Supporting Information for

Discovery of a Tetraarylhydrazine Catalyst for Electrocatalytic Synthesis of Imidazo-Fused N-Heteroaromatic Compounds

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Contents

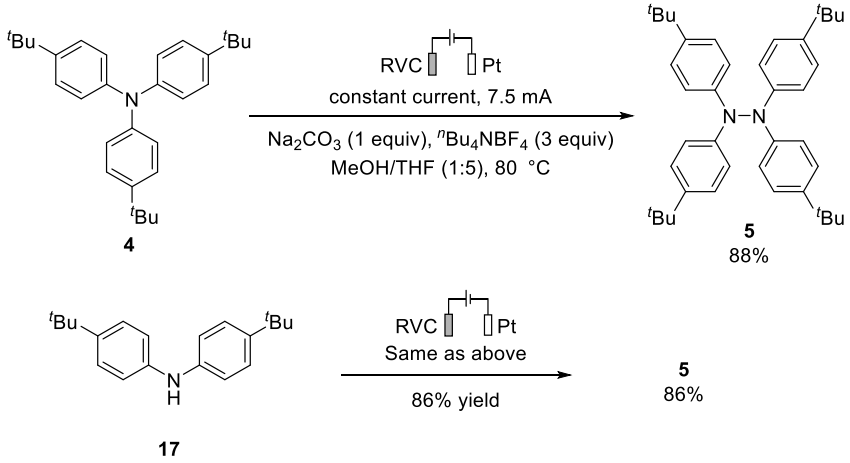
1. General Information

Anhydrous tetrahydrofuran was obtained by distillation under argon from sodium/benzophenone. Flash column chromatography was performed with silica gel (230–400 mesh). NMR spectra were recorded on Bruker AV-500 instruments. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.2 ppm) for ^{13}C. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectra (ESI HRMS) were recorded on a Micromass QTOF2 Quadruple/Time-of-FLight Tandem mass spectrometer by the instrumentation center of Department of Chemistry, Xiamen University. Cyclic voltammograms were obtained on a CHI 760E potentiostat. Infrared spectra (IR) were recorded on a Nicolet AVATER FTIR330 spectrometer.

2. General Procedure for the Electrolysis.

A 25 mL three-necked round-bottomed flask was charged with **4** or **5** (0.015 mmol), the carbamates (0.3 mmol), Et_4NBF_4 (0.3 mmol), and Na_2CO_3 (0.3 mmol). The flask was equipped with a condenser, a reticulated vitreous carbon (100 PPI, 1 cm x 1 cm x 1.2 cm) anode and a platinum plate (1 cm x 1 cm) cathode and then flushed with argon. THF (7.5 mL) and MeOH (2.5 mL) were added. The electrolysis was carried out at 80 °C (oil bath temperature) using a constant current of 7.5 mA until complete consumption of the substrate (monitored by TLC or ^{1}H NMR). The reaction mixture was cooled to RT and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired product.

3. Synthesis of 5 by Electrolyzing 4 and 17



A 25 mL three-necked round-bottomed flask was charged with **4** or **17** (0.3 mmol), $^{n}Bu_4NBF_4$ (0.9 mmol), and Na_2CO_3 (0.3 mmol). The flask was equipped with a condenser, a reticulated vitreous carbon (100 PPI, 1 cm x 1 cm x 1.2 cm) anode and a platinum plate (1 cm x 1 cm) cathode and then flushed with argon. THF (7.5 mL) and MeOH (1.5 mL) were added.

The electrolysis was carried out at 80 °C (oil bath temperature) using a constant current of 7.5 mA until complete consumption of the substrate (monitored by TLC or ^{1}H NMR). The reaction mixture was cooled to RT and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired product **5** as white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.16 (m, 16H), 1.26 (s, 36H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 141.9, 125.9, 117.7, 34.3, 31.6; IR (neat, cm^{-1}): 3361, 2962, 2867, 1605, 1511, 1364, 1266, 1115, 824; HRMS (ESI, *m/z*) calcd for $C_{40}H_{52}N_2Na$ ($M+Na^+$): 583.4023, obsd 583.4028.

4. Cyclic Voltammograms Studies

The cyclic voltammograms was recorded at rt in an electrolyte of Et_4NBF_4 (0.1 M) using a glassy carbon disk working electrode (diameter, 1 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate was 100 mV/s.

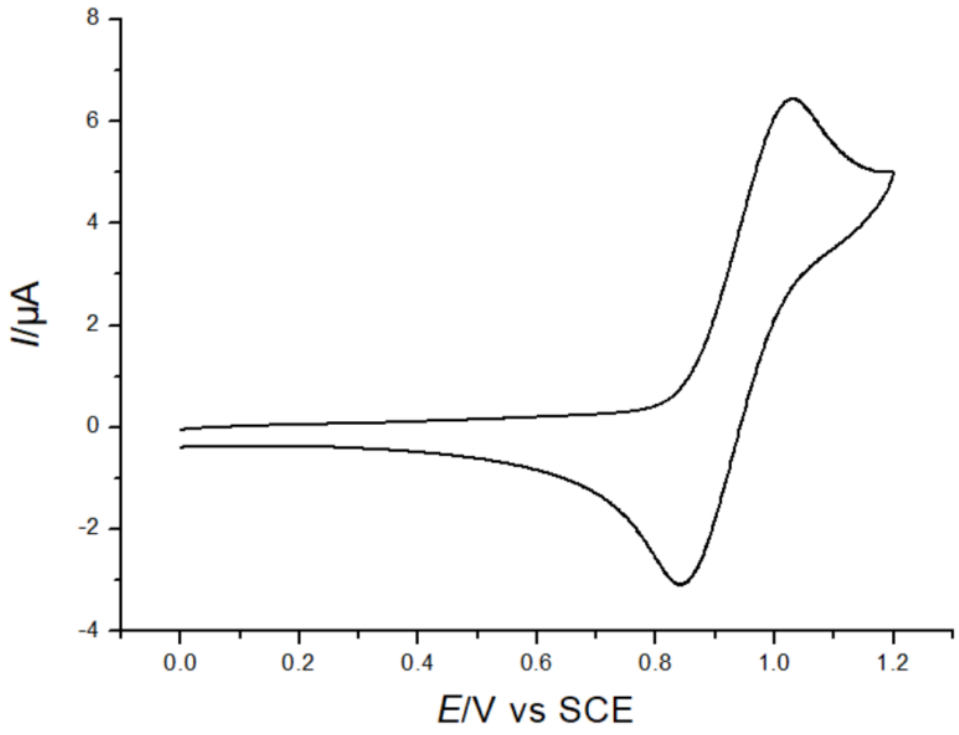


Figure S1. Cyclic voltammogram of **4** (3 mM) in MeOH/THF (1:3). $E_{p/2}$ = 0.92 V.

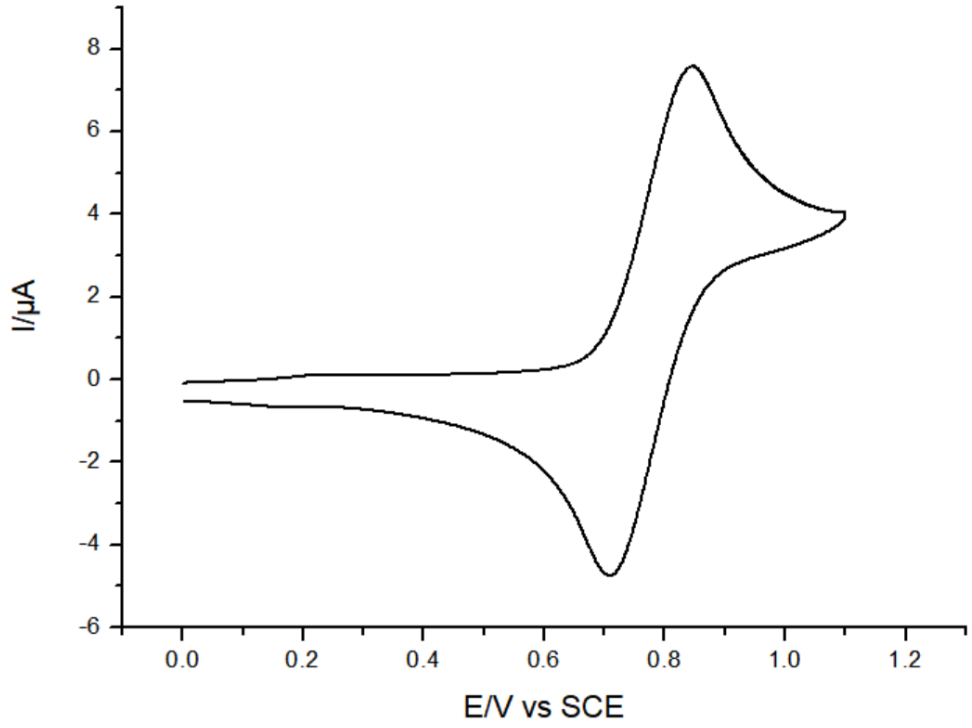


Figure S2. Cyclic voltammogram of **5** (3 mM) in MeOH/THF (1:3). $E_{p/2}$ = 0.76 V.

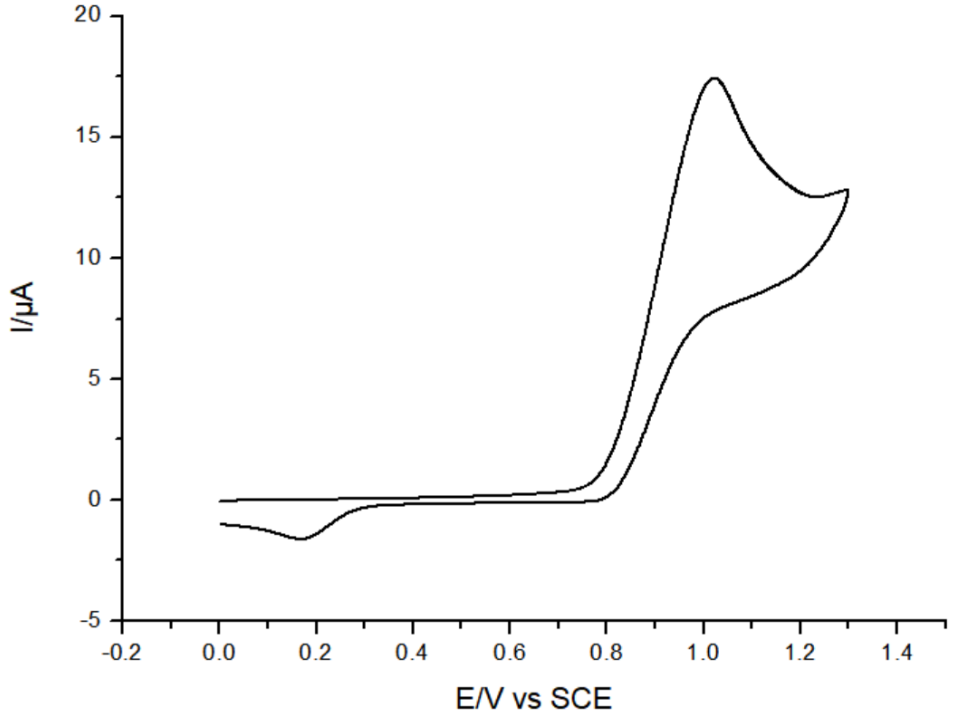
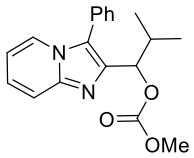
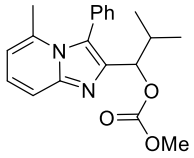


Figure S3. Cyclic voltammogram of **17** (3 mM) in MeOH/THF (1:3). $E_{p/2}$ = 0.89 V.

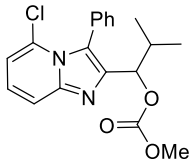
5. Characterization Data for Electrolysis Products.



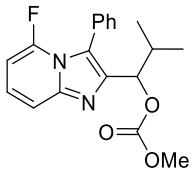
Methyl (2-methyl-1-(3-phenylimidazo[1,2-*a*]pyridin-2-yl)propyl) carbonate (7). Yield = 87%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98–7.91 (m, 1H), 7.64 (dt, *J* = 9.1, 1.1 Hz, 1H), 7.56 (d, *J* = 4.5 Hz, 4H), 7.52–7.45 (m, 1H), 7.22–7.14 (m, 1H), 6.76–6.68 (m, 1H), 5.45 (d, *J* = 8.7 Hz, 1H), 3.68 (s, 3H), 2.53–2.42 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 144.9, 141.2, 130.5, 129.4, 129.0, 128.7, 124.7, 123.6, 123.5, 118.1, 112.4, 79.3, 54.6, 32.8, 18.9 (2C); IR (neat, cm^{-1}): 2960, 2927, 2872, 1745, 1634, 1506, 1442, 1345, 1262, 967, 754, 702; HRMS (ESI, *m/z*) calcd for $C_{19}H_{20}N_2O_3Na$ ($M+Na^+$): 347.1366, obsd 347.1368.



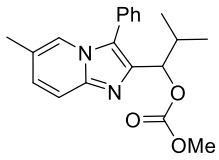
Methyl (2-methyl-1-(5-methyl-3-phenylimidazo[1,2-*a*]pyridin-2-yl)propyl) carbonate (18). Yield = 82%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68–7.62 (m, 1H), 7.60–7.54 (m, 1H), 7.51–7.44 (m, 2H), 7.44–7.36 (m, 1H), 7.34–7.30 (m, 1H), 7.13–7.05 (m, 1H), 6.44 (dt, *J* = 6.8, 1.2 Hz, 1H), 5.13 (d, *J* = 8.9 Hz, 1H), 3.67 (s, 3H), 2.52–2.38 (m, 1H), 2.04 (s, 3H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 146.2, 142.0, 136.7, 133.0, 132.8, 131.1, 129.1, 127.8, 127.2, 124.8, 124.4, 116.2, 113.5, 79.0, 54.6, 32.6, 21.6, 19.0, 18.9; IR (neat, cm^{-1}): 2960, 2927, 2872, 1745, 1638, 1516, 1442, 1261, 1082, 966, 770, 704; HRMS (ESI, *m/z*) calcd for $C_{20}H_{22}N_2O_3Na$ ($M+Na^+$): 361.1523, obsd 361.1522.



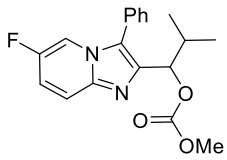
1-(5-Chloro-3-phenylimidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (19). Yield = 80%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68–7.59 (m, 2H), 7.47 (dd, *J* = 5.6, 3.4 Hz, 2H), 7.44–7.36 (m, 1H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.12 (dd, *J* = 9.0, 7.2 Hz, 1H), 6.76 (d, *J* = 7.2 Hz, 1H), 5.18 (d, *J* = 8.7 Hz, 1H), 3.68 (s, 3H), 2.48–2.37 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.76 (d, *J* = 6.7Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 146.6, 143.0, 133.0, 132.4, 130.0, 129.0, 127.7, 127.1 (2C), 124.9, 124.5, 116.8, 114.0, 78.6, 54.6, 32.6, 18.9, 18.8; IR (neat, cm^{-1}): 2960, 2927, 2872, 1746, 1627, 1490, 1442, 1291, 1260, 1083, 969, 766, 704; HRMS (ESI, *m/z*) calcd for $C_{19}H_{19}ClN_2O_3Na$ ($M+Na^+$):381.0976, obsd 381.0977.



1-(5-Fluoro-3-phenylimidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (20). Yield = 44%; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76–7.62 (m, 1H), 7.54–7.43 (m, 4H), 7.36 (s, 1H), 7.21–7.14 (m, 1H), 6.39–6.32 (m, 1H), 5.29 (d, *J* = 8.8 Hz, 1H), 3.69 (s, 3H), 2.48–2.37 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 150.6 (d, $J_{C–F}$ = 269.7 Hz), 146.9 (d, $J_{C–F}$ = 4.0 Hz), 142.3, 131.2, 129.3 (d, $J_{C–F}$ = 2.8 Hz), 128.8, 128.0 (d, $J_{C–F}$ = 58.7 Hz), 125.2 (d, $J_{C–F}$ = 6.5 Hz), 122.0 (d, $J_{C–F}$ = 2.3 Hz), 113.8 (d, $J_{C–F}$ = 4.9 Hz), 93.3 (d, $J_{C–F}$ = 17.1 Hz), 78.6, 54.7, 32.8, 18.8 (2C); ^{19}F NMR (471 MHz, $CDCl_3$) δ −102.0 (t, *J* = 6.4 Hz); IR (neat, cm^{-1}): 2959, 2920, 1745, 1655, 1519, 1442, 1290, 1259; HRMS (ESI, *m/z*) calcd for $C_{19}H_{19}FN_2O_3Na$ ($M+Na^+$): 365.1272, obsd 365.1272.

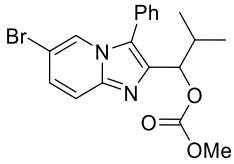


Methyl (2-methyl-1-(6-methyl-3-phenylimidazo[1,2-*a*]pyridin-2-yl)propyl) carbonate (21). Yield = 75%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.59–7.52 (m, 5H), 7.51–7.43 (m, 1H), 7.07–7.00 (m, 1H), 5.42 (d, *J* = 8.8 Hz, 1H), 3.68 (s, 3H), 2.55–2.40 (m, 1H), 2.24 (s, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.74 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 144.0, 140.9, 130.5, 129.3, 128.9, 128.9, 127.9, 123.2, 122.0, 121.1, 117.4, 79.3, 54.6, 32.8, 18.9 (2C), 18.4; IR (neat, cm^{-1}): 2919, 2927, 2872, 1644, 1490, 1417, 1300, 1083, 969, 766, 704; HRMS (ESI, *m/z*) calcd for $C_{20}H_{23}N_2O_3$ ($M+H^+$):339.1703, obsd 339.1703.

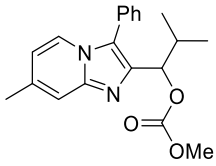


1-(6-Fluoro-3-phenylimidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (22). Yield = 80%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 4.4, 2.4 Hz, 1H), 7.66–7.46 (m, 6H), 7.15–7.07 (m, 1H), 5.43 (d, *J* = 8.6 Hz, 1H), 3.69 (s, 3H), 2.50–2.39 (m, 1H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 154.4, 152.5, 142.5, 130.2, 129.5, 129.3, 128.1, 124.8 (d, $J_{C–F}$ = 2.2 Hz), 118.6 (d, $J_{C–F}$ = 9.1 Hz), 116.8 (d, $J_{C–F}$ = 25.8 Hz), 110.1 (d, $J_{C–F}$ = 41.4 Hz), 79.1, 54.7, 32.8, 18.8 (2C); ^{19}F NMR (471 MHz, $CDCl_3$) δ –140.0; IR (neat, cm^{-1}): 2961, 2927, 2872, 1745, 1656, 1535, 1441,

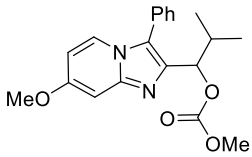
1395, 1261, 1134, 1083, 970, 766, 704; HRMS (ESI, *m/z*) calcd for $C_{19}H_{19}FN_2O_3Na$ ($M+Na^+$): 365.1272, obsd 365.1270.



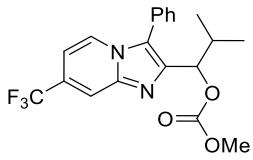
1-(6-Bromo-3-phenylimidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (23). Yield = 86%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.7 Hz, 1H), 7.61–7.50 (m, 6H), 7.24 (dd, *J* = 9.5, 1.9 Hz, 1H), 5.40 (d, *J* = 8.7 Hz, 1H), 3.69 (s, 3H), 2.49–2.38 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.74 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 143.3, 142.1, 130.5, 129.6, 129.4, 128.2, 128.0, 123.9, 123.7, 118.8, 107.3, 79.0, 54.8, 32.9, 18.9 (2C) ; IR (neat, cm^{-1}): 2958, 1498, 1441, 1284, 1260, 1196, 1132; HRMS (ESI, *m/z*) calcd for $C_{19}H_{19}BrN_2O_3Na$ ($M+Na^+$): 425.0471, obsd 425.0473.



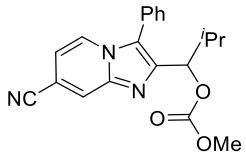
Methyl (2-methyl-1-(7-methyl-3-phenylimidazo[1,2-*a*]pyridin-2-yl)propyl) carbonate (24). Yield = 79%; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.0 Hz, 1H), 7.58–7.51 (m, 4H), 7.49–7.44 (m, 1H), 7.39 (s, 1H), 6.56 (dd, *J* = 7.0, 1.6 Hz, 1H), 5.41 (d, *J* = 8.8 Hz, 1H), 3.68 (s, 3H), 2.52–2.43 (m, 1H), 2.38 (s, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.74 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 145.4, 140.7, 135.7, 130.4, 129.3, 128.8 (2C), 123.0, 122.9, 116.4, 115.0, 79.4, 54.7, 32.8, 21.5, 19.0, 18.9; IR (neat, cm^{-1}): 2958, 1744, 1648, 1506, 1442, 1288, 1261; HRMS (ESI, *m/z*) calcd for $C_{20}H_{22}N_2O_3Na$ ($M+Na^+$): 361.1523, obsd 361.1523.



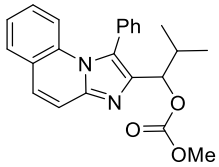
1-(7-Methoxy-3-phenylimidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (25). Yield = 76%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.58–7.42 (m, 5H), 6.91 (d, *J* = 2.5 Hz, 1H), 6.45 (dd, *J* = 7.5, 2.5 Hz, 1H), 5.38 (d, *J* = 8.8 Hz, 1H), 3.85 (s, 3H), 3.69 (s, 3H), 2.53–2.42 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 155.7, 146.4, 140.3, 130.4, 129.3, 128.8, 128.7, 124.1, 122.6, 107.5, 95.0, 79.4, 55.6, 54.6, 32.7, 19.0, 18.9; IR (neat, cm^{-1}): 2959, 2927, 2872, 1744, 1650, 1477, 1441, 1288, 1262, 1216, 966, 766, 704; HRMS (ESI, *m/z*) calcd for $C_{20}H_{22}N_2O_4Na$ ($M+Na^+$): 377.1472, obsd 377.1472.



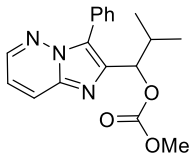
Methyl (2-methyl-1-(3-phenyl-7-(trifluoromethyl)imidazo[1,2-*a*]pyridin-2-yl)propyl) carbonate (26). Yield = 87%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.3 Hz, 1H), 7.89 (s, 1H), 7.54–7.43 (m, 5H), 6.83 (dd, *J* = 7.3, 1.7 Hz, 1H), 5.36 (d, *J* = 8.6 Hz, 1H), 3.62 (s, 3H), 2.42–2.31 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.68 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 143.6, 143.0, 130.4, 129.7, 129.6, 127.8, 126.6 (q, $J_{C–F}$ = 34.0 Hz), 124.9, 124.5, 123.5 (q, $J_{C–F}$ = 272.0 Hz), 116.2 (q, $J_{C–F}$ = 4.9 Hz), 108.4 (q, $J_{C–F}$ = 2.8 Hz), 78.9, 54.8, 32.9, 18.8 (2C); ^{19}F NMR (471 MHz, $CDCl_3$) δ −63.6; IR (neat, cm^{-1}): 2920, 1747, 1645, 1258, 1196, 1132, 1077; HRMS (ESI, *m/z*) calcd for $C_{20}H_{19}F_3N_2O_3Na$ ($M+Na^+$): 415.1240, obsd 415.1240.



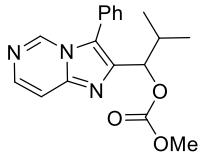
1-(7-Cyano-3-phenylimidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (27). Yield = 65%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 8.01 (d, *J* = 7.1, 1.0 Hz, 1H), 7.64–7.51 (m, 5H), 6.88 (dd, *J* = 7.2, 1.6 Hz, 1H), 5.44 (d, *J* = 8.4 Hz, 1H), 3.69 (s, 3H), 2.47–2.35 (m, 1H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 144.8, 142.7, 130.3, 129.9, 129.8, 127.2, 125.8, 124.4, 124.4, 117.8, 112.7, 107.4, 78.7, 54.9, 32.9, 18.8; IR (neat, cm^{-1}): 2961, 2225, 1633, 1417, 1132, 1082; HRMS (ESI, *m/z*) calcd for $C_{20}H_{19}N_3O_3Na$ ($M+Na^+$): 372.1319, obsd 372.1318.



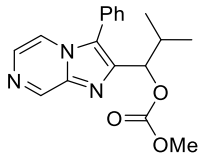
Methyl (2-methyl-1-(1-phenylimidazo[1,2-*a*]quinolin-2-yl)propyl) carbonate (28). Yield = 86%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76–7.69 (m, 2H), 7.65–7.51 (m, 4H), 7.48 (d, *J* = 9.1 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.34–7.26 (m, 1H), 7.23–7.13 (m, 2H), 5.21 (d, *J* = 6.1 Hz, 1H), 3.68 (s, 3H), 2.54–2.42 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.77 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 144.1, 141.0, 134.1, 131.6, 131.5, 131.3, 129.4, 129.3, 129.1, 128.8, 127.9, 126.7 (2C), 124.6, 124.4, 117.7, 116.8, 78.8, 54.5, 32.6, 19.0 (2C); IR (neat, cm^{-1}): 2960, 2927, 2872, 1745, 1621, 1444, 1261, 1132, 1083, 967, 806, 762, 704; HRMS (ESI, *m/z*) calcd for $C_{23}H_{22}N_2O_3Na$ ($M+Na^+$): 397.1523, obsd 397.1522.



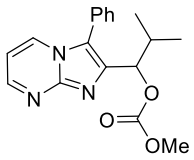
Methyl (2-methyl-1-(3-phenylimidazo[1,2-*b*]pyridazin-2-yl)propyl) carbonate (29). Yield = 74%; Light yellow oil;[1]H NMR (500 MHz, $CDCl_3$) δ 8.32–8.26 (m, 1H), 7.99 (dd, *J* = 9.2, 1.7 Hz, 1H), 7.75–7.69 (m, 2H), 7.58–7.53 (m, 2H), 7.50–7.45 (m, 1H), 7.06 (dd, *J* = 9.2, 4.3 Hz, 1H), 5.60 (d, *J* = 8.6 Hz, 1H), 3.71 (s, 3H), 2.50–2.41 (m, 1H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.76 (d, *J* = 6.7 Hz, 3H); [13]C NMR (126 MHz, $CDCl_3$) δ 155.8, 143.1, 141.8, 138.7, 130.3, 129.0, 128.9, 127.9, 127.3, 126.0, 117.2, 79.1, 54.8, 33.0, 18.9 (2C); IR (neat, cm^{-1}): 2962, 2927, 2872, 1745, 1619, 1489, 1442, 1288, 1261, 1165, 966, 792, 698; HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}N_3O_3Na$ ($M+Na^+$): 348.1319, obsd 348.1317.



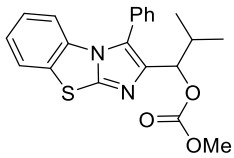
Methyl (2-methyl-1-(3-phenylimidazo[1,2-*c*]pyrimidin-2-yl)propyl) carbonate (30). Yield = 74%; Light yellow oil; [1]H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.98–7.90 (m, 1H), 7.63–7.50 (m, 6H), 5.44 (d, *J* = 8.5 Hz, 1H), 3.69 (s, 3H), 2.51–2.40 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H); [13]C NMR (126 MHz, $CDCl_3$) δ 155.7, 144.3, 142.5, 139.5, 137.9, 130.4, 129.7, 129.6, 127.1, 122.1, 112.7, 78.7, 54.8, 32.8, 18.8; IR (neat, cm^{-1}): 2959, 2927, 2872, 1746, 1650, 1494, 1444, 1385, 1261, 1083, 969, 766, 704; HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}N_3O_3Na$ ($M+Na^+$): 348.1319, obsd 348.1319.



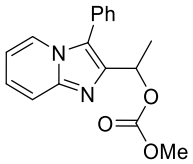
Methyl (2-methyl-1-(3-phenylimidazo[1,2-*a*]pyrazin-2-yl)propyl) carbonate (31). Yield = 80%; Light yellow oil; [1]H NMR (500 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.94–7.88 (m, 1H), 7.83 (d, *J* = 4.7 Hz, 1H), 7.62–7.52 (m, 5H), 5.50 (d, *J* = 8.4 Hz, 1H), 3.70 (s, 3H), 2.49–2.38 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.76 (d, *J* = 6.7 Hz, 3H); [13]C NMR (126 MHz, $CDCl_3$) δ 155.7, 144.4, 143.7, 140.1, 130.1, 129.8, 129.7 (2C), 127.2, 124.7, 116.5, 78.7, 54.8, 33.0, 18.8 (2C) ; IR (neat, cm^{-1}): 2920, 1745, 1659, 1631, 1441, 1286, 1260; HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}N_3NaO_3$ ($M+Na^+$): 348.1319, obsd 348.1320.



