Supporting Information

N-heterocyclic carbene-palladium(II)-1-methylimidazole complex catalyzed direct C-H bond arylation of imidazo[1,2-*a*]pyridines with aryl chlorides

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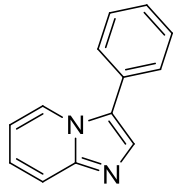
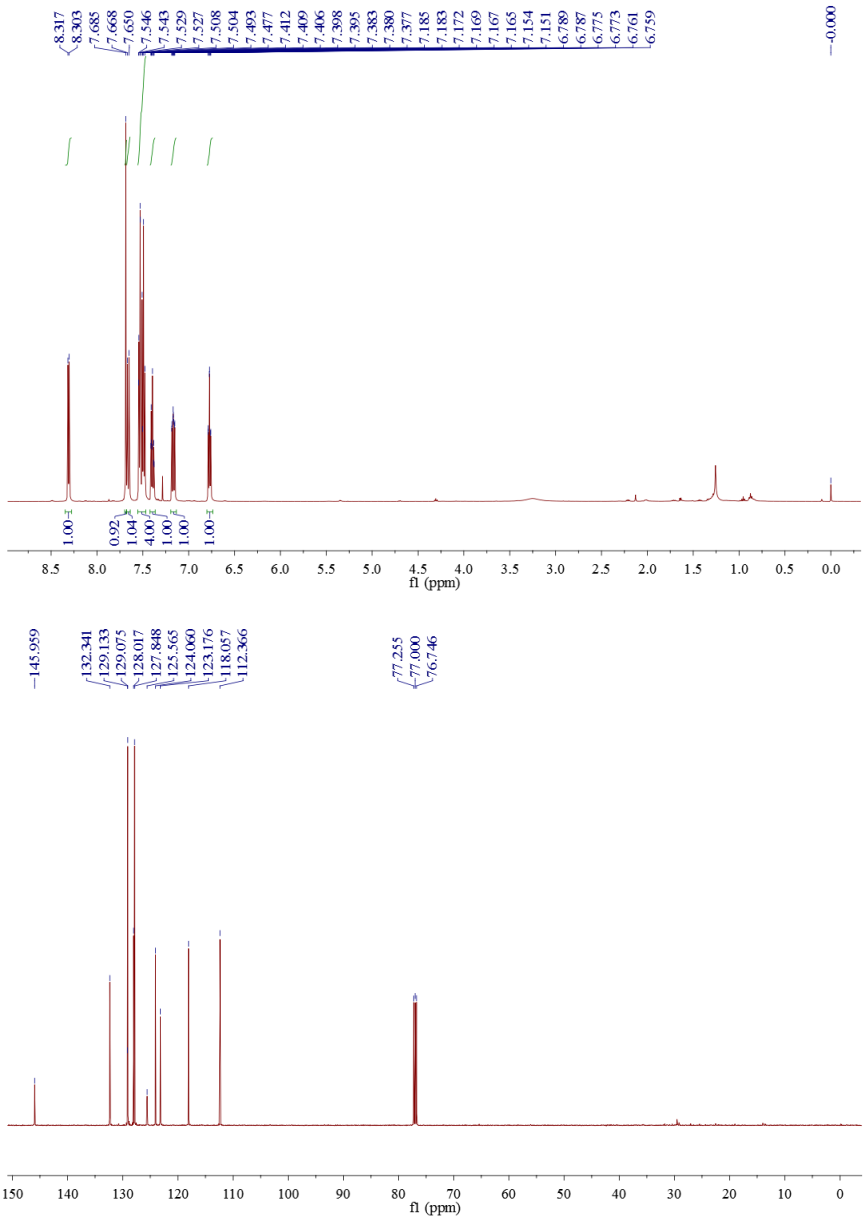
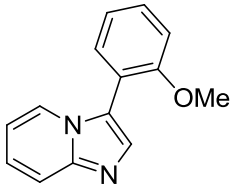
Synthesis of NHC-Pd(II)-Im complex **1**: under N_2 atmosphere, a mixture of 1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium chloride (2.2 mmol, 935 mg), $PdCl_2$ (2.0 mmol, 354 mg), K_2CO_3 (2.2 mmol, 304 mg) and 1-methylimidazole (637.7 ml, 8 mmol) was stirred in anhydrous THF (10 mL) under reflux for 20 h. The solvent was removed under reduced pressure, and the residue was purified by a flash chromatography on silica gel (petroleum ether/ethyl acetate) to give NHC-Pd(II)-Im complex **1** (1.166 g, 90%) as yellow solid.



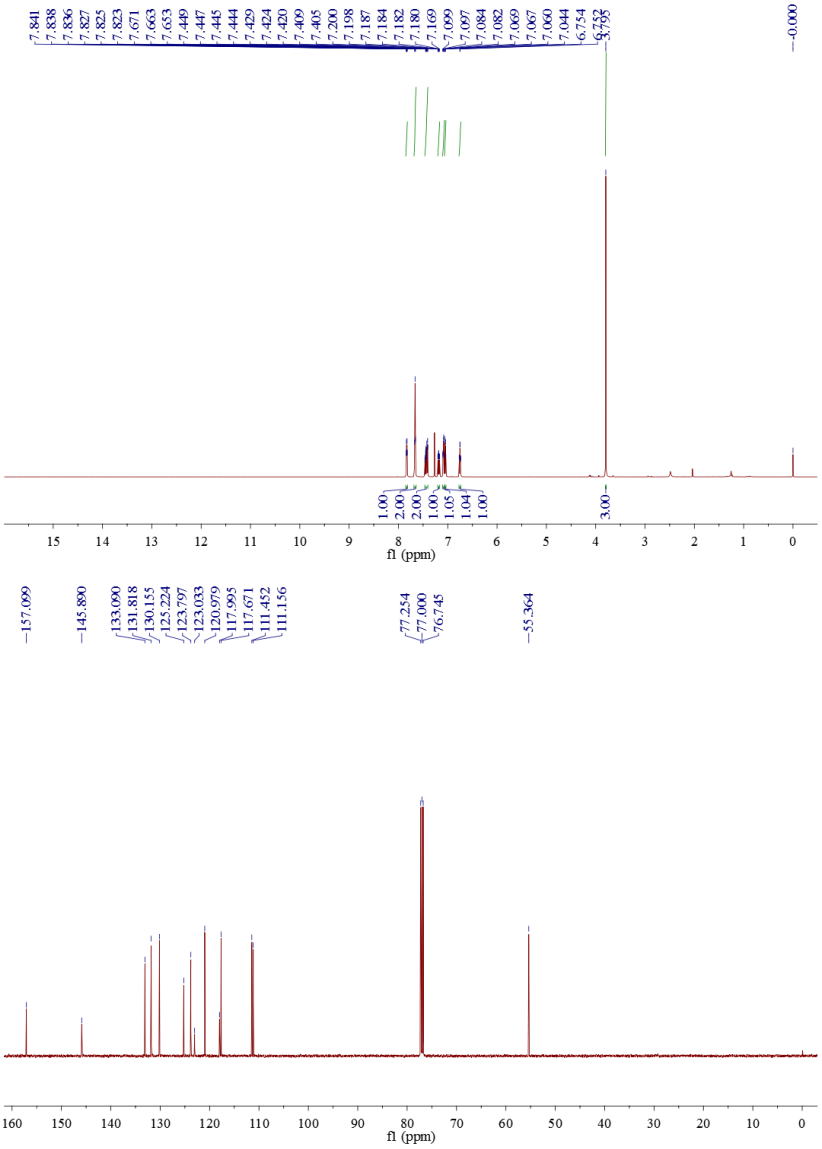
Compound **4a**:[1] yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.31 (d, *J* = 7.0 Hz, 1H), 7.69 (s, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.41-7.38 (m, 1H), 7.19-7.15 (m, 1H), 6.77 (td, *J* = 7.0, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0, 132.3, 129.13, 129.08, 128.0, 127.8, 125.6, 124.1, 123.2, 118.1, 112.4.



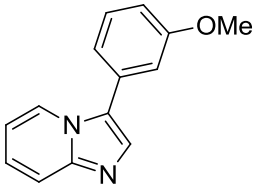
1) S. K. Lee and J. K. Park, *J. Org. Chem.*, 2015, **80**, 3723.



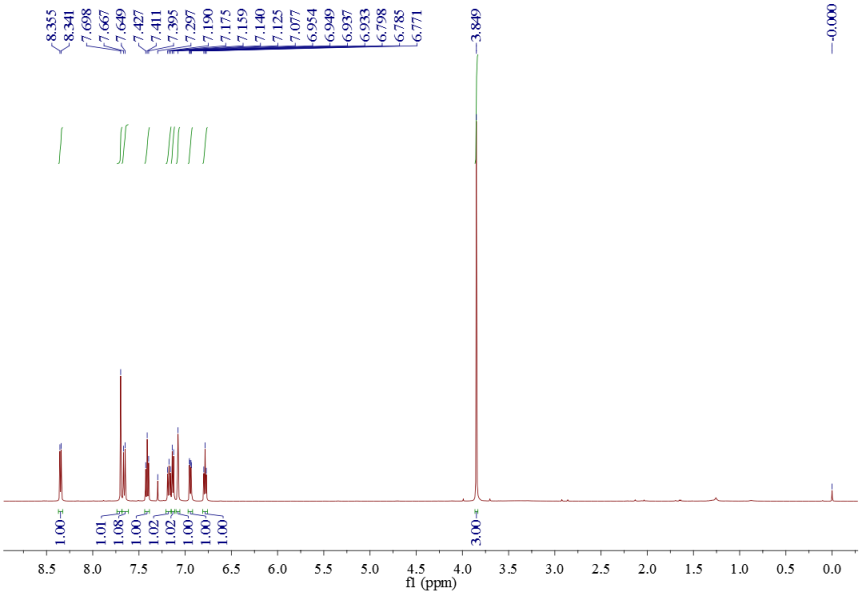
Compound **4b**:[2] brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.83 (dt, *J* = 6.5, 1.0 Hz, 1H), 7.66 (t, *J* = 4.5 Hz, 2H), 7.47-7.41 (m, 2H), 7.18 (ddd, *J* = 9.0, 6.5, 1.0 Hz, 1H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.75 (td, *J* = 7.0, 1.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 145.9, 133.1, 131.8, 130.2, 125.2, 123.8, 123.0, 121.0, 118.0, 117.7, 111.5, 111.2, 55.4.

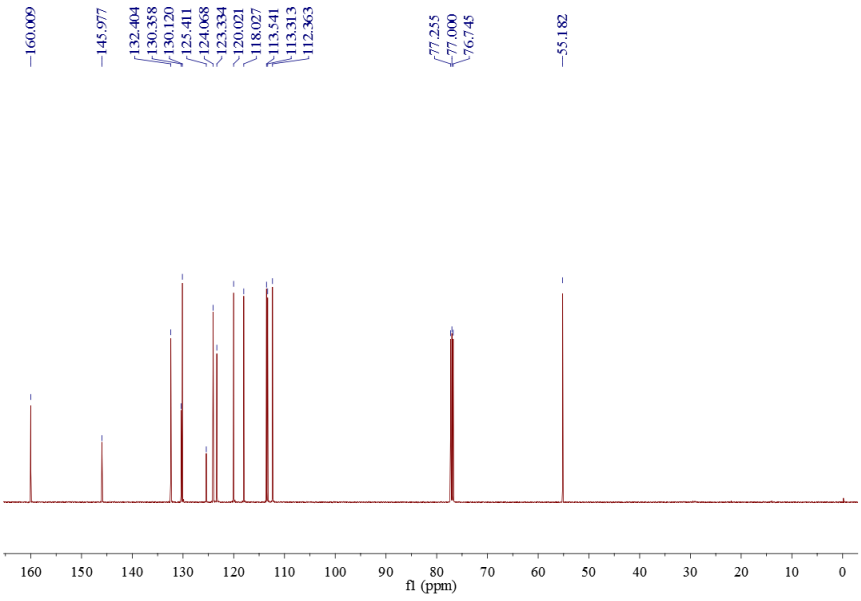


2) B. Mu, Y.-S. Wu, J.-G. Li, D.-P. Zou, J.-B. Chang and Y.-J. Wu, *Org. Biomol. Chem.*, 2016, **14**, 246.

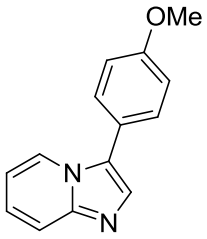


Compound **4c**:[3] white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.35 (d, *J* = 6.5 Hz, 1H), 7.70 (s, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.5 Hz,1H), 7.08 (s, 1H), 6.94 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.79 (t, *J* = 6.5 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 146.0, 132.4, 130.4, 130.1, 125.4, 124.1, 123.3, 120.0, 118.0, 113.5, 113.3, 112.4, 55.2.

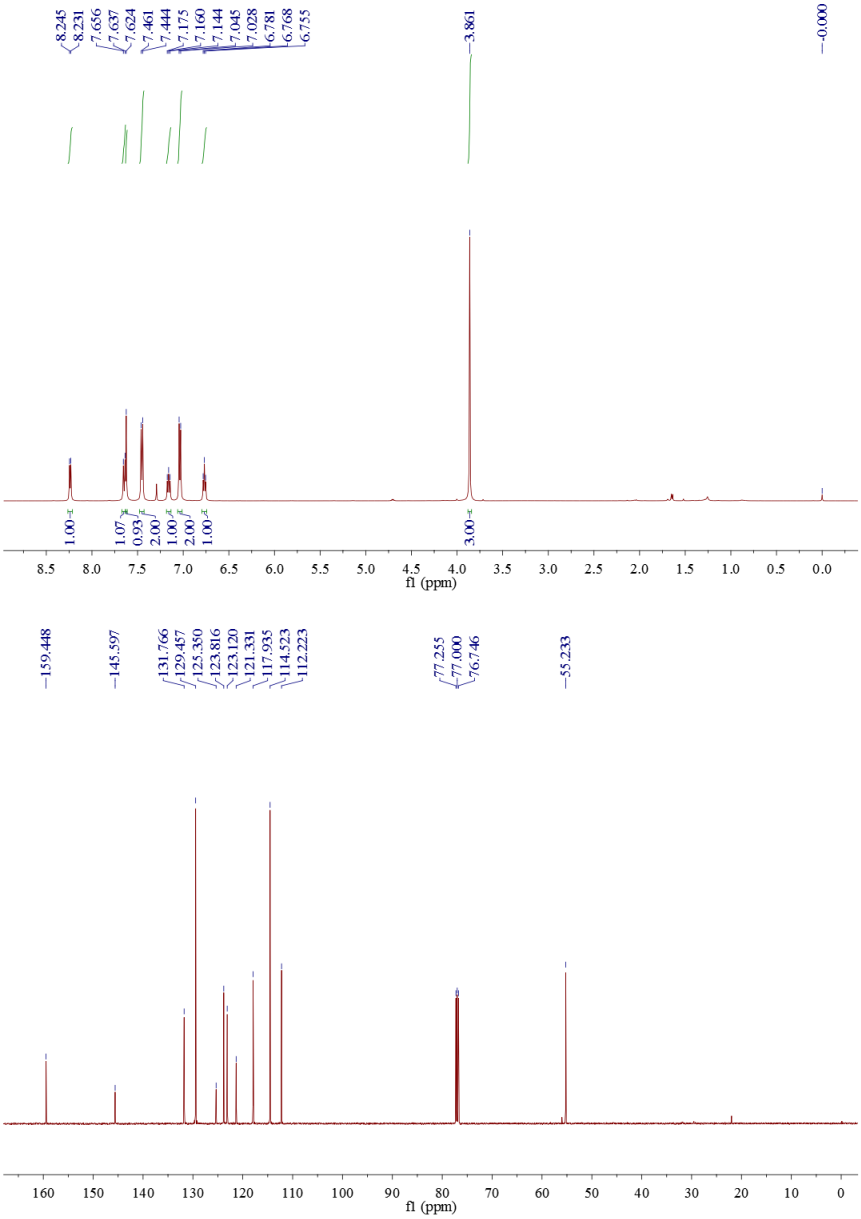


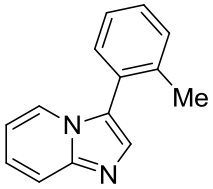


3) Z.-Q. Wu, Y.-Y. Pan and X.-G. Zhou, *Synthesis*, 2011, 2255.

