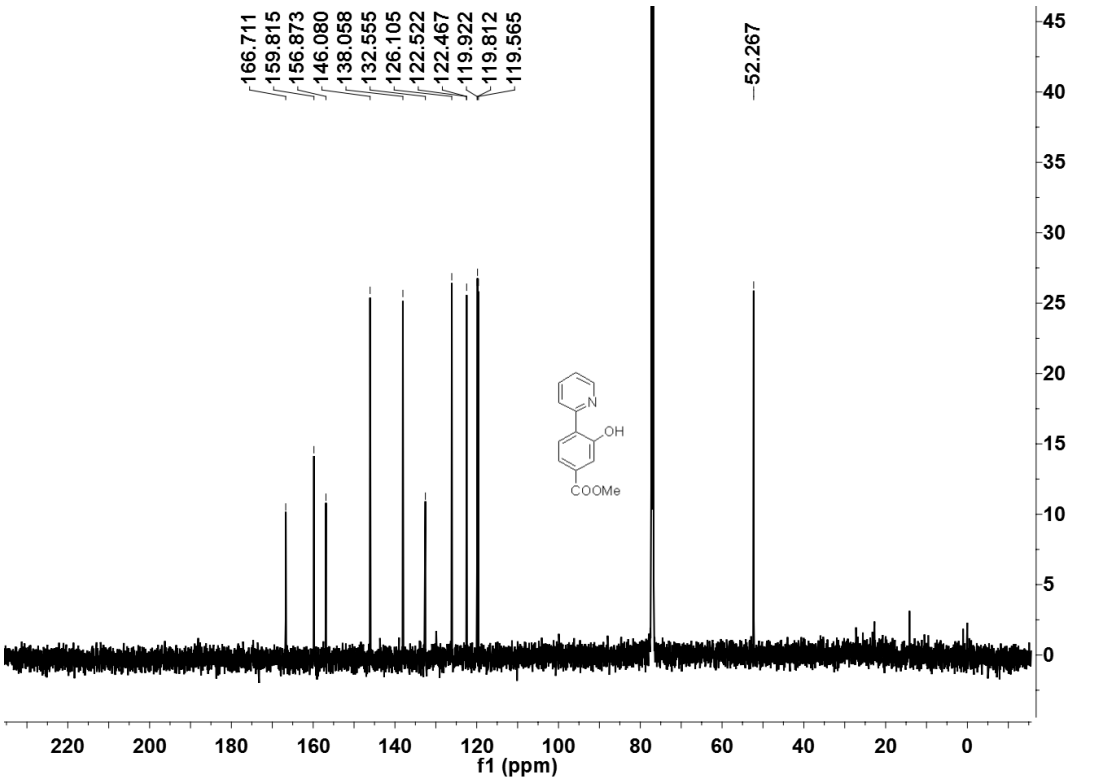
Compound **3g**


14.613
8.571
8.554
7.981
7.955
7.926
7.909
7.881
7.361
7.340
7.319
7.285
7.155
7.129
1.00
1.06
3.15
1.06
1.38
1.00
f1 (ppm)