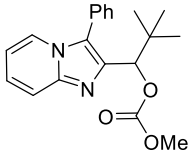
Methyl (2-methyl-1-(3-phenylimidazo[1,2-*a*]pyrimidin-2-yl)propyl) carbonate (32). Yield = 72%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 4.0, 2.0 Hz, 1H), 8.26 (dd, *J* = 6.9, 2.0 Hz, 1H), 7.61–7.50 (m, 5H), 6.83 (dd, *J* = 6.9, 4.0 Hz, 1H), 5.47 (d, *J* = 8.5 Hz, 1H), 3.67 (s, 3H), 2.61–2.49 (m, 1H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.78 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 150.3, 147.9, 142.7, 131.2, 130.4, 129.6, 129.5, 127.5, 122.0, 108.9, 108.3, 79.1, 54.7, 32.6, 18.9, 18.8; IR (neat, cm^{-1}): 2960, 2927, 2872, 1745, 1618, 1499, 1442, 1287, 1261, 1083, 969, 766, 704; HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}N_3O_3Na$ ($M+Na^+$): 348.1319, obsd 348.1315.



Methyl (2-methyl-1-(3-phenylbenzo[*d*]imidazo[2,1-*b*]thiazol-2-yl)propyl) carbonate (33). Yield = 78%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.63–7.49 (m, 3H), 7.46–7.40 (m, 1H), 7.26–7.20 (m, 1H), 7.14 (td, *J* = 7.8, 7.3, 1.2 Hz, 1H), 6.94–6.87 (m, 1H), 5.20 (d, *J* = 8.9 Hz, 1H), 3.70 (s, 3H), 2.50–2.36 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 147.5, 142.0, 133.0, 131.2, 131.1, 130.7, 129.5, 129.3, 128.8, 128.7, 127.2, 125.8, 124.7, 124.3, 113.7, 79.0, 54.7, 32.5, 19.0 (2C); IR (neat, cm^{-1}): 2960, 2927, 2872, 1745, 1615, 1485, 1305, 1260, 1083, 969, 766, 704; HRMS (ESI, *m/z*) calcd for $C_{21}H_{20}N_2O_3SNa$ ($M+Na^+$): 403.1087, obsd 403.1086.

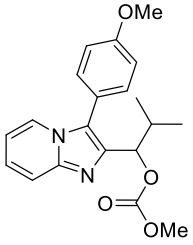


Methyl (1-(3-phenylimidazo[1,2-*a*]pyridin-2-yl)ethyl) carbonate (34). Yield = 77%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03–7.97 (m, 1H), 7.70–7.63 (m, 1H), 7.58–7.46 (m, 5H), 7.23–7.16 (m, 1H), 6.78–6.71 (m, 1H), 5.92 (q, *J* = 6.6 Hz, 1H), 3.69 (s, 3H), 1.73 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 144.9, 142.4, 130.2, 129.5, 129.1, 128.4, 125.0, 123.7, 122.4, 118.2, 112.6, 70.6, 54.7, 20.8; IR (neat, cm^{-1}): 2956, 2925, 1738, 1588, 1440, 1268, 1221, 1086, 757; HRMS (ESI, *m/z*) calcd for $C_{17}H_{16}N_2O_3Na$ ($M+Na^+$): 319.1053, obsd 319.1053.

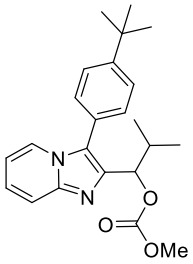


2,2-Dimethyl-1-(3-phenylimidazo[1,2-*a*]pyridin-2-yl)propyl methyl carbonate (35). Yield = 92%; White solid; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.97–7.91 (m, 1H), 7.70–7.53 (m, 5H),

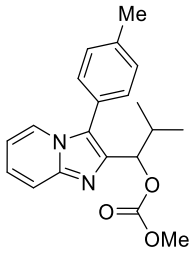
7.47 (dt, *J* = 8.6, 4.3 Hz, 1H), 7.20–7.12 (m, 1H), 6.71 (td, *J* = 6.8, 2.3 Hz, 1H), 5.52 (s, 1H), 3.73 (s, 3H), 0.94 (s, 9H); ^{13}CNMR (126 MHz, $CDCl_3$) δ 156.0, 144.5, 140.2, 130.5, 129.5, 129.1, 128.9, 124.4, 123.7, 123.4, 118.1, 112.3, 80.9, 54.6, 36.3, 26.3; IR (neat, cm^{-1}): 2957, 2868, 1744, 1635, 1506, 1442, 1345, 1268, 963, 752, 703; HRMS (ESI, *m/z*) calcd for $C_{20}H_{22}N_2O_3Na$ ($M+Na^+$): 361.1523, obsd 361.1524.



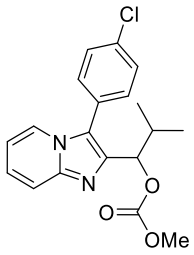
1-(3-(4-Methoxyphenyl)imidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (36). Yield = 83%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.63 (dd, *J* = 9.1, 1.2 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.20–7.15 (m, 1H), 7.11–7.05 (m, 2H), 6.75–6.68 (m, 1H), 5.40 (d, *J* = 8.8 Hz, 1H), 3.89 (s, 3H), 3.69 (s, 3H), 2.53–2.40 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 155.8, 144.8, 141.0, 131.9, 124.6, 123.7, 123.4, 120.6, 118.1, 114.8, 112.3, 79.4, 55.5, 54.7, 32.8, 19.0 (2C) ; IR (neat, cm^{-1}): 2957, 2921, 1744, 1634, 1505, 1441, 1289, 1260; HRMS (ESI, *m/z*) calcd for $C_{20}H_{22}N_2O_4Na$ ($M+Na^+$): 377.1472, obsd 377.1471.



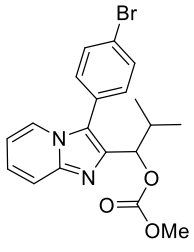
1-(3-(4-(*tert*-Butyl)phenyl)imidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (37). Yield = 79%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.0 Hz, 1H), 7.63 (d, *J* = 9.1 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.20–7.12 (m, 1H), 6.74–6.67 (m, 1H), 5.46 (d, *J* = 8.6 Hz, 1H), 3.68 (s, 3H), 2.54–2.43 (m, 1H), 1.40 (s, 9H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 152.0, 144.9, 141.0, 130.1, 126.3, 125.5, 124.6, 123.8, 123.6, 118.1, 112.2, 79.4, 54.7, 35.0, 32.9, 31.5, 19.0, 18.9; IR (neat, cm^{-1}): 2965, 2930, 2873, 1711, 1601, 1496, 1438, 1308, 1260, 770, 700; HRMS (ESI, *m/z*) calcd for $C_{23}H_{28}N_2O_3Na$ ($M+Na^+$): 403.1992, obsd 403.1994.



Methyl (2-methyl-1-(3-(p-tolyl)imidazo[1,2-*a*]pyridin-2-yl)propyl) carbonate (38). Yield = 82%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96–7.90 (m, 1H), 7.66–7.60 (m, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.20–7.13 (m, 1H), 6.74–6.68 (m, 1H), 5.43 (d, *J* = 8.8 Hz, 1H), 3.69 (s, 3H), 2.52–2.43 (m, 4H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 144.9, 141.0, 139.0, 130.4, 130.1, 125.6, 124.6, 123.7, 123.6, 118.1, 112.3, 79.3, 54.7, 32.8, 21.6, 19.0 (2C); IR (neat, cm^{-1}): 2958, 1744, 1505, 1441, 1343, 1289, 1260; HRMS (ESI, *m/z*) calcd for $C_{20}H_{22}N_2O_3Na$ ($M+Na^+$): 361.1523, obsd 361.1523.

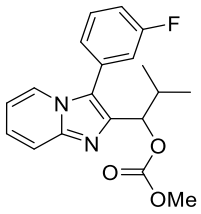


1-(3-(4-Chlorophenyl)imidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (39). Yield = 61%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93–7.88 (m, 1H), 7.67–7.64 (m, 1H), 7.55–7.49 (m, 4H), 7.23–7.18 (m, 1H), 6.76 (t, *J* = 6.8 Hz, 1H), 5.37 (d, *J* = 8.8 Hz, 1H), 3.69 (s, 3H), 2.50–2.43 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.73 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 145.1, 141.5, 135.2, 131.9, 129.8, 127.1, 125.0, 123.4, 122.3, 118.3, 112.7, 79.2, 54.8, 32.8, 19.0, 18.9; IR (neat, cm^{-1}): 2957, 2922, 1743, 1504, 1440, 1290, 1261, 1089; HRMS (ESI, *m/z*) calcd for $C_{19}H_{19}ClN_2O_3Na$ ($M+Na^+$): 381.0976, obsd 381.0976.

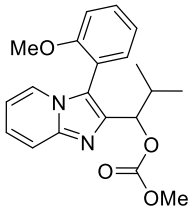


1-(3-(4-Bromophenyl)imidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (40). Yield = 68%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 6.9Hz, 1H), 7.72–7.62 (m, 3H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.24–7.17 (m, 1H), 6.79–6.70 (m, 1H), 5.38 (d, *J*

= 8.7 Hz, 1H), 3.69 (s, 3H), 2.54–2.40 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.74 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 145.1, 141.5, 132.7, 132.1, 127.6, 125.0, 123.4, 123.4, 122.3, 118.2, 112.7, 79.2, 54.7, 32.8, 18.9 (2C); IR (neat, cm^{-1}): 2959, 2927, 2872, 1745, 1633, 1581, 1440, 1343,1261, 1083, 966, 745; HRMS (ESI, *m/z*) calcd for $C_{19}H_{19}BrN_2O_3Na$ (M+Na^+): 425.0471, 427.0452; obsd 425.0472, 427.0451.



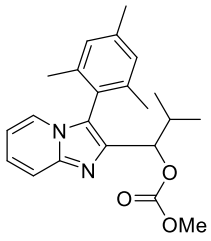
1-(3-(3-Fluorophenyl)imidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (41). Yield = 44%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00–7.94 (m, 1H), 7.69–7.62 (m, 1H), 7.57–7.50 (m, 1H), 7.41–7.36 (m, 1H), 7.35–7.30 (m, 1H), 7.23–7.16 (m, 2H), 6.76 (t, *J* = 6.8, 1.2 Hz, 1H), 5.43 (d, *J* = 8.8 Hz, 1H), 3.70 (s, 3H), 2.53–2.43 (m, 1H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 (d, $J_{C–F}$ = 247.7 Hz), 155.7, 145.1, 141.6, 131.1 (d, $J_{C–F}$ = 8.6 Hz), 130.8 (d, $J_{C–F}$ = 8.5 Hz), 126.2 (d, $J_{C–F}$ = 3.0 Hz), 125.0, 123.5, 122.2 (d, $J_{C–F}$ = 2.2 Hz), 118.2, 117.3 (d, $J_{C–F}$ = 21.8 Hz), 116.0 (d, $J_{C–F}$ = 20.9 Hz), 112.7, 79.1, 54.7, 32.8, 18.9 (2C); ^{19}F NMR (471 MHz, $CDCl_3$) δ −111.3 (d, *J* = 8.3 Hz); IR (neat, cm^{-1}): 2958, 2925, 1744, 1583, 1292, 261, 790; HRMS (ESI, *m/z*) calcd for $C_{19}H_{19}FN_2O_3Na$ (M+Na^+): 365.1272, obsd 365.1272.



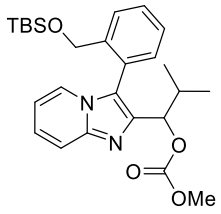
1-(3-(2-Methoxyphenyl)imidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (42). A mixture of stereoisomers were obtained in a ratio of 2.1:1. Yield = 84%; Major isomer: Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.67–7.63 (m, 1H), 7.59–7.55 (m, 1H), 7.52–7.47 (m, 1H), 7.19–7.14 (m, 2H), 7.06–7.03 (m, 1H), 6.72–6.67 (m, 1H), 5.37 (d, *J* = 8.5 Hz, 1H), 3.72 (s, 6H), 2.57–2.48 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.67 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 155.9, 145.1, 141.3, 133.2, 131.0, 125.0, 124.4, 121.4, 120.8, 117.8, 117.1, 111.6, 111.0, 79.4, 55.4, 54.7, 33.1, 18.9, 18.2.

Minor isomer: Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67–7.63 (m, 1H), 7.61 (dd, *J* = 6.8, 1.1 Hz, 1H), 7.52–7.47 (m, 1H), 7.31–7.28 (m, 1H), 7.19–7.14 (m, 1H), 7.12–7.06 (m, 2H), 6.72–6.67 (m, 1H), 5.47 (d, *J* = 8.9 Hz, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 2.57–2.48 (m,

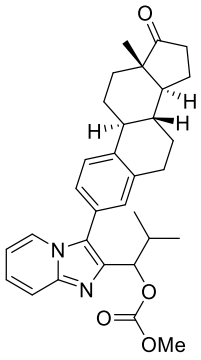
1H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 155.5, 144.8, 141.6, 133.1 (2C), 124.8, 124.5, 120.9 (2C), 117.9, 117.3, 111.8, 111.5, 79.5, 55.6, 54.5, 32.2, 19.4, 18.9; IR (neat, cm^{-1}): 2960, 2922, 1745, 1505, 1440, 1292, 1261, 1022, 754; HRMS (ESI, *m/z*) calcd for $C_{20}H_{22}N_2O_4Na$ ($M+Na^+$): 377.1472, obsd 377.1472.



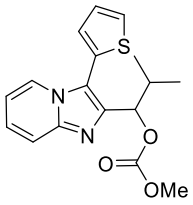
1-(3-Mesitylimidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (43). Yield = 83%; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 9.1 Hz, 1H), 7.39 (d, *J* = 6.7 Hz, 1H), 7.20–7.15 (m, 1H), 7.02 (d, *J* = 11.2 Hz, 2H), 6.73–6.65 (m, 1H), 5.53 (d, *J* = 7.1 Hz, 1H), 3.62 (s, 3H), 2.64–2.51 (m, *J* = 6.7 Hz, 1H), 2.37 (s, 3H), 1.93 (s, 3H), 1.88 (s, 3H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 144.8, 141.7, 140.0, 139.5 (2C), 128.8, 128.6, 124.3, 123.9, 123.3, 121.2, 118.0, 112.3, 79.3, 54.6, 32.3, 21.4, 19.8, 19.7, 19.4, 17.9; IR (neat, cm^{-1}): 2960, 1746, 1505, 1441, 1342, 1263, 948, 756; HRMS (ESI, *m/z*) calcd for $C_{22}H_{26}N_2O_3Na$ ($M+Na^+$): 389.1836, obsd 389.1835.



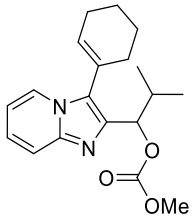
1-(3-(2-(((*tert*-Butyldimethylsilyl)oxy)methyl)phenyl)imidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (44). A mixture of stereoisomers were obtained in a ratio of 0.9:1. Yield = 80%; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72–7.68 (m, 1.9H), 7.65 (dt, *J* = 3.7, 1.1 Hz, 0.9H), 7.63 (dt, *J* = 3.7, 1.1 Hz, 1H), 7.56–7.47 (m, 4.8H), 7.43 (td, *J* = 7.4, 1.4 Hz, 0.9H), 7.38 (td, *J* = 7.5, 1.4 Hz, 1H), 7.20–7.15 (m, 2.8H), 6.70–6.65 (m, 1.9H), 5.39 (d, *J* = 8.0 Hz, 0.9H), 5.30 (d, *J* = 8.3 Hz, 1H), 4.55 (d, *J* = 13.4 Hz, 1H), 4.35 (d, *J* = 13.3 Hz, 0.9H), 4.26 (d, *J* = 2.4 Hz, 1H), 4.23 (d, *J* = 2.3 Hz, 0.9H), 3.64 (s, 2.7H), 3.59 (s, 3H), 2.58–2.51 (m, 0.9H), 2.50–2.42 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 2.7H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.82 (s, 8H), 0.81 (s, 9H), 0.79 (d, *J* = 6.8 Hz, 2.7H), −0.07–−0.10 (m, 5.7H), −0.12 (s, 2.7H), −0.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6 (2C), 144.9 (2C), 142.9, 142.2, 141.6 (2C), 132.4, 132.3, 130.1 (2C), 127.9, 127.8, 127.6, 127.4, 125.7, 125.5, 124.7 (2C), 124.3, 124.2, 121.8, 121.7, 117.9 (2C), 112.3, 112.2, 79.4, 79.1, 62.9, 62.5, 54.7, 54.6, 32.6, 32.5, 26.0 (2C), 19.4, 19.0, 18.7, 18.5, 18.4 (2C), −5.4 (3C), −5.5; IR (neat, cm^{-1}): 2956, 2027, 1747, 1635, 1441, 1262, 1081, 1023, 839; HRMS (ESI, *m/z*) calcd for $C_{26}H_{36}N_2O_4SiNa$ ($M+Na^+$): 491.2337, obsd 491.2336.



Methyl (2-methyl-1-(3-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)imidazo[1,2-*a*]pyridin-2-yl)propyl) carbonate (45). Yield = 79%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–7.97 (m, 1H), 7.97–7.94 (m, 1H), 7.66–7.63 (m, 1H), 7.63–7.60 (m, 1H), 7.47 (s, 1H), 7.46 (s, 1H), 7.34–7.30 (m, 2H), 7.27 (d, *J* = 1.8 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.18–7.14 (m, 2H), 6.74–6.67 (m, 2H), 5.46 (d, *J* = 3.5 Hz, 1H), 5.45 (d, *J* = 3.5 Hz, 1H), 3.70 (s, 3H), 3.70 (s, 3H), 3.06–2.95 (m, 4H), 2.57–2.46 (m, 6H), 2.43–2.38 (m, 2H), 2.21–2.06 (m, 6H), 2.04–2.00 (m, 2H), 1.76–1.61 (m, 6H), 1.61–1.51 (m, 6H),, 1.05 (d, *J* = 1.7 Hz, 3H), 1.03 (d, *J* = 1.7 Hz, 3H), 0.97 (s, 6H), 0.77 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.7, 155.7 (2C), 144.8 (2C), 140.9 (2C), 140.6 (2C), 137.5 (2C), 130.9 (2C), 127.7 (2C), 126.3, 125.9, 124.5, 123.7, 123.6 (2C), 118.0, 112.2, 79.2, 54.6, 50.7, 48.1, 44.6, 38.1, 35.9, 32.8 (2C), 31.7, 29.5 (2C), 26.5, 25.7, 21.7, 19.0 (2C), 18.9 (2C), 14.0; IR (neat, cm^{-1}): 2924, 1740, 1635, 1440, 1261, 1083, 755; HRMS (ESI, *m/z*) calcd for $C_{31}H_{36}N_2O_4Na$ ($M+Na^+$): 501.2748, obsd 501.2750.



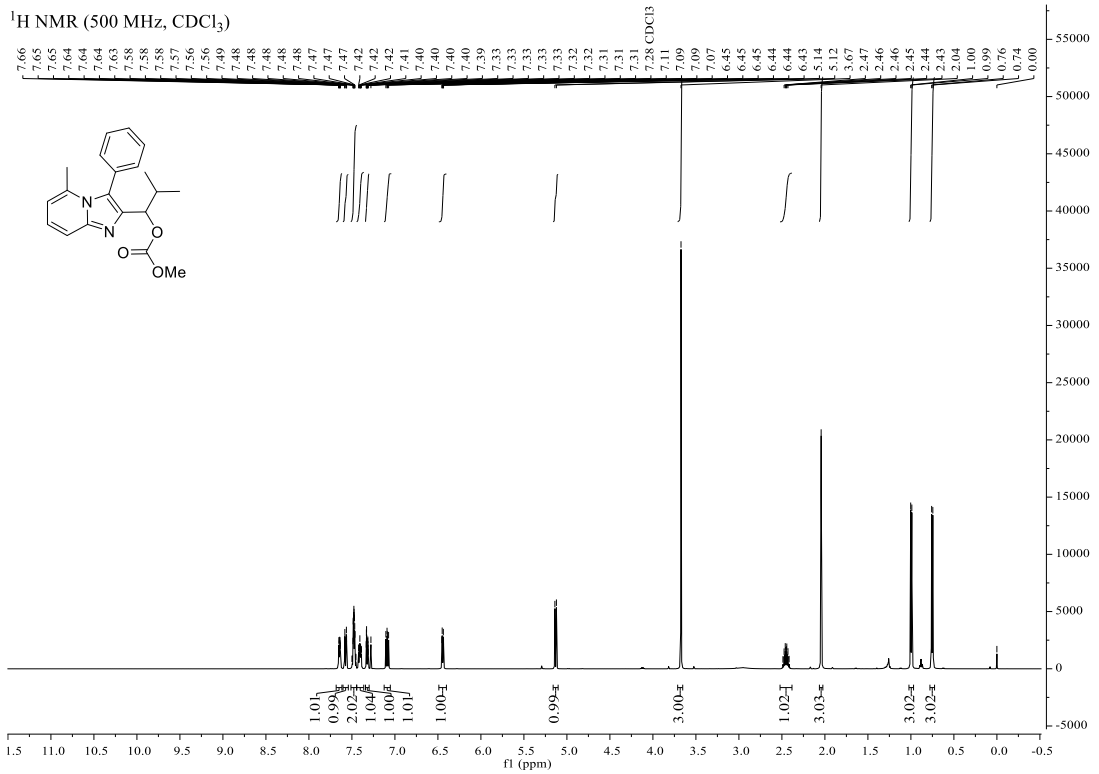
Methyl (2-methyl-1-(3-(thiophen-2-yl)imidazo[1,2-*a*]pyridin-2-yl)propyl) carbonate (46). Yield = 86%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.8 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.60–7.55 (m, 1H), 7.35–7.31 (m, 1H), 7.26–7.16 (m, 2H), 6.92–6.75 (m, 1H), 5.50 (d, *J* = 8.7 Hz, 1H), 3.69 (s, 3H), 2.55–2.43 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 145.5, 143.3, 130.2, 128.5, 128.3, 128.0, 125.3, 124.1, 118.1, 116.4, 112.7, 79.0, 54.7, 32.7, 19.0, 18.9; IR (neat, cm^{-1}): 2959, 2927, 2872, 1745, 1635, 1504, 1441, 1348,1260, 1083, 969, 754; HRMS (ESI, *m/z*) calcd for $C_{17}H_{18}N_2O_3SNa$ ($M+Na^+$): 353.0930, obsd 353.0933.



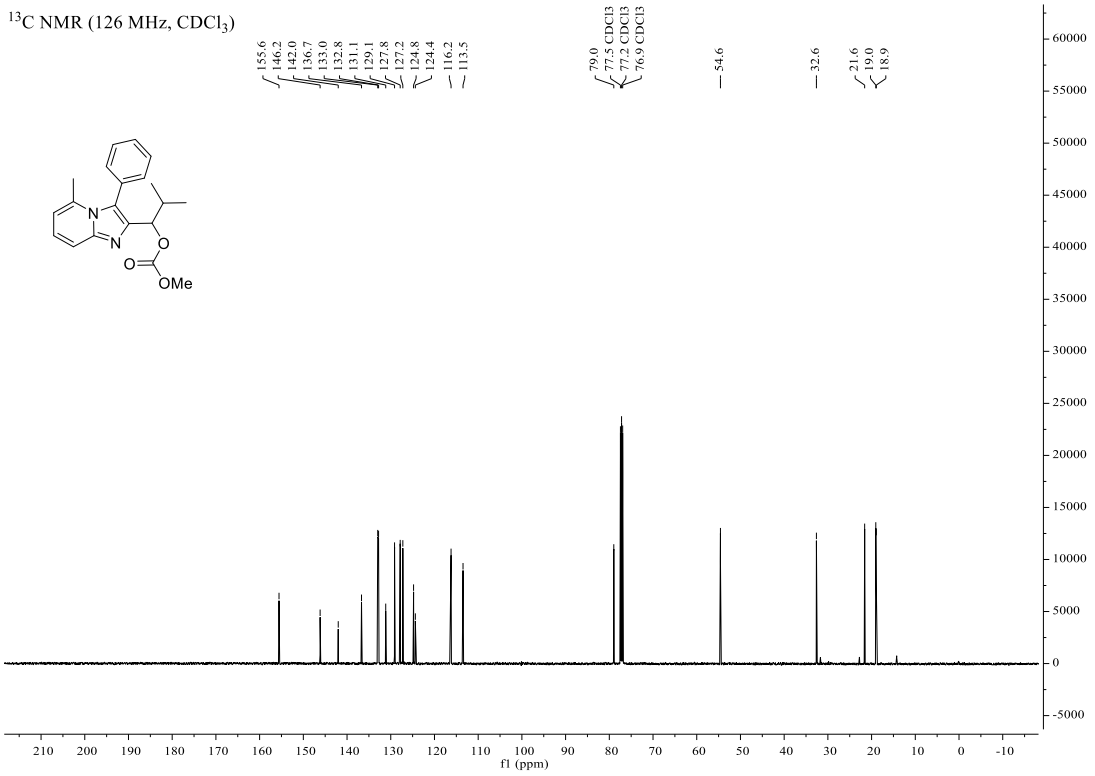
1-(3-(Cyclohex-1-en-1-yl)imidazo[1,2-*a*]pyridin-2-yl)-2-methylpropyl methyl carbonate (47). Yield = 74%; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.57 (dt, *J* = 9.2, 1.2 Hz, 1H), 7.15–7.09 (m, 1H), 6.74 (td, *J* = 6.8, 1.2 Hz, 1H), 6.06–5.99 (m, 1H), 5.48 (d, *J* = 8.9 Hz, 1H), 3.71 (s, 3H), 2.59–2.49 (m, 1H), 2.39–2.32 (m, 1H), 2.31–2.28 (m, 2H), 2.21–2.14 (m, 1H), 1.88–1.76 (m, 4H), 1.10 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 144.4, 139.7, 134.2, 126.3, 125.9, 124.1 (2C), 118.0, 112.0, 79.3, 54.6, 32.5, 28.4, 25.9, 22.9, 22.1, 19.2, 19.0; IR (neat, cm^{-1}): 2926, 1745, 1505, 1441, 1346, 1260; HRMS (ESI, *m/z*) calcd for $C_{19}H_{24}N_2NaO_3Na$ ($M+Na^+$): 351.1679, obsd 351.1679.