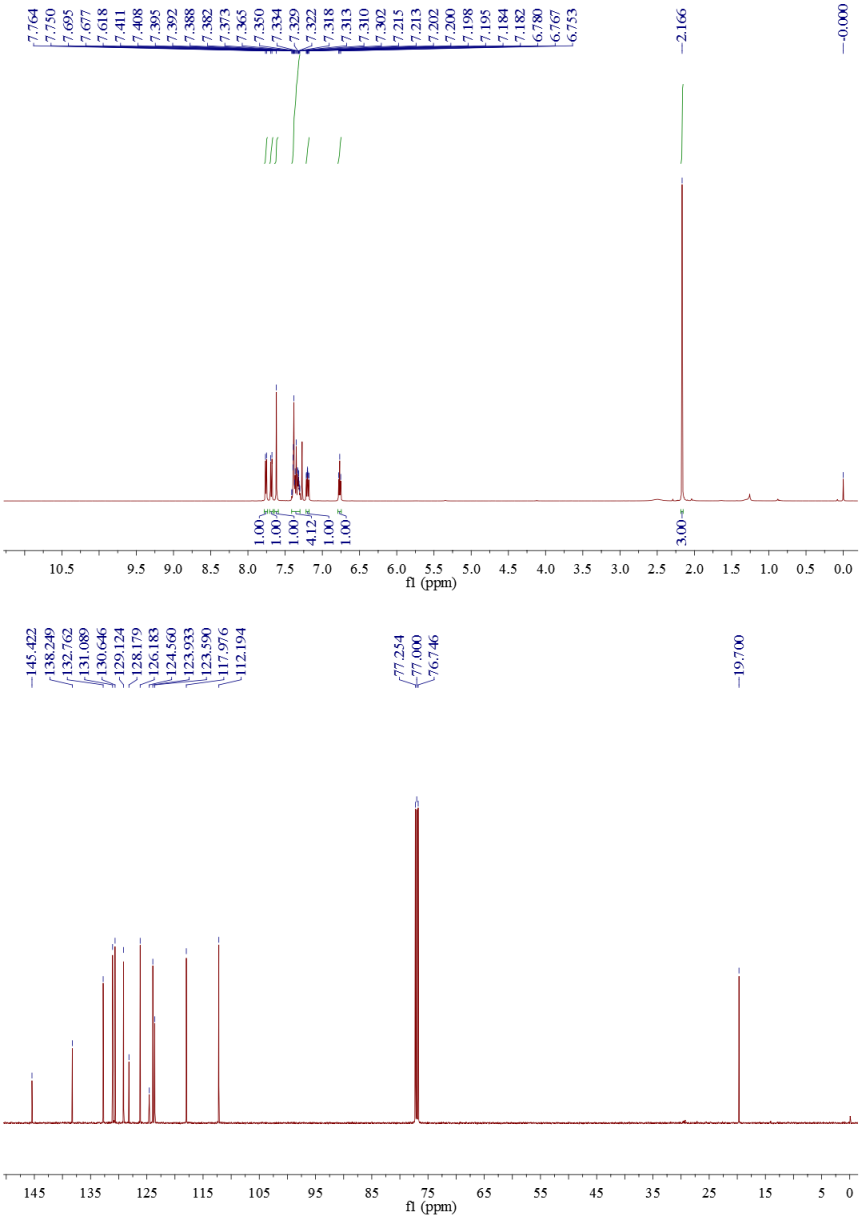


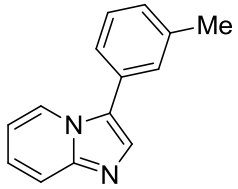
Compound **4d**:[2] white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.24 (d, *J* = 7.0 Hz, 1H), 7.65 (d, *J* = 9.5 Hz, 1H), 7.62 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.77 (t, *J* = 7.0 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 145.6, 131.8, 129.5, 125.4, 123.8, 123.1, 121.3, 117.9, 114.5, 112.2, 55.2.



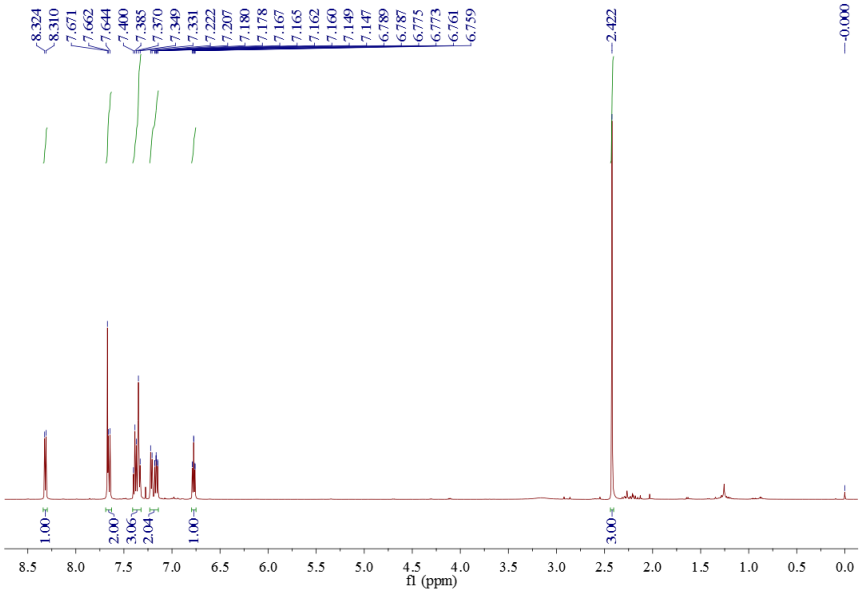


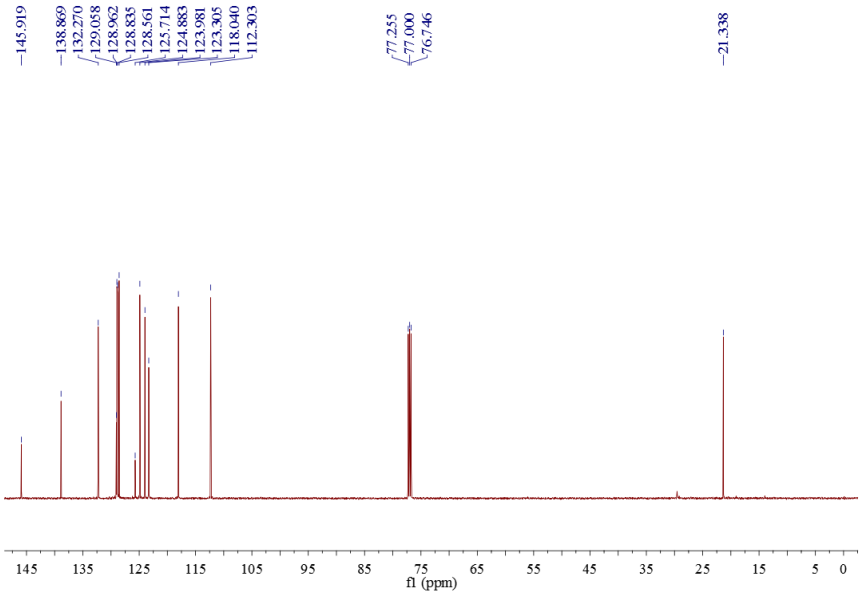
Compound **4e**:[1] brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.76 (d, *J* = 7.0 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.62 (s, 1H), 7.41-7.30 (m, 4H), 7.20 (ddd, *J* = 9.0, 6.5, 1.0 Hz, 1H), 6.77 (t, *J* = 6.5 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 138.2, 132.8, 131.1, 130.6, 129.1, 128.2, 126.2, 124.6, 123.9, 123.6, 118.0, 112.2, 19.7.

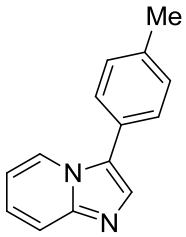




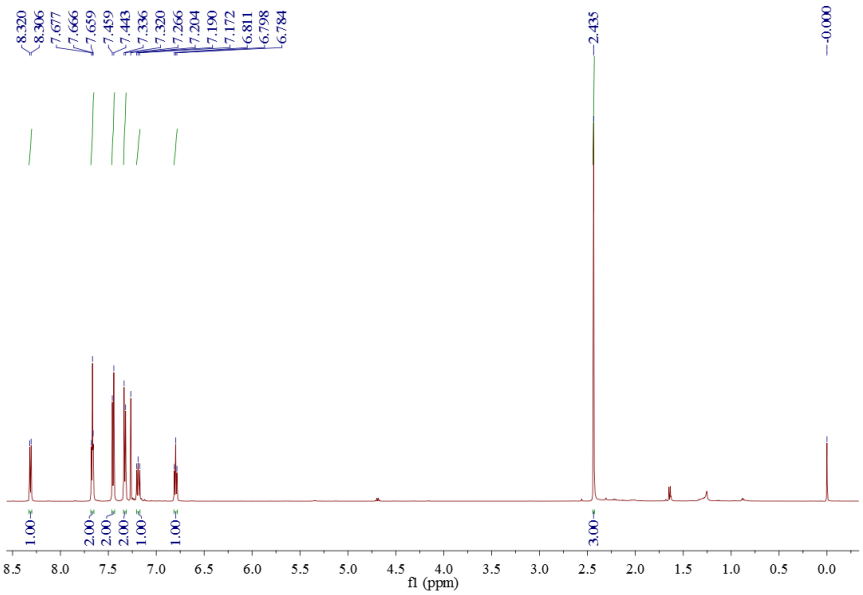
Compound **4f**:[3] brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.32 (d, *J* = 7.0 Hz, 1H), 7.67 (s, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.40-7.33 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.18-7.15 (m, 1H), 6.77 (td, *J* = 7.0, 1.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 138.9, 132.3, 129.1, 129.0, 128.8, 128.6, 125.7, 124.9, 124.0, 123.3, 118.0, 112.3, 21.3.

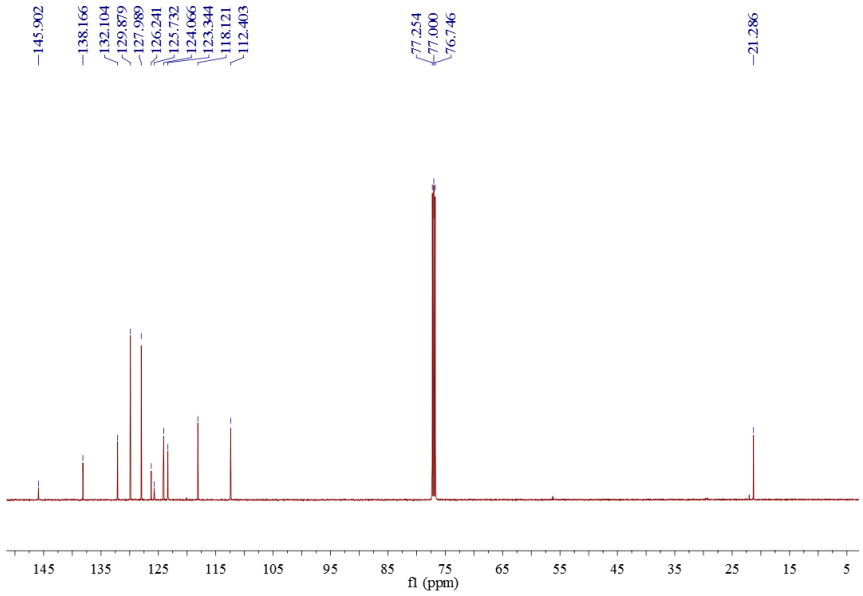


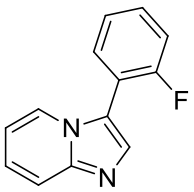




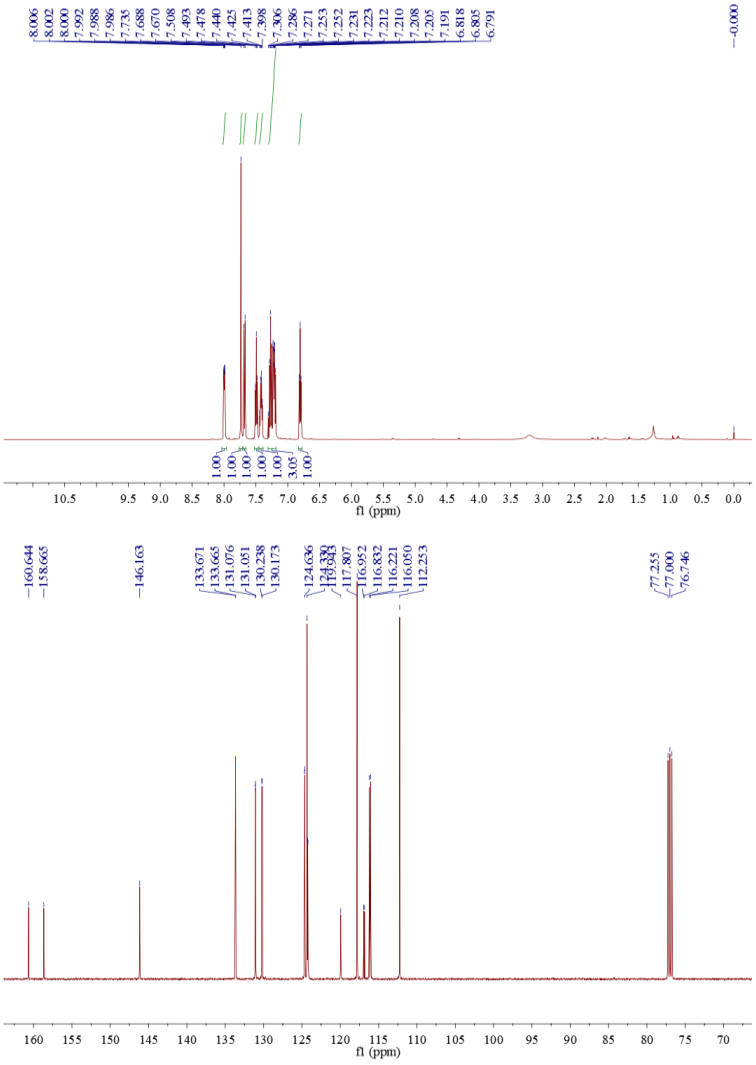
Compound **4g**:[1] yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.31 (d, *J* = 7.0 Hz, 1H), 7.68-7.66 (m, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.20-7.17 (m, 1H), 6.80 (t, *J* = 6.5 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 138.2, 132.1, 129.9, 128.0, 126.2, 125.7, 124.1, 123.3, 118.1, 112.4, 21.3.