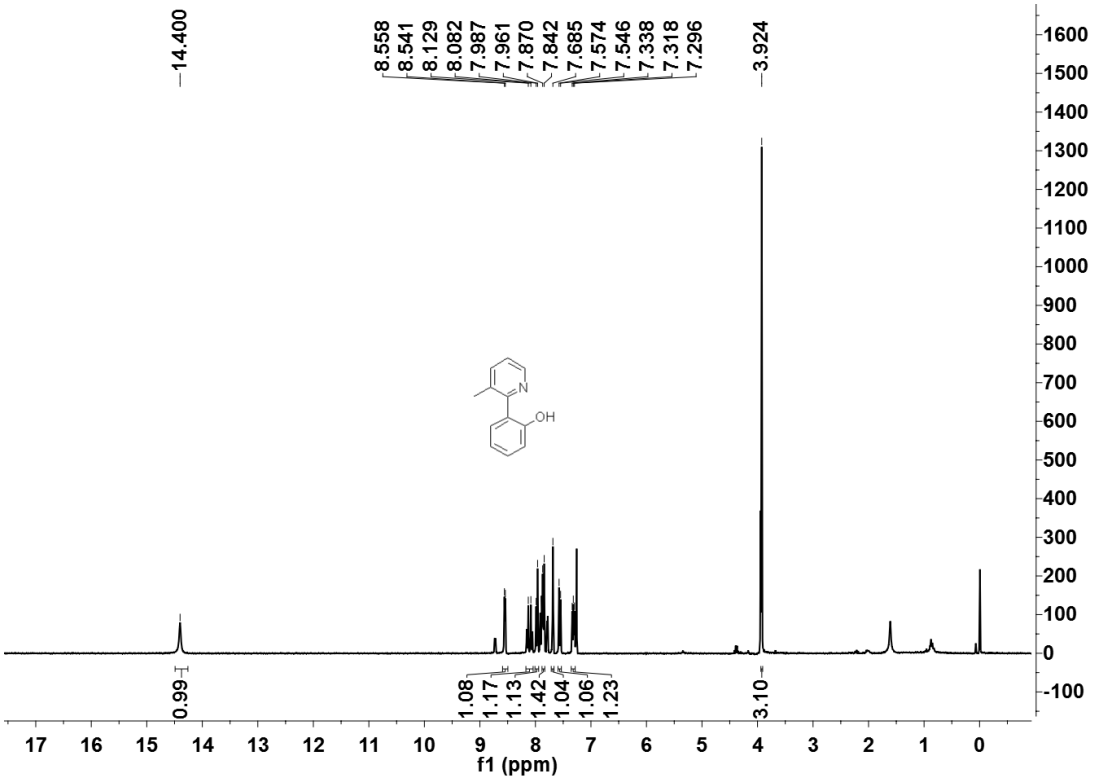

160.225
156.760
146.188
138.297
133.264
133.006
132.746
126.744
124.965
122.799
122.674
121.639
119.728
116.007
115.977
115.220
115.190
f1 (ppm)