6. NMR Spectra for Compounds

Compound 18

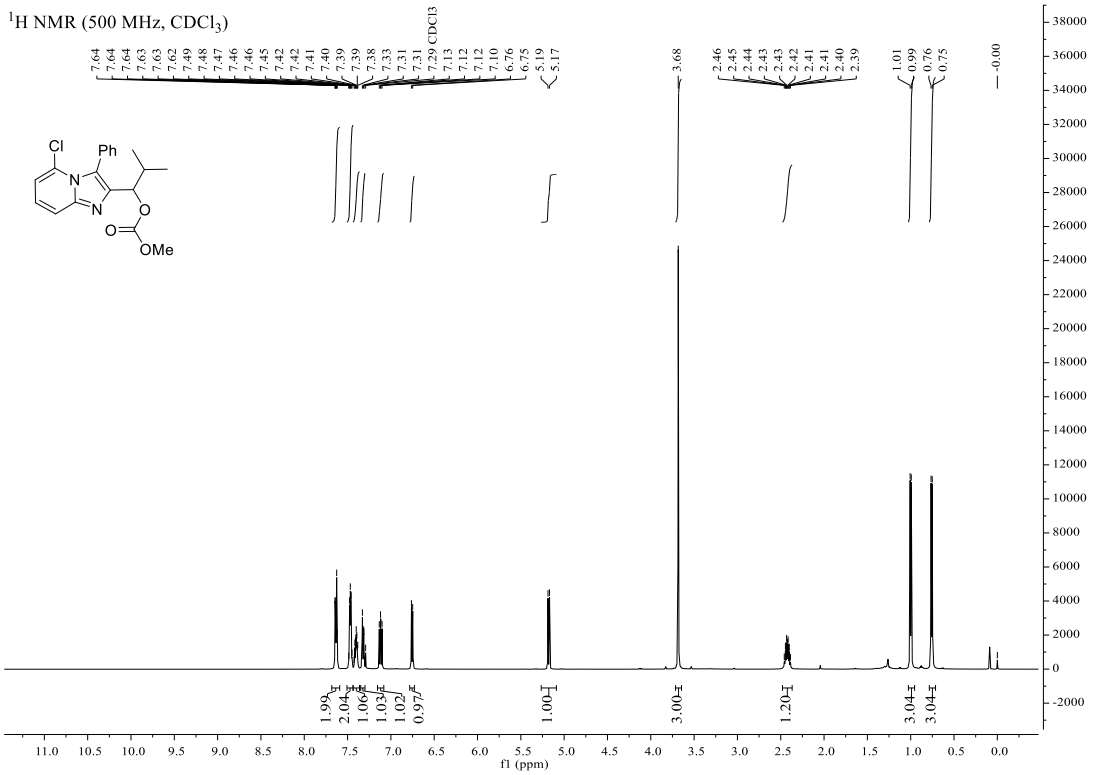


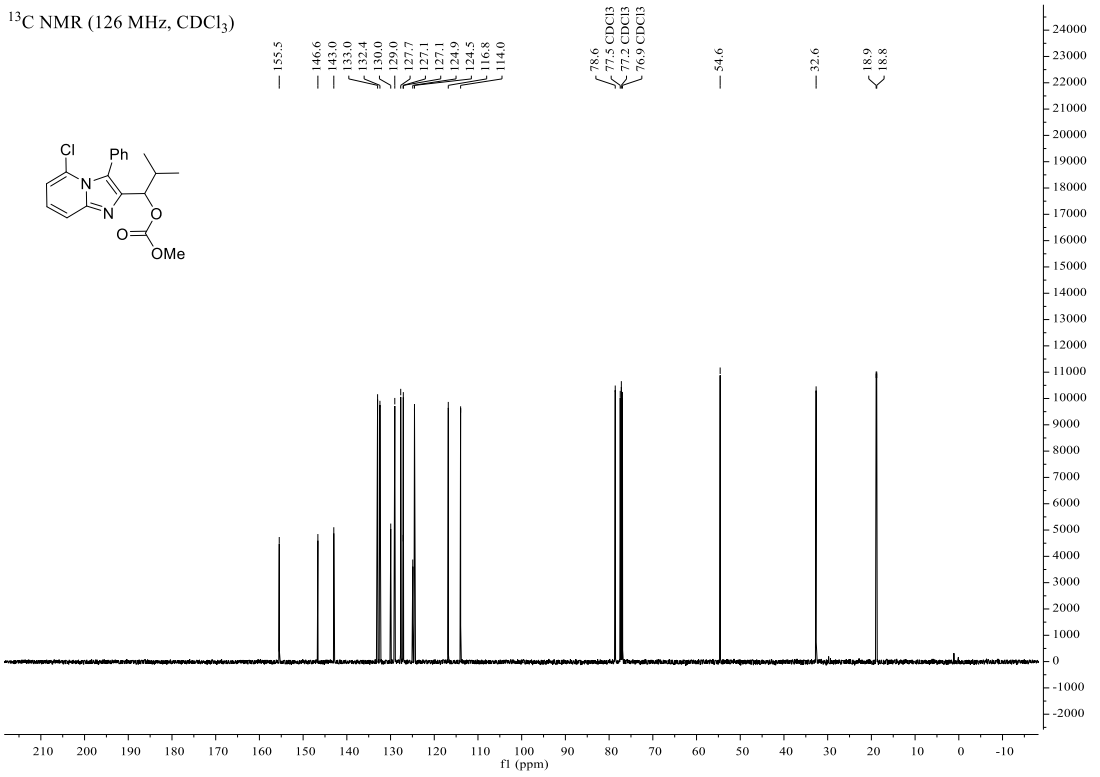
^{13}C NMR (126 MHz, $CDCl_3$)



Compound 19

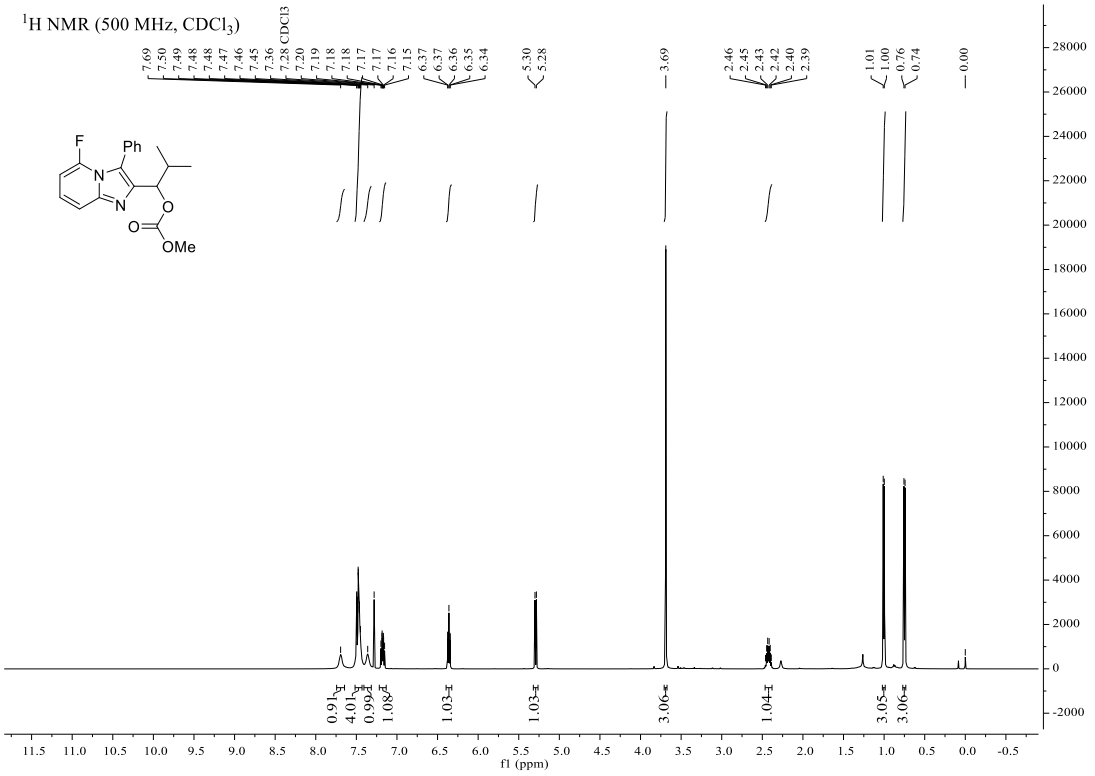
^{1}H NMR (500 MHz, $CDCl_3$)



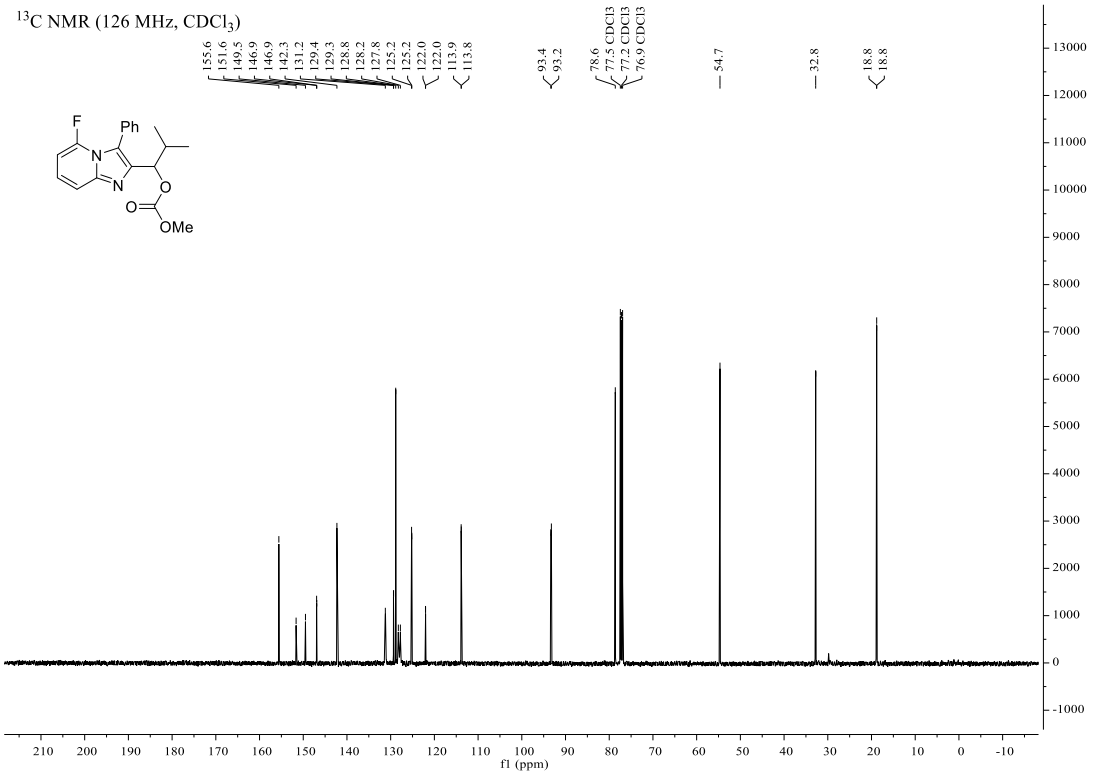

^{13}C NMR (126 MHz, $CDCl_3$)
155.5
146.6
143.0
133.0
132.4
130.0
129.0
127.7
127.1
127.1
124.9
124.5
116.8
114.0
78.6
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
54.6
32.6
18.9
18.8
Cl
Ph
N
N
O
O
OMe
f1 (ppm)

Compound 20

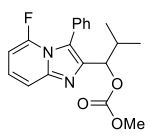
^{1}H NMR (500 MHz, $CDCl_3$)



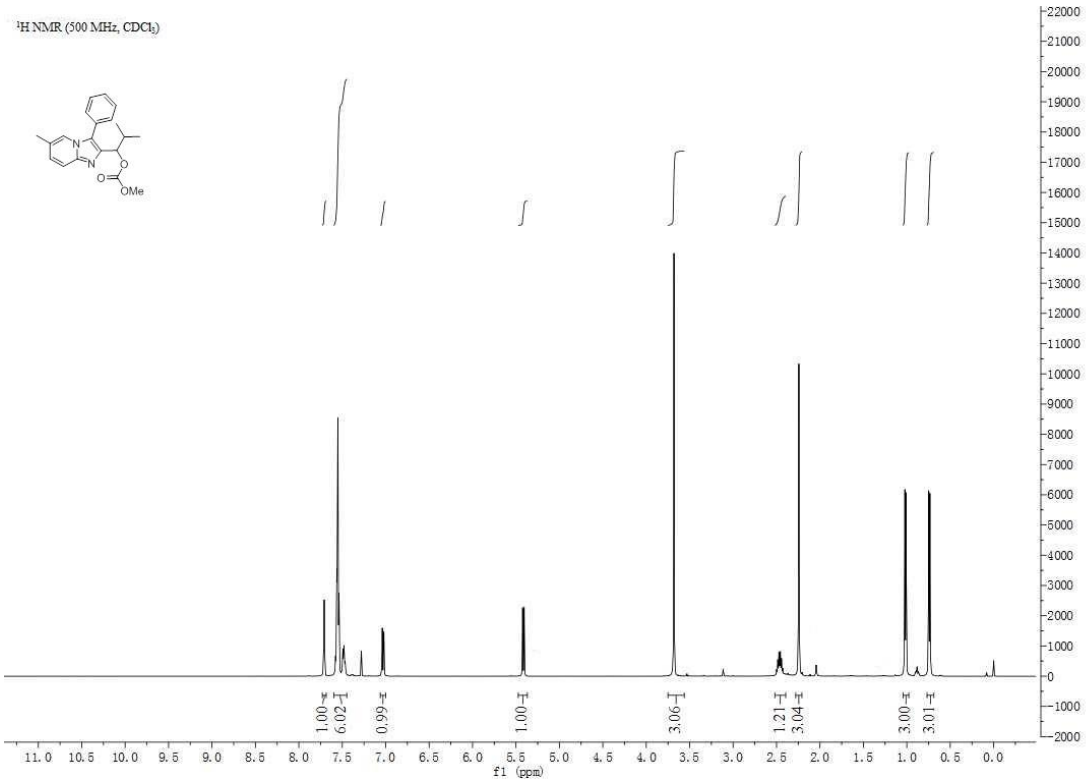
^{13}C NMR (126 MHz, $CDCl_3$)

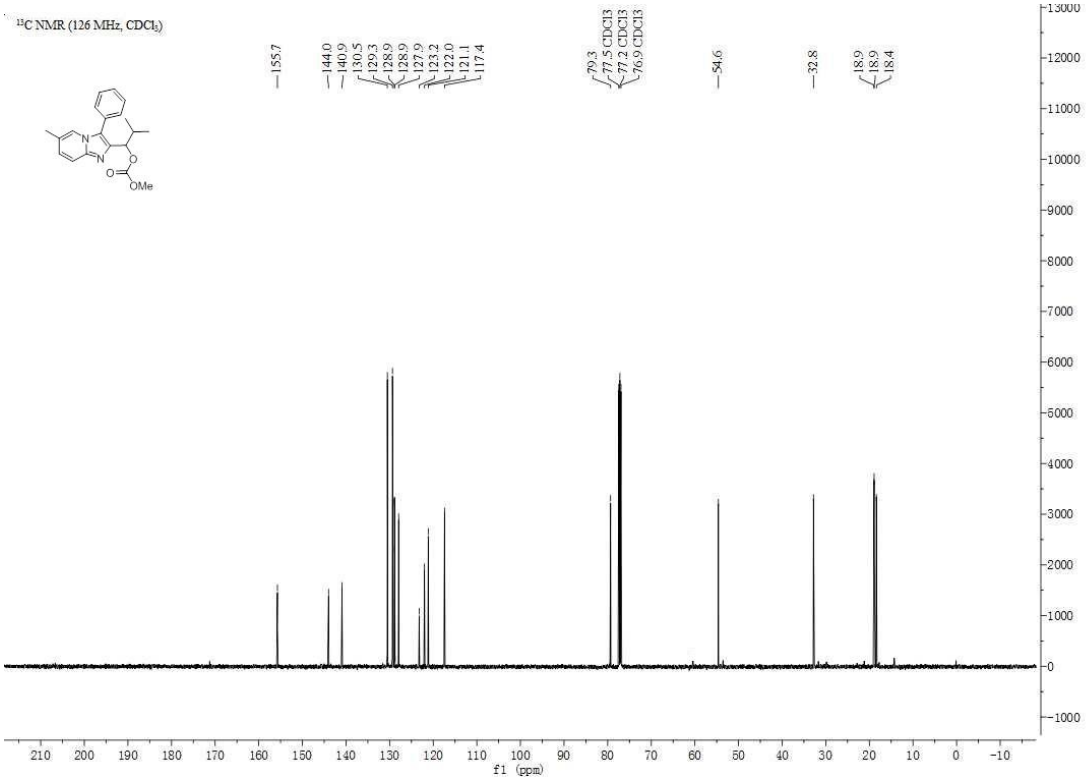


^{19}F NMR (471 MHz, $CDCl_3$)

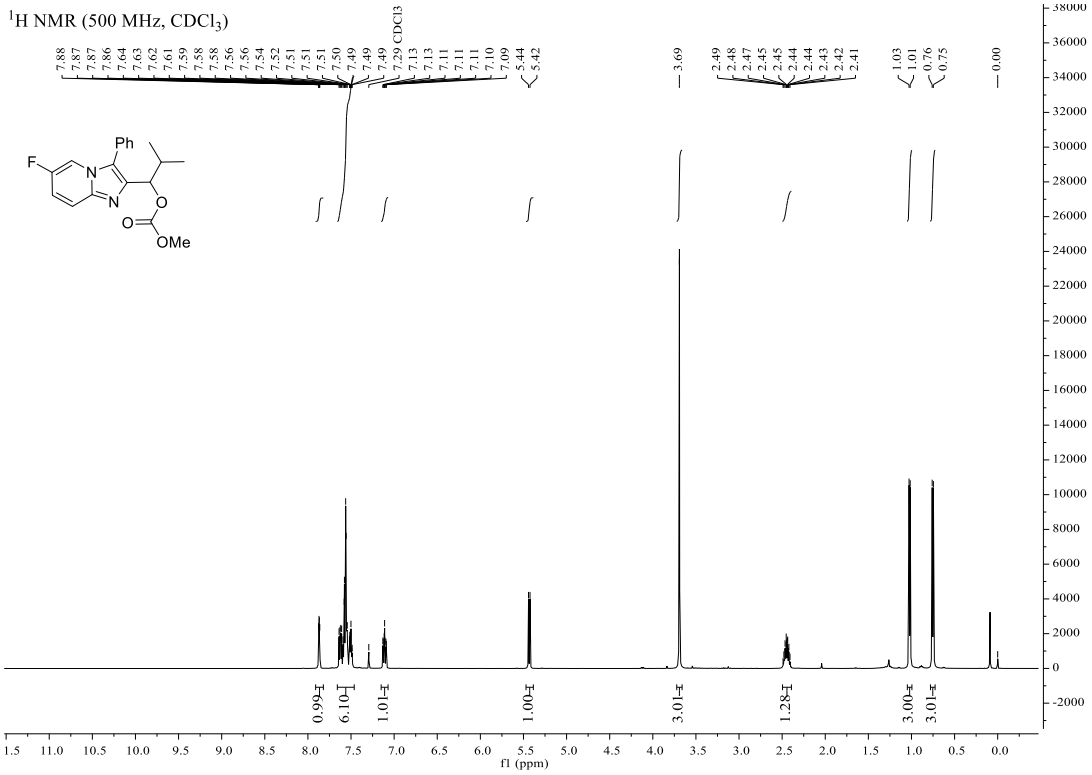


Compound 21

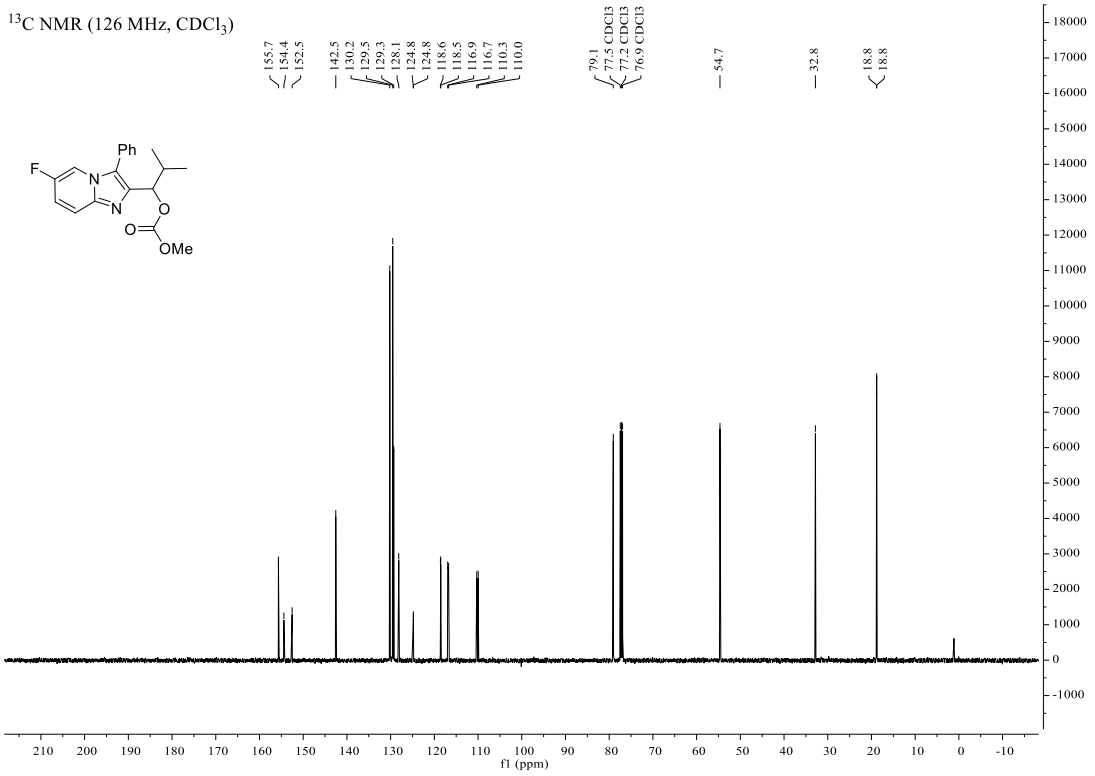

1H NMR (500 MHz, CDCl3)
1.00
6.02
0.99
1.00
3.06
1.21
3.04
3.00
3.01
f1 (ppm)


13C NMR (126 MHz, CDCl3)
155.7
144.0
140.9
130.5
129.3
128.9
128.9
127.9
123.2
122.0
121.1
117.4
79.3
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
54.6
32.8
18.9
18.9
18.4
f1 (ppm)

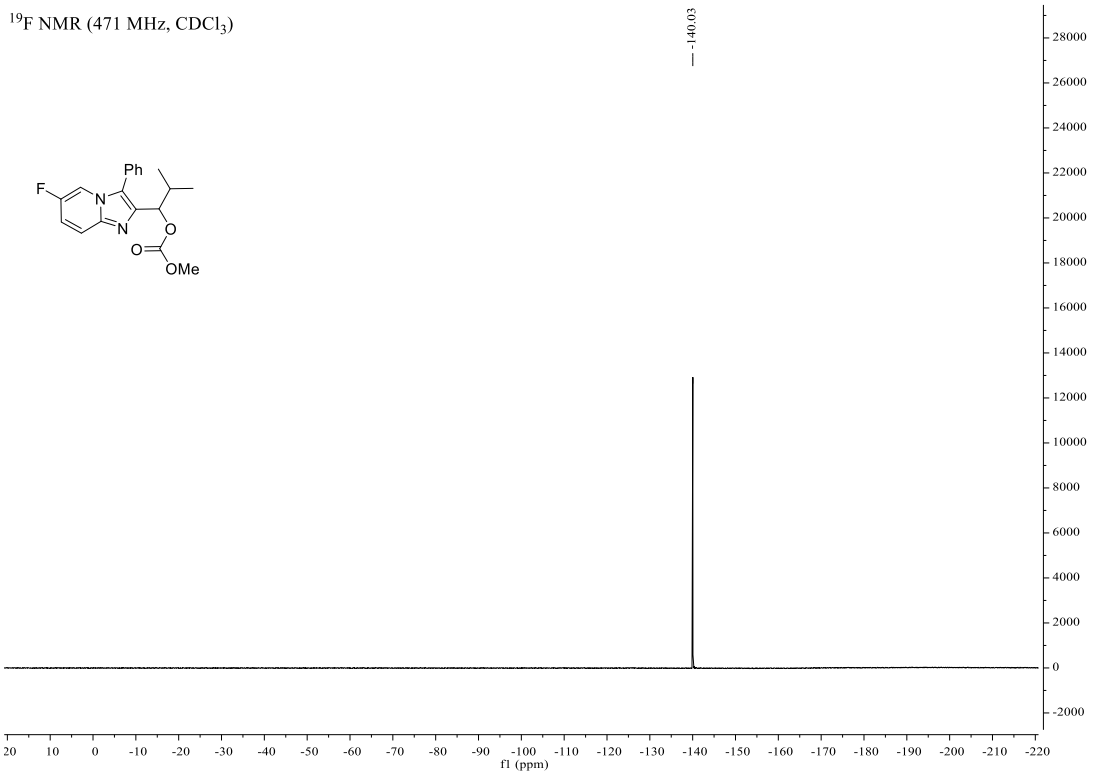
Compound 22


1H NMR (500 MHz, CDCl3)
Ph
F
N
N
O
O
OMe
7.88 7.87 7.87 7.86 7.64 7.63 7.62 7.61 7.59 7.58 7.58 7.56 7.56 7.54 7.52 7.51 7.51 7.51 7.50 7.49 7.49 7.49 7.29 CDCl3 7.13 7.13 7.11 7.11 7.11 7.10 7.09 5.44 5.42
3.69
2.49 2.48 2.47 2.45 2.45 2.44 2.44 2.43 2.42 2.41
1.03 1.01 0.76 0.75
0.00
0.99 6.10 1.01 1.00 3.01 1.28 3.00 3.01
f1 (ppm)

^{13}C NMR (126 MHz, $CDCl_3$)

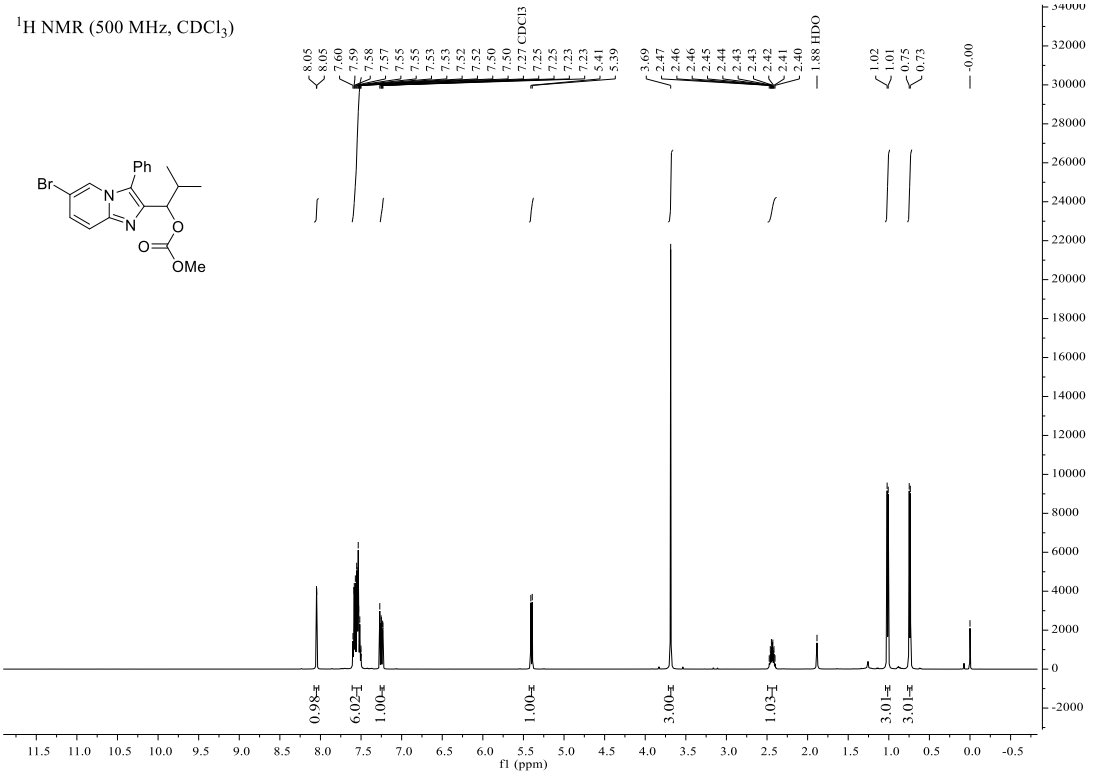


^{19}F NMR (471 MHz, $CDCl_3$)