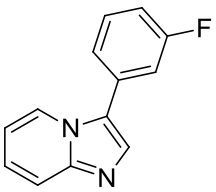




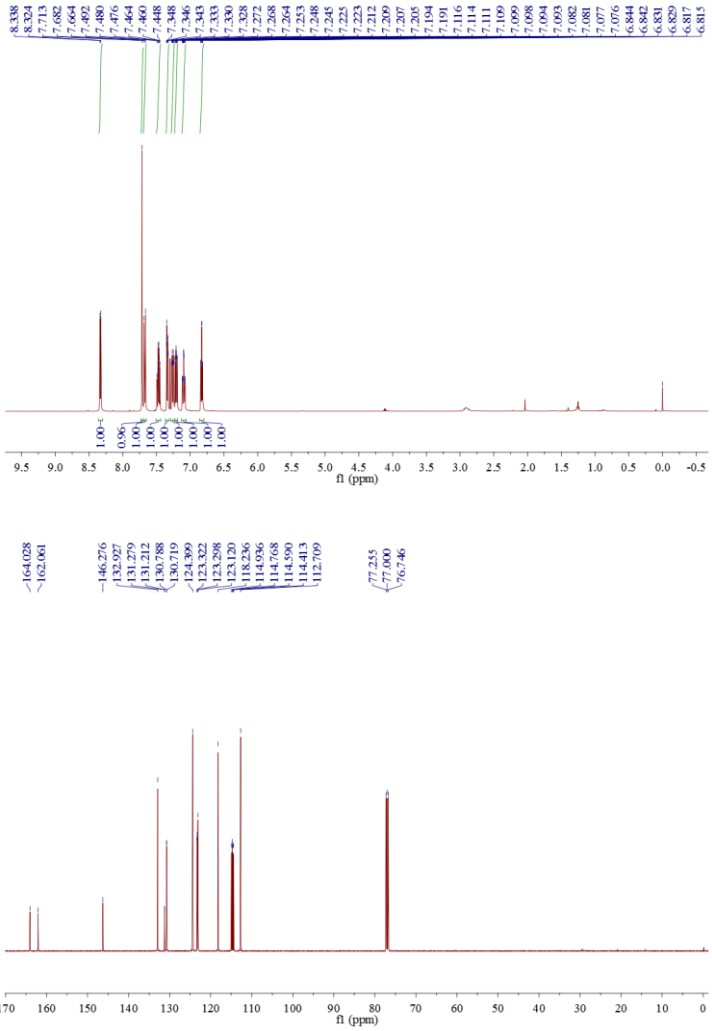


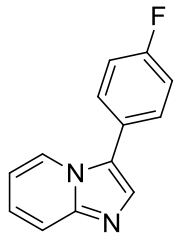
Compound **4h**: brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.01-7.99 (m, 1H), 7.74 (s, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.42 (dd, J = 13.5, 7.5 Hz, 1H), 7.31-7.19 (m, 3H), 6.81 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7 (d, $J_{C\text{-}F}$ = 247.375 Hz), 146.2, 133.7 (d, $J_{C\text{-}F}$ = 0.75 Hz), 131.1 (d, $J_{C\text{-}F}$ = 3.125 Hz), 130.2 (d, $J_{C\text{-}F}$ = 8.125 Hz), 124.7 (d, $J_{C\text{-}F}$ = 3.5 Hz), 124.3, 124.2 (d, $J_{C\text{-}F}$ = 4.625 Hz), 119.9, 117.8, 116.9 (d, $J_{C\text{-}F}$ = 15.0 Hz), 116.1 (d, $J_{C\text{-}F}$ = 21.375 Hz), 112.3. MS (ESI): 213 $[M+H]^+$; HRMS (ESI) calcd for $C_{13}H_{10}FN_2$ $[M+H]^+$: 213.0823; found: 213.0840; IR (neat) ν 1635, 1542, 1497, 1483, 1469, 1450, 1351, 1301, 1270, 1256, 1216, 1177, 1146, 1118, 1090, 1008, 970, 897, 865, 814, 779, 753, 737 cm^{-1}.



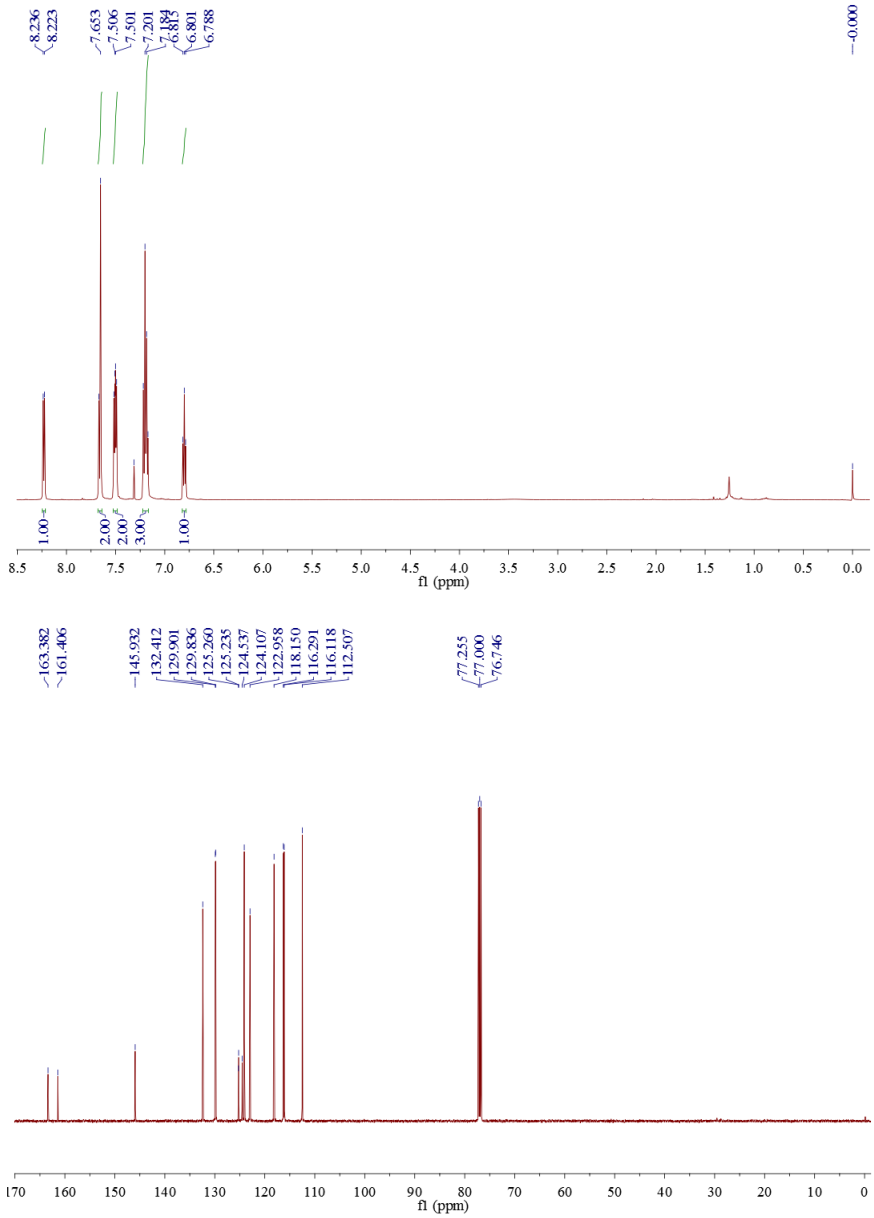


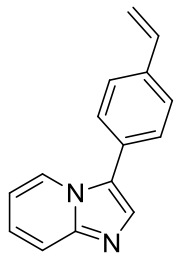
Compound **4i**: brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.33 (d, *J* = 7.0 Hz, 1H), 7.72 (s, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.47 (td, *J* = 8.0, 6.0 Hz, 1H), 7.34 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.26 (dt, *J* = 9.5, 2.0 Hz, 1H), 7.21 (ddd, *J* = 9.0, 6.5, 1.0 Hz, 1H), 7.10 (tdd, *J* = 8.5, 2.5, 1.0 Hz, 1H), 6.83 (td, *J* = 7.0, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 245.875 Hz), 146.3, 132.9, 131.2 (d, $J_{C\text{-}F}$ = 8.375 Hz), 130.8 (d, $J_{C\text{-}F}$ = 8.625 Hz), 124.4, 123.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 123.1, 118.2, 114.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.5 (d, $J_{C\text{-}F}$ = 22.125 Hz), 112.7. MS (ESI): 213 $[M+H]^+$; HRMS (ESI) calcd for $C_{13}H_{10}FN_2$ $[M+H]^+$: 213.0823; found: 213.0840; IR (neat) ν 1610, 1582, 1495, 1469, 1436, 1354, 1295, 1264, 1208, 1157, 1129, 1115, 848, 791, 750 cm^{-1}.



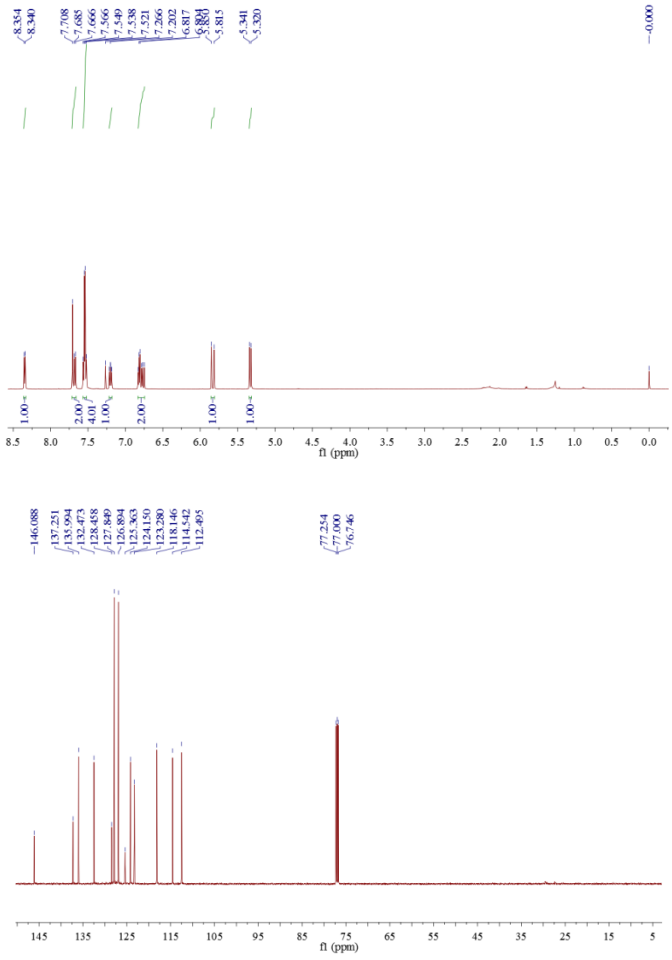


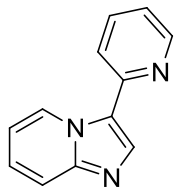
Compound **4j**:[1] brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.23 (d, J = 6.5 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.50 (dd, J = 8.0, 5.5 Hz, 2H), 7.22-7.17 (m, 3H), 6.80 (t, J = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 247.0 Hz), 145.9, 132.4, 129.9 (d, $J_{C\text{-}F}$ = 8.125 Hz), 125.2 (d, $J_{C\text{-}F}$ = 3.125 Hz), 124.5, 124.1, 123.0, 118.2, 116.2 (d, $J_{C\text{-}F}$ = 21.625 Hz), 112.5.



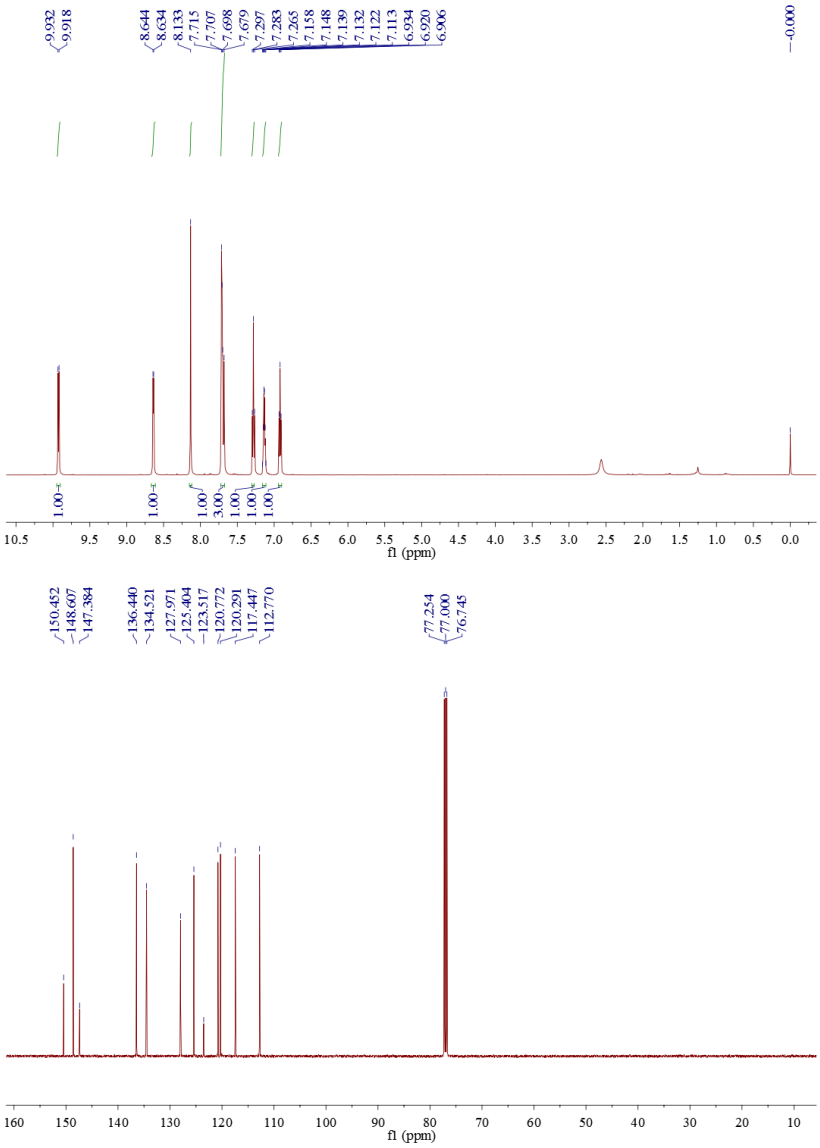


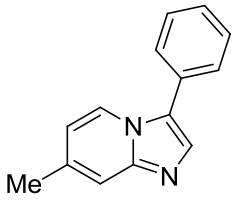
Compound **4k**: brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.35 (d, *J* = 7.0 Hz, 1H), 7.71 (s, 1H), 7.68 (d, *J* = 9.5 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.21 (td, *J* = 8.0, 1.0 Hz, 1H), 6.82 (d, *J* = 6.5 Hz, 1H), 6.78 (dd, *J* = 17.5, 10.5 Hz, 1H), 5.83 (d, *J* = 17.5 Hz, 1H), 5.33 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 137.3, 136.0, 132.5, 128.5, 127.8, 126.9, 125.4, 124.2, 123.3, 118.1, 114.5, 112.5. MS (ESI): 221 $[M+H]^+$; HRMS (ESI) calcd for $C_{15}H_{13}N_2$ $[M+H]^+$: 221.1073; found: 221.1091; IR (neat) ν 1627, 1604, 1540, 1483, 1407, 1351, 1301, 1273, 1253, 1163, 1149, 1129, 1115, 1008, 989, 962, 910, 903, 893, 858, 848, 843, 754, 738, 736 cm^{-1}.