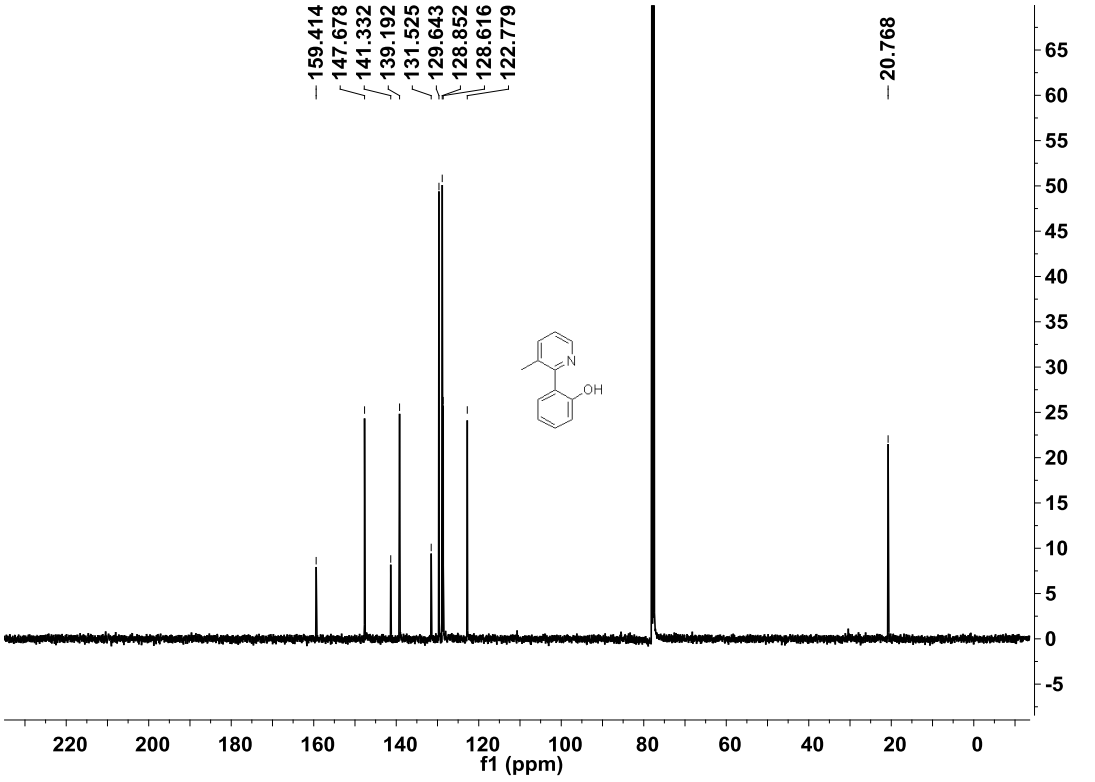
Compound **3h**


14.417
8.563
8.548
7.994
7.966
7.918
7.888
7.876
7.848
7.689
7.579
7.551
7.342
7.324
7.303
3.928
0.94
1.00
3.14
0.96
0.99
1.06
3.09
OH
COOMe
f1 (ppm)

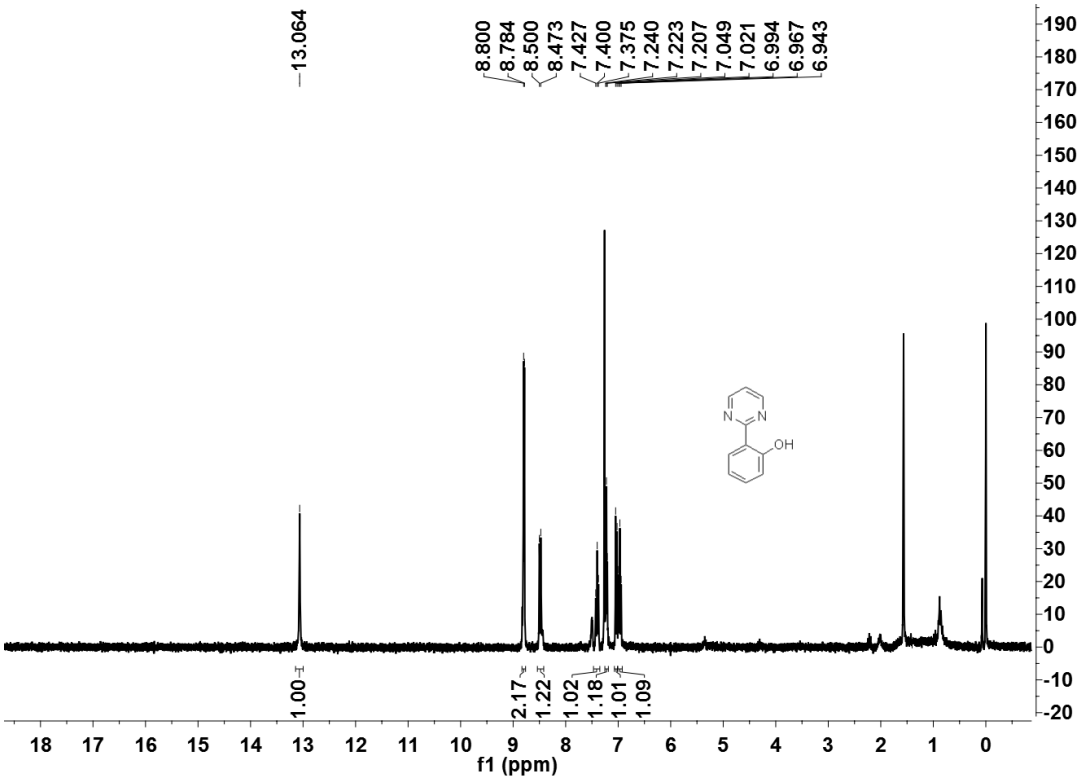

166.711
159.815
156.873
146.080
138.058
132.555
126.105
122.522
122.467
119.922
119.812
119.565
52.267
OH
COOMe
f1 (ppm)