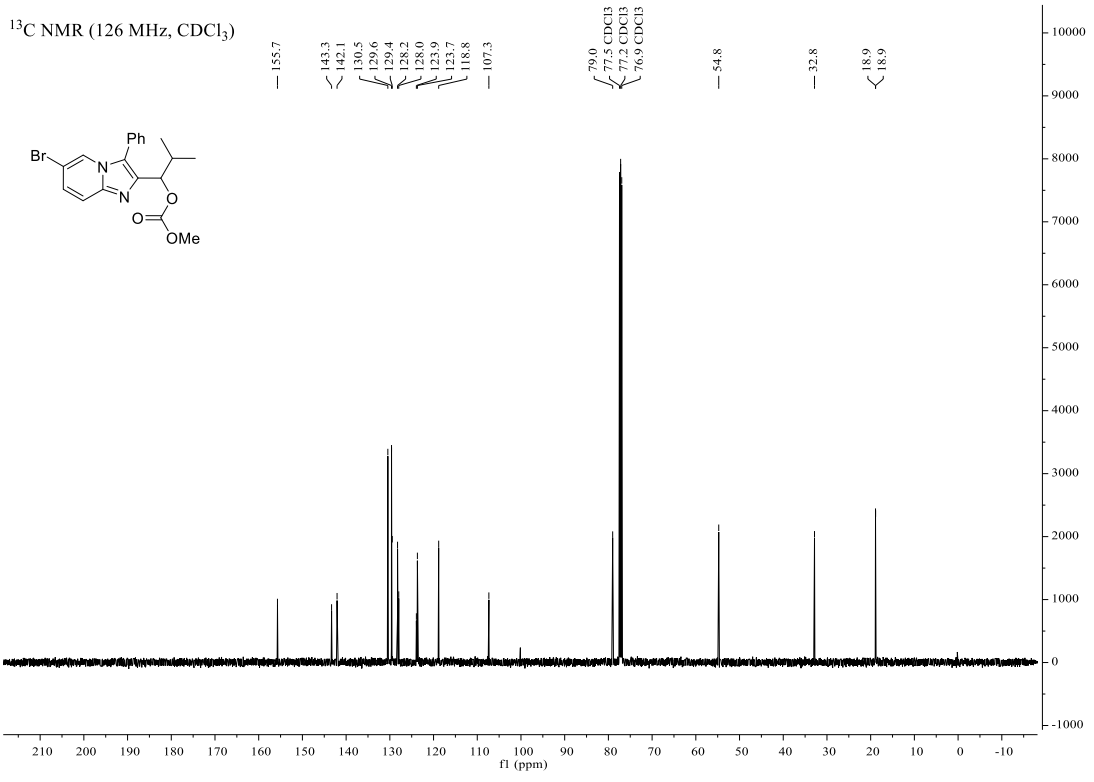


Compound 23

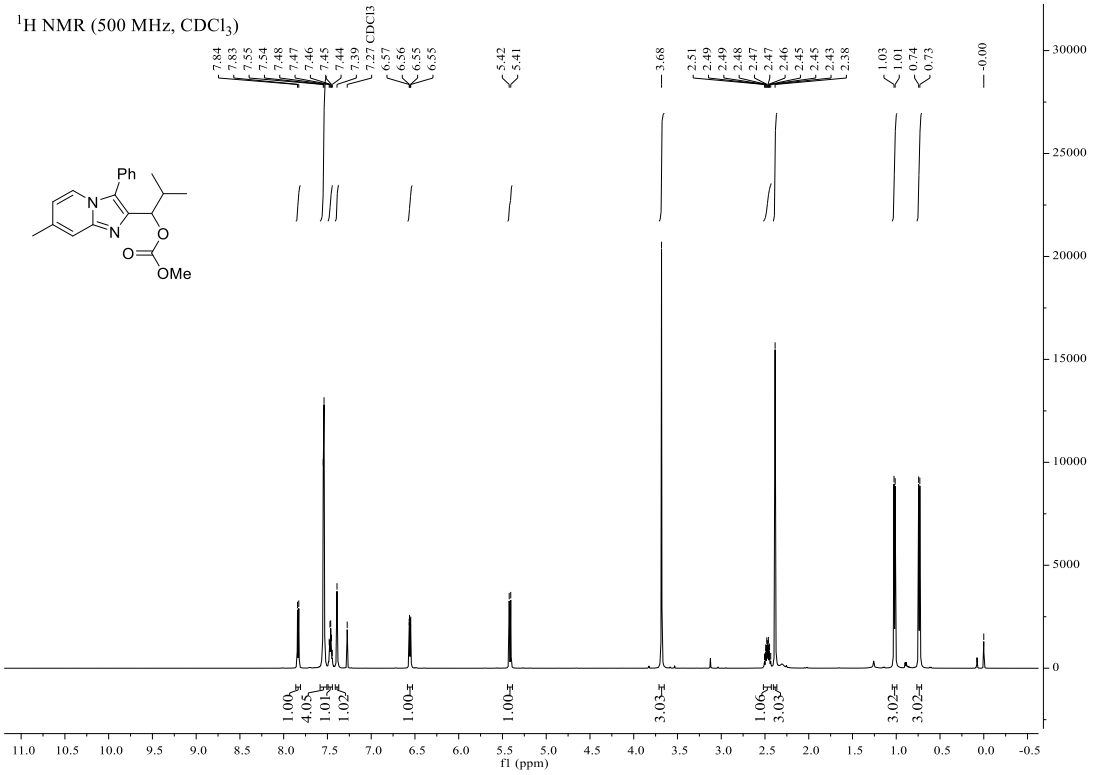
^{1}H NMR (500 MHz, $CDCl_3$)



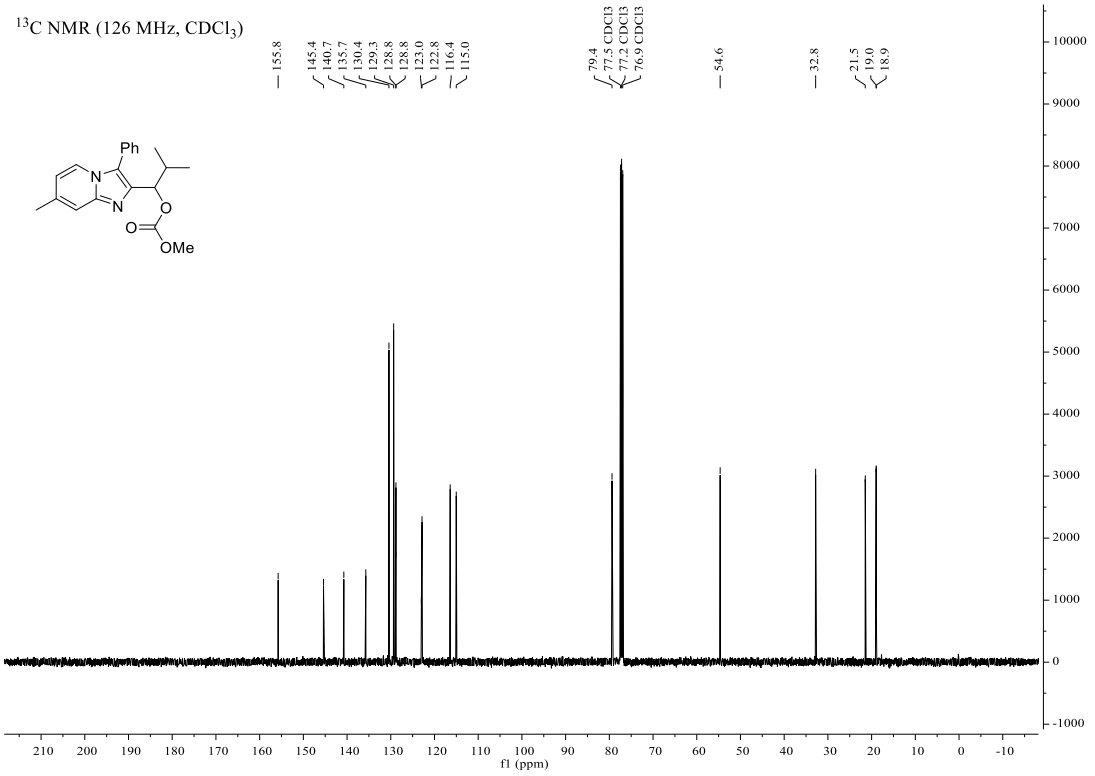
^{13}C NMR (126 MHz, $CDCl_3$)



Compound 24

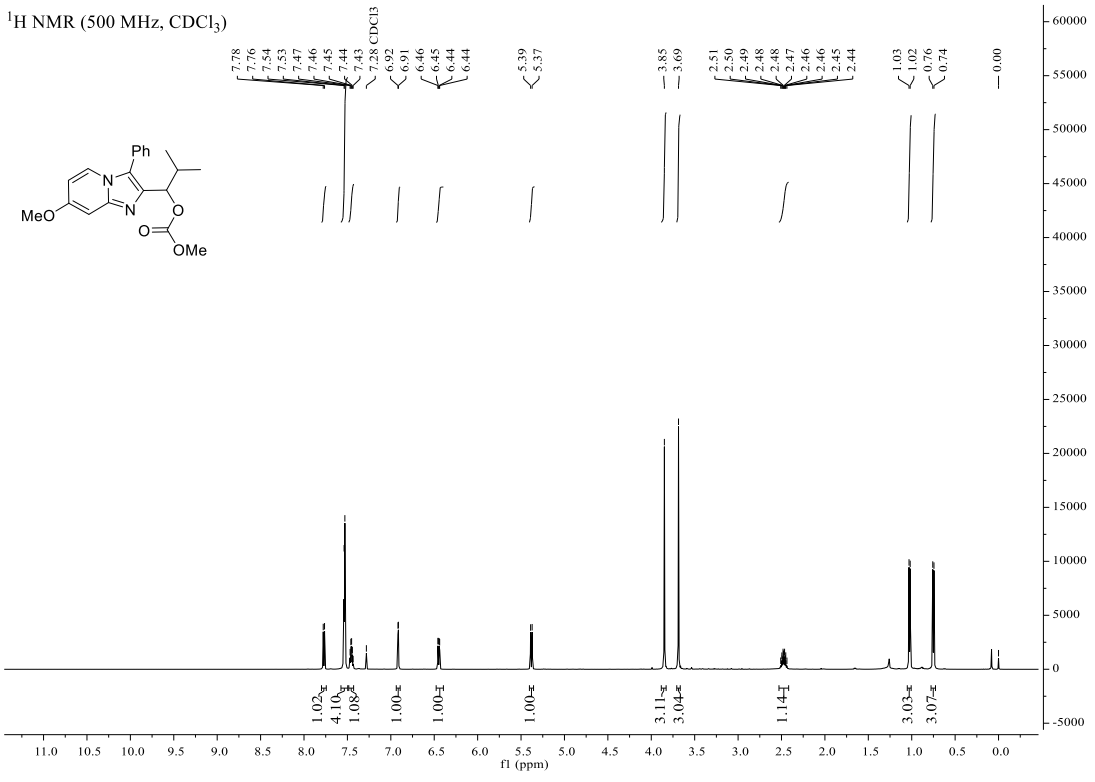

1H NMR (500 MHz, CDCl3)
Ph
N
N
O
O
OMe
7.84
7.83
7.55
7.54
7.48
7.47
7.46
7.45
7.44
7.39
7.27 CDCl3
6.57
6.56
6.55
6.55
5.42
5.41
3.68
2.51
2.49
2.49
2.48
2.47
2.47
2.46
2.45
2.45
2.43
2.38
1.03
1.01
0.74
0.73
-0.00
1.00
4.05
1.01
1.02
1.00
1.00
3.03
1.06
3.03
3.02
3.02
f1 (ppm)

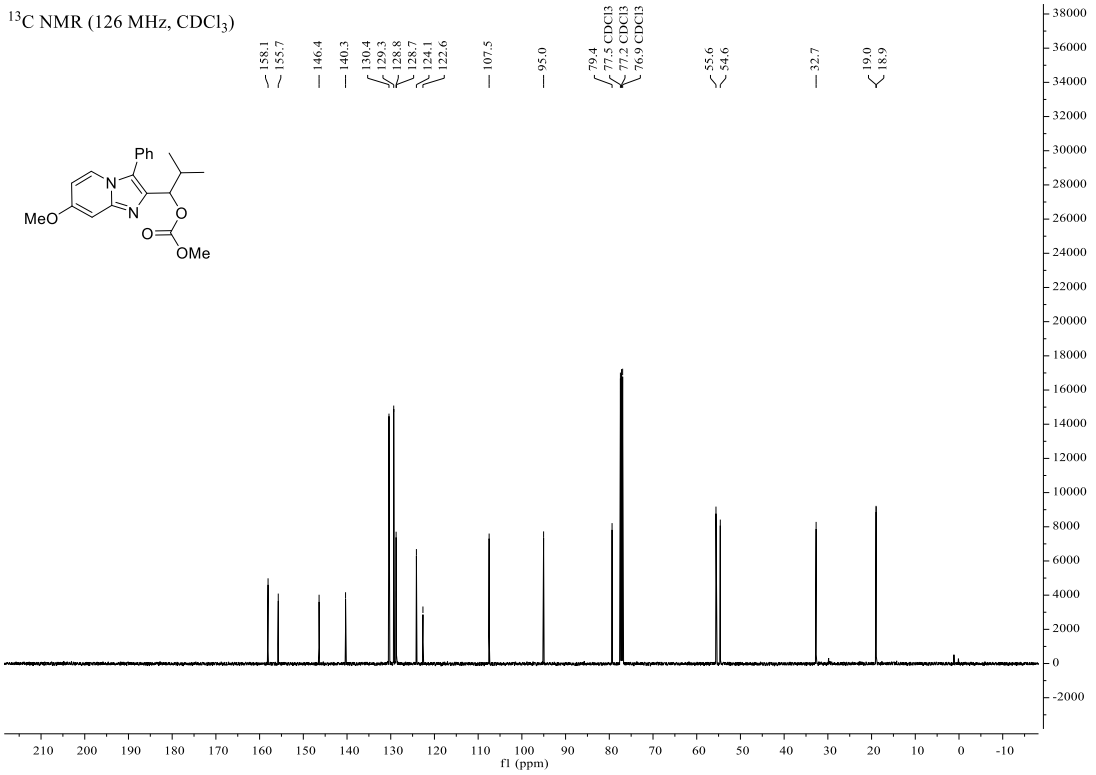
^{13}C NMR (126 MHz, $CDCl_3$)



Compound 25

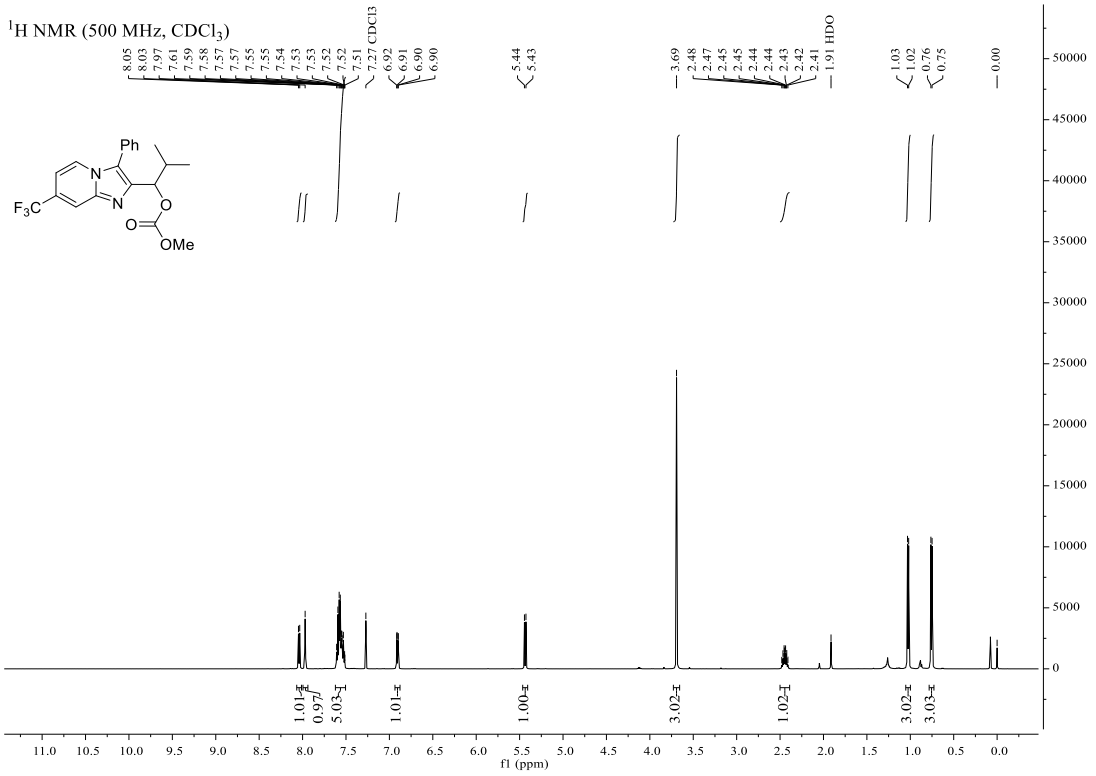
^{1}H NMR (500 MHz, $CDCl_3$)



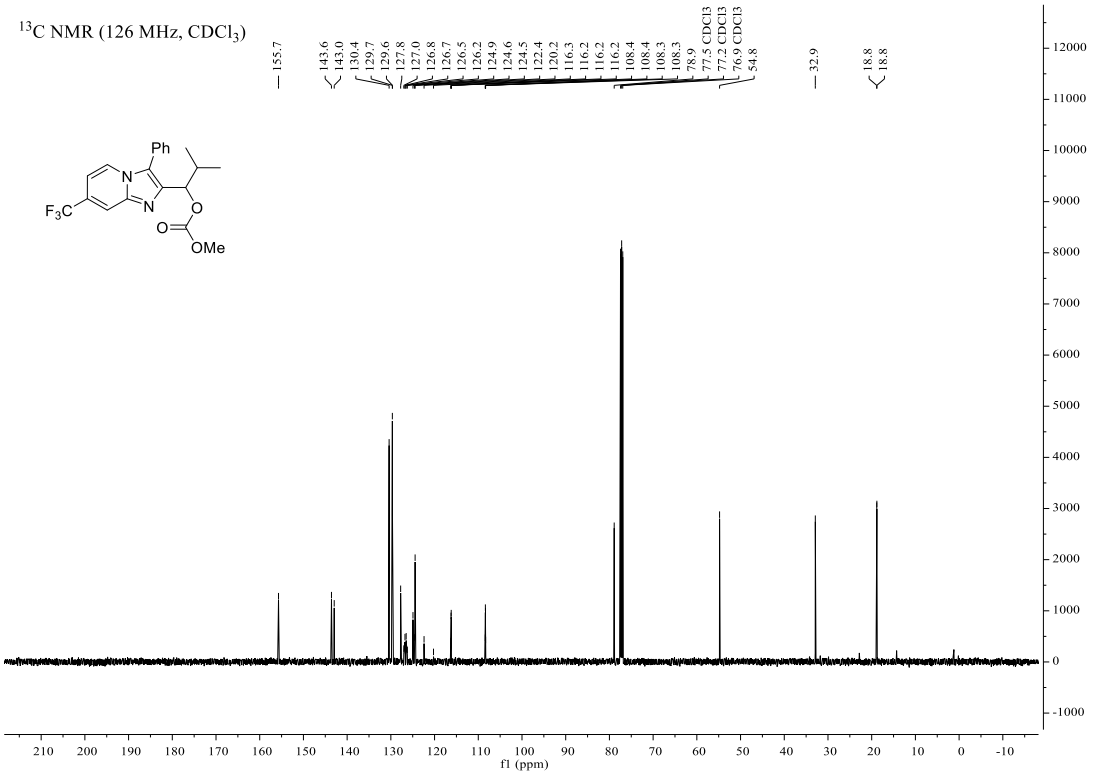

13C NMR (126 MHz, CDCl3)
158.1
155.7
146.4
140.3
130.4
129.3
128.8
128.7
124.1
122.6
107.5
95.0
79.4
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
55.6
54.6
32.7
19.0
18.9
Ph
MeO
OMe
f1 (ppm)

Compound 26

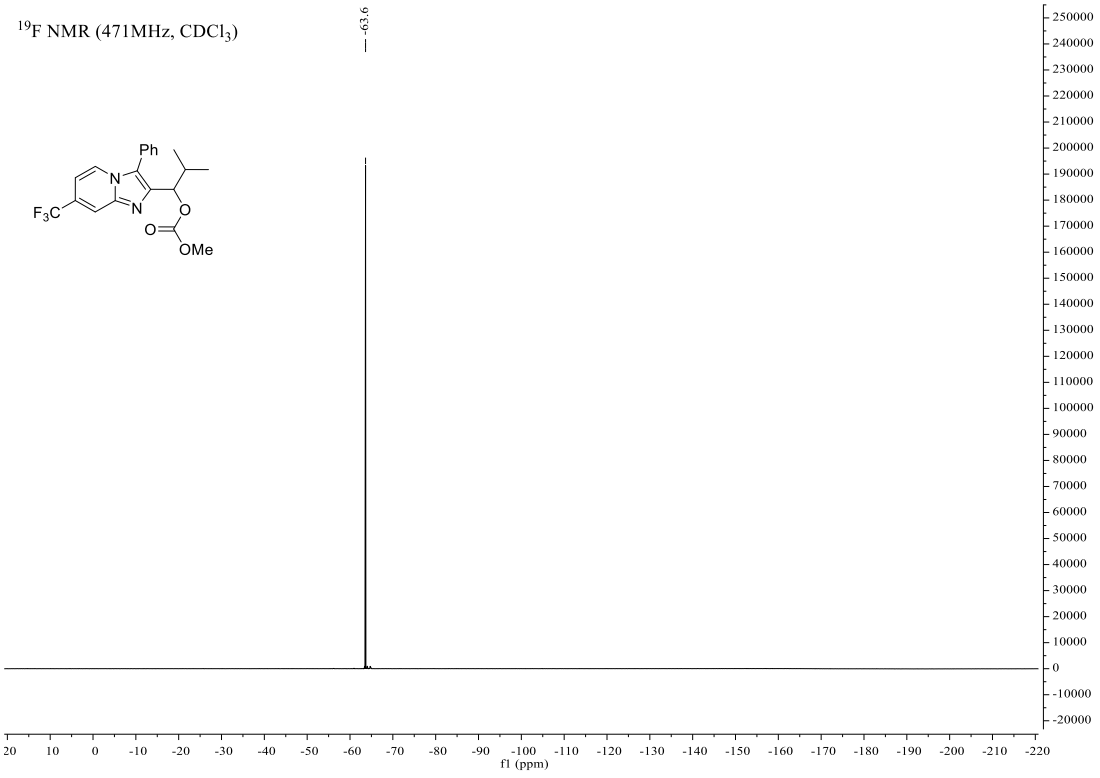
^{1}H NMR (500 MHz, $CDCl_3$)



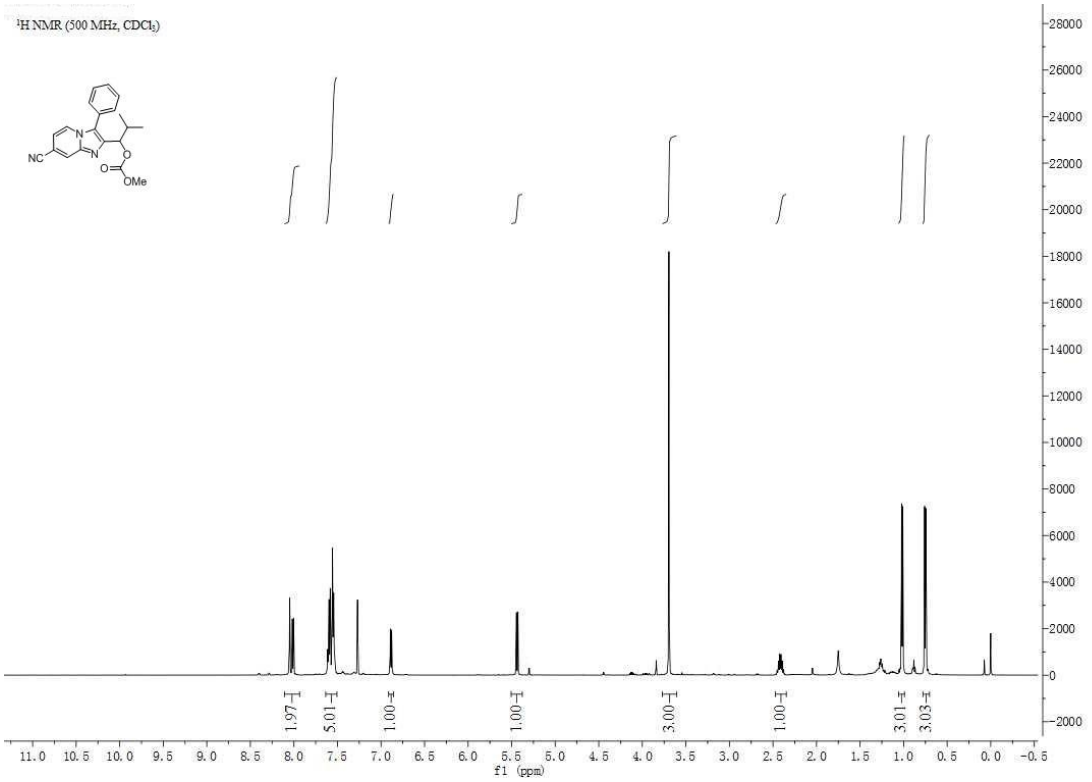
^{13}C NMR (126 MHz, $CDCl_3$)

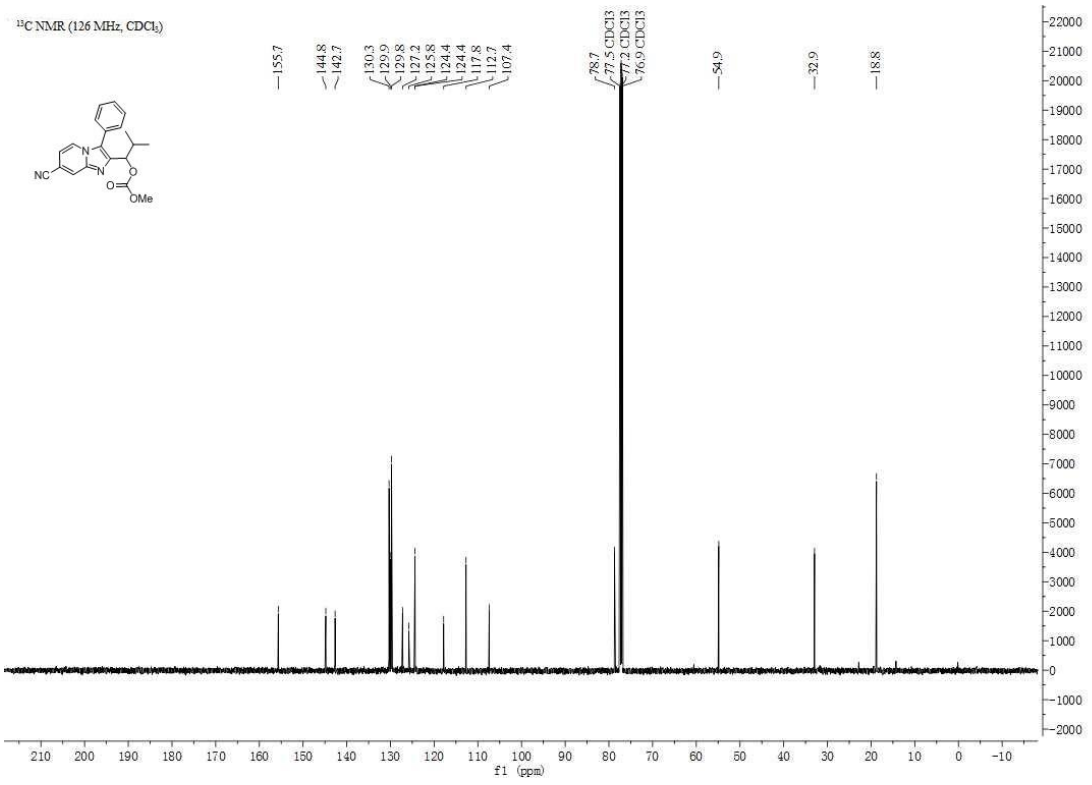


^{19}F NMR (471MHz, $CDCl_3$)