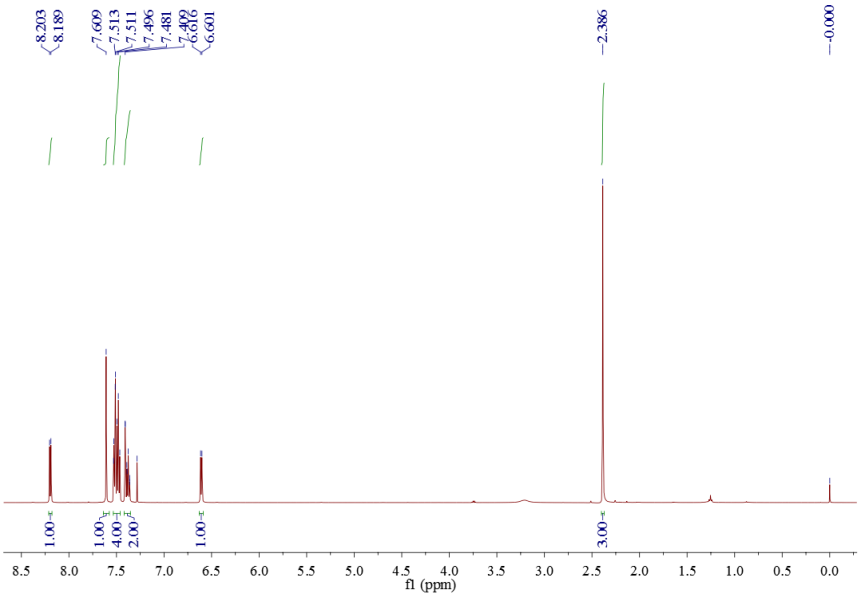


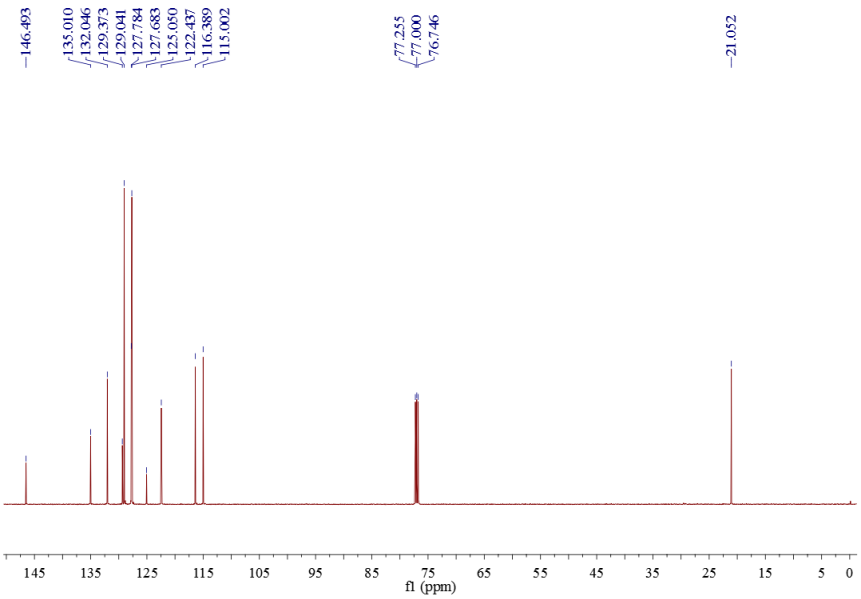
Compound **4l**: white solid. mp: 80-81 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 9.93 (d, *J* = 7.0 Hz, 1H), 8.64 (d, *J* = 5.0 Hz, 1H), 8.13 (s, 1H), 7.72-7.68 (m, 3H), 7.2t (t, *J* = 8.0 Hz, 1H), 7.16-7.11 (m, 1H), 6.92 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 148.6, 147.4, 136.4, 134.5, 128.0, 125.4, 123.5, 120.8, 120.3, 117.4, 112.8. MS (ESI): 196 $[M+H]^+$; HRMS (ESI) calcd for $C_{12}H_{10}N_3$ $[M+H]^+$: 196.0869; found: 196.0879; IR (neat) ν 1587, 1531, 1495, 1444, 1438, 1360, 1348, 1320, 1306, 1273, 1261, 1185, 1171, 1126, 1093, 1014, 992, 968, 888, 851, 837, 782, 751 cm^{-1}.

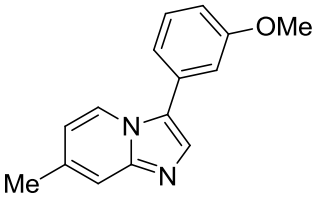




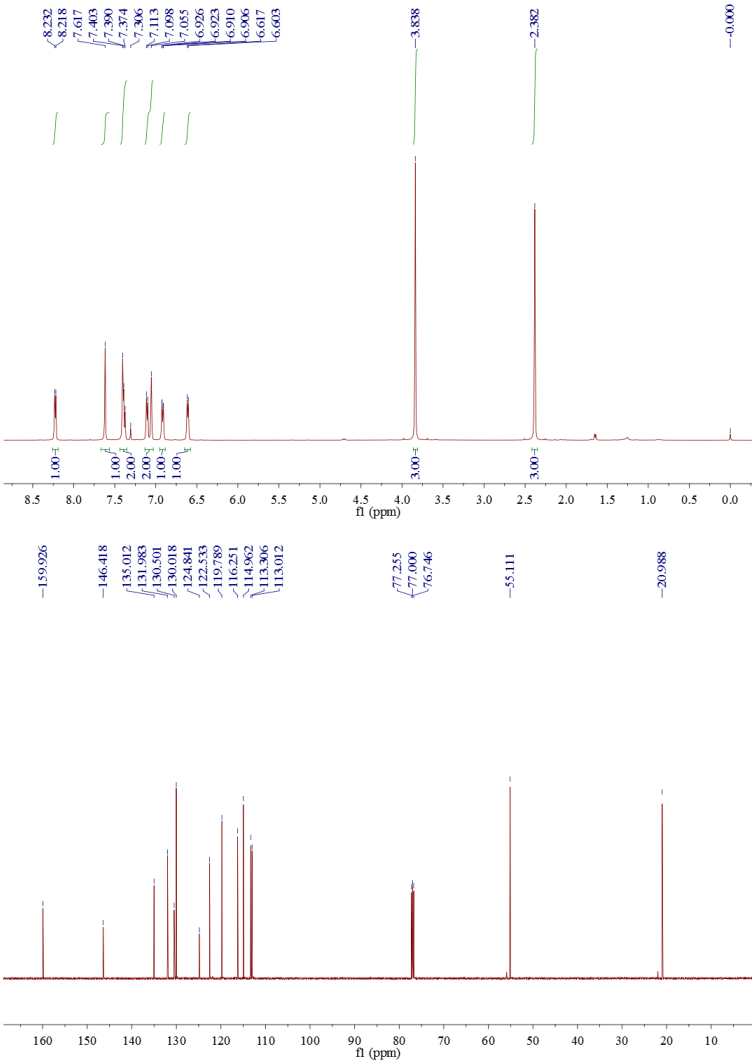
Compound **4m**:[1] brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.20 (d, *J* = 7.0 Hz, 1H), 7.61 (s, 1H), 7.53-7.47 (m, 4H), 7.41-7.36 (m, 2H), 6.61 (d, *J* = 7.5 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 135.0, 132.0, 129.4, 129.0, 127.8, 127.7, 125.1, 122.4, 116.4, 115.0, 21.1.

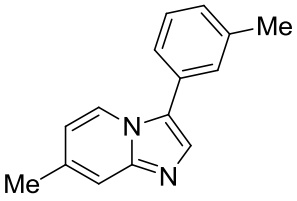




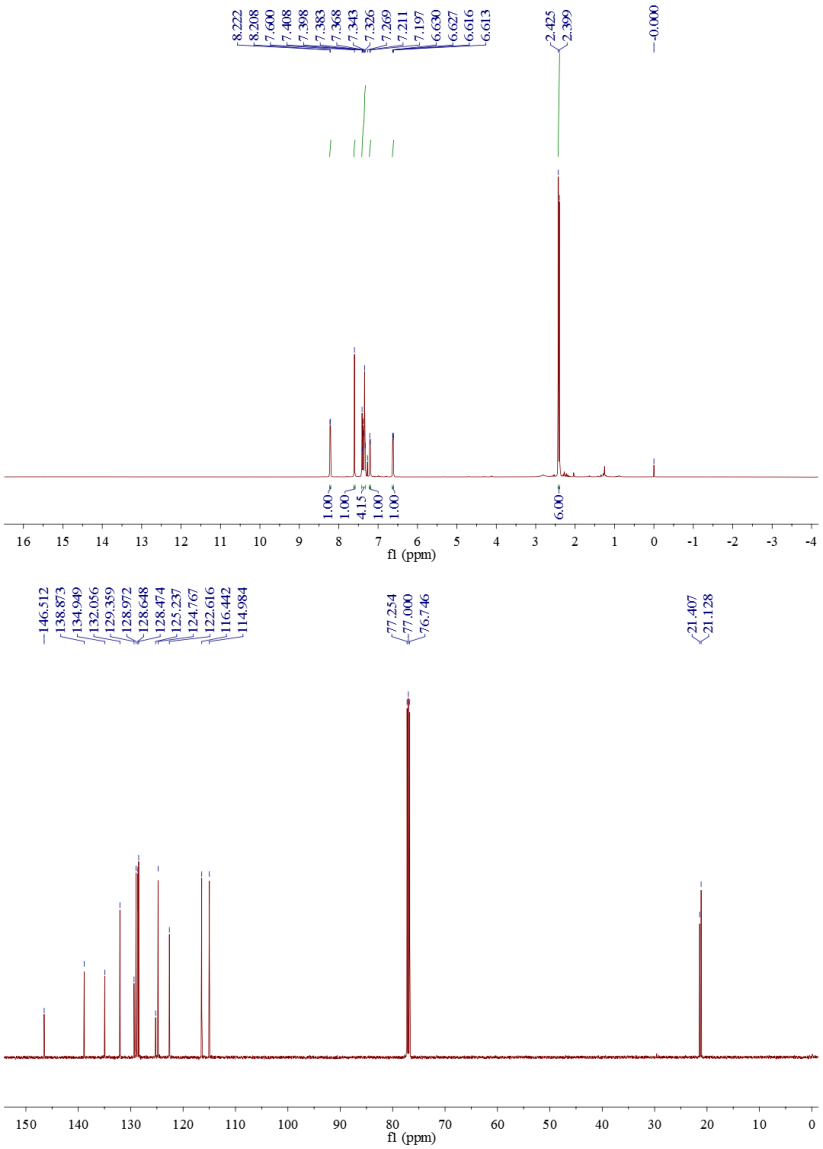


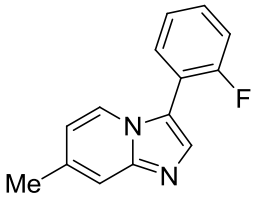
Compound **4n**: brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.22 (d, *J* = 7.0 Hz, 1H), 7.62 (s, 1H), 7.40-7.31 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 6.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.61 (d, *J* = 7.0 Hz, 1H), 3.84 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 146.4, 135.0, 132.0, 130.5, 130.0, 124.8, 122.5, 119.8, 116.3, 115.0, 113.3, 113.0, 55.1, 21.0. MS (ESI): 239 $[M+H]^+$; HRMS (ESI) calcd for $C_{15}H_{15}N_2O$ $[M+H]^+$: 239.1179; found: 239.1200; IR (neat) ν 1646, 1599, 1573, 1542, 1492, 1464, 1433, 1340, 1298, 1292, 1287, 1233, 1185, 1166, 1141, 1110, 1042, 989, 845, 776, 746 cm^{-1}.



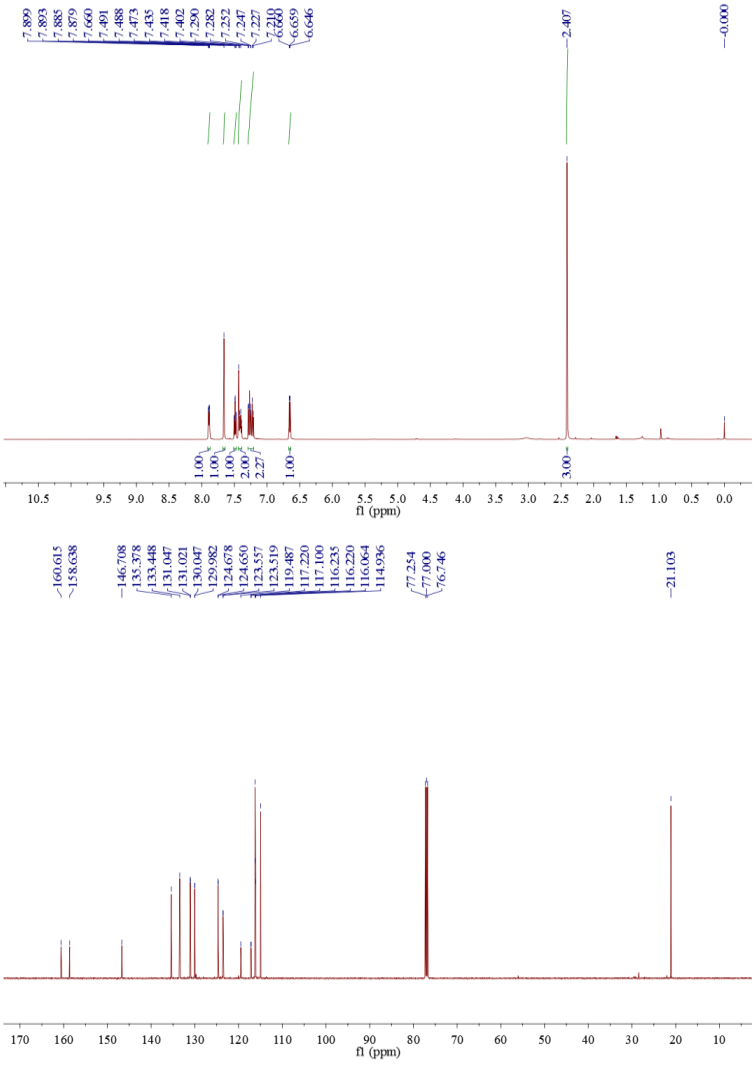


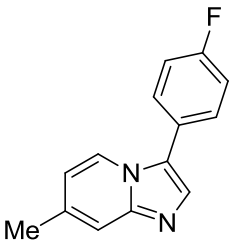
Compound **4o**: brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.22 (d, *J* = 7.0 Hz, 1H), 7.60 (s, 1H), 7.41-7.33 (m, 4H), 7.20 (d, *J* = 7.0 Hz, 1H), 6.62 (dd, *J* = 7.0, 1.5 Hz, 1H), 2.43 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 138.9, 134.9, 132.1, 129.4, 129.0, 128.6, 128.5, 125.2, 124.8, 122.6, 116.4, 115.0, 21.4, 21.1. MS (ESI): 223 $[M+H]^+$; HRMS (ESI) calcd for $C_{15}H_{15}N_2$ $[M+H]^+$: 223.1230; found: 223.1247; IR (neat) ν 1647, 1608, 1544, 1497, 1463, 1346, 1332, 1301, 1268, 1184, 1167, 1134, 1114, 1033, 905, 884, 858, 842, 789, 779, 742 cm^{-1}.