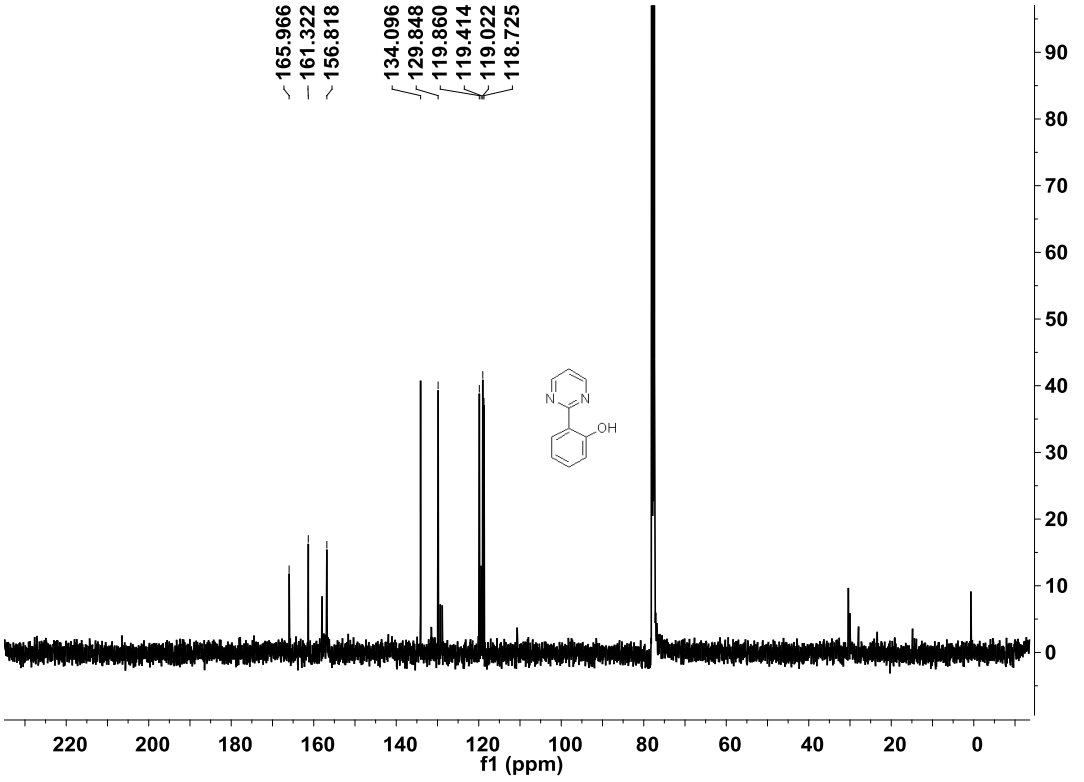
Compound **3i**


14.400
8.558
8.541
8.129
8.082
7.987
7.961
7.870
7.842
7.685
7.574
7.546
7.338
7.318
7.296
3.924
0.99
1.08
1.17
1.13
1.42
1.04
1.06
1.23
3.10
f1 (ppm)