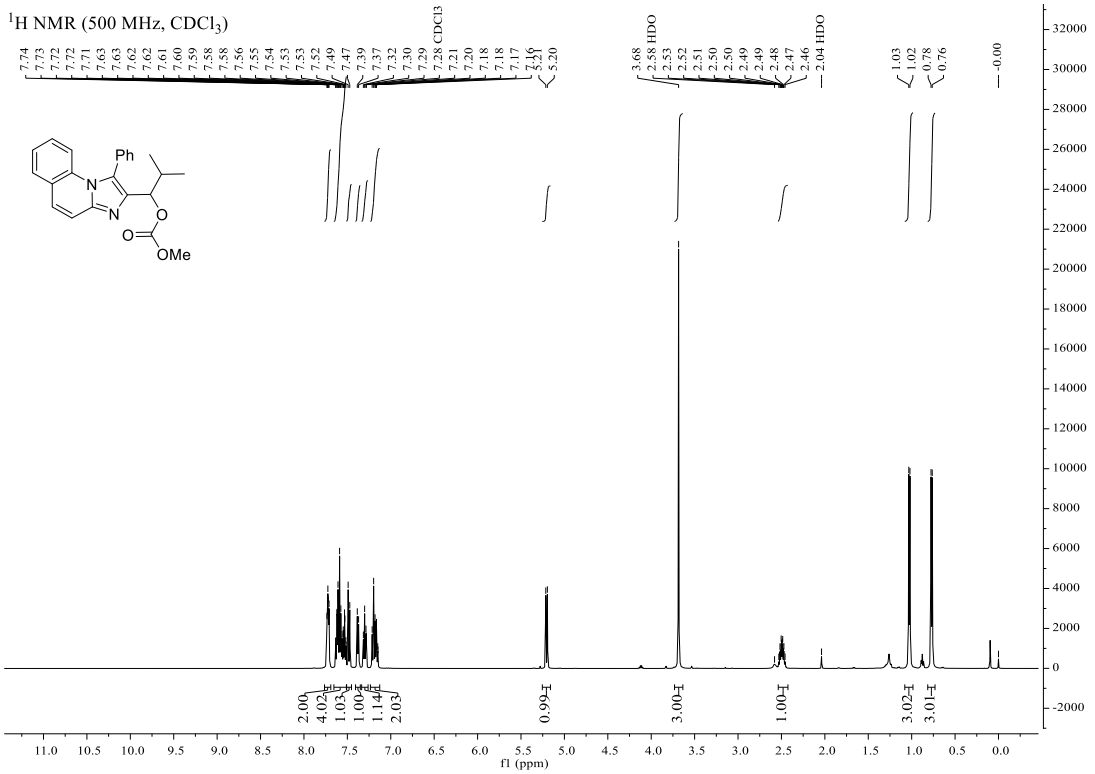


Compound 27

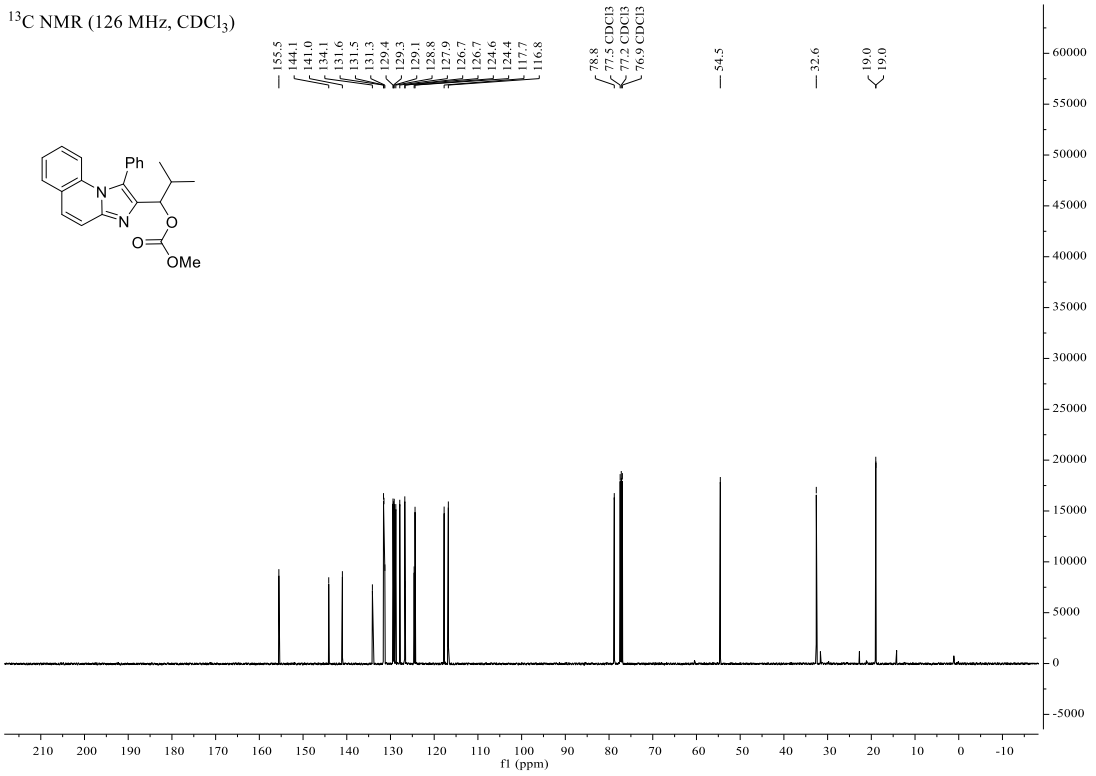

^{1}H NMR (500 MHz, $CDCl_3$)
NC
O
OMe
1.97
5.01
1.00
1.00
3.00
1.00
3.01
3.03
f1 (ppm)


^{13}C NMR (126 MHz, $CDCl_3$)
155.7
144.8
142.7
130.3
129.9
129.8
127.2
125.8
124.4
124.4
117.8
112.7
107.4
78.7
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
54.9
32.9
18.8
NC
O
OMe
f1 (ppm)

Compound 28

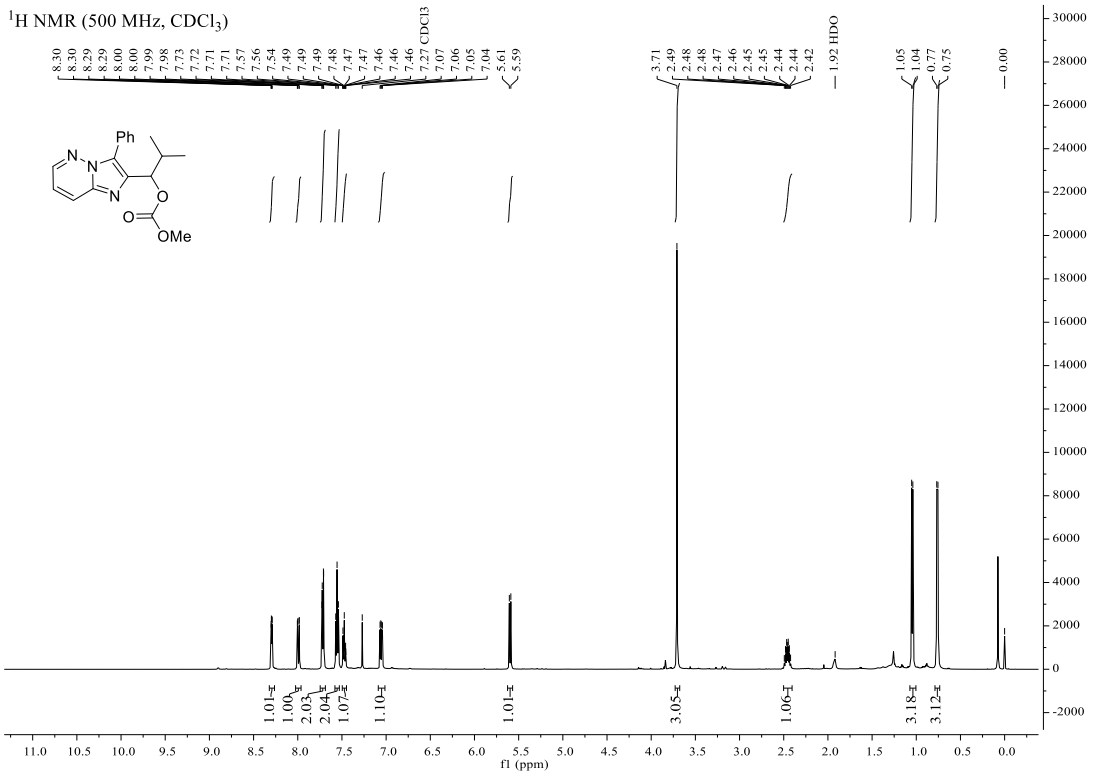


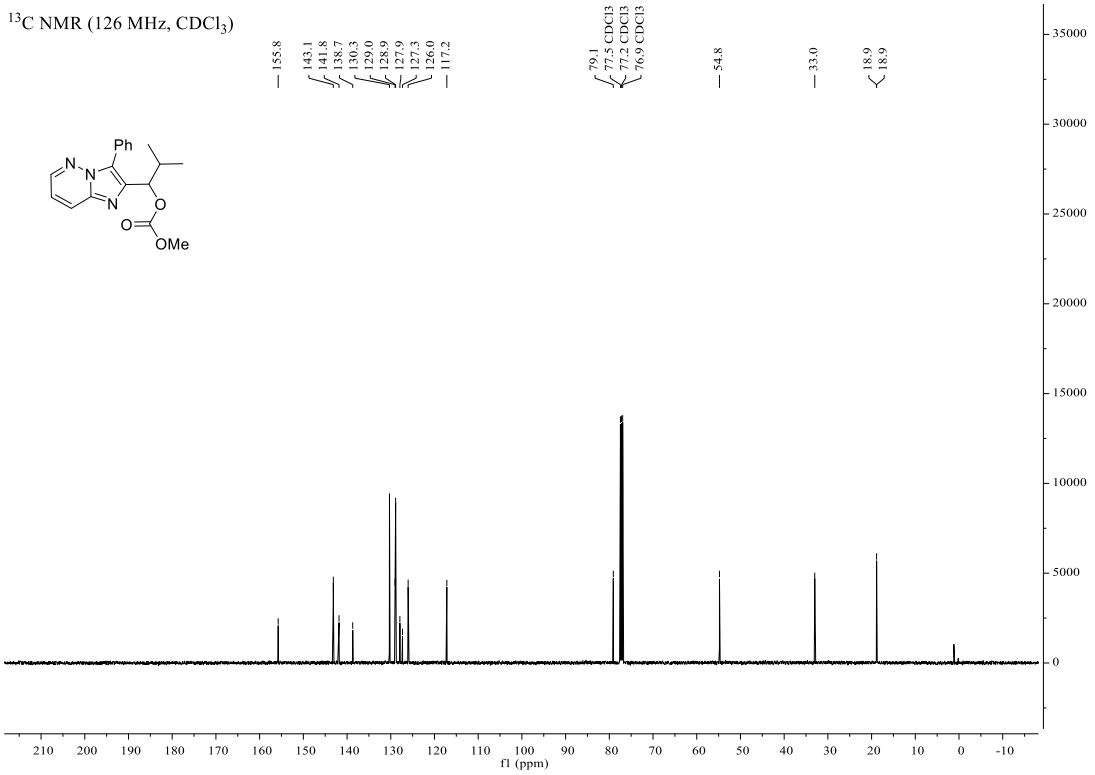
^{13}C NMR (126 MHz, $CDCl_3$)



Compound 29

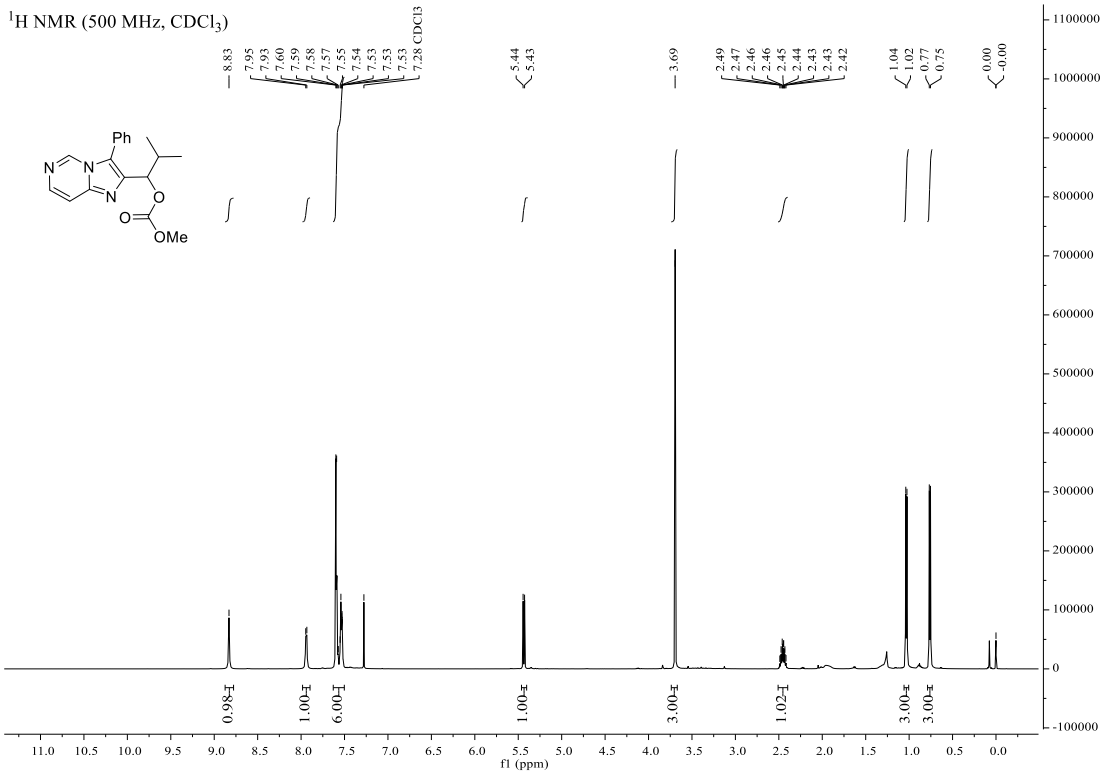
^{1}H NMR (500 MHz, $CDCl_3$)



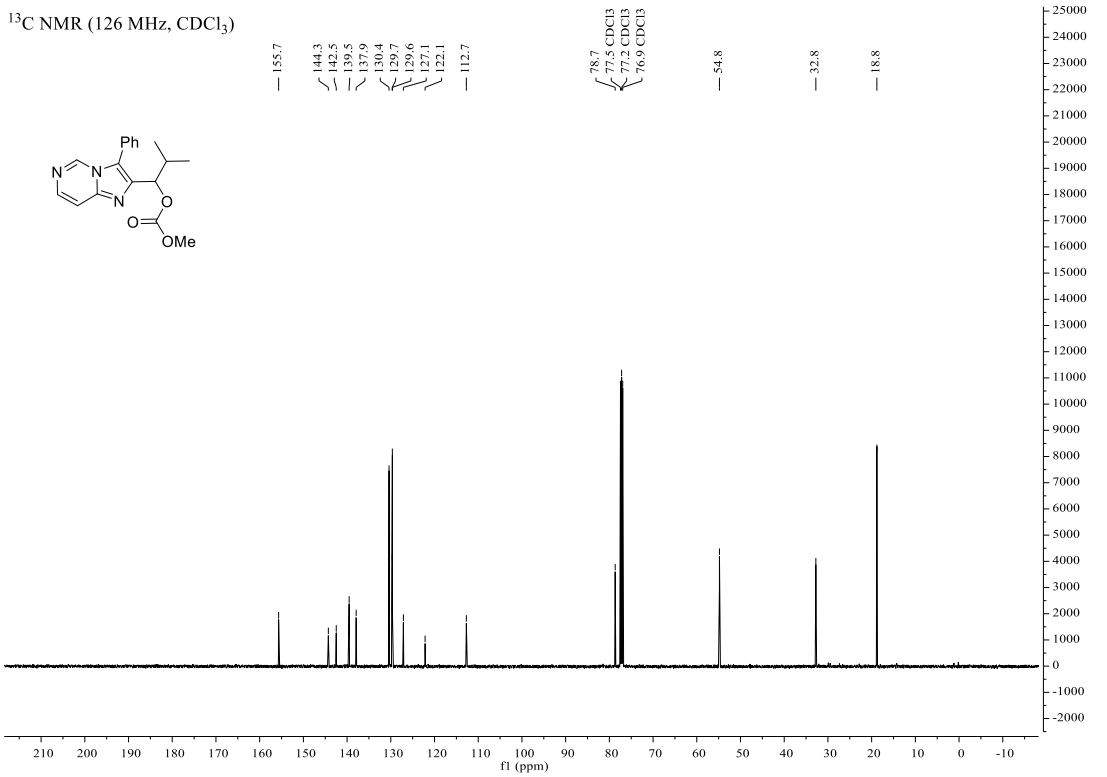

13C NMR (126 MHz, CDCl3)
155.8
143.1
141.8
138.7
130.3
129.0
128.9
127.9
127.3
126.0
117.2
79.1
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
54.8
33.0
18.9
18.9
Ph
N
N
N
O
O
OMe
35000
30000
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 30

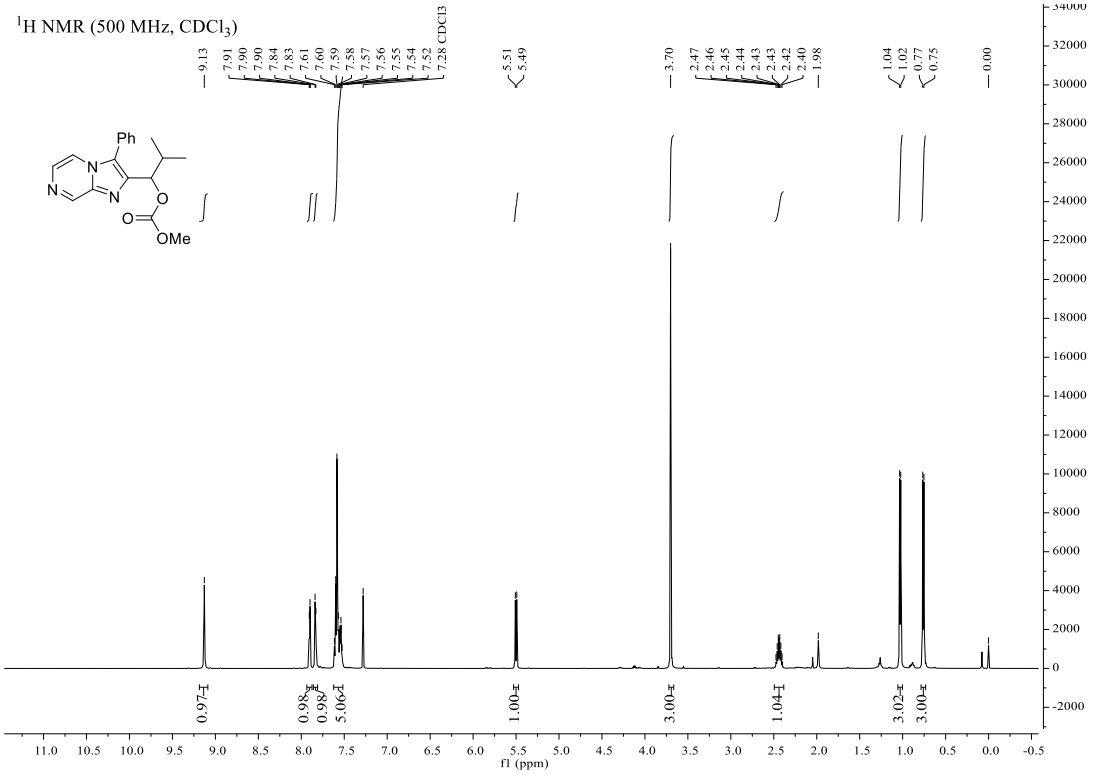
^{1}H NMR (500 MHz, $CDCl_3$)

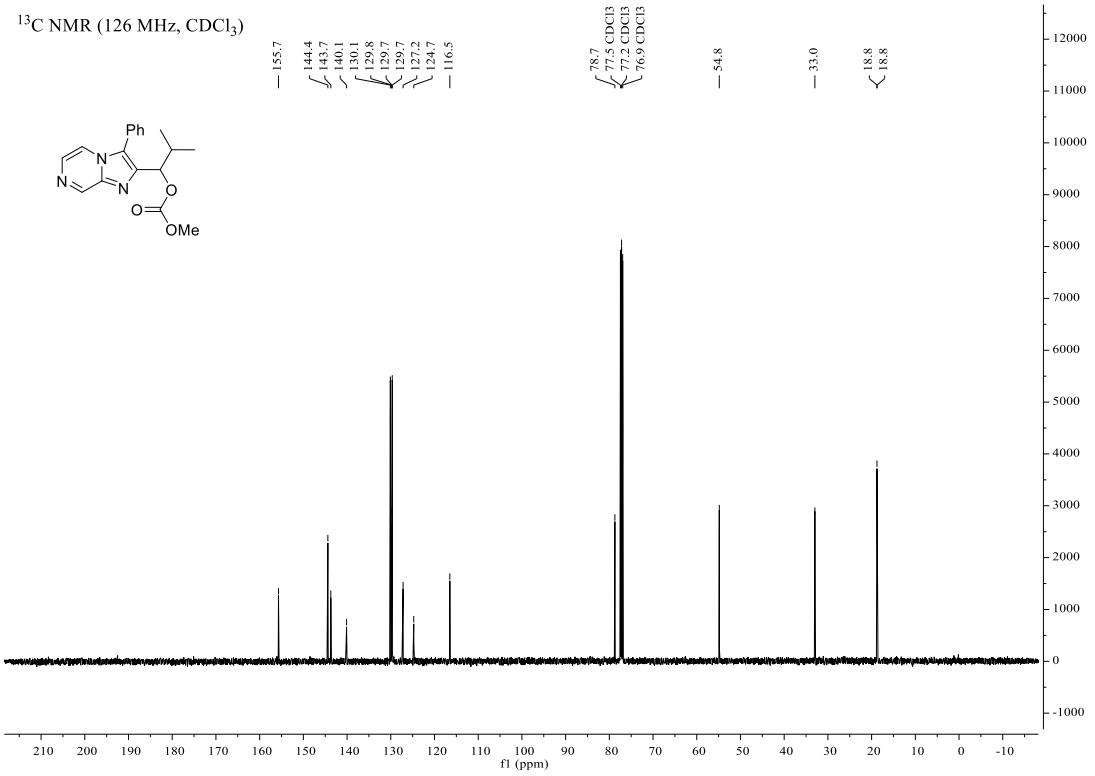


^{13}C NMR (126 MHz, $CDCl_3$)

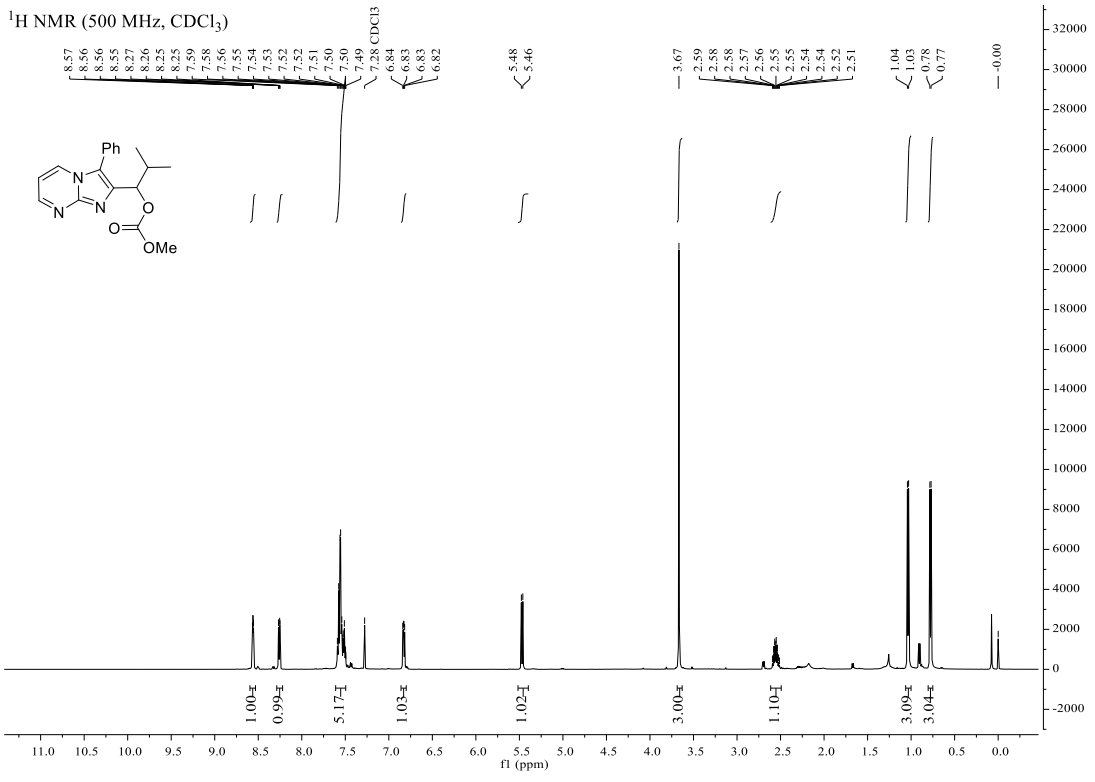


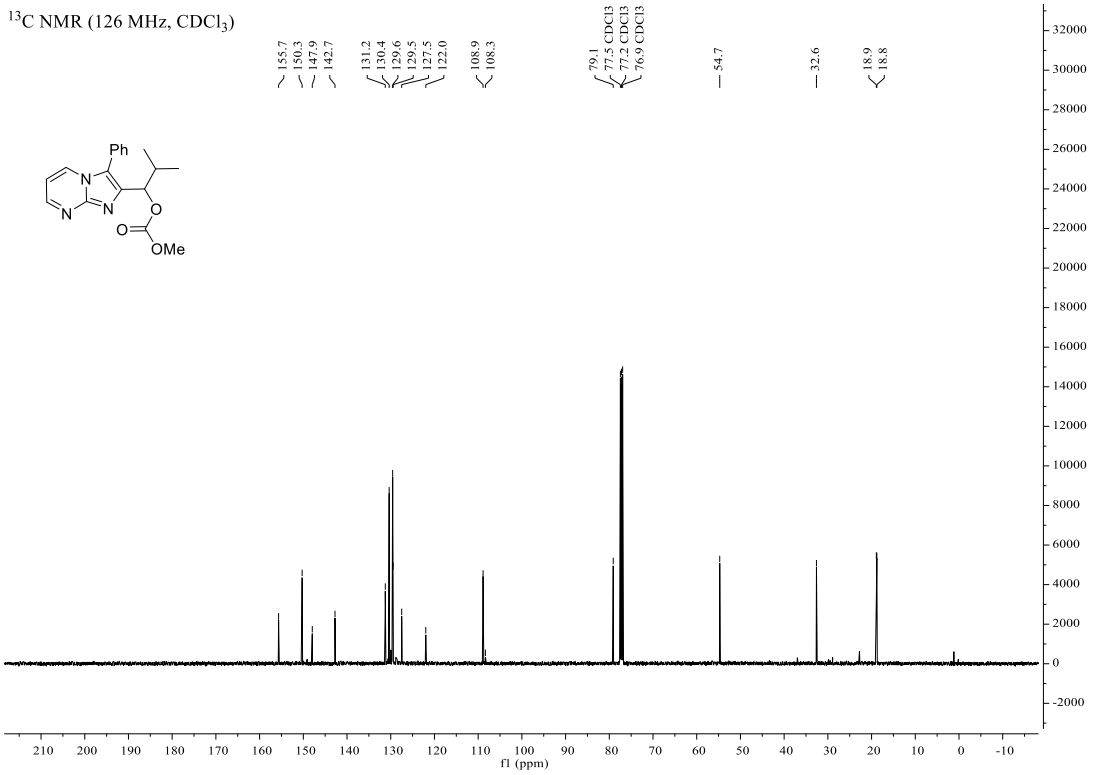
Compound 31


1H NMR (500 MHz, CDCl3)
9.13
7.91
7.90
7.90
7.84
7.83
7.61
7.60
7.59
7.58
7.57
7.56
7.55
7.54
7.52
7.28 CDCl3
5.51
5.49
3.70
2.47
2.46
2.45
2.44
2.43
2.43
2.42
2.40
1.98
1.04
1.02
0.77
0.75
0.00
Ph
N
N
N
O
O
OMe
0.97
0.98
0.98
5.06
1.00
3.00
1.04
3.02
3.00
f1 (ppm)


13C NMR (126 MHz, CDCl3)
155.7
144.4
143.7
140.1
130.1
129.8
129.7
129.7
127.2
124.7
116.5
78.7
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
54.8
33.0
18.8
18.8
Ph
N
N
O
O
OMe
f1 (ppm)

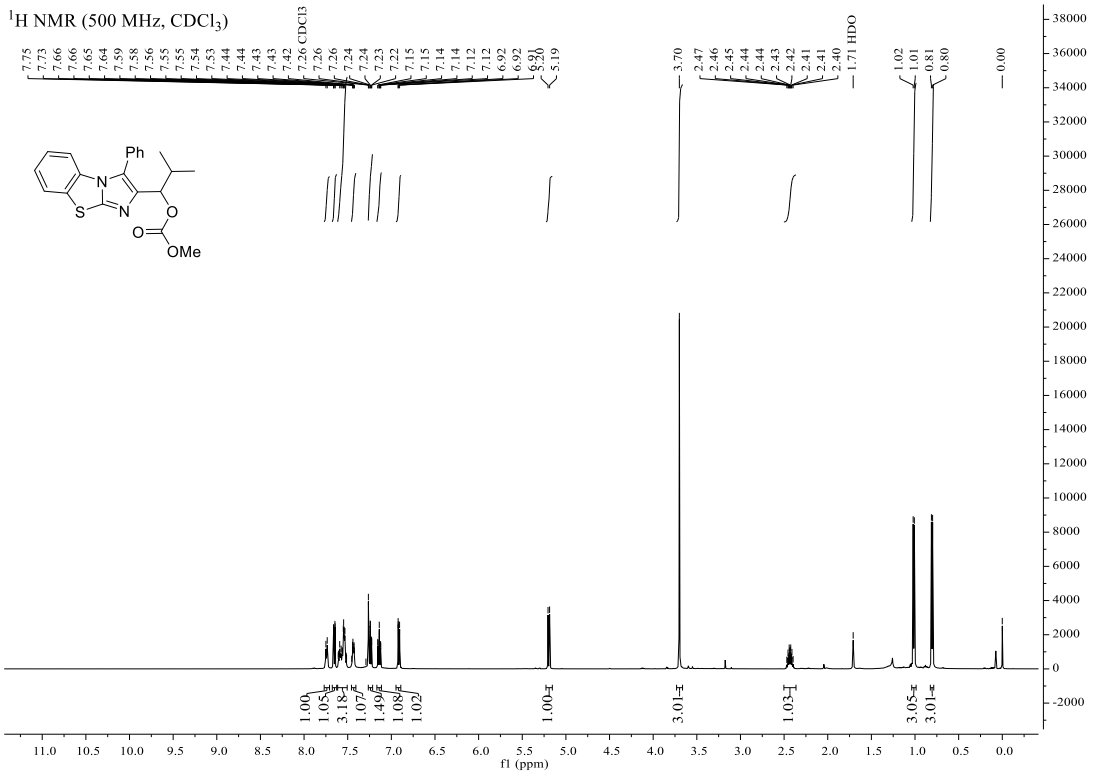
Compound 32


1H NMR (500 MHz, CDCl3)
8.57
8.56
8.56
8.55
8.55
8.27
8.26
8.25
8.25
7.59
7.58
7.56
7.55
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.28 CDCl3
6.84
6.83
6.83
6.82
5.48
5.46
3.67
2.59
2.58
2.58
2.57
2.56
2.55
2.55
2.54
2.54
2.52
2.51
1.04
1.03
0.78
0.77
-0.00
Ph
N
N
O
O
OMe
1.00
0.99
5.17
1.03
1.02
3.00
1.10
3.09
3.04
f1 (ppm)