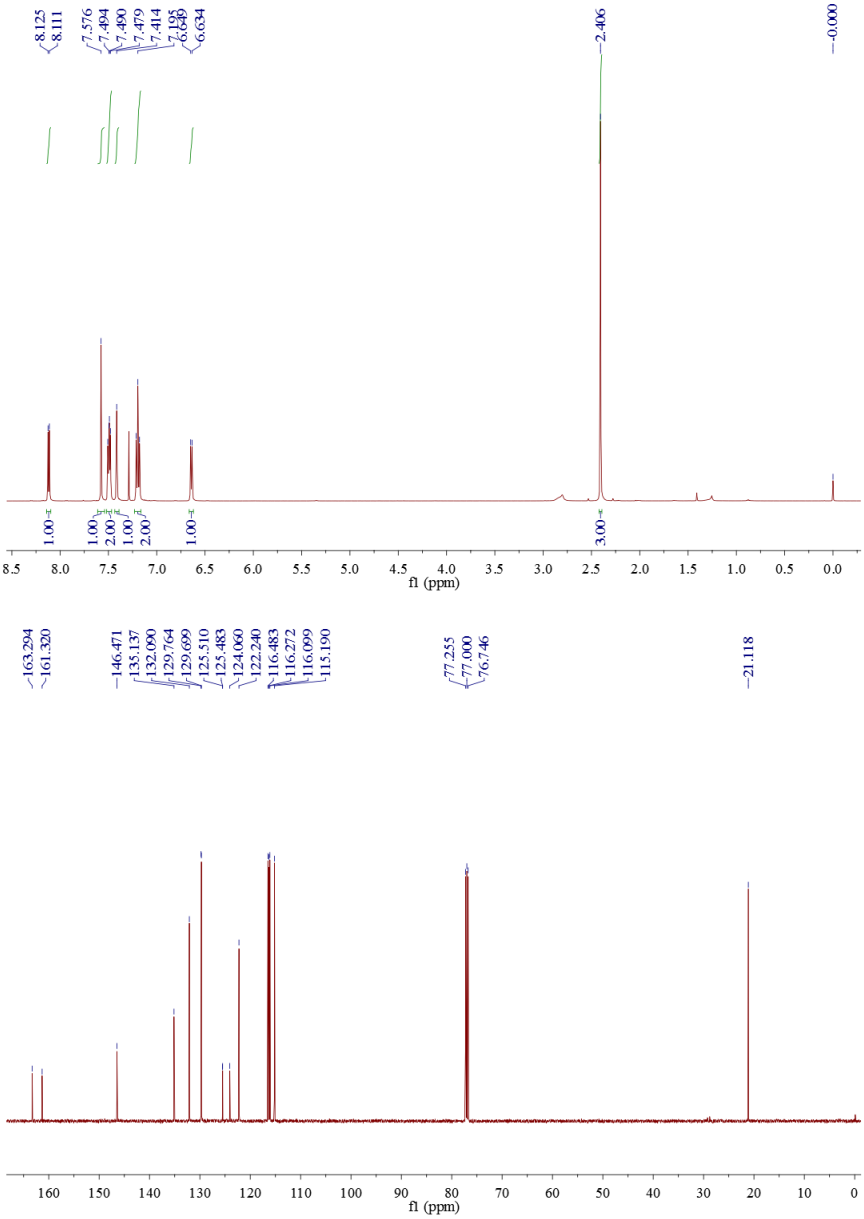


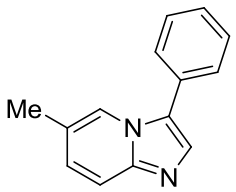
Compound **4p**: yellow solid. mp: 99-100 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.89 (dd, J = 7.0, 3.0 Hz, 1H), 7.66 (s, 1H), 7.49 (td, J = 7.5, 1.5 Hz, 1H), 7.44-7.39 (m, 2H), 7.29-7.21 (m, 2H), 6.67-6.64 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ 159.6 (d, J_{C-F} = 247.125 Hz), 146.7, 135.4, 133.4, 131.0 (d, J_{C-F} = 3.25 Hz), 130.0 (d, J_{C-F} = 8.125 Hz), 124.7 (d, J_{C-F} = 3.5 Hz), 123.5 (d, J_{C-F} = 4.75 Hz), 119.5, 117.2 (d, J_{C-F} = 15.0 Hz), 116.2 (d, J_{C-F} = 1.875 Hz), 116.1, 114.9, 21.1. MS (ESI): 227 $[M+H]^+$; HRMS (ESI) calcd for $C_{14}H_{12}FN_2$ $[M+H]^+$: 227.0979; found: 227.0998; IR (neat) ν 1647, 1545, 1496, 1449, 1340, 1300, 1275, 1213, 1186, 1139, 1117, 1092, 975, 867, 848, 825, 810, 787, 758, 748 cm^{-1}.



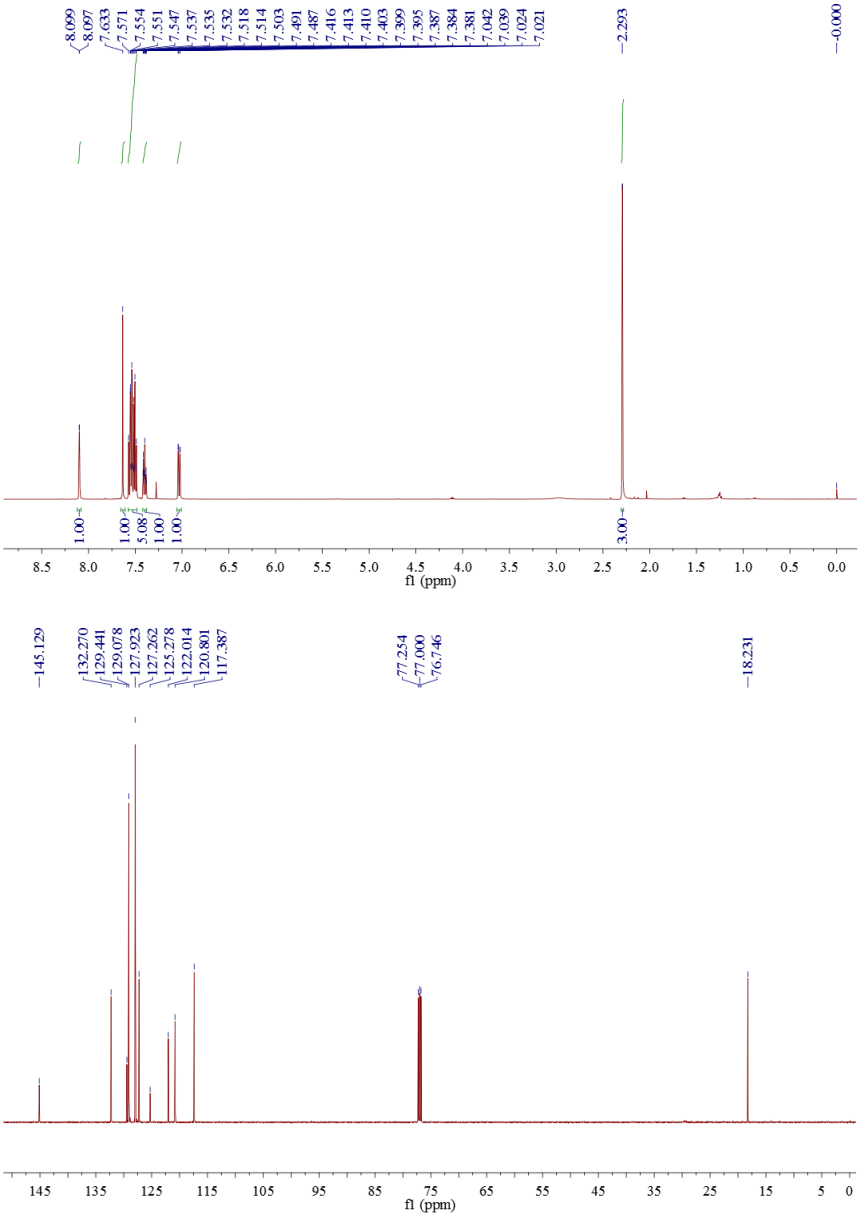


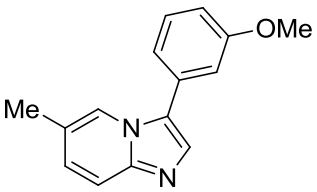
Compound **4q**:[1] yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.12 (d, J = 7.0 Hz, 1H), 7.58 (s, 1H), 7.49 (dd, J = 8.5, 6.0 Hz, 2H), 7.41 (s, 1H), 7.20 (t, J = 8.5 Hz, 2H), 6.64 (d, J = 7.0 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 246.75 Hz), 146.5, 135.1, 132.1, 129.7 (d, $J_{C\text{-}F}$ = 8.125 Hz), 125.5 (d, $J_{C\text{-}F}$ = 3.375 Hz), 124.1, 122.2, 116.5, 116.2 (d, $J_{C\text{-}F}$ = 21.625 Hz), 115.2, 21.1.



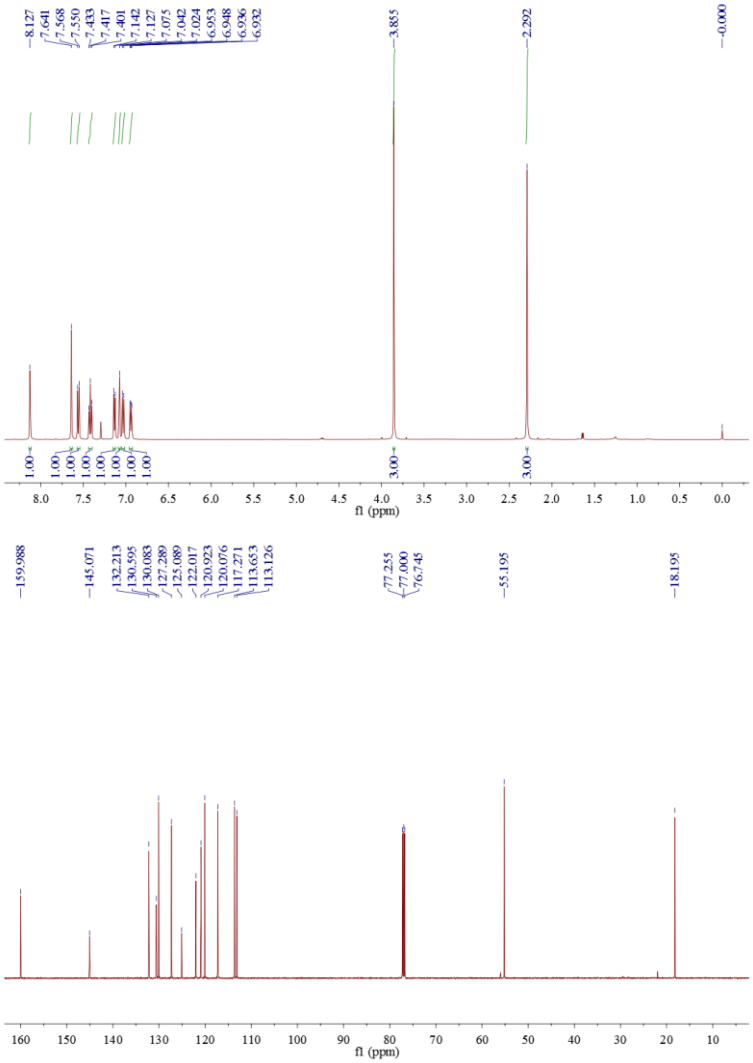


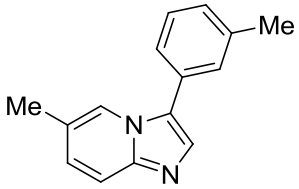
Compound **4r**:[3] brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.10 (d, *J* = 1.0 Hz, 1H), 7.63 (s, 1H), 7.57-7.49 (m, 5H), 7.40 (tt, *J* = 7.0, 1.5 Hz, 1H), 7.03 (dd, *J* = 9.0, 1.5 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 132.3, 129.4, 129.1, 127.9, 127.3, 125.3, 122.0, 120.8, 117.4, 18.2.



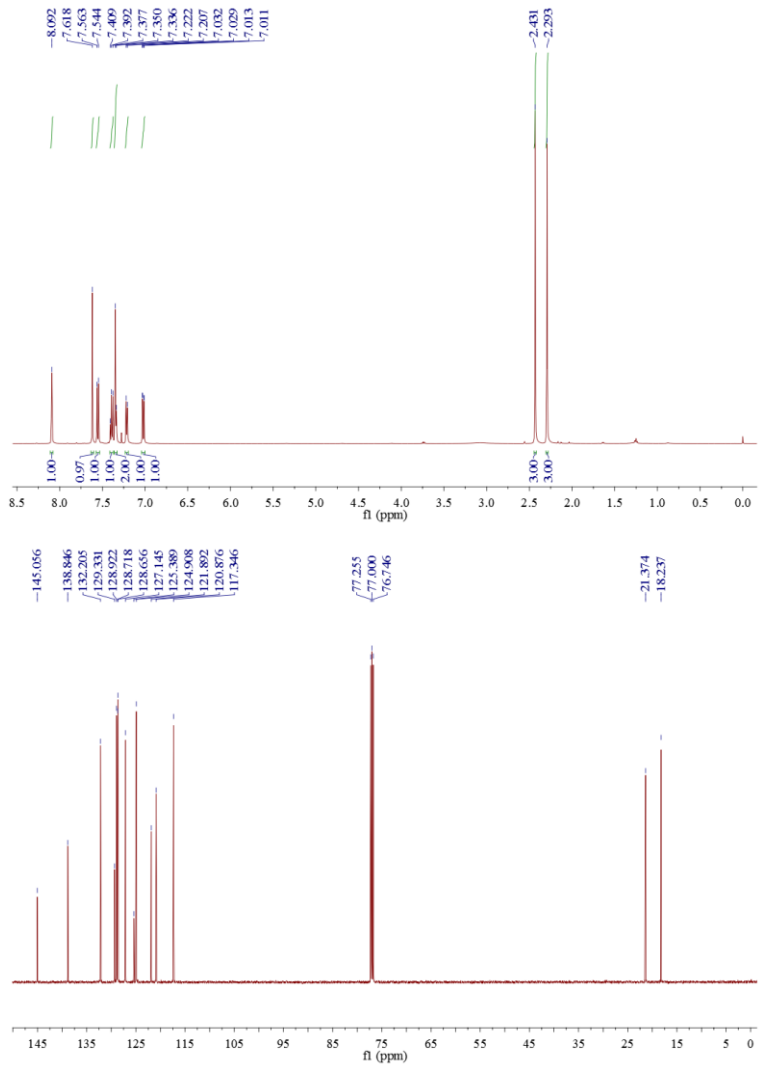


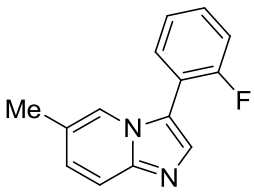
Compound **4s**: yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.13 (s, 1H), 7.64 (s, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.08 (s, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.86 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 145.1, 132.2, 130.6, 130.1, 127.3, 125.1, 122.0, 120.9, 120.1, 117.3, 113.7, 113.1, 55.2, 18.2. MS (ESI): 239 $[M+H]^+$; HRMS (ESI) calcd for $C_{15}H_{15}N_2O$ $[M+H]^+$: 239.1179; found: 239.1200; IR (neat) ν 1607, 1576, 1540, 1526, 1500, 1472, 1427, 1357, 1332, 1298, 1278, 1239, 1211, 1157, 1132, 1042, 978, 844, 799, 781, 753 cm^{-1}.