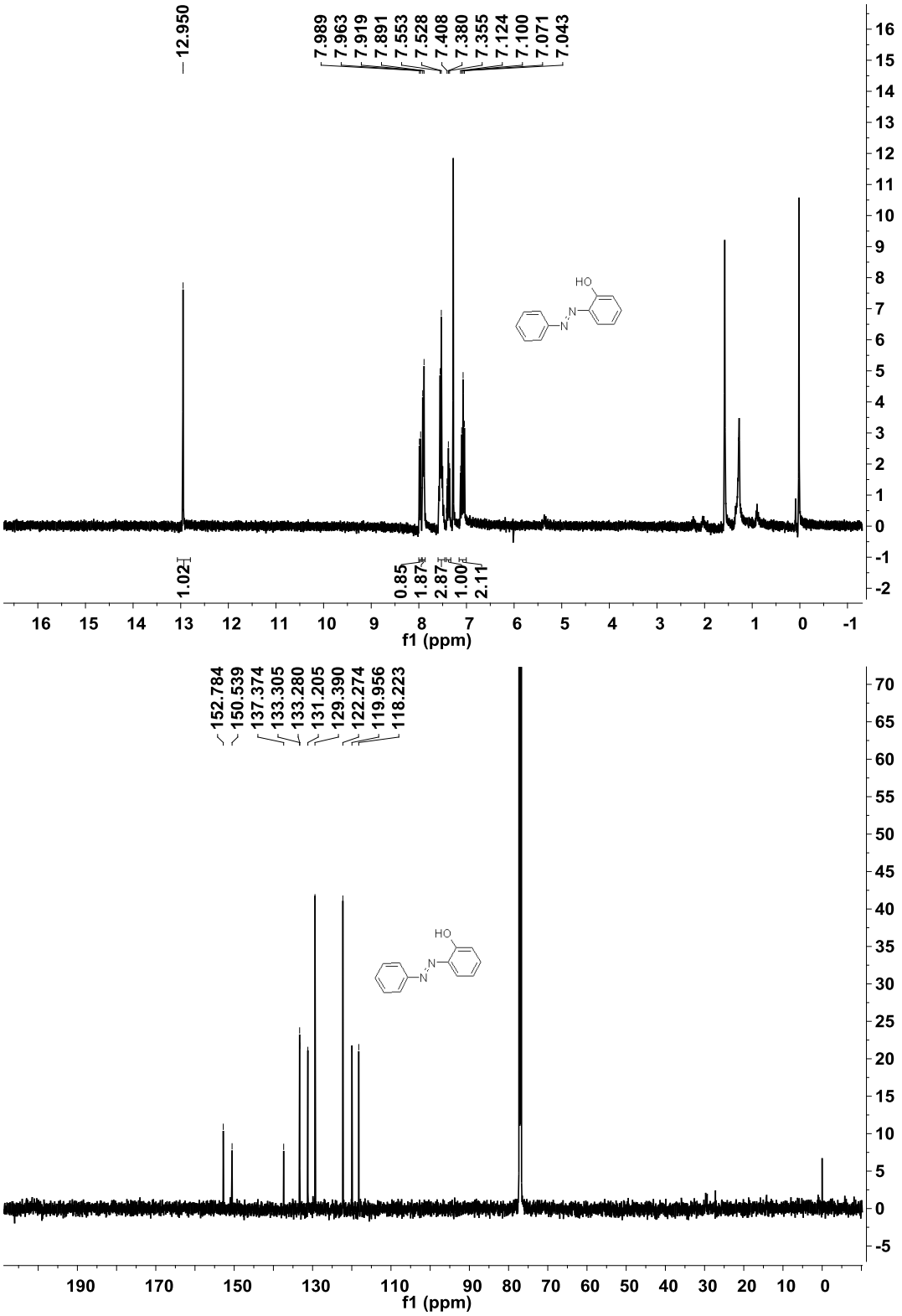

159.414
147.678
141.332
139.192
131.525
129.643
128.852
128.616
122.779
20.768
f1 (ppm)

Compound **3j**


13.064
8.800
8.784
8.500
8.473
7.427
7.400
7.375
7.240
7.223
7.207
7.049
7.021
6.994
6.967
6.943
1.00
2.17
1.22
1.02
1.18
1.01
1.09
f1 (ppm)


165.966
161.322
156.818
134.096
129.848
119.860
119.414
119.022
118.725
f1 (ppm)

Compound **3k**


12.950
7.989
7.963
7.919
7.891
7.553
7.528
7.408
7.380
7.355
7.124
7.100
7.071
7.043
1.02
0.85
1.87
2.87
1.00
2.11
f1 (ppm)
152.784
150.539
137.374
133.305
133.280
131.205
129.390
122.274
119.956
118.223
f1 (ppm)