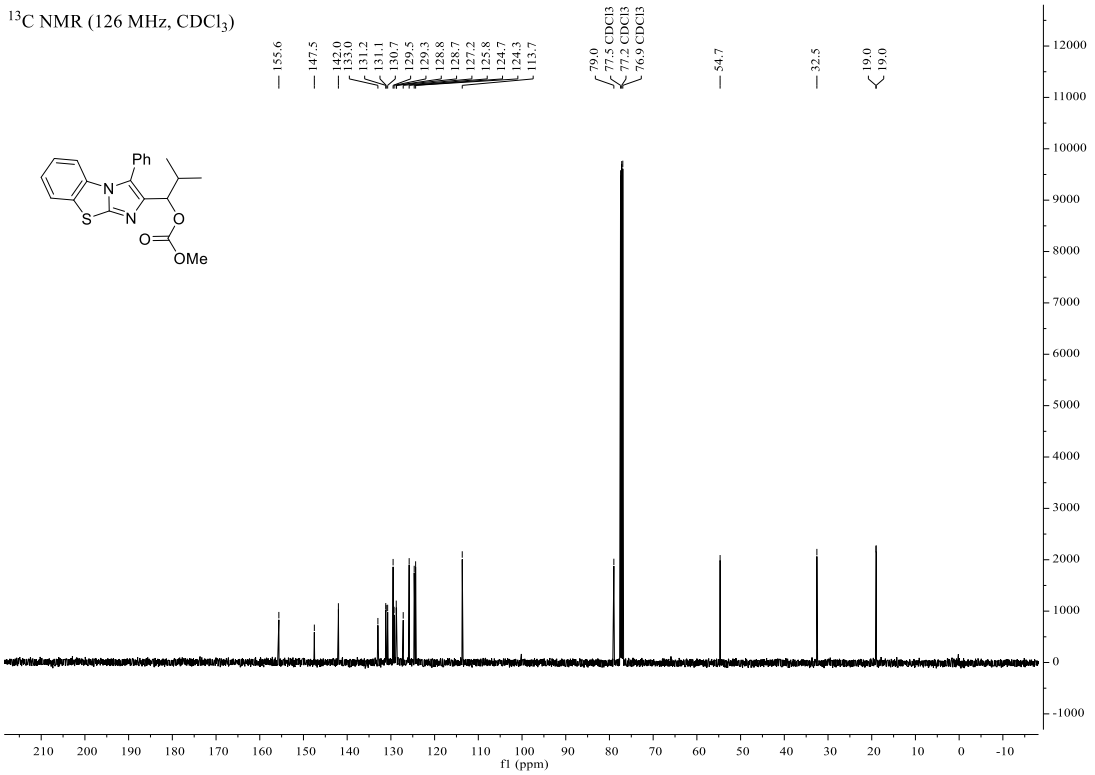

13C NMR (126 MHz, CDCl3)
155.7
150.3
147.9
142.7
131.2
130.4
129.6
129.5
127.5
122.6
108.9
108.3
79.1
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
54.7
32.6
18.9
18.8
Ph
N
N
N
O
O
OMe
f1 (ppm)

Compound 33

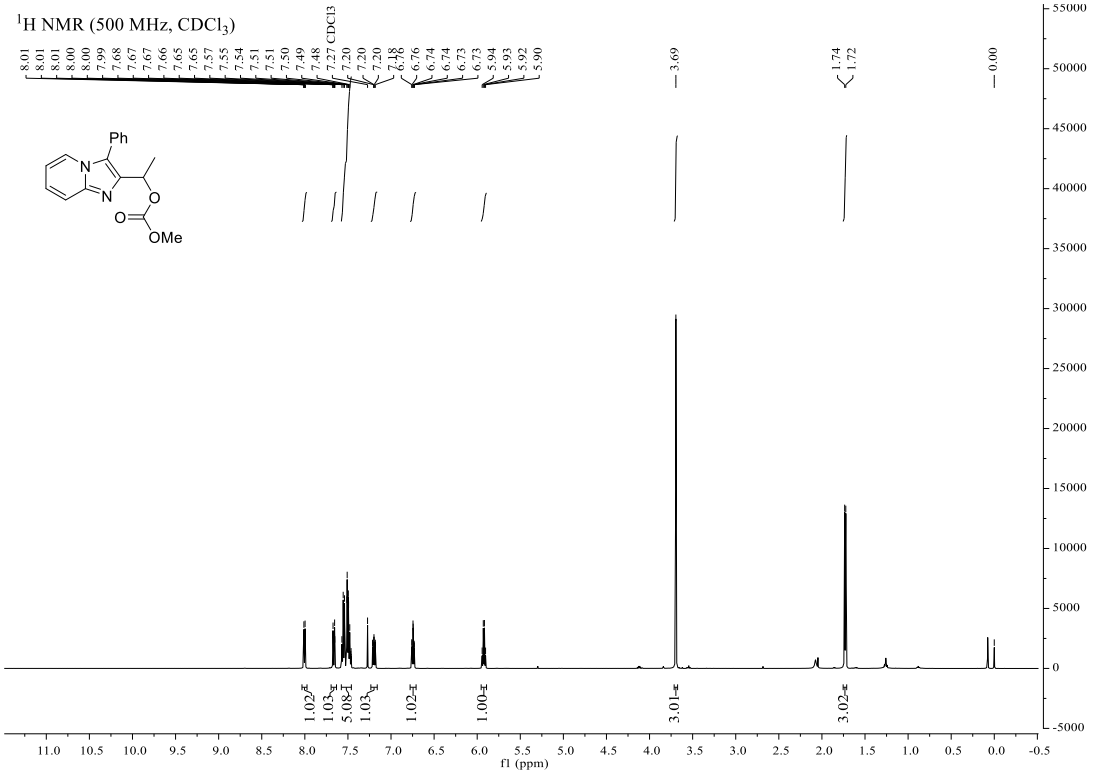
^{1}H NMR (500 MHz, $CDCl_3$)

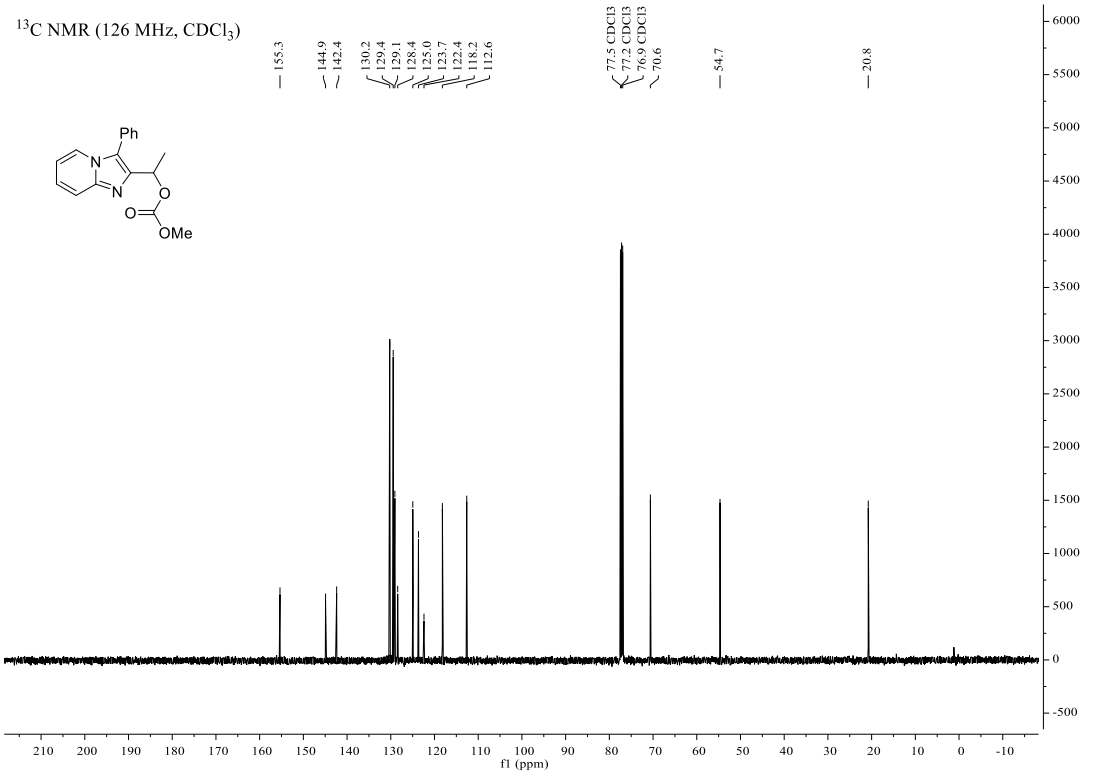


^{13}C NMR (126 MHz, $CDCl_3$)

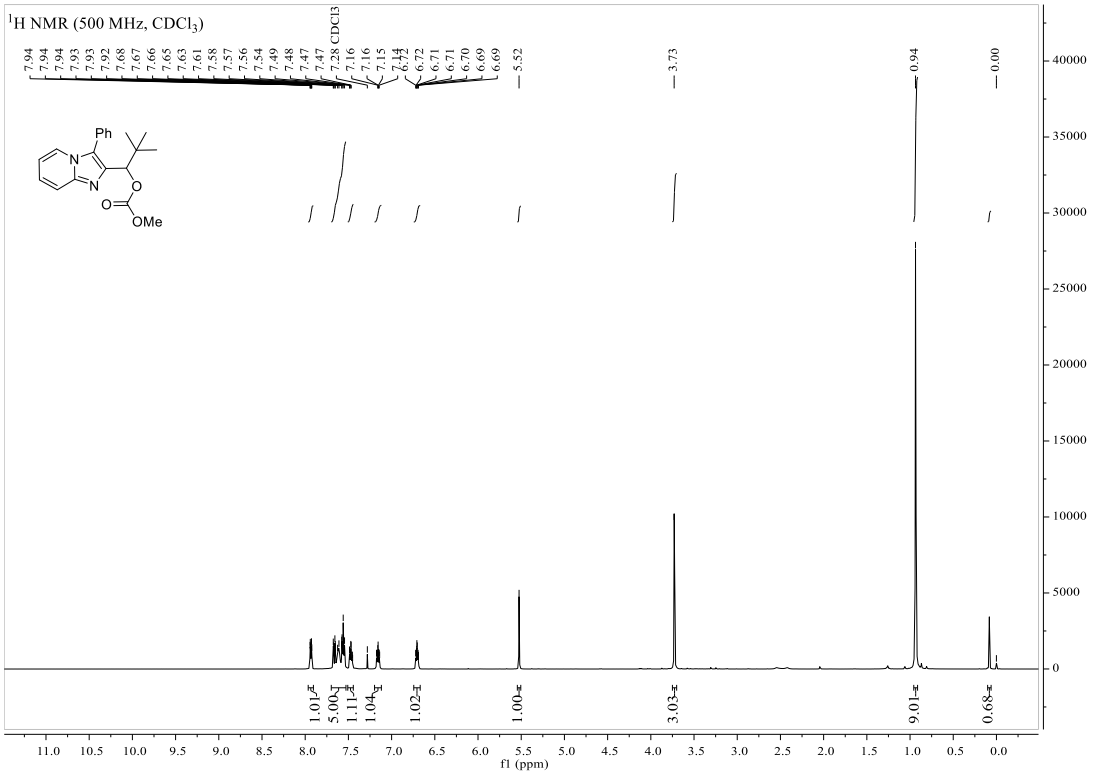


Compound 34

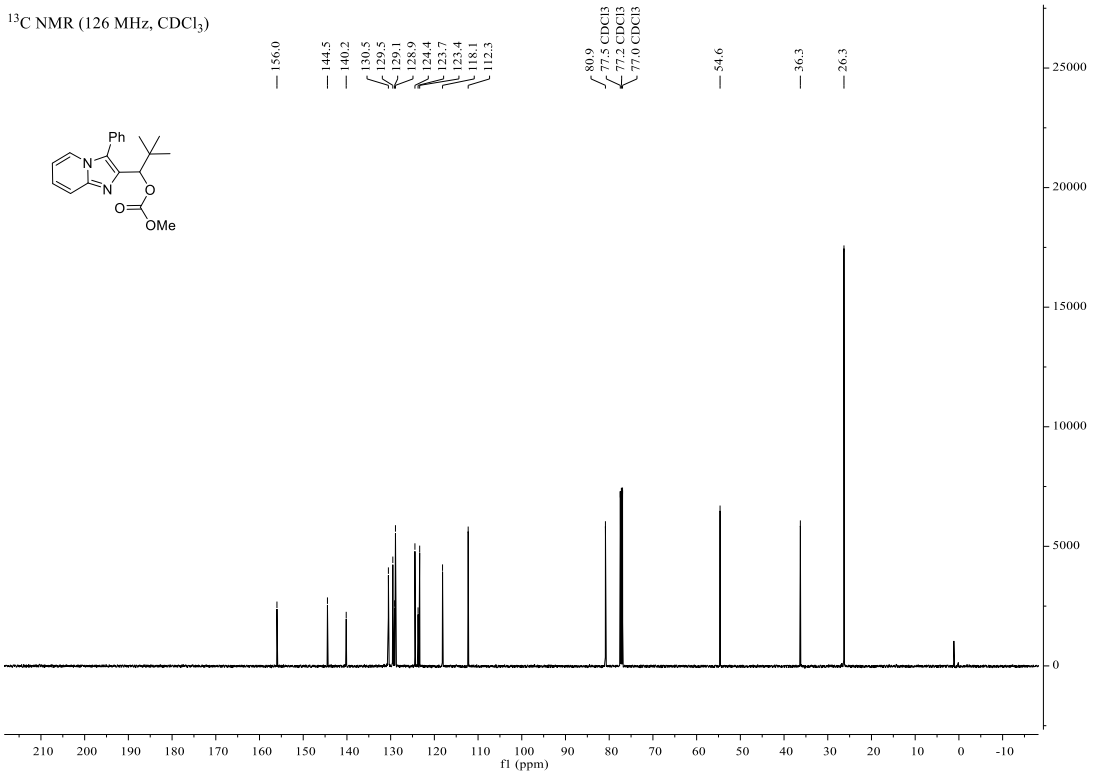

1H NMR (500 MHz, CDCl3)
8.01
8.01
8.01
8.00
8.00
7.99
7.68
7.67
7.67
7.66
7.65
7.57
7.55
7.54
7.51
7.51
7.50
7.49
7.48
7.27 CDCl3
7.20
7.20
7.20
7.18
6.76
6.76
6.74
6.74
6.73
5.94
5.93
5.92
5.90
3.69
1.74
1.72
0.00
Ph
N
N
O
O
OMe
1.02
1.03
5.08
1.03
1.02
1.00
3.01
3.02
f1 (ppm)


13C NMR (126 MHz, CDCl3)
155.3
144.9
142.4
130.2
129.4
129.1
128.4
125.0
123.7
122.4
118.2
112.6
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
70.6
54.7
20.8
Ph
N
N
O
O
OMe
f1 (ppm)

Compound 35

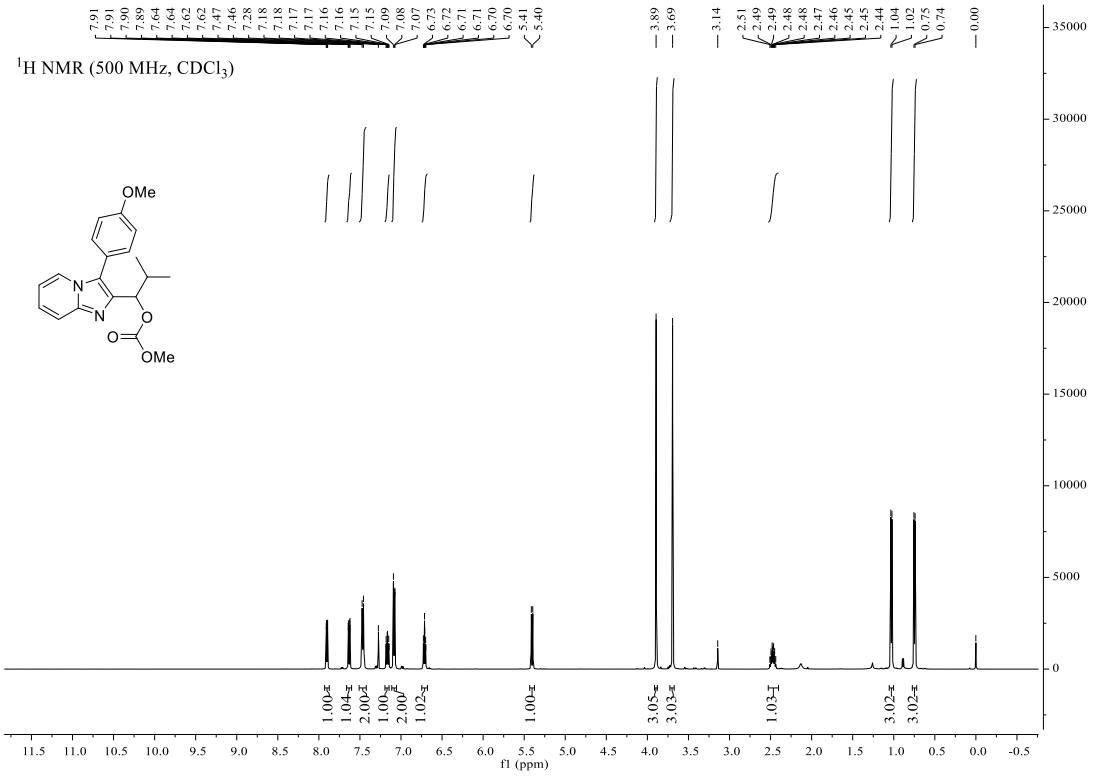

1H NMR (500 MHz, CDCl3)
7.94
7.94
7.94
7.93
7.93
7.92
7.68
7.67
7.66
7.65
7.63
7.61
7.58
7.57
7.56
7.54
7.49
7.48
7.47
7.47
7.28 CDCl3
7.16
7.16
7.15
6.72
6.71
6.71
6.70
6.69
6.69
5.52
3.73
0.94
0.00
Ph
N
N
O
O
OMe
1.01
5.00
1.11
1.04
1.02
1.00
3.03
9.01
0.68
f1 (ppm)

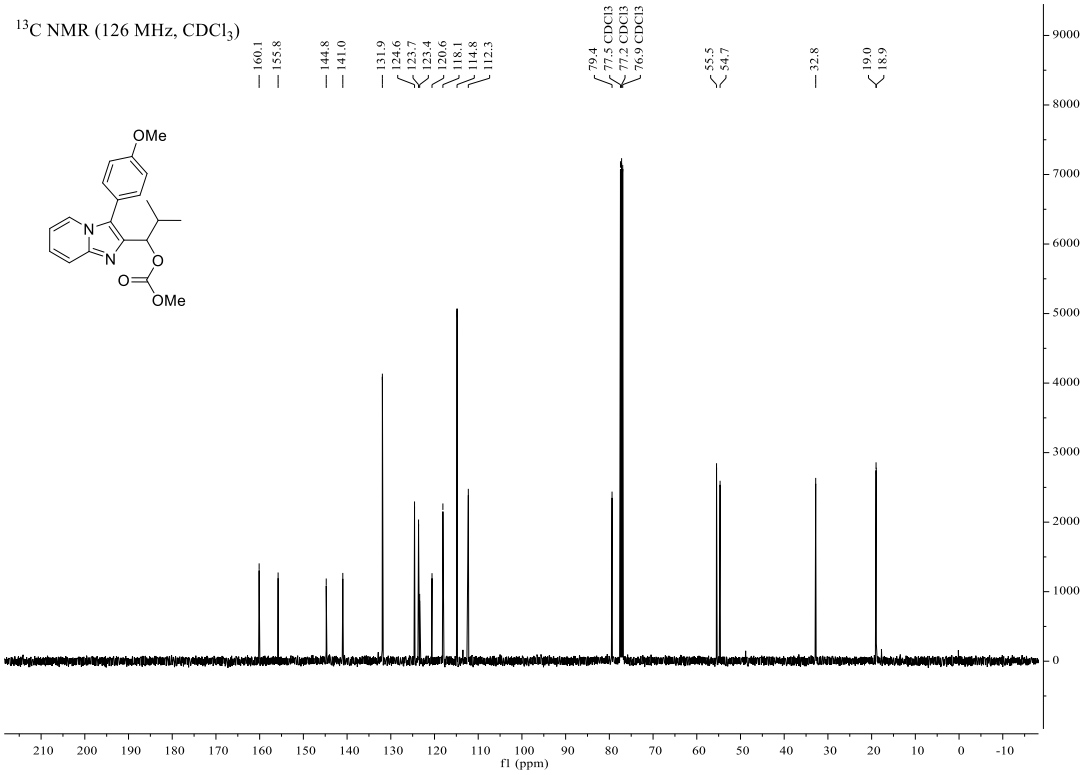
^{13}C NMR (126 MHz, $CDCl_3$)



Compound 36

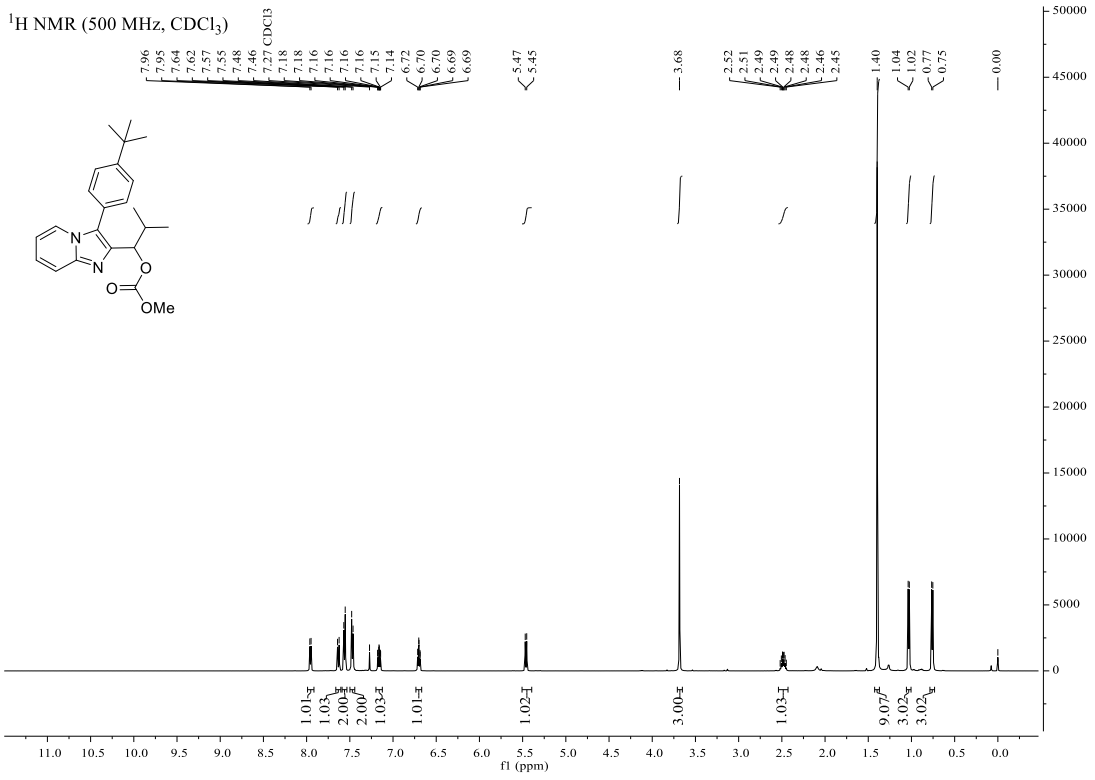
^{1}H NMR (500 MHz, $CDCl_3$)



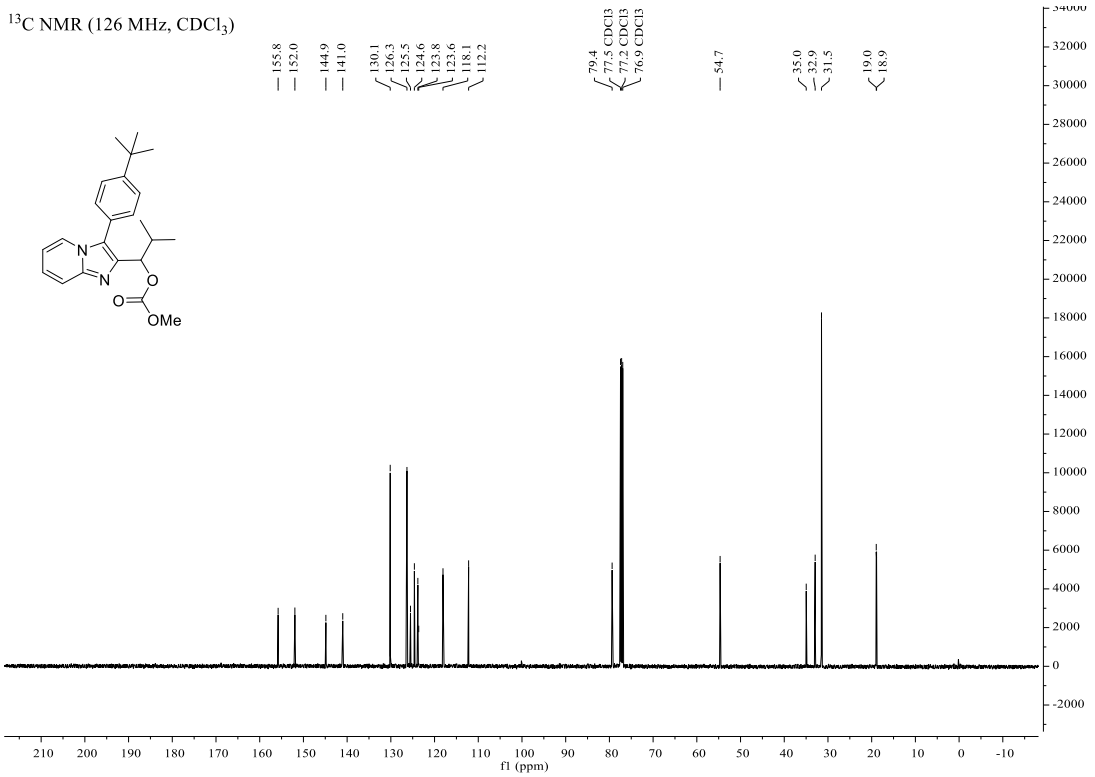

13C NMR (126 MHz, CDCl3)
160.1
155.8
144.8
141.0
131.9
124.6
123.7
123.4
120.6
118.1
114.8
112.3
79.4
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
55.5
54.7
32.8
19.0
18.9
OMe
N
N
O
O
OMe
f1 (ppm)