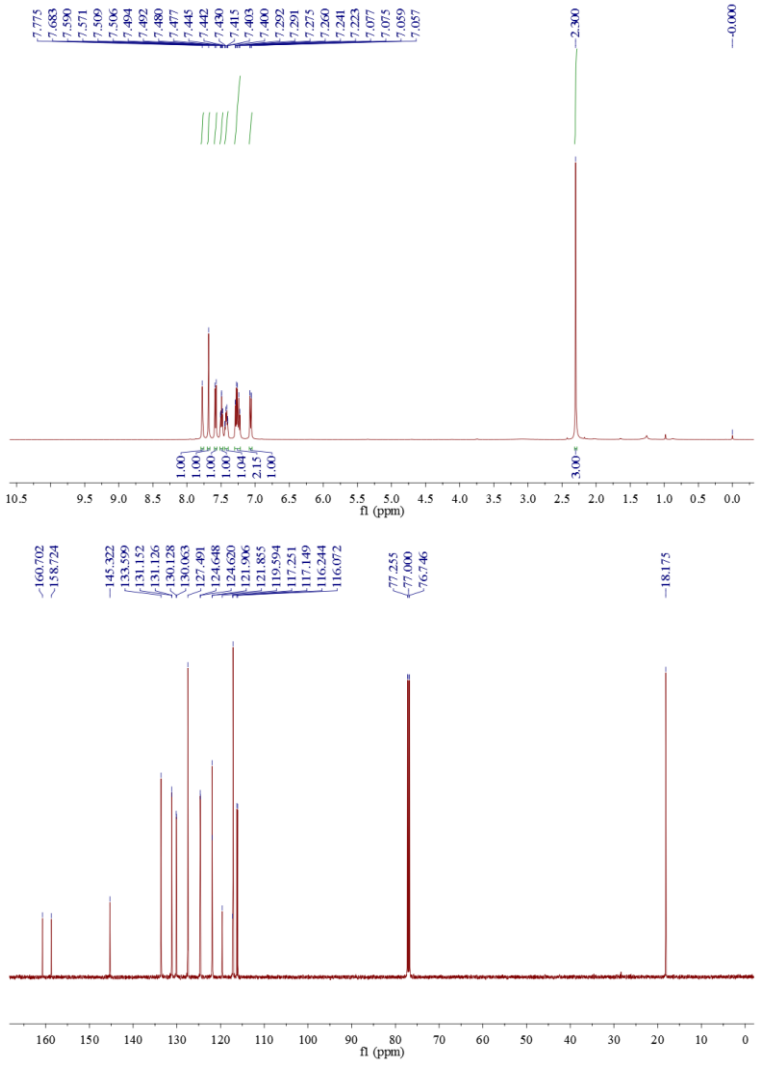


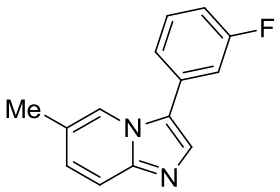
Compound **4t**: brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.09 (s, 1H), 7.62 (s, 1H), 7.55 (d, *J* = 9.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.02 (dd, *J* = 9.5, 1.5 Hz, 1H), 2.43 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 138.9, 132.2, 129.3, 128.9, 128.7, 128.6, 127.1, 125.4, 124.9, 121.9, 120.9, 117.3, 21.4, 18.2. MS (ESI): 223 $[M+H]^+$; HRMS (ESI) calcd for $C_{15}H_{15}N_2$ $[M+H]^+$: 223.1230; found: 223.1250; IR (neat) ν 1606, 1583, 1541, 1505, 1460, 1357, 1340, 1299, 1265, 1232, 1153, 1134, 1092, 1042, 856, 845, 786, 753 cm^{-1}.



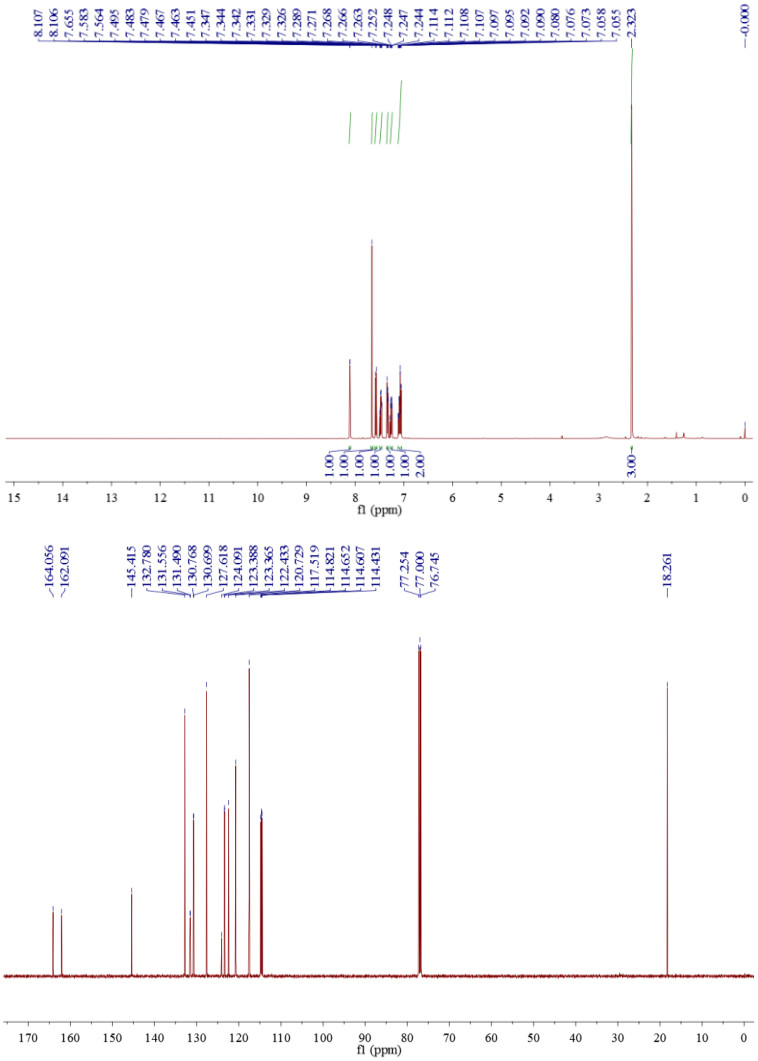


Compound **4u**: yellow solid. mp: 80-81 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.78 (s, 1H), 7.68 (s, 1H), 7.58 (d, *J* = 9.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 7.45-7.40 (m, 1H), 7.29-7.22 (m, 2H), 7.07 (dd, *J* = 9.0, 1.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7 (d, $J_{C\text{-}F}$ = 247.25 Hz), 145.3, 133.6, 131.1 (d, $J_{C\text{-}F}$ = 3.25 Hz), 130.1 (d, $J_{C\text{-}F}$ = 8.125 Hz), 127.5, 124.6 (d, $J_{C\text{-}F}$ = 3.5 Hz), 121.9 (d, $J_{C\text{-}F}$ = 6.375 Hz), 119.6, 117.3, 117.1, 116.2 (d, $J_{C\text{-}F}$ = 21.5 Hz), 18.2. MS (ESI): 227 $[M+H]^+$; HRMS (ESI) calcd for $C_{14}H_{12}FN_2$ $[M+H]^+$: 227.0979; found: 227.0998; IR (neat) ν 1548, 1528, 1503, 1469, 1458, 1436, 1354, 1334, 1301, 1264, 1230, 1208, 1152, 1138, 1118, 1084, 1037, 965, 930, 861, 830, 809, 795, 768, 753 cm^{-1}.

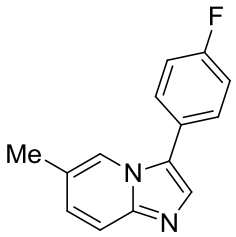




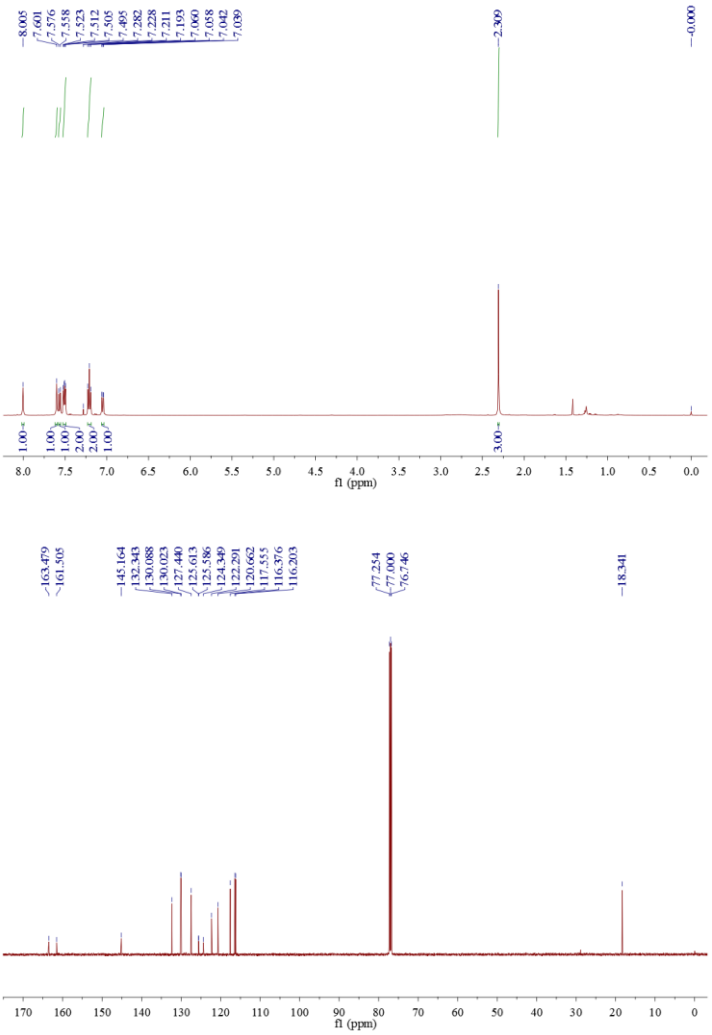
Compound **4v**:[4] brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.11 (d, J = 0.5 Hz, 1H), 7.66 (s, 1H), 7.57 (d, J = 9.5 Hz, 1H), 7.47 (td, J = 8.0, 6.0 Hz, 1H), 7.34 (dt, J = 8.0, 1.5 Hz, 1H), 7.26 (ddd, J = 9.5, 2.0, 1.5 Hz, 1H), 7.11-7.06 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1 (d, $J_{C\text{-}F}$ = 245.625 Hz), 145.4, 132.8, 131.5 (d, $J_{C\text{-}F}$ = 8.25 Hz), 130.7 (d, $J_{C\text{-}F}$ = 8.625 Hz), 127.6, 124.1, 123.4 (d, $J_{C\text{-}F}$ = 2.875 Hz), 122.4, 120.7, 117.5, 114.7 (d, $J_{C\text{-}F}$ = 21.125 Hz), 114.5 (d, $J_{C\text{-}F}$ = 22.0 Hz), 18.3.

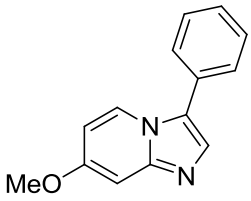


4) Y. Liu, L. He, G.-Q. Yin, G.-J. Wu and Y.-D. Cui, *Bull. Korean Chem. Soc.*, 2013, **34**, 2340.

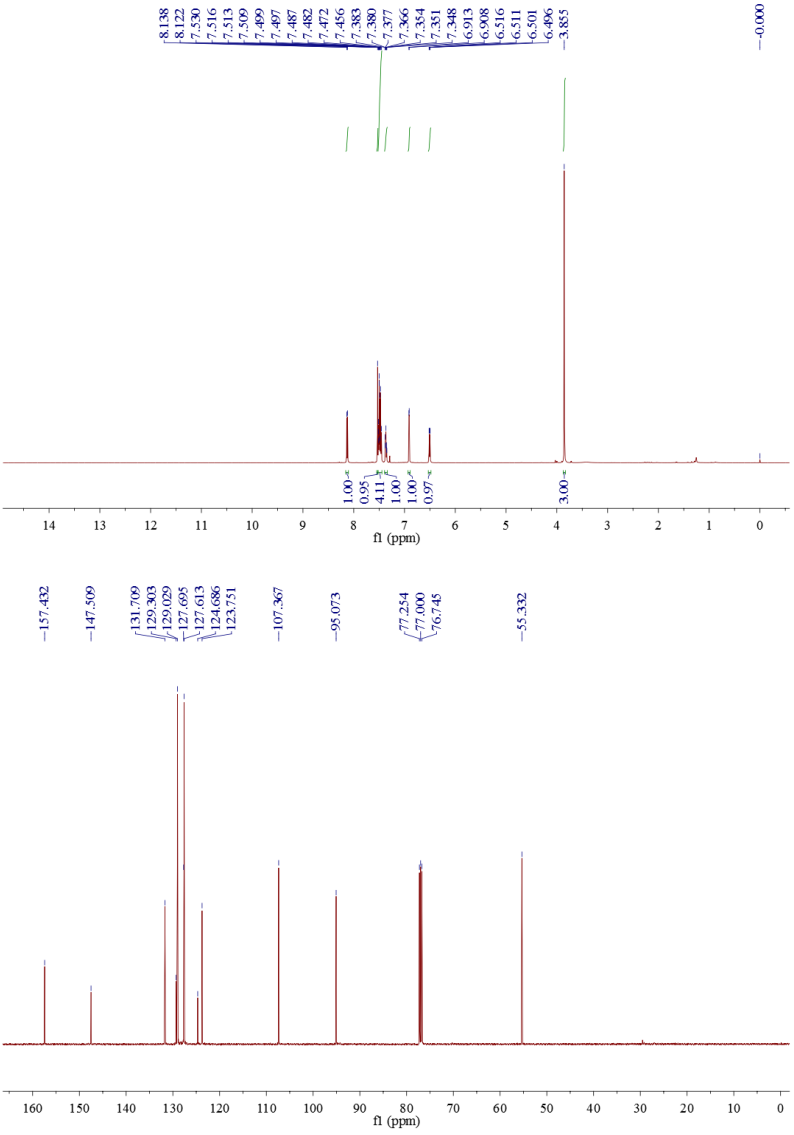


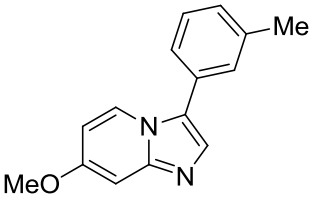
Compound **4w**: brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.01 (s, 1H), 7.60 (s, 1H), 7.57 (d, J = 9.0 Hz, 1H), 7.51 (dd, J = 8.5, 5.5 Hz, 2H), 7.21 (t, J = 8.5 Hz, 2H), 7.05 (dd, J = 9.0, 1.0 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$ = 246.75 Hz), 145.2, 132.3, 130.1 (d, $J_{C\text{-}F}$ = 8.125 Hz), 127.4, 125.6 (d, $J_{C\text{-}F}$ = 3.375 Hz), 124.3, 122.3, 120.7, 117.6, 116.3 (d, $J_{C\text{-}F}$ = 21.625 Hz), 18.3. MS (ESI): 227 $[M+H]^+$; HRMS (ESI) calcd for $C_{14}H_{12}FN_2$ $[M+H]^+$: 227.0979; found: 227.0985; IR (neat) ν 1551, 1531, 1506, 1490, 1358, 1338, 1305, 1229, 1151, 1134, 1095, 962, 931, 840, 835, 811, 798, 759, 744, 735 cm^{-1}.