Compound 37

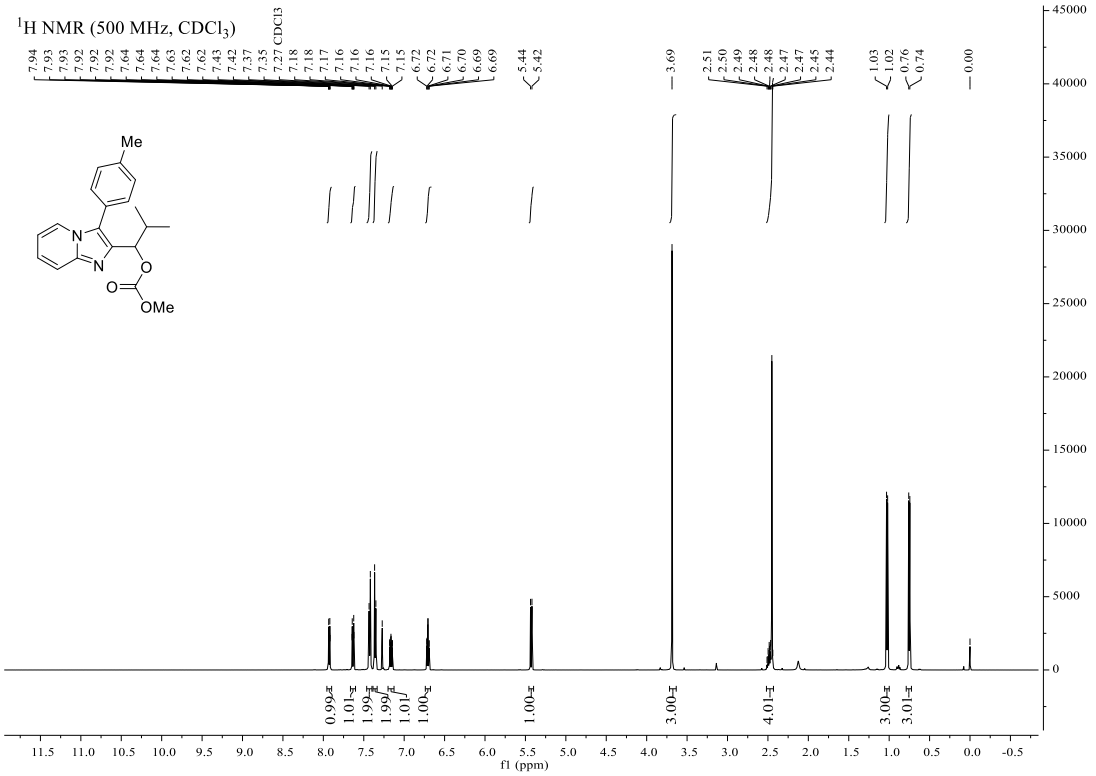
^{1}H NMR (500 MHz, $CDCl_3$)

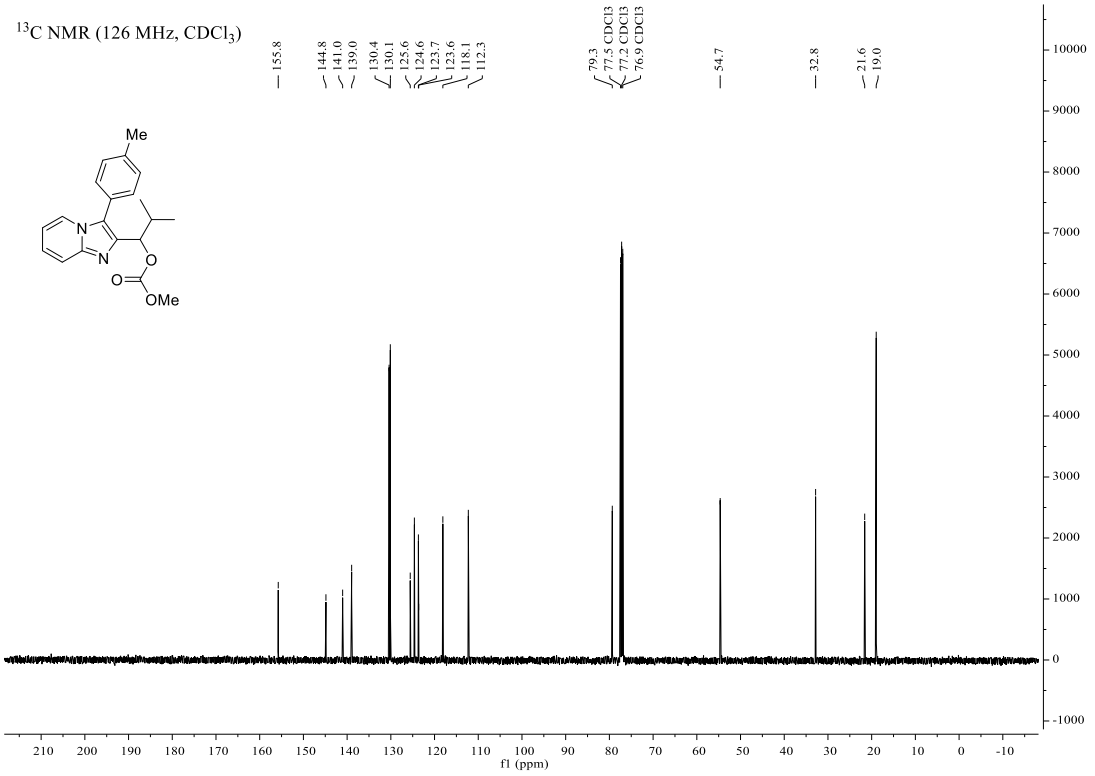


^{13}C NMR (126 MHz, $CDCl_3$)

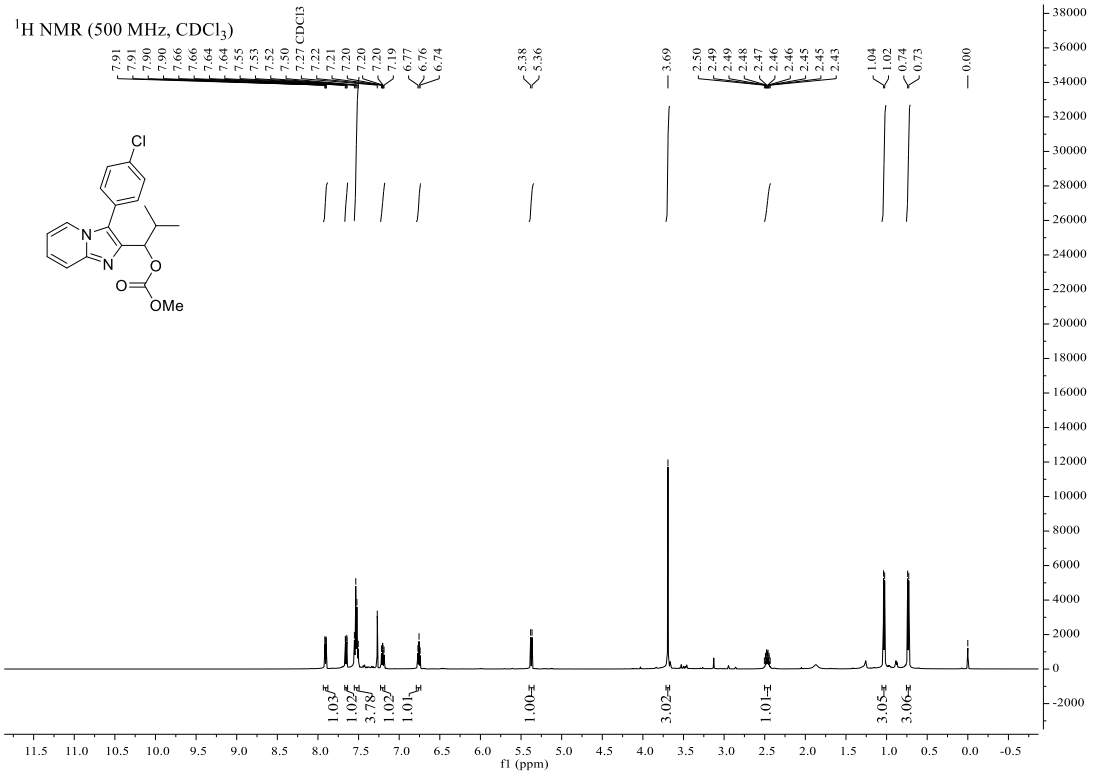


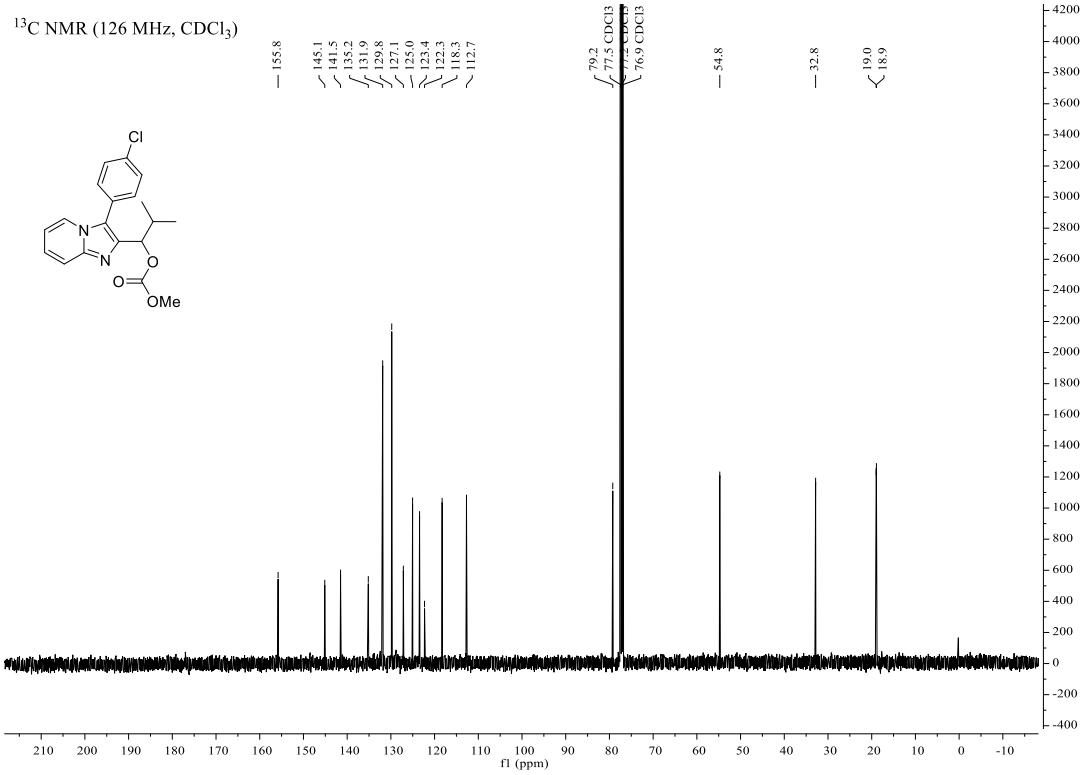
Compound 38




^{13}C NMR (126 MHz, $CDCl_3$)
155.8
144.8
141.0
139.0
130.4
130.1
125.6
124.6
123.7
123.6
118.1
112.3
79.3
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
54.7
32.8
21.6
19.0
Me
N
N
O
O
OMe
f1 (ppm)

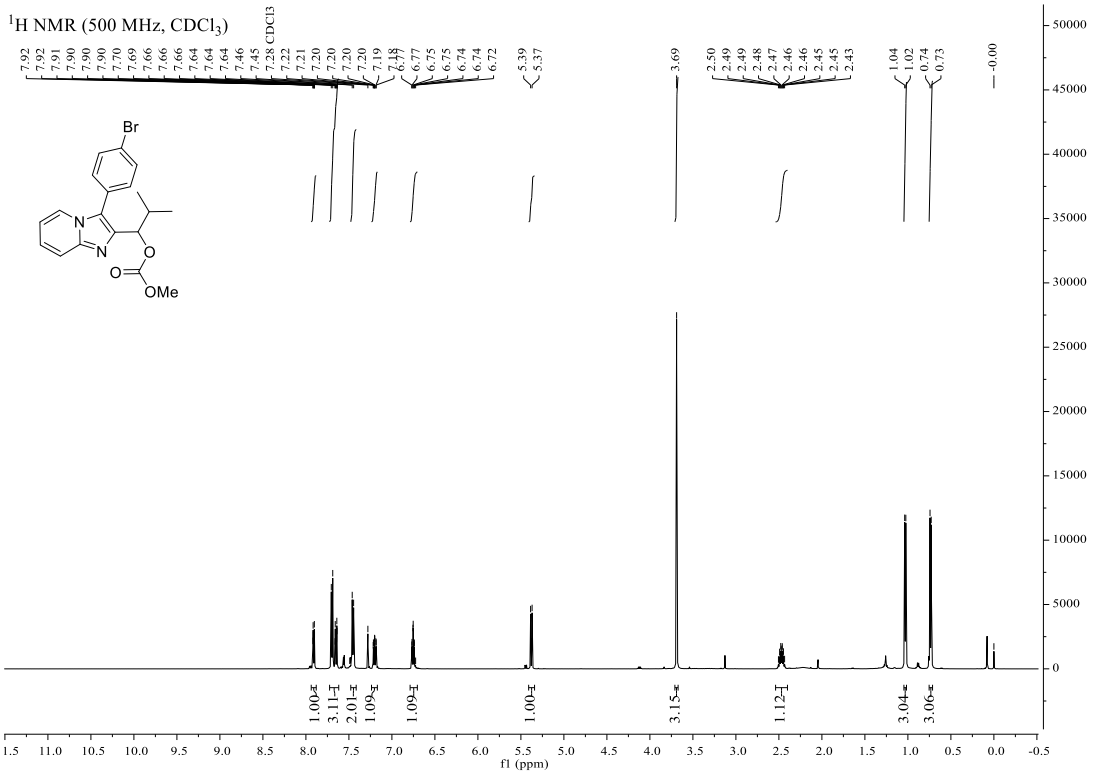
Compound 39


^{1}H NMR (500 MHz, $CDCl_3$)
7.91
7.91
7.90
7.90
7.66
7.66
7.64
7.64
7.55
7.53
7.52
7.50
7.27 CDCl3
7.22
7.21
7.20
7.20
7.20
7.19
6.77
6.76
6.74
5.38
5.36
3.69
2.50
2.49
2.49
2.48
2.47
2.46
2.46
2.45
2.45
2.45
2.43
1.04
1.02
0.74
0.73
0.00
Cl
N
N
O
O
OMe
1.03
1.02
3.78
1.02
1.01
1.00
3.02
1.01
3.05
3.06
f1 (ppm)

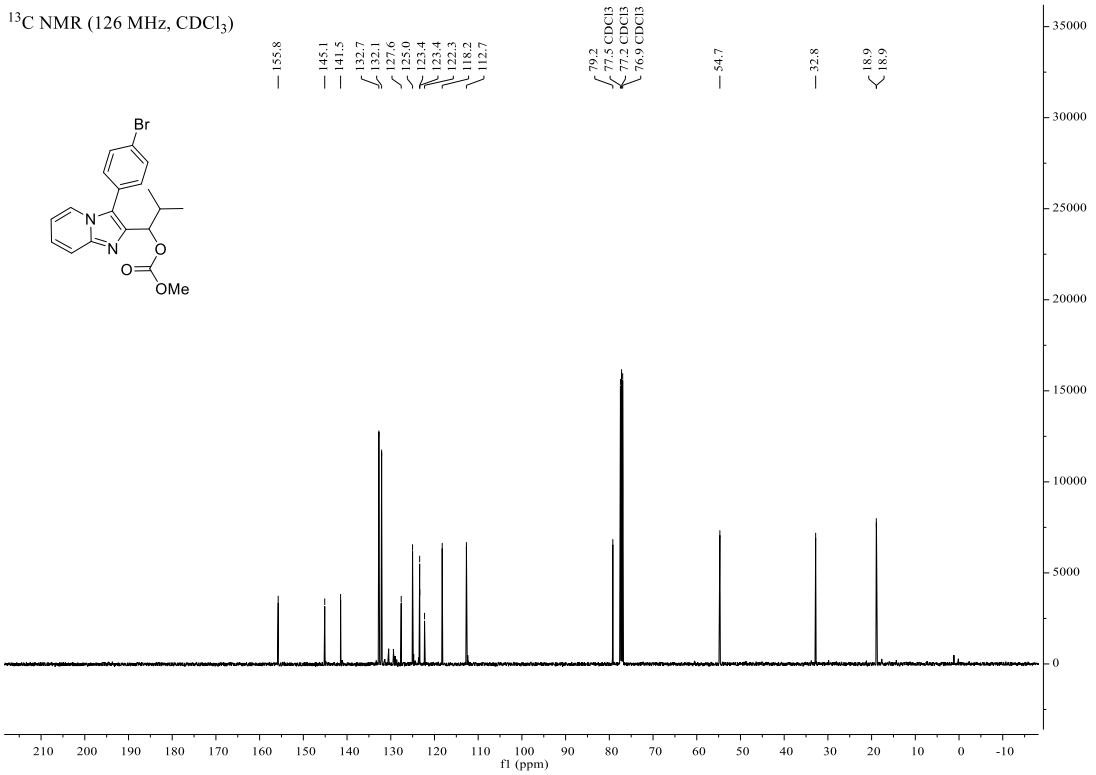

13C NMR (126 MHz, CDCl3)
155.8
145.1
141.5
135.2
131.9
129.8
127.1
125.0
123.4
122.3
118.3
112.7
79.2
77.5 CDCl3
76.9 CDCl3
54.8
32.8
19.0
18.9
Cl
N
N
O
O
OMe
f1 (ppm)

Compound 40

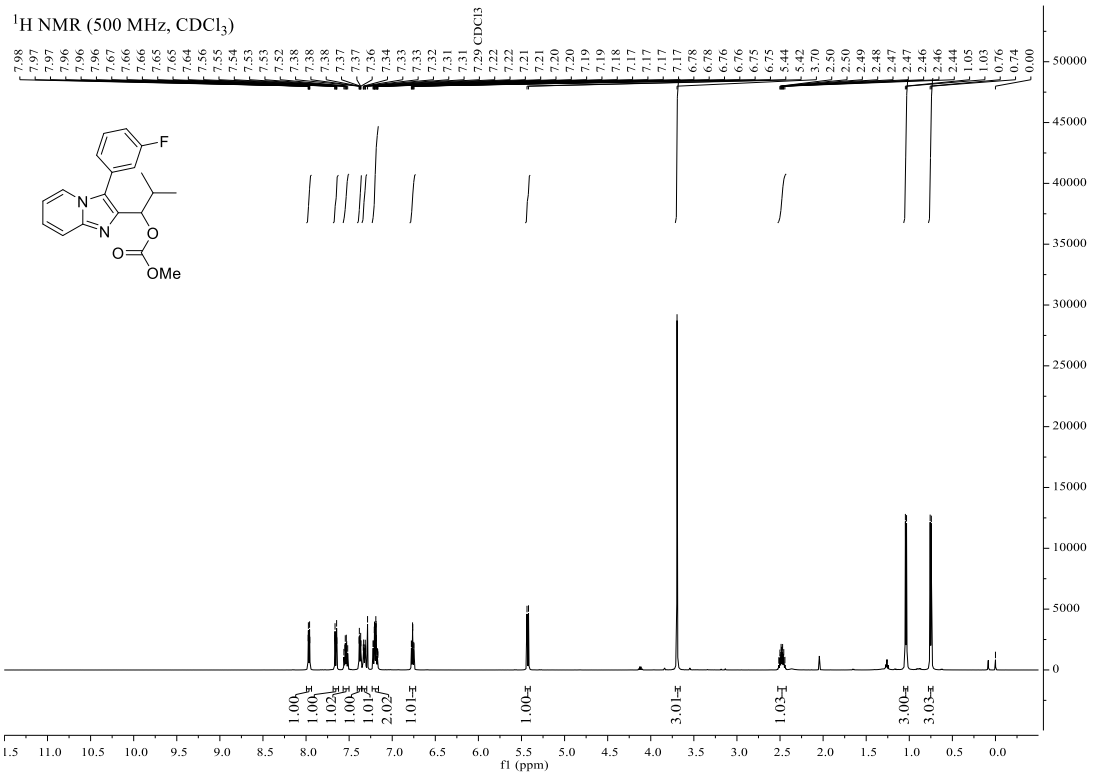
^{1}H NMR (500 MHz, $CDCl_3$)

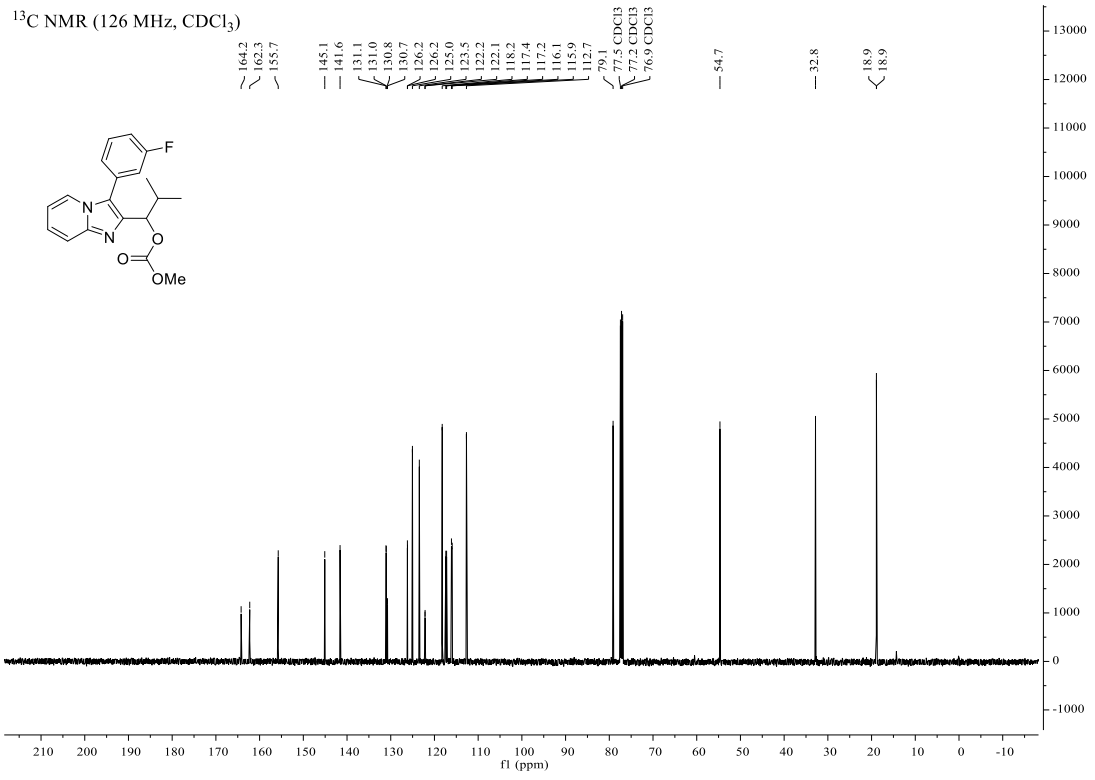


^{13}C NMR (126 MHz, $CDCl_3$)

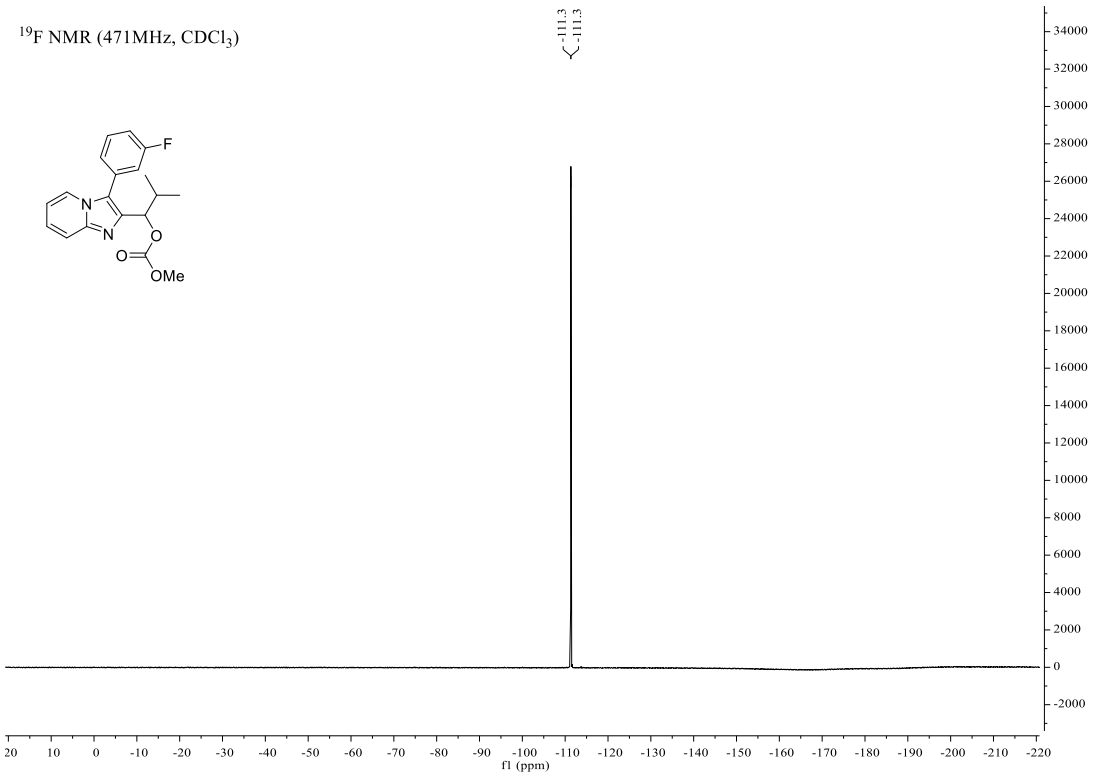


Compound 41

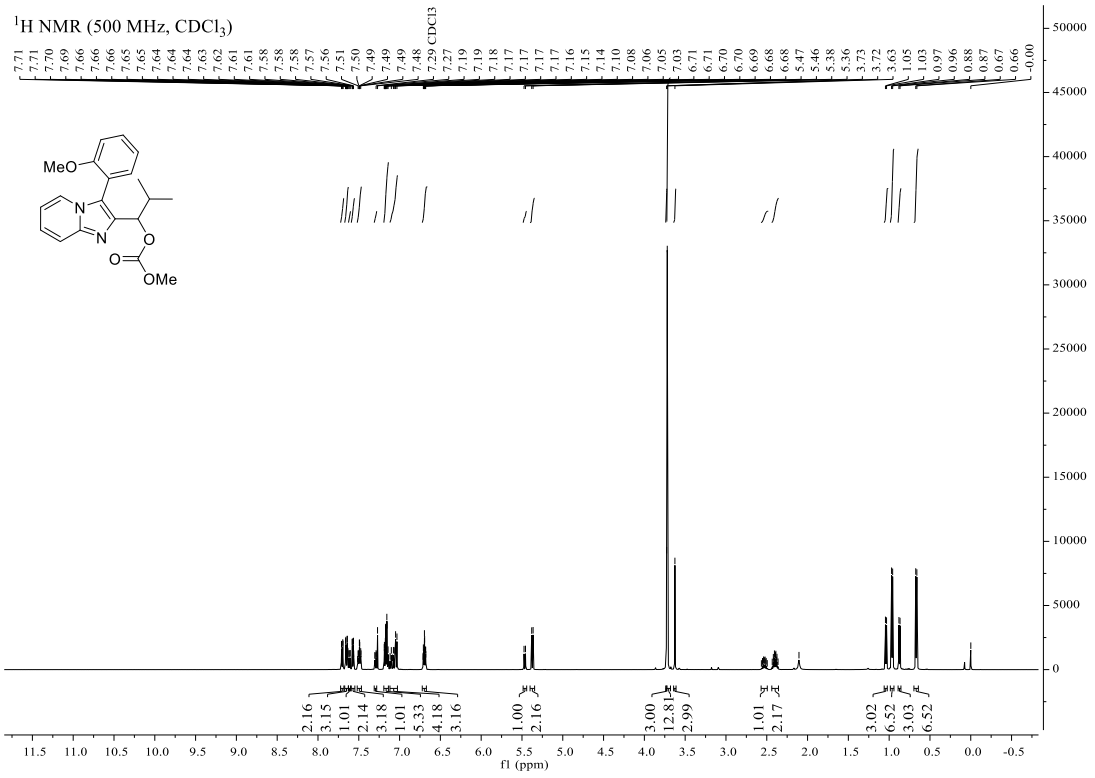

1H NMR (500 MHz, CDCl3)
F
N
N
O
O
OMe
f1 (ppm)

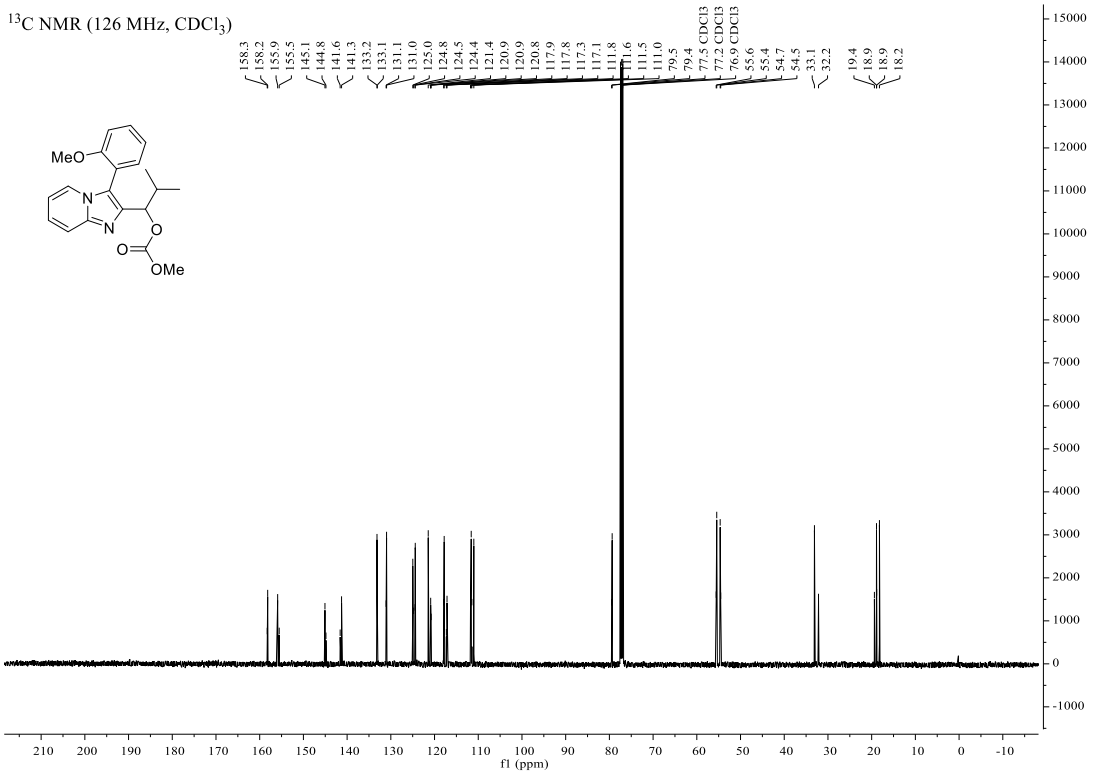

13C NMR (126 MHz, CDCl3)
F
N
N
O
O
OMe
f1 (ppm)

^{19}F NMR (471MHz, $CDCl_3$)

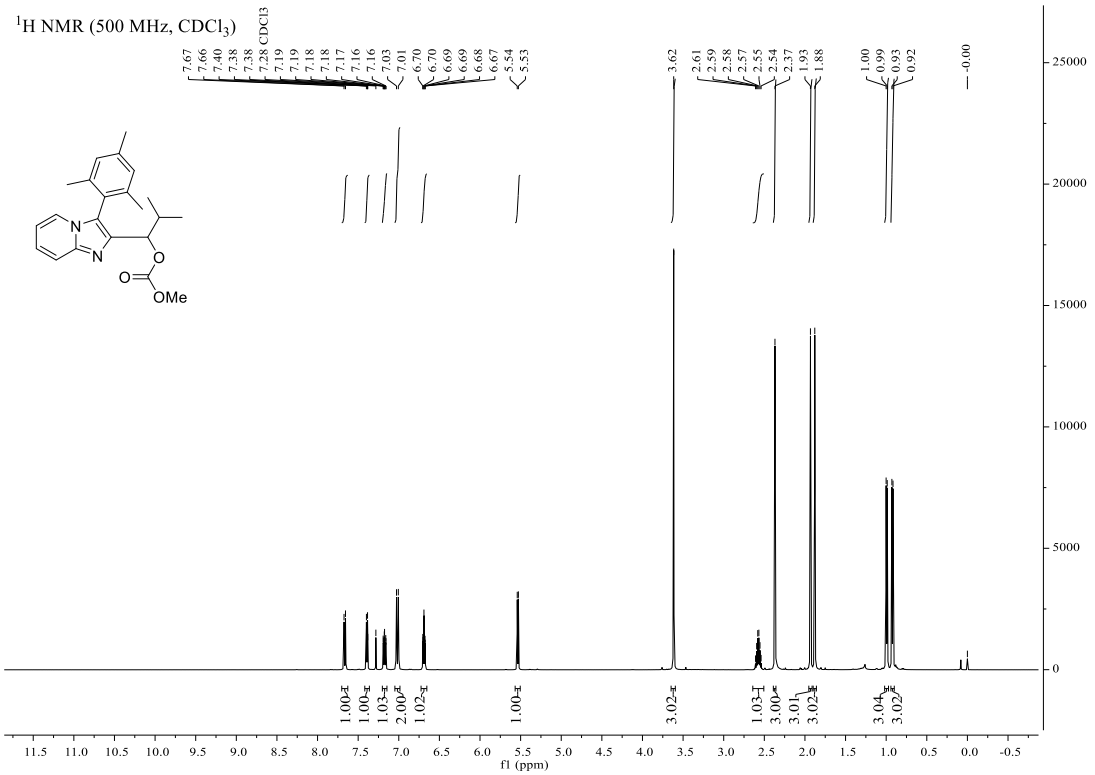


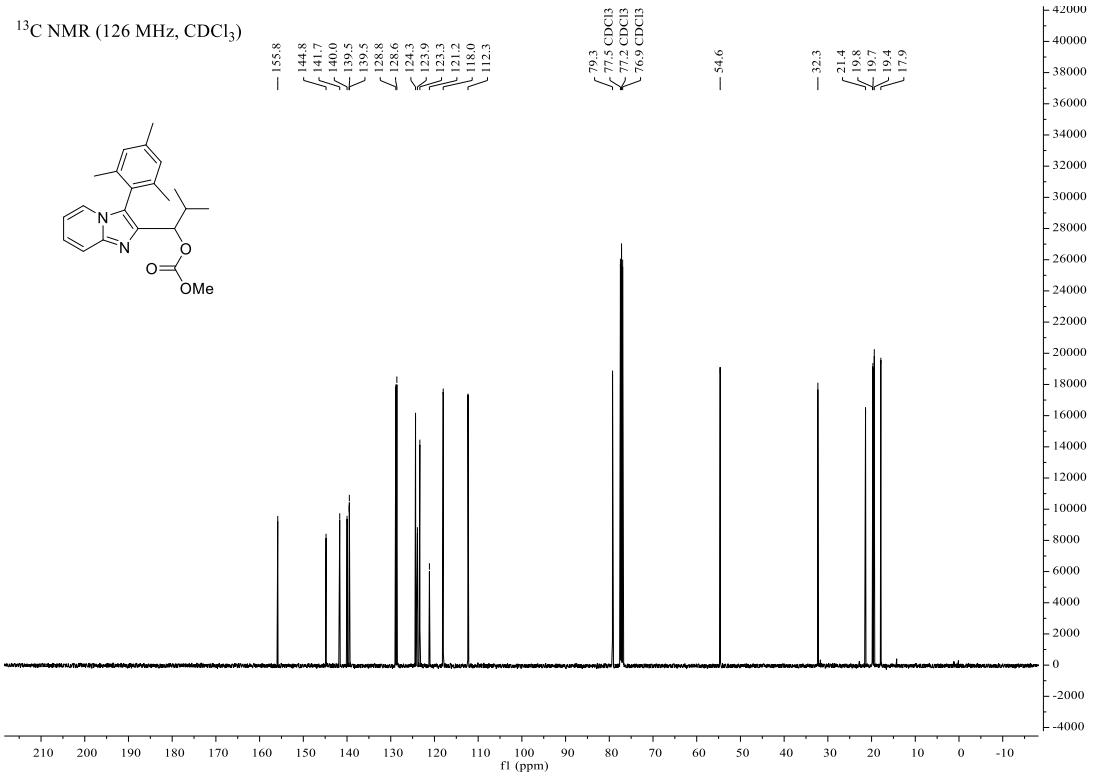
Compound 42 (A mixture of stereoisomers were obtained in a ratio of 2.1:1)



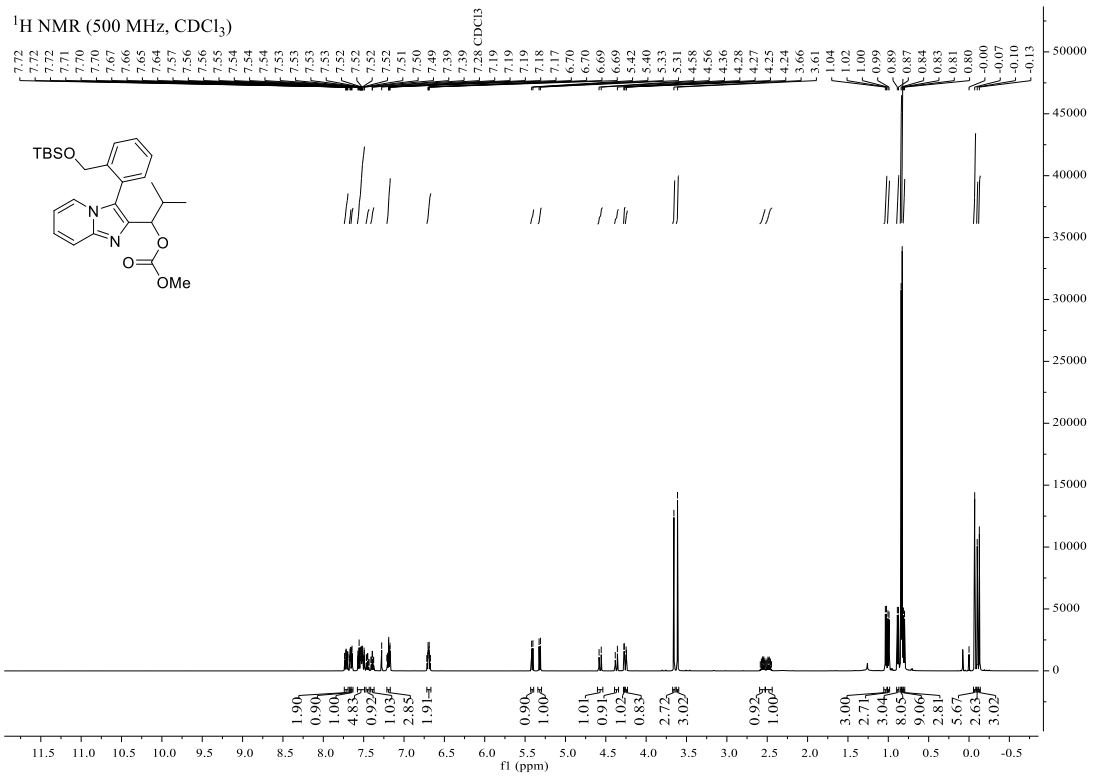

^{13}C NMR (126 MHz, $CDCl_3$)
MeO
N
N
O
O
OMe
158.3
158.2
155.9
155.5
145.1
144.8
141.6
141.3
133.2
133.1
131.1
131.0
125.0
124.8
124.5
124.4
121.4
120.9
120.9
120.8
117.9
117.8
117.3
117.1
111.8
111.6
111.5
111.0
79.5
79.4
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
55.6
55.4
54.7
54.5
33.1
32.2
19.4
18.9
18.9
18.2
f1 (ppm)

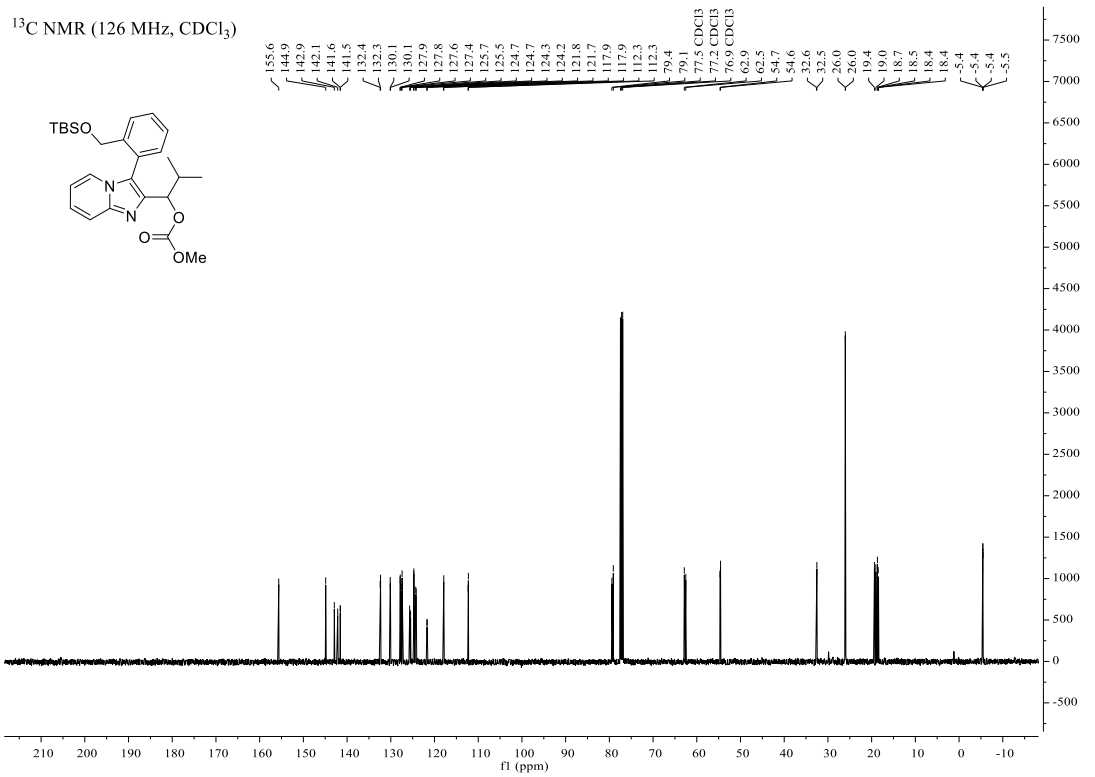
Compound 43


^{1}H NMR (500 MHz, $CDCl_3$)
MeO
N
N
O
O
OMe
7.67
7.66
7.40
7.38
7.38
7.28 CDCl3
7.19
7.19
7.18
7.18
7.17
7.16
7.16
7.03
7.01
6.70
6.70
6.69
6.69
6.68
6.67
5.54
5.53
3.62
2.61
2.59
2.58
2.57
2.55
2.54
2.37
1.93
1.88
1.00
0.99
0.93
0.92
-0.00
1.00
1.00
1.03
2.00
1.02
1.00
3.02
1.03
3.00
3.01
3.02
3.04
3.02
f1 (ppm)

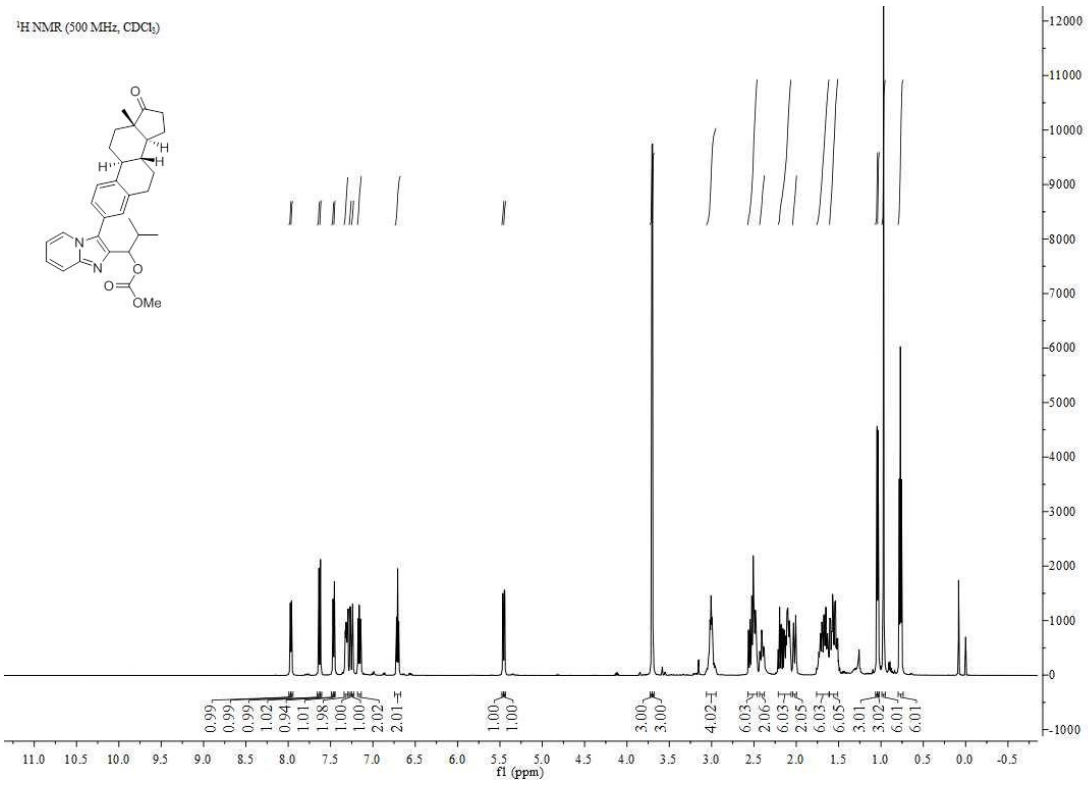


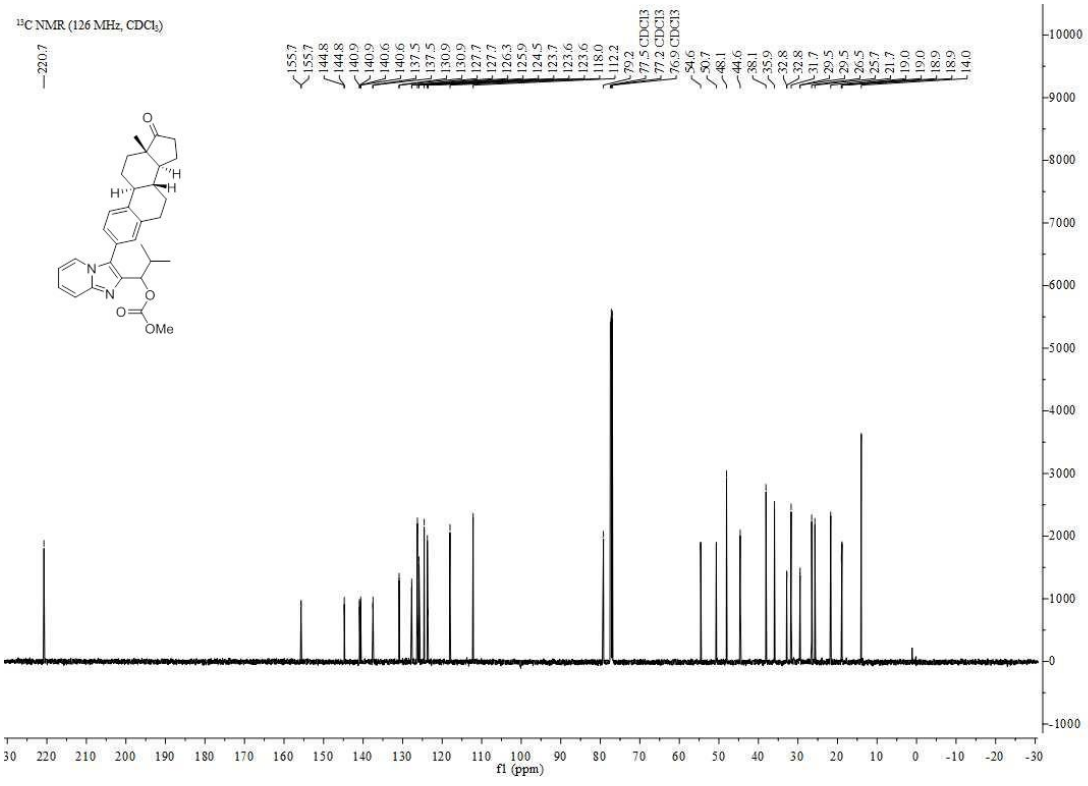
Compound 44 (A mixture of stereoisomers were obtained in a ratio of 0.9:1)


^{1}H NMR (500 MHz, $CDCl_3$)
TBSO
N
N
O
O
OMe
f1 (ppm)

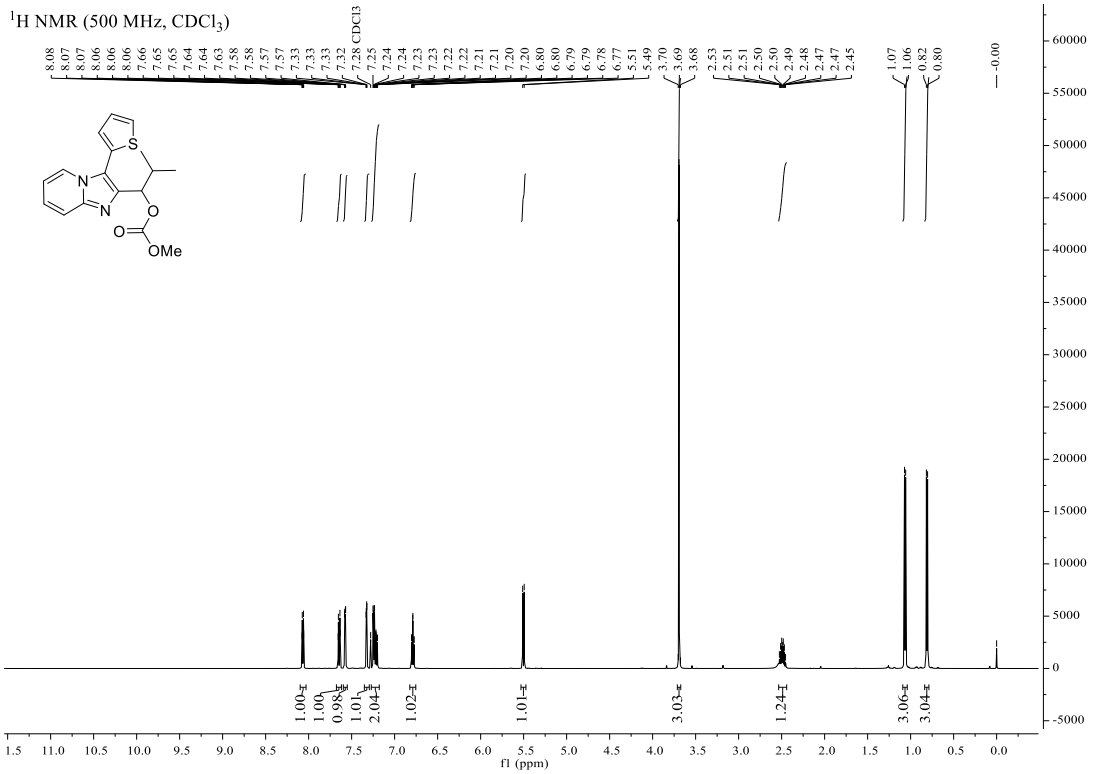

^{13}C NMR (126 MHz, $CDCl_3$)
TBSO
N
N
O
O
OMe
f1 (ppm)

Compound 45

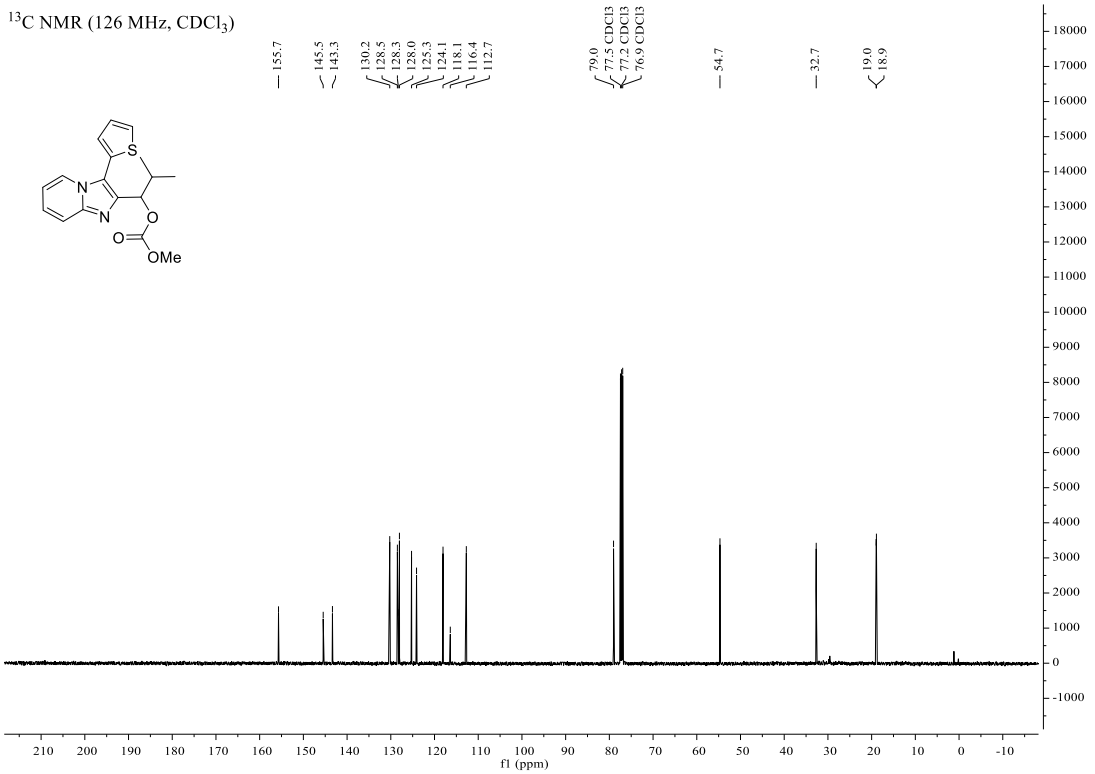




Compound 46

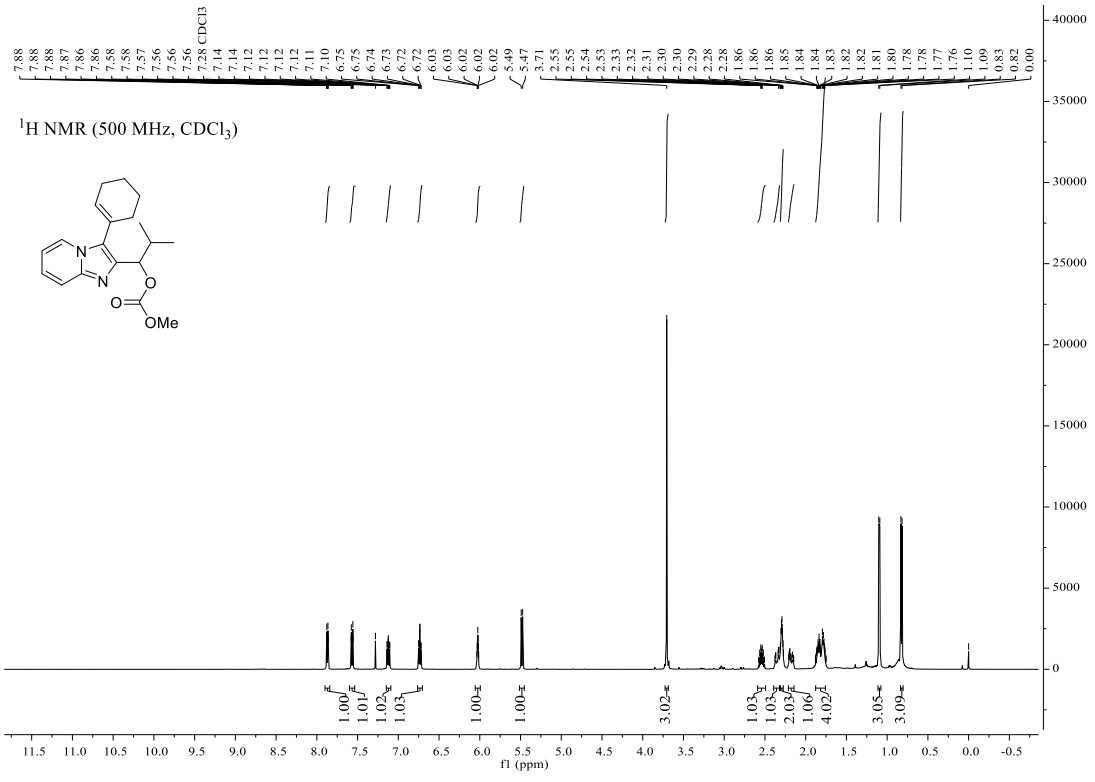

1H NMR (500 MHz, CDCl3)
8.08 8.07 8.07 8.06 8.06 8.06 7.66 7.65 7.65 7.64 7.64 7.63 7.58 7.58 7.57 7.57 7.33 7.33 7.32 7.28 CDCl3 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.20 6.80 6.80 6.79 6.79 6.78 6.77 5.51 5.49 3.70 3.69 3.68 2.53 2.51 2.51 2.50 2.50 2.49 2.48 2.47 2.47 2.45 1.07 1.06 0.82 0.80 -0.00
S
N
N
O
O
OMe
1.00 1.00 0.98 1.01 2.04 1.02 1.01 3.03 1.24 3.06 3.04
f1 (ppm)

^{13}C NMR (126 MHz, $CDCl_3$)



Compound 47

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)