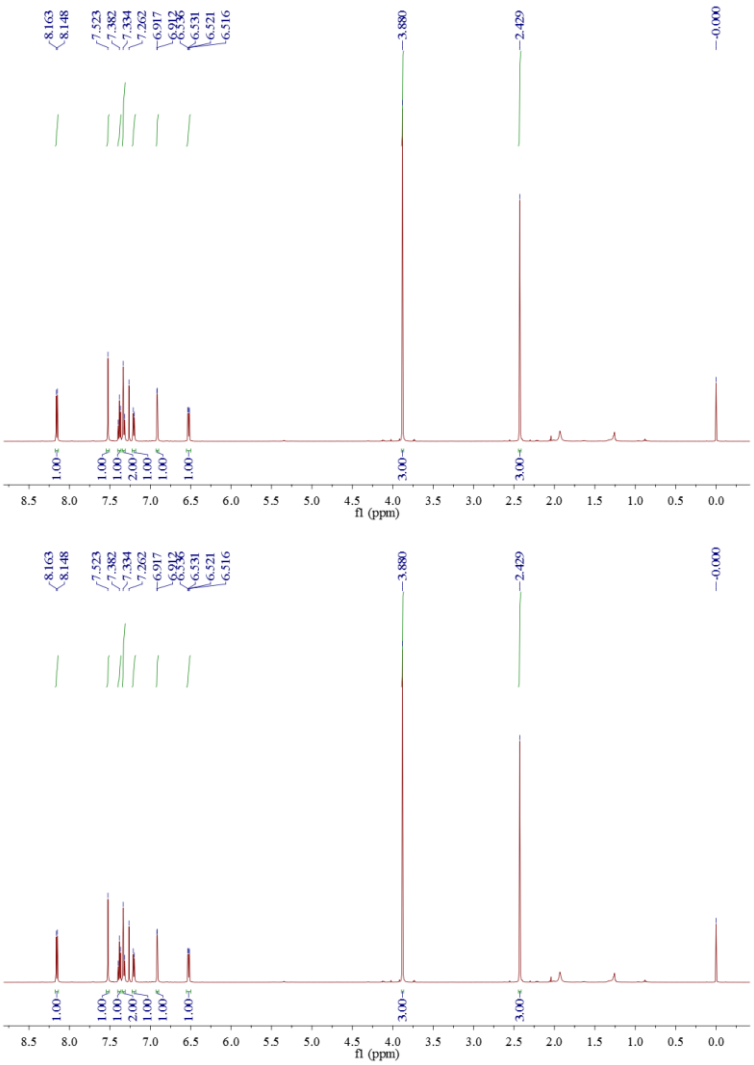


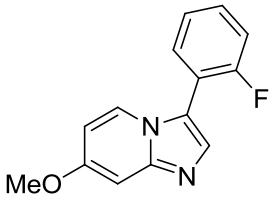
Compound **4x**: yellow solid. mp: 105-106 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.53 (s, 1H), 7.52-7.46 (m, 4H), 7.38-7.35 (m, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 6.51 (dd, *J* = 7.5, 2.5 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 147.5, 131.7, 129.3, 129.0, 127.7, 127.6, 124.7, 123.8, 107.4, 95.1, 55.3. MS (ESI): 225 $[M+H]^+$; HRMS (ESI) calcd for $C_{14}H_{13}N_2O$ $[M+H]^+$: 225.1022; found: 225.1038; IR (neat) ν 1646, 1601, 1548, 1507, 1475, 1434, 1301, 1233, 1162, 1180, 1139, 1109, 1028, 972, 947, 907, 864, 841, 831, 776, 766, 750, 738 cm^{-1}.



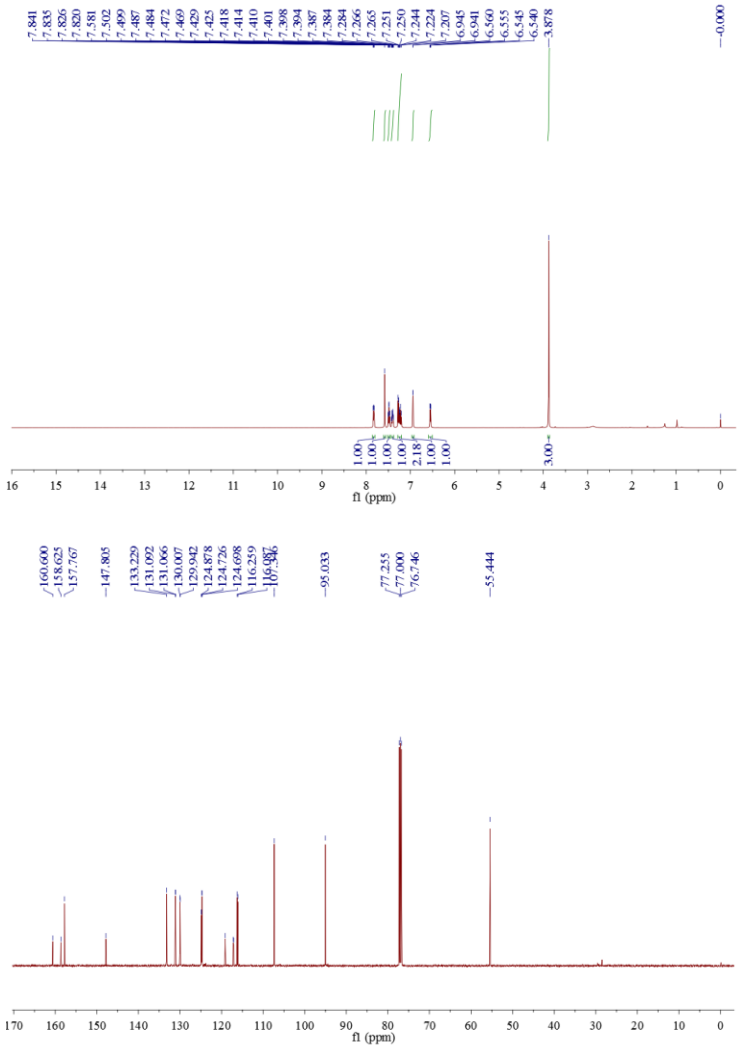


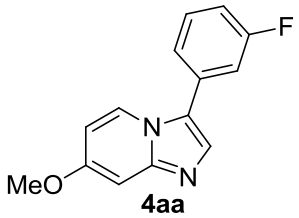
Compound **4y**: yellow solid. mp: 134-135 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.16 (d, *J* = 7.5 Hz, 1H), 7.52 (s, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 7.0 Hz, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 6.53 (dd, *J* = 7.5, 2.5 Hz, 1H), 3.88 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 147.6, 139.0, 131.8, 129.4, 129.0, 128.7, 128.5, 125.0, 124.8, 124.0, 107.4, 95.3, 55.5, 21.5. MS (ESI): 239 $[M+H]^+$; HRMS (ESI) calcd for $C_{15}H_{15}N_2O$ $[M+H]^+$: 239.1179; found: 239.1203; IR (neat) ν 1652, 1604, 1537, 1509, 1478, 1430, 1348, 1295, 1233, 1183, 1163, 1042, 951, 866, 860, 840, 809, 774, 743 cm^{-1}.





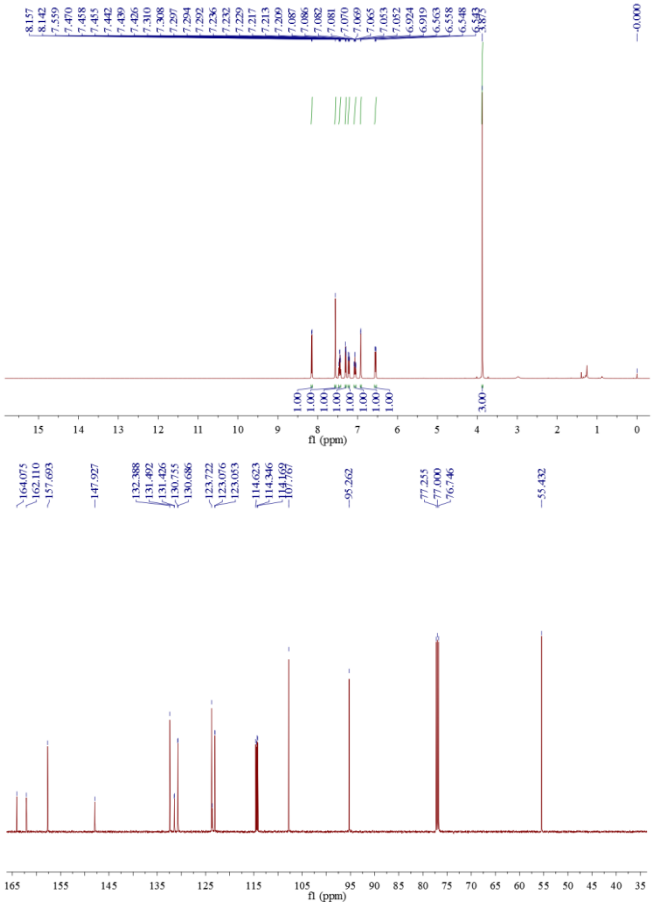
Compound **4z**: brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.83 (dd, *J* = 7.5, 3.0 Hz, 1H), 7.58 (s, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43-7.38 (m, 1H), 7.28-7.21 (m, 2H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.55 (dd, *J* = 7.5, 2.5 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6 (d, J_{C-F} = 246.875 Hz), 157.8, 147.8, 133.2, 131.1 (d, J_{C-F} = 3.25 Hz), 130.0 (d, J_{C-F} = 8.125 Hz), 124.9 (d, J_{C-F} = 4.875 Hz), 124.7 (d, J_{C-F} = 3.5 Hz), 119.1, 117.2 (d, J_{C-F} = 15.0 Hz), 116.2 (d, J_{C-F} = 21.5 Hz), 107.3, 95.0, 55.4. MS (ESI): 243 $[M+H]^+$; HRMS (ESI) calcd for $C_{14}H_{12}FN_2O$ $[M+H]^+$: 243.0928; found: 243.0929; IR (neat) ν 1647, 1617, 1575, 1547, 1494, 1449, 1338, 1304, 1276, 1212, 1187, 1145, 1092, 1036, 975, 946, 937, 869, 849, 825, 809, 789, 761, 747 cm^{-1}.

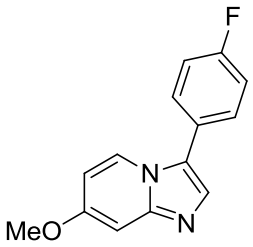




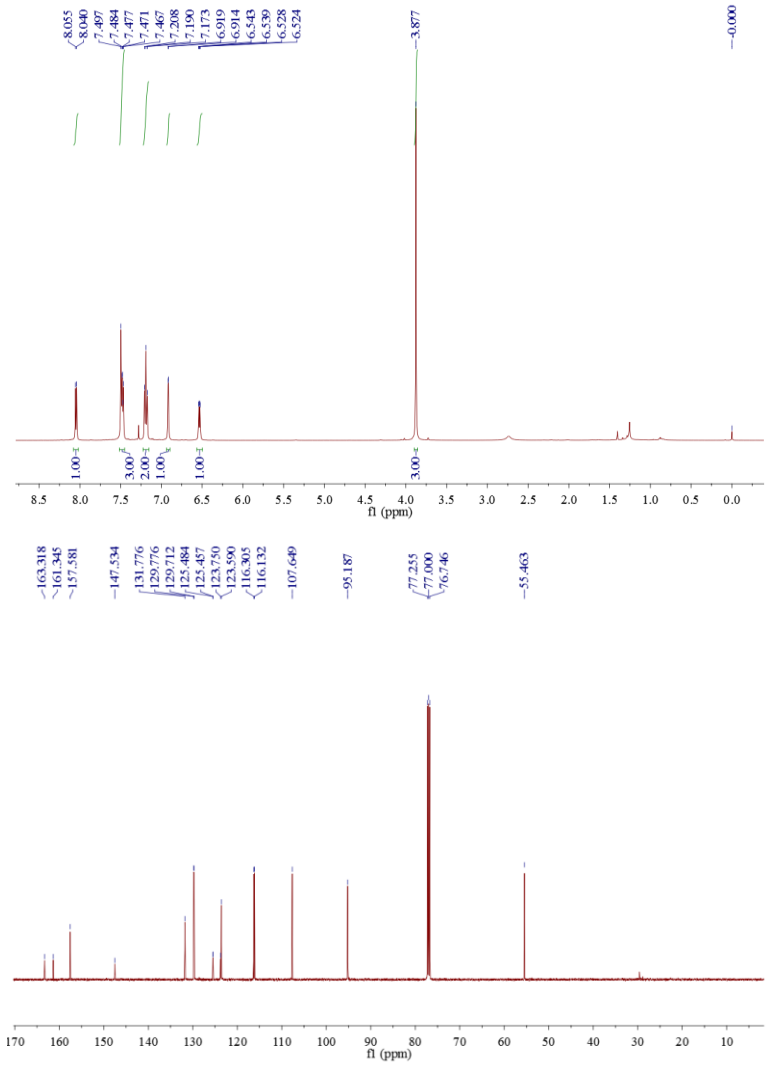
4aa

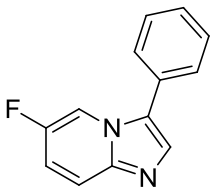
Compound **4aa**: yellow solid. mp: 132-133 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.15 (d, *J* = 7.5 Hz, 1H), 7.56 (s, 1H), 7.45 (td, *J* = 7.5, 6.0 Hz, 1H), 7.31-7.29 (m, 1H), 7.22 (dt, *J* = 10.0, 2.0 Hz, 1H), 7.09-7.05 (m, 1H), 6.92 (d, *J* = 2.5 Hz, 1H), 6.55 (dd, *J* = 7.5, 2.5 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1 (d, $J_{C\text{-}F}$ = 245.625 Hz), 157.7, 147.9, 132.4, 131.5 (d, $J_{C\text{-}F}$ = 8.25 Hz), 130.7 (d, $J_{C\text{-}F}$ = 8.625 Hz), 123.7, 123.1 (d, $J_{C\text{-}F}$ = 2.875 Hz), 114.6, 114.3 (d, $J_{C\text{-}F}$ = 22.125 Hz), 107.8, 95.3, 55.4. MS (ESI): 243 $[M+H]^+$; HRMS (ESI) calcd for $C_{14}H_{12}FN_2O$ $[M+H]^+$: 243.0928; found: 243.0963; IR (neat) ν 1652, 1610, 1582, 1542, 1534, 1506, 1483, 1467, 1436, 1346, 1337, 1298, 1236, 1202, 1180, 1163, 1143, 1104, 1022, 951, 871, 859, 843, 775, 760, 743 cm^{-1}.



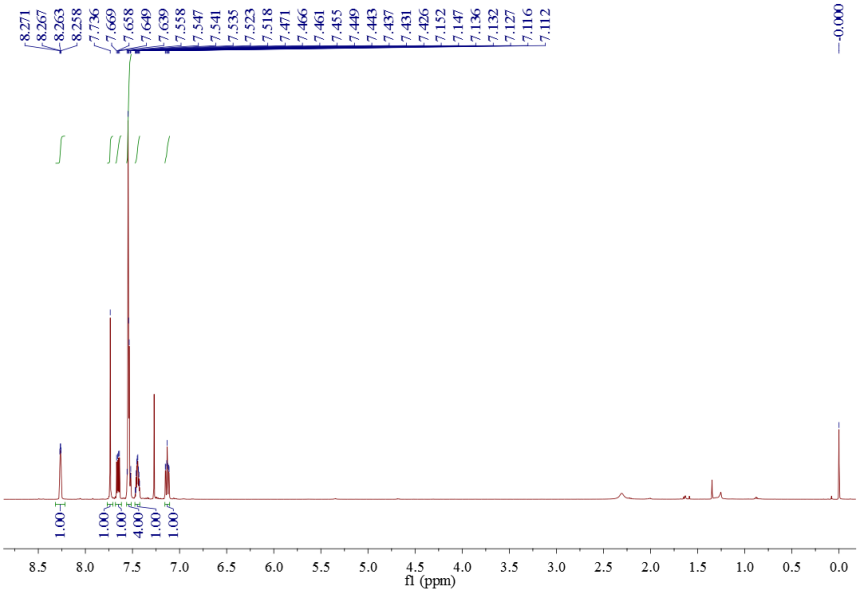


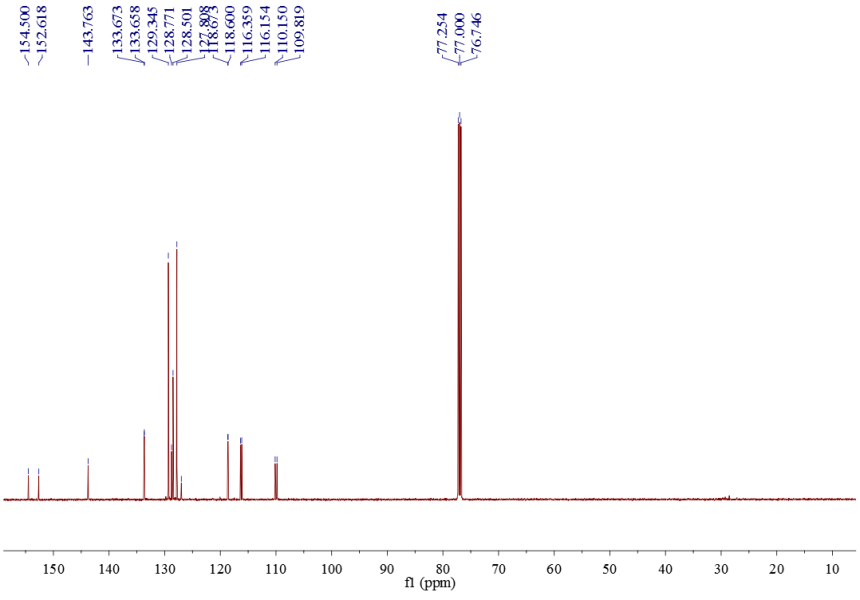
Compound **4ab**: yellow solid. mp: 135-136 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.05 (d, *J* = 7.5 Hz, 1H), 7.50-7.47 (m, 3H), 7.19 (t, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 2.5 Hz, 1H), 6.53 (dd, *J* = 7.5, 2.0 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 246.625 Hz), 157.6, 147.5, 131.8, 129.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 125.5 (d, $J_{C\text{-}F}$ = 3.375 Hz), 123.7 (d, $J_{C\text{-}F}$ = 20.0 Hz), 116.2 (d, $J_{C\text{-}F}$ = 21.625 Hz), 107.6, 95.2, 55.5. MS (ESI): 243 $[M+H]^+$; HRMS (ESI) calcd for $C_{14}H_{12}FN_2O$ $[M+H]^+$: 243.0928; found: 243.0963; IR (neat) ν 1649, 1557, 1545, 1506, 1491, 1475, 1431, 1345, 1295, 1219, 1180, 1156, 1139, 1106, 1020, 944, 851, 837, 821, 810, 789, 775, 736 cm^{-1}.

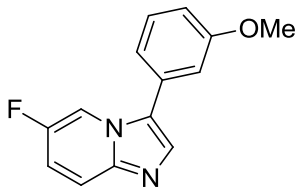




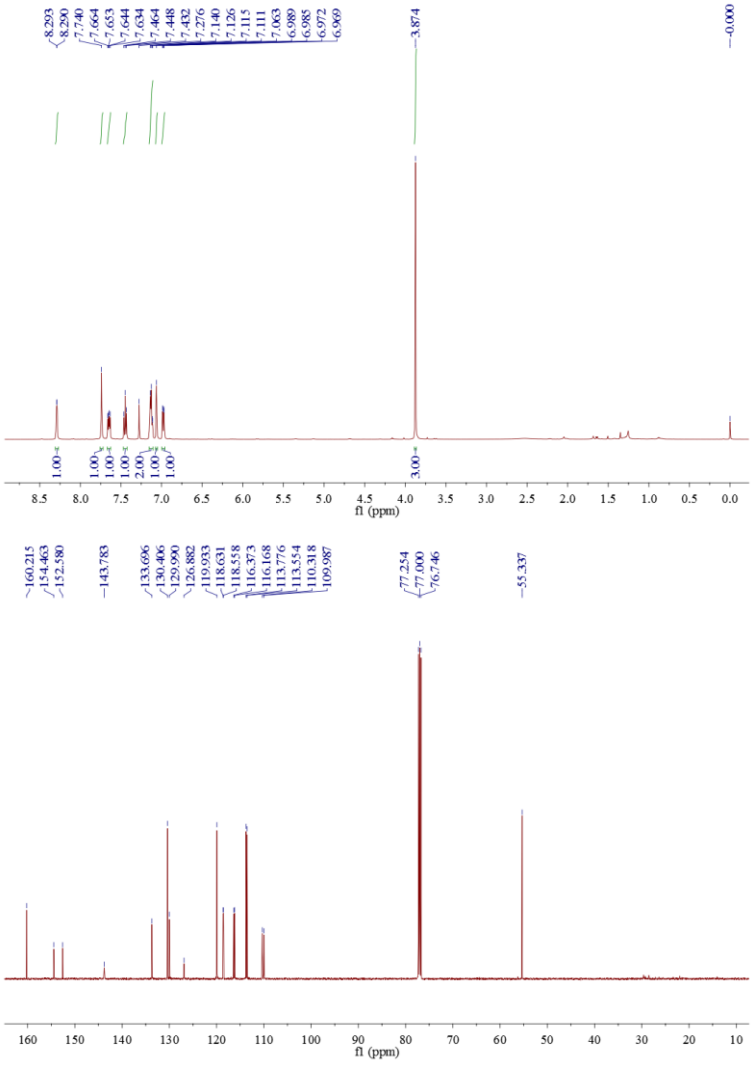
Compound **4ac**:[3] brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.26 (dd, J = 4.0, 2.0 Hz, 1H), 7.74 (s, 1H), 7.65 (dd, J = 10.0, 5.5 Hz, 1H), 7.56-7.52 (m, 4H), 7.47-7.43 (m, 1H), 7.15-7.11 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6 (d, $J_{C\text{-}F}$ = 235.25 Hz), 143.8, 133.7 (d, $J_{C\text{-}F}$ = 1.875 Hz), 129.3, 128.8, 128.5, 127.8, 127.0, 118.6 (d, $J_{C\text{-}F}$ = 9.125 Hz), 116.3 (d, $J_{C\text{-}F}$ = 25.625 Hz), 110.2, 109.8.

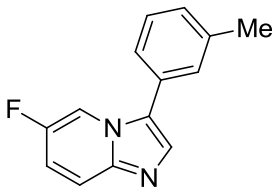




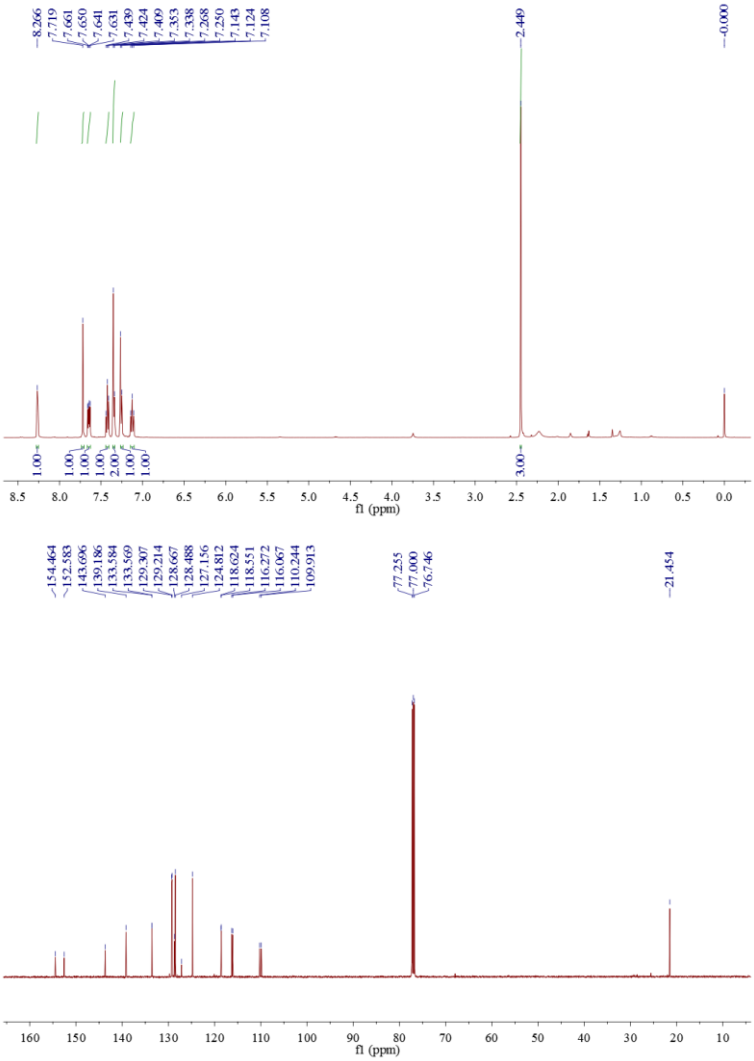


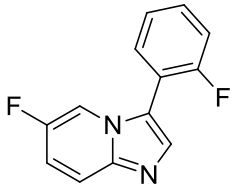
Compound **4ad**: yellow solid. mp: 86-87 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.29 (d, *J* = 1.5 Hz, 1H), 7.74 (s, 1H), 7.65 (dd, *J* = 10.0, 5.5 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.14-7.11 (m, 2H), 7.06 (s, 1H), 6.98 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 153.5 (d, $J_{C\text{-}F}$ = 235.375 Hz), 143.8, 133.7, 130.4, 130.0, 126.9, 119.9, 118.6 (d, $J_{C\text{-}F}$ = 9.125 Hz), 116.3 (d, $J_{C\text{-}F}$ = 25.625 Hz), 113.7 (d, $J_{C\text{-}F}$ = 27.75 Hz), 110.3, 110.0, 55.3. MS (ESI): 243 $[M+H]^+$; HRMS (ESI) calcd for $C_{14}H_{12}FN_2O$ $[M+H]^+$: 243.0928; found: 243.0963; IR (neat) ν 1652, 1599, 1585, 1540, 1503, 1483, 1461, 1441, 1329, 1304, 1259, 1239, 1219, 1146, 1121, 1039, 954, 859, 831, 817, 800, 789, 762 cm^{-1}.





Compound **4ae**: brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.27 (s, 1H), 7.72 (s, 1H), 7.65 (dd, *J* = 10.0, 5.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.25 (s, 1H), 7.12 (t, *J* = 9.5 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5 (d, $J_{C\text{-}F}$ = 235.125 Hz), 143.7, 139.2, 133.6 (d, $J_{C\text{-}F}$ = 1.875 Hz), 129.3 (d, $J_{C\text{-}F}$ = 11.625 Hz), 128.7, 128.5, 127.2, 124.8, 118.6 (d, $J_{C\text{-}F}$ = 9.125 Hz), 116.2 (d, $J_{C\text{-}F}$ = 25.625 Hz), 110.2, 109.9, 21.5. MS (ESI): 227 $[M+H]^+$; HRMS (ESI) calcd for $C_{14}H_{12}FN_2$ $[M+H]^+$: 227.0979; found: 227.0997; IR (neat) ν 1652, 1604, 1594, 1503, 1326, 1306, 1292, 1253, 1225, 1197, 1146, 1118, 1101, 948, 852, 816, 788, 757 cm^{-1}.





Compound **4af**: brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.95-7.93 (m, 1H), 7.77 (s, 1H), 7.66 (dd, J = 9.5, 5.0 Hz, 1H), 7.51-7.43 (m, 2H), 7.31-7.24 (m, 2H), 7.18-7.13 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6 (d, $J_{C\text{-}F}$ = 247.5 Hz), 153.3 (d, $J_{C\text{-}F}$ = 235.25 Hz), 143.9, 134.9, 130.9 (d, $J_{C\text{-}F}$ = 3.125 Hz), 130.6 (d, $J_{C\text{-}F}$ = 8.125 Hz), 124.8 (d, $J_{C\text{-}F}$ = 3.625 Hz), 121.4, 118.3 (d, $J_{C\text{-}F}$ = 9.125 Hz), 116.5 (d, $J_{C\text{-}F}$ = 15.0 Hz), 116.34 (d, $J_{C\text{-}F}$ = 25.625 Hz), 116.27 (d, $J_{C\text{-}F}$ = 21.25 Hz), 111.2 (d, $J_{C\text{-}F}$ = 4.75 Hz), 110.9 (d, $J_{C\text{-}F}$ = 4.875 Hz). MS (ESI): 231 $[M+H]^+$; HRMS (ESI) calcd for $C_{13}H_9F_2N_2$ $[M+H]^+$: 231.0728; found: 231.0736; IR (neat) ν 1652, 1545, 1529, 1506, 1467, 1336, 1299, 1266, 1229, 1199, 1159, 1129, 1084, 950, 867, 842, 814, 794, 755 cm^{-1}.